# Supporting Information

## Total Synthesis of (±)-Ganocins B and C

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## 1 . General Experimental Details

The solvents used were dried by distillation over the drying agents indicated in parentheses and were transferred under argon: THF (Na-benzophenone), diethyl ether (Na-benzophenone), dichloromethane ($CaH_2$). Anhydrous DMF was purchased from Acros Organics and stored under argon. Commercially available chemicals were obtained from commercial suppliers and used without further purification unless otherwise stated.

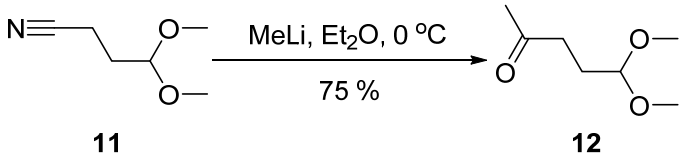
Proton ($^1H$), and Carbon NMR ($^{13}C$) were recorded at 400 MHz and 100 MHz NMR spectrometer, respectively. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br s: broad singlet for proton spectra. Coupling constants (*J*) are reported in Hertz (Hz).

High-resolution mass spectra (HRMS) were recorded on a BRUKER VPEXII spectrometer with EI and ESI mode unless otherwise stated.

Analytical thin layer chromatography was performed on Polygram SIL $G/UV_{254}$ and $G/UV_{365}$ plates. Visualization was accomplished with short wave UV light (254 nm and/or 365 mm) and/or phosphomolybdic acid or p-anisaldehyde stain or $KMnO_4$ staining solutions followed by heating. Flash column chromatography was performed using silica gel (200-300 mesh) with solvents distilled prior to use.

## 2 . Experimental Procedures

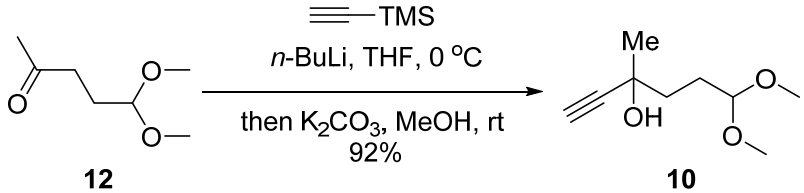
### 5,5-dimethoxypentan-2-one (16)[1]




**11** **12**

To a stirred solution of MeLi (3.1 M, 29.0 mL, 90 mmol, 3.0 equiv) in $Et_2O$ (100 mL) was added 4,4-dimethoxybutanenitrile (**11**) (3.9 mL, 30 mmol, 1.0 equiv) dropwise under argon at 0 °C. After stirring for 2 h, $NH_4Cl$ saturated solution (50 mL) was added and the mixture was stirred for an additional 10 min. The reaction was moved to room temperature, and the layers were separated. The aqueous layer was extracted with $Et_2O$ (5 x 30 mL) and the organic layers were combined, dried over $Na_2SO_4$, and concentrated under reduced pressure. The resulting residue was purified via flash chromatography (PE:EA 5:1) to afford **12** (3.3 g, 75% yield) as a clear oil. Compound **12** was put into next step immediately owing to its instability. Compound **12**: $R_f$ = 0.40 (PE:EA 2:1).

### 6,6-dimethoxy-3-methylhex-1-yn-3-ol (10)

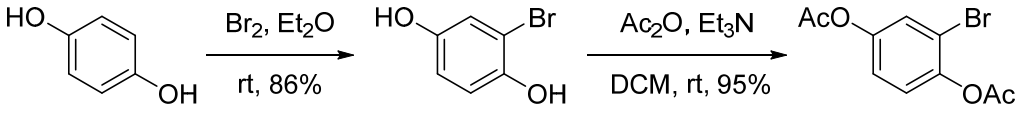



**12** **10**

To a stirred solution of ethynyltrimethylsilane (9.0 mL, 68.0 mmol, 1.51 equiv) in THF (70 mL) was added *n*-BuLi (42.2 mL, 1.6 M in hexane, 67.5 mmol, 1.50 equiv) dropwise at 0 °C under argon, and this solution was stirred for additional 30 min at the same temperature. After that, a solution of **12** (6.6 g, 45 mmol, 1.0 equive) in THF (10 mL) was added dropwise to the formed acetylide solution at 0 °C. The reaction was stirred for additional 2 h and then quenched with saturated $NH_4Cl$ at 0 °C. The resulting mixture was extracted with EA and the combined organic layers were washed with brine, dried over $Na_2SO_4$, and evaporated to give a residue, which was subjected to the next process without further purification.

The formed intermediate was dissolved in methanol (10 mL) and stirred with $K_2CO_3$ (6.9 g, 50 mmol, 1.1 equiv) for 6 h. The residue $K_2CO_3$ was removed by filtering. The organic layers were concentrated under reduced pressure. The mixture was washed with saturated $NH_4Cl$ and extracted with EA. The combined organic layers were washed with brine, dried over $Na_2SO_4$, and evaporated to give a residue, which was purified by column chromatography on silica gel (PE:EA 6:1) to afford compound **10** (7.1 g, 92%) as a pale yellow oil. Compound **10**: $R_f$ = 0.30 (PE:EA 2:1); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 4.44–4.40 (m, 1H), 3.34 (s, 6H), 2.91 (s, 1H), 2.44 (s, 1H), 2.01–1.92 (m, 1H), 1.88–1.80 (m, 1H), 1.78–1.73 (m, 2H), 1.50 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 104.5, 87.5, 71.4, 67.5, 52.9, 38.1 , 30.1, 28.0; HRMS–ESI (m/z) $[M + Na]^+$ calcd for $C_9H_{16}O_3Na$: 195.0992, found 195.0992.

**2-bromo-1,4-phenylene diacetate (9)**[2]



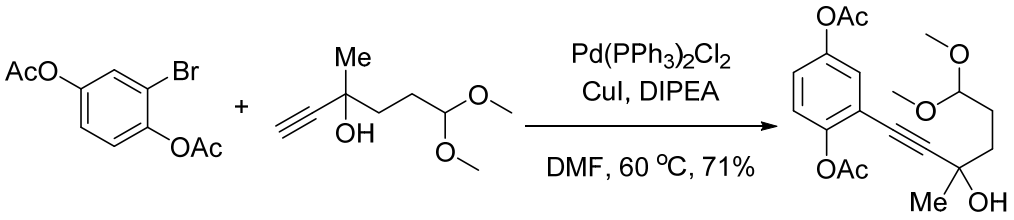

hydroquinone **S1** **9**

To a solution of hydroquinone (50.0 g, 454.0 mmol) in ethyl ether (200 mL) was added bromine (23.4 mL, 454.0 mmol) at 0 °C. The mixture was stirred at room temperature for 6 h. The reaction mixture was then quenched by using 10% aqueous sodium thiosulfate solution and extracted with ethyl ether. The organic layers were collected and washed with water, then brine, dried with anhydrous $Na_2SO_4$, and concentrated under vacuum. Compound **S1** was obtained as a white solid (74 g, 86% yield) after purification by flash column chromatography on silica gel (PE:EA 6:1). Compound **S1**: $R_f$ = 0.4 (PE:EA 4:1).

To a solution of **S1** (56.7 g, 300.0 mmol) in $CH_2C_2$ (400 mL) was added acetic anhydride (34 ml, 360.0 mmol) at 0 °C followed by triethylamine (62.4 mL, 450.0 mmol), then the mixture was stirred at room temperature. The reaction mixture was treated with aqueous ammonium chloride and extracted with $CH_2Cl_2$. The organic layer was washed with brine and dried ($Na_2SO_4$). The solvent was evaporated under reduced pressure, and the residue was purified by column chromatography (PE/EA 8:1) to afford **9** as a white solid (77.8 g, 95%). Compound **9**: mp: 71-73 $^o$C; $R_f$ = 0.5

(PE:EA 4:1); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.39 (d, $J$ = 2.6 Hz, 1H), 7.13 (d, $J$ = 8.7 Hz, 1H), 7.08 (dd, $J$ = 8.8, 2.6 Hz, 1H), 2.35 (s, 3H), 2.29 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 168.8, 168.4, 148.4, 145.9, 126.4, 123.9, 121.6, 116.2, 20.9, 20.7.

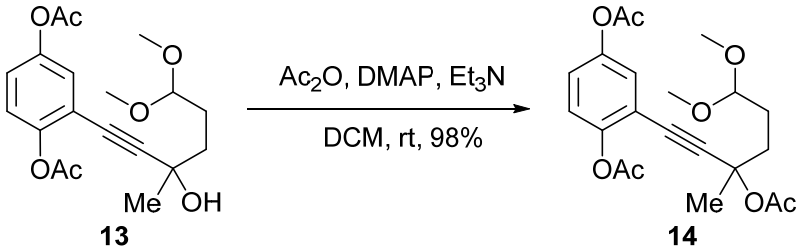
**2-(3-hydroxy-6,6-dimethoxy-3-methylhex-1-yn-1-yl)-1,4-phenylene diacetate (13)**




**9** **10** **13**

To a solution of **9** (1.23 g, 4.5 mmol, 1.5 equiv) and palladium catalyst (105 mg, 0.15 mmol, 5 mol %) and copper iodide (29 mg, 0.15 mmol, 5 mol %), in N,N-dimethylformamide (3.0 mL) were added **10** (516 mg, 3.0 mmol, 1.0 equiv) and DIPEA (2.1 mL, 12.0 mmol, 4.0 equiv) at room temperature. The resulting solution was then heated at 60 °C with stirring for 20 h under argon atmosphere. The reaction mixture was partitioned between ethyl acetate and aqueous ammonium chloride. The combined organic layers were washed three times with brine and concentrated in vacuo and the residue was purified by flash column chromatography (PE: EA 6:1) to give compound **13** (776 mg, 71%) as a pale yellow oil. Compound **13**: $R_f$ = 0.26 (PE:EA 2:1); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.19 (dd, $J$ = 2.0, 1.2 Hz, 1H), 7.08–7.04 (m, 2H), 4.43 (dd, $J$ = 5.7, 4.6 Hz, 1H), 3.34 (s, 6H), 3.05 (s, 1H), 2.33 (s, 3H), 2.28 (s, 3H), 2.06–1.92 (m, 1H), 1.90–1.76 (m, 3H), 1.55 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 169.0, 168.7, 149.0, 147.8, 125.8, 123.0, 122.7, 117.9, 104.4, 98.5, 68.0, 53.0, 53.00, 38.1, 30.1, 28.1, 21.0, 20.7; HRMS–ESI (m/z) $[M + Na]^+$ calcd for $C_{19}H_{24}O_7Na$: 387.1414, found 387.1412.

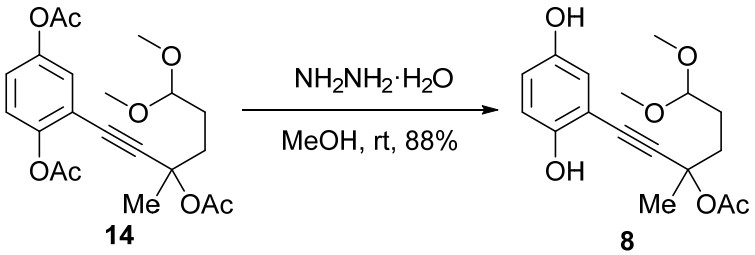
**2-(3-acetoxy-6,6-dimethoxy-3-methylhex-1-yn-1-yl)-1,4-phenylene diacetate (14)**




**13** **14**

To a solution of compound **13** (5.2 g, 14.3 mmol, 1.0 equiv) in DCM (15 mL) was added triethylamine (6 mL, 28.6 mmol, 2.0 equiv) and acetic anhydride (4 mL, 21.5 mmol, 1.0 equiv) and DMAP (200 mg, 1.6 mmol, 10 mol %) at room temperature. After stirring for 2 h, the reaction mixture was quenched with saturated $NH_4Cl$, concentrated under vacuum and then extracted with dichloromethane. The organic phases were combined and washed with brine, dried over anhydrous $Na_2SO_4$, filtered and concentrated concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE:EA 8:1) to give compound **14** (5.7 g, 98%) as a yellow oil. Compound **14**: $R_f$ =0.36 (PE:EA 2:1); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.20 (t, $J$ = 1.6 Hz, 1H), 7.06 (d, $J$ = 1.6 Hz, 2H), 4.41 (t, $J$ = 5.4 Hz, 1H), 3.33 (s, 6H), 2.36 (s, 3H), 2.27 (s, 3H), 2.02 (s, 3H), 2.07-1.99 (m, 1H), 1.94–1.80 (m, 4H), 1.73 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 169.0 (2C), 168.8, 149.1, 147.7, 126.1, 123.0, 122.9, 117.7, 104.1, 94.4, 79.5, 74.7, 52.8, 52.8, 36.6, 27.5, 26.5, 21.8, 21.0, 20.7; HRMS–ESI (m/z) $[M + Na]^+$ calcd for $C_{21}H_{26}O_8Na$: 429.1520, found 429.1519.

**1-(2,5-dihydroxyphenyl)-6,6-dimethoxy-3-methylhex-1-yn-3-yl acetate (8)**

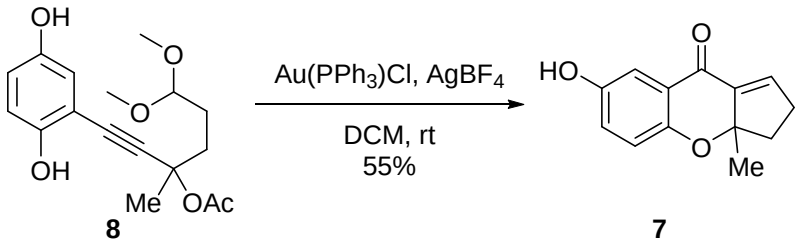



**14** **8**

To a stirred solution of compound **14** (5.7 g, 14.0 mmol, 1.0 equiv) in MeOH (10 mL) was added hydrazine hydrate (2.0 mL, 85 w% in $H_2O$, 35.0 mmol, 2.5 equiv) at 0 $^o$C under Ar and then the reaction mixture was moved to room temperature. After stirring at room temperature for 1 h, the reaction was quenched with saturated $NH_4Cl$ and extracted with ethyl acetate. The organic extract was dried over $Na_2SO_4$, followed

by filtration and solvent removal to give a dark yellow oil. The residue was purified by flash column chromatography (PE: EA 6:1) to give compound **8** (4.0 g, 88%) as a light yellow oil. Compound **8:** $R_f$ = 0.32 (PE:EA 2:1); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.79 (d, $J$ = 8.8 Hz, 1H), 6.75 (dd, $J$ = 8.8, 2.8 Hz, 1H), 6.69 (d, $J$ = 2.8 Hz, 1H), 5.68 (br s, 1H), 4.45 (t, $J$ = 5.5 Hz, 1H), 3.36 (d, $J$ = 1.4 Hz, 6H), 2.06 (s, 3H), 2.08–1.96 (m, 1H), 1.94 (m, 3H), 1.72 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 170.9, 152.7, 148.5, 118.4, 116.5, 115.8, 108.6, 104.0, 95.4, 81.4, 75.2, 52.9, 52.9, 36.2, 27.5, 26.6, 22.0; HRMS–ESI (m/z) $[M + Na]^+$ calcd for $C_{17}H_{22}O_6Na$: 345.1309, found 345.1319.

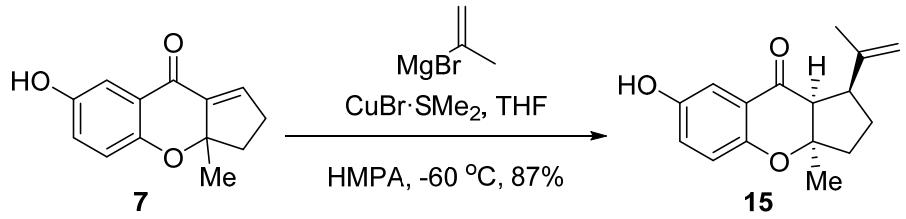
**7-hydroxy-3a-methyl-3,3a-dihydrocyclopenta[b]chromen-9(2H)-one (7)**




**8** **7**

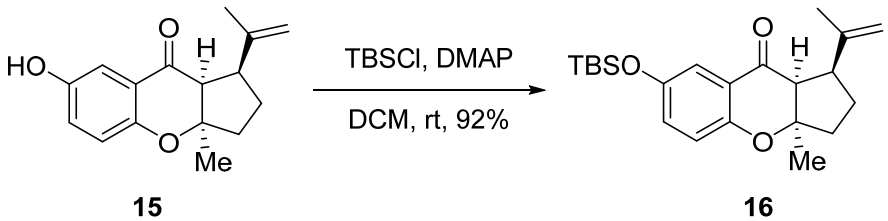
$Au(PPh_3)Cl$ (14 mg, 0.029 mmol, 10 mol %) was added to a solution of $AgBF_6$ (6 mg, 0.029 mmol, 10 mol %) in $CH_2Cl_2$ (0.6 mL, 0.025 M). The mixture was stirred for 20 min and compound **8** (94 mg, 0.29 mmol, 1.0 equiv) in 3.0 mL $CH_2Cl_2$ was added at room temperature. After stirring for 15min, *p*-$TsOH \cdot H_2O$ (55 mg, 0.29 mmol, 1.0 equiv) was added and the resulting mixture was stirred for 4 h at room temperature. Then the reaction mixture was washed with water and extracted with $CH_2Cl_2$. The combined organic phase was dried ($Na_2SO_4$) and concentrated under reduced pressure. The residue was purified by flash chromatography (PE:EA 8:1) to afford **7** as a yellow solid; yield: 34 mg (55%). Compound **7**: mp 133–135 $^o$C; $R_f$ = 0.40 (PE:EA 4:1); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.54 (d, $J$ = 3.1 Hz, 1H), 7.09 (dd, $J$ = 8.9, 3.1 Hz, 1H), 6.88 (dd, $J$ = 3.4, 2.0 Hz, 1H), 6.85 (d, $J$ = 8.8 Hz, 1H), 2.73–2.58 (m, 1H), 2.5 –2.40 (m, 2H), 2.38–2.24 (m, 1H), 1.43 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 181.5, 154.4, 150.5, 142.6, 140.6, 125.3, 121.6, 120.0, 111.6, 89.5, 40.1, 29.9, 23.2; HRMS–ESI (m/z) $[M + H]^+$ calcd for $C_{13}H_{13}O_3$: 217.0859, found 217.0853.

**Compound 15**




Isopropenylmagnesium bromide solution (14.4 mL, 0.5 M in hexane, 7.20 mmol, 3.0 equiv) was added to a mixture of $CuBr{\cdot}SMe_2$ (99 mg, 0.48 mmol, 0.2 equiv) in anhydrous THF (20 mL) at -60 $^oC$. HMPA (0.84 mL, 28.8 mmol, 12.0 equiv) was next introduced then stirred for 30 min. A solution of **7** (520 mg, 2.40 mmol, 1.0 equiv) in anhydrous THF (10 mL) was added dropwise to the mixture at -60 $^oC$ and stirred at the same temperature for another 30 min, water (15 mL) was added. The organic layer was washed with saturated $NH_4Cl$ (30 mL), dried over $Na_2SO_4$. Concentration and purification by flash column chromatography (PE/EA 8:1) gave **15** (537 mg, 87%) as light yellow solid. Compound **15**: mp 111–113 $^oC$; $R_f$ = 0.5 (PE:EA 4:1); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.28 (d, $J$ = 3.2 Hz, 1H), 7.02 (dd, $J$ = 8.8, 3.1 Hz, 1H), 6.79 (d, $J$ = 8.8 Hz, 1H), 5.36 (s, 1H), 4.70 (t, $J$ = 1.6 Hz, 1H), 4.69 (s, 1H), 3.26 (dt, $J$ = 11.9, 8.8 Hz, 1H), 2.87 (d, $J$ = 11.9 Hz, 1H), 2.30-2.21 (m, 1H), 2.20-2.09 (m, 1H), 2.01-1.94 (m, 1H), 1.83-1.75 (m, 1H), 1.54 (s, 1H), 1.44 (s, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 194.8, 154.6, 150.2, 144.4, 125.2, 120.6, 119.6, 113.6, 110.7, 89.2, 58.4, 50.6, 40.5, 30.3, 23.4, 22.8; HRMS–ESI (m/z) $[M + H]^+$ calcd for $C_{16}H_{19}O_3$: 259.1329, found 259.1291.

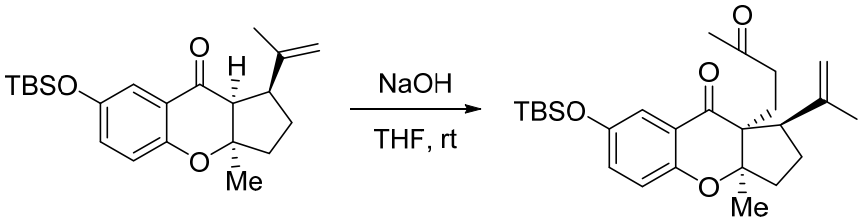
**Compound 16**




To a stirred solution of phenol **15** (900 mg, 3.5 mmol, 1.0 equiv) in dry $CH_2Cl_2$ (8 mL) was added DMAP (854 mg, 7.0 mmol, 2.0 equiv) and TBSCl (790 mg, 5.3 mmol, 1.5 equiv). The mixture was stirred at room temperature for 12 hours. After completion, the reaction mixture was quenched with saturated $NH_4Cl$, concentrated

under vacuum and then extracted with $CH_2Cl_2$. The organic phases were combined and washed with brine, dried over anhydrous $Na_2SO_4$, filtered and concentrated to yield the crude product. The residue was purified by column chromatography on silica gel (PE:EA 100:1), to give the desired product **16** (1.2 g, 92%) as a light yellow oil. Compound **16**: $R_f$ = 0.26 (PE:EA 64:1); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.22 (d, $J$ = 3.0 Hz, 1H), 6.95 (dd, $J$ = 8.8, 3.1 Hz, 1H), 6.75 (d, $J$ = 8.8 Hz, 1H), 4.69 (t, $J$ = 1.5 Hz, 1H), 4.67 (s, 1H), 3.24 (dt, $J$ = 12.0, 8.7 Hz, 1H), 2.86 (d, $J$ = 11.9 Hz, 1H), 2.28-2.22 (m, 1H), 2.18-2.08 (m, 1H), 2.00-1.93 (m, 1H), 1.83-1.74 (m, 1H), 1.53 (s, 3H), 1.44 (s, 3H), 0.96 (s, 9H), 0.17 (d, $J$ = 2.7 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 193.5, 154.8, 149.2, 144.5, 128.9, 120.8, 119.1, 115.5, 113.3, 89.1, 58.3, 50.3, 40.5, 30.1, 25.6, 23.4, 22.9, 18.1, -4.6, -4.6; HRMS–ESI (m/z) $[M + H]^+$ calcd for $C_{22}H_{33}O_3Si$: 373.2193, found 373.2208.

**Compound 17**

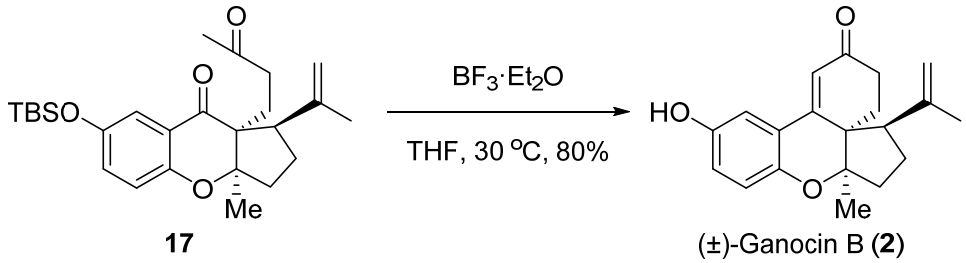



**16** **17**

To a stirred solution of compound **16** (112 mg, 0.30 mmol) in dry THF (3 mL) was added dry solid NaOH (6.0 mg, 0.15 mmol, 0.5 equiv) at 0 $^o$C and the mixture was stirred for 10 min and then warm to room temperature. Freshly prepared MVK (30 μL, 0.36 mmol, 1.2 equiv) was added very slowly (over 30 min) at the same temperature for 2 h. The reaction was quenched with saturated $NH_4Cl$, and the mixture was extracted with ethyl acetate. The combined organic layers were dried with $Na_2SO_4$ and concentrated in vacuo. The resulting crude product was purified by silica gel column chromatography, eluting with PE:EA 100:1 to 60:1 to 30:1. Compound **17** (light yellow oil) were obtained 51 mg (38%, 59% brsm) and compound **16** were recoveried 40 mg (36%). Compound **17** : $R_f$ = 0.26 (PE:EA 16:1); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.17 (d, $J$ = 3.0 Hz, 1H), 6.95 (dd, $J$ = 8.8, 3.1 Hz, 1H), 6.72 (d, $J$ = 8.8 Hz, 1H), 4.76 (s, 1H), 4.74 (s, 1H), 3.00 (ddd, $J$ = 18.1, 9.9, 5.4 Hz, 1H), 2.74 (t, $J$ = 8.5 Hz, 1H), 2.61 (ddd, $J$ = 18.3, 9.9, 5.7 Hz, 1H), 2.14 (s, 3H), 2.07–1.85 (m, 6H), 1.58 (s, 3H), 1.43 (s, 3H), 0.96 (s, 9H), 0.17 (d, $J$ = 2.2 Hz, 6H); $^{13}$C

NMR (100 MHz, $CDCl_3$) $\delta$ 208.5, 196.2, 154.0, 149.5, 144.6, 128.7, 122.1, 119.2, 115.7, 113.9, 92.3, 60.4, 55.5, 39.7, 37.9, 30.1, 29.7, 28.0, 25.6, 22.8, 21.2, 18.2, -4.5, -4.5; HRMS–ESI (m/z) $[M + H]^+$ calcd for $C_{26}H_{39}O_4Si$: 443.2612, found 443.2605.

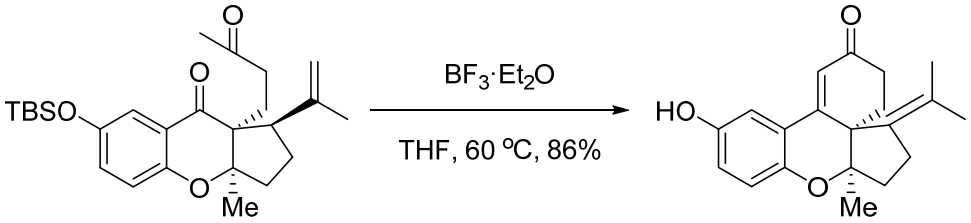
**(±)-Ganocin B (2)**




**17** (±)-Ganocin B (**2**)

To a stirred solution of compound **17** (32 mg, 0.072 mmol, 1.0 equiv) in THF (1 mL) was added $BF_3{\cdot}Et_2O$ (0.14 mL, 1.0 M, 2.0 equiv) dropwise at 30 °C. The reaction stirred at this temperature for 48 h. After completion, the mixture was concentrated under vacuum, distributed into water and ethyl acetate, extracted with ethyl acetate. The organic layers were combined and washed with brine, dried over anhydrous $Na_2SO_4$, filtered and concentrated to yield crude product. The product **2** was purified by column chromatography on silica gel (PE:EA 8:1), 17 mg (80% yield) of yellow solid product ganocin B was obtained. mp 166–169 °C; $R_f$ = 0.2 (PE:EA 4:1); $^1$H NMR (400 MHz, $C_5D_5N$) $\delta$ 7.65 (d, $J$ = 2.9 Hz, 1H), 7.22 (dd, $J$ = 8.8, 2.8 Hz, 1H), 6.95 (d, $J$ = 8.7 Hz, 1H), 6.93 (s, 1H), 4.82 (s, 1H), 4.74-4.73 (m, 1H), 3.16 (t, $J$ = 8.1 Hz, 1H), 2.83 (ddd, $J$ = 18.6, 14.0, 4.9 Hz, 1H), 2.58 (ddd, $J$ = 18.0, 5.0, 2.2 Hz, 1H), 2.34–2.21 (m, 1H), 2.18–2.09 (m, 1H), 2.02–1.87 (m, 3H), 1.69–1.60 (m, 1H), 1.50 (d, $J$ = 1.2 Hz, 3H), 1.28 (s, 3H); $^{13}$C NMR (100 MHz, $C_5D_5N$) $\delta$ 198.0, 152.7, 151.8, 148.4, 145.9, 135.7, 135.5, 135.2, 122.0, 121.0, 120.5, 119.4, 114.3, 110.0, 88.6, 53.2, 51.7, 37.8, 34.0, 33.7, 28.3, 22.6, 19.0; HRMS–ESI (m/z) $[M + H]^+$ calcd for $C_{20}H_{23}O_3$: 311.1642, found 311.1637.

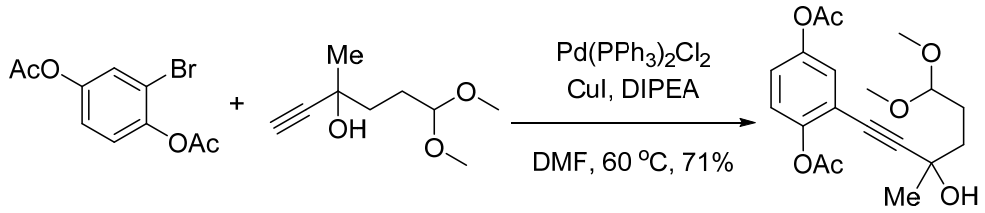
**(±)-Ganocin C (3)**




To a stirred solution of compound **17** (20 mg, 0.045 mmol, 1.0 equiv) in THF (1 mL) was added $BF_3{\cdot}Et_2O$ (0.09 mL, 1.0 M, 2.0 equiv) dropwise at room tmperture. The reaction was warmed to 60 $^oC$ and run for 24 h. After completion, the mixture was concentrated under vacuum, distributed into water and ethyl acetate, extracted with ethyl acetate. The organic layers were combined and washed with brine, dried over anhydrous $Na_2SO_4$, filtered and concentrated to yield crude product. The product **3** was purified by column chromatography on silica gel (PE:EA 8:1), 12 mg (86% yield) of yellow solid product ganocin C was obtained. mp 182–184 $^oC$; $R_f$ = 0.24 (PE:EA 4:1); $^1H$ NMR (400 MHz, $C_5D_5N$) $\delta$ 7.68 (d, $J$ = 2.9 Hz, 1H), 7.19 (dd, $J$ = 8.8, 2.9 Hz, 1H), 7.01 (s, 1H), 6.93 (d, $J$ = 8.8 Hz, 1H), 2.73–2.58 (m, 2H), 2.57–2.44 (m, 2H), 2.40–2.30 (m, 1H), 2.15–2.05 (m, 2H), 1.95–1.83 (m, 3H), 1.71 (ddd, $J$ = 12.9, 4.7, 2.9 Hz, 2H), 1.57 (s, 3H), 1.39 (s, 3H), 1.25 (s, 3H); $^{13}C$ NMR (100 MHz, $C_5D_5N$) $\delta$ 198.8, 154.6, 152.7, 148.1, 135.7, 135.5, 135.2, 134.5, 126.7, 122.5, 122.1, 119.0, 111.5, 90.7, 52.3, 34.7, 34.6, 31.0, 29.9, 28.6, 23.2, 18.8, 17.5; HRMS–ESI (m/z) $[M + H]^+$ calcd for $C_{20}H_{23}O_3$: 311.1642, found 311.1645.

## 3 . Optimization of Reaction Conditions

(1) Optimization of gold-catalyzed cascade reaction of compound **8**.[a]



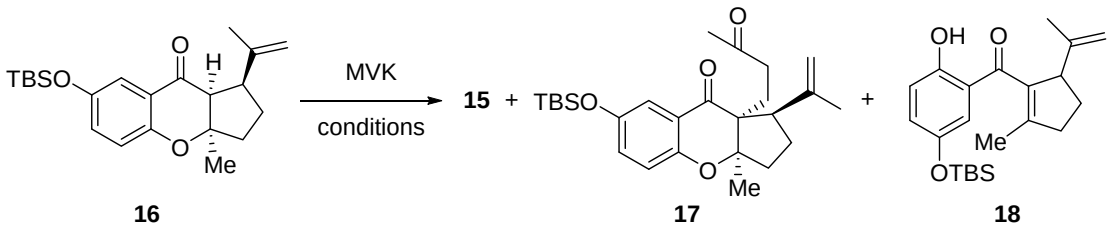

**9** **10** **13**

| entry | [Ag] | T/°C | **7** | **7a** |
|---|---|---|---|---|
| 1[b] | AgOTf | 40 | 0 | 38% |
| 2 | AgOTf | rt | 42% | 29% |
| 3[c] | AgOTf | rt | 34% | 0 |
| 4[c] | $AgBF_4$ | rt | 40% | 0 |
| 5 | $AgBF_4$ | rt | 55% | 0 |

[a] Reaction conditions: Compound **8** (0.1 mmol, 1.0 equiv)**,** $Au(PPh_3)Cl$ (10 mol %), [Ag] (10 mol %), $TsOH{\cdot}H_2O$ (1.0 equiv), DCM (0.2 mL + 1.0 mL); [b] Under Wong's conditions.[1] [c] Without addition of PTSA.

Compound **7a**: a light yellow solid; mp 162-164 °C; $R_f$ = 0.41 (PE:EA 4:1); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.59 (d, $J$ = 3.3 Hz, 1H), 7.05 (dd, $J$ = 8.9, 3.1 Hz, 1H), 6.86 (d, $J$ = 8.9 Hz, 1H), 6.31 (s, 1H), 5.39 (dq, $J$ = 6.6, 3.7, 3.2 Hz, 1H), 2.69–2.47 (m, 3H), 2.28 (s, 3H), 2.18–2.04 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 182.8, 158.3, 155.3, 150.6, 130.4, 124.2, 123.8, 119.3, 111.8, 85.6, 37.1, 29.8, 16.7; HRMS–ESI (m/z) $[M - H]^-$ calcd for $C_{13}H_{11}O_3$: 215.0714; found 215.0710.

(2) Optimization of Michael addition of compound **16** with MWK:




**16** **17** **18**

**General procedure**:

To a stirred solution of compound **16** (0.1 mmol) in solvent (1.0 mL) was added additive (0.05 mmol) and run for 10 min. Then freshly distilled MVK (0.15 mmol, 1.5

equiv) was added. After completion of the reaction, the resulting mixture was diluted with ethyl acetate and water and filtered through a pad of celite. Then the filtrate was extraced with ethyl acetate for three times. The combined organic layer was dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel with a mixture of petroleum ether and ethyl acetate as eluent.

| entry | additive | solvent | T/$^o$C | **15** | **16** | **17** | **18** |
|---|---|---|---|---|---|---|---|
| 1 | $Sc(OTf)_3$ | DCM | rt | 75% | 0 | 0 | 0 |
| 2 | NaOMe | MeOH | rt | 81% | 0 | 0 | 0 |
| 3 | t-BuOK | t-BuOH | rt | 0 | 77% | trace | 0 |
| 4 | piperidine | PhMe | 100 | 0 | 68% | 0 | 0 |
| 5 | LiHMDS | THF | -60 | 0 | 84% | trace | 0 |
| 6 | NaOH | THF | rt | 0 | 23% | 17% | 22% |
| 7 | $Na_2CO_3$ | THF | rt | 0 | 94% | 0 | 0 |
| 8 | DBU | THF | rt | 0 | 0 | 16% | 53% |

Conclusion: NaOH was found to be effective promoter.

**Optimization of varying temperature**:

| entry | additive | solvent | T/$^o$C | **16** | **17** | **18** |
|---|---|---|---|---|---|---|
| 1 | NaOH | THF | -10 | 91% | 0 | 0 |
| 2 | NaOH | THF | 0 | 92% | 0 | 0 |
| 3 | NaOH | THF | 0 to rt | 36% | 38% | 0 |

Compound **18** : $R_f$ = 0.28 (PE:EA 64:1), a yellow oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 11.81 (s, 1H), 7.08 (d, $J$ = 3.0 Hz, 1H), 7.00 (dd, $J$ = 8.9, 3.0 Hz, 1H), 6.86 (d, $J$ = 8.9 Hz, 1H), 4.74–4.71 (m, 1H), 4.67-4.66 (m, 1H), 3.92 (ddq, $J$ = 8.9, 6.7, 2.2 Hz, 1H), 2.66–2.54 (m, 1H), 2.5 –2.42 (m, 1H), 2.24 (dtd, $J$ = 13.4, 8.9, 4.7 Hz, 1H), 1.85–1.76 (m, 1H), 1.75–1.72 (m, 3H), 1.66 (s, 3H), 0.97 (s, 9H), 0.16 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 201.9, 157.2, 147.3, 147.2, 146.7, 137.3, 129.2, 121.7, 119.9, 118.9, 111.3, 56.9, 38.9, 29.1, 25.7, 19.8, 18.2, 16.6, -4.4, -4.4; HRMS–ESI (m/z) $[M + Na]^+$ calcd for $C_{22}H_{32}O_3SiNa$: 395.2013, found 395.2001.

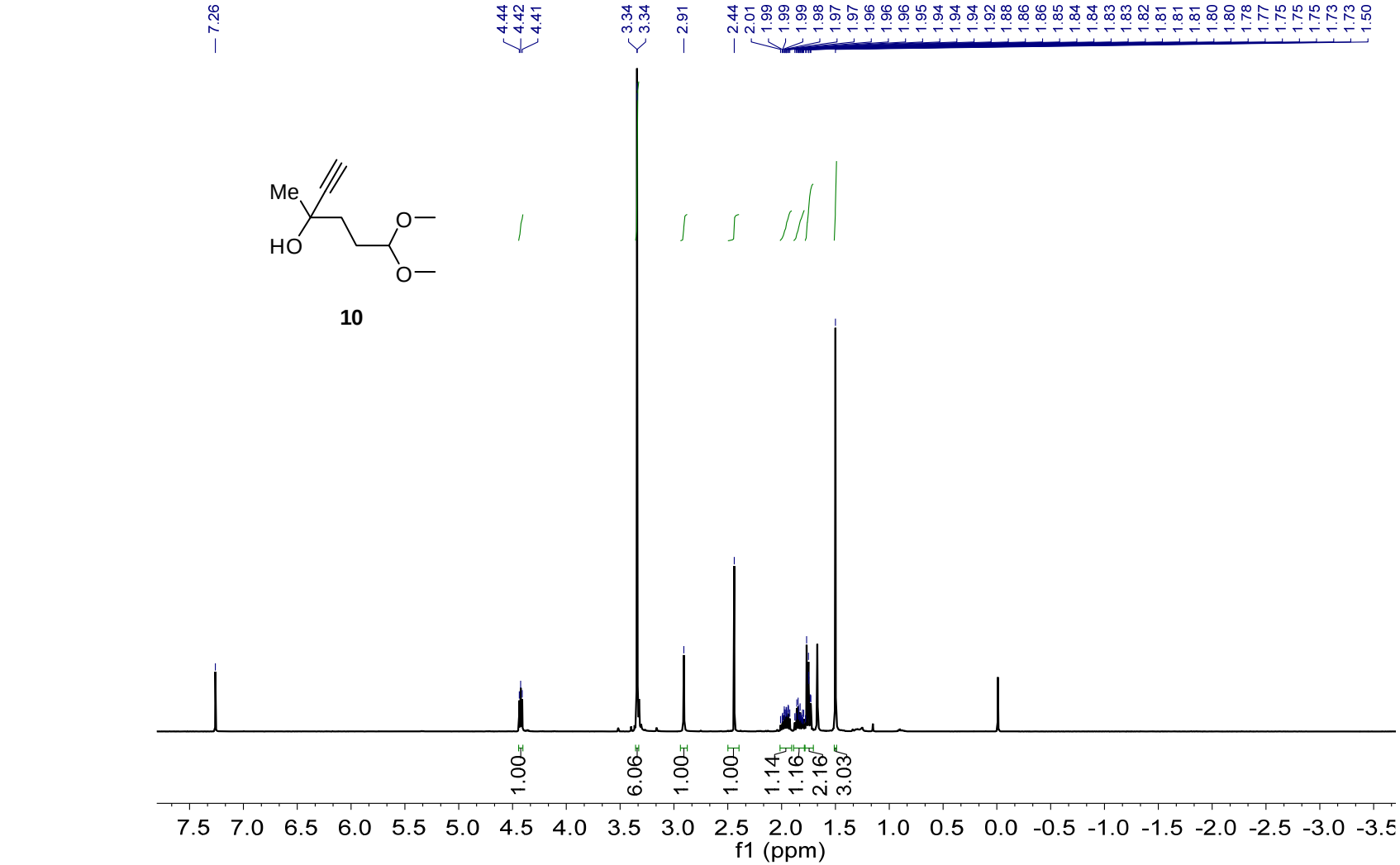
## 4 . References

1. Z. Li, Q. Li, G.-K. Liu, W. Chen, X.-S. Peng, and H. N. C. Wong, *Synlett*, 2015, **26**, 1461–1464.

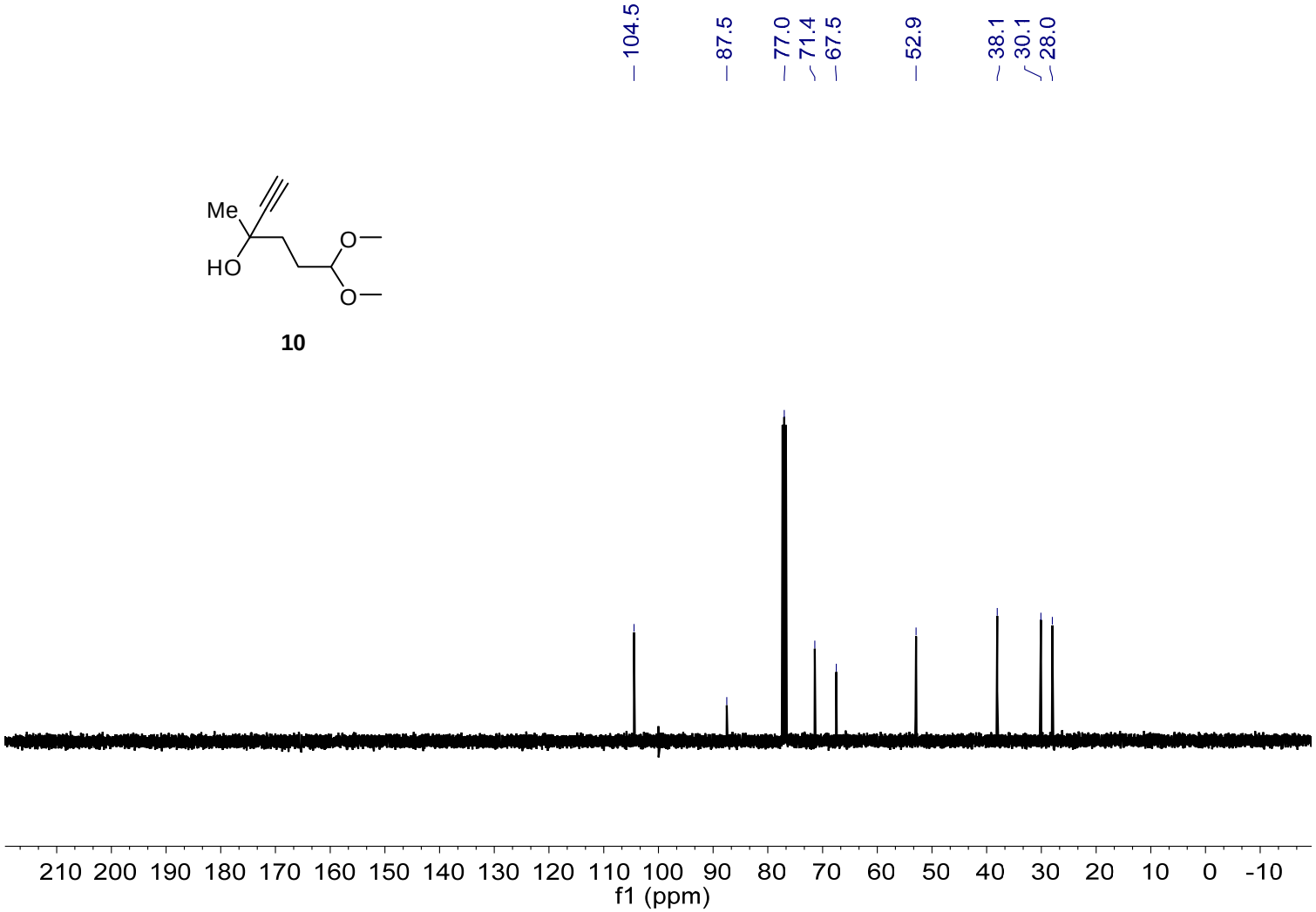
2. G. Viault, D. Grée, S. Das, J. S. Yadav, and R. Grée, *Eur. J. Org. Chem.*, 2011, 1233–1241.

## 5 . NMR Spectrum of Products

**$^{1}$H NMR of Compound 10 ($CDCl_3$, 400 MHz)**

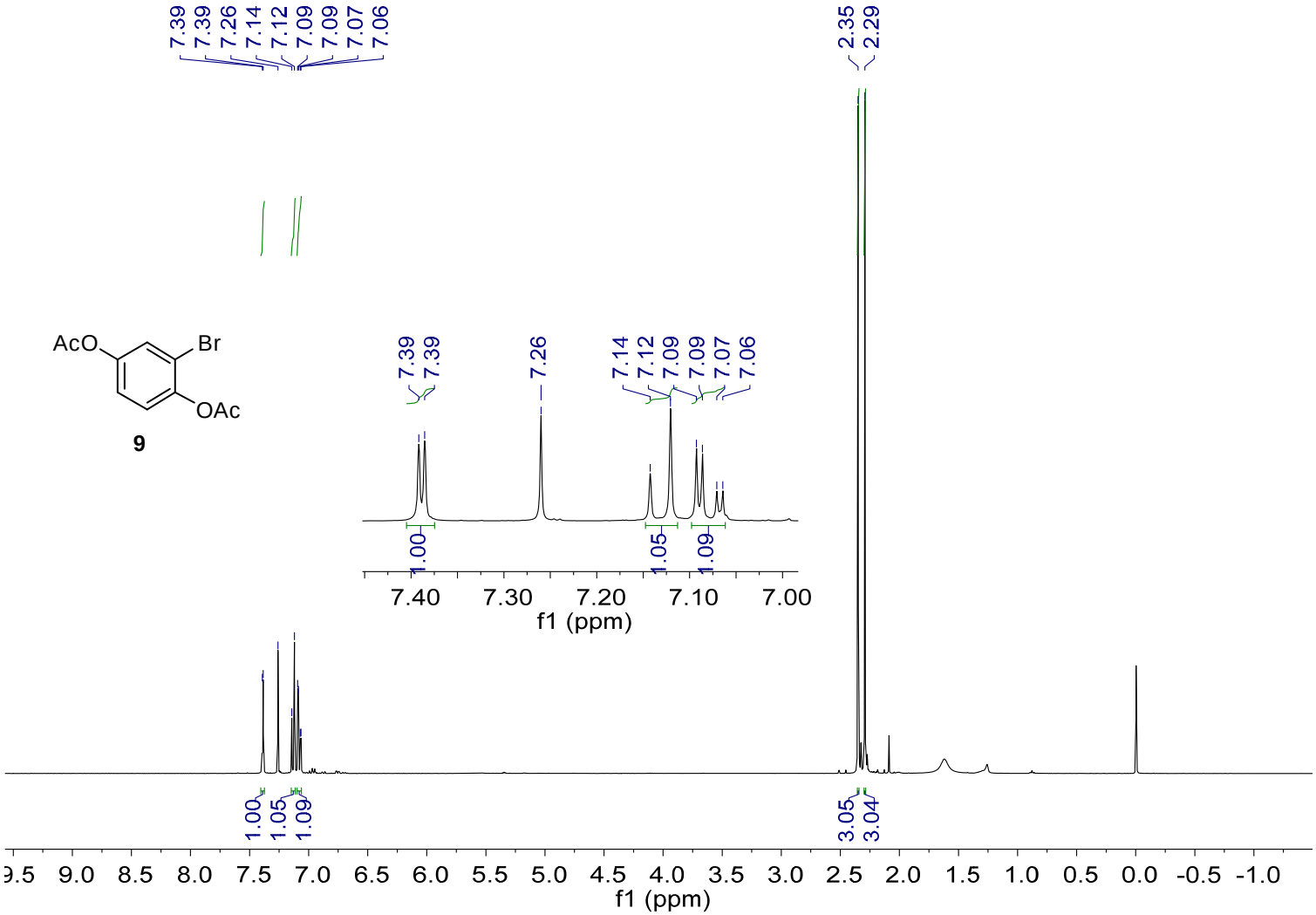


**$^{13}$C NMR of Compound 10 ($CDCl_3$, 100 MHz)**

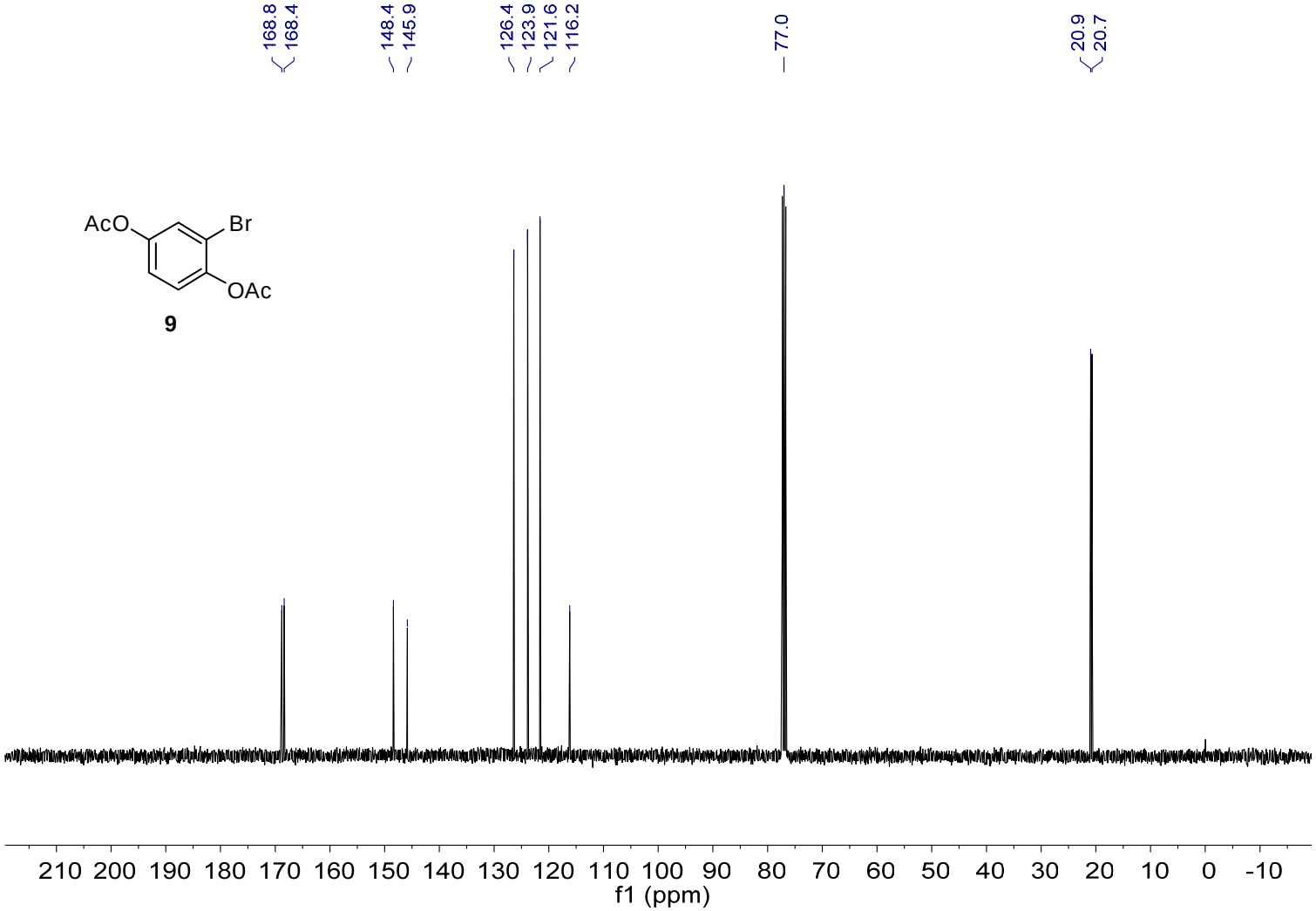



**10**

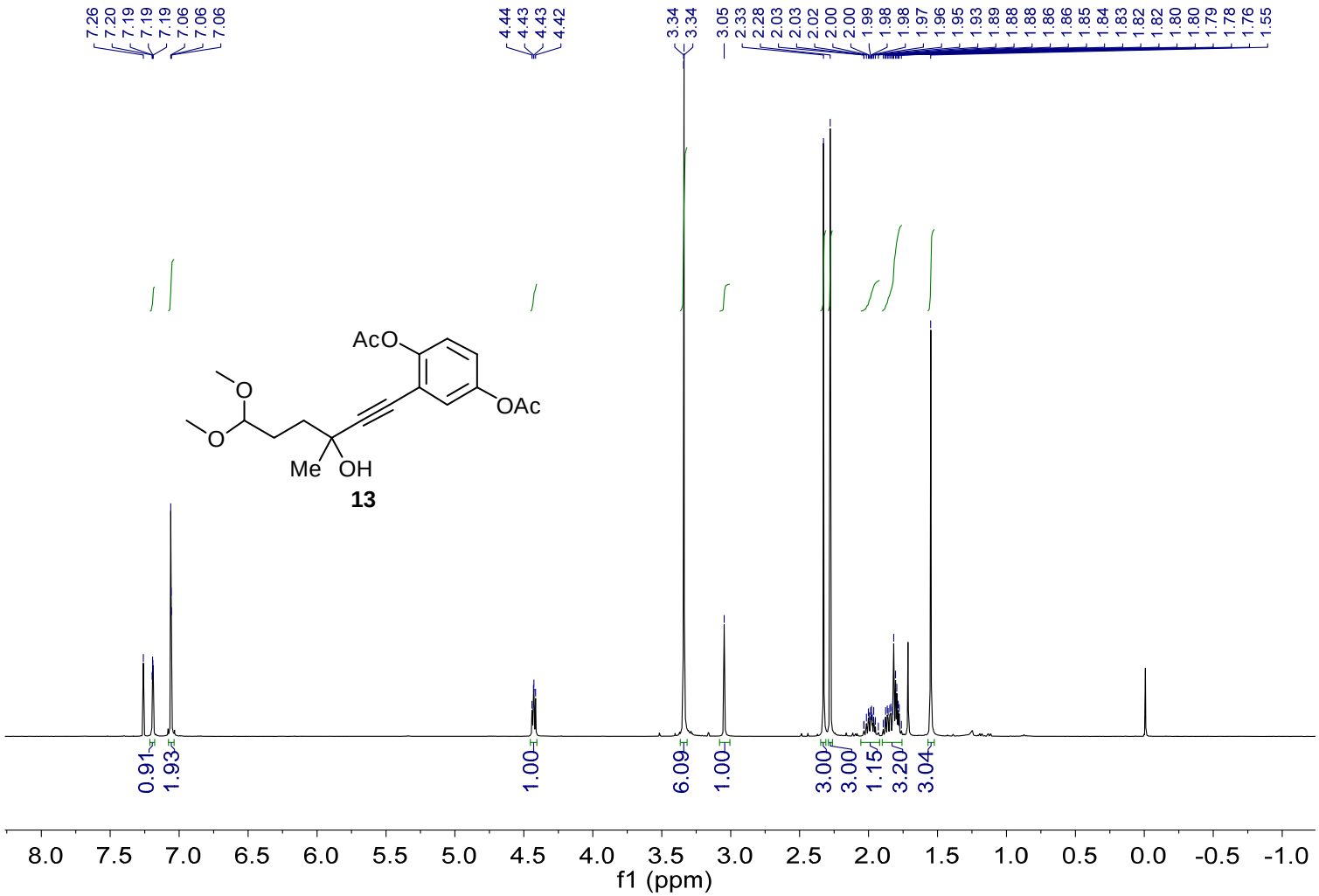
**$^{1}$H NMR of Compound 9 ($CDCl_3$, 400 MHz)**



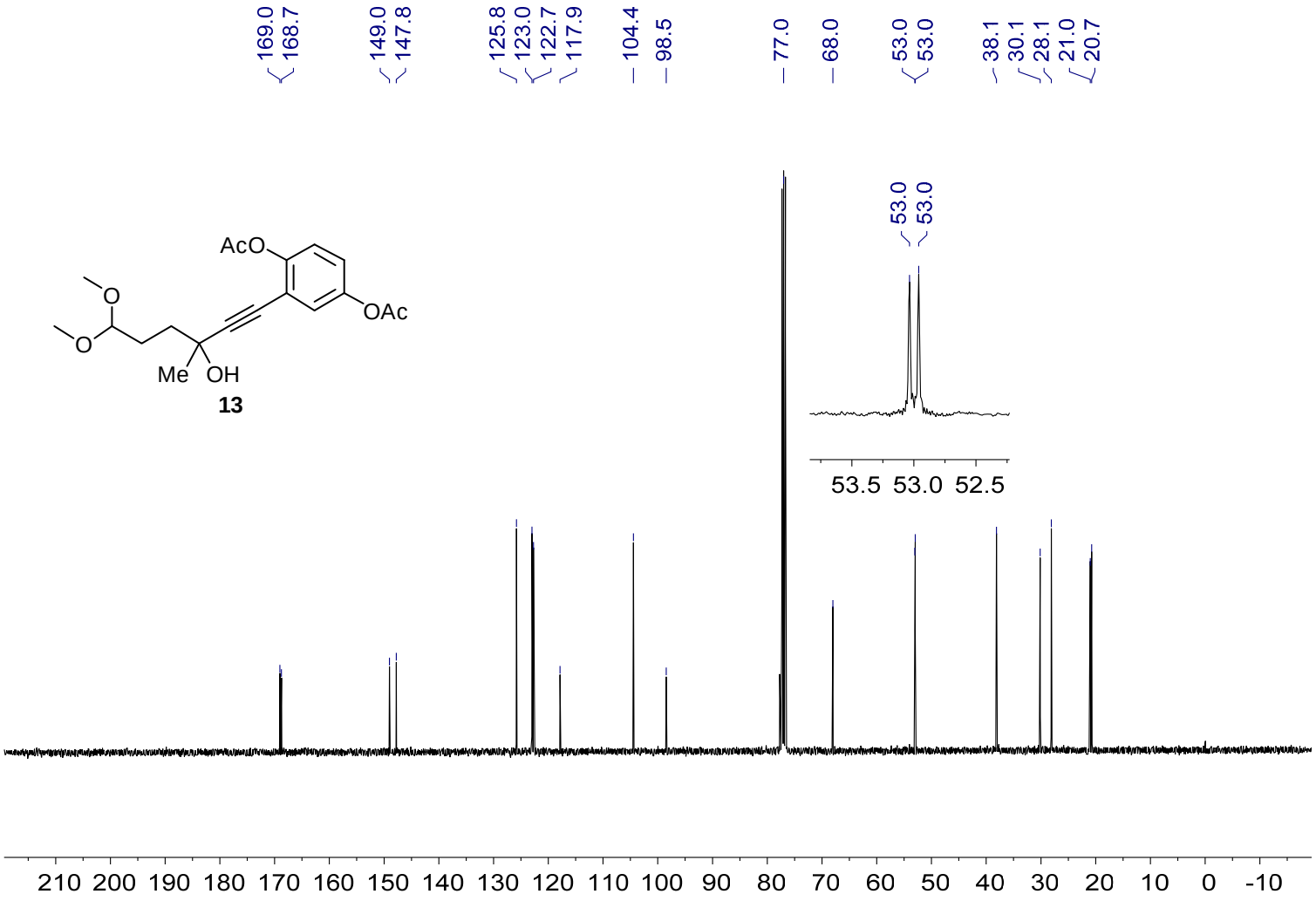
## $^{13}$C NMR of Compound 9 ($CDCl_3$, 100 MHz)



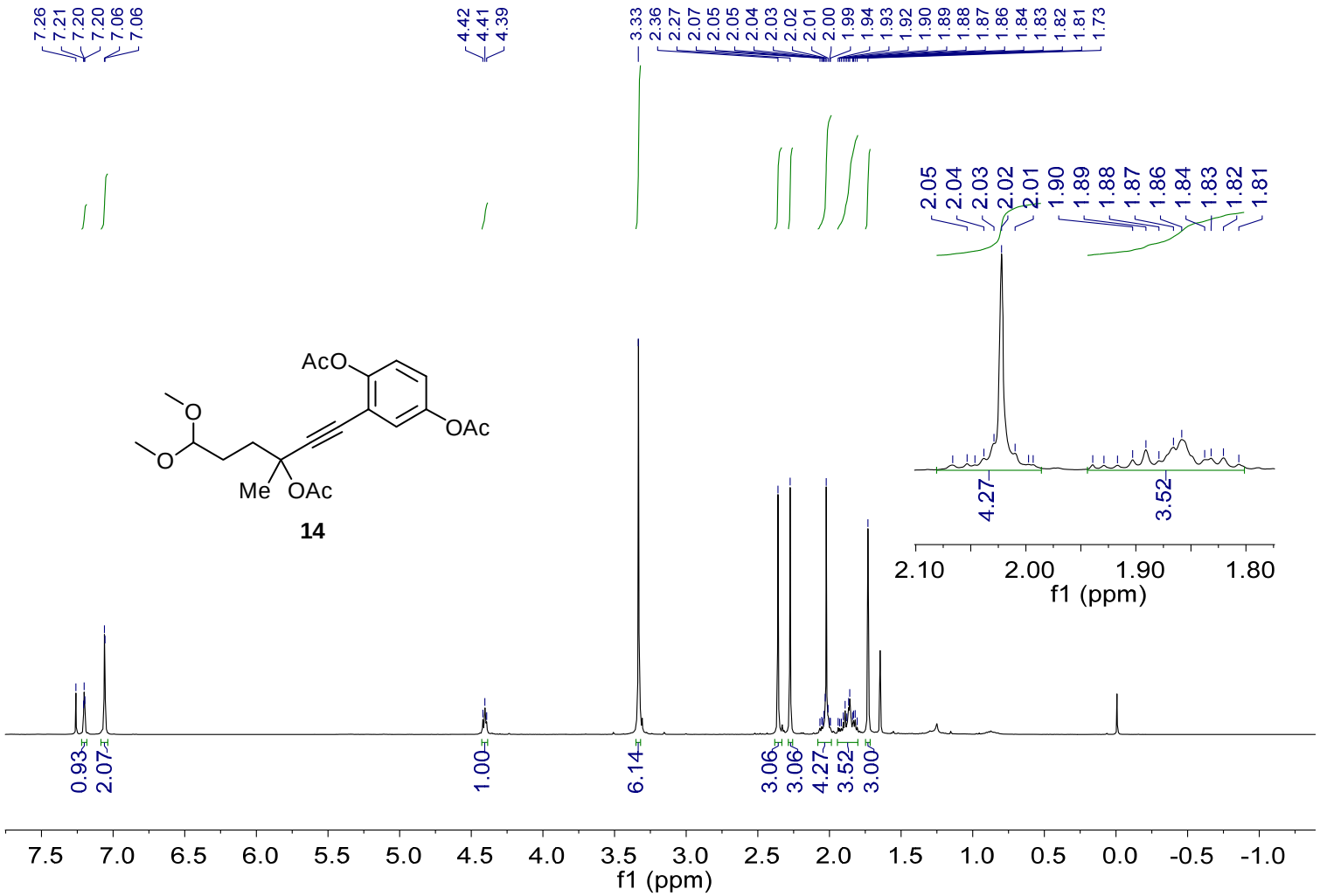
**$^{1}$H NMR of Compound 13 ($CDCl_3$, 400 MHz)**



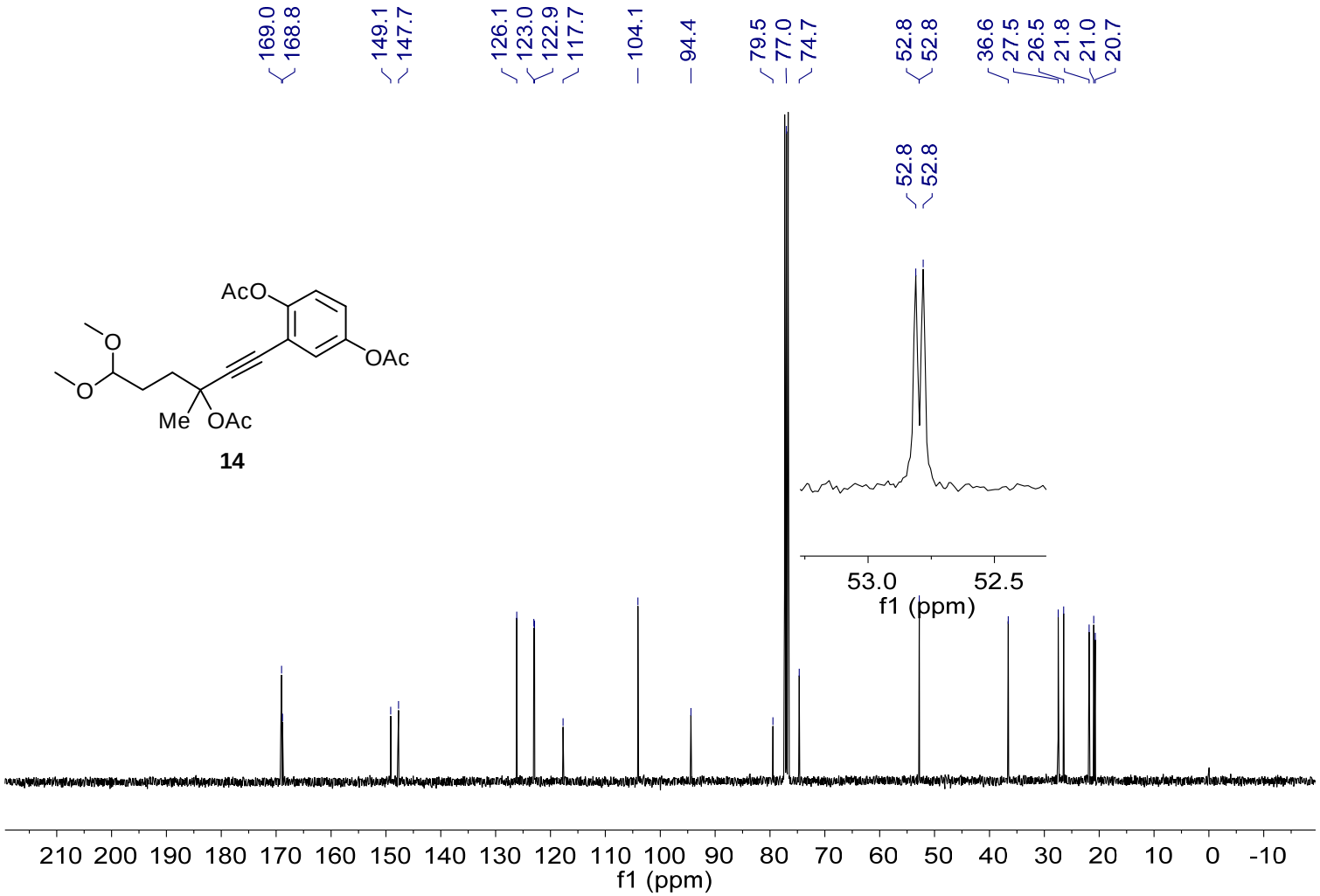
**$^{13}$C NMR of Compound 13 ($CDCl_3$, 100 MHz)**



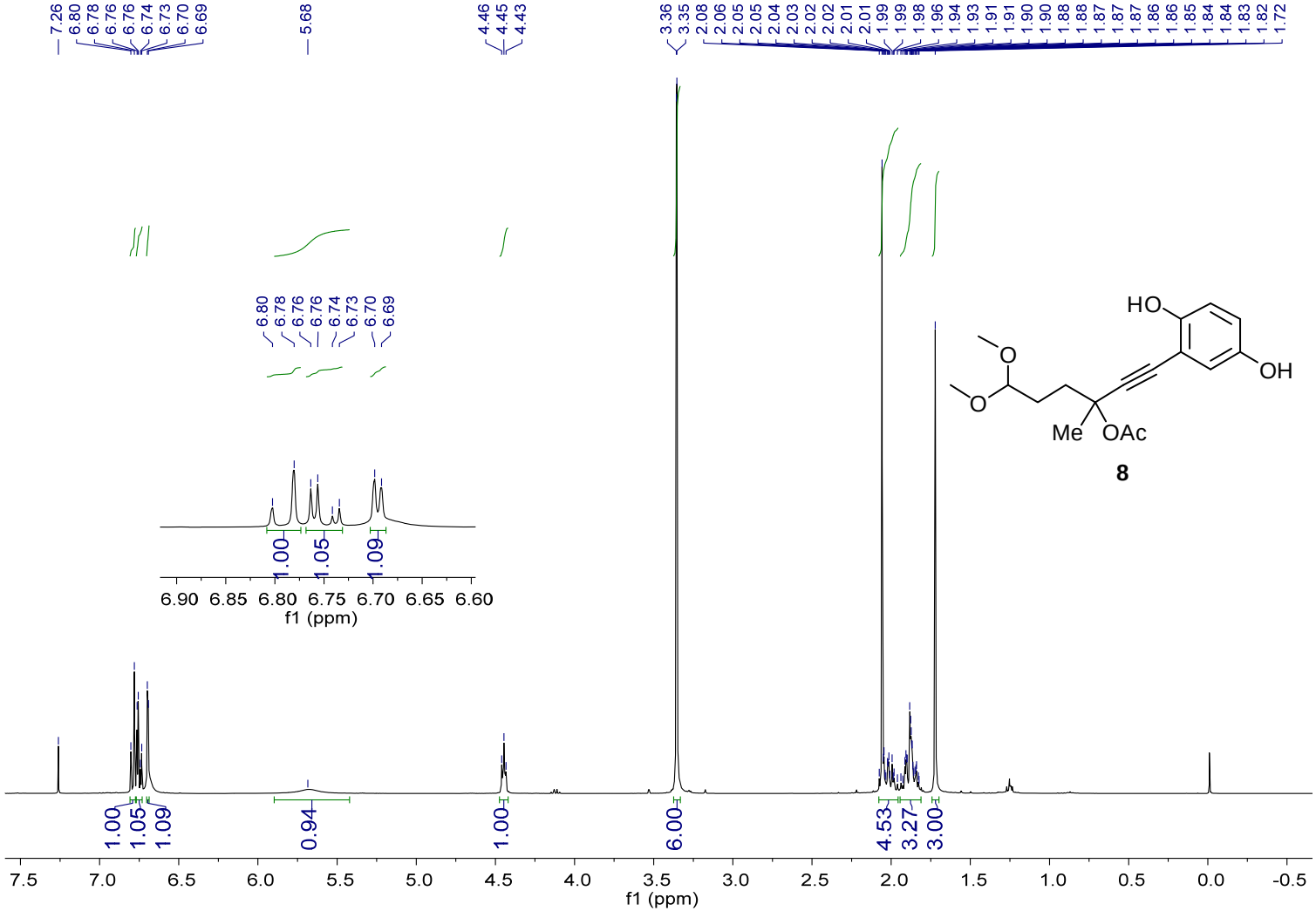
**$^{1}$H NMR of Compound 14 ($CDCl_3$, 400 MHz)**



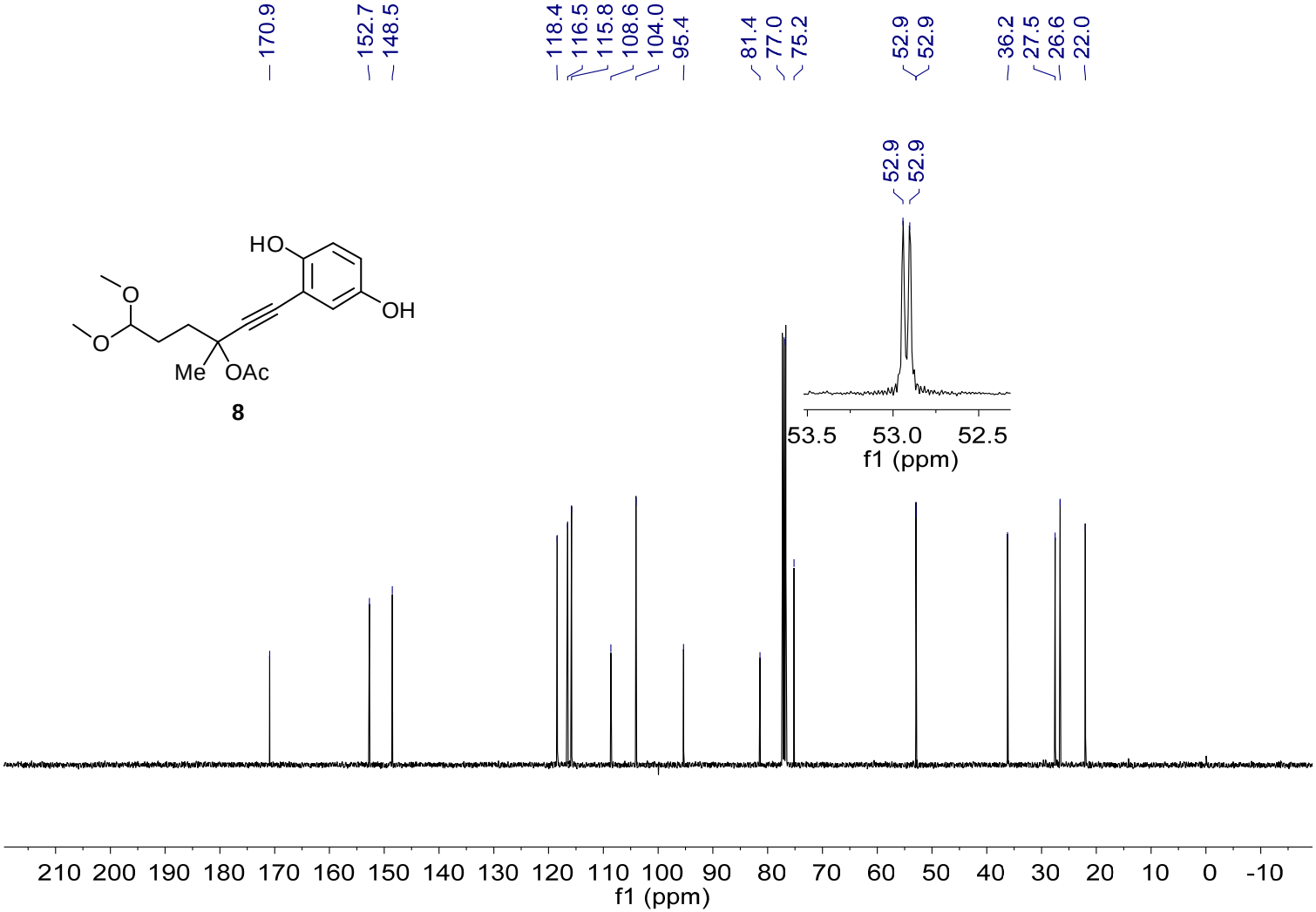
**$^{13}$C NMR of Compound 14 ($CDCl_3$, 100 MHz)**



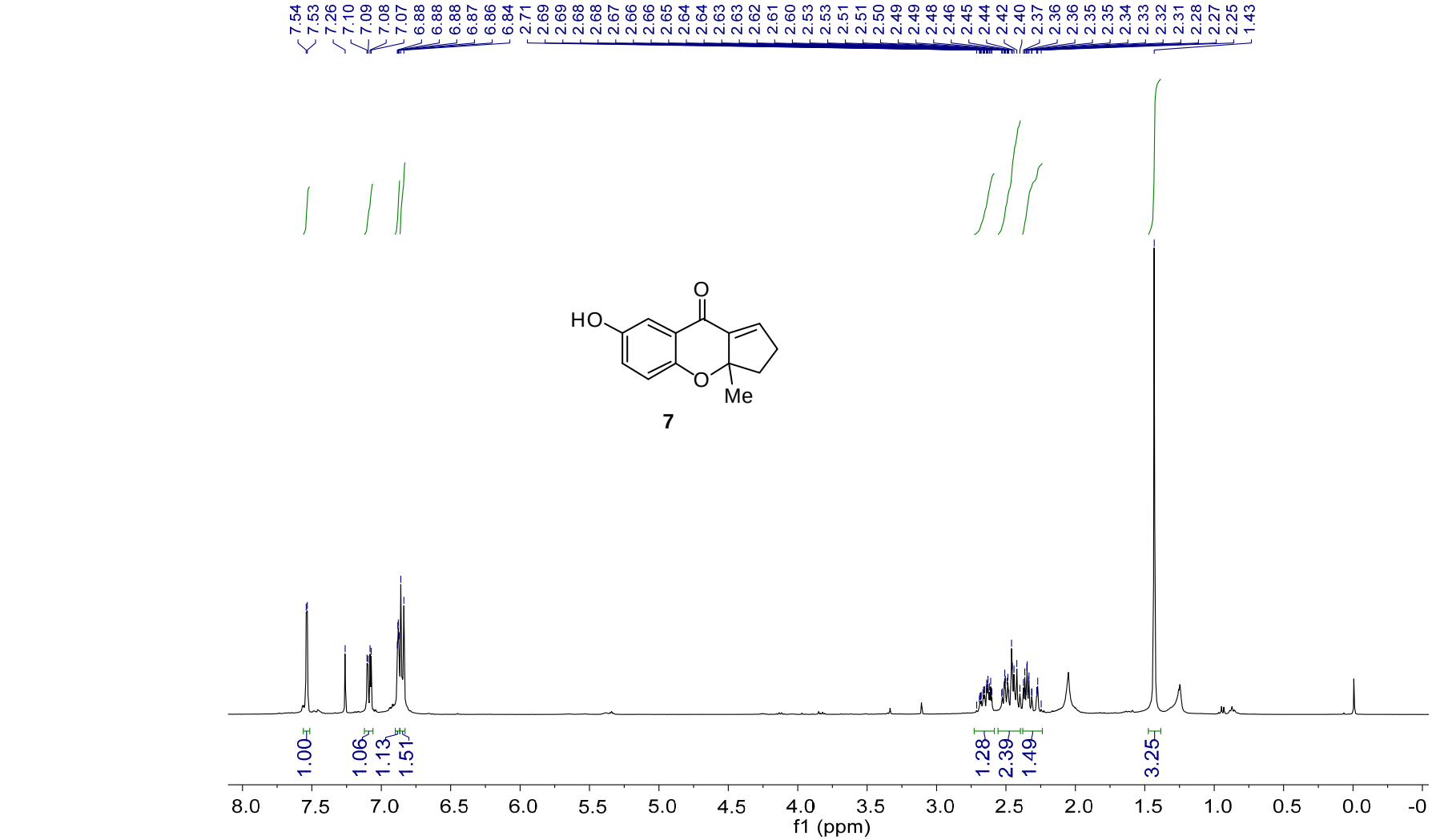
**$^{1}$H NMR of Compound 8 ($CDCl_3$, 400 MHz)**



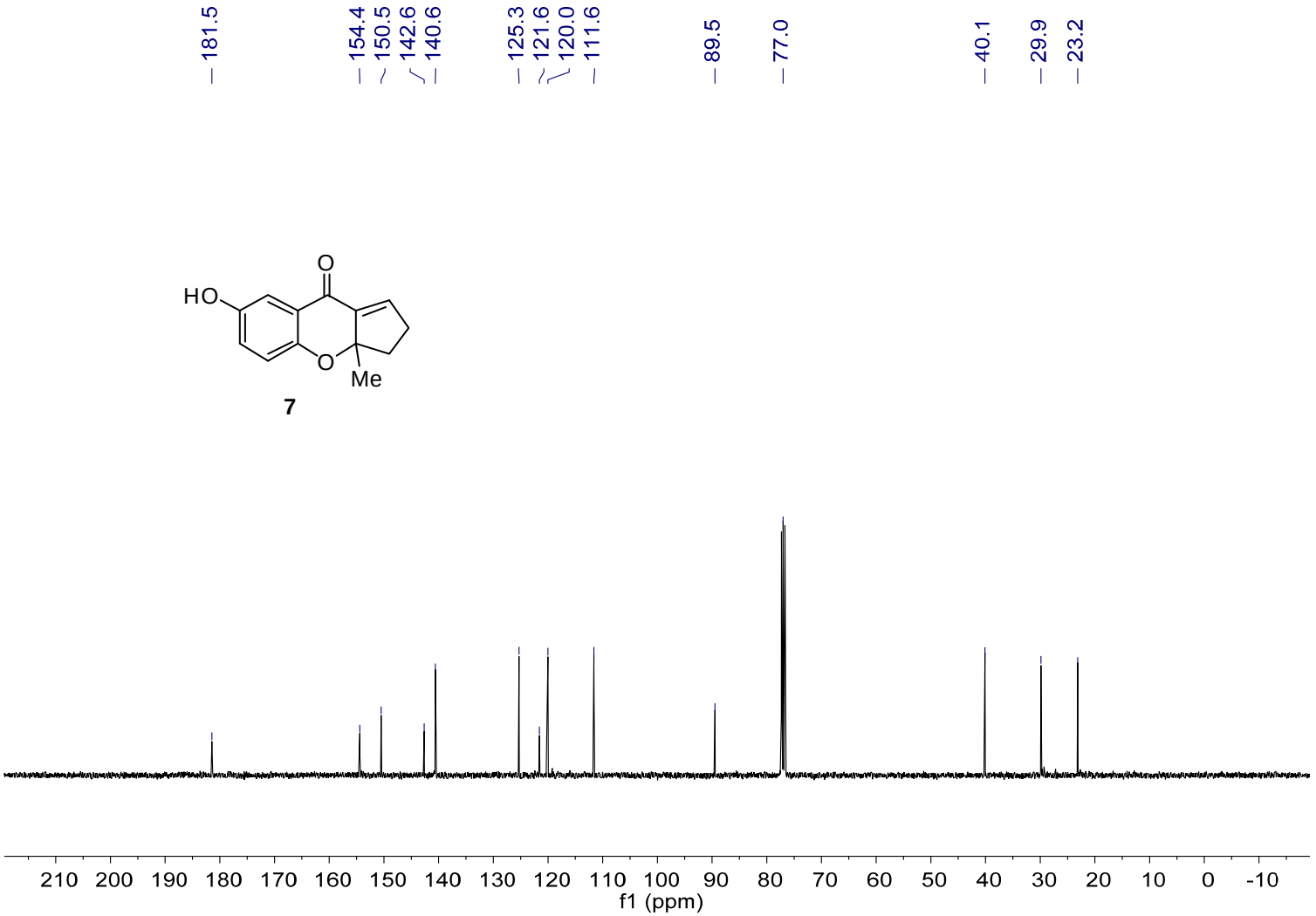
**$^{13}$C NMR of Compound 8 ($CDCl_3$, 100 MHz)**



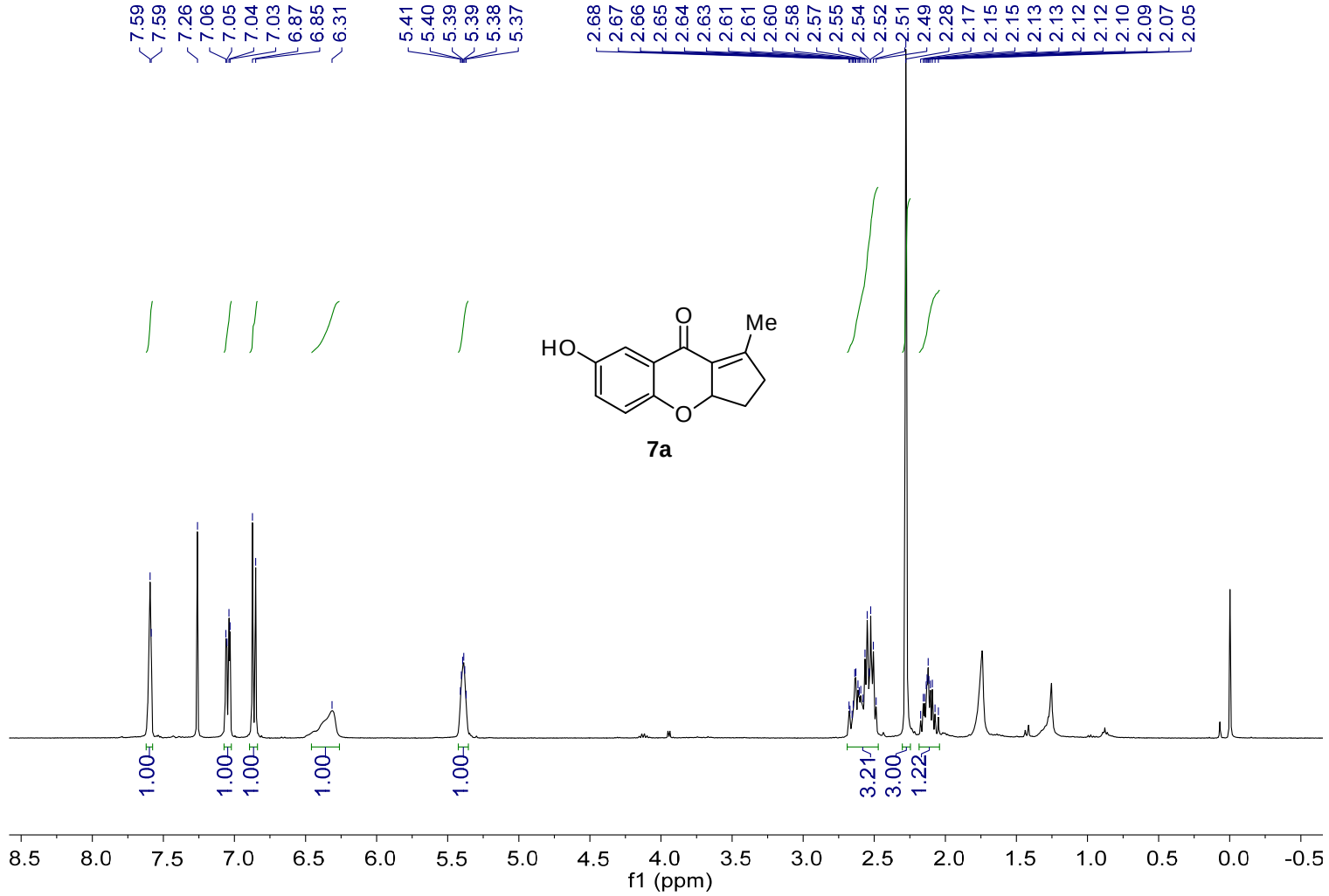
**$^{1}$H NMR of Compound 7 ($CDCl_3$, 400 MHz)**



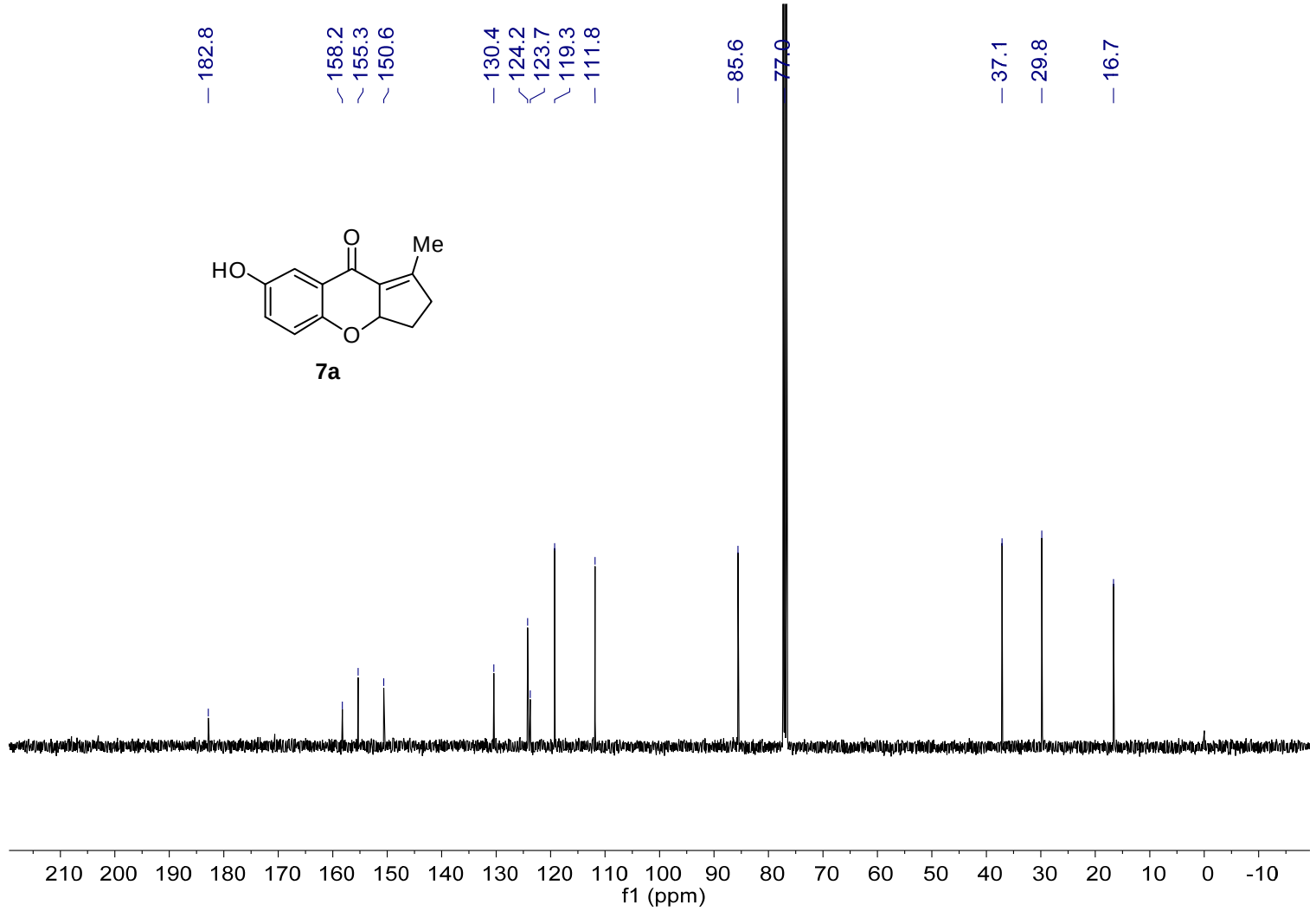
**$^{13}$C NMR of Compound 7 ($CDCl_3$, 100 MHz)**



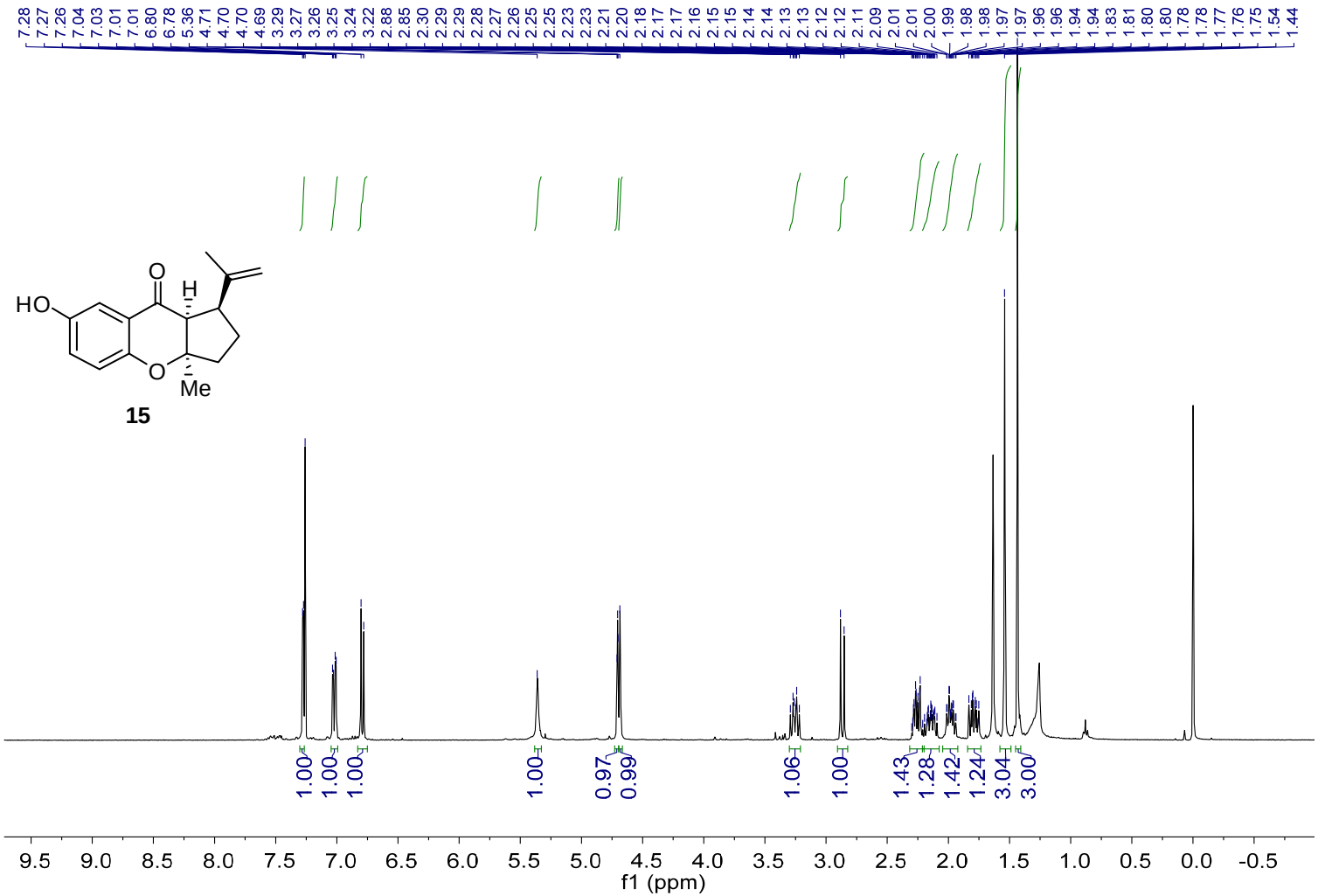
**$^{1}$H NMR of Compound 7a ($CDCl_3$, 100 MHz)**



**$^{13}$C NMR of Compound 7a ($CDCl_3$, 100 MHz)**

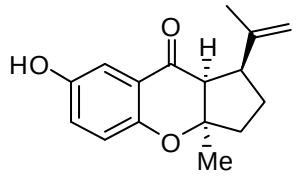


**$^{1}$H NMR of Compound 15 ($CDCl_3$, 400 MHz)**

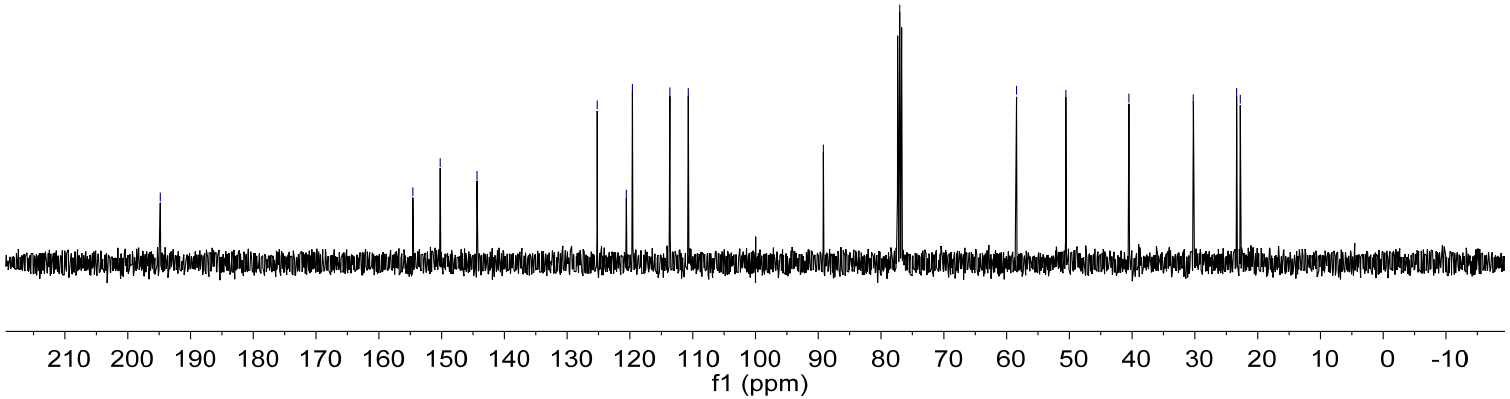


**$^{13}$C NMR of Compound 15 ($CDCl_3$, 100 MHz)**

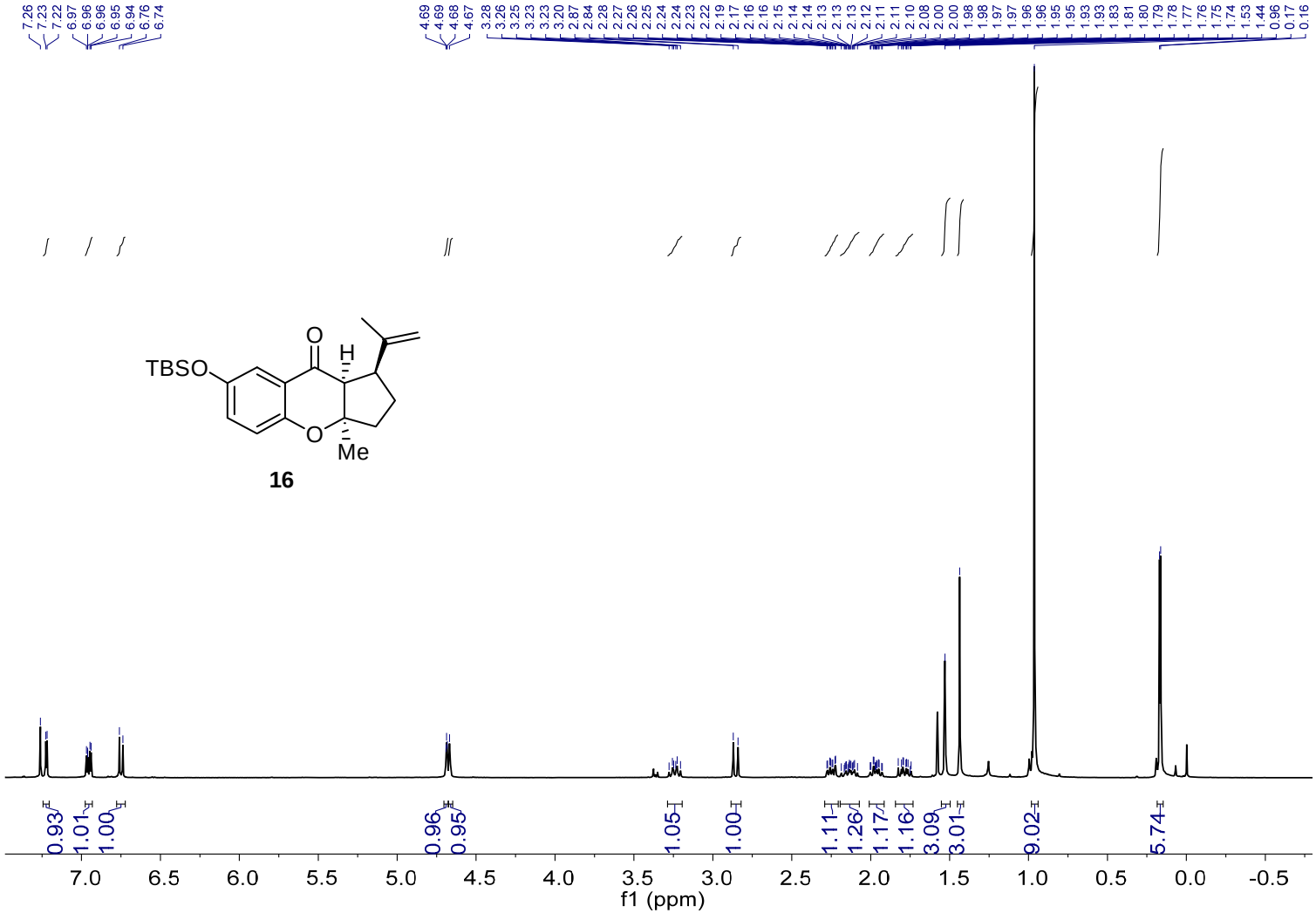
194.8
154.6
150.2
144.4
125.2
120.6
119.6
113.6
110.7
89.2
77.0
58.4
50.6
40.5
30.3
23.4
22.8



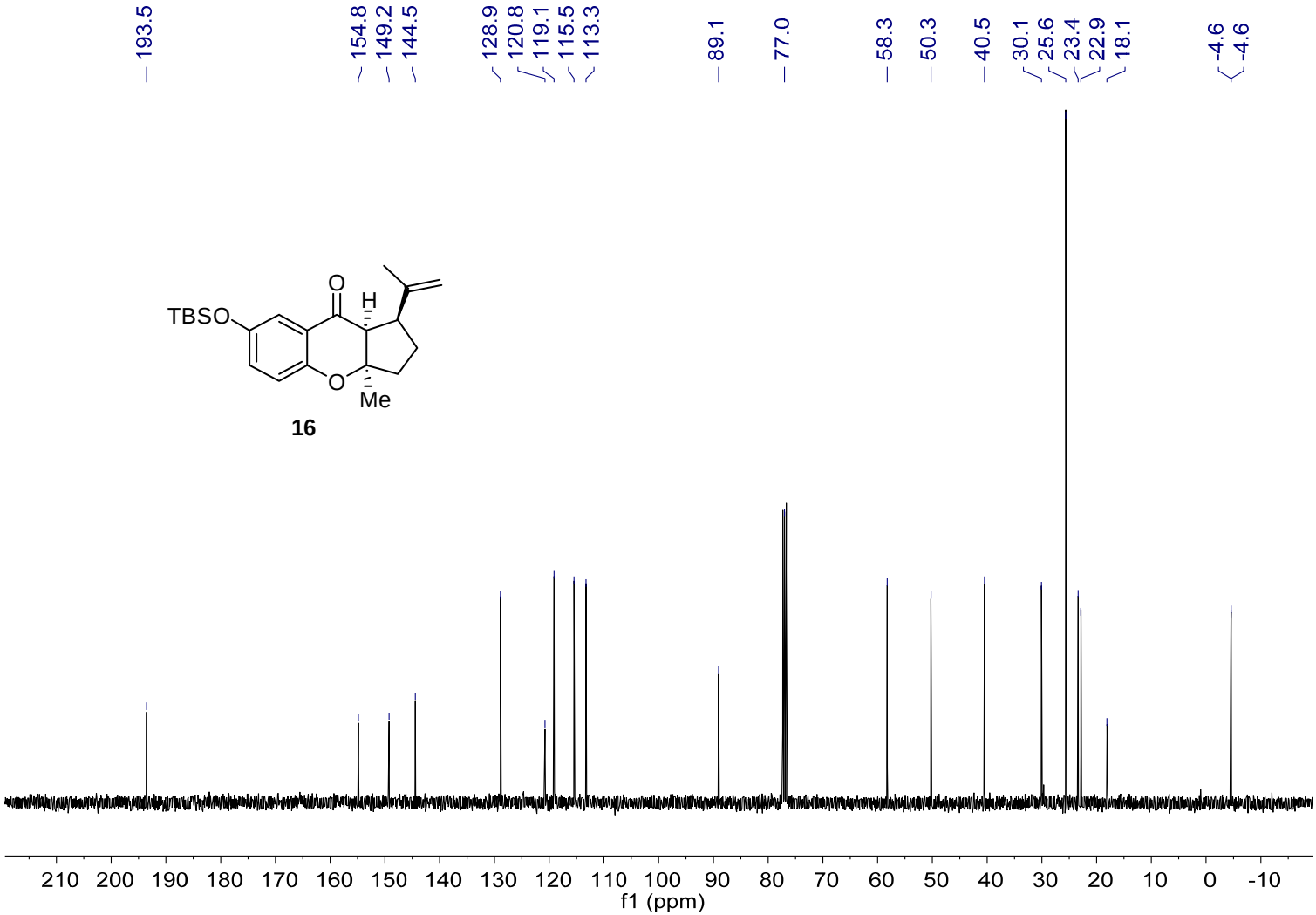

**15**



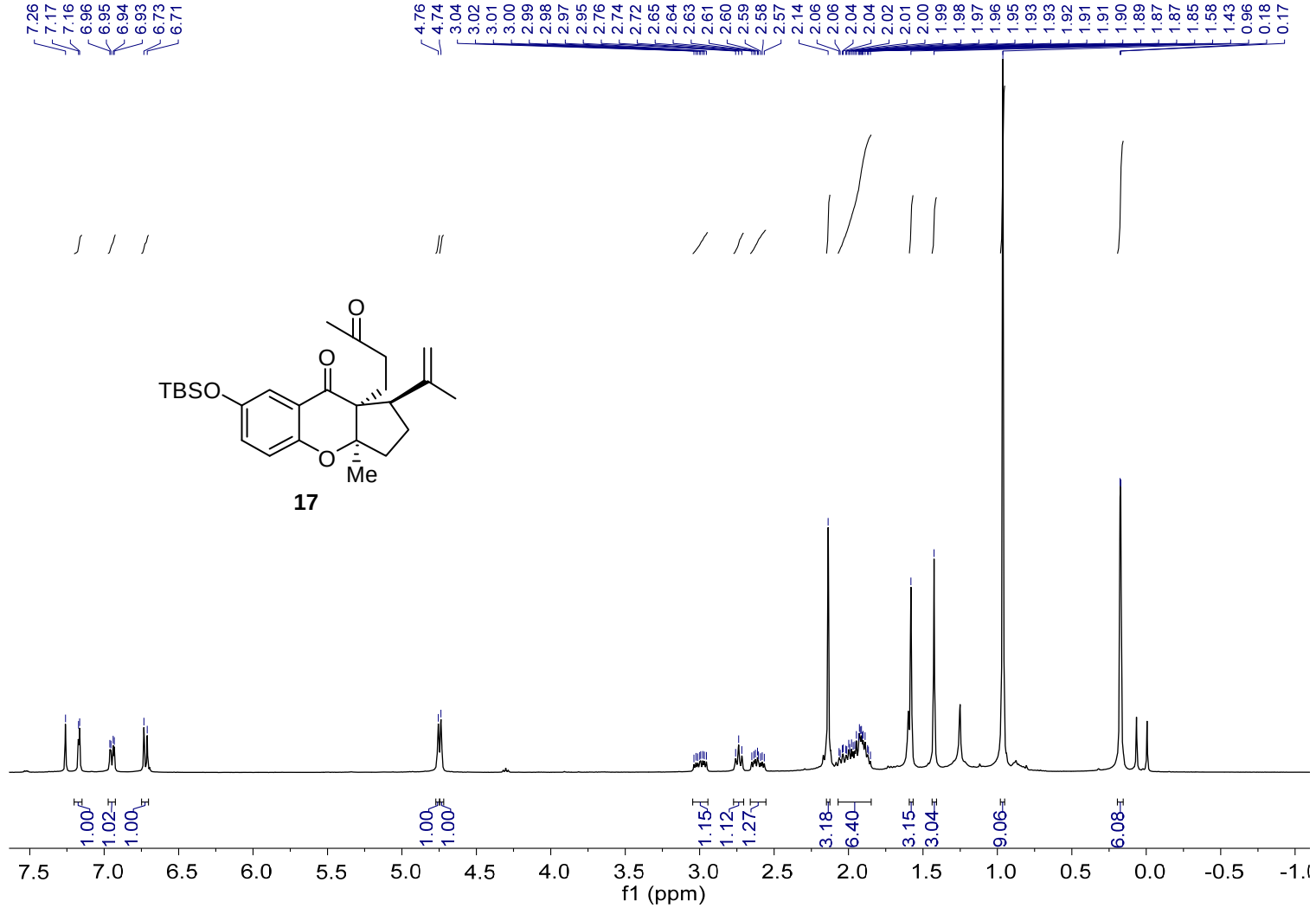
## $^{1}$H NMR of Compound 16 ($CDCl_3$, 400 MHz)



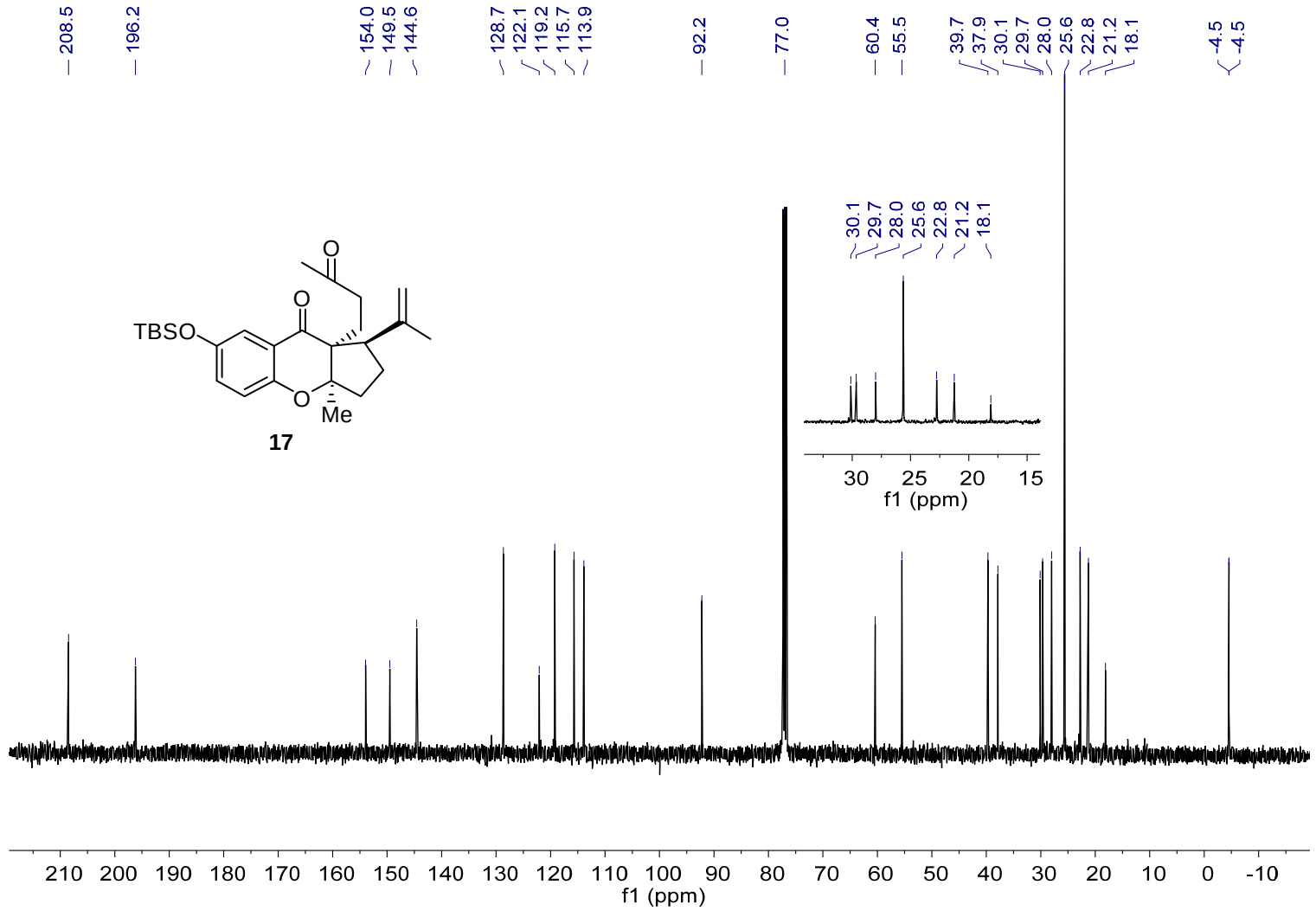
**$^{13}$C NMR of Compound 16 ($CDCl_3$, 100 MHz)**



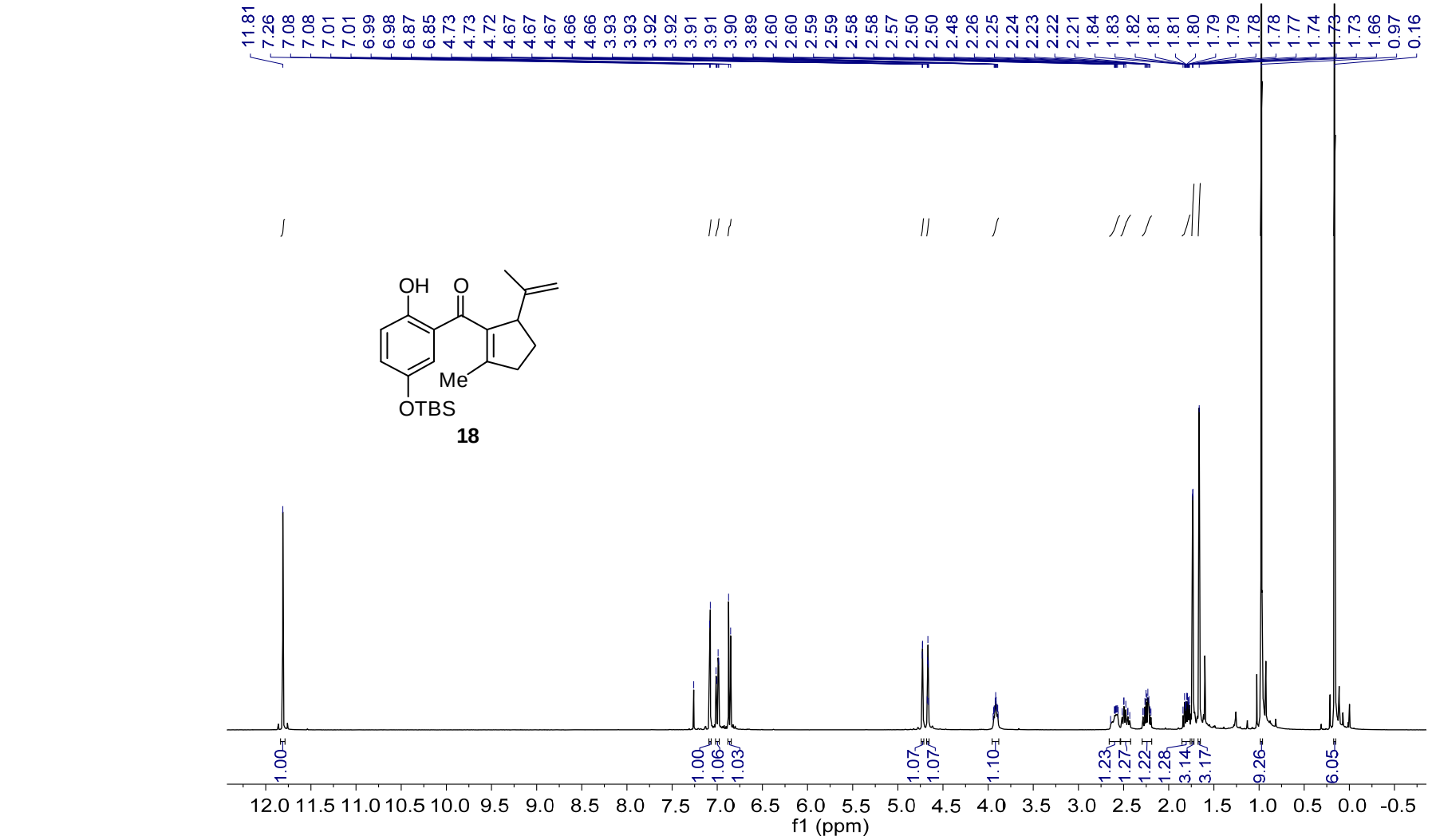
**$^{1}$H NMR of Compound 17 ($CDCl_3$, 400 MHz)**



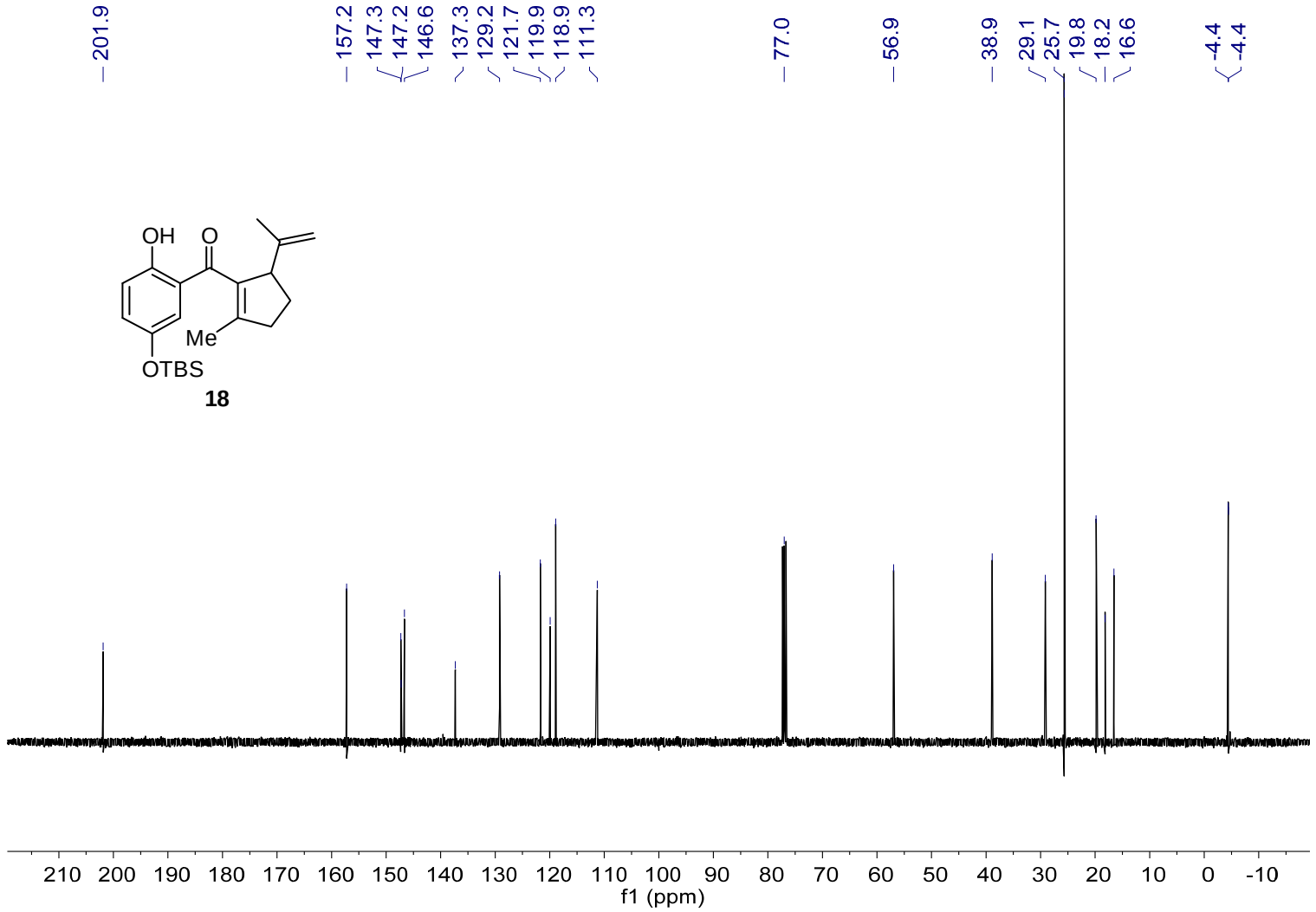
**$^{13}$C NMR of Compound 17 ($CDCl_3$, 100 MHz)**



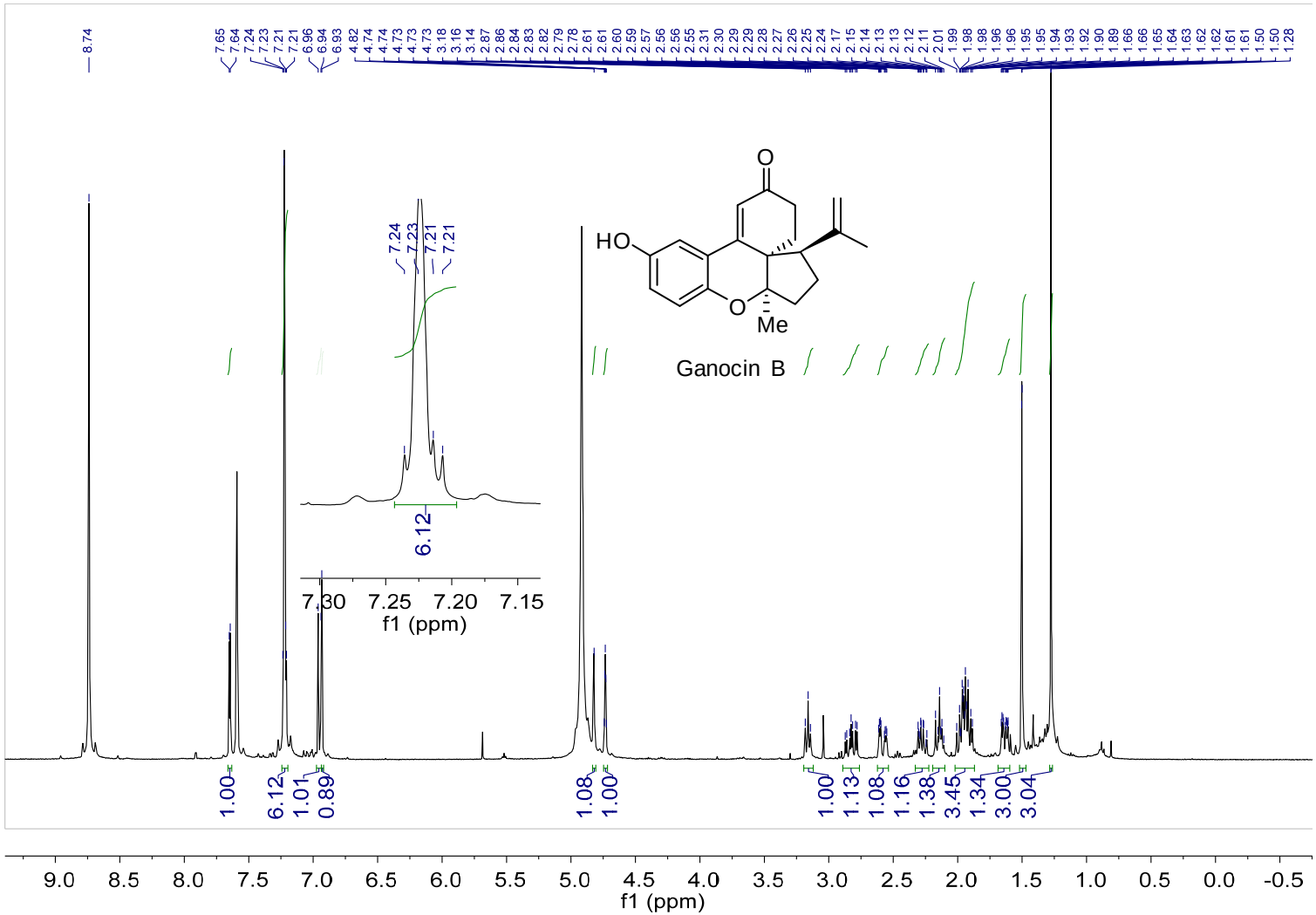
**$^{1}$H NMR of Compound 18 ($CDCl_3$, 400 MHz)**



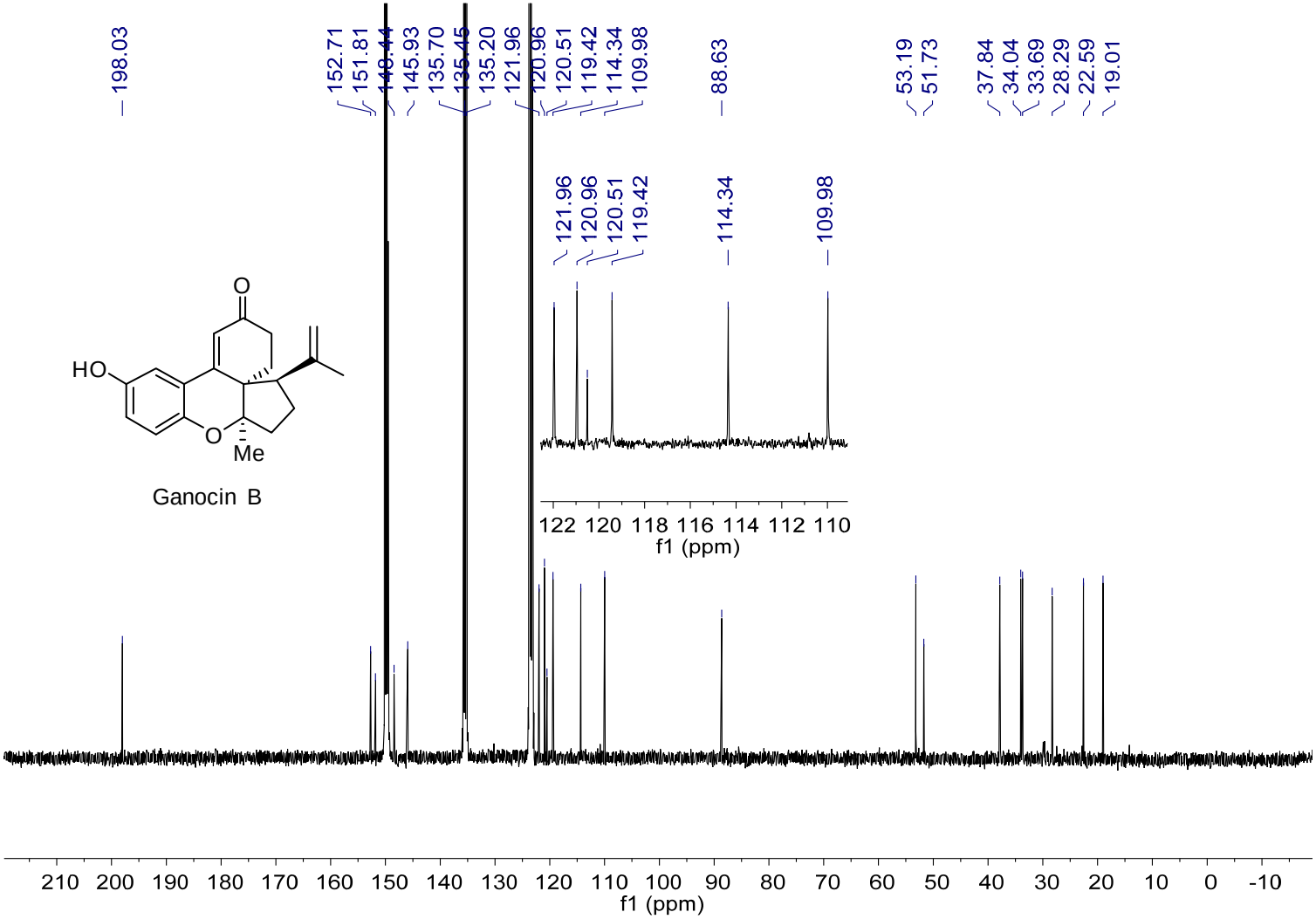
**$^{13}$C NMR of Compound 18 ($CDCl_3$, 400 MHz)**



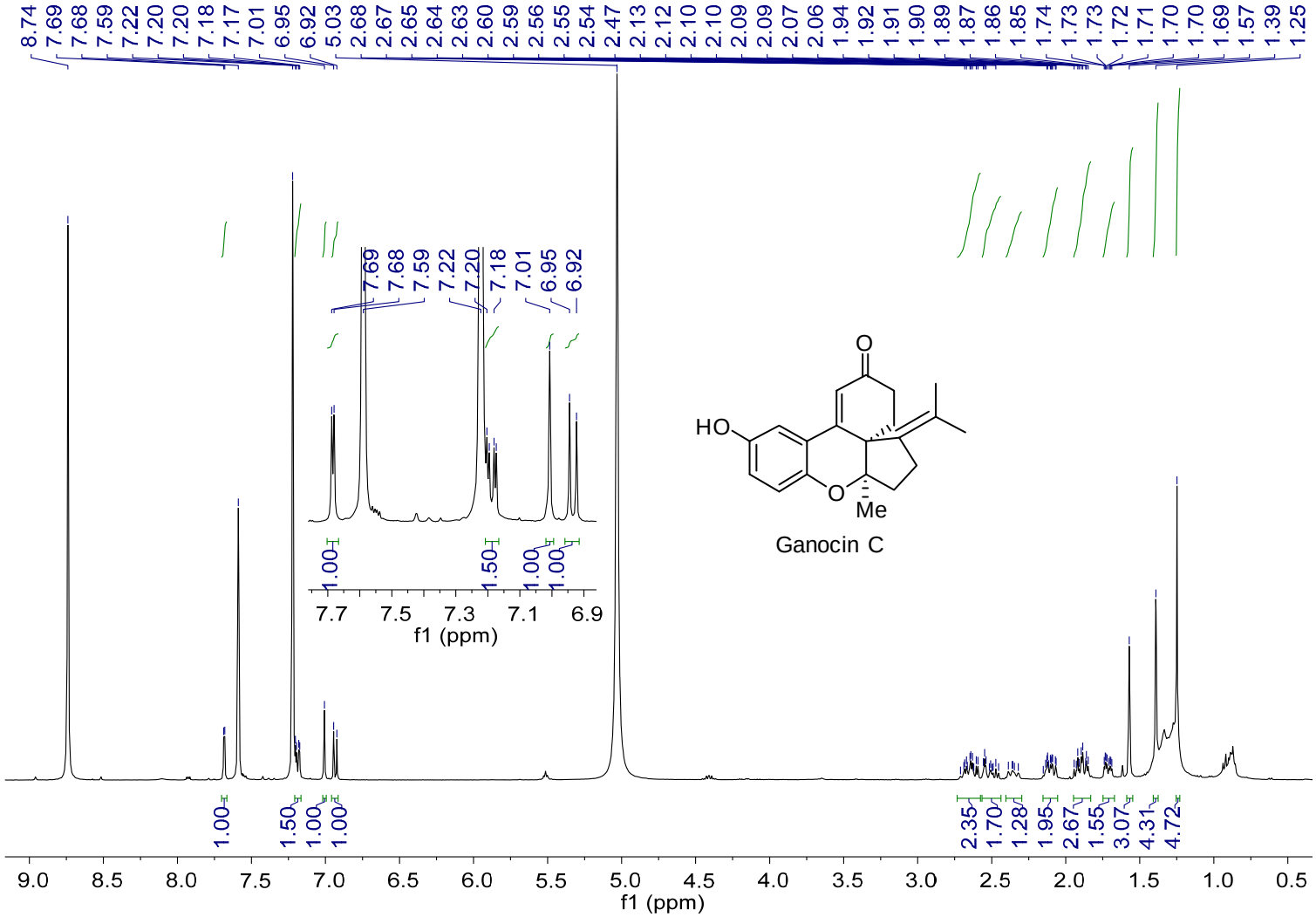
**$^{1}$H NMR of (±)-Ganocin B ($C_5D_5N$, 400 MHz)**



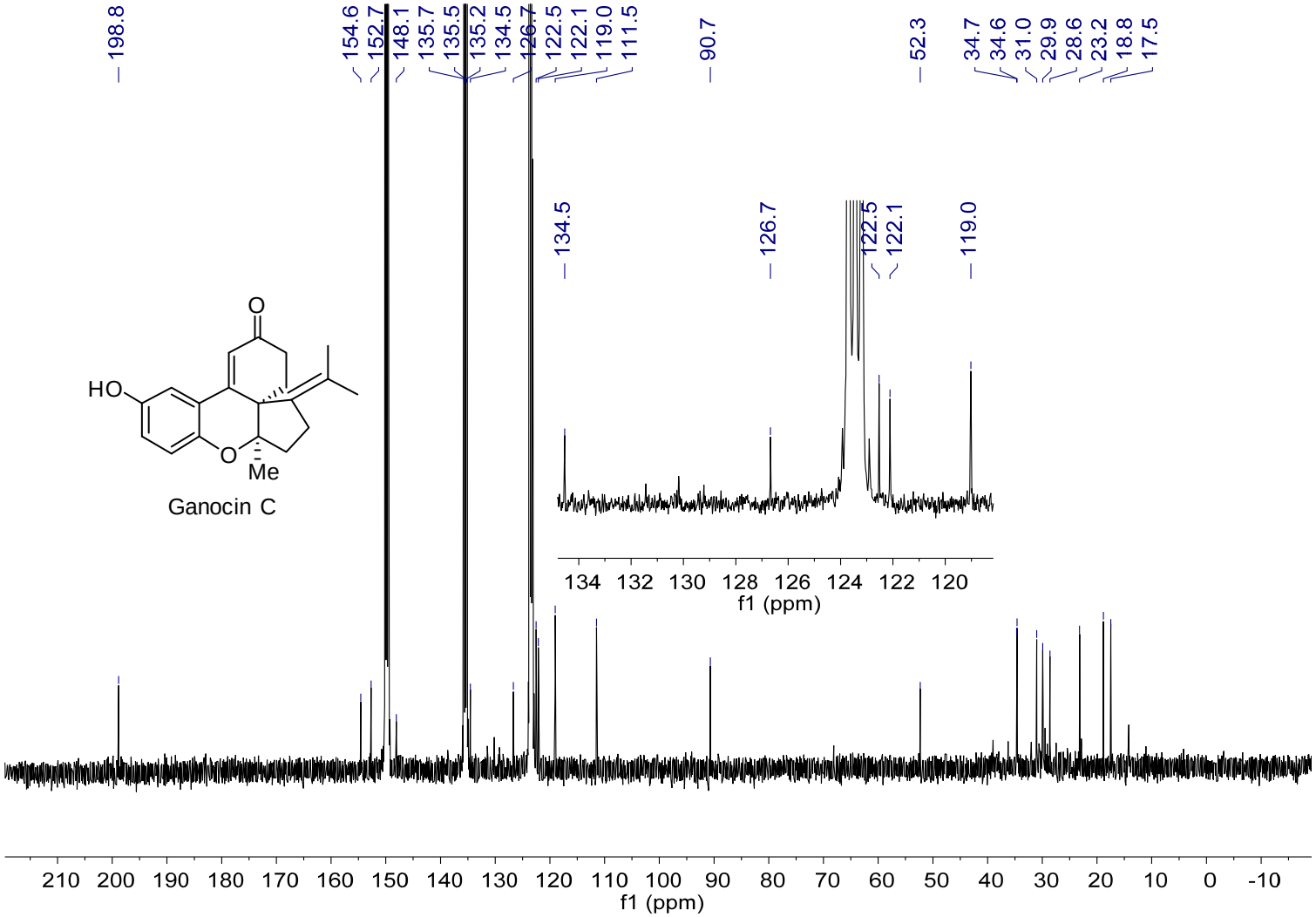
**$^{13}$C NMR of (±)-Ganocin B ($C_5D_5N$, 100 MHz)**



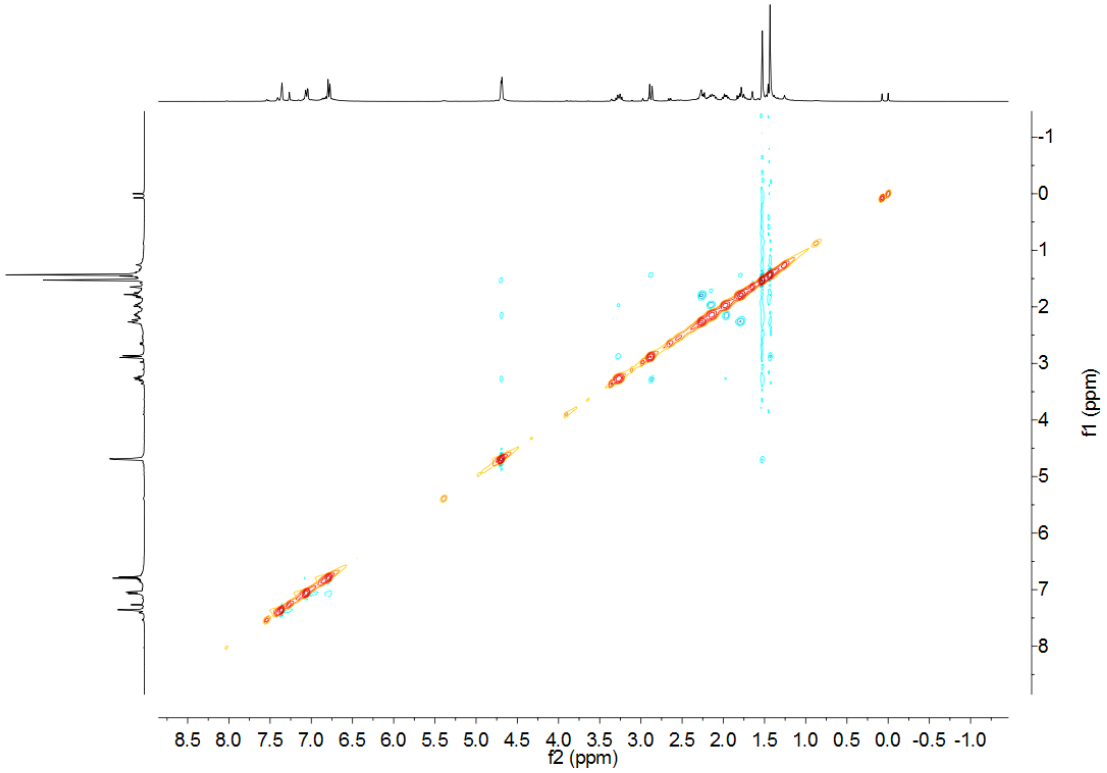
**$^{1}$H NMR of (±)-Ganocin C ($C_5D_5N$, 400 MHz)**



**$^{13}$C NMR of (±)-Ganocin C ($C_5D_5N$, 100 MHz)**



## NOE of Compound 15 ($CDCl_3$, 400 MHz)



# 6. High-Resolution Mass Spectra (HRMS) of Products

Formula Predictor Report - 038.lcd



Data File: F:\WangHongGen\LY\038.lcd

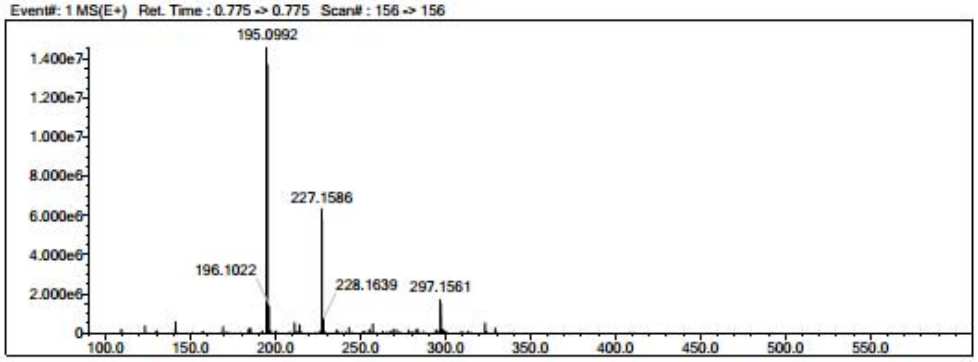
| Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Use Adduct |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | 1 | 0 | 33 | O | 2 | 0 | 8 | P | 3 | 0 | 1 | Cu | 2 | 0 | 0 | H |
| C | 4 | 0 | 24 | F | 1 | 0 | 0 | S | 2 | 0 | 2 | Br | 1 | 0 | 1 | Na |
| N | 3 | 0 | 4 | Si | 4 | 0 | 1 | Cl | 1 | 0 | 2 | I | 3 | 0 | 1 | |

Error Margin (mDa): 5.0
HC Ratio: unlimited
Max Isotopes: all
MSn Iso RI (%): 75.00

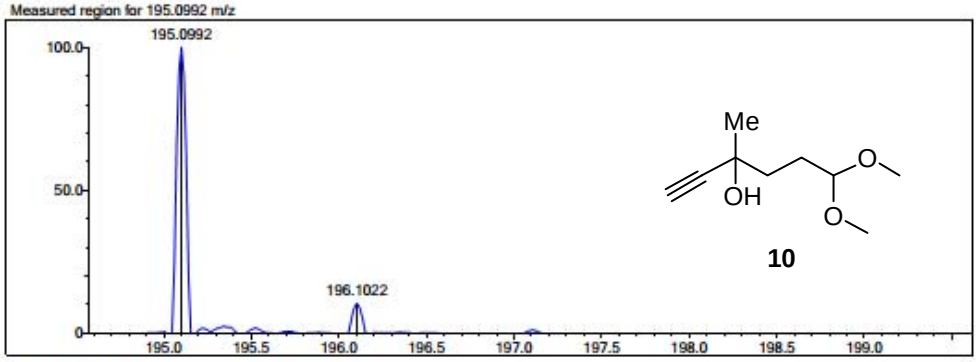
DBE Range: -2.0 - 1000.0
Apply N Rule: yes
Isotope RI (%): 1.00
MSn Logic Mode: AND

Electron Ions: both
Use MSn Info: yes
Isotope Res: 10000
Max Results: 800

Event#: 1 MS(E+) Ret. Time : 0.775 -> 0.775 Scan# : 156 -> 156

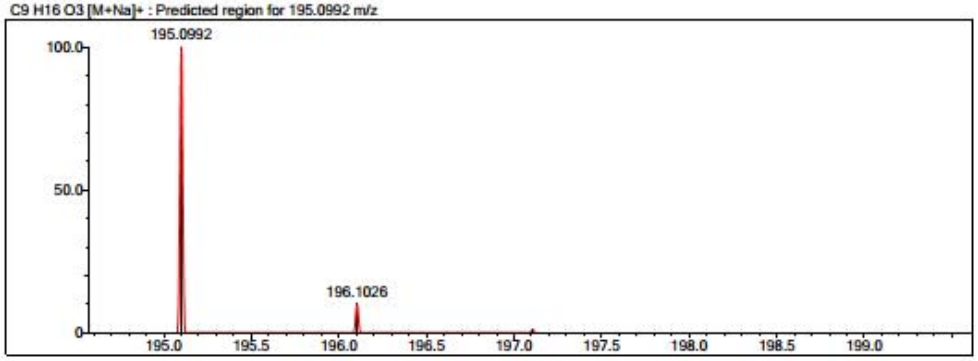



Measured region for 195.0992 m/z




**10**

C9 H16 O3 [M+Na]+ : Predicted region for 195.0992 m/z




| Rank | Score | Formula (M) | Ion | Meas. m/z | Pred. m/z | Df. (mDa) | Df. (ppm) | Iso | DBE |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 69.32 | C9 H16 O3 | [M+Na]+ | 195.0992 | 195.0992 | 0.0 | 0.00 | 69.32 | 2.0 |

Data File: F:\WangHongGen\LY\2.lcd

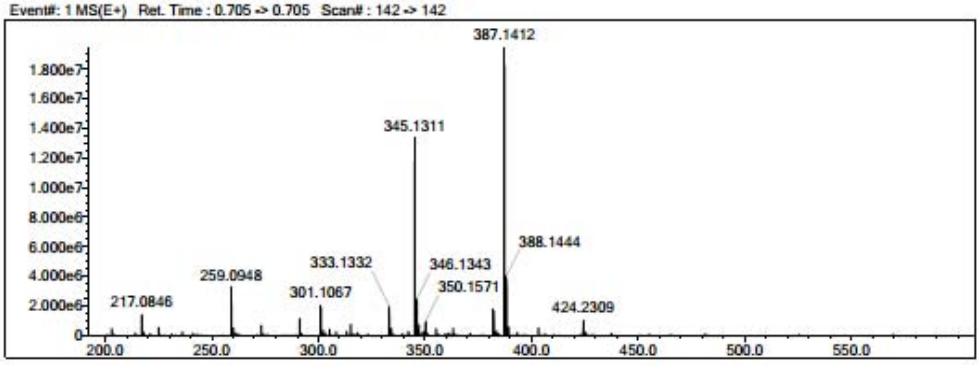
| Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Use Adduct |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | 1 | 0 | 26 | O | 2 | 0 | 8 | S | 2 | 0 | 2 | Br | 1 | 0 | 1 | H |
| C | 4 | 0 | 19 | F | 1 | 0 | 0 | Cl | 1 | 0 | 2 | I | 3 | 0 | 1 | Na |
| N | 3 | 0 | 4 | P | 3 | 0 | 1 | Cu | 2 | 0 | 0 | | | | | |

Error Margin (mDa): 5.0
HC Ratio: unlimited
Max Isotopes: all
MSn Iso RI (%): 75.00

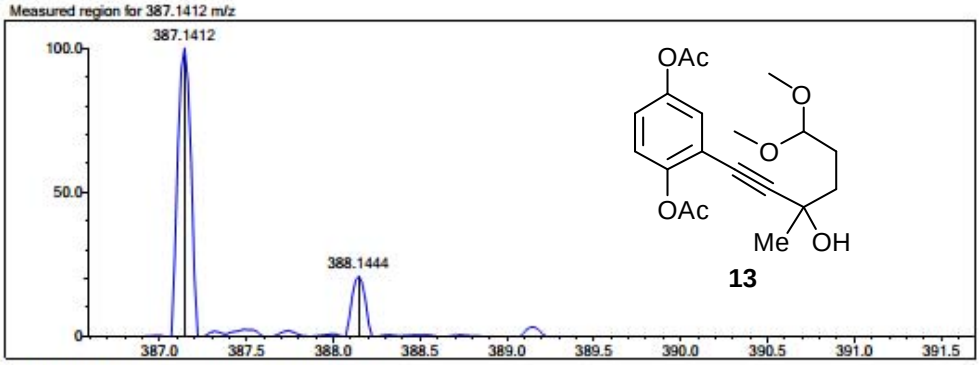
DBE Range: -2.0 - 1000.0
Apply N Rule: yes
Isotope RI (%): 1.00
MSn Logic Mode: AND

Electron Ions: both
Use MSn Info: yes
Isotope Res: 10000
Max Results: 800

Event#: 1 MS(E+) Ret. Time : 0.705 -> 0.705 Scan# : 142 -> 142

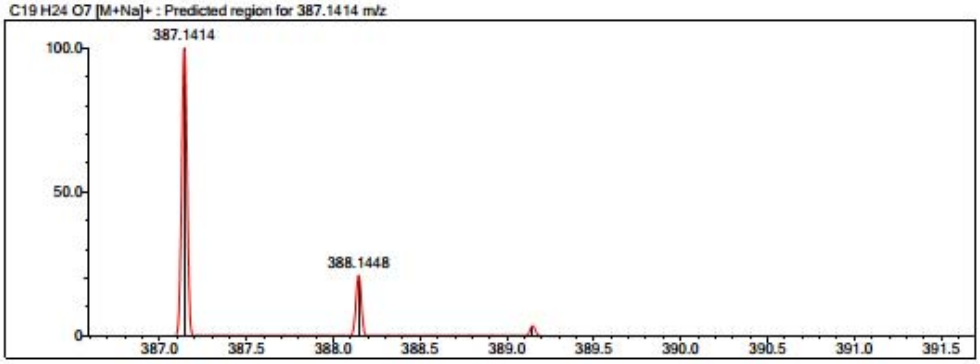



Measured region for 387.1412 m/z




**13**

C19 H24 O7 [M+Na]+ : Predicted region for 387.1414 m/z




| Rank | Score | Formula (M) | Ion | Meas. m/z | Pred. m/z | Df. (mDa) | Df. (ppm) | Iso | DBE |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 87.08 | C19 H24 O7 | [M+Na]+ | 387.1412 | 387.1414 | -0.2 | -0.52 | 87.08 | 8.0 |

Data File: F:\WangHongGen\LY\3.lcd

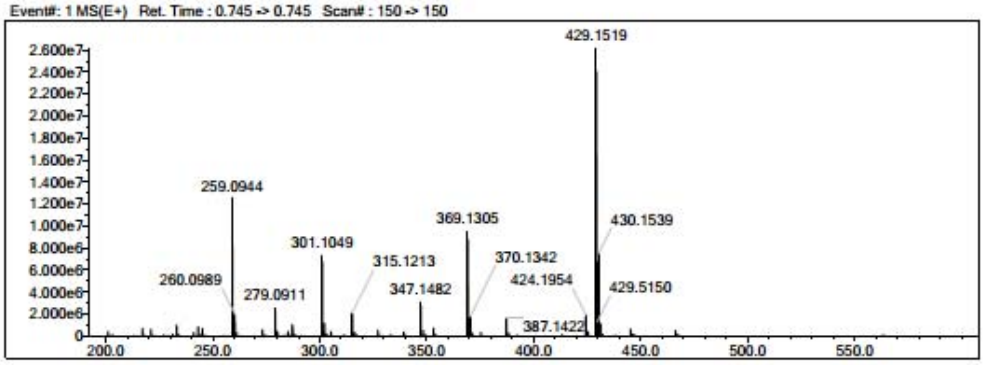
| Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Use Adduct |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | 1 | 0 | 26 | O | 2 | 0 | 8 | S | 2 | 0 | 2 | Br | 1 | 0 | 1 | H |
| C | 4 | 0 | 21 | F | 1 | 0 | 0 | Cl | 1 | 0 | 2 | I | 3 | 0 | 1 | Na |
| N | 3 | 0 | 4 | P | 3 | 0 | 1 | Cu | 2 | 0 | 0 | | | | | |

Error Margin (mDa): 5.0
HC Ratio: unlimited
Max Isotopes: all
MSn Iso RI (%): 75.00

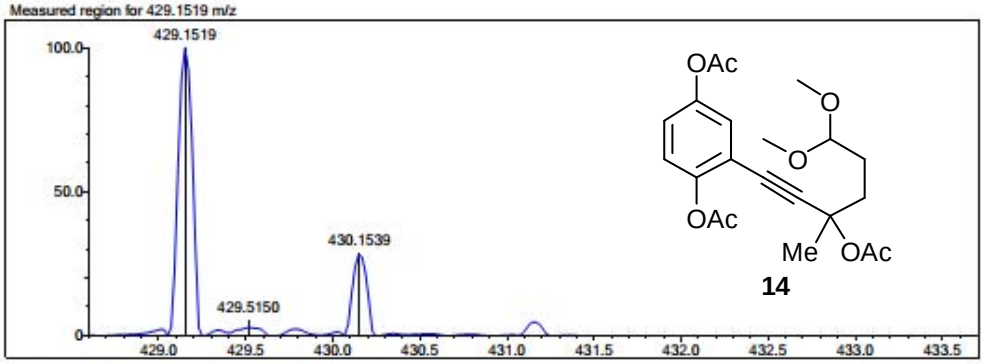
DBE Range: -2.0 - 1000.0
Apply N Rule: yes
Isotope RI (%): 1.00
MSn Logic Mode: AND

Electron Ions: both
Use MSn Info: yes
Isotope Res: 10000
Max Results: 800

Event#: 1 MS(E+) Ret. Time : 0.745 -> 0.745 Scan# : 150 -> 150

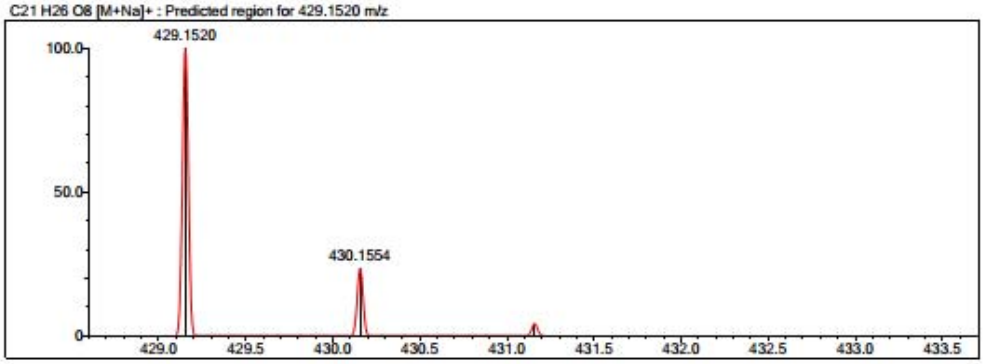



Measured region for 429.1519 m/z




**14**

C21 H26 O8 [M+Na]+ : Predicted region for 429.1520 m/z



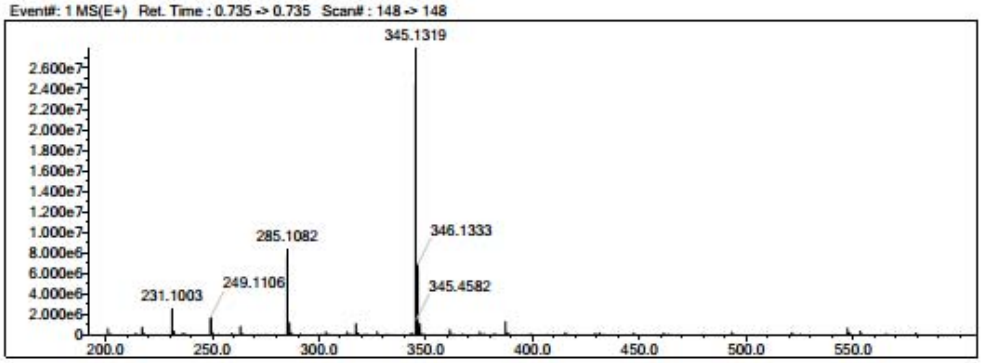

| Rank | Score | Formula (M) | Ion | Meas. m/z | Pred. m/z | Df. (mDa) | Df. (ppm) | Iso | DBE |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 85.72 | C21 H26 O8 | [M+Na]+ | 429.1519 | 429.1520 | -0.1 | -0.23 | 85.72 | 9.0 |

Data File: F:\WangHongGen\LY\4.lcd

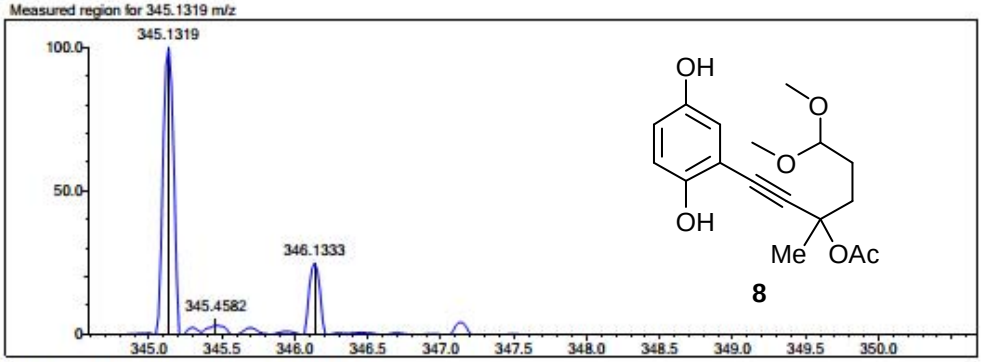
| Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Use Adduct |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | 1 | 0 | 26 | O | 2 | 0 | 8 | S | 2 | 0 | 2 | Br | 1 | 0 | 1 | H |
| C | 4 | 0 | 21 | F | 1 | 0 | 0 | Cl | 1 | 0 | 2 | I | 3 | 0 | 1 | Na |
| N | 3 | 0 | 4 | P | 3 | 0 | 1 | Cu | 2 | 0 | 0 | | | | | |

| | | | | | |
|---|---|---|---|---|---|
| Error Margin (mDa): | 5.0 | DBE Range: | -2.0 - 1000.0 | Electron Ions: | both |
| HC Ratio: | unlimited | Apply N Rule: | yes | Use MSn Info: | yes |
| Max Isotopes: | all | Isotope RI (%): | 1.00 | Isotope Res: | 10000 |
| MSn Iso RI (%): | 75.00 | MSn Logic Mode: | AND | Max Results: | 800 |

Event#: 1 MS(E+) Ret. Time : 0.735 -> 0.735 Scan# : 148 -> 148




Measured region for 345.1319 m/z

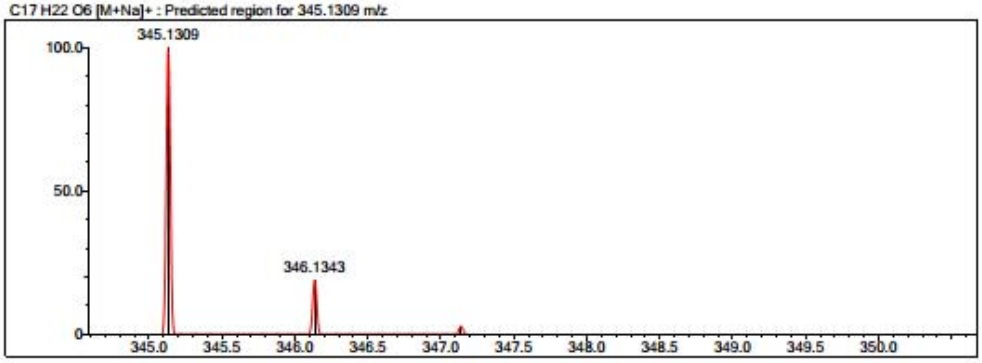






**8**

C17 H22 O6 [M+Na]+ : Predicted region for 345.1309 m/z




| Rank | Score | Formula (M) | Ion | Meas. m/z | Pred. m/z | Df. (mDa) | Df. (ppm) | Isc | DBE |
|---|---|---|---|---|---|---|---|---|---|
| 5 | 67.90 | C17 H22 O6 | [M+Na]+ | 345.1319 | 345.1309 | 1.0 | 2.90 | 71.29 | 7.0 |

Data File: F:\WangHongGen\LY\5.lcd

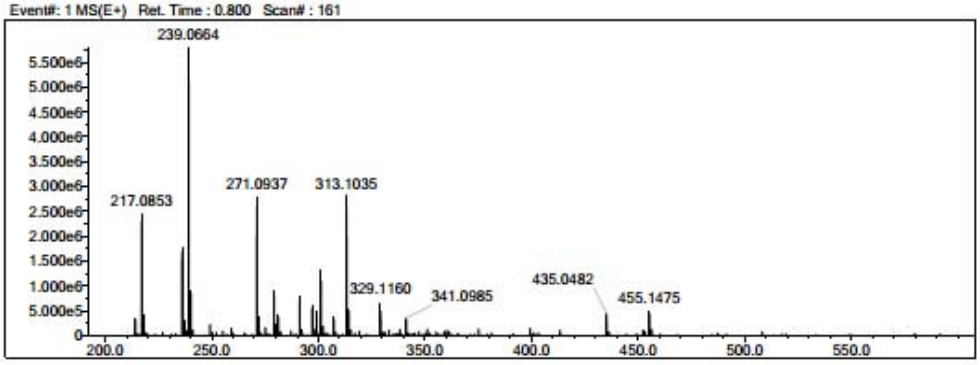
| Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Use Adduct |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | 1 | 0 | 26 | O | 2 | 0 | 8 | S | 2 | 0 | 2 | Br | 1 | 0 | 1 | H |
| C | 4 | 0 | 21 | F | 1 | 0 | 0 | Cl | 1 | 0 | 2 | I | 3 | 0 | 1 | Na |
| N | 3 | 0 | 4 | P | 3 | 0 | 1 | Cu | 2 | 0 | 0 | | | | | |

Error Margin (mDa): 5.0
HC Ratio: unlimited
Max Isotopes: all
MSn Iso RI (%): 75.00

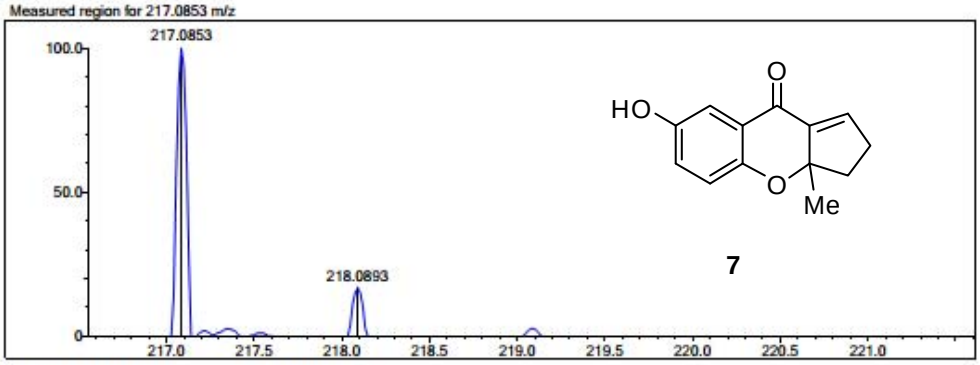
DBE Range: -2.0 - 1000.0
Apply N Rule: yes
Isotope RI (%): 1.00
MSn Logic Mode: AND

Electron Ions: both
Use MSn Info: yes
Isotope Res: 10000
Max Results: 800

Event#: 1 MS(E+) Ret. Time : 0.800 Scan# : 161




Measured region for 217.0853 m/z

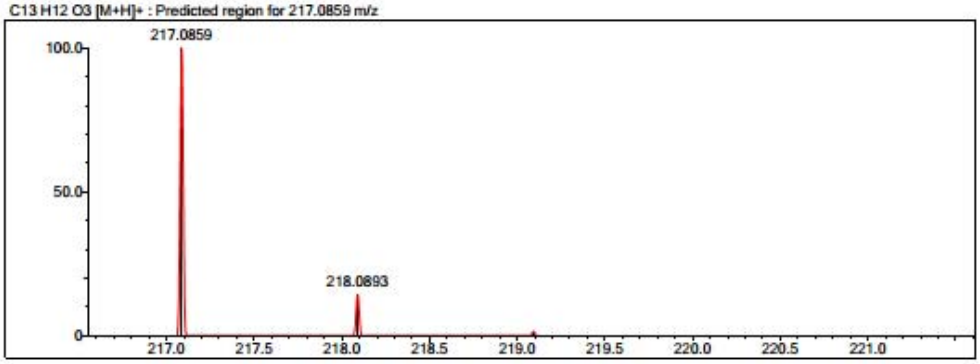






**7**

C13 H12 O3 [M+H]+ : Predicted region for 217.0859 m/z




| Rank | Score | Formula (M) | Ion | Meas. m/z | Pred. m/z | Df. (mDa) | Df. (ppm) | Iso | DBE |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 69.08 | C13 H12 O3 | [M+H]+ | 217.0853 | 217.0859 | -0.6 | -2.76 | 72.26 | 8.0 |

Formula Predictor Report - y-d-m1.lcd



Data File: F:\高分辨数据\wanghonggen\Liu Yaoly-d-m1.lcd

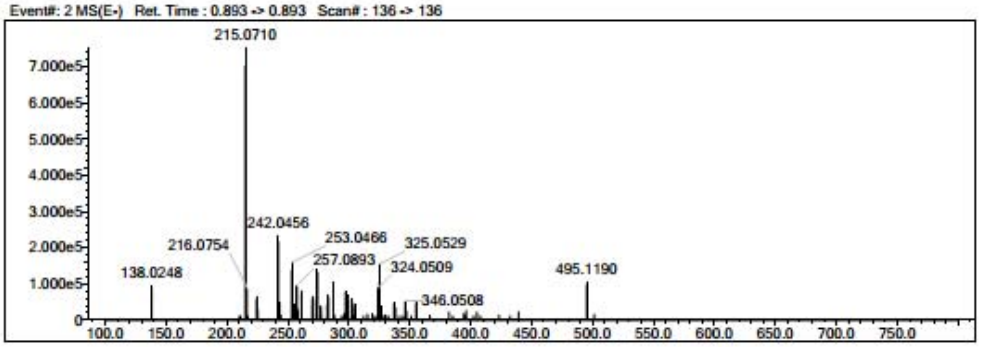
| Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Use Adduct |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | 1 | 0 | 12 | O | 2 | 0 | 3 | P | 3 | 0 | 0 | Se | 2 | 0 | 0 | H |
| 2H | 1 | 0 | 0 | 18O | 2 | 0 | 0 | S | 2 | 0 | 1 | Br | 1 | 0 | 0 | |
| B | 3 | 0 | 0 | F | 1 | 0 | 0 | Cl | 1 | 0 | 0 | I | 3 | 0 | 0 | |
| C | 4 | 0 | 13 | Na | 1 | 0 | 0 | K | 1 | 0 | 0 | | | | | |
| N | 3 | 0 | 0 | Si | 4 | 0 | 1 | Zn | 2 | 0 | 0 | | | | | |

Error Margin (ppm): 100
HC Ratio: unlimited
Max Isotopes: all
MSn Iso RI (%): 75.00

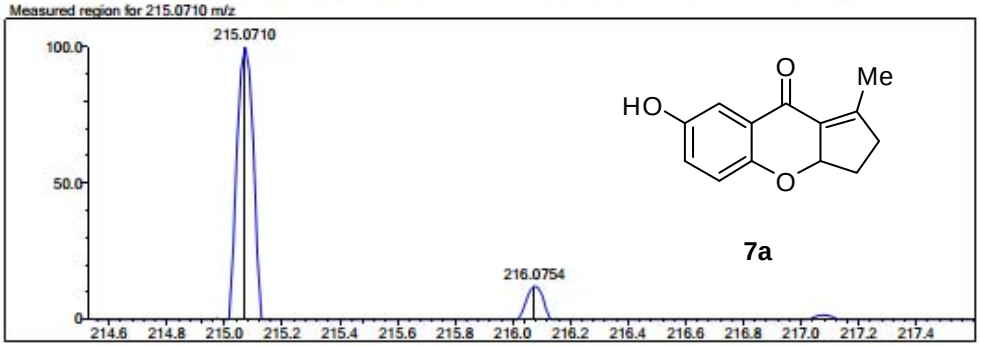
DBE Range: -0.5 - 1000.0
Apply N Rule: no
Isotope RI (%): 1.00
MSn Logic Mode: AND

Electron Ions: both
Use MSn Info: no
Isotope Res: 10000
Max Results: 500

Event#: 2 MS(E-) Ret. Time : 0.893 -> 0.893 Scan# : 136 -> 136




Measured region for 215.0710 m/z

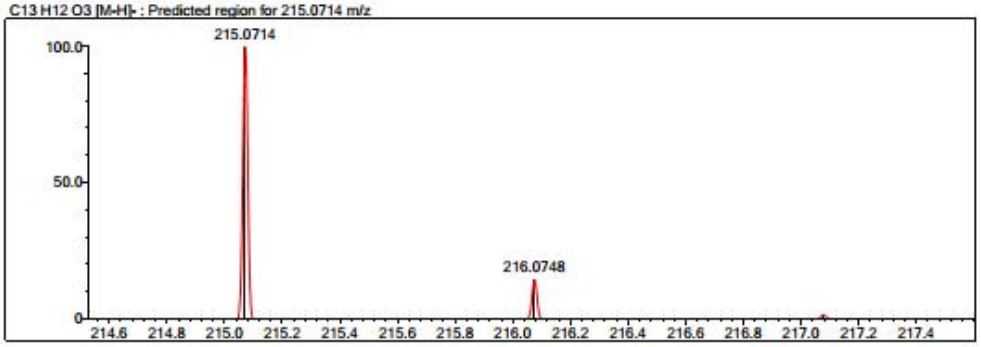






**7a**

C13 H12 O3 [M-H]- : Predicted region for 215.0714 m/z




| Rank | Score | Formula (M) | Ion | Meas. m/z | Pred. m/z | Df. (mDa) | Df. (ppm) | Iso | DBE |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 67.00 | C13 H12 O3 | [M-H]- | 215.0710 | 215.0714 | -0.4 | -1.86 | 68.47 | 8.0 |

Data File: F:\高分辨数据\wanghonggen\Liu Yao\New Folder\1.lcd

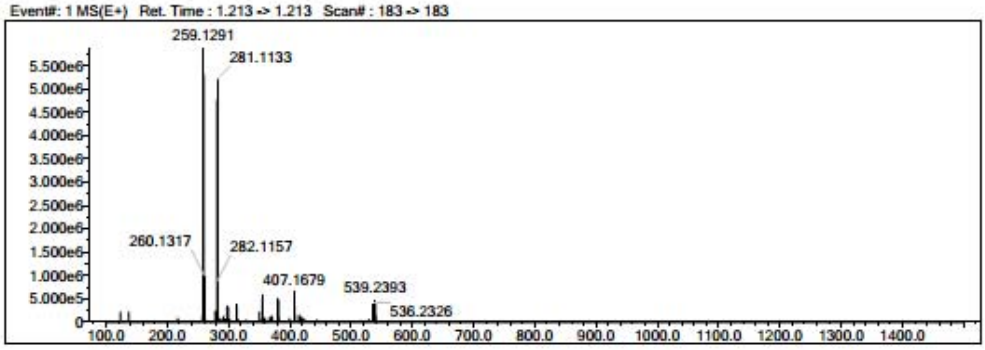
| Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Use Adduct |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | 1 | 0 | 40 | O | 2 | 0 | 3 | P | 3 | 0 | 0 | Se | 2 | 0 | 0 | H |
| 2H | 1 | 0 | 0 | 18O | 2 | 0 | 0 | S | 2 | 0 | 0 | Br | 1 | 0 | 0 | Na |
| B | 3 | 0 | 0 | F | 1 | 0 | 0 | Cl | 1 | 0 | 0 | I | 3 | 0 | 0 | |
| C | 4 | 0 | 16 | Na | 1 | 0 | 0 | K | 1 | 0 | 0 | | | | | |
| N | 3 | 0 | 0 | Si | 4 | 0 | 0 | Zn | 2 | 0 | 0 | | | | | |

Error Margin (ppm): 100
HC Ratio: unlimited
Max Isotopes: all
MSn Iso RI (%): 75.00

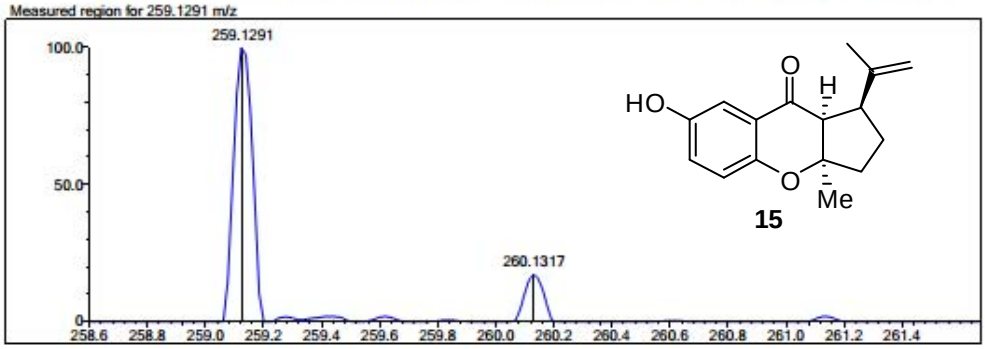
DBE Range: -0.5 - 1000.0
Apply N Rule: no
Isotope RI (%): 1.00
MSn Logic Mode: AND

Electron Ions: both
Use MSn Info: no
Isotope Res: 10000
Max Results: 500

Event#: 1 MS(E+) Ret. Time : 1.213 -> 1.213 Scan# : 183 -> 183

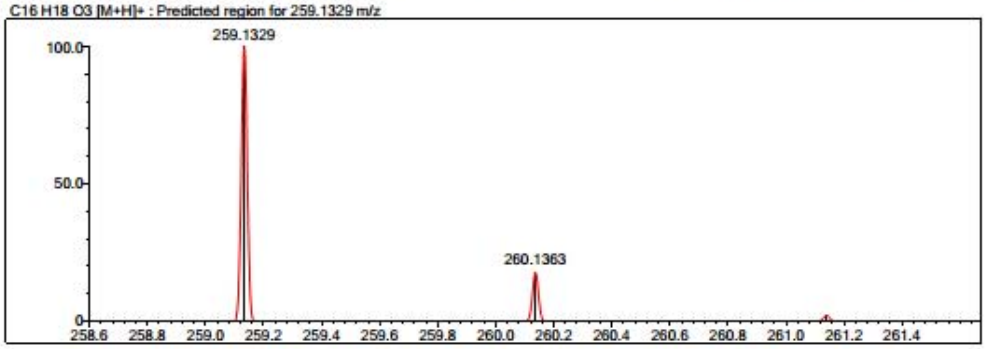



Measured region for 259.1291 m/z




**15**

C16 H18 O3 [M+H]+ : Predicted region for 259.1329 m/z




| Rank | Score | Formula (M) | Ion | Meas. m/z | Pred. m/z | Df. (mDa) | Df. (ppm) | Iso | DBE |
|---|---|---|---|---|---|---|---|---|---|
| 2 | 21.63 | C16 H18 O3 | [M+H]+ | 259.1291 | 259.1329 | -3.8 | -14.66 | 78.43 | 8.0 |

Data File: F:\WangHongGen\LY\8.lcd

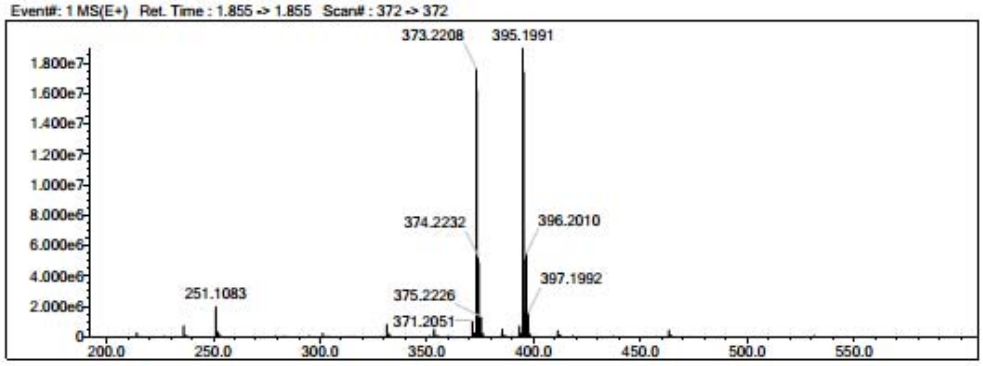
| Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Use Adduct |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | 1 | 0 | 33 | O | 2 | 0 | 8 | P | 3 | 0 | 1 | Cu | 2 | 0 | 0 | H |
| C | 4 | 0 | 24 | F | 1 | 0 | 0 | S | 2 | 0 | 2 | Br | 1 | 0 | 1 | Na |
| N | 3 | 0 | 4 | Si | 4 | 0 | 1 | Cl | 1 | 0 | 2 | I | 3 | 0 | 1 | |

Error Margin (mDa): 5.0
HC Ratio: unlimited
Max Isotopes: all
MSn Iso RI (%): 75.00

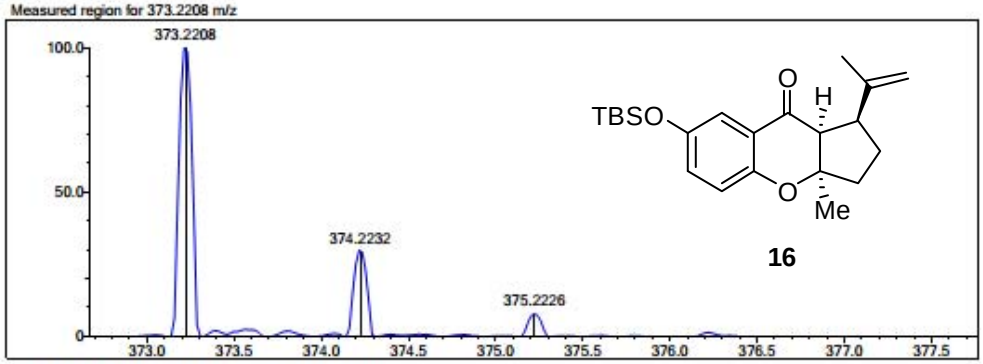
DBE Range: -2.0 - 1000.0
Apply N Rule: yes
Isotope RI (%): 1.00
MSn Logic Mode: AND

Electron Ions: both
Use MSn Info: yes
Isotope Res: 10000
Max Results: 800

Event#: 1 MS(E+) Ret. Time : 1.855 -> 1.855 Scan# : 372 -> 372




Measured region for 373.2208 m/z

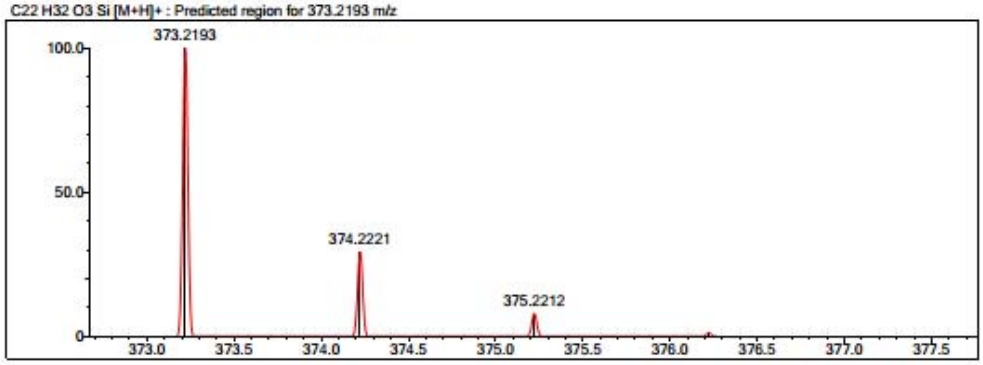






**16**

C22 H32 O3 Si [M+H]+ : Predicted region for 373.2193 m/z




| Rank | Score | Formula (M) | Ion | Meas. m/z | Pred. m/z | Df. (mDa) | Df. (ppm) | Iso | DBE |
|---|---|---|---|---|---|---|---|---|---|
| 2 | 83.32 | C22 H32 O3 Si | [M+H]+ | 373.2208 | 373.2193 | 1.5 | 4.02 | 90.12 | 8.0 |

Data File: F:\高分辨数据\wanghonggen\Liu Yaoly-d-m2.lcd

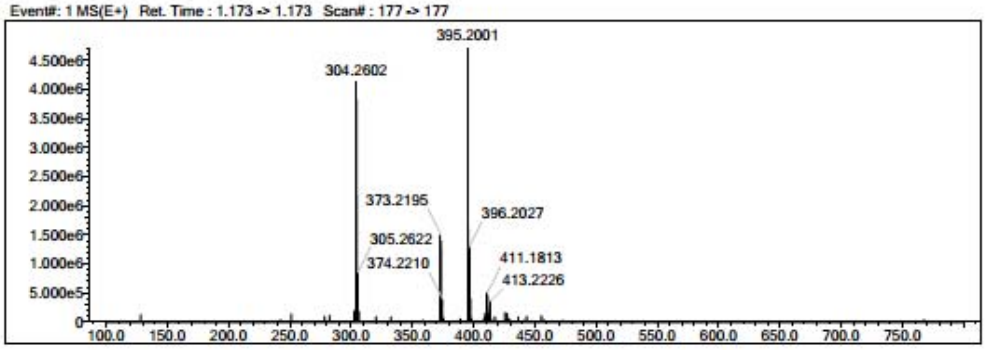
| Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Use Adduct |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | 1 | 0 | 40 | O | 2 | 0 | 4 | P | 3 | 0 | 0 | Se | 2 | 0 | 0 | H |
| 2H | 1 | 0 | 0 | 18O | 2 | 0 | 0 | S | 2 | 0 | 1 | Br | 1 | 0 | 0 | Na |
| B | 3 | 0 | 0 | F | 1 | 0 | 0 | Cl | 1 | 0 | 0 | I | 3 | 0 | 0 | |
| C | 4 | 0 | 40 | Na | 1 | 0 | 0 | K | 1 | 0 | 0 | | | | | |
| N | 3 | 0 | 0 | Si | 4 | 0 | 1 | Zn | 2 | 0 | 0 | | | | | |

Error Margin (ppm): 100
HC Ratio: unlimited
Max Isotopes: all
MSn Iso RI (%): 75.00

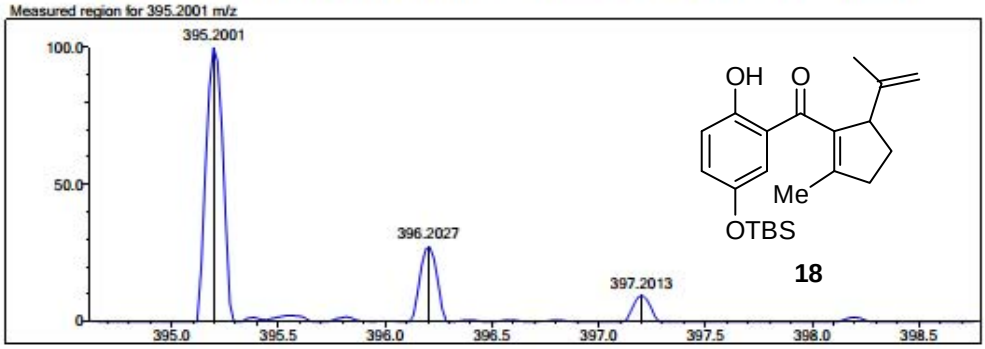
DBE Range: -0.5 - 1000.0
Apply N Rule: no
Isotope RI (%): 1.00
MSn Logic Mode: AND

Electron Ions: both
Use MSn Info: no
Isotope Res: 10000
Max Results: 500

Event#: 1 MS(E+) Ret. Time : 1.173 -> 1.173 Scan# : 177 -> 177

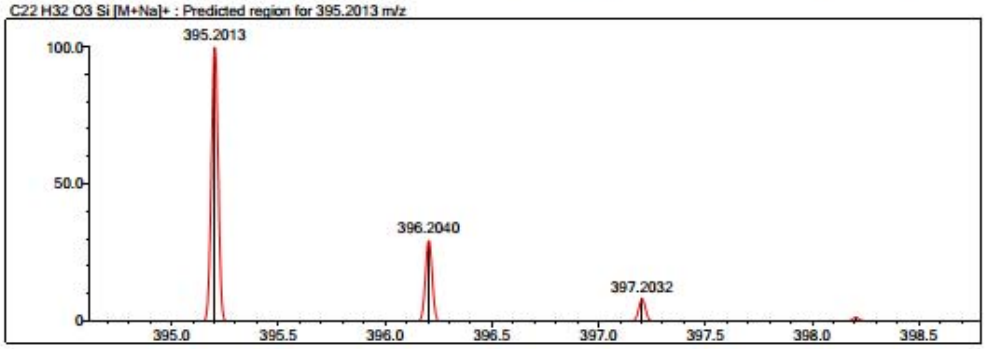



Measured region for 395.2001 m/z




**18**

C22 H32 O3 Si [M+Na]+ : Predicted region for 395.2013 m/z




| Rank | Score | Formula (M) | Ion | Meas. m/z | Pred. m/z | Df. (mDa) | Df. (ppm) | Iso | DBE |
|---|---|---|---|---|---|---|---|---|---|
| 2 | 78.91 | C22 H32 O3 Si | [M+Na]+ | 395.2001 | 395.2013 | -1.2 | -3.04 | 83.15 | 8.0 |

Data File: F:\高分辨数据\wanghonggen\Liu Yao\YAO-I-1.lcd

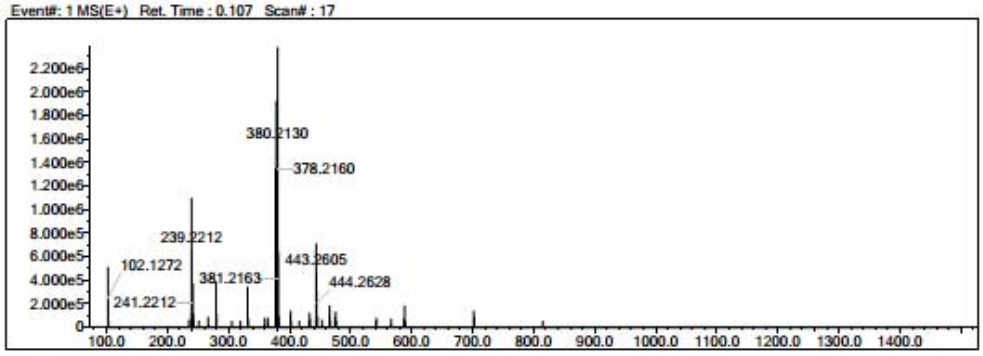
| Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Use Adduct |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | 1 | 0 | 50 | O | 2 | 0 | 4 | S | 2 | 0 | 0 | I | 3 | 0 | 0 | H |
| B | 3 | 0 | 0 | 18O | 2 | 0 | 0 | Cl | 1 | 0 | 2 | | | | | Na |
| C | 4 | 0 | 30 | F | 1 | 0 | 0 | K | 1 | 0 | 0 | | | | | |
| N | 3 | 0 | 2 | Si | 4 | 0 | 1 | Br | 1 | 0 | 0 | | | | | |

Error Margin (ppm): 100
HC Ratio: unlimited
Max Isotopes: all
MSn Iso RI (%): 75.00

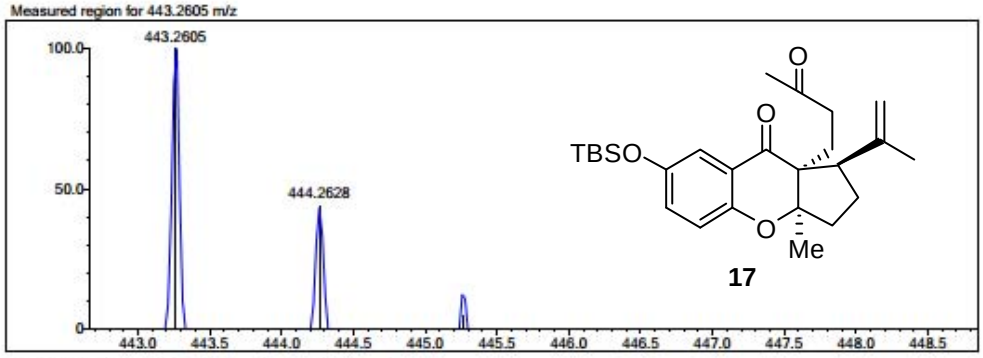
DBE Range: -0.5 - 1000.0
Apply N Rule: yes
Isotope RI (%): 1.00
MSn Logic Mode: AND

Electron Ions: both
Use MSn Info: no
Isotope Res: 10000
Max Results: 500

Event#: 1 MS(E+) Ret. Time : 0.107 Scan# : 17

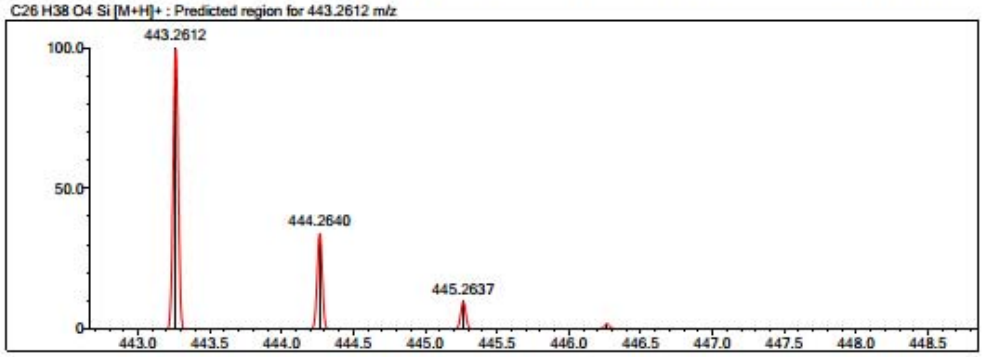



Measured region for 443.2605 m/z




**17**

C26 H38 O4 Si [M+H]+ : Predicted region for 443.2612 m/z




| Rank | Score | Formula (M) | Ion | Meas. m/z | Pred. m/z | Df. (mDa) | Df. (ppm) | Iso | DBE |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 71.66 | C26 H38 O4 Si | [M+H]+ | 443.2605 | 443.2612 | -0.7 | -1.58 | 72.72 | 9.0 |

Data File: F:\WangHongGen\YAO-I-001.lcd

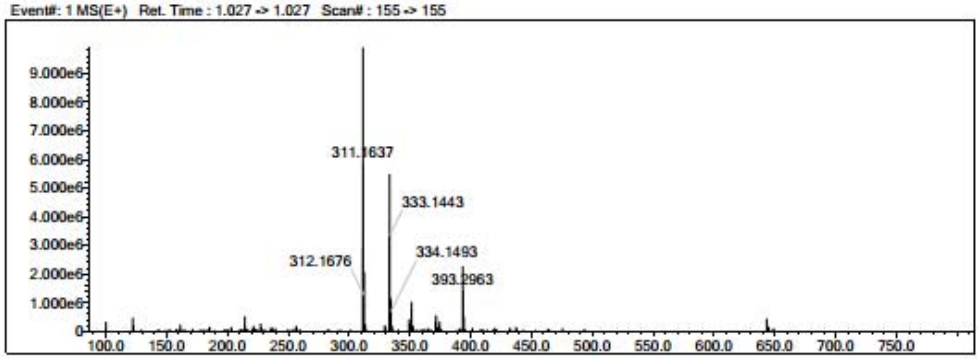
| Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Use Adduct |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | 1 | 0 | 29 | N | 3 | 0 | 6 | P | 3 | 0 | 0 | Cu | 2 | 0 | 0 | H |
| B | 3 | 0 | 0 | O | 2 | 0 | 6 | S | 2 | 0 | 1 | Br | 1 | 0 | 0 | Na |
| C | 4 | 0 | 28 | F | 1 | 0 | 0 | Cl | 1 | 0 | 1 | I | 3 | 0 | 0 | |

Error Margin (mDa): 20.0
HC Ratio: unlimited
Max Isotopes: all
MSn Iso RI (%): 75.00

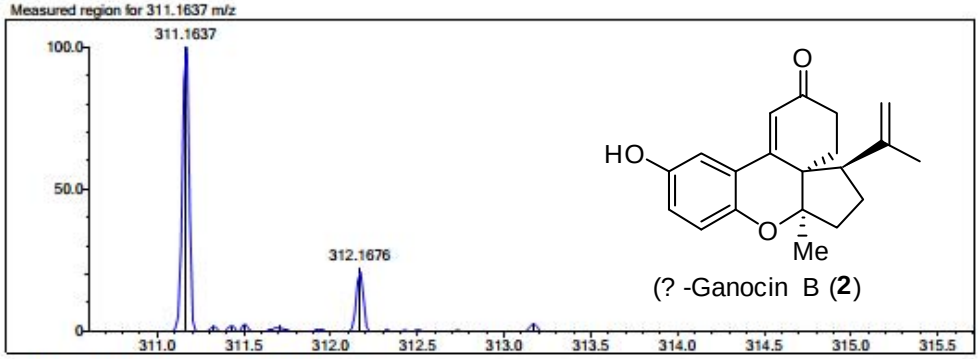
DBE Range: -2.0 - 1000.0
Apply N Rule: yes
Isotope RI (%): 1.00
MSn Logic Mode: AND

Electron Ions: both
Use MSn Info: yes
Isotope Res: 10000
Max Results: 800

Event#: 1 MS(E+) Ret. Time : 1.027 -> 1.027 Scan# : 155 -> 155




Measured region for 311.1637 m/z

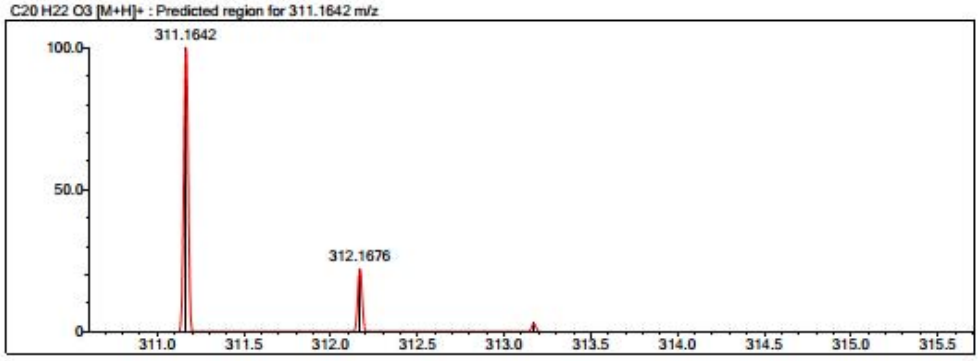






(? -Ganocin B (**2**)

C20 H22 O3 [M+H]+ : Predicted region for 311.1642 m/z




| Rank | Score | Formula (M) | Ion | Meas. m/z | Pred. m/z | Df. (mDa) | Df. (ppm) | Isc | DBE |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 95.38 | C20 H22 O3 | [M+H]+ | 311.1637 | 311.1642 | -0.5 | -1.61 | 96.85 | 10.0 |

Data File: F:\WangHongGen\YAO-I-003-2.lcd

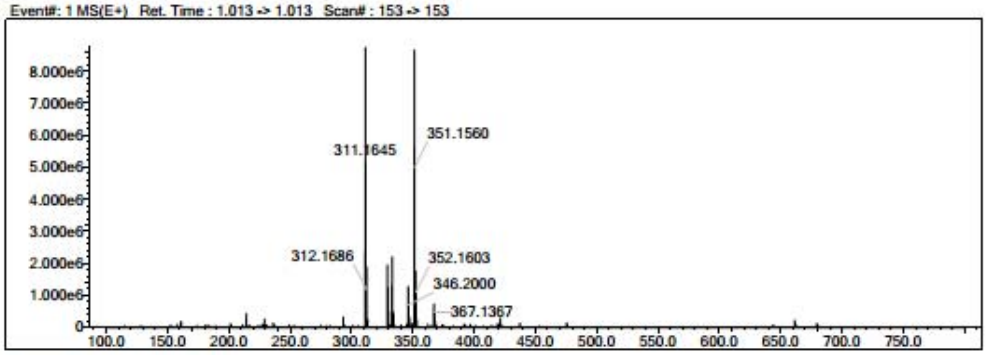
| Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Elmt | Val. | Min | Max | Use Adduct |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | 1 | 0 | 38 | O | 2 | 0 | 6 | S | 2 | 0 | 1 | I | 3 | 0 | 0 | H |
| B | 3 | 0 | 0 | F | 1 | 0 | 0 | Cl | 1 | 0 | 1 | | | | | Na |
| C | 4 | 0 | 28 | Si | 4 | 0 | 1 | Cu | 2 | 0 | 0 | | | | | |
| N | 3 | 0 | 6 | P | 3 | 0 | 0 | Br | 1 | 0 | 0 | | | | | |

Error Margin (mDa): 20.0
HC Ratio: unlimited
Max Isotopes: all
MSn Iso RI (%): 75.00

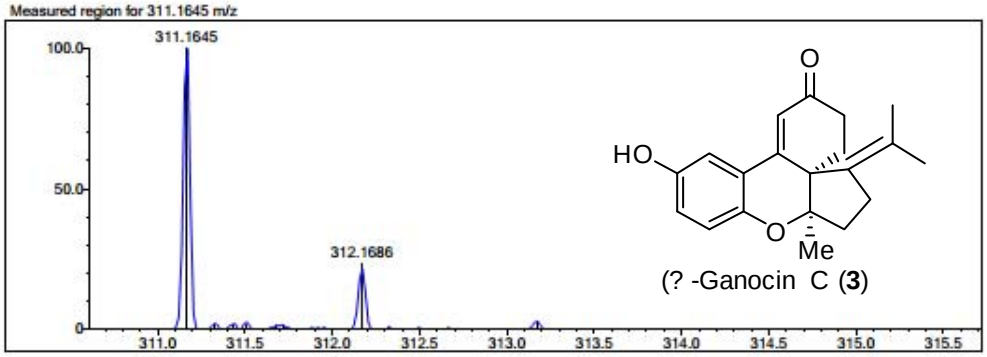
DBE Range: -2.0 - 1000.0
Apply N Rule: yes
Isotope RI (%): 1.00
MSn Logic Mode: AND

Electron Ions: both
Use MSn Info: yes
Isotope Res: 10000
Max Results: 800

Event#: 1 MS(E+) Ret. Time : 1.013 -> 1.013 Scan# : 153 -> 153




Measured region for 311.1645 m/z

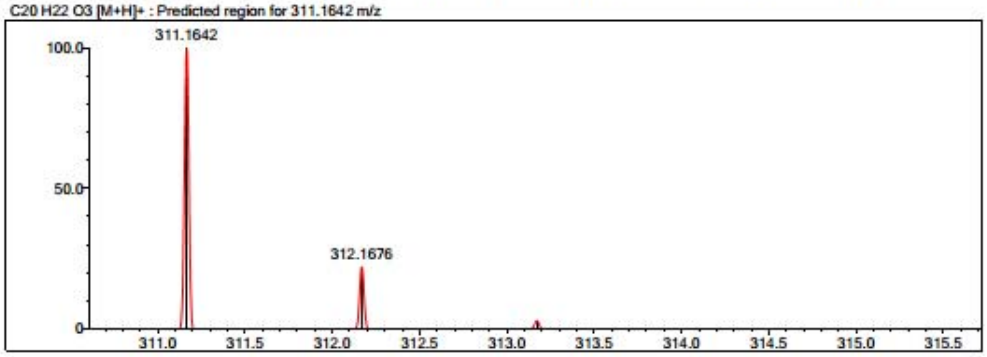






(? -Ganocin C (**3**)

C20 H22 O3 [M+H]+ : Predicted region for 311.1642 m/z




| Rank | Score | Formula (M) | Ion | Meas. m/z | Pred. m/z | Df. (mDa) | Df. (ppm) | Iso | DBE |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 95.28 | C20 H22 O3 | [M+H]+ | 311.1645 | 311.1642 | 0.3 | 0.96 | 95.28 | 10.0 |