

# Pd/P(*t*-Bu)<sub>3</sub>-Catalyzed Suzuki Cross-Couplings in the Presence of Water

Sha Lou and Gregory C. Fu\*

*Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

## Supporting Information

### Table of Contents

I.	General Information	S-1
II.	Suzuki Cross-Couplings (Tables 2 and 3)	S-1
III.	<sup>1</sup> H NMR Spectra (Tables 2 and 3)	S-11

### I. General Information

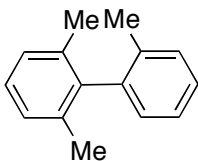
The cross-coupling partners were purchased and used without purification. THF ( $\geq 99.9\%$ ; inhibitor-free; Aldrich), Pd<sub>2</sub>(dba)<sub>3</sub> (Strem), HP(*t*-Bu)<sub>3</sub>BF<sub>4</sub> (Strem), and Pd<sub>2</sub>(dba)<sub>3</sub>/[HP(*t*-Bu)<sub>3</sub>]BF<sub>4</sub> (Pd:P(*t*-Bu)<sub>3</sub> = 1:1.2; Strem) were purchased and used without purification. KF•2H<sub>2</sub>O (Mallinckrodt Chemicals) was ground with a mortar and pestle before use.

**Procedure for preparing a mixture of Pd<sub>2</sub>(dba)<sub>3</sub>/[HP(*t*-Bu)<sub>3</sub>]BF<sub>4</sub> (Pd:P(*t*-Bu)<sub>3</sub> = 1:1.2).** Pd<sub>2</sub>(dba)<sub>3</sub> (458 mg, 0.50 mmol) and HP(*t*-Bu)<sub>3</sub>BF<sub>4</sub> (348 mg, 1.20 mmol) were weighed into a mortar. The mixture was ground and mixed well with a pestle. The resulting fine powder was stored under air in a capped 4-mL vial.

### II. Suzuki Cross-Couplings (Tables 2 and 3)

**General Procedure for Suzuki cross couplings.** Pd<sub>2</sub>(dba)<sub>3</sub>/[HP(*t*-Bu)<sub>3</sub>]BF<sub>4</sub> (Pd:P(*t*-Bu)<sub>3</sub> = 1:1.2; 8.1 mg, 0.0050 mmol of Pd<sub>2</sub>(dba)<sub>3</sub>), the boronic acid (1.10 mmol), and KF•2H<sub>2</sub>O (310 mg, 3.30 mmol) were added to a 4-mL vial that contained a stir bar. The vial was purged with argon for 3 min, and then it was sealed with a septum cap. THF (2.0 mL) and the aryl halide (1.00 mmol) were added, and the reaction mixture was stirred at room temperature. Next, the mixture was diluted with Et<sub>2</sub>O (2 mL) and filtered through a plug of silica gel (washed with Et<sub>2</sub>O (10 mL)). The filtrate was concentrated, and the residue was purified by flash chromatography on silica gel.

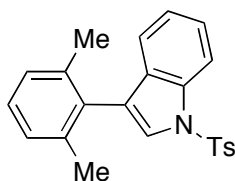
The first run was conducted with Pd<sub>2</sub>(dba)<sub>3</sub>/[HP(*t*-Bu)<sub>3</sub>]BF<sub>4</sub> that we prepared. The second run employed commercially available Pd<sub>2</sub>(dba)<sub>3</sub>/[HP(*t*-Bu)<sub>3</sub>]BF<sub>4</sub> (Strem).



**2,2',6-Trimethyl-1,1'-biphenyl (Table 2, entry 1) [10273-87-7].** The title compound was prepared according to the General Procedure with 2-bromo-1,3-dimethylbenzene (133  $\mu$ L; 185 mg, 1.00 mmol) and 2-methylbenzeneboronic acid (150 mg, 1.10 mmol). Reaction time: 2.5 h. After purification by flash chromatography (eluted with 5 $\rightarrow$ 15% Et<sub>2</sub>O in hexanes), the title compound was isolated as a colorless oil (192 mg, 98% yield).

The second run furnished the product as a colorless oil (184 mg, 94% yield).

The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra are in agreement with reported values.<sup>1</sup>



**3-(2,6-Dimethylphenyl)-1-tosyl-1H-indole (Table 2, entry 2).** The title compound was prepared according to the General Procedure with 2-bromo-1,3-dimethylbenzene (133  $\mu$ L; 185 mg, 1.00 mmol) and *N*-(toluenesulfonyl)indole-3-boronic acid (347 mg, 1.10 mmol). Reaction time: 4.0 h. After purification by flash chromatography (eluted with 15 $\rightarrow$ 50% Et<sub>2</sub>O in hexanes), the title compound was isolated as a colorless oil (332 mg, 94% yield).

The second run furnished the product as a colorless oil (360 mg, 96% yield).

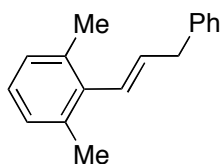
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  8.09 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.43 (s, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.24-7.18 (m, 4H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 1H), 2.35 (s, 3H), 1.99 (s, 6H);

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  145.1, 138.0 (2C), 135.4, 135.3, 131.5, 131.0, 130.0 (2C), 128.1, 127.5 (2C), 126.9 (2C), 125.0, 124.3, 123.6, 122.8, 120.6, 114.2, 21.7, 20.7 (2C);

IR (film) 3025, 1597, 1446, 1371, 1176, 1126, 1011, 931, 751, 693, 661 cm<sup>-1</sup>;

LRMS (ESI) calcd for C<sub>23</sub>H<sub>22</sub>NO<sub>2</sub>S (M+H) 376.1, found, 376.1.

[1] A. F. Littke, C. Dai, G. C. Fu, *J. Am. Chem. Soc.* **2000**, *122*, 4020–4028.



**(E)-1,3-Dimethyl-2-(3-phenylprop-1-en-1-yl)benzene (Table 2, entry 3).** The title compound was prepared according to the General Procedure with 2-bromo-1,3-dimethylbenzene (133  $\mu$ L; 185 mg, 1.00 mmol) and *trans*-3-phenyl-1-propen-1-ylboronic acid (178 mg, 1.10 mmol). Reaction time: 4.0 h. After purification by flash chromatography (eluted with 5 $\rightarrow$ 15% Et<sub>2</sub>O in hexanes), the title compound was isolated as a colorless oil (218 mg, 98% yield).

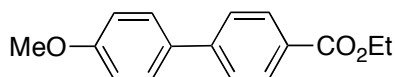
The second run furnished the product as a colorless oil (216 mg, 97% yield).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.32-7.19 (m, 3H), 7.02-7.00 (m, 3H), 6.40 (d, *J* = 16.0 Hz, 1H), 5.85-5.78 (m, 1H), 3.58 (d, *J* = 7.0 Hz, 2H), 2.29 (s, 6H);

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  140.5, 137.4, 136.0, 134.1 (2C), 129.0, 128.8 (2C), 128.6 (2C), 127.8 (2C), 126.5, 126.3, 40.0, 21.2 (2C);

IR (film) 3026, 1603, 1494, 1465, 1453, 1376, 1029, 974, 768, 732, 698 cm<sup>-1</sup>;

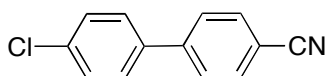
LRMS (ESI) calcd for C<sub>17</sub>H<sub>19</sub> (M+H) 223.1, found, 223.1.



**Ethyl 4'-methoxy-[1,1'-biphenyl]-4-carboxylate (Table 2, entry 4) [732-80-9].** The title compound was prepared according to the General Procedure with 4-bromoanisole (125  $\mu$ L; 187 mg, 1.00 mmol) and 4-(ethoxycarbonyl)phenylboronic acid (213 mg, 1.10 mmol). Reaction time: 36 h. After purification by flash chromatography (eluted with 15 $\rightarrow$ 50% Et<sub>2</sub>O in hexanes), the title compound was isolated as a colorless oil (223 mg, 87% yield).

The second run furnished the product as a colorless oil (208 mg, 81% yield).

The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra are in agreement with reported values.<sup>2</sup>



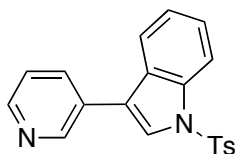
**4'-Chloro-[1,1'-biphenyl]-4-carbonitrile (Table 2, entry 5) [57774-36-4].** The title compound was prepared according to the General Procedure with 4-bromochlorobenzene (192 mg, 1.00 mmol) and 4-cyanophenylboronic acid (162 mg, 1.10 mmol). Reaction time: 4.0 h. After

[2] S. E. Denmark, M. H. Ober, *Adv. Synth. Catal.* **2004**, *346*, 1703–1714.

purification by flash chromatography (eluted with 5→15% Et<sub>2</sub>O in hexanes), the title compound was isolated as a colorless oil (212 mg, 99% yield).

The second run furnished the product as a colorless oil (207 mg, 97% yield).

The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra are in agreement with reported values.<sup>3</sup>



**3-(Pyridin-3-yl)-1-tosyl-1H-indole (Table 2, entry 6).** The title compound was prepared according to the General Procedure with 3-bromopyridine (96  $\mu$ L; 158 mg, 1.00 mmol) and *N*-(toluenesulfonyl)indole-3-boronic acid (347 mg, 1.10 mmol). Reaction time: 2.5 h. After purification by flash chromatography (eluted with 20→80% Et<sub>2</sub>O in hexanes), the title compound was isolated as a colorless oil (313 mg, 90% yield).

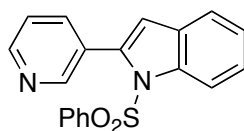
The second run furnished the product as a colorless oil (331 mg, 95% yield).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  8.85 (d, *J* = 2.5 Hz, 1H), 8.59 (d, *J* = 4.5 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.88 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.73 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 2.33 (s, 3H);

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  149.0, 148.9, 145.5, 136.8, 135.6, 135.3, 135.2, 130.3 (2C), 127.2 (2C), 125.5, 124.0, 123.9, 123.7, 120.5, 120.2, 114.1, 86.7, 21.8;

IR (film) 3031, 1596, 1446, 1372, 1175, 1134, 1089, 1009, 811, 746, 675 cm<sup>-1</sup>;

LRMS (ESI) calcd for C<sub>20</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub>S (M+H) 349.1, found 349.1.



**1-(Phenylsulfonyl)-2-(pyridin-3-yl)-1H-indole (Table 2, entry 7).** The title compound was prepared according to the General Procedure with 3-bromopyridine (96  $\mu$ L; 158 mg, 1.00 mmol) and 1-(phenylsulfonyl)-2-indoleboronic acid (331 mg, 1.10 mmol). Reaction time: 36 h. After purification by flash chromatography (eluted with 20→80% Et<sub>2</sub>O in hexanes), the title compound was isolated as a colorless oil (267 mg, 80% yield).

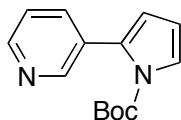
The second run furnished the product as a colorless oil (281 mg, 84% yield).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  8.61 (d, *J* = 5.0 Hz, 1H), 8.55 (s, 1H), 8.27 (d, *J* = 8.0 Hz, 1H), 7.87 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.43-7.29 (m, 6H), 7.25-7.20 (m, 3H), 6.57 (s, 1H);

---

[3] R. Martin, S. L. Buchwald, *J. Am. Chem. Soc.* **2007**, *129*, 3844–3845.

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  150.0, 149.7, 138.5, 138.3, 137.4, 134.1 (2C), 130.4, 129.0 (2C), 128.7, 126.7 (2C), 125.6, 124.8, 122.6, 121.2, 116.7, 114.9;  
IR (film) 3065, 1570, 1448, 1411, 1374, 1185, 1120, 1091, 753, 555  $\text{cm}^{-1}$ ;  
LRMS (ESI) calcd for  $\text{C}_{19}\text{H}_{15}\text{N}_2\text{O}_2\text{S}$  (M+H) 335.1, found 335.1.



**tert-Butyl 2-(pyridin-3-yl)-1H-pyrrole-1-carboxylate (Table 2, entry 8).** The title compound was prepared according to the General Procedure with 3-bromopyridine (96  $\mu\text{L}$ ; 158 mg, 1.00 mmol) and 1-*N*-Boc-pyrrole-2-boronic acid (232 mg, 1.10 mmol). Reaction time: 4.0 h. After purification by flash chromatography (eluted with 10 $\rightarrow$ 80%  $\text{Et}_2\text{O}$  in hexanes), the title compound was isolated as a yellow oil (234 mg, 96% yield).

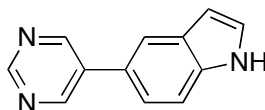
The second run furnished the product as a colorless oil (227 mg, 93% yield).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  8.59 (dd,  $J$  = 2.5, 1.0 Hz, 1H), 8.52 (dd,  $J$  = 5.0, 2.0 Hz, 1H), 7.65 (dt,  $J$  = 8.0, 2.0 Hz, 1H), 7.40 (dd,  $J$  = 4.0, 2.0 Hz, 1H), 7.26 (dd,  $J$  = 8.0, 4.5 Hz, 1H), 6.26-6.23 (m, 2H), 1.37 (s, 9H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  145.0, 149.2, 148.3, 136.5, 131.4, 130.5, 123.4, 122.6, 115.7, 111.0, 84.3, 27.8 (3C);

IR (film) 2982, 1743, 1569, 1458, 1394, 1313, 1148, 972, 842, 756, 732  $\text{cm}^{-1}$ ;

LRMS (ESI) calcd for  $\text{C}_{14}\text{H}_{17}\text{N}_2\text{O}_2$  (M+H) 245.1, found 245.1.



**5-(Pyrimidin-5-yl)-1H-indole (Table 2, entry 9).** The title compound was prepared according to the General Procedure with 5-bromopyrimidine (159 mg, 1.00 mmol) and indole-5-boronic acid (177 mg, 1.10 mmol). Reaction time: 36 h. After purification by flash chromatography (eluted with 10 $\rightarrow$ 80%  $\text{EtOAc}$  in  $\text{CH}_2\text{Cl}_2$ ), the title compound was isolated as a white solid (152 mg, 78% yield).

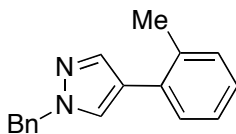
The second run furnished the product as a colorless oil (142 mg, 73% yield).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  9.15 (s, 1H), 8.99 (s, 2H), 8.46 (br, 1H), 7.84 (s, 1H), 7.52 (d,  $J$  = 8.5 Hz, 1H), 7.39 (d,  $J$  = 8.5 Hz, 1H), 7.29 (t,  $J$  = 2.5 Hz, 1H), 6.64 (s, 1H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  156.8, 155.2 (2C), 136.2, 135.8, 128.9, 126.2, 125.8, 121.3, 119.7, 112.3, 103.4;

IR (film) 3179, 1597, 1562, 1408, 1314, 882, 765, 716  $\text{cm}^{-1}$ ;

LRMS (ESI) calcd for  $\text{C}_{12}\text{H}_{10}\text{N}_3$  (M+H) 196.1, found 196.1.



**1-Benzyl-4-(*o*-tolyl)-1H-pyrazole (Table 2, entry 10).** The title compound was prepared according to the General Procedure with 4-bromo-1-benzyl-1H-pyrazole (237 mg, 1.00 mmol) and 2-methylbenzeneboronic acid (150 mg, 1.10 mmol). Reaction time: 2.5 h. After purification by flash chromatography (eluted with 10→40% Et<sub>2</sub>O in hexanes), the title compound was isolated as a colorless oil (219 mg, 88% yield).

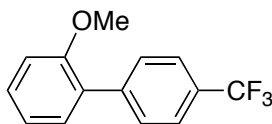
The second run furnished the product as a colorless oil (214 mg, 86% yield).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 7.72 (s, 1H), 7.51 (s, 1H), 7.40-7.37 (m, 2H), 7.35-7.33 (m, 2H), 7.30-7.24 (m, 3H), 7.22-7.19 (m, 2H), 5.38 (s, 2H), 2.40 (s, 3H);

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 139.4, 136.7, 135.4, 132.3, 130.9, 129.2, 129.1 (2C), 128.32, 128.28, 127.9 (2C), 126.9, 126.1, 122.7, 56.3, 21.5;

IR (film) 2918, 1561, 1453, 1376, 1187, 995, 760, 723 cm<sup>-1</sup>;

LRMS (ESI) calcd for C<sub>17</sub>H<sub>17</sub>N<sub>2</sub> (M+H) 249.1, found 249.1.

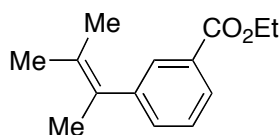


**2-Methoxy-4'-(trifluoromethyl)biphenyl (eq 3) [122801-55-2].** The title compound was prepared according to the General Procedure with 2-iodoanisole (133 μL; 234 mg, 1.00 mmol) and 4-(trifluoromethyl)phenylboronic acid (209 mg, 1.10 mmol). Reaction time: 36 h. After purification by flash chromatography (eluted with 10→60% benzene in hexanes), the title compound was isolated as a colorless oil (222 mg, 88% yield).

The second run furnished the product as a colorless oil (207 mg, 82% yield).

The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra are in agreement with reported values.<sup>4</sup>

[4] S. E. Denmark, R. C. Smith, W.-T. T. Chang, J. M. Muhuhi, *J. Am. Chem. Soc.* **2009**, *131*, 3104–3118.



**Ethyl 3-(3-methylbut-2-en-2-yl)benzoate (eq 4).** The title compound was prepared according to the General Procedure with 2-bromo-3-methyl-2-butene (116  $\mu$ L; 149 mg, 1.00 mmol) and 3-(ethoxycarbonyl)phenylboronic acid (213 mg, 1.10 mmol). Reaction time: 24 h. After purification by flash chromatography (eluted with 5 $\rightarrow$ 20% Et<sub>2</sub>O in hexanes), the title compound was isolated as a colorless oil (135 mg, 62% yield).

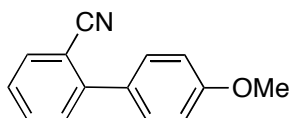
The second run furnished the product as a colorless oil (128 mg, 59% yield).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.89 (d, *J* = 7.5 Hz, 1H), 7.82 (s, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 4.38 (q, *J* = 7.0 Hz, 2H), 1.98 (s, 3H), 1.83 (s, 3H), 1.58 (s, 3H), 1.41 (t, *J* = 7.0 Hz, 3H);

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  167.1, 145.7, 133.2, 130.4, 129.7, 129.4, 128.4, 128.2, 127.2, 61.1, 22.3, 20.9, 20.8, 14.6;

IR (film) 2983, 1719, 1447, 1306, 1252, 1202, 1107, 1026, 758 cm<sup>-1</sup>;

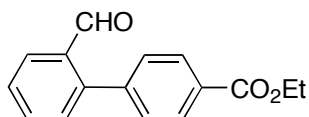
LRMS (ESI) calcd for C<sub>14</sub>H<sub>19</sub>O<sub>2</sub> (M+H) 219.1, found 219.1.



**4'-Methoxy-[1,1'-biphenyl]-2-carbonitrile (Table 3, entry 1) [125610-78-8].** The title compound was prepared according to the General Procedure with 2-chlorobenzonitrile (138 mg, 1.00 mmol) and 4-methoxyphenylboronic acid (167 mg, 1.10 mmol). Reaction time: 4.0 h. After purification by flash chromatography (eluted with 5 $\rightarrow$ 40% Et<sub>2</sub>O in hexanes), the title compound was isolated as a colorless oil (203 mg, 97% yield).

The second run furnished the product as a colorless oil (201 mg, 96% yield).

The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra are in agreement with reported values.<sup>5</sup>



**Ethyl 2'-formyl-[1,1'-biphenyl]-4-carboxylate (Table 3, entry 2).** The title compound was prepared according to the General Procedure with 2-chlorobenzaldehyde (113  $\mu$ L; 141 mg, 1.00 mmol) and 4-(ethoxycarbonyl)phenylboronic acid (213 mg, 1.10 mmol). Reaction time: 24 h.

[5] G. Manolikakes, P. Knochel, *Angew. Chem. Int. Ed.* **2009**, *48*, 205–209.

After purification by flash chromatography (eluted with 5→50% Et<sub>2</sub>O in hexanes), the title compound was isolated as a colorless oil (185 mg, 73% yield; 46 mg, 17% yield of the hydrate).

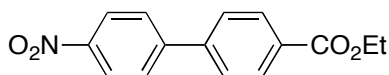
The second run furnished the product as a colorless oil (175 mg, 69% yield; 63 mg, 23% yield of the hydrate).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 9.94 (s, 1H), 8.13 (d, *J* = 7.0 Hz, 2H), 8.03 (d, *J* = 7.5 Hz, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 7.0 Hz, 2H), 7.42 (d, *J* = 7.5 Hz, 1H), 4.40 (q, *J* = 7.0 Hz, 2H), 1.41 (t, *J* = 7.0 Hz, 3H);

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 192.0, 166.4, 144.9, 144.5, 142.5, 133.9, 130.8, 130.3 (2C), 129.8 (2C), 128.6, 128.1, 127.4, 51.4, 14.6;

IR (film) 2982, 1716, 1694, 1596, 1396, 1277, 1104, 760 cm<sup>-1</sup>;

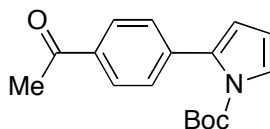
LRMS (ESI) calcd for C<sub>16</sub>H<sub>15</sub>O<sub>3</sub> (M+H) 255.1, found 255.1.



**Ethyl 4'-nitro-[1,1'-biphenyl]-4-carboxylate (Table 3, entry 3) [6242-99-5].** The title compound was prepared according to the General Procedure with 1-chloro-4-nitrobenzene (133 μL; 158 mg, 1.00 mmol) and 4-(ethoxycarbonyl)phenylboronic acid (213 mg, 1.10 mmol). Reaction time: 2.0 h. After purification by flash chromatography (eluted with 20→80% Et<sub>2</sub>O in hexanes), the title compound was isolated as a white solid (268 mg, 99% yield).

The second run furnished the product as a white solid (266 mg, 98% yield).

The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra are in agreement with reported values.<sup>6</sup>



**tert-Butyl 2-(4-acetylphenyl)-1H-pyrrole-1-carboxylate (Table 3, entry 4).** The title compound was prepared according to the General Procedure with 4'-chloroacetophenone (130 μL; 155 mg, 1.00 mmol) and 1-*N*-Boc-pyrrole-2-boronic acid (232 mg, 1.10 mmol). Reaction time: 1.0 h. After purification by flash chromatography (eluted with 5→15% Et<sub>2</sub>O in hexanes), the title compound was isolated as a colorless oil (280 mg, 98% yield).

The second run furnished the product as a colorless oil (277 mg, 97% yield).

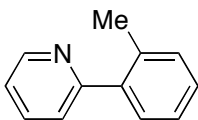
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 7.88 (d, *J* = 7.0 Hz, 2H), 7.42 (d, *J* = 7.0 Hz, 2H), 7.21 (t, *J* = 2.0 Hz, 1H), 6.20 (d, *J* = 2.0 Hz, 1H), 6.19 (d, *J* = 2.0 Hz, 1H), 2.57 (s, 3H), 1.57 (s, 9H);

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 197.0, 156.0, 139.7, 135.6, 129.9 (2C), 129.1 (2C), 120.1 (2C), 112.0 (2C), 83.7, 28.2 (3C), 26.8;

[6] P. Lan, D. Berta, J. A. Porco, Jr, M. S. South, J. J. Parlow, *J. Org. Chem.* **2003**, *68*, 9678–9686.



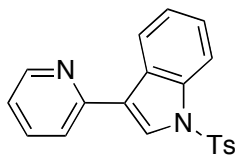
IR (film) 2981, 1747, 1685, 1590, 1472, 1399, 1343, 1319, 1260, 1154, 1094, 952, 828, 742  $\text{cm}^{-1}$ ;  
LRMS (ESI) calcd for  $\text{C}_{17}\text{H}_{20}\text{NO}_3$  (M+H) 286.1, found 286.1.



**2-*o*-Tolylpyridine (Table 3, entry 5) [10273-89-9].** The title compound was prepared according to the General Procedure with 2-chloropyridine (95  $\mu\text{L}$ ; 114 mg, 1.00 mmol) and 2-methylbenzeneboronic acid (150 mg, 1.10 mmol). Reaction time: 12 h. After purification by flash chromatography (eluted with 5 $\rightarrow$ 30%  $\text{Et}_2\text{O}$  in hexanes), the title compound was isolated as a colorless oil (156 mg, 92% yield).

The second run furnished the product as a colorless oil (154 mg, 91% yield).

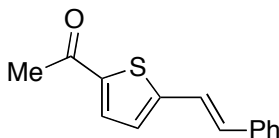
The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra are in agreement with reported values.<sup>1</sup>



**3-(Pyridin-2-yl)-1-tosyl-1H-indole (Table 3, entry 6) [758686-21-4].** The title compound was prepared according to the General Procedure with 2-chloropyridine (95  $\mu\text{L}$ ; 114 mg, 1.00 mmol) and *N*-(toluenesulfonyl)indole-3-boronic acid (347 mg, 1.10 mmol). Reaction time: 12 h. After purification by flash chromatography (eluted with 10 $\rightarrow$ 60%  $\text{Et}_2\text{O}$  in hexanes), the title compound was isolated as a colorless oil (324 mg, 93% yield).

The second run furnished the product as a colorless oil (338 mg, 97% yield).

The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra are in agreement with reported values.<sup>7</sup>



**(*E*)-1-(5-Styrylthiophen-2-yl)ethanone (Table 3, entry 7) [125972-78-3].** The title compound was prepared according to the General Procedure with 2-acetyl-5-chlorothiophene (161 mg, 1.00 mmol) and *trans*-2-phenylvinylboronic acid (163 mg, 1.10 mmol). Reaction time: 12 h. After

---

[7] T. Miyagi, Y. Hari, T. Aoyama, *Tetrahedron Lett.* **2004**, *45*, 6303–6305.

purification by flash chromatography (eluted with 5→15% Et<sub>2</sub>O in hexanes), the title compound was isolated as a colorless oil (196 mg, 86% yield).

The second run furnished the product as a colorless oil (205 mg, 90% yield).

The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra are in agreement with reported values.<sup>8</sup>

---

[8] C. J. O'Brien, E. A. B. Kantchev, C. Valente, N. Hadei, G. A. Chass, A. Lough, A. C. Hopkinson, M. G. Organ, *Chem. Eur. J.* **2006**, *12*, 4743–4748.

Table 2, entry 1

10-3-15-1

```

expt  s2pu1
SAMPLE Mar 15 2010 DEC. & VT 125.845
solvent CDC13 dn C13 30
file /data/export/~ dpwr 0
home/gfu/FUJ10U/ca~ dof mn 0
sper/10-3-15-1.fid dm mn C
ACQUISITION dmm 200
sfrq 500.435 dmf 200
tn HI dseq 1.0
dt 4.999 dres 1.0
np 120102 homo
sw 12012.0 wffile ft
fb not used wffile ft
tpwr 4 fn 262144
pw 56 math f
dl 8.0 math f
lof 0.100 werr f
nt 3003.2 wexp f
ct 16 wbs f
alock 8 wnt
gain not used wnt
flags not used wnt
il n
in n
dp y
hs mn
DISPLAY -228.5
wp 4473.3
vs 16
sc 0
wc 250
hzmm 17.89
ls 310.91
rfl 4139.3
rtp 3623.1
th 7
ins 9.000
ai cdc ph
  
```

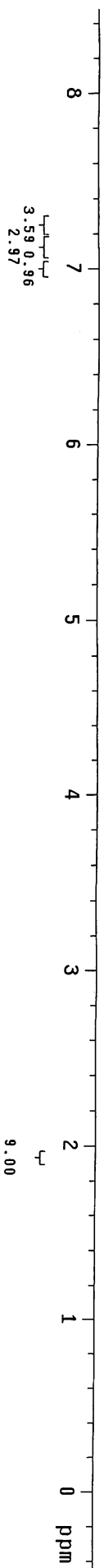
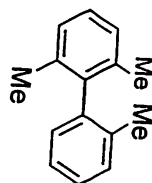


Table 2, entry 2

10-2-3-1

expt1 s2pu1

SAMPLE	3 2010	DEC. & VT	125.672
date	Feb	dfreq	C13
solvent	GDC13	dn	30
file	/data/export/~	dpwr	0
home/gfu/fusion/bu	do	do	nnn
llwinkle/10-2-3-1	dm	w	10000
fid	fid		
ACQUISITION			
sfrq	499.746	dmf	1.0
tn	H1	dseq	n
at	3.001	dres	n
np	63050	homo	n
sw	10504.2	wtfile	ft
fb	not used	proc	f
bs	4	fn	262144
tpwr	56	math	f
pv	8.6		
dl	2.000	weff	
tof	1519.5	wexp	
nt	16	wds	
ct	16	wnt	wft
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dd	y		
hs	nm		
DISPLAY			
SP	-243.5		
WP	5020.7		
VS	37		
SC	0		
WC	250		
h2mm	20.08		
is	486.99		
ftl	4857.1		
ftp	3618.1		
th	7		
ins	2.000		
al	cdc	ph	

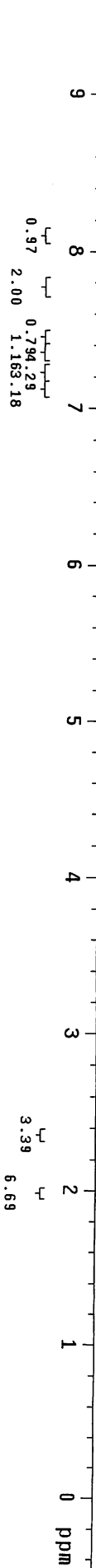
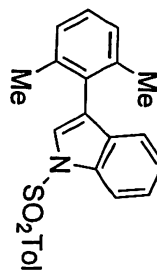


Table 2, entry 3

10-3-16-14

expi szpu1

SAMPLE	Mar 16 2010	DEC. & VT	125.845
date	Mar 16 2010	dfrq	C13
solvent	CDCl3	dn	30
file	/data/export/~	dpwr	0
home	/gfu/Fujiou/cav	dof	nnn
spcr	/10-3-16-14.fi~	dm	c
	d	dmr	200
ACQUISITION		dms	
sfrq	500.435	dseq	1.0
in	H1	drps	n
at	4.999	homo	
np	120102	PROCCESSING	
sw	12012.0	wfite	ft
fb	not used	proc	26214f
bs	4	fn	
tpwr	56	math	
pw	8.0	werr	
d1	0.100	wexp	
tof	3003.2	wbs	
nt	16	wnt	wft
ct	16		
atlock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	Y		
hs	nm		
DISPLAY			
sp	-236.1		
wp	4842.7		
vs	15		
sc	0		
wc	250		
hzmm	19.37		
is	238.87		
rfl	4138.8		
rfp	3623.1		
th	6		
ins	6.000		
ai	cdc		
ph			

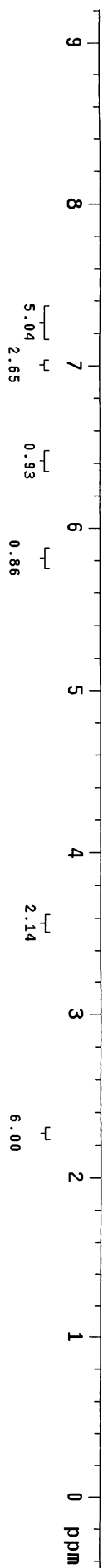
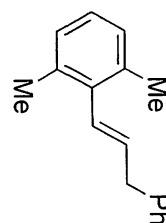
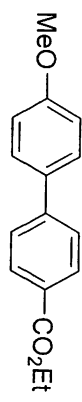


Table 2, entry 4

10-3-16-11

expt1 s2pu1

SAMPLE DEC. & VT  
 date Mar 16 2010 dfrq 125.845  
 solvent CDCl3 dn C13  
 file /data/export/~ dpwr 30  
 home/gfu/fujstou/ca~ dof 0  
 sper/10-3-16-11.f1~ dm nm  
 d dnm  
 d dnt 200  
 d dnt 200



ACQUISITION  
 sfrq 500.435  
 tn H1  
 at 4.999  
 np 120102  
 sw 12012.0  
 fb not used  
 ds 56  
 tpwr 8.0  
 pw 0.100  
 d1 3003.2  
 tof 16  
 nt 16  
 ct 16  
 atlock not used  
 gain not used  
 flags not used  
 i1 n  
 in n  
 dp y  
 hs nm  
 DISPLAY  
 sp -255.9  
 wp 4972.4  
 vs 21  
 sc 0  
 wc 250  
 hzmm 19.89  
 is 409.66  
 rfl 4138.7  
 rfp 3623.1  
 th 7  
 ins 3.000  
 ai cdc ph

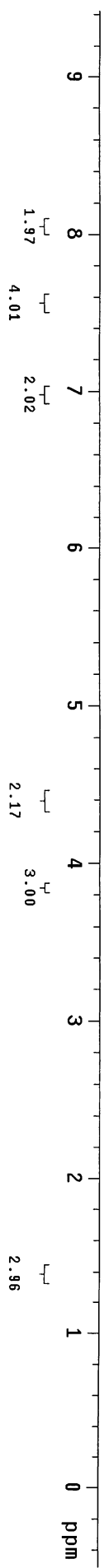


Table 2, entry 5

10-3-15-4  
 exp1 s2pu1

SAMPLE Mar 15 2010 DEC. & VT  
 solvent CDC13 dn C13  
 file /data/export/~ dpwr 30  
 home/gfu/fusion/ca~ dof 0  
 spcr/10-3-15-4.fid dm nnn  
 ACQUISITION c 200  
 sfrq 500.435 dmf 200  
 tn H1 dseq 1.0  
 at 4.999 homo n  
 np 120102  
 sw 12012.0  
 fb not used wfile  
 bs 4 proc ft  
 tpwr 56 fn 262144  
 pw 8.0 math f  
 dl 0.100  
 tof 3003.2 werr  
 nt 16 wexp  
 ct 8 wbs  
 gain not used wnt  
 alock n  
 flags not used  
 l1 n  
 ln n  
 dd y  
 hs nm  
 DISPLAY  
 sp -226.2  
 wp 4702.9  
 vs 17  
 sc 0  
 wc 250  
 hzmm 18.81  
 is 237.13  
 rfl 4198.9  
 rfp 3629.1  
 fh 4.000  
 ins  
 al cdc ph

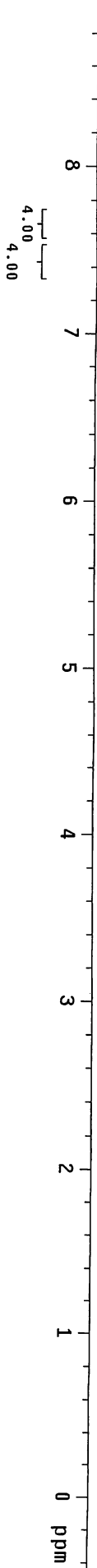
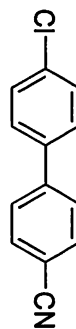


Table 2, entry 6

10-2-3-2

expt1 s2pu1

SAMPLE DEC. & VT  
 date Feb 3 2010 dfrq 125.672  
 solvent CDCl3 dn C13  
 file /data/export/~ dpwr 30  
 home/gnu/fusion/bu~ dof 0  
 1lwinkle/10-2-3-2.~ dm nm  
 fid dm w

ACQUISITION  
 sfrq 499.746 dseq 10000  
 tn H1 dres 1.0  
 at 3.001 homo n  
 np 63050  
 sw 10504.2 wtfile  
 fd not used proc 262144  
 bs 4 fn math f  
 tpwr 56  
 pw 8.6 warr ft  
 dl 2.000 wexp  
 tof 1519.5 wds  
 nt 16 wnt  
 ct 12  
 atlock n  
 gain not used wft

DISPLAY  
 sp -401.0  
 vp 5465.9  
 vs 38  
 sc 0  
 wc 250  
 hzmm 21.86  
 is 248.03  
 rfl 4866.1  
 rfp 3618.1  
 th 7  
 ins 2.000  
 ai cdc ph

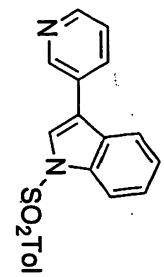
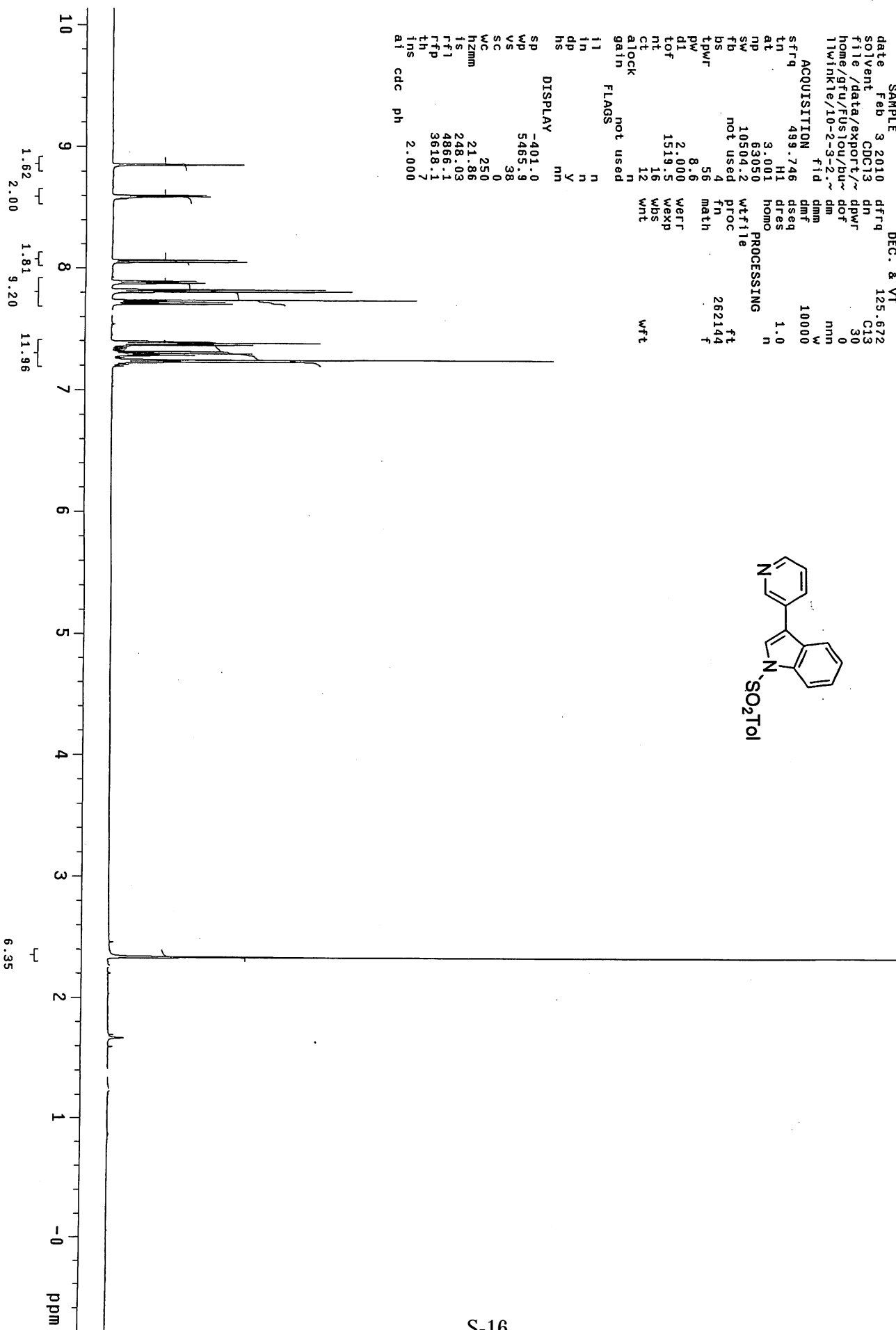




Table 2, entry 7

10-2-4-12

exp1 szpu1

date	Feb	4	2010	dfrq	DEC. & VT	125.845
solvent	CDCl3			dn		G13
file	/data/export/~			dpwr		30
home	/gfu/fls/10u/ca~			dof		0
spcr	/10-2-4-12.fid			dm		nmn
ACQUISITION				dmm		C
sfrq	500.435			dnt		200
ln	H1			dseq		
at	4.999			dres		1.0
np	120102			homo		n
sw	12012.0					
fb	not used			PROCESsing		
bs	4			wfite		ft
tpwr	56			proc		262144
pw	8.0			fn		f
di	0.100			math		
tof	3003.2			werr		
nt	16			wexp		
ct	4			wbs		
alock	n			wnt		wft
gain	not used					
FLAGS						
il	n					
in	n					
dp	y					
hs	mn					
DISPLAY						
SP	-241.0					
WP	5671.4					
VS	97					
WC	0					
SC	250					
hzm	22.69					
is	296.28					
rfl	500.6					
rffp	0					
th	7					
ins	1.000					
at	cdc					
ph						

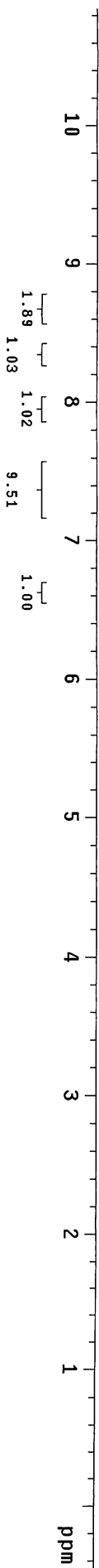
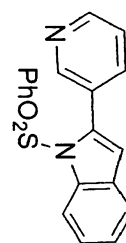


Table 2, entry 8

10-2-3-3

exptl szpui

date	Feb 3 2010	dfreq	125.672
solvent	CDCl3	dn	C13
file	/data/export/~	dpwr	30
home	gfu/fjstou/bu-	dof	0
lwinkle	/10-2-3-3	dm	mnn
		dmm	w
		dmt	10000
ACQUISITION			
sfrq	499.746	dseq	
in	H1	dres	1.0
at	3.001	homo	n
np	63050	PROCESSING	
sw	10504.2	vtfile	
fb	not used	proc	ft
bs	not used	fn	262144
tpwr	56	math	f
pw	8.6	werr	
d1	2.000	waxp	
tof	1519.5	wbs	
nt	16	wht	wft
ct	4		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	mn		
DISPLAY			
sp	-369.3		
wp	5177.8		
vs	6		
sc	0		
wc	250		
hzm	20.71		
is	263.36		
rfl	1233.8		
rff	0		
th	7		
ins	1.000		
al	cdc	ph	

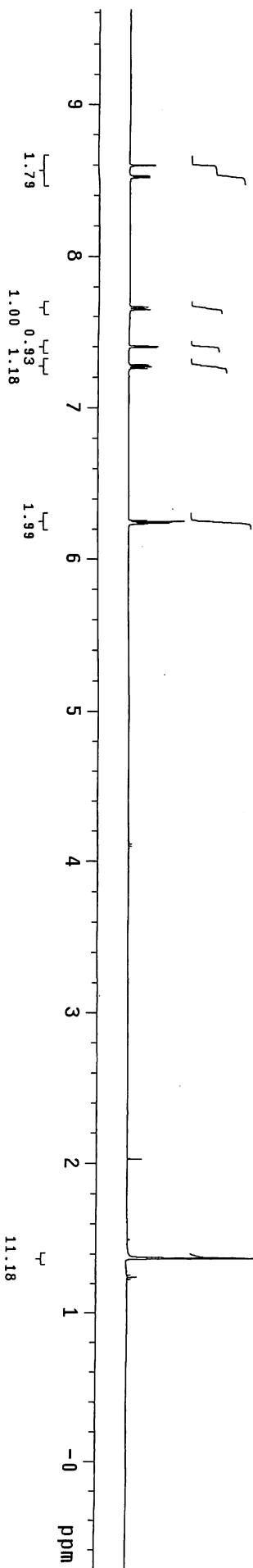
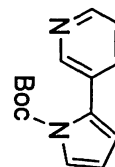


Table 2, entry 9

10-3-15-22  
 exp1 s2pu1

SAMPLE	date	Mar 15 2010	dfrq	125.794
solvent	CDCl3	dn	C13	
file	/data/export/~	dof	38	
home	/ofu/fujstou/ro~	dm	mm	
ckv	19-3-15-22.fid	dmm	C	
ACQUISITION		dnt	10000	
sfrq	500.231	dres	1.0	
in	H1	homo	n	
at	3.200	temp	20.0	
np	64000	PROCESSING		
sw	10000.0	ft	131072	
fb	not used	fn	math	
bs	not used	proc		
ss	1	wf		
tpwr	58	wrt		
pw	9.0			
d1	0			
tof	1498.2			
nt	16			
ct	16			
alock	n			
gain	not used			
flags	not used			
fl	n			
in	n			
dp	y			
hs	nm			
DISPLAY				
sp	-381.1			
wp	5403.0			
vs	94			
sc	0			
wc	250			
hzm	21.61			
is	478.26			
rfl	4684.6			
rfp	3821.6			
th	7			
ins	1.000			
nm				

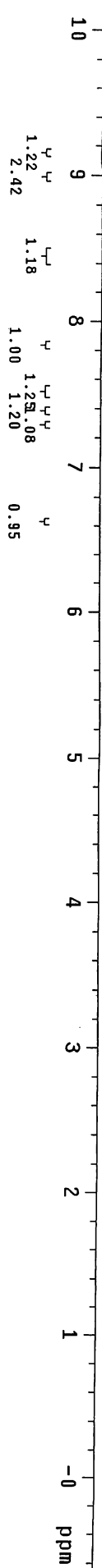
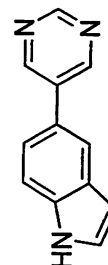
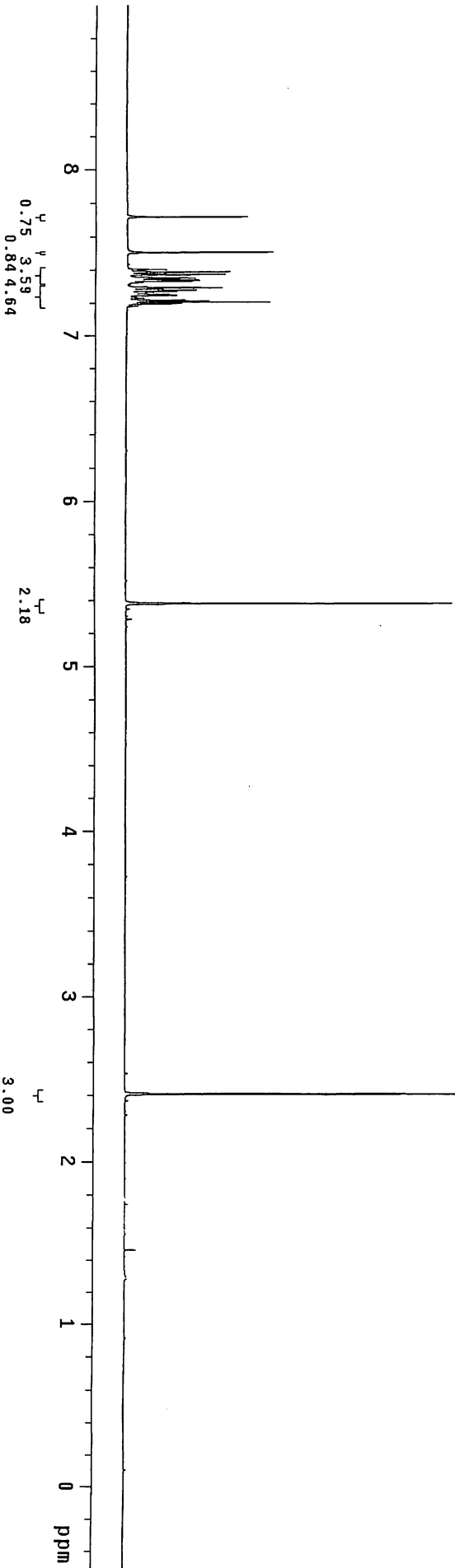
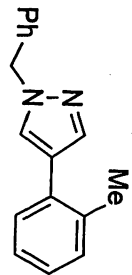


Table 2, entry 10

10-3-15-3

exp1 s2pu1

date	Mar 15 2010	DEC. & VT	125.845
solvent	CDCl3	C13	30
file	/data/export/~	dpwr	0
home/gfu/fusion/ca~		do	nmn
spe/10-3-15-3.fid		dm	c
ACQUISITION		dmm	200
sfrq	500.435	dmf	n
tn		dseq	1.0
at	4.939	dtes	
np	120102	homo	n
sw	12012.0	PROCESsing	
fb	not used	wfifile	ft
bs		proc	262144
tpwr	56	fn	f
pw	8.0	math	
d1	0.100	warr	
tof	3003.2	wexp	
nt	16	wbs	
ct	8	wrt	
alock	n		
gain	not used		
flags			
il	n		
in	n		
dp	y		
hs	nh		
DISPLAY			
sp	-261.0		
wp	4762.8		
vs	18		
sc	0		
wc	250		
hzmm	19.05		
ls	624.34		
rfl	500.6		
rflp	0		
th	7		
ins	3.000		
at	cdc	ph	



Eq. (3) product

10-3-24-11

expi s2pu1

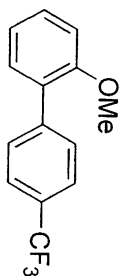
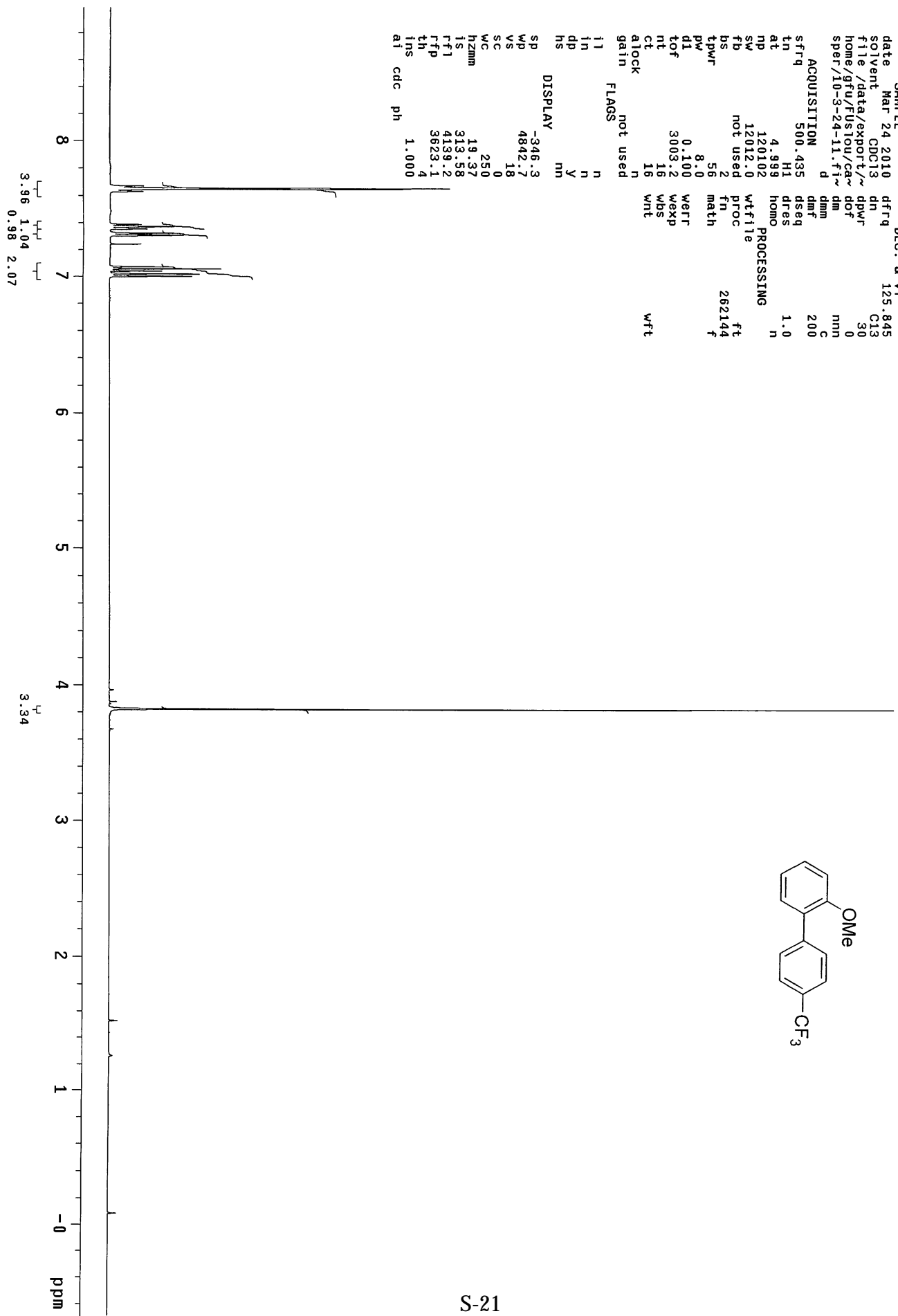
SAMPLE Mar 24 2010 DEC. & VT  
 date Mar 24 2010 125.845  
 solvent CDCl3 C13  
 file /data/export/~ dpwr 30  
 home/gfu/fusion/ca~ dof 0  
 sper/10-3-24-11.fi~ dm nnn  
 dmm nnc  
 dnm C  
 dnmr 200

ACQUISITION  
 sfrq 500.435  
 tn H1  
 at 4.999  
 np 120102  
 sw 12012.0  
 fb not used  
 bs 2  
 tpwr 56  
 pw 8.0  
 d1 0.100  
 tof 3003.2  
 nt 16  
 ct 16  
 alock n  
 gain not used

PROCESSING  
 wfft 1.0  
 homo n  
 dres  
 dseq  
 ft 262144  
 math  
 wfft  
 wft

DISPLAY  
 sp -346.3  
 wp 4842.7  
 vs 18  
 sc 0  
 wc 250  
 hzmm 19.37  
 is 313.58  
 rfl 4139.2  
 rfp 3623.1  
 th 4  
 ins 1.000  
 ai cdc ph

FLAGS  
 i1 n  
 in n  
 dp Y  
 hs nm



Eq.(4) product

10-3-22-21  
exptl s2pu1

SAMPLE Mar 23 2010 DEC. & VT  
 date Mar 23 2010 dfrq 125.845  
 solvent CDC13 dn C13  
 file /data/export/~ dpwr 30  
 home/gfu/fiuslou/ca~ dof 0  
 spcr/10-3-22-21.ft~ dm mnm  
 ACQUISITION d dmm 200  
 sfrq 500.435 dmf  
 tn H1 dseq  
 at 4.999 H1 dres 1.0  
 np 120102 homo  
 sw 12012.0 wffile  
 fb not used proc  
 bs 4 fn  
 tpwr 56 math 262144  
 pw 8.0  
 dl 0.100 werr  
 tof 3003.2 wexp  
 nt 16 wbs  
 ct 16 wnt  
 alock not used  
 gain not used  
 FLAGS  
 i1 n  
 in n  
 dp Y  
 hs nm  
 DISPLAY  
 SP -380.7  
 WP 5022.4  
 VS 129  
 WC 0  
 SC 250  
 hzmm 20.09  
 is 380.52  
 rfl 500.6  
 rfp 0  
 th 7  
 ins 2.000  
 ai cdc ph

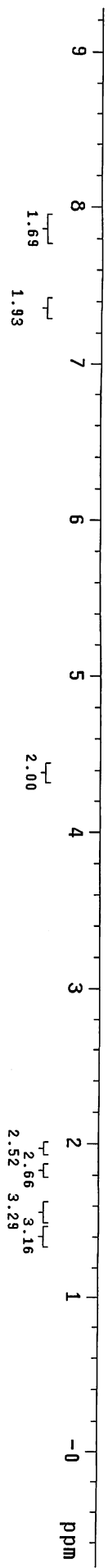
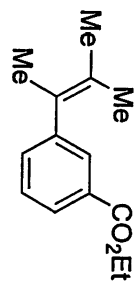


Table 3, entry 1

10-3-17-11  
 exp1 s2pu1

date	Mar 17 2010	DEC. & VT	125.794
solvent	CDCl3		C13
file	exp	dpwr	38
ACQUISITION		doF	0
sfrq	500.231	dm	nnn
tn	H1	dmm	c
at	3.200	dmf	10000
np	64000	dseq	
sw	10000.0	dres	1.0
td	not used	homo	n
ds	2	PROCESSING	
ss	1	wfFile	ft
tpwr	58	proc	fn
pw	9.0	fn	131072
di	0	math	f
tof	1498.2		
nt	16	WERR	
ct	16	WEXP	
alock	n	WDS	
gain	not used	wrt	
FLAGS			
i1	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-256.3		
wp	4846.9		
vs	151		
sc	0		
wc	250		
hzm	19.39		
fs	314.38		
rfl	4622.3		
rfp	3821.7		
tn	7		
ins	1.000		
nm			

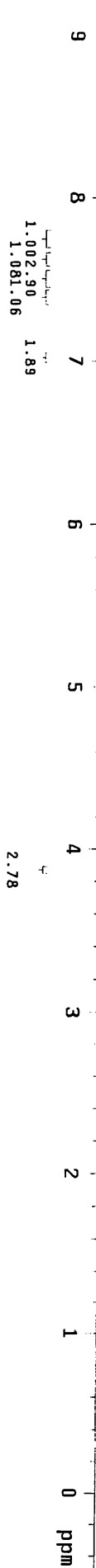
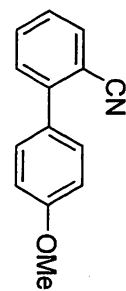
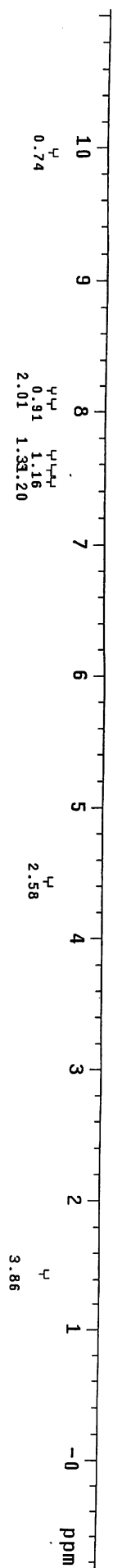
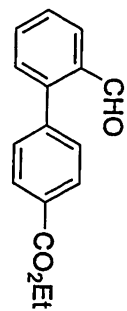


Table 3, entry 2

STANDARD PROTON PARAMETERS

```

exp1 s2pu1
SAMPLE Mar 19 2010 DEC. & VT 125.794
solvent Mar 19 CDC13 dn C13
file /data/export/~ dpwr 38
home/gfu/FUS10U/RO~ dof 0
ckv/10-9-19-41.fid dm nm
ACQUISITION dmm c
sfrq 500.231 dmf 10000
tn H1 dseq 1.0
at 3.200 dres n
np 64000 homo n
sw 10000.0 wfile PROCESSING
fb not used wfile ft
ss 2 proc 131072
bs 1 fn
tpwr 58 math
pv 9.0 weff
di 0 wexp
tof 1498.2 wbs
nt 16 wnt
ct 4
alock n
gain not used
flags not used
ii n
in n
dp y
hs nm
DISPLAY
sp -443.7
wp 5968.3
vs 151
sc 0
wc 250
hzmm 23.87
is 499.90
rfl 4622.3
rflp 3621.7
th 7
ins 1.200
nm ph
    
```

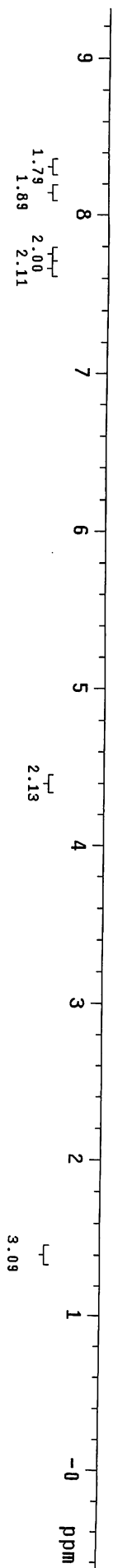
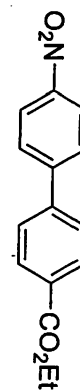




10-3-18-23  
 exp1 szpu1

SAMPLE DEC. & VT  
 date Mar 18 2010 dfrq 125.794  
 solvent CDCl3 dn C13  
 file /data/export/~ dpwr 38  
 home/gfu/fujiou/ro~ dof 0  
 cky/10-3-18-23.fid dm mnn  
 ACQUISITION c  
 sfrq 500.231 dmf C  
 tn 3.200 dseq 10000  
 dt 3.200 dres 1.0  
 np 64000 homo n  
 sw 10000.0  
 fb not used wffite  
 bs not used wffite  
 ss 4 proc ft  
 tpwr 58 math 131072  
 pw 9.0 f  
 d1 0 werr  
 tof 1498.2 wexp  
 nt 16 wbs  
 ct 16 wnt  
 alock n  
 gain not used  
 flags

DISPLAY  
 sp -330.8  
 wp 4987.3  
 vs 151  
 sc 0  
 wc 250  
 hzmm 19.95  
 fs 456.45  
 ft1 4634.2  
 rfp 3821.6  
 fh 7  
 fns 2.000  
 nm  
 ph



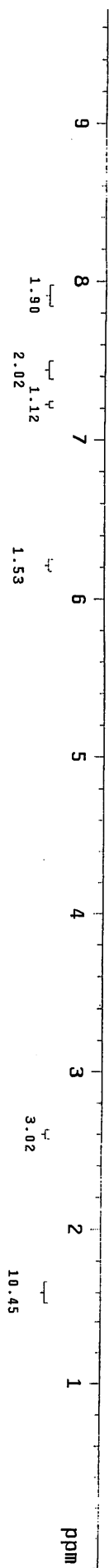
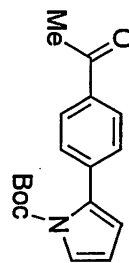


Table 3, entry 5

10-3-21-11

expi s2pu1

date	Mar 22 2010	dfrq	DEC. & VT	125.845
solvent	CDC13	dn	C13	0
file	/data/exprt/~	dpwr	30	0
home	/gfu/Fusion/ca~	dof	nm	nm
spe	/10-3-21-11.ft~	dm	nm	nm
ACQUISITION	d	dim	nm	nm
sfrq	500.435	dseq	200	200
tn	H1	dmf	1.0	1.0
at	4.999	homo	n	n
np	120102	dr	ft	ft
sw	12012.0	proc	262144	262144
fb	not used	math		
bs	4	fn		
tpwr	56	math		
pw	8.0	werf		
d1	0.100	wexp		
tof	3003.2	wbs		
nt	16	wnt		
ct	16			
atock	not used			
gain	not used			
FLAGS				
i1	n			
in	n			
dp	Y			
hs	nm			
DISPLAY				
sp	-280.9			
wp	5641.4			
vs	25			
sc	0			
wc	250			
h2mm	22.57			
IS	390.07			
rfl	500.6			
rflp	0			
th	7			
ins	1.000			
ai	cdc	ph		

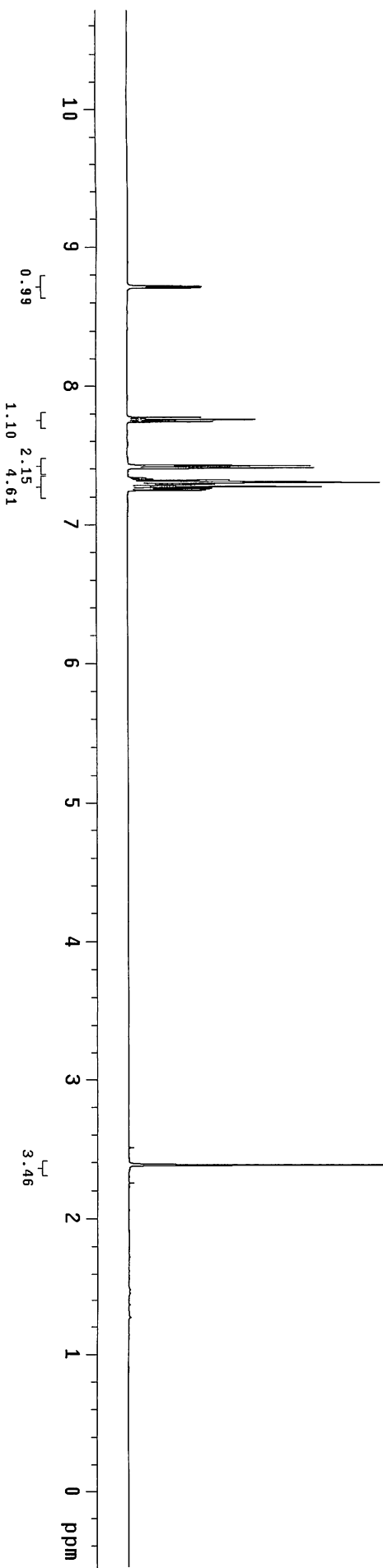
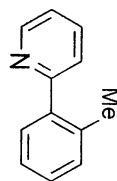


Table 3, entry 6

10-3-15-21  
 expt s2pu1

date	Mar 15 2010	dfrq	DEC. & VT	125.794
solvent	CDCl3	dn		613
file	/data/export/~	dpwr		38
home/gfu/fusion/ro~		dof		0
ckv/10-3-15-21.fid		dmm		mm
ACQUISITION		dmf		C
sfrq	500.231	dmf		10000
tn		dseq		
at	3.200	dtes		1.0
np	84000	homo		n
sw	10000.0	temp	PROCESSING	20.0
fb	not used	wf		
bs		math		
ss		proc		ft
tpwr	58	fn		131072
pw	9.0	wh		f
d1				
tof	1498.2	werr		
nt		wexp		
ct	16	wbs		
alock	16	wht		
gain	not used			
fl	FLAGS			
in	n			
in	n			
dp	y			
hs	nm			
sp	DISPLAY			
wp	-355.7			
vs	5112.0			
sc	151			
hzc	0			
h2mm	250			
is	20.45			
ftl	520.06			
rfl	4684.1			
th	3621.6			
ins	7			
nm	1.000			

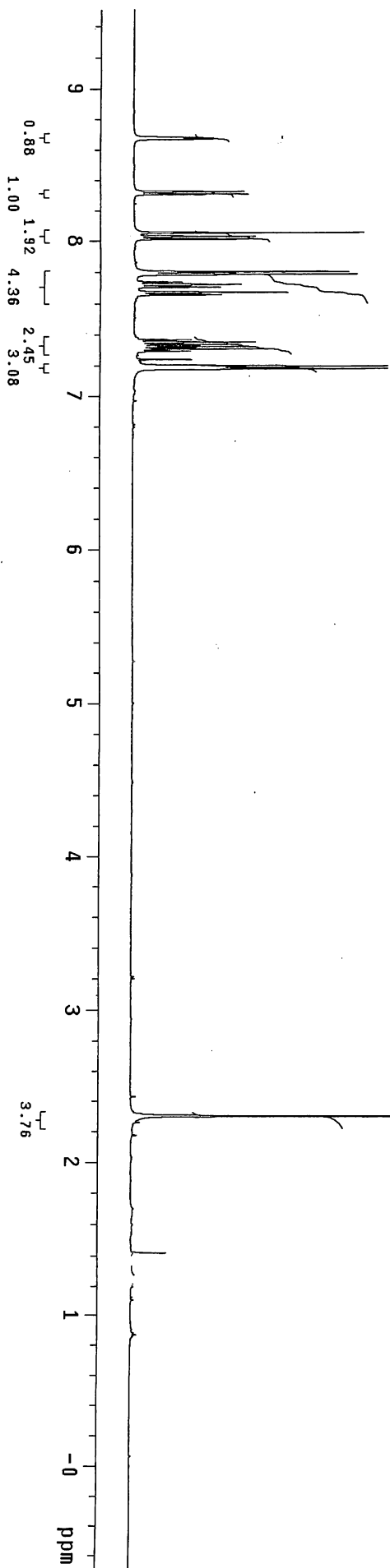
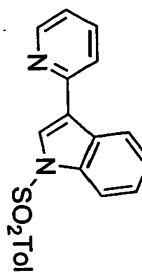


Table 3, entry 7

10-3-17-13  
 expt szpu1

SAMPLE Mar 17 2010 DEC. & VT  
 solvent CDC13 dn 125.794  
 file /data/export/~ dpwr C13  
 Home/gfu/fusion/ro~ dof 38  
 cky/10-3-17-13.fid dm nnn  
 ACQUISITION dmf c  
 sfreq 500.231 dms 10000  
 tn H1  
 at 3.200 dres 1.0  
 np 84000 homo  
 sw 10000.0 PROCESSING  
 fb not used wifile  
 bs 4 ft  
 ss 1 fn  
 tpwr 58 math 131072  
 pw 9.0  
 dl 0 wert  
 tof 1498.2 wexp  
 nt 16 wbs  
 ct 12 wnt  
 ct alock  
 gain not used  
 flags  
 i1 n  
 in n  
 dp Y  
 hs mh  
 DISPLAY  
 sp -323.1  
 wp 4837.8  
 vs 151  
 sc 0  
 hzmm 19.35  
 is 555.11  
 rf1 4084.7  
 rfp 3821.5  
 lns 3.000  
 nm  
 ph

