Supplementary Material (ESI) for Chemical Communications

ELECTRONIC SUPPLEMENTARY INFORMATION

Rapid Screening for Asymmetric Catalysts: Efficient Connection of Two Different Catalytic Asymmetric Reactions

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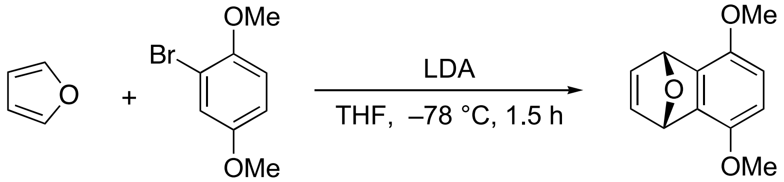
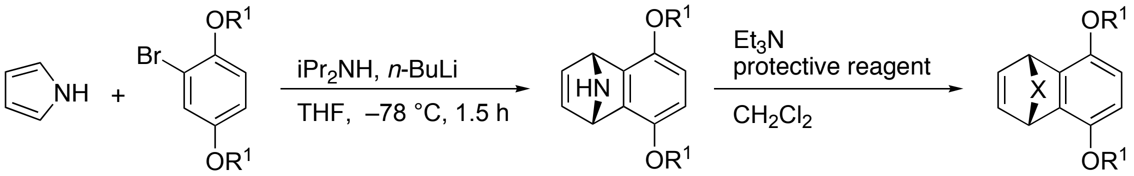
General. All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen. NMR spectra were recorded on a JEOL JNM LA-500 spectrometer (500 MHz for ^{1}H and 125 MHz for ^{13}C) and LA-400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C). Chemical shifts are reported in δ ppm referenced to an internal $SiMe_4$ standard for ^{1}H NMR and chloroform-d (δ 77.0) for ^{13}C NMR. HPLC analyses were performed using Shimadzu LC-10AD VP pump, SPD-10A VP UV detector, and Shimadzu CTO-10AC VP column oven with appropriate chiral columns.

Materials. THF was distilled from sodium benzophenone-ketyl under argon prior to use. Et_2O was distilled from sodium benzophenone-ketyl under argon prior to use. Toluene was distilled from sodium benzophenone-ketyl under nitrogen and stored in a glass flask with a Teflon stopcock under nitrogen. Dichloromethane was distilled from CaH_2 under nitrogen and stored in a glass flask with a Teflon stopcock under nitrogen. Hexane was distilled from sodium benzophenone-ketyl under nitrogen and stored in a glass flask with a Teflon stopcock under nitrogen. 1,4-Dialkoxy-2-bromobenzenes[1] and $PdCl_2$((*R*,*R*)-*t*-Bu-QuinoxP*)[2] were prepared according to the reported procedures. Diisopropylamine, *n*-buthyllithium solution, furan, pyrrole, triethylamine, benzoyl chloride, benzenesulfonyl chloride, *p*-toluenesulfonyl chloride, methanesulfonyl chloride, 1,2-dibromobenzene, dialkylzinc solutions, benzaldehyde, 2-naphthaldehyde, 3-methoxybenzaldehyde, 3-chlorobenzaldehyde, 4-methylbenzaldehyde, 4-chlorobenzaldehyde, and 3-phenylpropionaldehyde were used as received.

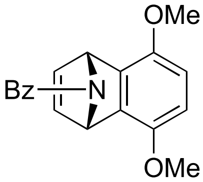
Procedures for the Preparation of 1



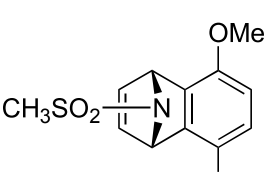
1,4-Dihydro-5,8-dimethoxy-1,4-epoxynaphthalene: To a mixture of LDA (1.1 mmol) and furan (15 ml) in THF (15ml) was slowly added a solution of 1-bromo-2,5-dimethoxybenzene (10 mmol) in THF (5 ml) at –78 °C under nitrogen. After stirring for 1.5 h at the same temperature, the mixture was quenched by addition of H_2O and left to warm up. The mixture was extracted with Et_2O, dried over Na_2SO_4, and concentrated under vacuum. The residue was purified by recrystallization to give the oxabenzonorbornene. This product was characterized by comparison of the spectroscopic data with those reported previously.[3]



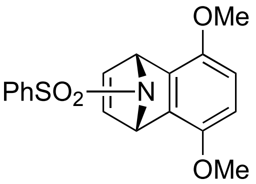
General Procedure A. To a mixture of diisopropylamine (13 mmol) and pyrrole (10 mmol) in THF (11.5 ml) was slowly added *n*-BuLi (1.55 M in hexane, 26 mmol, 16.8 ml) at –78 °C under nitrogen. After stirring for 10 min at the same temperature, a solution of 1,4-dialkoxy-2-bromobenzene in THF (8.5 ml) was slowly added to the mixture. After stirring for 1.5 h, the mixture was quenched by addition of H_2O and left to warm up. The mixture was extracted with Et_2O, dried over Na_2SO_4, and concentrated under vacuum. The residue was purified by silica gel column chromatography (AcOEt, then MeOH) to give corresponding azabenzonorbornene. To a solution of the azabenzonorbornene in CH_2Cl_2 were added triethylamine (1.0 eq) and protective reagent (1.0 eq). After stirring for 1.5 h, the mixture was quenched by addition of H_2O, extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated under vacuum. The residue was purified by silica gel column chromatography or reprecipitation to give desired *N*-protected azabenzonorbornene.



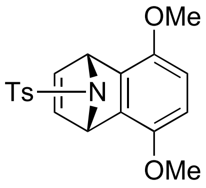
9-Benzoyl-5,8-dimethoxy-1,4-dihydro-1,4-epiazanonaphthalene: The reaction was carried out following the General Procedure A; benzoyl chloride was used; ^{1}H NMR ($CDCl_3$) δ 3.72 (br s, 3H), 3.82 (br s, 3H), 5.77 (br s, 1H), 6.23 (br s, 1H), 6.54-6.59 (m, 2H), 6.92-6.94 (m, 1H), 7.21-7.22 (m, 1H), 7.39-7.55 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 56.23, 56.37, 61.43, 65.44, 111.13, 111.48, 127.89, 128.36, 130.83, 134.44, 136.50, 136.58, 142.23, 144.78, 147.39, 147.40, 148.32, 148.35, 167.00; HRMS (FAB) calcd for $C_{19}H_{17}O_3N$ (M^+) 307.1208, found 307.1200.



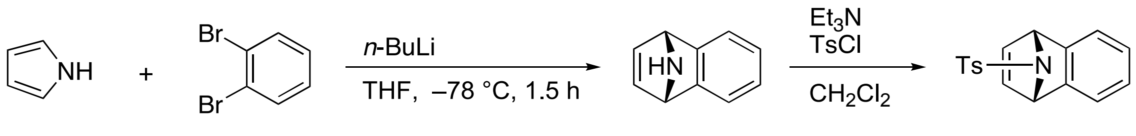
9-Methanesulfonyl-5,8-dimethoxy-1,4-dihydro-1,4-epiazanonaphthalene: The reaction was carried out following the General Procedure A; methanesulfonyl chloride was used; ^{1}H NMR (CDCl$_3$) δ 2.39 (s, 3H), 3.79 (s, 6H), 5.68 (t, *J* = 1.5 Hz, 2H), 6.58 (s, 2H), 7.11 (t, *J* = 1.5 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ 39.00, 56.23, 65.13, 111.67, 135.77, 143.03, 148.37; HRMS (FAB) calcd for $C_{13}H_{15}O_4NS$ (M$^+$) 281.0722, found 281.0712.



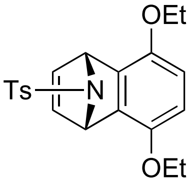
9-Benzenesulfonyl-5,8-dimethoxy-1,4-dihydro-1,4-epiazanonaphthalene: The reaction was carried out following the General Procedure A; benzenesulfonyl chloride was used; ^{1}H NMR (CDCl$_3$) δ 3.66 (s, 6H), 5.63 (s, 2H), 6.19 (s, 2H), 6.94 (s, 2H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ 55.88, 65.03, 110.99, 128.10, 128.29, 131.95, 135.03, 137.43, 142.64, 148.02; HRMS (FAB) calcd for $C_{18}H_{17}O_4NS$ (M$^+$+H) 344.0957, found 344.0948.



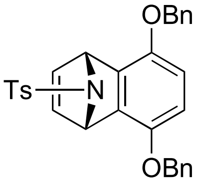
5,8-Dimethoxy-9-(4-toluenesulfonyl)-1,4-dihydro-1,4-epiazanonaphthalene: The reaction was carried out following the General Procedure A; *p*-toluenesulfonyl chloride was used; ^{1}H NMR (CDCl$_3$) δ 2.32 (s, 3H), 3.67 (s, 6H), 5.62 (t, *J* = 1.5 Hz, 2H), 6.23 (s, 2H), 6.91 (t, *J* = 1.5 Hz, 2H), 7.02 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ 21.46, 55.92, 65.05, 110.85, 128.10, 128.94, 134.62, 135.31, 142.58, 142.74, 148.04; HRMS (FAB) calcd for $C_{19}H_{20}O_4NS$ (M$^+$+H) 358.1113, found 358.1104.



9-(4-Toluenesulfonyl)-1,4-dihydro-1,4-epiazanonaphthalene: To a solution of pyrrole (24.0 mmol) in THF (40 ml) was slowly added *n*-BuLi (1.55 M in hexane, 44.0 mmol, 28.4 ml) at –78 °C under nitrogen. After stirring for 10 min at the same temperature, 1,2-dibromobenzene was slowly added to the mixture. After stirring for 1.5 h, the mixture was quenched by addition of H_2O and left to warm up. The mixture was extracted with Et_2O, dried over Na_2SO_4, and concentrated under vacuum. The residue was purified by silica gel column chromatography (AcOEt, then MeOH) to give azabenzonorbornene. To a solution of the azabenzonorbornene (0.30 mmol) in CH_2Cl_2 (2 ml) were added triethylamine (0.30 mmol) and *p*-toluenesulfonyl chloride (0.30 mmol). After stirring for 1.5 h, the mixture was quenched by addition of H_2O, extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated under vacuum. The residue was purified by reprecipitation to give the desired product. This product was characterized by comparison of the spectroscopic data with those reported previously.[4]

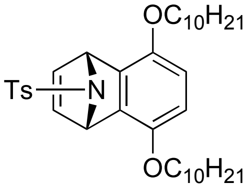


5,8-Diethoxy-9-(4-toluenesulfonyl)-1,4-dihydro-1,4-epiazanonaphthalene: The reaction was carried out following the General Procedure A; *p*-toluenesulfonyl chloride was used; ^{1}H NMR ($CDCl_3$) δ 1.36 (t, *J* = 7.0 Hz, 6H), 2.32 (s, 3H), 3.80 (dq, *J* = 9.4, 7.0 Hz, 2H), 3.91 (dq, *J* = 9.4, 7.0 Hz, 2H), 5.63 (t, *J* = 1.5 Hz, 2H), 6.20 (s, 2H), 6.89 (t, *J* = 1.5 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 15.04, 21.46, 64.49, 65.15, 112.18, 128.11, 128.96, 134.76, 135.50, 142.42, 142.72, 147.35; HRMS (FAB) calcd for $C_{21}H_{24}O_4NS$ (M^++H) 386.1426, found 386.1440.

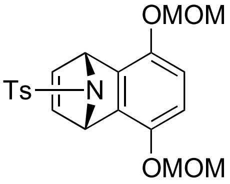


5,8-Bisbenzyloxy-9-(4-toluenesulfonyl)-1,4-dihydro-1,4-epiazanonaphthalene: The reaction was carried out following the General Procedure A; *p*-toluenesulfonyl chloride was used; ^{1}H

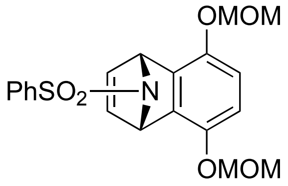
NMR ($CDCl_3$) δ 2.27 (s, 3H), 4.85 (d, *J* = 11.6 Hz, 2H), 4.90 (d, *J* = 11.9 Hz, 2H), 5.63 (t, *J* = 1.8 Hz, 2H), 6.27 (s, 2H), 6.80 (t, *J* = 1.8 Hz, 2H), 6.92 (d, *J* = 8.2 Hz, 2H), 7.34-7.44 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 21.45, 65.16, 71.03, 112.75, 127.41, 128.09, 128.60, 128.99, 134.56, 136.06, 136.95, 142.50, 142.74, 147.44; HRMS (FAB) calcd for $C_{31}H_{27}O_4NS$ (M^+) 509.1661, found 509.1663.



5,8-Bisdecyloxy-9-(4-toluenesulfonyl)-1,4-dihydro-1,4-epiazanonaphthalene: The reaction was carried out following the General Procedure A; *p*-toluenesulfonyl chloride was used; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, *J* = 7.1 Hz, 6H), 1.29-1.47 (m, 28H), 1.69-1.75 (m, 4H), 2.31 (s, 3H), 3.71 (dt, *J* = 9.2, 6.8 Hz, 2H), 3.82 (dt, *J* = 9.2, 6.5 Hz, 2H), 5.62 (t, *J* = 1.7 Hz, 2H), 6.18 (s, 2H), 6.91 (t, *J* = 1.7 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 12.69, 21.25, 24.64, 27.89, 28.00, 28.01, 28.17, 30.46, 63.67, 67.62, 110.71, 126.72, 127.53, 133.24, 133.88, 141.12, 141.24, 146.14; HRMS (FAB) calcd for $C_{37}H_{55}O_4NS$ (M^+) 609.3852, found 609.3859.



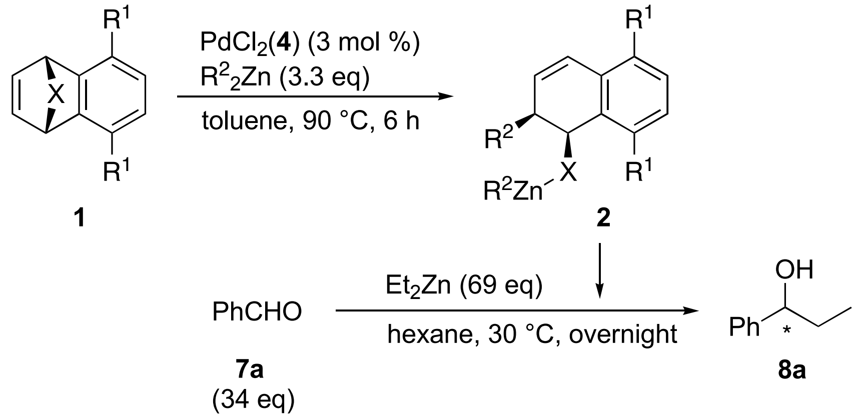
5,8-Bismethoxymethoxy-9-(4-toluenesulfonyl)-1,4-dihydro-1,4-epiazanonaphthalene: The reaction was carried out following the General Procedure A; *p*-toluenesulfonyl chloride was used; ^{1}H NMR ($CDCl_3$) δ 2.32 (s, 3H), 3.49 (s, 6H), 4.95 (d, *J* = 7.0 Hz, 2H), 5.01 (d, *J* = 7.0 Hz, 2H), 5.64 (t, *J* = 1.8 Hz, 2H), 6.41 (s, 2H), 6.92 (t, *J* = 1.9 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 7.44 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.48, 56.10, 65.29, 95.58, 115.61, 128.14, 129.09, 134.63, 136.30, 142.62, 142.97, 146.74; HRMS (FAB) calcd for $C_{21}H_{23}O_6NS$ (M^+) 417.1246, found 417.1234.



9-Benzenesulfonyl-5,8-bismethoxymethoxy-1,4-dihydro-1,4-epiazanonaphthalene:

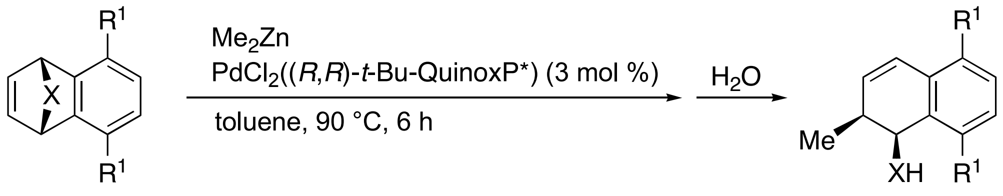
The reaction was carried out following the General Procedure A; benzenesulfonyl chloride was used; ^{1}H NMR ($CDCl_3$) δ 3.49 (s, 6H), 4.94 (d, *J* = 6.7 Hz, 2H), 5.01 (d, *J* = 6.7 Hz, 2H), 5.66 (t, *J* = 1.8, Hz, 2H), 6.38 (s, 2H), 6.94 (t, *J* = 1.8 Hz, 2H), 7.22-7.26 (m, 2H), 7.37 (tt, *J* = 7.3, 1.2 Hz, 1H), 7.56 (dd, *J* = 7.3, 1.2 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 56.09, 65.23, 95.50, 115.69, 128.10, 128.42, 132.14, 136.02, 137.40, 142.63, 146.67; HRMS (FAB) calcd for $C_{20}H_{22}O_6NS$ (M^++H) 404.1168, found 404.1163.

Procedures for the Screening for Asymmetric Catalysts 2 by Connecting Two Reactions



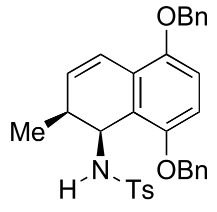
General Procedure B. To a solution of $PdCl_2$((*R*,*R*)-*t*-Bu-QuinoxP*) (0.00030 mmol) and **1** (0.0100 mmol) in toluene (0.5 ml) was added dialkylzinc (1.0 M in hexane, 0.033 ml, 0.033 mmol) under nitrogen. After stirring at 90 °C for 6 h, the mixture was cooled to room temperature and thoroughly pumped up under vacuum. To the residue were added hexane (4.0 ml), diethylzinc (1.0 M in hexane, 0.690 ml, 0.690 mmol), and benzaldehyde **7a** (0.340 mmol). The reaction mixture was stirred overnight at 30 °C. The mixture was then quenched by addition of 1N HCl aq and extracted with AcOEt three times. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under vacuum. The residue was purified by PTLC on silica gel (EtOAc/hexane = 1/4) to give 1-phenyl-1-propanol (**8a**). The ee value was determined by HPLC analysis with a stationary phase column (Daicel Chiralcel OD-H, hexane/i-PrOH = 98/2, 0.5 mL/min, t_1 = 26.0 min (major; *R*-enantiomer), t_2 = 30.8 min (minor; *S*-enantiomer).[5]

Procedures for the Asymmetric Ring Opening of 1 with Dialkylzinc Catalyzed by PdCl$_2$((*R*,*R*)-*t*-Bu-QuinoxP*)



1 **3**

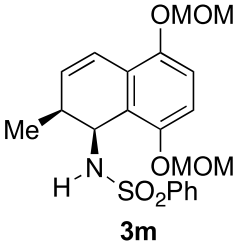
General Procedure C. To a mixture of PdCl$_2$((*R*,*R*)-*t*-Bu-QuinoxP*) (0.0060 mmol) and **1** (0.200 mmol) in toluene (5.0 ml) was added dimethylzinc (1.0 M in hexane, 0.600 ml, 0.600 mmol) under nitrogen. After stirring at 90 °C for 6 h, the mixture was cooled to room temperature and quenched by addition of few drops of water. The resulting mixture was stirred for 1.5 h, filtered through a short plug of Celite, and concentrated under vacuum. The residue was purified by PTLC on silica gel (EtOAc/hexane = 1/2) to give **3**.



3i

***N*-(5,8-Bisbenzyloxy-2-methyl-1,2-dihydronaphthalen-1-yl)-4-methylbenzenesulfonamide (3i):** The reaction was carried out following the General Procedure C; 91% yield; the ee value was determined by HPLC analysis with a stationary phase column (Daicel Chiralcel OD-H, hexane/i-PrOH = 9/1, 0.5 mL/min, t_1 = 38.6 min (major), t_2 = 53.8 min (minor); 95% ee; ^{1}H NMR (CDCl$_3$) δ 1.35 (d, *J* = 7.3 Hz, 3H), 2.29 (s, 3H), 2.59-2.63 (m, 1H), 4.60 (d, *J* = 12.2 Hz, 1H), 4.74 (d, *J* = 12.2 Hz, 1H), 4.87-5.03 (m, 4H), 5.70 (d, *J* = 9.8 Hz, 1H), 6.48 (d, *J* = 8.9 Hz, 1H), 6.70 (d, *J* = 8.9 Hz, 1H), 6.94 (d, *J* = 7.7 Hz, 2H), 6.97 (dd, *J* = 9.8, 3.1 Hz, 1H), 7.23-7.42 (m, 12H); ^{13}C NMR (CDCl$_3$) δ 15.98, 21.29, 34.16, 48.75, 69.81, 70.87, 111.58, 112.60, 122.11, 122.77, 124.62, 126.44, 126.66, 127.25, 127.52, 127.85, 128.34, 128.47, 128.67, 132.21, 136.98, 137.09, 139.07, 141.87, 148.40, 148.50; HRMS (FAB) calcd for $C_{32}H_{31}NO_4S$ (M^+) 525.1974, found 525.1975; a single reprecipitation in hexane increased the ee to >99% ee; $[\alpha]^{20}_D$ +62.2 (*c* 1.00, CHCl$_3$); mp =

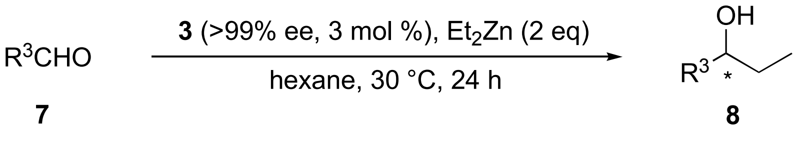
54-55 °C.



3m

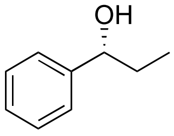
***N*-(5,8-Bismethoxymethoxy-2-methyl-1,2-dihydronaphthalen-1-yl)-benzenesulfonamide (3m):** The reaction was carried out following the General Procedure C; 93% yield; the ee value was determined by HPLC analysis with a stationary phase column (Daicel Chiralcel OD-H, hexane/i-PrOH = 9/1, 0.5 mL/min, t_1 = 18.9 min (major), t_2 = 23.8 min (minor); 93% ee; ^{1}H NMR ($CDCl_3$) δ 1.34 (d, *J* = 7.7 Hz, 3H), 2.61-2.64 (m, 1H), 3.34 (s, 3H), 3.46 (s, 3H), 4.58 (d, *J* = 7.0 Hz, 1H), 4.65 (d, *J* = 6.7 Hz, 1H), 4.87 (ddd, *J* = 9.8, 4.9, 1.2 Hz, 1H), 5.04 (d, *J* = 9.8 Hz, 1H), 5.08-5.12 (m, 2H), 5.71 (dt, *J* = 9.8, 1.5 Hz, 1H), 6.73 (d, *J* = 9.2 Hz, 1H), 6.88 (d, *J* = 8.9 Hz, 1H), 6.90 (dd, *J* = 9.8, 3.1 Hz, 1H), 7.33 (t, *J* = 7.9 Hz, 2H), 7.43 (tt, *J* = 7.7, 1.3 Hz, 1H), 7.63 (dd, *J* = 8.0, 1.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 16.05, 34.05, 48.90, 55.83, 56.03, 94.48, 95.35, 114.15, 115.50, 121.97, 123.09, 124.59, 126.28, 128.33, 131.62, 132.27, 142.34, 147.55, 148.00; HRMS (FAB) calcd for $C_{21}H_{25}NNaO_6S$ (M^++Na) 442.1300, found 442.1279; >99% ee of **3m** was obtained by separation using preparative HPLC (Daicel Chiralcel OD-H, 2 cm x 25 cm, hexane/i-PrOH = 9/1, 5.0 mL/min; $[\alpha]^{20}_D$ +63.7 (*c* 1.00, $CHCl_3$).

Procedures for the Asymmetric Addition of Diethylzinc to Aldehydes 7 Catalyzed by 2



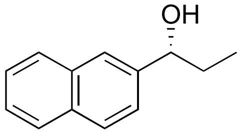
General Procedure D. A solution of **3** (1.0 M in AcOEt, 1.00 mL, 0.0100 mmol) was introduced to a Schlenk tube and concentrated under vacuum to remove AcOEt. To the residue were added hexane (4.0 mL) and diethylzinc (1.0 M in hexane, 692 µl, 0.692 mmol) at room temperature under nitrogen. After stirring for 1 h, the mixture was added aldehyde **7** (0.342 mmol) and stirred for 24 h (or 6 h) at 30 °C. The mixture was then quenched by addition of 1N HCl aq and extracted with

AcOEt three times. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under vacuum. The residue was purified by PTLC on silica gel (EtOAc/hexane = 1/4) to give **8**.

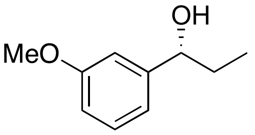


8a

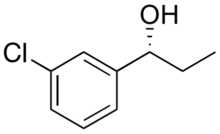
(*R*)-1-Phenylpropanol (8a): The reaction was carried out following the General Procedure D; 89% yield; this product was characterized by comparison of the spectroscopic data with those reported previously[6]; the ee value was determined by HPLC analysis with a stationary phase column (Daicel Chiralcel OD-H, hexane/i-PrOH = 98/2, 0.5 mL/min, t_1 = 26.0 min (major; *R*-enantiomer), t_2 = 30.8 min (minor; *S*-enantiomer)[5]; 84% ee; $[\alpha]^{20}_D$ +40.0 (*c* 1.00, $CHCl_3$)[5].



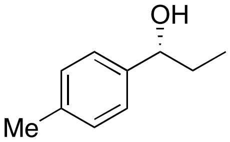
(*R*)-1-(2-Naphtyl)-1-propanol: The reaction was carried out following the General Procedure D; 99% yield; this product was characterized by comparison of the spectroscopic data with those reported previously[7]; the ee value was determined by HPLC analysis with a stationary phase column (Daicel Chiralcel OD-H, hexane/i-PrOH = 98/2, 0.5 mL/min, t_1 = 62.9 min (minor; *S*-enantiomer), t_2 = 70.2 min (major; *R*-enantiomer)[5]; 80% ee; $[\alpha]^{20}_D$ +31.7 (*c* 1.00, $CHCl_3$)[5].



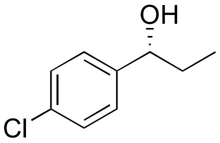
(*R*)-1-(3-Methoxyphenyl)-1-propanol: The reaction was carried out following the General Procedure D; 98% yield; this product was characterized by comparison of the spectroscopic data with those reported previously[7]; the ee value was determined by HPLC analysis with a stationary phase column (Daicel Chiralcel OD-H, hexane/i-PrOH = 98/2, 1.0 mL/min, t_1 = 22.5 min (major; *R*-enantiomer), t_2 = 28.0 min (minor; *S*-enantiomer)[8]; 82% ee; $[\alpha]^{20}_{D}$ +32.0 (*c* 1.00, $CHCl_3$)[8].



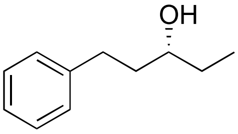
(*R*)-1-(3-Chlorophenyl)-1-propanol: The reaction was carried out following the General Procedure D; 80% yield; this product was characterized by comparison of the spectroscopic data with those reported previously[7]; the ee value was determined by HPLC analysis with a stationary phase column (Daicel Chiralcel AD-H, hexane/i-PrOH = 98/2, 1.0 mL/min, t_1 = 15.5 min (major; *R*-enantiomer), t_2 = 17.2 min (minor; *S*-enantiomer)[9]; 82% ee; $[\alpha]^{20}_{D}$ +28.8 (*c* 1.00, $CHCl_3$)[5].



(*R*)-1-(4-Methylphenyl)-1-propanol: The reaction was carried out following the General Procedure D; 88% yield; this product was characterized by comparison of the spectroscopic data with those reported previously[6]; the ee value was determined by HPLC analysis with a stationary phase column (Daicel Chiralcel OD-H, hexane/i-PrOH = 1000/1, 1.0 mL/min, t_1 = 49.0 min (major; *R*-enantiomer), t_2 = 63.0 min (minor; *S*-enantiomer)[10]; 85% ee; $[\alpha]^{20}_{D}$ +37.2 (*c* 1.00, $CHCl_3$)[5].

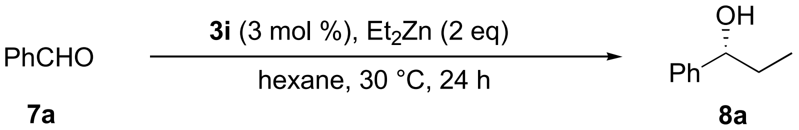


(*R*)-1-(4-Chlorophenyl)-1-propanol: The reaction was carried out following the General Procedure D; 65% yield; this product was characterized by comparison of the spectroscopic data with those reported previously[6]; the ee value was determined by HPLC analysis with a stationary phase column (Daicel Chiralcel OD-H, hexane/i-PrOH = 99/1, 0.5 mL/min, t_1 = 20.8 min (minor; *S*-enantiomer), t_2 = 26.7 min (major; *R*-enantiomer)[11]; 89% ee; $[\alpha]^{20}_{D}$ +34.2 (*c* 1.00, $CHCl_3$)[11].



(*R*)-1-Phenyl-3-pentanol: The reaction was carried out following the General Procedure D; 41% yield; this product was characterized by comparison of the spectroscopic data with those reported previously[12]; the ee value was determined by HPLC analysis with a stationary phase column (Daicel Chiralcel OD-H, hexane/i-PrOH = 98/2, 1.0 mL/min, t_1 = 16.5 min (major; *R*-enantiomer), t_2 = 27.0 min (minor; *S*-enantiomer)[12]; 83% ee; $[\alpha]^{20}_{D}$ –14.9 (*c* 1.00, $CHCl_3$)[12].

Table 1. Relationships between Enantioselectivity of the Ethylation Product **8a** and Enantiomeric Excess of **3i**[a]



entry	ee[b] of **3i** (%)	yield[c] of **8a** (%)	ee[b] of **8a** (%)
1	20	83	26
2	30	76	42
3	49	83	56
4	85	88	71
5	>99	89	84

[a] The reaction was carried out with benzaldehyde **7a** and Et_2Zn (2 eq) in the presence of **3i** (3 mol %) in hexane at 30 °C for 24 h. [b] Chiral HPLC analysis. [c] Isolated yield.

References

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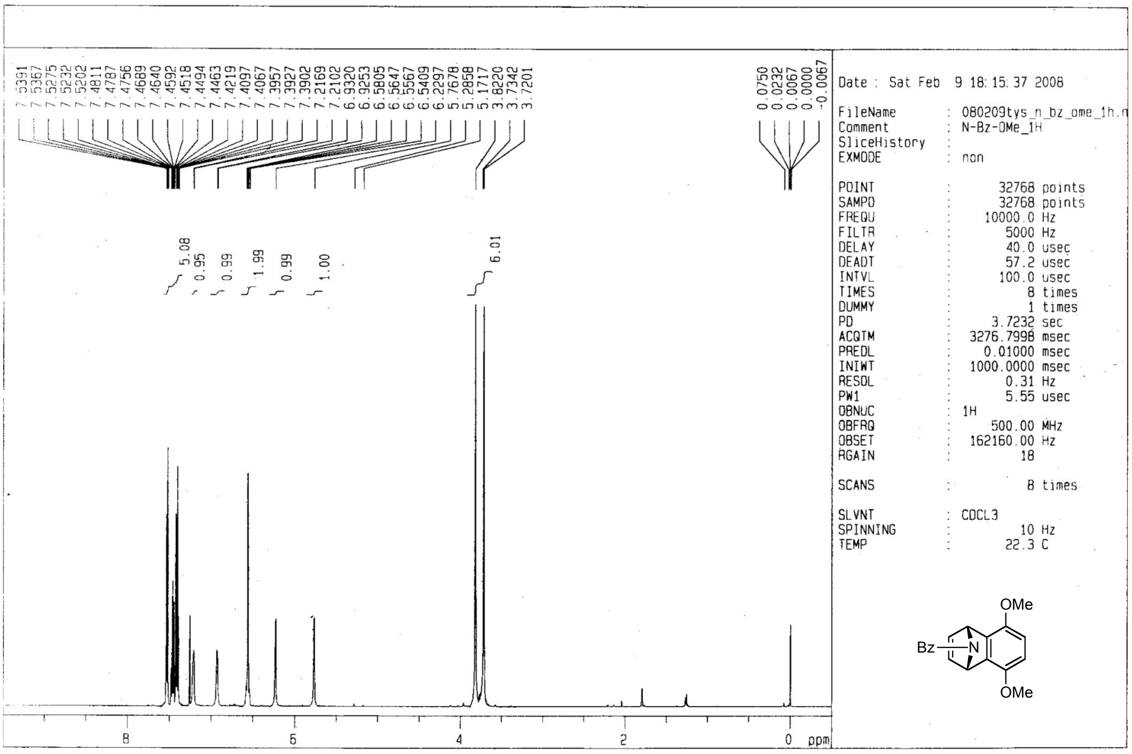
Spectra (^{1}H and ^{13}C NMR) of New Compounds



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OBNUC               :  1H
OBFRQ               :       500.00 MHz
OBSET               :    162160.00 Hz
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SCANS               :            8 times

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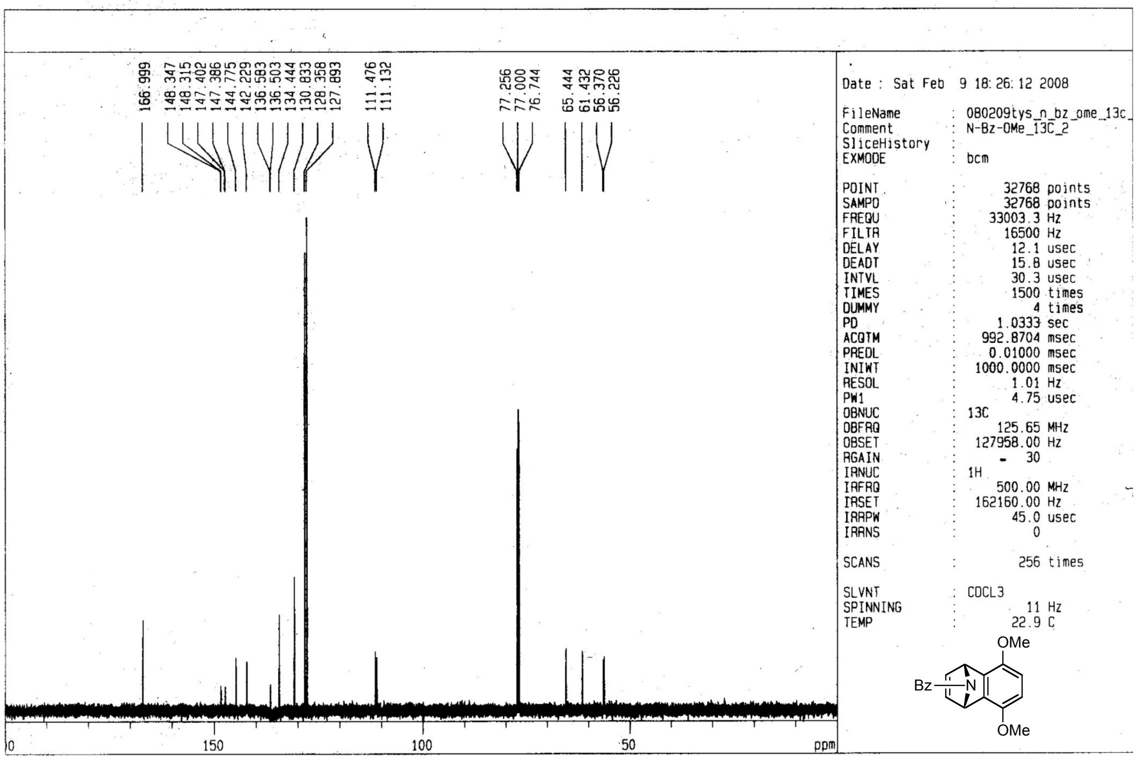

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OBFRQ               :       125.65 MHz
OBSET               :    127958.00 Hz
RGAIN               :  -        30
IRNUC               :  1H
IRFRQ               :       500.00 MHz
IRSET               :    162160.00 Hz
IRRPW               :         45.0 usec
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SCANS               :          256 times

SLVNT               :  CDCL3
SPINNING            :           11 Hz
TEMP                :         22.9 C
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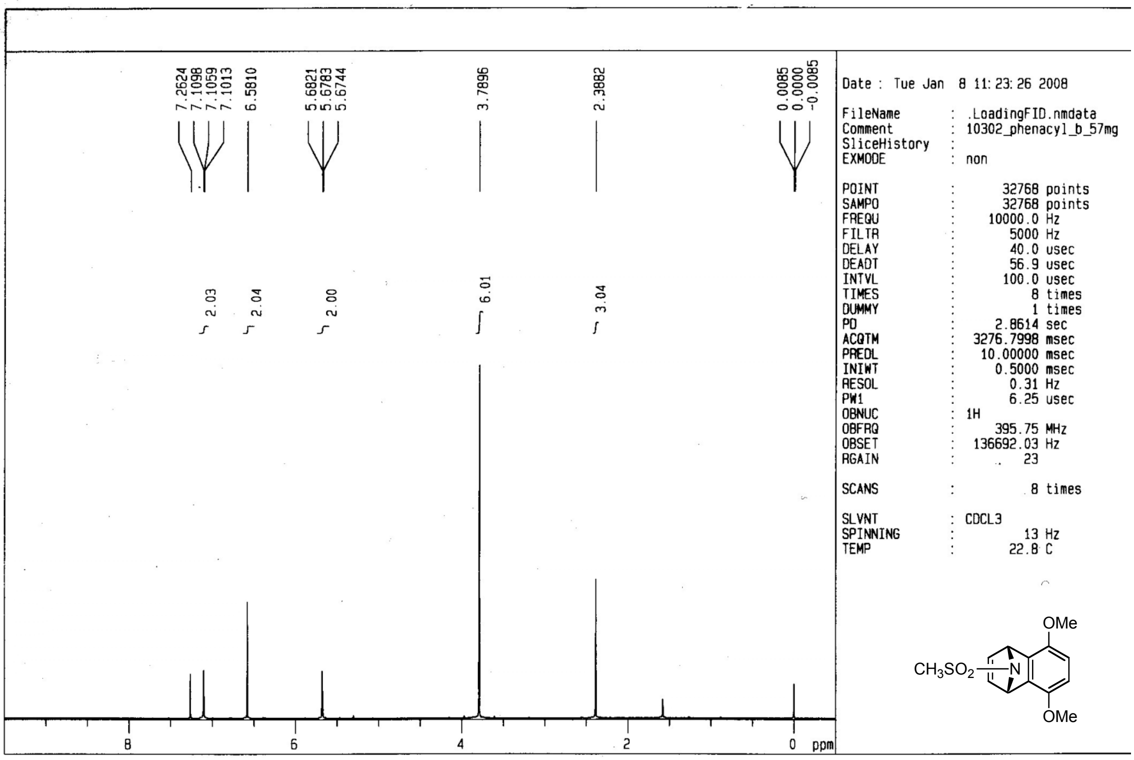

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PREDL         :   10.00000 msec
INIWT         :     0.5000 msec
RESOL         :       0.31 Hz
PW1           :       6.25 usec
OBNUC         : 1H
OBFRQ         :     395.75 MHz
OBSET         :  136692.03 Hz
RGAIN         :   ..    23

SCANS         :          8 times

SLVNT         : CDCL3
SPINNING      :         13 Hz
TEMP          :       22.8 C
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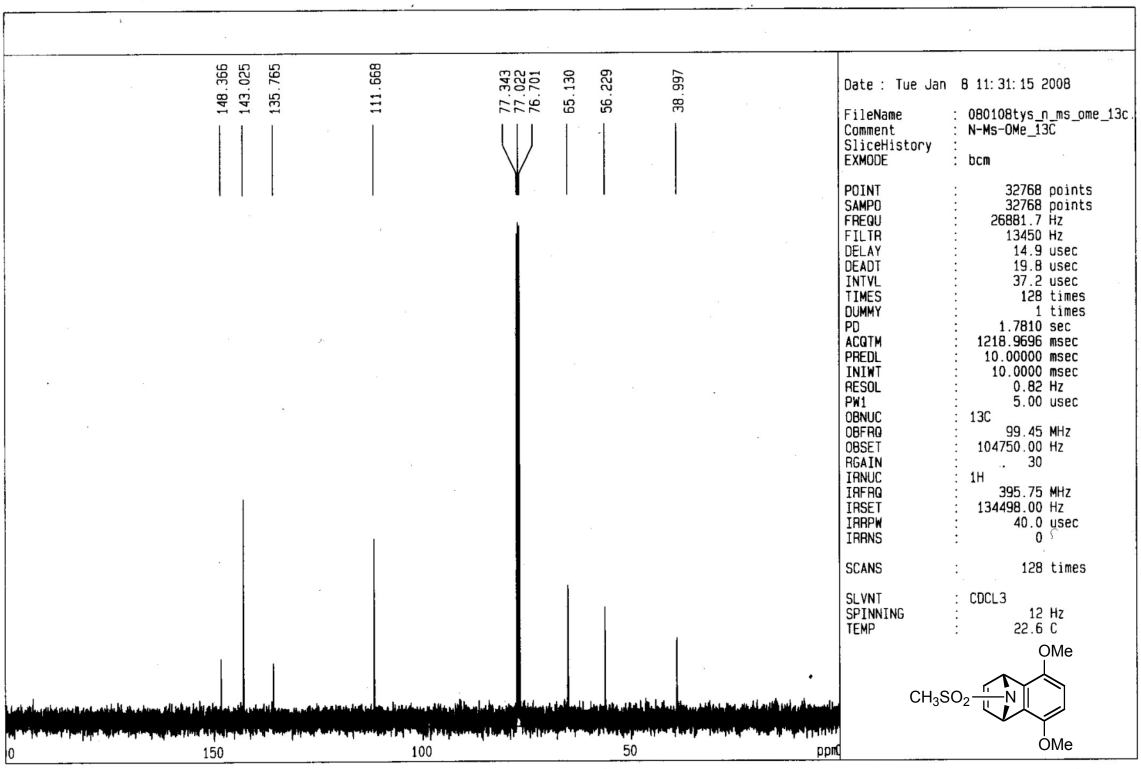

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INIWT         :    10.0000 msec
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OBNUC         : 13C
OBFRQ         :      99.45 MHz
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RGAIN         :   ..    30
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IRFRQ         :     395.75 MHz
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SPINNING      :         12 Hz
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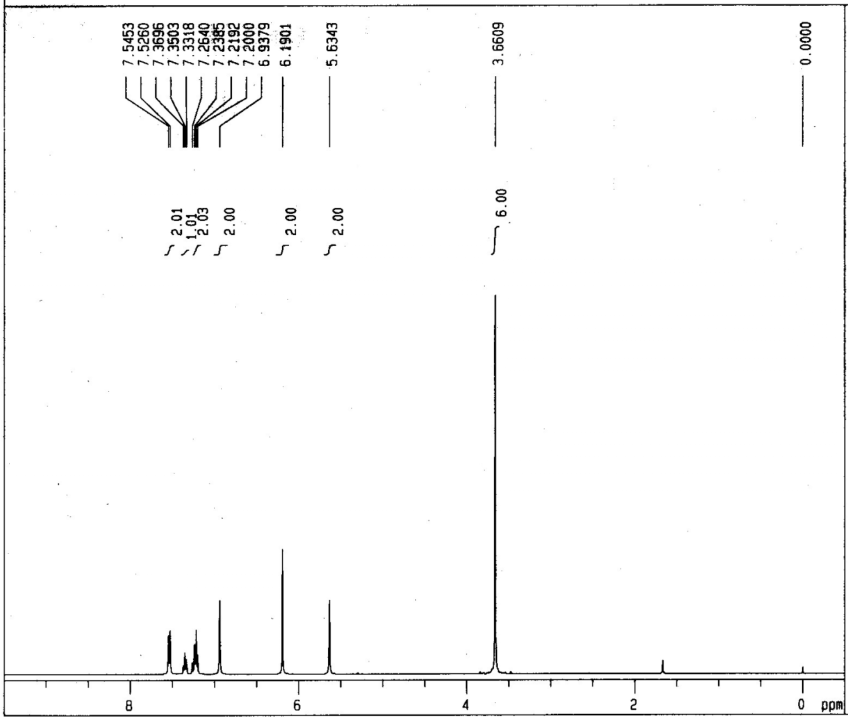

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INIWT           :      0.5000 msec
RESOL           :        0.31 Hz
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OBNUC           : 1H
OBFRQ           :      395.75 MHz
OBSET           :   136692.03 Hz
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SCANS           :           8 times

SLVNT           : CDCL3
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TEMP            :        22.7 C
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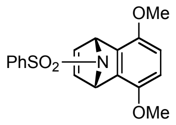

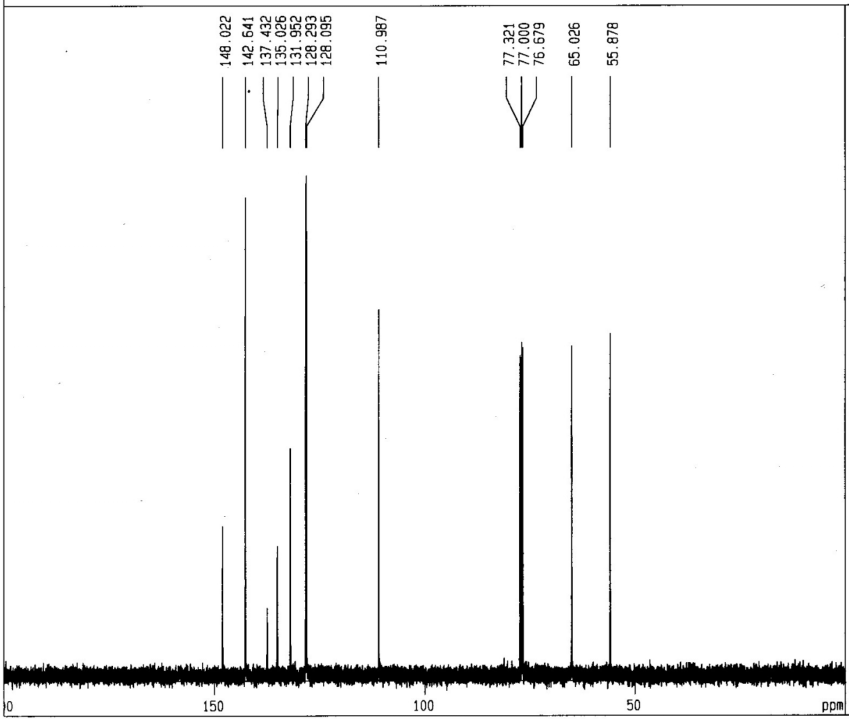

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OBFRQ           :       99.45 MHz
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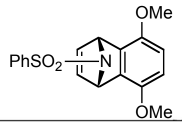

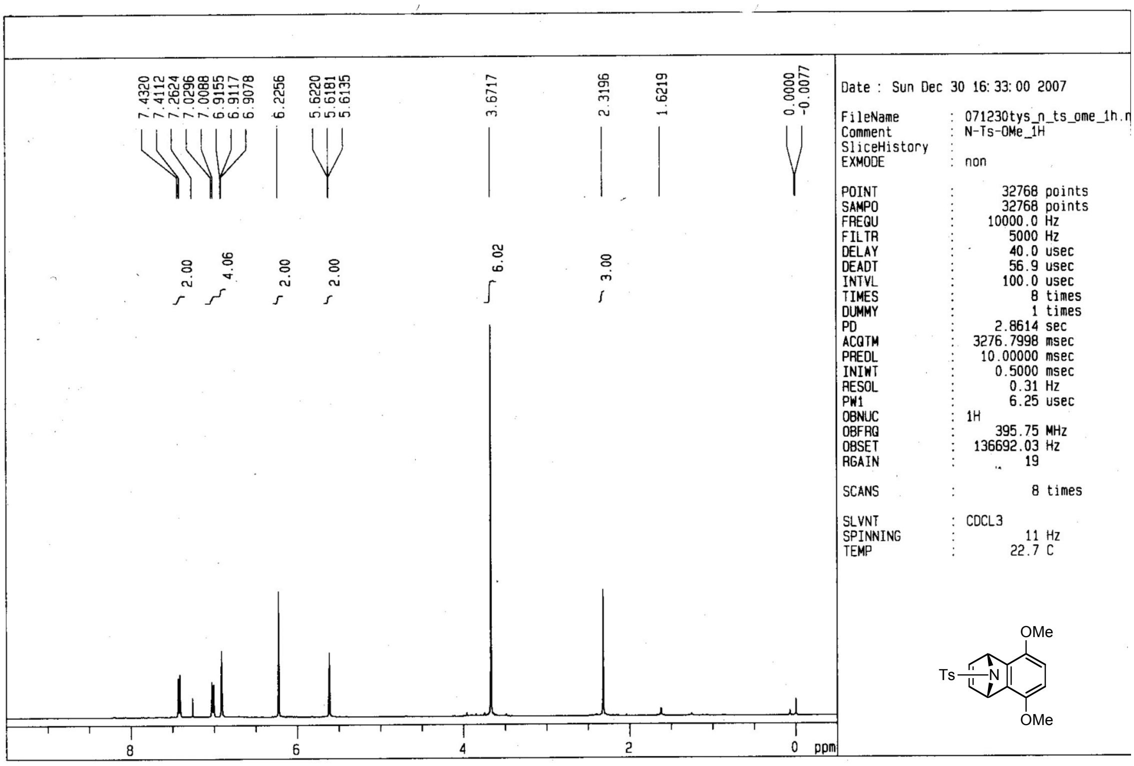

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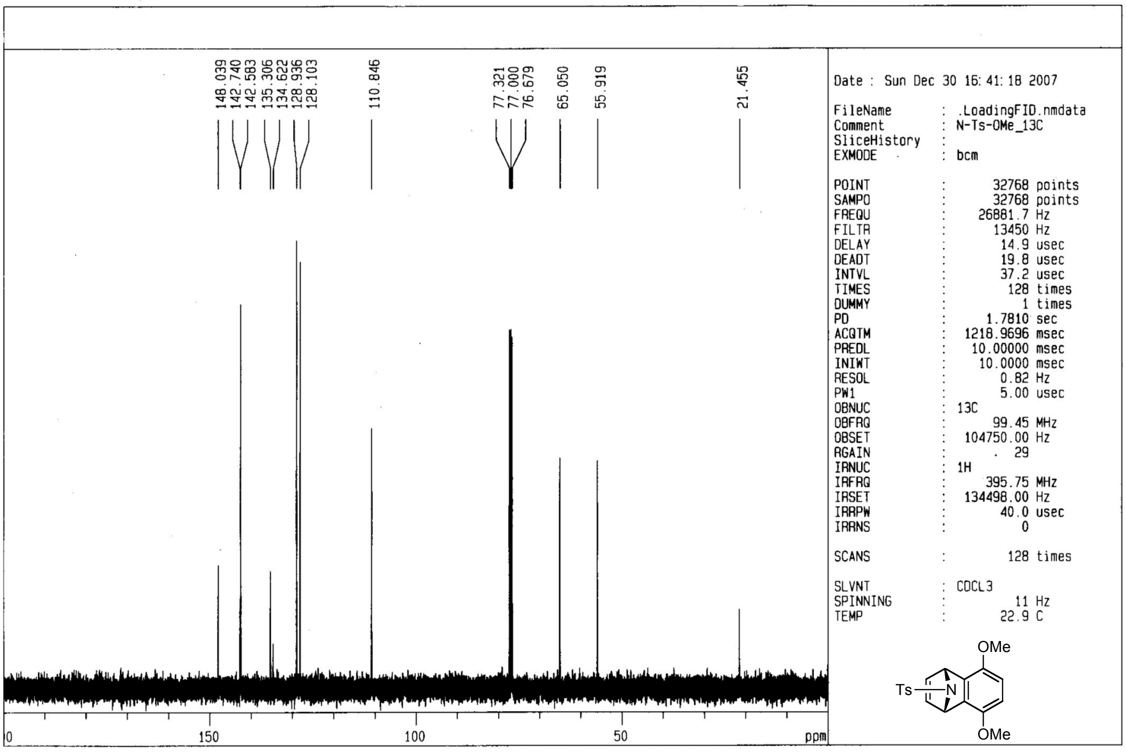

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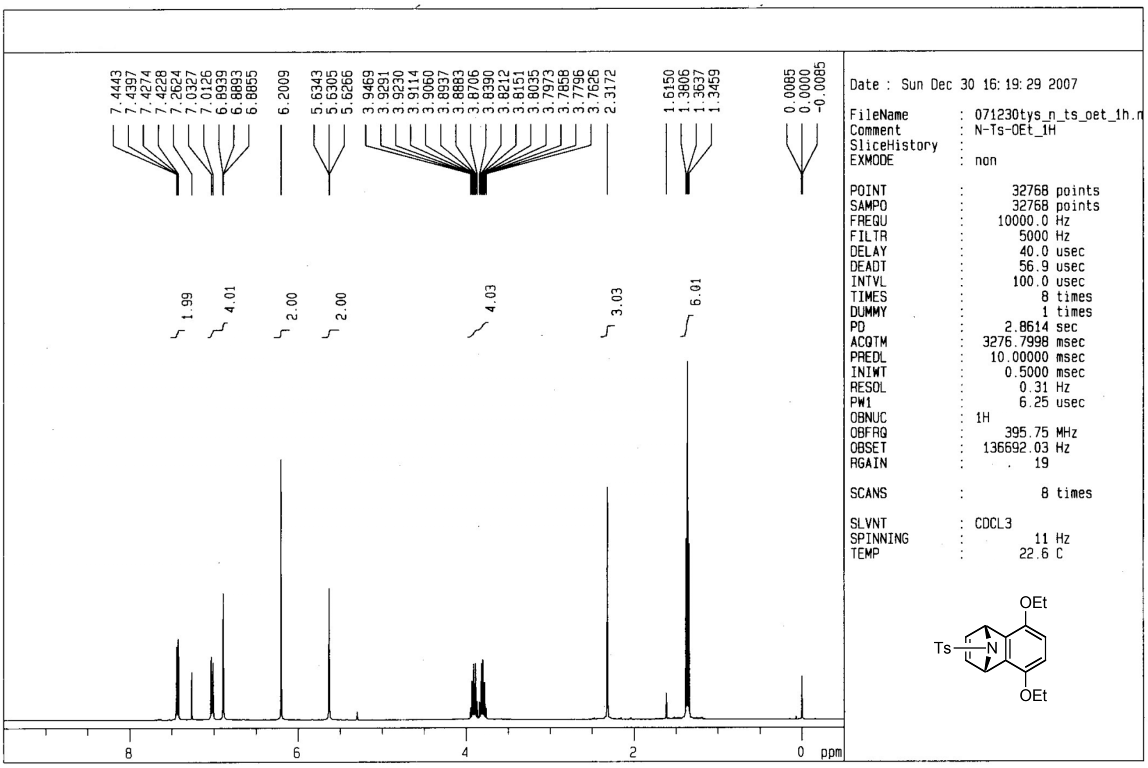

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RGAIN          :         . 19

SCANS          :           8 times

SLVNT          : CDCL3
SPINNING       :          11 Hz
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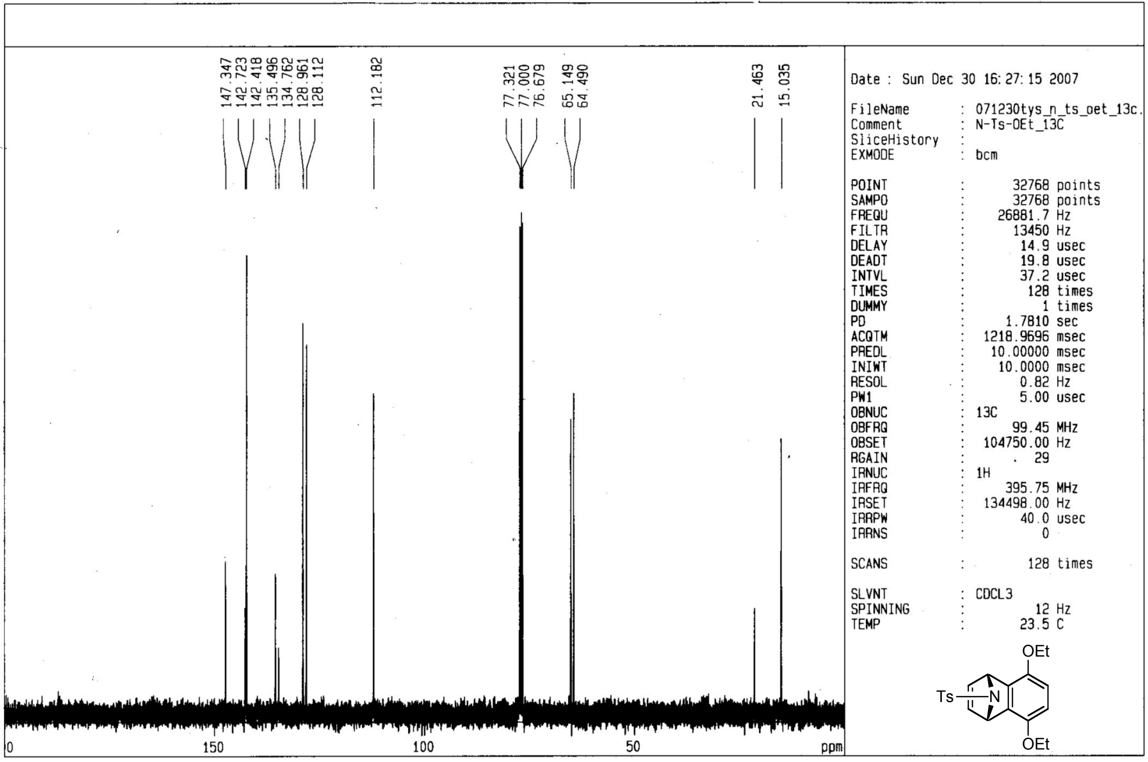

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PREDL          :    10.00000 msec
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RESOL          :        0.82 Hz
PW1            :        5.00 usec
OBNUC          : 13C
OBFRQ          :       99.45 MHz
OBSET          :   104750.00 Hz
RGAIN          :         . 29
IRNUC          : 1H
IRFRQ          :      395.75 MHz
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SCANS          :         128 times

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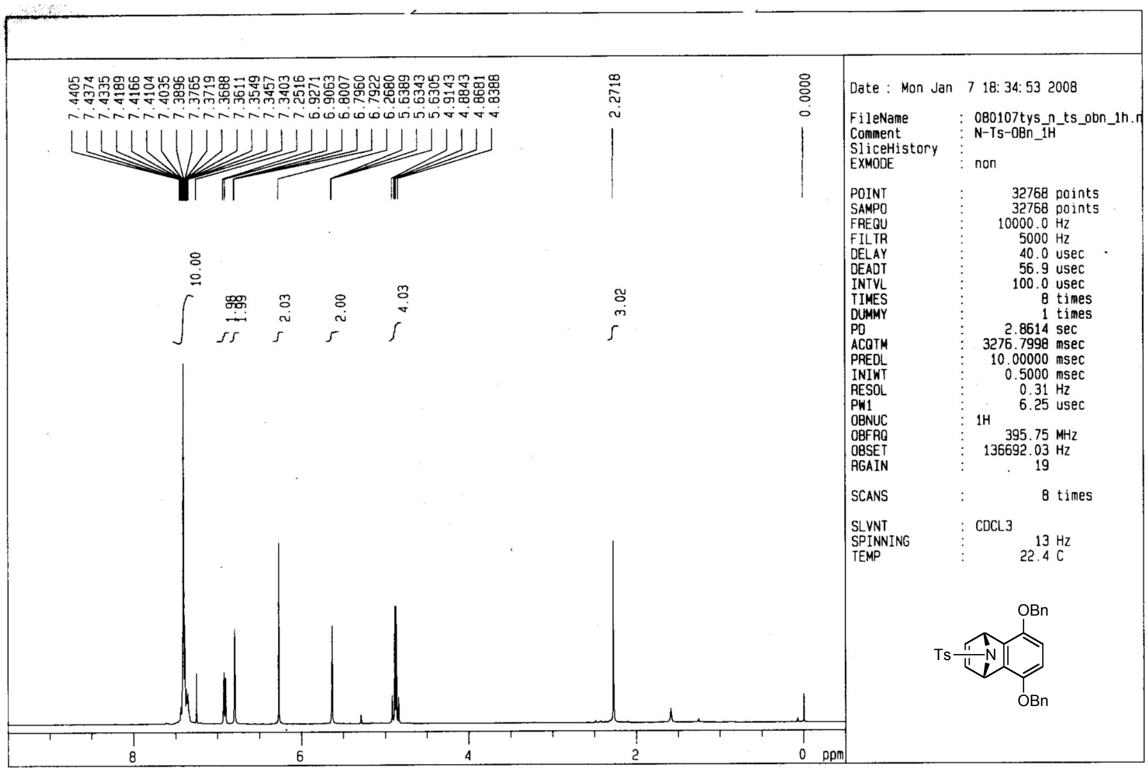

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TIMES          :            8 times
DUMMY          :            1 times
PD             :       2.8614 sec
ACQTM          :    3276.7998 msec
PREDL          :     10.00000 msec
INIWT          :       0.5000 msec
RESOL          :         0.31 Hz
PW1            :         6.25 usec
OBNUC          : 1H
OBFRQ          :       395.75 MHz
OBSET          :    136692.03 Hz
RGAIN          :           19

SCANS          :            8 times

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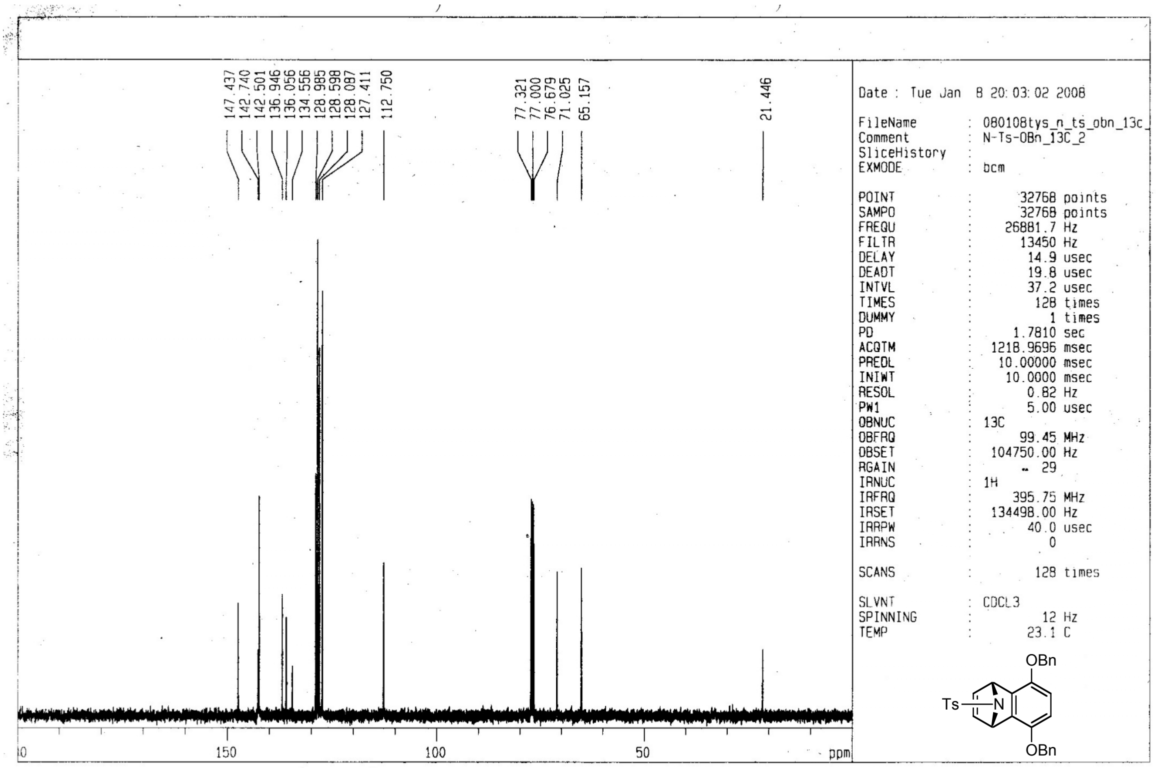

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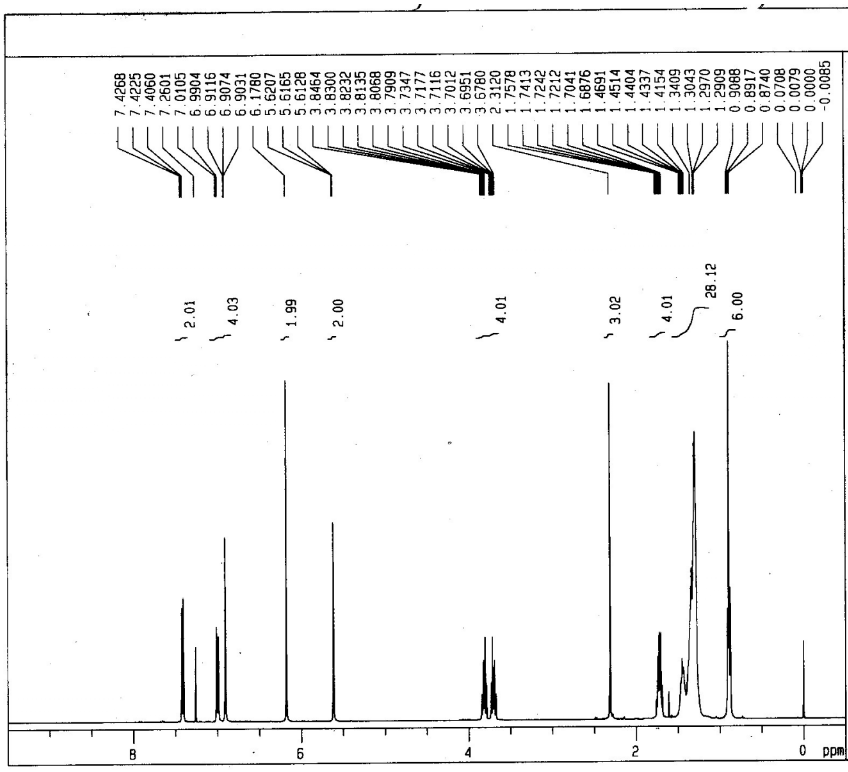
DEADT          :         19.8 usec
INTVL          :         37.2 usec
TIMES          :          128 times
DUMMY          :            1 times
PD             :       1.7810 sec
ACQTM          :    1218.9696 msec
PREDL          :     10.00000 msec
INIWT          :      10.0000 msec
RESOL          :         0.82 Hz
PW1            :         5.00 usec
OBNUC          : 13C
OBFRQ          :        99.45 MHz
OBSET          :    104750.00 Hz
RGAIN          :           29
IRNUC          : 1H
IRFRQ          :       395.75 MHz
IRSET          :    134498.00 Hz
IRRPW          :         40.0 usec
IRRNS          :            0

SCANS          :          128 times

SLVNT          : CDCL3
SPINNING       :           12 Hz
TEMP           :         23.1 C
```



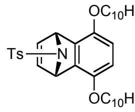
```
Date : Fri Jan 25 20:51:31 2008

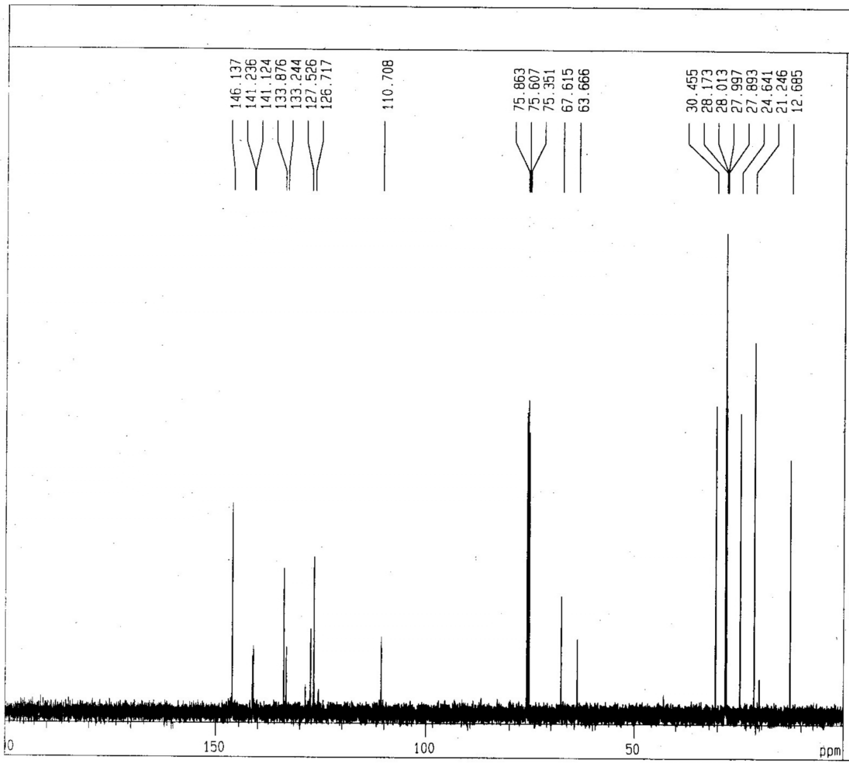
FileName      : 080125tys_n_ts_odec_1h.
Comment       : N-Ts-Odec_1H
SliceHistory  :
EXMODE        : non

POINT         :       32768 points
SAMPO         :       32768 points
FREQU         :      7917.7 Hz
FILTR         :        3950 Hz
DELAY         :        50.6 usec
DEADT         :        72.8 usec
INTVL         :       126.3 usec
TIMES         :           8 times
DUMMY         :           1 times
PD            :      2.8614 sec
ACQTM         :   4138.5986 msec
PREDL         :    10.00000 msec
INIWT         :      0.5000 msec
RESOL         :        0.24 Hz
PW1           :        6.25 usec
OBNUC         : 1H
OBFRQ         :      395.75 MHz
OBSET         :   134498.00 Hz
RGAIN         :   ..     15

SCANS         :           8 times

SLVNT         : CDCL3
SPINNING      :          13 Hz
TEMP          :        20.8 C
```





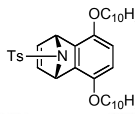
```
Date : Wed Jan 23 16:02:46 2008

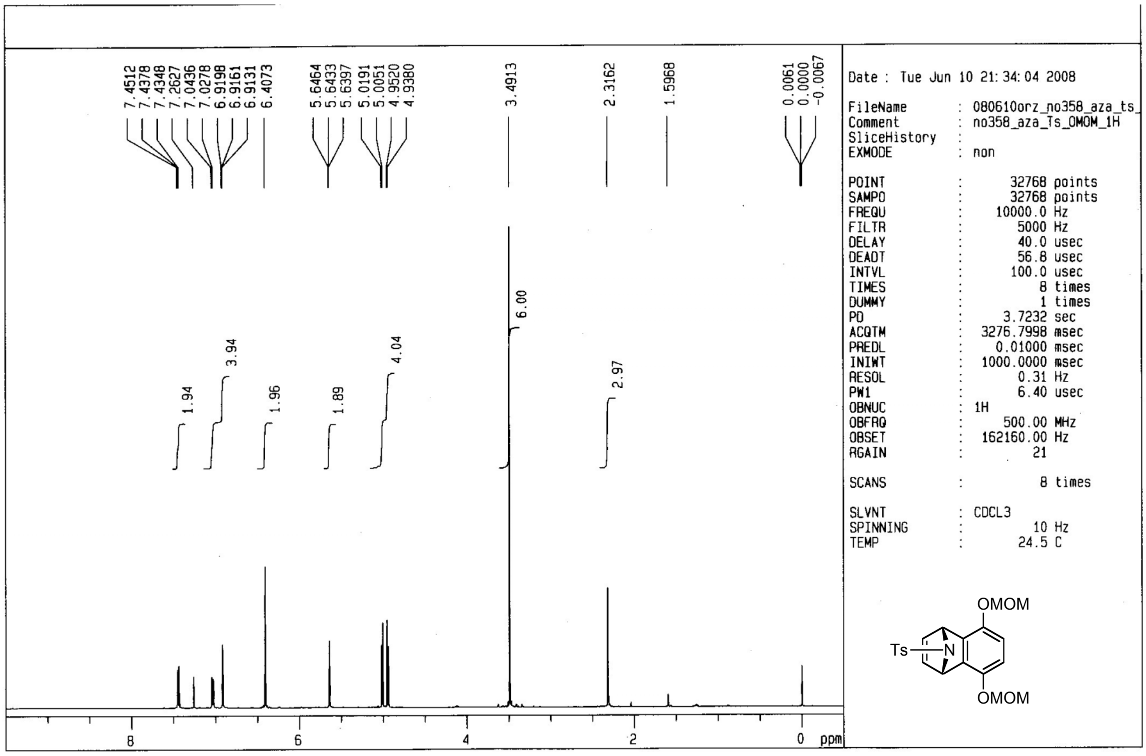
FileName      : 080123tys_n_ts_odec_13c
Comment       : N-Ts-Odec_13C
SliceHistory  :
EXMODE        : bcm

POINT         :       32768 points
SAMPO         :       32768 points
FREQU         :     33003.3 Hz
FILTR         :       16500 Hz
DELAY         :        12.1 usec
DEADT         :        15.8 usec
INTVL         :        30.3 usec
TIMES         :         128 times
DUMMY         :           4 times
PD            :      1.0333 sec
ACQTM         :    992.8704 msec
PREDL         :     0.01000 msec
INIWT         :   1000.0000 msec
RESOL         :        1.01 Hz
PW1           :        4.75 usec
OBNUC         : 13C
OBFRQ         :      125.65 MHz
OBSET         :   127958.00 Hz
RGAIN         :   ~      31
IRNUC         : 1H
IRFRQ         :      500.00 MHz
IRSET         :   162160.00 Hz
IRRPW         :        45.0 usec
IRRNS         :   .       0

SCANS         :         128 times

SLVNT         : CD2CL2
SPINNING      :          10 Hz
TEMP          :        22.8 C
```





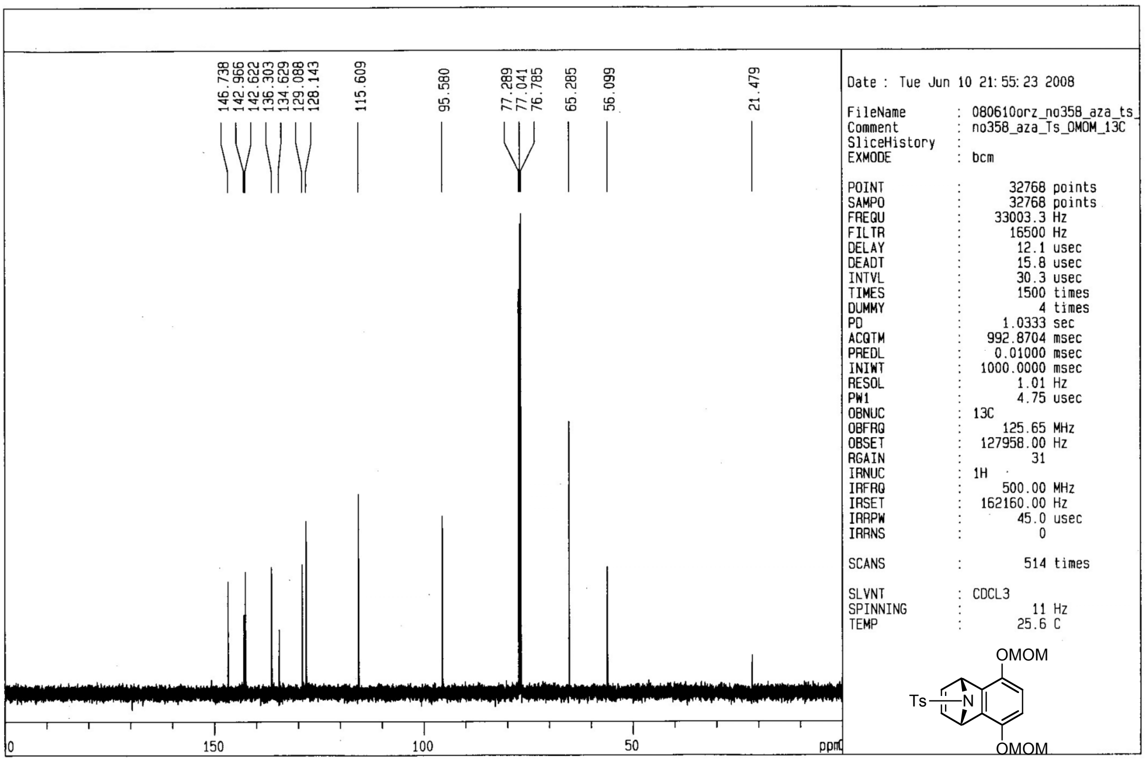
```
Date : Tue Jun 10 21:34:04 2008

FileName      : 080610orz_no358_aza_ts_
Comment       : no358_aza_Ts_OMOM_1H
SliceHistory  :
EXMODE        : non

POINT         :      32768 points
SAMPO         :      32768 points
FREQU         :    10000.0 Hz
FILTR         :       5000 Hz
DELAY         :       40.0 usec
DEADT         :       56.8 usec
INTVL         :      100.0 usec
TIMES         :          8 times
DUMMY         :          1 times
PD            :     3.7232 sec
ACQTM         :  3276.7998 msec
PREDL         :    0.01000 msec
INIWT         :  1000.0000 msec
RESOL         :       0.31 Hz
PW1           :       6.40 usec
OBNUC         : 1H
OBFRQ         :     500.00 MHz
OBSET         :  162160.00 Hz
RGAIN         :         21

SCANS         :          8 times

SLVNT         : CDCL3
SPINNING      :         10 Hz
TEMP          :       24.5 C
```



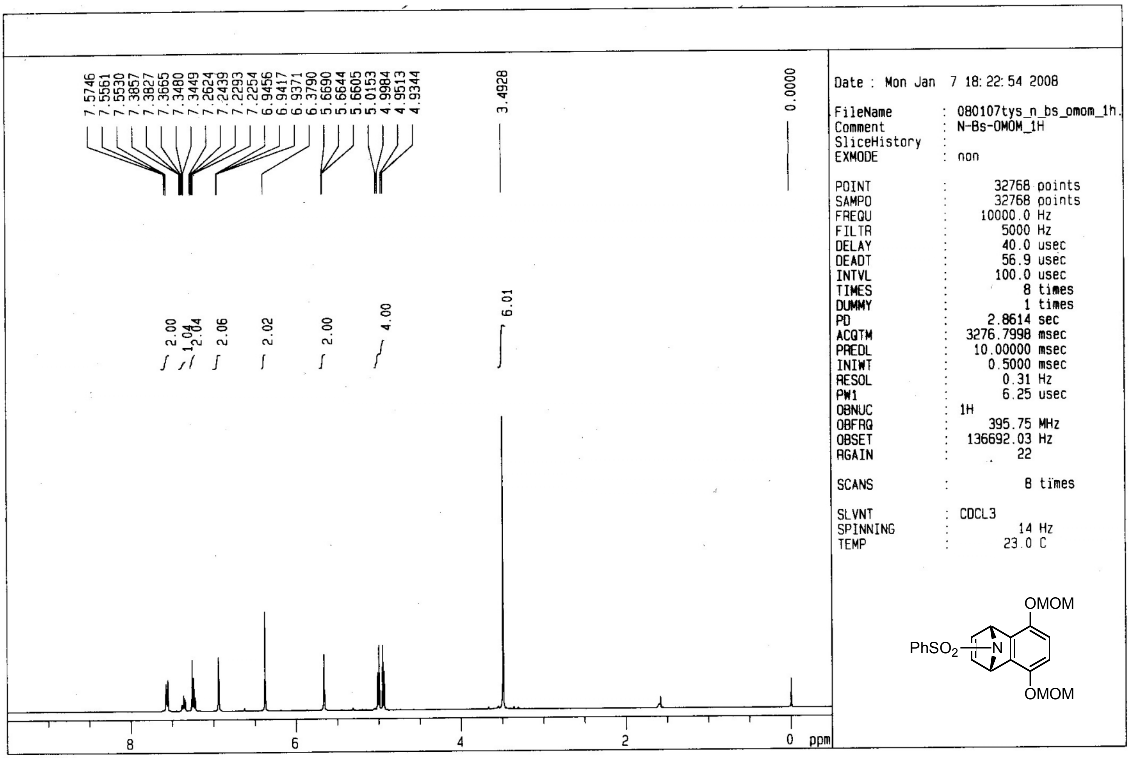
```
Date : Tue Jun 10 21:55:23 2008

FileName      : 080610orz_no358_aza_ts_
Comment       : no358_aza_Ts_OMOM_13C
SliceHistory  :
EXMODE        : bcm

POINT         :      32768 points
SAMPO         :      32768 points
FREQU         :    33003.3 Hz
FILTR         :      16500 Hz
DELAY         :       12.1 usec
DEADT         :       15.8 usec
INTVL         :       30.3 usec
TIMES         :       1500 times
DUMMY         :          4 times
PD            :     1.0333 sec
ACQTM         :   992.8704 msec
PREDL         :    0.01000 msec
INIWT         :  1000.0000 msec
RESOL         :       1.01 Hz
PW1           :       4.75 usec
OBNUC         : 13C
OBFRQ         :     125.65 MHz
OBSET         :  127958.00 Hz
RGAIN         :         31
IRNUC         : 1H
IRFRQ         :     500.00 MHz
IRSET         :  162160.00 Hz
IRRPW         :       45.0 usec
IRRNS         :          0

SCANS         :        514 times

SLVNT         : CDCL3
SPINNING      :         11 Hz
TEMP          :       25.6 C
```



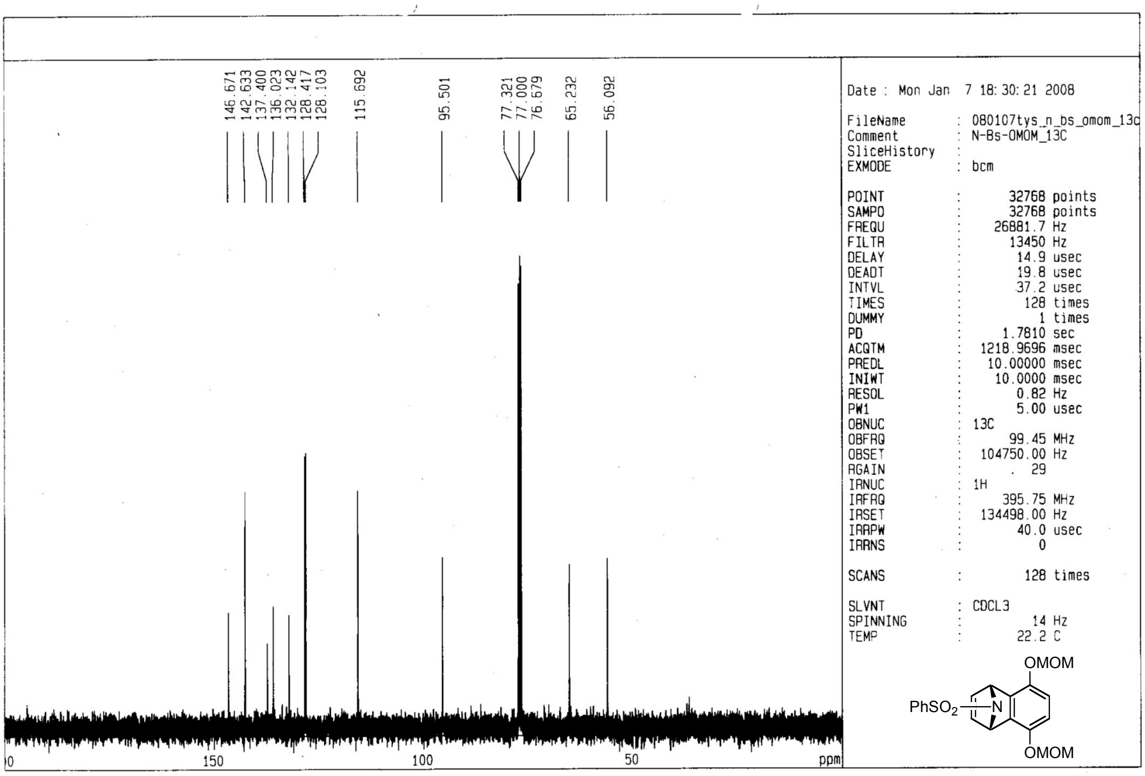
```
Date : Mon Jan  7 18:22:54 2008

FileName      : 080107tys_n_bs_omom_1h.
Comment       : N-Bs-OMOM_1H
SliceHistory  :
EXMODE        : non

POINT         :      32768 points
SAMPO         :      32768 points
FREQU         :    10000.0 Hz
FILTR         :       5000 Hz
DELAY         :       40.0 usec
DEADT         :       56.9 usec
INTVL         :      100.0 usec
TIMES         :          8 times
DUMMY         :          1 times
PD            :     2.8614 sec
ACQTM         :  3276.7998 msec
PREDL         :   10.00000 msec
INIWT         :     0.5000 msec
RESOL         :       0.31 Hz
PW1           :       6.25 usec
OBNUC         : 1H
OBFRQ         :     395.75 MHz
OBSET         :  136692.03 Hz
RGAIN         :         22

SCANS         :          8 times

SLVNT         : CDCL3
SPINNING      :         14 Hz
TEMP          :       23.0 C
```



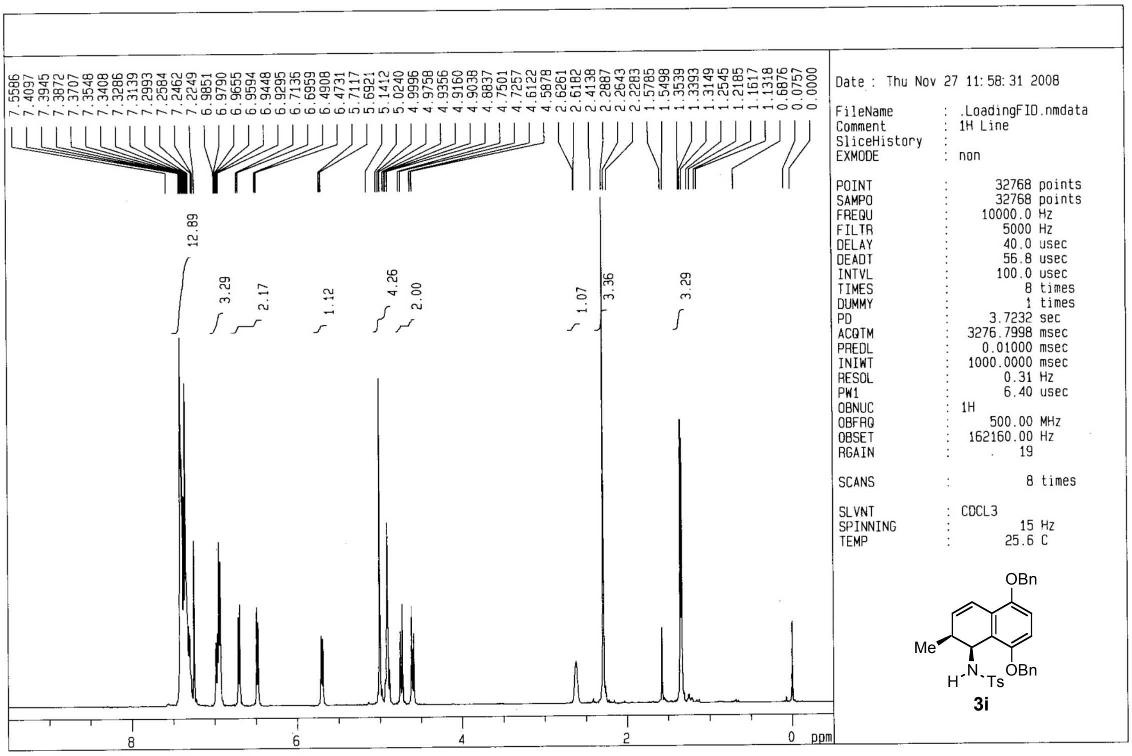
```
Date : Mon Jan  7 18:30:21 2008

FileName      : 080107tys_n_bs_omom_13c
Comment       : N-Bs-OMOM_13C
SliceHistory  :
EXMODE        : bcm

POINT         :      32768 points
SAMPO         :      32768 points
FREQU         :    26881.7 Hz
FILTR         :      13450 Hz
DELAY         :       14.9 usec
DEADT         :       19.8 usec
INTVL         :       37.2 usec
TIMES         :        128 times
DUMMY         :          1 times
PD            :     1.7810 sec
ACQTM         :  1218.9696 msec
PREDL         :   10.00000 msec
INIWT         :    10.0000 msec
RESOL         :       0.82 Hz
PW1           :       5.00 usec
OBNUC         : 13C
OBFRQ         :      99.45 MHz
OBSET         :  104750.00 Hz
RGAIN         :         29
IRNUC         : 1H
IRFRQ         :     395.75 MHz
IRSET         :  134498.00 Hz
IRRPW         :       40.0 usec
IRRNS         :          0

SCANS         :        128 times

SLVNT         : CDCL3
SPINNING      :         14 Hz
TEMP          :       22.2 C
```



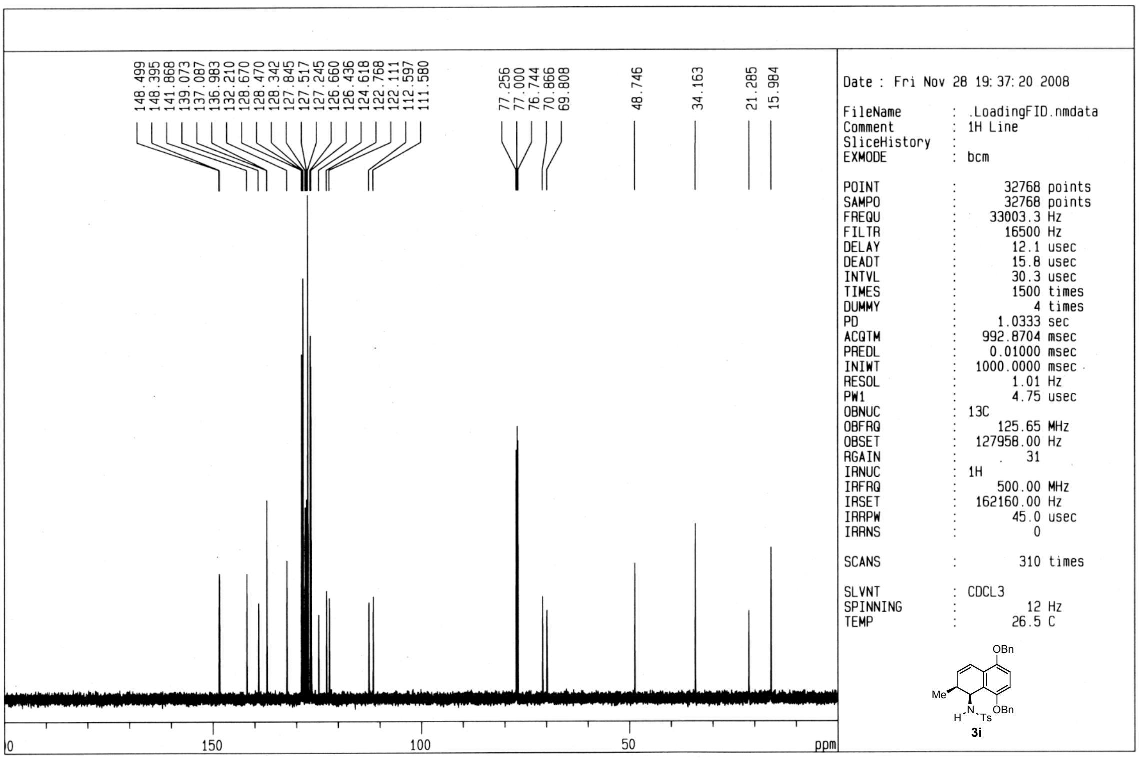
```
Date : Thu Nov 27 11:58:31 2008

FileName       : .LoadingFID.nmdata
Comment        : 1H Line
SliceHistory   :
EXMODE         : non

POINT          :        32768 points
SAMPO          :        32768 points
FREQU          :      10000.0 Hz
FILTR          :         5000 Hz
DELAY          :         40.0 usec
DEADT          :         56.8 usec
INTVL          :        100.0 usec
TIMES          :            8 times
DUMMY          :            1 times
PD             :       3.7232 sec
ACQTM          :    3276.7998 msec
PREDL          :      0.01000 msec
INIWT          :    1000.0000 msec
RESOL          :         0.31 Hz
PW1            :         6.40 usec
OBNUC          : 1H
OBFRQ          :       500.00 MHz
OBSET          :    162160.00 Hz
RGAIN          :           19

SCANS          :            8 times

SLVNT          : CDCL3
SPINNING       :           15 Hz
TEMP           :         25.6 C
```



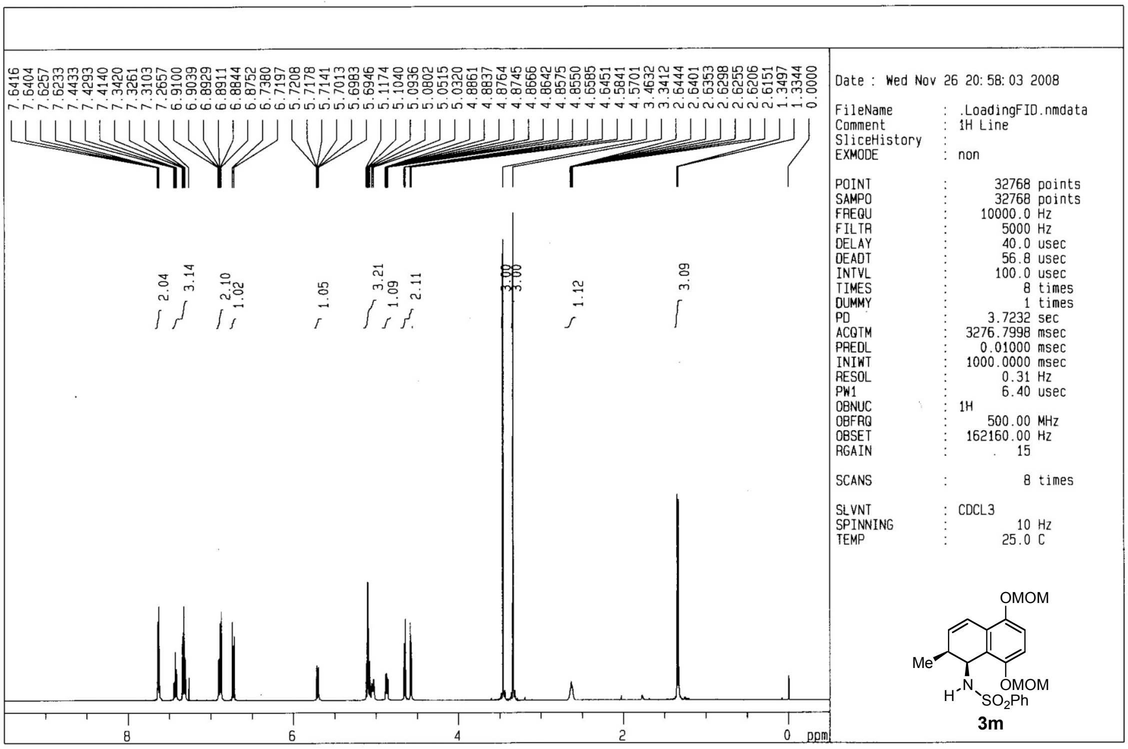
```
Date : Fri Nov 28 19:37:20 2008

FileName       : .LoadingFID.nmdata
Comment        : 1H Line
SliceHistory   :
EXMODE         : bcm

POINT          :        32768 points
SAMPO          :        32768 points
FREQU          :      33003.3 Hz
FILTR          :        16500 Hz
DELAY          :         12.1 usec
DEADT          :         15.8 usec
INTVL          :         30.3 usec
TIMES          :         1500 times
DUMMY          :            4 times
PD             :       1.0333 sec
ACQTM          :     992.8704 msec
PREDL          :      0.01000 msec
INIWT          :    1000.0000 msec
RESOL          :         1.01 Hz
PW1            :         4.75 usec
OBNUC          : 13C
OBFRQ          :       125.65 MHz
OBSET          :    127958.00 Hz
RGAIN          :           31
IRNUC          : 1H
IRFRQ          :       500.00 MHz
IRSET          :    162160.00 Hz
IRRPW          :         45.0 usec
IRRNS          :            0

SCANS          :          310 times

SLVNT          : CDCL3
SPINNING       :           12 Hz
TEMP           :         26.5 C
```



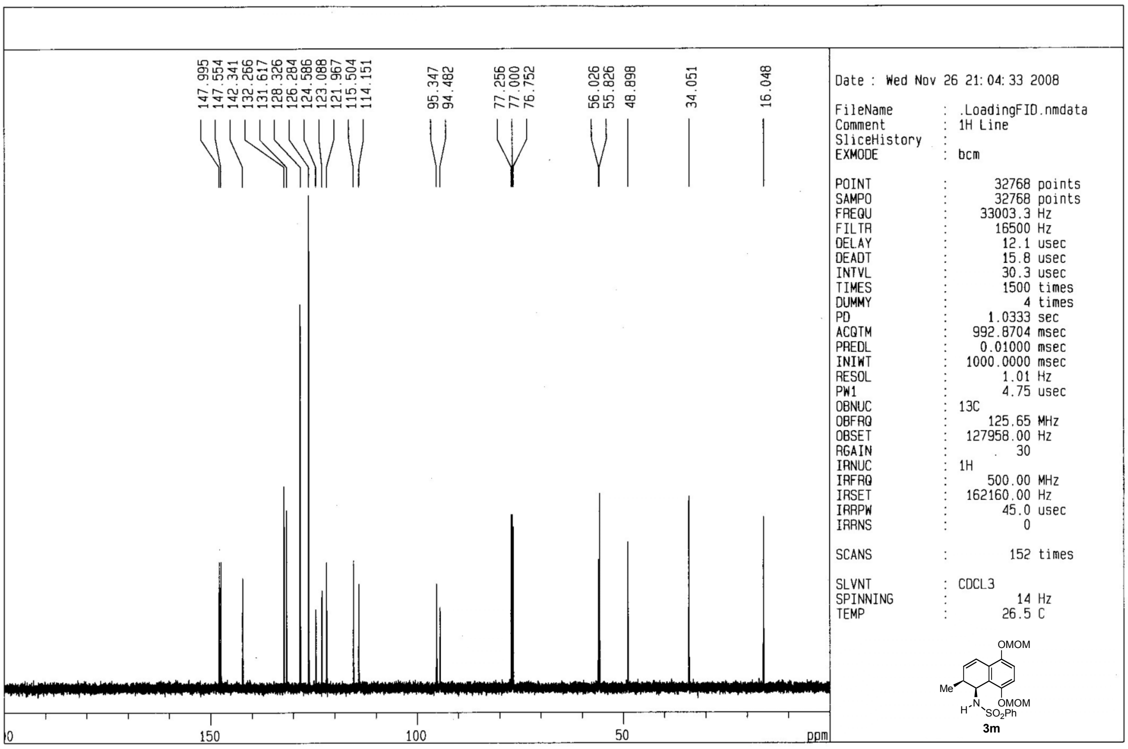
```
Date :  Wed Nov 26 20:58:03 2008

FileName        : .LoadingFID.nmdata
Comment         : 1H Line
SliceHistory    :
EXMODE          : non

POINT           :      32768 points
SAMPO           :      32768 points
FREQU           :    10000.0 Hz
FILTR           :       5000 Hz
DELAY           :       40.0 usec
DEADT           :       56.8 usec
INTVL           :      100.0 usec
TIMES           :          8 times
DUMMY           :          1 times
PD              :     3.7232 sec
ACQTM           :  3276.7998 msec
PREDL           :    0.01000 msec
INIWT           :  1000.0000 msec
RESOL           :       0.31 Hz
PW1             :       6.40 usec
OBNUC           : 1H
OBFRQ           :     500.00 MHz
OBSET           :  162160.00 Hz
RGAIN           :         15

SCANS           :          8 times

SLVNT           : CDCL3
SPINNING        :         10 Hz
TEMP            :       25.0 C
```



```
Date :  Wed Nov 26 21:04:33 2008

FileName        : .LoadingFID.nmdata
Comment         : 1H Line
SliceHistory    :
EXMODE          : bcm

POINT           :      32768 points
SAMPO           :      32768 points
FREQU           :    33003.3 Hz
FILTR           :      16500 Hz
DELAY           :       12.1 usec
DEADT           :       15.8 usec
INTVL           :       30.3 usec
TIMES           :       1500 times
DUMMY           :          4 times
PD              :     1.0333 sec
ACQTM           :   992.8704 msec
PREDL           :    0.01000 msec
INIWT           :  1000.0000 msec
RESOL           :       1.01 Hz
PW1             :       4.75 usec
OBNUC           : 13C
OBFRQ           :     125.65 MHz
OBSET           :  127958.00 Hz
RGAIN           :         30
IRNUC           : 1H
IRFRQ           :     500.00 MHz
IRSET           :  162160.00 Hz
IRRPW           :       45.0 usec
IRRNS           :          0

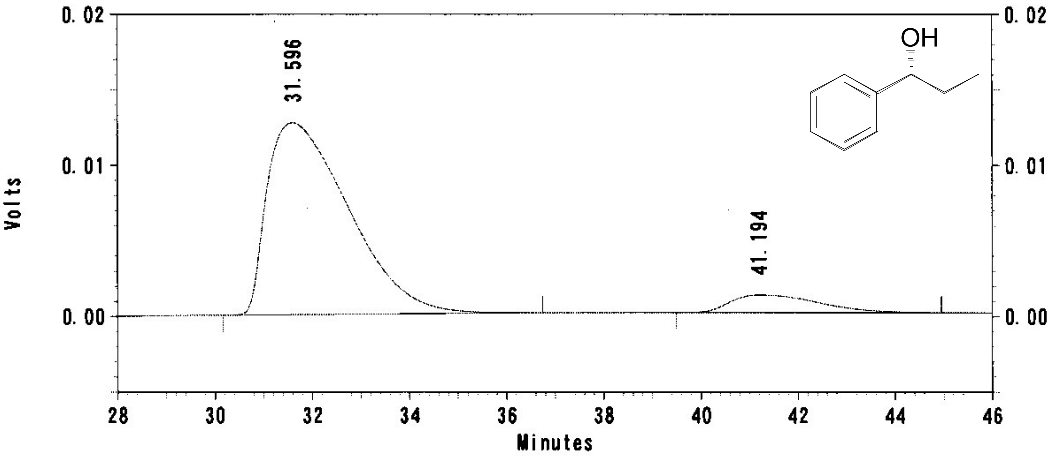
SCANS           :        152 times

SLVNT           : CDCL3
SPINNING        :         14 Hz
TEMP            :       26.5 C
```

Chiral HPLC Traces

Table 3, Entry 1

OD-H, Hexane/i-PrOH=98/2, 0.5ml/min, 254nm



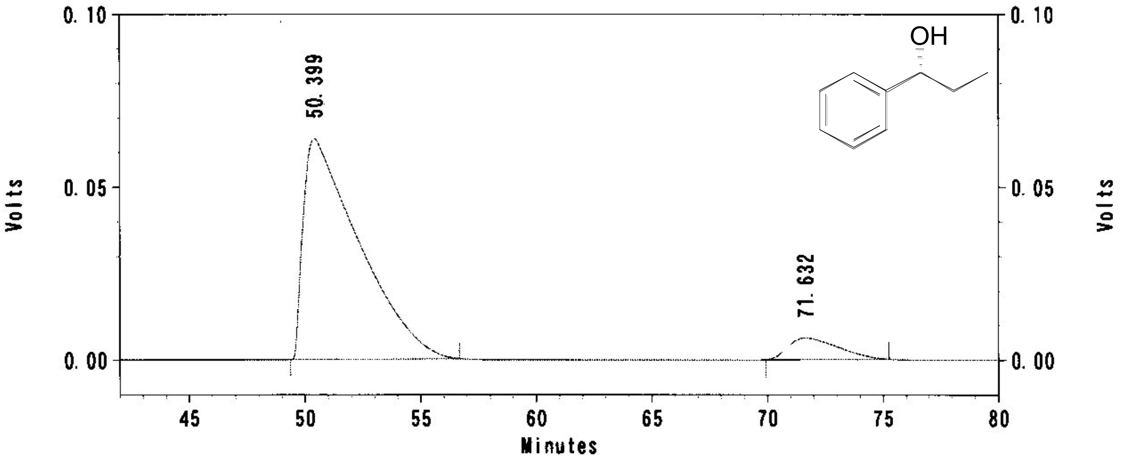
Detector 1 Results

保持時間	面積	Area Percent	高さ
31.596	1480220	90.872	12690
41.194	148680	9.128	1175

Totals			
	1628900	100.000	13865

Table 3, Entry 2

OD-H, Hexane/i-PrOH=98/2, 0.5ml/min, 254nm



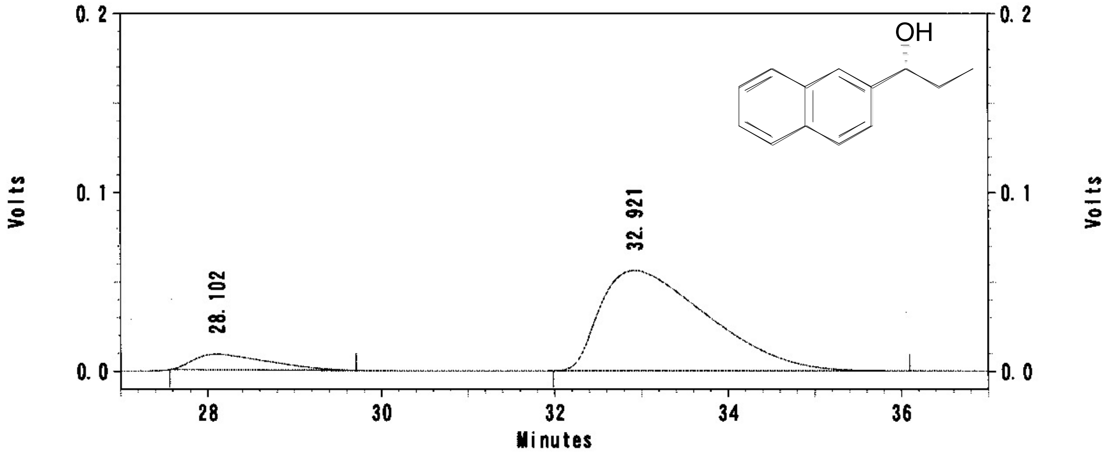
Detector 1 Results

保持時間	面積	Area Percent	高さ
50.399	10714638	91.987	63778
71.632	933308	8.013	6206

Totals			
	11647946	100.000	69984

Table 3, Entry 3

OD-H, Hexane/i-PrOH=9/1, 1.0ml/min, 254nm

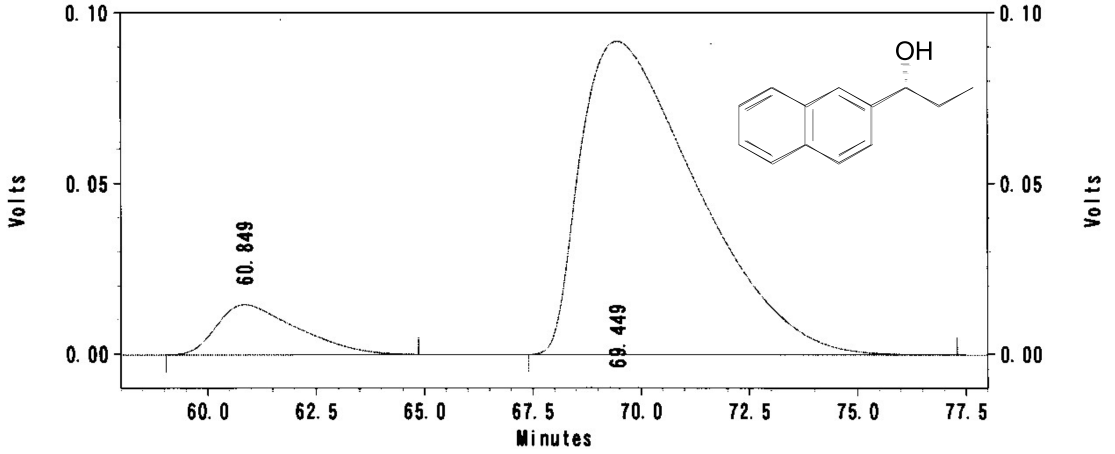


Detector 1 Results

保持時間	面積	Area Percent	高さ
28. 102	521765	9. 722	8835
32. 921	4844876	90. 278	56082
Totals	5366641	100. 000	64917

Table 3, Entry 4

OD-H, Hexane/i-PrOH=98/2, 0.5ml/min, 254nm

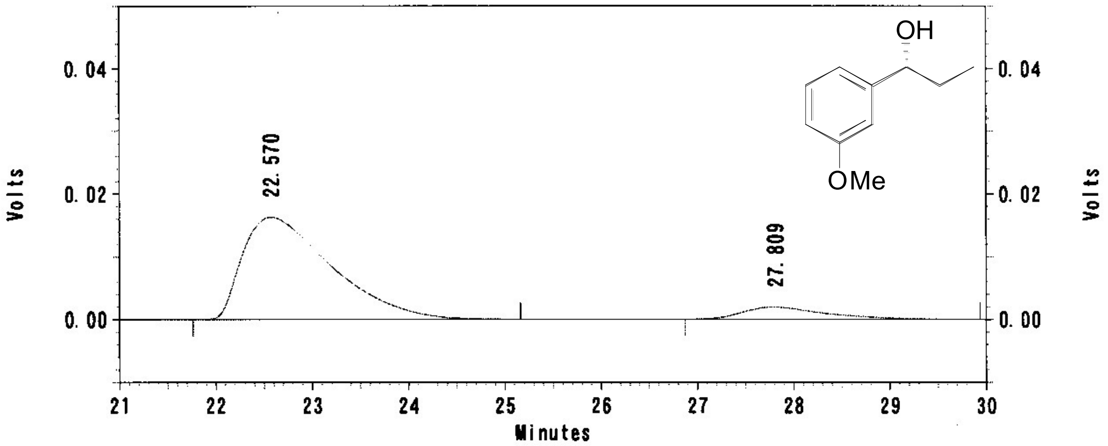


Detector 1 Results

保持時間	面積	Area Percent	高さ
60. 849	1896587	9. 920	14742
69. 449	17222599	90. 080	91812
Totals	19119186	100. 000	106554

Table 3, Entry 5

OD-H, Hexane/i-PrOH=98/2, 1.0ml/min, 254nm

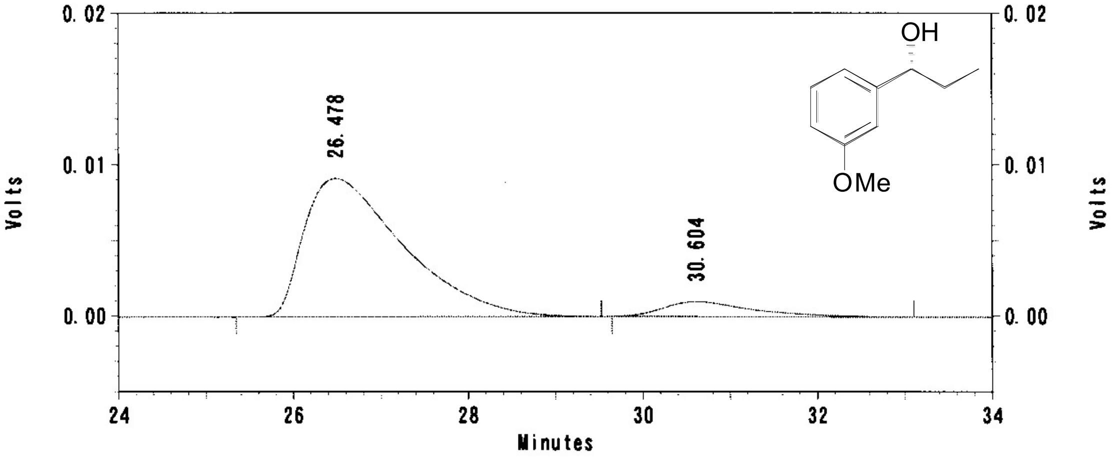


Detector 1 Results

保持時間	面積	Area Percent	高さ
22. 570	1044118	89. 836	16280
27. 809	118130	10. 164	1980
Totals	1162248	100. 000	18260

Table 3, Entry 6

OD-H, Hexane/i-PrOH=98/2, 1.0ml/min, 254nm

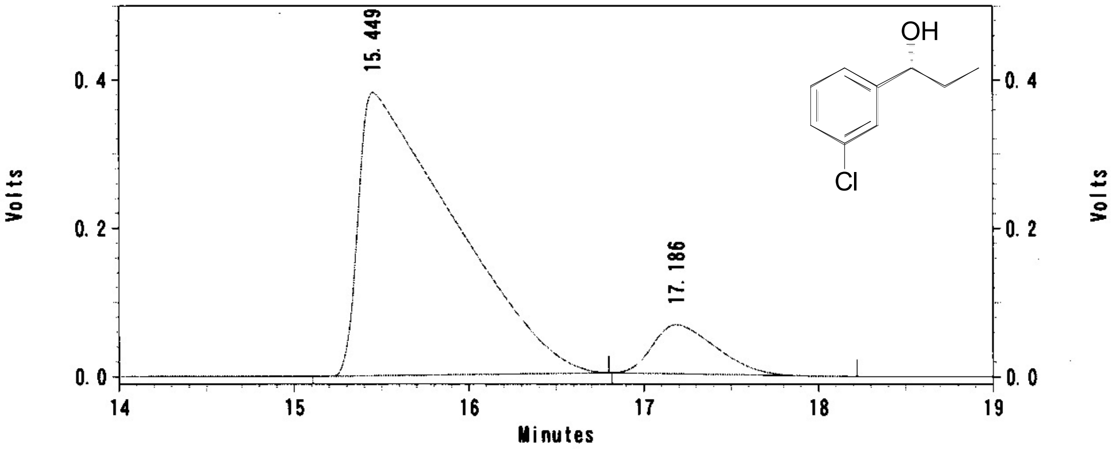


UV Results

保持時間	面積	Area Percent	高さ
26. 478	723324	91. 155	9158
30. 604	70185	8. 845	988
Totals	793509	100. 000	10146

Table 3, Entry 7

AD-H, Hexane/i-PrOH=98/2, 1.0ml/min, 254nm

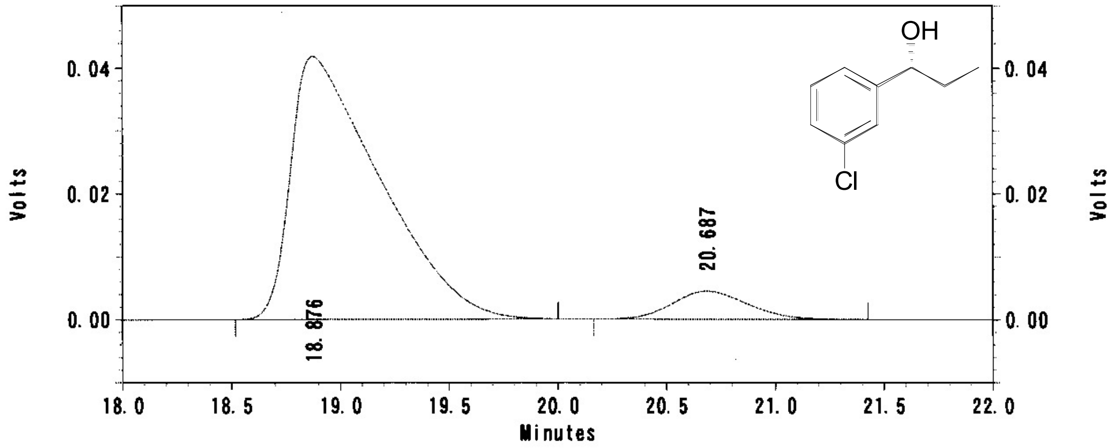


Detector 1 Results

保持時間	面積	Area Percent	高さ
15. 449	14462517	89. 731	381633
17. 186	1655129	10. 269	65880
Totals	16117646	100. 000	447513

Table 3, Entry 8

AD-H, Hexane/i-PrOH=98/2, 1.0ml/min, 254nm

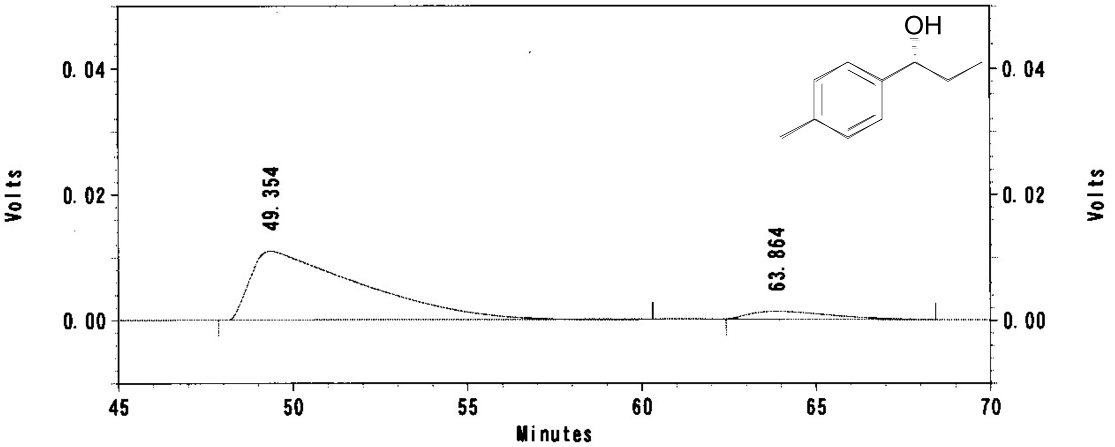


Detector 1 Results

保持時間	面積	Area Percent	高さ
18. 876	1191950	91. 648	41884
20. 687	108626	8. 352	4483
Totals	1300576	100. 000	46367

Table 3, Entry 9

OD-H, Hexane/i-PrOH=1000/1, 1.0ml/min, 254nm

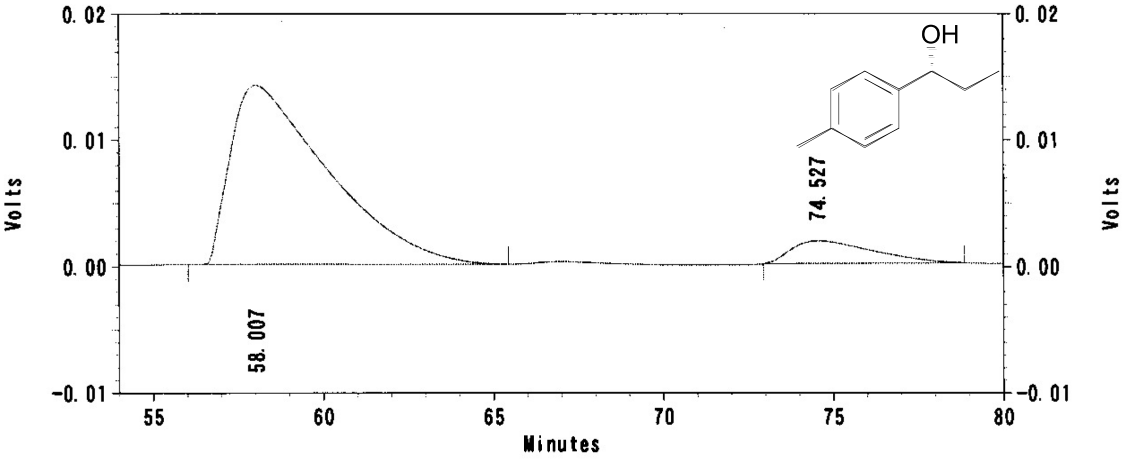


Detector 1 Results

保持時間	面積	Area Percent	高さ
49.354	2384603	92.310	10962
63.864	198666	7.690	1247
Totals	2583269	100.000	12209

Table 3, Entry 10

OD-H, Hexane/i-PrOH=1000/1, 1.0ml/min, 254nm

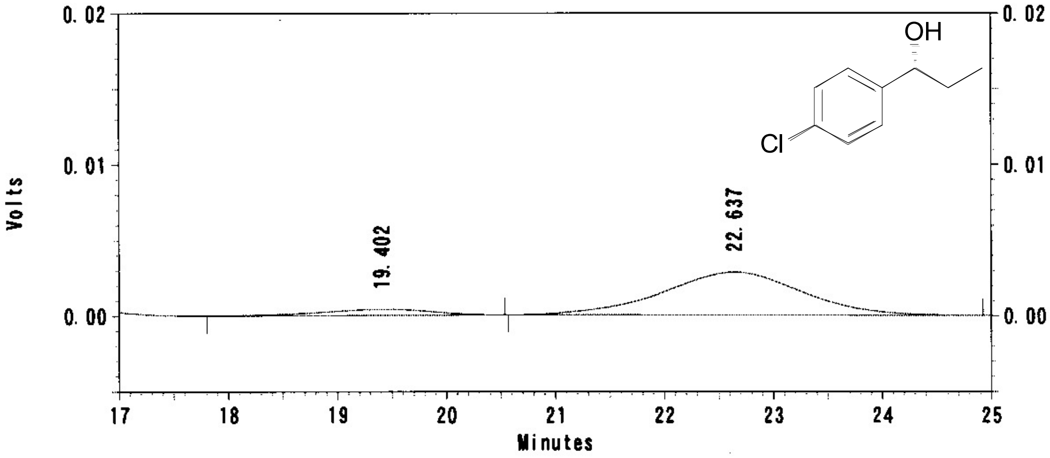


Detector 1 Results

保持時間	面積	Area Percent	高さ
58.007	2812119	90.478	14161
74.527	295950	9.522	1781
Totals	3108069	100.000	15942

Table 3, Entry 11

OB, Hexane/i-PrOH=98/2, 0.5ml/min, 254nm

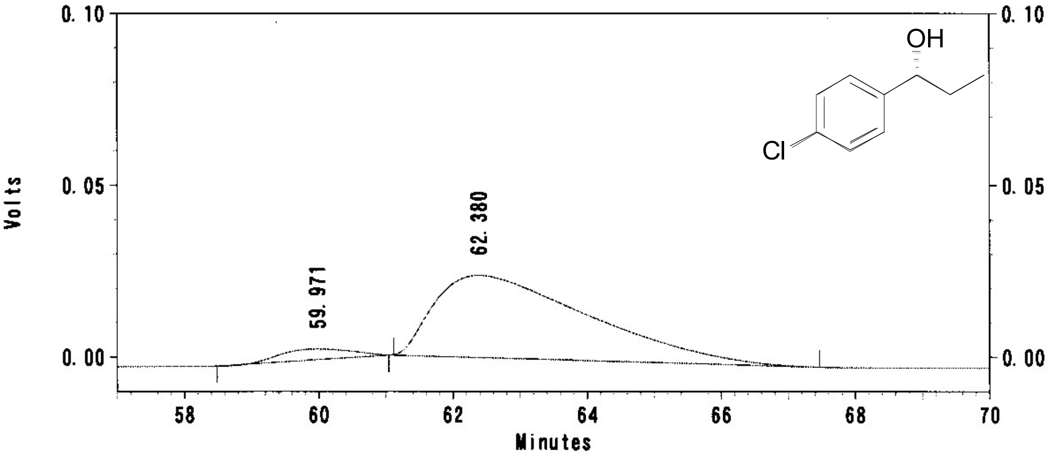


UV Results

保持時間	面積	Area Percent	高さ
19. 402	27786	9. 870	406
22. 637	253721	90. 130	2853
Totals	281507	100. 000	3259

Table 3, Entry 12

OD-H, Hexane/i-PrOH=99/1, 0.5ml/min, 254nm

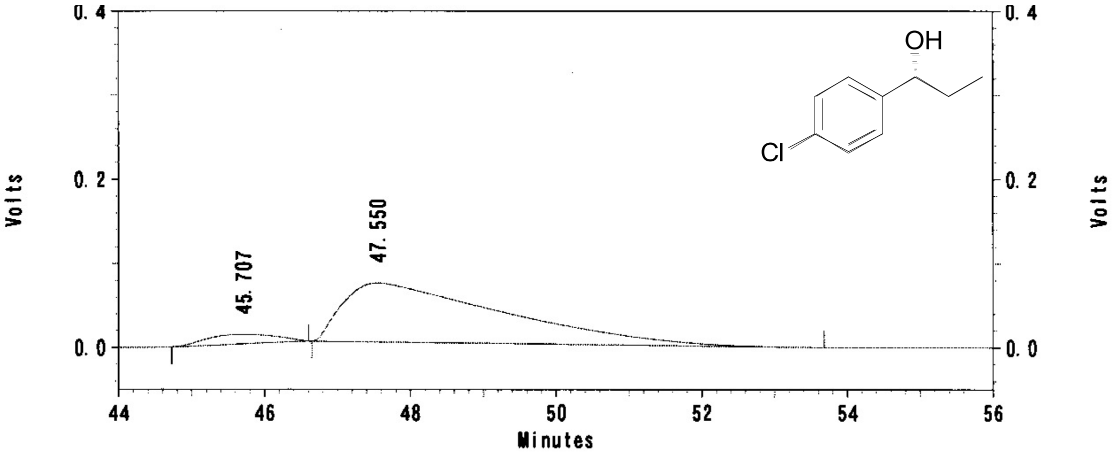


Detector 1 Results

保持時間	面積	Area Percent	高さ
59. 971	225564	5. 544	3077
62. 380	3842777	94. 456	23947
Totals	4068341	100. 000	27024

Table 3, Entry 13

OD-H, Hexane/i-PrOH=99/1, 0.5ml/min, 254nm

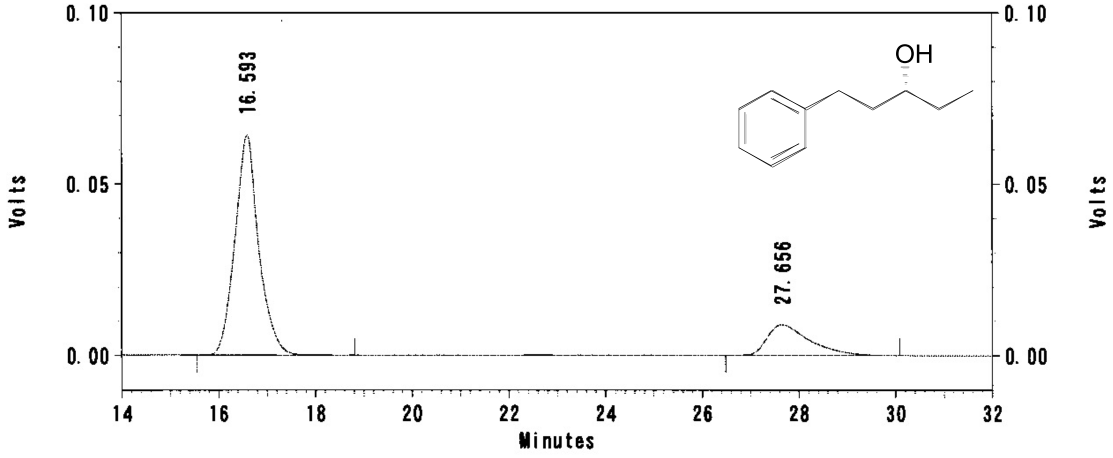


Detector 1 Results

保持時間	面積	Area Percent	高さ
45. 707	757909	6. 607	11269
47. 550	10713350	93. 393	70510
Totals	11471259	100. 000	81779

Table 3, Entry 14

OD-H, Hexane/i-PrOH=98/2, 1.0ml/min, 254nm

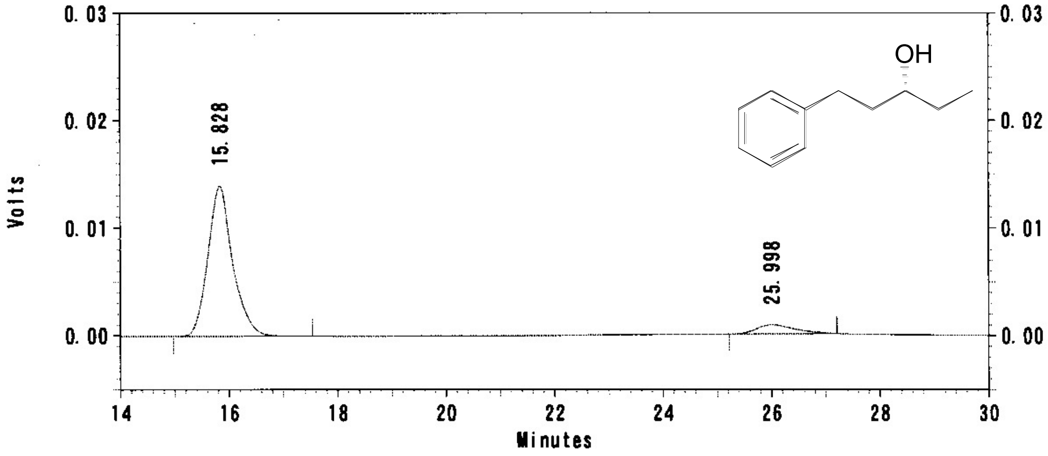


Detector 1 Results

保持時間	面積	Area Percent	高さ
16. 593	2192245	79. 981	64244
27. 656	548702	20. 019	8965
Totals	2740947	100. 000	73209

Table 3, Entry 15

OD-H, Hexane/i-PrOH=98/2, 1.0ml/min, 254nm



Detector 1 Results

保持時間	面積	Area Percent	高さ
15. 828	440433	91. 297	13974
25. 998	41986	8. 703	859
Totals	482419	100. 000	14833