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Supporting Information

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Quaternary Carbon Stereogenic Centers through Copper-Catalyzed Enantioselective Allylic Substitutions with Readily Accessible Aryl- or Heteroaryllithium Reagents and Aluminum Chlorides**

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SUPPORTING INFORMATION, PART A

General. Infrared (IR) spectra were recorded on a Bruker FT-IR Alpha (ATR mode) spectrophotometer, ν_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). ^{1}H NMR spectra were recorded on a Varian Unity INOVA 400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on a Varian Unity INOVA 400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: 77.16 ppm). High-resolution mass spectrometry was performed on a Micromass LCT ESI-MS (positive mode) at the Mass Spectrometry Facility, Boston College. Enantiomer ratios were determined by GLC analysis (Alltech Associated Chiral dex GTA column (30 m x 0.25 mm) and Betadex 120 column (30 m x 0.25 mm)) and HPLC analysis (high-performance liquid chromatography) with a Shimadzu chromatograph (Chiral Technologies Chiralcel OD (4.6 x 250 mm), Chiral Technologies Chiralpak AD (4.6 x 250 mm), Chiral Technologies Chiralcel OB-H (4.6 x 250 mm), Chiral Technologies Chiralcel OJ-H (4.6 x 250 mm), Chiral Technologies Chiralcel OD-H (4.6 x 250 mm), or Chiral Technologies Chiralpak AD-H (4.6 x 250 mm)) in comparison with authentic racemic materials. Specific rotations were measured on a Rudolph Research Analytical Autopol IV Polarimeter.

Unless otherwise noted, all reactions were carried out with distilled and degassed solvents under an atmosphere of dry N_2 in oven- (135 °C) or flame-dried glassware with standard dry box or vacuum-line techniques. Pentane and dichloromethane (Fisher Scientific) were purified by passing through two alumina columns under a positive pressure of dry argon by a modified Innovative Technologies purification system. Tetrahydrofuran (Aldrich Chemical Co.) was purified by distillation from sodium benzophenone ketyl immediately prior to use unless otherwise specified. All work-up and purification procedures were carried out with reagent grade solvents (purchased from Fisher Scientific) under air. All substrates are prepared according to previously reported procedures;[1] all substrates possess *E*-olefin geometry and purities are established by ^{1}H NMR analysis (400 MHz).

■ **Reagents and Ligands:**

Ag-NHC complex 1: prepared according to a previously reported procedure.[2]

Ag-NHC complex 2a: prepared according to a previously reported procedure.[3]

Ag-NHC complex 2b: prepared according to a previously reported procedure.[4]

Ag-NHC complex 2c: prepared according to a previously reported procedure.[5]

Ag-NHC complex 3 and 4: prepared according to a previously reported procedure.[6]

9-Borabicyclo[3.3.1]nonane (0.5 M in thf): purchased from Aldrich Chemical Co. and used as received.

4-Bromoanisole: purchased from Aldrich Chemical Co. and purified by distillation over CaH_2.

3-Bromofuran: purchased from Aldrich Chemical Co. and purified by distillation over sodium.

3-Bromothiophene: purchased from Aldrich Chemical Co. and purified by distillation over CaH_2.

1-Bromo-4-(trifluoromethyl)benzene: purchased from Aldrich Chemical Co. and purified by distillation over CaH_2.

***n*-Butyllithium (15% in hexanes):** purchased from Strem Chemicals Inc. and titrated before use.

***t*-Butyllithium (16% in pentane):** purchased from Strem Chemicals Inc. and titrated before use.

Copper(II) dichloride bishydrate: purchased from Aldrich Chemical Co. and used as received.

Diethylaluminum chloride: purchased from Aldrich Chemical Co. and used as received.

Diethylphenylaluminum: prepared according to a previously reported procedure.[7]

Furan: purchased from Aldrich Chemical Co. and purified by distillation over sodium.

Hydrogen peroxide (35% wt solution in water): purchased from Aldrich Chemical Co. and used as received.

Magnesium turning: purchased from Strem Chemicals Inc. and used as received.

Methylmagnesium iodide: prepared from iodomethane and Mg turning in Et_2O.

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[1] a) C. A. Luchaco-Cullis, H. Mizutani, K. E. Murphy, A. H. Hoveyda, *Angew. Chem. Int. Ed.* **2001**, *40*, 1456–1460. b) M. A. Kacprzynski, T. L. May, S. A. Kazane, A. H. Hoveyda, *Angew. Chem. Int. Ed.* **2007**, *46*, 4554–4558. c) Y. Lee, A. H. Hoveyda, *J. Am. Chem. Soc.* **2006**, *128*, 15604□15605. d) F. Gao, K. P. McGrath, Y. Lee, A. H. Hoveyda, *J. Am. Chem. Soc.* **2010**, Submitted for publication.

[2] J. J. Van Veldhuizen, J. E. Campbell, R. E. Giudici, A. H. Hoveyda, *J. Am. Chem. Soc.* **2005**, *127*, 6877–6882.

[3] M. K. Brown, T. L. May, C. A. Baxter, A. H. Hoveyda, *Angew. Chem. Int. Ed.* **2007**, *46*, 1097–1100.

[4] Y. Lee, K. Akiyama, D. G. Gillingham, M. K. Brown, A. H. Hoveyda, *J. Am. Chem. Soc.* **2008**, *130*, 446□447.

[5] K. Akiyama, F. Gao, A. H. Hoveyda, *Angew. Chem. Int. Ed.* **2010**, 49, 419□423.

[6] K-s. Lee, A. H. Hoveyda, *J. Org. Chem.* **2009**, *74*, 4455□4462.

[7] T. L. May, M. K. Brown, A. H. Hoveyda, *Angew. Chem. Int. Ed.* **2008**, *47*, 7358□7362.

***N*-Methylpyrrole:** purchased from Aldrich Chemical Co. and purified by distillation over CaH_2.

Phenyllithium (2.0 M in Bu_2O): purchased from Acros Organics and titrated before use.

Sodium perborate tetrahydrate: purchased from Aldrich Chemical Co. and used as received.

Thiophene: purchased from Aldrich Chemical Co. and purified by distillation over CaH_2.

■ **Representative Experimental Procedure for the Preparation of Diethylarylaluminum Reagents:**[7] Under a N_2 atmosphere, 4-bromoanisole (626 µL, 5.0 mmol) and tetrahydrofuran (thf, 700 µL) are placed in a flame-dried round bottom flask equipped with a stir bar. The solution is allowed to cool to –78 °C (dry ice/acetone bath). *n*-Butyllithium (1.61 M in hexanes, 3.10 mL, 5.0 mmol) is added through a syringe dropwise over ten minutes and the resulting mixture is allowed to stir at –78 °C for 1 h. Pentane (3.0 mL), followed by diethylaluminum chloride (690 µL, 5.5 mmol) is added to the solution through syringes and the suspension of white precipitate is allowed to warm to 22 °C and stir for 12 h. After that time, the resulting mixture is allowed to stand for 30 minutes to assist with the settling of white solid (LiCl) and the colorless supernatant (diethyl(4-methoxyphenyl)aluminum, 0.616 M) is used directly without further purification.

■ **Experimental Procedure for the Preparation of Diethyl(2-furyl)aluminum Reagent:** Under a N_2 atmosphere, furan (727 µL, 10.0 mmol) and tetrahydrofuran (thf, 1.4 mL) are added to a flame-dried round bottom flask equipped with a stir bar through syringes. The solution is allowed to cool to –78 °C (dry ice/acetone bath). *n*-Butyllithium (1.61 M in hexanes, 6.21 mL, 10.0 mmol) is added through a syringe and the resulting yellow solution is allowed to stir at 0 °C for 1 h, after which time the solution is allowed to cool to –78 °C again. Pentane (5.6 mL), followed by diethylaluminum chloride (1.38 mL, 11.0 mmol) is added to the solution through syringes and the mixture is allowed to warm to 22 °C and stir for 12 h. The resulting mixture is allowed to stand for 30 minutes to assist with the settling of white solid (LiCl) and the clear yellow supernatant (diethyl(2-furyl)aluminum, 0.653 M) is used directly without further purification.

■ **Diethyl(2-thienyl)aluminum Reagent:** prepared the same way as diethyl(2-furyl)aluminum reagent and used as supernatant without further purification.

■ **Experimental Procedure for the Preparation of Diethyl(3-furyl)aluminum Reagent:** Under a N_2 atmosphere, 3-bromofuran (449 µL, 5.0 mmol) and diethyl ether (Et_2O, 3.1 mL) are added to a flame-dried round bottom flask equipped with a stir bar through syringes. The solution is allowed to cool to –78 °C (dry ice/acetone bath). *n*-Butyllithium (1.61 M in hexanes, 3.1 mL, 5.0 mmol) is added through a syringe and the resulting yellow mixture is allowed to stir at –78 °C for 1 h. Diethylaluminum chloride (690 µL, 5.5 mmol) is added to the solution through a syringe and the mixture is allowed to warm to 22 °C and stir for 12 h. The resulting mixture is allowed to stand for 30 minutes to assist with the settling of white solid (LiCl) and the clear yellow supernatant (diethyl(3-furyl)aluminum, 0.681 M) is used directly without further purification.

■ **Diethyl(3-thienyl)aluminum Reagent:** prepared the same way as diethyl(3-furyl)aluminum reagent and used as supernatant without further purification.

■ **Experimental Procedure for the Preparation of Diethyl(2-pyrryl)aluminum Reagent:** Under an N_2 atmosphere, *N*-methylpyrrole (444 µL, 5.0 mmol) and diethyl ether (Et_2O, 3.1 mL) are added to a flame-dried round bottom flask equipped with a stir bar through syringes. The solution is allowed to cool to –78 °C (dry ice/acetone bath). *t*-Butyllithium (1.62 M in pentane, 3.1 mL, 5.0 mmol) is added through a syringe and the resulting yellow solution is allowed to stir at 0 °C for 1 h. White solid is generated and the mixture is allowed to cool to –78 °C. Diethylaluminum chloride (690 µL, 5.5 mmol) is added to the solution through a syringe and the mixture is allowed to warm to 22 °C and stir for 12 h. The resulting mixture is allowed to stand for 30 minutes to assist with the settling of white solid (LiCl) and the clear orange supernatant (diethyl(2-pyrryl)aluminum, 0.682 M) is used directly without further purification.

■ **Representative Experimental Procedure for Cu-Catalyzed Enantioselective Allylic Substitution Reactions of Diethylaryl/heteroarylaluminum Reagents to Allylic Phosphates:** In an N_2 filled glove box, an oven-dried vial (8 mL, 17 x 60 mm) with a magnetic stir bar is charged with NHC-Ag(I) complex **2a** (0.9 mg, 7.5 x 10^{-4} mmol) and sealed with a septum before removal from the glove box. To the vial under an N_2 atmosphere are added tetrahydrofuran (thf, 0.5 mL) and a solution of $CuCl_2$•$2H_2O$ (0.02 M in thf, 75 µL, 1.50 x 10^{-3} mmol). The light blue solution is allowed to stir at 22 °C for 30 minutes and a solution of *(E)*-*tert*-butyl-4-(diethoxyphosphoryloxy)-2-methylbut-2-enoate (46.2 mg, 0.150 mmol) in thf (0.5 mL) is added through a syringe. After stirring for 10 minutes, the reaction mixture is allowed to cool to –78 °C (dry ice/acetone bath). A solution of diethylphenylaluminum reagent (0.622 M in pentane, 723 µL, 0.450 mmol) is added slowly through a syringe. The vial is transferred to a –30 °C cryocool. After 1 h, the reaction solution is allowed to cool to –78 °C and quenched by addition of a saturated aqueous solution of Rochelle's salt (potassium sodium tartrate, 2 mL). The aqueous layer is washed with Et_2O (3 x 1 mL) and the combined organic layers are passed through a short plug of $MgSO_4$ and silica gel. The filtrate is concentrated under reduced pressure to provide colorless oil residue, which is purified by silica gel column chromatography (30:1 pentane:Et_2O) to afford product **6** as colorless oil (34.2 mg, 0.147 mmol, 98% yield). **(*R*)-*tert*-Butyl 2-methyl-2-phenylbut-3-enoate** (**6**): The compound has been previously reported and spectra data match those previously described).[8] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33–7.22 (5H, m), 6.37 (1H, dd, *J* = 17.6, 10.8 Hz), 5.25 (1H, dd, *J* = 10.8, 1.2 Hz), 5.13 (1H, dd, *J* = 17.6, 1.2 Hz), 1.58 (3H, s), 1.41 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.0, 144.3, 141.7, 128.4, 126.7, 126.5, 114.6, 81.1, 54.4, 28.0, 23.6. Specific Rotation: $[\alpha]_D^{20}$ +3.49 (*c* 1.06, $CHCl_3$) for an enantiomerically enriched sample of 90.5:9.5 er.

Proof of Stereochemistry: Literature value ($[\alpha]_D^{20}$ –3.05 (*c* 0.747, $CHCl_3$), 94.5:5.5 er) is assigned to the (*S*) enantiomer.[8]

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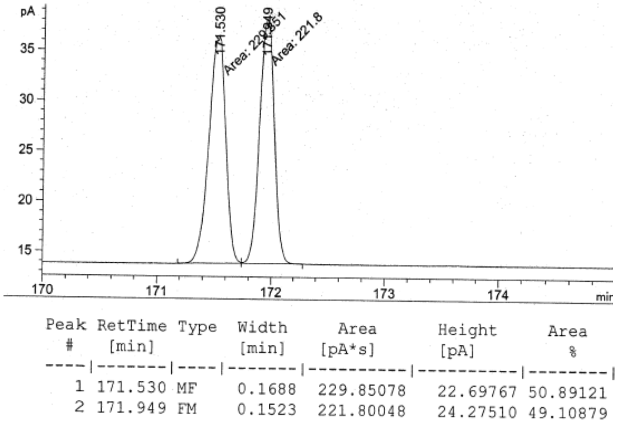
[8] K. E. Murphy, A. H. Hoveyda, *Org. Lett.* **2005**, *7*, 1255–1258.

Enantiomeric purity is determined by GLC analysis in comparison with authentic racemic material (91.1:8.9 er shown; *β*-dex column, 15 psi, 90 °C).



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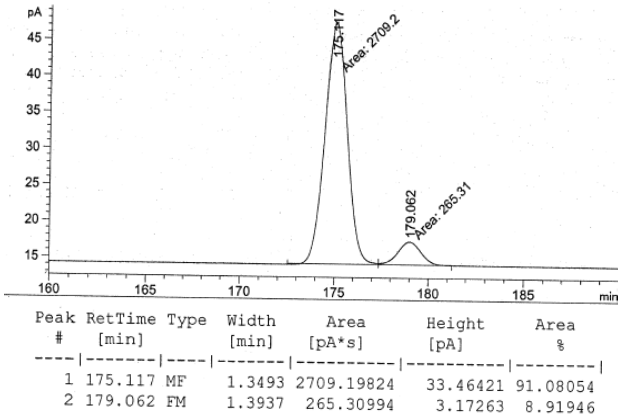

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   2 179.062 FM    1.3937  265.30994    3.17263  8.91946
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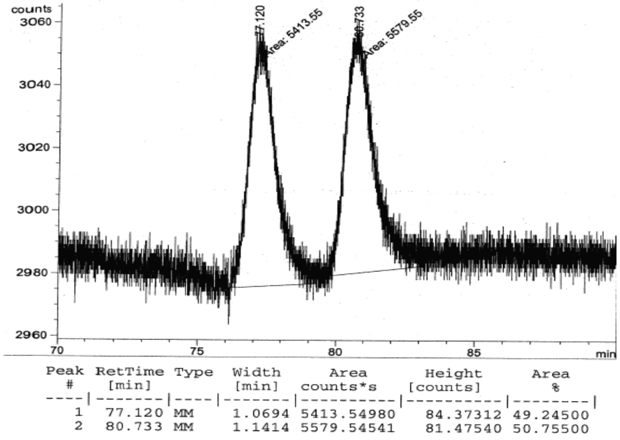
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	171.530	50.9	1	175.117	91.1
2	171.949	49.1	2	179.062	8.9

(*R*)-*tert*-Butyl 2-ethyl-2-phenylbut-3-enoate (**Entry 2, Table 2**)**:** The compound has been previously reported and spectra data match those described.[8] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31□7.18 (5H, m), 6.35 (1H, dd, *J* = 17.6, 10.8 Hz), 5.25 (1H, dd, *J* = 11.2, 1.2 Hz), 4.97 (1H, dd, *J* = 17.6, 1.2 Hz), 2.15 (1H, dq, *J* = 14.0, 7.6 Hz), 2.06 (1H, dq, *J* = 13.6, 7.2 Hz), 1.39 (9H, s), 0.84 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.6, 142.7, 140.3, 128.1, 127.4, 126.6, 115.7, 81.0, 58.5, 29.5, 28.0, 9.5. Specific Rotation: $[\alpha]_D^{20}$ □12.4 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 91:9 er.

Proof of Stereochemistry: Literature value ($[\alpha]_D^{20}$ +14.3 (*c* 0.493, $CHCl_3$), 89.5:10.5 er) is assigned to the (*S*) enantiomer.[8]

Enantiomeric purity was determined by GLC analysis in comparison with authentic racemic material obtained from the derived methyl ester derivative, which was prepared by deprotection of *tert*-butyl ester with trifluoroacetic acid in CH_2Cl_2, followed by methylation of the derived acid with MeI and K_2CO_3 in dmf (91.4:8.6 er shown; Chiral dex GTA column, 15 psi, 90 ºC).



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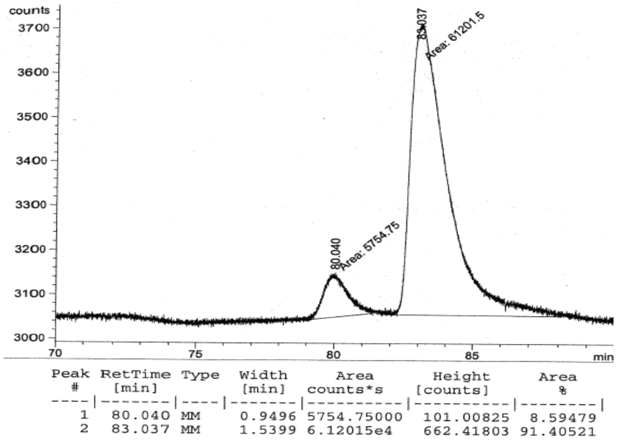

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  2  83.037 MM    1.5399 6.12015e4   662.41803 91.40521
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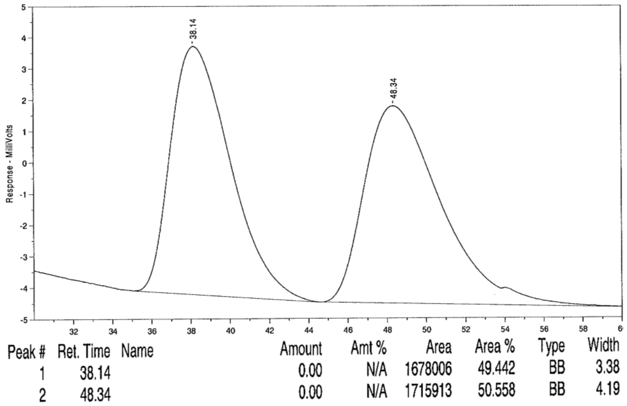
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	77.120	49.2	1	80.040	8.6
2	80.733	50.8	2	83.037	91.4

(*R*)-*tert*-Butyl 2-(4-methoxyphenyl)-2-methylbut-3-enoate (Entry 3, Table 2). IR (neat): 2979 (w), 1721 (s), 1610 (w), 1510 (s), 1367 (m), 1247 (s), 1161 (s), 1122 (s), 1034 (m), 920 (w), 831 (m) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.19 (2H, d, *J* = 8.8 Hz), 6.84 (2H, d, *J* = 9.2 Hz), 6.37 (1H, dd, *J* = 17.6, 10.4 Hz), 5.22 (1H, dd, *J* = 10.8, 1.2 Hz), 5.11 (1H, dd, *J* = 17.2, 0.8 Hz), 3.78 (3H, s), 1.54 (3H, s), 1.40 (9H, s); ^{13}C NMR (100 MHz, CDCl$_3$): δ 174.2, 158.3, 142.0, 136.3, 127.7, 114.3, 113.7, 81.0, 55.4, 53.7, 28.0, 23.6; HRMS (ESI+): Calcd for $C_{16}H_{26}N_1O_3$ $[M+NH_4]^+$: 280.1913, Found: 280.1914. Specific Rotation: $[\alpha]_D^{20}$ □4.11 (*c* 1.72, CHCl$_3$) for an enantiomerically enriched sample of 90.5:9.5 er.

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material obtained from the derived methyl ester derivative, which was prepared by deprotection of *tert*-butyl ester with trifluoroacetic acid in CH_2Cl_2, followed by methylation of the derived acid with MeI and K_2CO_3 in dmf (90.7:9.3 er shown; Chiralcel OB-H column, 99.8/0.2 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



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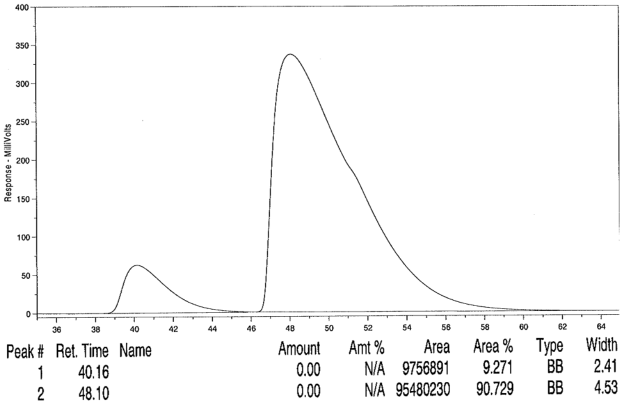

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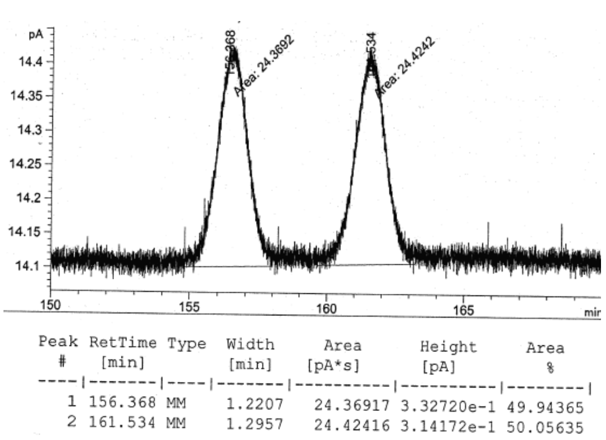
1	40.16		0.00	N/A	9756891	9.271	BB	2.41
2	48.10		0.00	N/A	95480230	90.729	BB	4.53

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	38.14	49.4	1	40.16	9.3
2	48.34	50.6	2	48.10	90.7

(*R*)-*tert*-Butyl 2-methyl-2-(4-(trifluoromethyl)phenyl)but-3-enoate (Entry 4, Table 2). IR (neat): 1725 (m), 1369 (m), 1324 (s), 1253 (m), 1161 (s), 1121 (s), 1078 (s), 1016 (s), 924 (m), 842 (m) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.56 (2H, d, *J* = 8.8 Hz), 7.38 (2H, d, *J* = 8.4 Hz), 6.33 (1H, dd, *J* = 17.6, 17.2 Hz), 5.30 (1H, d, *J* = 11.6 Hz), 5.15 (1H, d, *J* = 17.6 Hz), 1.58 (3H, s), 1.41 (9H, s); ^{13}C NMR (100 MHz, CDCl$_3$): δ 173.0, 148.0, 140.6, 128.8 (q, *J* = 32.0 Hz), 126.8, 126.1 (q, *J* = 270.9 Hz), 125.1 (q, *J* = 4.4 Hz), 115.2, 81.4, 54.3, 27.7, 23.3; HRMS (ESI+): Calcd for $C_{16}H_{23}F_3N_1O_2$ [M+NH$_4$]$^+$: 318.1681, Found: 318.1693. Specific Rotation: $[\alpha]_D^{20}$ +2.30 (*c* 1.57, CHCl$_3$) for an enantiomerically enriched sample of 83:17 er.

Enantiomeric purity was determined by GLC analysis in comparison with authentic racemic material (82.9:17.1 er shown; *β*-dex column, 15 psi, 90 °C).



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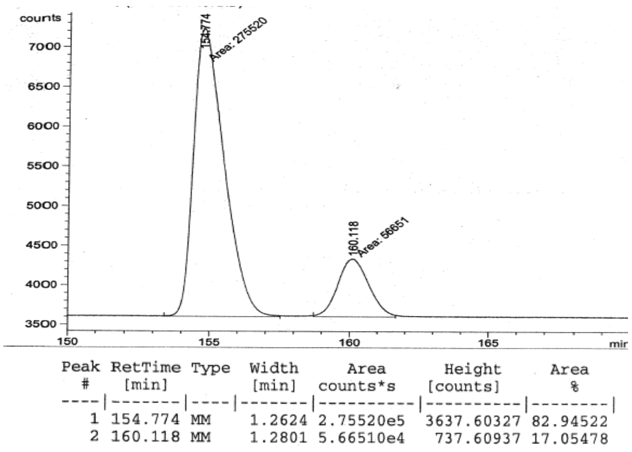

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   1 154.774 MM    1.2624 2.75520e5  3637.60327 82.94522
   2 160.118 MM    1.2801 5.66510e4   737.60937 17.05478
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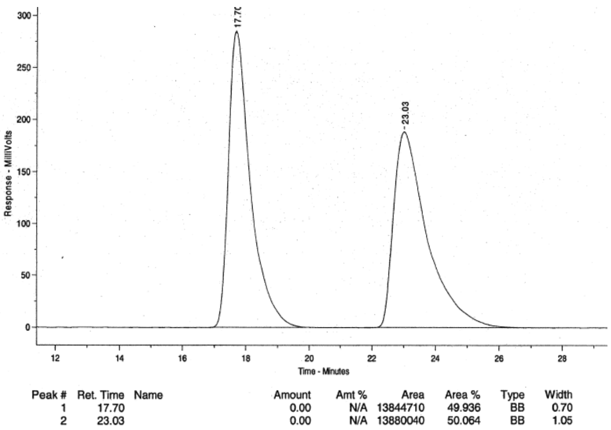
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	156.368	49.9	1	154.774	82.9
2	161.534	50.1	2	160.118	17.1

(*R*)-Dimethyl(phenyl)(2-phenylbut-3-en-2-yl)silane (Entry 5, Table 2): The compound has been previously reported and spectra data match those described.[1b] ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.37–7.06 (10H, m), 6.47 (1H, dd, *J* = 17.2, 10.8 Hz), 5.09 (1H, dd, *J* = 10.8, 1.6 Hz), 4.94 (1H, dd, *J* = 17.2, 1.2 Hz), 1.46 (3H, s), 0.24 (3H, s), 0.23 (3H, s); ^{13}C NMR (100 MHz, CDCl$_3$): δ 145.5, 143.1, 136.6, 135.0, 129.2, 127.9, 127.4, 126.6, 124.7, 111.4, 37.6, 19.0, −5.1, −5.2. Specific Rotation: $[\alpha]_D^{20}$ −15.7 (*c* 1.00, CHCl$_3$) for an enantiomerically enriched sample of 96:4 er.

Proof of Stereochemistry: Literature value ($[\alpha]_D^{20}$ □17.1 (*c* 0.513, $CHCl_3$), 92.5:7.5 er) is assigned to the (*R*) enantiomer.[1b]

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with H_2O_2) in comparison with authentic racemic material (95.8:4.2 er shown; Chiralcel OD column, 98/2 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



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Peak #  Ret. Time  Name                Amount   Amt %      Area   Area %   Type   Width
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     2      23.03                        0.00     N/A  13880040   50.064     BB    1.05
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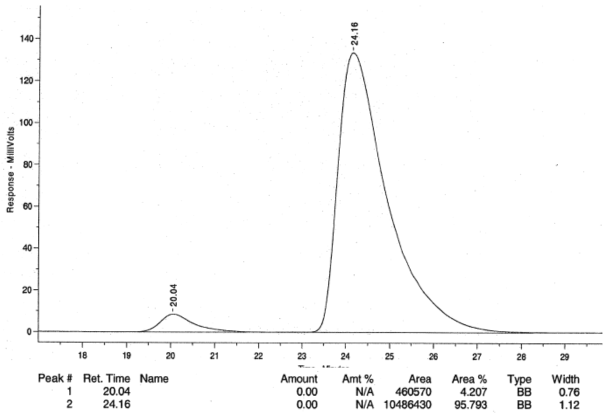

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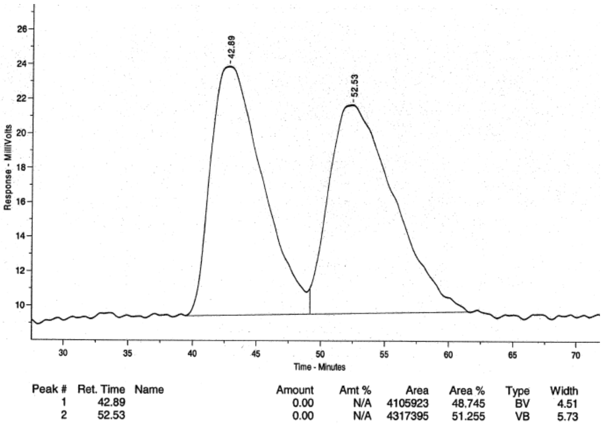
     1      20.04                        0.00     N/A    460570    4.207     BB    0.76
     2      24.16                        0.00     N/A  10486430   95.793     BB    1.12
```

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	17.70	49.9	1	20.04	4.2
2	23.03	50.1	2	24.16	95.8

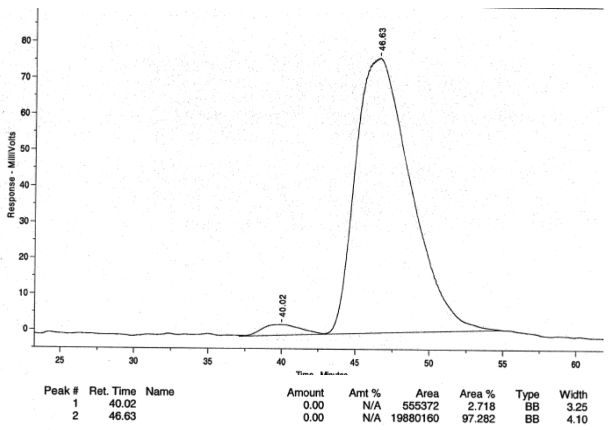
(*R*)-(2-(4-Methoxyphenyl)but-3-en-2-yl)dimethyl(phenyl)silane (**Entry 6, Table 2):** The compound has been previously reported and spectra data match those described.[1b] ^1H NMR (400 MHz, $CDCl_3$): δ 7.38□7.26 (5H, m), 6.99 (2H, d, *J* = 8.8 Hz), 6.76 (2H, d, *J* = 8.8 Hz), 6.41 (1H, dd, *J* = 17.2, 10.8 Hz), 5.07 (1H, dd, *J* = 10.8, 1.6 Hz), 4.98 (1H, dd, *J* = 17.2, 1.2 Hz), 3.78 (3H, s), 1.43 (3H, s), 0.24 (3H, s), 0.23 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.0, 143.4, 137.7, 136.9, 135.1, 129.3, 127.7, 127.5, 113.4, 111.3, 55.4, 36.8, 19.4, □5.0, □5.0. Specific Rotation: $[\alpha]_D^{20}$ –22.9 (*c* 2.22, $CHCl_3$) for an enantiomerically enriched sample of 97:3 er sample.

Proof of Stereochemistry: Literature value ($[\alpha]_D^{20}$ □4.38 (*c* 0.213, $CHCl_3$), 95:5 er) is assigned to the (*R*) enantiomer.[1b]

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with H_2O_2) in comparison with authentic racemic material (95.8:4.2 er shown; Chiralcel AD column, 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	42.89		0.00	N/A	4105923	48.745	BV	4.51
2	52.53		0.00	N/A	4317395	51.255	VB	5.73

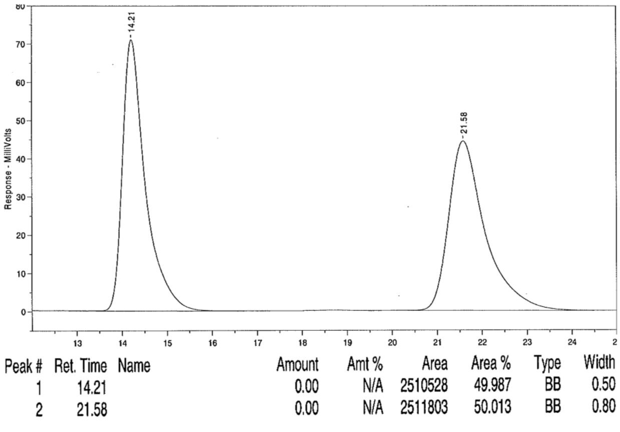


Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	40.02		0.00	N/A	555372	2.718	BB	3.25
2	46.63		0.00	N/A	19880160	97.282	BB	4.10

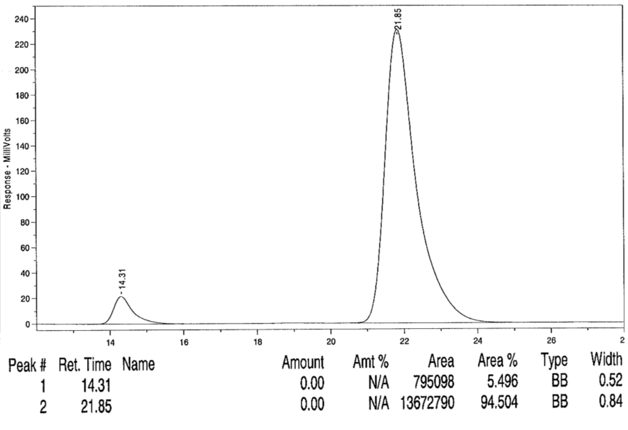
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	42.89	48.7	1	40.02	2.7
2	52.53	51.3	2	46.63	97.3

(*R*)-1-Bromo-2-(2-phenylbut-3-en-2-yl)benzene (8, Eq 1): IR (neat): 3084 (w), 3057 (w), 2977 (w), 1492 (w), 1467 (m), 1446 (m), 1425 (w), 1020 (m), 918 (m), 753 (s), 698 (s), 601 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (1H, dd, *J* = 8.0, 1.6 Hz), 7.53 (1H, dd, *J* = 8.0, 1.6 Hz), 7.33 (1H, ddd, *J* = 7.2, 7.2, 1.6 Hz), 7.29□7.23 (2H, m), 7.20□7.16 (1H, m), 7.13□7.08 (3H, m), 6.66 (1H, dd, *J* = 17.6, 10.8 Hz), 5.19 (1H, ddd, *J* = 10.8, 0.8, 0.4 Hz), 4.99 (1H, dd, *J* = 17.2, 0.8 Hz), 1.87 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 146.1, 145.1, 141.7, 135.7, 129.8, 128.6, 128.3, 128.2, 127.3, 127.0, 125.8, 124.3, 113.4, 51.5, 26.6; HRMS (ESI+): Calcd for $C_{16}H_{16}Br_1$ $[M+H]^+$: 287.0435, Found: 287.0439. Specific Rotation: $[\alpha]_D^{20}$ □17.3 (*c* 0.57, $CHCl_3$) for an enantiomerically enriched sample of 94.5:5.5 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with H_2O_2) in comparison with authentic racemic material (94.5:5.5 er shown; Chiralcel OD column, 95/5 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	14.21		0.00	N/A	2510528	49.987	BB	0.50
2	21.58		0.00	N/A	2511803	50.013	BB	0.80

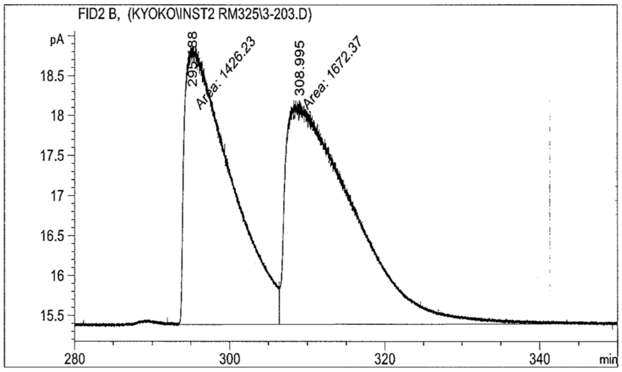


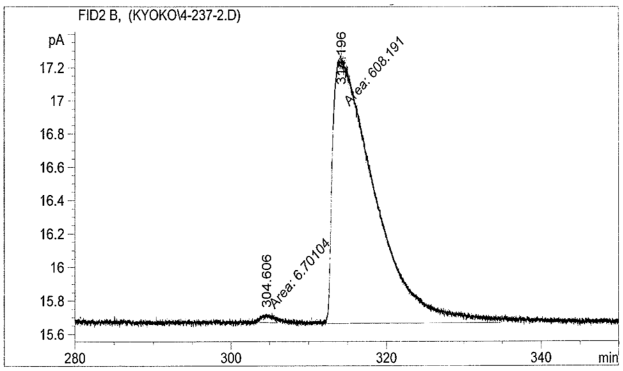
Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	14.31		0.00	N/A	795098	5.496	BB	0.52
2	21.85		0.00	N/A	13672790	94.504	BB	0.84

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	14.21	50.0	1	14.31	5.5
2	21.58	50.0	2	21.85	94.5

(*R*)-*tert*-Butyl 2-(furan-2-yl)-2-methylbut-3-enoate (9, Scheme 2). IR (neat): 2980 (w), 1729 (s), 1368 (m), 1253 (m), 1155 (s), 1116 (m), 1012 (w), 929 (w), 801 (w), 733 (m) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.35□7.33 (1H, m), 6.29 (1H, dd, *J* = 3.2, 1.6 Hz), 6.27 (1H, dd, *J* = 17.6, 10.8 Hz), 6.13 (1H, dd, *J* = 3.2, 0.8 Hz), 5.20 (1H, dd, *J* = 10.4, 0.8 Hz), 5.09 (1H, dd, *J* = 17.2, 0.8 Hz), 1.59 (3H, s), 1.40 (9H, s); ^{13}C NMR (100 MHz, CDCl$_3$): δ 172.1, 156.2, 141.8, 139.3, 114.9, 110.2, 106.0, 81.5, 51.2, 28.0, 21.6; HRMS (ESI+): Calcd for $C_{13}H_{19}O_3$ [M+H]$^+$: 223.1334, Found: 223.1329. Specific Rotation: $[\alpha]_D^{20}$ □2.38 (*c* 1.00, CHCl$_3$) for an enantiomerically enriched sample of 99:1 er.

Enantiomeric purity was determined by GLC analysis in comparison with authentic racemic material (98.9:1.1 er shown; Chiral dex GTA column, 10 psi, 50 °C).





```
Peak RetTime Type  Width     Area      Height     Area
 #   [min]         [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
  1 295.188 MF    6.7887 1426.23059    3.50149 46.02822
  2 308.995 FM    9.9466 1672.36975    2.80224 53.97178
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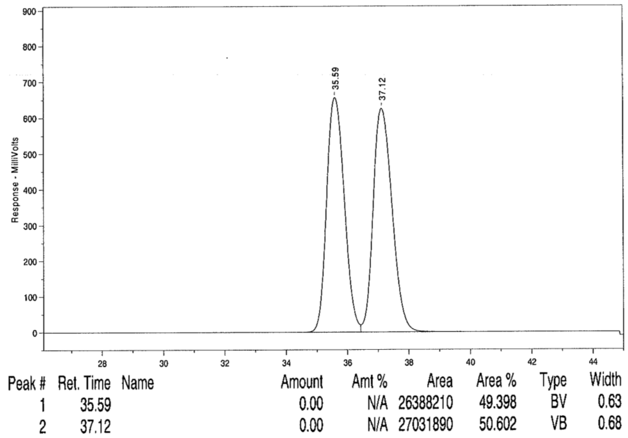
Peak RetTime Type  Width     Area      Height     Area
 #   [min]         [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
  1 304.606 MM    1.6802    6.70104 6.64691e-2  1.08979
  2 314.196 MM    6.0701  608.19061    1.66992 98.91021
```

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	295.188	46.0	1	304.606	1.1
2	308.995	54.0	2	314.196	98.9

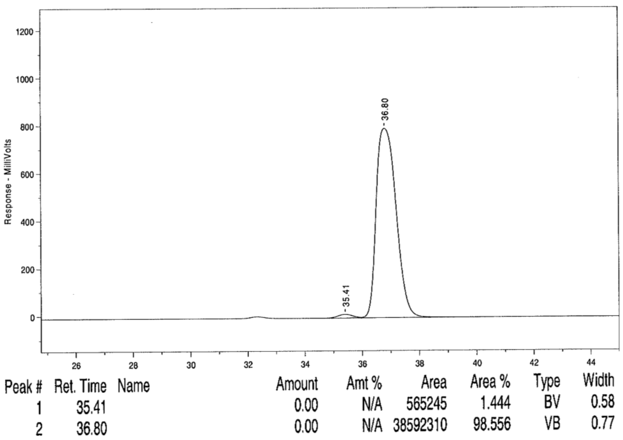
(*S*)-2-(2-Phenylbut-3-en-2-yl)furan (Entry 1, Table 3). IR (neat): 3085 (w), 3058 (w), 2979 (w), 2936 (w), 1491 (w), 1445 (w), 1409 (w), 1155 (w), 1009 (m), 922 (m), 759 (m), 730 (s), 697 (s) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.38□7.37 (1H, m), 7.33□7.28 (2H, m), 7.25□7.18 (3H, m), 6.38 (1H, dd, *J* = 17.2, 10.4 Hz), 6.35□6.34 (1H, m), 6.13 (1H, dd, *J* = 3.2, 0.8 Hz), 5.23 (1H, dd, *J* = 10.8, 1.2 Hz), 5.01 (1H, dd, *J* = 17.6, 1.2 Hz), 1.77 (3H, s); ^{13}C NMR (100 MHz, CDCl$_3$): δ 159.6, 145.8, 143.5, 141.7, 128.2, 127.1, 126.5, 113.7, 109.9, 106.3, 47.4, 25.2; HRMS (ESI+):

Calcd for $C_{14}H_{15}O_1$ $[M+H]^+$: 199.1123, Found: 199.1122. Specific Rotation: $[\alpha]_D^{20}$ □26.8 (*c* 1.19, $CHCl_3$) for an enantiomerically enriched sample of 99:1 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with $NaBO_3$•$4H_2O$) in comparison with authentic racemic material (98.6:1.4 er shown; Chiralcel AD-H column, 97/3 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	35.59		0.00	N/A	26388210	49.398	BV	0.63
2	37.12		0.00	N/A	27031890	50.602	VB	0.68

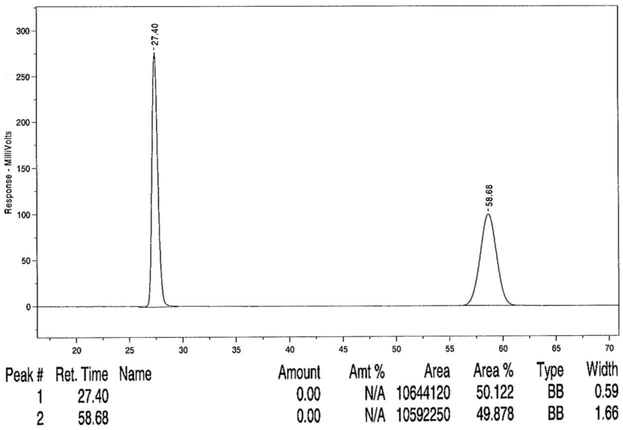


Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	35.41		0.00	N/A	565245	1.444	BV	0.58
2	36.80		0.00	N/A	38592310	98.556	VB	0.77

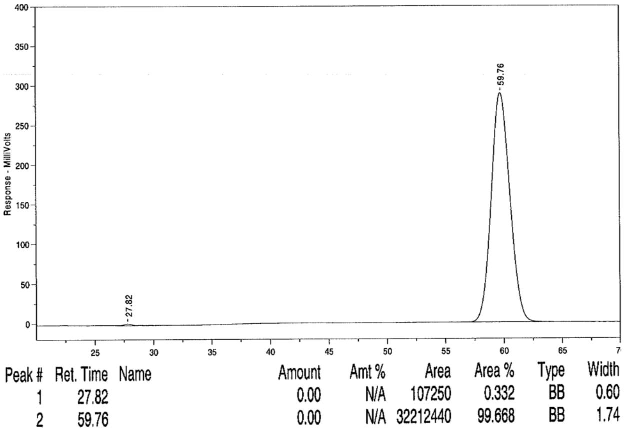
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	35.59	49.4	1	35.41	1.4
2	37.12	50.6	2	36.80	98.6

(*S*)-2-(2-(2-Bromophenyl)but-3-en-2-yl)furan (Entry 2, Table 3). IR (neat): 3059 (w), 2979 (w), 2939 (w), 1465 (w), 1427 (w), 1408 (w), 1368 (w), 1017 (m), 1009 (m), 922 (m), 799 (w), 751 (s), 723 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.55 (1H, dd, *J* = 7.6, 0.8 Hz), 7.34□7.24 (3H, m), 7.09 (1H, td, *J* = 7.6, 1.6 Hz), 6.45 (1H, dd, *J* = 17.2, 10.4 Hz), 6.33 (1H, dd, *J* = 3.2, 2.0 Hz), 6.05 (1H, d, *J* = 3.2 Hz), 5.20 (1H, d, *J* = 10.4 Hz), 4.97 (1H, d, *J* = 17.2 Hz), 1.88 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9, 144.0, 142.9, 141.0, 135.4, 129.8, 128.4, 127.2, 123.7, 113.7, 110.5, 106.3, 48.6, 24.3; HRMS (ESI+): Calcd for $C_{14}H_{14}Br_1O_1$ $[M+H]^+$: 277.0228, Found: 277.0217. Specific Rotation: $[\alpha]_D^{20}$ □39.8 (*c* 1.73, $CHCl_3$) for an enantiomerically enriched sample of 99.5:0.5 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with $NaBO_3$•$4H_2O$) in comparison with authentic racemic material (99.7:0.3 er shown; Chiralcel OJ-H column, 95/5 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	27.40		0.00	N/A	10644120	50.122	BB	0.59
2	58.68		0.00	N/A	10592250	49.878	BB	1.66

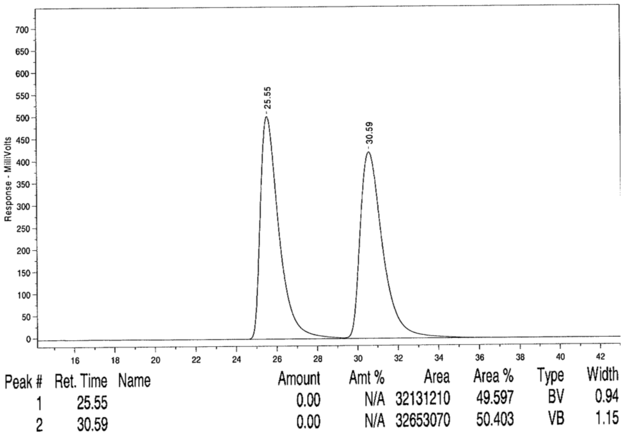


Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	27.82		0.00	N/A	107250	0.332	BB	0.60
2	59.76		0.00	N/A	32212440	99.668	BB	1.74

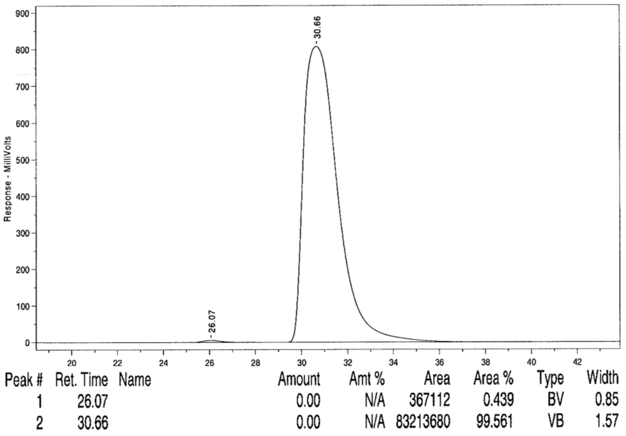
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	27.40	50.1	1	27.82	0.3
2	58.68	49.9	2	59.76	99.7

(*S*)-2-(2-(2-Methoxyphenyl)but-3-en-2-yl)furan (Entry 3, Table 3). IR (neat): 3081 (w), 2978 (w), 2936 (w), 2834 (w), 1598 (w), 1581 (w), 1488 (m), 1460 (m), 1434 (m), 1242 (s), 1027 (m), 1007 (m), 883 (m), 751 (s), 726 (s) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.31–7.30 (1H, m), 7.26–7.21 (1H, m), 7.05 (1H, dd, *J* = 7.6, 1.6 Hz), 6.92–6.86 (2H, m), 6.41 (1H, dd, *J* = 17.7, 10.8 Hz), 6.32–6.30 (1H, m), 6.02 (1H, dd, *J* = 3.2, 0.8 Hz), 5.13 (1H, dt, *J* = 10.4, 0.4 Hz), 4.93 (1H, dd, *J* = 17.2, 1.2 Hz), 3.62 (3H, s), 1.81 (3H, s); ^{13}C NMR (100 MHz, CDCl$_3$): δ 160.5, 157.9, 143.5, 140.6, 134.0, 128.3, 128.1, 120.5, 112.5, 112.4, 110.0, 104.6, 55.5, 46.2, 23.7; HRMS (ESI+): Calcd for $C_{15}H_{17}O_2$ [M+H]$^+$: 229.1229, Found: 229.1227. Specific Rotation: $[\alpha]_D^{20}$ −20.6 (*c* 1.52, CHCl$_3$) for an enantiomerically enriched sample of 99.5:0.5 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with $NaBO_3$•$4H_2O$) in comparison with authentic racemic material (99.6:0.4 er shown; Chiralcel OJ-H column, 96/4 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	25.55		0.00	N/A	32131210	49.597	BV	0.94
2	30.59		0.00	N/A	32653070	50.403	VB	1.15

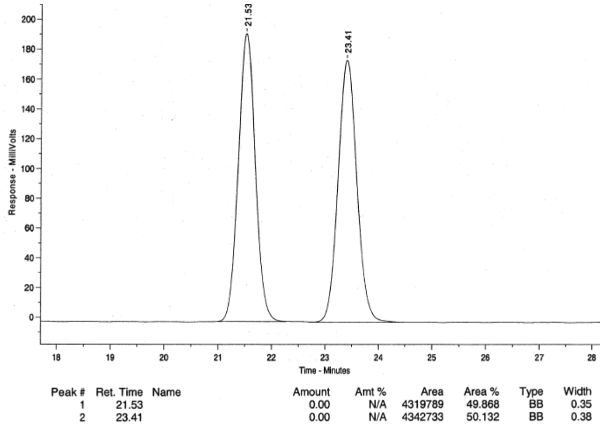


Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	26.07		0.00	N/A	367112	0.439	BV	0.85
2	30.66		0.00	N/A	83213680	99.561	VB	1.57

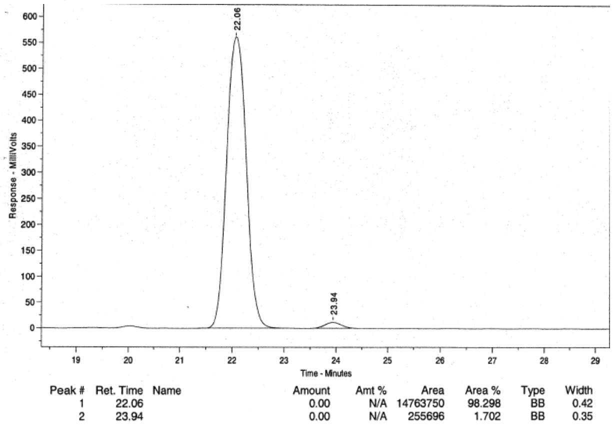
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	25.55	49.6	1	26.07	0.4
2	30.59	50.4	2	30.66	99.6

(*S*)-2-(2-*o*-Tolylbut-3-en-2-yl)furan (Entry 4, Table 3). IR (neat): 3059 (w), 3015 (w), 2978 (w), 2933 (w), 2876 (w), 1499 (w), 1486 (w), 1456 (w), 1153 (w), 1008 (m), 922 (m), 750 (m), 724 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34–7.33 (1H, m), 7.31–7.28 (1H, m), 7.20–7.16 (2H, m), 7.16–7.10 (1H, m), 6.48 (1H, dd, *J* = 17.2, 10.4 Hz), 6.33 (1H, dd, *J* = 3.2, 1.6 Hz), 6.05 (1H, dd, *J* = 2.8, 0.8 Hz), 5.16 (1H, dd, *J* = 10.4, 0.8 Hz), 4.92 (1H, dd, *J* = 17.2, 1.2 Hz), 1.99 (3H, s), 1.79 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4, 143.6, 143.1, 141.0, 137.3, 132.3, 127.6, 126.9, 125.8, 113.0, 110.2, 105.1, 47.5, 25.8, 21.0; HRMS (ESI+): Calcd for $C_{15}H_{17}O_1$ [M+H]$^+$: 213.1279, Found: 213.1273. Specific Rotation: $[\alpha]_D^{20}$ –21.1 (*c* 1.92, $CHCl_3$) for an enantiomerically enriched sample of 98:2 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with $NaBO_3$•$4H_2O$) in comparison with authentic racemic material (98.3:1.7 er shown; Chiralpak AD-H column, 95/5 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	21.53		0.00	N/A	4319789	49.868	BB	0.35
2	23.41		0.00	N/A	4342733	50.132	BB	0.38



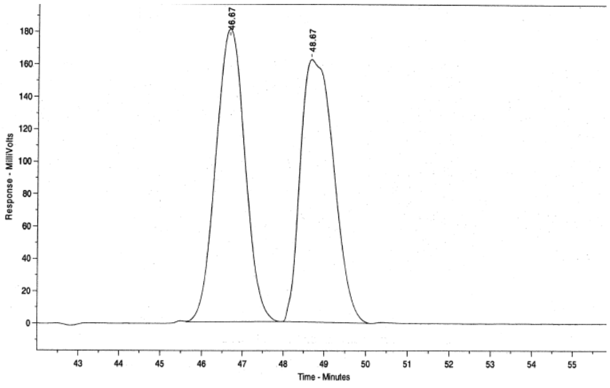
Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	22.06		0.00	N/A	14763750	98.298	BB	0.42
2	23.94		0.00	N/A	255696	1.702	BB	0.35

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	21.53	49.9	1	22.06	98.3
2	23.41	50.1	2	22.94	1.7

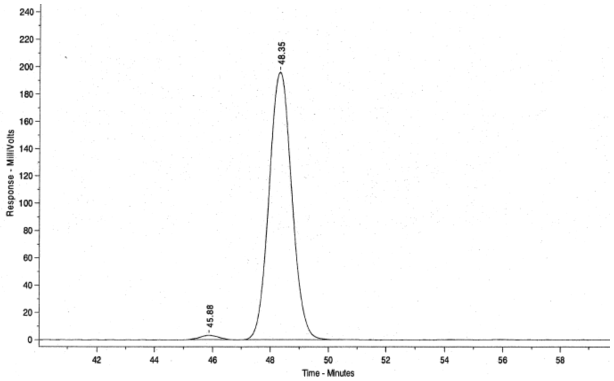
(*S*)-2-(2-(4-Nitrophenyl)but-3-en-2-yl)furan (Entry 5, Table 3). IR (neat): 1603 (w), 1514 (s), 1344 (s), 1316 (w), 1154 (w), 1110 (w), 1011 (m), 925 (m), 851 (m), 734 (m), 699 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15–8.11 (2H, m), 7.38–7.37 (1H, m), 7.33–7.30 (2H, m), 6.36–6.35 (1H, m), 6.32 (1H, dd, *J* = 17.6, 10.8 Hz), 6.18 (1H, dd, *J* = 3.2, 0.8 Hz), 5.29 (1H, dd, *J* = 10.4, 0.8 Hz), 5.03 (1H, dd, *J* = 17.6, 0.8 Hz), 1.77 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.0, 153.3, 146.6, 142.2, 142.1, 128.1, 123.5, 115.0, 110.2, 106.8, 47.6, 25.3; HRMS (ESI+):

Calcd for $C_{14}H_{14}N_1O_3$ $[M+H]^+$: 244.0974, Found: 244.0985. Specific Rotation: $[\alpha]_D^{20}$ □21.1 (*c* 1.92, $CHCl_3$) for an enantiomerically enriched sample of 98.5:1.5 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with $NaBO_3$•$4H_2O$) in comparison with authentic racemic material (98.6:1.4 er shown; Chiralpak AD-H column, 93/7 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	46.67		0.00	N/A	9050409	49.600	BB	0.79
2	48.67		0.00	N/A	9196202	50.400	BB	0.92

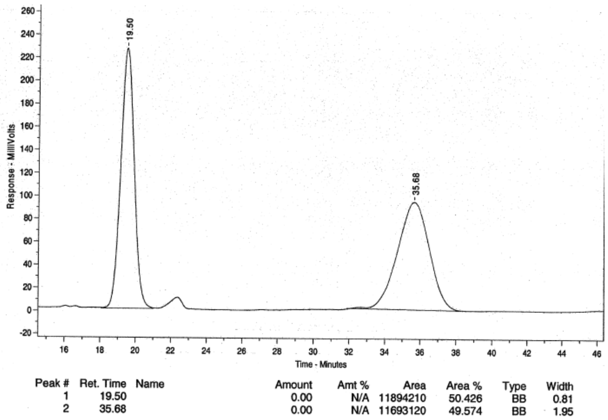


Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	45.88		0.00	N/A	147578	1.363	BB	0.72
2	48.35		0.00	N/A	10683510	98.637	BB	0.84

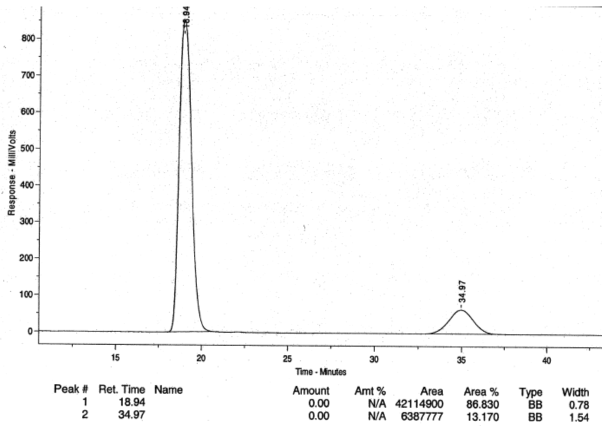
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	46.67	49.6	1	45.88	1.4
2	48.67	50.4	2	48.35	98.6

(*R*)-(2-(Furan-2-yl)but-3-en-2-yl)dimethyl(phenyl)silane (Entry 6, Table 3). IR (neat): 3079 (w), 3050 (w), 3010 (w), 2959 (w), 2929 (w), 1624 (w), 1500 (w), 1192 (m), 1160 (w), 1015 (w), 923 (w), 901 (w), 833 (m), 816 (s), 772 (m), 723 (s), 699 (s), 654 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37□7.27 (6H, m), 6.28□6.27 (1H, m), 6.26 (1H, dd, *J* = 17.6, 10.8 Hz), 5.77□5.76 (1H, m), 5.03 (1H, dd, *J* = 10.8, 1.6 Hz), 4.84 (1H, dd, *J* = 17.6, 1.2 Hz), 1.35 (3H, s), 0.36 (3H, s), 0.30 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 140.6, 140.4, 136.3, 134.6, 129.2, 127.3, 111.2, 110.3, 103.4, 35.8, 17.7, □4.9, □5.0; HRMS (ESI+): Calcd for $C_{16}H_{21}O_1Si_1$ $[M+H]^+$: 257.1362, Found: 257.1366. Specific Rotation: $[\alpha]_D^{20}$ □4.00 (*c* 1.37, $CHCl_3$) for an enantiomerically enriched sample of 85:15 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with H_2O_2) in comparison with authentic racemic material (86.8:13.2 er shown; Chiralcel OJ-H column, 95/5 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	19.50		0.00	N/A	11894210	50.426	BB	0.81
2	35.68		0.00	N/A	11693120	49.574	BB	1.95

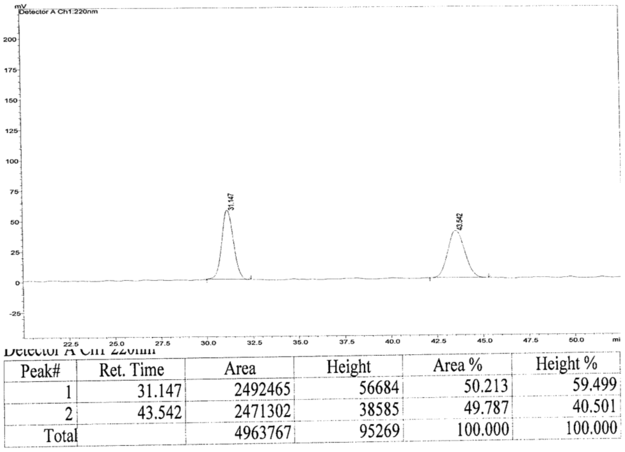


Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	18.94		0.00	N/A	42114900	86.830	BB	0.78
2	34.97		0.00	N/A	6387777	13.170	BB	1.54

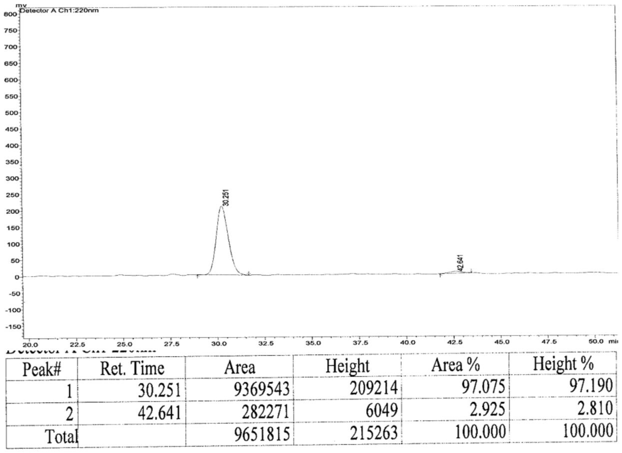
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	19.50	50.4	1	18.94	86.8
2	35.68	49.6	2	34.97	13.2

(*S*)-3-(2-Phenylbut-3-en-2-yl)furan (Entry 7, Table 3). IR (neat): 2976 (w), 1636 (w), 1599 (w), 1492 (w), 1445 (w), 1409 (w), 1368 (w), 1160 (w), 1060 (w), 1025 (m), 1000 (w), 954 (w), 918 (m), 873 (m), 785 (m), 758 (m), 728 (w), 698 (s), 599 (s), 553 (w), 532 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.38 (1H, m), 7.30–7.28 (4H, m), 7.23–7.19 (1H, m), 7.16–7.15 (1H, m), 6.26 (1H, dd, *J* = 17.6, 10.8 Hz), 6.19–6.18 (1H, m), 5.16 (1H, dd, *J* = 10.8, 1.2 Hz), 4.98 (1H, dd, *J* = 17.2, 1.2 Hz), 1.70 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.9, 145.6, 143.1, 139.5, 132.5, 128.2, 127.3, 126.4, 113.1, 110.7, 44.7, 27.2; HRMS (ESI+): Calcd for $C_{14}H_{15}O_1$ $[M+H]^+$: 199.1123, Found: 199.1120. Specific Rotation: $[\alpha]_D^{20}$ –4.32 (*c* 0.47, $CHCl_3$) for an enantiomerically enriched sample of 97:3 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with $NaBO_3•4H_2O$) in comparison with authentic racemic material (97.1:2.9 er shown; Chiralcel OJ-H column, 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.147	2492465	56684	50.213	59.499
2	43.542	2471302	38585	49.787	40.501
Total		4963767	95269	100.000	100.000

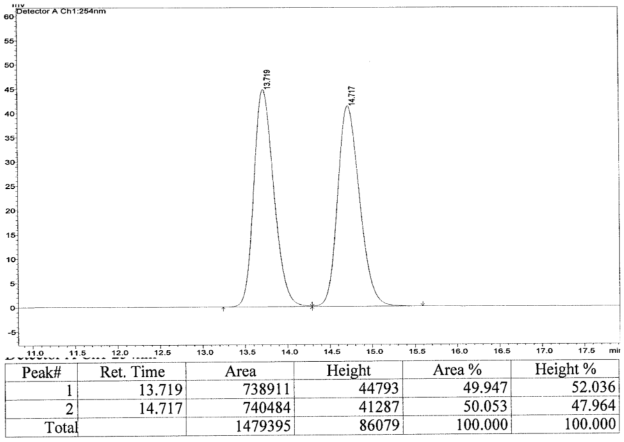


Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.251	9369543	209214	97.075	97.190
2	42.641	282271	6049	2.925	2.810
Total		9651815	215263	100.000	100.000

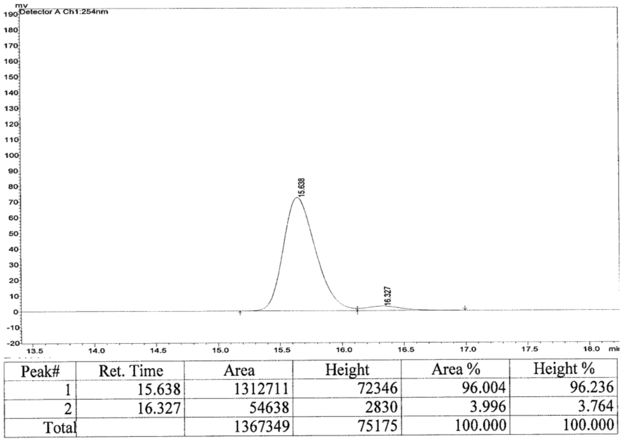
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	31.147	50.2	1	30.251	97.1
2	43.542	49.8	2	42.641	2.9

(*S*)-2-(2-Phenylbut-3-en-2-yl)thiophene (Entry 8, Table 3). IR (neat): 3084 (w), 3059 (w), 2976 (w), 2931 (w), 1634 (w), 1599 (w), 1491 (w), 1444 (w), 1407 (w), 1370 (w), 1237 (w), 999 (w), 918 (m), 853 (w), 828 (w), 759 (m), 692 (s), 527 (w) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.30–7.25 (4H, m), 7.24–7.19 (2H, m), 6.95 (1H, dd, *J* = 5.2, 3.6 Hz), 6.79 (1H, dd, *J* = 3.6, 1.2 Hz), 6.38 (1H, dd, *J* = 17.2, 10.4 Hz), 5.20 (1H, dd, *J* = 10.8, 1.2 Hz), 4.96 (1H, dd, *J* = 17.2, 1.2 Hz), 1.87 (3H, s); ^{13}C NMR (100 MHz, CDCl$_3$): δ 153.0, 147.5, 146.1, 128.2, 127.4, 126.6, 126.5, 125.0, 124.1, 113.5, 48.5, 28.8; HRMS (ESI+): Calcd for $C_{14}H_{15}S_1$ [M+H]$^+$: 215.0895, Found: 215.0892. Specific Rotation: $[\alpha]_D^{20}$ –22.6 (*c* 0.31, CHCl$_3$) for an enantiomerically enriched sample of 96:4 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (96.0:4.0 er shown; Chiralcel OD-H column, 100/0 hexanes/*i*-PrOH, 0.5 mL/min, 254 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.719	738911	44793	49.947	52.036
2	14.717	740484	41287	50.053	47.964
Total		1479395	86079	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.638	1312711	72346	96.004	96.236
2	16.327	54638	2830	3.996	3.764
Total		1367349	75175	100.000	100.000

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	13.719	49.9	1	15.638	96.0
2	14.717	50.1	2	16.327	4.0

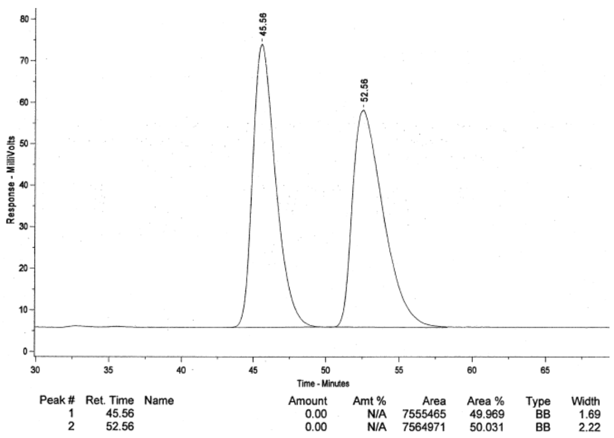
(*S*)-2-(2-(2-Bromophenyl)but-3-en-2-yl)thiophene (Entry 9, Table 3). IR (neat): 3064 (w), 2974 (w), 2933 (w), 1463 (w), 1430 (w), 1406 (w), 1368 (w), 1348 (w), 1018 (m), 910 (m), 852 (w), 824 (w), 805 (w), 753 (m), 732 (m), 689 (s), 644 (m) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.57 (1H, dd, *J* = 7.6, 1.6 Hz), 7.52 (1H, dd, *J* = 8.0, 1.6 Hz), 7.30 (1H, td, *J* = 7.6, 1.2 Hz), 7.19 (1H, dd, *J* = 4.4, 1.2 Hz), 7.12 (1H, td, *J* = 7.6, 1.6 Hz), 6.93 (1H, dd, *J* = 4.8, 3.2 Hz), 6.67 (1H, dd, *J* = 3.6, 1.2 Hz), 6.58 (1H, dd, *J* = 17.6, 10.8 Hz), 5.20 (1H, dd, *J* = 10.4, 0.4 Hz), 4.97 (1H, dd, *J* = 17.2, 0.4 Hz), 1.99 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5, 145.4, 145.1, 135.7, 129.6, 128.5, 127.1, 126.7, 124.5, 124.4, 123.4, 113.4, 49.5, 27.9; HRMS (ESI+): Calcd for $C_{14}H_{14}Br_1S_1$ $[M+H]^+$: 293.0000, Found: 293.0006. Specific Rotation: $[\alpha]_D^{20}$ □26.0 (*c* 2.93, $CHCl_3$) for an enantiomerically enriched sample of 98:2 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with $NaBO_3•4H_2O$) in comparison with authentic racemic material (98.4:1.6 er shown; Chiralcel OJ-H column, 94/6 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).

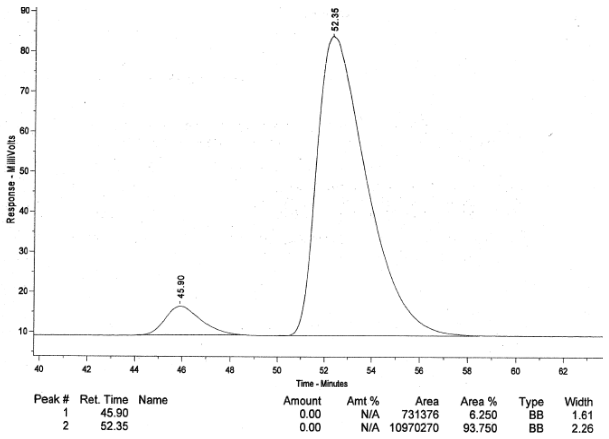
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	27.08	49.5	1	27.57	1.6
2	44.04	50.5	2	45.09	98.4

(*S*)-2-(2-(4-Nitrophenyl)but-3-en-2-yl)thiophene (Entry 10, Table 3). IR (neat): 3081 (w), 2977 (w), 2935 (w), 1602 (w), 1513 (s), 1342 (s), 1238 (w), 1012 (w), 924 (w), 849 (m), 830 (w), 804 (w), 694 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14□8.11 (2H, m), 7.43□7.41 (2H, m), 7.25□7.22 (1H, m), 6.98□6.96 (1H, m), 6.81□6.78 (1H, m), 6.35 (1H, ddd, *J* = 17.2, 10.4, 0.8 Hz), 5.27 (1H, dd, *J* = 10.4, 0.4 Hz), 4.98 (1H, d, *J* = 17.2 Hz), 1.89 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 151.1, 146.6, 144.7, 128.4, 126.7, 125.3, 124.7, 123.3, 114.7, 48.7, 28.6; HRMS (ESI+): Calcd for $C_{14}H_{14}N_1O_2S_1$ $[M+H]^+$: 260.0745, Found: 260.0754. Specific Rotation: $[\alpha]_D^{20}$ □2.70 (*c* 2.38, $CHCl_3$) for an enantiomerically enriched sample of 94:6 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with $NaBO_3•4H_2O$) in comparison with authentic racemic material (93.8:6.2 er shown; Chiralcel OD column, 96/4 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	45.56		0.00	N/A	7555465	49.969	BB	1.69
2	52.56		0.00	N/A	7564971	50.031	BB	2.22

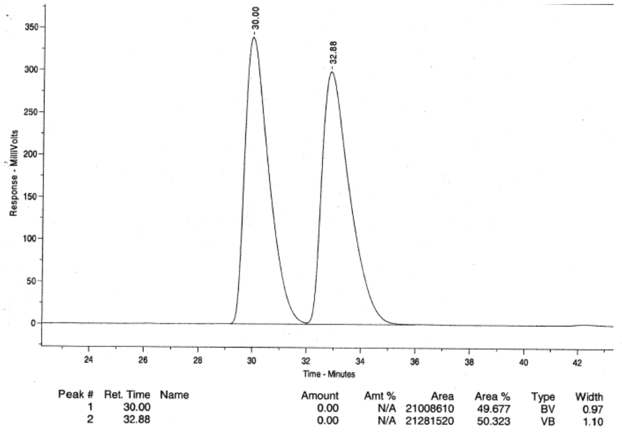


Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	45.90		0.00	N/A	731376	6.250	BB	1.61
2	52.35		0.00	N/A	10970270	93.750	BB	2.26

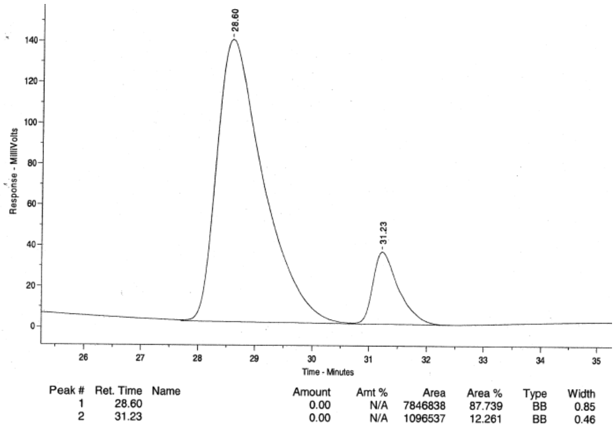
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	45.56	50.0	1	45.90	6.2
2	52.56	50.0	2	52.35	93.8

(*S*)-*tert*-Butyl 2-methyl-2-(thiophen-2-yl)but-3-enoate (Entry 11, Table 3). IR (neat): 2978 (w), 2935 (w), 1724 (s), 1455 (w), 1432 (w), 1419 (w), 1367 (m), 1253 (s), 1237 (m), 1154 (s), 1113 (s), 920 (m), 877 (m), 693 (s) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.20–7.18 (1H, m), 6.95–6.92 (2H, m), 6.38 (1H, dd, *J* = 17.2, 10.4 Hz), 5.20 (1H, dd, *J* = 11.2, 0.8 Hz), 5.15 (1H, d, *J* = 17.2 Hz), 1.70 (3H, s), 1.42 (9H, s); ^{13}C NMR (100 MHz, CDCl$_3$): δ 172.5, 147.6, 141.5, 126.4, 124.4, 124.3, 114.1, 81.6, 51.8, 27.9, 24.3; HRMS (ESI+): Calcd for $C_{13}H_{19}O_2S_1$ $[M+H]^+$: 239.1106, Found: 239.1105. Specific Rotation: $[\alpha]_D^{20}$ □2.41 (*c* 1.75, CHCl$_3$) for an enantiomerically enriched sample of 79:21 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (87.7:12.3 er shown; Chiralcel OD column, 100% hexanes, 0.5 mL/min, 220 nm).



Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	30.00		0.00	N/A	21008610	49.677	BV	0.97
2	32.88		0.00	N/A	21281520	50.323	VB	1.10



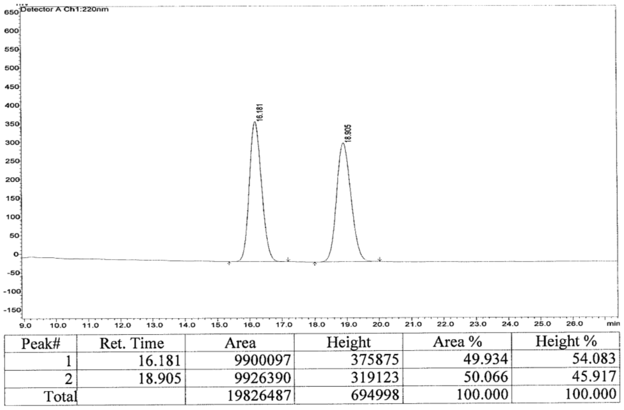
Peak #	Ret. Time	Name	Amount	Amt %	Area	Area %	Type	Width
1	28.60		0.00	N/A	7846838	87.739	BB	0.85
2	31.23		0.00	N/A	1096537	12.261	BB	0.46

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	30.00	49.7	1	28.60	87.7

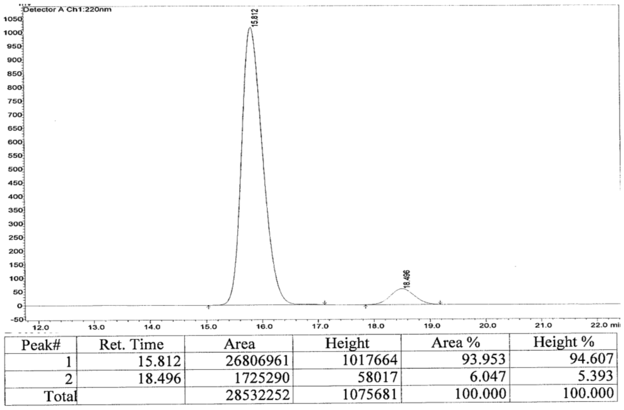
2	32.88	50.3	2	31.23	12.3

(*S*)-3-(2-Phenylbut-3-en-2-yl)thiophene (Entry 12, Table 3). IR (neat): 2974 (w), 1491 (w), 1444 (w), 1367 (w), 1000 (w), 918 (m), 838 (m), 755 (m), 698 (s), 664 (s), 528 (w) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.31–7.18 (6H, m), 6.97–6.96 (1H, m), 6.85–6.83 (1H, m), 6.36 (1H, ddd, *J* = 17.2, 10.4, 0.8 Hz), 5.17 (1H, dd, *J* = 10.8, 1.2 Hz), 4.92 (1H, dd, *J* = 17.2, 1.2 Hz), 1.79 (3H, s); ^{13}C NMR (100 MHz, CDCl$_3$): δ 149.0, 147.6, 146.0, 128.2, 127.5, 126.3, 125.3, 120.9, 113.1, 48.2, 27.5; HRMS (ESI+): Calcd for $C_{14}H_{15}S_1$ [M+H]$^+$: 215.0895, Found: 215.0899. Specific Rotation: $[\alpha]_D^{20}$ –6.69 (*c* 0.28, CHCl$_3$) for an enantiomerically enriched sample of 94:6 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with NaBO$_3$•4H$_2$O) in comparison with authentic racemic material (94.0:6.0 er shown; Chiralcel OD-H column, 95/5 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.181	9900097	375875	49.934	54.083
2	18.905	9926390	319123	50.066	45.917
Total		19826487	694998	100.000	100.000

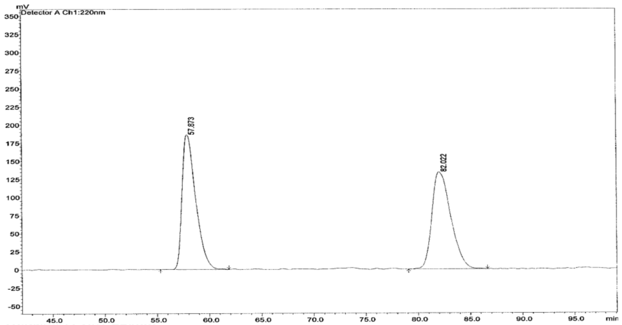


Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.812	26806961	1017664	93.953	94.607
2	18.496	1725290	58017	6.047	5.393
Total		28532252	1075681	100.000	100.000

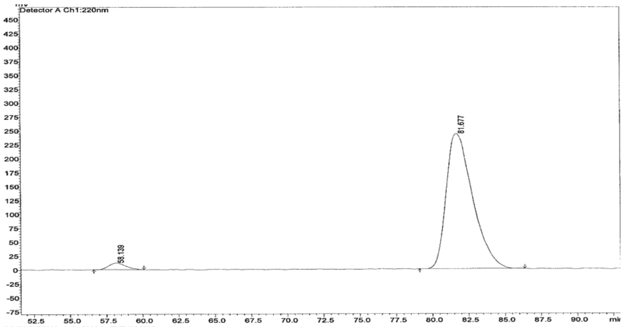
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	16.181	49.9	1	15.812	94.0
2	18.905	50.1	2	18.496	6.0

(*R*)-3-(2-(2-Bromophenyl)but-3-en-2-yl)thiophene (Entry 13, Table 3). IR (neat): 2974 (w), 1633 (w), 1464 (w), 1409 (w), 1367 (w), 1231 (w), 1198 (w), 1173 (w), 1084 (w), 1019 (m), 917 (m), 838 (m), 750 (s), 652 (m), 455 (w) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.55 (1H, dd, *J* = 7.6, 1.6 Hz), 7.51 (1H, dd, *J* = 8.0, 2.0 Hz), 7.30 (1H, ddd, *J* = 8.0, 7.2, 1.6 Hz), 7.23 (1H, dd, *J* = 5.2, 3.2 Hz), 7.10 (1H, ddd, *J* = 7.6, 7.2, 1.6 Hz), 6.90 (1H, dd, *J* = 3.2, 1.6 Hz), 6.74 (1H, dd, *J* = 5.2, 1.2 Hz), 6.56 (1H, dd, *J* = 17.6, 10.8 Hz), 5.17 (1H, dd, *J* = 10.4, 0.8 Hz), 4.94 (1H, dd, *J* = 17.2, 0.8 Hz), 1.91 (3H, s); ^{13}C NMR (100 MHz, CDCl$_3$): δ 148.2, 145.7, 145.1, 135.7, 129.5, 128.3, 127.6, 127.2, 125.1, 124.2, 120.7, 113.1, 49.3, 26.6; HRMS (ESI+): Calcd for $C_{14}H_{14}Br_1S_1$ [M+H]$^+$: 293.0000, Found: 292.9987. Specific Rotation: $[\alpha]_D^{20}$ –22.7 (*c* 1.19, CHCl$_3$) for an enantiomerically enriched sample of 97:3 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with $NaBO_3•4H_2O$) in comparison with authentic racemic material (97.0:3.0 er shown; Chiralcel OD-H column, 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	57.873	16932633	186036	50.063	58.098
2	82.022	16889813	134172	49.937	41.902
Total		33822446	320208	100.000	100.000

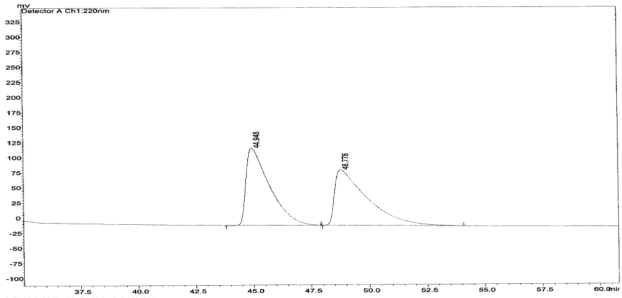


Peak#	Ret. Time	Area	Height	Area %	Height %
1	58.139	959740	11782	3.026	4.632
2	81.677	30758578	242577	96.974	95.368
Total		31718318	254359	100.000	100.000

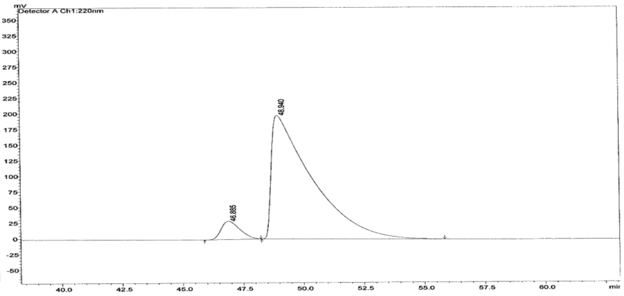
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	57.873	50.1	1	58.139	3.0
2	82.022	49.9	2	81.677	97.0

(*R*)-Dimethyl(phenyl)(2-(thiophen-3-yl)but-3-en-2-yl)silane (Entry 14, Table 3). IR (neat): 2959 (w), 1620 (w), 1427 (w), 1366 (w), 1247 (m), 1112 (m), 998 (w), 830 (s), 810 (s), 773 (s), 734 (s), 699 (s), 653 (s), 567 (m), 472 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.34 (1H, m), 7.31–7.25 (4H, m), 7.20 (1H, dd, *J* = 5.2, 2.8 Hz), 6.80 (1H, dd, *J* = 5.2, 1.6 Hz), 6.65 (1H, dd, *J* = 3.2, 1.6 Hz), 6.36 (1H, dd, *J* = 17.2, 10.8 Hz), 5.05 (1H, dd, *J* = 10.4, 1.2 Hz), 4.90 (1H, dd, *J* = 17.6, 1.2 Hz), 1.44 (3H, s), 0.26 (6H, d, *J* = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5, 142.8, 136.5, 134.9, 129.3, 127.4, 127.2, 124.5, 117.9, 110.8, 36.7, 19.4, –5.2, –5.4; HRMS (ESI+): Calcd for $C_{16}H_{21}S_1Si_1$ $[M+H]^+$: 273.1133, Found: 273.1132. Specific Rotation: $[\alpha]_D^{20}$ –18.7 (*c* 0.41, $CHCl_3$) for an enantiomerically enriched sample of 94:6 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (93.6:6.4 er shown; Chiralcel OD-H column, 100% hexanes, 0.2 mL/min, 220 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	44.948	9047280	128014	50.219	58.193
2	48.778	8968453	91967	49.781	41.807
Total		18015733	219981	100.000	100.000

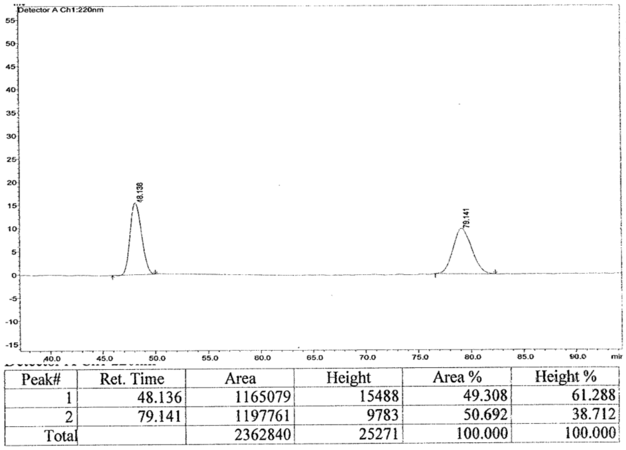


Peak#	Ret. Time	Area	Height	Area %	Height %
1	46.885	1577665	29319	6.361	12.912
2	48.940	23222851	197756	93.639	87.088
Total		24800517	227075	100.000	100.000

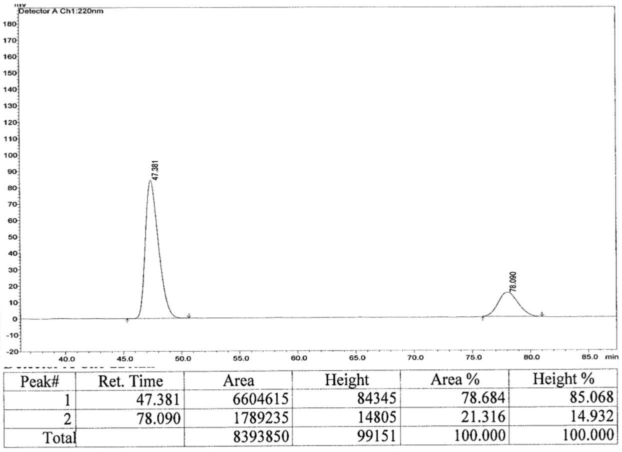
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	44.948	50.2	1	46.885	6.4
2	48.778	49.8	2	48.940	93.6

(*R*)-1-(3,7-Dimethylocta-1,6-dien-3-yl)-4-methoxybenzene (sporochnol methyl ether, not shown in Scheme 3). IR (neat): 2966 (m), 2927 (m), 2857 (w), 2835 (w), 1610 (w), 1511 (s), 1463 (w), 1295 (w), 1249 (s), 1182 (m), 1038 (m), 913 (w), 828 (m), 649 (w), 545 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25–7.22 (2H, m), 6.87–6.83 (2H, m), 6.02 (1H, dd, *J* = 17.6, 10.8 Hz), 5.11–5.07 (2H, m), 5.03 (1H, dd, *J* = 17.2, 1.2 Hz), 3.80 (3H, s), 1.91–1.67 (4H, m), 1.66 (3H, s), 1.53 (3H, s), 1.36 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.7, 147.4, 139.7, 131.4, 127.7, 124.9, 113.5, 111.6, 55.4, 43.8, 41.3, 25.8, 25.2, 23.4, 17.7; HRMS (ESI+): Calcd for $C_{17}H_{25}O_1$ $[M+H]^+$: 245.1905, Found: 245.1905. Specific Rotation: $[\alpha]_D^{20}$ –2.57 (*c* 0.79, $CHCl_3$) for an enantiomerically enriched sample of 78.5:21.5 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with $NaBO_3•4H_2O$) in comparison with authentic racemic material (78.7:21.3 er shown; Chiralcel OD-H column, 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	48.136	1165079	15488	49.308	61.288
2	79.141	1197761	9783	50.692	38.712
Total		2362840	25271	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	47.381	6604615	84345	78.684	85.068
2	78.090	1789235	14805	21.316	14.932
Total		8393850	99151	100.000	100.000

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	48.136	49.3	1	47.381	78.7
2	79.141	50.7	2	78.090	21.3

■ **Enantioselective Synthesis of *R*-(–)-sporochnol (Scheme 3): Procedure for Demethylation of Sporochnol Methyl Ether.** A flame-dried 6-dram vial is charged with sporochnol methyl ether (17.4 mg, 0.071 mmol) and a stir bar. The vial is sealed with a septum and purged with N_2 flow for 10 minutes. Freshly prepared MeMgI in diethyl ether (890 μL, 0.356 mmol) is added to the reaction vessel and solvent is carefully removed under reduced pressure. The resulting mixture is heated in a 180 °C oil bath for 10 minutes (white smoke generated as the reaction goes on and disappears in 10 minutes), after which time, it is allowed to cool to 22 °C and diluted with Et_2O (5 mL). A saturated solution of NH_4Cl is added to quench the reaction and layers are separated. The aqueous layer is washed with Et_2O (5 mL x 3) and the combined organic layers are dried with anhydrous $MgSO_4$, filtered and concentrated *in vacuo* to afford a slightly yellow oil, which is subjected to silica gel chromatography (10:1 hexanes:ethyl acetate) to furnish the desired product as colorless oil (14.1 mg, 0.061 mmol, 86% yield). ***R*-(–)-Sporochnol:** The compound has been previously reported and spectra data match those previously described.[9] IR (neat): 3332 (br), 2966 (w), 2922 (w), 2857 (w), 1611 (w), 1511 (s), 1439 (w), 1374 (w), 1232 (m), 1178 (m), 1013 (w), 912 (m), 828 (s), 651 (w), 541 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.20–7.17 (2H, m), 6.78–6.75 (2H, m), 6.00 (1H, dd, *J* = 17.6, 10.8 Hz), 5.10–5.00 (3H, m), 4.68 (1H, s), 1.86–1.61 (4H, m), 1.66 (3H, s), 1.52 (3H, s), 1.35 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.5, 147.3, 139.9, 131.4, 130.0, 124.8, 114.9, 111.6, 43.8, 41.3, 25.8, 25.1, 23.4, 17.7; HRMS (ESI+): Calcd for $C_{16}H_{23}O_1$ $[M+H]^+$: 231.1749, Found: 231.1751. Specific Rotation: $[\alpha]_D^{20}$ –2.03 (*c* 0.82, $CHCl_3$) for an enantiomerically enriched sample of 78.5:21.5 er.

Proof of Stereochemistry: Literature value ($[\alpha]_D^{20}$ □2.5 (*c* 1.00, $CHCl_3$), 98.5:1.5 er) is assigned to the (*R*) enantiomer.[9]

(*R*)-2-(3,7-Dimethylocta-1,6-dien-3-yl)furan (11, Scheme 3). IR (neat): 2970 (w), 2925 (w), 2857 (w), 1504 (w), 1452 (w), 1412 (w), 1376 (w), 1260 (w), 1156 (w), 1074 (w), 1012 (m), 916 (m), 799 (m), 730 (s), 598 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.34–7.33 (1H, m), 6.29–6.27 (1H, m), 6.05–5.98 (2H, m), 5.10–5.04 (2H, m), 4.99 (1H, dd, *J* = 17.6, 1.2 Hz), 1.91–1.76 (2H, m), 1.67 (3H, d, *J* = 1.2 Hz), 1.55 (3H, d, *J* = 0.4 Hz), 1.37 (3H, s), 1.35–1.21 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6, 144.5, 141.2, 131.6, 124.5, 112.4, 109.9, 104.6, 42.3, 40.0, 25.8, 23.3, 22.8, 17.7; HRMS (ESI+): Calcd for $C_{14}H_{21}O_1$ $[M+H]^+$: 205.1592, Found: 205.1596. Specific Rotation: $[\alpha]_D^{20}$ –19.6 (*c* 2.43, $CHCl_3$) for an enantiomerically enriched sample of 91:9 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with $NaBO_3 \bullet 4H_2O$) in comparison with authentic racemic material (91.1:8.9 er shown; Chiralcel OD-H column, 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).

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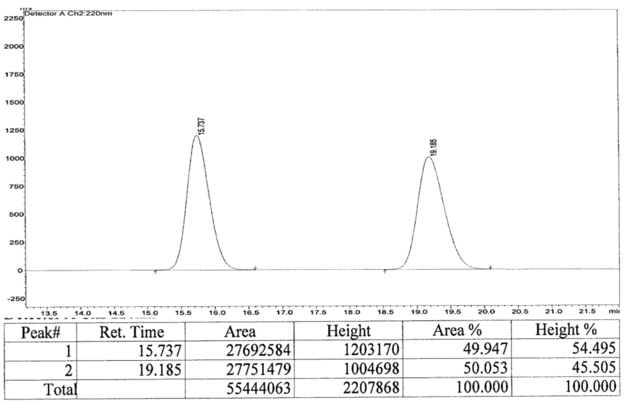
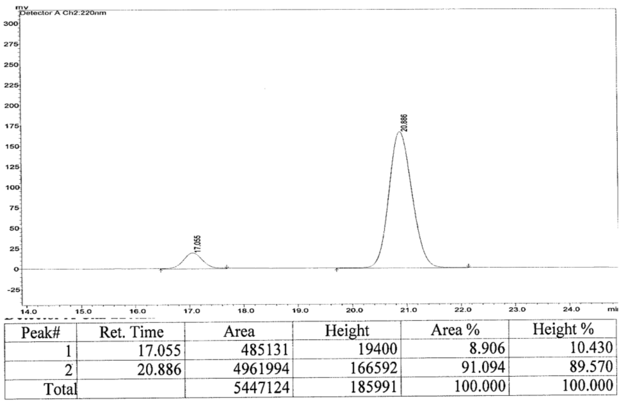
[9] A. Fadel, L. Vandromme, *Tetrahedron: Asymmetry* **1999**, *10*, 1153–1162.



Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.737	27692584	1203170	49.947	54.495
2	19.185	27751479	1004698	50.053	45.505
Total		55444063	2207868	100.000	100.000

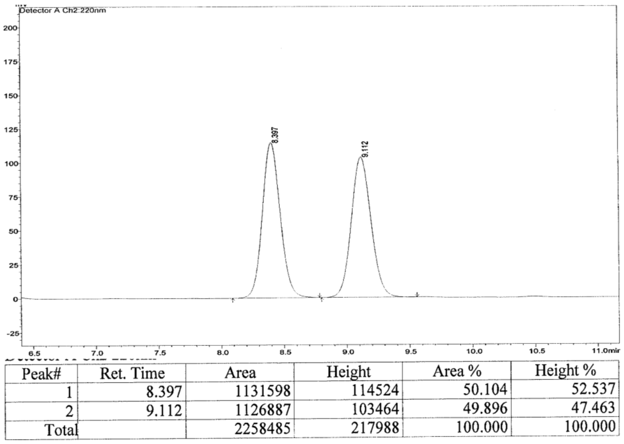


Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.055	485131	19400	8.906	10.430
2	20.886	4961994	166592	91.094	89.570
Total		5447124	185991	100.000	100.000

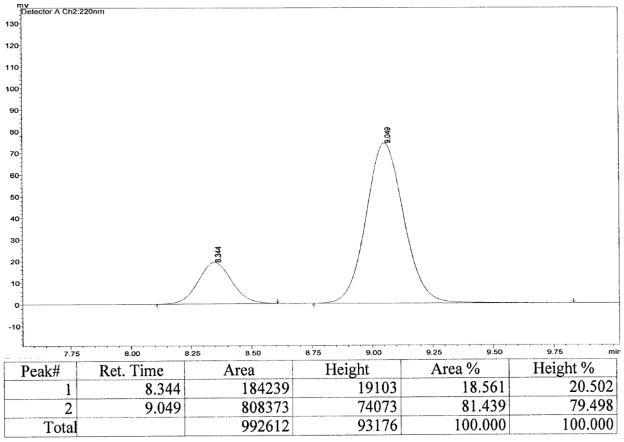
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	15.737	49.9	1	17.055	8.9
2	19.185	50.1	2	20.886	91.1

(*R*)-2-(3,7-Dimethylocta-1,6-dien-3-yl)thiophene (12, Scheme 3). IR (neat): 2967 (m), 2925 (m), 2856 (w), 1439 (w), 1375 (w), 1235 (w), 916 (w), 849 (w), 825 (w), 692 (s) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.16 (1H, dd, *J* = 4.8, 0.8 Hz), 6.94 (1H, dd, *J* = 5.2, 4.0 Hz), 6.83 (1H, dd, *J* = 3.6, 1.2 Hz), 6.08 (1H, dd, *J* = 17.6, 10.8 Hz), 5.13–5.05 (3H, m), 1.96–1.88 (2H, m), 1.85–1.71 (2H, m), 1.68 (3H, s), 1.56 (3H, s), 1.47 (3H, s); ^{13}C NMR (100 MHz, CDCl$_3$): δ 153.7, 146.4, 131.7, 126.5, 124.4, 123.2, 123.0, 112.0, 43.5, 43.0, 25.9, 25.8, 23.5, 17.7; HRMS (ESI+): Calcd for $C_{14}H_{21}S_1$ [M+H]$^+$: 221.1364, Found: 221.1374. Specific Rotation: $[\alpha]_D^{20}$ –9.44 (*c* 0.35, CHCl$_3$) for an enantiomerically enriched sample of 81:19 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (81.4:18.6 er shown; Chiralcel OJ-H column, 99/1 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.397	1131598	114524	50.104	52.537
2	9.112	1126887	103464	49.896	47.463
Total		2258485	217988	100.000	100.000



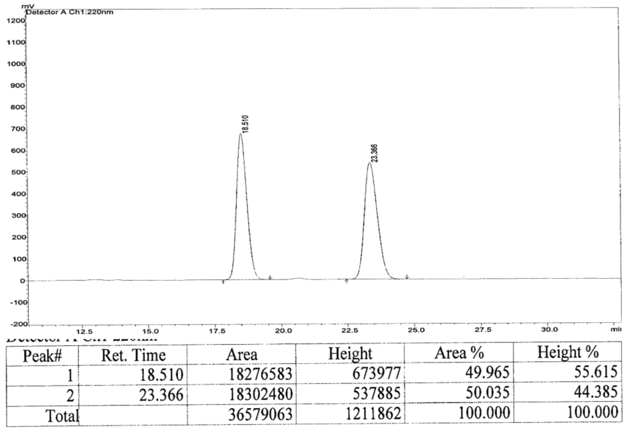
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.344	184239	19103	18.561	20.502
2	9.049	808373	74073	81.439	79.498
Total		992612	93176	100.000	100.000

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	8.397	50.1	1	8.344	18.6

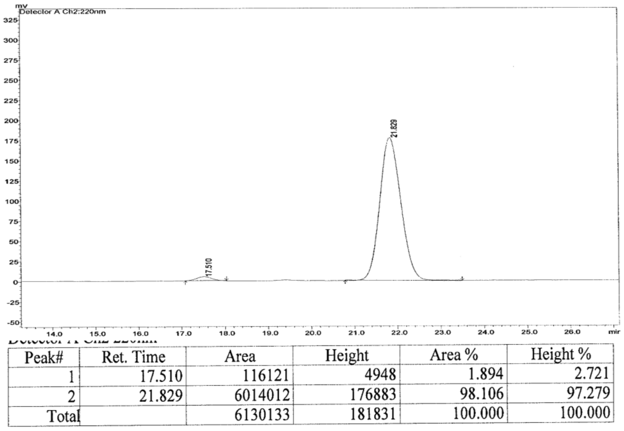
2	9.112	49.9	2	9.049	81.4

(*S*)-2-(2-Cyclohexylbut-3-en-2-yl)furan (13, Scheme 3). IR (neat): 2980 (w), 2926 (s), 2853 (m), 1635 (w), 1503 (w), 1450 (w), 1416 (w), 1370 (w), 1152 (w), 1014 (m), 914 (m), 802 (w), 731 (s), 598 (w) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.34–7.33 (1H, m), 6.27–6.26 (1H, m), 6.11 (1H, dd, *J* = 17.6, 10.8 Hz), 5.99–5.97 (1H, m), 5.08 (1H, dd, *J* = 10.8, 1.6 Hz), 4.98 (1H, dd, *J* = 17.6, 1.2 Hz), 1.78–1.59 (5H, m), 1.42–1.37 (1H, m), 1.30 (3H, s), 1.27–0.87 (5H, m); ^{13}C NMR (100 MHz, CDCl$_3$): δ 161.0, 143.4, 140.9, 112.9, 109.7, 104.9, 46.2, 45.6, 28.2, 27.9, 27.2, 27.1, 26.8, 18.4; HRMS (ESI+): Calcd for $C_{14}H_{21}O_1$ [M+H]$^+$: 205.1592, Found: 205.1595. Specific Rotation: $[\alpha]_D^{20}$ –84.2 (*c* 1.37, CHCl$_3$) for an enantiomerically enriched sample of 98:2 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with NaBO$_3$•4H$_2$O) in comparison with authentic racemic material (98.1:1.9 er shown; Chiralcel OD-H column, 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.510	18276583	673977	49.965	55.615
2	23.366	18302480	537885	50.035	44.385
Total		36579063	1211862	100.000	100.000

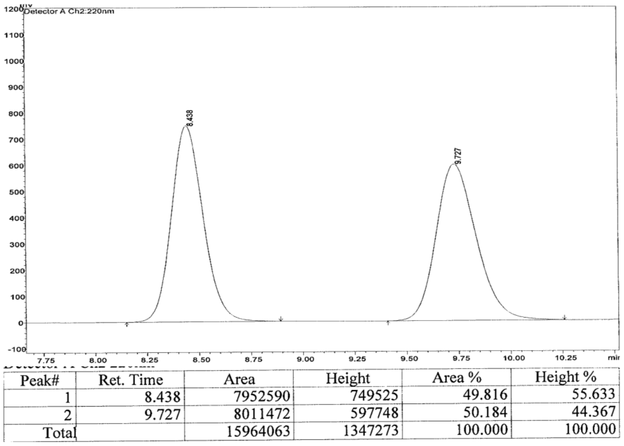


Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.510	116121	4948	1.894	2.721
2	21.829	6014012	176883	98.106	97.279
Total		6130133	181831	100.000	100.000

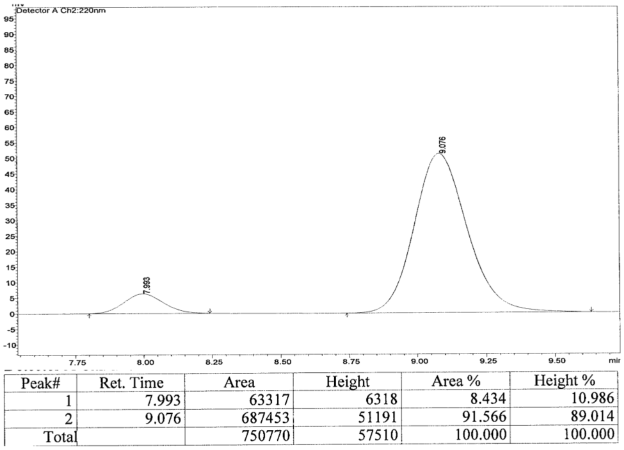
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	18.510	50.0	1	17.510	1.9
2	23.366	50.0	2	21.829	98.1

(*S*)-2-(2-Cyclohexylbut-3-en-2-yl)thiophene (14, Scheme 3). IR (neat): 2978 (w), 2923 (s), 2851 (m), 1449 (w), 1372 (w), 1235 (w), 1008 (w), 914 (w), 850 (w), 821 (w), 689 (s) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.15 (1H, dd, *J* = 5.2, 0.8 Hz), 6.93 (1H, dd, *J* = 5.2, 3.6 Hz), 6.80 (1H, dd, *J* = 3.6, 1.2 Hz), 6.14 (1H, dd, *J* = 17.6, 10.8 Hz), 5.11 (1H, dd, *J* = 10.8, 1.2 Hz), 5.05 (1H, dd, *J* = 17.2, 1.2 Hz), 1.76–1.57 (6H, m), 1.42 (3H, s), 1.27–0.91 (5H, m); ^{13}C NMR (100 MHz, CDCl$_3$): δ 154.2, 145.3, 126.3, 123.0, 122.8, 112.6, 49.6, 46.8, 28.2, 28.0, 27.2, 27.1, 26.8, 21.5; HRMS (ESI+): Calcd for $C_{14}H_{21}S_1$ [M+H]$^+$: 221.1364, Found: 221.1367. Specific Rotation: $[\alpha]_D^{20}$ –38.4 (*c* 0.34, CHCl$_3$) for an enantiomerically enriched sample of 91.5:8.5 er.

Enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (91.6:8.4 er shown; Chiralcel OJ-H column, 99/1 hexanes/*i*-PrOH, 0.5 mL/min, 220 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.438	7952590	749525	49.816	55.633
2	9.727	8011472	597748	50.184	44.367
Total		15964063	1347273	100.000	100.000

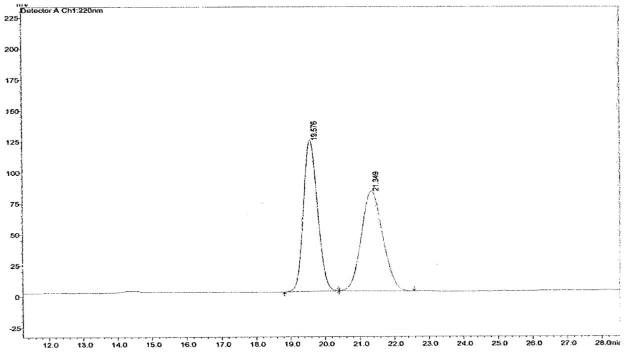


Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.993	63317	6318	8.434	10.986
2	9.076	687453	51191	91.566	89.014
Total		750770	57510	100.000	100.000

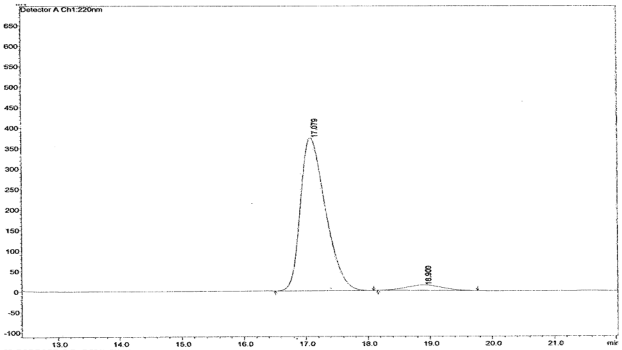
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	8.438	49.8	1	7.993	8.4
2	9.727	50.2	2	9.076	91.6

(*S*)-3-(2-Cyclohexylbut-3-en-2-yl)furan (15, Scheme 3). IR (neat): 2925 (s), 2853 (m), 1635 (w), 1501 (w), 1450 (w), 1413 (w), 1370 (w), 1159 (w), 1060 (w), 1027 (w), 914 (w), 873 (m), 778 (m), 726 (w), 600 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (1H, dd, *J* = 1.6, 1.6 Hz), 7.13 (1H, dd, *J* = 1.6, 0.8 Hz), 6.30 (1H, dd, *J* = 0.8, 0.8 Hz), 6.02 (1H, dd, *J* = 17.2, 10.8 Hz), 5.04 (1H, dd, *J* = 10.8, 1.6 Hz), 4.98 (1H, dd, *J* = 17.2, 1.6 Hz), 1.74–1.56 (6H, m), 1.48–1.40 (1H, m), 1.25 (3H, s), 1.22–1.02 (2H, m), 0.98–0.86 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.2, 142.7, 138.8, 132.4, 112.3, 109.7, 47.3, 42.5, 28.00, 27.98, 27.21, 27.18, 26.8, 20.4; HRMS (ESI+): Calcd for $C_{14}H_{21}O_1$ $[M+H]^+$: 205.1592, Found: 205.1600. Specific Rotation: $[\alpha]_D^{20}$ –9.48 (*c* 0.27, $CHCl_3$) for an enantiomerically enriched sample of 95:5 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with $NaBO_3 \cdot 4H_2O$) in comparison with authentic racemic material (95.0:5.0 er shown; Chiralcel OD-H column, 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.576	3447725	121592	49.930	60.225
2	21.349	3457334	80305	50.070	39.775
Total		6905058	201897	100.000	100.000

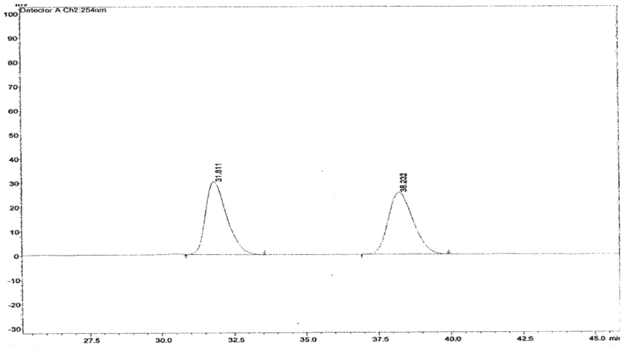


Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.079	10488798	373578	95.031	96.501
2	18.900	548394	13545	4.969	3.499
Total		11037192	387123	100.000	100.000

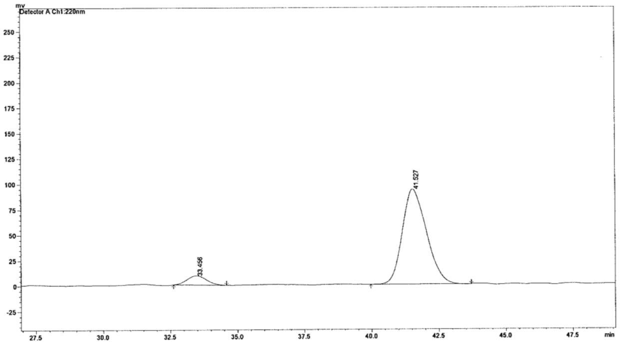
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	19.576	49.9	1	17.079	95.0
2	21.349	50.1	2	18.900	5.0

(*S*)-3-(2-Cyclohexylbut-3-en-2-yl)thiophene (16, Scheme 3). IR (neat): 2981 (w), 2926 (s), 2852 (m), 1449 (w), 913 (w), 770 (w), 652 (w) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.25 (1H, ddd, *J* = 5.2, 3.2, 0.4 Hz), 7.02 (1H, ddd, *J* = 5.2, 1.6, 0.4 Hz), 6.91 (1H, ddd, *J* = 2.8, 1.2, 0.4 Hz), 6.13 (1H, dd, *J* = 17.2, 10.8 Hz), 5.08 (1H, ddd, *J* = 11.2, 1.6, 0.4 Hz), 4.99 (1H, dd, *J* = 17.6, 1.2 Hz), 1.75–1.58 (5H, m), 1.50–1.44 (1H, m), 1.34 (3H, s), 1.25–1.01 (3H, m), 0.99–0.86 (2H, m); ^{13}C NMR (100 MHz, CDCl$_3$): δ 149.6, 145.3, 126.8, 125.0, 119.5, 112.4, 47.8, 46.1, 28.2, 28.0, 27.3, 27.2, 26.8, 20.6; HRMS (ESI+): Calcd for $C_{14}H_{21}S_1$ [M+H]$^+$: 221.1364, Found: 221.1371. Specific Rotation: $[\alpha]_D^{20}$ +1.39 (*c* 0.72, CHCl$_3$) for an enantiomerically enriched sample of 92.5:7.5 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with NaBO$_3$•4H$_2$O) in comparison with authentic racemic material (92.7:7.3 er shown; Chiralcel OD-H column, 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.811	1512039	29972	49.910	53.962
2	38.232	1517487	25571	50.090	46.038
Total		3029526	55544	100.000	100.000

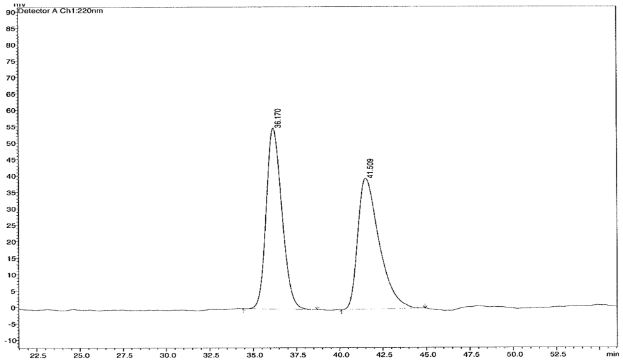


Peak#	Ret. Time	Area	Height	Area %	Height %
1	33.456	455015	9027	7.286	8.835
2	41.527	5790473	93152	92.714	91.165
Total		6245489	102179	100.000	100.000

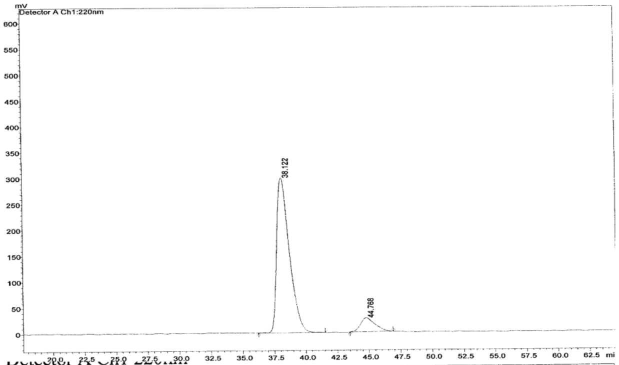
Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	31.811	49.9	1	33.456	7.3
2	38.232	50.1	2	41.527	92.7

(*R*)-2-(2-(Dimethyl(phenyl)silyl)but-3-en-2-yl)-1-methyl-1*H*-pyrrole (major isomer in endnote 16). IR (neat): 3070 (w), 2961 (w), 1617 (w), 1480 (w), 1427 (w), 1409 (w), 1294 (w), 1249 (w), 1109 (w), 1002 (w), 891 (w), 822 (m), 777 (w), 736 (w), 701 (s), 654 (w), 474 (w), 445 (w) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.55–7.52 (2H, m), 7.37–7.30 (3H, m), 6.47 (1H, dd, *J* = 2.8, 2.0 Hz), 6.10–6.03 (2H, m), 5.99 (1H, dd, *J* = 3.6, 2.8 Hz), 5.07 (1H, dd, *J* = 10.8, 1.2 Hz), 4.73 (1H, dd, *J* = 17.6, 1.2 Hz), 3.41 (3H, s), 1.50 (3H, s), 0.47 (3H, s), 0.43 (3H, s); ^{13}C NMR (100 MHz, CDCl$_3$): δ 143.2, 137.6, 135.4, 135.1, 129.1, 127.5, 123.3, 112.2, 108.4, 105.9, 36.7, 33.8, 20.6, –3.7, –3.8; HRMS (ESI+): Calcd for $C_{17}H_{24}N_1Si_1$ [M+H]$^+$: 270.1678, Found: 270.1666. Specific Rotation: $[\alpha]_D^{20}$ +41.9 (*c* 0.67, CHCl$_3$) for an enantiomerically enriched sample of 85:15 er.

Enantiomeric purity is determined by HPLC analysis of the derived primary alcohol (obtained from hydroboration of the terminal olefin with 9-BBN, followed by oxidation with NaBO$_3$•4H$_2$O) in comparison with authentic racemic material (90.7:9.3 er shown; Chiralcel OD-H column, 99/1 hexanes/*i*-PrOH, 1.0 mL/min, 220 nm).



Peak#	Ret. Time	Area	Height	Area %	Height %
1	36.170	3473016	55040	50.223	57.994
2	41.509	3442157	39866	49.777	42.006
Total		6915173	94906	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %
1	38.122	20939460	298663	90.723
2	44.768	2141304	26979	9.277
Total		23080764	325642	100.000

Peak #	Time (mins)	Area (%)	Peak #	Time (mins)	Area (%)
1	36.170	50.2	1	38.122	90.7
2	41.509	49.8	2	44.768	9.3

Quaternary Carbon Stereogenic Centers through Copper-Catalyzed Enantioselective Allylic Substitutions with Readily Accessible Aryl- and Hetero-aryllithium Reagents and Aluminum Chlorides

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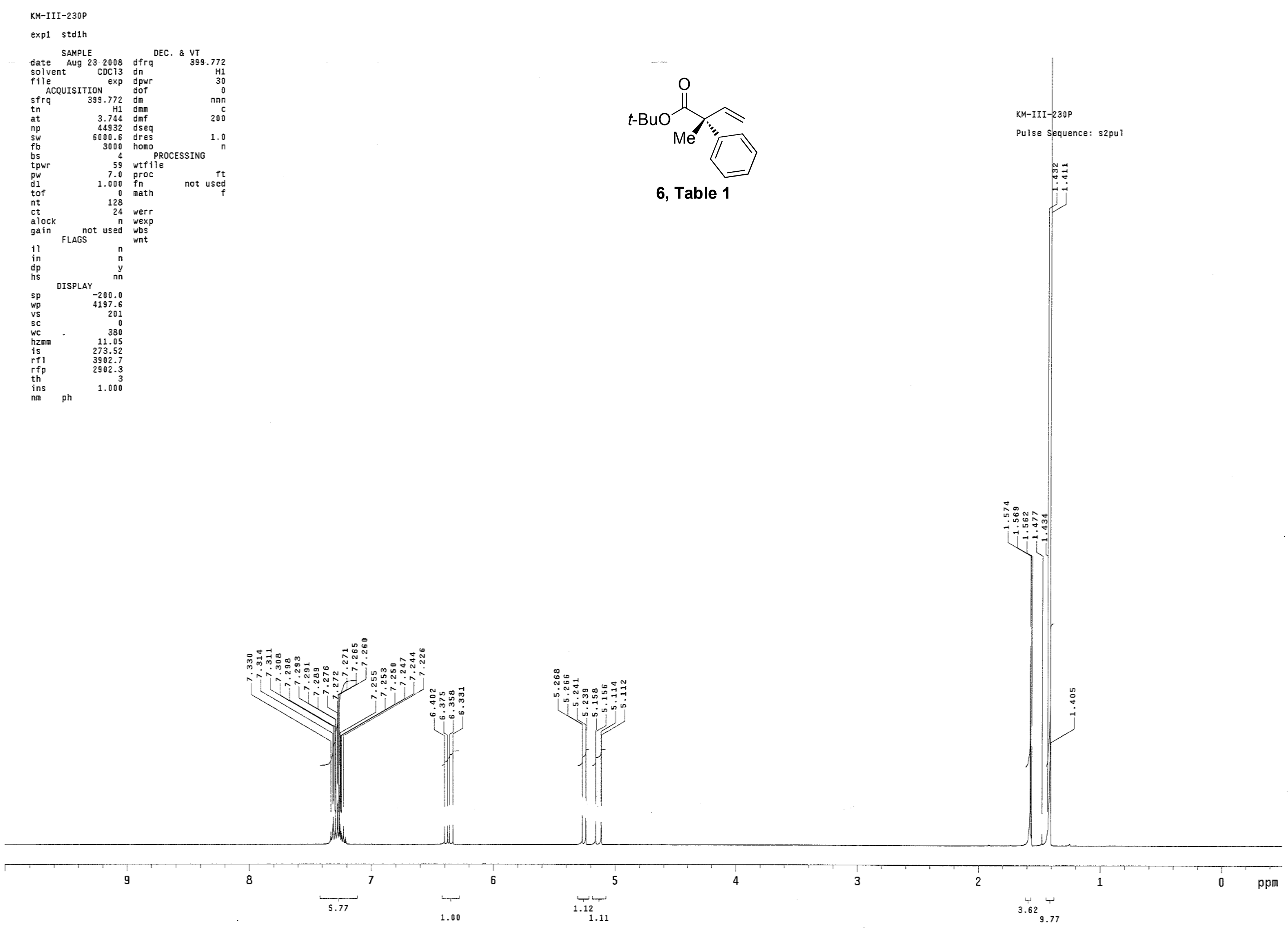
Department of Chemistry, Merkert Chemistry Center,
Boston College, Chestnut Hill, Massachusetts 02467

SUPPORTING INFORMATION, PART B

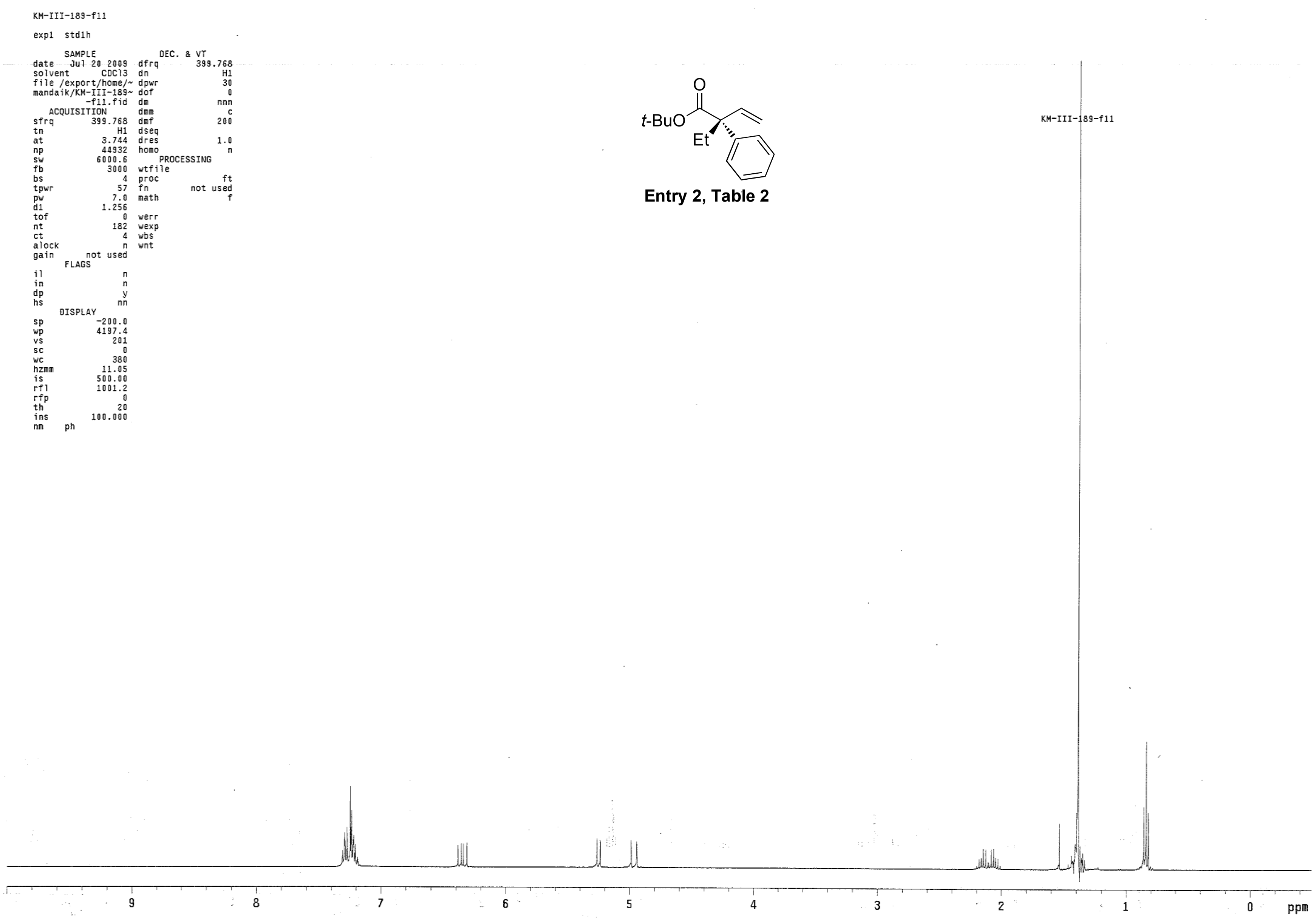


```
KM-III-230P

exp1  std1h

      SAMPLE              DEC. & VT
date   Aug 23 2008  dfrq         399.772
solvent      CDCl3  dn                H1
file           exp  dpwr              30
   ACQUISITION      dof                0
sfrq       399.772  dm               nnn
tn              H1  dmm                c
at           3.744  dmf              200
np           44932  dseq
sw          6000.6  dres             1.0
fb            3000  homo               n
bs               4      PROCESSING
tpwr            59  wtfile
pw             7.0  proc              ft
d1           1.000  fn          not used
tof              0  math               f
nt             128
ct              24  werr
alock            n  wexp
gain      not used  wbs
      FLAGS         wnt
il               n
in               n
dp               y
hs              nn
     DISPLAY
sp          -200.0
wp          4197.6
vs             201
sc               0
wc    .        380
hzmm         11.05
is          273.52
rfl         3902.7
rfp         2902.3
th               3
ins          1.000
nm    ph
```

6, Table 1



Entry 2, Table 2

```
KM-III-189-f11

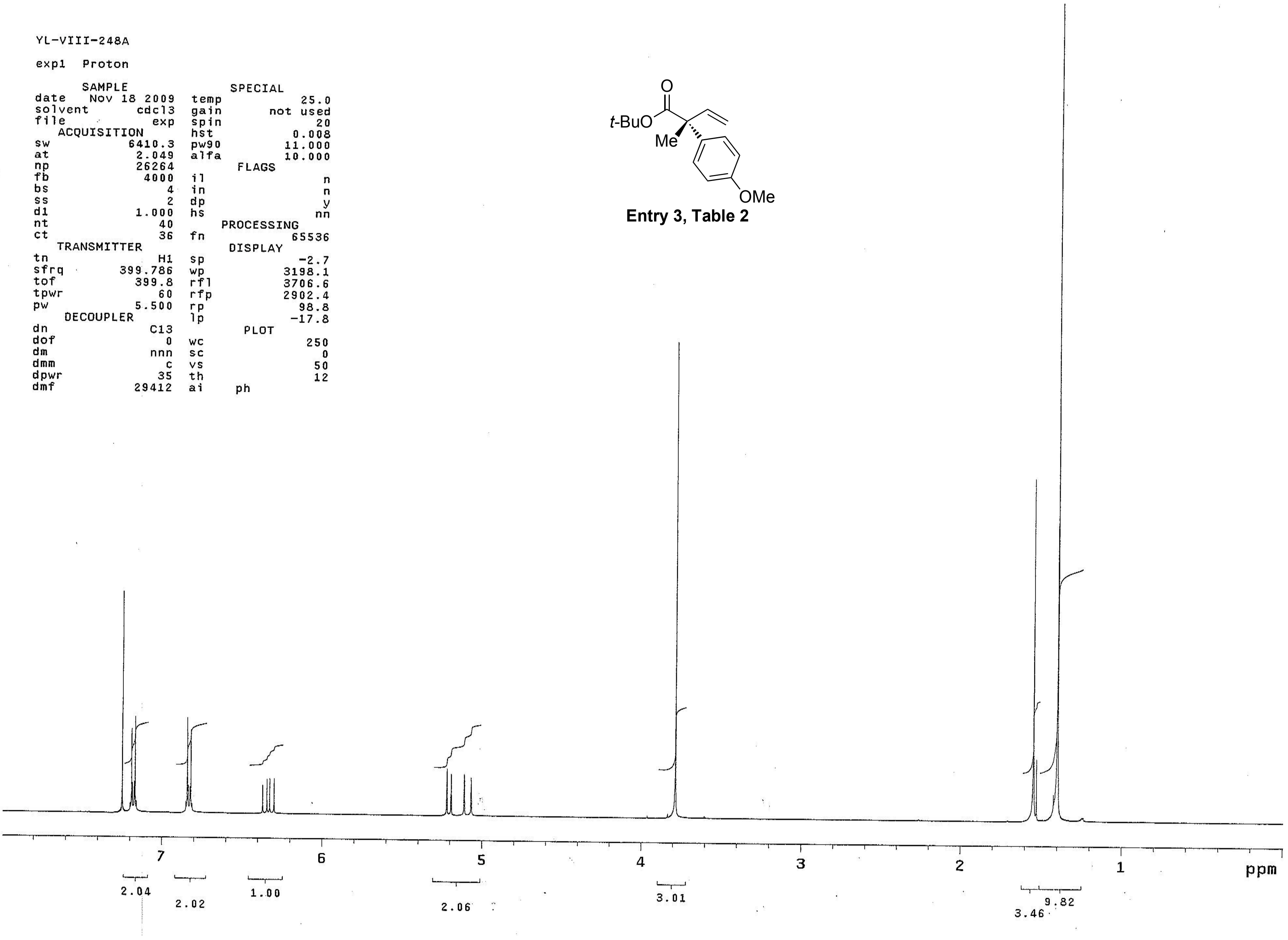
exp1  std1h

      SAMPLE           DEC. & VT
date   Jul 20 2009  dfrq       399.768
solvent       CDCl3  dn             H1
file /export/home/~  dpwr           30
mandaik/KM-III-189~  dof             0
          -f11.fid  dm             nnn
   ACQUISITION      dmm              c
sfrq       399.768  dmf            200
tn              H1  dseq
at           3.744  dres           1.0
np           44932  homo             n
sw          6000.6       PROCESSING
fb            3000  wtfile
bs               4  proc            ft
tpwr            57  fn        not used
pw             7.0  math             f
d1           1.256
tof              0  werr
nt             182  wexp
ct               4  wbs
alock            n  wnt
gain      not used
      FLAGS
il               n
in               n
dp               y
hs              nn
     DISPLAY
sp          -200.0
wp          4197.4
vs             201
sc               0
wc             380
hzmm         11.05
is          500.00
rfl         1001.2
rfp              0
th              20
ins        100.000
nm    ph
```

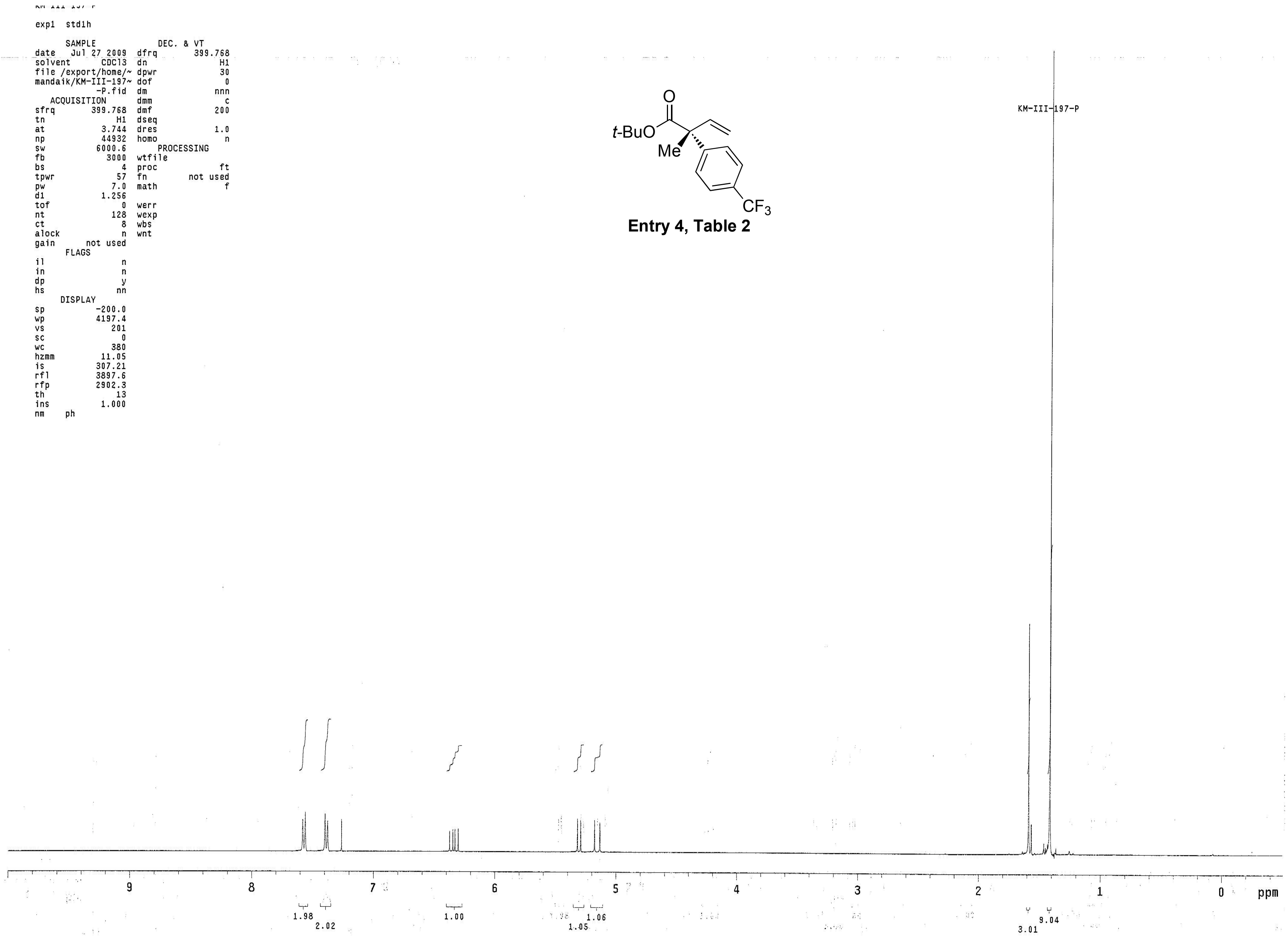
```
YL-VIII-248A

exp1  Proton

       SAMPLE                SPECIAL
date   Nov 18 2009   temp            25.0
solvent      cdcl3   gain        not used
file           exp   spin              20
   ACQUISITION       hst            0.008
sw          6410.3   pw90          11.000
at           2.049   alfa          10.000
np           26264          FLAGS
fb            4000   il                 n
bs               4   in                 n
ss               2   dp                 y
d1           1.000   hs                nn
nt              40        PROCESSING
ct              36   fn             65536
   TRANSMITTER              DISPLAY
tn              H1   sp              -2.7
sfrq       399.786   wp            3198.1
tof          399.8   rfl           3706.6
tpwr            60   rfp           2902.4
pw           5.500   rp              98.8
    DECOUPLER        lp             -17.8
dn             C13          PLOT
dof              0   wc               250
dm             nnn   sc                 0
dmm              c   vs                50
dpwr            35   th                12
dmf          29412   ai     ph
```



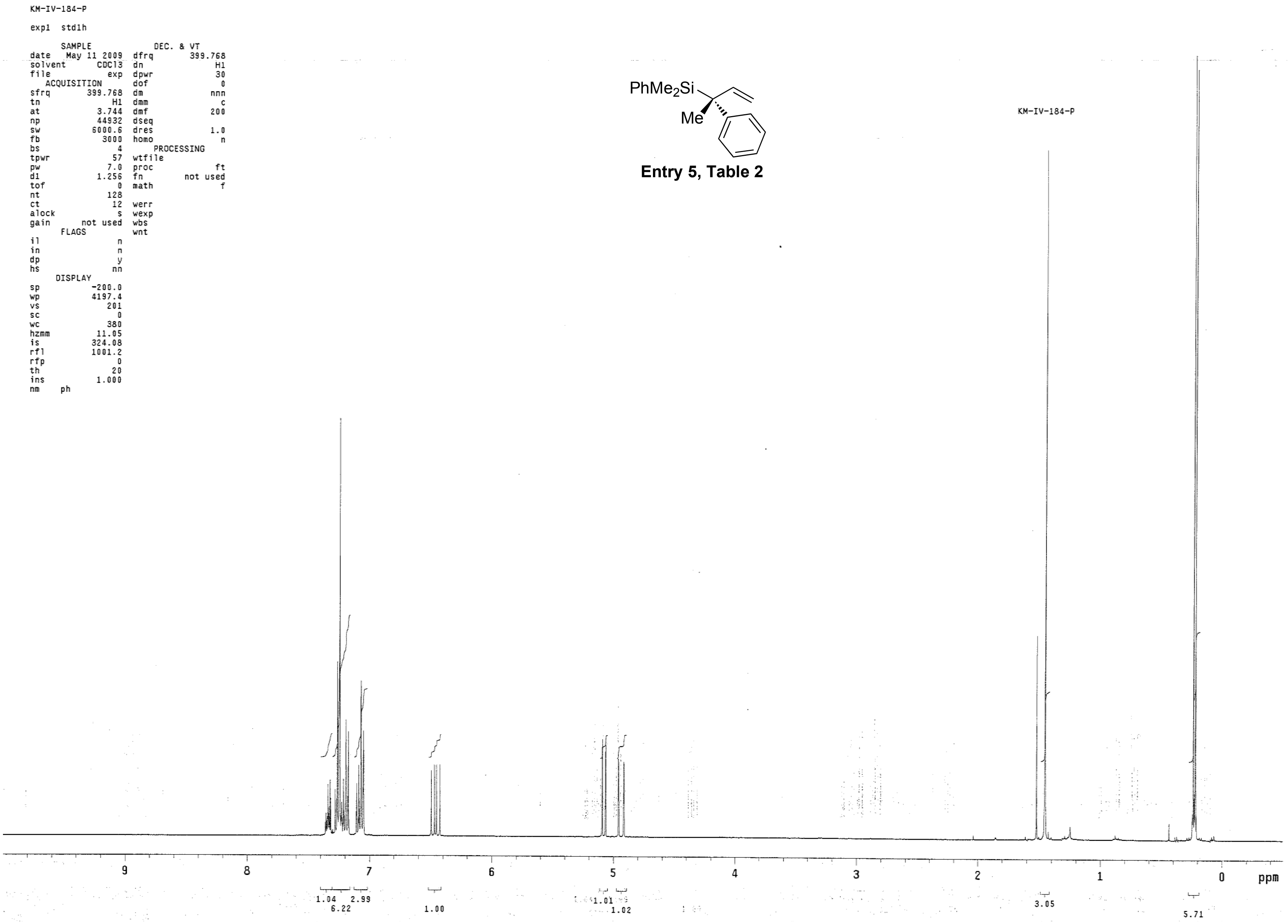
Entry 3, Table 2



```
exp1  stdlh

      SAMPLE            DEC. & VT
date   Jul 27 2009  dfrq        399.768
solvent      CDCl3  dn               H1
file /export/home/~ dpwr             30
mandaik/KM-III-197~ dof               0
            -P.fid  dm              nnn
   ACQUISITION      dmm               c
sfrq       399.768  dmf             200
tn              H1  dseq
at           3.744  dres            1.0
np           44932  homo              n
sw          6000.6      PROCESSING
fb            3000  wtfile
bs               4  proc             ft
tpwr            57  fn         not used
pw             7.0  math              f
d1           1.256
tof              0  werr
nt             128  wexp
ct               8  wbs
alock            n  wnt
gain      not used
      FLAGS
il               n
in               n
dp               y
hs              nn
     DISPLAY
sp          -200.0
wp          4197.4
vs             201
sc               0
wc             380
hzmm         11.05
is          307.21
rfl         3897.6
rfp         2902.3
th              13
ins          1.000
nm    ph
```

Entry 4, Table 2

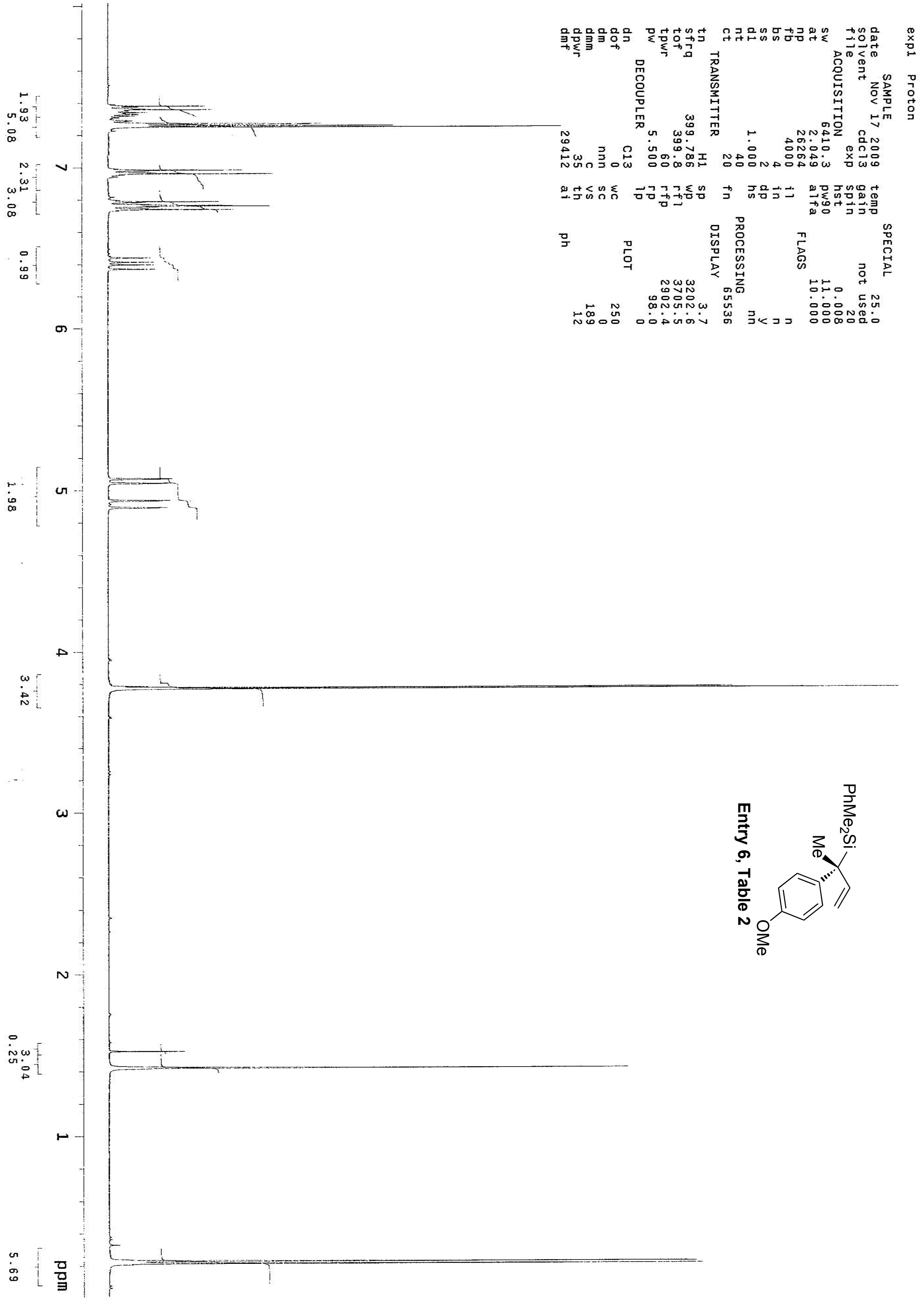


```
KM-IV-184-P

exp1  std1h

      SAMPLE             DEC. & VT
date   May 11 2009  dfrq        399.768
solvent      CDCl3  dn               H1
file           exp  dpwr             30
   ACQUISITION      dof               0
sfrq       399.768  dm              nnn
tn              H1  dmm               c
at           3.744  dmf             200
np           44932  dseq
sw          6000.6  dres            1.0
fb            3000  homo              n
bs               4      PROCESSING
tpwr            57  wtfile
pw             7.0  proc             ft
d1           1.256  fn         not used
tof              0  math              f
nt             128
ct              12  werr
alock            s  wexp
gain      not used  wbs
      FLAGS         wnt
il               n
in               n
dp               y
hs              nn
     DISPLAY
sp          -200.0
wp          4197.4
vs             201
sc               0
wc             380
hzmm         11.05
is          324.08
rfl         1001.2
rfp              0
th              20
ins          1.000
nm    ph
```

Entry 5, Table 2

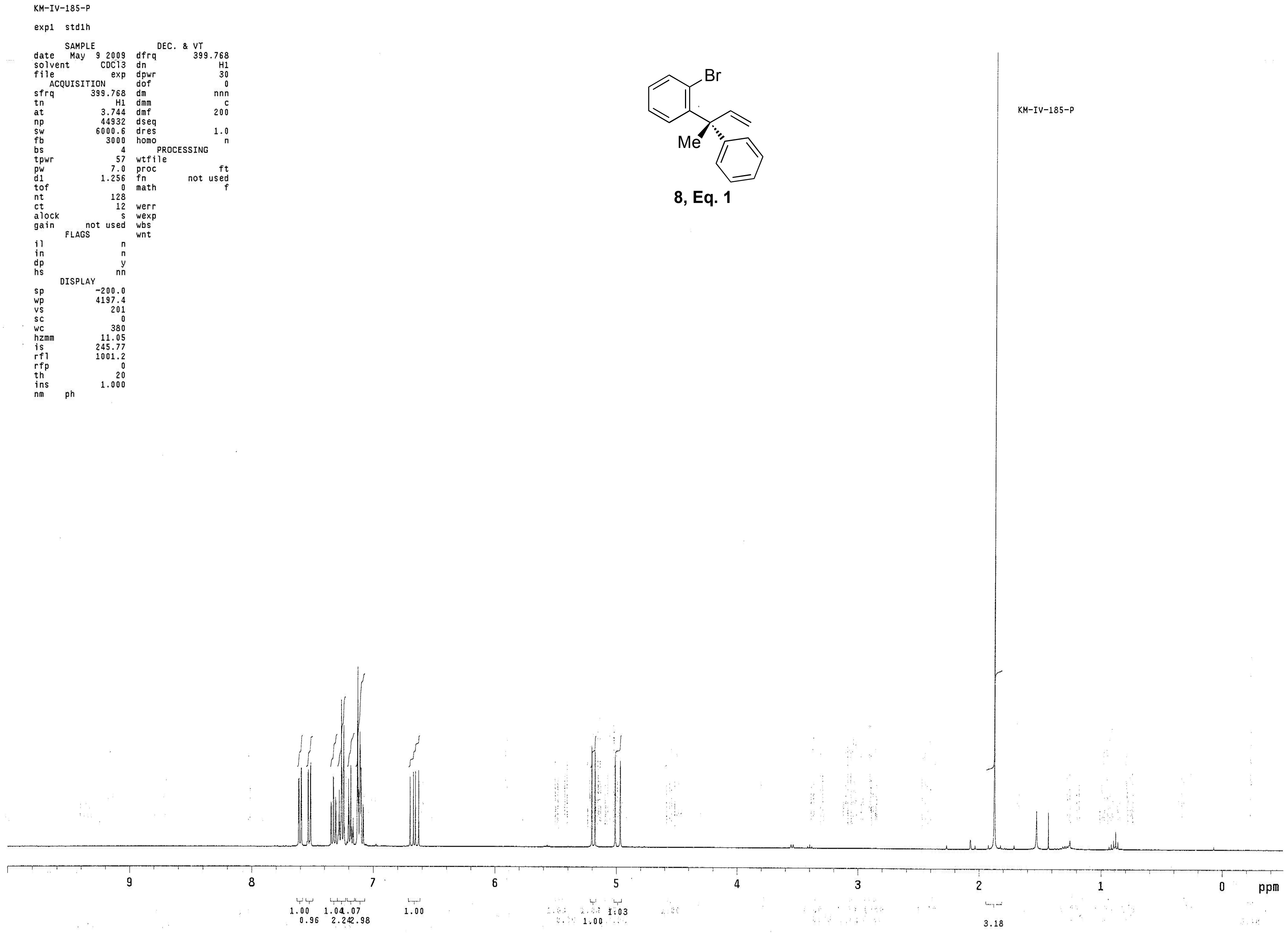


Entry 6, Table 2

```
YL-VIII-249A

exp1  Proton

        SAMPLE                  SPECIAL
date     Nov 17 2009    temp              25.0
solvent        cdcl3    gain          not used
file             exp    spin                20
    ACQUISITION         hst              0.008
sw            6410.3    pw90            11.000
at             2.049    alfa            10.000
np             26264             FLAGS
fb              4000    il                   n
bs                 4    in                   n
ss                 2    dp                   y
d1             1.000    hs                  nn
nt                40          PROCESSING
ct                20    fn               65536
    TRANSMITTER                 DISPLAY
tn                H1    sp                 3.7
sfrq         399.786    wp              3202.6
tof            399.8    rfl             3705.5
tpwr              60    rfp             2902.4
pw             5.500    rp                98.0
     DECOUPLER          lp                   0
dn               C13             PLOT
dof                0    wc                 250
dm               nnn    sc                   0
dmm                c    vs                 189
dpwr              35    th                  12
dmf            29412    ai         ph
```

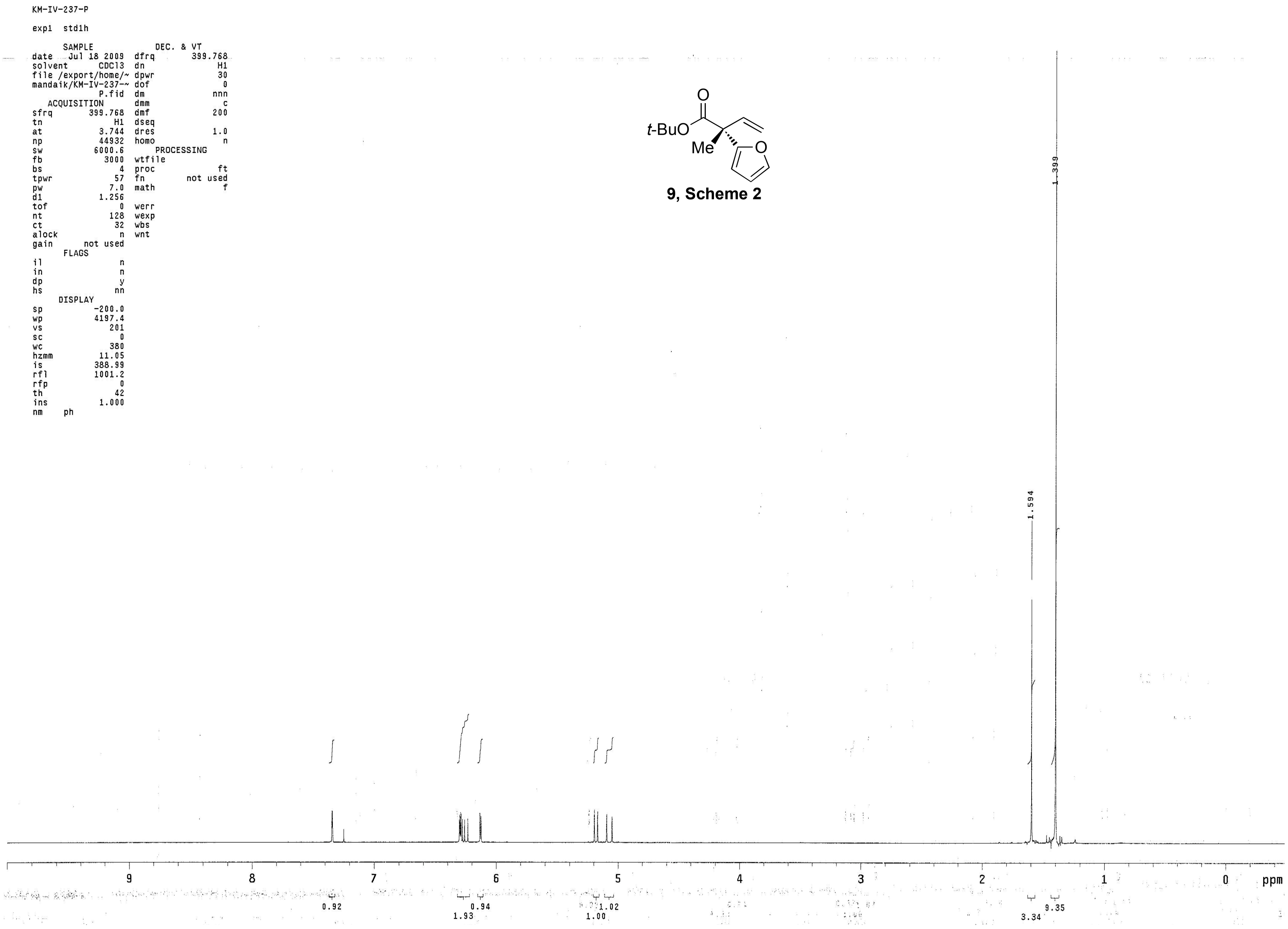


```
KM-IV-185-P

exp1  std1h

      SAMPLE              DEC. & VT
date   May  9 2009   dfrq        399.768
solvent      CDCl3   dn               H1
file           exp   dpwr             30
   ACQUISITION       dof               0
sfrq       399.768   dm              nnn
tn              H1   dmm               c
at           3.744   dmf             200
np           44932   dseq
sw          6000.6   dres            1.0
fb            3000   homo              n
bs               4       PROCESSING
tpwr            57   wtfile
pw             7.0   proc             ft
d1           1.256   fn         not used
tof              0   math              f
nt             128
ct              12   werr
alock            s   wexp
gain      not used   wbs
      FLAGS          wnt
il               n
in               n
dp               y
hs              nn
     DISPLAY
sp          -200.0
wp          4197.4
vs             201
sc               0
wc             380
hzmm         11.05
is          245.77
rfl         1001.2
rfp              0
th              20
ins          1.000
nm    ph
```

8, Eq. 1



```
KM-IV-237-P

exp1  std1h

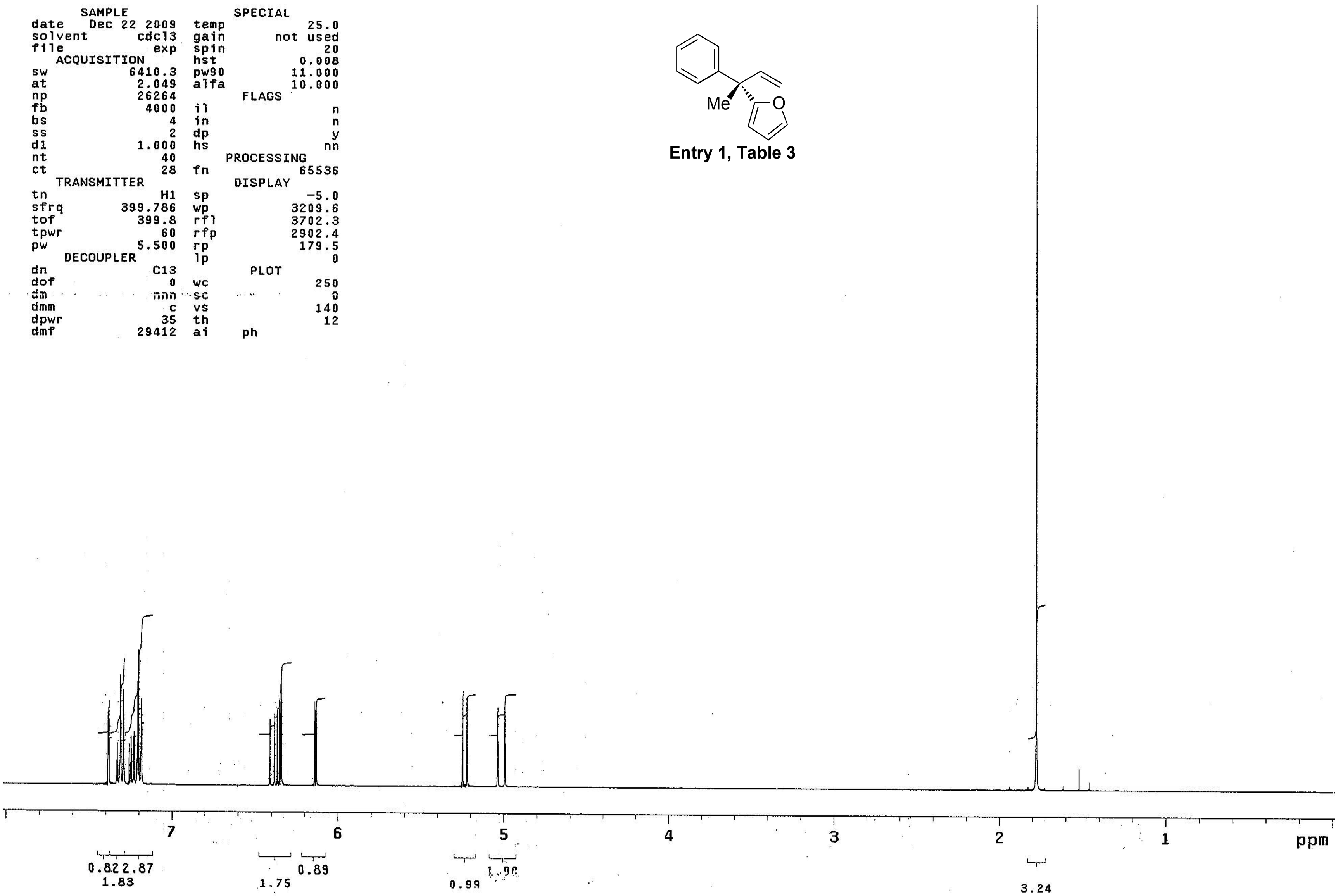
      SAMPLE            DEC. & VT
date   Jul 18 2009  dfrq       399.768
solvent       CDCl3  dn              H1
file /export/home/~  dpwr            30
mandaik/KM-IV-237-~  dof              0
              P.fid  dm             nnn
   ACQUISITION       dmm              c
sfrq        399.768  dmf            200
tn               H1  dseq
at            3.744  dres           1.0
np            44932  homo             n
sw           6000.6      PROCESSING
fb             3000  wtfile
bs                4  proc            ft
tpwr             57  fn        not used
pw              7.0  math             f
d1            1.256
tof               0  werr
nt              128  wexp
ct               32  wbs
alock             n  wnt
gain       not used
      FLAGS
il                n
in                n
dp                y
hs               nn
     DISPLAY
sp           -200.0
wp           4197.4
vs              201
sc                0
wc              380
hzmm          11.05
is           388.99
rfl          1001.2
rfp               0
th               42
ins           1.000
nm    ph
```

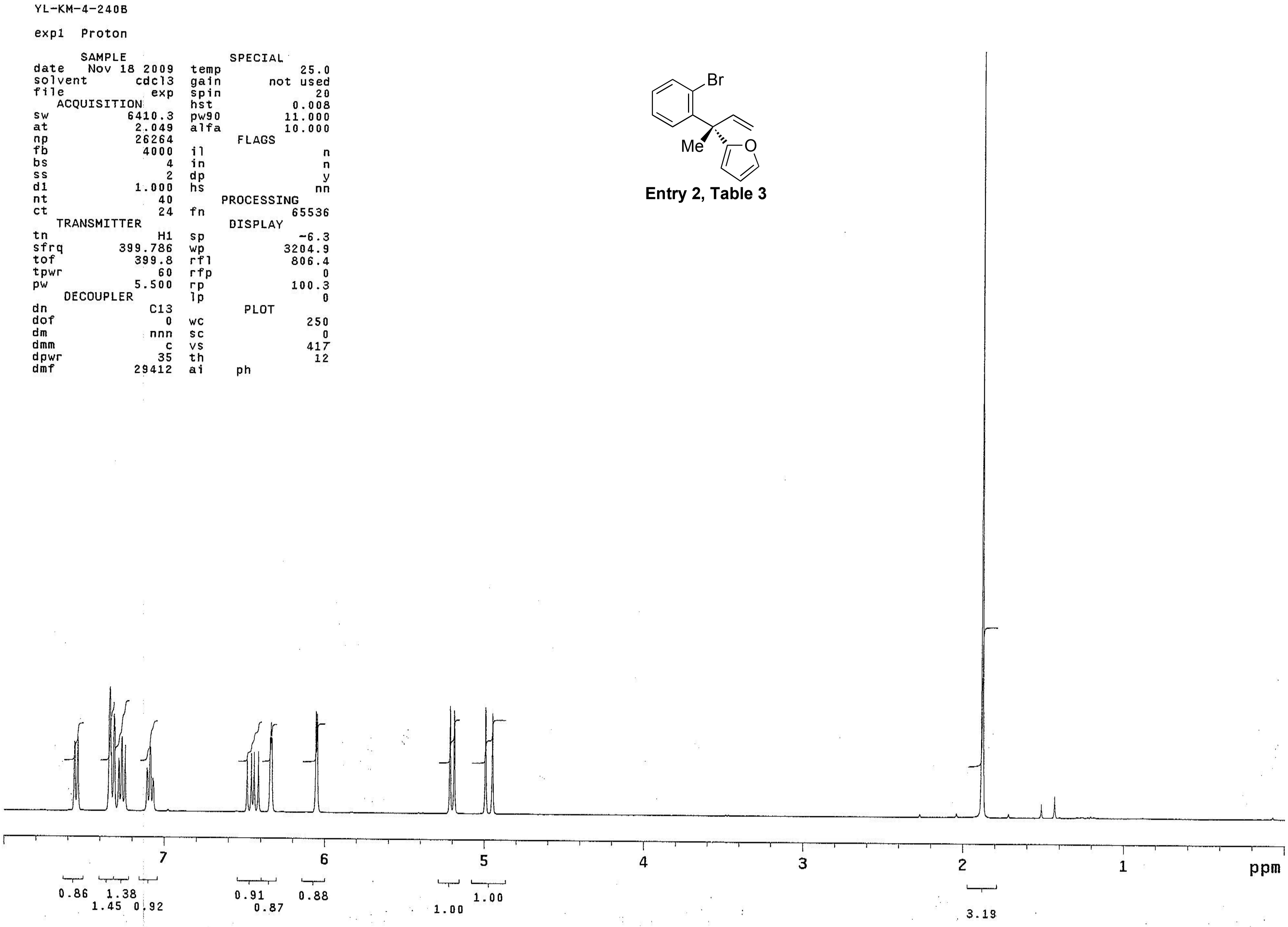
9, Scheme 2

```
YL-VIII-286A

exp26  Proton

      SAMPLE                    SPECIAL
date   Dec 22 2009  temp            25.0
solvent      cdcl3  gain        not used
file           exp  spin              20
   ACQUISITION      hst            0.008
sw          6410.3  pw90          11.000
at           2.049  alfa          10.000
np           26264            FLAGS
fb            4000  il                 n
bs               4  in                 n
ss               2  dp                 y
d1           1.000  hs                nn
nt              40          PROCESSING
ct              28  fn             65536
   TRANSMITTER                DISPLAY
tn              H1  sp              -5.0
sfrq       399.786  wp            3209.6
tof          399.8  rfl           3702.3
tpwr            60  rfp           2902.4
pw           5.500  rp             179.5
    DECOUPLER       lp                 0
dn             C13             PLOT
dof              0  wc               250
dm             nnn  sc                 0
dmm              c  vs               140
dpwr            35  th                12
dmf          29412  ai     ph
```


Entry 1, Table 3

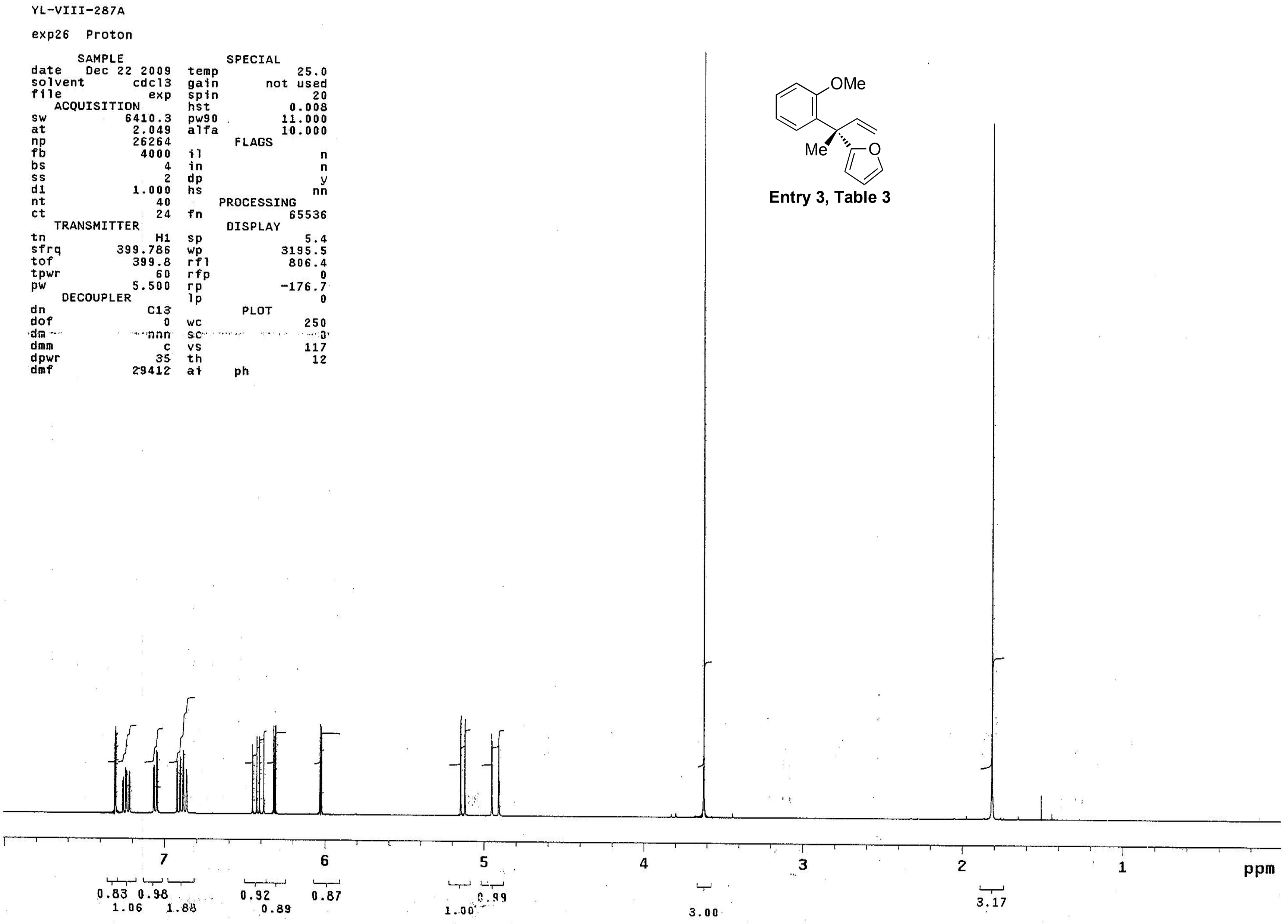


```
YL-KM-4-240B

exp1  Proton

      SAMPLE                  SPECIAL
date    Nov 18 2009   temp           25.0
solvent       cdcl3   gain       not used
file            exp   spin             20
   ACQUISITION        hst           0.008
sw           6410.3   pw90         11.000
at            2.049   alfa         10.000
np            26264            FLAGS
fb             4000   il                n
bs                4   in                n
ss                2   dp                y
d1            1.000   hs               nn
nt               40          PROCESSING
ct               24   fn            65536
   TRANSMITTER                DISPLAY
tn               H1   sp             -6.3
sfrq        399.786   wp           3204.9
tof           399.8   rfl           806.4
tpwr             60   rfp               0
pw            5.500   rp            100.3
    DECOUPLER         lp                0
dn              C13            PLOT
dof               0   wc              250
dm              nnn   sc                0
dmm               c   vs              417
dpwr             35   th               12
dmf           29412   ai     ph
```

Entry 2, Table 3

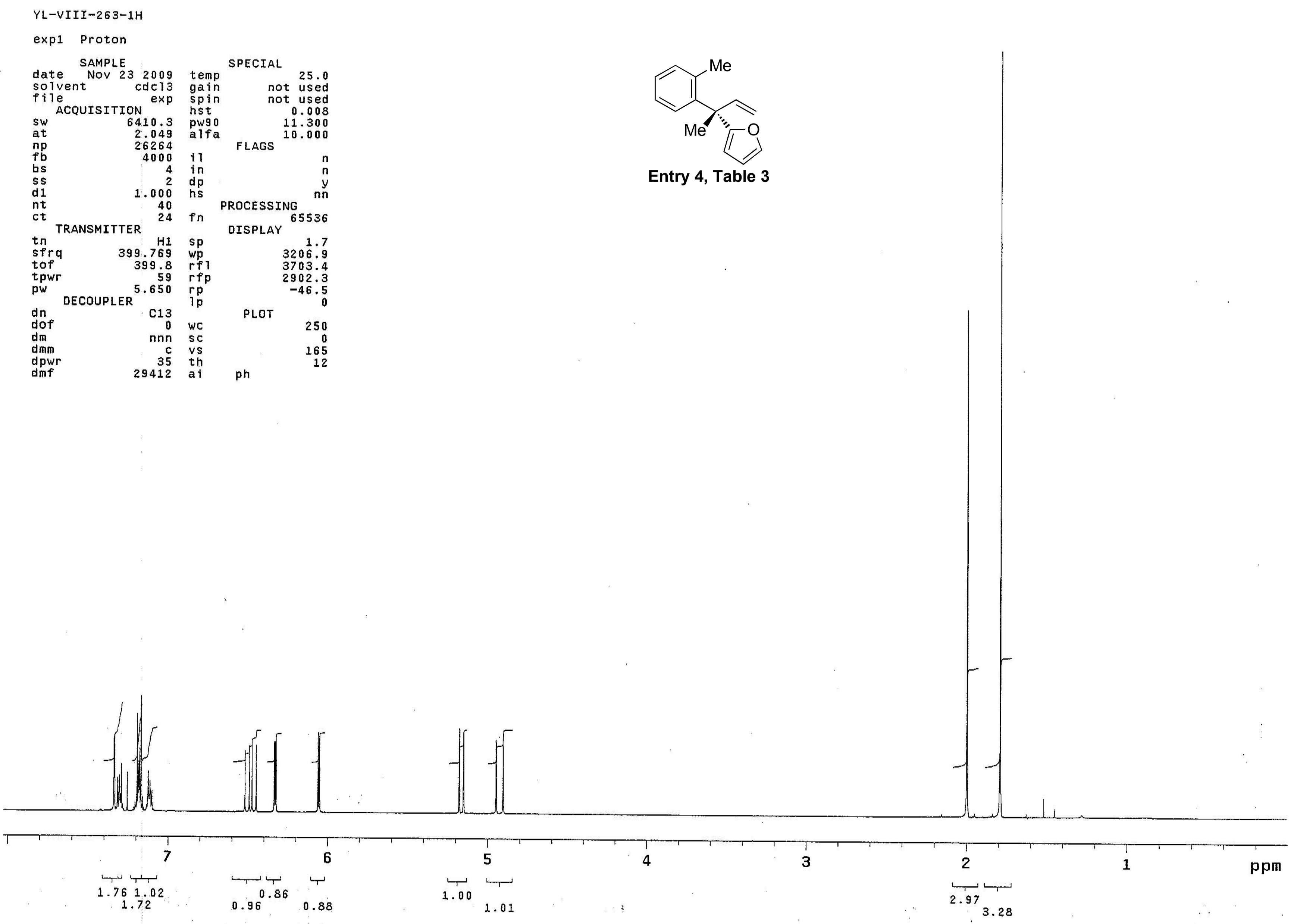


Entry 3, Table 3

```
YL-VIII-287A

exp26  Proton

      SAMPLE                SPECIAL
date   Dec 22 2009  temp            25.0
solvent       cdcl3  gain       not used
file            exp  spin             20
   ACQUISITION       hst           0.008
sw           6410.3  pw90         11.000
at            2.049  alfa         10.000
np            26264          FLAGS
fb             4000  il                n
bs                4  in                n
ss                2  dp                y
d1            1.000  hs               nn
nt               40        PROCESSING
ct               24  fn            65536
   TRANSMITTER              DISPLAY
tn               H1  sp              5.4
sfrq        399.786  wp           3195.5
tof           399.8  rfl           806.4
tpwr             60  rfp               0
pw            5.500  rp           -176.7
    DECOUPLER        lp                0
dn              C13          PLOT
dof               0  wc              250
dm              nnn  sc                0
dmm               c  vs              117
dpwr             35  th               12
dmf           29412  ai    ph
```



```
YL-VIII-263-1H

exp1  Proton

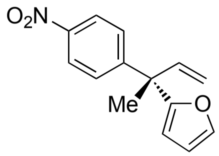
      SAMPLE                SPECIAL
date   Nov 23 2009   temp             25.0
solvent       cdcl3  gain         not used
file            exp  spin         not used
   ACQUISITION       hst             0.008
sw           6410.3  pw90           11.300
at            2.049  alfa           10.000
np            26264           FLAGS
fb             4000  il                  n
bs                4  in                  n
ss                2  dp                  y
d1            1.000  hs                 nn
nt               40         PROCESSING
ct               24  fn              65536
   TRANSMITTER               DISPLAY
tn               H1  sp                1.7
sfrq        399.769  wp             3206.9
tof           399.8  rfl            3703.4
tpwr             59  rfp            2902.3
pw            5.650  rp              -46.5
    DECOUPLER        lp                  0
dn              C13           PLOT
dof               0  wc                250
dm              nnn  sc                  0
dmm               c  vs                165
dpwr             35  th                 12
dmf           29412  ai     ph
```

Entry 4, Table 3

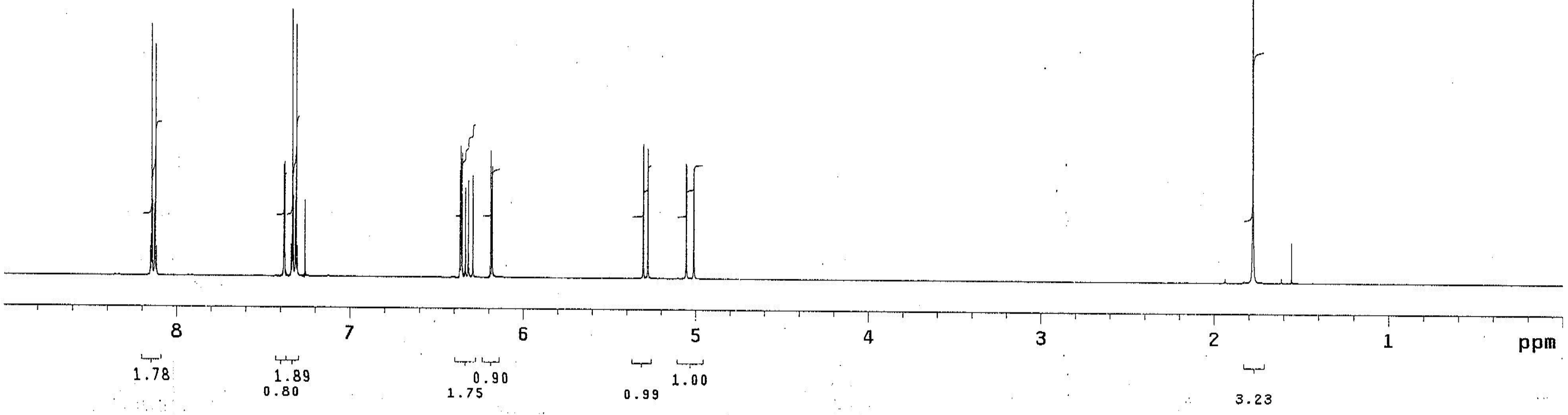
```
YL-VIII-268B

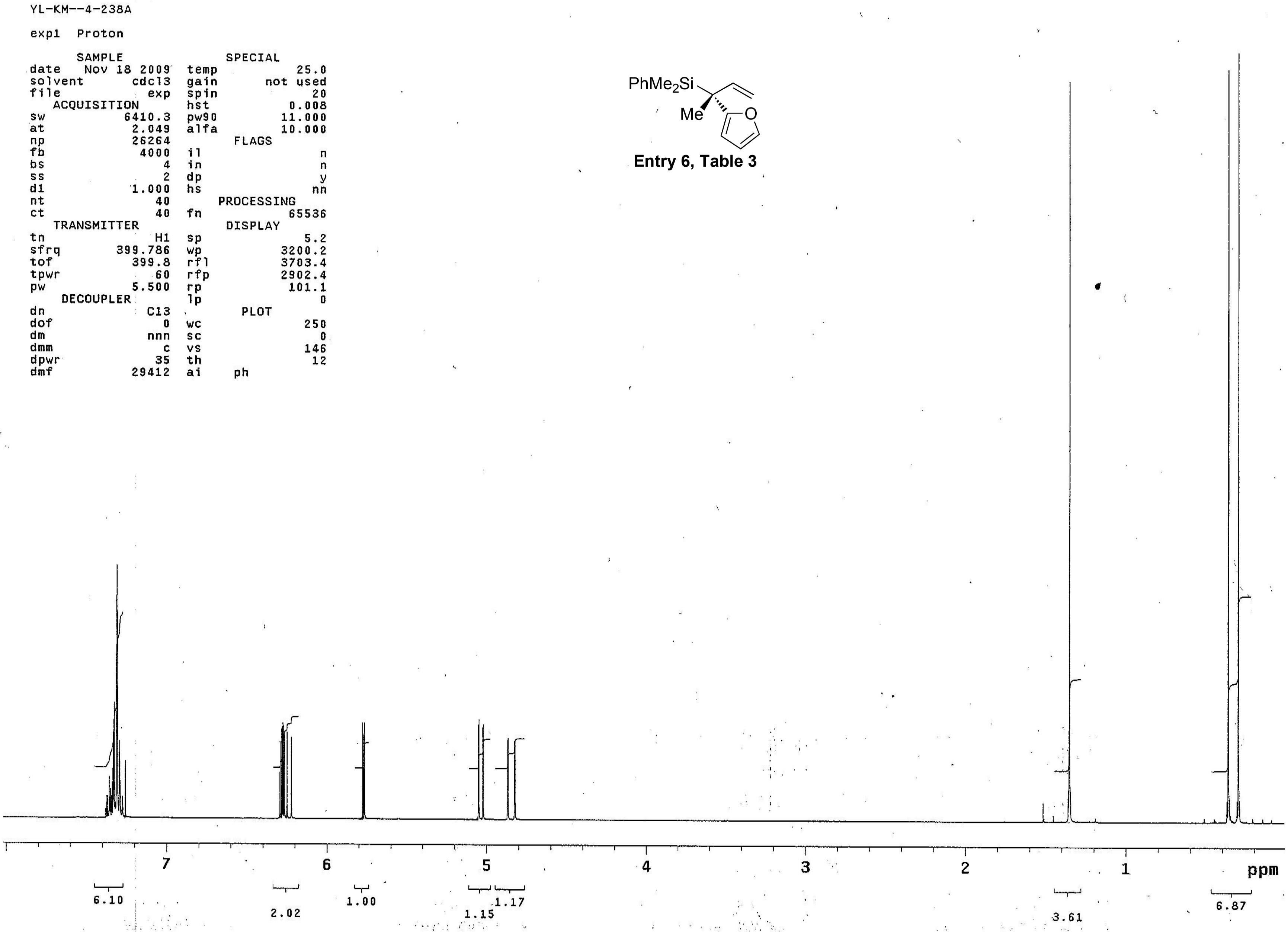
exp145  Proton

      SAMPLE               SPECIAL
date   Nov 25 2009  temp         25.0
solvent      cdcl3  gain     not used
file           exp  spin           20
   ACQUISITION      hst         0.008
sw          6410.3  pw90       11.000
at           2.049  alfa       10.000
np           26264         FLAGS
fb            4000  il              n
bs               4  in              n
ss               2  dp              y
d1           1.000  hs             nn
nt              40       PROCESSING
ct              24  fn          65536
   TRANSMITTER             DISPLAY
tn              H1  sp           -1.4
sfrq       399.786  wp         3597.2
tof          399.8  rfl        3702.7
tpwr            60  rfp        2902.4
pw           5.500  rp          143.8
   DECOUPLER        lp              0
dn             C13          PLOT
dof              0  wc            250
dm             nnn  sc              0
dmm              c  vs            167
dpwr            35  th             12
dmf          29412  ai     ph
```



Entry 5, Table 3



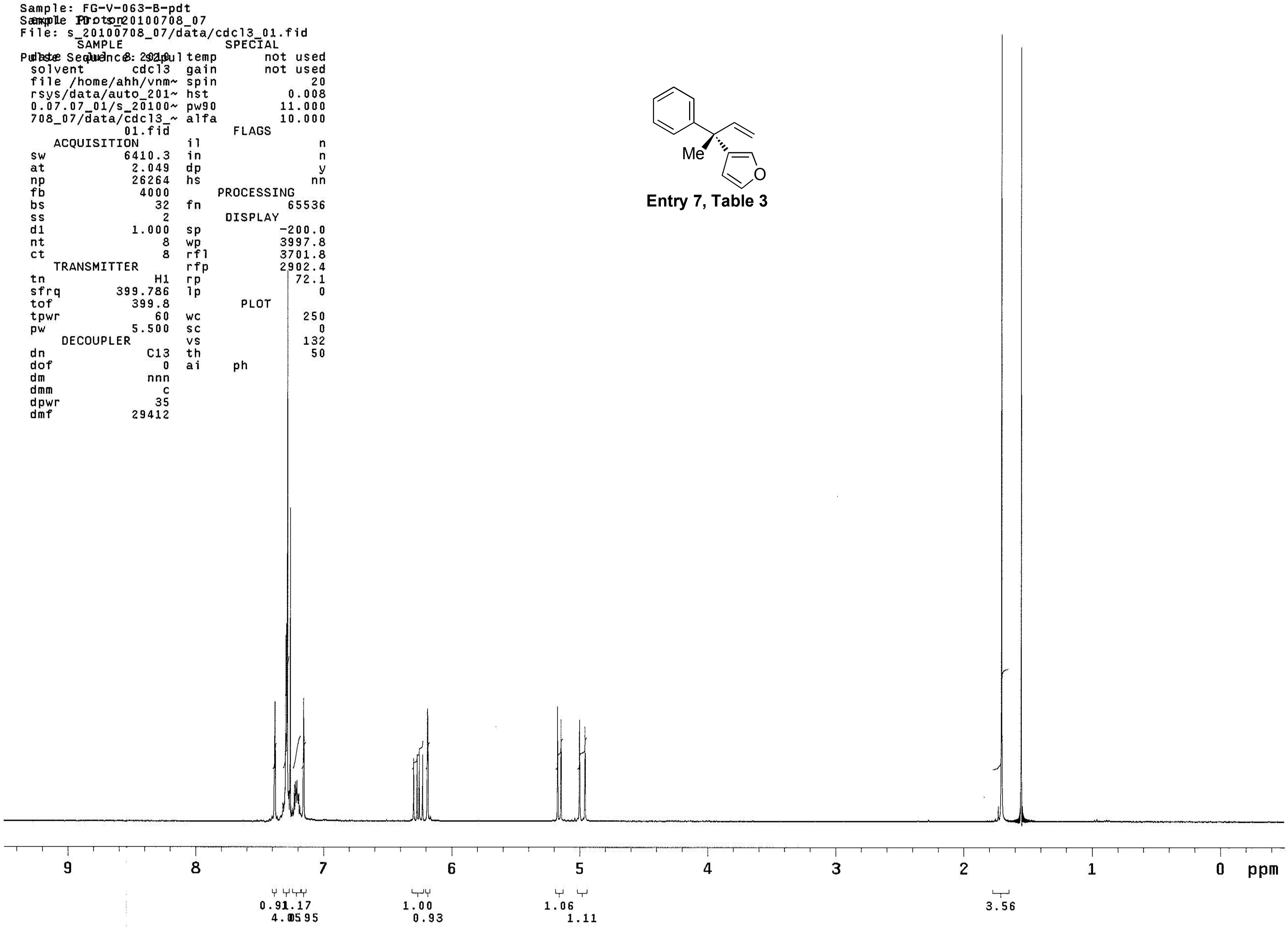


```
YL-KM--4-238A

exp1  Proton

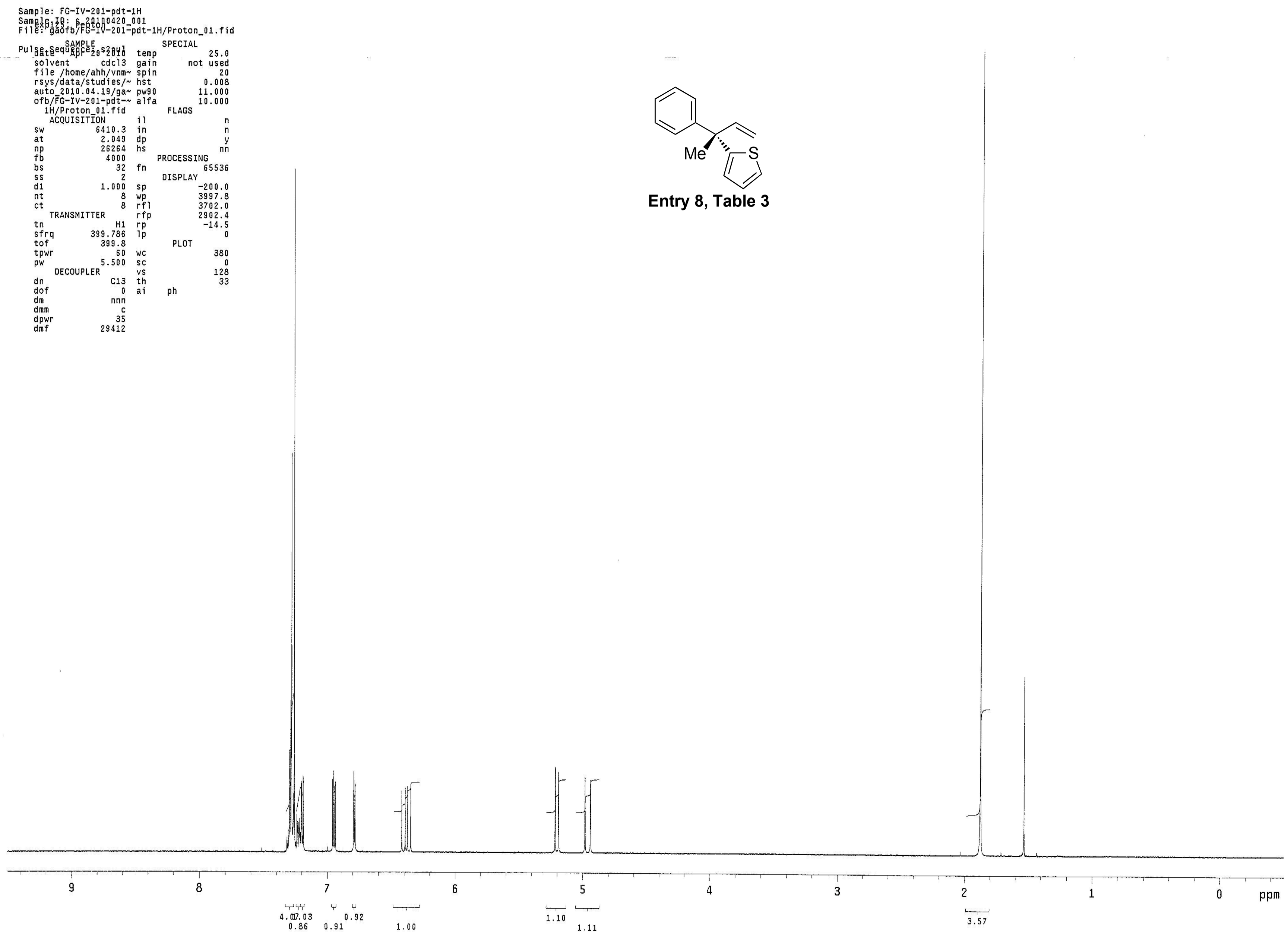
      SAMPLE              SPECIAL
date   Nov 18 2009  temp          25.0
solvent      cdcl3  gain      not used
file           exp  spin            20
   ACQUISITION      hst          0.008
sw          6410.3  pw90        11.000
at           2.049  alfa        10.000
np           26264          FLAGS
fb            4000  il               n
bs               4  in               n
ss               2  dp               y
d1           1.000  hs              nn
nt              40        PROCESSING
ct              40  fn           65536
   TRANSMITTER              DISPLAY
tn              H1  sp             5.2
sfrq       399.786  wp          3200.2
tof          399.8  rfl         3703.4
tpwr            60  rfp         2902.4
pw           5.500  rp           101.1
    DECOUPLER       lp               0
dn             C13          PLOT
dof              0  wc             250
dm             nnn  sc               0
dmm              c  vs             146
dpwr            35  th              12
dmf          29412  ai    ph
```

Entry 6, Table 3



```
Sample: FG-V-063-B-pdt
exp1  Proton
Sample: s_20100708_07
File: s_20100708_07/data/cdcl3_01.fid
        SAMPLE                  SPECIAL
date     Jul  8 2010  temp        not used
Pulse Sequence: s2pul
 solvent       cdcl3  gain        not used
 file /home/ahh/vnm~  spin              20
 rsys/data/auto_201~  hst            0.008
 0.07.07_01/s_20100~  pw90          11.000
 708_07/data/cdcl3_~  alfa          10.000
            01.fid            FLAGS
    ACQUISITION       il                 n
 sw           6410.3  in                 n
 at            2.049  dp                 y
 np            26264  hs                nn
 fb             4000        PROCESSING
 bs               32  fn             65536
 ss                2          DISPLAY
 d1            1.000  sp            -200.0
 nt                8  wp            3997.8
 ct                8  rfl           3701.8
    TRANSMITTER       rfp           2902.4
 tn               H1  rp              72.1
 sfrq        399.786  lp                 0
 tof           399.8           PLOT
 tpwr             60  wc               250
 pw            5.500  sc                 0
    DECOUPLER         vs               132
 dn              C13  th                50
 dof               0  ai      ph
 dm              nnn
 dmm               c
 dpwr             35
 dmf           29412
```

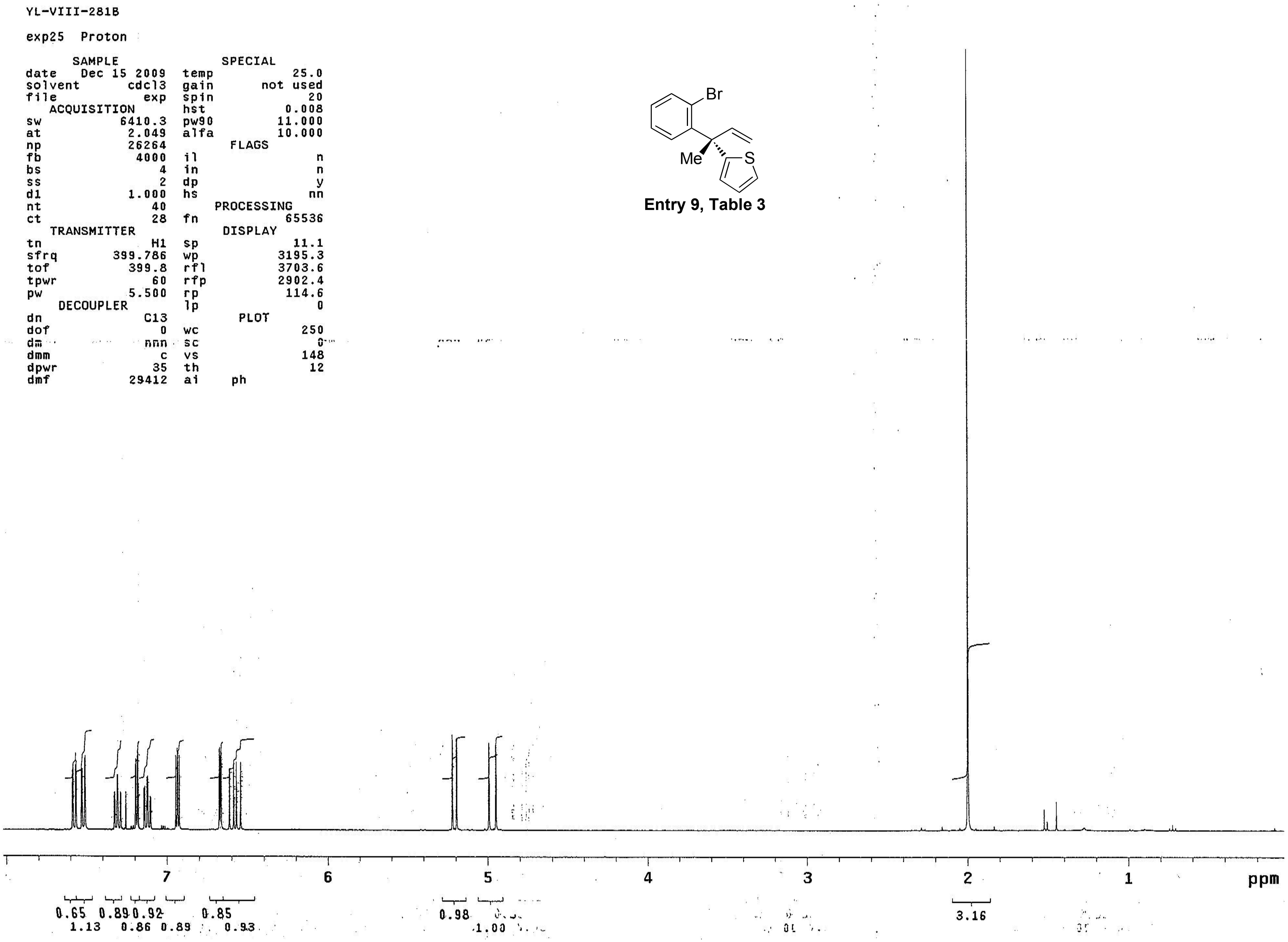
Entry 7, Table 3



```
Sample: FG-IV-201-pdt-1H
Sample ID: s_20100420_001
exp125: Proton
File: gaofb/FG-IV-201-pdt-1H/Proton_01.fid

Pulse Sequence: s2pul
        SAMPLE              SPECIAL
  date    Apr 20 2010  temp              25.0
  solvent       cdcl3  gain          not used
  file /home/ahh/vnm~  spin                20
  rsys/data/studies/~  hst              0.008
  auto_2010.04.19/ga~  pw90            11.000
  ofb/FG-IV-201-pdt-~  alfa            10.000
    1H/Proton_01.fid          FLAGS
      ACQUISITION      il                   n
  sw           6410.3  in                   n
  at            2.049  dp                   y
  np            26264  hs                  nn
  fb             4000         PROCESSING
  bs               32  fn               65536
  ss                2          DISPLAY
  d1            1.000  sp              -200.0
  nt                8  wp              3997.8
  ct                8  rfl             3702.0
      TRANSMITTER      rfp             2902.4
  tn               H1  rp               -14.5
  sfrq        399.786  lp                   0
  tof           399.8            PLOT
  tpwr             60  wc                 380
  pw            5.500  sc                   0
       DECOUPLER       vs                 128
  dn              C13  th                  33
  dof               0  ai     ph
  dm              nnn
  dmm               c
  dpwr             35
  dmf           29412
```

Entry 8, Table 3



```
YL-VIII-281B

exp25  Proton

      SAMPLE               SPECIAL
date   Dec 15 2009  temp           25.0
solvent      cdcl3  gain       not used
file           exp  spin             20
   ACQUISITION      hst           0.008
sw          6410.3  pw90         11.000
at           2.049  alfa         10.000
np           26264           FLAGS
fb            4000  il                n
bs               4  in                n
ss               2  dp                y
d1           1.000  hs               nn
nt              40        PROCESSING
ct              28  fn            65536
   TRANSMITTER             DISPLAY
tn              H1  sp             11.1
sfrq       399.786  wp           3195.3
tof          399.8  rfl          3703.6
tpwr            60  rfp          2902.4
pw           5.500  rp            114.6
    DECOUPLER       lp                0
dn             C13            PLOT
dof              0  wc              250
dm             nnn  sc                0
dmm              c  vs              148
dpwr            35  th               12
dmf          29412  ai     ph
```

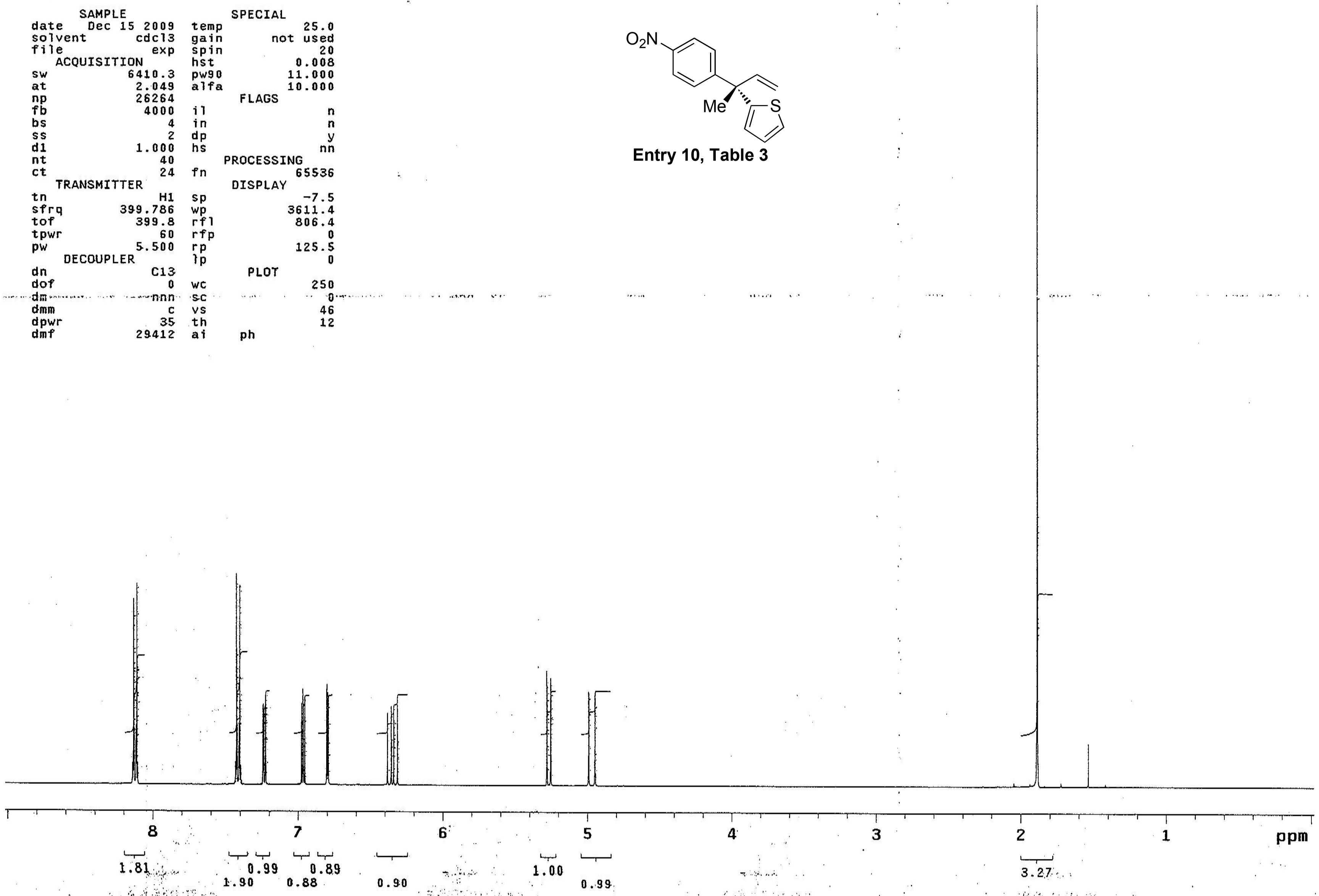
Entry 9, Table 3

```
YL-VIII-283A

exp25  Proton

      SAMPLE              SPECIAL
date   Dec 15 2009  temp           25.0
solvent      cdcl3  gain       not used
file           exp  spin             20
   ACQUISITION      hst           0.008
sw          6410.3  pw90         11.000
at           2.049  alfa         10.000
np           26264           FLAGS
fb            4000  il                n
bs               4  in                n
ss               2  dp                y
d1           1.000  hs               nn
nt              40         PROCESSING
ct              24  fn            65536
   TRANSMITTER             DISPLAY
tn              H1  sp             -7.5
sfrq       399.786  wp           3611.4
tof          399.8  rfl           806.4
tpwr            60  rfp               0
pw           5.500  rp            125.5
    DECOUPLER       lp                0
dn             C13           PLOT
dof              0  wc              250
dm             nnn  sc                0
dmm              c  vs               46
dpwr            35  th               12
dmf          29412  ai     ph
```

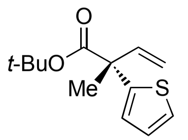
Entry 10, Table 3



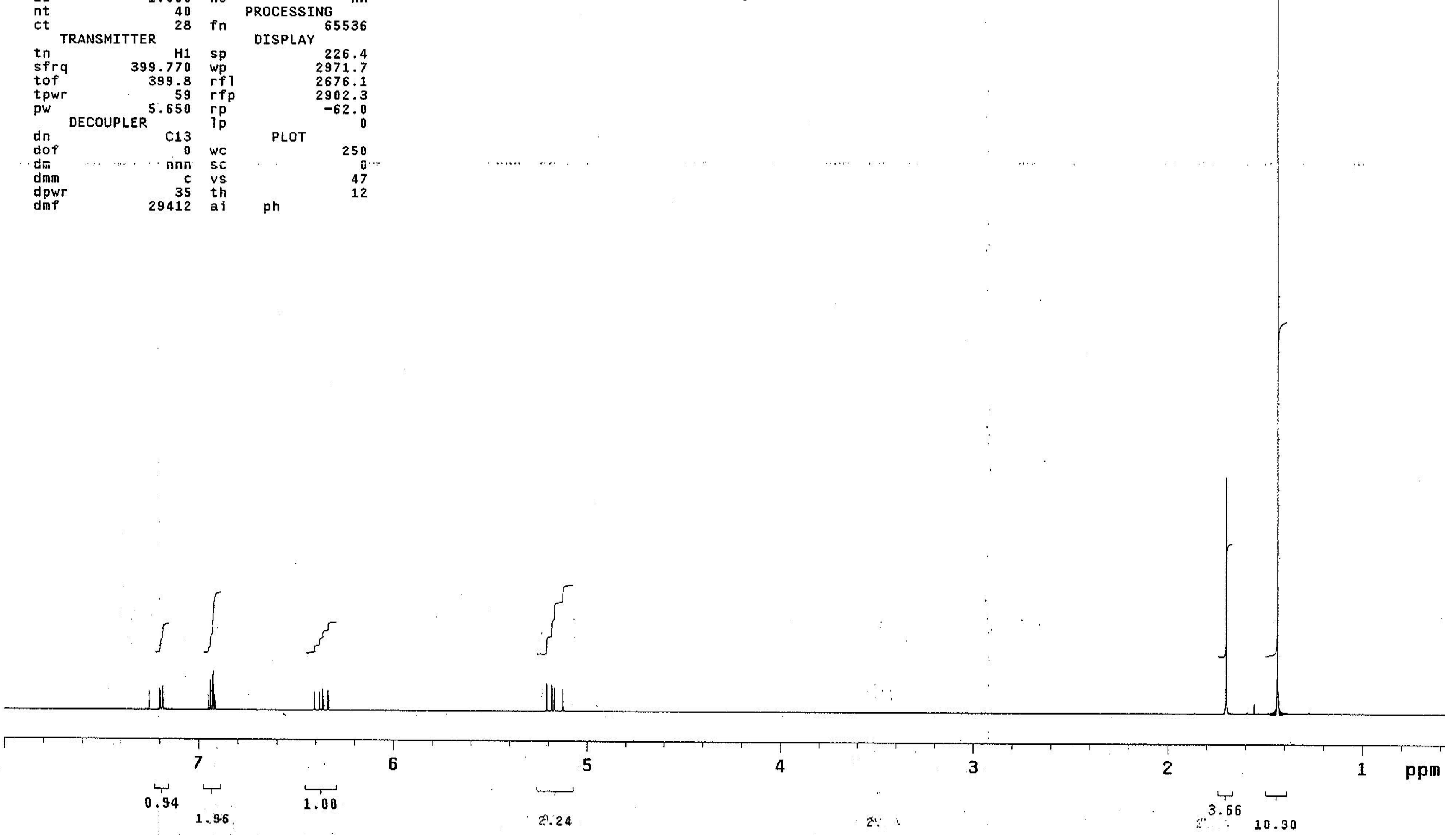
```
YL-VIII-280A

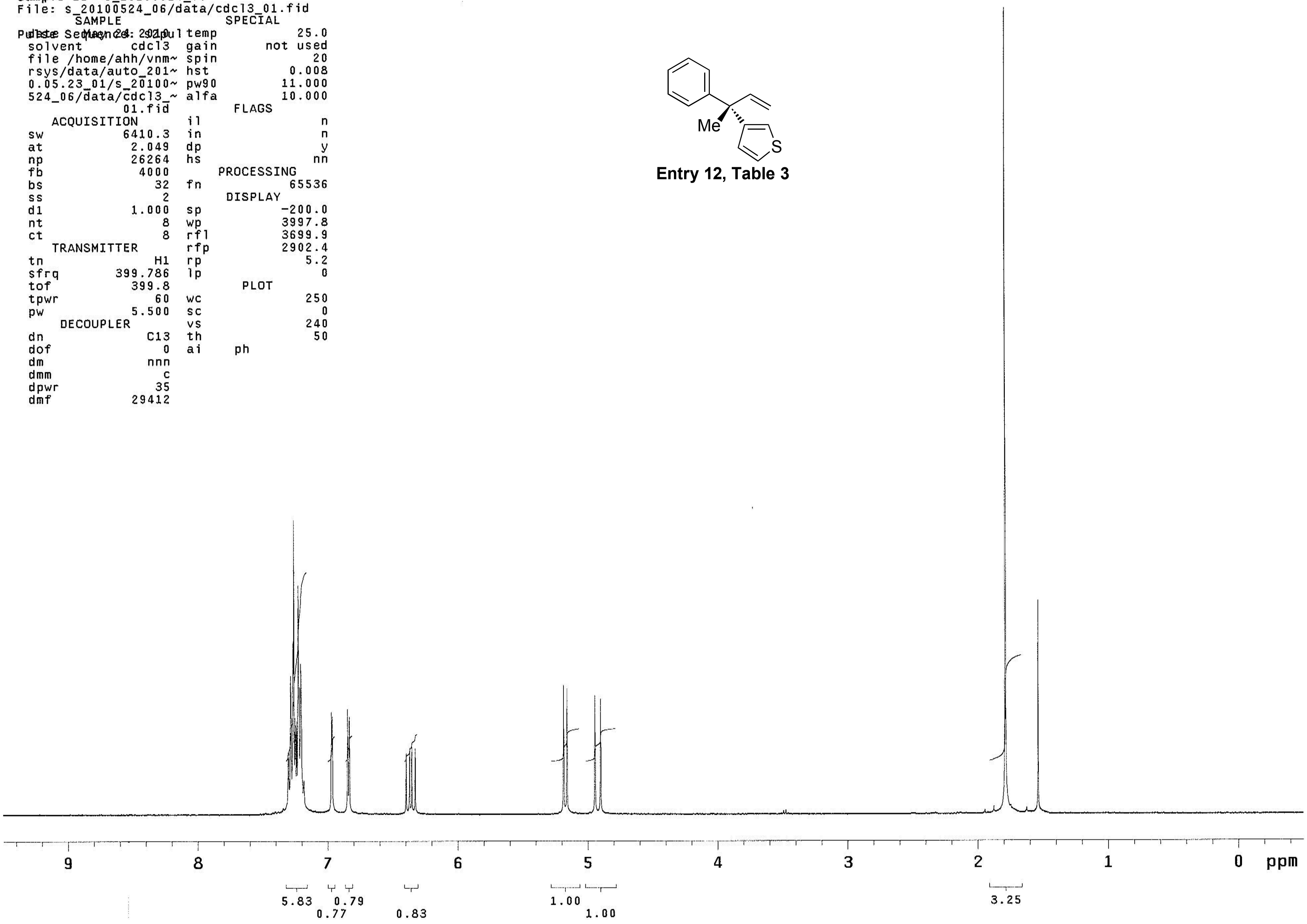
exp1  Proton

      SAMPLE              SPECIAL
date   Dec 11 2009  temp          25.0
solvent        d2o  gain      not used
file           exp  spin      not used
   ACQUISITION      hst          0.008
sw          6410.3  pw90        11.300
at           2.049  alfa        10.000
np           26264          FLAGS
fb            4000  il               n
bs               4  in               n
ss               2  dp               y
d1           1.000  hs              nn
nt              40        PROCESSING
ct              28  fn           65536
   TRANSMITTER            DISPLAY
tn              H1  sp           226.4
sfrq       399.770  wp          2971.7
tof          399.8  rfl         2676.1
tpwr            59  rfp         2902.3
pw           5.650  rp           -62.0
    DECOUPLER       lp               0
dn             C13          PLOT
dof              0  wc             250
dm             nnn  sc               0
dmm              c  vs              47
dpwr            35  th              12
dmf          29412  ai    ph
```



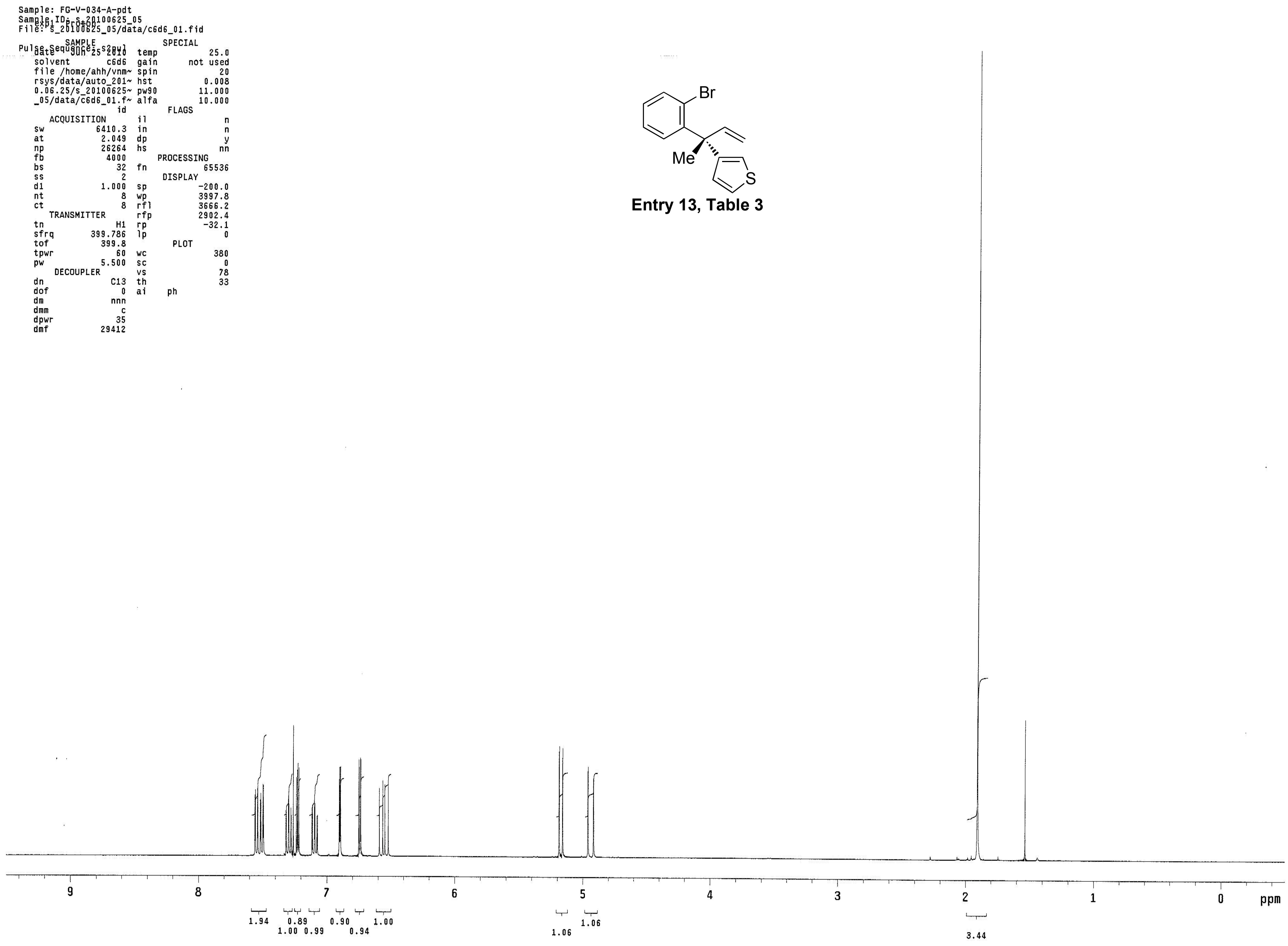
Entry 11, Table 3





```
Sample: FG-IV-287-pdt1
Sample ID: s_20100524_06
expt Proton
File: s_20100524_06/data/cdcl3_01.fid
        SAMPLE                  SPECIAL
Pulse Sequence: s2pul
date    May 24 2010   temp             25.0
 solvent       cdcl3  gain         not used
 file /home/ahh/vnm~  spin               20
 rsys/data/auto_201~  hst             0.008
 0.05.23_01/s_20100~  pw90           11.000
 524_06/data/cdcl3_~  alfa           10.000
            01.fid             FLAGS
   ACQUISITION        il                  n
 sw           6410.3  in                  n
 at            2.049  dp                  y
 np            26264  hs                 nn
 fb             4000        PROCESSING
 bs               32  fn              65536
 ss                2          DISPLAY
 d1            1.000  sp             -200.0
 nt                8  wp             3997.8
 ct                8  rfl            3699.9
   TRANSMITTER        rfp            2902.4
 tn               H1  rp                5.2
 sfrq        399.786  lp                  0
 tof           399.8          PLOT
 tpwr             60  wc                250
 pw            5.500  sc                  0
     DECOUPLER        vs                240
 dn              C13  th                 50
 dof               0  ai     ph
 dm              nnn
 dmm               c
 dpwr             35
 dmf           29412
```

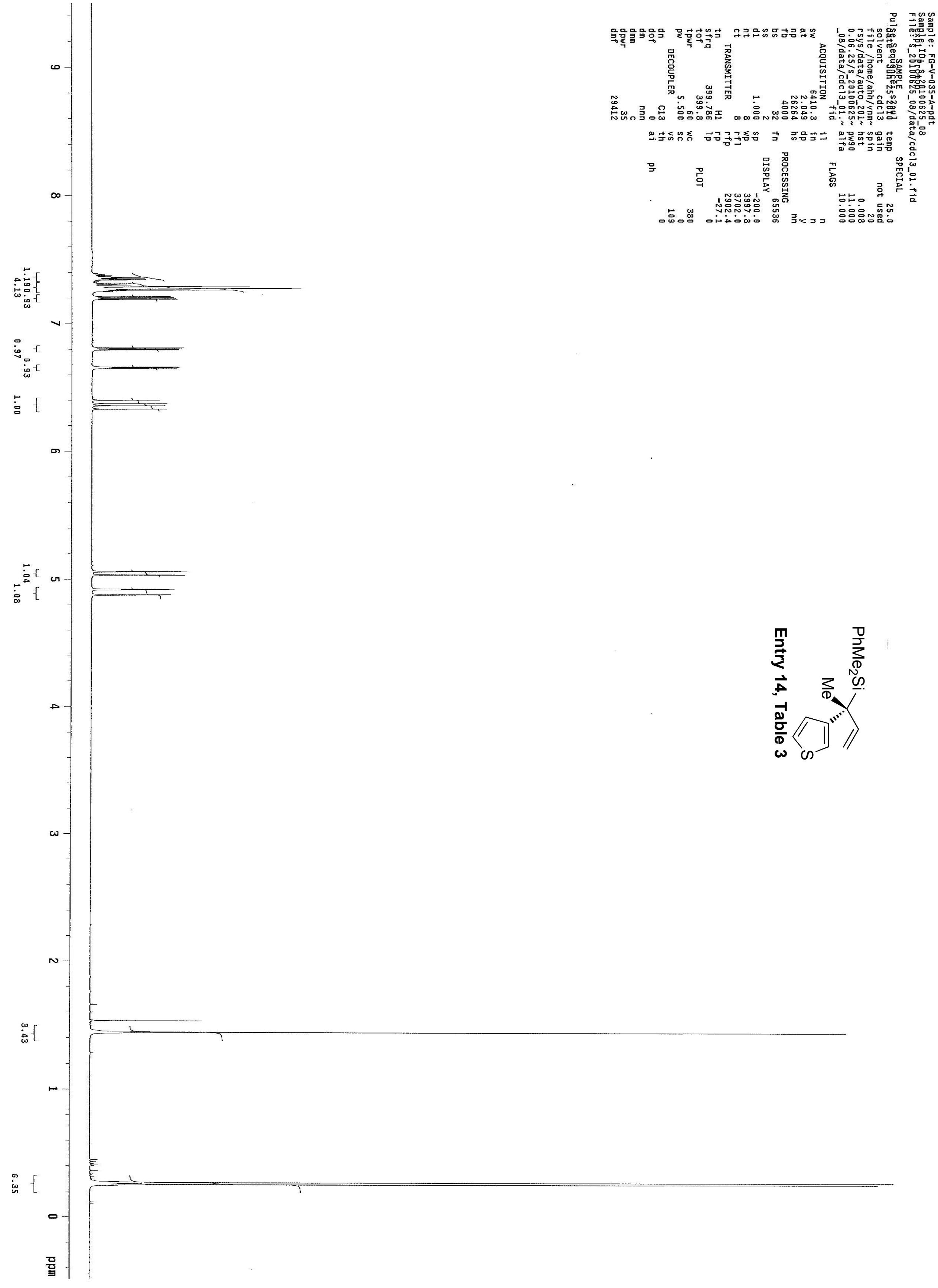
Entry 12, Table 3



Entry 13, Table 3

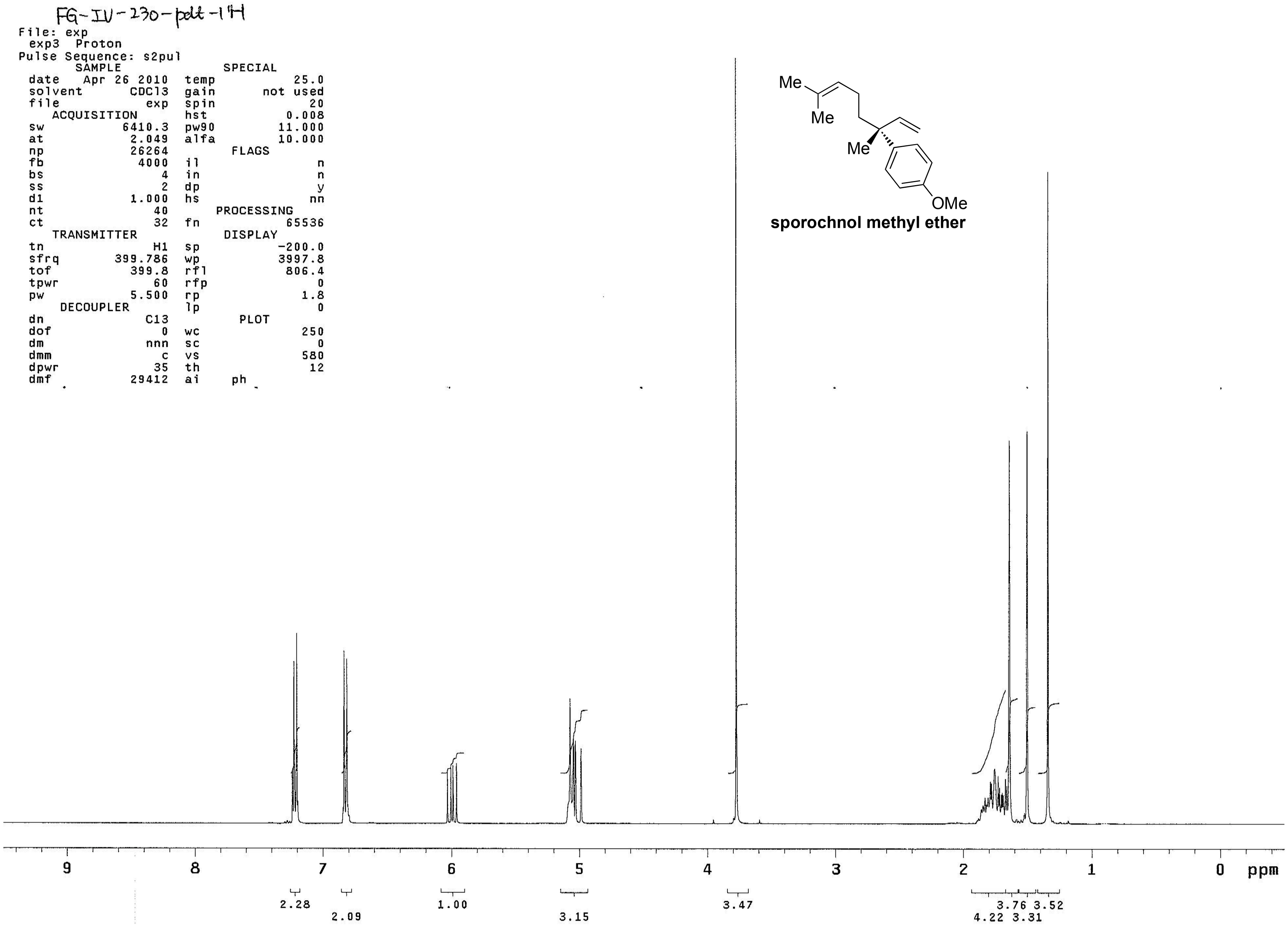
```
Sample: FG-V-034-A-pdt
Sample ID: s_20100625_05
exp1 Proton
File: s_20100625_05/data/c6d6_01.fid

Pulse Sequence: s2pul
         SAMPLE                SPECIAL
date      Jun 25 2010  temp          25.0
solvent          c6d6  gain      not used
file /home/ahh/vnm~   spin            20
rsys/data/auto_201~   hst          0.008
0.06.25/s_20100625~   pw90        11.000
_05/data/c6d6_01.f~   alfa        10.000
                 id          FLAGS
    ACQUISITION        il               n
sw             6410.3  in               n
at              2.049  dp               y
np              26264  hs              nn
fb               4000       PROCESSING
bs                 32  fn           65536
ss                  2        DISPLAY
d1              1.000  sp          -200.0
nt                  8  wp          3997.8
ct                  8  rfl         3666.2
    TRANSMITTER        rfp         2902.4
tn                 H1  rp           -32.1
sfrq          399.786  lp               0
tof             399.8          PLOT
tpwr               60  wc             380
pw              5.500  sc               0
     DECOUPLER         vs              78
dn                C13  th              33
dof                 0  ai    ph
dm                nnn
dmm                 c
dpwr               35
dmf             29412
```



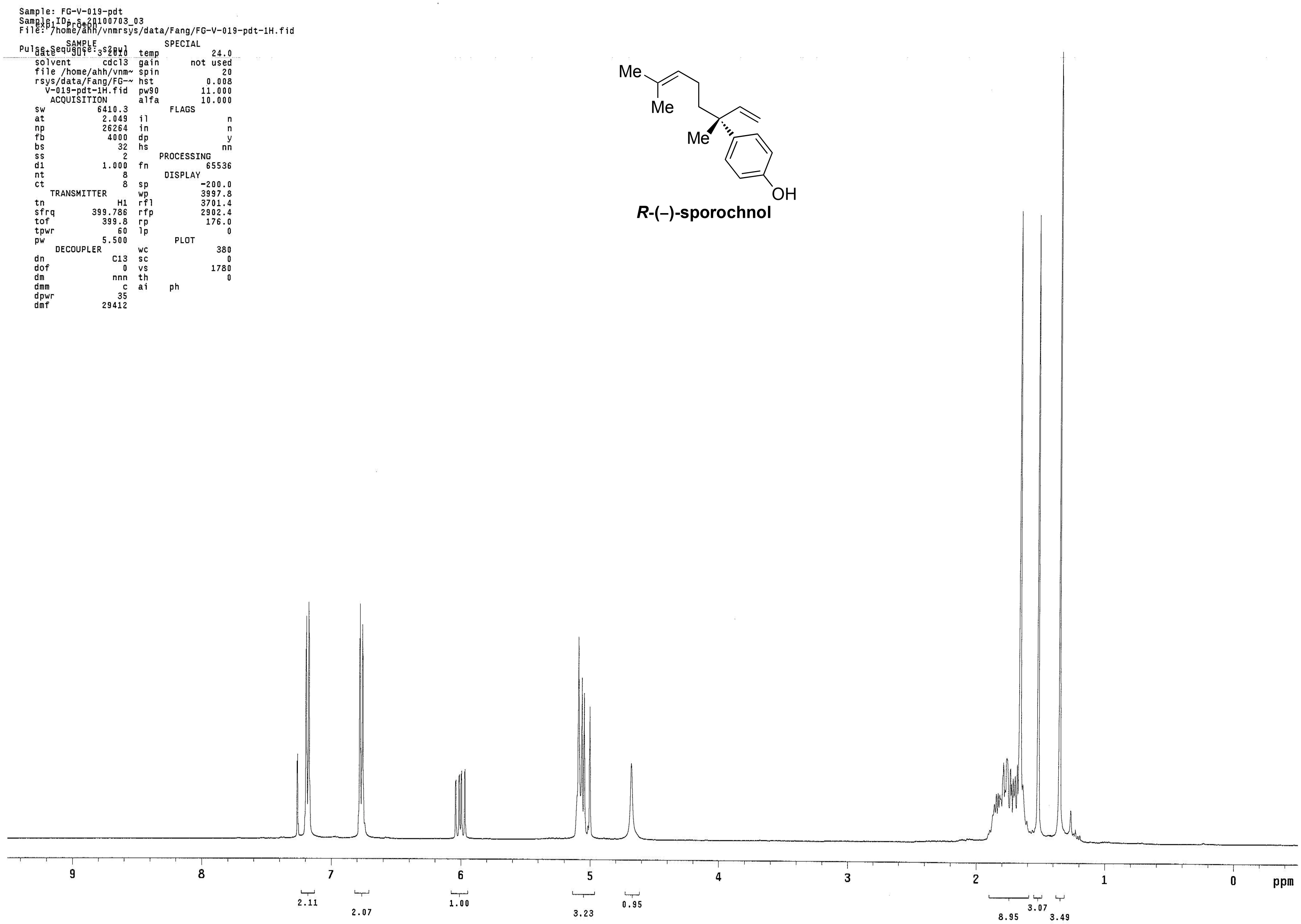
Entry 14, Table 3

FG-IV-230-pdt-1H



```
File: exp
 exp3  Proton
Pulse Sequence: s2pul
        SAMPLE                  SPECIAL
 date   Apr 26 2010  temp             25.0
 solvent      CDCl3  gain         not used
 file           exp  spin               20
     ACQUISITION     hst             0.008
 sw          6410.3  pw90           11.000
 at           2.049  alfa           10.000
 np           26264          FLAGS
 fb            4000  il                  n
 bs               4  in                  n
 ss               2  dp                  y
 d1           1.000  hs                 nn
 nt              40        PROCESSING
 ct              32  fn              65536
     TRANSMITTER             DISPLAY
 tn              H1  sp             -200.0
 sfrq       399.786  wp             3997.8
 tof          399.8  rfl             806.4
 tpwr            60  rfp                 0
 pw           5.500  rp                1.8
      DECOUPLER      lp                  0
 dn             C13           PLOT
 dof              0  wc                250
 dm             nnn  sc                  0
 dmm              c  vs                580
 dpwr            35  th                 12
 dmf          29412  ai     ph
```

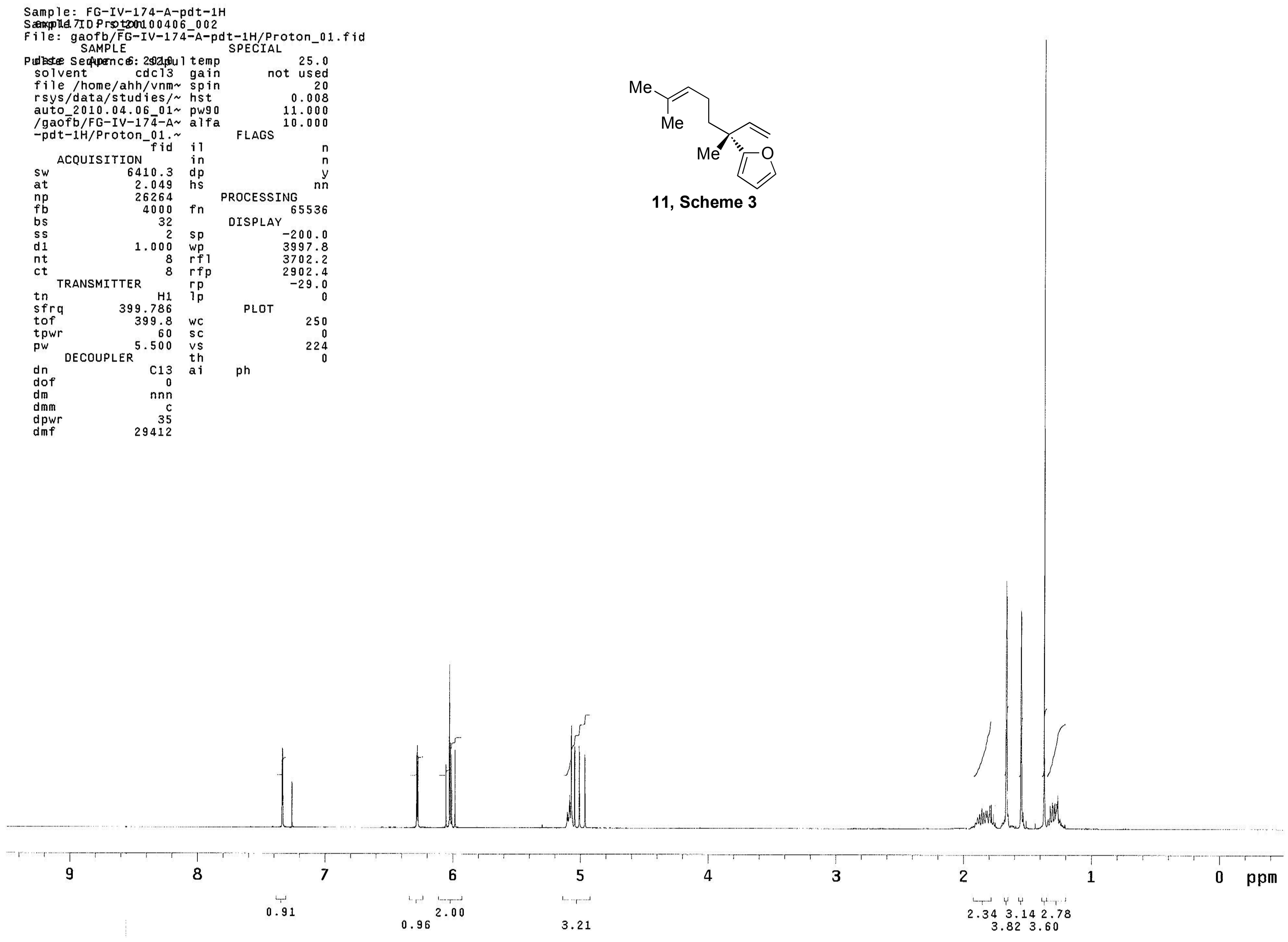
sporochnol methyl ether



```
Sample: FG-V-019-pdt
Sample ID: s_20100703_03
   exp1  Proton
File: /home/ahh/vnmrsys/data/Fang/FG-V-019-pdt-1H.fid

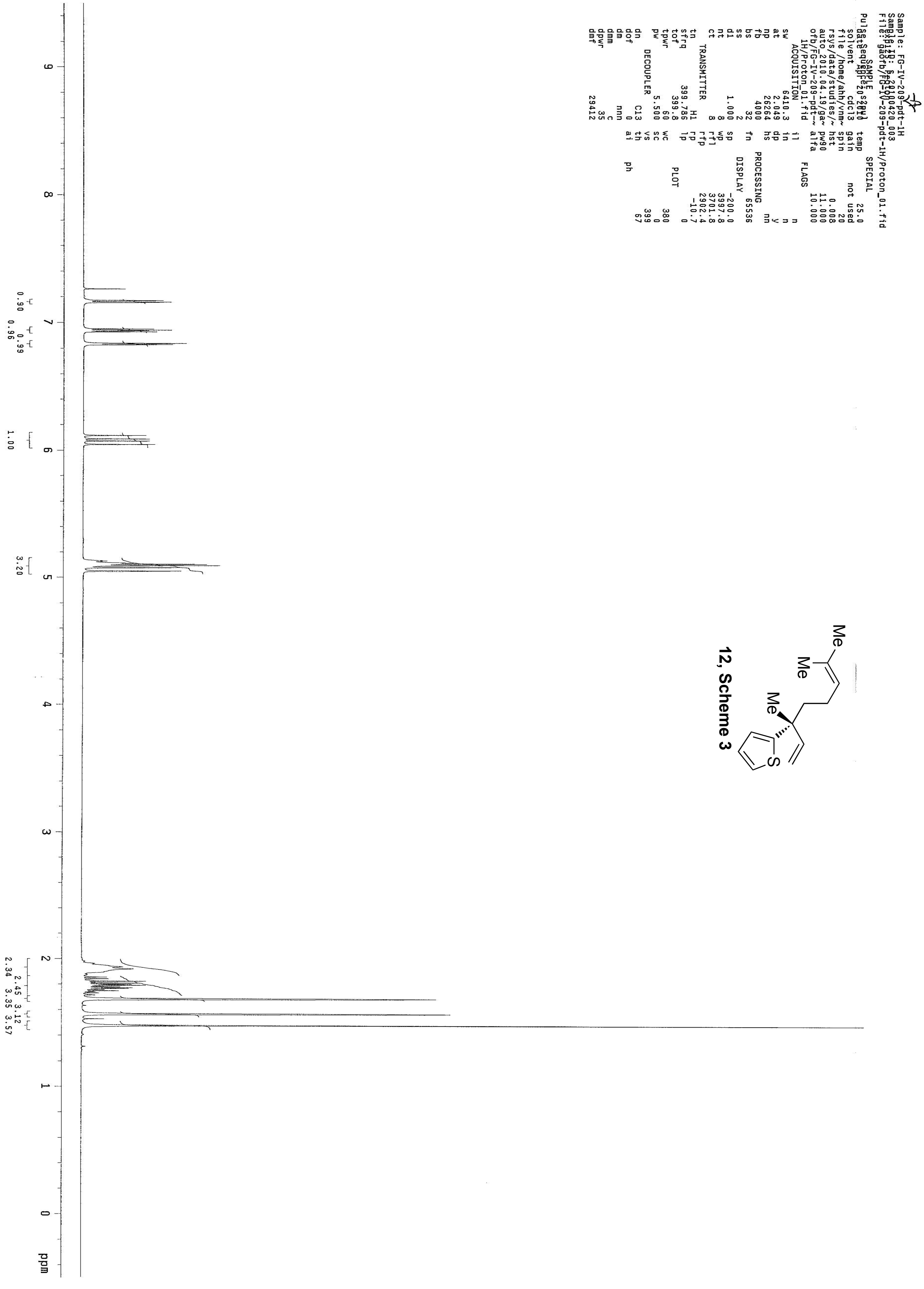
Pulse Sequence: s2pul
        SAMPLE                  SPECIAL
   date     Jul  3 2010  temp          24.0
   solvent        cdcl3  gain      not used
   file /home/ahh/vnm~  spin            20
   rsys/data/Fang/FG-~  hst          0.008
     V-019-pdt-1H.fid   pw90        11.000
      ACQUISITION       alfa        10.000
   sw           6410.3          FLAGS
   at            2.049  il               n
   np            26264  in               n
   fb             4000  dp               y
   bs               32  hs              nn
   ss                2        PROCESSING
   d1            1.000  fn           65536
   nt                8         DISPLAY
   ct                8  sp          -200.0
      TRANSMITTER       wp          3997.8
   tn               H1  rfl         3701.4
   sfrq        399.786  rfp         2902.4
   tof           399.8  rp           176.0
   tpwr             60  lp               0
   pw            5.500           PLOT
       DECOUPLER        wc             380
   dn              C13  sc               0
   dof               0  vs            1780
   dm              nnn  th               0
   dmm               c  ai    ph
   dpwr             35
   dmf           29412
```

R-(–)-sporochnol



11, Scheme 3

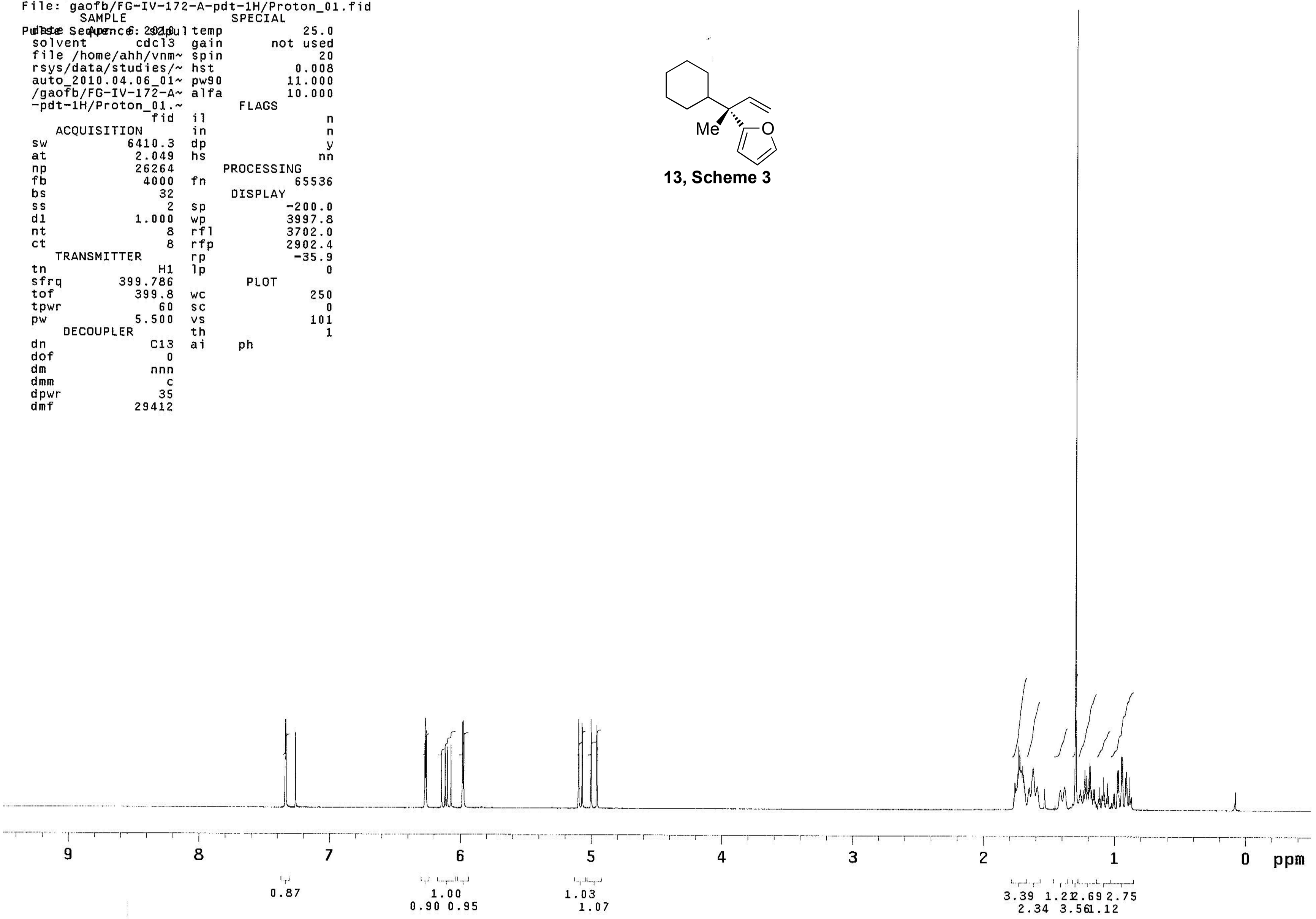
```
Sample: FG-IV-174-A-pdt-1H
Sample ID: 20100406_002
exp17 Proton
File: gaofb/FG-IV-174-A-pdt-1H/Proton_01.fid
         SAMPLE                SPECIAL
Date: Apr  6 2010      temp           25.0
Pulse Sequence: s2pul
 solvent      cdcl3    gain       not used
 file /home/ahh/vnm~   spin             20
 rsys/data/studies/~   hst           0.008
 auto_2010.04.06_01~   pw90         11.000
 /gaofb/FG-IV-174-A~   alfa         10.000
 -pdt-1H/Proton_01.~         FLAGS
                 fid   il                n
    ACQUISITION        in                n
 sw           6410.3   dp                y
 at            2.049   hs               nn
 np            26264        PROCESSING
 fb             4000   fn            65536
 bs               32         DISPLAY
 ss                2   sp           -200.0
 d1            1.000   wp           3997.8
 nt                8   rfl          3702.2
 ct                8   rfp          2902.4
    TRANSMITTER        rp            -29.0
 tn               H1   lp                0
 sfrq        399.786          PLOT
 tof           399.8   wc              250
 tpwr             60   sc                0
 pw            5.500   vs              224
    DECOUPLER          th                0
 dn              C13   ai     ph
 dof               0
 dm              nnn
 dmm               c
 dpwr             35
 dmf           29412
```


Sample: FG-IV-209-pdt-1H
File: gaofb/FG-IV-209-pdt-1H/Proton_01.fid
SAMPLE
solvent cdcl3
file /home/ahh/vnm~
rsys/data/studies/~
auto_2010.04.19/ga~
ofb/FG-IV-209-pdt-~
1H/Proton_01.fid
ACQUISITION
sw 6410.3
at 2.049
np 26264
fb 4000
bs 32
ss 2
d1 1.000
nt 8
ct 8
TRANSMITTER
tn H1
sfrq 399.786
tof 399.8
tpwr 60
pw 5.500
DECOUPLER
dn C13
dof 0
dm nnn
dmm c
dpwr 35
dmf 29412
SPECIAL
temp 25.0
gain not used
spin 20
hst 0.008
pw90 11.000
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
fn 65536
DISPLAY
sp -200.0
wp 3997.8
rfl 3701.8
rfp 2902.4
rp -10.7
lp 0
PLOT
wc 380
sc 0
vs 399
th 67
ai ph
Me
Me
Me
S
0.90
0.96
0.99
1.00
3.20
2.34
2.45
3.35
3.12
3.57
9
8
7
6
5
4
3
2
1
0
ppm

12, Scheme 3

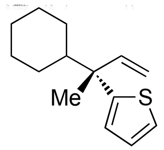
```
Sample: FG-IV-172-A-pdt-1H
Sample ID: 20100406_001   exp17 Proton
File: gaofb/FG-IV-172-A-pdt-1H/Proton_01.fid
Pulse Sequence: s2pul   date Apr 6 2010
      SAMPLE                 SPECIAL
                           temp              25.0
 solvent        cdcl3      gain          not used
 file /home/ahh/vnm~       spin                20
 rsys/data/studies/~       hst              0.008
 auto_2010.04.06_01~       pw90            11.000
 /gaofb/FG-IV-172-A~       alfa            10.000
 -pdt-1H/Proton_01.~             FLAGS
                  fid      il                   n
    ACQUISITION            in                   n
 sw            6410.3      dp                   y
 at             2.049      hs                  nn
 np             26264         PROCESSING
 fb              4000      fn               65536
 bs                32          DISPLAY
 ss                 2      sp              -200.0
 d1             1.000      wp              3997.8
 nt                 8      rfl             3702.0
 ct                 8      rfp             2902.4
    TRANSMITTER            rp               -35.9
 tn                H1      lp                   0
 sfrq         399.786           PLOT
 tof            399.8      wc                 250
 tpwr              60      sc                   0
 pw             5.500      vs                 101
    DECOUPLER              th                   1
 dn               C13      ai     ph
 dof                0
 dm               nnn
 dmm                c
 dpwr              35
 dmf            29412
```

13, Scheme 3

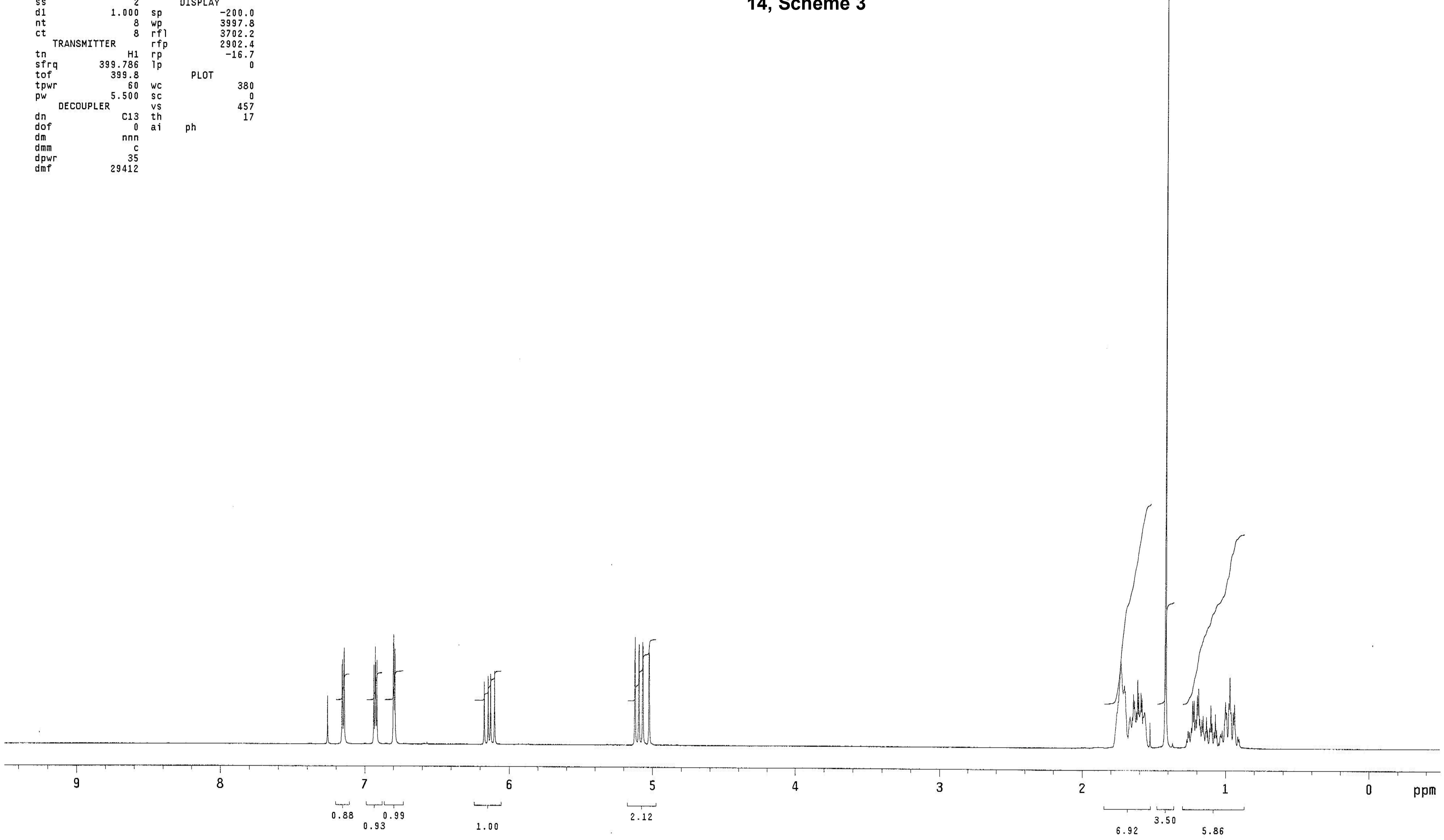


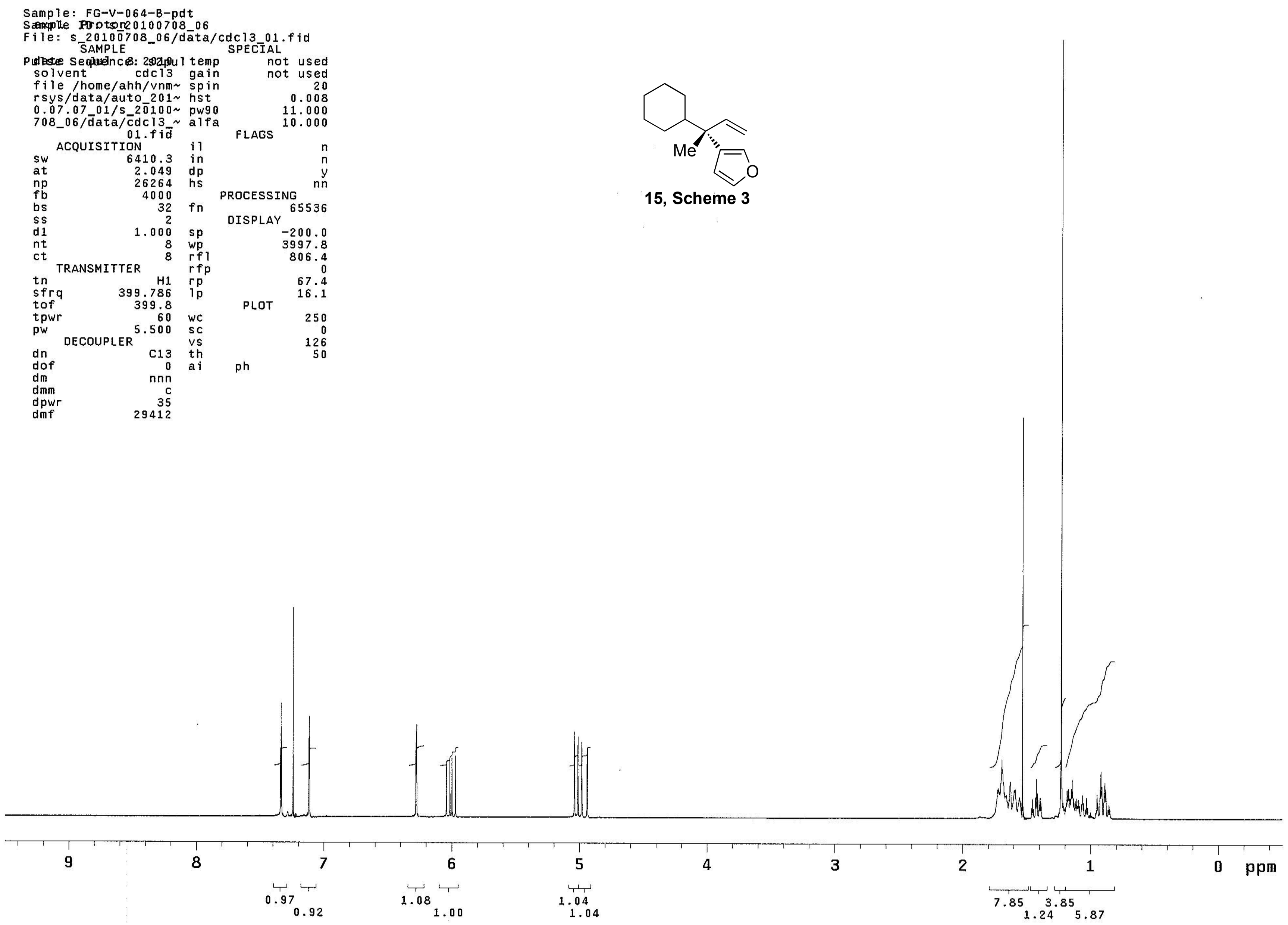
```
Sample: FG-IV-203-pdt-1H
Sample ID: s_20100420_002
    exp125: Proton
File: gaofb/FG-IV-203-pdt-1H/Proton_01.fid

         SAMPLE                SPECIAL
Pulse Sequence: s2pul
   date   Apr 20 2010  temp           25.0
   solvent       cdcl3  gain       not used
   file /home/ahh/vnm~  spin             20
   rsys/data/studies/~  hst           0.008
   auto_2010.04.19/ga~  pw90         11.000
   ofb/FG-IV-203-pdt-~  alfa         10.000
     1H/Proton_01.fid          FLAGS
      ACQUISITION       il                n
   sw           6410.3  in                n
   at            2.049  dp                y
   np            26264  hs               nn
   fb             4000       PROCESSING
   bs               32  fn            65536
   ss                2         DISPLAY
   d1            1.000  sp           -200.0
   nt                8  wp           3997.8
   ct                8  rfl          3702.2
      TRANSMITTER       rfp          2902.4
   tn               H1  rp            -16.7
   sfrq        399.786  lp                0
   tof           399.8          PLOT
   tpwr             60  wc              380
   pw            5.500  sc                0
       DECOUPLER        vs              457
   dn              C13  th               17
   dof               0  ai    ph
   dm              nnn
   dmm               c
   dpwr             35
   dmf           29412
```



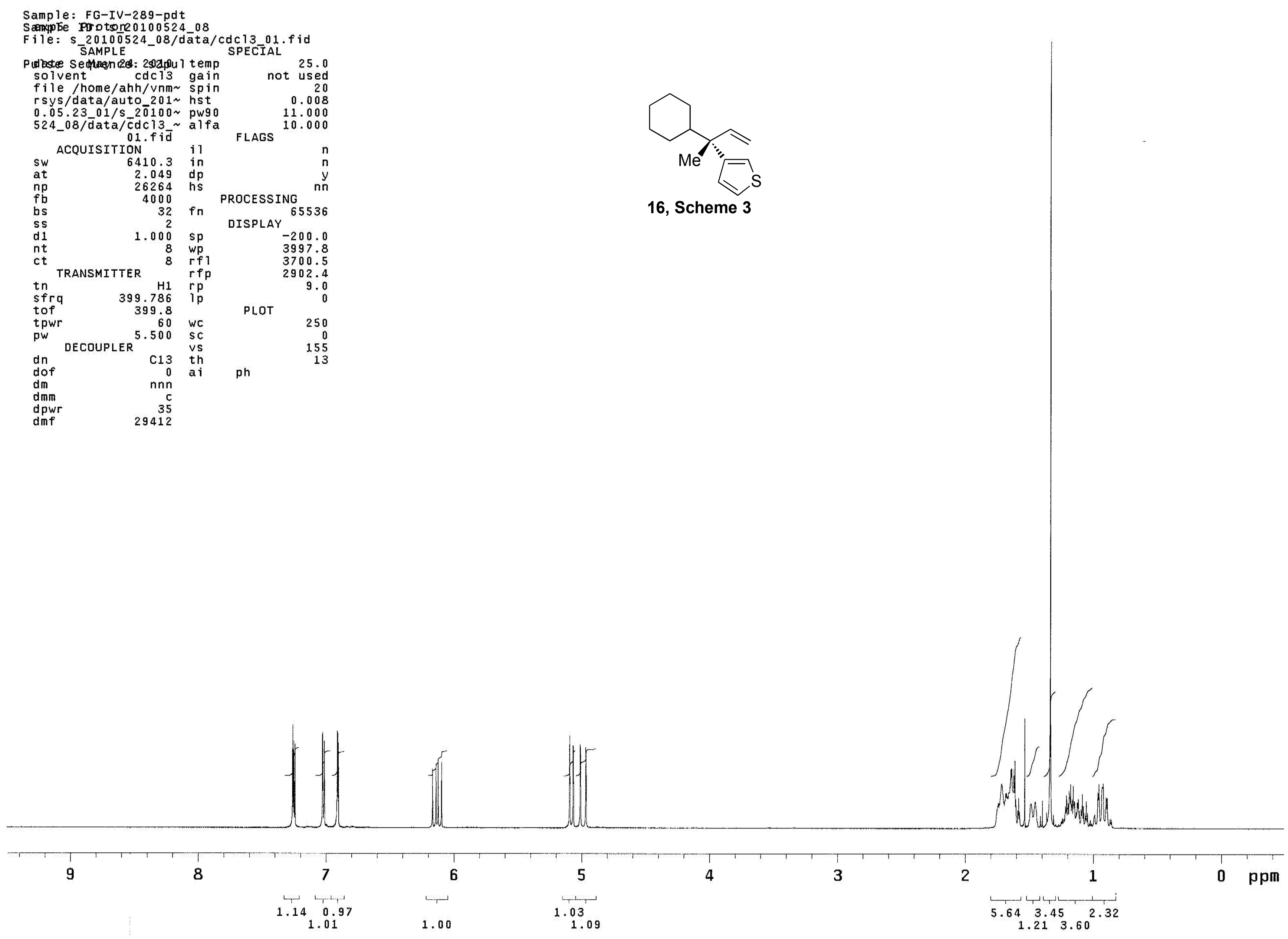
14, Scheme 3





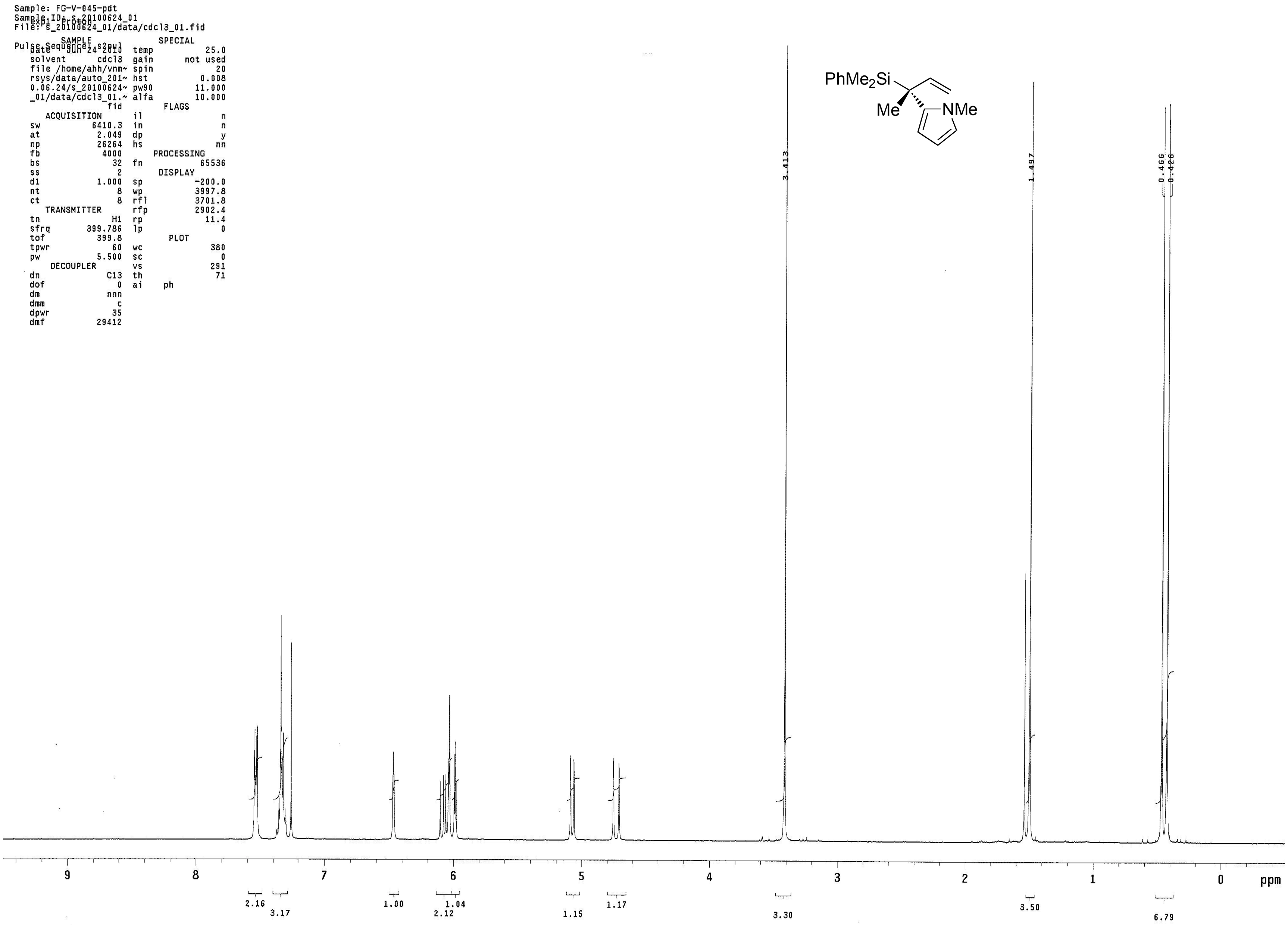
```
Sample: FG-V-064-B-pdt
Sample Proton_20100708_06
File: s_20100708_06/data/cdcl3_01.fid
       SAMPLE                    SPECIAL
Pulse Sequence: s2pul  temp       not used
 solvent       cdcl3   gain       not used
 file /home/ahh/vnm~   spin             20
 rsys/data/auto_201~   hst           0.008
 0.07.07_01/s_20100~   pw90         11.000
 708_06/data/cdcl3_~   alfa         10.000
              01.fid          FLAGS
    ACQUISITION        il                n
 sw           6410.3   in                n
 at            2.049   dp                y
 np            26264   hs               nn
 fb             4000        PROCESSING
 bs               32   fn            65536
 ss                2          DISPLAY
 d1            1.000   sp           -200.0
 nt                8   wp           3997.8
 ct                8   rfl           806.4
    TRANSMITTER        rfp               0
 tn               H1   rp             67.4
 sfrq        399.786   lp             16.1
 tof           399.8          PLOT
 tpwr             60   wc              250
 pw            5.500   sc                0
     DECOUPLER         vs              126
 dn              C13   th               50
 dof               0   ai     ph
 dm              nnn
 dmm               c
 dpwr             35
 dmf           29412
```

15, Scheme 3



```
Sample: FG-IV-289-pdt
Sample ID: s_20100524_08
exp5 Proton
File: s_20100524_08/data/cdcl3_01.fid
        SAMPLE                  SPECIAL
Pulse Sequence: s2pul  temp          25.0
date May 24 2010
 solvent        cdcl3  gain      not used
 file /home/ahh/vnm~   spin            20
 rsys/data/auto_201~   hst          0.008
 0.05.23_01/s_20100~   pw90        11.000
 524_08/data/cdcl3_~   alfa        10.000
              01.fid           FLAGS
    ACQUISITION        il               n
 sw            6410.3  in               n
 at             2.049  dp               y
 np             26264  hs              nn
 fb              4000        PROCESSING
 bs                32  fn           65536
 ss                 2          DISPLAY
 d1             1.000  sp          -200.0
 nt                 8  wp          3997.8
 ct                 8  rfl         3700.5
    TRANSMITTER        rfp         2902.4
 tn                H1  rp             9.0
 sfrq         399.786  lp               0
 tof            399.8          PLOT
 tpwr              60  wc             250
 pw             5.500  sc               0
     DECOUPLER         vs             155
 dn               C13  th              13
 dof                0  ai     ph
 dm               nnn
 dmm                c
 dpwr              35
 dmf            29412
```

16, Scheme 3



```
Sample: FG-V-045-pdt
Sample ID: s_20100624_01
exp1 Proton
File: s_20100624_01/data/cdcl3_01.fid
Pulse Sequence: s2pul
         SAMPLE                    SPECIAL
   date     Jun 24 2010   temp              25.0
   solvent        cdcl3   gain          not used
   file /home/ahh/vnm~    spin                20
   rsys/data/auto_201~    hst              0.008
   0.06.24/s_20100624~    pw90            11.000
   _01/data/cdcl3_01.~    alfa            10.000
                   fid            FLAGS
      ACQUISITION         il                   n
   sw            6410.3   in                   n
   at             2.049   dp                   y
   np             26264   hs                  nn
   fb              4000         PROCESSING
   bs                32   fn               65536
   ss                 2          DISPLAY
   d1             1.000   sp              -200.0
   nt                 8   wp              3997.8
   ct                 8   rfl             3701.8
      TRANSMITTER         rfp             2902.4
   tn                H1   rp                11.4
   sfrq         399.786   lp                   0
   tof            399.8            PLOT
   tpwr              60   wc                 380
   pw             5.500   sc                   0
       DECOUPLER          vs                 291
   dn               C13   th                  71
   dof                0   ai      ph
   dm               nnn
   dmm                c
   dpwr              35
   dmf            29412
```