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

Supporting Information

Thermolysis and Radiofluorination of Diaryliodonium Salts Derived from Anilines

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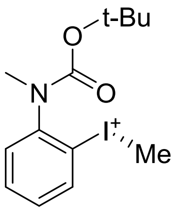
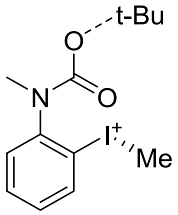
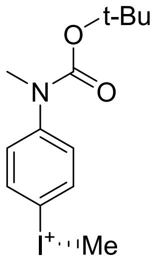
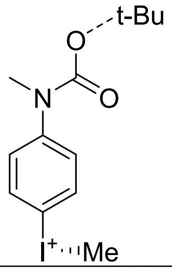
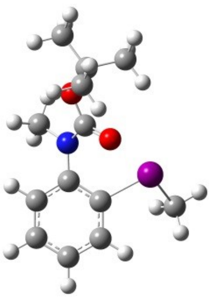
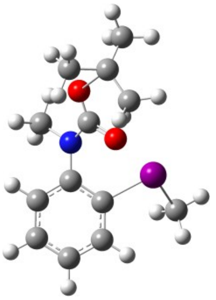
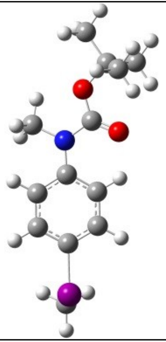
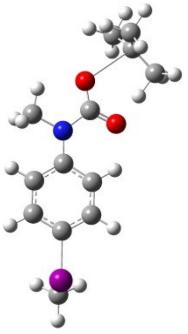
General information:

All materials were obtained from commercial sources and used as received unless otherwise noted. Trimethylsilyl acetate (TMSOAc), trimethylsilyl trifluoroacetate (TMSTFA), and trimethylsilyl triflate (TMSOTf) were distilled under reduced pressure into flame-dried storage tubes and stored under nitrogen. Acetonitrile and d_3-acetonitrile (Cambridge Isotope Laboratories) were stirred over P_2O_5 (12 h), distilled into flame-dried storage tubes, and transferred into an inert atmosphere glove box. Benzene and d_6-benzene (Sigma-Aldrich) were dried over Na/benzophenone (12 h), distilled directly into flame-dried storage tubes, and stored under dry nitrogen. Tetrahydrofuran (THF) was dried over Na/benzophenone and distilled into a flame dried storage flask under dry nitrogen. Acetate buffer is (0.5 mol:0.5 mol, HOAc:NaOAc) unless otherwise noted. All glassware and NMR tubes were oven dried (140 °C) for 24 h before they were transferred into the glove box for use. Glove box manipulations were performed under nitrogen in an MBraun Labmaster 130, equipped with a recirculating purifier, which removed oxygen and water. All NMR experiments reported were performed using a Bruker Avance 300 MHz, 400 MHz, 500 MHz, 600 MHz, or 700 MHz NMR spectrometers in the NMR laboratory at the University of Nebraska or at the University of Illinois at Chicago and calibrated using residual protonated solvent. Yields from NMR scale reactions were determined by using the residual solvent peak as an internal standard. All *J* coupling values are given in Hz. Computational work was performed using the Gaussian 09[1] suite of programs.

Computational Studies

All density functional theory calculations were performed with the B3LYP functional. The basis set for iodine was MIDIX and 6-311G (d,p) for all other atoms. Results are summarized in the table below.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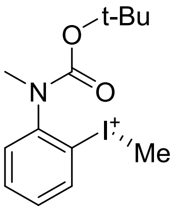
Barrier		21.398 kcal/mol		23.509 kcal/mol
Imaginary Frequencies		-123.58		-282.73

Cartesian coordinates



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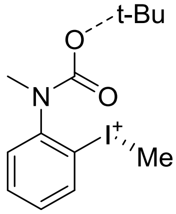

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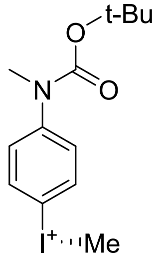

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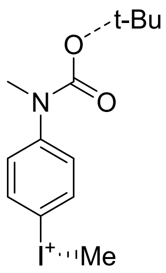

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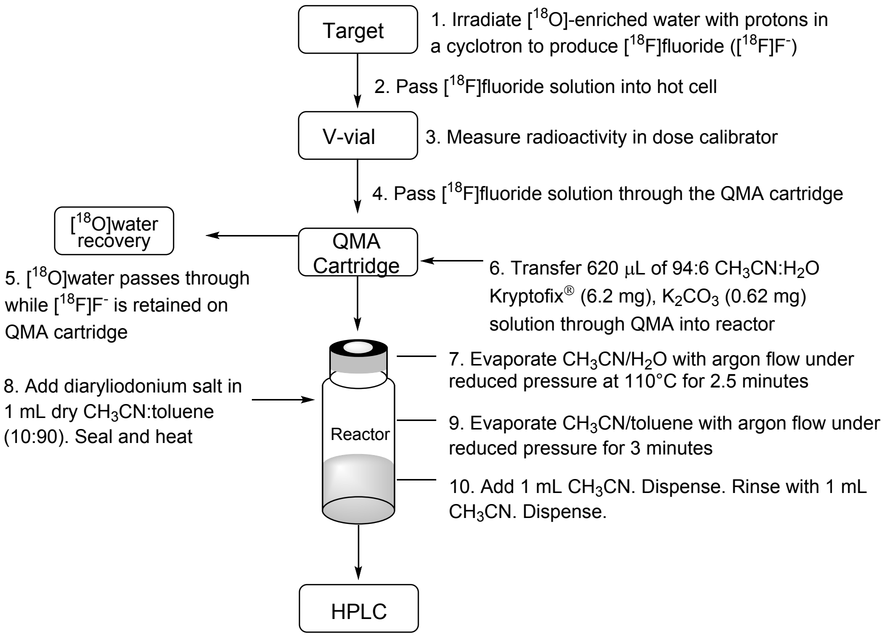
Radiosynthetic Methods

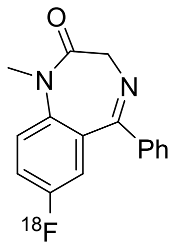
Figure S1. Radiosynthesis Steps



General radiosynthesis procedure

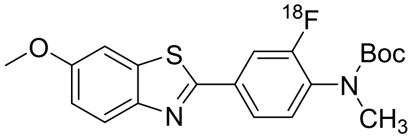
The diaryliodonium salt precursor and organic solvents for radiosynthesis were stored in an anaerobic chamber under argon. All organic solvents used were anhydrous grade, and used as received. The radiofluorinated product was synthesized by thermolysis of the appropriate diaryliodonium fluoride using an IBA Synthera automated synthesizer equipped with an integrated fluidic processor (ABX) and an automated script, following the steps outlined in Figure S1. Aqueous [^{18}F]fluoride produced in an IBA Cyclone 18/9 cyclotron from 97% ^{18}O-enriched water was passed through a QMA cartridge (pretreated with 1 M sodium bicarbonate (2 mL) followed by a water (5 mL) rinse) to trap the [^{18}F]fluoride while the [^{18}O]water passed through to waste. The [^{18}F]fluoride was eluted from the QMA resin with 620 μL of 4% water in acetonitrile containing potassium carbonate (0.62 mg) and Kryptofix [2.2.2] (6.2 mg). The solvent was removed by azeotropic distillation under argon flow with reduced pressure and heating to 110 °C for 2.5 min. The diaryliodonium salt precursor, pre-dissolved in 10% acetonitrile in toluene (1 mL), was added to the reactor and the mixture was heated for 10 min to give the product. Identity of the product was confirmed by comparison of its HPLC trace against a trace of the ^{19}F compound standard.

7-^{18}Fluoro-1-methyl-5-phenyl-1,3-dihydro-2H-benzo[e][1,4]diazepin-2-one



According to the general radiosynthesis procedure, 8 mg of diaryliodonium salt precursor **15** was heating to 140 °C for 10 min to give the product in 32.1 ± 4.0% (n=3) radiochemical yield, decay corrected to end of bombardment (t = 27 min). HPLC purification (Zorbax SB-Aq column 3.5 μm 4.6x100 mm, 30% acetonitrile in pH 2 phosphate buffer, 1 mL/min, 254 nm, 7 min) gave the product (30.2 ± 4.7% RCY) in 97% radiochemical purity.

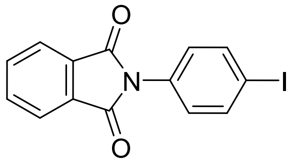
2-(4-(*N*-*Boc*-3-^{18}fluoro-*N*-methyl)phenyl)-6-methoxybenzothiazole



According to the general radiosynthesis procedure, 4 mg of diaryliodonium salt precursor **18** was heated gradually to 120 °C over the course of 10 min to give the product in 51.7 ± 1.9% (n=3) radiochemical yield, decay corrected to end of bombardment. Synthesis time was 27 minutes.

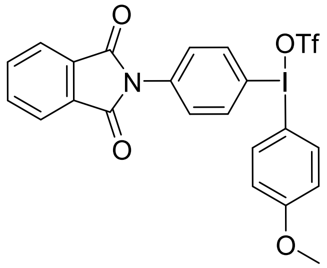
Experimental Procedures

Phthalimido-4-iodobenzene[2-5]



To a 250 mL round bottom flask was added phthalic anhydride (3.40 g, 22.83 mmol), 4-iodoaniline (5.00 g, 22.83 mmol), a catalytic amount of p-toluenesulfonic acid, and toluene (75 mL). A Dean-Stark trap was affixed to the flask and the stirred solution was heated at reflux for 60 h. The solution was allowed to cool to room temperature and precipitated solids were removed by vacuum filtration. The filtrate washed with sat. aq. bicarbonate (3 x 200 mL) and brine (2 x 200 mL), and the organic solution was dried over sodium sulfate and filtered. The solvent was removed by rotary evaporation, and the remaining solid recrystallized from boiling 1:1 ethanol/ethyl acetate, which was slowly cooled to 0 °C. The resulting crystals were collected by vacuum filtration, giving a light-gray fluffy solid (2.83 g, 35%). ^{1}H NMR (CD_3CN, 400 MHz, 25 °C): δ 7.92-7.94 (m, 2H), 7.89 (d, *J* = 8.6, 2H), 7.85-7.87 (m, 2H), 7.24 (d, *J* = 8.6, 2H). ^{13}C NMR ($(CD_3)_2CO$, 100 MHz, 25 °C): δ 168.0, 139.4, 136.0, 133.8, 133.4, 130.4, 124.8, 93.8. HRMS (ESI) calculated for $C_{14}H_8N$348.9600, found 348.9597.

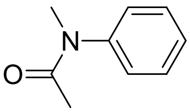
(4-Phthalimidophenyl)(4'-methoxyphenyl)iodonium triflate[6]



In a glove box under nitrogen, Selectfluor™ (2.65 g, 7.48 mmol) and TMSOAc (1.72 mL, 11.42 mmol) were dissolved in dry acetonitrile (30 mL). Phthalimido-4-iodobenzene[5] (2.00 g, 5.73 mmol) was dissolved in dry acetonitrile (30 mL) and placed in a 250 mL Schlenk-style flask. The Selectfluor™/TMSOAc solution was added slowly to the stirred solution of aryl iodide. The reaction flask was sealed and the reaction mixture was heated at 60 °C for 12 h; (a parallel NMR scale reaction in dry CD_3CN indicated the reaction was 98% complete at this time). After allowing the reaction mixture to cool to room temperature, potassium (4-methoxyphenyl)trifluoroborate (1.21 g, 5.65 mmol) was added, followed by TMSOTf (1.0 mL, 5.52 mmol) diluted in 2 mL dry acetonitrile. The reaction was removed from the glove box and allowed to stand for 2 hours. Precipitated product was removed via filtration and the mother liquor chilled overnight at -10 °C to provide a second crop of product. The product was dried under dynamic high vacuum overnight to give a colorless solid 1.92 g (56%). ^{1}H NMR ($(CD_3)_2CO$, 300 MHz, 25 °C): δ

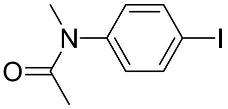
8.45 (d, *J* = 8.9, 2H), 8.34 (d, *J* = 9.1, 2H), 7.92-8.02 (m, 4H), 7.79 (d, *J* = 8.9, 2H), 7.16 (d, *J* = 9.2, 2H), 3.90 (s, 3H). ^{13}C NMR ($(CD_3)_2CO$, 75 MHz, 25 °C): δ 167.3, 164.3, 139.0, 137.3, 136.7, 135.9, 132.8, 130.9, 124.5, 119.0, 113.5, 103.7, 56.4. ^{19}F NMR ($(CD_3)_2CO$, 282 MHz, 25 °C): δ -78.8 (s, 3F). HRMS (ESI): calculated for $C_{21}H_{15}NO_3I$ $[M\text{-}OTf^-]^+$ 456.0091, found 456.0105.

N-Methylacetanilide[7-9]



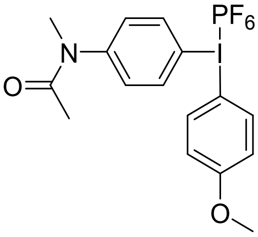
N-Methylaniline (6.1 mL, 56.3 mmol) and a catalytic amount of conc. sulfuric acid were combined in acetic anhydride (12 mL) in a 50 mL round bottom flask at 0 °C. This mixture was warmed to room temperature and stirred for 5 hours. The solution was poured into CH_2Cl_2 (50 mL), transferred to a separatory funnel, washed with bicarbonate (2 x 50 mL), brine (2 x 50 mL), and dried over sodium sulfate. Removal of CH_2Cl_2 yielded purple crystals (7.62 g, 91%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.39 (t, *J* = 7.6, 2H), 7.31 (t, *J* = 7.3, 1H), 7.17 (d, *J* = 7.5, 2H), 3.28 (s, 3H), 1.88 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 170.6, 144.7, 129.8, 127.8, 127.2, 37.2, 22.5. HRMS (ESI) calculated for $C_9H_{11}ON$ 149.0841, found 148.0762.

4-Iodo-N-methylacetanilide [10] [11]



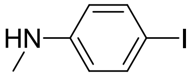
N-Iodosuccinimide (6.64 g, 29.5 mmol), N-methylacetanilide (4.00 g, 26.8 mmol) and trifluoracetic acid (cat.) were combined in a 250 mL round bottom flask in acetonitrile (100 mL), and the resulting solution was heated at reflux for 15 hours. The solvent was removed and the resulting solid was dissolved in EtOAc (100 mL). The solution was washed with bicarbonate (3 x 25 mL), water (25 mL), dried over sodium sulfate, and the solvent removed by rotary evaporation. Recrystallization from water/acetonitrile (1200 mL/25 mL) gave light purple crystals (5.47 g, 74%). ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 7.67 (d, *J* = 7.9, 2H), 6.90 (d, *J* = 8.0, 2H), 3.16 (s, 3H), 1.80 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, 25 °C): δ 170.1, 144.2, 138.9, 129.0, 92.7, 37.0, 22.4. HRMS (ESI) calculated for $C_9H_{10}ONI$ 274.9807, found 274.9807.

(4-(N-Methyl-N-acetamido)phenyl)(4'-methoxyphenyl) iodonium hexafluorophosphate[6]



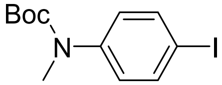
In a glove box under nitrogen, 4-iodo-N-methylacetanilide[12] (0.80 g, 2.92 mmol) and Selectfluor™ (1.35g, 3.80 mmol) were dissolved in dry acetonitrile (75 mL) and placed in a 250 mL Schlenk flask. TMSOAc (1.14mL, 7.604 mmol) was added to the mixture dropwise. The reaction was heated at 40 °C for 6 h. Potassium (4-methoxyphenyl)trifluoroborate (0.69 mg, 3.22 mmol) was added, followed by TMSTFA (0.51 mL, 2.93 mmol). The mixture was stirred for 30 min at RT before the flask was removed from the glove box. The reaction mixture was poured directly into a solution of sodium hexafluorophosphate (1.96g, 11.67 mmol) in 5 mL of water. Acetonitrile was removed and the residual was extracted with CH_2Cl_2 (10 x 20 mL). The combined organic extracts were dried over sodium sulfate and the solvent was removed by rotary evaporation. The remaining oil was crystallized from a solution of EtOAc/CH_2Cl_2 to provide the product as a colorless solid (0.46 g, 30%). ^{1}H NMR (CD_3CN, 400 MHz, 25 °C): δ 8.05 (d, *J* = 8.8, 2H), 8.03 (d, *J* = 9.2, 2H), 7.42 (d, *J* = 8.9, 2H), 7.07 (d, *J* = 9.2, 2H), 3.84 (s, 3H), 3.22 (s, 3H), 1.93 (s, 3H). ^{13}C NMR (CD_3CN, 100 MHz, 25 °C): δ 171.3, 164.8, 149.8, 139.1, 137.3, 131.6, 119.6, 111.4, 102.7, 57.1, 38.2, 23.2. ^{19}F NMR (CD_3CN, 376 MHz, 25 °C): δ -73.42 (d, *J* = 707.6, 6F). HRMS (ESI) calculated for $C_{16}H_{17}O_2NI$ [M-PF_6^-] 382.0298, found 382.0305.

4-Iodo-N-methylaniline[13]



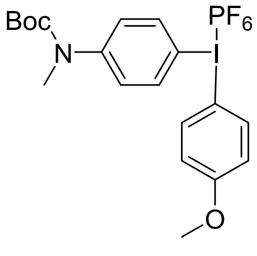
In a 250 mL round bottom flask, 4-iodo-N-methylacetanilide (2.0 g, 7.27 mmol) and potassium hydroxide (2.45 g, 43.66 mmol) were dissolved in an ethanol/water (80 mL/20 mL) solution. The reaction was refluxed for 48 hours. Ethanol was removed by rotary evaporation and ethyl acetate (40 mL) was added. The mixture was brought to neutral pH with sat. aq. ammonium chloride, washed with water (10 mL), dried over sodium sulfate, and the solvent removed. The compound was purified by column chromatography in 20% ethyl acetate/hexanes to give an amber liquid (1.40 g, 83%). ^1H NMR (CD_3CN, 400 MHz, 25 °C): δ 7.39 (d, *J* = 8.8, 2H), 6.41 (d, *J* = 8.8, 2H), 4.50 (s, 1H), 2.71 (d, *J* = 5.2, 3H). ^{13}C NMR (CD_3CN, 100 MHz, 25 °C): δ 151.1, 138.9, 115.8, 77.1, 30.7. HRMS (ESI) calculated for C_7H_8NI 232.9701, found 232.9702.

N-Boc-4-iodo-N-methylaniline[14]



In a 100 mL round bottom flask N-methyl-4-iodoaniline (0.50 g, 2.15 mmol), di-*tert*-butyl dicarbonate (0.94 g, 4.30 mmol), triethylamine (1.2 mL, 6.6 mmol), and DMAP (0.1 g, 0.82 mmol) were dissolved in acetonitrile (15 mL). The resulting solution was and stirred for 14 h at room temperature. All volatiles were removed by rotary evaporation and the compound was purified by flash column chromatography (silica, 10% ethyl acetate/hexanes). The resulting oil was recrystallized from pentane to give colorless crystals (0.38 g, 54%). ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.64 (d, *J* = 8.7, 2H), 7.02 (d, *J* = 8.6, 2H), 3.25 (s, 3H), 1.47 (s, 9H). ^{13}C NMR (CD_3CN, 100 MHz, 25 °C): δ 155.4, 145.4, 138.9, 129.0, 90.1, 81.5, 37.9, 28.8. HRMS (ESI) calculated for $C_{12}H_{16}O_2NI$ 333.0226, found 333.0226.

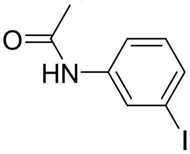
(4-(N-methyl-N-Boc)anilino)(4'-methoxyphenyl)iodonium hexafluorophosphate[6]



In a glove box under nitrogen, N-Boc-4-iodo-N-methylaniline[14] (1.0 g, 3.00 mmol), Selectfluor™ (1.38 g, 3.90 mmol) and TEDA-PF_6 (0.10 g, 0.21 mmol) were dissolved in 5 mL of dry acetonitrile. TMSOAc (1.3 mL, 8.40 mmol) was added to this stirred mixture in a dropwise fashion. The reaction mixture was stirred for 1 h at room temperature and at 40 °C for 3 h. Potassium (4-methoxyphenyl)trifluoroborate (0.71 g, 3.30 mmol) and TMSTFA (0.57 mL, 3.30 mmol) were added and the reaction mixture stirred for 1 h at room temperature. The reaction vessel was removed from the glove box and the mixture concentrated by rotary evaporation. The resulting oil was added to an aqueous solution (8 mL) of sodium hexafluorophosphate (2.5 g, 15.0 mmol). The acetonitrile was removed by rotary evaporation. The remaining aqueous mixture was treated with EtOAc (25 mL) and the contents of the flask were transferred to a separatory funnel with the aid of additional water and ethyl acetate. The ethyl acetate solution was washed with acetate buffer (3 x 10 mL) and water (3 x 10 mL). The organic layer was separated, dried over sodium sulfate and evaporated. The resulting oil was sonicated in benzene (200 mL) to dissolve it, and allowed to stand at room temperature for 1 h. The product crystallized from solution and was isolated by vacuum filtration.

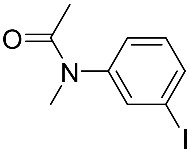
Residual solvent was removed to give 1.00 g of the title compound (57%). ^{1}H NMR (CD_3CN, 400 MHz, 25 °C): δ 8.00 (d, *J* = 9.2, 2H), 7.96 (d, *J* = 9.1, 2H), 7.46 (d, *J* = 9.1, 2H), 7.06 (d, *J* = 9.2, 2H), 3.84 (s, 3H), 3.23 (s, 3H), 1.44 (s, 9H). ^{13}C NMR (CD_3CN, 100 MHz, 25 °C): δ 164.8, 154.9, 138.9, 136.7, 129.4, 119.6, 108.5, 103.0, 82.5, 57.1, 37.5, 28.7 ^{19}F NMR (CD_3CN, 376 MHz, 25 °C): δ -72.85 (d, *J* = 705.9, 6F). HRMS (ESI) calculated for $C_{19}H_{23}O_3NI$ [M-PF_6^-] 440.0717, found 440.0723.

N-acetyl-3-iodoaniline



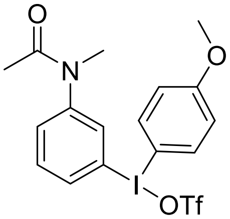
3-Iodoaniline (2.25 g, 10.3 mmol) is dissolved in acetic anhydride (20 mL) and stirred for 4 h at RT. The reaction solution was poured into cold water and neutralized with a 1M potassium hydroxide solution. The product is extracted with DCM (20 mL x 4), dried over sodium sulfate, and the solvent removed to provide a colorless solid (2.6 g, 97%), which was sufficiently pure for further use. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.90 (s, 1H), 7.72 (br s, 1H), 7.46 (d, *J* = 7.9, 1H), 7.42 (d, *J* = 7.7, 1H), 7.01 (t, *J* = 7.9, 1H), 2.16 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 168.7, 139.1, 133.3, 130.5, 128.7, 119.2, 94.1, 24.6. HRMS (ESI) calculated for C_8H_9NOI [M+H$^+$] 261.9723, found 261.9707.

N-acetyl-3-iodo-N-methylaniline



N-Acetyl-3-iodoaniline (2.1 g, 8.04 mmol) was dissolved in DMF (80 mL) in a Schlenk-style storage tube equipped with a PTFE closure. Cesium bicarbonate (6.6 g, 20.1 mmol) and iodomethane (1.3 mL, 20.1 mmol) were added, the tube sealed and heated at 40 °C overnight with stirring. The solution is poured into water, extracted with ethyl acetate (50 mL x 6), the combined organic extracts washed with water (25 mL x 3), dried over sodium sulfate, and the solvent removed under dynamic high vacuum to provide a colorless solid (2.1 g, 95%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.67 (d, *J* = 6.6, 1H), 7.17 (dd, *J* = 8.0, 1.8; 1H), 7.13 (d, *J* = 7.8, 1H), 3.24 (s, 3H), 1.88 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 170.2, 145.8, 136.8, 136.2, 131.1, 126.6, 94.4, 37.2, 22.5. HRMS (ESI) calculated for $C_9H_{11}NOI$ [M+H$^+$] 275.9880, found 275.9863.

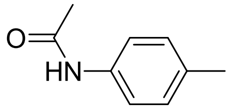
(3-(N-Methyl-N-acetamido)phenyl)(4'-methoxyphenyl)iodonium trifluoromethansulfonate



In a glovebox under nitrogen, N-acetyl-3-iodo-N-methylaniline (1.0 g, 3.64 mmol) and Selectfluor™ (1.67 g, 4.73 mmol) were dissolved in dry acetonitrile (40 mL). TMSOAc (0.97 mL, 1.02 mmol) was added dropwise to the solution. The reaction was heated to 40 °C in a sealed vessel for 4 h. The solution was allowed to cool to room temperature and potassium (4-methoxyphenyl)trifluoroborate (0.87 g, 4.00 mmol) was added, followed by a slow addition of TMSTFA (0.69 mL, 4.00 mmol). The reaction was stirred for 10 min before the reaction vessel was removed from the glove box. The solvent was removed by rotary evaporation and the remainder was dissolved in 100 mL of acetate buffer and transferred to a separatory funnel. The mixture was extracted with ethyl acetate (25 x 4 mL) and the combined organic extracts dried over Na_2SO_4, filtered, and the solvent was removed by rotary evaporation. The resulting solid was dissolved in minimal acetonitrile and added to an aqueous solution of sodium triflate (3.1 g, 18.2 mmol). The mixture was extracted with ethyl acetate (25 mL x 3) and the solvent removed. Recrystallization using acetonitrile, MTBE, and pentane provided the product as a colorless solid (120 mg, 6%).

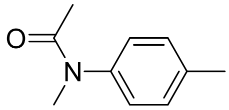
^{1}H NMR (CDCl$_3$, 400 MHz, 25 °C): δ 8.03 (d, *J* = 9.2, 2H), 8.02 (s, 1H), 7.94 (d, *J* = 7.4, 1H), 7.58 (dd, *J* = 8.1, 1.7; 1H), 7.54 (t, *J* = 7.9, 1H), 7.06 (d, *J* = 9.1, 2H), 3.84 (s, 3H), 3.21 (s, 3H), 1.82 (br s, 3H). ^{13}C NMR (CD$_3$CN, 100 MHz, 25 °C): δ 164.4, 148.0, 138.8, 134.3, 133.6, 132.3, 123.6, 120.4, 119.2, 114.5, 102.6, 56.7, 37.9, 22.8. ^{19}F NMR (CD$_3$CN, 376 MHz, 25 °C): δ -79.35 (s, 3F). HRMS (ESI) calculated for $C_{16}H_{17}NO_2I$ [M-OTf$^-$] 382.0298, found 382.0261.

N-Acetyltoluidine[9, 15] [16]



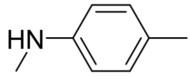
In a 100 mL round bottom flask, toluidine (1.0 g, 9.33 mmol) was treated with acetic anhydride (10 mL) and the mixture was stirred for 4 h at RT. The reaction solution was poured into ethyl acetate (25 mL), transferred to a separatory funnel, neutralized with saturated aqueous bicarbonate, and washed with water (10 mL). The organic layer was dried over sodium sulfate, filtered, and evaporated to provide a colorless solid (1.34 g, 97%) which was sufficiently pure for further use. ^{1}H NMR (CD$_3$CN, 400 MHz, 25 °C): δ 8.21 (s, 1H), 7.40 (d, *J* = 8.3, 2H), 7.10 (d, *J* = 8.3, 2H), 2.28 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (CD$_3$CN, 100 MHz, 25 °C): δ 169.7, 138.0, 134.4, 130.5, 120.8, 24.6, 21.2. HRMS (ESI) calculated for $C_9H_{11}ON$ 149.0841, found 149.0841.

N-acetyl-N-methyltoluidine[17, 18] [19]



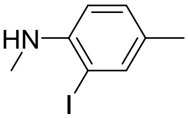
N-Acetyltoluidine (1.0g, 6.70 mmol) was dissolved in THF (10 mL) in a Schlenk-style storage tube equipped with a PTFE closure. Sodium hydride (0.48 g, 20.12 mmol) was added cautiously. Once the vigorous gas evolution was completed, methyl iodide (4.2 mL, 67.03 mmol) was added and the storage tube was sealed. The stirred reaction mixture was heated at 80 °C for 12 h. Upon completion of the reaction, the mixture was allowed to cool to RT, the solvent was removed by rotary evaporation, and the resulting solid was dissolved in ethyl acetate and transferred to a separatory funnel. The organic layer was washed with ammonium chloride until the washes were acidic, washed with water (10 mL), and dried over sodium sulfate. The solvent was removed to give a pale yellow solid (1.05g, 96%). ^{1}H NMR (CD$_3$CN, 400 MHz, 25 °C): δ 7.25 (d, *J* = 7.8, 2H), 7.13 (d, *J* = 8.3, 2H), 3.15 (s, 3H), 2.35 (s, 3H), 1.75 (s, 3H). ^{13}C NMR (CD$_3$CN, 100 MHz, 25 °C): δ 171.0, 143.8, 138.9, 131.5, 128.4, 37.6, 23.0, 21.5. HRMS (ESI) calculated for $C_{10}H_{13}ON$ 163.0997, found 163.0997.

N-methyl-toluidine[9, 20, 21] [22]



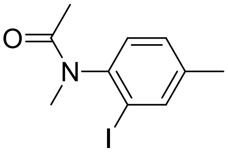
N-Acetyltoluidine (5.0g, 30.63 mmol) was dissolved in (400 mL) 80% Ethanol/water. Potassium hydroxide (17.2 g, 306.34 mmol) was added, and the stirred solution was heated at reflux for 36 hours. The ethanol was removed by rotary evaporation and the remaining aqueous solution was neutralized with sat. aq. ammonium chloride. The neutralized aqueous solution was extracted with diethyl ether (3 x 50 mL), and the combined organic extracts were washed with water (3 x 10 mL) and dried over sodium sulfate. Filtration to remove the drying agent and evaporation of the solvent afforded the product as an amber liquid (3.19 g, 86%). ^{1}H NMR (CDCl$_3$, 400 MHz, 25 °C): δ 7.03 (d, *J* = 8.36, 2H), 6.57 (d, *J* = 8.35, 2H), 3.57 (br, 1H), 2.84 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (CDCl$_3$, 100 MHz, 25°C): δ 147.4, 129.9, 126.7, 112.8, 31.3, 20.6. HRMS (ESI) calculated for $C_8H_{11}N$ 121.0891, found 121.0891

2-Iodo-N-methyltoluidine[23] [24]



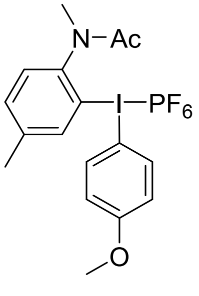
N-Methyltoluidine (1.0 g, 8.25 mmol) was dissolved in CH_2Cl_2 (20 mL) and sat. aq. bicarbonate (10 mL) was added. Iodine (2.3 g, 9.08 mmol) was added in portions, and the reaction mixture was allowed to stir slowly for 12 h at RT. The solution was transferred to a separatory funnel and extracted with CH_2Cl_2 (3 x 25 mL). The combined organic extracts were washed with brine (5 mL), dried over sodium sulfate, filtered and evaporated. The crude product was purified using silica gel flash chromatography (5% ethyl acetate in hexanes) to give a yellow oil (1.3g, 64%). [Note: The product co-eluted on the column with a small amount (7%) of the starting material, but it was sufficiently pure to carry through to the next step.] ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.51 (d, *J* = 1.6, 1H), 7.06 (dd, *J* = 8.2, 1.7; 1H), 6.49 (d, *J* = 8.2, 1H), 4.03 (s, 3H), 2.87 (d, *J* = 5.2, 3H), 2.22 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 146.3, 139.4, 130.3, 110.2, 85.4, 31.5, 20.0. HRMS (ESI) calculated for $C_8H_{10}IN$ 246.9858, found 246.9858.

N-acetyl-2-iodo-N-methyltoluidine[6]



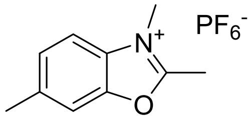
2-Iodo-N-methyltoluidine[23] (0.50 g, 2.02 mmol) was dissolved in acetic anhydride (10 mL) and the solution was stirred for 12 h. Saturated aqueous bicarbonate was added to bring the solution to neutral pH and the mixture was transferred to a separatory funnel. The mixture was extracted with diethyl ether (3 x 25 mL) and the combined organic extracts were dried over sodium sulfate, filtered, and evaporated, leaving a yellow oil (0.31 g, 58%). [Note: two rotamers (R: rotamer) are visible due to restricted rotation of the amide bond.] ^1H NMR (CD_3CN, 400 MHz, 25 °C): δ 7.82 (s, 0.9H), 7.75 [R] (s, 0.1H), 7.29 (d, *J* = 9.0, 0.9H), 7.26 (d, *J* = 8.0, 0.9H), 7.23 [R] (d, *J* = 9.0, 0.1H) 7.11 [R] (d, *J* = 8.0, 0.1H), 3.20 [R] (s, 0.2H), 3.05 (s, 2.8H), 2.33 (s, 0.8H) 2.30 [R] (s, 0.2H), 2.15 [R] (s, 0.2H), 1.68 (s, 2.8H). ^{13}C NMR (CD_3CN, 100 MHz, 25 °C): δ 170.8, 145.5, 141.9, 141.5, 132.3, 130.1, 118.7, 100.4, 36.4, 23.1, 20.9. HRMS (ESI) calculated for $C_{10}H_{12}NOI$ 288.9964, found 288.9964.

(5-Methyl-2-(N-methyl-N-acetamido)phenyl)(4'-methoxyphenyl)iodonium hexafluorophosphate[6]



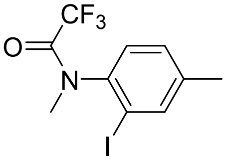
In a glovebox under nitrogen, N-acetyl-2-iodo-N-methyltoluidine (2.00 g, 6.92 mmol) and Selectfluor™ (3.19 g, 8.99 mmol) were dissolved in dry acetonitrile (20 mL). TMSOAc (2.90 mL, 19.37 mmol) was added dropwise to the solution. The reaction was heated to 60 °C in a sealed vessel for 5 h. The solution was allowed to cool to room temperature and potassium (4-methoxyphenyl)trifluoroborate (1.48 g, 6.92 mmol) was added, followed by a slow addition of TMSTFA (1.31 mL, 7.61 mmol). The reaction was stirred for 10 min before the reaction vessel was removed from the glove box. The solvent was removed by rotary evaporation and the remainder was dissolved in 150 mL of acetate buffer and transferred to a separatory funnel. The mixture was washed with EtOAc (50 mL), and extracted with CH_2Cl_2 (25 mL x 10). The CH_2Cl_2 extracts were combined, dried over Na_2SO_4, filtered, and the solvent was removed by rotary evaporation. The resulting solid was dissolved in minimal acetonitrile and added to an aqueous solution of sodium hexafluorophosphate (5.81g, 34.6 mmol) to precipitate the desired product. After decanting the liquid, the solid was dissolved in CH_2Cl_2 (400mL) and ethyl ether added until the cloud point was reached. Upon standing overnight, a colorless solid formed. The precipitated solid was isolated by vacuum filtration, triturated with pentane and placed under dynamic high vacuum for 12 h, yielding a colorless solid (1.92 g, 51%). [Note: two rotamers (R: rotamer) are visible due to restricted rotation of the amide bond.] ^1H NMR (CD_3CN, 400 MHz, 25 °C): δ 8.01 (d, $J = 8.8$, 2H), 7.93 [R] (br), 7.60 [R] (br), 7.55 (s, 1H), 7.50 (d, $J = 8.1$, 1H), 7.41 (d, $J = 8.2$, 1H), 7.08 (d, $J = 9.0$, 2H), 3.86 (s, 3H), 3.50 (s, 2.3H), 3.09 [R] (s, 0.7H), 2.44 [R] (s, 0.7H), 2.33 (s, 2.3H), 2.28 (s, 2.3H) 1.35 [R] (s, 0.7H). ^{13}C NMR (CD_3CN, 100 MHz, 25 °C): δ 176.1, 164.9, 142.1, 142.0, 139.8, 135.6, 134.9, 127.7, 119.4, 116.6, 103.4, 57.1, 40.6, 23.3, 21.1 ^{19}F NMR (CD_3CN, 376 MHz, 25 °C): δ -73.0 (d, $J = 707.0$, 6F). HRMS (ESI) calculated for $C_{17}H_{19}O_2NI$ [M-PF_6^-] 396.0455, found 396.0461.

2,3,6-trimethylbenzoxazolium hexafluorophosphate.



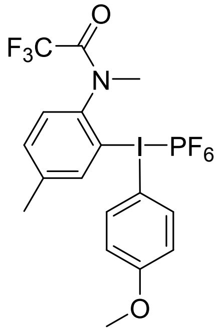
In a sealed tube (5-methyl-2-(N-methyl-N-acetimido)phenyl)(4'-methoxyphenyl)iodonium hexafluorophosphate was dissolved in dry acetonitrile and heated at 100 °C for 2 hours. Upon removal of the solvent and drying of the remaining solid under dynamic high vacuum for 12 h, the title compound was recovered in quantitative yield. ^1H NMR (CD_3CN, 400 MHz, 25 °C): δ 7.74 (d, $J = 8.6$, 1H), 7.73 (d, $J = 8.6$, 1H), 7.59 (d, $J = 8.6$, 1H), 3.98 (s, 3H), 2.96 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (CD_3CN, 100 MHz, 25 °C): 142.0, 130.4, 114.6, 113.7, 33.8, 21.8, 13.7. ^{19}F NMR (CD_3CN, 376 MHz, 25 °C): δ -73.0 (d, $J = 706.7$, 6F). MS (ESI) calculated for $C_{10}H_{12}ON^+$ [M-PF_6^-] 162.0913, found 162.07.

N-trifluoroacetyl-2-iodo-N-methyltoluidine[6]



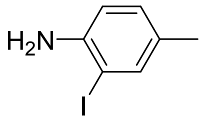
2-Iodo-N-methyltoluidine[23] (9.0g, 31.13 mmol) was dissolved in anhydrous THF (50 mL) and chilled to -78 °C under nitrogen. Trifluoroacetic anhydride (8.66 mL, 62.26 mmol) was added dropwise and the reaction was stirred for 10 min. The solution was allowed to warm to room temperature and stirred for an additional 1 h. The solvent was removed by rotary evaporation and the remaining material was treated with sat. aq. bicarbonate and transferred to a separatory funnel with the aid of methylene chloride. The mixture was extracted with CH_2Cl_2 (25mL x 3) and the combined organic extracts were dried over sodium sulfate, filtered, and evaporated. The remaining solid was recrystallized from boiling pentane to yield amber crystals, which were isolated by filtration and dried in vacuo (9.90 g, 93%). [Note: two rotamers (R: rotamer) are visible due to restricted rotation of the amide bond.] ^1H NMR (CD_3CN, 400 MHz, 25 °C): δ 7.83 (d, $J = 0.8$, 0.8H), 7.82[R] (d, $J = 0.8$, 0.2H), 7.34 (d, $J = 8.0$, 0.8H) 7.29 (dd, $J = 8.1,0.6$, 1H), 7.25 [R] (d, $J = 8.0$, 0.2H), 3.36 [R] (q, $J = 1.65$, 0.5H), 3.22 (s, 2.5H), 2.33 (s, 3H). ^{13}C NMR (CD_3CN, 100 MHz, 25 °C): δ 157.7, 157.4, 143.1, 142.4, 141.7, 141.6, 132.3, 131.7, 130.4, 129.0, 119.1, 116.2, 99.6, 39.3, 21.0 ^{19}F NMR (CD_3CN, 376 MHz, 25 °C): δ -68.99 (s, 2.5F), -71.05 [R] (q, $J = 1.64$, 0.5F). HRMS (ESI) calculated for $C_{10}H_9F_3NIO$ 342.9681, found 342.9681.

(5-Methyl-2-(N-methyl-N-trifluoroacetamido)phenyl) (4'-methoxyphenyl)iodonium hexafluorophosphate[6]



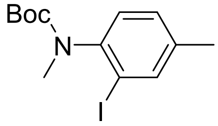
In a glove box under nitrogen, N-trifluoroacetyl-2-iodo-N-methyltoluidine (5.00 g, 14.57 mmol) and Selectfluor™ (6.71 g, 18.94 mmol) were dissolved in dry acetonitrile (50 mL). TMSOAc (6.12 mL, 40.80 mmol) was added to the solution dropwise. The stirred reaction mixture was heated in a sealed container to 40 °C for 2 h and 60 °C for 4 h. The stirred reaction mixture was allowed to cool to room temperature before potassium (4-methoxyphenyl)trifluoroborate (3.27 g, 15.30 mmol) was added, followed by TMSTFA (2.77 mL, 16.03 mmol), which was added dropwise. After 10 min the reaction vessel was removed from the glove box and the mixture concentrated by rotary evaporation. The remaining oil was added to an aqueous solution of sodium hexafluorophosphate (12.2g, 72.64 mmol). This solution was extracted with 50 mL of CH_2Cl_2, and the organic extract was washed with acetate buffer (3 x 20 mL) and water (3 x 20 mL), and dried over sodium sulfate. The organic extract was filtered and evaporated, and the remaining oil was triturated with pentane and placed under dynamic high vacuum, forming an amber solid. The solid was dissolved in 5 mL CH_2Cl_2 and MTBE was added dropwise to reach the cloud point. This cloudy mixture was added dropwise to hexane to precipitate the product as a white solid (4.80 g, 52%), which was isolated by filtration and dried under reduced pressure for 12 h. [Note: two rotamers are visible due to restricted rotation of the amide bond.] ^{1}H NMR (CD_3CN, 400 MHz, 25 °C): δ 8.02 (s, 0.5H), 8.01 (s, 0.5H), 7.97 (d, *J* = 9.2 0.5H), 7.94 (d, *J* = 9.2, 0.5H), 7.64 (br d, 0.5H), 7.62 (br d, 0.5H), 7.56 (br d, 0.5H), 7.54 (br d, 0.5H), 7.08 (d, *J* = 8.8, 1H), 7.06 (d, *J* = 8.8, 1H), 3.85 (s, 3H), 3.44 (s, 1.5H), 3.28 (s, 1.5H), 2.43 (s, 1.5H), 2.41 (s, 1.5H). ^{13}C NMR (CD_3CN, 100 MHz, 25 °C): δ 165.2, 164.9, 145.9, 144.9, 141.6, 140.1, 139.2, 138.9, 138.6, 137.3, 136.8, 131.9, 130.0, 119.9, 119.6, 116.0, 115.7, 102.5, 101.2, 57.2, 27.2, 40.8, 40.3, 21.4, 21.3. ^{19}F NMR (CD_3CN, 376 MHz, 25 °C): δ -68.49 (s, 1.5F), -70.78 (s, 1.5F), -72.87 (d, *J* = 706.5, 6F). HRMS (ESI) calculated for $C_{17}H_{16}NO_2F_3I$ [M-PF_6^-] 450.0172, found 450.0178.

2-Iodotoluidine[25]



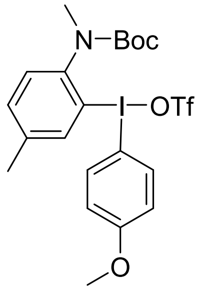
Toluidine (5.0 g, 46.7 mmol) was dissolved in dichloromethane (40 mL) and saturated aqueous sodium bicarbonate (40 mL) was added. Iodine (11.9 g, 46.9 mmol) was added in portions to the slowly stirred biphasic solution, and the reaction mixture was stirred at room temperature for 3 days. The organic layer was separated, and the aqueous layer extracted with CH_2Cl_2 (10 mL x 3). The combined organic extracts were washed once with an aqueous solution of sodium thiosulfate (10 g/L $Na_2S_2O_3$ in brine, 10 mL), dried over sodium sulfate, filtered and evaporated. The product was purified by column chromatography (5% ethyl acetate in hexanes) to give a red oil (10.9 g, 84%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.48 (d, J = 1.1, 1H), 6.96 (dd, J = 8.1, 1.4, 1H), 6.67 (d, J = 8.1, 1H), 3.95 (br s, 2H), 2.22 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 144.4, 139.2, 130.2, 129.6, 114.8, 84.4, 20.0. HRMS (ESI) calculated for C_7H_8NI 232..9701, found 232.9102.

N-Boc-N-methyl-2-iodotoluidine[26]



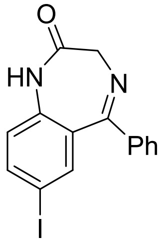
Lithium hexamethyldisilazide solution (1 M in THF, 42.9 mL, 42.9 mmol) was transferred to a dry Schlenk tube and chilled to -40 °C with stirring. 2-Iodotoluidine (5.0 g, 21.5 mmol) was dissolved in dry THF (17.5 mL), and added slowly to the stirred LiHMDS solution. After 10 minutes, di-*tert*-butyl dicarbonate (4.78 g, 21.9 mmol) dissolved in dry THF (17.5 mL) was added. After a further 10 min at -40 °C, the reaction flask was placed in an ice bath and the stirred reaction mixture was held at 0 °C 1 h. Methyliodide (2.67 mL, 42.9 mmol) was added dropwise, the ice bath was removed, and the reaction was allowed to stir at RT for 1 hour. Water (50 mL) and CH_2Cl_2 (50 mL) were added and the organic layer was separated. The aqueous layer was extracted further with CH_2Cl_2 (50 mL x 3), and the combined organic extracts were dried over sodium sulfate, filtered, and evaporated. The remainder was purified by column chromatography (5% ethyl acetate in hexanes) to obtain a viscous pale amber oil (6.51 g, 87%). ^1H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.68 (s, 1H), 7.14 (d, J = 8.9, 1H), 7.07 (d, J = 8.0, 1H), 3.12 (s, 3H), 2.32 (s, 3H), 1.54 (s, 2H), 1.36 (s, 7H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 154.5, 143.5, 140.1, 139.8, 138.8, 130.1, 128.0, 99.3, 80.1, 36.6, 28.6, 28.4, 20.6. HRMS (ESI) calculated for $C_{13}H_{18}O_2NI$ 347.0382, found 347.0382.

(2-((Boc)(methyl)amino)-5-methylphenyl)(4'-methoxyphenyl)iodonium trifluoromethansulfonate



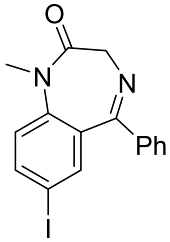
N-Boc-N-methyl-2-iodotoluidine (525 mg, 1.51 mmol) was dissolved in dry THF. The solution was chilled to -78 °C and *iso*-propylmagnesium chloride (2 M in THF, 1.13 mL, 2.26 mmol) was added slowly with stirring. This reaction mixture was stirred for 1 hour at -78 °C to effect the transmetalation. 4-Methoxyphenyliodonium diacetate (1.6 g, 4.54 mmol) was dissolved in dry THF and this solution was also chilled to -78 °C. The Grignard reagent solution was added through a chilled cannula to the stirred solution of iodonium diacetate. The reaction mixture was allowed to warm slowly to room temperature overnight. The reaction was poured into acetate buffer (50 mL), extracted with ethyl acetate (25 mL x 4), washed with water (10 mL), dried over sodium sulfate, and the solvents were removed under reduced pressure. Acetonitrile (10 mL) was added to the residue and sodium trifluoromethanesulfonate (1.3 g, 7.6 mmol, in 10 mL water) was added. After stirring for 1.5 hours, the acetonitrile was removed by rotary evaporation. The remaining aqueous solution was extracted with ethyl acetate (25 mL x 3), and the combined organic extracts were washed with water (10 mL), dried over sodium sulfate, and evaporated. The residue was dissolved in acetonitrile (10 mL), MTBE (25 mL) added and the mixture was allowed to stand overnight. The solution was filtered to yield the product as colorless crystals (0.090 g, 5%). ^1H NMR (CD_3CN, 700 MHz, 60 °C): δ 7.98 (d, J = 9.0, 2H), 7.62 (s, 1H), 7.50 (d, J = 8.1, 1H), 7.44 (d, J = 8.1, 1H), 7.09 (d, J = 9.0, 2H), 3.88 (s, 3H), 3.28 (s, 3H), 2.32 (s, 3H), 1.52 (br s, 9H). ^{13}C NMR (CD_3CN, 175 MHz, 60 °C): δ 164.6, 142.5, 142.0, 139.5, 135.7, 135.5, 128.4, 123.5, 121.7, 119.5, 102.8, 84.4, 57.1, 38.7, 28.8, 21.0. ^{19}F NMR (CD_3CN, 376 MHz, 25 °C): δ -79.33 (s, 3F). HRMS (ESI) calculated for $C_{20}H_{25}O_3NI$ 454.0874 [M-OTf$^-$], found 454.0879.

7-Iodo-5-phenyl-1,3-dihydro-2H-benzo[e][1,4]diazepin-2-one



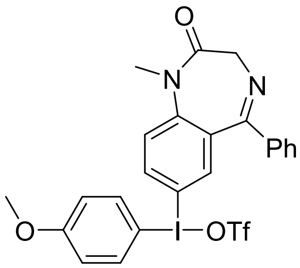
2-Amino-5-iodo-benzophenone[27] (5.0 g, 15.5 mmol), glycine methyl ester hydrochloride (3.9 g, 31 mmol), and a catalytic amount of piperidine were dissolved in pyridine (31 mL). The solution was heated at reflux for 24 h in a Dean-Stark apparatus in which 4 Å molecular sieves were placed in the recirculation sidearm. The solvent was removed at 60 °C by rotary evaporation to give a tarry residue, which was partitioned between water (50 mL) and ethyl acetate (50 mL). The organic layer was separated and the aqueous layer was treated with 1 M KOH until it was strongly basic. The aqueous solution was extracted with ethyl acetate (3 x 50 mL), the combined organic layers washed with brine (25 mL), dried over sodium sulfate and the solvent was removed by rotary evaporation. The remainder was purified by silica gel column chromatography (2:1 ethyl acetate:hexanes) to give a light brown solid (2.9 g, 52%). ^{1}H NMR (CDCl$_3$, 600 MHz, 25 °C): δ 9.42 (s, 1H), 7.54 (d, *J* = 7.6, 2H), 7.51 (t, *J* = 7.6, 1H), 7.45 (t, *J* = 7.1, 1H), 7.38 (t, *J* = 7.4, 2H), 7.33 (d, *J* = 7.7, 1H), 7.20 (d, *J* = 8.1, 1H), 7.15 (t, *J* = 7.5, 1H), 4.34 (br s, 2H). ^{13}C NMR (CDCl$_3$, 150 MHz, 25 °C): δ 172.4, 171.3, 139.7, 139.0, 131.9, 131.6, 130.5, 129.9, 128.4, 127.5, 123.5, 121.4, 56.9. HRMS (ESI) calculated for $C_{15}H_{11}N_2OI$ 361.9916, found 361.9916.

7-iodo-1-methyl-5-phenyl-1,3-dihydro-2H-benzo[e][1,4]diazepin-2-one[28]



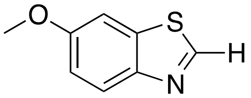
7-Iodo-5-phenyl-1,3-dihydro-2H-benzo[e][1,4]diazepin-2-one (0.10 g, 0.28 mmol) was dissolved in dry DMF (10 mL) and stirred magnetically while sodium hydride (8 mg, 0.33 mmol) was added in portions. Methyl iodide (26 µL, 0.42 mmol) was added to the precipitated sodium salt and the flask was shaken to free the stir bar. The solution was stirred at RT for a further 30 minutes before ethyl acetate (25 mL) and water (5 mL) were added. The reaction mixture was transferred to a separatory funnel and the organic layer was washed with brine (3 x 10 mL), dried over sodium sulfate, filtered, and the solvent was removed by rotary evaporation. After drying under dynamic high vacuum overnight, the product was recovered as a light tan solid (63 mg, 61%). ^{1}H NMR (CDCl$_3$, 700 MHz, 25 °C): δ 7.84 (dd, *J* = 8.7, 1.9; 1H), 7.6 (d, *J* = 2.0, 1H), 7.60 (d, *J* = 7.5, 2H), 7.48 (d, *J* = 7.4, 1H), 7.11 (d, *J* = 8.7, 1H), 4.84 (d, *J* = 10.8, 1H), 3.78 (d, *J* = 10.9, 1H), 3.39 (s, 3H). ^{13}C NMR (CDCl$_3$, 176 MHz, 25 °C): δ 169.9, 168.8, 143.8, 140.2, 138.8, 138.2, 130.7, 129.5, 128.4, 122.9, 87.4, 56.9, 34.8. HRMS (ESI) calculated for $C_{16}H_{13}N_2OI$ 376.0073, found 376.0073.

(7-Iodo-1-methyl-5-phenyl-1,3-dihydro-2H-benzo[e][1,4]diazepin-2-one)(4'-methoxyphenyl)iodonium trifluoromethansulfonate



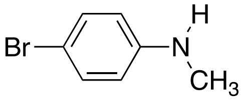
In a glove box under nitrogen, 7-iodo-1-methyl-5-phenyl-1,3-dihydro-2H-benzo[e][1,4]diazepin-2-one (3.00 g, 7.97 mmol) and Selectfluor^{TM} (3.67 g, 10.36 mmol) were dissolved in dry acetonitrile (30 mL). TMSOAc (3.36 mL, 22.32 mmol) was added to the solution dropwise. The reaction mixture was heated in a sealed container at 60 °C for 3 h with stirring and then allowed to cool to room temperature. Potassium (4-methoxyphenyl)trifluoroborate (1.92 g, 8.76 mmol) was added to the stirred reaction mixture, followed by dropwise addition of TMSTFA (1.38 mL, 8.0 mmol). The solution was stirred for 10 min before the reaction vessel was removed from the glove box and the solvent was removed under reduced pressure. The remainder was treated with the minimum amount of acetonitrile needed to dissolve it, and this solution was added to an aqueous solution of sodium hexafluorophosphate (6.7 g, 40 mmol). The solution was filtered and the solid was retained. The filtrate was extracted with CH_2Cl_2 (3 x 25 mL). The combined organic layers were added to the recovered solid and the resulting solution was dried over sodium sulfate, filtered to remove the drying agent, and the solvent was removed by rotary evaporation. The resulting oil was dissolved in acetonitrile (40 mL) diluted with ethyl acetate (200 mL). MTBE was added until the solution reached the cloud point (250 mL). The solution was allowed to stand at room temperature overnight to precipitate the product. The solution was filtered and more MTBE added until the solution again reached the cloud point and the process was repeated to obtain a second crop. The product was recovered as a colorless crystalline solid (3.0 g, 60%). The initially isolated hexafluorophosphate salt (2 g, 3.2 mmol) was converted to the triflate salt using an IRA-400 ion exchange column. Removal of the solvent followed by recrystallization as above yielded the colorless crystalline product (1.5 g, 75%). ^{1}H NMR (CD_3CN, 400 MHz, 25 °C): δ 8.16 (dd, *J* = 9.0, 2.3; 1H), 7.93 (d, *J* = 9.1, 2H), 7.84 (d, *J* = 2.2, 1H), 7.53 (t, *J* = 8.1, 2H), 7.45 (d, *J* = 7.1, 2H), 7.39 (t, *J* = 7.6, 2H), 7.03 (d, *J* = 9.1, 2H), 4.65 (d, *J* = 10.8, 1H), 3.86 (s, 3H), 3.74 (d, *J* = 10.8, 1H), 3.33 (s, 3H). ^{13}C NMR (CD_3CN, 176 MHz, 25 °C): δ 170.3, 169.1, 164.4, 148.4, 138.9, 138.7, 138.7, 138.0, 137.9, 132.5, 131.8, 130.4, 129.4, 126.1, 119.1, 107.4, 102.8, 57.8, 56.8, 35.2. ^{19}F NMR (CD_3CN, 376 MHz, 25 °C): δ -79.31 (s, 3F). HRMS (ESI) calculated for $C_{23}H_{20}N_2O_2I$ [M-(OTf)] 483.0564, found 483.0569.

6-Methoxybenzothiazole[29]



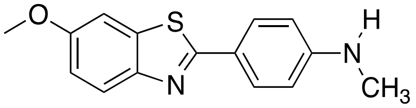
Tert-butyl nitrite (18.5 mL, 155.2 mmol) was dissolved in 50 mL of THF and heated at reflux under N_2. 2-Amino-6-methoxybenzothiazole (14.00 g, 77.6 mmol) was dissolved in 150 mL THF and added dropwise with a pressure-equalizing addition funnel over 1 h. The solution was heated at reflux for an additional 3 h under N_2 before it was cooled to room temperature. The solution was diluted with ethyl ether (100 mL) and washed three times with sodium thiosulfate in brine (10 g/L). The aqueous layers were extracted once with ethyl ether. The combined organic layers were dried over sodium sulfate, filtered, and the solvent was removed under reduced pressure. The crude oil was precipitated with ether and filtered. The filtrate was concentrated in vacuo to yield an oily orange solid, which was chromatographed on silica with ethyl acetate/hexanes (1:1, v/v). The orange solid was sublimated under high dynamic vacuum, at 60 °C to give a pale yellow solid. This crude product was dissolved in boiling hexanes and cooled slowly to room temperature to yield a colorless solid (8.05 g, 63 %). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 8.83 (s, 1H), 8.01 (d, *J* = 9.0, 1H), 7.40 (d, *J*=2.4, 1H), 7.13 (dd, *J*=9.0, 2.4, 1H), 3.89 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 158.3, 151.7, 147.9, 135.3, 124.2, 116.1, 104.2, 56.0; HRMS: (EI) calculated for C_8H_7NOS $[M]^+$ 165.0248 found 165.0248.

4-Bromo-*N*-methylaniline[30]



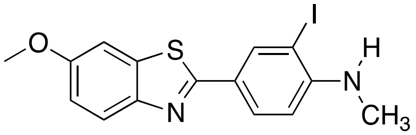
N-methylaniline (10.8 mL, 0.10 mol) was dissolved in DCM (85 mL) in a 500 mL round bottom flask. The solution was cooled to -20 °C with a sodium chloride/ice bath. Tetraethylammonium chloride (1.66 g, 0.01 mol) was dissolved in methanol (2.0 mL) and added to the flask. Bromine (5.64 mL, 0.11 mmol) was dissolved in 15 mL of DCM and added by syringe pump over the course of 1 hour. The flask was protected from light and solution was allowed to warm slowly to room temperature (12 h). The reaction mixture was neutralized with saturated aqueous sodium bicarbonate and transferred to a separatory funnel. The organic layer was washed twice with saturated aqueous sodium bicarbonate and once with brine, dried over sodium sulfate, filtered, and solvent was removed in vacuo. The crude liquid was fractionally distilled at 100 mTorr (boiling point 58–61 °C) to yield a yellow liquid (12.53 g, 67 %). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.28 (d, *J* = 8.7, 2H), 6.50 (d, *J* = 8.7, 2H), 3.74 (br s, 1H), 2.83 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 148.4, 132.1, 114.2, 109.1, 31.0; HRMS: (EI) calculated for C_7H_8BrN $[M]^+$ 184.9840 found 184.9840.

2-(4-(Methylamino)phenyl)-6-methoxybenzothiazole[31]



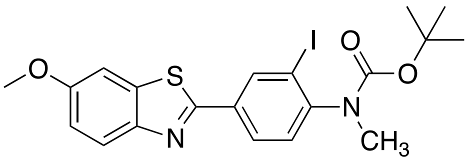
In a nitrogen-charged glove box, 6-methoxybenzothiazole (7.00 g, 42.4 mmol), 4-bromo-*N*-methylaniline (9.46 g, 50.9 mmol), palladium(II) acetate (0.48 g, 2.1 mmol), tri(*tert*-butyl)phosphine (0.86 g, 4.2 mmol), and copper(I) bromide (1.22 g, 8.5 mmol) were dissolved in dry DMF (200 mL). The mixture was transferred to a 500 mL airfree storage flask equipped with a threaded PTFE closure. Solid cesium carbonate (15.19 g, 46.6 mmol) was added directly to the flask. The reaction flask was sealed and the stirred solution was heated at 150 °C for 4 h. The mixture was cooled to RT, diluted with ether, transferred to a separatory funnel, and washed five times with water. The aqueous layers were extracted three times with ether. The combined organic layers were washed with brine, dried over sodium sulfate, and filtered. The solvent was removed in vacuo and the crude oil was chromatographed on silica with ethyl acetate/hexanes/dichloromethane (1:4:5 v/v/v) to yield a pale yellow solid (7.94 g, 69%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.88 (d, *J* = 8.6, 1H), 7.87 (d, *J* = 9.0, 1H), 7.33 (d, *J* = 2.5, 1H), 7.05 (dd, *J* = 9.0, 2.5, 1H), 6.65 (d, *J* = 8.6, 1H), 4.10 (br q, *J* =5.0, 1H), 2.91 (d, *J* = 5.0, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 166.7, 157.4, 151.5, 149.0, 135.9, 129.0, 123.0, 122.9, 115.2, 112.3, 104.6, 77.5, 77.2, 76.9, 56.0, 30.6; HRMS: (ESI) calculated for $C_{15}H_{14}N_2NaOS$ $[M + Na]^+$ 293.0725 found 293.0737.

2-(3-Iodo-4-(methylamino)phenyl)-6-methoxybenzothiazole



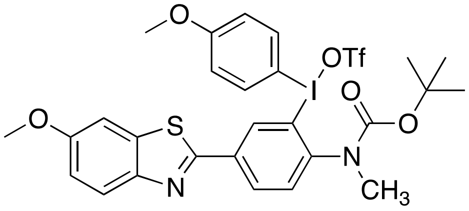
In a Schlenk storage tube equipped with a threaded PTFE closure, 2-(4-(methylamino)phenyl)-6-methoxybenzothiazole (1.00 g, 2.5 mmol) was dissolved in DCM (20 mL). Iodine (1.28 g, 5.0 mmol) and saturated aqueous sodium bicarbonate (5 mL) were added and the biphasic reaction mixture was heated to 50 °C for 3 days (unstirred). After the solution was cooled to RT, more iodine (1.92g, 7.5 mmol) was added, the solution was stirred briefly to mix and heated for an additional 2 days at 50 °C (unstirred). The solution was diluted with DCM and brine, transferred to a separatory funnel, and the layers were separated. The organic layer was washed three times with small portions of sodium thiosulfate in brine (10 g/L), and washed once with brine. The organic layer was dried over sodium sulfate, filtered, and the solvent was removed in vacuo. The black solid was triturated three times with boiling MTBE and filtered. MTBE was removed in vacuo, and the crude solid was chromatographed on silica with ethyl acetate/hexanes (90:10 v/v) to yield a light orange solid (468.0 mg, 32%). ^{1}H NMR (CD_2Cl_2, 400 MHz, 25 °C): δ 8.38 (d, *J* = 2.0, 1H), 7.88 (dd, *J* = 8.6, 2.0, 1H), 7.82 (d, *J* = 8.9, 1H), 7.35 (d, *J* = 2.5, 1H), 7.04 (dd, *J* = 8.9, 2.5, 1H), 6.61 (d, *J* = 8.6, 1H), 4.64 (q, *J* = 5.0, 1H), 3.87 (s, 3H), 2.96 (d, *J* = 5.0, 3H); ^{13}C NMR (CD_2Cl_2, 100 MHz, 25 °C): δ 164.7, 158.0, 150.6, 149.3, 138.0, 136.5, 129.3, 124.6, 123.4, 115.7, 109.8, 104.9, 84.9, 56.3, 31.2; HRMS: (ESI) calculated for $C_{15}H_{14}IN_2NaOS$ $[M + Na]^+$ 418.9691 found 418.9680.

2-(4-(*N*-*Boc*-3-iodo-*N*-methyl)phenyl)-6-benzothiazole



2-(3-Iodo-4-(methylamino)phenyl)-6-methoxybenzothiazole (1.43 g, 3.60 mmol) was dissolved in 25 mL of THF. DMAP (1.32 g, 10.80 mmol) and triethylamine (1.5 mL, 10.80 mmol) were added. Di-*tert*-butyl dicarbonate (4.71 g, 21.60 mmol) was added in portions to the stirred solution, and the mixture was stirred for 3 days under N_2. The solvent was removed in vacuo, and the remaining oily solid was dissolved the minimum amount of DCM. Impurities were precipitated by adding 10% diethyl ether in hexanes, and they were removed by filtration. The filtrate was reduced in vacuo and chromatographed on silica (deactivated with triethylamine/hexanes (5:95 v/v)) with triethylamine/ethyl acetate/hexanes (0.5:15:84.5 v/v). The crude solid crystallized from ethyl acetate/ether/hexanes after the solution was cooled from RT to -4 °C, to yield a white solid (1.25 g, 70%). [Note: two rotamers are visible due to restricted rotation of the carbamate bond] ^{1}H NMR (CD_3CN, 400 MHz, 25 °C): δ 8.50 (d, *J* = 1.9, 1H), 7.99 (br d, *J* = 8.2, 1H), 7.88 (d, *J* = 9.0, 1H), 7.51 (d, *J* = 2.5, 1H), 7.38 (d, *J* = 8.2, 1H), 7.11 (dd, *J* = 9.0, 2.5, 1H), 3.86 (s, 3H), 3.13 (br s, 1.2H), 3.10 (br s, 1.8H), 1.52 (br s, 2.6H), 1.33 (br s, 6.4H); ^{13}C NMR (CD_3CN, 100 MHz, 25 °C): δ 163.4, 159.3, 154.5, 149.5, 138.2, 137.8, 134.9, 130.2, 129.1, 124.8, 117.1, 105.5, 101.0, 81.0, 56.6, 36.8, 28.5, 28.2; HRMS: (ESI) calculated for $C_{20}H_{21}IN_2NaO_3S$ $[M + Na]^+$ 519.0215 found 519.0224.

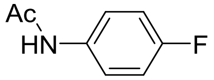
(2-(*N*-Boc-*N*-methyl)amino-5-(6-methoxybenzothiazolyl))(4-methoxyphenyl)iodonium triflate



In a nitrogen-charged glovebox, 2-(3-iodo-4-(*N*-Boc-*N*-methyl)phenyl)-6-benzothiazole (550.14 mg, 1.11 mmol) was dissolved in 5 mL of dry THF and placed in a (flame-dried) 50 mL Schlenk tube. The solution was chilled to -78 °C before *i*PrMgCl (2.0 M in THF, 1.1 mL, 2.22 mmol) was added dropwise, with stirring. The solution was stirred for 5 minutes, and transferred by cannula to another 50 mL flame-dried Schlenk tube, containing *bis*(acetoxy)iodoanisole (1.17 g, 3.33 mmol) in 10 mL of dry THF, at -78 ˚C. The solution was stirred for 15 minutes at -78 ˚C, the reaction vessel was shielded from light using aluminum foil, and the reaction mixture was allowed to warm slowly to room temperature over the course of 12 h. The solution was concentrated in vacuo and diluted with 15 mL of methanol. Sodium triflate (1.91 g, 11.10 mmol) was dissolved in 10 mL of water/methanol (1:2, v/v) and added dropwise to the vigorously stirred solution. After 30 minutes, the mixture was concentrated in vacuo to remove methanol, and the remaining aqueous solution was transferred to a separatory funnel and extracted three times with DCM. The organic layers were dried over sodium sulfate and solvent was removed in vacuo. The crude oil was sonicated with hexanes and filtered. The solid was sonicated in 15 mL ethyl acetate, chilled to 0 ˚C, and filtered. The solid was sonicated again in 15 mL ethyl acetate, chilled to 0 ˚C, and filtered to yield a pale yellow solid (0.243 g, 29.1%). ^{1}H NMR (CD_3CN, 400 MHz, 25 °C): δ 8.36 (br s, 1H), 8.22 (dd, *J* = 8.5, 1.8, 1H), 8.08 (d, *J* = 9.0, 2H), 7.88 (d, *J* = 8.9, 1H), 7.64 (d, *J* = 8.5, 1H), 7.54 (d, *J* = 2.5, 1H), 7.14 (dd, *J* = 8.9, 2.5, 1H), 7.12 (d, *J* = 9.0, 2H), 3.87 (s, 3H), 3.86 (s, 3H), 3.37 (br s, 3H), 1.56 (s, 9H); ^{19}F NMR (CD3CN, 376 MHz, 25 °C): δ -79.30 (s, 1F); ^{13}C NMR (CD_3CN, 100 MHz, 25 °C): δ 187.3, 164.7, 164.7, 162.4, 159.5, 149.3, 139.6, 137.9, 132.7, 124.9, 123.8, 119.2, 118.4, 117.5, 105.6, 56.8, 56.7, 38.5, 28.5, 1.8, 1.6, 1.4, 1.2, 1.0; HRMS: (ESI) calculated for $C_{27}H_{28}IN_2O_4S$ $[M-(OTf)]^+$ 603.0809 found 603.0795.

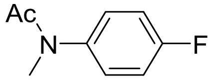
Synthesis of fluorinated standards

4-Fluoroacetanilide[32, 33] [34]



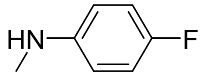
4-Fluoraniline (5 mL, 52 mmol) was dissolved in acetic anhydride and stirred at room temperature for two hours. The reaction solution was poured into ice water and neutralized with bicarbonate. The product was extracted with ethyl ether (3 x 50 mL), dried over sodium sulfate, and the solvent removed. The product was recrystallized from 1:1 ethanol:water to yield light purple crystals (3.35 g, 42%). ^{1}H NMR (CDCl$_3$, 400 MHz, 25 °C): δ 7.46 (dd, *J* = 9.0, 4.8, 2H), 7.13 (s, 1H), 7.02 (t, *J* = 8.7, 2H), 2.18 (s, 3H) ^{13}C NMR (CDCl$_3$, 100 MHz, 25 °C): δ 168.7, 159.6 (d, *J* = 243.5), 134.0, 129.9, 122.1 (d, *J* = 7.9), 115.8 (d, *J* = 22.5), 24.5 ^{19}F NMR (CDCl$_3$, 376 MHz, 25 °C): δ -118.0 (sept, *J* = 4.4, 1F).

4-Fluoro-N-methylacetanilide[35]



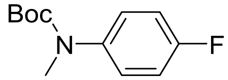
In a resealable flask equipped with a PTFE closure, 4-fluoroacetanilide (3.0 g, 20 mmol) was dissolved in THF (30 mL). Sodium hydride (1.41 g, 60 mmol) was added carefully followed by methyl iodide (6.1 mL, 100 mmol). The storage flask was sealed and the reaction mixture was stirred and heated at 80 °C for 12 h. The solution was allowed to cool to RT, neutralized with sat. aq. ammonium chloride, and transferred to a separatory funnel. The solution was extracted with ether (3 x 25 mL), and the organic extracts were dried over sodium sulfate, filtered, and the solvent was removed by rotary evaporation. After drying under dynamic high vacuum overnight, the product was obtained as a pale yellow solid (2.5 g, 76%). [Note: two rotamers (R: rotamer) are visible due to restricted rotation about the amide bond.] ^{1}H NMR (CD$_3$CN, 400 MHz, 25 °C): δ 7.29 (br dd, 2H), 7.17 (t, *J* = 8.3, 2H), 3.15 (s, 3H), 1.75 (s, 2.6H), 0.96 [R] (s, 0.4) ^{13}C NMR (CD$_3$CN, 100 MHz, 25 °C): δ 171.0, 162.9 (d, *J* = 244.3), 142.6, 130.7 (d, *J* = 8.4), 117.6 (d, *J* = 22.8), 37.6, 23.0 ^{19}F NMR (CD$_3$CN, 376 MHz, 25 °C): δ -116.2 (s, 0.9F), -118.1 [R] (s, 0.1F).

4-Fluoro-N-methylaniline[33] [36]



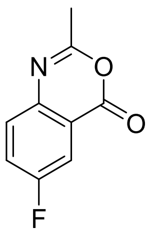
4-Fluoro-N-methylacetanilide (1.5 g, 8.97 mmol) was dissolved in 80% ethanol/water (30 mL) along with potassium hydroxide (5 g, 90 mmol). The solution was heated at reflux for 36 hours, cooled to RT, and the ethanol was removed by rotary evaporation. The product was extracted from water with CH$_2$Cl$_2$ (3 x 20 mL). The combined organic extracts were dried over sodium sulfate, filtered, and the solvent was removed by rotary evaporation. The product was purified using flash silica gel column chromatography (10% EtOAc in hexanes) to yield a colorless oil (0.13 g, 12%). ^{1}H NMR (CDCl$_3$, 400 MHz, 25 °C): δ 6.91 (t, *J* = 8.8, 2H), 6.55 (dd, *J* = 9.0, 4.4, 2H), 3.59 (s, 1H), 2.82 (s, 3H) ^{13}C NMR (CDCl$_3$, 100 MHz, 25 °C): δ 156.0 (d, *J* = 234.2), 145.9, 115.8 (d, *J* = 22.5), 113.3 (d, *J* = 7.4), 31.5 ^{19}F NMR (CDCl$_3$, 376 MHz, 25 °C): δ -128.5 (sept, *J* = 4.3, 1F).

N-Boc-4-fluoro-N-methylaniline[37]



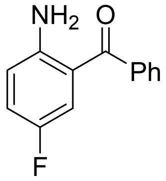
4-Fluoro-N-methylaniline (0.12 g, 0.96 mmol) was dissolved in triethylamine (0.54 mL, 3.84 mmol). DMAP (0.35 g, 2.88 mmol) and di-*tert*-butyl dicarbonate (1.05 g, 4.81 mmol) were added and the mixture was allowed to stir at RT for 3 d. The triethylamine was removed by rotary evaporation and the resulting oil was extracted with pentane (3 x 10 mL) and filtered. The product was purified by silica gel flash chromatography (10% EtOAc in hexanes) to yield a colorless oil (0.20 g, 93%). ^{1}H NMR (CD_3CN, 400 MHz, 25 °C): δ 7.26 (dd, *J* = 9.1, 5.0, 2H), 7.07 (t, *J* = 8.7, 2H), 3.17 (s, 3H), 1.40 (s, 9H) ^{13}C NMR (CD_3CN, 100 MHz, 25 °C): δ 161.5 (d, *J* = 242.1), 155.8, 141.8, 129.1 (d *J* = 8.5), 116.5 (d, *J* = 22.7), 81.1, 38.3, 28.8 ^{19}F NMR (CD_3CN, 376 MHz, 25 °C): δ -119.0 (sept, *J* = 4.4 1F). HRMS (ESI) calculated for $C_{12}H_{16}NO_2F$ 225.1165, found 225.1165.

6-Fluoro-2-methyl-4H-benzo[d][1,3]oxazin-4-one



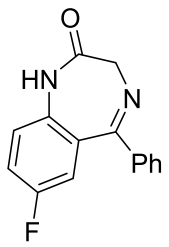
One part 2-amino-5-fluorobenzoic acid was dissolved in three parts acetic anhydride with stirring and heated to 120-130 °C.[38] Once half the volume had been distilled off, the solution was allowed to cool to room temperature. Residual acetic anhydride was removed under dynamic high vacuum at 50 °C for 12 h to afford the crude product as a tan solid (5.3 g, 92%), which was used without further purification.

2-Amino-5-fluoro-benzophenone



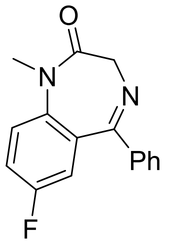
Magnesium turnings (0.29 g, 11.9 mmol) and a single crystal of iodine were placed in a Schlenk tube under N_2 and dry THF (11 mL) was added. Bromobenzene (1.12 mL, 10.8 mmol) was added to the solution, which was heated with stirring at 65 °C for 2 h, and then allowed to cool to room temperature. In a separate Schlenk tube, 6-fluoro-2-methyl-4H-benzo[d][1,3]oxazin-4-one (1.75 g, 9.77 mmol) was suspended in dry THF (10 mL) and the mixture was cooled to -78 °C. The Grignard reagent was added to the substrate slowly over 30 minutes with stirring. The reaction flask was removed from the dry ice/ethanol bath and the solution was allowed to warm to room temperature overnight. Water (5 mL), and ethyl acetate (10 mL) were added in succession before the mixture was acidified to pH 1 with 10% HCl. The organic layer was separated and retained, and the water layer was extracted with $CHCl_3$ (3 x 50 mL). The combined organic extracts were dried over sodium sulfate, filtered, and the solvent was removed by rotary evaporation. Flash silica gel column chromatography (20% ethyl acetate in hexanes) followed by evaporation of the collected fractions yielded a pale yellow oil, which proved to be 2-acetamido-5-fluoro-benzophenone. This intermediate was immediately subjected to hydrolysis. Ethanol (25 mL, 95%) was added an the solution was heated at reflux while conc. HCl (15 mL) was added in three portions over four hours. The solution was carefully basicified with KOH to precipitate the product from solution. Filtration yielded the product as a yellow solid (0.44 g, 21%). ^{1}H NMR ($CDCl_3$, 700 MHz, 25 °C): δ 7.65, (dd, *J* = 8.2, 1.3; 2H), 7.56 (br t, *J* = 7.39, 1H), 7.48 (t, *J* = 7.6, 2H), 7.16 (dd, *J* = 9.6, 3.0; 1H), 7.08 (ddd, *J* = 8.9, 7.8, 3.0; 1H) 6.71 (dd, *J* = 9.0, 4.5; 2H), 5.91 (bs s, 2H). ^{13}C NMR ($CDCl_3$, 176 MHz, 25 °C): δ 198.0, 153.2 (d, *J* = 234.9), 147.3, 139.4, 131.5, 129.1, 128.3, 122.2 (d, *J* = 23.5), 119.0 (d, *J* = 22.7), 118.2 (d, *J* = 7.0), 117.9. ^{19}F NMR (CD_3CN, 376 MHz, 25 °C): δ -118.54-118.60 (m, 1F). HRMS (ESI) calculated for $C_{13}H_{10}NOF$ 215.0746, found 215.0746.

7-Fluoro-5-phenyl-1,3-dihydro-2H-benzo[e][1,4]diazepin-2-one



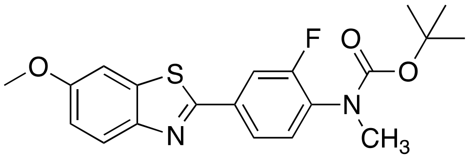
2-Amino-5-fluoro-benzophenone (0.15 g, 0.70 mmol), glycine methyl ester hydrochloride (175 mg, 1.4 mmol), and a catalytic amount of piperidine were dissolved in pyridine (25 mL). The stirred solution was heated at reflux for 36 h in a recirculating Dean-Stark apparatus equipped with 4Å molecular sieves in the side arm. The solvent was removed at 60 °C by rotary evaporation to give a tarry residue, which was partitioned between water (5 mL) and ethyl acetate (5 mL). The organic layer was separated and the aqueous layer was basicified with 1 M KOH. The aqueous solution was extracted with ethyl acetate (3 x 10 mL), and the combined organic layers were washed with brine (5 mL), dried over sodium sulfate, filtered, and the solvent was removed by rotary evaporation. The compound was purified by flash silica gel column chromatography (2:1 ethyl acetate:hexanes) yielding a light purple solid (0.10 g, 56%). ^{1}H NMR ($CDCl_3$, 600 MHz, 25 °C): δ 9.14 (s, 1H), 7.55 (d, *J* = 7.3, 2H), 7.48 (t, *J* = 7.4, 1H), 7.41 (t, *J* = 7.5, 2H), 7.24 (td, *J* = 8.2, 2.7; 1H), 7.17 (dd, *J* = 8.8, 4.7; 1H), 7.03, (dd, *J* = 8.7, 2.6; 1H), 4.34 (s, 2H). ^{13}C NMR ($CDCl_3$, 150 MHz, 25 °C): δ 172.0, 170.1, 139.0, 135.8, 129.8, 128.91 (d, *J* = 6.7), 128.6, 123.2 (d, *J* = 7.9), 119.6 (d, *J* = 23.3), 117.4 (d, *J* = 23.0), 108.3, 56.8. ^{19}F NMR (CD_3CN, 376 MHz, 25 °C): δ -117.06 (sept, *J* = 4.2, 1F). HRMS (ESI) calculated for $C_{15}H_{11}N_2OF$ 254.0855, found 254.0855.

7-Fluoro-1-methyl-5-phenyl-1,3-dihydro-2H-benzo[e][1,4]diazepin-2-one



7-Fluoro-5-phenyl-1,3-dihydro-2H-benzo[e][1,4]diazepin-2-one (200 mg, 0.79 mmol) was dissolved in dry DMF (20 mL). Sodium hydride (22.7 mg, 0.95 mmol) was added in portions to the stirred solution, causing the compound to precipitate as the sodium salt. Methyl iodide (74 µL, 1.2 mmol) was added and the solution was shaken to release the stir bar, and the solution was stirred for a further 30 minutes. The reaction mixture treated with ethyl acetate (50 mL) and water (10 mL) and transferred to a separatory funnel. The organic layer was washed with brine (10 mL) and water (3 x 10 mL), and the combined aqueous layers were back extracted once with ethyl acetate (10 mL). The combined organic extracts were dried over sodium sulfate, filtered, and the solvent was removed by rotary evaporation. The product was obtained as colorless crystals after recrystallization from hot ethyl acetate and hexanes (158 mg, 75%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.63 (d, 7.0, 2H), 7.48 (t, *J* = 7.3, 1H), 7.42 (t, *J* = 7.3, 2H), 7.35 (dd, *J* = 9.1, 4.8; 1H), 7.26-7.30 (m, 2H), 7.02 (dd, *J* = 8.6, 2.9; 1H), 4.84 (d, *J* = 10.8, 1H), 3.79 (d, *J* = 10.7, 1H), 3.40 (s, 3H). ^{13}C NMR ($CDCl_3$, 150 MHz, 25 °C): δ 170.3, 169.1, 158.1 (d, *J* = 247.2), 140.6, 138.4, 130.9, 130.5 (d, *J* = 7.1), 129.6, 128.6, 123.2 (d, *J* = 8.0), 119.0 (d. *J* = 23.1), 116.6 (d, *J* = 23.1), 57.2, 35.2. ^{19}F NMR (CD_3CN, 376 MHz, 25 °C): δ -116.50-116.56 (m, 1F). HRMS (ESI) calculated for $C_{16}H_{13}N_2OF$ 268.1012, found 268.1012.

2-(4-(*N*-Boc-3-fluoro-*N*-methyl)phenyl)-6-methoxybenzothiazole

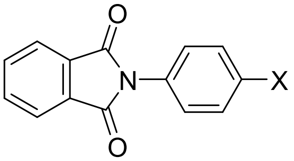


In a nitrogen-charged glove box, (2-(N-Boc-N-methyl)amino-5-(6-methoxybenzothiazolyl))(4-methoxyphenyl)iodonium triflate (10.0 mg, 0.013 mmol) was dissolved in 0.6 mL of acetonitrile-d_3 in an NMR tube equipped with a PTFE screw top closure. An aliquot (0.1 mL, 0.0034 mmol, 0.25 eq.) of a stock solution of tetramethyl ammonium fluoride (3.2 mg, 0.034 mmol) in 1.0 mL CD_3CN was added. ^{1}H- and ^{19}F-NMR spectra were acquired and the solvent was removed in vacuo. Dry benzene-d_6 (0.6 mL) was added and the tube was heated to 60 ˚C for 1 hour in the dark (0.0028 mmol product, 83% yield, by internal ^{1}H-NMR standard). The solvent was removed in vacuo, and the crude oil was chromatographed on silica (deactivated with triethylamine/hexanes (5:95 v/v)) with ethyl acetate/hexanes (20:80 v/v) to yield a pale yellow oil. The product was crystallized from boiling hexanes, cooled to 0 ˚C, filtered, and washed with cold hexanes to yield a colorless solid (1 mg). ^{1}H NMR (CD_3CN, 400 MHz, 25 °C): δ 7.91 (d, J = 9.0, 1H), 7.85 (dd, J = 11.4, 1.9, 1H), 7.83 (ddd, J = 8.6, 2.0, 1.3; 1H), 7.56 (d, J = 2.5, 1H), 7.44 (dd, J = 8.6, 7.9, 1H), 7.14 (dd, J = 11.4, 1.8, 1H), 3.88 (s, 3H), 3.20 (s, 3H), 1.41 (br s, 9H). ^{13}C NMR (CD_3CN, 100 MHz, 25 °C): δ 164.1, 159.2, 158.8 (d, J = 248.7), 154.9, 149.4, 137.7, 134.6 (d, J = 12.6), 134.5 (d, J = 7.5), 130.3, 124.7, 124.1 (d, J = 2.9), 117.1, 115.2 (d, J = 23.2), 105.5, 81.3, 56.6, 37.4, 28.3. ^{19}F NMR (CD3CN, 376 MHz, 25 °C): δ -120.88 (br s, 1F); HRMS: (ESI) calculated for $C_{20}H_{21}FN_2NaO_3S$ $[M + Na]^+$ 411.1155 found 411.1161.

General procedure for thermolysis of diaryliodonium salts

In a nitrogen atmosphere glove box, ion exchange of various nucleophilic anions (X) for the triflate or hexafluorophosphate counterions in the aniline-derived diaryliodonium salts was accomplished with 1.1 equivalents of TBA-X, TMA-X, or Na-X dissolved in dry acetonitrile. Fluoridation was performed using a substoichiometric amount of TMAF (0.25 eq) to avoid equilibration of aryl groups in the diaryliodonium salts. The reaction solutions were placed in sealed containers, removed from the glove box and heated for 1 hour. The reactions were monitored by NMR to determine the appropriate thermolysis temperatures. Products ratios were determined by ^{1}H NMR spectroscopy using authentic, isolated functionalized arenes as standards. Literature references for known compounds are provided.

2-(4-X-phenyl)isoindoline-1,3-dione

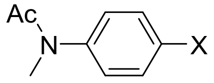


X = Acetato,[5] fluoro,[5] chloro,[5] bromo.[5]

X = Azido
^{1}H NMR (CD_3CN, 400 MHz, 25 °C): δ 7.93 (q, J = 2.8, 2H), 7.86 (q, J = 2.9, 2H), 7.45 (d, J = 9.1, 2H), 7.22 (d, J = 8.8, 2H). ^{13}C NMR (CD_3CN, 100 MHz, 25 °C): δ 168.8, 141.3, 136.0, 133.3, 130.2, 130.0, 124.7, 120.9. HRMS (ESI) calculated for $C_{14}H_8N_4O_2$ 264.06, found 264.0647.

X = *iso*-Thiocyanato
^{1}H NMR (CD_3CN, 400 MHz, 25 °C): δ 7.95 (q, J = 2.9, 2H), 7.88 (q, J = 2.9, 2H), 7.75 (d, J = 8.9, 2H), 7.60 (d, J = 8.9, 2H). ^{13}C NMR (CD_3CN, 176 MHz, 25 °C): δ 168.1, 135.9, 134.6, 132.9, 131.8, 129.6, 125.4, 124.5, 111.6. HRMS (EI) calculated for $C_{15}H_8N_2O_2S$ 280.03, found 280.0307.

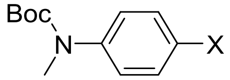
N-(4-X-phenyl)-N-methylacetamide



X = Azido,[39] acetato,[40], fluoro,[35] chloro,[9] bromo.[9]

X = iso-Thiocyanato
^{1}H NMR (CD_3CN, 400 MHz, 25 °C): δ 7.65 (d, *J* = 8.6, 2H), 7.40 (d, *J* = 8.7, 2H), 3.21 (s, 3H), 1.87 (s-broad, 3H). ^{13}C NMR (CD_3CN, 176 MHz, 25 °C): δ 170.6, 147.2, 132.5, 130.0, 124.5, 111.8, 37.3, 22.8. HRMS (ESI) calculated for $C_{10}H_{10}N_2OS$ 206.05, found 206.0514.

tert-Butyl-(4-X-phenyl)(methyl)carbamate



X = Bromo.[41]

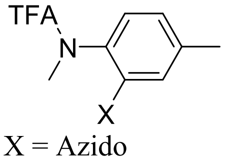
X = Azido (with 12.5% Iodo)
^{1}H NMR (CD_3CN, 700 MHz, 25 °C): δ 7.27 (d, *J* = 8.7, 2H), 7.03 (d, *J* = 8.8, 2H), 3.18 (s, 3H), 1.41 (s, 9H). ^{13}C NMR (CD_3CN, 176 MHz, 25 °C): δ 155.4, 142.1, 138.6, 138.0, 128.2, 120.1, 80.9, 37.8. HRMS (ESI) calculated for $C_{12}H_{16}N_4O_2$ 248.1273, found 248.1273

X = Acetato
^{1}H NMR (CD_3CN, 400 MHz, 25 °C): δ 7.27 (d, *J* = 8.8, 2H), 7.05 (d, *J* = 8.8, 2H), 3.76 (s, 3H), 3.19 (s, 3H), 1.42 (s, 9H). ^{13}C NMR (CD_3CN, 100 MHz, 25 °C): δ 170.6, 155.4, 149.1, 142.7, 127.6, 122.8, 80.8, 37.8, 28.5, 21.2 HRMS (ESI) calculated for $C_{14}H_{19}NO_4$ 265.1314, found 265.1314.

X = iso-Thiocyanato
^{1}H NMR (CD_3CN, 700 MHz, 25 °C): δ 7.57 (d, *J* = 8.8, 2H), 7.41 (d, *J* = 8.8, 2H), 3.22 (s, 3H), 1.43 (s, 9H). ^{13}C NMR (CD_3CN, 176 MHz, 25 °C): δ 153.9, 145.7, 131.1, 126.9, 119.8, 111.1, 80.5, 36.4. HRMS (ESI) calculated for $C_{13}H_{16}N_2O_2S$ 264.0933, found 264.0933.

X = Chloro (with 17% Iodo)
^{1}H NMR (CD_3CN, 400 MHz, 25 °C): δ 7.34 (d, *J* = 8.9, 2H), 7.25 (d, *J* = 8.8, 2H), 3.19 (s, 3H), 1.41 (s, 9H). ^{13}C NMR (CD_3CN, 100 MHz, 25 °C): δ 155.1, 143.9, 138.5, 129.4, 128.1, 81.0, 37.6, 28.4 HRMS (ESI) calculated for $C_{12}H_{16}NO_2Cl$ 241.0870, found 241.0877

2,2,2-Trifluoro-N-(2-X-4-methylphenyl)-N-methylacetamide



X = Azido
^{1}H NMR (CD_3CN, 700 MHz, 25 °C): δ 7.24 (d, *J* = 8.1, 1H), 7.18 (s, 0.8H), 7.17 [R] (s, 0.2H), 7.08 [R] (d, *J* = 7.6, 0.2H), 7.05 (d, *J* = 7.8, 0.8H), 3.35 [R] (br q, 0.5H), 3.20 (s, 2.5H), 2.39 (s, 3H). ^{13}C NMR (CD_3CN, 176 MHz, 25 °C): δ 157.7, 157.5, 142.6, 138.4, 130.6, 129.6, 129.2, 127.6, 127.1, 121.3, 121.0, 38.9, 21.2. ^{19}F NMR (CD_3CN, 376 MHz, 25 °C): δ -71.02 (s, 2.7F), -72.44 [R] (s, 0.3F). HRMS (ESI) calculated for $C_{10}H_9F_3N_4O$ 258.07, found 258.0728.

X = Acetato

^{1}H NMR (CD_3CN, 300 MHz, 25 °C): δ 7.31 (d, *J* = 8.0, 0.8H), 7.28 [R] (d, *J* = 8.1, 0.2H), 7.19 [R] (br d, 0.2H), 7.16 (br d, 0.8H), 7.12 (s, (0.8H), 7.08 [R], (s, 0.2H), 3.33 [R] (br q, 0.5H), 3.17 (s, 2.5H), 2.38 (s, 3H), 2.24 (s, 2.5H), 2.20 [R] (s, 0.5H). ^{13}C NMR (CD_3CN, 176 MHz, 25 °C): δ 169.0, 146.7, 141.2, 130.1, 129.1, 127.7, 127.4, 127.3, 124.2, 124.1, 115.5, 38.16, 20.2, 20.0. ^{19}F NMR (CD_3CN, 282 MHz, 25 °C): δ -69.3 (s, 2.5F) -70.9 [R] (s, 0.5F). HRMS (ESI) calculated for $C_{12}H_{12}F_3NO_3$ 275.08, found 275.0769.

X = iso-Thiocyanato
^{1}H NMR (CD_3CN, 700 MHz, 25 °C): δ 7.66 [R] (s, 0.2H), 7.65 (s, 0.8H) 7.44 (d, *J* = 7.9, 0.2H), 7.42 (d *J* = 8.1, 0.8H), 7.39 (d, *J* = 8.3, 0.8H), 7.38 (d, *J* = 8.3, 0.2H), 3.46 [R] (br q, 1H), 3.28 (s, 2H), 2.43 (s, 2H), 2.42 [R] (s, 1H). ^{13}C NMR (CD_3CN, 176 MHz, 25 °C): δ 157.7, 157.5, 143.4, 142.3, 140.5, 138.1, 134.1, 133.8, 132.93, 132.87, 131.1, 129.2, 125.4, 123.8, 116.4, 111.1, 110.4, 39.1, 21.2. ^{19}F NMR (CD_3CN, 376 MHz, 25 °C): δ -70.9 (s, 2F), -72.6 [R] (s, 1F). HRMS (ESI) calculated for $C_{11}H_9F_3N_2OS$ 274.04, found 274.0388.

X = Fluoro
^{1}H NMR (CD_3CN, 400 MHz, 25 °C): δ 7.39-7.48 (m, 1H), 7.22-7.30 (m, 1H), 7.10 (t, *J* = 9.7, 1H), 3.42 [R] (br q 1H), 3.26 (s, 2H), 2.41 [R] (s, 1H), 2.38 (s, 2H). ^{13}C NMR (CD_3CN, 176 MHz, 25 °C): δ 158.2, 157.1, 143.7, 142.7, 141.3, 141.2, 132.9, 131.9, 131.4, 131.0, 130.8, 130.2, 130.0, 129.63, 129.60, 129.5, 129.2, 128.9, 128.6, 126.6, 40.0, 39.2, 39.0, 21.3, 21.2, 20.6. ^{19}F NMR (CD_3CN, 376 MHz, 25 °C): δ -70.7 (s, 1.5F) -70.3 (s, 1.5F), 126.4 (sept, *J* = 3.7, 1F). HRMS (EI) calculated for $C_{10}H_9NOF_4$ 235.06, found 235.062.

X = Chloro
^{1}H NMR (CD_3CN, 400 MHz, 25 °C): δ 7.41 (s, 1H), 7.36 (d, *J* = 8.0, 1H), 7.23 (d, *J* = 8.1, 1H), 3.38 [R] (br q, 0.5H), 3.24 (s, 2.5H), 2.37 (s, 3H). ^{13}C NMR (CD_3CN, 100 MHz, 25 °C): δ 157.6, 157.3, 142.9, 142.7, 142.0, 121.2, 136.1, 133.2, 131.9, 131.7, 131.6, 131.3, 130.9, 130.3, 130.0, 129.8, 129.4, 128.6, 115.9, 99.3, 38.5, 21.0. ^{19}F NMR (CD_3CN, 376 MHz, 25 °C): δ -70.6 [R] (s, 1F), -71.3 (s, 2F). HRMS (ESI) calculated for $C_{10}H_9F_3NOCl$ 251.03, found 251.0325.

X = Bromo
^{1}H NMR (CD_3CN, 700 MHz, 25 °C): δ 7.59 (s, 0.8H), 7.58 [R] (s, 0.2H), 7.36 (d, *J* = 8.1, 1H), 7.27 (d, *J* = 8.8, 1H), 3.37 [R] (br q, 0.5H), 3.23 (s, 2.5H), 2.37 (s, 3H). ^{13}C NMR (CD_3CN, 176 MHz, 25 °C): δ 157.7, 157.4, 157.3, 157.2, 157.1, 157.0, 143.1, 143.0, 142.7, 142.2, 142.0, 141.34, 141.27, 141.25, 139.5, 137.7, 134.9, 134.8, 131.9, 131.4, 131.0, 130.9, 130.5, 130.0, 129.5, 128.6, 123.4, 121.7, 119.8, 118.2, 118.1, 116.52, 116.46, 114.9, 99.3, 97.1, 39.0, 38.8, 38.7, 20.9, 20.7. ^{19}F NMR (CD_3CN, 376 MHz, 25 °C): δ -70.7 [R] (s, 1F), -71.1 (s, 2F). HRMS (ESI) calculated for $C_{10}H_9F_3NOBr$ 294.98, found 294.9819.

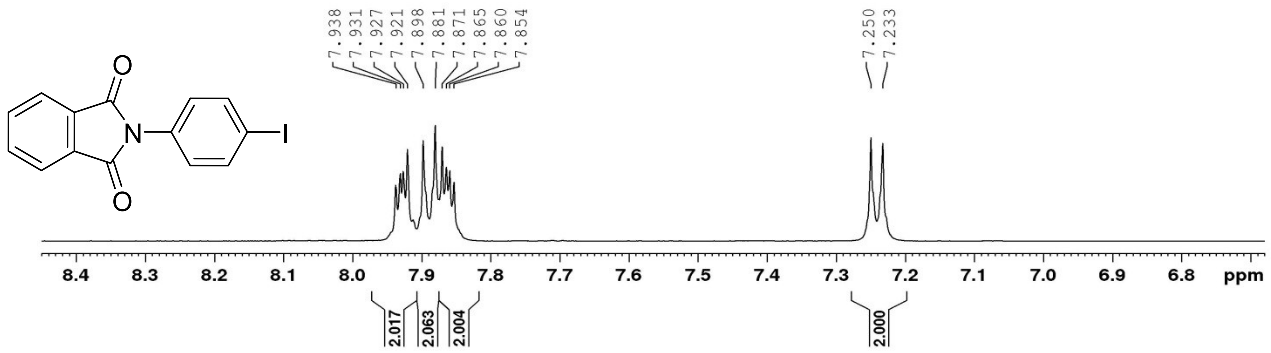
References:

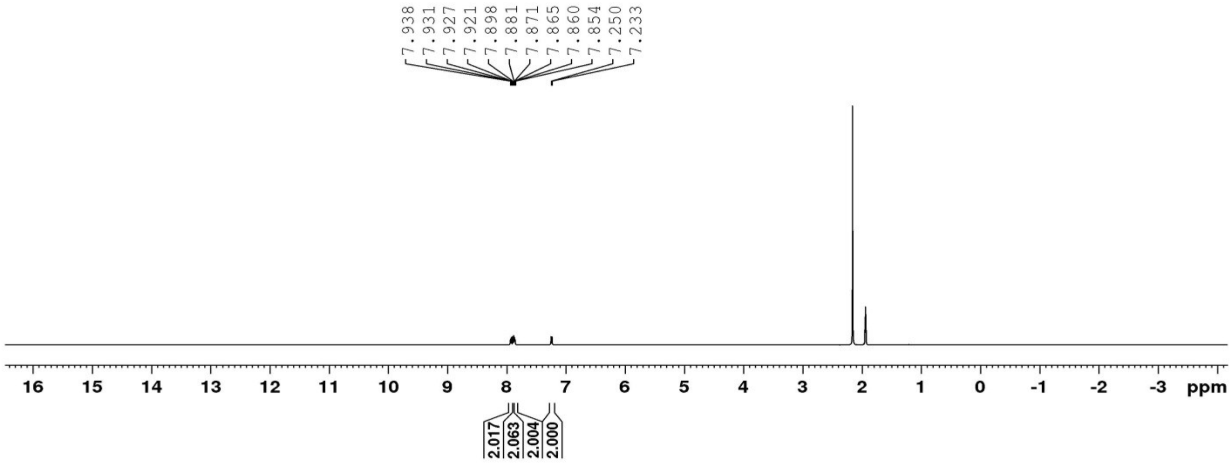
1. M. J. T. Frish, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewsi, V. G.; Voth, G. A.; Salvador, P.; Dannenber, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J., *Gaussian 09*, *Revision A. 02,* Gaussian Inc., Wallingord, CT, 2009.
2. G. Wanag and A. Veinbergs, *Chem. Ber.*, 1942, **75**, 1558-1569.
3. S. A. Soomro, A. Schulz and H. Meier, *Tetrahedron*, 2006, **62**, 8089-8094.
4. F. D. Chattaway and A. Constable, *Proc. Chem. Soc., London*, 1914, **29**, 304.
5. R. Shrestha, P. Mukherjee, Y. Tan, Z. C. Litman and J. F. Hartwig, *J. Am. Chem. Soc.*, 2013, **135**, 8480-8483.

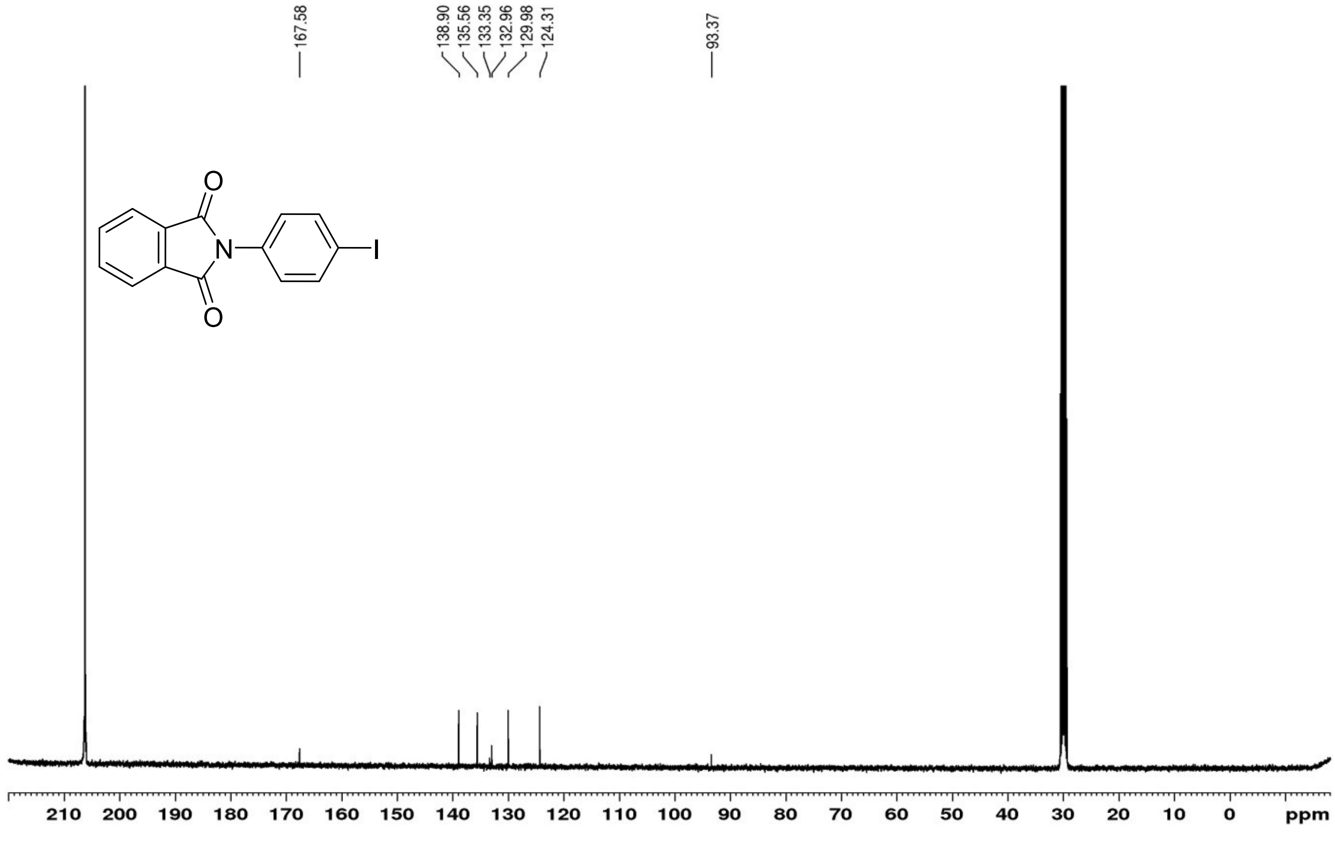
6. L. Qin, B. Hu, K. D. Neumann, E. J. Linstad, K. McCauley, J. Veness, J. J. Kempinger and S. G. DiMagno, *Eur. J. Org. Chem.*, 2015, **2015**, 5919-5924.
7. A. Pictet and P. Crépieux, *Chem. Ber.*, 1888, **21**, 1106-1111.
8. G. D. Lander, *J. Chem. Soc., Trans.*, 1901, **79**, 690-700.
9. Y. Peng, H. Liu, M. Tang, L. Cai and V. Pike, *Chin. J. Chem.*, 2009, **27**, 1339-1344.
10. G. Galliani, B. Rindone and P. L. Beltrame, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1803-1805.
11. T. Knauber, F. Arikan, G.-V. Röschenthaler and L. J. Gooßen, *Chemistry – A European Journal*, 2011, **17**, 2689-2697.
12. L. Horner, E. Winkelmann, K. H. Knapp and W. Ludwig, *Chem. Ber.*, 1959, **92**, 288-292.
13. C. H. Chui, Q. Wang, W. C. Chow, M. C. W. Yuen, K. L. Wong, W. M. Kwok, G. Y. M. Cheng, R. S. M. Wong, S. W. Tong, K. W. Chan, F. Y. Lau, P. B. S. Lai, K. H. Lam, E. Fabbri, X. M. Tao, R. Gambari and W. Y. Wong, *Chem. Commun. (Cambridge, U. K.)*, 2010, **46**, 3538-3540.
14. D.-H. Wang, X.-S. Hao, D.-F. Wu and J.-Q. Yu, *Org. Lett.*, 2006, **8**, 3387-3390.
15. P. P. Bedson and A. J. King, *J. Chem. Soc., Trans.*, 1880, **37**, 752-757.
16. S. R. Thopate, S. R. Kote, S. V. Rohokale and N. M. Thorat, *J. Chem. Res.*, 2011, **35**, 124-125.
17. E. Thielepape, *Chem. Ber.*, 1935, **68**, 751-753.
18. W. H. Mills and R. M. Kelham, *Journal of the Chemical Society (Resumed)*, 1937, 274-278.
19. S. Hanada, A. Yuasa, H. Kuroiwa, Y. Motoyama and H. Nagashima, *Eur. J. Org. Chem.*, 2010, **2010**, 1021-1025.
20. F. Reverdin, *Bull. Soc. Chim. Fr.*, 1911, **9**, 43-49.
21. J. V. Braun, *Ber. Dtsch. Chem. Ges.*, 1908, **41**, 2100-2113.
22. I. González, J. Mosquera, C. Guerrero, R. Rodríguez and J. Cruces, *Org. Lett.*, 2009, **11**, 1677-1680.
23. d. T. F. Gonzalez-Lopez and D. P. Curran, *Org. Lett.*, 2005, **7**, 151-154.
24. F. González-López de Turiso and D. P. Curran, *Org. Lett.*, 2005, **7**, 151-154.
25. G. Venkateshwarlu, A. Premalatha, A. Chakradhar, K. C. Rajanna and P. K. S. Prakash, *Helv. Chim. Acta*, 2010, **93**, 345-349.
26. O. S. Morozov, A. V. Lunchev, A. A. Bush, A. A. Tukov, A. F. Asachenko, V. N. Khrustalev, S. S. Zalesskiy, V. P. Ananikov and M. S. Nechaev, *Chemistry – A European Journal*, 2014, **20**, 6162-6170.
27. S. Patterson, M. S. Alphey, D. C. Jones, E. J. Shanks, I. P. Street, J. A. Frearson, P. G. Wyatt, I. H. Gilbert and A. H. Fairlamb, *J. Med. Chem.*, 2011, **54**, 6514-6530.
28. L. Guandalini, C. Cellai, A. Laurenzana, S. Scapecchi, F. Paoletti and M. N. Romanelli, *Bioorg. Med. Chem. Lett.*, 2008, **18**, 5071-5074.
29. J. Hyvl and J. Srogl, *Eur. J. Org. Chem.*, 2010, **2010**, 2849-2851.
30. Z.-G. Le, Z.-C. Chen, Y. Hu and Q.-G. Zheng, *Synthesis*, 2004, **2004**, 2809-2812.
31. G. B. Cole, G. Keum, J. Liu, G. W. Small, N. Satyamurthy, V. Kepe and J. R. Barrio, *Proceedings of the National Academy of Sciences*, 2010, **107**, 6222-6227.
32. S. Stavber and M. Zupan, *The Journal of Organic Chemistry*, 1985, **50**, 3609-3612.
33. A. Zakrzewska, E. Kolehmainen, B. Osmialowski and R. Gawinecki, *J. Fluorine Chem.*, 2001, **111**, 1-10.
34. K. Kajihara, M. Arisawa and S. Shuto, *The Journal of Organic Chemistry*, 2008, **73**, 9494-9496.
35. H. G. Lee, P. J. Milner and S. L. Buchwald, *Org. Lett.*, 2013, **15**, 5602-5605.
36. N. Sun, S. Wang, W. Mo, B. Hu, Z. Shen and X. Hu, *Tetrahedron*, 2010, **66**, 7142-7148.
37. T. Niwa, H. Ochiai, Y. Watanabe and T. Hosoya, *J. Am. Chem. Soc.*, 2015, **137**, 14313-14318.
38. M. T. Bogert, R. A. Gortner and C. G. Amend, *J. Am. Chem. Soc.*, 1911, **33**, 949-962.
39. P. H. Ruane and R. A. McClelland, *Can. J. Chem.*, 2001, **79**, 1875-1880.
40. H. Liu, X. Wang and Y. Gu, *Org. Biomol. Chem.*, 2011, **9**, 1614-1620.
41. S. Yoshida, K. Igawa and K. Tomooka, *J. Am. Chem. Soc.*, 2012, **134**, 19358-19361.

NMR Spectra

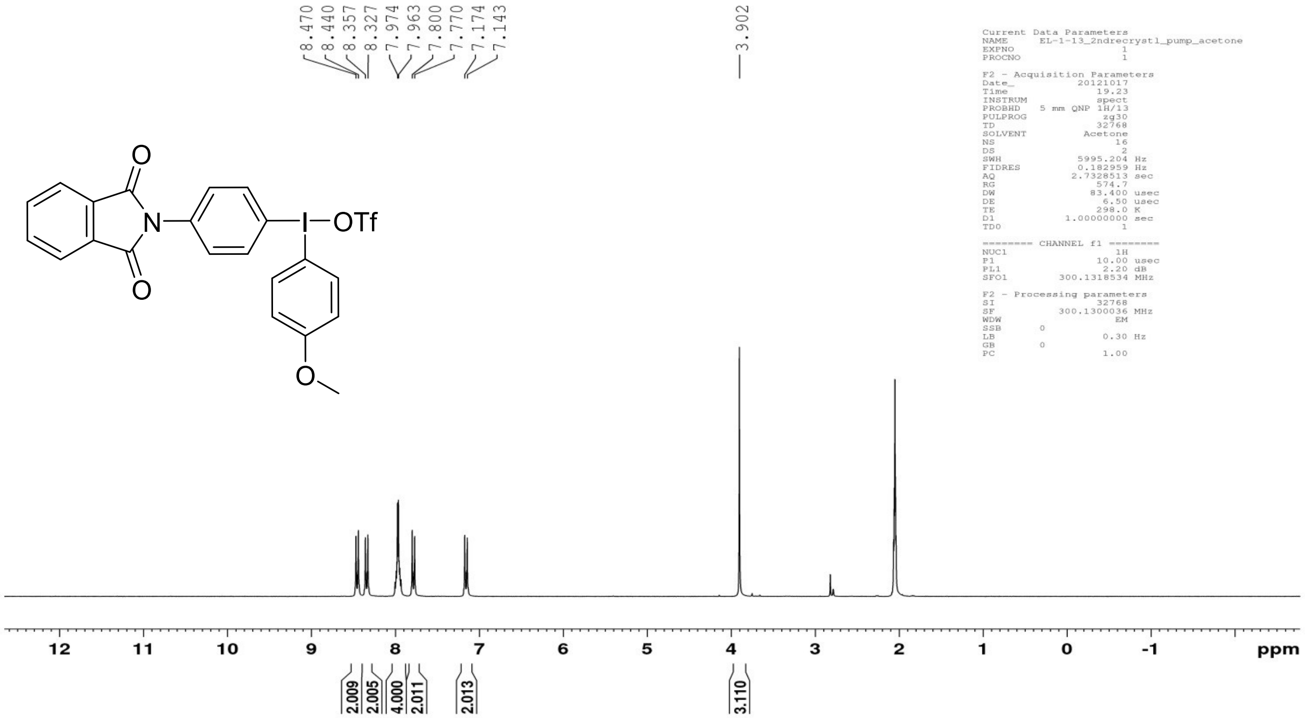
Phthalimido-4-iodobenzene







(4-Phthalimidophenyl)(4'-methoxyphenyl)iodonium triflate



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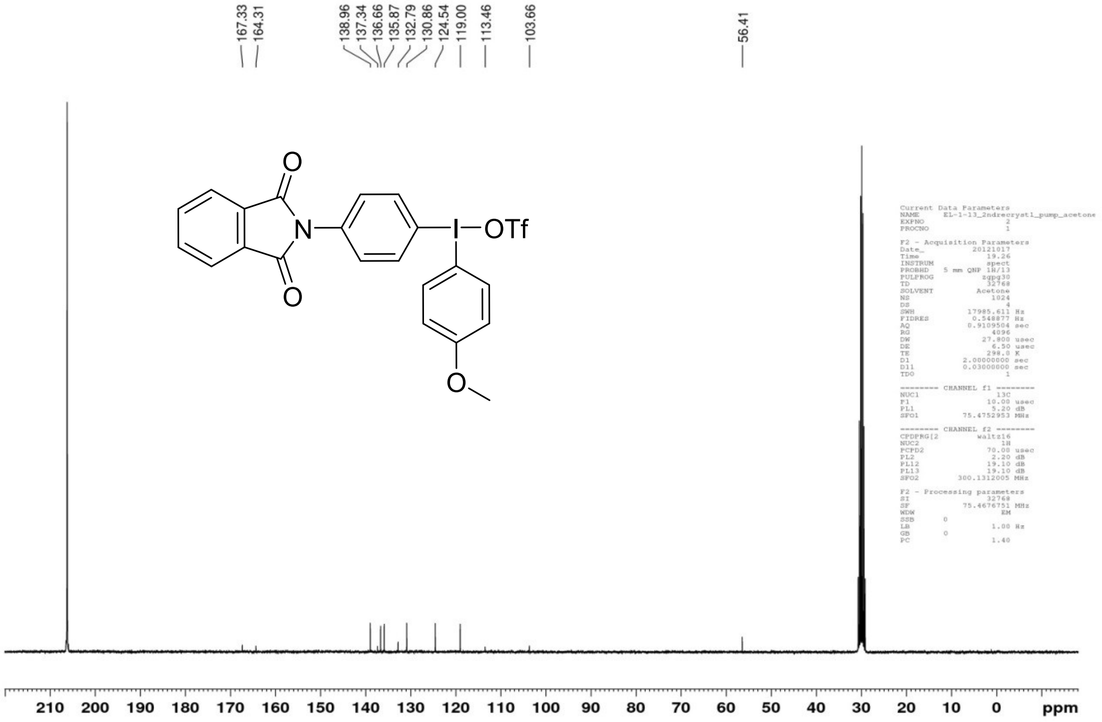

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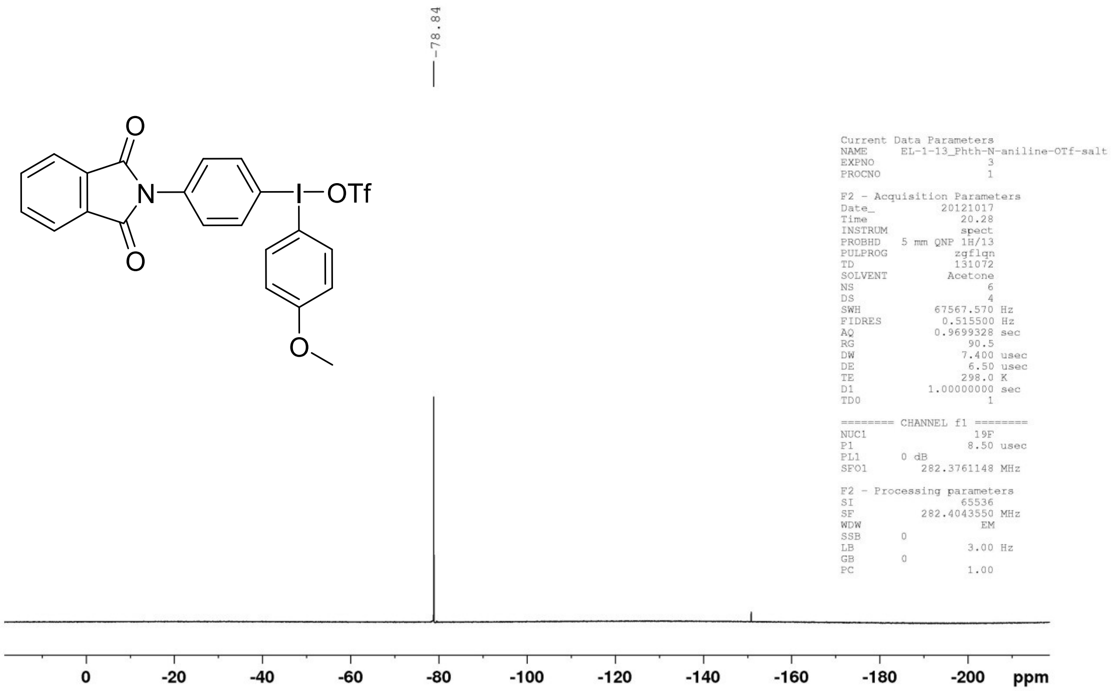

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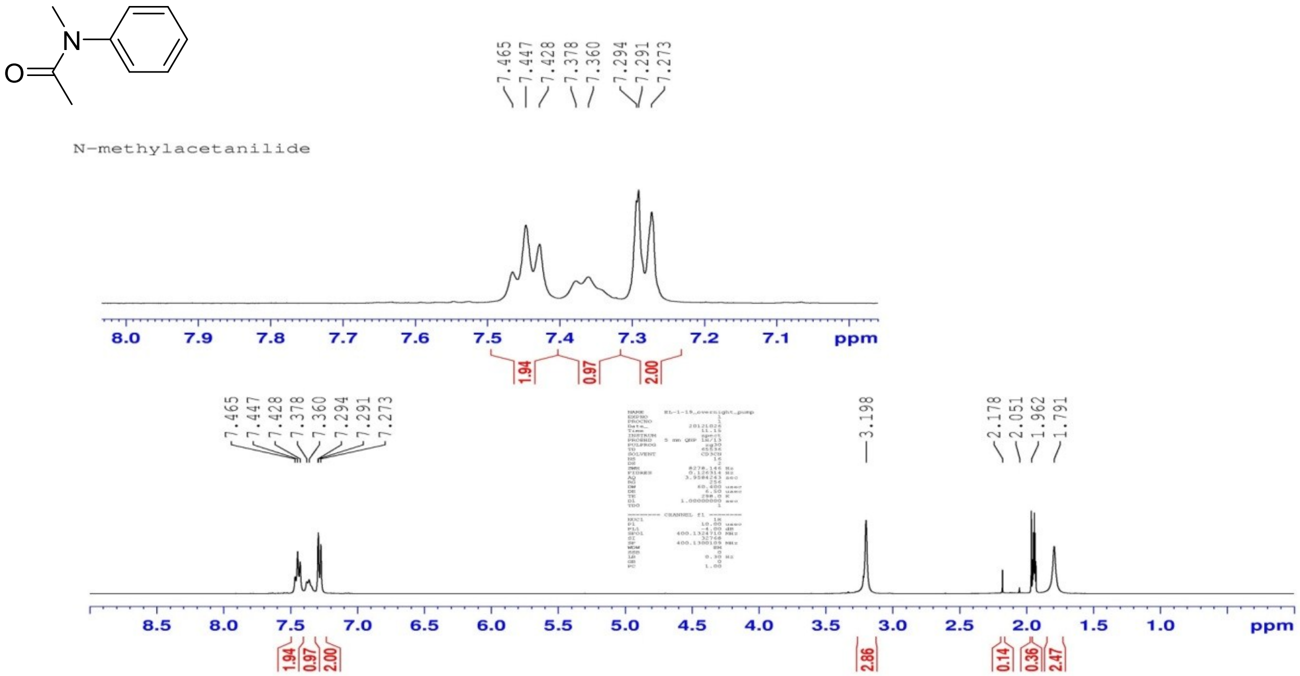
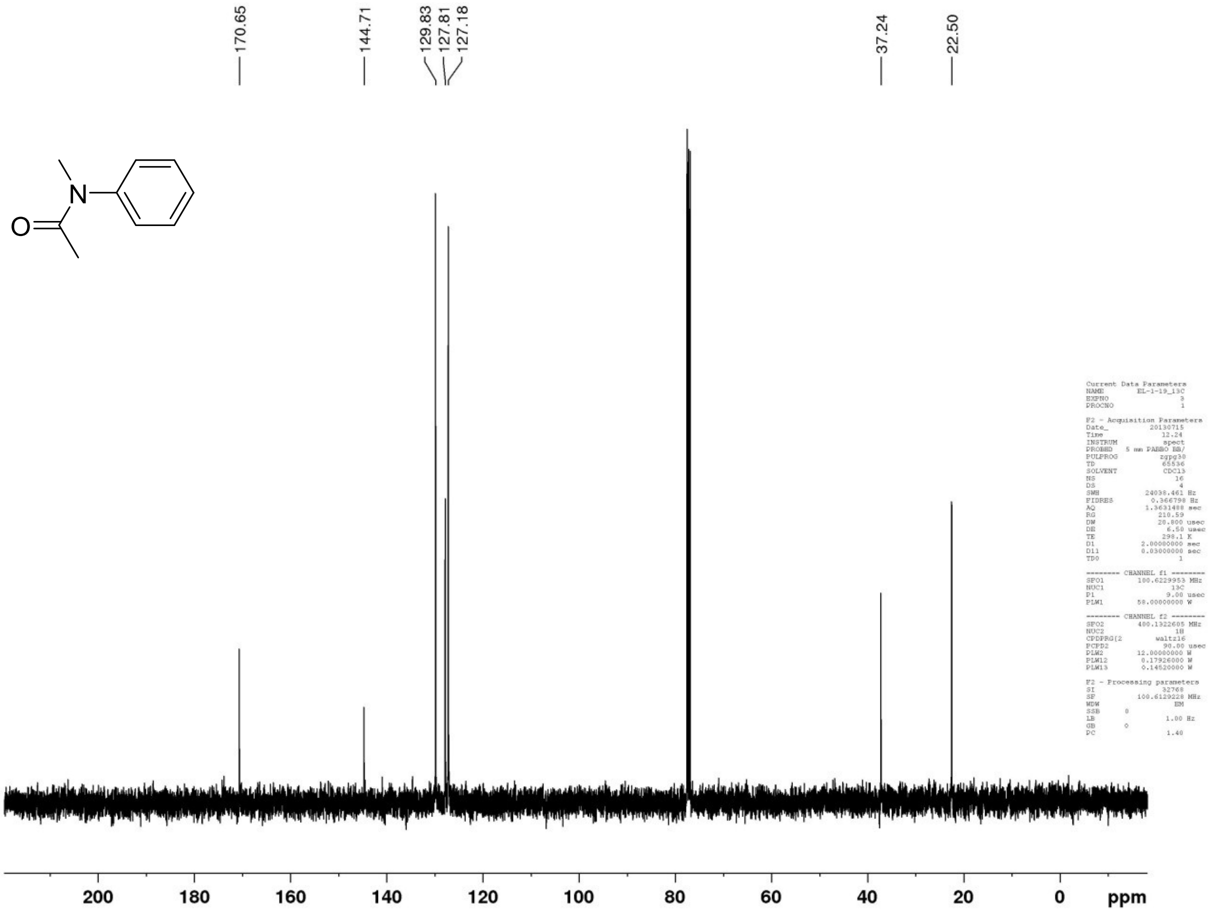
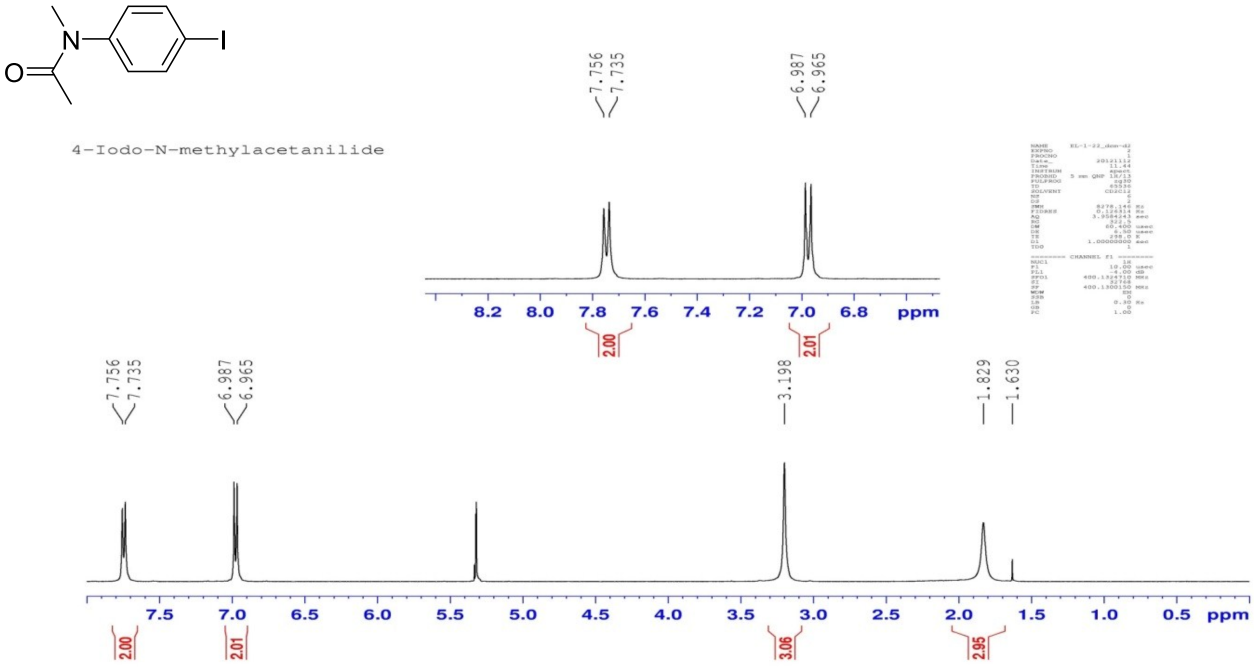
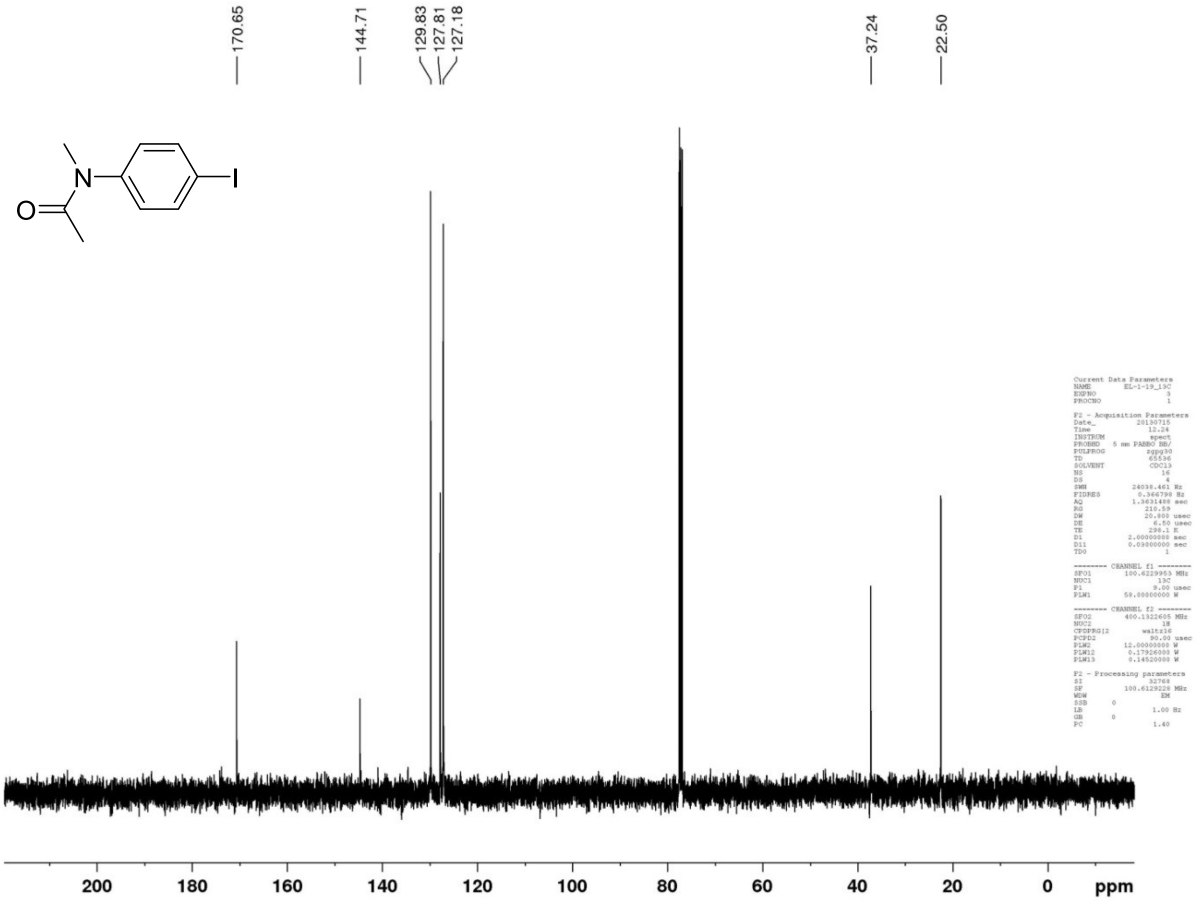




4-Iodo-N-methylacetanilide





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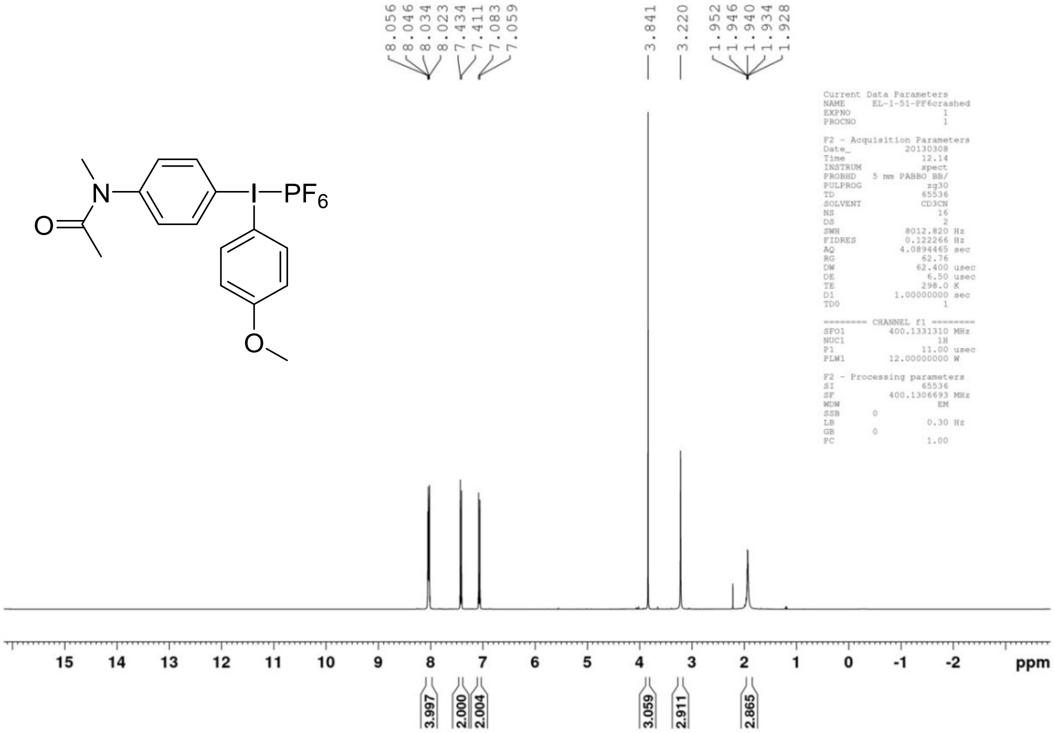
Time              12.24
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631488 sec
RG               210.59
DW               20.800 usec
DE                 6.50 usec
TE                298.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        100.6229953 MHz
NUC1                13C
P1                 9.00 usec
PLW1        58.00000000 W

======== CHANNEL f2 ========
SFO2        400.1322605 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             90.00 usec
PLW2        12.00000000 W
PLW12        0.17926000 W
PLW13        0.14520000 W

F2 - Processing parameters
SI                32768
SF          100.6129228 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```

(4-(N-methyl-N-acetamido)phenyl)(4'-methoxyphenyl) iodonium hexafluorophosphate

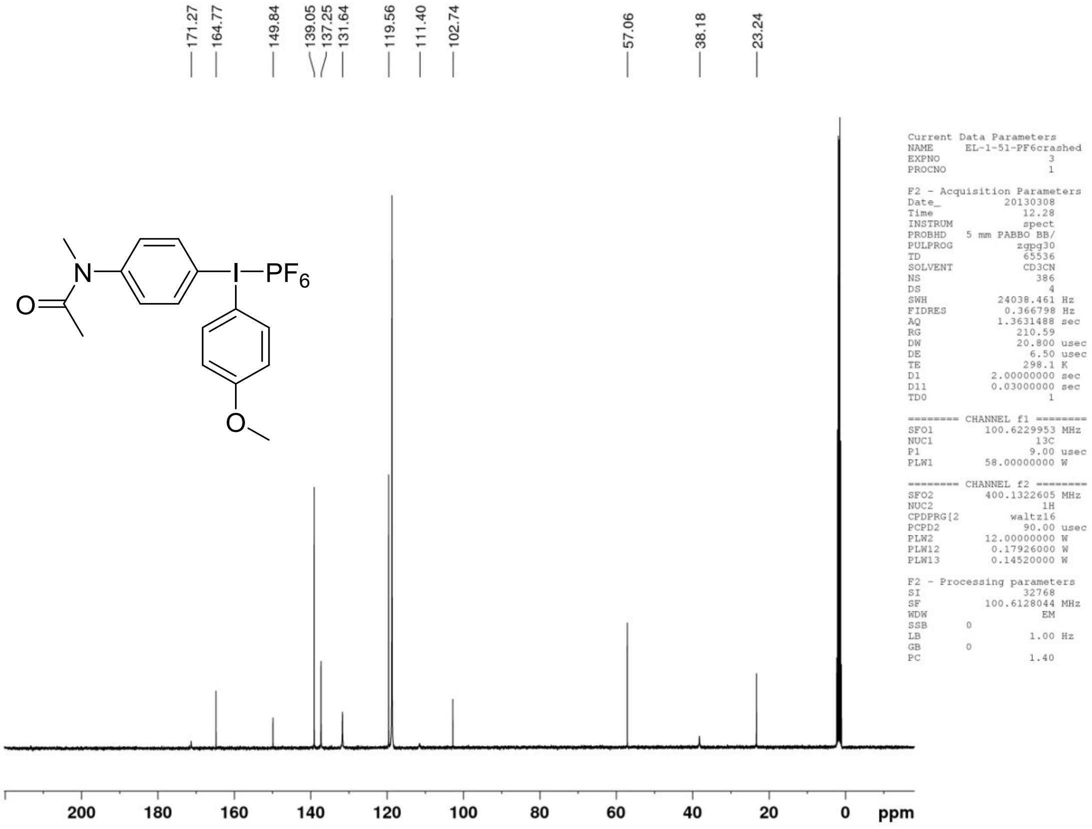


```
Current Data Parameters
NAME     EL-1-51-PF6crashed
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20130308
Time              12.14
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CD3CN
NS                   16
DS                    2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894465 sec
RG                62.76
DW               62.400 usec
DE                 6.50 usec
TE                298.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        400.1331310 MHz
NUC1                 1H
P1                11.00 usec
PLW1        12.00000000 W

F2 - Processing parameters
SI                65536
SF          400.1306693 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```



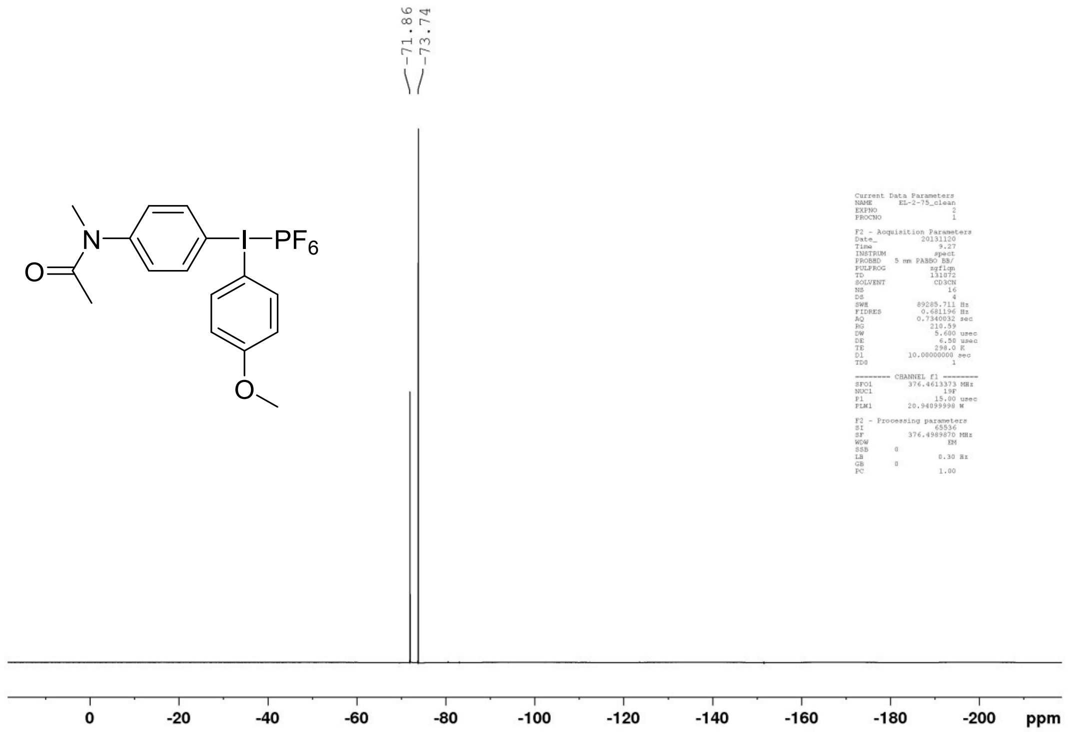
```
Current Data Parameters
NAME     EL-1-51-PF6crashed
EXPNO                     3
PROCNO                    1

F2 - Acquisition Parameters
Date_              20130308
Time                  12.28
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                    65536
SOLVENT               CD3CN
NS                      386
DS                        4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631488 sec
RG                   210.59
DW                   20.800 usec
DE                     6.50 usec
TE                    298.1 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           100.6229953 MHz
NUC1                    13C
P1                     9.00 usec
PLW1           58.00000000 W

======== CHANNEL f2 ========
SFO2           400.1322605 MHz
NUC2                     1H
CPDPRG[2            waltz16
PCPD2                 90.00 usec
PLW2           12.00000000 W
PLW12           0.17926000 W
PLW13           0.14520000 W

F2 - Processing parameters
SI                    32768
SF             100.6128044 MHz
WDW                      EM
SSB      0
LB                     1.00 Hz
GB       0
PC                     1.40
```



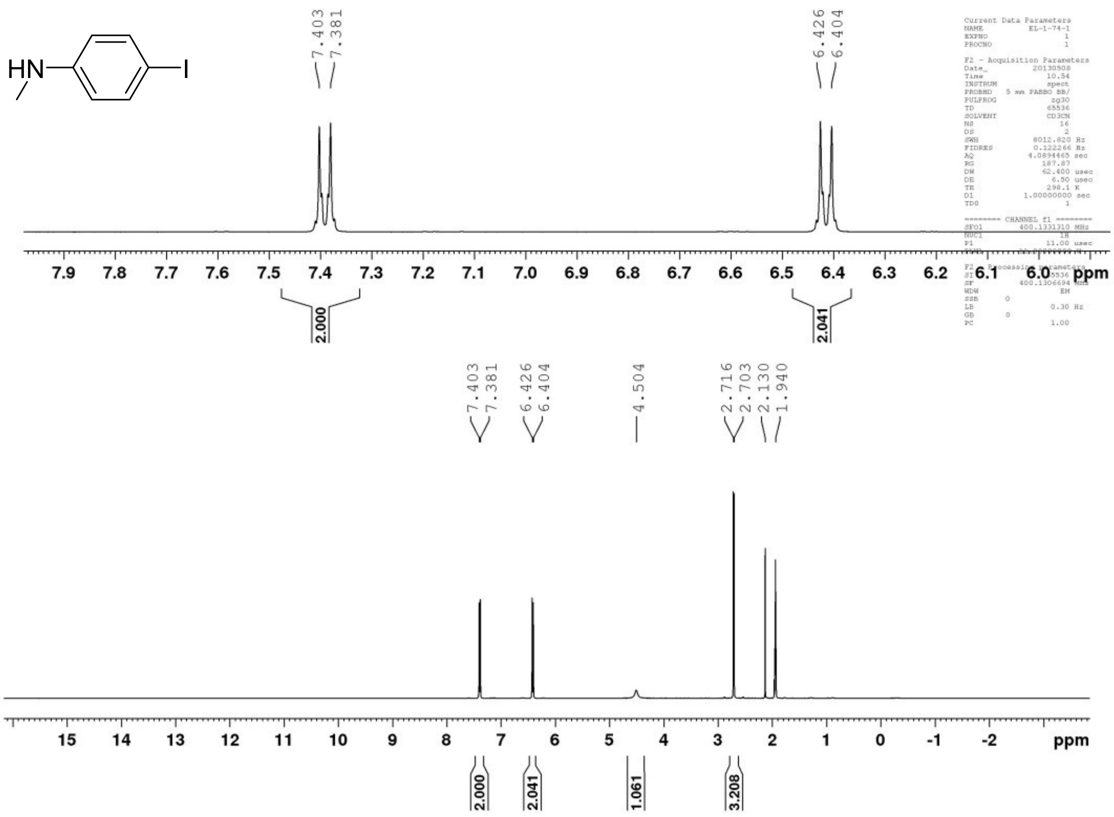
```
Current Data Parameters
NAME        EL-2-75_clean
EXPNO                   2
PROCNO                  1

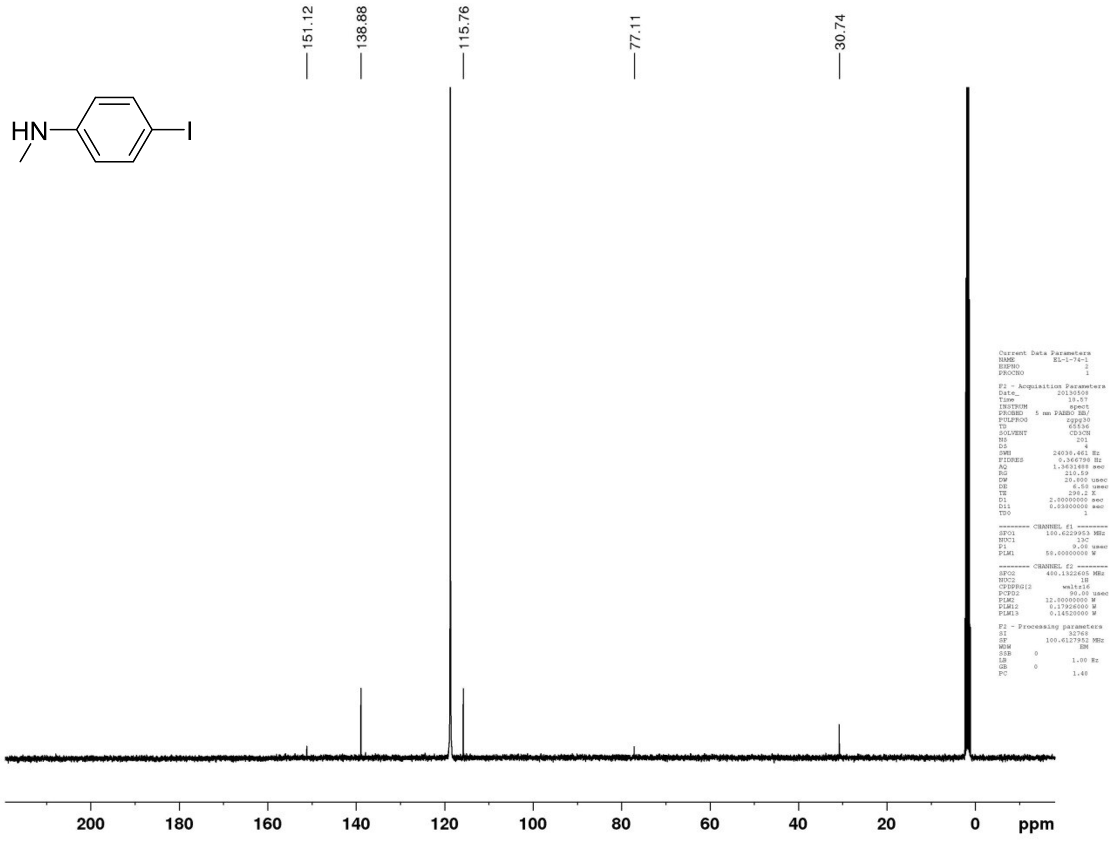
F2 - Acquisition Parameters
Date_            20131120
Time                 9.27
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG            zgflqn
TD                 131072
SOLVENT             CD3CN
NS                     16
DS                      4
SWH             89285.711 Hz
FIDRES           0.681196 Hz
AQ              0.7340032 sec
RG                 210.59
DW                  5.600 usec
DE                   6.50 usec
TE                  298.0 K
D1            10.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          376.4613373 MHz
NUC1                  19F
P1                  15.00 usec
PLW1          20.94099998 W

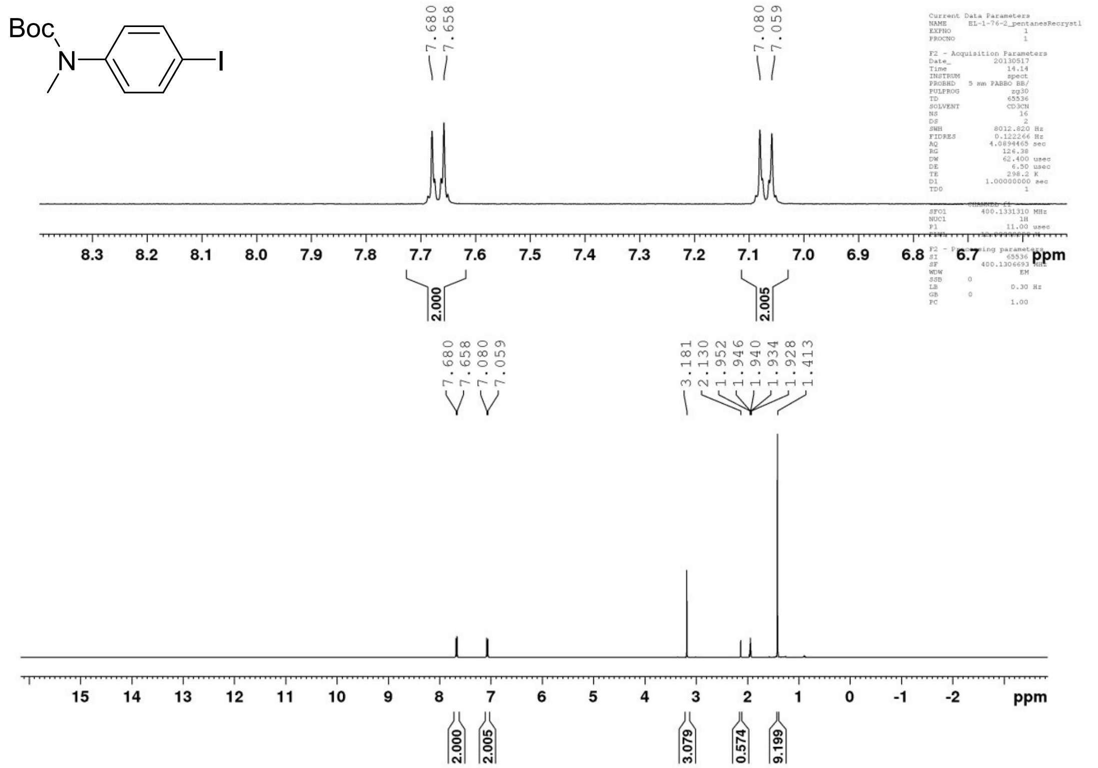
F2 - Processing parameters
SI                  65536
SF            376.4989870 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

4-Iodo-N-methylaniline





N-Boc-4-iodo-N-methylaniline

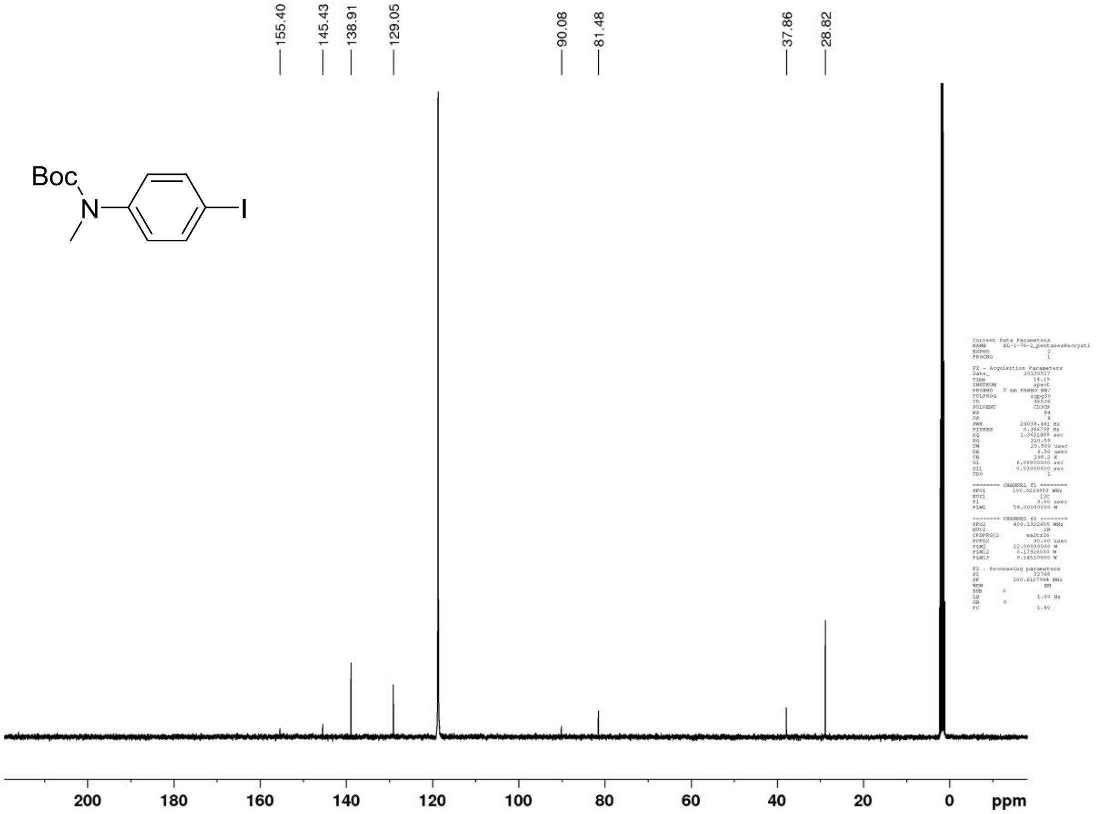


```
Current Data Parameters
NAME     EL-1-76-2_pentanesRecrystl
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20130517
Time                  14.14
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CD3CN
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES             0.122266 Hz
AQ                4.0894465 sec
RG                   126.38
DW                   62.400 usec
DE                     6.50 usec
TE                    298.2 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            400.1331310 MHz
NUC1                     1H
P1                    11.00 usec

F2 - Processing parameters
SI                    65536
SF              400.1306693 MHz
WDW                      EM
SSB      0
LB                     0.30 Hz
GB       0
PC                     1.00
```



```
Current Data Parameters
NAME     EL-1-76-2_pentanesRecrystl
EXPNO                     2
PROCNO                    1

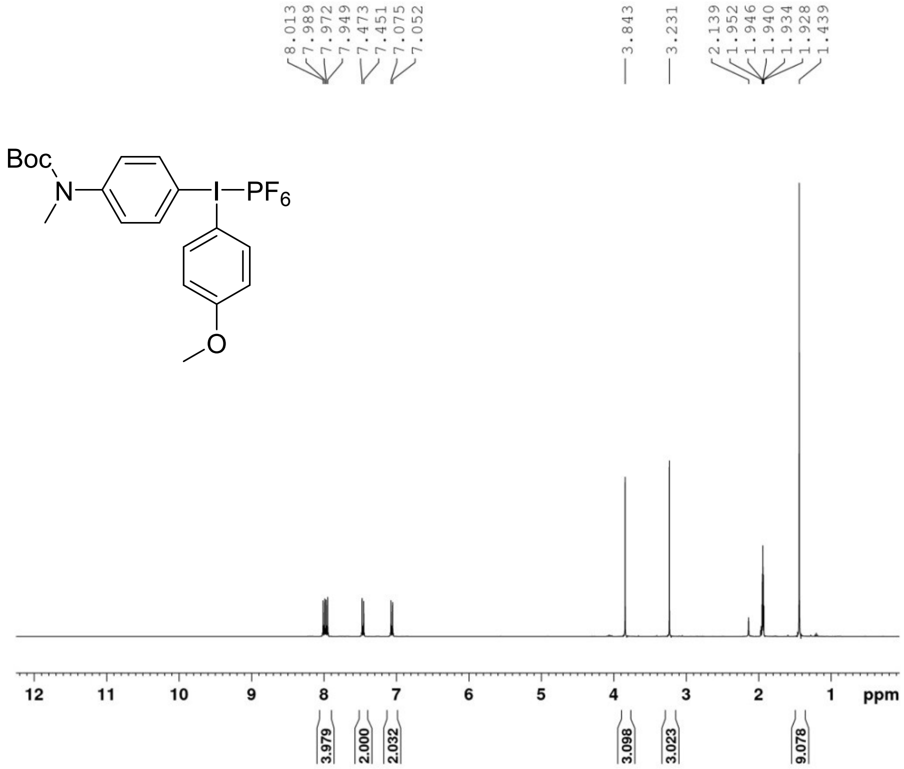
F2 - Acquisition Parameters
Date_              20130517
Time                  14.19
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                    65536
SOLVENT               CD3CN
NS                       84
DS                        4
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                1.3631988 sec
RG                   210.59
DW                   20.800 usec
DE                     6.50 usec
TE                    298.2 K
D1               6.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            100.6229953 MHz
NUC1                    13C
P1                     9.00 usec
PLW1            58.00000000 W

======== CHANNEL f2 ========
SFO2            400.1322405 MHz
NUC2                     1H
CPDPRG[2            waltz16
PCPD2                 90.00 usec
PLW2            12.00000000 W
PLW12            0.17926000 W
PLW13            0.14520000 W

F2 - Processing parameters
SI                    32768
SF              100.6127944 MHz
WDW                      EM
SSB      0
LB                     1.00 Hz
GB       0
PC                     1.40
```

(4-(N-methyl-N-Boc)anilino)(4'-methoxyphenyl)iodonium hexafluorophosphate

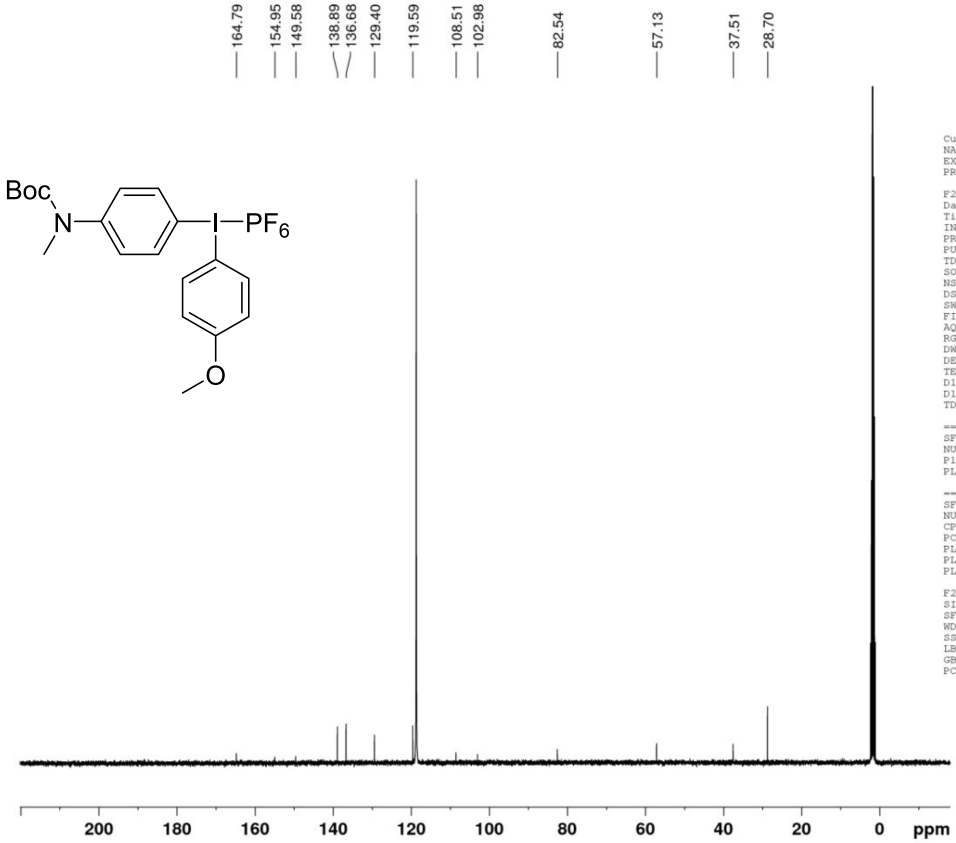


```
Current Data Parameters
NAME        EL-2-40_1wk
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20130913
Time               9.43
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CD3CN
NS                   16
DS                    2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894465 sec
RG               142.43
DW               62.400 usec
DE                 6.50 usec
TE                298.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        400.1331310 MHz
NUC1                 1H
P1                11.00 usec
PLW1        12.00000000 W

F2 - Processing parameters
SI                65536
SF          400.1306693 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```



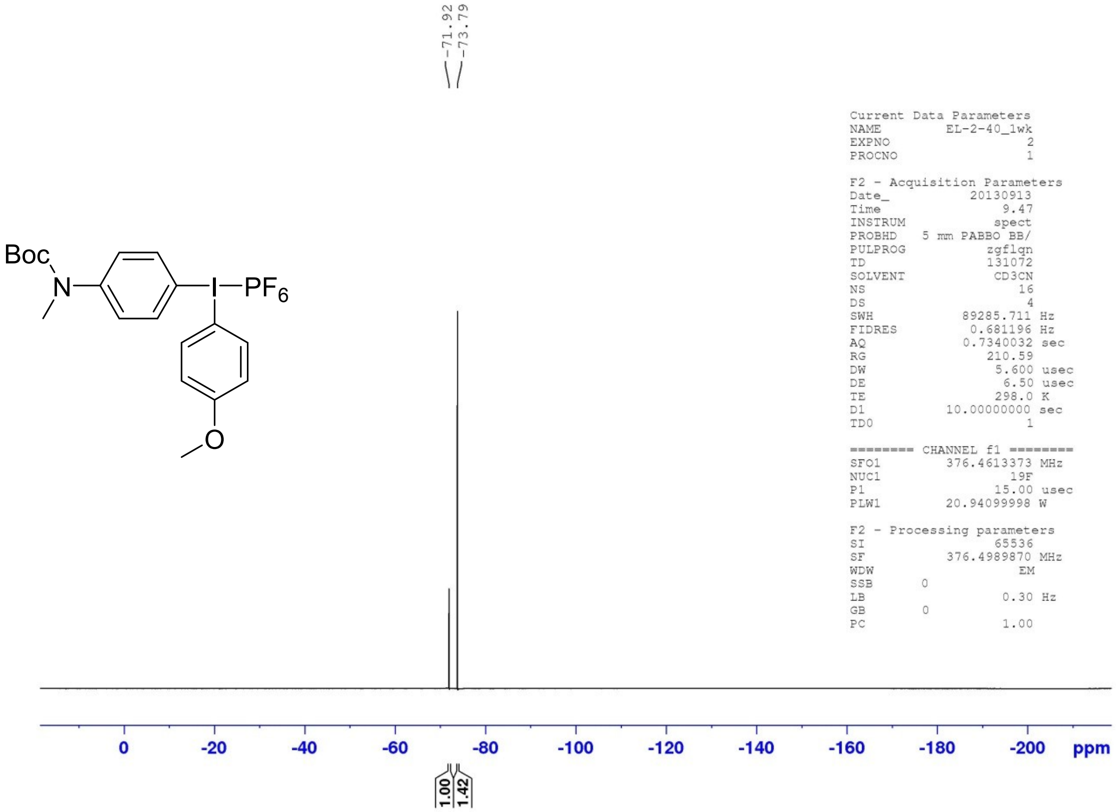
```
Current Data Parameters
NAME        EL-2-40_1wk
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20130913
Time               9.57
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CD3CN
NS                  111
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631488 sec
RG               210.59
DW               20.800 usec
DE                 6.50 usec
TE                298.0 K
D1           5.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        100.6229953 MHz
NUC1                13C
P1                 9.00 usec
PLW1        58.00000000 W

======== CHANNEL f2 ========
SFO2        400.1322605 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             90.00 usec
PLW2        12.00000000 W
PLW12        0.17926000 W
PLW13        0.14520000 W

F2 - Processing parameters
SI                32768
SF          100.6127963 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```



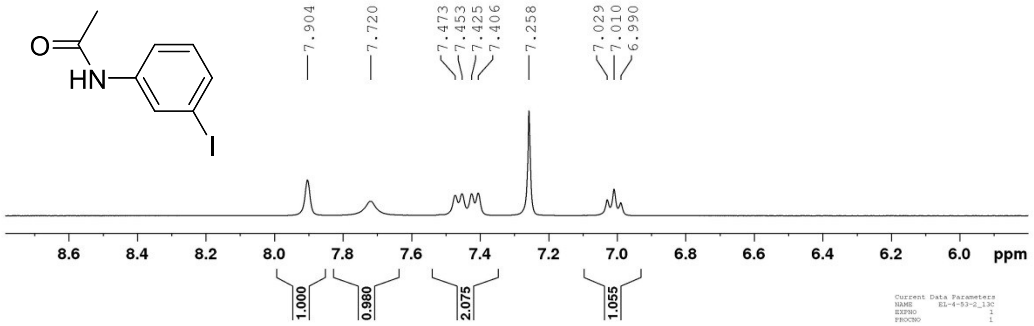
```
Current Data Parameters
NAME        EL-2-40_1wk
EXPNO                 2
PROCNO                1

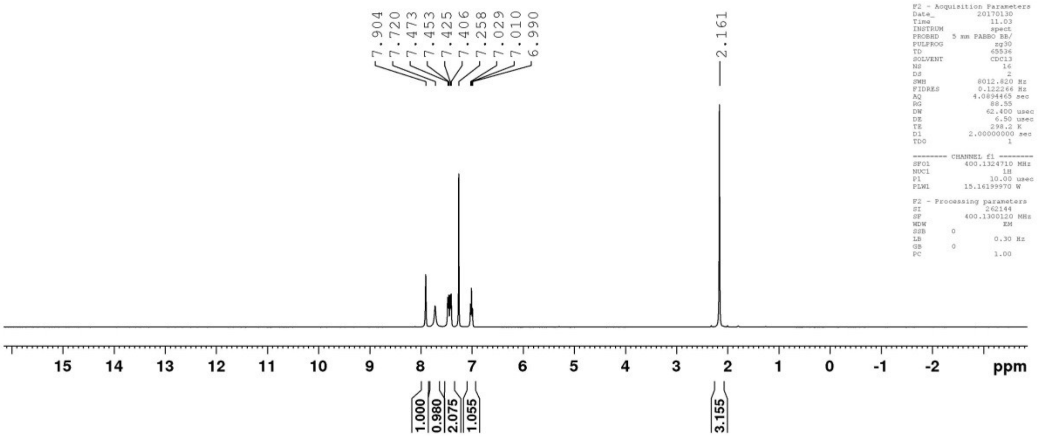
F2 - Acquisition Parameters
Date_          20130913
Time               9.47
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgflqn
TD               131072
SOLVENT           CD3CN
NS                   16
DS                    4
SWH          89285.711 Hz
FIDRES        0.681196 Hz
AQ           0.7340032 sec
RG               210.59
DW                5.600 usec
DE                 6.50 usec
TE                298.0 K
D1          10.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1       376.4613373 MHz
NUC1                19F
P1                15.00 usec
PLW1       20.94099998 W

F2 - Processing parameters
SI                65536
SF         376.4989870 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

N-acetyl-3-iodoaniline



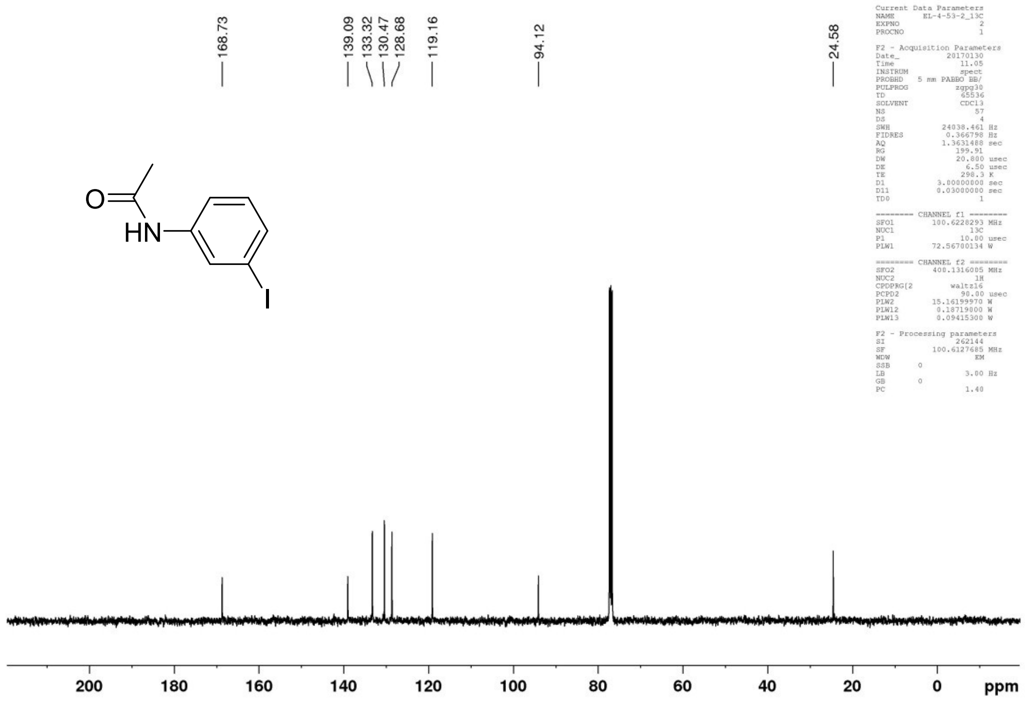


```
Current Data Parameters
NAME      EL-4-53-2_13C
EXPNO                 1
PROCNO                1

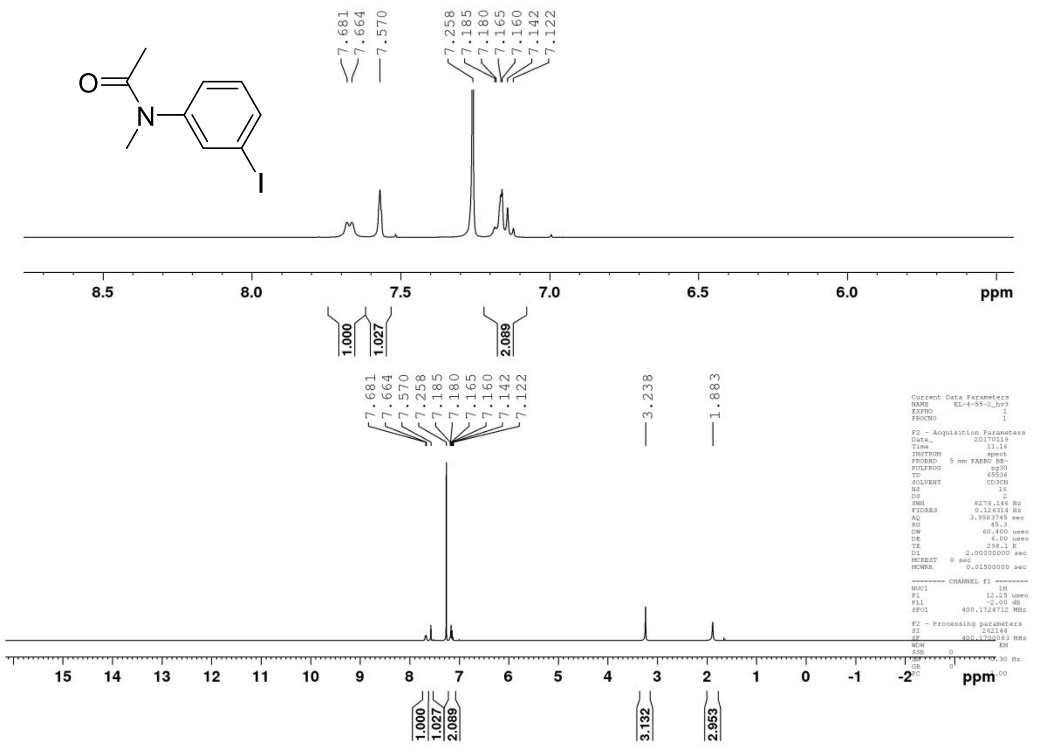
F2 - Acquisition Parameters
Date_          20170130
Time              11.03
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894465 sec
RG                88.55
DW               62.400 usec
DE                 6.50 usec
TE                298.2 K
D1           2.00000000 sec
TD0                   1

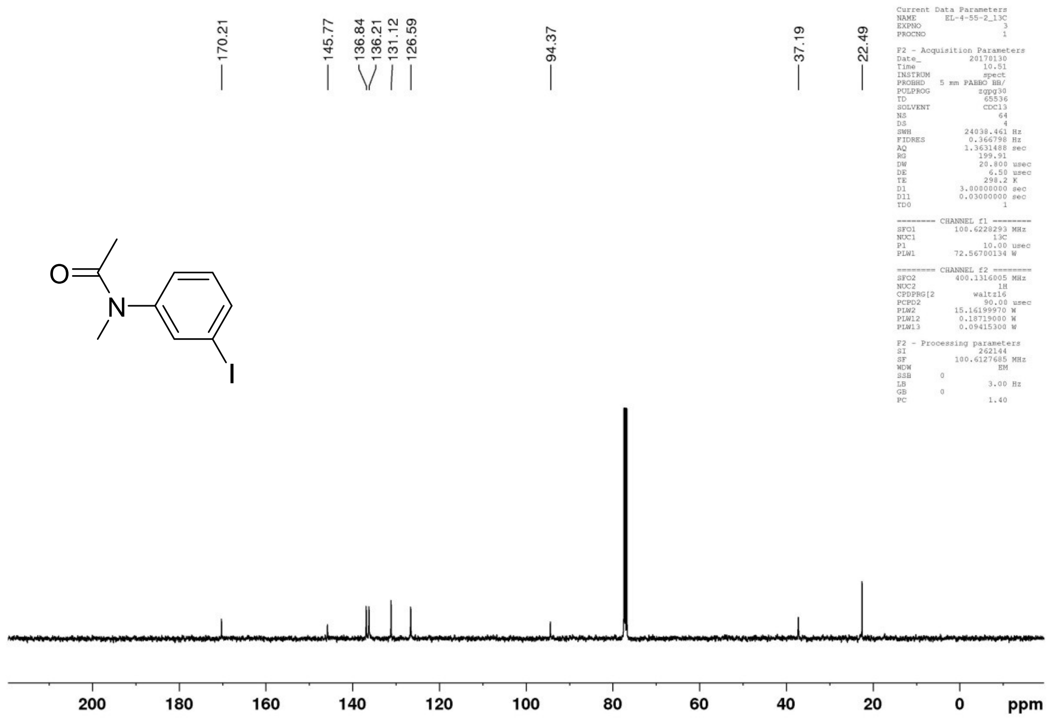
======== CHANNEL f1 ========
SFO1        400.1324710 MHz
NUC1                 1H
P1                10.00 usec
PLW1        15.16199970 W

F2 - Processing parameters
SI               262144
SF          400.1300120 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```



N-acetyl-3-iodo-N-methylaniline





```
Current Data Parameters
NAME      EL-4-55-2_13C
EXPNO                 3
PROCNO                1

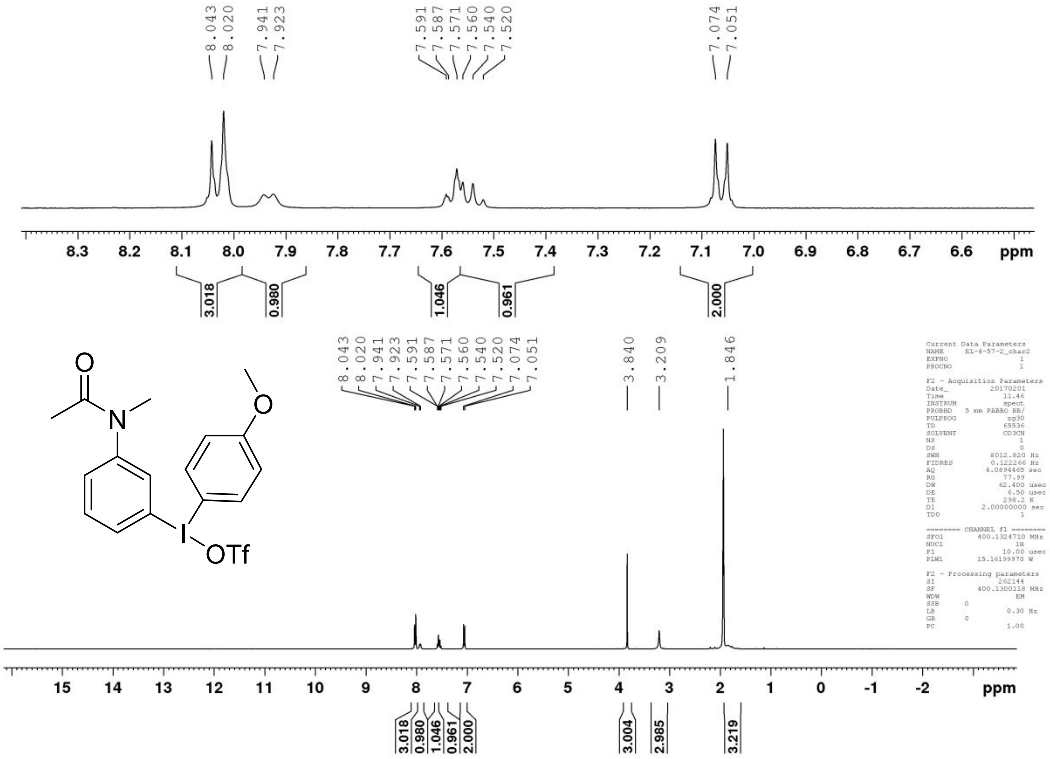
F2 - Acquisition Parameters
Date_          20170130
Time              10.51
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                   64
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631488 sec
RG               199.91
DW               20.800 usec
DE                 6.50 usec
TE                298.2 K
D1           3.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        100.6228293 MHz
NUC1                13C
P1                10.00 usec
PLW1        72.56700134 W

======== CHANNEL f2 ========
SFO2        400.1316005 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             90.00 usec
PLW2        15.16199970 W
PLW12        0.18719000 W
PLW13        0.09415300 W

F2 - Processing parameters
SI               262144
SF          100.6127685 MHz
WDW                  EM
SSB      0
LB                 3.00 Hz
GB       0
PC                 1.40
```

(3-(N-Methyl-N-acetamido)phenyl)(4'-methoxyphenyl)iodonium trifluoromethansulfonate

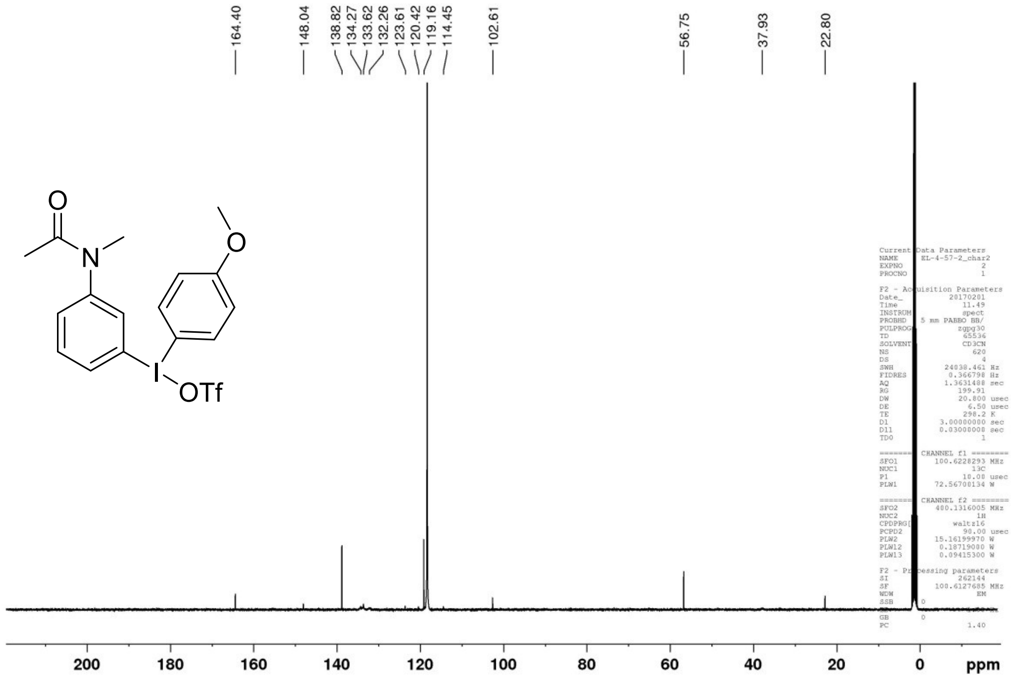


```
Current Data Parameters
NAME     EL-4-57-2_char2
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20170201
Time              11.46
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CD3CN
NS                    1
DS                    0
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894465 sec
RG                77.99
DW               62.400 usec
DE                 6.50 usec
TE                298.2 K
D1           2.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        400.1324710 MHz
NUC1                 1H
P1                10.00 usec
PLW1        15.16199970 W

F2 - Processing parameters
SI               262144
SF          400.1300118 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```



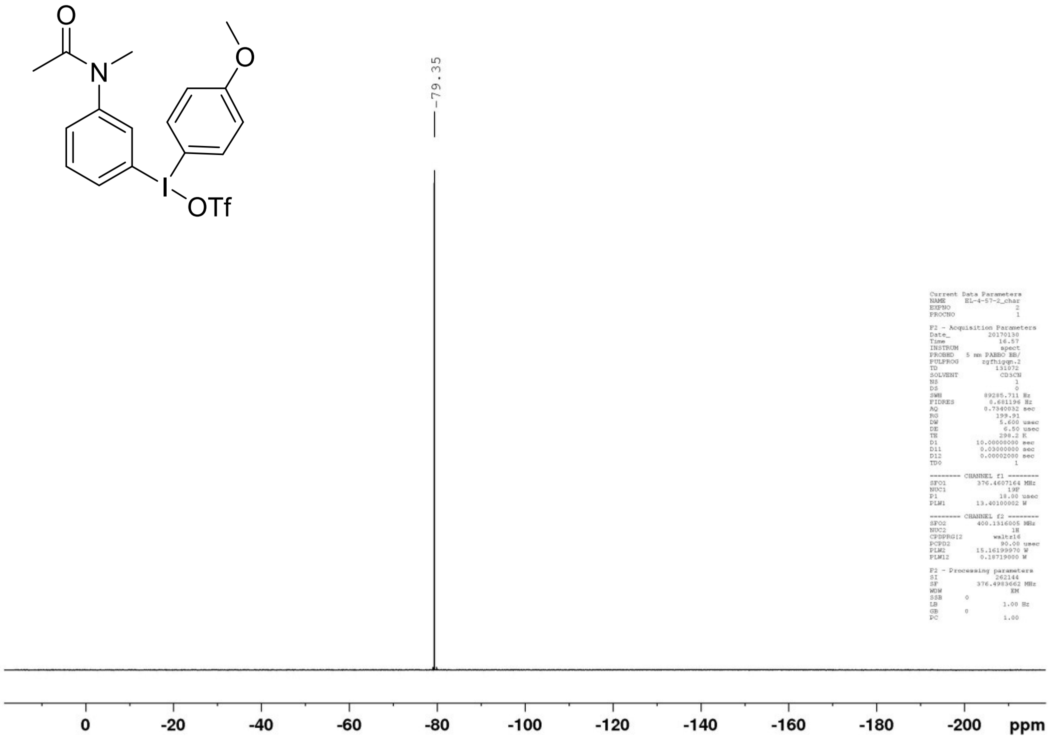
```
Current Data Parameters
NAME      EL-4-57-2_char2
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20170201
Time                11.49
INSTRUM             spect
PROBHD    5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT             CD3CN
NS                    620
DS                      4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631488 sec
RG                 199.91
DW                 20.800 usec
DE                   6.50 usec
TE                  298.2 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          100.6228293 MHz
NUC1                  13C
P1                  10.00 usec
PLW1          72.56700134 W

======== CHANNEL f2 ========
SFO2          400.1316005 MHz
NUC2                   1H
CPDPRG[            waltz16
PCPD2               90.00 usec
PLW2          15.16199970 W
PLW12          0.18719000 W
PLW13          0.09415300 W

F2 - Processing parameters
SI                 262144
SF            100.6127685 MHz
WDW                    EM
SSB      0
[illegible]
GB       0
PC                   1.40
```



```
Current Data Parameters
NAME      EL-4-57-2_char
EXPNO                  2
PROCNO                 1

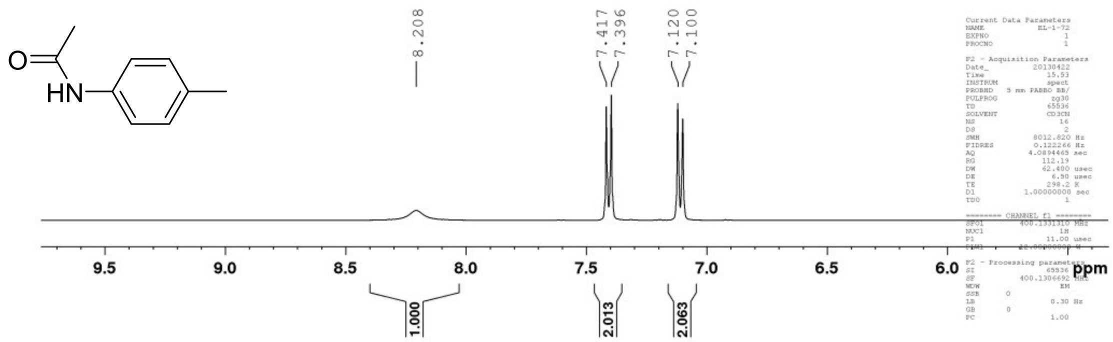
F2 - Acquisition Parameters
Date_           20170130
Time               16.57
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG       zgfhigqn.2
TD                131072
SOLVENT            CD3CN
NS                     1
DS                     0
SWH            89285.711 Hz
FIDRES          0.681196 Hz
AQ             0.7340032 sec
RG                199.91
DW                 5.600 usec
DE                  6.50 usec
TE                 298.2 K
D1           10.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
TD0                    1

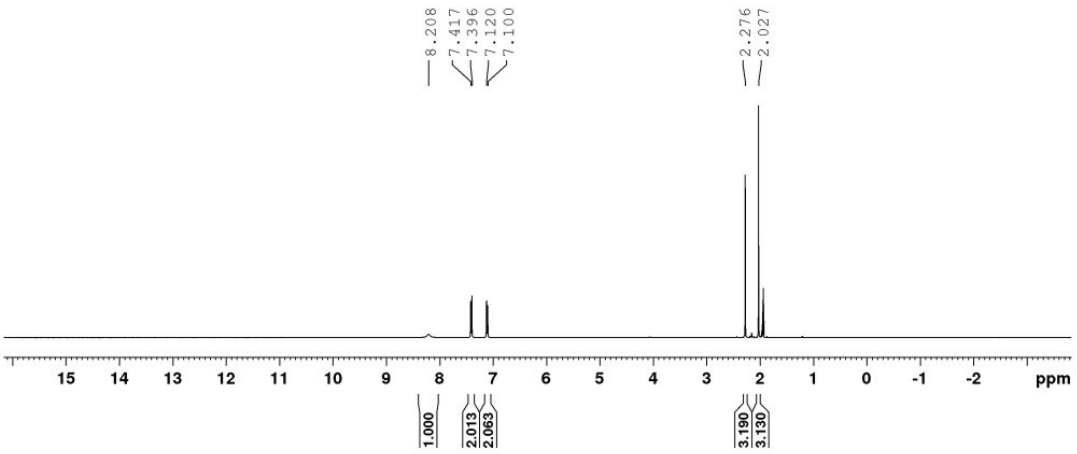
======== CHANNEL f1 ========
SFO1         376.4607164 MHz
NUC1                 19F
P1                 18.00 usec
PLW1         13.40100002 W

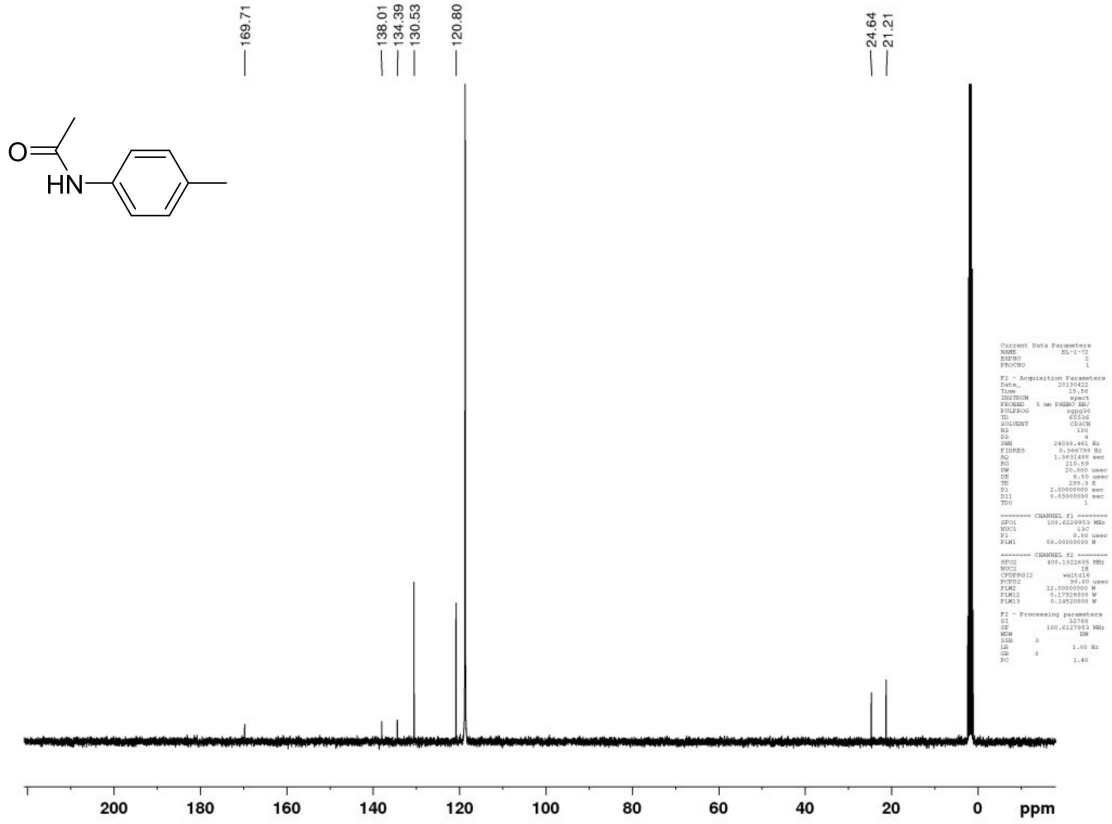
======== CHANNEL f2 ========
SFO2         400.1316005 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2              90.00 usec
PLW2         15.16199970 W
PLW12         0.18719000 W

F2 - Processing parameters
SI                262144
SF           376.4983662 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.00
```

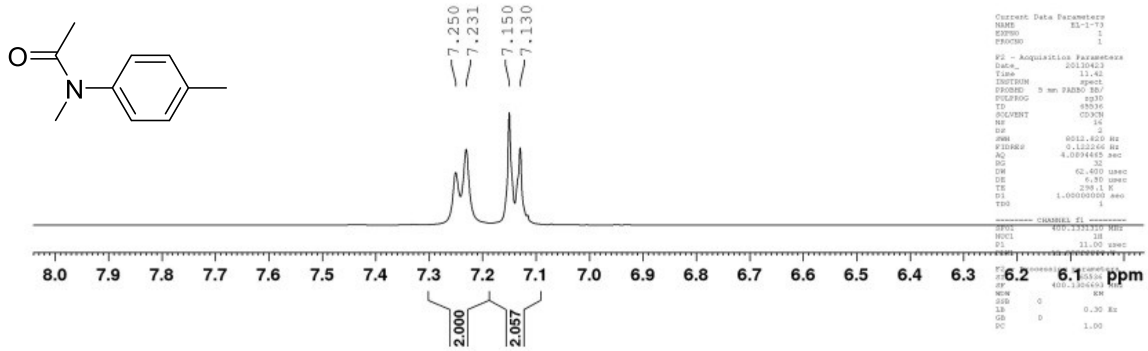
N-acetyltoluidine

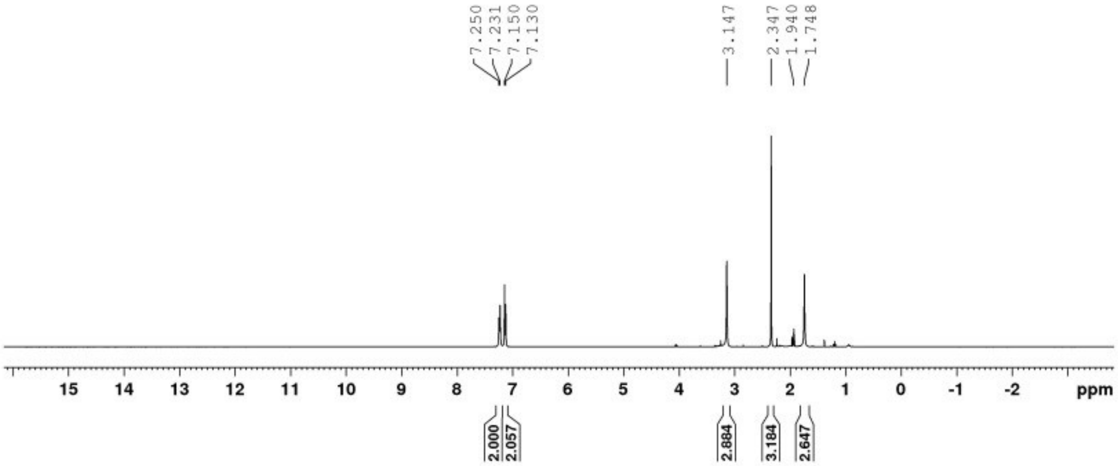


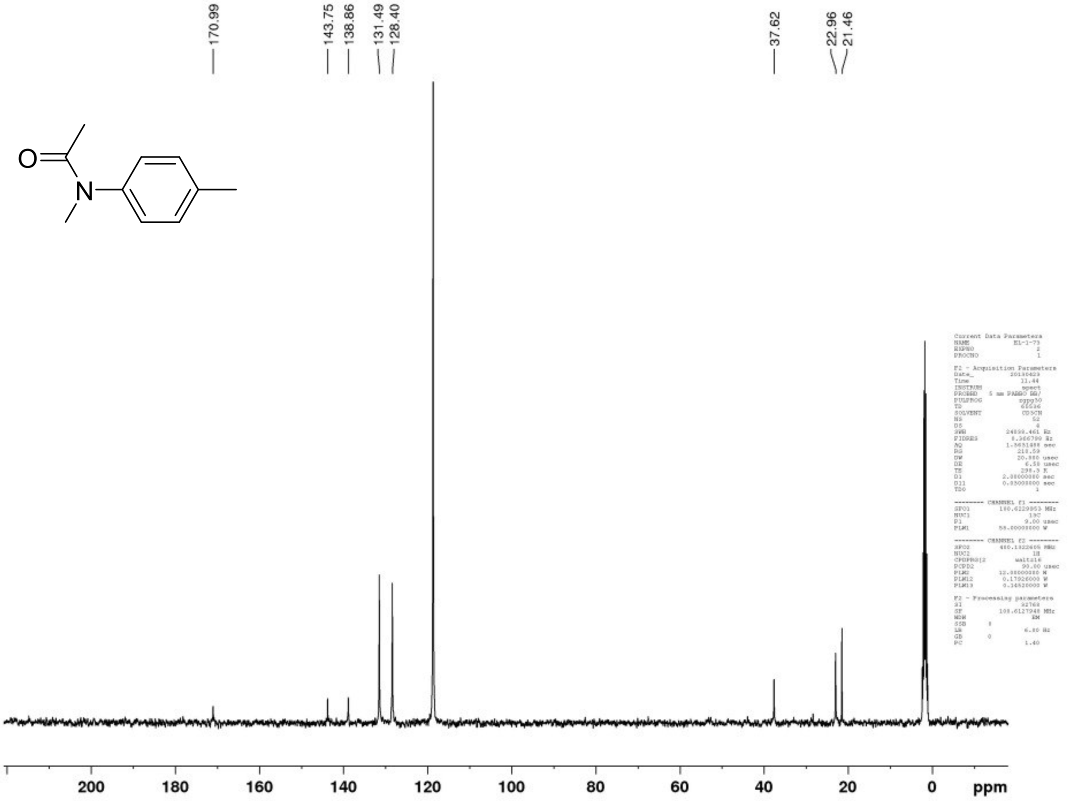




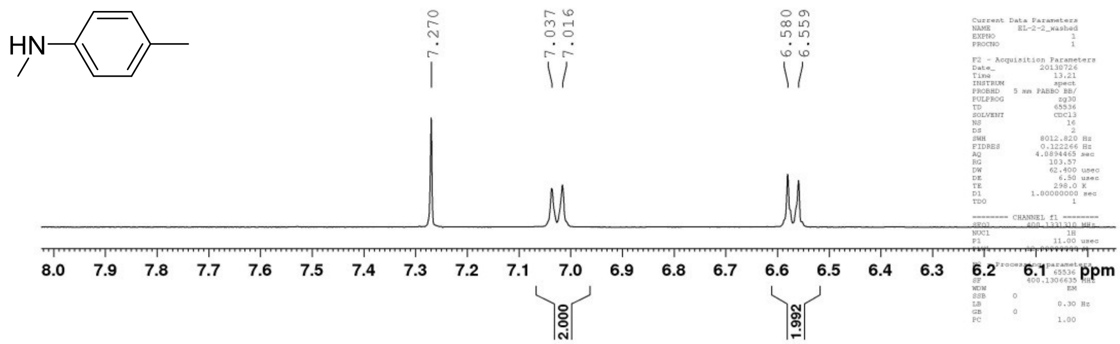
N-acetyl-N-methyltoluidine

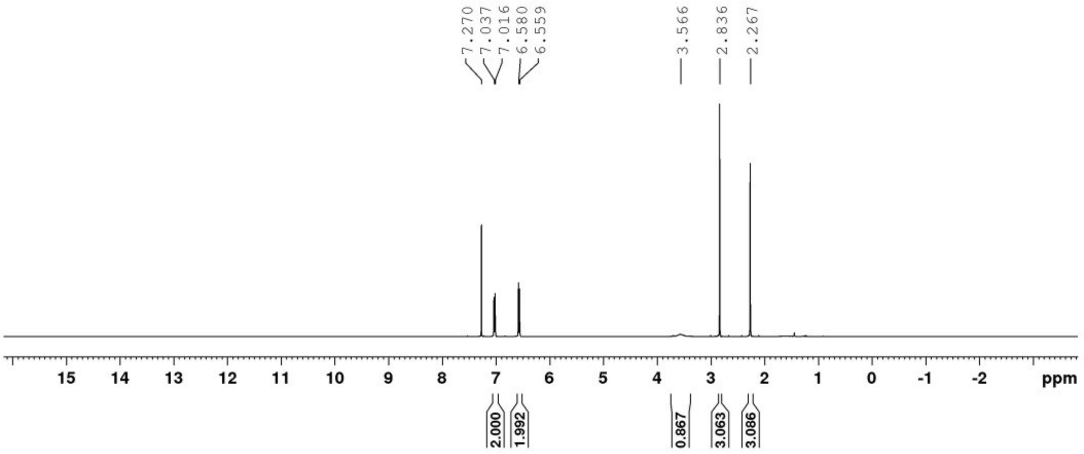


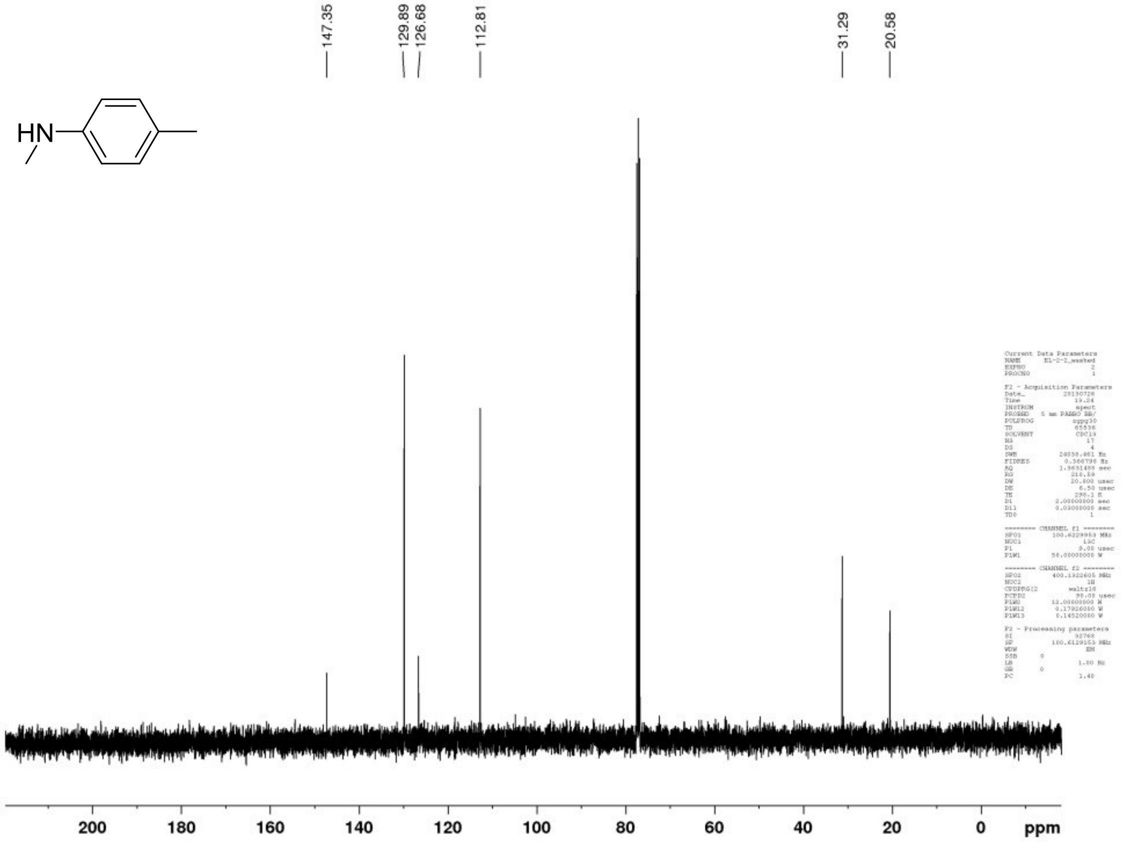




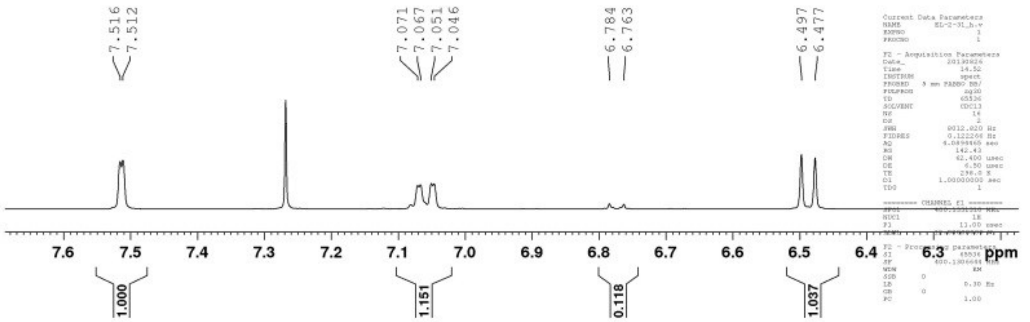
N-methyl-toluidine

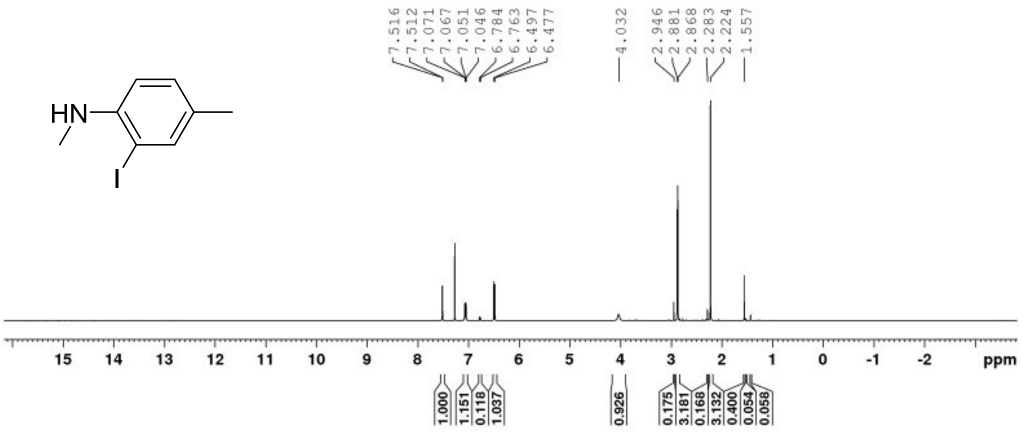


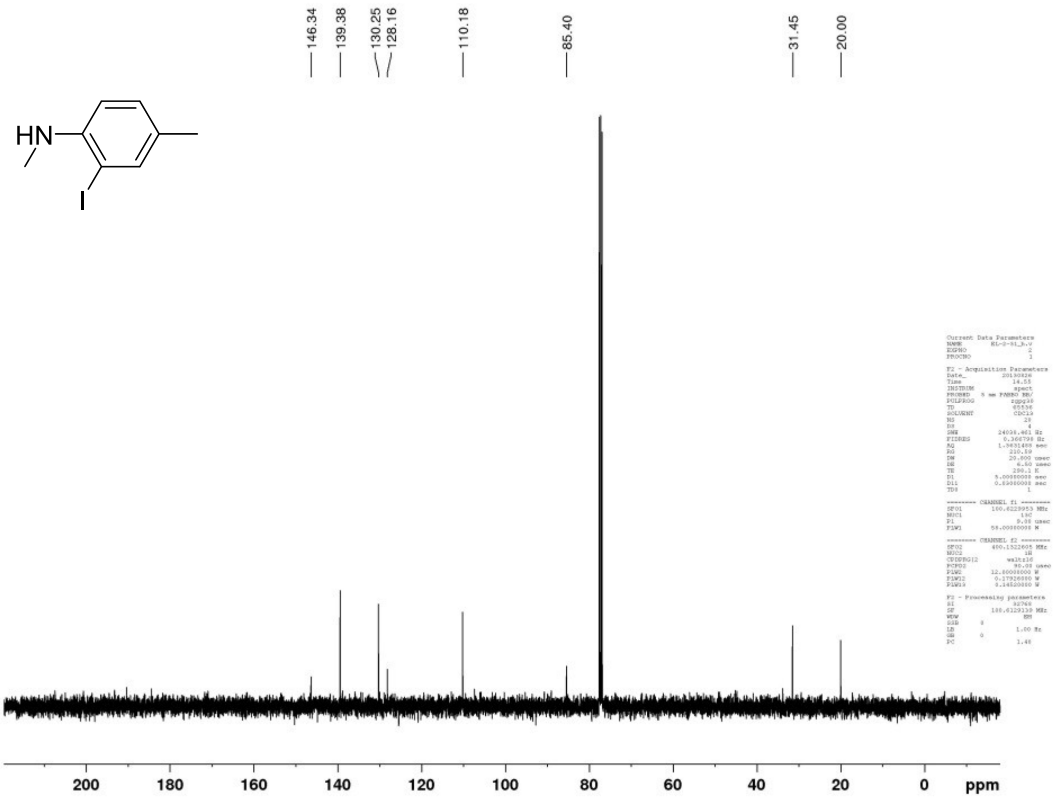




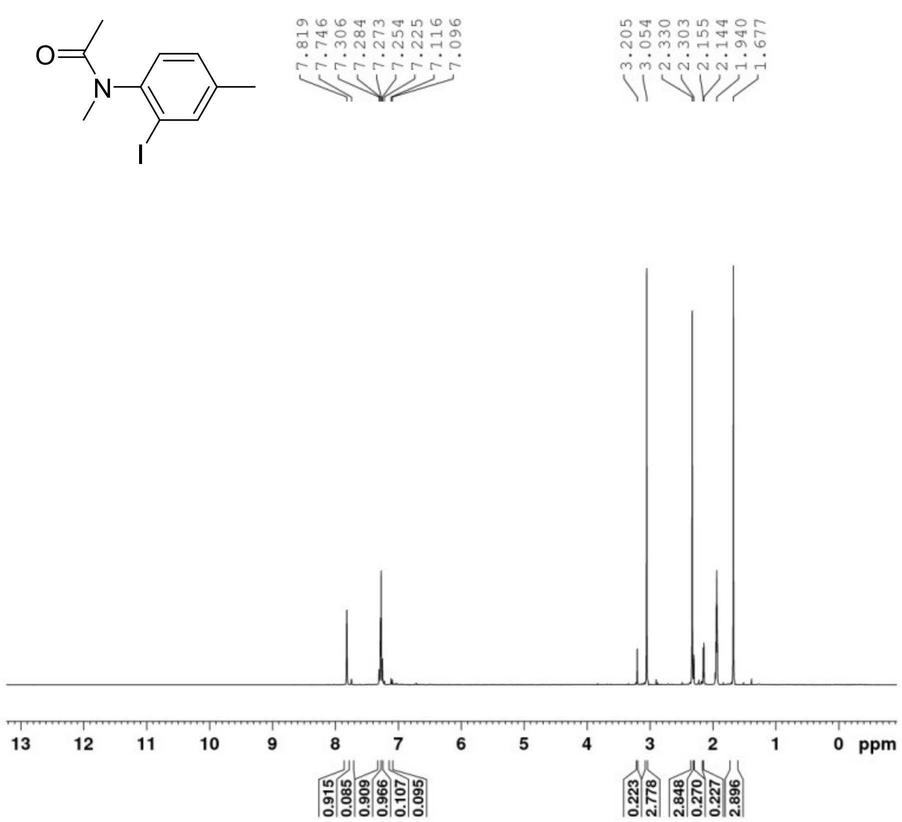
2-Iodo-N-methyltoluidine







N-acetyl-2-iodo-N-methyltoluidine

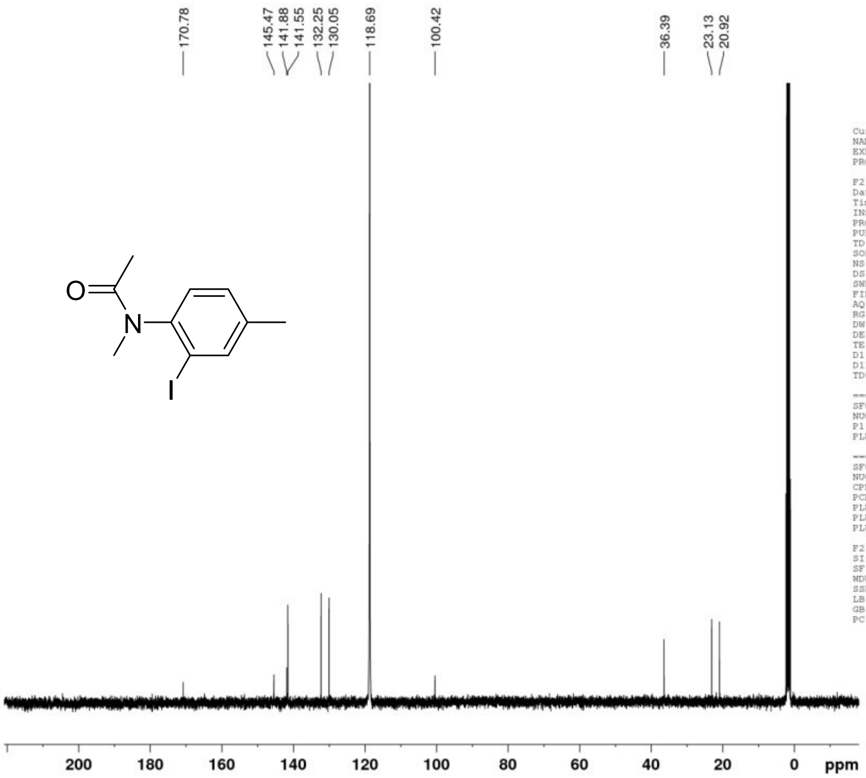


```
Current Data Parameters
NAME      EL-2-55_washed-2
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20131014
Time                  9.48
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zg30
TD                   65536
SOLVENT              CD3CN
NS                      16
DS                       2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894465 sec
RG                  103.57
DW              62.400 usec
DE                6.50 usec
TE               298.0 K
D1           1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1        400.1331310 MHz
NUC1                    1H
P1               11.00 usec
PLW1        12.00000000 W

F2 - Processing parameters
SI                   65536
SF          400.1306692 MHz
WDW                     EM
SSB      0
LB                 0.30 Hz
GB       0
PC                    1.00
```



```
Current Data Parameters
NAME      EL-2-55_washed-2
EXPNO                    3
PROCNO                   1

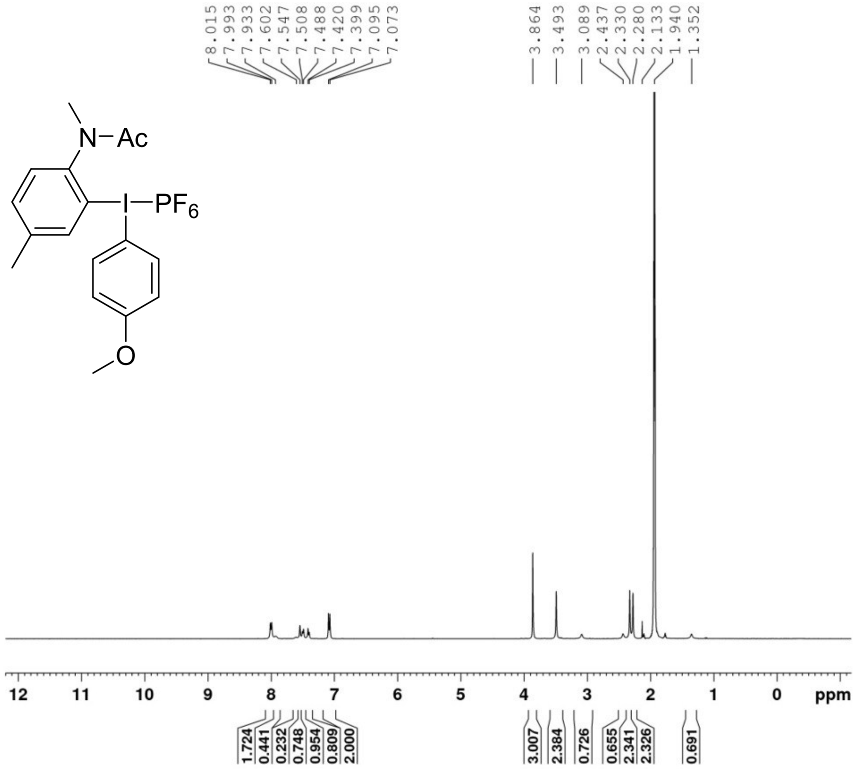
F2 - Acquisition Parameters
Date_             20131014
Time                  9.58
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                   65536
SOLVENT              CD3CN
NS                      86
DS                       4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631488 sec
RG                  210.59
DW              20.800 usec
DE                6.50 usec
TE               298.0 K
D1           4.00000000 sec
D11          0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1        100.6229953 MHz
NUC1                   13C
P1                9.00 usec
PLW1        58.00000000 W

======== CHANNEL f2 ========
SFO2        400.1322605 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2            90.00 usec
PLW2        12.00000000 W
PLW12        0.17926000 W
PLW13        0.14520000 W

F2 - Processing parameters
SI                   32768
SF          100.6127952 MHz
WDW                     EM
SSB      0
LB                 1.00 Hz
GB       0
PC                    1.40
```

(5-Methyl-2-(N-methyl-N-acetamido)phenyl)(4'-methoxyphenyl)iodonium hexafluorophosphate

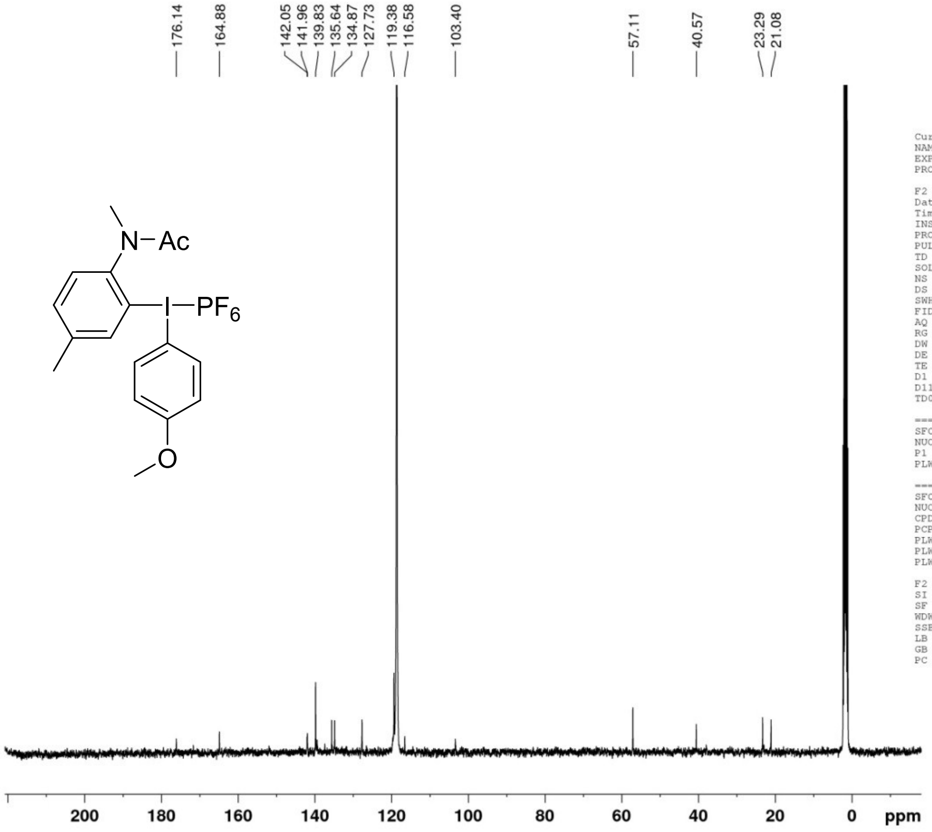


```
Current Data Parameters
NAME       EL-2-64-2_1H
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20131115
Time              11.31
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CD3CN
NS                   16
DS                    2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894465 sec
RG                88.85
DW               62.400 usec
DE                 6.50 usec
TE                298.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        400.1331310 MHz
NUC1                 1H
P1                11.00 usec
PLW1        12.00000000 W

F2 - Processing parameters
SI                65536
SF          400.1306693 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.00
```



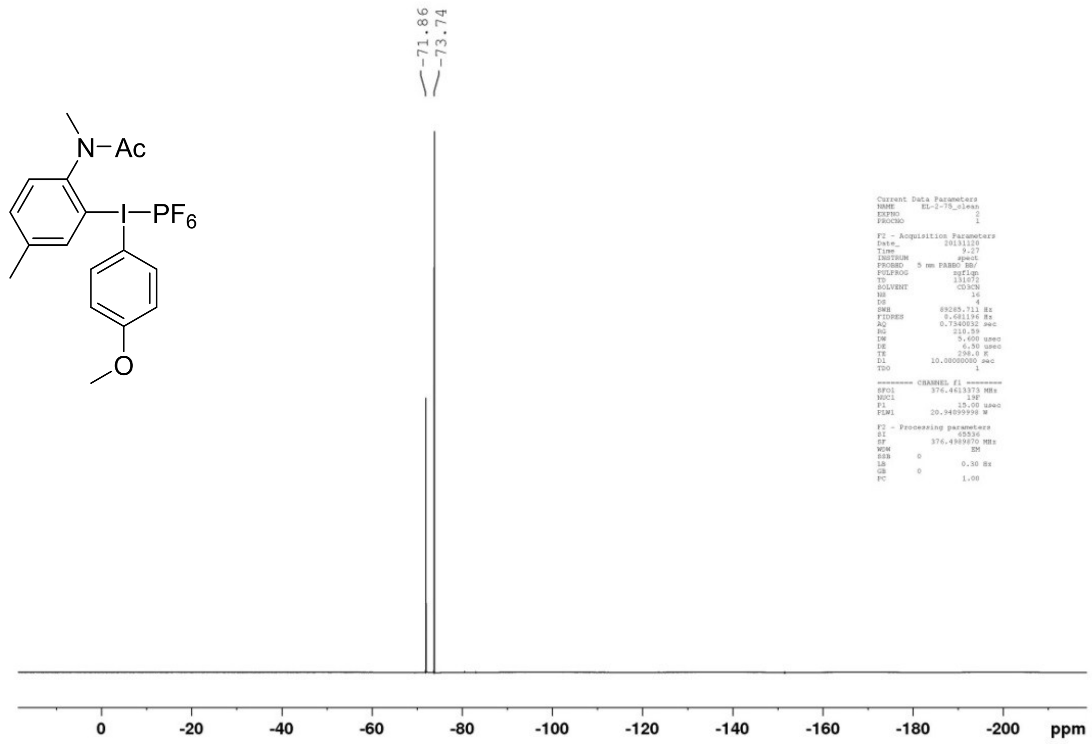
```
Current Data Parameters
NAME       EL-2-64-2_13C
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20131112
Time              13.01
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CD3CN
NS                  526
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631488 sec
RG               210.59
DW               20.800 usec
DE                 6.50 usec
TE                297.5 K
D1           5.00000000 sec
D11          0.03000000 sec
TD0                   1

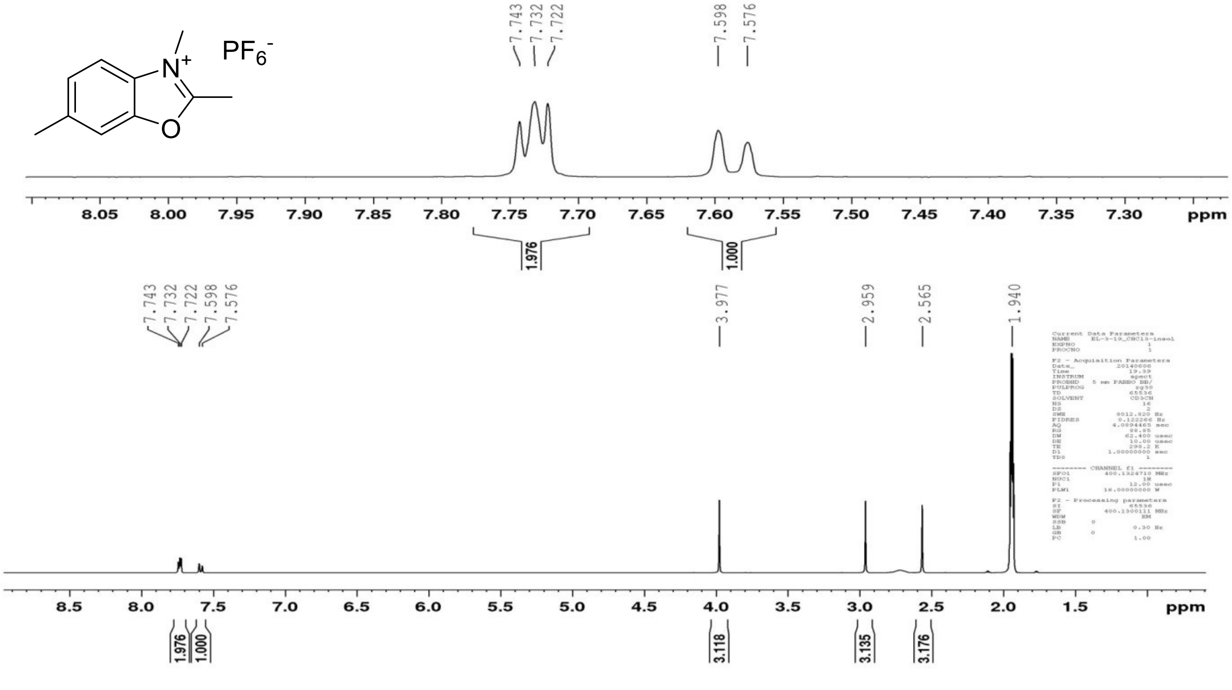
======== CHANNEL f1 ========
SFO1        100.6229953 MHz
NUC1                13C
P1                 9.00 usec
PLW1        58.00000000 W

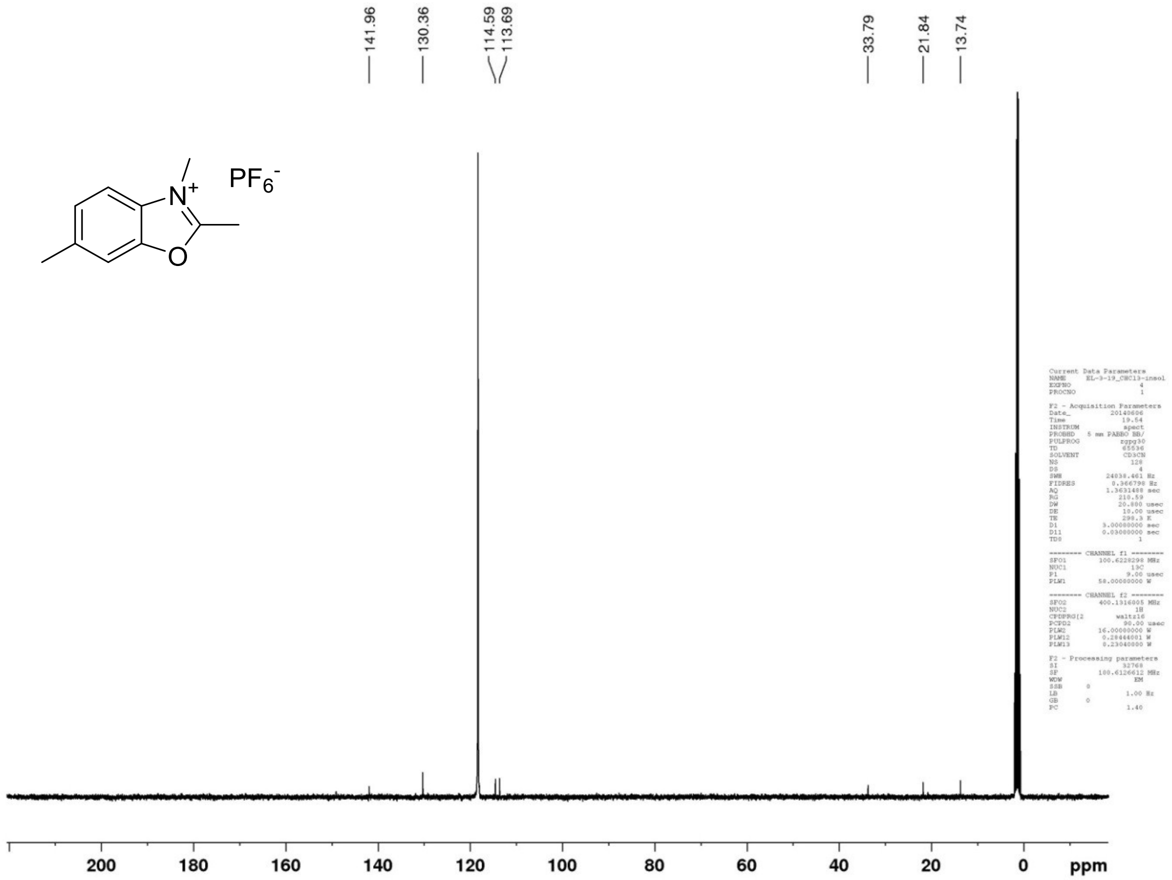
======== CHANNEL f2 ========
SFO2        400.1322605 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             90.00 usec
PLW2        12.00000000 W
PLW12        0.17926000 W
PLW13        0.14520000 W

F2 - Processing parameters
SI                32768
SF          100.6127978 MHz
WDW                  EM
SSB      0
LB                 3.00 Hz
GB       0
PC                 1.40
```



2,3,6-trimethylbenzoxazolium hexafluorophosphate





```
Current Data Parameters
NAME     EL-3-19_CHCl3-insol
EXPNO                     4
PROCNO                    1

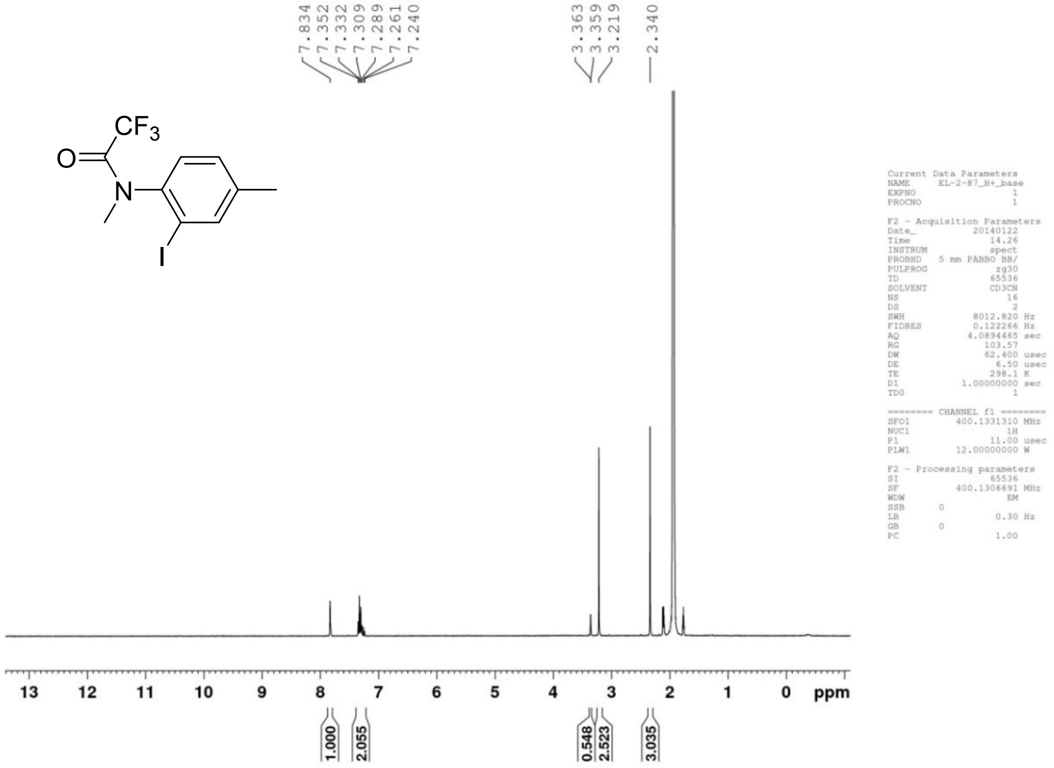
F2 - Acquisition Parameters
Date_              20140606
Time                  19.54
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                   65536
SOLVENT              CD3CN
NS                     128
DS                       4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631488 sec
RG                 210.59
DW                 20.800 usec
DE                  10.00 usec
TE                  298.3 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          100.6228298 MHz
NUC1                  13C
P1                   9.00 usec
PLW1          58.00000000 W

======== CHANNEL f2 ========
SFO2          400.1316005 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               90.00 usec
PLW2          16.00000000 W
PLW12          0.28444001 W
PLW13          0.23040000 W

F2 - Processing parameters
SI                  32768
SF            100.6126612 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.40
```

N-trifluoroacetyl-2-iodo-N-methyltoluidine

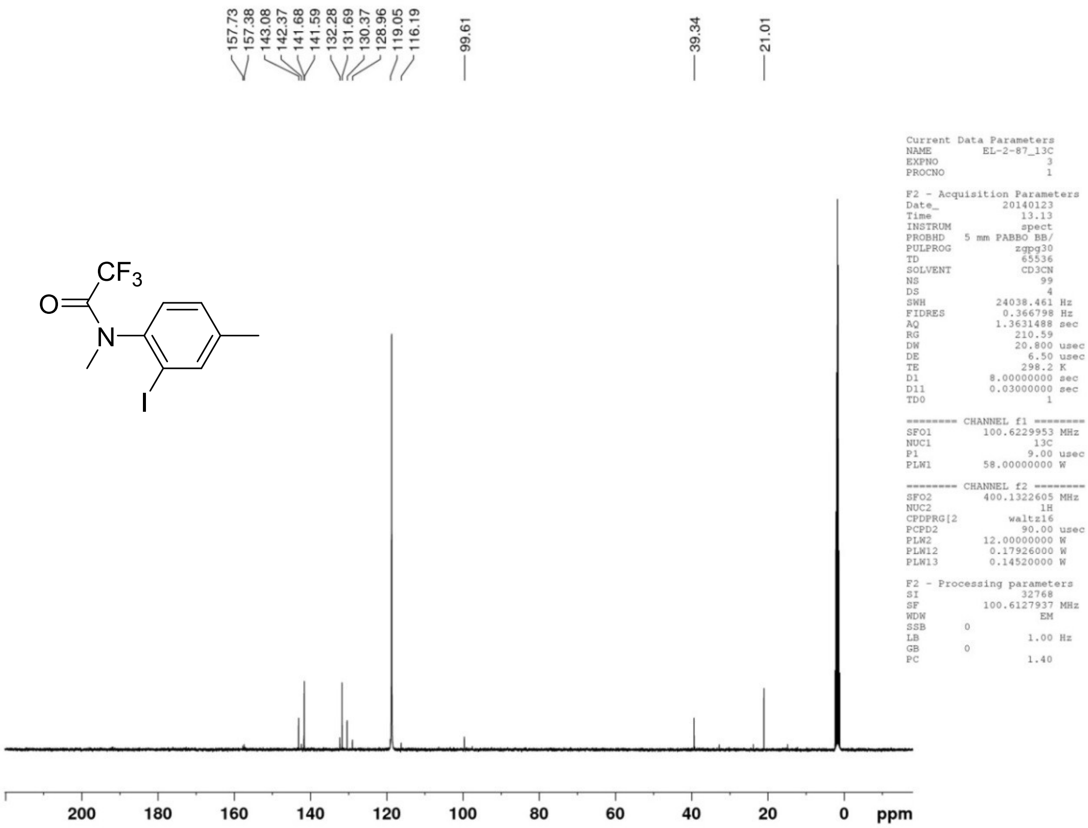


```
Current Data Parameters
NAME      EL-2-87_H+_base
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20140122
Time                14.26
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CD3CN
NS                     16
DS                      2
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894465 sec
RG                 103.57
DW                 62.400 usec
DE                   6.50 usec
TE                  298.1 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          400.1331310 MHz
NUC1                   1H
P1                  11.00 usec
PLW1          12.00000000 W

F2 - Processing parameters
SI                  65536
SF            400.1306691 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



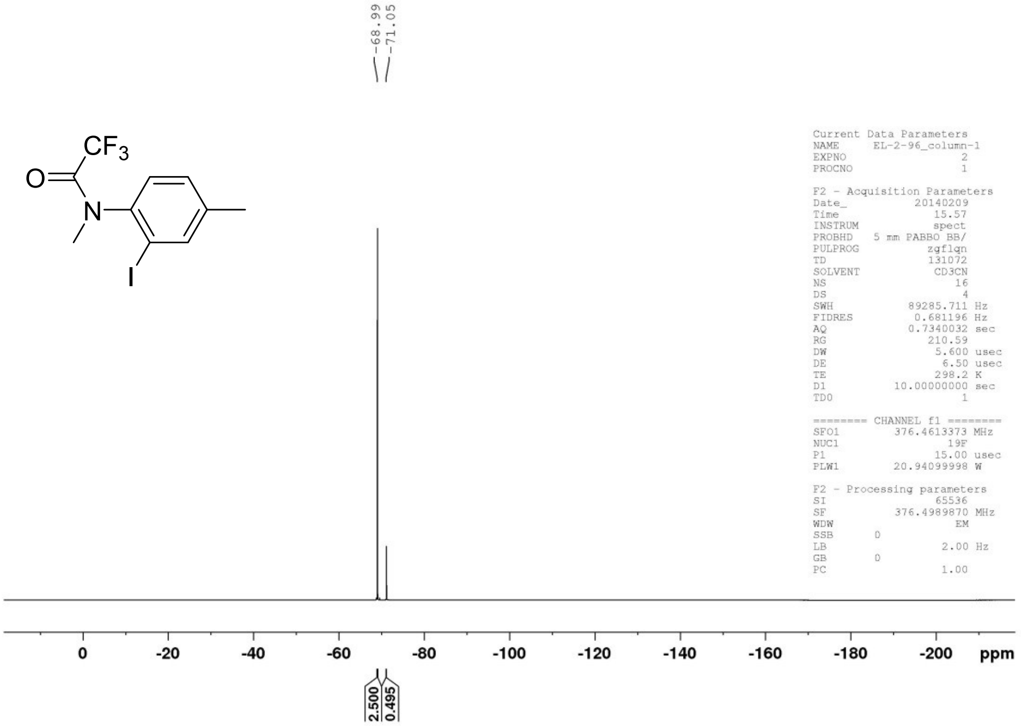
```
Current Data Parameters
NAME        EL-2-87_13C
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20140123
Time              13.13
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CD3CN
NS                   99
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631488 sec
RG               210.59
DW               20.800 usec
DE                 6.50 usec
TE                298.2 K
D1           8.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        100.6229953 MHz
NUC1                13C
P1                 9.00 usec
PLW1        58.00000000 W

======== CHANNEL f2 ========
SFO2        400.1322605 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             90.00 usec
PLW2        12.00000000 W
PLW12        0.17926000 W
PLW13        0.14520000 W

F2 - Processing parameters
SI                32768
SF          100.6127937 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```



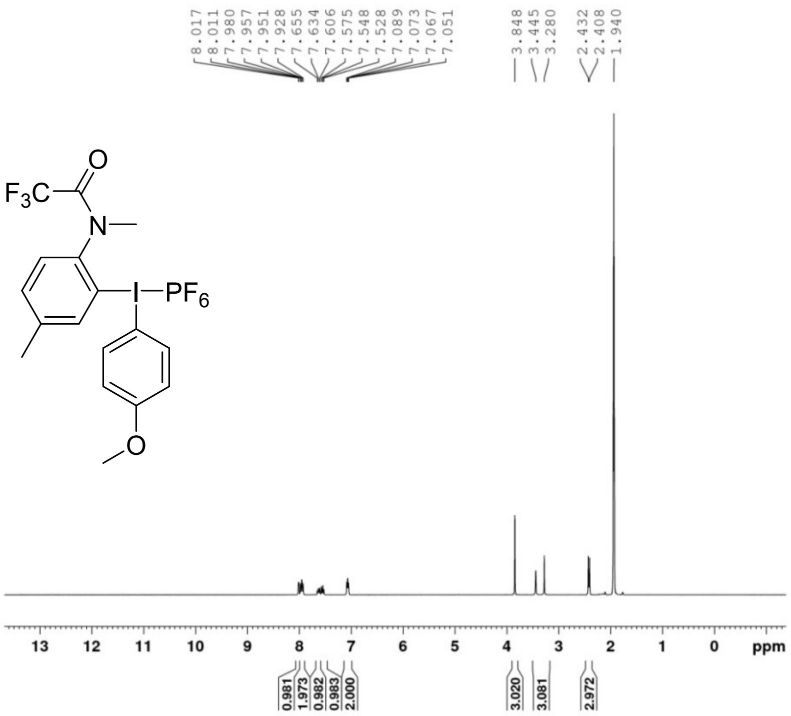
```
Current Data Parameters
NAME     EL-2-96_column-1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140209
Time               15.57
INSTRUM            spect
PROBHD    5 mm PABBO BB/
PULPROG           zgflqn
TD                131072
SOLVENT            CD3CN
NS                    16
DS                     4
SWH            89285.711 Hz
FIDRES          0.681196 Hz
AQ             0.7340032 sec
RG                210.59
DW                 5.600 usec
DE                  6.50 usec
TE                 298.2 K
D1           10.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         376.4613373 MHz
NUC1                 19F
P1                 15.00 usec
PLW1         20.94099998 W

F2 - Processing parameters
SI                 65536
SF           376.4989870 MHz
WDW                   EM
SSB      0
LB                  2.00 Hz
GB       0
PC                  1.00
```

(5-Methyl-2-(N-methyl-N-trifluoroacetamido)phenyl) (4'-methoxyphenyl)iodonium hexafluorophosphate

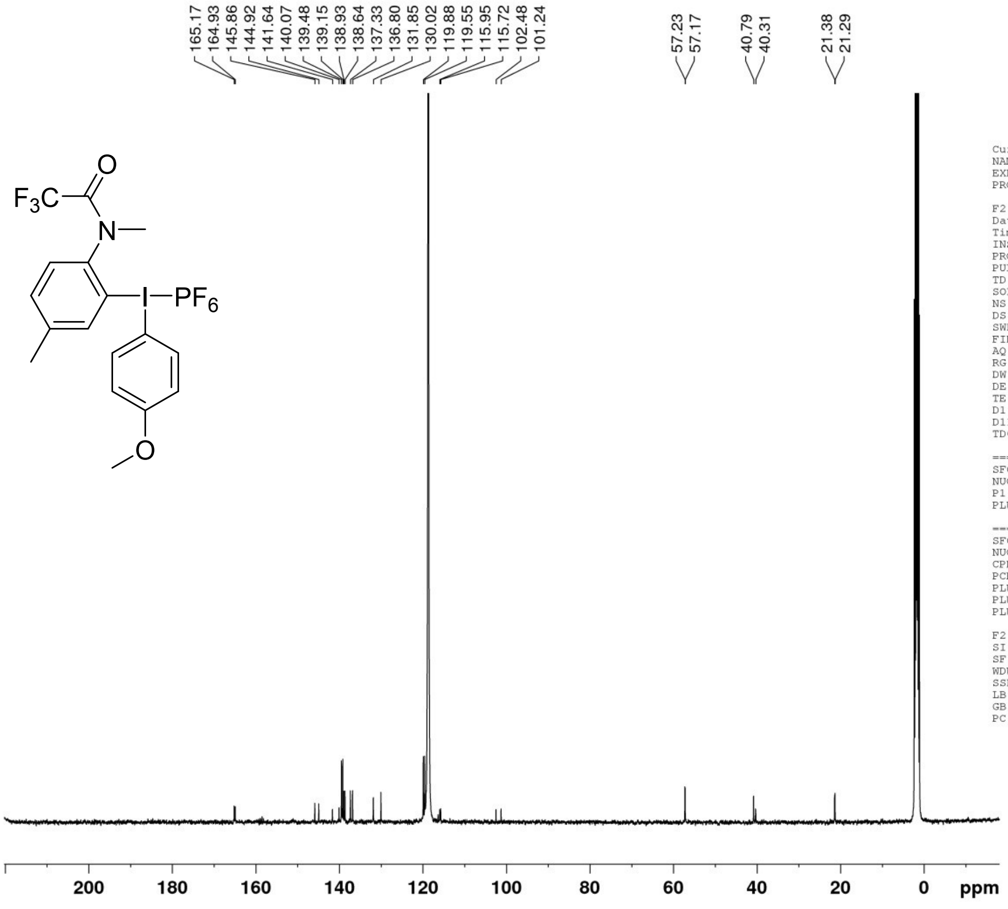


```
Current Data Parameters
NAME          EL-3-6_A
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_         20140303
Time             18.32
INSTRUM          spect
PROBHD   5 mm PABBO BB/
PULPROG           zg30
TD               65536
SOLVENT          CD3CN
NS                  16
DS                   2
SWH           8012.820 Hz
FIDRES        0.122266 Hz
AQ           4.0894465 sec
RG               88.85
DW              62.400 usec
DE                6.50 usec
TE               298.0 K
D1          4.00000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1       400.1331310 MHz
NUC1                1H
P1               11.00 usec
PLW1       12.00000000 W

F2 - Processing parameters
SI               65536
SF         400.1306695 MHz
WDW                 EM
SSB      0
LB                0.30 Hz
GB       0
PC                1.00
```



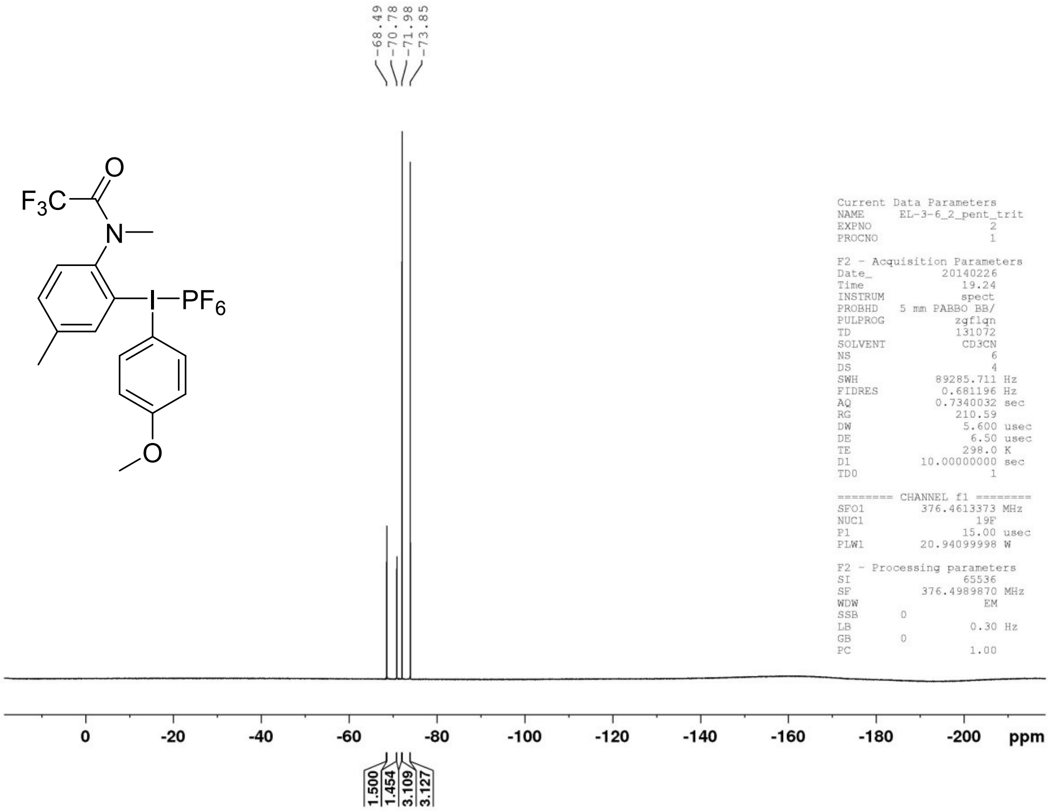
```
Current Data Parameters
NAME       EL-3-6_A-13C
EXPNO                2
PROCNO               1

F2 - Acquisition Parameters
Date_         20140305
Time             23.10
INSTRUM          spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD               65536
SOLVENT          CD3CN
NS                3490
DS                   4
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ           1.3631488 sec
RG              210.59
DW              20.800 usec
DE                6.50 usec
TE               298.1 K
D1          8.00000000 sec
D11         0.03000000 sec
TD0                  1

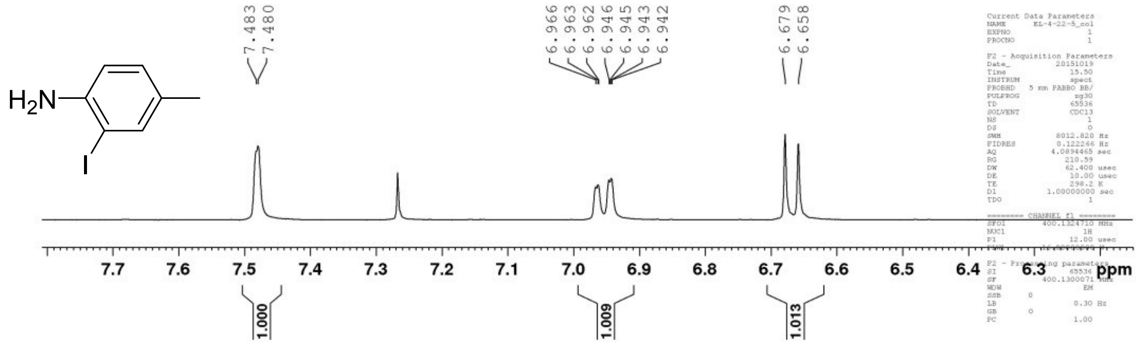
======== CHANNEL f1 ========
SFO1       100.6229953 MHz
NUC1               13C
P1                9.00 usec
PLW1       58.00000000 W

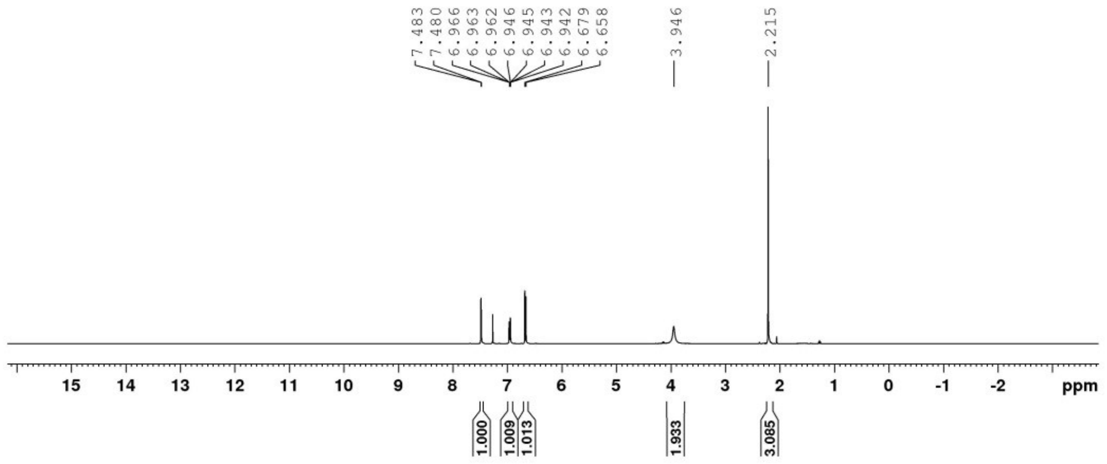
======== CHANNEL f2 ========
SFO2       400.1322605 MHz
NUC2                1H
CPDPRG[2        waltz16
PCPD2            90.00 usec
PLW2       12.00000000 W
PLW12       0.17926000 W
PLW13       0.14520000 W

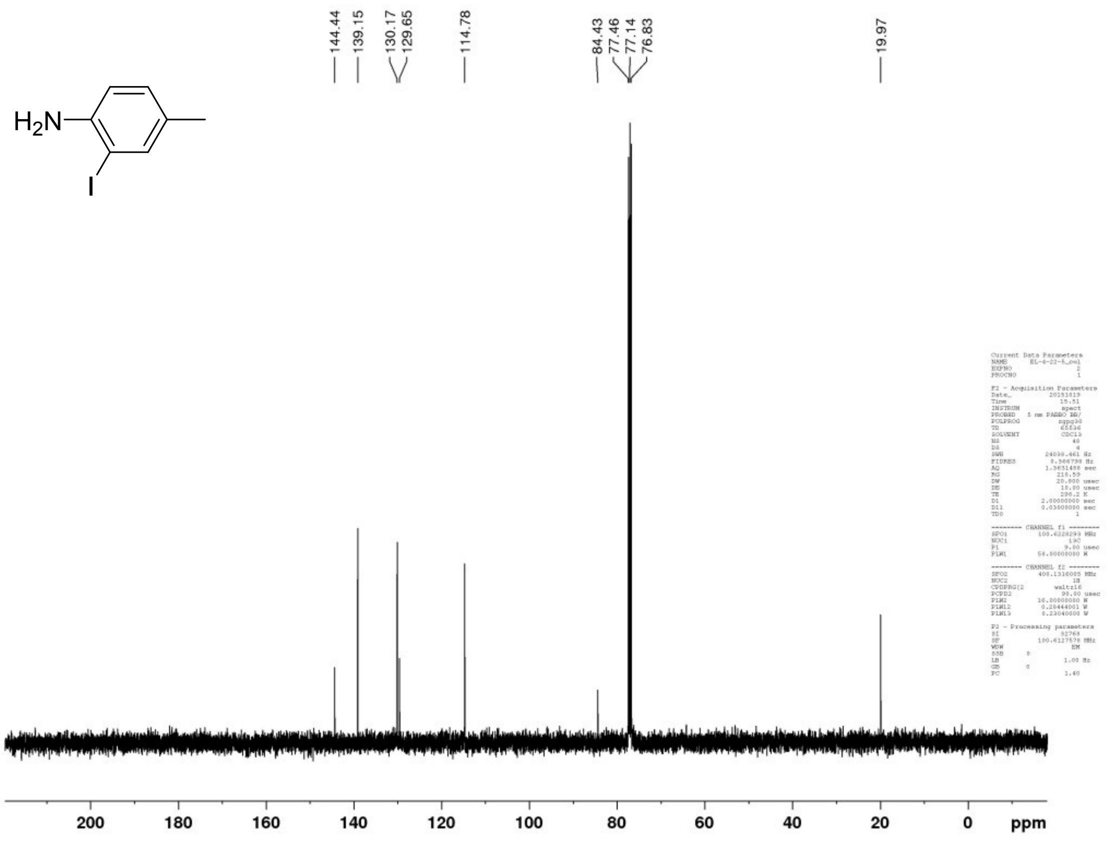
F2 - Processing parameters
SI               32768
SF         100.6127962 MHz
WDW                 EM
SSB      0
LB                3.00 Hz
GB       0
PC                1.40
```



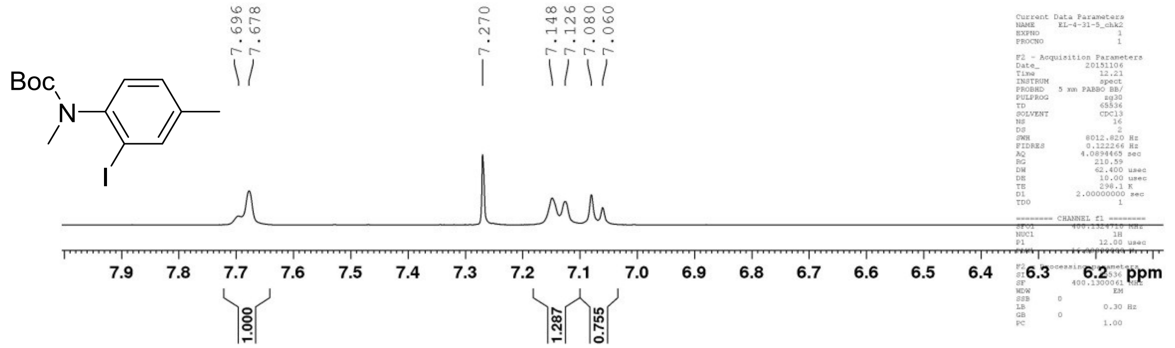
2-Iodotoluidine

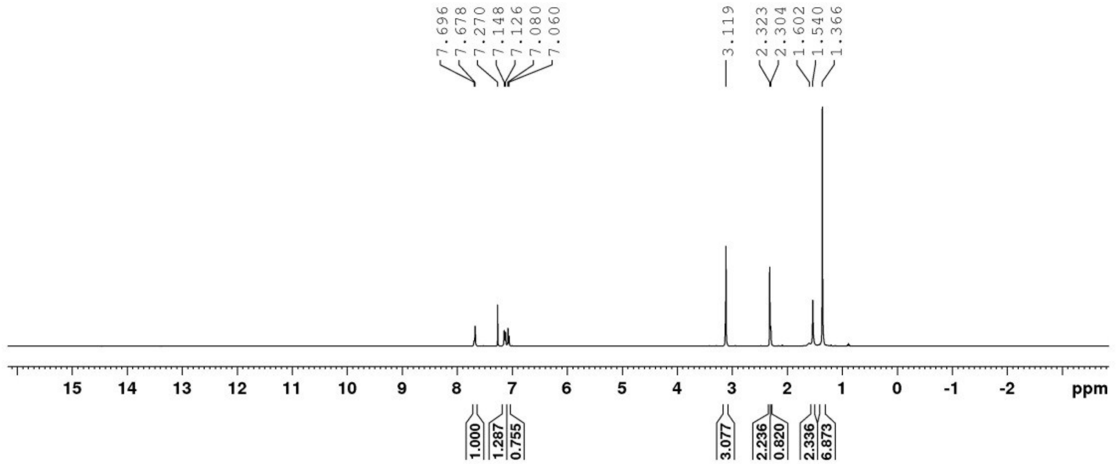


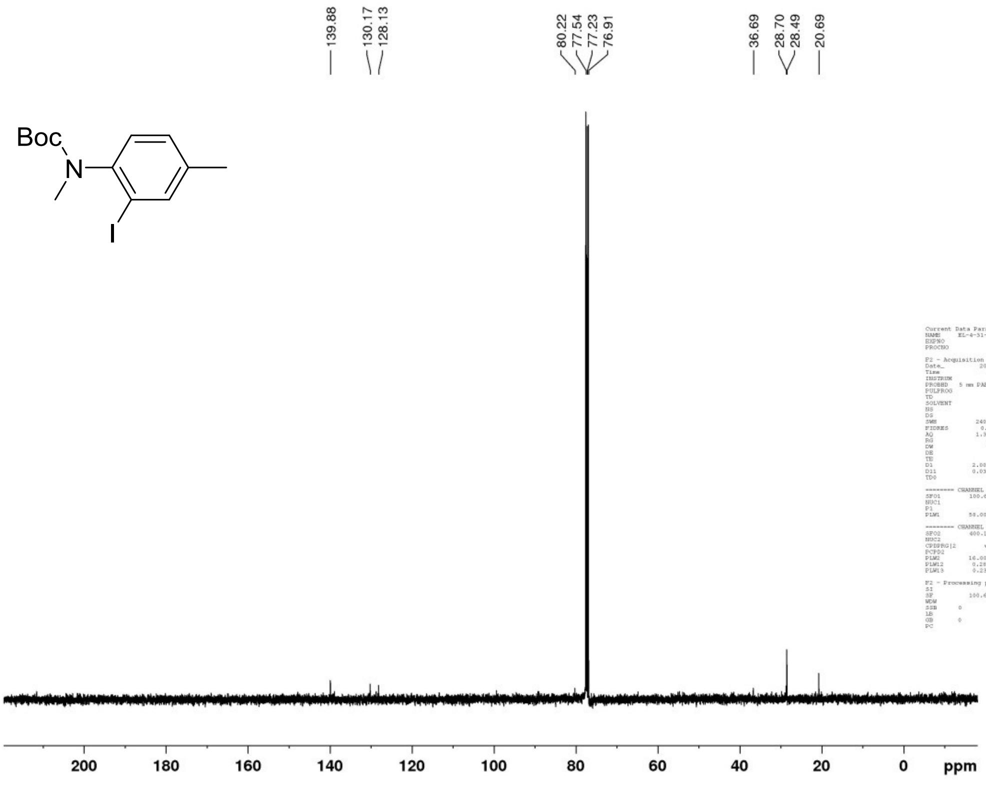




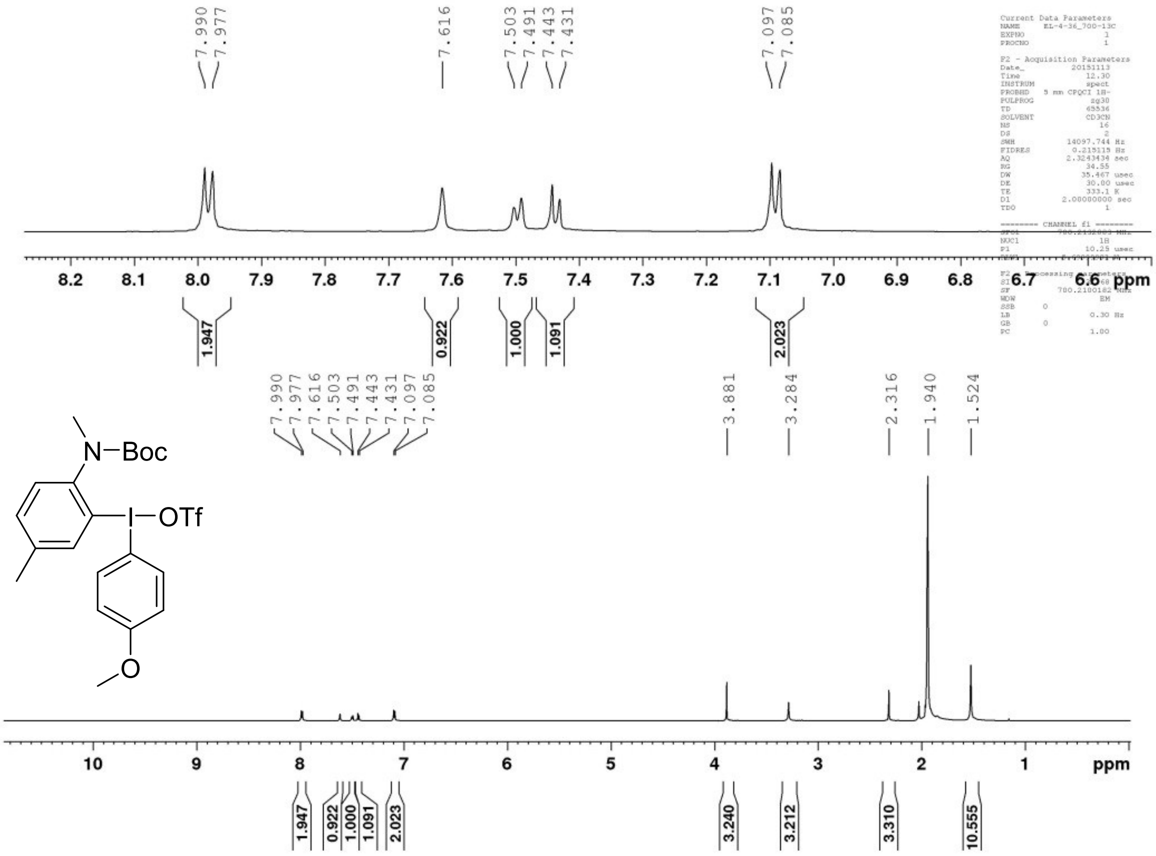
N-Boc-N-methyl-2-iodotoluidine

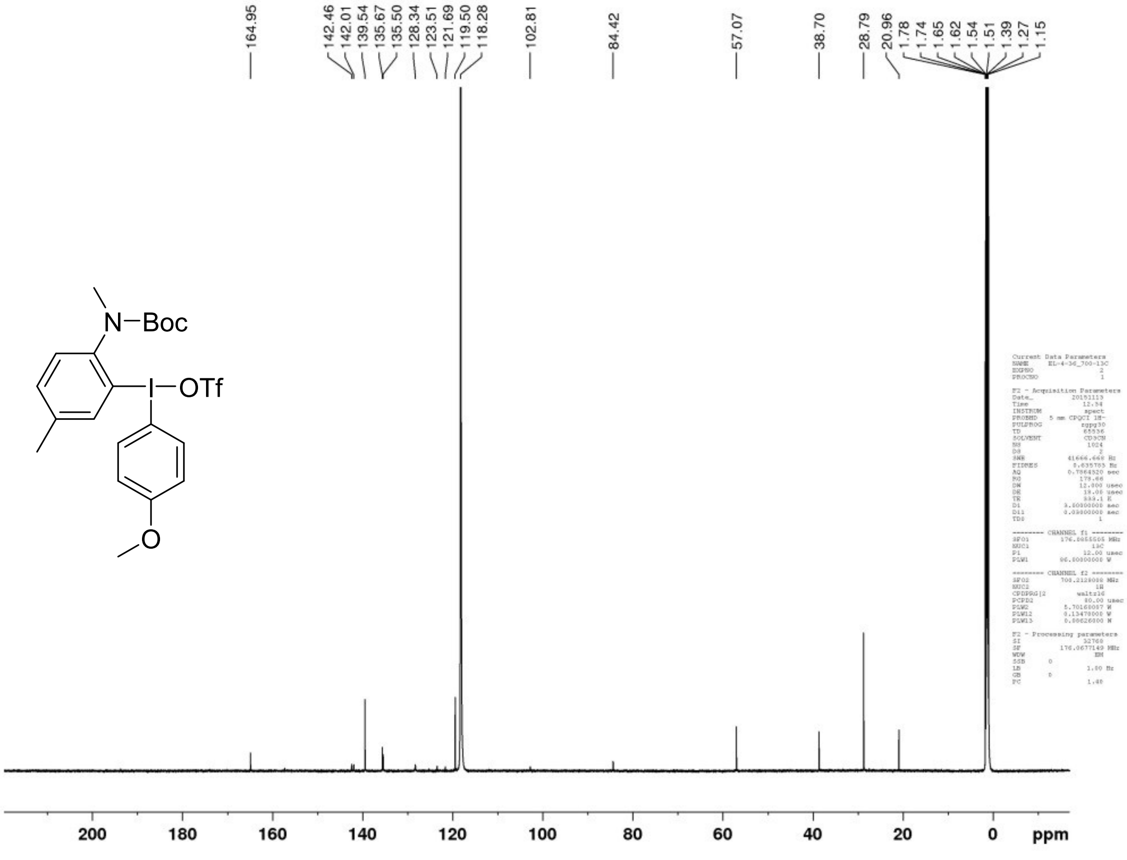


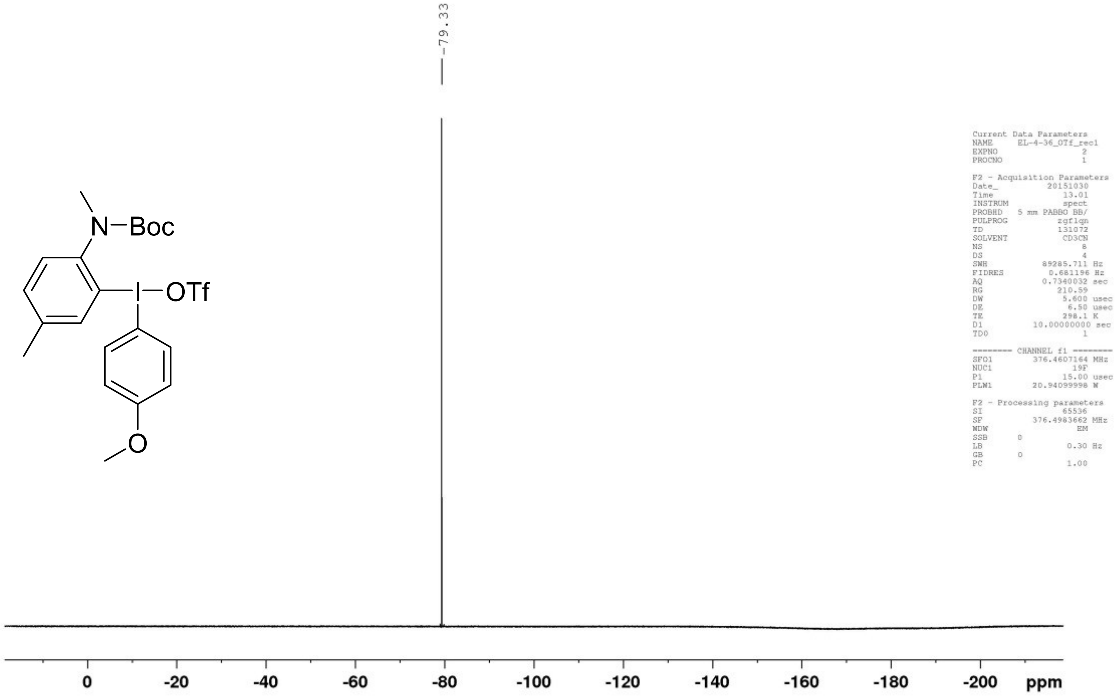




(2-((Boc)(methyl)amino)-5-methylphenyl)(4'-methoxyphenyl)iodonium trifluoromethansulfonate


7.990
7.977
7.616
7.503
7.491
7.443
7.431
7.097
7.085
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
ppm
1.947
0.922
1.000
1.091
2.023
Current Data Parameters
NAME EL-4-36_700-13C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20151113
Time 12.30
INSTRUM spect
PROBHD 5 mm CPQCI 1H-
PULPROG zg30
TD 65536
SOLVENT CD3CN
NS 16
DS 2
SWH 14097.744 Hz
FIDRES 0.215115 Hz
AQ 2.3243434 sec
RG 34.55
DW 35.467 usec
DE 30.00 usec
TE 333.1 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.25 usec
F2 - Processing parameters
SF 700.2100182 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
N−Boc
I−OTf
O
7.990
7.977
7.616
7.503
7.491
7.443
7.431
7.097
7.085
3.881
3.284
2.316
1.940
1.524
10
9
8
7
6
5
4
3
2
1
ppm
1.947
0.922
1.000
1.091
2.023
3.240
3.212
3.310
10.555


164.95
142.46
142.01
139.54
135.67
135.50
128.34
123.51
121.69
119.50
118.28
102.81
84.42
57.07
38.70
28.79
20.96
1.78
1.74
1.65
1.62
1.54
1.51
1.39
1.27
1.15
N−Boc
I−OTf
O
Current Data Parameters
NAME EL-4-36_700-13C
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20151113
Time 12.34
INSTRUM spect
PROBHD 5 mm CPQCI 1H-
PULPROG zgpg30
TD 65536
SOLVENT CD3CN
NS 1024
DS 2
SWH 41666.668 Hz
FIDRES 0.635783 Hz
AQ 0.7864320 sec
RG 178.66
DW 12.000 usec
DE 18.00 usec
TE 333.1 K
D1 3.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 176.0855505 MHz
NUC1 13C
P1 12.00 usec
PLW1 96.00000000 W
======== CHANNEL f2 ========
SFO2 700.2128000 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 5.70160007 W
PLW12 0.13470000 W
PLW13 0.06626000 W
F2 - Processing parameters
SI 32768
SF 176.0677149 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
0
ppm



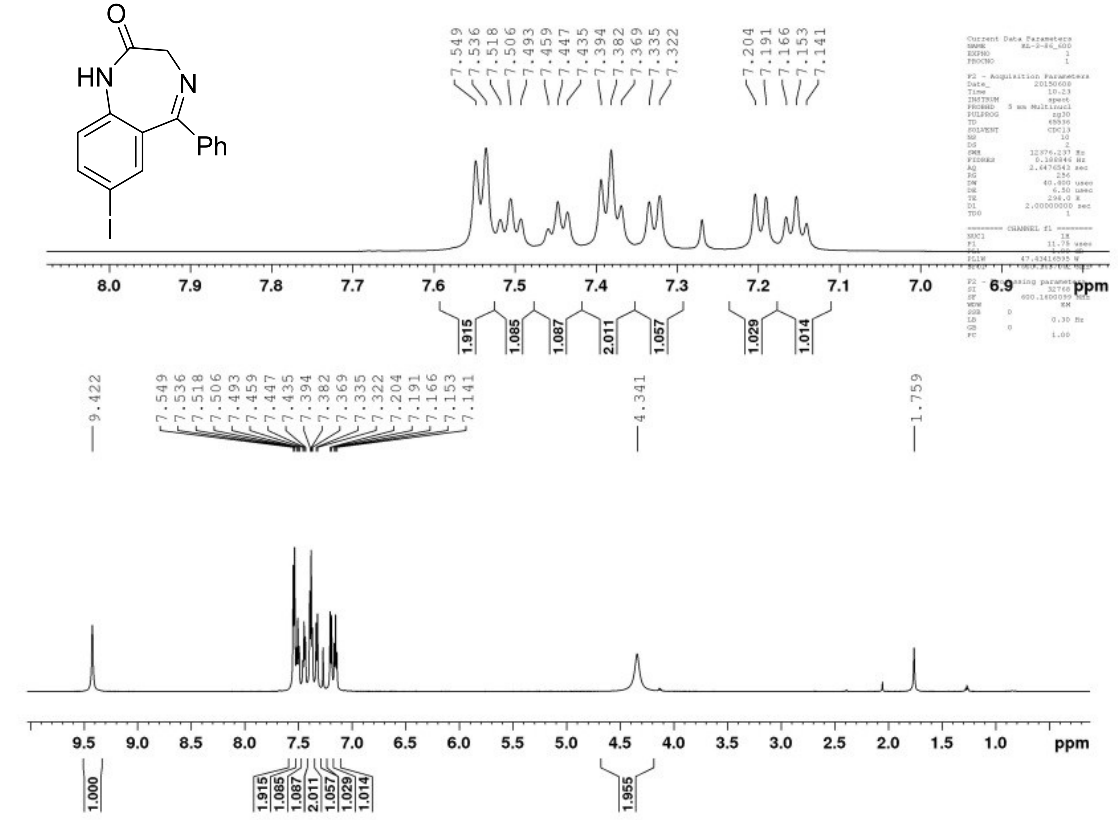
```
Current Data Parameters
NAME     EL-4-36_OTf_rec1
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20151030
Time                13.01
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG            zgflqn
TD                 131072
SOLVENT             CD3CN
NS                      8
DS                      4
SWH           89285.711 Hz
FIDRES         0.681196 Hz
AQ            0.7340032 sec
RG                 210.59
DW                  5.600 usec
DE                   6.50 usec
TE                  298.1 K
D1          10.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1        376.4607164 MHz
NUC1                  19F
P1                  15.00 usec
PLW1        20.94099998 W

F2 - Processing parameters
SI                  65536
SF          376.4983662 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

7-Iodo-5-phenyl-1,3-dihydro-2H-benzo[e][1,4]diazepin-2-one

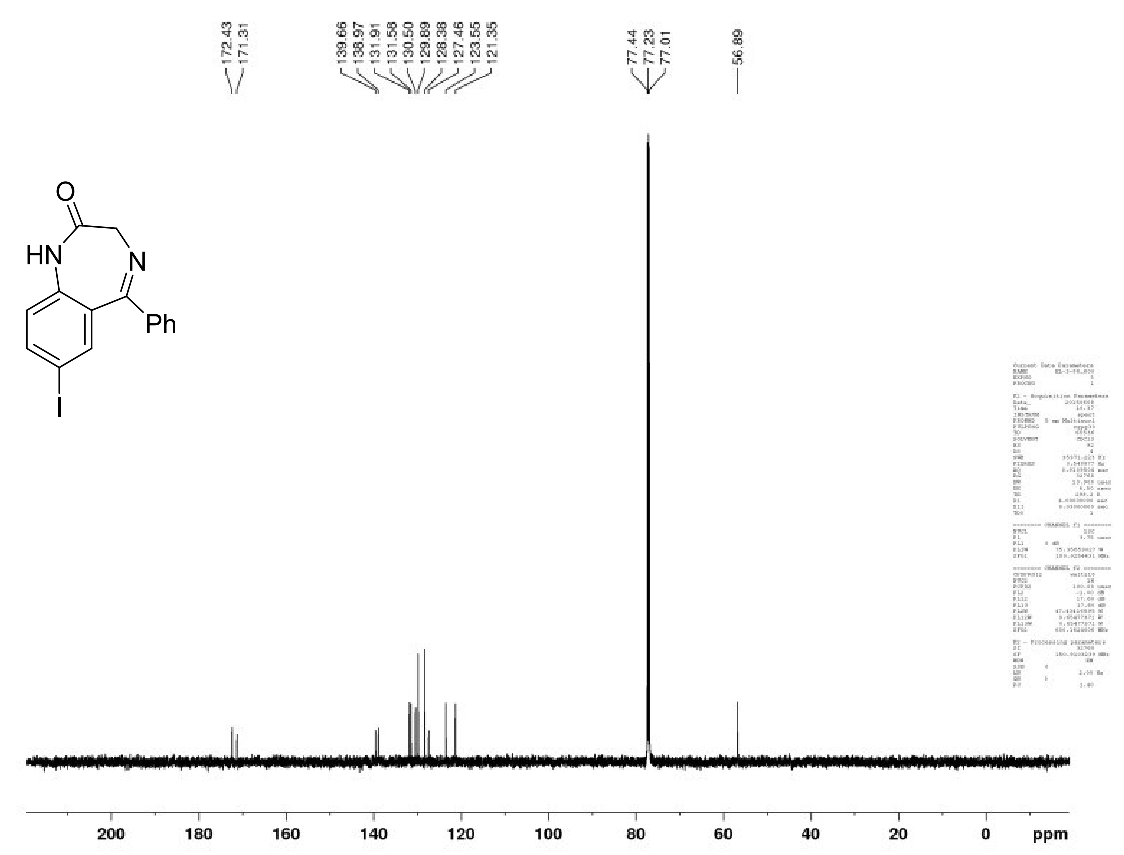


```
Current Data Parameters
NAME        EL-2-86_600
EXPNO                 1
PROCNO                1

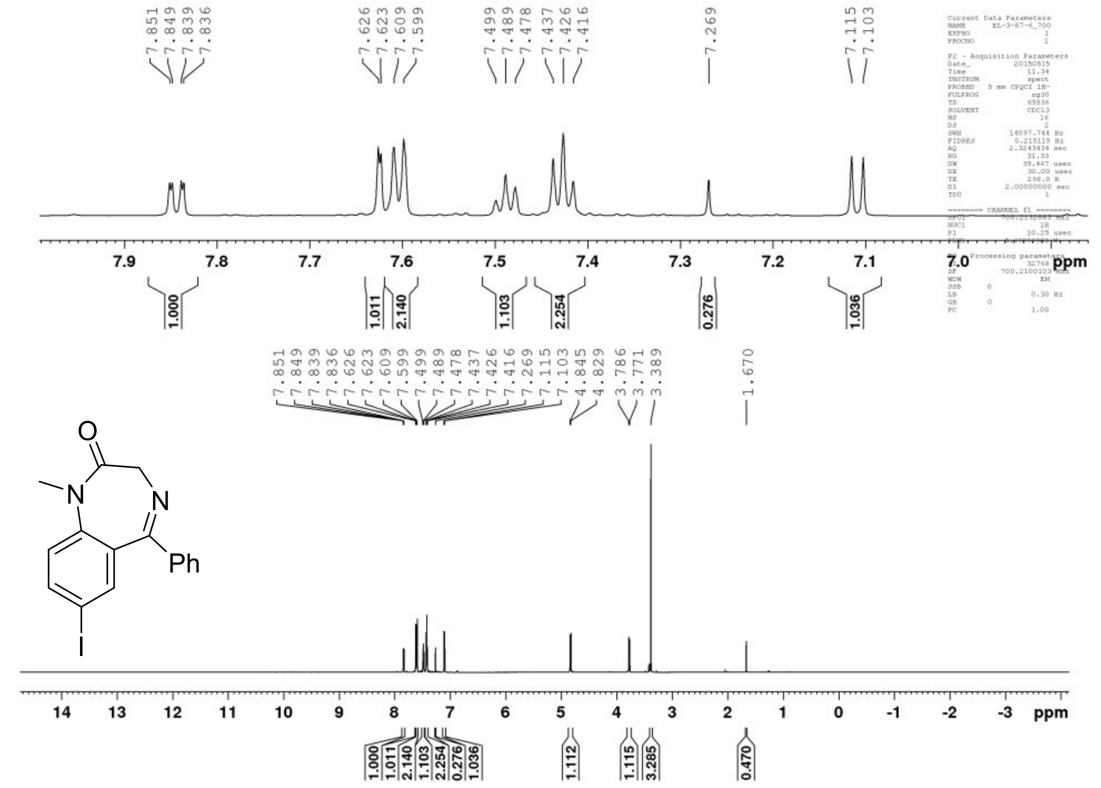
F2 - Acquisition Parameters
Date_          20150608
Time              10.23
INSTRUM           spect
PROBHD   5 mm Multinucl
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   10
DS                    2
SWH          12376.237 Hz
FIDRES        0.188846 Hz
AQ           2.6476543 sec
RG                  256
DW               40.400 usec
DE                 6.50 usec
TE                298.0 K
D1           2.00000000 sec
TD0                   1

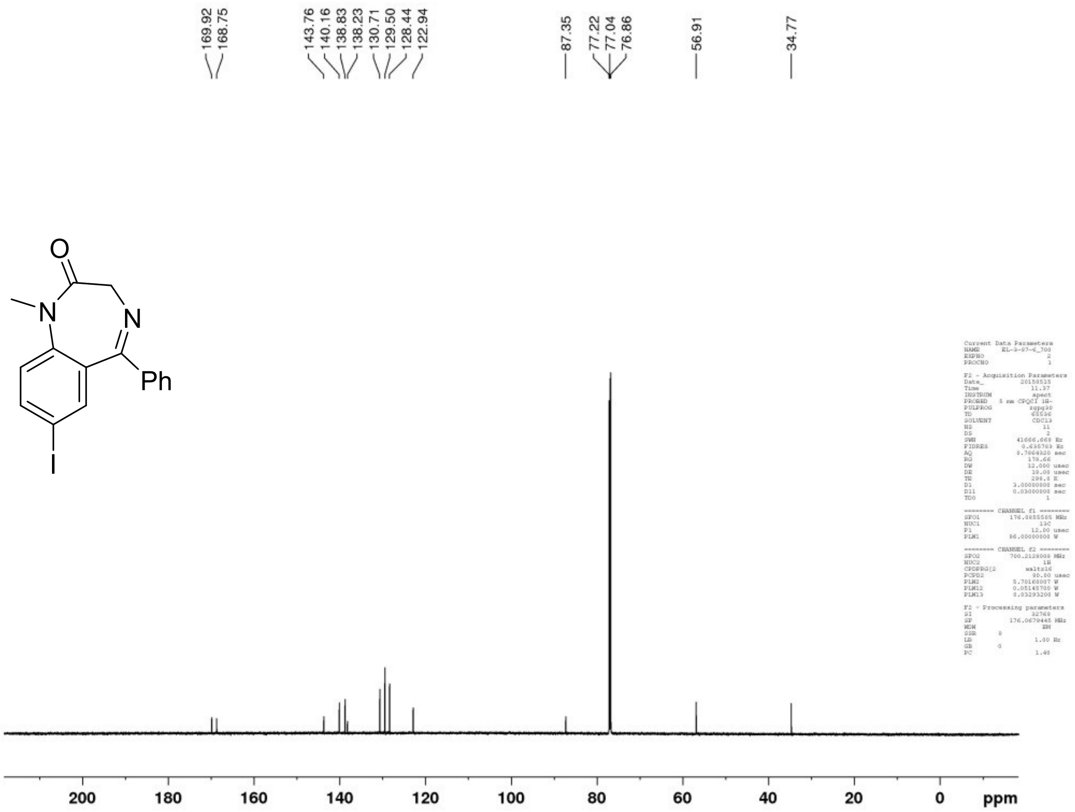
======== CHANNEL f1 ========
NUC1                 1H
P1                11.75 usec
PL1                1.00 dB
PLW1        47.43416595 W
SFO1       [illegible] MHz

F2 - Processing parameters
SI                32768
SF         600.1800099 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

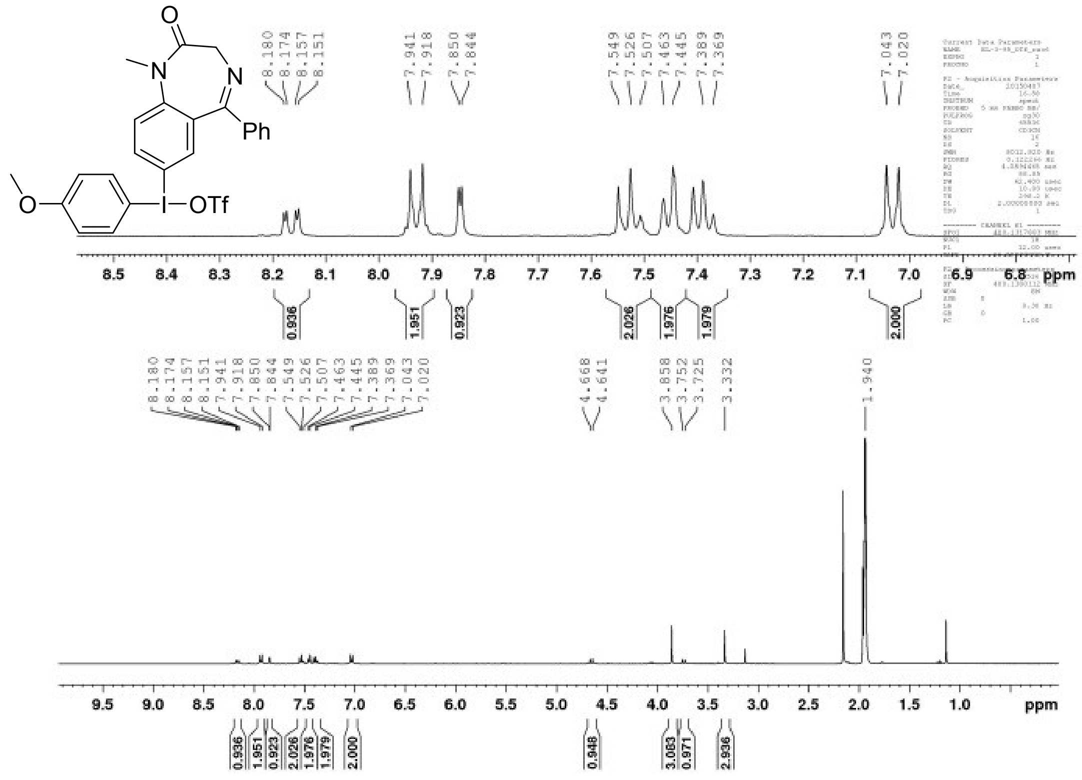


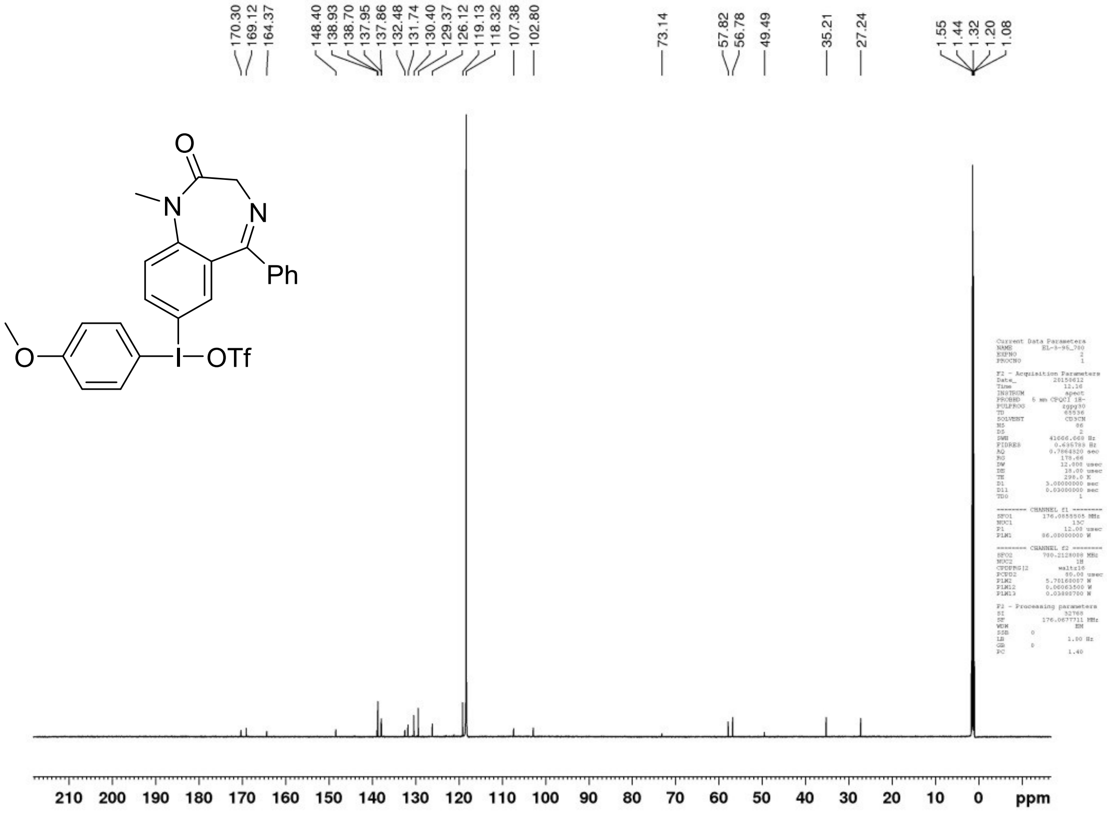
7-iodo-1-methyl-5-phenyl-1,3-dihydro-2H-benzo[e][1,4]diazepin-2-one





(7-Iodo-1-methyl-5-phenyl-1,3-dihydro-2H-benzo[e][1,4]diazepin-2-one)(4'-methoxyphenyl)iodonium trifluoromethansulfonate





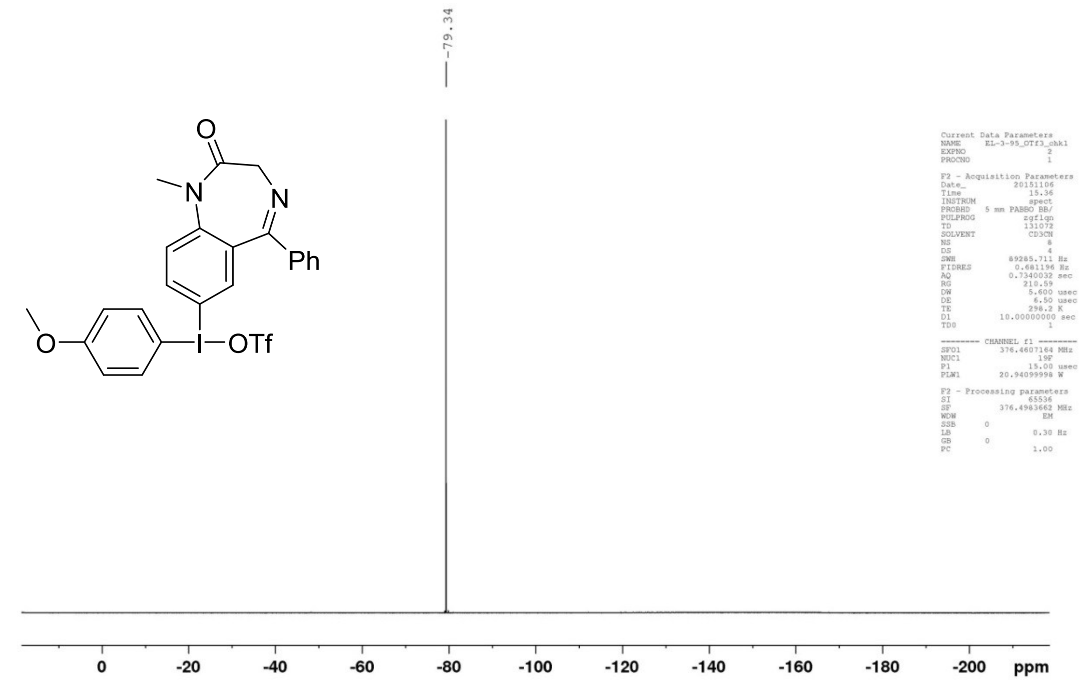
```
Current Data Parameters
NAME          EL-3-95_700
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150612
Time                12.16
INSTRUM             spect
PROBHD   5 mm CPQCI 1H-
PULPROG            zgpg30
TD                  65536
SOLVENT             CD3CN
NS                     86
DS                      2
SWH             41666.668 Hz
FIDRES           0.635788 Hz
AQ              0.7864820 sec
RG                 178.66
DW                 12.000 usec
DE                  18.00 usec
TE                  298.0 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         176.0855505 MHz
NUC1                  13C
P1                  12.00 usec
PLW1          86.00000000 W

======== CHANNEL f2 ========
SFO2         700.2128008 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2           5.70168007 W
PLW12          0.06063500 W
PLW13          0.03898700 W

F2 - Processing parameters
SI                  32768
SF           176.0677711 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.40
```



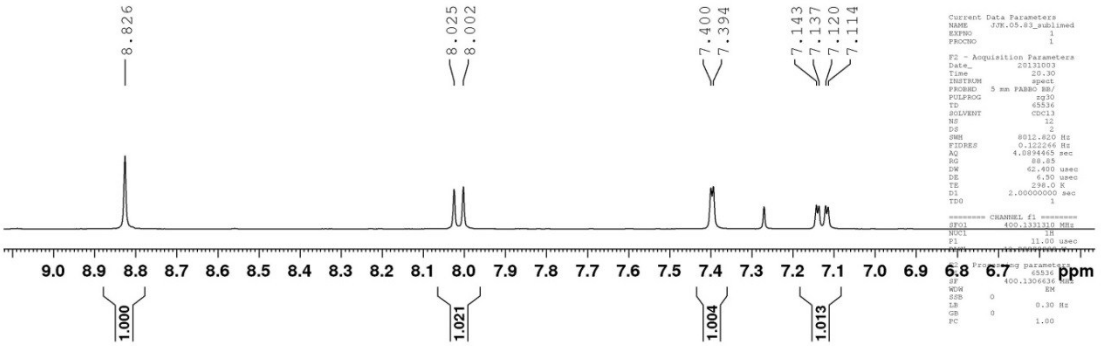
```
Current Data Parameters
NAME      EL-3-95_OTf3_chk1
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20151106
Time                15.36
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG            zgflqn
TD                 131072
SOLVENT             CD3CN
NS                      8
DS                      4
SWH             89285.711 Hz
FIDRES           0.681196 Hz
AQ              0.7340032 sec
RG                 210.59
DW                  5.600 usec
DE                   6.50 usec
TE                  298.2 K
D1            10.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         376.4607164 MHz
NUC1                  19F
P1                  15.00 usec
PLW1          20.94099998 W

F2 - Processing parameters
SI                  65536
SF           376.4983662 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

6-Methoxybenzothiazole

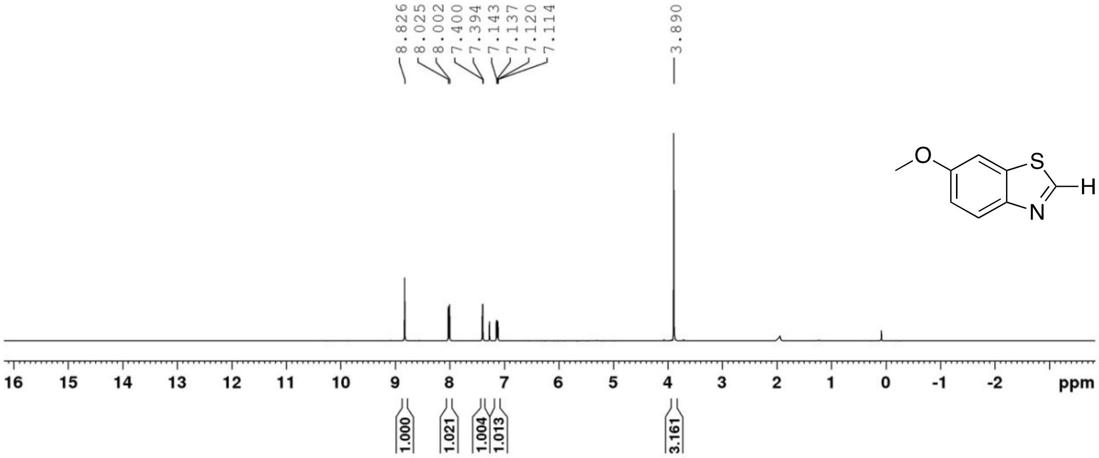


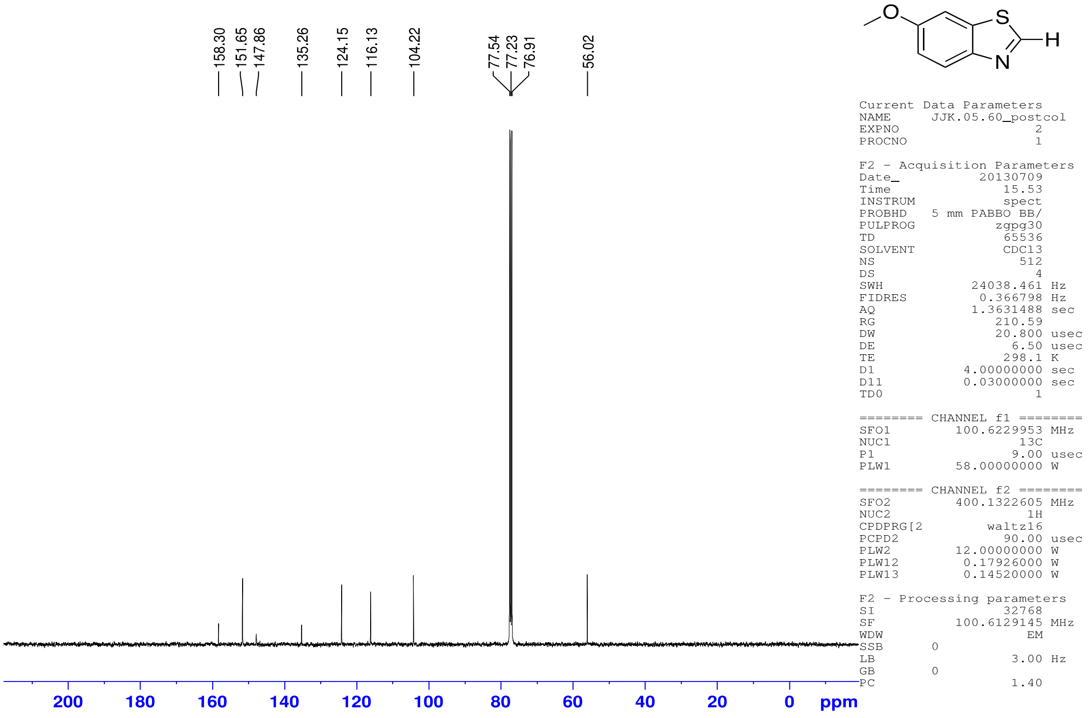
```
Current Data Parameters
NAME     JJK.05.83_sublimed
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20131003
Time                  20.30
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       12
DS                        2
SWH                8012.820 Hz
FIDRES             0.122266 Hz
AQ                4.0894465 sec
RG                    88.85
DW                   62.400 usec
DE                     6.50 usec
TE                    298.0 K
D1               2.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            400.1331310 MHz
NUC1                     1H
P1                    11.00 usec

F2 - Processing parameters
                      65536
SF              400.1306636 MHz
WDW                      EM
SSB        0
LB                     0.30 Hz
GB         0
PC                     1.00
```





```
Current Data Parameters
NAME      JJK.05.60_postcol
EXPNO                     2
PROCNO                    1

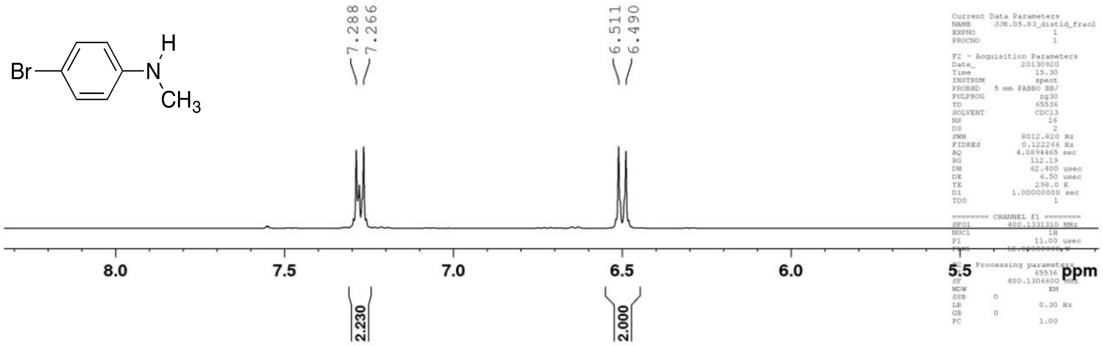
F2 - Acquisition Parameters
Date_              20130709
Time                  15.53
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      512
DS                        4
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                1.3631488 sec
RG                   210.59
DW                   20.800 usec
DE                     6.50 usec
TE                    298.1 K
D1               4.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            100.6229953 MHz
NUC1                    13C
P1                     9.00 usec
PLW1            58.00000000 W

======== CHANNEL f2 ========
SFO2            400.1322605 MHz
NUC2                     1H
CPDPRG[2            waltz16
PCPD2                 90.00 usec
PLW2            12.00000000 W
PLW12            0.17926000 W
PLW13            0.14520000 W

F2 - Processing parameters
SI                    32768
SF              100.6129145 MHz
WDW                      EM
SSB        0
LB                     3.00 Hz
GB         0
PC                     1.40
```

4-Bromo-*N*-methylaniline

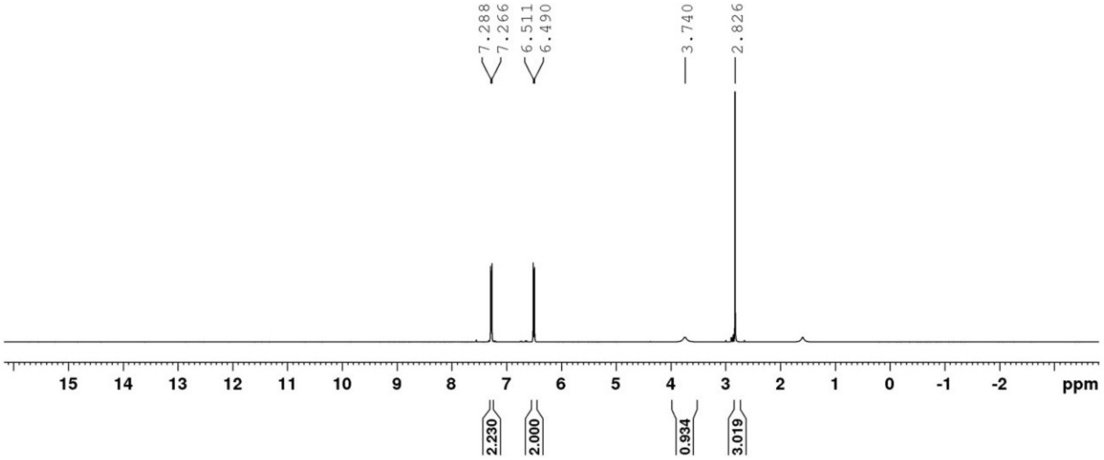


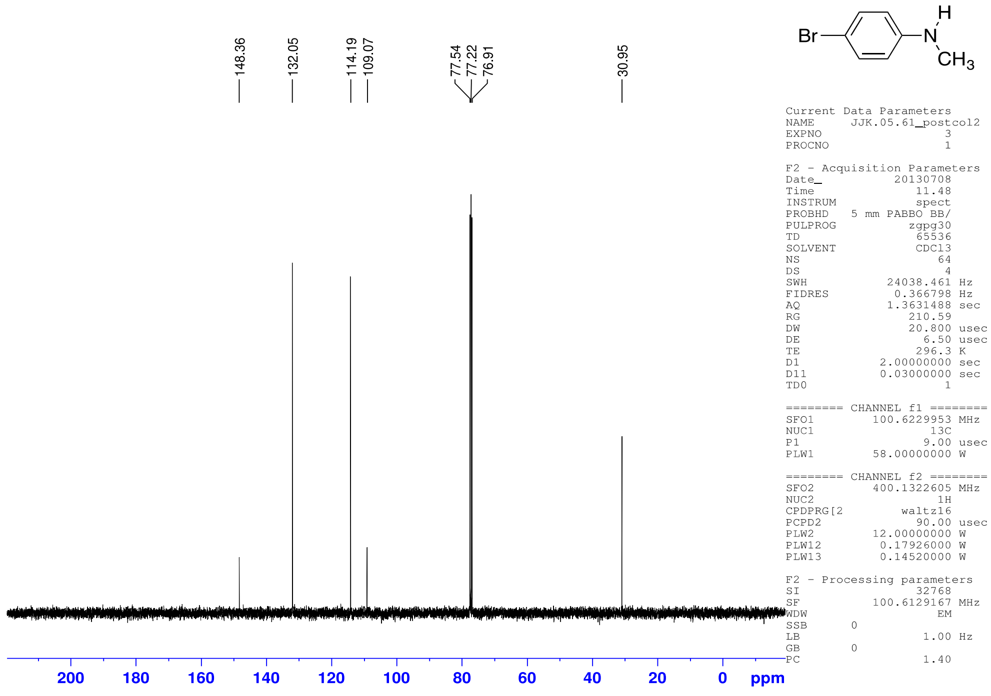
```
Current Data Parameters
NAME     JJK.05.83_distld_frac2
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20130920
Time              15.30
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894465 sec
RG               112.19
DW               62.400 usec
DE                 6.50 usec
TE                298.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        400.1331310 MHz
NUC1                 1H
P1                11.00 usec
PLW1        12.00000000 W

F2 - Processing parameters
SI                65536
SF          400.1306600 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```





```
Current Data Parameters
NAME      JJK.05.61_postcol2
EXPNO                  3
PROCNO                 1

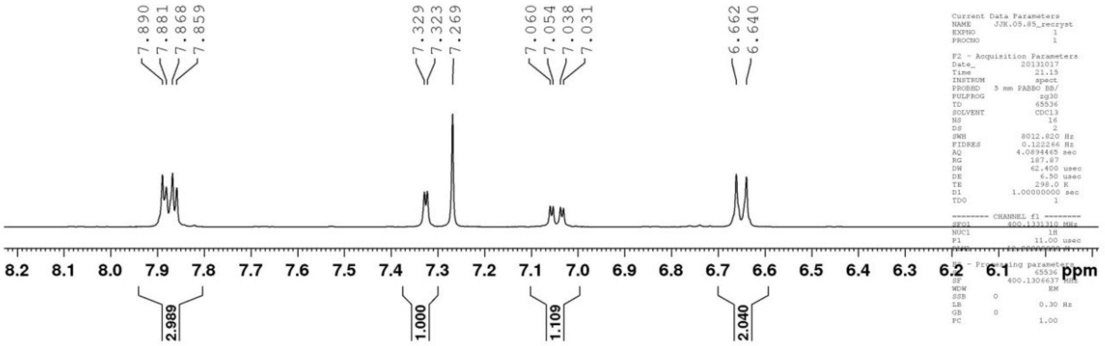
F2 - Acquisition Parameters
Date_           20130708
Time               11.48
INSTRUM            spect
PROBHD    5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631488 sec
RG                210.59
DW                20.800 usec
DE                  6.50 usec
TE                 296.3 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6229953 MHz
NUC1                  13C
P1                  9.00 usec
PLW1         58.00000000 W

======== CHANNEL f2 ========
SFO2         400.1322605 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2              90.00 usec
PLW2         12.00000000 W
PLW12         0.17926000 W
PLW13         0.14520000 W

F2 - Processing parameters
SI                 32768
SF           100.6129167 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```

2-(4-(Methylamino)phenyl)-6-methoxybenzothiazole

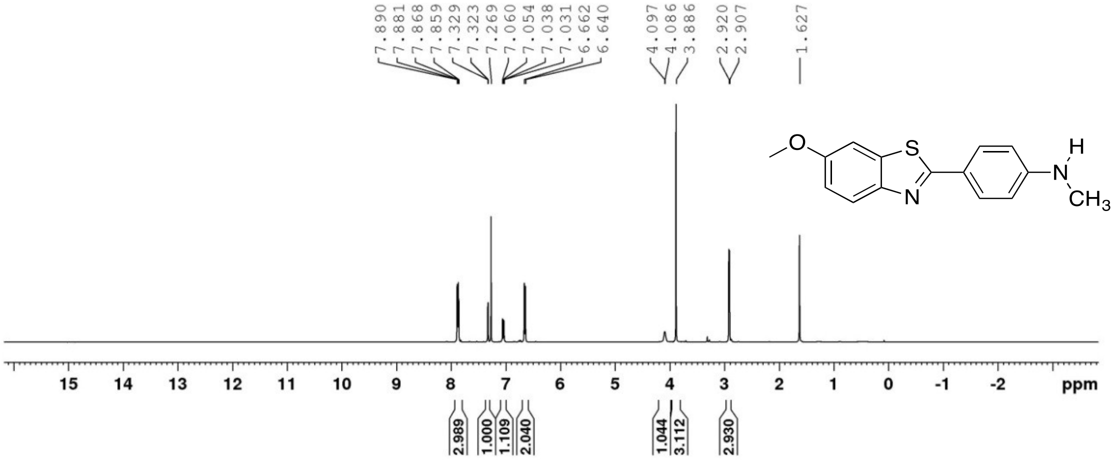


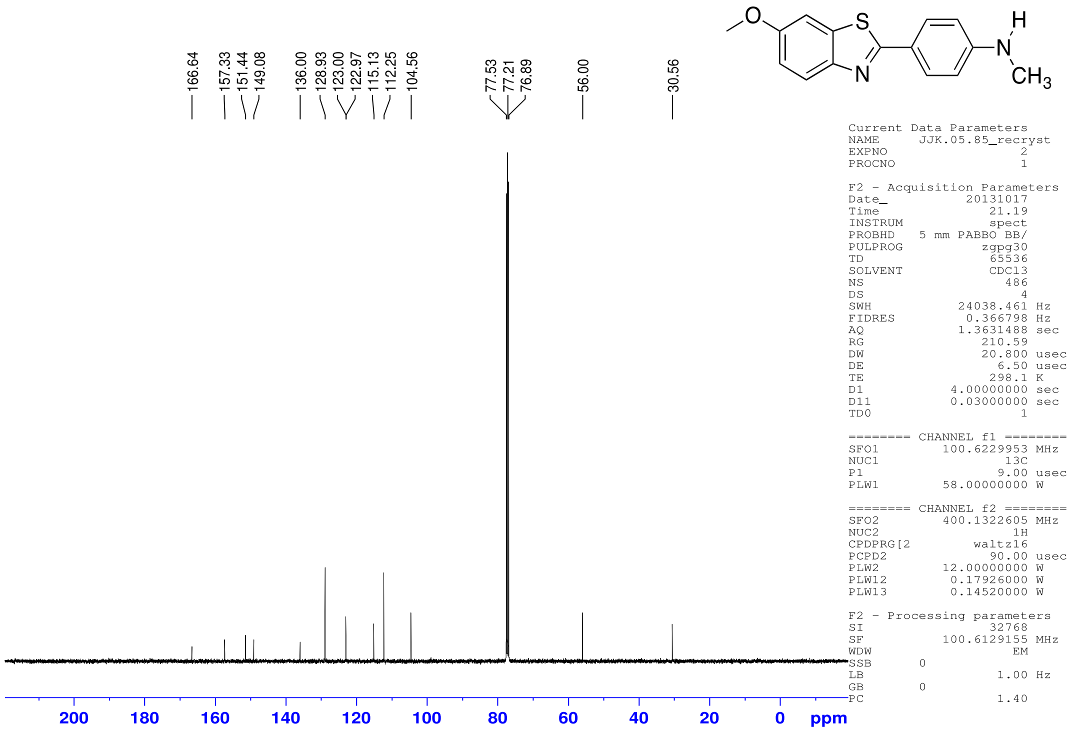
```
Current Data Parameters
NAME      JJK.05.85_recryst
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20131017
Time                  21.15
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894465 sec
RG                   187.87
DW               62.400 usec
DE                 6.50 usec
TE                298.0 K
D1           1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1        400.1331310 MHz
NUC1                     1H
P1                11.00 usec
[illegible]

F2 - Processing parameters
[illegible]           65536
SF          400.1306637 MHz
WDW                      EM
SSB       0
LB                  0.30 Hz
GB        0
PC                     1.00
```





```
Current Data Parameters
NAME      JJK.05.85_recryst
EXPNO                     2
PROCNO                    1

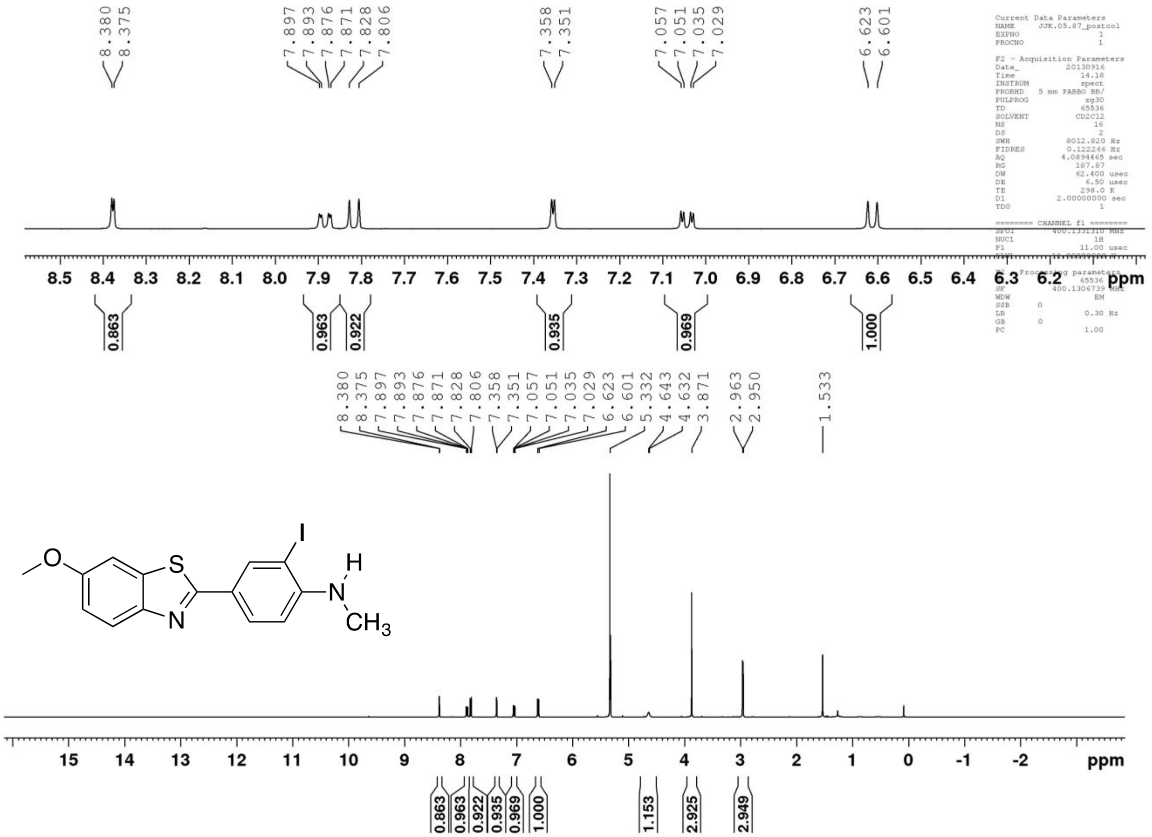
F2 - Acquisition Parameters
Date_              20131017
Time                  21.19
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      486
DS                        4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631488 sec
RG                   210.59
DW               20.800 usec
DE                 6.50 usec
TE                298.1 K
D1           4.00000000 sec
D11          0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1        100.6229953 MHz
NUC1                    13C
P1                 9.00 usec
PLW1        58.00000000 W

======== CHANNEL f2 ========
SFO2        400.1322605 MHz
NUC2                     1H
CPDPRG[2            waltz16
PCPD2             90.00 usec
PLW2        12.00000000 W
PLW12        0.17926000 W
PLW13        0.14520000 W

F2 - Processing parameters
SI                    32768
SF          100.6129155 MHz
WDW                      EM
SSB       0
LB                  1.00 Hz
GB        0
PC                     1.40
```

2-(3-Iodo-4-(methylamino)phenyl)-6-methoxybenzothiazole

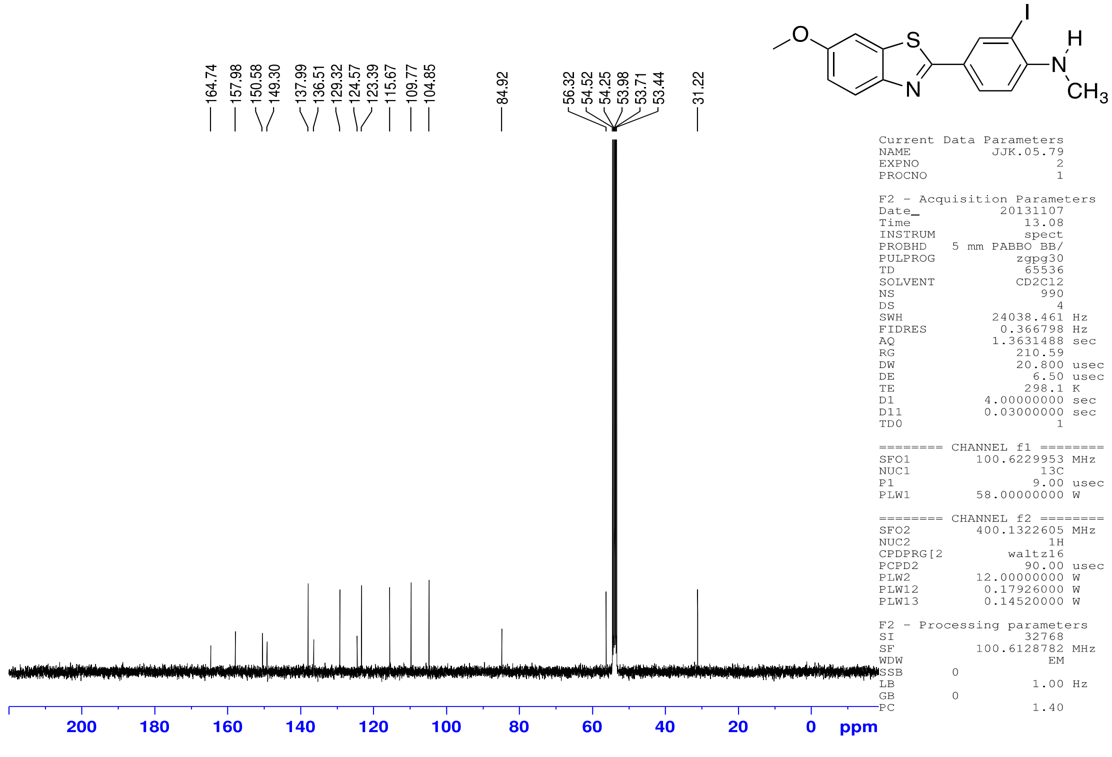


```
Current Data Parameters
NAME       JJK.05.87_postcol
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_               20130916
Time                   14.18
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG                 zg30
TD                     65536
SOLVENT               CD2Cl2
NS                        16
DS                         2
SWH                 8012.820 Hz
FIDRES              0.122266 Hz
AQ                 4.0894465 sec
RG                    187.87
DW                    62.400 usec
DE                      6.50 usec
TE                     298.0 K
D1                2.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             400.1331310 MHz
NUC1                      1H
P1                     11.00 usec

F2 - Processing parameters
                       65536
SF               400.1306739 MHz
WDW                       EM
SSB       0
LB                      0.30 Hz
GB        0
PC                      1.00
```



```
Current Data Parameters
NAME            JJK.05.79
EXPNO                   2
PROCNO                  1

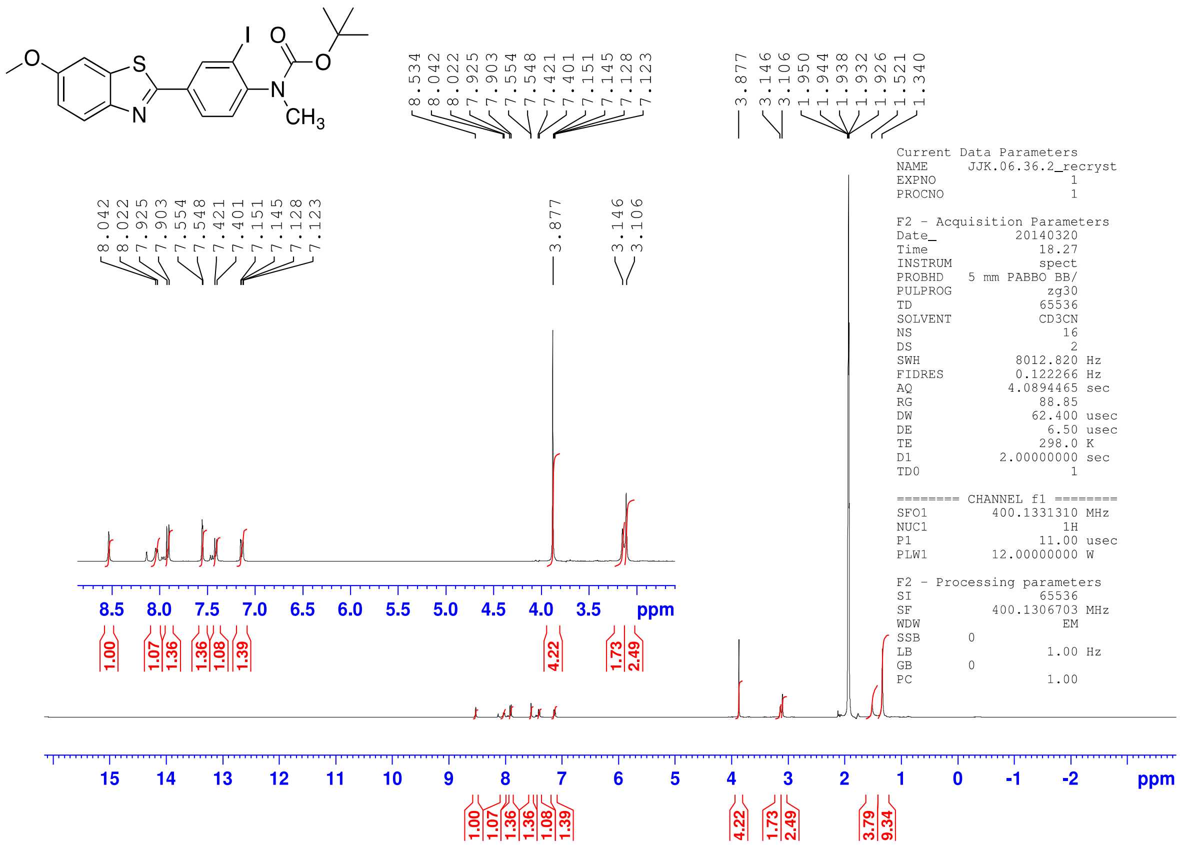
F2 - Acquisition Parameters
Date_            20131107
Time                13.08
INSTRUM             spect
PROBHD    5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT           CD2Cl2
NS                   990
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631488 sec
RG                210.59
DW                20.800 usec
DE                  6.50 usec
TE                 298.1 K
D1            4.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6229953 MHz
NUC1                 13C
P1                  9.00 usec
PLW1         58.00000000 W

======== CHANNEL f2 ========
SFO2         400.1322605 MHz
NUC2                  1H
CPDPRG[2            waltz16
PCPD2               90.00 usec
PLW2         12.00000000 W
PLW12         0.17926000 W
PLW13         0.14520000 W

F2 - Processing parameters
SI                  32768
SF           100.6128782 MHz
WDW                    EM
SSB       0
LB                   1.00 Hz
GB        0
PC                   1.40
```

2-(4-(*N*-*Boc*-3-iodo-*N*-methyl)phenyl)-6-benzothiazole

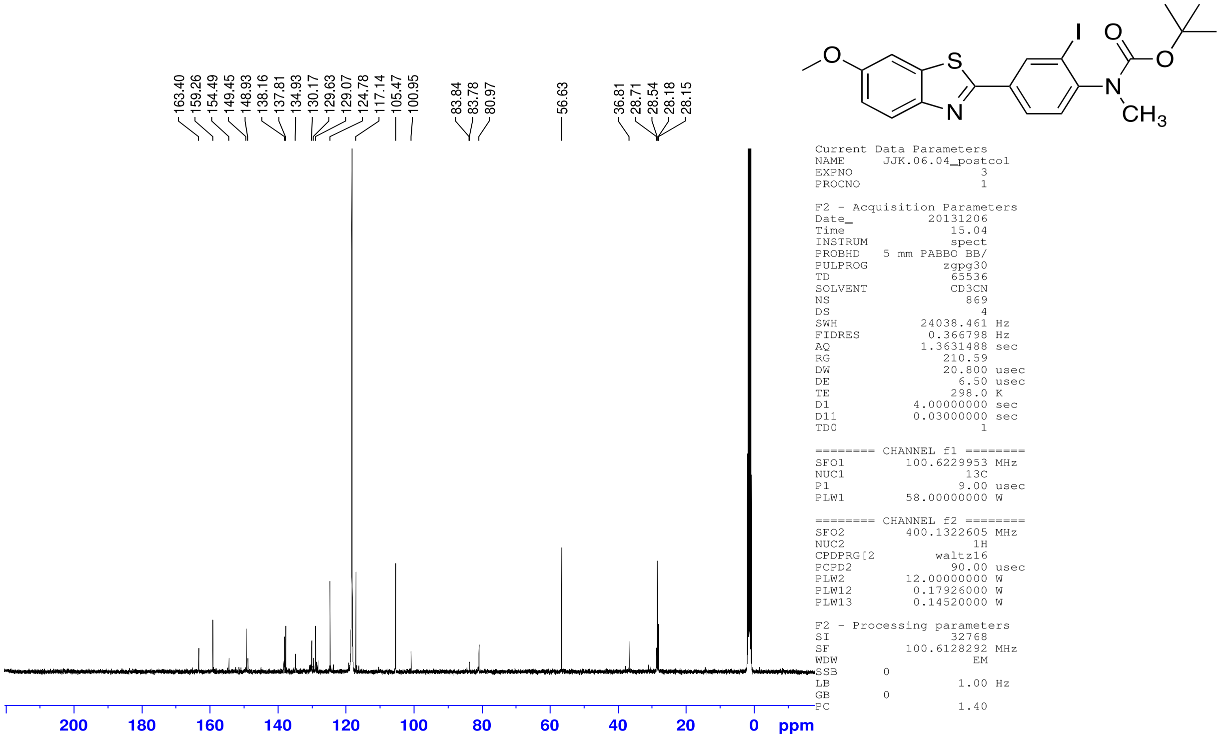


```
Current Data Parameters
NAME     JJK.06.36.2_recryst
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_               20140320
Time                   18.27
INSTRUM                spect
PROBHD   5 mm PABBO BB/
PULPROG                 zg30
TD                     65536
SOLVENT                CD3CN
NS                        16
DS                         2
SWH                 8012.820 Hz
FIDRES              0.122266 Hz
AQ                 4.0894465 sec
RG                     88.85
DW                    62.400 usec
DE                      6.50 usec
TE                     298.0 K
D1                2.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1            400.1331310 MHz
NUC1                      1H
P1                     11.00 usec
PLW1             12.00000000 W

F2 - Processing parameters
SI                     65536
SF              400.1306703 MHz
WDW                       EM
SSB      0
LB                      1.00 Hz
GB       0
PC                      1.00
```



```
Current Data Parameters
NAME     JJK.06.04_postcol
EXPNO                    3
PROCNO                   1

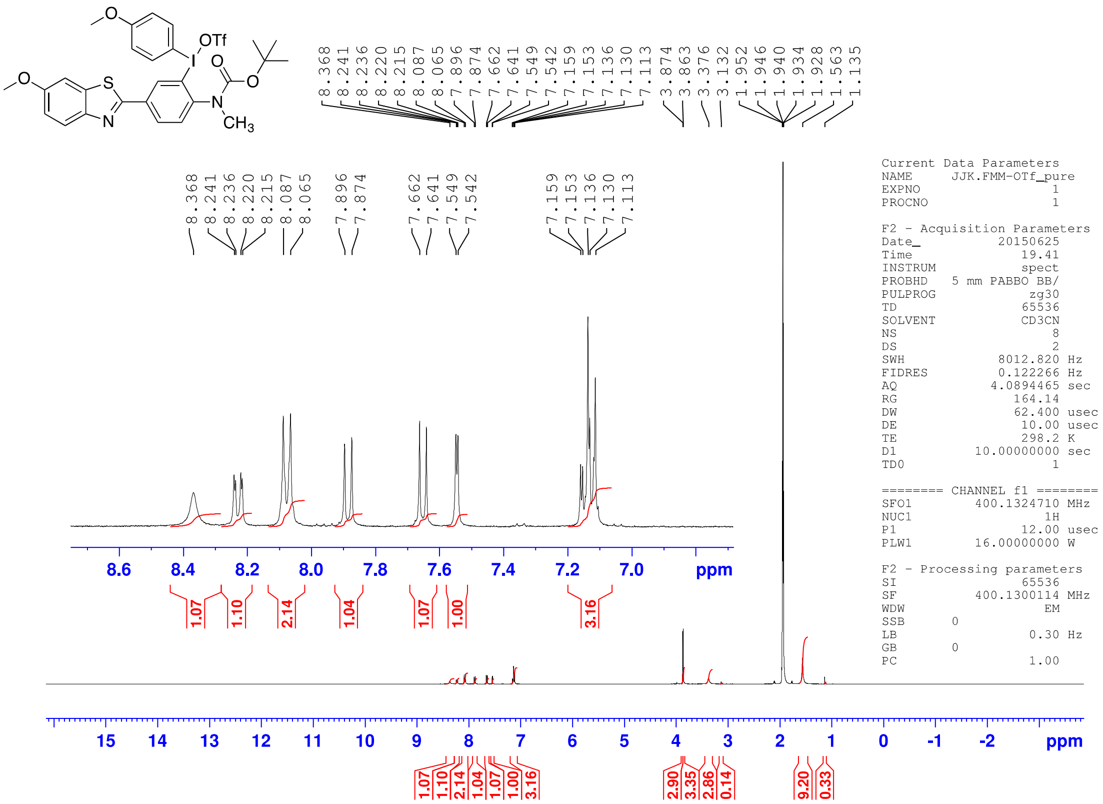
F2 - Acquisition Parameters
Date_             20131206
Time                 15.04
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG            zgpg30
TD                  65536
SOLVENT             CD3CN
NS                    869
DS                      4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631488 sec
RG                 210.59
DW                 20.800 usec
DE                   6.50 usec
TE                  298.0 K
D1             4.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          100.6229953 MHz
NUC1                  13C
P1                   9.00 usec
PLW1          58.00000000 W

======== CHANNEL f2 ========
SFO2          400.1322605 MHz
NUC2                   1H
CPDPRG[2           waltz16
PCPD2               90.00 usec
PLW2          12.00000000 W
PLW12          0.17926000 W
PLW13          0.14520000 W

F2 - Processing parameters
SI                  32768
SF            100.6128292 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.40
```

(2-(*N*-Boc-*N*-methyl)amino-5-(6-methoxybenzothiazolyl))(4-methoxyphenyl)iodonium triflate

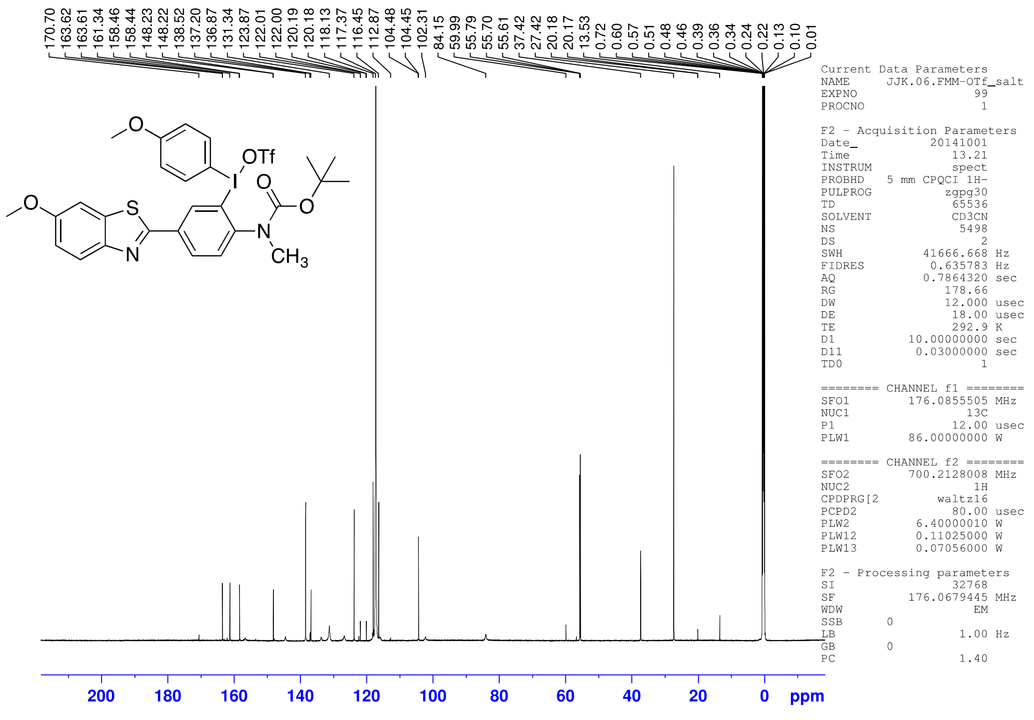


```
Current Data Parameters
NAME      JJK.FMM-OTf_pure
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150625
Time                 19.41
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zg30
TD                   65536
SOLVENT              CD3CN
NS                       8
DS                       2
SWH               8012.820 Hz
FIDRES            0.122266 Hz
AQ               4.0894465 sec
RG                  164.14
DW                  62.400 usec
DE                   10.00 usec
TE                   298.2 K
D1             10.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1        400.1324710 MHz
NUC1                     1H
P1                   12.00 usec
PLW1          16.00000000 W

F2 - Processing parameters
SI                   65536
SF             400.1300114 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```



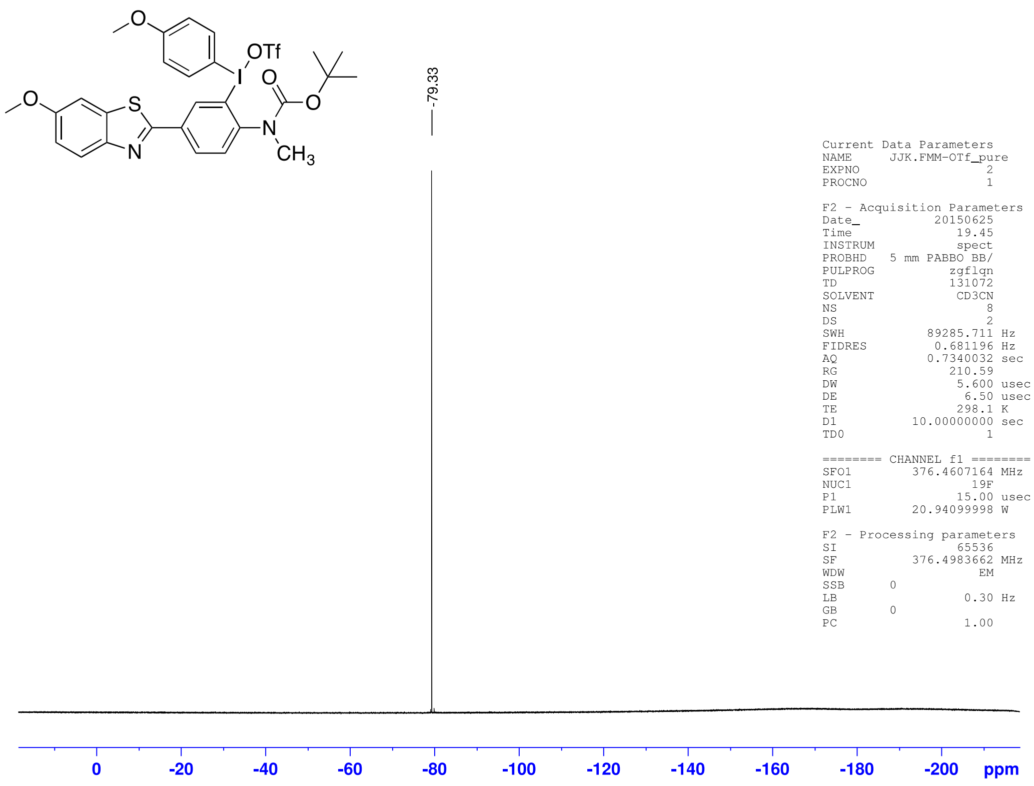
```
Current Data Parameters
NAME     JJK.06.FMM-OTf_salt
EXPNO                   99
PROCNO                   1

F2 - Acquisition Parameters
Date_             20141001
Time                 13.21
INSTRUM              spect
PROBHD   5 mm CPQCI 1H-
PULPROG             zgpg30
TD                   65536
SOLVENT              CD3CN
NS                    5498
DS                       2
SWH              41666.668 Hz
FIDRES            0.635783 Hz
AQ               0.7864320 sec
RG                  178.66
DW                  12.000 usec
DE                   18.00 usec
TE                   292.9 K
D1             10.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1        176.0855505 MHz
NUC1                    13C
P1                   12.00 usec
PLW1          86.00000000 W

======== CHANNEL f2 ========
SFO2        700.2128008 MHz
NUC2                     1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2            6.40000010 W
PLW12           0.11025000 W
PLW13           0.07056000 W

F2 - Processing parameters
SI                   32768
SF             176.0679445 MHz
WDW                     EM
SSB      0
LB                    1.00 Hz
GB       0
PC                    1.40
```



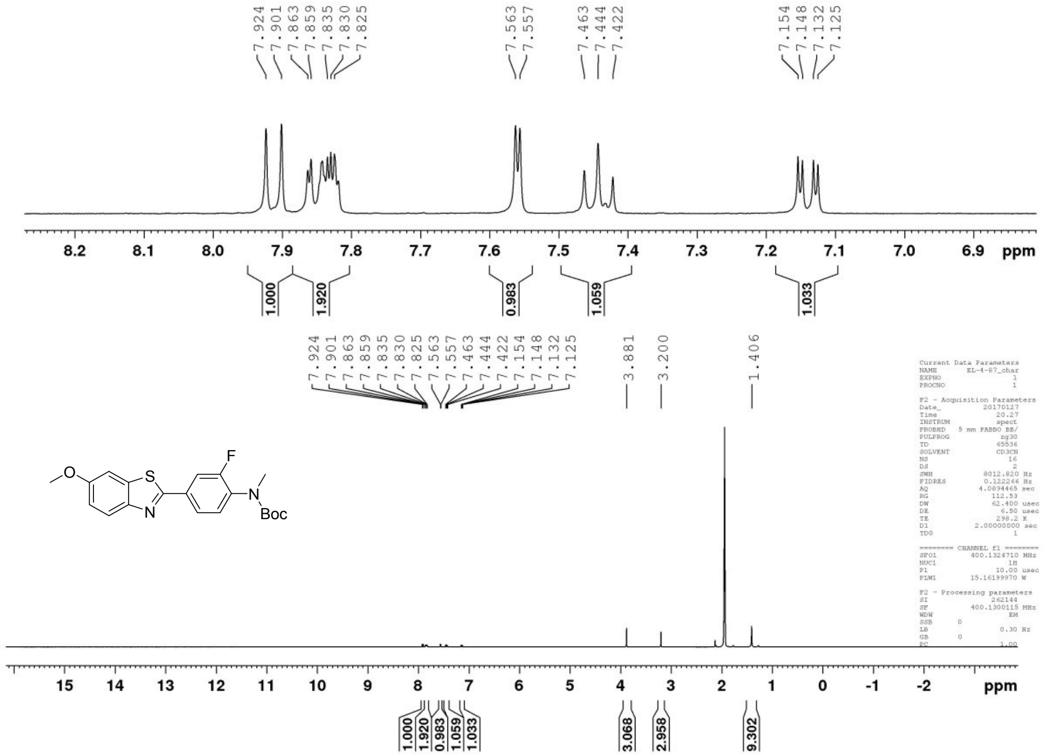
```
Current Data Parameters
NAME     JJK.FMM-OTf_pure
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20150625
Time                19.45
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG            zgflqn
TD                 131072
SOLVENT              CD3CN
NS                      8
DS                      2
SWH            89285.711 Hz
FIDRES          0.681196 Hz
AQ             0.7340032 sec
RG                 210.59
DW                  5.600 usec
DE                   6.50 usec
TE                  298.1 K
D1          10.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         376.4607164 MHz
NUC1                   19F
P1                   15.00 usec
PLW1          20.94099998 W

F2 - Processing parameters
SI                   65536
SF           376.4983662 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```

2-(4-(*N*-Boc-3-fluoro-*N*-methyl)phenyl)-6-benzothiazole

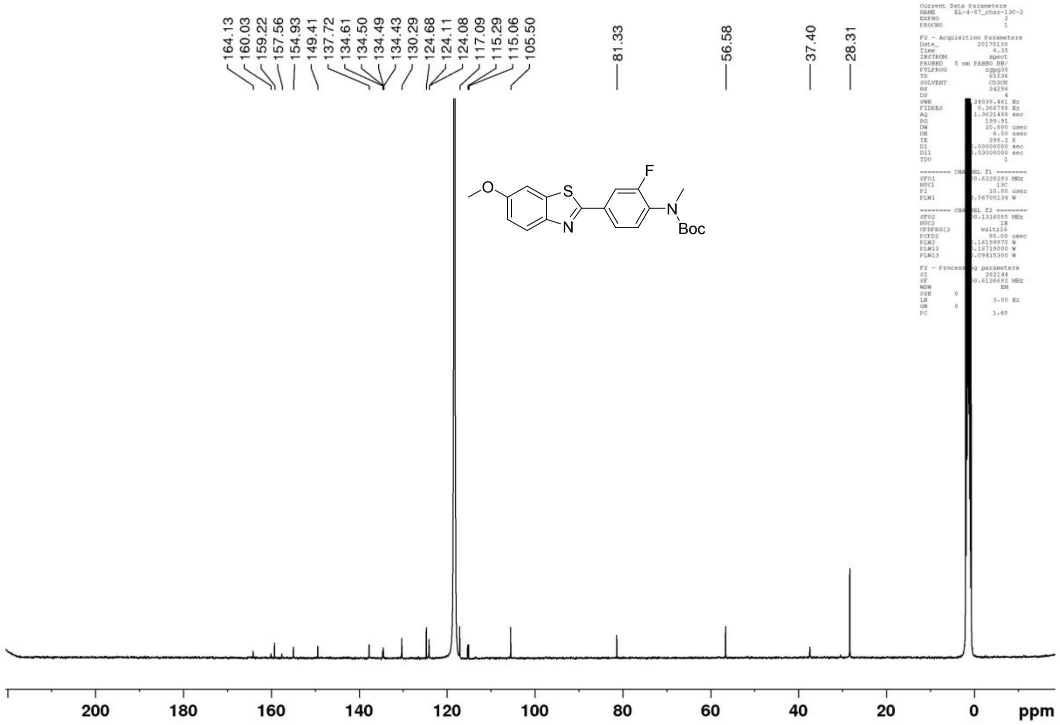


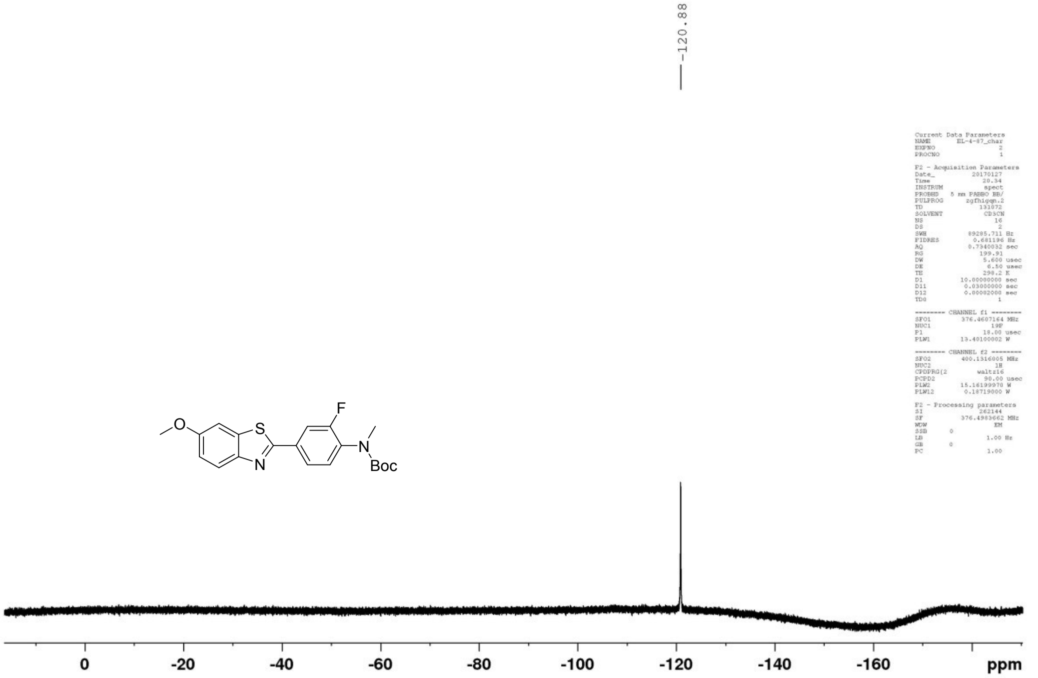
```
Current Data Parameters
NAME        EL-4-87_char
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170127
Time               20.27
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CD3CN
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894465 sec
RG                112.53
DW                62.400 usec
DE                  6.50 usec
TE                 298.2 K
D1            2.00000000 sec
TD0                    1

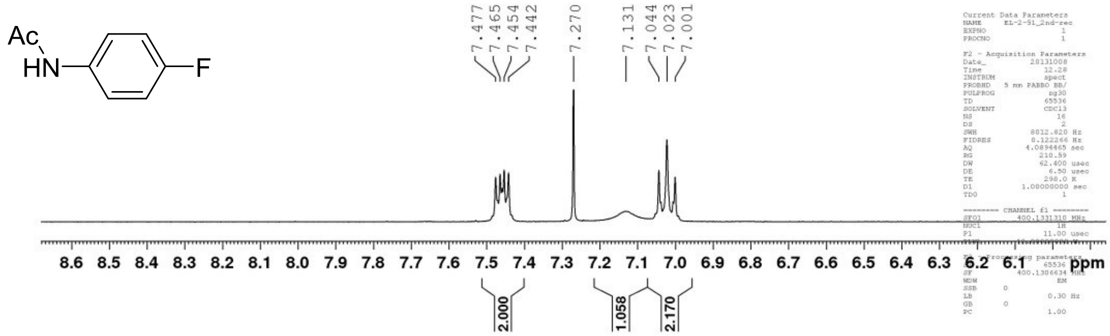
======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                  1H
P1                 10.00 usec
PLW1         15.16199970 W

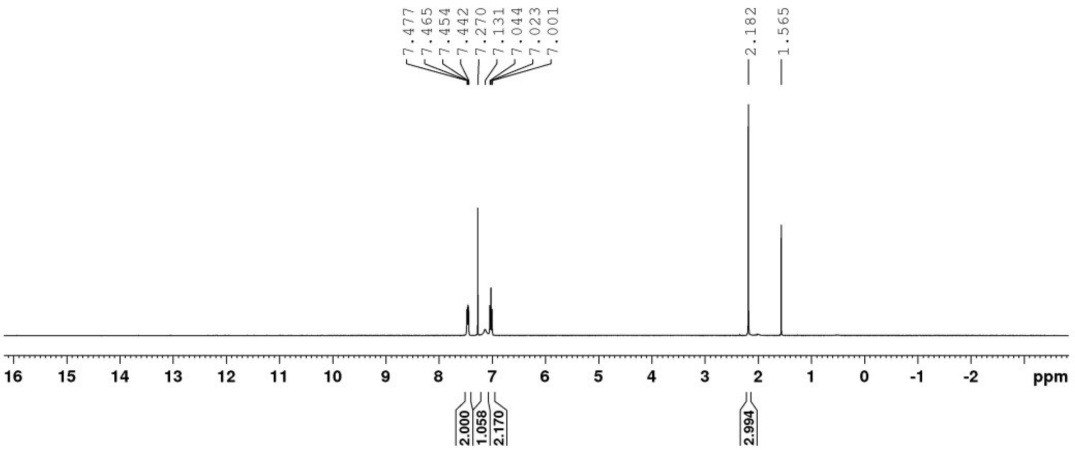
F2 - Processing parameters
SI                262144
SF          400.1300115 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

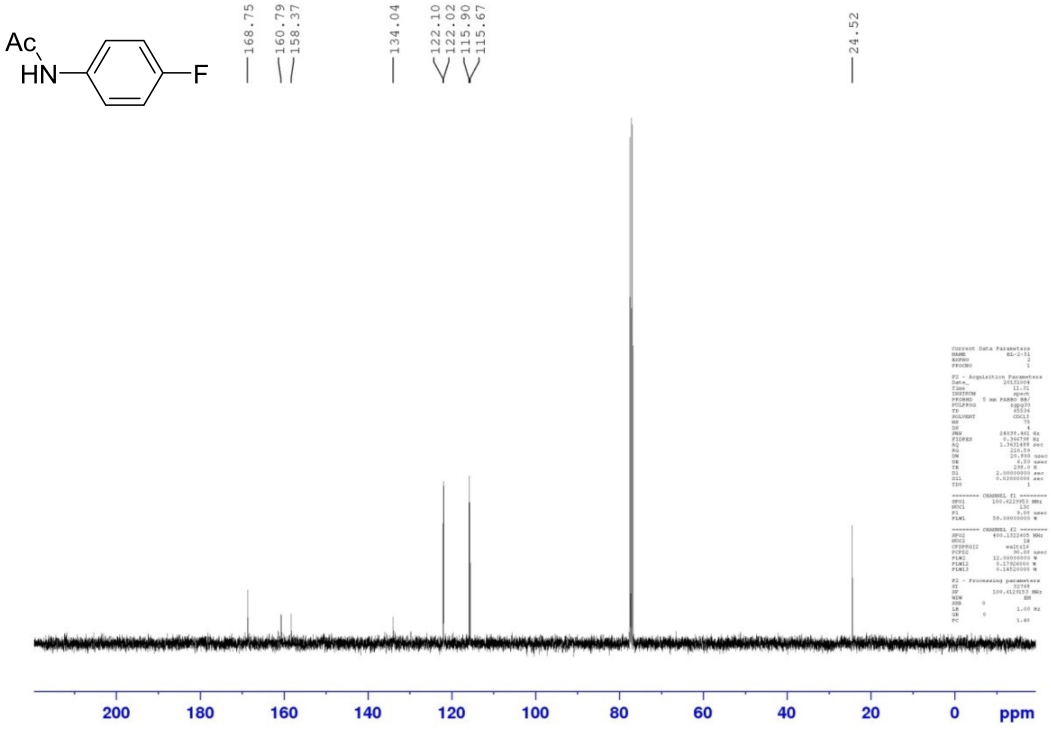

164.13
160.03
159.22
157.56
154.93
149.41
137.72
134.61
134.50
134.49
134.43
130.29
124.68
124.11
124.08
117.09
115.29
115.06
105.50
81.33
56.58
37.40
28.31
S
N
F
N
Boc
Current Data Parameters
NAME EL-4-87_char-13C-2
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170130
Time 8.35
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CD3CN
NS 24296
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 199.91
DW 20.800 usec
DE 6.50 usec
TE 298.2 K
D1 .00000000 sec
D11 .03000000 sec
TD0 1
======== CHA EL f1 ========
SFO1 0.6228293 MHz
NUC1 13C
P1 10.00 usec
PLW1 .56700134 W
======== CHA EL f2 ========
SFO2 0.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 .16199970 W
PLW12 .18719000 W
PLW13 .09415300 W
F2 - Process g parameters
SI 262144
SF 0.6126692 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
0
ppm

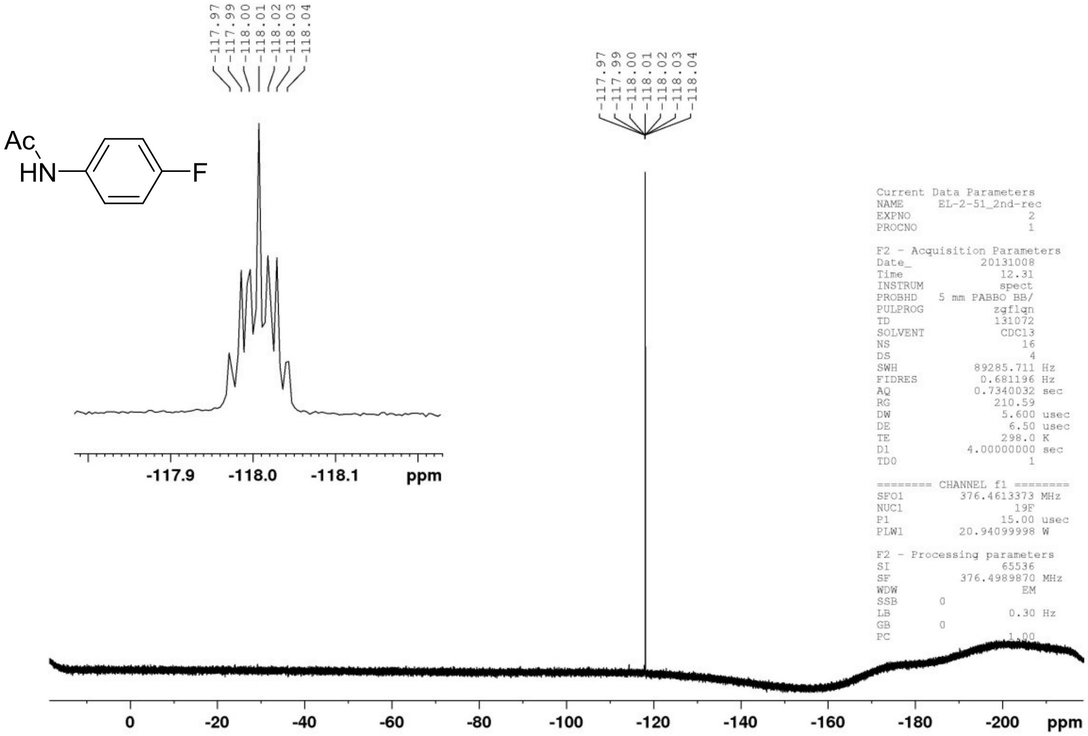

-120.88
Current Data Parameters
NAME EL-4-87_char
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170127
Time 20.34
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgfhigqn.2
TD 131072
SOLVENT CD3CN
NS 16
DS 2
SWH 89285.711 Hz
FIDRES 0.681196 Hz
AQ 0.7340032 sec
RG 199.91
DW 5.600 usec
DE 6.50 usec
TE 298.2 K
D1 10.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 376.4607164 MHz
NUC1 19F
P1 18.00 usec
PLW1 13.40100002 W
======== CHANNEL f2 ========
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 15.16199970 W
PLW12 0.18719000 W
F2 - Processing parameters
SI 262144
SF 376.4983662 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
S
N
F
N
Boc
0
-20
-40
-60
-80
-100
-120
-140
-160
ppm

4-Fluoroacetanilide









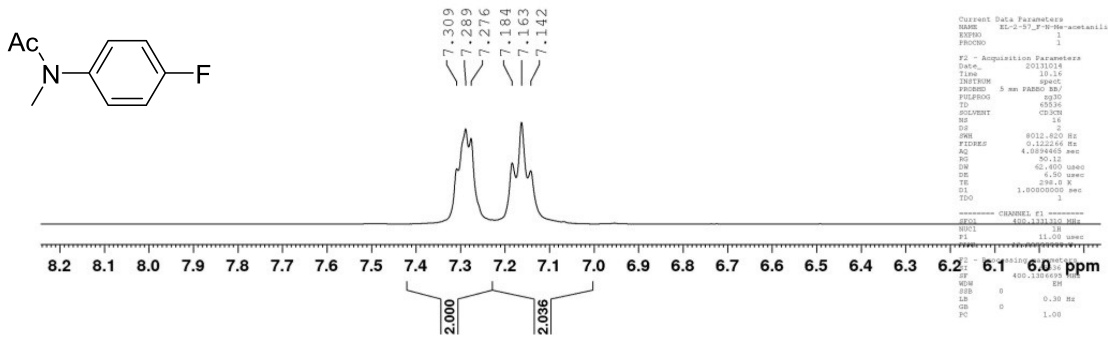
```
Current Data Parameters
NAME      EL-2-51_2nd-rec
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20131008
Time                12.31
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG            zgflqn
TD                 131072
SOLVENT             CDCl3
NS                     16
DS                      4
SWH           89285.711 Hz
FIDRES         0.681196 Hz
AQ            0.7340032 sec
RG                 210.59
DW                  5.600 usec
DE                   6.50 usec
TE                  298.0 K
D1             4.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1        376.4613373 MHz
NUC1                  19F
P1                  15.00 usec
PLW1          20.94099998 W

F2 - Processing parameters
SI                  65536
SF          376.4989870 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

4-Fluoro-N-methylacetanilide

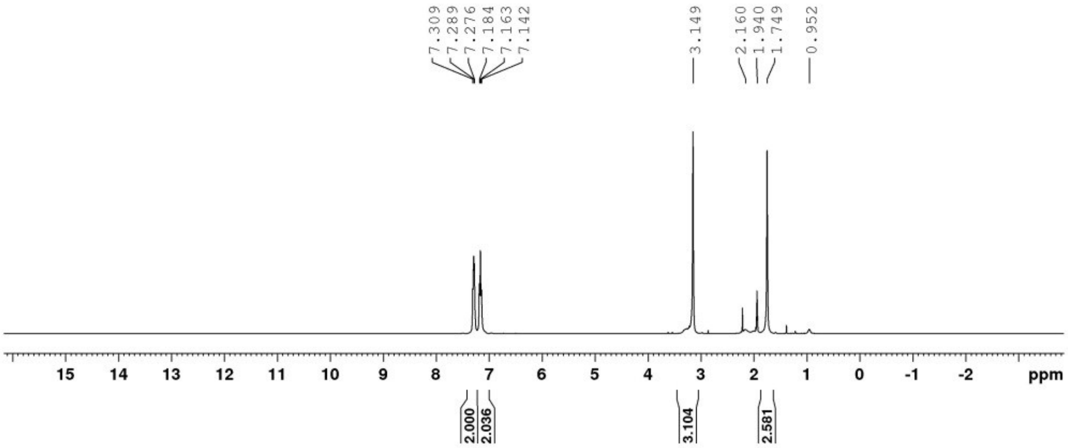


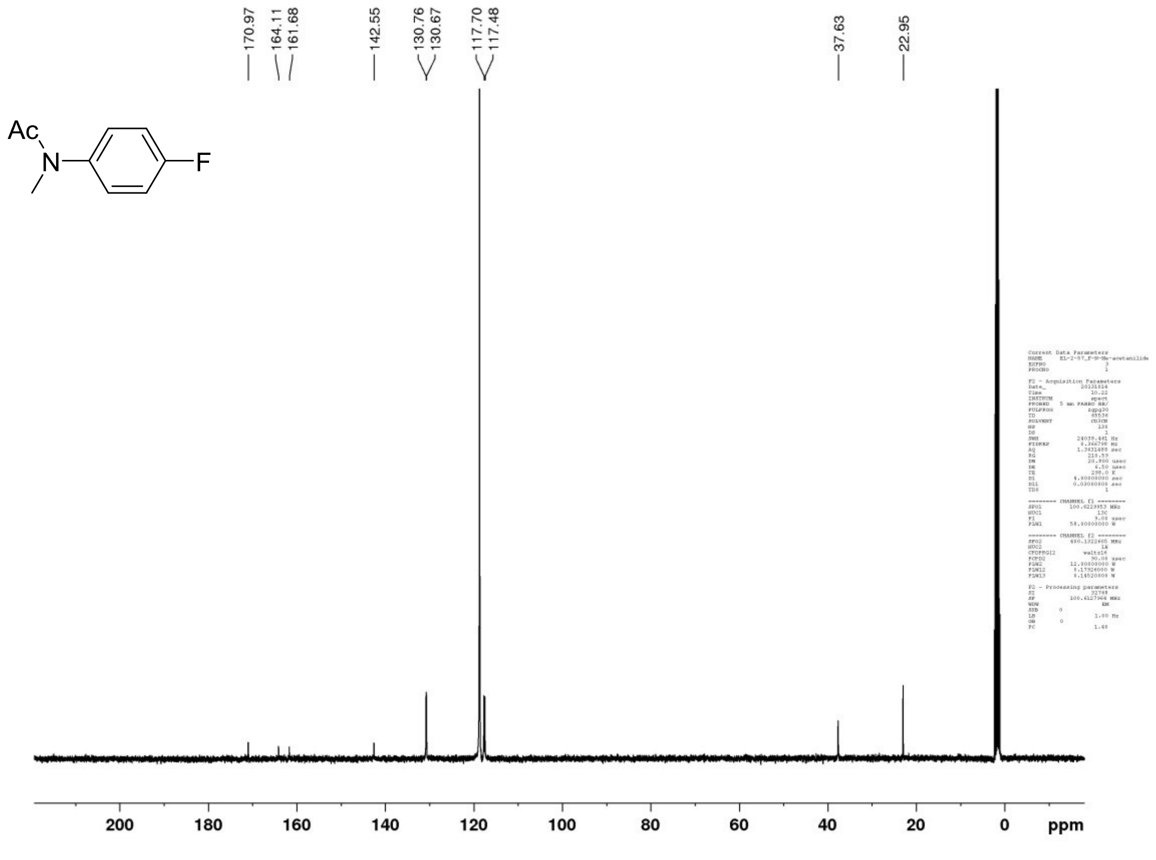
```
Current Data Parameters
NAME      EL-2-57_F-N-Me-acetanilide
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20131014
Time                 10.16
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zg30
TD                   65536
SOLVENT              CD3CN
NS                      16
DS                       2
SWH               8012.820 Hz
FIDRES            0.122266 Hz
AQ               4.0894465 sec
RG                   50.12
DW                  62.400 usec
DE                    6.50 usec
TE                   298.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           400.1331310 MHz
NUC1                    1H
P1                   11.00 usec

F2 - Processing parameters
SF             400.1306695 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```





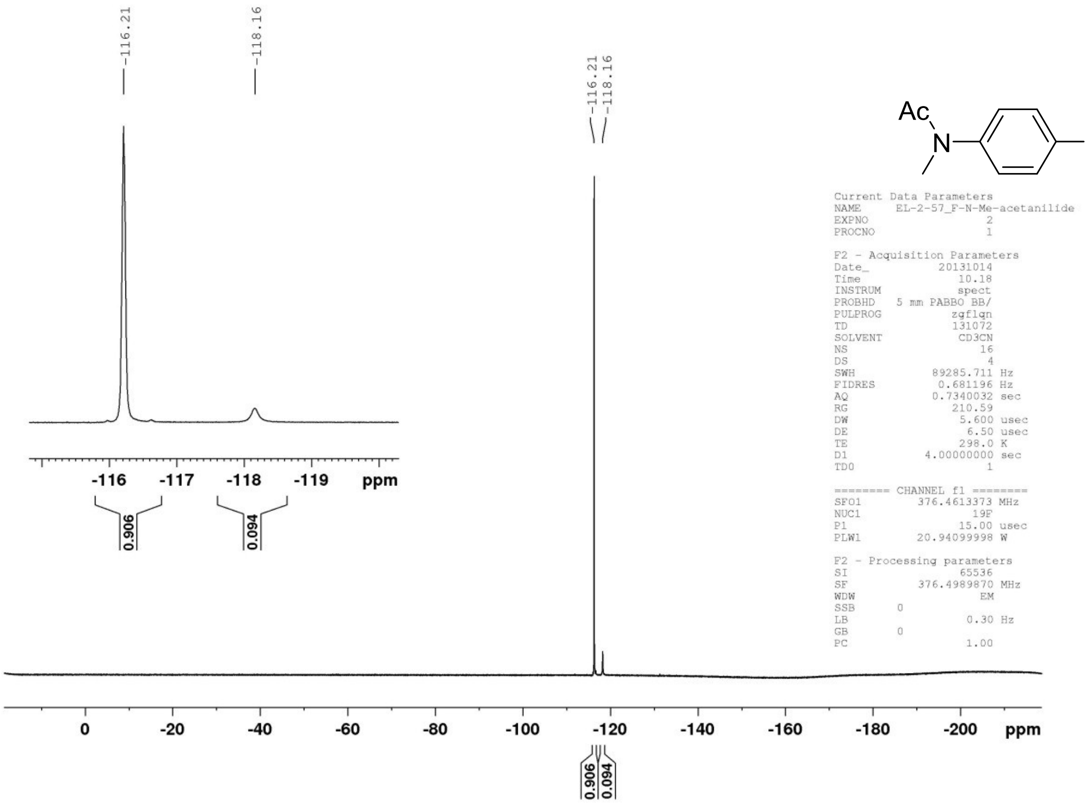
```
Current Data Parameters
NAME      EL-2-57_F-N-Me-acetanilide
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_             20131014
Time                 10.22
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG            zgpg30
TD                   65536
SOLVENT              CD3CN
NS                     128
DS                       4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631488 sec
RG                  210.59
DW                  20.800 usec
DE                    6.50 usec
TE                   298.0 K
D1              4.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           100.6229353 MHz
NUC1                   13C
P1                    9.00 usec
PLW1           58.00000000 W

======== CHANNEL f2 ========
SFO2           400.1322405 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                90.00 usec
PLW2           12.00000000 W
PLW12           0.17326000 W
PLW13           0.14520000 W

F2 - Processing parameters
SI                   32768
SF             100.6127964 MHz
WDW                     EM
SSB      0
LB                    1.00 Hz
GB       0
PC                    1.40
```



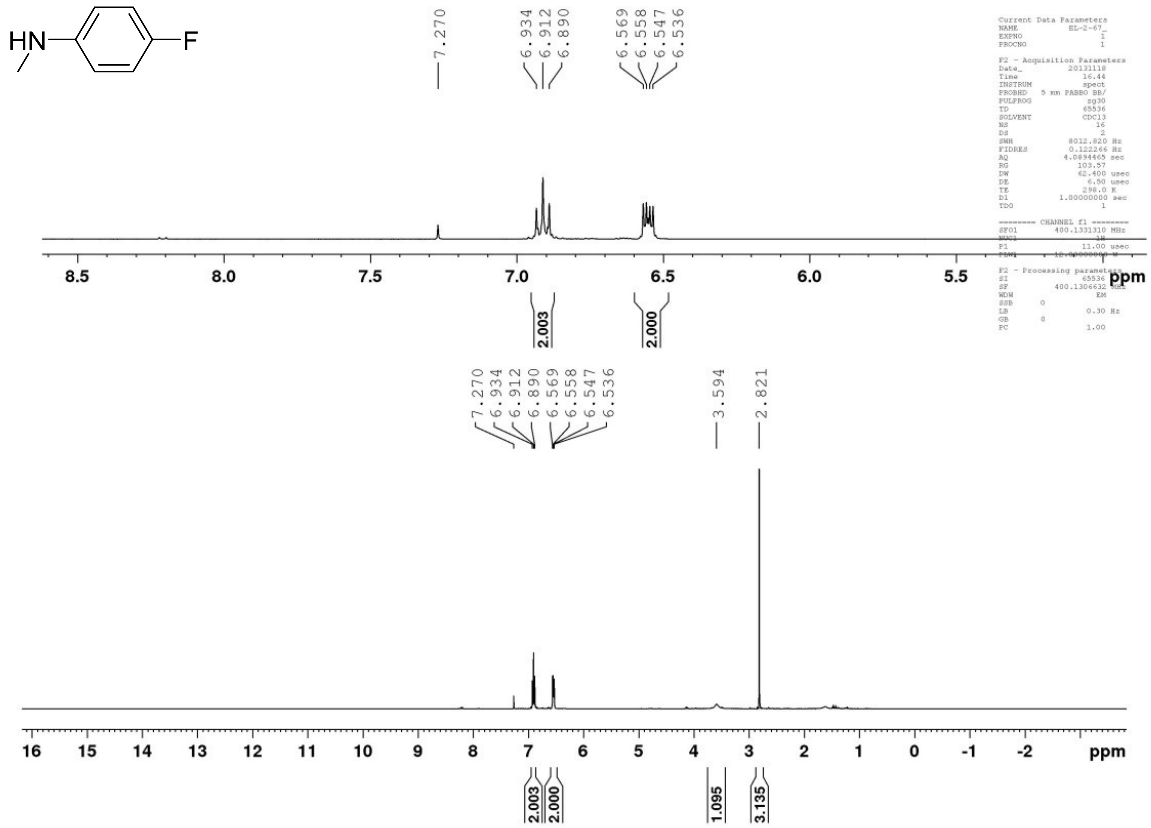
```
Current Data Parameters
NAME      EL-2-57_F-N-Me-acetanilide
EXPNO                  2
PROCNO                 1

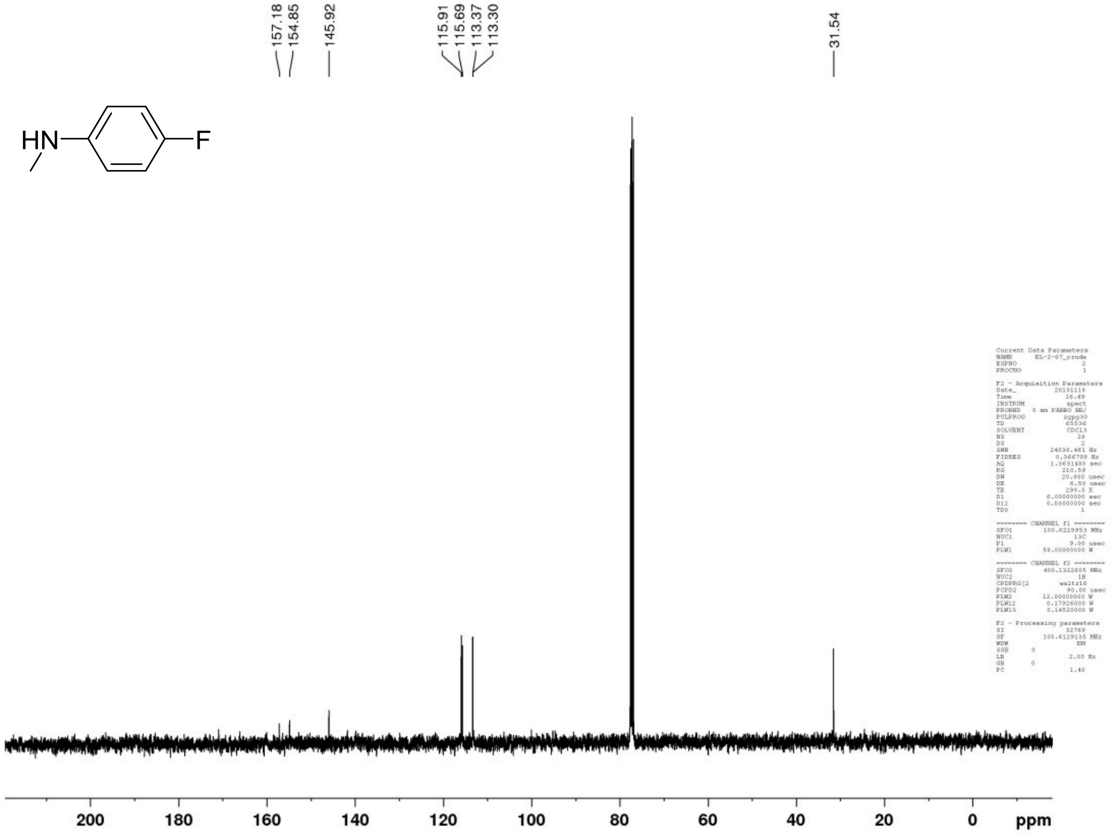
F2 - Acquisition Parameters
Date_           20131014
Time               10.18
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgflqn
TD                131072
SOLVENT            CD3CN
NS                    16
DS                     4
SWH           89285.711 Hz
FIDRES         0.681196 Hz
AQ            0.7340032 sec
RG                210.59
DW                 5.600 usec
DE                  6.50 usec
TE                 298.0 K
D1           4.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        376.4613373 MHz
NUC1                19F
P1                15.00 usec
PLW1        20.94099998 W

F2 - Processing parameters
SI                 65536
SF          376.4989870 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

4-Fluoro-N-methylaniline





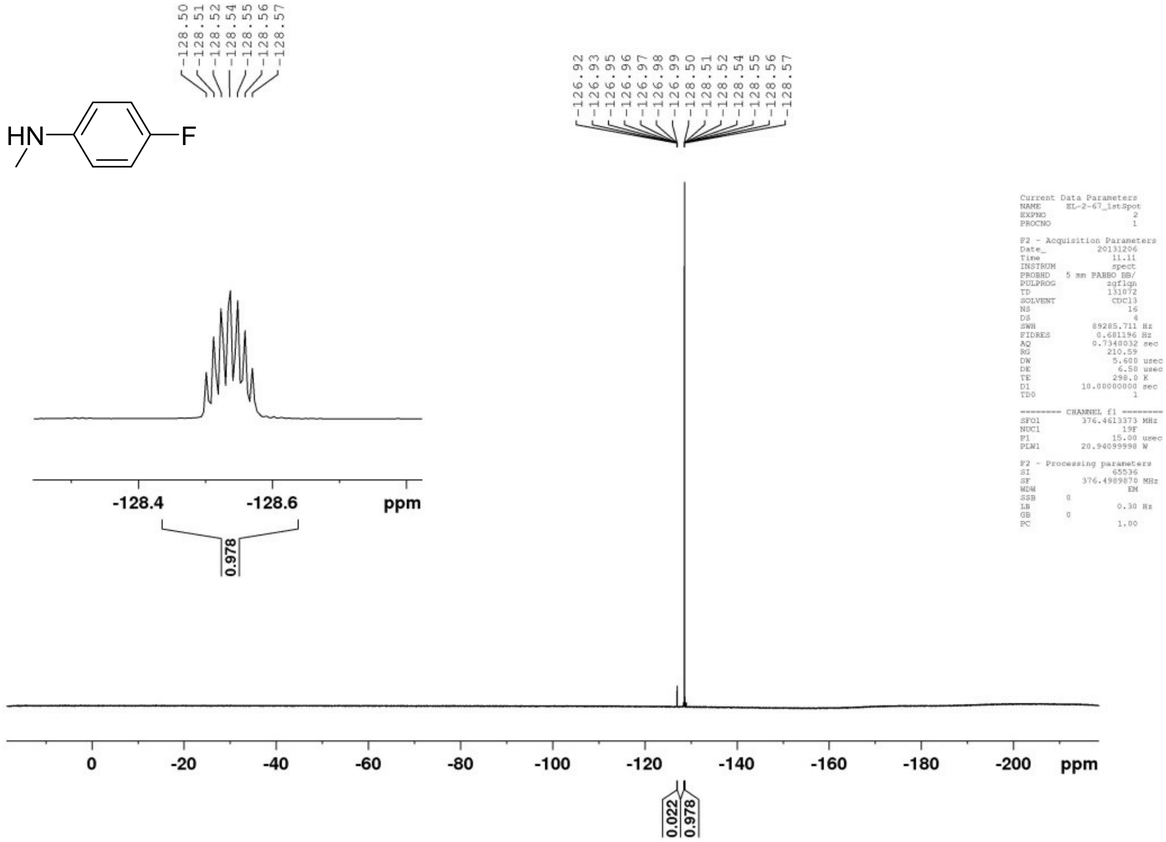
```
Current Data Parameters
NAME       EL-2-67_crude
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20131118
Time               16.49
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDC13
NS                    28
DS                     2
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ           1.3631488 sec
RG               210.59
DW               20.800 usec
DE                 6.50 usec
TE                298.0 K
D1           6.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        100.6229953 MHz
NUC1                13C
P1                 9.00 usec
PLW1        58.00000000 W

======== CHANNEL f2 ========
SFO2        400.1322605 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2        12.00000000 W
PLW12        0.17926000 W
PLW13        0.14520000 W

F2 - Processing parameters
SI                 32768
SF          100.6129135 MHz
WDW                   EM
SSB      0
LB                  2.00 Hz
GB       0
PC                  1.40
```



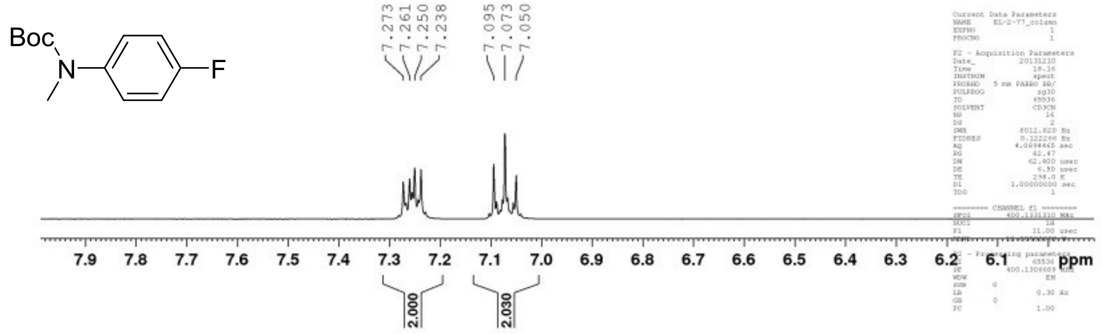
```
Current Data Parameters
NAME       EL-2-67_1stSpot
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20131206
Time               11.11
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgflqn
TD                131072
SOLVENT            CDC13
NS                    16
DS                     4
SWH          89285.711 Hz
FIDRES        0.681196 Hz
AQ           0.7340032 sec
RG               210.59
DW                5.600 usec
DE                 6.50 usec
TE                298.0 K
D1          10.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        376.4613373 MHz
NUC1                19F
P1                15.00 usec
PLW1        20.94099998 W

F2 - Processing parameters
SI                 65536
SF          376.4989870 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

N-Boc-4-fluoro-N-methylaniline

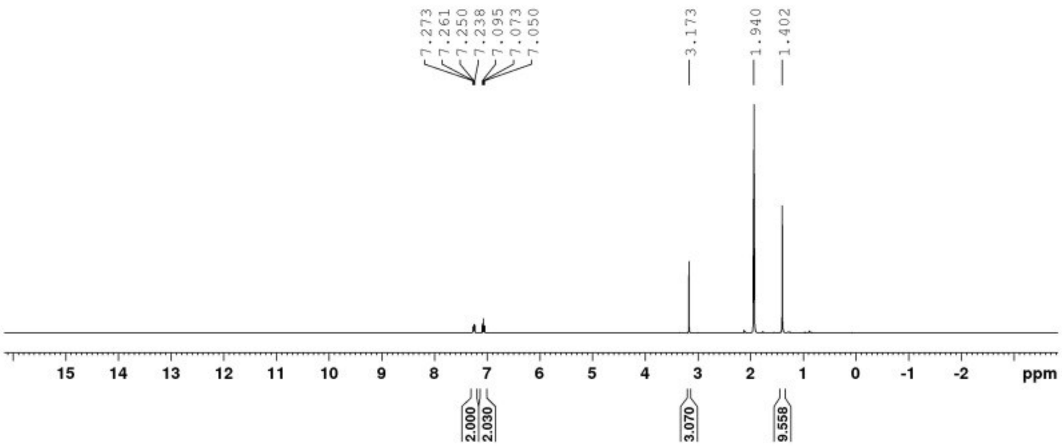


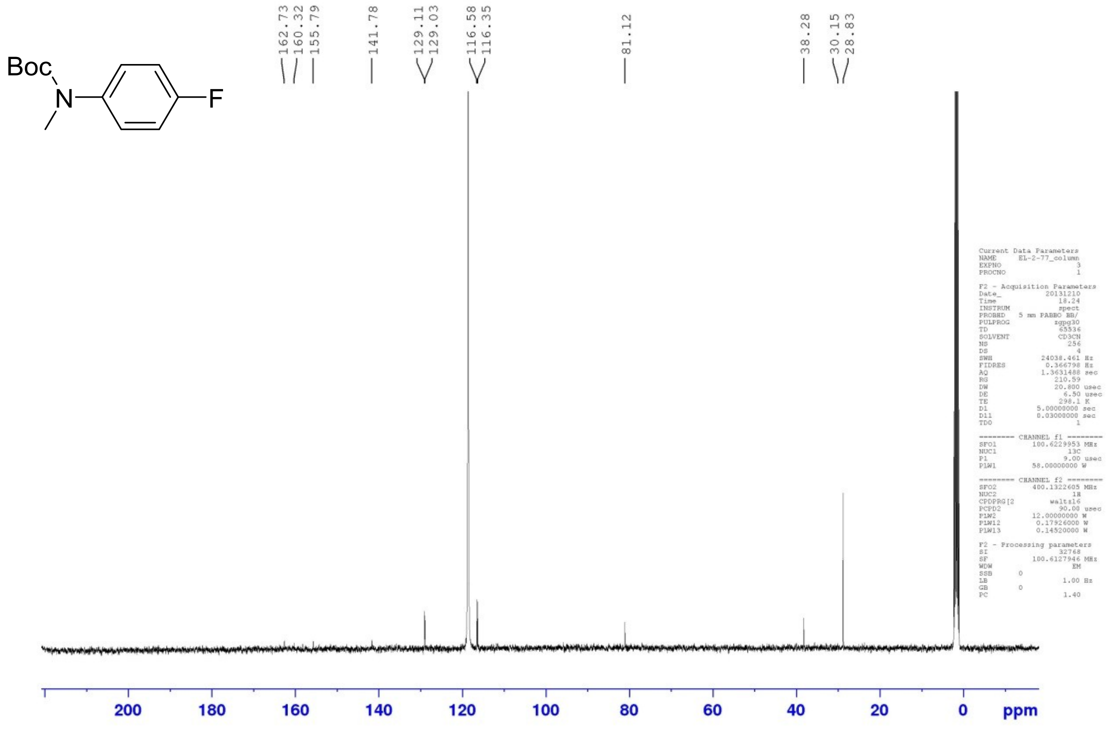
```
Current Data Parameters
NAME      EL-2-77_column
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20131210
Time               18.16
INSTRUM            spect
PROBHD    5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CD3CN
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894465 sec
RG                 82.47
DW                62.400 usec
DE                  6.50 usec
TE                 298.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1321310 MHz
NUC1                  1H
P1                 11.00 usec

F2 - Processing parameters
SI                 65536
SF           400.1304603 MHz
WDW                   EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```





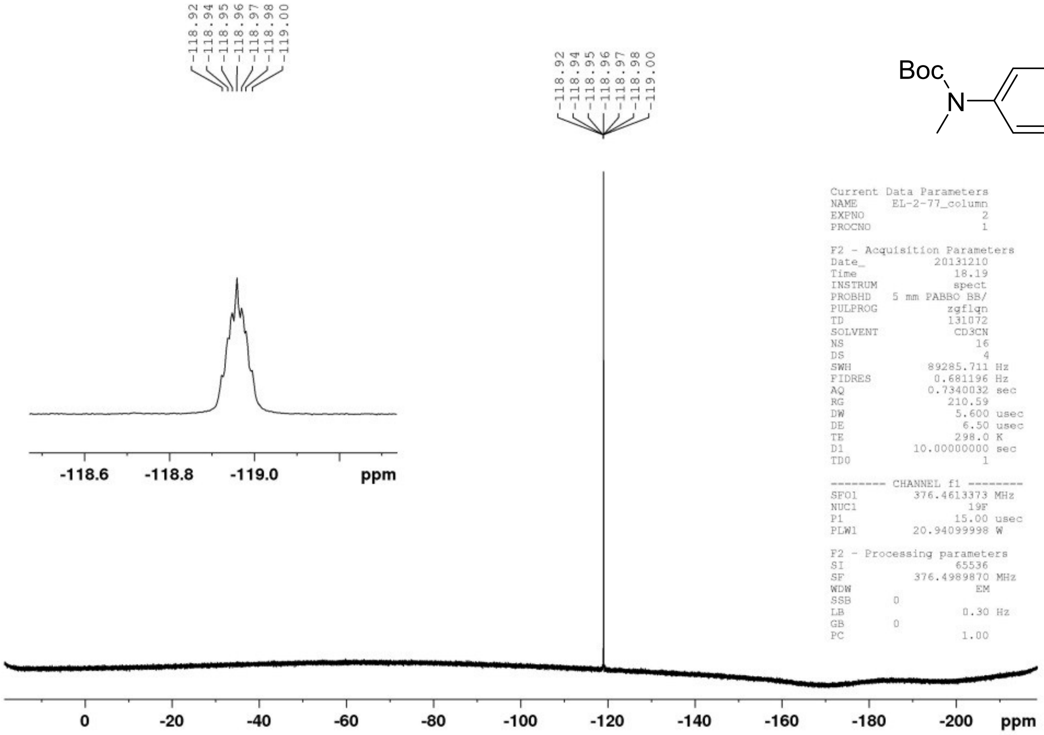
```
Current Data Parameters
NAME      EL-2-77_column
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20131210
Time               18.24
INSTRUM            spect
PROBHD    5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT            CD3CN
NS                   256
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631488 sec
RG                210.59
DW                20.800 usec
DE                  6.50 usec
TE                 298.1 K
D1            5.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6229953 MHz
NUC1                 13C
P1                  9.00 usec
PLW1         58.00000000 W

======== CHANNEL f2 ========
SFO2         400.1322605 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2              90.00 usec
PLW2         12.00000000 W
PLW12         0.17926000 W
PLW13         0.14520000 W

F2 - Processing parameters
SI                 32768
SF           100.6127946 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```



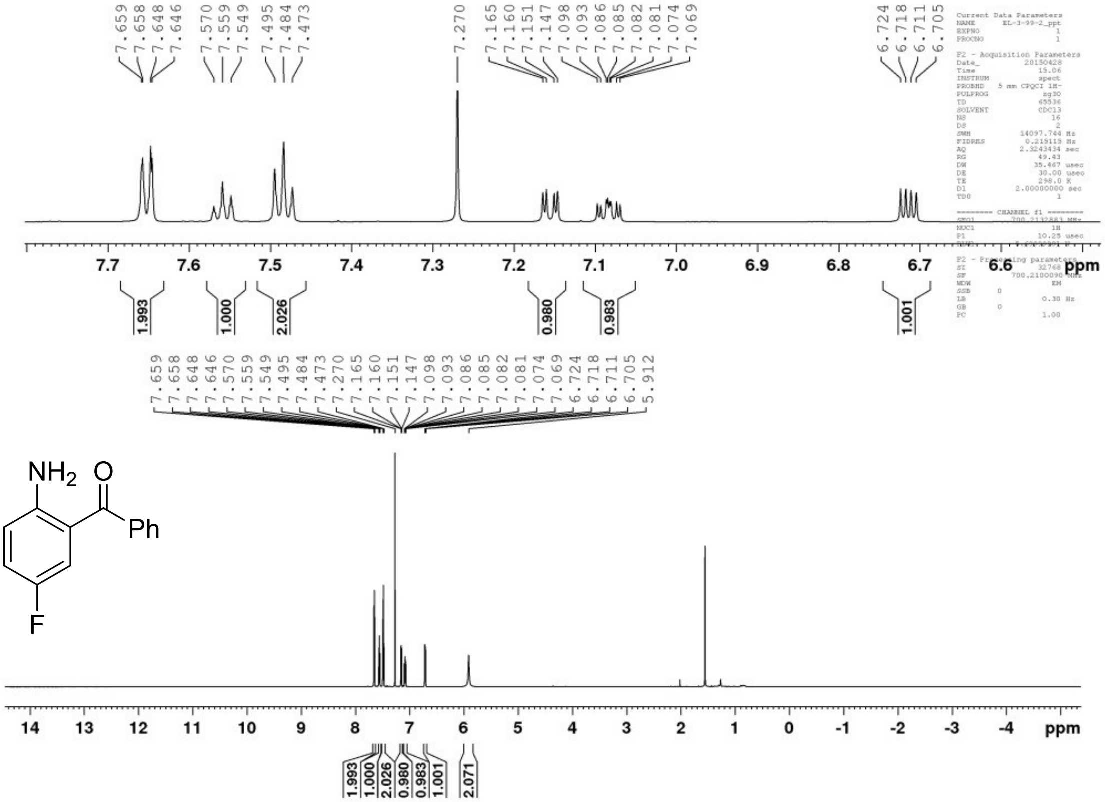
```
Current Data Parameters
NAME      EL-2-77_column
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20131210
Time               18.19
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgflqn
TD                131072
SOLVENT            CD3CN
NS                    16
DS                     4
SWH           89285.711 Hz
FIDRES         0.681196 Hz
AQ            0.7340032 sec
RG                210.59
DW                 5.600 usec
DE                  6.50 usec
TE                 298.0 K
D1           10.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         376.4613373 MHz
NUC1                 19F
P1                 15.00 usec
PLW1         20.94099998 W

F2 - Processing parameters
SI                 65536
SF           376.4989870 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

2-Amino-5-fluoro-benzophenone

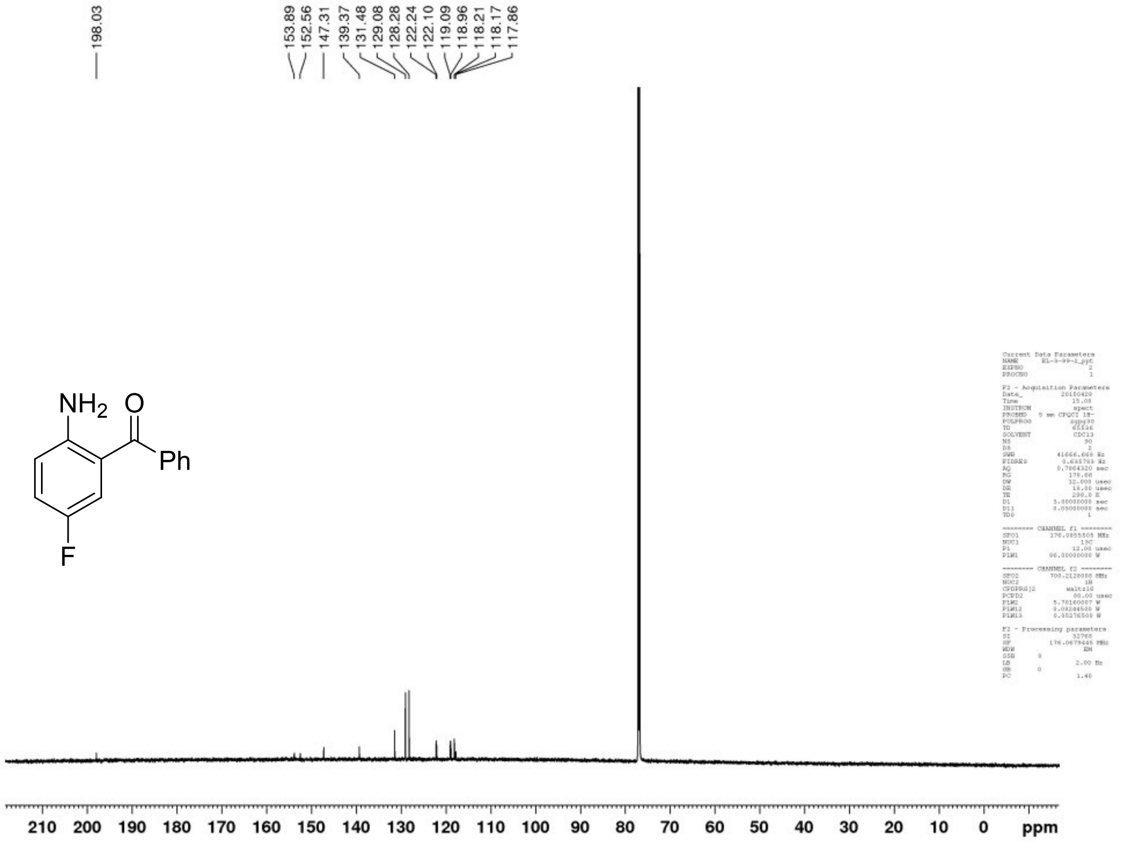


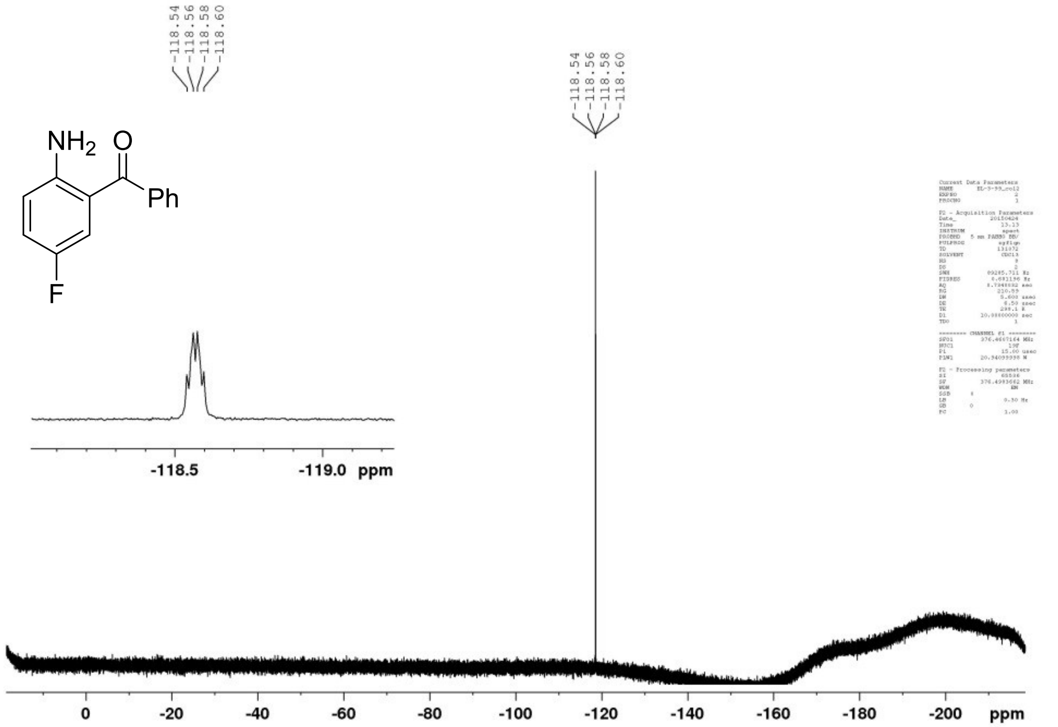
```
Current Data Parameters
NAME       EL-3-99-2_ppt
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150428
Time               15.06
INSTRUM            spect
PROBHD   5 mm CPQCI 1H-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH           14097.744 Hz
FIDRES         0.215119 Hz
AQ             2.3243434 sec
RG                 49.43
DW                35.467 usec
DE                 30.00 usec
TE                 298.0 K
D1            2.00000000 sec
TD0                    1

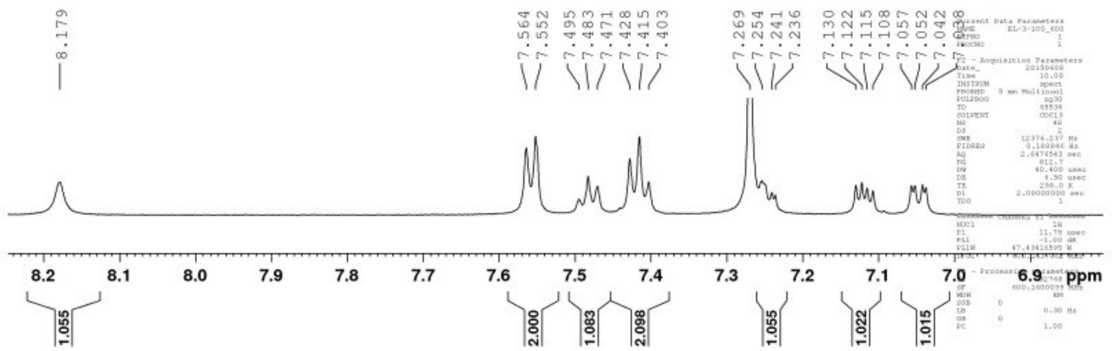
======== CHANNEL f1 ========
SFO1         700.2132883 MHz
NUC1                  1H
P1                 10.25 usec
PLW1         [illegible]

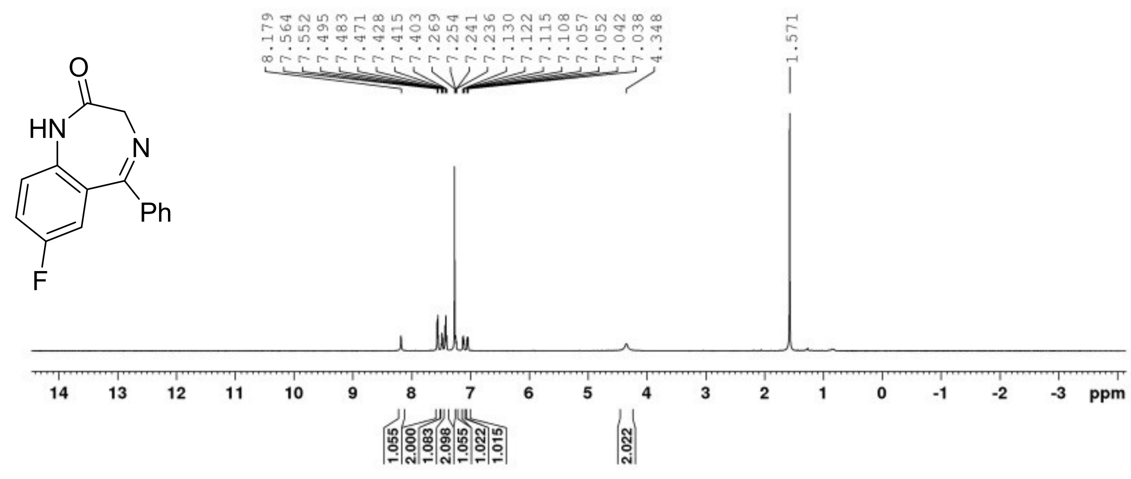
F2 - Processing parameters
SI                 32768
SF           700.2100090 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

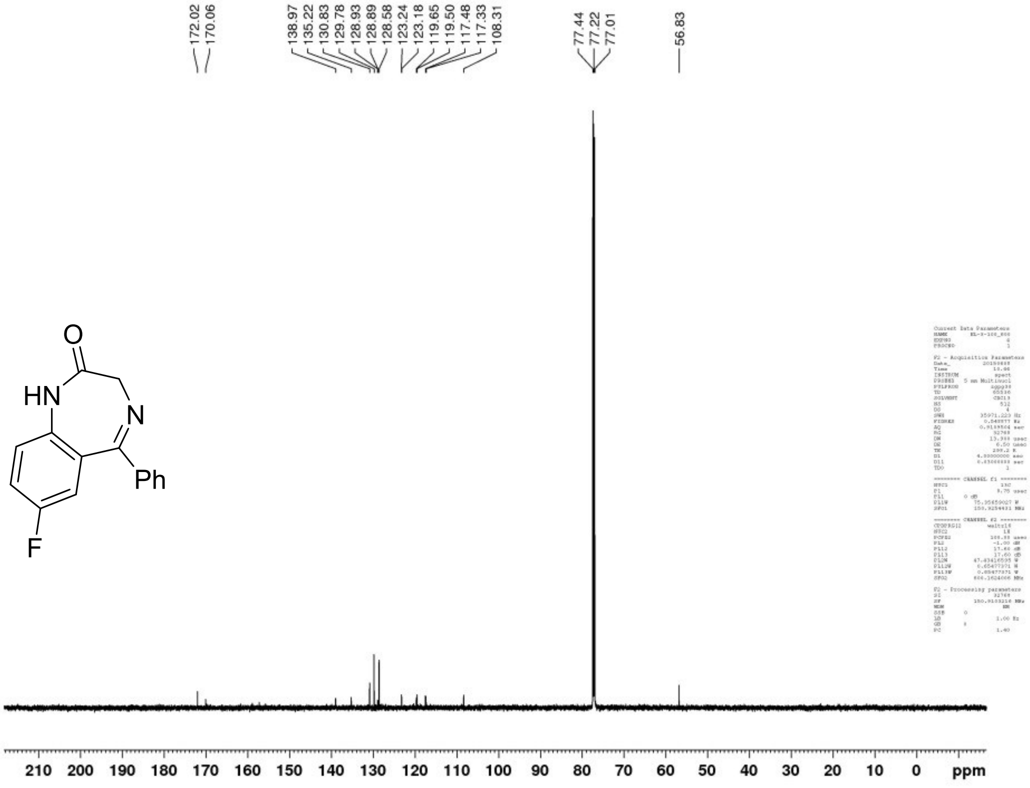

198.03
153.89
152.56
147.31
139.37
131.48
129.08
128.28
122.24
122.10
119.09
118.96
118.21
118.17
117.86
NH2
O
Ph
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

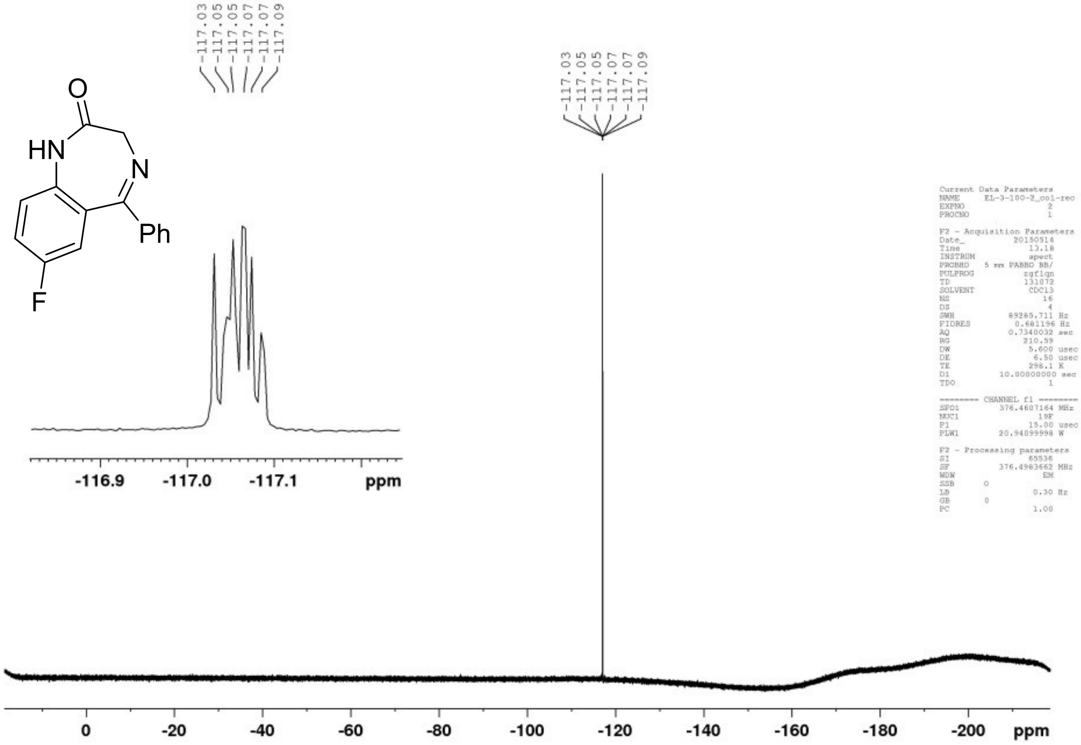

-118.54
-118.56
-118.58
-118.60
NH2
O
Ph
F
-118.5
-119.0 ppm
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

7-Fluoro-5-phenyl-1,3-dihydro-2H-benzo[e][1,4]diazepin-2-one

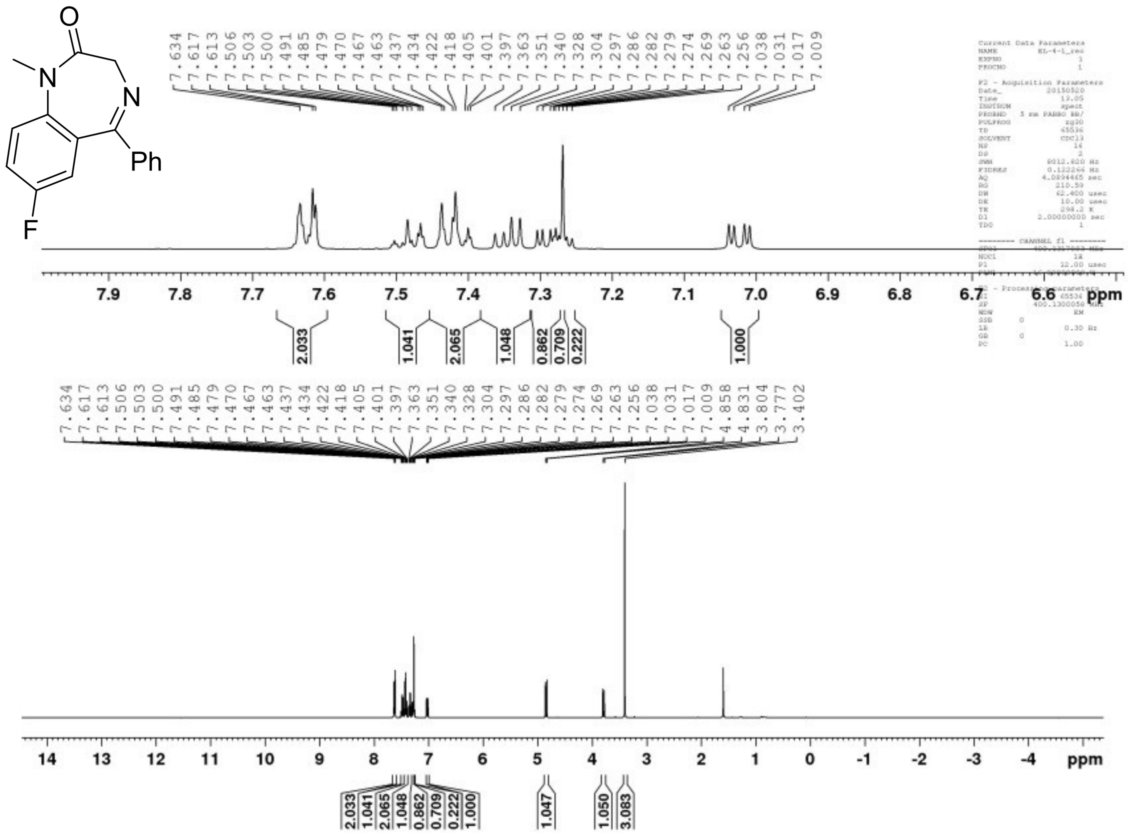


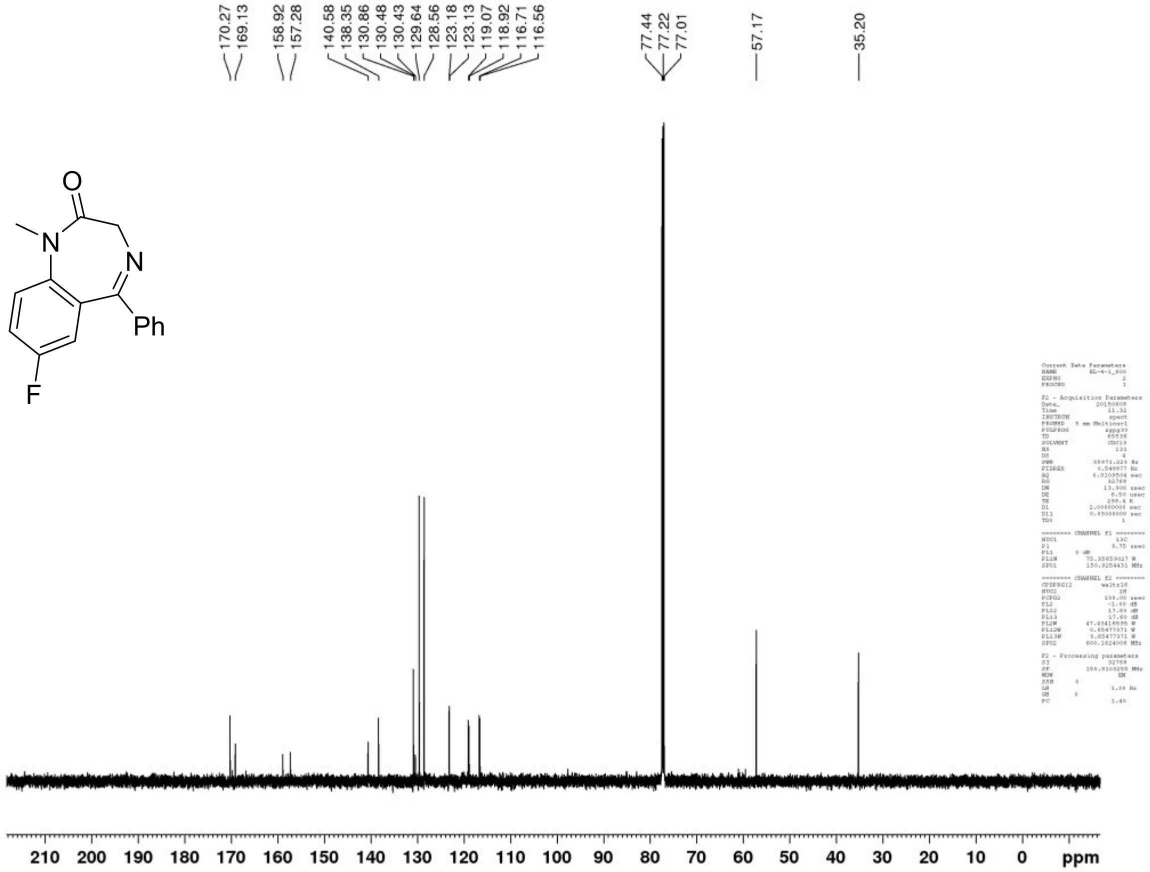






7-Fluoro-1-methyl-5-phenyl-1,3-dihydro-2H-benzo[e][1,4]diazepin-2-one





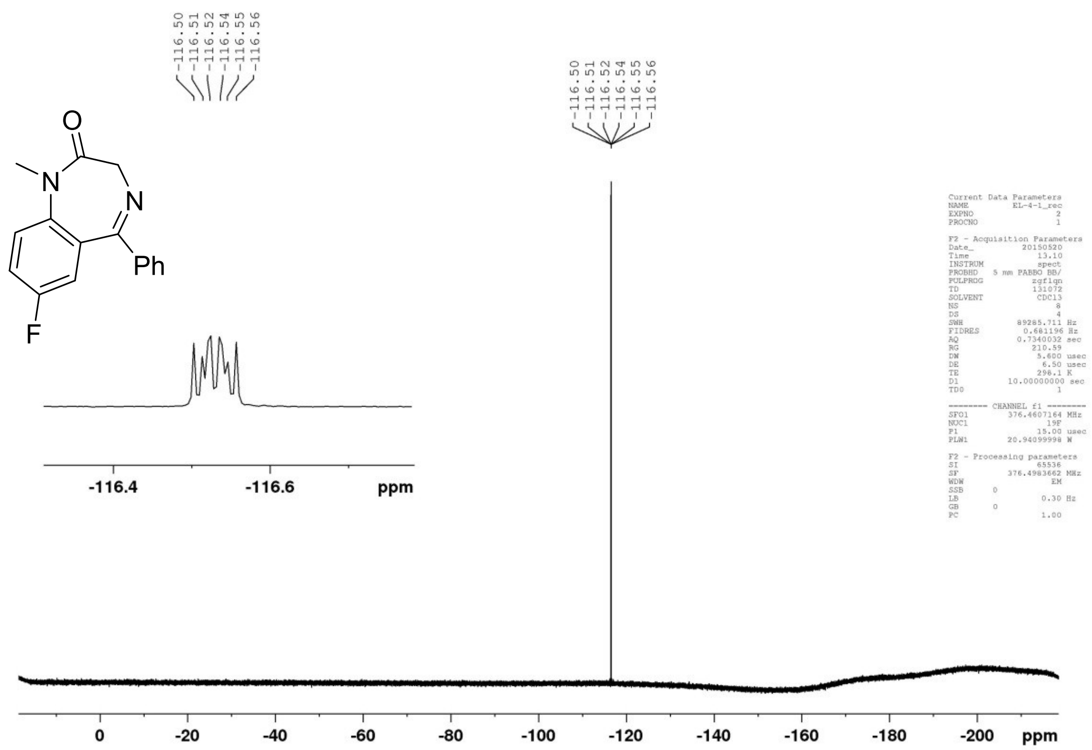
```
Current Data Parameters
NAME          EL-4-1_600
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150608
Time               11.32
INSTRUM            spect
PROBHD   5 mm Multinucl
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   121
DS                     4
SWH            35971.223 Hz
FIDRES          0.548877 Hz
AQ             0.9109504 sec
RG                 32768
DW                13.900 usec
DE                  6.50 usec
TE                 298.4 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.75 usec
PL1       0 dB
PL1W         75.35659027 W
SFO1         150.9254431 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                -1.40 dB
PL12               17.60 dB
PL13               17.60 dB
PL2W         47.03416595 W
PL12W         0.65477371 W
PL13W         0.65477371 W
SFO2         600.1624008 MHz

F2 - Processing parameters
SI                 32768
SF           150.9103258 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```



```
Current Data Parameters
NAME          EL-4-1_rec
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150520
Time               13.10
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgflqn
TD                131072
SOLVENT            CDCl3
NS                     8
DS                     4
SWH            89285.711 Hz
FIDRES          0.681196 Hz
AQ             0.7340032 sec
RG                210.59
DW                 5.600 usec
DE                  6.50 usec
TE                 298.1 K
D1           10.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         376.4607164 MHz
NUC1                 19F
P1                 15.00 usec
PLW1         20.94099998 W

F2 - Processing parameters
SI                 65536
SF           376.4983662 MHz
WDW                   EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```