# Fine-tuning Monophosphine Ligands for Enhanced Enantioselectivity. Influence of Chiral Hemilabile Pendant Groups

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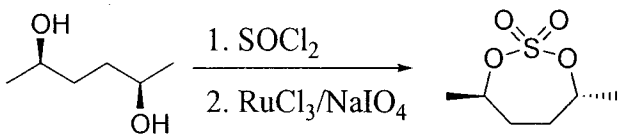
## Supporting Information

**General methods.** Reactions requiring air–sensitive manipulations were conducted under an inert atmosphere of nitrogen by using Schlenk techniques or a Vacuum Atmospheres drybox. Methylene chloride and DMSO were distilled from calcium hydride under nitrogen and stored over molecular sieves. Tetrahydrofuran, hexane and benzene were distilled under nitrogen from sodium/benzophenone ketyl. 2-Bromobenzaldehyde, (2*R*, 3*R*)-butanediol, (2*S*, 3*S*)-butanediol, (2*R*, 5*R*)-hexanediol, (2*S*, 5*S*)-hexanediol, (2*S*, 4*S*)-pentanediol, *N,N*-diisopropylethylamine, 4-methylstyrene, 4-bromostyrene, 4-methoxystyrene and 2-methyl-2-butene were purchased from Acros. $LiAlH_4$ (1M in diethyl ether), diethyl phosphite, styrene and 2-vinylnaphthalene were purchased from Aldrich. Allylic nickel bromide[1], $Na^+[[3,5\text{-}(CF_3)_2C_6H_3]_4B]^-$ ($Na^+$ $^-$BARF)[2], 4-isobutylstyrene[3], 6-methoxy-2-vinylnaphthalene[3] were prepared according to the literature. Ethylene (99.5%) was purchased from Matheson Inc., and passed through Drierite before use. For ozonolysis, ozone gas was delivered using a Welsbach ozone generator. Analytical TLC was performed on E. Merck precoated (0.25 mm) silica gel 60 $F_{254}$ plates. Flash column chromatography was carried out on silica gel 40 (Scientific Adsorbents Incorporated, Microns Flash). Gas chromatographic analyses were performed on a Hewlett-Packard 5890 equipped with an HP-ultra-1 crosslinked methyl silicone capillary column (25 m length x 0.2 mm i.d.) and a FID detector connected to a HP 3396 integrator. Helium was used as the carrier gas. Chiral gas chromatographic separations were accomplished using Chirasil-L-Val on WCOT fused silica (25 m x 0.25 mm, 0.12 mm film thickness) capillary GC column purchased from Chrompack. Enatiomeric excesses of all compounds were determined by HPLC using a Daicel Chiralcel OJ column using hexane/isopropanol as solvents where base-line separation was obtained. Optical rotations were recorded in solution on a Perkin-Elmer Model 241 polarimeter at the sodium

D line in chloroform. The optical rotations of ligands were not measured because of their air-sensitivity.

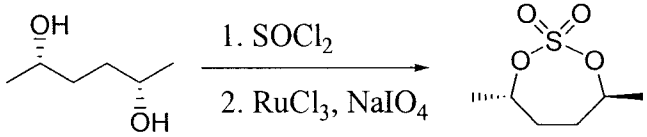
## Preparation of Ligands

**Preparation of (2*R*,5*R*)-hexanediol cyclic sulfate[4]:**



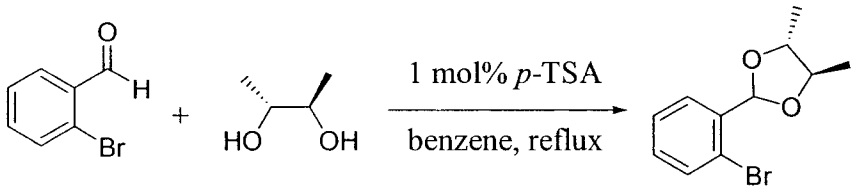

To a solution of (2*R*,5*R*)-hexanediol (1.18g, 10 mmol) in $CCl_4$ (7 mL) was added via syringe thionyl chloride (1.2 mL, 16.5 mmol). The resulting brown solution was then heated at reflux for 1.5 h. After the solution was cooled to r.t., the reaction mixture was concentrated on a rotary evaporator to afford a brown oil. The oil was then dissolved in a mixture of $CCl_4$ (7 mL), $CH_3CN$ (7 mL) and $H_2O$ (10 mL) and the mixture was cooled to 0°C. To the cold mixture was added $RuCl_3 \cdot 3H_2O$ (7.3 mg, 0.028 mmol), followed by $NaIO_4$ (4.43 g, 20.7 mmol). The reaction was allowed to stir at r.t. for 1 h. $H_2O$ (40 mL) was added, the reaction mixture was extracted with diethyl ether (4x40 mL) and the combined extracts were washed with brine. After drying over $MgSO_4$ and the solution was filtered through a pad of silica gel, the colorless solution was concentrated to yield white solid (1.57 g, 87%) which was used without further purification. $^1$H NMR ($CDCl_3$, 250 MHz) $\delta$ 4.95-4.75 (m, 2H), 2.10-1.80 (m, 4H), 1.46 (d, $J$ = 6.35 Hz, 6H).

**Preparation of (2*S*,5*S*)-hexanediol cyclic sulfate[4]:**



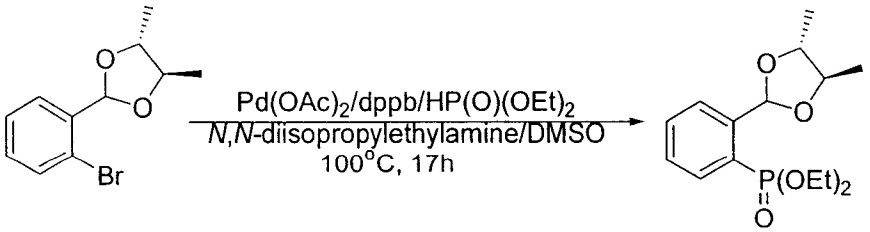

The procedure is the same as the above. Starting from (2*S*,5*S*)-hexanediol (1.18 g, 10 mmol) to get 1.55g (86%) of (2S,5S)-hexanediol cyclic sulfate. $^1$H NMR ($CDCl_3$, 250 MHz) $\delta$ 4.90-4.65 (m, 2H), 2.10-1.80 (m, 4H), 1.41 (d, $J$ = 6.35 Hz, 6H).

**Preparation of 2-(2-bromophenyl)-(4*R*,5*R*)-dimethyl-[1,3]dioxolane[5]:**




To a solution of 2-bromobenzaldehyde (1.76 g, 9.5 mmol) and (2*R*,3*R*)-butanediol (0.94 g, 10.4 mmol) in benzene (5 mL) was added *p*-toluenesulfonic acid monohydrate (19 mg, 0.1 mmol). The resulting solution was heated under reflux with Dean-Stark trap for 5 h. The reaction mixture was poured into aqueous $NaHCO_3$ and extracted with diethyl ether. The organic layers were combined, dried and concentrated to afford the crude product which was purified by flash chromatography (eluent: hexane:ethyl acetate=40:1) to give 2.04 g (84%) of 2-(2-bromophenyl)-(4*R*,5*R*)-dimethyl-[1,3]dioxolane. $^1$H NMR ($CDCl_3$, 250 MHz) $\delta$ 7.62 (dd, $J$ = 7.75, 1.75 Hz, 1H), 7.53 (dd, $J$ = 7.75, 1.03 Hz, 1H), 7.32 (td, $J$ = 7.50, 0.83 Hz, 1H), 7.18 (td, $J$ = 7.75, 1.78 Hz, 1H), 6.22 (s, 1H), 3.90-3.70 (m, 2H), 1.38 (t, $J$ = 5.50 Hz, 3H), 1.32 (t, $J$ = 5.50 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 62.9 MHz) $\delta$ 16.75, 17.06, 78.66, 80.43, 101.47, 122.93, 127.43, 128.09, 130.46, 132.91, 137.31.

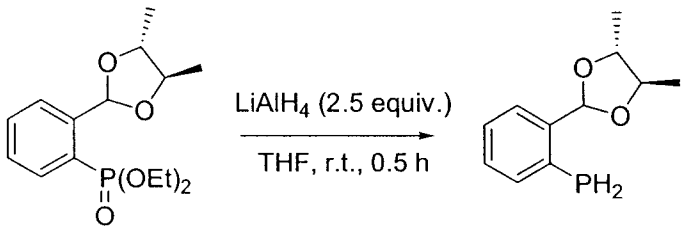
**Preparation of [2-((4*R*,5*R*)-dimethyl-[1,3]dioxolan-2-yl)-phenyl]-phosphonic acid diethyl ester**[6]:




A mixture of 2-(2-bromophenyl)-(4*R*,5*R*)-dimethyl-[1,3]dioxolane (1.99 g, 7.74 mmol), diethylphosphite (2.3 mL, 17.8 mmol), $Pd(OAc)_2$ (87 mg, 0.39 mmol), dppb (165 mg, 0.39 mmol) and *N*,*N*-diisopropylethylamine (5.4 mL, 31 mmol) in DMSO (11 mL) was heated with stirring at 100°C under nitrogen atmosphere overnight. After the mixture was cooled to r.t., 10 mL of water was added slowly and the mixture was extracted with ethyl acetate. The extracts were combined, washed with water, dried over $MgSO_4$ and concentrated *in vacuo* to give a crude oil which was purified by column chromatography

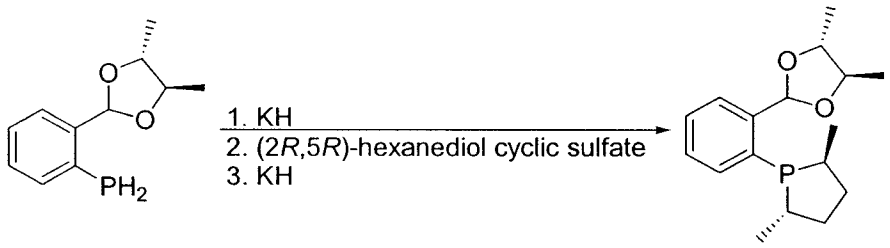
(eluent: hexane:ethyl acetate = 4:1) to afford 1.28 g (53%) of [2-((4*R*,5*R*)-dimethyl-[1,3]dioxolan-2-yl)-phenyl]-phosphonic acid diethyl ester and 100 mg (5%) of 2-(2-bromophenyl)-(4*R*,5*R*)-dimethyl-[1,3]dioxolane was recovered. $^{1}$H NMR ($CDCl_3$, 250 MHz) $\delta$ 7.83 (dd, $J$ = 14.0, 7.75 Hz, 1H), 7.70 (t, $J$ = 5.50 Hz, 1H), 7.46 (t, $J$ = 7.50 Hz, 1H), 7.40-7.25 (m, 1H), 6.43 (s, 1H), 4.15-3.85 (m, 4H), 3.80-3.60 (m, 2H), 1.40-1.05(m, 12H); $^{13}$C NMR ($CDCl_3$, 62.9 MHz) $\delta$ 15.90 (d, $J_{P,C}$ = 6.60 Hz), 16.62, 17.06, 61.86 (d, $J_{P,C}$ = 5.2 Hz), 78.62, 80.13, 98.96 (d, $J_{P,C}$ = 3.8 Hz), 125.18, 127.30 (d, $J_{P,C}$ = 13.5 Hz), 128.30 (t, $J_{P,C}$ = 14.5 Hz), 132.42 (d, $J_{P,C}$ = 2.8 Hz), 133.49 (d, $J_{P,C}$ = 9.1 Hz), 141.65 (d, $J_{P,C}$ = 10.1 Hz); $^{31}$P NMR ($C_6D_6$, 101.3 MHz) $\delta$ 18.94.

**Preparation of 2-[(4*R*,5*R*)-dimethyl-[1,3]dioxolan-2-yl]-phenyl-phosphane**[7]:



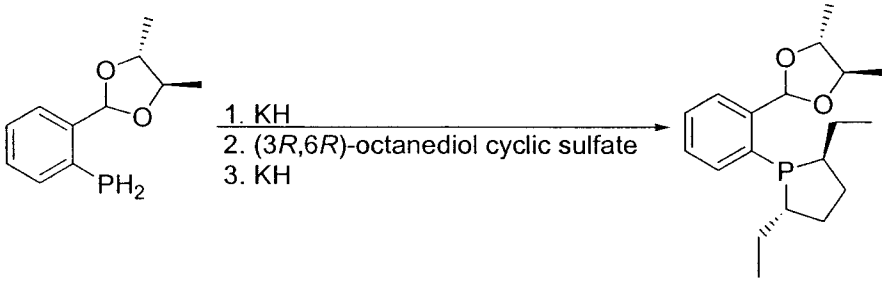

To a solution of [2-((4*R*,5*R*)-dimethyl-[1,3]dioxolan-2-yl)-phenyl]-phosphonic acid diethyl ester (314 mg, 1mmol) in THF (10 mL) was added a solution of $LiAlH_4$ (2.5 mL, 1 M in ether, 2.5 mmol) slowly at r.t. in drybox. After the addition, the reaction mixture was stirred for additional 30 min at r.t. The reaction was quenched with minimum amount of saturated aqueous $NH_4Cl$ and the solvent was removed under reduced pressure. Dry benzene (2x5 mL) was added to remove water azetropically from the solid residue. The solid was extracted with hexane three times and the extracts were combined and concentrated to afford a crude oil which was purified by flash column chromatography (eluent: hexane:ether = 40:1) to get 52 mg (25%) of 2-[(4*R*,5*R*)-dimethyl-[1,3]dioxolan-2-yl]-phenyl-phosphane. $^{1}$H NMR ($CDCl_3$, 250 MHz) $\delta$ 7.55-7.35 (m, 2H), 7.25-7.05(m, 2H), 6.03 (d, $J_{P,H}$ = 2.0 Hz, 1H), 3.90 (d, $J_{P,H}$ = 206 Hz, 2H), 3.85-3.65 (m, 2H), 1.29 (d, $J$ = 4.50 Hz, 3H), 1.23 (d, $J$ = 4.50 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 62.9 MHz) $\delta$ 16.79, 17.35, 78.60, 80.62, 101.80 (d, $J_{P,C}$ = 9.0 Hz), 127.00 (d, $J_{P,C}$ = 3.4 Hz), 128.28, 128.73 (d, $J_{P,C}$ = 3.2 Hz), 128.92, 136.93 (d, $J_{P,C}$ = 6.4 Hz), 140.92 (d, $J_{P,C}$ = 10.9 Hz); $^{31}$P NMR ($C_6D_6$, 101.3 MHz) $\delta$ -126.08.

**Preparation of 2-[2-((2*S*,5*S*)-dimethyl-phospholan-1-yl)-phenyl]-(4*R*,5*R*)-dimethyl-[1,3]dioxolane (1a)**[8]:



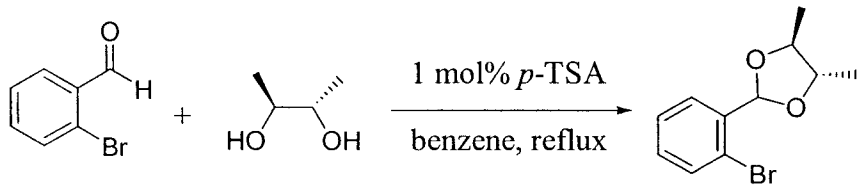

To a solution of 2-[(4*R*,5*R*)-dimethyl-[1,3]dioxolan-2-yl]-phenyl-phosphane (52 mg, 0.25 mmol) in THF (10 mL) was added KH (10.3 mg, 0.26 mmol in 0.5 mL of THF) at -30°C in drybox. The mixture was allowed to warm to r.t. and stirred for 1.5h. To the resulting solution was added slowly a solution of (2*R*,5*R*)-hexanediol cyclic sulfate (45 mg, 0.25mmol) in THF (1mL) and the mixture was stirred for 2h at r.t. Finally KH (10.3 mg, 0.26 mmol in 0.5 mL of THF) was added at r.t. and stirred for additional 2 h. The reaction was quenched with a few drops of methanol and the solvents were removed under vacuum to get a crude oil. Purification by column chromatography (eluent:hexane:ether = 40:1) afforded 31 mg (42%) of 2-[2-((2*S*,5*S*)-dimethyl-phospholan-1-yl)-phenyl]-(4*R*,5*R*)-dimethyl-[1,3]dioxolane. $^{1}$H NMR ($C_6D_6$, 250 MHz) $\delta$ 7.98 (ddd, $J$ = 7.75, 3.25, 1.48 Hz, 1H), 7.35 (dt, $J$ = 7.50, 1.65 Hz, 1H), 7.24 (td, $J$ = 7.50, 1.30 Hz, 1H), 7.18-7.08 (m, 2H), 3.85-3.50 (m, 2H), 2.60-2.42 (m, 1H), 2.40-2.18 (m, 1H), 2.14-1.92 (m,1 H), 1.92-1.73 (m, 1H), 1.55-1.35 (m,1 H), 1.30-1.10 (m, 4H), 1.08 (d, $J$ = 5.80 Hz, 3H), 1.04 (d, $J$ = 6.0 Hz, 3H), 0.91 (dd, $J$ = 9.75, 7.0 Hz, 3H); $^{13}$C NMR ($C_6D_6$, 62.9 MHz) $\delta$ 16.53 (d, $J_{P,C}$ = 1.3 Hz), 16.94, 17.52, 21.03 (d, $J$ = 36.5 Hz), 35.17 (d, $J_{P,C}$ = 7.6 Hz), 35.36 (d, $J_{P,C}$ = 5.0 Hz), 36.70 (d, $J_{P,C}$ = 2.1 Hz), 37.17 (d, $J_{P,C}$ = 2.6 Hz), 79.10, 80.52, 100.66 (d, $J_{P,C}$ = 31.5 Hz), 127.06 (d, $J_{P,C}$ = 5.5 Hz), 128.19, 128.72, 132.74 (d, $J_{P,C}$ = 3.7 Hz), 136.75 (d, $J_{P,C}$ = 36.2 Hz), 145.22 (d, $J_{P,C}$ = 20.7 Hz); $^{31}$P NMR ($C_6D_6$, 101.3 MHz) $\delta$ -5.35; HRMS (ESI) m/z 293.1649 ([M+H]$^+$, exact mass calcd for $C_{17}H_{26}O_2P$ 293.1665).

**Preparation of 2-[2-((2*S*,5*S*)-diethyl-phospholan-1-yl)-phenyl]-(4*R*,5*R*)-dimethyl-[1,3]dioxolane (1b)**[8]:




The procedure is the same as the above. Starting from 2-[(4*R*,5*R*)-dimethyl-[1,3]dioxolan-2-yl]-phenyl-phosphane (58 mg, 0.28 mmol) and (3*R*,6*R*)-octanediol cyclic sulfate (57.4 mg, 0.28 mmol) to get 40 mg (45%) of 2-[2-((2*S*,5*S*)-diethyl-phospholan-1-yl)-phenyl]-(4*R*,5*R*)-dimethyl-[1,3]dioxolane. $^1$H NMR ($C_6D_6$, 250 MHz) $\delta$ 8.0-7.9 (m, 1H), 7.39 (dt, $J$ = 6.0, 1.5 Hz, 1H), 7.30-7.05 (m, 3H), 3.75-3.45 (m, 2H), 2.40-2.25 (m, 1H), 2.15-1.80 (m, 3H), 1.75-1.35 (m, ca.5H), 1.25-1.10 (m, ca.1H), 1.07 (d, $J$ = 6.0 Hz, 3H), 1.03 (d, $J$ = 6.0 Hz, 3H), 0.91 (t, $J$ = 7.25 Hz, 3H), 0.80 (t, $J$ = 7.13 Hz, 3H); $^{13}$C NMR ($C_6D_6$, 62.9 MHz) $\delta$ 14.35 (d, $J_{P,C}$ = 1.7 Hz), 14.50 (d, $J_{P,C}$ = 5.4 Hz), 16.93, 17.51, 24.50, 29.33 (d, $J_{P,C}$ = 33.1 Hz), 34.35 (d, $J_{P,C}$ = 1.5 Hz), 34.52 (d, $J_{P,C}$ = 3.2 Hz), 43.06 (d, $J_{P,C}$ = 12.6 Hz), 45.25 (d, $J_{P,C}$ = 11.3 Hz), 79.06, 80.52, 100.65 (d, $J_{P,C}$ = 33.5 Hz), 127.19 (d, $J_{P,C}$ = 5.8 Hz), 128.10, 128.84, 133.86 (d, $J_{P,C}$ = 3.9 Hz), 137.49 (d, $J_{P,C}$ = 35.4 Hz), 145.45 (d, $J_{P,C}$ = 21.4 Hz); $^{31}$P NMR ($C_6D_6$, 101.3 MHz) $\delta$ -14.81; HRMS (ESI) m/z 359.1736 ([M+O+Na]$^+$, exact mass calcd for $C_{19}H_{29}O_3PNa$ 359.1747).

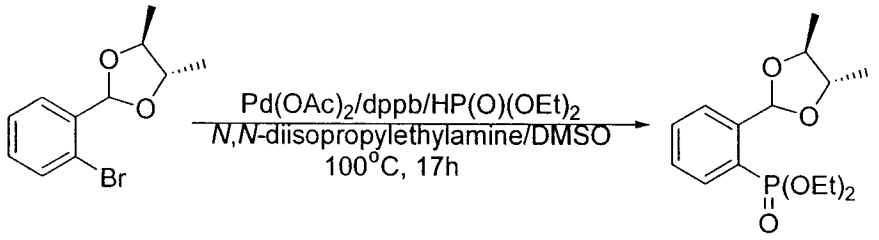
**Preparation of 2-(2-bromophenyl)-(4*S*,5*S*)-dimethyl-[1,3]dioxolane**[5]:




The procedure is the same as the above. Starting from 2-bromobenzaldehyde (0.59 mL, 5 mmol) and (2*S*,3*S*)-butanediol (0.5 g, 5.58 mmol) to get 1.11 g (85%) of 2-(2-bromophenyl)-(4*S*,5*S*)-dimethyl-[1,3]dioxolane. $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.63 (dd, $J$ = 7.72, 1.74 Hz, 1H), 7.54 (dd $J$ = 7.96, 1.12 Hz, 1H), 7.34 (td, $J$ = 7.60, 0.96 Hz, 1H), 7.20 (td, $J$ = 7.84, 1.72 Hz, 1H), 6.24 (s, 1H), 3.95-3.75 (m, 2H), 1.39 (d, $J$ = 5.80 Hz,

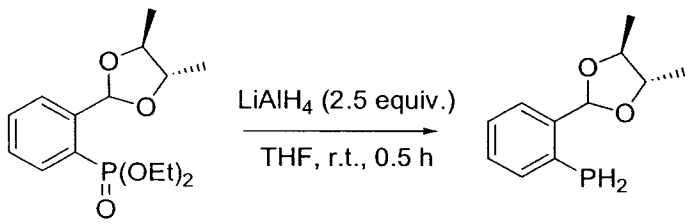
3H), 1.34 (d, $J$ = 5.80 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100.6 MHz) $\delta$ 17.19, 17.51, 79.07, 80.84, 101.89, 123.35, 127.87, 128.55, 130.90, 133.32, 137.76.

**Preparation of [2-((4*S*,5*S*)-dimethyl-[1,3]dioxolan-2-yl)-phenyl]-phosphonic acid diethyl ester**[6]:



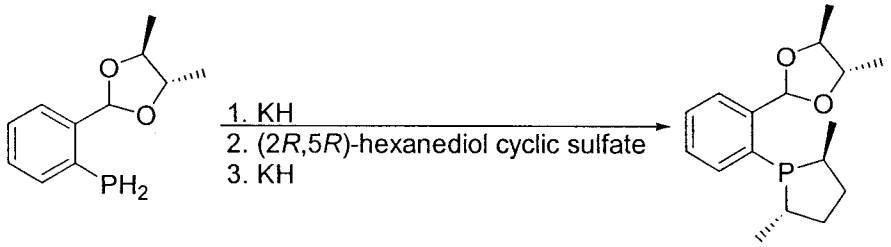

The procedure is the same as the above. Starting from 2-(2-bromophenyl)-(4*S*,5*S*)-dimethyl-[1,3]dioxolane (1.765 g, 6.87 mmol), diethylphosphite (2.0 mL, 15.8 mmol), $Pd(OAc)_2$ (76 mg, 0.34 mmol), dppb (145 mg, 0.34 mmol) and *N*,*N*-diisopropylethylamine (4.8 mL, 28 mmol) to get 1.2 g (58%) of [2-((4*S*,5*S*)-dimethyl-[1,3]dioxolan-2-yl)-phenyl]-phosphonic acid diethyl ester and 500 mg (28%) of 2-(2-bromophenyl)-(4*S*,5*S*)-dimethyl-[1,3]dioxolane was recovered. $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.90 (ddd, $J$ = 14.0, 6.50, 1.20 Hz, 1H), 7.76 (td, $J$ = 5.50, 1.20 Hz, 1H), 7.54 (t, $J$ = 7.50 Hz, 1H), 7.45-7.30 (m, 1H), 6.50 (s, 1H), 4.20-3.90 (m, 4H), 3.85-3.70 (m, 2H), 1.40-1.15 (m,12H); $^{13}$C NMR ($CDCl_3$, 100.6 MHz) $\delta$ 16.47, 17.14, 17.58, 62.36, 79.11, 80.63, 99.48, 126.25, 127.90 (t, $J_{P,C}$ = 14.1 Hz), 128.92 (d, $J_{P,C}$ = 14.1 Hz), 132.93, 133.93 (d, $J_{P,C}$ = 8.1 Hz), 142.22 (d, $J_{P,C}$ = 10.1 Hz); $^{31}$P NMR ($CDCl_3$, 101.3 MHz) $\delta$ 19.02; HRMS (ESI) m/z 337.1188 ([M+Na]$^+$, exact mass calcd for $C_{15}H_{23}O_5PNa$ 337.1175).

**Preparation of 2-[(4*S*,5*S*)-dimethyl-[1,3]dioxolan-2-yl]-phenyl-phosphane**[7]:



The procedure is the same as the above. Starting from [2-((4*S*,5*S*)-dimethyl-[1,3]dioxolan-2-yl)-phenyl]-phosphonic acid diethyl ester (315 mg, 1mmol) to get 53 mg (25%) of 2-[(4*S*,5*S*)-dimethyl-[1,3]dioxolan-2-yl]-phenyl-phosphane. $^1$H NMR ($CDCl_3$, 250 MHz) $\delta$ 7.65-7.45 (m, 2H), 7.40-7.10 (m, 2H), 6.09 (d, $J_{P,H}$ = 2.0 Hz, 1H), 3.96 (d, $J_{P,H}$ = 205 Hz, 2H), 3.90-3.70 (m, 2H), 1.35 (d, $J$ = 5.80 Hz, 3H), 1.27 (d, $J$ = 5.80 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 62.9 MHz) $\delta$ 17.22, 17.78, 79.02, 81.04, 102.23, 127.44 (d, $J_{P,C}$ = 3.4 Hz), 128.70, 129.16 (d, $J_{P,C}$ = 3.2 Hz), 129.35, 136.82 (d, $J_{P,C}$ = 6.3 Hz), 141.34 (d, $J_{P,C}$ = 10.7 Hz); $^{31}$P NMR ($CDCl_3$, 101.3 MHz) $\delta$ -126.05; HRMS (ESI) m/z 249.0645 ($[M+O+Na]^+$, exact mass calcd for $C_{11}H_{15}O_3PNa$ 249.0651).

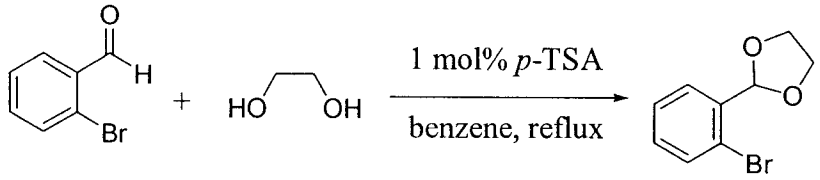
**Preparation of 2-[2-((2*S*,5*S*)-dimethyl-phospholan-1-yl)-phenyl]-(4*S*,5*S*)-dimethyl-[1,3]dioxolane (2)**[8]:




The procedure is the same as the above. Starting from 2-[(4*S*,5*S*)-dimethyl-[1,3]dioxolan-2-yl]-phenyl-phosphane (52 mg, 0.25 mmol) and (2*R*,5*R*)-hexanediol cyclic sulfate (45 mg, 0.25 mmol) to get 34 mg (47%) of 2-[2-((2*S*,5*S*)-dimethyl-phospholan-1-yl)-phenyl]-(4S,5S)-dimethyl-[1,3]dioxolane. $^1$H NMR ($C_6D_6$, 250 MHz) $\delta$ 7.97 (ddd, $J$ = 7.75, 3.25, 1.50 Hz, 1H), 7.33 (dt, $J$ = 7.50, 1.50 Hz, 1H), 7.22 (td, $J$ = 7.50, 1.25 Hz, 1H), 7.15-7.05 (m, 2H), 3.70-3.45 (m, 2H), 2.60-2.40 (m, 1H), 2.40-2.15 (m, 1H), 2.10-1.92 (m, 1H), 1.90-1.72 (m, 1H), 1.53-1.30 (m, 1H), 1.30-1.12 (m, 4H), 1.09 (d, $J$ = 5.75 Hz, 3H), 1.05 (d, $J$ = 6.75 Hz, 3H), 0.89 (dd, $J$ = 9.75, 7.0 Hz, 3H); $^{13}$C NMR ($C_6D_6$, 62.9 MHz) $\delta$ 16.94 (d, $J_{P,C}$ = 5.25 Hz), 17.42, 17.89, 21.45(d, $J_{P,C}$ = 36.5 Hz), 35.52 (d, $J_{P,C}$ = 16.25 Hz), 35.71 (d, $J_{P,C}$ = 6.25 Hz), 37.05 (d, $J_{P,C}$ = 9.3 Hz), 37.50 (d, $J_{P,C}$ = 10.0Hz), 79.08, 80.80, 100.97 (d, $J_{P,C}$ = 31.1 Hz), 127.66 (d, $J_{P,C}$ = 5.7 Hz), 128.61, 129.04, 133.14 (d, $J_{P,C}$ = 3.6 Hz), 137.15 (d, $J_{P,C}$ = 28.9 Hz), 145.60 (d, $J_{P,C}$ = 20.4 Hz); $^{31}$P NMR ($C_6D_6$,

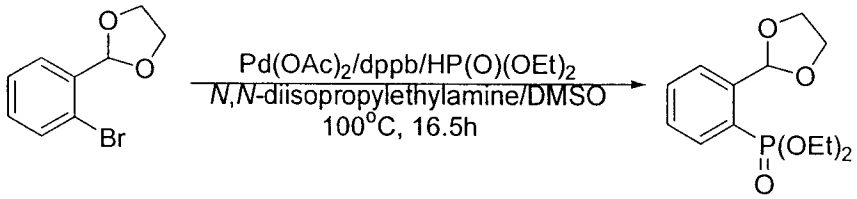
101.3 MHz) $\delta$ -5.03; HRMS (ESI) m/z 293.1681 ([M+H]$^+$, exact mass calcd for $C_{17}H_{26}O_2P$ 293.1665).

**Preparation of 2-(2-bromophenyl)-[1,3]dioxolane**[5]:



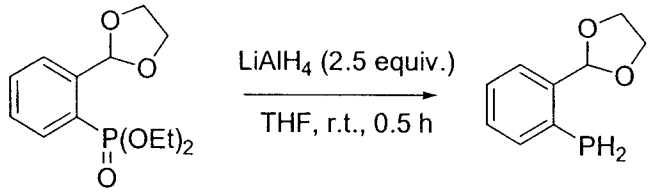

The procedure is the same as the above. Starting from 2-bromobenzaldehyde (3.7g, 20 mmol) and ethylene glycol (1.36g, 22 mmol) to get 4.2 g (92%) of 2-(2-bromophenyl)-[1,3]dioxolane. $^1$H NMR ($CDCl_3$, 250 MHz) $\delta$ 7.47 (td, $J$ = 7.75, 1.75 Hz, 2H), 7.22 (t, $J$ = 7.5 Hz, 1H), 7.12 (td, $J$ = 5.25, 1.55 Hz, 1H), 5.99 (s, 1H), 4.15-3.90 (m, 4H); $^{13}$C NMR ($CDCl_3$, 62.9 MHz) $\delta$ 65.68, 103.52, 127.23, 128.66, 129.23, 136.83, 140.66.

**Preparation of (2 -[1,3]dioxolan-2-yl-phenyl)-phosphonic acid diethyl ester**[6]:



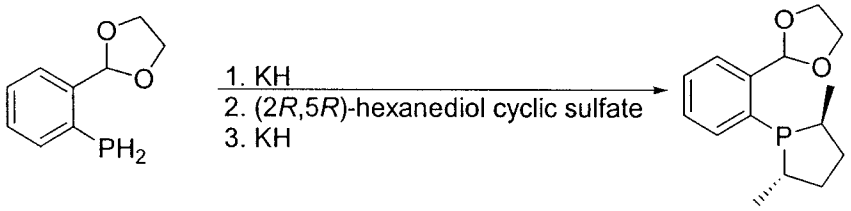

The procedure is the same as the above. Starting from 2-(2-bromophenyl)-[1,3]dioxolane (4.04 g, 17.6 mmol), diethylphosphite (5.2 mL, 40.5 mmol), $Pd(OAc)_2$ (198 mg, 0.88 mmol), dppb (375 mg, 0.88 mmol) and *N,N*-diisopropylethylamine (12.3 mL, 70.4 mmol) in DMSO (20 mL) to get 2.82 g (56%) of (2 -[1,3]dioxolan-2-yl-phenyl)-phosphonic acid diethyl ester and 1.45 g (36 %) of 2-(2-bromophenyl)-[1,3]dioxolane was recovered. $^1$H NMR ($CDCl_3$, 250 MHz) $\delta$ 7.94 (dd, $J$ = 14.0, 7.75 Hz, 1H), 7.76 (t, $J$ = 6.50 Hz, 1H), 7.56 (t, $J$ = 7.50 Hz, 1H), 7.50-7.35 (m, 1H), 6.40 (s, 1H), 4.30-3.95 (m, 8H), 1.30 (t, $J$ = 7.0 Hz, 6H); $^{31}$P NMR ($CDCl_3$, 101.3 MHz) $\delta$ 18.94.

**Preparation of 2 -[1,3]dioxolan-2-yl-phenyl-phosphane**[7]:



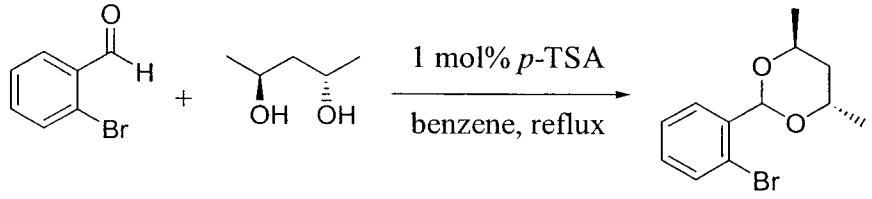

The procedure is the same as the above. Starting from (2 -[1,3]dioxolan-2-yl-phenyl)-phosphonic acid diethyl ester (572 mg, 2 mmol) to get 56 mg (15.4%) of 2 -[1,3]dioxolan-2-yl-phenyl-phosphane. $^{1}$H NMR ($CDCl_3$, 250 MHz) $\delta$ 7.55-7.35 (m, 2H), 7.30-7.05 (m, 2H), 5.90 (s, 1H), 3.89 (d, $J_{P,H}$ = 205 Hz, 2H), 4.20-3.90 (m, 4H); $^{31}$P NMR ($CDCl_3$, 101.3 MHz) $\delta$ -126.04.

**Preparation of 2-[2-((2*S*,5*S*)-dimethyl-phospholan-1-yl)-phenyl]-[1,3]dioxolane (3)**[8]:



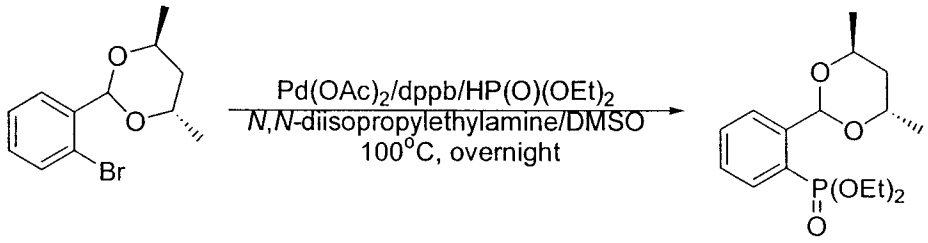

The procedure is the same as the above. Starting from 2 -[1,3]dioxolan-2-yl-phenyl-phosphane (56 mg, 0.31 mmol) and (2*R*,5*R*)-hexanediol cyclic sulfate (55.4 mg, 0.31mmol) to get 37 mg (45%) of 2-[2-((2S,5S)-dimethyl-phospholan-1-yl)-phenyl]-[1,3]dioxolane. $^{1}$H NMR ($CDCl_3$, 250 MHz) $\delta$ 7.75-7.60 (m, 1H), 7.50-7.40 (m, 1H), 7.40-7.28 (m, 2H), 6.60 (d, $J_{P,H}$ = 6.7 Hz, 1H), 4.25-4.00 (m, 4H), 2.80-2.60 (m, 1H), 2.50-2.20 (m, 2H), 2.15-1.95 (m, 1H), 1.70-1.45 (m, 1H), 1.45-1.25 (m, 4H), 0.76 (dd, J = 10.1, 7.25 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 62.9 MHz) $\delta$ 15.99 (d, $J_{P,C}$ = 1.3 Hz), 20.84 (d, $J_{P,C}$ = 35.2 Hz), 34.80 (d, $J_{P,C}$ = 7.6 Hz), 34.96 (d, $J_{P,C}$ = 5.4 Hz), 36.39 (d, $J_{P,C}$ = 2.3 Hz), 36.83 (d, $J_{P,C}$ = 2.7 Hz), 65.42 (d, $J_{P,C}$ = 5.7 Hz), 101.31 (d, $J_{P,C}$ = 30.2 Hz), 126.10 (d, $J_{P,C}$ = 5.7 Hz), 128.29, 128.68, 132.50 (d, $J_{P,C}$ = 3.5 Hz), 136.06 (d, $J_{P,C}$ = 33.9 Hz), 143.08 (d, $J_{P,C}$ = 20.1 Hz); $^{31}$P NMR ($CDCl_3$, 101.3 MHz) $\delta$ -4.64; HRMS (ESI) m/z 303.1126 ([M+O+Na]$^{+}$, exact mass calcd for $C_{15}H_{21}O_3PNa$ 303.1121).

**Preparation of 2-(2-bromophenyl)-(4*S*,6*S*)-dimethyl-[1,3]-dioxane**[5]:




The procedure is the same as the above. Starting from 2-bromobenzaldehyde (0.80 g, 4.36 mmol mmol) and (2*S*,4*S*)-pentanediol (0.5 g, 4.8 mmol) to get 1.05 g (90%) of 2-(2-bromophenyl)-(4*S*,6*S*)-dimethyl-[1,3]-dioxane. $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.73 (dd, $J$ = 7.96, 1.68 Hz, 1H), 7.51 (dd, $J$ = 7.96, 0.99 Hz, 1H), 7.32 (td, $J$ = 7.96, 0.99 Hz, 1H), 7.16 (td, $J$ = 7.96, 1.68 Hz, 1H), 6.11 (s, 1H), 4.53-4.40 (m, 1H), 4.28-4.15 (m, 1H), 2.05-1.90 (m, 1H), 1.52 (d, $J$ = 7.0 Hz, 3H), 1.42 (d, $J$ = 13.6 Hz, 1H), 1.28 (d, $J$ = 6.4 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100.6 MHz) $\delta$ 16.94, 21.83, 36.66, 68.33, 69.04, 93.26, 122.38, 127.48, 128.20, 130.05, 132.47, 137.76.

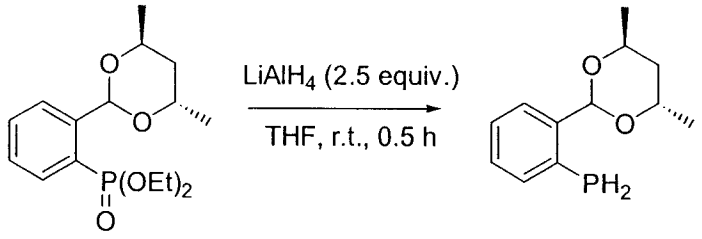
**Preparation of [2-((4*S*,6*S*)-dimethyl-[1,3]dioxan-2-yl)phenyl]-phosphonic acid diethyl ester**[6]:




The procedure is the same as the above. Starting from 2-(2-bromophenyl)-(4*S*,6*S*)-dimethyl-[1,3]-dioxane (0.79 g, 2.9 mmol), diethylphosphite (0.86 mL, 6.7 mmol), $Pd(OAc)_2$ (33 mg, 0.15 mmol), dppb (62 mg, 0.15 mmol) and *N*,*N*-diisopropylethylamine (2.0 mL, 11.6 mmol) in DMSO (6 mL) to get 0.69 g (73%) of [2 -((4*S*,6*S*)-dimethyl-[1,3]dioxan-2-yl)phenyl]-phosphonic acid diethyl ester. $^1$H NMR ($CDCl_3$, 250 MHz) $\delta$ 8.00-7.85 (m, 2H), 7.57 (t, $J$ = 7.50 Hz, 1H), 7.45-7.30 (m, 1H), 6.54 (s, 1H), 4.55-4.40 (m, 1H), 4.30-3.90 (m, 5H), 2.10-1.90 (m, 1H), 1.50 (d, $J$ = 7.0 Hz, 3H), 1.42 (t, $J$ = 13.5 Hz, 1H), 1.35-1.20 (m, 9H); $^{13}$C NMR ($CDCl_3$, 100.6 MHz) $\delta$ 16.65 (t, $J_{P,C}$ = 6.5 Hz), 17.63, 22.33, 37.34, 62.46 (t, $J_{P,C}$ = 5.2 Hz), 68.73, 69.50, 91.91 (d, $J_{P,C}$ = 3.9 Hz), 125.80 (d, $J_{P,C}$ = 181 Hz), 128.13 (d, $J_{P,C}$ = 13.6 Hz), 128.75 (d, $J_{P,C}$ = 14.1 Hz), 133.34 (d, $J_{P,C}$ =

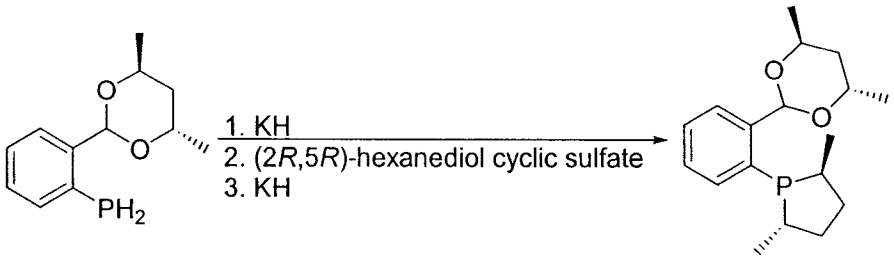
2.5 Hz), 133.95 (d, $J_{P,C}$ = 9.1 Hz), 142.78 (d, $J_{P,C}$ = 10.1 Hz); $^{31}$P NMR ($CDCl_3$, 101.3 MHz) $\delta$ 19.47.

**Preparation of [2-((4*S*,6*S*)-dimethyl-[1,3]dioxan-2-yl)phenyl]-phosphane**[7]:




The procedure is the same as the above. Starting from [2 -((4*S*,6*S*)-dimethyl-[1,3]dioxan-2-yl)phenyl]-phosphonic acid diethyl ester (328 mg, 1 mmol) to get 73 mg (32.6%) of [2 -((4*S*,6*S*)-dimethyl-[1,3]dioxan-2-yl)phenyl]-phosphane. $^1$H NMR ($C_6D_6$, 400 MHz) $\delta$ 8.00-7.85 (m, 1H), 7.30 (t, J = 6.60 Hz, 1H), 7.10 (t, $J$ = 7.40 Hz, 1H), 6.93 (t, $J$ = 7.40 Hz, 1H), 6.01 (s, 1H), 4.35-4.15 (m, 2H), 3.90-3.75 (m, 1H), 3.74 (s, 1H), 1.80-1.65 (m, 1H), 1.18 (d, $J$ = 6.96 Hz, 3H), 1.09 (d, $J$ = 6.2 Hz, 3H), 0.86 (d, $J$ = 13.2 Hz, 3H); $^{13}$C NMR ($C_6D_6$, 62.9 MHz) $\delta$ 16.95, 21.94, 36.76, 67.87, 68.76, 93.26 (d, $J_{P,C}$ = 9.7 Hz), 126.81 (d, $J_{P,C}$ = 3.4 Hz), 128.22 (d, $J_{P,C}$ = 2.0 Hz), 128.28, 128.83, 136.21 (d, $J_{P,C}$ = 4.7 Hz), 143.01 (d, $J_{P,C}$ = 12.3 Hz); $^{31}$P NMR ($C_6D_6$, 101.3 MHz) $\delta$ -112.92.

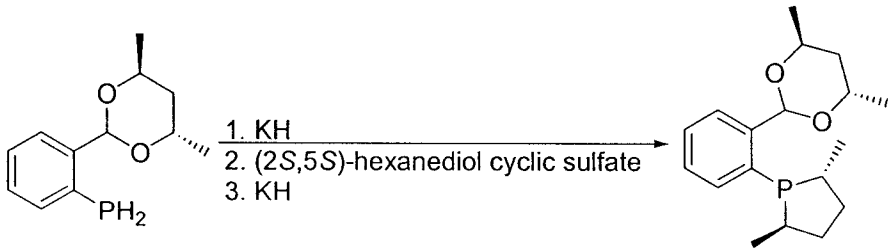
**Preparation of 2-[2-((2*S*,5*S*)-dimethyl-phospholan-1-yl)-phenyl]-(4*S*,6*S*)-dimethyl-[1,3]dioxane (4)**[8]:




The procedure is the same as the above. Starting from [2 -((4*S*,6*S*)-dimethyl-[1,3]dioxan-2-yl)phenyl]-phosphane (39 mg, 0.17 mmol) and (2R,5R)-hexanediol cyclic sulfate (31.3 mg, 0.17mmol) to get 20 mg (38%) of 2-[2-((2*S*,5*S*)-dimethyl-phospholan-1-yl)-phenyl]-

(4*S*,6*S*)-dimethyl-[1,3]dioxane. $^1$H NMR ($C_6D_6$, 400 MHz) $\delta$ 8.18 (ddd, $J$ = 7.8, 3.3, 1.4 Hz, 1H), 7.32 (dt, $J$ =7.5, 1.6 Hz, 1H), 7.22 (td, $J$ = 7.5, 1.4 Hz, 1H), 7.11 (td, $J$ = 7.5, 1.6 Hz, 1H), 6.96 (d, $J_{P,H}$ = 7.4 Hz, 1H), 4.30-4.20 (m, 1H), 4.00-3.90 (m, 1H), 2.60-2.45 (m, 1H), 2.40-2.25 (m, 1H), 2.10-1.95 (m, 1H), 1.90-1.70 (m, 2H), 1.53-1.40 (m, 1H), 1.39 (d, $J$ = 7.0 Hz, 3H), 1.30-1.15 (m, 4H), 1.12 (d, $J$ = 6.1 Hz, 3H), 0.95-0.85 (m, 4H); $^{13}$C NMR ($C_6D_6$, 100.6 MHz) $\delta$ 16.70, 17.57 (d, $J_{P,C}$ = 2.0 Hz), 20.98 (d, $J_{P,C}$ = 36.2 Hz), 22.18, 35.02 (d, $J_{P,C}$ = 12.6 Hz), 35.16 (d, $J_{P,C}$ = 10.1 Hz), 36.66 (d, $J_{P,C}$ = 2.8 Hz), 37.02, 37.13 (d, $J_{P,C}$ = 2.5 Hz), 67.98, 69.14, 92.36 (d, $J_{P,C}$ = 31.2 Hz), 127.46 (d, $J_{P,C}$ = 5.4 Hz), 127.85, 128.74, 132.36 (d, $J_{P,C}$ = 3.7 Hz), 135.10 (d, $J_{P,C}$ = 33.2 Hz), 146.02 (d, $J_{P,C}$ = 21.1 Hz); $^{31}$P NMR ($C_6D_6$, 101.3 MHz) $\delta$ 8.28; HRMS (ESI) m/z 345.1588 ($[M+O+Na]^+$, exact mass calcd for $C_{18}H_{27}O_3PNa$ 345.1590).

**Preparation of 2-[2-((2*R*,5*R*)-dimethyl-phospholan-1-yl)-phenyl]-(4*S*,6*S*)-dimethyl-[1,3]dioxane (5)**[8]:



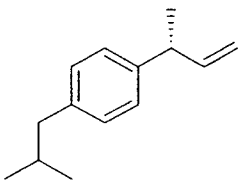

The procedure is the same as the above. Starting from [2 -((4*S*,6*S*)-dimethyl-[1,3]dioxan-2-yl)phenyl]-phosphane (53 mg, 0.24 mmol) and (2S,5S)-hexanediol cyclic sulfate (43.2 mg, 0.24mmol) to get 27 mg (36%) of 2-[2-((2*R*,5*R*)-dimethyl-phospholan-1-yl)-phenyl]-(4S,6S)-dimethyl-[1,3]dioxane. $^1$H NMR ($C_6D_6$, 400 MHz) $\delta$ 8.18 (ddd, $J$ = 7.8, 3.3, 1.4 Hz, 1H), 7.34 (dt, $J$ =7.5, 1.6 Hz, 1H), 7.22 (td, $J$ = 7.5, 1.4 Hz, 1H), 7.11 (td, $J$ = 7.5, 1.6 Hz, 1H), 6.85 (d, $J_{P,H}$ = 7.2 Hz, 1H), 4.35-4.25 (m, 1H), 4.20-4.05 (m, 1H), 2.60-2.45 (m, 1H), 2.45-2.30 (m, 1H), 2.10-1.95 (m, 1H), 1.95-1.80 (m, 1H), 1.80-1.70 (m, 1H), 1.55-1.40 (m, 1H), 1.35-1.15 (m, 7H), 1.11 (d, $J$ = 6.2 Hz, 3H), 0.98-0.85 (m, 4H); $^{13}$C NMR ($C_6D_6$, 100.6 MHz) $\delta$ 16.86 (d, $J_{P,C}$ = 2.0 Hz), 17.14, 20.93 (d, $J_{P,C}$ = 36.2 Hz), 22.13, 35.01 (d, $J_{P,C}$ = 10.4 Hz), 35.12 (d, $J_{P,C}$ = 7.3 Hz), 36.54 (d, $J_{P,C}$ = 2.9 Hz), 36.99, 37.14 (d, $J_{P,C}$ = 2.4 Hz), 67.74, 68.77, 92.26 (d, $J_{P,C}$ = 29.9 Hz), 126.99 (d, $J_{P,C}$ = 5.5 Hz),

128.63, 132.49 (d, $J_{P,C}$ = 3.6 Hz), 135.58 (d, $J_{P,C}$ = 33.6 Hz), 145.88 (d, $J_{P,C}$ = 21.1 Hz); $^{31}P$ NMR ($C_6D_6$, 101.3 MHz) $\delta$ 9.42; HRMS (ESI) m/z 345.1582 ($[M+O+Na]^+$, exact mass calcd for $C_{18}H_{27}O_3PNa$ 345.1590).

## Asymmetric Hydrovinylation Reactions of Vinylarene Compounds

**General procedure for asymmetric hydrovinylation reaction of Vinylarene compounds using [(allyl)NiBr]$_2$ and ligands in the presence of NaBARF in $CH_2Cl_2$:**
To a solution of [(allyl)NiBr]$_2$ in $CH_2Cl_2$ (1.5 mL) at room temperature was added a solution of ligand in $CH_2Cl_2$ (1.5 mL) in drybox. The resulting solution was added to a suspension of NaBARF in $CH_2Cl_2$ (1 mL). After stirring at room temperature for 1.5 h, the mixture was filtered through a small plug of celite and the precipitate was rinsed with $CH_2Cl_2$ (1 mL). The filtrate was collected in a Schlenk flask and was taken out of drybox. The catalyst solution was cooled to the desigated temperature in the table. Under one atmosphere of ethylene, the solution of vinylarene compounds in $CH_2Cl_2$ (3 mL) was added dropwise to the catalyst solution. After stirring for 2h at this temperature, the mixture was quenched with half-saturated aqueous $NH_4Cl$ solution and extracted three times with 10 mL portions of $CH_2Cl_2$. The combined organic layers were dried over anhydrous $MgSO_4$ and passed through a small plug of silica gel. The filtrate was concentrated to afford the crude products which were analyzed by GC. The enantiomeric excess of the alkene products were determined by HPLC on Chiracel OJ column (hexane/isopropanol system).

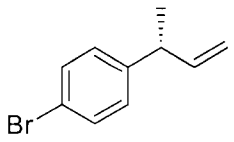
**Asymmetric hydrovinylation reaction of 4-isobutylstyrene using [(allyl)NiBr]$_2$, ligand in the presence of NaBARF in $CH_2Cl_2$:**



**1-Isobutyl-4-[(*R*)-1-methylallyl]benzene**: catalyst amount: 0.35 mol%; $[\alpha]_D$ = -7.63 (91%ee) (c 2.19 $CHCl_3$) [lit.: $[\alpha]_D$ = -5.84 (83%ee, neat),[9] -6.80 (c 2.09 $CHCl_3$, 74%ee)[10]]; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.10 (d, $J$ = 6.0 Hz, 2H), 7.05 (d, $J$ = 6.0 Hz, 2H), 6.05-5.95 (m, 1H), 5.05-4.95 (m, 2H), 3.50-3.35 (m, 1H), 2.42 (d, $J$ = 7.2 Hz, 2H), 1.90-1.75 (m, 1H), 1.33 (d, $J$ = 7.0 Hz, 3H), 0.88 (d, $J$ = 6.6 Hz, 6H); GC conditions: 1.0 mL helium/min, 10 min at 100°C, 4°C/min, 10 min at 200°C; HPLC conditions: 100% hexane, 0.25 mL/min, retention time (min): 21.57 (*R*), 24.08 (*S*).

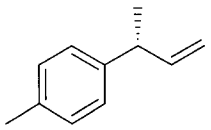
| Ligand | Temp. (°C) | Conv. (%) | Regioselectivity (%) | Ee (%) | Configuration |
|---|---|---|---|---|---|
| **1a** | -55 | 99.9 | 99.6 | 91 | *R* |
| **1a** | -70 | 100 | 97.5 | 88 | *R* |
| **1a** | -40 | 100 | 99 | 90 | *R* |
| **1b** | -55 | 83.4 | 100 | 88 | *R* |
| **2** | -55 | 99.2 | 89.8 | 71 | *R* |
| **3** | -55 | 100 | 100 | 85 | *R* |
| **4** | -55 | 100 | 100 | 85 | *R* |
| **5** | -55 | 100 | 100 | 90 | *S* |

**Asymmetric hydrovinylation reaction of 4-bromostyrene using [(allyl)NiBr]$_2$, ligand 1a in the presence of NaBARF in $CH_2Cl_2$**:



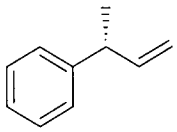

**1-Bromo-4-[(*R*)-1-methylallyl]benzene**: catalyst amount: 0.35 mol%; reaction temperature: -55°C, conversion:100%, regioselectivity:100%, 71% ee, configuration: *R*; $[\alpha]_D$ = -8.65 (c 3.07 $CHCl_3$) (lit.[10]: $[\alpha]_D$ = +9.9 (89%ee, c 7.02 $CHCl_3$)); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.39 (d, $J$ = 9.2 Hz, 2H), 7.07 (d, $J$ = 9.2 Hz, 2H), 6.00-5.90 (m, 1H), 5.05-4.95 (m, 2H), 3.45-3.35 (m, 1H), 1.32 (d, $J$ = 7.0 Hz, 3H); GC conditions: 1.0 mL helium/min, 10 min at 100°C, 4°C/min, 25 min at 200°C; HPLC conditions: 100% hexane, 0.30 mL/min, retention time (min): 21.57 (*S*), 27.70 (*R*).

**Asymmetric hydrovinylation reaction of 4-methylstyrene using [(allyl)NiBr]$_2$, ligand 1a in the presence of NaBARF in $CH_2Cl_2$:**



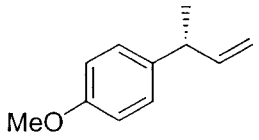
**1-Methyl-4-[(*R*)-1-methylallyl]benzene**: catalyst amount: 0.35 mol%; reaction temperature: -55°C, conversion:100%, regioselectivity:100%, 87% ee, configuration: *R*; $[\alpha]_D$ = -9.11 (c 2.13 $CHCl_3$) (lit[9]: $[\alpha]_D$ = +6.78 (83%ee, neat)); $^1$H NMR (250 MHz, $CDCl_3$) $\delta$ 7.10 (s, 4H), 6.10-5.90 (m, 1H), 5.10-4.95 (m, 2H), 3.50-3.35 (m, 1H), 2.31 (s, 3H), 1.32 (d, J = 7.0 Hz, 3H); GC conditions: 1.0 mL helium/min, 5 min at 80°C, 4°C/min, 15 min at 180°C; HPLC conditions: 100% hexane, 0.30 mL/min, retention time (min): 23.97 (*S*), 25.03 (*R*).

**Asymmetric hydrovinylation reaction of styrene using [(allyl)NiBr]$_2$, ligand 1a in the presence of NaBARF in $CH_2Cl_2$:**



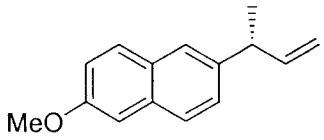
**[(*R*)-1-methylallyl]benzene**: catalyst amount:0.35 mol%; reaction temperature: -55°C, conversion:100%, regioselectivity: 99.7%, 88% ee, configuration: *R*; $[\alpha]_D$ = -4.90 (c 2.06 $CHCl_3$) (lit.[9,11]: $[\alpha]_D$ = -5.91 (neat)); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.35-7.25 (m, 2H), 7.25-7.10 (m, 3H), 6.15-5.90 (m, 1H), 5.10-4.95 (m, 2H), 3.50-3.40 (m, 1H), 1.35 (d, J = 7.0 Hz, 3H); GC conditions: 1.0 mL helium/min, 5 min at 80°C, 4°C/min, 15 min at 180°C; HPLC conditions: 100% hexane, 0.30 mL/min, retention time (min): 19.84 (*R*), 22.62 (*S*).

**Asymmetric hydrovinylation reaction of 4-methoxystyrene using [(allyl)NiBr]$_2$, ligand 1a in the presence of NaBARF in $CH_2Cl_2$:**



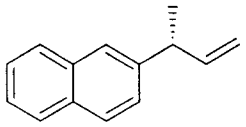

**1-Methoxy-4-[(*R*)-1-methylallyl]benzene**: catalyst amount:0.35 mol%; reaction temperature: -55°C, conversion:80.2%, regioselectivity: 100%, 73% ee, configuration: *R*; GC conditions: 1.0 mL helium/min, 15 min at 120°C, 4°C/min, 30 min at 220°C; HPLC conditions: hexane:isopropanol=95:5, 0.50 mL/min, retention time (min): 26.37 (*R*), 27.90 (*S*).

**Asymmetric hydrovinylation reaction of 6-methoxy-2-vinylnaphthalene using [(allyl)NiBr]$_2$, ligand 1a in the presence of NaBARF in $CH_2Cl_2$:**



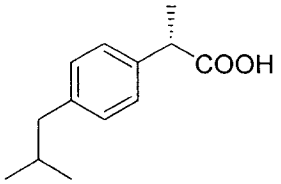

**2-Methoxy-6-[(*R*)-1-methylallyl]naphthalene**: catalyst amount:1.40 mol%; reaction temperature: -55°C, conversion:72.8%, regioselectivity: 100%, 86% ee, configuration: *R*; GC conditions: 1.0 mL helium/min, 15 min at 150°C, 4°C/min, 15 min at 250°C; HPLC conditions: hexane:isopropanol=95:5, 0.50 mL/min, retention time (min): 29.74 (*R*), 33.10 (*S*).

**Asymmetric hydrovinylation reaction of 2-vinylnaphthalene using [(allyl)NiBr]$_2$, ligand 1a in the presence of NaBARF in $CH_2Cl_2$:**



**2-[(*R*)-1-methylallyl]naphthalene**: catalyst amount:0.70 mol%; reaction temperature: -55°C, conversion: 21%, regioselectivity: 100%, 86% ee, configuration: *R*; GC conditions: 1.0 mL Helium/min, 5 min at 130°C, 4°C/min, 15 min at 230°C; HPLC conditions: 100% hexane, 0.50 mL/min, retention time (min): 36.36 (*R*), 39.58 (*S*).

**Synthesis of (*S*)-(-)-ibuprofen: Oxidation of 1-isobutyl-4-[(*R*)-1-methylallyl]benzene**




1-Isobutyl-4-[(*R*)-1-methylallyl]benzene (92 mg, 0.49 mmol) was dissolved in a mixture of $CH_2Cl_2$ and $CH_3OH$ (1:1, 8 mL) and cooled to -78°C. Ozone was passed through the solution until it became blue. At that time ozone flow was stopped and nitrogen was bubbled for about 20 min to expel all the dissolved ozone from the solution. Excess of $Me_2S$ (1 mL) was added and the solution was warmed to room temperature and stirred for 30 min. Excess of water was added and the mixture was extracted with diethyl ether. The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure to get the crude aldehyde which was used for the next step without purification.

To the solution of the crude aldehyde in diethyl ether (2 mL) was added 2-methyl-2-butene (2 mL) and cooled to 0°C. Sodium chlorite (93 mg, 80%, 0.82 mmol) which has been powered well was added to the resulting mixture at 0°C and stirred vigorously. The reaction mixture was allowed to warm to room temperature for 10 minutes. 5 mL of water was added and stirred for 3 mintues, then 3 mL of 2N HCl was added and stirred for additional 5 minutes. The reaction mixture was extracted with diethyl ether. The combined extracts were washed with brine, dried over anhydrous $MgSO_4$ and concentrated to get 95 mg of crude (S)-(+)-ibuprofen. $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 7.20 (d, $J$ = 7.80 Hz, 2H), 7.08 (d, $J$ = 7.80 Hz, 2H), 3.69 (q, $J$ = 7.20 Hz, 1H), 2.43 (d, $J$ = 7.20 Hz, 2H), 1.90-1.75 (m, 1H), 1.48 (d, $J$ = 7.20 Hz, 3H), 0.88 (d, $J$ = 6.6 Hz, 6H).

Determination of enantiomeric excess of ibuprofen: To the solution of ibuprofen (1 mg) in $CH_2Cl_2$ (1 mL) was added 40 uL of esterification solution which was prepared by mixing (-)-menthol (350 mg), DCC (120 mg), DMAP (6 mg), 25 uL of 1M HCl and $CH_2Cl_2$ (1 mL). The mixture was shaken for about 15 min and analyzed by Chirasil-L-Val on WCOT fused silica (25 m x 0.25 mm, 0.12 μm film thickness) capillary GC

column to give 89%ee. GC conditions: 1.0 mL helium/min, 20 min at 150°C, 0.5°C/min, 30 min at 180°C, retention time (min): 23.568 (*S*), 24.307 (*R*).

**Asymmetric hydrovinylation reaction of 4-isobutylstyrene using 0.035 mol% of [(allyl)NiBr]$_2$:**

To a solution of [(allyl)NiBr]$_2$ (2.5 mg, 0.007 mol) in $CH_2Cl_2$ (1 mL) at room temperature was added a solution of ligand **1a** (4.3 mg, 0.014 mmol) in $CH_2Cl_2$ (1 mL) in drybox. The resulting solution was added to a suspension of NaBARF (12.9 mg, 0.0146 mmol) in $CH_2Cl_2$ (1 mL). 1 mL of $CH_2Cl_2$ was used to rinse the vial and combined with the above mixture and the resulting mixture was stirred for 1.5 h at room temperature. The above solution (0.4 mL) was transferred into a dry Schlenk flask and taken out of drybox. The catalyst solution was cooled to -55°C and added dropwise the solution of 4-isobutylstyrene (320 mg, 2mmol) in $CH_2Cl_2$ (1 mL) under 1 atm of ethylene. After stirring at -55°C for 4h, the mixture was quenched with half-saturated aqueous $NH_4Cl$ solution and extracted three times with 10 mL portions of $CH_2Cl_2$. The combined organic layers were dried over anhydrous $MgSO_4$ and passed through a small plug of silica gel. The filtrate was concentrated to afford the crude products which were analyzed by GC to get 86% conversion and 100% regioselectivity. The enantiomeric excess of product was determined by HPLC on Chiracel OJ column to be 76%.

**References**: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7. Reduction of diethoxyphosphoryl compounds: (a) Kalbitz, J.; Leibring, E.; Schmidt, H. Z. *Anorg. Allg. Chem.* **1994**, *620*, 2041; (b) Kyba, E. P.; Liu, S. T.; Harris, R. L. *Organometallics* **1983**, *2*, 1877.
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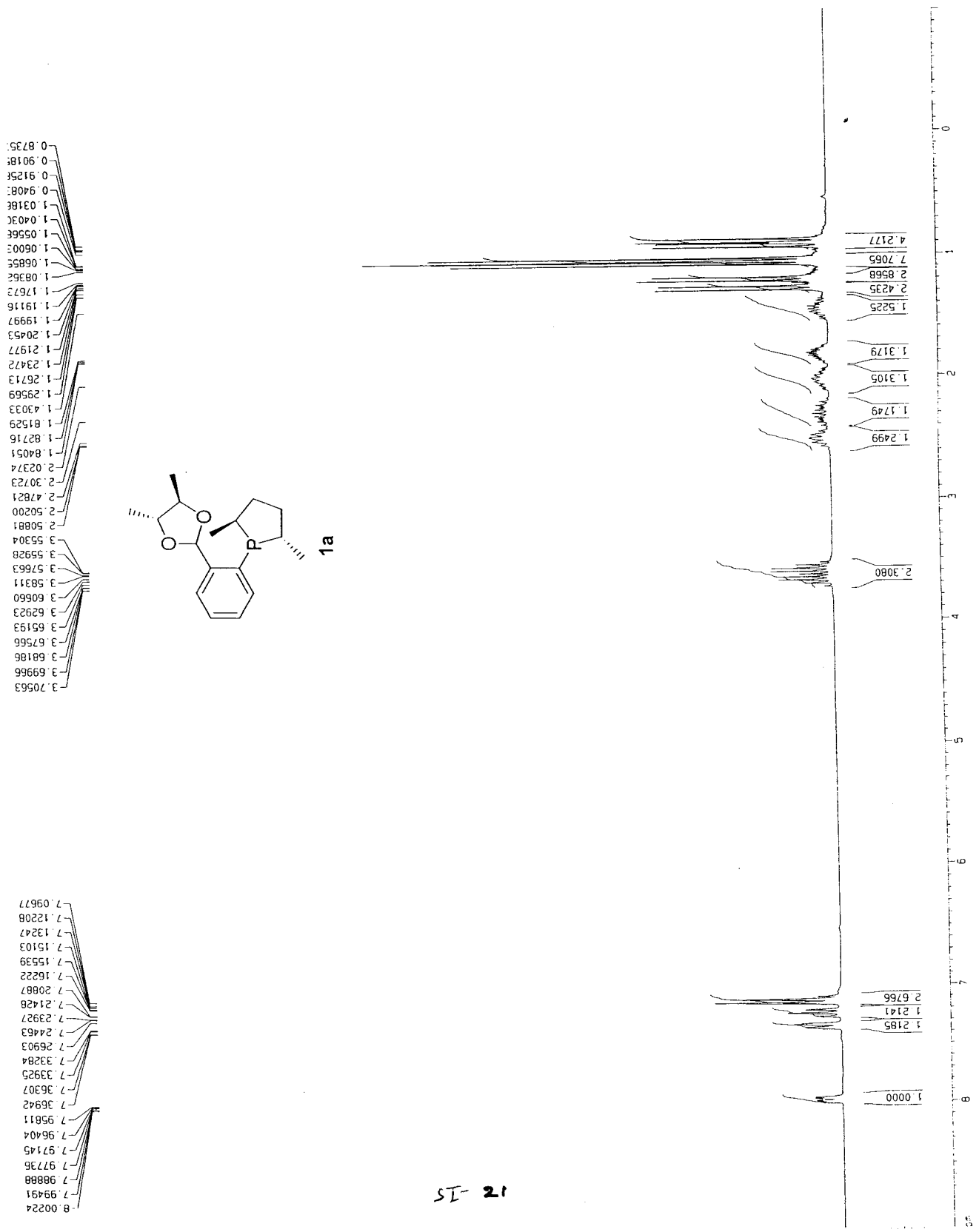
11. Hayashi, T.; Konishi, M.; Fukushima, M.; Mise, T.; Kagotani, M.; Tajika, M.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 180.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SOLVENT C606
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DS 2
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FIDRES 0.315917 Hz
AQ 1.5827444 sec
RG 203.2
DW 96.600 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
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PL1 -4.00 dB
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F2 - Processing parameters
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SF 250.1300312 MHz
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LB 0.30 Hz
GB 0
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2.8568
2.4235
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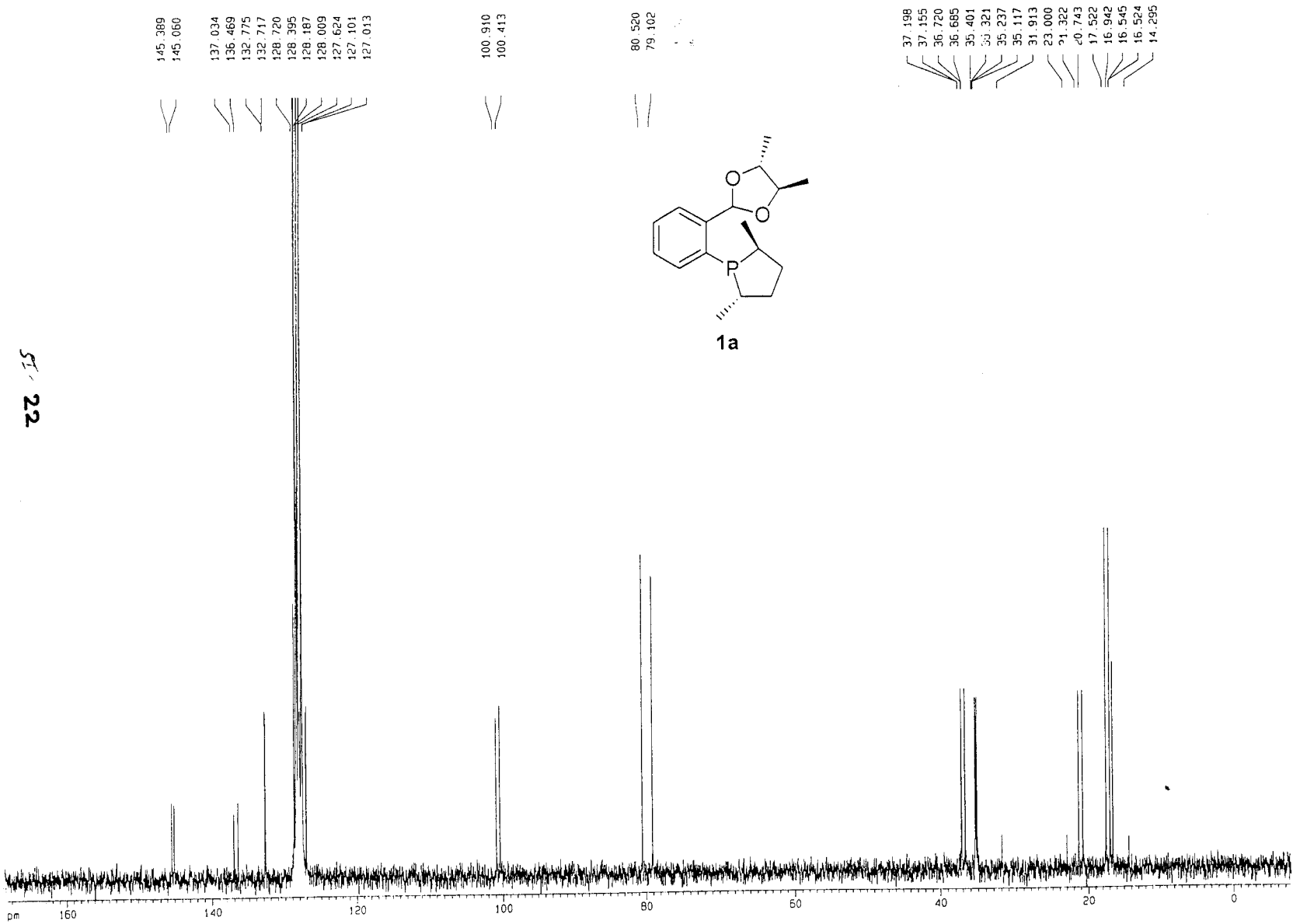


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RG 11585.2
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d12 0.00002000 sec

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PL1 0.00 dB
SFO1 62.9021320 MHz

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PCPD2 80.00 usec
PL2 -4.00 dB
PL12 16.00 dB
PL13 17.00 dB
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F2 - Processing parameters
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SSB 0
LB 1.00 Hz
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1D NMR plot parameters
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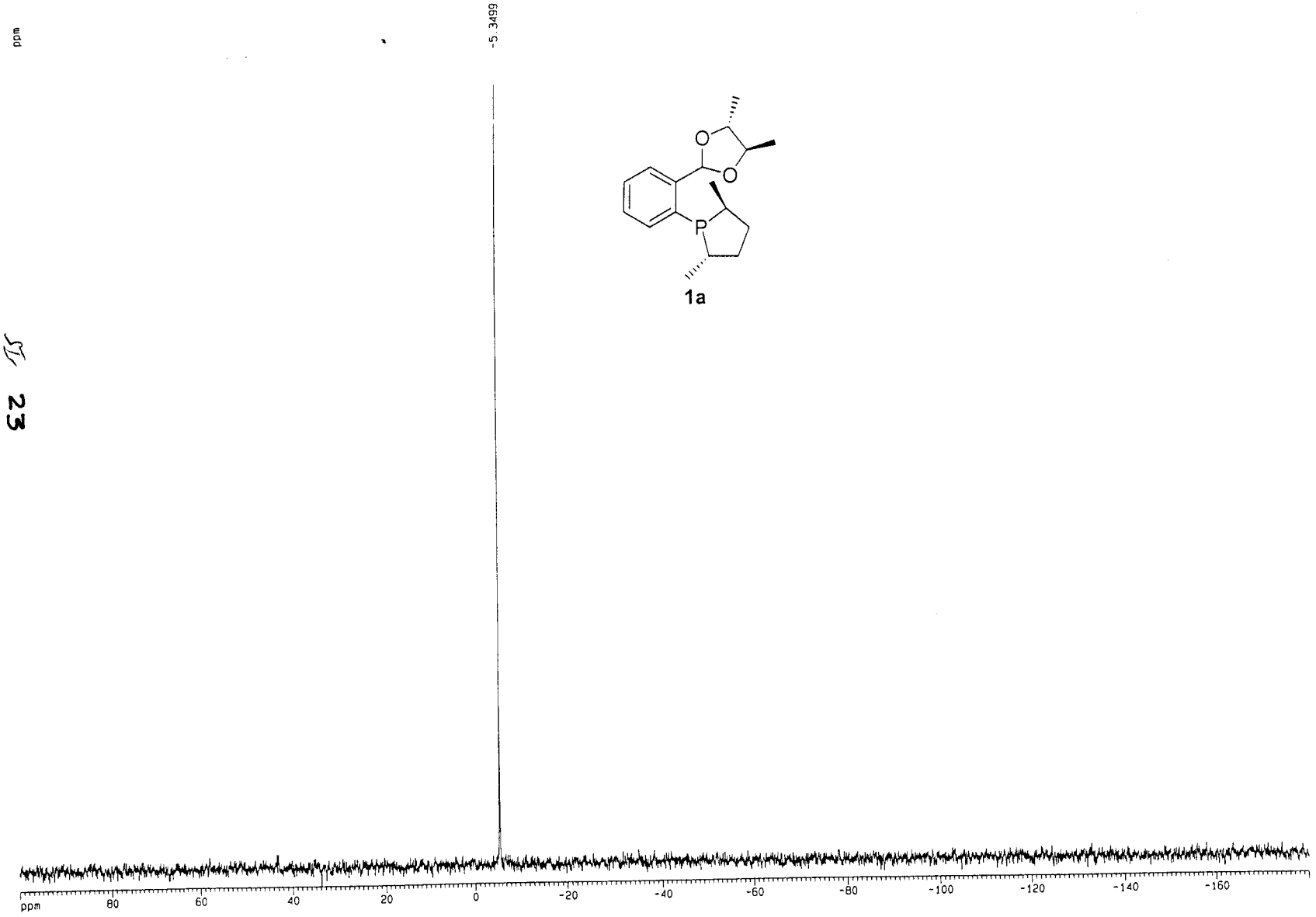





1a

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PROCNO 1

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SOLVENT C6D6
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DS 4
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DW 12.300 usec
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TE 300.0 K
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SFO1 101.2492922 MHz

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PCPD2 80.00 usec
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F2 - Processing parameters
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SF 101.2543550 MHz
WDW EM
SSB 0
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GB 0
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1D NMR plot parameters
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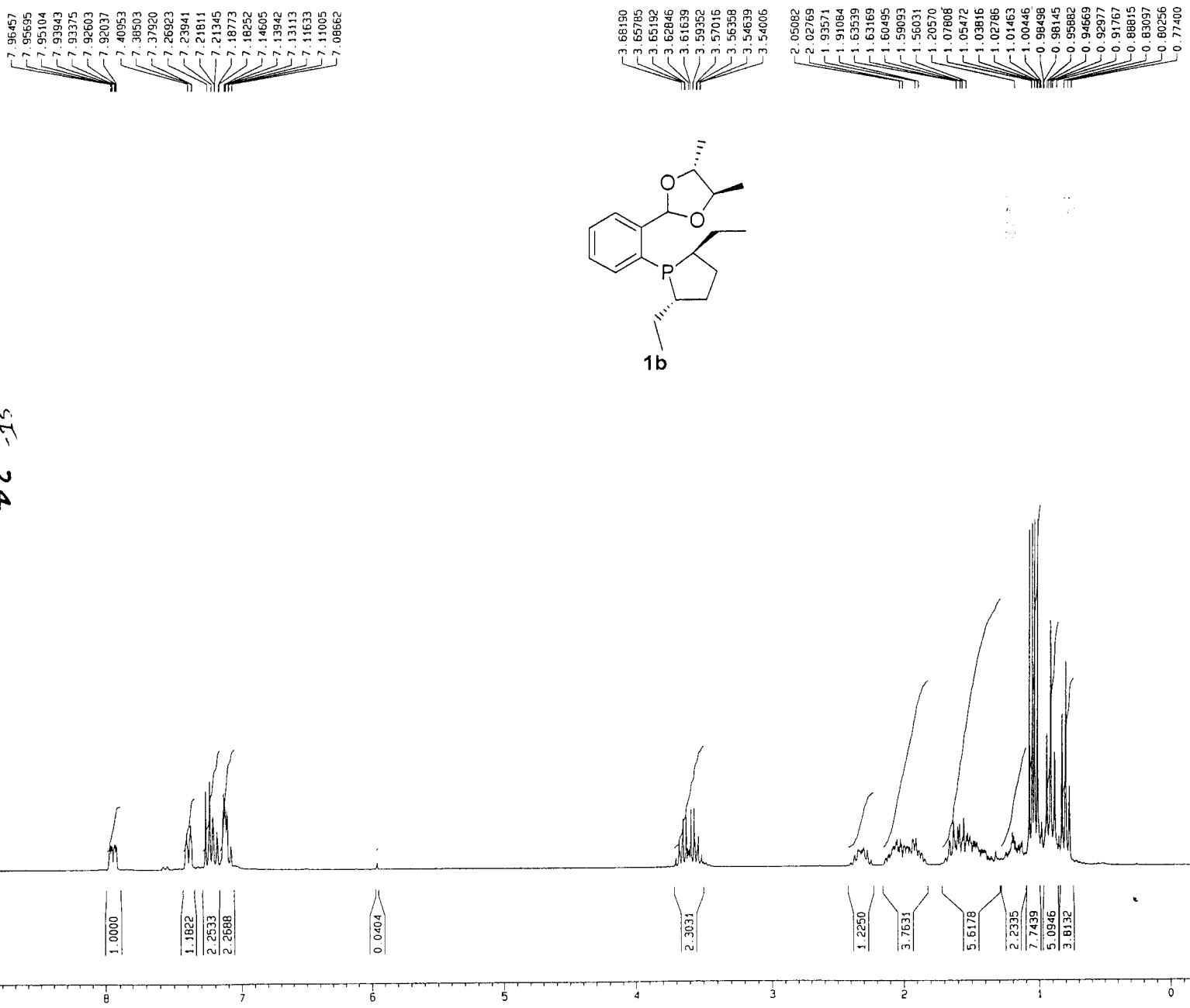
23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TE 300.0 K
D1 1.00000000 sec
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P1 7.20 usec
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LB 0.30 Hz
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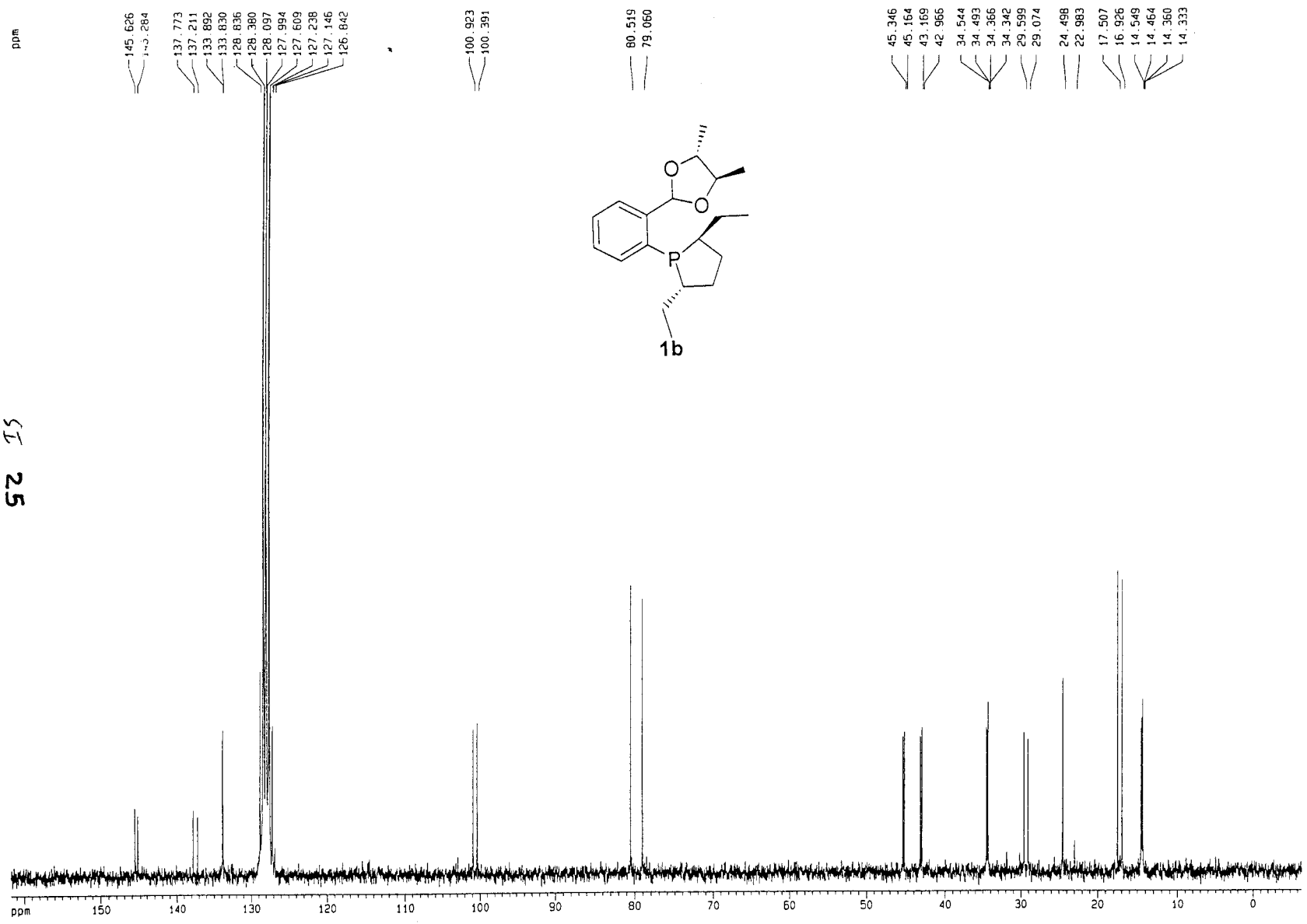
S1-24

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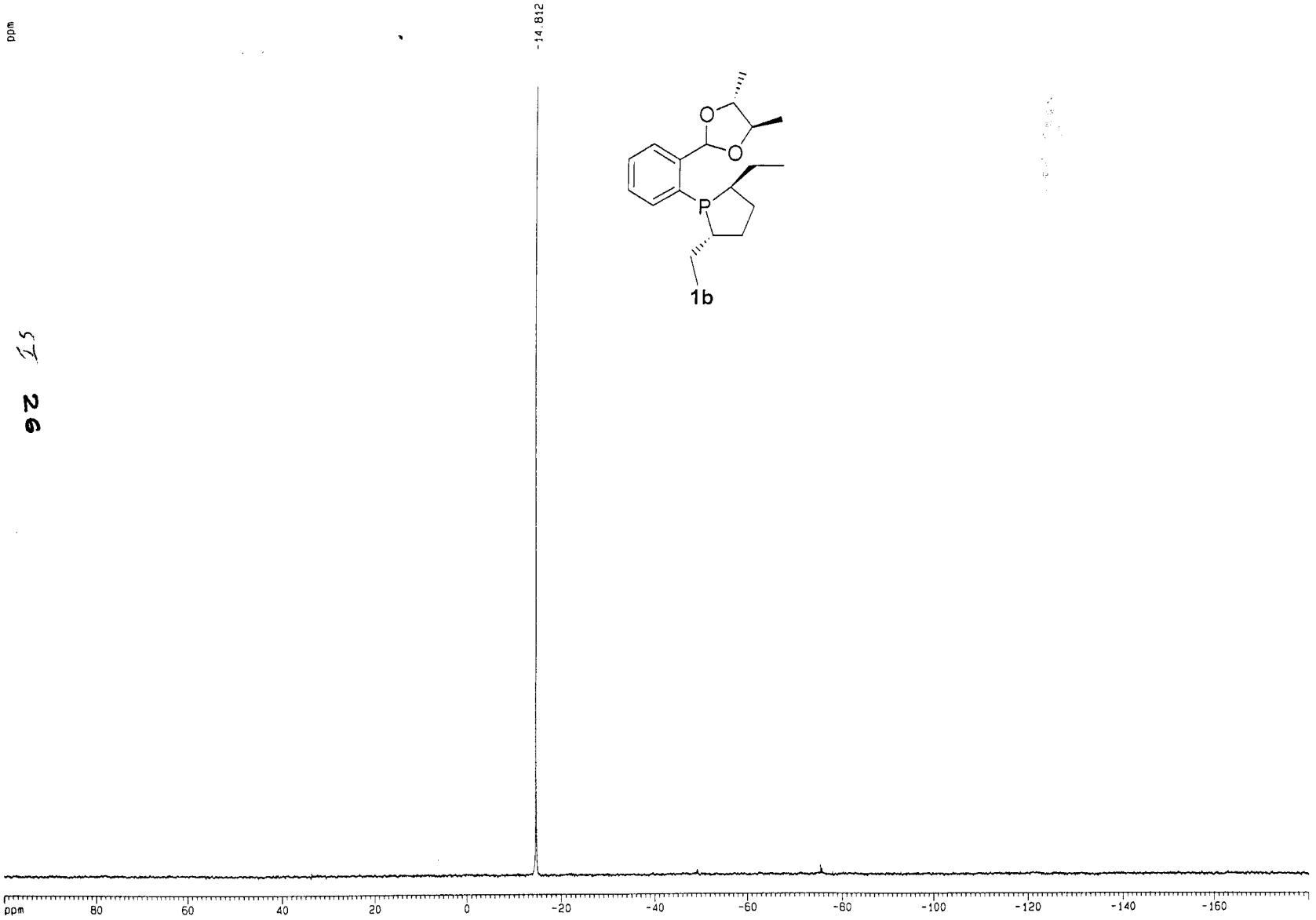





1b

15
26

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PROCNO                  1

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TE               300.0 K
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PL13             17.00 dB
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1D NMR plot parameters
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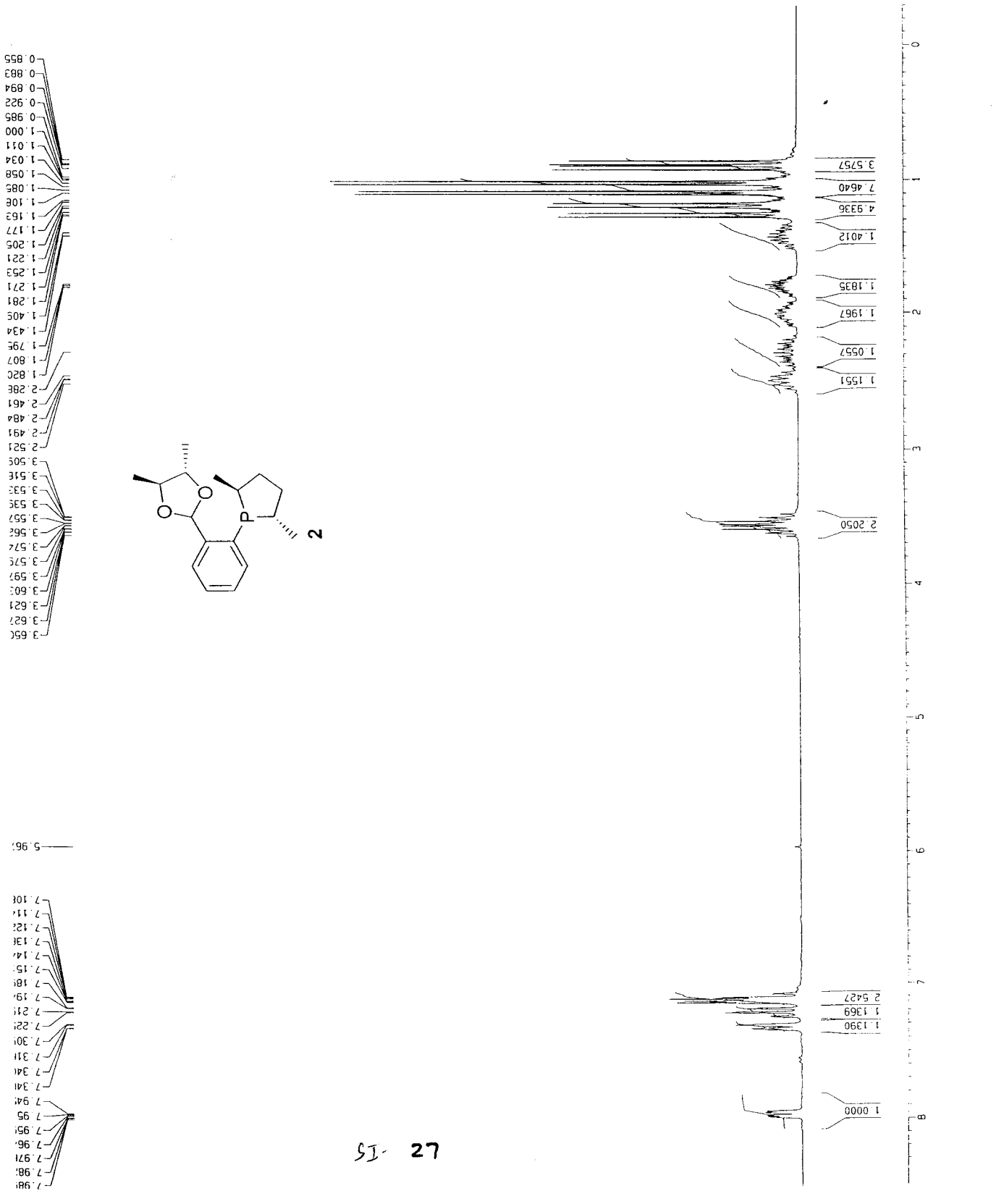
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SOLVENT C6D6
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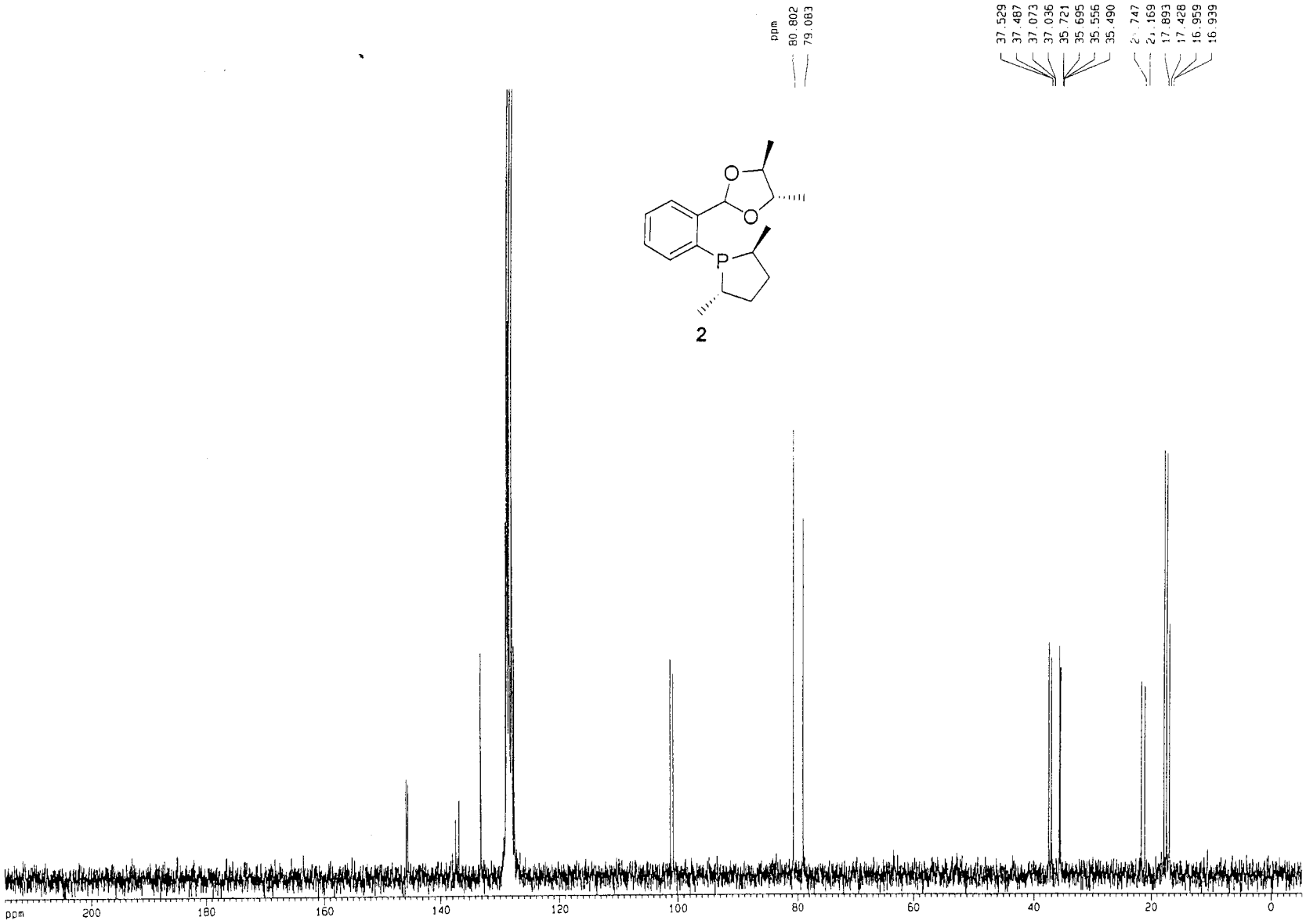
F2 - Processing parameters
SI 32768
SF 250.1300356 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 34.00 cm
F1P 8.692 ppm
F1 2174.14 Hz
F2P -0.301 ppm
F2 -75.24 Hz
PPMCM 0.26449 ppm/cm
HZCM 66.15812 Hz/cm
3.5757
7.4640
4.9336
1.4012
1.1835
1.1967
1.0557
1.1551
2.2050
2.5427
1.1369
1.1390
1.0000
2
0.855
0.883
0.894
0.922
0.985
1.000
1.011
1.034
1.058
1.085
1.108
1.162
1.177
1.205
1.221
1.253
1.271
1.281
1.405
1.434
1.796
1.807
1.820
2.288
2.461
2.484
2.491
2.521
3.506
3.516
3.533
3.539
3.557
3.562
3.574
3.576
3.597
3.603
3.621
3.627
3.650
5.961
7.108
7.114
7.122
7.138
7.144
7.151
7.181
7.192
7.219
7.225
7.301
7.311
7.340
7.941
7.95
7.951
7.961
7.971
7.981
7.987




Current Data Parameters
NAME ZAB-1-66
EXPNO 12
PROCNO 1

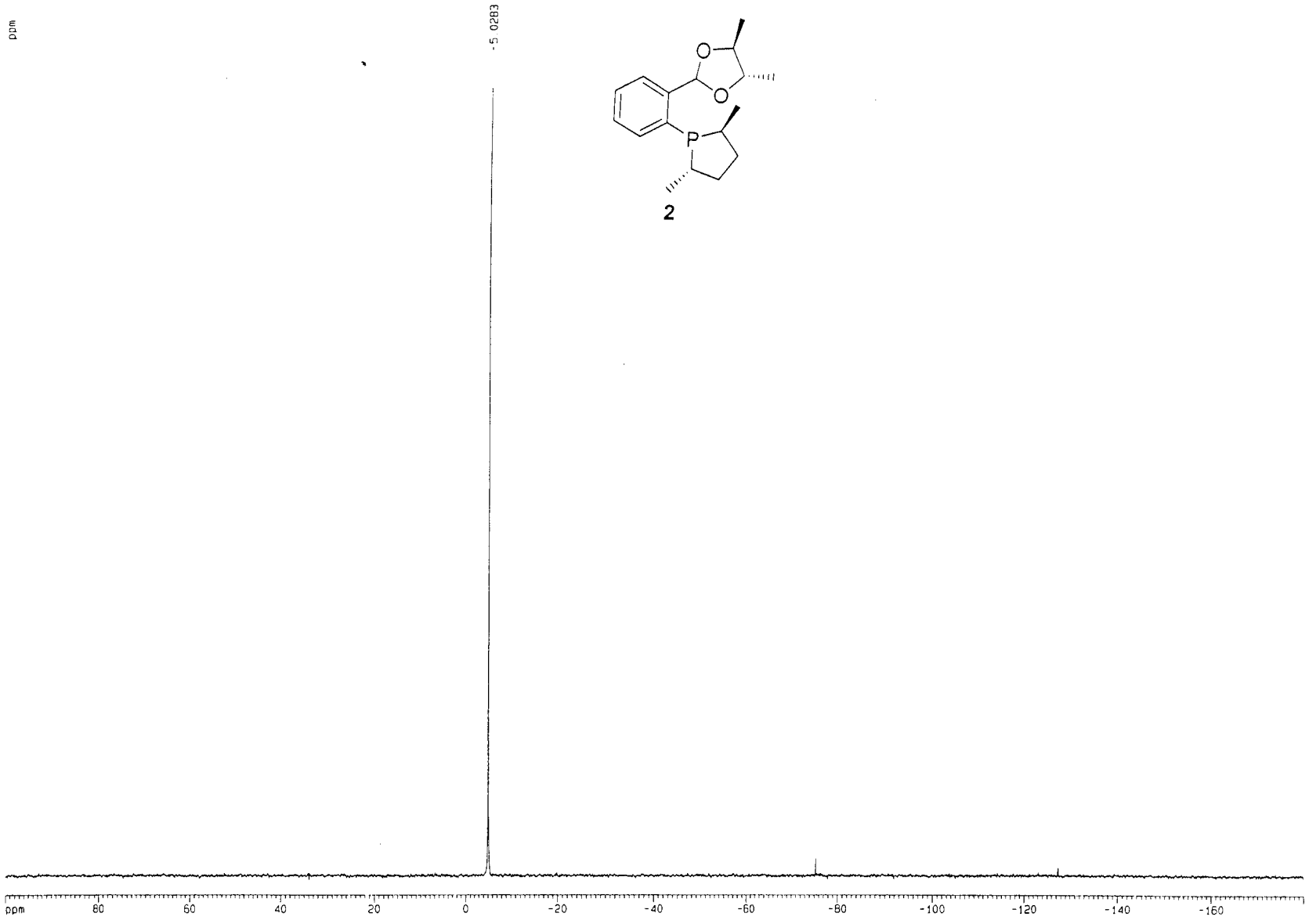
F2 - Acquisition Parameters
Date_ 20030412
Time 10.22
INSTRUM spect
PROBHD 5 mm QNP 1H/
PULPROG zgpg30
TD 65536
SOLVENT C606
NS 343
DS 4
SWH 15723.271 Hz
FIDRES 0.239918 Hz
AQ 2.0840948 sec
RG 11585.2
DW 31.800 usec
DE 30.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

********** CHANNEL f1 **********
NUC1 13C
P1 8.00 usec
PL1 0.00 dB
SF01 62.9021320 MHz

********** CHANNEL f2 **********
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 16.00 dB
PL13 17.00 dB
SF02 250.1310005 MHz

F2 - Processing parameters
SI 32768
SF 62.8952002 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 34.00 cm
F1P 215.000 ppm
F1 13522.47 Hz
F2P -5.000 ppm
F2 -314.48 Hz
PPMCM 6.47059 ppm/cm
HZCM 406.96893 Hz/cm






2

Current Data Parameters
NAME ZAB-1-66
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030412
Time 10.19
INSTRUM spect
PROBHD 5 mm ONP 1H/
PULPROG zgpg30
TD 65536
SOLVENT C606
NS 16
DS 4
SWH 40650.406 Hz
FIDRES 0.620276 Hz
AQ 0.8061428 sec
RG 9195.2
DW 12.300 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

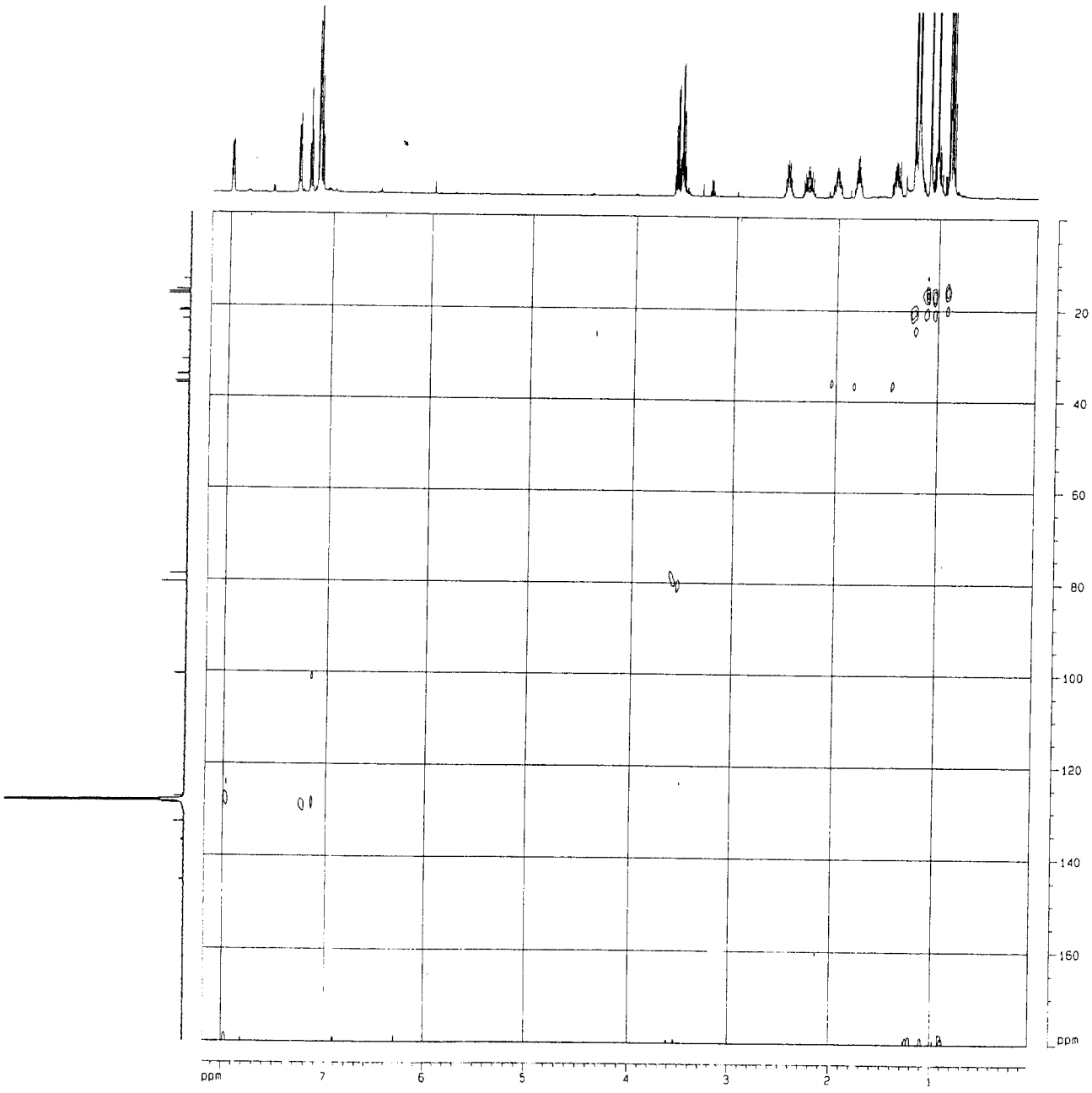
********** CHANNEL f1 **********
NUC1 31P
P1 6.00 usec
PL1 -4.00 dB
SFO1 101.2492922 MHz

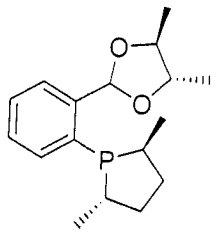
********** CHANNEL f2 **********
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 16.00 dB
PL13 17.00 dB
SFO2 250.1310005 MHz

F2 - Processing parameters
SI 32768
SF 101.2543550 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 34.00 cm
F1P 100.000 ppm
F1 10125.44 Hz
F2P -180.000 ppm
F2 -18225.78 Hz
PPMCM 8.23529 ppm/cm
HZCM 833.85938 Hz

SI- 30




2

Current Data Parameters

| | |
|---|---|
| NAME | ZAP-1-62 |
| EXPNO | 4 |
| PROCNO | 1 |

F2 - Acquisition Parameters

| | |
|---|---|
| Date_ | 20030409 |
| Time | 17.59 |
| INSTRUM | spect |
| PROBHD | 5 mm BBO BB-1 |
| PULPROG | inv4gs1d |
| TD | 1024 |
| SOLVENT | CDCl3 |
| NS | 2 |
| DS | 0 |
| SWH | 4084.967 Hz |
| FIDRES | 3.989226 Hz |
| AQ | 0.1253876 sec |
| RG | 7298.2 |
| DW | 122.400 usec |
| DE | 6.00 usec |
| TE | 300.0 K |
| D0 | 0.00000300 sec |
| D1 | 1.50000000 sec |
| D2 | 0.00345000 sec |
| d4 | 0.00172500 sec |
| D11 | 0.03000000 sec |
| D13 | 0.00000300 sec |
| D16 | 0.00020000 sec |
| d20 | 0.00052500 sec |
| d21 | 0.00224600 sec |
| IN0 | 0.00001104 sec |

********** CHANNEL f1 **********

| | |
|---|---|
| NUC1 | 1H |
| P1 | 14.75 usec |
| P2 | 29.50 usec |
| PL1 | -1.00 dB |
| SFO1 | 500.0220501 MHz |

********** CHANNEL f2 **********

| | |
|---|---|
| CPDPRG2 | garp |
| NUC2 | 13C |
| P3 | 13.00 usec |
| P4 | 26.00 usec |
| PCPD2 | 88.00 usec |
| PL2 | 3.00 dB |
| PL12 | 22.50 dB |
| SFO2 | 125.7413947 MHz |

********** GRADIENT CHANNEL ********

| | |
|---|---|
| P16 | 1000.00 usec |

F1 - Acquisition parameters

| | |
|---|---|
| NDO | 4 |
| TD | 90 |
| SFO1 | 125.7414 MHz |
| FIDRES | 251.667297 Hz |
| SW | 180.132 ppm |

F2 - Processing parameters

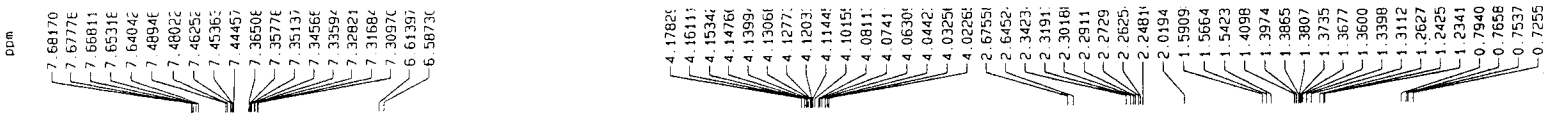
| | |
|---|---|
| SI | 1024 |
| SF | 500.0200000 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 5.00 Hz |
| GB | 0 |
| PC | 1.40 |

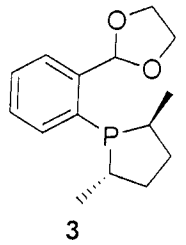
F1 - Processing parameters

| | |
|---|---|
| SI | 512 |
| MC2 | TPPI |
| SF | 125.7300790 MHz |
| WDW | QSINE |
| SSB | 4 |
| LB | 0.00 Hz |
| GB | 0 |

2D NMR plot parameters

| | |
|---|---|
| CX2 | 20.00 cm |
| CA1 | 20.00 cm |
| F2PLO | 8.185 ppm |
| F2LO | 4092.57 Hz |
| F2PHI | 2.015 ppm |
| F2HI | 7.60 Hz |
| F1PLO | 180.074 ppm |
| F1LO | 22640.73 Hz |
| F1PHI | -0.074 ppm |
| F1HI | 7.33 Hz |
| F2PPMCM | 0.40846 ppm/cm |
| F2HZCM | 204.24837 Hz/cm |
| F1PPMCM | 9.00741 ppm/cm |





3

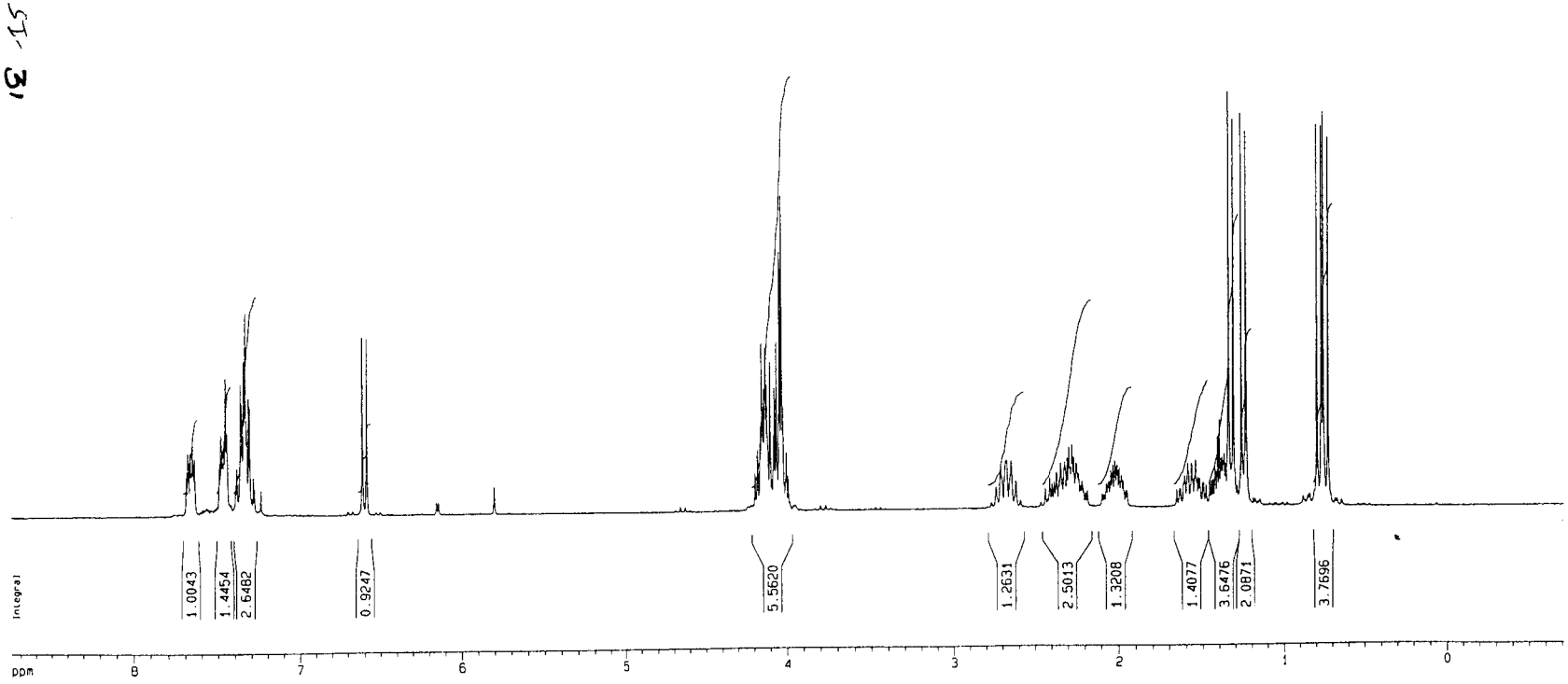
Current Data Parameters
NAME ZAB-1-122
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030607
Time 13.00
INSTRUM spect
PROBHD 5 mm QNP 1H/
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 16
DS 2
SWH 5175.983 Hz
FIDRES 0.315917 Hz
AQ 1.5827444 sec
RG 181
DW 96.600 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

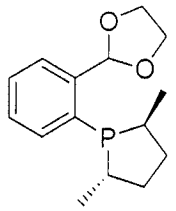
========== CHANNEL f1 ==========
NUC1 1H
P1 7.20 usec
PL1 -4.00 dB
SFO1 250.1315447 MHz

F2 - Processing parameters
SI 32768
SF 250.1300124 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 34.00 cm
F1P 8.764 ppm
F1 2192.13 Hz
F2P -0.713 ppm
F2 -178.35 Hz
PPMCM 0.27874 ppm/cm
HZCM 69.72019 Hz/cm

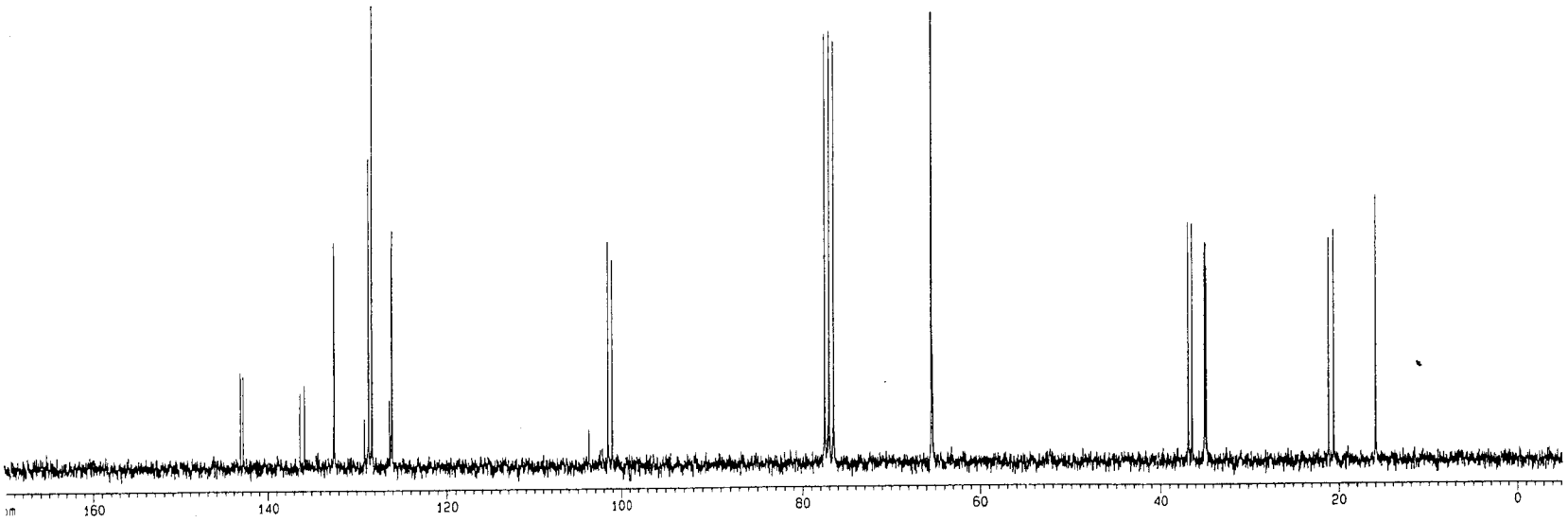


143.245
142.924
136.330
135.797
132.525
132.469
128.676
128.286
126.153
126.064
101.553
101.075
77.510
77.001
76.493
65.463
65.372
65.264
36.848
36.805
36.410
36.376
35.008
34.924
34.864
34.746
21.125
20.567
16.004
15.983

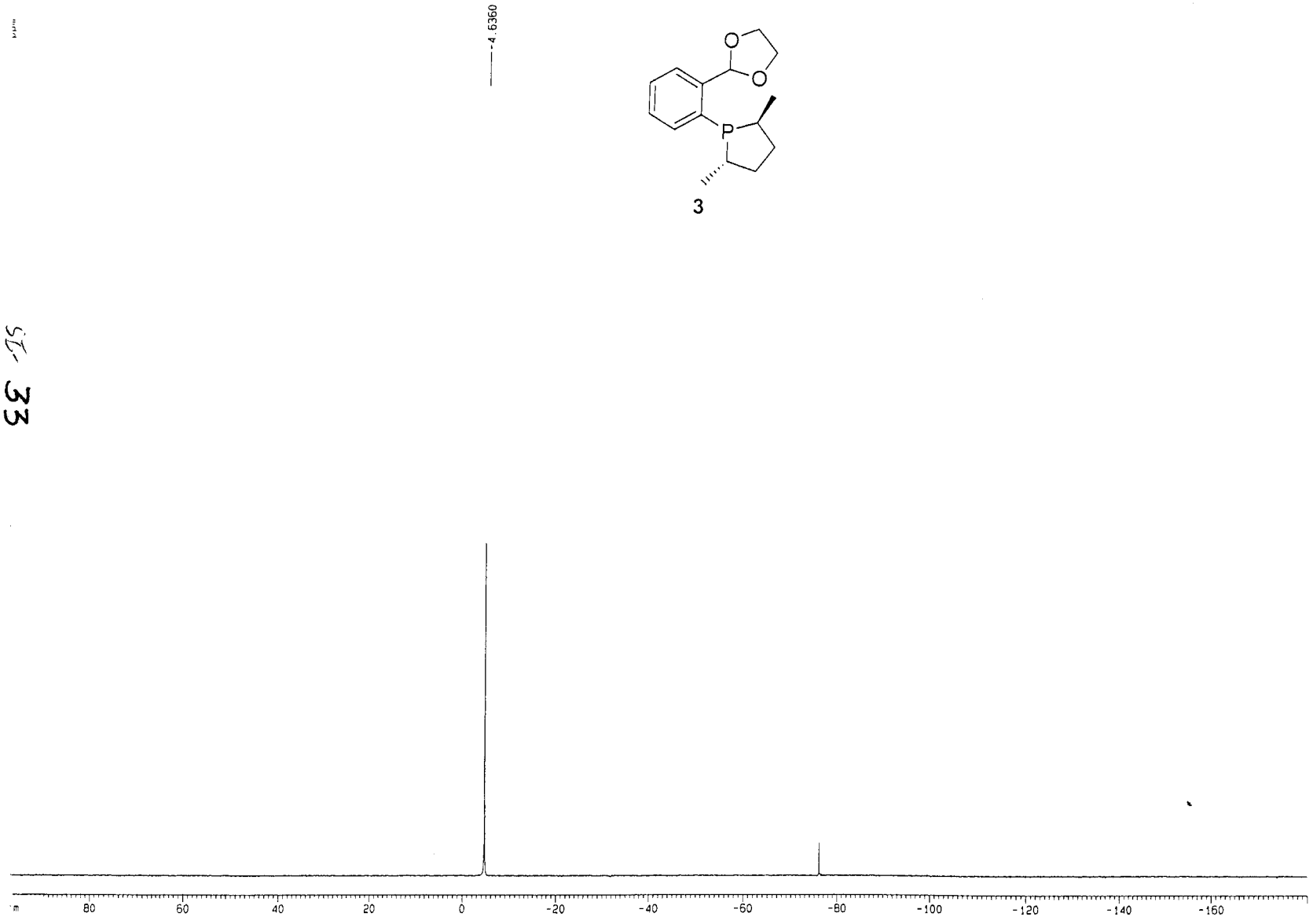


3

ST- 32




```
Current Data Parameters
NAME                ZAB-1-122
EXPNO                      12
PROCNO                      1

F2 - Acquisition Parameters
Date_               20030607
Time                   13.05
INSTRUM                spect
PROBHD     5 mm QNP 1H/
PULPROG             zgpg30
TD                      65536
SOLVENT                CDCl3
NS                        421
DS                          4
SWH                15723.271 Hz
FIDRES              0.239918 Hz
AQ                  2.0840948 sec
RG                      16384
DW                     31.800 usec
DE                     30.00 usec
TE                     300.0 K
D1                  2.00000000 sec
d11                 0.03000000 sec
d12                 0.00002000 sec

========== CHANNEL f1 ==========
NUC1                       13C
P1                        8.00 usec
PL1                       0.00 dB
SFO1               62.9021320 MHz

========== CHANNEL f2 ==========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                    80.00 usec
PL2                      -4.00 dB
PL12                     16.00 dB
PL13                     17.00 dB
SFO2              250.1310005 MHz

F2 - Processing parameters
SI                         32768
SF                 62.8952416 MHz
WDW                           EM
SSB                            0
LB                        1.00 Hz
GB                             0
PC                         1.40

1D NMR plot parameters
CX                        34.00 cm
F1P                     171.518 ppm
F1                    10787.70 Hz
F2P                      -5.089 ppm
F2                     -320.09 Hz
PPMCM                   5.19435 ppm/cm
HZCM                  326.69974 Hz/cm
```




ST-33

Current Data Parameters
NAME ZAB-1-122
EXPNO 10
PROCNO 1

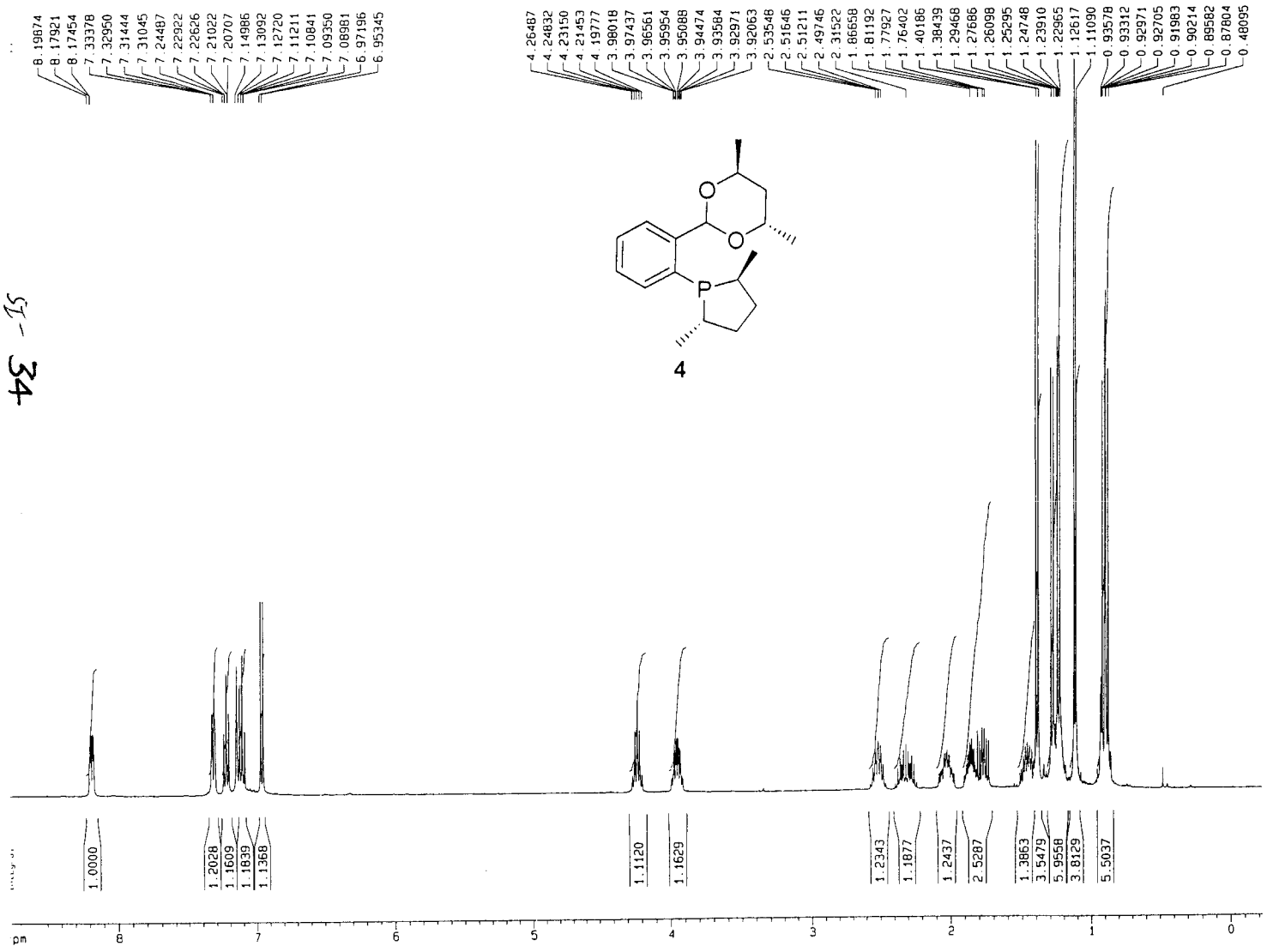
F2 - Acquisition Parameters
Date_ 20030607
Time 12.56
INSTRUM spect
PROBHD 5 mm QNP 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 16
DS 4
SWH 40650.406 Hz
FIDRES 0.620276 Hz
AQ 0.8061428 sec
RG 9195.2
DW 12.300 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

********** CHANNEL f1 **********
NUC1 31P
P1 6.00 usec
PL1 -4.00 dB
SFO1 101.2492922 MHz

********** CHANNEL f2 **********
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 16.00 dB
PL13 17.00 dB
SFO2 250.1310005 MHz

F2 - Processing parameters
SI 32768
SF 101.2543550 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 34.00 cm
F1P 100.000 ppm
F1 10125.44 Hz
F2P -180.000 ppm
F2 -18225.78 Hz
PPMCM 8.23529 ppm/cm
HZCM 833.85938 Hz/cm




4

St-34

Current Data Parameters

| | |
|---|---|
| NAME | ZAB-1-170 |
| EXPNO | 10 |
| PROCNO | 1 |

F2 - Acquisition Parameters

| | |
|---|---|
| Date_ | 20030723 |
| Time | 17.07 |
| INSTRUM | spect |
| PROBHD | 5 mm BBO BB- |
| PULPROG | zg30 |
| TD | 32768 |
| SOLVENT | C6D6 |
| NS | 16 |
| DS | 2 |
| SWH | 8278.146 Hz |
| FIDRES | 0.252629 Hz |
| AQ | 1.9792372 sec |
| RG | 90.5 |
| DW | 60.400 usec |
| DE | 6.00 usec |
| TE | 300.0 K |
| D1 | 1.00000000 sec |

========== CHANNEL f1 ==========

| | |
|---|---|
| NUC1 | 1H |
| P1 | 7.50 usec |
| PL1 | -6.00 dB |
| SFO1 | 400.1324710 MHz |

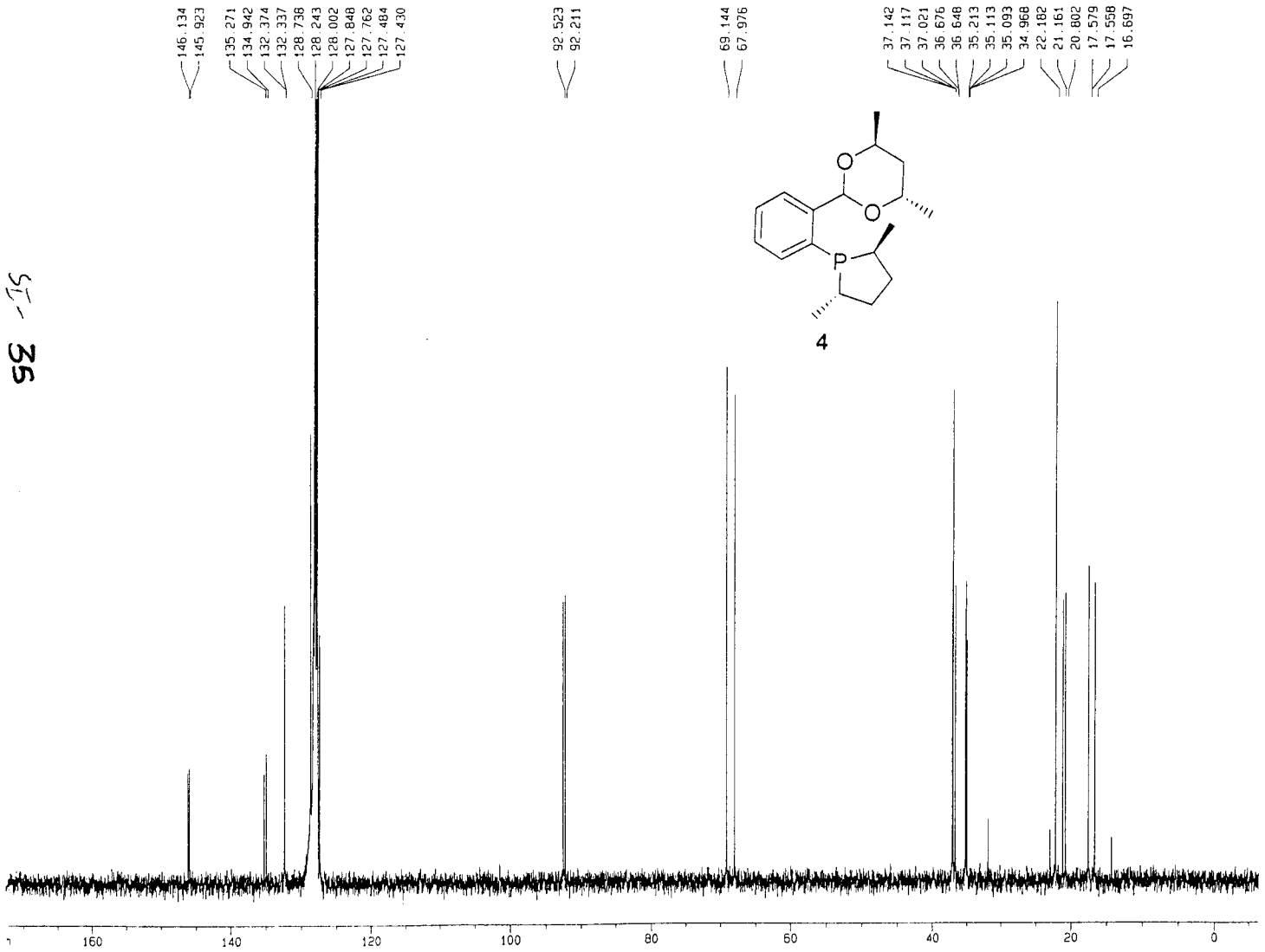
F2 - Processing parameters

| | |
|---|---|
| SI | 32768 |
| SF | 400.1300478 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 0.30 Hz |
| GB | 0 |
| PC | 1.00 |

1D NMR plot parameters

| | |
|---|---|
| CX | 30.00 cm |
| F1P | 8.815 ppm |
| F1 | 3527.19 Hz |
| F2P | -0.226 ppm |
| F2 | -90.39 Hz |
| PPMCM | 0.30137 ppm/cm |
| HZCM | 120.58592 Hz/cm |

S1- 35




4

Current Data Parameters

| | |
|---|---|
| NAME | ZAB-1-170 |
| EXPNO | 11 |
| PROCNO | 1 |

F2 - Acquisition Parameters

| | |
|---|---|
| Date_ | 20030723 |
| Time | 17.20 |
| INSTRUM | spect |
| PROBHD | 5 mm BBO BB- |
| PULPROG | zgpg30 |
| TD | 65536 |
| SOLVENT | C6D6 |
| NS | 610 |
| DS | 4 |
| SWH | 25125.629 Hz |
| FIDRES | 0.383387 Hz |
| AQ | 1.3042164 sec |
| RG | 8192 |
| DW | 19.900 usec |
| DE | 6.00 usec |
| TE | 300.0 K |
| D1 | 2.00000000 sec |
| d11 | 0.03000000 sec |
| d12 | 0.00002000 sec |

========== CHANNEL f1 ==========

| | |
|---|---|
| NUC1 | 13C |
| P1 | 5.90 usec |
| PL1 | -6.00 dB |
| SFO1 | 100.6237959 MHz |

========== CHANNEL f2 ==========

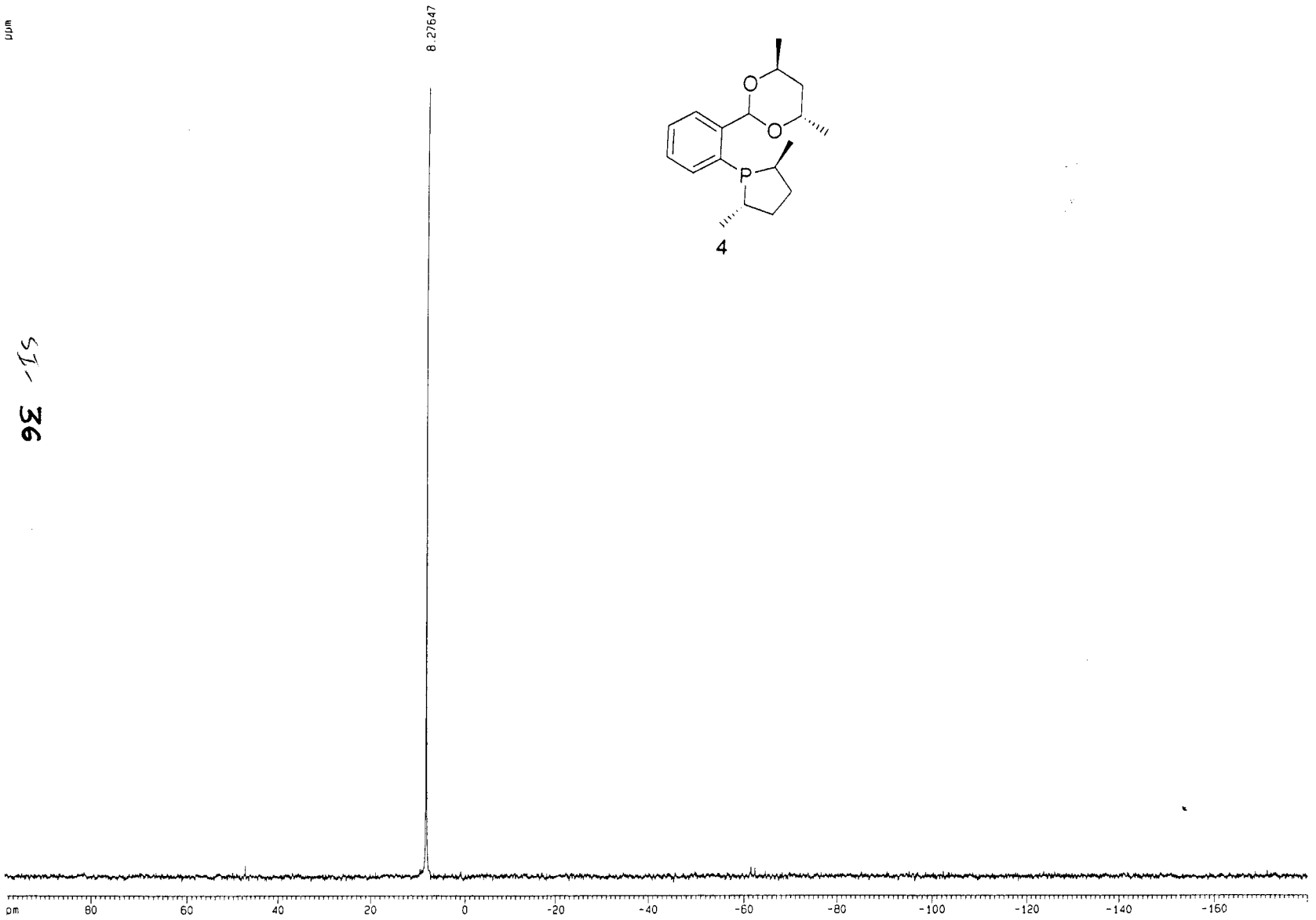
| | |
|---|---|
| CPDPRG2 | waltz16 |
| NUC2 | 1H |
| PCPD2 | 80.00 usec |
| PL2 | -6.00 dB |
| PL12 | 15.80 dB |
| PL13 | 15.80 dB |
| SFO2 | 400.1316005 MHz |

F2 - Processing parameters

| | |
|---|---|
| SI | 32768 |
| SF | 100.6127464 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 1.00 Hz |
| GB | 0 |
| PC | 1.40 |

1D NMR plot parameters

| | |
|---|---|
| CX | 30.00 cm |
| F1P | 174.971 ppm |
| F1 | 17604.36 Hz |
| F2P | -6.441 ppm |
| F2 | -648.09 Hz |
| PPMCM | 6.04710 ppm/cm |
| HZCM | 608.41504 Hz/cm |







4

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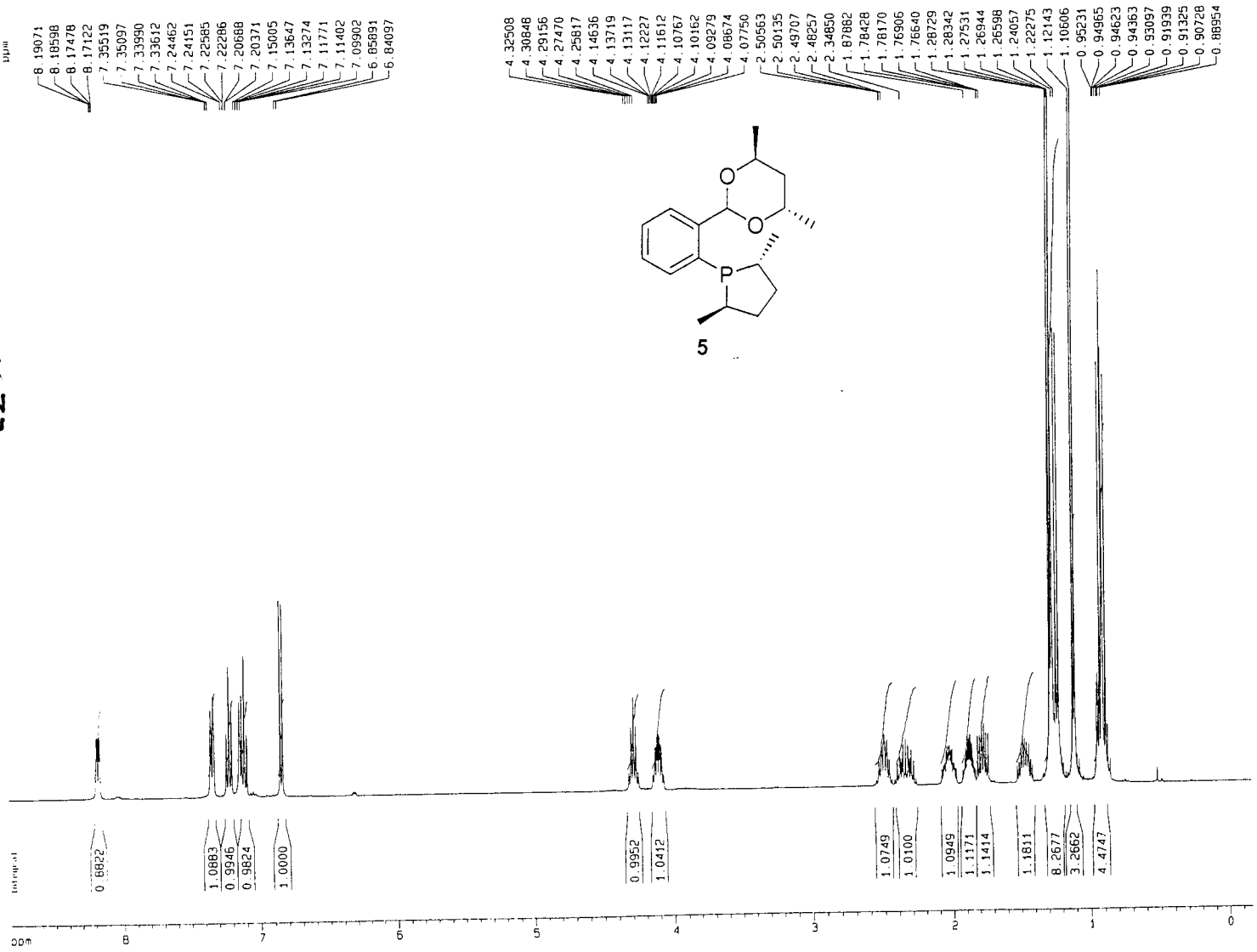
S1-15

```
Current Data Parameters
NAME            ZAB-1-170
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_            20030723
Time                17.09
INSTRUM             spect
PROBHD     5 mm QNP 1H/
PULPROG          zgpg30
TD                 65536
SOLVENT             C6D6
NS                    16
DS                     4
SWH           40650.406 Hz
FIDRES        0.620276 Hz
AQ            0.8061428 sec
RG               9195.2
DW              12.300 usec
DE               6.00 usec
TE              300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
d12          0.00002000 sec

********** CHANNEL f1 **********
NUC1                31P
P1                6.00 usec
PL1              -4.00 dB
SFO1        101.2492922 MHz

********** CHANNEL f2 **********
CPDPRG2         waltz16
NUC2                1H
PCPD2            80.00 usec
PL2              -4.00 dB
PL12             16.00 dB
PL13             17.00 dB
SFO2        250.1310005 MHz

F2 - Processing parameters
SI                 32768
SF          101.2530027 MHz
WDW                   EM
SSB                    0
LB                5.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                34.00 cm
F1P              100.000 ppm
F1              10125.30 Hz
F2P             -180.000 ppm
F2            -18225.54 Hz
PPMCM           8.23529 ppm/cm
HZCM          833.84827 Hz/cm
```




5

Current Data Parameters

| | |
|---|---|
| NAME | ZAB-1-176 |
| EXPNO | 10 |
| PROCNO | 1 |

F2 - Acquisition Parameters

| | |
|---|---|
| Date_ | 20030728 |
| Time | 10.06 |
| INSTRUM | spect |
| PROBHD | 5 mm BBO BB- |
| PULPROG | zg30 |
| TD | 32768 |
| SOLVENT | C6D6 |
| NS | 16 |
| DS | 2 |
| SWH | 8278.146 Hz |
| FIDRES | 0.252629 Hz |
| AQ | 1.9792372 sec |
| RG | 90.5 |
| DW | 60.400 usec |
| DE | 6.00 usec |
| TE | 300.0 K |
| D1 | 1.00000000 sec |

========== CHANNEL f1 ==========

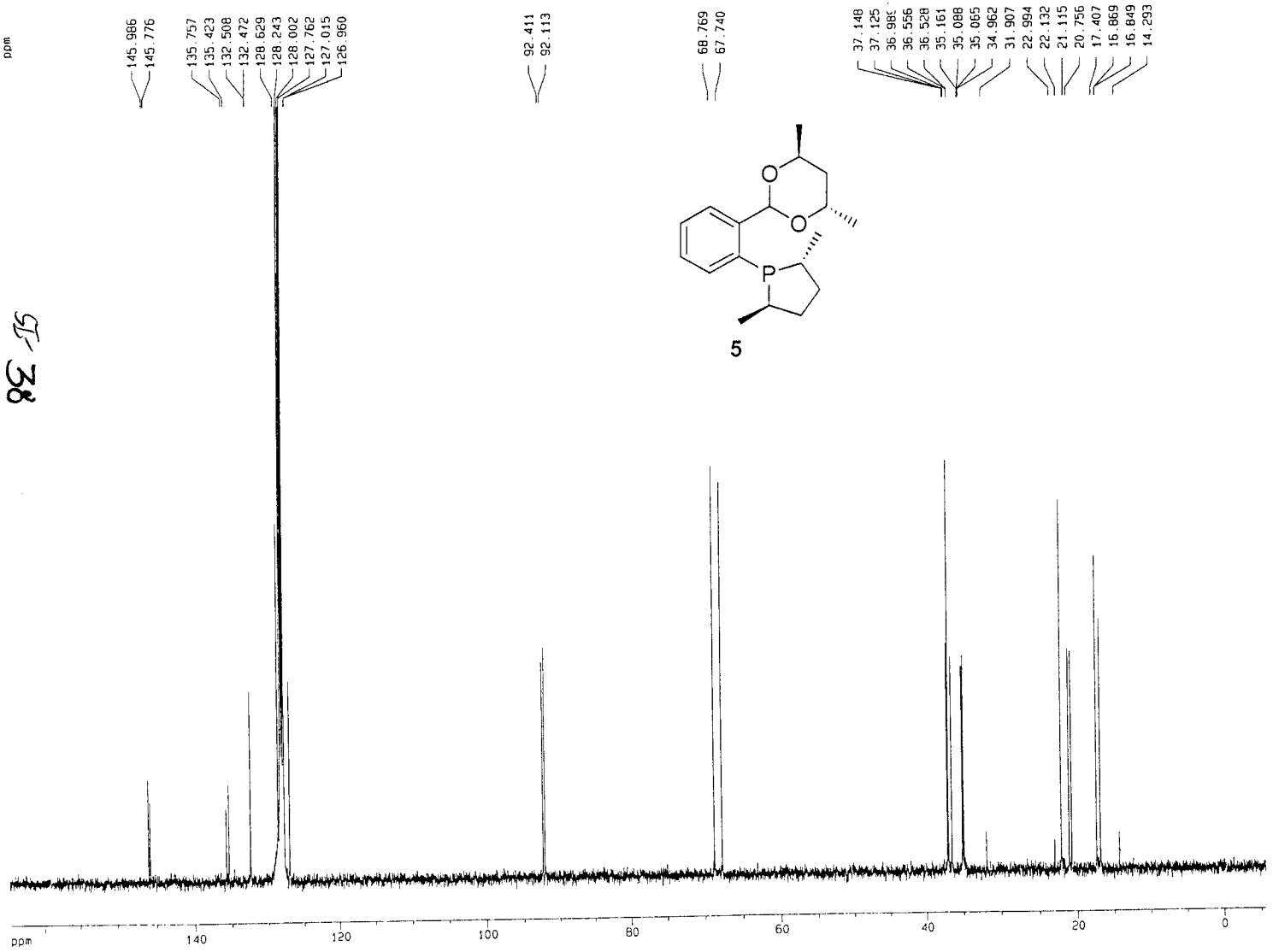
| | |
|---|---|
| NUC1 | 1H |
| P1 | 7.50 usec |
| PL1 | -6.00 dB |
| SFO1 | 400.1324710 MHz |

F2 - Processing parameters

| | |
|---|---|
| SI | 32768 |
| SF | 400.1300476 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 0.30 Hz |
| GB | 0 |
| PC | 1.00 |

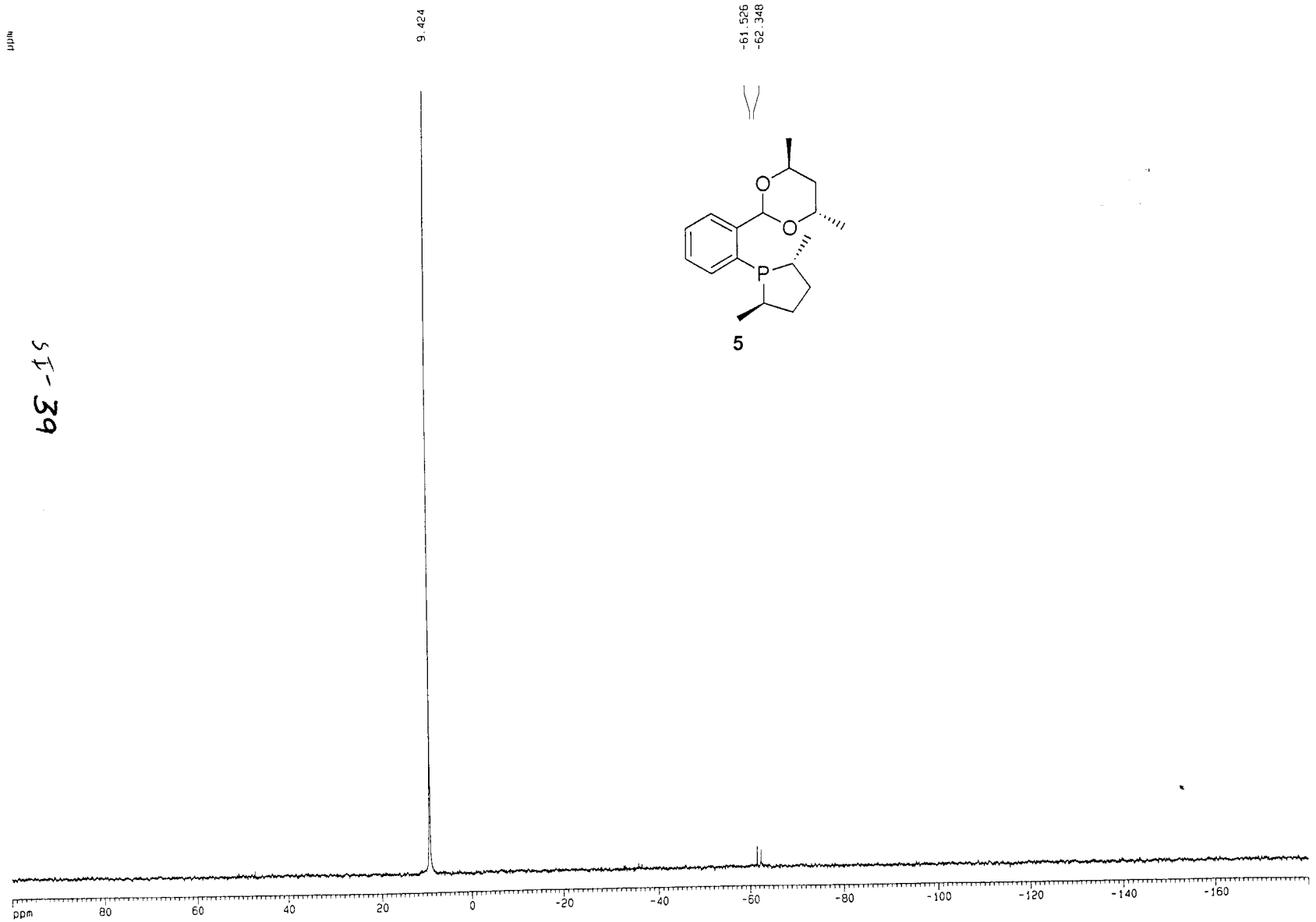
1D NMR plot parameters

| | |
|---|---|
| CX | 30.00 cm |
| F1P | 8.851 ppm |
| F1 | 3541.63 Hz |
| F2P | -0.165 ppm |
| F2 | -65.83 Hz |
| PPMCM | 0.30052 ppm/cm |
| HZCM | 120.24883 Hz/cm |




T-38

```
Current Data Parameters
NAME                  ZAB-1-176
EXPNO                        11
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20030728
Time                      10.14
INSTRUM                   spect
PROBHD       5 mm BBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                   C6D6
NS                         458
DS                           4
SWH                  25125.629 Hz
FIDRES               0.383387 Hz
AQ                   1.3042164 sec
RG                        4096
DW                      19.900 usec
DE                       6.00 usec
TE                      300.0 K
D1                   2.00000000 sec
d11                  0.03000000 sec
d12                  0.00002000 sec

========== CHANNEL f1 ==========
NUC1                        13C
P1                         5.90 usec
PL1                       -6.00 dB
SFO1                100.6237959 MHz

========== CHANNEL f2 ==========
CPDPRG2                 waltz16
NUC2                        1H
PCPD2                     80.00 usec
PL2                       -6.00 dB
PL12                      15.80 dB
PL13                      15.80 dB
SFO2                400.1316005 MHz

F2 - Processing parameters
SI                         32768
SF                  100.6127464 MHz
WDW                           EM
SSB                            0
LB                         1.00 Hz
GB                             0
PC                          1.40

1D NMR plot parameters
CX                        30.00 cm
F1P                      164.960 ppm
F1                     16597.09 Hz
F2P                       -5.642 ppm
F2                      -567.65 Hz
PPMCM                    5.68673 ppm/cm
HZCM                   572.15796 Hz/cm
```




ST-39

Current Data Parameters
NAME ZAB-1-176
EXPNO 10
PROCNO 1

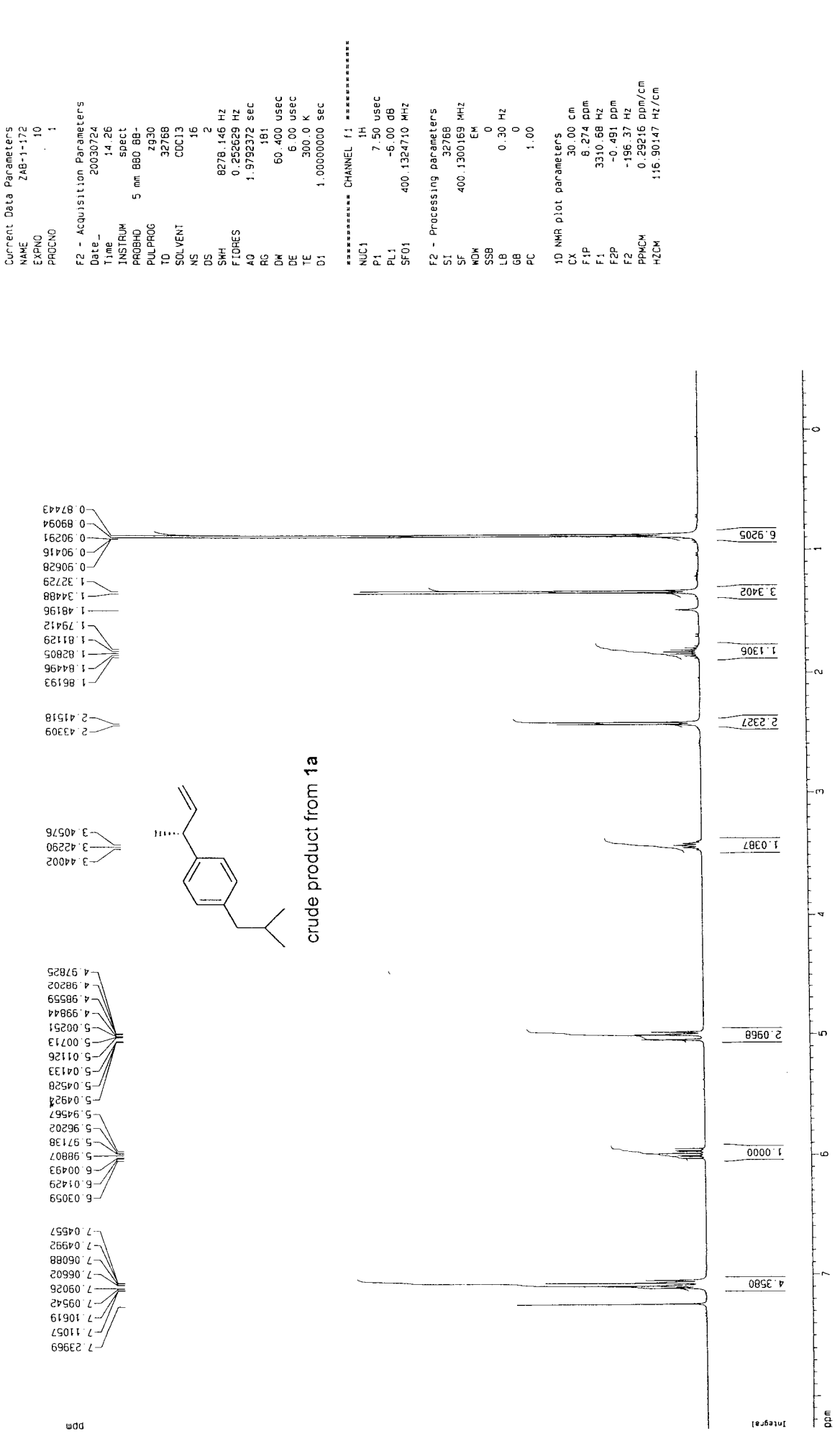
F2 - Acquisition Parameters
Date_ 20030729
Time 10.20
INSTRUM spect
PROBHD 5 mm QNP 1H/
PULPROG zgpg30
TD 65536
SOLVENT C6D6
NS 16
DS 4
SWH 40650.406 Hz
FIDRES 0.620276 Hz
AQ 0.8051428 sec
RG 9195.2
DW 12.300 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

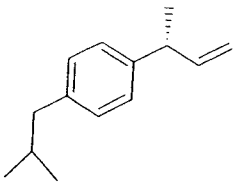
========== CHANNEL f1 ==========
NUC1 31P
P1 6.00 usec
PL1 -4.00 dB
SFO1 101.2492922 MHz

========== CHANNEL f2 ==========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 16.00 dB
PL13 17.00 dB
SFO2 250.1310005 MHz

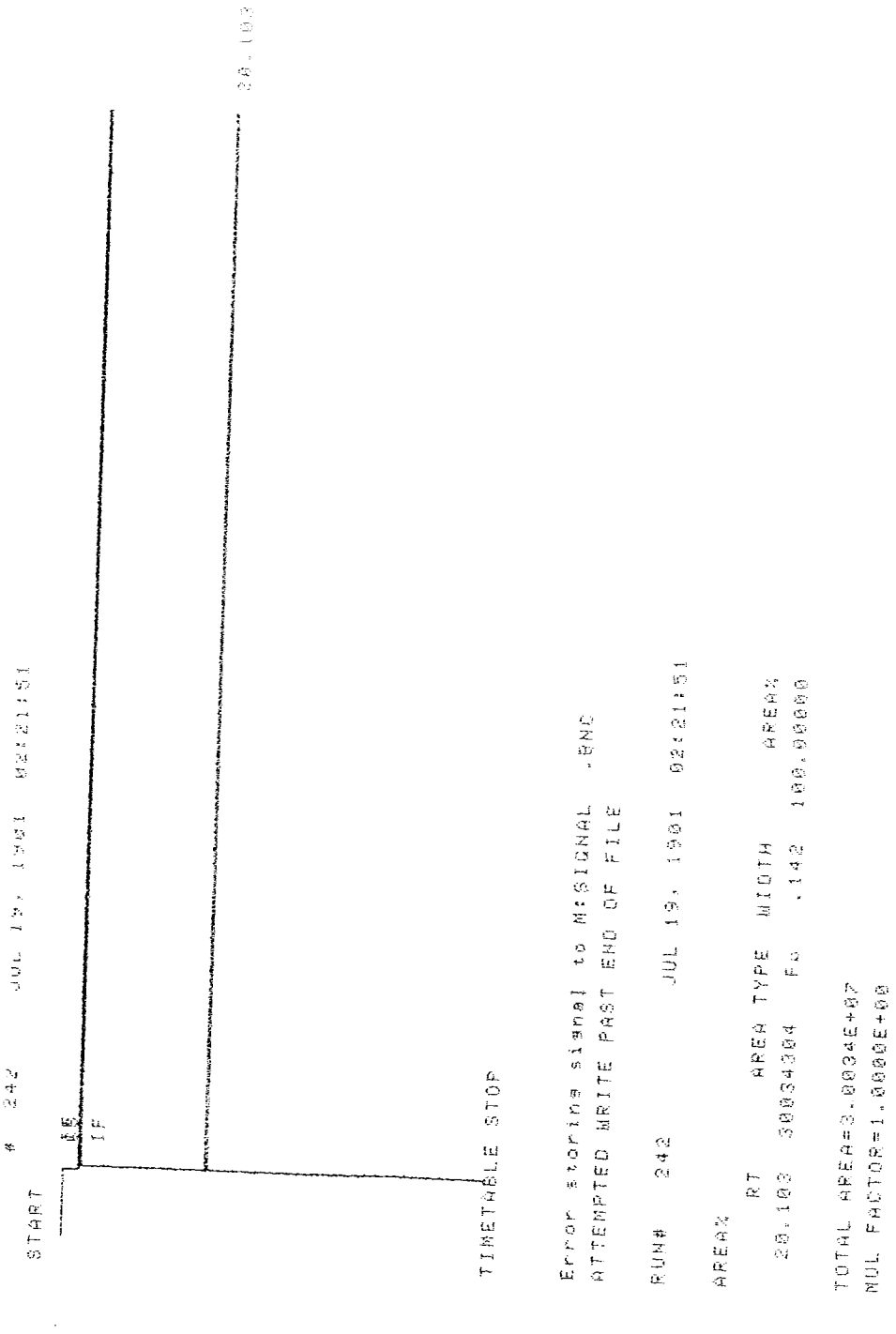
F2 - Processing parameters
SI 32768
SF 101.2530027 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 34.00 cm
F1P 100.000 ppm
F1 10125.30 Hz
F2P -180.000 ppm
F2 -18225.54 Hz
PPMCM 8.23529 ppm/cm
HZCM 833.84827 Hz/cm

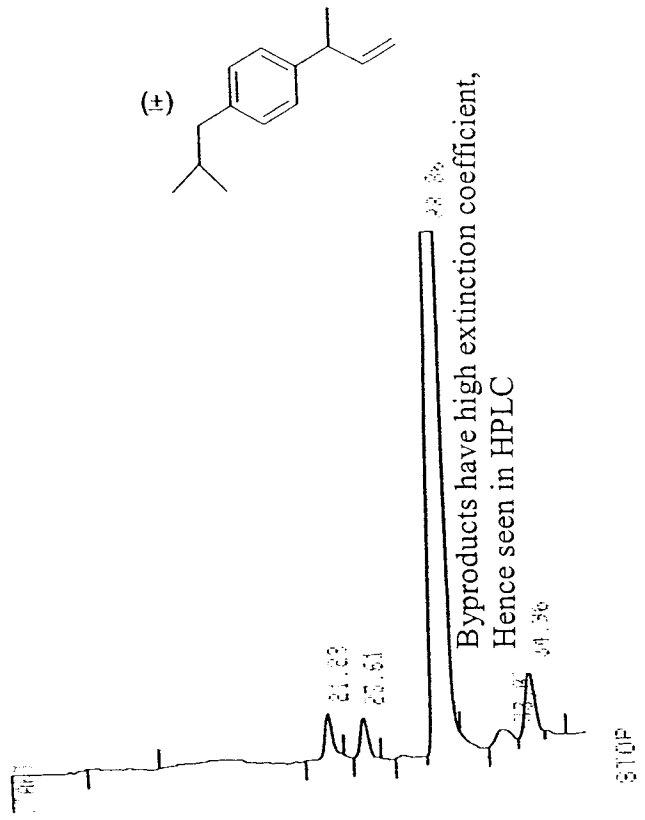

Current Data Parameters
NAME ZAB-1-172
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20030724
Time 14.26
INSTRUM spect
PROBHD 5 mm BBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.252629 Hz
AQ 1.9792372 sec
RG 181
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
CHANNEL f1
NUC1 1H
P1 7.50 usec
PL1 -6.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300169 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 30.00 cm
F1P 8.274 ppm
F1 3310.68 Hz
F2P -0.491 ppm
F2 -196.37 Hz
PPMCM 0.29216 ppm/cm
HZCM 116.90147 Hz/cm
crude product from 1a
7.23969
7.11057
7.10619
7.09542
7.09026
7.06602
7.06088
7.04992
7.04557
6.03059
6.01429
6.00493
5.98807
5.97138
5.96202
5.94567
5.04924
5.04528
5.04133
5.01126
5.00751
4.99844
4.98559
4.98202
4.97825
3.44002
3.42290
3.40576
2.43309
2.41518
1.86193
1.84496
1.82805
1.81129
1.79412
1.48196
1.34488
1.32729
0.90528
0.90416
0.90291
0.89094
0.87443
6.9205
3.3402
1.1306
2.2327
1.0387
2.0968
1.0000
4.3580
Integral
ppm
ppm



crude product from **1a**




1.0 mL helium/min, 10 min at 100°C, 4°C/min, 10 min at 200°C

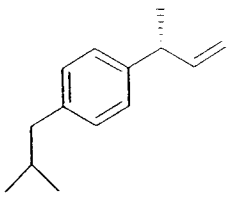



RUN # 47

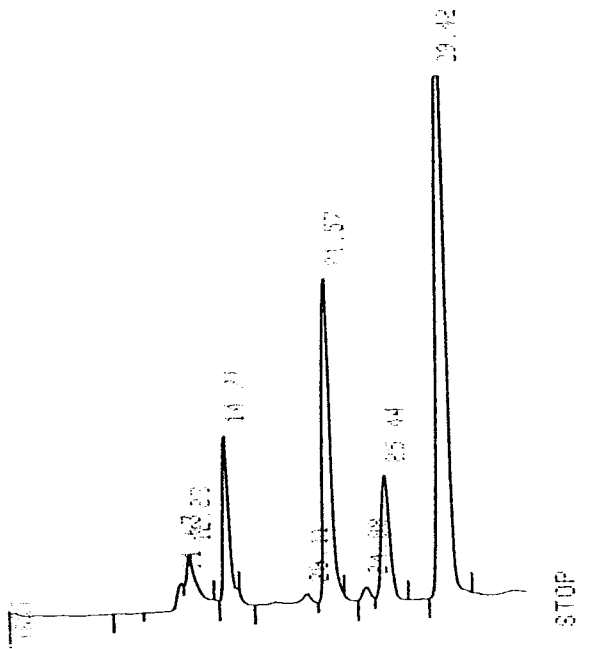
| AREA% RT | AREA | TYPE | AR/HT | AREA% |
|---|---|---|---|---|
| 21.28 | 21926 | BB | 0.563 | 1.786 |
| 23.51 | 21602 | PB | 0.591 | 1.762 |
| 28.86 | 1114600 | PB | 0.675 | 90.810 |
| 33.03 | 17507 | PV | 1.157 | 1.426 |
| 34.96 | 50402 | VV | 0.799 | 4.111 |

R S

TOTAL AREA= 1226000
MUL FACTOR= 1.0000E+00



crude product from **1a**



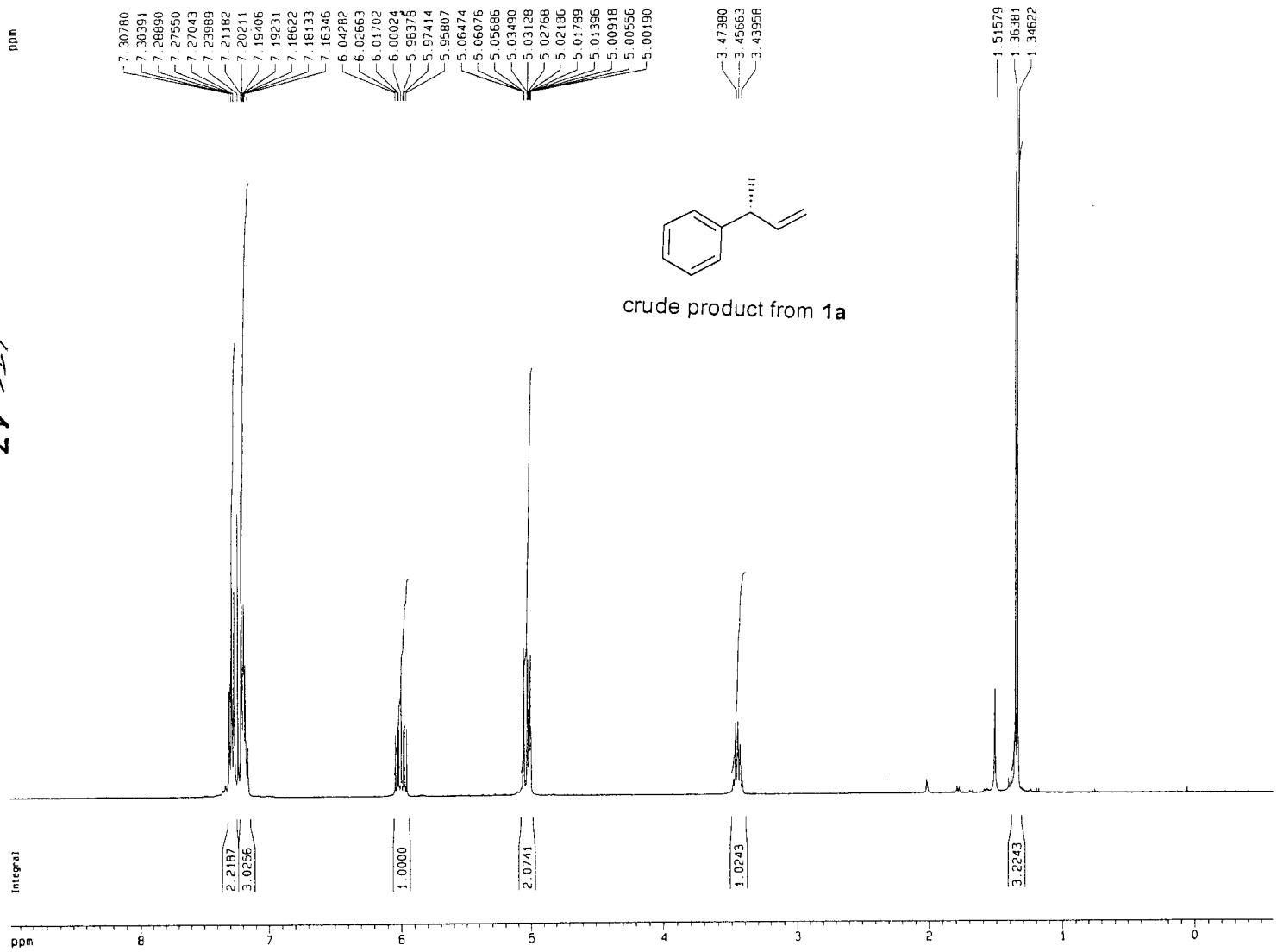

RUN # 61

| AREA% RT | AREA | TYPE | AR/HT | AREA% |
|---|---|---|---|---|
| 11.63 | 3535 | PV | 0.227 | 0.653 |
| 12.23 | 61265 | D VB | 0.696 | 4.192 |
| 14.71 | 122890 | PB | 3.434 | 8.410 |
| 20.11 | 16241 | PP | 0.918 | 1.111 |
| 21.57 | 326610 | PB | 3.563 | 22.351 |
| 24.88 | 15364 | BV | 0.567 | 1.045 |
| 25.44 | 146220 | VB | 0.662 | 10.013 |
| 29.42 | 763160 | PB | 0.680 | 52.225 |

R S 91%ee

TOTAL AREA= 1461300
MUL FACTOR= 1.0000E+00

Daicel Chiralcel OJ Column, 100% hexane, 0.25 mL/min




ST-43

Current Data Parameters

| | |
|---|---|
| NAME | ZAB-1-146 |
| EXPNO | 10 |
| PROCNO | 1 |

F2 - Acquisition Parameters

| | |
|---|---|
| Date_ | 20030701 |
| Time | 17.08 |
| INSTRUM | spect |
| PROBHD | 5 mm BBO BB- |
| PULPROG | zg30 |
| TD | 32768 |
| SOLVENT | CDCl3 |
| NS | 16 |
| DS | 2 |
| SWH | 8278.146 Hz |
| FIDRES | 0.252629 Hz |
| AQ | 1.9792372 sec |
| RG | 181 |
| DW | 60.400 usec |
| DE | 6.00 usec |
| TE | 300.0 K |
| D1 | 1.00000000 sec |

********** CHANNEL f1 **********

| | |
|---|---|
| NUC1 | 1H |
| P1 | 7.50 usec |
| PL1 | -6.00 dB |
| SFO1 | 400.1324710 MHz |

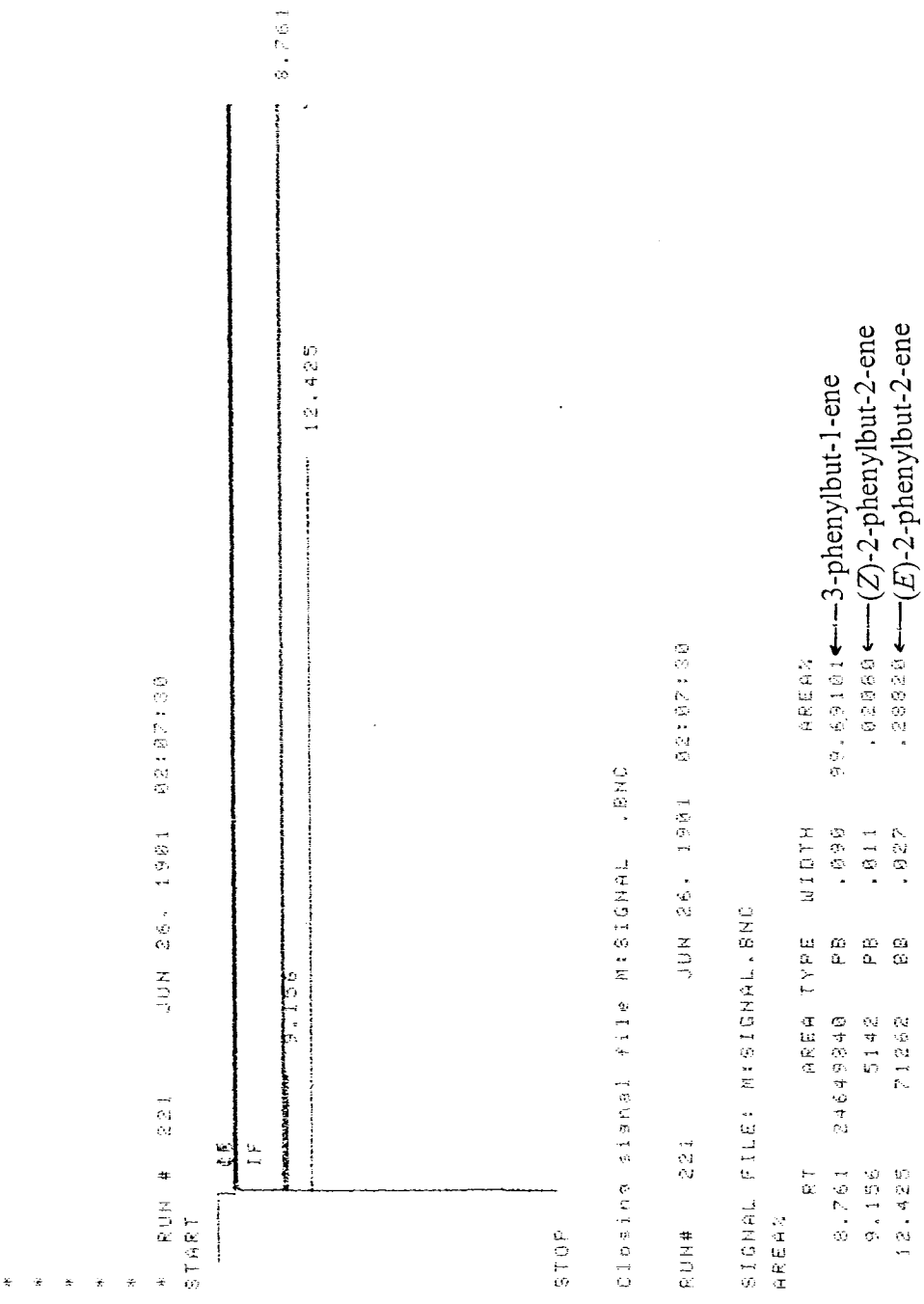
F2 - Processing parameters

| | |
|---|---|
| SI | 32768 |
| SF | 400.1300171 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 0.30 Hz |
| GB | 0 |
| PC | 1.00 |

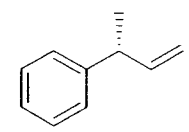
1D NMR plot parameters

| | |
|---|---|
| CX | 30.00 cm |
| F1P | 8.971 ppm |
| F1 | 3589.67 Hz |
| F2P | -0.587 ppm |
| F2 | -234.80 Hz |
| PPMCM | 0.31860 ppm/cm |
| HZCM | 127.48212 Hz/cm |

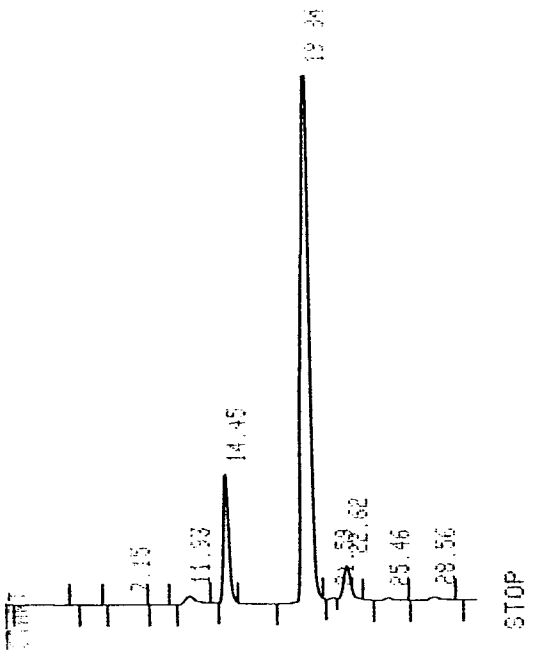
crude product from **1a**




1.0 mL helium/min, 5 min at 80°C, 4°C/min, 15 min at 180°C



crude product from **1a**




RUN # 147

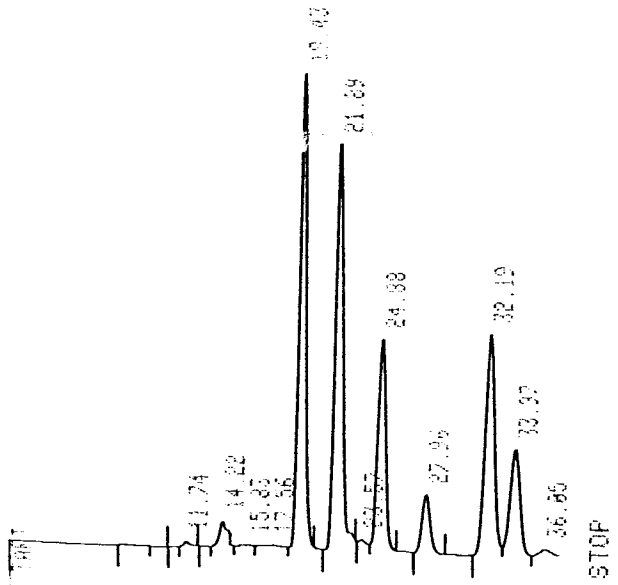
| AREA% RT | AREA | TYPE | AR/HT | AREA% |
|---|---|---|---|---|
| 2.15 | 11037 | BB | 1.089 | 0.398 |
| 11.53 | 39615 | PB | 0.744 | 1.428 |
| 14.45 | 371920 | D PB | 0.404 | 13.402 |
| 19.84 | 2187000 | PB | 0.524 | 78.811 |
| 21.59 | 4237 | D PV | 0.395 | 0.153 |
| 22.62 | 132900 | VB | 0.572 | 4.789 |
| 25.46 | 12070 | BB | 0.647 | 0.435 |
| 28.56 | 16217 | PB | 0.861 | 0.584 |

TOTAL AREA= 2775000
MUL FACTOR= 1.0000E+00

*R* — 19.84
*S* — 22.62

88%ee

(±)



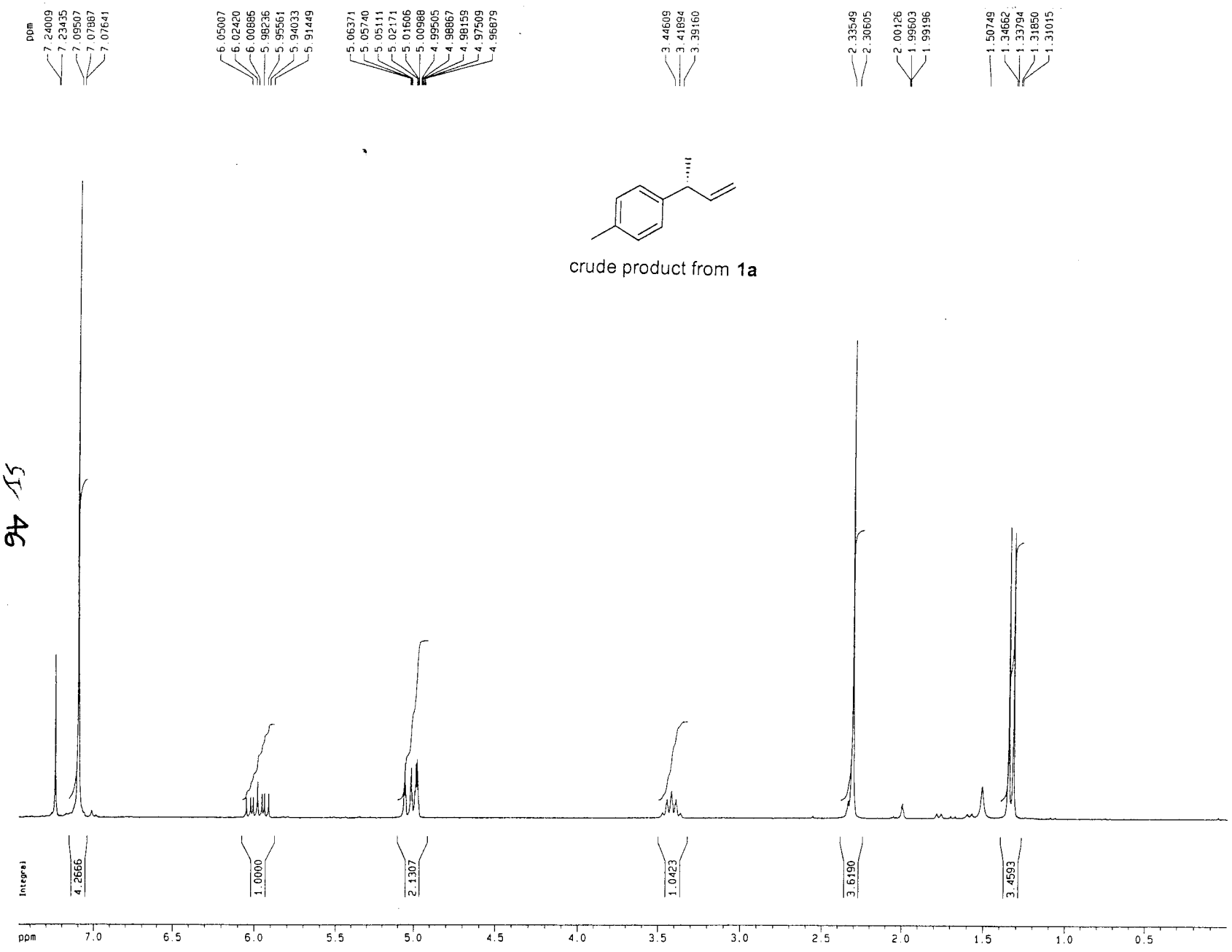

RUN # 148

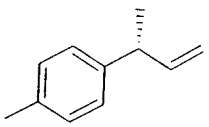
| AREA% RT | AREA | TYPE | AR/HT | AREA% |
|---|---|---|---|---|
| 11.74 | 15610 | VB | 0.514 | 0.239 |
| 14.22 | 83721 | PV | 0.468 | 1.280 |
| 15.83 | 11467 | VV | 0.910 | 0.175 |
| 17.56 | 18372 | VV | 1.367 | 0.281 |
| 19.43 | 1744900 | VB | 0.507 | 26.662 |
| 21.89 | 1649200 | PB | 0.567 | 25.207 |
| 23.57 | 8296 | D BV | 0.376 | 0.127 |
| 24.88 | 887810 | VB | 0.583 | 13.569 |
| 27.96 | 275240 | BB | 0.655 | 4.207 |
| 32.19 | 1190000 | BV | 0.733 | 18.189 |
| 33.92 | 609760 | VV | 0.784 | 9.320 |
| 36.85 | 48388 | I VP | 0.943 | 0.746 |

TOTAL AREA= 5542700
MUL FACTOR= 1.0000E+00

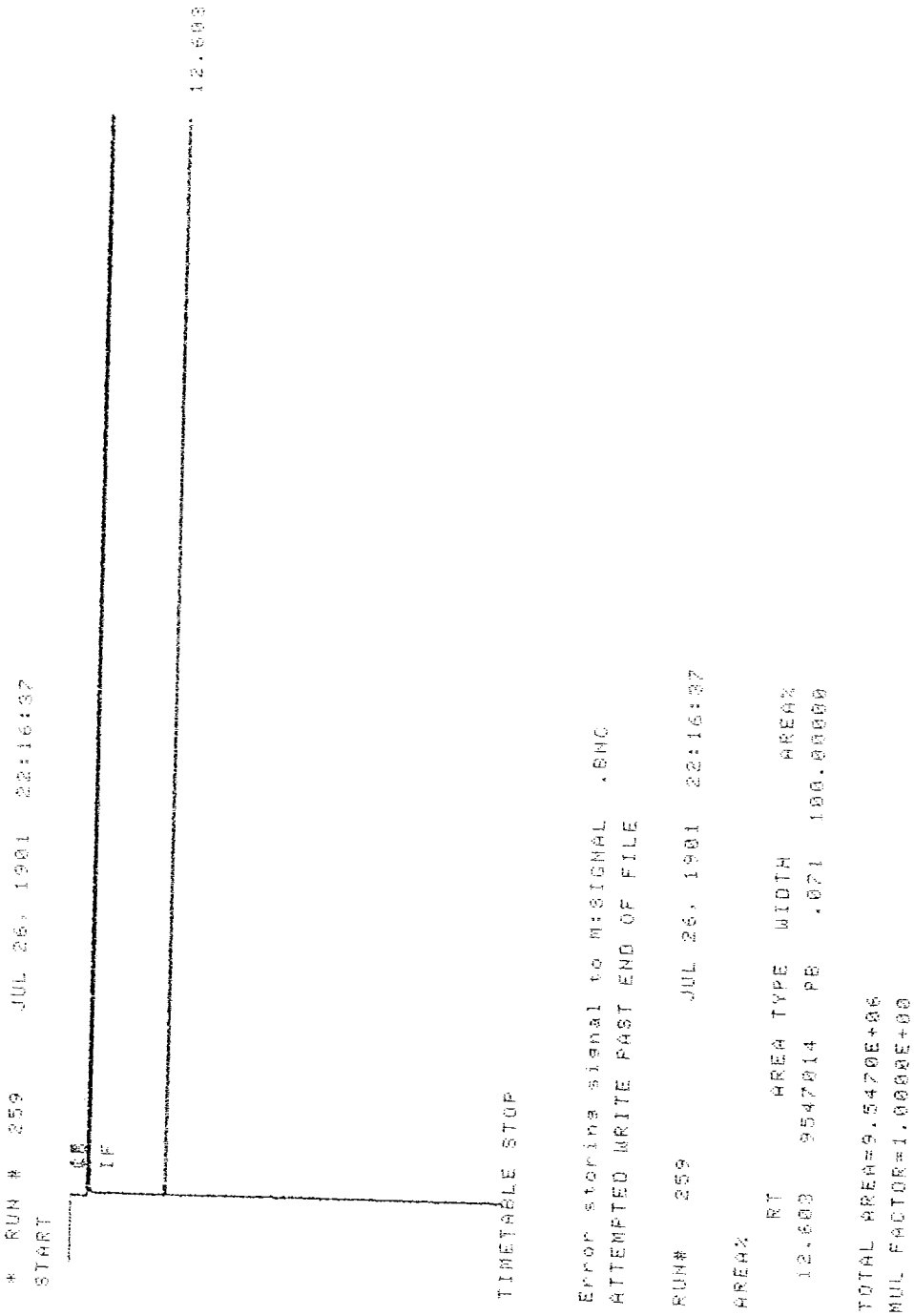
*R* — 21.89
*S* — 23.57

Daicel Chiralcel OJ Column, 100% hexane, 0.30 mL/min

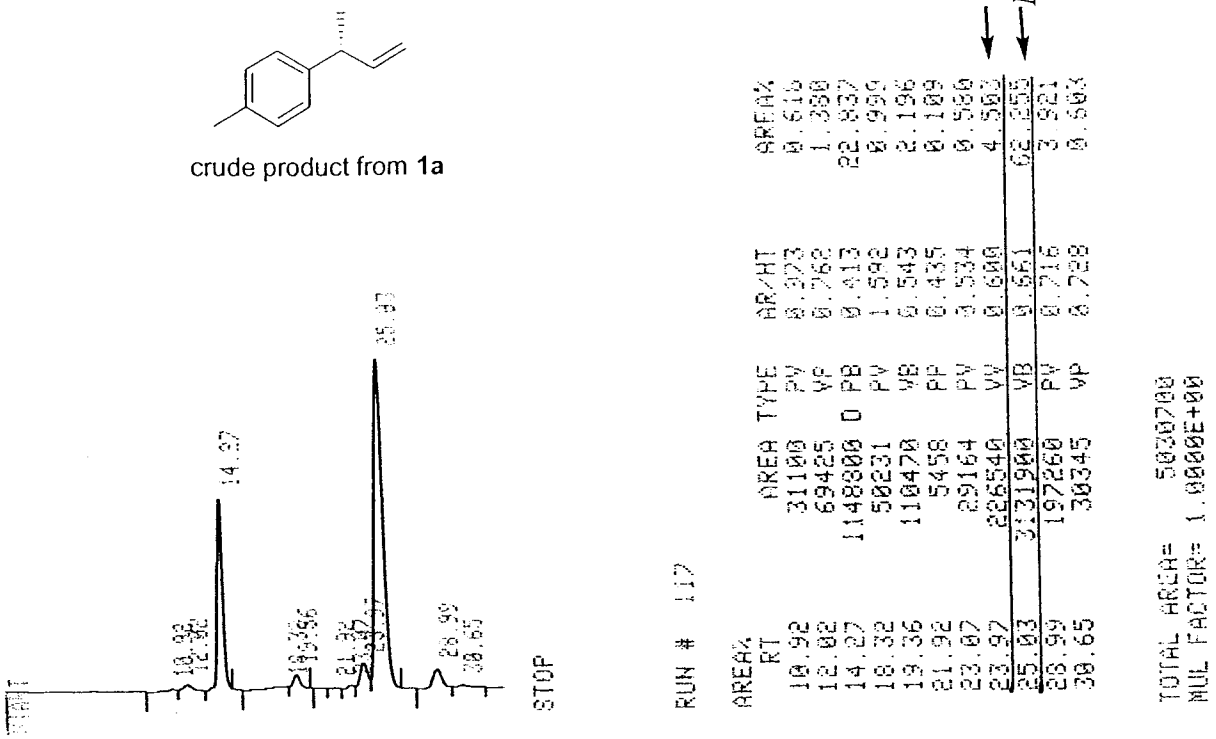

ppm
7.24009
7.23435
7.09507
7.07987
7.07641
6.05007
6.02420
6.00886
5.98236
5.95561
5.94033
5.91449
5.06371
5.05740
5.05111
5.02171
5.01606
5.00988
4.99505
4.98867
4.98159
4.97509
4.96879
3.44609
3.41894
3.39160
2.33549
2.30605
2.00126
1.99603
1.99196
1.50749
1.34662
1.33794
1.31850
1.31015
crude product from 1a
Current Data Parameters
NAME ZAB-1-138
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20030521
Time 14.36
INSTRUM spect
PROBHD 5 mm QNP 1H/
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 16
DS 2
SWH 5175.983 Hz
FIDRES 0.315917 Hz
AQ 1.5827444 sec
RG 912.3
DW 96.600 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
CHANNEL f1
NUC1 1H
P1 7.20 usec
PL1 -4.00 dB
SFO1 250.1315447 MHz
F2 - Processing parameters
SI 32768
SF 250.1300123 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 34.00 cm
F1P 7.473 ppm
F1 1869.33 Hz
F2P 0.002 ppm
F2 0.57 Hz
PPMCM 0.21974 ppm/cm
HZCM 54.96364 Hz/cm
Integral
4.2666
1.0000
2.1307
1.0423
3.6190
3.4593
ppm
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

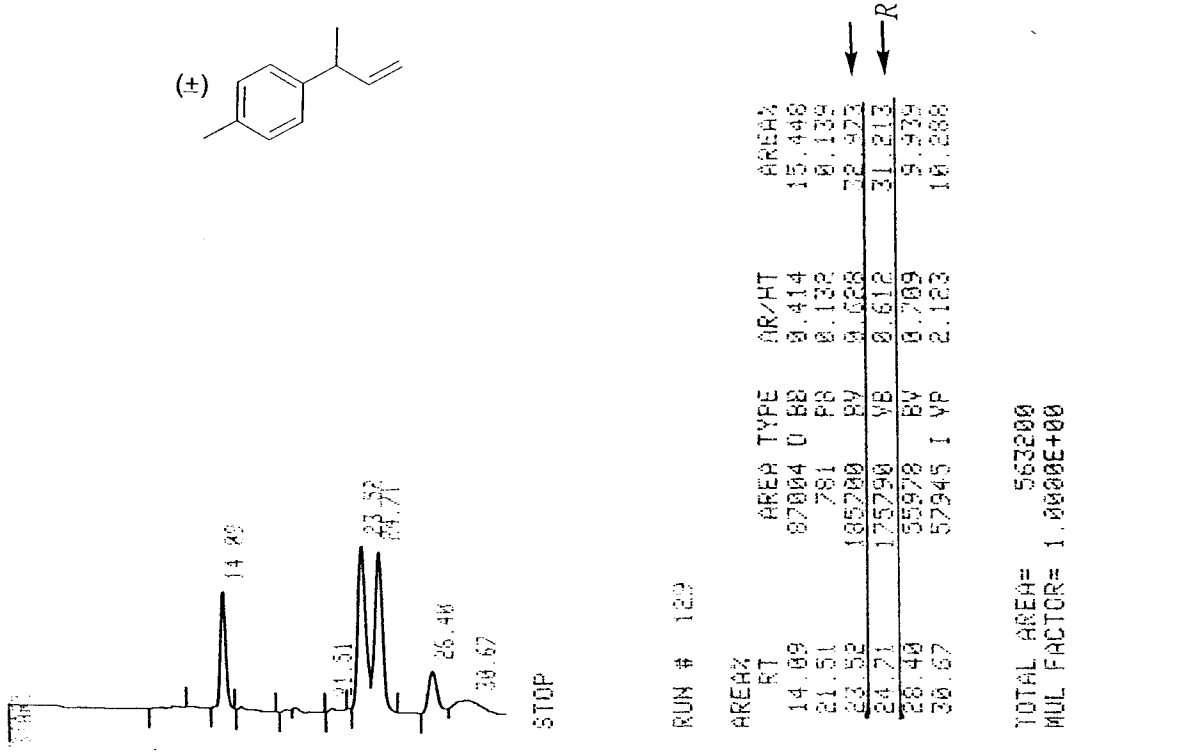


crude product from **1a**

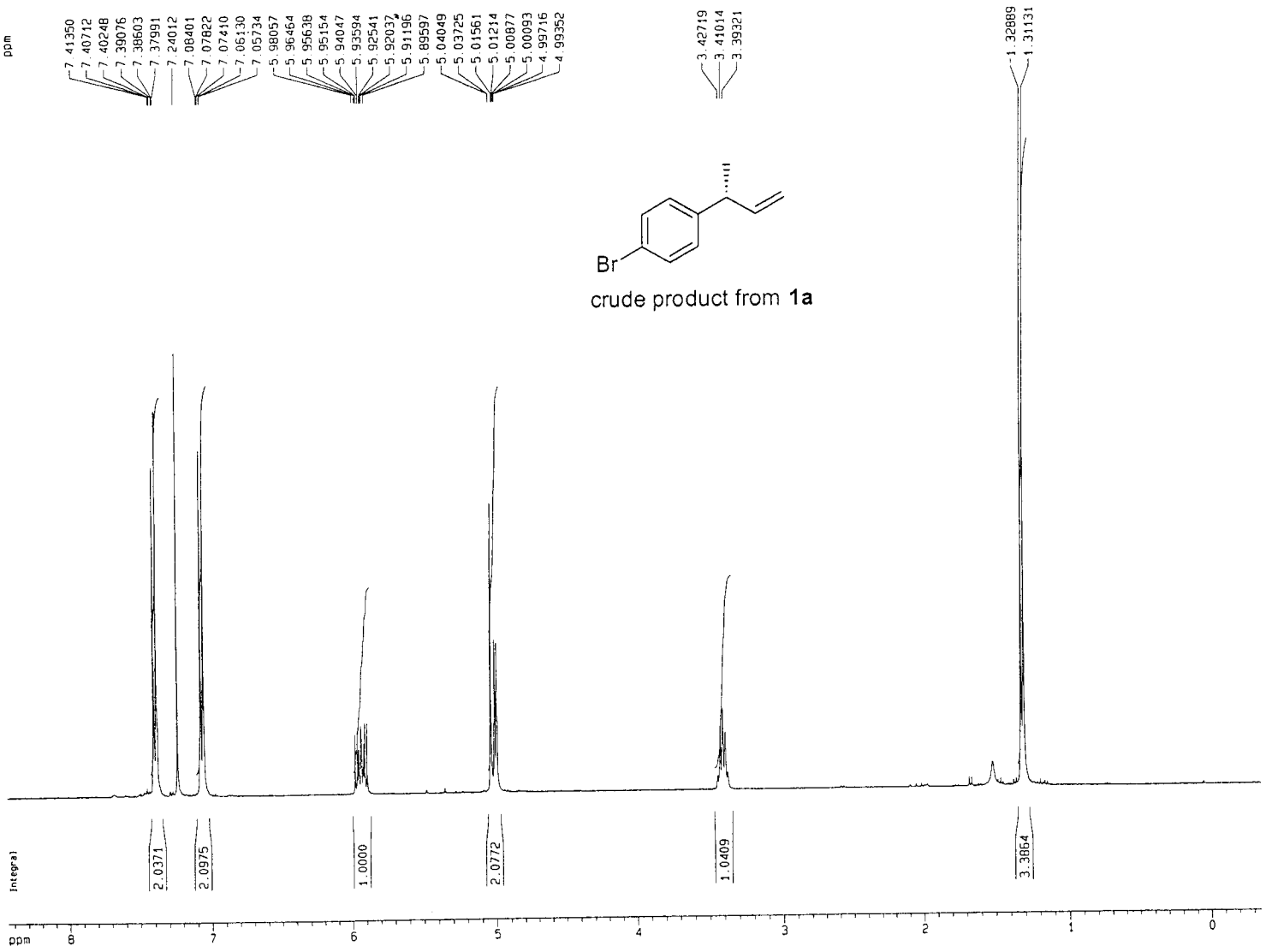



1.0 mL helium/min, 5 min at 80°C, 4°C/min, 15 min at 180°C




Daicel Chiralcel OJ Column, 100% hexane, 0.30 mL/min




49

Current Data Parameters

| | |
|---|---|
| NAME | ZAB-1-156 |
| EXPNO | 10 |
| PROCNO | 1 |

F2 - Acquisition Parameters

| | |
|---|---|
| Date_ | 20030710 |
| Time | 14.50 |
| INSTRUM | spect |
| PROBHD | 5 mm BBO BB- |
| PULPROG | zg30 |
| TD | 32768 |
| SOLVENT | CDCl3 |
| NS | 16 |
| DS | 2 |
| SWH | 8278.146 Hz |
| FIDRES | 0.252629 Hz |
| AQ | 1.9792372 sec |
| RG | 362 |
| DW | 60.400 usec |
| DE | 6.00 usec |
| TE | 300.0 K |
| D1 | 1.00000000 sec |

CHANNEL f1

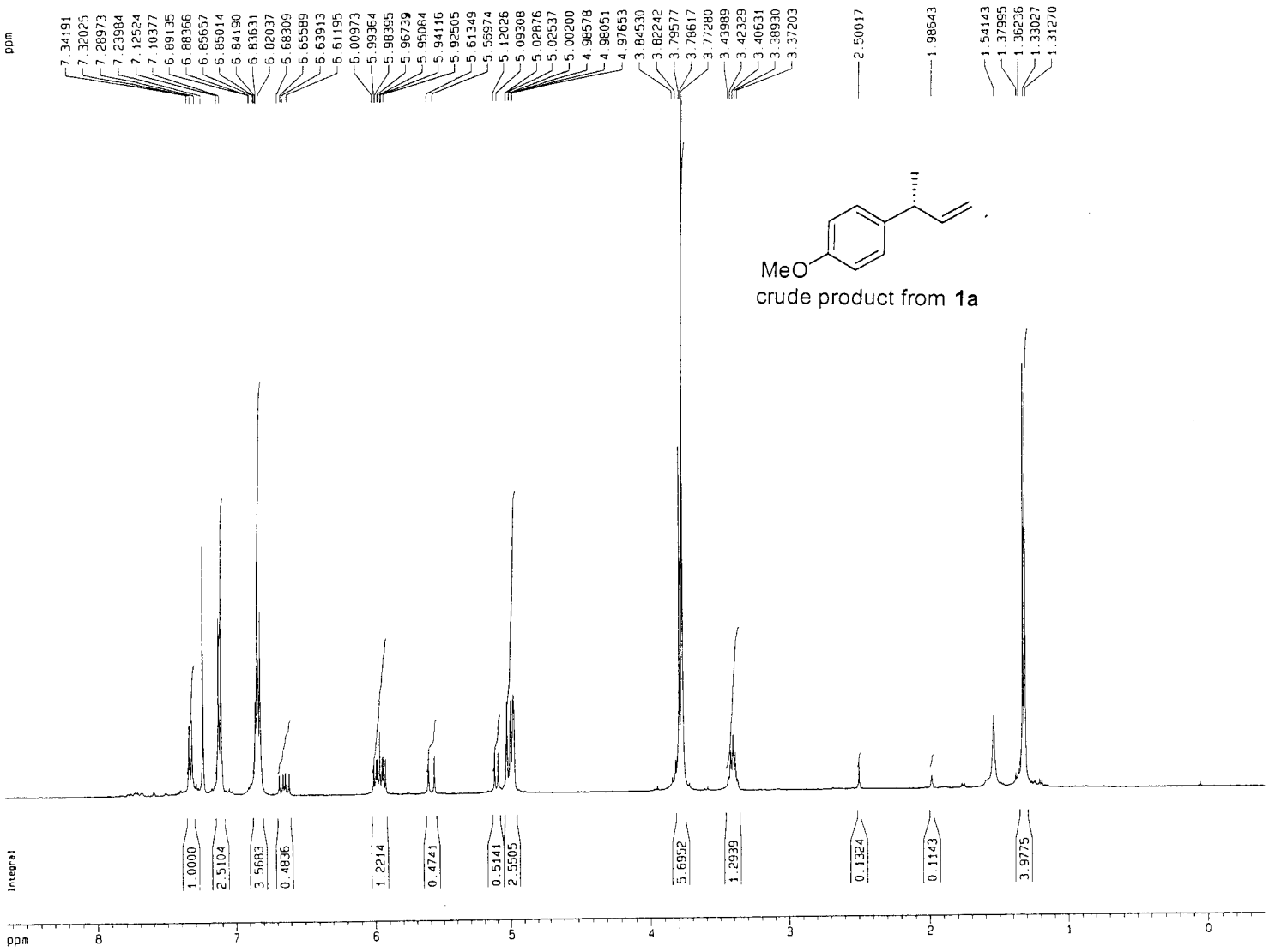
| | |
|---|---|
| NUC1 | 1H |
| P1 | 7.50 usec |
| PL1 | -6.00 dB |
| SFO1 | 400.1324710 MHz |

F2 - Processing parameters

| | |
|---|---|
| SI | 32768 |
| SF | 400.1300171 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 0.30 Hz |
| GB | 0 |
| PC | 1.00 |

1D NMR plot parameters

| | |
|---|---|
| CX | 30.00 cm |
| F1P | 8.446 ppm |
| F1 | 3379.62 Hz |
| F2P | -0.348 ppm |
| F2 | -139.25 Hz |
| PPMCM | 0.29314 ppm/cm |
| HZCM | 117.29572 Hz/cm |




Current Data Parameters

| | |
|---|---|
| NAME | ZAB-1-147 |
| EXPNO | 10 |
| PROCNO | 1 |

F2 - Acquisition Parameters

| | |
|---|---|
| Date_ | 20030702 |
| Time | 16.07 |
| INSTRUM | spect |
| PROBHD | 5 mm BBO BB- |
| PULPROG | zg30 |
| TD | 32768 |
| SOLVENT | CDCl3 |
| NS | 16 |
| DS | 2 |
| SWH | 8278.146 Hz |
| FIDRES | 0.252629 Hz |
| AQ | 1.9792372 sec |
| RG | 181 |
| DW | 60.400 usec |
| DE | 6.00 usec |
| TE | 300.0 K |
| D1 | 1.00000000 sec |

========== CHANNEL f1 ==========

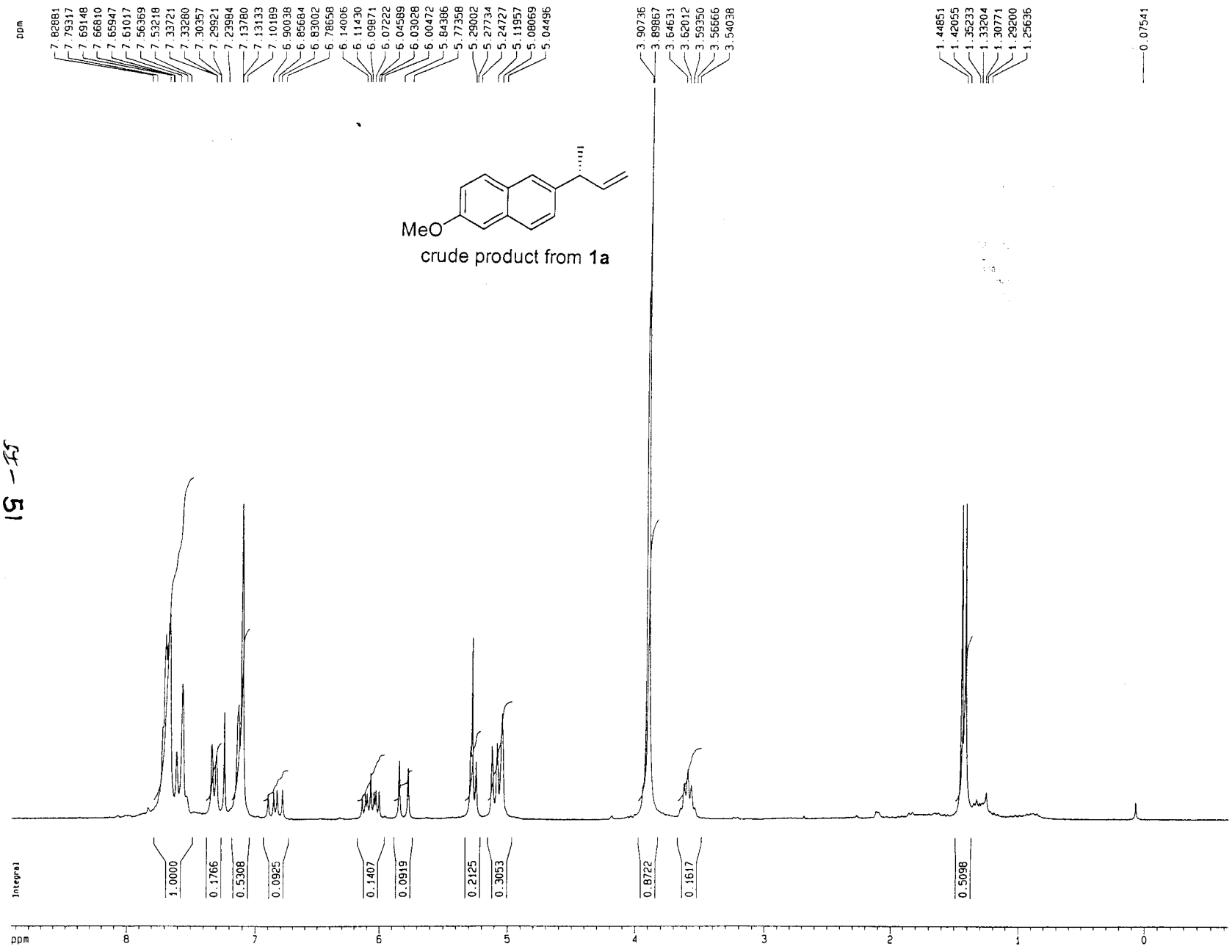
| | |
|---|---|
| NUC1 | 1H |
| P1 | 7.50 usec |
| PL1 | -6.00 dB |
| SFO1 | 400.1324710 MHz |

F2 - Processing parameters

| | |
|---|---|
| SI | 32768 |
| SF | 400.1300169 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 0.30 Hz |
| GB | 0 |
| PC | 1.00 |

1D NMR plot parameters

| | |
|---|---|
| CX | 30.00 cm |
| F1P | 8.645 ppm |
| F1 | 3459.09 Hz |
| F2P | -0.401 ppm |
| F2 | -160.28 Hz |
| PPMCM | 0.30152 ppm/cm |
| HZCM | 120.64562 Hz/cm |



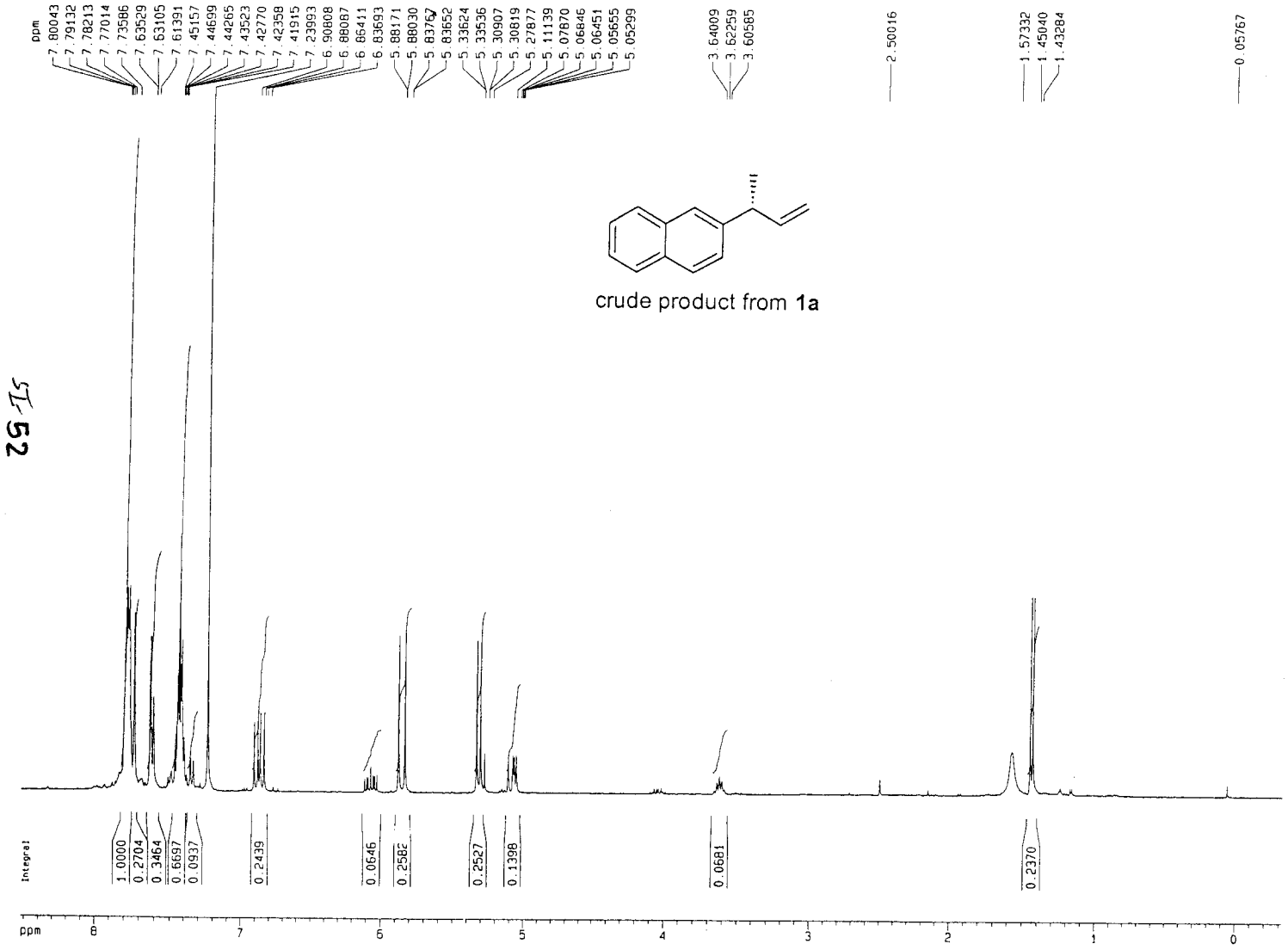

Current Data Parameters
NAME ZAB-1-166
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030718
Time 15.39
INSTRUM spect
PROBHD 5 mm QNP 1H/
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 16
DS 2
SWH 5175.983 Hz
FIDRES 0.315917 Hz
AQ 1.5827444 sec
RG 362
DW 96.600 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

CHANNEL f1
NUC1 1H
P1 7.20 usec
PL1 -4.00 dB
SFO1 250.1315447 MHz

F2 - Processing parameters
SI 32768
SF 250.1300127 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 34.00 cm
F1P 8.938 ppm
F1 2235.55 Hz
F2P -0.628 ppm
F2 -157.18 Hz
PPMCM 0.26135 ppm/cm
HZCM 70.37442 Hz/cm




IT52

Current Data Parameters

| | |
|---|---|
| NAME | ZAB-1-153 |
| EXPNO | 20 |
| PROCNO | 1 |

F2 - Acquisition Parameters

| | |
|---|---|
| Date_ | 20030709 |
| Time | 14.47 |
| INSTRUM | spect |
| PROBHD | 5 mm BBO BB- |
| PULPROG | zg30 |
| TD | 32768 |
| SOLVENT | CDCl3 |
| NS | 16 |
| DS | 2 |
| SWH | 8278.146 Hz |
| FIDRES | 0.252629 Hz |
| AQ | 1.9792372 sec |
| RG | 362 |
| DW | 60.400 usec |
| DE | 6.00 usec |
| TE | 300.0 K |
| D1 | 1.00000000 sec |

********** CHANNEL f1 **********

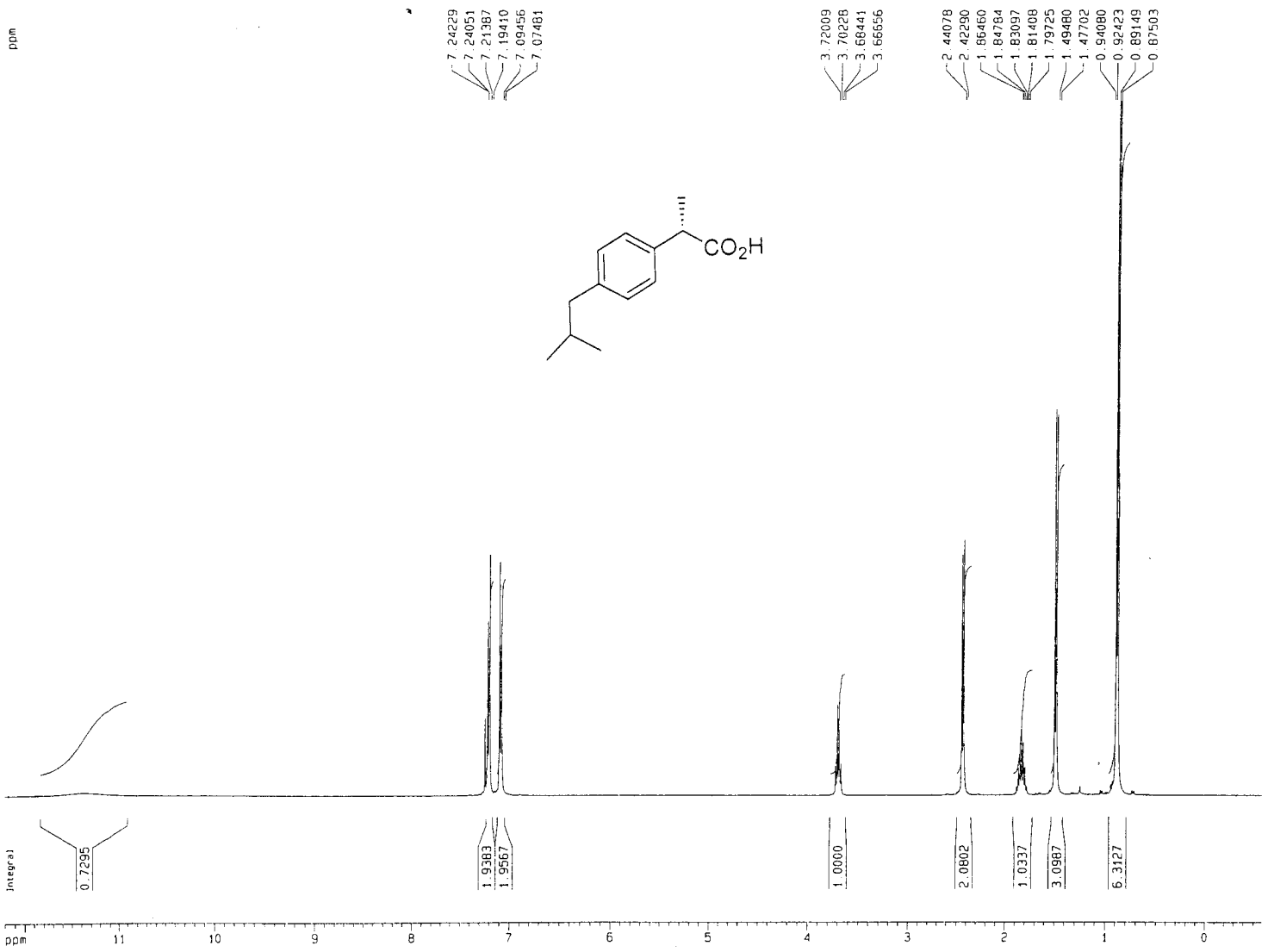
| | |
|---|---|
| NUC1 | 1H |
| P1 | 7.50 usec |
| PL1 | -6.00 dB |
| SFO1 | 400.1324710 MHz |

F2 - Processing parameters

| | |
|---|---|
| SI | 32768 |
| SF | 400.1300171 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 0.30 Hz |
| GB | 0 |
| PC | 1.00 |

1D NMR plot parameters

| | |
|---|---|
| CX | 30.00 cm |
| F1P | 8.524 ppm |
| F1 | 3410.53 Hz |
| F2P | -0.322 ppm |
| F2 | -128.75 Hz |
| PPMCM | 0.29484 ppm/cm |
| HZCM | 117.97598 Hz/cm |




S1-53

Current Data Parameters

| | |
|---|---|
| NAME | ZAB-1-212 |
| EXPNO | 10 |
| PROCNO | 1 |

F2 - Acquisition Parameters

| | |
|---|---|
| Date_ | 20031022 |
| Time | 17.29 |
| INSTRUM | spect |
| PROBHD | 5 mm BBO BB- |
| PULPROG | zg30 |
| TD | 32768 |
| SOLVENT | CDCl3 |
| NS | 16 |
| DS | 2 |
| SWH | 8278.146 Hz |
| FIDRES | 0.252629 Hz |
| AQ | 1.9792372 sec |
| RG | 181 |
| DW | 60.400 usec |
| DE | 6.00 usec |
| TE | 300.0 K |
| D1 | 1.00000000 sec |

========== CHANNEL f1 ==========

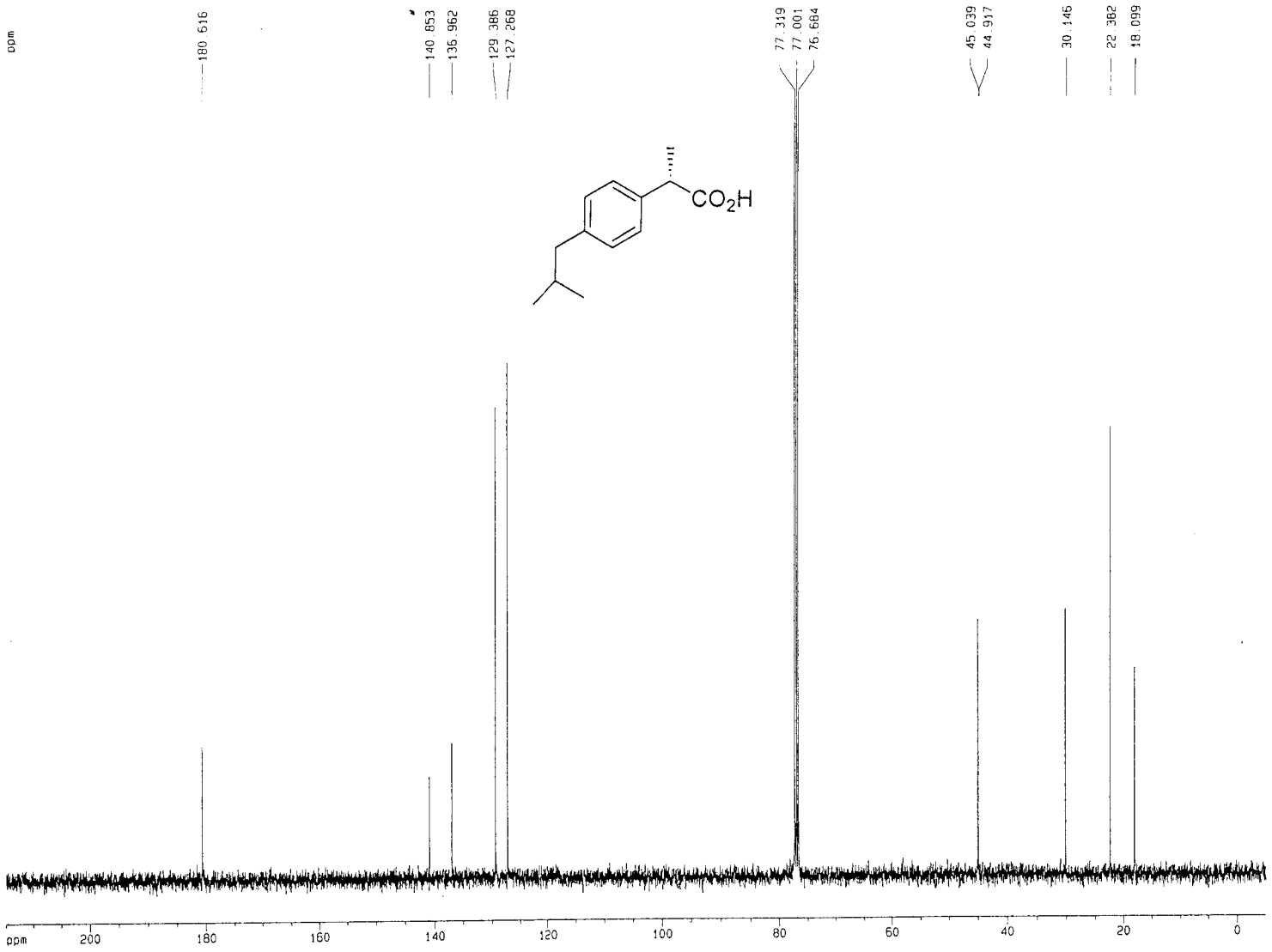
| | |
|---|---|
| NUC1 | 1H |
| P1 | 7.50 usec |
| PL1 | -6.00 dB |
| SFO1 | 400.1324710 MHz |

F2 - Processing parameters

| | |
|---|---|
| SI | 32768 |
| SF | 400.1300164 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 0.30 Hz |
| GB | 0 |
| PC | 1.00 |

1D NMR plot parameters

| | |
|---|---|
| CX | 30.00 cm |
| F1P | 12.202 ppm |
| F1 | 4882.46 Hz |
| F2P | -0.593 ppm |
| F2 | -237.44 Hz |
| PPMCM | 0.42652 ppm/cm |
| HZCM | 170.66316 Hz/cm |




ST-54

Current Data Parameters

| | |
|---|---|
| NAME | ZAB-1-212 |
| EXPNO | 11 |
| PROCNO | 1 |

F2 - Acquisition Parameters

| | |
|---|---|
| Date_ | 20031022 |
| Time | 17.44 |
| INSTRUM | spect |
| PROBHD | 5 mm BBO BB- |
| PULPROG | zgpg30 |
| TD | 65536 |
| SOLVENT | CDCl3 |
| NS | 263 |
| DS | 4 |
| SWH | 25125.629 Hz |
| FIDRES | 0.383387 Hz |
| AQ | 1.3042164 sec |
| RG | 4096 |
| DW | 19.900 usec |
| DE | 6.00 usec |
| TE | 300.0 K |
| D1 | 2.00000000 sec |
| d11 | 0.03000000 sec |
| d12 | 0.00002000 sec |

========== CHANNEL f1 ==========

| | |
|---|---|
| NUC1 | 13C |
| P1 | 5.90 usec |
| PL1 | -6.00 dB |
| SFO1 | 100.6237959 MHz |

========== CHANNEL f2 ==========

| | |
|---|---|
| CPDPRG2 | waltz16 |
| NUC2 | 1H |
| PCPD2 | 80.00 usec |
| PL2 | -6.00 dB |
| PL12 | 15.80 dB |
| PL13 | 15.80 dB |
| SFO2 | 400.1316005 MHz |

F2 - Processing parameters

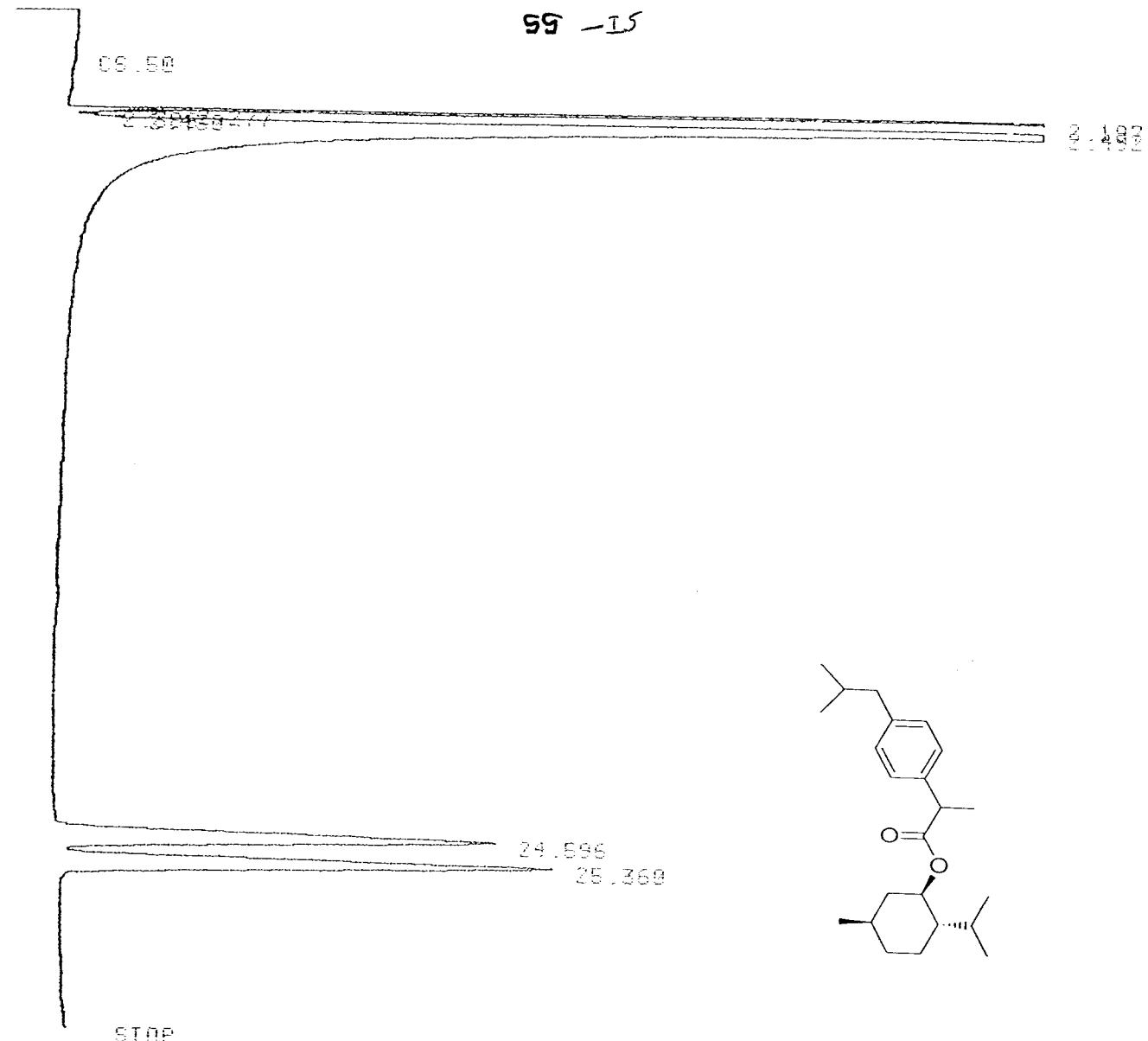
| | |
|---|---|
| SI | 32768 |
| SF | 100.6127686 MHz |
| WDW | EM |
| SSB | 0 |
| LB | 1.00 Hz |
| GB | 0 |
| PC | 1.40 |

1D NMR plot parameters

| | |
|---|---|
| CX | 30.00 cm |
| F1P | 215.000 ppm |
| F1 | 21631.75 Hz |
| F2P | -5.000 ppm |
| F2 | -503.06 Hz |
| PPMCM | 7.33333 ppm/cm |
| HZCM | 737.82697 Hz/cm |

```
*  RUN # 1257      OCT 15, 1903  22:48:39
START; not ready
```

59 -15





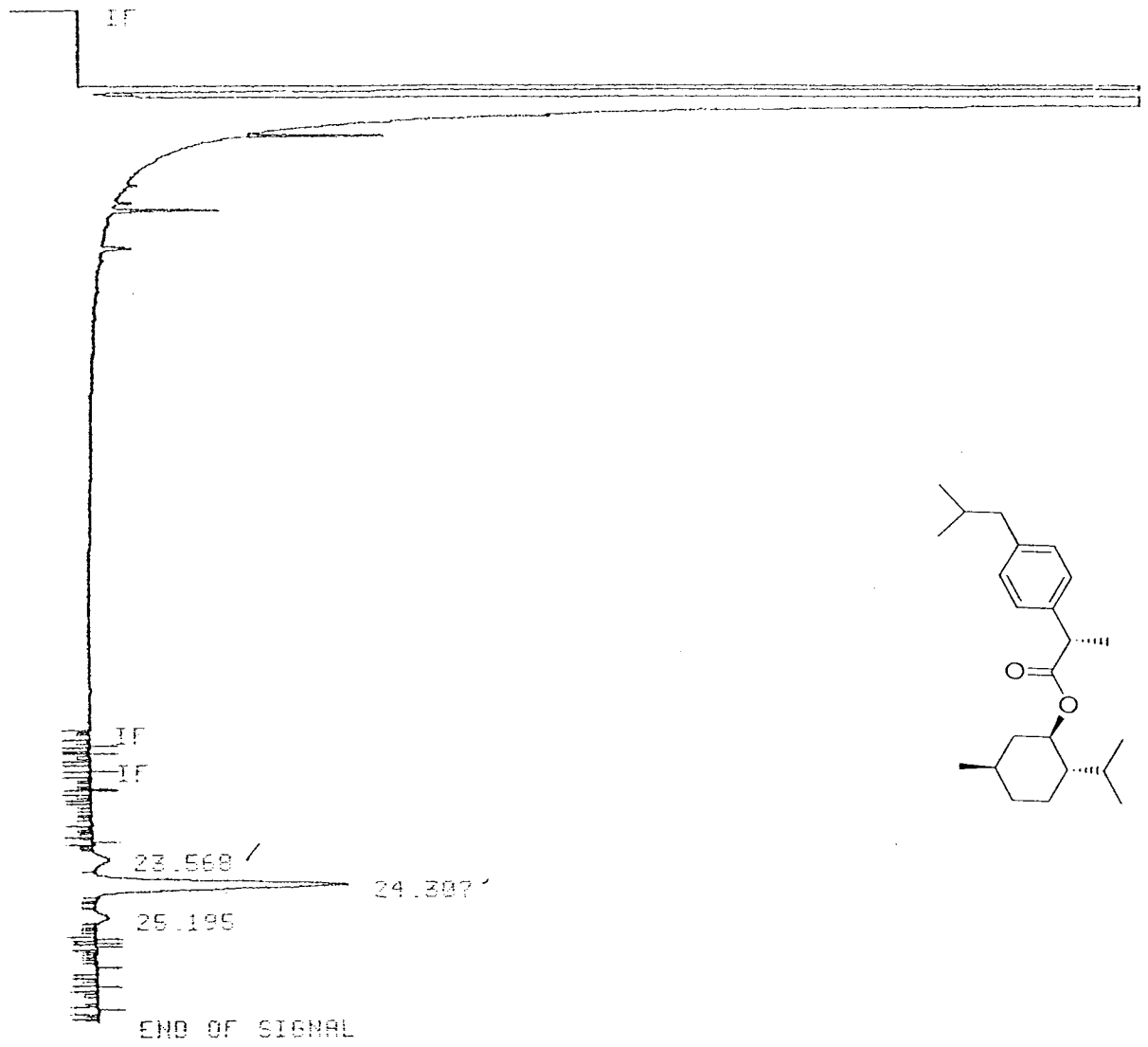

```
Closing signal file M:SIGNAL   .BNC

RUN#  1257           OCT 15, 1903  22:48:39

SIGNAL FILE: M:SIGNAL.BNC
AREAX
```

| RT | AREA | TYPE | WIDTH | AREAX | |
|---|---|---|---|---|---|
| 2.197 | 1084114 | BV | .029 | 62.03448 | |
| 2.277 | 1496 | VP | .031 | .08560 | |
| 2.492 | 507139 | PB | .025 | 29.01919 | |
| 24.596 | 77193 | BV | .356 | 4.41709 | ← *R* |
| 25.360 | 77657 | VV | .317 | 4.44364 | ← *S* |

```
TOTAL AREA=1747599
MUL FACTOR=1.0000E+00
```

Chirasil-L-Val Column, 1.0 mL helium/min,
20 min at 150°C, 0.5°C/min, 30 min at 180°C

*MN
RUN # 1266 OCT 18, 1993 17:39:21
START






Closing signal file M:SIGNAL .BNA

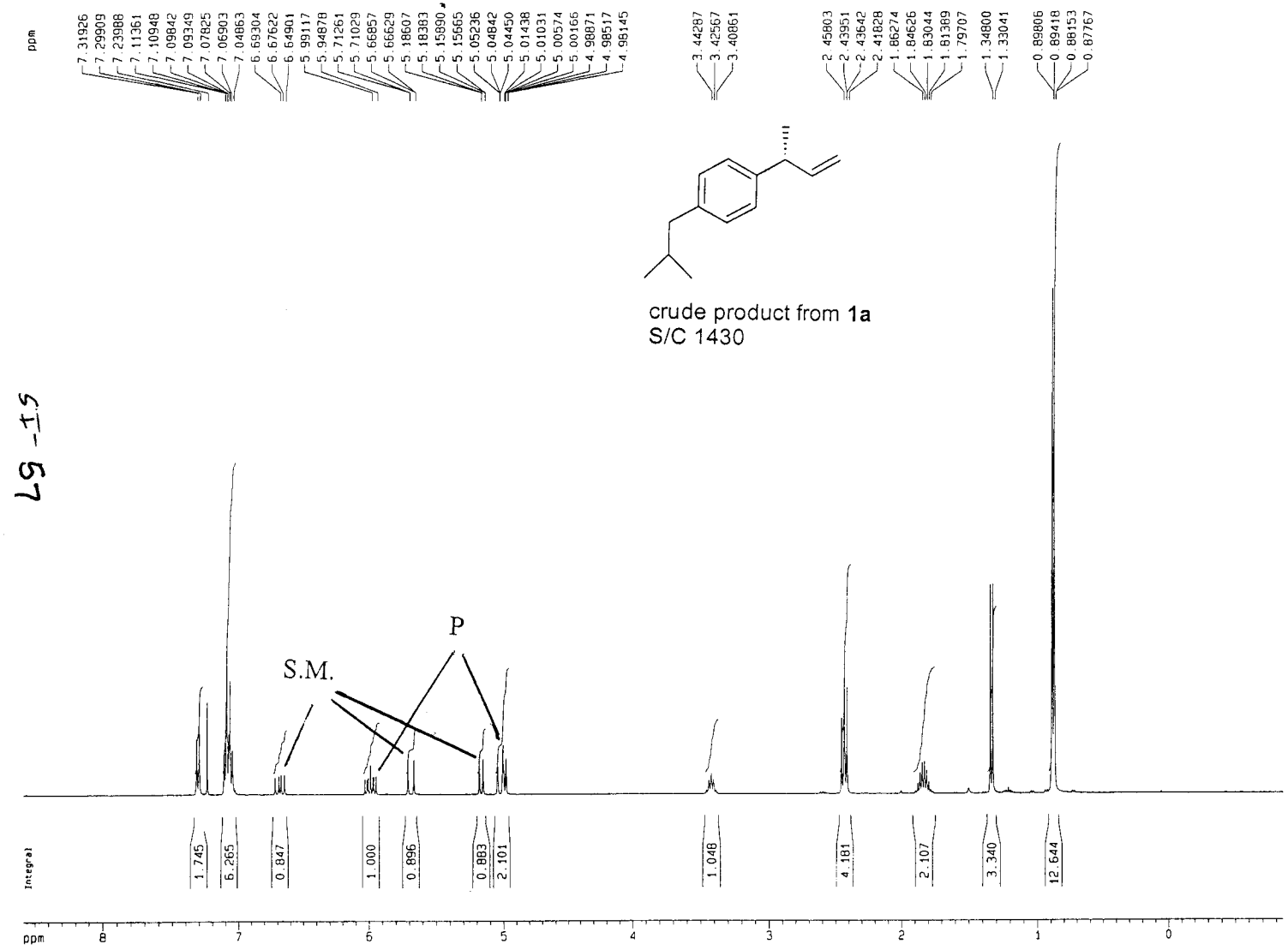
RUN# 1266 OCT 18, 1993 17:39:21

SIGNAL FILE: M:SIGNAL.BNA
AREA%

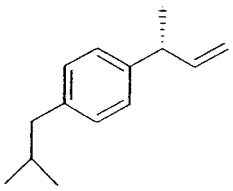
| RT | AREA | TYPE | WIDTH | AREA% | |
|---|---|---|---|---|---|
| 23.568 | 1768 | VV | .232 | 5.41183 | ← *R* |
| 24.307 | 29629 | VV | .257 | 90.68067 | ← *S* 89%ee |
| 25.195 | 1277 | VV | .211 | 3.90831 | |

TOTAL AREA= 32674
MUL FACTOR=1.0000E+00

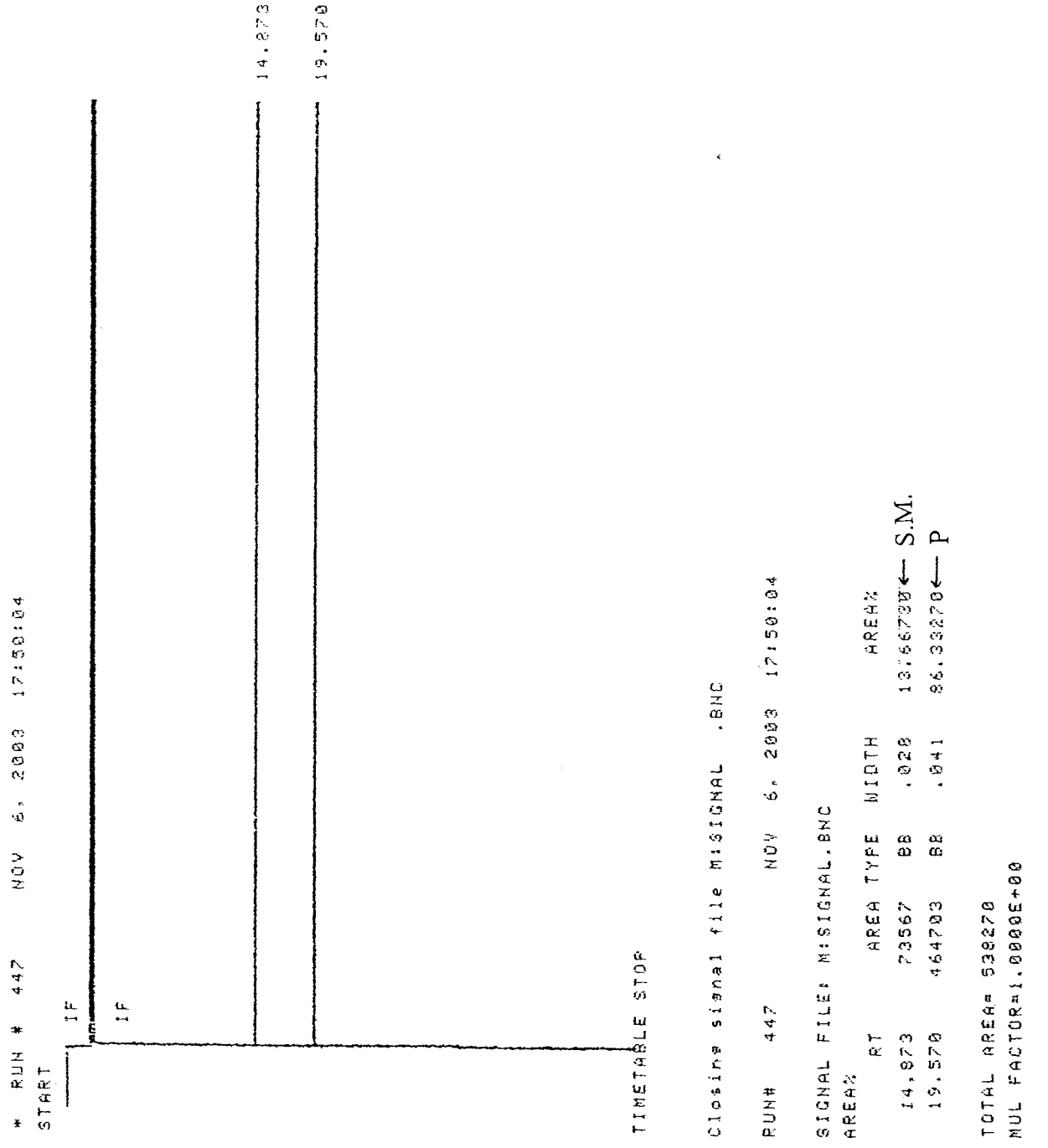
Chirasil-L-Val Column, 1.0 mL helium/min, 20 min at 150°C, 0.5°C/min, 30 min at 180°C



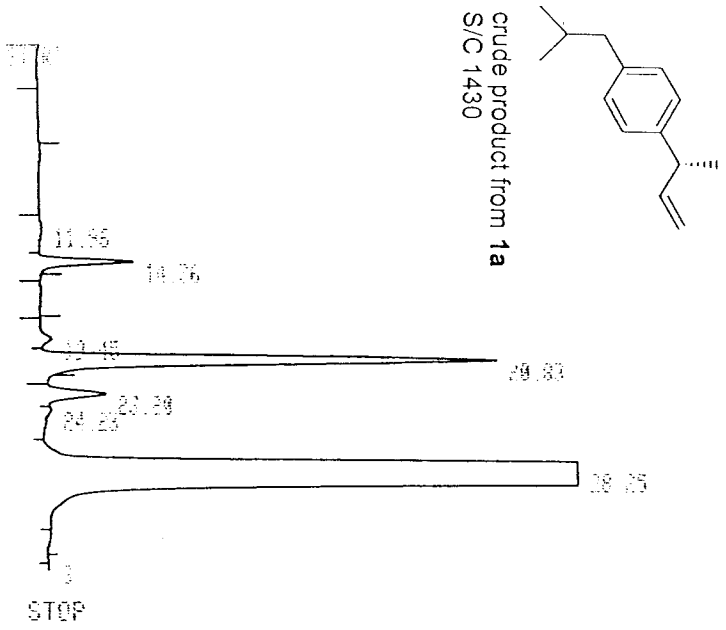

```
Current Data Parameters
NAME                  ZAB-1-279
EXPNO                        10
PROCNO                        1

F2 - Acquisition Parameters
Date_               20031106
Time                     18.08
INSTRUM                  spect
PROBHD       5 mm BBO BB-
PULPROG                  zg30
TD                      32768
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                 8278.146 Hz
FIDRES              0.252629 Hz
AQ                  1.9792372 sec
RG                         181
DW                    60.400 usec
DE                     6.00 usec
TE                     300.0 K
D1                  1.00000000 sec

============ CHANNEL f1 =============
NUC1                         1H
P1                     7.50 usec
PL1                    -6.00 dB
SFO1                400.1324710 MHz

F2 - Processing parameters
SI                      32768
SF                  400.1300171 MHz
WDW                        EM
SSB                         0
LB                     0.30 Hz
GB                          0
PC                      1.00

1D NMR plot parameters
CX                     30.00 cm
F1P                    8.590 ppm
F1                  3437.11 Hz
F2P                   -0.849 ppm
F2                  -339.79 Hz
PPMCM                0.31464 ppm/cm
HZCM                125.89680 Hz/cm
```



crude product from **1a**
S/C 1430




1.0 mL helium/min, 10 min at 100°C, 4°C/min, 10 min at 200°C




RUN # 284

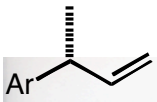
AREA%

| RT | AREA | TYPE | AR/HT | AREA% | |
|---|---|---|---|---|---|
| 11.96 | 12000 | BP | 1.047 | 0.015 | |
| 14.36 | 148410 | PB | 0.438 | 0.182 | |
| 19.45 | 18934 | PP | 0.512 | 0.023 | |
| 20.83 | 900280 | PB | 0.553 | 1.104 | ← *R* |
| 23.20 | 122470 | BV | 0.568 | 0.150 | ← *S* |
| 24.23 | 14917 | D VP | 0.696 | 0.018 | |
| 28.25 | 8.0340E+07 | SPB | 0.684 | 98.508 | |

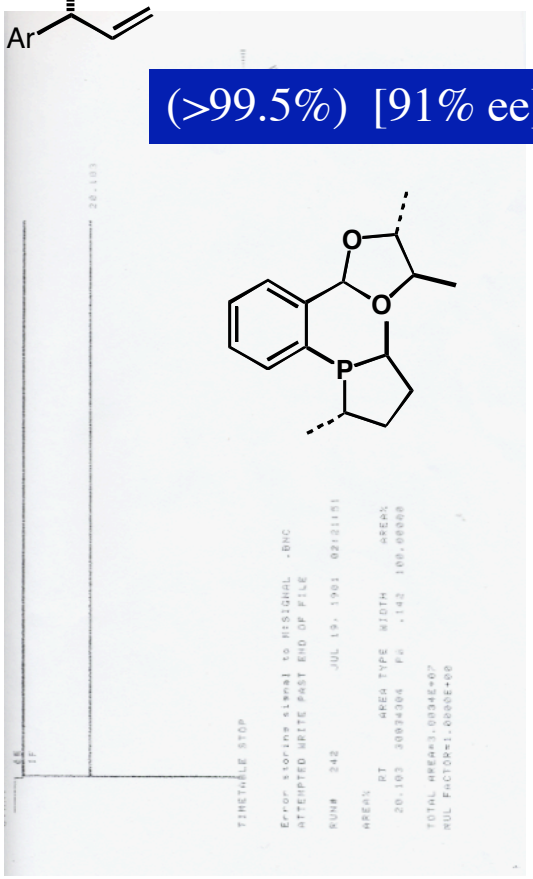
76%ee

TOTAL AREA= 8.1557E+07
MUL FACTOR= 1.0000E+00

# Effect of Side-chain Chirality




(>99.5%) [91% ee]





(3%, 90%, 7%) [70% ee]