A General and Efficient Approach to Aryl Thiols: CuI-catalyzed Coupling of Aryl Iodides with Sulfur and Subsequent Reduction

Yongwen Jiang,[1]* Yuxia Qin,[2] Siwei Xie,[2] Xiaojing Zhang,[2] Jinhua Dong,[2] and Dawei Ma[1]*

[1]*State Key Laboratory of Bioorganic and Natural Products Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China,*
[2]*Shenyang Pharmaceutical University, 103 Wenhua Lu, Shenyang 110016, China*

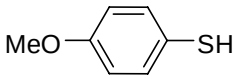
Jiangyw@mail.sioc.ac.cn & Madw@mail.sioc.ac.cn

Supporting information

Table of contents

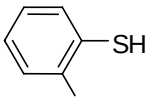
Experimental

General procedure for preparation of aryl thiols: An oven-dried Schlenk tube was charged with CuI (19 mg, 0.1 mmol), aryl iodide (1 mmol), S powder (96 mg, 3 mmol) and K_2CO_3 (276 mg, 2 mmol). The tube was evacuated and backfilled with argon before DMF (2 mL) were added. The reaction mixture was stirred at 90 ^oC until the corresponding aryl iodide was completely consumed as monitored by TLC. To this reaction mixture $NaBH_4$ (0.111 g, 3 mmol) was added with cooling by ice-water (for **4a**-**4s**). [For **4t**-**4v**, Ph_3P (0.78 g, 3 mmol), dioxane (3 mL), H_2O (1 mL) and concentrated HCl (0.2 mL) were added into this mixture] After the resultant reaction solution was stirred at 40 ^oC for 5 h, 3 N HCl (2 mL) was added to quench the reaction. The mixture was extracted with ethyl acetate, and the combined organic layers were treated with 20% NaOH. The aqueous layer was separated, washed with ethyl acetate, acidified with concentrated HCl, and then extracted with ethyl acetate. The organic layer was washed with H_2O and brine, and dried over Na_2SO_4. Removal of solvent in vacuo provided the desired product with satisfactory purity. Some relatively stable products were purified via column chromatography.



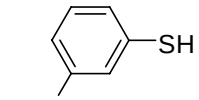
4a

4-Methoxythiophenol 4a.[1] ^1H NMR ($CDCl_3$, 300 MHz) δ 7.27 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 2H), 3.78 (s, 3H), 3.36 (s, 1H); EI-MS *m/z* 140 (M^+).



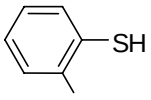
4b

2-Methoxythiophenol 4b.[2] ^1H NMR ($CDCl_3$, 300 MHz) δ 7.24-7.27 (m, 1H), 7.12 (t, *J* = 7.8 Hz, 1H), 6.83-6.88 (m, 2H), 3.89 (s, 3H), 3.81 (s, 1H); EI-MS *m/z* 140 (M^+).



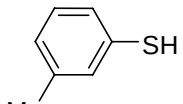
4c

3-Methoxythiophenol 4c.[2] ^1H NMR ($CDCl_3$, 300 MHz) δ 7.14 (t, *J* = 8.1 Hz, 1H), 6.81-6.86 (m, 2H), 6.70 (d, *J* = 8.7 Hz, 1H), 3.78 (s, 3H), 3.46 (s, 1H); EI-MS *m/z* 140 (M^+).



4d

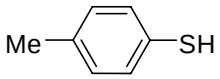
2-Methylthiophenol 4d.[3] ^1H NMR ($CDCl_3$, 300 MHz) δ 7.27 (d, *J* = 7.2 Hz, 1H), 7.14-7.17 (m, 1H), 7.08-7.05 (m, 2H), 3.29 (s, 1H), 2.33 (s, 3H); EI-MS *m/z* 124 (M^+).



4e

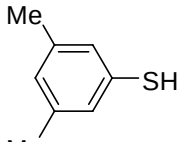
3-Methylthiophenol 4e.[4] ^1H NMR ($CDCl_3$, 300 MHz) δ 7.06-7.15 (m, 3H), 6.96 (d, *J*

= 7.5 Hz, 1H), 3.40 (s, 1H), 2.30 (s, 3H); EI-MS *m/z* 124 (M^+).



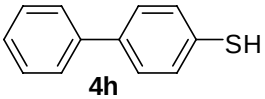
4f

4-Methylthiophenol 4f.[1] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.18 (d, 2H, *J* = 7.8 Hz), 7.05 (d, 2H, *J* = 8.1 Hz), 3.38 (s, 1H), 2.29 (s, 3H); EI-MS *m/z* 124 (M^+).



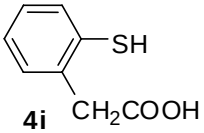
4g

3,5-Dimethyl-thiophenol 4g.[5] ^{1}H NMR (DMSO-d_6, 300 MHz) δ 6.90 (s, 2H), 6.78 (s, 1H), 3.35 (s, 1H), 2.25 (s, 6H); EI-MS *m/z* 138 (M^+).



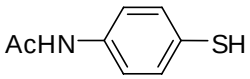
4h

Biphenyl-4-thiol 4h.[6] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.55 (d, *J* = 7.2 Hz, 2H), 7.49-7.41 (m, 4H), 7.33-7.36 (m, 3H), 3.50 (s, 1H); EI-MS *m/z* 186 (M^+).



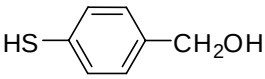
4i

2-Mercapto-benzeneacetic acid 4i.[7] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.42-7.39 (m, 1H), 7.25-7.17 (m, 3H), 3.82 (s, 2H), 3.50 (s, 1H); EI-MS *m/z* 168 (M^+).



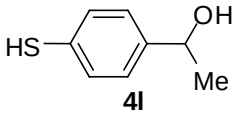
4j

4-Acetamidthiophenol 4j.[8] mp 157-158 °C (lit.[8] mp 155-158 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.40 (d, *J* = 8.7 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 2H), 3.43 (s, 1H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.9, 139.9, 130.6 (2C), 129.8, 120.1 (2C), 24.4; EI-MS *m/z* 167 (M^+).



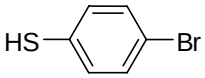
4k

4-Mercapto-benzyl alcohol 4k.[9] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.28 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 4.64 (s, 2H), 3.45 (s, 1H); EI-MS *m/z* 140 (M^+).



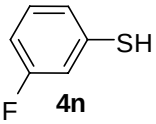
4l

1-(4-Mercapto-phenyl)ethanol 4l. ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.19 (m, 4H), 5.26 (s, 1H), 5.08 (d, *J* = 4.5 Hz, 1H), 4.66-4.58 (m, 1H), 1.25 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 129.2, 129.1 (2C), 125.8 (2C), 69.5, 24.7; EI-MS *m/z* 154 (M^+); EI-HRMS calcd for $C_8H_{10}OS$ (M^+), 154.0452, found 154.0455.



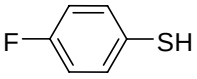
4m

4-Bromothiophenol 4m.[10] mp 70.2-70.6 °C (lit.[10] mp 70-71 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.35 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.7 Hz, 2H), 3.44 (s, 1H); EI-MS *m/z* 188 (M^+), 190 (M^+).



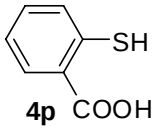
4n

3-Fluorothiophenol 4n.[11] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.23-7.16 (m, 1H), 7.04-7.00 (m, 2H), 6.85 (dt, *J* = 8.4, 2.4 Hz, 1H), 3.52 (s, 1H); EI-MS *m/z* 128 (M^+).



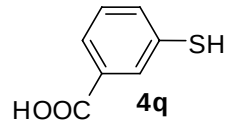
4o

4-Fluorothiophenol 40.[1] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.30-7.25 (m, 2H), 6.80 (t, *J* = 8.1 Hz, 2H), 3.43 (s, 1H); EI-MS *m/z* 128 (M^+).



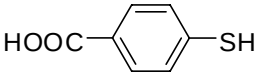
4p

2-Mercapto-benzoic acid 4p.[12] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.13 (d, *J* = 7.8 Hz, 1H), 7.40-7.32 (m, 2H), 7.23-7.17 (m, 1H), 4.67 (s, 1H); ESI-MS *m/z* 153 $(M - H)^+$.



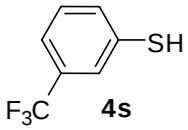
4q

3-Mercapto-benzoic acid 4q.[13] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.02 (s, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 3.58 (s, 1H); EI-MS *m/z* 154 (M^+).



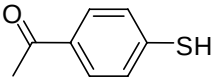
4r

4-Mercapto-benzoic acid 4r.[9] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.94 (d, *J* = 8.7 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 3.65 (s, 1H); EI-MS *m/z* 154 (M^+).



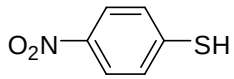
4s

3-Trifluoromethylthiophenol 4s.[1] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.52 (s, 1H), 7.45-7.32 (m, 3H), 3.58 (s, 1H); EI-MS *m/z* 178 (M^+).



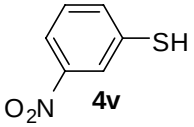
4t

1-(4-Mercapto-phenyl)ethanone 4t.[9] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.7 Hz, 2H), 3.63 (s, 1H), 2.56 (s, 3H); EI-MS *m/z* 152 (M^+).



4u

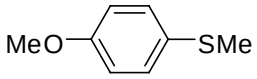
4-Nitrothiophenol 4u.[14] mp 79-80 °C (lit.[20] mp 80 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.10 (d, *J* = 8.7 Hz, 2H), 7.36 (d, *J* = 8.7 Hz, 2H), 3.76 (s, 1H); EI-MS *m/z* 155 (M^+).



4v

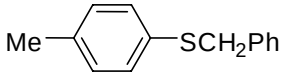
3-Nitrothiophenol 4v.[15] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.14 (d, *J* = 1.8 Hz, 1H), 8.0 (d, *J* = 8.7 Hz, 2H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 8.1 Hz, 1H), 3.71 (s, 1H); EI-MS *m/z* 155 (M^+).

General procedure for synthesis of aryl alkyl thioethers: An oven-dried Schlenk tube was charged with CuI (19 mg, 0.1 mmol), aryl iodide (1 mmol), S powder (96 mg, 3 mmol) and K_2CO_3 (276 mg, 2 mmol). The tube was evacuated and backfilled with argon before DMF (2 mL) were added. The reaction mixture was stirred at 90 °C until till aryl iodide was consumed as monitored by TLC. To this mixture $NaBH_4$ (0.111 g, 3 mmol) was added with cooling by ice-water. After the solution was stirred at 40 °C for 5 h, alkyl bromide was added. The reaction mixture was stirred at room temperature for 5 h before 3 N HCl (2 mL) was added. The mixture was extracted with ethyl acetate, and the organic layer was washed with H_2O and brine, and dried over Na_2SO_4. After removal of the solvent in vacuo, the residue was purified by flash chromatography to get the thioether.



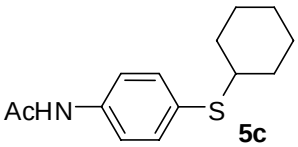
5a

4-Methoxythioanisole 5a.[16] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.28 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 2.45 (s, 3H); EI-MS *m/z* 154 (M^+).



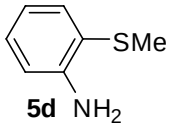
5b

Methyl-4-[(phenylmethyl)thio]benzene 5b.[17] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.27-7.19 (m, 7H), 7.06 (d, *J* = 7.5 Hz, 2H), 4.06 (s, 2H), 2.30 (s, 3H); EI-MS *m/z* 214 (M^+).



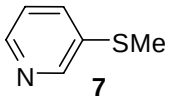
5c

Cyclohexylsulfanyl-4-acetamid-benzene 5c. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.43 (d, *J* = 8.7 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.12 (s, 1H), 2.98-3.02 (m, 1H), 2.18 (s, 3H), 1.93-1.96 (m, 2H), 1.75-1.79 (m, 2H),1.23-1.35 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 137.1, 133.5 (2C), 129.8, 120.3 (2C), 47.3, 33.3 (2C), 26.0, 25.7 (2C), 24.5; EI-MS *m/z* 249 (M^+). EI-HRMS calcd for $C_{14}H_{19}NOS$ (M^+), 249.1187, found 249.1188.



5d

2-Methylsulfanyl phenylamine 5d.[18] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.35 (d, *J* = 7.8 Hz, 1H), 7.09 (t, *J* = 7.8 Hz, 2H), 6.74-6.69 (m, 2 H), 4.0 (br s, 2H), 2.35 (s, 3H); EI-MS *m/z* 139 (M^+).

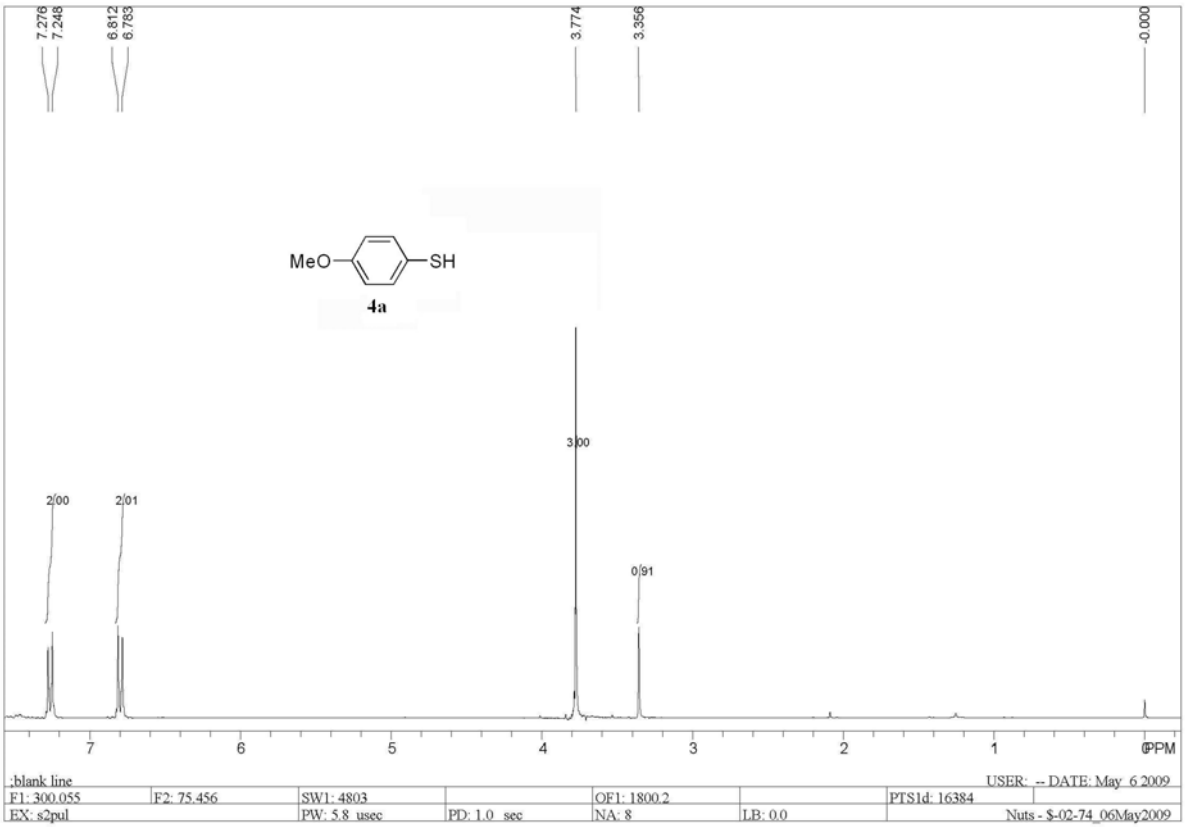


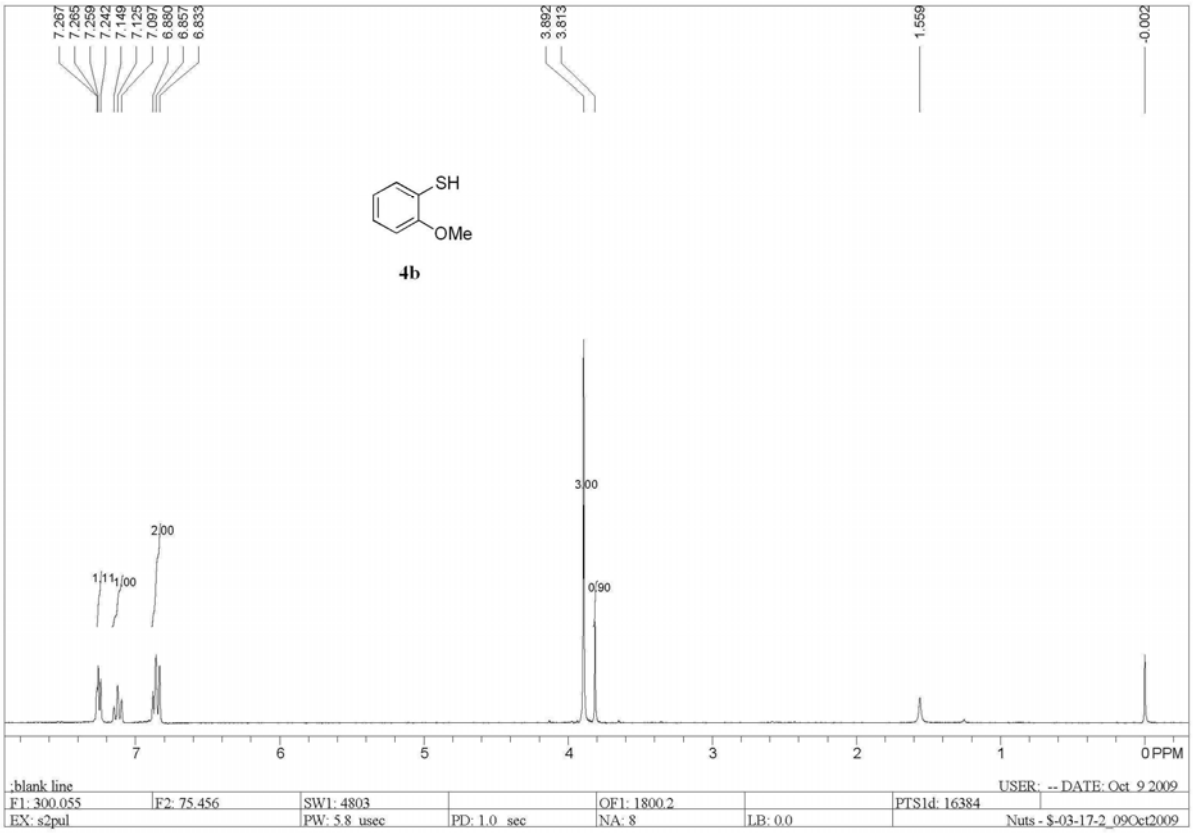
7

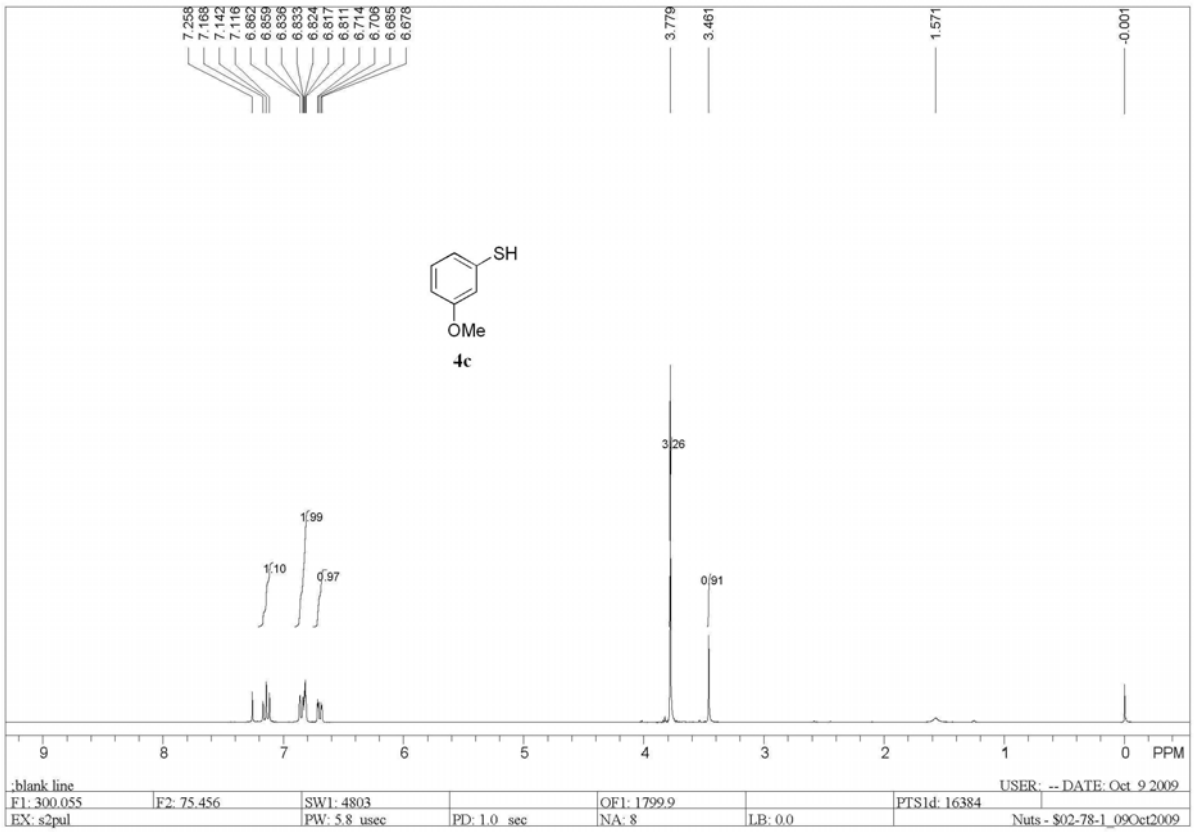
3-Methylsulfanyl-pyridine 7.[19] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.41 (s, 1H), 8.35 (d, *J* = 5.4 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.40 (t, *J* = 6.0 Hz, 1H), 2.56 (s, 3H); EI-MS *m/z* 125 (M^+).

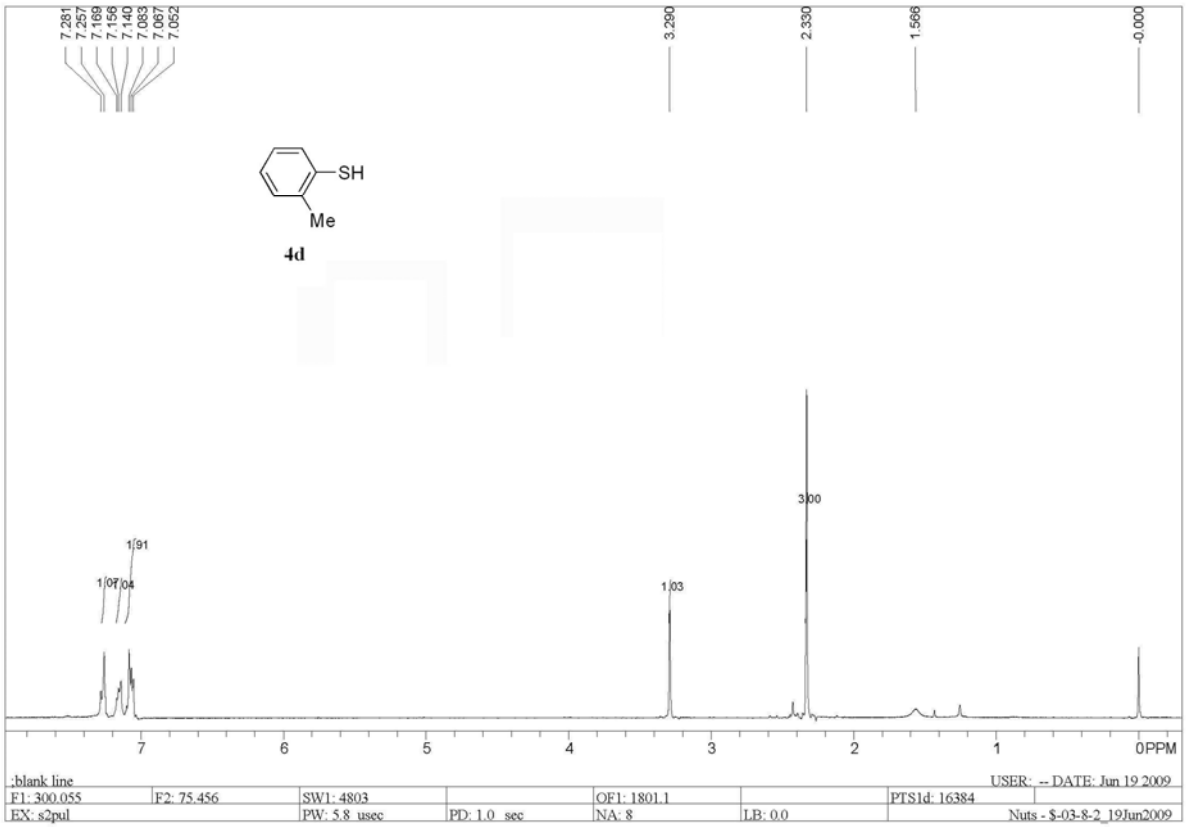
References:

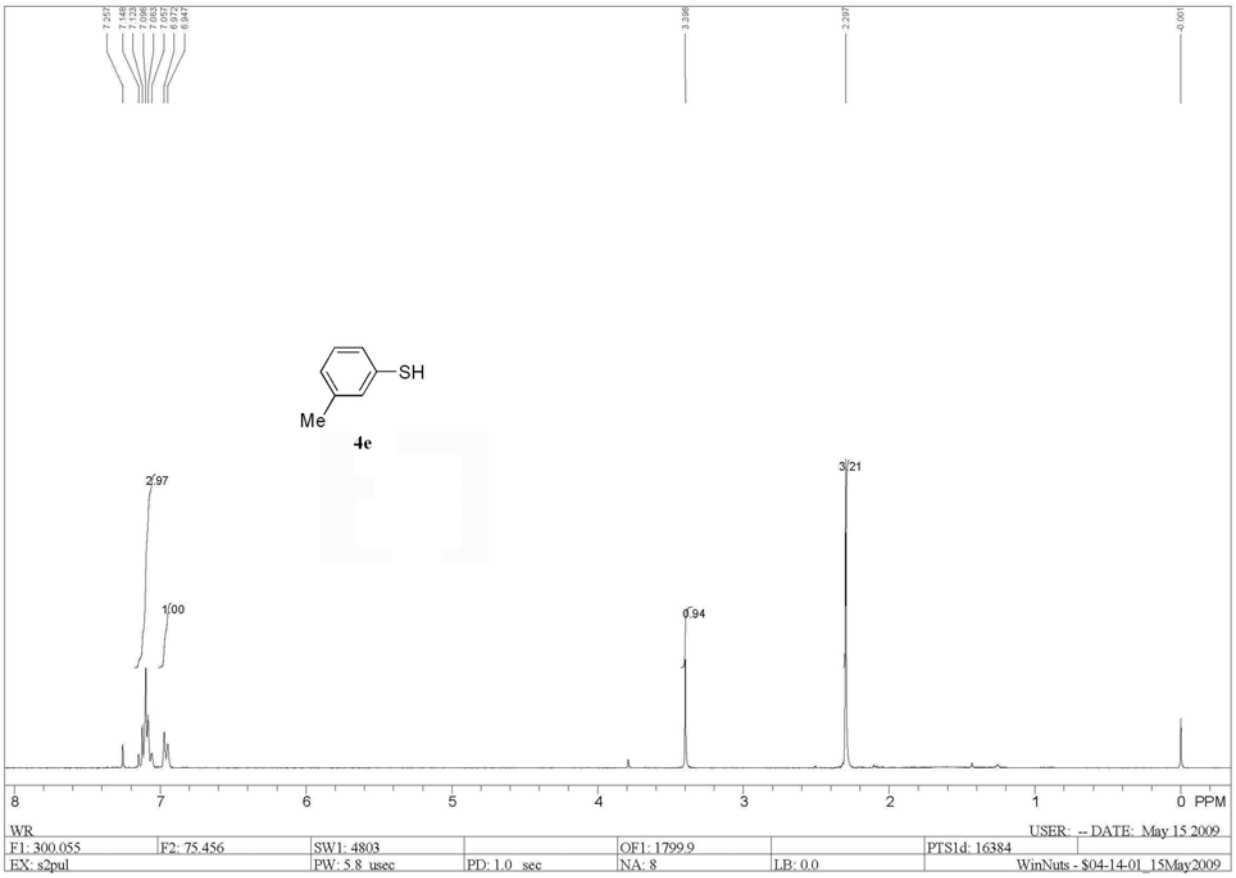
1. Still, I. W. J.; Watson, I. D. G. *Synth. Commun*. **2001**, *31*, 1355.
2. Testaferri, L.; Tiecco, M.; Tingoli, M. *Tetrahedron.* **1982**, *38*, 2721-2724.
3. Dittmer, D. C.; Nelsen, T. R. *J. Org. Chem*. **1976**, *41*, 3044.
4. D′Souza, V. T.; Nanjundiah, R.; Baeza H., J. *J. Org. Chem*. **1987**, *52*, 1720-1725.
5. Jikei, M.; Katoh, J.; Sato, N.; Yamamoto, K. *Bull. Chem. Soc. Jpn*. **1992**, *65*, 2029-2036.
6. Itoh, T.; Mase, T. *J. Org. Chem*. **2006**, *71*, 2203-2206.
7. Ojima, I. *US 2005232928*
8. Sengar, R. S.; Nemykin, V. N.; Basu, P. *New. J. Chem*. **2003**, *27*,1115-1123.
9. Decollo, T. V.; Lees, W. J. *J. Org. Chem*. **2001**, *66*, 4244-4249.
10. Jen, K.-Y.; Cava, M. P. *Tetrahedron Lett*. **1982**; *23*, 2001.
11. Kravtsov, D. N.; Kvasov, B. A.; Pombrik, S. I.; Fedin, E. I. *J. Organometal. Chem*. **1975**, *86*, 383.
12. Figuly, G D.; Loop, C. K.; Martin, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 654.
13. Starnes, W. H.; Kim, S. *US* 2003220429
14. Khalfina, I. A.; Beregovaya, I.V.; Vlasov, V.M. *Russ. J. Org. Chem.,* **2003**, *39*, 1104.
15. Turos, E.; Revell, K. D.; Ramaraju, P. *Bioorg. Med. Chem*. **2008**, *16*, 6501-6508.
16. Allaire, F. S.; Lyga, J. W. *Synth. Commun*. **2001**, *31*, 1857-1862.
17. Ajiki, K.; Hirano, M.; Tanaka, K. *Org. Lett*, **2005**, *7*, 4193-4195.
18. Chhikara, B. S.; Mishra, A. K.; Tandon, V. *Heterocycles*, **2004**, *63*, 1057.
19. Doudouh, A.; Woltermann, C.; Gros, P. C. *J. Org. Chem*. **2007**, *72*, 4978-4980.
20. Frankfater, A., Kezdy, F. J. *J. Am. Chem. Soc*. **1971**, *93*, 4039.

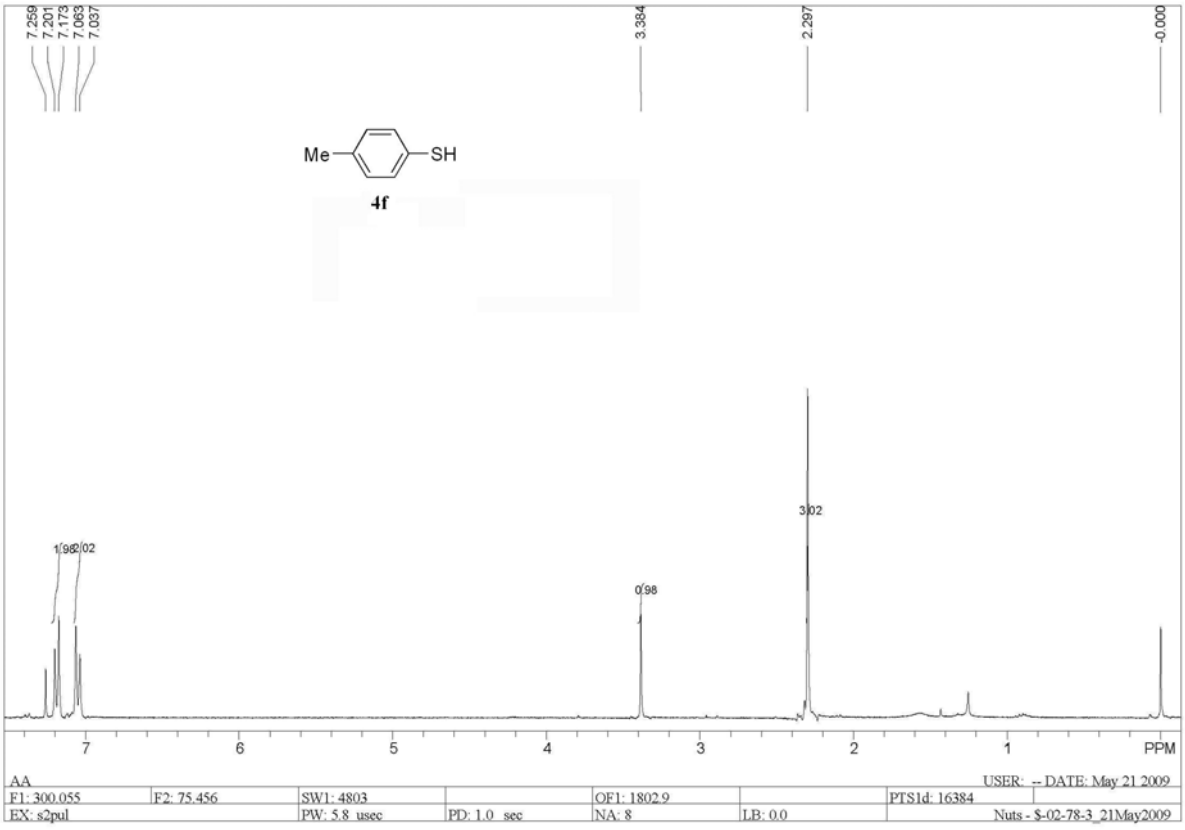

7.276
7.248
6.812
6.783
3.774
3.356
0.000
MeO
SH
4a
3.00
2.00
2.01
0.91
7
6
5
4
3
2
1
0PPM
;blank line
USER: -- DATE: May 6 2009
F1: 300.055
F2: 75.456
SW1: 4803
OF1: 1800.2
PTS1d: 16384
EX: s2pul
PW: 5.8 usec
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $-02-74_06May2009

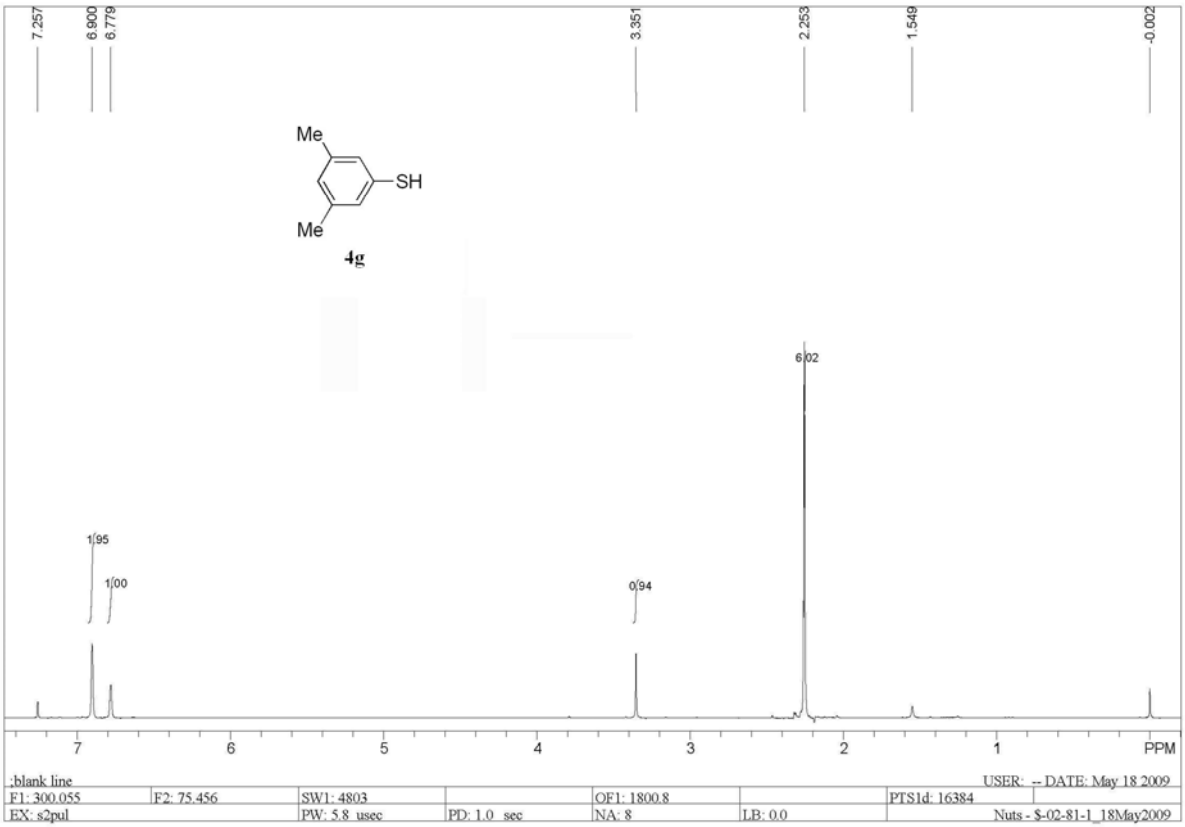

7.267
7.265
7.259
7.242
7.149
7.125
7.097
6.880
6.857
6.833
3.892
3.813
1.559
0.002
SH
OMe
4b
3.00
2.00
1.11
1.00
0.90
7
6
5
4
3
2
1
0 PPM
;blank line
USER: -- DATE: Oct 9 2009
F1: 300.055
F2: 75.456
SW1: 4803
OF1: 1800.2
PTS1d: 16384
EX: s2pul
PW: 5.8 usec
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $-03-17-2_09Oct2009

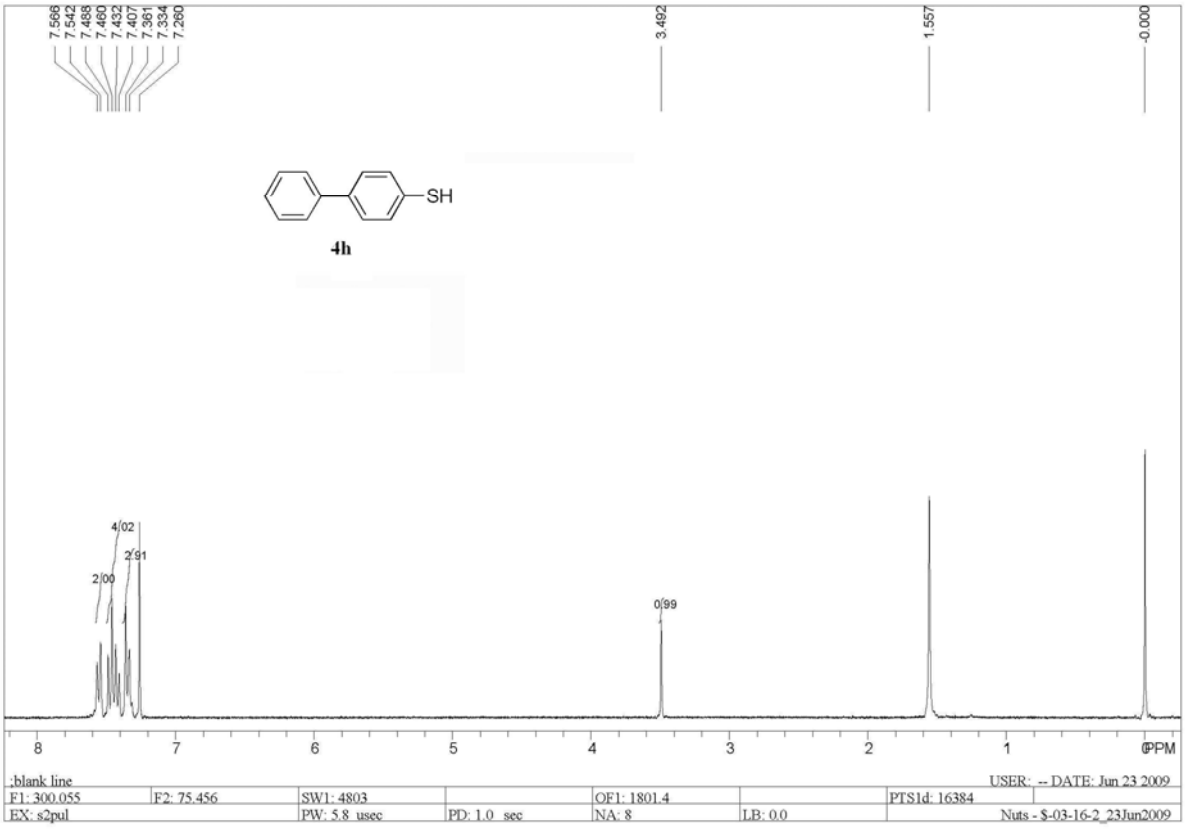

7.258
7.168
7.142
7.116
6.862
6.859
6.836
6.833
6.824
6.817
6.811
6.714
6.708
6.685
6.678
3.779
3.461
1.571
-0.001
SH
OMe
4c
3.26
1.99
1.10
0.97
0.91
9
8
7
6
5
4
3
2
1
0
PPM
;blank line
USER: -- DATE: Oct 9 2009
F1: 300.055
F2: 75.456
SW1: 4803
OF1: 1799.9
PTS1d: 16384
EX: s2pul
PW: 5.8 usec
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $02-78-1_09Oct2009

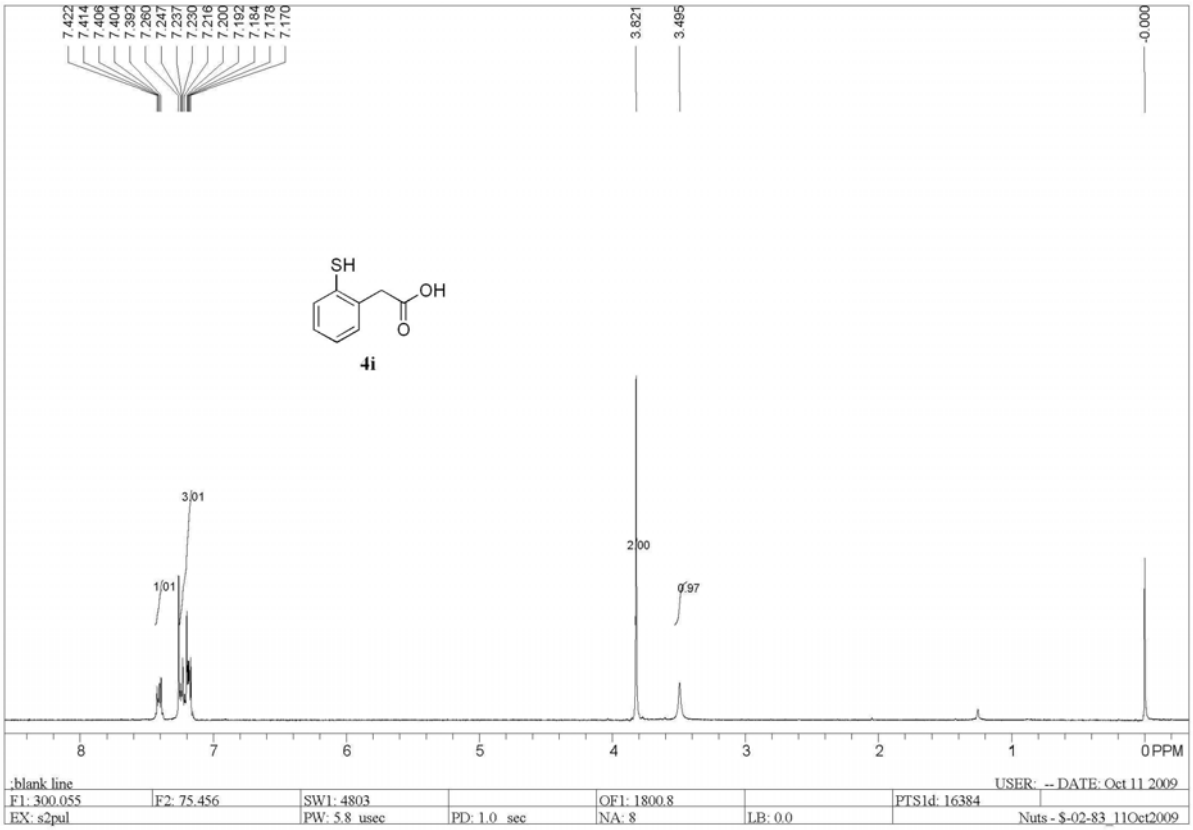

7.281
7.257
7.169
7.156
7.140
7.083
7.067
7.052
3.290
2.330
1.566
-0.000
SH
Me
4d
3.00
1.91
1.07
1.04
1.03
7
6
5
4
3
2
1
0PPM
;blank line
USER: -- DATE: Jun 19 2009
F1: 300.055
F2: 75.456
SW1: 4803
OF1: 1801.1
PTS1d: 16384
EX: s2pul
PW: 5.8 usec
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $-03-8-2_19Jun2009

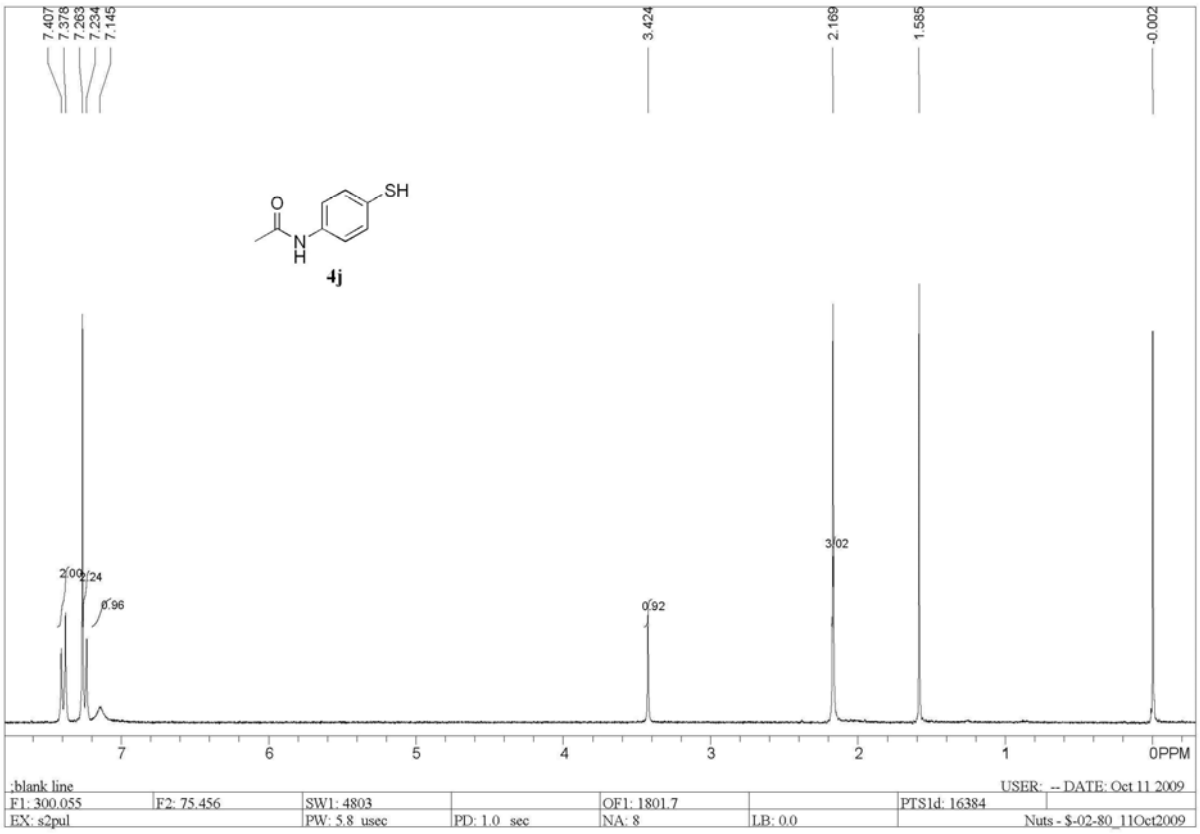

SH
Me
4e
2.97
1.00
0.94
3.21
8
7
6
5
4
3
2
1
0 PPM
WR
USER: -- DATE: May 15 2009
F1: 300.055
F2: 75.456
SW1: 4803
OF1: 1799.9
PTS1d: 16384
EX: s2pul
PW: 5.8 usec
PD: 1.0 sec
NA: 8
LB: 0.0
WinNuts - $04-14-01_15May2009

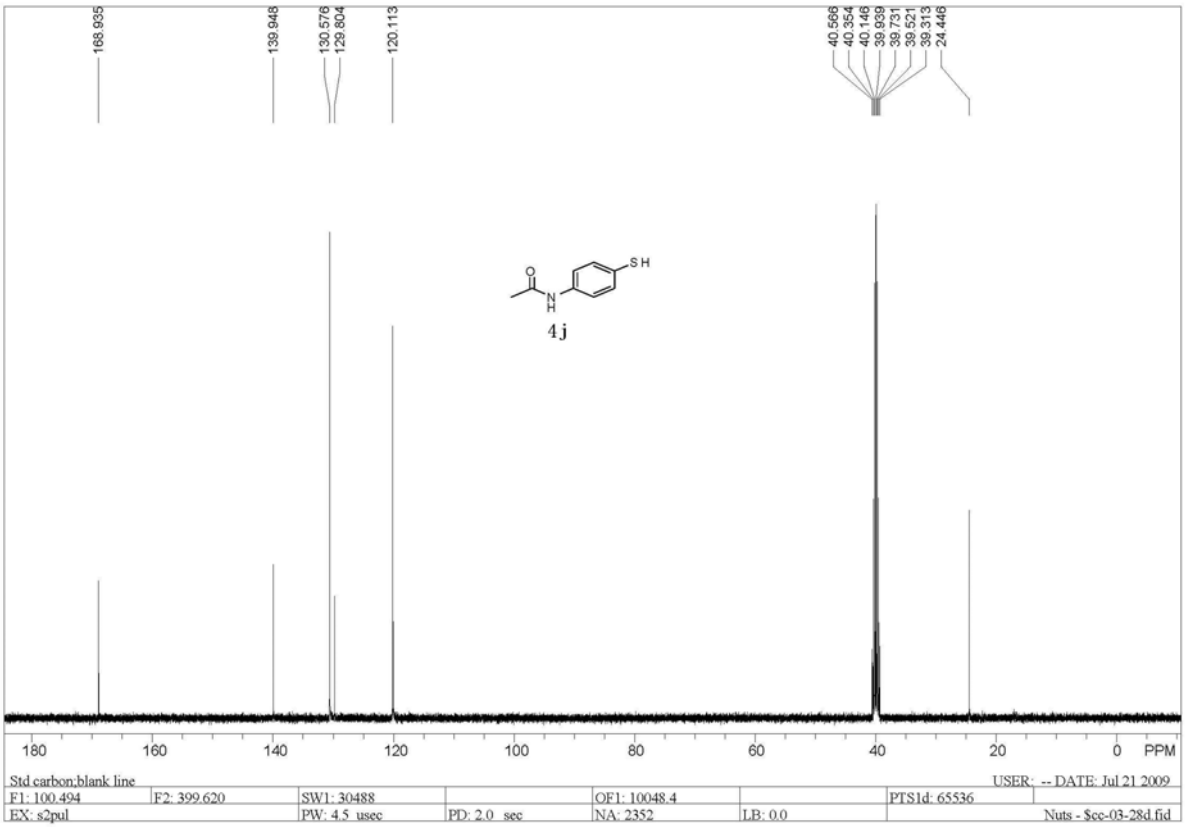

Me
SH
4f
1.98
2.02
0.98
3.02
7
6
5
4
3
2
1
PPM
AA
USER: -- DATE: May 21 2009
F1: 300.055
F2: 75.456
SW1: 4803
OF1: 1802.9
PTS1d: 16384
EX: s2pul
PW: 5.8 usec
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $-02-78-3_21May2009

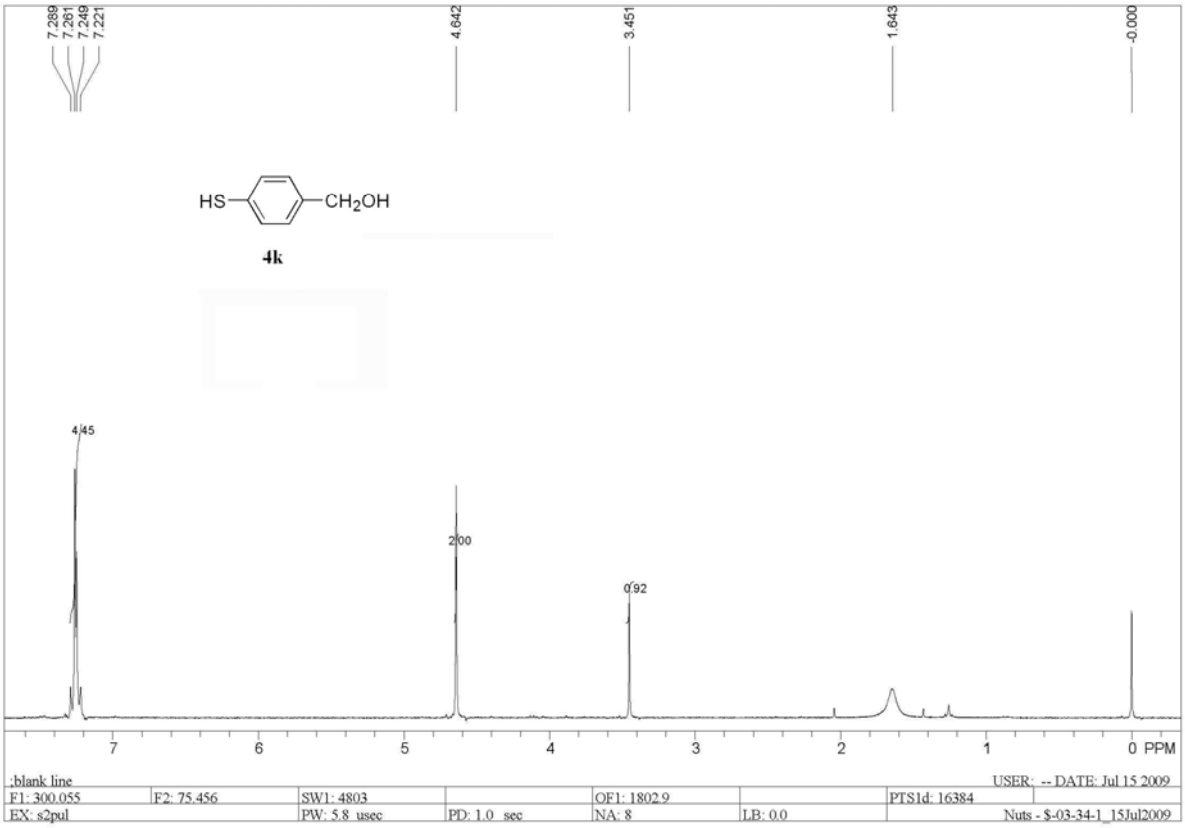

7.257
6.900
6.779
3.351
2.253
1.549
-0.002
Me
SH
Me
4g
6.02
1.95
1.00
0.94
7
6
5
4
3
2
1
PPM
;blank line
USER: -- DATE: May 18 2009
F1: 300.055
F2: 75.456
SW1: 4803
OF1: 1800.8
PTS1d: 16384
EX: s2pul
PW: 5.8 usec
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $-02-81-1_18May2009

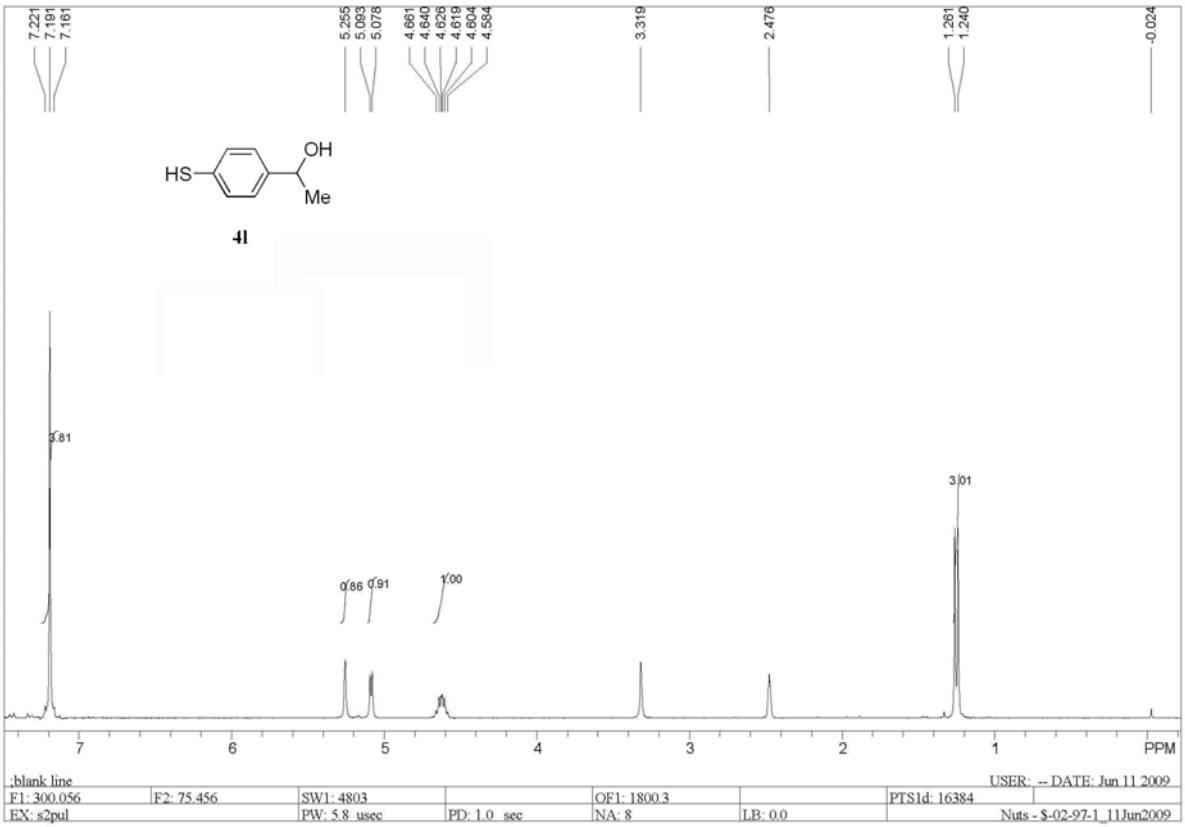

7.566
7.542
7.488
7.460
7.432
7.407
7.381
7.334
7.260
3.492
1.557
-0.000
SH
4h
4.02
2.91
2.00
0.99
8
7
6
5
4
3
2
1
0
PPM
;blank line
USER: -- DATE: Jun 23 2009
F1: 300.055
F2: 75.456
SW1: 4803
OF1: 1801.4
PTS1d: 16384
EX: s2pul
PW: 5.8 usec
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $-03-16-2_23Jun2009


7.422
7.414
7.406
7.404
7.392
7.260
7.247
7.237
7.230
7.216
7.200
7.192
7.184
7.178
7.170
3.821
3.495
0.000
SH
OH
O
4i
3.01
2.00
1.01
0.97
8
7
6
5
4
3
2
1
0 PPM
;blank line
USER: -- DATE: Oct 11 2009
F1: 300.055
F2: 75.456
SW1: 4803
OF1: 1800.8
PTS1d: 16384
EX: s2pul
PW: 5.8 usec
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $-02-83_11Oct2009

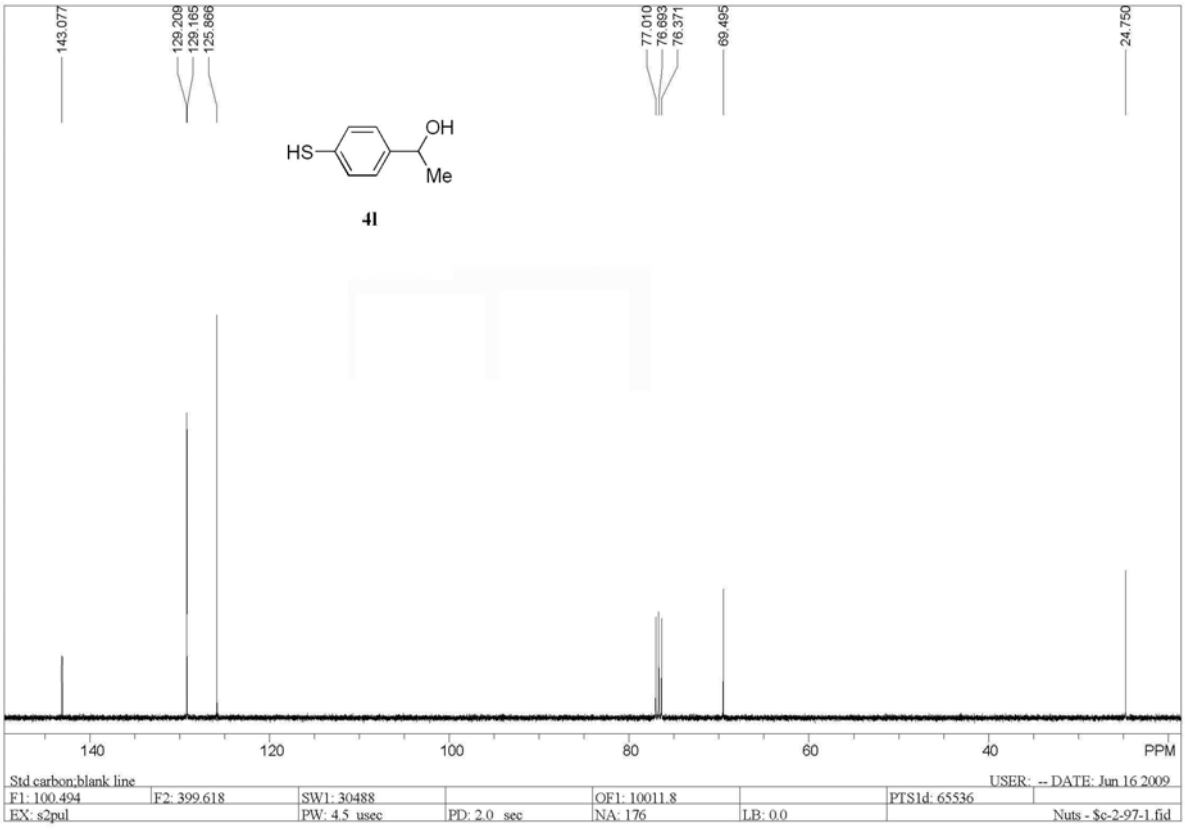

7.407
7.378
7.263
7.234
7.145
3.424
2.169
1.585
0.002
O
N
H
SH
4j
3.02
2.00
2.24
0.96
0.92
7
6
5
4
3
2
1
0 PPM
;blank line
USER: -- DATE: Oct 11 2009
F1: 300.055
F2: 75.456
SW1: 4803
OF1: 1801.7
PTS1d: 16384
EX: s2pul
PW: 5.8 usec
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $-02-80_11Oct2009


168.935
139.948
130.576
129.804
120.113
40.566
40.354
40.146
39.939
39.731
39.521
39.313
24.446
SH
O
N
H
4j
180
160
140
120
100
80
60
40
20
0 PPM
Std carbon;blank line
USER: -- DATE: Jul 21 2009
F1: 100.494
F2: 399.620
SW1: 30488
OF1: 10048.4
PTS1d: 65536
EX: s2pul
PW: 4.5 usec
PD: 2.0 sec
NA: 2352
LB: 0.0
Nuts - $cc-03-28d.fid

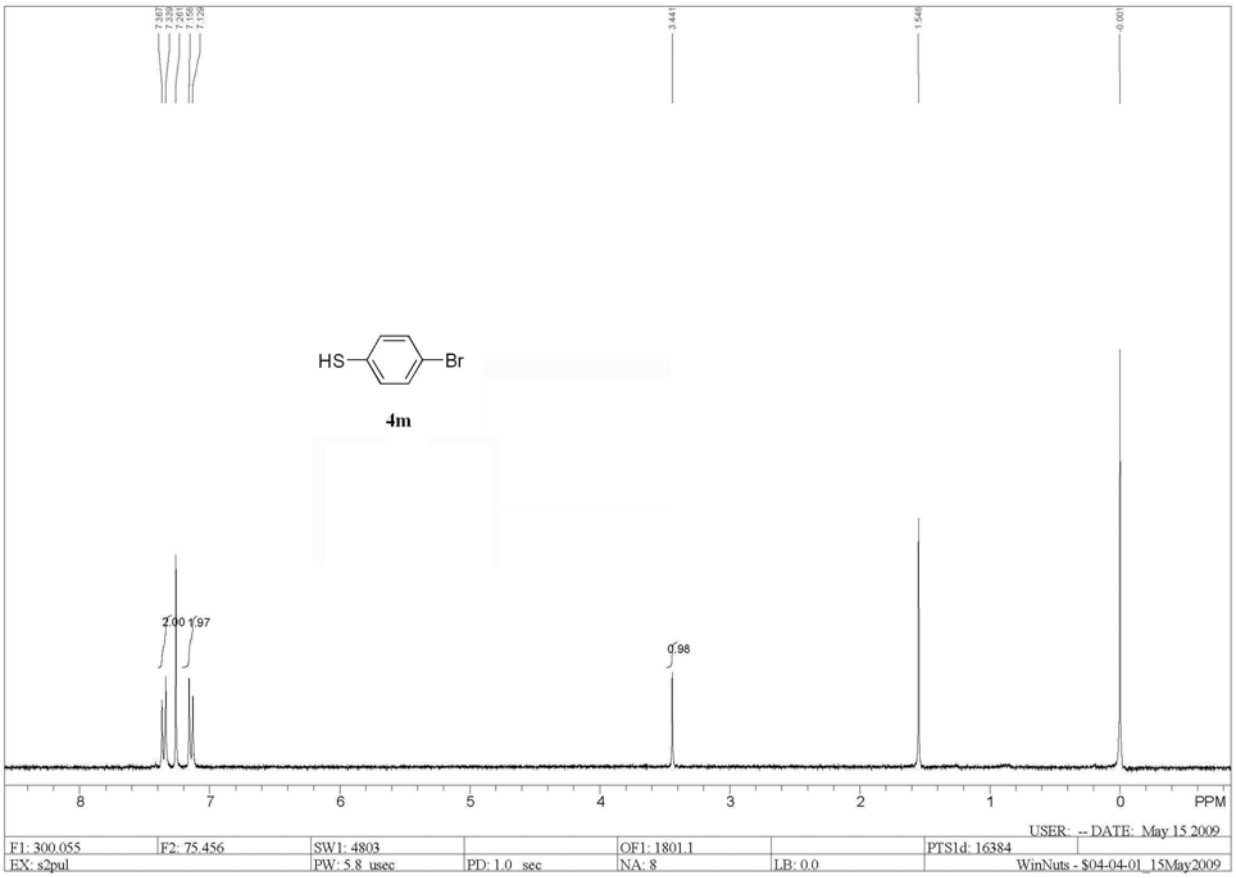

7.289
7.261
7.248
7.221
4.642
3.451
1.643
-0.000
HS
CH2OH
4k
4.45
2.00
0.92
7
6
5
4
3
2
1
0 PPM
;blank line
USER: -- DATE: Jul 15 2009
F1: 300.055
F2: 75.456
SW1: 4803
OF1: 1802.9
PTS1d: 16384
EX: s2pul
PW: 5.8 usec
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $-03-34-1_15Jul2009

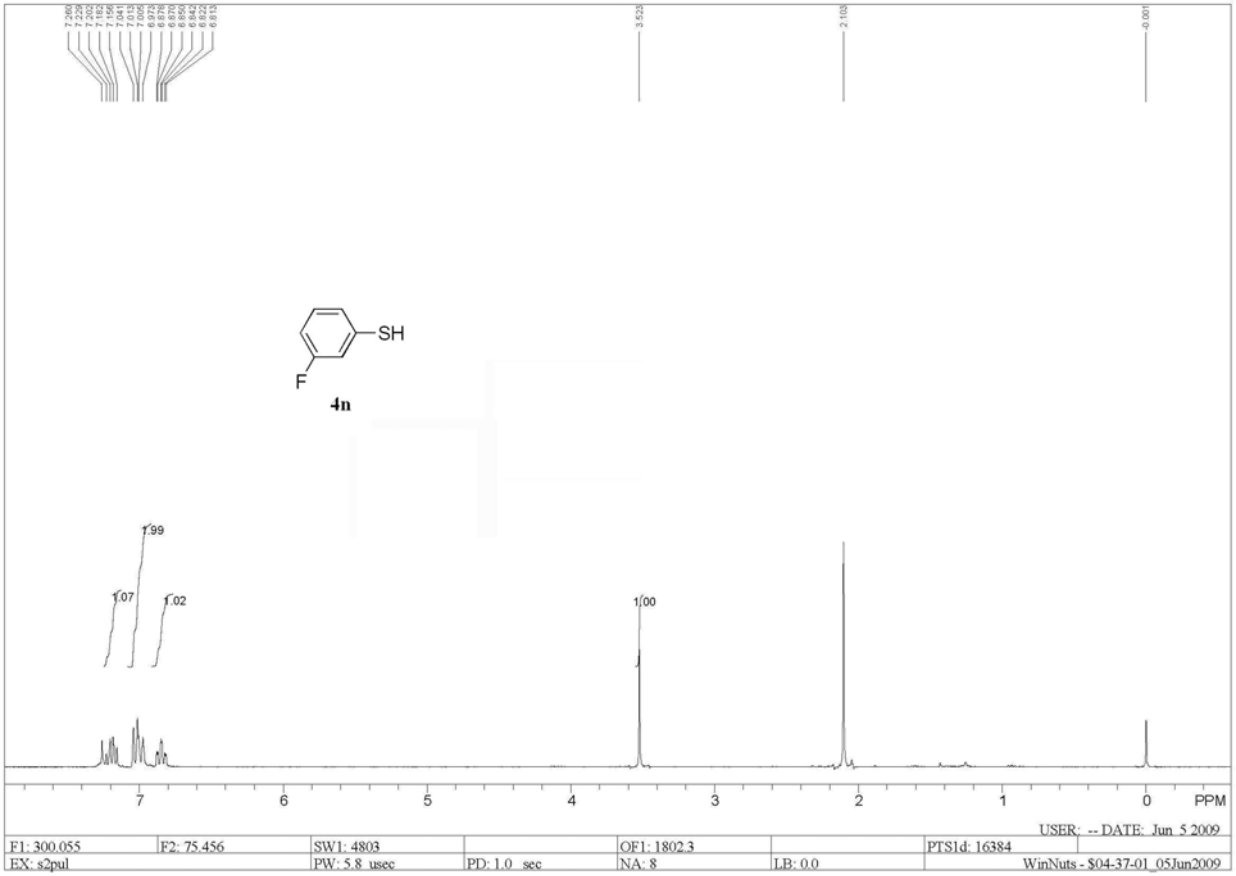

7.221
7.191
7.161
5.255
5.093
5.078
4.661
4.640
4.626
4.619
4.604
4.584
3.319
2.476
1.261
1.240
-0.024
HS
OH
Me
3.81
0.86
0.91
1.00
3.01
7
6
5
4
3
2
1
PPM
;blank line
USER: -- DATE: Jun 11 2009
F1: 300.056
F2: 75.456
SW1: 4803
OF1: 1800.3
PTS1d: 16384
EX: s2pul
PW: 5.8 usec
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $-02-97-1_11Jun2009

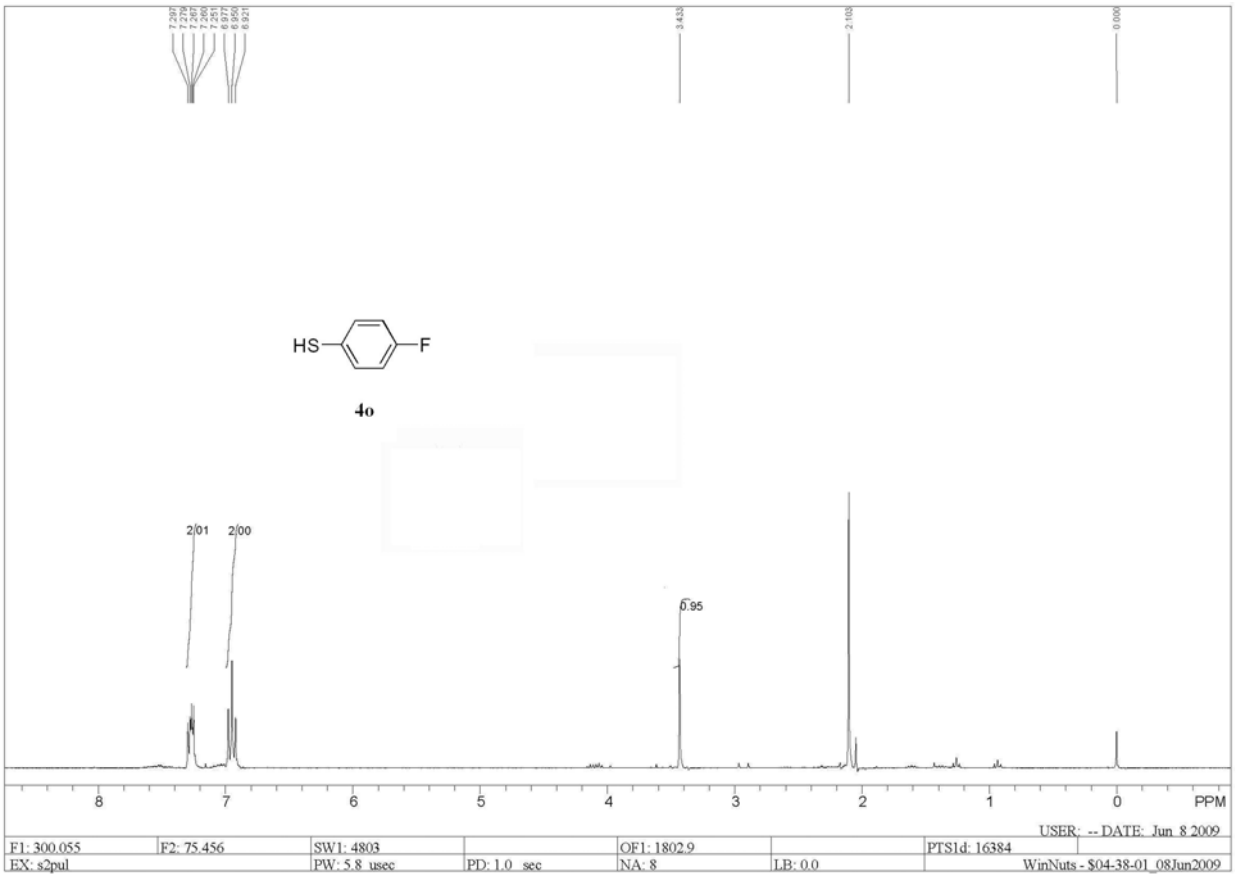
4l

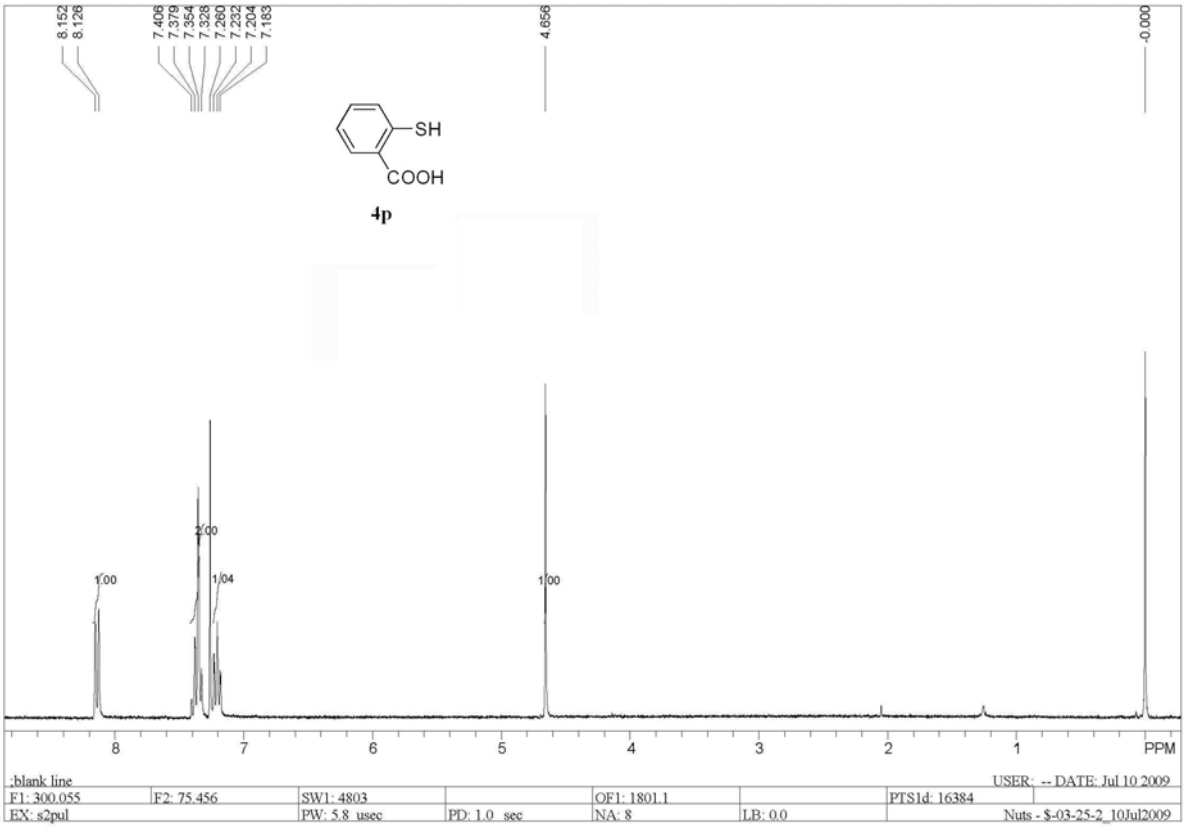

143.077
129.209
129.165
125.866
77.010
76.693
76.371
69.495
24.750
HS
OH
Me
140
120
100
80
60
40
PPM
Std carbon;blank line
USER: -- DATE: Jun 16 2009
F1: 100.494
F2: 399.618
SW1: 30488
OF1: 10011.8
PTS1d: 65536
EX: s2pul
PW: 4.5 usec
PD: 2.0 sec
NA: 176
LB: 0.0
Nuts - $c-2-97-1.fid

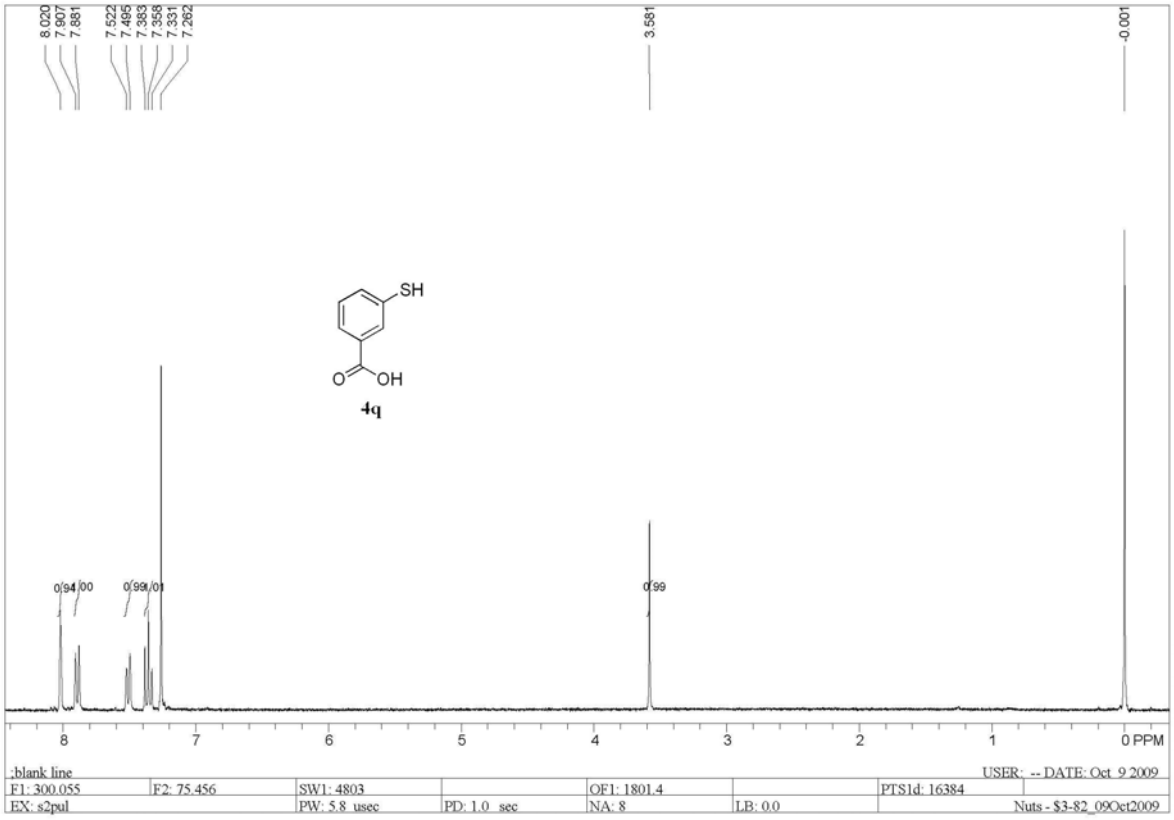
4l

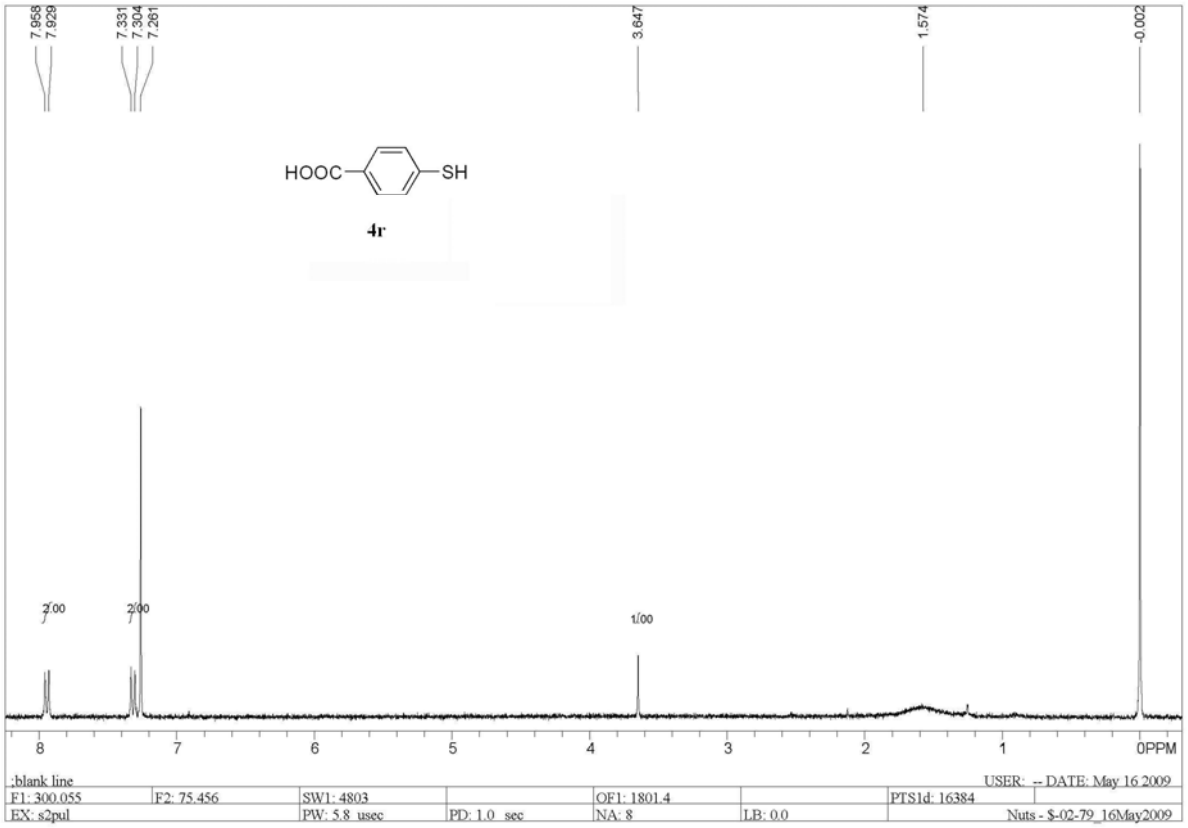

HS
Br
4m
2.00
1.97
0.98
8
7
6
5
4
3
2
1
0
PPM
USER: -- DATE: May 15 2009
F1: 300.055
F2: 75.456
SW1: 4803
OF1: 1801.1
PTS1d: 16384
EX: s2pul
PW: 5.8 usec
PD: 1.0 sec
NA: 8
LB: 0.0
WinNuts - $04-04-01_15May2009

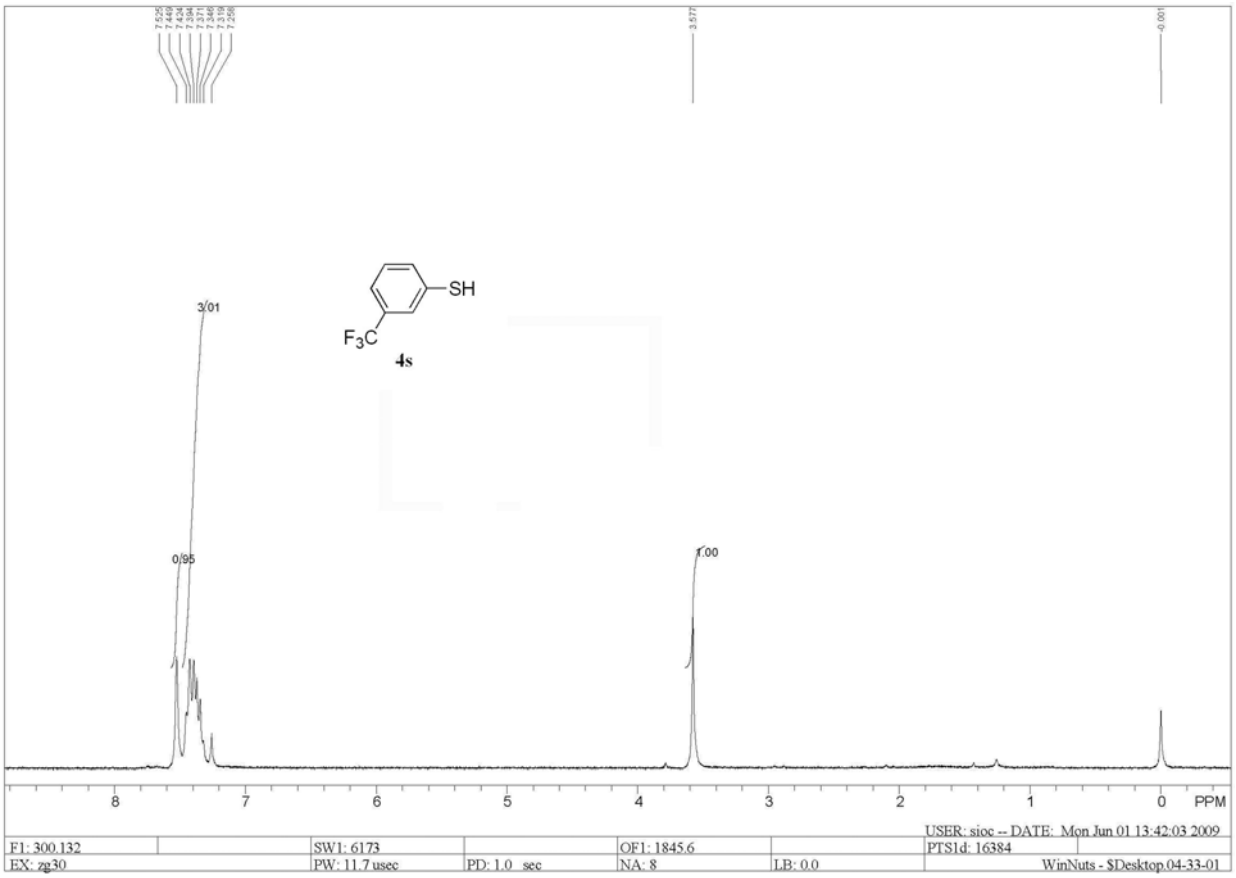

SH
F
4n
1.99
1.07
1.02
1.00
7
6
5
4
3
2
1
0
PPM
USER: -- DATE: Jun 5 2009
F1: 300.055
F2: 75.456
SW1: 4803
OF1: 1802.3
PTS1d: 16384
EX: s2pul
PW: 5.8 usec
PD: 1.0 sec
NA: 8
LB: 0.0
WinNuts - $04-37-01_05Jun2009

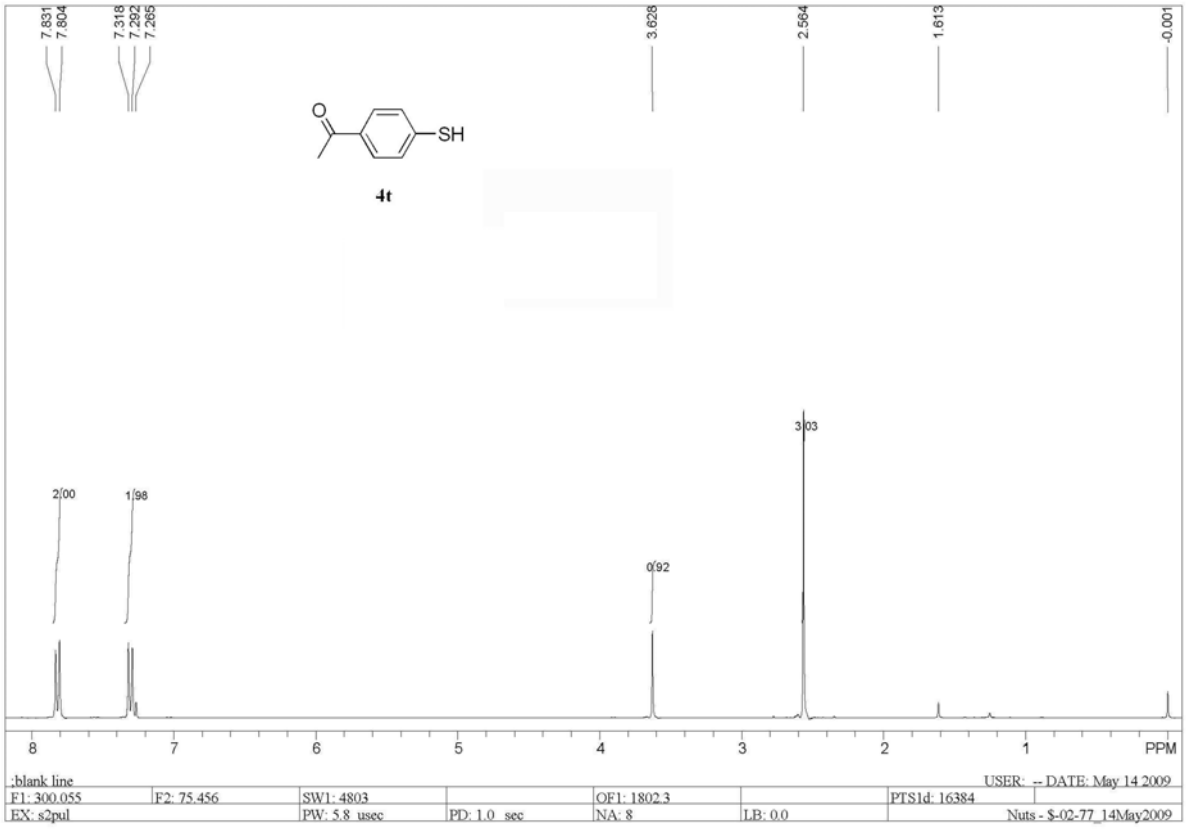

HS
F
4o
2.01
2.00
0.95
8
7
6
5
4
3
2
1
0
PPM
USER: -- DATE: Jun 8 2009
F1: 300.055
F2: 75.456
SW1: 4803
OF1: 1802.9
PTS1d: 16384
EX: s2pul
PW: 5.8 usec
PD: 1.0 sec
NA: 8
LB: 0.0
WinNuts - $04-38-01_08Jun2009

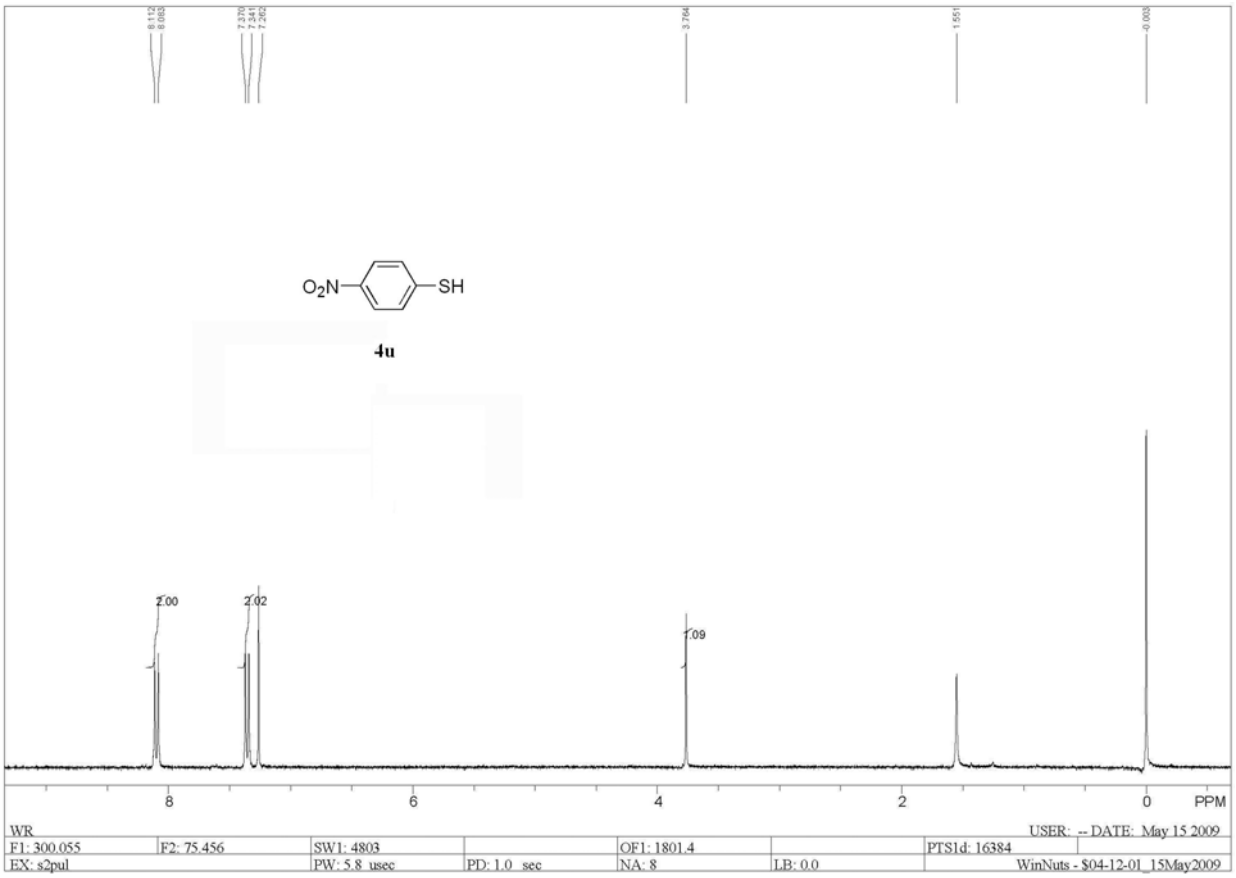

8.152
8.128
7.406
7.379
7.354
7.328
7.260
7.232
7.204
7.183
4.656
-0.000
SH
COOH
4p
2.00
1.00
1.04
1.00
8
7
6
5
4
3
2
1
PPM
;blank line
USER: -- DATE: Jul 10 2009
F1: 300.055
F2: 75.456
SW1: 4803
OF1: 1801.1
PTS1d: 16384
EX: s2pul
PW: 5.8 usec
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $-03-25-2_10Jul2009

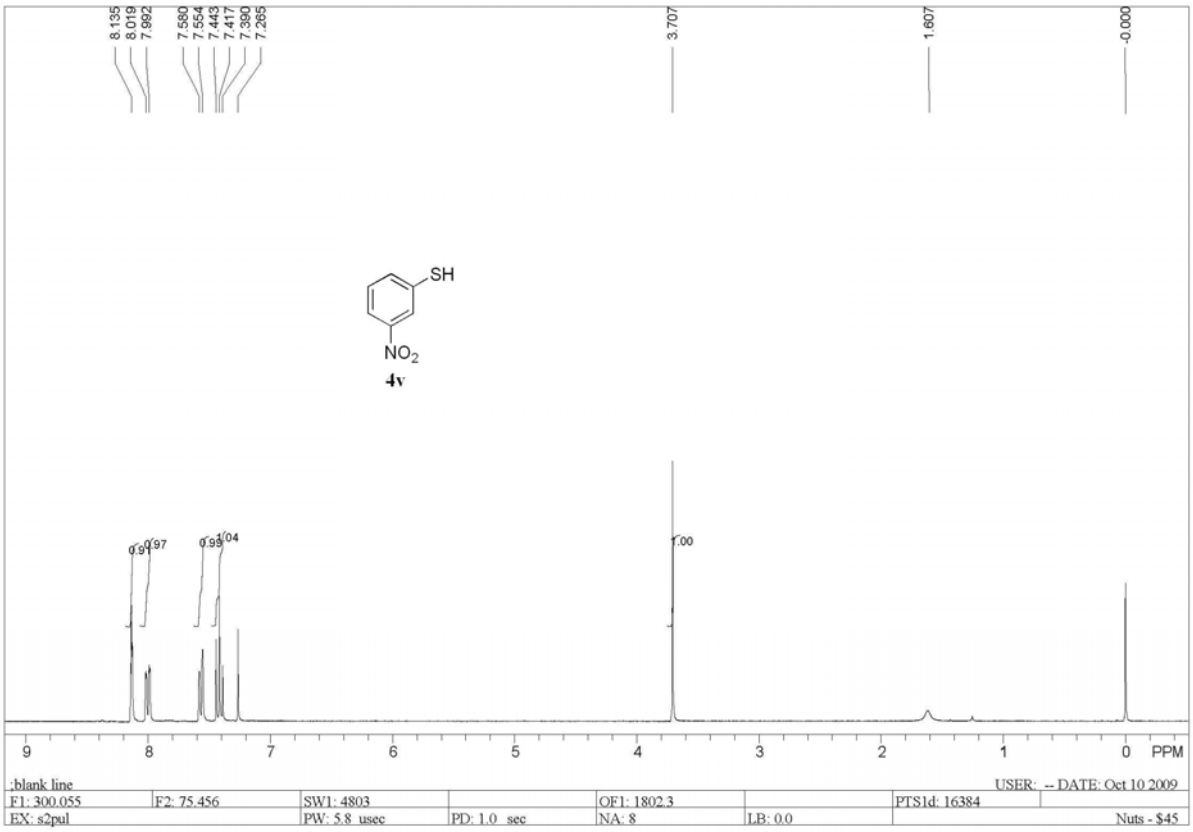

8.020
7.907
7.881
7.522
7.495
7.383
7.358
7.331
7.282
3.581
-0.001
SH
O
OH
4q
0.94
0.99
0.99
8
7
6
5
4
3
2
1
0 PPM
;blank line
USER: -- DATE: Oct 9 2009
F1: 300.055
F2: 75.456
SW1: 4803
OF1: 1801.4
PTS1d: 16384
EX: s2pul
PW: 5.8 usec
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $3-82_09Oct2009

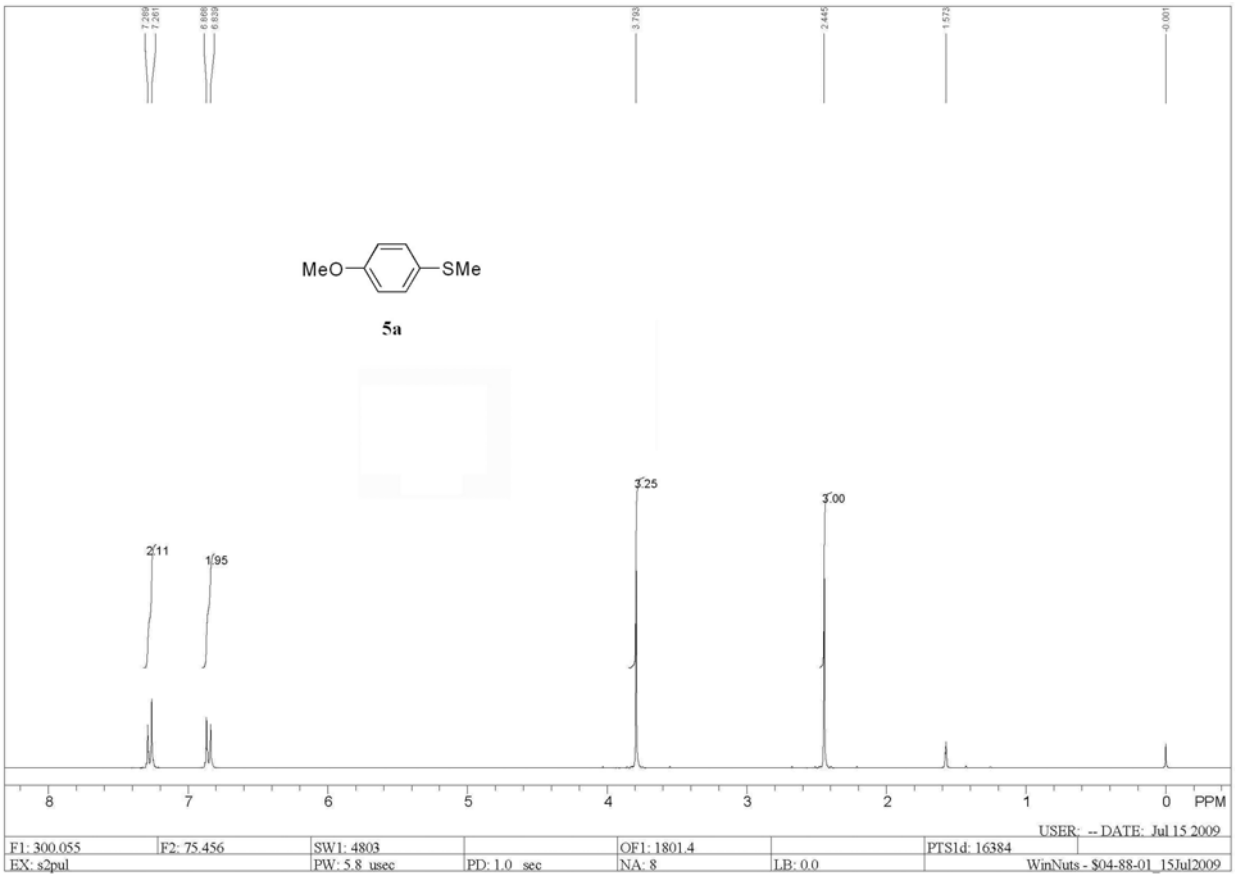

7.958
7.929
7.331
7.304
7.261
3.647
1.574
-0.002
HOOC
SH
4r
2.00
2.00
1.00
8
7
6
5
4
3
2
1
0PPM
;blank line
USER: -- DATE: May 16 2009
F1: 300.055
F2: 75.456
SW1: 4803
OF1: 1801.4
PTS1d: 16384
EX: s2pul
PW: 5.8 usec
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $-02-79_16May2009

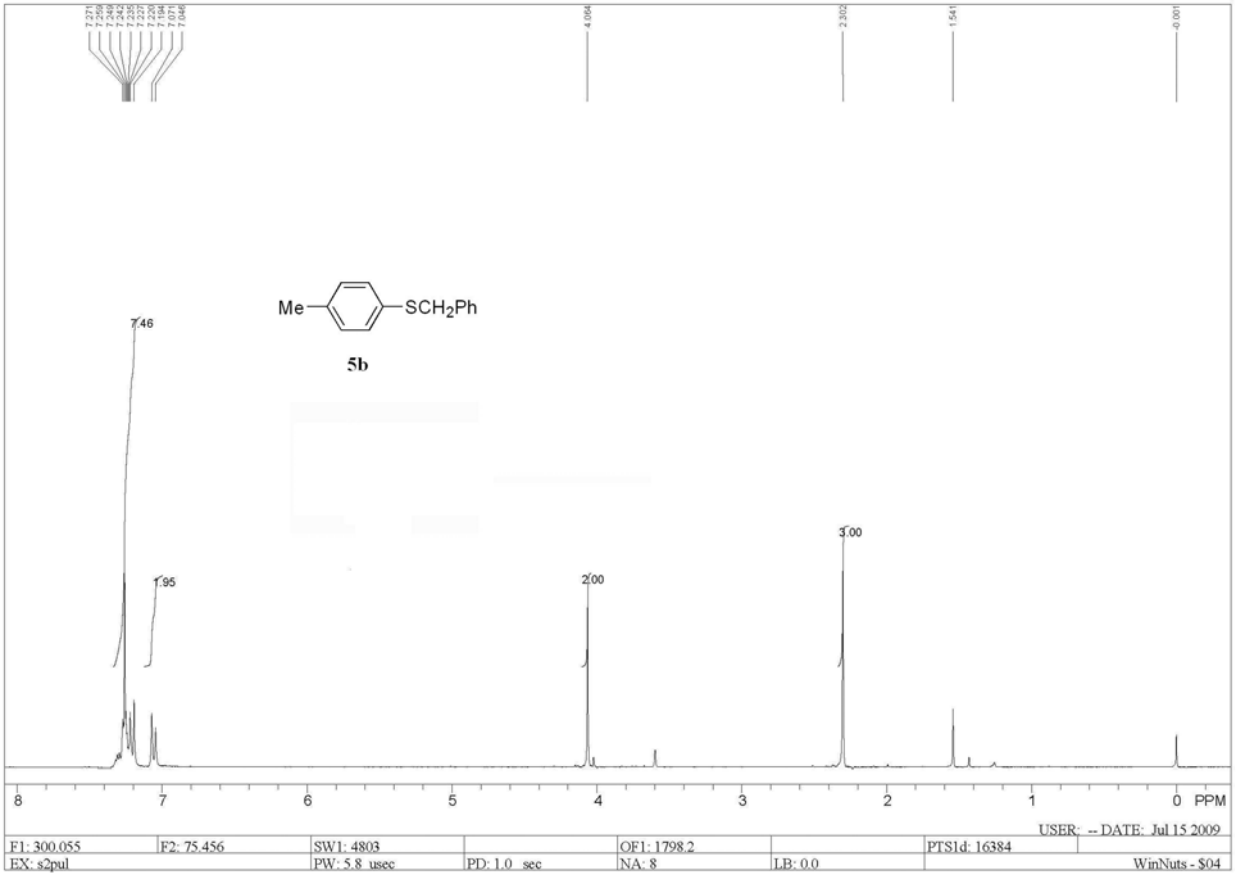

7.505
7.469
7.454
7.394
7.371
7.346
7.319
7.298
3.577
0.001
SH
F3C
4s
3.01
0.95
1.00
8
7
6
5
4
3
2
1
0
PPM
USER: sioc -- DATE: Mon Jun 01 13:42:03 2009
F1: 300.132
SW1: 6173
OF1: 1845.6
PTS1d: 16384
EX: zg30
PW: 11.7 usec
PD: 1.0 sec
NA: 8
LB: 0.0
WinNuts - $Desktop.04-33-01

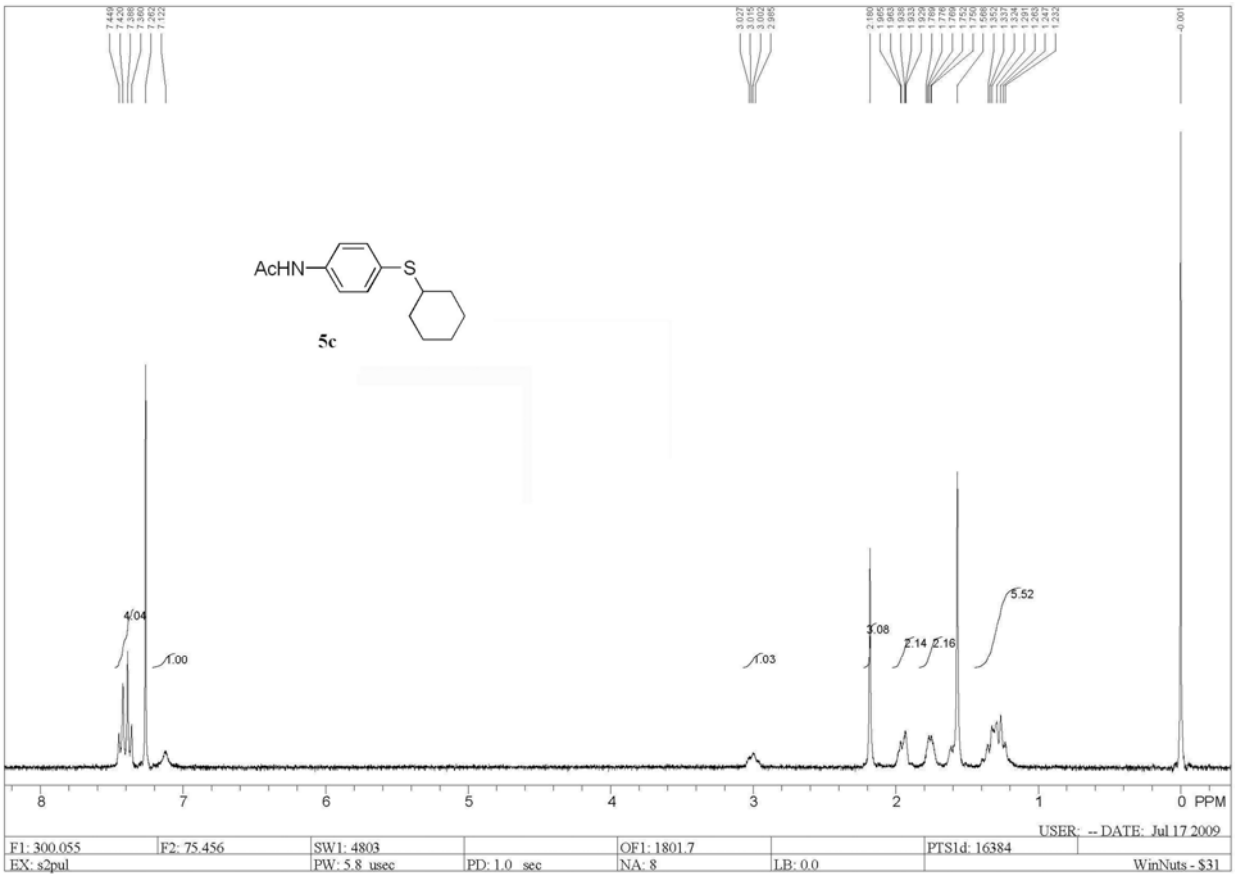

7.831
7.804
7.318
7.292
7.265
3.628
2.564
1.613
0.001
O
SH
4t
3.03
2.00
1.98
0.92
8
7
6
5
4
3
2
1
PPM
;blank line
USER: -- DATE: May 14 2009
F1: 300.055
F2: 75.456
SW1: 4803
OF1: 1802.3
PTS1d: 16384
EX: s2pul
PW: 5.8 usec
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $-02-77_14May2009

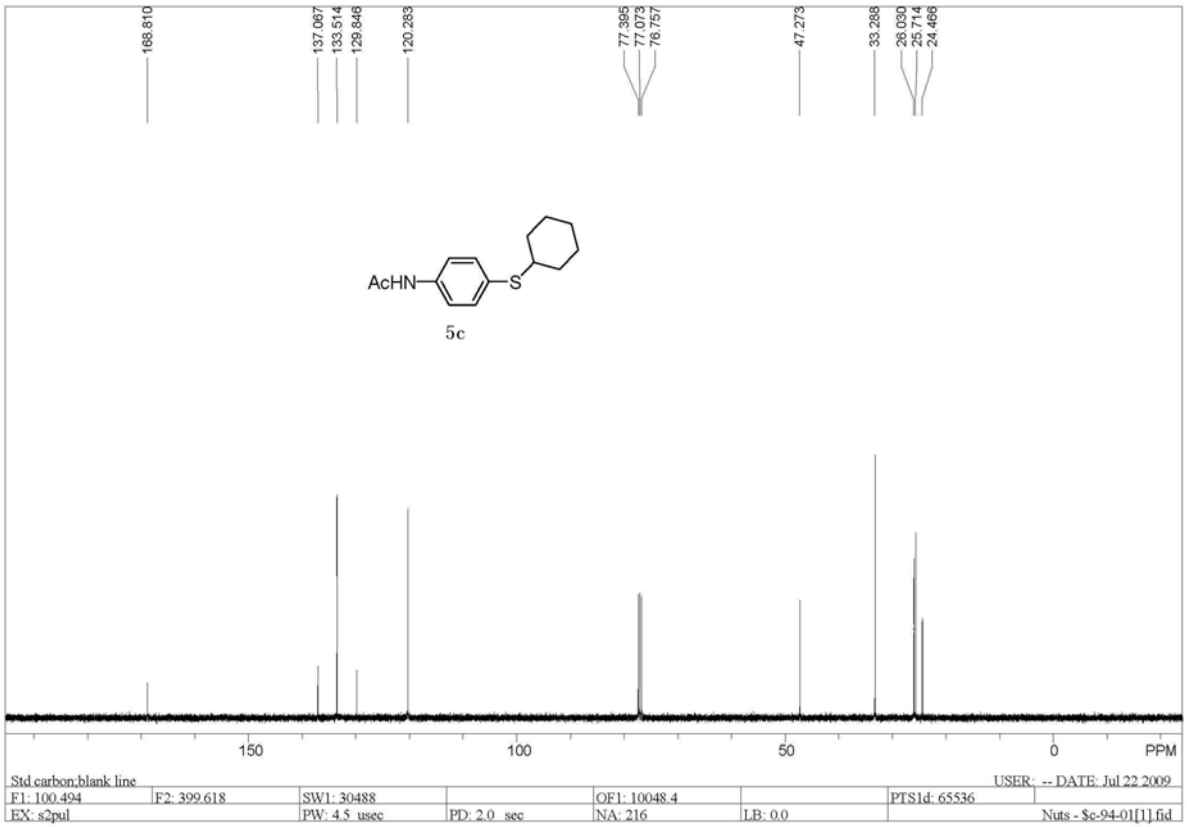

8.112
8.093
7.370
7.341
7.262
3.764
1.551
-0.000
O2N
SH
4u
2.00
2.02
1.09
8
6
4
2
0
PPM
WR
USER: -- DATE: May 15 2009
F1: 300.055
F2: 75.456
SW1: 4803
OF1: 1801.4
PTS1d: 16384
EX: s2pul
PW: 5.8 usec
PD: 1.0 sec
NA: 8
LB: 0.0
WinNuts - $04-12-01_15May2009

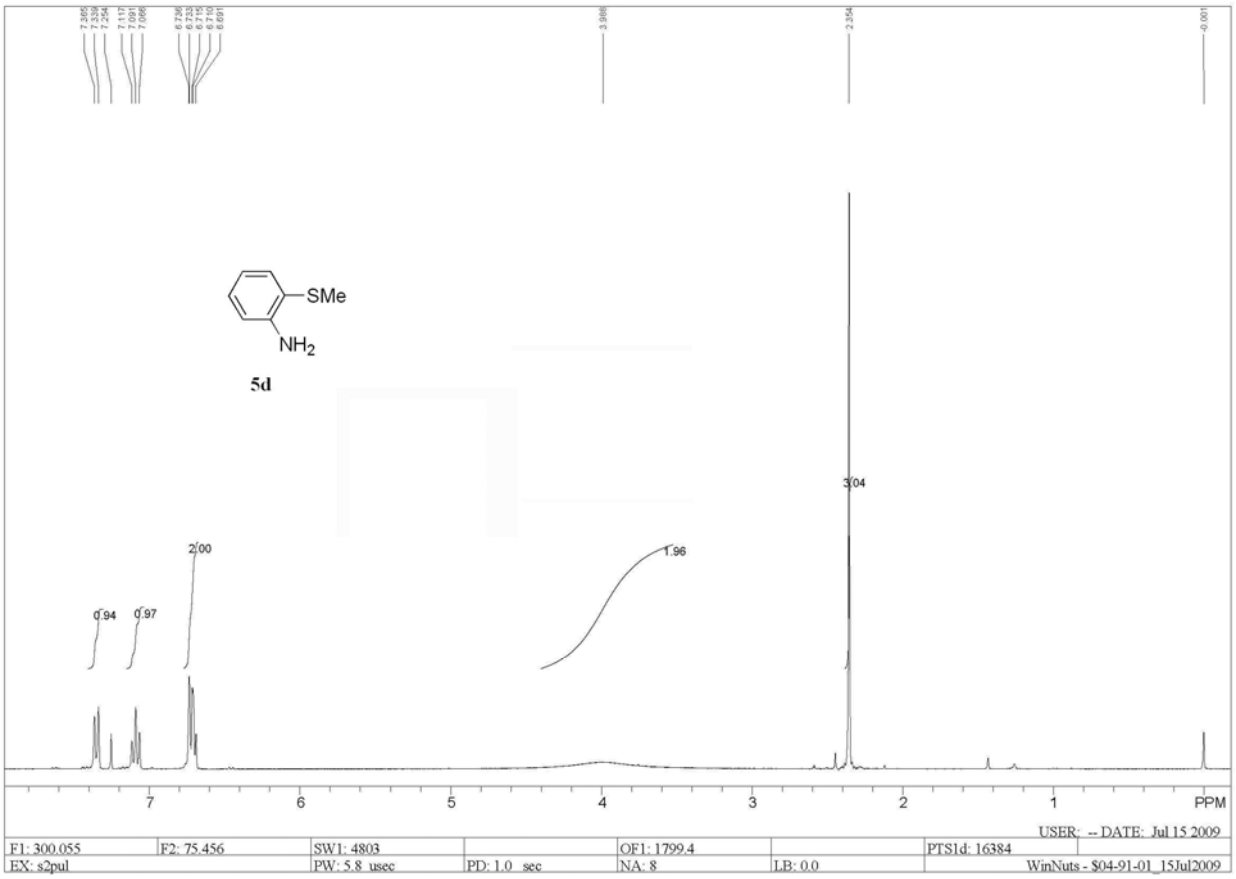

8.135
8.019
7.992
7.580
7.554
7.443
7.417
7.390
7.265
3.707
1.607
-0.000
SH
NO2
4v
0.99
0.97
0.99
1.04
1.00
9
8
7
6
5
4
3
2
1
0
PPM
;blank line
USER: -- DATE: Oct 10 2009
F1: 300.055
F2: 75.456
SW1: 4803
OF1: 1802.3
PTS1d: 16384
EX: s2pul
PW: 5.8 usec
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $45

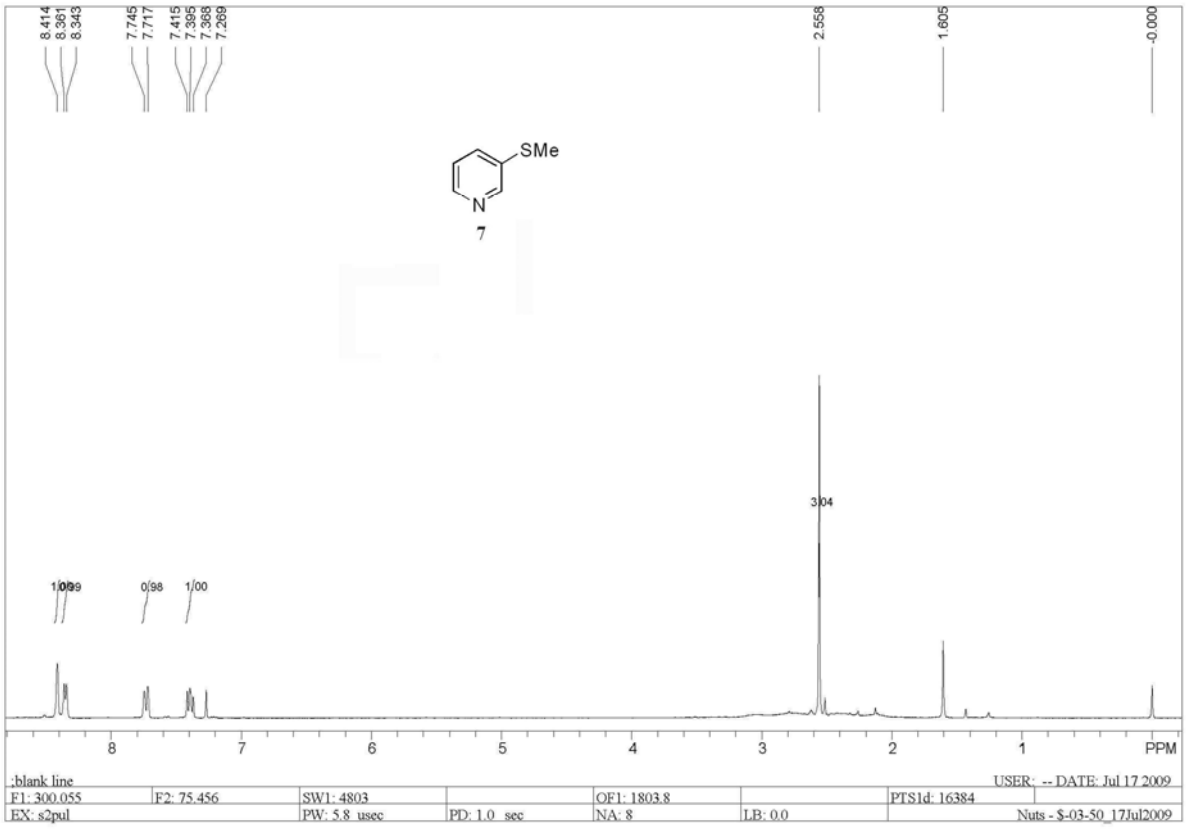

MeO
SMe
5a
3.25
3.00
2.11
1.95
8
7
6
5
4
3
2
1
0 PPM
USER: -- DATE: Jul 15 2009
F1: 300.055
F2: 75.456
SW1: 4803
OF1: 1801.4
PTS1d: 16384
EX: s2pul
PW: 5.8 usec
PD: 1.0 sec
NA: 8
LB: 0.0
WinNuts - $04-88-01_15Jul2009


Me
SCH2Ph
5b
7.46
3.00
2.00
1.95
8
7
6
5
4
3
2
1
0 PPM
USER: -- DATE: Jul 15 2009
F1: 300.055
F2: 75.456
SW1: 4803
OF1: 1798.2
PTS1d: 16384
EX: s2pul
PW: 5.8 usec
PD: 1.0 sec
NA: 8
LB: 0.0
WinNuts - $04


AcHN
S
5c
4.04
1.00
1.03
3.08
2.14
2.16
5.52
8
7
6
5
4
3
2
1
0 PPM
USER: -- DATE: Jul 17 2009
F1: 300.055
F2: 75.456
SW1: 4803
OF1: 1801.7
PTS1d: 16384
EX: s2pul
PW: 5.8 usec
PD: 1.0 sec
NA: 8
LB: 0.0
WinNuts - $31


168.810
137.067
133.514
129.846
120.283
77.395
77.073
76.757
47.273
33.288
26.030
25.714
24.466
AcHN
S
5c
150
100
50
0
PPM
Std carbon;blank line
USER: -- DATE: Jul 22 2009
F1: 100.494
F2: 399.618
SW1: 30488
OF1: 10048.4
PTS1d: 65536
EX: s2pul
PW: 4.5 usec
PD: 2.0 sec
NA: 216
LB: 0.0
Nuts - $c-94-01[1].fid


SMe
NH2
5d
3.04
2.00
1.96
0.94
0.97
PPM
USER: -- DATE: Jul 15 2009
F1: 300.055
F2: 75.456
SW1: 4803
OF1: 1799.4
PTS1d: 16384
EX: s2pul
PW: 5.8 usec
PD: 1.0 sec
NA: 8
LB: 0.0
WinNuts - $04-91-01_15Jul2009


SMe
N
7
3.04
1.00
0.98
1.00
PPM
:blank line
USER: -- DATE: Jul 17 2009
F1: 300.055
F2: 75.456
SW1: 4803
OF1: 1803.8
PTS1d: 16384
EX: s2pul
PW: 5.8 usec
PD: 1.0 sec
NA: 8
LB: 0.0
Nuts - $-03-50_17Jul2009