Enantioselective Synthesis of Tatanans A-C and Reinvestigation of Their Glucokinase-Activating Properties

Qing Xiao,[1] Jeffrey J. Jackson,[1] Joseph M. Bowler,[2] Ashok Basak,[1] Brian G. Miller,[2] Armen Zakarian[1]

[1] Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA 93106, Telephone: (805)-893-3717; Fax: (805)-893-4120; E-mail: zakarian@chem.ucsb.edu

[2] Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306-4390, Telephone: (850)-645-6570; Fax: (850)-644-8281; E-mail: miller@chem.fsu.edu

Supplementary Information

Table of contents

Bioassays

Materials and Methods

Enzyme production

Recombinant human pancreatic glucokinase was produced as an N-terminal hexa-histidine tagged polypeptide in *Escherichia coli* BL21(DE3). Cultures were inoculated to an initial OD_{600} of 0.01 and were grown at 37 °C in Luria-Bertani broth supplemented with ampicillin (150 μg/mL). When the OD_{600} reached 0.8, IPTG (1 mM) was added and the temperature was reduced to 20 °C, where growth was continued for 20 h. Cells were harvested by centrifugation and 5 g of wet cell pellet was resuspended in 17 mL of buffer A containing HEPES (50 mM, pH 7.6), KCl (50 mM), imidazole (25 mM), dithiothreitol (10 mM), and glycerol (25%, w/v). Cells were lysed using a microfluidizer and subjected to centrifugation at 25,000x g at 4 °C. The supernatant was immediately loaded onto a 5 mL HisTrap Fast Flow Affinity Column (GE Healthcare) previously equilibrated in buffer A. Following loading, the column was washed with 10 column volumes of buffer A followed by 5 columns of buffer A containing 50 mM imidazole. Glucokinase was eluted with buffer A containing 250 mM imidazole, and the enzyme was dialyzed for 1.5 h at 4 °C against 1 L of buffer containing HEPES (50 mM, pH 7.6), KCl (50 mM), glycerol (5%), imidazole (40 mM), EDTA (0.25 mM), and dithiothreitol (10 mM). Dialyzed glucokinase was concentrated to 500 μL via centrifugation at 4000x g and 4° C using a 10,000 MWCO filter (Millipore Amicon Ultra). The concentrated sample was injected onto a Superdex 200 10/300 GL size-exclusion column (GE Healthcare) pre-equilibrated in a buffer containing HEPES (50 mM, pH 7.6), KCl (50 mM), and TCEP (4 mM). The gel filtration column was run at a flow rate of 0.02 mL/min, and fractions containing the highest A_{280} readings were pooled and stored at −80°C.

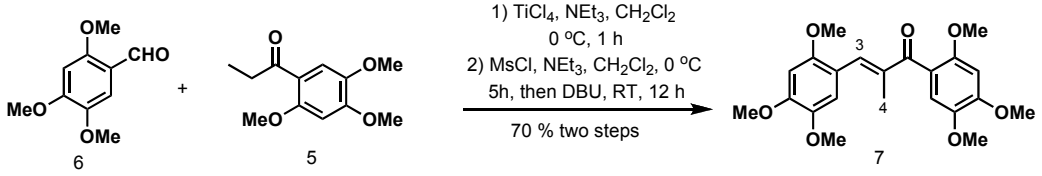
Enzyme Assays

Glucokinase activity was measured in the absence and presence of candidate activators (20 μM) using a spectrophotomertic assay that couples the production of glucose 6-phosphate to the reduction of $NADP^+$ via glucose 6-phosphate dehydrogenase. Stock solutions of tatanan A, tatanan C, and RO-28-1675 were prepared in HEPES buffer (10 mM, pH 7.6) containing DMSO (25%) and dilution were performed into assay mixtures such that DMSO concentrations did not exceed 5% w/v. Assay reactions were initiated by the addition of ATP following pre-equilibration with glucose and activator. Initial rate data were extracted from the linear portions of progress curves and fitted to the Hill equation to obtain values for k_{cat}, $K_{0.5}$ and Hill number, as previously described[1].

[1] M. Larion, B. G. Miller, 23-residue C-terminal α-helix governs kinetic cooperativity in monomeric human glucokinase. *Biochemistry* **48**, 6157-6165 (2009).

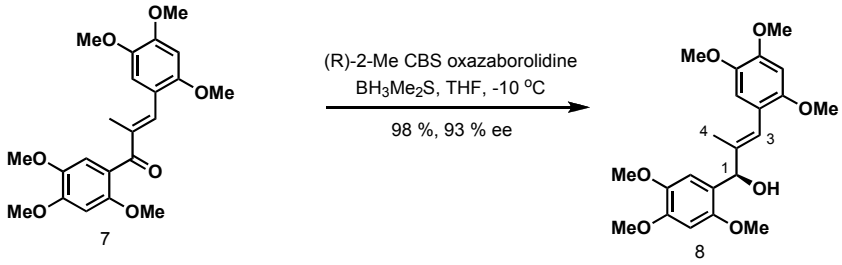
Synthesis

General Information. All reactions were carried out under an inert atmosphere of dry argon in oven or flame-dried glassware, unless the reaction procedure states otherwise. Tetrahydrofuran (THF) and ether (Et_2O) were distilled from sodium-benzophenone in a continuous still under an atmosphere of argon. Dichloromethane, di-*iso*-propylamine, pyridine, triethylamine, and chlorotrimethylsilane were distilled from calcium hydride in a continuous still under and atmosphere of argon. Chlorotriethylsilane (TESCl), and di-*iso*-propylethylamine (Hunig's Base) were distilled from calcium hydride under an inert atmosphere of dry argon and stored over calcium hydride. Reaction temperatures were controlled by IKA ETS-D4 fuzzy thermo couples. Room temperature reactions were carried out between 22-24 °C. Analytical thin-layer chromatography (TLC) was performed using pre-coated TLC plates with Silica Gel 60 F_{254} (EMD no. 5715-7) and visualized using combinations of UV, anisaldehyde, ceric ammonium molybdate (CAM), potassium permanganate, and iodine staining. Flash column chromatography was preformed using 40-63 μm silica gel (Merck, Geduran, no. 11567-1) as the stationary phase. Proton magnetic resonance spectra were recorded at 400, 500, and 600 MHz on Varian Unity Inova, and Varian Unity Inova spectrometers and at 800 MHz on a Bruker Avance II 800 Ultrashield Plus. Carbon magnetic resonance spectra were recorded at 50 MHz, 100 MHz, and 125 MHz on Varian Varian Unity Inova, and Varian Unity Inova spectrometers and at 200 MHz on a Bruker Avance II 800 Ultrashield Plus. All Chemical shifts were reported in δ units relative to tetramethylsilane. Optical Rotations were measured on a Rudolph DIP-1000 polarimeter. High-performance liquid chromatography (HPLC) was performed on Shimadzu instruments (LC-20AB or LC-8A). High Resolution mass spectral data were obtained by the Mass Spectrometry laboratory at the University of California, Santa Barbara.

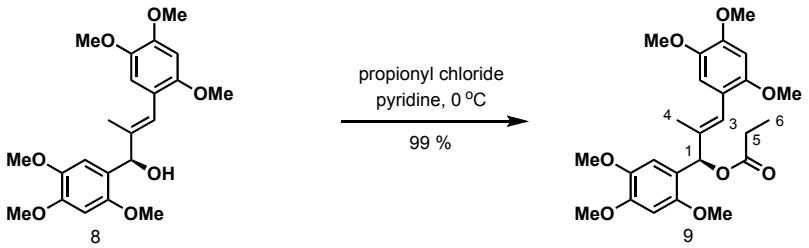


(*E*)-2-Methyl-1,3-bis(2,4,5-trimethoxyphenyl)prop-2-en-1-one 7. Titanium tetrachloride (1.0 M in CH_2Cl_2, 1.1 ml, 1.1 mmol) was added to a solution of 2,4,5-trimethoxybenzaldehyde (0.170 g, 0.86 mmol) and 2,4,5-trimethoxyphenyl ethyl ketone (0.194 g, 0.86 mmol) in dry CH_2Cl_2 (6.0 mL) at 0 °C. After 5 min, triethylamine (0.15 mL, 1.08 mmol) was added dropwise. The resultant mixture was allowed to stir at 0 °C for 1 h. The mixture was poured over ice water and extracted with diethyl ether (25 mL). The organic phase was separated, washed with 1M HCl (2 x 5 mL), 1M NaOH (2 x 5 mL), and brine (10 mL). The organic layer was dried with Na_2SO_4, filtered, and concentrated in vacuo. The crude material was dissolved in 6 ml of CH_2Cl_2 and cooled to 0 °C, then triethylamine (0.36 mL, 2.58 mmol) was added. After stirring for 5 min, methanesulfonyl chloride (0.17 mL, 2.24 mmol) was added and the resultant solution was allowed to stir for 5 h, then DBU (0.5 mL, 3.44 mmol) was added dropwise and the reaction mixture was warmed to room temperature and stirred for 12 h. The reaction was diluted with CH_2Cl_2 (20 mL), washed with 1 M HCl (2 x 5 mL), saturated aqueous $NaHCO_3$ (2 x 5 mL) and brine (10 mL). The organic layer was dried with Na_2SO_4, filtered, and concentrated in vacuo. The crude material was purified by column chromatography (silica, 60% ethyl acetate – hexanes, then 70% ethyl acetate – hexanes) to obtain the desired enone (0.243 g, 0.60 mmol, 70% yield)

as a yellow solid. mp 140-142 °C; ^{1}H NMR (400 MHz, $CDCl_3$); δ(ppm): 7.38 (d, J = 1.2 Hz, 1H, H-3), 6.99 (s, 1H, H-Ar), 6.93 (s, 1H, H-Ar), 6.56 (s, 1H, H-Ar), 6.49 (s, 1H, H-Ar), 3.95 (s, 3H, OMe), 3.92 (s, 3H, OMe), 3.87 (s, 3H, OMe), 3.86 (s, 3H, OMe), 3.79 (s, 3H, OMe), 3.75 (s, 3H, OMe), 2.19 (d, J = 1.6 Hz, 3H, H-4); ^{13}C NMR (150 MHz, $CDCl_3$) ; δ(ppm): 198.4, 152.9, 152.3, 151.2, 150.5, 142.7, 142.5, 138.1, 136.2,120.9, 116.6, 113.7, 113.0, 97.8, 96.8, 56.9, 56.6, 56.4, 56.3, 56.1, 56.0, 13.6; HRMS (EI) calculated for $C_{22}H_{26}O_7$: 402.1679 found 402.1684.

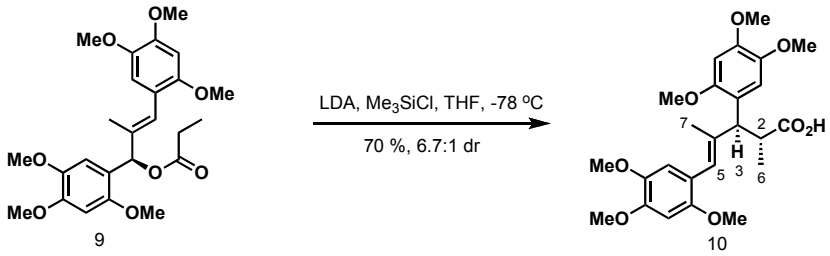


(*R*,*E*)-2-Methyl-1,3-bis(2,4,5-trimethoxyphenyl)prop-2-en-1-ol (*R*)-8. (*R*)-2-Me-CBS oxazaborolidine (1.0 M in toluene, 0.50 mL, 0.5 mmol) was added to a stirred solution of the starting enone **7** (0.200 g, 0.49 mmol) in THF (10 mL) at -10 °C. Then, BH_3•Me_2S (0.14 mL, 1.48 mmol) was added dropwise via syringe over a period of 15 min. The reaction mixture was stirred for 5 min and quenched with MeOH (1.0 mL), H_2O (2.5 mL), and diluted with ethyl acetate (50 mL). The combined organic layers were washed with aqueous $NaHCO_3$ (2x20 mL), dried over Na_2SO_4 and evaporated. The crude product was purified by column chromatography (silica gel buffered with Et_3N, 40:59:1 acetone:hexanes:Et_3N as eluent) to obtain the allylic alcohol **8** as a colorless oil (0.195 g, 0.48 mmol, 98% yield); ee 93% by chiral HPLC analysis (Daicel Chiralcel OD-H, 20% i-PrOH/hexanes, λ= 215 nm, r = 1.0 ml/min, R_t = 24.9 min (minor), R_t = 33.93 (major)); $[\alpha]_D^{22}$ +22.15 (c 1.0, MeOH); ^{1}H NMR (500 MHz, $CDCl_3$); δ(ppm): 7.00 (s, 1H, H-Ar), 6.79 (s, 1H, H-Ar), 6.73 (s, 1H, H-3), 6.55 (s, 1H, H-Ar), 6.53 (s, 1H, H-Ar), 5.54 (d, J = 4.5 Hz, 1H, H-1), 3.90 (s, 3H, OMe), 3.89 (s, 3H, OMe), 3.85 (s, 6H, OMe), 3.81 (s, 3H, OMe), 3.79 (s, 3H, OMe), 2.54 (d, J = 4.5 Hz, 1H, OH), 1.73 (s, 3H, H-4); ^{13}C NMR (125 MHz, $CDCl_3$); δ(ppm): 151.7, 151.4, 148.9, 148.4, 143.2, 142.4, 138.2, 122.5, 120.3, 118.5, 114.3, 111.6, 97.7, 97.6, 73.4, 56.6, 56.5, 56.4, 56.4, 56.0, 56.0, 14.8; HRMS (EI) calculated for $C_{22}H_{28}O_7$: 404.1835 found 404.1848.



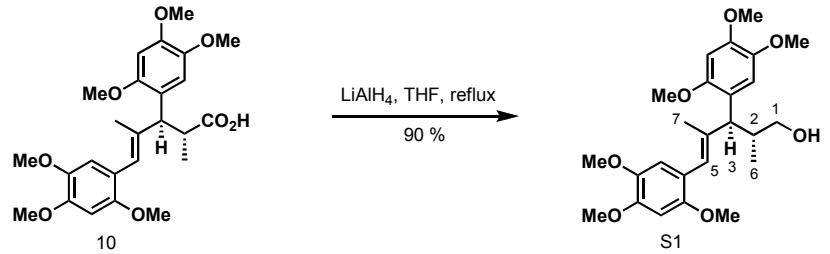
(*R*,*E*)-2-Methyl-1,3-bis(2,4,5-trimethoxyphenyl)allyl propionate 9. Propionyl chloride (0.16 mL, 1.78 mmol) was added dropwise via syringe to a stirred solution of alcohol **8** (0.240 g, 0.59 mmol) in pyridine (3.0 mL) at 0 °C. The deep brown mixture was stirred at 0 °C for 30 min and then diluted with ethyl acetate (50 mL) and washed with saturated aqueous $NaHCO_3$ solution (2×20 mL). Aqueous layer back extracted with ethyl acetate (2×20 mL). Combined ethyl acetate layers were dried over Na_2SO_4 and evaporated. The crude product was purified by column chromatography (silica buffered with Et_3N, 50:49.5:0.5 EtOAc:hexanes:Et_3N as eluent) to obtain propionate **9** as a brown viscous oil (0.270 g, 0.86

mmol, 99% yield). $[\alpha]_D^{22}$ +52.6 (c 1.0, MeOH); ^{1}H NMR (600 MHz, C_6D_6); δ(ppm): 7.49 (s, 1H, H-Ar), 7.44 (s, 1H, H-3), 7.29 (s, 1H, H-1), 7.03 (s, 1H, H-Ar), 6.46 (s, 1H, H-Ar), 6.43 (s, 1H, H-Ar), 3.70 (s, 3H, OMe), 3.56 (s, 3H, OMe), 3.54 (s, 3H, OMe), 3.52 (s, 3H, OMe), 3.51 (s, 3H, OMe), 3.47 (s, 3H, OMe) 2.33-2.25 (m, 2H, H-5), 2.09 (d, J = 1.8 Hz, 3H, H-4), 1.11 (t, J = 7.2 Hz, 3H, H-6); ^{13}C NMR (125 MHz, $CDCl_3$); δ(ppm): 173.3, 151.9, 151.8, 149.5, 148.6, 143.2, 142.5, 135.0, 121.2, 118.9, 118.3, 114.2, 111.7, 97.8, 97.7, 73.0, 56.8, 56.6, 56.6, 56.5, 56.1, 56.0, 27.9, 15.1, 9.2; HRMS (ESI) calculated for $C_{25}H_{32}O_8Na$[M+Na]: 483.1995 found 483.1982.



9 10

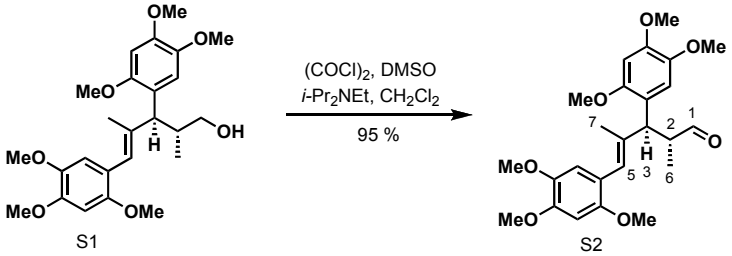
(2*R*,3*S*,*E*)-2,4-Dimethyl-3,5-bis(2,4,5-trimethoxyphenyl)pent-4-enoic acid 10. A flame-dried round bottomed flask fitted with a stir bar, nitrogen inlet, and a septum was charged with THF (45 mL) and cooled to -78 °C. Diisopropylamine (0.94 mL, 6.65 mmol) was added followed by *n*-BuLi (2.50 M in hexanes, 2.32 mL, 5.97 mmol) via syringe. After 15 min, a solution of the starting material **9** (2.75 g, 5.97 mmol) in THF (15 mL) was added via syringe over 5 min. The reaction mixture was stirred at -78 °C for 15 min, and then TMSCl (0.87 mL, 6.87 mmol) was added carefully. After stirring at -78 °C for 30 min, the reaction mixture was allowed to warm to room temperature over a period of 1 h and stirred at room temperature for 1 h. The reaction mixture was quenched with aqueous 1N HCl (50 mL) at 0 °C and the mixture was stirred for 15 min. The mixture was then extracted with ethyl acetate (3×100 mL). Combined ethyl acetate layers were dried over Na_2SO_4 and evaporated. The crude product was purified by column chromatography (silica gel, 60% ether-hexanes to 100% ether then 10% MeOH-DCM) to obtain the diastereomerically pure carboxylic acid **10** as light-brown oil (1.64 g, 3.56 mmol, 60% yield). $[\alpha]_D^{22}$ +30.4 (c 1.0, DCM); ^{1}H NMR (400 MHz, $CDCl_3$); δ(ppm): 6.87 (s, 1H, H-Ar), 6.68 (s, 1H, H-Ar), 6.56 (s, 1H, H-5), 6.50 (s, 1H, H-Ar), 6.49 (s, 1H, H-Ar), 4.05 (d, J = 12.0 Hz, 1H, H-3), 3.88 (s, 3H, OMe), 3.86 (s, 3H, OMe), 3.82 (s, 3H, OMe), 3.79 (s, 3H, OMe), 3.77 (s, 3H, OMe), 3.76 (s, 3H, OMe), 3.22-3.14 (m, 1H, H-2), 1.63 (s, 3H, H-7), 1.32 (d, J = 6.8 Hz, 3H, H-6); ^{13}C NMR (125 MHz, $CDCl_3$); δ(ppm): 180.4, 152.0, 151.8, 148.4, 148.1, 142.7, 142.5, 135.8, 123.0, 121.6 119.1, 114.4 112.3, 98.3, 98.1, 56.8, 56.7, 56.6, 56.1, 56.0, 49.7, 41.0, 16.9, 15.1; HRMS (ESI) calculated for $C_{25}H_{32}O_8Na$[M+Na]: 483.1995 found 483.1978.



10 S1

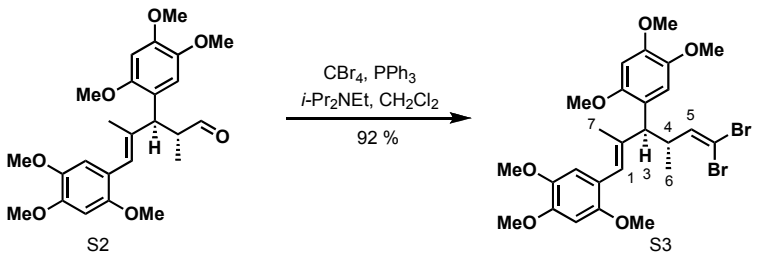
(2*R*,3*S*,*E*)-2,4-Dimethyl-3,5-bis(2,4,5-trimethoxyphenyl)pent-4-en-1-ol S1. Lithium aluminum hydride (41 mg, 1.08 mmol) was added in one-portion to a stirred solution of the starting carboxylic acid **10** (0.247 g, 0.53 mmol) in THF (6 mL) at 0 °C. The mixture was warmed to room temperature and heated under reflux for 4 h. The reaction mixture cooled to 0 °C and

quenched carefully with saturated aqueous Na_2SO_4. The white precipitate was filtered off using a small pad of Celite and washed with ethyl acetate (3×20 mL). The solvent was evaporated and residue was purified by column chromatography (silica gel, 50% ethyl acetate-hexanes) to obtain alcohol **10a** as light brown oil (0.216 g, 0.48 mmol, 90% yield). $[\alpha]_D^{22}$ -56.1 (c 1.0, DCM); ^{1}H NMR (400 MHz, $CDCl_3$); δ(ppm): 6.94 (s, 1H, H-Ar), 6.72 (s, 1H, H-Ar), 6.54 (s, 2H, H-Ar, H-5), 6.53 (s, 1H, H-Ar), 3.89 (s, 3H, OMe), 3.88 (s, 3H, OMe), 3.87 (s, 3H, OMe), 3.81 (s, 3H, OMe), 3.80 (s, 3H, OMe), 3.78 (s, 3H, OMe), 3.68 (d, J = 11.6 Hz, 1H, H-3), 3.44-3.34 (m, 1H, H-1), 3.31-3.23 (m, 1H, H-1), 2.22-2.07 (m, 2H, H-2, OH), 1.68 (s, 3H, H-7), 1.21 (d, J = 6.8 Hz, 3H, H-6); δ(ppm): 151.7, 151.4, 148.3, 147.9, 143.7, 142.5, 138.1, 122.7, 120.9, 119.3, 114.5, 111.8, 98.0, 97.8, 66.5, 57.2, 56.7, 56.5, 56.3, 56.1, 56.0, 47.4, 37.9, 18.2, 16.1; HRMS (ESI) calculated for $C_{25}H_{34}O_7Na$[M+Na]: 469.2202 found 469.2186.



S1 S2

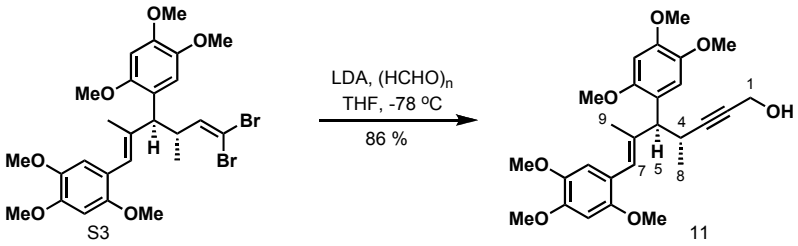
(2*R*,3*S*,*E*)-2,4-Dimethyl-3,5-bis(2,4,5-trimethoxyphenyl)pent-4-enal S2. Dimethylsulfoxide (0.66 mL, 9.29 mmol) was added to a stirred solution of oxalyl chloride (0.40 mL, 4.65 mmol) in CH_2Cl_2 (16 mL) at -78 °C. After 15 min, a solution of the starting alcohol **S1** (1.38 g, 3.10 mmol) in dichloromethane (15 mL) was added via syringe. The resulting mixture was stirred -78 °C for 45 min after which Hunig base (3.23 mL, 18.6 mmol) was added. After stirring for 30 min at -78 °C, the reaction mixture was placed in an ice-bath and stirred for 30 min, then diluted with ethyl acetate (150 mL) and washed with aqueous 1N HCl (1x50 mL). The aqueous layer was back-extracted with ethyl acetate (1x20 mL). Combined ethyl acetate layers were washed with brine (1×50 mL), dried over Na_2SO_4 and evaporated. Crude aldehyde was purified by column chromatography (silica gel, 30%→50% ethyl acetate-hexanes) to obtain the target aldehyde **S2** as a white solid (1.31 g, 2.95 mmol, 95% yield); mp 143-145 °C; $[\alpha]_D^{22}$ +6.5 (c 1.0, DCM); ^{1}H NMR (400 MHz, $CDCl_3$); δ(ppm): 9.41 (d, J = 3.2 Hz, 1H, H-1), 6.85 (s, 1H, H-Ar), 6.71 (s, 1H, H-Ar), 6.52 (s, 2H, H-Ar, H-5), 6.51 (s, 1H, H-Ar), 4.03 (d, J = 11.2 Hz, 1H, H-3), 3.89 (s, 3H, OMe), 3.87 (s, 3H, OMe), 3.82 (s, 6H, OMe), 3.81 (s, 3H, OMe), 3.78 (s, 3H, OMe), 3.08-2.99 (m, 1H, H-2), 1.67 (s, 3H, H-7), 1.21 (d, J = 6.8 Hz, 3H, H-6); ^{13}C NMR (125 MHz, $CDCl_3$); δ(ppm): 205.2, 151.8, 151.7, 148.5, 148.4, 143.1, 142.5, 136.0, 122.4, 120.4, 118.9, 114.4, 112.8, 97.8, 97.0, 56.7, 56.6, 56.5, 56.4, 56.1, 56.0, 48.0, 47.7, 16.5, 13.4; HRMS (ESI) calculated for $C_{25}H_{32}O_7Na$[M+Na]: 467.2046 found 467.2036.



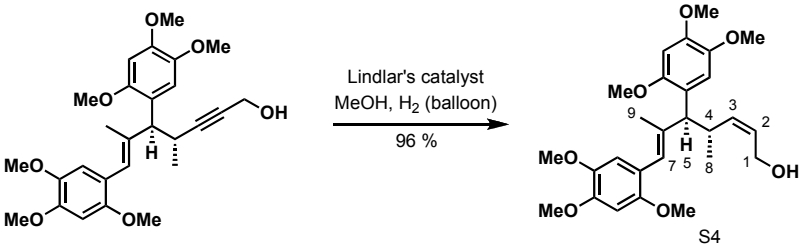
S2 S3

5,5'-((3*S*,4*R*,*E*)-6,6-Dibromo-2,4-dimethylhexa-1,5-diene-1,3-diyl)-bis-(1,2,4-trimethoxy-benzene) S3. Carbon tetrabromide (1.96 g, 5.92 mmol) was added to a stirred solution of

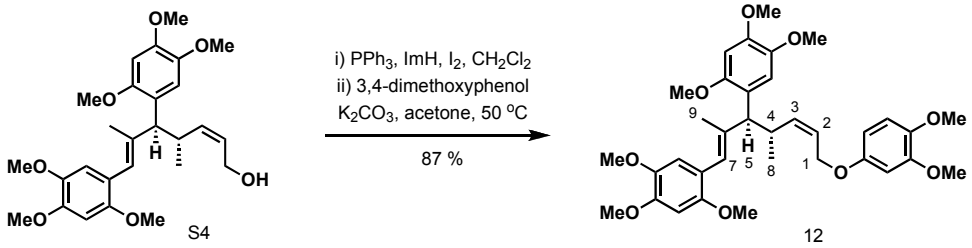
Ph_3P (3.10 g, 11.8 mmol) in dichloromethane (20 mL) at 0 °C and the mixture was stirred for 20 min. Hunig base (3.10 mL, 5.92 mmol) was added via syringe. After 2 min, a solution of the aldehyde **S2** (1.31 g, 2.94 mmol) in dichloromethane (10 mL) was added via syringe. The reaction mixture was stirred at 0 °C for 20 min and then at room temperature for 30 min. The reaction mixture was quenched with aqueous $NaHCO_3$ solution (30 mL) and extracted with dichloromethane (3×30 mL). Combined organic layers were dried over Na_2SO_4 and evaporated. The product was purified by column chromatography (silica gel, 30% ethyl acetate-hexanes) to obtain the desired dibromoalkene **S3** as a brown oil (1.63 g, 2.71 mmol, 92% yield). $[\alpha]_D^{22}$ +25.7 (c 1.0, DCM); ^{1}H NMR (400 MHz, $CDCl_3$); δ(ppm): 7.24 (s, 1H, H-Ar), 7.08 (s, 1H, H-1), 6.98 (s, 1H, H-Ar), 6.48 (s, 1H, H-Ar), 6.41 (s, 1H, H-Ar), 6.33 (d, J = 9.6 Hz, 1H, H-5), 4.15 (d, J = 11.2 Hz, 1H, H-3), 3.85 (s, 3H, OMe), 3.56 (s, 3H, OMe), 3.55 (s, 3H, OMe), 3.53 (s, 3H, OMe), 3.52 (s, 3H, OMe), 3.49 (s, 3H, OMe), 3.35-3.29 (m, 1H, H-4), 1.91 (d, J = 1.2 Hz, 3H, H-7), 1.30 (d, J = 6.8 Hz, 3H, H-6); ^{13}C NMR (125 MHz, $CDCl_3$); δ(ppm): 151.8, 151.7, 148.4, 147.9, 143.5, 142.8, 142.5, 136.8, 122.3, 121.7, 119.2, 114.4, 112.5, 98.0, 97.7, 87.4, 56.7, 56.6, 56.6, 56.6, 56.1, 56.0, 51.1, 40.0, 18.0, 15.8; HRMS (ESI) calculated for $C_{26}H_{32}Br_2O_6Na$[M+Na]: 621.0463 found 621.0435.



(4*R*,5*S*,*E*)-4,6-Dimethyl-5,7-bis(2,4,5-trimethoxyphenyl)hept-6-en-2-yn-1-ol 11. A flame dried round bottomed flask fitted with a stir bar, nitrogen inlet, and a septum was charged with THF (2.0 mL) and cooled to -78 °C. Diisopropylamine (0.47 mL, 3.32 mmol) followed by *n*-BuLi (2.43 M in hexanes, 1.29 mL, 3.14 mmol) were added via syringe. After 15 min, a solution of the starting material **S3** (0.420 g, 0.70 mmol) in THF (5.0 mL) was added via syringe. The reaction mixture was stirred at -78 °C for 45 min and then placed in an ice-bath and stirred for 10 min. Azeotropically dried paraformaldehyde (100 mg, 3.33 mmol) was added at once and the mixture was stirred at room temperature for 4 h. After quenching with aqueous NH_4Cl solution (20 ml), the reaction mixture was diluted with ethyl acetate (100 mL), washed with 1N HCl (20 mL), aqueous $NaHCO_3$ solution (20 mL), brine (20 mL), dried over Na_2SO_4, and evaporated. The crude product was purified by column chromatography (silica gel, 50% ethyl acetate-hexanes) to give the propargyllic alcohol **11** as a brown oil (0.284 g, 0.47 mmol, 86% yield). $[\alpha]_D^{22}$ +4.6 (c 1.0, CH_2Cl_2) ^{1}H NMR (400 MHz, C_6D_6); δ(ppm): 7.51 (s, 1H, H-Ar), 7.21 (s, 1H, H-7), 7.01 (s, 1H, H-Ar), 6.49 (s, 1H, H-Ar), 6.46 (s, 1H, H-Ar), 4.38 (d, J = 8.0 Hz, 1H, H-5), 4.00 (brs, 2H, H-1), 3.84 (s, 3H, OMe), 3.56 (s, 3H, OMe), 3.55 (s, 6H, OMe), 3.44 (s, 3H, OMe), 3.36-3.28 (m, 1H, H-4), 1.93 (s, 1H, H-9), 1.54 (d, J = 6.8 Hz, 3H, H-8); ^{13}C NMR (125 MHz, C_6D_6); δ(ppm): 153.4, 152.8, 150.1, 149.9, 144.7, 144.4, 138.4, 123.1, 122.6, 120.5, 116.8, 115.7, 99.8, 99.7, 90.1, 81.8, 57.3, 57.1, 56.7, 56.6, 56.5, 56.4, 51.7, 51.6, 29.3, 20.8, 17.4; HRMS (ESI) calculated for $C_{27}H_{34}O_7Na$[M+Na]: 493.2202 found 493.2180.



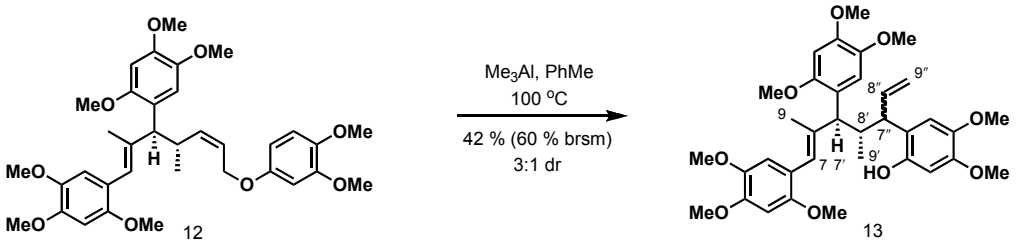
(2*Z*,4*S*,5*S*,6*E*)-4,6-Dimethyl-5,7-bis(2,4,5-trimethoxyphenyl)hepta-2,6-dien-1-ol S4. A 50 mL round bottomed flask was charged with propargyl alcohol **11** (0.280 g, 0.59 mmol). The flask was evacuated and with filled with hydrogen (balloon). The process was repeated for 3 times. Methanol (8.0 mL) was added and the solution was stirred for 5 min. Lindlar's catalyst (5% Pd on $CaCO_3$ poisoned with Pb, 0.127 g) was added at once and the mixture was stirred at room temperature for 10 min. The hydrogen balloon was removed and the mixture was filtered quickly through a small pad of silica and washed with ethyl acetate (3x15 mL). Combined organic layers were evaporated and the crude product was purified by column chromatography (silica gel, 50%→70% ethyl acetate-hexanes) to give the *Z*-allylic alcohol **S4** (0.271 g, 0.57 mmol, 96% yield) as colorless oil. $[\alpha]_D^{22}$ -14.0 (c 1.0, DCM); ^{1}H NMR (500 MHz, $CDCl_3$); δ(ppm): 6.86 (s, 1H, H-Ar), 6.71 (s, 1H, H-Ar), 6.56 (s, 1H, H-7), 6.53 (s, 1H, H-Ar), 6.50 (s, 1H, H-Ar), 5.37-5.28 (m, 2H, H-2, H-3), 4.13-4.00 (m, 2H, H-1), 3.89 (s, 3H, OMe), 3.86 (s, 3H, OMe), 3.83 (s, 3H, OMe), 3.81 (s, 3H, OMe), 3.80 (s, 3H, OMe), 3.79 (s, 3H, OMe), 3.68 (d, J = 11.0 Hz, 1H, H-5), 3.20-3.12 (m, 1H, H-4), 1.69 (s, 3H, H-9), 1.14 (d, J = 6.5 Hz, 3H, H-8); ^{13}C NMR (125 MHz, $CDCl_3$); δ(ppm): 152.0, 151.7, 148.2, 147.7, 142.8, 142.5, 138.3, 137.7, 126.4, 123.1, 121.4, 119.3, 114.4, 112.5, 98.0, 97.9, 58.7, 56.8, 56.7, 56.6, 56.6, 56.1, 56.0, 51.7, 34.2, 20.3, 17.1; HRMS (ESI) calculated for $C_{27}H_{36}O_7Na$[M+Na]: 495.2359 found 495.2345.



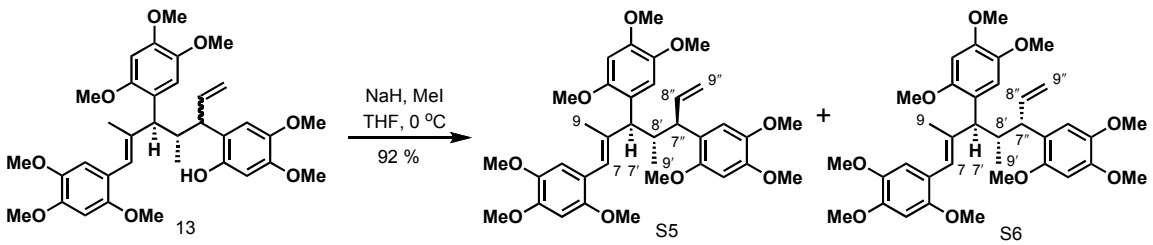
5,5'-((1*E*,3*S*,4*S*,5*Z*)-7-(3,4-Dimethoxyphenoxy)-2,4-dimethylhepta-1,5-diene-1,3-diyl)bis-(1,2,4-trimethoxybenzene) 12. Triphenylphosphine (0.108 g, 0.41 mmol), imidazole (62 mg, 0.90 mmol) and powdered iodine (0.112 g, 0.44 mmol) were added to a stirred solution of the starting alcohol **S4** (0.130 g, 0.27 mmol) in dichloromethane (2.80 mL) at 0 °C sequentially. The mixture was stirred at 0 °C for 10 min and quenched with saturated aqueous $Na_2S_2O_3$:$NaHCO_3$ solution (1:1, 20 mL). The dichloromethane layer was separated and the aqueous layer was extracted with dichloromethane (2×10 mL). Combined organic layers were dried over Na_2SO_4 and evaporated under reduced pressure (the water bath was kept at 15 °C). The crude product was purified by a short column chromatography (silica gel, 20% ethyl acetate-hexanes) to obtain the intermediate allylic iodide as a light brown oil (0.150 g, 0.257 mmoml, 94% yield).

The allylic iodide was immediately dissolved in acetone (2.57 mL). Powdered anhydrous K_2CO_3 (0.356 g, 2.57 mmol) and 3,4-dimethoxyphenol (79 mg, 0.512 mmol) were added to this solution. After stirring for 15 min at room temperature, the mixture was heated at 50 °C for 3 h. The mixture was then cooled to room temperature and acetone was

evaporated. Ethyl acetate (100 mL) and water (30 mL) were added to the residue. The ethyl acetate layers were separated and the aqueous layer was extracted with ethyl acetate (2x20 mL). The combined ethyl acetate layers were dried over Na_2SO_4 and evaporated. The crude product was purified by a column chromatography (silica gel, 30% ethyl acetate-hexanes) to obtain the requisite aryl ether **12** as a colorless oil (0.145 g, 0.24 mmol, 93% yield). $[\alpha]_D^{22}$ +37.0 (c 1.0, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$); δ(ppm): 6.86 (s, 1H, H-Ar), 6.75 (d, J = 8.4 Hz, 1H, H-Ar), 6.71 (s, 1H, H-Ar), 6.56 (s, 1H, H-7), 6.52 (s, 1H, H-Ar), 6.50 (s, 1H, H-Ar), 6.48 (d, J = 2.4 Hz, 1H, H-Ar), 6.29 (dd, J1 = 9.0 Hz, J2 = 2.4 Hz, 1H, H-Ar), 5.43-5.38 (m, 2H, H-2, H-3), 4.38 (m, 2H, H-1), 3.87 (s, 3H, OMe), 3.86 (s, 3H, OMe), 3.83 (s, 3H, OMe), 3.82 (s, 3H, OMe), 3.81 (s, 3H, OMe), 3.80 (s, 3H, OMe), 3.78 (s, 3H, OMe), 3.77 (s, 3H, OMe), 3.72 (d, J = 10.8 Hz, H-5), 3.19-3.11 (m, 1H, H-4), 1.69 (s, 3H, H-9), 1.17 (d, J = 6.6 Hz, 3H, H-8); ^{13}C NMR (150 MHz, $CDCl_3$); δ(ppm): 153.2, 152.0, 151.7, 149.8, 148.2, 147.7, 143.4, 142.7, 142.5, 138.8, 137.7, 123.3, 122.8, 121.6, 119.3, 114.4, 112.6, 111.6, 103.6, 101.0, 97.9, 97.8, 64.6, 56.7, 56.7, 56.6, 56.5, 56.4, 56.1, 55.9, 55.8, 51.8, 34.5, 20.1, 16.8; HRMS (ESI) calculated for $C_{35}H_{44}O_9Na$[M+Na]: 631.2883 found 631.2857.



Alkenes 13. Trimethylaluminum (2.0 M solution in toluene, 2.84 mL, 5.67 mmol) was added to an azeotropically dried neat aryl ether **12** (0.115 g, 0.19 mmol) at room temperature under argon atmosphere. The solution was then heated at 100 °C for 2 h. The reaction mixture was then cooled to 0 °C, diluted with dichloromethane (30 mL), and quenched carefully with 1N HCl (50 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (2×30 mL). The combined organic layers were dried over Na_2SO_4 and evaporated. The crude mixture of products was purified by a column chromatography (silica gel, 30% ethyl acetate-hexanes) to give an inseparable mixture of diastereomers as a light brown oil (48 mg, 0.078 mmol, 42% yield) along with the starting material (21 mg, 0.034 mmol, 18%). ^{1}H NMR for the major diastereomer: ^{1}H NMR (600 MHz, $CDCl_3$); δ(ppm): 6.91 (s, 1H, H-Ar), 6.64 (s, 1H, H-Ar), 6.58 (s, 1H, H-Ar), 6.48 (s, 1H, H-Ar), 6.47 (s, 1H, H-Ar), 6.44 (s, 1H, H-Ar), 6.40 (s, 1H, H-7), 6.19-6.13 (m, 1H, H-8″), 5.18-5.12 (m, 2H, H-9″), 4.57 (s, 1H, OH), 3.90 (s, 3H, OMe), 3.86 (s, 3H, OMe), 3.85 (s, 3H, OMe), 3.83 (s, 3H, OMe), 3.81 (s, 3H, OMe), 3.79 (s, 3H, OMe), 3.78 (s, 3H, OMe), 3.72 (s, 3H, OMe), 3.65-3.62 (m, 1H, H-7″), 3.62 (d, J = 11.5 Hz, 1H, H-7′), 2.78-2.70 (m, 1H, H-8′), 1.58 (s, 3H, H-9), 0.98 (d, J = 6.6 Hz, 3H, H-9′); HRMS (ESI) calculated for $C_{34}H_{44}O_9Na$[M+Na]: 631.2883 found 631.2854.

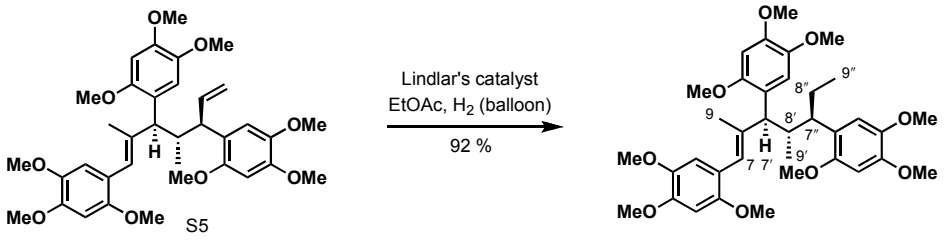


5,5'-((3*S*,4*S*,5*R*,*E*)-2,4-Dimethyl-5-(2,4,5-trimethoxyphenyl)hepta-1,6-diene-1,3-diyl)bis-(1,2,4-trimethoxybenzene) S5 and 5,5'-((3*S*,4*S*,5*S*,*E*)-2,4-dimethyl-5-(2,4,5-trimethoxy-

phenyl)hepta-1,6-diene-1,3-diyl)bis(1,2,4-trimethoxybenzene) S6. Sodium hydride (60% in mineral oil, 20 mg, 0.48 mmol) was added to as stirred solution of the starting phenol **13** (59 mg, 0.096 mmol) and iodomethane (30 μL, 0.48 mol) in THF (1.0 mL) at 0 °C and stirred for 15 min. The ice-bath was removed and the reaction mixture was stirred at room temperature for 1 h. The reaction mixture was then cooled to 0 °C and quenched with ice. The reaction mixture was diluted with ethyl acetate (50 mL) and washed with brine (10 mL). The organic layer was dried over Na_2SO_4 and evaporated. The crude product was purified by column chromatography (silica gel, 20→40% ethyl acetate-hexanes) to obtain the desired product **S5** and its diastereomer **S6.**

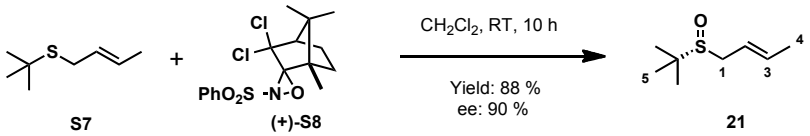
S5: (13.6 mg, 0.021 mmol, 22% yield); $[\alpha]_D^{22}$ +45.3 (c 0.54, DCM); ^{1}H NMR (500 MHz, $CDCl_3$); δ(ppm): 7.15 (s, 1H, H-Ar), 6.74 (s, 1H, H-Ar), 6.66 (s, 1H, H-Ar), 6.53 (s, 1H, H-Ar), 6.52 (s, 1H, H-7), 6.50 (s, 1H, H-Ar), 6.49 (s, 1H, H-Ar), 6.21 (ddd, J1 = 17.0 Hz, J2 = 10.0 Hz, J3 = 10.0 Hz, 1H, H-8″), 5.08 (dd, J1 = 10.0 Hz, J2 = 2.5 Hz, 1H, H-9″), 4.72 (dd, J1 = 17.0 Hz, J2 = 2.0 Hz, 1H, H-9″), 3.92 (s, 3H, OMe), 3.90 (s, 3H, OMe), 3.86 (s, 6H, OMe), 3.83 (d, J = 12.0 Hz, 1H, H-7′), 3.82 (s, 3H, OMe), 3.80 (s, 3H, OMe), 3.77 (s, 3H, OMe), 3.76 (s, 3H, OMe), 3.74 (s, 3H, OMe), 3.68 (dd, J1 = 9.5 Hz, J2 = 3.5 Hz, 1H, H-7″), 2.53-2.44 (m, 1H, H-8′), 1.65 (s, 3H, H-9), 0.92 (d, J = 7.0 Hz, 3H, H-9′); ^{13}C NMR (150 MHz, $CDCl_3$); δ(ppm): 152.7, 151.8, 151.1, 148.1, 147.9, 147.6, 142.6, 142.6, 142.5, 138.7, 136.2, 125.3, 122.6, 121.7, 120.0, 117.3, 114.9, 114.5, 113.9, 98.5, 98.3, 97.9, 57.4, 57.0, 56.8, 56.7, 56.6, 56.1, 56.0, 55.9, 50.4, 43.8, 36.8, 14.9, 13.4.

S6: (40.7 mg, 0.065 mmol, 68% yield); $[\alpha]_D^{22}$ +63.8(c 1.0, DCM); ^{1}H NMR (500 MHz, $CDCl_3$); δ(ppm): 6.88 (s, 1H, H-Ar), 6.66 (s, 1H, H-Ar), 6.56 (s, 1H, H-Ar), 6.51 (s, 1H, H-Ar), 6.49 (s, 1H, H-Ar), 6.44 (s, 1H, H-Ar), 6.41 (s, 1H, H-7), 6.17 (ddd, J1 = 17.0 Hz, J2 = 10.0 Hz, J3 = 8.5 Hz, 1H, H-8″), 5.00-4.92 (m, 2H, H-9″), 3.89 (s, 3H, OMe), 3.86 (s, 3H, OMe), 3.85 (s, 3H, OMe), 3.84 (s, 3H, OMe), 3.80 (dd, J1 = 10.0 Hz, J2 = 6.0 Hz, 1H, H-7″), 3.78 (s, 3H, OMe), 3.77 (s, 3H, OMe), 3.76 (s, 3H, OMe), 3.73 (s, 3H, OMe), 3.67 (d, J = 11.0 Hz, 1H, H-7′), 2.70-2.62 (m, 1H, H-8′), 1.61 (s, 3H, H-9), 0.93 (d, J = 7.0 Hz, 3H, H-9′); ^{13}C NMR (150 MHz, $CDCl_3$); δ(ppm): 152.3, 151.8, 151.7, 148.1, 147.7, 147.5, 142.5, 142.4, 142.3, 141.8, 138.3, 123.6, 122.3, 122.0, 120.0, 114.6, 114.5, 113.7, 112.9, 98.4, 98.1, 97.5, 56.9, 56.6, 56.5, 56.5, 56.4, 56.1, 56.0, 56.0, 55.9, 50.5, 45.7, 37.6, 15.6, 15.1; HRMS (ESI) calculated for $C_{36}H_{46}O_9Na$[M+Na]: 645.3040 found 645.3010.

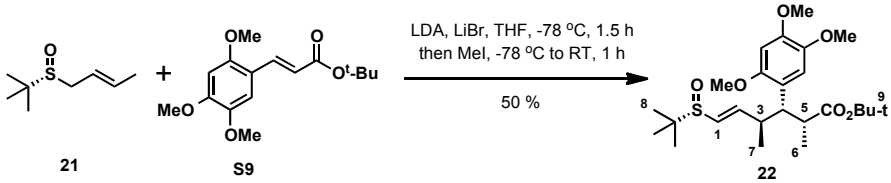


(+)-Tatanan A. A 50 mL round bottomed flask was charged with substrate **S5** (28 mg, 0.045 mmol). The flask was evacuated and with filled with hydrogen. The process was repeated 3 times. Ethyl acetate was added and the solution was stirred for 5 min. Lindlar's catalyst (5% Pd on $CaCO_3$ poisoned with Pb, 95 mg) was added at once and the mixture was stirred at room temperature for 20 min. The hydrogen balloon was removed and the mixture was filtered quickly through a small pad of silica and washed with ethyl acetate (3×20 mL). The filtrate was evaporated and crude product was purified by column chromatography (silica, 30% ethyl acetate-hexanes) to give pure tatanan A (26 mg, 0.041 mmol, 92% yield)

as a colorless oil. A sample of tatanan A was recrystallized from CD_3OD; mp 123-125 °C; $[\alpha]_D^{23}$ +55.1 (c 0.1, MeOH); ^1H NMR (500 MHz, CD_3OD); δ(ppm): 6.86 (s, 1H, H-Ar), 6.65 (s, 1H H-Ar), 6.63 (s, 1H H-Ar), 6.59 (s, 1H H-Ar), 6.53 (s, 2H, H-Ar), 6.26 (s, 1H, H-7), 3.86 (s, 3H, OMe), 3.83 (s, 3H, OMe), 3.81 (s, 3H, OMe), 3.77 (s, 3H, OMe), 3.76 (s, 3H, OMe), 3.71 (s, 3H, OMe), 3.70 (s, 6H, OMe), 3.52 (s, 3H, OMe), 3.50 (d, J = 11.5 Hz, 1H, H-7′) 3.16-3.02 (m, 1H, H-7″), 2.58-2.51 (m, 1H, H-8′), 1.85-1.67 (m, 2H, H-8″), 1.55 (s, 3H, H-9), 0.95 (d, J = 6.5 Hz, 3H, H-9′), 0.75 (t, J = 7.5 Hz, 3H, H-9″); ^{13}C NMR (125 MHz, CD_3OD); δ(ppm): 154.9, 154.5, 153.8, 150.1, 149.5, 149.4, 144.1, 144.0, 143.6, 139.9, 125.3, 123.9, 123.3, 121.6, 116.8, 116.8, 115.4, 100.1, 100.1, 98.8, 57.9, 57.8, 57.7, 57.4, 57.04, 56.97, 56.9, 56.8, 56.2, 52.2, 38.5, 27.3, 16.0, 15.0, 13.4; HRMS (ESI) calculated for $C_{36}H_{48}O_9Na$[M+Na]: 647.3196 found 647.3181.



(*R*)-*tert*-Butyl (*E*)-2-buten-1-yl sulfoxide 21. A solution of *tert*-butyl (*E*)-2-buten-1-yl sulfide[2] **S7** (0.53 g, 3.7 mmol) in 24 mL of CH_2Cl_2 was added to a solution of oxaziridine[3] **S8** (1.31 g, 3.5 mmol) in 100 mL of CH_2Cl_2 under the atmosphere of argon. The reaction mixture was stirred at room temperature for 10 h, the solvent was removed under reduced pressure and the residue was purified by column chromatography (silica, 20% acetone – DCM) to give the desired product (0.52 g, 3.30 mmol, 88%) as colorless oil. The enantiomeric excess was found to be 90% by chiral HPLC analysis (Daicel Chiralcel AD-H, 2% iPrOH/hexanes, λ= 200 nm, r = 1.0 ml/min, R_t = 18.3 min (minor), R_t = 20.8 (major)); $[\alpha]_D^{23}$ +198.8° (c 1.0, CH_2Cl_2); ^1H NMR (500 MHz, *t* = 23 °C, $CDCl_3$); δ(ppm): 5.76 (dq, J = 14.1, 6.5 Hz, 1H, H-3), 5.59 – 5.49 (m, 1H, H-2), 3.23 – 3.14 (m, 1H, Ha-1), 3.09 – 3.01 (m, 1H, Hb-1), 1.71 (dd, J = 6.5, 1.3 Hz, 3H, H-4), 1.20 (s, 9H, H-5); ^{13}C NMR (125 MHz, *t* = 23 °C, $CDCl_3$); δ(ppm): 133.55, 120.36, 53.15, 49.73, 22.86, 22.83, 18.09; LRMS (ESI) calcd for $C_8H_{16}OSNa$ [M+Na] 183.08, found 183.09.

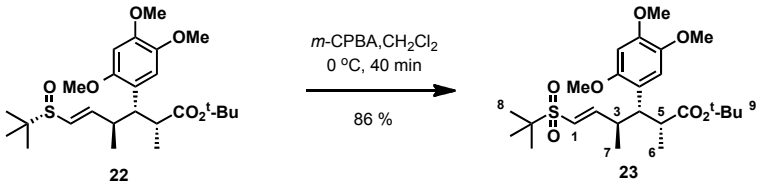


(2*R*,3*S*,4*R*,*E*)-*tert*-Butyl 6-((*R*)-*tert*-butylsulfinyl)-2,4-dimethyl-3-(2,4,5-trimethoxyphenyl)hex-5-enoate 22. A solution of (*S*)-*tert*-butyl (*E*)-2-buten-1-yl sulfoxide (21) (0.88 g, 5.50 mmol) in THF (6.0 ml total with rinses) was added slowly dropwise to a slight excess of lithium diisopropylamide, generated from *n*-butyllithium (1.99 M in hexanes, 2.76 ml, 5.50 mmol) and diisopropylamine (0.77 ml, 5.50 mmol), in THF (70 mL) at -78 °C under argon. The resulting solution was stirred for 15 min, and then a solution of ester **S9** (1.40 g, 4.80 mmol) and lithium bromide (0.83 g, 9.60 mmol) in THF (6.0 ml total with rinses) was added at -78 °C. Addition of the solution was carried out slowly to ensure that the temperature of the reaction remained constant. The reaction mixture was stirred at -78 °C for 90 min, and then iodomethane (3.00 ml, 24.0 mmol) was added slowly. The

[2] Binns, M. R.; Haynes, R. K.; Katsifis, A. G.; Schober, P. A.; Vonwiller, S. C. *J. Am. Chem. Soc.* **1988**, *110*, 5411-5423.

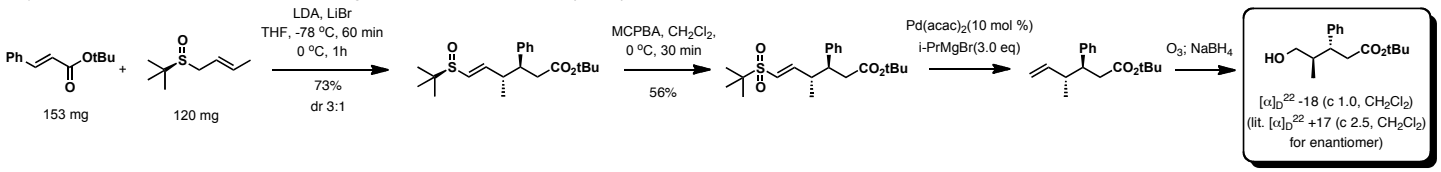
[3] Davis, F. A.; Reddy, R. T.; Han, W.; Carroll, P. J. *J. Am. Chem. Soc.* **1992**, *114*, 1428-1437.

reaction mixture was allowed to warm to ambient temperature during 30 min and stirred at ambient temperature for 1 h. The mixture was then quenched with saturated aqueous ammonium chloride and extracted with ethyl acetate (3×50 ml). The combined organic layers were washed with brine, dried with sodium sulfate, concentrated, and the residue was purified by column chromatography (silica, 50% ethyl acetate – hexanes) to give the desired product **22** (1.13 g, 2.40 mmol, 50%). $[\alpha]_D^{23}$ +142.9° (c 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, *t* = 23 °C, $CDCl_3$); δ(ppm): 6.48 (s, 1H, H-Ar), 6.46 (s, 1H, H-Ar), 6.37 (dd, J = 15.0, 8.8 Hz, 1H, H-2), 6.00 (d, J = 14.9 Hz, 1H, H-1), 3.85 (s, 3H, OMe), 3.81 (s, 3H, OMe), 3.75 (s, 3H, OMe), 3.48 (s, 1H, H-4), 2.78 (dd, J = 13.0, 6.8 Hz, 1H, H-3), 2.73 – 2.69 (m, 1H, H-5), 1.47 (s, 9H, H-9), 1.17 (s, 9H, H-8), 0.92 (d, J = 6.7 Hz, 3H, H-7), 0.84 (d, J = 6.9 Hz, 3H, H-6);^{1}H NMR (500 MHz, *t* = 50 °C, $CDCl_3$); δ(ppm): 6.49 (s, 1H), 6.38 (dd, J = 15.2, 8.6 Hz, 1H), 6.01 (d, J = 15.3 Hz, 1H), 3.85 (s, 2H), 3.81 (s, 1H), 3.75 (s, 2H), 3.47 (s, 1H), 2.80 (dt, J = 13.3, 6.6 Hz, 1H), 2.73 (dt, J = 13.1, 6.7 Hz, 1H), 1.48 (s, 9H), 1.17 (s, 9H), 0.94 (d, J = 6.7 Hz, 3H), 0.85 (d, J = 6.9 Hz, 3H);^{13}C NMR (125 MHz, *t* = 23 °C, $CDCl_3$); δ(ppm): 176.15, 152.69, 148.90, 147.91, 143.96, 142.71, 127.74, 118.13, 97.57, 80.28, 56.56, 56.40, 55.94, 54.39, 43.37, 39.75, 28.07, 22.80, 18.53, 16.67; LRMS (ESI) calcd for $C_{25}H_{40}O_6SNa$ [M+Na] 491.24, found 491.25.[4]

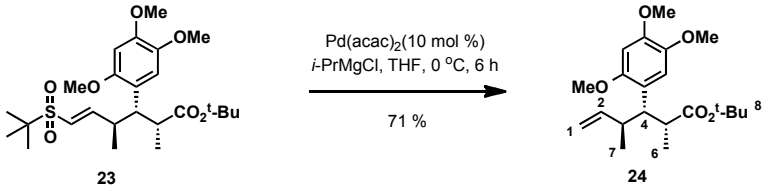


(2*R*,3*S*,4*R*,*E*)-*tert*-Butyl 6-(*tert*-butylsulfonyl)-2,4-dimethyl-3-(2,4,5-trimethoxyphenyl)-hex-5-enoate 23. *m*-Chloroperoxybenzoic acid (~77% pure, 0.59 g, 2.65 mmol) was added to a solution of the starting sulfoxide **22** (1.13 g, 2.41 mmol) in dry CH_2Cl_2 (40 mL) at 0 °C . After the addition was complete, the solution was stirred at the same temperature for 40 min. A 20 mL portion of saturated aqueous sodium sulfite was added, and the aqueous phase was extracted with CH_2Cl_2 (3×50 ml). The combined organic layers were washed with saturated aqueous sodium carbonate and brine, dried with sodium sulfate, concentrated, and the residue was purified by column chromatography (silica, 30% ethyl acetate – hexanes) to give the desired product **23** (1.01 g, 2.10 mmol, 86%). $[\alpha]_D^{23}$ +42.1° (c 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, *t* = 23 °C, $CDCl_3$); δ(ppm): 6.84 (dd, J = 15.2, 8.9 Hz, 1H, H-2), 6.49 (s, 1H, H-Ar), 6.44 (s, 1H, H-Ar), 6.13 (d, J = 15.2 Hz, 1H, H-1), 3.87 (s, 3H, OMe), 3.82 (s, 3H, OMe), 3.77 (s, 3H, OMe), 3.66 – 3.26 (m, 1H, H-4), 2.91 – 2.63 (m, 2H, H-3,5), 1.49 (s, 9H, H-9), 1.29 (s, 9H, H-8), 0.97 (d, J = 6.7 Hz, 3H, H-7), 0.87 (d, J = 6.9 Hz, 3H, H-6); ^{1}H NMR (500 MHz, *t* = 50 °C, $CDCl_3$); δ(ppm): 6.84 (dd, J = 15.2, 8.8 Hz, 1H), 6.50 (s, 1H), 6.47 (s, 1H), 6.13 (d, J = 15.2 Hz, 1H), 3.86 (s, 3H), 3.82 (s, 3H), 3.77 (s, 3H), 3.47 (s, 1H), 2.84 (dd, J = 13.6, 6.9 Hz, 1H), 2.77 (s, 1H), 1.50 (s, 9H),

[4] The absolute configuration was confirmed by the follwing transformations and correlation of the final product to a known compound: Hanessian, S.; Gomtsyan, A.; Payne, A.; Herve, Y.; Beaudoin, S. J. Org. Chem. **58**, 5032-5034 (1993).

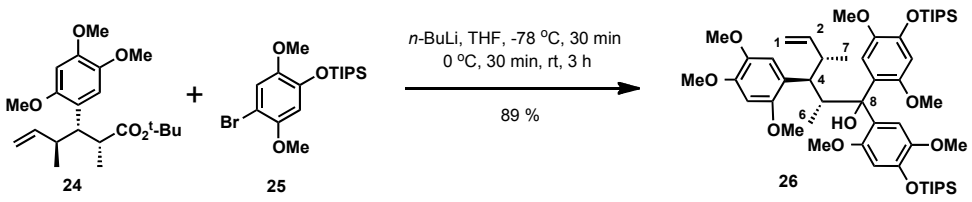


1.29 (s, 9H), 0.99 (d, J = 6.7 Hz, 3H), 0.88 (d, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, *t* = 23 °C, $CDCl_3$); δ(ppm): 175.96, 153.51, 152.52, 148.22, 142.82, 123.46, 117.54, 113.38, 97.51, 80.47, 58.06, 56.53, 56.23, 55.96, 43.17, 39.64, 28.03, 23.15, 18.02, 16.63. LRMS (ESI) calcd for $C_{25}H_{40}O_7SNa$ [M+Na] 507.24, found 507.25.



23 24

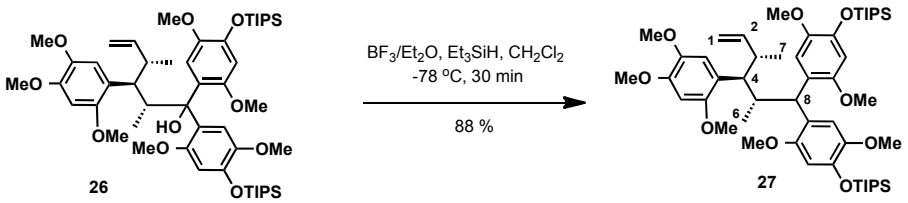
***tert*-Butyl (2*R*,3*S*,4*S*)-2,4-dimethyl-3-(2,4,5-trimethoxyphenyl)hex-5-enoate 24.** A solution of *i*-PrMgCl (1.3 mL, 1.1 M in THF) was added dropwise to a solution of the starting sulfone **23** (0.232 g, 0.47 mmol) and $Pd(acac)_2$ (15 mg, 0.047 mmol) in dry THF (10 mL) at 0 °C. The resulting solution was stirred at 0 °C for 1.5 h. The mixture was then quenched with aqueous ammonium chloride and extracted with ethyl acetate (3×20 ml). The organic layer was washed with aqueous saturated sodium carbonate and brine, dried over with sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography (silica, 15% ethyl acetate – hexanes) to give the desired product **24** (0.121 g, 0.33 mmol, 71%). $[\alpha]_D^{23}$ +30.9° (c 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, *t* = 23 °C, $CDCl_3$); δ(ppm): 6.54 (s, 1H, H-Ar), 6.51 (s, 1H, H-Ar), 5.74 (ddd, J = 17.3, 10.4, 8.2 Hz, 1H, H-2), 5.01 (dd, J = 10.3, 1.4 Hz, 1H, H-1a), 4.95 (d, J = 17.2 Hz, 1H, H-1b), 3.87 (s, 3H, OMe), 3.78 (s, 3H, OMe), 3.76 (s, 3H, OMe), 3.45 (s, 1H, H-4), 2.72 (dq, J = 13.5, 6.8 Hz, 1H, H-5), 2.56 – 2.48 (m, 1H, H-3), 1.50 (s, 9H, H-8), 0.86 (d, J = 7.1 Hz, 3H, H-6), 0.84 (d, J = 7.4 Hz, 3H, H-7); ^{13}C NMR (125 MHz, *t* = 23 °C, $CDCl_3$); δ(ppm): 176.35, 152.94, 147.58, 142.34, 141.00, 119.21, 114.56, 113.42, 97.49, 79.90, 56.60, 56.46, 55.79, 45.39, 43.28, 40.29, 27.99, 18.33, 16.69; LRMS (ESI) calcd for $C_{21}H_{32}O_5Na$ [M+Na] 387.21, found 387.23.



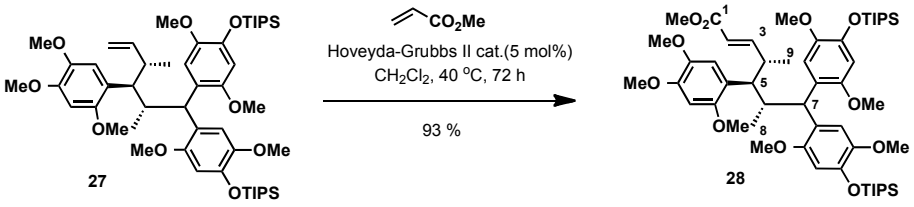
24 25 26

(2*R*,3*S*,4*S*)-1,1-Bis(2,5-dimethoxy-4-((triisopropylsilyl)oxy)phenyl)-2,4-dimethyl-3-(2,4,5-trimethoxyphenyl)hex-5-en-1-ol 26. *n*-Butyllithium (1.99 M in hexane, 1.0 mL, 1.99 mmol) was added dropwise to a solution of (4-bromo-2,5-dimethoxyphenoxy)triisopropylsilane **S10** (0.77 g, 1.98 mmol) in THF (3 mL) at -78 °C. After stirring at -78 °C for 1 h, the reaction flask was placed in an ice-water bath and stirred for 10 min. The reaction mixture was then cooled back to -78 °C and a solution of ester **24** (0.24 g, 0.65 mmol) in THF (3.0 ml total with rinses) was added via syringe drop by drop, and stirring was continued at the same temperature for 30 min. After warming to 0 °C for 30 min and room temperature for 3 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution (10 mL). The mixture was extracted with ethyl acetate (3×20 mL). The combined organic layers were washed with brine, dried with sodium sulfate, concentrated, and the residue was purified by column chromatographyraphy (silica, 8% first then 15% ethyl acetate – hexanes) to give the desired product **26** (0.53 g, 0.58 mmol, 89%). $[\alpha]_D^{23}$ -25.3° (c 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, *t* = 23 °C, $CDCl_3$); δ(ppm): 7.33 (s, 1H, H-Ar), 7.18 (s, 1H, H-Ar), 6.74 (s, 1H, H-Ar), 6.39 (s, 2H, H-Ar), 6.33 (s, 1H, H-Ar), 5.73 – 5.51 (m, 1H, H-

2), 4.94 (s, 1H, OH), 4.75 (d, J = 17.3 Hz, 1H, H-1a), 4.72 (d, J = 10.2 Hz, 1H, H-1b), 3.86 (s, 3H, OMe), 3.82 (s, 3H, OMe), 3.79 (s, 3H, OMe), 3.75 (s, 3H, OMe), 3.55 (d, J = 5.7 Hz, 1H, H-4), 3.45 (broad s, 3H, OMe), 3.41 (s, 3H, OMe), 3.38 (s, 3H, OMe), 2.51 (s, 1H, H-3), 1.30 – 1.16 (m, 6H, H-TIPS), 1.12 – 1.02 (m, 39H H-TIPS, Me), 0.95 – 0.90 (m, 3H); ^{13}C NMR (125 MHz, *t* = 23 °C, $CDCl_3$); δ(ppm): 152.77, 146.83, 144.22, 144.05, 143.91, 143.67, 141.57, 128.03, 124.25, 114.80, 112.75, 106.48, 97.32, 81.10, 56.62, 56.26, 55.53, 41.95, 37.96, 18.97, 17.83, 17.78, 17.48, 17.44, 14.11, 12.82, 12.81, 12.76, 12.75; LRMS (ESI) calcd for $C_{51}H_{82}O_{10}Si_2Na$ [M+Na] 933.53, found 933.58.

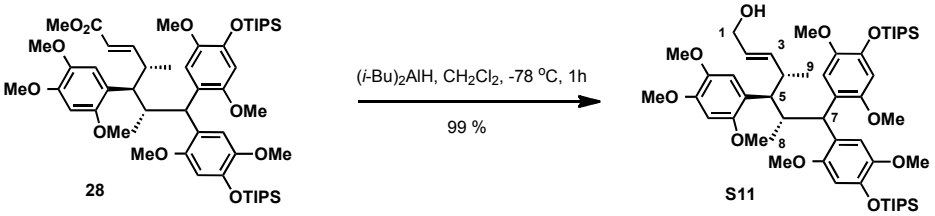


((((2*R*,3*S*,4*S*)-2,4-Dimethyl-3-(2,4,5-trimethoxyphenyl)hex-5-ene-1,1-diyl)bis(2,5-dimethoxy-4,1-phenylene))bis(oxy))bis(triisopropylsilane) 27. Triethylsilane (1.6 mL, 10 mmol) followed by BF_3•OEt_2(0.26 mL, 2.1 mmol) were added to a solution of alcohol **26** (0.47 g, 0.52 mmol) in dichloromethane (40 mL) at -78 °C under an atmosphere of argon. The resultant solution was stirred at -78 °C for 30 min. Aqueous ammonium chloride (30 mL) was added, the layers were separated, the aqueous layer was further extracted with dichloromethane (3×20 mL). The combined organic layers were washed with brine, dried with sodium sulfate, concentrated, and the residue was purified by column chromatography (silica, 10% ethyl acetate – hexanes) to give the desired product **27** (0.41 g, 0.46 mmol, 88 %). $[\alpha]_D^{23}$ -41.4° (c 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, *t* = 40 °C, $CDCl_3$); δ(ppm): 6.96 (s, 1H, H-Ar), 6.69 (s, 1H, H-Ar), 6.61 (s, 1H, H-Ar), 6.42 (s, 1H, H-Ar), 6.41 (s, 1H, H-Ar), 6.40 (s, 1H, H-Ar), 5.69 – 5.58 (m, 1H, H-2), 4.86 – 4.79 (m, 1H, H-1a), 4.75 (d, J = 10.3 Hz, 1H, H-1b), 4.34 (s, 1H, H-6), 3.87 (s, 3H, OMe), 3.77 (s, 3H, OMe), 3.76 (s, 3H, OMe), 3.66 (s, 3H, OMe), 3.55 (s, 3H, OMe), 3.53 (s, 3H, OMe), 3.48 (s, 3H, OMe), 3.21 (s, 1H, H-4), 2.92 (s, 1H, H-3), 2.78 (s, 1H, H-5), 1.24 (ddt, J = 14.6, 10.8, 7.4 Hz, 9H, H-6 and TIPS), 1.09 (ddd, J = 13.2, 7.4, 1.5 Hz, 36H, H-TIPS), 0.69 (d, J = 7.0 Hz, 3H, H-7); ^{13}C NMR (125 MHz, *t* = 50 °C, $CDCl_3$); δ(ppm): 153.23, 152.19, 147.56, 144.62, 144.33, 143.80, 143.75, 142.22, 126.57, 126.26, 122.00, 116.19, 115.93, 114.87, 112.68, 106.41, 106.10, 97.36, 56.85, 56.73, 56.62, 56.56, 56.29, 56.11, 55.70, 39.09, 35.68, 29.69, 18.97, 17.94, 17.89, 17.59, 17.55, 14.13, 12.98, 12.94; LRMS (ESI) calcd for $C_{51}H_{82}O_9Si_2Na$ [M+Na] 917.54, found 917.60.

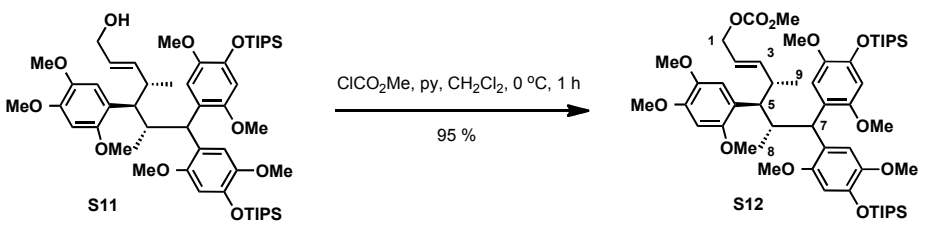


Methyl (4*S*,5*S*,6*R*,*E*)-7,7-bis(2,5-dimethoxy-4-((triisopropylsilyl)oxy)phenyl)-4,6-dimethyl-5-(2,4,5-trimethoxyphenyl)hept-2-enoate 28. Alkene **27** (0.45 g, 0.50 mmol) and methyl acrylate (0.27 mL, 3.0 mmol) were dissolved in CH_2Cl_2 (4 mL), and Hoveyda-Grubbs second-generation catalyst (15 mg, 0.025 mmol) was added as a solid in one portion. The reaction was stirred at 45 °C for 72 h and then concentrated. The residue was purified by column chromatography (silica, 15% ethyl acetate – hexanes) to give the desired product **28** (0.44

g, 0.46 mmol, 93 %) as a yellow solid. $[\alpha]_D^{23}$ -9.6° (c 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, *t* = 50 °C, $CDCl_3$); δ(ppm): 7.02 (broad, 1H, H-3), 6.89 (s, 1H, H-Ar), 6.80 (s, 1H, H-Ar), 6.53 (s, 1H, H-Ar), 6.46 (s, 1H, H-Ar), 6.45 (s, 1H, H-Ar), 6.42 (s, 1H, H-Ar), 5.68 (d, J = 15.8 Hz, 1H, H-2), 4.65 (s, 1H, H-7), 3.86 (s, 3H, OMe), 3.75 (s, 3H, OMe), 3.72 (s, 3H, OMe), 3.69 (s, 3H, OMe), 3.67 (s, 3H, OMe), 3.66 (s, 3H, OMe), 3.57 (s, 3H, OMe), 3.56 (s, 3H, OMe), 3.30 (s, 1H, H-5), 2.90 (s, 2H, H-4 and 6), 1.34 – 1.19 (m, 6H, H-TIPS), 1.15 – 1.02 (m, 36H, H-TIPS), 0.94 (d, J = 3.4 Hz, 3H, H-8), 0.70 (t, J = 5.6 Hz, 3H, H-9); ^{13}C NMR (125 MHz, *t* = 50 °C, $CDCl_3$); δ(ppm): 167.29, 154.14, 152.98, 152.20, 151.97, 147.81, 144.65, 144.33, 144.05, 143.98, 142.49, 125.93, 125.11, 121.11, 119.70, 115.95, 115.24, 106.62, 105.89, 97.65, 56.71, 56.67, 56.58, 56.21, 56.12, 55.92, 51.02, 37.58, 35.97, 17.92, 17.91, 17.88, 17.57, 17.54, 14.72, 12.97, 12.94; LRMS (ESI) calcd for $C_{53}H_{84}O_{11}Si_2Na$ [M+Na] 975.54, found 975.54.

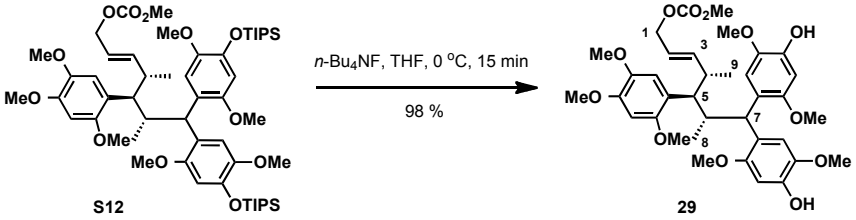


(4*S*,5*S*,6*R*,*E*)-7,7-Bis(2,5-dimethoxy-4-((triisopropylsilyl)oxy)phenyl)-4,6-dimethyl-5-(2,4,5-trimethoxyphenyl)hept-2-en-1-ol S11. Diisobutylaluminum hydride (1 M in toluene, 2.3 ml, 2.3 mmol) was added dropwise to a solution of ester **28** (0.43 g, 0.46 mmol) in dry dichloromethane (25 ml) at -78 °C. After 1 h, the reaction mixture was quenched with 20 ml of Rochelle's salt solution and diluted with 50 ml of ethyl acetate. The mixture was stirred vigorously for 2 h at room temperature. The layers were separated and the aqueous layer was extracted with ethyl acetate (3×20 ml). The organic layers were dried with sodium sulfate and concentrated to give the crude alcohol, which was purified by column chromatographyraphy (silica, 30% ethyl acetate – hexanes) to give the desired product **S11** (0.42 g, 0.45 mmol, 99 %) as a colorless solid. $[\alpha]_D^{23}$ -29.7° (c 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, *t* = 50 °C, $CDCl_3$); δ(ppm): 6.90 (s, 1H, H-Ar), 6.74 (s, 1H, H-Ar), 6.59 (s, 1H, H-Ar), 6.42 (s, 1H, H-Ar), 6.41 (s, 1H, H-Ar), 6.40 (s, 1H, H-Ar), 5.51 (dd, J = 15.4, 7.2 Hz, 1H, H-3), 5.43 (dt, J = 15.4, 5.8 Hz, 1H, H-2), 4.39 (s, 1H, H-7), 3.89 (d, J = 5.8 Hz, 2H, H-1), 3.86 (s, 3H, OMe), 3.77 (s, 3H, OMe), 3.75 (s, 3H, OMe), 3.67 (s, 3H, OMe), 3.55 (s, 3H, OMe), 3.55 (s, 3H, OMe), 3.49 (s, 3H, OMe), 3.20 (s, 1H, H-5), 2.92 (s, 1H, H-4), 2.76 (s, 1H, H-6), 1.30 – 1.19 (m, 6H, H-TIPS), 1.11 – 1.06 (m, 36H, H-TIPS), 1.04 (d, J = 6.5 Hz, 3H, H-8), 0.71 (d, J = 7.0 Hz, 3H, H-9); ^{13}C NMR (125 MHz, *t* = 50 °C,$CDCl_3$); δ(ppm): 153.17, 152.16, 152.13, 147.64, 144.64, 144.36, 143.87, 143.82, 142.28, 138.49, 127.61, 126.40, 126.03, 122.06, 115.88, 114.95, 106.45, 106.11, 97.36, 63.98, 56.89, 56.71, 56.65, 56.57, 56.35, 56.17, 55.73, 18.98, 17.93, 17.93, 17.89, 17.58, 17.54, 14.28, 12.98, 12.94; LRMS (ESI) calcd for $C_{52}H_{84}O_{10}Si_2Na$ [M+Na] 947.55, found 947.59.

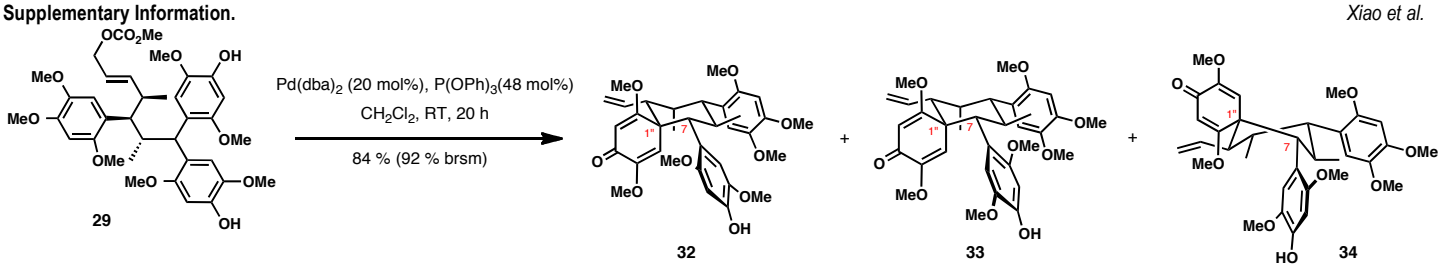


(4*S*,5*S*,6*R*,*E*)-7,7-Bis(2,5-dimethoxy-4-((triisopropylsilyl)oxy)phenyl)-4,6-dimethyl-5-(2,4,5-trimethoxyphenyl)hept-2-en-1-yl methyl carbonate S12. Methyl chloroformate (0.10 mL, 1.3 mmol) was slowly added to a stirred solution of allyl alcohol **S11** (0.41 g, 0.44

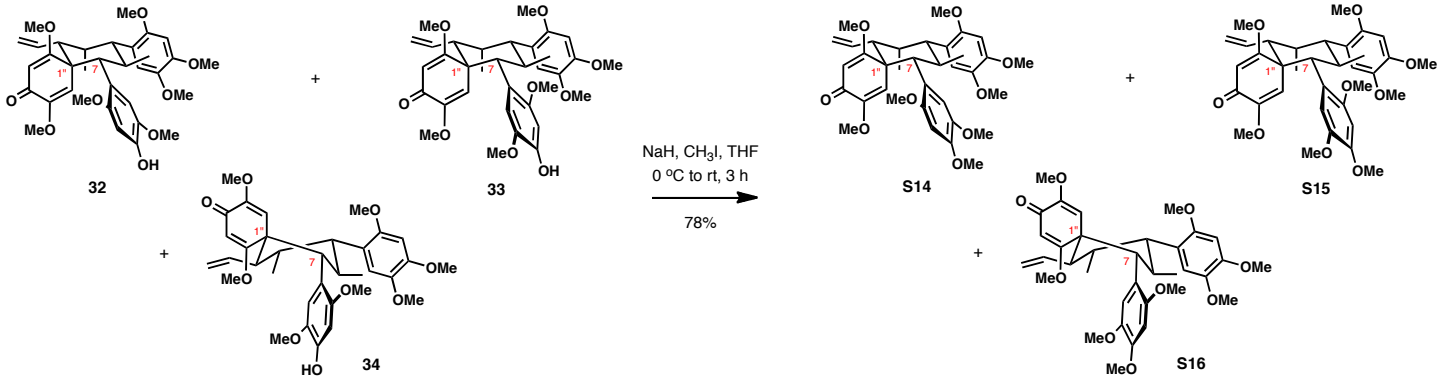
mmol) and pyridine (0.23 mL, 2.7 mmol) in dry dichloromethane (25 mL) at 0 °C. The mixture was stirred at 0 °C for 60 min and then concentrated. The residue was purified by column chromatography (silica, 25% ethyl acetate – hexanes) to give the desired product **S12** (0.42 g, 0.43 mmol, 95%) as a white powder. $[\alpha]_D^{23}$ -24.9° (c 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, *t* = 50 °C, $CDCl_3$); δ(ppm): 6.89 (s, 1H, H-Ar), 6.76 (s, 1H, H-Ar), 6.57 (s, 1H, H-Ar), 6.43 (s, 1H, H-Ar), 6.41 (s, 1H, H-Ar), 6.40 (s, 1H, H-Ar), 5.67 (dd, J = 15.1, 7.5 Hz, 1H, H-2), 5.44 – 5.35 (m, 1H, H-3), 4.47 – 4.36 (m, 3H, H-1 and 7), 3.87 (s, 3H, OMe), 3.76 (s, 3H, OMe), 3.74 (s, 3H, OMe), 3.72 (s, 3H, OMe), 3.68 (s, 3H, OMe), 3.57 (s, 3H, OMe), 3.55 (s, 3H, OMe), 3.50 (s, 3H, OMe), 3.19 (s, 1H, H-5), 2.90 (s, 1H, H-4), 2.79 (s, 1H, H-6), 1.29 – 1.20 (m, 6H, H-TIPS), 1.12 – 1.06 (m, 36H, H-TIPS), 1.01 (d, J = 6.4 Hz, 3H, H-8), 0.69 (d, J = 7.0 Hz, 3H, H-9); ^{13}C NMR (125 MHz, *t* = 50 °C,$CDCl_3$); δ(ppm): 155.56, 153.07, 152.11, 152.07, 147.59, 144.56, 144.28, 143.82, 143.78, 142.27, 141.93, 126.24, 125.82, 121.77, 115.85, 114.94, 106.39, 105.96, 97.39, 56.76, 56.62, 56.58, 56.50, 56.23, 56.06, 55.65, 54.37, 37.55, 18.72, 17.85, 17.81, 17.51, 17.47, 14.27, 12.91, 12.86; LRMS (ESI) calcd for $C_{54}H_{86}O_{12}Si_2Na$ [M+Na] 1005.56, found 1005.59.



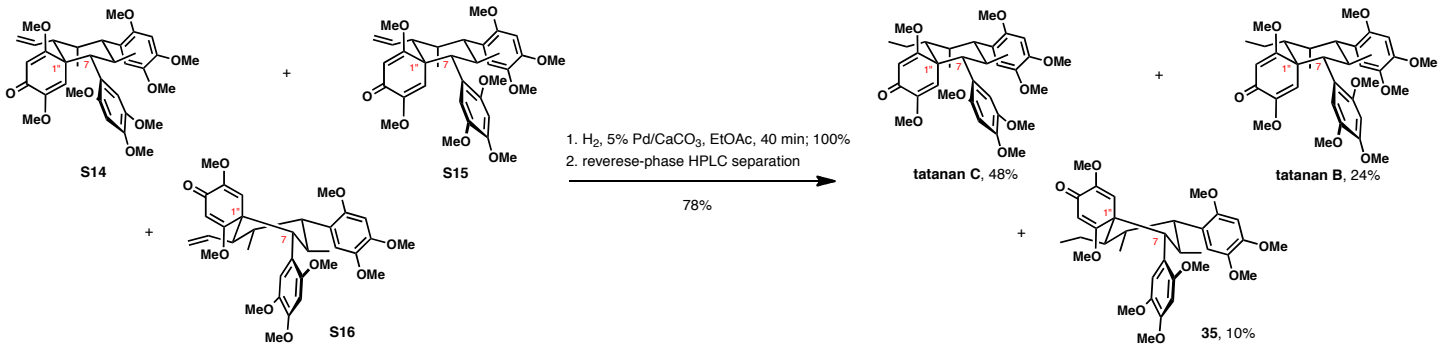
(4*S*,5*S*,6*R*,*E*)-7,7-Bis(4-hydroxy-2,5-dimethoxyphenyl)-4,6-dimethyl-5-(2,4,5-trimethoxyphenyl)hept-2-en-1-yl methyl carbonate 29. Tetra-*n*-butylammonium fluoride (1.0 M in THF, 1.2 ml, 1.2 mmol) was added to a solution of silyl ether **S12** (0.39 g, 0.39 mmol) in THF (30 ml) at 0 °C. After 15 min, the reaction was quenched with 1M aqueous solution of hydrogen chloride (2 ml). The aqueous layer was extracted with ethyl acetate (3x10 ml). The combined organic layers were washed with brine, dried with sodium sulfate, concentrated, and the residue was purified by column chromatography (silica, 50% ethyl acetate – hexanes then 60% ethyl acetate – hexanes) to give the desired product **29** (0.28 g, 0.40 mmol, 100%) as a yellow solid. $[\alpha]_D^{23}$ -66.4° (c 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, *t* = 50 °C, $CDCl_3$); δ(ppm): 6.88 (s, 1H, H-Ar), 6.80 (s, 1H, H-Ar), 6.57 (s, 1H, H-Ar), 6.47 (s, 1H, H-Ar), 6.43 (s, 1H, H-Ar), 6.35 (s, 1H, H-Ar), 5.54 (dd, J = 15.4, 7.8 Hz, 1H, H-3), 5.41 (s, 1H, OH), 5.37 (s, 1H, OH), 5.36 – 5.27 (m, 1H, H-2), 4.33 (d, J = 6.5 Hz, 2H, H-1), 4.13 (s, 1H, H-7), 3.87 (s, 3H, OMe), 3.83 (s, 3H, OMe), 3.77 (s, 6H, OMe), 3.71 (s, 3H, OMe), 3.63 (s, 3H, OMe), 3.62 (s, 3H, OMe), 3.43 (s, 3H, OMe), 3.43 (s, 3H, OMe), 3.08 (s, 2H, H-5 and 4), 2.75 (s, 1H, H-6), 1.12 (d, J = 6.6 Hz, 3H, H-8), 0.78 (d, J = 6.9 Hz, 3H, H-9); ^{13}C NMR (125 MHz, *t* = 23 °C, $CDCl_3$); δ(ppm): 171.22, 155.47, 152.73, 152.18, 152.12, 147.19, 143.83, 143.72, 142.36, 141.62, 139.85, 139.54, 124.04, 123.74, 121.38, 113.70, 112.81, 99.68, 99.25, 96.07, 68.80, 64.31, 60.34, 56.66, 56.56, 56.08, 55.82, 55.64, 55.18, 54.48, 30.58, 19.06, 18.94, 14.17, 14.14, 13.64; LRMS (ESI) calcd for $C_{36}H_{46}O_{12}Na$ [M+Na] 693.29, found 693.32.



Mixture of cyclohexadienones 32, 33, and 34. Bis-phenol **29** (0.100 g, 0.149 mmol), $Pd(dba)_2$ (17 mg, 0.030 mmol), and $P(OPh)_3$ (22 mg, 0.072 mmol) were dissolved in CH_2Cl_2 (3.0 mL) and the resulting solution was degassed with argon and stirred at room temperature. After 20 h, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography (SiO_2, 50% ethyl acetate – hexanes, then 100% ethyl acetate) to give products **32**, **33** and **34** (75 mg, 0.0126 mmol, 84%), as an inseparable mixture in a 6:3:2 ratio, respectively, along with the recovered starting material (9 mg, 0.0134 mmol, 9%). LRMS (ESI) calcd for $C_{34}H_{42}O_9Na$ [M+Na] 617.27, found 617.30.



Mixture of aryl methyl ethers S14, S15, and S16. Sodium hydride (60% in mineral oil, 54 mg, 1.35 mmol) was added to as stirred solution of **32**, **33** and **34** (6:3:2, 80 mg, 0.134 mmol) and iodomethane (84 μL, 1.35 mol) in dry THF (5.0 mL) at 0 °C. The resultant mixture was stirred for 10 min. Then ice-water bath was removed and the stirring was continued at room temperature for 3 h. The reaction mixture was then cooled to 0 °C and quenched with pieces of ice. The reaction mixture was diluted with ethyl acetate (50 mL) and washed with brine (10 mL). The organic layer was dried over Na_2SO_4 and evaporated. The crude product was purified by column chromatography (silica gel, 100% ethyl acetate) to obtain products **S14**, **S15** and **S16** as a 6:3:2 mixture (63 mg, 0.103 mmol, 78%).



Tatanans B and C. A 50 mL round bottomed flask was charged with the mixture of substrates **S14**, **S15** and **S16** (3:6:2, 63 mg, 0.103 mmol). The flask was evacuated and filled with hydrogen. The process was repeated 3 times. Ethyl acetate was added and the solution was

stirred for 40 min. Lindlar's catalyst (5% Pd on $CaCO_3$ poisoned with Pb, 95 mg) was added at once and the mixture was stirred at room temperature for 20 min. The balloon supplying hydrogen was removed and the reaction mixture was filtered rapidly through a small pad of silica and the pad was washed with ethyl acetate (3×20 mL). The filtrate was evaporated and the crude product was purified by column chromatography (silica, 100% ethyl acetate) to obtain a mixture of tatanan B, tatanan C, and isomer **35** (3:6:2, 64 mg, 0.103 mol, 100%). The isomers were separated by reverse-phase HPLC (YMC ODS-AM column, 250mm·20mm, 254 nm, 40% MeCN-H_2O, 18.0 ml/min) affording **35** (R_t=108.6 min, 6 mg, 10%), tatanan C (R_t=110.4 min, 30 mg, 48%), tatanan B (R_t=115.8 min, 15 mg, 24%), and a mixture of **35**/tatanan B/tatanan C (12 mg, 2:1:2, 18%).

35: $[\alpha]_D^{23}$ +54.5°(c 0.10, CH_3OH); ^{1}H NMR (600 MHz, *t* = 23 °C, $(CD_3)_2CO$); δ(ppm): 7.28 (s, 1H, H-6), 6.73 (s, 1H, H-3), 6.68 (s, 1H, H-6′), 6.52 (s, 1H, H-3′), 5.89 (s, 1H, H-6′′), 5.28 (s, 1H, H-3′′), 3.93 (s, 3H, OMe), 3.88 (s, 3H, OMe), 3.85 (s, 3H, OMe), 3.82 (s, 3H, OMe), 3.76 (s, 3H, OMe), 3.73 (s, 3H, OMe), 3.70 (s, 3H, OMe), 3.67 (d, J = 12.7 Hz, 1H, H-7), 3.65 (s, 3H, OMe), 3.37 (dd, J = 9.7, 8.2 Hz, 1H, H-7′), 2.92 (ddd, J = 12.6, 9.9, 6.4 Hz, 1H, H-8), 2.69 (ddd, J = 11.9, 7.0, 4.6 Hz, 1H, 7′′), 2.52 - 2.43 (m, 1H, 8′), 1.26 - 1.19 (m, 1H, H-8′′a), 1.00 (ddd, J = 14.5, 7.5, 4.6 Hz, 1H, H-8′′b), 0.74 (t, J = 7.5 Hz, 3H, H-9′′), 0.63 (d, J = 7.1 Hz, 3H, H-9′), 0.50 (d, J = 6.4 Hz, 3H, H-9); ^{13}C NMR (150 MHz, *t* = 23 °C, $(CD_3)_2CO$); δ(ppm): 180.77, 177.57, 152.91, 152.79, 149.96, 148.82, 148.19, 143.43, 142.71, 123.51, 118.31, 116.37, 115.26, 113.08, 104.54, 98.37, 97.52, 56.62, 56.03, 55.91, 55.49, 55.44, 55.32, 55.00, 54.37, 53.78, 45.92, 44.88, 43.60, 34.35, 32.22, 29.42, 22.71, 19.91, 15.32, 14.24. HRMS (ESI) calcd for $C_{35}H_{46}O_9Na$ [M+Na] 633.3040, found 693.3010.

Tatanan B: $[\alpha]_D^{23}$ -29.9° (c 0.10, CH_3OH); ^{1}H NMR (800 MHz, *t* = 23 °C, $(CD_3)_2CO$); δ(ppm): 6.89 (s, 1H), 6.73 (s, 1H), 6.52 (s, 1H), 6.49 (s, 1H), 6.26 (s, 1H), 5.36 (s, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 3.84 (s, 3H), 3.84 (s, 3H), 3.77 (s, 3H), 3.74 (s, 3H), 3.70 (s, 3H), 3.64 (s, 3H), 3.43 (ddd, J = 18.1, 12.1, 6.3 Hz, 1H), 3.24 (dd, J = 11.9, 4.4 Hz, 1H), 3.14 (d, J = 11.2 Hz, 1H), 2.40 (dt, J = 10.7, 4.4 Hz, 1H), 2.32 — 2.26 (m, 1H), 1.26 — 1.20 (m, 1H), 1.15 — 1.09 (m, 1H), 0.91 (d, J = 7.5 Hz, 3H), 0.76 (t, J = 7.4 Hz, 3H), 0.60 (d, J = 6.2 Hz, 3H); ^{13}C NMR (200 MHz, *t* = 23 °C, $(CD_3)_2CO$); δ(ppm): 181.31, 177.50, 153.30, 153.24, 150.90, 149.66, 149.52, 143.62, 143.04, 123.90, 119.83, 118.87, 117.00, 116.21, 105.72, 99.45, 99.06, 60.99, 57.92, 56.87, 56.82, 56.26, 56.06, 56.04, 55.98, 54.62, 49.83, 48.07, 33.61, 27.33, 21.52, 19.43, 12.29, 11.98; LRMS (ESI) calcd for $C_{35}H_{46}O_9Na$ [M+Na] 633.30, found 633.30. HRMS (ESI) calcd for $C_{35}H_{46}O_9Na$ [M+Na] 633.3040, found 693.3016.

Tatanan C: $[\alpha]_D^{23}$ -47.3° (c 0.11, CH_3OH); ^{1}H NMR (600 MHz, *t* = 23 °C, $(CD_3)_2CO$); δ(ppm): 6.96 (s, 1H), 6.83 (s, 1H), 6.73 (s, 1H), 6.50 (s, 1H), 6.29 (s, 1H), 5.23 (s, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 3.84 (d, J = 2.5 Hz, 1H),3.79 (s, 3H), 3.75 (s, 3H), 3.74 (s, 3H), 3.71 (s, 6H), 3.62 (s, 3H), 3.39 (dd, J = 11.6, 4.6 Hz, 1H), 2.85 — 2.79 (m, 1H), 2.52 (dt, J = 10.8, 4.3 Hz, 1H), 2.37 — 2.31 (m, 1H), 1.25 (m, 1H), 1.17 — 1.10 (m, 1H), 0.99 (d, J = 7.5 Hz, 3H), 0.78 (t, J = 7.4 Hz, 3H), 0.51 (d, J = 6.2 Hz, 3H) ; ^{13}C NMR (150 MHz, *t* = 23 °C, $(CD_3)_2CO$); δ(ppm): 181.25, 178.86, 153.72, 153.43, 152.82, 149.82, 149.69, 143.74, 142.79, 124.00, 120.76, 117.95, 117.41, 114.85, 104.62, 99.40, 97.65, 58.49, 57.87, 56.92, 56.65, 56.39, 56.23, 56.09, 55.28, 55.06, 50.72, 49.41, 48.34, 33.46,

30.35, 22.03, 19.10, 12.46, 12.15; HRMS (ESI) calcd for $C_{35}H_{46}O_9Na$ [M+Na] 633.3040, found 693.3027.

Supplementary Table 1. Comparison of ^{1}H NMR data for the synthetic tatanans A, B, and C with those published for the natural material.

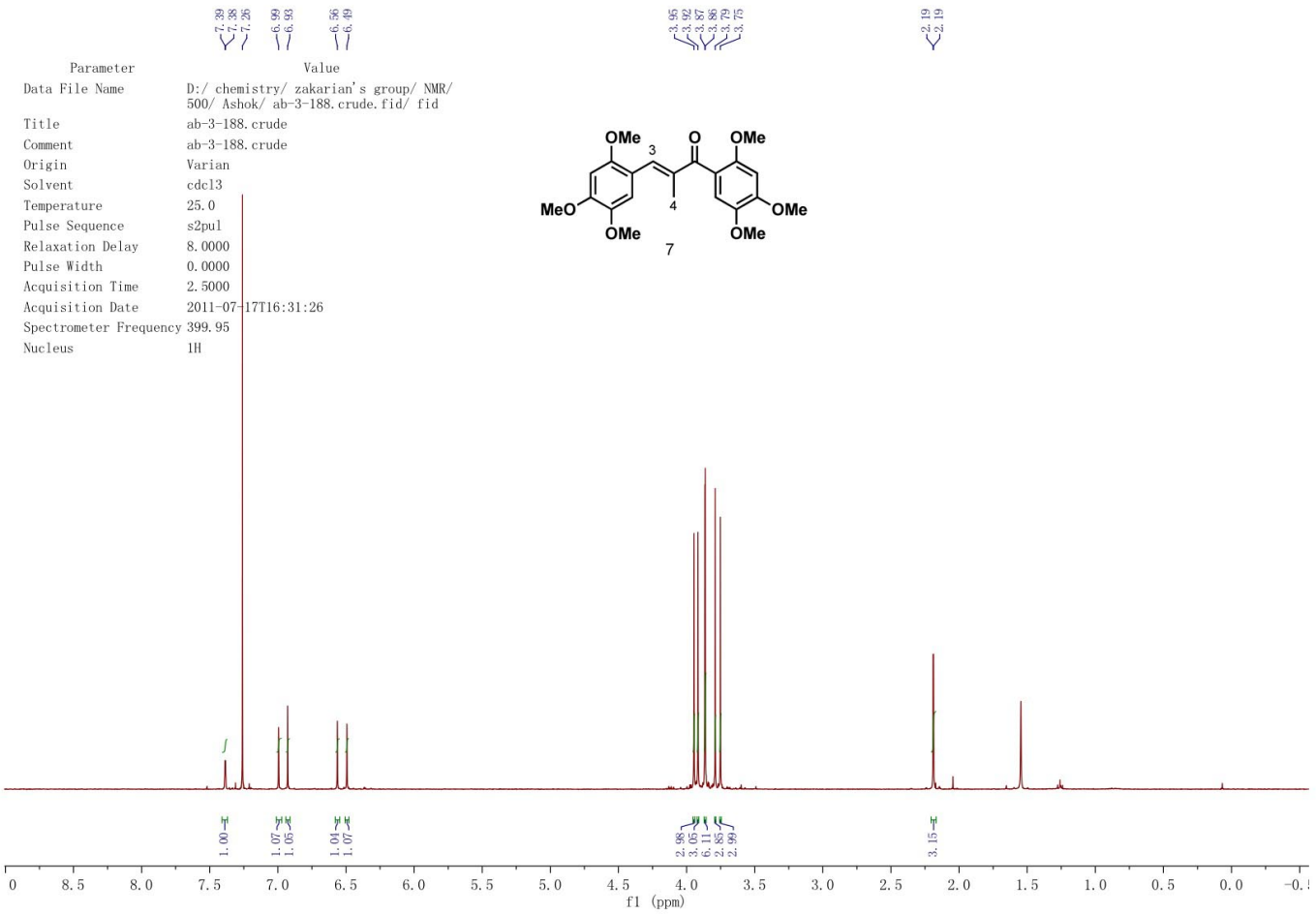
comparison of ^{1}H NMR data δ (ppm)						
no.	tatanan A[a]		tatanan B[b]		tatanan C[b]	
	Ni et al. natural δ_H m(J,Hz)	This work δ_H m(J,Hz)	Ni et al. natural δ_H m(J,Hz)	This work δ_H m(J,Hz)	Ni et al. natural δ_H m(J,Hz)	This work δ_H m(J,Hz)
1						
2						
3	6.59(s)	6.58(s)	6.55(s)	6.52(s)	6.49(s)	6.50(s)
4						
5						
6	6.64(s)	6.62(s)	6.51(s)	6.48(s)	6.82(s)	6.83(s)
7	6.28(s)	6.26(s)	3.17(d,11.0)	3.14(d,11.2)	3.84(d,11.4)	3.84(d,10.8)
8			3.45(m)	3.42(m)	2.81(m)	2.82(m)
9	1.57(s)	1.55(s)	0.63(d,6.0)	0.60(d,6.2)	0.50(d,6.0)	0.51(d,6.2)
1′						
2′						
3′	6.66(s)	6.65(s)	6.76(s)	6.73(s)	6.72(s)	6.73(s)
4′						
5′						
6′	6.87(s)	6.85(s)	6.92(s)	6.89(s)	6.95(s)	6.96(s)
7′	3.53(overlap)	3.50(d,11.5)	3.27(dd, 12.0,4.5)	3.24(dd, 11.9,4.4)	3.39(dd, 12.0,4.2)	3.39(dd, 11.6,4.6)
8′	2.56(1H,m)	2.55(m)	2.32(m)	2.30(m)	2.33(m)	2.34(m)
9′	0.97(d,6.5)	0.95(d,6.5)	0.94(d,7.5)	0.91(d,7.5)	0.94(d,7.2)	0.99(d,7.5)
1″						
2″						
3″	6.54(s)	6.53(s)	5.38(s)	5.35(s)	5.22(s)	5.23(s)
4″						
5″						
6″	6.54(s)	6.53(s)	6.29(s)	6.26(s)	6.27(s)	6.29(s)
7″	3.11(m)	3.10(m)	2.43(dt, 11.0,4.5)	2.40(dt, 10.7,4.4)	2.51(dt, 11.8,4.8)	2.52(dt, 10.8,4.3)
8″	a 1.74(m) b 1.80(m)	a 1.73(m) b 1.78(m)	a 1.15(m) b 1.24(m)	a 1.12(m) b 1.21(m)	a 1.13(m) b 1.27(m)	a 1.14(m) b 1.25(m)
9″	0.77(t,6.5)	0.75(t,7.5)	0.79(t,6.5)	0.76(t,7.4)	0.78(t,6.5)	0.78(t,7.4)
OMe	3.53(s)	3.51(s)	3.67(s)	3.64(s)	3.61(s)	3.62(s)
OMe	3.71(9H, overlap)	3.70(9H, overlap)	3.72(s)	3.69(s)	3.70(6H, overlap)	3.71(6H, overlap
OMe	3.77(s)	3.76(s)	3.77(s)	3.74(s)	3.73(overlap)	3.74(s)
OMe	3.78(s)	3.77(s)	3.80(s)	3.77(s)	3.74(overlap)	3.75(s)
OMe	3.82(S)	3.81(s)	3.86(overlap)	3.83(s)	3.78(s)	3.79(s)
OMe	3.84(s)	3.83(s)	3.87(overlap)	3.84(s)	3.83(s)	3.84(s)
OMe	3.87(s)	3.86(s)	3.88(overlap)	3.84(s)	3.86(s)	3.87(s)
OMe			3.89(overlap)	3.86(s)		

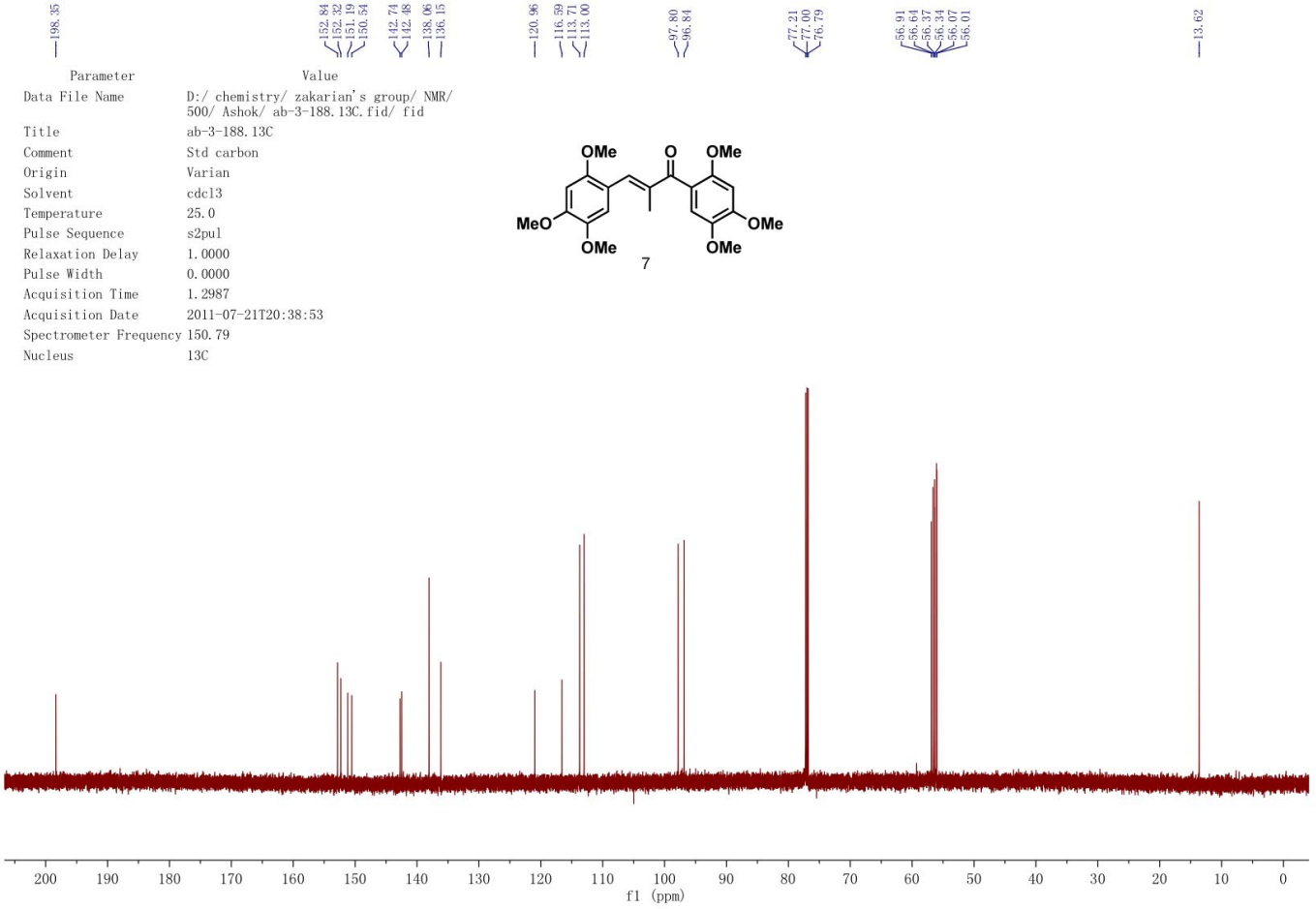
[a]In CD_3OD. [b]In acetone-d_6

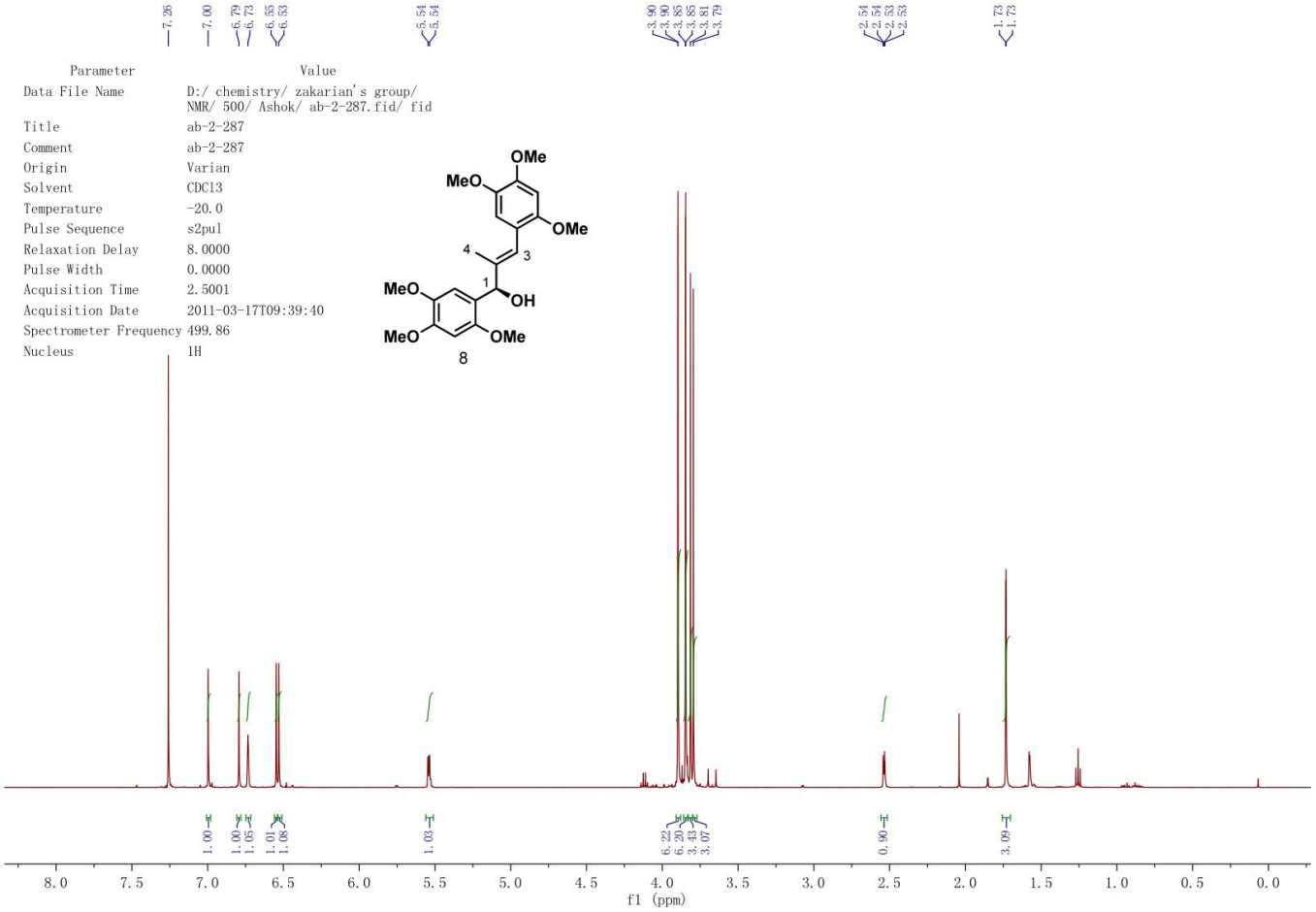
Supplementary Table 2. Comparison of ^{13}C NMR data for the synthetic tatanans A, B, and C with those published for the natural material

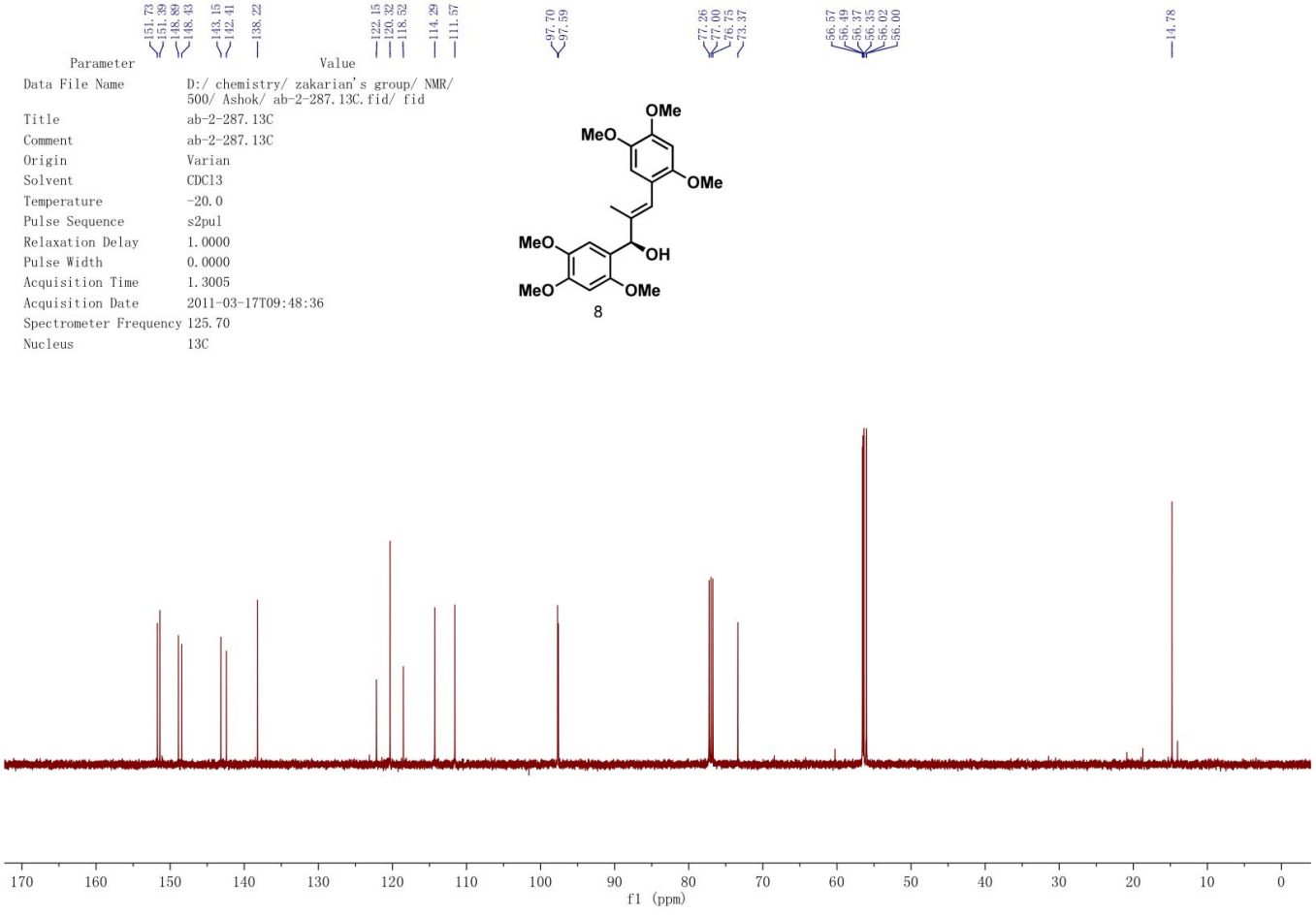
comparison of ^{13}C NMR data δ (ppm)						
no.	tatanan A[a]		tatanan B[b]		tatanan C[b]	
	Ni et al. natural δ_H m(J,Hz)	This work δ_H m(J,Hz)	Ni et al. natural δ_H m(J,Hz)	This work δ_H m(J,Hz)	Ni et al. natural δ_H m(J,Hz)	This work δ_H m(J,Hz)
1	121.4	121.6	119.9	119.8	120.7	120.7
2	153.5	153.8	153.4	153.3	153.7	153.7
3	98.7	98.8	99.2	99.1	97.6	97.6
4	149.8	150.1	149.7	149.7	149.8	149.8
5	143.8	144.1	143.1	143.0	142.7	142.8
6	116.6	116.8	119.0	118.9	114.7	114.8
7	123.0	123.3	61.0	61.0	50.6	50.7
8	139.7	139.9	27.4	27.3	30.3	30.3
9	14.9	15.0	19.5	19.4	19.0	19.1
1′	125.1	125.3	124.0	123.9	123.9	124.0
2′	154.2	154.5	153.3	153.2	153.4	153.4
3′	100.0	100.0	99.6	99.5	99.3	99.4
4′	149.2	149.5	149.6	149.5	149.6	149.7
5′	143.7	144.0	143.7	143.6	143.7	143.7
6′	115.2	115.4	117.1	117.0	117.9	117.9
7′	52.0	52.2	48.1	48.1	48.3	48.3
8′	38.3	38.5	33.7	33.6	33.4	33.4
9′	15.8	16.0	12.3	12.3	12.4	12.4
1″	123.8	123.9	56.3	56.3	55.2	55.2
2″	154.6	154.9	177.5	177.5	178.6	178.8
3″	99.9	100.0	105.8	105.7	104.6	104.6
4″	149.2	149.4	181.3	181.3	181.1	181.3
5″	143.4	143.6	151.0	150.9	152.8	152.8
6″	116.6	116.8	116.3	116.2	117.4	117.4
7″	29.5		49.9	49.8	49.3	49.4
8″	27.2	27.3	21.6	21.5	21.9	22.0
9″	13.3	13.4	12.0	12.0	12.0	12.1
OMe	56.1	56.2	54.7	54.6	55.0	55.0
OMe	56.7	56.8	55.7	55.7	56.0	56.0
OMe	56.8	56.9	56.1	56.0	56.1	56.2
OMe	56.8	57.0	56.1	56.0	56.3	56.4
OMe	56.9	57.0	56.1	56.1	56.5	56.6
OMe	57.3	57.4	56.9	56.8	56.8	56.9
OMe	57.6	57.7	57.0	56.9	57.8	57.8
OMe	57.6	57.8	58.0	57.9	58.4	58.4
OMe	57.8	57.9				

[a]In CD_3OD. [b]In acetone-d_6


7.39
7.38
7.26
6.99
6.93
6.56
6.49
3.95
3.92
3.87
3.86
3.79
3.75
2.19
2.19
Parameter Value
Data File Name D:/ chemistry/ zakarian's group/ NMR/ 500/ Ashok/ ab-3-188.crude.fid/ fid
Title ab-3-188.crude
Comment ab-3-188.crude
Origin Varian
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Relaxation Delay 8.0000
Pulse Width 0.0000
Acquisition Time 2.5000
Acquisition Date 2011-07-17T16:31:26
Spectrometer Frequency 399.95
Nucleus 1H
OMe
O
OMe
3
MeO
4
OMe
OMe
7
1.00
1.07
1.05
1.04
1.07
2.98
3.05
6.11
2.85
2.99
3.15
f1 (ppm)


198.35
152.84
152.32
151.19
150.54
142.74
142.48
138.06
136.15
120.96
116.59
113.71
113.00
97.80
96.84
77.21
77.00
76.79
56.91
56.64
56.37
56.34
56.07
56.01
13.62
Parameter Value
Data File Name D:/ chemistry/ zakarian's group/ NMR/ 500/ Ashok/ ab-3-188.13C.fid/ fid
Title ab-3-188.13C
Comment Std carbon
Origin Varian
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Relaxation Delay 1.0000
Pulse Width 0.0000
Acquisition Time 1.2987
Acquisition Date 2011-07-21T20:38:53
Spectrometer Frequency 150.79
Nucleus 13C
OMe
O
OMe
MeO
OMe
OMe
7
f1 (ppm)


7.26
7.00
6.79
6.73
6.55
6.53
5.54
5.54
3.90
3.90
3.85
3.85
3.81
3.79
2.54
2.54
2.53
2.53
1.73
1.73
Parameter Value
Data File Name D:/ chemistry/ zakarian's group/ NMR/ 500/ Ashok/ ab-2-287.fid/ fid
Title ab-2-287
Comment ab-2-287
Origin Varian
Solvent CDCl3
Temperature -20.0
Pulse Sequence s2pul
Relaxation Delay 8.0000
Pulse Width 0.0000
Acquisition Time 2.5001
Acquisition Date 2011-03-17T09:39:40
Spectrometer Frequency 499.86
Nucleus 1H
OMe
MeO
OMe
4
3
1
OH
MeO
MeO
OMe
8
1.00
1.00
1.05
1.01
1.08
1.03
6.22
6.20
3.43
3.07
0.90
3.09
f1 (ppm)


151.73
151.39
148.89
148.43
143.15
142.41
138.22
122.15
120.32
118.52
114.29
111.57
97.70
97.59
77.26
77.00
76.75
73.37
56.57
56.49
56.37
56.35
56.02
56.00
14.78
Parameter Value
Data File Name D:/ chemistry/ zakarian's group/ NMR/ 500/ Ashok/ ab-2-287.13C.fid/ fid
Title ab-2-287.13C
Comment ab-2-287.13C
Origin Varian
Solvent CDCl3
Temperature -20.0
Pulse Sequence s2pul
Relaxation Delay 1.0000
Pulse Width 0.0000
Acquisition Time 1.3005
Acquisition Date 2011-03-17T09:48:36
Spectrometer Frequency 125.70
Nucleus 13C
OMe
MeO
OMe
OH
MeO
MeO
OMe
8
f1 (ppm)

7/26/2012 17:56:39 1 / 1

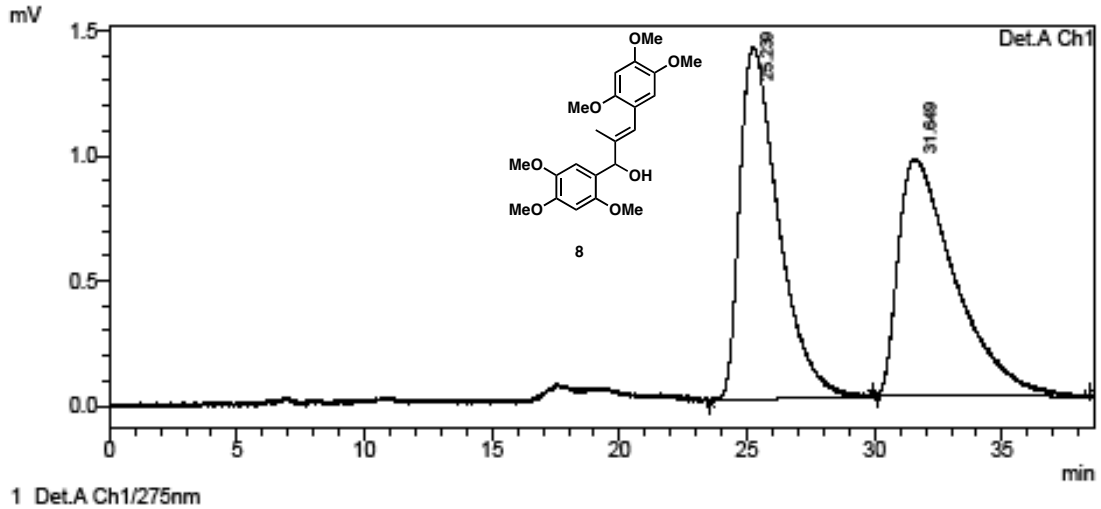
==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\ab\ab-3-097-03.lcd

Acquired by	: Admin
Sample Name	: ab-3-139
Sample ID	: ab-3-139
Vail #	:
Injection Volume	: 25 uL
Data File Name	: ab-3-097-03.lcd
Method File Name	: ces-OD-H-analytical 0.46cm x 25cm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 6/11/2011 3:55:22 PM
Data Processed	: 6/11/2011 4:37:44 PM

<Chromatogram>

C:\LabSolutions\Data\ab\ab-3-097-03.lcd



1 Det.A Ch1/275nm

PeakTable

Detector A Ch1 275nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.239	149571	1409	50.601	59.885
2	31.649	146019	944	49.399	40.115
Total		295590	2353	100.000	100.000

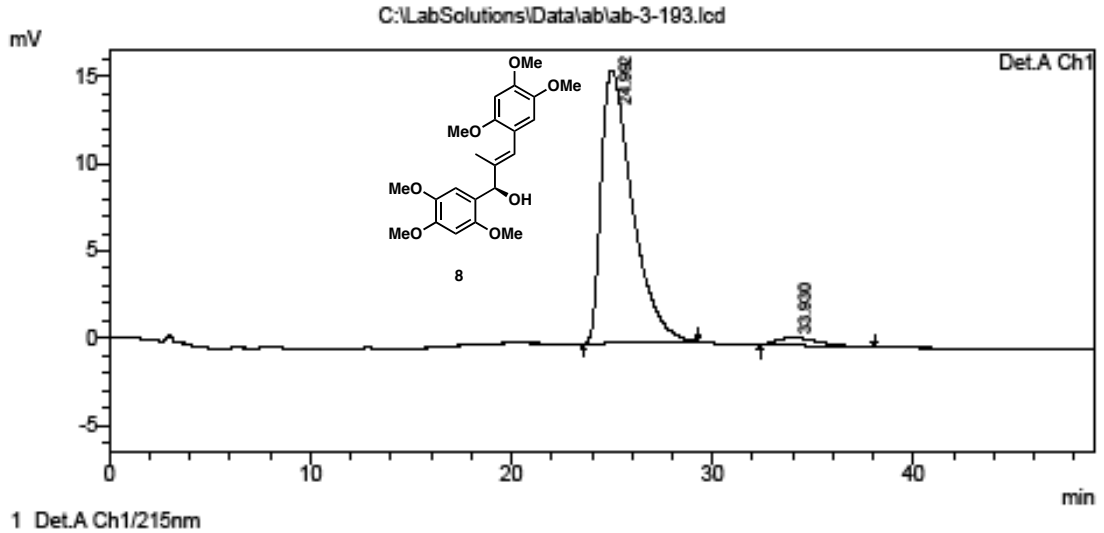
C:\LabSolutions\Data\ab\ab-3-097-03.lcd

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\ab\ab-3-193.lcd

Acquired by	: Admin
Sample Name	: ab-3-193
Sample ID	: ab-3-193
Vail #	:
Injection Volume	: 25 uL
Data File Name	: ab-3-193.lcd
Method File Name	: ces-OD-H-analytical 0.46cm x 25cm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 7/21/2011 5:44:58 PM
Data Processed	: 7/21/2011 6:34:01 PM

<Chromatogram>



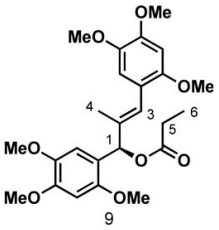
1 Det.A Ch1/215nm

PeakTable

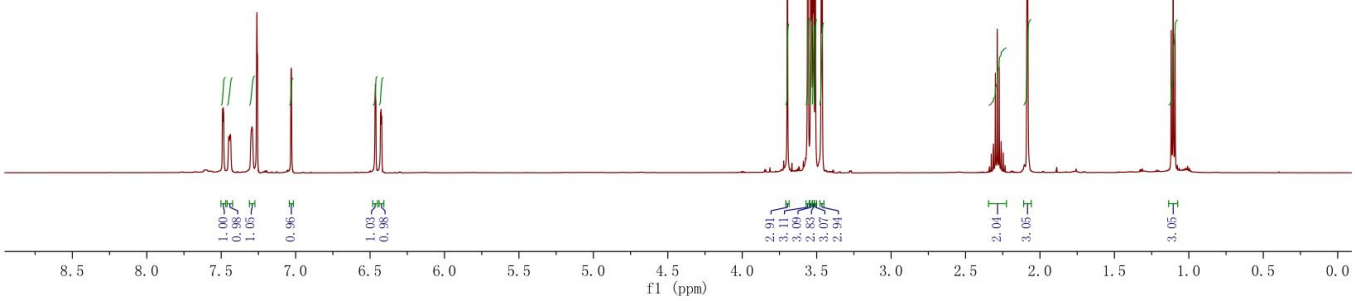
Detector A Ch1 215nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.992	1689324	15639	96.437	97.213
2	33.930	62407	448	3.563	2.787
Total		1751731	16087	100.000	100.000

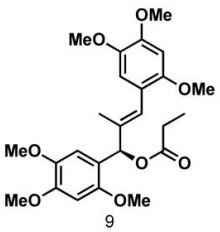
Parameter	Value
Data File Name	D:/ chemistry/ zakarian's group/ NMR/ 500/ Ashok/ ab-3-196.fid/ fid
Title	ab-3-196
Comment	
Origin	Varian
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Relaxation Delay	4.8000
Pulse Width	0.0000
Acquisition Time	2.5000
Acquisition Date	2011-07-23T15:35:28
Spectrometer Frequency	599.63
Nucleus	1H



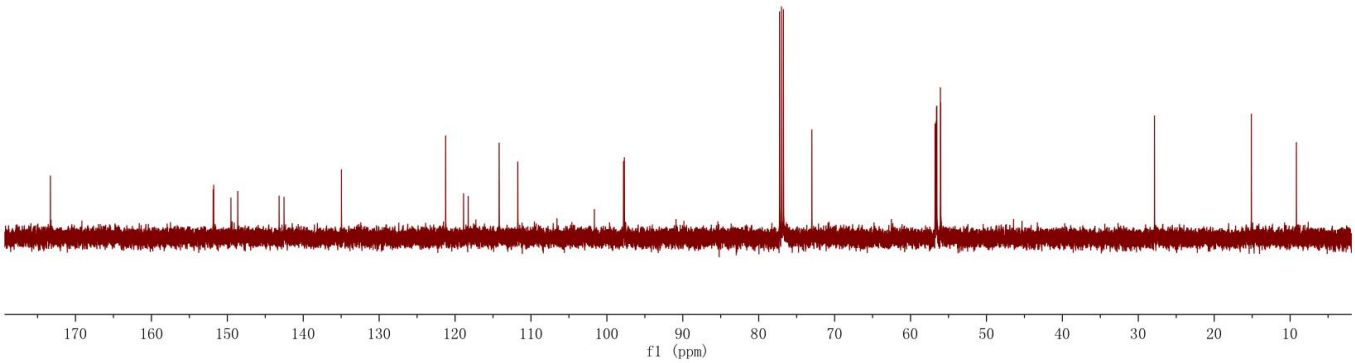
9

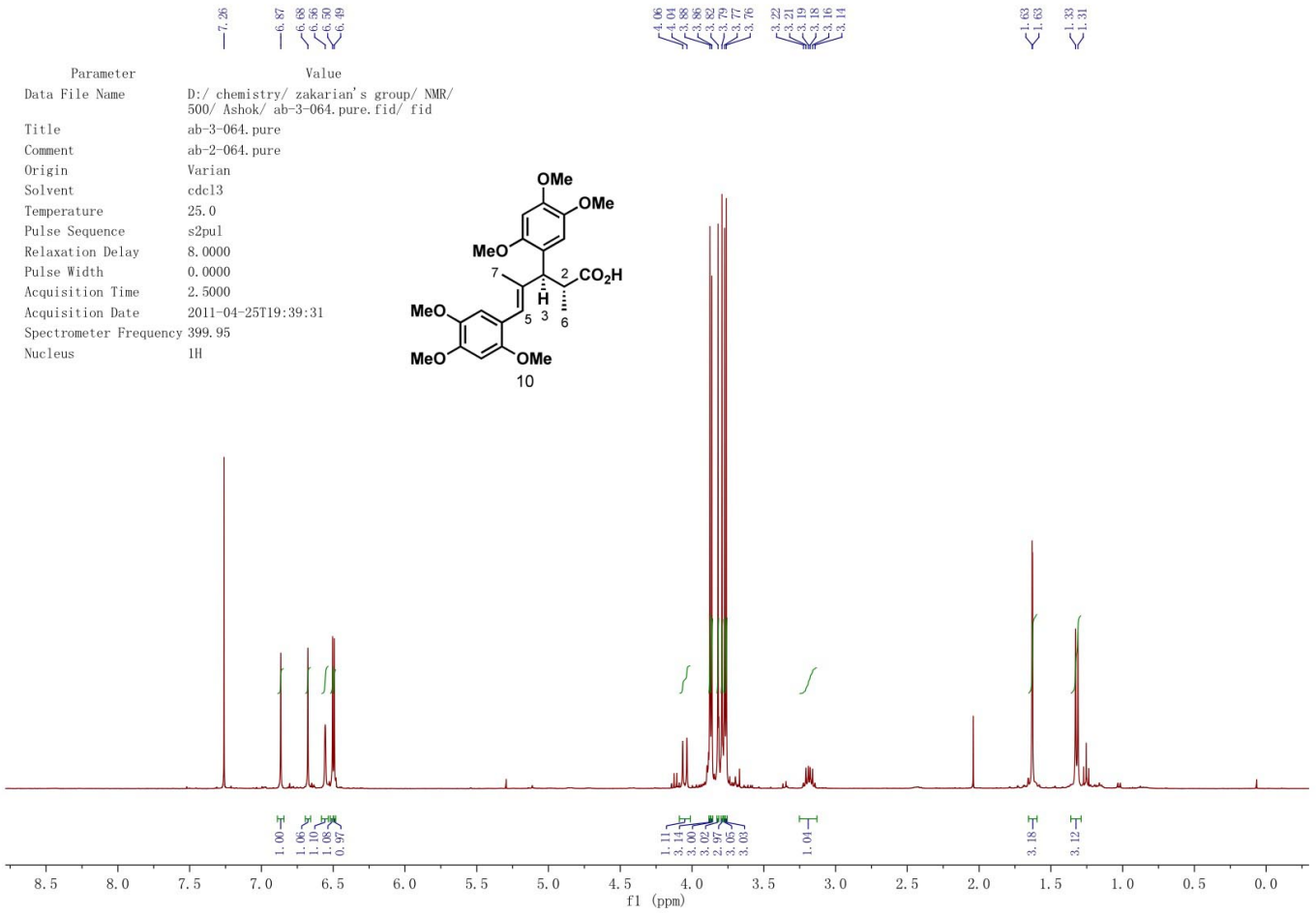


Parameter	Value
Data File Name	D:/ chemistry/ zakarian's group/ NMR/ 500/ Ashok/ ab-3-120.13C.fid/ fid
Title	ab-3-120.13C
Comment	STANDARD CARBON PARAMETERS
Origin	Varian
Solvent	CDCl3
Temperature	22.0
Pulse Sequence	s2pul
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.3005
Acquisition Date	2011-05-27T16:25:30
Spectrometer Frequency	125.70
Nucleus	13C



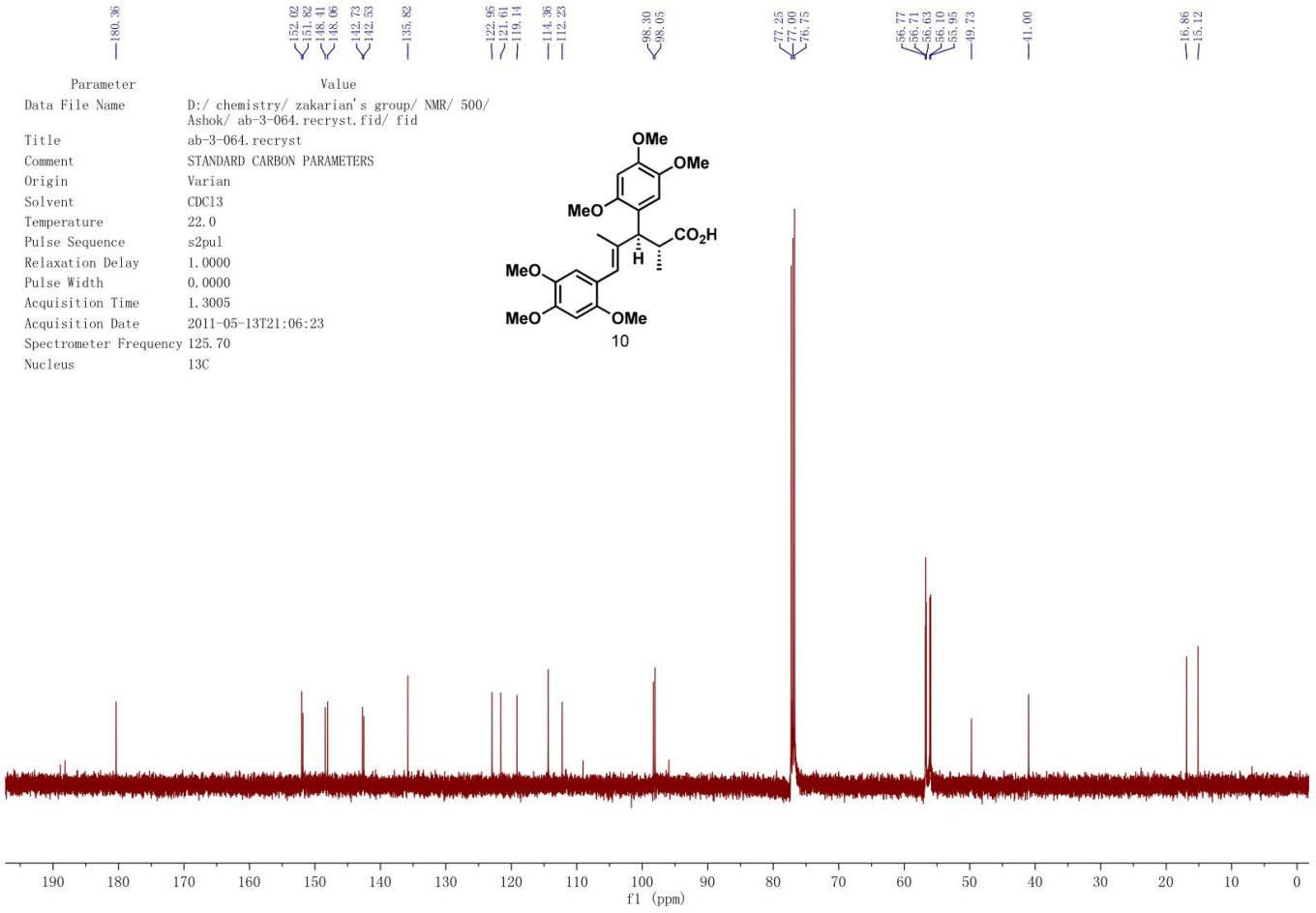
9





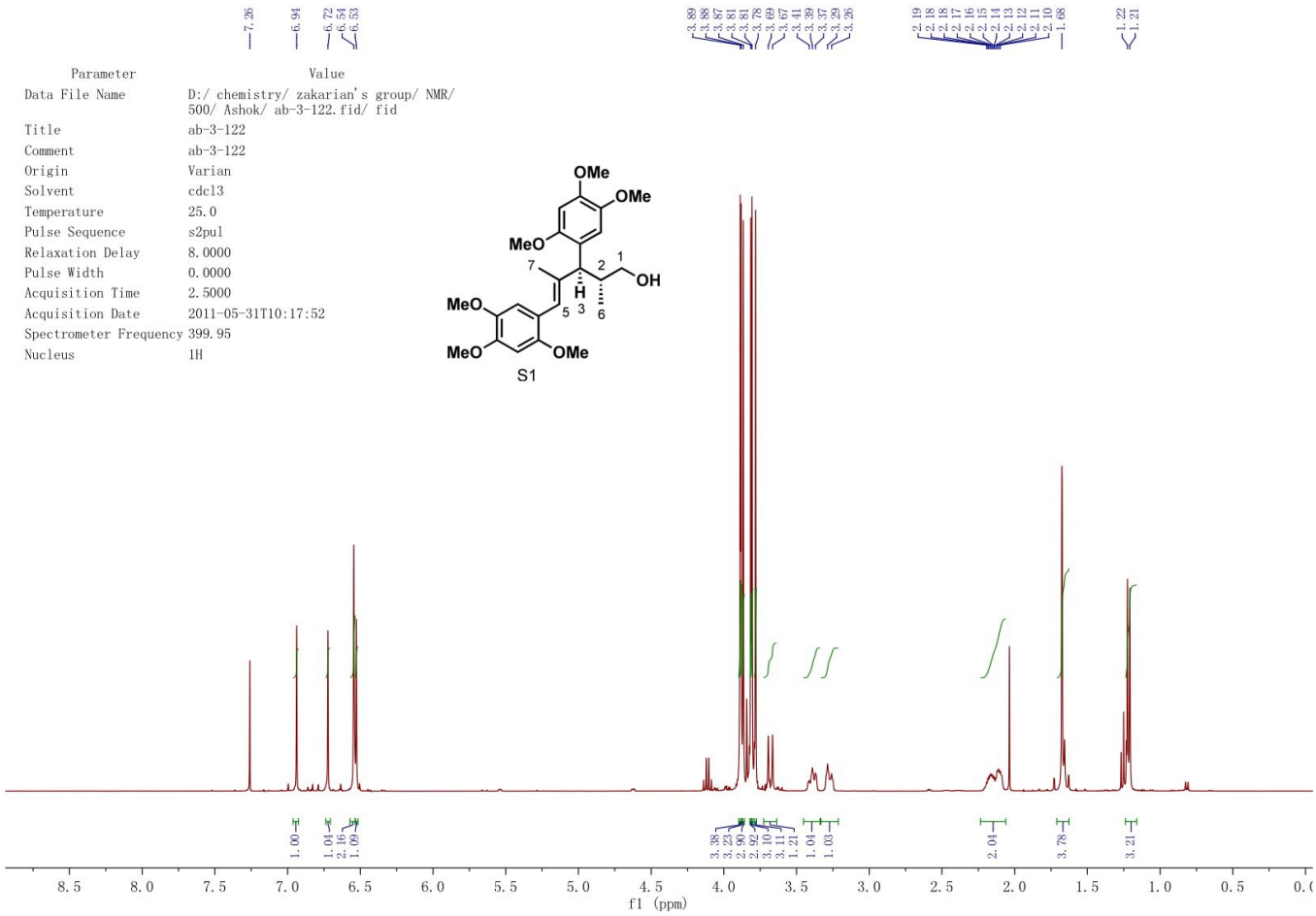
Parameter	Value
Data File Name	D:/ chemistry/ zakarian's group/ NMR/ 500/ Ashok/ ab-3-064.pure.fid/ fid
Title	ab-3-064.pure
Comment	ab-2-064.pure
Origin	Varian
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Relaxation Delay	8.0000
Pulse Width	0.0000
Acquisition Time	2.5000
Acquisition Date	2011-04-25T19:39:31
Spectrometer Frequency	399.95
Nucleus	1H

10

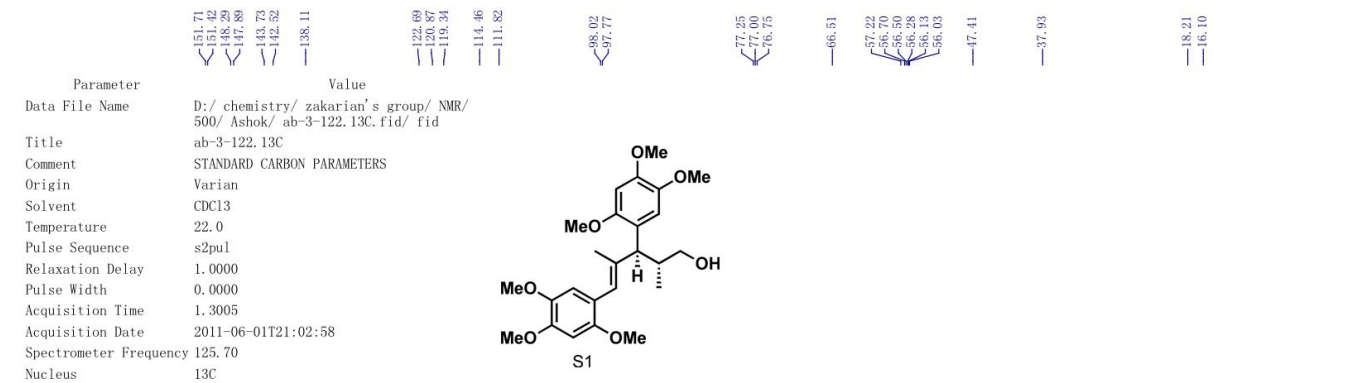


Parameter	Value
Data File Name	D:/ chemistry/ zakarian's group/ NMR/ 500/ Ashok/ ab-3-064.recryst.fid/ fid
Title	ab-3-064.recryst
Comment	STANDARD CARBON PARAMETERS
Origin	Varian
Solvent	CDCl3
Temperature	22.0
Pulse Sequence	s2pul
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.3005
Acquisition Date	2011-05-13T21:06:23
Spectrometer Frequency	125.70
Nucleus	13C

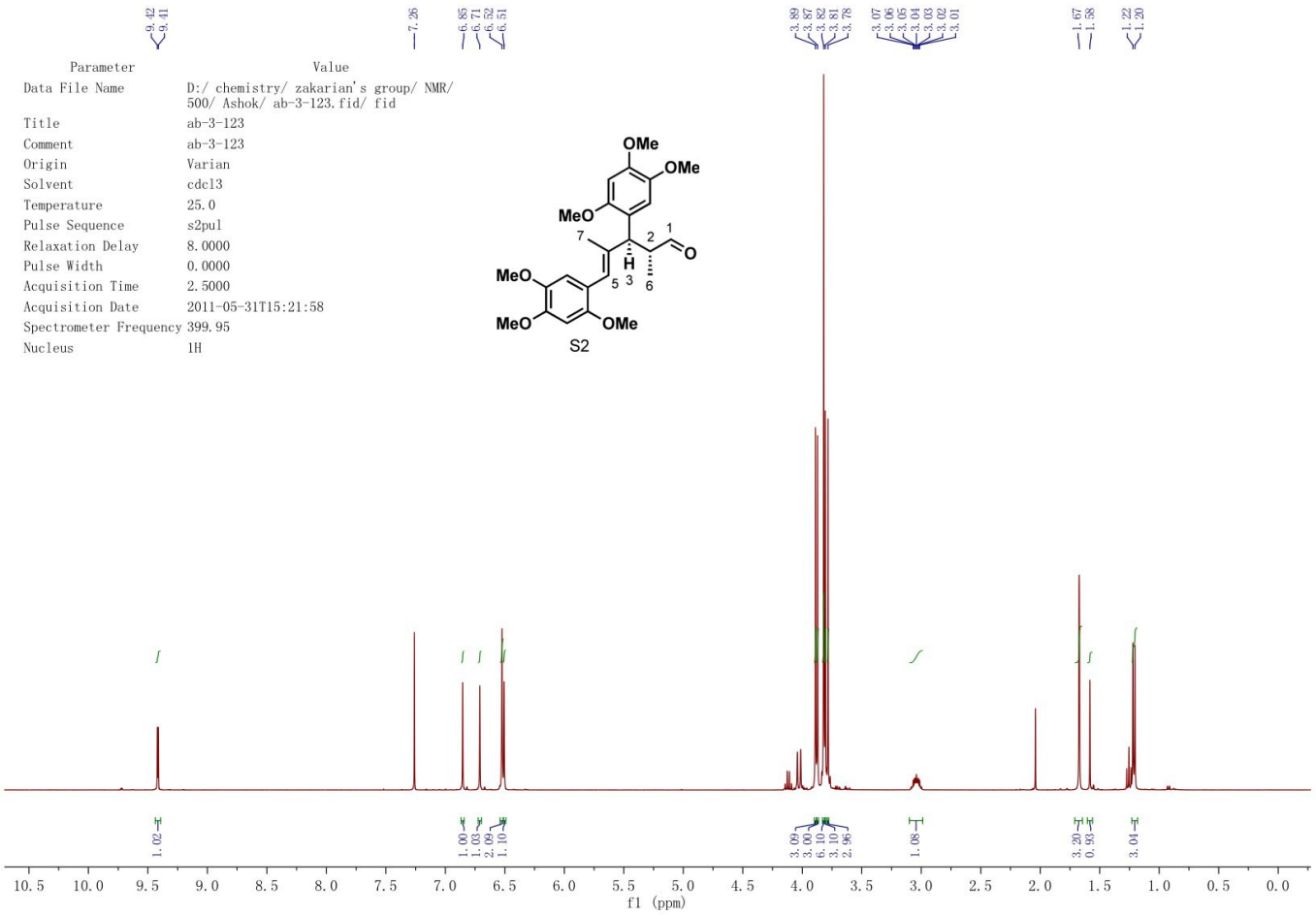
10

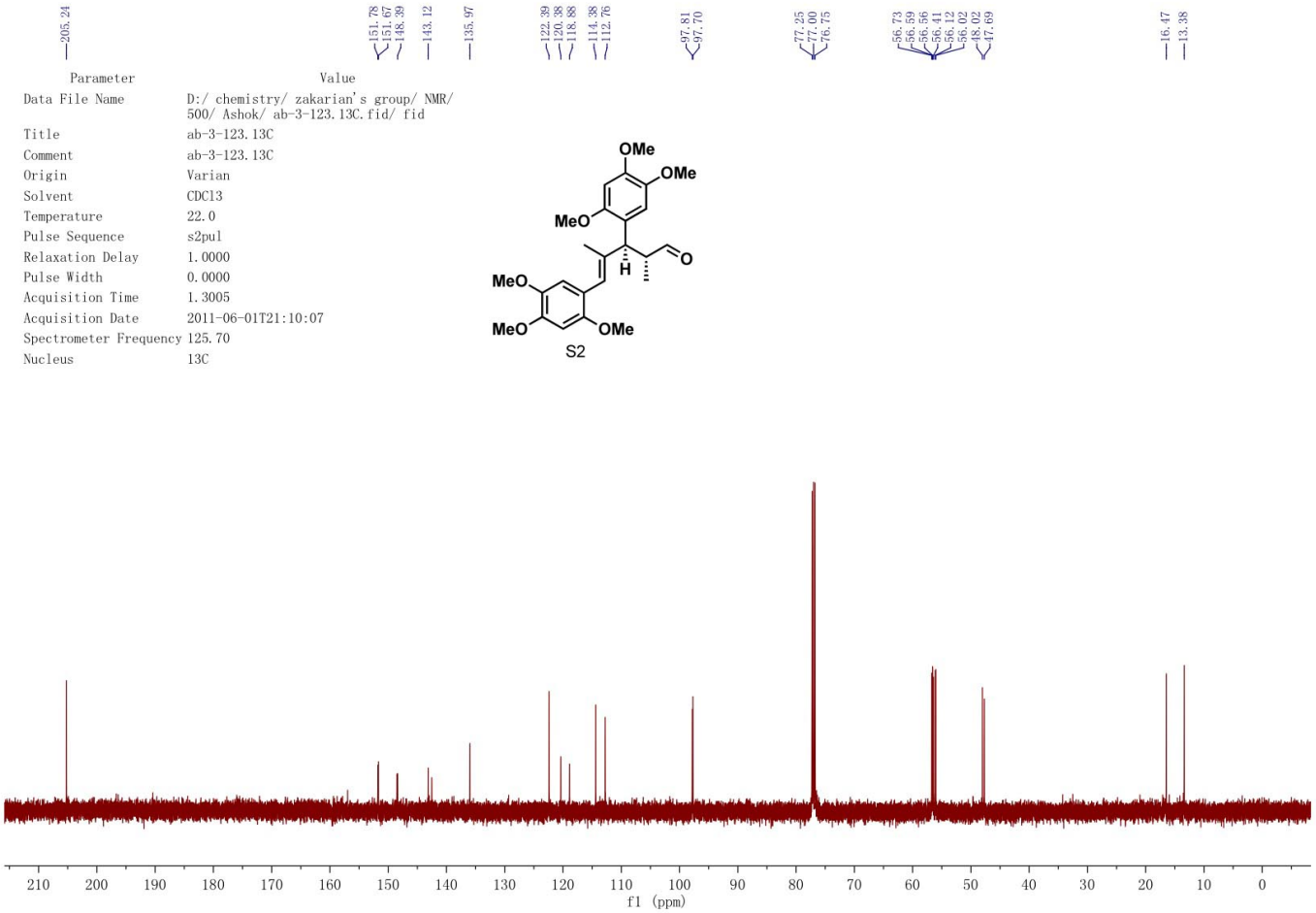


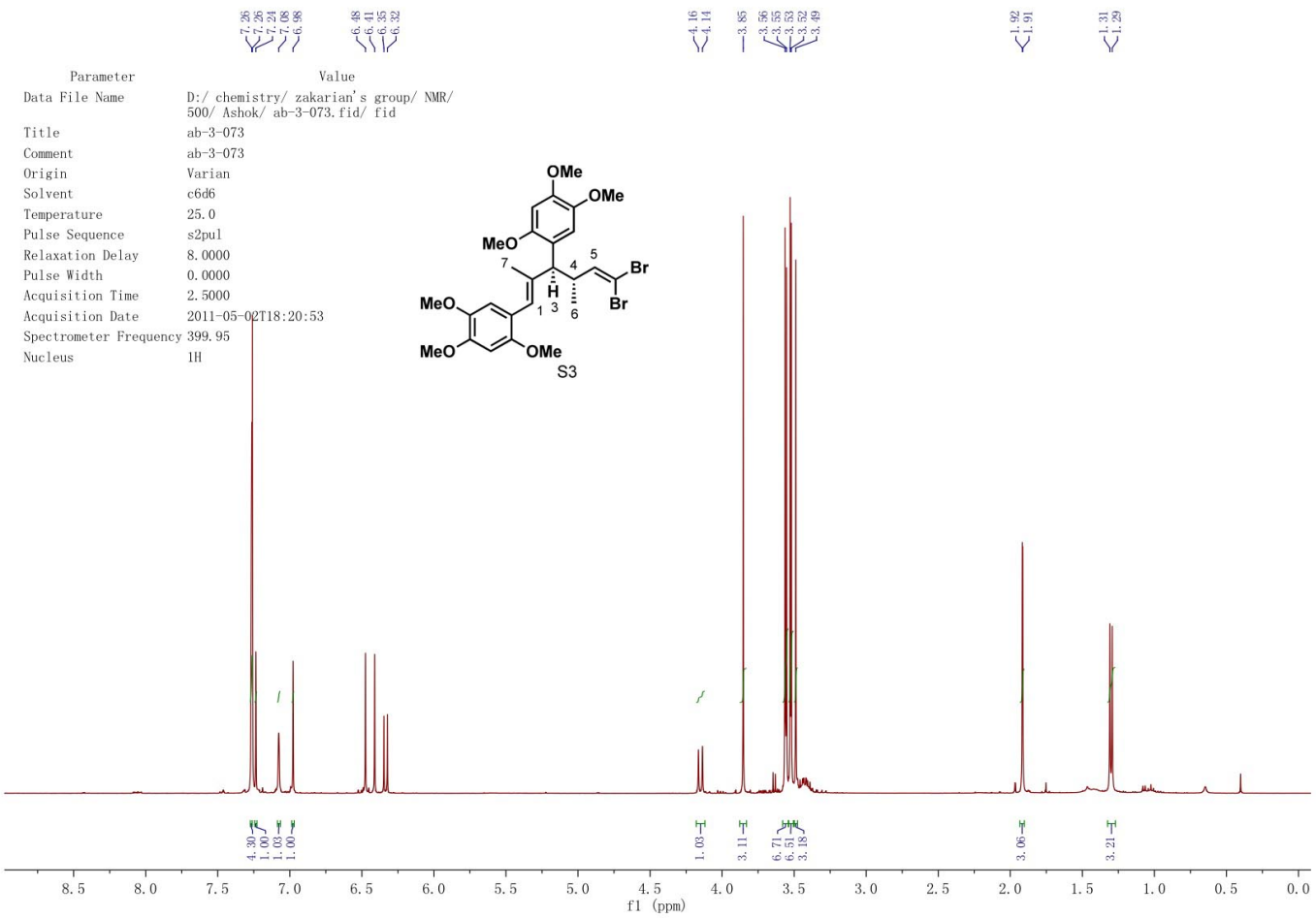
Parameter	Value
Data File Name	D:/ chemistry/ zakarian's group/ NMR/ 500/ Ashok/ ab-3-122.fid/ fid
Title	ab-3-122
Comment	ab-3-122
Origin	Varian
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Relaxation Delay	8.0000
Pulse Width	0.0000
Acquisition Time	2.5000
Acquisition Date	2011-05-31T10:17:52
Spectrometer Frequency	399.95
Nucleus	1H



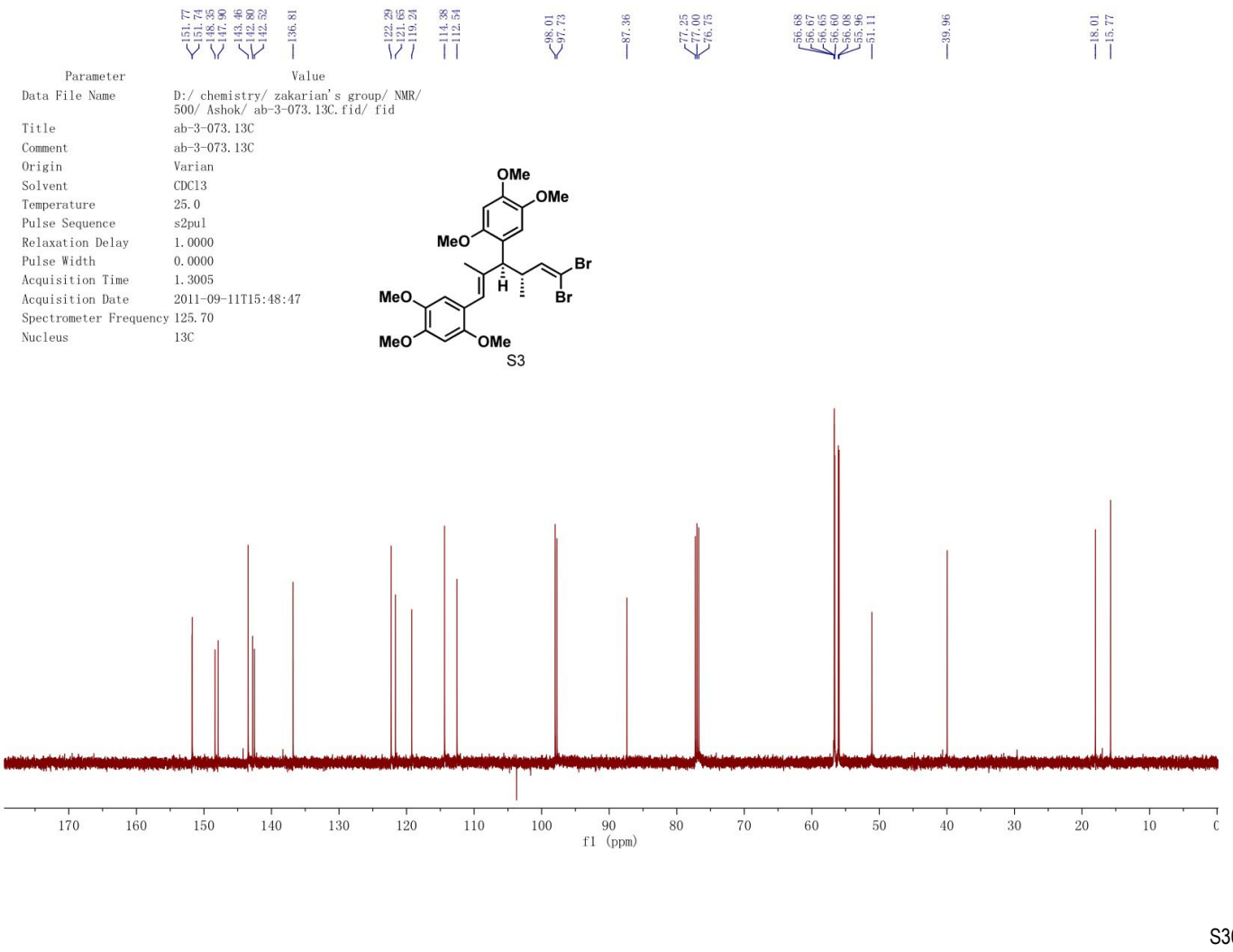
Parameter	Value
Data File Name	D:/ chemistry/ zakarian's group/ NMR/ 500/ Ashok/ ab-3-122.13C.fid/ fid
Title	ab-3-122.13C
Comment	STANDARD CARBON PARAMETERS
Origin	Varian
Solvent	CDCl3
Temperature	22.0
Pulse Sequence	s2pul
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.3005
Acquisition Date	2011-06-01T21:02:58
Spectrometer Frequency	125.70
Nucleus	13C


9.42
9.41
7.26
6.85
6.71
6.52
6.51
3.89
3.87
3.82
3.81
3.78
3.07
3.06
3.05
3.04
3.03
3.02
3.01
1.67
1.58
1.22
1.20
Parameter Value
Data File Name D:/ chemistry/ zakarian's group/ NMR/ 500/ Ashok/ ab-3-123.fid/ fid
Title ab-3-123
Comment ab-3-123
Origin Varian
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Relaxation Delay 8.0000
Pulse Width 0.0000
Acquisition Time 2.5000
Acquisition Date 2011-05-31T15:21:58
Spectrometer Frequency 399.95
Nucleus 1H
OMe
OMe
MeO
MeO
OMe
MeO
S2
1.02
1.00
1.03
2.09
1.10
3.09
3.00
6.10
3.10
2.96
1.08
3.20
0.93
3.04
f1 (ppm)

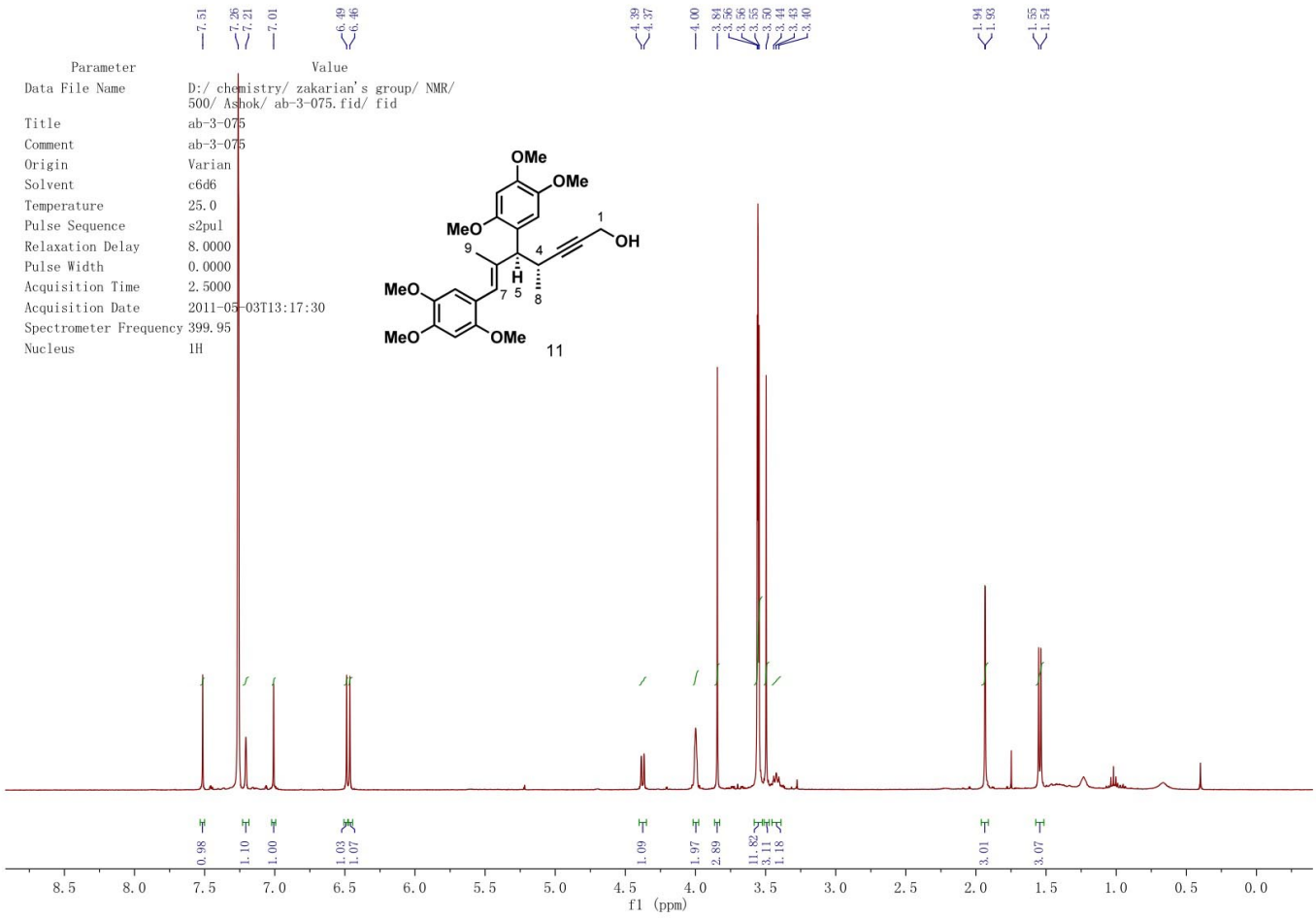

205.24
151.78
151.67
148.39
143.12
135.97
122.39
120.38
118.88
114.38
112.76
97.81
97.70
77.25
77.00
76.75
56.73
56.59
56.56
56.41
56.12
56.02
48.02
47.69
16.47
13.38
Parameter Value
Data File Name D:/ chemistry/ zakarian's group/ NMR/ 500/ Ashok/ ab-3-123.13C.fid/ fid
Title ab-3-123.13C
Comment ab-3-123.13C
Origin Varian
Solvent CDCl3
Temperature 22.0
Pulse Sequence s2pul
Relaxation Delay 1.0000
Pulse Width 0.0000
Acquisition Time 1.3005
Acquisition Date 2011-06-01T21:10:07
Spectrometer Frequency 125.70
Nucleus 13C
OMe
OMe
MeO
MeO
OMe
MeO
S2
f1 (ppm)

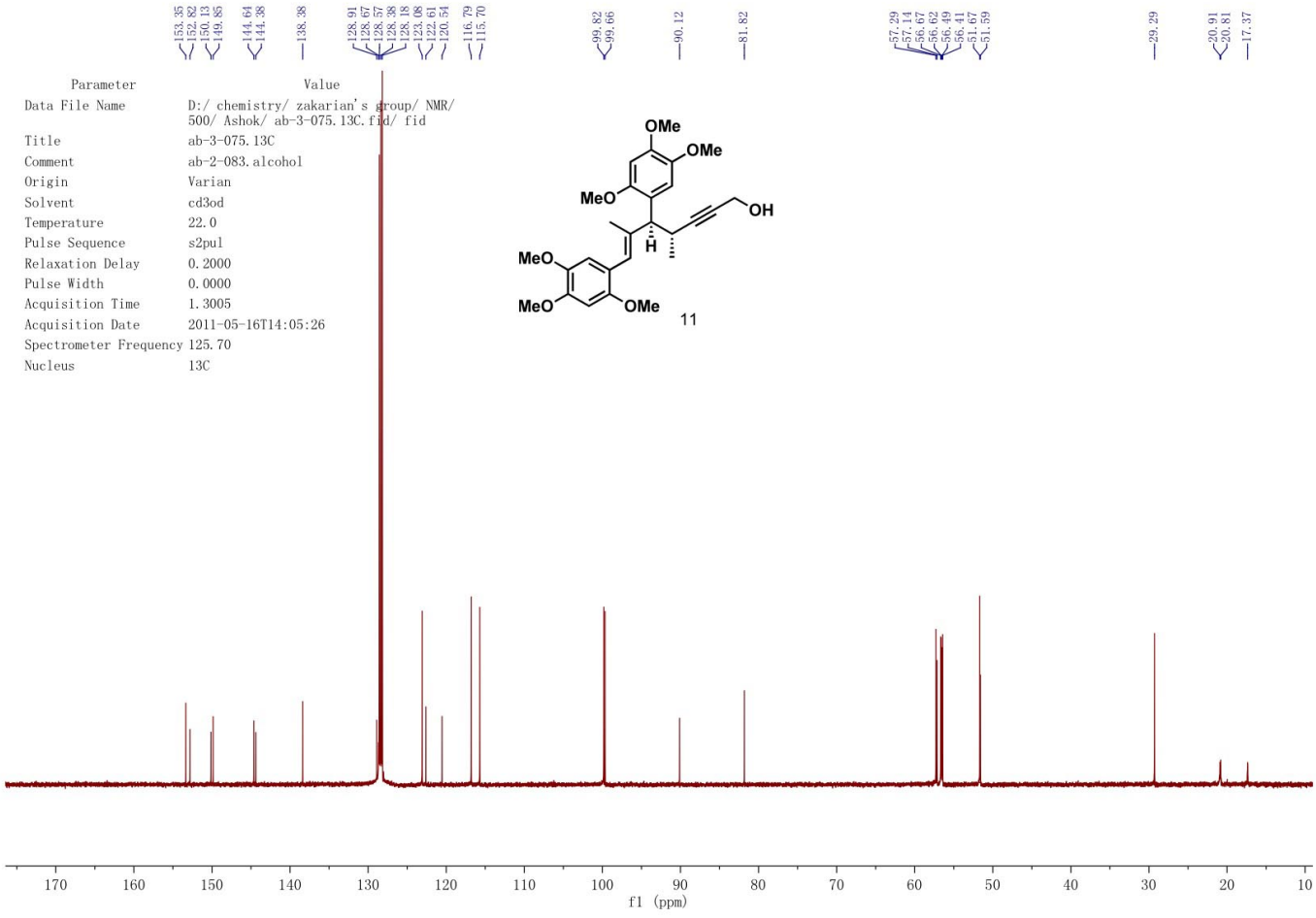


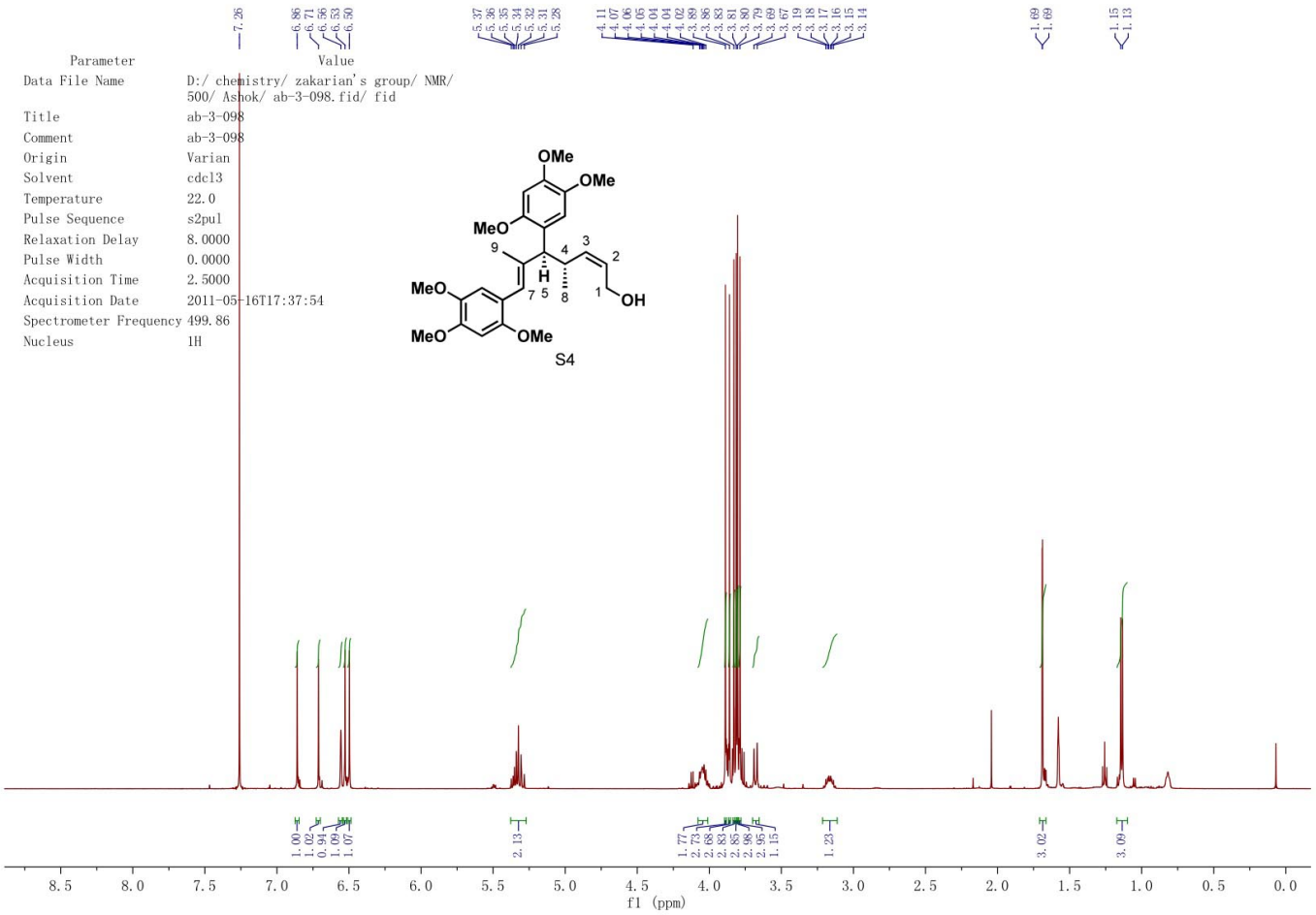
Parameter	Value
Data File Name	D:/ chemistry/ zakarian's group/ NMR/ 500/ Ashok/ ab-3-073.fid/ fid
Title	ab-3-073
Comment	ab-3-073
Origin	Varian
Solvent	c6d6
Temperature	25.0
Pulse Sequence	s2pul
Relaxation Delay	8.0000
Pulse Width	0.0000
Acquisition Time	2.5000
Acquisition Date	2011-05-02T18:20:53
Spectrometer Frequency	399.95
Nucleus	1H



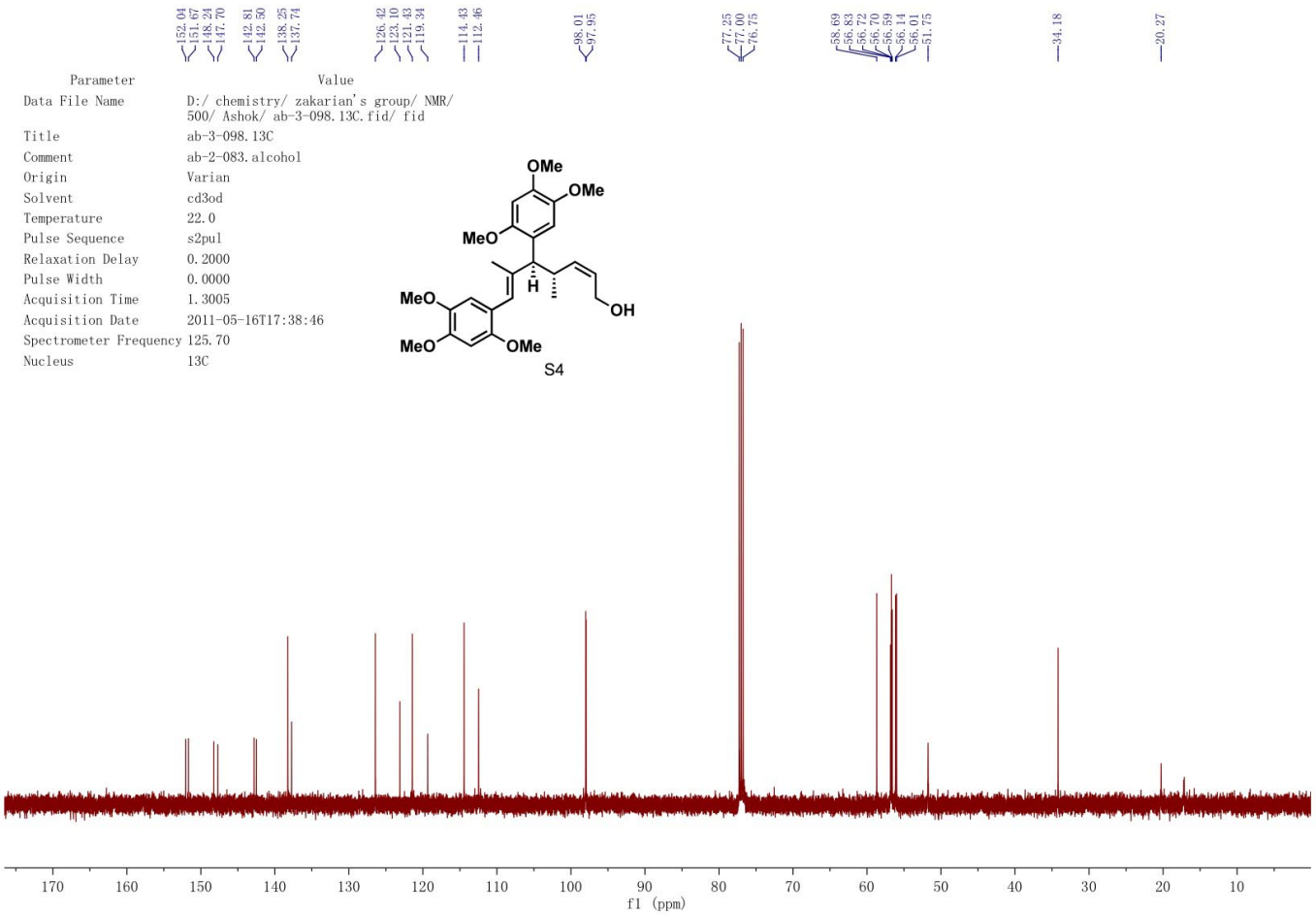
Parameter	Value
Data File Name	D:/ chemistry/ zakarian's group/ NMR/ 500/ Ashok/ ab-3-073.13C.fid/ fid
Title	ab-3-073.13C
Comment	ab-3-073.13C
Origin	Varian
Solvent	CDCl3
Temperature	25.0
Pulse Sequence	s2pul
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.3005
Acquisition Date	2011-09-11T15:48:47
Spectrometer Frequency	125.70
Nucleus	13C


7.51
7.26
7.21
7.01
6.49
6.46
4.39
4.37
4.00
3.84
3.56
3.55
3.50
3.44
3.43
3.40
1.94
1.93
1.55
1.54
Parameter Value
Data File Name D:/ chemistry/ zakarian's group/ NMR/ 500/ Ashok/ ab-3-075.fid/ fid
Title ab-3-075
Comment ab-3-075
Origin Varian
Solvent c6d6
Temperature 25.0
Pulse Sequence s2pul
Relaxation Delay 8.0000
Pulse Width 0.0000
Acquisition Time 2.5000
Acquisition Date 2011-05-03T13:17:30
Spectrometer Frequency 399.95
Nucleus 1H
OMe
OMe
MeO
OH
MeO
OMe
MeO
OMe
11
0.98
1.10
1.00
1.03
1.07
1.09
1.97
2.89
11.82
3.11
1.18
3.01
3.07
f1 (ppm)


153.35
152.82
150.13
149.85
144.64
144.38
138.38
128.91
128.67
128.57
128.38
128.18
123.08
122.61
120.54
116.79
115.70
99.82
99.66
90.12
81.82
57.29
57.14
56.67
56.62
56.49
56.41
51.67
51.59
29.29
20.91
20.81
17.37
Parameter Value
Data File Name D:/ chemistry/ zakarian's group/ NMR/ 500/ Ashok/ ab-3-075.13C.fid/ fid
Title ab-3-075.13C
Comment ab-2-083.alcohol
Origin Varian
Solvent cd3od
Temperature 22.0
Pulse Sequence s2pul
Relaxation Delay 0.2000
Pulse Width 0.0000
Acquisition Time 1.3005
Acquisition Date 2011-05-16T14:05:26
Spectrometer Frequency 125.70
Nucleus 13C
OMe
OMe
MeO
OH
MeO
OMe
MeO
OMe
11
f1 (ppm)


7.26
6.86
6.71
6.58
6.53
6.50
5.37
5.36
5.35
5.34
5.32
5.31
5.28
4.11
4.07
4.06
4.05
4.04
4.04
4.02
3.89
3.86
3.83
3.81
3.80
3.79
3.69
3.67
3.19
3.18
3.17
3.16
3.15
3.14
1.09
1.09
1.15
1.13
Parameter Value
Data File Name D:/ chemistry/ zakarian's group/ NMR/ 500/ Ashok/ ab-3-098.fid/ fid
Title ab-3-098
Comment ab-3-098
Origin Varian
Solvent cdcl3
Temperature 22.0
Pulse Sequence s2pul
Relaxation Delay 8.0000
Pulse Width 0.0000
Acquisition Time 2.5000
Acquisition Date 2011-05-16T17:37:54
Spectrometer Frequency 499.86
Nucleus 1H
OMe
OMe
MeO
MeO
MeO
OMe
OH
H
1.00
1.02
0.94
1.09
1.07
2.13
1.77
2.73
2.68
2.83
2.85
2.98
2.95
1.15
1.23
3.02
3.09
f1 (ppm)

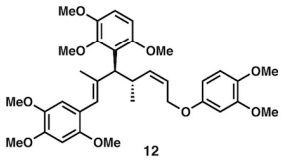
S4


152.04
151.67
148.24
147.70
142.81
142.50
138.25
137.74
126.42
123.10
121.43
119.34
114.43
112.46
98.01
97.95
77.25
77.00
76.75
58.69
56.83
56.72
56.70
56.59
56.14
56.01
51.75
34.18
20.27
Parameter Value
Data File Name D:/ chemistry/ zakarian's group/ NMR/ 500/ Ashok/ ab-3-098.13C.fid/ fid
Title ab-3-098.13C
Comment ab-2-083.alcohol
Origin Varian
Solvent cd3od
Temperature 22.0
Pulse Sequence s2pul
Relaxation Delay 0.2000
Pulse Width 0.0000
Acquisition Time 1.3005
Acquisition Date 2011-05-16T17:38:46
Spectrometer Frequency 125.70
Nucleus 13C
OMe
OMe
MeO
MeO
MeO
OMe
OH
H
f1 (ppm)

S4

jjj-2-219-a-a
jjj-2-219-a-a

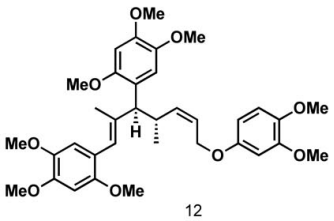
	Parameter	Value
1	Data File Name	/ Users/ Jeff/ Downloads/ jjj-2-219-a-a.fid/ fid
2	Title	jjj-2-219-a-a
3	Comment	jjj-2-219-a-a
4	Origin	Varian
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	s2pul
8	Relaxation Delay	4.8000
9	Pulse Width	0.0000
10	Acquisition Time	2.5000
11	Acquisition Date	2012-11-20T15:38:09
12	Spectrometer Frequency	599.64
13	Nucleus	1H



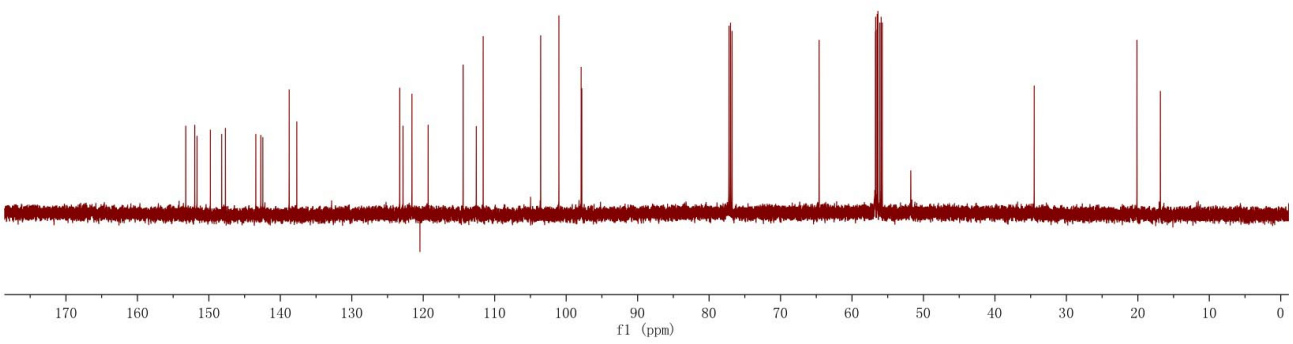
12

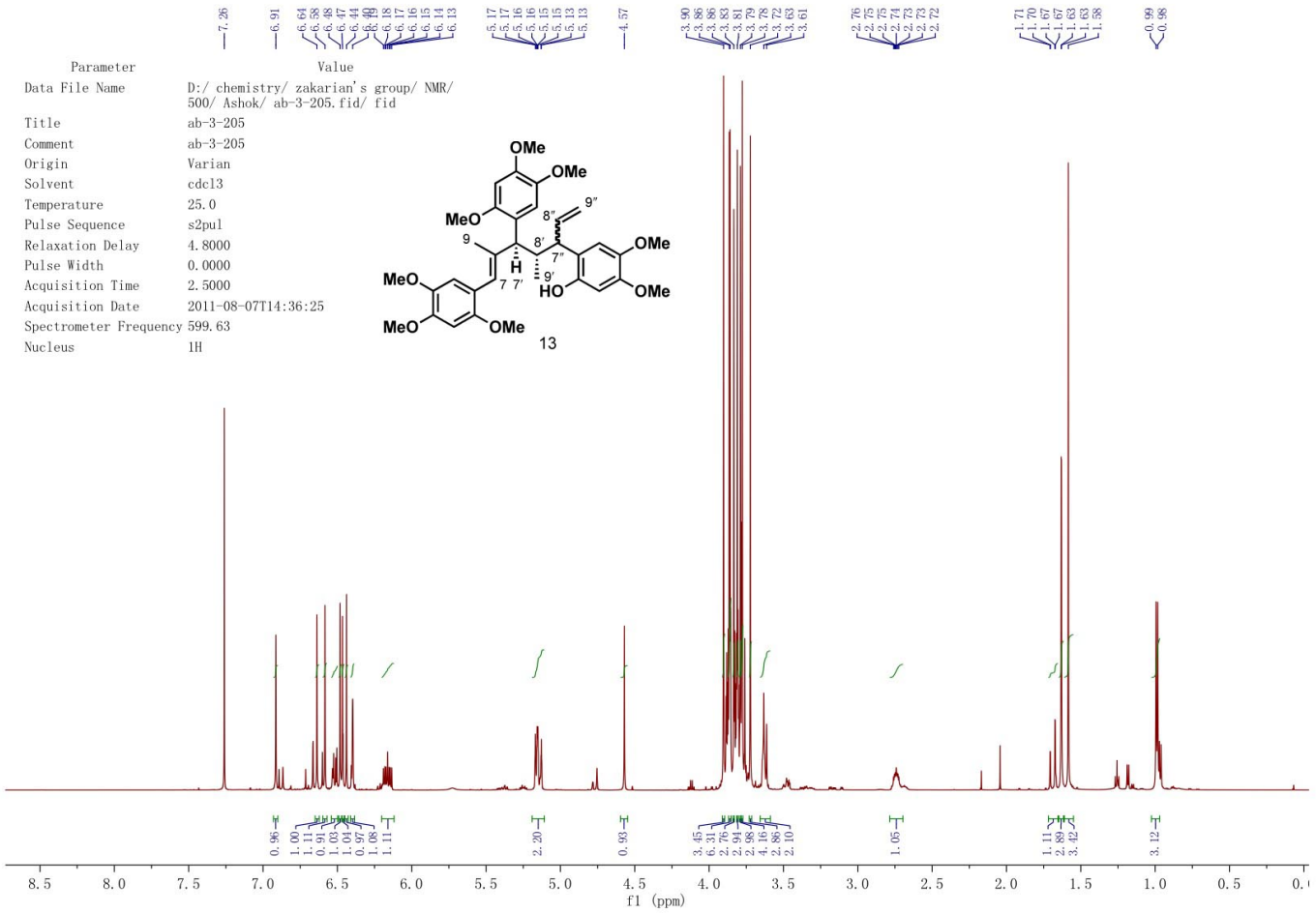
153.23
151.97
151.66
149.79
148.20
147.69
143.43
142.73
142.46
138.76
137.70
123.29
122.83
121.58
119.31
114.42
112.58
111.61
103.57
101.02
97.91
97.81
77.21
77.00
76.79
64.60
56.69
56.47
56.37
56.10
55.92
55.77
34.50
20.12
16.84

Parameter	Value
Data File Name	D:/ chemistry/ zakarian's group/ NMR/ 500/ Ashok/ ab-3-128.13C.fid/ fid
Title	ab-3-128.13C
Comment	ab-3-128.13C
Origin	Varian
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.2987
Acquisition Date	2011-07-28T21:49:15
Spectrometer Frequency	150.79
Nucleus	13C

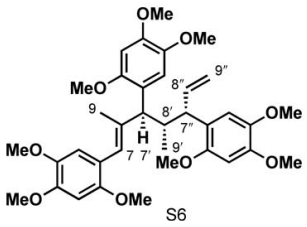


12



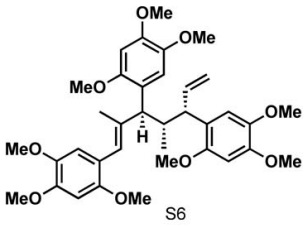

7.26
6.91
6.64
6.58
6.48
6.47
6.44
6.43
6.18
6.17
6.16
6.15
6.14
6.13
5.17
5.17
5.16
5.16
5.15
5.15
5.13
5.13
4.57
3.90
3.86
3.86
3.83
3.81
3.79
3.78
3.72
3.63
3.61
2.76
2.75
2.75
2.74
2.73
2.73
2.72
1.71
1.70
1.67
1.67
1.63
1.63
1.58
0.99
0.98
Parameter
Value
Data File Name
D:/ chemistry/ zakarian's group/ NMR/ 500/ Ashok/ ab-3-205.fid/ fid
Title
ab-3-205
Comment
ab-3-205
Origin
Varian
Solvent
cdcl3
Temperature
25.0
Pulse Sequence
s2pul
Relaxation Delay
4.8000
Pulse Width
0.0000
Acquisition Time
2.5000
Acquisition Date
2011-08-07T14:36:25
Spectrometer Frequency
599.63
Nucleus
1H
OMe
OMe
MeO
9
8′
8″
9″
7″
9′
HO
OMe
MeO
H
7 7′
OMe
MeO
OMe
13
0.96
1.00
1.11
0.91
1.03
1.04
0.97
1.08
1.11
2.20
0.93
3.45
6.31
2.76
2.94
2.98
4.16
2.86
2.10
1.05
1.11
2.89
3.42
3.12
8.5
8.0
7.5
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
f1 (ppm)

Parameter	Value
Data File Name	D:/ chemistry/ zakarian's group/ NMR/ 500/ Ashok/ ab-3-135.a.fid/ fid
Title	ab-3-135.a
Comment	ab-3-135.a
Origin	Varian
Solvent	cdcl3
Temperature	22.0
Pulse Sequence	s2pul
Relaxation Delay	8.0000
Pulse Width	0.0000
Acquisition Time	2.5000
Acquisition Date	2011-06-07T09:56:01
Spectrometer Frequency	499.86
Nucleus	1H

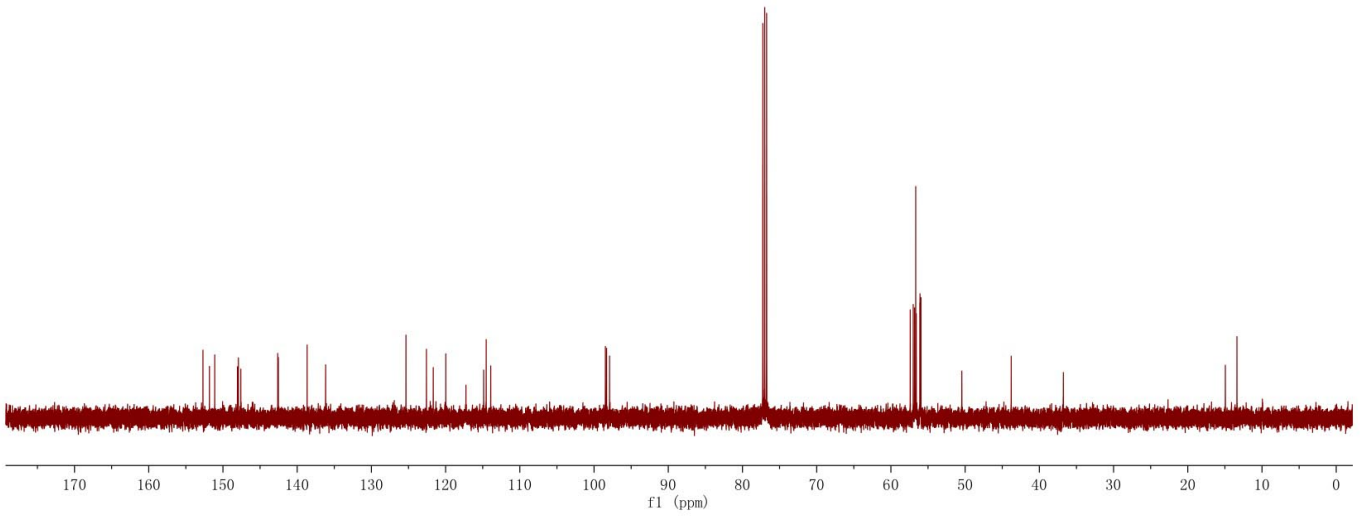


S6

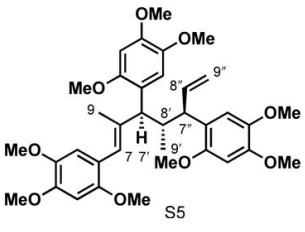
Parameter	Value
Data File Name	D:/ chemistry/ zakarian's group/ NMR/ 500/ Ashok/ ab-3-135.a.13C.fid/ fid
Title	ab-3-135.a.13C
Comment	ab-3-135.a.13C
Origin	Varian
Solvent	CDCl3
Temperature	22.0
Pulse Sequence	s2pul
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.3005
Acquisition Date	2011-06-07T09:56:58
Spectrometer Frequency	125.70
Nucleus	13C



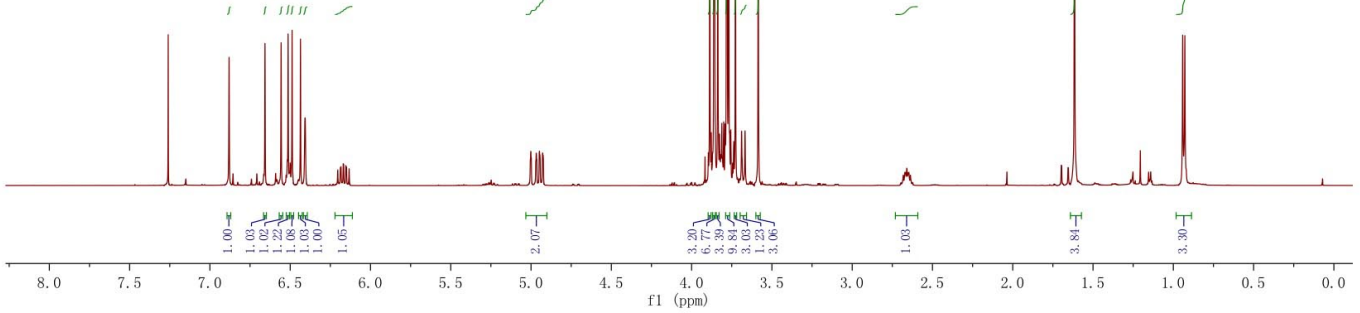
S6



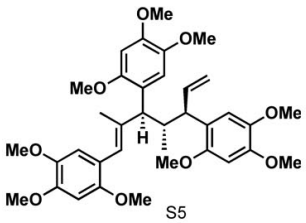
Parameter	Value
Data File Name	D:/ chemistry/ zakarian's group/ NMR/ 500/ Ashok/ ab-3-135.b.fid/ fid
Title	ab-3-135.b
Comment	ab-3-135.b
Origin	Varian
Solvent	cdcl3
Temperature	22.0
Pulse Sequence	s2pul
Relaxation Delay	8.0000
Pulse Width	0.0000
Acquisition Time	2.5000
Acquisition Date	2011-06-06T18:07:41
Spectrometer Frequency	499.86
Nucleus	1H



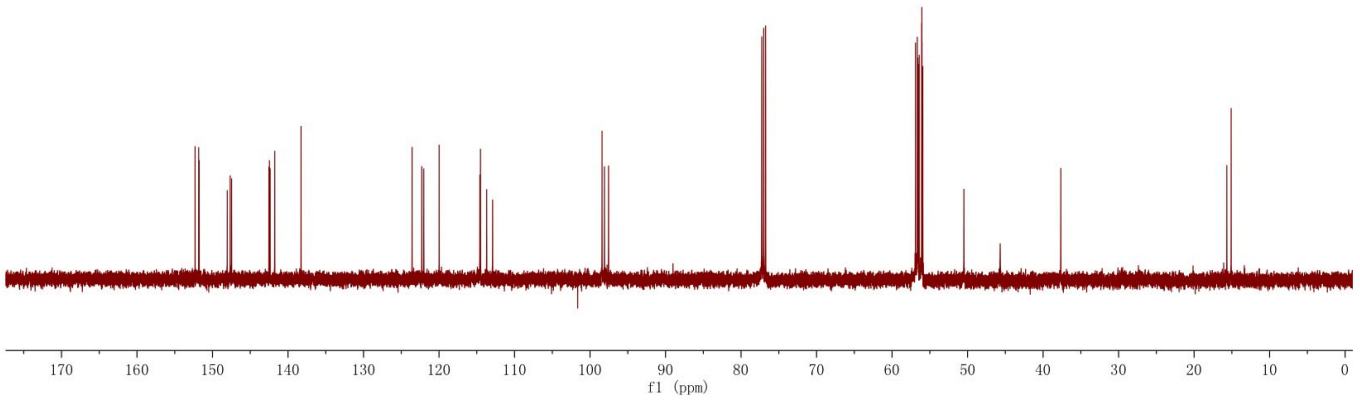
S5

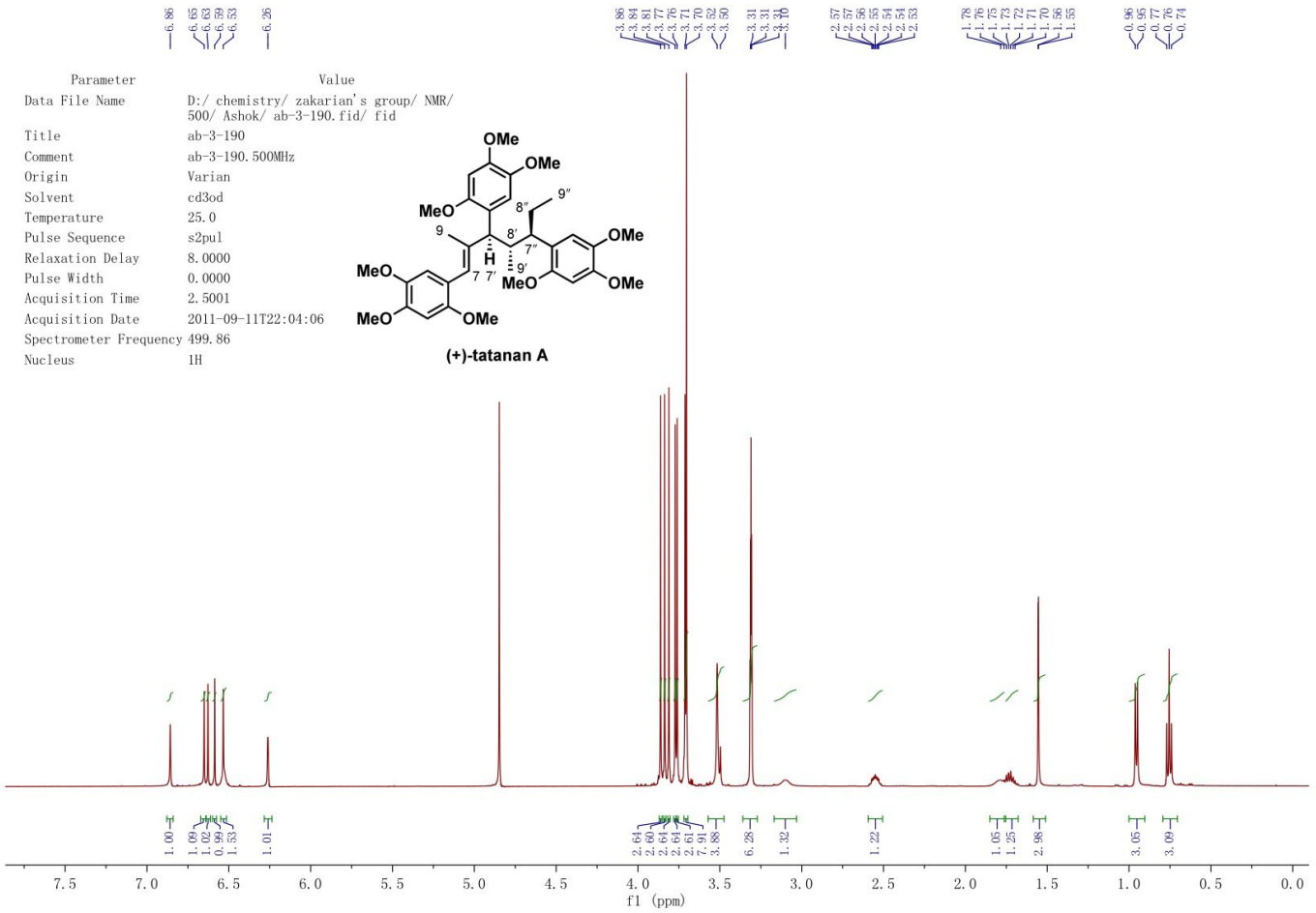


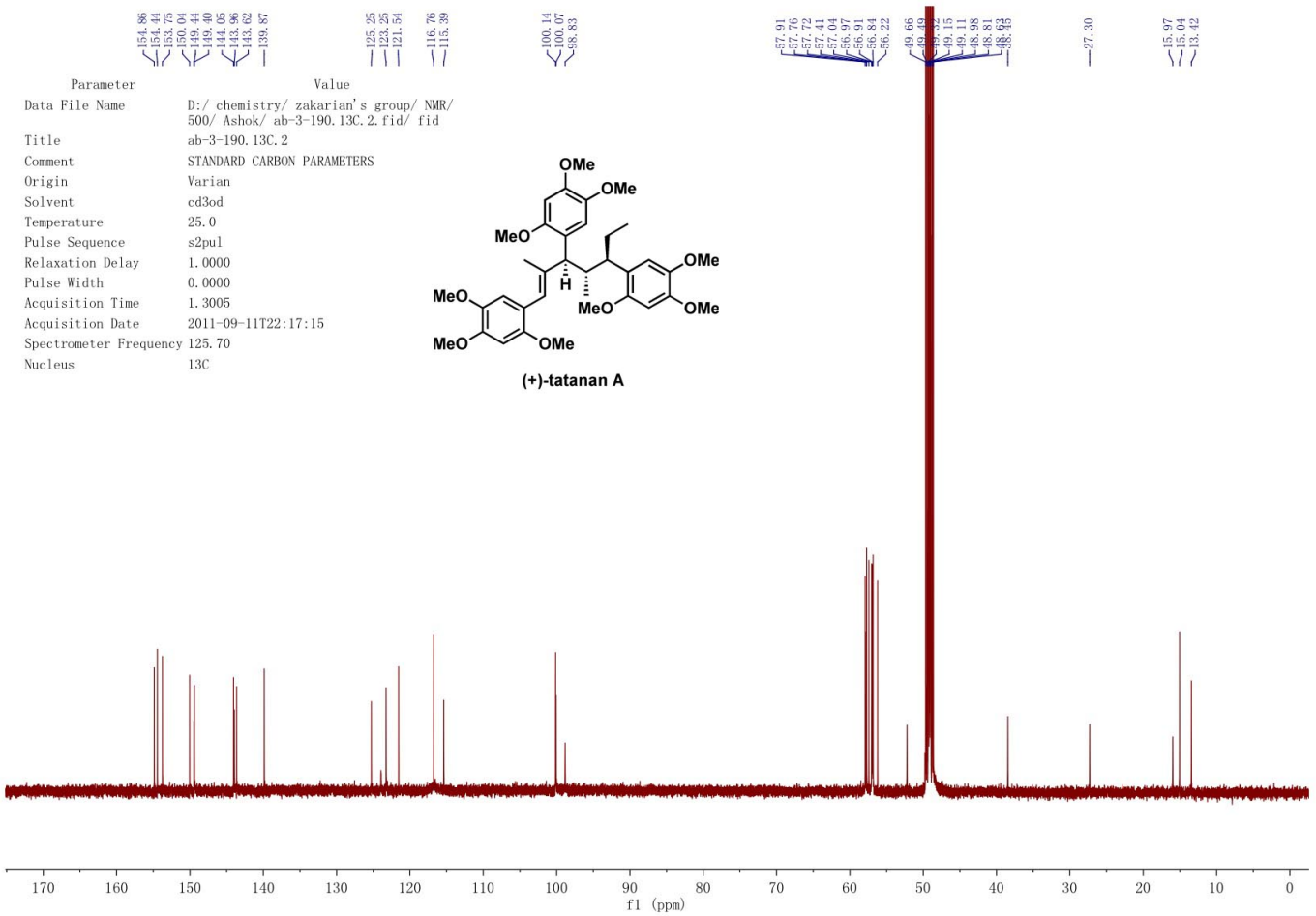
Parameter	Value
Data File Name	D:/ chemistry/ zakarian's group/ NMR/ 500/ Ashok/ ab-3-135.b.13C.fid/ fid
Title	ab-3-135.b.13C
Comment	ab-3-135.b.13C
Origin	Varian
Solvent	CDCl3
Temperature	22.0
Pulse Sequence	s2pul
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.3005
Acquisition Date	2011-06-06T18:10:49
Spectrometer Frequency	125.70
Nucleus	13C

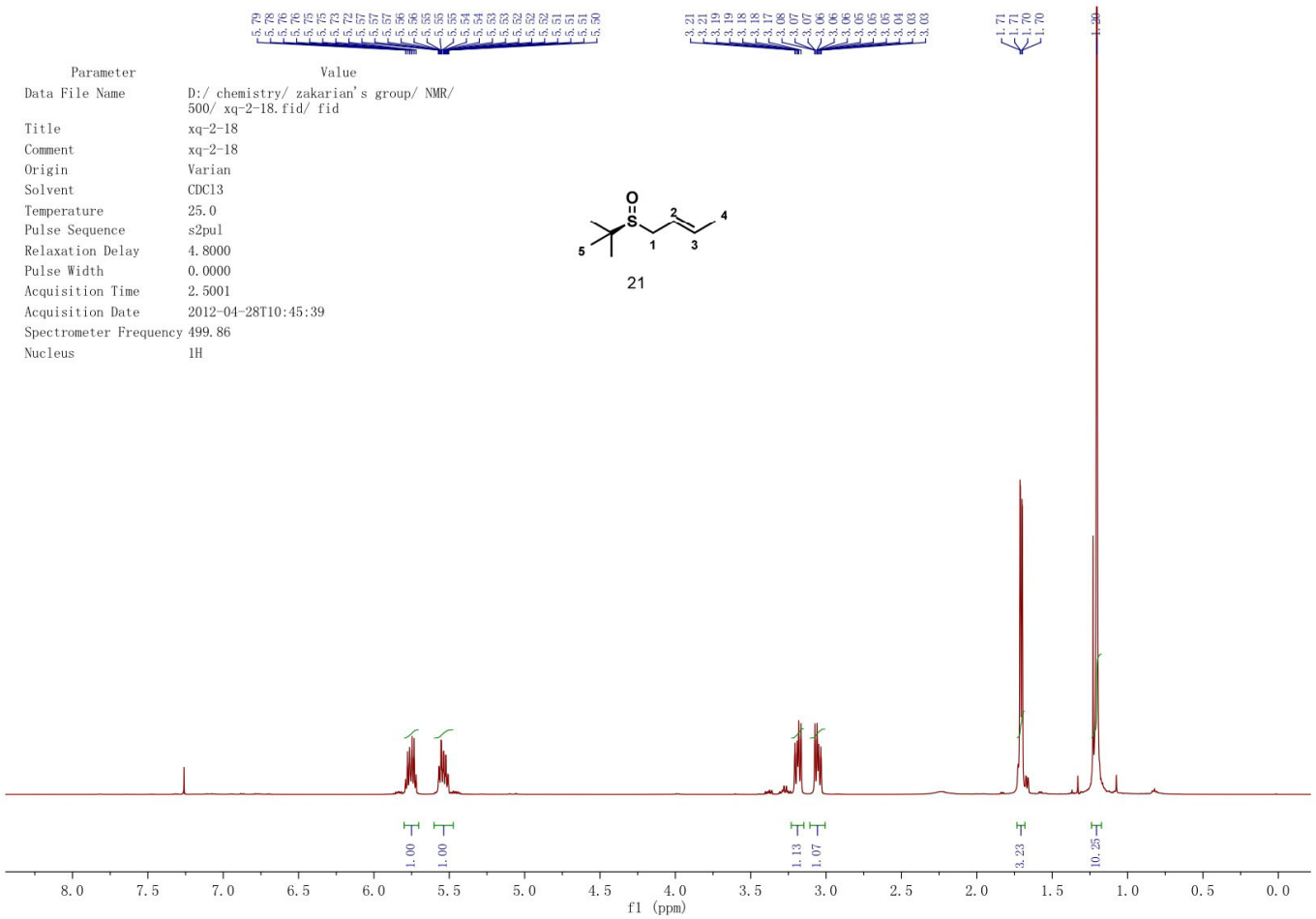


S5



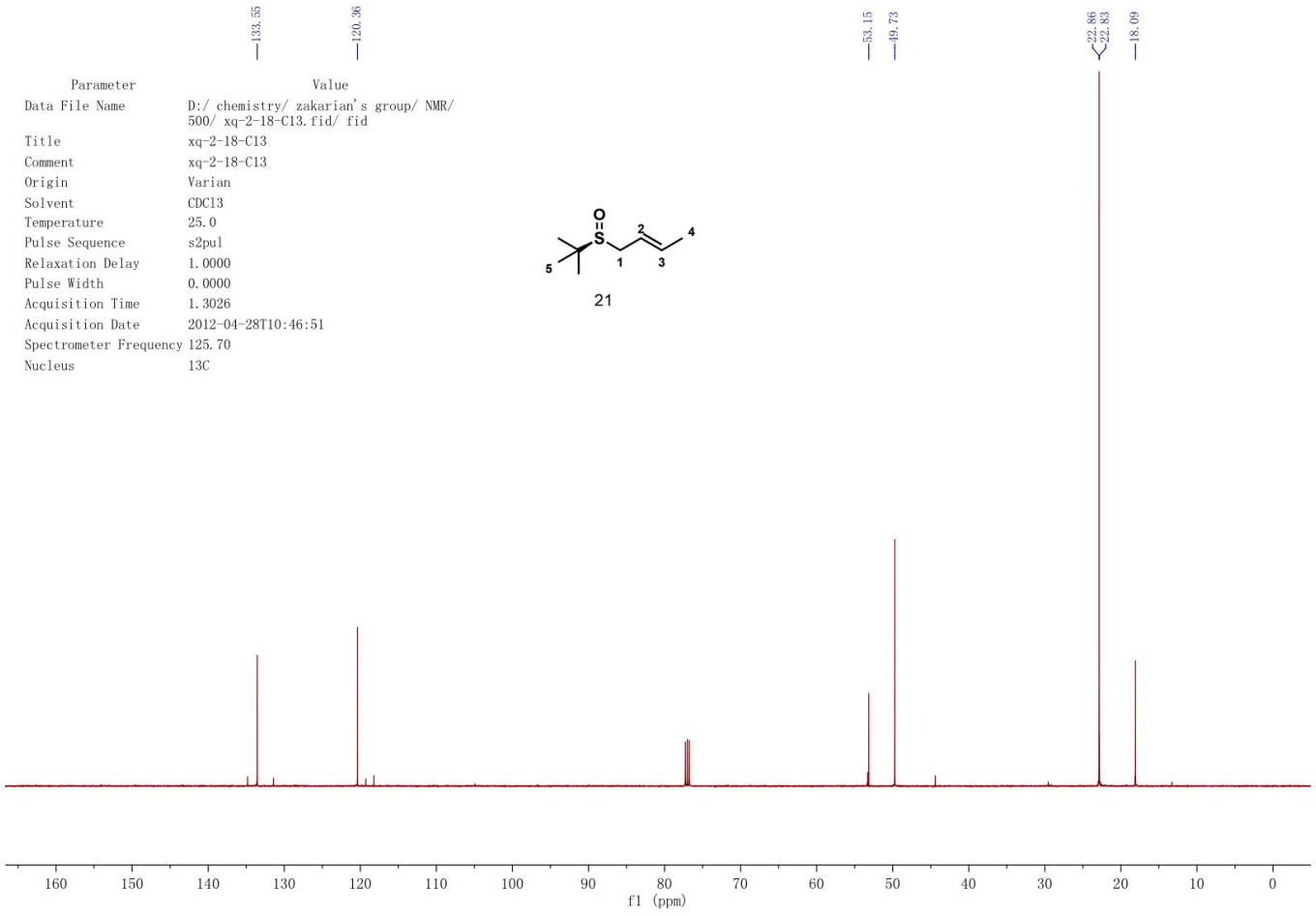

6.86
6.65
6.63
6.59
6.53
6.26
3.86
3.84
3.81
3.77
3.76
3.71
3.70
3.52
3.50
3.31
3.31
3.10
2.57
2.57
2.56
2.55
2.54
2.54
2.53
1.78
1.76
1.75
1.73
1.72
1.71
1.70
1.56
1.55
0.96
0.95
0.77
0.76
0.74
Parameter Value
Data File Name D:/ chemistry/ zakarian's group/ NMR/ 500/ Ashok/ ab-3-190.fid/ fid
Title ab-3-190
Comment ab-3-190.500MHz
Origin Varian
Solvent cd3od
Temperature 25.0
Pulse Sequence s2pul
Relaxation Delay 8.0000
Pulse Width 0.0000
Acquisition Time 2.5001
Acquisition Date 2011-09-11T22:04:06
Spectrometer Frequency 499.86
Nucleus 1H
(+)-tatanan A
1.00
1.09
1.02
0.99
1.53
1.01
2.64
2.60
2.64
2.61
2.61
7.98
3.88
6.28
1.32
1.22
1.05
1.25
2.98
3.05
3.09
f1 (ppm)


154.86
154.44
153.75
150.04
149.44
149.40
144.05
143.96
143.62
139.87
125.25
123.25
121.54
116.76
115.39
100.14
100.07
98.83
57.91
57.76
57.72
57.41
57.04
56.97
56.91
56.84
56.22
49.66
49.49
49.15
49.11
48.98
48.81
48.63
38.43
27.30
15.97
15.04
13.42
Parameter Value
Data File Name D:/ chemistry/ zakarian's group/ NMR/ 500/ Ashok/ ab-3-190.13C.2.fid/ fid
Title ab-3-190.13C.2
Comment STANDARD CARBON PARAMETERS
Origin Varian
Solvent cd3od
Temperature 25.0
Pulse Sequence s2pul
Relaxation Delay 1.0000
Pulse Width 0.0000
Acquisition Time 1.3005
Acquisition Date 2011-09-11T22:17:15
Spectrometer Frequency 125.70
Nucleus 13C
(+)-tatanan A
f1 (ppm)



Parameter	Value
Data File Name	D:/ chemistry/ zakarian's group/ NMR/ 500/ xq-2-18.fid/ fid
Title	xq-2-18
Comment	xq-2-18
Origin	Varian
Solvent	CDCl3
Temperature	25.0
Pulse Sequence	s2pul
Relaxation Delay	4.8000
Pulse Width	0.0000
Acquisition Time	2.5001
Acquisition Date	2012-04-28T10:45:39
Spectrometer Frequency	499.86
Nucleus	1H

21



Parameter	Value
Data File Name	D:/ chemistry/ zakarian's group/ NMR/ 500/ xq-2-18-C13.fid/ fid
Title	xq-2-18-C13
Comment	xq-2-18-C13
Origin	Varian
Solvent	CDCl3
Temperature	25.0
Pulse Sequence	s2pul
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.3026
Acquisition Date	2012-04-28T10:46:51
Spectrometer Frequency	125.70
Nucleus	13C

21

==== Shimadzu LCsolution Analysis Report ====

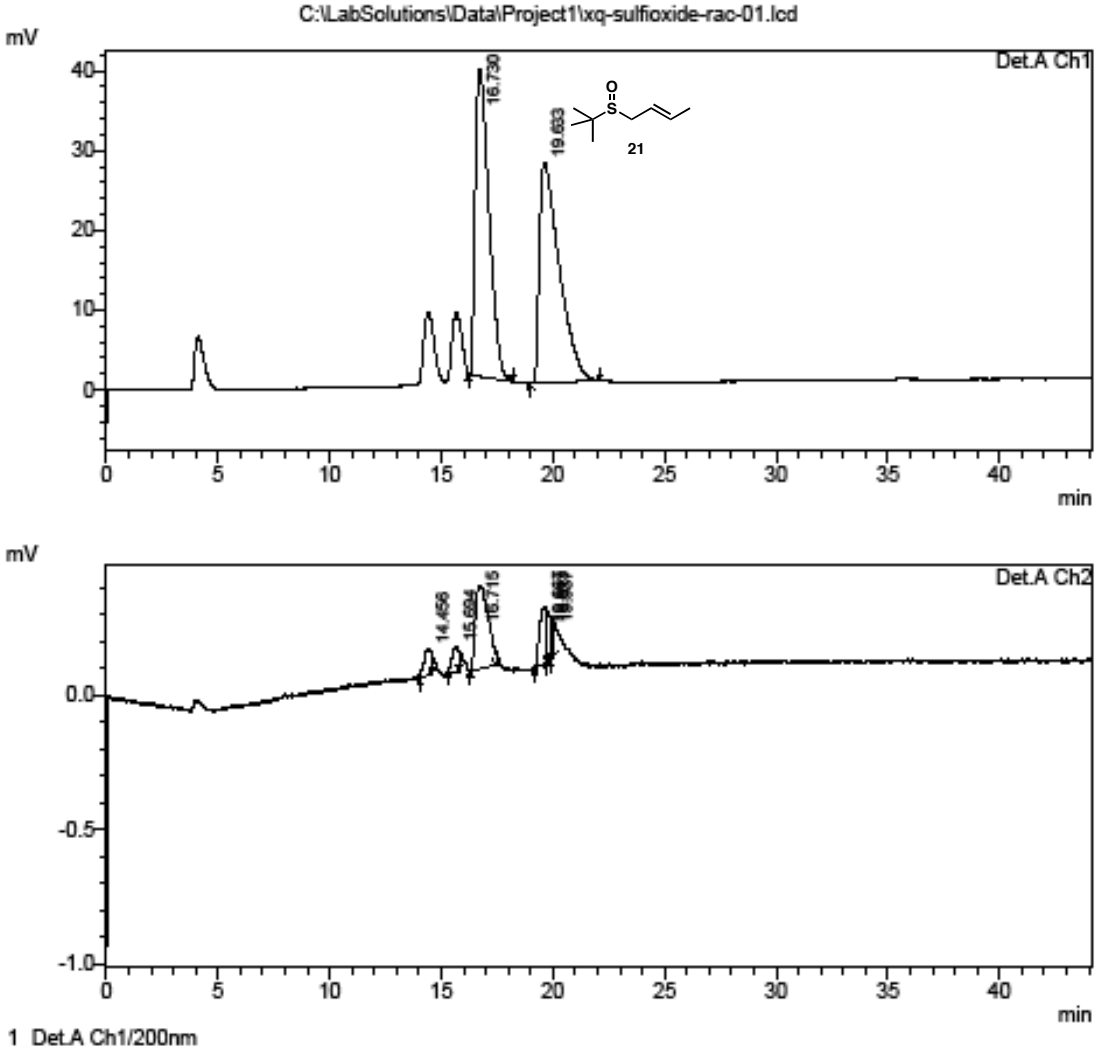
C:\LabSolutions\Data\Project1\xq-sulfioxide-rac-01.lcd

Acquired by	: Admin
Sample Name	: xq-sulfioxide-rac
Sample ID	: xq-sulfioxide-rac
Vail #	:
Injection Volume	: 25 uL
Data File Name	: xq-sulfioxide-rac-01.lcd
Method File Name	: JB-test-1.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 5/4/2012 8:40:22 PM
Data Processed	: 7/26/2012 4:33:16 PM2% iPrOH-hexane

1 ml/min
1 mg/ml concentration
30 uL injection
200 nm
chiral-AD-H

<Chromatogram>

C:\LabSolutions\Data\Project1\xq-sulfioxide-rac-01.lcd



1 Det.A Ch1/200nm
2 Det.A Ch2/254nm

PeakTable

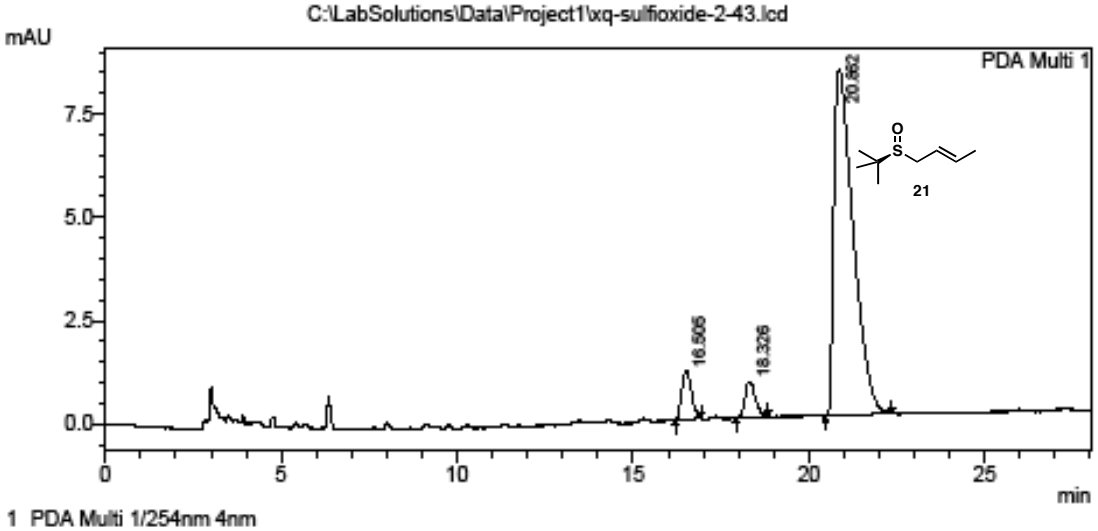
==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\Project1\xq-sulfioxide-2-43.lcd

2%iPrOH in Hex
1ml/min AD-H
1 mg/ml
20 ulAcquired by : Admin
Sample Name : xq-sulfioxide-2-43.lcd
Sample ID : xq-sulfioxide-2-43
Vail # :
Injection Volume : 20 uL
Data File Name : xq-sulfioxide-2-43.lcd
Method File Name : hk-standard.lcm
Batch File Name :
Report File Name : Default.lcr
Data Acquired : 5/21/2012 12:07:47 PM
Data Processed : 5/21/2012 8:08:47 PM

<Chromatogram>

C:\LabSolutions\Data\Project1\xq-sulfioxide-2-43.lcd

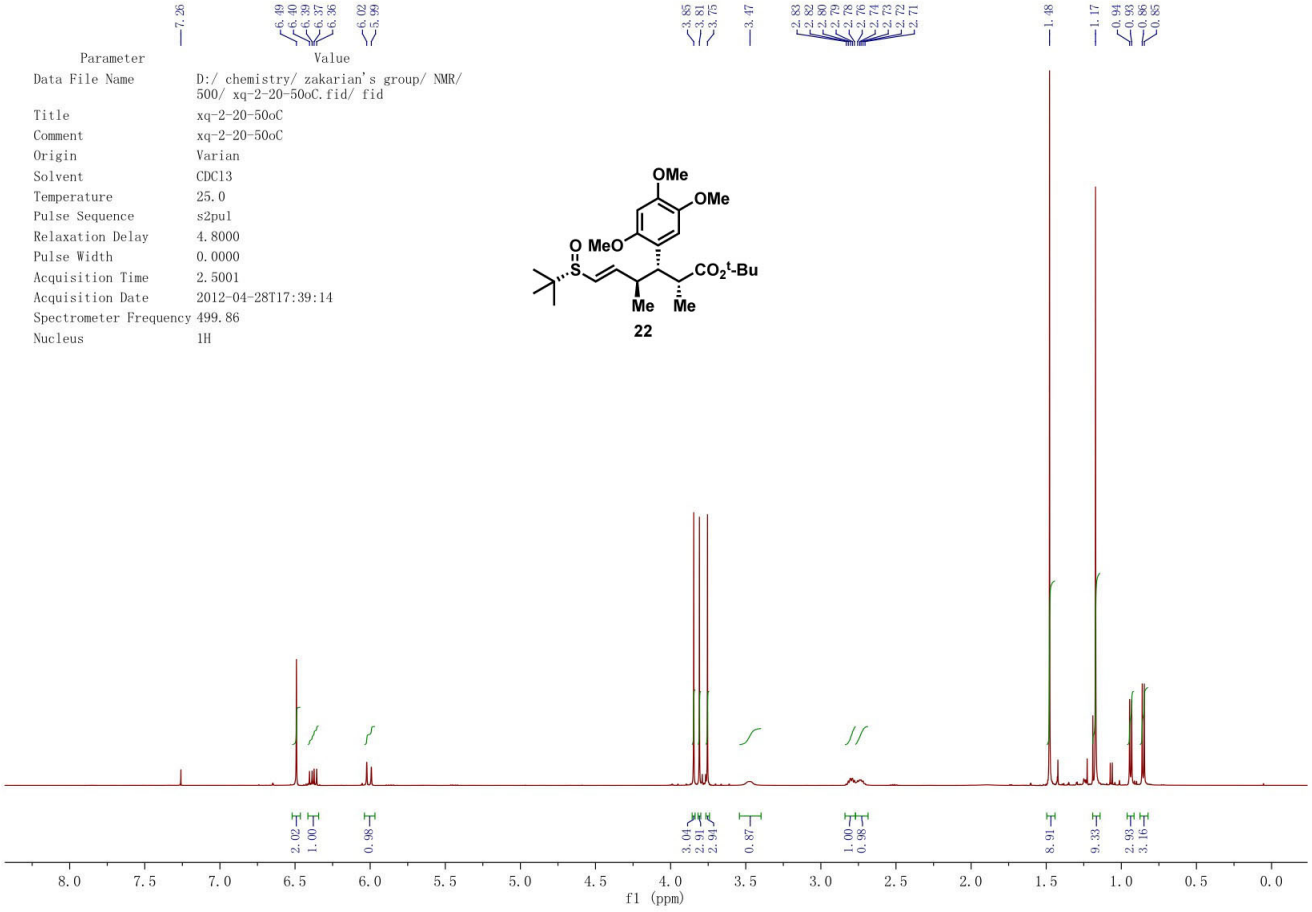


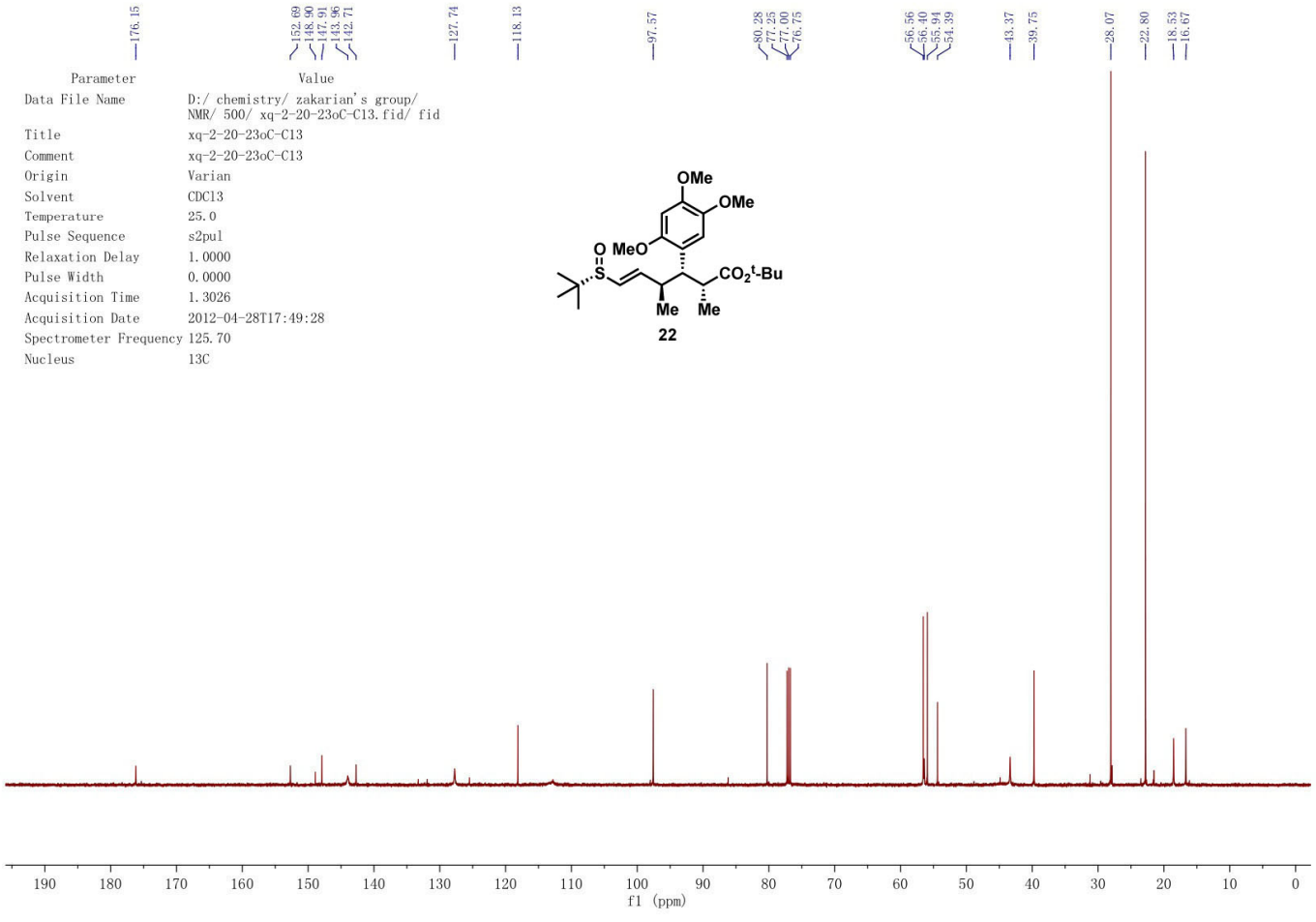
1 PDA Multi 1/254nm 4nm

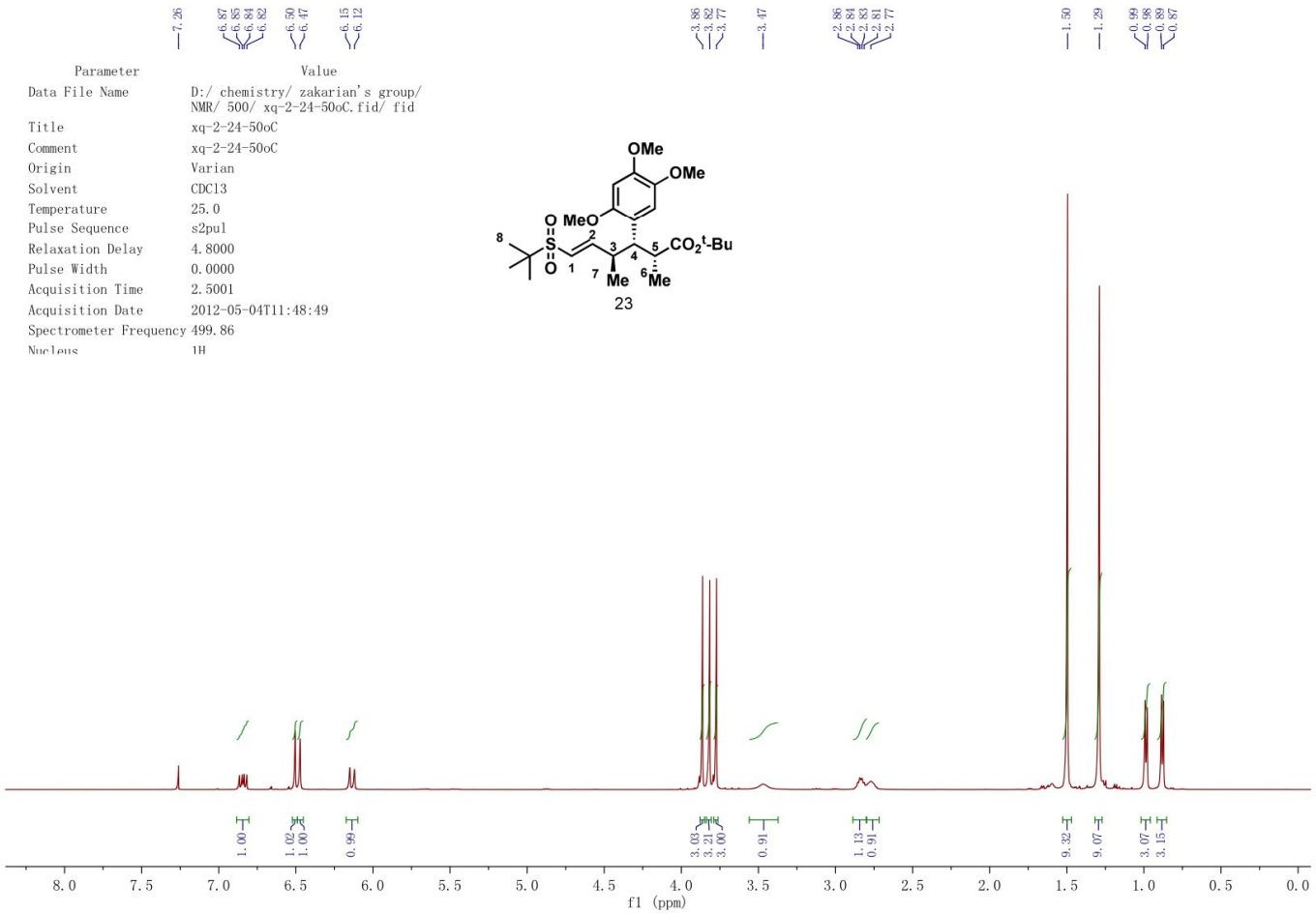
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.505	22128	1161	6.110	11.158
2	18.326	18122	859	5.004	8.258
3	20.862	321895	8382	88.886	80.584
Total		362145	10401	100.000	100.000

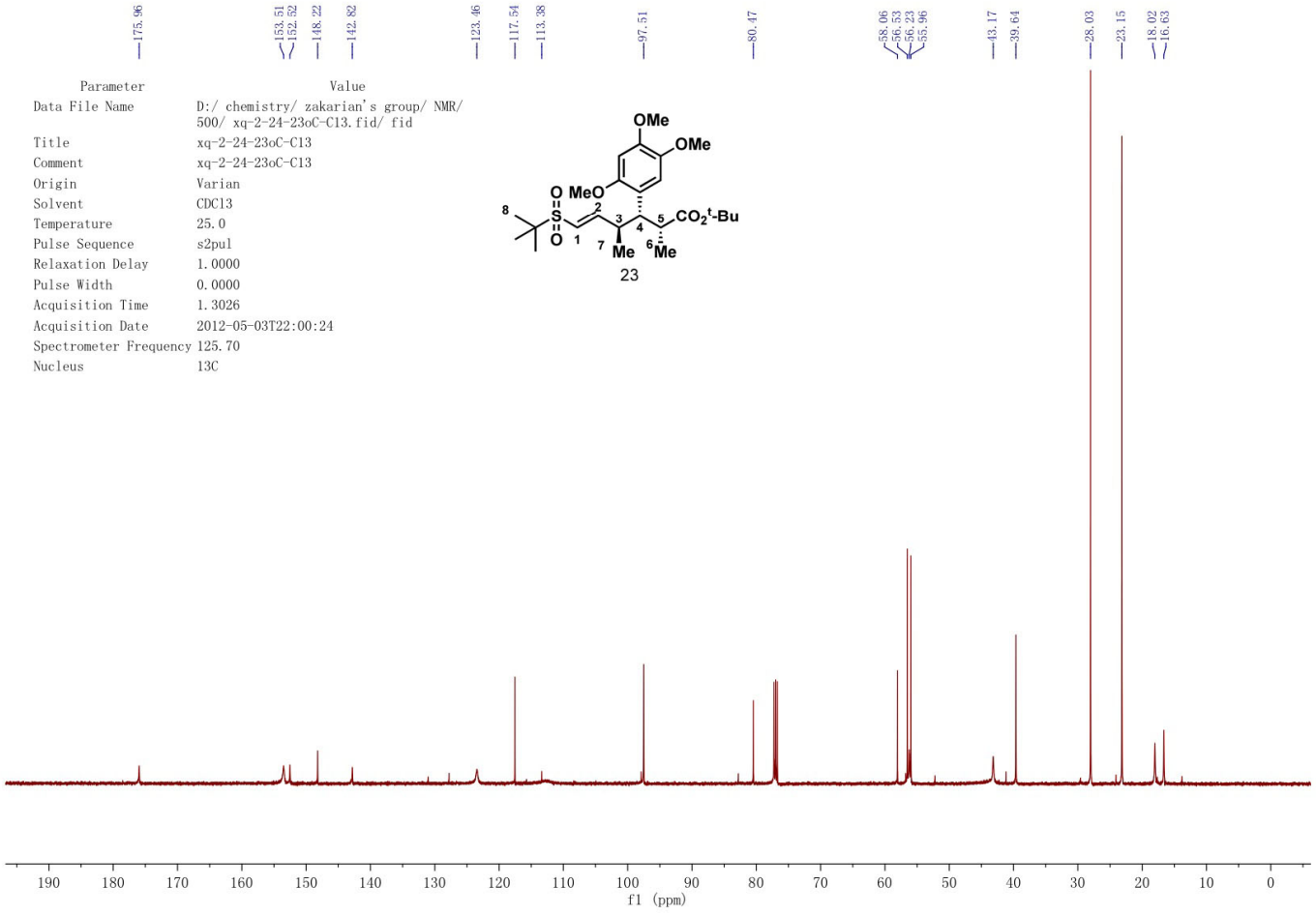

7.26
6.49
6.40
6.39
6.37
6.36
6.02
5.99
3.85
3.81
3.75
3.47
2.83
2.82
2.80
2.79
2.78
2.76
2.74
2.73
2.72
2.71
1.48
1.17
0.94
0.93
0.86
0.85
Parameter Value
Data File Name D:/ chemistry/ zakarian's group/ NMR/ 500/ xq-2-20-50oC.fid/ fid
Title xq-2-20-50oC
Comment xq-2-20-50oC
Origin Varian
Solvent CDCl3
Temperature 25.0
Pulse Sequence s2pul
Relaxation Delay 4.8000
Pulse Width 0.0000
Acquisition Time 2.5001
Acquisition Date 2012-04-28T17:39:14
Spectrometer Frequency 499.86
Nucleus 1H
OMe
OMe
O MeO
S
CO2t-Bu
Me
Me
22
2.02
1.00
0.98
3.04
2.91
2.94
0.87
1.00
0.98
8.91
9.33
2.93
3.16
8.0
7.5
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
0.0
f1 (ppm)


176.15
152.69
148.90
147.91
143.96
142.71
127.74
118.13
97.57
80.28
77.25
77.00
76.73
56.56
56.40
55.94
54.39
43.37
39.75
28.07
22.80
18.53
16.67
Parameter Value
Data File Name D:/ chemistry/ zakarian's group/ NMR/ 500/ xq-2-20-23oC-C13.fid/ fid
Title xq-2-20-23oC-C13
Comment xq-2-20-23oC-C13
Origin Varian
Solvent CDCl3
Temperature 25.0
Pulse Sequence s2pul
Relaxation Delay 1.0000
Pulse Width 0.0000
Acquisition Time 1.3026
Acquisition Date 2012-04-28T17:49:28
Spectrometer Frequency 125.70
Nucleus 13C
OMe
OMe
O MeO
S
CO2t-Bu
Me
Me
22
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



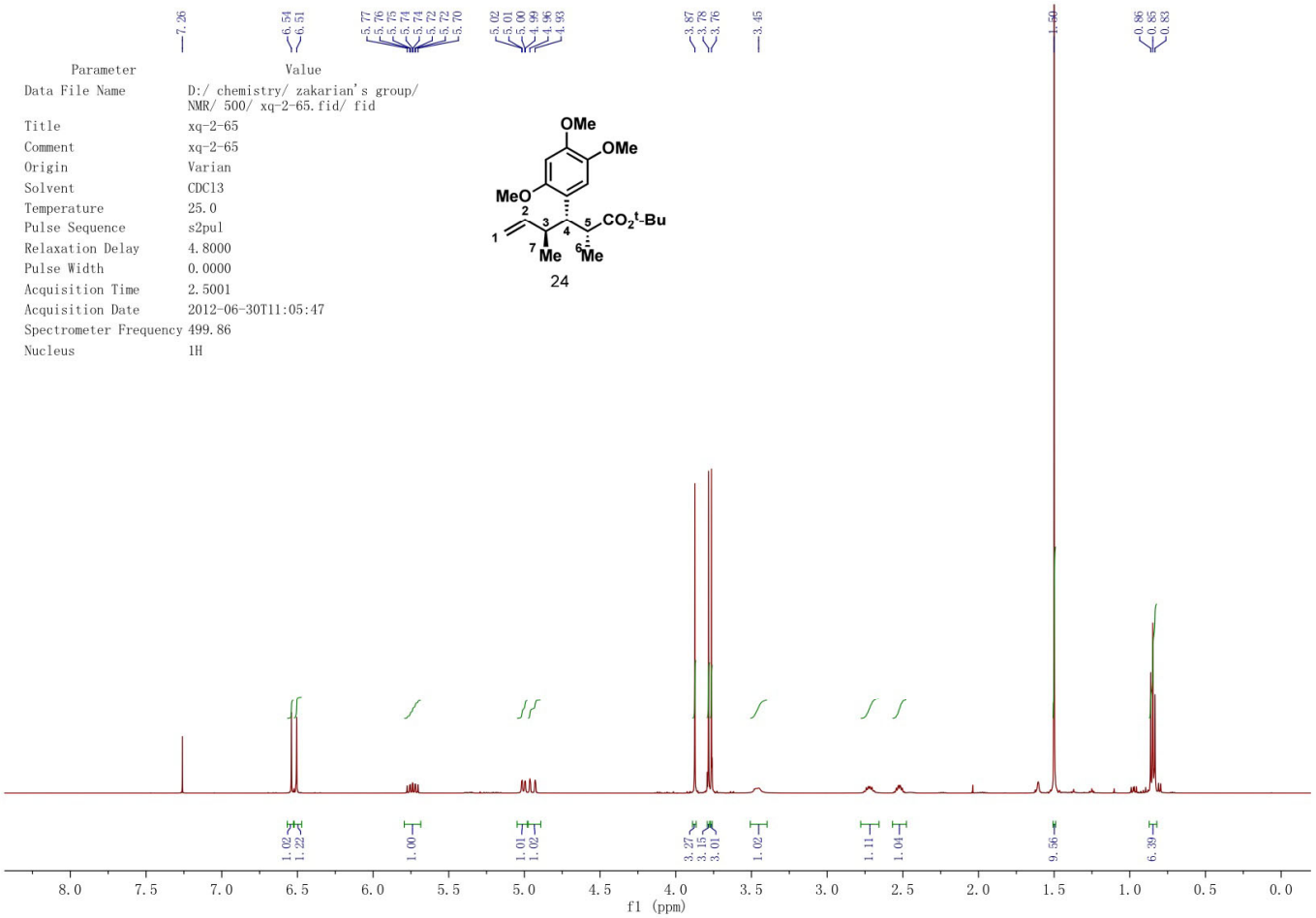
Parameter	Value
Data File Name	D:/ chemistry/ zakarian's group/ NMR/ 500/ xq-2-24-50oC.fid/ fid
Title	xq-2-24-50oC
Comment	xq-2-24-50oC
Origin	Varian
Solvent	CDCl3
Temperature	25.0
Pulse Sequence	s2pul
Relaxation Delay	4.8000
Pulse Width	0.0000
Acquisition Time	2.5001
Acquisition Date	2012-05-04T11:48:49
Spectrometer Frequency	499.86
Nucleus	1H

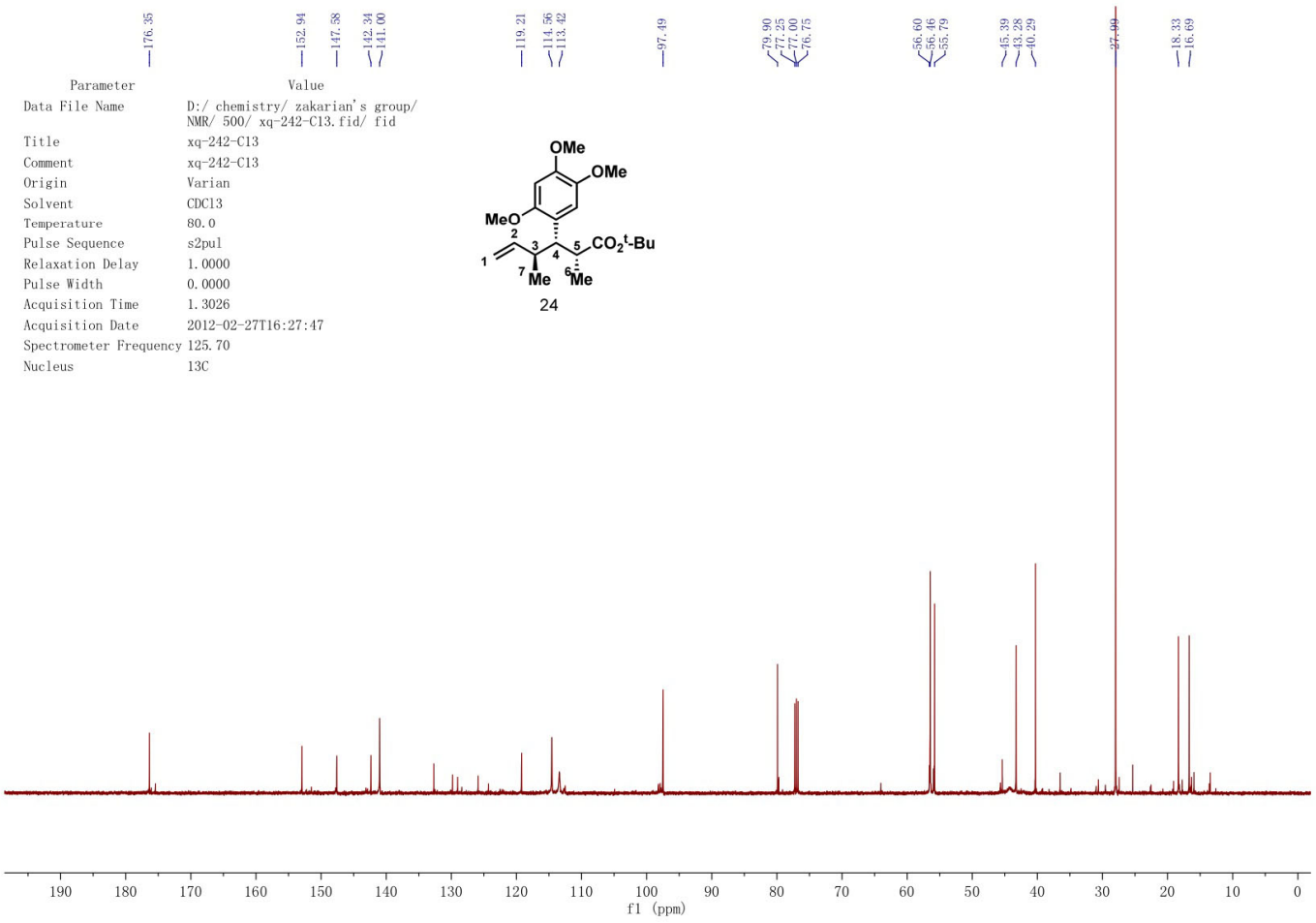
23

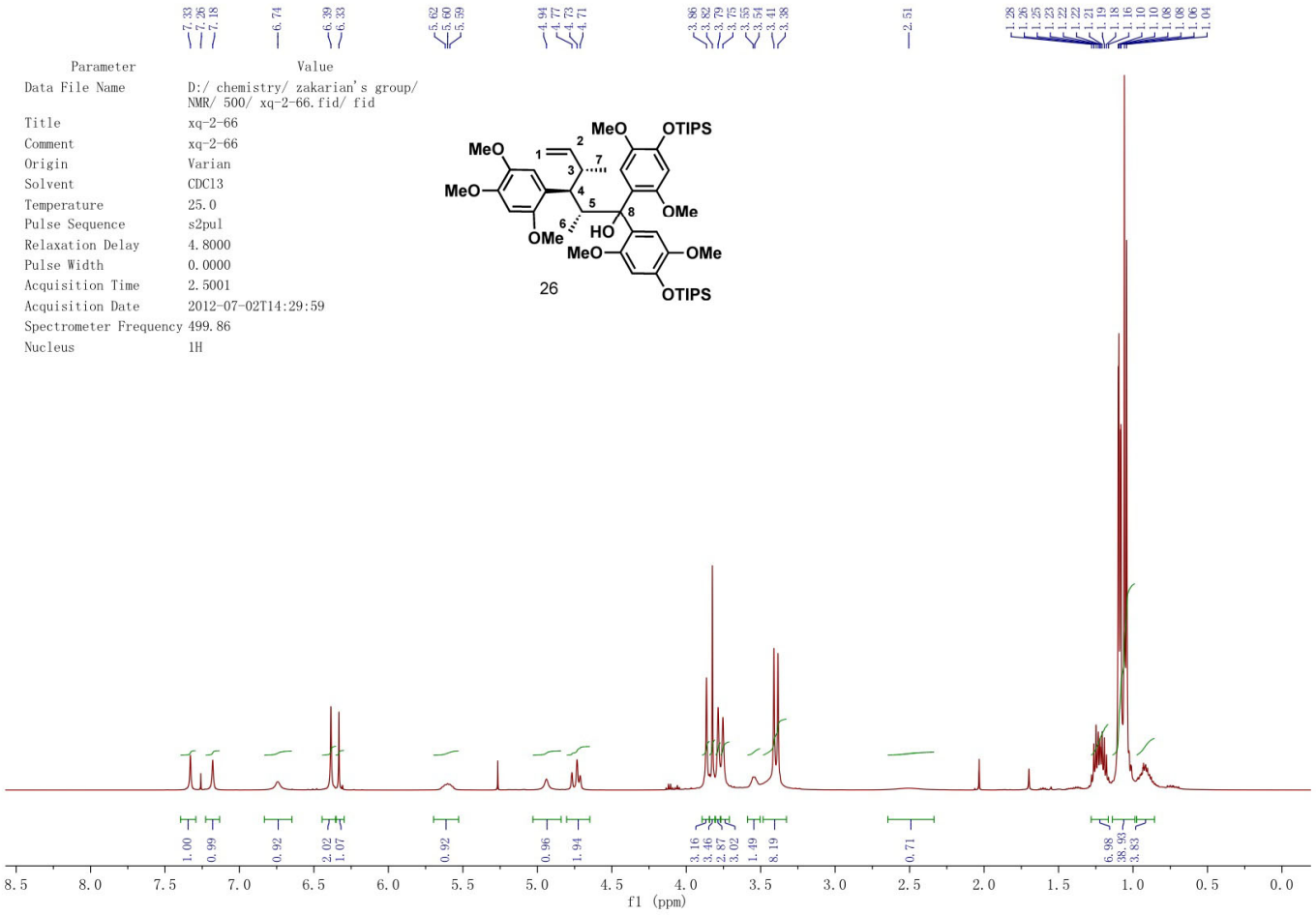


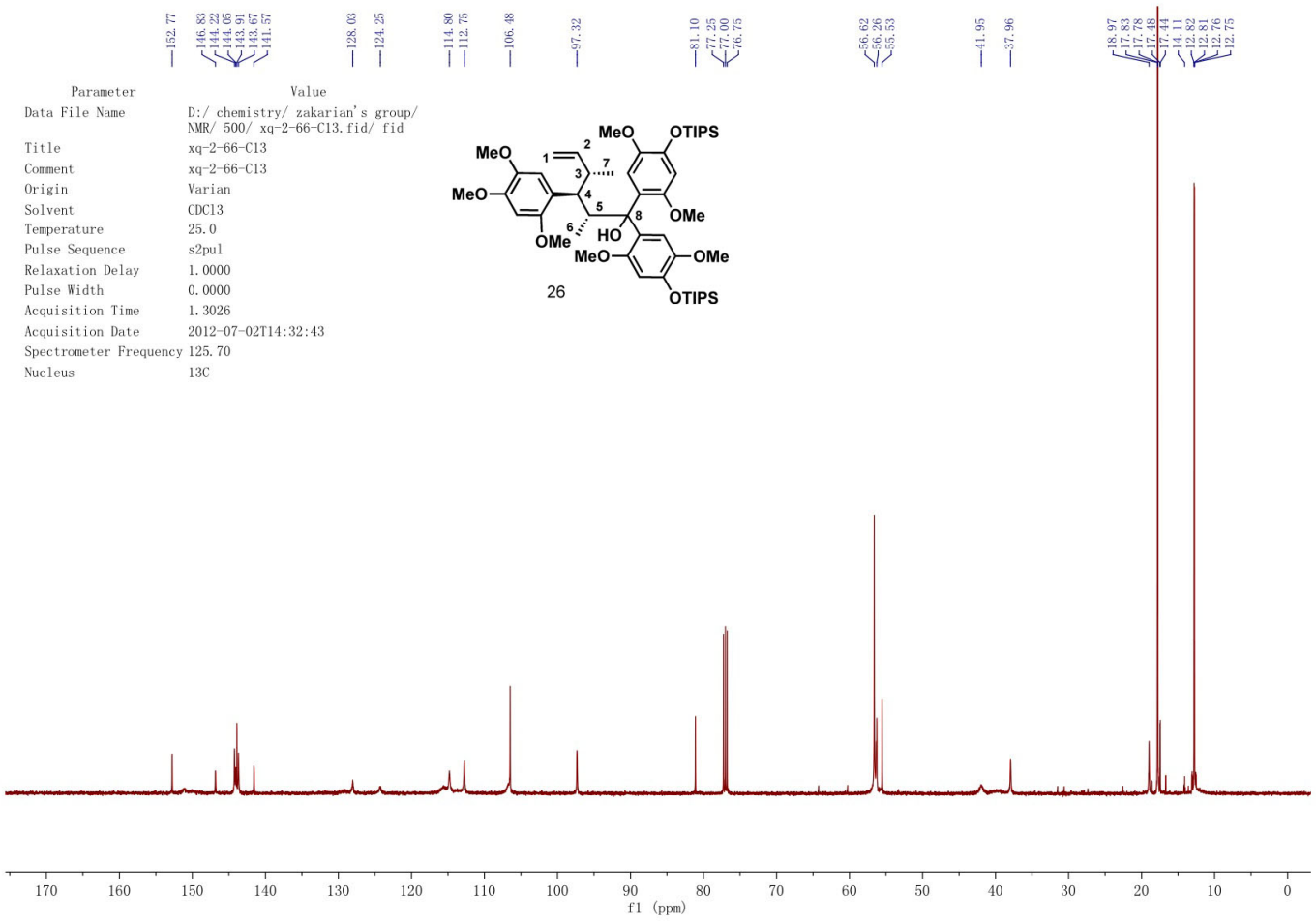
Parameter	Value
Data File Name	D:/ chemistry/ zakarian's group/ NMR/ 500/ xq-2-24-23oC-C13.fid/ fid
Title	xq-2-24-23oC-C13
Comment	xq-2-24-23oC-C13
Origin	Varian
Solvent	CDCl3
Temperature	25.0
Pulse Sequence	s2pul
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.3026
Acquisition Date	2012-05-03T22:00:24
Spectrometer Frequency	125.70
Nucleus	13C

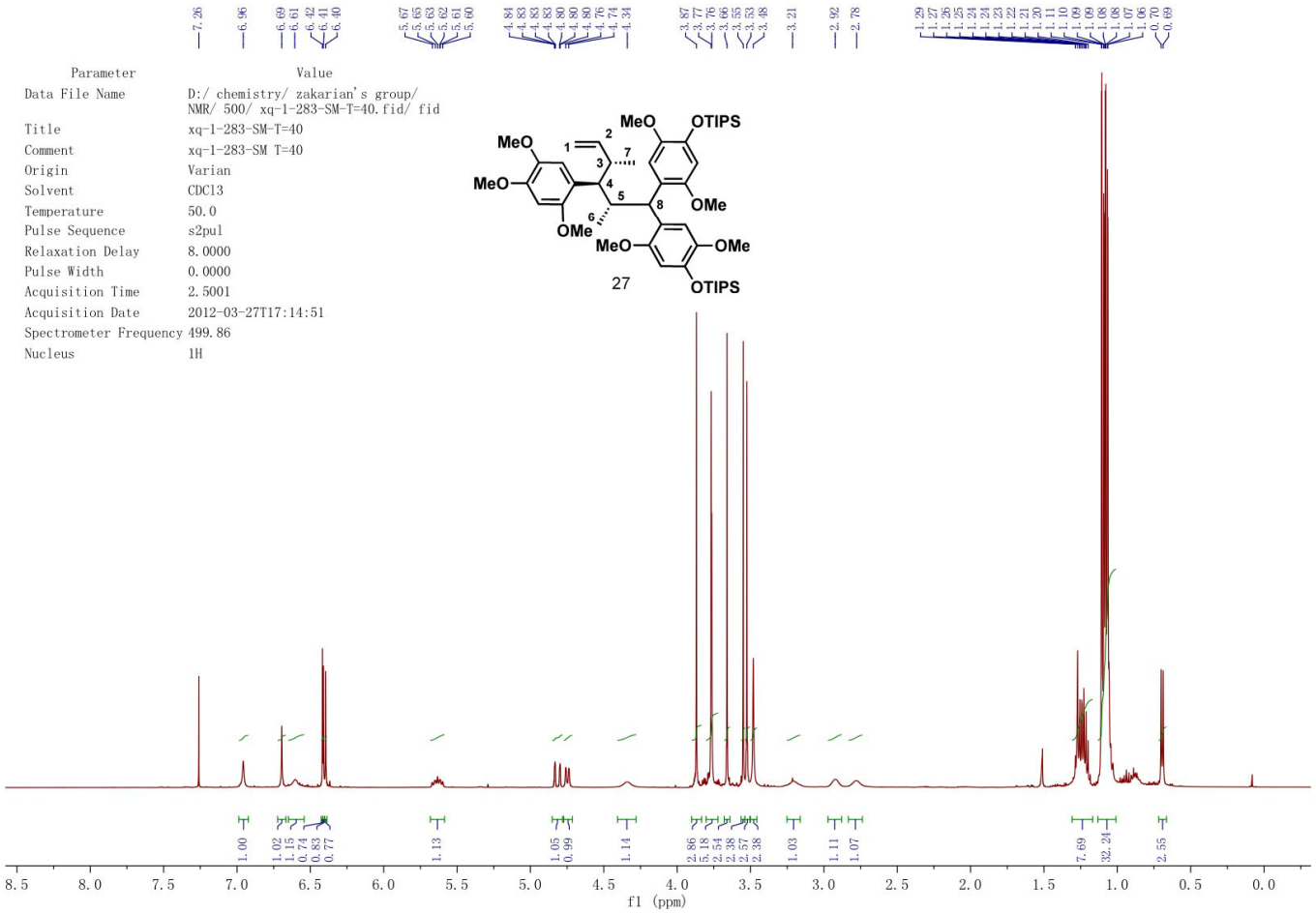
23

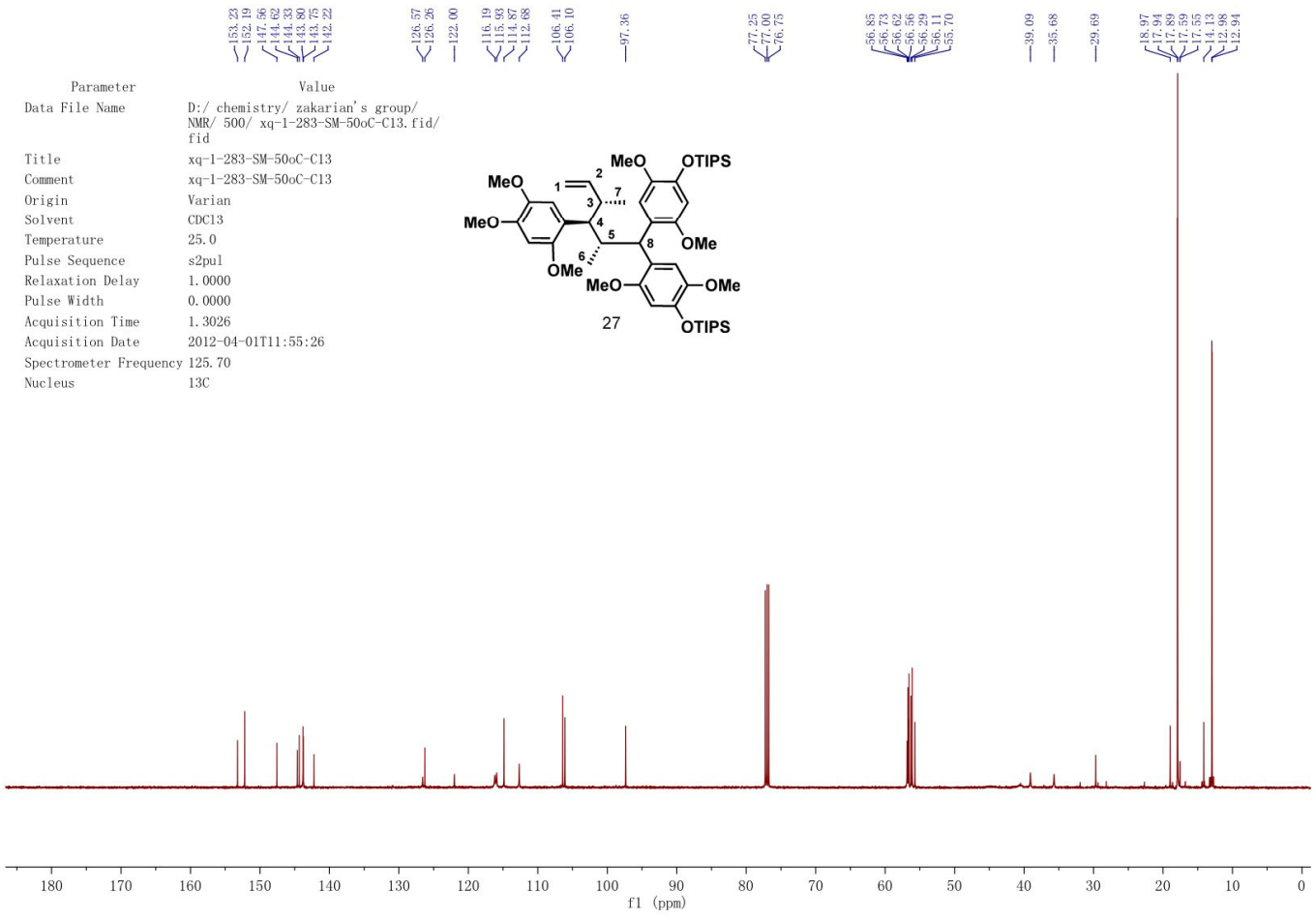

7.26
6.54
6.51
5.77
5.76
5.75
5.74
5.74
5.72
5.72
5.70
5.02
5.01
5.00
4.99
4.96
4.93
3.87
3.78
3.76
3.45
1.50
0.86
0.85
0.83
Parameter Value
Data File Name D:/ chemistry/ zakarian's group/ NMR/ 500/ xq-2-65.fid/ fid
Title xq-2-65
Comment xq-2-65
Origin Varian
Solvent CDCl3
Temperature 25.0
Pulse Sequence s2pul
Relaxation Delay 4.8000
Pulse Width 0.0000
Acquisition Time 2.5001
Acquisition Date 2012-06-30T11:05:47
Spectrometer Frequency 499.86
Nucleus 1H
OMe
OMe
MeO
CO2t-Bu
Me
Me
24
1.02
1.22
1.00
1.01
1.02
3.27
2.15
3.01
1.02
1.11
1.04
9.56
6.39
f1 (ppm)


176.35
152.94
147.58
142.34
141.00
119.21
114.56
113.42
97.49
79.90
77.25
77.00
76.75
56.60
56.46
55.79
45.39
43.28
40.29
27.99
18.33
16.69
Parameter Value
Data File Name D:/ chemistry/ zakarian's group/ NMR/ 500/ xq-242-C13.fid/ fid
Title xq-242-C13
Comment xq-242-C13
Origin Varian
Solvent CDCl3
Temperature 80.0
Pulse Sequence s2pul
Relaxation Delay 1.0000
Pulse Width 0.0000
Acquisition Time 1.3026
Acquisition Date 2012-02-27T16:27:47
Spectrometer Frequency 125.70
Nucleus 13C
OMe
OMe
MeO
CO2t-Bu
Me
Me
24
f1 (ppm)

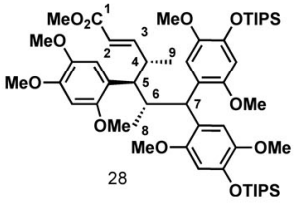

7.33
7.25
7.18
6.74
6.39
6.33
5.62
5.60
5.59
4.94
4.77
4.73
4.71
3.86
3.82
3.79
3.75
3.55
3.54
3.41
3.38
2.51
1.28
1.26
1.25
1.23
1.22
1.22
1.21
1.19
1.18
1.16
1.10
1.10
1.08
1.08
1.06
1.04
Parameter Value
Data File Name D:/ chemistry/ zakarian's group/ NMR/ 500/ xq-2-66.fid/ fid
Title xq-2-66
Comment xq-2-66
Origin Varian
Solvent CDCl3
Temperature 25.0
Pulse Sequence s2pul
Relaxation Delay 4.8000
Pulse Width 0.0000
Acquisition Time 2.5001
Acquisition Date 2012-07-02T14:29:59
Spectrometer Frequency 499.86
Nucleus 1H
MeO
OTIPS
MeO
MeO
OMe
HO
OMe
MeO
OMe
OTIPS
26
1.00
0.99
0.92
2.02
1.07
0.92
0.96
1.94
3.16
3.46
2.87
3.02
1.49
8.19
0.71
6.98
38.93
3.83
8.5
8.0
7.5
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
0.0
f1 (ppm)


152.77
146.83
144.22
144.06
143.91
143.67
141.57
128.03
124.25
114.80
112.75
106.48
97.32
81.10
77.25
77.00
76.75
56.62
56.26
55.53
41.95
37.96
18.97
17.83
17.78
17.48
17.44
14.11
12.82
12.51
12.26
12.15
Parameter Value
Data File Name D:/ chemistry/ zakarian's group/ NMR/ 500/ xq-2-66-C13.fid/ fid
Title xq-2-66-C13
Comment xq-2-66-C13
Origin Varian
Solvent CDCl3
Temperature 25.0
Pulse Sequence s2pul
Relaxation Delay 1.0000
Pulse Width 0.0000
Acquisition Time 1.3026
Acquisition Date 2012-07-02T14:32:43
Spectrometer Frequency 125.70
Nucleus 13C
MeO
OTIPS
MeO
MeO
OMe
HO
OMe
MeO
OMe
OTIPS
26
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.26 6.96 6.69 6.61 6.42 6.41 6.40 5.67 5.65 5.63 5.62 5.61 5.60 4.84 4.83 4.83 4.83 4.80 4.80 4.80 4.76 4.74 4.34 3.87 3.77 3.76 3.66 3.55 3.53 3.48 3.21 2.92 2.78 1.29 1.27 1.25 1.25 1.24 1.24 1.23 1.22 1.21 1.20 1.11 1.10 1.09 1.09 1.08 1.08 1.07 1.06 0.70 0.69
Parameter Value
Data File Name D:/ chemistry/ zakarian's group/ NMR/ 500/ xq-1-283-SM-T=40.fid/ fid
Title xq-1-283-SM-T=40
Comment xq-1-283-SM T=40
Origin Varian
Solvent CDCl3
Temperature 50.0
Pulse Sequence s2pul
Relaxation Delay 8.0000
Pulse Width 0.0000
Acquisition Time 2.5001
Acquisition Date 2012-03-27T17:14:51
Spectrometer Frequency 499.86
Nucleus 1H
MeO OTIPS MeO MeO OMe OMe MeO OMe OTIPS
27
1.00 1.02 1.15 0.74 0.83 0.77 1.13 1.05 0.99 1.14 2.86 5.18 2.54 2.38 2.57 2.38 1.03 1.11 1.07 7.69 32.24 2.55
8.5 8.0 7.5 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 0.0
f1 (ppm)

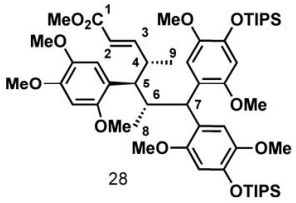

153.23 152.19 147.56 144.62 144.33 143.80 143.75 142.22 126.57 126.26 122.00 116.19 115.83 114.57 112.68 106.41 106.10 97.36 77.25 77.00 76.75 56.85 56.73 56.62 56.56 56.29 56.11 55.70 39.09 35.68 29.69 18.97 17.94 17.89 17.59 17.55 14.13 12.98 12.94
Parameter Value
Data File Name D:/ chemistry/ zakarian's group/ NMR/ 500/ xq-1-283-SM-50oC-C13.fid/ fid
Title xq-1-283-SM-50oC-C13
Comment xq-1-283-SM-50oC-C13
Origin Varian
Solvent CDCl3
Temperature 25.0
Pulse Sequence s2pul
Relaxation Delay 1.0000
Pulse Width 0.0000
Acquisition Time 1.3026
Acquisition Date 2012-04-01T11:55:26
Spectrometer Frequency 125.70
Nucleus 13C
MeO OTIPS MeO MeO OMe OMe MeO OMe OTIPS
27
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Parameter	Value
Data File Name	D:/ chemistry/ zakarian's group/ NMR/ 500/ xq-1-292-HPLC-2-50oC.fid/ fid
Title	xq-1-292-HPLC-2-50oC
Comment	xq-1-292-HPLC-2-50oC
Origin	Varian
Solvent	CDCl3
Temperature	25.0
Pulse Sequence	s2pul
Relaxation Delay	4.8000
Pulse Width	0.0000
Acquisition Time	2.5001
Acquisition Date	2012-04-15T13:56:44
Spectrometer Frequency	499.86
Nucleus	1H

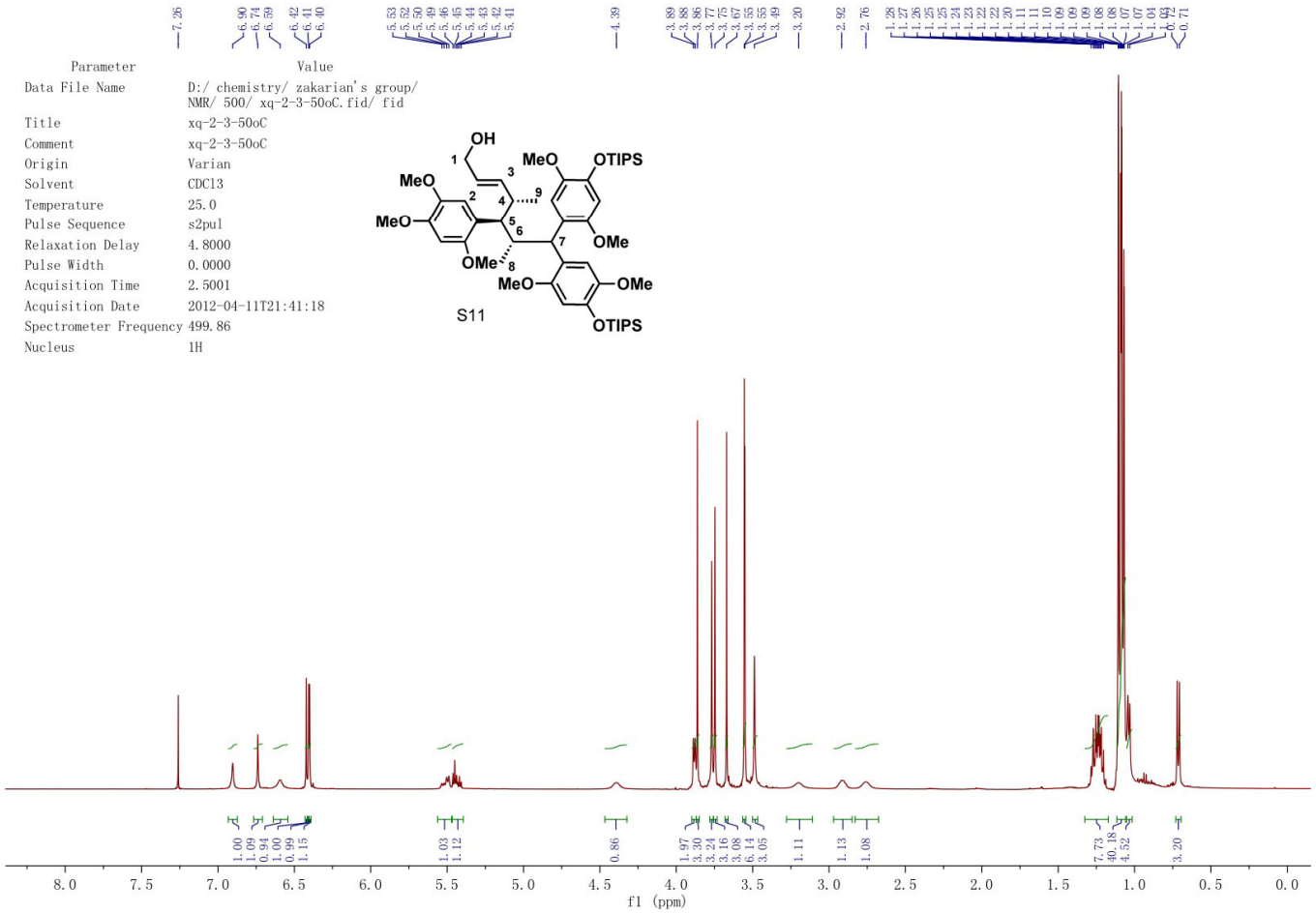


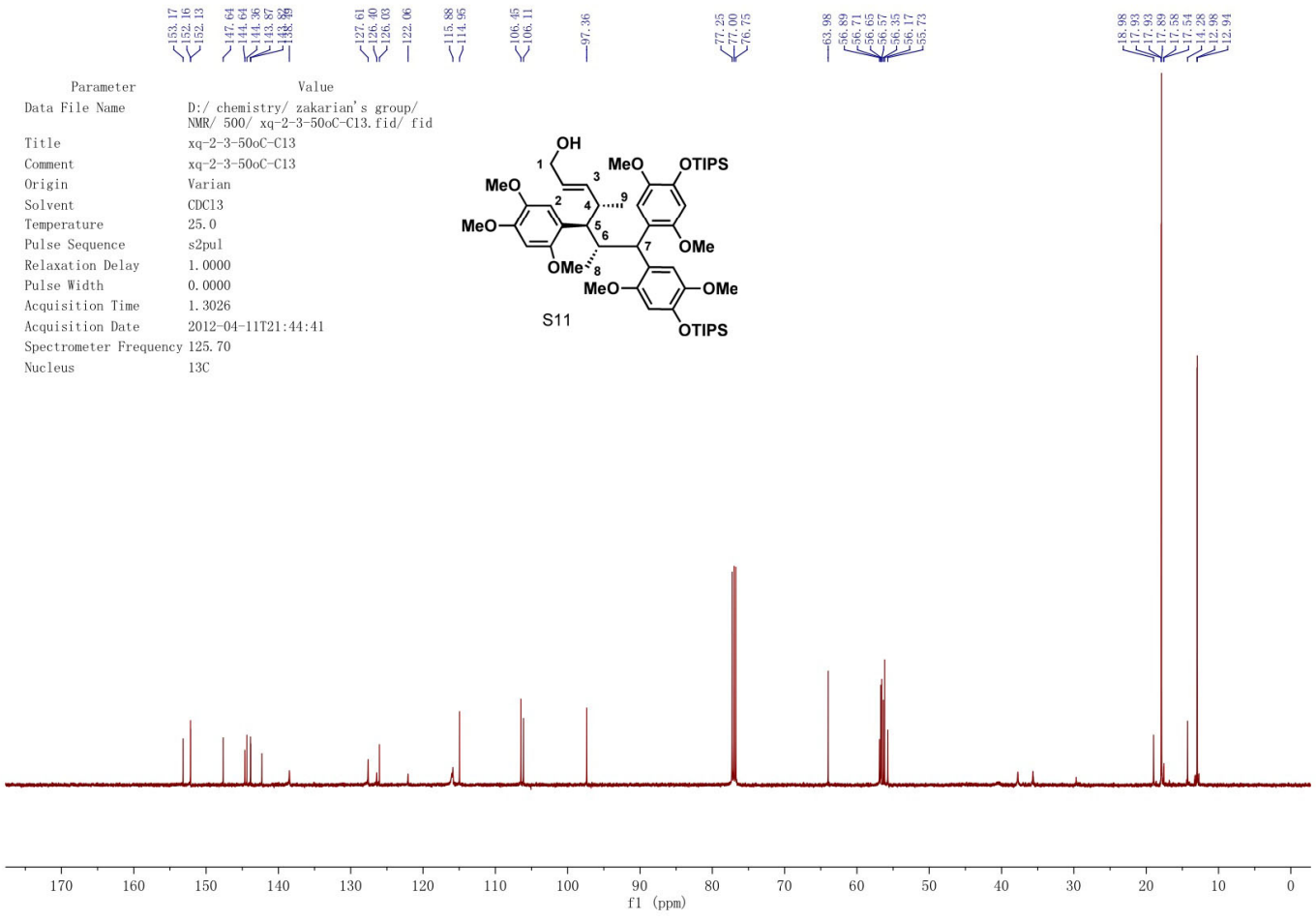
28

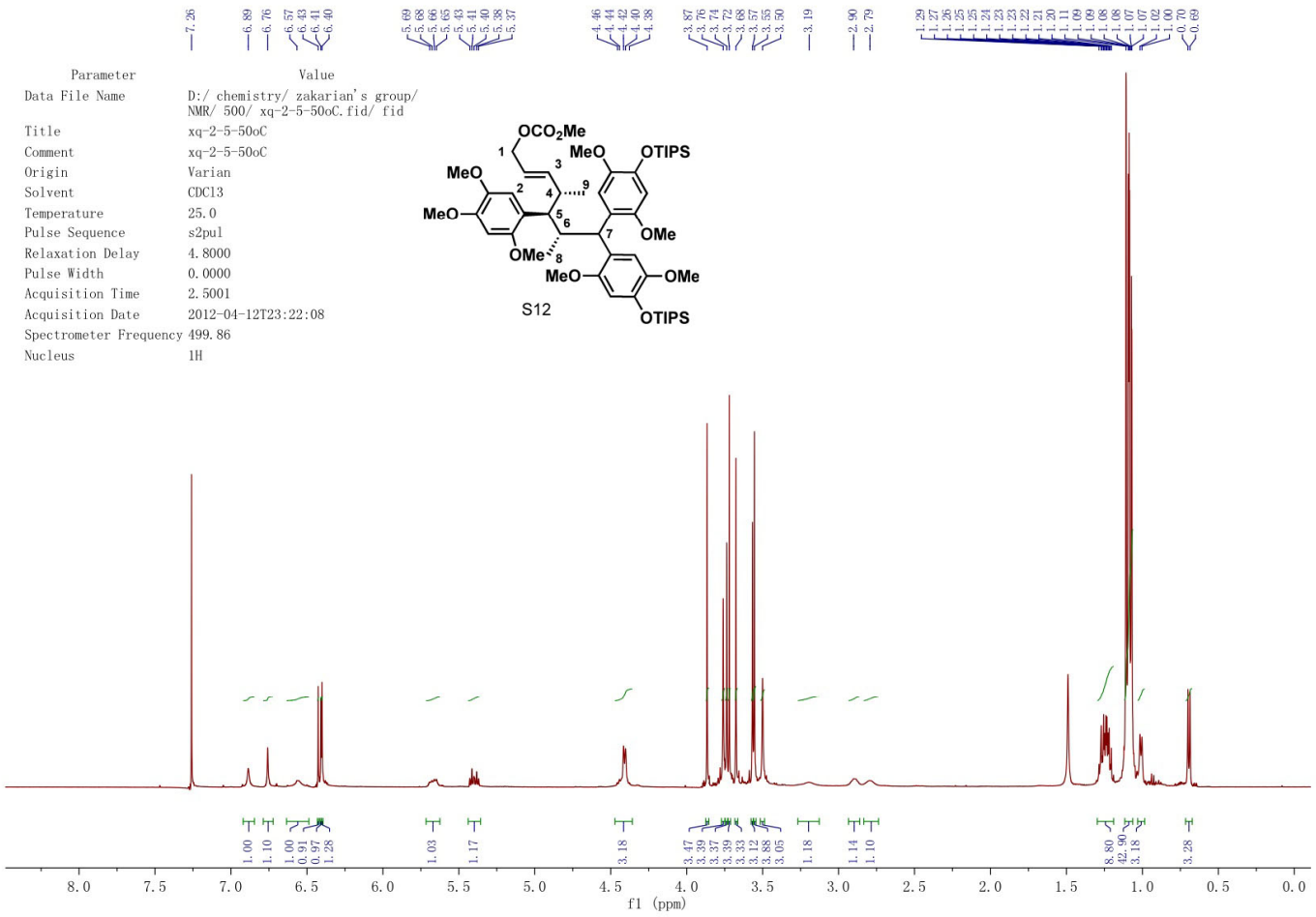
Parameter	Value
Data File Name	D:/ chemistry/ zakarian's group/ NMR/ 500/ xq-1-292-HPLC-2-50oC-C13.fid/ fid
Title	xq-1-292-HPLC-2-50oC-C13
Comment	xq-1-292-HPLC-2-50oC-C13
Origin	Varian
Solvent	CDCl3
Temperature	25.0
Pulse Sequence	s2pul
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.3026
Acquisition Date	2012-04-15T13:59:08
Spectrometer Frequency	125.70
Nucleus	13C

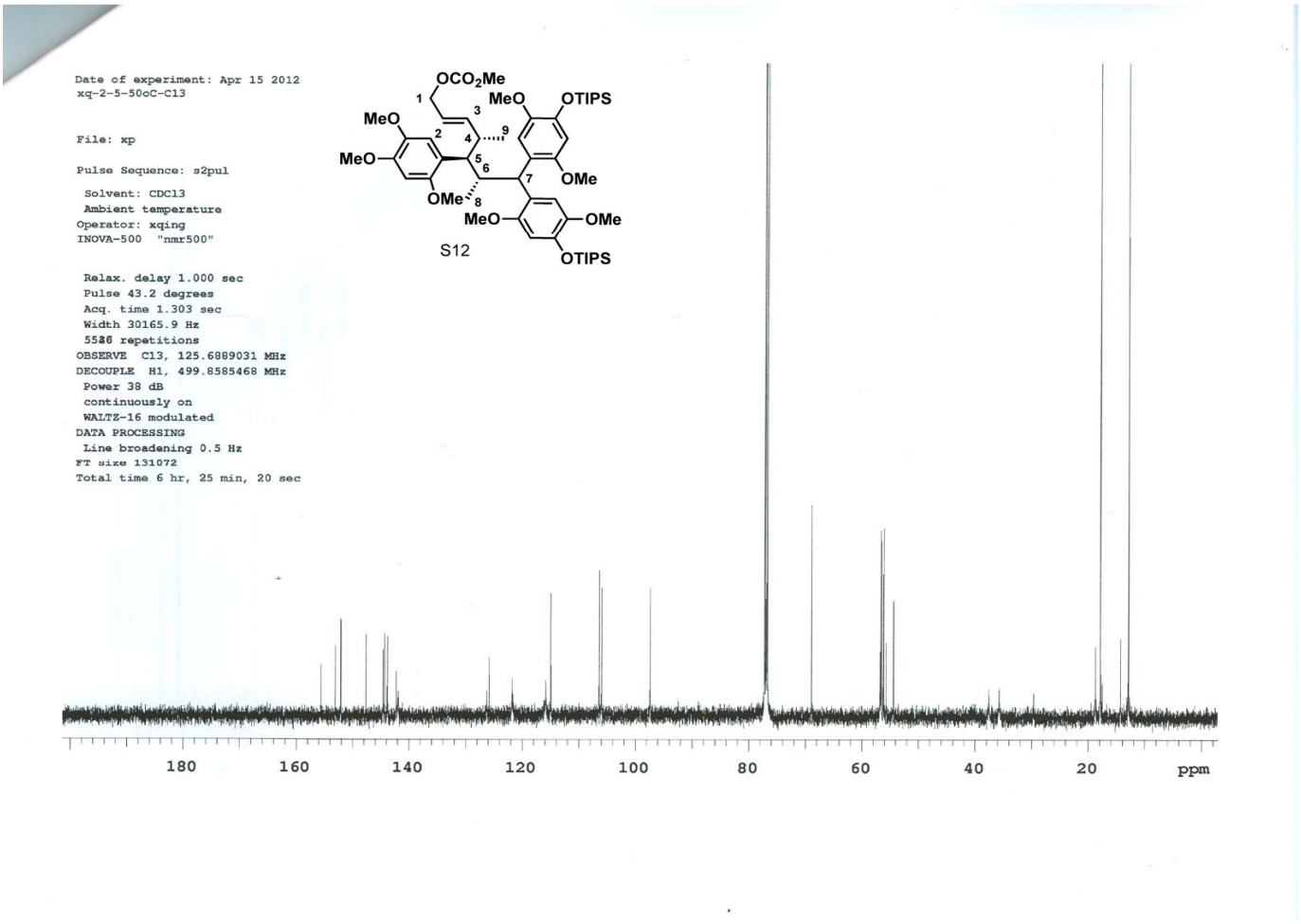


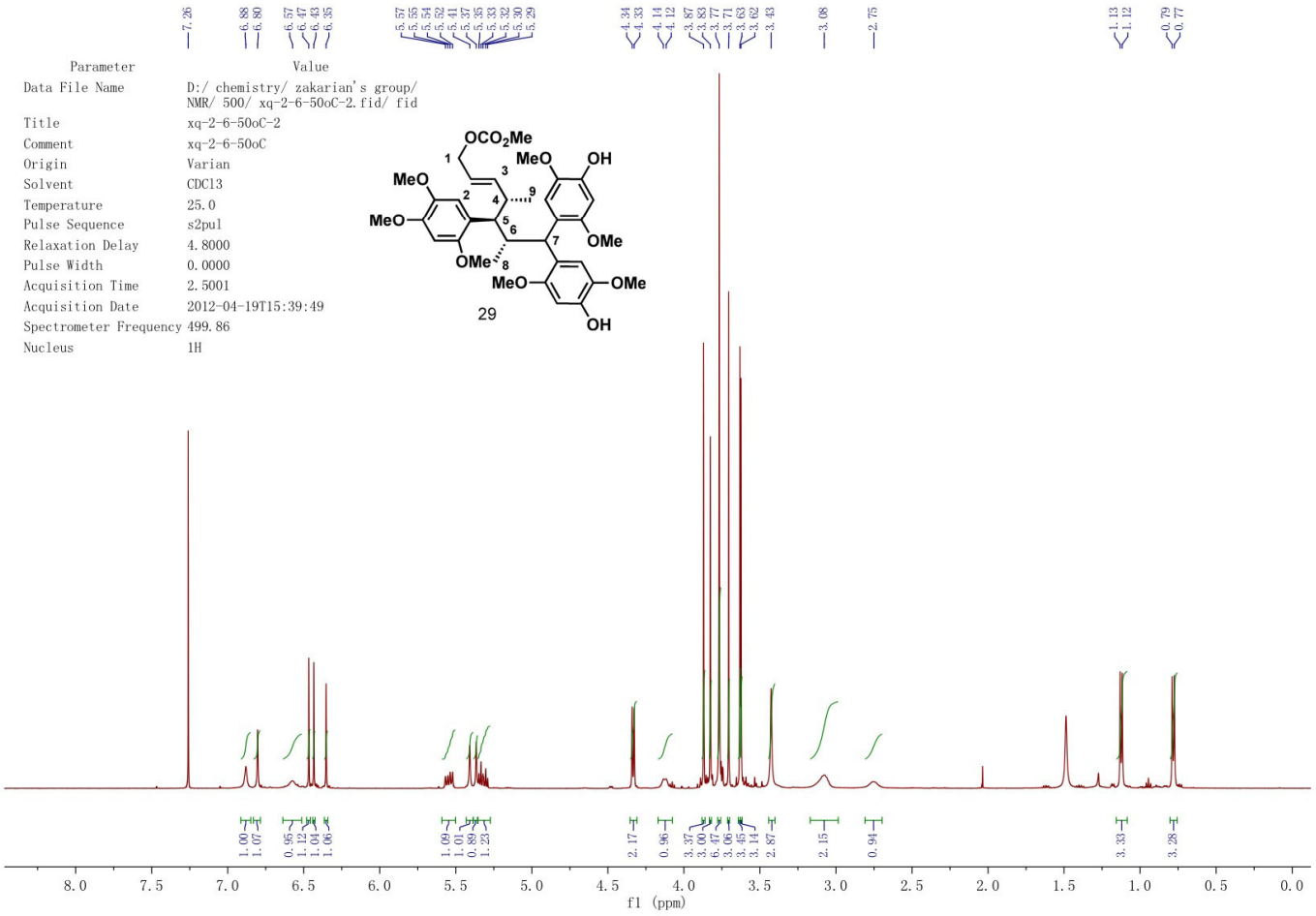
28

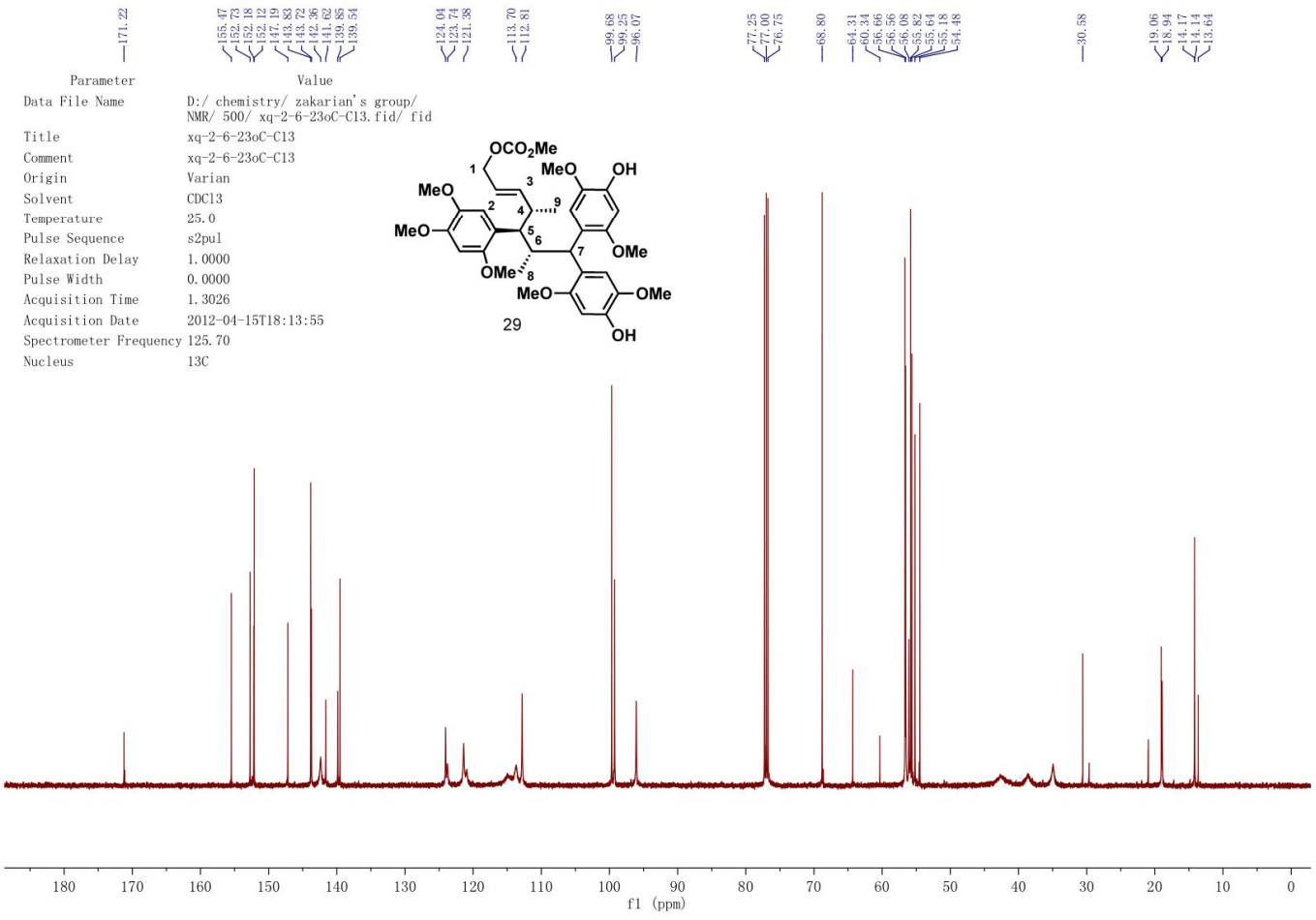

7.26
6.90
6.74
6.69
6.42
6.41
6.40
5.53
5.52
5.50
5.49
5.46
5.45
5.44
5.43
5.42
5.41
4.39
3.89
3.88
3.86
3.77
3.75
3.67
3.55
3.55
3.49
3.20
2.92
2.76
1.28
1.27
1.26
1.25
1.25
1.24
1.23
1.22
1.22
1.20
1.11
1.11
1.10
1.09
1.09
1.09
1.08
1.08
1.07
1.07
1.04
0.93
0.71
Parameter Value
Data File Name D:/ chemistry/ zakarian's group/ NMR/ 500/ xq-2-3-50oC.fid/ fid
Title xq-2-3-50oC
Comment xq-2-3-50oC
Origin Varian
Solvent CDCl3
Temperature 25.0
Pulse Sequence s2pul
Relaxation Delay 4.8000
Pulse Width 0.0000
Acquisition Time 2.5001
Acquisition Date 2012-04-11T21:41:18
Spectrometer Frequency 499.86
Nucleus 1H
OH
MeO
OTIPS
MeO
MeO
OMe
OMe
MeO
OMe
MeO
OTIPS
S11
1.00
1.09
0.94
1.00
0.99
1.15
1.03
1.12
0.86
1.97
3.30
3.24
3.16
3.08
6.14
3.05
1.11
1.13
1.08
7.73
40.18
4.52
3.20
f1 (ppm)

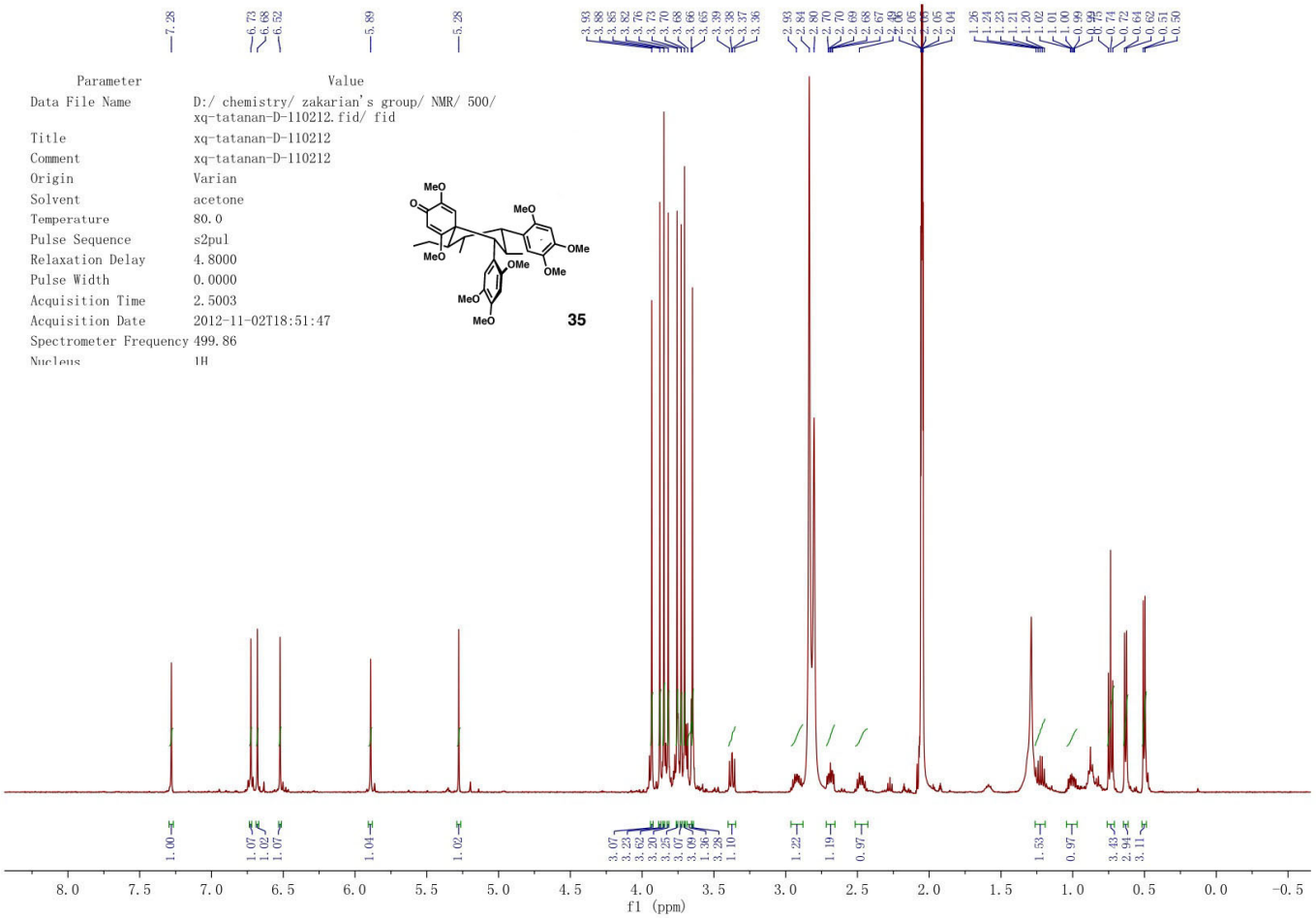

153.17
152.16
152.13
147.64
144.64
144.36
143.57
143.49
138.99
127.61
126.40
126.03
122.06
115.88
114.96
106.45
106.11
97.36
77.25
77.00
76.75
63.98
56.89
56.71
56.65
56.57
56.35
56.17
55.73
18.98
17.93
17.93
17.89
17.58
17.54
14.28
12.98
12.94
Parameter Value
Data File Name D:/ chemistry/ zakarian's group/ NMR/ 500/ xq-2-3-50oC-C13.fid/ fid
Title xq-2-3-50oC-C13
Comment xq-2-3-50oC-C13
Origin Varian
Solvent CDCl3
Temperature 25.0
Pulse Sequence s2pul
Relaxation Delay 1.0000
Pulse Width 0.0000
Acquisition Time 1.3026
Acquisition Date 2012-04-11T21:44:41
Spectrometer Frequency 125.70
Nucleus 13C
OH
MeO
OTIPS
MeO
MeO
OMe
OMe
MeO
OMe
MeO
OTIPS
S11
f1 (ppm)

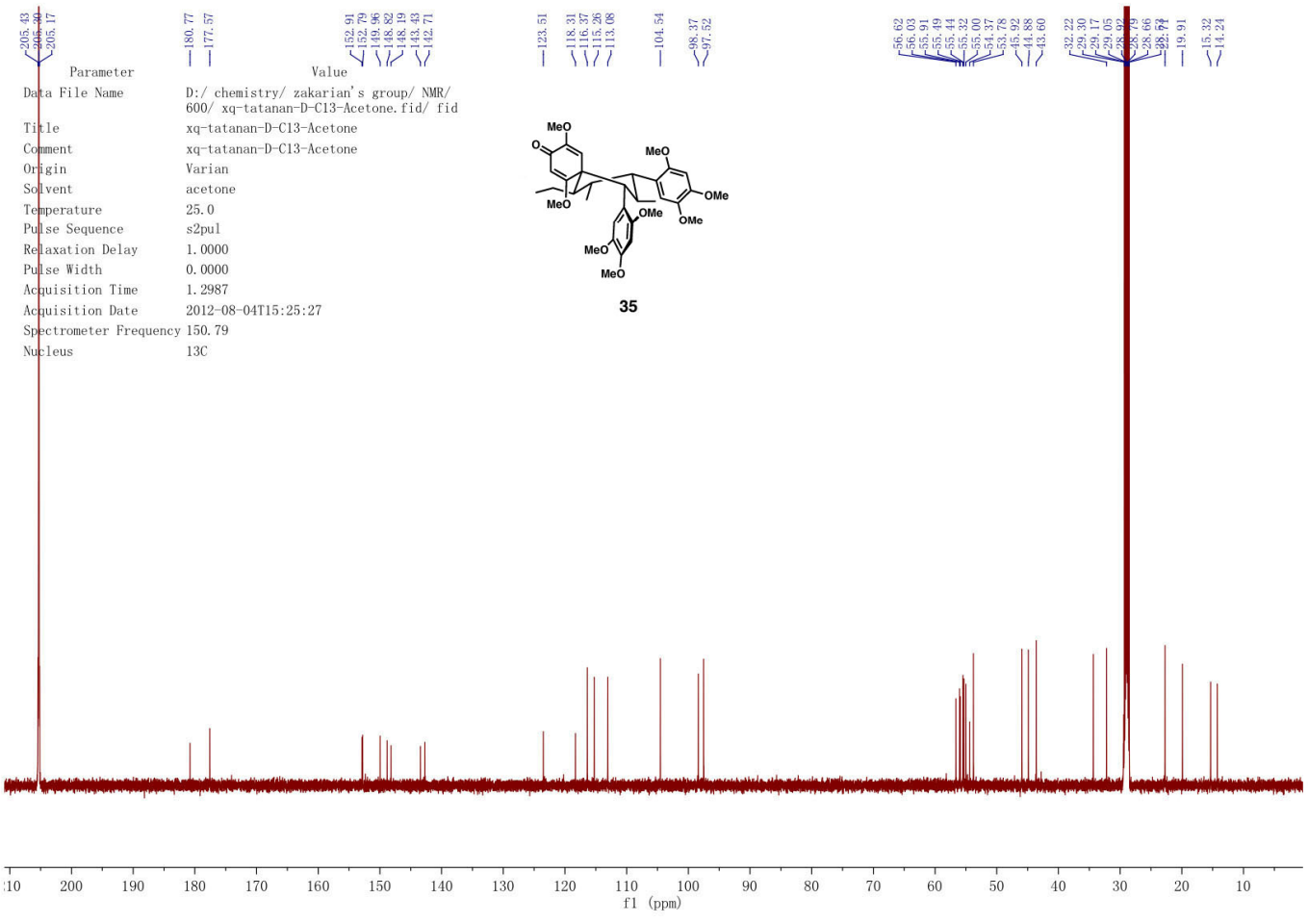

Parameter Value
Data File Name D:/ chemistry/ zakarian's group/ NMR/ 500/ xq-2-5-50oC.fid/ fid
Title xq-2-5-50oC
Comment xq-2-5-50oC
Origin Varian
Solvent CDCl3
Temperature 25.0
Pulse Sequence s2pul
Relaxation Delay 4.8000
Pulse Width 0.0000
Acquisition Time 2.5001
Acquisition Date 2012-04-12T23:22:08
Spectrometer Frequency 499.86
Nucleus 1H
S12
f1 (ppm)

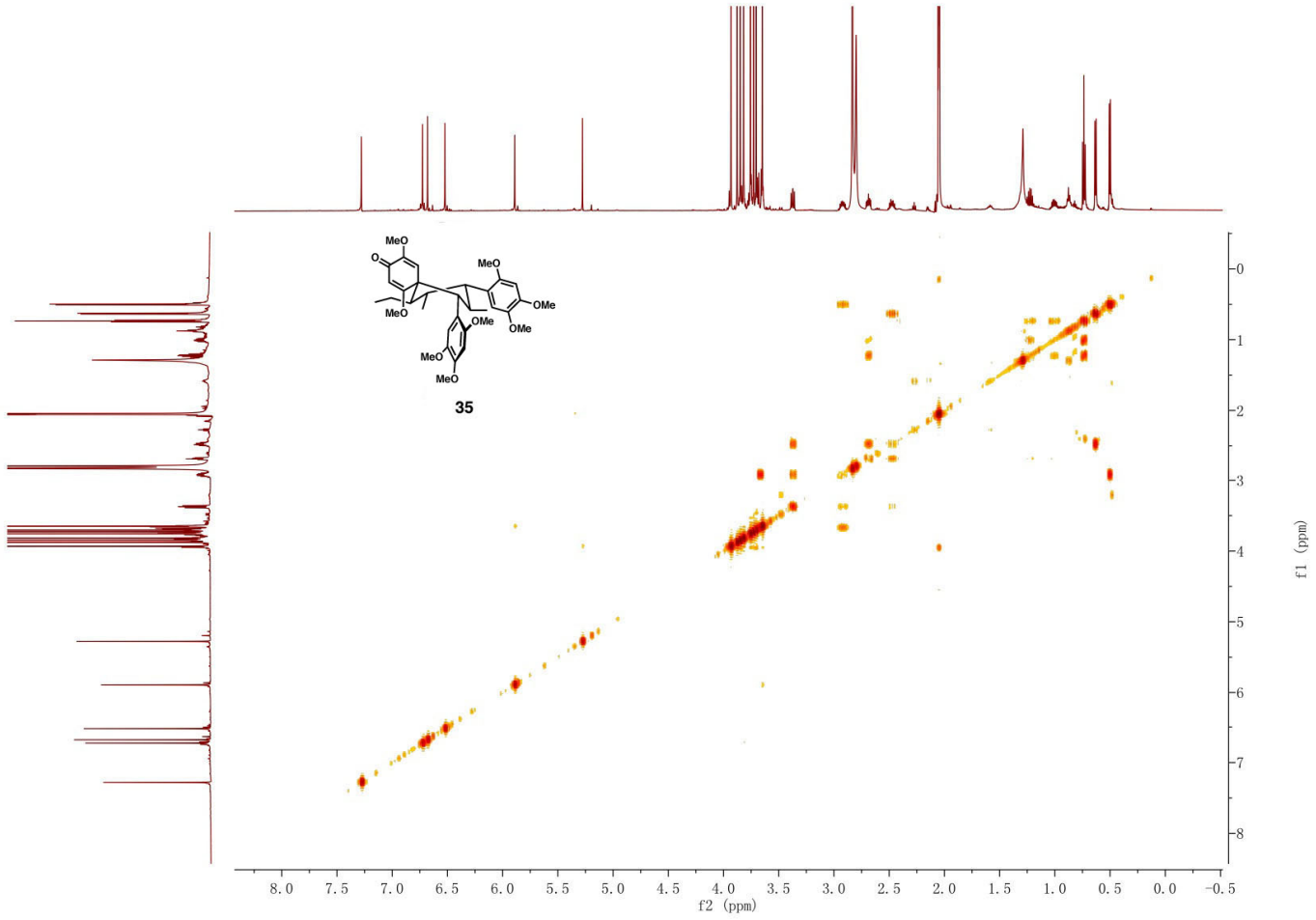

Date of experiment: Apr 15 2012
xq-2-5-50oC-C13
File: xp
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Operator: xqing
INOVA-500 "nmr500"
Relax. delay 1.000 sec
Pulse 43.2 degrees
Acq. time 1.303 sec
Width 30165.9 Hz
repetitions
OBSERVE C13, 125.6889031 MHz
DECOUPLE H1, 499.8585468 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 6 hr, 25 min, 20 sec
S12
ppm


7.26
6.88
6.80
6.57
6.47
6.43
6.35
5.57
5.55
5.54
5.52
5.41
5.37
5.35
5.33
5.32
5.30
5.29
4.34
4.33
4.14
4.12
3.87
3.85
3.77
3.71
3.63
3.62
3.43
3.08
2.75
1.13
1.12
0.79
0.77
Parameter Value
Data File Name D:/ chemistry/ zakarian's group/ NMR/ 500/ xq-2-6-50oC-2.fid/ fid
Title xq-2-6-50oC-2
Comment xq-2-6-50oC
Origin Varian
Solvent CDCl3
Temperature 25.0
Pulse Sequence s2pul
Relaxation Delay 4.8000
Pulse Width 0.0000
Acquisition Time 2.5001
Acquisition Date 2012-04-19T15:39:49
Spectrometer Frequency 499.86
Nucleus 1H
OCO2Me
MeO
OH
MeO
OMe
MeO
OMe
MeO
OMe
OH
29
1.00
1.07
0.95
1.12
1.04
1.06
1.09
1.01
0.89
1.23
2.17
0.96
3.37
3.00
6.06
3.45
3.14
2.87
2.15
0.94
3.33
3.28
f1 (ppm)

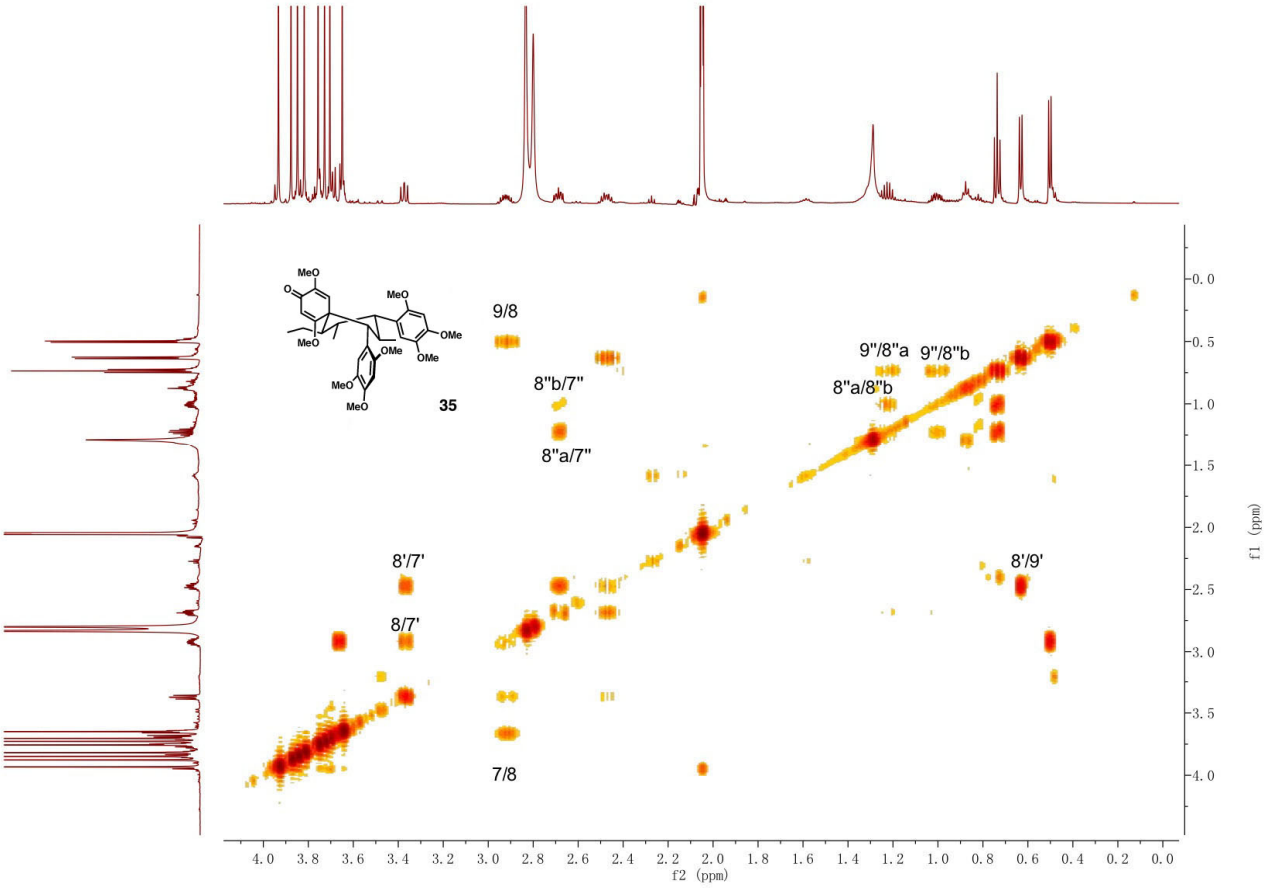

171.22
155.47
152.73
152.18
152.12
147.19
143.83
143.72
142.36
141.62
139.85
139.54
124.04
123.74
121.38
113.70
112.81
99.68
99.25
96.07
77.25
77.00
76.75
68.80
64.31
60.34
56.56
56.08
55.82
55.64
55.18
54.48
30.58
19.06
18.94
14.17
14.14
13.64
Parameter Value
Data File Name D:/ chemistry/ zakarian's group/ NMR/ 500/ xq-2-6-23oC-C13.fid/ fid
Title xq-2-6-23oC-C13
Comment xq-2-6-23oC-C13
Origin Varian
Solvent CDCl3
Temperature 25.0
Pulse Sequence s2pul
Relaxation Delay 1.0000
Pulse Width 0.0000
Acquisition Time 1.3026
Acquisition Date 2012-04-15T18:13:55
Spectrometer Frequency 125.70
Nucleus 13C
OCO2Me
MeO
OH
MeO
OMe
MeO
OMe
MeO
OMe
OH
29
f1 (ppm)


Parameter Value
Data File Name D:/ chemistry/ zakarian's group/ NMR/ 500/ xq-tatanan-D-110212.fid/ fid
Title xq-tatanan-D-110212
Comment xq-tatanan-D-110212
Origin Varian
Solvent acetone
Temperature 80.0
Pulse Sequence s2pul
Relaxation Delay 4.8000
Pulse Width 0.0000
Acquisition Time 2.5003
Acquisition Date 2012-11-02T18:51:47
Spectrometer Frequency 499.86
Nucleus 1H
35
f1 (ppm)

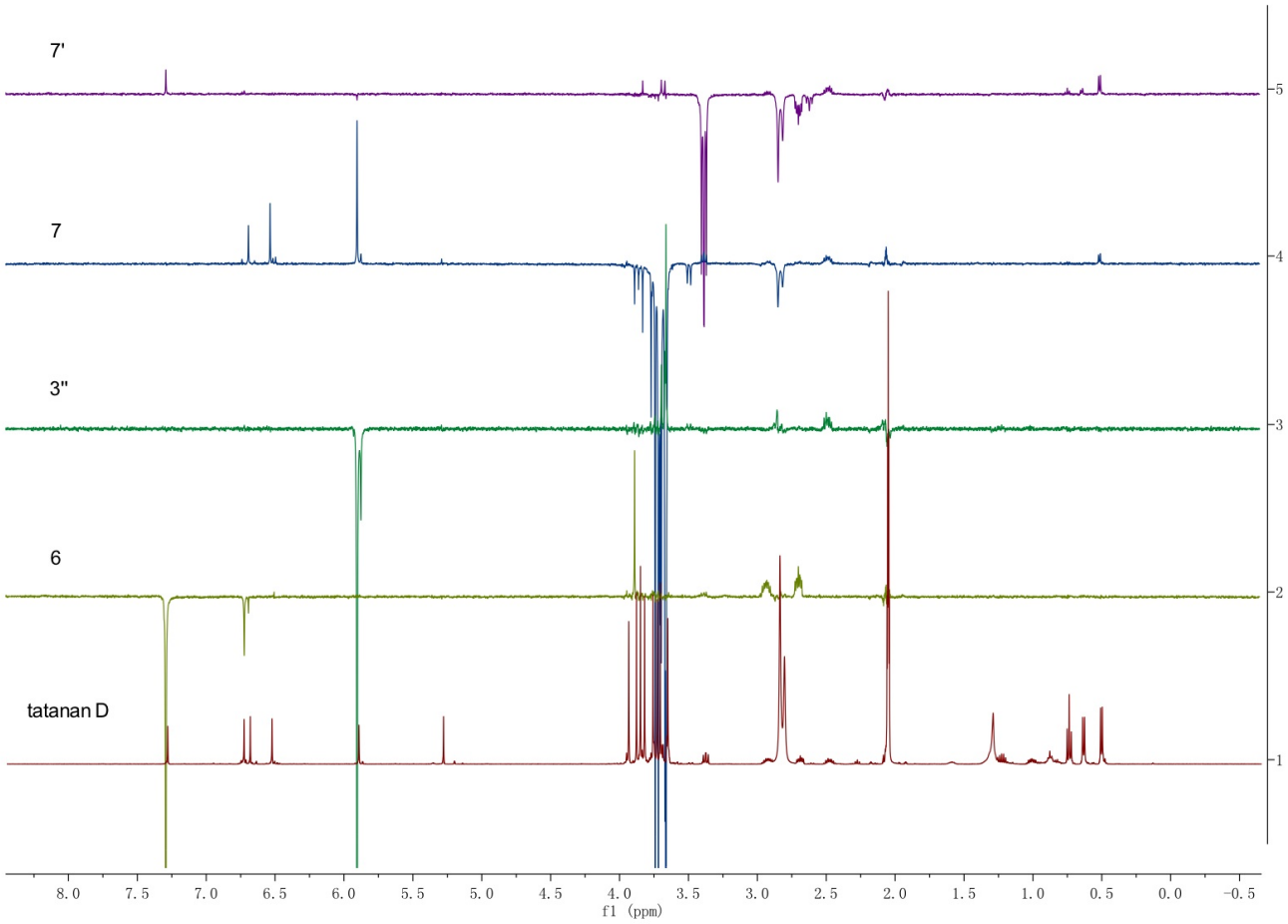

Parameter Value
Data File Name D:/ chemistry/ zakarian's group/ NMR/ 600/ xq-tatanan-D-C13-Acetone.fid/ fid
Title xq-tatanan-D-C13-Acetone
Comment xq-tatanan-D-C13-Acetone
Origin Varian
Solvent acetone
Temperature 25.0
Pulse Sequence s2pul
Relaxation Delay 1.0000
Pulse Width 0.0000
Acquisition Time 1.2987
Acquisition Date 2012-08-04T15:25:27
Spectrometer Frequency 150.79
Nucleus 13C
35
f1 (ppm)

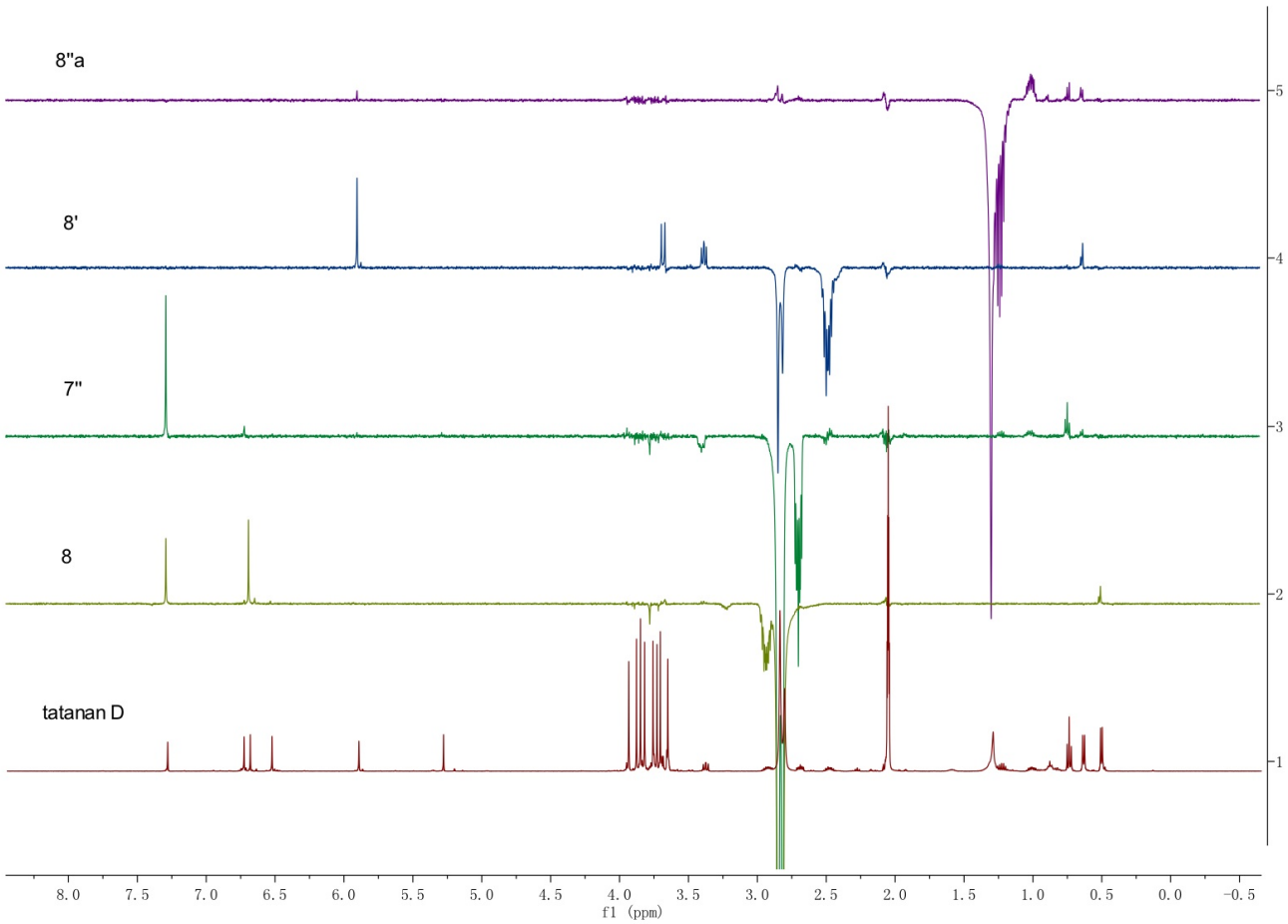


2D H,H-COSY spectrum of **35** in CD_3COCD_3(600 MHz)

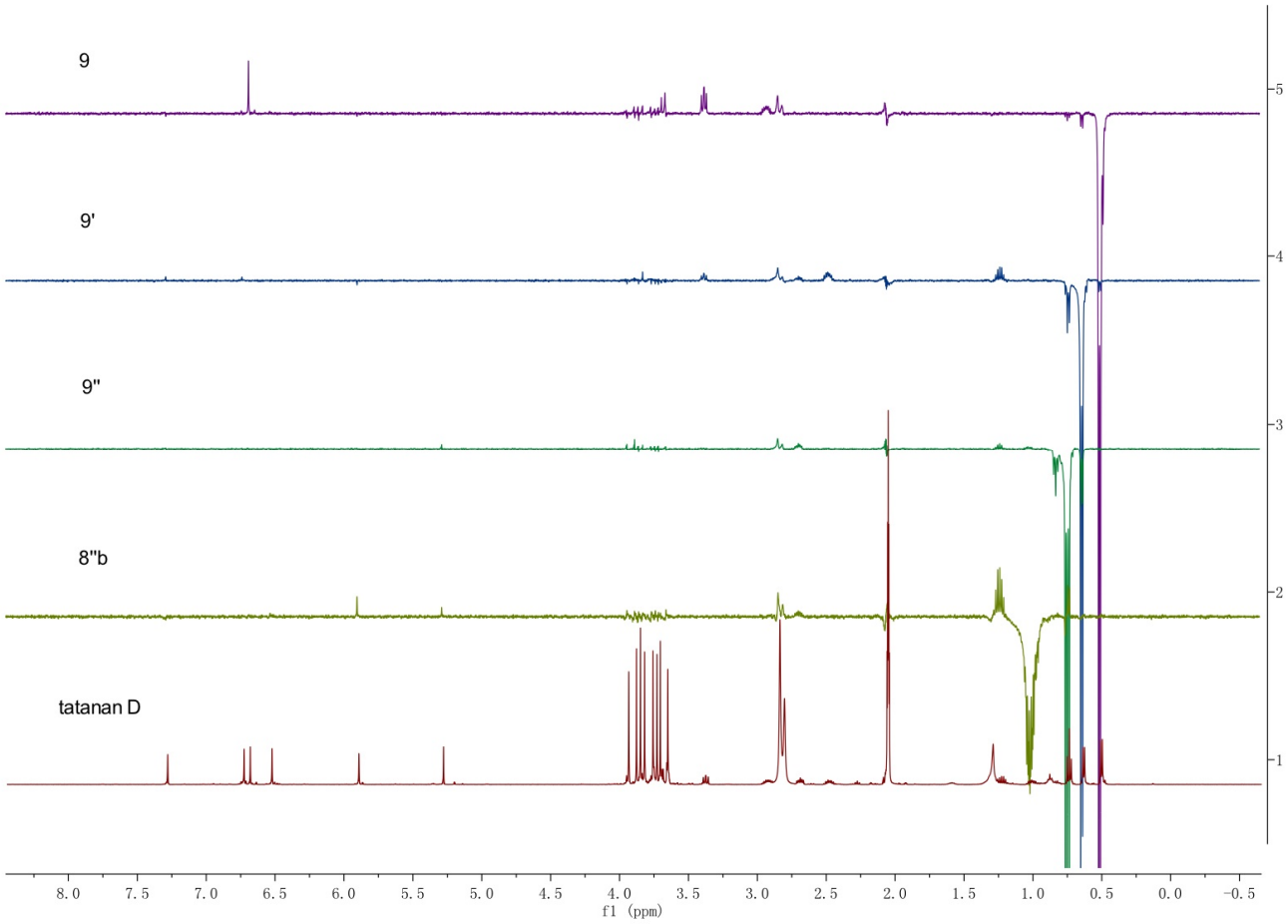


Enlarged 2D H,H-COSY spectrum of **35** in CD_3COCD_3(600 MHz)

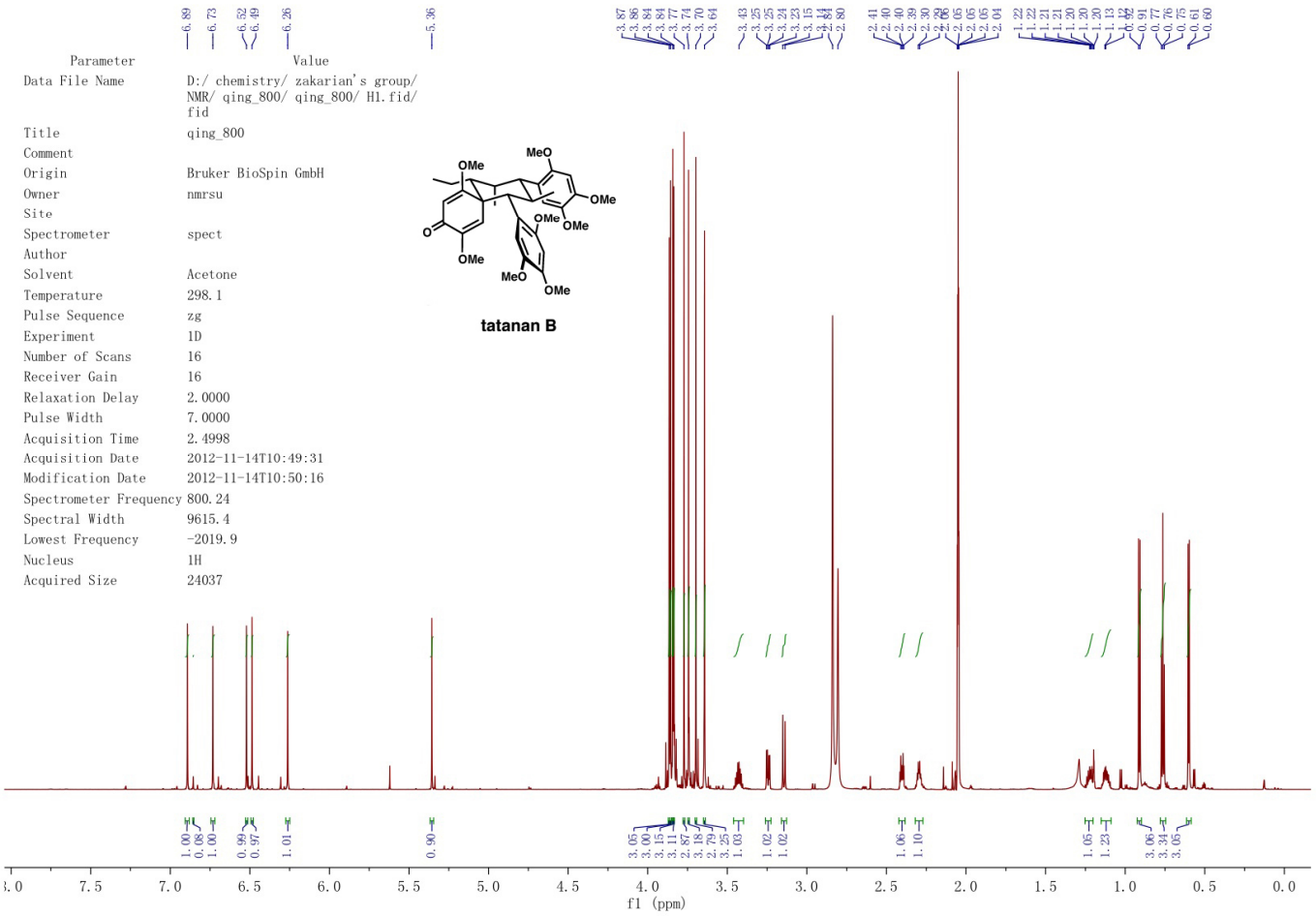




NOE spectrum of **35** in CD_3COCD_3(500 MHz)

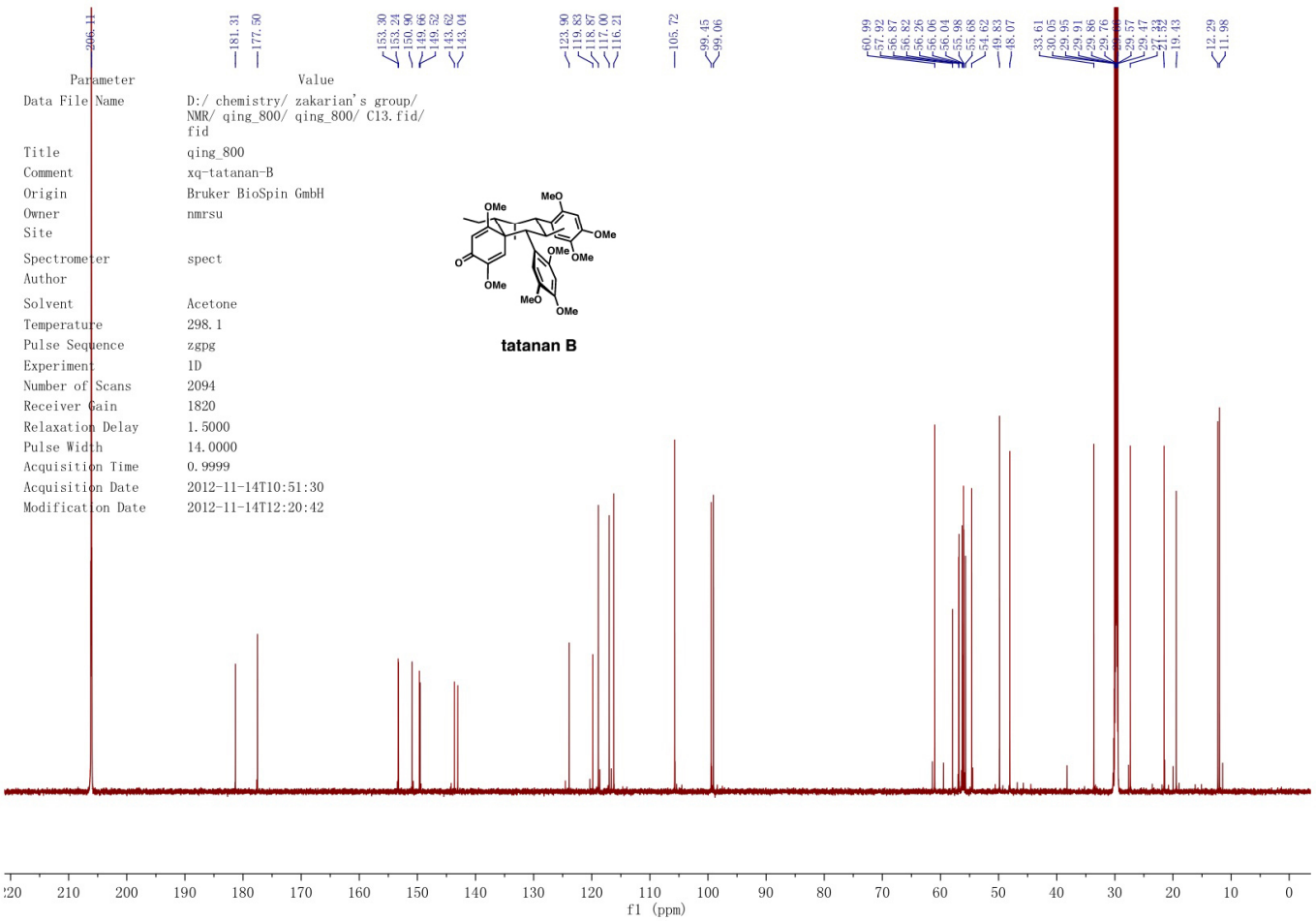


NOE spectrum of **35** in CD_3COCD_3(500 MHz)



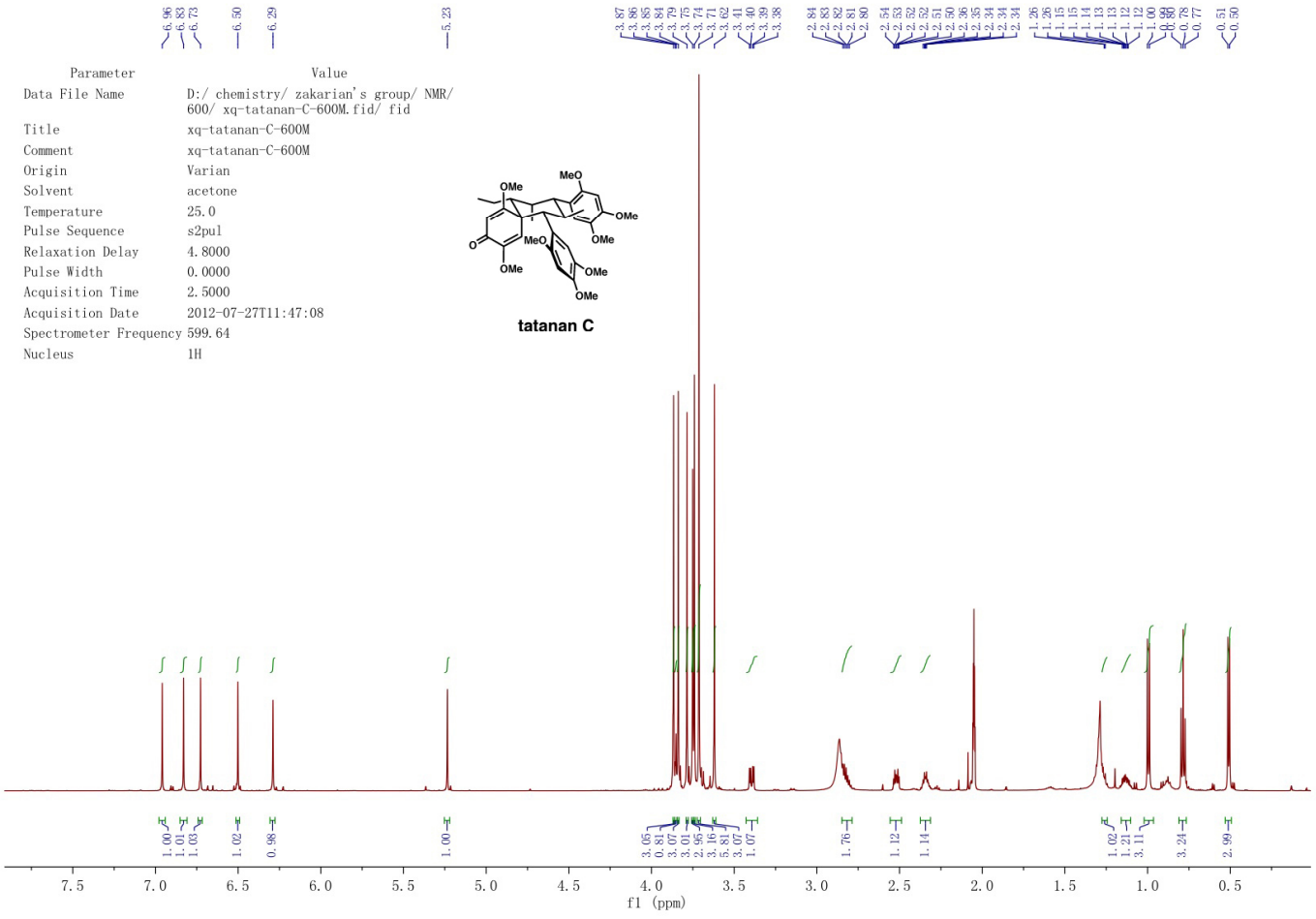
Parameter	Value
Data File Name	D:/ chemistry/ zakarian's group/ NMR/ qing_800/ qing_800/ H1.fid/ fid
Title	qing_800
Comment	
Origin	Bruker BioSpin GmbH
Owner	nmrsu
Site	
Spectrometer	spect
Author	
Solvent	Acetone
Temperature	298.1
Pulse Sequence	zg
Experiment	1D
Number of Scans	16
Receiver Gain	16
Relaxation Delay	2.0000
Pulse Width	7.0000
Acquisition Time	2.4998
Acquisition Date	2012-11-14T10:49:31
Modification Date	2012-11-14T10:50:16
Spectrometer Frequency	800.24
Spectral Width	9615.4
Lowest Frequency	-2019.9
Nucleus	1H
Acquired Size	24037

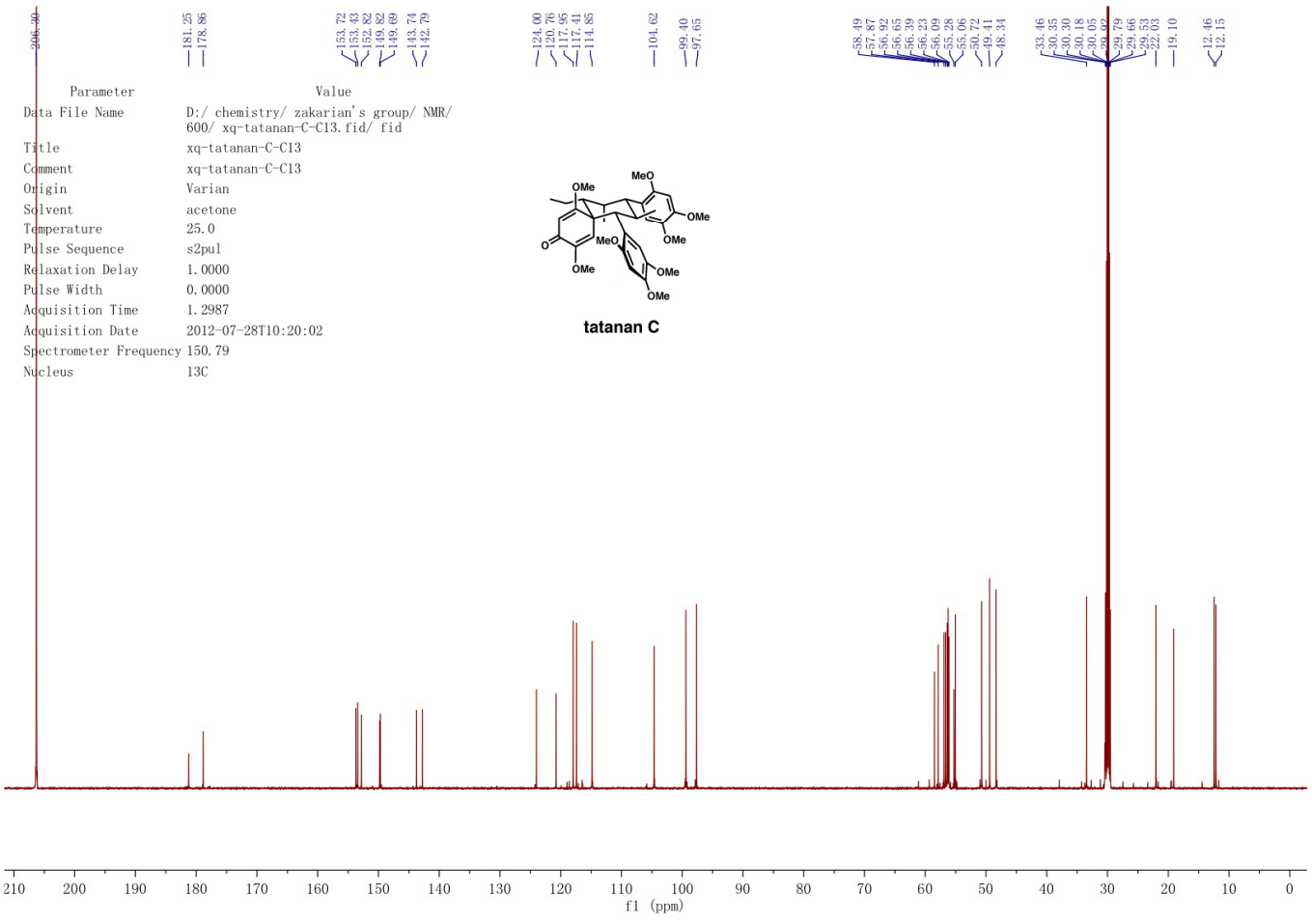
tatanan B



Parameter	Value
Data File Name	D:/ chemistry/ zakarian's group/ NMR/ qing_800/ qing_800/ C13.fid/ fid
Title	qing_800
Comment	xq-tatanan-B
Origin	Bruker BioSpin GmbH
Owner	nmrsu
Site	
Spectrometer	spect
Author	
Solvent	Acetone
Temperature	298.1
Pulse Sequence	zgpg
Experiment	1D
Number of Scans	2094
Receiver Gain	1820
Relaxation Delay	1.5000
Pulse Width	14.0000
Acquisition Time	0.9999
Acquisition Date	2012-11-14T10:51:30
Modification Date	2012-11-14T12:20:42

tatanan B


6.96
6.83
6.73
6.50
6.29
5.23
3.87
3.86
3.85
3.84
3.79
3.75
3.74
3.71
3.62
3.41
3.40
3.39
3.38
2.84
2.83
2.82
2.81
2.80
2.54
2.53
2.52
2.52
2.51
2.50
2.36
2.35
2.34
2.34
2.34
1.26
1.26
1.15
1.15
1.14
1.13
1.13
1.12
1.12
1.00
0.80
0.78
0.77
0.51
0.50
Parameter Value
Data File Name D:/ chemistry/ zakarian's group/ NMR/ 600/ xq-tatanan-C-600M.fid/ fid
Title xq-tatanan-C-600M
Comment xq-tatanan-C-600M
Origin Varian
Solvent acetone
Temperature 25.0
Pulse Sequence s2pul
Relaxation Delay 4.8000
Pulse Width 0.0000
Acquisition Time 2.5000
Acquisition Date 2012-07-27T11:47:08
Spectrometer Frequency 599.64
Nucleus 1H
tatanan C
1.00
1.01
1.03
1.02
0.98
1.00
3.05
0.81
3.07
3.01
2.95
3.16
5.81
3.07
1.07
1.76
1.12
1.14
1.02
1.21
3.11
3.24
2.99
7.5
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
f1 (ppm)


206.30
181.25
178.86
153.72
153.43
152.82
149.82
149.69
143.74
142.79
124.00
120.76
117.96
117.41
114.85
104.62
99.40
97.65
58.49
57.87
56.92
56.65
56.39
56.23
56.09
55.28
55.06
50.72
49.41
48.34
33.46
30.35
30.30
30.18
30.05
29.92
29.79
29.66
29.53
22.03
19.10
12.46
12.15
Parameter Value
Data File Name D:/ chemistry/ zakarian's group/ NMR/ 600/ xq-tatanan-C-C13.fid/ fid
Title xq-tatanan-C-C13
Comment xq-tatanan-C-C13
Origin Varian
Solvent acetone
Temperature 25.0
Pulse Sequence s2pul
Relaxation Delay 1.0000
Pulse Width 0.0000
Acquisition Time 1.2987
Acquisition Date 2012-07-28T10:20:02
Spectrometer Frequency 150.79
Nucleus 13C
tatanan C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

==== Shimadzu LCsolution Analysis Report ====

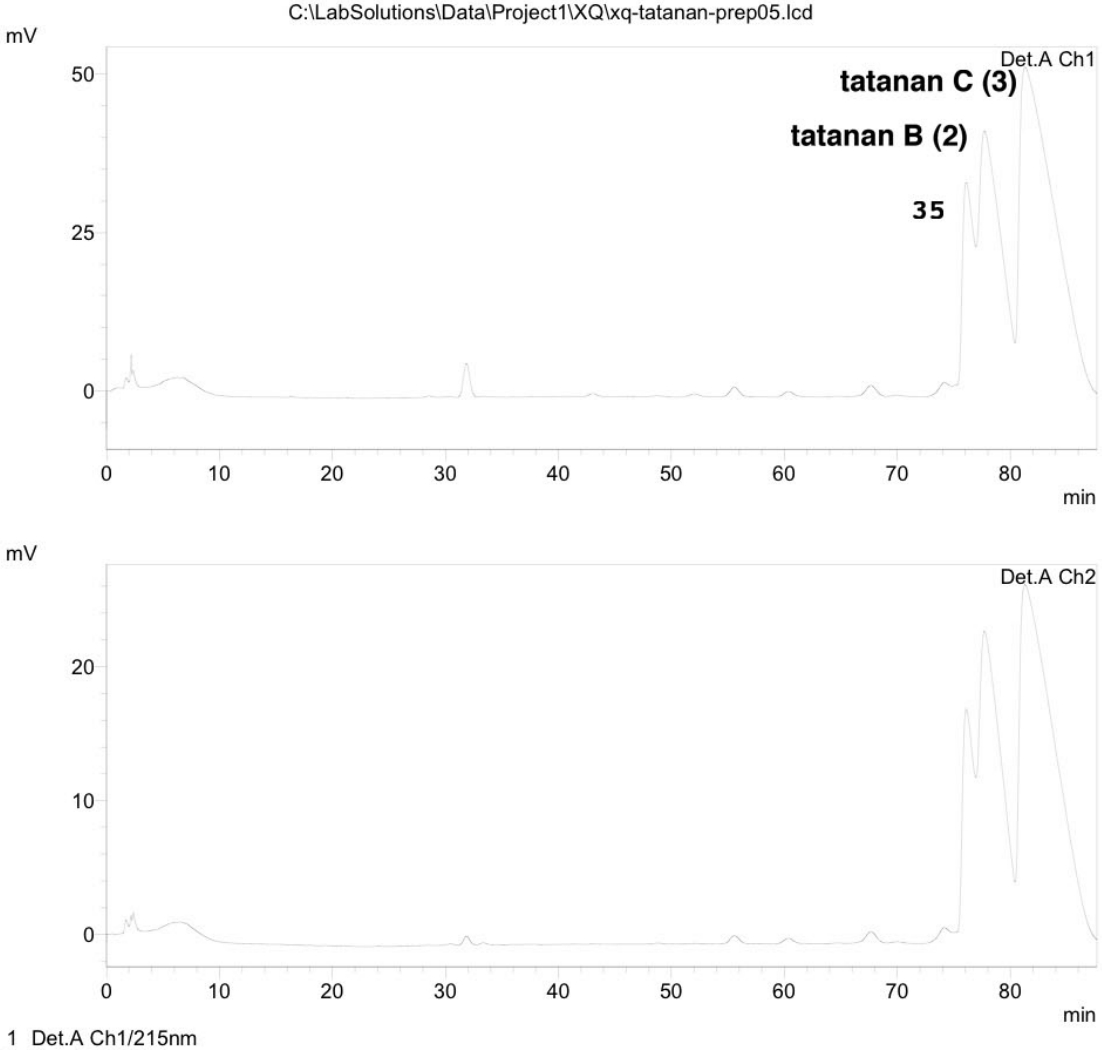
C:\LabSolutions\Data\Project1\XQ\xq-tatanan-prep05.lcd

xq-tatanan-prep
ODS-AM 250mm*20mm
20ml/min 40% CH3CN in H2O
2.5 ml in 50:50 CH3CN/H2O
sampl injection

Acquired by	: Admin
Sample Name	: xq-tatanan-prep
Sample ID	: xq-tatanan-prep
Vail #	:
Injection Volume	: 2.5 uL
Data File Name	: xq-tatanan-prep05.lcd
Method File Name	: ath-YMC-Pack SIL, 250x30 mm, S-10 um, 12 nm.lcm
Batch File Name	:
Report File Name	: Default.lcr
Data Acquired	: 7/25/2012 10:15:04 AM
Data Processed	: 7/25/2012 2:09:21 PM

<Chromatogram>

C:\LabSolutions\Data\Project1\XQ\xq-tatanan-prep05.lcd



1 Det.A Ch1/215nm
2 Det.A Ch2/254nm