Stereoselectivity of Intramolecular S_N' Cyclizations of Alkyllithium Reagents on Methoxy Alkenes

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Supporting information

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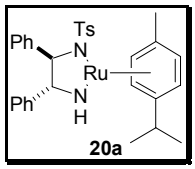
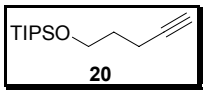
General Experimental. ^{1}H NMR spectra were recorded at 500 MHz and ^{13}C NMR spectra were recorded at 125 MHz. Chemical shifts of the ^{1}H NMR spectra were referenced to residual chloroform at 7.26 ppm. Chemical shifts of ^{13}C NMR spectra were referenced to $CDCl_3$ at 77.0 ppm. Coupling constants (*J* values) are reported in Hz. Tetrahydrofuran (THF), Et_2O, and CH_2Cl_2 were dried by filtration through alumina according to the procedure described by Grubbs.[1] Liquid chromatography was performed using forced flow (flash chromatography) of the indicated solvent system on silica gel. Enantiomeric excess was determined by HPLC utilizing a chiralcel OD-H column. Moisture sensitive reactions were performed under an atmosphere of argon using flame or oven dried glassware, and standard syringe/septa techniques.

Preparation of a stock solution of LiDBB in THF (*ca*. 0.4 M). To a two-necked round-bottom flask equipped with a glass stir-bar was added 4, 4'-di-*tert*-butylbiphenyl (DBB) (0.747 g, 2.72 mmol), THF (6.80 mL), and the solution was stirred under argon. To the stirring solution of DBB was introduced 1.0 mg of 1,10-phenanthroline, the mixture was cooled to 0 °C, and titrated with *n*-BuLi (2.5 M in hexanes, added to remove any residual trace of water) until a dark red end point persisted. Fresh lithium metal (0.226 g, 32.5 mmol) was prepared by submerging the wire in hexanes while scraping off the oxidized surface with an Exacto® knife. The shiny metal was then cut directly into the DBB solution under a stream of argon forming a dark green color within 5 minutes. The resulting mixture was allowed to stir at 0 °C for 5 h to form the desired LiDBB solution (*ca*. 0.4 M).

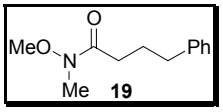


20a

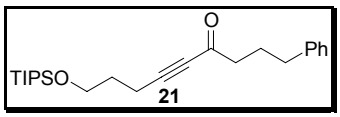
Ru[(*R*,*R*)-TsDPEN](η^6-*p*-cymene) (20a). The titled asymmetric hydrogen-transfer catalyst was prepared by a procedure developed by Noyori *et al*.[2, 3]



1-(Triisopropylsilyl)oxy-4-pentyne (20). The known title compound was synthesized from commercially available 4-pentyn-1-ol using a literature procedure.[4]

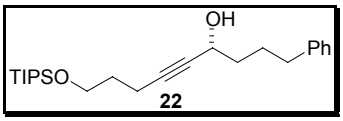


***N*-Methoxy-*N*-Methyl-4-phenylbutyramide (19)**. A flask was charged with 4-phenylbutyric acid (9.00 g, 55.0 mmol), CH_2Cl_2 (274 mL) and cooled to 0 °C. To this suspension was added triethylamine (15.3 mL, 110 mmol), isobutyl chloroformate (7.80 mL, 60.0 mmol), then *N,O*-dimethylhydroxylamine (5.60 g, 58.0 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 20 h. The excess isobutyl chloroformate was quenched with saturated aqueous $NaHCO_3$ (50 mL). The aqueous layer was extracted with ether (3 x 100 mL), and washed with brine (3 x 50 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to give a yellow oil that was purified by flash chromatography (40% EtOAc/Hexanes) to afford 10.5 g (92%) of the desired amide as a colorless oil: R_f = 0.36 (40% EtOAc/Hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (m, 2H), 7.19 (m, 3H), 3.59 (s, 3H), 2.93 (s, 3H), 2.68 (t, 2H, *J* = 7.5), 2.43 (t, 2H, *J* = 6.7), 1.98 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.0, 141.5, 128.2, 128.0, 125.4, 60.8, 35.0, 31.8, 30.8, 25.8 ppm; IR (neat) 3563, 2938, 1667, 1497, 1454, 1179, 1105 cm^{-1}; HRMS (CI/ammonia) *m/z* calcd for $C_{12}H_{17}NO_2$ $[M]^+$ 207.1259; found 207.1259.



1-Phenyl-9-triisopropylsilanyloxynon-5-yn-4-one (21). A solution of alkyne **20** (8.00 g, 33.0 mmol) in THF (221 mL) was cooled to 0 °C at which time *n*-butyllithium (2.5 M in

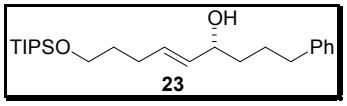
hexanes, 14.0 mL, 35.0 mmol) was added dropwise over a five min. period. The solution was stirred at 0 °C for 20 min., then a solution of *N*-methoxy-*N*-methyl-4-phenylbutyramide (**19**) (6.90 g, 33.3 mmol) in THF (56.0 mL, precooled to 0 °C) was added dropwise over a 10 min. period. The colorless solution was stirred at 0 °C for 1.5 h, the excess anion was then quenched with saturated aqueous NH_4Cl (120 mL), and the mixture was extracted with hexanes (2 x 200 mL). The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated in *vacuo*. The resulting oil was purified by silica gel chromatography (5% EtOAc/Hexanes) to afford 12.2 g (95% yield) of the title compound as a colorless oil: R_f = 0.39 (5% EtOAc/Hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (m, 2H), 7.19 (m, 2H), 3.78 (t, 2H, *J* = 5.9), 2.65 (t, 2H, *J* = 7.4), 2.55 (t, 2H, *J* = 7.5), 2.51 (t, 2H, *J* = 7.1), 2.00 (dt, 2H *J* = 15.2, 7.7), 1.81 (m, 2H), 1.09 (m, 21H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 187.7, 141.3, 128.4, 128.4, 125.9, 94.0, 80.2, 61.4, 44.6, 34.8, 30.9, 25.5, 17.9, 15.4, 11.9 ppm; IR (neat) 2944, 2213, 1675, 1463, 1383, 1238 cm^{-1}; HRMS (CI/ammonia) *m/z* calcd for $C_{24}H_{39}O_2Si$ $[M + H]^+$ 387.2719; found 387.2723.



22

(*R*)-1-Phenyl-9-triiopropylsilanyloxynon-5-yn-4-ol (22). A solution of 1-phenyl-9-triisopropylsilanyloxynon-5-yn-4-one **21** (7.00 g, 18.1 mmol) in freshly distilled isopropanol (181 mL) was sparged with argon for 20 min. To this solution was added Ru[(*R*,*R*)-TsDPEN](η^6-*p*-cymene) (**21a)** (0.109 g, 0.181 mmol) at room temperature. The solution immediately turned purple then red and finally, after 2h, an orange color. At the end of the 2 h period another portion of the catalyst (0.109 g, 0.181 mmol) was added to the solution and the mixture was allowed to stir for another 2 h. Another portion of the catalyst was added (0.109 g

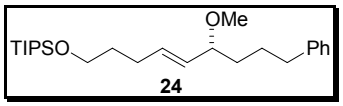
0.181 mmol) and the solution was stirred for 2 h. The resulting brown solution was concentrated and the brown residue was purified by passing it through a silica gel column (10% EtOAc/Hexanes) (three times) to give 5.72 g (81% yield, 97% *ee*) of the title compound as a slightly yellow oil: R_f = 0.32 (10% EtOAc/Hexanes); $[\alpha]_D$ –4.2 (*c* 0.10, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (m, 2H), 7.20 (m, 3H), 4.37 (m, 1H), 3.77 (t, 2H, *J* = 6.1), 2.67 (t, 2H, *J* = 7.6), 2.34 (dt, 2H, *J* = 7.1, 1.8), 1.75 (m, 7H), 1.08 (m, 21H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.1, 128.4, 128.3, 125.7, 85.3, 81.2, 62.5, 61.8, 37.6, 35.5, 31.9, 26.9, 18.0, 15.1, 11.9 ppm; IR (neat) 3350, 2942, 1604, 1463, 1384, 1248, cm^{-1}; HRMS (CI/ammonia) *m/z* calcd for $C_{21}H_{33}O_2Si$ $[M - i\text{-}Pr]^+$ 345.2250; found 345.2246.



23

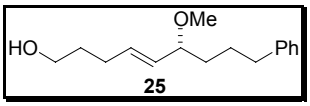
(*R*)-1-Phenyl-9-triisopropylsilanyloxynon-5-en-4-ol (23). A flask was charged with RedAl® (65% solution in toluene, 7.67 mL, 29.9 mmol) and THF (99.8 mL), and the resulting solution was cooled to 0 °C. To the cool stirring mixture was added a solution of alcohol **22** (2.91 g, 7.49 mmol) in THF (74.9 mL) dropwise over a five minute period. Once the exotherm was complete, the solution was warmed to room temperature and stirred for 8 h. The vigorously stirred mixture was cooled to 0 °C and an aqueous solution of potassium tartrate (2.0 M, 30 mL) and diethyl ether (30 mL) were sequentially introduced into the reaction vessel. The mixture was warmed to room temperature and stirred for 0.5 h. The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 30 mL). The combined organic layers were washed with brine (3 x 20 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting yellow residue was purified by flash chromatography (10% EtOAc/Hexanes) to give 2.63 g (90% yield) of the desired alcohol as a colorless oil: R_f = 0.32 (10% EtOAc/Hexanes); $[\alpha]_D$ –1.5 (*c* 0.20, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (m, 2H),

7.20 (m, 3H), 5.67 (dt, 1H, J = 15.1, 6.6), 5.49 (dd, 1H, J = 15.4, 7.1), 4.07 (m, 1H), 3.70 (t, 2H, J = 6.4), 2.65 (t, 2H, J = 7.4), 2.13 (q, 2H, J = 7.3), 1.77–1.60 (m, 5H), 1.57–1.52 (m, 2H), 1.08 (m, 21H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.3, 133.1, 131.7, 128.4, 128.2, 125.7, 73.0, 62.6, 36.8, 35.8, 32.4, 28.5, 27.3, 18.0, 12.0 ppm; IR (neat) 3350, 2939, 1669, 1604, 1455, 1383, 1248, 1110 cm^{-1}; HRMS (CI/ammonia) *m/z* calcd for $C_{21}H_{35}O_2Si$ $[M - i\text{-Pr}]^+$ 347.2406; found 347.2411.

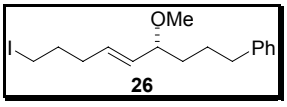


24

(*R*)-Triisopropyl-(6-methoxy-9-phenylnon-4-enyloxy)-silane (24). A solution of alcohol **23** (4.66 g, 11.9 mmol) in THF (23.6 mL) was cooled to 0 °C. Sodium hydride (60% dispersion in mineral oil, 2.06 g, 53.6 mmol), and methyl iodide (3.71 mL, 59.6 mmol) were sequentially added to the reaction mixture. The resulting grey mixture was allowed to stir for 15 h, cooled to 0 °C, and the excess sodium hydride was quenched with MeOH (20 mL). The mixture was poured into a separatory funnel containing 50 mL of water, the aqueous layer was extracted with Et_2O (3 x 40 mL), the combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash chromatography (5% EtOAc/Hexanes) to afford 4.59 g (95% yield) of the desired methyl ether **24** as a colorless oil: R_f = 0.56 (5% EtOAc/Hexanes); $[\alpha]_D$ +2.6 (*c* 0.10, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (m, 2H), 7.19 (m, 3H), 5.65 (dt, 1H, J = 15.2, 6.7), 5.30 (dd, 1H, J = 15.4, 8.3), 3.73 (t, 1H, J = 6.5), 3.50 (m, 1H), 3.26 (s, 3H), 2.64 (t, 2H, J = 7.1), 2.18 (q, 2H, J = 7.0), 1.75–1.63 (m, 5H), 1.55–1.48 (m, 1H), 1.10 (m, 21H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.5, 133.8, 130.7, 128.4, 128.2, 125.6, 82.4, 62.7, 55.87, 35.9, 35.3, 32.5, 28.5, 27.4, 18.0, 12.0 ppm; IR (neat) 2941, 1668, 1604, 1463, 1383, 1106 cm^{-1}; HRMS (CI/ammonia) *m/z* calcd for $C_{24}H_{41}O_2Si$ $[M - MeO]^+$ 373.2927; found 373.2934.

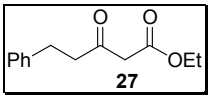


(*R*)-6-Methoxy-9-phenylnon-4-en-1-ol (25). To a solution of allyl ether **24** (3.60 g, 8.90 mmol) in THF (44.5 mL), cooled to 0 °C, was added TBAF (1.0 M solution in THF, 2.75 mL, 11.6 mmol) in one portion. The solution was warmed to room temperature, stirred for 10 h, and then brine (30 mL) was introduced into the reaction vessel. The mixture was extracted with Et_2O (3 x 40 mL), the combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated. The resulting oil was purified by silica gel chromatography (40% EtOAc/Hexanes) to give 2.18 g of the desired alcohol **25** as a colorless oil in 99% yield: R_f = 0.51 (40% EtOAc/Hexanes); $[\alpha]_D$ +19 (*c* 0.19, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.29 (m, 2H), 7.18 (m, 3H), 5.64 (dt, 1H, *J* = 15.4, 6.7), 5.29 (ddt, 1H, *J* = 15.4, 8.2, 1.4), 3.63 (m, 2H), 3.49 (m, 1H), 3.24 (s, 3H), 2.62 (t, 2H, *J* = 7.2), 2.15 (m, 2H), 2.00 (s, 1H), 1.70–1.61 (m, 5H), 1.52–1.47 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.4, 133.3, 130.8, 128.3, 128.2, 125.6, 82.3, 62.0, 55.7, 35.8, 35.1, 32.0, 28.4, 27.2 ppm; IR (neat) 3392, 2934, 1667, 1603, 1496, 1453, 1364, 1094 cm^{-1}; HRMS (CI/ammonia) *m/z* calcd for $C_{16}H_{23}O_2$ $[M - H]^+$ 247.1698; found 247.1692.



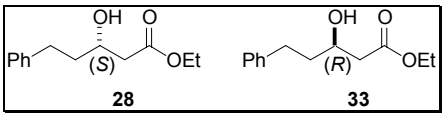
(*R*)-(9-Iodo-4-methoxynon-5-enyl)-benzene (26). To a solution of alcohol **25** (1.60 g, 6.44 mmol) in Et_2O (64.4 mL) at room temperature was added PPh_3 (3.38 g, 12.9 mmol) and imidazole (0.875 g, 12.9 mmol). A 0.3 M solution of I_2 (1.43 g, 11.3 mmol) in Et_2O (37.6 mL) was added dropwise over a 10 min. period. At the end of the addition of I_2, TLC analysis of the reaction mixture indicated that all starting material had been consumed. At this point another portion of I_2 (10 mL of a 0.3 M solution in Et_2O) was added to the reaction mixture, which was

then followed by the addition of MeOH (10 mL) to remove excess PPh_3. The excess I_2 was quenched with aqueous $NaHSO_3$ (2.0 M solution**,** 20 mL). The layers were separated, and the aqueous layer was extracted with hexanes (3 x 20 mL). The combined organic layers were washed with a saturated aqueous solution of $NaHCO_3$ (2 x 10 mL), brine (3 x 10 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the resulting oil by silica gel chromatography (10% EtOAc/Hexanes) gave the title compound (iodide **26**, 2.23 g, 97% yield) as a colorless oil: R_f = 0.64 (10% EtOAc/Hexanes); $[\alpha]_D$ +12 (*c* 0.29, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (m, 2H), 7.18 (m, 3H), 5.55 (dt, 1H, *J* = 15.2, 6.7), 5.36 (ddt, 1H, *J* = 15.4, 8.0, 1.3), 3.48 (m, 1H), 3.23 (s, 3H), 3.18 (t, 2H, *J* = 6.9), 2.62 (t, 2H, *J* = 7.2), 2.18 (m, 2H), 1.92 (app quintet, 2H, *J* = 7.0), 1.72–1.60 (m, 3H), 1.53–1.45 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.4, 132.1, 131.5, 128.4, 128.3, 125.7, 82.1, 55.9, 35.9, 35.2, 32.8, 32.6, 27.3, 6.2 ppm; IR (neat) 2930, 1667, 1603, 1496, 1452, 1214 cm^{-1}; HRMS (CI/ammonia) *m/z* calcd for $C_{16}H_{23}IO$ $[M]^+$ 358.0794; found 358.0790.



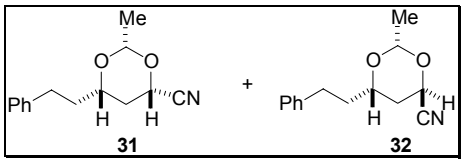
27

3-Oxo-5-phenyl-pentanoic acid ethyl ester (27). A literature procedure was used for the synthesis of β-keto ester **27**.[5]



28 **33**

(*S*)- and (*R*)-3-Hydroxy-5-phenyl-pentanoic acid ethyl ester (28 and 33). β-Hydroxy esters **28** and **33** were synthesized by using a literature procedure.[6]

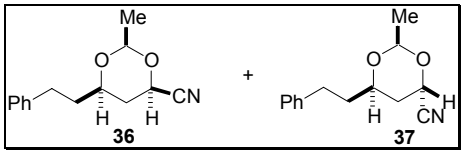


31 **32**

cis- and trans- acetals 31 and 32. (*S*)-3-Hydroxy-5-phenyl-pentanoic acid ethyl ester (1.80 g, 8.09 mmol) and *N,N*-dimethyl-(trimethylsilyl)amine (1.37 mL, 8.58 mmol) were combined neat and stirred for 16 h. The reaction mixture was then passed through a silica plug, eluting with diethyl ether, and concentrated under reduced pressure to give 2.36 g of the TMS-protected product **29**. Ester **29** (2.20 g, 6.79 mmol) was dissolved in 67.9 mL of anhydrous diethyl ether and the solution was cooled to –78 °C. DIBALH (1.0 M in toluene, 8.15 mL, 8.15 mmol) was added dropwise over a five minute period, and the reaction mixture was stirred for 1.5 h. The excess DIBALH was quenched at –78 °C with 1 mL of ethyl formate followed by 25 mL of 10% aqueous acetic acid solution and the reaction mixture was warmed to 0 °C. The resulting layers were separated, and the aqueous phase was extracted with Et_2O (3 x 50 mL). The combined organic layers were washed with 50 mL of water, saturated $NaHCO_{3(aq)}$ (3 x 50 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to give 1.83 g of the desired aldehyde **30** as a colorless oil. The aldehyde **30** (1.83 g, 7.31 mmol) was cooled to 0 °C, then TMSCN (0.590 mL, 4.41 mmol) was introduced into the reaction vessel followed by 1 mg of KCN/18-crown-6 complex. The reaction mixture was warmed to room temperature, stirred for 1 hour 15 minutes, and then 10 mL acetaldehyde and CSA (0.170 g, 0.731 mmol) were added to the reaction vessel. The resulting pale yellow mixture was allowed to stir at room temperature for 20 h. Saturated $NaHCO_{3(aq)}$ (30 mL) was added, the layers were separated, and the aqueous layer was extracted with Et_2O (3 x 70 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure, and the resulting residue was purified by flash chromatography (20% Et_2O/Pentane) to give 1.32 g (78% overall yield) of cis/trans acetals **31** and **32** (1:1.1 cis/trans) (contaminated with ~3-5% of the axial epimer at C2). A small portion was further purified to give diastereomers **31** and **32**.

Cis isomer **31**: R_f = 0.32 (15% Et_2O/Pentane); $[\alpha]_D$ –32 (*c* 0.5, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.30 (m, 2H), 7.20 (m, 3H), 4.67 (q, 1H, *J* = 5.1), 4.50 (d, 1H, *J* = 2.9), 3.56 (m, 1H), 2.78 (ddd, 1H, *J* = 14.1, 9.1, 5.6), 2.70 (dt, 1H, *J* = 14.1, 8.0), 1.93 (m, 2H), 1.79 (m, 2H), 1.41 (d, 3H, *J* = 5.1); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.1, 128.5, 128.4, 126.0, 117.1, 99.3, 74.2, 64.1, 36.7, 34.3, 30.7, 20.8 ppm; IR (neat) 2930, 1602, 1496, 1412, 1333, 1137 cm^{-1}; HRMS (CI/ammonia) *m/z* calcd for $C_{14}H_{18}NO_2$ $[M]^+$ 231.1259 found 231.1259.

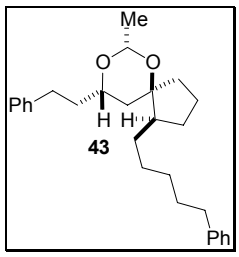
Trans isomer **32**: R_f = 0.39 (15% Et_2O/Pentane); $[\alpha]_D$ –81 (*c* 0.5, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.31 (m, 2H), 7.20 (m, 3H), 5.12 (q, 1H, *J* = 5.0), 4.95 (m, 1H), 3.94 (d, 1H, *J* = 4.7), 2.82 (ddd, 1H, *J* = 14.1, 9.9, 5.4), 2.68 (ddd, 1H, *J* = 13.9, 9.6, 6.8), 1.93 (m, 2H), 1.79 (m, 1H), 1.69 (ddd, 1H, *J* = 13.7, 2.1, 1.5), 1.38 (d, 3H, *J* = 5.1) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.2, 128.5, 128.3, 126.0, 117.4, 96.1, 72.3, 63.1, 37.0, 33.0, 30.9, 20.7; IR (neat) 2938, 1604, 1496, 1414, 1335, 1138 cm^{-1} ppm; HRMS (CI/ammonia) *m/z* calcd for $C_{14}H_{18}NO_2$ $[M]^+$ 231.1259 found 231.1260.



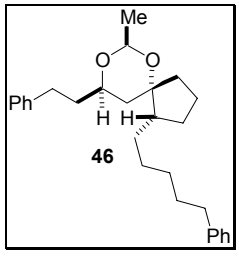
cis- and trans- acetals 36 and 37. Starting with β-hydroxy ester **33**, and the experimental procedure employed for the synthesis of acetals **31** and **32** led to the synthesis of acetals **36** and **37** in 78% overall yield (1:1.1 cis/trans) (contaminated with ~3-5% of the C2 epimer).

Cis isomer **36**: $[\alpha]_D$ +31 (*c* 0.5, $CHCl_3$); R_f, ^1H NMR, ^{13}C NMR, and IR spectra data were identical to that of acetal **31**.

Trans isomer **37**: $[\alpha]_D$ +80 (*c* 0.5, $CHCl_3$); R_f, ^1H NMR, ^{13}C NMR, and IR spectra data were identical to that of acetal **32**.



Hydrogenation of alkene 41 to acetal 43. To a solution of alkene **41** (19 mg, 47 μmol) in MeOH (1 mL) was added 10% Pd/C. The resulting mixture was kept under an atmosphere of H_2 (1 atm of pressure) and allowed to stir at room temperature for 20 h. The solution was filtered through a plug of silica eluting with pentane, and the solution was concentrated under reduced pressure. The resulting oil was purified by flash chromatography (10% Et_2O/Pentane) to give 15 mg (79% yield) of the desired product (acetal **43**) as a colorless oil: R_f = 0.54 (10% Et_2O/Pentane); $[\alpha]_D$ –78 (*c* 1.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (m, 4H), 7.20 (m, 6H), 4.67 (q, 1H, *J* = 5.1), 3.72 (m, 1H), 2.80 (ddd, 1H, *J* = 14.0, 10.0, 5.7), 2.69 (ddd, 1H, *J* = 13.9, 9.7, 6.6) 2.62 (t, 2H, *J* = 7.8), 2.00 (m, 1H), 1.87 (m, 2H), 1.74–1.62 (m, 6H), 1.55–1.47 (m, 2H), 1.46–1.29 (m, 9H), 1.24–1.16 (m, 1H), 1.04–0.97 (m, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.8, 142.0, 128.5, 128.4, 128.3, 128.2, 125.8, 125.6, 95.1, 83.6, 72.5, 40.8, 40.3, 38.1, 37.6, 36.0, 31.6, 31.4, 29.6, 28.1, 27.8, 27.2, 21.4, 17.8 ppm; IR (neat) 2928, 1601, 1496, 1454, 1378, 1143 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{28}H_{38}O_2Na$ $[M + Na]^+$ 429.2769; found 429.2765.



Hydrogenation of mixture of alkenes to acetal 46. The mixture comprised of olefin isomers **44 and 45** (6.0 mg, 15 μmol) were hydrogenated by using same experimental protocol developed

for the hydrogenation of alkene **41.** The reduced product **46** was isolated as a single diastereomer: R_f = 0.54 (10% Et_2O/Pentane); $[\alpha]_D$ +66 (*c* 1.4, $CHCl_3$); ^1H NMR, ^{13}C NMR, and IR spectra of acetal **46** were identical to the spectra of acetal **43**.

References:

1. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

2. Matsumura, K.; Hashiguchi, S.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1997**, *119*, 8738–8739.

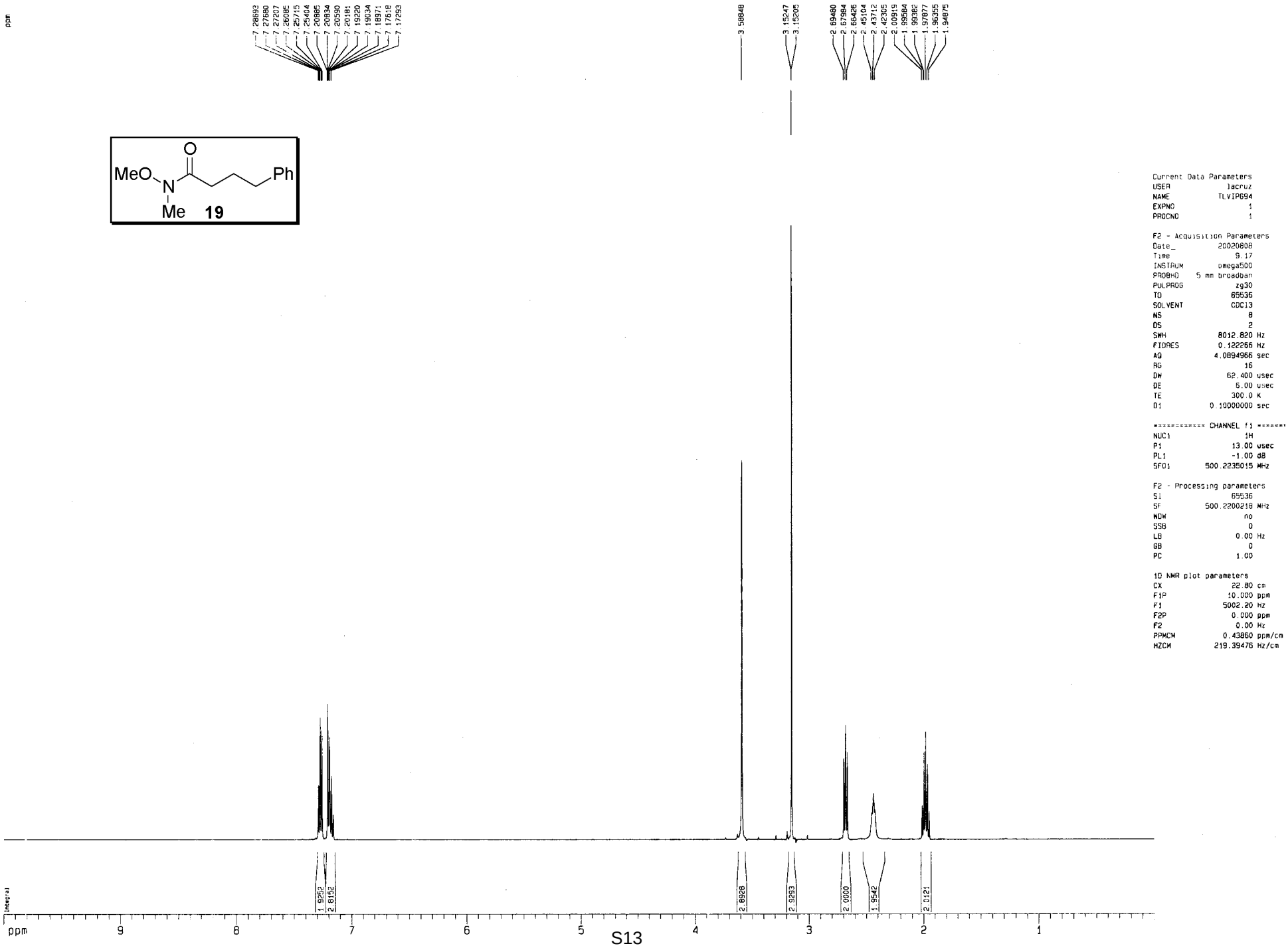
3. Haack, K.; Hashiguchi, S.; Fujii, A.; Ikariya, T.; Noyori, R. *Angew. Chem. Int. Ed. Engl*. **1997**, *36*, 285–290.

4. Dussault, P. H.; Eary, C. T.; Woller, K. R. *J. Org. Chem.* **1999**, *64*, 1789–1797.

5. Holmquist, C. R.; Roskamp, E. J. *J. Org. Chem*. **1989**, *54*, 3258–3260.

6. (a) Rychnovsky, S. D.; Sinz C. J. *Tetrahedron Lett.* **1998***, 39,* 6811-6814. (b) Sumida, S; Ohga, M.; Mitani, J.; Nokami, J. *J. Am. Chem. Soc*. **2000**, *122*, 310–1313.

1H spectrum



Current Data Parameters

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EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

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PROBHD	5 mm broadban
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	8012.820 Hz
FIDRES	0.122266 Hz
AQ	4.0894966 sec
RG	16
DW	62.400 usec
DE	6.00 usec
TE	300.0 K
D1	0.10000000 sec

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PL1	-1.00 dB
SFO1	500.2235015 MHz

F2 - Processing parameters

SI	65536
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PC	1.00

1D NMR plot parameters

CX	22.80 cm
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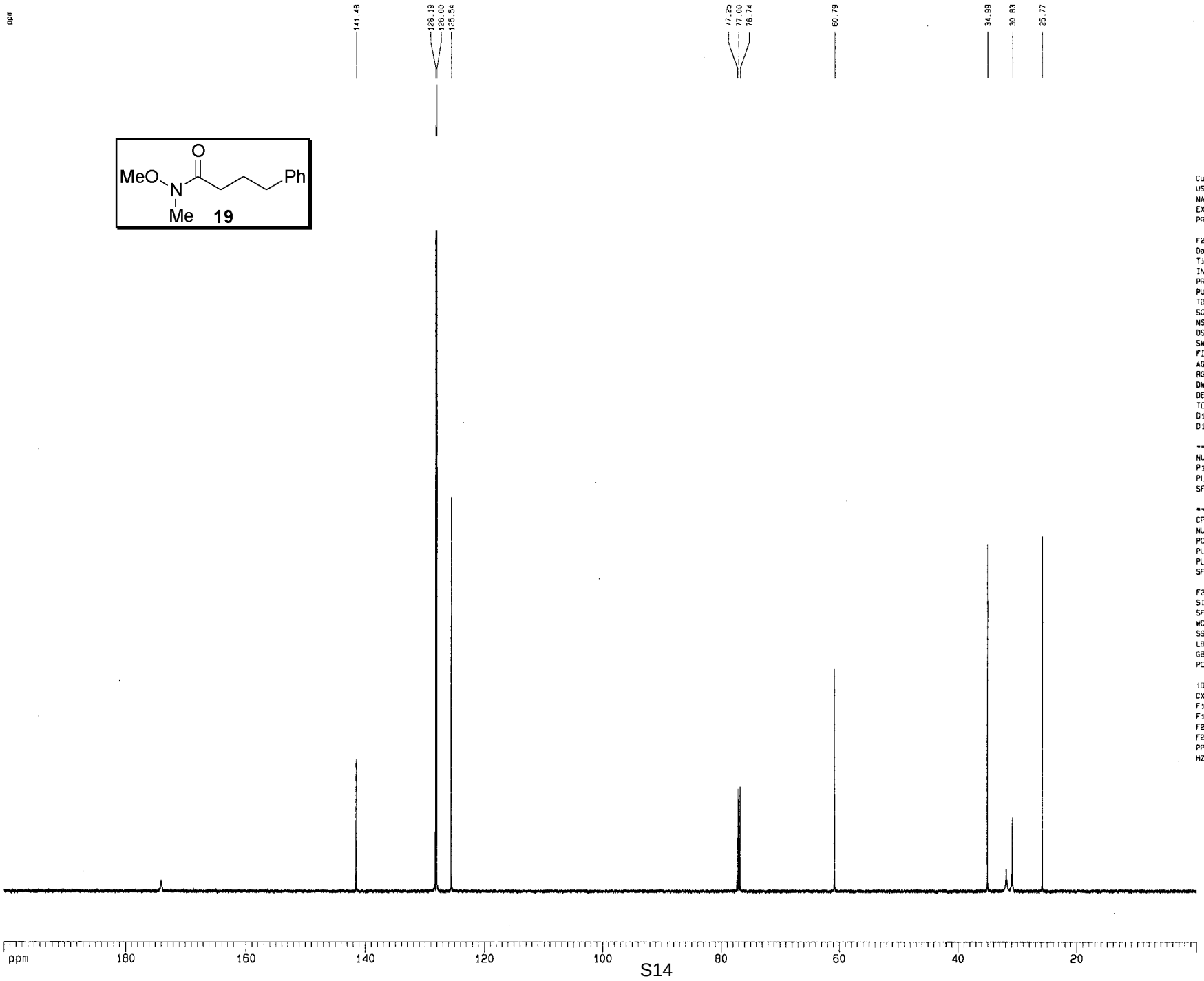
F1	5002.20 Hz
F2P	0.000 ppm
F2	0.00 Hz
PPMCM	0.43860 ppm/cm
HZCM	219.39476 Hz/cm

13C spectrum with 1H decoupling



Current Data Parameters
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EXPNO 1
PROCNO 1

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TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 10321.3
DW 16.500 usec
DE 4.50 usec
TE 300.0 K
D1 0.25000000 sec
D11 0.03000000 sec

========== CHANNEL f1 =======
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PL1 -3.00 dB
SFO1 125.7942048 MHz

========== CHANNEL f2 =======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 120.00 dB
PL12 14.40 dB
SFO2 500.2230013 MHz

F2 - Processing parameters
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LB 1.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
F1P 200.000 ppm
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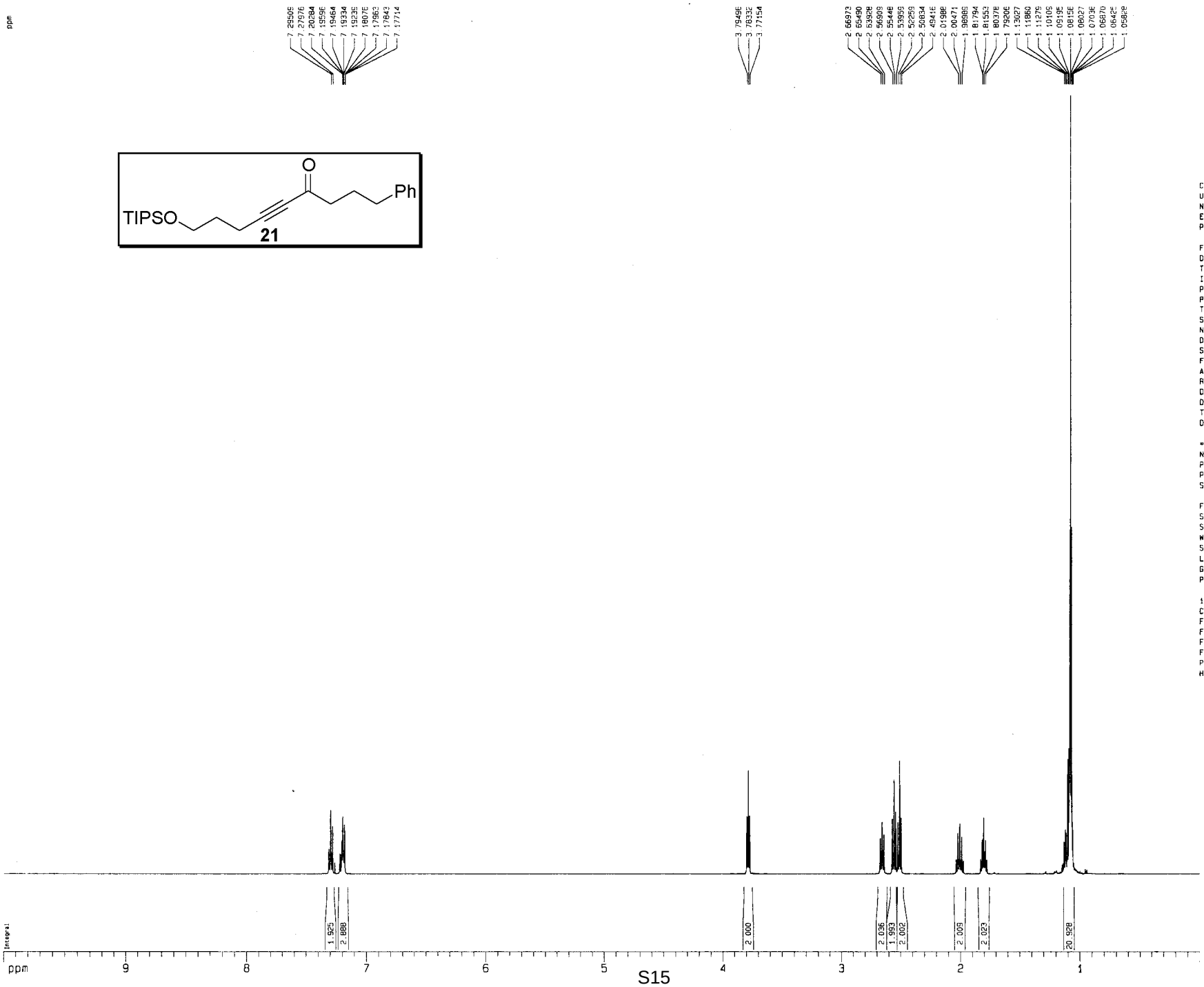
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 8.77193 ppm/cm
HZCM 1103.33740 Hz/cm

1H spectrum



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PROCNO 1

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PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 16
DW 62.400 usec
DE 6.00 usec
TE 300.0 K
D1 0.10000000 sec

========== CHANNEL f1 =======
NUC1 1H
P1 13.00 usec
PL1 -1.00 dB
SFO1 500.2235015 MHz

F2 - Processing parameters
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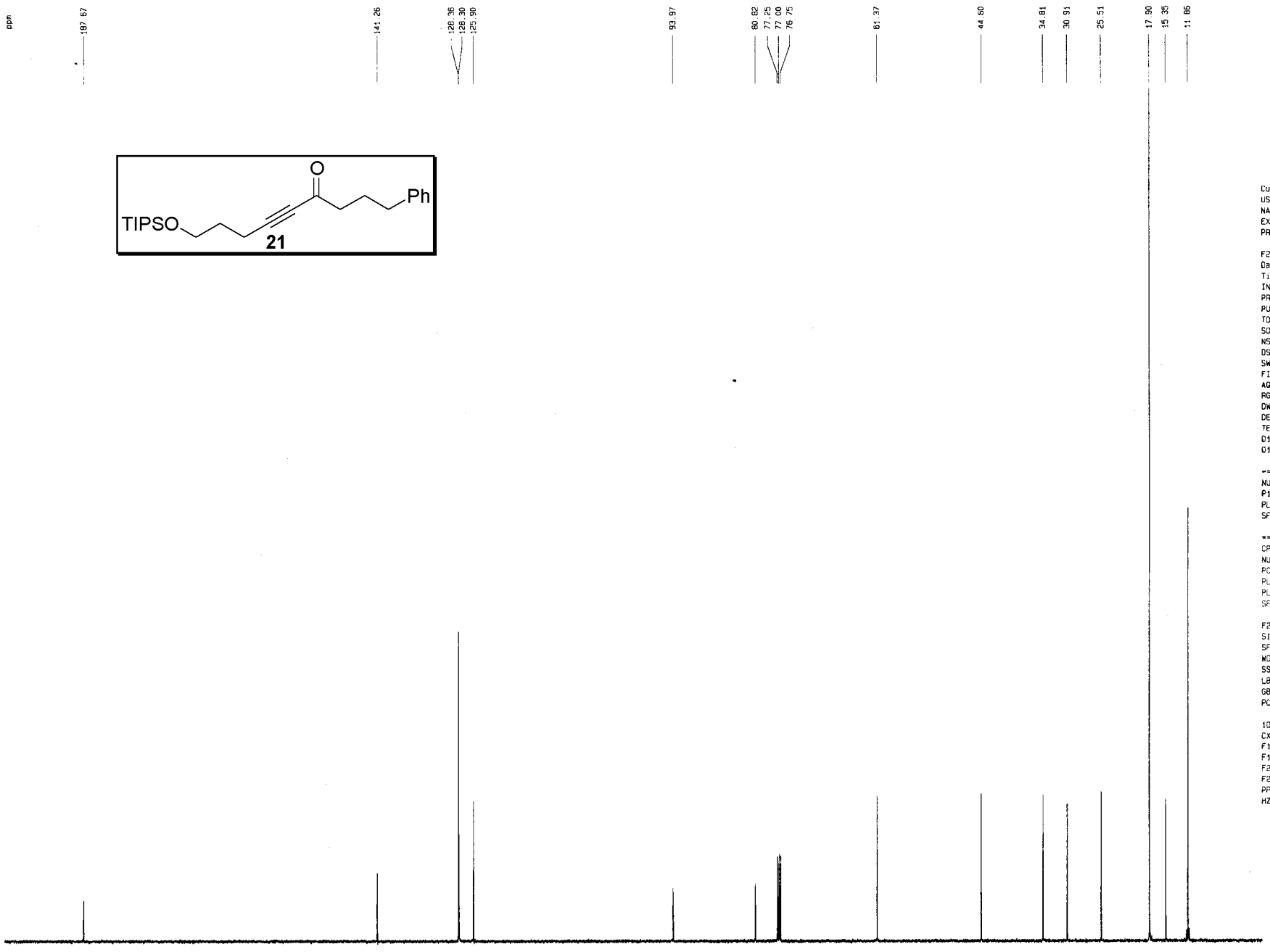
SF 500.2200310 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
F1P 10.000 ppm
F1 5002.20 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.43860 ppm/cm
HZCM 219.39476 Hz/cm

13C spectrum with 1H decoupling



Current Data Parameters
USER lacruz
NAME TLV1PG95Carbon
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
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TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 7298.2
DW 16.500 usec
DE 4.50 usec
TE 300.0 K
D1 0.25000000 sec
D11 0.03000000 sec

========== CHANNEL f1 =======
NUC1 13C
P1 29.00 usec
PL1 -3.00 dB
SFO1 125.7942048 MHz

========== CHANNEL f2 =======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 120.00 dB
PL12 14.40 dB
SFO2 500.2230013 MHz

F2 - Processing parameters
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LB 1.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
F1P 200.000 ppm
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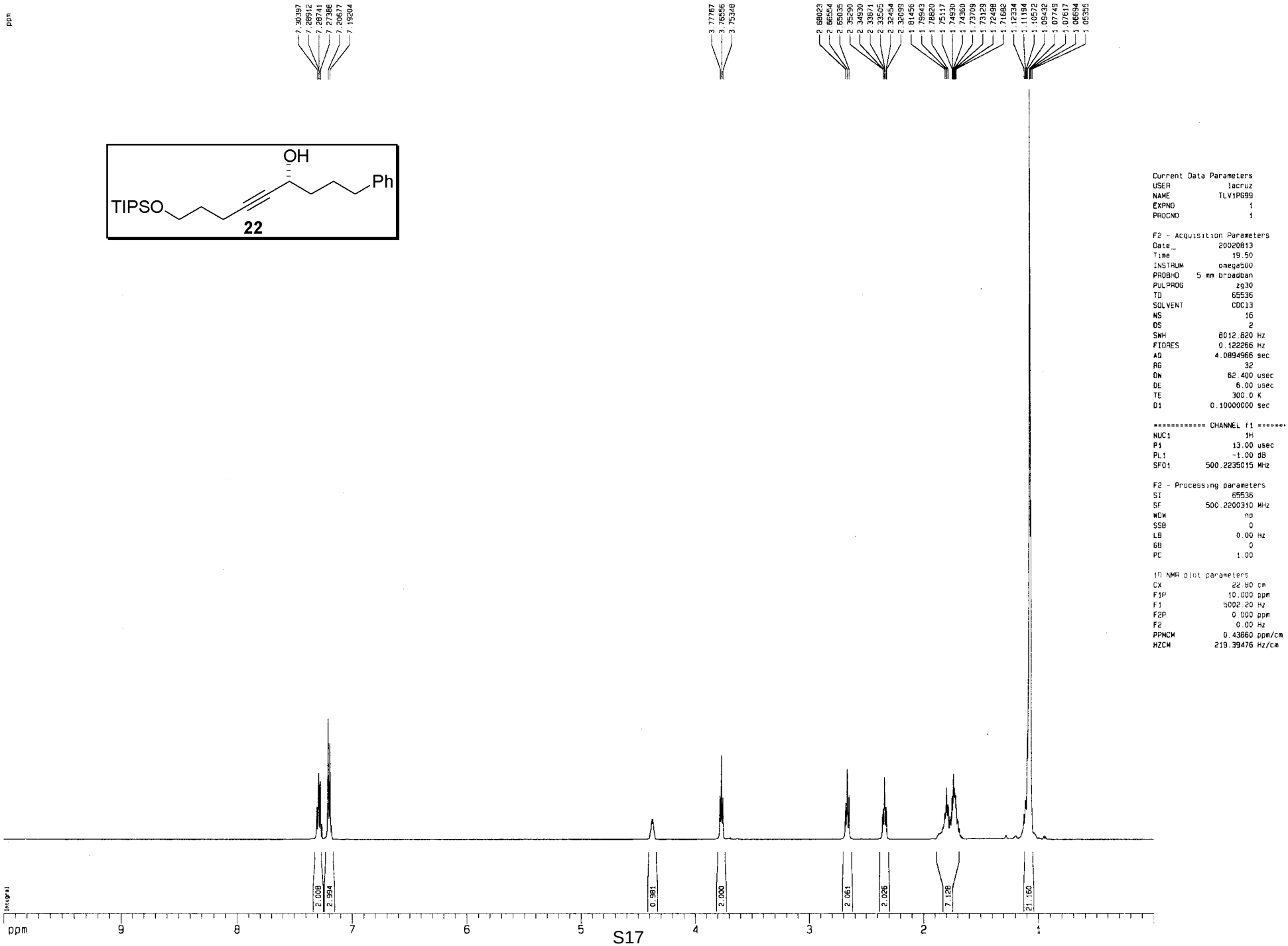
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 8.77193 ppm/cm
HZCM 1103.33728 Hz/cm

1H spectrum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2.65035
2.35290
2.34930
2.33871
2.33505
2.32454
2.32099
1.81496
1.79943
1.78820
1.75117
1.74930
1.74360
1.73709
1.73129
1.72498
1.71682
1.12334
1.11194
1.10572
1.09432
1.07745
1.07617
1.06694
1.05355
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Ph
TIPSO
22
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NAME TLV1PG99
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
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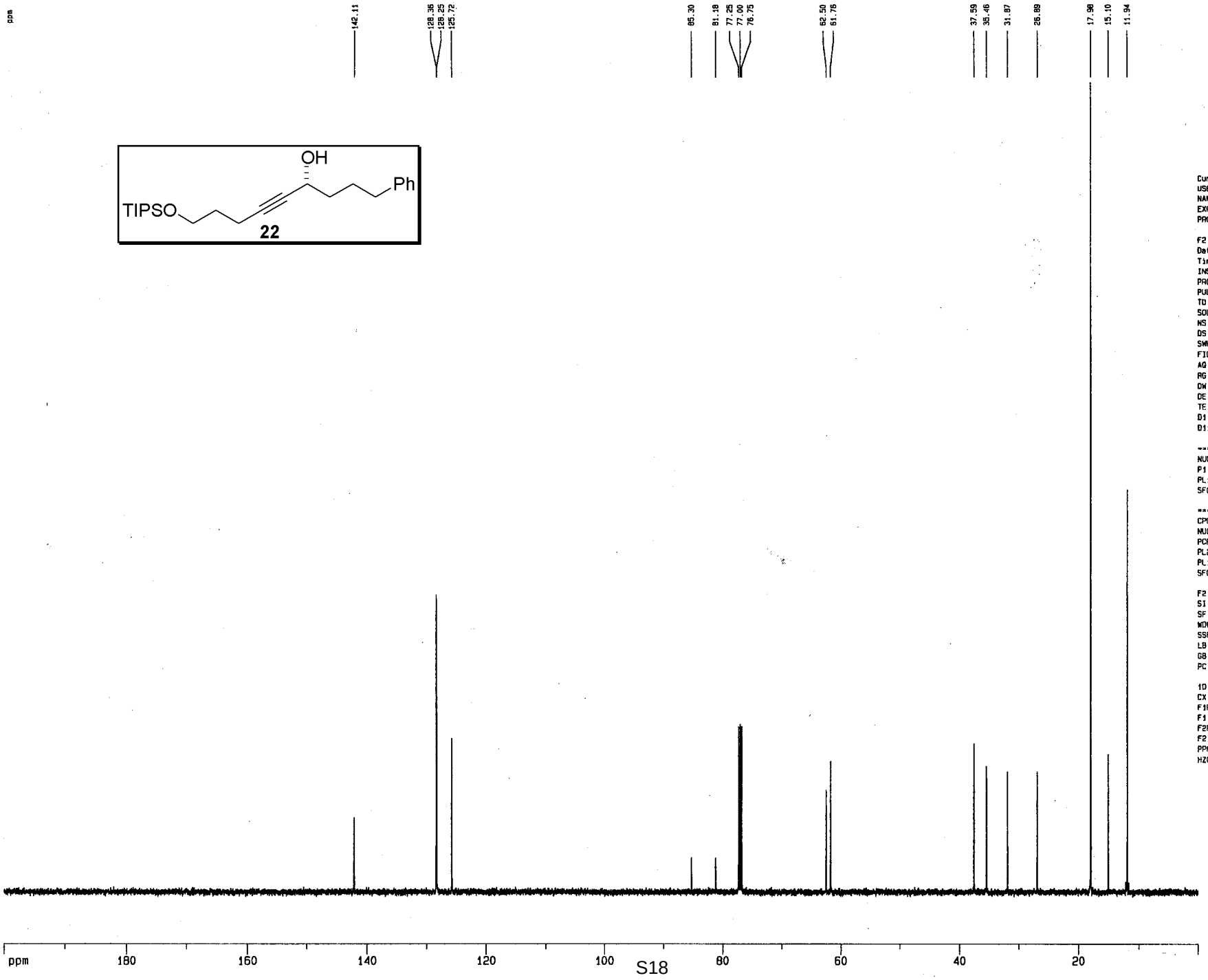
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 32
DW 62.400 usec
DE 6.00 usec
TE 300.0 K
D1 0.10000000 sec
========== CHANNEL f1 ======
NUC1 1H
P1 13.00 usec
PL1 -1.00 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200310 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.80 cm
F1P 10.000 ppm
F1 5002.20 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.43860 ppm/cm
HZCM 219.39476 Hz/cm
Integral
2.008
2.994
0.981
2.000
2.061
2.026
7.128
21.160
ppm
9
8
7
6
5
4
3
2
1

13C spectrum with 1H decoupling



Current Data Parameters
USER lacruz
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EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
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Time 19.42
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TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 7298.2
DW 16.500 usec
DE 4.50 usec
TE 300.0 K
D1 0.25000000 sec
D11 0.03000000 sec

========== CHANNEL f1 =======
NUC1 13C
P1 29.00 usec
PL1 -3.00 dB
SFO1 125.7942048 MHz

========== CHANNEL f2 =======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 120.00 dB
PL12 14.40 dB
SFO2 500.2230013 MHz

F2 - Processing parameters
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SF 125.7804332 MHz
WDW EM
SSB 0
LB 1.00 Hz
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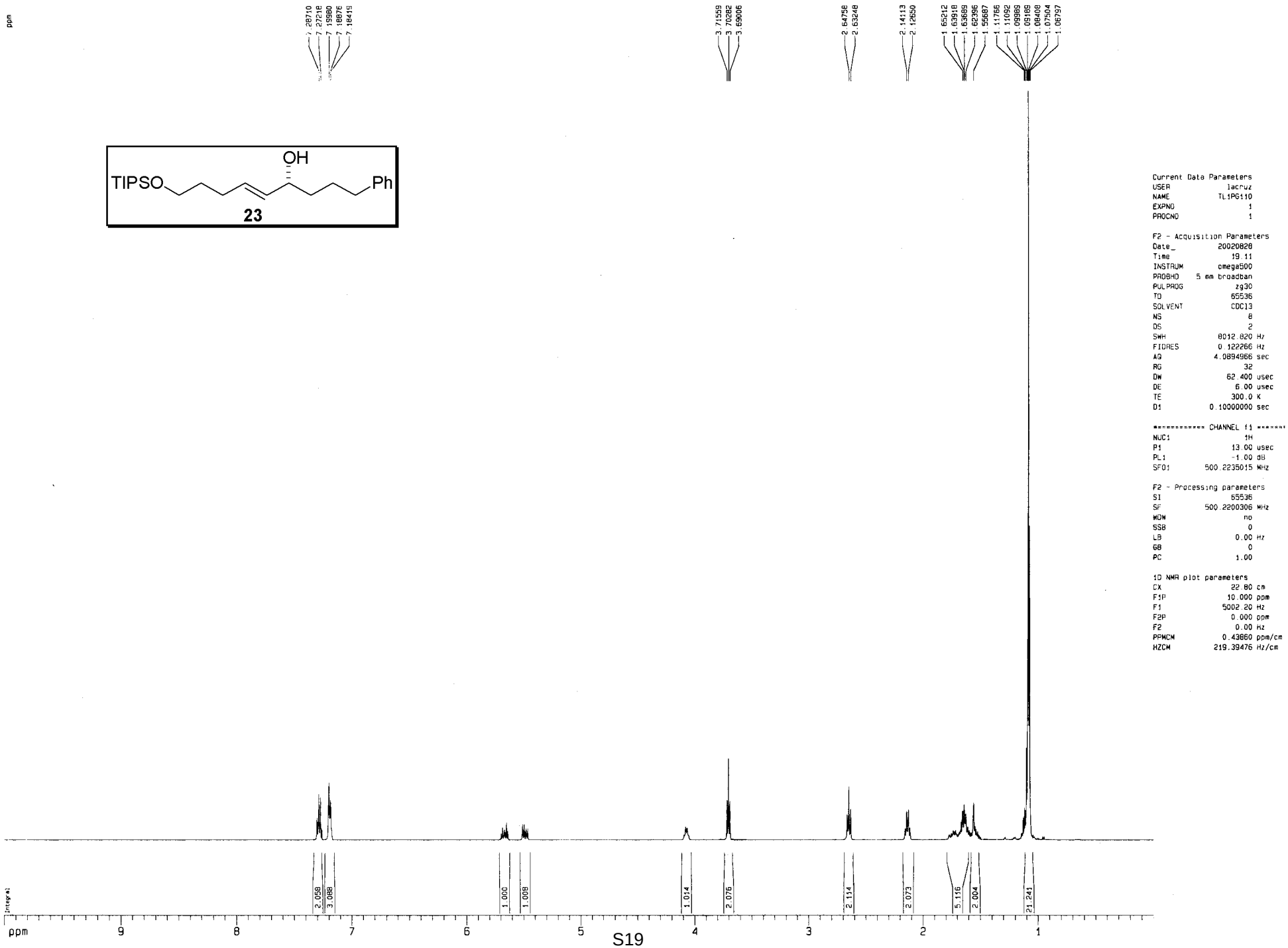
PC 1.00

1D NMR plot parameters
CX 22.80 cm
F1P 200.000 ppm
F1 25156.09 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 8.77193 ppm/cm
HZCM 1103.33716 Hz/cm

1H spectrum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1.62396
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TIPSO
Ph
23
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USER lacruz
NAME TL1PG110
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
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Time 19.11
INSTRUM omega500
PROBHD 5 mm broadban
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TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 32
DW 62.400 usec
DE 6.00 usec
TE 300.0 K
D1 0.10000000 sec
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NUC1 1H
P1 13.00 usec
PL1 -1.00 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200306 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.80 cm
F1P 10.000 ppm
F1 5002.20 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.43860 ppm/cm
HZCM 219.39476 Hz/cm
Integral
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1.000
1.008
1.014
2.076
2.114
2.073
5.116
2.004
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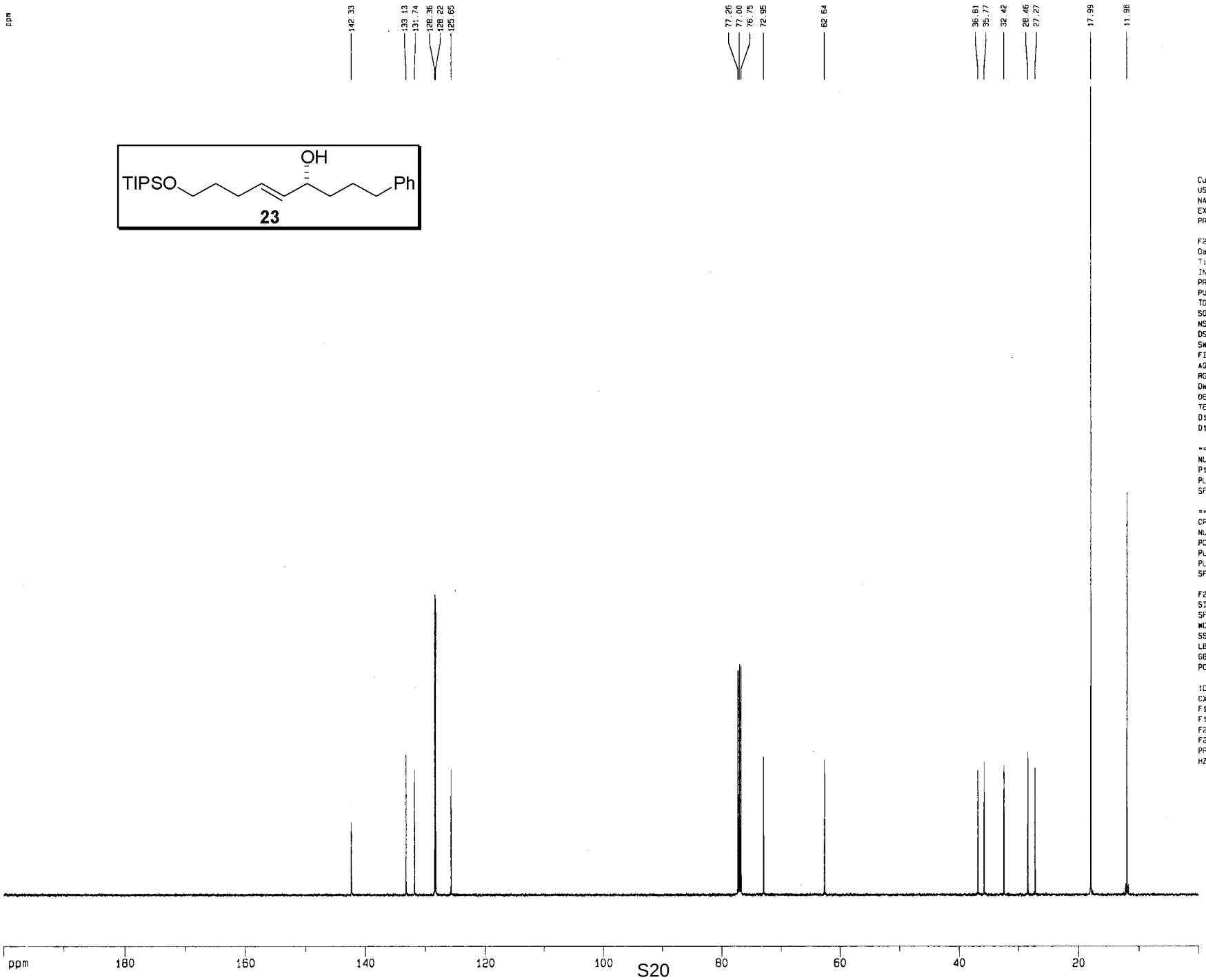
ppm
9
8
7
6
5
4
3
2
1

13C spectrum with 1H decoupling



Current Data Parameters

USER	lacruz
NAME	TL1PG110Carbon
EXPNO	1
PROCNO	1

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SOLVENT	CDCl3
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DS	4
SWH	30303.031 Hz
FIDRES	0.462388 Hz
AQ	1.0813940 sec
RG	2896.3
DW	16.500 usec
DE	4.50 usec
TE	300.0 K
D1	0.25000000 sec
D11	0.03000000 sec

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

NUC1	13C
P1	29.00 usec
PL1	-3.00 dB
SF01	125.7942048 MHz

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

CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	120.00 dB
PL12	14.40 dB
SF02	500.2230013 MHz

F2 - Processing parameters

SI	65536
SF	125.7804341 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	22.80 cm
F1P	200.000 ppm
F1	25156.09 Hz
F2P	0.000 ppm
F2	0.00 Hz
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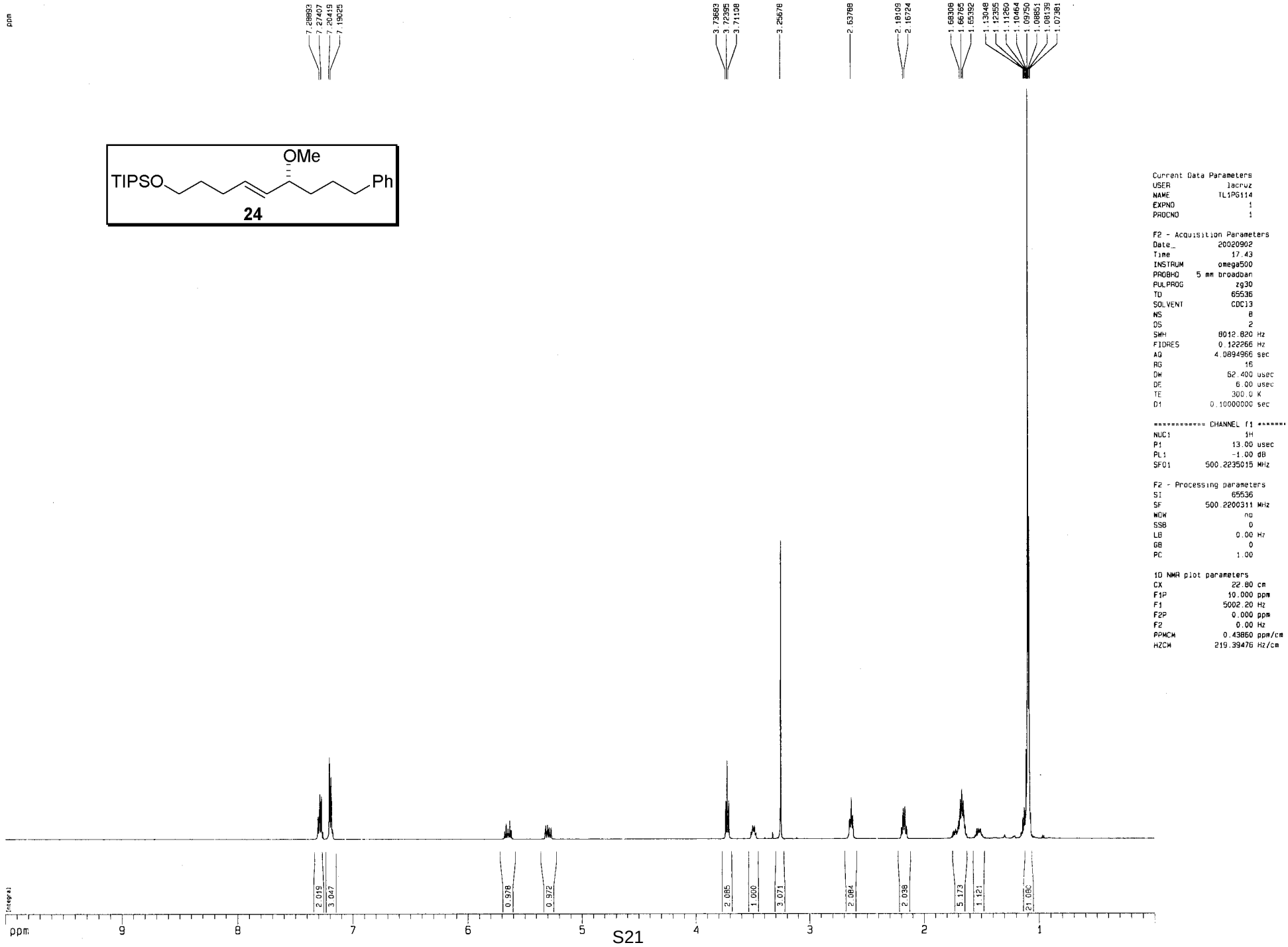
HZCM	1103.33716 Hz/cm

1H spectrum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1.66765
1.65392
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1.12355
1.11260
1.10464
1.09750
1.08851
1.08135
1.07381
OMe
TIPSO
Ph
24
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NAME TL1PG114
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
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Time 17.43
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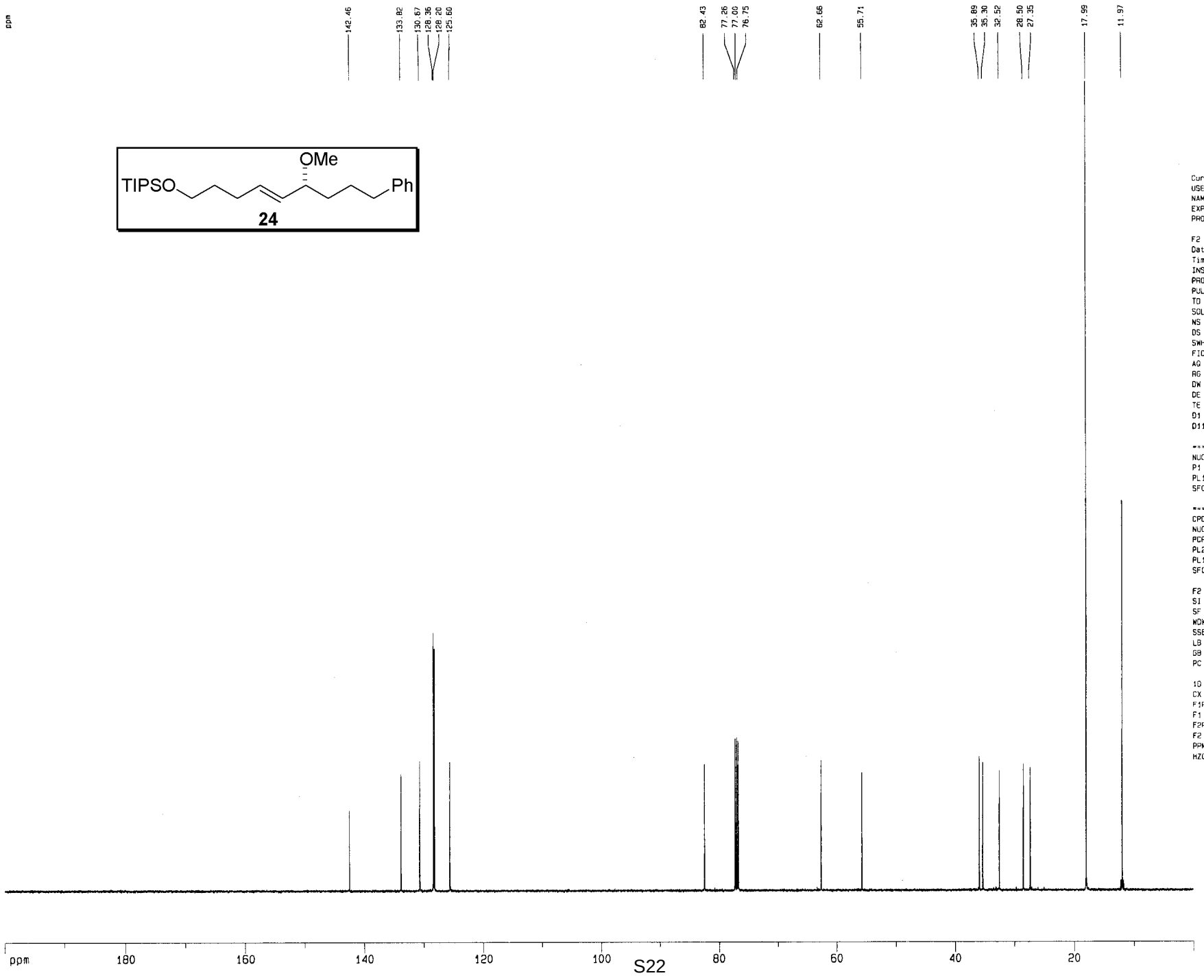
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 16
DW 62.400 usec
DE 6.00 usec
TE 300.0 K
D1 0.10000000 sec
========== CHANNEL f1 =======
NUC1 1H
P1 13.00 usec
PL1 -1.00 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200311 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.80 cm
F1P 10.000 ppm
F1 5002.20 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.43860 ppm/cm
HZCM 219.39476 Hz/cm
Integral
2.019
3.047
0.978
0.972
2.085
1.000
3.071
2.084
2.038
5.173
1.121
21.080
ppm
9
8
7
6
5
4
3
2
1

13C spectrum with 1H decoupling



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EXPNO 1
PROCNO 1

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TD 65536
SOLVENT CDCl3
NS 1024
DS 4
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FIDRES 0.462368 Hz
AQ 1.0813940 sec
RG 2580.3
DW 16.500 usec
DE 4.50 usec
TE 300.0 K
D1 0.25000000 sec
D11 0.03000000 sec

========== CHANNEL f1 ======
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P1 29.00 usec
PL1 -3.00 dB
SFO1 125.7942048 MHz

========== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 120.00 dB
PL12 14.40 dB
SFO2 500.2230013 MHz

F2 - Processing parameters
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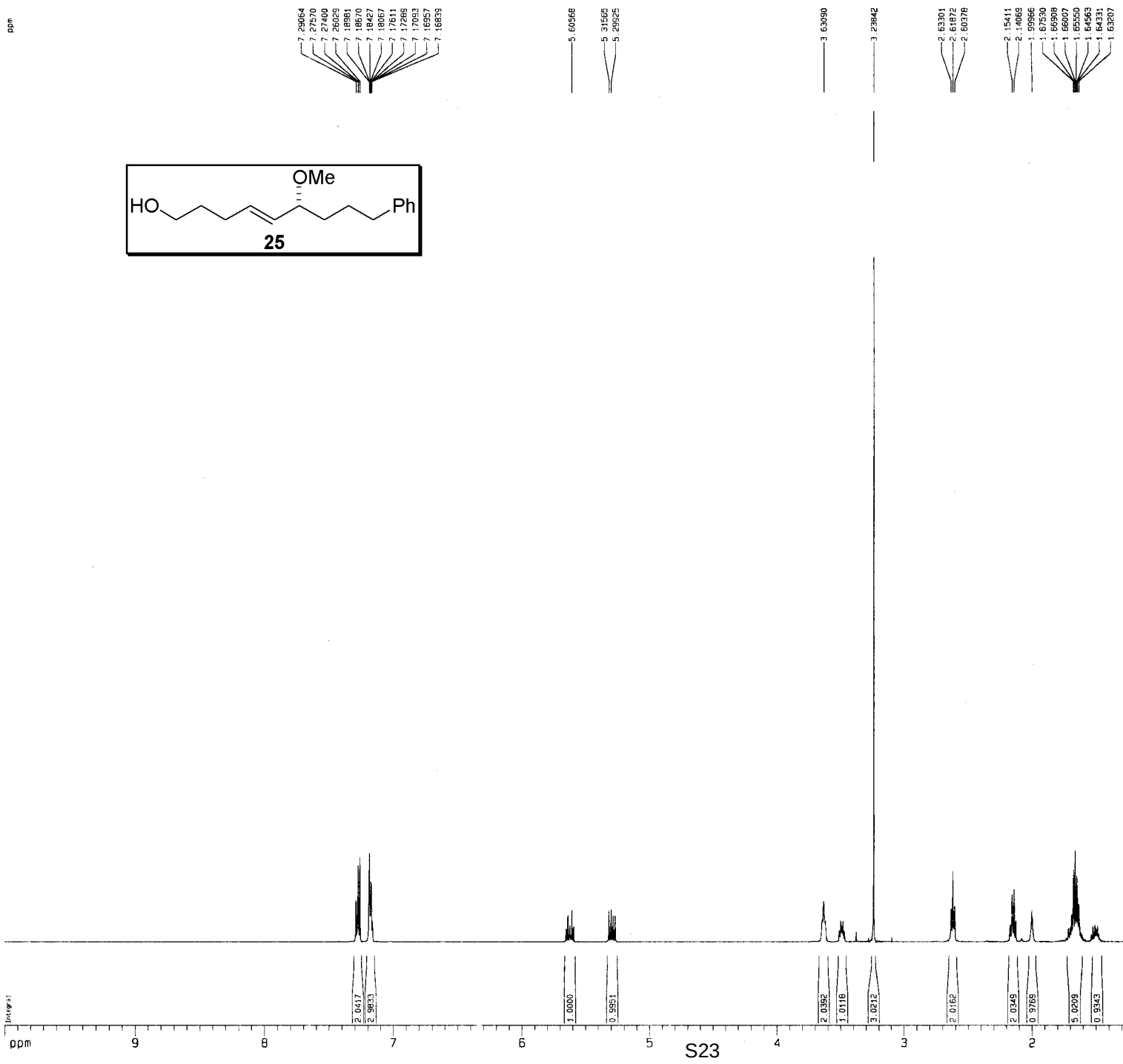
SF 125.7804341 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 22.80 cm
F1P 200.000 ppm
F1 25156.09 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 8.77193 ppm/cm
HZCM 1103.33716 Hz/cm

1H spectrum



Current Data Parameters

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NAME	TL1PG115
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

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Time	22.57
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PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	8012.820 Hz
FIDRES	0.122266 Hz
AQ	4.0894966 sec
RG	32
DW	62.400 usec
DE	6.00 usec
TE	300.0 K
D1	0.10000000 sec

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

NUC1	1H
P1	13.00 usec
PL1	-1.00 dB
SFO1	500.2235015 MHz

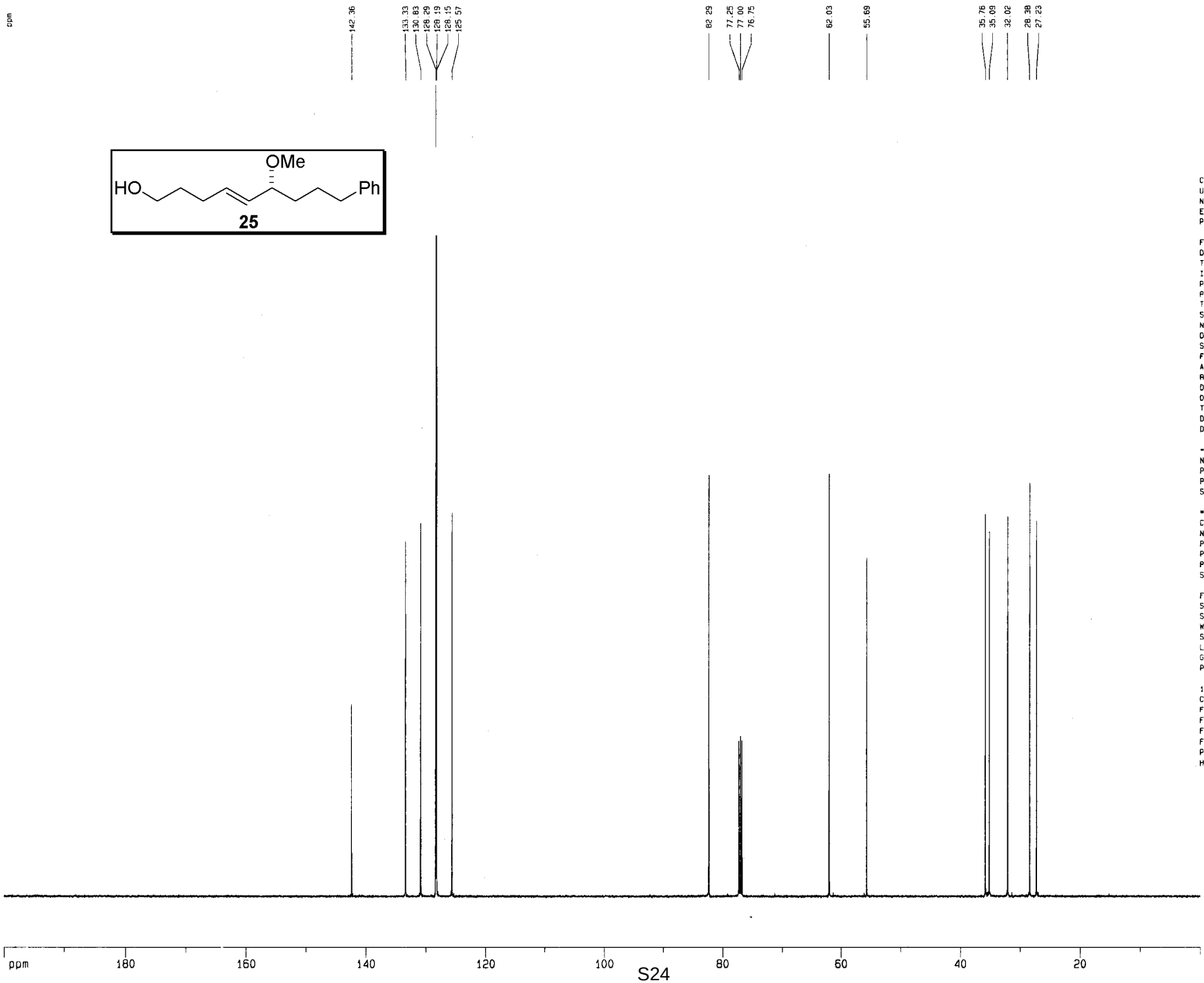
F2 - Processing parameters

SI	65536
SF	500.2200307 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	22.80 cm
F1P	10.000 ppm
F1	5002.20 Hz
F2P	0.000 ppm
F2	0.00 Hz
PPMCM	0.43860 ppm/cm
HZCM	219.39476 Hz/cm

13C spectrum with 1H decoupling



Current Data Parameters

USER	lacruz
NAME	TL1PG115Carbon
EXPNO	1
PROCNO	1

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SOLVENT	CDCl3
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DS	4
SWH	30303.031 Hz
FIDRES	0.462388 Hz
AQ	1.0813940 sec
RG	5160.6
DW	16.500 usec
DE	4.50 usec
TE	300.0 K
D1	0.25000000 sec
D11	0.03000000 sec

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

NUC1	13C
P1	29.00 usec
PL1	-3.00 dB
SFO1	125.7942048 MHz

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

CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	120.00 dB
PL12	14.40 dB
SFO2	500.2230013 MHz

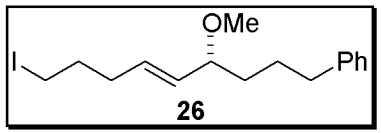
F2 - Processing parameters

SI	65536
SF	125.7804420 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	22.80 cm
F1P	200.000 ppm
F1	25156.09 Hz
F2P	0.000 ppm
F2	0.00 Hz
PPMCM	8.77193 ppm/cm
HZCM	1103.33728 Hz/cm

1H spectrum



Current Data Parameters
USER lacruz
NAME TL-1-116
EXPNO 1
PROCNO 1

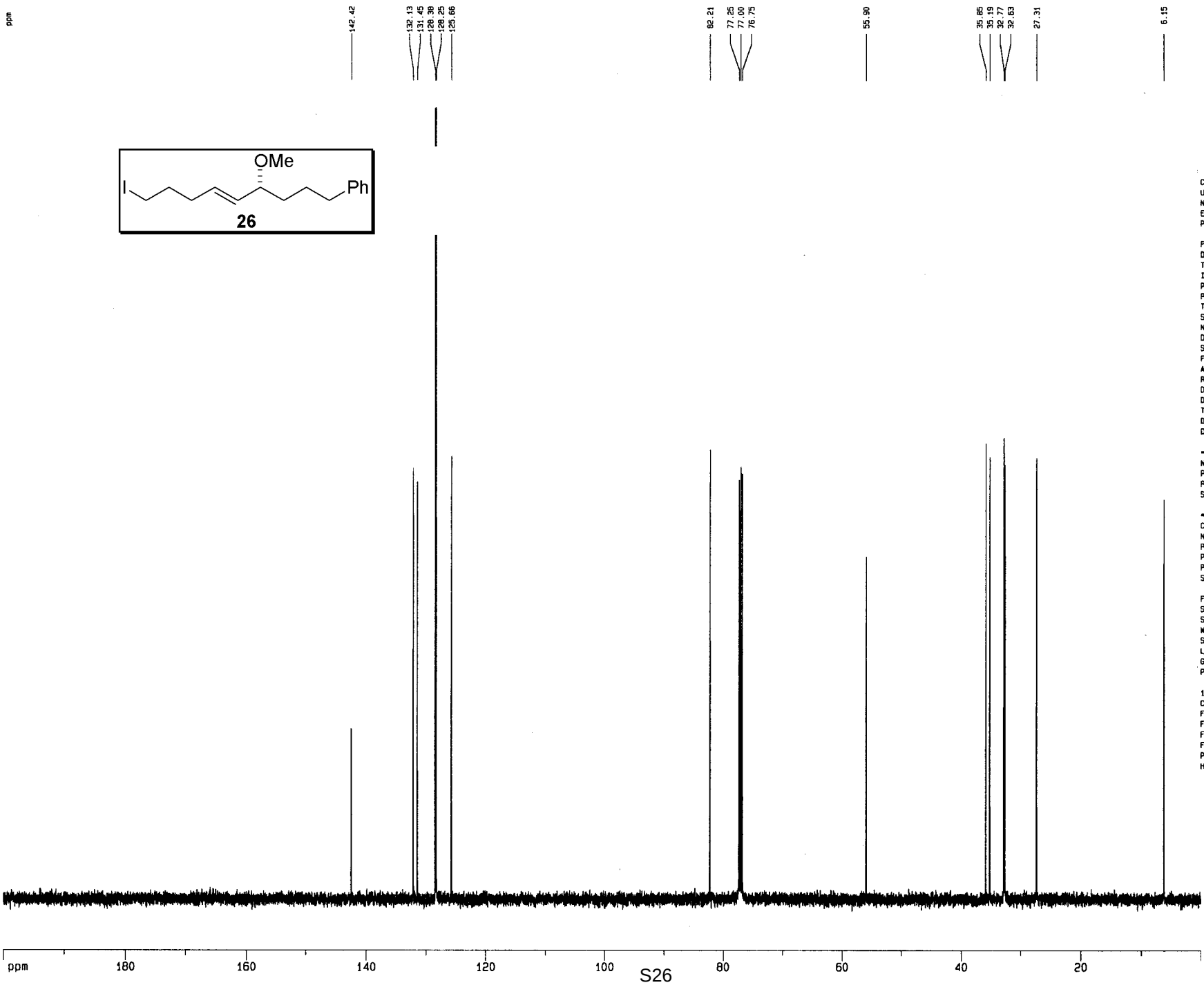
F2 - Acquisition Parameters
Date_ 20021124
Time 2.56
INSTRUM omega500
PROBHD 5 mm broadban
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 128
DW 62.400 usec
DE 6.00 usec
TE 300.0 K
D1 0.10000000 sec

========== CHANNEL f1 =======
NUC1 1H
P1 13.00 usec
PL1 -1.00 dB
SFO1 500.2235015 MHz

F2 - Processing parameters
SI 65536
SF 500.2200321 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.80 cm
F1P 10.000 ppm
F1 5002.20 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.43860 ppm/cm
HZCM 219.39476 Hz/cm

13C spectrum with 1H decoupling



Current Data Parameters
USER lacruz
NAME TL-1-116Carbo
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20021124
Time 3.12
INSTRUM omega500
PROBHD 5 mm broadban
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 583
DS 4
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 2896.3
DW 16.500 usec
DE 4.50 usec
TE 300.0 K
D1 0.25000000 sec
D11 0.03000000 sec

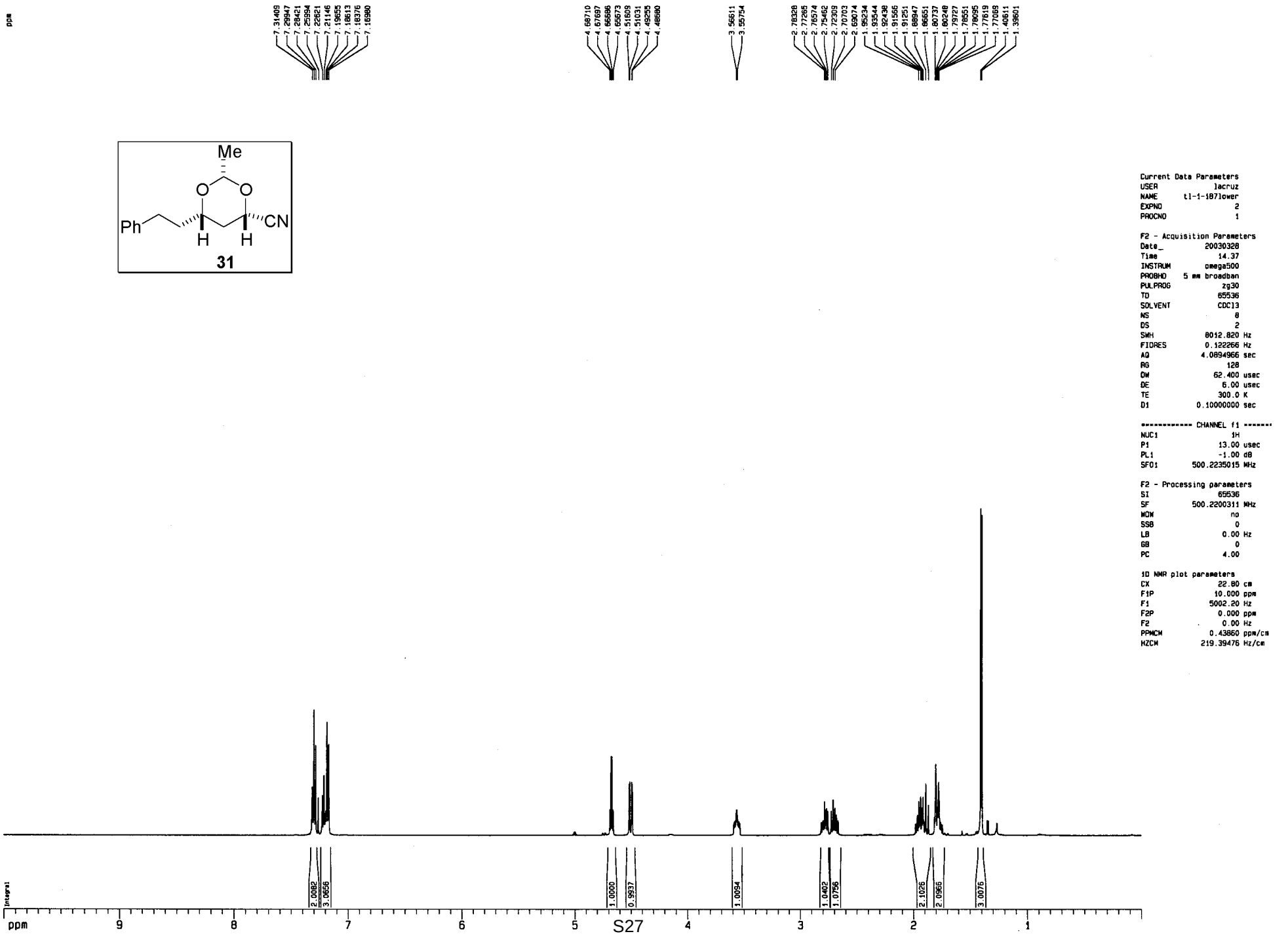
========== CHANNEL f1 =======
NUC1 13C
P1 29.00 usec
PL1 -6.00 dB
SFO1 125.7942048 MHz

========== CHANNEL f2 =======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 120.00 dB
PL12 14.40 dB
SFO2 500.2230013 MHz

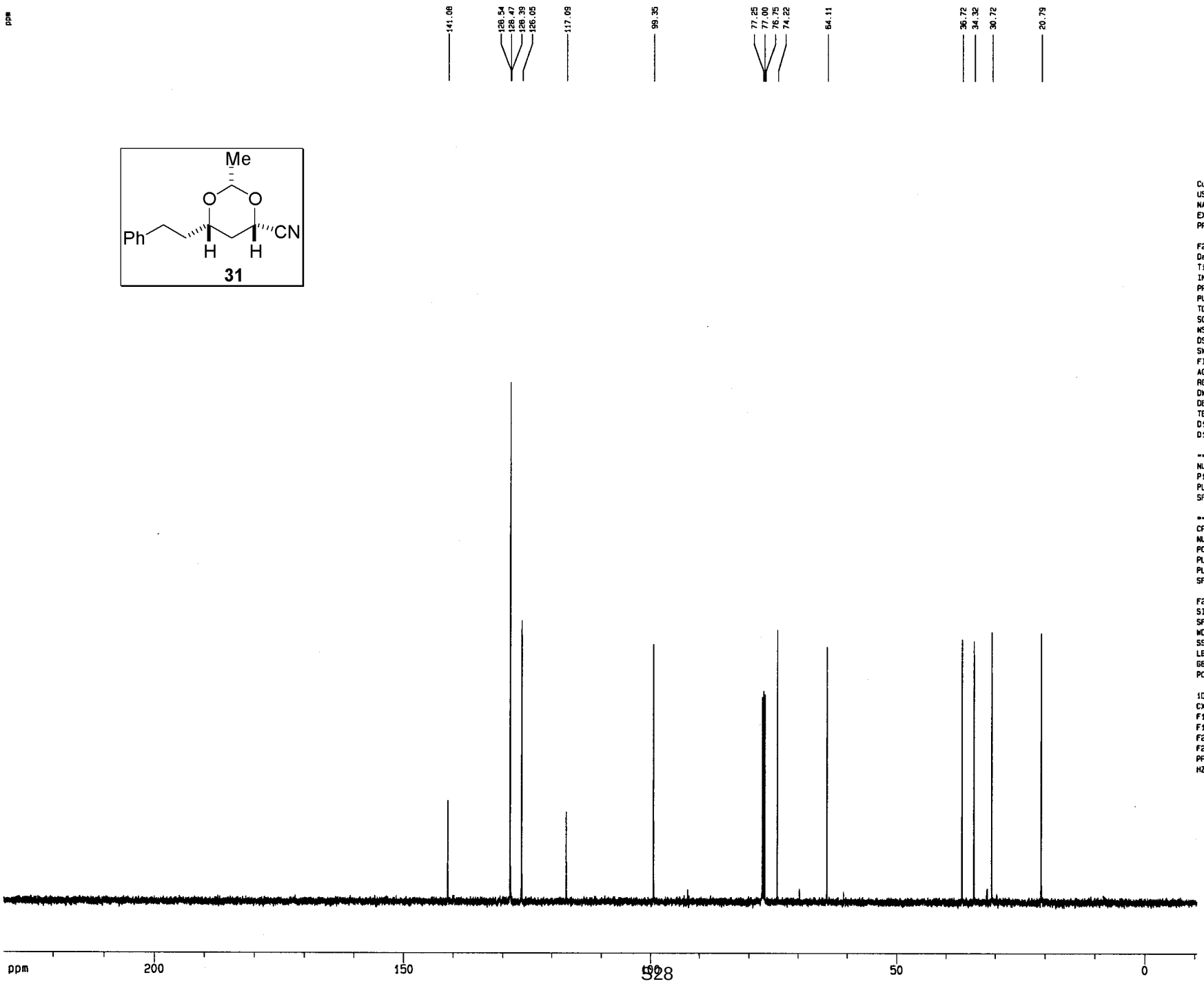
F2 - Processing parameters
SI 65536
SF 125.7804309 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
F1P 200.000 ppm
F1 25156.09 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 8.77193 ppm/cm
HZCM 1103.33716 Hz/cm

1H spectrum


ppm
7.31409
7.29947
7.28421
7.25994
7.22621
7.21146
7.19655
7.18613
7.18376
7.16980
4.68710
4.67697
4.66686
4.65673
4.51609
4.51031
4.49255
4.48680
3.56611
3.55754
2.78328
2.77265
2.76574
2.75462
2.72309
2.70703
2.69074
1.95234
1.93544
1.92438
1.91566
1.91251
1.88947
1.86651
1.80737
1.80248
1.79727
1.78651
1.78095
1.77619
1.77069
1.40611
1.39601
Me
O
O
Ph
CN
H
H
31
Current Data Parameters
USER lacruz
NAME tl-1-187lower
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20030328
Time 14.37
INSTRUM omega500
PROBHD 5 mm broadban
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 128
DW 62.400 usec
DE 6.00 usec
TE 300.0 K
D1 0.10000000 sec
========== CHANNEL f1 =======
NUC1 1H
P1 13.00 usec
PL1 -1.00 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200311 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 4.00
1D NMR plot parameters
CX 22.80 cm
F1P 10.000 ppm
F1 5002.20 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.43860 ppm/cm
HZCM 219.39476 Hz/cm
Integral
2.0082
3.0656
1.0000
0.9937
1.0094
1.0402
1.0796
2.1026
2.0966
3.0076
ppm
9
8
7
6
5
4
3
2
1

13C spectrum with 1H decoupling



Current Data Parameters

USER	lacruz
NAME	tl-1-187lowcar
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20030328
Time	14.48
INSTRUM	omega500
PROBHD	5 mm broadban
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	418
DS	4
SWH	30303.031 Hz
FIDRES	0.462388 Hz
AQ	1.0813940 sec
RG	4096
DW	16.500 usec
DE	4.50 usec
TE	300.0 K
D1	0.25000000 sec
D11	0.03000000 sec

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

NUC1	13C
P1	26.50 usec
PL1	-6.00 dB
SFO1	125.7942048 MHz

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

CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-1.00 dB
PL12	14.40 dB
SFO2	500.2230013 MHz

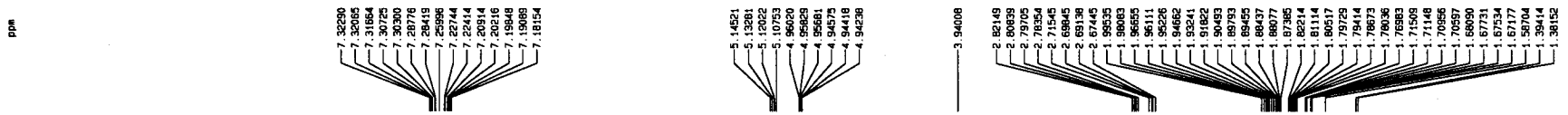
F2 - Processing parameters

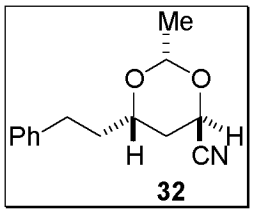
SI	65536
SF	125.7804313 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	2.00

1D NMR plot parameters

CX	22.80 cm
F1P	230.460 ppm
F1	28987.37 Hz
F2P	-10.460 ppm
F2	-1315.67 Hz
PPMCM	10.56668 ppm/cm
HZCM	1329.08093 Hz/cm

1H spectrum





32

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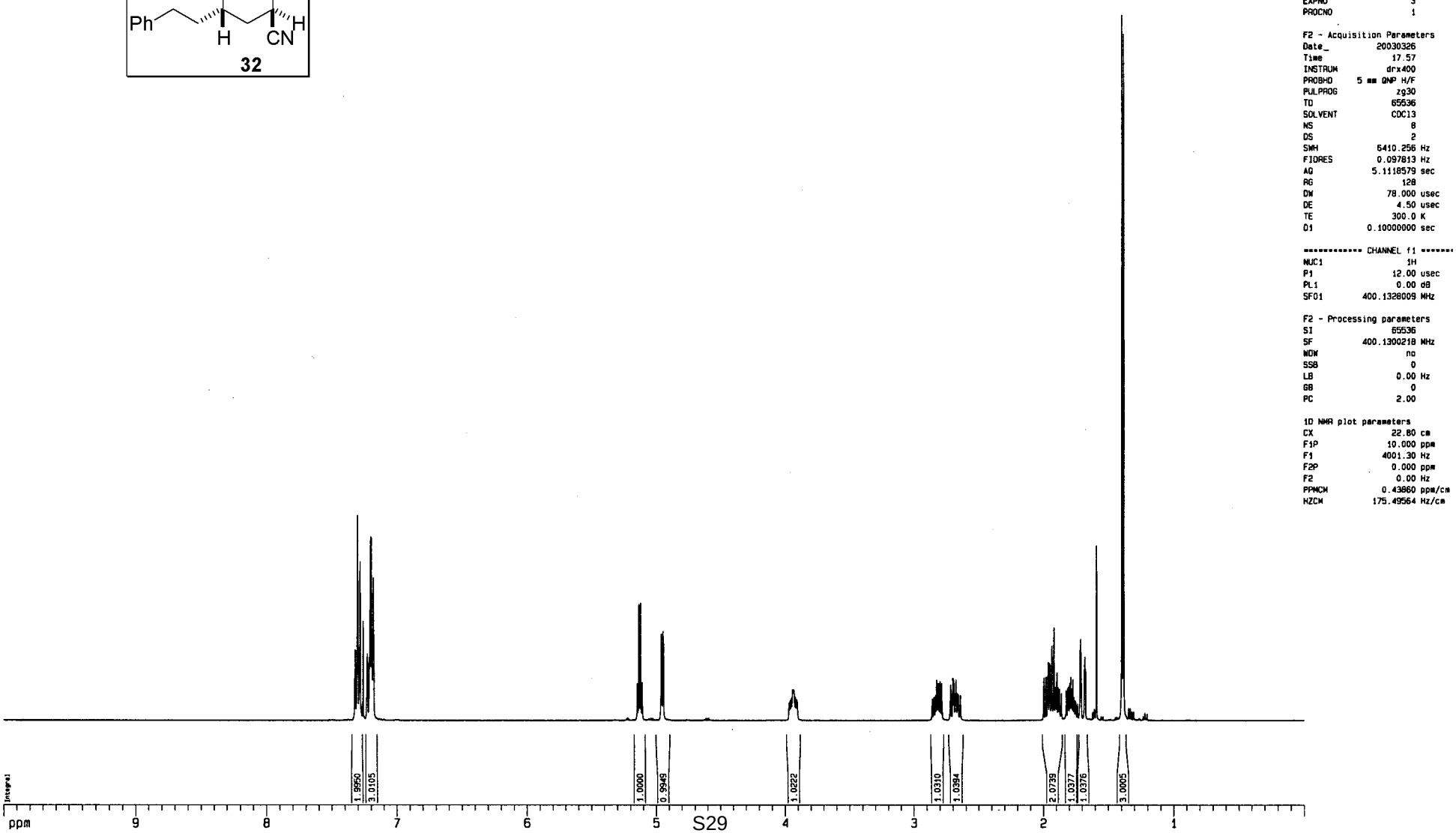
Current Data Parameters
USER              lacruz
NAME              test *
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_          20030326
Time              17.57
INSTRUM         drx400
PROBHD     5 mm QNP H/F
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                   8
DS                   2
SWH           6410.256 Hz
FIDRES        0.097813 Hz
AQ            5.1118579 sec
RG                 128
DW              78.000 usec
DE               4.50 usec
TE              300.0 K
D1           0.10000000 sec

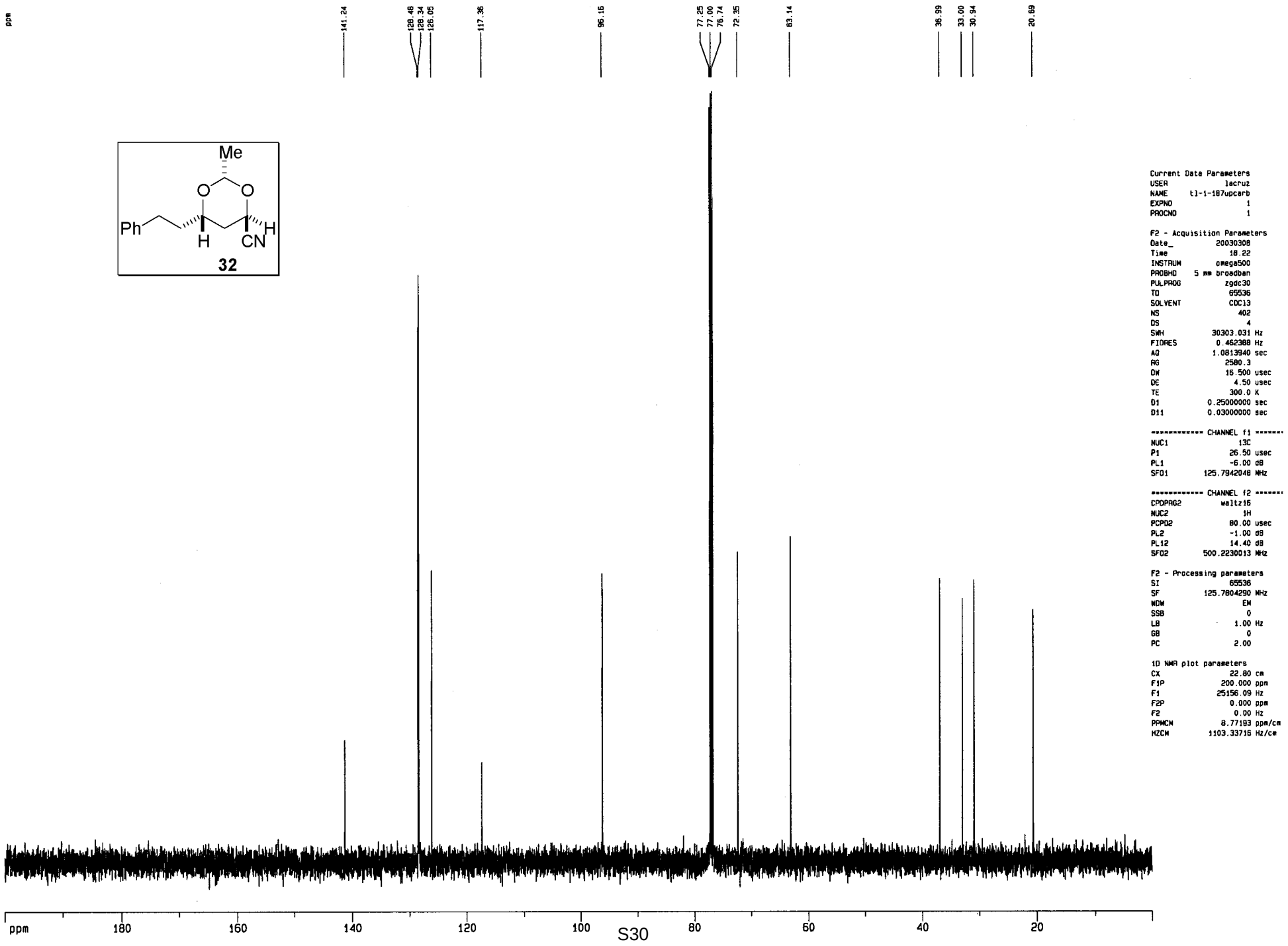
============ CHANNEL f1 =======
NUC1                1H
P1              12.00 usec
PL1              0.00 dB
SF01        400.1328009 MHz

F2 - Processing parameters
SI               65536
SF          400.1300218 MHz
WDW                 no
SSB                  0
LB              0.00 Hz
GB                   0
PC                2.00

1D NMR plot parameters
CX              22.80 cm
F1P            10.000 ppm
F1             4001.30 Hz
F2P             0.000 ppm
F2              0.00 Hz
PPMCM         0.43860 ppm/cm
HZCM        175.49564 Hz/cm
```



13C spectrum with 1H decoupling



Current Data Parameters
USER lacruz
NAME tl-i-187upcarb
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030308
Time 18.22
INSTRUM omega500
PROBHD 5 mm broadban
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 402
DS 4
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 2580.3
DW 16.500 usec
DE 4.50 usec
TE 300.0 K
D1 0.25000000 sec
D11 0.03000000 sec

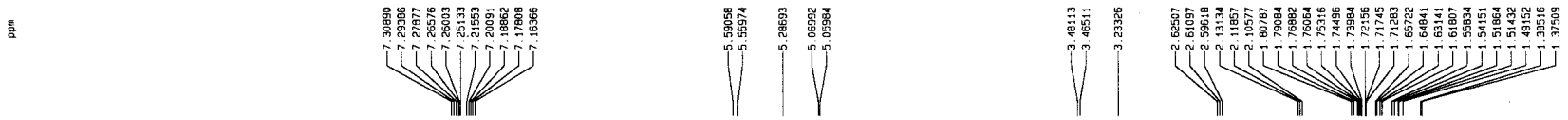
========== CHANNEL f1 ========
NUC1 13C
P1 26.50 usec
PL1 -6.00 dB
SFO1 125.7942048 MHz

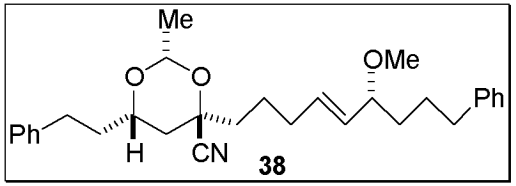
========== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.40 dB
SFO2 500.2230013 MHz

F2 - Processing parameters
SI 65536
SF 125.7804290 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
F1P 200.000 ppm
F1 25156.09 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 8.77193 ppm/cm
HZCM 1103.33716 Hz/cm

1H spectrum





38

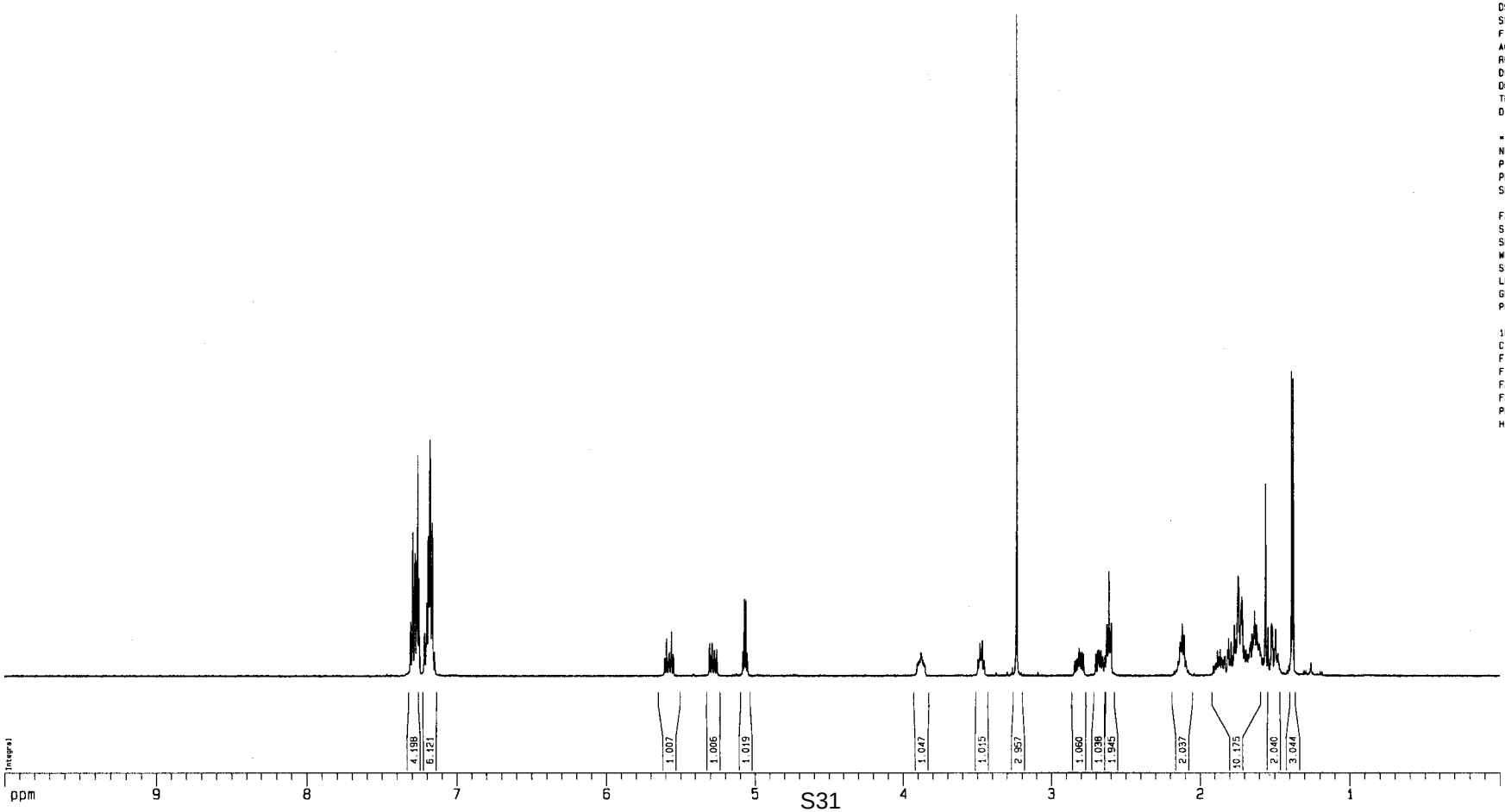
```
Current Data Parameters
USER                lacruz
NAME              tl-1-189
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20030325
Time                 14.37
INSTRUM            omega500
PROBHD     5 mm broadban
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        2
SWH               8012.820 Hz
FIDRES               0.122266 Hz
AQ                4.0894966 sec
RG                      256
DW                   62.400 usec
DE                    6.00 usec
TE                   300.0 K
D1              0.10000000 sec

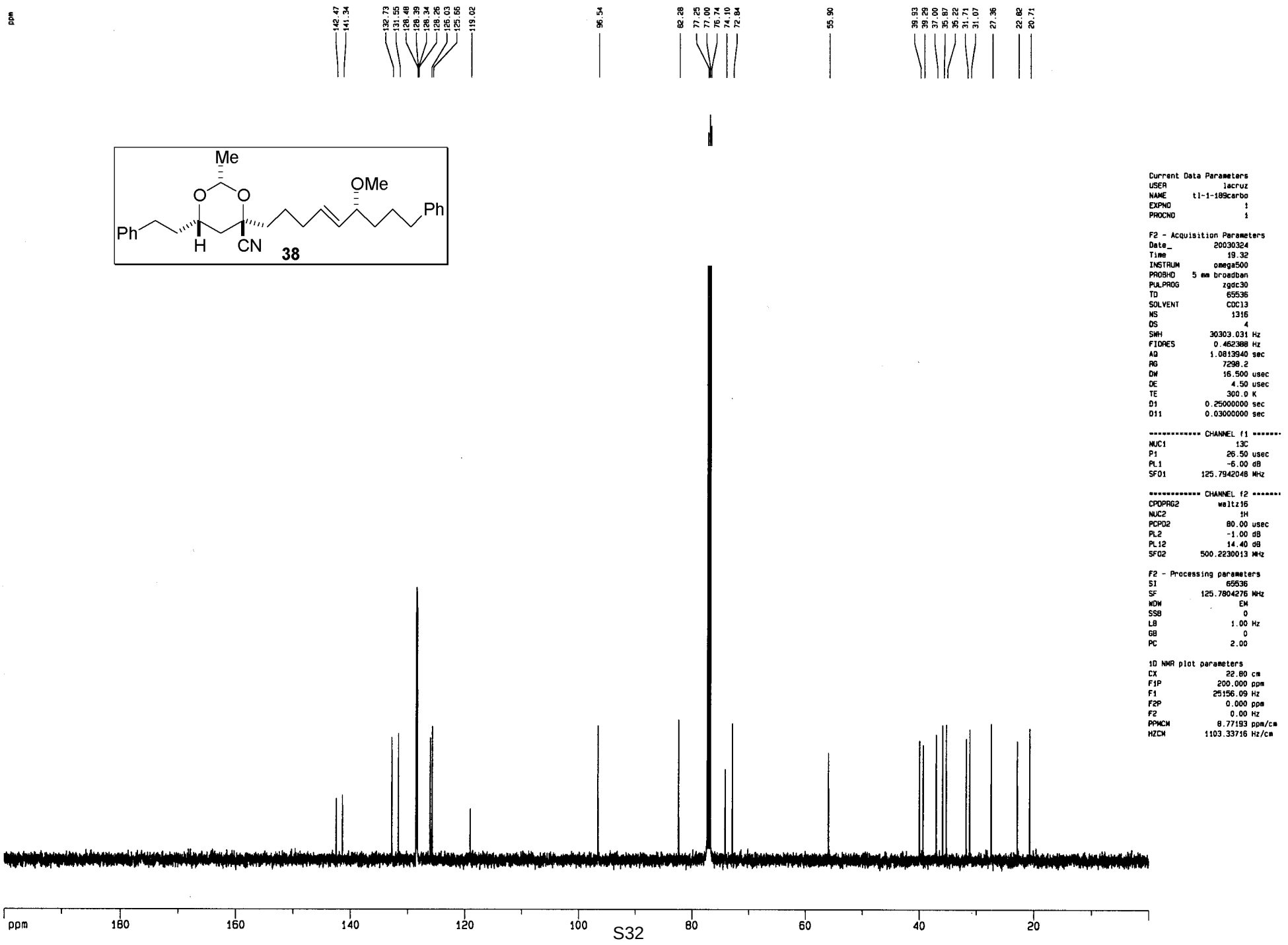
========== CHANNEL f1 =======
NUC1                     1H
P1                   13.00 usec
PL1                  -1.00 dB
SFO1            500.2235015 MHz

F2 - Processing parameters
SI                    65536
SF              500.2200313 MHz
WDW                      no
SSB                       0
LB                    0.00 Hz
GB                        0
PC                    4.00

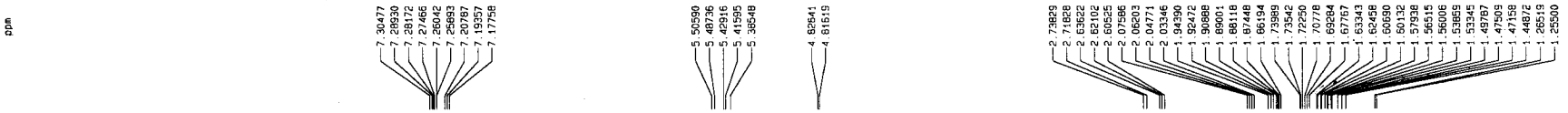
1D NMR plot parameters
CX                   22.80 cm
F1P                 10.000 ppm
F1                5002.20 Hz
F2P                  0.000 ppm
F2                   0.00 Hz
PPMCM             0.43860 ppm/cm
HZCM            219.39476 Hz/cm
```

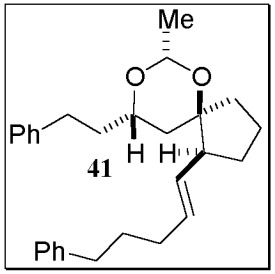


13C spectrum with 1H decoupling



1H spectrum





Current Data Parameters

USER	lacruz
NAME	tl-1-193
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20030320
Time	16.19
INSTRUM	omega500
PROBHD	5 mm broadban
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	8012.820 Hz
FIDRES	0.122266 Hz
AQ	4.0894966 sec
RG	128
DW	62.400 usec
DE	6.00 usec
TE	300.0 K
D1	0.10000000 sec

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

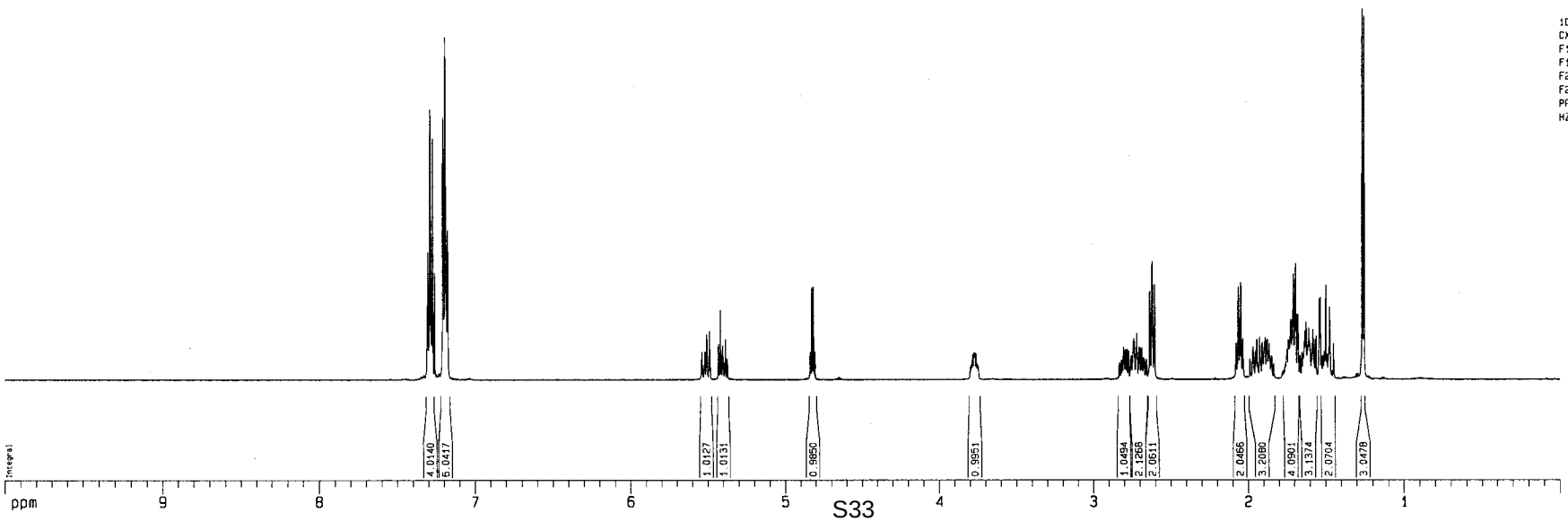
NUC1	1H
P1	13.00 usec
PL1	-1.00 dB
SFO1	500.2235015 MHz

F2 - Processing parameters

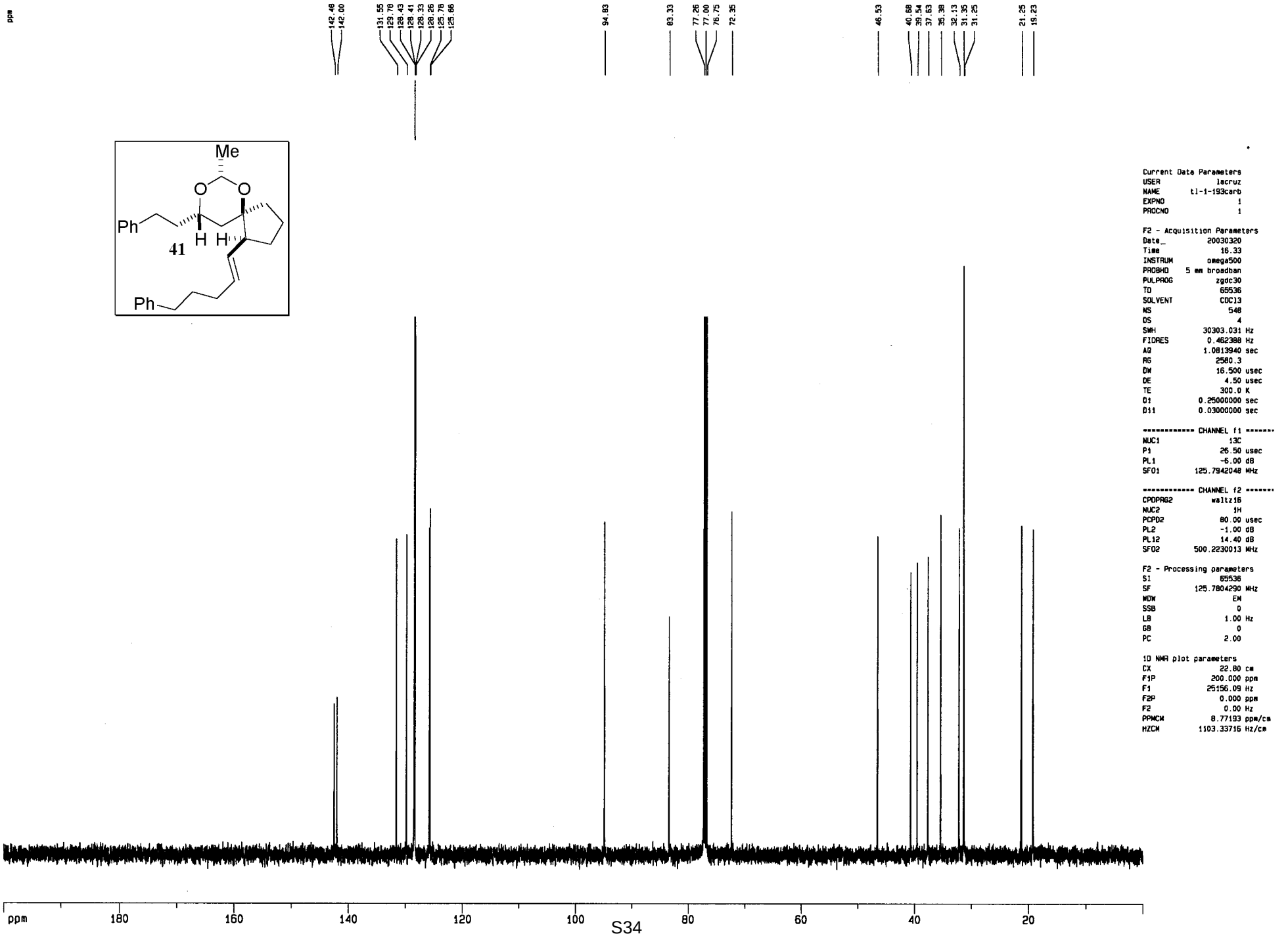
SI	65536
SF	500.2200313 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	4.00

1D NMR plot parameters

CX	22.80 cm
F1P	10.000 ppm
F1	5002.20 Hz
F2P	0.000 ppm
F2	0.00 Hz
PPMCM	0.43860 ppm/cm
HZCM	219.39476 Hz/cm



13C spectrum with 1H decoupling



Current Data Parameters
USER lacruz
NAME tl-1-193carb
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030320
Time 16.33
INSTRUM omega500
PROBHD 5 mm broadban
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 548
DS 4
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 2580.3
DW 16.500 usec
DE 4.50 usec
TE 300.0 K
D1 0.25000000 sec
D11 0.03000000 sec

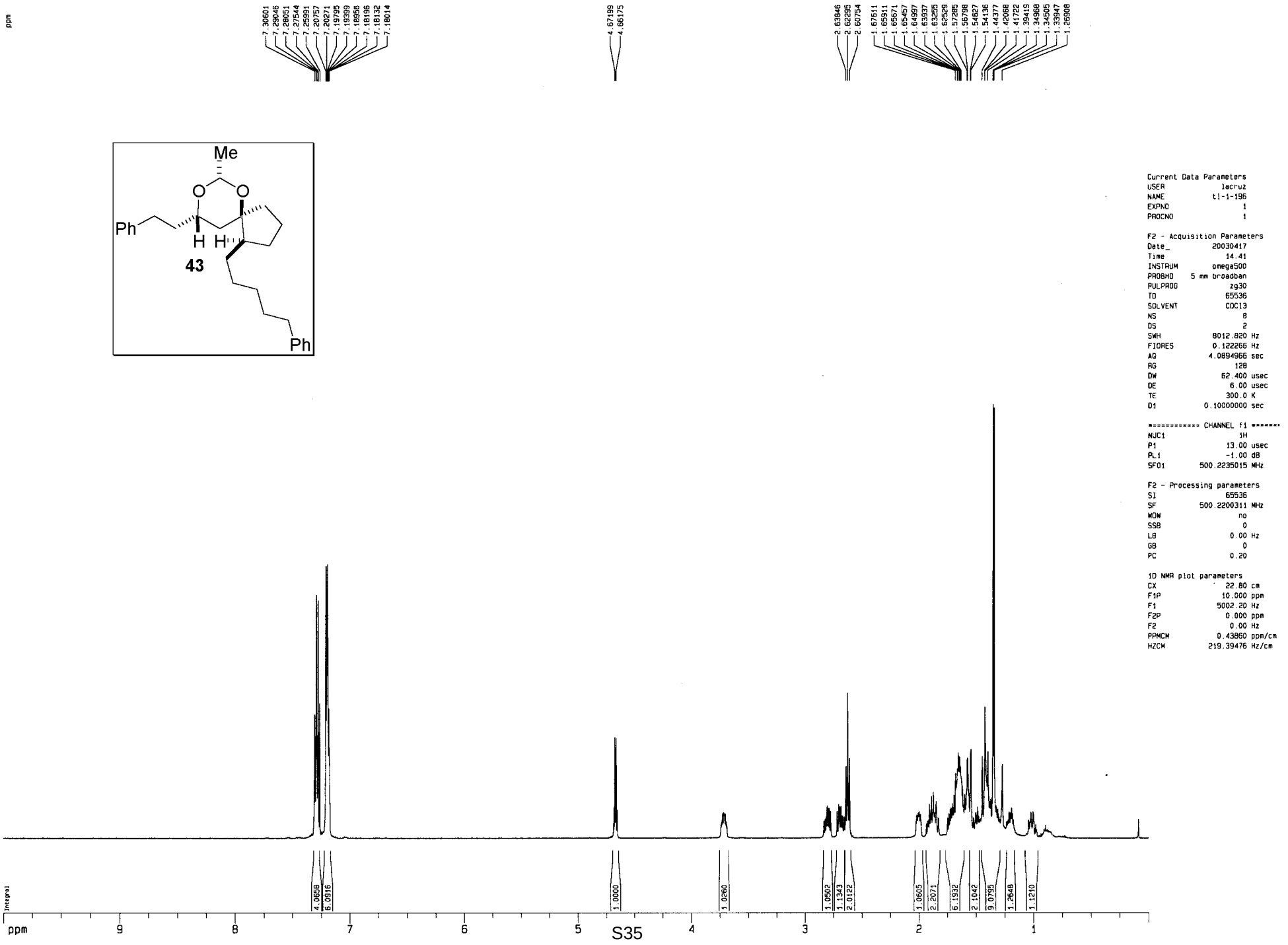
========== CHANNEL f1 =======
NUC1 13C
P1 26.50 usec
PL1 -6.00 dB
SFO1 125.7942048 MHz

========== CHANNEL f2 =======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.40 dB
SFO2 500.2230013 MHz

F2 - Processing parameters
SI 65536
SF 125.7804290 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
F1P 200.000 ppm
F1 25156.09 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 8.77193 ppm/cm
HZCM 1103.33716 Hz/cm

1H spectrum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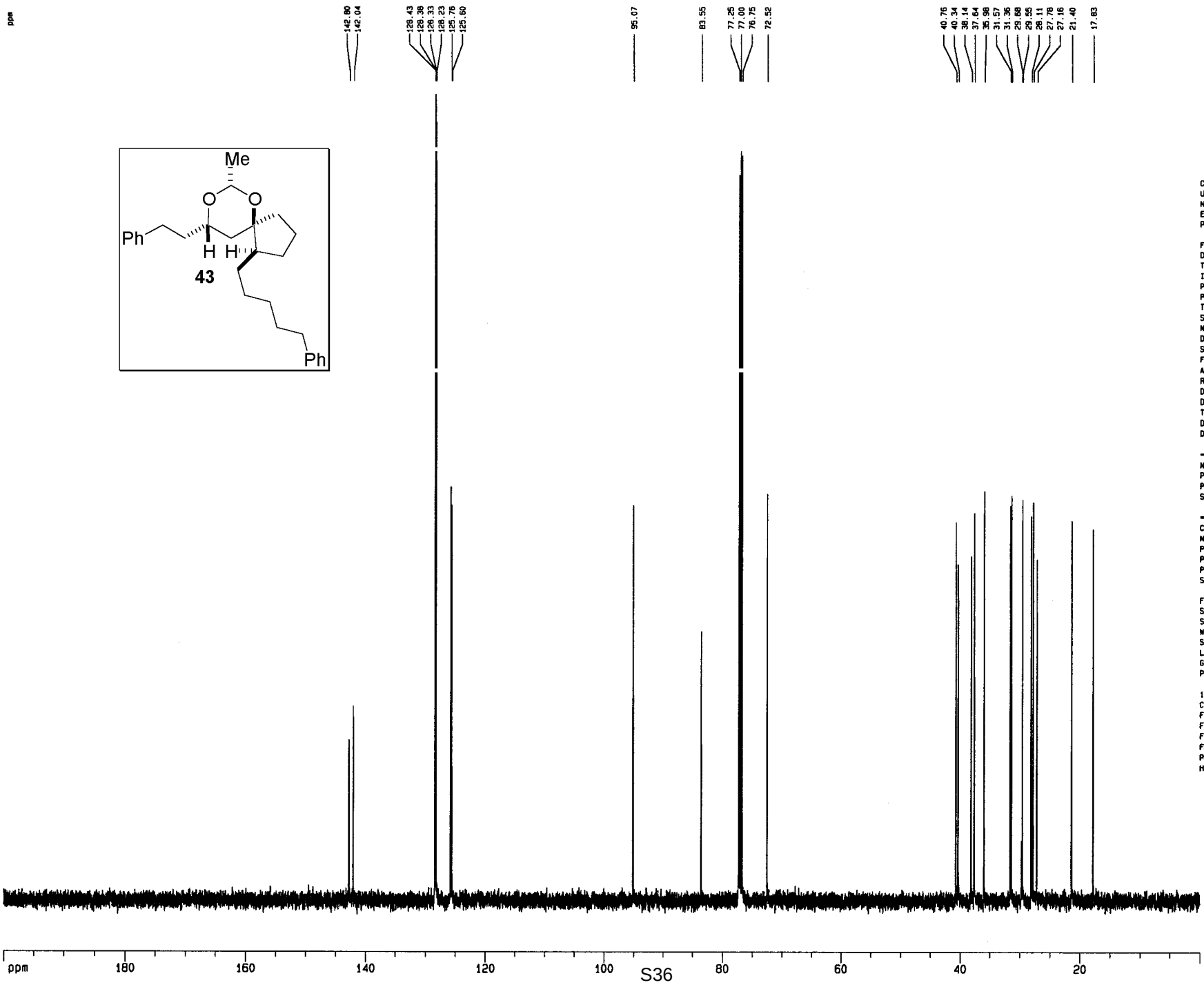
7.20271
7.19795
7.19399
7.18956
7.18196
7.18132
7.18014
4.67199
4.66175
2.63846
2.62295
2.60754
1.67611
1.65911
1.65671
1.65457
1.64997
1.63937
1.63255
1.62529
1.57285
1.56798
1.54627
1.54136
1.44377
1.42068
1.41722
1.39419
1.34968
1.34505
1.33947
1.26908
Me
O
O
Ph
H
H
43
Ph
Current Data Parameters
USER lacruz
NAME tl-1-196
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20030417
Time 14.41
INSTRUM omega500
PROBHD 5 mm broadban
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 128
DW 62.400 usec
DE 6.00 usec
TE 300.0 K
D1 0.10000000 sec
========== CHANNEL f1 =======
NUC1 1H
P1 13.00 usec
PL1 -1.00 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200311 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 0.20
1D NMR plot parameters
CX 22.80 cm
F1P 10.000 ppm
F1 5002.20 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.43860 ppm/cm
HZCM 219.39476 Hz/cm
Integral
4.0658
6.0916
1.0000
1.0260
1.0502
1.1343
2.0122
1.0605
2.2071
6.1932
2.1042
9.0795
1.2648
1.1210
ppm
9
8
7
6
5
4
3
2
1

13C spectrum with 1H decoupling



Current Data Parameters

USER	lacruz
NAME	tl-1-196
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20030417
Time	14.48
INSTRUM	omega500
PROBHD	5 mm broadban
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	764
DS	4
SWH	30303.031 Hz
FIDRES	0.462388 Hz
AQ	1.0813940 sec
RG	8192
DW	16.500 usec
DE	4.50 usec
TE	300.0 K
D1	0.25000000 sec
D11	0.03000000 sec

---------- CHANNEL f1 -------

NUC1	13C
P1	26.50 usec
PL1	-6.00 dB
SFO1	125.7942048 MHz

---------- CHANNEL f2 -------

CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-1.00 dB
PL12	14.40 dB
SFO2	500.2230013 MHz

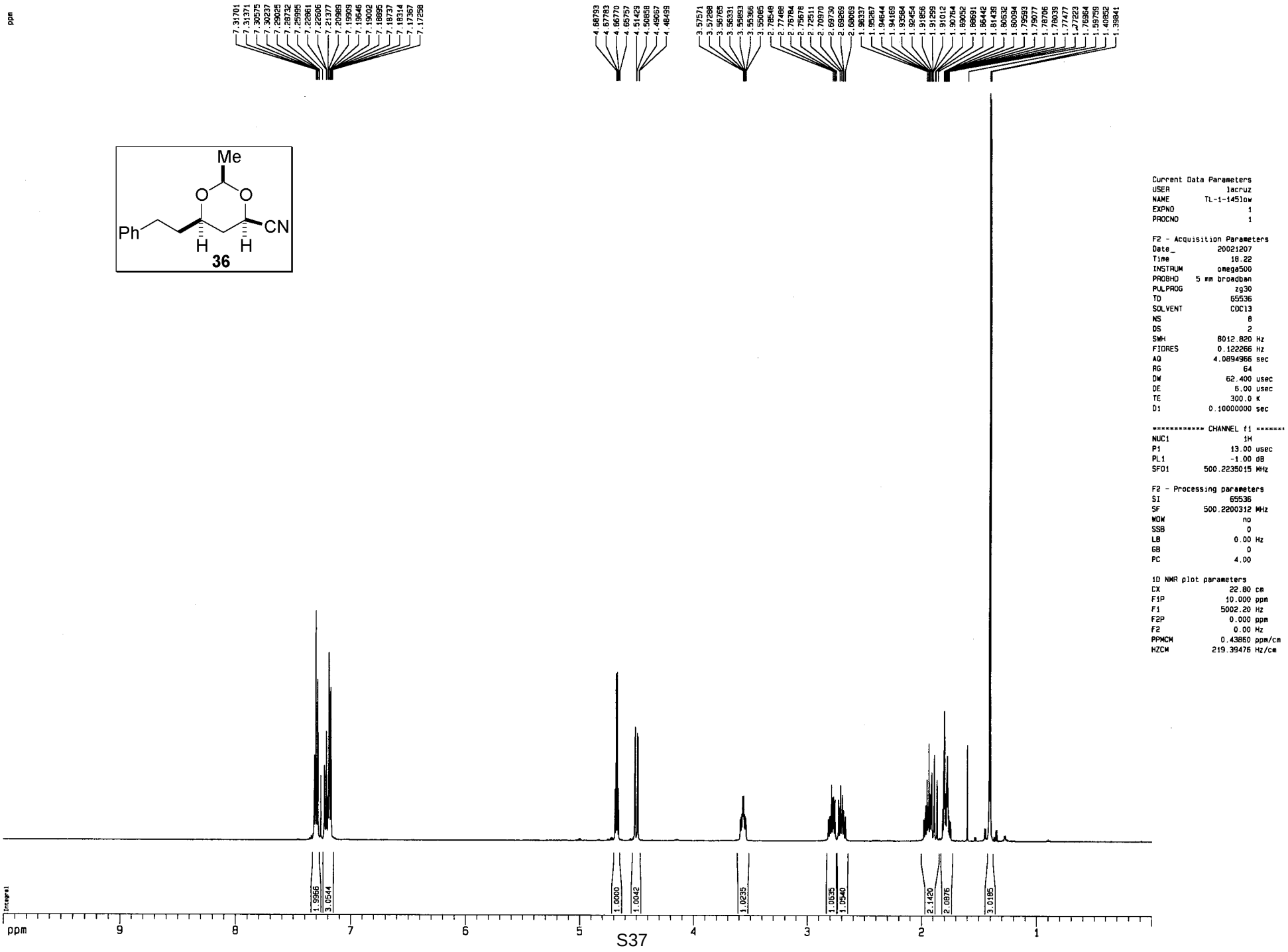
F2 - Processing parameters

SI	65536
SF	125.7804285 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	2.00

1D NMR plot parameters

CX	22.80 cm
F1P	200.000 ppm
F1	25156.09 Hz
F2P	0.000 ppm
F2	0.00 Hz
PPMCM	8.77193 ppm/cm
HZCM	1103.33716 Hz/cm

1H spectrum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7.30575
7.30237
7.29025
7.28732
7.25995
7.22861
7.22606
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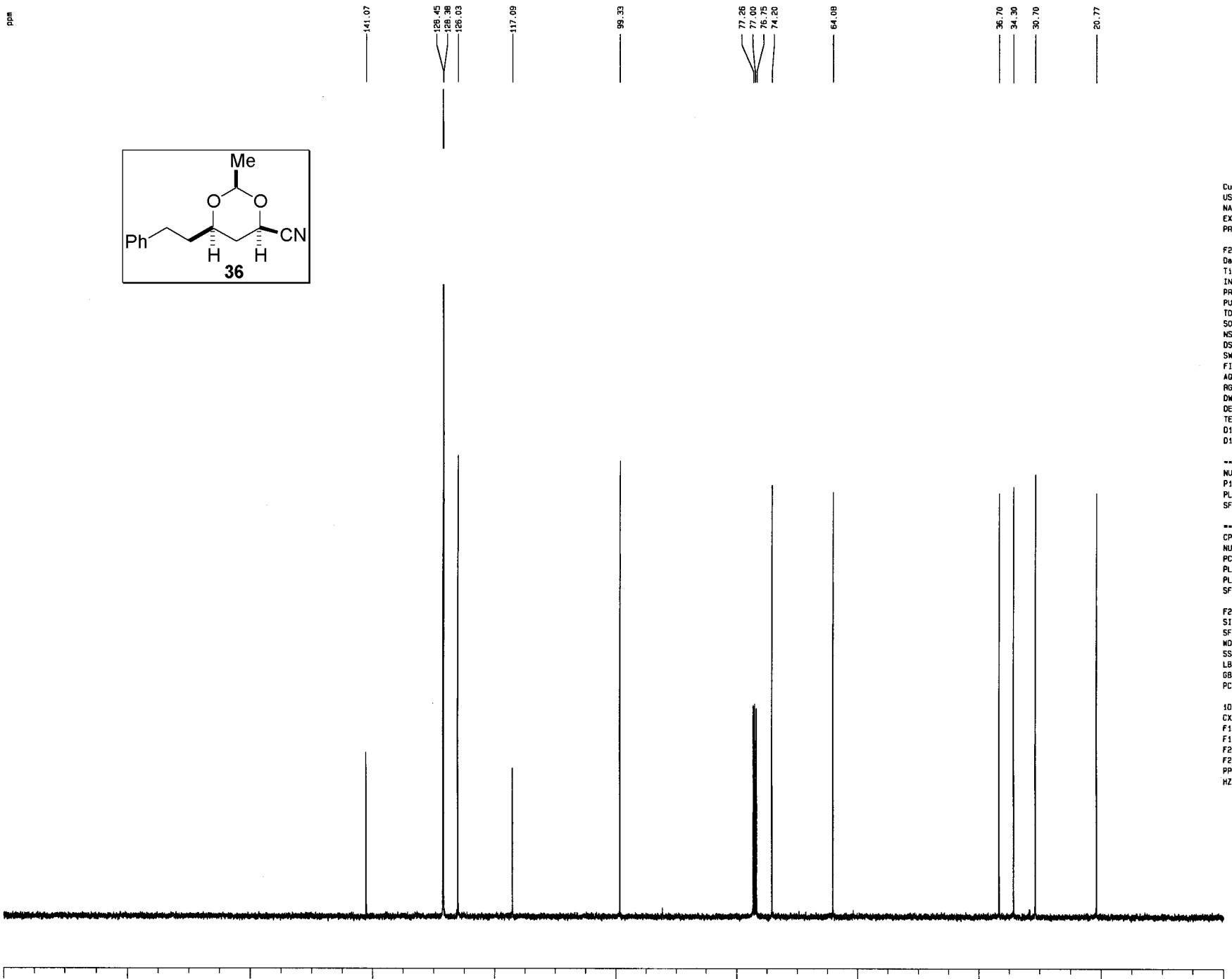
7.20969
7.19569
7.19646
7.19002
7.18895
7.18737
7.18314
7.17367
7.17258
4.68793
4.67783
4.66770
4.65757
4.51429
4.50858
4.49067
4.48499
3.57571
3.57288
3.56765
3.56331
3.55893
3.55366
3.55065
2.78548
2.77488
2.76784
2.75678
2.72511
2.70970
2.69730
2.69269
2.68069
1.96337
1.95567
1.94644
1.94169
1.93584
1.92454
1.91956
1.91259
1.91012
1.90764
1.89052
1.88691
1.86442
1.81438
1.80532
1.80094
1.79593
1.79077
1.78706
1.78039
1.77477
1.77223
1.76964
1.59759
1.40852
1.39841
Me
O
O
Ph
CN
H
H
36
Current Data Parameters
USER lacruz
NAME TL-1-145low
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20021207
Time 18.22
INSTRUM omega500
PROBHD 5 mm broadban
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 64
DW 62.400 usec
DE 6.00 usec
TE 300.0 K
D1 0.10000000 sec
CHANNEL f1
NUC1 1H
P1 13.00 usec
PL1 -1.00 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200312 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 4.00
1D NMR plot parameters
CX 22.80 cm
F1P 10.000 ppm
F1 5002.20 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.43860 ppm/cm
HZCM 219.39476 Hz/cm
Integral
1.9966
3.0544
1.0000
1.0042
1.0235
1.0535
1.0540
2.1420
2.0876
3.0185
ppm
9
8
7
6
5
4
3
2
1

13C spectrum with 1H decoupling



Current Data Parameters
USER lacruz
NAME TL-1-145lowcar
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20021207
Time 18.38
INSTRUM omega500
PROBHD 5 mm broadban
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 749
DS 4
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 6502
DW 16.500 usec
DE 4.50 usec
TE 300.0 K
D1 0.25000000 sec
D11 0.03000000 sec

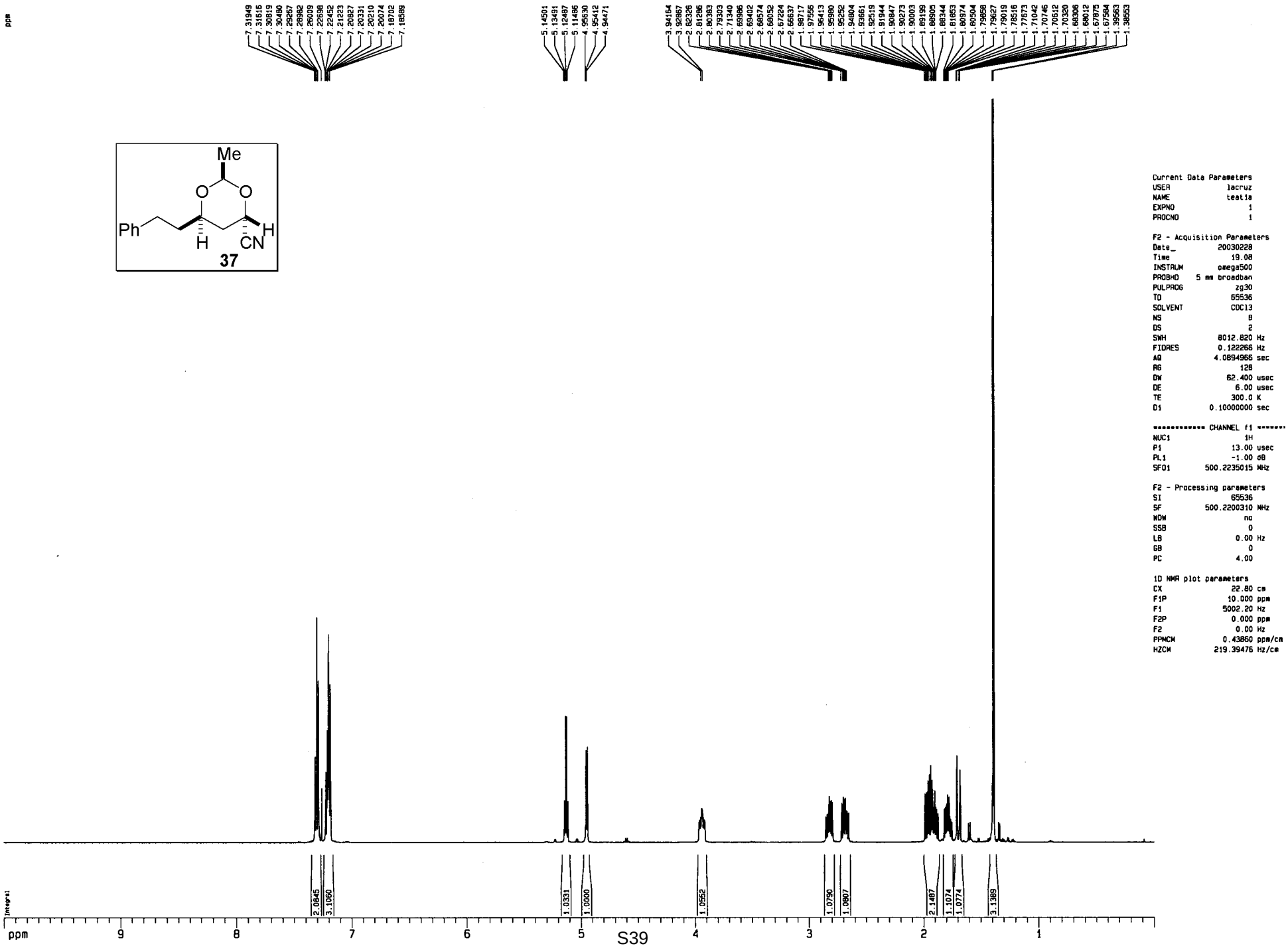
========== CHANNEL f1 ========
NUC1 13C
P1 29.00 usec
PL1 -6.00 dB
SFO1 125.7942048 MHz

========== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 120.00 dB
PL12 14.40 dB
SFO2 500.2230013 MHz

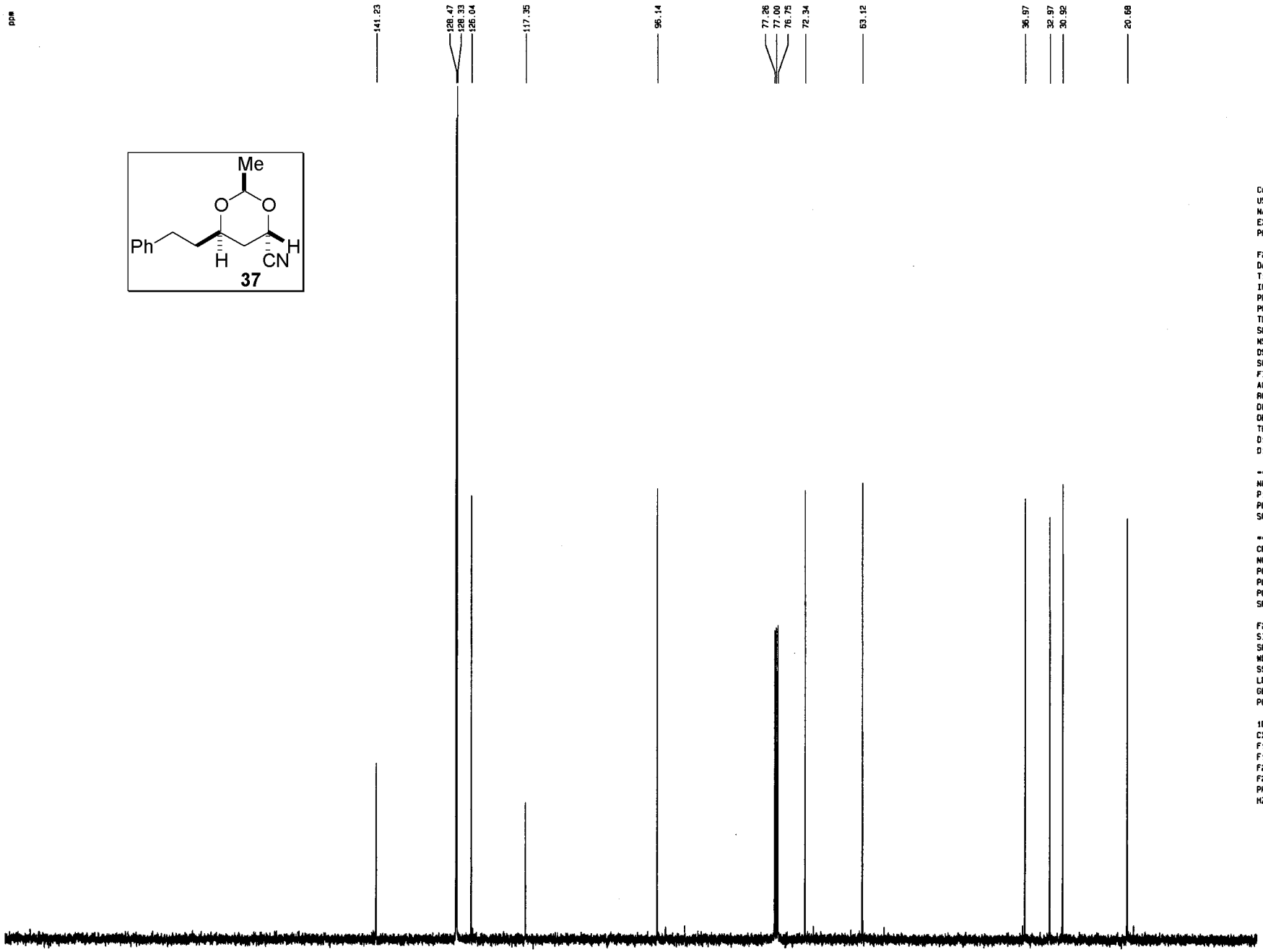
F2 - Processing parameters
SI 65536
SF 125.7804346 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
F1P 200.000 ppm
F1 25156.09 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 8.77193 ppm/cm
HZCM 1103.33716 Hz/cm

1H spectrum


ppm
7.31949
7.31616
7.30819
7.30480
7.29267
7.28982
7.26009
7.22698
7.22452
7.21223
7.20827
7.20331
7.20210
7.20074
7.18702
7.18589
5.14501
5.13491
5.12487
5.11486
4.95630
4.95412
4.94471
3.94164
3.92867
2.82326
2.81286
2.80383
2.79303
2.71340
2.69986
2.69402
2.68574
2.68052
2.67224
2.66637
1.98717
1.97556
1.96413
1.95980
1.95252
1.94804
1.93661
1.92519
1.91944
1.90847
1.90273
1.90003
1.89199
1.88805
1.88344
1.81653
1.80974
1.80504
1.79858
1.79627
1.79019
1.78516
1.77673
1.77042
1.70746
1.70612
1.70320
1.68306
1.68012
1.67875
1.67584
1.39563
1.38553
Me
O
O
Ph
H
CN
H
37
Current Data Parameters
USER lacruz
NAME teat1a
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20030228
Time 19.08
INSTRUM omega500
PROBHD 5 mm broadban
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 128
DW 62.400 usec
DE 6.00 usec
TE 300.0 K
D1 0.10000000 sec
CHANNEL f1
NUC1 1H
P1 13.00 usec
PL1 -1.00 dB
SFO1 500.2235015 MHz
F2 - Processing parameters
SI 65536
SF 500.2200310 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 4.00
1D NMR plot parameters
CX 22.80 cm
F1P 10.000 ppm
F1 5002.20 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.43860 ppm/cm
HZCM 219.39476 Hz/cm
Integral
2.0845
3.1060
1.0331
1.0000
1.0552
1.0790
1.0807
2.1497
1.1074
1.0774
3.1389
ppm
9
8
7
6
5
4
3
2
1

13C spectrum with 1H decoupling



Current Data Parameters

USER	lacruz
NAME	tl-1-165upcarb
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20030228
Time	19.37
INSTRUM	omega500
PROBHD	5 mm broadban
PULPROG	zgdc30
TD	65536
SOLVENT	CDCl3
NS	569
DS	4
SWH	30303.031 Hz
FIDRES	0.462388 Hz
AQ	1.0813940 sec
RG	4597.6
DW	16.500 usec
DE	4.50 usec
TE	300.0 K
D1	0.25000000 sec
D11	0.03000000 sec

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

NUC1	13C
P1	26.50 usec
PL1	-6.00 dB
SFO1	125.7942048 MHz

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

CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-1.00 dB
PL12	14.40 dB
SFO2	500.2230013 MHz

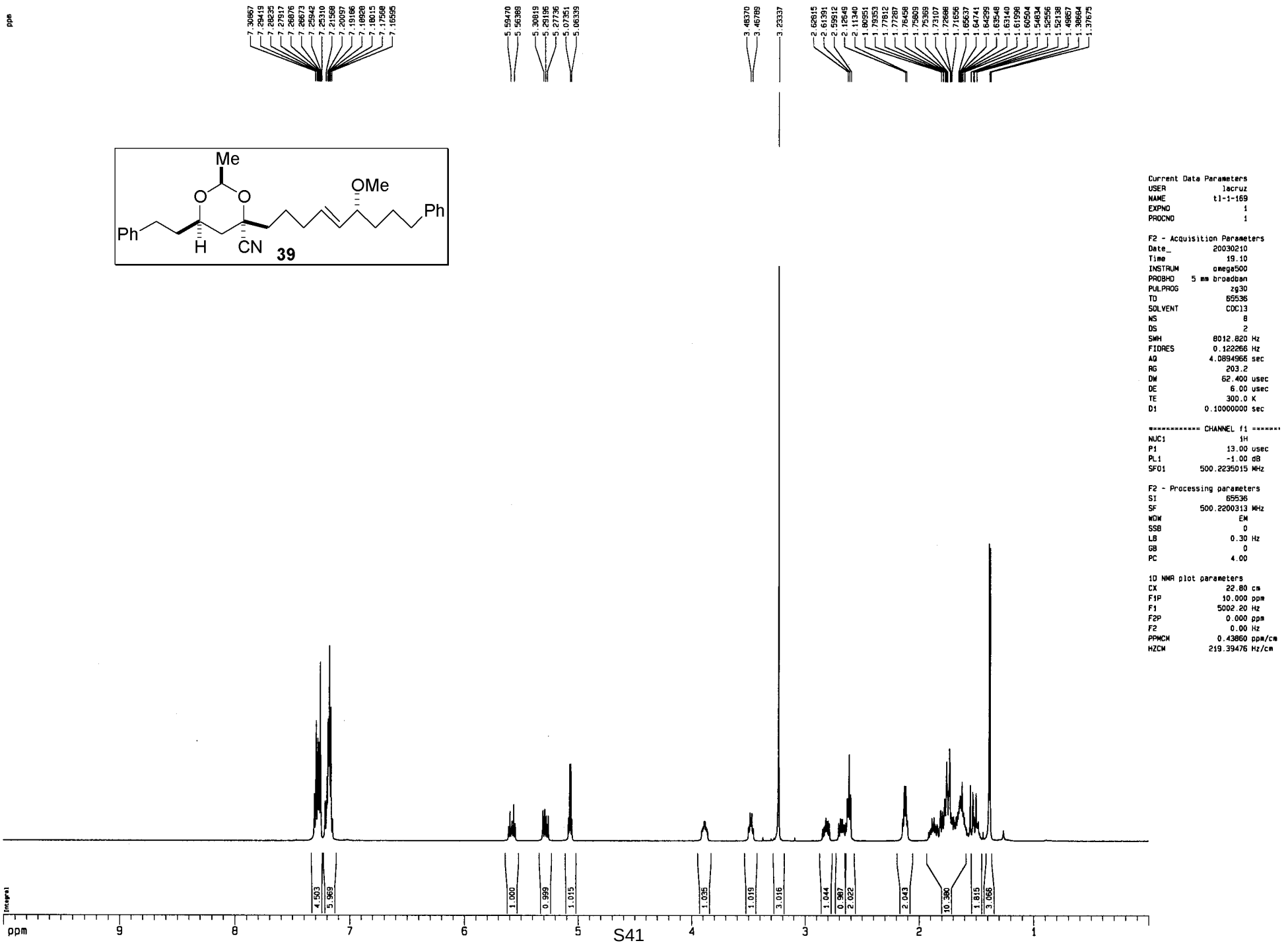
F2 - Processing parameters

SI	65536
SF	125.7804318 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	2.00

1D NMR plot parameters

CX	22.80 cm
F1P	200.000 ppm
F1	25156.09 Hz
F2P	0.000 ppm
F2	0.00 Hz
PPMCM	8.77193 ppm/cm
HZCM	1103.33716 Hz/cm

1H spectrum



Current Data Parameters

USER	lacruz
NAME	tl-1-169
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20030210
Time	19.10
INSTRUM	omega500
PROBHD	5 mm broadban
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	8012.820 Hz
FIDRES	0.122266 Hz
AQ	4.0894966 sec
RG	203.2
DW	62.400 usec
DE	6.00 usec
TE	300.0 K
D1	0.10000000 sec

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

NUC1	1H
P1	13.00 usec
PL1	-1.00 dB
SFO1	500.2235015 MHz

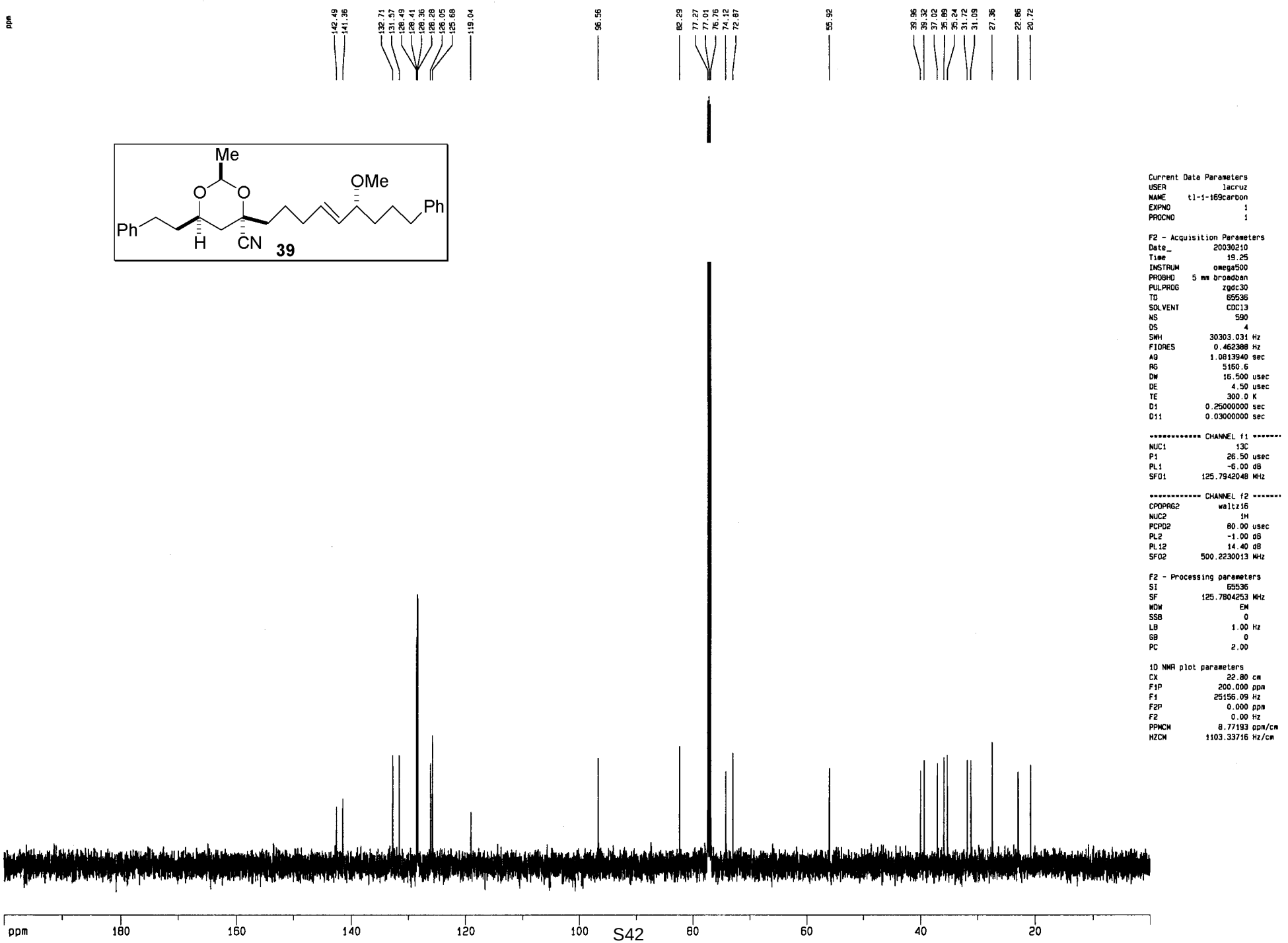
F2 - Processing parameters

SI	65536
SF	500.2200313 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	4.00

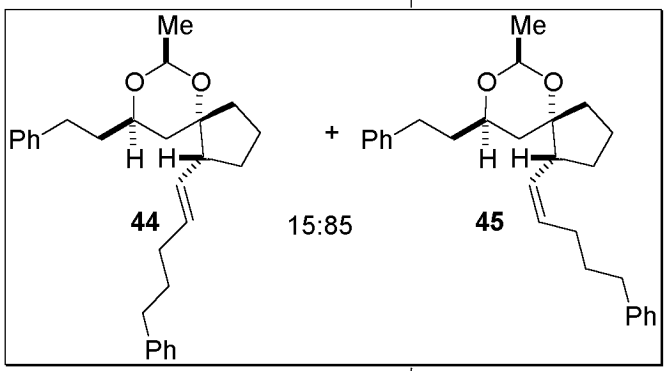
1D NMR plot parameters

CX	22.80 cm
F1P	10.000 ppm
F1	5002.20 Hz
F2P	0.000 ppm
F2	0.00 Hz
PPMCM	0.43860 ppm/cm
HZCM	219.39476 Hz/cm

13C spectrum with 1H decoupling



1H spectrum



Current Data Parameters
USER lacruz
NAME tl-1-177pure
EXPNO 2
PROCNO 1

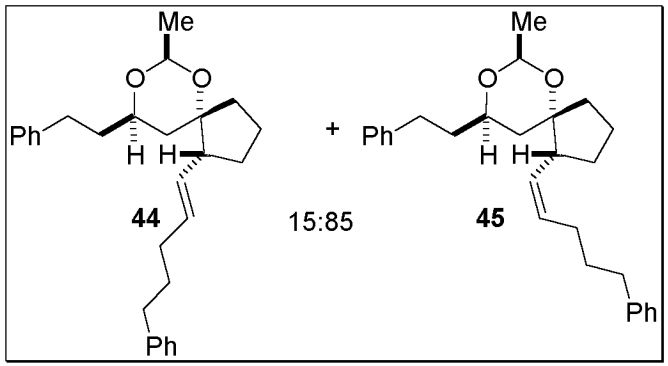
F2 - Acquisition Parameters
Date_ 20030215
Time 16.18
INSTRUM omega500
PROBHD 5 mm broadban
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 574.7
DW 62.400 usec
DE 6.00 usec
TE 300.0 K
D1 0.10000000 sec

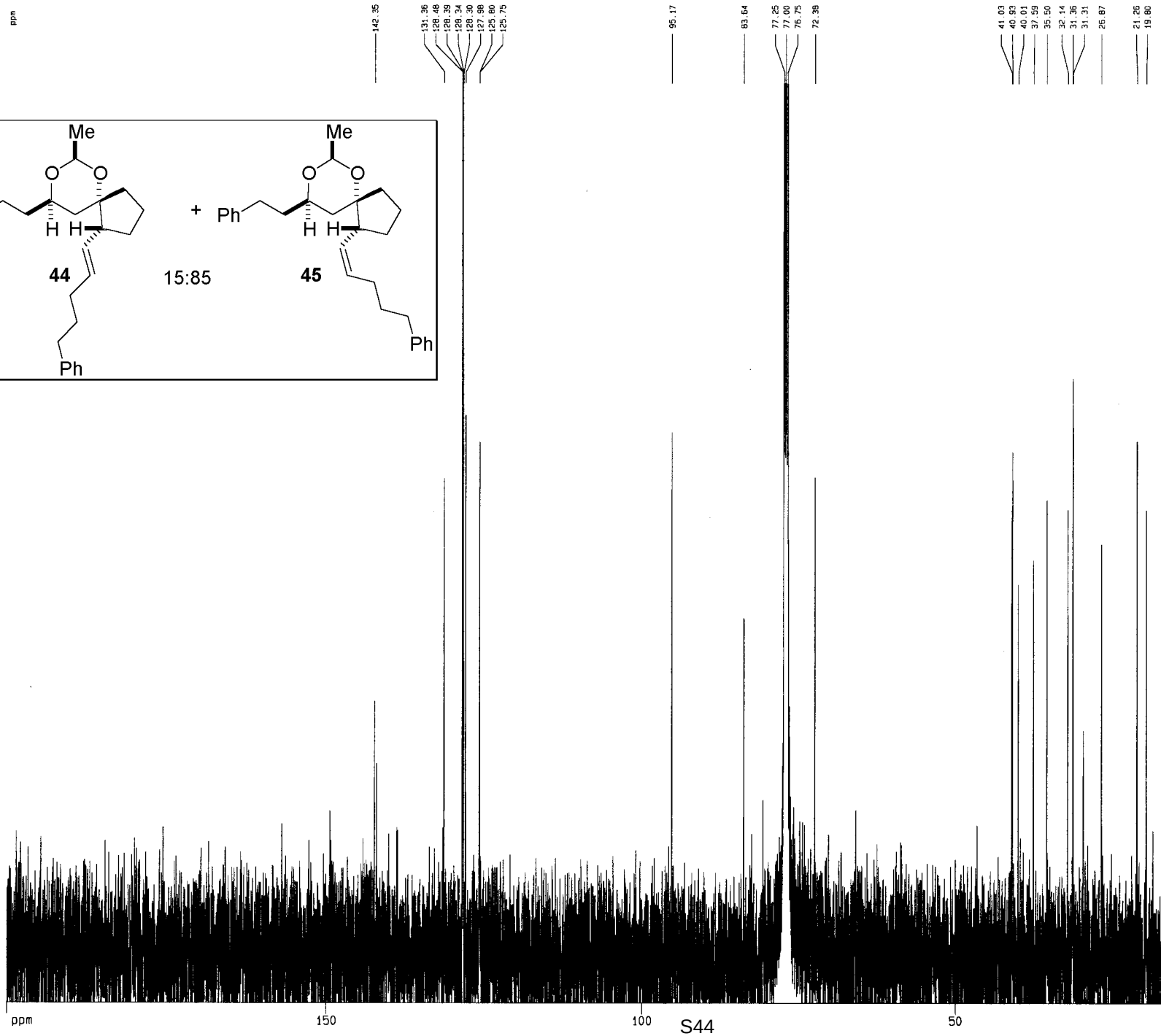
========== CHANNEL f1 ======
NUC1 1H
P1 13.00 usec
PL1 -1.00 dB
SFO1 500.2235015 MHz

F2 - Processing parameters
SI 65536
SF 500.2200312 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.80 cm
F1P 10.000 ppm
F1 5002.20 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.43860 ppm/cm
HZCM 219.39476 Hz/cm

13C spectrum with 1H decoupling






```
Current Data Parameters
USER              lacruz
NAME        tl-1-176carbo
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20030209
Time               7.54
INSTRUM         omega500
PROBHD    5 mm broadban
PULPROG          zgdc30
TD                65536
SOLVENT           CDCl3
NS                21504
DS                    4
SWH           30303.031 Hz
FIDRES        0.462388 Hz
AQ            1.0813940 sec
RG               2896.3
DW               16.500 usec
DE                4.50 usec
TE              300.0 K
D1            0.25000000 sec
D11           0.03000000 sec

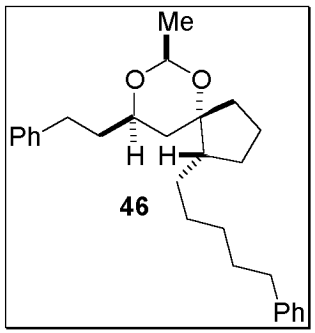
========== CHANNEL f1 =======
NUC1               13C
P1               26.50 usec
PL1              -6.00 dB
SFO1        125.7942048 MHz

========== CHANNEL f2 =======
CPDPRG2          waltz16
NUC2                1H
PCPD2            80.00 usec
PL2              -1.00 dB
PL12             14.40 dB
SFO2        500.2230013 MHz

F2 - Processing parameters
SI                65536
SF          125.7804258 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
F1P              200.000 ppm
F1              25156.09 Hz
F2P                0.000 ppm
F2                 0.00 Hz
PPMCM          8.77193 ppm/cm
HZCM         1103.33716 Hz/cm
```

1H spectrum



Current Data Parameters
USER lacruz
NAME tl-1-195
EXPNO 1
PROCNO 1

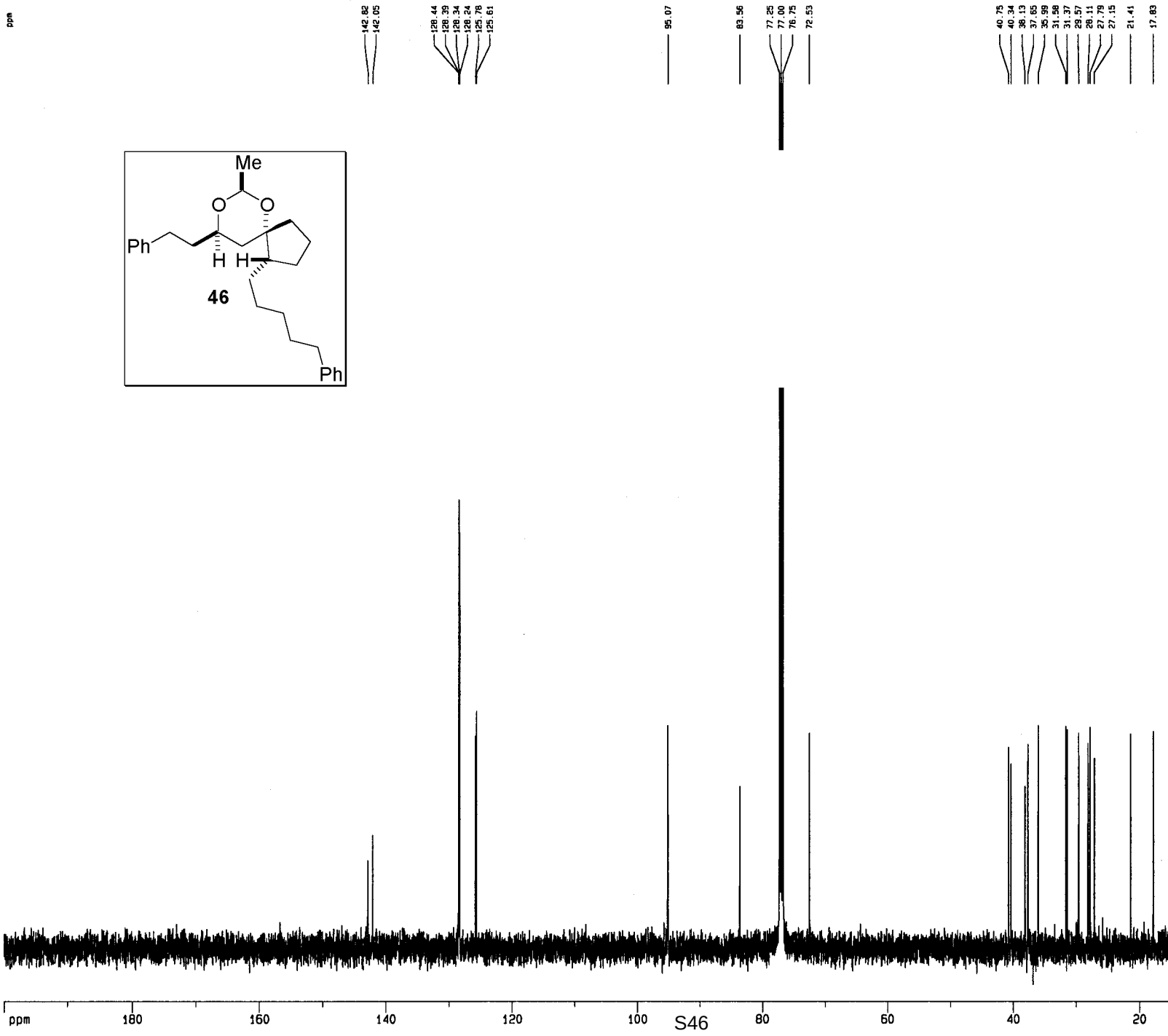
F2 - Acquisition Parameters
Date_ 20030415
Time 13.41
INSTRUM omega500
PROBHD 5 mm broadban
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 48
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 362
DW 62.400 usec
DE 6.00 usec
TE 300.0 K
D1 0.10000000 sec

========== CHANNEL f1 =======
NUC1 1H
P1 13.00 usec
PL1 -1.00 dB
SFO1 500.2235015 MHz

F2 - Processing parameters
SI 65536
SF 500.2200315 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 4.00

1D NMR plot parameters
CX 22.80 cm
F1P 10.000 ppm
F1 5002.20 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.43850 ppm/cm
HZCM 219.39476 Hz/cm

13C spectrum with 1H decoupling



Current Data Parameters
USER lacruz
NAME t1-1-195
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20030414
Time 19.44
INSTRUM omega500
PROBHD 5 mm broadban
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 3072
DS 4
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 8192
DW 16.500 usec
DE 4.50 usec
TE 300.0 K
D1 0.25000000 sec
D11 0.03000000 sec

========== CHANNEL f1 =======
NUC1 13C
P1 26.50 usec
PL1 -6.00 dB
SFO1 125.7942048 MHz

========== CHANNEL f2 =======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.40 dB
SFO2 500.2230013 MHz

F2 - Processing parameters
SI 65536
SF 125.7804262 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.80 cm
F1P 200.000 ppm
F1 25156.09 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 8.77193 ppm/cm
HZCM 1103.33716 Hz/cm