



Supporting Information

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A General and Efficient Method for the Suzuki-Miyaura Coupling of 2-Pyridyl Nucleophilics

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Experimental Section

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General. All reactions were carried out under an argon atmosphere. 1,4-Dioxane (anhydrous) was purchased from Aldrich Chemical Co. in a SureSeal® bottle. Commercially available materials were used without further purification unless otherwise noted. Diphenylphosphine oxide was purchased from Alfa Aesar, and di-*tert*-butylphosphine oxide was purchased from Strem Chemicals, Inc. Both ligands are hygroscopic and must be stored in a benchtop desiccator. Aryl halides were purchased from Aldrich Chemical Co. Liquid aryl halides were purified by passage through a pad of basic alumina prior to use. Potassium fluoride (anhydrous, Alfa Aesar) and Pd₂dba₃ (Strem Chemicals, Inc.) were stored in a benchtop desiccator. All lithium triisopropyl 2-pyridylborates were prepared in our laboratories via the procedure described in this experimental (Page 2). These were stored in a round bottom flask under an argon atmosphere inside a benchtop desiccator for up to a month.

All new compounds were characterized by ¹H NMR, ¹³C NMR, IR spectroscopy, melting points (for solids) and, in most cases, elemental analysis. Known compounds were characterized by ¹H NMR, ¹³C NMR and melting points (for solids) and compared to their literature values. ¹H and ¹³C NMR spectra were recorded on a Varian Mercury

300. Infrared spectra were recorded on an ASI Applied Systems ReactIR 1000 (neat samples were placed directly on the DiComp probe). Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, GA. All ^1H NMR experiments are reported in δ units, parts per million (ppm) downfield of TMS and were measured relative to the signals for the residual benzene (7.16 ppm), chloroform (7.26 ppm), dimethylsulfoxide (2.50 ppm) or methanol (3.31 ppm). All ^{13}C NMR spectra were reported in ppm relative to residual chloroform (77 ppm), dimethylsulfoxide (39.5 ppm) or methanol (49 ppm) and were obtained with ^1H decoupling. Melting points were obtained on a Mel-Temp capillary melting point apparatus and are uncorrected. Gas chromatographic analyses were performed on Hewlett-Packard 6890 gas chromatography instrument with a FID detector using 25 m x 0.20 mm capillary column with cross-linked methyl siloxane as a stationary phase.

The yields in tables 2 and 3 refer to isolated yields (average of two runs) of compounds estimated to be $\geq 95\%$ pure as determined by ^1H NMR and GC analysis and/or combustion analysis.

I. Experimental for Preparation of Lithium Triisopropyl 2-Pyridylborates

General Procedure for the Preparation of Lithium Triisopropyl 2-Pyridylborates.¹

An oven-dried round-bottomed flask equipped with a magnetic stir bar and fitted with a rubber septum was charged with toluene (60 mL) and THF (15 mL) and placed under an argon atmosphere. The flask was charged with triisopropylborate (3.81 mL, 3.10 g, 16.5 mmol) and the heteroaryl bromide (15.0 mmol). The reaction mixture was cooled to -78°C using a dry ice/acetone bath. *n*-Butyllithium (2.5 M in hexanes, 6.6 mL, 16.5 mmol) was added dropwise via a syringe pump over 1.5 h, and the mixture was stirred for an additional 0.5 h while the temperature was held at -78°C . The reaction mixture was then allowed to warm to room temperature overnight (15 h). The resulting solution was then concentrated under reduced pressure, followed by further drying under high vacuum at 110°C for 12 h to yield the desired borate.

¹ For a related protocol for the synthesis of 3-Pyridine boronic acid, see: Li, W.; Nelson, D. P.; Jensen, M. S.; Hoerner, R. S.; Cai, D.; Larsen, R. D.; Reider, P. J. *J. Org. Chem.* **2002**, *67*, 5394-5397.

Lithium Triisopropyl 2-Pyridyl Borate (A). The general procedure was followed on a larger scale using toluene (120 mL), THF (30 mL), triisopropylborate (8.03 mL, 6.55 g, 34.8 mmol), 2-bromopyridine (31.6 mmol), *n*-Butyllithium (2.5 M in hexanes, 13.9 mL, 34.8 mmol) to provide the title compound in a 99% yield (8.67 g) as a brown solid, mp >250 °C. ¹H NMR (300 MHz, CD₃OD) δ: 8.38 (d, J = 5 Hz, 1H), 7.58 (dt, J = 8,1 Hz, 1H), 7.54 (t, J = 8 Hz, 1H), 7.07 (dt, J = 8,1 Hz, 1H), 3.93 (sept, J = 6 Hz, 3H), 1.15 (d, J = 6 Hz, 18H). ¹³C NMR (75 MHz, CD₃OD) δ: 148.2, 135.5, 128.5, 121.7, 64.7, 25.4. (No C-B Signal) IR (neat, cm⁻¹): 3372, 2941, 2913, 1653, 1557, 1538, 1421, 1149, 1004, 931. ¹H and ¹³C NMR spectrum included.

Lithium Triisopropyl 2-(6-Methoxypyridyl) Borate (B). The general procedure was followed to provide the title compound in a 90% yield (4.10 g) as a white solid, mp 226-227 °C. ¹H NMR (300 MHz, CD₃OD) δ: 7.52 (t, J = 8 Hz, 1H), 7.13 (d, J = 8 Hz, 1H), 6.52 (d, J = 8 Hz, 1H), 3.93 (sept, J = 6 Hz, 3H), 3.87 (s, 3H), 1.15 (d, J = 6 Hz, 18H). ¹³C NMR (75 MHz, CD₃OD) δ: 165.4, 138.9, 121.9, 105.3, 64.7, 54.4, 25.3. (No C-B Signal) IR (neat, cm⁻¹): 3284, 2952, 2901, 2851, 1647, 1589, 1559, 1487, 1425, 1401, 1282, 1226, 1043, 934, 903. ¹H and ¹³C NMR spectrum included.

Lithium Triisopropyl 2-(5-fluoropyridyl) Borate (C). The general procedure was followed on a smaller scale using toluene (40 mL), THF (10 mL), triisopropylborate (2.88 mL, 2.35 g, 12.5 mmol), 2-bromo-5-fluoropyridine (2.00 g, 11.4 mmol), *n*-Butyllithium (2.5 M in hexanes, 5.00 mL, 12.5 mmol) to provide the title compound in a 96% yield (3.24 g) as a brown solid, mp >250 °C. ¹H NMR (300 MHz, CD₃OD) δ: 8.26 (s, 1H), 7.55 (dd, J = 8,6 Hz, 1H), 7.39 (dt, J = 8,6 Hz, 1H), 3.93 (sept, J = 6 Hz, 3H), 1.15 (d, J = 6 Hz, 18H). ¹³C NMR (75 MHz, CD₃OD) δ: 161.0, 159.0, 135.8, 129.4, 122.6, 64.7, 25.5. IR (neat, cm⁻¹): 3282, 2959, 171, 1471, 1375, 1326, 1171, 1129, 950. ¹H and ¹³C NMR spectrum included.

Lithium Triisopropyl 2-(6-(1,3-dioxolan-2-yl)pyridin-2-yl) Borate (D). The general procedure was followed on a smaller scale using toluene (16.0 mL), THF (4.0 mL),

triisopropylborate (1.05 mL, 0.856 g, 4.55 mmol), 2-bromo-6-(1,3-dioxolan-2-yl)pyridine (0.952 g, 4.14 mmol), *n*-Butyllithium (2.5 M in hexanes, 1.82 mL, 4.55 mmol) to provide the title compound in a 73% yield (1.04 g) as a brown solid, mp 159-161 °C. ¹H NMR (300 MHz, CD₃OD) δ: 7.64 (t, J = 8 Hz, 1H), 7.55 (dd, J = 8,1 Hz, 1H), 7.30 (dd, J = 8,1 Hz, 1H), 5.81 (s, 1H), 3.95-4.10 (m, 4H), 3.92 (sept, J = 6 Hz, 3H), 1.15 (d, J = 6 Hz, 18H). ¹³C NMR (75 MHz, CD₃OD) δ: 155.9, 136.2, 128.7, 121.0, 119.0, 105.2, 66.4, 64.7, 25.5. IR (neat, cm⁻¹): 2964, 2892, 1593, 1464, 1376, 1202, 1127, 1007. ¹H and ¹³C NMR spectrum included.

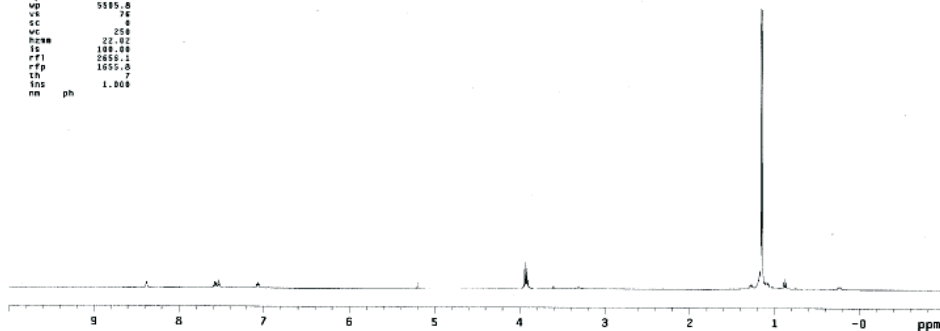
Lithium Triisopropyl 2-(5-cyanopyridyl) Borate (E). The general procedure was followed on a smaller scale using toluene (20.0 mL), THF (5.0 mL), triisopropylborate (1.27 mL, 1.03 g, 5.50 mmol), 6-bromopyridine-3-carbonitrile (0.915 g, 5.00 mmol), *n*-Butyllithium (2.5 M in hexanes, 2.20 mL, 5.50 mmol) to provide the title compound in a 95% yield (1.42 g) as a brown solid, mp >250 °C. ¹H NMR (300 MHz, CD₃OD) δ: 8.73 (d, J = 3 Hz, 1H), 7.93 (dd, J = 8,3 Hz, 1H), 7.71 (d, J = 8 Hz, 1H), 3.93 (sept, J = 6 Hz, 3H), 1.15 (d, J = 6 Hz, 18H). ¹³C NMR (75 MHz, CD₃OD) δ: 151.1, 138.3, 132.0, 128.8, 118.6, 107.8, 64.8, 25.4. IR (neat, cm⁻¹): 2952, 2862, 2218, 1591, 1448, 1363, 1126, 999. ¹H and ¹³C NMR spectrum included.

STANDARD PROTON PARAMETERS

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Lithium Triisopropyl 2-Pyridyl Boronate (A).

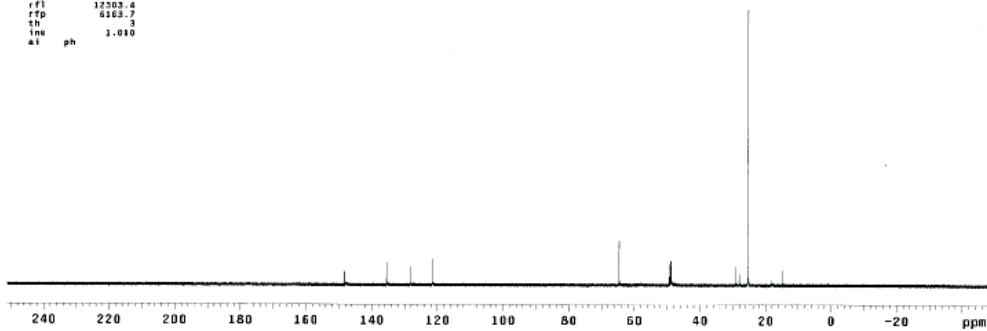


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Lithium Triisopropyl 2-Pyridyl Boronate (A).



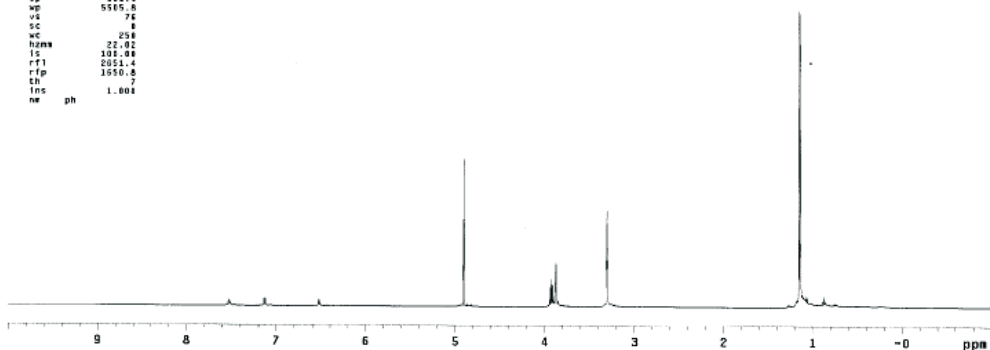
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Lithium Triisopropyl 2-(6-Methoxypyridyl) Boronate (B).



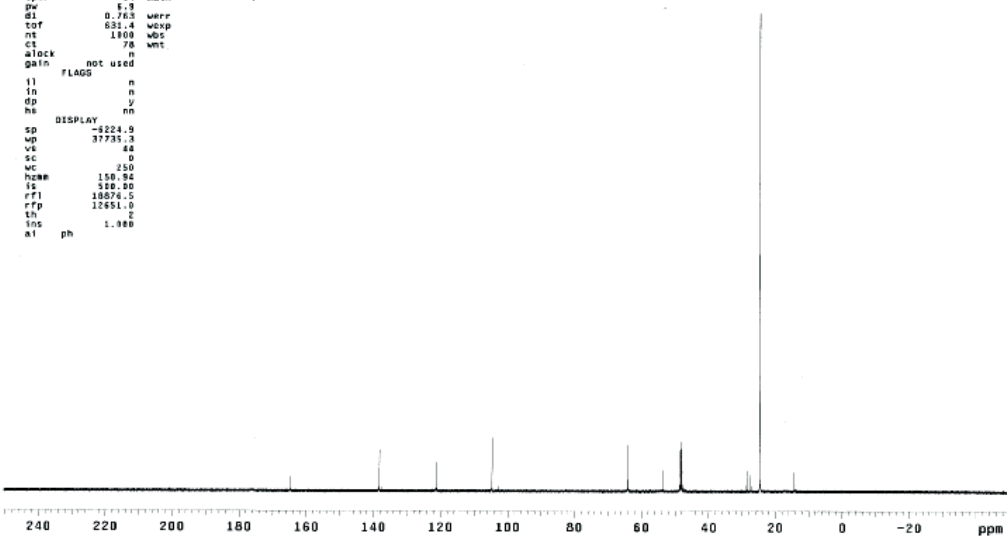
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at ph

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Lithium Triisopropyl 2-(6-Methoxypyridyl) Boronate (B).



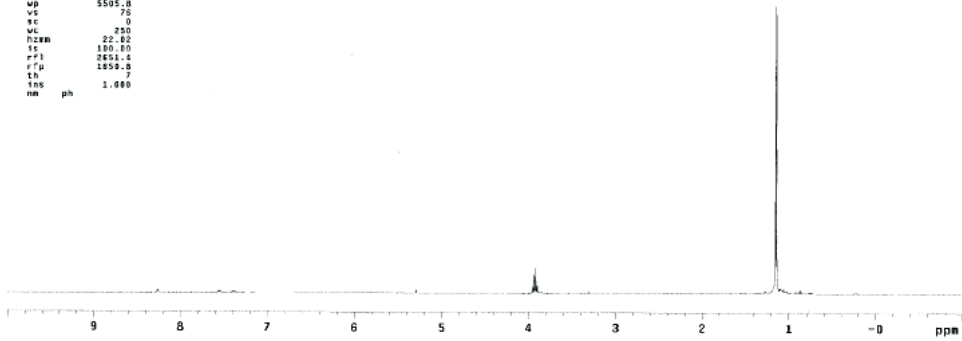
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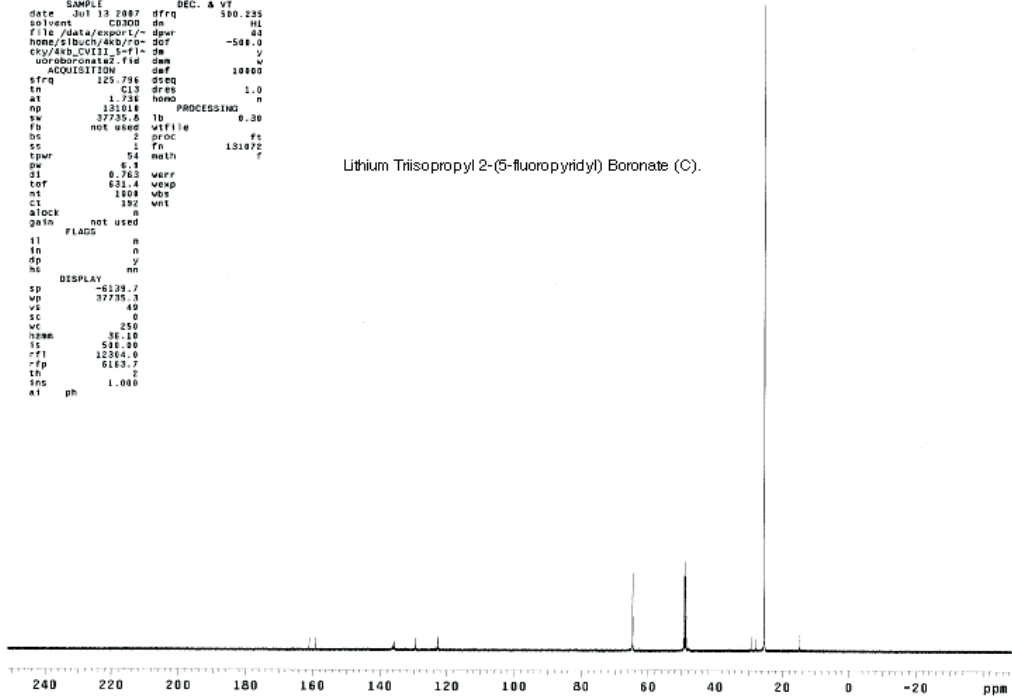
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Lithium Triisopropyl 2-(5-fluoropyridyl) Boronate (C).



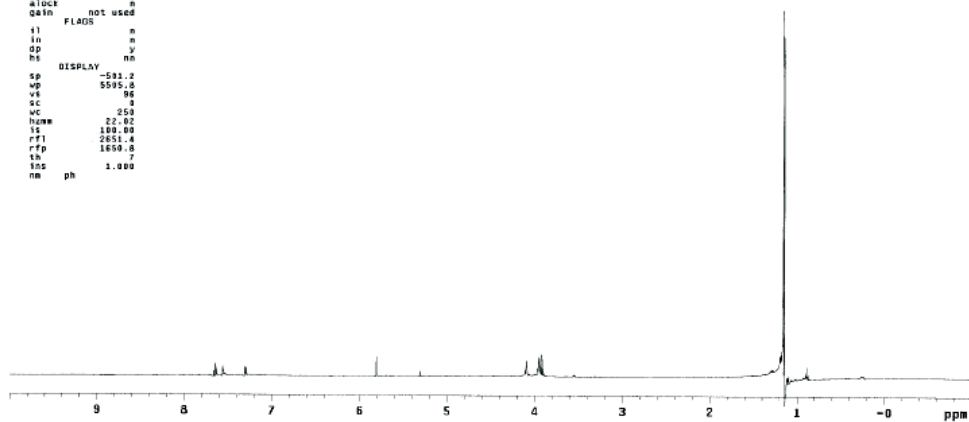
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Lithium Triisopropyl 2-(6-(1,3-dioxolan-2-yl)pyridin-2-yl) Boronate (D)



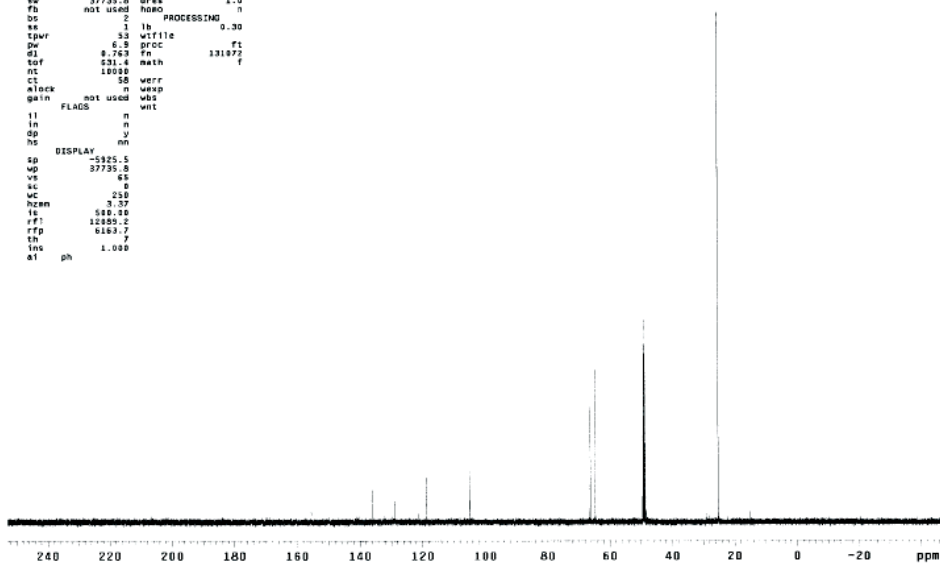
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Lithium Triisopropyl 2-(6-(1,3-dioxolan-2-yl)pyridin-2-yl) Boronate (D)

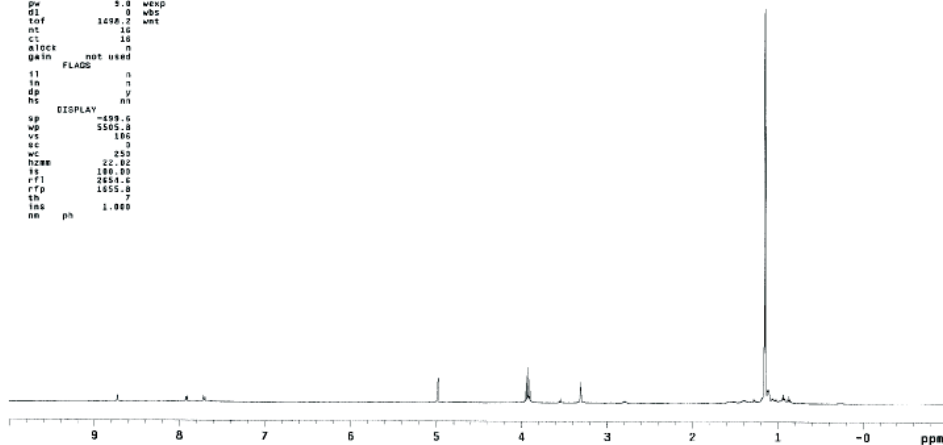


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Lithium Trisopropyl 2-(5-cyanopyridyl) Boronate (E)

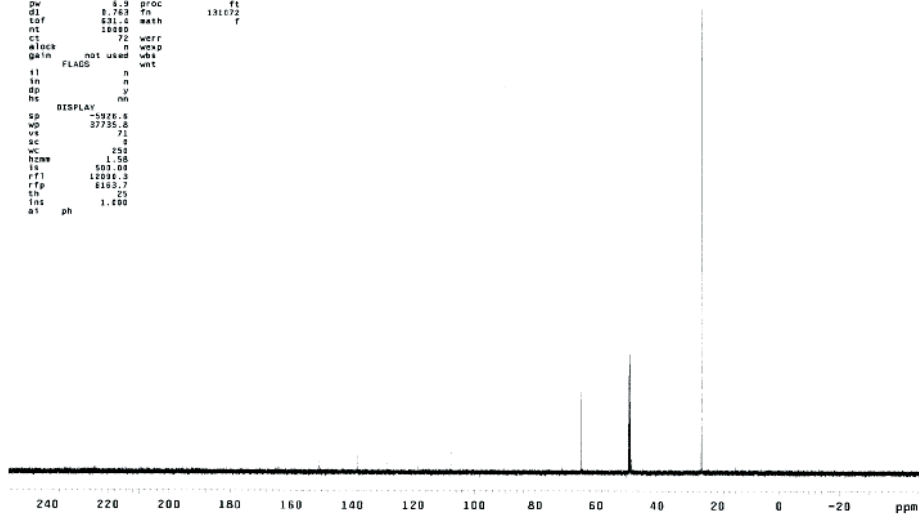


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```

Lithium Trisopropyl 2-(5-cyanopyridyl) Boronate (E)



II. Experimental for the Reactions with Aryl Bromides

General Procedure A: Pd-Catalyzed Suzuki-Miyaura Reaction of Lithium Triisopropyl 2-Pyridylborates with Aryl Halides.

An oven-dried resealable Schlenk tube possessing a Teflon screw valve was charged with Pd₂dba₃ (2.0-3.0%), ligand (6.0-9.0%), lithium triisopropyl 2-pyridylborate (0.375 mmol) and anhydrous KF (43.5 mg, 0.75 mmol). The Schlenk tube was capped with a rubber septum and then evacuated and backfilled with argon (this sequence was carried out two times). 1,4-Dioxane (0.75 mL) was added via syringe, through the septum, followed by the addition of the aryl halide (0.25 mmol) in a like manner (aryl halides that were solids were added with the other solid reagents). The septum was then replaced with a Teflon screw valve and the Schlenk tube was sealed. The reaction mixture was heated to 110 °C until the aryl halide had been completely consumed as determined by gas chromatography and was allowed to cool to room temperature. The reaction solution was then filtered through a thin pad of silica gel (eluting with ethyl acetate) and the eluent was concentrated under reduced pressure. The crude material so obtained was purified via flash chromatography on silica gel.

2-(4-butylphenyl)pyridine (Table 2, Entry 1).² Following general procedure A, a mixture of 4-*n*-butylbromobenzene (44.1 μL, 53.3 mg, 0.25 mmol), lithium triisopropyl 2-pyridylborate (104 mg, 0.375 mmol), KF, Pd₂dba₃ (2.3 mg, 0.0025 mmol) and **1** (3.0 mg, 0.015 mmol) was heated for 20 h. Flash column chromatography (10% EtOAc/Hexanes) yielded the title compound in 45 mg (85% yield) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ: 8.66 (dt, J = 6,1 Hz, 1H), 7.88 (d, J = 8 Hz, 2H), 7.67-7.71 (m, 2H), 7.26 (d, J = 8 Hz, 2H), 7.16 (dt, J = 6,1 Hz, 1H), 2.64 (t, J = 8 Hz, 2H), 1.62 (pent, J = 8 Hz, 2H), 1.36 (hex, J = 8 Hz, 2H), 0.92 (t, J = 8 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ: 157.4, 149.5, 143.9, 136.7, 136.6, 128.8, 126.7, 121.7, 120.2, 35.4, 33.5, 22.3, 13.9. ¹H and ¹³C NMR spectrum included.

2-(3,5-bis(trifluoromethyl)phenyl)pyridine (Table 2, Entry 2).³ Following general procedure A, a mixture of 3,5-bis(trifluoromethyl)bromobenzene (43.1 μL, 73.3 mg, 0.25

² Iwasawa, T.; Ajami, D.; Rebek, Jr. *J. Org. Lett.* **2006**, *8*, 2925.

³ Coppo, P.; Plummer, E. A.; Cola, L. D. *Chem. Commun.* **2004**, 1774.

mmol), lithium triisopropyl 2-pyridylborate (104 mg, 0.375 mmol), KF, Pd₂dba₃ (2.3 mg, 0.0025 mmol) and **1** (3.0 mg, 0.015 mmol) was heated for 20 h. Flash column chromatography (10% EtOAc/Hexanes) yielded the title compound in 60 mg (82% yield) as a white solid, mp 45-46 °C. ¹H NMR (300 MHz, CDCl₃) δ: 8.75 (dt, J = 5,1 Hz, 1H), 8.48 (s, 2H), 7.91 (s, 1H), 7.81-7.86 (m, 2H), 7.35 (dt, J = 5,1 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ: 154.1, 150.1, 141.3, 137.2, 132.1, 126.9, 124.4, 123.6, 122.4, 120.6. ¹H and ¹³C NMR spectrum included.

2-(4-methoxyphenyl)pyridine (Table 2, Entry 3).⁴ Following general procedure A, a mixture of 4-bromoanisole (31.3 μL, 46.8 mg, 0.25 mmol), lithium triisopropyl 2-pyridylborate (104 mg, 0.375 mmol), KF, Pd₂dba₃ (2.3 mg, 0.0025 mmol) and **1** (3.0 mg, 0.015 mmol) was heated for 20 h. Flash column chromatography (15% EtOAc/Hexanes) yielded the title compound in 34 mg (74% yield) as a white solid, mp 47-48 °C. ¹H NMR (300 MHz, CDCl₃) δ: 8.65 (dt, J = 5,1 Hz, 1H), 7.96 (d, J = 9 Hz, 2H), 7.71 (dt, J = 8,2 Hz, 1H), 7.66 (dt, J = 8,1 Hz, 1H), 7.17 (dd, J = 5,1 Hz, 1H), 7.00 (d, J = 9 Hz, 2H), 3.86 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ: 160.4, 157.0, 149.4, 136.6, 132.0, 128.1, 121.4, 119.8, 114.1, 55.3. ¹H and ¹³C NMR spectrum included.

2-(2,5-dimethylphenyl)pyridine (Table 2, Entry 4). Following general procedure A, a mixture of 2-bromo-*p*-xylene (34.5 μL, 46.3 mg, 0.25 mmol), lithium triisopropyl 2-pyridylborate (104 mg, 0.375 mmol), KF, Pd₂dba₃ (2.3 mg, 0.0025 mmol) and **1** (3.0 mg, 0.015 mmol) was heated for 20 h. Flash column chromatography (10% EtOAc/Hexanes) yielded the title compound in 39 mg (87% yield) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ: 8.71 (dt, J = 5,1 Hz, 1H), 7.74 (dt, J = 7,1 Hz, 1H), 7.42 (dt, J = 8,1 Hz, 1H), 7.23-7.26 (m, 2H), 7.16 (dt, J = 6,1 Hz, 1H), 7.20 (d, J = 8 Hz, 1H), 7.14 (dt, J = 8,1 Hz, 1H), 2.38 (s, 3H), 2.34 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ: 160.0, 149.2, 140.2, 135.9, 135.2, 132.4, 130.6, 130.2, 128.9, 124.0, 121.5, 20.9, 19.7. IR (neat, cm⁻¹): 3394, 3014, 2922, 1598, 1563, 1501, 1471, 1426, 1378, 1149, 1039, 992, 792, 749. ¹H and ¹³C NMR spectrum included.

2-(pyridin-2-yl)benzotrile (Table 2, Entry 5).⁵ Following general procedure A, a mixture of 2-bromobenzotrile (45.5 mg, 0.25 mmol), lithium triisopropyl 2-

⁴ Andersson, H.; Almqvist, F.; Olsson, R. *Org. Lett.* **2007**, *9*, 1335.

⁵ Chen, X.; Hao, X.-S.; Goodhue, C. E.; Yu, J.-Q. *J. Am. Chem. Soc.* **2006**, *127*, 6790.

pyridylborate (104 mg, 0.375 mmol), KF, Pd₂dba₃ (2.3 mg, 0.0025 mmol) and **1** (3.0 mg, 0.015 mmol) was heated for 20 h. Flash column chromatography (25% EtOAc/Hexanes) yielded the title compound in 41 mg (90% yield) as a yellow oil. ¹H NMR (300 MHz, CDCl₃) δ: 8.77 (dt, J = 5,1 Hz, 1H), 7.76-7.84 (m, 4H), 7.79 (dt, J = 8,2 Hz, 1H), 7.50 (dt, J = 8,2 Hz, 1H), 7.35 (ddd, J = 8,5,1 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ: 155.2, 149.9, 143.4, 136.8, 134.1, 132.8, 129.9, 128.7, 123.3, 123.2, 118.7, 111.0. ¹H and ¹³C NMR spectrum included.

5-(pyridin-2-yl)pyrimidine (Table 2, Entry 6).⁶ Following general procedure A, a mixture of 5-bromopyrimidine (39.7 mg, 0.25 mmol), lithium triisopropyl 2-pyridylborate (104 mg, 0.375 mmol), KF, Pd₂dba₃ (2.3 mg, 0.0025 mmol) and **1** (3.0 mg, 0.015 mmol) was heated for 20 h. Recrystallization (Hexanes) yielded the title compound in 36 mg (91% yield) as a brown solid, mp 129-130 °C. ¹H NMR (300 MHz, CDCl₃) δ: 9.33 (s, 2H), 9.25 (s, 1H), 8.75 (dt, J = 5,1 Hz, 1H), 7.83 (dt, J = 8,2 Hz 1H), 7.76 (dt, J = 8,1 Hz, 1H), 7.35 (ddd, J = 8,5,2 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ: 158.6, 155.1, 152.0, 150.4, 137.2, 132.4, 123.6, 120.5. ¹H and ¹³C NMR spectrum included.

4-(pyridin-2-yl)isoquinoline (Table 2, Entry 7).⁷ Following general procedure A, a mixture of 4-bromoisoquinoline (52.0 mg, 0.25 mmol), lithium triisopropyl 2-pyridylborate (104 mg, 0.375 mmol), KF, Pd₂dba₃ (2.3 mg, 0.0025 mmol) and **1** (3.0 mg, 0.015 mmol) was heated for 20 h. Flash column chromatography (50% EtOAc/Hexanes) yielded the title compound in 42 mg (82% yield) as a yellow oil. ¹H NMR (300 MHz, CDCl₃) δ: 9.29 (s, 1H), 8.82 (dt, J = 5,1 Hz, 1H), 8.64 (s, 1H), 8.20 (d, J = 8 Hz, 1H), 8.03 (d, J = 8 Hz, 1H), 7.86 (dt, J = 8,1 Hz, 1H), 7.70 (dt, J = 8,1 Hz, 1H), 7.63 (t, J = 8 Hz, 1H), 7.37 (ddd, J = 8,5,1 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ: 156.3, 153.0, 149.7, 143.4, 136.8, 133.7, 131.5, 130.9, 128.5, 127.9, 127.3, 124.9, 124.7, 122.5. ¹H and ¹³C NMR spectrum included.

2,3'-bipyridine (Table 2, Entry 8).⁸ Following general procedure A, a mixture of 3-bromopyridine (24.1 μL, 39.5 mg, 0.25 mmol), lithium triisopropyl 2-pyridylborate (104

⁶ Berghian, C.; Darabantu, M.; Turck, A.; Pié, N. *Tetrahedron* **2005**, *61*, 9637.

⁷ Ishikura, M.; Oda, I.; Terashima, M. *Heterocycles* **1987**, *26*, 1603.

⁸ Cioffi, C. L.; Spencer, W. T.; Richards, J. J.; Herr, R. J. *J. Org. Chem.* **2004**, *69*, 2210.

mg, 0.375 mmol), KF, Pd₂dba₃ (2.3 mg, 0.0025 mmol) and **1** (3.0 mg, 0.015 mmol) was heated for 20 h. Flash column chromatography (EtOAc) yielded the title compound in 29 mg (73% yield) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ: 9.17 (d, J = 3 Hz, 1H), 8.71 (dt, J = 5,1 Hz, 1H), 8.64 (dt, J = 5,1 Hz, 1H), 8.31 (dt, J = 8,1 Hz, 1H), 7.79 (dt, J = 8,1 Hz, 1H), 7.75 (dt, J = 8,1 Hz, 1H), 7.39 (dd, J = 8,3 Hz, 1H), 7.28 (ddd, J = 8,5,1 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ: 154.7, 150.0, 149.9, 148.2, 136.9, 134.8, 134.3, 123.5, 122.8, 120.6. ¹H and ¹³C NMR spectrum included.

2-(4-butylphenyl)-6-methoxypyridine (Table 2, Entry 9). Following general procedure A, a mixture of 4-*n*-butylbromobenzene (44.1 μL, 53.3 mg, 0.25 mmol), lithium triisopropyl 2-(6-methoxypyridyl)borate (114 mg, 0.375 mmol), KF, Pd₂dba₃ (3.4 mg, 0.00375 mmol) and **2** (3.6 mg, 0.0225 mmol) was heated for 20 h. Flash column chromatography (5% EtOAc/Hexanes) yielded the title compound in 54 mg (90% yield) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ: 7.97 (d, J = 8 Hz, 2H), 7.62 (t, J = 8 Hz, 1H), 7.32 (d, J = 8 Hz, 1H), 7.28 (d, J = 8 Hz, 2H), 6.67 (d, J = 8 Hz, 1H), 4.05 (s, 3H), 2.67 (t, J = 8 Hz, 2H), 1.65 (pent, J = 8 Hz, 2H), 1.39 (hex, J = Hz, 2H), 0.96 (t, J = 8 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ: 163.6, 154.7, 143.8, 139.1, 136.5, 128.7, 126.5, 112.4, 108.8, 53.1, 35.4, 33.6, 22.3, 14.0. IR (neat, cm⁻¹): 3060, 2955, 2929, 2857, 1587, 1514, 1463, 1435, 1398, 1324, 1302, 1255, 1151, 1075, 1025, 795. ¹H and ¹³C NMR spectrum included.

2-methoxy-6-(4-methoxyphenyl)pyridine (Table 2, Entry 10).⁹ Following general procedure A, a mixture of 4-bromoanisole (31.3 μL, 46.8 mg, 0.25 mmol), lithium triisopropyl 2-(6-methoxypyridyl)borate (114 mg, 0.375 mmol), KF, Pd₂dba₃ (3.4 mg, 0.00375 mmol) and **2** (3.6 mg, 0.0225 mmol) was heated for 20 h. Flash column chromatography (5% EtOAc/Hexanes) yielded the title compound in 33 mg (61% yield) as a white solid, mp 120-121 °C. ¹H NMR (300 MHz, CDCl₃) δ: 8.01 (d, J = 7 Hz, 2H), 7.59 (dt, J = 7,2 Hz, 1H), 7.27 (d, J = 7 Hz, 1H), 6.98 (d, J = 7 Hz, 2H), 6.63 (d, J = 7 Hz, 2H), 4.03 (s, 3H), 3.86 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ: 163.6, 160.3, 154.4, 139.1, 131.7, 127.9, 113.9, 111.9, 108.2, 55.3, 53.1. ¹H and ¹³C NMR spectrum included.

4-(5-fluoropyridin-2-yl)benzotrile (Table 2, Entry 11). Following general procedure A, a mixture of 4-bromobenzotrile (45.5 mg, 0.25 mmol), lithium triisopropyl 2-(5-

⁹ Gosmini, C.; Nédélec, J. Y.; Périchon, R. *Tetrahedron Lett.* **2000**, *41*, 5039.

fluoropyridyl)borate (109 mg, 0.375 mmol), KF, Pd₂dba₃ (3.4 mg, 0.00375 mmol) and **2** (3.6 mg, 0.0225 mmol) was heated for 20 h. Recrystallization (Hexanes) yielded the title compound in 32 mg (65% yield) as a brown solid, mp 61-62 °C. ¹H NMR (300 MHz, CDCl₃) δ: 8.57 (d, J = 3 Hz, 1H), 8.06 (d, J = 8 Hz, 2H), 7.78 (dd, J = 8,3 Hz, 1H), 7.75 (d, J = 8 Hz, 2H), 7.52 (dt, J = 8,3 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ: 160.3, 158.3, 142.3, 138.3, 132.6, 127.2, 123.7, 121.8, 118.6, 112.4. IR (neat, cm⁻¹): 2917, 2226, 1585, 1476, 1225, 1069, 1014, 791. Anal. Calcd. For C₁₂H₇N₂F: C, 72.72; H, 3.56. Found C, 72.52; H, 3.55.

2-(2,5-dimethylphenyl)-5-fluoropyridine (Table 2, Entry 12). Following general procedure A, a mixture of 2-bromo-*p*-xylene (34.5 μL, 46.3 mg, 0.25 mmol), lithium triisopropyl 2-(5-fluoropyridyl)borate (109 mg, 0.375 mmol), KF, Pd₂dba₃ (3.4 mg, 0.00375 mmol) and **2** (3.6 mg, 0.0225 mmol) was heated for 20 h. Flash column chromatography (5% EtOAc/Hexanes) yielded the title compound in 20 mg (40% yield) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ: 8.55 (d, J = 3 Hz, 1H), 7.45 (dt, J = 8,3 Hz, 1H), 7.39 (dd, J = 8,3 Hz, 1H), 7.20 (s, 1H), 7.17 (d, J = 8 Hz, 1H), 7.12 (d, J = 8 Hz, 1H), 2.36 (s, 3H), 2.30 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ: 159.3, 157.2, 139.1, 137.2, 135.4, 132.5, 130.7, 130.2, 129.1, 124.8, 122.8, 20.9, 19.8. IR (neat, cm⁻¹): 3019, 2923, 2862, 1630, 1580, 1479, 1380, 1237, 1220, 1020, 812. ¹H and ¹³C NMR spectrum included.

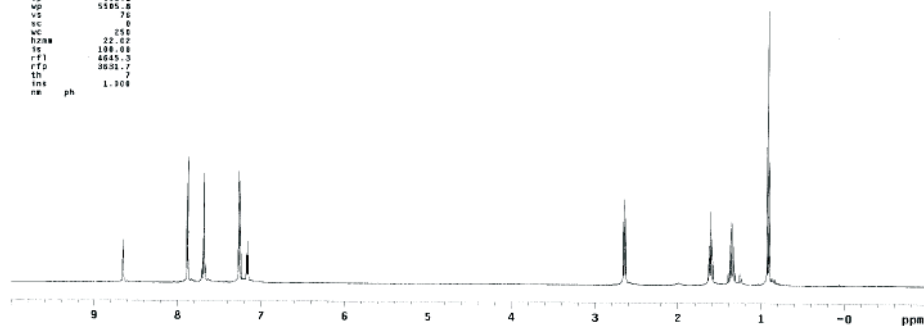
4-(6-(1,3-dioxolan-2-yl)pyridin-2-yl)benzotrile (Table 2, Entry 13). Following general procedure A, a mixture 4-bromobenzotrile (45.5 mg, 0.25 mmol), lithium triisopropyl 2-(6-(1,3-dioxolan-2-yl)pyridin-2-yl)borate (129 mg, 0.375 mmol), KF, Pd₂dba₃ (3.4 mg, 0.00375 mmol) and **1** (4.5 mg, 0.0225 mmol) was heated for 20 h. Flash column chromatography (25% EtOAc/Hexanes) yielded the title compound in 38 mg (63% yield) as a white solid, mp 80-81 °C. ¹H NMR (300 MHz, CDCl₃) δ: 8.14 (d, J = 8 Hz, 2H), 7.85 (t, J = 8 Hz, 1H), 7.73-7.76 (m, 3H), 7.57 (d, J = 8 Hz, 1H), 5.92 (s, 1H), 4.11-4.22 (m, 4H). ¹³C NMR (75 MHz, CDCl₃) δ: 157.6, 154.6, 143.0, 137.9, 132.4, 127.5, 121.0, 120.1, 118.8, 112.4, 103.7, 65.7. IR (neat, cm⁻¹): 2955, 2876, 2223, 1593, 1459, 1367, 1110. ¹H and ¹³C NMR spectrum included.

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at 2.230 homo n
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2-(4-butylphenyl)pyridine (Table 2, Entry 1)

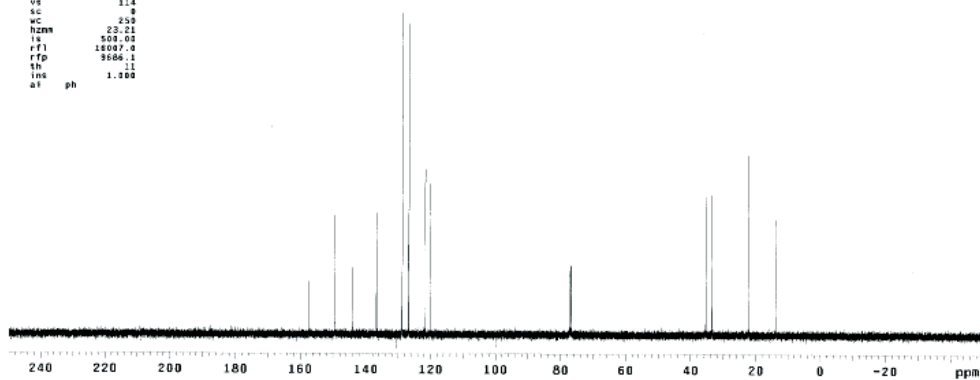


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2-(4-butylphenyl)pyridine (Table 2, Entry 1)



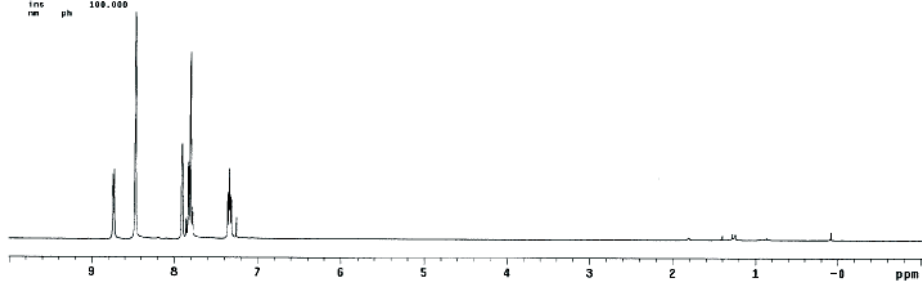
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2-(3,5-bis(trifluoromethyl)phenyl)pyridine (Table 2, Entry 2)



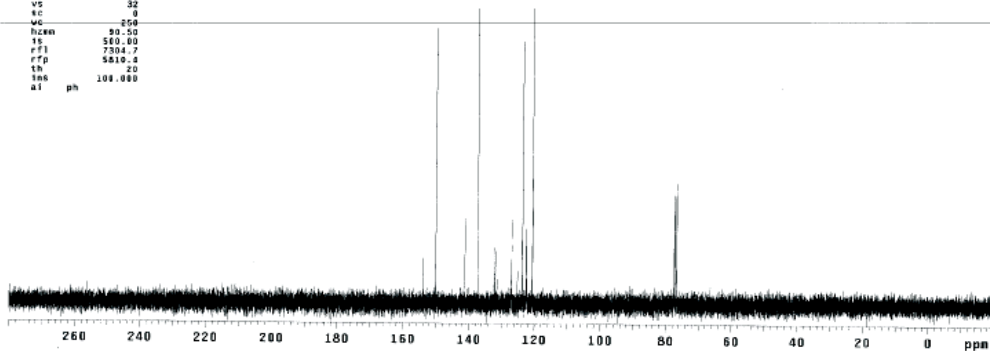
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at 1.000 sbs -1.100
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2-(3,5-bis(trifluoromethyl)phenyl)pyridine (Table 2, Entry 2)



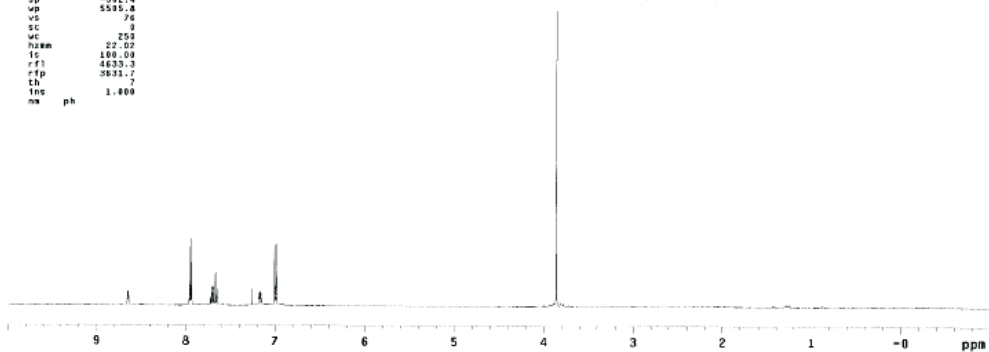
STANDARD PROTON PARAMETERS

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2-(4-methoxyphenyl)pyridine (Table 2, Entry 3)



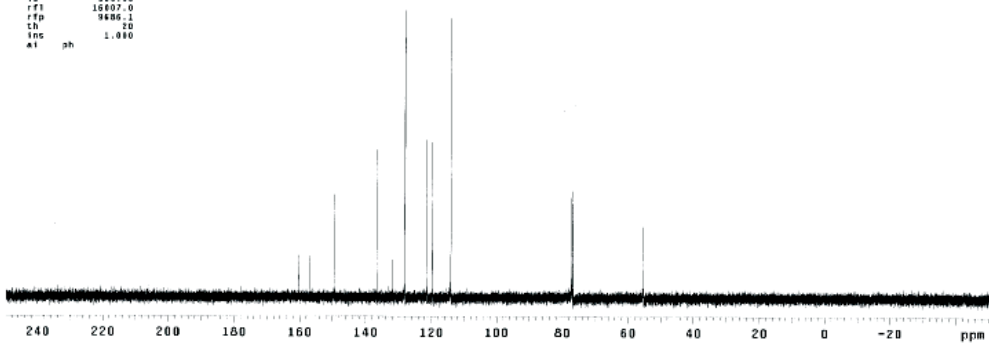
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2-(4-methoxyphenyl)pyridine (Table 2, Entry 3)



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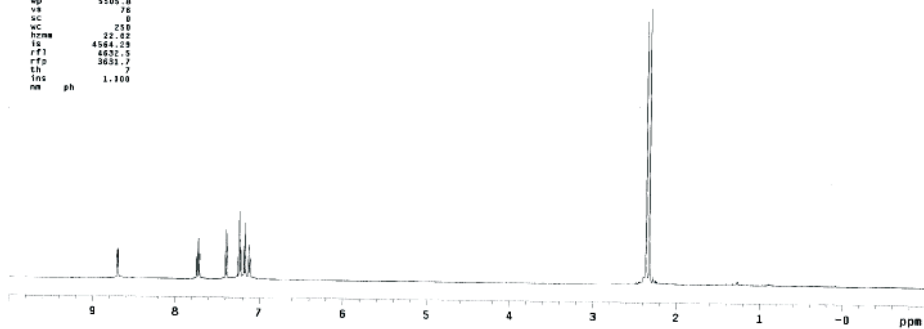
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2-(2,5-dimethylphenyl)pyridine (Table 2, Entry 4).



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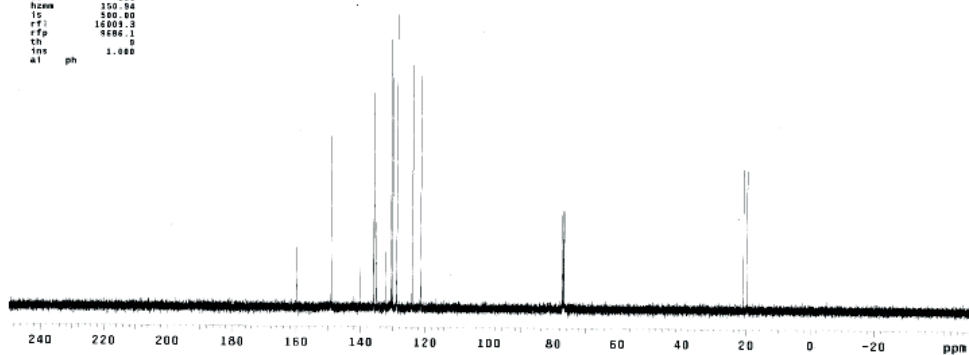
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 ps nn

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2-(2,5-dimethylphenyl)pyridine (Table 2, Entry 4).



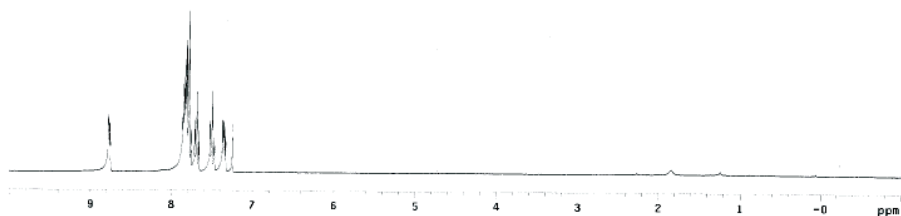
STANDARD IN OBSERVE

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007.116 dmw c
ACQUISITION def 200
=====
PROCCESSING
stfrq 300.101
tn HI wffile
ac 0.003 p'roc
np 00032 fn 131072
sw 6032.4
fb not used werr
ds not used werr
tpwr 50 wds
ps 6.0 wnt
d1 0.050
tof 007.7
ct 16
a'lock n
gain not used
=====
FLAGS
ii n
in n
dp DISPLAY y
=====
sp -300.5
wp 3012.7
vs 45
sc 0
wc 250
hzwa 13.15
is 500.00
rf1 100.4
rtp 0
ts 0
ins ph 103.000
=====

```

2-(pyridin-2-yl)benzonitrile (Table 2, Entry 5)



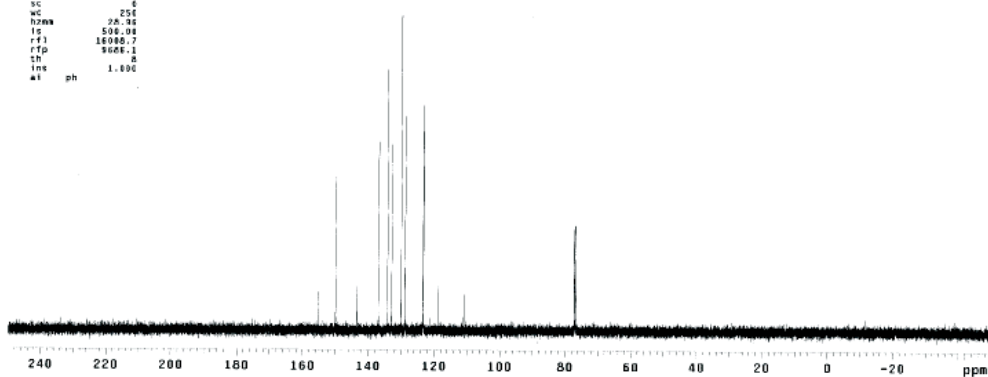
STANDARD CARBON PARAMETERS

```

=====
expt sEpu1
SAMPLE DEC. & VT
date Jul 2 2007 dfrq 510.233
solvent CDCl3 dn HI
file /data/export/~spur 44
home/stouch/44b/ser- dof -500.0
ckp/sk_VII174_01- deo y
0207.116 dmw w
ACQUISITION def 10000
=====
PROCCESSING
stfrq 125.796
tn C13 s'ocq 1.0
at 1.706 hnoo
np 131011
sw 37735.0 fb 0.30
fb not used wffile
ds 4 p'roc
es 1 fn 131072
tpwr 54 wds
ps 6.3
d1 0.763 werr
tof 021.4 wds
ct 60 wnt
a'lock n
gain not used
=====
FLAGS
ii n
in n
dp DISPLAY y
hs DISPLAY nn
=====
sp -6322.1
wp 37735.0
vs 170
sc 0
wc 250
hzwa 26.00
is 500.00
rf1 10000.7
rtp 9000.1
ts 0
ins ph 1.000
=====

```

2-(pyridin-2-yl)benzonitrile (Table 2, Entry 5)

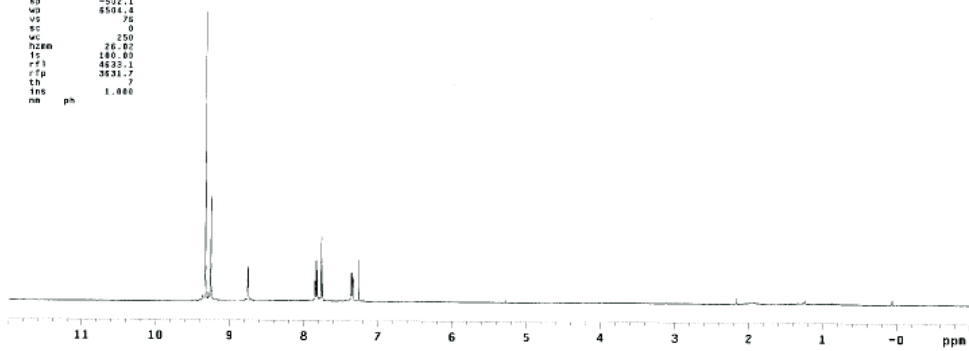


STANDARD PROTON PARAMETERS

```

exp1 s2pu1
SAMPLE DEC. & VT
date Jul 2 2007 dfrq 125.785
solvent CDCl3 dn C13
file /data/export/~dpwr 44
home /ibuch/440/r0-007 8
cky/45b_V11275_07-08 nm
207.fid dne C
ACQUISITION dnef 10000
f1rq 500.235 dseq
t1 n1 drag 1.0
at 3.200 homo n
np 64800 PROCESSING
sw 10509.0 wtf1ic
f0 not used proc ft
bs 1 fe 131972
ss 1 math f
tpr 63
pw 9.0 werr
d1 8 wexp
tof 1489.2 wbc
nt 16 wnt
ct 15
alock n
gain not used
FLAGS
i1 n
i2 n
sp y
ds nm
DISPLAY
sp -532.1
wp 6504.4
vs 76
sc 0
wc 250
hzmw 26.82
f1 180.00
r1 6535.1
r2 3531.7
t1 7
t2 1.000
nm ph
    
```

5-(pyridin-2-yl)pyrimidine (Table 2, Entry 6)

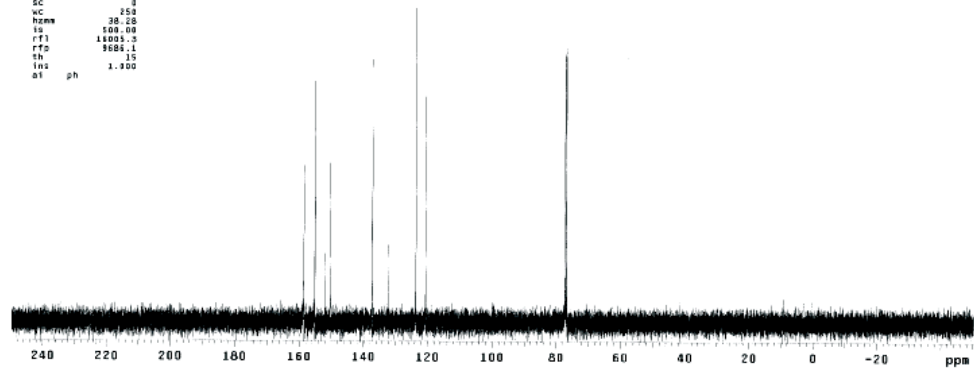


STANDARD CARBON PARAMETERS

```

exp1 s2pu1
SAMPLE DEC. & VT
date Jul 2 2007 dfrq 500.233
solvent CDCl3 dn C13
file /data/export/~dpwr 44
home /ibuch/440/r0-007 -500.0
cky/45b_V11275_07-08 dn y
0287.fid dne w
ACQUISITION dnef 10000
f1rq 125.786 dseq
t1 n1 drag 1.0
at 1.736 homo n
np 131010 PROCESSING
sw 2735.8 lb 0.30
f0 not used wtf1ic ft
bs 1 fe 131972
ss 1 math f
tpr 54
pw 6.9
d1 8 wexp
tof 631.4 wbc
nt 1080 wnt
ct 98
alock n
gain not used
FLAGS
i1 n
i2 n
sp y
ds nm
DISPLAY
sp -6315.6
wp 2735.3
vs 63
sc 0
wc 250
hzmw 38.20
f1 180.00
r1 16005.3
r2 9685.1
t1 15
t2 1.000
nm ph
    
```

5-(pyridin-2-yl)pyrimidine (Table 2, Entry 6)



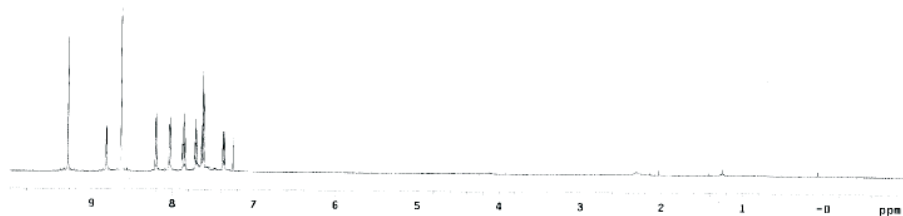
STANDARD PROTON PARAMETERS

```

expl 12pu1
SAMPLE
date Jul 13 2107 dfrq DEC. & VT 125.795
solvent CDCl3 dm C13
file /data/export/~dpuv 44
home/1buch/44b/ro-007 0
cxy/44b_47118_07-06 nm
ACQUISITION def 13000
sfrq 500.235 dseq 1.0
in 10 hz dres 1.0
at 2.200 homo n
np 64000 PROCESSING n
sw 10036.0 wtf file ft
td not used proc 131872 f
bs 1 fn 131872
ss 1 meth
tpwr 6.3 werr
dl 0 wexp
srf 1488.2 wbs
nt 16 wnt
ct 16
atlock n
gain not used
ii FLAGS n
in n
sp y
ms nm
SP DISPLAY
sp -391.7
wp 5585.8
vs 46
sc 0
wc 28
hnm 22.32
is 131.88
rf1 4532.8
rfp 3631.7
th 10
ins 1.000
ph

```

4-(pyridin-2-yl)isoquinoline (Table 2, Entry 7)



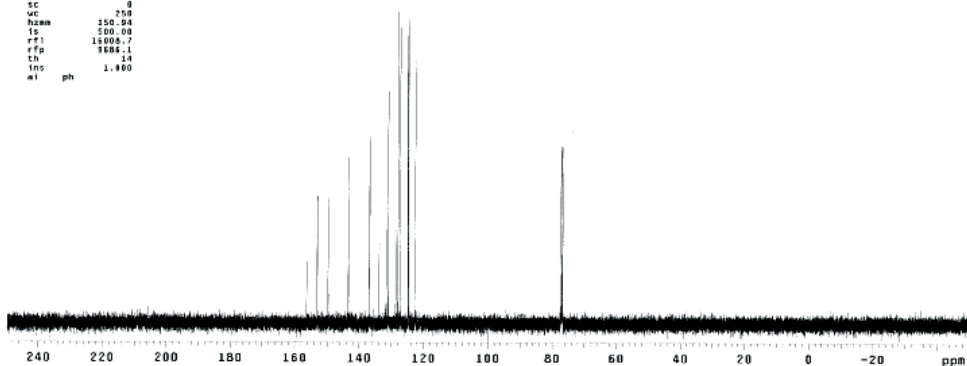
STANDARD CARBON PARAMETERS

```

expl 12pu1
SAMPLE
date Jul 13 2107 dfrq DEC. & VT 500.233
solvent CDCl3 dm h1
file /data/export/~dpuv 44
home/1buch/44b/ro-007 -508.0
cxy/44b_47118_07-06 y
ACQUISITION def 10100
sfrq 125.796 dseq 1.0
in 10 hz dres 1.0
at 1.730 homo n
np 131010 PROCESSING n
sw 37735.0 lb 0.30
td not used wtf file ft
bs 1 fn 131872
ss 1 meth
tpwr 6.3 werr
dl 0 wexp
srf 631.4 wbs
nt 256 wnt
ct 16
atlock n
gain not used
ii FLAGS n
in n
sp y
ms nm
SP DISPLAY
sp -632.1
wp 37735.3
vs 313
sc 0
wc 26
hnm 150.94
is 500.00
rf1 16085.7
rfp 3685.1
th 10
ins 1.000
ph

```

4-(pyridin-2-yl)isoquinoline (Table 2, Entry 7)



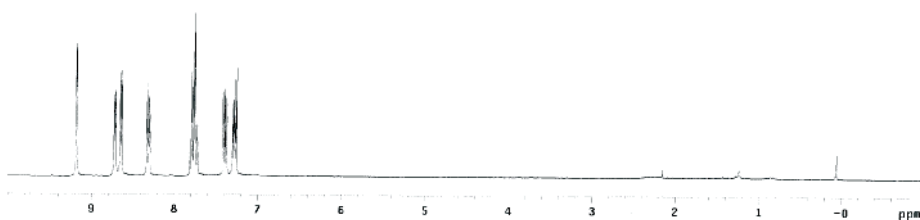
STANDARD 1H OBSERVE

```

expl st01h
SAMPLE DEC. & VT
date Aug 14 2007 #frq 300.109
solvent CDCl3 dn H1
file /data/export/~spur 34
home/51bucy/80/ro- sof 4
nat/440_VII1195_30- dn nnn
1407.714 cm c
ACQUISITION def 200
#frq 300.109 PROCESSING
in H1 wfile ft
at 1.803 proc 131072
ap 4802.0 in
sw 2042.4
fu not used verr
ns 1 wexp
tpr 1.4 wds
pw 6.5 wnt
SI 0.155
tof 857.2
nt 20
ct 14
#lock n
gain not used
flags n
in n
op 2
DISPLAY
sp -300.6
wd 3384.8
vs 45
sc 0
wc 238
hznm 13.22
ls 638.00
rfl 640.4
rfp 8
th 20
ins ph 100.009

```

2,3'-bipyridine (Table 2, Entry 8)



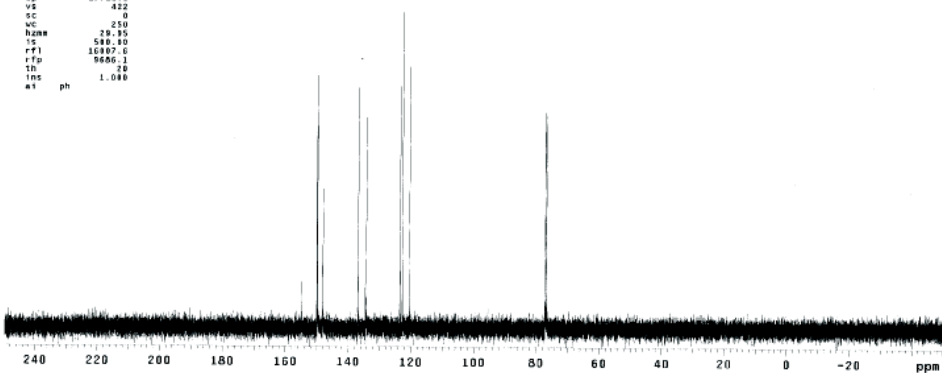
STANDARD CARBON PARAMETERS

```

expl s2ou1
SAMPLE DEC. & VT
date Jul 13 2007 #frq 100.233
solvent CDCl3 dn H1
file /data/export/~spur 44
home/51bucy/400/ro- sof -540.0
csp/440_VII1187_1- dn v
71387.714 dn w
ACQUISITION def 18004
#frq 100.233 dseq 1.4
in C13 drcz n
at 1.736 homo n
ap 13192.0 PROCESSING 0.38
sw 37735.0 lb wfile ft
ns not used proc 131072
tpr 1.4 wnt
pw 6.5 wexp
SI 0.263 verr
tof 631.4 wds
nt 250 wnt
ct 02
#lock n
gain not used
flags n
in n
op 2
ns nn
DISPLAY
sp -520.9
wd 37735.3
vs 422
sc 0
wc 230
hznm 29.95
ls 586.00
rfl 10307.0
rfp 8686.1
th 20
ins ph 1.080

```

2,3'-bipyridine (Table 2, Entry 8)



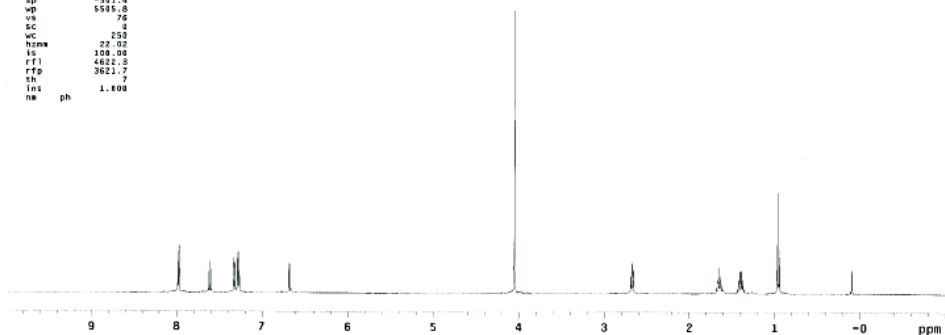
STANDARD PROTON PARAMETERS

```

expt s2p1
SAMPLE DEC. & VT
date Jul 13 2007 dfrq 125.705
solvent CDCl3 dn 013
file /data/export/ dpr 44
home/sibuch/480/rw dof 3
ckv/480_VIII118_07- dn nnn
1307.716 dm 19800
ACQUISITION def
f1q 598.235 dseq 1.0
t1 n1 drc 1.0
at 3.280 homo n
n0 14880 PROCESSING n
sw 10880.0 wfile fc
fb not used proc fc
ss 1 fn 131872
s2 1 math f
tpr 83
pw 9.0 werr
ds 0 wep
tof 1498.2 wbs
nt 16 wnt
ct 16
alock n
gain not used
FLAGS
f1 n
f2 n
f3 y
f4 n
hs DISPLAY nn
sp -581.4
wp 5595.8
vs 76
sc 6
wc 250
hnm 22.02
ls 108.08
rf1 4825.3
rfp 3921.7
th 7
ins 1.000
ns ph

```

2-(4-butylphenyl)-6-methoxypyridine (Table 2, Entry 9)



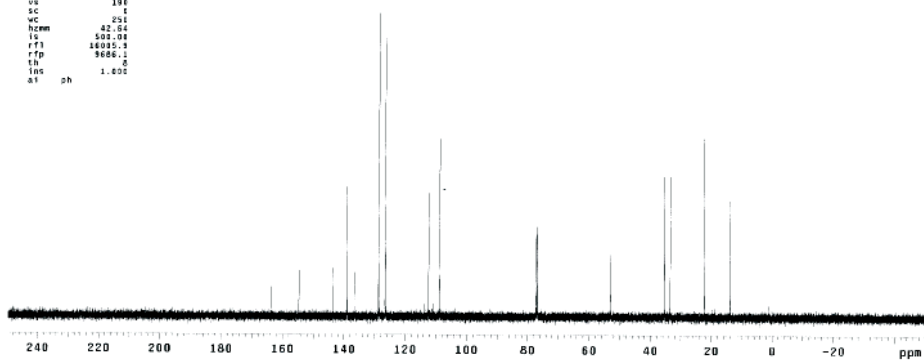
STANDARD CARBON PARAMETERS

```

expt s2p1
SAMPLE DEC. & VT
date Jul 13 2007 dfrq 125.733
solvent CDCl3 dn 013
file /data/export/ dpr 44
home/sibuch/480/rw dof -508.0
ckv/480_VIII118_07- dn y
71307.716 dm w
ACQUISITION def
f1q 125.733 dseq 1.0
t1 n1 drc 1.0
at 1.736 homo n
n0 13180 PROCESSING n
sw 37735.8 lb 0.36
fb not used wfile fc
ss 2 proc fc
s2 1 fn 131072
tpr 84 math f
pw 8.3
ds 0 wep
tof 831.4 wep
nt 250 wbs
ct 76 wnt
alock n
gain not used
FLAGS
f1 n
f2 n
f3 y
f4 n
hs DISPLAY nn
sp -8319.1
wp 37735.3
vs 198
sc 4
wc 251
hnm 42.84
ls 502.08
rf1 14030.3
rfp 3686.1
th 0
ins 1.000
ns ph

```

2-(4-butylphenyl)-6-methoxypyridine (Table 2, Entry 9)

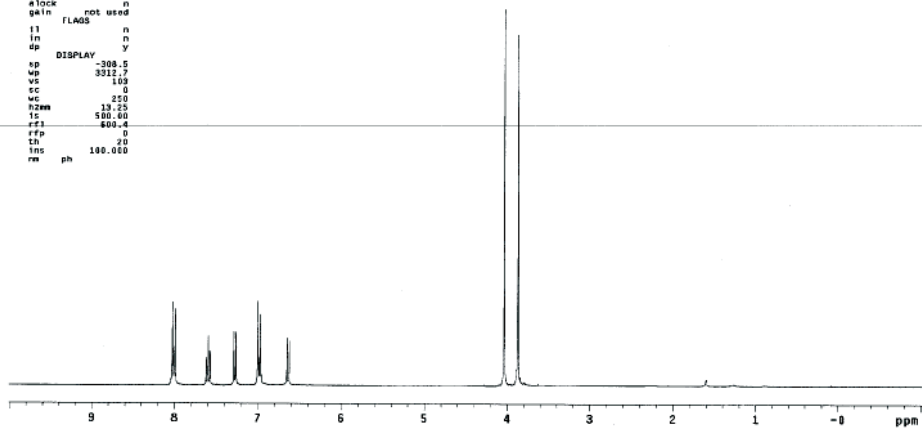


STANDARD IN OBSERVE

```

exp3 s1dih
SAMPLE
date Aug 15 2007 dfrq DEC. & WT 500.100
solvent CDCl3 dn H1
file ACQUISITION exp dpr 30
sfrq 300.101 dm 0
tn C13 dem min
at 4.303 def 200
np 48952 PROCESSING
sw 1607.6 wfile ft
fb not used proc 131072
ts 1
lprv 54
pw 8.8 warr
d1 8.050 wexp
tof 867.7 wps
nt 18 wnt
ct 15
nlock n
gain not used
flags n
in n
dp y
DISPLAY
sp -308.5
wp 3312.7
vs 103
sc 0
wc 250
hzms 13.25
fg 500.00
rfs 600.4
rfa 0
th 20
ins 100.000
rs ph
    
```

2-methoxy-6-(4-methoxyphenyl)pyridine (Table 2, Entry 10)

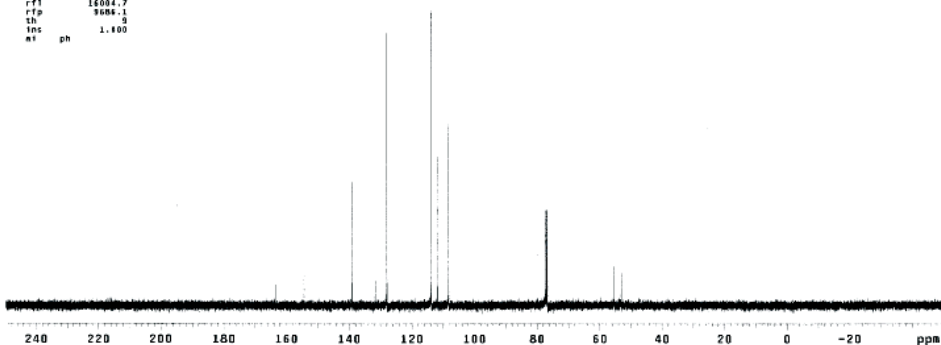


STANDARD CARBON PARAMETERS

```

exp2 s2pu1
SAMPLE
date Aug 15 2007 dfrq DEC. & WT 500.233
solvent CDCl3 dn H1
file ACQUISITION exp dpr 44
sfrq 125.756 dm -500.0
tn C13 dem w
at 1.736 def 10000
np 131010 GSEQ 1.0
sw 37759.0 dres
fb not used hbro n
ts 2 PROCESSING
lprv 54 wfile ft
pw 8.3 dpc 131072
d1 8.763 fn
tof 631.4 math r
nt 10000
ct 160 warr
nlock n wexp
gain not used wnt
flags n
in n
dp y
ns nm
DISPLAY
sp -4318.5
wp 37735.8
vs 244
sc 0
wc 250
hzms 150.00
fg 500.00
rfs 16004.7
rfa 9684.1
th 0
ins 1.400
rs ph
    
```

2-methoxy-6-(4-methoxyphenyl)pyridine (Table 2, Entry 10)

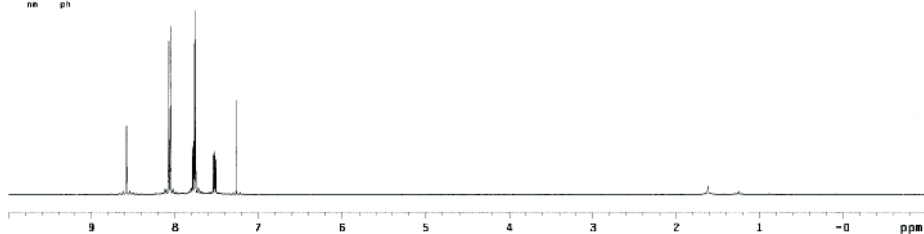


STANDARD PROTON PARAMETERS

```

exp2 s2pu1
SAMPLE
date Aug 21 2007 dfrq DEC. & VT 125.785
solvent CCl3 dn 125.785
file /data/export/~dpuw 44
home/sbuck/44b/rom dof 1
cxy/sb_VII1121_3- dn dn
82197.FID dms dn
ACQUISITION dof 10800
sfrq 108.233 dseq
in HI dres 1.3
at 3.250 hnmw
np 64000 PROCESSING n
wv 10288.0 wffile ft
Tb not used PROC
bs 1 fm 131072
rs 1 math T
spwr 8.0
pw 9.0 werr
dl 0 wexp
LOF 1458.0 wha
nt 10 wnt
ct 0
alock not used
gain not used
ii FLAGS
in n
op v
rs nk
DISPLAY
sp -581.1
wp 5545.0
vs 5.0
vc 0
wc 25.0
hzmw 22.32
is 108.00
rfl 4622.3
rfp 3621.7
th 1.000
int ph
  
```

4-(5-fluoropyridin-2-yl)benzonitrile (Table 2, Entry 11)

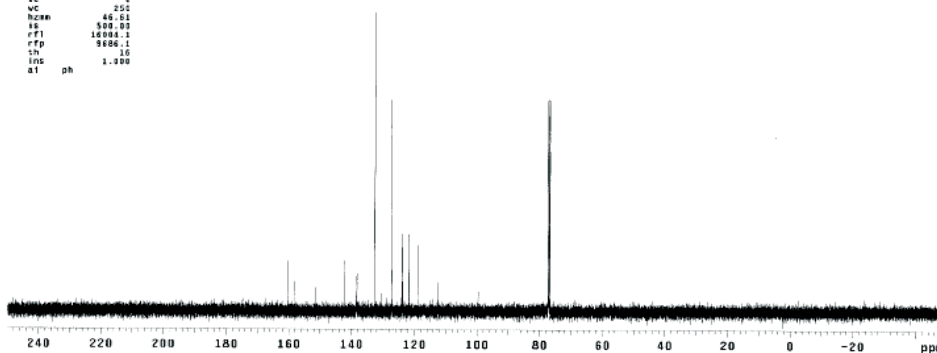


STANDARD CARBON PARAMETERS

```

exp2 s2pu1
SAMPLE
date Aug 21 2007 dfrq DEC. & VT 500.233
solvent CCl3 dn 500.233
file /data/export/~dpuw 44
home/sbuck/44b/rom dof -500.4
cxy/sb_VII1121_3- dn v
82197.FID dms w
ACQUISITION dof 10800
sfrq 125.786 dseq
in C13 dres 1.3
at 1.736 hnmw
np 13100 PROCESSING n
wv 37725.0 lb PROC 0.30
Tb not used wffile ft
bs 2 fm 131072
rs 1 math T
spwr 8.3
pw 9.760 werr
dl 0 wexp
LOF 431.4 wha
nt 8 wnt
ct 0
alock not used
gain not used
ii FLAGS
in n
op v
rs nk
DISPLAY
sp -5317.1
wp 27725.0
vs 390
vc 0
wc 25.0
hzmw 46.01
is 500.00
rfl 16086.1
rfp 9886.1
th 1.000
int ph
  
```

4-(5-fluoropyridin-2-yl)benzonitrile (Table 2, Entry 11)



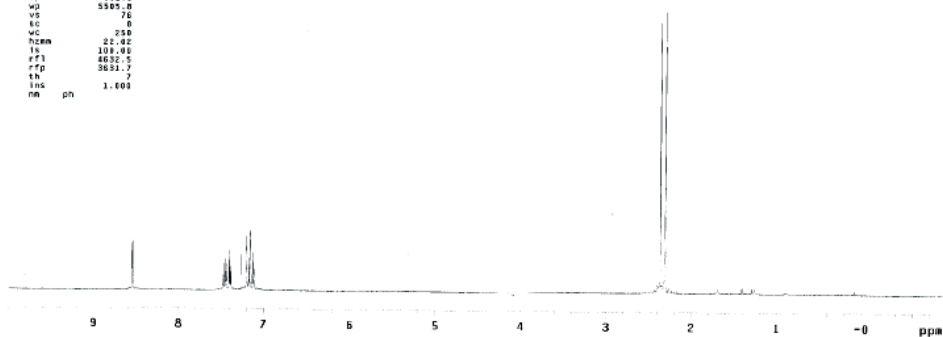
STANDARD PROTON PARAMETERS

```

exp1 s2pul

SAMPLE DEC. & VT
date Jul 17 2007 dfrq 125.755
solvent CDCl3 dn C13
file /data/export/ dpwr 44
home/s1bucl/4kb/ro- dof 3
ckj/4kb_VIIII18_07- dn nnn
1737.FID dm c
ACQUISITION dmf 10100
sfreq 510.135 dseg
tn H1 dres 1.0
at 3.203 homo
nd 64408 PROCESSING n
sw 19809.0 wfile ft
fb not used proc 131072
ss 1 fn
ss 1 math f
tpwr 63
sw 9.0 werr
d1 8 wexp
tof 1498.2 wds
nt 16 wnt
ct 16
atock n
gain not used
FLAGS
f3 n
f4 n
sp y
ds DISPLAY nm
sp -800.5
wp 5305.0
vs 76
sc 0
wc 250
h2cm 22.02
is 100.00
rf1 4830.5
rfp 3831.7
tn 2
ins 1.601
na ph
  
```

2-(2,5-dimethylphenyl)-5-fluoropyridine (Table 2, Entry 12)



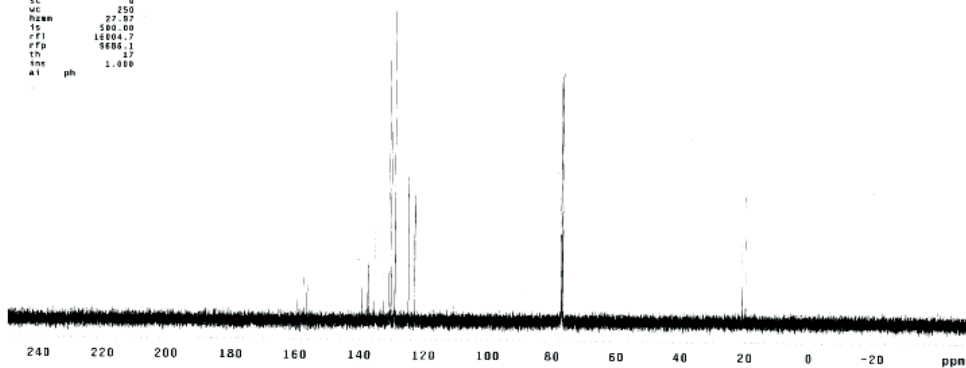
STANDARD CARBON PARAMETERS

```

exp1 s2pul

SAMPLE DEC. & VT
date Jul 17 2007 dfrq 500.233
solvent CDCl3 dn H1
file /data/export/ dpwr 44
home/s1bucl/4kb/ro- dof -500.3
ckj/4kb_VIIII18_07- dn y
1737.FID dm w
ACQUISITION dmf 10100
sfreq 125.746 dseg
tn C13 dres 1.0
at 1.738 homo
nd 131018 PROCESSING n
sw 37735.0 lb 0.30
fb not used wfile ft
ss 2 proc 131072
ss 1 fn
spwr 5 math f
sw 6.9
d1 0.763 werr
tof 831.4 wexp
nt 256 wds
ct 174 wnt
atock n
gain not used
FLAGS
f3 n
f4 n
sp y
ds DISPLAY nm
sp -8310.1
wp 37735.3
vs 394
sc 0
wc 250
h2cm 27.97
is 500.00
rf1 16104.7
rfp 9836.1
tn 2
ins 1.040
at ph
  
```

2-(2,5-dimethylphenyl)-5-fluoropyridine (Table 2, Entry 12)

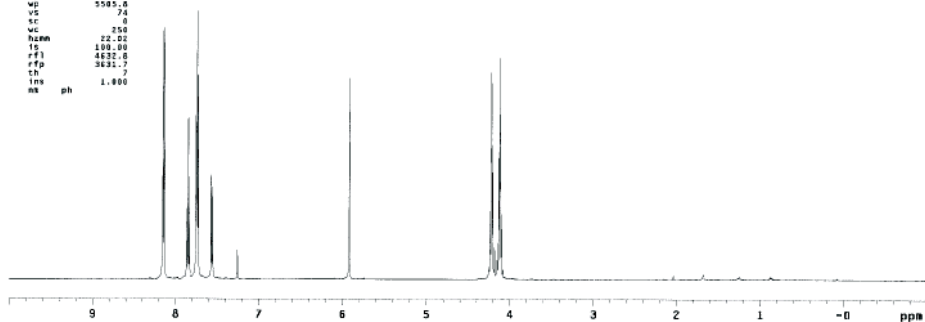


STANDARD PROTON PARAMETERS

```

exp2 s2pu1
SAMPLE
date DEC 10 2007 dfrq 125.755
solvent CDCl3 dn C13
file /data/exp0071- dpuv 37
home/61buch/4kb/r0- dof 0
cxy/4kb_vii1290_12- de nm
1807.TID dm C
ACQUISITION def 10000
sfrq 500.235 dscq
tn HI dres 1.0
at 3.288 homo n
np 84088 PROCESSING n
sv 10000.0 wfile
fb not used proc 151072
ss 1 math
tpwr 55
pw 0.1 verr
d1 148.0 vexp
tot 14 vnt
ct 14
atock not used
path
FLAGS
il n
in n
op 3
ns ns
DISPLAY
sp -591.0
wp 5585.0
vc 70
sc 0
wc 500
hzmm 22.02
ls 1000.00
rf1 4832.0
rfp 3832.0
th 7
ins ph 1.000
  
```

4-(6-(1,3-dioxolan-2-yl)pyridin-2-yl)benzonitrile (Table 2, Entry 13)

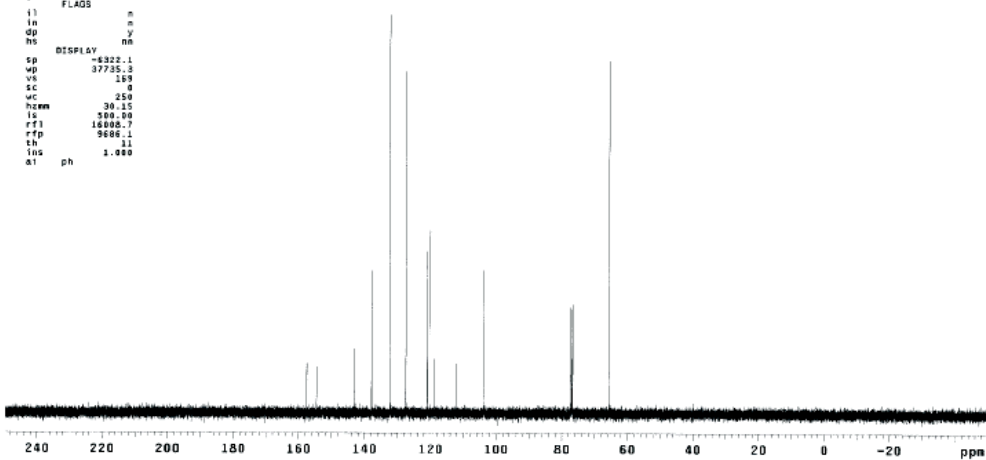


STANDARD CARBON PARAMETERS

```

exp2 s2pu1
SAMPLE
date DEC 10 2007 dfrq 125.755
solvent CDCl3 dn C13
file /data/exp0071- dpuv 37
home/61buch/4kb/r0- dof -590.3
cxy/4kb_vii1290_12- de v
21807.TID dm v
ACQUISITION def 10000
sfrq 125.755 dscq
tn C13 dres 1.0
at 1.700 homo n
np 131010 PROCESSING n
sv 37735.0 v
fb not used wfile 0.30
bs 1 proc
ss 1 ft 131072
tpwr 53 math
pw 6.9
d1 0.763 verr
tot 631.1 vexp
nt 11801 vnt
ct 42
atock not used
path
FLAGS
il n
in n
op v
ns ns
DISPLAY
sp -6322.1
wp 37735.3
vc 150
sc 0
wc 250
hzmm 30.15
ls 1000.00
rf1 16000.7
rfp 9600.1
th 11
ins ph 1.000
at
  
```

4-(6-(1,3-dioxolan-2-yl)pyridin-2-yl)benzonitrile (Table 2, Entry 13)



III. Experimental for the Reactions with Aryl Chlorides

4-(pyridin-2-yl)benzotrile (Table 3, Entry 1).¹⁰ Following general procedure A, a mixture of 4-chlorobenzotrile (34.4 mg, 0.25 mmol), lithium triisopropyl 2-pyridylborate (104 mg, 0.375 mmol), KF, Pd₂dba₃ (2.3 mg, 0.0025 mmol) and **2** (3.0 mg, 0.015 mmol) was heated for 20 h. Flash column chromatography (15% EtOAc/Hexanes) yielded the title compound in 33 mg (73% yield) as a white solid, mp 91-92 °C. ¹H NMR (300 MHz, CDCl₃) δ: 8.72 (dt, J= 8,1 Hz, 1H), 8.11 (d, J = 8 Hz, 2H), 7.81 (dt, J = 8,1 Hz, 1H), 7.74-7.77 (m, 3H), 7.31 (dt, J = 8,1 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ: 155.1, 150.0, 143.4, 137.0, 132.5, 127.4, 123.3, 120.9, 118.8, 112.3. ¹H and ¹³C NMR spectrum included.

2-(4-butylphenyl)pyridine (Table 3, Entry 2).² Following general procedure A, a mixture of 4-*n*-butylchlorobenzene (41.0 μL, 42.2 mg, 0.25 mmol), lithium triisopropyl 2-pyridylborate (104 mg, 0.375 mmol), KF, Pd₂dba₃ (2.3 mg, 0.0025 mmol) and **2** (2.4 mg, 0.015 mmol) was heated for 20 h. Flash column chromatography (10% EtOAc/Hexanes) yielded the title compound in 39 mg (76% yield) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ: 8.66 (dt, J = 6,1 Hz, 1H), 7.88 (d, J = 8 Hz, 2H), 7.67-7.71 (m, 2H), 7.26 (d, J = 8 Hz, 2H), 7.16 (dt, J = 6,1 Hz, 1H), 2.64 (t, J = 8 Hz, 2H), 1.62 (pent, J = 8 Hz, 2H), 1.36 (hex, J = 8 Hz, 2H), 0.92 (t, J = 8 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ: 157.4, 149.5, 143.9, 136.7, 136.6, 128.8, 126.7, 121.7, 120.2, 35.4, 33.5, 22.3, 13.9. ¹H and ¹³C NMR spectrum included.

2-(2,5-dimethylphenyl)pyridine (Table 3, Entry 3). Following general procedure A, a mixture of 2-chloro-*p*-xylene (33.5 μL, 35.1 mg, 0.25 mmol), lithium triisopropyl 2-pyridylborate (104 mg, 0.375 mmol), KF, Pd₂dba₃ (2.3 mg, 0.0025 mmol) and **2** (2.4 mg, 0.015 mmol) was heated for 20 h. Flash column chromatography (10% EtOAc/Hexanes) yielded the title compound in 32 mg (70% yield) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ: 8.71 (dt, J = 5,1 Hz, 1H), 7.74 (dt, J = 7,1 Hz, 1H), 7.42 (dt, J = 8,1 Hz, 1H), 7.23-7.26 (m, 2H), 7.16 (dt, J = 6,1 Hz, 1H), 7.20 (d, J = 8 Hz, 1H), 7.14 (dt, J = 8,1 Hz, 1H), 2.38 (s, 3H), 2.34 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ: 160.0, 149.2, 140.2, 135.9, 135.2, 132.4, 130.6, 130.2, 128.9, 124.0, 121.5, 20.9, 19.7. IR (neat, cm⁻¹): 3394,

¹⁰ Gosmini, C.; Lasry, S.; Nedelec, J.-Y.; Perichon, J. *Tetrahedron* **1998**, *54*, 1289.

3014, 2922, 1598, 1563, 1501, 1471, 1426, 1378, 1149, 1039, 992, 792, 749. ¹H and ¹³C NMR spectrum included.

2-(4-methoxyphenyl)pyridine (Table 3, Entry 4).³ Following general procedure A, a mixture of 4-chloroanisole (30.4 μ L, 35.6 mg, 0.25 mmol), lithium triisopropyl 2-pyridylborate (104 mg, 0.375 mmol), KF, Pd₂dba₃ (2.3 mg, 0.0025 mmol) and **2** (2.4 mg, 0.015 mmol) was heated for 20 h. Flash column chromatography (15% EtOAc/Hexanes) yielded the title compound in 36 mg (78% yield) as a white solid, mp 47-48 °C. ¹H NMR (300 MHz, CDCl₃) δ : 8.65 (dt, J = 5,1 Hz, 1H), 7.96 (d, J = 9 Hz, 2H), 7.71 (dt, J = 8,2 Hz, 1H), 7.66 (dt, J = 8,1 Hz, 1H), 7.17 (dd, J = 5,1 Hz, 1H), 7.00 (d, J = 9 HZ, 2H), 3.86 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ : 160.4, 157.0, 149.4, 136.6, 132.0, 128.1, 121.4, 119.8, 114.1, 55.3. ¹H and ¹³C NMR spectrum included.

2-(3-(trifluoromethyl)phenyl)pyridine (Table 3, Entry 5). Following general procedure A, a mixture of 3-chlorobenzotrifluoride (33.9 μ L, 45.1 mg, 0.25 mmol), lithium triisopropyl 2-pyridylborate (104 mg, 0.375 mmol), KF, Pd₂dba₃ (2.3 mg, 0.0025 mmol) and **2** (2.4 mg, 0.015 mmol) was heated for 20 h. Flash column chromatography (10% EtOAc/Hexanes) yielded the title compound in 32 mg (57% yield) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ : 8.70 (dt, J = 5,1 Hz, 1H), 8.26 (s, 1H), 8.15 (d, J = 8 Hz, 1H), 7.71-7.77 (m, 2H), 7.64 (d, J = 8 Hz, 1H), 7.56 (t, J = 8 Hz, 1H), 7.26 (ddd, J = 8,5,1 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ : 155.8, 149.9, 140.1, 137.0, 130.5, 130.0, 129.2, 125.5, 123.7, 122.8, 120.6, 112.3. IR (neat, cm⁻¹): 2963, 2913, 1631, 1586, 1464, 1437, 1417, 1301, 1262, 1166, 1123, 1073, 775. Anal. Calcd. for C₁₂H₈NF₃: C, 64.58; H, 3.61. Found C, 64.68; H, 3.56.

2,3'-bipyridine (Table 3, Entry 6).⁸ Following general procedure A, a mixture of 3-chloropyridine (23.8 μ L, 28.3 mg, 0.25 mmol), lithium triisopropyl 2-pyridylborate (104 mg, 0.375 mmol), KF, Pd₂dba₃ (2.3 mg, 0.0025 mmol) and **2** (2.4 mg, 0.015 mmol) was heated for 20 h. Flash column chromatography (EtOAc) yielded the title compound in 36 mg (92% yield) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ : 9.17 (d, J = 3 Hz, 1H), 8.71 (dt, J = 5,1 Hz, 1H), 8.64 (dt, J = 5,1 Hz, 1H), 8.31 (dt, J = 8,1 Hz, 1H), 7.79 (dt, J = 8,1 Hz, 1H), 7.75 (dt, J = 8,1 Hz, 1H), 7.39 (dd, J = 8,3 Hz, 1H), 7.28 (ddd, J = 8,5,1 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ : 154.7, 150.0, 149.9, 148.2, 136.9, 134.8, 134.3, 123.5, 122.8, 120.6. ¹H and ¹³C NMR spectrum included.

2-(6-methoxypyridin-2-yl)benzotrile (Table 3, Entry 7). Following general procedure A, a mixture of 2-chlorobenzotrile (34.4 mg, 0.25 mmol), lithium triisopropyl 2-(6-methoxypyridyl)borate (114 mg, 0.375 mmol), KF, Pd₂dba₃ (3.4 mg, 0.00375 mmol) and **2** (3.6 mg, 0.0225 mmol) was heated for 20 h. Flash column chromatography (5% EtOAc/Hexanes) yielded the title compound in 40 mg (76% yield) as a white solid, mp 48-49 °C. ¹H NMR (300 MHz, CDCl₃) δ: 7.79-7.83 (m, 2H), 7.63-7.70 (m, 2H), 7.48 (dt, J = 8,1 Hz, 1H), 7.31 (d, J = 8 Hz, 1H), 6.80 (d, J = 8 Hz, 1H), 4.09 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ: 163.8, 152.4, 142.9, 139.2, 134.7, 132.5, 129.4, 128.5, 119.2, 115.2, 111.0, 99.7, 54.0. IR (neat, cm⁻¹): 2969, 2946, 2223, 1602, 1574, 1461, 1426, 1406, 1325, 1247, 1152, 1017, 804, 780. ¹H and ¹³C NMR spectrum included.

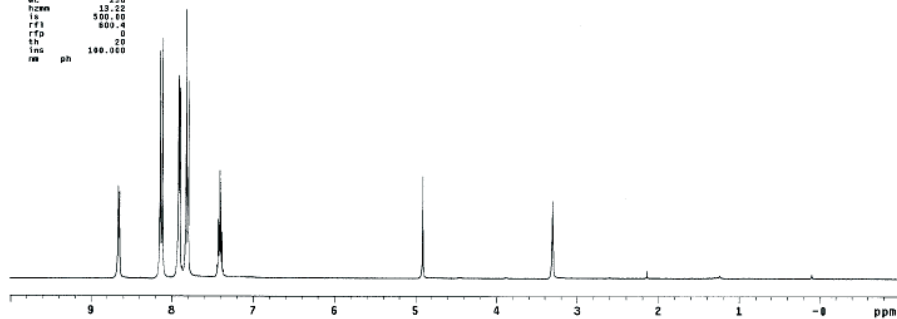
STANDARD 1H OBSERVE

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bs 1 tn 131972
lprw 54
pw 8.0 wscr
d5 8.350 wexp
tdr 867.7 wds
nt 16 wnt
ct alock n
gain not used
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in n
dp DISPLAY y
sp -309.8
wp 3304.8
vs 76
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hznm 13.82
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rfd 0
th 20
ins 199.050
nm ph

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4-(pyridin-2-yl)benzonitrile (Table 3, Entry 1) CD3OD



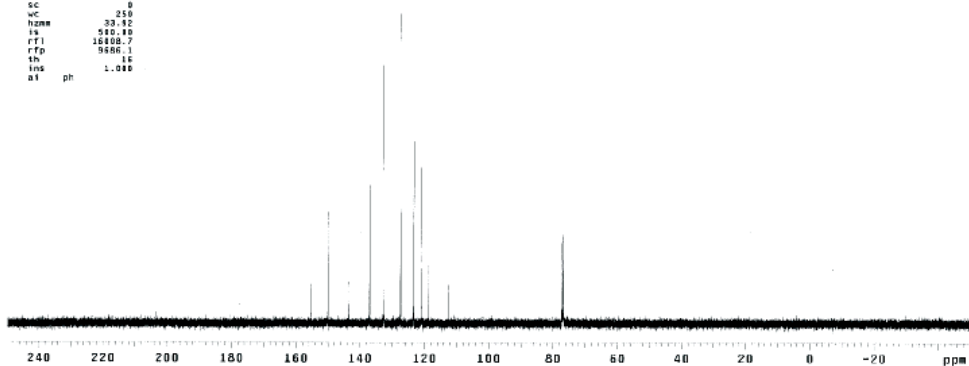
STANDARD CARBON PARAMETERS

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cky/4b_CDCl3112.dn v
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sfrq 125.796 dseq
tn C13 dres 1.4
at 1.736 hose
np 131618 PROCESSING
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fb not used vtfile ft
bs 1 tn 131672
lprw 54 math
pw 4.8
d5 9.763 wscr
tdr 881.4 wexp
nt 256 wds
ct alock n
gain not used
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in n
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wp 37735.3
vs 245
sc 8
wc 250
hznm 33.82
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rfd 9686.1
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nl ph

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4-(pyridin-2-yl)benzonitrile (Table 3, Entry 1)

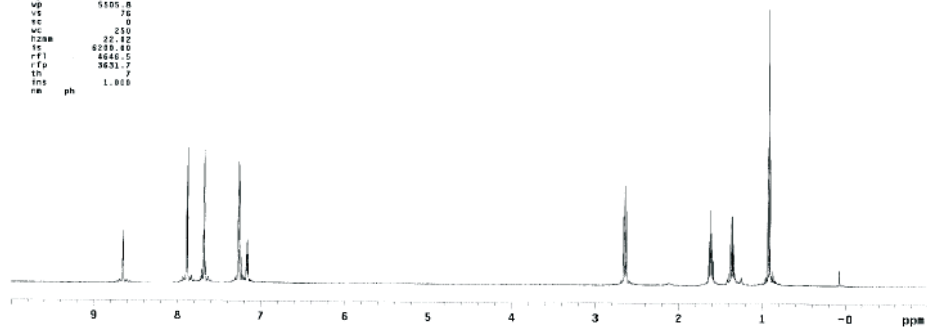



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tn H1 dres 1.0
at 5.230 homo
np 54000 PROCESSING n
sw 10000.0 vfile
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ss 1 math f
tpwr 50
pw 8.0 verr
d1 8 verr
tof 1498.0 vds
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ct 16
atock n
gain not used
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in n
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ms m
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2-(4-butylphenyl)pyridine (Table 3, Entry 2).

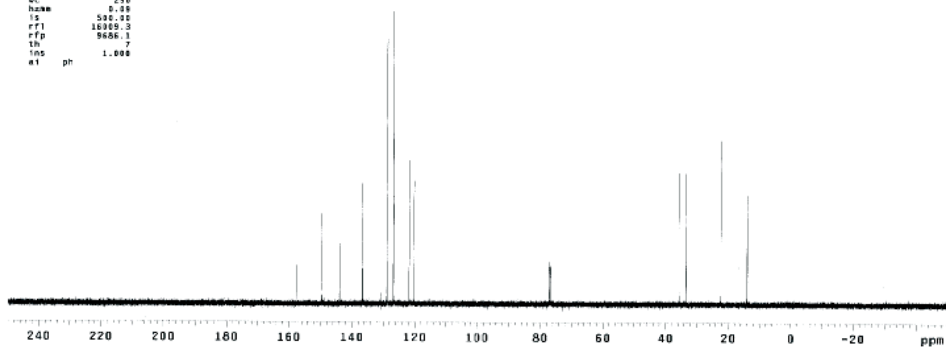


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tn C13 dres 1.0
at 1.725 homo
np 131610 PROCESSING n
sw 37725.0 lb
fb not used vfile ft
bs 1 fn 131072
ss 1 math f
tpwr 50
pw 8.0 verr
d1 8.763 verr
tof 1831.0 vds
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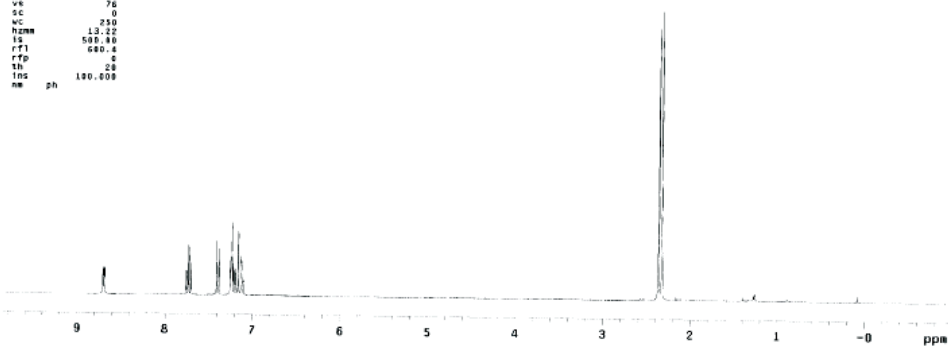
2-(4-butylphenyl)pyridine (Table 3, Entry 2).



STANDARD IN OBSERVE

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pw 0.0 wnt
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in n
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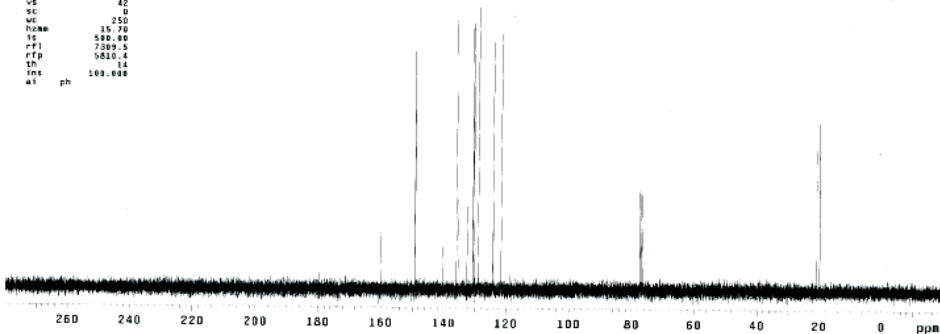
2-(2,5-dimethylphenyl)pyridine (Table 3, Entry 3).



13C OBSERVE

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np 6757.6 wffile -1.500
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fd 12400 fn 262144
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2-(2,5-dimethylphenyl)pyridine (Table 3, Entry 3).

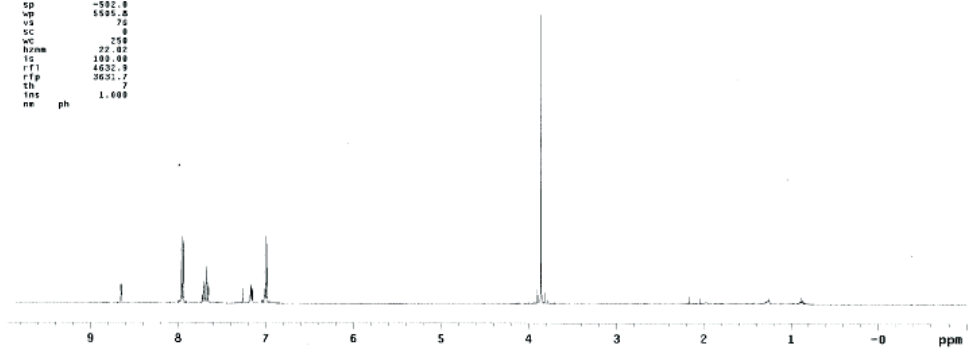


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2-(4-methoxyphenyl)pyridine (Table 3, Entry 4)

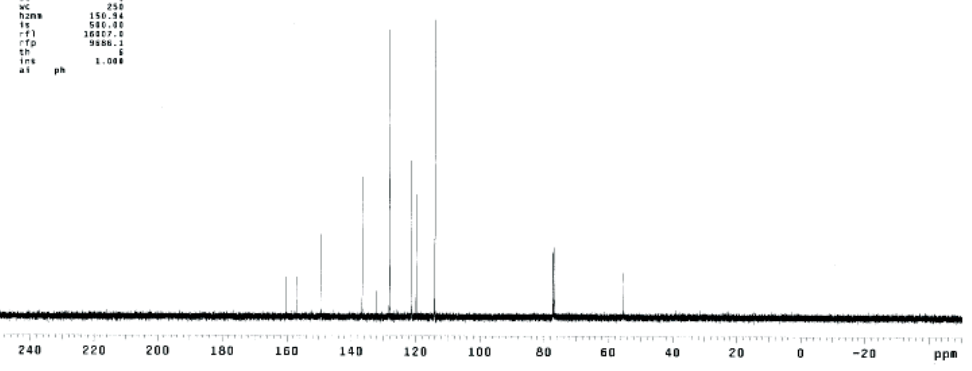


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2-(4-methoxyphenyl)pyridine (Table 3, Entry 4)



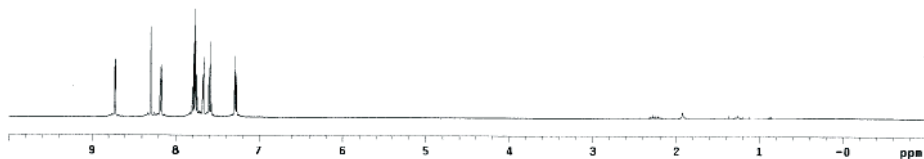
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4187-Flu den
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spwr 60
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2-(3-(trifluoromethyl)phenyl)pyridine (Table 3, Entry 5)



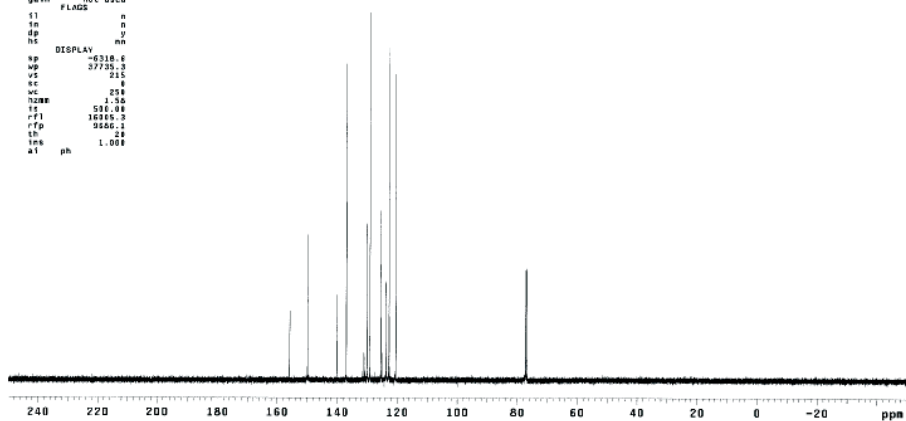
STANDARD CARBON PARAMETERS

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4187-Flu den
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np 131018 PROCESSING n
dv 37735.0 lb 1.38
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spwr 60 math
dv 6.0
dl 8 wepp
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dahn not used
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vc 215
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rfd 9586.1
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na ph

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2-(3-(trifluoromethyl)phenyl)pyridine (Table 3, Entry 5)



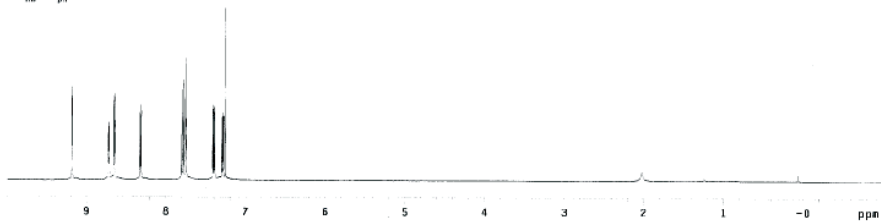
STANDARD PROTON PARAMETERS

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s1 1 math
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p1 8.4 werr
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t1 16 wnt
a1 lock 0
gain not used
FLAS n
in n
dp y
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sp -502.6
wp 559.5
vs 50
vc 0
wc 250
hzm 21.22
ls 104.92
rfl 463.2
rfd 3631.7
th 10
ins 1.000
ph

```

2,3'-bipyridine (Table 3, Entry 6)



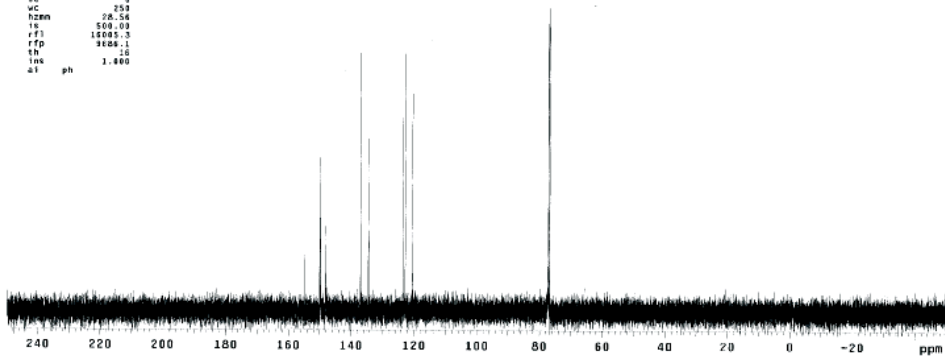
STANDARD CARBON PARAMETERS

```

exp1 s2pu1
SAMPLE DEC. & VT
date Jun 16 2007 dfrq 509.233
solvent CCl4 d1 H1
file /data/export/- spwr 44
home/ibuch/440/440- d0f -100.0
cky/ark_VI1262_05- d0f 8
247.710 d0f C
ACQUISITION daf 10030
f1rq 125.795 d1c0q
t1 C13 d1c1 1.0
a1 1.736 homo n
p1 131810 PROCESSING
s1 37735.8 lb 8.30
f1 not used wfile ft
b1 4 proc
s1 1 t1 131072
t1 50 math
p1 8.0 werr
d1 87.6 wep
t1 16 wnt
a1 lock 0
gain not used
FLAS n
in n
dp y
hs DISPLAY mn
sp -6310.6
wp 5775.5
vs 50
vc 0
wc 250
hzm 28.56
ls 500.02
rfl 1608.3
rfd 3668.1
th 10
ins 1.000
ph

```

2,3'-bipyridine (Table 3, Entry 6).

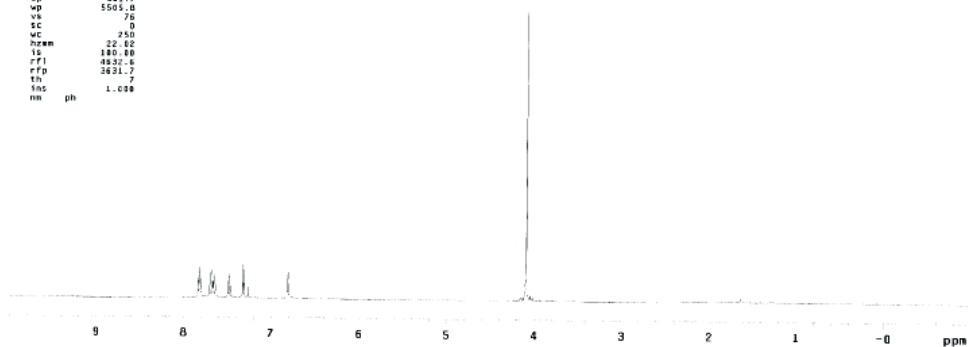


```

STANDARD PROTON PARAMETERS
exp1 szpu1
SAMPLE DEC. & WT
date Jul 9 2007 freq 125.795
solvent CDCl3 dn C13
file /data/export/~dswr 44
home/1bucl/13c/13c-dof 8
ckv/4kb_VI1136_070-0n mn
227.714 dm C
ACQUISITION def 10000
sfreq 500.235 dsq 1.0
in 101 drsc
at 3.200 homo n
ns 64000 PROCESSING
sw 10000.0 wfile ft
fn not used proc 131072
se 1 fn 131072
sc 1 math f
tdwr 63
sw 9.0 wepp
ds 0 weop
tof 1498.2 wds
nt 16 wnt
ct 16
atock n
gain not used
flags n
in n
op y
ns DISPLAY nn
sp -501.7
wp 5605.8
vc 70
sc 0
wc 250
hzab 22.62
fs 180.00
rfi 4832.5
rfd 3621.7
th
ins ph 1.009

```

2-(6-methoxypyridin-2-yl)benzotrile (Table 3, Entry 7)



```

STANDARD CARBON PARAMETERS
exp1 szpu1
SAMPLE DEC. & WT
date Jul 13 2007 freq 500.233
solvent CDCl3 dn M1
file /data/export/~dswr 44
home/1bucl/13c/13c-dof -500.0
ckv/4kb_VI1136_070-0n mn
71307.719 dm w
ACQUISITION def 10010
sfreq 125.795 dsq 1.0
in 101 drsc
at 1.735 homo n
ns 131072 PROCESSING
sw 37735.8 lb 1.38
fn not used wfile ft
fn 131072
se 1 math f
tdwr 6.9
sw 1.763 wepp
ds 0 weop
tof 831.4 wds
nt 256 wnt
ct 16
atock n
gain not used
flags n
in n
op y
ns DISPLAY nn
sp -6320.9
wp 37735.8
vc 137
sc 0
wc 250
hzab 150.10
fs 180.00
rfi 16307.0
rfd 8626.3
th
ins ph 1.009

```

2-(6-methoxypyridin-2-yl)benzotrile (Table 3, Entry 7)

