The Role of Aryne Distortions, Steric Effects, and Charges on Regioselectivities of Aryne Reactions

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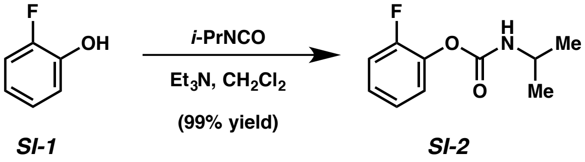
Supporting Information – Table of Contents

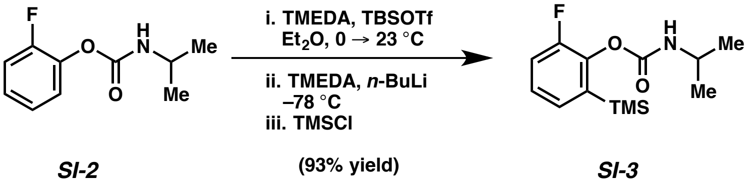
Materials and Methods. Unless stated otherwise, reactions were conducted in flame-dried glassware under an atmosphere of nitrogen using anhydrous solvents (freshly distilled or passed through activated alumina columns). All commercially obtained reagents were used as received unless otherwise specified. Cesium fluoride (CsF) was obtained from Strem Chemicals and stored on the bench-top at ambient temperature under an N_2 atmosphere. 2,6-Dibromophenol was obtained from Combi-Blocks, Inc. *N*-Phenylbis (trifluoromethanesulfonimide) was obtained from Oakwood Products, Inc. Finely powdered anhydrous K_3PO_4 was obtained from Acros Organics. 3-Furanylboronic acid was obtained from Combi-Blocks, Inc. 2-Methoxypyridine-3-boronic acid was obtained from Frontier Scientific. 2-Methyltetrahydrofuran (2-Me-THF), anhydrous, was obtained from Acros Organics. $NiCl_2$(DME) and $NiCl_2(PCy_3)_2$ were obtained from Strem Chemicals. NaO*t*Bu was obtained from Alfa Aesar. Morpholine, 2-pyridylpiperazine, SIPr•HCl, and Ph–B(pin) were obtained from Sigma Aldrich and Alfa Aesar. The following reagents were distilled prior to use: Trifluoromethanesulfonic anhydride (Tf_2O), pyridine, and *tert*-butyldimethylsilyl trifluoromethanesulfonate (TBSOTf). Trimethylsilyl chloride (TMSCl) and tetramethylethylenediamine (TMEDA) were stirred over CaH_2 for 1 h prior to distillation. Dioxane was distilled over sodium benzophenone ketyl. Diethylamine (Et_2NH) was dried over KOH and then passed over basic Brockman Grade I 58 Å Al_2O_3 (Activity 1). 1,8-Diazabicycloundec-7-ene (DBU), and *N*-methylaniline were dried over 3 Å molecular sieves and then passed over basic Brockman Grade I 58 Å Al_2O_3 (Activity 1) prior to use. *n*-Pentane was dried over $MgSO_4$ prior to use. Reaction temperatures were controlled using an IKAmag temperature modulator and, unless stated otherwise, reactions were performed at room temperature (rt, approximately 23 °C). Thin-layer chromatography (TLC) was conducted with EMD gel 60 F254 pre-coated plates (0.25 mm) and visualized using a combination of UV light and potassium permanganate staining. Silicycle Siliaflash P60 (particle size 0.040–0.063 mm) was used for flash column chromatography. ^{1}H NMR and 2D-NOESY spectra were recorded on Bruker spectrometers (at 300 MHz, 400 MHz, or 500 MHz) and are reported relative to deuterated solvent signals. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. ^{13}C NMR spectra were recorded on Bruker spectrometers (at 125 MHz) and are reported relative to deuterated solvent signals. Data for ^{13}C NMR spectra are reported in terms of chemical shift and, when necessary, multiplicity, and coupling constant (Hz). IR spectra were recorded on a Perkin-Elmer 100 spectrometer and are reported in terms of frequency of absorption (cm^{-1}). High-resolution mass spectra were obtained on Waters LCT Premier with ACQUITY LC and Thermo Scientific^{TM} Exactive Mass Spectrometers with DART ID-CUBE.

Experimental Procedures.

A. Synthesis of 3-Fluorobenzyne Precursor 4b.

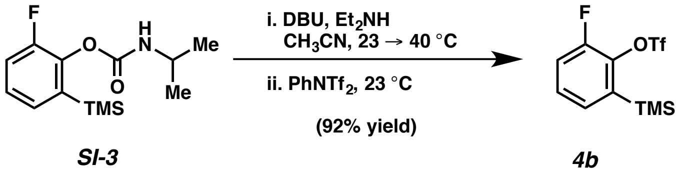


Fluorocarbamate SI-2. To a stirred solution of 2-fluorophenol (**SI-1**) (0.95 mL, 10.6 mmol) in CH_2Cl_2 (35 mL) was added *i*-PrNCO (1.56 mL, 15.9 mmol, 1.5 equiv), followed by Et_3N (0.30 mL, 2.1 mmol, 0.2 equiv). The solution was stirred at 23 °C for 12 h and then quenched with saturated aqueous $NaHCO_3$ (20 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The organic layers were combined and washed with brine (50 mL), and then dried over $MgSO_4$. Evaporation of the solvent under reduced pressure afforded the crude product, which was further purified by flash chromatography (20:1 Hexanes:EtOAc) to furnish carbamate **SI-2** (2.09 g, 99% yield) as a white solid. Spectral data match those previously reported.[1]



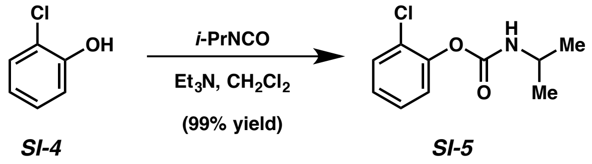
Fluorosilylcarbamate SI-3. To a solution of fluorocarbamate **SI-2** (2.09 g, 10.5 mmol) in diethyl ether (100 mL) at 0 °C was added TMEDA (1.77 mL, 11.8 mmol, 1.1 equiv), followed by a solution of TBSOTf in *n*-pentane (1.30 M, 8.70 mL, 11.8 mmol, 1.1 equiv). The mixture was allowed to stir at 0 °C for 5 min and was then warmed to 23 °C over 30 min. Additional TMEDA (3.22 mL, 21.4 mmol, 2.0 equiv) was added and the reaction was cooled to –78 °C. A solution of *n*-BuLi in hexanes (2.20 M, 9.75 mL, 21.4 mmol, 2.0 equiv) was added dropwise over 70 min. The mixture was stirred at –78 °C for an additional 1 h and then neat TMSCl (4.76 mL, 37.5 mmol, 3.5 equiv) was added dropwise over 35 min. The resulting mixture was stirred at –78 °C for 85 min, quenched with saturated aqueous $NaHSO_4$ (60 mL), and allowed to warm to 23 °C over 45 min with vigorous stirring. The organic layer was separated, washed successively with 1

M $NaHSO_4$ (60 mL) and brine (60 mL), and then dried over Na_2SO_4. Evaporation under reduced pressure afforded crude product, which was further purified by flash chromatography (95:5 Hexanes:EtOAc) to afford **SI-3** (2.62 g, 93% yield) as a white solid. Spectral data match those previously reported.[1]

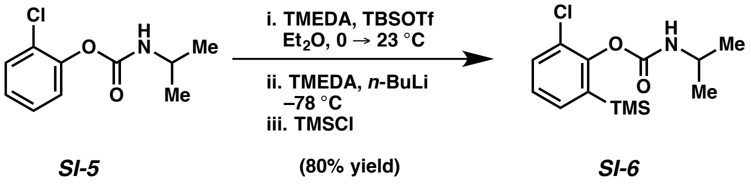


Fluorosilyltriflate 4b. To a solution of fluorosilylcarbamate **SI-3** (2.62 g, 9.7 mmol) in CH_3CN (100 mL) was added DBU (2.20 mL, 14.6 mmol, 1.5 equiv) and Et_2NH (1.20 mL, 11.7 mmol, 1.2 equiv). The resulting mixture was placed in an oil bath maintained at 40 °C for 45 min and then allowed to cool to 23 °C. Next, a solution of $PhNTf_2$ (5.20 g, 14.6 mmol, 1.5 equiv) in CH_3CN (30 mL) was added via cannula over 20 min. After stirring for 2 h, the reaction mixture was washed successively with saturated aqueous $NaHSO_4$ (2 x 60 mL) and 10% aqueous NaOH (2 x 60 mL), and then dried over Na_2SO_4. Evaporation under reduced pressure afforded the crude product, which was further purified by flash chromatography (200:1 Hexanes:Et_2O) to provide fluorosilyltriflate **4b** (2.83 g, 92% yield) as a colorless oil. **4b**: R_f 0.52 (10:1 Hexanes:Et_2O); ^1H NMR (400 MHz, $CDCl_3$): δ 7.36–7.28 (m, 2H), 7.26–7.21 (m, 1H), 0.41 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.4 (d, J = 254.2), 140.8 (d, J = 11.8), 137.3 (d, J = 3.1), 131.0 (d, J = 4.3), 129.4 (d, J = 6.6), 118.9 (q, J = 320.3, CF_3), 118.5 (d, J = 19.4), 0.4; IR (film): 2961, 1604, 1578, 1420, 1269, 1207 cm^{-1}; HRMS-ESI (*m/z*) $[M - H]^-$ calcd for $C_{10}H_{11}F_4O_3SSi$, 315.01288; found, 315.01429.

B. Synthesis of 3-Chlorobenzyne Precursor 4c.

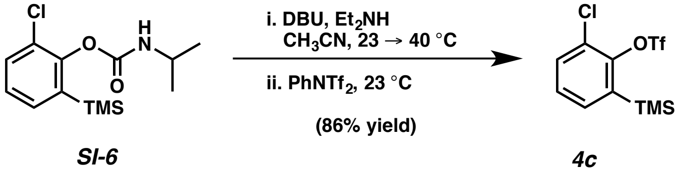


Chlorocarbamate SI-5. To a stirred solution of 2-chlorophenol (**SI-4**) (1.37 g, 10.6 mmol) in CH_2Cl_2 (35 mL) was added *i*-PrNCO (1.56 mL, 15.9 mmol, 1.5 equiv), followed by NEt_3 (0.30 mL, 2.1 mmol, 0.2 equiv). The solution was stirred at 23 °C for 12 h and then quenched with saturated aqueous $NaHCO_3$ (20 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The organic layers were combined and washed with brine (50 mL), and then dried over $MgSO_4$. Evaporation of the solvent under reduced pressure afforded the crude product, which was further purified by flash chromatography (20:1 Hexanes:EtOAc) to furnish chlorocarbamate **SI-5** (2.29 g, 99% yield) as a white solid. Spectral data match those previously reported.[2]



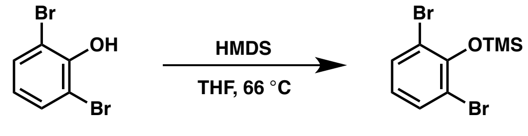
Chlorosilylcarbamate SI-6. To a solution of chlorocarbamate **SI-5** (2.29 g, 10.5 mmol) in diethyl ether (105 mL) at 0 °C was added TMEDA (1.77 mL, 11.8 mmol, 1.1 equiv), followed by a solution of TBSOTf in *n*-pentane (1.30 M, 8.70 mL, 11.8 mmol, 1.1 equiv). The mixture was allowed to stir at 0 °C for 5 min and was then warmed to 23 °C over 30 min. Additional TMEDA (3.22 mL, 21.4 mmol, 2.0 equiv) was added and the reaction was cooled to –78 °C. A solution of *n*-BuLi in hexanes (2.20 M, 9.75 mL, 21.4 mmol, 2.0 equiv) was added dropwise over 70 min. The mixture was stirred at –78 °C for an additional 1 h and then neat TMSCl (4.76 mL, 37.5 mmol, 3.5 equiv) was added dropwise over 35 min. The resulting mixture was stirred at –78 °C for 85 min, quenched with saturated aqueous $NaHSO_4$ (60 mL), and allowed to warm to 23 °C over 45 min with vigorous stirring. The organic layer was separated, washed successively with 1 M $NaHSO_4$ (60 mL) and brine (60 mL), and then dried over Na_2SO_4. Evaporation under reduced pressure afforded crude product, which was further purified by flash chromatography (95:5

Hexanes:EtOAc) to afford chlorosilylcarbamate **SI-6** (2.39 g, 80% yield) as a white solid. Spectral data match those previously reported.[2]



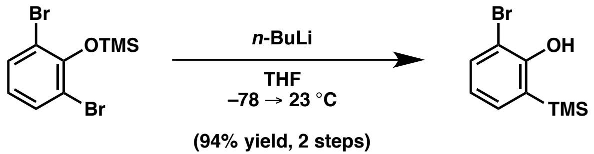
Chlorosilyltriflate 4c. To a solution of chlorosilylcarbamate **SI-6** (2.39 g, 8.36 mmol) in CH_3CN (100 mL) was added DBU (1.87 mL, 12.5 mmol, 1.5 equiv) and Et_2NH (1.04 mL, 10.0 mmol, 1.2 equiv). The resulting mixture was placed in a heating bath maintained at 40 °C for 45 min and then allowed to cool to 23 °C. Next, a solution of $PhNTf_2$ (4.48 g, 12.5 mmol, 1.5 equiv) in CH_3CN (30 mL) was added via cannula over 20 min. After stirring for 2 h, the reaction mixture was washed successively with saturated aqueous $NaHSO_4$ (2 x 60 mL) and 10% aqueous NaOH (2 x 60 mL), and then dried over Na_2SO_4. Evaporation under reduced pressure afforded the crude product, which was further purified by flash chromatography (100% Hexanes) to provide chlorosilyltriflate **4c** (2.16 g, 86% yield) as a colorless oil. **4c**: R$_f$ 0.55 (200:1 Hexanes:Et_2O); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (dd, *J* = 7.8, 1.6, 1H), 7.46 (dd, *J* = 7.5, 1.6, 1H), 7.31 (t, *J* = 7.8, 1H), 0.41 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.3, 137.7, 135.0, 132.6, 129.0, 127.6, 118.7 (q, *J* = 320, CF_3), 0.0; IR (film): 2958, 1556, 1397, 1254, 1208 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{10}H_{13}ClF_3O_3SSi$, 332.99898; found, 332.99871.

C. Synthesis of 3-Bromobenzyne Precursor 4d.



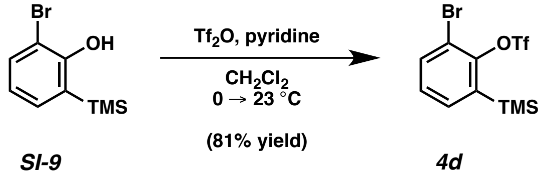
SI-7 *SI-8*

Silylether SI-8. Silylether **SI-8** was prepared following the general procedure described by Díaz.[3] To a solution of 2,6-dibromophenol (**SI-7**) (1.09 g, 4.3 mmol) in THF (5 mL) was added HMDS (1.81 mL, 8.7 mmol, 2.0 equiv). The reaction vessel was sealed and placed in an aluminum heating block maintained at 66 °C for 24 h. After cooling to 23 °C, evaporation of the solvent under reduced pressure afforded crude **SI-8** as a colorless oil, which was used in the subsequent step without further purification.



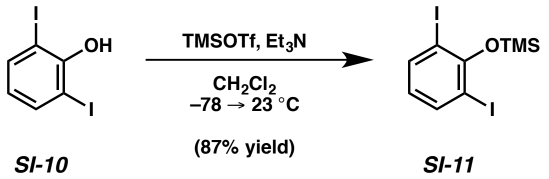
SI-8 *SI-9*

Bromosilylphenol SI-9. Compound **SI-9** was prepared following a modification of the procedure described by Booker.[4] Silylether **SI-8** (1.40 g, 4.3 mmol) was dissolved in THF (43 mL) and cooled to –78 °C. A solution of *n*-BuLi in hexanes (2.20 M, 1.97 mL, 4.3 mmol, 1.0 equiv) was added dropwise over 15 min. After stirring at –78 °C for 1 h, the solution was removed from the bath and allowed to warm to 23 °C. After stirring for an additional 4.5 h, the reaction was quenched with saturated aqueous NH_4Cl (30 mL). The biphasic mixture was further diluted with Et_2O (50 mL). The layers were separated, and then the aqueous layer was extracted with Et_2O (3 x 50 mL). The combined organic layers were washed with H_2O (50 mL), and then dried over $MgSO_4$. Evaporation of the solvent under reduced pressure afforded the crude product, which was further purified by flash chromatography (100% Hexanes) to afford **SI-9** (1.02 g, 94% yield, 2 steps) as a colorless oil. Spectral data match those previously reported.[4]

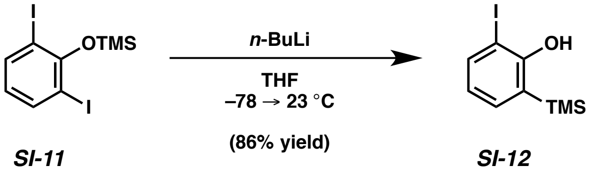


Bromosilyltriflate 4d. Bromosilyltriflate **4d** was prepared following a modified procedure described by Shimizu.[5] To a solution of bromosilylphenol **SI-9** (1.00 g, 4.1 mmol) in CH_2Cl_2 (15 mL) at 0 °C was added Tf_2O (1.02 mL, 6.1 mmol, 1.5 equiv) followed by pyridine (1.64 mL, 20.4 mmol, 5.0 equiv). The reaction was stirred at 0 °C for 5 min and then at 23 °C for 16 h. The reaction was quenched with saturated aqueous $NaHCO_3$ (20 mL). The layers were separated, and the aqueous layer was extracted with hexanes (3 x 20 mL). The combined organic layers were washed with brine (50 mL), and then dried over $MgSO_4$. Evaporation of the solvent under reduced pressure afforded the crude product, which was further purified by flash chromatography (100% Hexanes) to afford bromosilyltriflate **4d** (1.25 g, 81% yield) as a colorless oil. Spectral data match those previously reported.[6]

D. Synthesis of 3-Iodobenzyne Precursor 4e.

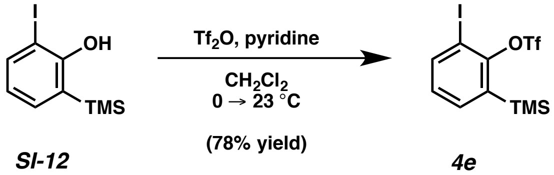


Silylether SI-11. To a solution of 2,6-diiodophenol (**SI-10**)[7] (2.63 g, 7.6 mmol) in CH_2Cl_2 (20 mL) at –78 °C was added Et_3N (5.90 mL, 42.0 mmol, 5.5 equiv) followed by TMSOTf in *n*-pentane (3.80 M, 16.8 mL, 38.0 mmol, 5.0 equiv) over 20 min. The reaction was stirred at –78 °C for 1 h. After warming to 23 °C, the mixture was loaded directly onto a silica gel column and purified by flash chromatography (100% Hexanes) to afford **SI-11** (2.76 g, 87% yield) as a colorless oil. **SI-11**: R_f 0.60 (100% Hexanes); ^{1}H NMR (300 MHz, C_6D_6): δ 7.44 (d, *J* = 7.8, 2H), 5.82 (t, *J* = 7.9, 1H), 0.44 (s, 9H); ^{13}C NMR (125 MHz, C_6D_6): δ 156.5, 140.2, 125.1, 89.8, 2.8; IR (film): 2954, 1542, 1432, 1267, 1253, 1076 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_9H_{13}I_2OSi$, 418.88195; found, 418.88285.



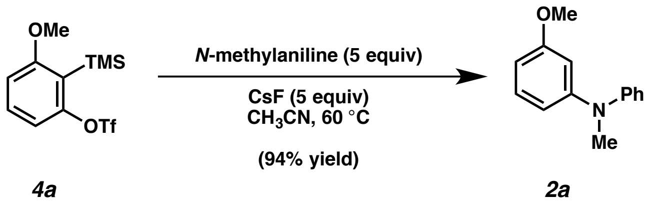
Iodosilylphenol SI-12. Iodosilylphenol **SI-12** was prepared following a modification of the procedure described by Booker.[4] Silylether **SI-11** (3.40 g, 8.1 mmol) was dissolved in THF (85 mL) and cooled to –78 °C. A solution of *n*-BuLi in hexanes (2.54 M, 3.20 mL, 8.1 mmol, 1.0 equiv) was added dropwise over 15 min. After stirring at –78 °C for 2 h, the solution was removed from the bath and allowed to warm to 23 °C. After stirring for an additional 4.5 h, the reaction was quenched with H_2O (20 mL) and the biphasic mixture was further diluted with Et_2O (50 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 50 mL). The combined organic layers were washed with brine (50 mL), and then dried over $MgSO_4$. Evaporation of the solvent under reduced pressure afforded the crude product, which was further purified by flash chromatography (100% Hexanes) to afford **SI-12** (2.05 g, 86% yield) as a colorless oil. **SI-12**: R_f 0.50 (100% Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66 (dd, *J* = 7.9, 1.6, 1H), 7.32 (dd, *J* = 7.2, 1.5, 1H), 6.66 (t, *J* = 7.6, 1H), 5.45 (s, 1H), 0.30 (s, 9H); ^{13}C NMR

(125 MHz, $CDCl_3$): δ 158.7, 139.5, 135.8, 126.5, 122.3, 87.1, -1.1; IR (film): 3491, 2954, 1576, 1416, 1319, 1229 cm^{-1}; HRMS-ESI (*m/z*) $[M - H]^-$ calcd for $C_9H_{12}IOSi$, 290.9665; found, 290.9714.



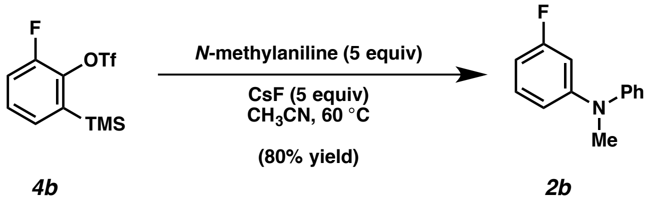
Iodosilyltriflate 4e. Iodosilyltriflate **4e** was prepared following the general procedure described by Shimizu.[5] To a solution of **SI-12** (2.05 g, 7.0 mmol) in CH_2Cl_2 (25 mL) at 0 °C was added Tf_2O (1.80 mL, 10.6 mmol, 1.5 equiv) followed by pyridine (2.83 mL, 35.2 mmol, 5.0 equiv). The reaction was stirred at 0 °C for 5 min and then at 23 °C for 16 h. The reaction was quenched with saturated aqueous $NaHCO_3$ (20 mL). The organic layers were separated, and the aqueous layer was extracted with hexane (3 x 20 mL). The organic layers were combined and washed with brine (50 mL), and then dried over $MgSO_4$. Evaporation of the solvent under reduced pressure afforded the crude product, which was further purified by flash chromatography (100% Hexanes) to afford iodosilyltriflate **4e** (2.33 g, 78% yield) as a colorless oil. **4e**: R_f 0.50 (100% Hexanes); ^1H NMR (300 MHz, $CDCl_3$): δ 7.92 (dd, J = 7.7, 1.7, 1H), 7.54 (dd, J = 7.4, 1.7, 1H), 7.07 (t, J = 7.6, 1H), 0.38 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.2, 142.6, 137.6, 137.0, 129.4, 118.6 (q, J = 319.6, CF_3), 90.0, 0.3; IR (film): 2957, 1574, 1544, 1401, 1384, 1206 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{10}H_{13}F_3IO_3SSi$, 424.9346; found, 424.9342.

E. *N*-Methylaniline Trapping Experiments.

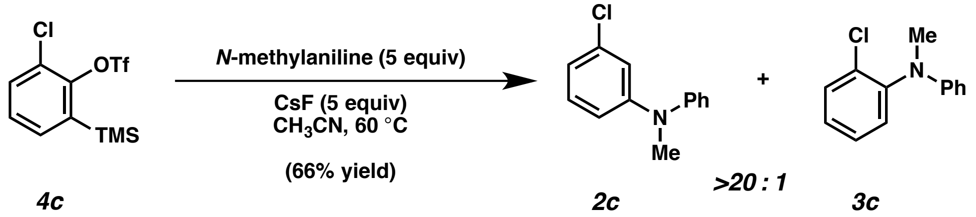


Representative Procedure (Preparation of adduct 2a is used as an example). 2a (Table 1, entry 1). To a stirred solution of silyltriflate **4a** (21.0 mg, 0.064 mmol) and *N*-methylaniline (34.5 μL, 0.320 mmol, 5.0 equiv) in CH_3CN (2.50 mL) was added CsF (51.0 mg, 0.320 mmol, 5.0 equiv). The reaction vessel was sealed and placed in an aluminum heating block maintained at 60 °C for 2 h. After cooling to 23 °C, the heterogeneous reaction mixture was filtered over silica gel (EtOAc eluent). Evaporation under reduced pressure afforded the crude product **2a** and the yield was determined by ^{1}H NMR analysis using hexamethylbenzene as an external standard (94% yield, average of three experiments). An analytical sample of **2a** was isolated as a colorless oil by preparative thin layer chromatography (95:5 Hexanes:EtOAc). Spectral data match those previously reported.[8]

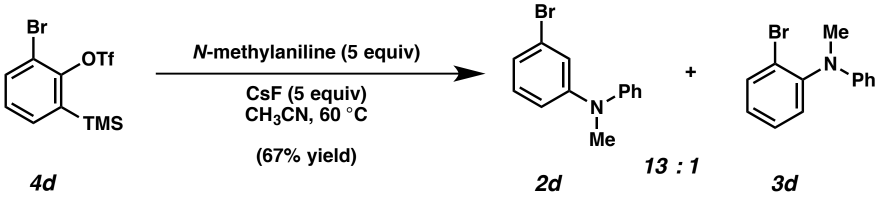
Any modifications of the conditions shown in this representative procedure are specified in the following schemes, which depict all of the results shown in Table 1.



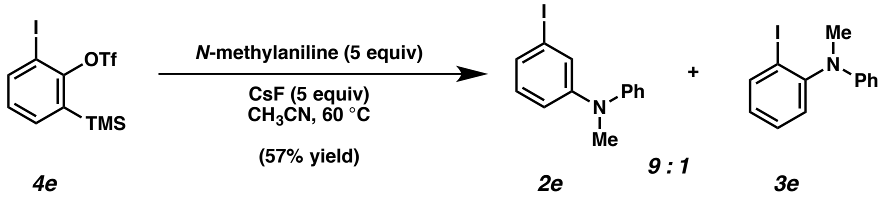
2b (Table 1, entry 2). The yield was determined by ^{1}H NMR analysis using hexamethylbenzene as an external standard (80% yield, average of three experiments). An analytical sample of **2b** was isolated as a colorless oil by preparative thin layer chromatography (95:5 Hexanes:EtOAc). **2b**: R_f 0.62 (95:5 Hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36–7.32 (m, 2H), 7.17–7.12 (m, 3H), 7.10 (tt, *J* = 7.3, 1.2, 1H), 6.65 (ddd, *J* = 8.4, 2.4, 0.9, 1H), 6.58 (dt, *J* = 12.1, 2.4, 1H), 6.53 (tdd, *J* = 8.3, 2.5, 0.8, 1H), 3.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.8 (d, *J* = 245.8), 150.9 (d, *J* = 10.4), 148.4, 130.1 (d, *J* = 10.0), 129.7, 123.9, 123.8, 112.9 (d, *J* = 2.6), 106.1 (d, *J* = 21.4), 104.3 (d, *J* = 24.7), 40.4; IR (film): 2917, 1616, 1590, 1492, 1348, 1259 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{13}H_{13}FN$, 202.10265; found, 202.10178.



2c and 3c (Table 1, entry 3). The yield and product ratio were determined by ^{1}H NMR analysis using hexamethylbenzene as an external standard (>20:1 ratio of **2c**:**3c**, 66% yield, average of three experiments). Analytical samples of **2c** and **3c**, both isolated as colorless oils, were obtained by preparative thin layer chromatography (95:5 Hexanes:EtOAc). **2c**: R$_f$ 0.50 (95:5 Hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36–7.32 (m, 2H), 7.15–7.07 (m, 4H), 6.89 (t, *J* = 2.1, 1H), 6.83 (ddd, *J* = 7.9, 2.0, 0.9, 1H), 6.78 (ddd, *J* = 8.4, 2.4, 0.9, 1H), 3.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.4, 148.4, 134.9, 130.1, 129.7, 123.6, 123.5, 119.6, 117.6, 115.9, 40.4; IR (film): 3063, 2881, 2814, 1583, 1561, 1494 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{13}H_{13}ClN$, 218.07310; found, 218.07204. Spectral data for **3c** match those previously reported.[9]

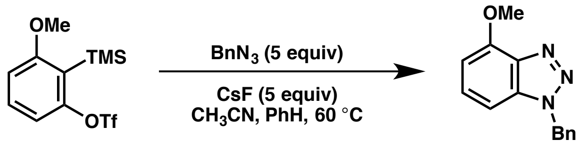


2d and 3d (Table 1, entry 4). The yield and product ratio were determined by ^{1}H NMR analysis using hexamethylbenzene as an external standard (13:1 ratio of **2d**:**3d**, 67% yield, average of three experiments). Analytical samples of **2d** and **3d**, both isolated as colorless oils, were obtained by preparative thin layer chromatography (95:5 Hexanes:EtOAc). **2d**: R$_f$ 0.52 (95:5 Hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36–7.32 (m, 2H), 7.13–7.04 (m, 5H), 6.98 (br d, *J* = 7.8, 1H), 6.82 (dd, *J* = 8.3, 2.3, 1H), 3.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.5, 148.3, 130.4, 129.7, 123.6, 123.4, 123.1, 122.6, 120.5, 116.4, 40.4; IR (film): 3062, 2880, 2813, 1582, 1560, 1495 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{13}H_{13}BrN$, 262.02259; found, 262.02160. Spectral data for **3d** match those previously reported.[10]



2e and 3e (Table 1, entry 5). The yield and product ratio were determined by ^{1}H NMR analysis using hexamethylbenzene as an external standard (9:1 ratio of **2e**:**3e**, 57% yield). Analytical samples of **2e** and **3e**, both isolated as colorless oils, were obtained by preparative thin layer chromatography (95.5 Hexanes:EtOAc). **2e**: R_f 0.55 (95:5 Hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35–7.31 (m, 2H), 7.26 (app. t, *J* = 2.0, 1H), 7.20 (ddd, *J* = 7.6, 1.6, 1.1, 1H), 7.11–7.06 (m, 3H), 6.93 (dd, *J* = 7.6, 7.6, 1H), 6.87 (ddd, *J* = 8.3, 2.3, 1.0, 1H), 3.29 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.4, 148.3, 130.5, 129.7, 128.9, 126.8, 123.4, 123.0, 117.5, 95.1, 40.4; IR (film): 3059, 2877, 2812, 1577, 1555, 1476 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{13}H_{13}IN$, 310.00872; found, 310.01013. Spectral data for **3e** match those previously reported.[11]

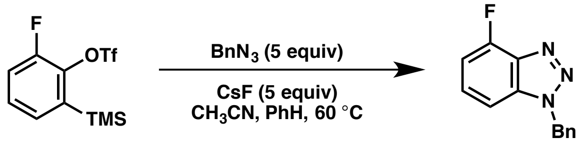
F. Benzylazide Trapping Experiments.



4a *5a*

Representative Procedure (Preparation of adduct 5a is used as an example). 5a (Table 2, entry 1). To a stirred solution of silyltriflate **4a** (19.6 mg, 0.060 mmol) in CH_3CN (2.50 mL) was added a solution of benzylazide[12] in benzene (0.80 M, 0.38 mL, 0.300 mmol, 5.0 equiv) followed by CsF (48.0 mg, 0.300 mmol, 5.0 equiv). The reaction vessel was sealed and placed in an aluminum heating block maintained at 60 °C for 2 h. After cooling to 23 °C, the reaction mixture was filtered over silica gel (EtOAc eluent). Evaporation under reduced pressure afforded the crude product **5a** and the yield was determined by ^{1}H NMR analysis using hexamethylbenzene as an external standard (94% yield, average of three experiments). An analytical sample of **5a** was isolated as a colorless oil by preparative thin layer chromatography (9:1 Hexanes:EtOAc). Spectral data match those previously reported.[13]

Any modifications of the conditions shown in this representative procedure are specified in the following schemes, which depict all of the results shown in Table 2.

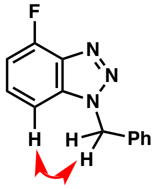


4b *5b*

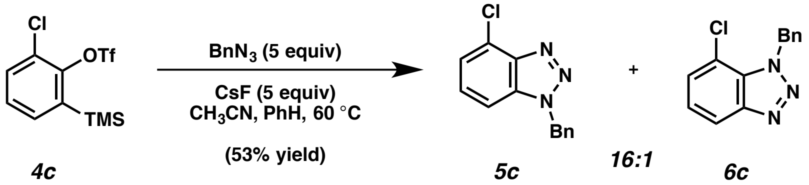
5b (Table 2, entry 2). The yield was determined by ^{1}H NMR analysis using hexamethylbenzene as an external standard (68% yield, average of three experiments). An analytical sample of **5b** was isolated as amorphous solids by preparative thin layer chromatography (9:1 Hexanes:EtOAc). **5b**: R_f 0.23 (9:1 Hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37–7.31 (m, 4H), 7.29–7.26 (m, 2H), 7.13 (dd, *J* = 8.4, 0.5, 1H), 7.00 (ddd, *J* = 10.1, 7.8, 0.5, 1H), 5.85 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.6 (d, *J* = 259.5), 136.8 (d, *J* = 19.0), 135.8 (d, *J* = 6.5), 134.4. 129.2, 128.8, 128.4 (d, *J* = 6.9), 127.7, 108.7 (d, *J* = 17.2), 105.9 (d, *J* = 5.0), 52.7;

IR (film): 3088, 3033, 1632, 1594, 1509, 1495 cm^{-1}; HRMS-ESI (*m/z*) [M + H]$^+$ calcd for $C_{13}H_{11}FN_3$, 228.09315; found, 228.09291.

The structure of **5b** was confirmed by a 2D-NOESY experiment, as the following interaction was observed:

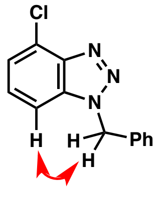


5b

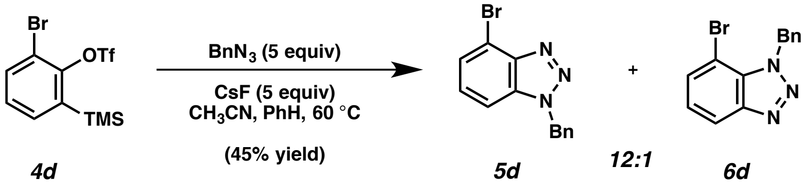


5c and 6c (Table 2, entry 3). The yield and product ratio were determined by ^{1}H NMR analysis using hexamethylbenzene as an external standard (16:1 ratio of **5c**:**6c**, 53% yield). Analytical samples of **5c** and **6c**, both isolated as amorphous solids, were obtained by preparative thin layer chromatography (7:2:1 Hexanes:EtOAc:Benzene). **5c**: R_f 0.25 (9:1 Hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37–7.29 (m, 5H), 7.28–7.23 (m, 3H), 5.85 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.2, 134.4, 134.2, 129.2, 128.8, 128.1, 127.7, 125.7, 124.0, 108.6, 52.8; IR (film): 3068, 1610, 1580, 1561, 1495, 1456 cm^{-1}; HRMS-ESI (*m/z*) [M + H]$^+$ calcd for $C_{13}H_{11}ClN_3$, 244.06360; found, 244.06295. **6c**: R_f 0.45 (7:2:1 Hexanes:EtOAc:Benzenes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (dd, *J* = 8.4, 0.8, 1H), 7.42 (dd, *J* = 7.6, 0.9, 1H), 7.32–7.24 (m, 6H), 6.15 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.9, 136.2, 130.2, 129.0, 128.4, 128.3, 127.4, 124.9, 119.1, 116.1, 53.0; IR (film): 3067, 2918, 1575, 1497, 1456, 1442 cm^{-1}; HRMS-ESI (*m/z*) [M + H]$^+$ calcd for $C_{13}H_{11}ClN_3$, 244.06360; found, 244.06316.

The structure of **5c** was confirmed by a 2D-NOESY experiment, as the following interaction was observed:

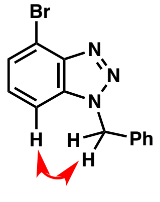


5c

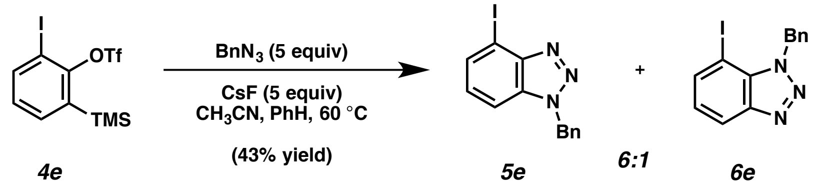


5d and 6d (Table 2, entry 4). The yield and product ratio were determined by ^{1}H NMR analysis using hexamethylbenzene as an external standard (12:1 ratio of **5d**:**6d**, 45% yield). Analytical samples of **5d** and **6d**, both isolated as amorphous solids, were obtained by preparative thin layer chromatography (7:2:1 Hexanes:EtOAc:Benzene). **5d**: R$_f$ 0.25 (9:1 Hexanes:EtOAc); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.51 (dd, *J* = 7.0, 1.2, 1H), 7.35–7.28 (m, 4H), 7.27–7.22 (m, 3H), 5.85 (s, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 145.5, 134.4, 133.8, 129.2, 128.8, 128.4, 127.7, 127.2, 113.7, 109.2, 52.9; IR (film): 3067, 3033, 1608, 1580, 1490, 1455 cm^{-1}; HRMS-ESI (*m/z*) [M + H]$^+$ calcd for $C_{13}H_{11}BrN_3$, 288.01309; found, 288.01228. **6d**: R$_f$ 0.35 (7:2:1 Hexanes:EtOAc:Benzene); ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.04 (dd, *J* = 8.2, 0.8, 1H), 7.62 (dd, *J* = 7.5, 0.8, 1H), 7.33–7.28 (m, 3H), 7.24–7.21 (m, 3H), 6.19 (s, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 147.6, 136.4, 131.9, 131.5, 128.9, 128.3, 127.2, 125.3, 119.7, 102.6, 52.6; IR (film): 3034, 1607, 1569, 1496, 1455, 1436 cm^{-1}; HRMS-ESI (*m/z*) [M + H]$^+$ calcd for $C_{13}H_{11}BrN_3$, 288.01309; found, 288.01250.

The structure of **5d** was confirmed by a 2D-NOESY experiment, as the following interaction was observed:

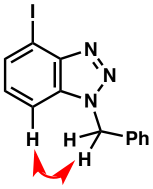


5d



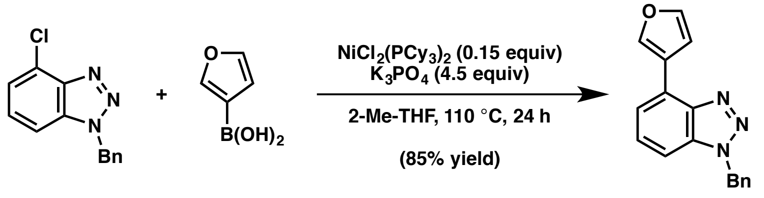
5e and 6e (Table 2, entry 5). The yield and product ratio were determined by ^{1}H NMR analysis using hexamethylbenzene as an external standard (6:1 ratio of **5e**:**6e**, 43% yield). Analytical samples of **5e** and **6e**, both isolated as colorless oils, were obtained by preparative thin layer chromatography (7:2:1 Hexanes:EtOAc:Benzene). **5e**: R$_f$ 0.30 (7:2:1 Hexanes:EtOAc:Benzene); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.76 (dd, J = 7.3, 0.8, 1H), 7.33–7.28 (m, 4H), 7.26–7.23 (m, 2H), 7.13 (dd, J = 8.4, 7.3, 1H), 5.83 (s, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 147.1, 133.4, 132.6, 131.6, 128.2, 127.7, 127.5, 126.7, 109.0, 84.8, 52.0; IR (film): 1573, 1487, 1456, 1433, 1248 cm^{-1}; HRMS-ESI (m/z) [M + H]$^+$ calcd for $C_{13}H_{11}IN_3$, 335.99922; found, 335.99803. **6e**: R$_f$ 0.35 (7:2:1 Hexanes:EtOAc:Benzene); ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.09 (dd, J = 8.4, 0.9, 1H), 7.92 (dd, J = 7.4, 0.8, 1H), 7.33–7.27 (m, 3H), 7.16 (br d, J = 7.4, 2H), 7.09 (dd, J = 8.3, 7.4, 1H), 6.22 (s, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 145.6, 138.2, 135.4, 133.0, 128.0, 127.2, 126.0, 124.8, 119.7, 70.5, 50.8; IR (film): 3031, 2950, 1601, 1561, 1494, 1484, 1455 cm^{-1}; HRMS-ESI (m/z) [M + H]$^+$ calcd for $C_{13}H_{11}IN_3$, 335.99922; found, 335.99835.

The structure of **5e** was confirmed by a 2D-NOESY experiment, as the following interaction was observed:



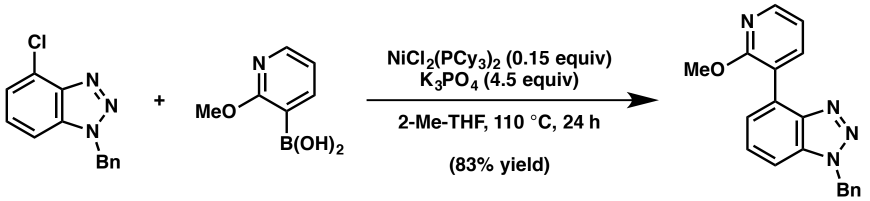
5e

G. Derivatization using Cross-Coupling



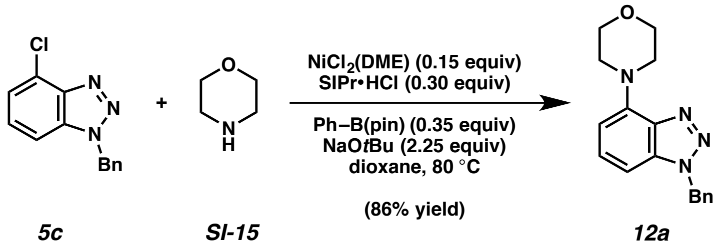
5c *SI-13* *11a*

11a (Figure 10). The cross-coupling was performed using a general procedure reported by our laboratory.[14] To a 4 mL vial was added anhydrous powdered K_3PO_4 (79.0 mg, 0.370 mmol, 4.5 equiv) and a magnetic stir bar. The vial was then flame-dried under reduced pressure and allowed to cool under N_2. $NiCl_2(PCy_3)_2$ (8.5 mg, 0.012 mmol, 0.15 equiv), boronic acid **SI-13** (23.0 mg, 0.205 mmol, 2.5 equiv), and triazole **5c** (18.3 mg, 0.075 mmol, 1.0 equiv) were added. The vial was then evacuated and backfilled with N_2. To the vial, 2-Me-THF (0.6 mL) was added and the vial was sealed with a Teflon-lined screw cap. The mixture was stirred at 23 °C for 1 h, and then at 110 °C for 24 h in a preheated aluminum block. After cooling the reaction vessel to 23 °C, the reaction was diluted with 1 M aqueous HCl (1 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3 x 2 mL). The combined organic layers were then dried over $MgSO_4$, filtered by passage through a plug of silica gel (EtOAc eluent, 12 mL), and concentrated under reduced pressure. The crude residue was purified by preparative thin layer chromatography (3:1 Hexanes:EtOAc) to afford **11a** (17.5 mg, 85% yield) as a colorless oil: R_f 0.48 (3:1 Hexanes:EtOAc); ^1H NMR (500 MHz, $CDCl_3$): δ 8.74 (app. s, 1H), 7.56 (t, J = 1.7, 1H), 7.46 (dd, J = 7.2, 0.9, 1H), 7.40 (dd, J = 8.2, 7.3, 1H), 7.36–7.27 (m, 5H), 7.22 (dd, J = 8.2, 0.9, 1H), 7.05 (dd, J = 1.8, 0.8, 1H), 5.86 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.9, 143.4, 143.3, 134.9, 133.5, 129.1, 128.6, 127.8, 127.7, 125.0, 121.9, 120.3, 108.7, 107.9, 52.4; IR (film): 3034, 1611, 1519, 1456, 1164 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{17}H_{14}N_3O$, 276.11314; found, 276.11239.

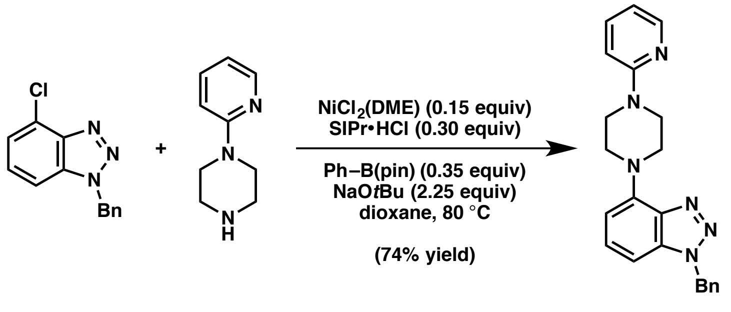


5c *SI-14* *11b*

11b (Figure 10). The cross-coupling was performed using a general procedure reported by our laboratory.[14] To a 4 mL vial was added anhydrous powdered K_3PO_4 (79.2 mg, 0.370 mmol, 4.5 equiv) and a magnetic stir bar. The vial was then flame-dried under reduced pressure and allowed to cool under N_2. $NiCl_2(PCy_3)_2$ (8.4 mg, 0.012 mmol, 0.15 equiv), boronic acid **SI-14** (32.0 mg, 0.205 mmol, 2.5 equiv), and triazole **5c** (17.9 mg, 0.074 mmol, 1 equiv) were added. The vial was then evacuated and backfilled with N_2. To the vial, 2-Me-THF (0.6 mL) was added and the vial was sealed with a Teflon-lined screw cap. The mixture was stirred at 23 °C for 1 h, and then at 110 °C for 24 h in a preheated aluminum block. After cooling the reaction vessel to 23 °C, the mixture was diluted with 1 M aqueous HCl (1 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3 x 2 mL). The combined organic layers were then dried over $MgSO_4$, filtered by passage through a plug of silica gel (EtOAc eluent, 12 mL), and concentrated under reduced pressure. The crude residue was further purified by preparative thin layer chromatography (3:1 Hexanes:EtOAc) to afford **11b** (19.2 mg, 83% yield) as a colorless oil: R_f 0.23 (3:1 Hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 (dd, *J* = 4.9, 2.0, 1H), 8.20 (dd, *J* = 7.3, 2.0, 1H), 7.63 (app. d, *J* = 7.3, 1H), 7.45 (app. t, *J* = 7.9, 1H), 7.36–7.28 (m, 6H), 7.08 (dd, *J* = 7.4, 5.0, 1H), 5.88 (s, 2H), 3.98 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.2, 146.7, 145.0, 141.0, 134.9, 133.4, 129.1, 128.9, 128.6, 127.8, 127.3, 125.1, 119.9, 117.1, 109.1, 53.8, 52.5; IR (film): 2949, 1577, 1464, 1396, 1257 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{19}H_{17}N_4O$, 317.13969; found, 317.13870.



12a (Figure 10). The cross-coupling was performed using a general procedure reported by our laboratory.[15] A 4 mL vial containing a magnetic stir bar was flame-dried under reduced pressure and allowed to cool under N_2. The vial was then charged with $NiCl_2$(DME) (2.9 mg, 0.013 mmol, 0.15 equiv), SIPr•HCl (10.7 mg, 0.025 mmol, 0.30 equiv), Ph–B(pin) (5.9 mg, 0.029 mmol, 0.35 equiv), anhydrous powdered NaO*t*Bu (17.7 mg, 0.185 mmol, 2.25 equiv), and triazole **5c** (19.3 mg, 0.079 mmol, 1 equiv). The vial was then evacuated and backfilled with N_2. Subsequently, dioxane (0.45 mL) and morpholine **SI-15** (13 µL, 0.148 mmol, 1.8 equiv) were added successively. The resulting mixture was stirred for 1 min and the vial was then sealed with a Teflon-lined screw cap. The mixture was allowed to stir at 23 °C for 1 h, and then at 80 °C for 16 h in a preheated aluminum block. After cooling the reaction vessel to 23 °C, the mixture was filtered by passage through a plug of silica gel (EtOAc eluent, 12 mL) and concentrated under reduced pressure. The crude residue was purified by preparative thin layer chromatography (3:1 Hexanes:EtOAc) to afford **12a** (20.0 mg, 86% yield) as a white solid: Mp: 112–114 °C; R_f 0.27 (3:1 Hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34–7.22 (m, 6H), 6.82 (dd, *J* = 8.2, 0.5, 1H), 6.51 (d, *J* = 7.6, 1H), 5.79 (s, 2H), 3.98 (app. t, *J* = 4.7, 4H), 3.74 (app. t, *J* = 4.7, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.6, 139.2, 135.1, 134.9, 129.0, 128.7, 128.4, 127.6, 106.2, 100.7, 67.1, 52.2, 49.9; IR (film): 2960, 2853, 1603, 1510, 1239 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{17}H_{19}N_4O$, 295.15534; found, 295.15426.



5c ***SI-16*** ***12b***

12b (Figure 10). The cross-coupling was performed using a general procedure reported by our laboratory.[15] A 4 mL vial containing a magnetic stir bar was flame-dried under reduced pressure and allowed to cool under N_2. The vial was then charged with $NiCl_2$(DME) (2.8 mg, 0.013 mmol, 0.15 equiv), SIPr•HCl (10.7 mg, 0.025 mmol, 0.30 equiv), Ph–B(pin) (6.1 mg, 0.029 mmol, 0.35 equiv), anhydrous powdered NaO*t*Bu (17.5 mg, 0.185 mmol, 2.25 equiv), and triazole **5c** (20.7 mg, 0.084 mmol, 1 equiv). The vial was then evacuated and backfilled with N_2. Subsequently, dioxane (0.45 mL) and piperazine **SI-16** (24.1 mg, 0.148 mmol, 1.8 equiv) were added successively. The resulting mixture was stirred for 1 min and the vial was then sealed with a Teflon-lined screw cap. The mixture was allowed to stir at 23 °C for 1 h, and then at 80 °C for 16 h on a preheated aluminum block. After cooling the reaction vessel to 23 °C, the mixture was filtered by passage through a plug of silica gel (EtOAc eluent, 12 mL), and concentrated under reduced pressure. The crude residue was further purified by preparative thin layer chromatography (3:1 Hexanes:EtOAc) to afford **12b** (22.5 mg, 74% yield) as a white solid: Mp: 118–120 °C; R_f 0.22 (3:1 Hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (ddd, J = 4.9, 2.0, 0.8, 1H), 7.52 (ddd, J = 8.8, 7.2, 2.0, 1H), 7.34–7.23 (m, 6H), 6.82 (d, J = 8.0, 1H), 6.73 (d, J = 8.5, 1H), 6.66 (ddd, J = 5.5, 4.9, 0.6, 1H), 6.56 (d, J = 7.6, 1H), 5.80 (s, 2H), 3.92–3.86 (m, 4H), 3.85–3.79 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.7, 148.2, 143.4, 139.3, 137.7, 135.1, 134.9, 129.0, 128.8, 128.4, 127.6, 113.7, 107.4, 106.6, 100.4, 52.2, 49.3, 45.4 ; IR (film): 3006, 2835, 1592, 1436, 1235 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{22}H_{22}N_6$, 371.19787; found, 371.19664.

Computational Methods.

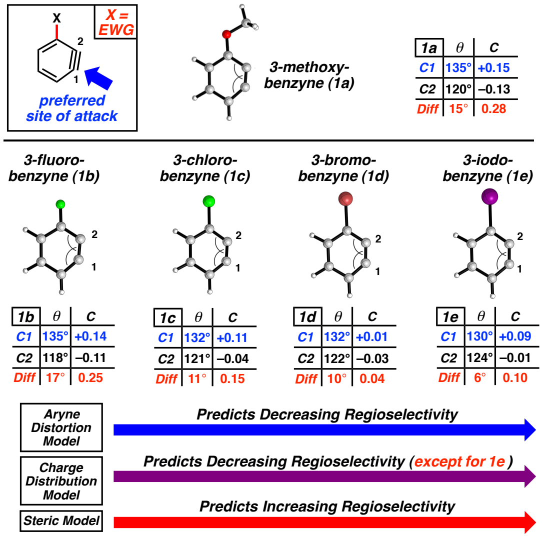
H. Complete citation for reference 15

Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

I. Computational details

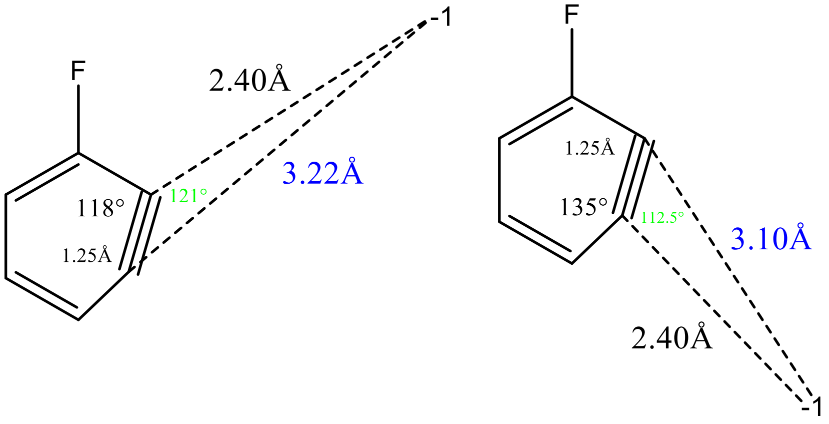
All reported energies in the paper are Gibbs free energies. Low frequencies (less then 100 cm^{-1}) have been corrected using the method discussed in a recent Truhlar paper.[16] All reactants were optimized to their ground state with a tight convergence criteria and a frequency calculation was performed with an ultrafine integration grid to verify no imaginary frequencies. Transition states for methyl azide were optimized to a saddle point with a tight convergence criteria and then a frequency calculation was performed with an ultrafine integration grid to verify only one imaginary frequencies and the correct saddle point was obtained. The transition state for attack of N-methylaniline is a variational transition state. It was obtained by doing a bond scan from 1.8Å out to 3.2Å with a step size of 0.04Å. At each of these points, the structure was optimized tight convergence citeria with only the distance between the nitrogen of *N*-methylaniline and either the *meta* or *ortho* carbon of the aryne fixed. Frequencies were computed at each of these points with an ultrafine integration grid and a free energy reaction coordinate was obtained.

J. Summary of Steric, Charge, and Distortion Models



Geometry-optimized structures of 1a–1e (B3LYP), internal angles (θ), NBO charges (C), and predictions based on the aryne distortion, charge distribution, and steric models. Of note, the general trends predicted by the distortion model correlate to both experimental results and computed transition state energies. The steric model predicts the opposite trend. The charge model incorrectly predicts the regioselectivity for 1e.

K. Point Charge analysis



Attack at C2 Attack at C1

To determine the distance of the point charge to the more distal carbon, the law of cosines must be used. To use the law of cosines, two sides and the angle between them are needed. The two sides used are the 2.4Å and the alkyne bond length. To obtain the angle in between these sides, we bisect the alkyne angle with the point charge, allowing the angle labeled in green to be calculated by subtracting 180 from ½ of the alkyne angle. Once the sides are known and the angle, we use the equation shown below.

Point charge attacking at C2

$$\begin{gathered} c^2 = a^2 + b^2 - 2 * a * b * \cos\gamma \\ c^2 = 1.25^2 + 2.4^2 - 2 * 1.25 * 2.4 * \cos 121 \\ c^2 = 7.3225 - -3.0902 \\ c^2 = 10.4127 \\ c = 3.22 \end{gathered}$$

Point charge attacking at C1

$$\begin{gathered} c^2 = a^2 + b^2 - 2 * a * b * \cos\gamma \\ c^2 = 1.25^2 + 2.4^2 - 2 * 1.25 * 2.4 * \cos 112.5 \\ c^2 = 7.3225 - -2.2961 \\ c^2 = 9.6186 \\ c = 3.10 \end{gathered}$$

Now that we know the distance of the point charge to both carbons of the alkyne, we can use Coulombs law to determine the attractive or repulsive energy felt by the point charge at each attack. The equations are shown below.

Coulomb's Law:

$$E = 332\frac{q_1 * q_2}{\epsilon * r_{q1q2}}$$

Attack at C2:

Interaction between point charge and C2

$$E = 332\frac{-1 * -0.11}{36 * 2.40}$$

$$E = 0.42 \text{ kcal/mol}$$

Interaction between point charge and C1

$$E = 332\frac{-1 * 0.14}{36 * 3.22}$$

$$E = -0.40 \text{ kcal/mol}$$

Attack at C1:

Interaction between point charge and C2

$$E = 332\frac{-1 * -0.11}{36 * 3.10}$$

$$E = 0.33 \text{ kcal/mol}$$

Interaction between point charge and C1

$$E = 332\frac{-1 * 0.14}{36 * 2.40}$$

$$E = -0.54 \text{ kcal/mol}$$

For attack at the C2 position the net energy is 0.0 kcal/mol. The attack at the C1 position is net attractive by 0.2 kcal/mol.

L. M06-2X discussion

Due to no electronic barrier for *N*-methylaniline attacking at the *meta* position for fluorobenzyne (**1b**), a bond scan was performed to get the free energy pathway or variational transition state. When done with B3LYP, a transition state was found in which the energy converged at a transition state as *N*-methylaniline approached fluorobenzyne and then decreased to the products. Frequencies were studied to assure that the only imaginary frequency was nucleophilic attack. This was performed for the *ortho* pathway as well and similar behavior was observed, however with M06-2X the energies did not converge on a transition state, instead they became erratic, as the imaginary frequency that was calculated was no longer that of a nucleophilic attack of *N*-methylaniline to the benzyne. Regioselectivities computed at the B3LYP level of theory have done a good job of estimating not only the trend in decreasing regioselectivities as the angle distortion decreases, but also the magnitude of the selectivity as stated in the paper.

M. Angles of alkynes computed at several levels of theory.

	B3LYP 6-311+g(d,p)		**M06-2X 6-311+g(d,p)**		**MP2 6-311+g(d,p)**	
Reactant Angles	**Ortho**	**Meta**	**Ortho**	**Meta**	**Ortho**	**Meta**
Methoxybenzyne	120°	135°	119°	136°	123°	131°
Fluorobenzyne	118°	135°	117°	136°	122°	130°
Chlorobenzyne	121°	132°	121°	133°	125°	128°
Bromobenzyne	122°	132°	121°	133°	126°	127°
Iodobenzyne	124°	130°	124°	131°	127°	127°
TMSbenzyne	134°	122°	134°	122°	130°	125°

B3LYP and M06-2X agree well with each other and follow the trend of F- and OMe-substituents having the greatest angle distortions, thus the greatest regioselectivities, and as we move down the halogens, that selectivity is eroded. The calculations at MP2 also have the correct trend with F- and OMe- displaying the greatest distortion of the alkyne angles, but moving down the halogens shows little to no distortion from benzyne but experimental there is selectivity. We previously have seen similar subtle variations in distortion using MP2.[17] It appears that B3LYP does a good job of getting angle distortion correct and should be sufficient when performing calculations on reactants to predict selectivities.

N. Cartesian coordinates for all reactants and transition states found in paper and SI

<u>Reactants reported in paper. B3LYP/6-311+G(d,p)</u>

Benzyne (**7**)

Electronic	H(Enthalpy)	G(Free Energy)
-230.972681596	-230.892389	-230.925154

6,4.209646,-0.466587,0.000505
6,5.614767,-0.466693,0.000703
6,6.371317,0.724086,-0.000478
6,5.534692,1.824756,-0.001792
6,4.290076,1.824845,-0.001959
6,3.453279,0.724308,-0.000891
1,3.683911,-1.416101,0.001460
1,6.140356,-1.416288,0.001804
1,7.453459,0.726395,-0.000330
1,2.371137,0.726787,-0.001042

Methoxybenzyne (**1a**)

Electronic	H(Enthalpy)	G(Free Energy)
-345.535293279	-345.420048	-345.459517

6,-1.996082,-0.200536,0.000413
6,-1.281230,1.022951,-0.000027
6,0.115172,1.083303,-0.000273
6,0.912964,-0.085307,-0.000097
6,0.172941,-1.267821,0.000336
6,-1.073856,-1.213709,0.000528
1,-3.073774,-0.265305,0.000608
1,-1.846827,1.949596,-0.000178
1,0.617507,2.043945,-0.000609
8,2.256441,0.035946,-0.000350
6,3.002607,-1.181015,-0.000147
1,4.051630,-0.890955,-0.000383
1,2.777401,-1.772017,0.892502
1,2.777128,-1.772482,-0.892419

Fluorobenzyne (**1b**)

Electronic	H(Enthalpy)	G(Free Energy)
-330.241810632	-330.168665	-330.203474

6,-0.173951,1.093694,-0.000024
6,1.226277,1.023958,0.000035
6,1.921163,-0.207252,0.000068
6,0.990720,-1.212399,0.000030
6,-0.256278,-1.266233,-0.000021
6,-0.950824,-0.074162,-0.000054
1,-0.674560,2.054823,-0.000046
1,1.801859,1.943834,0.000056
1,2.998127,-0.285633,0.000113
9,-2.292725,0.018157,-0.000112

Chlorobenzyne (**1c**)

Electronic	H(Enthalpy)	G(Free Energy)
-690.5946925	-690.522622	-690.558805

6,0.268537,1.086635,-0.000002
6,1.670034,1.030918,0.000006
6,2.381190,-0.190127,0.000012
6,1.475214,-1.222226,0.000009
6,0.229870,-1.247257,0.000002
6,-0.513395,-0.085535,-0.000005
1,-0.229646,2.048969,-0.000007

1,2.231623,1.959587,0.000007
1,3.460131,-0.248284,0.000018
17,-2.262215,-0.000273,-0.000015

Bromobenzyne (**1d**)

Electronic	H(Enthalpy)	G(Free Energy)
-243.530200799	-243.458625	-243.49632

6,-3.020543,-0.190038,0.000041
6,-2.309065,1.030641,0.000029
6,-0.906590,1.086472,0.000009
6,-0.130452,-0.087586,0.000002
6,-0.872395,-1.243935,0.000015
6,-2.118066,-1.225852,0.000032
1,-4.099685,-0.246599,0.000056
1,-2.869949,1.959788,0.000034
1,-0.410047,2.049329,0.000000
35,1.815607,0.000682,-0.000024

Iodobenzyne (**1e**)

Electronic	H(Enthalpy)	G(Free Energy)
-241.748528986	-241.677127	-241.71579

6,-3.485998,-0.190124,0.000048
6,-2.774093,1.029646,0.000035
6,-1.371214,1.087404,0.000016
6,-0.585160,-0.084167,0.000008
6,-1.345320,-1.228024,0.000021
6,-2.590531,-1.235387,0.000038
1,-4.565700,-0.242998,0.000063
1,-3.334148,1.959444,0.000041
1,-0.881005,2.053799,0.000007
53,1.542036,-0.000680,-0.000021

N-methyl Aniline

Electronic	H(Enthalpy)	G(Free Energy)
-327.001942843	-326.849025	-326.888634

6,0.006236,0.207955,1.189624
6,-0.045136,-1.178363,1.213727
6,-0.046889,-1.914078,0.025818
6,0.007931,-1.230172,-1.184969
6,0.064774,0.162634,-1.224063
6,0.059954,0.906686,-0.032285
1,-0.001508,0.767065,2.120616
1,-0.085123,-1.690511,2.169105

1,-0.088024,-2.996390,0.047829
1,0.010912,-1.782160,-2.118836
1,0.110235,0.665622,-2.181562
7,0.072337,2.296365,-0.027862
1,0.351029,2.709808,0.847857
6,0.403169,3.070223,-1.209252
1,-0.358894,2.941083,-1.983390
1,0.420761,4.127084,-0.940423
1,1.378749,2.803930,-1.641344

Methyl Azide

Electronic	H(Enthalpy)	G(Free Energy)
-204.15334968	-204.097854	-204.12982

7,-1.792321,0.271304,0.000013
7,-0.717832,-0.096220,0.000002
7,0.389258,-0.628951,-0.000012
6,1.547923,0.281987,-0.000004
1,2.436405,-0.345193,-0.000018
1,1.560882,0.915282,-0.893070
1,1.560891,0.915254,0.893082

Constrained structures used for charge analysis in paper. B3LYP/6-311+G(d,p). Charges in paper are NBO charges

Constrained Fluorobenzyne with F removed

Electronic	H(Enthalpy)	G(Free Energy)
-230.970848726	-230.89058	-230.923338

6,-0.457024,-1.239396,0.000022
6,0.792606,-1.228301,0.000010
6,1.435650,0.020175,-0.000014
6,0.569440,1.125327,-0.000022
6,-0.826019,0.985909,-0.000007
6,-1.438749,-0.283755,0.000017
1,0.999429,2.121492,-0.000040
1,-1.456114,1.869194,-0.000014
1,-2.510390,-0.426932,0.000029
1,2.511213,0.156332,-0.000025

Constrained Benzyne with F added

Electronic	H(Enthalpy)	G(Free Energy)
-330.23953544	-330.166357	-330.201253

6,1.039979,-1.251898,0.000001
6,-0.201059,-1.196791,-0.000001
6,-0.978615,-0.074020,-0.000002
6,-0.197787,1.095962,0.000000
6,1.207325,1.029608,0.000002
6,1.925138,-0.189040,0.000003
1,-0.696722,2.058977,0.000000
1,1.768267,1.958907,0.000004
1,3.005139,-0.230914,0.000005
9,-2.316348,-0.030069,-0.000004

Constrained TMSBenzyne with TMS removed

Electronic	H(Enthalpy)	G(Free Energy)
-230.971655439	-230.891442	-230.924195

6,1.465087,-0.053789,0.000014
6,0.632068,1.088415,0.000017
6,-0.774378,1.011960,0.000003
6,-1.469806,-0.224213,-0.000017
6,-0.526269,-1.214992,-0.000018
6,0.716170,-1.226304,-0.000006
1,2.545302,0.020486,0.000025
1,1.095433,2.070125,0.000032
1,-1.349372,1.932764,0.000007
1,-2.547126,-0.309478,-0.000028

Constrained Benzyne with TMS added

Electronic	H(Enthalpy)	G(Free Energy)
-639.713377767	-639.524363	-639.575867

6,1.226030,-1.202526,-0.000046
6,2.471257,-1.268172,-0.000046
6,3.365570,-0.212309,-0.000008
6,2.684282,1.017699,0.000033
6,1.283452,1.092536,0.000033
6,0.438660,-0.045165,-0.000008
1,4.446163,-0.278129,-0.000008
1,3.263888,1.935431,0.000066
1,0.822035,2.075392,0.000067
14,-1.457559,-0.002579,-0.000008
6,-2.075238,-0.893525,-1.544237
1,-1.709057,-1.923921,-1.575416
1,-3.169106,-0.927218,-1.567602

1,-1.734820,-0.392854,-2.455183
6,-2.075241,-0.893614,1.544169
1,-1.734823,-0.392995,2.455144
1,-3.169109,-0.927307,1.567530
1,-1.709060,-1.924012,1.575289
6,-2.045361,1.791043,0.000043
1,-1.699171,2.332927,-0.885127
1,-3.139183,1.830344,0.000042
1,-1.699175,2.332876,0.885246

Transition state structures found in paper. B3LYP/6-311+G(d,p)

N-methyl anline attacking fluorobenzyne at C1 (**TS1**)

Electronic	H(Enthalpy)	G(Free Energy)
-657.251445278	-657.023771	-657.080412

6,3.519848,1.243958,-0.173949
6,2.259997,1.858036,-0.184875
6,1.072449,1.103653,-0.088828
6,1.402093,-0.220556,0.008372
6,2.467371,-0.909383,0.032602
6,3.617794,-0.147632,-0.064996
1,4.422523,1.838927,-0.247971
1,2.191676,2.937600,-0.267419
1,0.083968,1.539570,-0.093875
9,4.856687,-0.703996,-0.058482
6,-2.550787,-0.419741,1.290825
6,-3.681579,0.390827,1.203394
6,-4.121347,0.876355,-0.025158
6,-3.412305,0.540299,-1.179766
6,-2.281687,-0.263127,-1.104845
6,-1.834368,-0.754516,0.133333
1,-2.234655,-0.788480,2.257759
1,-4.223576,0.638121,2.109441
1,-5.003380,1.502487,-0.085148
1,-3.742005,0.905055,-2.146174
1,-1.733004,-0.513554,-2.007506
7,-0.656231,-1.520102,0.175957
1,-0.445635,-1.953070,-0.713667
6,-0.365782,-2.397969,1.305623
1,0.597519,-2.874464,1.124115
1,-0.274239,-1.814106,2.222296
1,-1.135576,-3.166305,1.446505

N-methyl aniline attacking fluorobenzyne at C2 (**TS2**)

Electronic	H(Enthalpy)	G(Free Energy)

-657.246127866	-657.018044	-657.073

6,-3.063294,0.792539,-0.750406
6,-3.618327,-0.474654,-0.993817
6,-3.032901,-1.641791,-0.482197
6,-1.865169,-1.472191,0.272330
6,-1.396810,-0.298532,0.461704
6,-1.901786,0.890370,0.011236
1,-3.522396,1.693686,-1.140133
1,-4.523277,-0.540927,-1.590689
1,-3.483723,-2.609085,-0.679054
9,-1.345047,2.106485,0.284540
6,2.068647,-1.322841,0.372958
6,3.137854,-1.357272,-0.520448
6,3.641794,-0.182840,-1.073194
6,3.062381,1.039056,-0.729085
6,1.995210,1.086097,0.160010
6,1.497112,-0.095607,0.722277
1,1.678495,-2.245368,0.781846
1,3.574293,-2.313395,-0.786186
1,4.474162,-0.217227,-1.766022
1,3.442031,1.960976,-1.154631
1,1.538085,2.036678,0.413884
7,0.375896,-0.030778,1.593172
1,0.226184,0.911099,1.933387
6,0.234180,-1.046844,2.637839
1,-0.481459,-0.688116,3.377040
1,-0.177780,-1.958366,2.192067
1,1.191117,-1.261058,3.120679

Methyl azide attacking fluorobenzyne at C1 (**TS3**)

Electronic	H(Enthalpy)	G(Free Energy)
-534.397765787	-534.268016	-534.317279

6,-0.486438,1.717841,-0.300423
6,-1.891328,1.740340,-0.191118
6,-2.628672,0.567437,0.021721
6,-1.971567,-0.663438,0.129350
6,-0.594536,-0.700664,0.024570
6,-0.048567,0.427257,-0.159158
1,0.107646,2.602632,-0.478606
1,-2.410967,2.688343,-0.281092
1,-3.709037,0.603180,0.098104
1,4.103600,0.954200,0.516955
6,3.030213,1.075801,0.684130
7,2.252674,0.305217,-0.306030

1,2.769400,2.121204,0.536410
1,2.777959,0.782587,1.707118
7,2.376900,-0.925537,-0.266605
7,2.277142,-2.050484,-0.323451
9,-2.718036,-1.776378,0.328748

Methyl azide attacking fluorobenzyne at C2 (**TS4**)

Electronic	H(Enthalpy)	G(Free Energy)
-534.394007287	-534.264251	-534.313486

6,-1.545496,-1.789211,0.156620
6,-2.677431,-0.951170,0.163485
6,-2.565037,0.442550,0.049564
6,-1.307027,1.041113,-0.079117
6,-0.215079,0.205180,-0.081846
6,-0.397303,-1.043070,0.019301
1,-1.611392,-2.865225,0.239864
1,-3.663351,-1.395048,0.256087
1,-3.449243,1.069291,0.060633
1,4.103596,1.104120,0.309018
6,3.030056,1.192349,0.496101
7,2.274540,0.329767,-0.426127
1,2.718239,2.212241,0.283104
1,2.813686,0.955473,1.541031
7,2.263537,-0.882260,-0.219355
7,1.830977,-1.939421,-0.132420
9,-1.220361,2.388677,-0.180911

N-methyl anline attacking chlorobenzyne at C1 (**TS5**)

Electronic	H(Enthalpy)	G(Free Energy)
-1017.60417472	-1017.377425	-1017.434899

6,2.990952,1.357232,0.689985
6,1.722833,1.590962,1.239045
6,0.564048,1.015370,0.681415
6,0.913001,0.257602,-0.404269
6,2.000081,-0.033429,-0.999146
6,3.132280,0.536476,-0.439240
1,3.865036,1.813288,1.139125
1,1.628510,2.229523,2.111034
1,-0.428484,1.174187,1.079171
17,4.761619,0.272539,-1.095722
6,-2.497350,-1.090313,0.510886
6,-3.647714,-0.783528,1.227067
6,-4.511600,0.218796,0.783355
6,-4.207385,0.905305,-0.389285

6,-3.057877,0.603829,-1.117777
6,-2.187837,-0.399441,-0.671617
1,-1.827463,-1.866961,0.866586
1,-3.870730,-1.331620,2.135538
1,-5.408928,0.456505,1.341869
1,-4.870743,1.683586,-0.749637
1,-2.847363,1.149098,-2.028311
7,-0.982090,-0.700191,-1.338970
1,-0.643816,-1.625555,-1.106021
6,-0.819222,-0.406404,-2.762091
1,-0.914368,0.665338,-2.937025
1,0.191073,-0.697742,-3.049745
1,-1.550231,-0.939409,-3.380450

N-methyl anline attacking chlorobenzyne at C2 (**TS6**)

Electronic	H(Enthalpy)	G(Free Energy)
-1017.60116879	-1017.374177	-1017.430296

6,-3.087750,0.058554,-0.826235
6,-3.363587,-1.314385,-0.906973
6,-2.544773,-2.264038,-0.278003
6,-1.439979,-1.761407,0.416685
6,-1.230979,-0.502170,0.451135
6,-1.968701,0.504443,-0.112111
1,-3.735569,0.781002,-1.308193
1,-4.236038,-1.637295,-1.467358
1,-2.781950,-3.321005,-0.344680
17,-1.625640,2.238919,0.033600
6,2.294010,-1.219655,0.623162
6,3.384767,-1.366890,-0.232278
6,3.836061,-0.297649,-1.001027
6,3.182076,0.932124,-0.913020
6,2.093113,1.090951,-0.064636
6,1.645812,0.016267,0.714735
1,1.946838,-2.064334,1.202733
1,3.879862,-2.329204,-0.296850
1,4.685750,-0.418865,-1.662407
1,3.521212,1.773051,-1.507221
1,1.581016,2.045466,-0.008561
7,0.503792,0.182476,1.540826
1,0.275318,1.160096,1.673838
6,0.407139,-0.602883,2.771879
1,-0.372756,-0.171713,3.399211
1,0.106509,-1.624756,2.519429
1,1.355805,-0.616295,3.315850

Methyl azide attacking chlorobenzyne at C1 (**TS7**)

Electronic	H(Enthalpy)	G(Free Energy)
-894.749878317	-894.62123	-894.67164

6,0.242658,1.972181,-0.240843
6,-1.130516,2.275149,-0.152767
6,-2.098466,1.269886,-0.018199
6,-1.721700,-0.082073,0.031966
6,-0.371914,-0.371096,-0.055228
6,0.415304,0.614055,-0.165939
1,1.005845,2.729143,-0.357517
1,-1.445698,3.312381,-0.196387
1,-3.146737,1.537011,0.041768
1,4.555462,0.206315,0.523635
6,3.535904,0.558308,0.700187
7,2.605283,-0.008333,-0.294672
1,3.511285,1.637392,0.566656
1,3.229738,0.313857,1.721252
7,2.436916,-1.235003,-0.263294
7,2.038916,-2.291945,-0.330900
17,-2.973403,-1.319410,0.193424

Methyl azide attacking chlorobenzyne at C1 (**TS8**)

Electronic	H(Enthalpy)	G(Free Energy)
-894.748005641	-894.619246	-894.66937

6,-1.378167,-2.297297,0.143748
6,-2.522905,-1.479304,0.163746
6,-2.440125,-0.081228,0.070874
6,-1.195270,0.558638,-0.049043
6,-0.131423,-0.306356,-0.058493
6,-0.210345,-1.562525,0.019491
1,-1.443495,-3.375775,0.213041
1,-3.502962,-1.938116,0.249747
1,-3.342833,0.518030,0.090136
1,3.688227,1.595441,0.327352
6,2.646867,1.375388,0.576088
7,2.099844,0.358289,-0.339146
1,2.049313,2.271215,0.426267
1,2.573047,1.059899,1.620528
7,2.507231,-0.802535,-0.224493
7,2.521966,-1.940190,-0.210661
17,-1.087873,2.312613,-0.164426

Methyl azide attacking benzyne

Electronic	H(Enthalpy)	G(Free Energy)

-435.124208036	-434.98737	-435.03418

6,-2.030927,2.636423,0.111951
6,-0.698865,3.076523,0.198693
6,0.383292,2.182075,0.149124
6,0.188472,0.794454,0.009895
6,-1.154279,0.501116,-0.055621
6,-2.167997,1.255373,-0.025398
1,-2.856886,3.338367,0.145866
1,-0.497070,4.138244,0.301731
1,1.396038,2.566134,0.215427
1,-1.609387,-3.686776,0.388813
6,-1.254382,-2.683198,0.637319
7,-1.778352,-1.689750,-0.314459
1,-0.171214,-2.663540,0.537555
1,-1.526188,-2.438907,1.668366
7,-2.996610,-1.460961,-0.285278
7,-3.982401,-0.898904,-0.344571
1,1.013803,0.094959,-0.037530

<u>Reactants using M06-2X/6-311+G(d,p) found in SI</u>

3-TMSbenzyne

Electronic	H(Enthalpy)	G(Free Energy)
-639.503331653	-639.313123	-639.365288

6,-3.358970,-0.212034,-0.000039
6,-2.668578,1.010630,-0.000037
6,-1.265968,1.088730,-0.000021
6,-0.416537,-0.047325,-0.000004
6,-1.252262,-1.147304,-0.000008
6,-2.484328,-1.293264,-0.000023
1,-4.440285,-0.262752,-0.000053
1,-3.240265,1.932585,-0.000049
1,-0.805618,2.072797,-0.000021
14,1.469137,-0.008754,0.000017
6,2.074126,-0.893218,1.538030
1,1.706758,-1.922326,1.561664
1,3.166454,-0.924906,1.568013
1,1.723150,-0.391787,2.442884
6,2.074159,-0.893285,-1.537944
1,1.723191,-0.391902,-2.442827
1,3.166488,-0.924963,-1.567909
1,1.706802,-1.922398,-1.561534

6,2.017199,1.785645,-0.000016
1,1.655855,2.314719,0.885604
1,3.108568,1.847510,-0.000009
1,1.655869,2.314681,-0.885666

Fluorobenzyne

Electronic	H(Enthalpy)	G(Free Energy)
-330.109036805	-330.034948	-330.069662

6,-0.173237,1.089910,-0.000024
6,1.225192,1.020371,0.000035
6,1.920473,-0.204487,0.000070
6,0.984133,-1.203090,0.000027
6,-0.257638,-1.267225,-0.000018
6,-0.948789,-0.073410,-0.000055
1,-0.676352,2.049100,-0.000042
1,1.798607,1.940696,0.000053
1,2.996390,-0.285316,0.000114
9,-2.278970,0.022239,-0.000114

Reactants using MP2/6-311+G(d,p) found in SI

3-TMSbenzyne

Electronic	H(Enthalpy)	G(Free Energy)
-636.711746917	-637.925639	-637.97856

6,-3.380710,-0.219080,-0.000046
6,-2.686957,1.011357,-0.000033
6,-1.275008,1.092958,-0.000016
6,-0.413225,-0.041158,-0.000010
6,-1.219646,-1.187794,-0.000024
6,-2.484284,-1.287920,-0.000040
1,-4.464629,-0.277237,-0.000060
1,-3.264258,1.934017,-0.000036
1,-0.821951,2.083862,-0.000007
14,1.470183,-0.001496,0.000017
6,2.070984,-0.890565,1.539633
1,1.705291,-1.922598,1.558167
1,3.165513,-0.919851,1.580164
1,1.711172,-0.391972,2.445485
6,2.071029,-0.890635,-1.539542
1,1.711252,-0.392076,-2.445427
1,3.165559,-0.919933,-1.580035
1,1.705326,-1.922665,-1.558046

6,2.040968,1.787644,-0.000015
1,1.684916,2.322952,0.886381
1,3.135230,1.840078,-0.000007
1,1.684929,2.322916,-0.886438

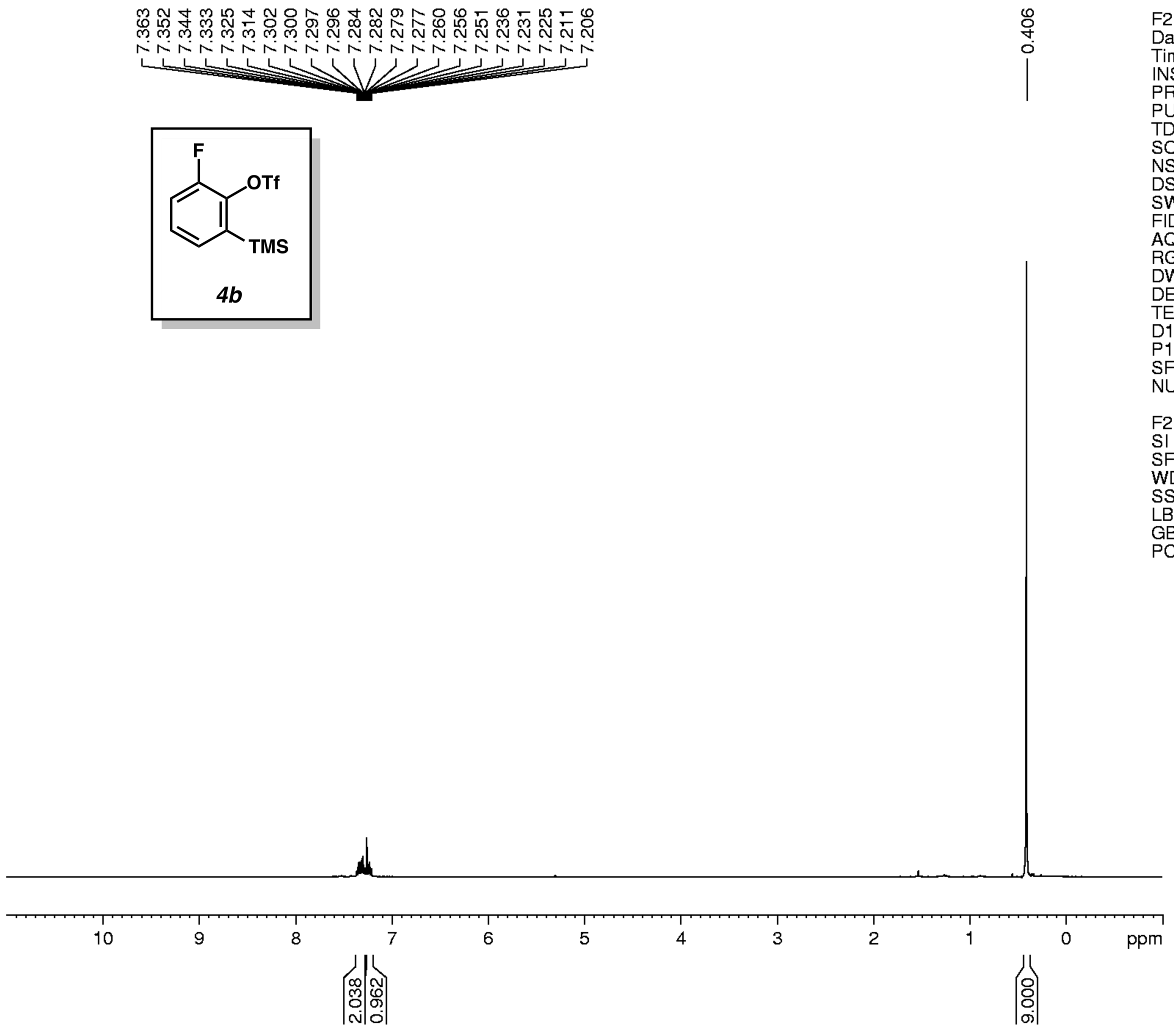
Fluorobenzyne

Electronic	H(Enthalpy)	G(Free Energy)
-328.315603255	-329.277612	-329.312797

6,-0.180930,1.096545,-0.000026
6,1.228263,1.018281,0.000035
6,1.926052,-0.209905,0.000068
6,1.015475,-1.258320,0.000034
6,-0.252262,-1.247658,-0.000021
6,-0.971279,-0.063587,-0.000054
1,-0.678794,2.062259,-0.000049
1,1.801586,1.943043,0.000055
1,3.007559,-0.273762,0.000114
9,-2.305859,0.021892,-0.000111

^{1}H NMR Spectra:

Account No. nkg539
JMM-1-30b



Current Data Parameters

NAME	JMM-1-30b
EXPNO	40
PROCNO	1

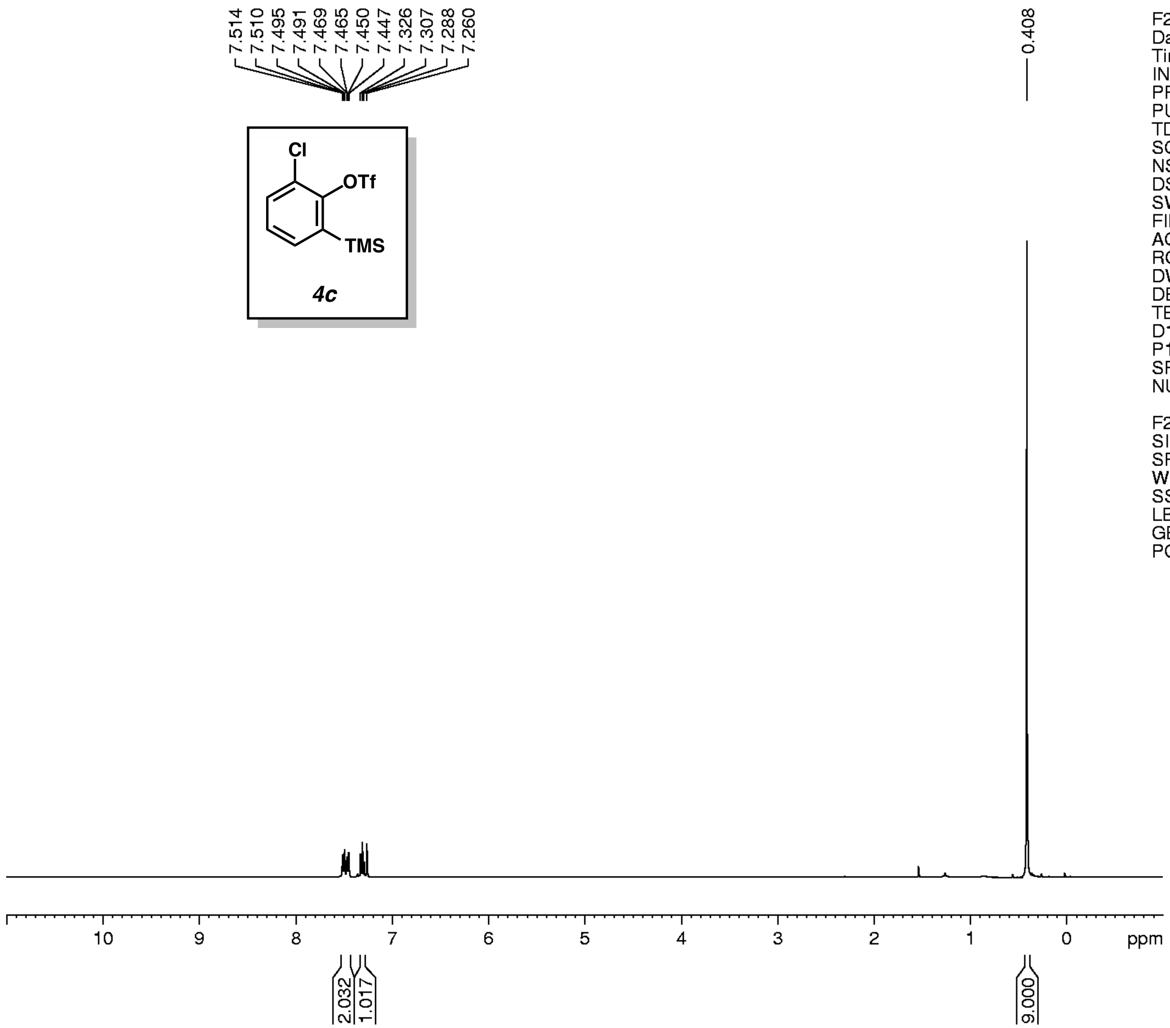
F2 – Acquisition Parameters

Date_	20130108
Time	21.42
INSTRUM	arx400
PROBHD	5 mm QNP 1H
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	32
DS	0
SWH	8064.516 Hz
FIDRES	0.123055 Hz
AQ	4.0632820 sec
RG	1024
DW	62.000 usec
DE	88.57 usec
TE	300.0 K
D1	2.00000000 sec
P1	8.80 usec
SFO1	400.1324008 MHz
NUCLEUS	1H

F2 – Processing parameters

SI	65536
SF	400.1300173 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Account No. nkg539
JMM-1-27h

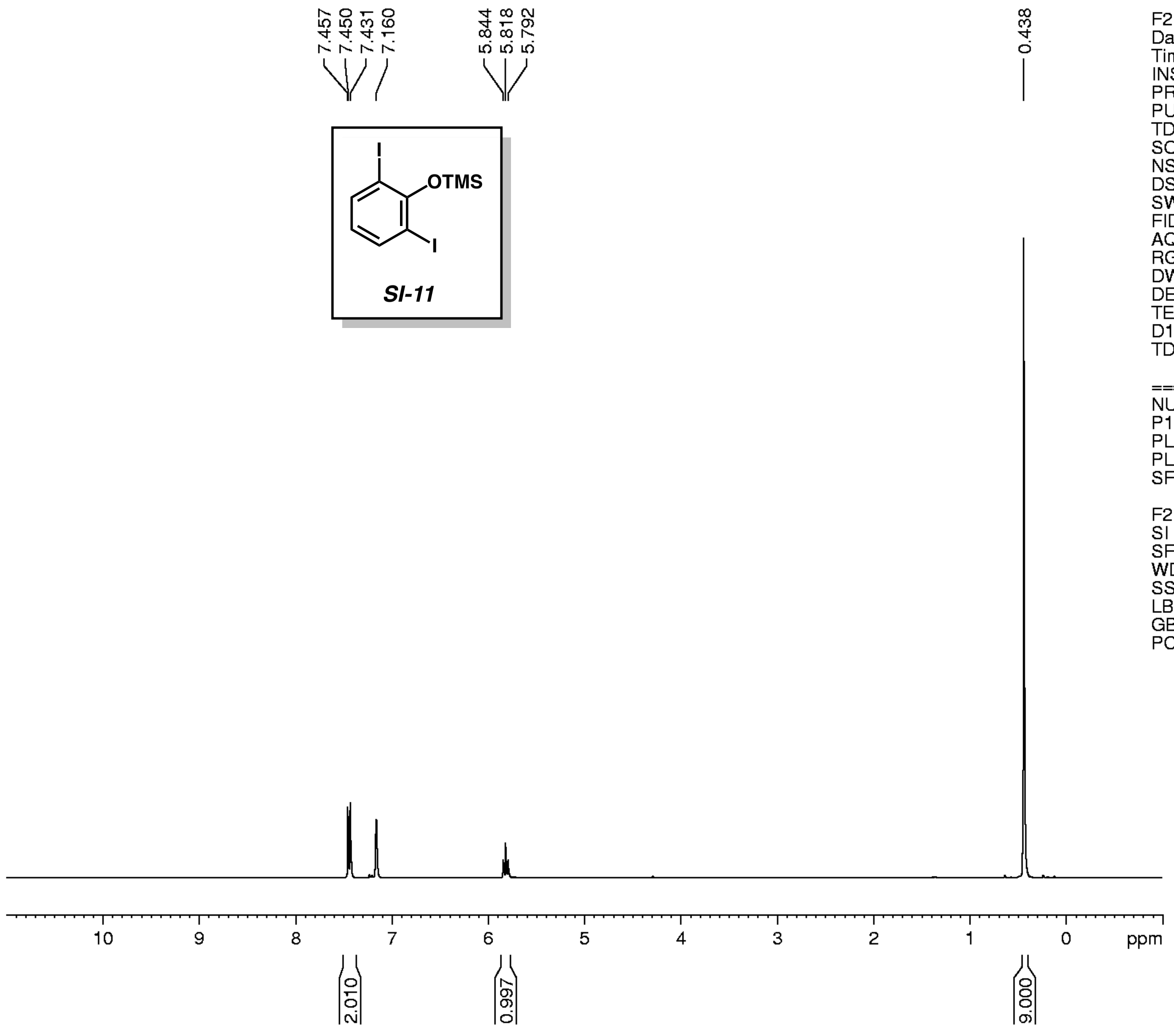


Current Data Parameters
NAME JMM-1-27h
EXPNO 20
PROCNO 1

F2 – Acquisition Parameters
Date_ 20130107
Time 21.38
INSTRUM arx400
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 0
SWH 8064.516 Hz
FIDRES 0.123055 Hz
AQ 4.0632820 sec
RG 1024
DW 62.000 usec
DE 88.57 usec
TE 300.0 K
D1 2.00000000 sec
P1 8.80 usec
SFO1 400.1324008 MHz
NUCLEUS 1H

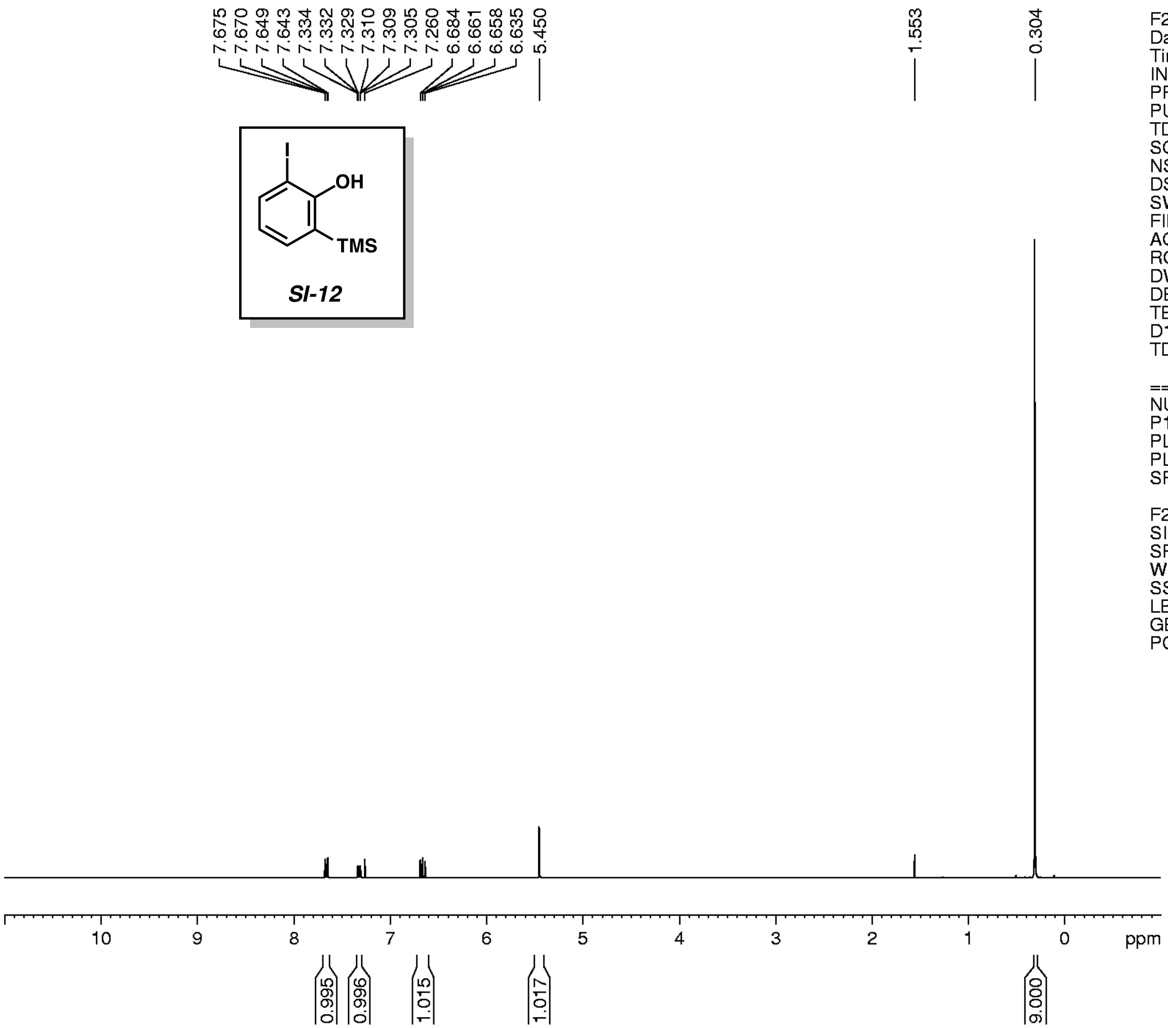
F2 – Processing parameters
SI 65536
SF 400.1300179 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

default proton parameters



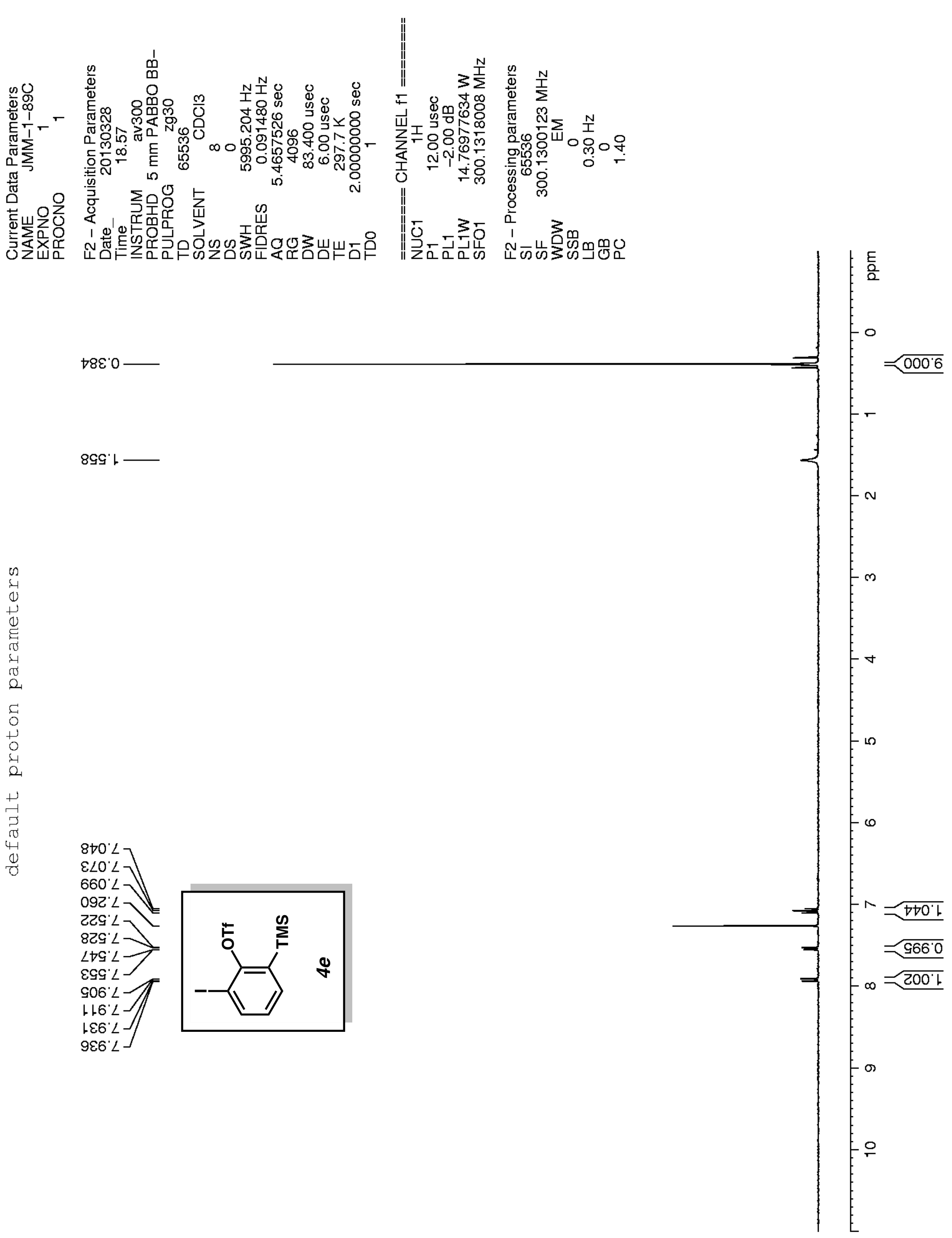
```
Current Data Parameters
NAME          JMM–1–87
EXPNO                1
PROCNO               1

F2 – Acquisition Parameters
Date_          20130325
Time              21.04
INSTRUM           av300
PROBHD   5 mm PABBO BB–
PULPROG            zg30
TD                65536
SOLVENT            C6D6
NS                    8
DS                    0
SWH         5995.204 Hz
FIDRES      0.091480 Hz
AQ        5.4657526 sec
RG                456.1
DW           83.400 usec
DE             6.00 usec
TE              297.5 K
D1       2.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1            12.00 usec
PL1            –2.00 dB
PL1W      14.76977634 W
SFO1    300.1318008 MHz

F2 – Processing parameters
SI                65536
SF      300.1300326 MHz
WDW                  EM
SSB                   0
LB              0.30 Hz
GB                    0
PC                 1.40
```

default proton parameters



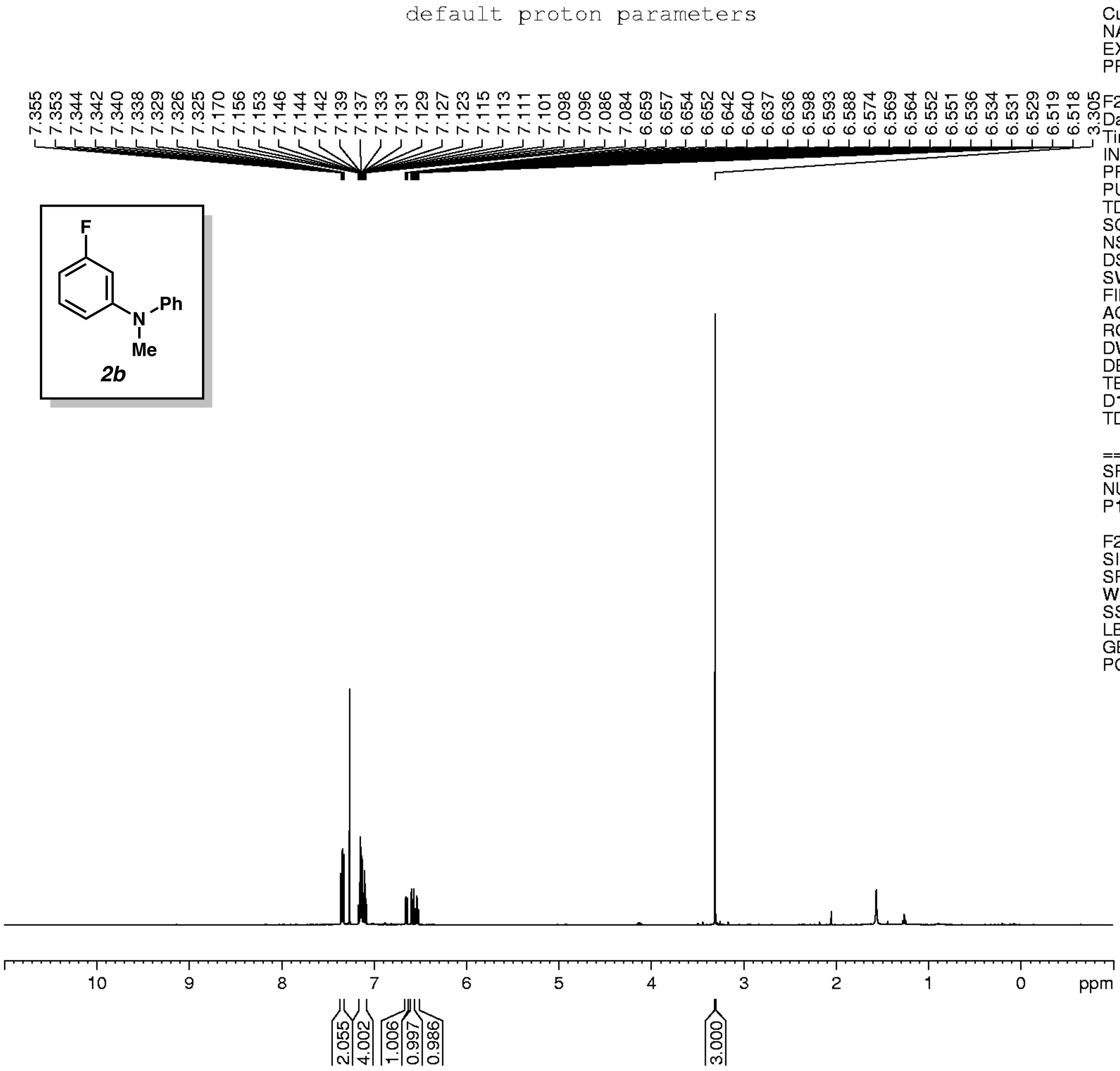
SI-12

```
Current Data Parameters
NAME         JMM-1-88B
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_        20130327
Time            10.06
INSTRUM         av300
PROBHD   5 mm PABBO BB-
PULPROG          zg30
TD              65536
SOLVENT         CDCl3
NS                  8
DS                  0
SWH          5995.204 Hz
FIDRES       0.091480 Hz
AQ          5.4657526 sec
RG              812.7
DW             83.400 usec
DE               6.00 usec
TE              297.5 K
D1         2.00000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1               1H
P1              12.00 usec
PL1             -2.00 dB
PL1W      14.76977634 W
SFO1     300.1318008 MHz

F2 - Processing parameters
SI              65536
SF       300.1300122 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               1.40
```

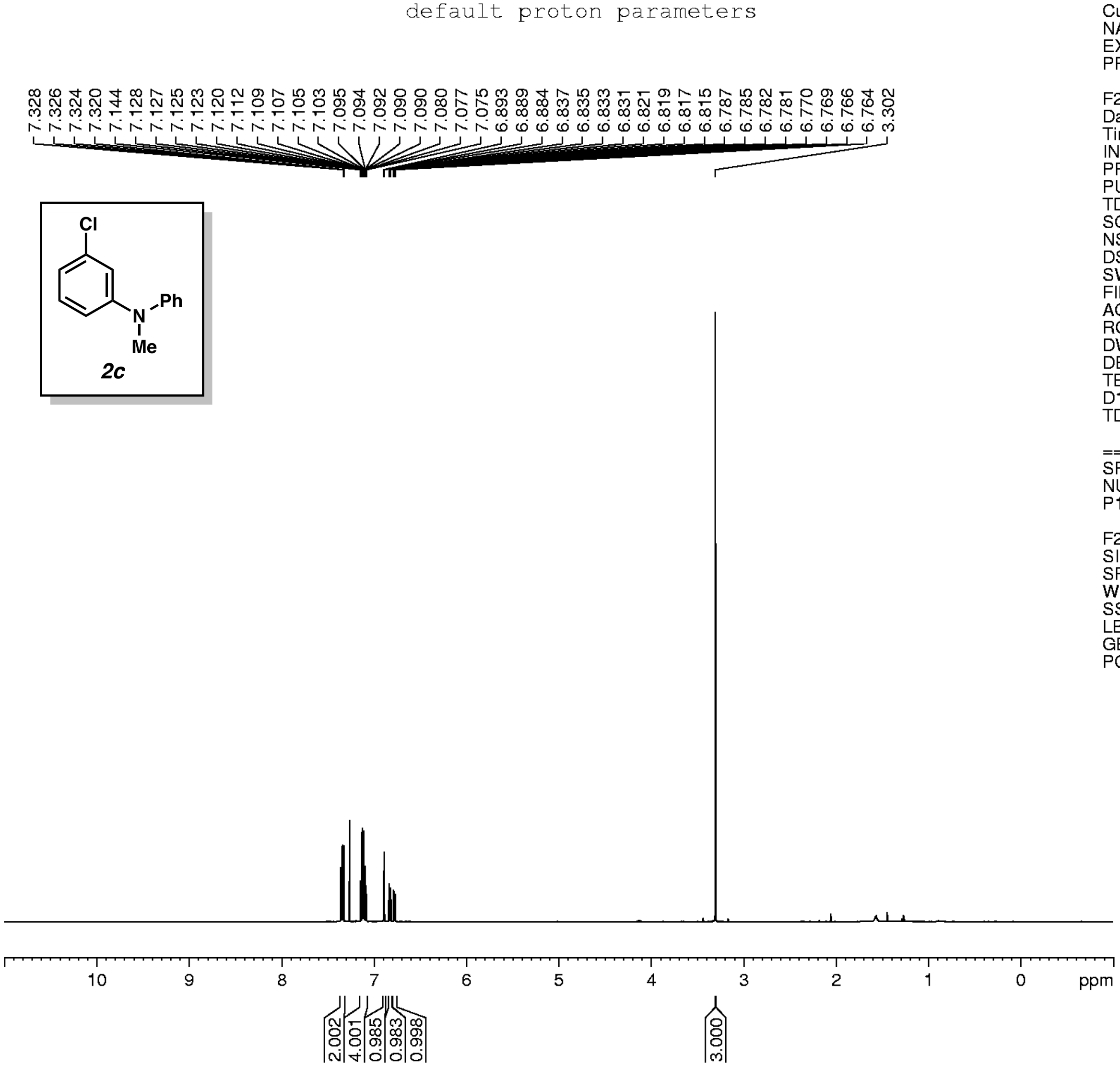


4e

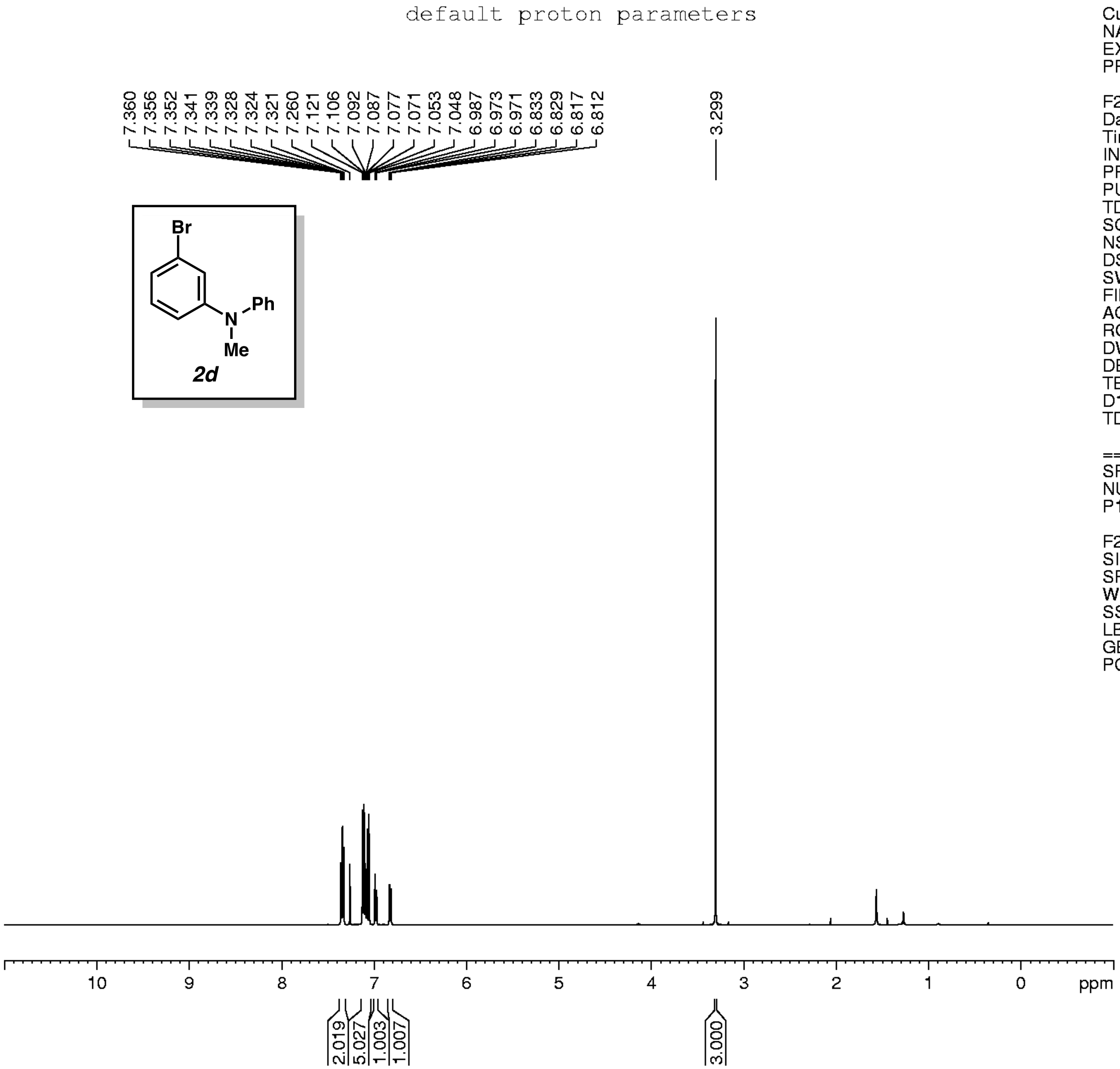
```
Current Data Parameters
NAME       JMM-1-89C
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_       20130328
Time           18.57
INSTRUM        av300
PROBHD   5 mm PABBO BB-
PULPROG         zg30
TD             65536
SOLVENT        CDCl3
NS                 8
DS                 0
SWH         5995.204 Hz
FIDRES      0.091480 Hz
AQ         5.4657526 sec
RG              4096
DW            83.400 usec
DE              6.00 usec
TE             297.7 K
D1        2.00000000 sec
TD0                1

======== CHANNEL f1 ========
NUC1              1H
P1             12.00 usec
PL1            -2.00 dB
PL1W     14.76977634 W
SFO1    300.1318008 MHz

F2 - Processing parameters
SI             65536
SF      300.1300123 MHz
WDW               EM
SSB                0
LB              0.30 Hz
GB                 0
PC              1.40
```



```
Current Data Parameters
NAME          JMM-2-119B
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130812
Time               15.22
INSTRUM            av500
PROBHD   5 mm DCH 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH         10000.000 Hz
FIDRES       0.152588 Hz
AQ         3.2768500 sec
RG                    11
DW            50.000 usec
DE            10.00 usec
TE               298.0 K
D1        2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1      500.1330008 MHz
NUC1                  1H
P1            10.00 usec

F2 - Processing parameters
SI                 65536
SF        500.1300126 MHz
WDW                   EM
SSB                    0
LB               0.00 Hz
GB                     0
PC                  1.00
```

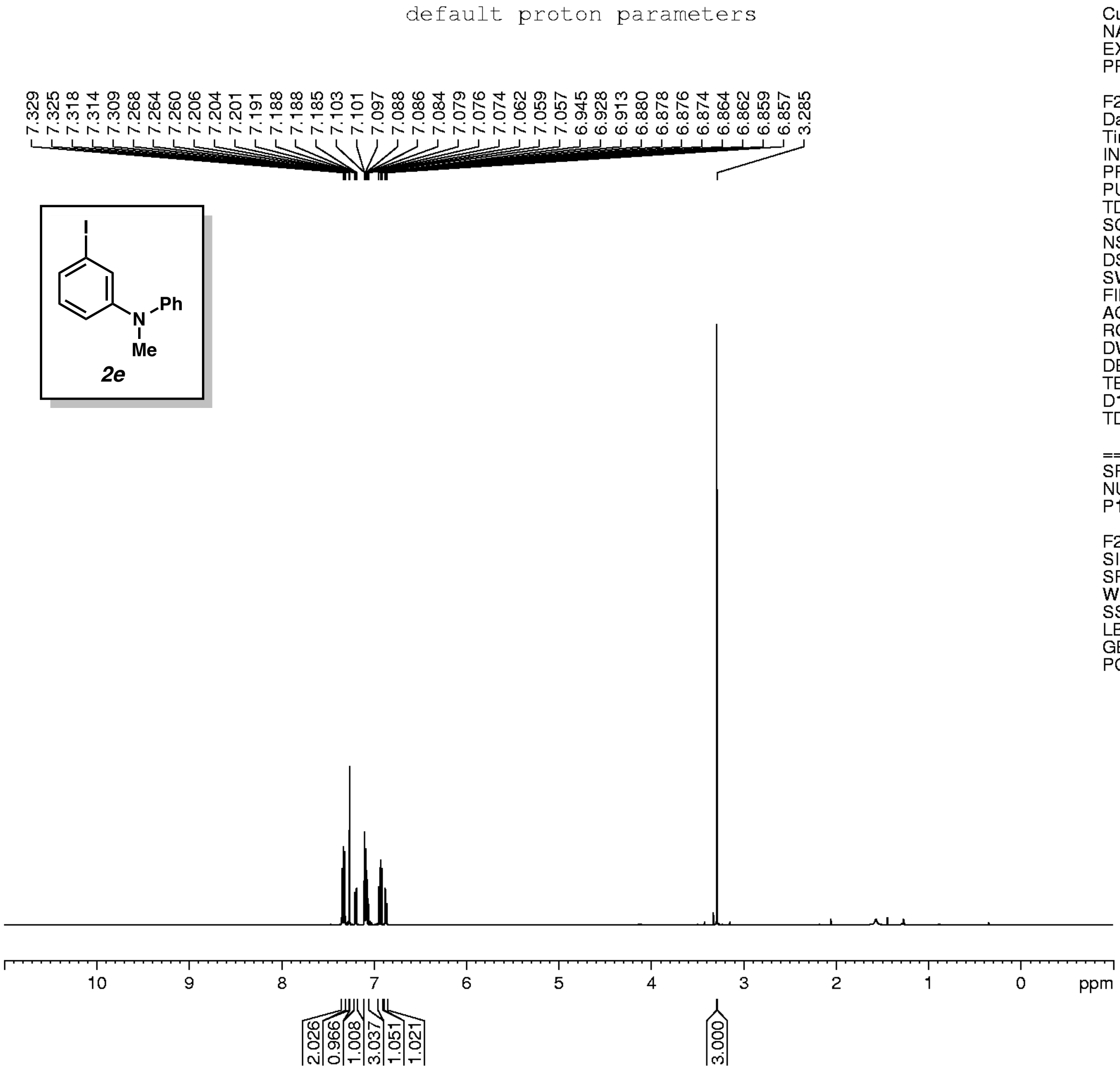


```
Current Data Parameters
NAME        JMM-2-118
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_       20130812
Time           11.39
INSTRUM        av500
PROBHD   5 mm DCH 13C-1
PULPROG         zg30
TD             65536
SOLVENT        CDCl3
NS                 8
DS                 0
SWH       10000.000 Hz
FIDRES     0.152588 Hz
AQ        3.2768500 sec
RG                11
DW           50.000 usec
DE            10.00 usec
TE            298.0 K
D1      2.00000000 sec
TD0                1

======== CHANNEL f1 ========
SFO1     500.1330008 MHz
NUC1              1H
P1            10.00 usec

F2 - Processing parameters
SI             65536
SF       500.1300126 MHz
WDW               EM
SSB                0
LB              0.00 Hz
GB                 0
PC              1.00
```



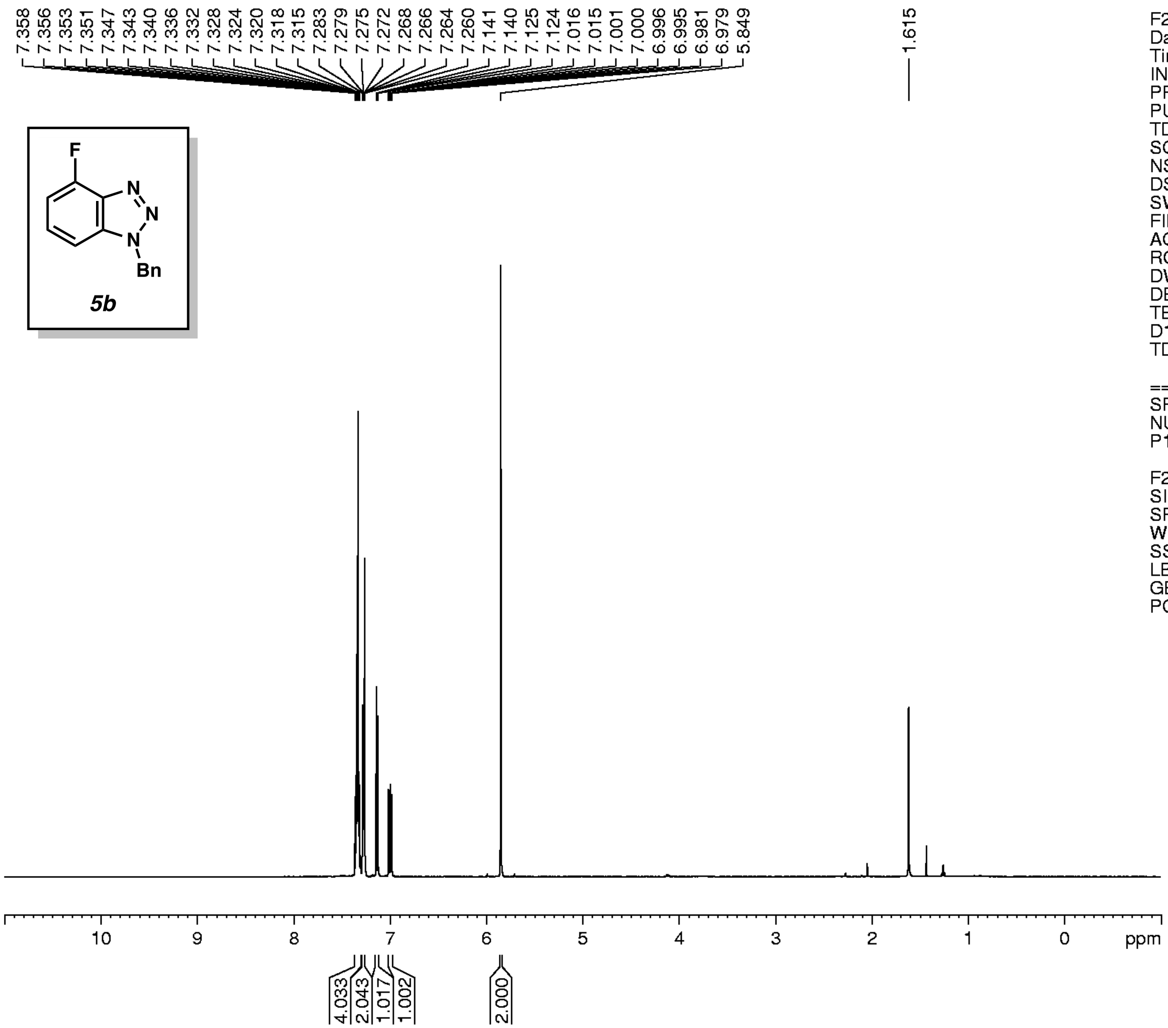
2d

```
Current Data Parameters
NAME         JMM-2-116
EXPNO               1
PROCNO              1

F2 - Acquisition Parameters
Date_        20130812
Time            11.33
INSTRUM         av500
PROBHD   5 mm DCH 13C-1
PULPROG          zg30
TD              65536
SOLVENT         CDCl3
NS                  8
DS                  0
SWH        10000.000 Hz
FIDRES      0.152588 Hz
AQ        3.2768500 sec
RG                 11
DW         50.000 usec
DE          10.00 usec
TE             298.0 K
D1       2.00000000 sec
TD0                 1

======== CHANNEL f1 ========
SFO1    500.1330008 MHz
NUC1                1H
P1          10.00 usec

F2 - Processing parameters
SI              65536
SF      500.1300125 MHz
WDW                EM
SSB                 0
LB            0.30 Hz
GB                  0
PC               1.00
```



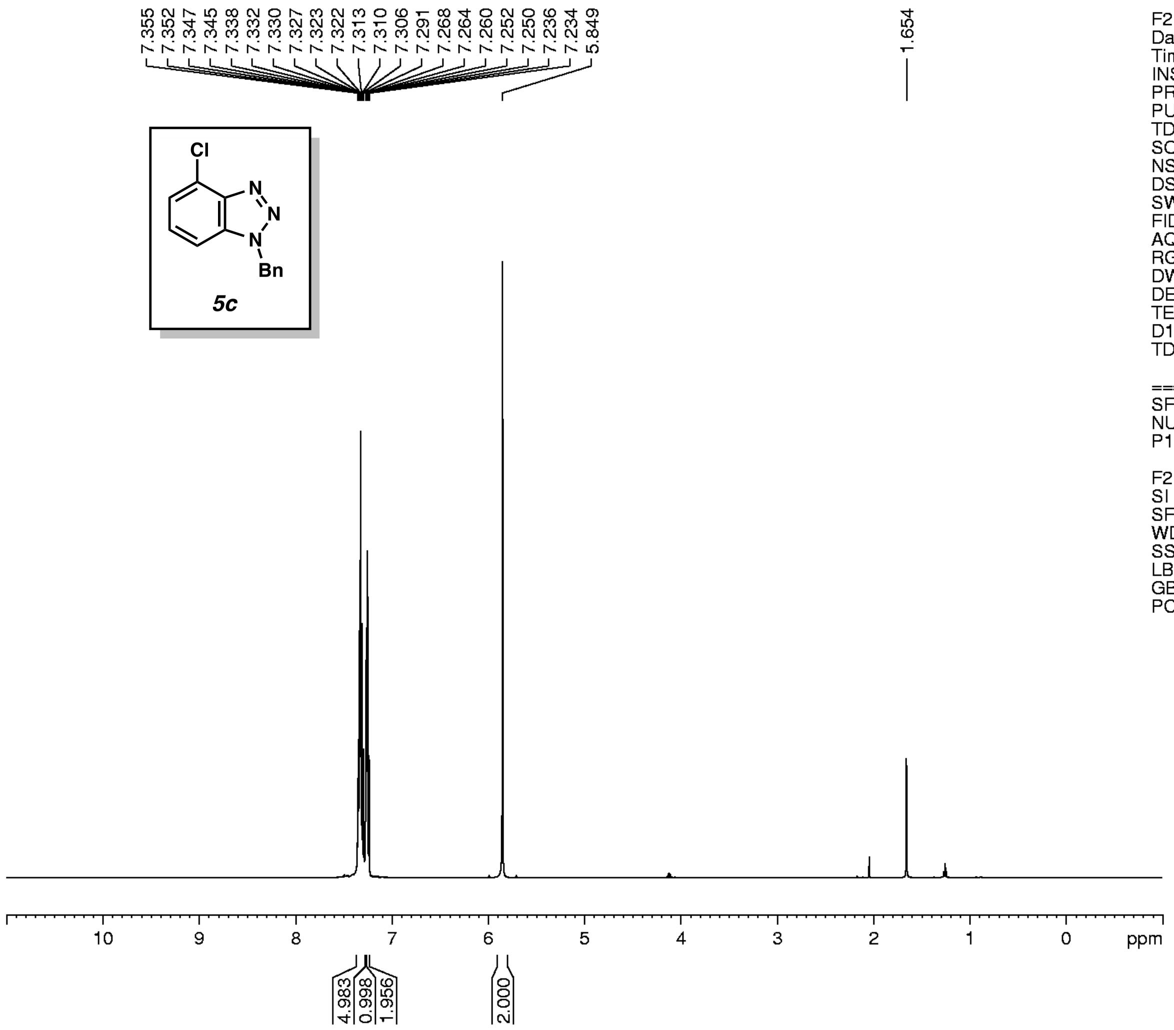
```
Current Data Parameters
NAME        JMM-2-123
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_       20130812
Time           11.57
INSTRUM        av500
PROBHD  5 mm DCH 13C-1
PULPROG         zg30
TD             65536
SOLVENT        CDCl3
NS                 8
DS                 0
SWH      10000.000 Hz
FIDRES    0.152588 Hz
AQ      3.2768500 sec
RG                11
DW        50.000 usec
DE         10.00 usec
TE            298.0 K
D1     2.00000000 sec
TD0                1

======== CHANNEL f1 ========
SFO1    500.1330008 MHz
NUC1              1H
P1         10.00 usec

F2 - Processing parameters
SI             65536
SF      500.1300126 MHz
WDW               EM
SSB                0
LB           0.00 Hz
GB                 0
PC              1.00
```

default proton parameters

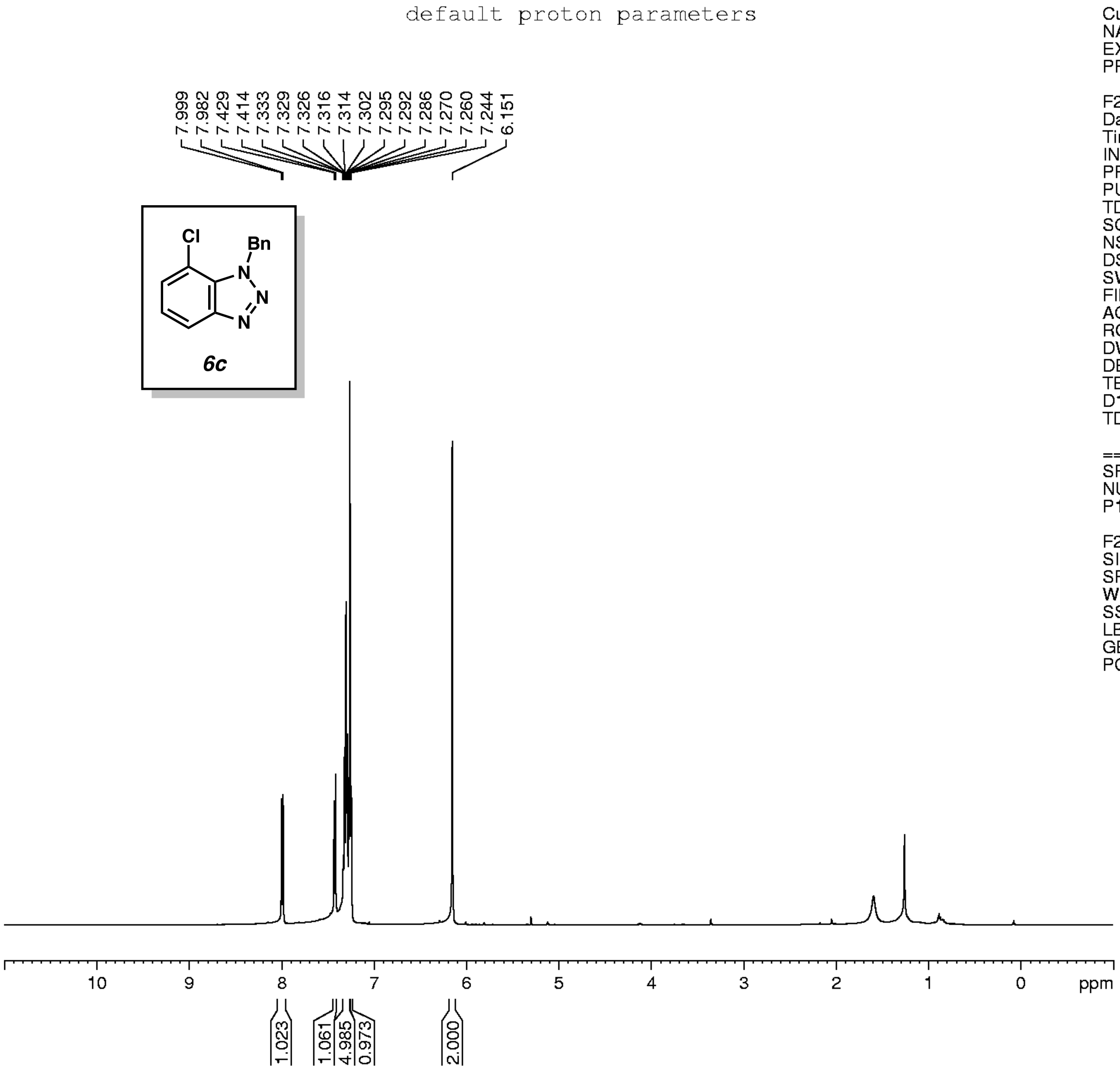


```
Current Data Parameters
NAME       JMM-2-200(1)
EXPNO             1
PROCNO            1

F2 - Acquisition Parameters
Date_        20131024
Time            11.42
INSTRUM         av500
PROBHD   5 mm DCH 13C-1
PULPROG          zg30
TD              65536
SOLVENT          CDCl3
NS                 15
DS                  0
SWH        10000.000 Hz
FIDRES      0.152588 Hz
AQ         3.2768500 sec
RG                 11
DW            50.000 usec
DE            10.00 usec
TE            298.0 K
D1       2.00000000 sec
TD0                 1

======== CHANNEL f1 ========
SFO1     500.1330008 MHz
NUC1              1H
P1            10.00 usec

F2 - Processing parameters
SI              65536
SF       500.1300122 MHz
WDW                EM
SSB                 0
LB            0.00 Hz
GB                  0
PC               1.00
```

default proton parameters



```
Current Data Parameters
NAME     JMM-2-208(1new)
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_          20131108
Time             14.46
INSTRUM          av500
PROBHD   5 mm DCH 13C-1
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                  19
DS                   0
SWH        10000.000 Hz
FIDRES      0.152588 Hz
AQ        3.2768500 sec
RG                  11
DW          50.000 usec
DE           10.00 usec
TE             298.0 K
D1       2.00000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1     500.1330008 MHz
NUC1                1H
P1           10.00 usec

F2 - Processing parameters
SI               65536
SF       500.1300122 MHz
WDW                 EM
SSB                  0
LB             0.30 Hz
GB                   0
PC                1.00
```



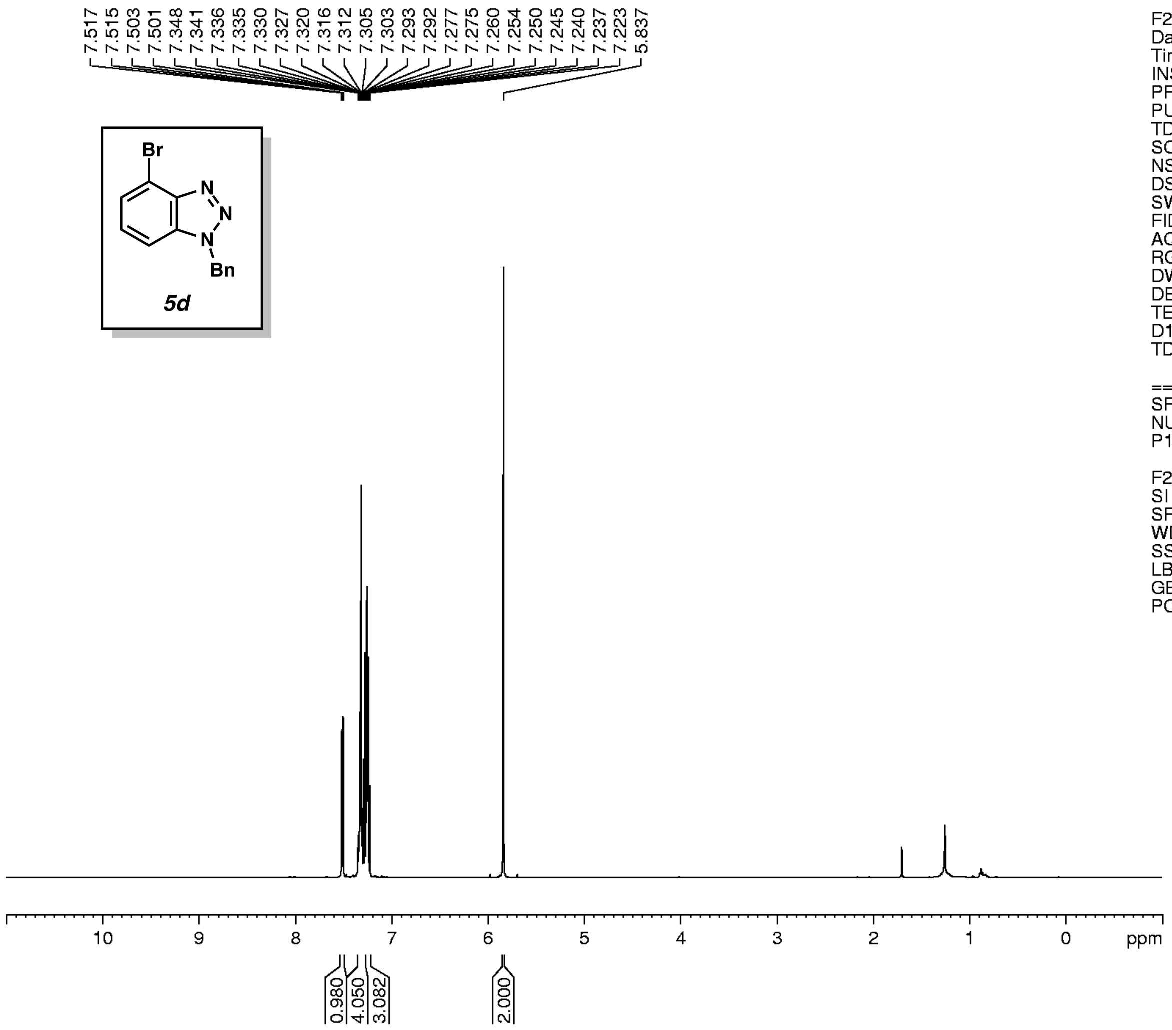
Current Data Parameters
NAME JMM-3-30(b)
EXPNO 1
PROCNO 1

F2 – Acquisition Parameters
Date_ 20140210
Time 9.09
INSTRUM av500
PROBHD 5 mm DCH 13C-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2768500 sec
RG 11
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec

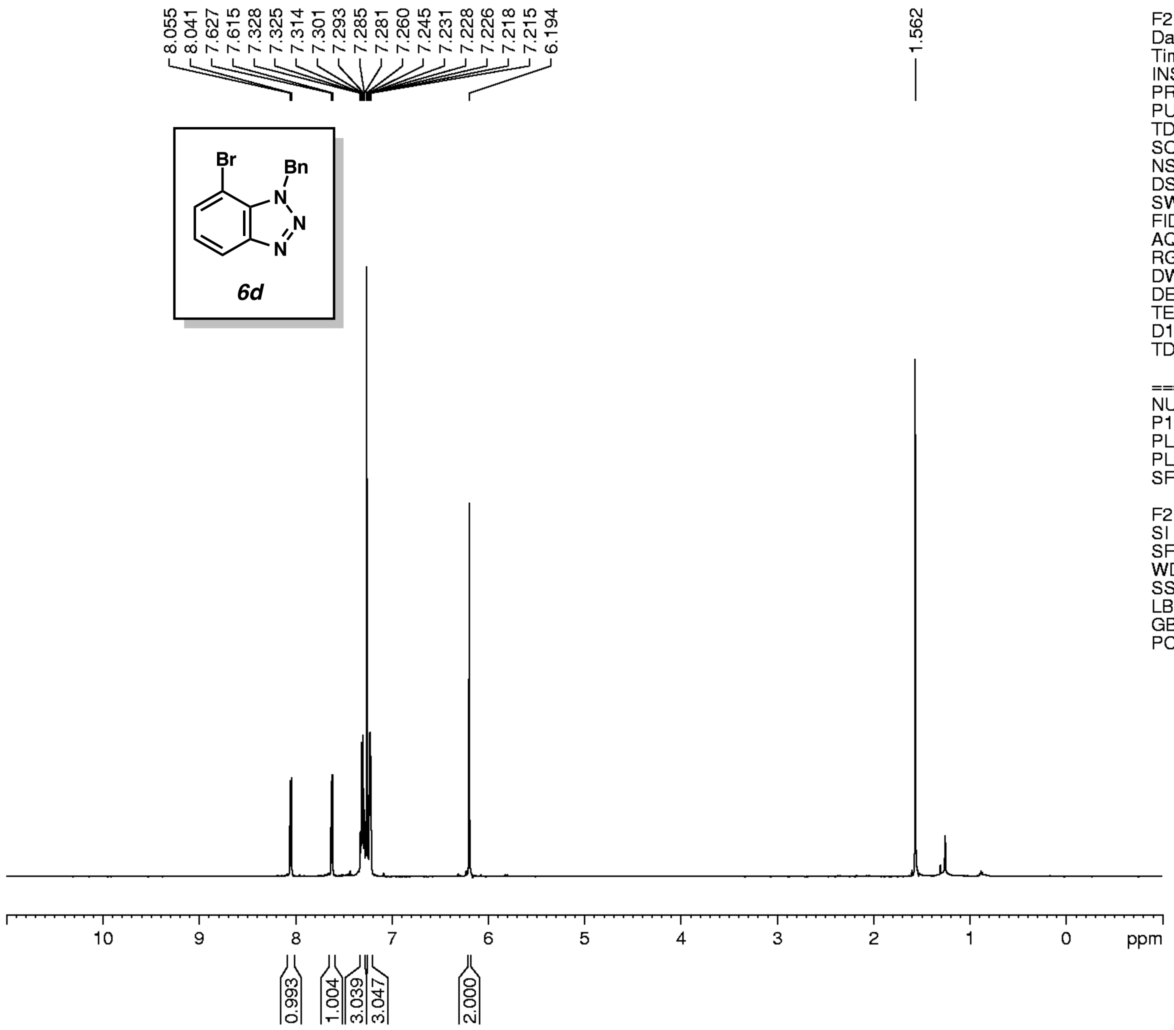
F2 – Processing parameters
SI 65536
SF 500.1300125 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

default proton parameters



```
Current Data Parameters
NAME      JMM-2-215(1)
EXPNO             1
PROCNO            1

F2 - Acquisition Parameters
Date_        20131115
Time             9.25
INSTRUM         av500
PROBHD   5 mm DCH 13C-1
PULPROG          zg30
TD              65536
SOLVENT         CDCl3
NS                 21
DS                  0
SWH        10000.000 Hz
FIDRES       0.152588 Hz
AQ          3.2768500 sec
RG                 11
DW             50.000 usec
DE              10.00 usec
TE              298.0 K
D1         2.00000000 sec
TD0                 1

======== CHANNEL f1 ========
SFO1      500.1330008 MHz
NUC1               1H
P1              10.00 usec

F2 - Processing parameters
SI              65536
SF        500.1300123 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               1.00
```

default carbon parameters



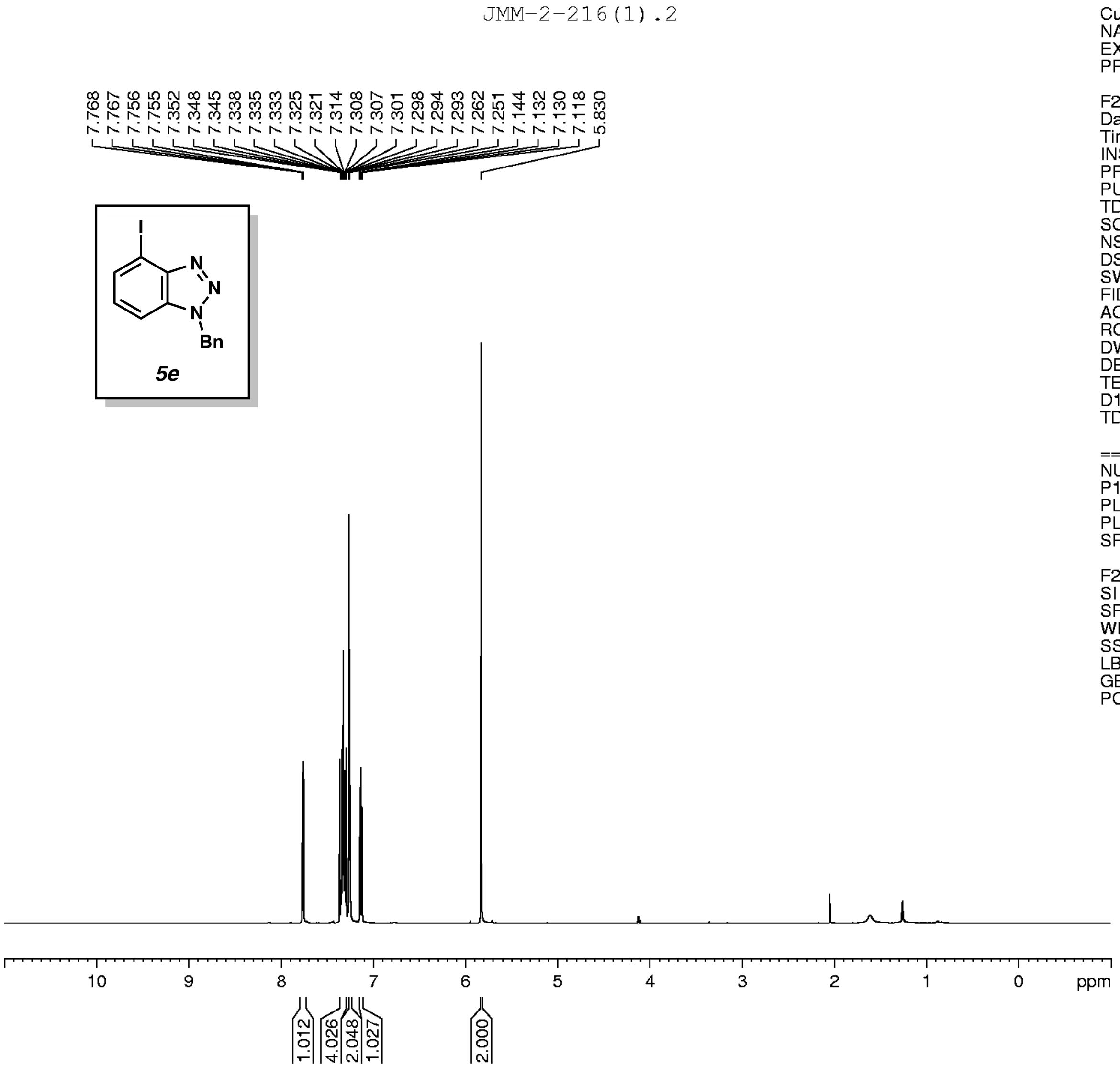
6d

Current Data Parameters
NAME JMM–2–215(2)
EXPNO 1
PROCNO 1

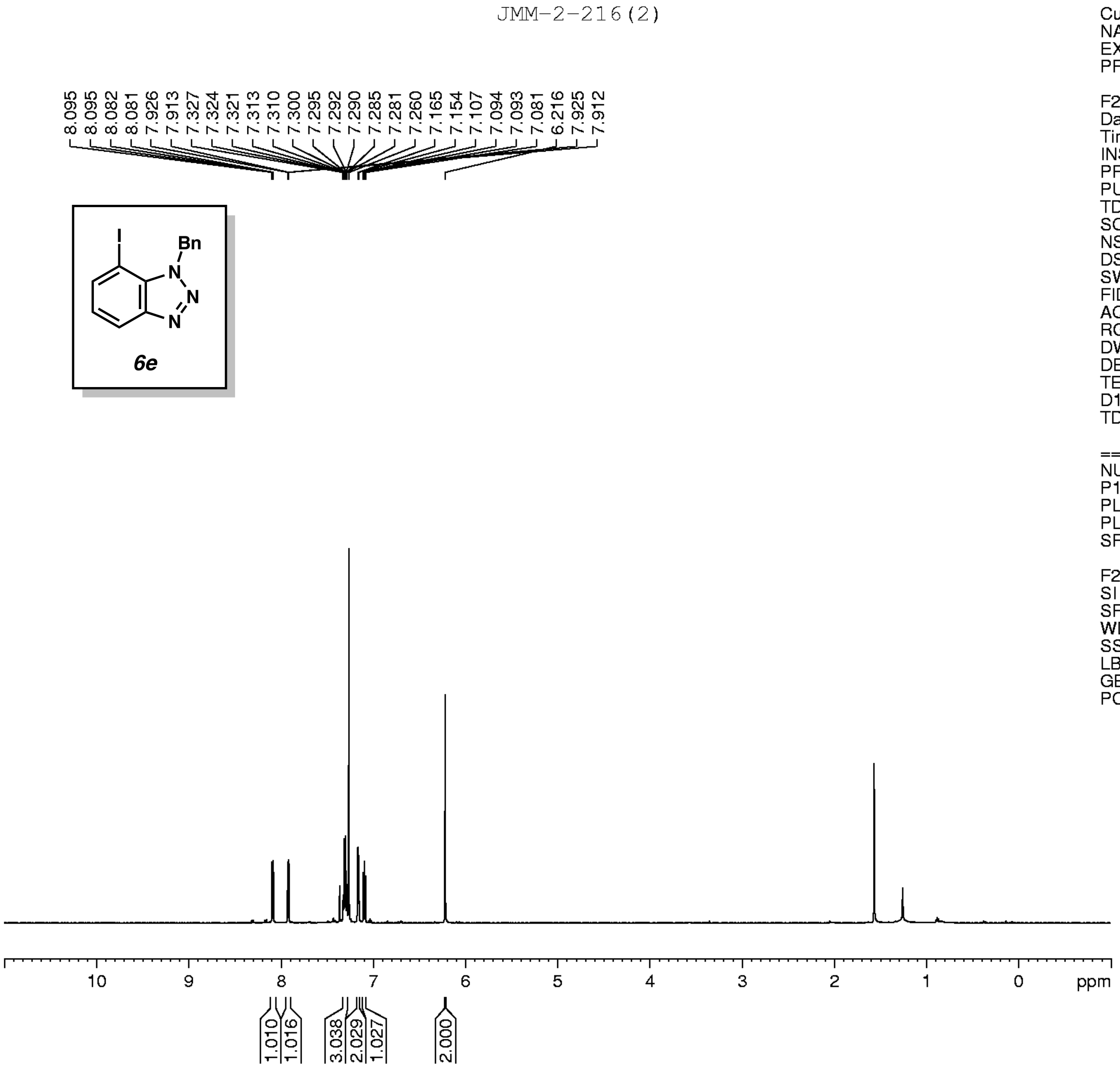
F2 – Acquisition Parameters
Date_ 20131119
Time 9.53
INSTRUM av600
PROBHD 5 mm BB5
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 23
DS 0
SWH 12376.237 Hz
FIDRES 0.188846 Hz
AQ 2.6477449 sec
RG 362
DW 40.400 usec
DE 6.50 usec
TE 294.1 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 15.38 usec
PL1 –1.00 dB
PL1W 31.62277603 W
SFO1 600.1336008 MHz

F2 – Processing parameters
SI 65536
SF 600.1300288 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

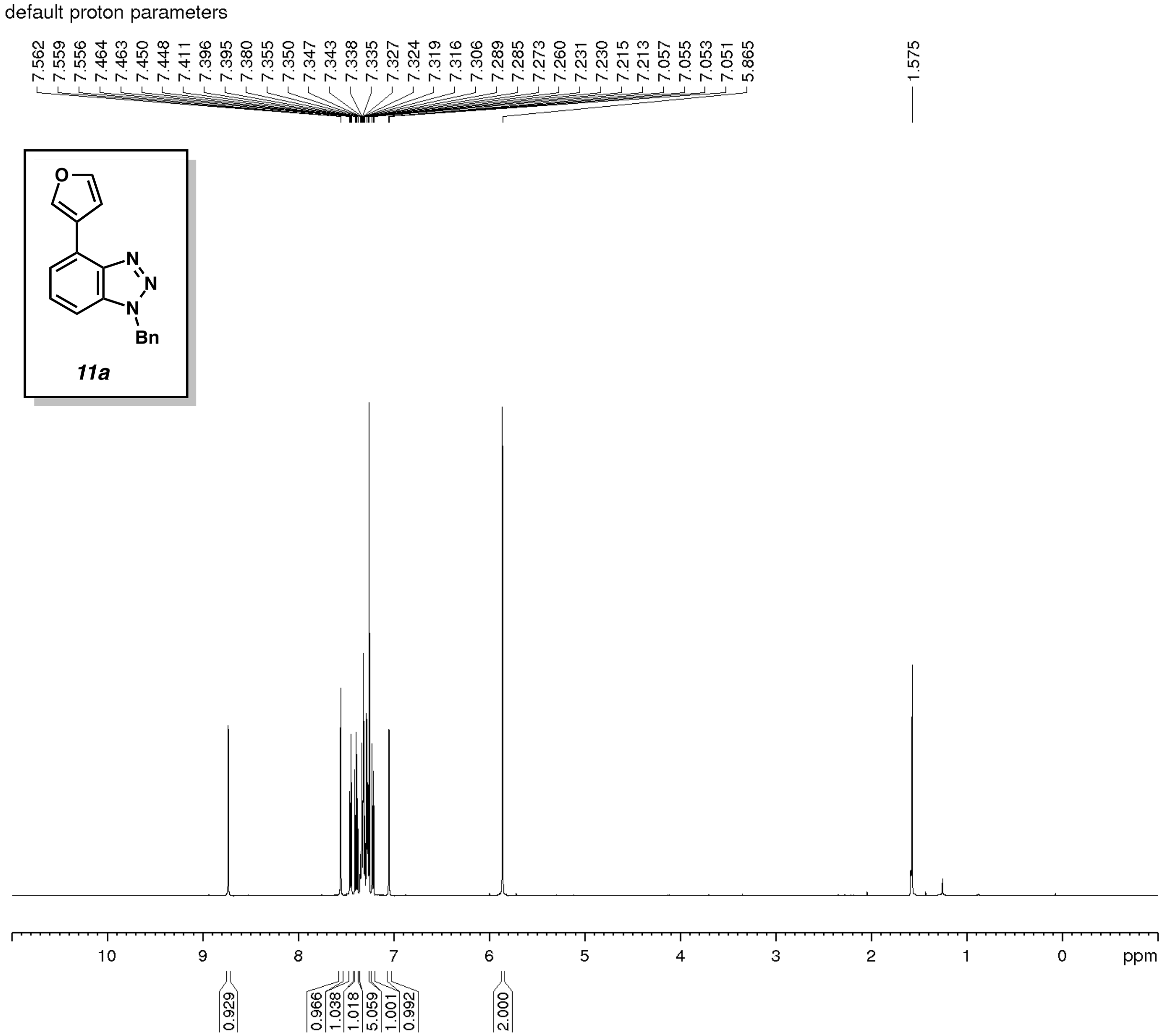


```
Current Data Parameters
NAME     JMM-2-216(1) 600
EXPNO              2
PROCNO             1

F2 - Acquisition Parameters
Date_        20131118
Time            13.56
INSTRUM         av600
PROBHD   5 mm BB5
PULPROG          zg30
TD            65536
SOLVENT         CDCl3
NS               16
DS                0
SWH       12376.237 Hz
FIDRES     0.188846 Hz
AQ        2.6477449 sec
RG              256
DW           40.400 usec
DE             6.50 usec
TE            294.6 K
D1       2.00000000 sec
TD0               1

======== CHANNEL f1 ========
NUC1             1H
P1            15.38 usec
PL1           -1.00 dB
PL1W    31.62277603 W
SFO1    600.1336008 MHz

F2 - Processing parameters
SI            65536
SF      600.1300288 MHz
WDW              EM
SSB               0
LB             0.30 Hz
GB                0
PC             1.00
```

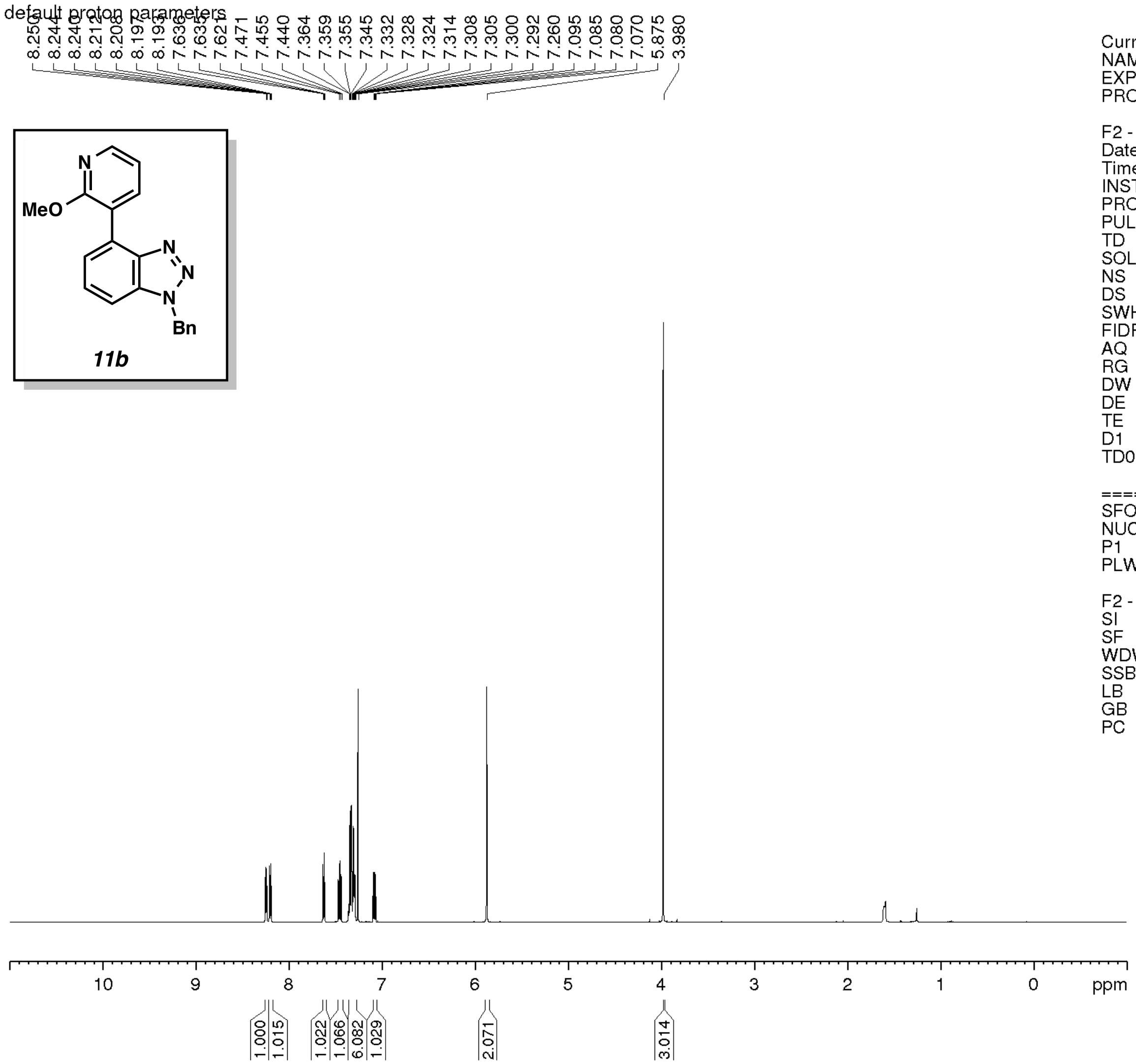


```
Current Data Parameters
NAME     JMM-2-216(2) 600
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_         20131118
Time            13.19
INSTRUM         av600
PROBHD   5 mm BB5
PULPROG          zg30
TD             65536
SOLVENT         CDCl3
NS                16
DS                 0
SWH        12376.237 Hz
FIDRES      0.188846 Hz
AQ         2.6477449 sec
RG               362
DW            40.400 usec
DE              6.50 usec
TE             294.3 K
D1        2.00000000 sec
TD0                1

======== CHANNEL f1 ========
NUC1              1H
P1             15.38 usec
PL1            -1.00 dB
PL1W     31.62277603 W
SFO1     600.1336008 MHz

F2 - Processing parameters
SI             65536
SF        600.1300290 MHz
WDW               EM
SSB                0
LB              0.30 Hz
GB                 0
PC              1.00
```

11a



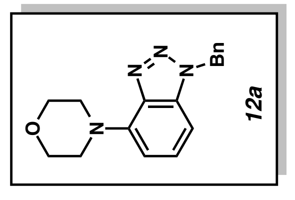
```
Current Data Parameters
NAME          JMM-3-79a
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20140412
Time              14.47
INSTRUM           av500
PROBHD   5 mm DCH 13C-1
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   19
DS                    0
SWH        10000.000 Hz
FIDRES      0.152588 Hz
AQ        3.2767999 sec
RG                   11
DW           50.000 usec
DE            10.00 usec
TE              298.0 K
D1       2.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1      500.1330008 MHz
NUC1                 1H
P1           10.00 usec
PLW1     13.50000000 W

F2 - Processing parameters
SI                65536
SF        500.1300120 MHz
WDW                  EM
SSB      0
LB              0.30 Hz
GB       0
PC                 1.00
```



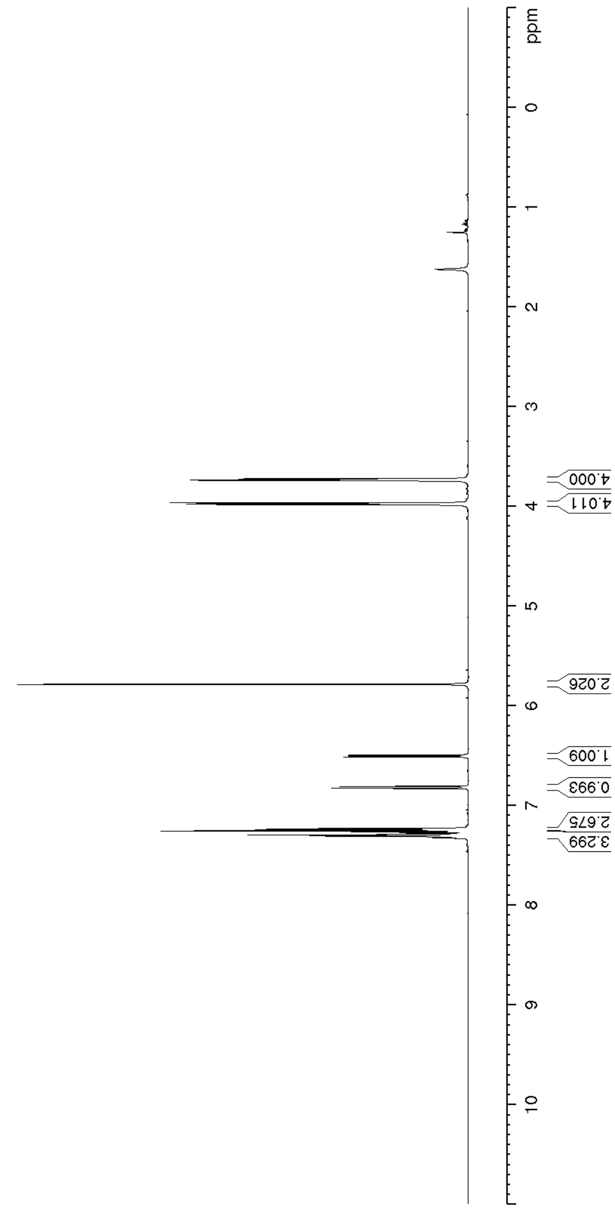
11b

```
Current Data Parameters
NAME         JMM-3-81a
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_         20140412
Time            14.55
INSTRUM         av500
PROBHD   5 mm DCH 13C-1
PULPROG          zg30
TD             65536
SOLVENT         CDCl3
NS                22
DS                 0
SWH        10000.000 Hz
FIDRES      0.152588 Hz
AQ         3.2767999 sec
RG             24.37
DW            50.000 usec
DE            10.00 usec
TE             298.0 K
D1        2.00000000 sec
TD0                1

======== CHANNEL f1 ========
SFO1      500.1330008 MHz
NUC1             1H
P1            10.00 usec
PLW1       13.50000000 W

F2 - Processing parameters
SI            65536
SF       500.1300120 MHz
WDW              EM
SSB    0
LB             0.30 Hz
GB     0
PC              1.00
```

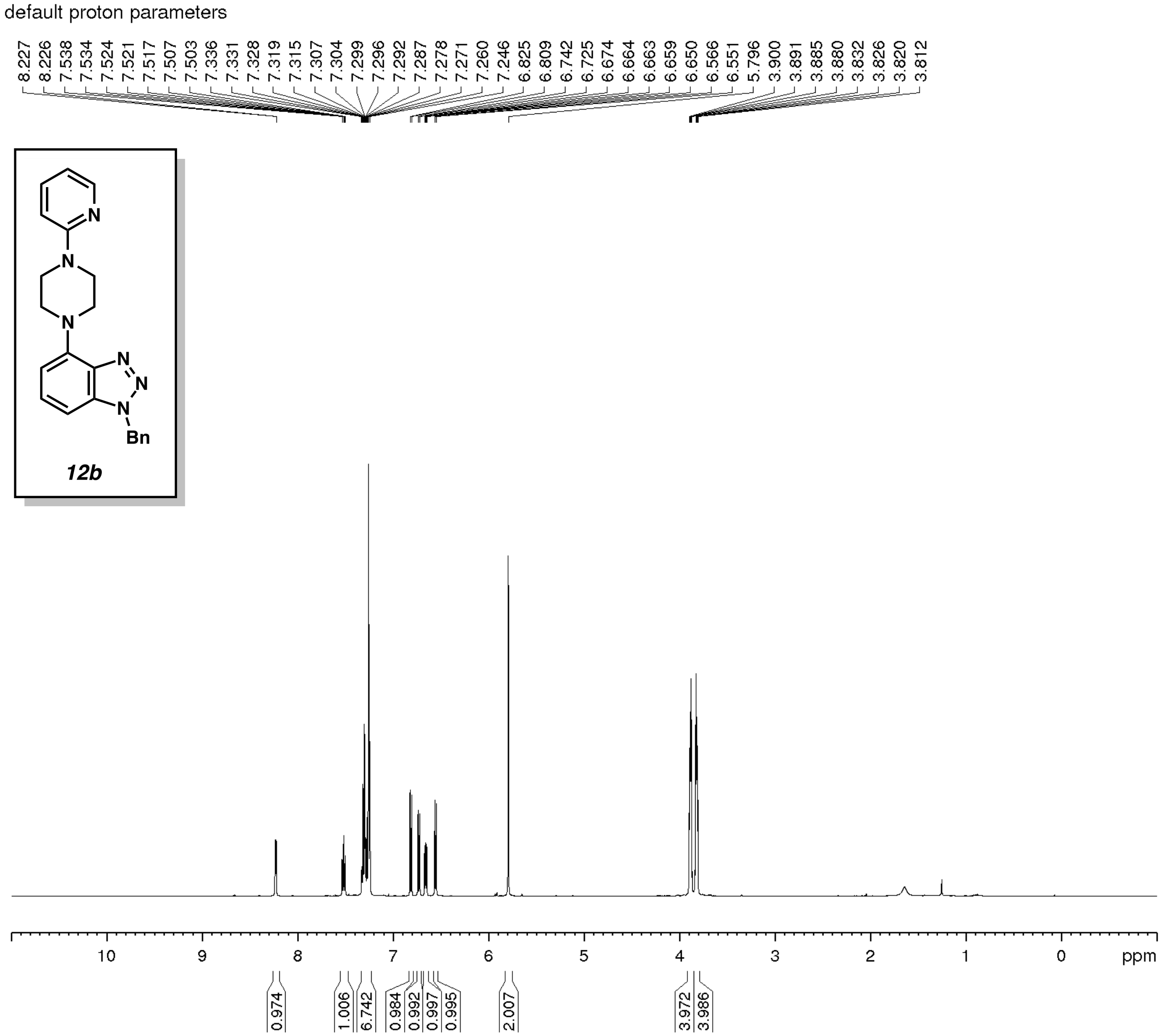
default proton parameters



12a



```
Current Data Parameters
NAME       JMM-3-133a
EXPNO               1
PROCNO              1

F2 - Acquisition Parameters
Date_       20140412
Time           15.10
INSTRUM        av500
PROBHD   5 mm DCH 13C-1
PULPROG         zg30
TD             65536
SOLVENT        CDCl3
NS                15
DS                 0
SWH       10000.000 Hz
FIDRES     0.152588 Hz
AQ        3.2767999 sec
RG             22.82
DW            50.000 usec
DE             10.00 usec
TE             298.0 K
D1       2.00000000 sec
TD0                1

======== CHANNEL f1 ========
SFO1     500.1330008 MHz
NUC1              1H
P1             10.00 usec
PLW1     13.50000000 W

F2 - Processing parameters
SI             65536
SF       500.1300120 MHz
WDW               EM
SSB    0
LB              0.30 Hz
GB     0
PC              1.00
```



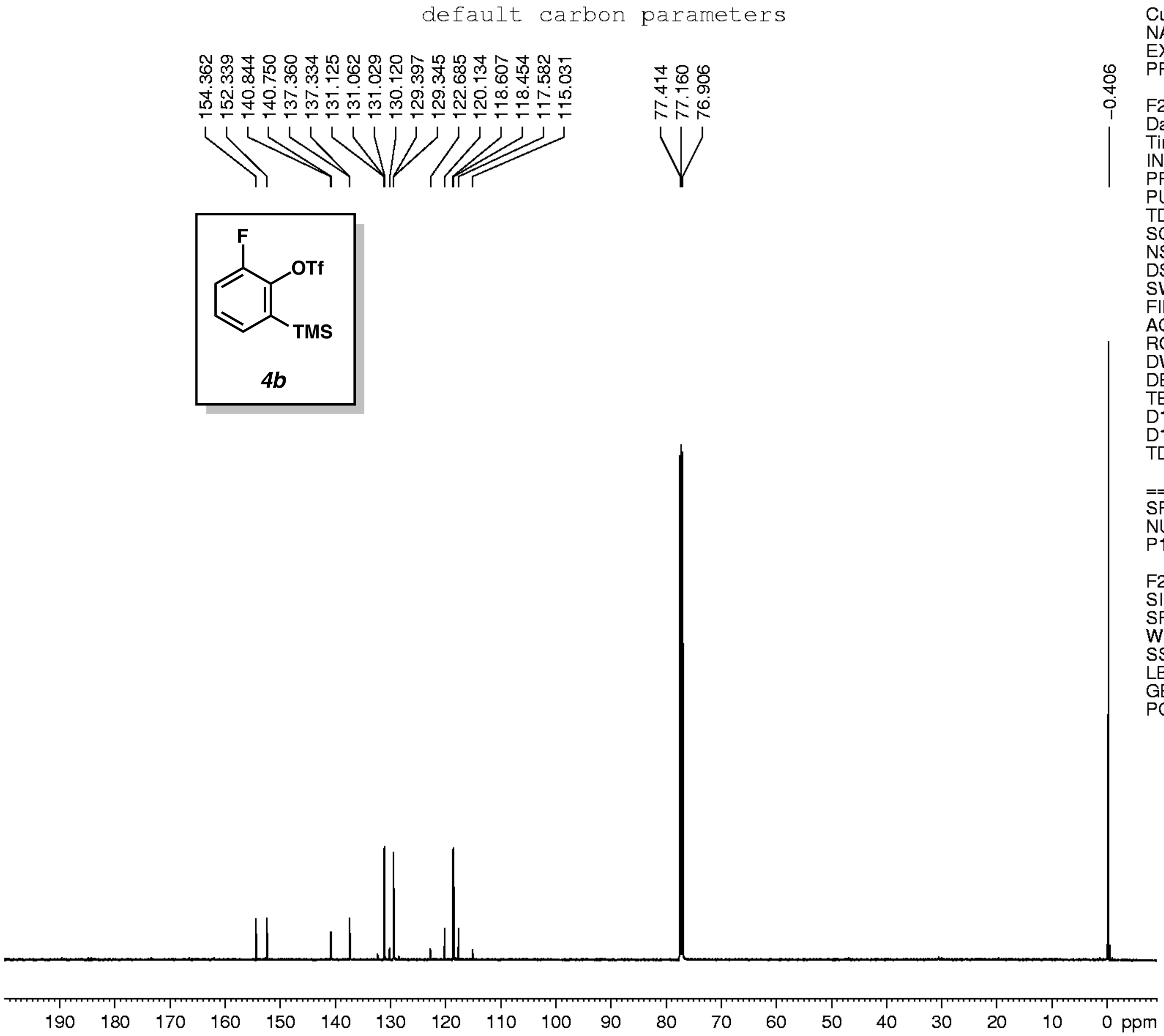
Current Data Parameters
NAME JMM-3-94a
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140412
Time 15.02
INSTRUM av500
PROBHD 5 mm DCH 13C-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 14
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 24.37
DW 50.000 usec
DE 10.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1

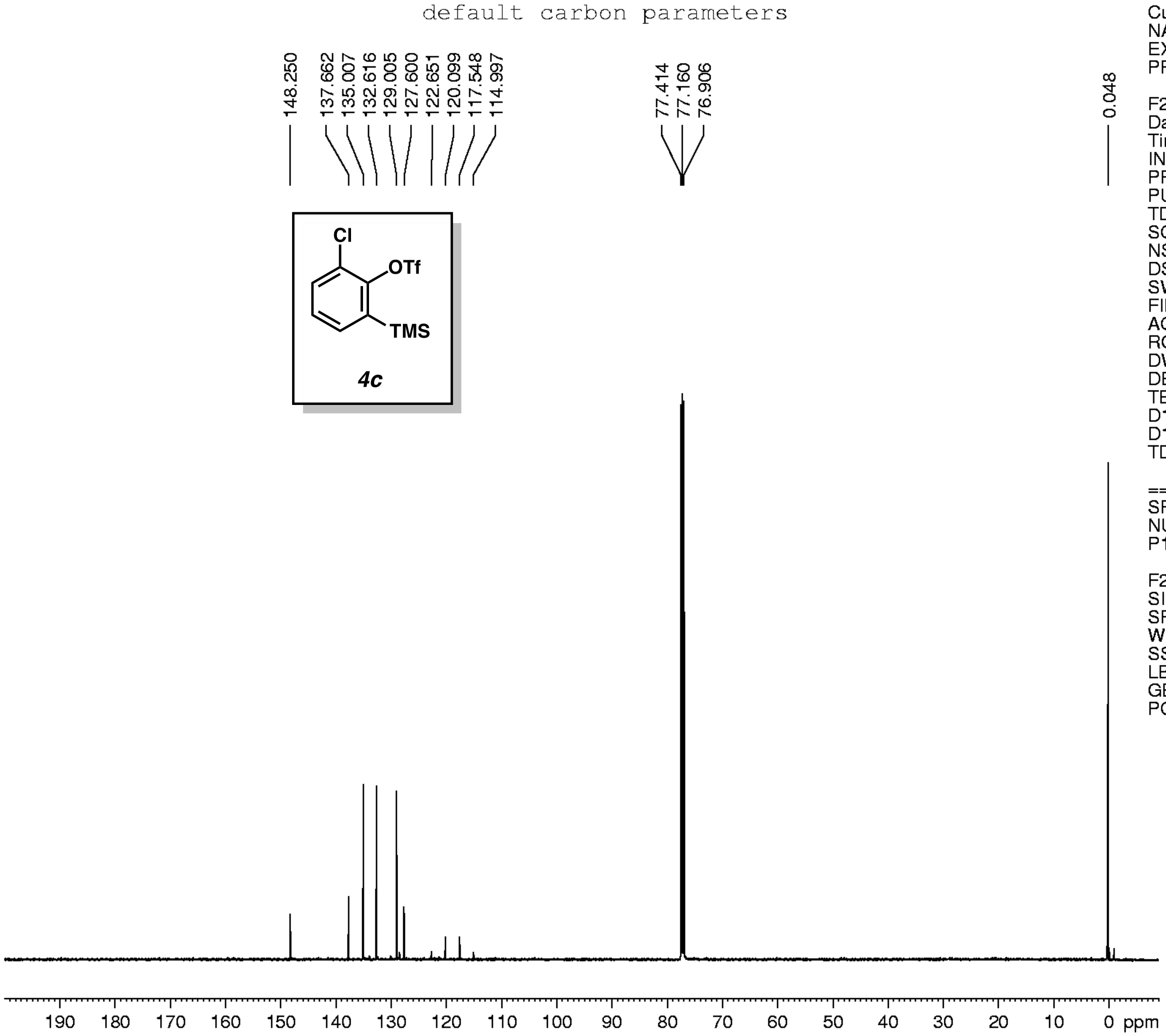
======== CHANNEL f1 ========
SFO1 500.1330008 MHz
NUC1 1H
P1 10.00 usec
PLW1 13.50000000 W

F2 - Processing parameters
SI 65536
SF 500.1300120 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

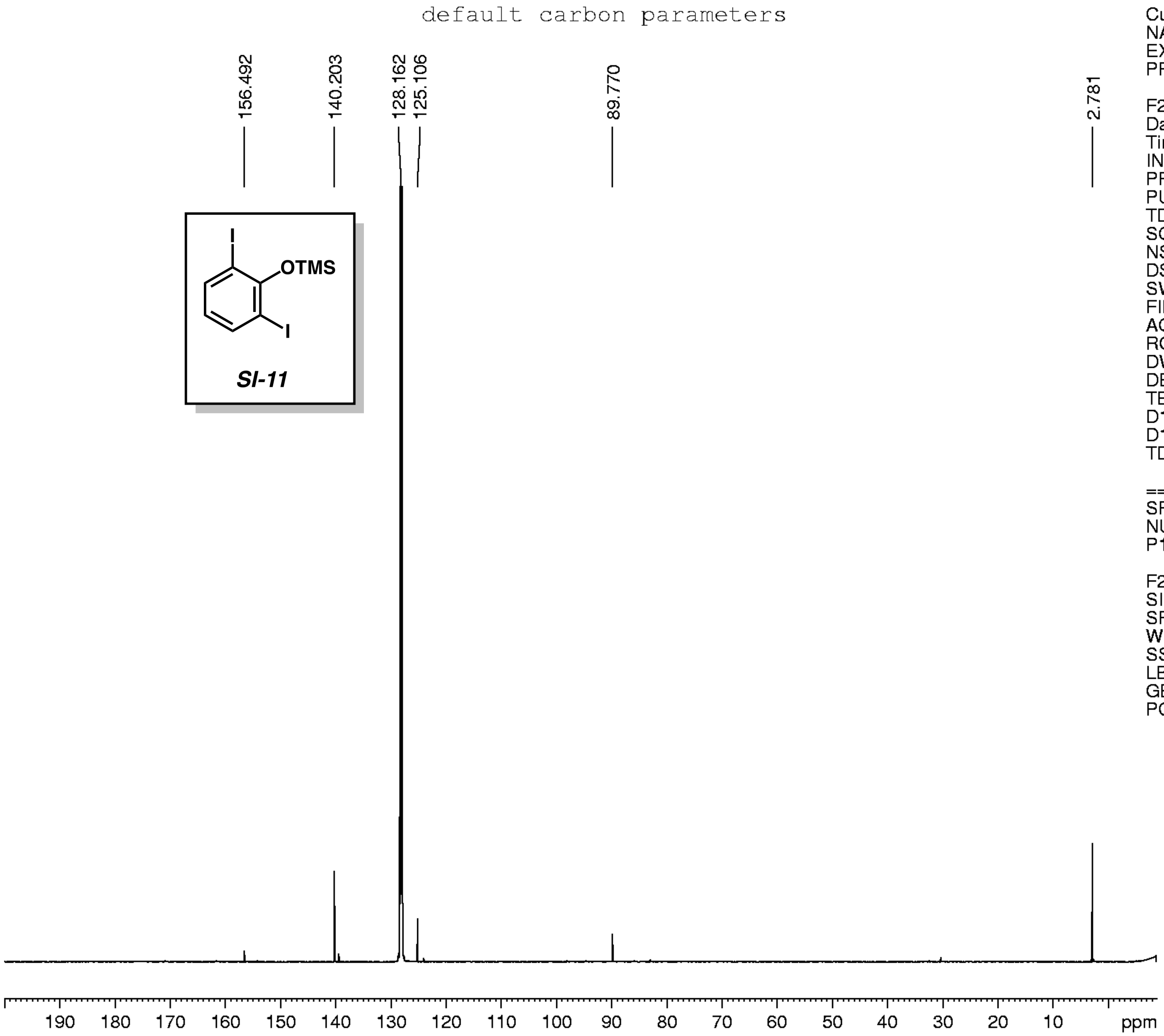
^{13}C NMR Spectra:



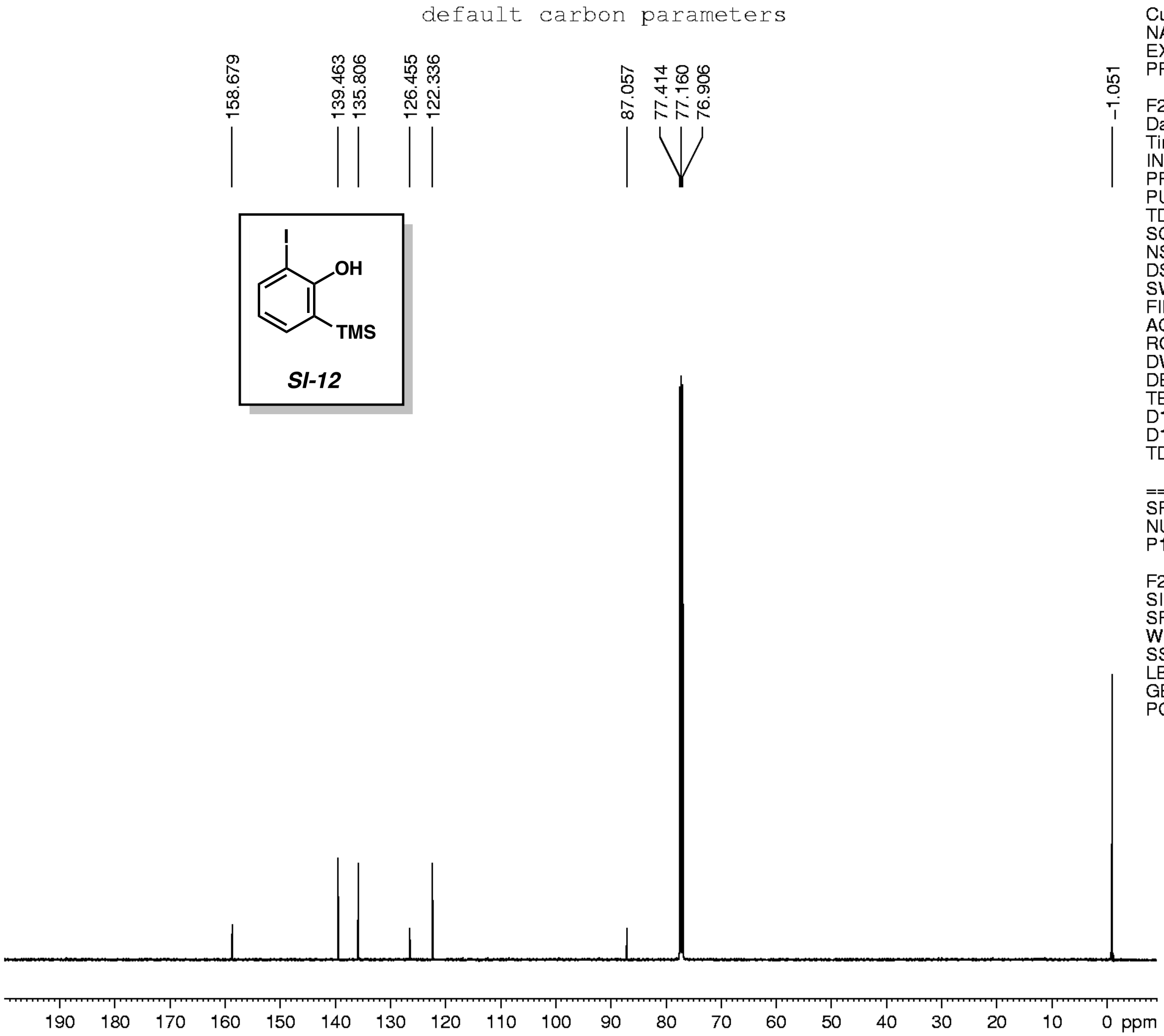
```
Current Data Parameters
NAME       JMM-2-B(F)
EXPNO               1
PROCNO              1

F2 - Acquisition Parameters
Date_        20131001
Time            15.13
INSTRUM         av500
PROBHD   5 mm DCH 13C-1
PULPROG        zgpg30
TD              65536
SOLVENT         CDCl3
NS                 64
DS                  2
SWH        31250.000 Hz
FIDRES      0.476837 Hz
AQ         1.0486259 sec
RG               12.4
DW             16.000 usec
DE              18.00 usec
TE              298.0 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
SFO1      125.7722511 MHz
NUC1              13C
P1               9.63 usec

F2 - Processing parameters
SI             131072
SF        125.7577708 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```



```
Current Data Parameters
NAME       JMM-2-A(Cl)
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_        20131001
Time            15.07
INSTRUM         av500
PROBHD   5 mm DCH 13C-1
PULPROG        zgpg30
TD              65536
SOLVENT         CDCl3
NS                 50
DS                  2
SWH         31250.000 Hz
FIDRES       0.476837 Hz
AQ          1.0486259 sec
RG             202.91
DW             16.000 usec
DE              18.00 usec
TE              298.0 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
SFO1      125.7722511 MHz
NUC1              13C
P1               9.63 usec

F2 - Processing parameters
SI             131072
SF        125.7577713 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```

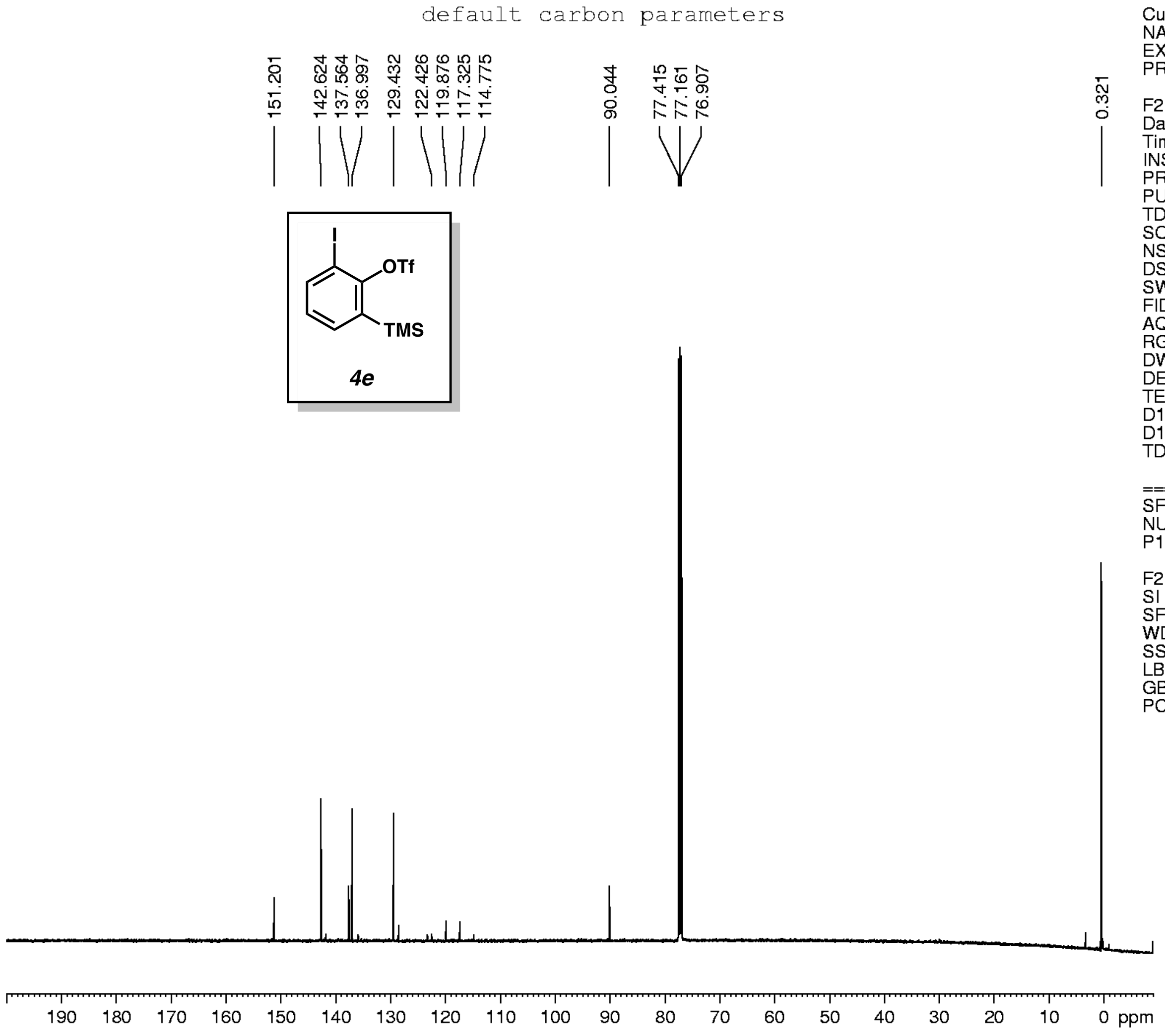


```
Current Data Parameters
NAME       JMM-2-178(2)
EXPNO              3
PROCNO             1

F2 - Acquisition Parameters
Date_         20131013
Time             10.16
INSTRUM          av500
PROBHD   5 mm DCH 13C-1
PULPROG        zgpg30
TD              65536
SOLVENT           C6D6
NS                 455
DS                   2
SWH       31250.000 Hz
FIDRES     0.476837 Hz
AQ       1.0486259 sec
RG              202.91
DW          16.000 usec
DE           18.00 usec
TE             298.0 K
D1      2.00000000 sec
D11     0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1     125.7722511 MHz
NUC1               13C
P1            9.63 usec

F2 - Processing parameters
SI              131072
SF       125.7577428 MHz
WDW                 EM
SSB                  0
LB             1.00 Hz
GB                   0
PC                1.40
```

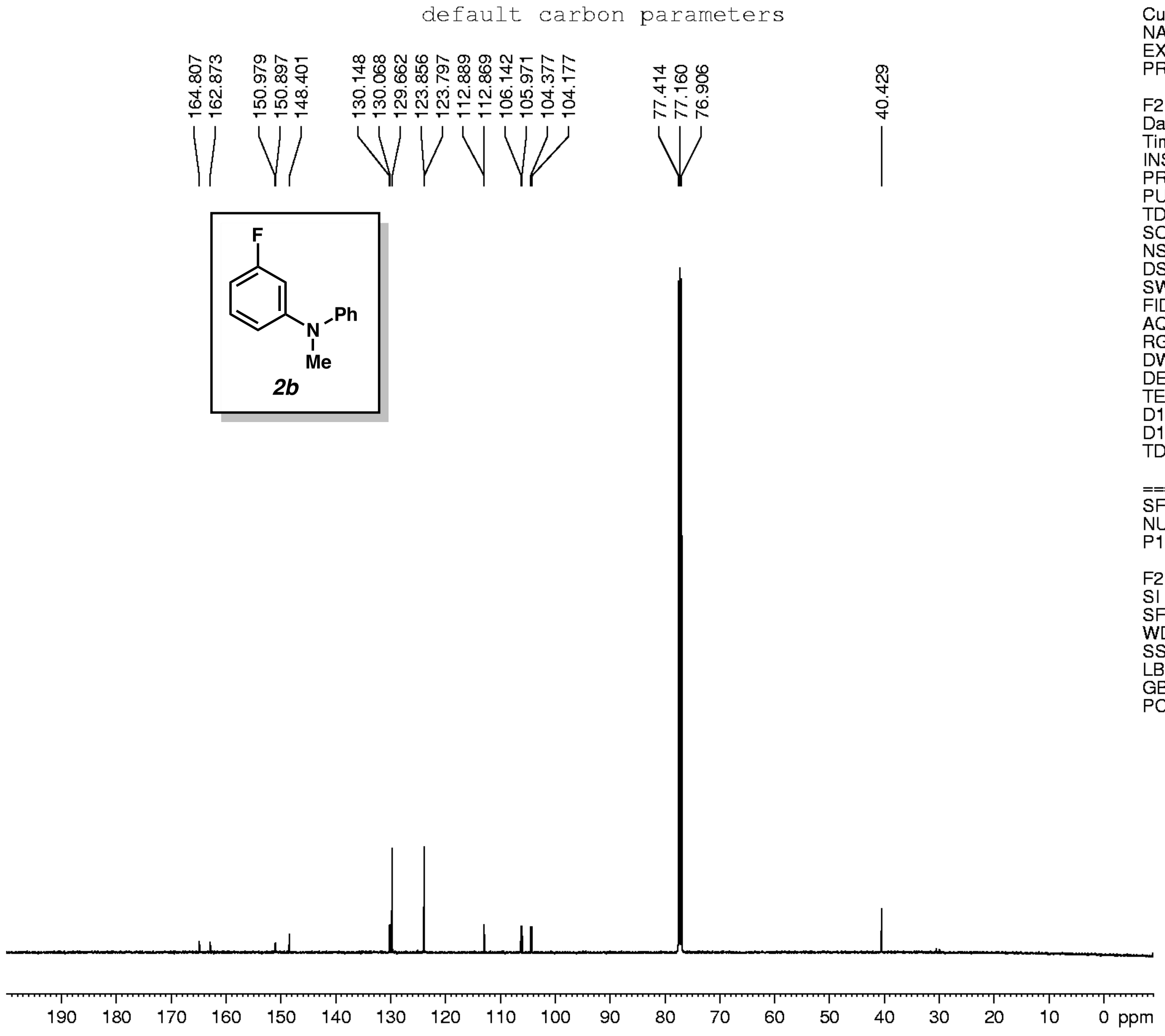


SI-12

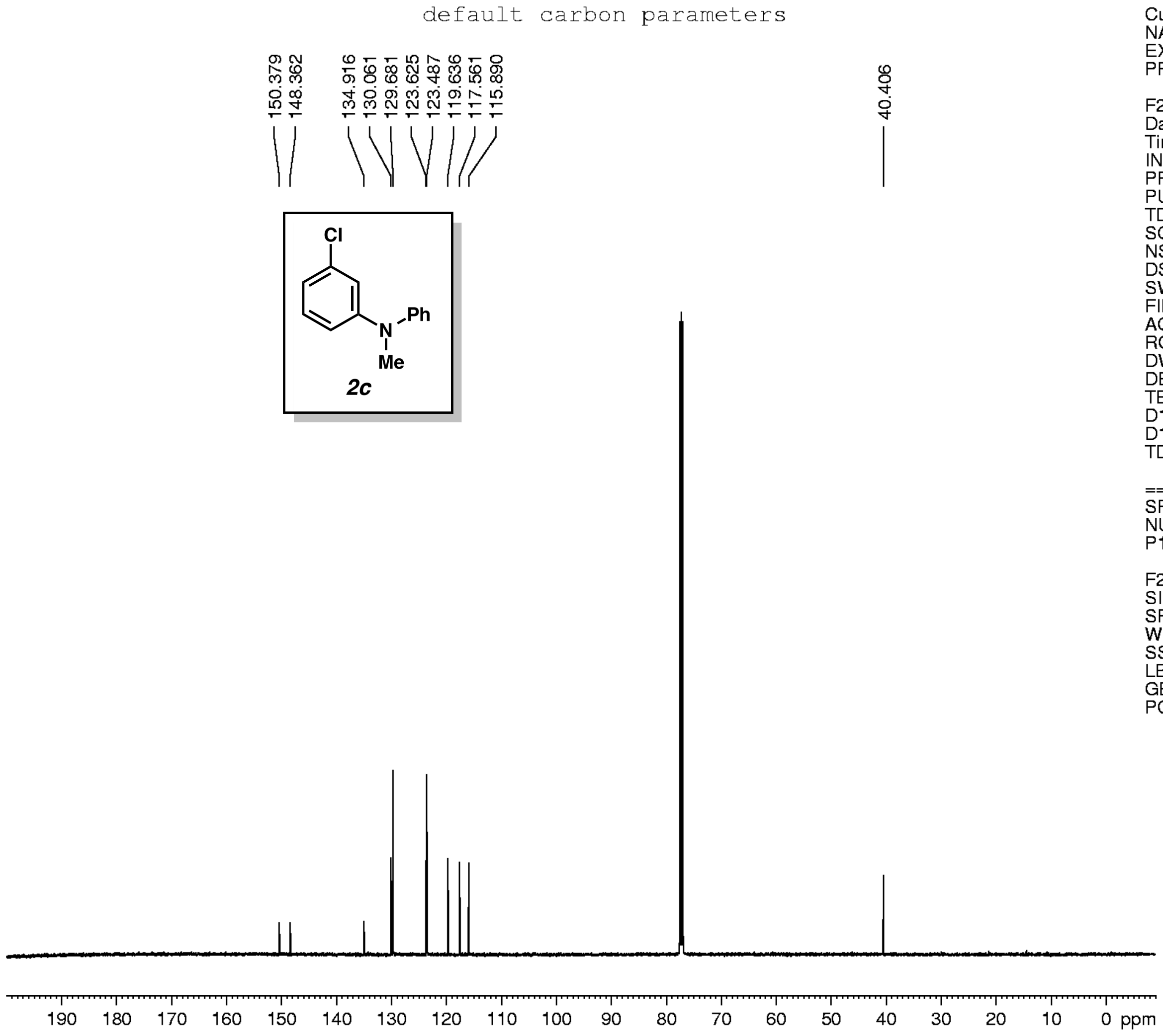
```
Current Data Parameters
NAME       JMM−2−179(1)
EXPNO             2
PROCNO            1

F2 − Acquisition Parameters
Date_        20131014
Time             9.28
INSTRUM         av500
PROBHD   5 mm DCH 13C−1
PULPROG        zgpg30
TD              65536
SOLVENT         CDCl3
NS                 66
DS                  2
SWH       31250.000 Hz
FIDRES     0.476837 Hz
AQ       1.0486259 sec
RG                 11
DW         16.000 usec
DE          18.00 usec
TE            298.0 K
D1      2.00000000 sec
D11     0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
SFO1     125.7722511 MHz
NUC1               13C
P1           9.63 usec

F2 − Processing parameters
SI             131072
SF       125.7577720 MHz
WDW                EM
SSB                 0
LB            1.00 Hz
GB                  0
PC               1.40
```



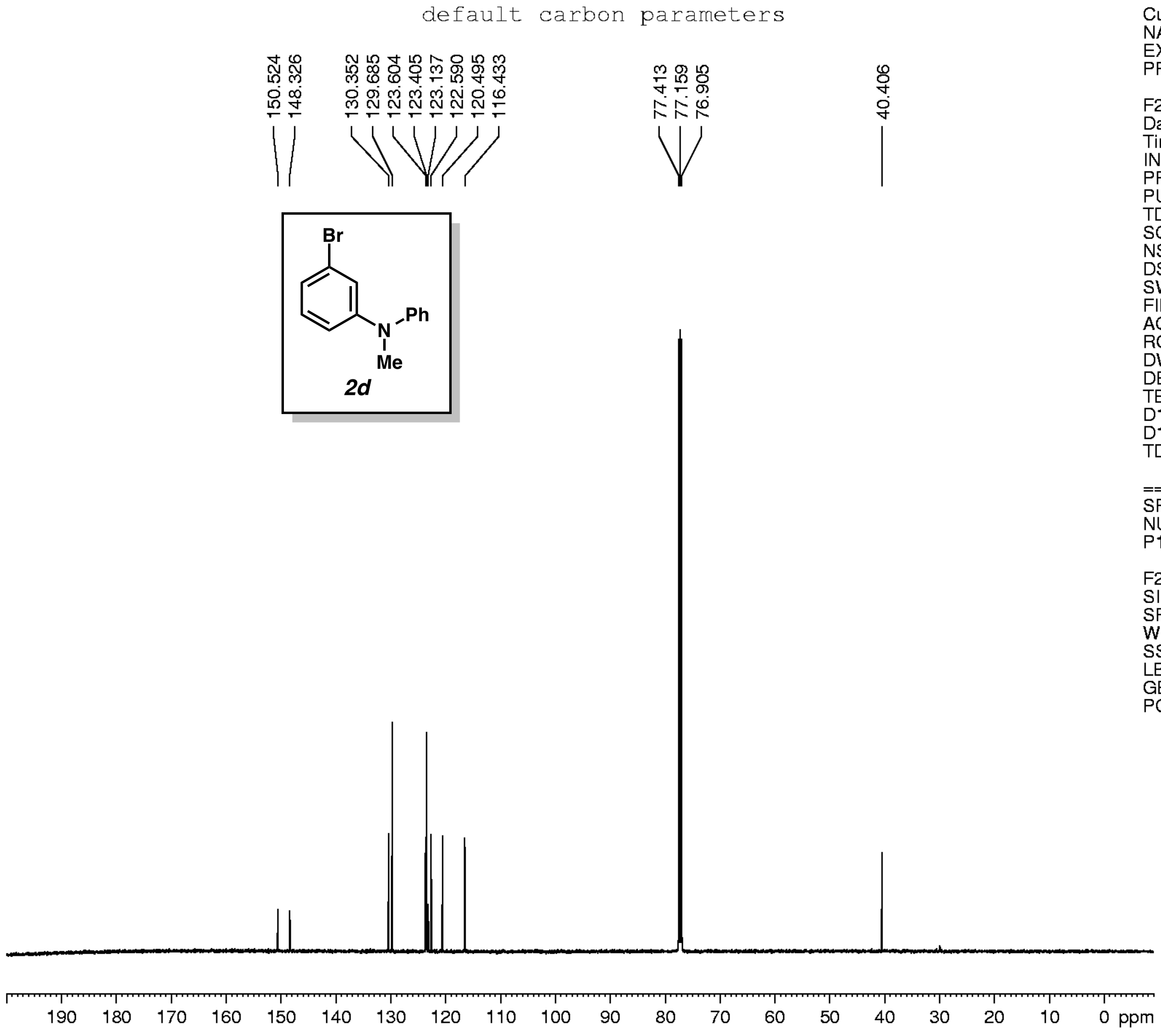
```
Current Data Parameters
NAME         JMM-2-C(I)
EXPNO               1
PROCNO              1

F2 - Acquisition Parameters
Date_        20131001
Time            15.23
INSTRUM         av500
PROBHD   5 mm DCH 13C-1
PULPROG        zgpg30
TD              65536
SOLVENT         CDCl3
NS                 64
DS                  2
SWH        31250.000 Hz
FIDRES      0.476837 Hz
AQ         1.0486259 sec
RG             202.91
DW             16.000 usec
DE              18.00 usec
TE              298.0 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
SFO1     125.7722511 MHz
NUC1             13C
P1              9.63 usec

F2 - Processing parameters
SI             131072
SF        125.7577718 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```



```
Current Data Parameters
NAME     JMM-2-119B(char)
EXPNO              2
PROCNO             1

F2 - Acquisition Parameters
Date_         20131021
Time             12.34
INSTRUM          av500
PROBHD   5 mm DCH 13C-1
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                  82
DS                   2
SWH         31250.000 Hz
FIDRES       0.476837 Hz
AQ          1.0486259 sec
RG              202.91
DW              16.000 usec
DE               18.00 usec
TE               298.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1       125.7722511 MHz
NUC1               13C
P1                9.63 usec

F2 - Processing parameters
SI              131072
SF         125.7577720 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```



```
Current Data Parameters
NAME     JMM-2-118(char)
EXPNO              2
PROCNO             1

F2 - Acquisition Parameters
Date_         20131021
Time            12.45
INSTRUM         av500
PROBHD   5 mm DCH 13C-1
PULPROG        zgpg30
TD             65536
SOLVENT         CDCl3
NS                46
DS                 2
SWH        31250.000 Hz
FIDRES      0.476837 Hz
AQ         1.0486259 sec
RG            202.91
DW            16.000 usec
DE             18.00 usec
TE             298.0 K
D1        2.00000000 sec
D11       0.03000000 sec
TD0                1

======== CHANNEL f1 ========
SFO1     125.7722511 MHz
NUC1            13C
P1             9.63 usec

F2 - Processing parameters
SI             131072
SF       125.7577727 MHz
WDW               EM
SSB                0
LB              1.00 Hz
GB                 0
PC              1.40
```



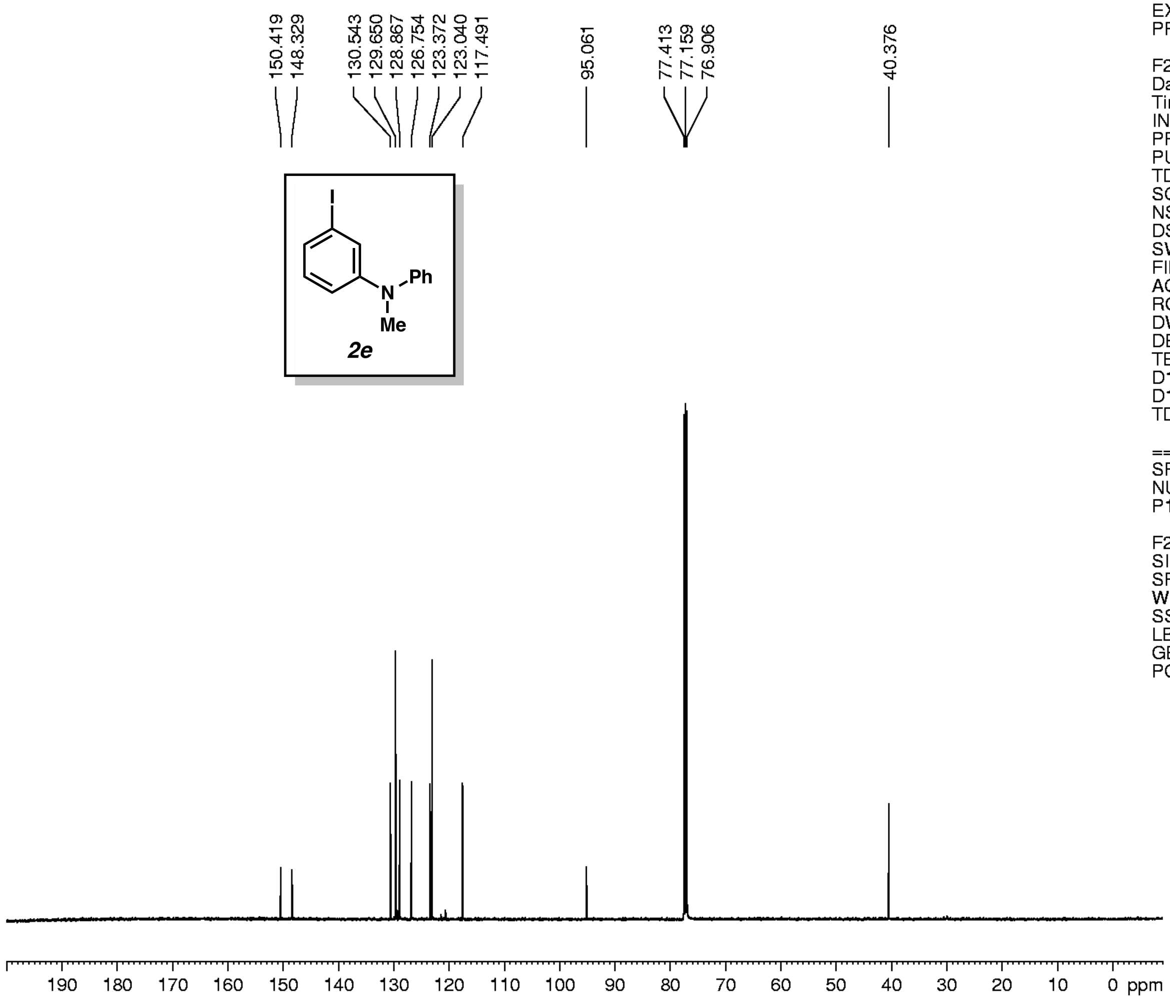
Current Data Parameters
NAME JMM-2-116(char)
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20131021
Time 12.54
INSTRUM av500
PROBHD 5 mm DCH 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 35
DS 2
SWH 31250.000 Hz
FIDRES 0.476837 Hz
AQ 1.0486259 sec
RG 202.91
DW 16.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

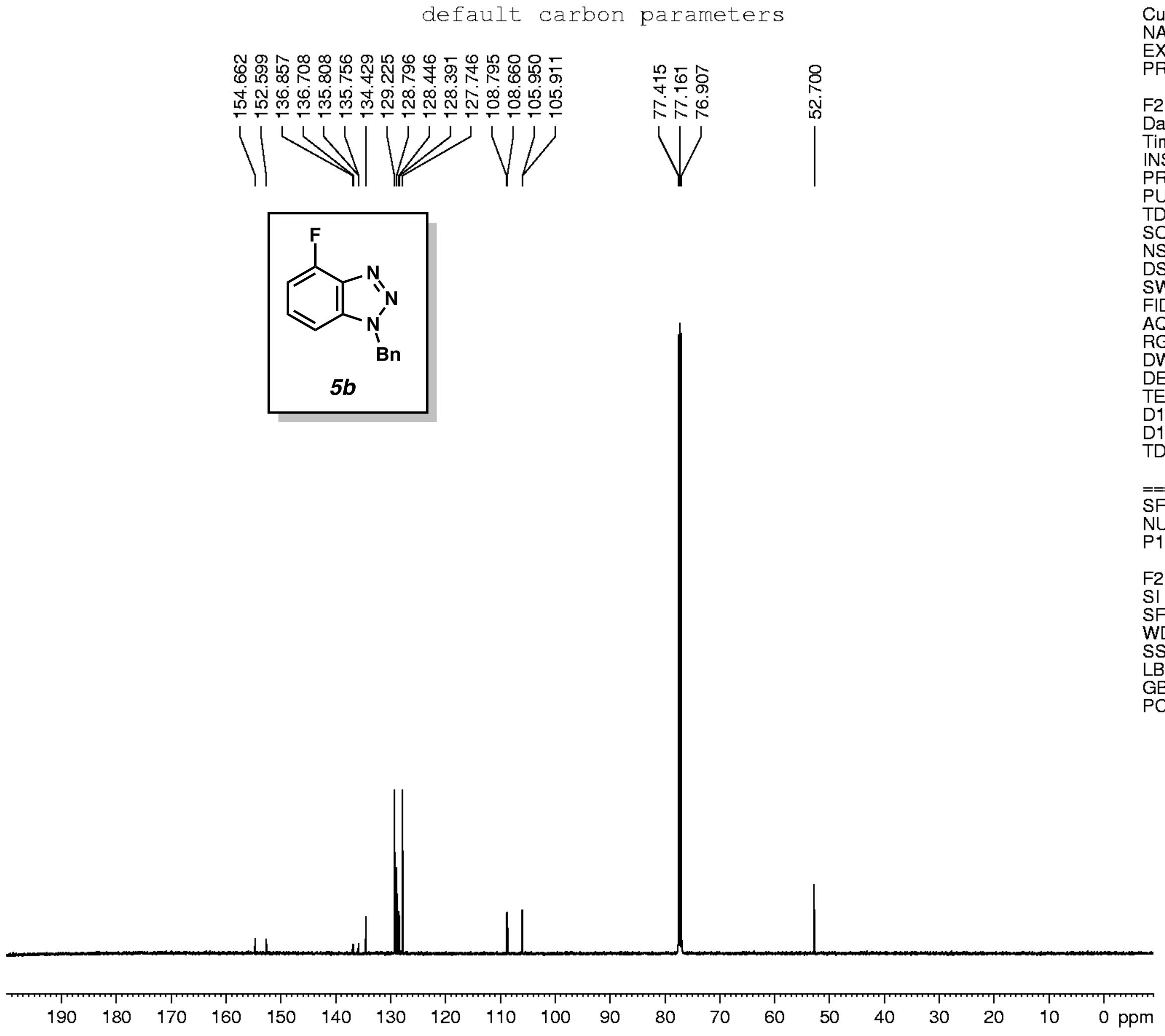
======== CHANNEL f1 ========
SFO1 125.7722511 MHz
NUC1 13C
P1 9.63 usec

F2 - Processing parameters
SI 131072
SF 125.7577735 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

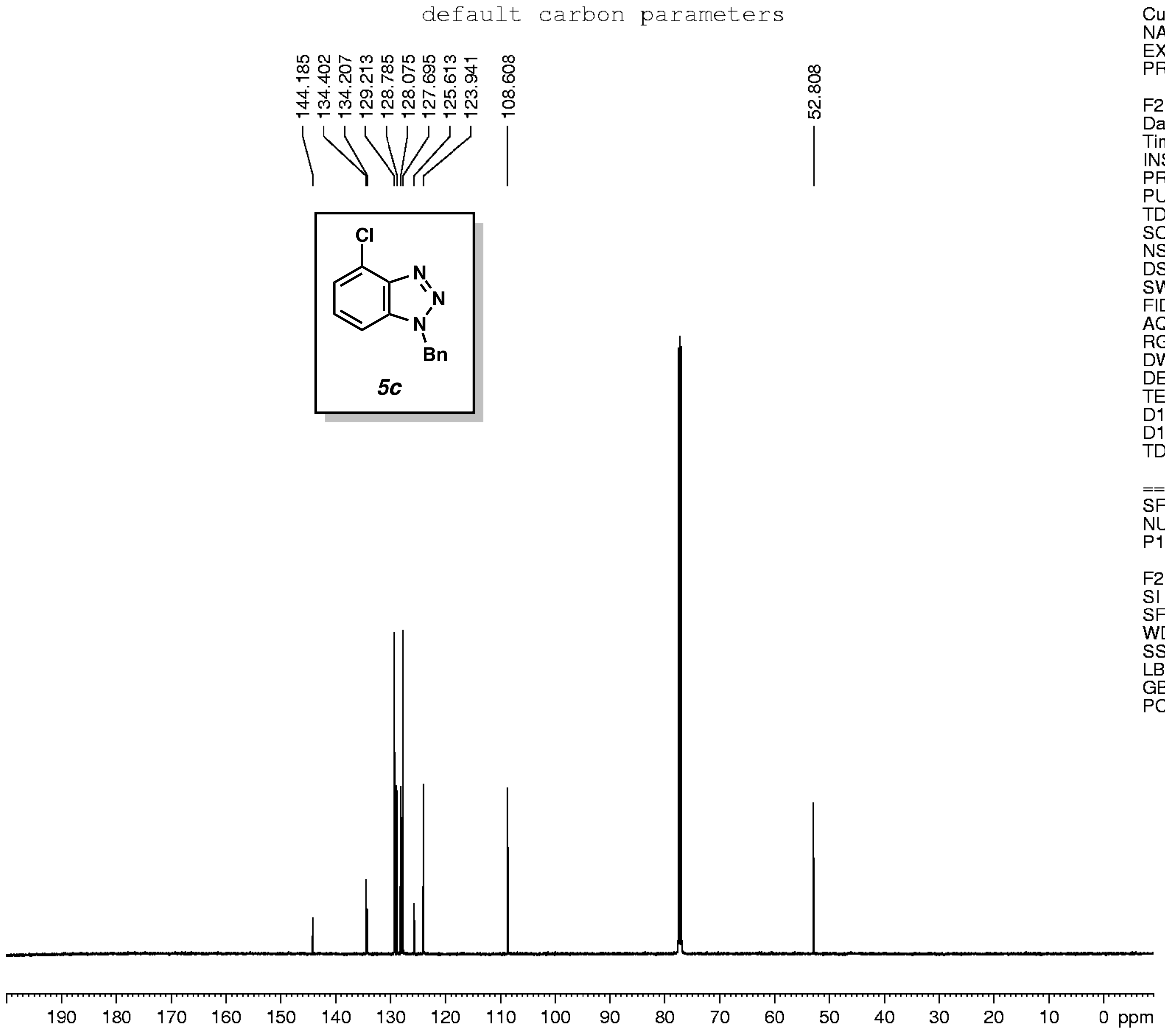
default carbon parameters



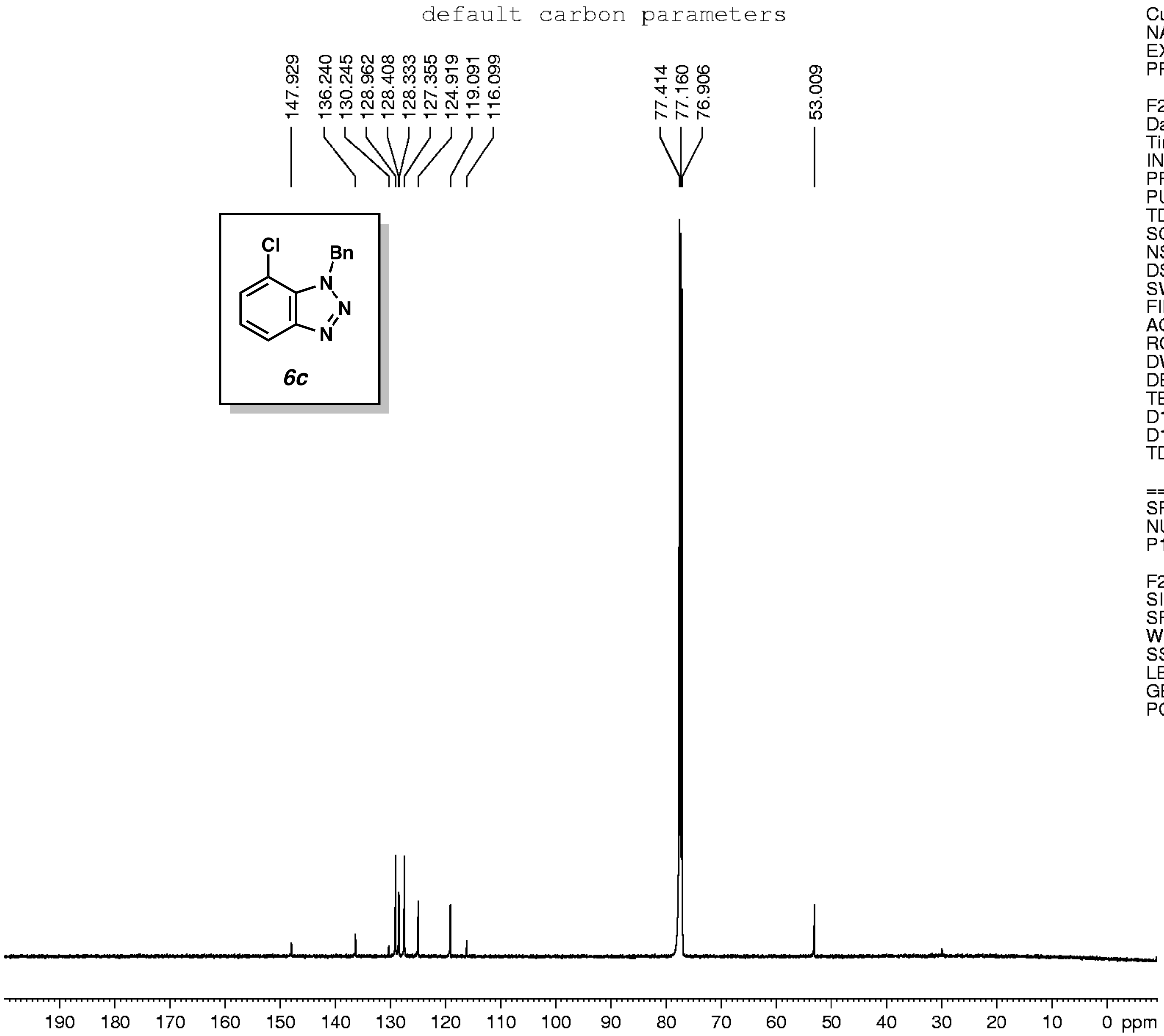
```
Current Data Parameters
NAME     JMM-2-123(char)
EXPNO              2
PROCNO             1

F2 - Acquisition Parameters
Date_        20131021
Time            13.03
INSTRUM         av500
PROBHD   5 mm DCH 13C-1
PULPROG        zgpg30
TD              65536
SOLVENT         CDCl3
NS                 48
DS                  2
SWH        31250.000 Hz
FIDRES      0.476837 Hz
AQ         1.0486259 sec
RG             202.91
DW            16.000 usec
DE             18.00 usec
TE              298.0 K
D1        2.00000000 sec
D11       0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
SFO1      125.7722511 MHz
NUC1              13C
P1               9.63 usec

F2 - Processing parameters
SI             131072
SF        125.7577749 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```



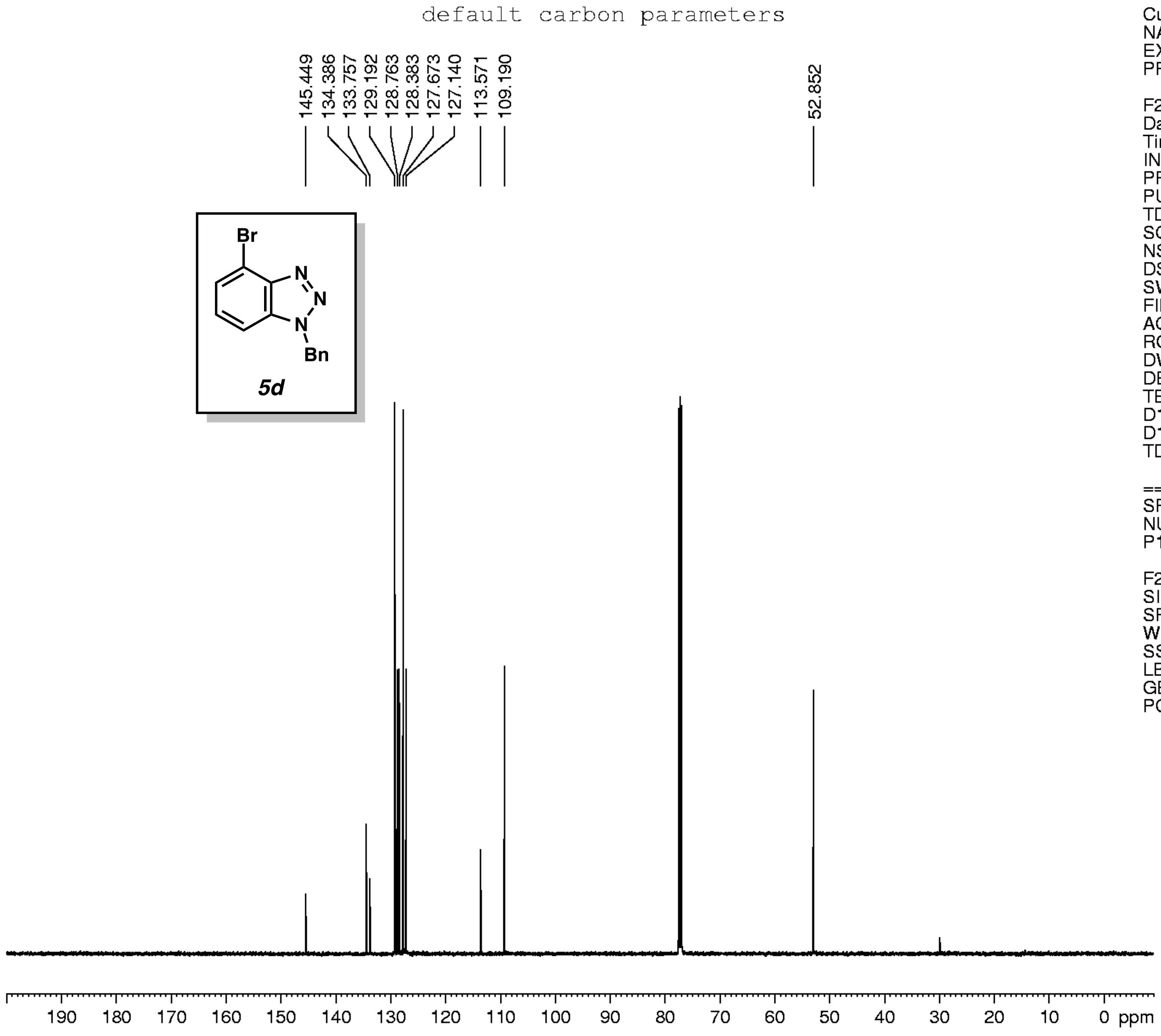
```
Current Data Parameters
NAME      JMM-2-200(1)
EXPNO              2
PROCNO             1

F2 - Acquisition Parameters
Date_        20131024
Time            11.45
INSTRUM         av500
PROBHD   5 mm DCH 13C-1
PULPROG        zgpg30
TD              65536
SOLVENT         CDCl3
NS                 31
DS                  2
SWH        31250.000 Hz
FIDRES      0.476837 Hz
AQ         1.0486259 sec
RG             202.91
DW             16.000 usec
DE              18.00 usec
TE              298.0 K
D1       2.00000000 sec
D11      0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
SFO1     125.7722511 MHz
NUC1              13C
P1               9.63 usec

F2 - Processing parameters
SI             131072
SF       125.7577730 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.40
```



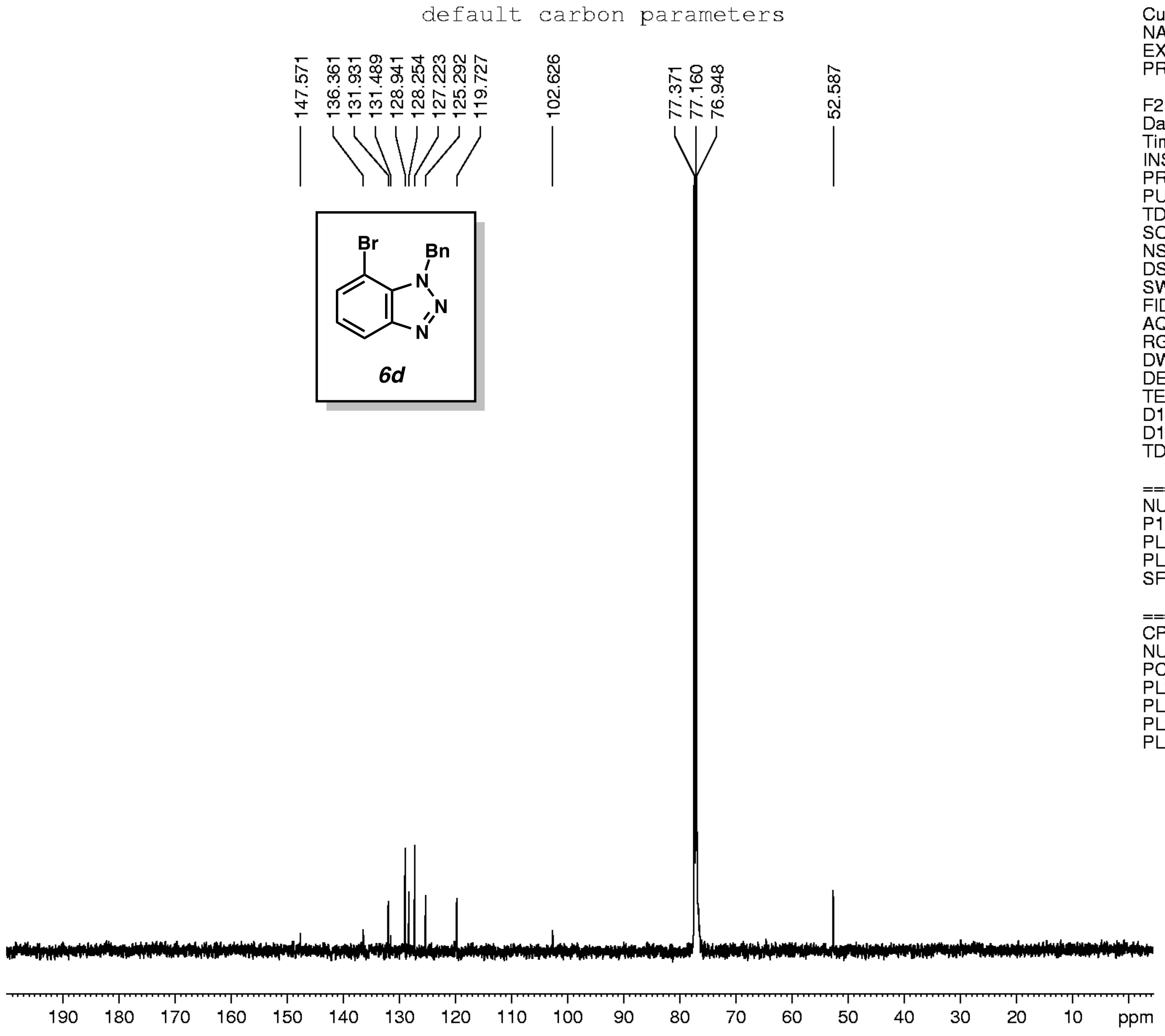
```
Current Data Parameters
NAME     JMM-2-208(1new)
EXPNO              2
PROCNO             1

F2 - Acquisition Parameters
Date_        20131108
Time            14.52
INSTRUM         av500
PROBHD   5 mm DCH 13C-1
PULPROG        zgpg30
TD              65536
SOLVENT         CDCl3
NS                 51
DS                  2
SWH       31250.000 Hz
FIDRES     0.476837 Hz
AQ       1.0486259 sec
RG             202.91
DW         16.000 usec
DE          18.00 usec
TE              298.0 K
D1     2.00000000 sec
D11    0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
SFO1     125.7722511 MHz
NUC1             13C
P1            9.63 usec

F2 - Processing parameters
SI             131072
SF      125.7577747 MHz
WDW                EM
SSB                 0
LB            1.00 Hz
GB                  0
PC               1.40
```



```
Current Data Parameters
NAME        JMM-3-30(b)
EXPNO               2
PROCNO              1

F2 - Acquisition Parameters
Date_         20140210
Time              9.13
INSTRUM          av500
PROBHD   5 mm DCH 13C-1
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 365
DS                   2
SWH        31250.000 Hz
FIDRES      0.476837 Hz
AQ        1.0486259 sec
RG              202.91
DW          16.000 usec
DE           18.00 usec
TE               298.0 K
D1       2.00000000 sec
D11      0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1     125.7722512 MHz
NUC1               13C
P1            9.63 usec

F2 - Processing parameters
SI              131072
SF       125.7577725 MHz
WDW                 EM
SSB                  0
LB             1.00 Hz
GB                   0
PC                1.40
```

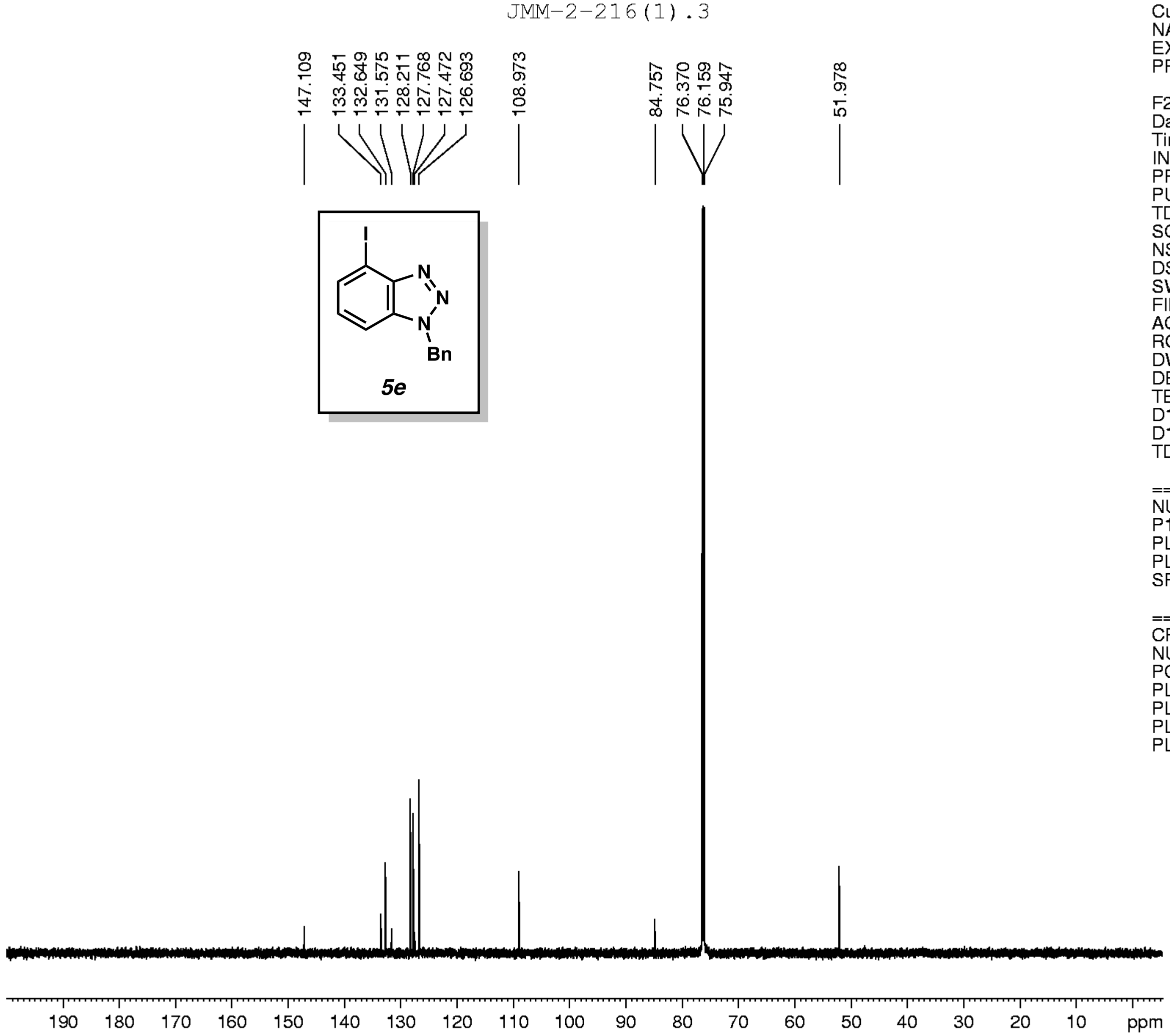


```
Current Data Parameters
NAME       JMM-2-215(1)
EXPNO              2
PROCNO             1

F2 - Acquisition Parameters
Date_        20131115
Time             9.30
INSTRUM         av500
PROBHD   5 mm DCH 13C-1
PULPROG        zgpg30
TD              65536
SOLVENT         CDCl3
NS                 24
DS                  2
SWH        31250.000 Hz
FIDRES      0.476837 Hz
AQ         1.0486259 sec
RG             202.91
DW         16.000 usec
DE          18.00 usec
TE            298.0 K
D1       2.00000000 sec
D11      0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
SFO1     125.7722511 MHz
NUC1              13C
P1            9.63 usec

F2 - Processing parameters
SI             131072
SF       125.7577763 MHz
WDW                EM
SSB                 0
LB            1.00 Hz
GB                  0
PC               1.40
```



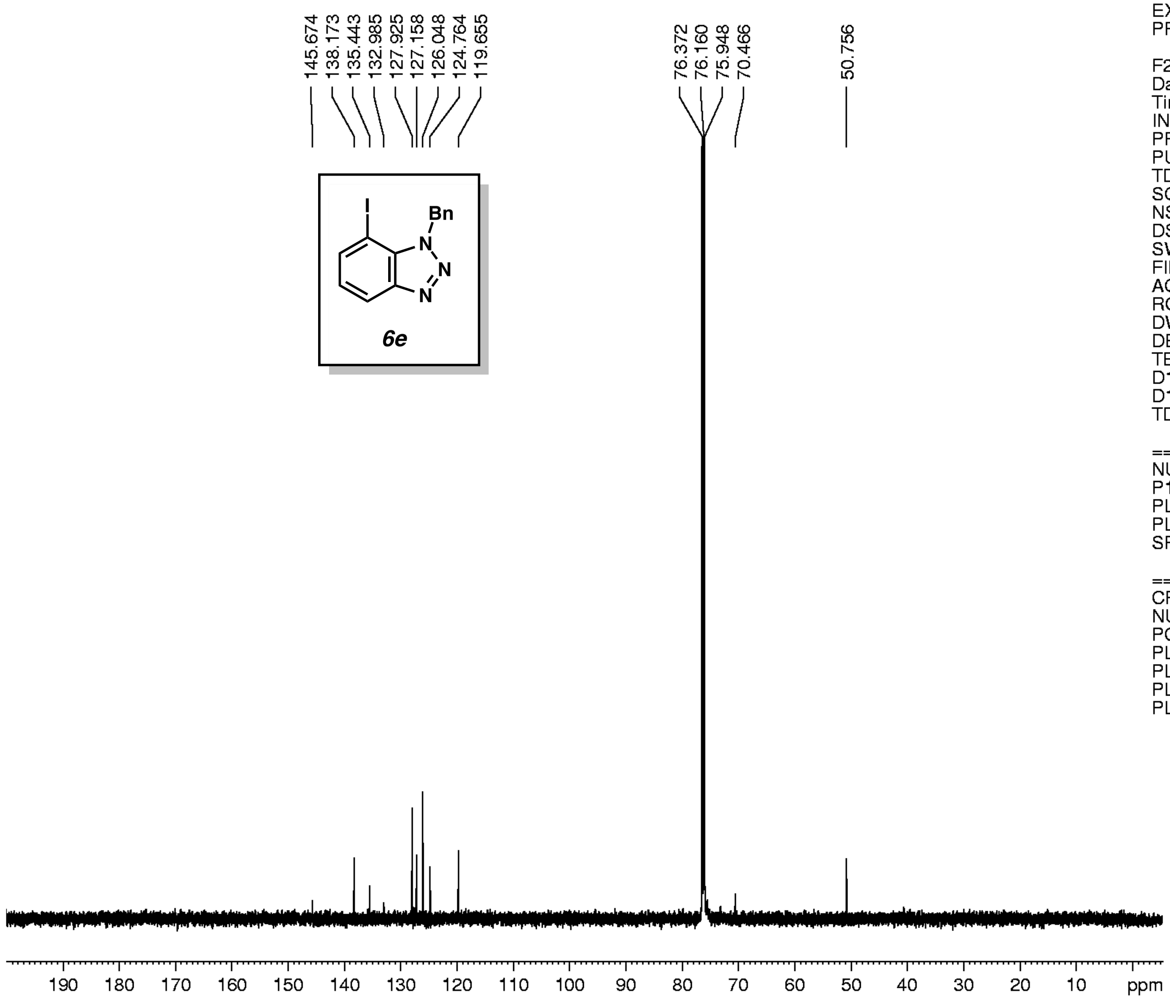
6d

```
Current Data Parameters
NAME       JMM-2-215(2)
EXPNO              2
PROCNO             1

F2 - Acquisition Parameters
Date_         20131119
Time             10.02
INSTRUM          av600
PROBHD   5 mm BB5
PULPROG         zgdc30
TD               65536
SOLVENT          CDCl3
NS                 810
DS                   0
SWH          37593.984 Hz
FIDRES        0.573639 Hz
AQ           0.8716921 sec
RG             18390.4
DW              13.300 usec
DE                6.50 usec
TE               295.7 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1               10.00 usec
PL1               0.00 dB
PL1W       75.35659027 W
SFO1       150.9209173 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2            80.00 usec
PL2              -1.00 dB
PL12             13.33 dB
PL2W       31.62277603 W
PL12W       1.16680968 W
```

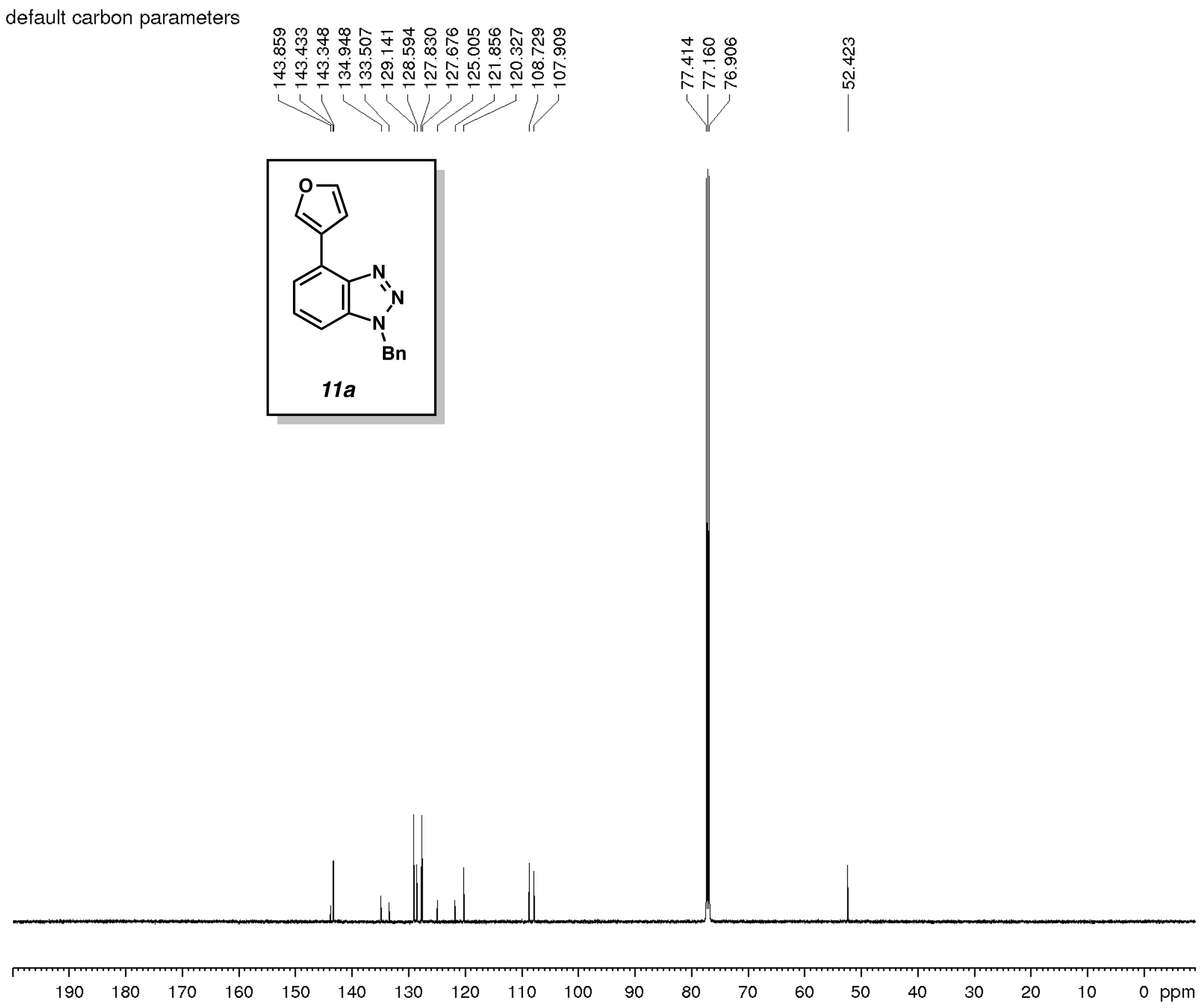


```
Current Data Parameters
NAME     JMM-2-216(1) 600
EXPNO               3
PROCNO              1

F2 - Acquisition Parameters
Date_         20131118
Time            13.59
INSTRUM          av600
PROBHD   5 mm BB5
PULPROG         zgdc30
TD              65536
SOLVENT          CDCl3
NS                217
DS                  0
SWH         37593.984 Hz
FIDRES       0.573639 Hz
AQ          0.8716921 sec
RG            20642.5
DW             13.300 usec
DE               6.50 usec
TE              295.1 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1              13C
P1               9.75 usec
PL1              0.00 dB
PL1W      75.35659027 W
SFO1     150.9209173 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2           80.00 usec
PL2             -1.00 dB
PL12            14.14 dB
PL2W      31.62277603 W
PL12W      0.96827775 W
```

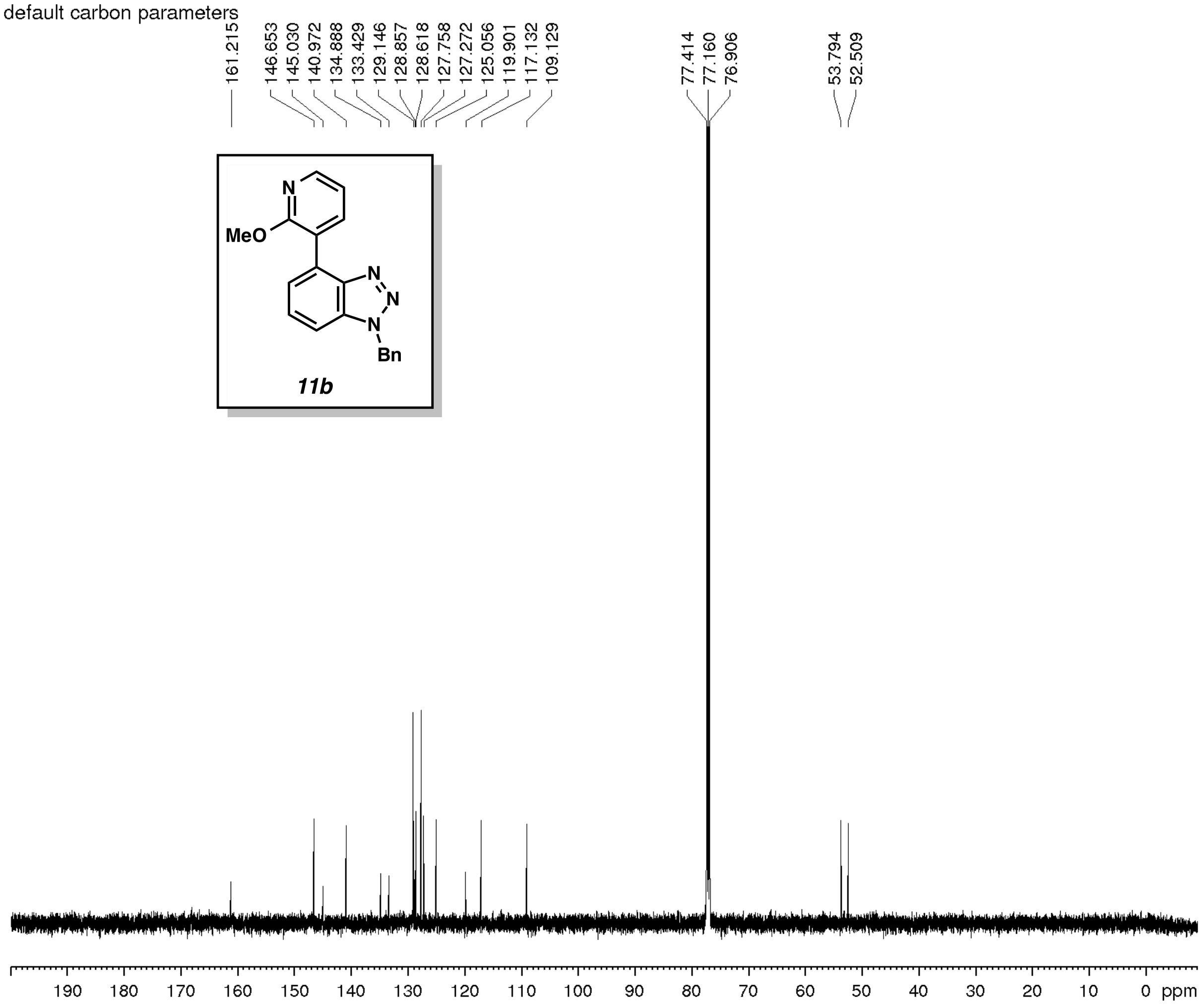
JMM-2-216(2).2



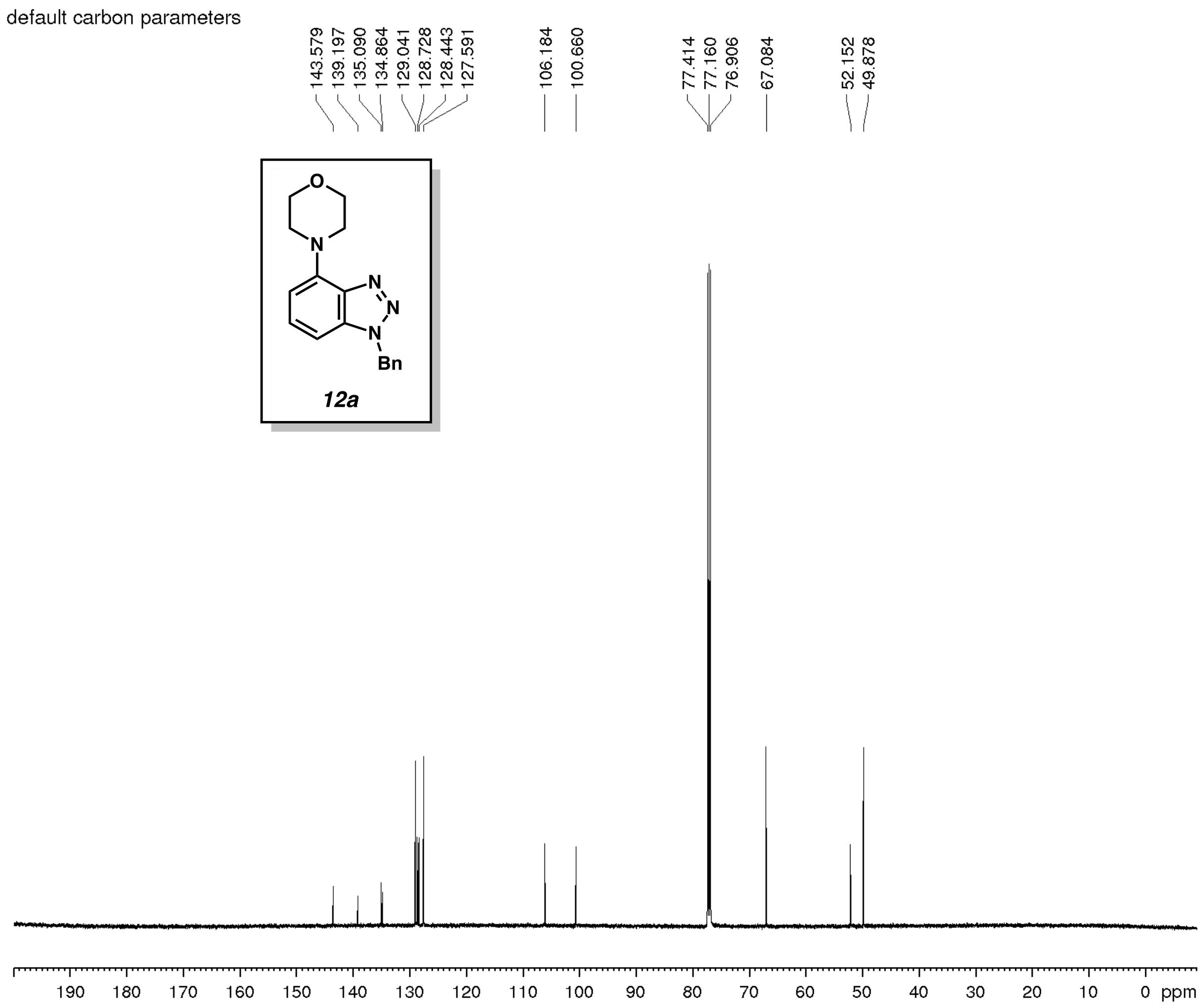
```
Current Data Parameters
NAME     JMM-2-216(2) 600
EXPNO              2
PROCNO             1

F2 - Acquisition Parameters
Date_        20131118
Time            13.24
INSTRUM         av600
PROBHD   5 mm BB5
PULPROG        zgdc30
TD             65536
SOLVENT         CDCl3
NS                501
DS                  0
SWH        37593.984 Hz
FIDRES      0.573639 Hz
AQ         0.8716921 sec
RG            14596.5
DW           13.300 usec
DE             6.50 usec
TE            295.0 K
D1       2.00000000 sec
D11      0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1              13C
P1               9.75 usec
PL1              0.00 dB
PL1W      75.35659027 W
SFO1      150.9209173 MHz

======== CHANNEL f2 ========
CPDPRG2       waltz16
NUC2               1H
PCPD2           80.00 usec
PL2             -1.00 dB
PL12            14.14 dB
PL2W      31.62277603 W
PL12W      0.96827775 W
```



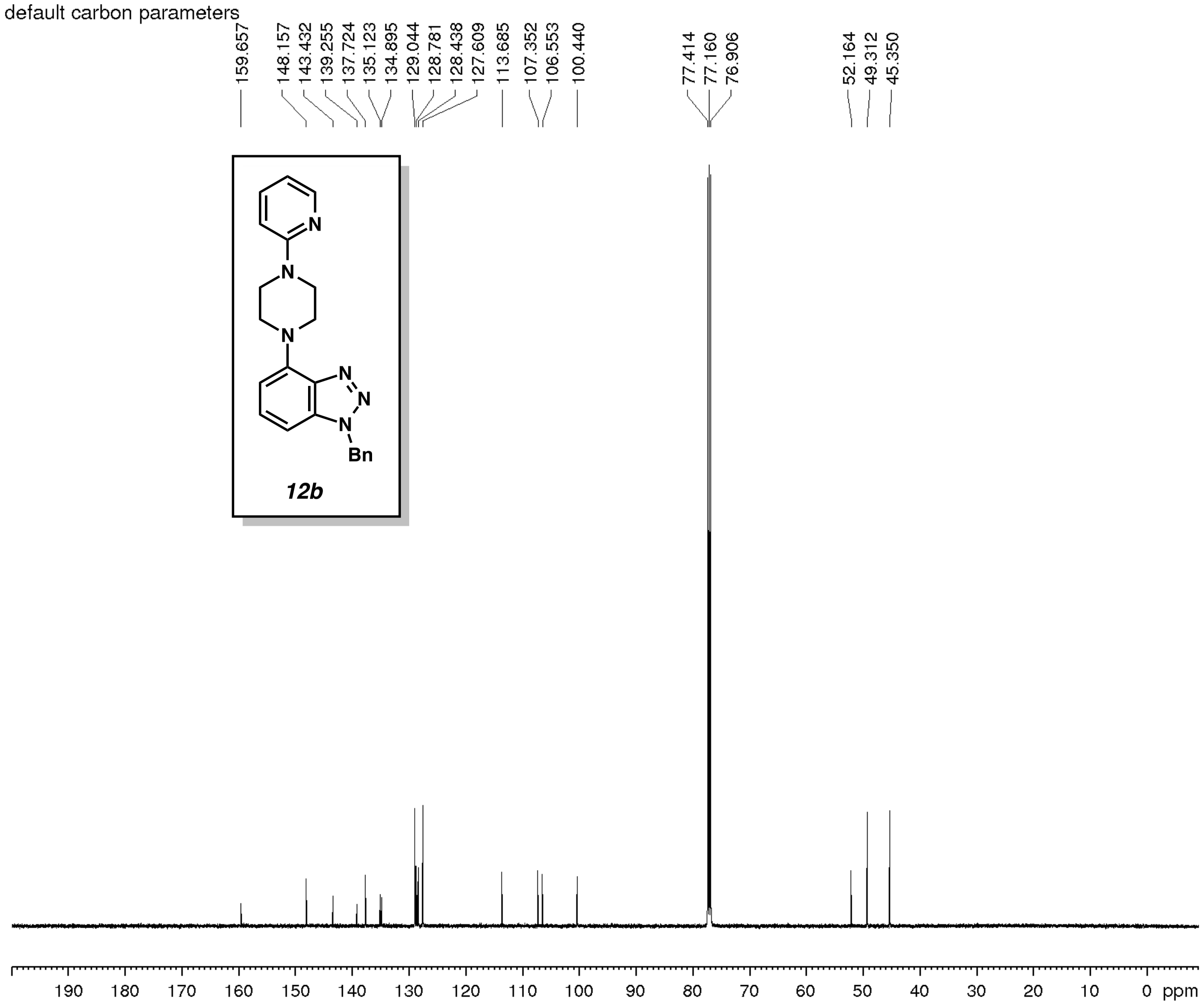
```
Current Data Parameters
NAME          JMM-3-79a
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20140412
Time              14.50
INSTRUM           av500
PROBHD   5 mm DCH 13C-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH          31250.000 Hz
FIDRES        0.476837 Hz
AQ           1.0485760 sec
RG               202.91
DW               16.000 usec
DE                18.00 usec
TE                298.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1       125.7722512 MHz
NUC1                13C
P1                 9.63 usec
PLW1        23.00000000 W

======== CHANNEL f2 ========
SFO2       500.1330008 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2        13.50000000 W
PLW12        0.21094000 W
PLW13        0.13500001 W

F2 - Processing parameters
SI               131072
SF         125.7577730 MHz
WDW                  EM
SSB     0
LB                 1.00 Hz
GB      0
PC                 1.40
```



```
Current Data Parameters
NAME          JMM-3-81a
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20140412
Time              14.57
INSTRUM           av500
PROBHD   5 mm DCH 13C-1
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                   18
DS                    2
SWH        31250.000 Hz
FIDRES      0.476837 Hz
AQ        1.0485760 sec
RG               202.91
DW           16.000 usec
DE            18.00 usec
TE              298.0 K
D1       2.00000000 sec
D11      0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1     125.7722512 MHz
NUC1                13C
P1            9.63 usec
PLW1     23.00000000 W

======== CHANNEL f2 ========
SFO2     500.1330008 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2        80.00 usec
PLW2     13.50000000 W
PLW12     0.21094000 W
PLW13     0.13500001 W

F2 - Processing parameters
SI               131072
SF       125.7577727 MHz
WDW                  EM
SSB      0
LB              1.00 Hz
GB       0
PC                 1.40
```



```
Current Data Parameters
NAME        JMM-3-133a
EXPNO               2
PROCNO              1

F2 - Acquisition Parameters
Date_        20140412
Time            15.12
INSTRUM         av500
PROBHD   5 mm DCH 13C-1
PULPROG        zgpg30
TD              65536
SOLVENT         CDCl3
NS                 27
DS                  2
SWH        31250.000 Hz
FIDRES      0.476837 Hz
AQ        1.0485760 sec
RG                 11
DW          16.000 usec
DE           18.00 usec
TE            298.0 K
D1      2.00000000 sec
D11     0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
SFO1     125.7722512 MHz
NUC1              13C
P1             9.63 usec
PLW1     23.00000000 W

======== CHANNEL f2 ========
SFO2     500.1330008 MHz
NUC2               1H
CPDPRG[2       waltz16
PCPD2         80.00 usec
PLW2     13.50000000 W
PLW12     0.21094000 W
PLW13     0.13500001 W

F2 - Processing parameters
SI             131072
SF       125.7577739 MHz
WDW                EM
SSB     0
LB            1.00 Hz
GB      0
PC              1.40
```



```
Current Data Parameters
NAME         JMM-3-94a
EXPNO               2
PROCNO              1

F2 - Acquisition Parameters
Date_         20140412
Time              15.05
INSTRUM           av500
PROBHD   5 mm DCH 13C-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   26
DS                    2
SWH         31250.000 Hz
FIDRES       0.476837 Hz
AQ          1.0485760 sec
RG               202.91
DW           16.000 usec
DE            18.00 usec
TE               298.0 K
D1       2.00000000 sec
D11      0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1      125.7722512 MHz
NUC1                 13C
P1              9.63 usec
PLW1      23.00000000 W

======== CHANNEL f2 ========
SFO2      500.1330008 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2          80.00 usec
PLW2      13.50000000 W
PLW12      0.21094000 W
PLW13      0.13500001 W

F2 - Processing parameters
SI               131072
SF        125.7577736 MHz
WDW                  EM
SSB     0
LB              1.00 Hz
GB      0
PC                 1.40
```

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