

Ligand and Base Free Copper(II)-Catalyzed C-N Bond Formation: Cross-coupling Reactions of Organoboron Compounds with Aliphatic Amines and Anilines

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General Synthetic Methods

CH₂Cl₂ was distilled from CaH₂ under argon. All other commercial solvents and reagents were used as received from the Aldrich Chemical Company, Fischer Scientific Ltd., EMD Chemicals Inc., Strem or BDH. The 4Å molecular sieves were purchased through the Aldrich Chemical Company in powdered form, activated and stored in a oven at 210 °C until their use. All glassware was oven dried at 210 °C and allowed to cool under a stream of dry oxygen. The oxygen gas (UHP/zero grade) was purchased from Air Products and was dried through a tube of Drierite (anhydrous CaSO₄) prior to connection to a manifold for delivery into the reaction flask.

Silica gel (60Å, 230-400 mesh) used in flash column chromatography was obtained from Silicycle and was used as received. Analytical thin-layer chromatography (TLC) was performed on pre-coated silica gel plates (Ultra Pure Silica Gel Plates purchased from Silicycle), visualized with a Spectroline UV₂₅₄ lamp, and stained with a 20% phosphomolybdic acid in ethanol solution. Solvent systems associated with R_f values and flash column chromatography are reported as v/v ratios.

Melting points were obtained using a Fisher-Johns melting point apparatus and are uncorrected. Specific optical rotations were determined on a Perkin-Elmer 243B Polarimeter under the conditions indicated using the sodium D line (589 nm). Sample concentrations are reported as grams per 100 mL solvent. Analytical chiral HPLC (of **3f**, **3n** and **3s**) was performed on a Chiralcel OD column (4.6 x 250 mm) obtained from Daicel Chemical Industries, Ltd. ¹H and ¹³C NMR were recorded at 300 MHz and 75 MHz respectively on a Varian Gemini 300 or Mercury 300 spectrometer. Proton chemical shifts were internally referenced to the residual proton resonance in CDCl₃ (δ 7.26 ppm). Carbon chemical shifts were internally referenced to the deuterated solvent signals in CDCl₃ (δ 77.20 ppm). FT-IR spectra were recorded on a Perkin-Elmer Spectrum 1000 spectrometer with samples loaded as neat films on NaCl plates. Low and high resolution mass spectra were recorded on a Bell and Howell 21-490 spectrometer and an AEI MS3074 spectrometer respectively.

References following compound names indicate literature articles where ¹H and ¹³C NMR data have previously been reported.

Synthetic Methods and Characterization Data

Representative Procedure for the Cross-Coupling of $\text{PhBF}_3^-\text{K}^+$ with Aliphatic Amines

A suspension of $\text{PhBF}_3^-\text{K}^+$ (0.368 g, 2.00 mmol), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (20.0 mg, 0.100 mmol), and powdered 4Å molecular sieves (0.750 g) in CH_2Cl_2 (8.00 mL) was stirred for 5 minutes at room temperature. To this stirring suspension was added *n*-butylamine (0.072 g, 99.0 µL, 1.00 mmol). The reaction mixture was then sealed with a rubber septa (heated if necessary), and stirred under an atmosphere of O_2 . Following a period of 24 h, the crude reaction mixture was filtered through a plug of celite to remove the molecular sieves and any insoluble byproducts and then concentrated *in vacuo* to afford the crude product mixture. The product (**3a**) was isolated by silica gel column chromatography (eluting with hexanes:EtOAc 9:1 ~ 3:1 gradient) as a pale yellow oil in 89% yield (0.133 g, 0.89 mmol).

Representative Procedure for the Cross-Coupling of $\text{PhB}(\text{OH})_2$ with Aliphatic Amines

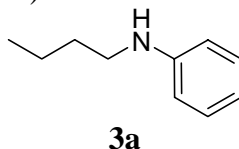
The above procedure was followed with substitution of $\text{PhB}(\text{OH})_2$ (0.244 g, 2.00 mmol) in place of the potassium organotrifluoroborate salt. The product (**3a**) was isolated as a pale yellow oil in 92% yield (0.137 g, 0.89 mmol).

Representative Procedure for the Activation of Amine Hydrohalide Salts and Subsequent Cross-Coupling with $\text{PhB}(\text{OH})_2$

To a stirring solution of 3-bromopropylamine hydrobromide (0.219 g, 1.00 mL) in acetonitrile (10.0 mL) was added Amberlyst A-21 resin (0.750 g). The suspension was stirred at room temperature for 30 min, then filtered and washed with CH_2Cl_2 to remove the resin. The filtrant was collected and concentrated *in vacuo*. The residue was then redissolved in acetonitrile (1.00 mL) and added to a prestirring suspension of $\text{PhB}(\text{OH})_2$ (0.244 g, 2.00 mmol), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (20.0 mg, 0.100 mmol), and powdered 4Å molecular sieves (0.750 g) in CH_2Cl_2 (8.00 mL). The reaction mixture was then sealed with a rubber septa, heated to 40 °C, and stirred under an atmosphere of O_2 . Following a period of 24 h, the crude reaction mixture was filtered through a plug of celite to remove the molecular sieves and any insoluble byproducts, and then concentrated *in vacuo* to afford the crude product mixture. The product (**3l**) was isolated by silica gel column chromatography (eluting with hexanes:EtOAc 9:1 ~ 3:1 gradient) as a clear oil in 86% yield (0.184 g, 0.860 mmol).

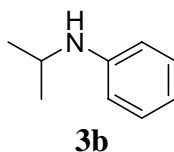
Products of Experiments Summarized in Table 1

***n*-Butylphenylamine** (Alberti, A.; Cane, F.; Dembech, P.; Lazzari, D.; Ricci, A.; Seconi, G. *J. Org. Chem.* **1996**, *61*, 1677-1681.)



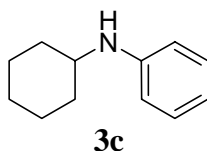
Reactions were performed at room temperature. Product was isolated as a pale yellow oil in 89% yield from $\text{PhBF}_3^-\text{K}^+$ and in 92% yield from PhB(OH)_2 : $R_f = 0.80$ (3:1 hexanes:EtOAc); ^1H NMR (300 MHz, CDCl_3) δ 7.22 (2H, ddd, $J = 8.5, 7.5, 1.0$ Hz), 6.74 (1H, tt, $J = 7.5, 1.0$ Hz), 6.65 (2H, dd, $J = 8.5, 1.0$ Hz), 3.62 (1H, br s), 3.15 (2H, tt, $J = 7.0$ Hz), 1.65 (2H, quintet, $J = 7.0$ Hz), 1.48 (2H, sextet, $J = 7.0$ Hz), 1.01 (3H, t, $J = 7.5$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 148.70, 129.35, 117.19, 112.81, 43.80, 31.83, 20.48, 14.06.

Isopropylphenylamine (Shaffer, C. L.; Morton, M. D.; Hanzlik, R. P. *J. Am. Chem. Soc.* **2001**, *123*, 8502-8508.)



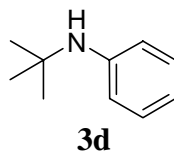
Reactions were performed at room temperature. Product was isolated as a clear oil in 98% yield from both $\text{PhBF}_3^-\text{K}^+$ and PhB(OH)_2 : $R_f = 0.70$ (9:1 hexanes:EtOAc); ^1H NMR (300 MHz, CDCl_3) δ 7.25 (2H, ddd, $J = 8.0, 7.5, 1.0$ Hz), 6.75 (1H, tt, $J = 7.5, 1.0$ Hz), 6.66 (2H, dd, $J = 8.0, 1.0$ Hz), 3.71 (1H, septet, $J = 6.5$ Hz), 3.50 (1H, br s), 1.28 (6H, d, $J = 6.5$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 147.64, 129.40, 117.05, 113.34, 44.28, 23.14.

Cyclohexylphenylamine (Kawakami, T.; Sugimoto, T.; Shibata, I.; Baba, A.; Matsuda, H.; Sonoda, N. *J. Org. Chem.* **1995**, *60*, 2677-2682.)



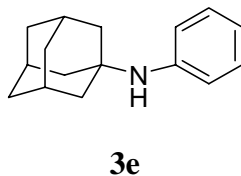
Product was isolated as a clear oil in 79% yield from $\text{PhBF}_3^-\text{K}^+$ at room temperature; and in 85% yield from PhB(OH)_2 at 40 °C: $R_f = 0.60$ (3:1 hexanes:EtOAc); ^1H NMR (300 MHz, CDCl_3) δ 7.17 (2H, ddd, $J = 8.5, 7.5, 2.0$ Hz), 6.67 (1H, tt, $J = 7.5, 1.0$ Hz), 6.61 (2H, ddd, $J = 8.5, 2.0, 1.0$ Hz), 3.53 (1H, br s), 3.27 (1H, dddd, $J = 14.0, 7.5, 6.5, 4.0$ Hz), 2.14 - 2.02 (2H, m), 1.84 - 1.62 (3H, m), 1.48 - 1.10 (5H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 147.59, 129.43, 116.99, 113.30, 51.86, 33.68, 26.13, 25.21.

***t*-Butylphenylamine** (Arnauld, T.; Barton, D. H. R.; Doris, E. *Tetrahedron* **1997**, 53, 4137-4144.)



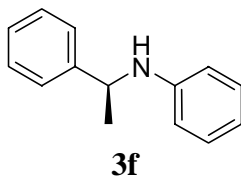
Product was isolated as a light beige oil in 26% yield from $\text{PhBF}_3^-\text{K}^+$ at room temperature; and in 39% yield from $\text{PhB}(\text{OH})_2$ at 40 °C: $R_f = 0.40$ (9:1 hexanes:EtOAc); ^1H NMR (300 MHz, CDCl_3) δ 7.16 (2H, t, $J = 7.5$ Hz), 6.8 - 6.72 (3H, m), 3.34 (1H, br s), 1.34 (9H, s); ^{13}C NMR (75 MHz, CDCl_3) δ 147.06, 129.08, 118.49, 117.68, 51.66, 30.28.

Adamantan-1-ylphenylamine (Olifirov, D. I.; Koshchii, V. A.; Kozlikovskii, Y. B. *J. Org. Chem. USSR (Engl. Transl.)*, **1992**, 28, 152-157.)

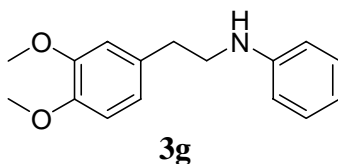


Reactions were performed at 40 °C. Product was isolated as a pale beige solid in 57% yield from $\text{PhBF}_3^-\text{K}^+$ and in 67% yield from $\text{PhB}(\text{OH})_2$: $R_f = 0.60$ (3:1 hexanes:EtOAc); ^1H NMR (300 MHz, CDCl_3) δ 7.19 - 7.13 (2H, m), 6.83 - 6.77 (3H, m), 3.31 (1H, br s), 2.12 (3H, m), 1.88 (6H, d, $J = 3.0$ Hz), 1.77 - 1.71 (6H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 146.21, 128.89, 119.25, 119.19, 52.35, 43.62, 36.63, 29.87; LRMS (EI): m/z (rel. intensity) = 229 (9), 227 (51), 171 (15), 170 (100), 135 (41), 133 (9), 107 (5), 94 (5), 93 (21), 92 (11), 91 (7), 79 (14), 77 (12), 67 (6); HRMS (EI): m/z calcd. for (M^+) = 227.1674, found = 227.1673.

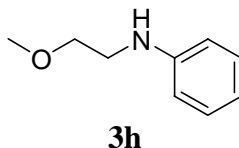
S-(-)-N-(1-Phenylethyl)aniline (Landor, S. R.; Sonola, O. O.; Tatchell, A. R. *Bull. Chem. Soc. Jpn.* **1984**, 57, 1658-1661.)



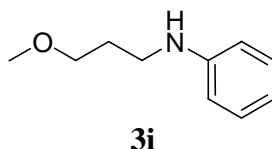
Product was isolated as a clear oil in 91% yield from $\text{PhBF}_3^-\text{K}^+$ at room temperature: $R_f = 0.44$ (9:1 hexanes:EtOAc); $[\alpha]_D^{22} = -5.15^\circ$ ($c = 10$, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.37 - 7.15 (5H, m), 7.07 (2H, t, $J = 7.5$ Hz), 6.63 (1H, t, $J = 7.5$ Hz), 6.49 (2H, d, $J = 7.5$ Hz), 4.46 (1H, q, $J = 7.0$ Hz), 3.98 (1H, br s), 1.48 (3H, d, $J = 7.0$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 147.42, 145.37, 129.24, 128.77, 127.00, 125.98, 117.36, 113.43, 53.57, 25.16.

[2-(3,4-Dimethoxyphenyl)ethyl]phenylamine

Product was isolated as a clear oil in 90% yield from $\text{PhBF}_3^-\text{K}^+$ at room temperature; and in 95% yield from $\text{PhB}(\text{OH})_2$ at 40 °C: $R_f = 0.70$ (1:1 hexanes:EtOAc); ^1H NMR (300 MHz, CDCl_3) δ 7.20 (2H, ddd, $J = 8.0, 7.5, 1.0$ Hz), 6.86 - 6.70 (4H, m), 6.63 (2H, dd, $J = 7.5, 1.0$ Hz), 3.88 (3H, s), 3.87 (3H, s), 3.68 (1H, br s), 3.40 (2H, t, $J = 7.0$ Hz), 2.88 (2H, t, $J = 7.0$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 149.13, 148.15, 147.78, 131.94, 129.39, 120.80, 117.59, 113.16, 112.17, 111.53, 56.06, 55.96, 45.23, 35.13; IR (film) ν 3394, 2932, 2360, 1603, 1513, 1465, 1419, 1319, 1261, 1235, 1156, 1140, 1027, 809, 750, 693 cm^{-1} ; LRMS (EI): m/z (rel. intensity) = 257 (12), 152 (23), 151 (8), 107 (12), 106 (100), 86 (7), 84 (11), 79 (5), 77 (15); HRMS (EI): m/z calcd. for (M^+) = 257.1416, found = 257.1418.

(2-Methoxyethyl)phenylamine

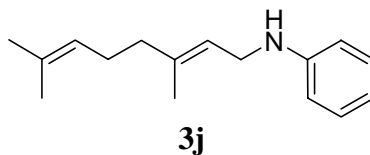
Product was isolated as a clear oil in 32% yield from $\text{PhBF}_3^-\text{K}^+$ at room temperature; and in 79% yield from $\text{PhBF}_3^-\text{K}^+$ and 94% yield from $\text{PhB}(\text{OH})_2$ at 40 °C: $R_f = 0.40$ (3:1 hexanes:EtOAc); ^1H NMR (300 MHz, CDCl_3) δ 7.19 (2H, t, $J = 7.5$ Hz), 6.70 (1H, t, $J = 7.5$ Hz), 6.61 (2H, d, $J = 7.5$ Hz), 4.02 (1H, br s), 3.57 (2H, t, $J = 5.0$ Hz), 3.37 (3H, s), 3.26 (2H, t, $J = 5.0$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 148.31, 129.31, 117.67, 113.17, 71.09, 58.81, 43.53; IR (film) ν 3051, 2925, 2891, 1603, 1506, 1472, 1319, 1259, 1193, 1117, 1071, 1025, 871, 750, 693 cm^{-1} ; LRMS (EI): m/z (rel. intensity) = 152 (9), 151 (48), 107 (14), 106 (100), 94 (7), 79 (12), 78 (5), 77 (24), 65 (7), 51 (11); HRMS (EI): m/z calcd. for (M^+) = 151.0997, found = 151.0991.

(3-Methoxypropyl)phenylamine

Product was isolated as a clear oil in 78% yield from $\text{PhBF}_3^-\text{K}^+$ at room temperature; and in 85% yield from $\text{PhB}(\text{OH})_2$ at 40 °C: $R_f = 0.50$ (3:1 hexanes:EtOAc); ^1H NMR (300 MHz, CDCl_3) δ 7.19 (2H, ddd, $J = 7.5, 3.0, 1.0$ Hz), 6.70 (1H, tt, $J = 7.5, 1.0$ Hz), 6.63 (2H, dd, $J = 7.5, 1.0$ Hz), 3.94 (1H, br s), 3.53 (2H, t, $J = 6.0$ Hz), 3.37 (3H, s), 3.24 (2H, t, $J = 6.0$ Hz), 1.90 (2H, quintet, $J = 6.0$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 148.66, 129.37, 117.27, 112.87, 71.37, 58.88, 41.92, 29.54; IR (film) ν 3394, 3051, 3021, 2924, 2871, 1604, 1508, 1478, 1433, 1389, 1321,

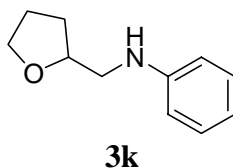
1262, 1180, 1117, 749, 693 cm^{-1} ; LRMS (EI): m/z (rel. intensity) = 166 (6), 165 (37), 107 (13), 106 (100), 104 (6), 93 (11), 79 (10), 77 (18), 65 (6), 51 (7); HRMS (EI): m/z calcd. for (M^+) = 165.1154, found = 165.1150.

(3,7-Dimethylocta-2,6-dienyl)phenylamine (Ranu, B. C.; Majee, A.; Sarkar, A. *J. Org. Chem.* **1998**, 63, 370-373.)



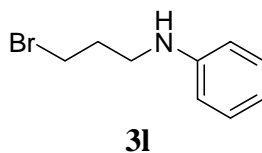
Reactions were performed at 40 °C. Product was isolated as a yellow oil in 80% yield from $\text{PhBF}_3^-\text{K}^+$ and in 89% yield from PhB(OH)_2 ; R_f = 0.75 (3:1 hexanes:EtOAc); ^1H NMR (300 MHz, CDCl_3) δ 7.29 (2H, ddd, J = 8.5, 7.5, 2.0 Hz), 6.82 (1H, tt, J = 7.5, 1.0 Hz), 6.72 (2H, ddd, J = 8.5, 2.0, 1.0 Hz), 5.49 - 5.41 (1H, m), 5.25 - 5.18 (1H, m), 3.81 (2H, d, J = 6.5 Hz), 3.67 (1H, br s), 2.28 - 2.14 (4H, m), 1.82 (3H, s), 1.81 (3H, s), 1.73 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 148.58, 139.10, 131.81, 129.33, 124.10, 121.70, 117.40, 113.02, 42.10, 39.67, 26.59, 25.86, 17.86, 16.51.

Phenyl(tetrahydrofuran-2-ylmethyl)amine



Reactions were performed at 40 °C. Product was isolated as a pale yellow oil in 83% yield from $\text{PhBF}_3^-\text{K}^+$ and in 91% yield from PhB(OH)_2 ; R_f = 0.33 (3:1 hexanes:EtOAc); ^1H NMR (300 MHz, CDCl_3) δ 7.20 (2H, ddd, J = 8.5, 7.5, 2.0 Hz), 6.74 (1H, tt, J = 7.5, 1.0 Hz), 6.66 (2H, ddd, J = 8.5, 2.0, 1.0 Hz), 4.15 (1H, dddd, J = 7.0, 7.0, 7.0, 4.0 Hz), 4.05 (1H, br s), 3.92 (1H, ddd, J = 8.0, 7.0, 7.0 Hz), 3.81 (1H, ddd, J = 8.0, 7.0, 7.0 Hz), 3.28 (1H, dd, J = 12.5, 4.0 Hz), 3.10 (1H, dd, J = 12.5, 7.5 Hz), 2.11 - 1.90 (3H, m), 1.74 - 1.62 (1H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 148.50, 129.28, 117.53, 113.10, 77.64, 68.12, 48.24, 29.19, 25.89; IR (film) ν 3390, 3051, 3021, 2971, 2869, 1603, 1506, 1459, 1433, 1378, 1360, 1320, 1256, 1180, 1070, 749, 693 cm^{-1} ; LRMS (EI): m/z (rel. intensity) = 178 (7), 177 (27), 107 (17), 106 (100), 79 (7), 77 (16), 71 (9), 50 (6); HRMS (EI): m/z calcd. for (M^+) = 177.1154, found = 177.1156.

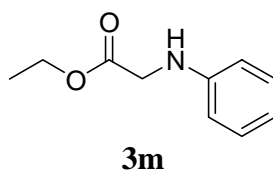
(3-Bromopropyl)phenyl amine



The amine hydrobromide salt was pretreated with Amberlyst A-21 resin. Reaction was performed at 40 °C. Product was isolated as a clear oil in 86% yield from PhB(OH)_2 over both

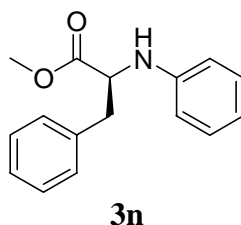
steps: $R_f = 0.30$ (9:1 hexanes:EtOAc); ^1H NMR (300 MHz, CDCl_3) δ 7.29 (2H, ddd, $J = 7.5, 2.0, 1.5$ Hz), 6.83 (1H, tt, $J = 7.5, 1.5$ Hz), 6.73 (2H, dd, $J = 7.5, 2.0$ Hz), 3.95 (1H, br s), 3.60 (2H, t, $J = 6.5$ Hz), 3.42 (2H, t, $J = 6.5$ Hz), 2.24 (2H, quintet, $J = 6.5$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 147.82, 129.46, 117.77, 113.01, 42.14, 32.07, 31.37; IR (film) ν 3410, 3051, 3021, 2961, 1603, 1507, 1431, 1322, 1255, 1180, 1100, 991, 870, 751, 693 cm^{-1} ; LRMS (EI): m/z (rel. intensity) = 215 (19), 213 (18), 107 (15), 106 (100), 104 (7), 79 (11), 78 (7), 77 (27), 65 (8); HRMS (EI): m/z calcd. for (M^+) = 213.0153, found = 213.0151.

N-Phenyl-glycine ethyl ester (Anderson, W. K.; Bhattacharjee, D.; Houston, D. M.; *J. Med. Chem.* **1989**, 32, 119-127.)



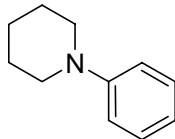
The amine hydrochloride salt was pretreated with Amberlyst A-21 resin. Reaction was performed at 40 °C. Product was isolated as a clear crystalline solid in 84% yield from PhB(OH)_2 over both steps: $R_f = 0.50$ (9:1 hexanes:EtOAc); ^1H NMR (300 MHz, CDCl_3) δ 7.21 (2H, t, $J = 7.5$ Hz), 6.76 (1H, dt, $J = 7.5, 1.0$ Hz), 6.62 (2H, dd, $J = 7.5, 1.0$ Hz), 4.28 (1H, br s), 4.25 (2H, q, $J = 7.0$ Hz), 3.91 (2H, s), 1.31 (3H, t, $J = 7.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 171.33, 147.20, 129.48, 118.37, 113.19, 61.49, 46.05, 14.36.

S-N-Phenyl-phenylalanine methyl ester (Tunge, J. A.; Gately, D. A.; Norton, J. R. *J. Amer. Chem. Soc.* **1999**, 121, 4520-4521.)



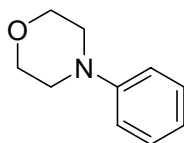
The amine hydrochloride salt was pretreated with Amberlyst A-21 resin. Reaction was performed at 40 °C. Product was isolated as a light beige oil in 90% yield from PhB(OH)_2 over both steps: $R_f = 0.40$ (3:1 hexanes:EtOAc); $[\alpha]_D^{22} = +25.88^\circ$ ($c = 10$, CH_2Cl_2) for >99% ee (Chiralcel OD, 10% ethanol/hexanes, 1.0 mL/min, retention times for R and S enantiomers are 7.16 and 9.78 min respectively) with determination of the absolute stereochemistry by comparison of the specific rotation with the literature value; ^1H NMR (300 MHz, CDCl_3) δ 7.48 - 7.28 (7H, m), 6.90 (1H, t, $J = 7.5$ Hz), 6.75 (2H, d, $J = 7.5$ Hz), 4.53 (1H, t, $J = 6.5$ Hz), 4.36 (1H, br s), 3.79 (3H, s), 3.28 (2H, ddd, $J = 20.0, 13.5, 6.5$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 173.62, 146.39, 136.38, 129.39, 129.28, 128.55, 127.03, 118.41, 113.56, 57.70, 52.03, 38.62.

N-Phenylpiperidine (Brenner, E.; Schneider, R.; Fort, Y.; *Tetrahedron*, **1999**, 55, 12829-12842.)

**3o**

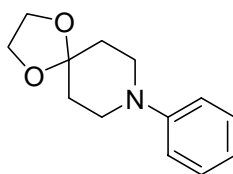
Product was isolated as a clear oil in 78% yield from $\text{PhBF}_3^-\text{K}^+$ at room temperature; and in 86% yield from PhB(OH)_2 at 40 °C: R_f = 0.40 (3:1 hexanes:EtOAc); ^1H NMR (300 MHz, CDCl_3) δ 7.25 (2H, dt, J = 7.5, 1.0 Hz), 6.94 (2H, dd, J = 7.5, 1.0 Hz), 6.82 (1H, dt, J = 7.5, 1.0 Hz), 3.16 (4H, t, J = 5.5 Hz), 1.76 - 1.66 (4H, m), 1.62 - 1.53 (2H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 152.47, 129.19, 119.36, 116.72, 50.87, 26.07, 24.52.

4-Phenyl-morpholine (Ishikawa, T.; Uedo, E.; Tani, R.; Saito, S. *J. Org. Chem.* **2001**, 66, 186-191.)

**3p**

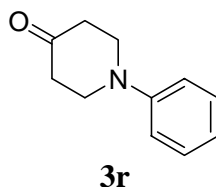
Reactions were performed at 40 °C. Product was isolated as a pale light beige, crystalline solid in 81% yield from $\text{PhBF}_3^-\text{K}^+$ and in 90% yield from PhB(OH)_2 : R_f = 0.45 (3:1 hexanes:EtOAc); ^1H NMR (300 MHz, CDCl_3) δ 7.31 (2H, ddd, J = 9.0, 7.5, 1.5 Hz), 6.96 - 6.88 (3H, m), 3.91 - 3.85 (4H, m), 3.20 - 3.15 (4H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 151.41, 129.33, 120.17, 115.83, 67.08, 49.48.

8-Phenyl-1,4-dioxo-8-azaspiro[4.5]decane

**3q**

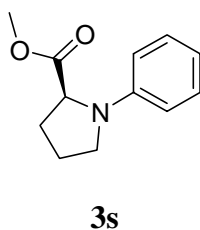
Reactions were performed at 40 °C. Product was isolated as a clear oil in 87% yield from $\text{PhBF}_3^-\text{K}^+$ and in 86% yield from PhB(OH)_2 : R_f = 0.40 (3:1 hexanes:EtOAc); ^1H NMR (300 MHz, CDCl_3) δ 7.34 (2H, ddd, J = 7.5, 2.0, 1.5 Hz), 7.04 (2H, dd, J = 7.5, 2.0 Hz), 6.93 (1H, dt, J = 7.5, 1.5 Hz), 4.07 (4H, s), 3.42 (4H, dd, J = 6.0, 6.0 Hz), 1.94 (4H, dd, J = 6.0, 6.0 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 151.08, 129.19, 119.49, 116.70, 107.27, 64.41, 47.83, 34.64; IR (film) ν 2956, 2882, 2828, 1599, 1497, 1466, 1365, 1228, 1143, 1105, 1037, 962, 946, 929, 896, 757, 693, 529 cm^{-1} ; LRMS (EI): m/z (rel. intensity) = 220 (18), 219 (100), 218 (10), 174 (28), 158 (20), 133 (18), 132 (55), 106 (11), 105 (73), 104 (25), 77 (21); HRMS (EI): m/z calcd. for (M^+) = 219.1259, found = 219.1265.

1-Phenyl-piperidin-4-one (Hermant, R. M.; Bakker, N. A. C.; Scherer, T.; Krijnen, B.; Verhoeven, J. W. *J. Amer. Chem. Soc.* **1990**, *112*, 1214-1221.)



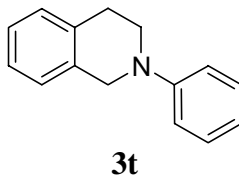
The amine hydrochloride salt was pretreated with Amberlyst A-21 resin. Reaction was performed at 40 °C. Product was isolated as a light beige solid in 83% yield from PhB(OH)₂ over both steps: R_f = 0.33 (3:1 hexanes:EtOAc); ¹H NMR (300 MHz, CDCl₃) δ 7.29 (2H, ddd, J = 7.5, 2.0, 1.5 Hz), 6.97 (2H, dd, J = 7.5, 2.0 Hz), 6.91 (1H, dt, J = 7.5, 1.5 Hz), 3.60 (4H, t, J = 6.0 Hz), 2.54 (4H, t, J = 6.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 208.35, 149.25, 129.58, 119.96, 116.01, 48.96, 40.86.

N-Phenyl-L-proline methyl ester (Ishikawa, T.; Uedo, E.; Tani, R.; Saito, S. *J. Org. Chem.* **2001**, *66*, 186-191.)



The amine hydrochloride salt was pretreated with Amberlyst A-21 resin. Reaction was performed at 40 °C. Product was isolated as a pale yellow oil in 74% yield from PhB(OH)₂ over both steps: R_f = 0.50 (3:1 hexanes:EtOAc); $[\alpha]_D^{22}$ = -13.81 ° (c = 1.0, CHCl₃) for >99% ee (Chiralcel OD, 10% ethanol/hexanes, 1.0 mL/min, retention times for R and S enantiomers are 6.19 and 8.77 min respectively) with determination of the absolute stereochemistry by comparison of the specific rotation with the literature value; ¹H NMR (300 MHz, CDCl₃) δ 7.32 (2H, ddd, J = 7.5, 2.0, 1.5 Hz), 6.81 (1H, dt, J = 7.5, 1.5 Hz), 6.64 (2H, dd, J = 7.5, 2.0 Hz), 4.34 (1H, dd, J = 8.0, 2.0 Hz), 3.80 (3H, s), 3.70 - 3.66 (1H, m), 3.49 - 3.40 (1H, m), 2.45 - 2.07 (4H, m); ¹³C NMR (100 MHz, CDCl₃) δ 175.10, 146.79, 129.35, 116.77, 112.04, 52.20, 48.37, 31.02, 23.99.

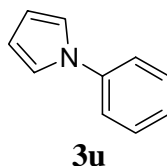
2-Phenyl-1,2,3,4-tetrahydroisoquinoline (Almena, J.; Foubelo, F.; Yus, M. *Tetrahedron* **1996**, *52*, 8545-8564.)



Reactions were performed at room temperature. Product was isolated as a clear oil in 72% yield from both PhBF₃⁻K⁺ and PhB(OH)₂: R_f = 0.50 (9:1 hexanes:EtOAc); ¹H NMR (300 MHz,

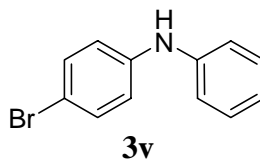
CDCl_3) δ 7.36 - 7.13 (6H, m), 7.02 (2H, d, $J = 7.5$ Hz), 6.87 (1H, t, $J = 7.5$ Hz), 4.45 (2H, s), 3.60 (2H, t, $J = 6.0$ Hz), 3.03 (2H, t, $J = 6.0$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 150.44, 134.41, 129.16, 128.98, 128.48, 126.51, 126.30, 126.00, 118.66, 115.16.

1-Phenyl-pyrrole (Lee, C. K.; Jun, J. H.; Yu, J. S. *J. Heterocycl. Chem.* **2000**, 37, 15-24.)



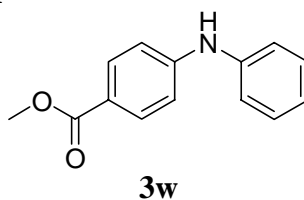
Reactions were performed at 40 °C. Product was isolated as a clear, crystalline solid in 80% yield from $\text{PhBF}_3^-\text{K}^+$ and in 89% yield from PhB(OH)_2 : $R_f = 0.60$ (9:1 hexanes:EtOAc); ^1H NMR (300 MHz, CDCl_3) δ 7.56 - 7.48 (4H, m), 7.38 - 7.31 (1H, m), 7.20 (2H, t, $J = 2.0$ Hz), 6.46 (2H, t, $J = 2.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 140.89, 129.69, 125.75, 120.66, 119.46, 110.55.

4-Bromodiphenylamine (Barchiesi, E.; Bradamante, S.; Pagani, G. A. *J. Chem. Soc. Perkin Trans. 2* **1987**, 1091-1096.)

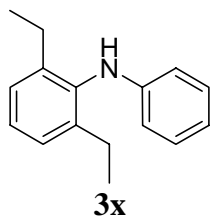


Reactions were performed at 40 °C. Product was isolated as a clear, crystalline solid in 30% yield from $\text{PhBF}_3^-\text{K}^+$ and in 53% yield from PhB(OH)_2 : $R_f = 0.40$ (3:1 hexanes:EtOAc); ^1H NMR (300 MHz, CDCl_3) δ 7.35 - 7.22 (4H, m), 7.06 - 6.88 (5H, m), 5.63 (1H, br s); ^{13}C NMR (100 MHz, CDCl_3) δ 142.56, 142.53, 132.31, 129.90, 121.79, 119.17, 118.43, 112.74.

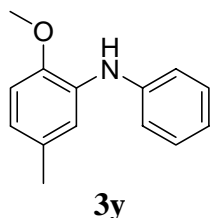
4-Anilinobenzoic acid methyl ester



Reactions were performed at room temperature. Product was isolated as a beige, crystalline solid in 35% yield from $\text{PhBF}_3^-\text{K}^+$ and in 40% yield from PhB(OH)_2 : $R_f = 0.60$ (1:1 hexanes:EtOAc); ^1H NMR (300 MHz, CDCl_3) δ 7.92 (2H, d, $J = 8.5$ Hz), 7.34 (2H, t, $J = 8.0$ Hz), 7.17 (2H, d, $J = 8.0$ Hz), 7.07 (1H, t, $J = 8.0$ Hz), 6.99 (2H, d, $J = 8.5$ Hz), 6.07 (1H, br s), 3.88 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 167.16, 148.27, 141.03, 131.65, 129.67, 123.28, 121.26, 120.62, 114.75, 51.89; IR (film) ν 3343, 1695, 1591, 1521, 1496, 1434, 1328, 1282, 1172, 1109, 850, 769, 747, 693 cm^{-1} ; LRMS (EI): m/z (rel. intensity) = 228 (24), 227 (100), 197 (21), 196 (95), 168 (23), 167 (56), 166 (14), 98 (11), 84 (20), 77 (15), 51 (11); HRMS (EI): m/z calcd. for (M^+) = 227.0946, found = 227.0919.

(2,6-Diethylphenyl)phenylamine

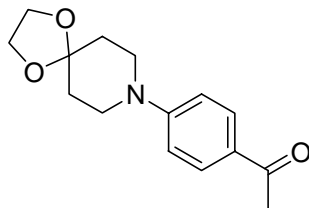
Reactions were performed at room temperature. Product was isolated as an amber oil in 34% yield from $\text{PhBF}_3^-\text{K}^+$ and in 49% yield from $\text{PhB}(\text{OH})_2$: $R_f = 0.70$ (3:1 hexanes:EtOAc); ^1H NMR (300 MHz, CDCl_3) δ 7.23 - 7.06 (5H, m), 6.71 (1H, tt, $J = 7.5, 1.0$ Hz), 6.47 (2H, dd, $J = 8.5, 1.0$ Hz), 5.13 (1H, br s), 2.58 (4H, q, $J = 7.5$ Hz), 1.14 (6H, t, $J = 7.5$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 147.45, 142.52, 129.91, 129.36, 126.84, 126.69, 118.10, 113.41, 24.86, 14.86; IR (film) ν 3396, 3044, 2965, 2872, 1603, 1497, 1454, 1412, 1374, 1306, 1237, 1175, 1106, 1077, 1026, 994, 866, 798, 747, 693 cm^{-1} ; LRMS (EI): m/z (rel. intensity) = 226 (29), 225 (100), 211 (24), 210 (92), 208 (20), 196 (18), 194 (14), 193 (13), 182 (15), 181 (32), 180 (53), 170 (15), 168 (11), 167 (13), 148 (12), 134 (13), 91 (12), 77 (19), 51 (12); HRMS (EI): m/z calcd. for (M^+) = 225.1518, found = 225.1519.

(2-Methoxy-5-methylphenyl)phenylamine

Reactions were performed at room temperature. Product was isolated as an orange oil in 51% yield from $\text{PhBF}_3^-\text{K}^+$ and in 66% yield from $\text{PhB}(\text{OH})_2$: $R_f = 0.60$ (3:1 hexanes:EtOAc); ^1H NMR (300 MHz, CDCl_3) δ 7.31 (2H, t, $J = 7.5$ Hz), 7.17 (3H, d, $J = 7.5$ Hz), 6.97 (1H, tt, $J = 7.5, 1.0$ Hz), 6.80 (1H, d, $J = 8.0$ Hz), 6.67 (1H, dd, $J = 8.0, 1.0$ Hz), 6.13 (1H, br s), 3.88 (3H, s), 2.29 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 146.45, 142.97, 132.90, 130.41, 129.42, 121.23, 120.26, 118.82, 115.64, 110.70, 55.94, 21.16; IR (film) ν 3410, 3047, 2935, 2860, 2833, 1594, 1526, 1496, 1463, 1413, 1311, 1293, 1244, 1221, 1176, 1156, 1079, 1033, 956, 865, 795, 748, 725, 708, 694, 620 cm^{-1} ; LRMS (EI): m/z (rel. intensity) = 214 (19), 213 (100), 199 (15), 198 (89), 197 (17), 183 (33), 170 (26), 155 (11), 154 (11), 77 (12); HRMS (EI): m/z calcd. for (M^+) = 213.1154, found = 213.1160.

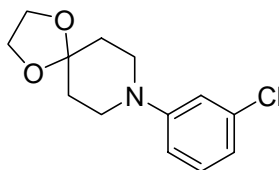
Products of Experiments Summarized in Table 3

8-(4-Acetylphenyl)-1,4-dioxaspiro[4.5]decane (Ogawa, K.; Kaji, M.; Kagawa, H.; Sagawa, M.; Kakuta, A. *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **1994**, 50, 95-97.)

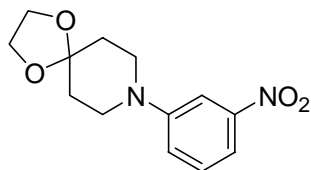
**4a**

Reaction was performed at 40 °C. Product was isolated as a clear, crystalline solid in 93% yield from PhB(OH)₂: R_f = 0.10 (3:1 hexanes:EtOAc); ¹H NMR (300 MHz, CDCl₃) δ 7.84 (2H, ddd, J = 10.0, 5.0, 3.0 Hz), 6.85 (2H, ddd, J = 10.0, 5.0, 3.0 Hz), 3.98 (4H, s), 3.50 (4H, dd, J = 6.0, 6.0 Hz), 2.50 (3H, s), 1.78 (4H, dd, J = 6.0, 6.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 196.54, 153.58, 130.63, 127.21, 113.60, 107.14, 64.55, 45.95, 34.38, 26.22.

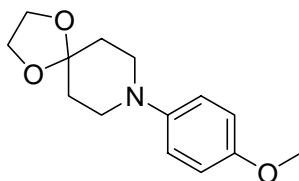
8-(3-Chlorophenyl)-1,4-dioxaspiro[4.5]decane

**4b**

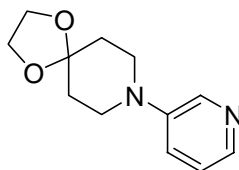
Reaction was performed at 40 °C. Product was isolated as a clear oil in 85% yield from PhB(OH)₂: R_f = 0.30 (3:1 hexanes:EtOAc); ¹H NMR (300 MHz, CDCl₃) δ 7.14 (1H, t, J = 8.0 Hz), 6.89 (1H, t, J = 2.0 Hz), 6.82 - 6.75 (2H, m), 3.98 (4H, s), 3.33 (4H, dd, J = 6.0, 6.0 Hz), 1.81 (4H, dd, J = 6.0, 6.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 152.00, 135.03, 130.18, 119.01, 116.27, 114.42, 107.15, 64.50, 47.35, 34.47; IR (film) ν 2958, 2883, 1595, 1563, 1487, 1466, 1365, 1231, 1144, 1097, 1037, 945, 768, 683 cm⁻¹; LRMS (EI): m/z (rel. intensity) = 255 (37), 254 (21), 253 (100), 210 (10), 208 (30), 194 (11), 192 (21), 168 (16), 167 (18), 166 (42), 141 (26), 140 (15), 139 (74), 138 (20), 111 (13), 86 (11); HRMS (EI): m/z calcd. for (M⁺) = 253.0869, found = 253.0870.

8-(3-Nitrophenyl)-1,4-dioxaspiro[4.5]decane**4c**

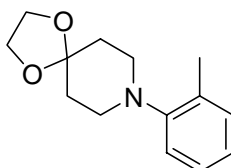
Reaction was performed at 40 °C. Product was isolated as a bright yellow oil in 84% yield from PhB(OH)₂: R_f = 0.25 (3:1 hexanes:EtOAc); ¹H NMR (300 MHz, CDCl₃) δ 7.68 (1H, t, J = 2.0 Hz), 7.57 (1H, ddd, J = 8.0, 2.0, 1.0 Hz), 7.32 (1H, t, J = 8.0 Hz), 7.16 (1H, ddd, J = 8.0, 2.0, 1.0 Hz), 3.97 (4H, s), 3.40 (4H, dd, J = 6.0, 6.0 Hz), 1.78 (4H, dd, J = 6.0, 6.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 151.34, 149.35, 129.79, 121.52, 113.27, 109.96, 106.86, 64.51, 46.98, 34.27; IR (film) ν 2960, 2886, 1616, 1526, 1349, 1234, 1144, 1112, 1036, 946, 856, 737, 674 cm⁻¹; LRMS (EI): m/z (rel. intensity) = 265 (19), 264 (93), 219 (46), 204 (12), 203 (35), 178 (24), 177 (48), 151 (13), 150 (100), 149 (10), 132 (12), 105 (15), 104 (15), 99 (17), 86 (14), 77 (15); HRMS (EI): m/z calcd. for (M⁺) = 264.1110, found = 264.1109.

8-(4-Methoxyphenyl)-1,4-dioxaspiro[4.5]decane**4d**

Reaction was performed at 40 °C. Product was isolated as a clear, crystalline solid in 95% yield from PhB(OH)₂: mp = 60 - 61 °C (hexanes); R_f = 0.20 (3:1 hexanes:EtOAc); ¹H NMR (300 MHz, CDCl₃) δ 6.92 (2H, ddd, J = 10.0, 6.0, 3.5 Hz), 6.82 (2H, ddd, J = 10.0, 6.0, 3.5 Hz), 3.98 (4H, s), 3.76 (3H, s), 3.18 (4H, dd, J = 5.5, 5.5 Hz), 1.86 (4H, dd, J = 5.5, 5.5 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 153.82, 145.74, 119.05, 114.44, 107.16, 64.41, 55.62, 49.47, 34.95; IR (film) ν 2956, 2821, 1512, 1466, 1442, 1417, 1368, 1288, 1249, 1224, 1180, 1115, 1036, 949, 896, 832, 704 cm⁻¹; LRMS (EI): m/z (rel. intensity) = 250 (26), 249 (100), 235 (11), 234 (51), 204 (12), 188 (10), 163 (13), 162 (42), 136 (12), 135 (63), 133 (18), 121 (11), 120 (41), 99 (11), 92 (10), 86 (11), 84 (16), 55 (12), 51 (12); HRMS (EI): m/z calcd. for (M⁺) = 249.1365, found = 249.1361.

8-(Pyridin-3-yl)-1,4-dioxaspiro[4.5]decane**4e**

Reaction was performed at 40 °C. Product was isolated as light orange oil in 55% yield from PhB(OH)₂: R_f = 0.10 (1:1 CH₂Cl₂:EtOAc); ¹H NMR (300 MHz, CDCl₃) δ 8.31 (1H, s), 8.05 (1H, d, J = 3.5 Hz), 7.18 (1H, ddd, J = 8.5, 3.5, 1.5 Hz), 7.11 (1H, dd, J = 8.5, 3.5 Hz), 3.98 (4H, s), 3.34 (4H, dd, J = 5.5, 5.5 Hz), 1.82 (4H, dd, J = 5.5, 5.5 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 146.77, 140.50, 139.20, 123.60, 122.90, 106.98, 64.53, 47.24, 34.46; IR (film) ν 2958, 2884, 1672, 1582, 1488, 1426, 1365, 1235, 1144, 1102, 1052, 1035, 946, 930, 799, 708, 670, 614 cm⁻¹; LRMS (EI): m/z (rel. intensity) = 221 (14), 220 (82), 175 (32), 159 (26), 134 (17), 133 (55), 107 (15), 106 (100), 105 (29), 99 (20), 86 (20), 78 (21), 55 (11), 51 (10); HRMS (EI): m/z calcd. for (M⁺) = 220.1212, found = 220.1217.

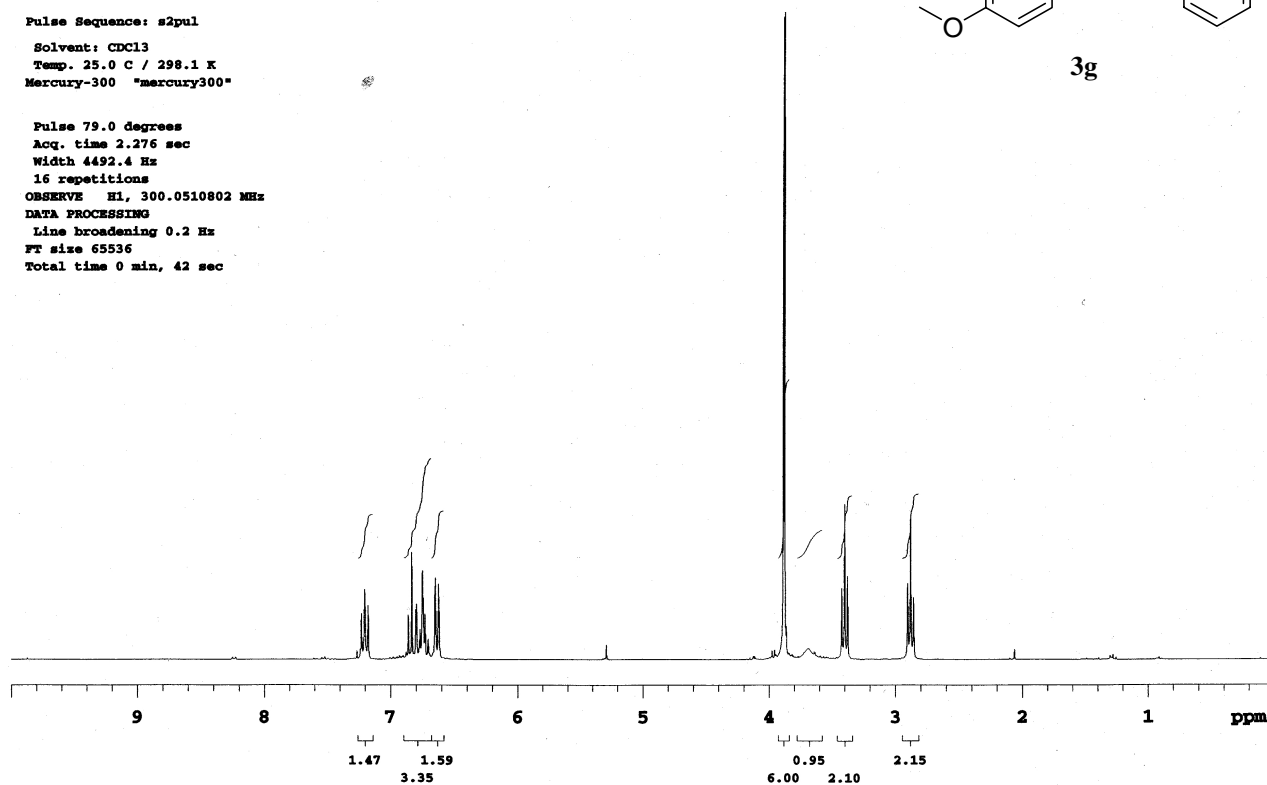
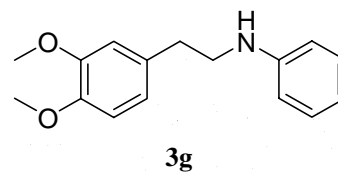
8-*o*-Tolyl-1,4-dioxaspiro[4.5]decane**4f**

Reaction was performed at 40 °C. Product was isolated as a pale yellow oil in 61% yield from PhB(OH)₂: R_f = 0.33 (9:1 hexanes:EtOAc); ¹H NMR (300 MHz, CDCl₃) δ 7.24 - 7.18 (2H, m), 7.07 (1H, dd, J = 7.5, 1.0 Hz), 6.99 (1H, dt, J = 7.5, 1.0 Hz), 4.02 (4H, s), 3.01 (4H, dd, J = 5.5, 5.5 Hz), 2.34 (3H, s), 1.91 (4H, dd, J = 5.5, 5.5 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 151.95, 132.76, 131.05, 126.60, 123.14, 119.38, 107.30, 64.41, 50.27, 35.79, 17.90; IR (film) ν 2955, 2880, 2823, 1599, 1493, 1470, 1363, 1328, 1217, 1142, 1101, 1038, 931, 899, 762, 724, 666 cm⁻¹; LRMS (EI): m/z (rel. intensity) = 234 (22), 233 (100), 232 (16), 188 (41), 172 (19), 147 (15), 146 (55), 132 (17), 119 (42), 118 (44), 91 (18); HRMS (EI): m/z calcd. for (M⁺) = 233.1416, found = 233.1411.

STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl₃
Temp. 25.0 C / 298.1 K
Mercury-300 "mercury300"

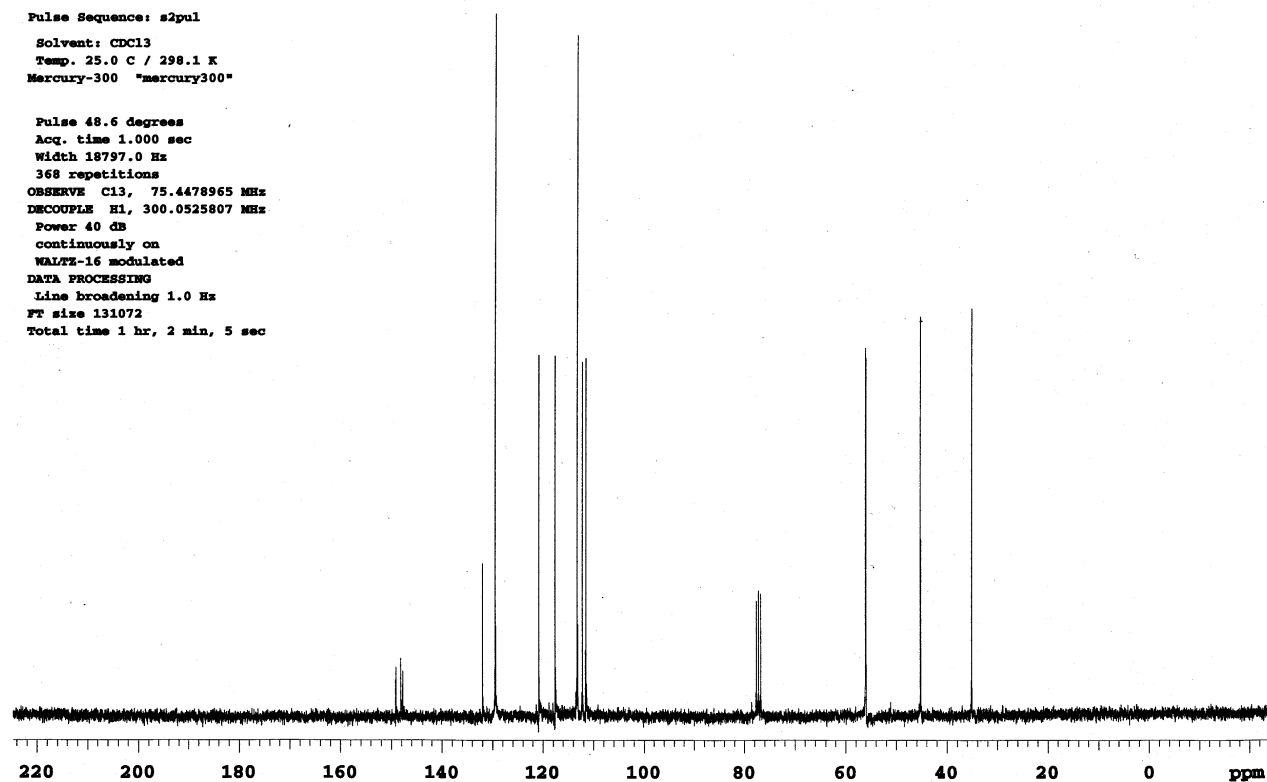
Pulse 79.0 degrees
Acq. time 2.276 sec
Width 4492.4 Hz
16 repetitions
OBSERVE H1, 300.0510802 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 0 min, 42 sec

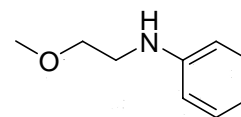


13C OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl₃
Temp. 25.0 C / 298.1 K
Mercury-300 "mercury300"

Pulse 48.6 degrees
Acq. time 1.000 sec
Width 18797.0 Hz
368 repetitions
OBSERVE C13, 75.4478965 MHz
DECOUPLE H1, 300.0525807 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 1 hr, 2 min, 5 sec





3h

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

GEMINI-300BB "gemin300"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.998 sec

Width 4500.5 Hz

16 repetitions

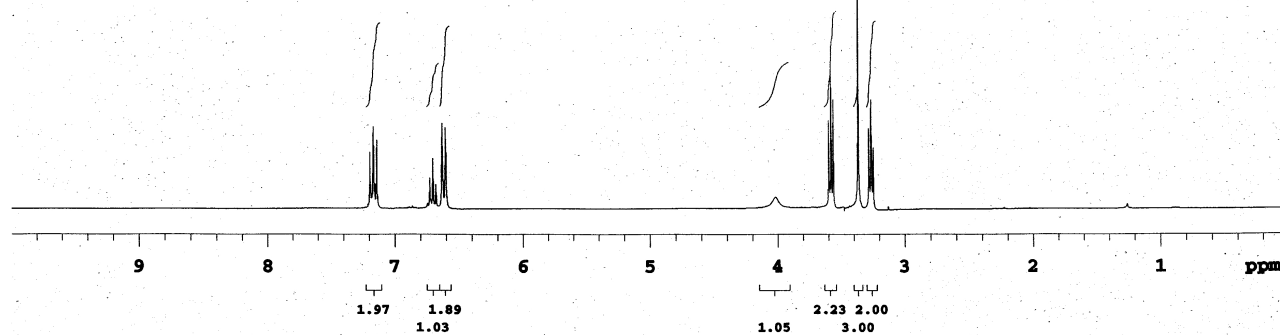
OBSERVE H1, 300.0738366 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 32768

Total time 0 min, 53 sec



13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

GEMINI-300BB "gemin300"

Pulse 28.6 degrees

Acq. time 1.815 sec

Width 18761.7 Hz

136 repetitions

OBSERVE C13, 75.4536182 MHz

DECOUPLE H1, 300.0753189 MHz

Power 33 dB

continuously on

WALTZ-16 modulated

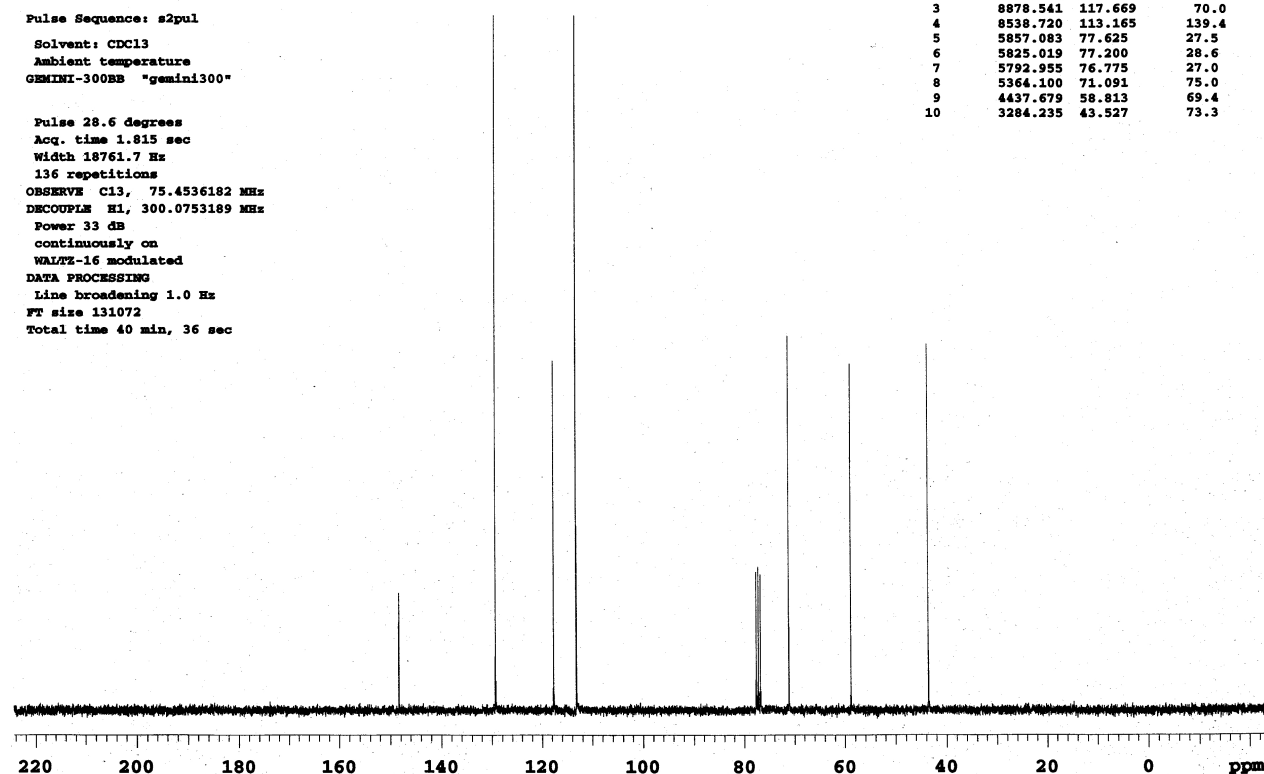
DATA PROCESSING

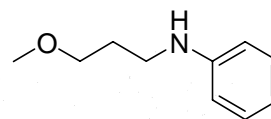
Line broadening 1.0 Hz

FT size 131072

Total time 40 min, 36 sec

INDEX	FREQUENCY	PPM	HEIGHT
1	11190.298	148.307	23.3
2	9757.152	129.313	139.5
3	8878.541	117.669	70.0
4	8538.720	113.165	139.4
5	5857.083	77.625	27.5
6	5825.019	77.200	28.6
7	5792.955	76.775	27.0
8	5364.100	71.091	75.0
9	4437.679	58.813	69.4
10	3284.235	43.527	73.3





3i

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Temp. 25.0 C / 298.1 K

Mercury-300 "mercury300"

Relax. delay 5.000 sec

Pulse 79.0 degrees

Acq. time 2.276 sec

Width 4492.4 Hz

16 repetitions

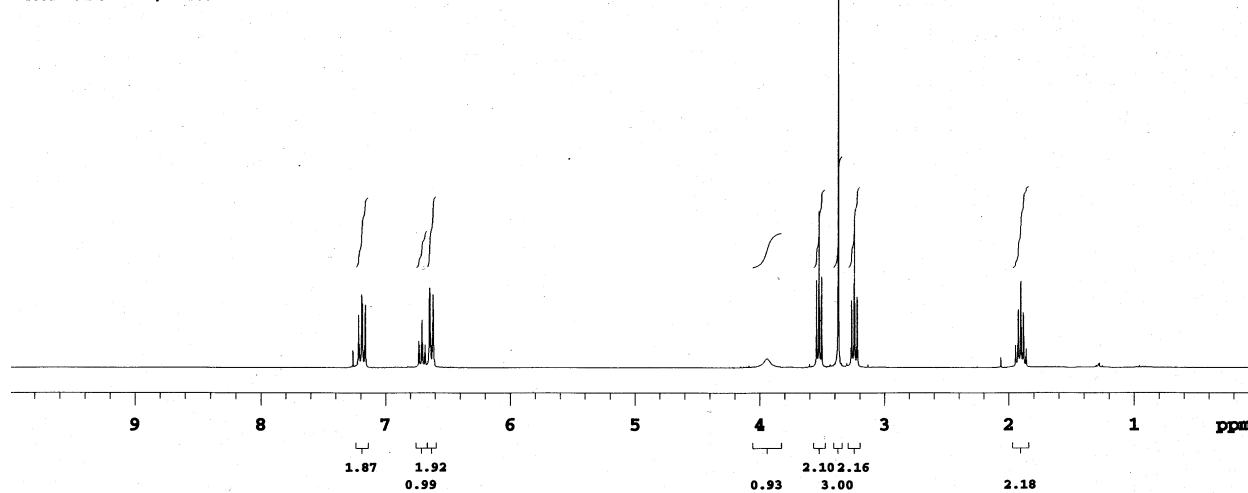
OBSERVE H1, 300.0510805 MHz

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 2 min, 2 sec



13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3

Temp. 25.0 C / 298.1 K

Mercury-300 "mercury300"

Pulse 48.6 degrees

Acq. time 1.000 sec

Width 18797.0 Hz

424 repetitions

OBSERVE C13, 75.4478928 MHz

DECOUPLE H1, 300.0525807 MHz

Power 40 dB

continuously on

WALTZ-16 modulated

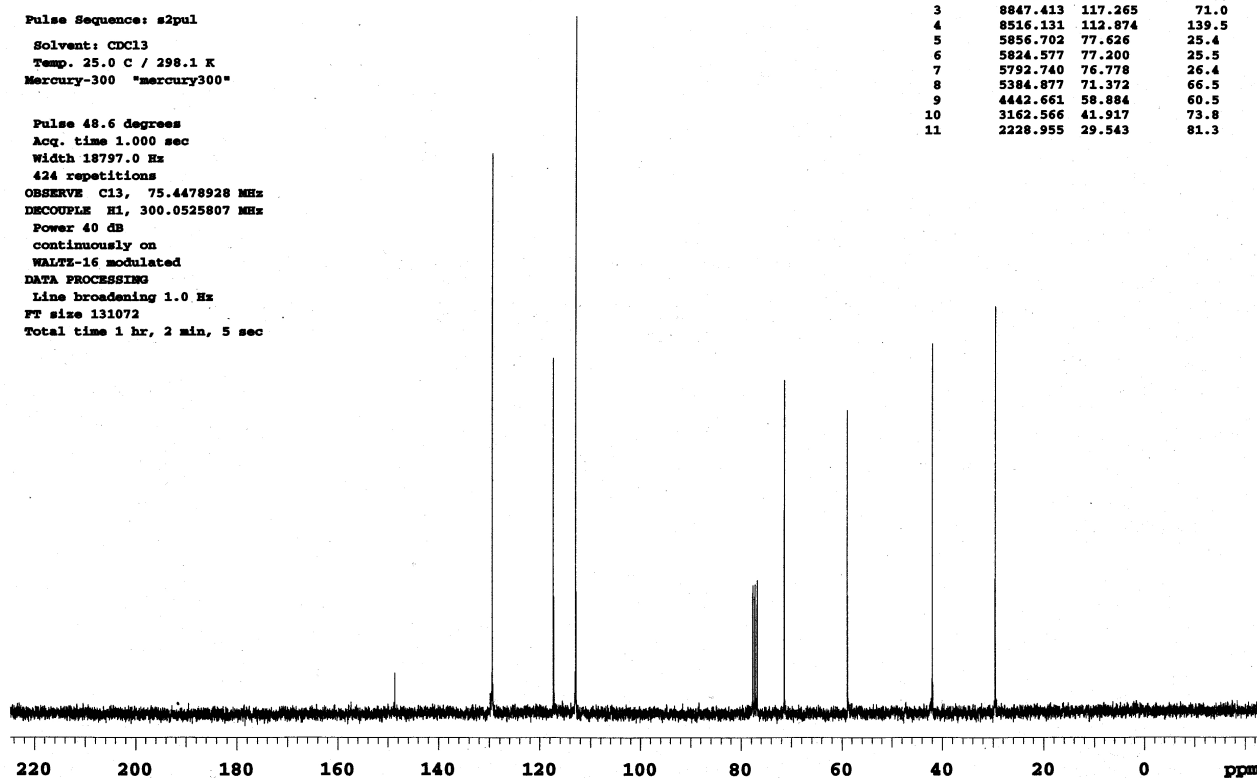
DATA PROCESSING

Line broadening 1.0 Hz

FT size 131072

Total time 1 hr, 2 min, 5 sec

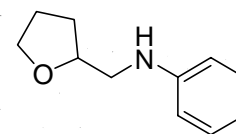
INDEX	FREQUENCY	PPM	HEIGHT
1	11216.290	148.663	7.9
2	9760.659	129.370	112.0
3	8847.413	117.265	71.0
4	8516.131	112.874	139.5
5	5856.702	77.626	25.4
6	5824.577	77.200	25.5
7	5792.740	76.778	26.4
8	5384.877	71.372	66.5
9	4442.661	58.884	60.5
10	3162.566	41.917	73.8
11	2228.955	29.543	81.3



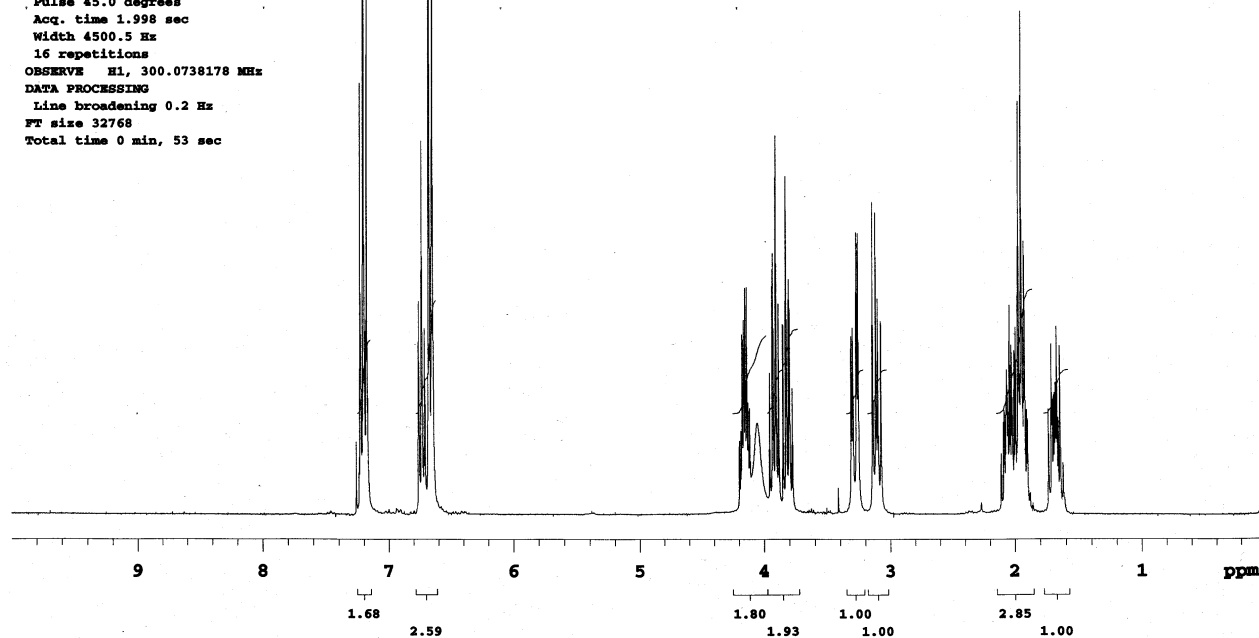
STANDARD 1H OBSERVE

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 GEMINI-300BS "gemin300"

Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.998 sec
 Width 4500.5 Hz
 16 repetitions
 OBSERVE H1, 300.0738178 MHz
 DATA PROCESSING
 Line broadening 0.2 Hz
 FT size 32768
 Total time 0 min, 53 sec



3k

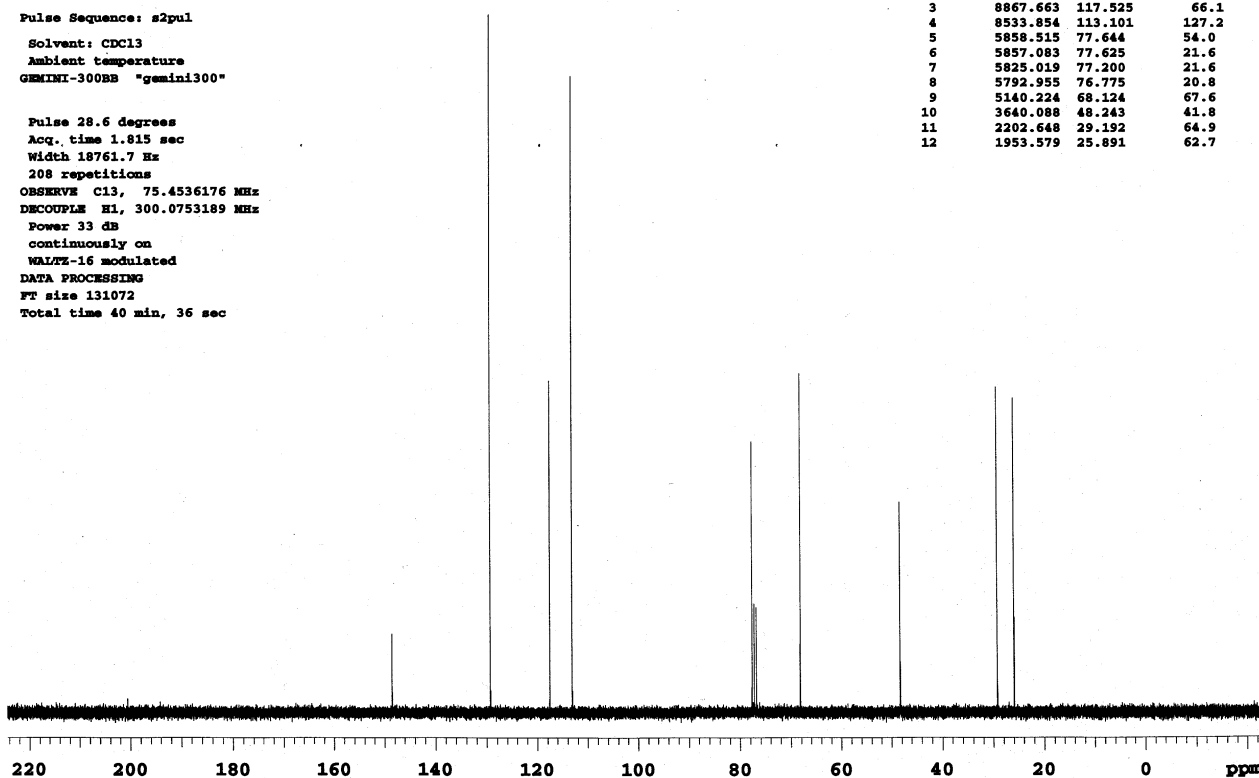


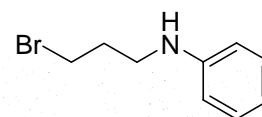
13C OBSERVE

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 GEMINI-300BS "gemin300"

Pulse 28.6 degrees
 Acq. time 1.815 sec
 Width 18761.7 Hz
 208 repetitions
 OBSERVE C13, 75.4536176 MHz
 DECOUPLE H1, 300.0753189 MHz
 Power 33 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 FT size 131072
 Total time 40 min, 36 sec

INDEX	FREQUENCY	PPM	HEIGHT
1	11204.612	148.497	15.6
2	9754.862	129.283	139.5
3	8867.663	117.525	66.1
4	8533.854	113.101	127.2
5	5858.515	77.644	54.0
6	5857.083	77.625	21.6
7	5825.019	77.200	21.6
8	5792.955	76.775	20.8
9	5140.224	68.124	67.6
10	3640.088	48.243	41.8
11	2202.648	29.192	64.9
12	1953.579	25.891	62.7



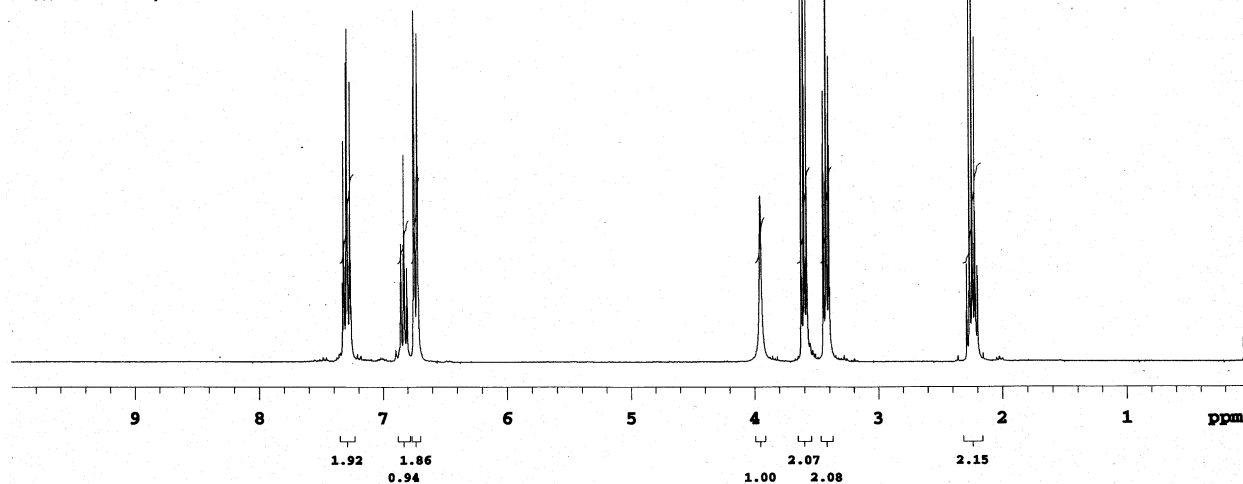


3l

STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300BB "gemin300"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.998 sec
Width 4500.5 Hz
16 repetitions
OBSERVE H1, 300.0737984 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 0 min, 53 sec

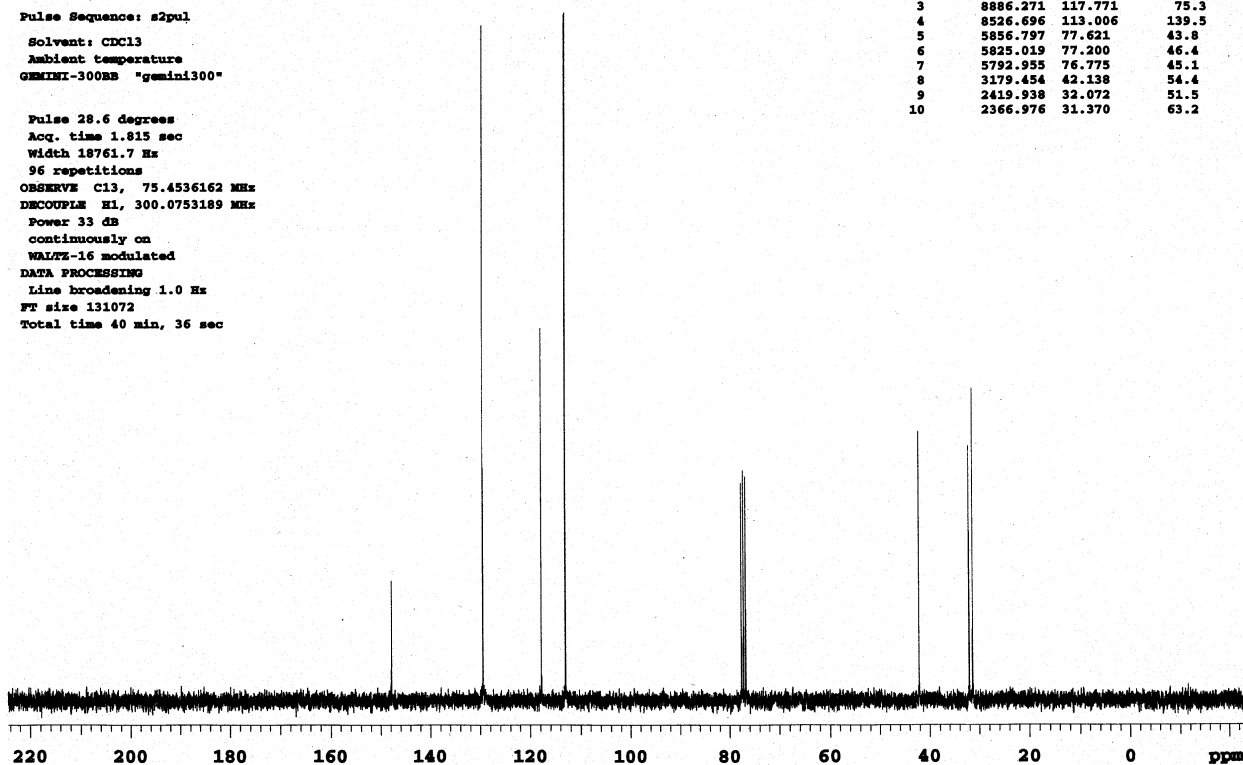


13C OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300BB "gemin300"

Pulse 28.6 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
96 repetitions
OBSERVE C13, 75.4536162 MHz
DECOUPLE H1, 300.0753189 MHz
Power 33 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 40 min, 36 sec

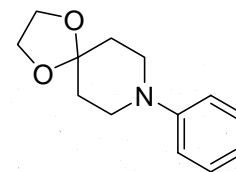
INDEX	FREQUENCY	PPM	HEIGHT
1	11153.367	147.818	24.1
2	9768.317	129.461	136.9
3	8886.271	117.771	75.3
4	8526.696	113.006	139.5
5	5856.797	77.621	43.8
6	5825.019	77.200	46.4
7	5792.955	76.775	45.1
8	3179.454	42.138	54.4
9	2419.938	32.072	51.5
10	2366.976	31.370	63.2



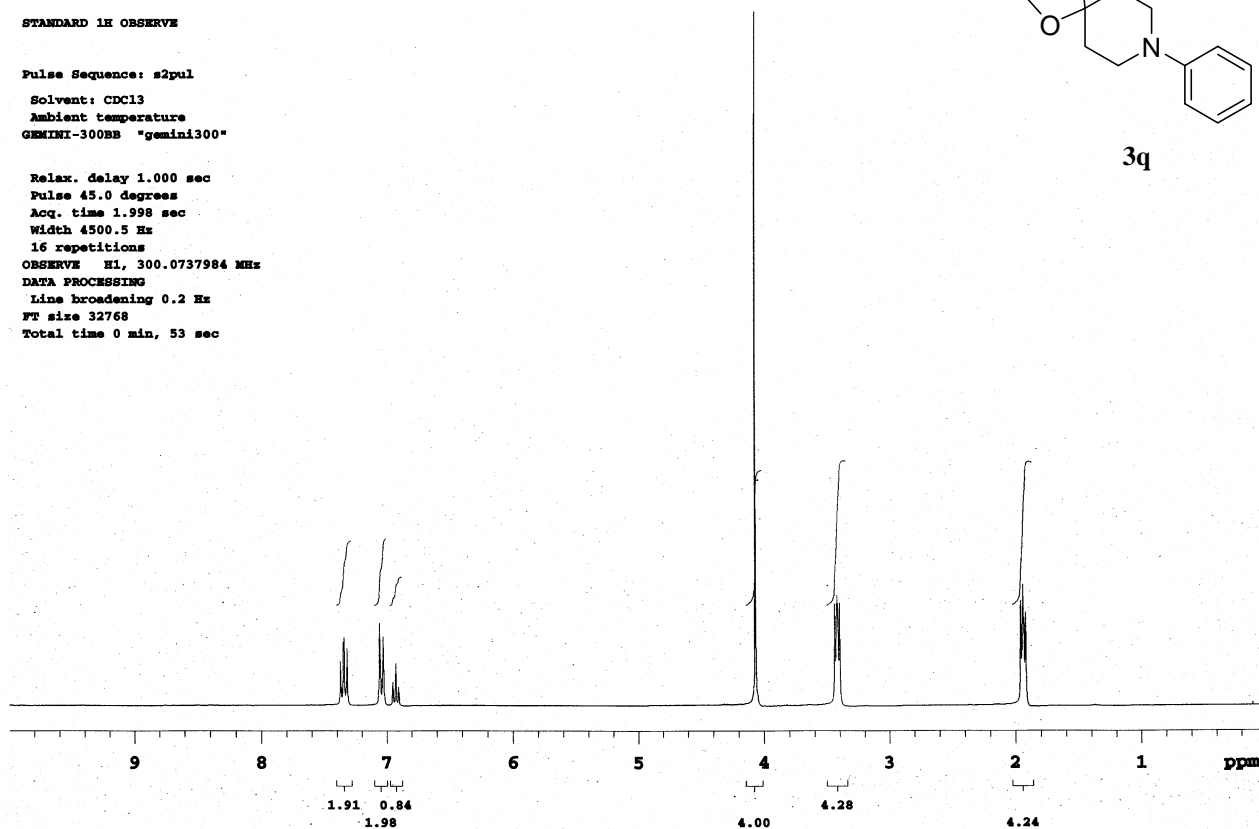
STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300BB "gemin300"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.998 sec
Width 4500.5 Hz
16 repetitions
OBSERVE H1, 300.0737984 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 0 min, 53 sec



3q

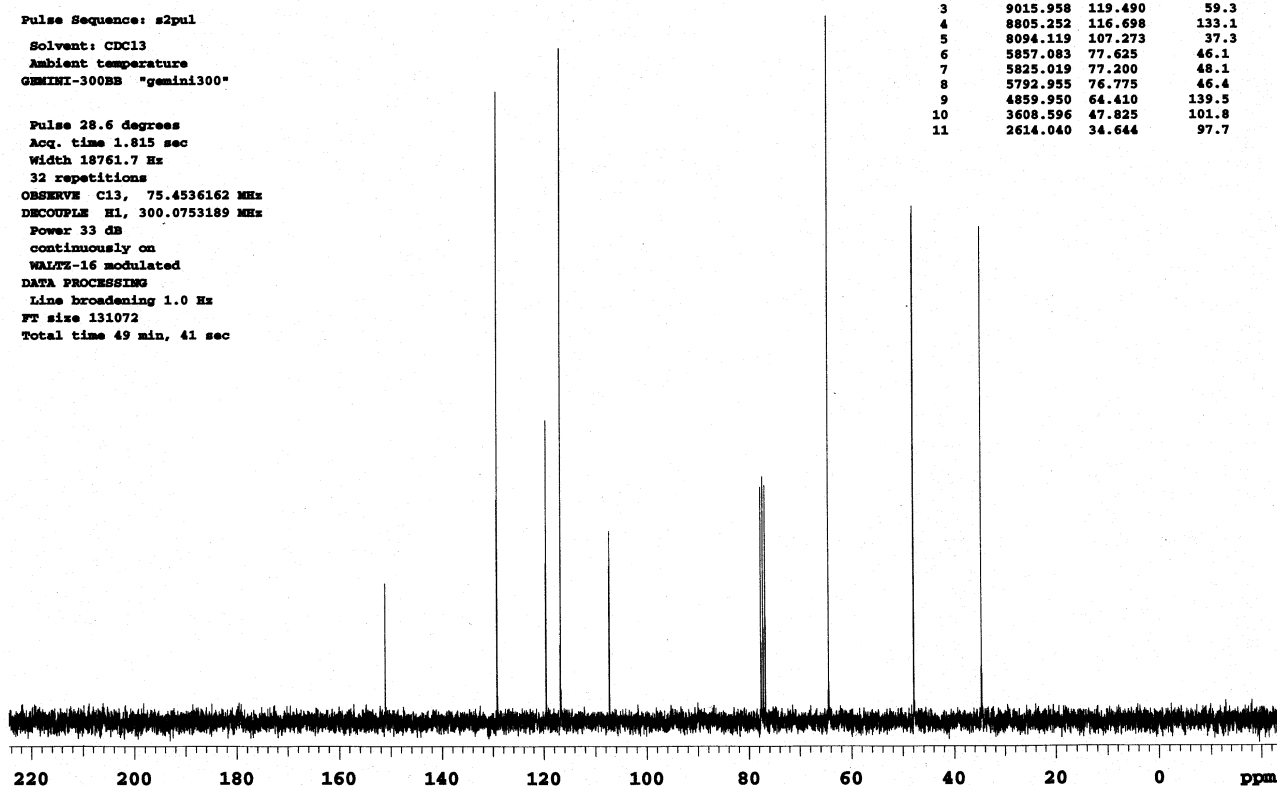


13C OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300BB "gemin300"

Pulse 28.6 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
32 repetitions
OBSERVE C13, 75.4536162 MHz
DECOUPLE H1, 300.0753189 MHz
Power 33 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 49 min, 41 sec

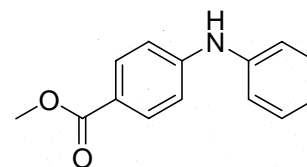
INDEX	FREQUENCY	PPM	HEIGHT
1	11399.286	151.077	27.0
2	9747.704	129.188	124.4
3	9015.958	119.490	59.3
4	8805.252	116.698	133.1
5	8094.119	107.273	37.3
6	5857.083	77.625	46.1
7	5825.019	77.200	48.1
8	5792.955	76.775	46.4
9	4859.950	64.410	139.5
10	3608.596	47.825	101.8
11	2614.040	34.644	97.7



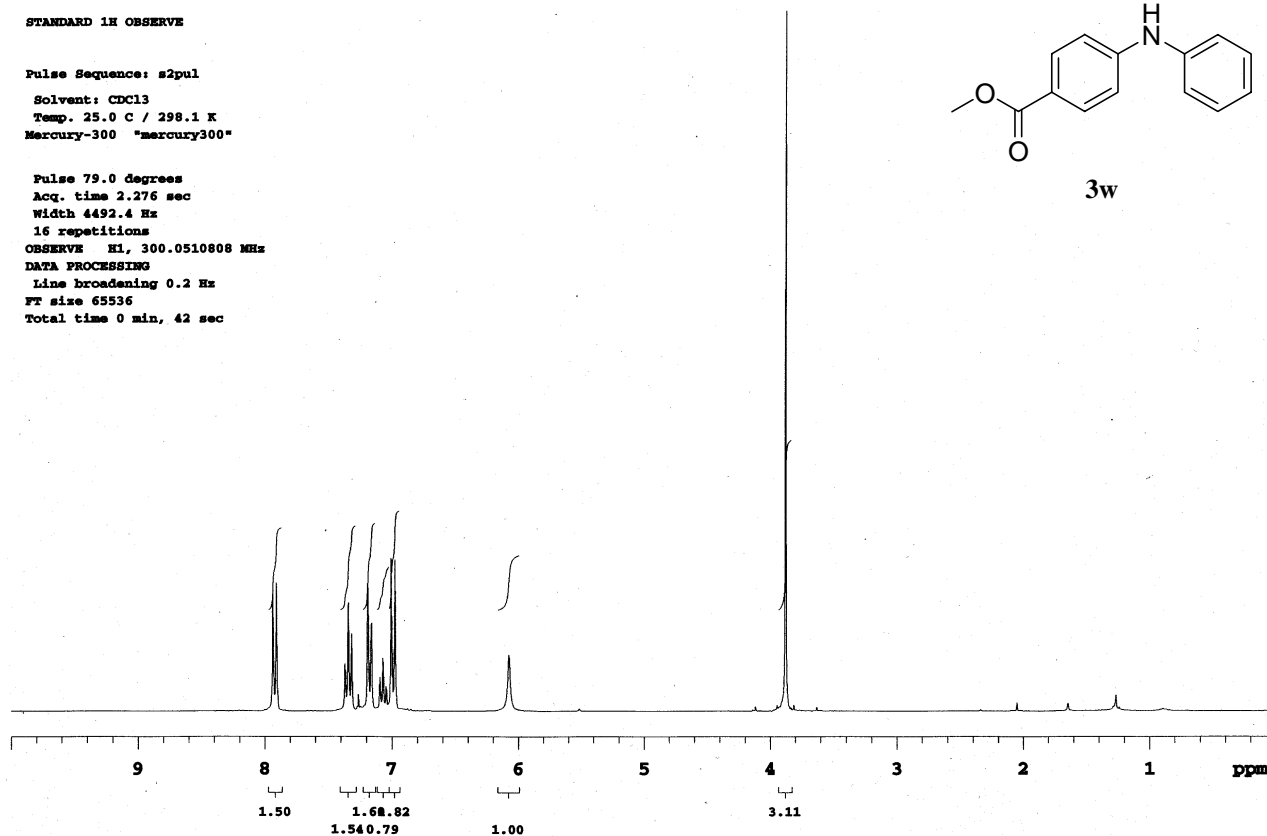
STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl₃
Temp. 25.0 C / 298.1 K
Mercury-300 "mercury300"

Pulse 79.0 degrees
Acq. time 2.276 sec
Width 4492.4 Hz
16 repetitions
OBSERVE H1, 300.0510808 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 0 min, 42 sec



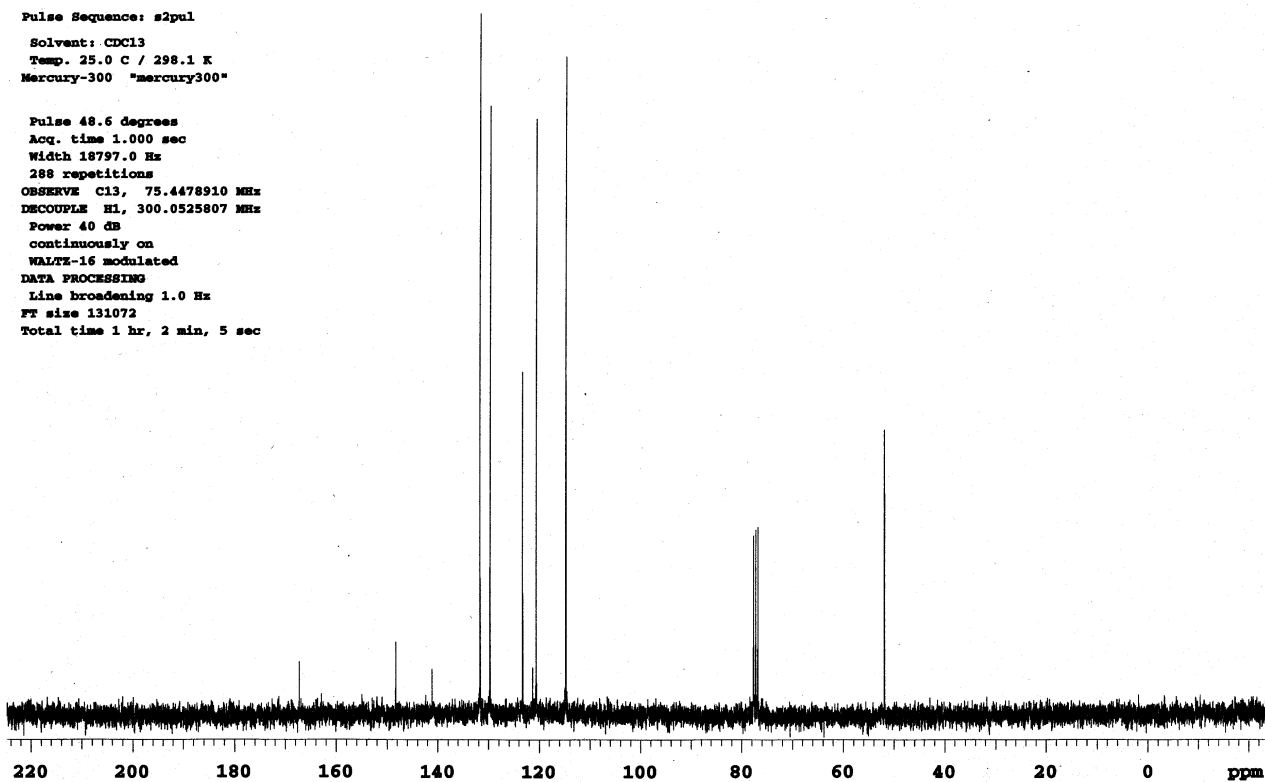
3w



13C OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl₃
Temp. 25.0 C / 298.1 K
Mercury-300 "mercury300"

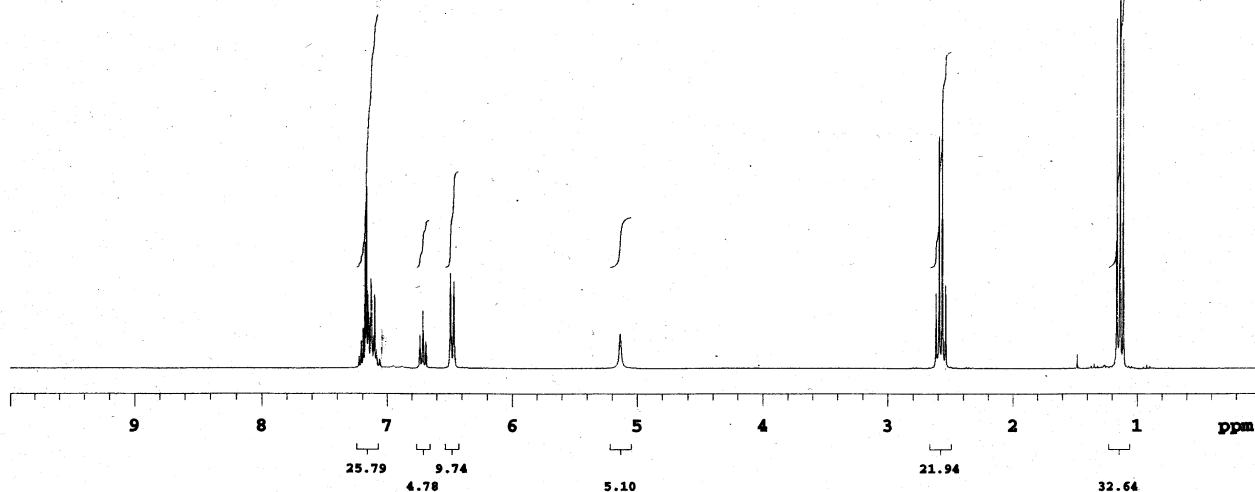
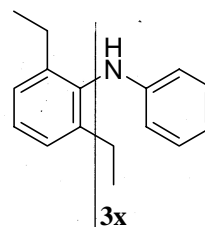
Pulse 48.6 degrees
Acq. time 1.000 sec
Width 18797.0 Hz
288 repetitions
OBSERVE C13, 75.4478910 MHz
DECOUPLE H1, 300.0525807 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 1 hr, 2 min, 5 sec



STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl₃
Temp. 25.0 C / 298.1 K
Mercury-300 "mercury300"

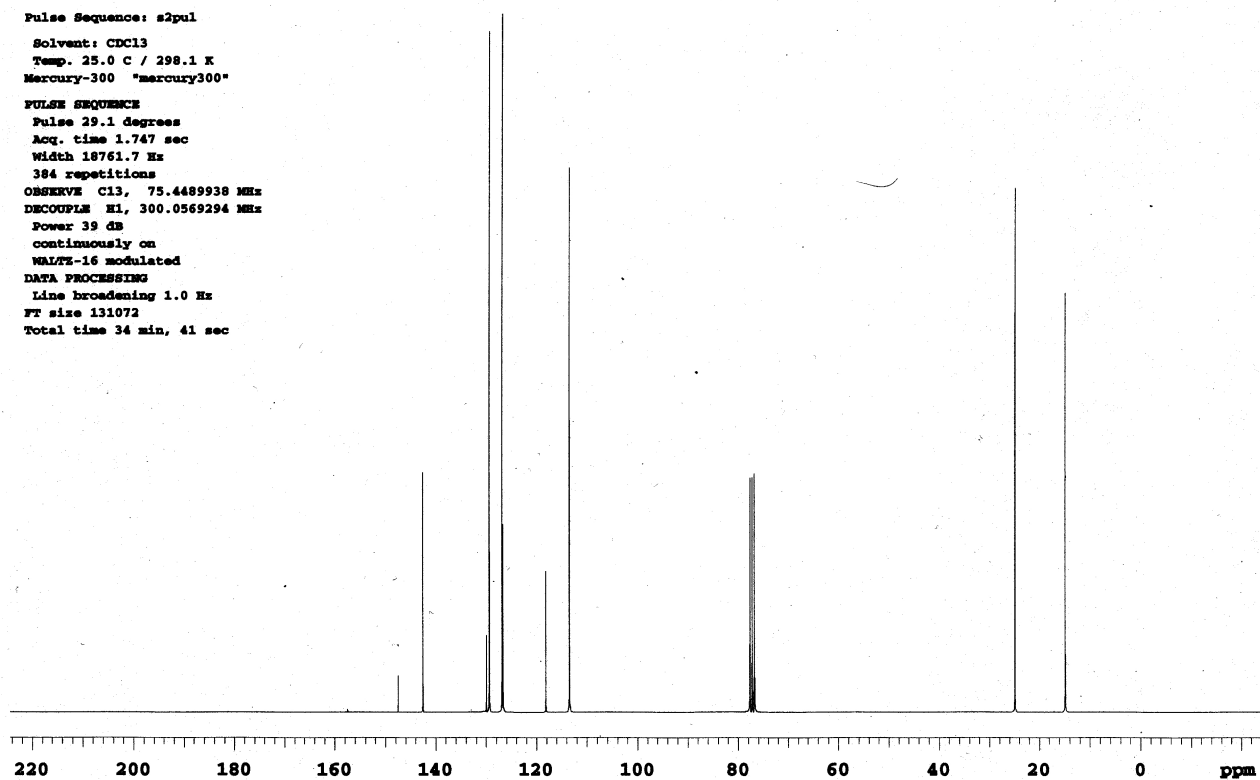
PULSE SEQUENCE
Pulse 65.6 degrees
Acq. time 2.276 sec
Width 4492.4 Hz
16 repetitions
OBSERVE H1, 300.054728 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 0 min, 42 sec



13C OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl₃
Temp. 25.0 C / 298.1 K
Mercury-300 "mercury300"

PULSE SEQUENCE
Pulse 29.1 degrees
Acq. time 1.747 sec
Width 18761.7 Hz
384 repetitions
OBSERVE C13, 75.4489938 MHz
DECOUPLE H1, 300.0569294 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 34 min, 41 sec



STANDARD 1H OBSERVE

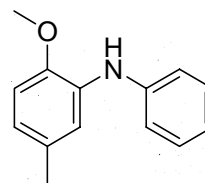
Pulse Sequence: s2pul

Solvent: CDCl₃

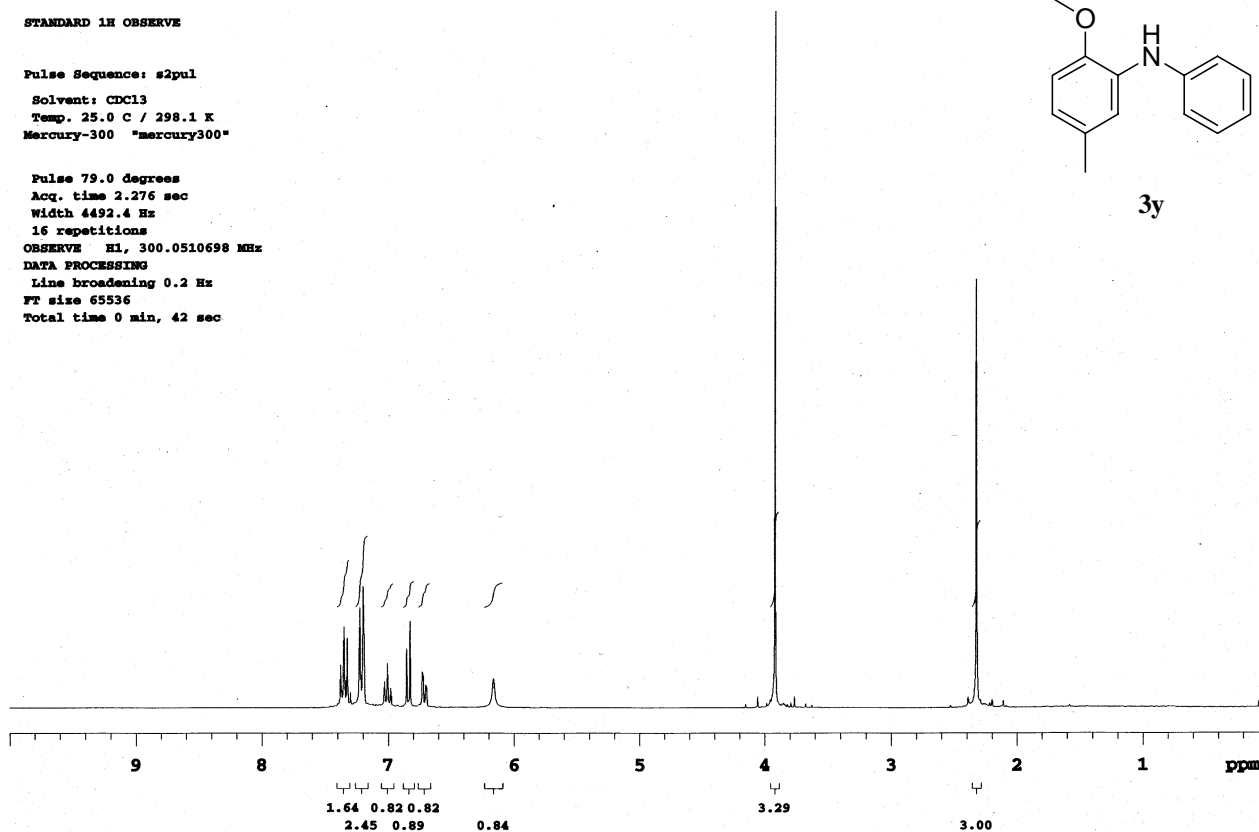
Temp. 25.0 C / 298.1 K

Mercury-300 "mercury300"

Pulse 79.0 degrees
Acq. time 2.276 sec
Width 4492.4 Hz
16 repetitions
OBSERVE H1, 300.0510698 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 0 min, 42 sec



3y



13C OBSERVE

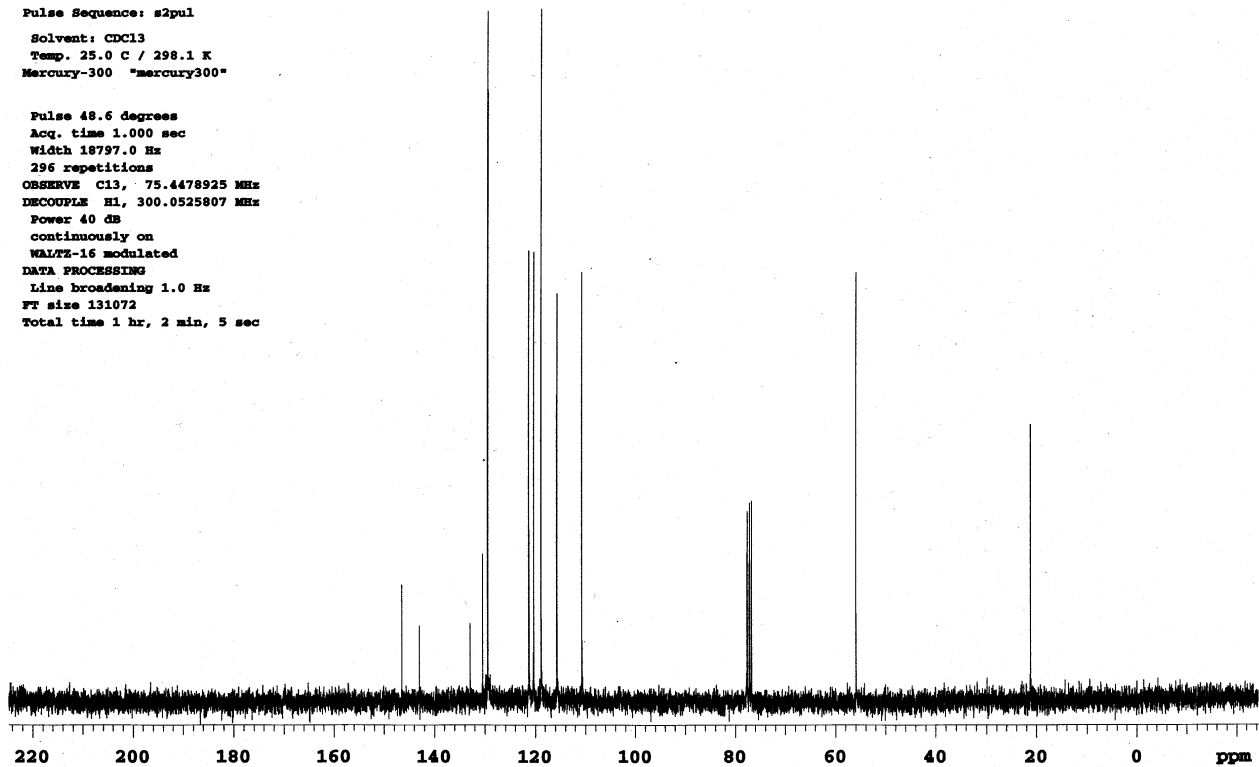
Pulse Sequence: s2pul

Solvent: CDCl₃

Temp. 25.0 C / 298.1 K

Mercury-300 "mercury300"

Pulse 48.6 degrees
Acq. time 1.000 sec
Width 18797.0 Hz
296 repetitions
OBSERVE C13, 75.4478925 MHz
DECOUPLE H1, 300.0525807 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 1 hr, 2 min, 5 sec



STANDARD 1H OBSERVE

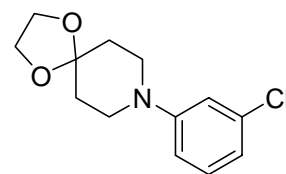
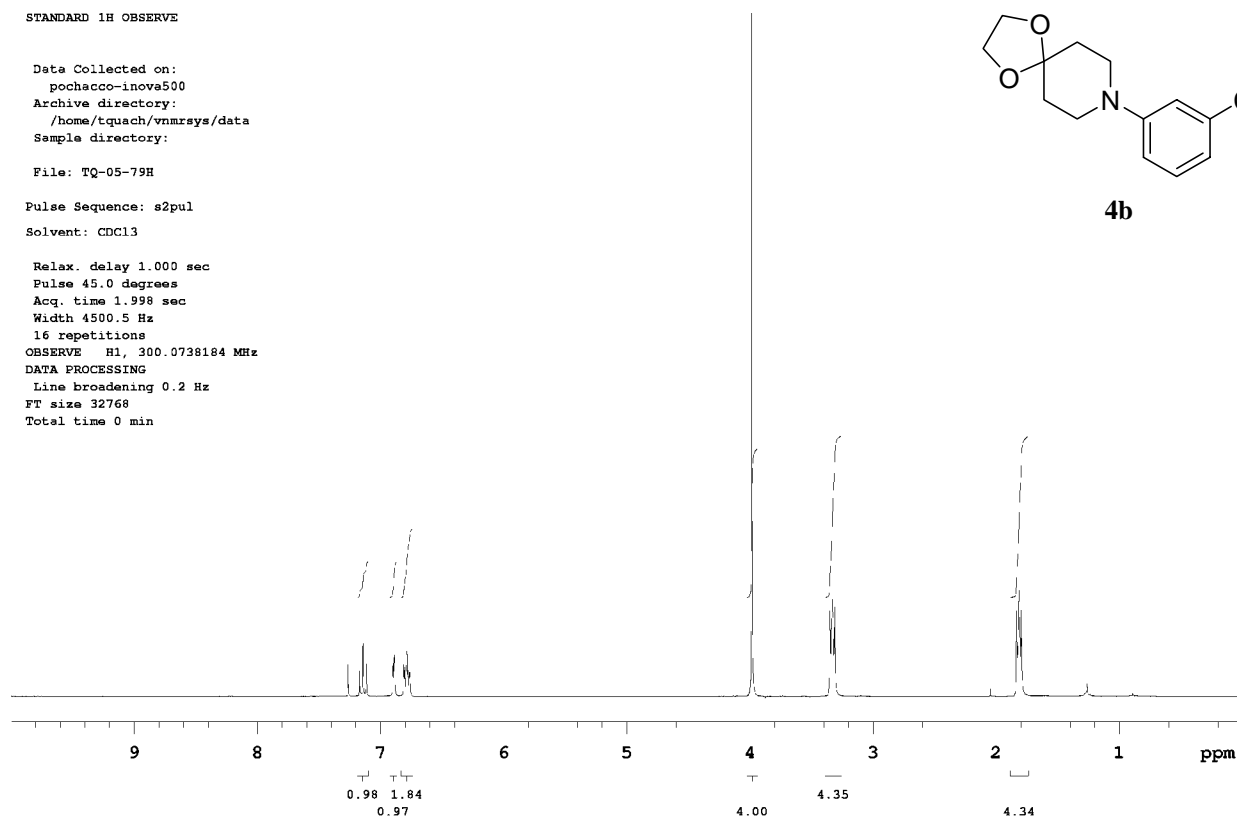
Data Collected on:
pochacco-inova500
Archive directory:
/home/tquach/vnmrsys/data
Sample directory:

File: TQ-05-79H

Pulse Sequence: s2pul

Solvent: CDCl3

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.998 sec
Width 4500.5 Hz
16 repetitions
OBSERVE H1, 300.0738184 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 0 min

**4b**

13C OBSERVE

Data Collected on:
pochacco-inova500
Archive directory:
/home/tquach/vnmrsys/data
Sample directory:

File: TQ-05-79C

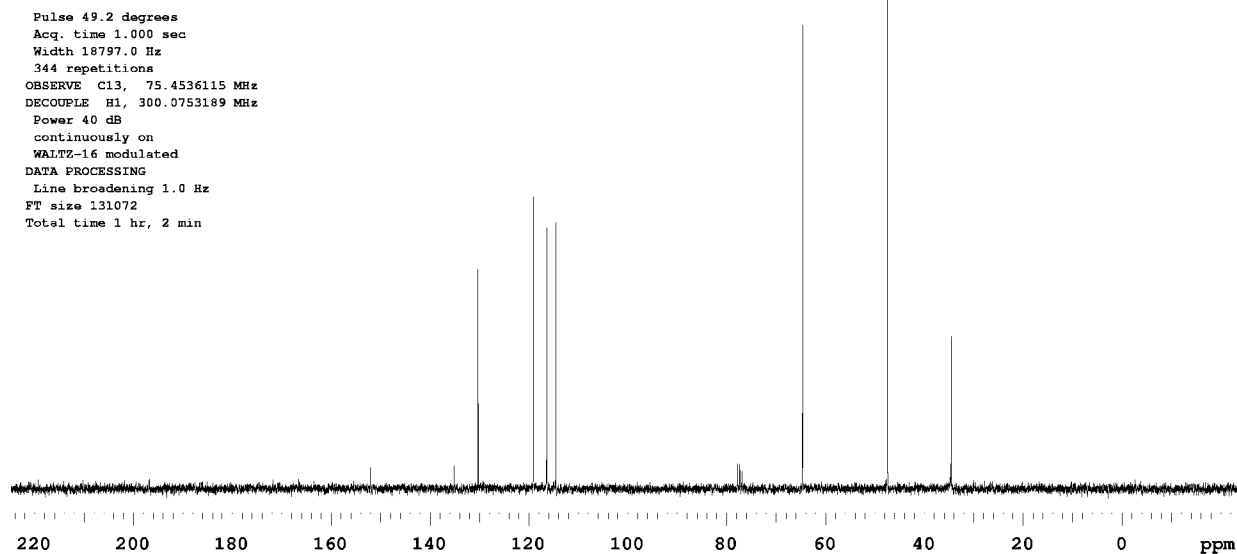
Pulse Sequence: s2pul

Solvent: CDCl3

Temp. 25.0 C / 298.1 K

Pulse 49.2 degrees
Acq. time 1.000 sec
Width 18797.0 Hz
344 repetitions
OBSERVE C13, 75.4536115 MHz
DECOUPLE H1, 300.0753189 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 1 hr, 2 min

INDEX	FREQUENCY	PPM	RELINT
1	11468.849	151.999	4.3
2	10188.468	135.030	4.6
3	9822.194	130.175	44.4
4	8979.793	119.011	80.1
5	8772.706	116.266	52.8
6	8633.597	114.423	53.8
7	8084.616	107.147	20.5
8	5857.430	77.630	5.0
9	5825.019	77.200	4.8
10	5793.181	76.778	5.3
11	4866.454	64.496	93.9
12	3572.879	47.352	139.5
13	2600.547	34.466	132.1



STANDARD 1H OBSERVE

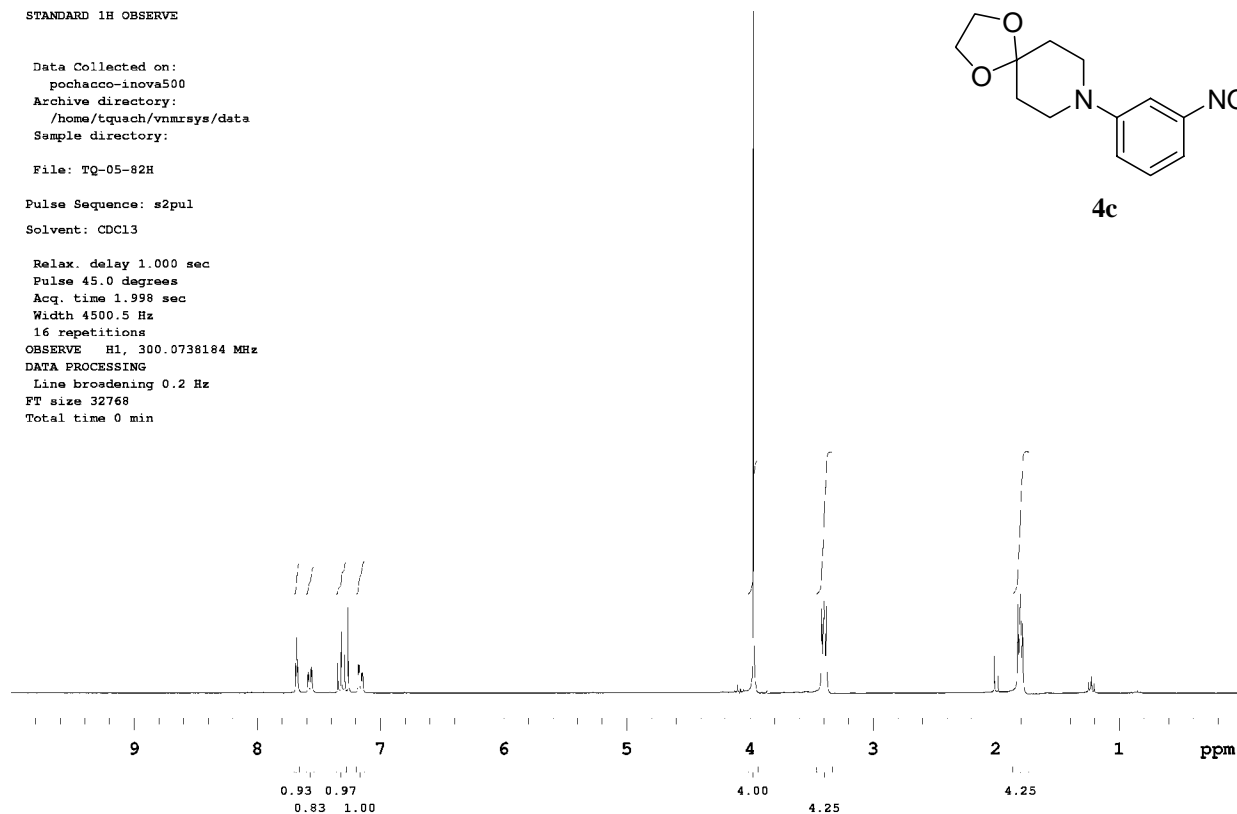
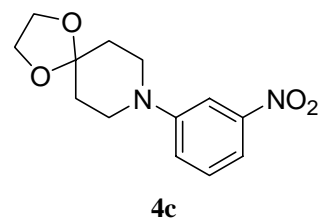
Data Collected on:
pochacco-inova500
Archive directory:
/home/tquach/vnmrsys/data
Sample directory:

File: TQ-05-82H

Pulse Sequence: s2pul

Solvent: CDCl₃

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.998 sec
Width 4500.5 Hz
16 repetitions
OBSERVE H1, 300.0738184 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 0 min



13C OBSERVE

Data Collected on:
pochacco-inova500
Archive directory:
/home/tquach/vnmrsys/data
Sample directory:

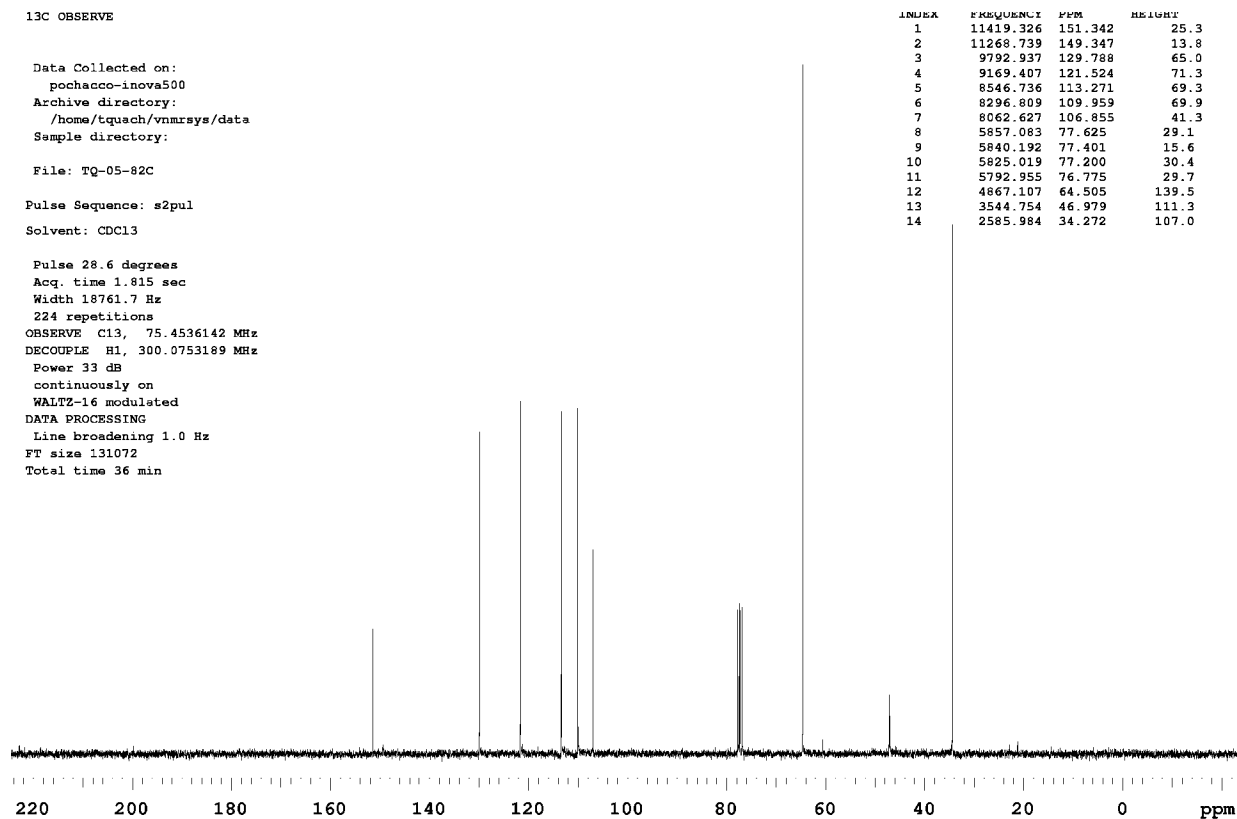
File: TQ-05-82C

Pulse Sequence: s2pul

Solvent: CDCl₃

Pulse 28.6 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
224 repetitions
OBSERVE C13, 75.4536142 MHz
DECOUPLE H1, 300.0753189 MHz
Power 33 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 36 min

INDEX	FREQUENCY	PPM	HEIGHT
1	11419.326	151.342	25.3
2	11268.739	149.347	13.8
3	9792.937	129.788	65.0
4	9169.407	121.524	71.3
5	8546.736	113.271	69.3
6	8296.809	109.959	69.9
7	8062.627	106.855	41.3
8	5857.083	77.625	29.1
9	5840.192	77.401	15.6
10	5825.019	77.200	30.4
11	5792.955	76.775	29.7
12	4867.107	64.505	139.5
13	3544.754	46.979	111.3
14	2585.984	34.272	107.0



STANDARD 1H OBSERVE

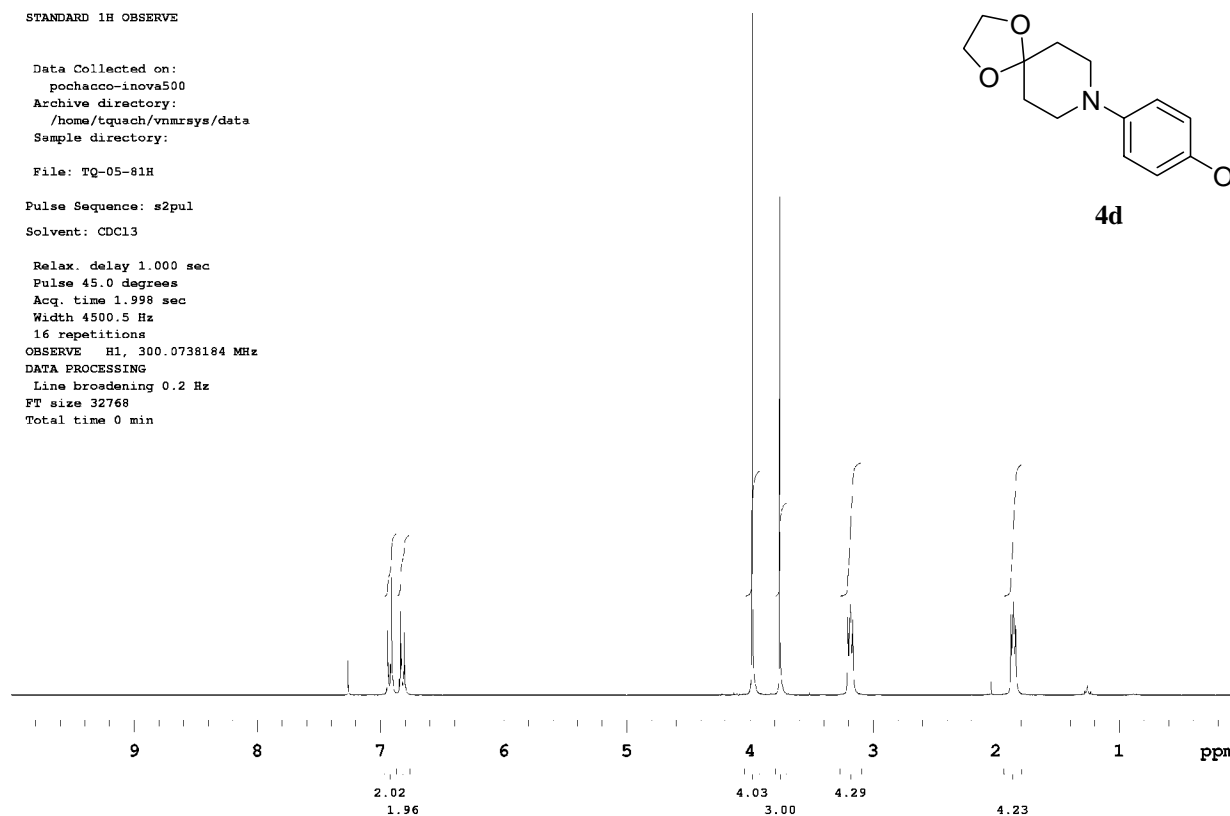
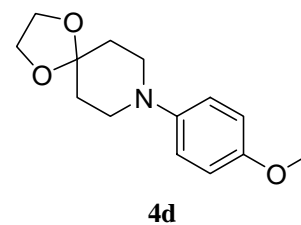
Data Collected on:
pochacco-inova500
Archive directory:
/home/tquach/vnmrsys/data
Sample directory:

File: TQ-05-81H

Pulse Sequence: s2pul

Solvent: CDCl₃

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.998 sec
Width 4500.5 Hz
16 repetitions
OBSERVE H1, 300.0738184 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 0 min



13C OBSERVE

Data Collected on:
pochacco-inova500
Archive directory:
/home/tquach/vnmrsys/data
Sample directory:

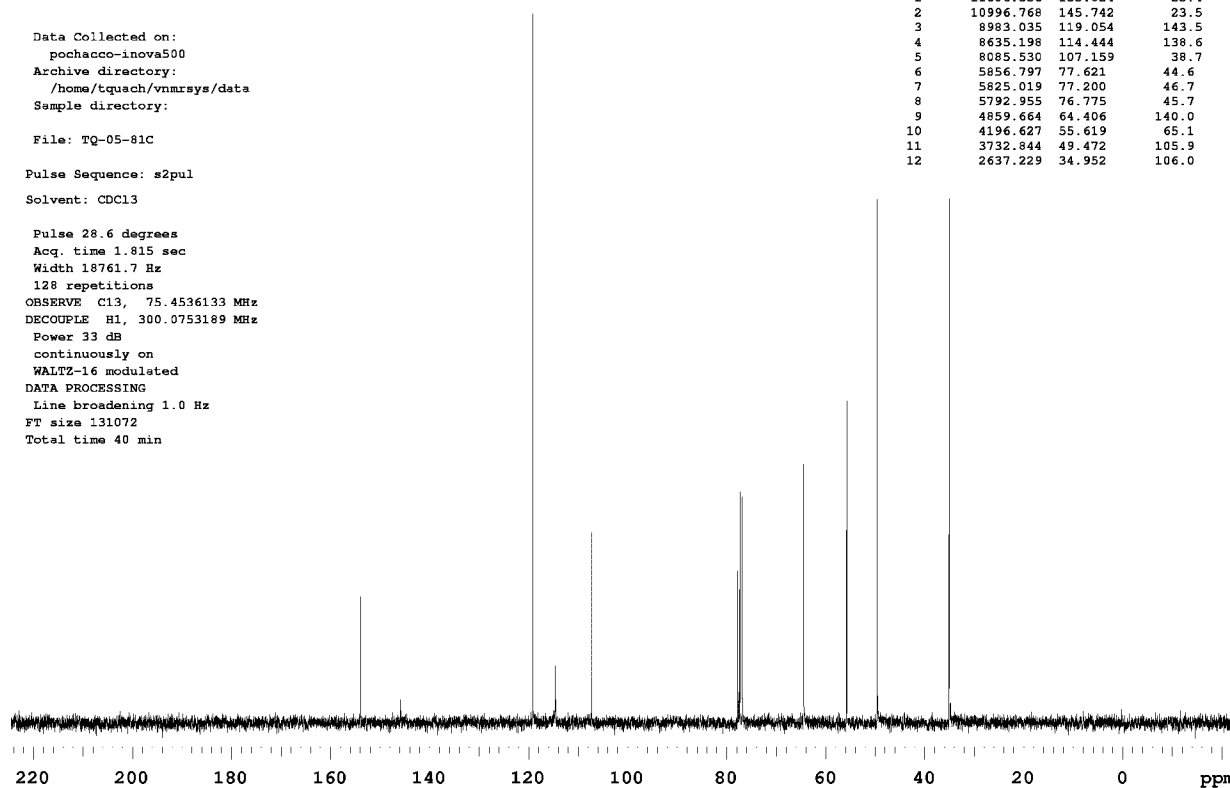
File: TQ-05-81C

Pulse Sequence: s2pul

Solvent: CDCl₃

Pulse 28.6 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
128 repetitions
OBSERVE C13, 75.4536133 MHz
DECOUPLE H1, 300.0753189 MHz
Power 33 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 40 min

INDEX	FREQUENCY	PPM	HEIGHT
1	11606.556	153.824	25.4
2	10996.768	145.742	23.5
3	8983.035	119.054	143.5
4	8635.198	114.444	138.6
5	8085.530	107.159	38.7
6	5856.797	77.621	44.6
7	5825.019	77.200	46.7
8	5792.955	76.775	45.7
9	4859.664	64.406	140.0
10	4196.627	55.619	65.1
11	3732.844	49.472	105.9
12	2637.229	34.952	106.0



STANDARD 1H OBSERVE

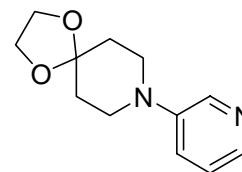
Data Collected on:
pochacco-inova500
Archive directory:
/home/tquach/vnmrsys/data
Sample directory:

File: TQ-05-83H

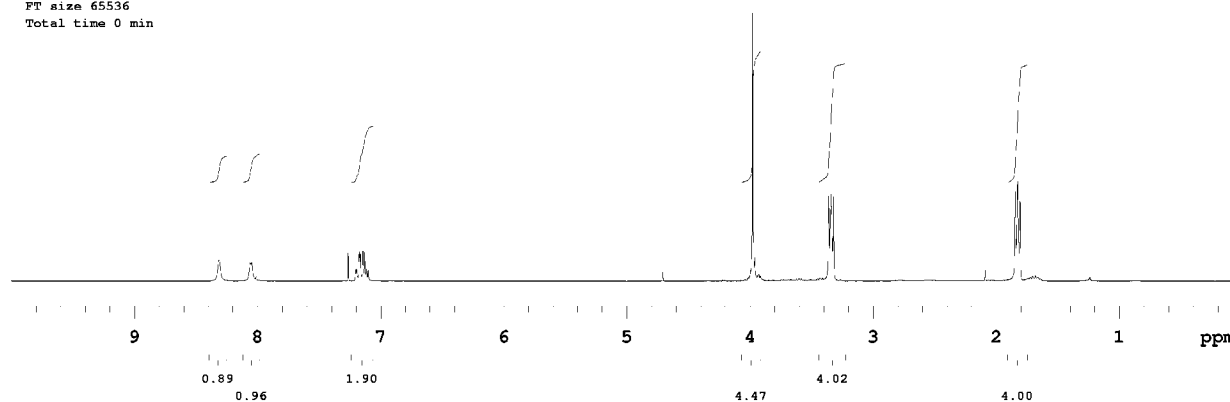
Pulse Sequence: s2pul

Solvent: CDCl₃
Temp. 25.0 C / 298.1 K

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.276 sec
Width 4492.4 Hz
16 repetitions
OBSERVE H1, 300.0510802 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 0 min



4e



13C OBSERVE

Data Collected on:
pochacco-inova500
Archive directory:
/home/tquach/vnmrsys/data
Sample directory:

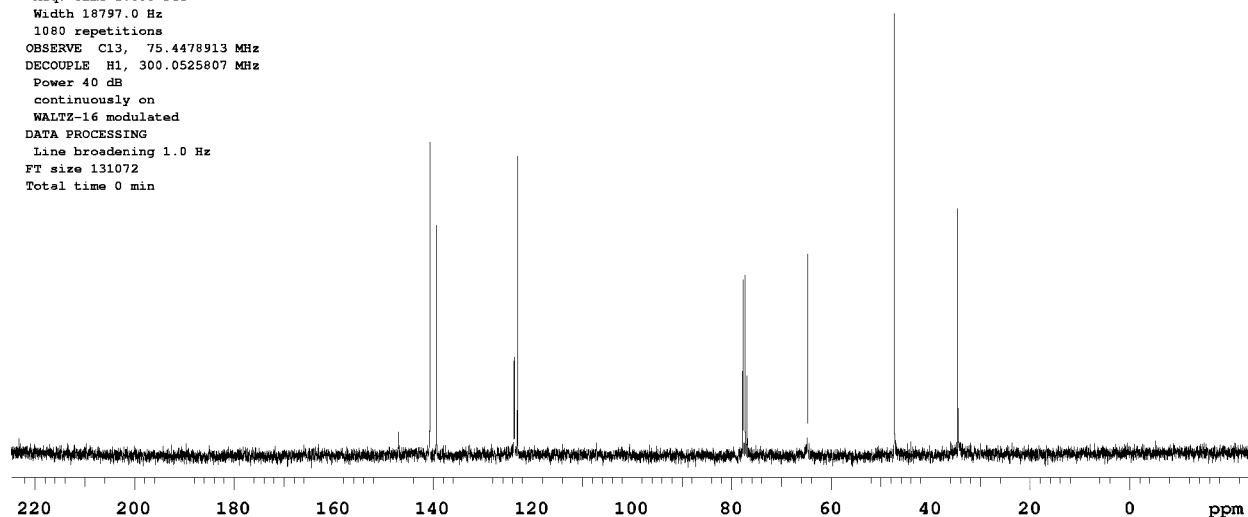
File: TQ-05-83C

Pulse Sequence: s2pul

Solvent: CDCl₃
Temp. 25.0 C / 298.1 K

Pulse 49.2 degrees
Acq. time 1.000 sec
Width 18797.0 Hz
1080 repetitions
OBSERVE C13, 75.4478913 MHz
DECOUPLE H1, 300.0525807 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 0 min

INDEX	FREQUENCY	PPM	HEIGHT
1	11074.025	146.777	4.1
2	10600.479	140.501	64.1
3	10502.385	139.201	45.8
4	9325.548	123.602	19.3
5	9272.772	122.903	59.8
6	8071.554	106.982	18.1
7	5856.701	77.626	34.9
8	5824.864	77.204	35.9
9	5792.740	76.778	36.0
10	4868.881	64.533	139.5
11	3564.406	47.243	131.6
12	2599.818	34.458	128.7



STANDARD 1H OBSERVE

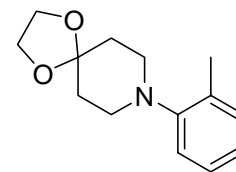
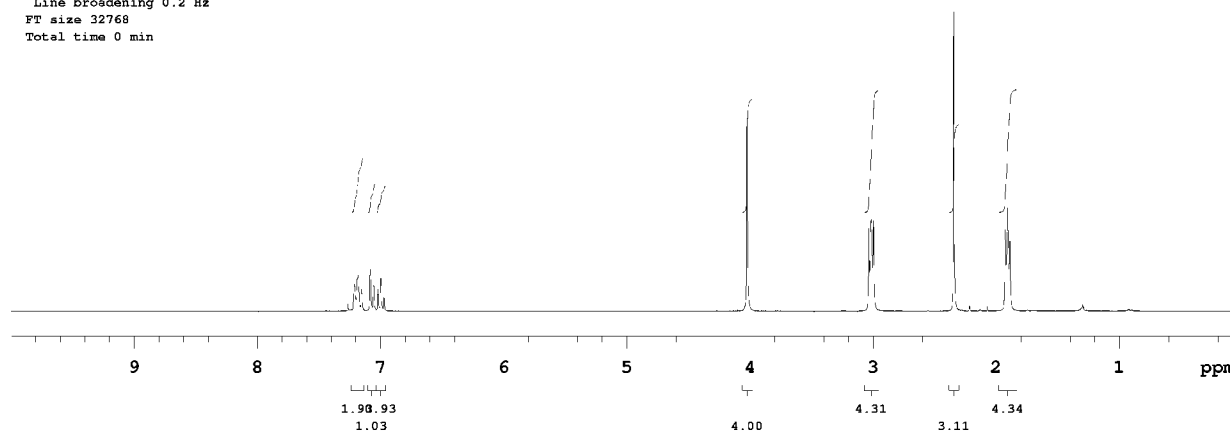
Data Collected on:
pochacco-inova500
Archive directory:
/home/tquach/vnmrsys/data
Sample directory:

File: TQ-05-84H

Pulse Sequence: s2pul

Solvent: CDCl3

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.998 sec
Width 4500.5 Hz
16 repetitions
OBSERVE H1, 300.0738181 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 0 min

**4f**

13C OBSERVE

Data Collected on:
pochacco-inova500
Archive directory:
/home/tquach/vnmrsys/data
Sample directory:

File: TQ-05-84C

Pulse Sequence: s2pul

Solvent: CDCl3

Pulse 28.6 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
176 repetitions
OBSERVE C13, 75.4536136 MHz
DECOUPLE H1, 300.0753189 MHz
Power 33 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 40 min

INDEX	FREQUENCY	PPM	HEIGHT
1	11465.131	151.949	30.6
2	10016.813	132.755	33.0
3	9887.984	131.047	68.4
4	9552.171	126.597	79.0
5	9291.651	123.144	68.8
6	9007.370	119.376	72.1
7	8096.123	107.299	38.7
8	5857.083	77.625	40.2
9	5825.019	77.200	40.2
10	5793.241	76.779	39.0
11	4859.950	64.410	139.5
12	3792.678	50.265	117.0
13	2700.498	35.790	113.6
14	1350.948	17.904	63.1

