Supplementary Information

Secure route to the epoxybicyclo[7.3.0]dodecadienediyne core of kedarcidin chromophore

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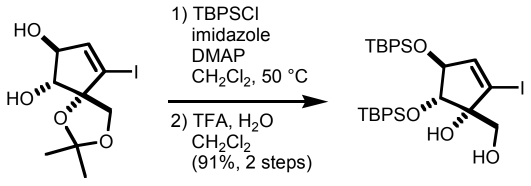
General Methods. All reactions using air- and moisture-sensitive compounds were conducted under an atmosphere of argon. For thin-layer chromatography (TLC) analysis, Merck pre-coated plates (silica gel 60 F254, Art 5715, 0.25 mm) were used. Silica Gel 60N (100–210 μm, Kanto Chemical Co., Inc.) was used for flash column chromatography on silica gel. Melting point (mp) determinations were performed by using a Yanaco MP-S3 micro melting point instruments and are uncorrected. ^{1}H-NMR (400, 500 and 600 MHz) and ^{13}C-NMR (100, 125 and 150 MHz) spectra were measured on a Varian INOVA 400-MR, a Varian INOVA 500 and a JEOL ECA-600 spectrometers. Chemical shifts are expressed in ppm relative to tetramethylsilane. Infrared (IR) spectra were recorded on a PERKIN ELMER Spectrum BX FT-IR System spectrometer. Optical rotations ($[\alpha]_D$) were measured on a JASCO DIP-370 polarimeter. MALDI-TOF MS spectra were measured on an Applied Biosystems Voyager DE STR SI-3 instrument. ESI-TOF MS spectra were measured on a BRUKER DALTONICS APEX III (HRMS).

All compounds given below bear the same formula numbers as used in the main text. Compounds unlabeled in the main text are labeled with letters [**A** and **B**]. The carbon numbers of intermediates are labeled according to those of the natural kedarcidin chromophore (**1**).[1]

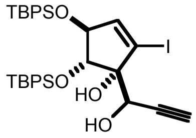


A[2] **2**

t-Butyldiphenylsilyl Ether 2

To a solution of **A**[2] (674.0 mg, 2.16 mmol), DMAP (106.0 mg, 0.86 mmol) and imidazole (1.47 g, 21.6 mmol) in dry CH_2Cl_2 (72.0 mL) was added TBPSCl (2.81 mL, 10.8 mmol) at 0 °C. The mixture was warm to 50 °C and stirred for 48 h. The reaction mixture was diluted with CH_2Cl_2 and filtered through a pad of Celite. The organic layer was concentrated to afford crude product which was directly used in the next reaction.

To a solution of the crude mixture in CH_2Cl_2 (4.7 mL) were added H_2O (57.0 μL, 3.14 mmol) and trifluoroacetic acid (0.47 mL) at 0 °C. After 15 min, the reaction was quenched by the addition of sat. aq. $NaHCO_3$ and the mixture was extracted with EtOAc. The combined organic extracts was dried over $MgSO_4$ and concentrated *in vacuo*. The crude mixture was purified by flash column chromatography on silica gel (hexane/EtOAc = 20/1–5/1) to afford **2** (107.3 mg, 0.143 mmol, 91% for 2 steps) as a colorless amorphous; R_f = 0.38 (hexane/EtOAc = 5/1); $[\alpha]_D^{26}$ +53.9 (*c* 0.72, $CHCl_3$); FT-IR (film) ν 3512, 2931, 2858, 1734, 1427, 1111, 1072, 702, 507 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.88 (9H, s, TBPS), 1.00 (9H, s, TBPS), 2.11 (1H, dd, *J* = 12.0, 3.0 Hz, C8-OH), 3.48 (1H, s, C9-OH), 3.58 (1H, dd, *J* = 12.0, 12.0 Hz, H8), 3.71 (1H, dd, *J* = 12.0, 3.0 Hz, H8), 4.36 (1H, s, H10), 4.42 (1H, d, *J* = 3.0 Hz, H11), 5.92 (1H, d, *J* = 3.0 Hz, H12), 7.40 (12H, m, TBPS), 7.73 (8H, m, TBPS); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.1, 19.5, 26.8, 27.1, 65.5, 78.1, 82.1, 85.0, 110.9, 127.75, 127.80, 127.9, 128.1, 129.95, 129.97, 130.2, 130.3, 132.1, 132.6, 133.3, 135.76, 135.79, 135.9, 136.0, 142.1; HRMS (MALDI), calcd for $C_{38}H_{45}INaO_4Si_2^+$ 771.1793 ($M+Na^+$), found 771.1771.

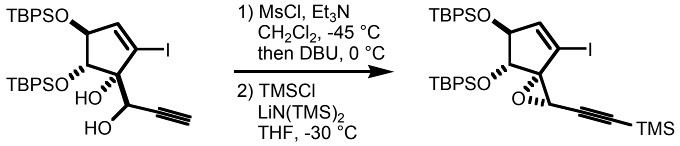


3

Alkyne 3

The diol **2** was dissolved in a mixed solvent of DMSO (20.3 mL) and CH_2Cl_2 (57.7 mL). Et_3N (7.32 mL, 52.5 mmol) and SO_3·pyridine (4.17 g, 26.3 mmol) was added portionwise at room temperature. After stirring for 5 h, the mixture was diluted with Et_2O and the reaction was quenched by the addition of water. The mixture was successively washed with water and brine. The combined organic extracts was dried over $MgSO_4$ and concentrated *in vacuo* to afford crude aldehyde (1.31 g, 100%). This aldehyde was used in the next reaction without further purification.

A solution of aldehyde (0.250 g, 0.335 mmol) in CH_2Cl_2 (34.0 mL) was cooled to –78 °C. To this solution was added dropwise a THF solution of ethynylmagnesium bromide (0.5 M, 13.4 mL, 6.70 mmol). After the mixture was warmed to 0 °C over a period of 1 h, sat. aq. NH_4Cl was added at 0 °C. The mixture was exacted by the EtOAc and combined organic extracts was dried over $MgSO_4$ and concentrated *in vacuo*. The crude mixture was purified by column chromatography on silica gel (hexane/EtOAc 1/0–20/1) to afford **3** (160.0 mg, 0.207 mmol, 62% for 2 steps, colorless oil) and the recovered starting material **2** (114.6 mg, 0.153 mmol, 38%); $R_f = 0.50$ (hexane/EtOAc = 3/1); $[\alpha]_D^{21}$ +53.0 (*c* 0.72, $CHCl_3$); FT-IR (film) ν 3467, 3307, 2931, 2858, 1427, 1111, 703, 506 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.80 (9H, s, TBPS), 1.03 (9H, s, TBPS), 2.31 (1H, d, *J* = 5.0 Hz, C8-OH), 2.39 (1H, d, *J* = 2.0 Hz, H6), 3.85 (1H, s, C9-OH), 4.58 (1H, d, *J* = 2.0 Hz, H11), 4.61 (1H, dd, *J* = 5.0, 2.0 Hz, H8), 4.64 (1H, s, H10), 5.93 (1H, d, *J* = 2.0 Hz, H12), 7.26-7.71 (20H, m, TBPS); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.1, 19.5, 26.7, 27.1, 68.4, 75.7, 79.0, 80.6, 83.5, 84.6, 105.3, 127.6, 127.87, 127.93, 128.1, 129.8, 130.0, 130.2, 130.4, 131.8, 132.6, 132.8, 133.6, 135.8, 135.96, 135.98, 136.3, 143.9; HRMS (MALDI), calcd for $C_{40}H_{45}INaO_4Si_2^+$ 795.1793 ($M+Na^+$), found 795.1731.



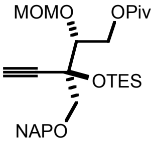
3 **4**

TMS-protected Alkyne 4

To a solution of **3** (0.97 g, 1.26 mmol) and Et_3N (3.5 mL, 25.1 mmol) in dry CH_2Cl_2 (126.0 mL) was added MsCl (0.975 mL, 12.6 mmol) at –45 °C. After stirring for 2 h, DBU (7.5 mL, 50.4 mmol) was added the mixture. After stirring for 1 h at 0 °C, the reaction was quenched by the addition of sat. aq. NH_4Cl and the mixture was extracted with EtOAc. The combined organic extracts was dried over $MgSO_4$ and concentrated *in vacuo*. The crude mixture was purified by flash column chromatography on silica gel (hexane/EtOAc 1/0–20/1) to afford propargylic oxirane (682.5 mg, 0.904 mmol, 72%) as a colorless oil.

To a solution of propargylic oxirane (686.4 mg, 0.909 mmol) and LiN(TMS)$_2$ (1.54 mL, 8.18 mmol) in THF (18.2 mL) was added TMSCl (1.54 mL, 8.18 mmol) at –68 °C. After stirring at –68 °C for 20 min, the reaction was quenched by the addition of sat. aq. NH$_4$Cl and the mixture was extracted with Et$_2$O. The combined organic extracts was dried over MgSO$_4$ and concentrated *in vacuo*. The crude mixture was purified by flash column chromatography on silica gel (hexane/EtOAc 1/0–50/1) to afford **4** (719.6 mg, 0.870 mmol, 96%) as a colorless amorphous.

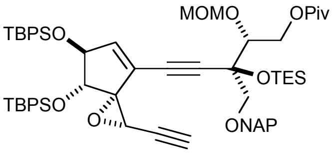
4: R_f = 0.69 (hexane/EtOAc = 5/1); $[\alpha]_D^{22}$ +88.2 (*c* 1.59, CHCl$_3$); FT-IR (film) ν 3071, 2959, 2932, 2858, 1427, 1112, 844, 703, 611 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.19 (9H, s, TMS), 0.95 (9H, s, TBPS), 0.97 (9H, s, TBPD), 3.02 (1H, s, H8), 3.83 (1H, s, H10), 4.61 (1H, d, *J* = 3.0 Hz, H11), 6.36 (1H, d, *J* = 3.0 Hz, H12), 7.36 (12H, m, TBPS), 7.55 (8H, m, TBPD); ^{13}C NMR (100 MHz, CDCl$_3$) δ –0.3, 19.2, 19.3, 26.7, 26.9, 49.6, 73.9, 78.2, 82.4, 95.9, 98.3, 101.1, 127.6, 127.7, 127.8, 127.9, 129.79, 129.83, 129.9, 130.0, 133.1, 133.2, 133.5, 133.7, 135.7, 135.8, 135.9, 136.0, 136.3, 147.4; HRMS (MALDI), cal for $C_{43}H_{51}INaO_3Si_3^+$ 849.2083 (M+Na$^+$), found 849.2079.



5

Alkyne 5

5: R_f = 0.57 (hexane/EtOAc = 3/1); $[\alpha]_D^{21}$ +31.0 (*c* 1.10, CHCl$_3$); FT-IR (film) ν 2957, 2876, 1729, 1155, 1032, 745 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.72 (6H, t, *J* = 7.5 Hz, TES), 0.95 (9H, q, *J* = 7.5 Hz, TES), 1.20 (9H, s, Piv), 2.56 (1H, s, H2), 3.40 (3H, s, MOM), 3.63 (1H, d, *J* = 10.0 Hz, H5), 3.71 (1H, d, *J* = 10.0 Hz, H5), 4.00 (1H, dd, *J* = 7.5, 2.5 Hz, H13), 4.21 (1H, dd, *J* = 11.5, 7.5 Hz, H14), 4.63 (1H, dd, *J* = 11.5, 2.5 Hz, H14), 4.78 (1H, d, *J* = 6.0 Hz, NAP), 4.79 (2H, s, MOM), 4.84 (1H, d, *J* = 6.0 Hz, NAP), 7.47 (3H, m, NAP), 7.82 (4H, m, NAP); ^{13}C NMR (125 MHz, CDCl$_3$) δ 6.2, 7.1, 27.3, 38.8, 56.3, 65.8, 73.6, 73.9, 74.0, 75.5, 80.4, 84.1, 97.9, 125.9, 126.0, 126.2, 126.5, 127.8, 128.0, 128.2, 133.1, 133.4, 135.7, 178.5; HRMS (MALDI), cal for $C_{30}H_{44}NaO_6Si^+$ 551.2799 (M+Na$^+$), found 551.2814.

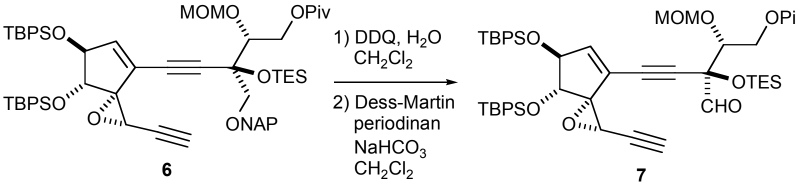


6

2-Naphthylmethyl (NAP) Ether 6

To a solution of **4** (22.3 mg, 0.0270 mmol) and **5** (15.7 mg, 0.0297 mol) in dry DMF (27.8 mL) was added *i*-Pr_2NEt (47.0 μL, 0.270 mmol). The solution was degassed by freeze-pump-thaw cycles (three times). To the solution was added CuI (5.1 mg, 0.0270 mmol) and $Pd_2(dba)_3 \cdot CHCl_3$ (7.0 mg, 6.75 μmol) under N_2 stream. After the mixture was stirred at room temperature for 2 h in the dark. The mixture was diluted with Et_2O and sat. aq. NH_4Cl was added at 0 °C. The mixture was stirred vigorously at room temperature for 1 h umtil the color of the aqueous phase turned into dark blue. After extraction with Et_2O, the combined organic extracts was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo* to afford the coupling product which was directly used in the next reaction.

To a solution of the coupling product (25.8 mg, 0.0210mmol) in MeOH (1.0 mL) was added K_2CO_3 (2.4 mg, 0.0174 mmol) at room temperature. After stirring for 2 h, the reaction mixture was diluted with EtOAc and the reaction was quenched with sat. aq. NH_4Cl. The mixture was then extracted with EtOAc. The combined organic extracts was dried over $MgSO_4$ and concentrated *in vacuo*. The crude mixture was purified by flash column chromatography on silica gel (hexane/EtOAc 50/1–20/1) to afford **6** (17.5 mg, 0.0151 mmol, 72% for 2 steps) as a colorless oil; R_f = 0.55 (hexane/EtOAc = 5/1); $[\alpha]_D^{25}$ +92.4 (*c* 1.26, $CHCl_3$); FT-IR (film) ν 3287, 2957, 1728, 1158, 1111, 741, 703 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.69 (6H, q, *J* = 8.0 Hz, TES), 0.90 (9H, s, TBPS), 0.93 (9H, t, *J* = 8.0 Hz, TES), 0.99 (9H, s, TBPS), 1.02 (9H, s, Piv), 2.38 (1H, d, *J* = 1.5 Hz, H6), 3.10 (1H, d, *J* = 1.5 Hz, H8), 3.38 (3H, s, MOM), 3.66 (1H, d, *J* = 9.0 Hz, H5), 3.68 (1H, d, *J* = 9.0 Hz, H5), 3.94 (1H, s, H10), 4.02 (1H, dd, *J* = 8.0, 1.5 Hz, H13), 4.29 (1H, dd, *J* = 12.0, 8.0 Hz, H14), 4.64 (1H, dd, *J* = 12.0, 1.5 Hz, H14), 4.67 (1H d, *J* = 3.0 Hz, H11), 4.76 (2H, s, MOM or NAP), 4.76 (1H, d, *J* = 6.5 Hz, MOM or NAP), 4.85 (1H, d, *J* = 6.5 Hz, MOM or NAP), 6.09 (1H, d, *J* = 3.0 Hz, H12), 7.24-7.78 (17H, m, NAP, TBPS); ^{13}C NMR (125 MHz, $CDCl_3$) δ 6.1, 7.1, 19.2, 19.5, 26.8, 27.0, 27.3, 38.8, 48.8, 56.3, 60.5, 66.4, 73.0, 73.6, 73.8, 73.9, 74.0, 76.3, 78.0, 79.6, 80.3, 96.2, 97.9, 125.8, 125.9, 126.08, 126.14, 126.3, 127.4, 127.58, 127.62, 127.7, 127.8, 127.9, 128.0, 128.08, 128.13, 129.5, 129.78, 129.82, 129.9, 133.06, 133.08, 133.2, 133.4, 133.6, 133.7, 135.6, 135.7, 135.8, 135.86, 135.88, 136.0, 136.1, 136.5, 143.7, 178.4; HRMS (MALDI), calcd for $C_{70}H_{85}NaO_9Si_3^+$ 1177.5472 ($M+Na^+$), found 1177.5441.



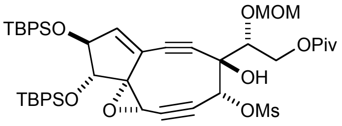
Aldehyde 7

To a solution of **6** (602.4 mg, 0.521 mmol) in H_2O (2.0 mL) and CH_2Cl_2 (10.0 mL) was added DDQ (236.5 mg, 1.04 mmol) at room temperature. After stirring for 2 h, the reaction was quenched by the addition of sat. aq. $NaHCO_3$ and the mixture was extracted with Et_2O. The combined organic extracts was dried over $MgSO_4$ and concentrated *in vacuo*. The crude mixture was purified by flash column chromatography on silica gel (hexane/EtOAc 20/1–5/1) to afford alcohol(475.4 mg, 0.468 mmol, 90%) as a colorless oil.

To a solution of alcohol (475.4 mg, 0.468 mmol) and $NaHCO_3$ (235.9 mg, 2.81 mmol) in CH_2Cl_2 (31.2 mL) was added Dess-Martin periodinane (397.0 mg, 0.936 mmol). After stirring at room temperature for 2 h, the reaction mixture was diluted with Et_2O and sat. aq. $NaHCO_3$ and sat. aq. $Na_2S_2O_3$ were successively added to the mixture. After stirring for 0.5 h, the mixture was washed with sat. aq. $NaHCO_3$. The aqueous layer was extracted with Et_2O and the extracts were combined. The combined organic extracts was dried over $MgSO_4$ and concentrated *in vacuo*. The crude mixture was purified by flash column chromatography on silica gel (hexane/EtOAc = 1/0–10/1) to afford **7** (445.6 mg, 0.440 mmol, 94%) as a colorless amorphous.

7: $R_f = 0.60$ (hexane/EtOAc = 5/1); $[\alpha]_D^{25}$ +50.5 (*c* 1.31, CH_2Cl_2); FT-IR (film) ν 2957, 1737, 1152, 1112, 740, 703 cm^{-1}; ^1H NMR (600 MHz, C_6D_6) δ 0.87 (6H, q, $J = 7.8$ Hz, TES), 0.99 (9H, s, Piv), 1.10 (9H, t, $J = 7.8$ Hz, TES), 1.11 (9H, s, TBPS), 1.14 (9H, s, TBPS), 2.47 (1H, d, $J = 1.8$ Hz, H6), 3.09 (1H, d, $J = 1.8$ Hz, H8), 3.20 (3H, s, MOM), 4.15 (1H, s, H10), 4.19 (1H, dd, $J = 5.1$, 2.9 Hz, H13), 4.43 (1H, dd, $J = 11.9$, 5.1 Hz, H14), 4.67 (2H, s, MOM), 4.71 (1H, dd, $J = 11.9$, 2.9 Hz, H14), 4.88 (1H, d, $J = 2.9$ Hz, H11), 6.18 (1H, d, $J = 2.9$ Hz, H12), 7.21 (12H, m, TBPS), 7.62 (8H, m, TBPS), 9.69 (1H, s, H5); ^{13}C NMR (150 MHz, C_6D_6) δ 6.5 (3C, TES), 7.3 (3C, TES), 19.3 (TBPS), 19.6 (TBPS), 26.9 (3C, TBPS), 27.1 (3C, TBPS), 27.2 (3C, Piv), 38.8 (Piv), 49.2 (C8), 56.0 (MOM), 63.6 (C14), 73.6 (C9), 76.9 (C6), 78.2 (C7), 78.3 (C3), 79.9 (C10), 80.4 (C13), 80.9 (C11), 84.2 (C2), 92.0 (C4),

97.4 (MOM), 127.8 (C1), 130.0 (TBPS), 130.1 (TBPS), 130.2 (TBPS), 133.3 (TBPS), 133.4 (TBPS), 133.8 (TBPS), 134.0 (TBPS), 135.9 (TBPS), 136.0 (TBPS), 136.1 (TBPS), 136.4 (TBPS), 144.3 (C12), 177.6 (Piv), 193.6 (C5); HRMS (MALDI), calcd for $C_{59}H_{76}NaO_9Si_3^+$ 1035.4689 (M+Na$^+$), found 1035.4669.



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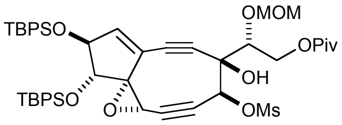


12

Nine-Membered Diyne 10 and 12

Anhydrous $CeCl_3$ (947.9 mg, 3.84 mmol, purchased from Aldrich) was dried under vacuum at 90 °C. Under the above conditions, particles of $CeCl_3$ was ground with vigorous stirring using a magnetic stirrer bar for 2h. After the introduction of N_2 into the flask, the flask was cooled to 0 °C. Freshly distilled THF (32.5 mL) was then added to the flask in one portion. The resulting suspension was stirred vigorously at room temperature for 19 h. To a separate solution of HN(TMS)$_2$ (608 μL, 2.88 mmol) in THF (19.5 mL) was added *n*-BuLi (1.57 M in hexane, 1.83 mL, 2.88 mmol) dropwise at 0 °C over 2 min. The resulting solution of LiN(TMS)$_2$ was stirred at 0 °C for 0.5 h. The suspension of $CeCl_3$ was added in one portion at –45 °C via cannula over 2 min. The mixture was allowed to warm to –25 °C over a period of 1 h with vigorous stirring. To the suspension of $CeCl_3$ and LiN(TMS)$_2$ was added a solution of **7** (95.3 mg, 0.0940 mmol) in THF (13.0 ml) at –25 °C via cannula. After stirring at –25 °C for 2.0 h, the reaction was quenched with aqueous phosphate buffer (pH 7.0) and the mixture was diluted with EtOAc. The precipitate was filtered through a pad of Celite and washed with EtOAc. The combined organic extracts was washed with brine, and dried over $MgSO_4$. After concentration, the crude product was purified by column chromatography on silica gel (hexane/EtOAc = 1/0–5/1) to give a 4:1 mixture of **8** and **9** (55.6 mg, 0.0549 mmol, 53%, combined yield).

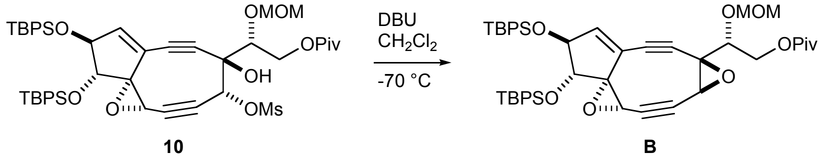
To a solution of the mixture of **8** and **9** (43.4 mg, 0.0428 mmol) in THF (7.1 mL) was added TBAF (1.0 M in THF, 85.6 μL) at –78 °C. After stirring at –78 °C for 15 min, sat. aq. NH_4Cl was added and the mixture was diluted with EtOAc. After the mixture was extracted with EtOAc, the combined organic exacts was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel to afford diol (38.5 mg, 0.0428 mmol) as a mixture of diastereomers.

To a solution of diol (37.4 mg, 0.0416 mmol) and pyridine (20 μL, 0.250 mmol) in

CH_2Cl_2 (5.0 mL) was added Ms_2O (22.4 mg, 0.125 mmol) at 0 °C. After stirring for 1 h, the reaction was quenched by adding with sat. aq. $NaHCO_3$. The mixture was diluted and extracted with Et_2O. The combined organic extracts was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 6/1–3/1) to afford **10** (28.9 mg, 0.0296 mmol, 71% for 2 steps) and **12** (10.3 mg, 0.0105 mmol, 25% for 2 steps) as a colorless oil, respectively.

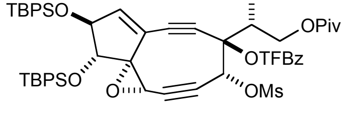
10: R_f = 0.40 (hexane/EtOAc = 2/1); $[\alpha]_D^{26}$ +83.5 (*c* 1.00, CH_2Cl_2); FT-IR (film) ν 3341, 2934, 2859, 1734, 1370, 1157, 1110, 1075, 825, 704 cm^{-1}; ^1H NMR (600 MHz, C_6D_6) δ 1.00 (9H, s, Piv), 1.08 (9H, s, TBPS), 1.15 (9H, s, TBPS), 2.50 (3H, s, Ms), 2.68 (1H, s, H8), 2.87 (3H, s, MOM), 4.07 (1H, dd, *J* = 8.5, 3.2 Hz, H13), 4.27 (1H, d, *J* = 6.8 Hz, MOM), 4.33 (1H, d, *J* = 6.8 Hz, MOM), 4.45 (1H, dd, *J* = 12.1, 8.5 Hz, H14), 4.49 (1H, d, *J* = 2.4 Hz, H10), 4.90 (1H, dd, *J* = 12.1, 3.2 Hz, H14), 4.91 (1H, s, C4-OH), 5.21 (1H, dd, *J* = 2.4, 2.4 Hz, H11), 5.70 (1H, s, H5), 5.93 (1H, d, *J* = 2.4 Hz, H12), 7.15-7.21 (12H, m, TBPS), 7.56-7.82 (8H, m, TBPS); ^{13}C NMR (150 MHz, C_6D_6) δ 19.3 (TBPS), 19.7 (TBPS), 26.9 (3C, Piv), 27.2 (6C, TBPS), 38.3 (Ms), 38.7 (Piv), 47.9 (C8), 55.8 (MOM), 64.1 (C14), 70.8 (C9), 77.8 (C5), 78.7 (C10), 79.2 (C4), 82.8 (C11), 83.5 (C13), 83.7 (C6), 86.1 (C2), 93.7 (C7), 98.5 (C3), 98.9 (MOM), 123.5 (C1), 128.5 (TBPS), 130.2 (TBPS), 130.3 (TBPS), 133.3 (TBPS), 133.4 (TBPS), 133.6 (TBPS), 134.1 (TBPS), 135.9 (TBPS), 136.3 (TBPS), 136.4 (TBPS), 142.0 (C12), 177.3 (Piv); HRMS (ESI), calcd for $C_{54}H_{64}NaO_{11}SSi_2^+$ 999.3600 ($M+Na^+$), found 999.3595.

12: R_f = 0.34 (hexane/EtOAc = 2/1); $[\alpha]_D^{26}$ +132.0 (*c* 1.28, CH_2Cl_2); FT-IR (film) ν 3437, 2960, 2859, 1731, 1367, 1179, 1157, 1111, 1023, 704 cm^{-1}; ^1H NMR (600 MHz, C_6D_6) δ1.01 (9H, s, Piv), 1.07 (9H, s, TBPS), 1.14 (9H, s, TBPS), 2.33 (1H, s, C4-OH), 2.35 (3H, s, Ms), 2.54 (1H, s, H8), 3.13 (3H, s, MOM), 3.96 (1H, dd, *J* = 6.1, 3.6 Hz, H13), 4.32 (1H, d, *J* = 6.8 Hz, MOM), 4.44 (1H, dd, *J* = 11.9, 6.1 Hz, H14), 4.49 (1H, d, *J* = 6.8 Hz, MOM), 4.50 (1H, d, *J* = 2.4 Hz, H10), 4.57 (1H, dd, *J* = 11.9, 3.6 Hz, H14), 5.17 (1H, dd, *J* = 2.4, 2.4 Hz, H11), 5.66 (1H, s, H5), 5.92 (1H, d, *J* = 2.4 Hz, H12), 7.15-7.20 (12H, m, TBPS), 7.57-7.82 (8H, m, TBPS); ^{13}C NMR (150 MHz, C_6D_6) δ 19.3 (TBPS), 19.7 (TBPS), 27.0 (3C, PIv), 27.2 (6C, TBPS), 38.2 (Ms), 38.7 (Piv), 48.0 (C8), 56.5 (MOM), 64.5 (C14), 74.1 (C9), 76.1 (C5), 78.4 (C13), 78.6 (C10), 79.9 (C4), 83.3 (C11), 84.3 (C6), 87.0 (C2), 93.1 (C7), 96.3 (C3), 97.5 (MOM), 123.6 (C1), 128.5 (TBPS), 130.2 (TBPS), 130.3 (TBPS), 130.4 (TBPS), 133.2 (TBPS), 133.5 (TBPS), 133.7 (TBPS), 133.9 (TBPS), 136.00 (TBPS), 136.03 (TBPS), 136.3 (TBPS), 136.4 (TBPS), 142.0 (C12), 177.4 (Piv); HRMS (ESI), calcd for $C_{54}H_{64}NaO_{11}SSi_2^+$ 999.3600 (M+Na$^+$), found 999.3594.



Diepoxide B

To a solution of **10** (18.5 mg, 0.0189 mmol) in CH_2Cl_2 (5.0 mL) was added DBU (22.7 μL, 0.189 mmol) at –70 °C. After stirring for 0.5 h, the reaction mixture was diluted with Et_2O and sat. aq. NH_4Cl was added. The mixture was then extracted with Et_2O. The combined organic extracts was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 20/1–5/1) to afford **B** (12.9 mg, 0.0146 mmol, 77%) as a colorless amorphous; R_f = 0.72 (hexane/EtOAc = 2/1); $[\alpha]_D^{25}$ +139.1 (*c* 1.29, $CHCl_3$); FT-IR (film) ν 2959, 2933, 2895, 2858, 1736, 1242, 1154, 1110, 1038, 704 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) δ 1.00 (9H, s, Piv), 1.14 (9H, s, TBPS), 1.15 (9H, s, TBPS), 2.69 (1H, s, H8), 3.02 (3H, s, MOM), 3.10 (1H, s, H5), 3.52 (1H, t, *J* = 6.5 Hz, H13), 4.18 (2H, d, *J* = 6.5 Hz, H14), 4.29 (1H, d, *J* = 6.5 Hz, MOM), 4.51 (1H, d, *J* = 6.5 Hz, MOM), 4.55 (1H, d, *J* = 3.5 Hz, H10), 5.23 (1H, dd, *J* = 3.5, 2.0 Hz, H11), 5.93 (1H, d, *J* = 2.0 Hz, H12),7.12-7.21 (12H, m, TBPS), 7.53-7.75 (8H, m, TBPS); ^{13}C NMR (125 MHz, C_6D_6) δ 19.3, 19.8, 27.1, 27.3, 27.4, 38.8, 47.0, 51.6, 55.5, 63.58, 63.62, 72.5, 74.7, 78.8, 82.8, 83.6, 85.8, 89.0, 96.1, 123.4, 128.2, 128.3, 130.2, 130.30, 130.35, 130.4, 133.2, 133.6, 133.8, 134.1, 136.0, 136.1, 136.4, 136.5, 144.0, 177.3; HRMS (ESI), calcd for $C_{62}H_{67}F_3NaO_{12}Si_2^+$ 903.3719 (M+Na$^+$), found 903.3713.

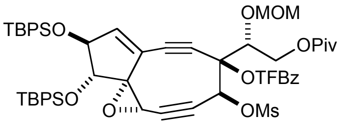


11

p-Trifluoromethylbenzoate 11

To a solution of **10** (28.9 mg, 0.0296 mmol) and *p*-trifluoromethylbenzoyl chloride (22.0 μL, 0.148 mmol) in CH_2Cl_2 (5.0 mL) was added DMAP (36.2 mg, 0.296 mmol) at 0 °C. After stirring for 0.5 h, the reaction mixture was diluted with Et_2O and sat. aq. $NaHCO_3$ was added. The mixture was then extracted with Et_2O. The combined organic extracts was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 20/1–5/1) to afford **11** (28.1

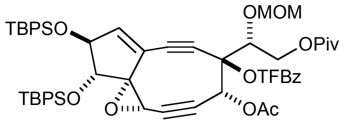
mg, 0.0244 mmol, 83%) as a colorless oil; R_f = 0.26 (hexane/EtOAc = 5/1); $[\alpha]_D^{24}$ +109.1 (*c* 2.05, CH_2Cl_2); FT-IR (film) ν 2934, 2859, 1735, 1372, 1267, 1111, 1041, 956, 824, 704 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.91 (9H, s, Piv), 1.04 (9H, s, TBPS), 1.20 (9H, s, TBPS), 2.79 (1H, s, H8), 3.14 (3H, s, Ms), 3.28 (3H, s, MOM), 4.05 (1H, dd, *J* = 12.0, 8.0 Hz, H14), 4.36 (1H, d, *J* = 4.0 Hz, H10), 4.37 (1H, dd, *J* = 8.0, 2.5 Hz, H13), 4.76 (1H, dd, *J* = 12.0, 2.5 Hz, H14), 4.77 (1H, d, *J* = 7.0 Hz, MOM), 4.81 (1H, d, *J* = 7.0 Hz, MOM), 5.13 (1H, dd, *J* = 4.0, 2.5 Hz, H11), 5.94 (1H, d, *J* = 2.5 Hz, H12), 6.09 (1H, s, H5), 7.31-7.72 (22H, m, TBPS, TFBz), 8.15 (2H, d, *J* = 8.5 Hz, TFBz); ^1H NMR (500 MHz, C_6D_6) δ 1.03 (9H, s, TBPS), 1.13 (9H, s, Piv), 1.16 (9H, s, TBPS), 2.29 (3H, s, Ms), 2.68 (1H, s, H8), 3.15 (3H, s, MOM), 4.56 (1H, dd, *J* = 12.5, 7.0 Hz, H14), 4.56 (1H, d, *J* = 2.0 Hz, H10), 4.74 (1H, dd, *J* = 7.0, 2.5 Hz, H13), 4.81 (1H, d, *J* = 6.5 Hz, MOM), 4.85 (1H, d, *J* = 6.5 Hz, MOM), 5.22 (1H, dd, *J* = 2.0, 2.0 Hz, H11), 5.25 (1H, dd, *J* = 12.5, 2.5 Hz, H14), 5.95 (1H, d, *J* = 2.0 Hz, H12), 6.50 (1H, s, H5), 7.20-7.99 (24H, m, TBPS, TFBz); ^{13}C NMR (125 MHz, C_6D_6) δ 19.4, 19.8, 27.1, 27.3, 38.0, 38.8, 48.0, 56.1, 65.0, 70.4, 74.6, 78.7, 80.3, 82.6, 82.9, 84.2, 90.2, 94.7, 94.7, 98.9, 122.9, 124.3 (q, CF_3), 125.6, 125.6, 128.1, 128.3, 130.3, 130.39, 130.42, 130.7, 132.9, 133.2, 133.56, 133.64, 134.0, 134.8 (q, $\underline{C}$-CF_3), 136.08, 136.12, 136.4, 136.5, 142.6, 163.9, 177.6; HRMS (ESI), calcd for $C_{62}H_{67}F_3NaO_{12}Si_2^+$ 1171.3736 (M+Na^+), found 1171.3729.



13

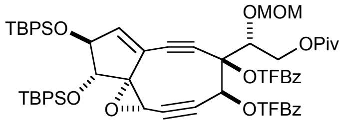
p-Trifluoromethylbenzoate 13

To a solution of **12** (10.3 mg, 0.0105 mmol) and *p*-trifluoromethylbenzoyl chloride (15.6 μL, 0.105 mmol) in CH_2Cl_2 (5.0 mL) was added DMAP (25.7 mg, 0.210 mmol) at 0 °C. After stirring for 2 h, the reaction mixture was diluted with Et_2O and sat. aq. $NaHCO_3$ was added. The mixture was then extracted with Et_2O. The combined organic extracts was dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 10/1–7/1) to afford **13** (8.9 mg, 0.00774 mmol, 74%) as a colorless oil; R_f = 0.26 (hexane/EtOAc = 5/1); $[\alpha]_D^{23}$ +153.0 (*c* 1.14, CH_2Cl_2); FT-IR (film) ν 2960, 2934, 2859, 1738, 1372, 1326, 1266, 1135, 1111, 704 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 0.99 (9H, s, Piv), 1.08 (9H, s, TBPS), 1.15 (9H, s, TBPS), 2.22 (3H, s, Ms), 2.73 (1H, d, *J* = 1.0 Hz, H8), 3.24 (3H, s, MOM), 4.51 (1H, dd, *J* = 11.5, 6.5 Hz, H14), 4.55 (1H, d, *J* = 2.5 Hz, H10), 4.57 (1H, dd, *J* = 6.5, 2.5 Hz, H13), 4.58 (1H, d, *J* = 6.5 Hz, MOM), 4.69 (1H, d, *J* = 6.5 Hz, MOM), 4.86 (1H, dd, *J* = 11.5, 2.5 Hz, H14), 5.15 (1H, dd, *J* = 2.5, 2.5 Hz, H11), 6.00 (1H, d, *J* = 2.5 Hz, H12), 6.21 (1H, d, *J* = 1.0 Hz, H5), 7.21 (12H, m, TBPS), 7.63 (8H, m, TBPS), 7.90 (4H, m, TFBz); ^{13}C NMR (125 MHz, C_6D_6) δ 19.3, 19.8, 27.1, 27.2, 27.3, 38.4, 38.8, 47.9, 56.5, 64.9, 74.4, 74.5, 78.8, 79.3, 82.0, 83.0, 83.3, 90.5, 93.7, 94.0, 98.3, 123.1, 123.8 (q, CF_3), 125.61, 125.64, 128.2, 128.4, 130.25, 130.33, 130.36, 130.41, 130.8, 132.9, 133.1, 133.59, 133.63, 133.9, 134.6 (q, $\underline{\text{C}}$-CF_3), 136.1, 136.4, 136.5, 143.1, 163.2, 177.4; HRMS (ESI), calcd for $C_{62}H_{67}F_3NaO_{12}Si_2^+$ 1171.3736 (M+Na$^+$), found 1171.3725.



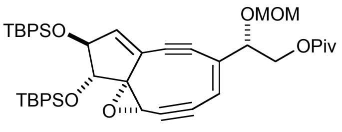
14

14: *R*$_f$ = 0.40 (hexane/EtOAc = 5/1); $[\alpha]_D^{33}$ +130.2 (*c* 0.59, $CHCl_3$); FT-IR (film) ν 2959, 2932, 2858, 1737, 1325, 1268, 1137, 1111, 1043, 704 cm^{-1}; ^{1}H NMR (600 MHz, C_6D_6) δ 1.03 (9H, s, Piv), 1.14 (9H, s, TBPS), 1.14 (9H, s, TBPS), 1.63 (3H, s, Ac), 2.60 (1H, s, H8), 3.12 (3H, s, MOM), 4.51 (1H, d, *J* = 2.2 Hz, H10), 4.57 (1H, dd, *J* = 11.9, 8.4 Hz, H14), 4.70 (1H, dd, *J* = 8.4, 2.4 Hz, H13), 4.81 (1H, d, *J* = 6.8 Hz, MOM), 4.84 (1H, d, *J* = 6.8 Hz, MOM), 5.21 (1H, dd, *J* = 2.2, 2.2 Hz, H11), 5.23 (1H, dd, *J* = 11.9, 2.4 Hz, H14), 5.93 (1H, d, *J* = 2.2 Hz, H12), 6.96 (1H, s, H5), 7.13-7.23 (14H, m, TBPS, TFBz), 7.61-7.92 (10H, m, TBPS, TFBz); ^{13}C NMR (150 MHz, C_6D_6) δ 19.3, 19.7, 19.9, 27.0, 27.3, 38.8, 48.1, 56.1, 65.3, 68.9, 70.4, 78.6, 80.4, 82.9, 84.3, 85.0, 90.0, 91.9, 95.2, 98.8, 123.4, 124.2 (q, CF_3), 125.47, 125.49, 128.4, 128.6, 130.2, 130.26, 130.30, 130.5, 133.2, 133.3, 133.6, 133.7, 134.0, 134.5 (q, $\underline{\text{C}}$-CF_3), 136.0, 136.1, 136.4, 136.5, 142.0, 163.6, 169.1, 177.7; HRMS (ESI), calcd for $C_{63}H_{67}F_3NaO_{11}Si_2^+$ 1135.4066 (M+Na$^+$), found 1135.4057.

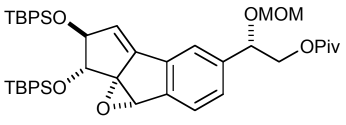


15

15: *R*$_f$ = 0.46 (hexane/EtOAc = 5/1); $[\alpha]_D^{25}$ +5.3 (*c* 0.27, CH_2Cl_2); FT-IR (film) ν 2927, 2856, 1738, 1325, 1270, 1325, 1270, 1134, 1110, 1018, 703 cm^{-1}; ^{1}H NMR (600 MHz, C_6D_6) δ 1.00 (9H, s, Piv), 1.11 (9H, s, TBPS), 1.14 (9H, s, TBPS), 2.63 (1H, d, *J* = 1.2 Hz, H8), 3.26 (3H, s, MOM), 4.53 (1H, dd, *J* = 12.1, 6.3 Hz, H14), 4.53 (1H, d, *J* = 2.4 Hz, H10), 4.62 (1H, d, $J = 7.0$ Hz, MOM), 4.65 (1H, dd, $J = 6.3, 3.9$ Hz, H13), 4.72 (1H, d, $J = 7.0$ Hz, MOM), 4.86 (1H, dd, $J = 12.1, 3.9$ Hz, H14), 5.21 (1H, dd, $J = 2.4, 2.4$ Hz, H11), 6.03 (1H, d, $J = 2.4$ Hz, H12), 6.82 (1H, d, $J = 1.2$ Hz, H5), 6.93-7.01 (4H, m, TFBz), 7.13-7.20 (8H, m, TBPS), 7.58-7.80 (12H, m, TBPS, TFBz); ^{13}C NMR (150 MHz, C_6D_6) δ 19.3, 19.7, 27.0, 27.2, 27.3, 38.8, 47.9, 56.5, 64.8, 69.5, 74.2, 78.7, 79.3, 83.1, 82.3, 84.0, 90.7, 92.2, 94.0, 98.2, 123.4, 125.40, 125.42, 128.6, 128.8, 130.16, 130.18, 130.2, 130.3, 130.5, 132.2, 132.8, 133.1, 133.60, 133.62, 134.0, 136.0, 136.1, 136.3, 136.4, 142.6, 163.0, 164.0, 177.5; HRMS (ESI), calcd for $C_{69}H_{68}F_6NaO_{11}Si_2^+$ 1265.4097 (M+Na$^+$), found 1265.4089.



16

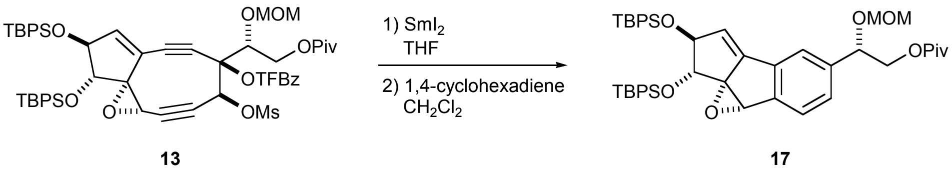


17

The typical procedure of SmI$_2$ mediated reductive elimination (Table 1, entry 2)

A 0.1 M THF solution of SmI$_2$ was prepared from samarium and diiodomethane according to the procedure reported by Kagan[3)]. To a solution of **13** (4.2 mg, 3.7 μmol) in fleshly distilled THF (0.64 mL) was added a solution of SmI$_2$ (0.1 M, 90 μL, 9.1 μmol) at –20 °C. After stirring for 10 min, the mixture was allowed for the exposure to open air and diluted by diethyl ether. The suspension was filtrated through pads of Celite and silica gel. Concentration under the reduced pressure and the silica gel flash chromatography (hexane/ethyl acetate) gave a mixture of enediyne **16** and aromatized product **17** in the ratio of 3:2 (2.3 mg, 72% as a combined yield).

16: $R_f = 0.36$ (hexane/EtOAc = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.93 (9H, s, Piv), 1.06 (9H, s, TBPS), 1.15 (1H, s, TBPS), 3.06 (1H, d, $J = 2.0$ Hz, H8), 3.33 (3H, s, MOM), 4.10 (2H, m, H14), 4.40 (1H, m, H13), 4.47 (1H, d, $J = 3.5$ Hz, H10), 4.59 (2H, s, MOM), 5.08 (1H, dd, $J = 3.5, 2.0$ Hz, H11), 5.94 (1H, d, $J = 2.0$ Hz, H12), 5.96 (1H, brs, H5), 7.30-7.82 (20H, m, TBPS); HRMS (MALDI), calcd for $C_{53}H_{60}NaO_7Si_2^+$ 887.3770 (M+Na$^+$), found 887.1913.



13 **17**

The procedure for reductive elimination and cycloaromatization (Table 1, entry 3)

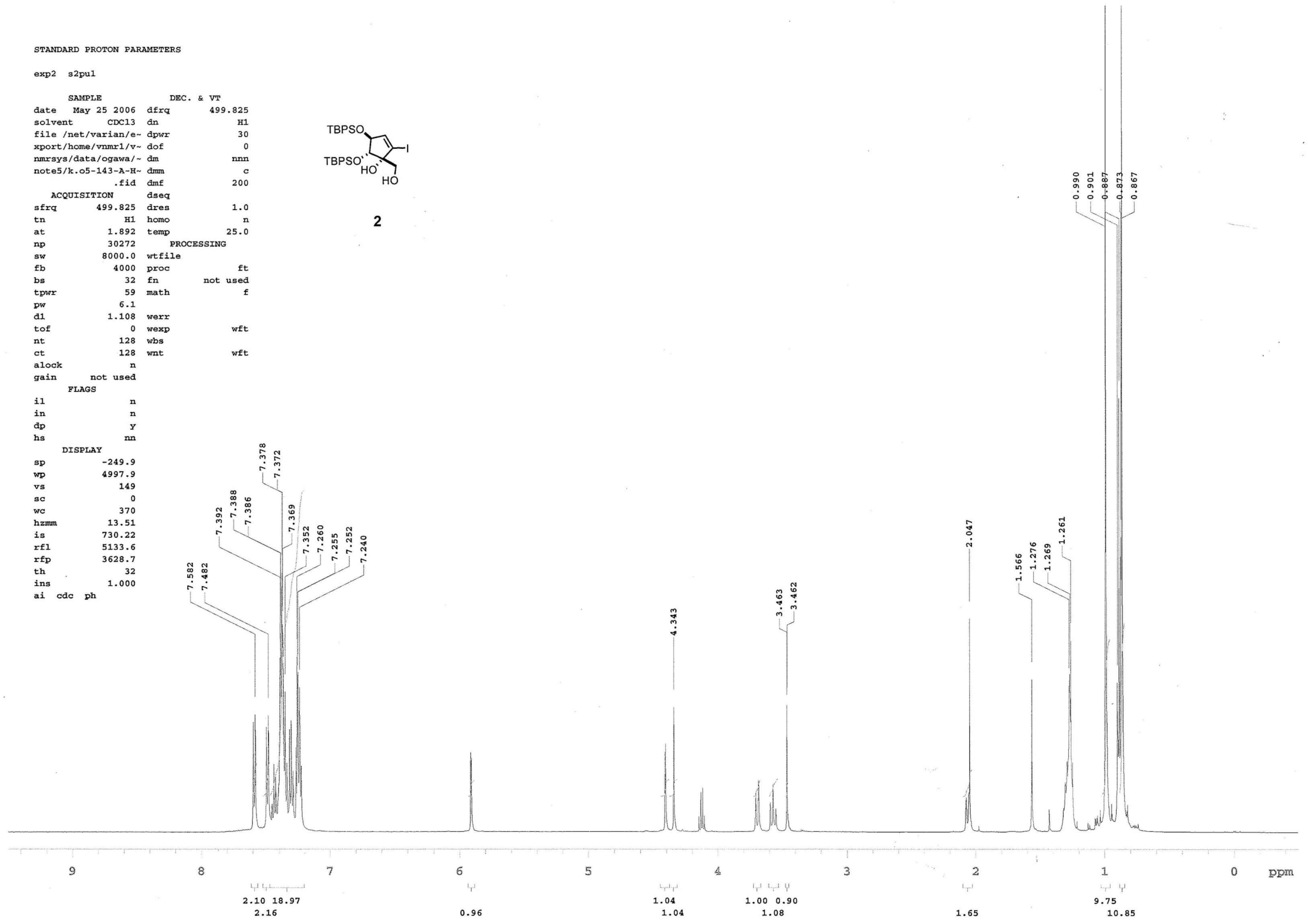
To a solution of **13** (5.2 mg, 4.5 μmol) in fleshly distilled THF was added a solution of SmI_2 (0.1 M, 136 μL, 13.6 μmol) at –15 °C. After stirring for 10 min, the mixture was allowed for the exposure to open air and diluted by diethyl ether. The suspension was filtrated through pads of Celite and silica gel and concentrated. The residue was dissolved in CH_2Cl_2 (0.3 mL), and 1,4-cyclohexadiene (0.3 mL) was added at room temperature. After stirring for 2.0 h, the mixture was concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 20/1–5/1) to afford **17** (2.3 mg, 2.65 μmol, 59%) as a colorless oil.

17: R_f = 0.59 (hexane/EtOAc = 1/1); $[\alpha]_D^{25}$ +116.6 (*c* 0.62, CH_2Cl_2); FT-IR (film) ν 2932, 2858, 1734, 1152, 1111, 1033, 823, 704 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.12 (9H, s, Piv), 1.13 (9H, s, TBPS), 1.15 (9H, s, TBPS), 2.61 (1H, s, H8), 3.28 (3H, s, MOM), 4.03 (1H, dd, *J* = 12.0, 4.5 Hz, H14), 4.13 (1H, dd, *J* = 12.0, 7.5 Hz, H14), 4.43 (1H, d, *J* = 6.5 Hz, MOM), 4.53 (1H, d, *J* = 6.5 Hz, MOM), 4.74 (1H, dd, *J* = 7.5, 4.5 Hz, H13), 5.00 (1H, d, *J* = 4.0 Hz, H10), 5.54 (1H, d, *J* = 2.0 Hz, H12), 5.65 (1H, dd, *J* = 4.0, 2.0 Hz, H11), 7.11 (1H, d, *J* = 8.5 Hz, H5 or H6), 7.14 (1H, d, *J* = 8.5 Hz, H5 or H6), 7.19 (1H, s, H3), 7.33 (12H, m, TBPS), 7.82 (8H, m, TBPS) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.4, 19.6, 26.7, 27.2, 27.26, 27.30, 29.9, 38.6, 55.7, 57.9, 67.5, 72.9, 75.5, 79.5, 88.6, 94.5, 123.0, 125.9, 126.9, 127.3, 127.7, 127.8, 127.9, 128.0, 129.8, 129.9, 130.0, 133.4, 134.0, 134.2, 134.5, 134.9, 135.4, 136.0, 136.1, 136.5, 138.8, 141.3, 145.2, 178.3; HRMS (ESI), calcd for $C_{53}H_{62}NaO_7Si_2^+$ 889.3926 ($M+Na^+$), found 889.3922.

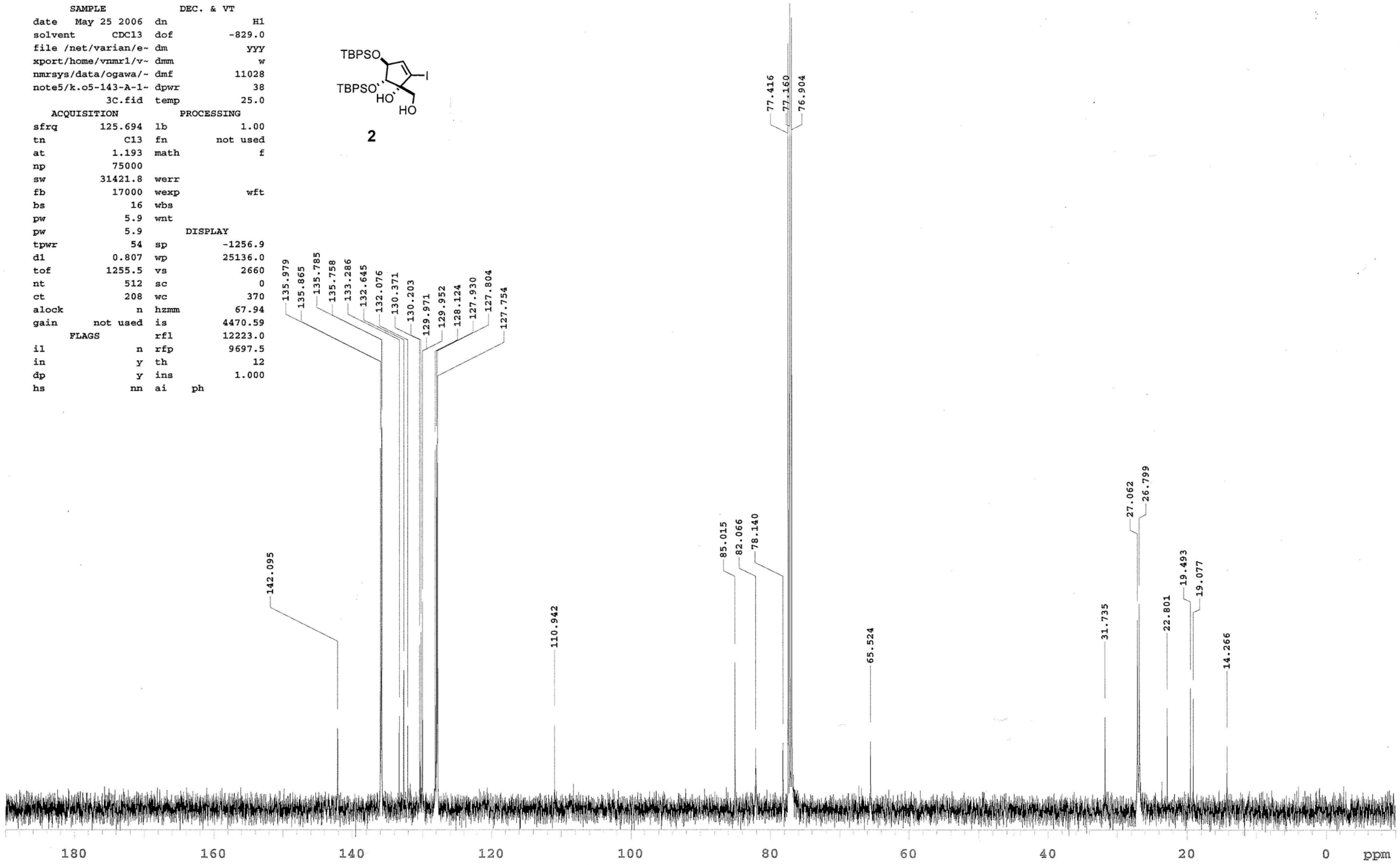
1) Leet, J. E.; Schroeder, D. R.; Langley, D. R.; Colson, K. L.; Huang, S.; Klohr, S. E.; Lee, M. S.; Golik, J.; Hofstead, S. J.; Doyle, T. W.; Matson, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 8432.

2) Koyama, Y.; Lear, M. J.; Yoshimura, F.; Ohashi, I.; Mashimo, T.; Hirama, M. *Org. Lett.* **2005**, *7*, 267.

3) a) Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.*, **1980**, *102*, 2693.
b) Namy, J. L.; Girard, P.; Kagan, H. B.; Caro, P. E. *Nouv. J. Chim.,* **1981**, *5*, 479.

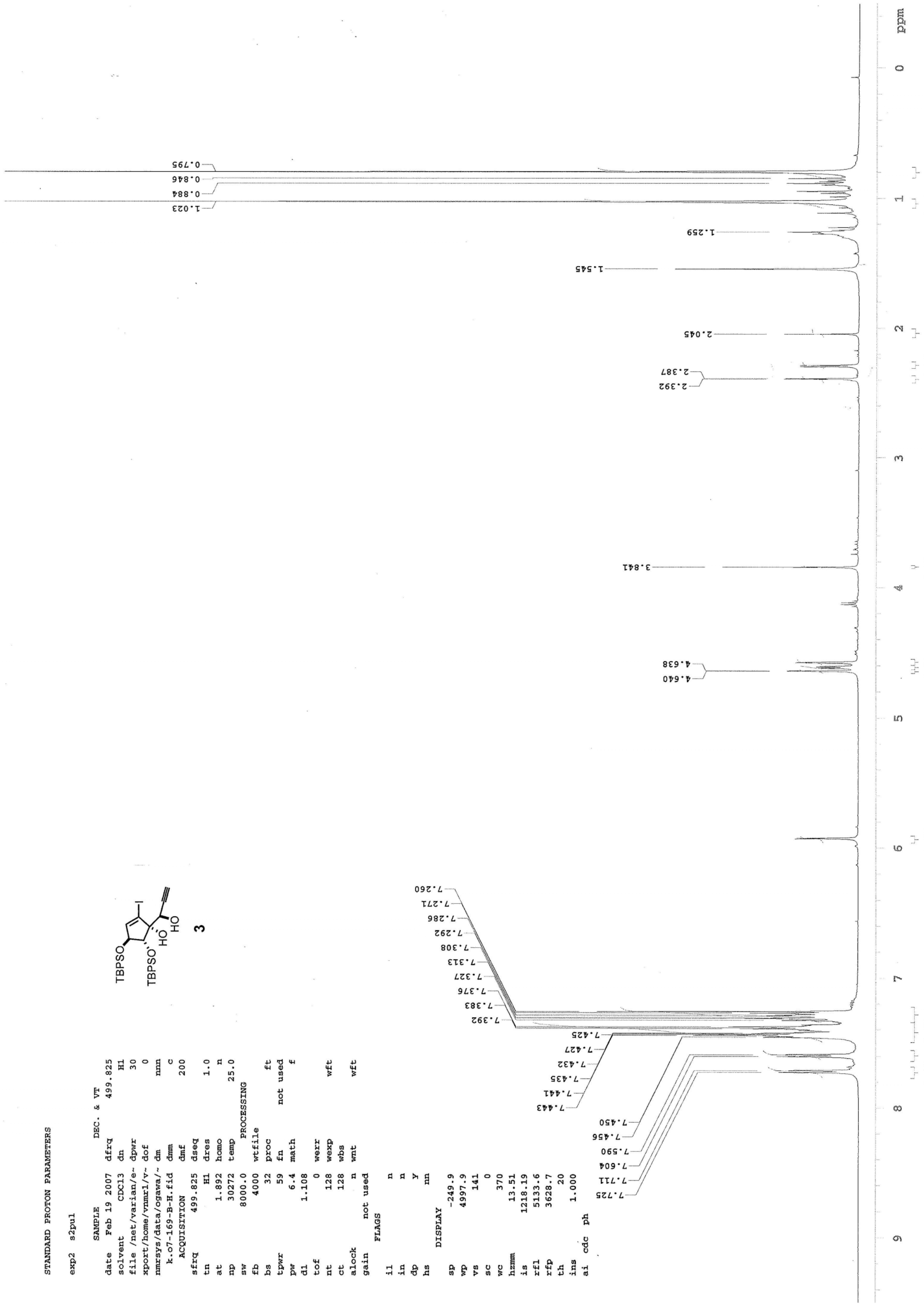


```
STANDARD PROTON PARAMETERS

exp2  s2pul

      SAMPLE              DEC. & VT
date   May 25 2006  dfrq        499.825
solvent      CDCl3  dn               H1
file /net/varian/e~ dpwr             30
xport/home/vnmr1/v~ dof               0
nmrsys/data/ogawa/~ dm              nnn
note5/k.o5-143-A-H~ dmm               c
              .fid  dmf             200
   ACQUISITION      dseq
sfrq       499.825  dres            1.0
tn              H1  homo              n
at           1.892  temp           25.0
np           30272        PROCESSING
sw          8000.0  wtfile
fb            4000  proc             ft
bs              32  fn         not used
tpwr            59  math              f
pw             6.1
d1           1.108  werr
tof              0  wexp            wft
nt             128  wbs
ct             128  wnt             wft
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
hs              nn
     DISPLAY
sp          -249.9
wp          4997.9
vs             149
sc               0
wc             370
hzmm         13.51
is          730.22
rfl         5133.6
rfp         3628.7
th              32
ins          1.000
ai  cdc  ph
```

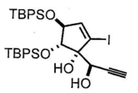


2

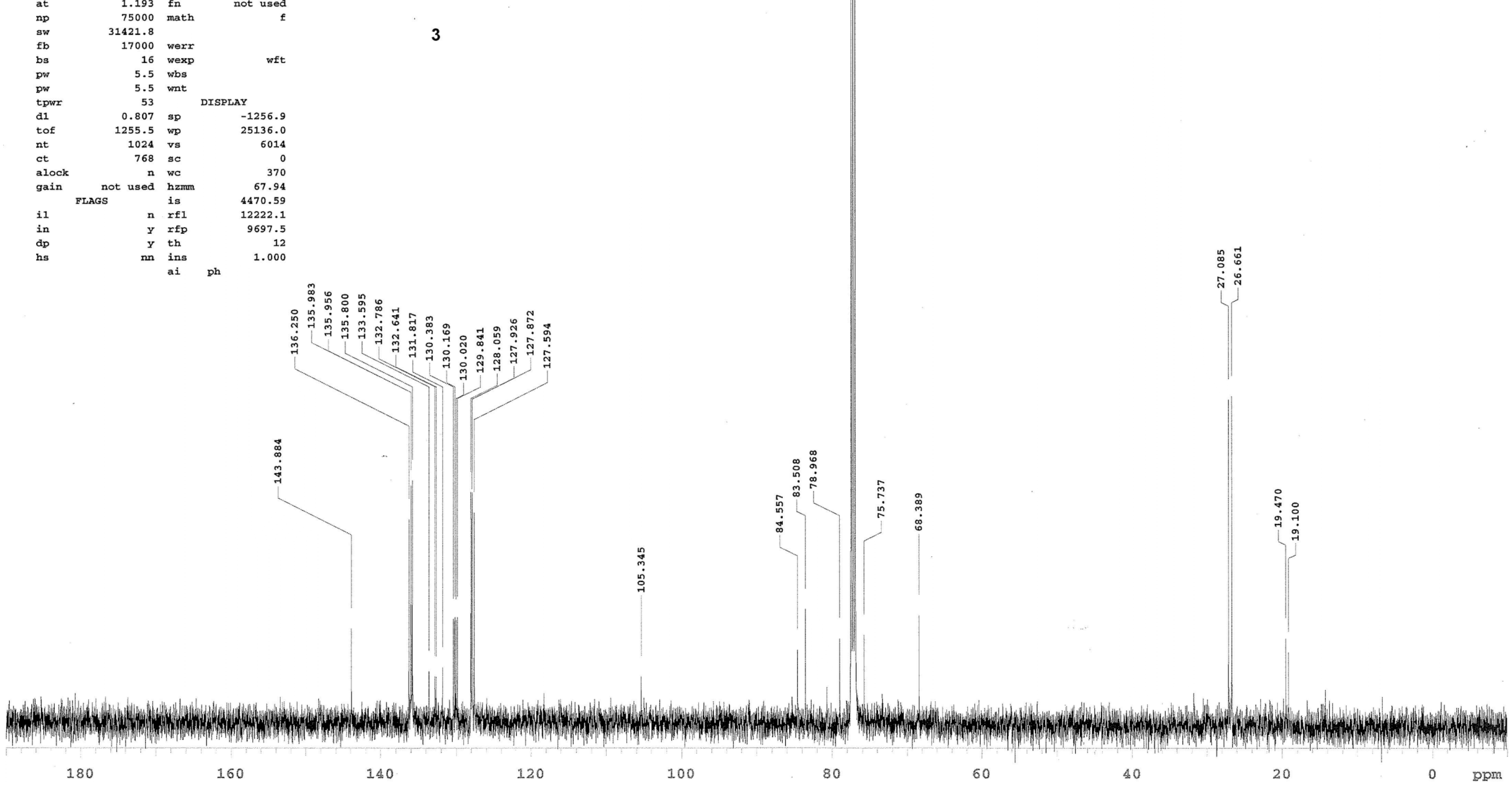
```
13C SENSITIVITY
ASTM SAMPLE

exp2  s2pul

      SAMPLE             DEC. & VT
date   May 25 2006  dn              H1
solvent      CDCl3  dof         -829.0
file /net/varian/e~ dm             yyy
xport/home/vnmr1/v~ dmm              w
nmrsys/data/ogawa/~ dmf          11028
note5/k.o5-143-A-1~ dpwr            38
             3C.fid temp          25.0
   ACQUISITION         PROCESSING
sfrq       125.694  lb            1.00
tn             C13  fn        not used
at           1.193  math             f
np           75000
sw         31421.8  werr
fb           17000  wexp           wft
bs              16  wbs
pw             5.9  wnt
pw             5.9         DISPLAY
tpwr            54  sp         -1256.9
d1           0.807  wp         25136.0
tof         1255.5  vs            2660
nt             512  sc               0
ct             208  wc             370
alock            n  hzmm         67.94
gain      not used  is         4470.59
     FLAGS          rfl        12223.0
il               n  rfp         9697.5
in               y  th              12
dp               y  ins          1.000
hs              nn  ai    ph
```


STANDARD PROTON PARAMETERS
exp2 s2pul
SAMPLE
date Feb 19 2007
solvent CDCl3
file /net/varian/e~
xport/home/vnmr1/v~
nmrsys/data/ogawa/~
k.o7-169-B-H.fid
DEC. & VT
dfrq 499.825
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
ACQUISITION
sfrq 499.825
tn H1
at 1.892
np 30272
sw 8000.0
fb 4000
bs 32
tpwr 59
pw 6.4
d1 1.108
tof 0
nt 128
ct 128
alock n
gain not used
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
wtfile
proc ft
fn not used
math f
werr
wexp wft
wbs
wnt wft
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -249.9
wp 4997.9
vs 141
sc 0
wc 370
hzmm 13.51
is 1218.19
rfl 5133.6
rfp 3628.7
th 20
ins 1.000
ai cdc ph
TBPSO
TBPSO
HO
HO
I
3
7.260
7.271
7.286
7.292
7.308
7.313
7.327
7.376
7.383
7.392
7.425
7.427
7.432
7.435
7.441
7.443
7.450
7.456
7.590
7.604
7.711
7.725
4.640
4.638
3.841
2.392
2.387
2.045
1.545
1.259
1.023
0.884
0.846
0.795
2.18
2.35
11.50
8.01
0.88
0.94
0.95
0.50
0.77
0.84
0.82
0.45
9.51
8.97
9
8
7
6
5
4
3
2
1
0
ppm

```
13C SENSITIVITY
ASTM SAMPLE

exp2  s2pul

      SAMPLE            DEC. & VT
date   Feb 19 2007  dn              H1
solvent      CDC13  dof         -829.0
file /net/varian/e~ dm             yyy
xport/home/vnmr1/v~ dmm              w
nmrsys/data/ogawa/~ dmf          10768
k.o7-169-B-13C.fid  dpwr            39
   ACQUISITION      temp          25.0
sfrq       125.694       PROCESSING
tn             C13  lb            1.00
at           1.193  fn        not used
np           75000  math             f
sw         31421.8
fb           17000  werr
bs              16  wexp           wft
pw             5.5  wbs
pw             5.5  wnt
tpwr            53        DISPLAY
d1           0.807  sp         -1256.9
tof         1255.5  wp         25136.0
nt            1024  vs            6014
ct             768  sc               0
alock            n  wc             370
gain      not used  hzmm         67.94
      FLAGS         is         4470.59
il               n  rfl        12222.1
in               y  rfp         9697.5
dp               y  th              12
hs              nn  ins          1.000
                    ai    ph
```

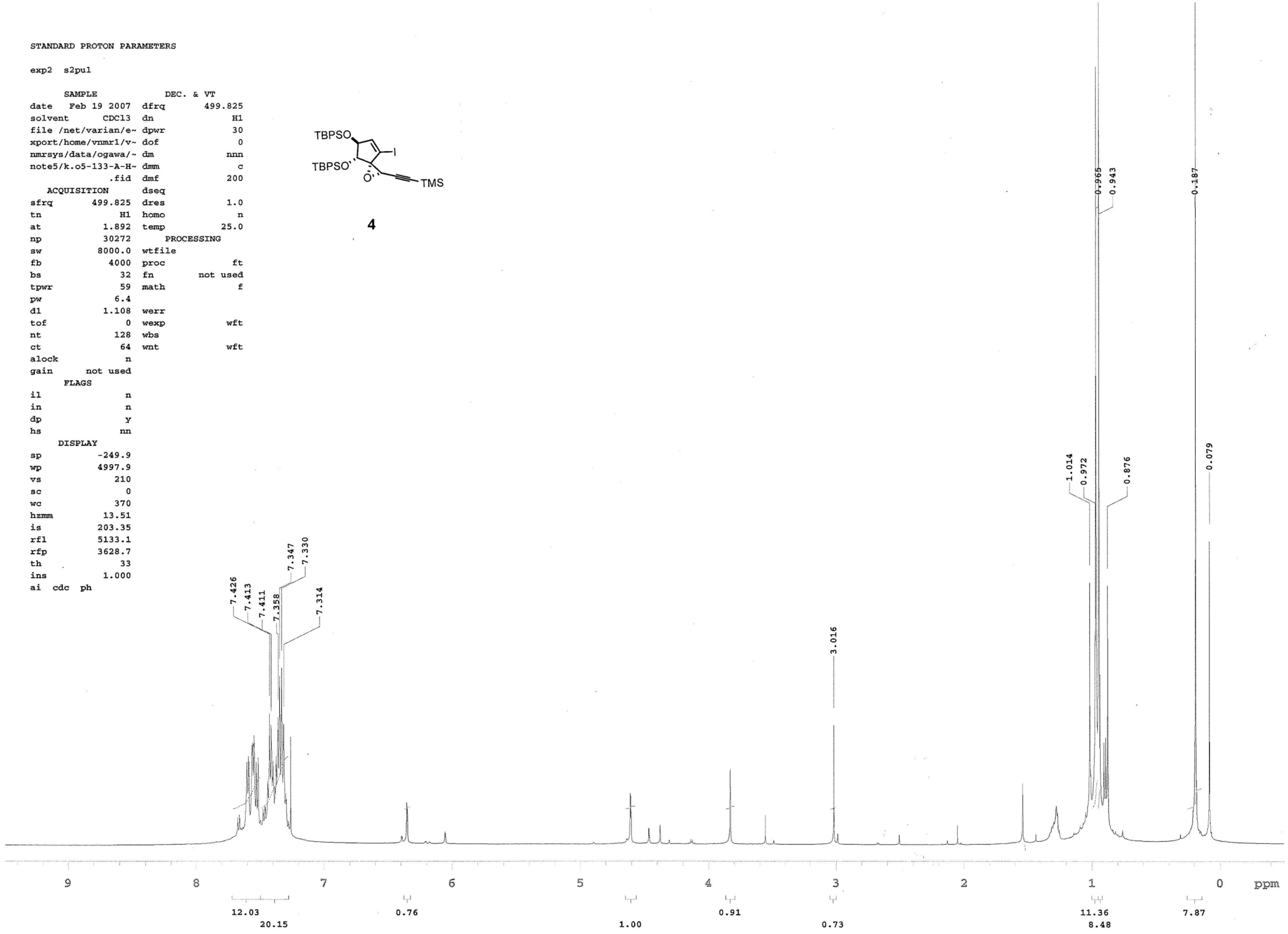


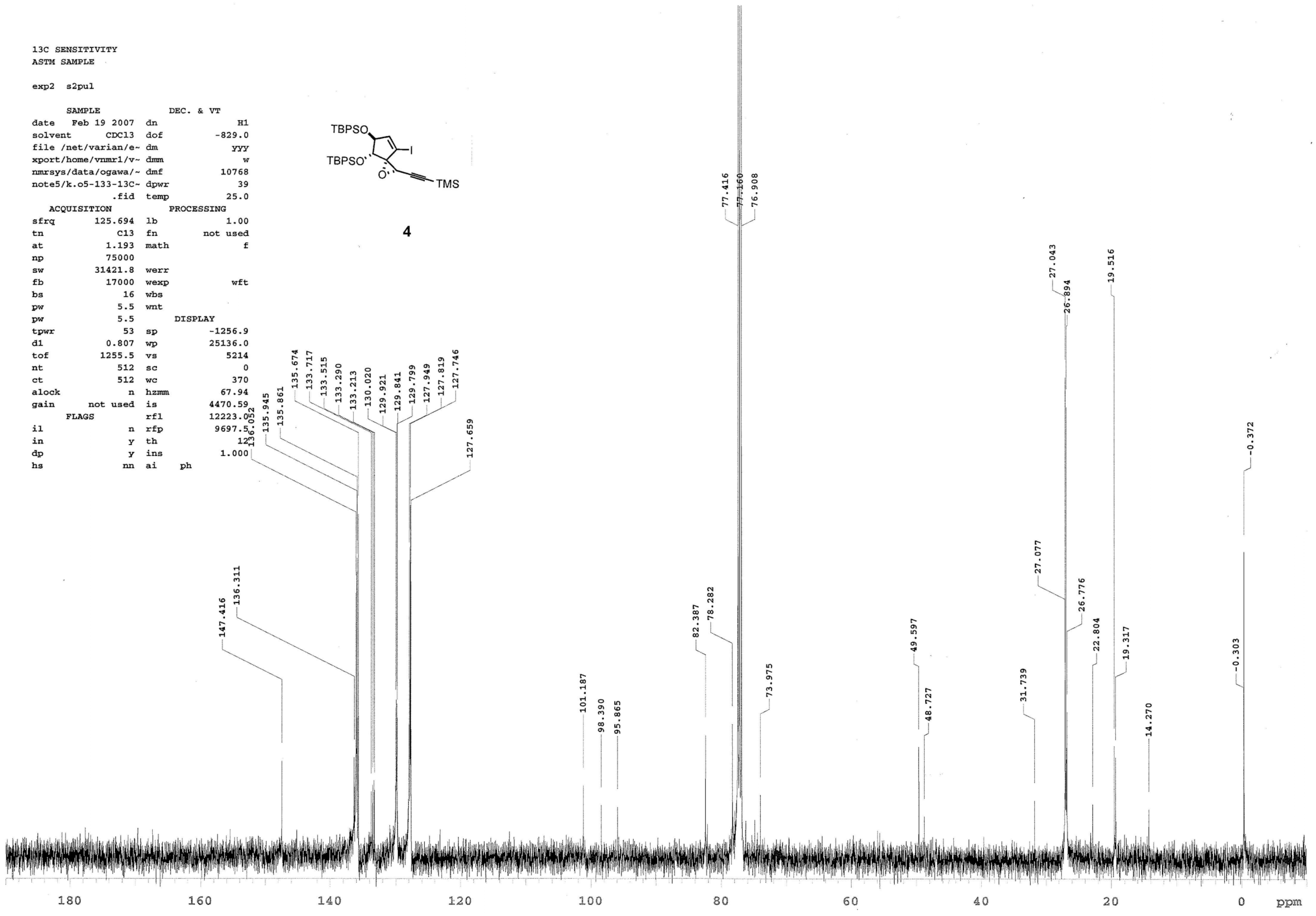
3



```
STANDARD PROTON PARAMETERS

exp2  s2pul

      SAMPLE            DEC. & VT
date   Feb 19 2007  dfrq       499.825
solvent      CDCl3  dn              H1
file /net/varian/e~ dpwr            30
xport/home/vnmr1/v~ dof              0
nmrsys/data/ogawa/~ dm             nnn
note5/k.o5-133-A-H~ dmm              c
              .fid  dmf            200
   ACQUISITION      dseq
sfrq       499.825  dres           1.0
tn              H1  homo             n
at           1.892  temp          25.0
np           30272      PROCESSING
sw          8000.0  wtfile
fb            4000  proc            ft
bs              32  fn        not used
tpwr            59  math             f
pw             6.4
d1           1.108  werr
tof              0  wexp           wft
nt             128  wbs
ct              64  wnt            wft
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
hs              nn
     DISPLAY
sp          -249.9
wp          4997.9
vs             210
sc               0
wc             370
hzmm         13.51
is          203.35
rfl         5133.1
rfp         3628.7
th              33
ins          1.000
ai  cdc  ph
```

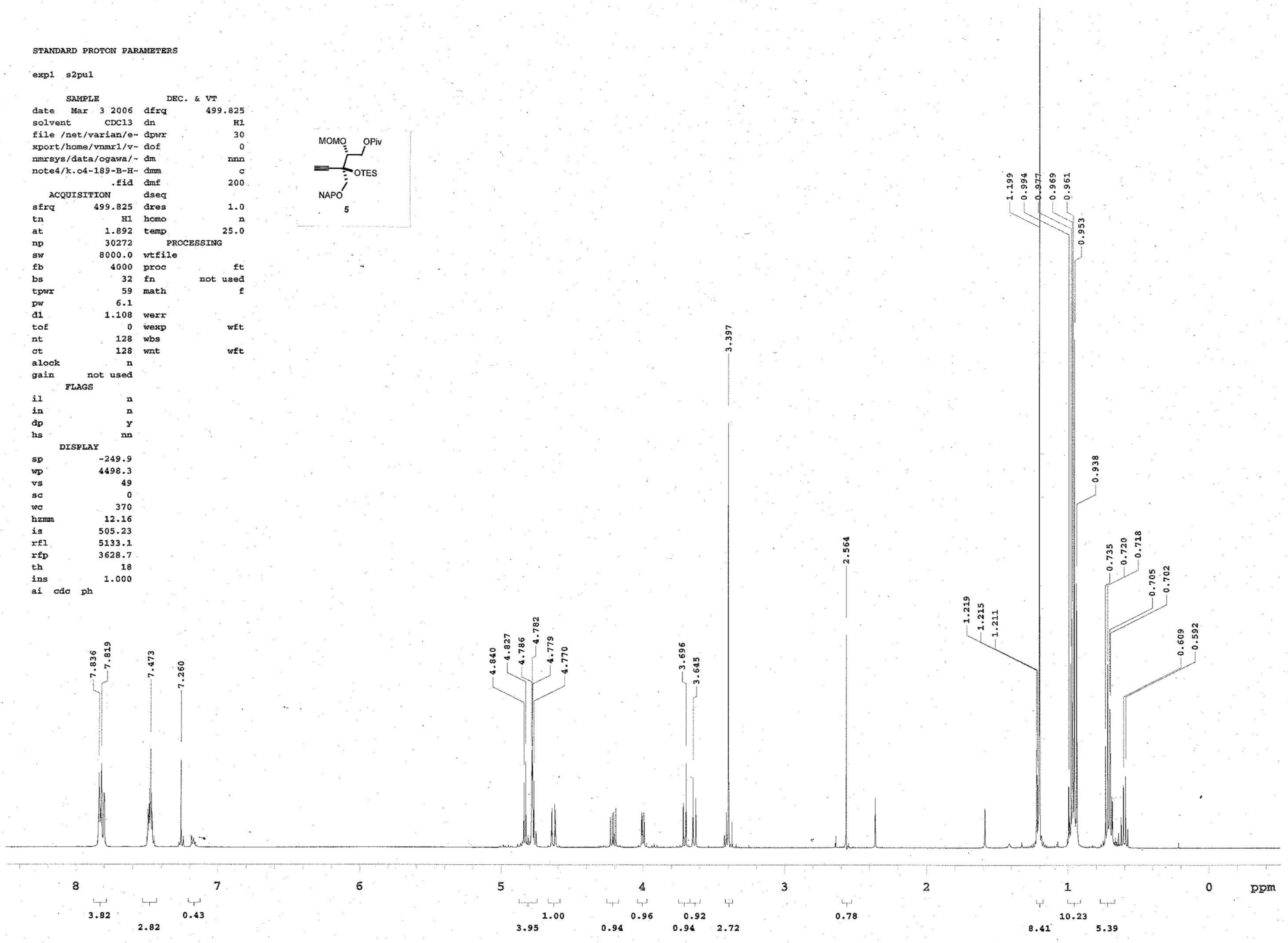
4





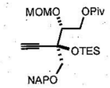
```
13C SENSITIVITY
ASTM SAMPLE

exp2  s2pul

      SAMPLE              DEC. & VT
date   Feb 19 2007  dn              H1
solvent       CDCl3  dof          -829.0
file /net/varian/e~  dm             yyy
xport/home/vnmr1/v~  dmm              w
nmrsys/data/ogawa/~  dmf          10768
note5/k.o5-133-13C~  dpwr            39
               .fid  temp          25.0
   ACQUISITION          PROCESSING
sfrq        125.694  lb            1.00
tn              C13  fn        not used
at            1.193  math             f
np            75000
sw          31421.8  werr
fb            17000  wexp           wft
bs               16  wbs
pw              5.5  wnt
pw              5.5       DISPLAY
tpwr             53  sp         -1256.9
d1            0.807  wp         25136.0
tof          1255.5  vs            5214
nt              512  sc               0
ct              512  wc             370
alock             n  hzmm         67.94
gain       not used  is         4470.59
      FLAGS          rfl        12223.0
il                n  rfp         9697.5
in                y  th              12
dp                y  ins          1.000
hs               nn  ai     ph
```

4

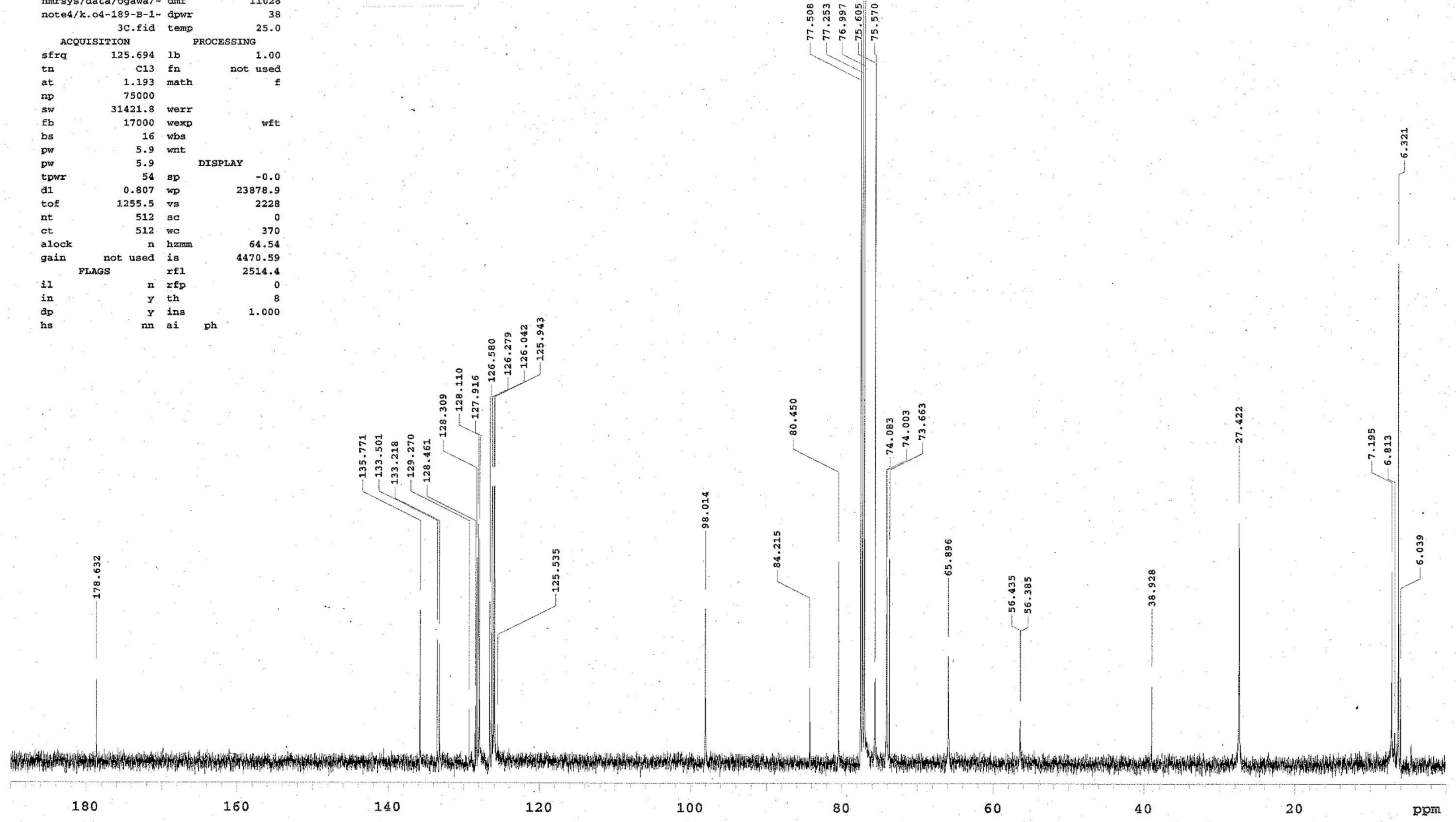


```
STANDARD PROTON PARAMETERS

exp1  s2pul

      SAMPLE            DEC. & VT
date   Mar  3 2006  dfrq        499.825
solvent       CDC13  dn               H1
file /net/varian/e~ dpwr              30
xport/home/vnmr1/v~ dof                0
nmrsys/data/ogawa/~ dm               nnn
note4/k.o4-189-B-H~ dmm                c
               .fid dmf              200
   ACQUISITION      dseq
sfrq        499.825 dres             1.0
tn               H1 homo               n
at            1.892 temp            25.0
np            30272      PROCESSING
sw           8000.0 wtfile
fb             4000 proc              ft
bs               32 fn          not used
tpwr             59 math               f
pw              6.1
d1            1.108 werr
tof               0 wexp             wft
nt              128 wbs
ct              128 wnt              wft
alock             n
gain       not used
      FLAGS
il                n
in                n
dp                y
hs               nn
     DISPLAY
sp           -249.9
wp           4498.3
vs               49
sc                0
wc              370
hzmm          12.16
is           505.23
rfl          5133.1
rfp          3628.7
th               18
ins           1.000
ai  cdc  ph
```

```
13C SENSITIVITY
ASTM SAMPLE

exp1  s2pul

      SAMPLE              DEC. & VT
date   Mar  3 2006  dn              H1
solvent      CDCl3  dof         -829.0
file /net/varian/e~ dm             yyy
xport/home/vnmr1/v~ dmm              w
nmrsys/data/ogawa/~ dmf          11028
note4/k.o4-189-B-1~ dpwr            38
            3C.fid  temp          25.0
   ACQUISITION           PROCESSING
sfrq       125.694  lb            1.00
tn             C13  fn        not used
at           1.193  math             f
np           75000
sw         31421.8  werr
fb           17000  wexp           wft
bs              16  wbs
pw             5.9  wnt
pw             5.9        DISPLAY
tpwr            54  sp            -0.0
d1           0.807  wp         23878.9
tof         1255.5  vs            2228
nt             512  sc               0
ct             512  wc             370
alock            n  hzmm         64.54
gain      not used  is         4470.59
      FLAGS         rfl         2514.4
il               n  rfp              0
in               y  th               8
dp               y  ins          1.000
hs              nn  ai    ph
```

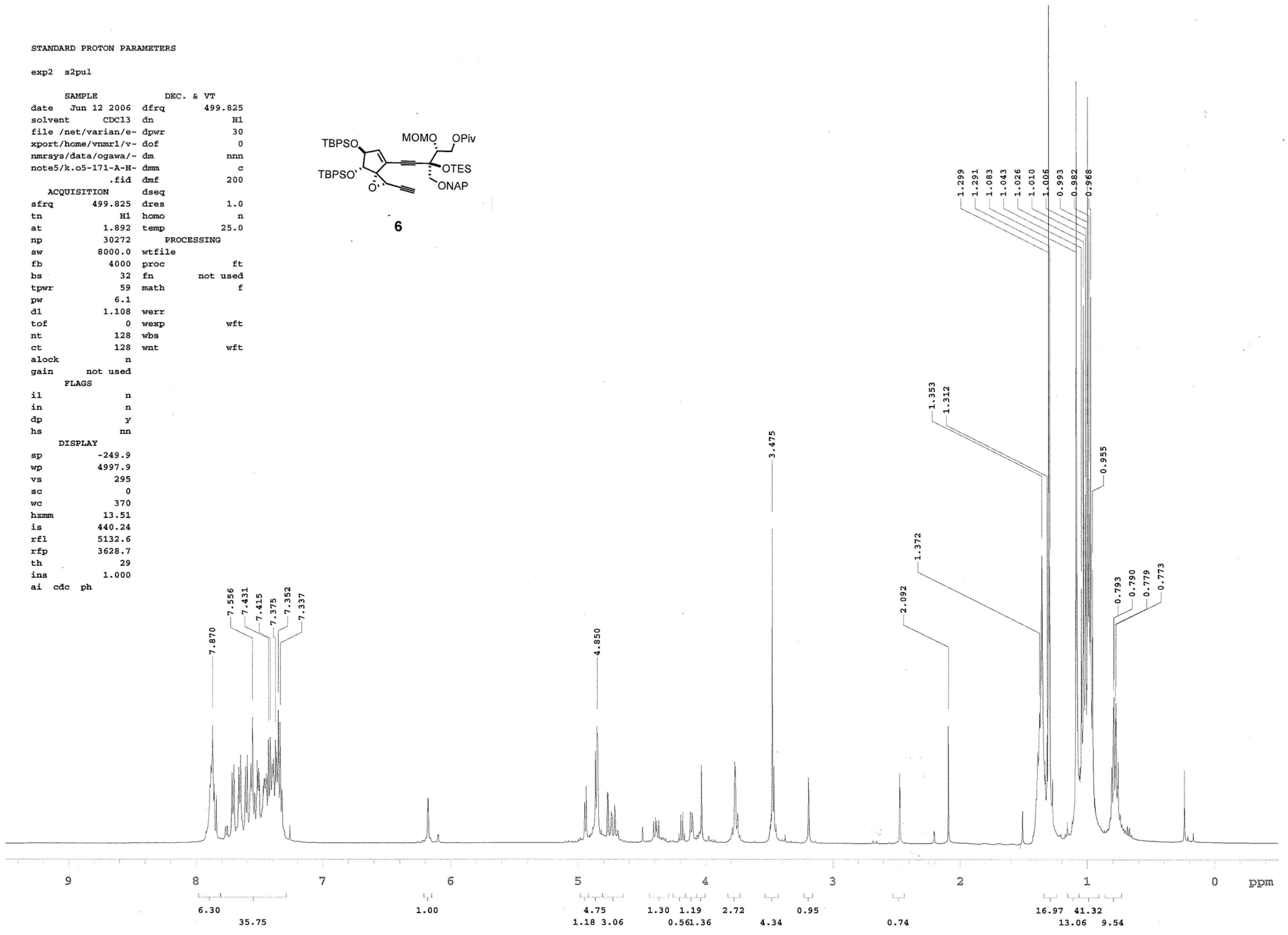


5

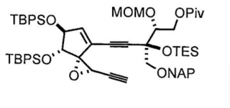


```
STANDARD PROTON PARAMETERS

exp2  s2pul

      SAMPLE              DEC. & VT
date   Jun 12 2006  dfrq        499.825
solvent      CDCl3  dn               H1
file /net/varian/e~ dpwr             30
xport/home/vnmr1/v~ dof               0
nmrsys/data/ogawa/~ dm              nnn
note5/k.o5-171-A-H~ dmm               c
              .fid  dmf             200
   ACQUISITION      dseq
sfrq       499.825  dres            1.0
tn              H1  homo              n
at           1.892  temp           25.0
np           30272      PROCESSING
sw          8000.0  wtfile
fb            4000  proc             ft
bs              32  fn         not used
tpwr            59  math              f
pw             6.1
d1           1.108  werr
tof              0  wexp            wft
nt             128  wbs
ct             128  wnt             wft
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
hs              nn
     DISPLAY
sp          -249.9
wp          4997.9
vs             295
sc               0
wc             370
hzmm         13.51
is          440.24
rfl         5132.6
rfp         3628.7
th              29
ins          1.000
ai  cdc  ph
```

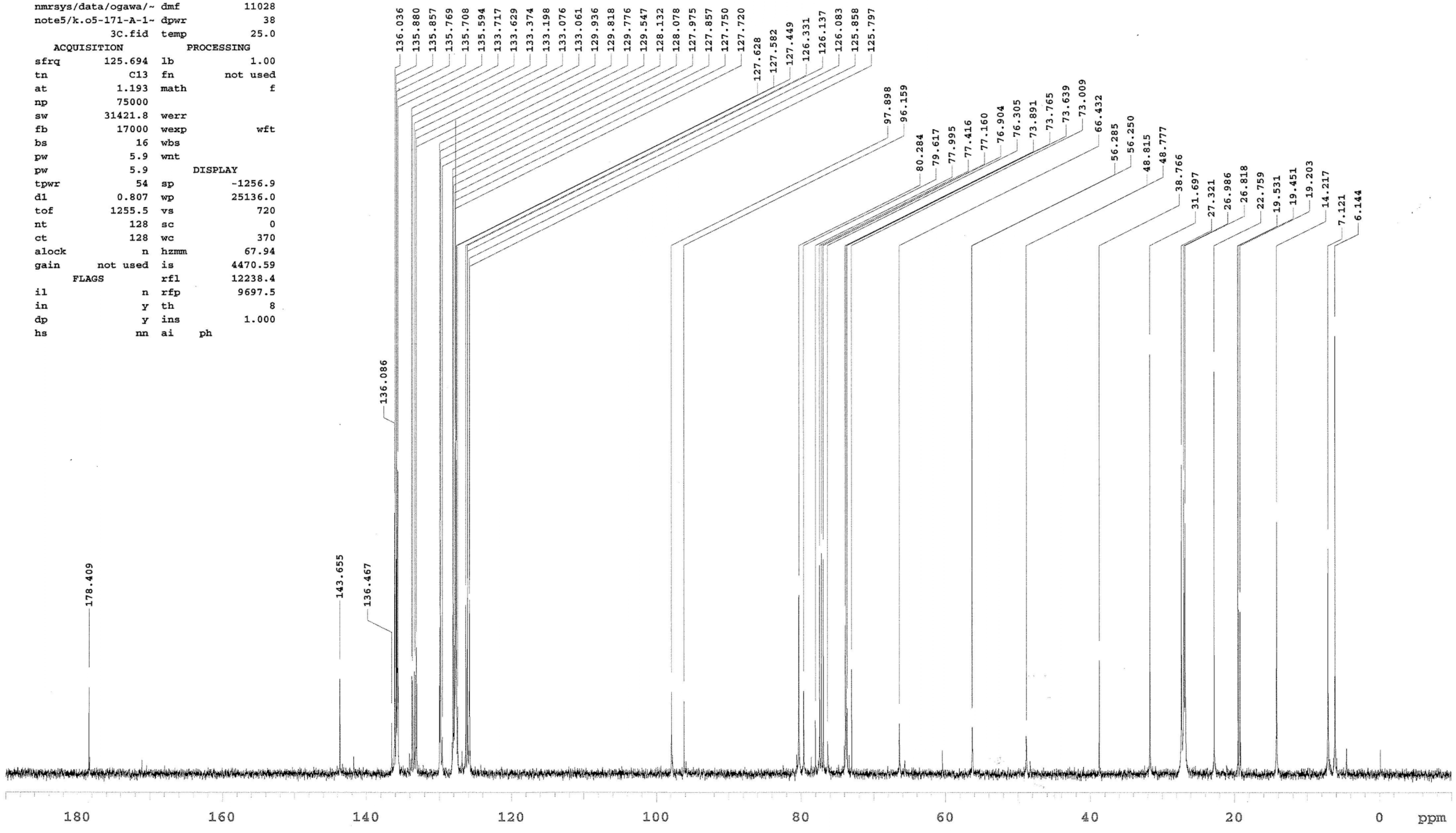
6

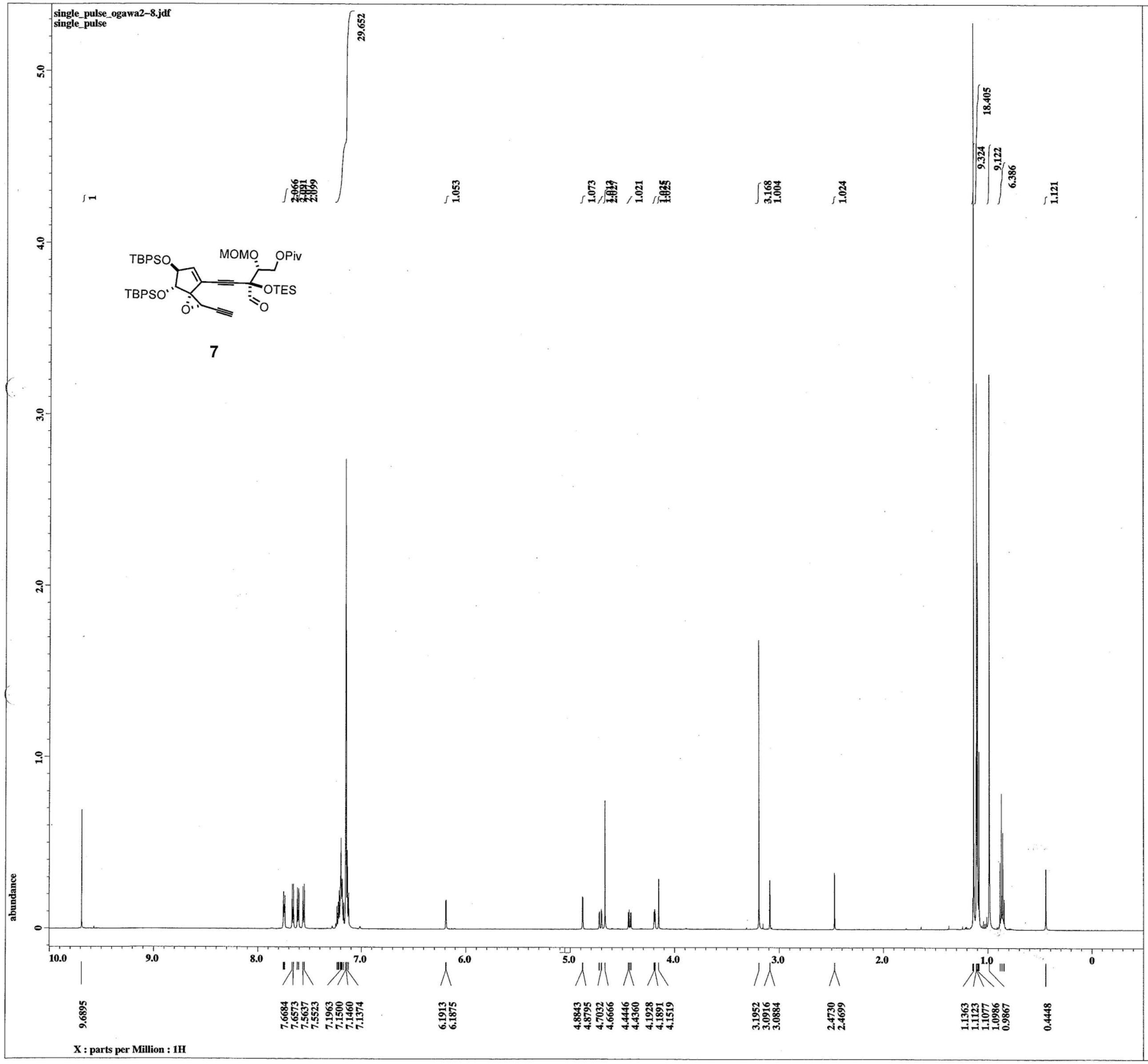


```
13C SENSITIVITY
ASTM SAMPLE

exp2  s2pul

      SAMPLE              DEC. & VT
date   Jun 12 2006  dn            H1
solvent       CDCl3  dof        -829.0
file /net/varian/e~  dm            yyy
xport/home/vnmr1/v~  dmm             w
nmrsys/data/ogawa/~  dmf         11028
note5/k.o5-171-A-1~  dpwr           38
            3C.fid  temp          25.0
   ACQUISITION           PROCESSING
sfrq        125.694  lb            1.00
tn              C13  fn       not used
at            1.193  math            f
np            75000
sw          31421.8  werr
fb            17000  wexp          wft
bs               16  wbs
pw              5.9  wnt
pw              5.9        DISPLAY
tpwr             54  sp        -1256.9
d1            0.807  wp        25136.0
tof          1255.5  vs            720
nt              128  sc              0
ct              128  wc            370
alock             n  hzmm        67.94
gain       not used  is        4470.59
      FLAGS          rfl       12238.4
il                n  rfp        9697.5
in                y  th              8
dp                y  ins         1.000
hs               nn  ai    ph
```

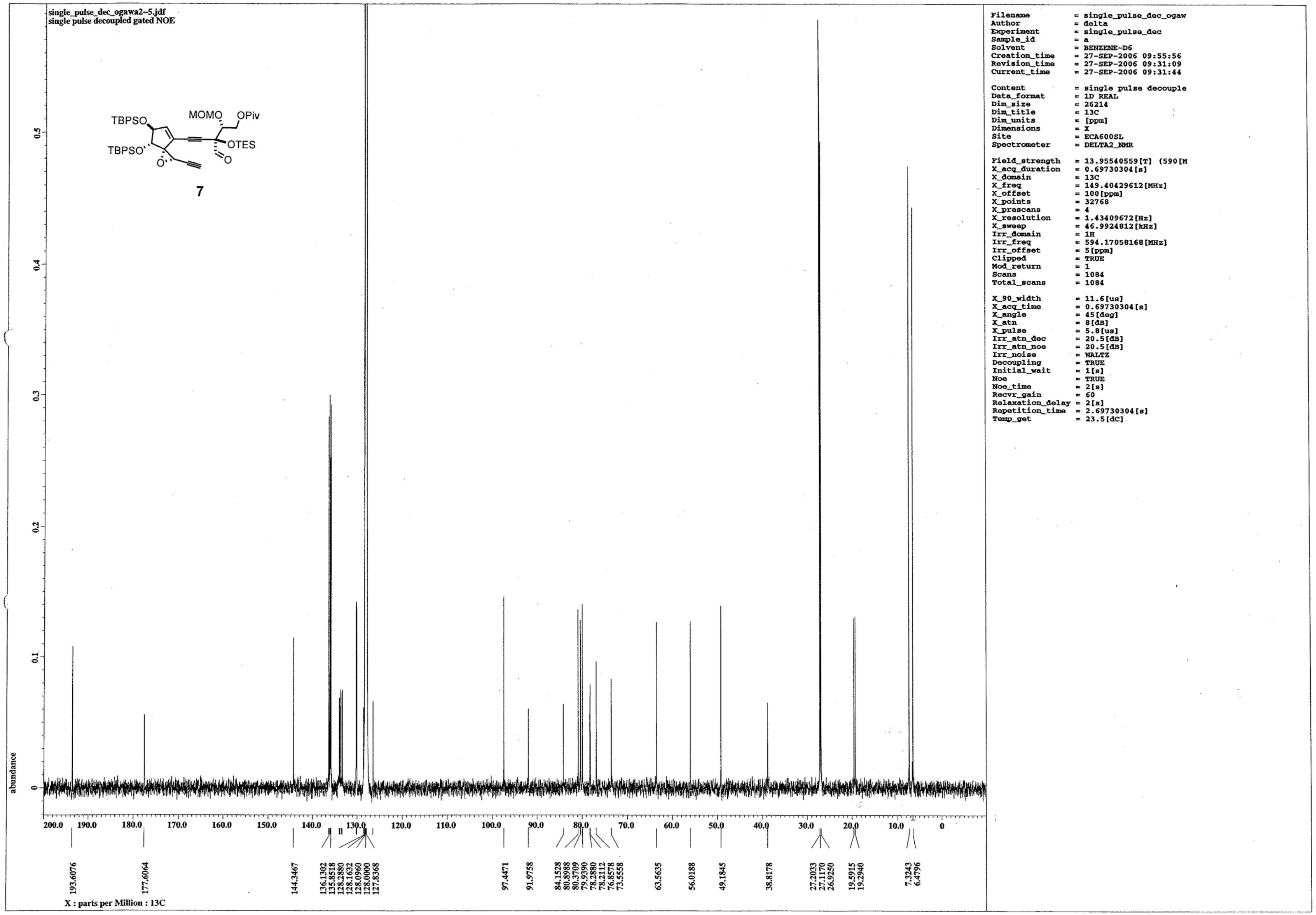


6

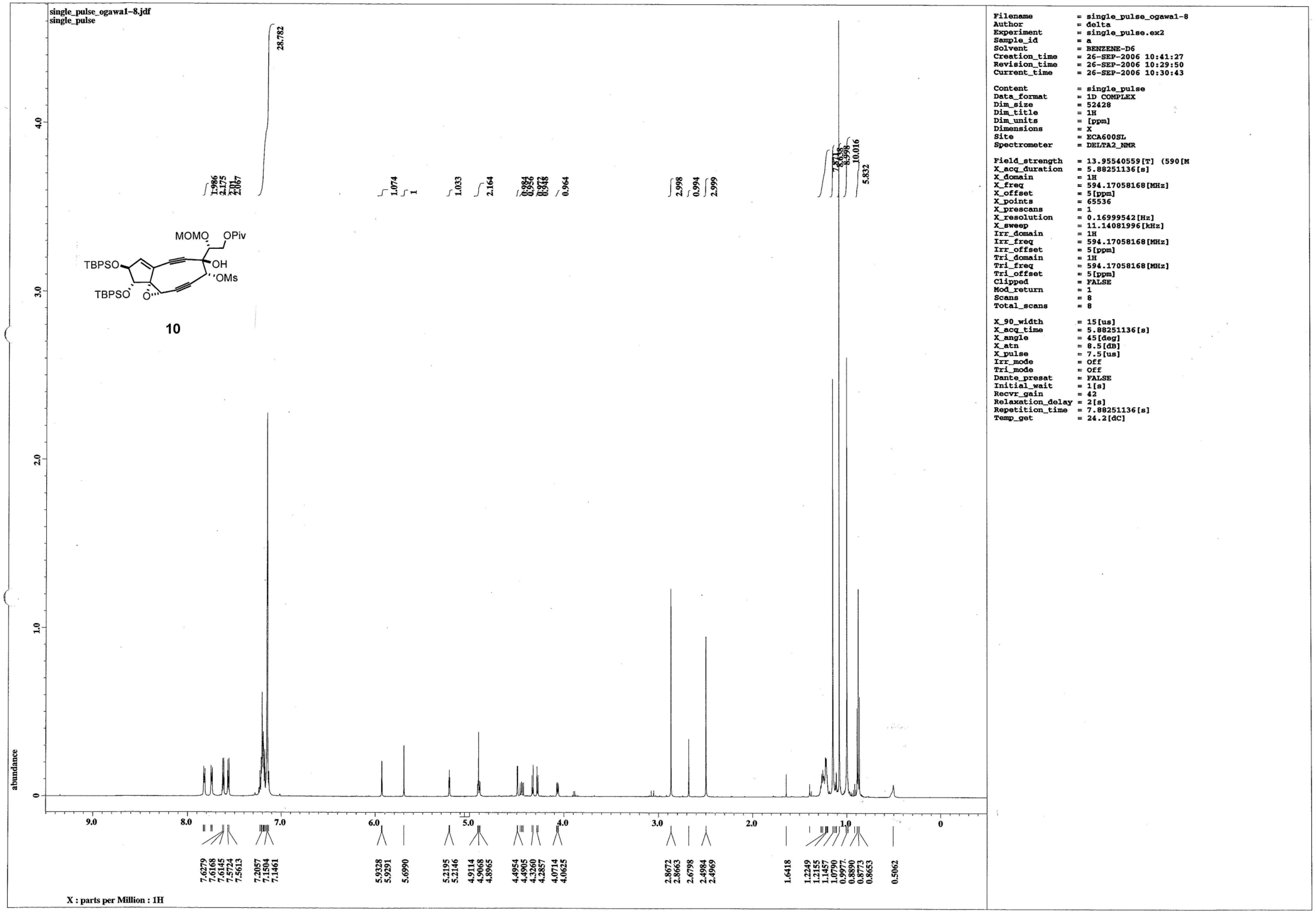




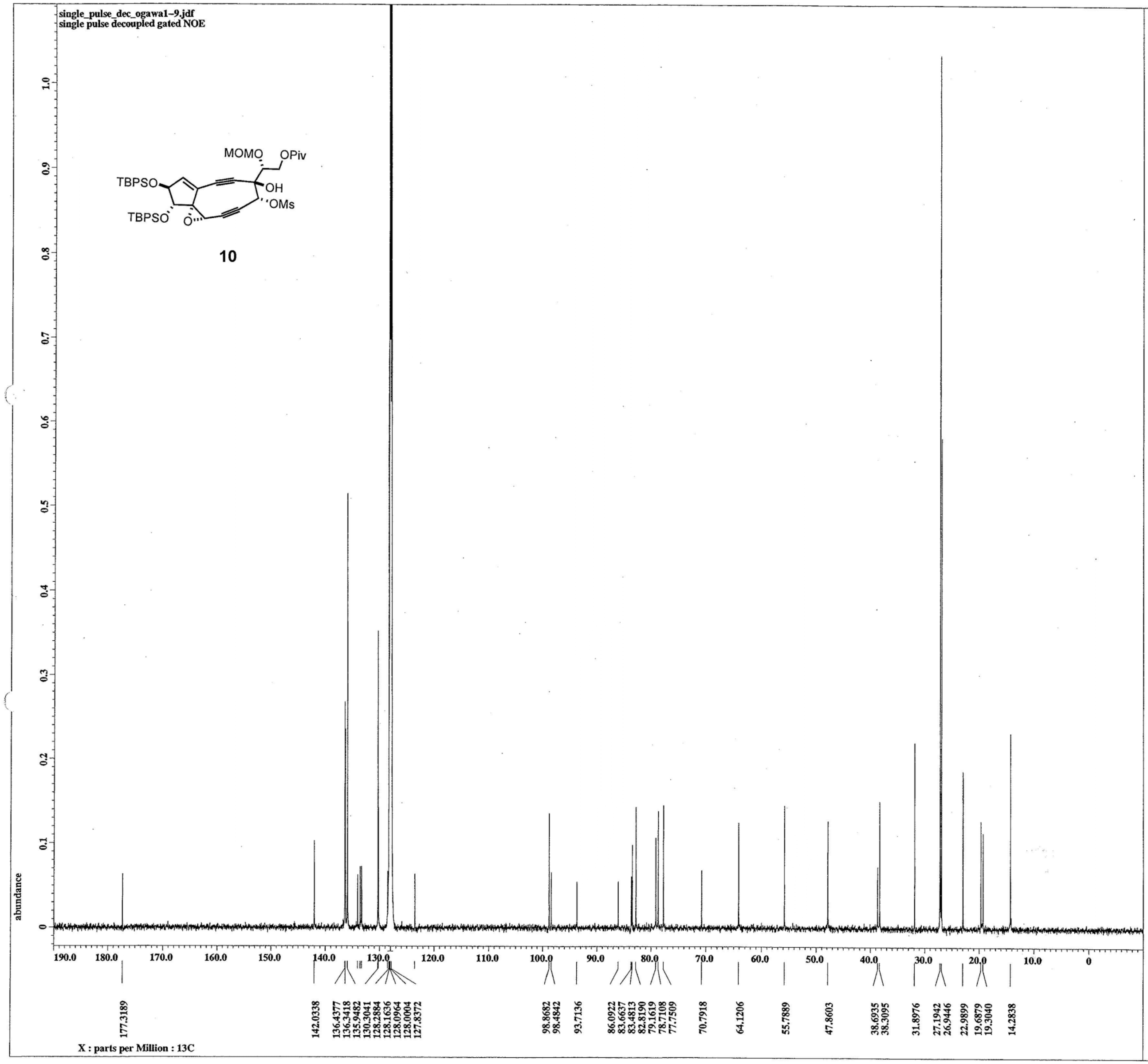
```
Filename           = single_pulse_ogawa2-8
Author             = delta
Experiment         = single_pulse.ex2
Sample_id          = a
Solvent            = BENZENE-D6
Creation_time      = 27-SEP-2006 08:49:25
Revision_time      = 27-SEP-2006 08:51:22
Current_time       = 27-SEP-2006 08:52:52

Content            = single_pulse
Data_format        = 1D COMPLEX
Dim_size           = 52428
Dim_title          = 1H
Dim_units          = [ppm]
Dimensions         = X
Site               = ECA600SL
Spectrometer       = DELTA2_NMR

Field_strength     = 13.95540559[T] (590[M
X_acq_duration     = 5.88251136[s]
X_domain           = 1H
X_freq             = 594.17058168[MHz]
X_offset           = 5[ppm]
X_points           = 65536
X_prescans         = 1
X_resolution       = 0.16999542[Hz]
X_sweep            = 11.14081996[kHz]
Irr_domain         = 1H
Irr_freq           = 594.17058168[MHz]
Irr_offset         = 5[ppm]
Tri_domain         = 1H
Tri_freq           = 594.17058168[MHz]
Tri_offset         = 5[ppm]
Clipped            = FALSE
Mod_return         = 1
Scans              = 8
Total_scans        = 8

X_90_width         = 15[us]
X_acq_time         = 5.88251136[s]
X_angle            = 45[deg]
X_atn              = 8.5[dB]
X_pulse            = 7.5[us]
Irr_mode           = Off
Tri_mode           = Off
Dante_presat       = FALSE
Initial_wait       = 1[s]
Recvr_gain         = 42
Relaxation_delay   = 2[s]
Repetition_time    = 7.88251136[s]
Temp_get           = 22.1[dC]
```



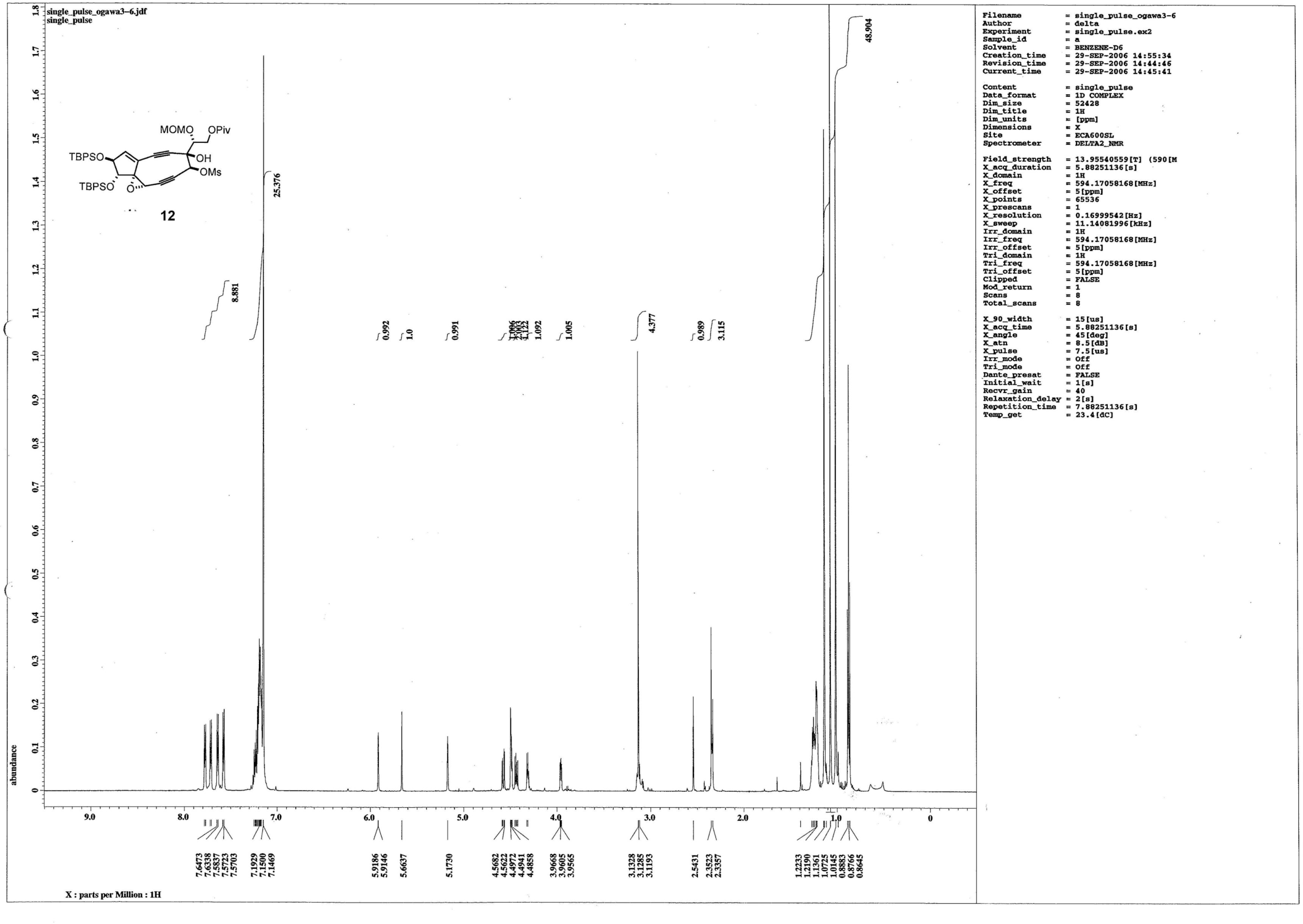
```
Filename          = single_pulse_dec_ogaw
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = a
Solvent           = BENZENE-D6
Creation_time     = 27-SEP-2006 09:55:56
Revision_time     = 27-SEP-2006 09:31:09
Current_time      = 27-SEP-2006 09:31:44

Content           = single pulse decouple
Data_format       = 1D REAL
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA600SL
Spectrometer      = DELTA2_NMR

Field_strength    = 13.95540559[T] (590[M
X_acq_duration    = 0.69730304[s]
X_domain          = 13C
X_freq            = 149.40429612[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.43409672[Hz]
X_sweep           = 46.9924812[kHz]
Irr_domain        = 1H
Irr_freq          = 594.17058168[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 1084
Total_scans       = 1084

X_90_width        = 11.6[us]
X_acq_time        = 0.69730304[s]
X_angle           = 45[deg]
X_atn             = 8[dB]
X_pulse           = 5.8[us]
Irr_atn_dec       = 20.5[dB]
Irr_atn_noe       = 20.5[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 60
Relaxation_delay  = 2[s]
Repetition_time   = 2.69730304[s]
Temp_get          = 23.5[dC]
```

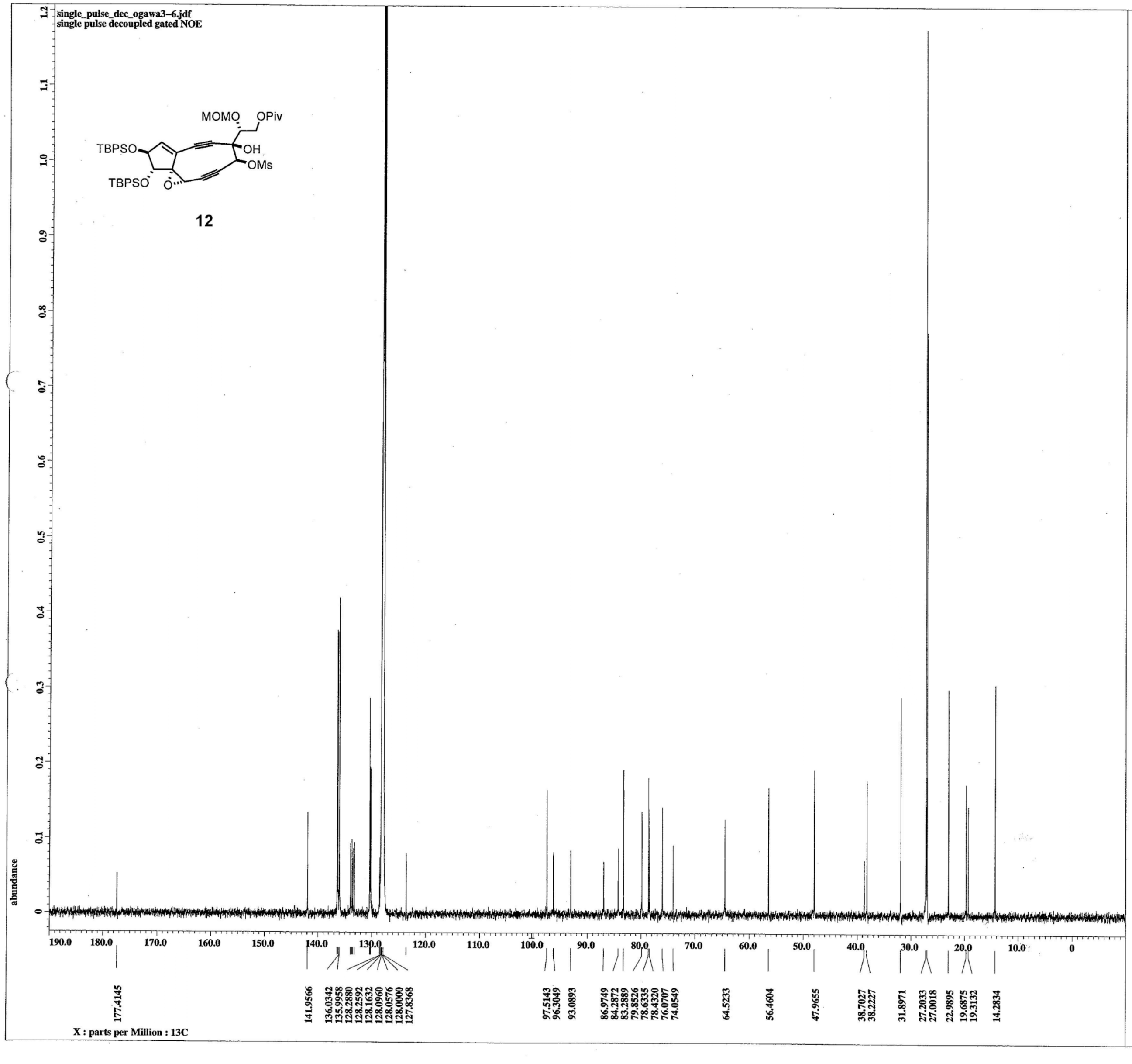


```
Filename          = single_pulse_ogawa1-8
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = a
Solvent           = BENZENE-D6
Creation_time     = 26-SEP-2006 10:41:27
Revision_time     = 26-SEP-2006 10:29:50
Current_time      = 26-SEP-2006 10:30:43

Content           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 52428
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA600SL
Spectrometer      = DELTA2_NMR

Field_strength    = 13.95540559[T] (590[M
X_acq_duration    = 5.88251136[s]
X_domain          = 1H
X_freq            = 594.17058168[MHz]
X_offset          = 5[ppm]
X_points          = 65536
X_prescans        = 1
X_resolution      = 0.16999542[Hz]
X_sweep           = 11.14081996[kHz]
Irr_domain        = 1H
Irr_freq          = 594.17058168[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 594.17058168[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 15[us]
X_acq_time        = 5.88251136[s]
X_angle           = 45[deg]
X_atn             = 8.5[dB]
X_pulse           = 7.5[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 42
Relaxation_delay  = 2[s]
Repetition_time   = 7.88251136[s]
Temp_get          = 24.2[dC]
```



```
Filename           = single_pulse_dec_ogaw
Author             = delta
Experiment         = single_pulse_dec
Sample_id          = a
Solvent            = BENZENE-D6
Creation_time      = 26-SEP-2006 12:57:12
Revision_time      = 26-SEP-2006 14:17:39
Current_time       = 26-SEP-2006 14:18:51

Content            = single pulse decouple
Data_format        = 1D REAL
Dim_size           = 26214
Dim_title          = 13C
Dim_units          = [ppm]
Dimensions         = X
Site               = ECA600SL
Spectrometer       = DELTA2_NMR

Field_strength     = 13.95540559[T] (590[M
X_acq_duration     = 0.69730304[s]
X_domain           = 13C
X_freq             = 149.40429612[MHz]
X_offset           = 100[ppm]
X_points           = 32768
X_prescans         = 4
X_resolution       = 1.43409672[Hz]
X_sweep            = 46.9924812[kHz]
Irr_domain         = 1H
Irr_freq           = 594.17058168[MHz]
Irr_offset         = 5[ppm]
Clipped            = TRUE
Mod_return         = 1
Scans              = 2883
Total_scans        = 2883

X_90_width         = 11.6[us]
X_acq_time         = 0.69730304[s]
X_angle            = 45[deg]
X_atn              = 8[dB]
X_pulse            = 5.8[us]
Irr_atn_dec        = 20.5[dB]
Irr_atn_noe        = 20.5[dB]
Irr_noise          = WALTZ
Decoupling         = TRUE
Initial_wait       = 1[s]
Noe                = TRUE
Noe_time           = 2[s]
Recvr_gain         = 60
Relaxation_delay   = 2[s]
Repetition_time    = 2.69730304[s]
Temp_get           = 25.3[dC]
```

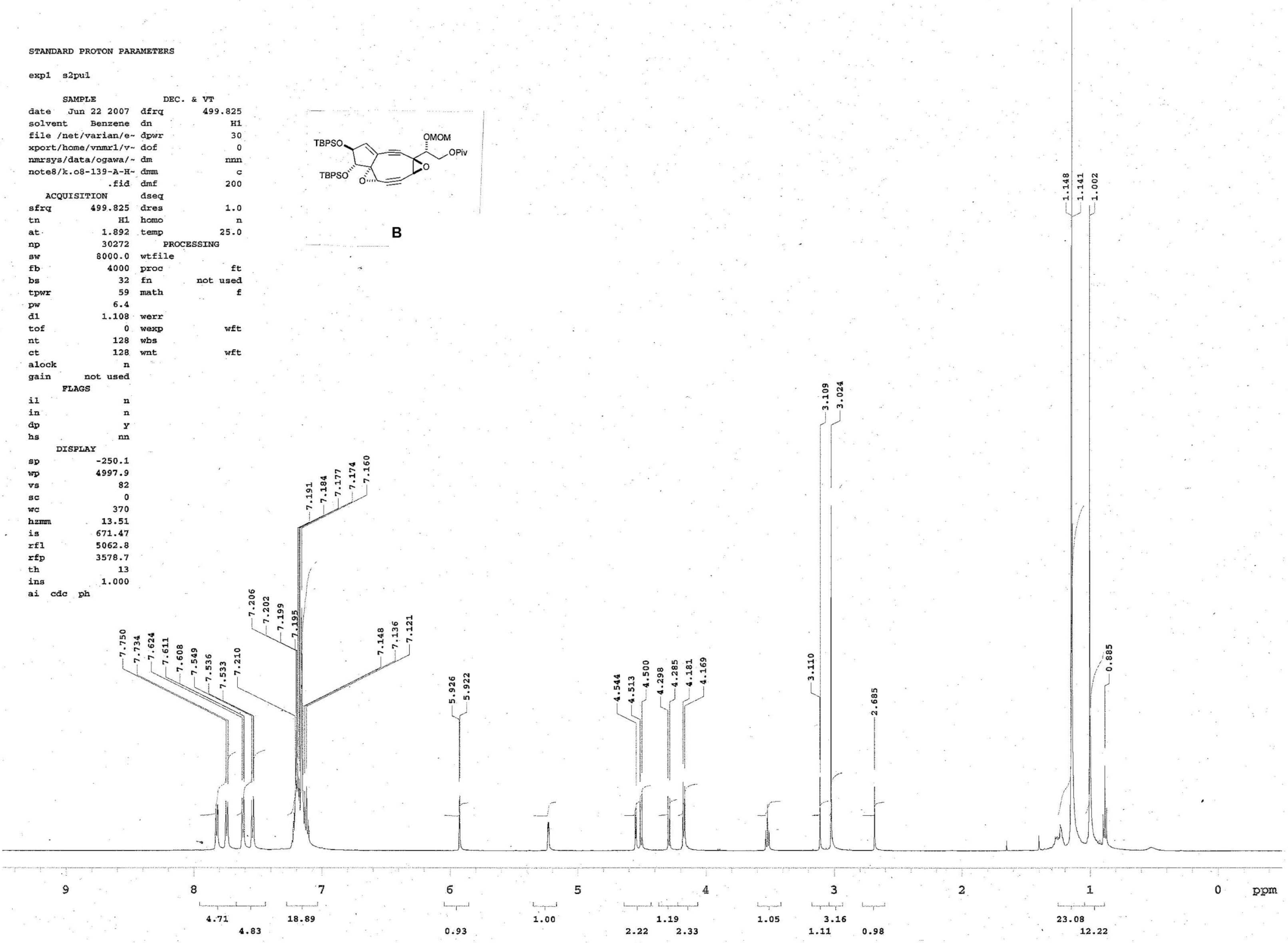

single_pulse_ogawa3–6.jdf
single_pulse
MOMO
OPiv
TBPSO
OH
OMs
TBPSO
O
12
8.881
25.376
0.992
1.0
0.991
1.006
2.003
1.122
1.092
1.005
4.377
0.989
3.115
48.904
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.6473
7.6338
7.5837
7.5723
7.5703
7.1929
7.1500
7.1469
5.9186
5.9146
5.6637
5.1730
4.5682
4.5622
4.4972
4.4941
4.4858
3.9668
3.9605
3.9565
3.1328
3.1285
3.1193
2.5431
2.3523
2.3357
1.2233
1.2190
1.1361
1.0725
1.0145
0.8883
0.8766
0.8645
X : parts per Million : 1H
Filename = single_pulse_ogawa3-6
Author = delta
Experiment = single_pulse.ex2
Sample_id = a
Solvent = BENZENE-D6
Creation_time = 29-SEP-2006 14:55:34
Revision_time = 29-SEP-2006 14:44:46
Current_time = 29-SEP-2006 14:45:41
Content = single_pulse
Data_format = 1D COMPLEX
Dim_size = 52428
Dim_title = 1H
Dim_units = [ppm]
Dimensions = X
Site = ECA600SL
Spectrometer = DELTA2_NMR
Field_strength = 13.95540559[T] (590[M
X_acq_duration = 5.88251136[s]
X_domain = 1H
X_freq = 594.17058168[MHz]
X_offset = 5[ppm]
X_points = 65536
X_prescans = 1
X_resolution = 0.16999542[Hz]
X_sweep = 11.14081996[kHz]
Irr_domain = 1H
Irr_freq = 594.17058168[MHz]
Irr_offset = 5[ppm]
Tri_domain = 1H
Tri_freq = 594.17058168[MHz]
Tri_offset = 5[ppm]
Clipped = FALSE
Mod_return = 1
Scans = 8
Total_scans = 8
X_90_width = 15[us]
X_acq_time = 5.88251136[s]
X_angle = 45[deg]
X_atn = 8.5[dB]
X_pulse = 7.5[us]
Irr_mode = Off
Tri_mode = Off
Dante_presat = FALSE
Initial_wait = 1[s]
Recvr_gain = 40
Relaxation_delay = 2[s]
Repetition_time = 7.88251136[s]
Temp_get = 23.4[dC]



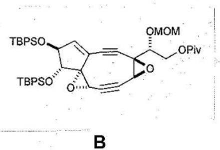
```
Filename          = single_pulse_dec_ogaw
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = a
Solvent           = BENZENE-D6
Creation_time     = 29-SEP-2006 15:51:32
Revision_time     = 29-SEP-2006 15:23:55
Current_time      = 29-SEP-2006 15:24:53

Content           = single pulse decouple
Data_format       = 1D REAL
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA600SL
Spectrometer      = DELTA2_NMR

Field_strength    = 13.95540559[T] (590[M
X_acq_duration    = 0.69730304[s]
X_domain          = 13C
X_freq            = 149.40429612[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.43409672[Hz]
X_sweep           = 46.9924812[kHz]
Irr_domain        = 1H
Irr_freq          = 594.17058168[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 1116
Total_scans       = 1116

X_90_width        = 11.6[us]
X_acq_time        = 0.69730304[s]
X_angle           = 50[deg]
X_atn             = 8[dB]
X_pulse           = 6.44444444[us]
Irr_atn_dec       = 20.5[dB]
Irr_atn_noe       = 20.5[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 60
Relaxation_delay  = 2[s]
Repetition_time   = 2.69730304[s]
Temp_get          = 24.7[dC]
```

```
STANDARD PROTON PARAMETERS

exp1  s2pul

      SAMPLE              DEC. & VT
date   Jun 22 2007  dfrq        499.825
solvent    Benzene  dn               H1
file /net/varian/e~ dpwr             30
xport/home/vnmr1/v~ dof               0
nmrsys/data/ogawa/~ dm              nnn
note8/k.o8-139-A-H~ dmm               c
              .fid  dmf             200
   ACQUISITION      dseq
sfrq       499.825  dres            1.0
tn              H1  homo              n
at           1.892  temp           25.0
np           30272      PROCESSING
sw          8000.0  wtfile
fb            4000  proc             ft
bs              32  fn         not used
tpwr            59  math              f
pw             6.4
d1           1.108  werr
tof              0  wexp            wft
nt             128  wbs
ct             128  wnt             wft
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
hs              nn
     DISPLAY
sp          -250.1
wp          4997.9
vs              82
sc               0
wc             370
hzmm         13.51
is          671.47
rfl         5062.8
rfp         3578.7
th              13
ins          1.000
ai  cdc  ph
```

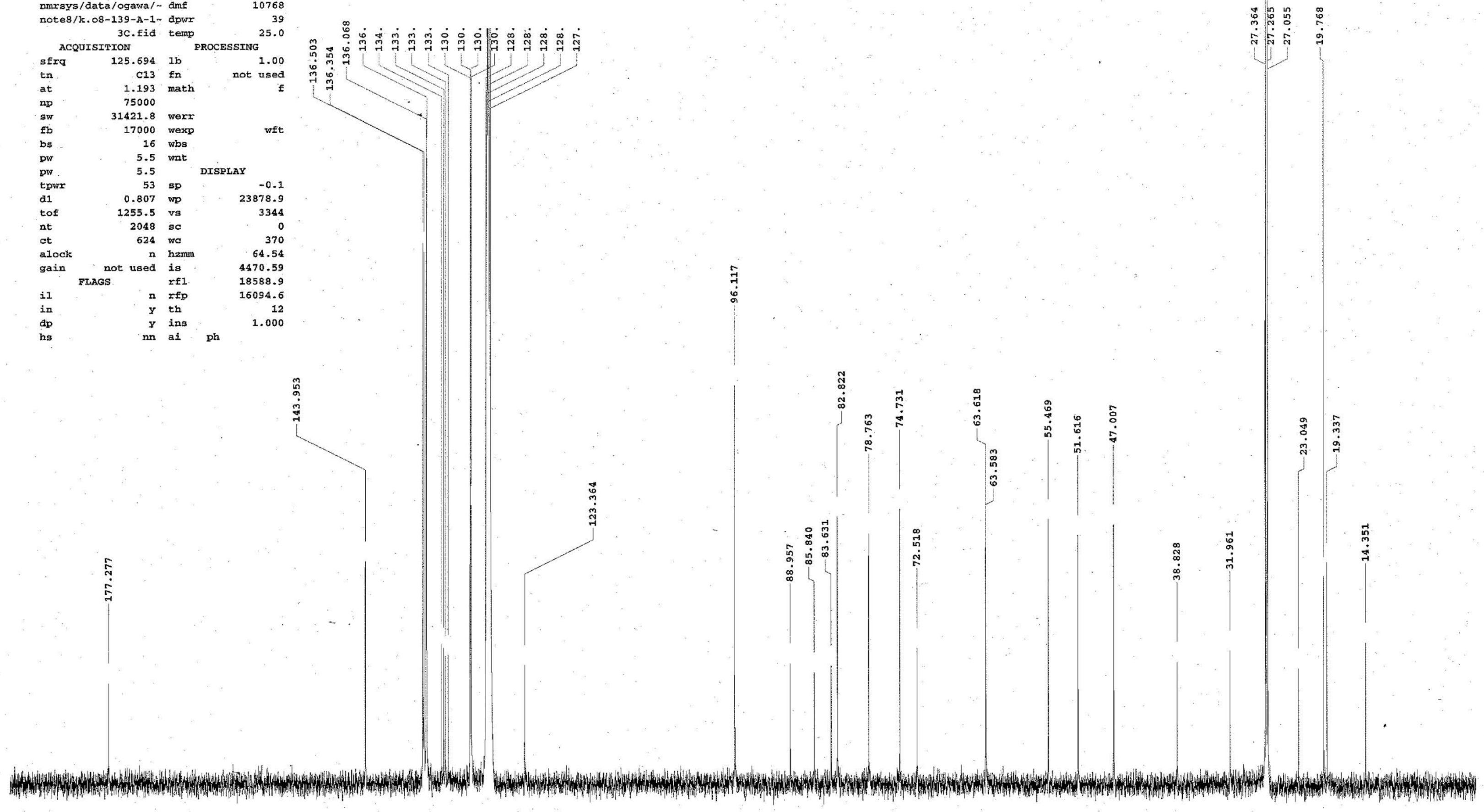
B

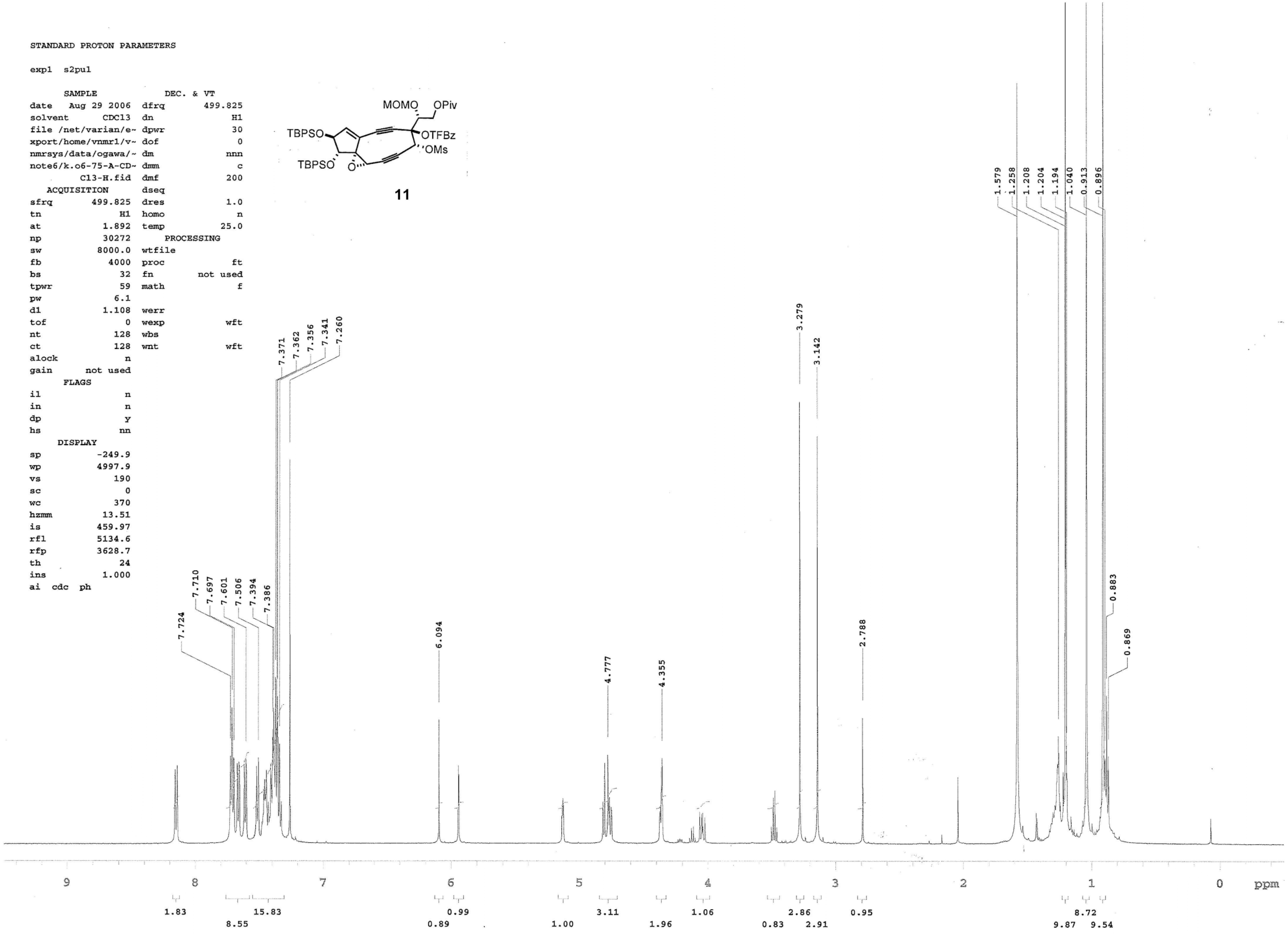


```
13C SENSITIVITY
ASTM SAMPLE

exp1  s2pul

      SAMPLE            DEC. & VT
date   Jun 22 2007  dn            H1
solvent    Benzene  dof       -829.0
file /net/varian/e~ dm           yyy
xport/home/vnmr1/v~ dmm            w
nmrsys/data/ogawa/~ dmf        10768
note8/k.o8-139-A-1~ dpwr          39
           3C.fid   temp        25.0
   ACQUISITION         PROCESSING
sfrq       125.694  lb          1.00
tn             C13  fn      not used
at           1.193  math           f
np           75000
sw         31421.8  werr
fb           17000  wexp         wft
bs              16  wbs
pw             5.5  wnt
pw             5.5      DISPLAY
tpwr            53  sp          -0.1
d1           0.807  wp       23878.9
tof         1255.5  vs          3344
nt            2048  sc             0
ct             624  wc           370
alock            n  hzmm       64.54
gain      not used  is       4470.59
     FLAGS          rfl      18588.9
il               n  rfp      16094.6
in               y  th            12
dp               y  ins        1.000
hs              nn  ai    ph
```



B

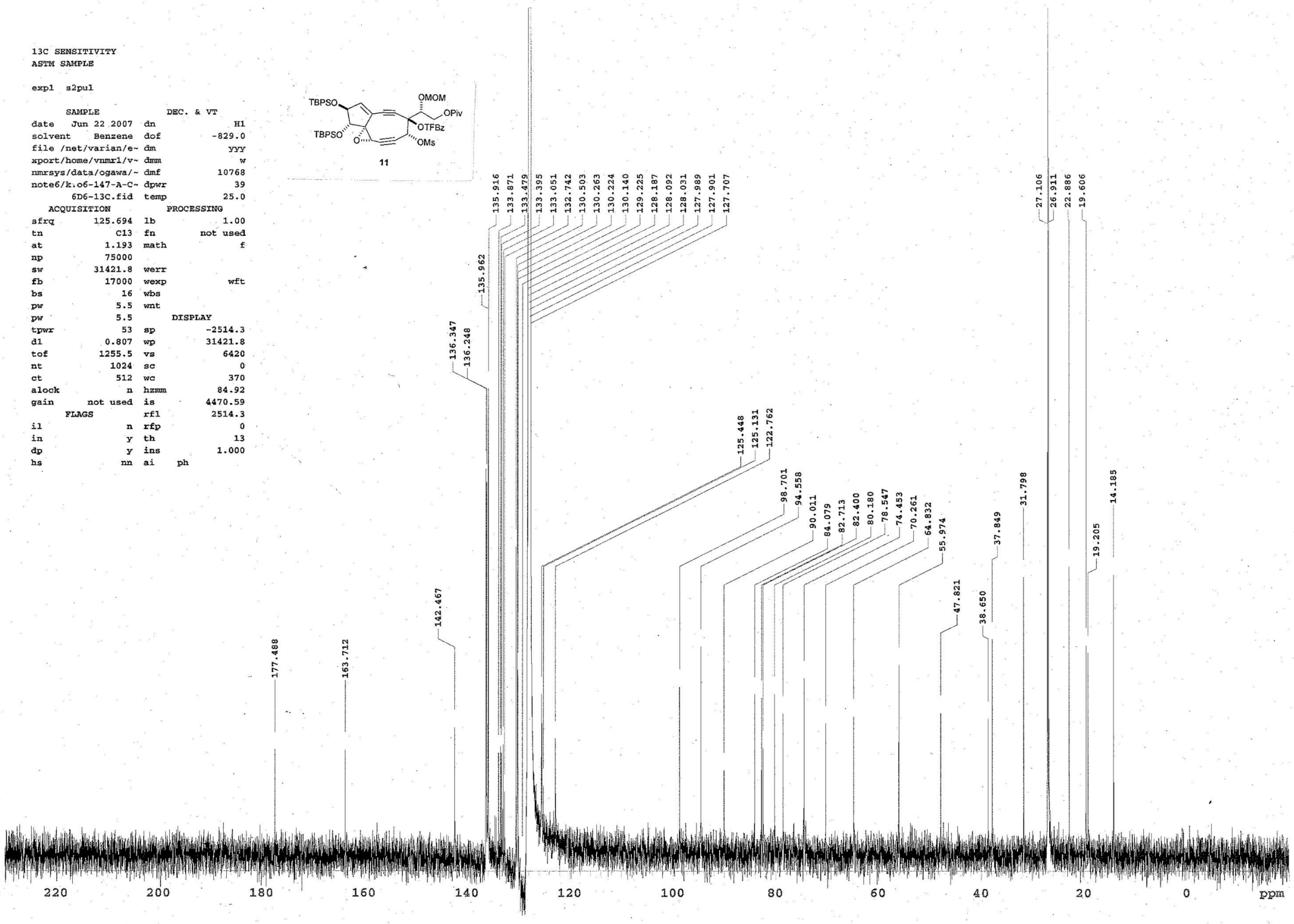




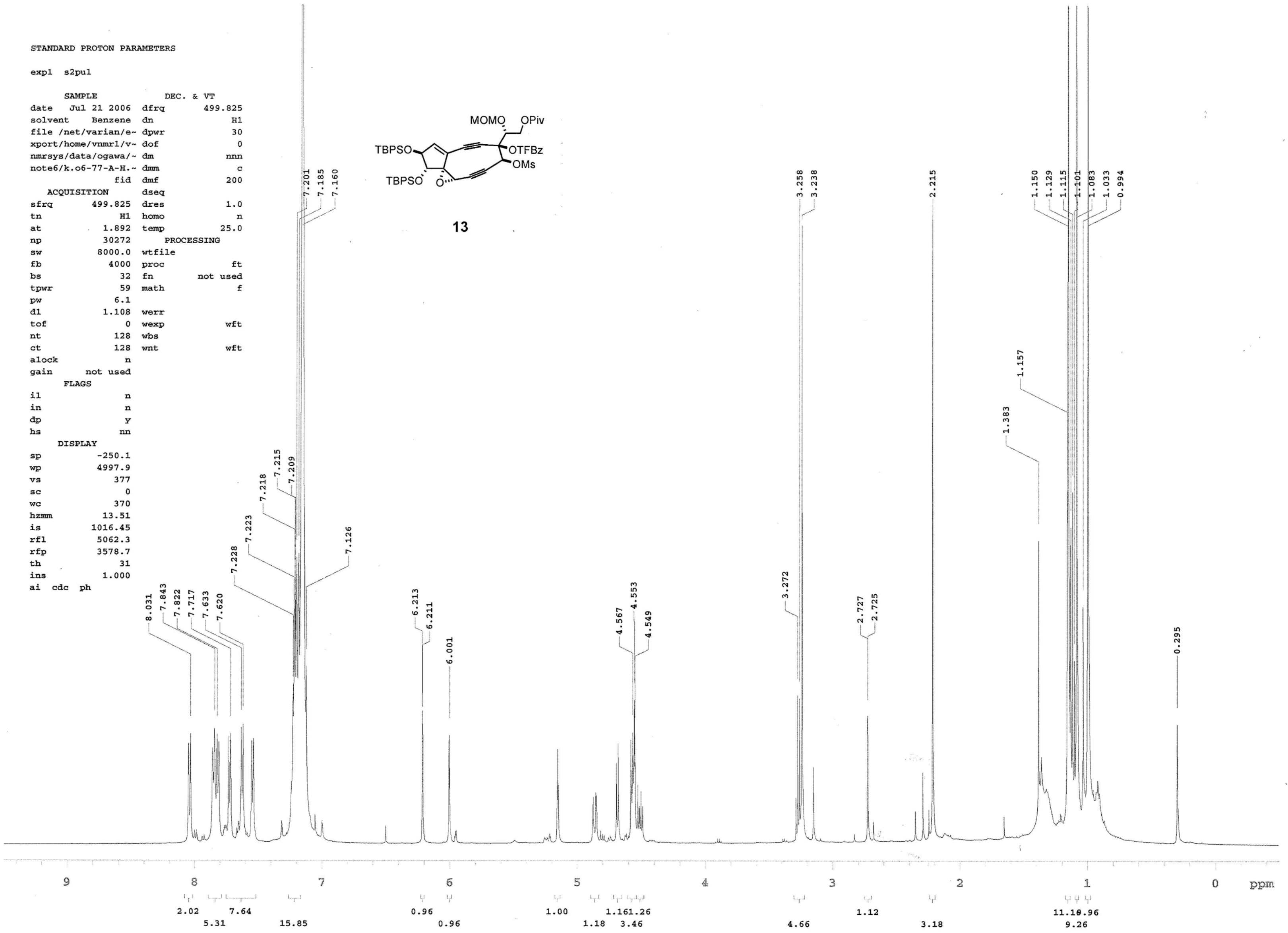
```
STANDARD PROTON PARAMETERS

exp1  s2pul

      SAMPLE            DEC. & VT
date   Aug 29 2006  dfrq        499.825
solvent      CDCl3  dn               H1
file /net/varian/e~ dpwr             30
xport/home/vnmr1/v~ dof               0
nmrsys/data/ogawa/~ dm              nnn
note6/k.o6-75-A-CD~ dmm               c
         C13-H.fid  dmf             200
   ACQUISITION      dseq
sfrq       499.825  dres            1.0
tn              H1  homo              n
at           1.892  temp           25.0
np           30272      PROCESSING
sw          8000.0  wtfile
fb            4000  proc             ft
bs              32  fn         not used
tpwr            59  math              f
pw             6.1
d1           1.108  werr
tof              0  wexp            wft
nt             128  wbs
ct             128  wnt             wft
alock            n
gain      not used
       FLAGS
il               n
in               n
dp               y
hs              nn
      DISPLAY
sp          -249.9
wp          4997.9
vs             190
sc               0
wc             370
hzmm         13.51
is          459.97
rfl         5134.6
rfp         3628.7
th              24
ins          1.000
ai  cdc  ph
```

11

```
13C SENSITIVITY
ASTM SAMPLE

exp1  s2pul

      SAMPLE              DEC. & VT
date   Jun 22 2007  dn               H1
solvent    Benzene  dof          -829.0
file /net/varian/e~ dm              yyy
xport/home/vnmr1/v~ dmm               w
nmrsys/data/ogawa/~ dmf           10768
note6/k.o6-147-A-C~ dpwr             39
       6D6-13C.fid  temp           25.0
   ACQUISITION          PROCESSING
sfrq       125.694  lb             1.00
tn             C13  fn         not used
at           1.193  math              f
np           75000
sw         31421.8  werr
fb           17000  wexp            wft
bs              16  wbs
pw             5.5  wnt
pw             5.5       DISPLAY
tpwr            53  sp          -2514.3
d1           0.807  wp          31421.8
tof         1255.5  vs             6420
nt            1024  sc                0
ct             512  wc              370
alock            n  hzmm          84.92
gain      not used  is          4470.59
      FLAGS         rfl          2514.3
il               n  rfp               0
in               y  th               13
dp               y  ins           1.000
hs              nn  ai    ph
```

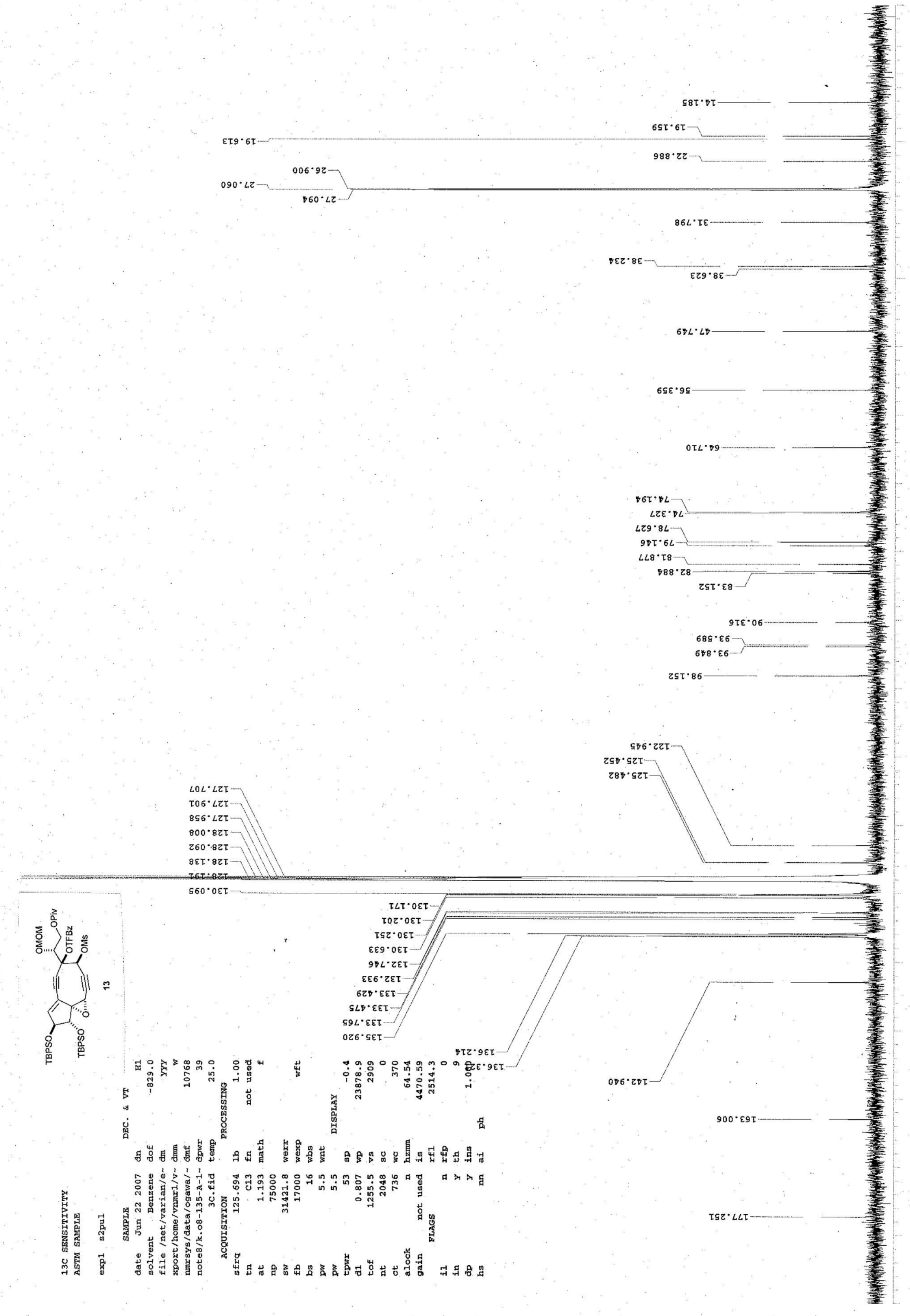


11

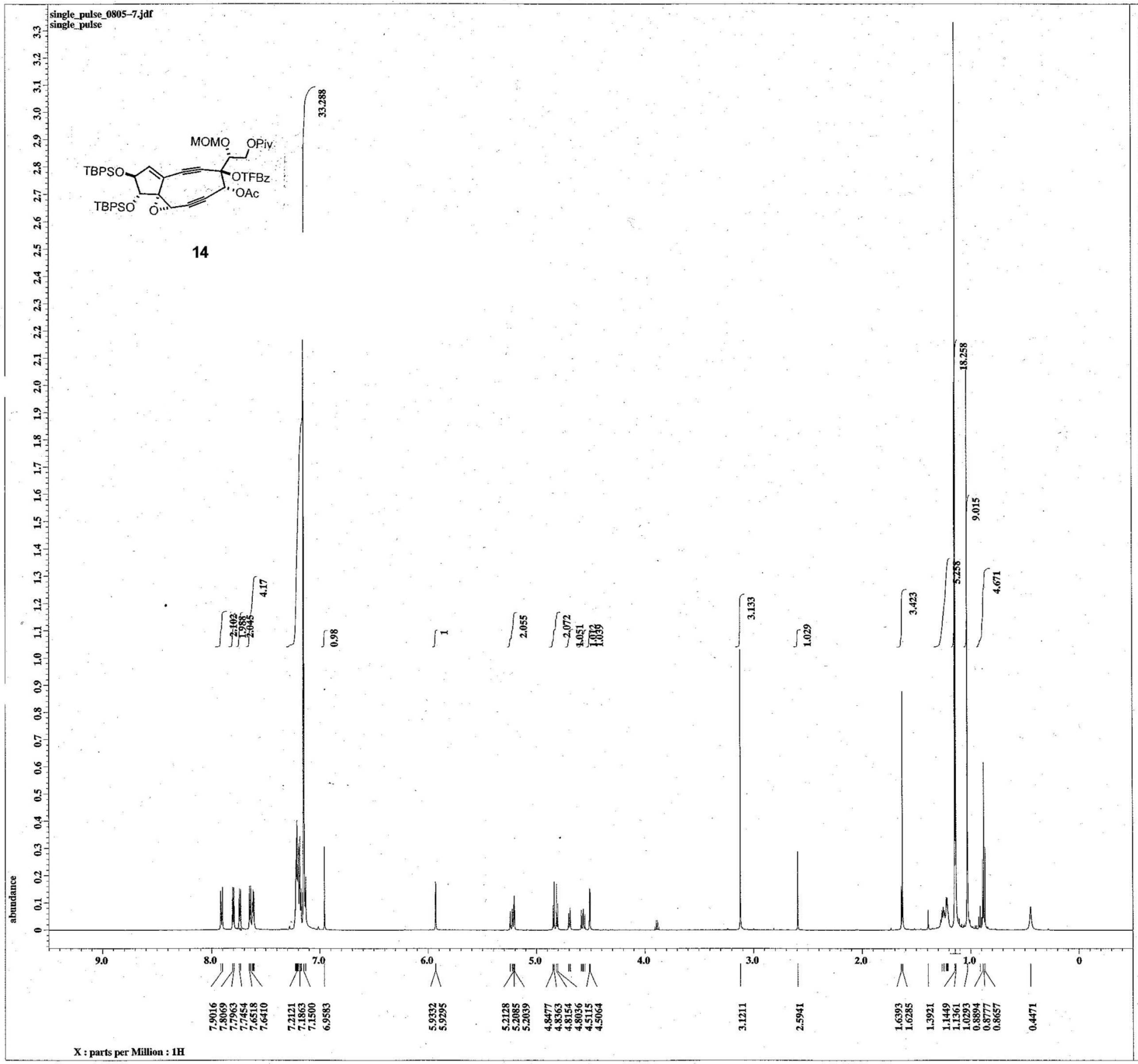


13

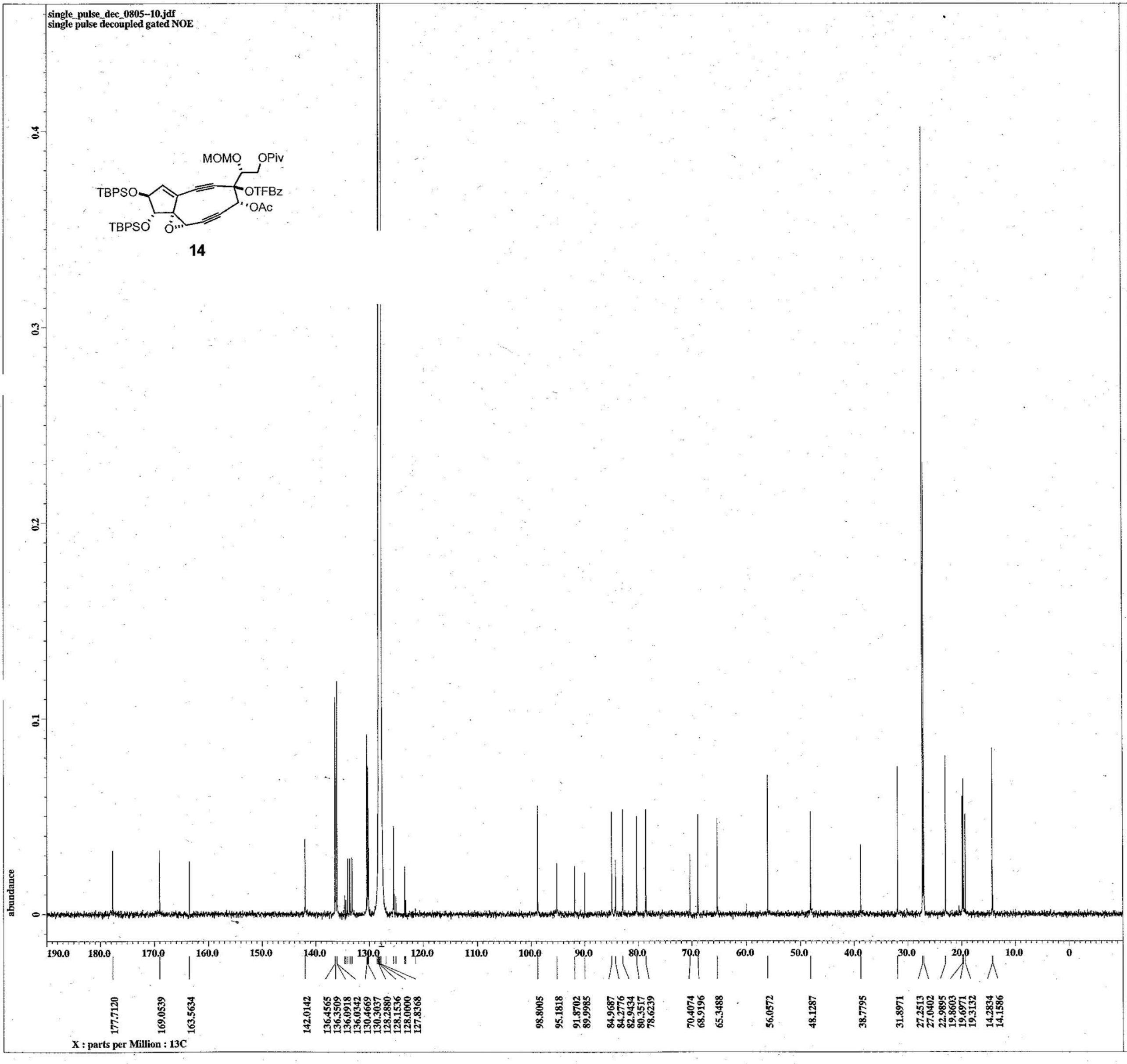
```
STANDARD PROTON PARAMETERS

exp1  s2pul

      SAMPLE              DEC. & VT
date   Jul 21 2006  dfrq        499.825
solvent    Benzene  dn               H1
file /net/varian/e~ dpwr             30
xport/home/vnmr1/v~ dof               0
nmrsys/data/ogawa/~ dm              nnn
note6/k.o6-77-A-H.~ dmm               c
               fid  dmf             200
   ACQUISITION      dseq
sfrq       499.825  dres            1.0
tn              H1  homo              n
at           1.892  temp           25.0
np           30272       PROCESSING
sw          8000.0  wtfile
fb            4000  proc             ft
bs              32  fn         not used
tpwr            59  math              f
pw             6.1
d1           1.108  werr
tof              0  wexp            wft
nt             128  wbs
ct             128  wnt             wft
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
hs              nn
     DISPLAY
sp          -250.1
wp          4997.9
vs             377
sc               0
wc             370
hzmm         13.51
is         1016.45
rfl         5062.3
rfp         3578.7
th              31
ins          1.000
ai  cdc  ph
```



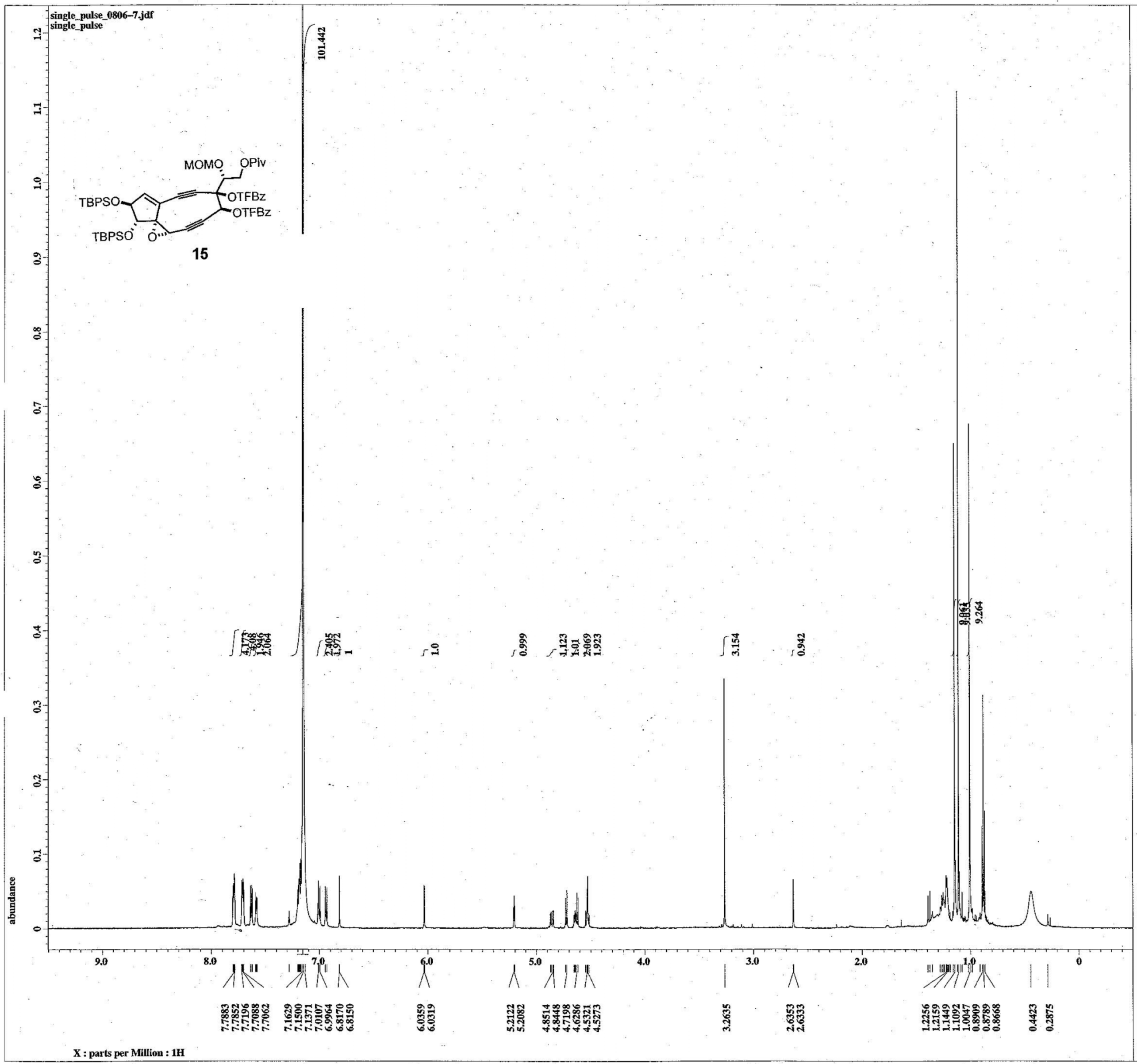
```
13C SENSITIVITY
ASTM SAMPLE

exp1  s2pul

      SAMPLE              DEC. & VT
date   Jun 22 2007   dn            H1
solvent    Benzene   dof       -829.0
file /net/varian/e~  dm           yyy
xport/home/vnmr1/v~  dmm            w
nmrsys/data/ogawa/~  dmf        10768
note8/k.o8-135-A-1~  dpwr          39
           3C.fid    temp        25.0
   ACQUISITION          PROCESSING
sfrq       125.694   lb          1.00
tn             C13   fn      not used
at           1.193   math           f
np           75000
sw         31421.8   werr
fb           17000   wexp         wft
bs              16   wbs
pw             5.5   wnt
pw             5.5       DISPLAY
tpwr            53   sp          -0.4
d1           0.807   wp       23878.9
tof         1255.5   vs          2909
nt            2048   sc             0
ct             736   wc           370
alock            n   hzmm       64.54
gain      not used   is       4470.59
      FLAGS          rfl       2514.3
il               n   rfp            0
in               y   th             9
dp               y   ins        1.000
hs              nn   ai    ph
```



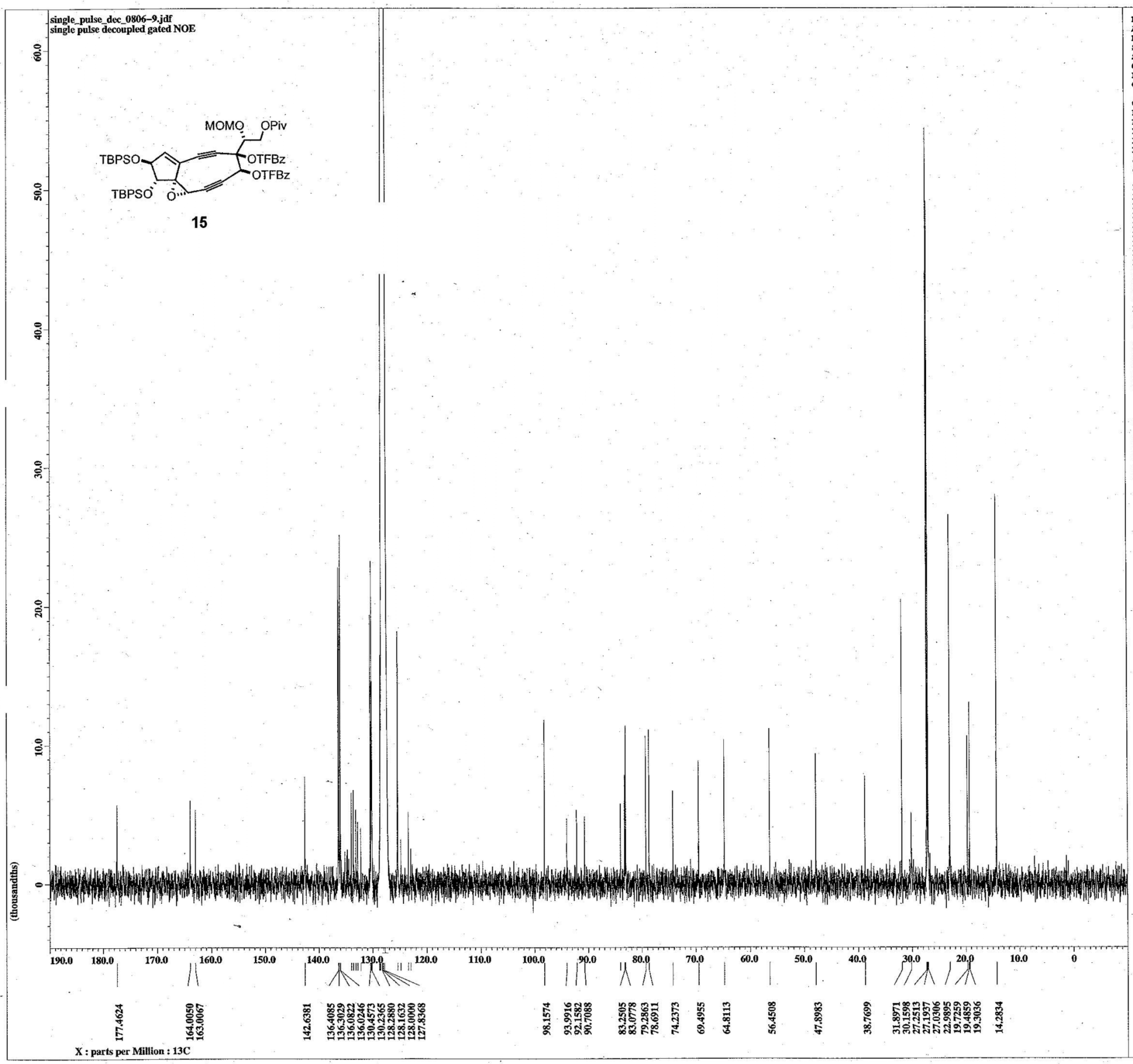
```
Filename          = single_pulse_0805-7.j
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = a
Solvent           = BENZENE-D6
Creation_time     =  6-AUG-2007 14:47:00
Revision_time     =  6-AUG-2007 15:12:20
Current_time      =  6-AUG-2007 15:12:27

Content           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 52428
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA600SL
Spectrometer      = DELTA2_NMR

Field_strength    = 13.95540559[T] (590[M
X_acq_duration    = 5.88251136[s]
X_domain          = 1H
X_freq            = 594.17058168[MHz]
X_offset          = 5[ppm]
X_points          = 65536
X_prescans        = 1
X_resolution      = 0.16999542[Hz]
X_sweep           = 11.14081996[kHz]
Irr_domain        = 1H
Irr_freq          = 594.17058168[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 594.17058168[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 16
Total_scans       = 16

X_90_width        = 14[us]
X_acq_time        = 5.88251136[s]
X_angle           = 45[deg]
X_atn             = 8.5[dB]
X_pulse           = 7[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 44
Relaxation_delay  = 2[s]
Repetition_time   = 7.88251136[s]
Temp_get          = 23.1[dC]
```



```
Filename          = single_pulse_dec_0805
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = a
Solvent           = BENZENE-D6
Creation_time     =  7-AUG-2007 01:11:41
Revision_time     =  7-AUG-2007 08:45:46
Current_time      =  7-AUG-2007 08:46:55

Content           = single pulse decouple
Data_format       = 1D REAL
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA600SL
Spectrometer      = DELTA2_NMR

Field_strength    = 13.95540559[T] (590[M
X_acq_duration    = 0.69730304[s]
X_domain          = 13C
X_freq            = 149.40429612[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.43409672[Hz]
X_sweep           = 46.9924812[kHz]
Irr_domain        = 1H
Irr_freq          = 594.17058168[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 10000
Total_scans       = 10000

X_90_width        = 11.2[us]
X_acq_time        = 0.69730304[s]
X_angle           = 40[deg]
X_atn             = 8[dB]
X_pulse           = 4.97777778[us]
Irr_atn_dec       = 20.5[dB]
Irr_atn_noe       = 20.5[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 3[s]
Recvr_gain        = 58
Relaxation_delay  = 3[s]
Repetition_time   = 3.69730304[s]
Temp_get          = 24.8[dC]
```

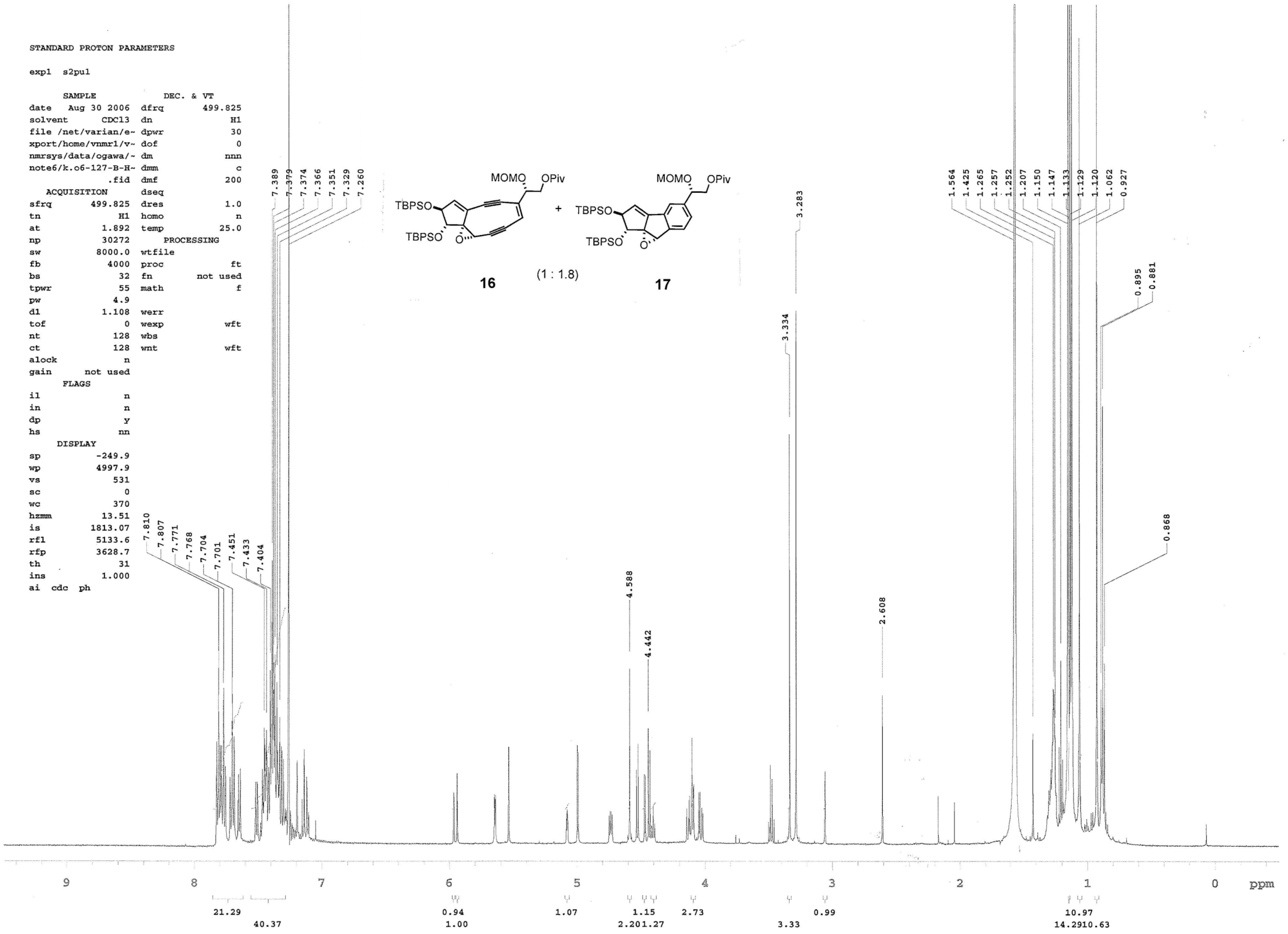


```
Filename          = single_pulse_0806-7.j
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = a
Solvent           = BENZENE-D6
Creation_time     =  7-AUG-2007 10:53:55
Revision_time     =  7-AUG-2007 11:04:00
Current_time      =  7-AUG-2007 11:04:25

Content           = single_pulse
Data_format       = 1D COMPLEX
Dim_size          = 52428
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA600SL
Spectrometer      = DELTA2_NMR

Field_strength    = 13.95540559[T] (590[M
X_acq_duration    = 5.88251136[s]
X_domain          = 1H
X_freq            = 594.17058168[MHz]
X_offset          = 5[ppm]
X_points          = 65536
X_prescans        = 1
X_resolution      = 0.16999542[Hz]
X_sweep           = 11.14081996[kHz]
Irr_domain        = 1H
Irr_freq          = 594.17058168[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 594.17058168[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 32
Total_scans       = 32

X_90_width        = 14[us]
X_acq_time        = 5.88251136[s]
X_angle           = 45[deg]
X_atn             = 8.5[dB]
X_pulse           = 7[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 48
Relaxation_delay  = 2[s]
Repetition_time   = 7.88251136[s]
Temp_get          = 22.7[dC]
```

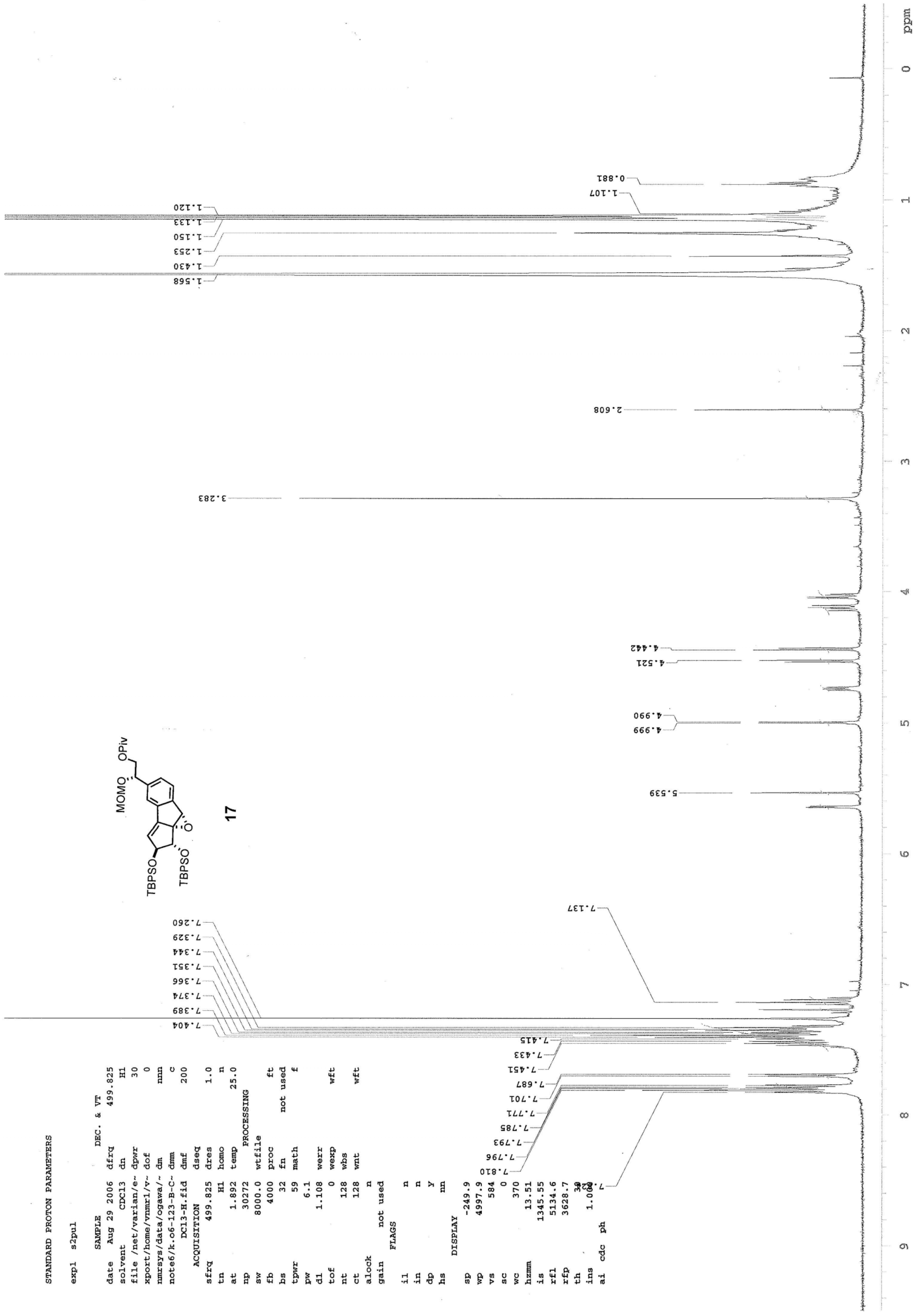


```
Filename          = single_pulse_dec_0806
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = a
Solvent           = BENZENE-D6
Creation_time     =  8-AUG-2007 07:31:01
Revision_time     =  8-AUG-2007 08:45:28
Current_time      =  8-AUG-2007 08:46:06

Content           = single pulse decouple
Data_format       = 1D REAL
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECA600SL
Spectrometer      = DELTA2_NMR

Field_strength    = 13.95540559[T] (590[M
X_acq_duration    = 0.69730304[s]
X_domain          = 13C
X_freq            = 149.40429612[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.43409672[Hz]
X_sweep           = 46.9924812[kHz]
Irr_domain        = 1H
Irr_freq          = 594.17058168[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 20000
Total_scans       = 20000

X_90_width        = 11.2[us]
X_acq_time        = 0.69730304[s]
X_angle           = 40[deg]
X_atn             = 8[dB]
X_pulse           = 4.97777778[us]
Irr_atn_dec       = 20.5[dB]
Irr_atn_noe       = 20.5[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 3[s]
Recvr_gain        = 58
Relaxation_delay  = 3[s]
Repetition_time   = 3.69730304[s]
Temp_get          = 24.6[dC]
```

```
STANDARD PROTON PARAMETERS

exp1  s2pul

      SAMPLE            DEC. & VT
date   Aug 30 2006 dfrq        499.825
solvent      CDCl3 dn               H1
file /net/varian/e~ dpwr             30
xport/home/vnmr1/v~ dof               0
nmrsys/data/ogawa/~ dm              nnn
note6/k.o6-127-B-H~ dmm               c
              .fid dmf              200
   ACQUISITION     dseq
sfrq       499.825 dres             1.0
tn              H1 homo               n
at           1.892 temp            25.0
np           30272       PROCESSING
sw          8000.0 wtfile
fb            4000 proc              ft
bs              32 fn          not used
tpwr            55 math               f
pw             4.9
d1           1.108 werr
tof              0 wexp             wft
nt             128 wbs
ct             128 wnt              wft
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
hs              nn
     DISPLAY
sp          -249.9
wp          4997.9
vs             531
sc               0
wc             370
hzmm         13.51
is         1813.07
rfl         5133.6
rfp         3628.7
th              31
ins          1.000
ai  cdc  ph
```

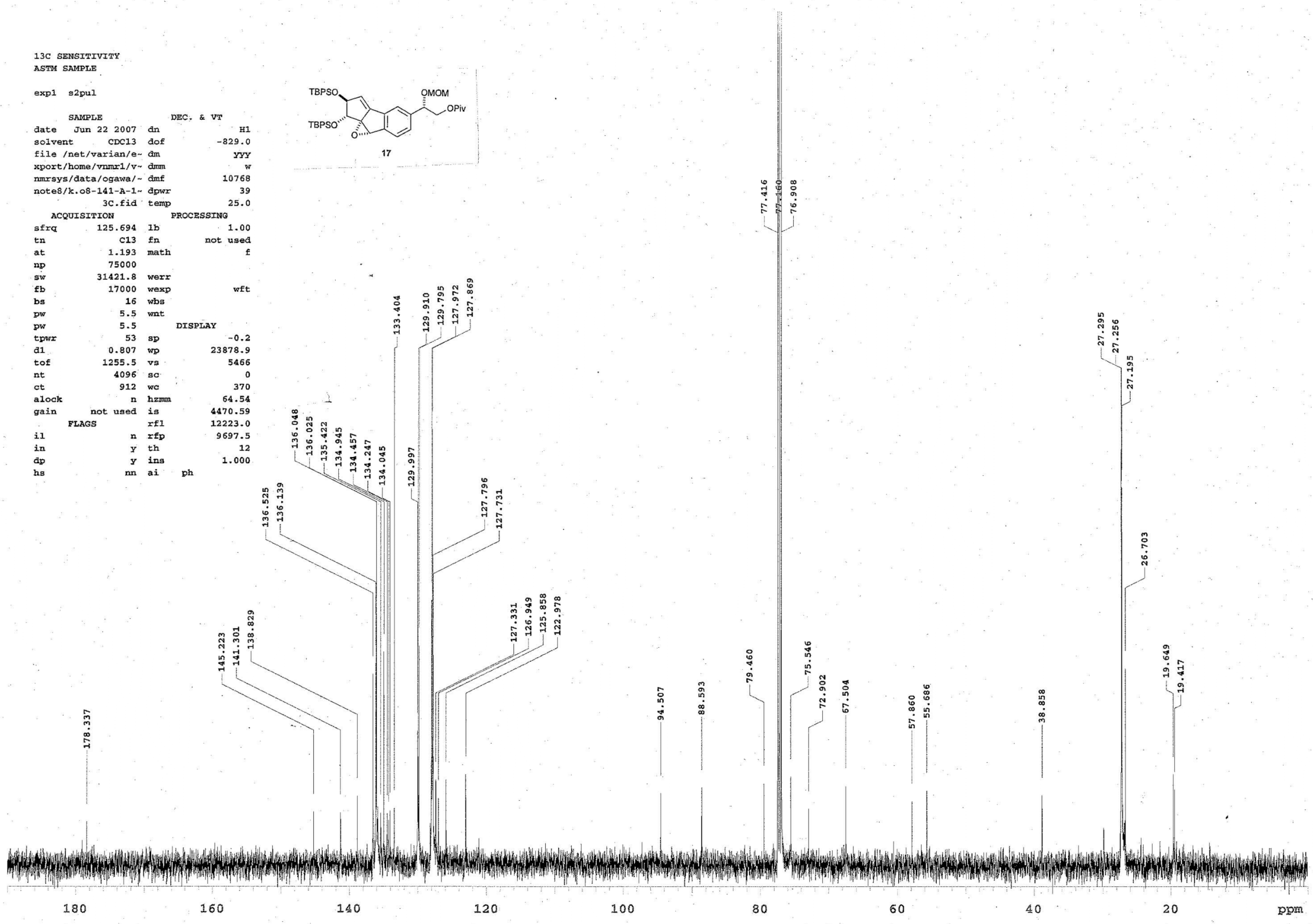


16 (1 : 1.8) **17**



17

```
STANDARD PROTON PARAMETERS

exp1  s2pul

     SAMPLE              DEC. & VT
date  Aug 29 2006   dfrq      499.825
solvent     CDCl3   dn             H1
file /net/varian/e~ dpwr           30
xport/home/vnmr1/v~ dof             0
nmrsys/data/ogawa/~ dm            nnn
note6/k.o6-123-B-C~ dmm             c
     DC13-H.fid     dmf           200
    ACQUISITION     dseq
sfrq      499.825   dres          1.0
tn             H1   homo            n
at          1.892   temp         25.0
np          30272        PROCESSING
sw         8000.0   wtfile
fb           4000   proc           ft
bs             32   fn       not used
tpwr           59   math            f
pw            6.1
d1          1.108   werr
tof             0   wexp          wft
nt            128   wbs
ct            128   wnt           wft
alock           n
gain     not used
      FLAGS
il              n
in              n
dp              y
hs             nn
     DISPLAY
sp         -249.9
wp         4997.9
vs            584
sc              0
wc            370
hzmm        13.51
is        1345.55
rfl        5134.6
rfp        3628.7
th             30
ins         1.000
ai  cdc  ph
```



```
13C SENSITIVITY
ASTM SAMPLE

exp1  s2pul

      SAMPLE            DEC. & VT
date   Jun 22 2007  dn              H1
solvent      CDC13  dof         -829.0
file /net/varian/e~ dm             yyy
xport/home/vnmr1/v~ dmm              w
nmrsys/data/ogawa/~ dmf          10768
note8/k.o8-141-A-1~ dpwr            39
           3C.fid   temp          25.0
   ACQUISITION          PROCESSING
sfrq       125.694  lb            1.00
tn             C13  fn        not used
at           1.193  math             f
np           75000
sw         31421.8  werr
fb           17000  wexp           wft
bs              16  wbs
pw             5.5  wnt
pw             5.5       DISPLAY
tpwr            53  sp            -0.2
d1           0.807  wp         23878.9
tof         1255.5  vs            5466
nt            4096  sc               0
ct             912  wc             370
alock            n  hzmm         64.54
gain      not used  is         4470.59
      FLAGS         rfl        12223.0
il               n  rfp         9697.5
in               y  th              12
dp               y  ins          1.000
hs              nn  ai    ph
```