Supporting Information

A Model Study for the Concise Construction of the Cortistatins Oxapentacyclic Core through Intramolecular Diels-Alder Reaction and Oxidative Dearomatization Cyclization

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General Information

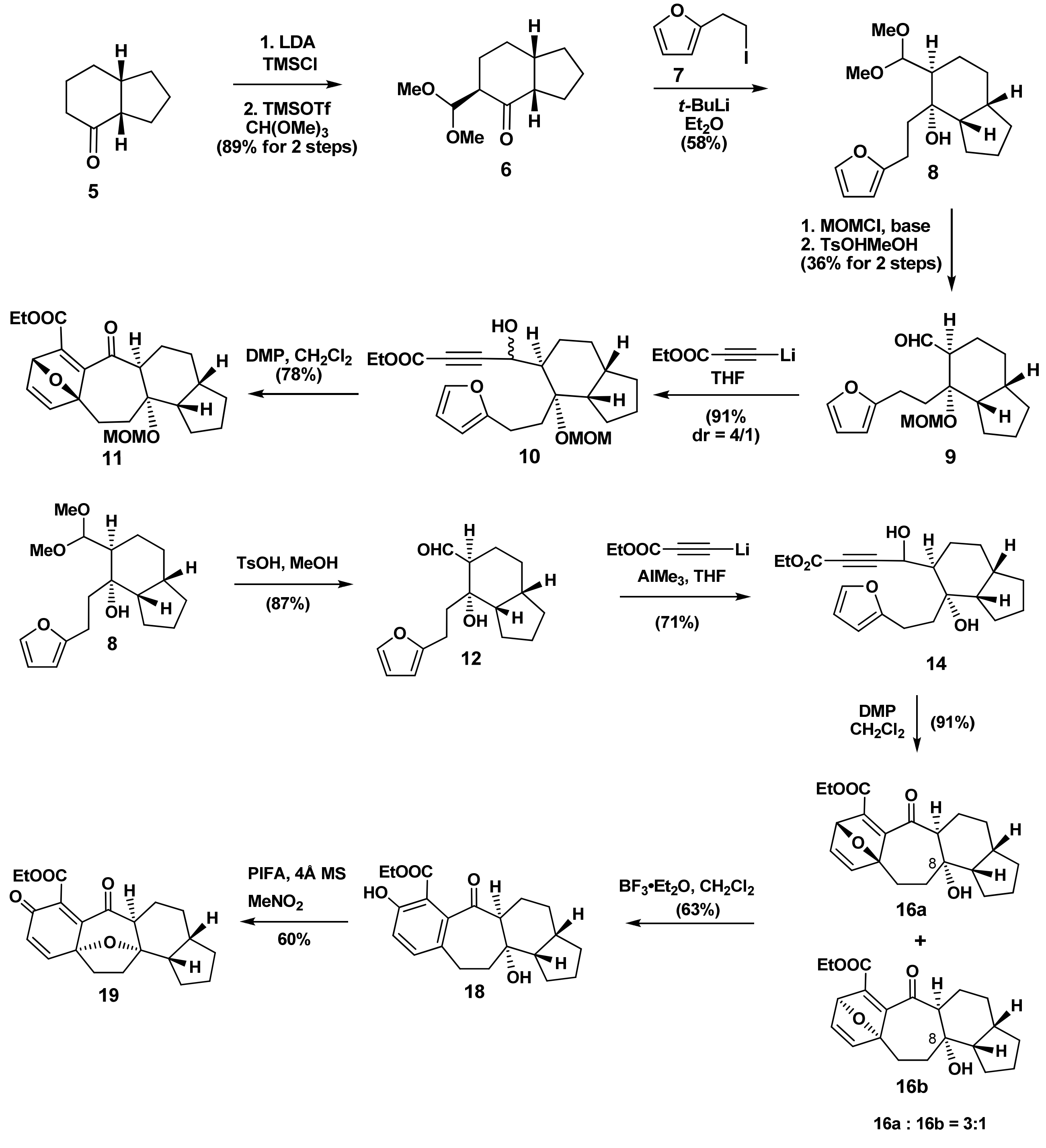
All reactions were carried out under a nitrogen atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. All the chemicals were purchased commercially, and used without further purification. Anhydrous THF and diethyl ether were distilled from sodium-benzophenone, and dichloromethane was distilled from calcium hydride. Yields refer to chromatographically, unless otherwise stated.

Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Tsingdao silica gel plates (60F-254) using UV light as visualizing agent and an ethanolic solution of phosphomolybdic acid and cerium sulfate, and heat as developing agents. Tsingdao silica gel (60, particle size 0.040–0.063 mm) was used for flash column chromatography.

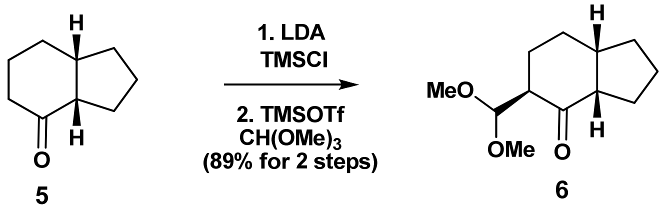
Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. NMR spectra were recorded on either a Brüker Advance 300 (^{1}H: 300 MHz, ^{13}C: 75.5 MHz), Brüker Advance 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz). High resolution mass spectrometric (HRMS) data were obtained using Bruker Apex IV RTMS.

The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad.

Overall Synthetic Route：



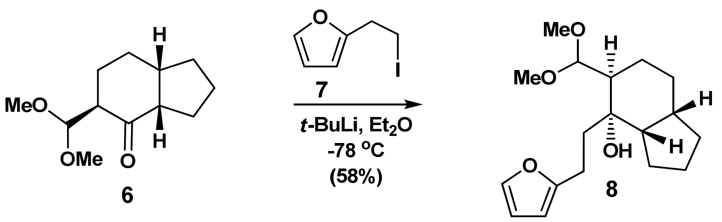
Synthesis of Compound 6:



To a solution of diisopropylamine (0.3 mL, 2.17 mmol) in THF (10 mL) was added *n*-BuLi (2.5 *M*, 0.9 mL, 2.17 mmol) at -78 °C in dropwise manner, and the mixture was stirred at 0 °C for 30 min. To this solution was added **5** (2.59 g, 18.8 mmol) in THF (3 mL) at -78 °C slowly, and the formed mixture was stirred at the same temperature for 30 min. followed by addition of TMSCl (3.6 mL, 28.2 mmol). The mixture was then warmed up room temperature, and the mixture was stirred at the same temperature for 2 h. Solvent was removed under vacuum, and the residue was diluted with hexane, and then filtered through a silica gel pad. The filtrate was concentrated under vacuum, and the residue was used for next step without further purification.

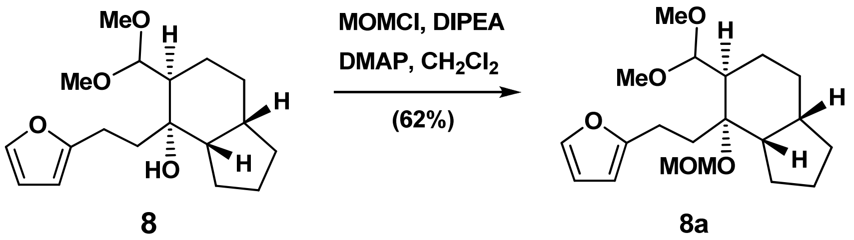
To a solution of the crude product made above in CH_2Cl_2 (100 mL) was added $CH(OMe)_3$ (2.5 mL, 22.6 mmol), and the mixture was stirred at room temperature for 10 min. To this solution was added TMSOTf (170 μL, 0.94 mmol) in a dropwise manner at -78 °C, and the reaction mixture was stirred at this temperature for 12 h. The reaction was quenched with saturated aqueous solution of $NaHCO_3$ (60 mL) and extracted with Et_2O (60 mL × 3). The combined organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 20/1) to give acetal **6** (3.55 g) in 89%): R_f = 0.5 (hexane/EtOAc = 15/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.65 (d, *J* = 5.3 Hz, 1 H), 3.39 (s, 3 H), 3.39 (s, 3 H), 2.67 – 2.64 (m, 2 H), 2.46 – 2.41 (m, 1H), 1.99 – 1.95 (m, 2 H), 1.89 – 1.86 (m, 1H), 1.75 – 1.70 (m, 4 H), 1.56 – 1.50 (m, 1 H), 1.32 – 1.30 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.2, 104.6, 55.4, 55.1, 52.6, 51.5, 42.9, 32.5, 27.0, 26.9, 24.3, 23.7; HRMS (ESI) calcd for $C_{12}H_{20}Na_1O_3$ $[M+Na]^+$: 235.1304; found: 235.1300.

Synthesis of Compound 8:



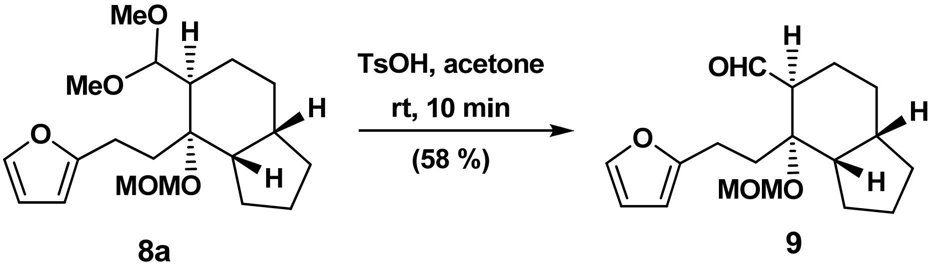
To a solution of iodide **7** (4.48 g, 20.2 mmol) in Et_2O (100 mL) in a flame-dried flask was added *t*-BuLi (1.5 *M*, 27mL, 40.5 mmol) at -78 ^{o}C in a drop-wise manner, and the mixture was stirred at the same temperature for 30 min. To this solution was added ketone **6** (3.31 g, 15.6 mmol) in Et_2O (20 mL) at -78 ^{o}C slowly, and the mixture was stirred at the same temperature for 3 h. The reaction was quenched with saturated aqueous solution of NH_4Cl (60 mL), and the mixture was extracted with Et_2O (5 x 50 mL), and the combined organic phase was dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, the residue was purified by a flash column chromatography (hexane/EtOAc = 20/1) to give product **8** (2.78 g) in 58%: $R_f = 0.5$ (hexane/EtOAc = 15/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, $J = 1.7$ Hz, 1H), 6.29 (dd, $J = 2.9$ Hz, 1.7 Hz, 1 H), 5.99 (d, $J = 2.9$ Hz, 1 H), 4.42 (d, $J = 8.7$ Hz, 1 H), 4.00 (s, 1 H), 3.43 (s, 3 H), 3.33 (s, 3 H), 2.91 – 2.85 (m, 1 H), 2.74 – 2.67 (m, 1 H), 2.19 - 2.14 (m, 1 H), 2.12 – 2.06 (m, 2 H), 1.90 – 1.86 (m, 1 H), 1.74 – 1.60 (m, 7 H), 1.44 – 1.38 (m, 2 H), 1.20 – 1.14 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.2, 140.7, 110.1, 107.1, 104.4, 73.6, 54.8, 51.5, 47.1, 42.3, 38.1, 33.7, 31.7, 26.5, 25.5, 23.8, 21.9, 20.7; HRMS (ESI) calcd for $C_{18}H_{28}Na_1O_4$ $[M + Na]^+$ 331.1880; found: 331.1879.

Synthesis of Compound 8a:



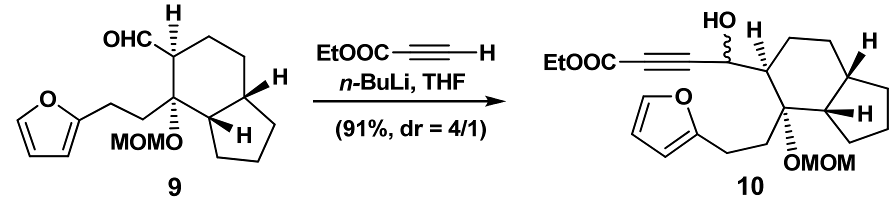
To a solution of alcohol **8** (2.13 g, 6.9 mmol) in CH_2Cl_2 (100 mL) in a flame-dried flask was added DIPEA (13.7 mL, 83 mmol) and DMAP (84.3 mg, 0.69 mmol), and the mixture was cooled to 0 ^{o}C. To this solution was added MOMCl (5.2 mL, 69 mmol) was added, and the mixture was first stirred at 0 ^{o}C for 10 min, and then stirred at room temperature for 4 days. The reaction was quenched with saturated aqueous NH_4Cl solution (60 mL), and the mixture was extracted with Et_2O (60 mL x 2), and the combined organic phase was dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography in silica gel (hexane/EtOAc = 60/1) to give product **8a** (1.50 g) in 62% yield: $R_f = 0.6$ (hexane/EtOAc = 15/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, $J = 1.8$ Hz, 1 H) , 6.27 (dd, $J = 3.0$ Hz, 1.9 Hz, 1 H), 5.97 (d, *J* = 3.1 Hz, 1 H), 4.88 (d, *J* = 6.8 Hz, 1 H), 4.67 (d, *J* = 6.8 Hz, 1 H), 4.57 (d, *J* = 1.2 Hz, 1 H), 3.42 (s, 3 H), 3.41 (s, 3 H), 3.39 (s, 3 H), 2.90 - 2.83 (m, 1 H), 2.73 – 2.67 (m, 1 H), 2.26 – 2.21 (m, 1 H), 2.13 – 2.01 (m, 3 H), 1.91 – 1.85 (m, 1 H), 1.78 – 1.69 (m, 3 H), 1.63 – 1.59 (m, 3 H), 1.50 – 1.41 (m, 3 H), 1.17 – 1.08 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.0, 140.7, 110.0, 105.4, 104.1, 90.5, 79.5, 56.0, 55.4, 54.9, 47.3, 45.0, 38.7, 33.2, 31.7, 26.6, 24.1, 22.5, 22.1, 20.5; HRMS (ESI) calcd for $C_{20}H_{32}Na_1O_5$ [M+Na]$^+$: 375.2142; found: 375.2136.

Synthesis of Compound 9:



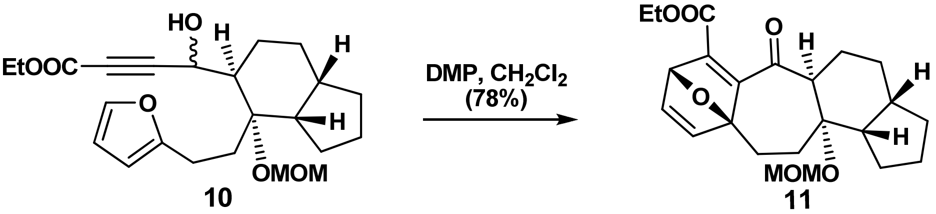
To a solution of substrate **8a** (705 mg, 2.0 mmol) in acetone (20 mL) was added *p*-TsOH (34.4 mg, 0.20 mmol) at room temperature, and the mixture was stirred at the same temperature for 10 min. The reaction was quenched with saturated aqueous $NaHCO_3$ solution (15 mL), the organic solvent was removed under vacuum, and the residue was extracted with Et_2O (20 mL × 3), and the combined organic phase was dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 30/1) to give product **9** (355 mg) in 58% yield: R_f = 0.6 (hexane/EtOAc = 15/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.20 (s, 1 H), 7.28 (d, *J* = 1.8 Hz, 1 H), 6.25 (dd, *J* = 2.9 Hz, 1.8 Hz, 1 H), 5.96 (d, *J* = 3.0 Hz, 1 H), 4.95 (d, *J* = 7.1 Hz, 1 H), 4.69 (d, *J* = 7.1 Hz, 1 H), 3.44 (s, 3 H), 2.71 – 2.65 (m, 1 H), 2.60 (dd, *J* = 12.4 Hz, 3.1 Hz, 1 H), 2.55 – 2.49 (m, 1 H), 2.27 – 2.20 (m, 2 H), 2.11 – 2.04 (m, 1 H), 2.01 – 1.96 (m, 2 H), 1.79 – 1.66 (m, 5 H), 1.54 – 1.51 (m, 1 H) , 1.46 – 1.37 (m, 2 H) , 1.15 – 1.06 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.3, 155.5, 140.9, 110.1, 104.6, 90.3, 81.1, 56.0, 53.6, 48.7, 38.7, 34.1, 31.6, 26.3, 23.9, 22.7, 22.1, 20.9; HRMS (ESI) calcd for $C_{18}H_{26}Na_1O_4$ [M+Na]$^+$ 329.1723; found: 329.1721.

Synthesis of Compound 10:



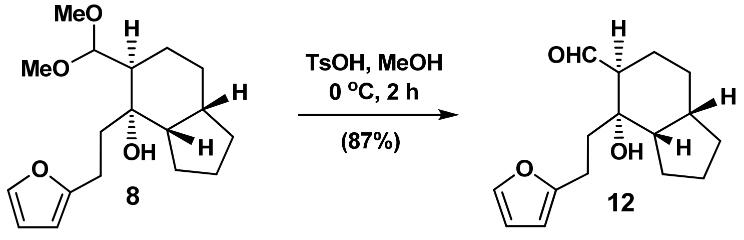
To a solution of ethyl propiolate (0.33 mL, 3.3 mmol) in THF (10 mL) in a flame-dried flask was added *n*-BuLi solution (2.5 *M*, 1.3 mL, 3.3 mmol) at -78 °C in a drop-wise manner, and the mixture was stirred at the same temperature for 30 min. To this solution was added aldehyde **9** (337 mg, 1.1 mmol) in THF (10 mL), and the reaction mixture was stirred at -78 °C for 1 h. The reaction was quenched with saturated aqueous NH_4Cl solution (20 mL), and the mixture was extracted with Et_2O (20 mL × 3), and the combined organic phase was dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 12/1) to give product **10** (404 mg) in 91% yield as two inseparable epimers **(dr = 4/1):** R_f = 0.5 (hexane/EtOAc = 8/1); HRMS (ESI) calcd for $C_{23}H_{32}Na_1O_6$ $[M+Na]^+$: 427.2091; found: 427.2091.

Synthesis of Compound 11:



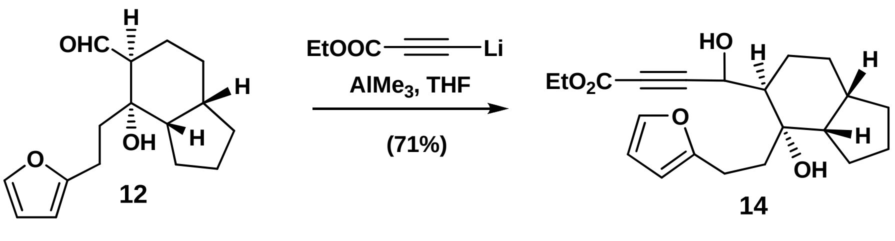
To a solution of alcohol **10** (307 mg, 0.76 mmol) in CH_2Cl_2 (8 mL) in a flame-dried flask was sequentially added $NaHCO_3$ (126 mg, 1.5 mmol) and DMP (466 mg, 1.1 mmol) at room temperature, and the mixture was stirred at the same temperature for 2 h. The reaction was first quenched with saturated aqueous $NaHCO_3$ solution (10 mL) and $Na_2S_2O_3$ solution (10 mL), then the aqueous phase was extracted with Et_2O (20 mL × 3), and the combined organic phase was dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 10/1) to give product **11** (240 mg) in 78% yield: R_f = 0.3 (hexane/EtOAc = 8/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 5.3 Hz, 1.9 Hz, 1 H), 6.79 (d, *J* = 5.3 Hz, 1 H), 5.61 (d, *J* = 1.9 Hz, 1 H), 4.84 (d, *J* = 6.7 Hz, 1 H), 4.63 (d, *J* = 6.7 Hz, 1 H), 4.17 (q, *J* = 7.1 Hz, 2 H), 3.41 (s, 3 H), 2.90 (dd, *J* = 13.3 Hz, 3.2 Hz, 1 H), 2.67 – 2.50 (m, 2 H), 2.17 – 2.07 (m, 2 H), 2.04 – 2.00 (m, 1 H), 1.91 – 1.85 (m, 2 H), 1.75 – 1.62 (m, 6 H), 1.48 – 1.45 (m, 2 H), 1.24 (t, *J* = 7.1 Hz, 3 H), 1.19 – 1.10 (m, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 204.2, 165.9, 162.3, 147.6, 146.4, 144.8, 95.6, 90.0, 83.2, 78.6, 61.0, 56.4, 56.2, 51.1, 38.3, 31.7, 29.9, 25.6, 25.4, 24.2, 24.0, 20.3, 14.0; HRMS (ESI) calcd for $C_{23}H_{31}O_6$ $[M+H]^+$: 403.2115; found: 403.2110.

Synthesis of Compound 12:



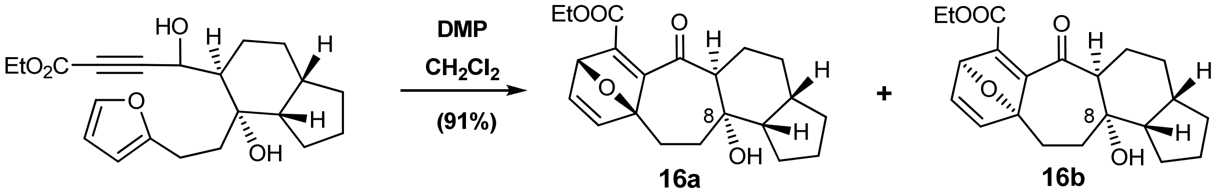
To a solution of acetal **8** (500 mg, 1.6 mmol) in acetone (30 mL) was added TsOH·H_2O (33 mg, 0. 16 mmol) in one portion at 0 °C, and the reaction mixture was stirred at 0 °C for 3 h. The reaction was quenched with saturated aqueous $NaHCO_3$ solution, and the mixture was evaporated under vacuum to remove organic solvent. The residue was extracted with Et_2O (3 × 50 mL), and the combined organic layer was dried with anhydrous Na_2SO_4. The solvent was removed under vacuum and the residue obtained was purified by a flash column chromatography on silica gel (hexane/EtOAc = 7/1) to give aldehyde **12** (370 mg) in 87% as colorless oil: R_f = 0.26 (hexane/EtOAc = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.97 (s, 1 H), 7.29 (d, *J* = 0.7 Hz, 1 H), 6.27 (dd, *J* = 3.1 Hz, 1.9 Hz, 1 H), 5.99 (dd, *J* = 3.1 Hz , 0.7 Hz, 1 H), 2.84 – 2.78 (m, 1 H), 2.76 – 2.70 (m, 1 H), 2.58 (dd, *J* = 13.0 Hz, 3.5 Hz, 1 H), 2.41 (s, 1 H), 2.24 – 2.19 (m, 1 H), 2.12 – 2.06 (m, 1 H), 1.99 – 1.95 (m, 2 H), 1.86 – 1.83 (m, 1 H), 1.81 – 1.77 (m, 1 H), 1.76 – 1.74 (m, 1 H), 1.73 – 1.65 (m, 3 H), 1.57 – 1.47 (m, 2 H), 1.46 – 1.43 (m, 1 H), 1.22 – 1.15 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.4, 155.7, 140.9, 110.1, 104.8, 75.3, 54.2, 47.8, 38.2, 34.3, 31.6, 26.0, 23.5, 22.9, 21.8, 20.9; HRMS (ESI-TOF) calcd for $C_{16}H_{22}Na_1O_3$ $[M+Na]^+$: 285.1461; found: 285.1460.

Synthesis of Compound 14:



To a solution of **12** (350 mg, 1.3 mmol) in THF (15 mL) was added Me_3Al (1.0 *M*, 1.3 mL, 1.3 mmol) at -78 °C slowly, followed by addition of a solution of lithium ethyl propiolate generated by addition of *n*-BuLi (2.5 *M*, 1.6 mL, 4.0 mmol) to a solution of ethyl propiolate (0.4 mL, 4.0 mmol) in THF (10 mL) at -78 °C, and the resulting suspension was stirred vigorously at -78 °C for 1 h. The reaction was first quenched with saturated aqueous NH_4Cl solution, and then extracted with Et_2O (4 × 50 mL), and the combined organic phase was dried with anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 7/1) to give **14** (340 mg) in 71% yield: $R_f = 0.35$ (hexane/EtOAc = 5/1). ^1H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, *J* = 1.8 Hz, 1 H), 6.28 (dd, *J* =3.0 Hz, 1.8 Hz, 1 H), 6.02 (d, *J* = 3.0 Hz, 1 H), 4.62 (d, *J* = 10.2 Hz, 1 H), 4.45 (s, 1 H), 4.23 (t, *J* = 7.2 Hz, 2 H), 2.93 (s, 1 H), 2.86 – 2.72 (m, 2 H), 2.22 – 2.15 (m, 2 H), 2.07 – 1.96 (m, 2 H), 1.92 – 1.85 (m, 2 H), 1.69 – 1.66 (m, 5 H), 1.47 – 1.44 (m, 2 H), 1.30 (t, *J* = 7.2 Hz, 3 H), 1.28 – 1.15 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.1, 153.4, 140.9, 110.2, 104.8, 87.6, 76.8, 76.5, 65.3, 62.1, 47.7, 46.0, 38.2, 31.8, 31.7, 26.4, 26.3, 23.3, 21.7, 20.8, 14.0; HRMS (ESI) calcd for $C_{21}H_{29}O_5[M+H]^+$: 361.2009; found: 361.2010.

Synthesis of Compound 16a and 16b:



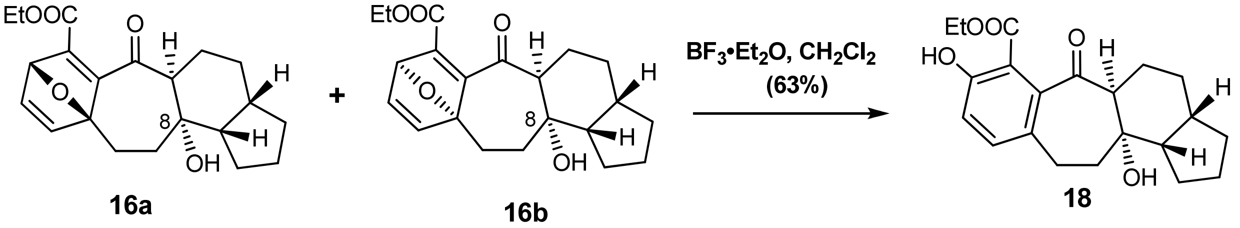
14 **16a** **16b**

16a : 16b = 3:1

To a solution of **14** (300 mg, 0.83 mmol) in CH_2Cl_2 (30 mL) was sequentially added $NaHCO_3$ (210 mg, 2.5 mmol) and DMP (540 mg, 1.25 mmol), and the mixture was stirred at room temperature for 1 h. The reaction was quenched with aqueous $Na_2S_2O_3$ (30 mL and $NaHCO_3$ (30 mL), and the formed mixture was extracted with diethyl ether (3 × 60 mL), and the combined organic phase was dried with Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 5/1) to give two isomers **16a** and **16b** (**16a**/**16b**= 3:1) (270 mg) in 91% yield. **16a**. ^1H NMR (500 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 5.3 Hz, 1.9 Hz, 1 H), 6.81 (d, *J* = 5.3 Hz, 1 H), 5.62 (d, *J* = 1.8 Hz, 1 H), 4.19 – 4.15 (m, 2 H), 2.80 – 2.78 (m, 2 H), 2.61 – 2.55 (m, 1 H), 2.11 – 2.05 (m, 2 H), 2.00 – 1.91 (m, 2 H), 1.79 – 1.61 (m, 7 H), 1.51 – 1.44 (m, 2 H), 1.26 – 1.23 (m, 4 H), 1.16 – 1.08 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$)

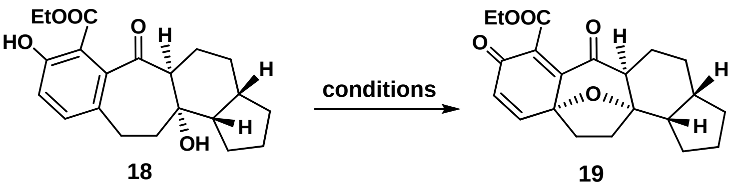
δ 205.3, 166.0, 162.2, 147.7, 146.4, 144.8, 95.8, 83.2, 72.6, 61.0, 58.2, 55.2, 38.3, 33.3, 31.9, 25.9, 25.7, 23.9, 23.4, 20.5, 14.1; HRMS (ESI) calcd for $C_{21}H_{27}O_5[M+H]^+$: 359.1853; found: 359.1857; **16b**: ^{1}H NMR (500 MHz, MeOD) δ 7.49 (d, *J* = 5.3 Hz, 1 H), 7.27 (m, 1 H), 5.52 (d, *J* = 2.1 Hz, 1 H), 4.16 (q, *J* = 7.1 Hz, 2 H), 2.82 (dd, *J* = 2.1 Hz, 13.5 Hz , 1 H), 2.74 – 2.68 (m, 1 H), 2.50 – 2.45 (m, 1 H), 2.21 – 2.16 (m, 1 H), 1.98 – 1.94 (m, 2 H), 1.90 – 1.85 (m, 1 H), 1.80 – 1.68 (m, 4 H), 1.64 – 1.59 (m, 1 H), 1.53 – 1.47 (m, 1 H), 1.46 – 1.40 (m, 2 H), 1.36 – 1.28 (m, 1 H), 1.22 (t, *J* = 7.1 Hz, 3 H), 1.18 – 1.11 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.6, 165.4, 162.3, 151.7, 144.7, 143.4, 94.2, 83.7, 74.3, 61.2, 58.4, 54.4, 38.9, 34.5, 31.9, 26.7, 24.2, 24.0, 23.6, 21.1, 13.9.

Synthesis of Compound 18:

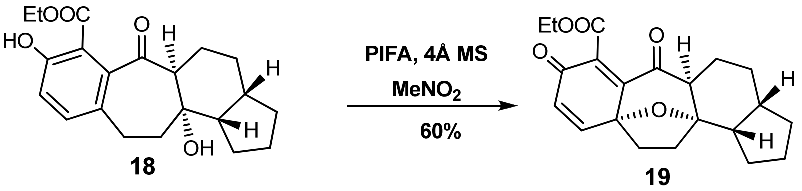


To a solution of **16a** and **16b** (40 mg, 0.11 mmol) in CH_2Cl_2 (5 mL) was added $BF_3{\cdot}Et_2O$ (48%, 42uL, 0.33 mmol) in a drop-wise manner at -20 °C, and the formed dark brown solution was stirred at the same temperature for 20 min. The reaction was first quenched with saturated aqueous $NaHCO_3$ solution (5 mL), and then extracted with Et_2O (3 × 10 mL), and the combined organic layer was finally dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 10/1) to give **18** (25 mg) in 63% yield as slight yellow solid; R_f = 0.65 (hexane/EtOAc = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.71 (s, 1 H), 7.24 (d, *J* = 8.3 Hz, 1 H), 6.90 (d, *J* = 8.3 Hz, 1 H), 4.38 - 4.33 (m, 2 H), 3.03 (t, *J* = 14.4 Hz, 1 H), 2.74 (d, *J* = 12.7 Hz, 1 H), 2.62 (bs, 1 H), 2.41 (dd, *J*= 15.3, 6.0 Hz, 1 H), 2.28 (t, *J* = 13.5 Hz, 1 H), 1.97 – 1.69 (m, 9 H), 1.42 – 1.33 (m, 6 H), 1.15 – 1.10 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.6, 168.8, 160.2, 143.5, 136.2, 127.1, 117.9, 108.7, 75.1, 62.1, 55.6, 53.7, 38.4, 36.6, 31.8, 28.1, 26.3, 25.6, 23.9, 20.6, 13.5; HRMS (ESI) calcd for $C_{21}H_{27}O_5$ $[M+H]^+$: 359.1853; found: 359.1854.

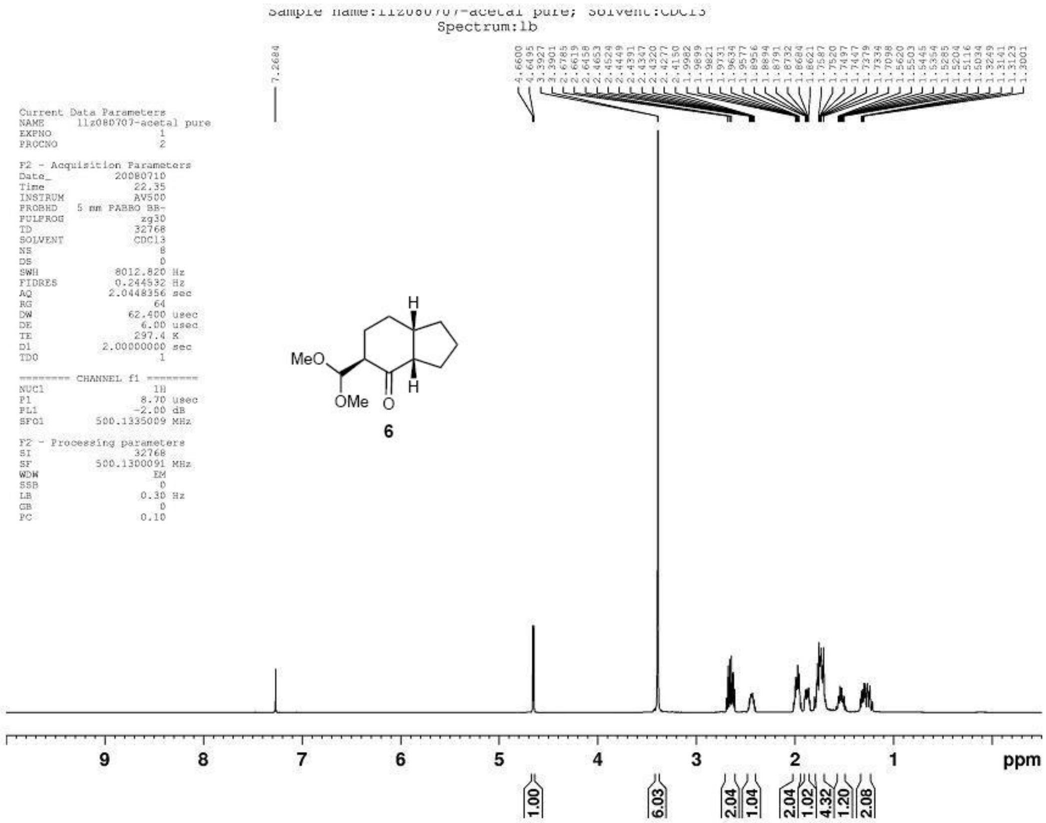
Synthesis of Compound 19:



entry	oxidant	solvent	product 19
1	$PhI(OAc)_2$	CH_2Cl_2	no reaction
2	$PhI(OAc)_2$	TFE	decomposition
3	IBX	CH_2Cl_2	no reaction
4	DDQ	THF	no reaction
5	Pb(OAc)	CH_2Cl_2	decomposition
6	$Tl(NO_3)_3$	CH_2Cl_2	decomposition
7	$PhI(OOCCF_3)_2$	CH_2Cl_2	decomposition
8	$PhI(OOCCF_3)_2$	THF	decomposition
9	$PhI(OOCCF_3)_2$	CH_3NO_2	30%
10	$PhI(OOCCF_3)_2$	CH_3CN	decomposition
11	$PhI(OOCCF_3)_2$	TFE	decomposition
12	$PhI(OOCCF_3)_2$	CH_3NO_2, 4ÅMS	60%



To a solution of compound **18** (40 mg, 0.11 mmol) in dry nitromethane (10 mL) in a flame-dried flask was added activated 4 Å molecular sieves (50 mg) was added $PhI(OOCCF_3)_2$ (58 mg, 0.13 mmol), and the formed suspension was stirred at room temperature for 30 min. The reaction was quenched with aqueous $NaHCO_3$ (10 mL), followed by filtration through a silica gel pad. The filtrate was extracted with Et_2O (4 × 20 mL), and combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 5/1) to give the desired product **19** (24 mg) in 60% yield: $R_f = 0.7$ (hexane/EtOAc = 2/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.91 (d, $J = 10.1$ Hz, 1 H), 6.35 (d, $J = 10.1$ Hz, 1 H), 4.39 – 4.31 (m, 2 H), 2.80 (dd, $J = 11.4$ Hz, 1.5 Hz, 1 H), 2.29 – 2.19 (m, 3 H), 2.15 – 2.11 (m, 1 H), 2.04 – 2.00 (m, 1 H), 1.96 – 1.92 (m, 1 H), 1.92 – 1.85 (m, 2 H), 1.82 – 1.79 (m, 1 H), 1.73 – 1.69 (m, 3 H), 1.48 – 1.43 (m, 1 H), 1.34 (t, $J = 7.2$ Hz, 3 H), 1.26 (m, 3 H), 1.19 – 1.10 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.4, 182.0, 164.4, 148.0, 147.5, 129.2, 129.1, 87.5, 78.7, 61.9, 54.8, 50.8, 39.6, 37.5, 34.4, 31.4, 26.1, 24.3, 22.8, 21.3, 13.9; DEPT 135 (500 MHz, $CDCl_3$) δ CH and CH_3: 147.6, 129.2, 54.8, 50.8, 39.6, 13.9; CH_2: 61.9, 37.5, 34.4, 31.4, 26.1, 24.3, 22.8, 21.3; HRMS (ESI) calcd for $C_{21}H_{25}O_5$ $[M+H]^+$ 357.1697; found: 357.1700.


Sample name:11z080707-acetal pure; Solvent:CDCl3
Spectrum:1b
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4.6495
3.3927
3.3901
2.6785
2.6619
2.6458
2.4653
2.4524
2.4449
2.4391
2.4347
2.4320
2.4277
2.4150
1.9982
1.9899
1.9821
1.9731
1.9634
1.9577
1.8956
1.8894
1.8791
1.8732
1.8684
1.8621
1.7587
1.7520
1.7497
1.7447
1.7379
1.7334
1.7098
1.5620
1.5503
1.5445
1.5354
1.5285
1.5204
1.5116
1.5034
1.3249
1.3141
1.3123
1.3001
Current Data Parameters
NAME 11z080707-acetal pure
EXPNO 1
PROCNO 2
F2 - Acquisition Parameters
Date_ 20080710
Time 22.35
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 2.0448356 sec
RG 64
DW 62.400 usec
DE 6.00 usec
TE 297.4 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 8.70 usec
PL1 -2.00 dB
SFO1 500.1335009 MHz
F2 - Processing parameters
SI 32768
SF 500.1300091 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 0.10
MeO
OMe
O
H
H
6
9
8
7
6
5
4
3
2
1
ppm
1.00
6.03
2.04
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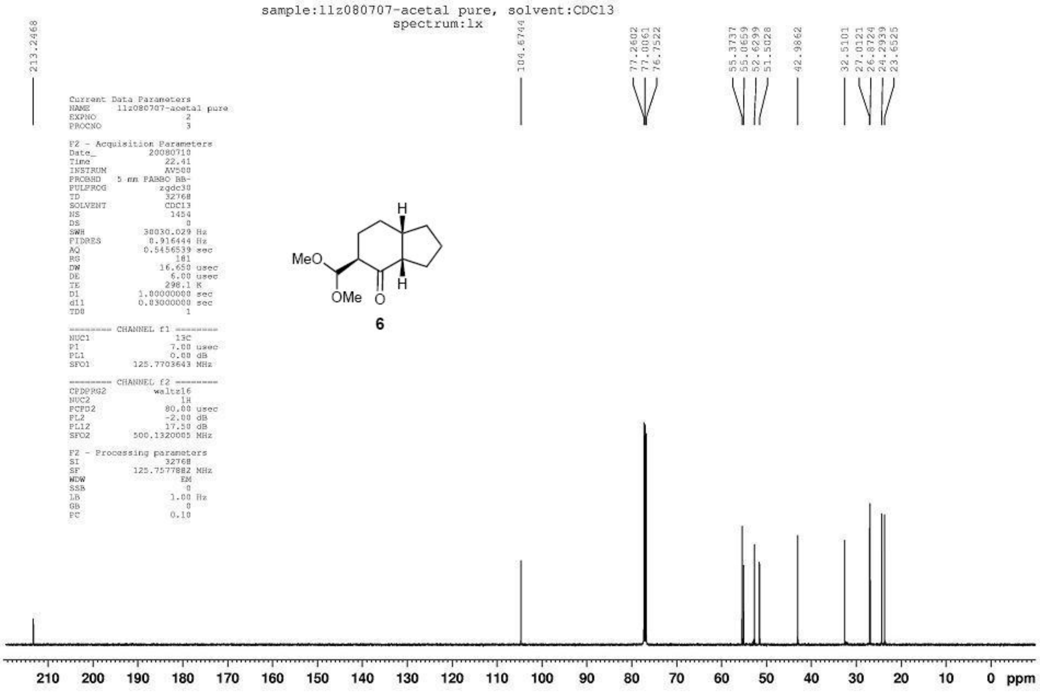
1.02
4.32
1.20
2.08


sample:11z080707-acetal pure, solvent:CDCl3
spectrum:1x
213.2468
104.6744
77.2602
77.0061
76.7522
55.3737
55.0659
52.6299
51.5028
42.9862
32.5101
27.0121
26.8724
24.2939
23.6525
Current Data Parameters
NAME 11z080707-acetal pure
EXPNO 2
PROCNO 3
F2 - Acquisition Parameters
Date_ 20080710
Time 22.41
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zgdc30
TD 32768
SOLVENT CDCl3
NS 1454
DS 0
SWH 30030.029 Hz
FIDRES 0.916444 Hz
AQ 0.5456539 sec
RG 181
DW 16.650 usec
DE 6.00 usec
TE 298.1 K
D1 1.00000000 sec
d11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.00 usec
PL1 0.00 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 17.50 dB
SFO2 500.1320005 MHz
F2 - Processing parameters
SI 32768
SF 125.7577882 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 0.10
MeO
OMe
O
H
H
6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
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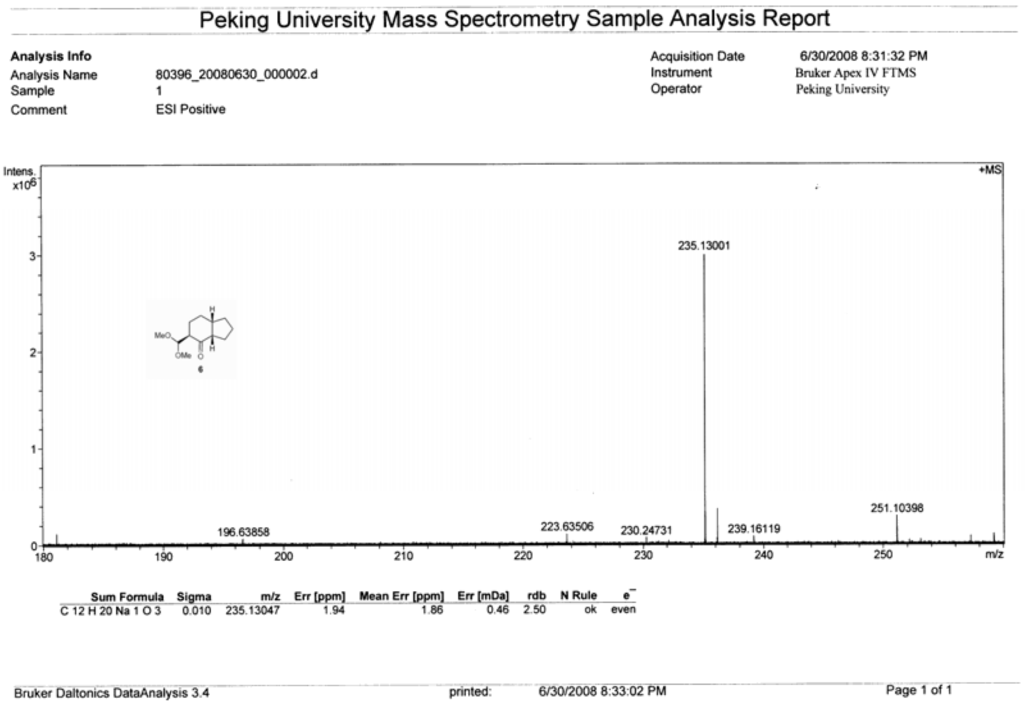
60
50
40
30
20
10
0
ppm



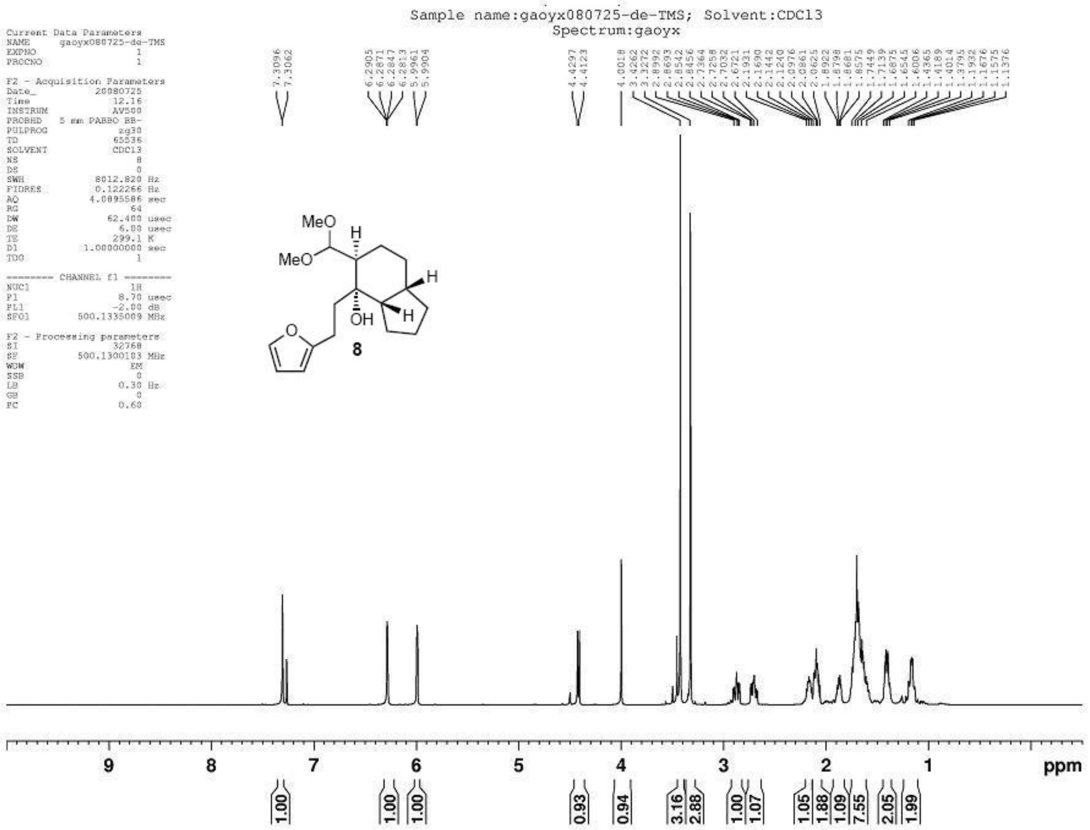
Peking University Mass Spectrometry Sample Analysis Report

Analysis Info
Analysis Name 80396_20080630_000002.d
Sample 1
Comment ESI Positive

Acquisition Date 6/30/2008 8:31:32 PM
Instrument Bruker Apex IV FTMS
Operator Peking University

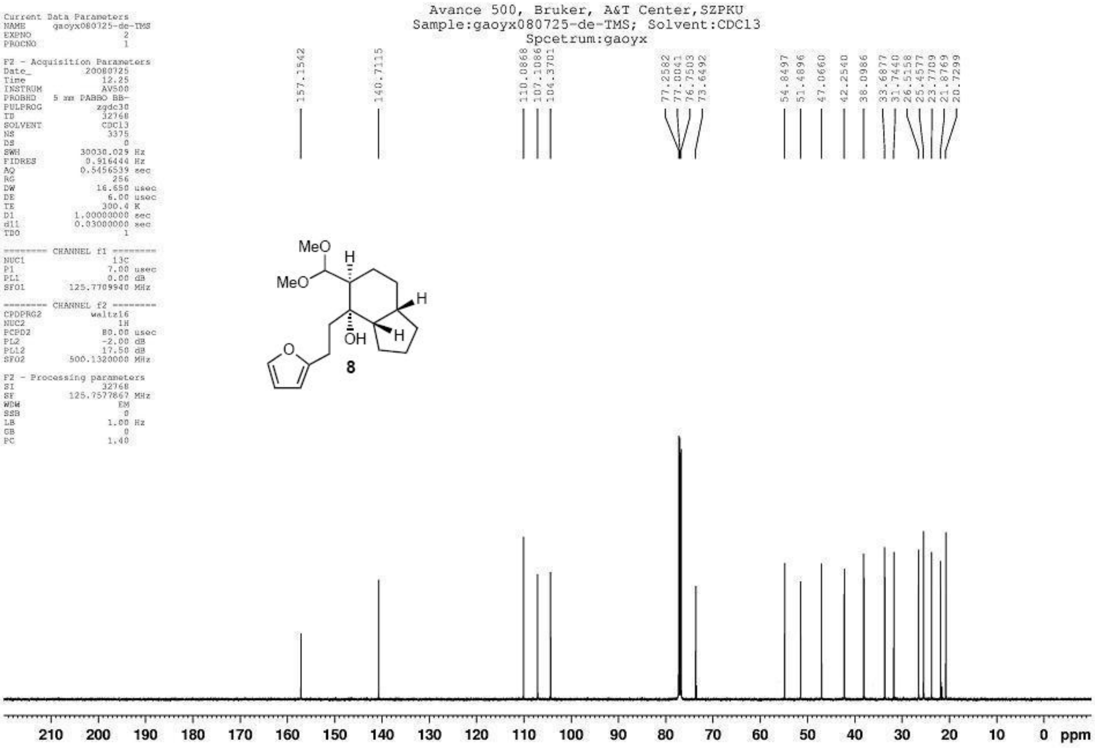
Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 12 H 20 Na 1 O 3	0.010	235.13047	1.94	1.86	0.46	2.50	ok	even

Bruker Daltonics DataAnalysis 3.4 printed: 6/30/2008 8:33:02 PM Page 1 of 1



```
Sample name:gaoyx080725-de-TMS; Solvent:CDCl3
Spectrum:gaoyx
```

```
Current Data Parameters
NAME     gaoyx080725-de-TMS
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20080725
Time                  12.16
INSTRUM               AV500
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        0
SWH                8012.820 Hz
FIDRES             0.122266 Hz
AQ                4.0895586 sec
RG                       64
DW                   62.400 usec
DE                     6.00 usec
TE                    299.1 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                     8.70 usec
PL1                   -2.00 dB
SFO1            500.1335009 MHz

F2 - Processing parameters
SI                    32768
SF              500.1300103 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     0.60
```



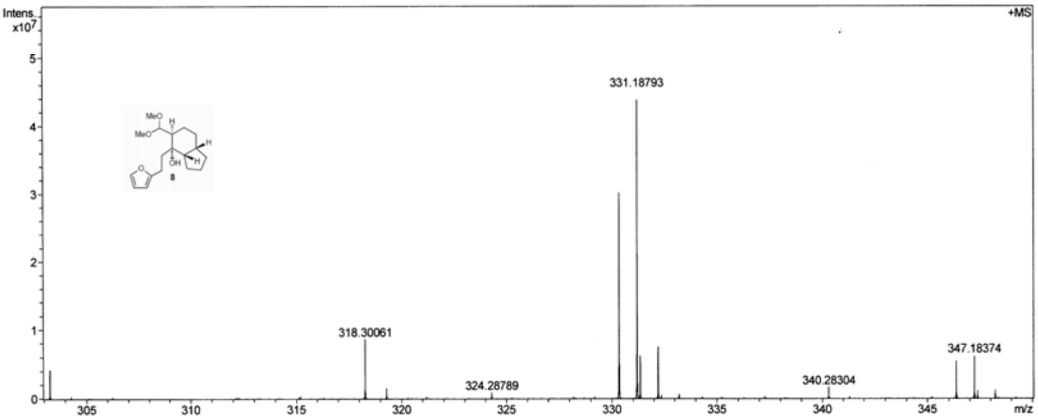
```
Avance 500, Bruker, A&T Center,SZPKU
Sample:gaoyx080725-de-TMS; Solvent:CDCl3
Spcetrum:gaoyx
```

```
Current Data Parameters
NAME     gaoyx080725-de-TMS
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20080725
Time                  12.25
INSTRUM               AV500
PROBHD    5 mm PABBO BB-
PULPROG             zgdc30
TD                    32768
SOLVENT               CDCl3
NS                     3375
DS                        0
SWH              30030.029 Hz
FIDRES            0.916444 Hz
AQ               0.5456539 sec
RG                      256
DW                   16.650 usec
DE                     6.00 usec
TE                    300.4 K
D1               1.00000000 sec
d11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                     7.00 usec
PL1                    0.00 dB
SFO1            125.7709940 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 80.00 usec
PL2                   -2.00 dB
PL12                  17.50 dB
SFO2            500.1320000 MHz

F2 - Processing parameters
SI                    32768
SF              125.7577867 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

Peking University Mass Spectrometry Sample Analysis Report

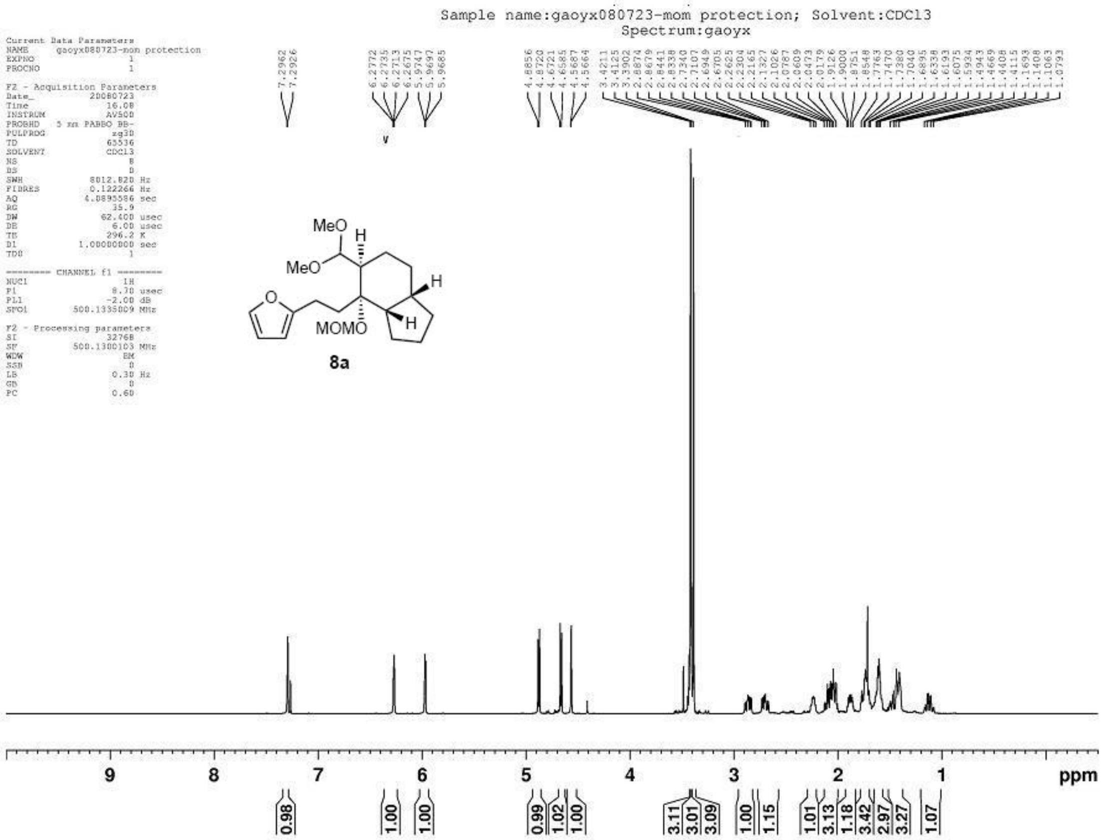
Analysis Info

Analysis Name	80397_20080630_000002.d	Acquisition Date	6/30/2008 8:37:38 PM
Sample	2	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University

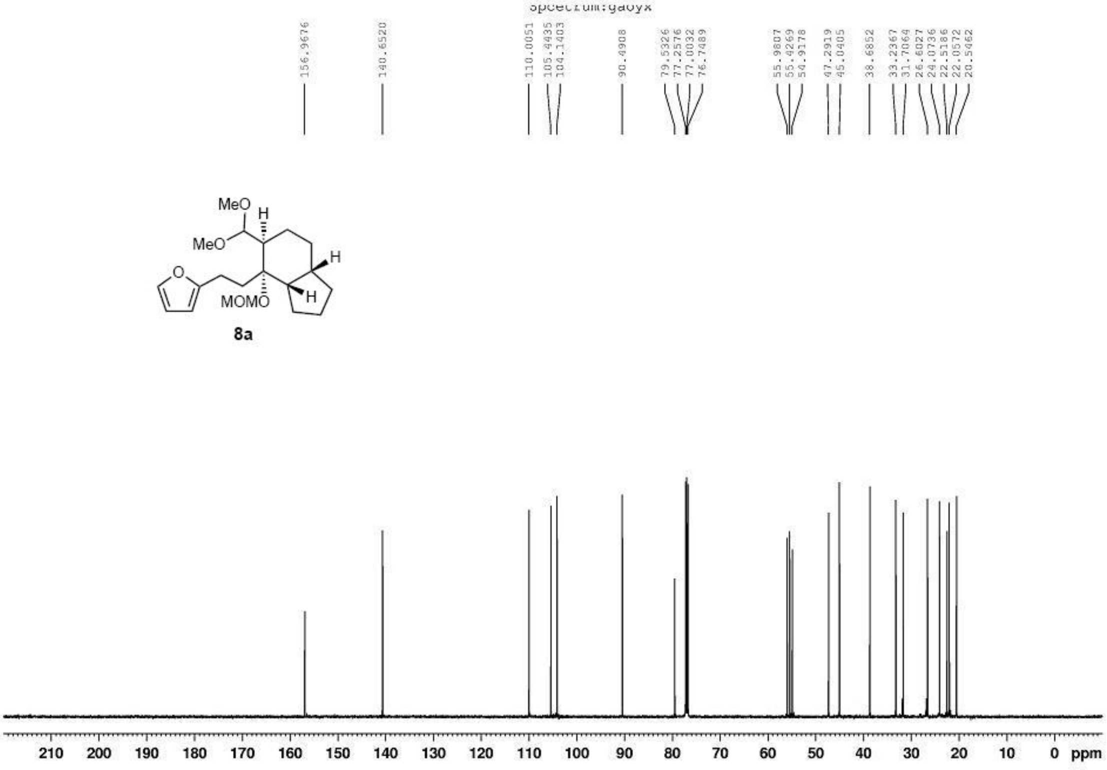


Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 18 H 28 Na 1 O 4	0.019	331.18798	0.15	-0.19	0.05	4.50	ok	even

Bruker Daltonics DataAnalysis 3.4 printed: 6/30/2008 8:38:57 PM Page 1 of 1


Sample name:gaoyx080723-mom protection; Solvent:CDCl3
Spectrum:gaoyx
Current Data Parameters
NAME gaoyx080723-mom protection
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080723
Time 16.08
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0895586 sec
RG 35.9
DW 62.400 usec
DE 6.00 usec
TE 296.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 8.70 usec
PL1 -2.00 dB
SFO1 500.1335009 MHz
F2 - Processing parameters
SI 32768
SF 500.1300103 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 0.60
7.2962
7.2926
6.2772
6.2735
6.2713
6.2675
5.9747
5.9697
5.9685
4.8856
4.8720
4.6721
4.6585
4.5687
4.5664
3.4211
3.4125
3.3902
2.8874
2.8679
2.8441
2.8338
2.7340
2.7107
2.6949
2.6705
2.2625
2.2304
2.2165
2.1327
2.1026
2.0787
2.0609
2.0473
2.0179
1.9126
1.9000
1.8751
1.8548
1.7763
1.7470
1.7380
1.7040
1.6895
1.6338
1.6193
1.6075
1.5934
1.4943
1.4669
1.4408
1.4115
1.1693
1.1408
1.1063
1.0793
MeO
MeO
H
H
H
O
MOMO
9
8
7
6
5
4
3
2
1
ppm
0.98
1.00
1.00
0.99
1.02
1.00
3.11
3.01
3.09
1.00
1.15
1.01
3.13
1.18
3.42
2.97
3.27
1.07

8a


Spectrum:gaoyx
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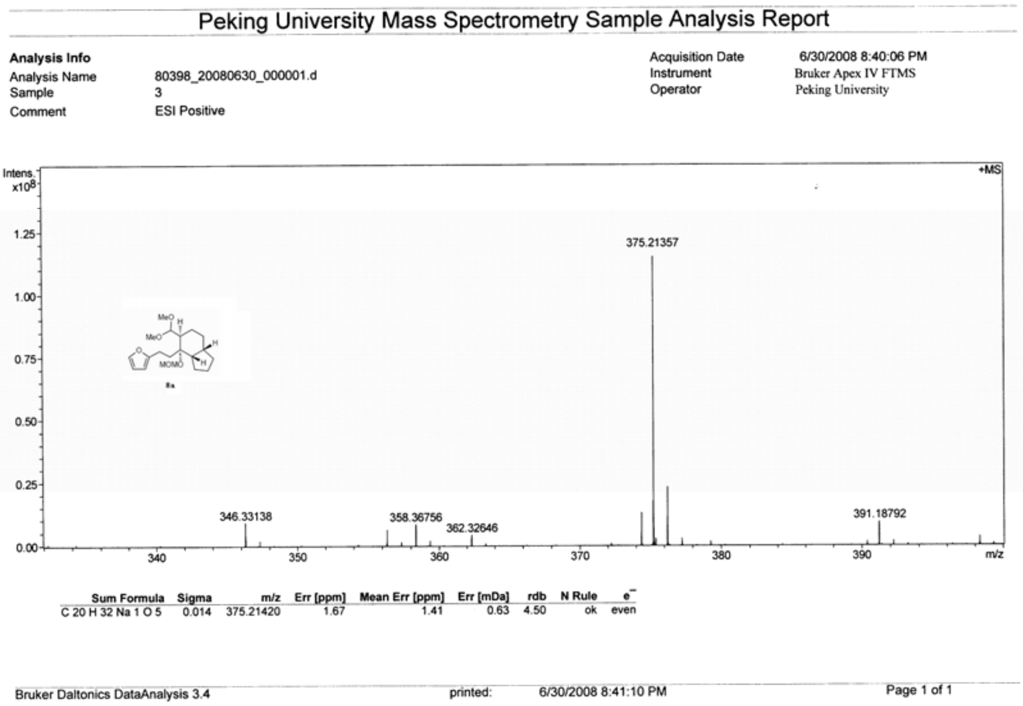
110.0051
105.4435
104.1403
90.4908
79.5326
77.2576
77.0032
76.7489
55.9807
55.4269
54.9178
47.2919
45.0405
38.6852
33.2367
31.7064
26.6027
24.0736
22.5786
22.0572
20.5462
MeO
MeO
H
H
H
O
MOMO
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

8a



Peking University Mass Spectrometry Sample Analysis Report

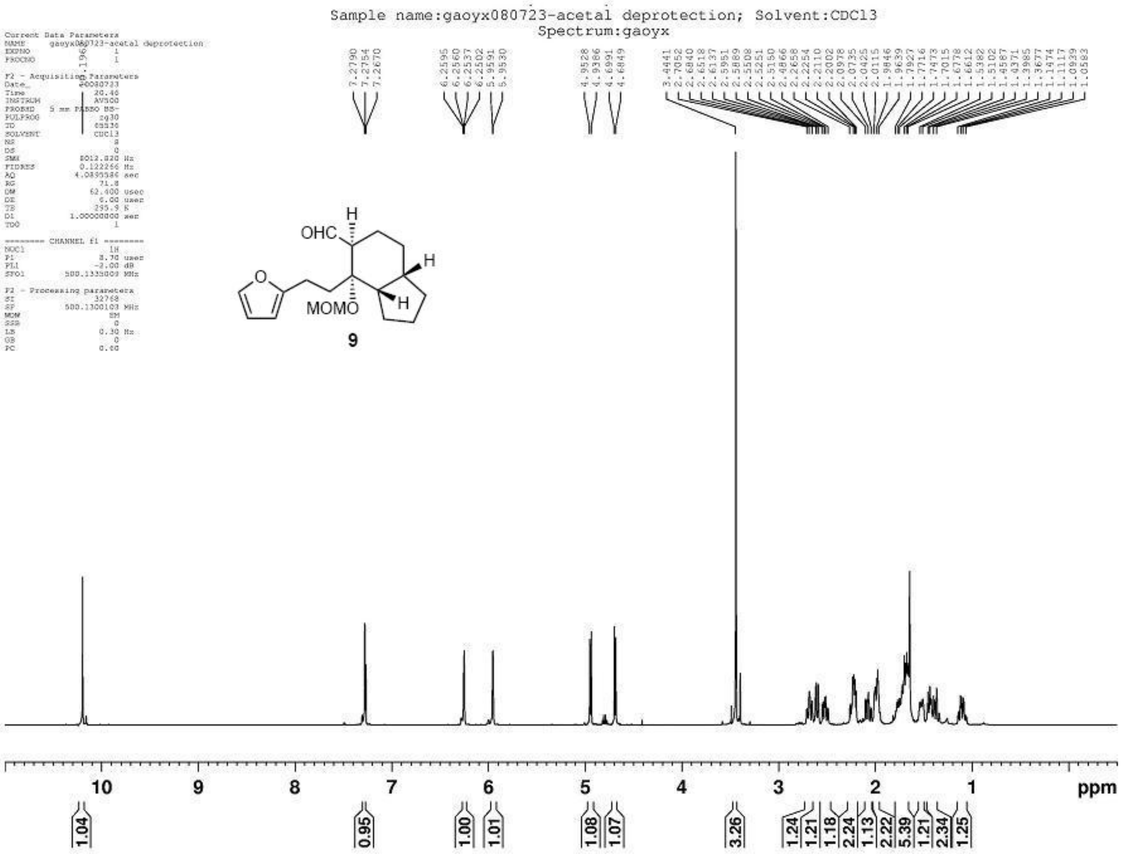
Analysis Info

Analysis Name 80398_20080630_000001.d
Sample 3
Comment ESI Positive

Acquisition Date 6/30/2008 8:40:06 PM
Instrument Bruker Apex IV FTMS
Operator Peking University

Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 20 H 32 Na 1 O 5	0.014	375.21420	1.67	1.41	0.63	4.50	ok	even

Bruker Daltonics DataAnalysis 3.4 printed: 6/30/2008 8:41:10 PM Page 1 of 1

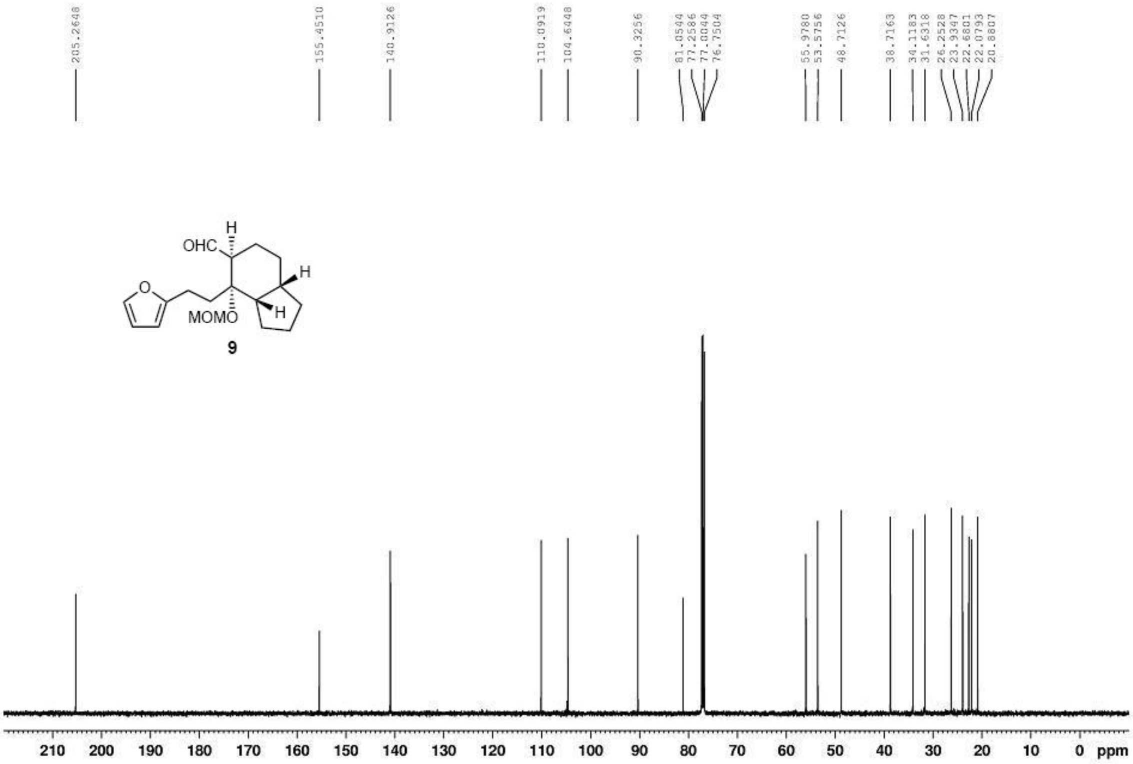


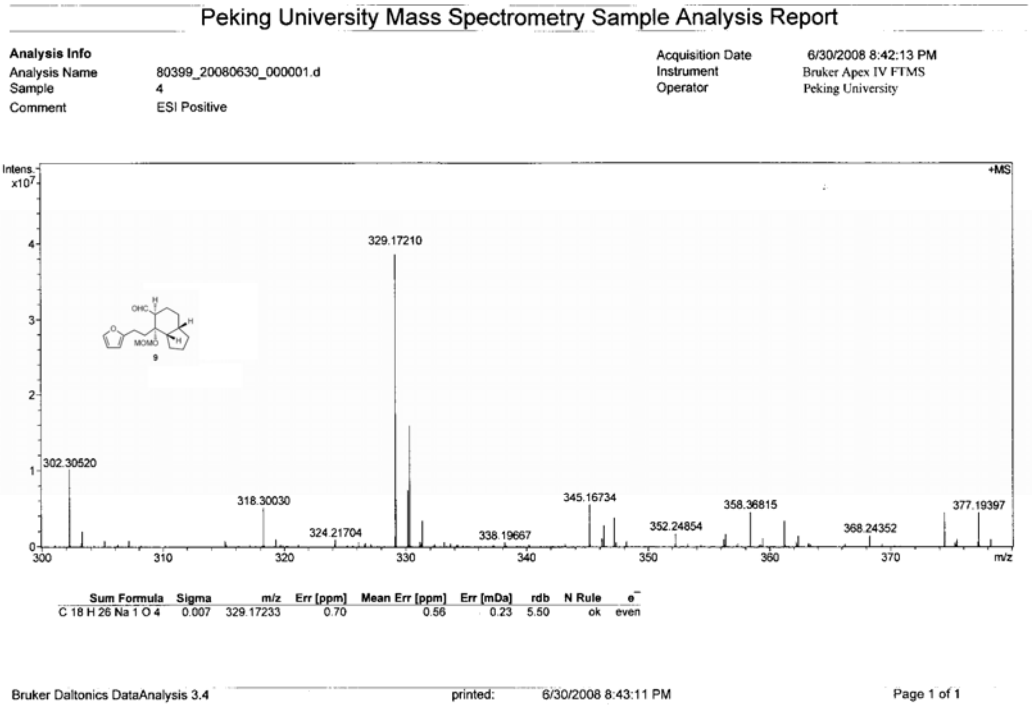
```
Current Data Parameters
NAME     gaoyx080723-acetal deprotection
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080723
Time               20.46
INSTRUM            AV500
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0895586 sec
RG                  71.8
DW                62.400 usec
DE                  6.00 usec
TE                 295.9 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  8.70 usec
PL1                -2.00 dB
SFO1         500.1335009 MHz

F2 - Processing parameters
SI                 32768
SF           500.1300103 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  0.40
```



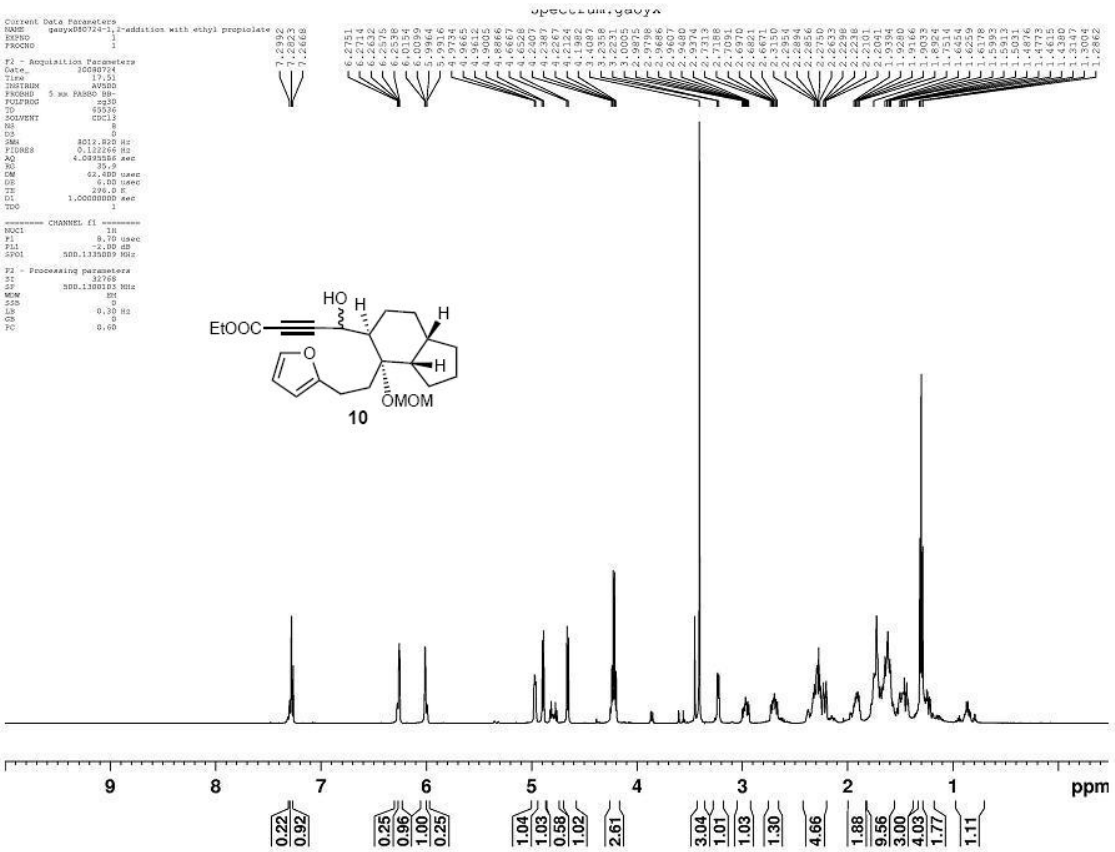


Peking University Mass Spectrometry Sample Analysis Report

Analysis Info		Acquisition Date	6/30/2008 8:42:13 PM
Analysis Name	80399_20080630_000001.d	Instrument	Bruker Apex IV FTMS
Sample	4	Operator	Peking University
Comment	ESI Positive		

Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 18 H 26 Na 1 O 4	0.007	329.17233	0.70	0.56	0.23	5.50	ok	even

Bruker Daltonics DataAnalysis 3.4 printed: 6/30/2008 8:43:11 PM Page 1 of 1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7.2668
6.2751
6.2714
6.2632
6.2575
6.2538
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6.0099
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5.9916
4.9734
4.9665
4.9612
4.9005
4.8866
4.6667
4.6528
4.2407
4.2387
4.2267
4.2124
4.1982
3.4087
3.2358
3.2231
3.0005
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2.9798
2.9686
2.9607
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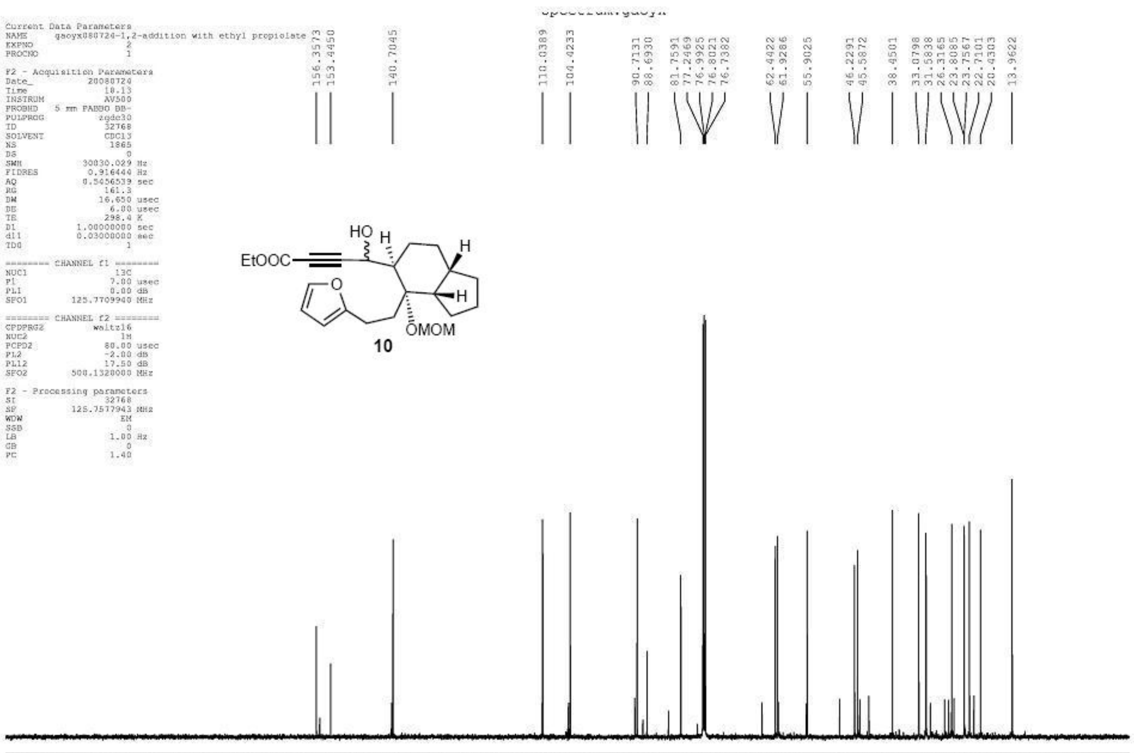
2.7091
2.6970
2.6821
2.6671
2.3150
2.2954
2.2894
2.2856
2.2750
2.2633
2.2298
2.2238
2.2101
2.2041
1.9394
1.9280
1.9166
1.9033
1.8924
1.7514
1.6454
1.6259
1.6178
1.5993
1.5913
1.5031
1.4876
1.4773
1.4615
1.4380
1.3147
1.3004
1.2862
HO
H
H
EtOOC
O
H
OMOM
10
9
8
7
6
5
4
3
2
1
ppm
0.22
0.92
0.25
0.96
1.00
0.25
1.04
1.03
0.58
1.02
2.61
3.04
1.01
1.03
1.30
4.66
1.88
9.56
3.00
4.03
1.77
1.11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140.7045
110.0389
104.4233
90.7131
88.6930
81.7591
77.2469
76.9925
76.8021
76.7382
62.4422
61.9286
55.9025
46.2291
45.5872
38.4501
33.0798
31.5838
26.3165
23.8085
23.7567
22.7101
20.4303
13.9622
HO
H
H
EtOOC
O
H
OMOM
10
210
200
190
180
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160
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140
130
120
110
100
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80
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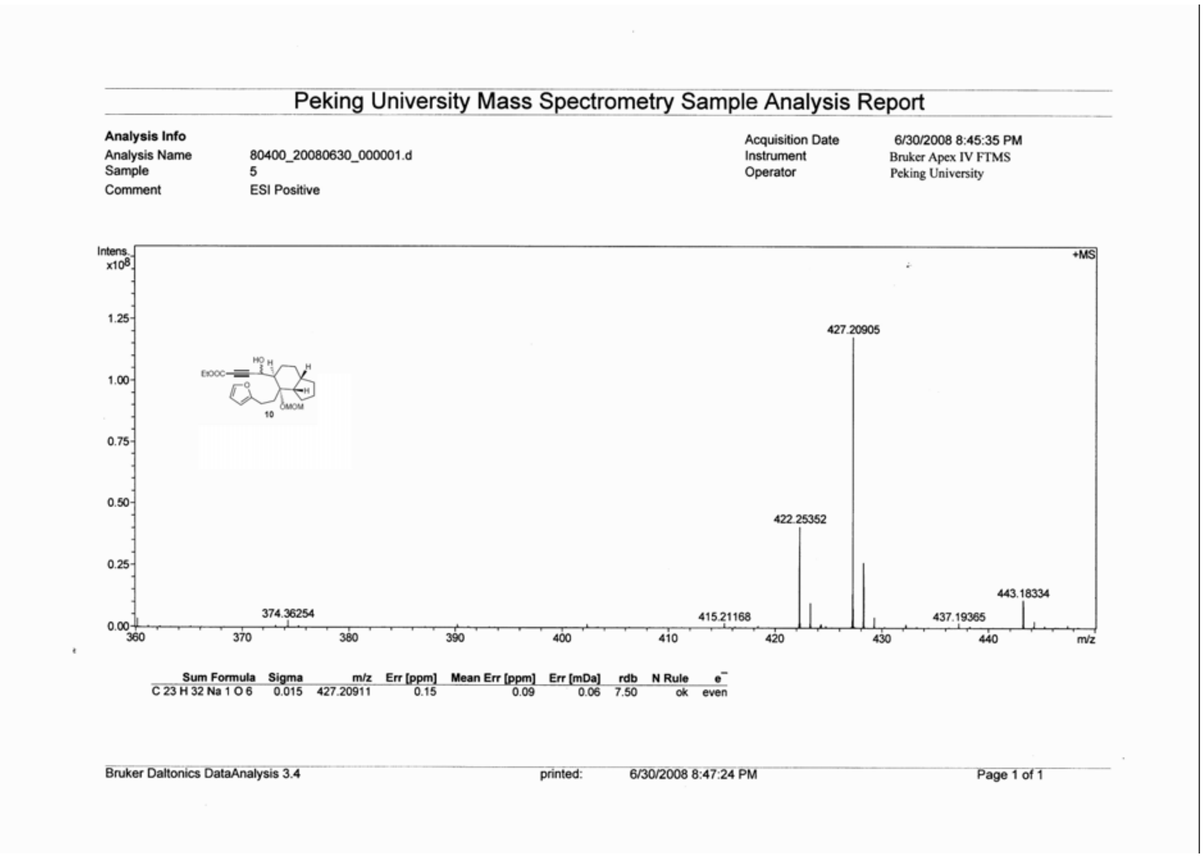
60
50
40
30
20
10
0
ppm



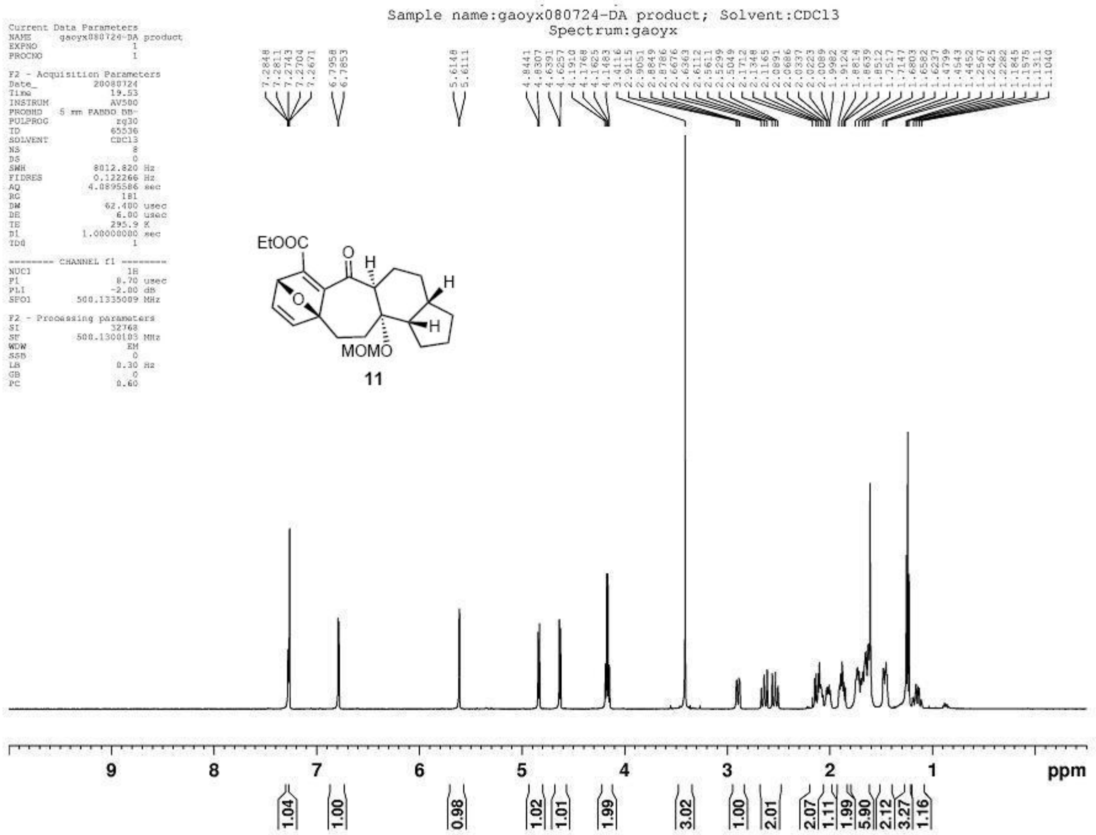
Peking University Mass Spectrometry Sample Analysis Report

Analysis Info
Analysis Name 80400_20080630_000001.d
Sample 5
Comment ESI Positive

Acquisition Date 6/30/2008 8:45:35 PM
Instrument Bruker Apex IV FTMS
Operator Peking University

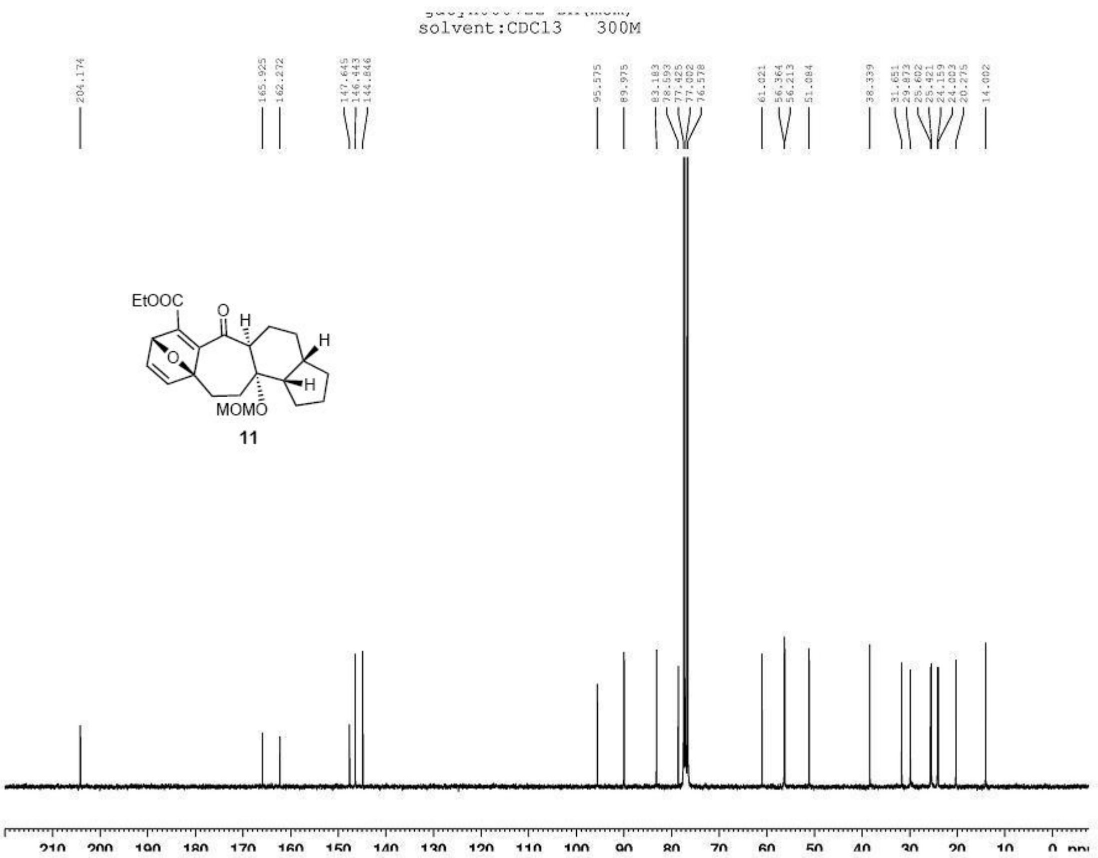
Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 23 H 32 Na 1 O 6	0.015	427.20911	0.15	0.09	0.06	7.50	ok	even

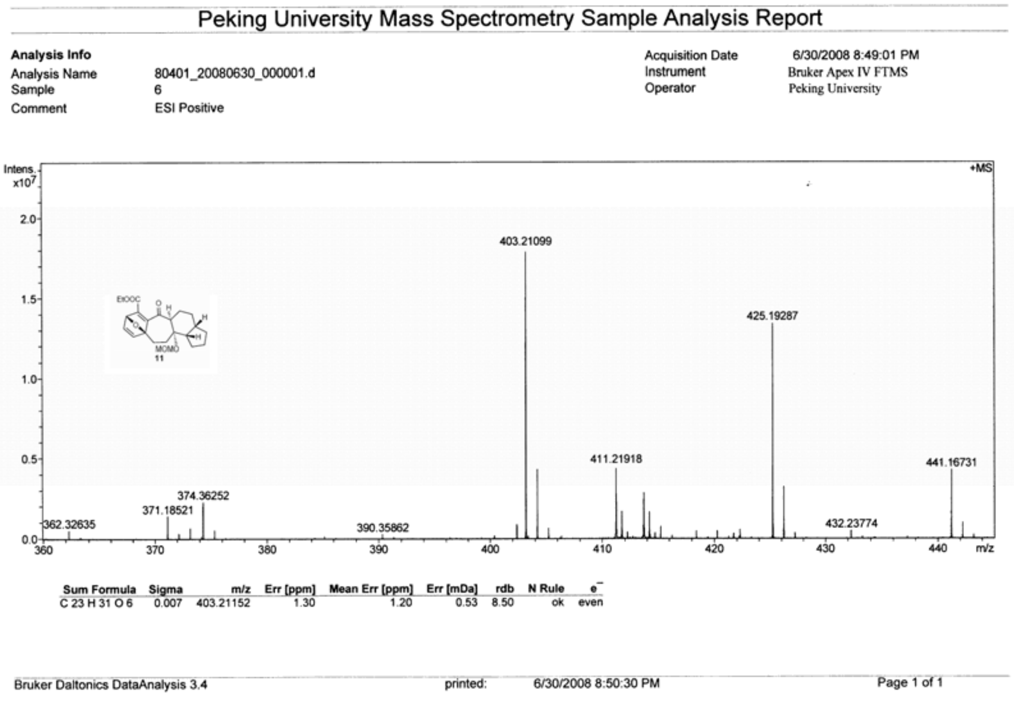
Bruker Daltonics DataAnalysis 3.4 printed: 6/30/2008 8:47:24 PM Page 1 of 1



Sample name:gaoyx080724-DA product; Solvent:CDCl3
Spectrum:gaoyx

```
Current Data Parameters
NAME     gaoyx080724-DA product
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20080724
Time                 19.53
INSTRUM              AV500
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       0
SWH               8012.820 Hz
FIDRES            0.122266 Hz
AQ               4.0895586 sec
RG                     181
DW                  62.400 usec
DE                    6.00 usec
TE                   295.9 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                    8.70 usec
PL1                  -2.00 dB
SFO1         500.1335009 MHz

F2 - Processing parameters
SI                   32768
SF           500.1300103 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    0.60
```





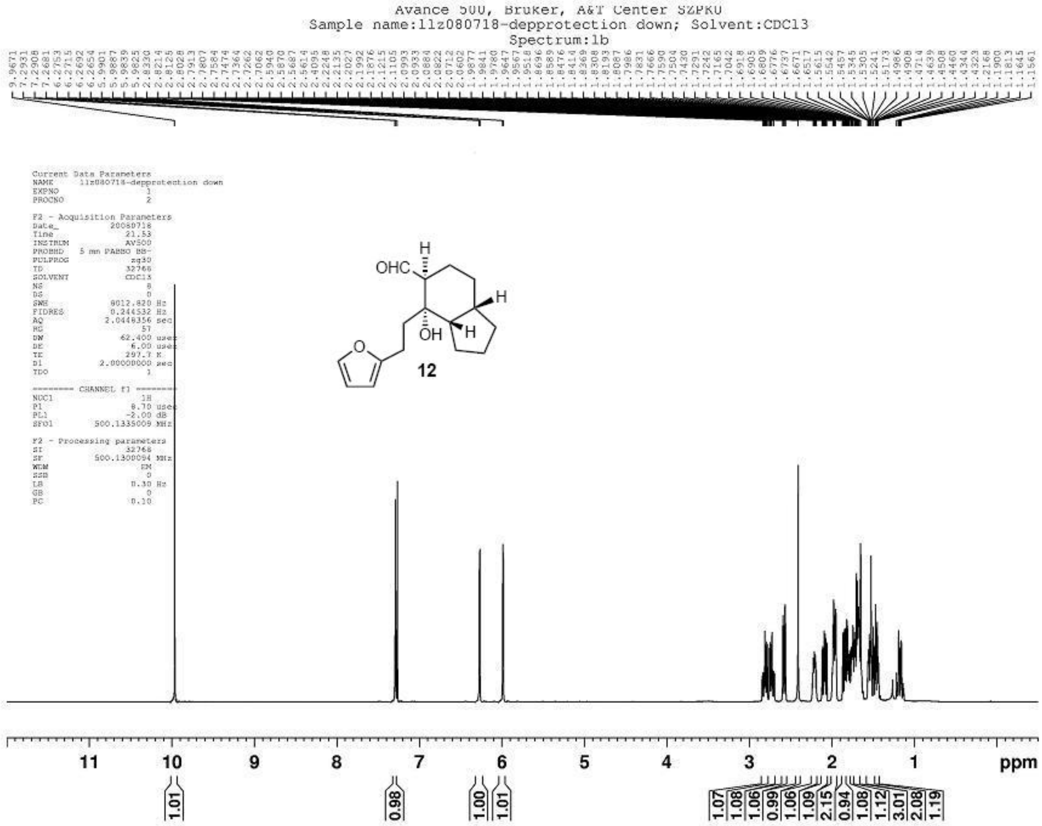
Peking University Mass Spectrometry Sample Analysis Report

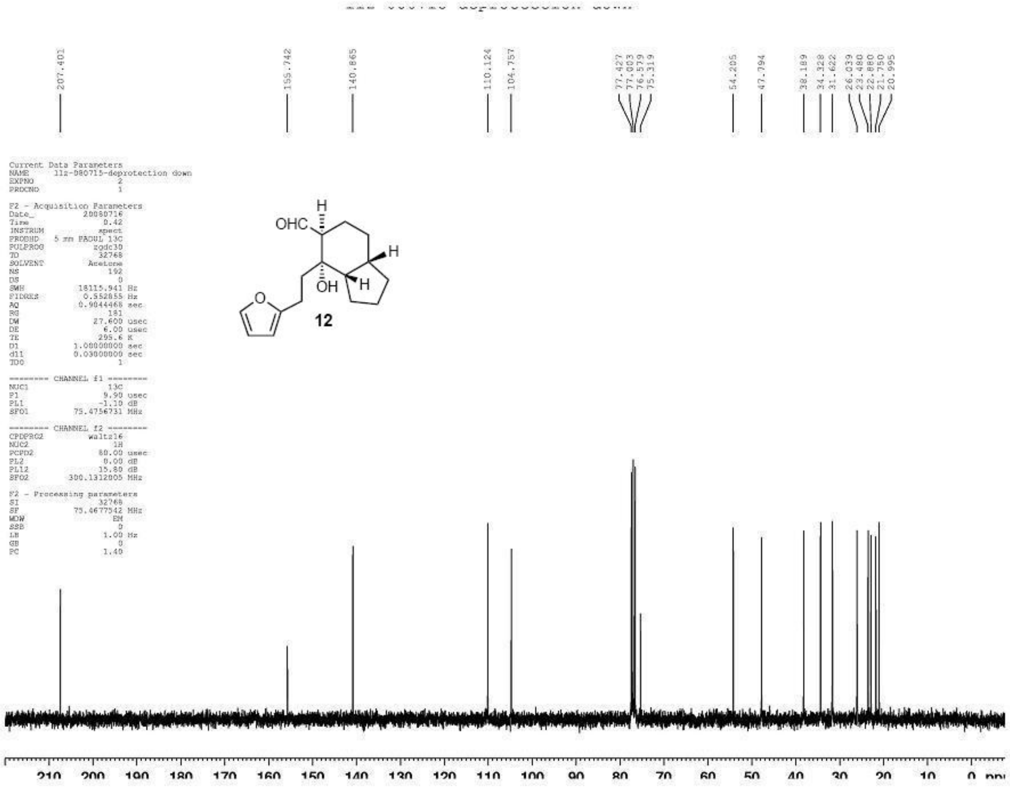
Analysis Info

Analysis Name	80401_20080630_000001.d	Acquisition Date	6/30/2008 8:49:01 PM
Sample	6	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University

Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 23 H 31 O 6	0.007	403.21152	1.30	1.20	0.53	8.50	ok	even

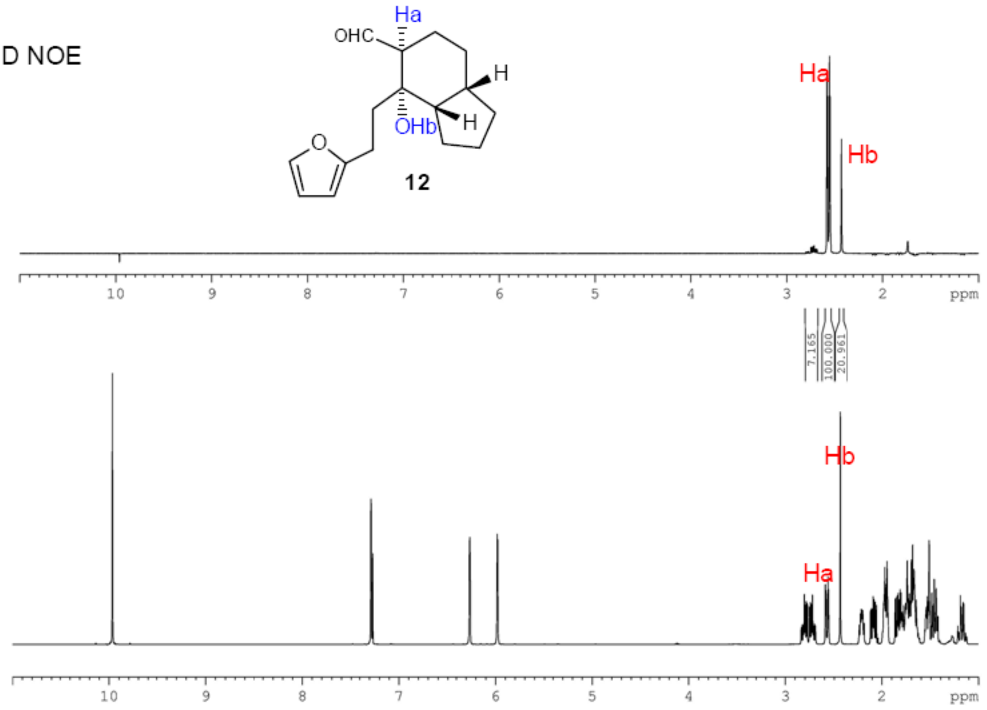
Bruker Daltonics DataAnalysis 3.4 printed: 6/30/2008 8:50:30 PM Page 1 of 1


Avance 500, Bruker, A&T Center SZPKU
Sample name:11z080718-depprotection down; Solvent:CDCl3
Spectrum:1b
OHC
H
OH
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.01
0.98
1.00
1.01
1.07
1.08
1.06
0.99
1.06
1.09
2.15
0.94
1.08
1.12
3.01
2.08
1.19

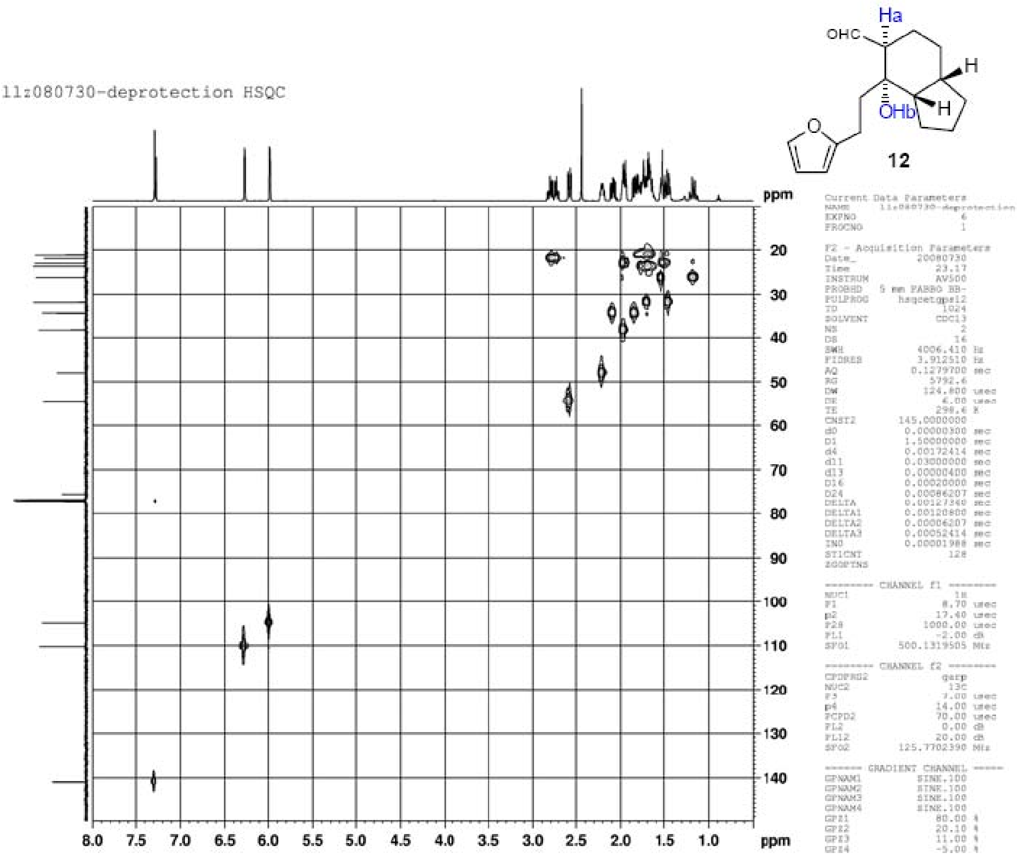

207.401
155.742
140.865
110.124
104.757
77.427
77.003
76.579
75.319
54.205
47.794
38.189
34.328
31.622
26.039
23.480
22.880
21.750
20.995
OHC
H
OH
12
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

1 D NOE, HSQC and deuteration result of compound 12

1D NOE

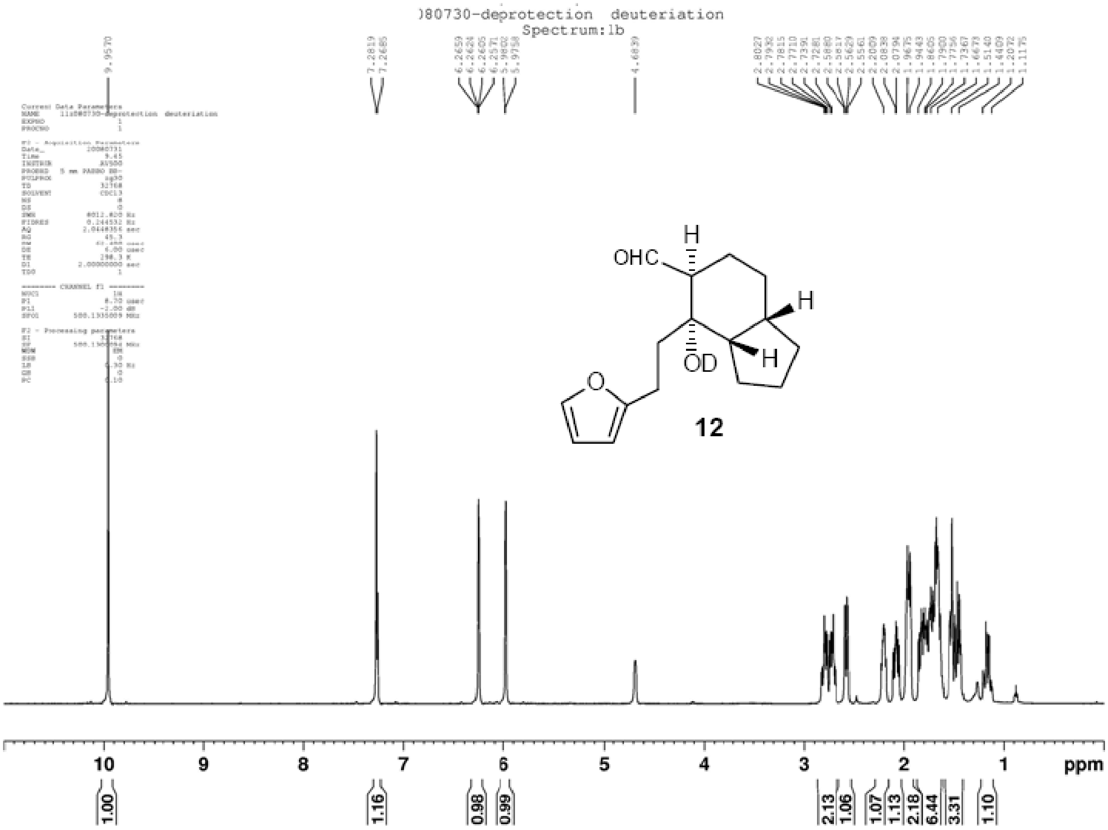


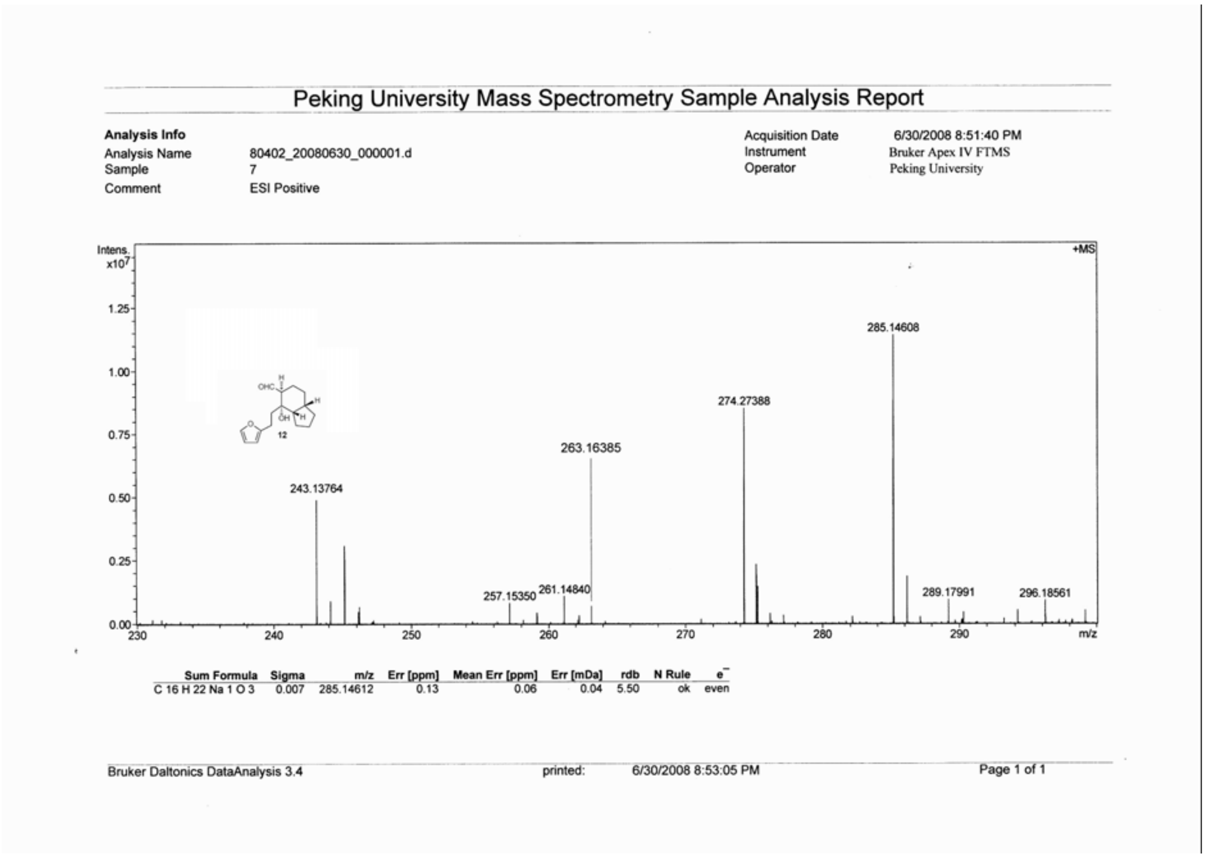
HSQC



```
Current Data Parameters
NAME      11z080730-deprotection
EXPNO                6
PROCNO               1

F2 - Acquisition Parameters
Date_          20080730
Time              23.17
INSTRUM           AV500
PROBHD   5 mm PABBO BB-
PULPROG     hsqcetgpsi2
TD                 1024
SOLVENT           CDCl3
NS                    2
DS                   16
SWH            4006.410 Hz
FIDRES         3.912510 Hz
AQ            0.1279700 sec
RG               5792.6
DW              124.800 usec
DE                 6.00 usec
TE                298.4 K
CNST2       145.0000000
d0           0.00000300 sec
D1           1.50000000 sec
d4           0.00172414 sec
d11          0.03000000 sec
d13          0.00000400 sec
D16          0.00020000 sec
D24          0.00086207 sec
DELTA        0.00127340 sec
DELTA1       0.00120800 sec
DELTA2       0.00006207 sec
DELTA3       0.00052414 sec
IN0          0.00001988 sec
ST1CNT              128
ZGOPTNS

======== CHANNEL f1 ========
NUC1                 1H
P1                 8.70 usec
p2                17.40 usec
P28             1000.00 usec
PL1               -2.00 dB
SFO1        500.1319505 MHz

======== CHANNEL f2 ========
CPDPRG2            garp
NUC2                13C
P3                 7.00 usec
p4                14.00 usec
PCPD2             70.00 usec
PL2                0.00 dB
PL12              20.00 dB
SFO2        125.7702390 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPNAM3         SINE.100
GPNAM4         SINE.100
GPZ1              80.00 %
GPZ2              20.10 %
GPZ3              11.00 %
GPZ4              -5.00 %
```

Deuteration



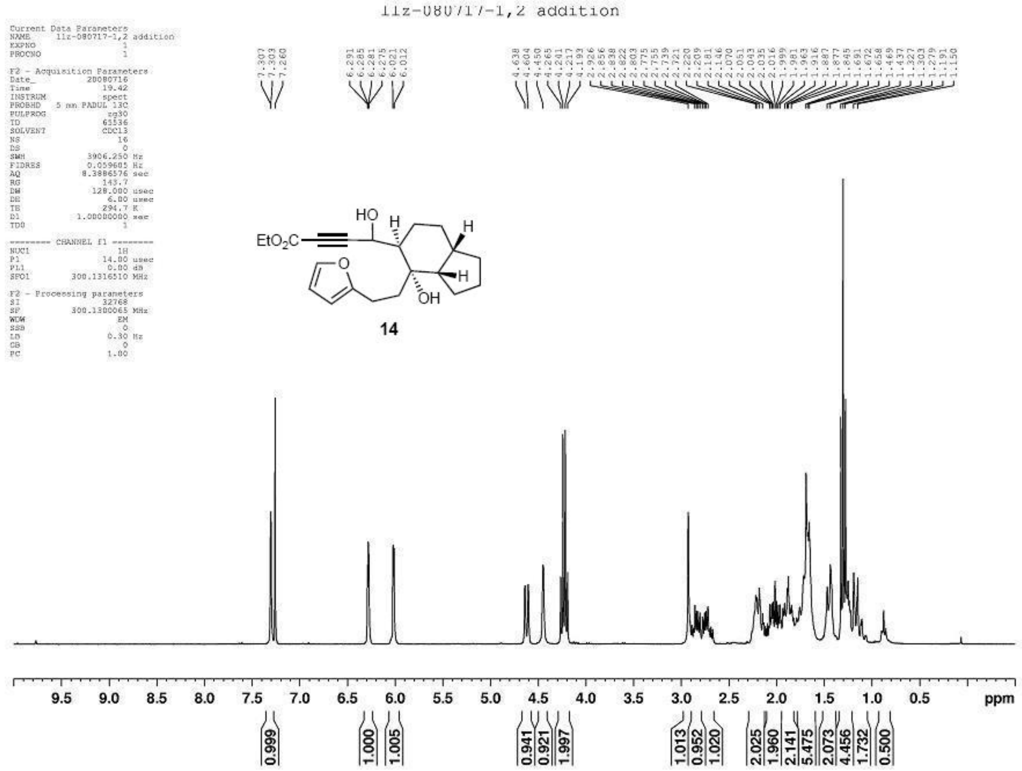


Peking University Mass Spectrometry Sample Analysis Report

Analysis Info		Acquisition Date	6/30/2008 8:51:40 PM
Analysis Name	80402_20080630_000001.d	Instrument	Bruker Apex IV FTMS
Sample	7	Operator	Peking University
Comment	ESI Positive		

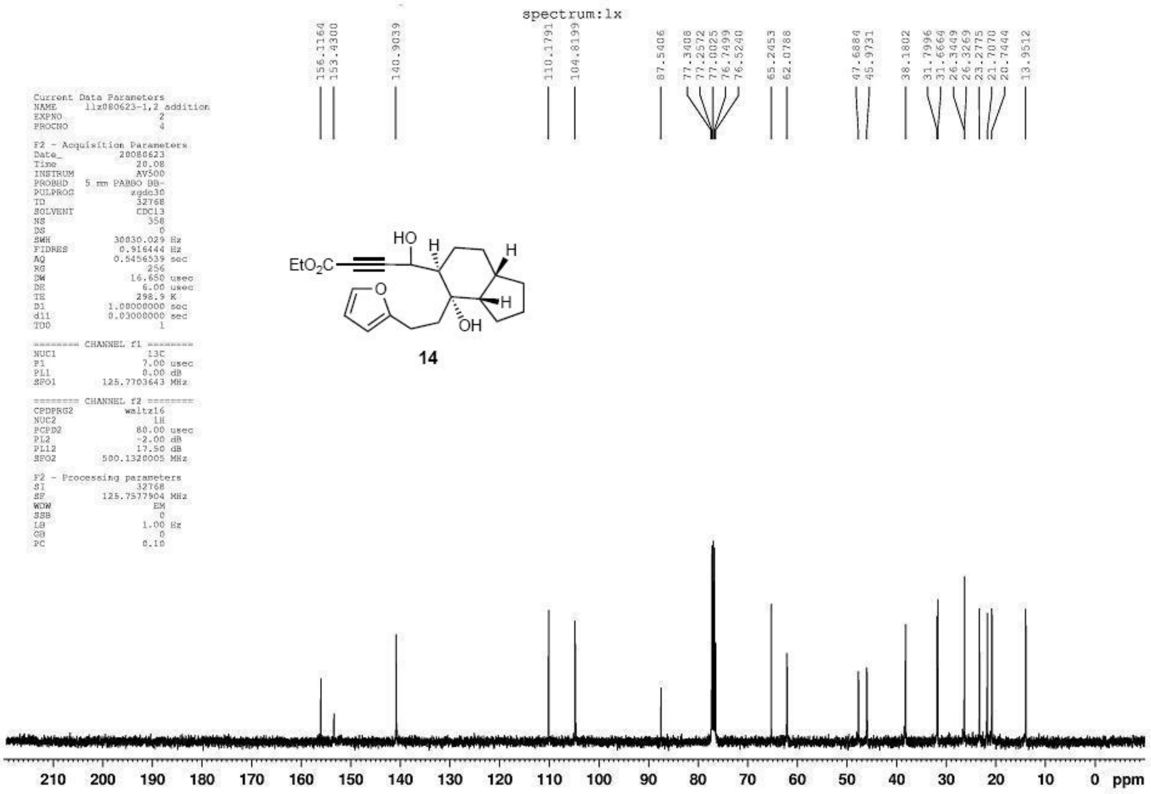
Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 16 H 22 Na 1 O 3	0.007	285.14612	0.13	0.06	0.04	5.50	ok	even

Bruker Daltonics DataAnalysis 3.4 printed: 6/30/2008 8:53:05 PM Page 1 of 1



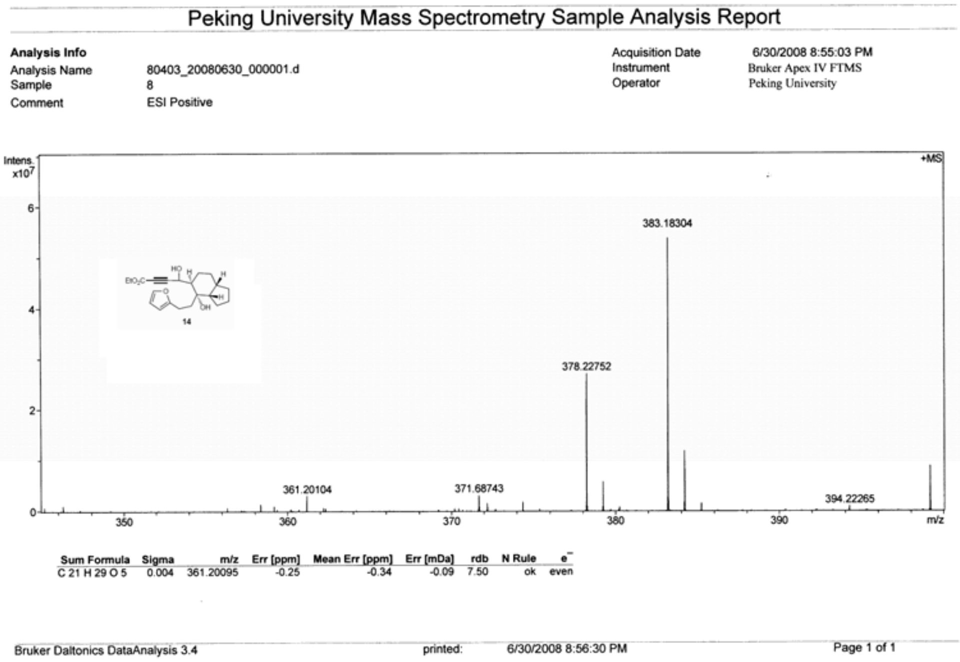
14

```
Current Data Parameters
NAME      11z-080717-1,2 addition
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20080716
Time                 19.42
INSTRUM              spect
PROBHD   5 mm PADUL 13C
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       0
SWH               3906.250 Hz
FIDRES            0.059605 Hz
AQ               8.3886576 sec
RG                   143.7
DW                 128.000 usec
DE                    6.00 usec
TE                   294.7 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   14.00 usec
PL1                   0.00 dB
SFO1           300.1316510 MHz

F2 - Processing parameters
SI                   32768
SF             300.1300065 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



14

```
Current Data Parameters
NAME      11z080623-1,2 addition
EXPNO                    2
PROCNO                   4

F2 - Acquisition Parameters
Date_             20080623
Time                 20.08
INSTRUM              AV500
PROBHD   5 mm PABBO BB-
PULPROG            zgdc30
TD                   32768
SOLVENT              CDCl3
NS                     358
DS                       0
SWH              30030.029 Hz
FIDRES            0.916444 Hz
AQ               0.5456539 sec
RG                     256
DW                  16.650 usec
DE                    6.00 usec
TE                   298.9 K
D1              1.00000000 sec
d11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    7.00 usec
PL1                   0.00 dB
SFO1           125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                  -2.00 dB
PL12                 17.50 dB
SFO2           500.1320005 MHz

F2 - Processing parameters
SI                   32768
SF             125.7577904 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    0.10
```

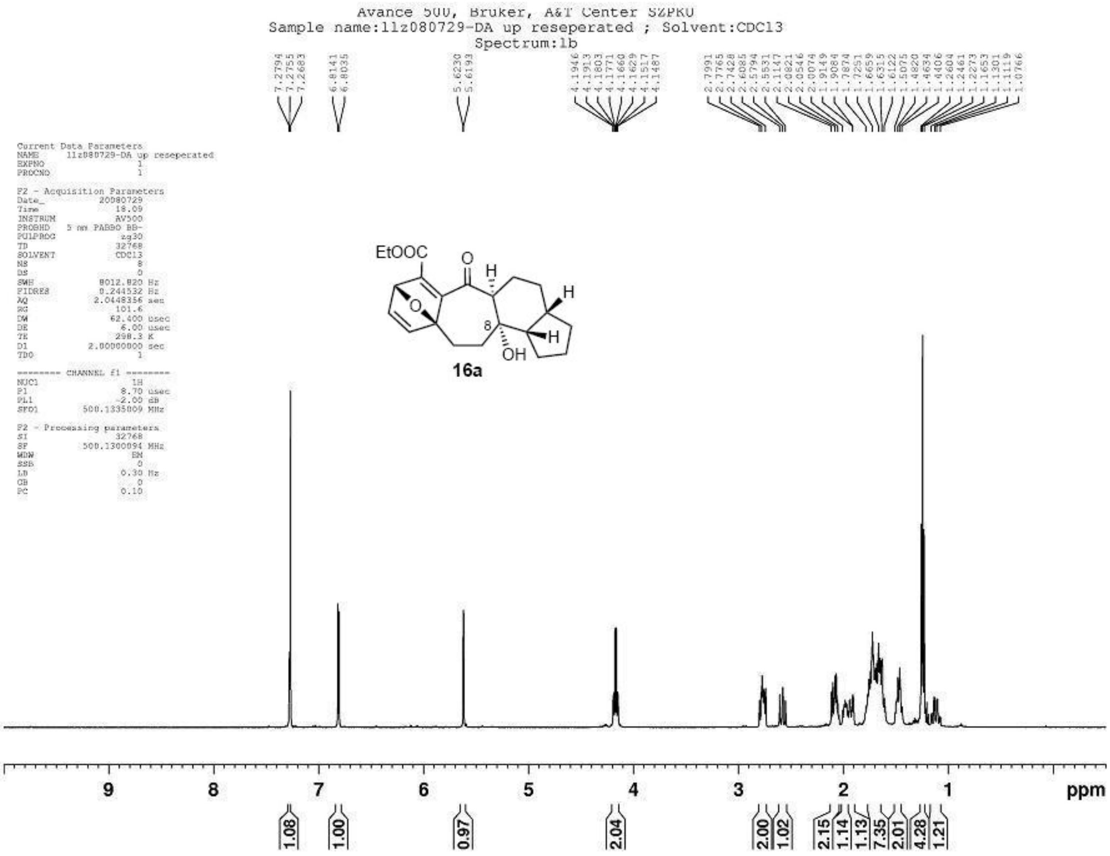


Peking University Mass Spectrometry Sample Analysis Report

Analysis Info		Acquisition Date	6/30/2008 8:55:03 PM
Analysis Name	80403_20080630_000001.d	Instrument	Bruker Apex IV FTMS
Sample	8	Operator	Peking University
Comment	ESI Positive		

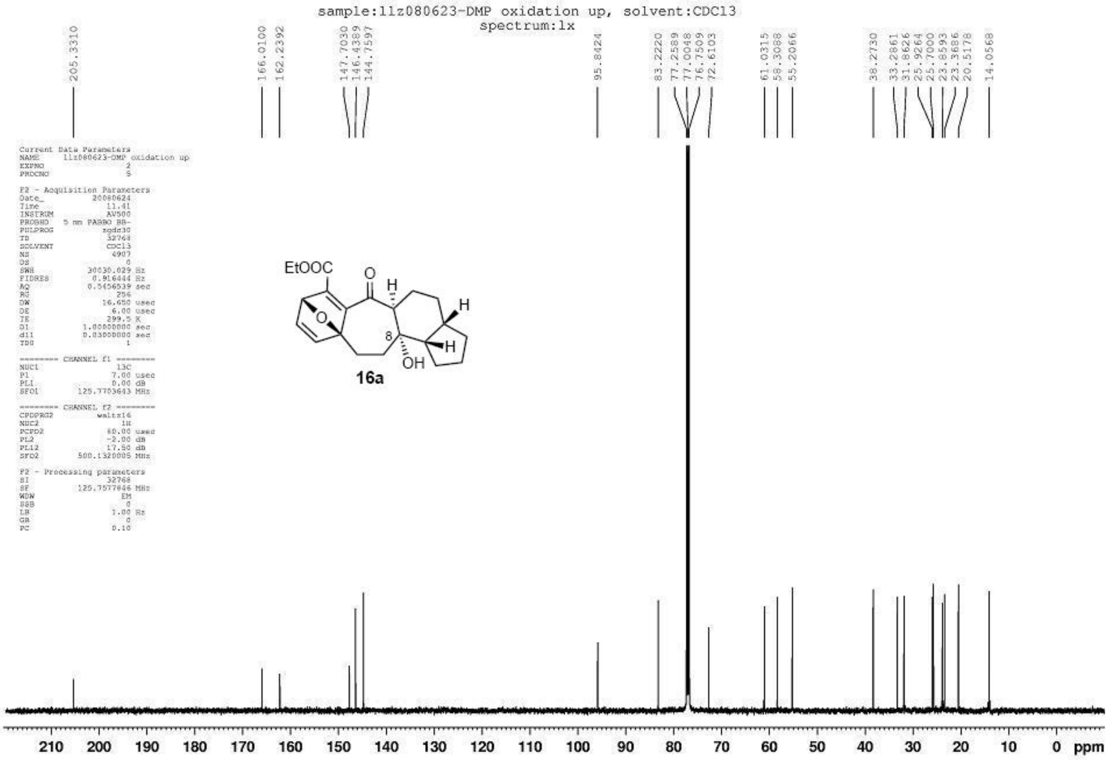
Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 21 H 29 O 5	0.004	361.20095	-0.25	-0.34	-0.09	7.50	ok	even

Bruker Daltonics DataAnalysis 3.4 printed: 6/30/2008 8:56:30 PM Page 1 of 1

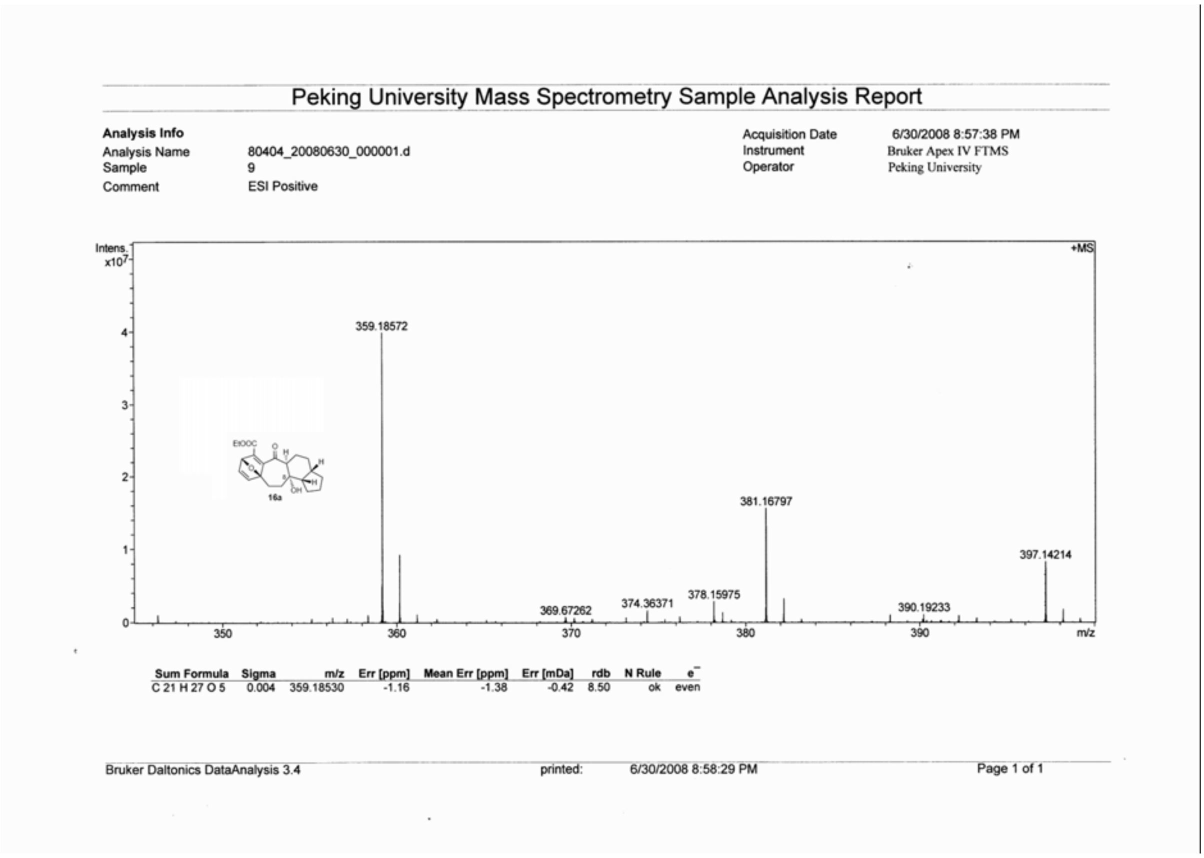


Avance 500, Bruker, A&T Center SZPKU
Sample name:llz080729-DA up reseperated ; Solvent:CDCl3
Spectrum:1b

```
Current Data Parameters
NAME     llz080729-DA up reseperated
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20080729
Time                  18.09
INSTRUM               AV500
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                        8
DS                        0
SWH             8012.820 Hz
FIDRES          0.244532 Hz
AQ             2.0448356 sec
RG                    101.6
DW               62.400 usec
DE                 6.00 usec
TE                 298.3 K
D1           2.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                 8.70 usec
PL1                -2.00 dB
SFO1        500.1335009 MHz

F2 - Processing parameters
SI                    32768
SF          500.1300094 MHz
WDW                      EM
SSB                       0
LB                  0.30 Hz
GB                        0
PC                     0.10
```



```
Current Data Parameters
NAME     llz080623-DMP oxidation up
EXPNO                 2
PROCNO                5

F2 - Acquisition Parameters
Date_          20080624
Time              11.41
INSTRUM           AV500
PROBHD   5 mm PABBO BB-
PULPROG          zgdc30
TD                32768
SOLVENT           CDCl3
NS                 4907
DS                    0
SWH           30030.029 Hz
FIDRES         0.916444 Hz
AQ            0.5456539 sec
RG                  256
DW               16.650 usec
DE                 6.00 usec
TE                299.5 K
D1           1.00000000 sec
d11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 7.00 usec
PL1                0.00 dB
SFO1        125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -2.00 dB
PL12              17.50 dB
SFO2        500.1320005 MHz

F2 - Processing parameters
SI                32768
SF          125.7577846 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 0.10
```



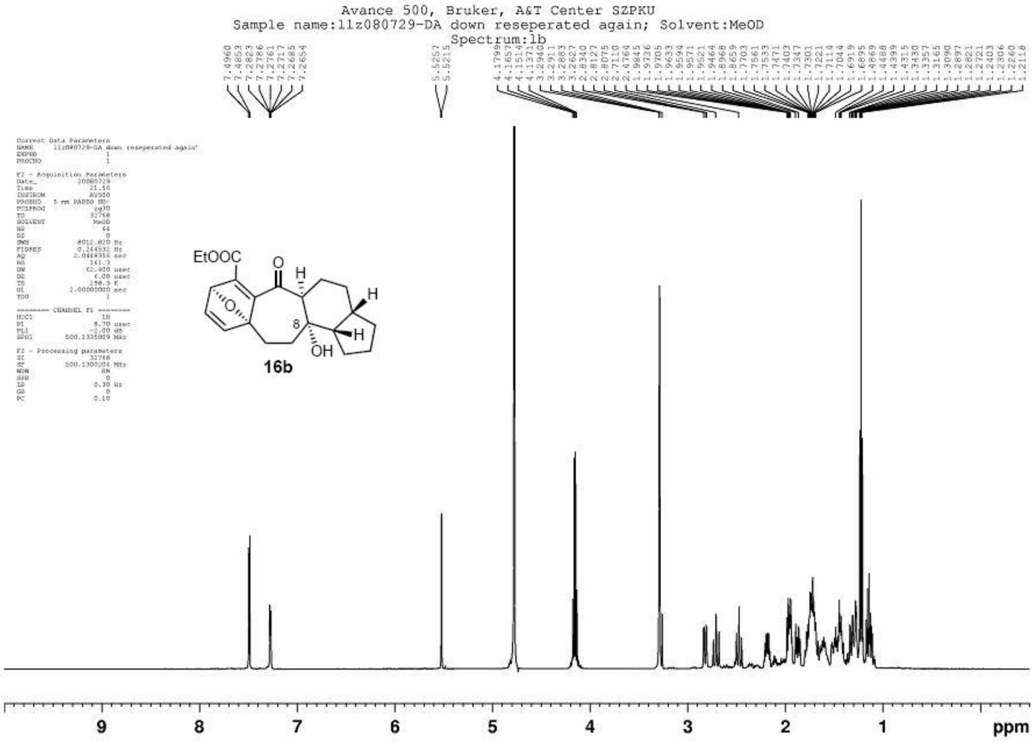
Peking University Mass Spectrometry Sample Analysis Report

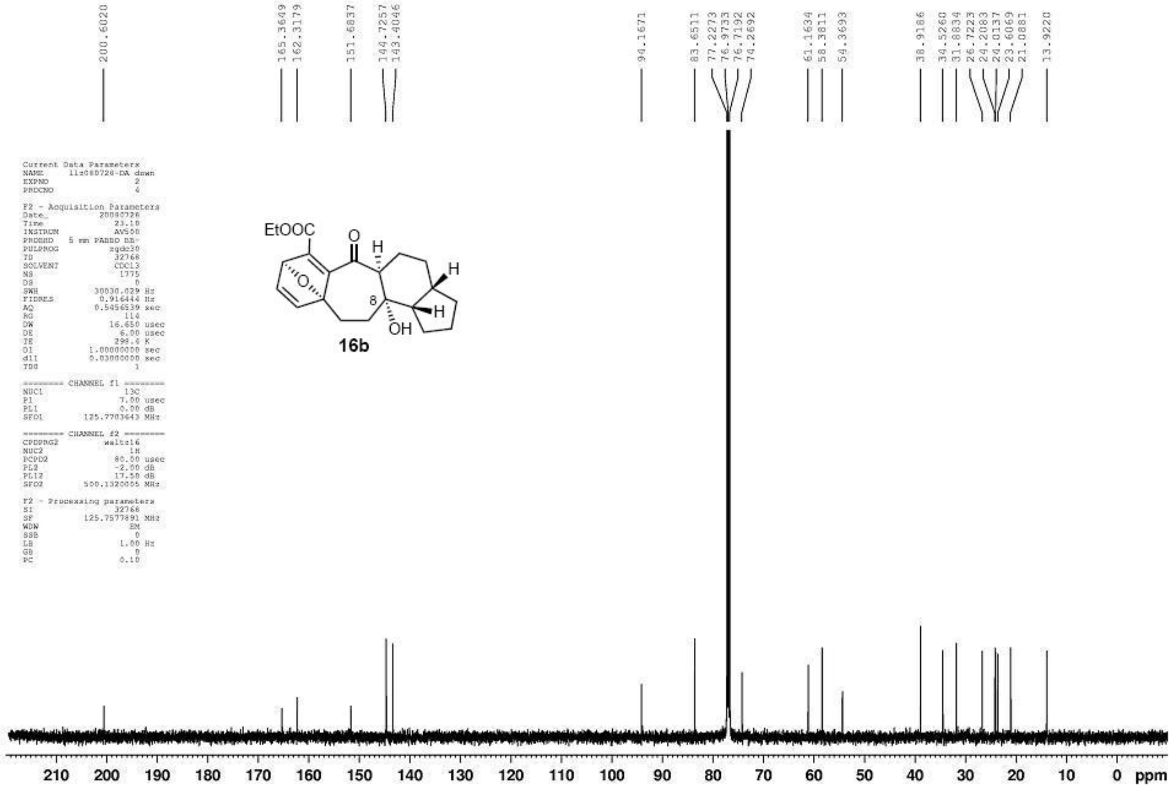
Analysis Info

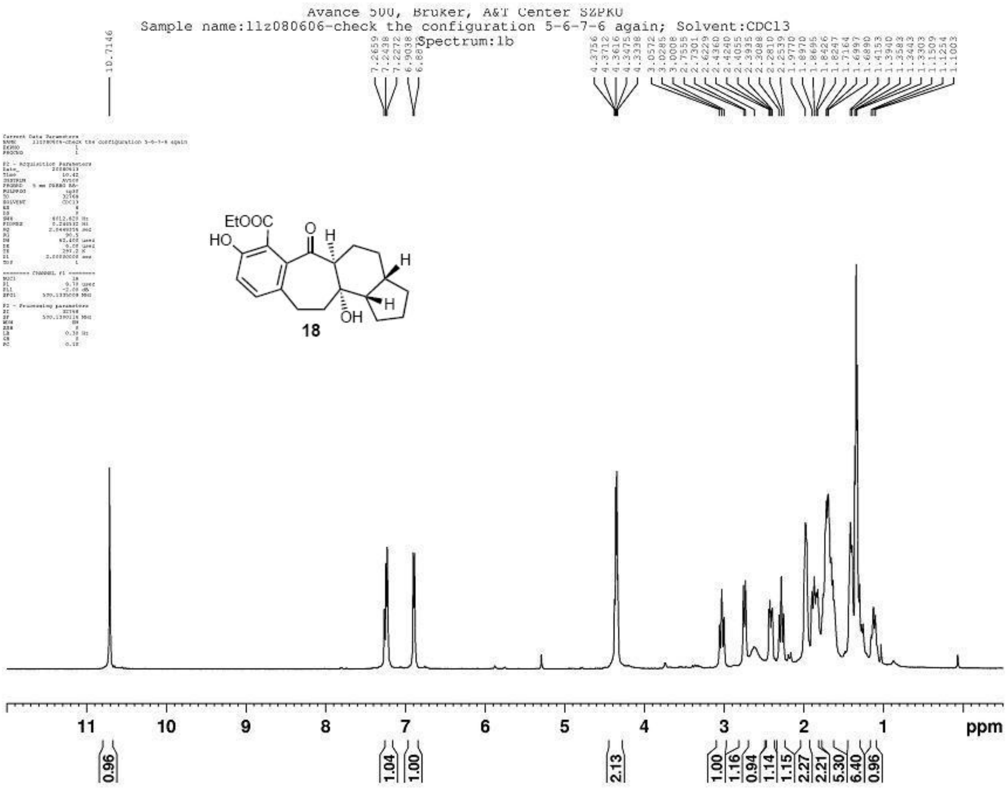
Analysis Name	80404_20080630_000001.d	Acquisition Date	6/30/2008 8:57:38 PM
Sample	9	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University

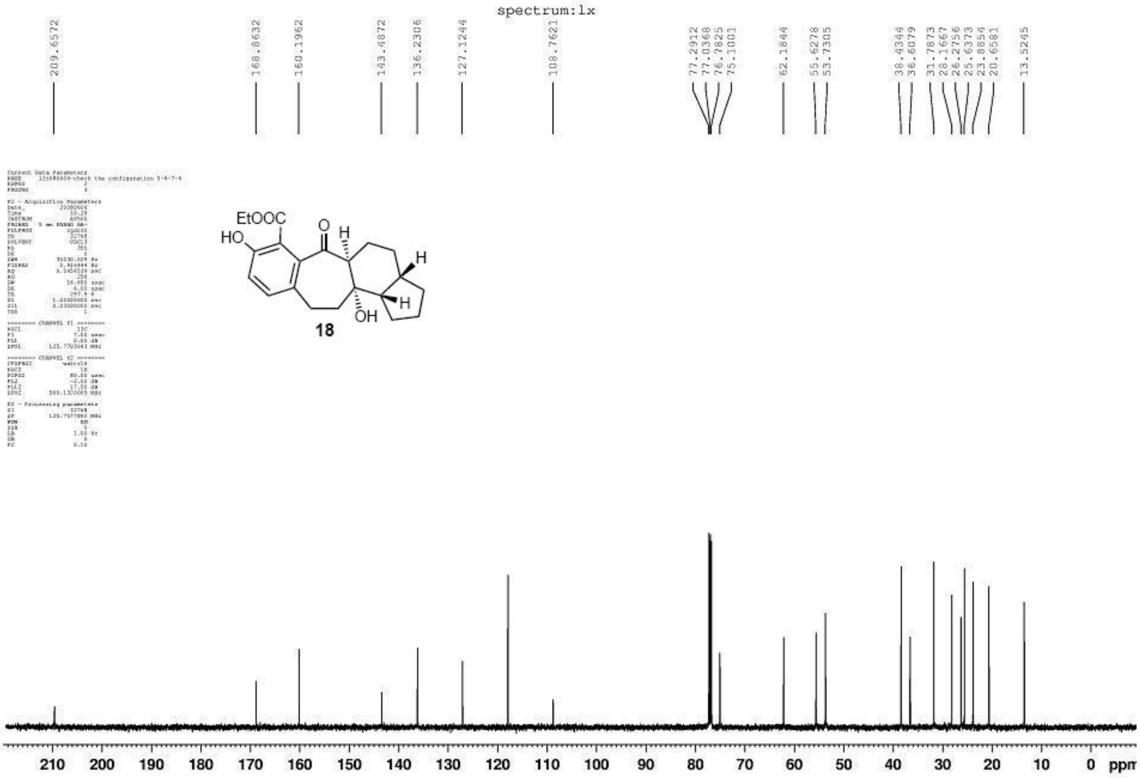
Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 21 H 27 O 5	0.004	359.18530	-1.16	-1.38	-0.42	8.50	ok	even

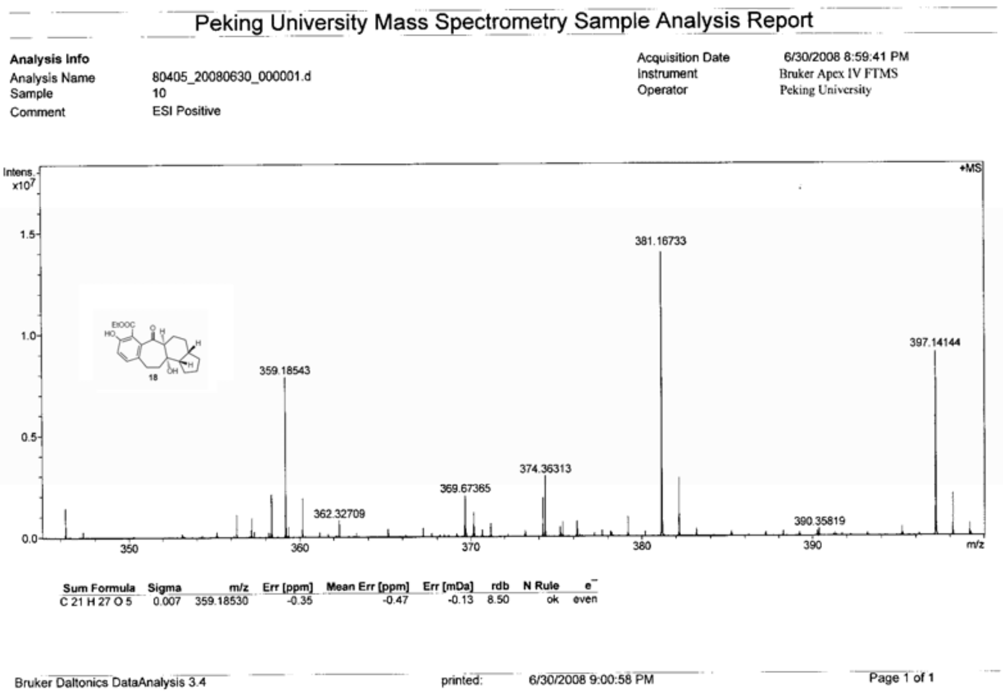
Bruker Daltonics DataAnalysis 3.4 printed: 6/30/2008 8:58:29 PM Page 1 of 1


Avance 500, Bruker, A&T Center SZPKU
Sample name:11z080729-DA down reseperated again; Solvent:MeOD
Spectrum:1b
7.4960
7.4853
7.2823
7.2786
7.2761
7.2717
7.2685
7.2654
5.5257
5.5215
4.1799
4.1657
4.1514
4.1371
3.2940
3.2911
3.2883
3.2627
2.8340
2.8127
2.8075
2.7110
2.4764
1.9845
1.9736
1.9705
1.9633
1.9594
1.9571
1.9521
1.9464
1.8968
1.8659
1.7703
1.7561
1.7533
1.7471
1.7403
1.7347
1.7301
1.7221
1.7114
1.7044
1.6919
1.6895
1.4869
1.4488
1.4399
1.4315
1.3430
1.3357
1.3165
1.3090
1.2897
1.2821
1.2721
1.2403
1.2306
1.2260
1.2118
Current Data Parameters
NAME 11z080729-DA down reseperated again
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080729
Time 21.56
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT MeOD
NS 64
DS 0
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 2.0448356 sec
RG 161.3
DW 62.400 usec
DE 6.00 usec
TE 298.3 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 8.70 usec
PL1 -2.00 dB
SFO1 500.1335009 MHz
F2 - Processing parameters
SI 32768
SF 500.1300204 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 0.10
EtOOC
O
H
H
H
8
OH
O
16b
9
8
7
6
5
4
3
2
1
ppm


200.6020
165.3649
162.3179
151.6837
144.7257
143.4046
94.1671
83.6511
77.2273
76.9733
76.7192
74.2692
61.1634
58.3811
54.3693
38.9186
34.5260
31.8834
26.7223
24.2083
24.0137
23.6069
21.0881
13.9220
Current Data Parameters
NAME 11z080728-DA down
EXPNO 2
PROCNO 4
F2 - Acquisition Parameters
Date_ 20080728
Time 23.10
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zgdc30
TD 32768
SOLVENT CDCl3
NS 1775
DS 0
SWH 30030.029 Hz
FIDRES 0.916444 Hz
AQ 0.5456539 sec
RG 114
DW 16.650 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
d11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.00 usec
PL1 0.00 dB
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 17.50 dB
SFO2 500.1320005 MHz
F2 - Processing parameters
SI 32768
SF 125.7577891 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 0.10
EtOOC
O
H
H
H
8
OH
O
16b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


Avance 500, Bruker, A&T Center SZPKU
Sample name:11z080606-check the configuration 5-6-7-6 again; Solvent:CDCl3
Spectrum:1b
10.7146
7.2659
7.2438
7.2272
6.9038
6.88
4.3756
4.3712
4.3616
4.3475
4.3338
3.0572
3.0285
3.0008
2.7555
2.7301
2.6229
2.4360
2.4240
2.4055
2.3935
2.3088
2.2810
2.2539
1.9770
1.8970
1.8695
1.8426
1.8247
1.7164
1.6997
1.6890
1.4153
1.3940
1.3583
1.3443
1.3303
1.1509
1.1254
1.1003
EtOOC
HO
O
H
H
H
OH
18
11
10
9
8
7
6
5
4
3
2
1
ppm
0.96
1.04
1.00
2.13
1.00
1.16
0.94
1.14
1.15
2.27
2.21
5.30
6.40
0.96


spectrum:1x
209.6572
168.8632
160.1962
143.4872
136.2306
127.1244
108.7621
77.2912
77.0368
76.7825
75.1001
62.1844
55.6278
53.7305
38.4344
36.6079
31.7873
28.1667
26.2756
25.6373
23.8854
20.6581
13.5245
EtOOC
HO
O
H
H
H
OH
18
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



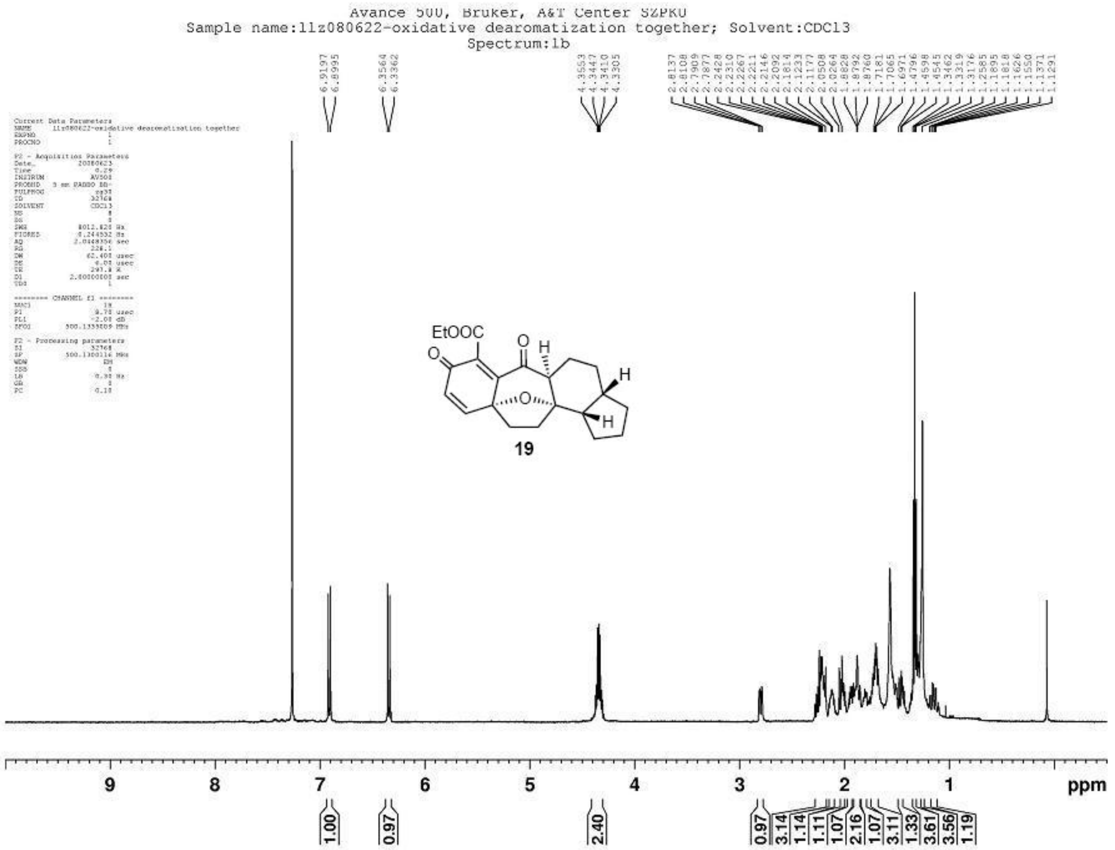
Peking University Mass Spectrometry Sample Analysis Report

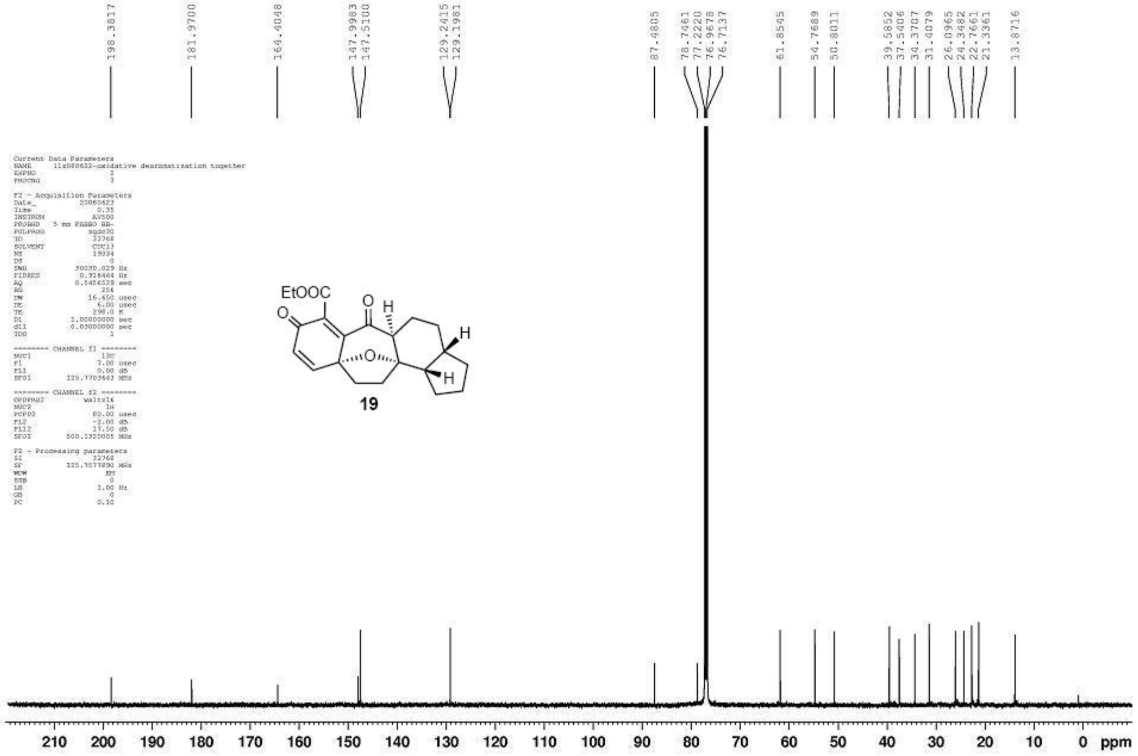
Analysis Info
Analysis Name 80405_20080630_000001.d
Sample 10
Comment ESI Positive

Acquisition Date 6/30/2008 8:59:41 PM
Instrument Bruker Apex IV FTMS
Operator Peking University

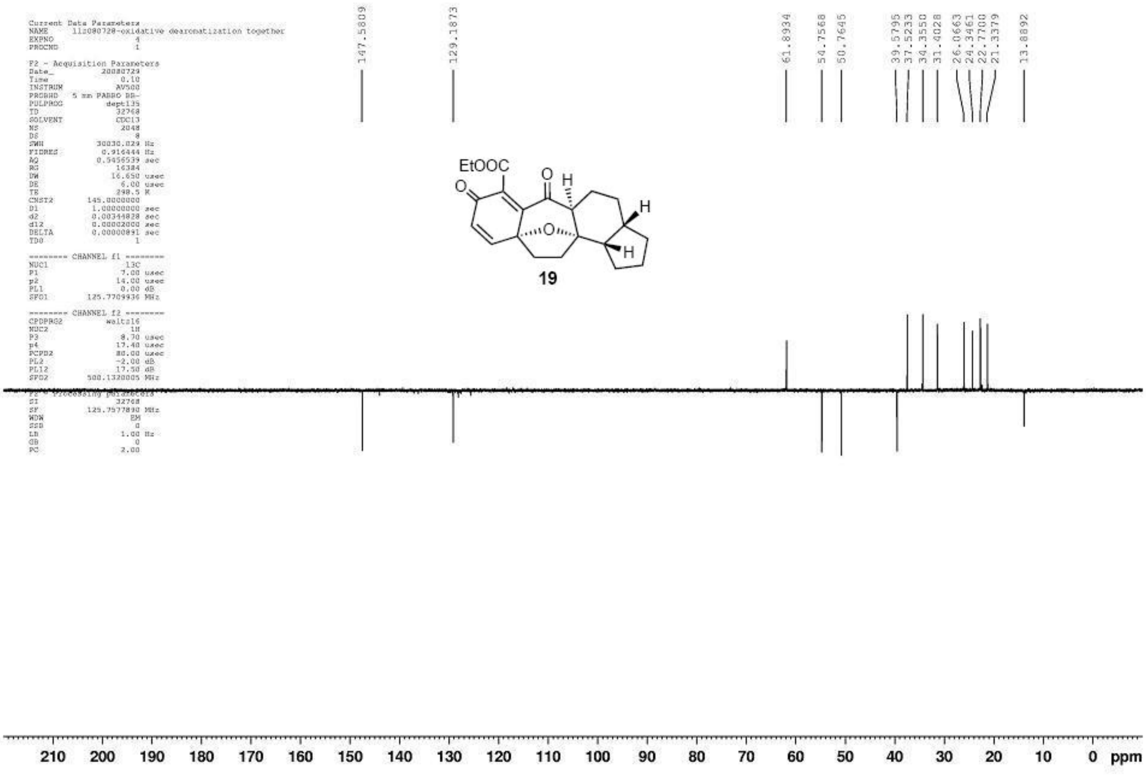
Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 21 H 27 O 5	0.007	359.18530	-0.35	-0.47	-0.13	8.50	ok	even

Bruker Daltonics DataAnalysis 3.4   printed: 6/30/2008 9:00:58 PM   Page 1 of 1





```
Current Data Parameters
NAME       11z080622-oxidative dearomatization together
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080623
Time                0.35
INSTRUM            AV500
PROBHD   5 mm PABBO BB-
PULPROG          zgdc30
TD                 32768
SOLVENT            CDCl3
NS                 19334
DS                     0
SWH            30030.029 Hz
FIDRES          0.916444 Hz
AQ             0.5456539 sec
RG                   256
DW                16.650 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
d11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  7.00 usec
PL1                 0.00 dB
SFO1         125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -2.00 dB
PL12               17.50 dB
SFO2         500.1320005 MHz

F2 - Processing parameters
SI                 32768
SF           125.7577890 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  0.10
```



```
Current Data Parameters
NAME       11z080728-oxidative dearomatization together
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080729
Time                0.10
INSTRUM            AV500
PROBHD   5 mm PABBO BB-
PULPROG         dept135
TD                 32768
SOLVENT            CDCl3
NS                  2048
DS                     8
SWH            30030.029 Hz
FIDRES          0.916444 Hz
AQ             0.5456539 sec
RG                 16384
DW                16.650 usec
DE                  6.00 usec
TE                 298.5 K
CNST2        145.0000000
D1            1.00000000 sec
d2            0.00344828 sec
d12           0.00002000 sec
DELTA         0.00000891 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  7.00 usec
p2                 14.00 usec
PL1                 0.00 dB
SFO1         125.7709936 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
P3                  8.70 usec
p4                 17.40 usec
PCPD2              80.00 usec
PL2                -2.00 dB
PL12               17.50 dB
SFO2         500.1320005 MHz

F2 - Processing parameters
SI                 32768
SF           125.7577890 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  2.00
```