SUPPORTING INFORMATION

New Facile Enantio- and Diastereo-selective Syntheses of (-)-Triptonide and (-)-Triptolide

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CONTENT

1. General Procedures.

All solvents were dried and distilled prior to use by standard procedures. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC), carried out on 0.25 mm silica gel plates using UV light as visualizing agent and phosphomolybdic acid hydrate in ethanol for staining. Column chromatography was performed using silica gel F254 (particle size 0.2−0.3 mm). Unless stated otherwise, all of the yields refer to isolated products after flash column chromatography. The solvent mixtures employed in TLC analysis and in flash column chromatography purifications are reported as volume by volume and in percentages. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded using 300 MHz and 400 MHz equipments. For ^{1}H NMR spectra, chemical shifts (δ) are referenced from $CDCl_3$ (7.27 ppm). Coupling constants (J) are reported in Hz. For multiplicities the following abbreviations were used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, double doublet; bs; broad singlet; dt, double triplet. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded using an NMR spectrometer at 75 MHz and 100 MHz. For ^{13}C NMR spectra, chemical shifts (δ) are given from $CDCl_3$ (77.0 ppm) or DMSO-*d6* (39.5 ppm). The ee value was detected by chiral HPLC using isopropanol and n-hexane as eluants. HRMS data were determined using ESI-MS. Optical rotations were measured using sodium D line. The enantiomeric excess values were determined by chiral stationary phase HPLC analysis (hexane:i-propanol 95:05~95:15 v/v, flow rate 1~1.1 mL/min) using OD-H chiral column and photodiode array detecter (210-400 nm).

2. Experimental section

2.1 *Synthesis of ethyl 3-oxopent-4-enoate* ***(11).*** This compound was prepared according to the literature.[13a] To a solution of (*i*-Pr)$_2$NH (1.54 mL, 11 mmol, 1.1 equiv) in dry THF (20mL), under argon atmosphere and at -78 °C, was slowly added dropwise to n-C_4H_9Li in dry THF (4.4 mL, 11 mmol, 2.5 M, 1.1 equiv). After the mixture was stirred for 15 min at this temperature, dry AcOEt (0.96 mL, 10 mmol, 1.0 equiv) was added dropwised slowly and stirred for another 45 min after the completion of addition. Dry acrolein (0.67 mL, 10 mmol) wad added dropwise. The reaction mixture was stirred for 5 min and a saturated aqueous NH_4Cl solution (5 mL) was added and the result solution was extracted with Et_2O (3 × 50 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and evaporated in rotary evaporator. Column chromatography (20% AcOEt/hexanes) of the residue afforded compound **11a** (1.18 g, 8.19 mmol, 82%) as a pale yellow oil. **Compound 11a**: **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 5.82~5.90 (m, 1H), 5.26~5.31 (dd, 1H), 5.11~5.14 (dd, 1H), 4.50~4.53 (q, 1H), 4.12~4.17 (q, 2H), 3.16 (s, 1H), 2.46~2.57 (m, 2H), 1.22~1.26 (t, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 172.1, 138.8, 115.2, 68.8, 60.7, 41.2, 14.1.

To a solution of compound **11a** (1.18 g, 8.19 mmol) in acetone (20 mL) at 0 °C, Jone's reagent (8.75 mL) was added slowly. The reaction mixture was stirred at 0 °C for about 10 min and then at room temperature for 3 h. Methanol (1 mL) was added to quench it followed by the addition of H_2O (40mL). The mixture was extracted with AcOEt (3 × 50 mL), and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and evaporated in rotary evaporator to afford Nazarov's reagent **11** (1.02 g, 88%) as a pale yellow oil with no need for purification. **Compound 11: ^{1}H NMR** (300 MHz, CDCl3) δ 11.80 (s, enol OH), 6.48-5.95 (m, 2H), 5.58 (m, 1H), 5.06 (s, 1H), 4.22-4.17 (m, 2H), 3.63 (s, 2H), 1.31-1.25 (m, 3H).

2.2 *Synthesis of (S)-ethyl 8-methoxy-4a-methyl-2-oxo-2,3,4,4a,9,10-hexahydro phenanthrene-1-carboxylate* ***(9)*** and *(R)-ethyl 2-hydroxy-8-methoxy-4a-methyl- 3,4,4a,9-tetrahydrophenanthrene-1-carboxylate* ***(15).*** A solution of 5-methoxy-1- methyl-2-tetralone (**10**, 9.5 g, 50 mmol), (R)-(+)-α-phenylethylamine (**12**, 6.7 g, 55 mmol, 1.1 equiv), and *p*-toluenesulfonic acid (0.95 g, 5 mmol, 0.1 equiv) in toluene (100 mL) in three-necked flask equipped with a Dean-Stark trap and water condenser was heated to reflux for 24 h under argon atmosphere, then cooled to 0 °C. Nazarov's reagent (ethyl 3-oxopent-4-enoate, **11**, 10.0 g, 70 mmol, 1.4 equiv) was added to the reaction mixture slowly. Then the

mixture was warmed to 40 °C and stirred for another 48 h. After the reaction mixture was cooled to 0 °C, AcOH (5 mL) and H_2O (5 mL) was added and the result mixture was heated to reflux for 3 h. After the reaction mixture was evaporated in rotary evaporator, AcOEt (100 mL) was added to dissolve the residue and washed with H_2O (2 × 60 mL), saturated aqueous $NaHCO_3$ solution (2 × 60 mL), and brine in turn, and then dried over Na_2SO_4, filtered, and evaporated in rotary evaporator to form the crude product **14** (which could be purified by flash column chromatography eluting with 20% AcOEt/hexanes) as a reddish brown oil.

2.3 To a solution of the crude product **14** (8.2 g, 24.7 mmol, 1.0 equiv) in anhydrous ethanol (50 mL), under argon atmosphere and at 0 °C, was added dropwise a 2.50 M solution of KOH (2.8 g, 50 mmol, 2.0 equiv) in ethanol. Then the solution was warmed to room temperature and stirred for 3 h and concentrated in rotary evaporator. AcOEt (100 mL) was added to dissolve the residue. The solution was washed with H_2O (2 × 80 mL) and brine in turn, and then dried over Na_2SO_4, filtered, and evaporated in rotary evaporator. Purification by flash column chromatography (20% AcOEt/hexanes) afforded compound **9** (which was then triturated from diethyl ether and gave purified compound 6.27 g, 20.0 mmol, 56% yield from **10,** 90%ee) as a pale yellow solid and **15** (0.63 g, 2.0 mmol, 5.6% from **10**, 95%ee) as a pale yellow oil.

2.4 Compound 14: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.22~7.26 (t, 1H), 6.84~6.86 (d, *J* = 8.0 Hz, 1H), 6.72~6.74 (d, *J* = 8.0 Hz, 1H), 4.18~4.23 (q, 2H), 3.85 (s, 1H), 3.83 (s, 3H), 3.14~3.19 (d, 1H), 2.99~3.06 (q, 1H), 2.81~2.83 (d, 1H), 2.62~2.74 (q, 2H), 2.19~2.27 (dt, 2H), 1.58~1.69 (m, 2H), 1.48~1,56 (m, 1H), 1.47 (s, 3H), 1.28~1.32 (t, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 213.3, 172.0, 156.0, 144.2, 128.2, 122.6, 117.0, 107.5, 78.2, 61.0, 55.2, 54.3, 48.4, 42.5, 39.3, 30.9, 29.2, 20.1, 14.1; **MS** (ESI): [M+H$^+$] 333.3, [M+H$^+$-H_2O] 315.2; **HRMS** (ESI) for $C_{19}H_{24}O_5Na$ [M+Na$^+$]: calcd 355.1516, found 355.1511, error 1.4ppm.

Compound 9: $[\alpha]_D^{25}$ = +209.4° (c 0.53, CH_2Cl_2); **M.p.** 85-86°C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.21~7.25 (t, *J* = 8.0 Hz, 1H), 6.90~6.92 (d, *J* = 8.0 Hz, 1H), 6.71~6.73 (d, *J* = 8.0 Hz, 1H), 4.29~4.38 (m, 2H), 3.83 (s, 3H), 3.20~3.26 (m, 1H), 2.49~2.79 (m, 5H), 2.34~2.40 (dt, 1H), 2.02~2.11 (dt, 1H), 1.63 (s, 3H), 1.33~1.37 (t, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 194.4, 166.9, 166.2, 156.3, 130.6, 127.5, 123.7, 117.8, 107.4, 61.2, 55.3, 39.2, 36.1, 34.1, 27.7, 27.1, 24.1, 14.2; **MS** (ESI): [M+H]$^+$ 315.1; **HRMS** (ESI) for $C_{19}H_{22}O_4Na$ [M+Na$^+$]: calcd 337.1410, found 337.1408, error 0.6 ppm.

Compound 15: **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 13.1 (s, 1H), 7.21~7.25 (t, J = 8.0 Hz, 1H), 7.00~7.02 (d, J = 8.0 Hz, 1H), 6.71~6.73 (d, J = 8.0 Hz, 1H), 4.38~4.47 (m, 1H), 4.24~4.36 (m, 1H), 3.86 (s, 3H), 3.35~3.52 (m, 2H), 2.66~2.76 (m, 1H), 2.48~2.56 (m, 1H), 2.23~2.28 (q, 1H), 1.82~1.91 (m, 1H), 1.38~1.42 (t, 3H), 1.35 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 173.1, 172.4, 156.2, 144.6, 131.1, 126.5, 121.7, 118.9, 118.0, 106.6, 100.9, 60.9, 55.2, 36.5, 34.5, 27.4, 26.1, 25.1, 14.2; **MS** (ESI): [M+H$^+$] 315.1; **HRMS** (ESI) for $C_{19}H_{22}O_4Na$ [M+Na$^+$]: calcd 337.1410, found 337.1409, error 0.3 ppm.

2.5 *Synthesis of (R)-ethyl 8-methoxy-4a-methyl-2-(((trifluoromethyl)sulfonyl)oxy)- 3,4,4a,9-tetrahydrophenanthrene-1-carboxylate* ***(16).*** To a solution of the mixture of compound **9** and **15** (6.28 g, 20 mmol, 1.0 equiv) obtained from the above reaction in dry CH_2Cl_2 (100 mL), was added pyridine (3.16 g, 3.22 mL, 40 mmol, 2.0 equiv), under argon atmosphere and at 0 °C, which was followed by slow addition of trifluoromethanesulfonic anhydride (10.7 g, 6.47 mL, 38 mmol, 1.9 equiv). The solution was warmed to room temperature and stirred for 2 h, then was quenched with water. After separation, the organic layer was washed with H_2O (2 × 60 mL) and brine (60 mL), and then dried over Na_2SO_4, filtered, and evaporated in rotary evaporator to form the crude product **16** (the residue could be purified on column chromatography eluting with 20% AcOEt/hexanes to furnish 8.83 g/19.8 mmol pure compound **16** with 96%ee in 95% yield as a colorless oil). **Compound 16**: $[\alpha]_D^{25}$ = +113.3° (c 0.60, CH_2Cl_2); **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 7.23~7.27 (t, 1H), 6.97~6.99 (d, *J* = 6.0 Hz, 1H), 6.75~6.77 (d, *J* = 6.0 Hz, 1H), 6.05~6.07 (dd, 1H), 4.36~4.42 (m, 2H), 3.85 (s, 3H), 3.60~3.66 (dd, *J* = 17.7 Hz, 1H), 3.26~3.31 (d, 1H), 2.82~2.91 (m, 1H), 2.57~2.63 (dd, *J* = 17.7 Hz, 1H), 2.43~2.48 (dd, 1H), 1.91~1.99 (dt, 1H), 1.39~1.42 (t, 3H), 1.30 (s, 3H); **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 164.9, 156.3, 144.8, 143.5, 133.0, 127.2, 126.8, 126.4, 126.1, 123.0, 121.5, 119.8, 116.6, 116.5, 113.5, 107.3, 62.1, 55.3, 35.5, 32.7, 27.0, 25.0, 13.9; **MS** (ESI): [M +H$^+$] 447.1; **HRMS** (ESI) for $C_{20}H_{21}O_6SF_3Na$ [M+Na$^+$]: calcd 469.0903, found 469.0898, error 1.1ppm.

2.6 *Synthesis of (R)-1-(hydroxymethyl)-8-methoxy-4a-methyl-3,4,4a,9-tetrahydro- phenanthren-2-yl trifluoromethanesulfonate* ***(17).*** To a solution of compound **16** (8.47 g, 19 mmol, 1.0 equiv) in dry CH_2Cl_2 (100 mL), under argon atmosphere and at -78 °C, was added dropwise a 1.5 M solution of DiBAl-H (27.9 mL, 41.8 mmol, 2.2 equiv) in toluene. After the solution was stirred for 2 h at -40 °C, it was poured into cool aqueous solution (200mL) of seignette salt (20 g) carefully. After the mixture was stirred for 30 min, it was extracted with AcOEt (3 × 100 mL),

and the combined organic layers were washed with brine, and then dried over Na_2SO_4, filtered, and evaporated in rotary evaporator to form the crude product **17** (the residue could be purified on column chromatography eluting with 20% AcOEt/hexanes to furnish 7.06 g/17.5 mmol pure compound **17** with 97%ee in 92% yield) as a colorless oil. **Compound 17**: $[\alpha]_D^{25}$ = +74.5° (c 1.02, CH_2Cl_2); **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 7.23~7.27 (t, 1H), 6.98~7.00 (d, *J* = 6.0 Hz, 1H), 6.75~6.77 (d, *J* = 8.0 Hz, 1H), 6.43~6.45 (dd, 1H), 4.49~4.57 (q, 2H), 3.86 (s, 3H), 3.64~3.71 (dd, *J* = 1.8, 17.7 Hz, 1H), 3.30~3.36 (d, *J* = 17.7 Hz, 1H), 2.81~2.90 (m, 1H), 2.53~2.59 (dd, *J* = 17.7 Hz, 1H), 2.41~2.46 (q, 1H), 1.87~1.95 (m, 2H), 1.26 (s, 3H); **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 156.3, 145.2, 144.1, 134.8, 128.3, 127.0, 124.1, 123.1, 121.7, 119.9, 116.7, 116.4, 113.6, 107.2, 56.0, 55.3, 35.8, 33.0, 27.0, 25.6, 25.0; **MS** (ESI): $[M+H^+]$ 405.2; **HRMS** (ESI) for $C_{18}H_{19}O_5SF_3Na$ $[M+Na^+]$: calcd 427.0798, found 427.0801, error 0.7 ppm.

2.7 *Synthesis of (R)-6-methoxy-9b-methyl-5,9b,10,11-tetrahydrophenanthro[1,2-c]- furan-1(3H)-one* ***(6).*** To a solution of compound **17** (6.87 g, 17 mmol, 1.0 equiv) in DMF (85 mL), was added PPh_3 (178 mg, 0.68 mmol, 0.04 equiv), $Pd(OAc)_2$ (38.1 mg, 0.17 mmol, 0.01 equiv), Et_3N (12 mL, 85 mmol, 5 equiv), and methanol (1.4 mL, 34 mmol, 2 equiv), then carbon monoxide was introduced into the solution. After the solution was heated to 60 °C and stirred for 3 h under carbon monoxide atmosphere, the solvent was evaporated in rotary evaporator. The residue was dissolved in CH_2Cl_2, and the organic layer was washed with H_2O and brine, and then dried over Na_2SO_4, filtered, and evaporated in rotary evaporator. Purification of the residue by recrystallization from CH_2Cl_2/Et_2O afforded compound **6** (3.84 g, 13.6 mmol, 85% yield, 98%ee) as a yellow solid. **Compound 6**: $[\alpha]_D^{25}$ = +21.0° (c 1.00, CH_2Cl_2); **M.p.** 110-112 °C; **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 7.25~7.29 (t, 1H), 7.05~7.07 (d, *J* = 6.0 Hz, 1H), 7.77~7.79 (d, *J* = 6.0 Hz, 1H), 6.15~6.17 (dd, *J* = 1.8, 4.2 Hz, 1H), 5.01~5.06 (dt, *J* = 12.0 Hz, 1H), 4.89~4.94 (dd, *J* = 12.0 Hz, 1H), 3.86 (s, 3H), 3.68~3.75 (dd, *J* = 4.2, 17.7 Hz, 1H), 2.25~2.31 (d, *J* = 1.8, 17.7 Hz, 1H), 2.46~2.62 (m, 3H), 1.77~1.83 (m, 1H), 1.20 (s, 3H); **^{13}C NMR** ($CDCl_3$, 75 MHz): δ 174.1, 156.3, 155.0, 144.3, 134.5, 127.4, 125.8, 123.4, 121.5, 116.7, 107.4, 69.1, 55.4, 36.8, 32.8, 27.6, 24.6, 18.0; **MS** (ESI): $[M+H^+]$ 283.3; **HRMS** (ESI) for $C_{18}H_{19}O_3$ $[M+H^+]$: calcd 283.1329, found 283.1332, error 1.1ppm; **IR** (ν) (CH_2Cl_2) 2922.5, 1754.1, 1664.7, 1578.3, 1470.8, 1265.9, 1042.4, 785.5, 727.7 cm^{-1}.

2.8 *Synthesis of (R)-6-methoxy-9b-methyl-10,11-dihydrophenanthro[1,2-c]furan- 1,5(3H,9bH)-dione* ***(18).*** To a solution of compound **6**

(3.95 g, 14 mmol, 1.0 equiv) in 30 mL of 9:1 acetic acid/H_2O at 0 °C was added dropwise a solution of CrO_3 (2.52 g, 25.2 mmol, 1.8 equiv) in 20 mL of 9:1 acetic acid/H_2O. After the solution was stirred for 2 h at room temperature, it was added to H_2O (100 mL) and extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were washed with brine, and then dried over Na_2SO_4, filtered, and evaporated in rotary evaporator. Purification by triturating with diethyl ether afforded compound **18** (3.73 g, 12.6 mmol, 72% yield, 98%ee) as a yellow solid. **Compound 18**: $[\alpha]_D^{25}$ = -72.5° (c 0.80, CH_2Cl_2); **M.p.** 168-169 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.54~7.58 (t, 1H), 7.16~7.18 (d, J = 8.0 Hz, 1H), 6.96~6.98 (d, J = 8.0 Hz, 1H), 6.27 (s, 1H), 5.10~5.14 (d, J = 16.0 Hz, 1H), 4.93~4.97 (d, J = 16.0 Hz, 1H), 2.57~2.71 (m, 3H), 1.81~1.88 (m, 1H), 1.37 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 183.7, 172.3, 160.4, 152.9, 151.7, 148.4, 134.2, 131.0, 126.1, 120.4, 117.2, 110.3, 68.8, 56.2, 38.6, 33.0, 29.7, 18.4; **MS** (ESI): [M+H$^+$] 297.1; **HRMS** (ESI) for $C_{18}H_{17}O_4$ [M+H$^+$]: calcd 297.1121, found 297.1124, error 1.0 ppm; **IR** (ν) (CH_2Cl_2) 2970.7, 1753.0, 1649.9, 1592.1, 1472.0, 1264.6, 1042.9, 731.2 cm^{-1}.

2.9 *Synthesis of (R)-6-hydroxy-9b-methyl-10,11-dihydrophenanthro[1,2-c]furan- 1,5(3H,9bH)-dione* ***(19).*** To a solution of compound **18** (2.96 g, 10 mmol, 1.0 equiv) in dry CH_2Cl_2 (50 mL), under argon atmosphere and at -78 °C, was added dropwise BBr_3 (3g, 1.1 mL, 12 mmol, 1.2 equiv). The solution was stirred for 2 h at this temperature, then quenched with saturated aqueous NH_4Cl solution carefully. After separation, the organic layer was wash with H_2O (2 × 60 mL) and brine, and then dried over Na_2SO_4, filtered, and evaporated in rotary evaporator. Purification by flash column chromatography (33% AcOEt/hexanes) afforded compound **19** (2.79 g, 9.9 mmol, 90% yield, 98%ee) as a yellow solid. **Compound 19**: $[\alpha]_D^{25}$ = -72.9° (c 0.62, CH_2Cl_2); **M.p.** 185-187 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 12.7 (s, 1H), 7.51~7.55 (t, 1H), 7.03~7.05 (d, J = 8.0 Hz, 1H), 6.91~6.93 (s, J = 8.0 Hz, 1H), 6.32 (s, 1H), 5.13~5.18 (m, 1H), 4.96~5.01 (m, 1H), 2.68~2.76 (m, 2H), 2.57~2.67 (m, 1H), 1.88~1.96 (m, 1H), 1.40 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 189.0, 172.0, 162.8, 153.4, 152.2, 150.1, 136.1, 132.6, 123.5, 115.9, 115.9, 115.2, 68.6, 39.1, 33.1, 29.8, 18.5; **MS** (ESI): [M+H$^+$] 283.1; **HRMS** (ESI) for $C_{17}H_{15}O_4$ [M+H$^+$]: calcd 283.0962, found 283.0969, error 1.4 ppm; **IR** (v) (CH_2Cl_2) 2925.2, 1751.9, 1636.1, 1591.5, 1455.5, 1375.5, 1229.9, 1024.1, 758.1 cm^{-1}.

2.10 *Synthesis of (R)-6-hydroxy-7-isopropyl-9b-methyl-10,11-dihydrophenanthro[1,2-c]- furan-1,5(3H, 9bH)-dione* ***(5).*** To sulfuric acid (8 mL) in a three-necked round-bottomed flask was added portionwise compound **19** (2.68 g, 9.5 mmol, 1.0 equiv) under argon atmosphere at 0

°C under stirring. After the completion of addition, to the reaction mixture was slowly added isopropanol (3.5 mL), then it was heated to 65 °C and stirred for 3 h. The reaction mixture was poured into trash ice (100 g), and the aqueous layer was extracted with CH_2Cl_2 (3 × 80 mL). The combined organic layers were washed with H_2O, saturated aqueous $NaHCO_3$ solution, and brine, and then dried over Na_2SO_4, filtered, and evaporated in rotary evaporator. Purification of the crude product by recrystallization from CH_2Cl_2/Et_2O afforded compound **5** (2.40 g, 7.4 mmol, 71% yield, 99.0%ee) as a pale yellow solid. **Compound 5**: $[\alpha]_D^{25}$ = -195.7° (c 0.46, CH_2Cl_2); **M.p.** 133-135 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 13.08 (s, 1H), 7.46~7.48 (d, J = 8.0 Hz, 1H), 6.99~7.01 (d, J = 8.0 Hz, 1H), 6.31 (s, 1H), 5.13~5.18 (m, 1H), 4.96~5.01 (m, 1H), 3.33~3.43 (m, 1H), 2.56~2.73 (m, 3H), 1.86~1.93 (m, 1H), 1.27 (s, 3H), 1.23~1.38 (t, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 189.3, 172.1, 160.2, 153.2, 152.3, 147.2, 135.1, 132.7, 132.4, 123.6, 115.4, 114.5, 68.6, 38.8, 33.1, 29.8, 26.1, 22.2, 22.1, 18.5; **MS** (ESI): [M+H$^+$] 325.1; **HRMS** (ESI) for $C_{20}H_{21}O_4$ [M+H$^+$]: calcd 325.1434, found 325.1430, error 1.2 ppm; **IR** (v) (CH_2Cl_2) 3491.0, 2965.0, 1760.3, 1632.9, 1591.4, 1428.8, 1377.8, 1251.6, 1026.6, 733.7 cm^{-1}.

2.11 *Synthesis of (3bR,9bS)-6-hydroxy-7-isopropyl-9b-methyl-3b,4,10,11-tetrahydro phenanthro[1,2-c]furan-1,5(3H,9bH)-dione* **(4)** and *(3bS,9bS)-6-hydroxy-7-isopropyl -9b-methyl-3b,4,10,11-tetrahydrophenanthro[1,2-c]-furan-1,5(3H,9bH)-dione* **(20).** To a solution of compound **5** (2.27 g, 7 mmol, 1.0 equiv) in AcOEt (50 mL) was added 10% Pd on charcoal (0.23g, 0.1 w/w equiv). The solution was stirred under hydrogen atmosphere for 2 h and filtered over filter paper. The filtrate was then evaporated in a rotary evaporator, and purification of the residue by flash column chromatography (33% AcOEt/hexanes) afforded a mixture of compound **4** and **20** in a ratio of 2:1 in a 97% total yield. Recrystallization of the mixture from CH_2Cl_2/Et_2O afforded pure compound **4** with more than 99.0%ee value and the mixture of **4** and **20** in a 2:5 ratio.

Compound 4: **M.p.** 174-175 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 13.02 (s, 1H), 7.38~7.40 (d, J = 8.0 Hz, 1H), 6.75~6.77 (d, J = 8.0 Hz, 1H), 4.72~4.83 (m, 2H), 4.34~4.47 (sept, 1H), 3.17~3.19 (m, 1H), 2.38~2.86 (m, 5H), 1.77~1.85 (m, 1H), 1.14 (s, 3H), 1.23~1.25 (d, 3H), 1.21~1.23 (d, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 203.4, 178.5, 161.2, 159.7, 151.7, 135.5, 133.6, 126.0, 114.7, 112.7, 68.5, 39.0, 36.3, 29.6, 26.1, 22.2, 22.1, 21.1, 17.7; **MS** (ESI): [M+H$^+$] 327.2; **HRMS** (ESI) for $C_{20}H_{23}O_4$ [M+H$^+$]: calcd 327.1591, found 327.1595, error 1.2 ppm; **IR** (ν) (CH_2Cl_2) 3454.5, 2967.0, 1755.4, 1625.6, 1424.2, 1265.3, 739.7, 705.2 cm^{-1}.

Compound 20: **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 13.05 (s, 1H), 7.41~7.43 (d, J = 8.0 Hz, 1H), 6.88~6.90 (d, J = 8.0 Hz, 1H), 4.72~4.83 (m, 2H), 3.31~3.90 (sept, 1H), 3.17~3.19 (m, 1H), 2.38~2.86 (m, 5H), 1.77~1.85 (m, 1H), 1.23~1.25 (d, 3H), 1.21~1.23 (d, 3H), 1.14 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 202.2, 173.3, 161.7, 159.7, 149.1, 136.0, 133.7, 126.0, 114.7, 113.6, 69.9, 40.3, 36.4, 31.6, 26.1, 22.2, 22.1, 21.7, 17.7; **MS** (ESI): [M+H$^+$] 327.2; **HR-MS (ESI)** for $C_{20}H_{23}O_4$ [M+H$^+$]: calcd 327.1591, found 327.1597, error 1.8 ppm .

2.12 *Synthesis of (4aS,10aS)-ethyl 8-methoxy-4a-methyl-2-oxo-1,2,3,4,4a,9,10,10a- octahydrophenanthrene-1-carboxylate* ***(8).*** To a solution of the crude compound **9** and **15** (6.28 g, 20 mmol, 1.0 equiv) in dry CH_2Cl_2 (100 mL), was added pyridine (3.16 g, 3.22 mL, 40 mmol, 2.0 equiv), under argon atmosphere and at 0 °C, then was added dropwise TESOTf (10.7 g, 6.4 mL, 38 mmol, 1.9 equiv). After the solution was warmed naturally to room temperature and stirred for another 2 h, it was quenched with H_2O, then separated, and the organic layer was washed with H_2O (2 × 60 mL) and brine (60 mL). The combined organic layers were dried over Na_2SO_4, filtered, and evaporated in rotary evaporator to furnish compound **21** as reddish brown oil, which was then dissolved in AcOEt (60 mL), followed by the addition of 10% Pd on charcoal (0.428 g, 0.1 w/w equiv). The reaction was stirred under hydrogen atmosphere for 2 h, then filtered. The filtrate was evaporated in rotatory evaporator furnished a compound as light yellow soild, which was then dissolved in THF (60 mL), followed by the addition of TBAF (5.22 g, 20 mmol, 1.0 equiv). After stirred for 1 h, the mixture was concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2, and the organic layer was washed with HCl solution (1 mol/L), H_2O, saturated aqueous $NaHCO_3$ solution, and brine in turn, and then dried over Na_2SO_4, filtered, and evaporated in rotary evaporator to afford compound **8** as a yellow solid along with trace of **22** as a white solid.

Compound **8** was then recrystallized from CH_2Cl_2/Et_2O afforded light yellow crystals (5.88 g, 18.6 mmol, 83% yield) with a 98% ee value. **Compound 8**: $[\alpha]_D^{25}$ = +80.0° (c 0.40, CH_2Cl_2); **M.p.** 134-136 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): *δ* 7.16~7.20 (t, 1H), 6.94~6.96 (d, 1H), 6.71~6.73 (d, 1H), 4.21~4.35 (m, 2H), 3.82 (s, 3H), 3.37~3.40 (d, *J* = 12 Hz, 1H), 2.88~2.95 (m, 1H), 2.54~2.70 (m, 4H), 2.38~2.45 (m, 1H), 1.87~1.95 (m, 1H), 1.66~1.80 (m, 2H), 1.36 (s, 3H), 1.30~1.33 (t, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): *δ* 205.5, 169.7, 157.2, 146.2, 126.4, 124.0, 116.9, 107.3, 61.0, 60.0, 55.3, 55.2, 44.2, 37.9, 37.2, 36.1, 23.4, 23.2, 21.9, 14.2; **MS** (ESI): [M+H$^+$] 317.3;

Compound 22: $[\alpha]_D^{25}$ = +155.6° (c 0.36, CH_2Cl_2); **M.p.** 97-98 °C; **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 1.34 (3H, s, Me), 1.35 (3H, t, J=7.1 Hz,

Me) 1.47 (1H, m), 1.75 (1H, m), 2.06 (2H, m), 2.26 (1H, m), 2.39-2.54 (3H, m), 2.89 (1H, m), 3.81 (3H, s, MeO), 4.21~4.35 (2H, m), 6.66 (1H, d, J=8.1 Hz), 6.94 (1H, d, *J* = 8.2 Hz), 7.16 (1H, t, *J* = 8.1 Hz), 12.43 (1H, s, OH); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 173.0, 171.4, 156.7, 146.8, 126.2, 125.2, 119.1, 106.6, 101.1, 60.3, 55.3, 39.7, 36.0, 32.2, 27.3, 26.6, 25.6, 23.8, 14.2; **MS** (ESI): [M+H$^+$] 317.3; **HRMS** (ESI) for $C_{19}H_{25}O_4$ [M+Na$^+$]: calcd 317.1747, found 317.1749, error 0.6 ppm.

2.13 *Synthesis of (4aS,10aR)-ethyl 8-methoxy-4a-methyl-2-(((trifluoromethyl)sulfonyl)- oxy)-3,4,4a,9,10,10a-hexahydrophenanthrene-1-carboxylate* ***(23).*** To a solution of crude compound **8** (6.28 g, 20 mmol, 1.0 equiv) in dry THF (50 mL), under argon atmosphere and at 0 °C, was added KHMDS (1.6M in THF, 25.0 mL, 40 mmol, 2.0 equiv) carefully. After the solution was stirred for 3 h at this temperature, it was added dropwise to a solution of $PhNTf_2$ (10.7 g, 6.4 mL, 38 mmol, 1.9 equiv) in THF. After the solution was warmed to room temperature naturally and stirred for 2 h at this temperature. The solution was quenched with saturated aqueous NH_4Cl solution, and the solvent was removed under reduced pressure. The residue was dissolved in AcOEt and washed with H_2O (2 × 60 mL) and brine (60 mL), and then dried over Na_2SO_4, filtered, and evaporated in rotary evaporator to furnish compound **23** with no need for purification for next step (it could be purified by silica gel column chromatography eluting with 20% EtOAc/petroleum ether to form 8.10 g/18.1 mmol pure **23** as a white solid with 90%ee in 93% yield). **Compound 23**: $[\alpha]_D^{25}$ = -19.0° (c 0.74, CH_2Cl_2); **M.p.** 78-79 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.16~7.20 (t, 1H), 6.91~6.93 (d, 1H), 6.73~6.75 (d, 1H), 4.27~4.41 (m, 2H), 3.83 (s, 3H), 2.88~2.95 (dd, 1H), 2.66~2.83 (m, 3H), 2.47~2.54 (m, 2H), 1.91~1.96 (t, 1H), 1.75~1.87 (m, 2H), 1.36~1.40 (t, 3H), 1.18 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 165.1, 157.4, 146.7, 145.7, 132.1, 131.0, 130.0, 127.9, 126.3, 123.7, 119.9, 116.7, 115.8, 107.5, 61.7, 55.3, 41.8, 35.6, 32.8, 25.2, 22.8, 22.2, 20.3, 14.0; **MS** (ESI): [M+H]$^+$ 449.2; **HRMS** (ESI) for $C_{20}H_{23}O_6SF_3Na$ [M+Na$^+$]: calcd 471.1060, found 471.1055, error 1.1ppm.

2.14 *Synthesis of (4aS,10aR)-1-(hydroxymethyl)-8-methoxy-4a-methyl-3,4,4a,9,10,10a- hexahydrophenanthren-2-yl trifluoromethane-sulfonate* ***(24).*** To a solution of compound **23** (8.06 g, 18 mmol, 1.0 equiv) in dry toluene (100 mL) was added dropwise a 1.5 M solution of DiBAl-H (26.4 mL, 39.6 mmol, 2.2 equiv) in toluene under argon atmosphere and at -78 °C. After the solution was stirred for 2 h at -40 °C, it was poured into ice solution (500mL) of seignette salt (20 g) and stirred for 30 min, then extracted with AcOEt (3 × 100 mL). The combined organic

layers were washed with brine, and then dried over Na_2SO_4, filtered, evaporated in rotary evaporator. The residue was triturated with Et_2O and afforded compound **24** (6.72 g, 15 mmol, 90% yield, 95%ee) as a white solid. **Compound 24**: $[\alpha]_D^{25}$ = +28.7° (c 1.50, CH_2Cl_2); **M.p.** 126–127 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.15~7.19 (t, 1H), 6.93~6.95 (d, 1H), 6.72~6.74 (d, 1H), 4.43~4.46 (d, 1H), 4.24~4.31 (m, 1H), 3.84 (s, 3H), 2.95~3.01 (dd, 1H), 2.63~2.82 (m, 3H), 2.35~2.52 (m, 3H), 1.69~1.86 (m, 2H), 1.34~1.38 (m, 1H), 1.13 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 157.4, 146.3, 144.9, 132.1, 126.1, 123.9, 116.8, 116.1, 197.3, 56.9, 55.2, 42.4, 35.8, 26.8, 25.7, 23.3, 22.1, 19.7; **MS** (EI, 20 eV) m/z 406 (M^+, 15), 111 (57), 71 (100); **HRMS** (ESI) for $C_{18}H_{21}O_5SF_3Na$ [$M+Na^+$]: calcd 429.0954, found 429.0954, error 0 ppm.

2.15 *Synthesis of (3bR,9bS)-6-methoxy-9b-methyl-3b,4,5,9b,10,11-hexahydrophenanthro [1,2-c]furan-1(3H)-one* ***(7).*** To a solution of compound **24** (6.87 g, 17 mmol, 1.0 equiv) in DMF (85 mL) was added PPh_3 (178 mg, 0.68 mmol, 0.04 equiv), Et_3N (12 mL, 85 mmol, 5.0 equiv), Methanol (1.4 mL, 34 mmol, 2.0 equiv), and $Pd(OAc)_2$ (38.1 mg, 0.17 mmol, 0.01 equiv) in turn. The solution was heated to 60 °C and stirred under carbon monoxide atmosphere for 3 h. Next, the solvent was removed in vacuum and the residue was dissolved in CH_2Cl_2, washed with H_2O and brine, then dried over Na_2SO_4, filtered, and evaporated in rotary evaporator. The crude product was purified by crystallization from CH_2Cl_2/Et_2O and afforded compound **7** (4.56 g, 16 mmol, 89% yield, 98%ee) as a pale yellow solid. **Compound 7**: **$[\alpha]_D^{25}$** = +51.8° (c 1.10, CH_2Cl_2); **M.p**. 246-248 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): *δ* 7.18~7.22 (t, 1H), 6.99~7.01 (d, 1H), 6.74~6.76 (d, 1H), 4.74~4.85 (m, 2H), 3.84 (s, 3H), 2.92~2.98 (q, 1H), 2.76~2.86 (m, 1H), 2.68~2.69 (d, 1H), 2.49~2.57 (m, 2H), 2.36~2.44 (m, 1H), 1.81~2.00 (m, 2H), 1.67~1.74 (m, 1H), 1.04 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): *δ* 174.1, 163.0, 157.4, 146.3, 126.4, 124.9, 123.4, 116.2, 107.5, 70.4, 55.2, 40.9, 36.4, 32.7, 22.4, 22.2, 19.6, 18.2; **MS** (EI, 20 eV) *m/z* 284 (M^+, 100), 269 (58), 159 (23); **HRMS** (ESI) for $C_{18}H_{21}O_3$ [$M+H^+$]: calcd 285.1485, found 285.1482, error 1.1 ppm; **IR** (ν) (CH_2Cl_2) 2932.4, 1788.2, 1751.7, 1596.7, 1469.7, 1294.1, 1050.7, 739.9 cm^{-1}.

2.16 *Synthesis of (3bR,9bS)-6-methoxy-9b-methyl-3b,4,10,11-tetrahydrophenanthro [1,2-c]furan-1,5(3H, 9bH)-dione* ***(25).*** To a solution of compound **7** (2.84 g, 10 mmol, 1.0 equiv) in 20 mL AcOH/ H_2O (9:1) at 0 °C was slowly added a solution of CrO_3 (1.80 g, 18.0 mmol, 1.8equiv) in 20 mL AcOH/ H_2O (9:1). After the solution was stirred for 2 h at room temperature, H_2O (50 mL) was added and the result mixture was extracted with CH_2Cl_2 (3 × 80 mL). The combined organic layers were washed with brine, and then dried over Na_2SO_4, filtered, and

evaporated in rotary evaporator. Purification by flash column chromatography (33% AcOEt/hexanes) afforded compound **25** (2.66 g, 9 mmol, 81% yield, 98%ee) as a yellow solid. **Compound 25**: $[\alpha]_D^{25}$ = +12.7° (c 0.79, CH_2Cl_2); **M.p.** 281-283 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): *δ* 7.47~7.51 (t, *J* = 8 Hz, 1H), δ 7.02~7.04 (d, *J* = 8 Hz, 1H), δ 6.93~6.95 (d, *J* = 8 Hz, 1H), δ 4.73~4.75 (m, 2H), δ 3.90 (s, 3H), 3.08~3.14 (m, 1H), δ 2.76~2.82 (m, 1H), δ 2.61~2.66 (m, 1H), δ 2.48~2.58 (m, 2H), δ 2.33~2.43 (m, 1H), δ 1.77~1.85 (m, 1H), δ 1.10 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): *δ* 194.5, 173.3, 160.4, 160.1, 153.4, 134.6, 125.5, 120.9, 115.1, 110.9, 70.0, 56.0, 39.5, 37.7, 36.8, 31.9, 21.3, 17.6; **MS** (EI, 20 eV) *m/z* 298 (M^+, 100), 265 (27), 175 (60); **HRMS** (ESI) for $C_{18}H_{19}O_4$ (M^+): calcd 299.1278, found 299.1281, error 1.0 ppm; **IR** (CH_2Cl_2) 2967.2, 1751.1, 1678.0, 1590.5, 1471.4, 1275.8, 1045.4, 1017.7, 770.3, 734.7 cm^{-1}.

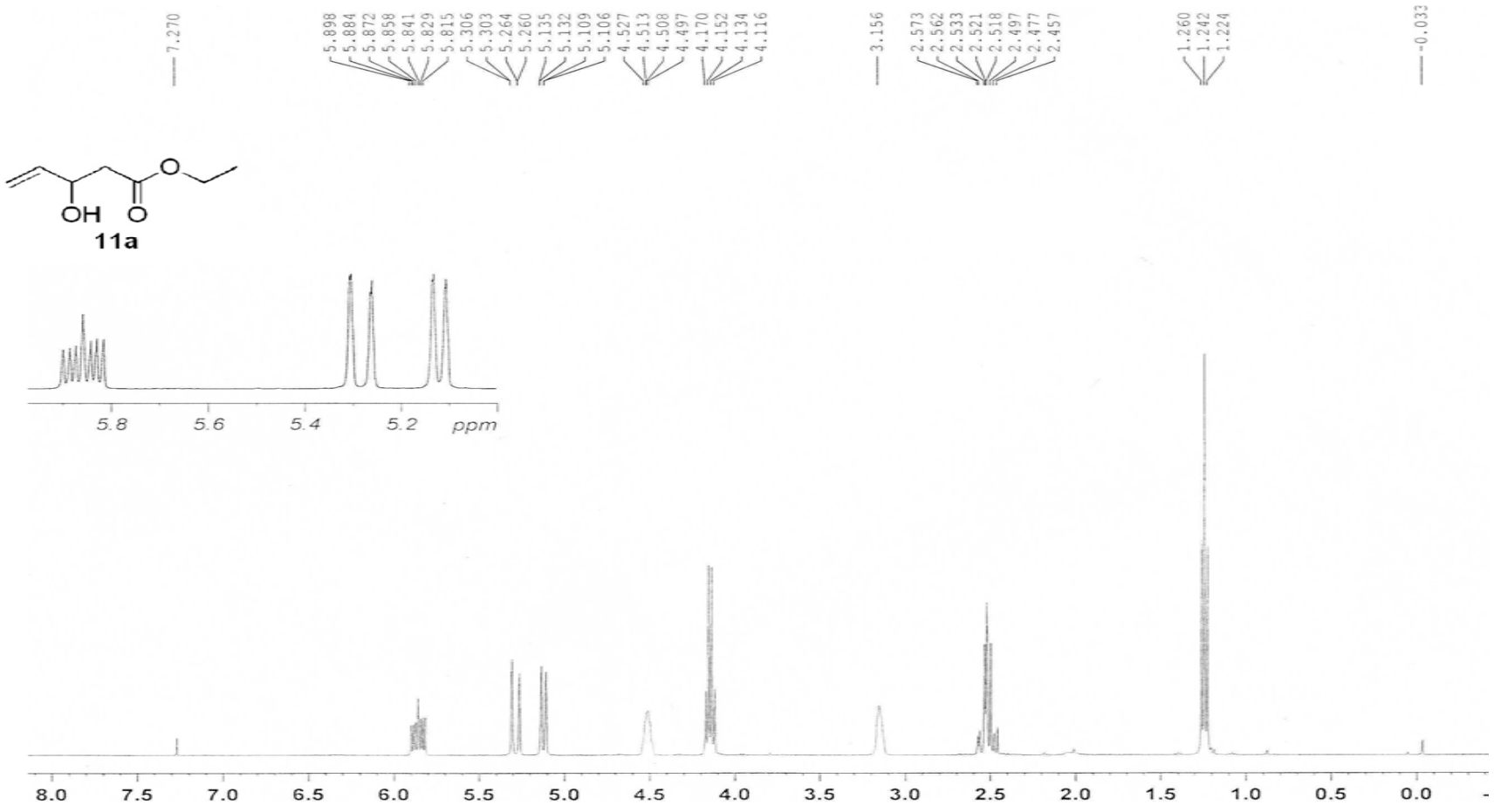
2.17 *Synthesis of (3bR,9bS)-6-hydroxy-9b-methyl-3b,4,10,11-tetrahydrophenanthro [1,2-c]furan-1,5(3H, 9bH)-dione* ***(26).*** To a solution of compound **25** (2.38 g, 8 mmol, 1.0 equiv) in dry CH_2Cl_2 (40 mL) was added dropwise BBr_3 (2.40 g, 0.9 mL, 9.6 mmol, 1.2 equiv) under argon atmosphere and at -78 °C. After the solution was stirred for 2 h at this temperature, it was quenched with saturated aqueous NH_4Cl solution carefully and warmed to room temperature naturally. Then the mixture was separated and the organic layer was washed with H_2O (2 × 60 mL) and brine, and then dried over Na_2SO_4, filtered, and evaporated in rotary evaporator. After triturated with Et_2O, pure compound **26** was obtained (2.25 g, 7.9 mmol, 87% yield, 99%ee) as a yellow solid. **Compound 26**: $[\alpha]_D^{25}$ = -50.8° (c 0.61, CH_2Cl_2) ; **M.p.** 265-266 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): *δ* 12.59 (s, 1H), δ 7.45~7.49 (t, *J* = 8 Hz, 1H), δ 6.91~6.93 (d, *J* = 8 Hz, 1H), δ 6.86~6.88 (d, *J* = 8 Hz, 1H), δ 4.78~4.83 (dd, *J* = 16, 4 Hz, 1H), δ 4.71~4.76 (dt, *J* = 16, 4 Hz, 1H), δ 3.18~3.23 (m, 1H), δ 3.09~3.15 (q, *J* = 8 Hz, 1H), δ 2.81(d, 1H), δ 2.51~2.59 (m, 2H), δ 2.35~2.46 (m, 1H), δ 1.78~1.86 (m, 1H), δ 1.15 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): *δ* 201.9, 173.1, 163.9, 159.5, 152.0, 137.3, 126.0, 116.9, 115.3, 114.1, 69.9, 40.2, 36.6, 36.2, 31.6, 21.7, 17.7; **MS** (EI, 20 eV) *m/z* 284 (M^+, 100), 269 (17), 187 (35); **HRMS** (ESI) for $C_{17}H_{17}O_4$ [$M+H^+$]: calcd 285.1121, found 285.1124, error 1.2 ppm; **IR** (ν) (CH_2Cl_2) 2936.5, 1749.5, 1636.8, 1452.0, 1344.2, 1249.0, 769.7 cm^{-1}.

2.18 *Synthesis of (3bR,9bS)-6-hydroxy-7-isopropyl-9b-methyl-3b,4,10,11-tetrahydro phenanthro[1,2-c]furan-1,5(3H, 9bH)-dione* ***(4).*** To cool concentrated sulfuric acid (5 mL) in a three-necked round-bottom flask was added compound **26** (1.70 g, 6 mmol, 1.0 equiv) under argon atmosphere at 0 °C slowly, then to the solution was added dropwise isopropanol (2.1 mL). The mixture was heated to 65 °C and stirred for 3 h,

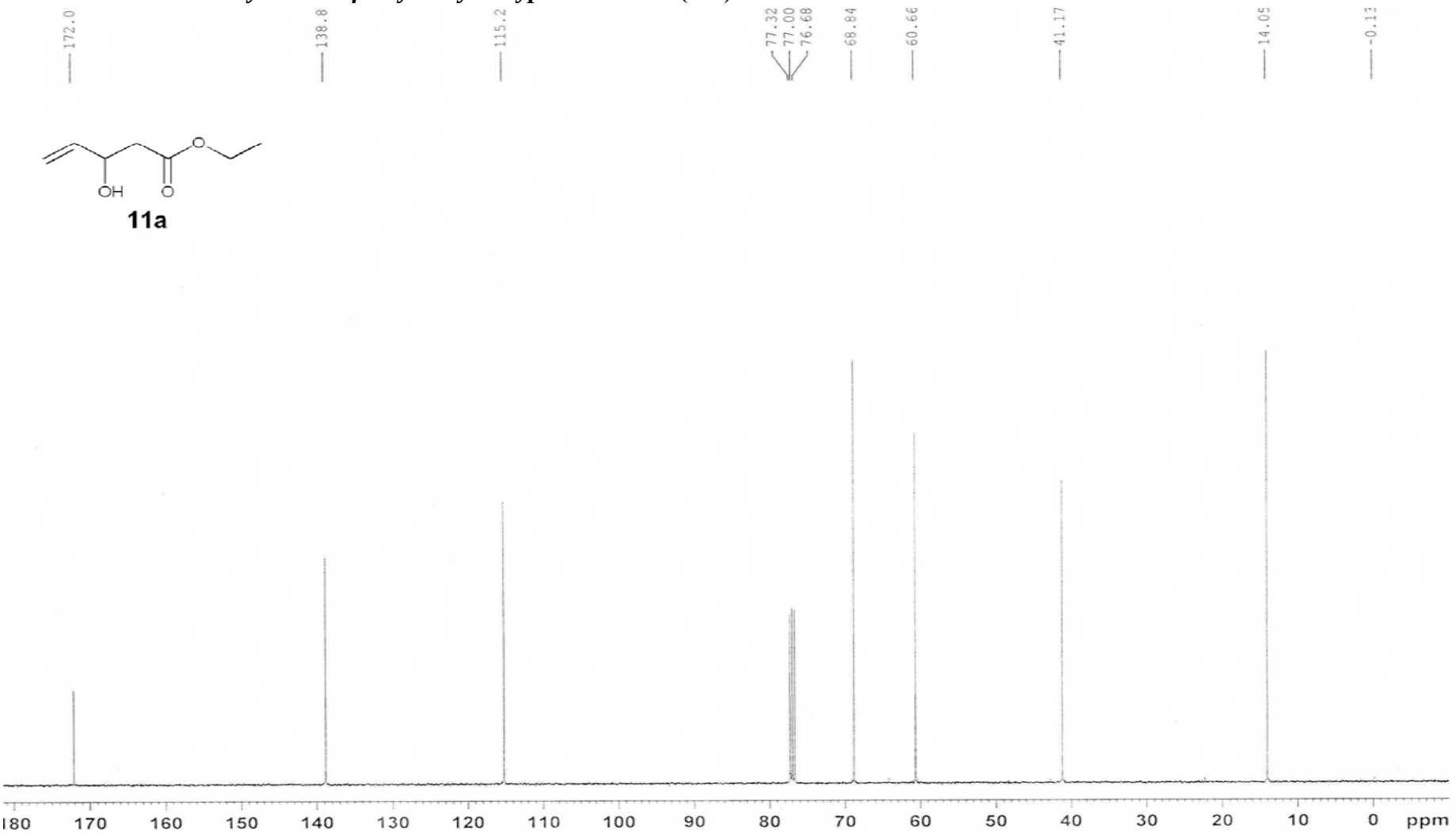
then poured into trash ice (80 g), extracted with CH_2Cl_2 (3 × 60 mL). The combined organic layers were washed with H_2O, saturated aqueous $NaHCO_3$ solution, and brine in turn, and then dried over Na_2SO_4, filtered, and evaporated in rotary evaporator. Purification of crude product by recrystallization from CH_2Cl_2/Et_2O afforded compound **4** (1.54 g, 4.7 mmol, 69% yield, 99% ee by HPLC) as a yellow solid. **Compound 4**: $[\alpha]_D^{25}$ = -42.0° (c 0.14, CH_2Cl_2) [literature -43.5° (c 0.17, MeOH)]; **M.p.** 174-175 °C (Et_2O/*n*-hexane) (lit. 175.5-176 °C); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 13.02 (s, 1H), 7.38~7.40 (d, J = 8.0 Hz, 1H), 6.75~6.77 (d, J = 8.0 Hz, 1H), 4.72~4.83 (m, 2H), 4.34~4.47 (sept, 1H), 3.17~3.19 (m, 1H), 2.38~2.86 (m, 5H), 1.77~1.85 (m, 1H), 1.14 (s, 3H), 1.23~1.25 (d, 3H), 1.21~1.23 (d, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 203.4, 178.5, 161.2, 159.7, 151.7, 135.5, 133.6, 126.0, 114.7, 112.7, 68.5, 39.0, 36.3, 29.6, 26.1, 22.2, 22.1, 21.1, 17.7; **MS** (EI, 20 eV) *m*/*z* 326 (M+, 57), 311(100); **HRMS (ESI)** for $C_{20}H_{23}O_4$ [$M+H^+$]: calcd 327.1591, found 327.1595, error 1.2 ppm; **IR** (ν) (CH_2Cl_2) 3454.5, 2967.0, 1755.4, 1625.6, 1424.2, 1265.3, 739.7, 705.2 cm^{-1}.

3. Spectra Copy of Intermediates and Targets

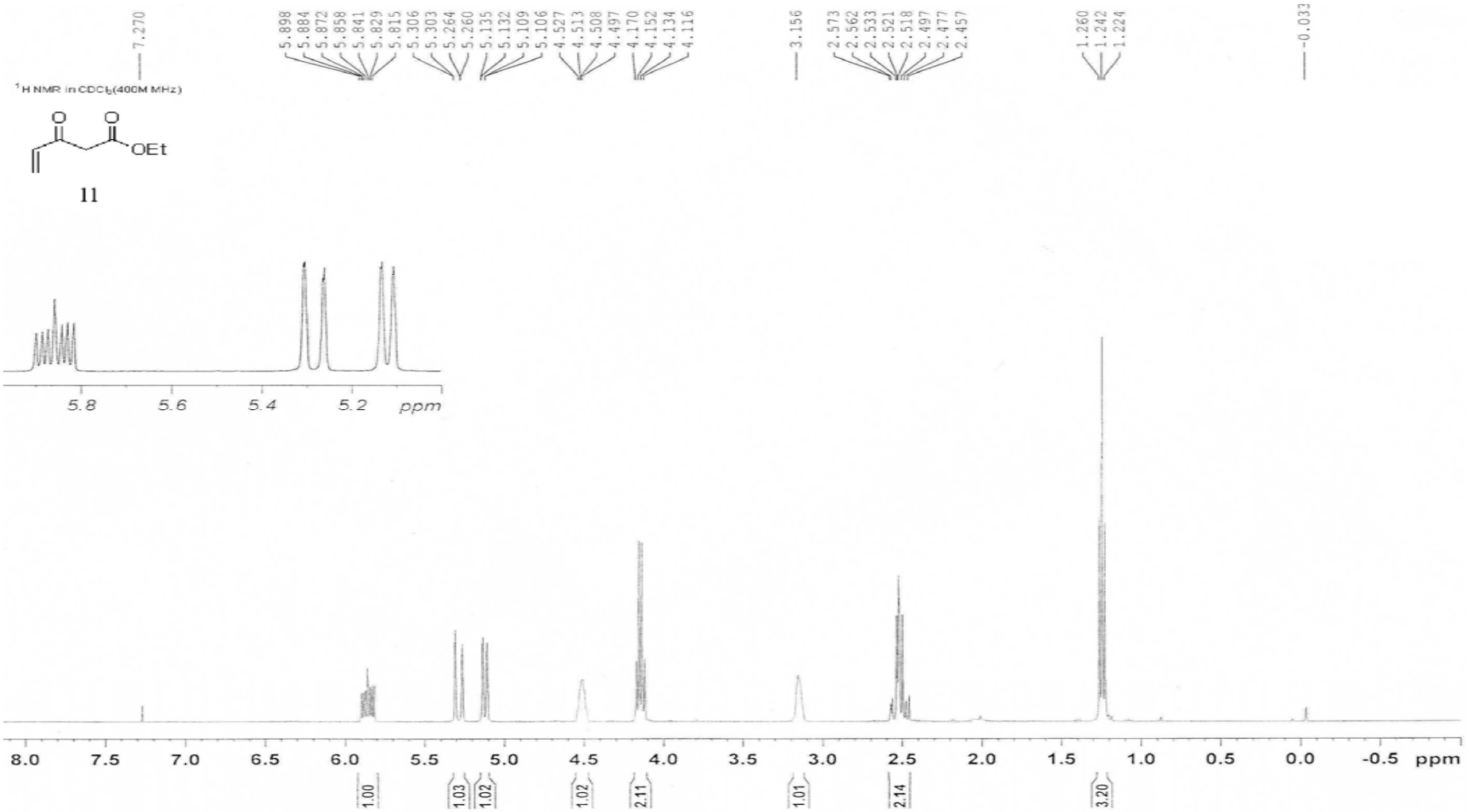
2.1. ^{1}H NMR of *Synthesis of ethyl 3-hydroxypent-4-enoate* (11a).



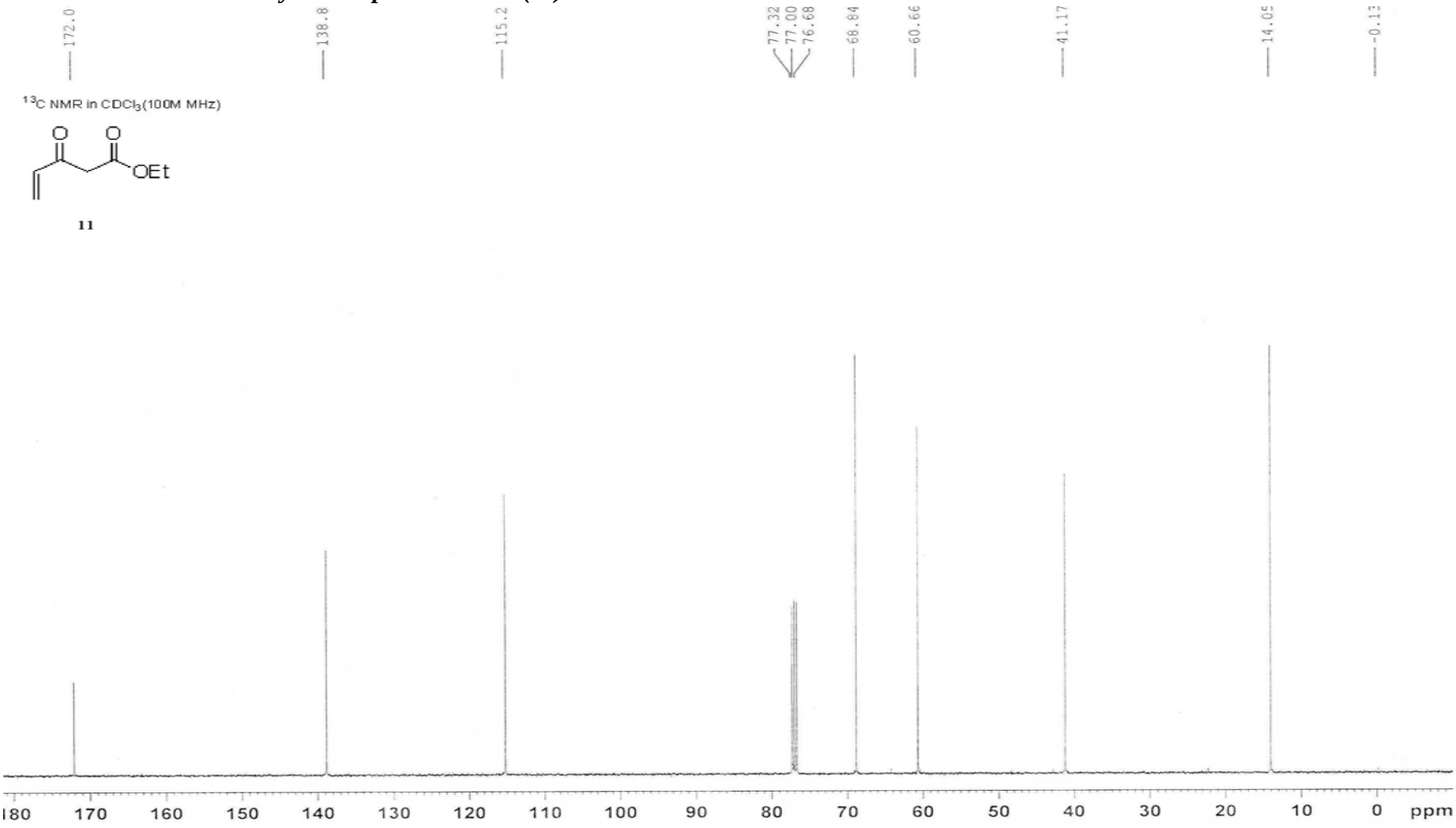
^{13}C NMR of of *Synthesis of ethyl 3-hydroxypent-4-enoate* (11a).



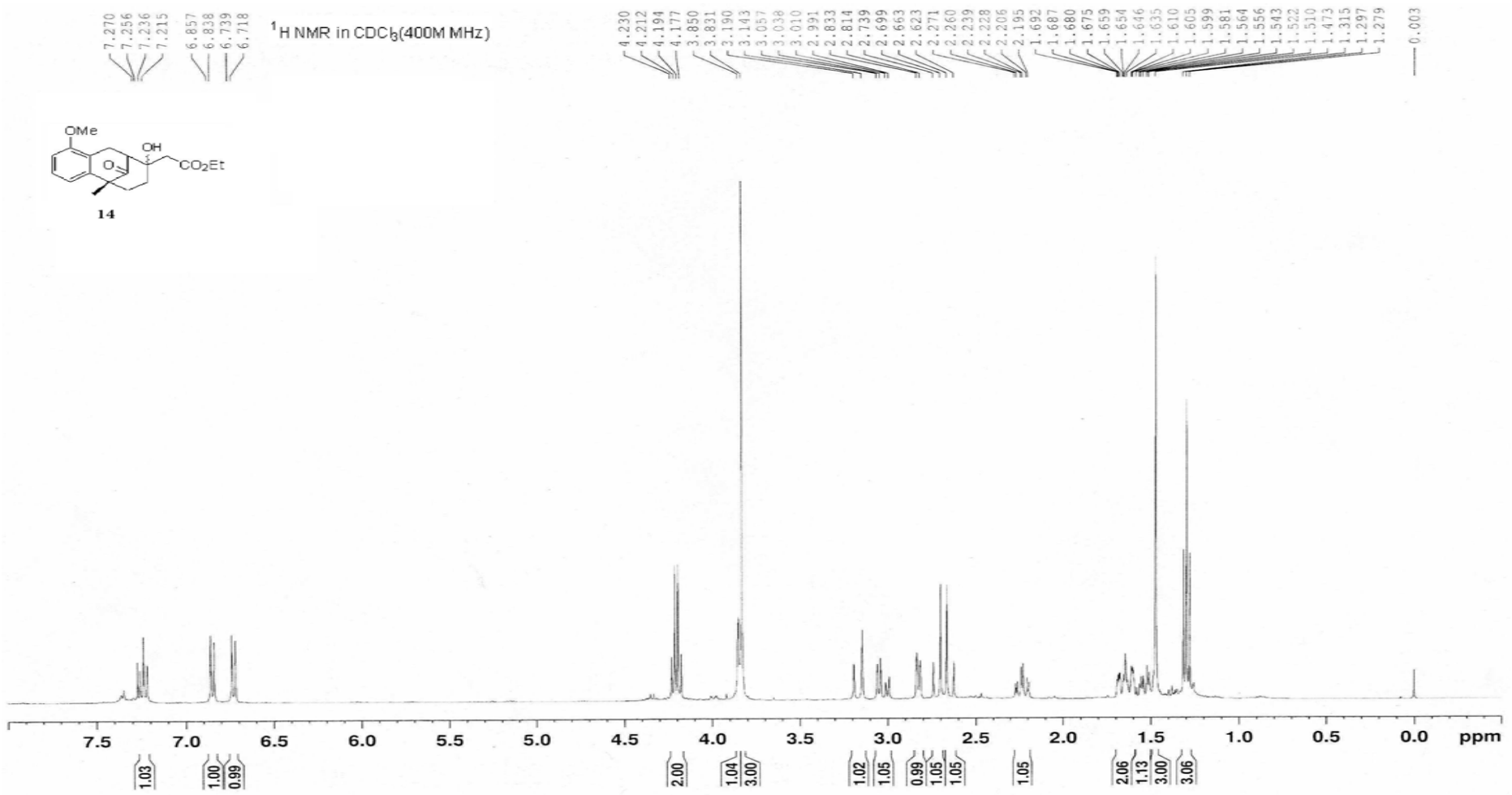
3.2. ^{1}H NMR of *ethyl 3-oxo-pent-4-enoate (11).*



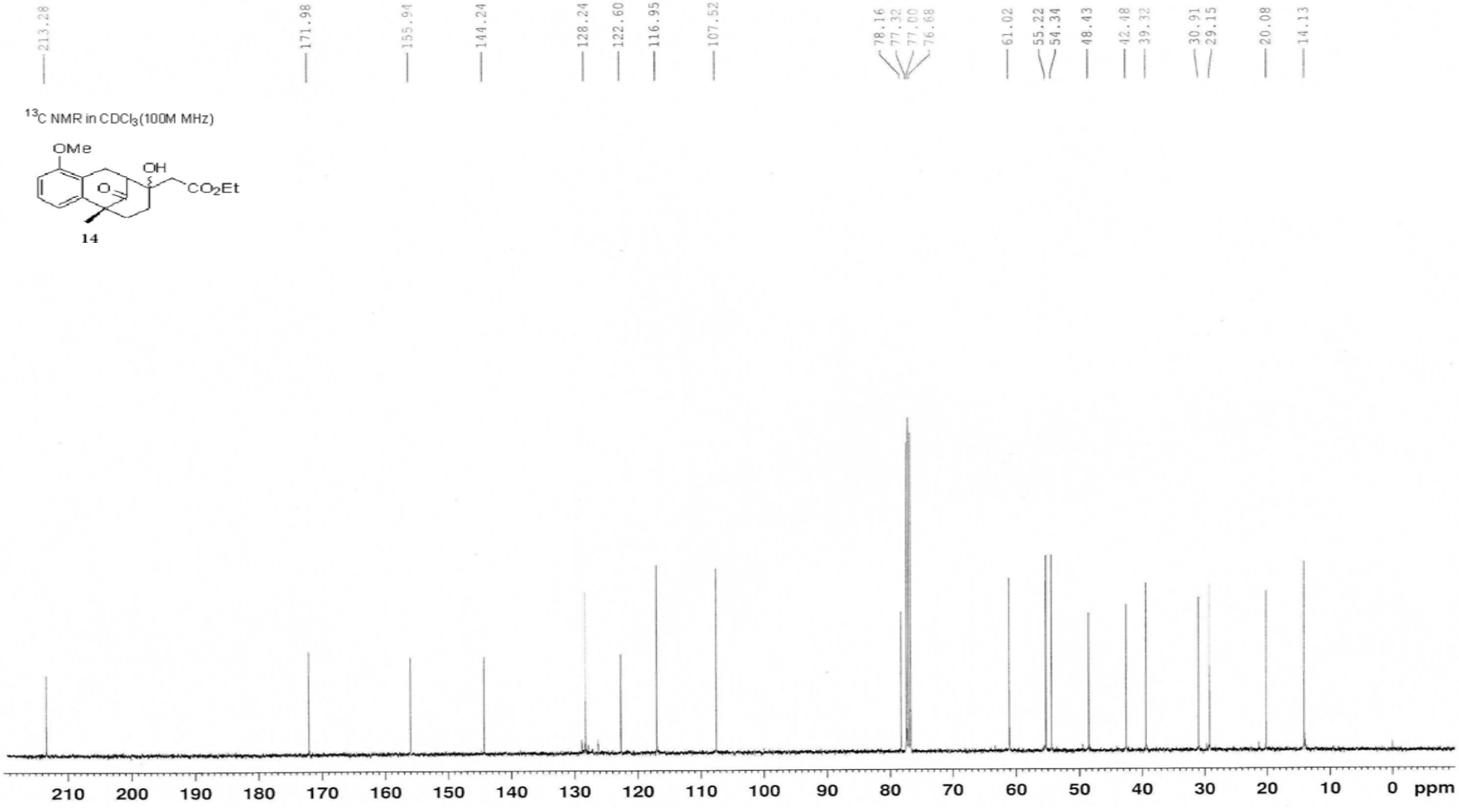
13 C NMR of *ethyl 3-oxo-pent-4-enoate (11).*



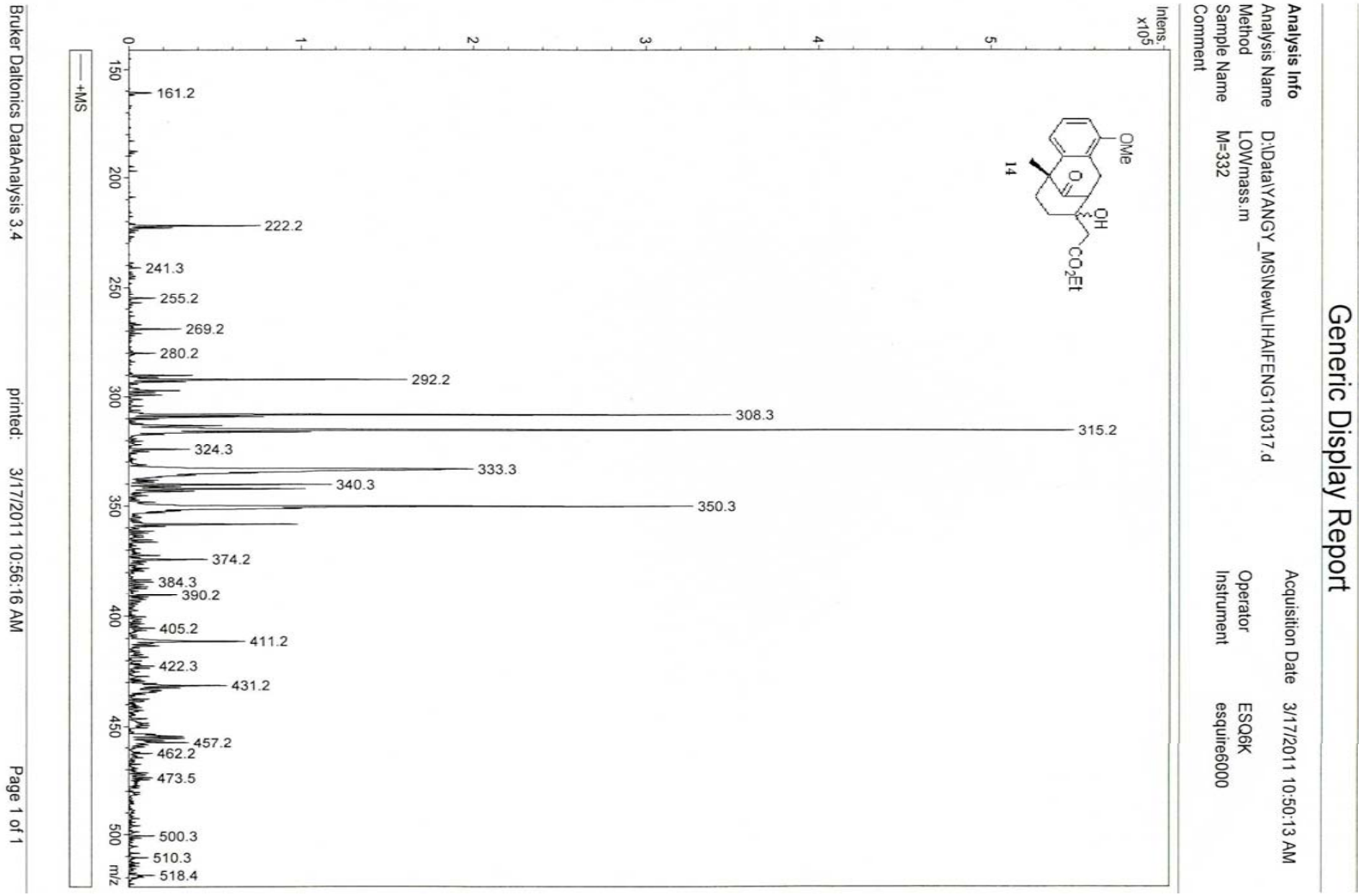
3.3. **^{1}H NMR of *ethyl 2-((5R)-8-hydroxy-1-methoxy-5-methyl-11-oxo-5,6,7,8,9,10-hexahydro-5,9-methanobenzo[8]-annulen-8-yl)acetate (14).***



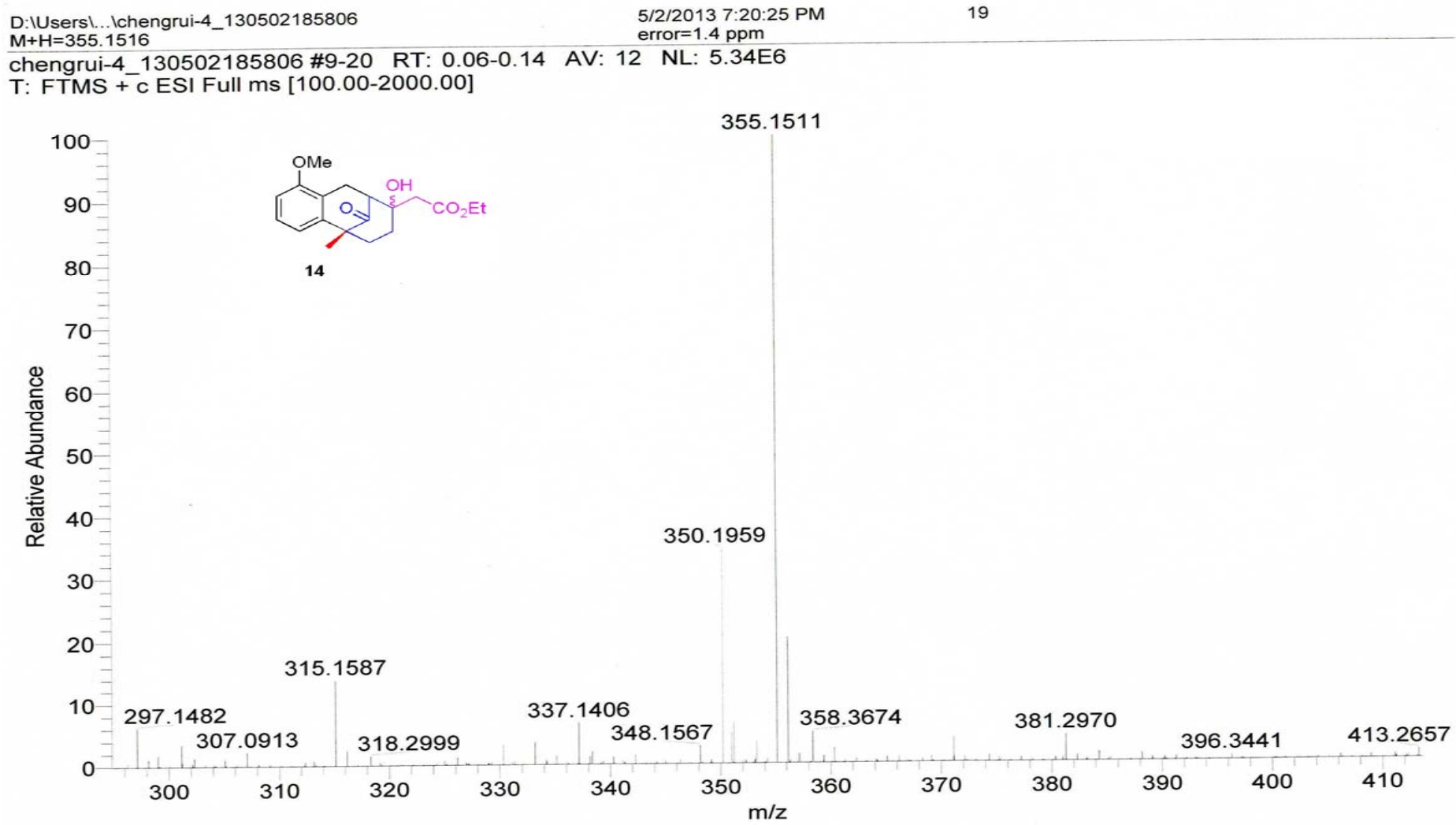
^{13}C NMR of *ethyl 2-((5R)-8-hydroxy-1-methoxy-5-methyl-11-oxo-5,6,7,8,9,10-hexahydro-5,9- methanobenzo [8]annulen-8-yl)acetate (14).*



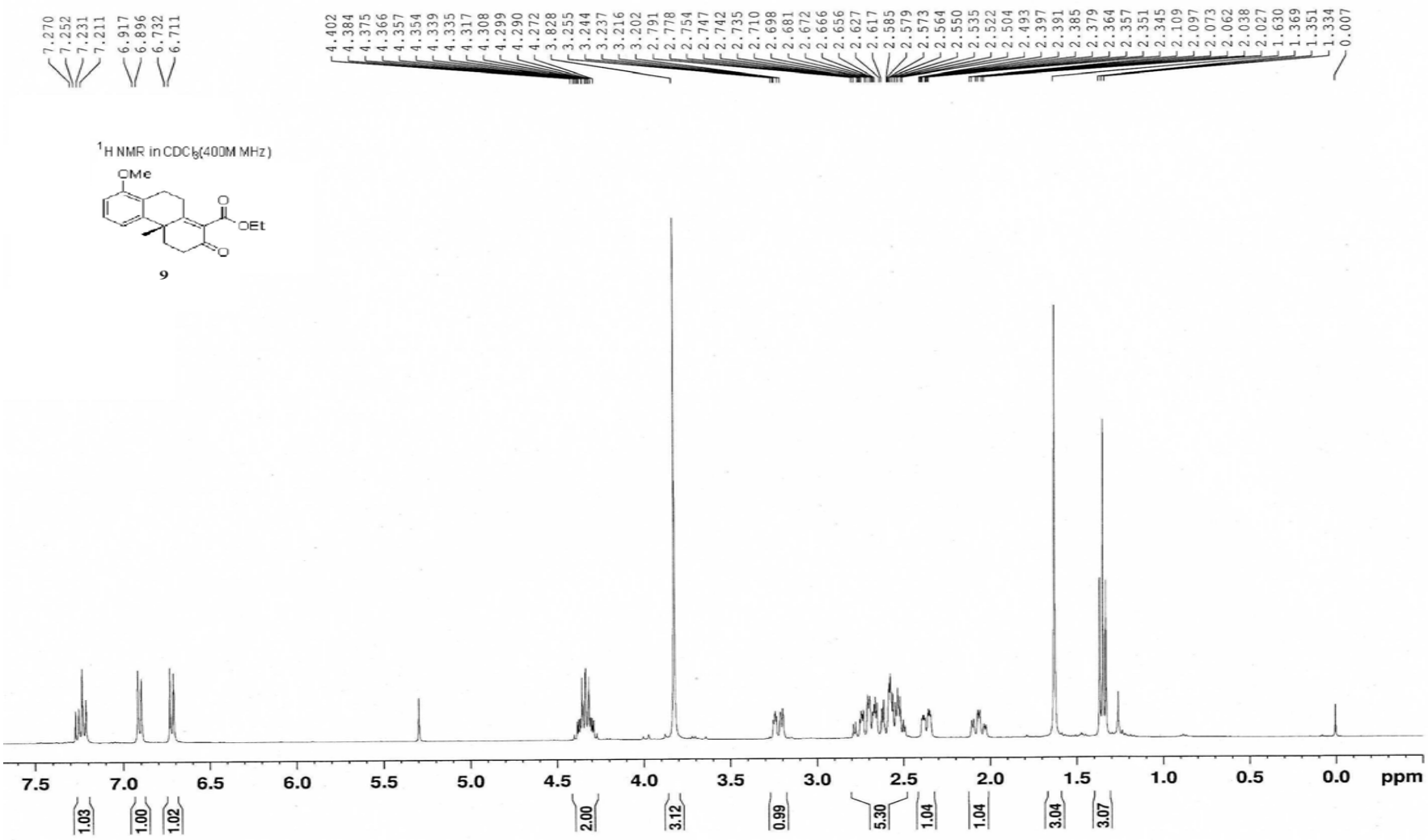
ESI-MS of *ethyl 2-((5R)-8-hydroxy-1-methoxy-5-methyl-11-oxo-5,6,7,8,9,10-hexahydro-5,9-methanobenzo[8] annulen-8-yl)acetate (14).*



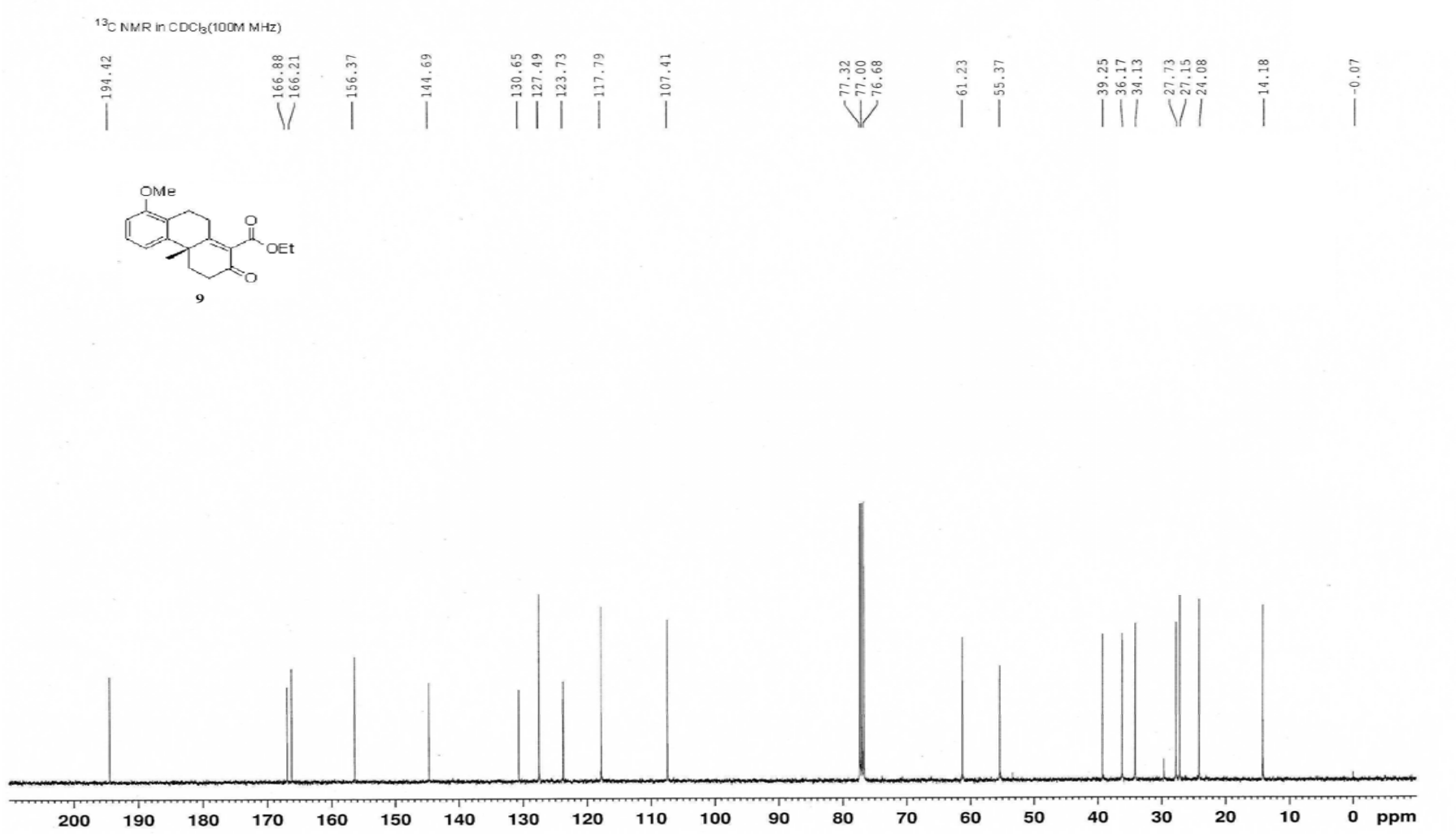
HR-MS of *ethyl 2-((5R)-8-hydroxy-1-methoxy-5-methyl-11-oxo-5,6,7,8,9,10-hexahydro-5,9- methanobenzo[8] annulen-8-yl)acetate (14).*



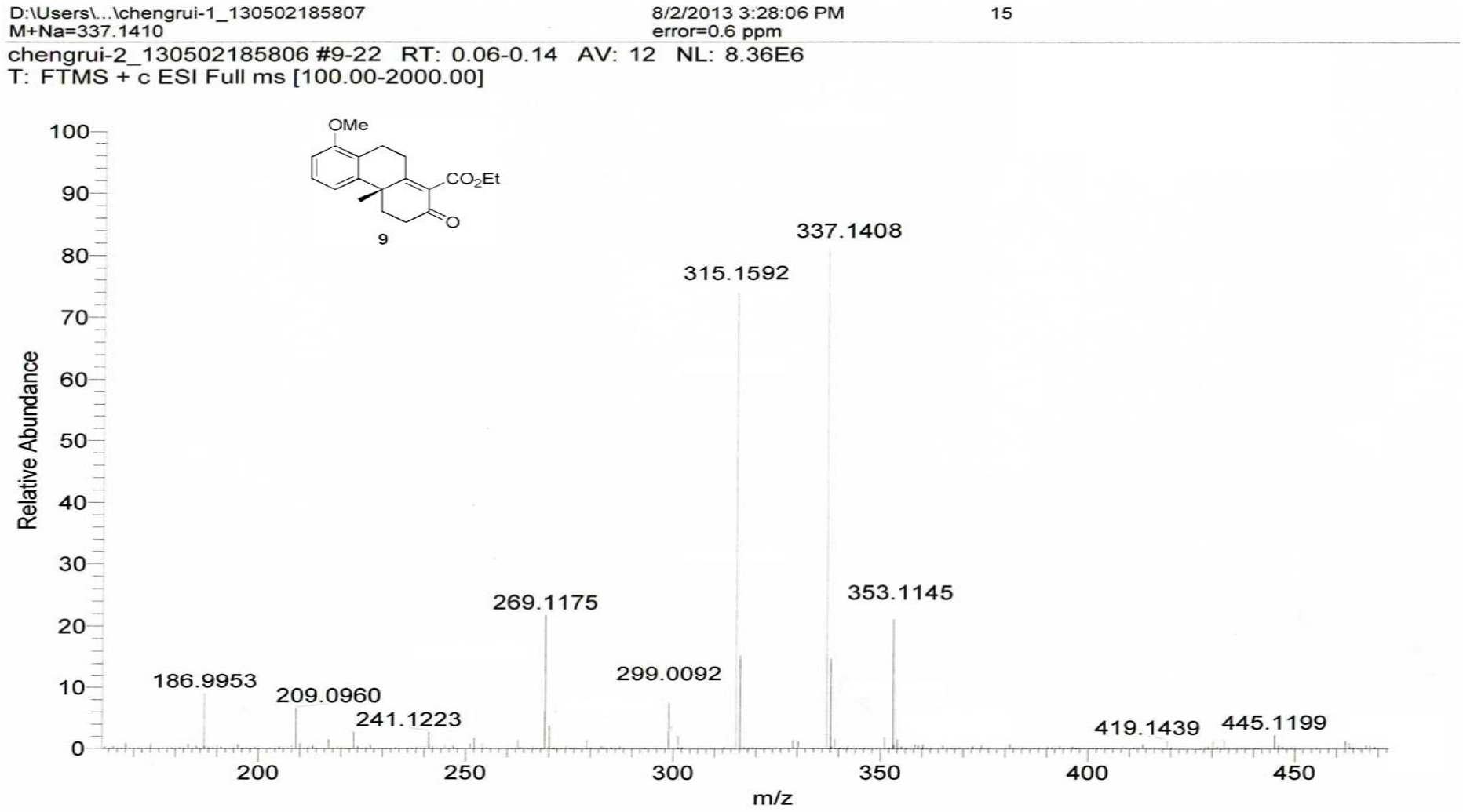
3.4. ^{1}H NMR of *(S)-ethyl 8-methoxy-4a-methyl-2-oxo-2,3,4,4a,9,10-hexahydrophenanthrene-1- carboxylate (9).*



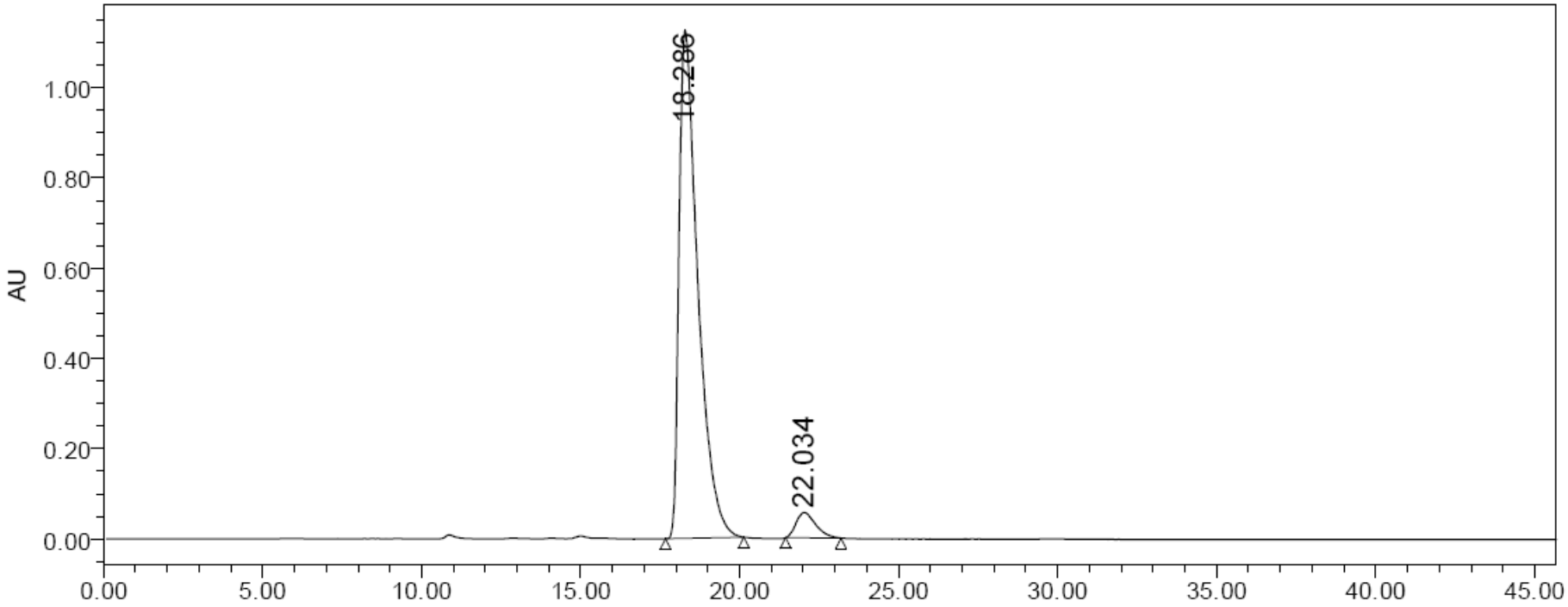
^{13}C NMR of *(S)-ethyl 8-methoxy-4a-methyl-2-oxo-2,3,4,4a,9,10-hexahydrophenanthrene-1- carboxylate (9).*



HRMS of *(S)-ethyl 8-methoxy-4a-methyl-2-oxo-2,3,4,4a,9,10-hexahydrophenanthrene-1- carboxylate (9).*

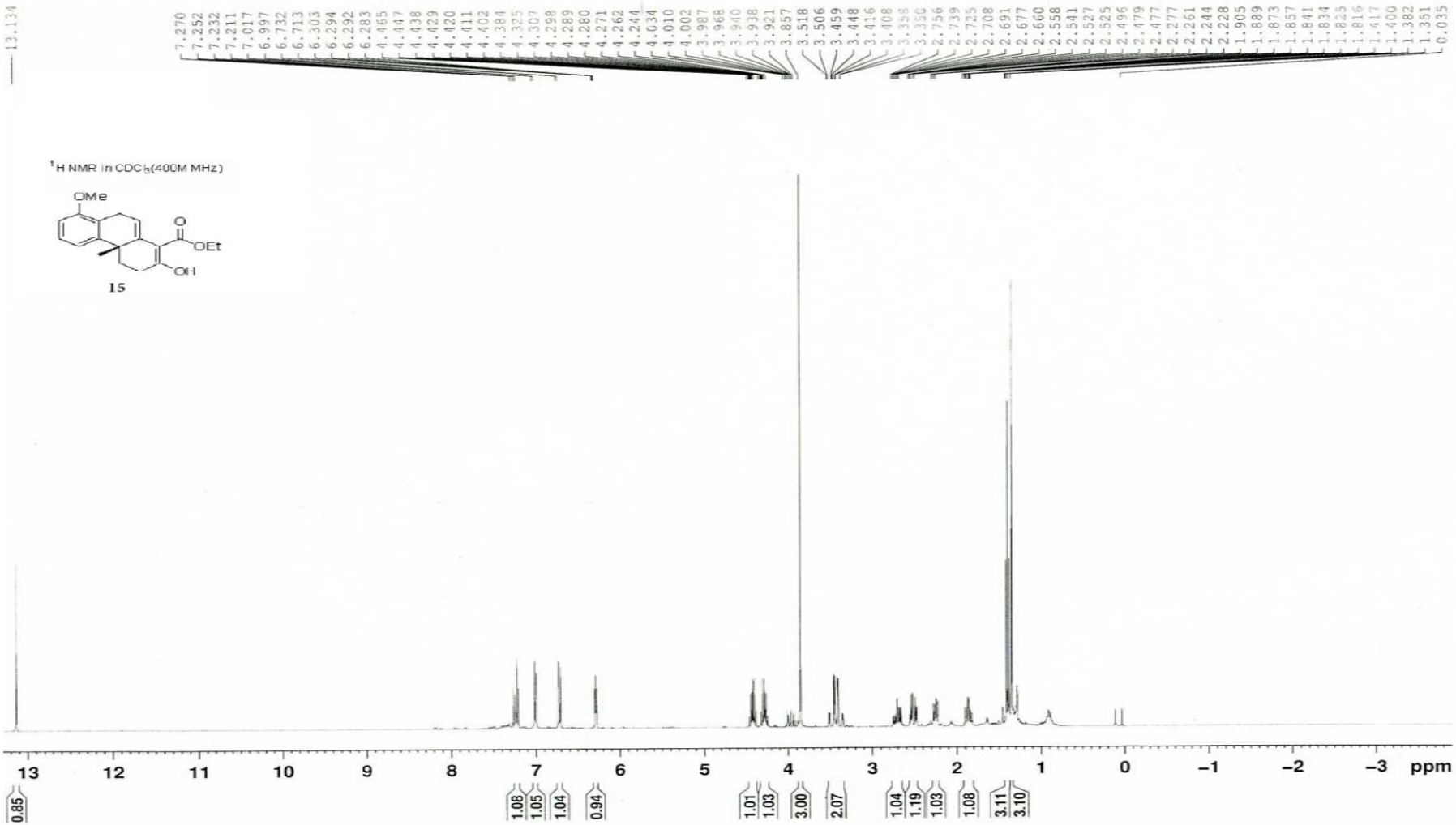


Chiral HPLC for ee value of *(S)-ethyl 8-methoxy-4a-methyl-2-oxo-2,3,4,4a,9,10-hexahydrophenanthrene-1- carboxylate (9).*

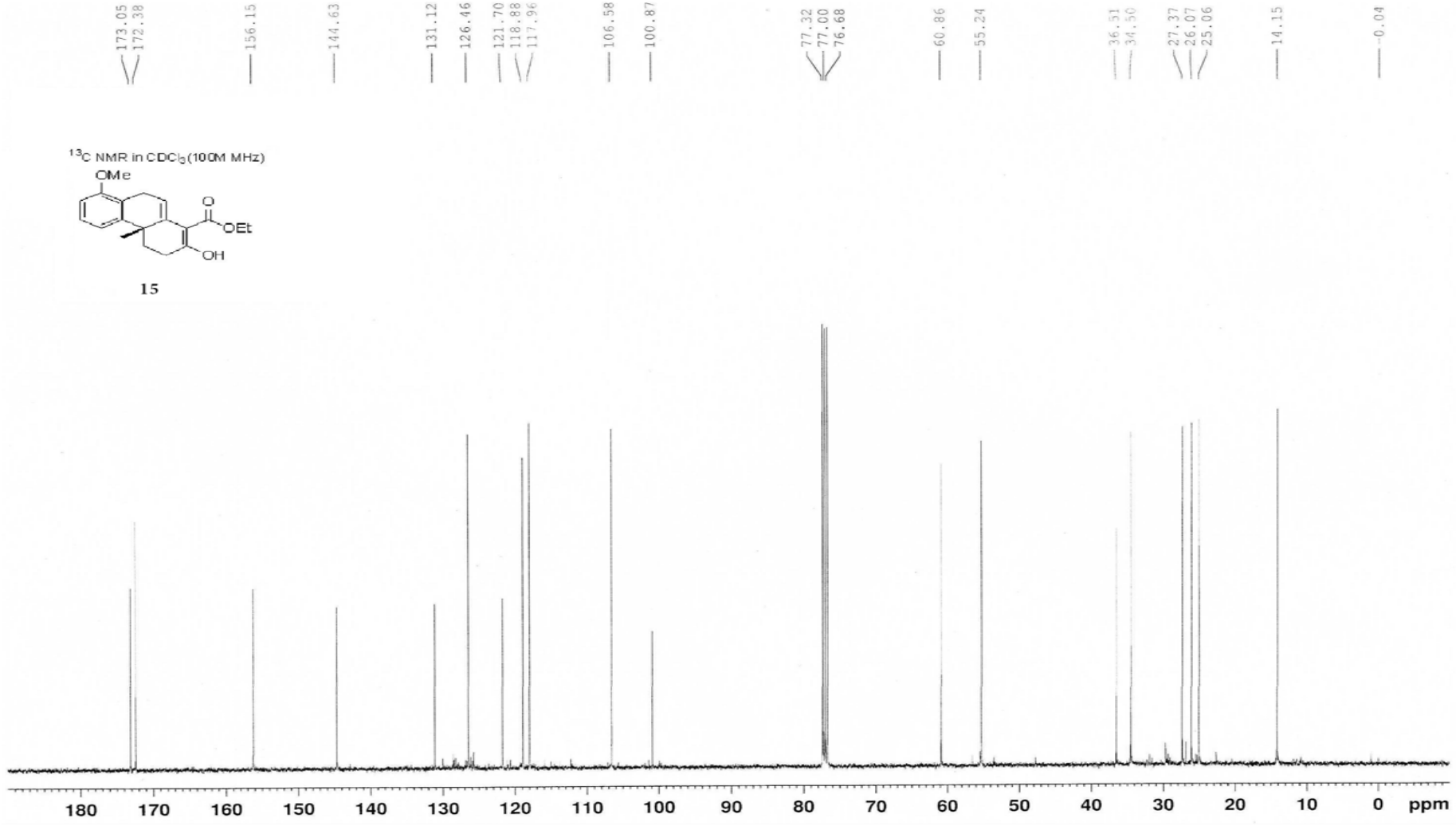


	channel	retenttion time(min)	area	%area	height
1	2998 (210-400)	18.286	46404737	95.07	1125338
2	2998 (210-400)	22.034	2406733	4.93	56264

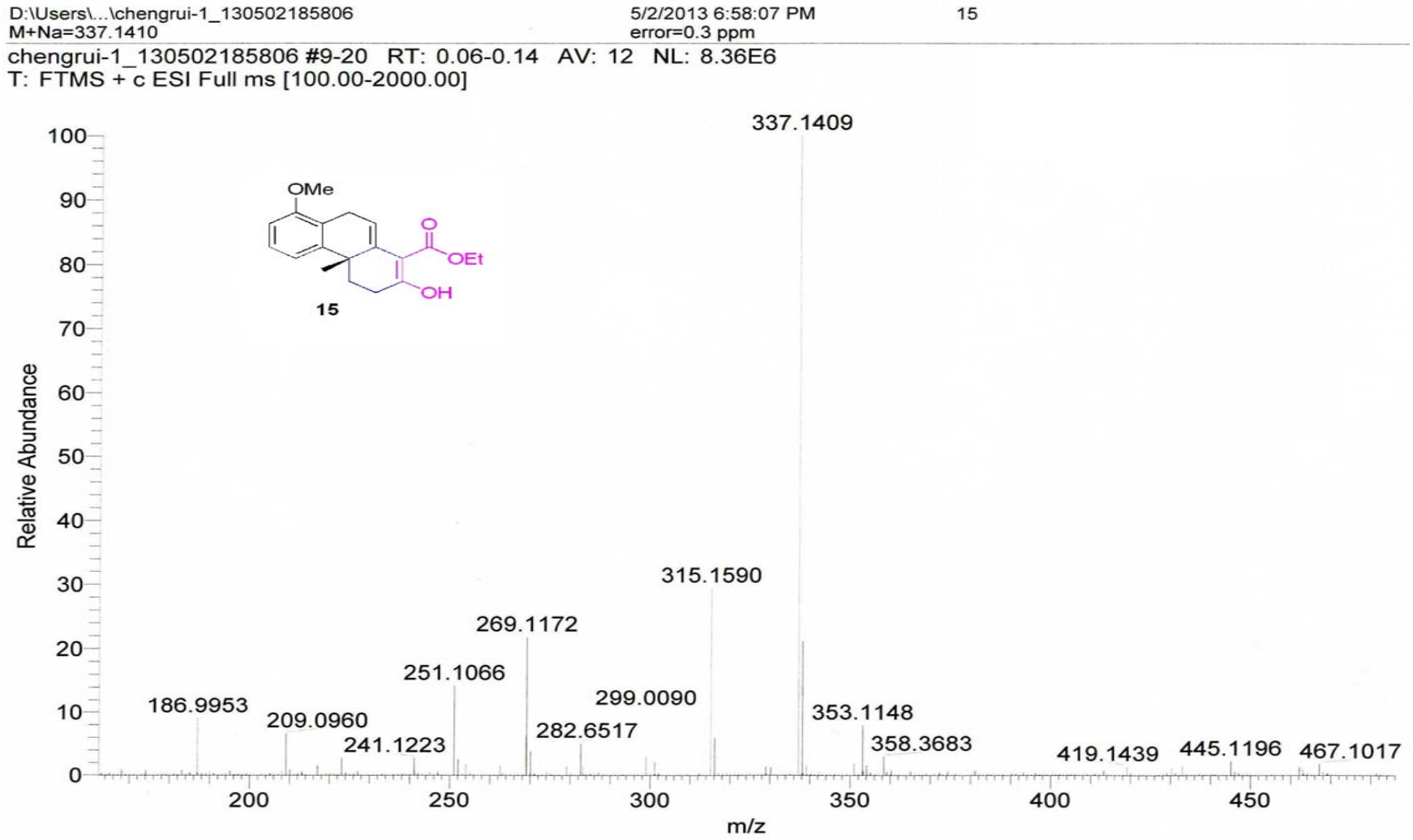
3.5. **^{1}H NMR of *(R)-ethyl 2-hydroxy-8-methoxy-4a-methyl-3,4,4a,9-tetrahydrophenanthrene-1- carboxylate (15).***



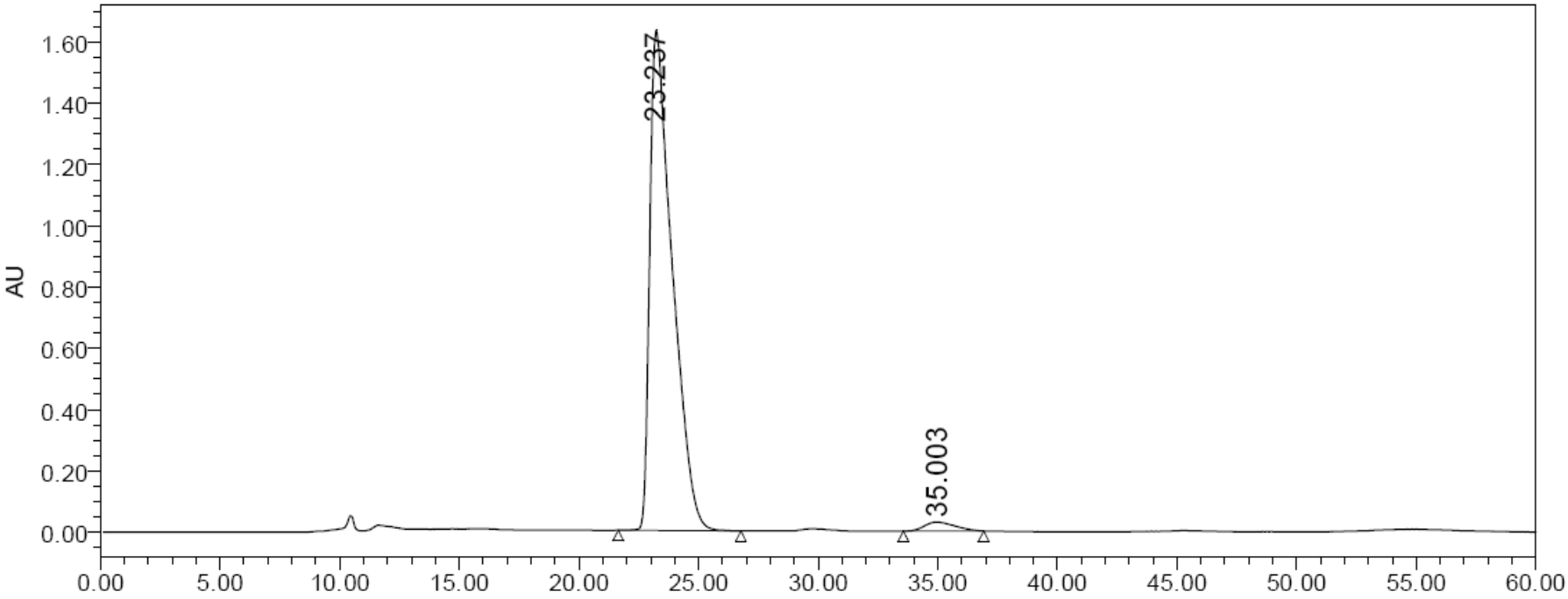
^{13} C NMR of *(R)-ethyl 2-hydroxy-8-methoxy-4a-methyl-3,4,4a,9-tetrahydrophenanthrene-1- carboxylate (15).*



HR-MS of *(R)-ethyl 2-hydroxy-8-methoxy-4a-methyl-3,4,4a,9-tetrahydrophenanthrene-1- carboxylate (15).*

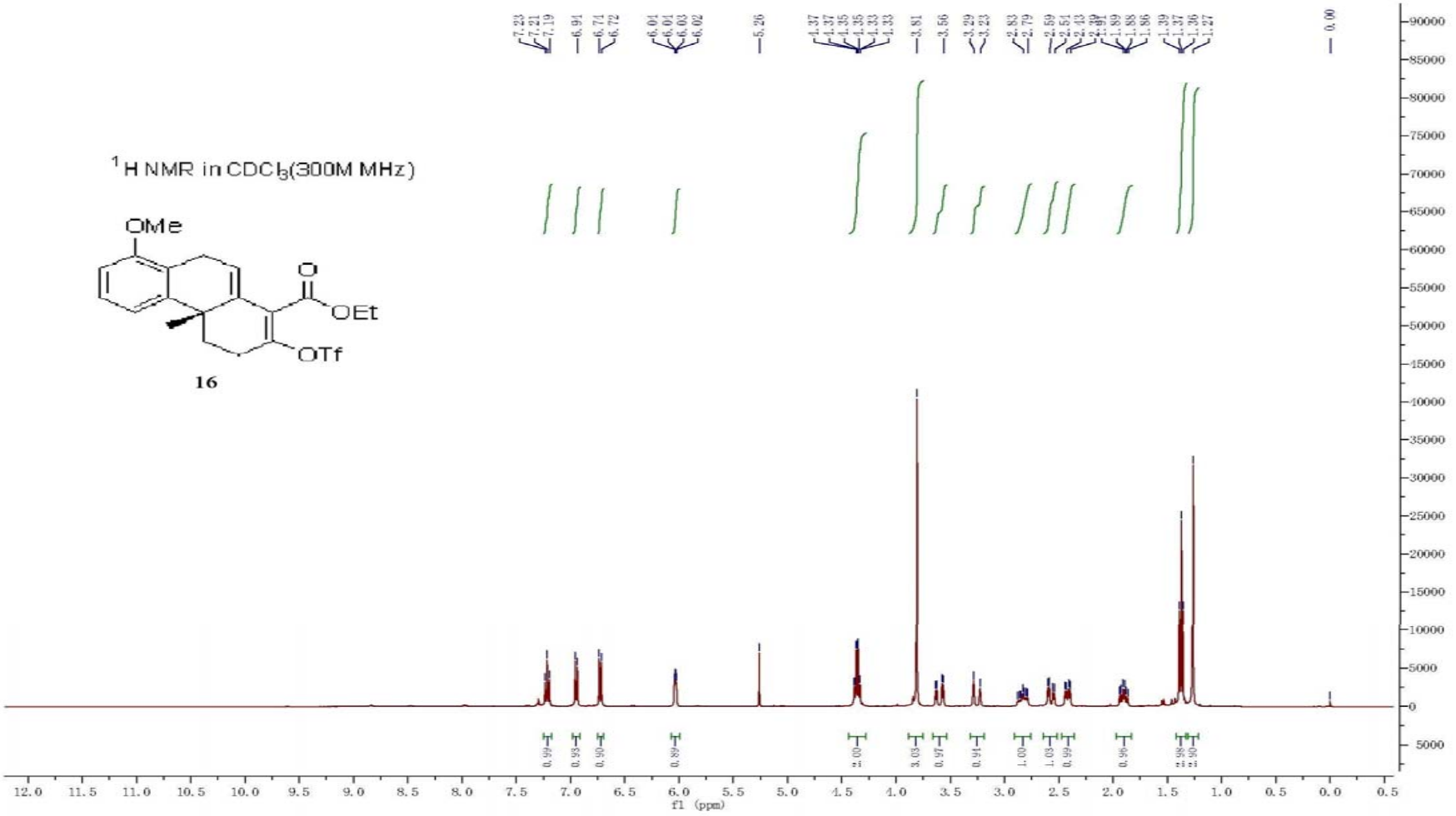


Chiral HPLC for ee value of *(R)-ethyl 2-hydroxy-8-methoxy-4a-methyl-3,4,4a,9-tetrahydrophenanthrene-1- carboxylate (15)*.

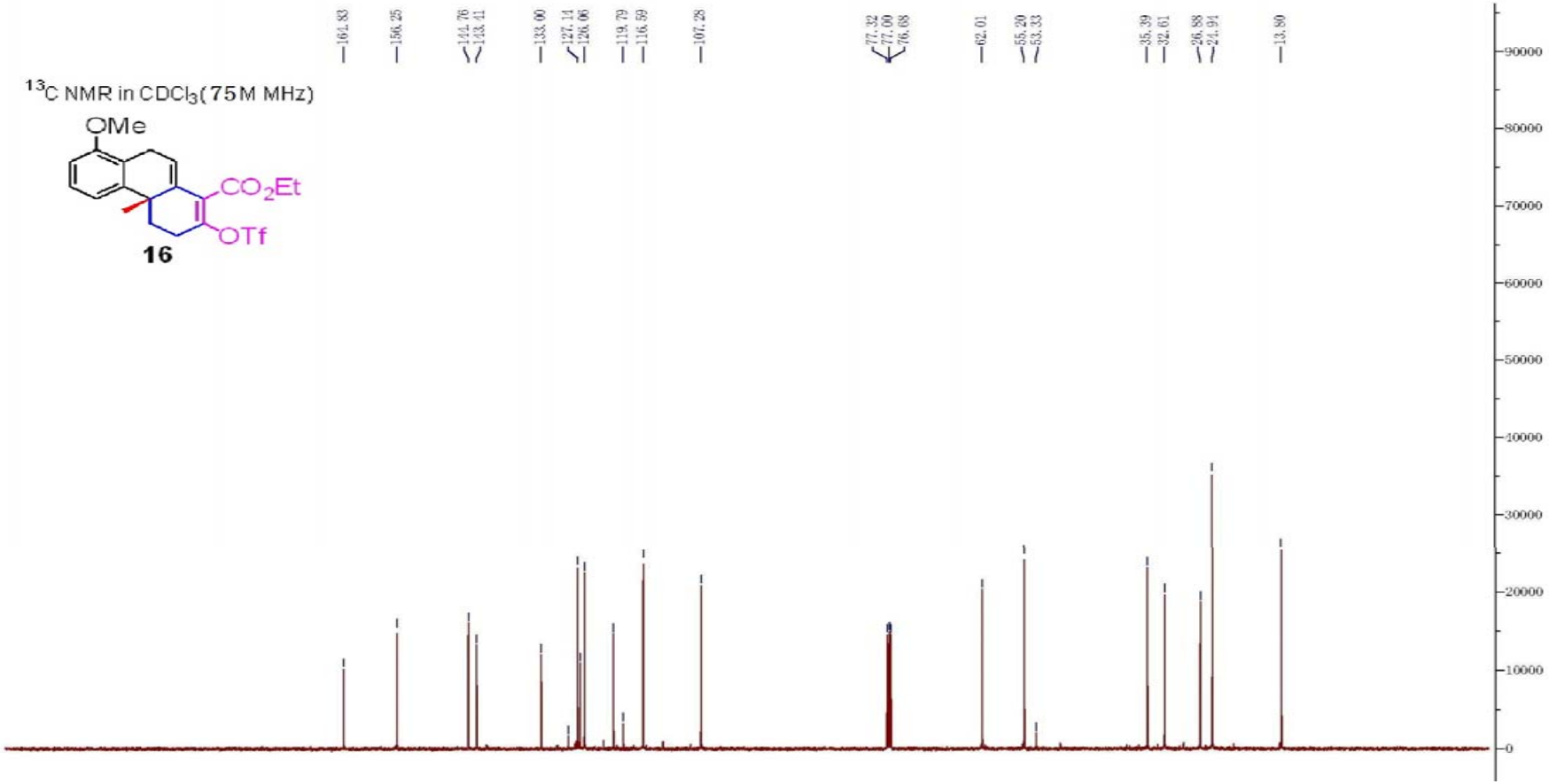


	channel	retenttion time(min)	area	%area	height
1	2998 (210-400)	23.237	106876374	97.65	1634163
2	2998 (210-400)	35.003	2568442	2.35	29179

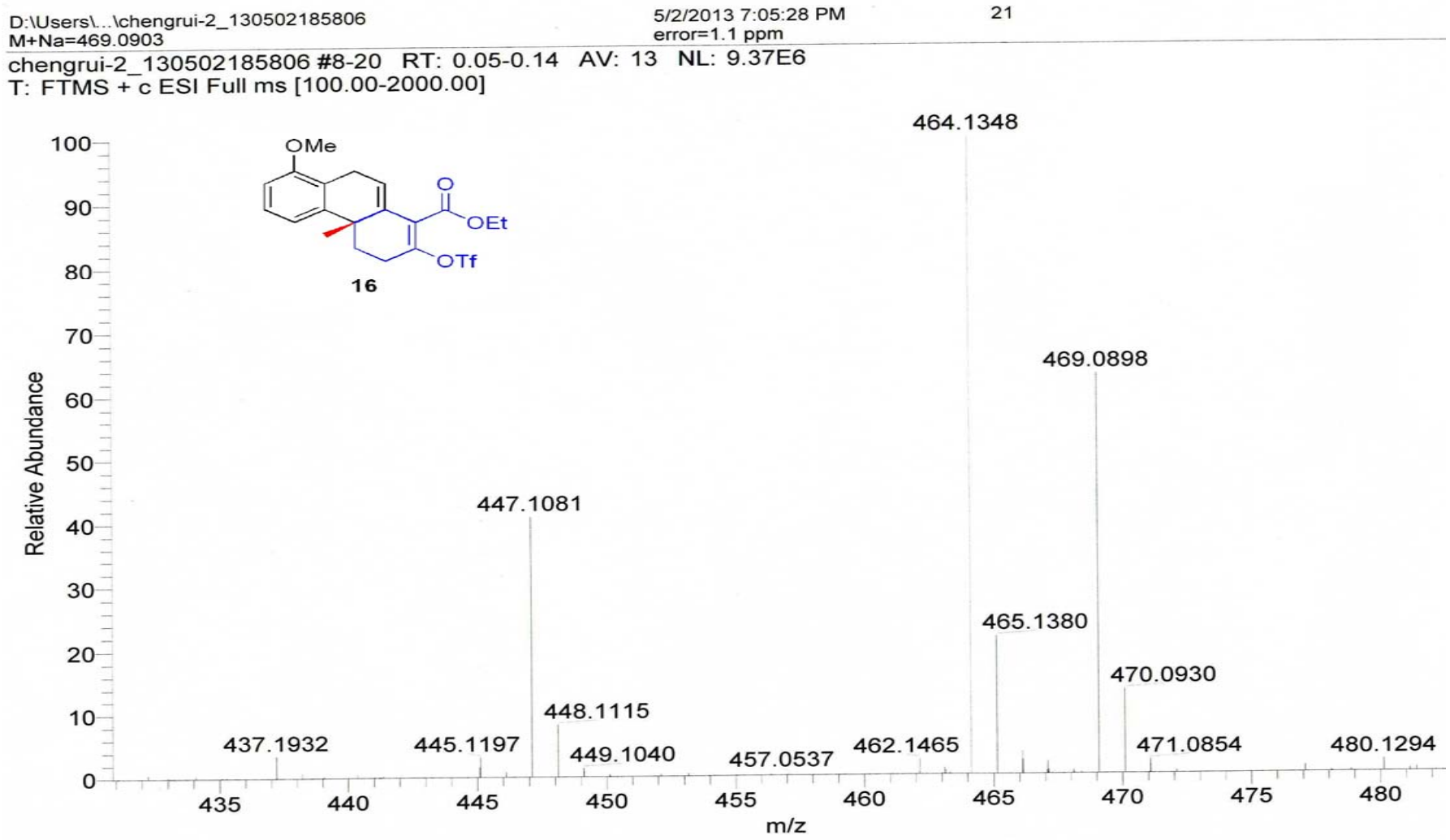
3.6. ^{1}H NMR of *(R)-ethyl 8-methoxy-4a-methyl-2-(((trifluoromethyl)sulfonyl)oxy)-3,4,4a,9-tetrahydrophenan-threne-1-carboxylate (16).*



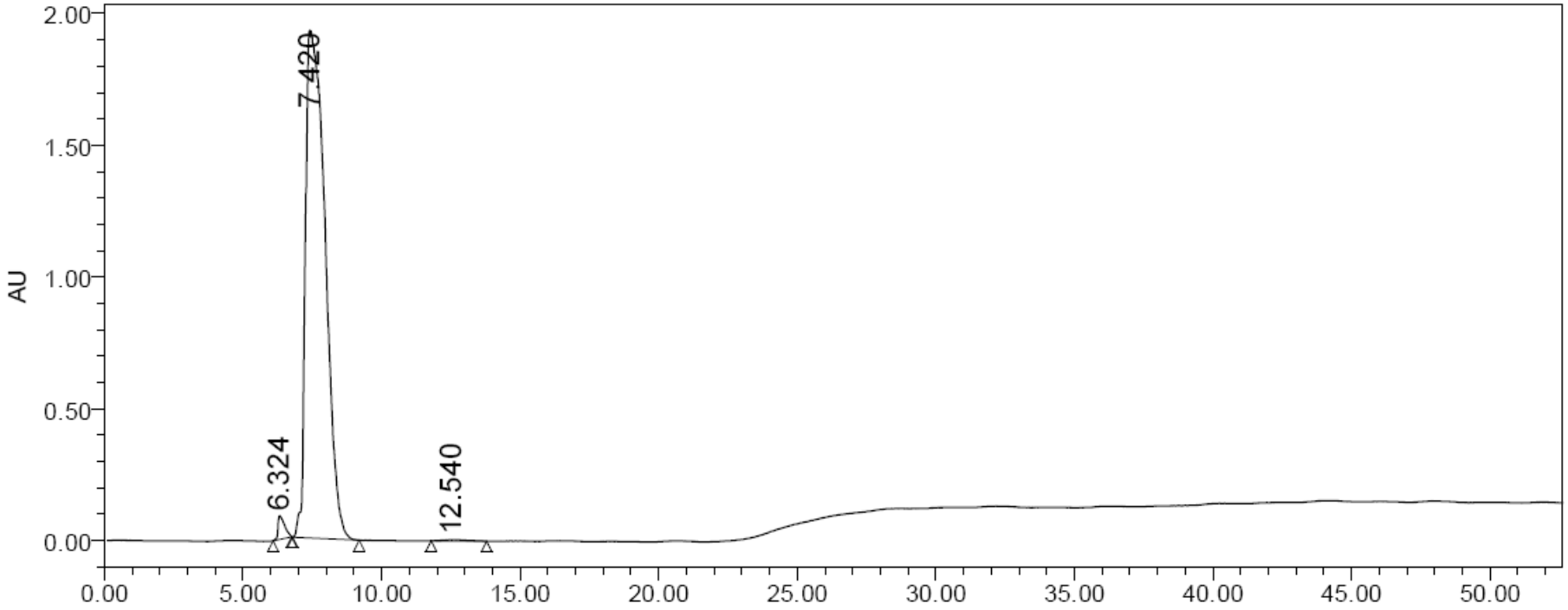
^{13}C NMR of *(R)-ethyl 8-methoxy-4a-methyl-2-(((trifluoromethyl)sulfonyl)oxy)-3,4,4a,9- tetrahydrophenan- threne-1-carboxylate (16).*



HR-MS of *(R)-ethyl 8-methoxy-4a-methyl-2-(((trifluoromethyl)sulfonyl)oxy)-3,4,4a,9- tetrahydrophenan- threne-1-carboxylate (16).*

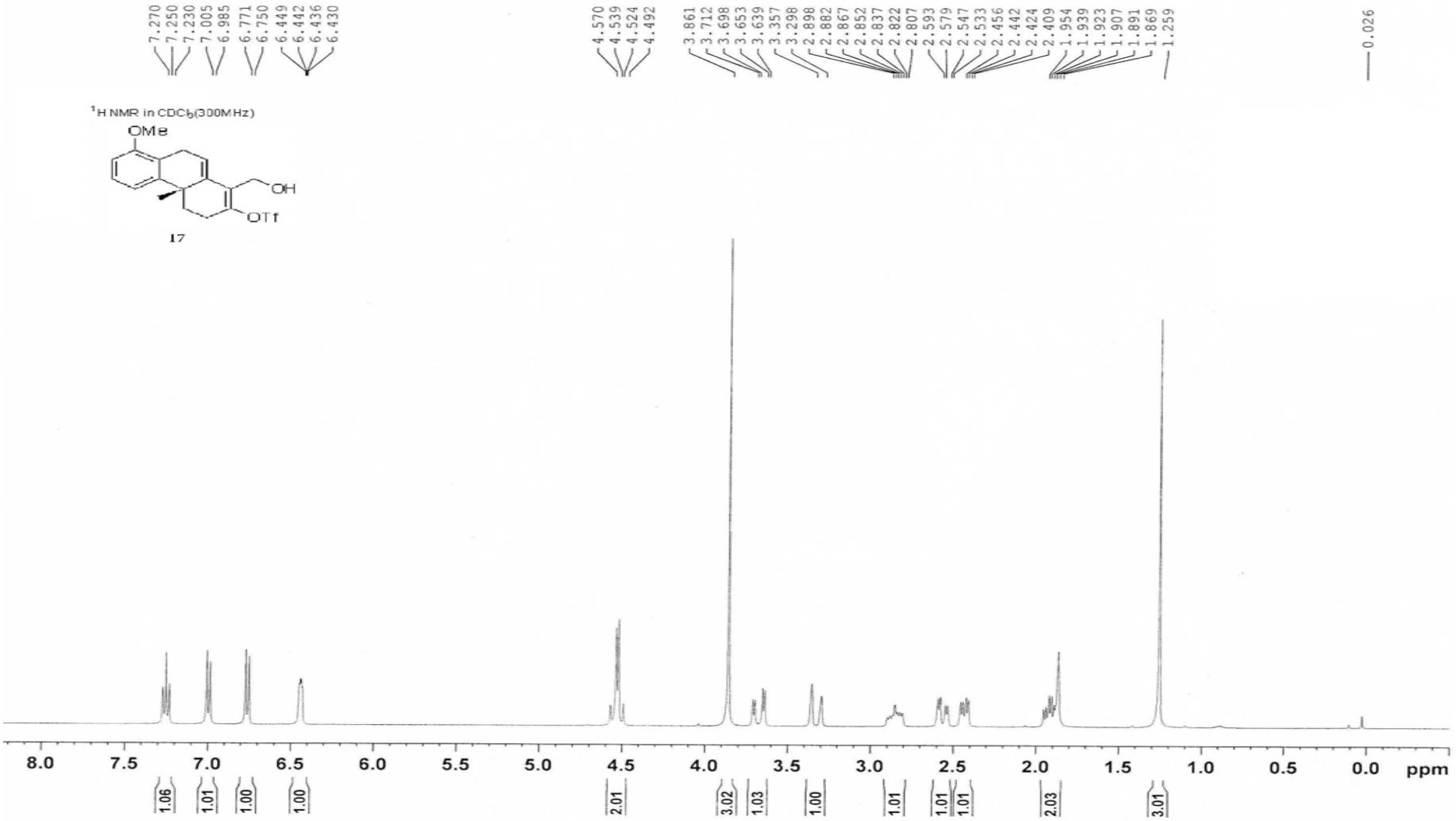


Chiral HPLC for ee value of *(R)-ethyl 8-methoxy-4a-methyl-2-(((trifluoromethyl)sulfonyl)oxy)-3,4,4a,9- tetrahydrophenanthrene-1-carboxylate (16)*

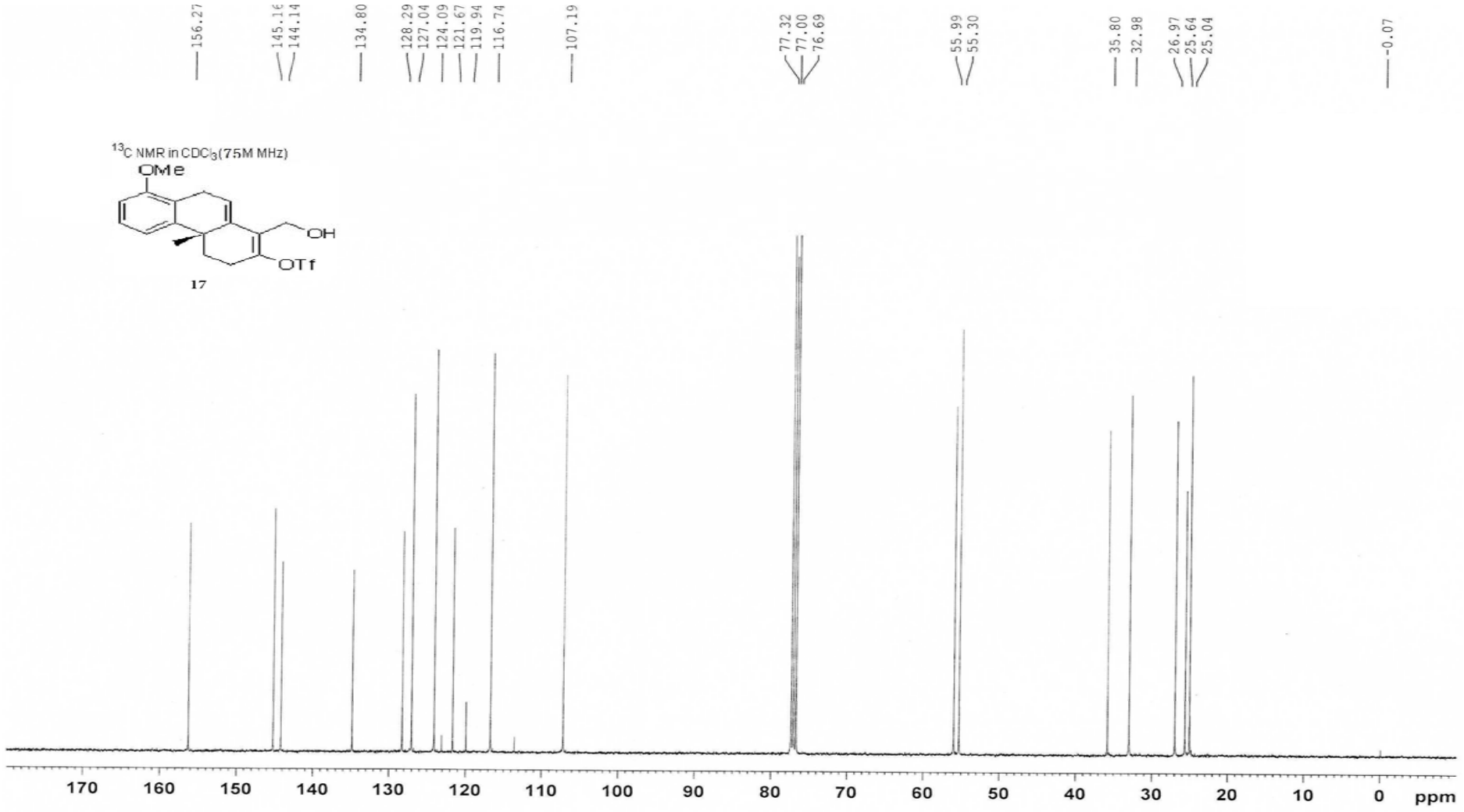


	channel	retenttion time(min)	area	%area	height
1	2998 (210-400)	6.324	1474260	1.53	89154
2	2998 (210-400)	7.420	94726744	98.21	1926167

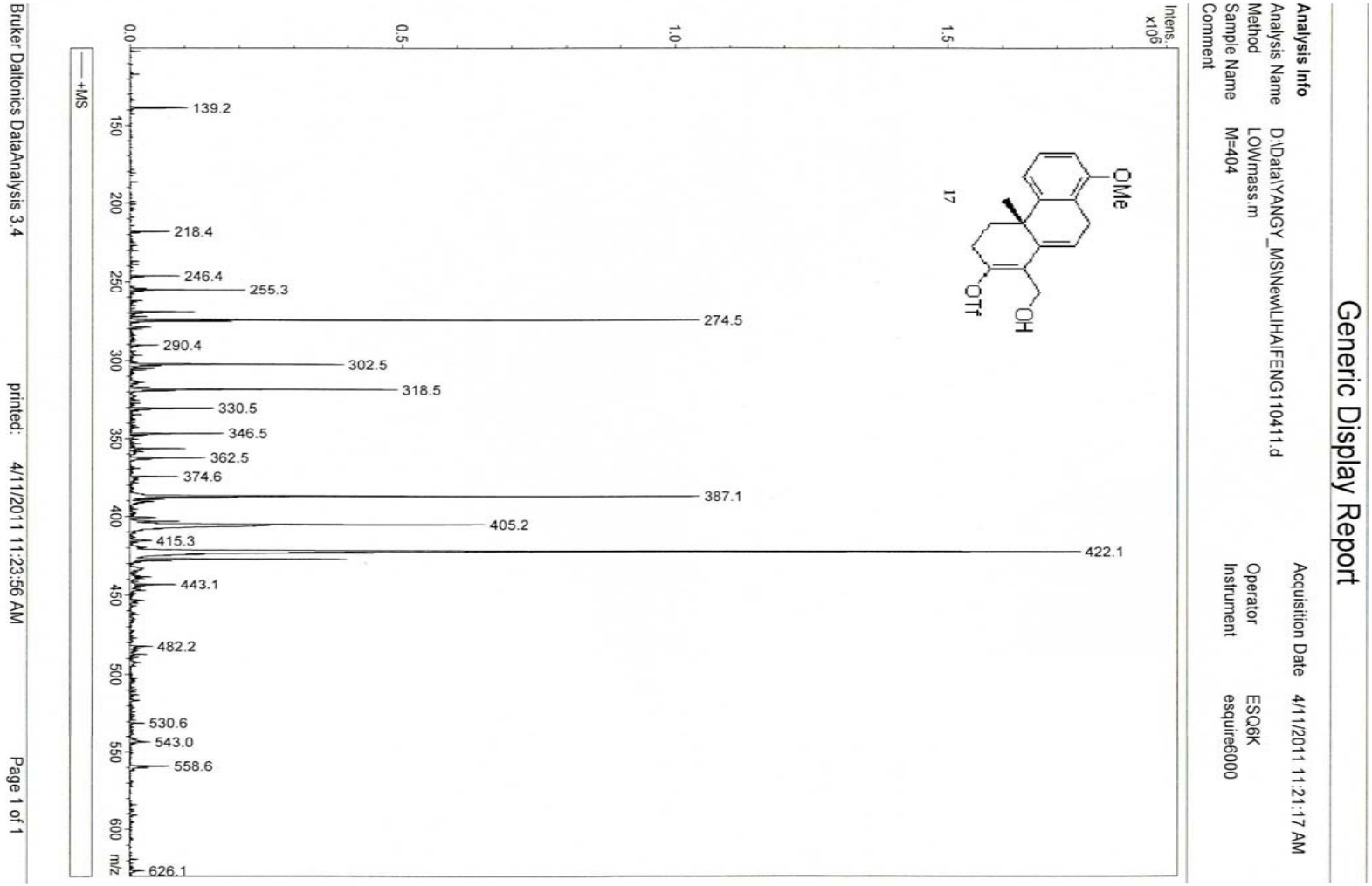
3.7. **^{1}H NMR of *(R)-1-(hydroxymethyl)-8-methoxy-4a-methyl-3,4,4a,9-tetrahydrophenanthren-2-yl trifluoromethanesulfonate (17).***



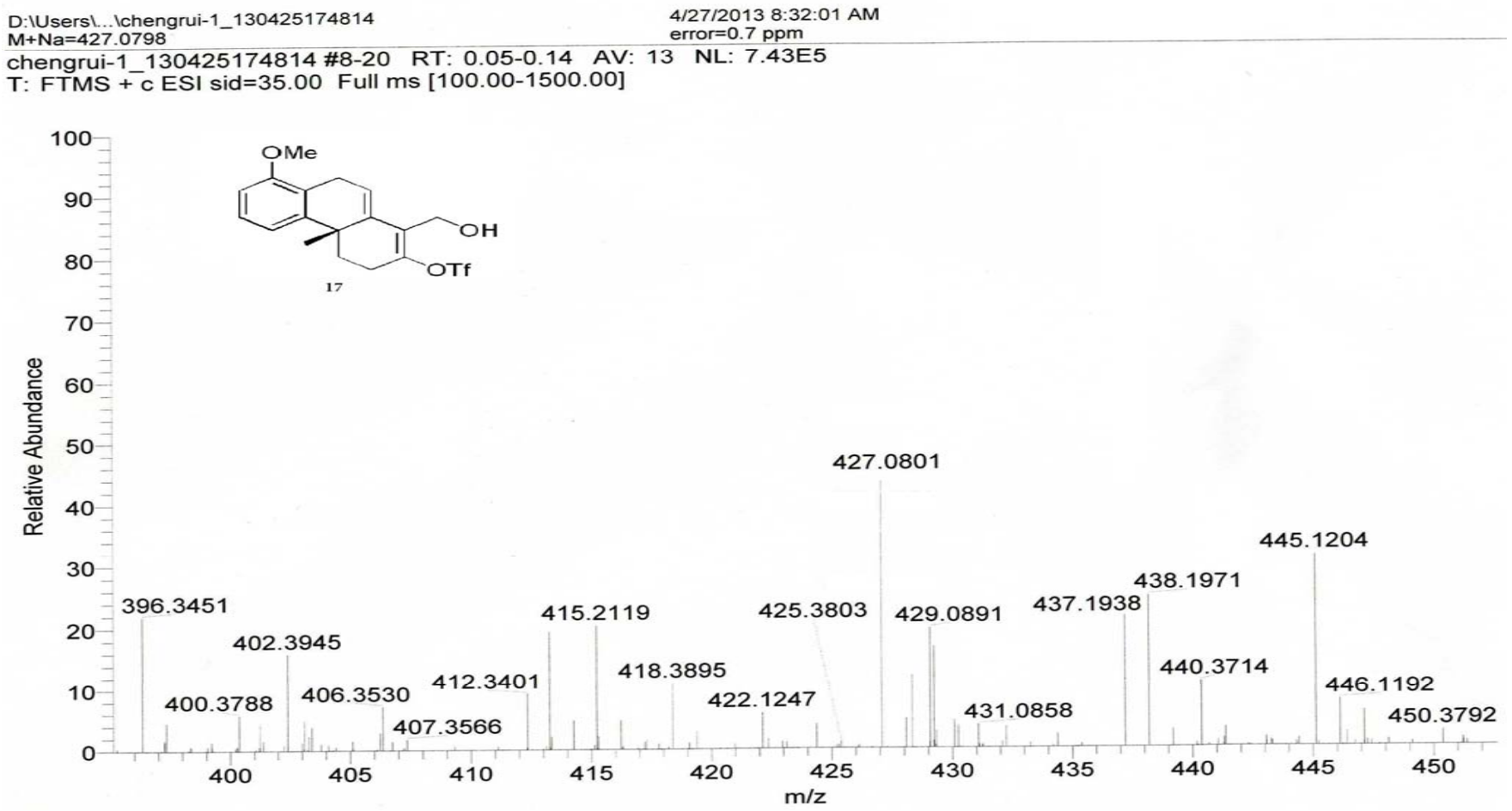
^{13}C NMR of *(R)-1-(hydroxymethyl)-8-methoxy-4a-methyl-3,4,4a,9-tetrahydrophenanthren- 2-yl trifluoromethanesulfonate (17).*



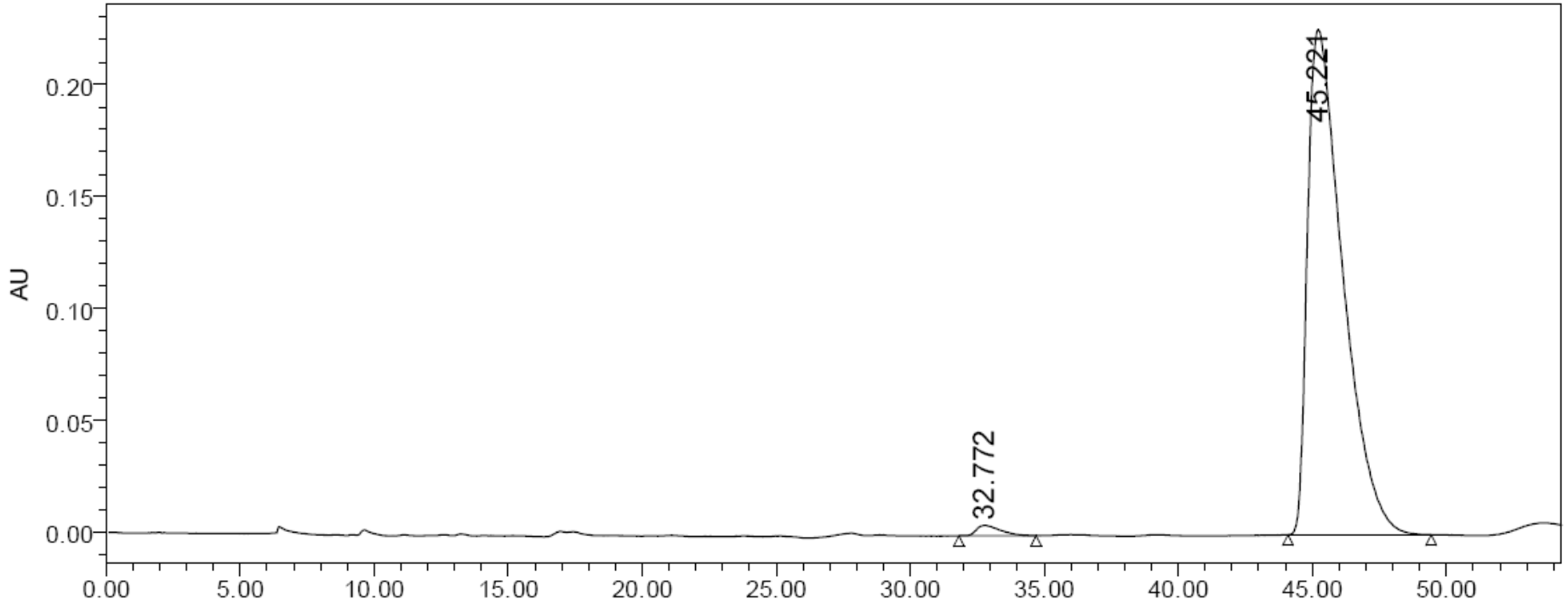
ESI-MS of *(R)-1-(hydroxymethyl)-8-methoxy-4a-methyl-3,4,4a,9-tetrahydrophenanthren- 2-yl trifluoro- methanesulfonate (17).*



HR-MS of *(R)-1-(hydroxymethyl)-8-methoxy-4a-methyl-3,4,4a,9-tetrahydrophenanthren- 2-yl trifluoro- methanesulfonate (17).*

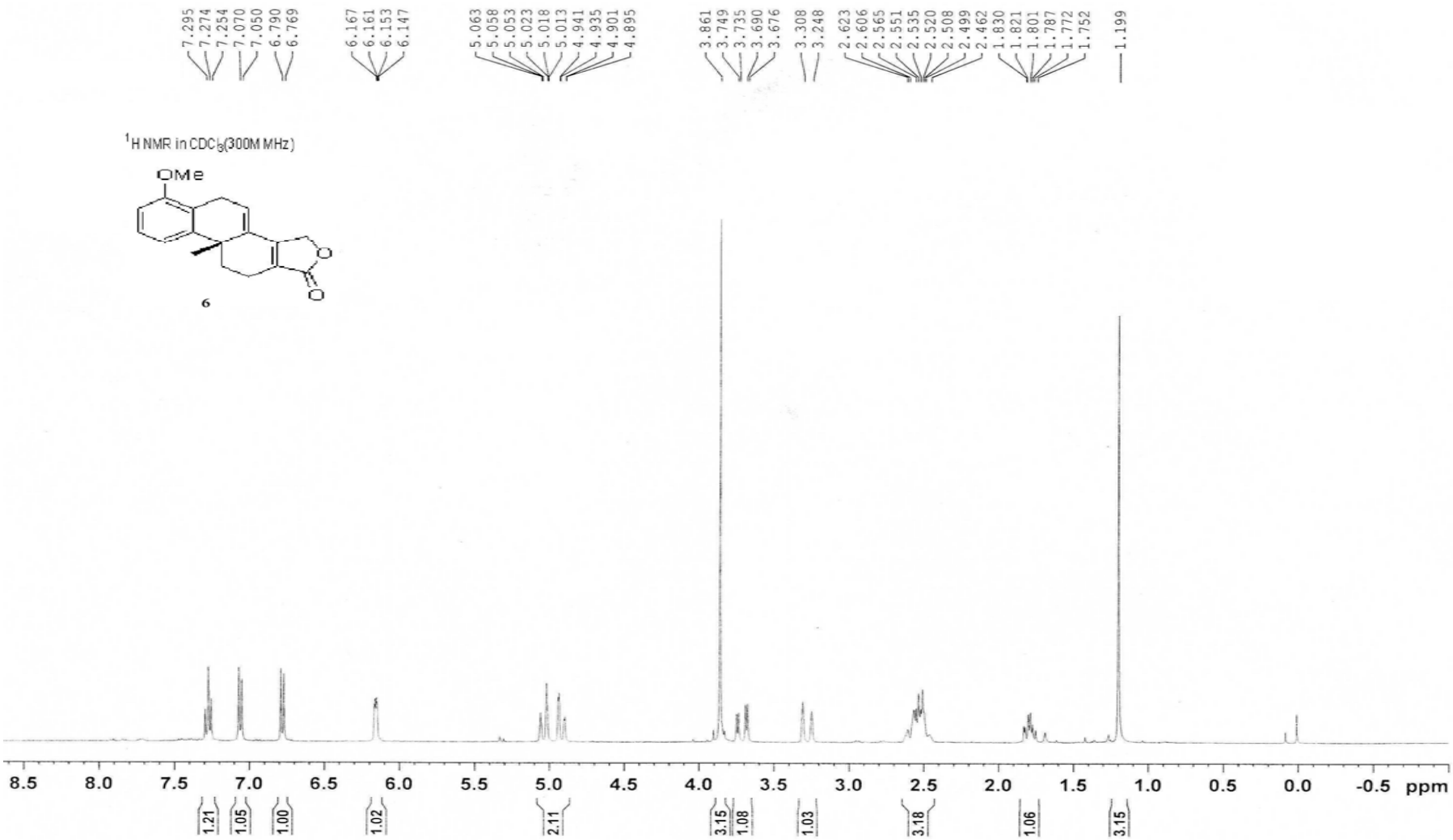


Chiral HPLC for ee value of *(R)-1-(hydroxymethyl)-8-methoxy-4a-methyl-3,4,4a,9-tetrahydrophenanthren-2-yl trifluoro -methanesulfonate (17)*

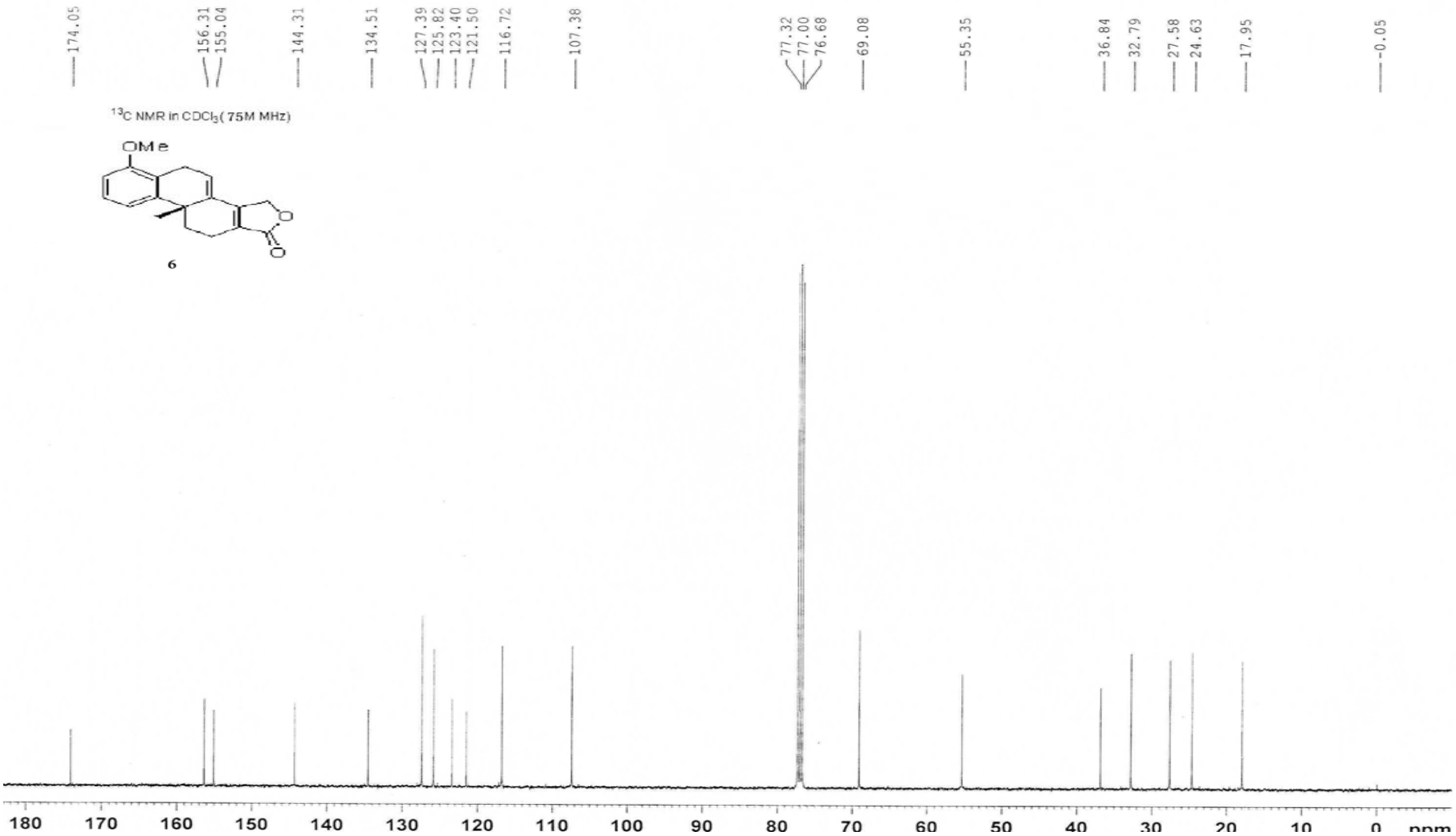


	channel	retenttion time(min)	area	%area	height
1	2998 (210-400)	32.772	286445	1.37	4665
2	2998 (210-400)	45.221	20641571	98.63	225425

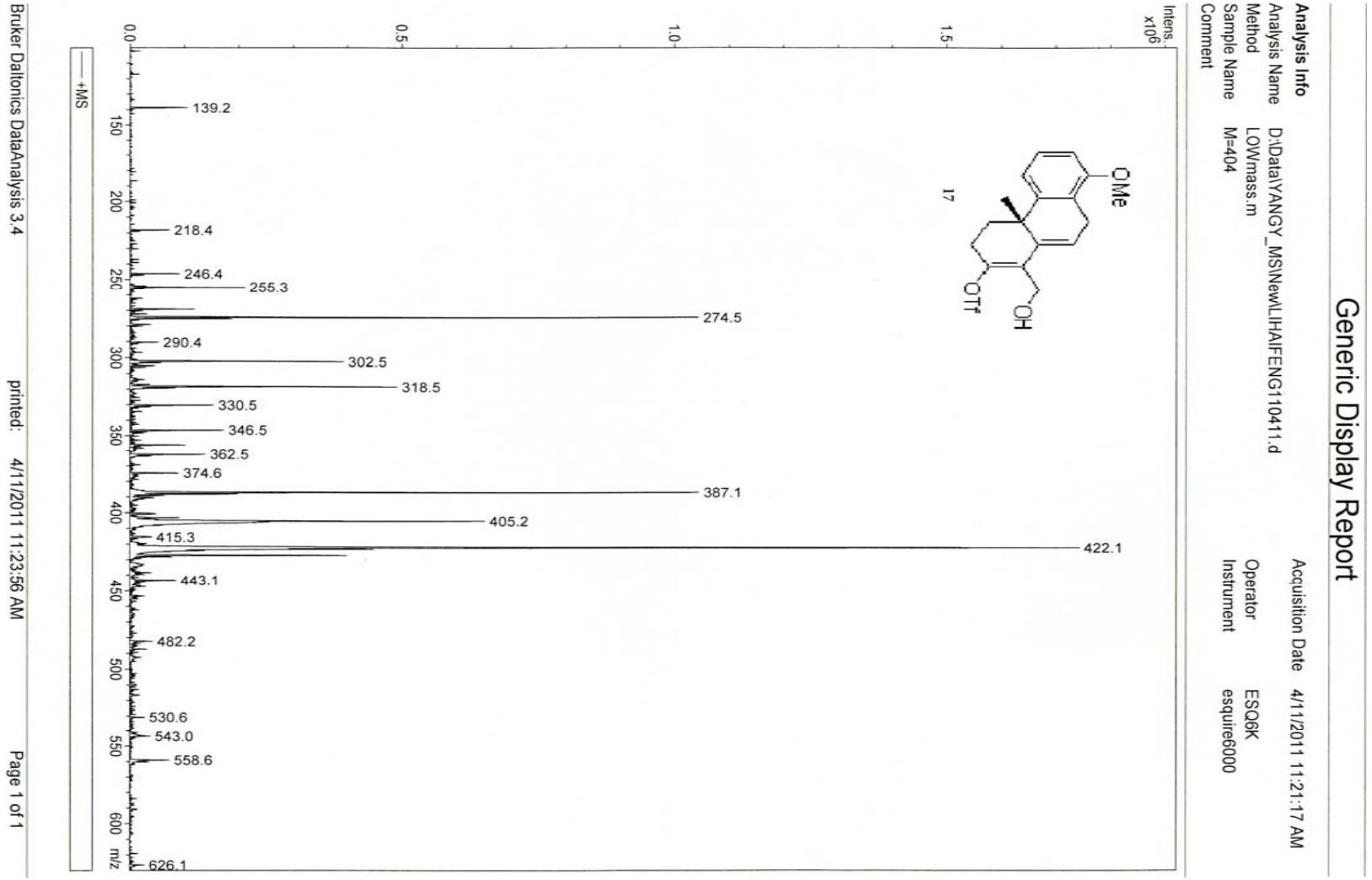
3.8. **^{1}H NMR of *(R)-6-methoxy-9b-methyl-5,9b,10,11-tetrahydrophenanthro[1,2-c]furan-1(3H)-one (6)*.**



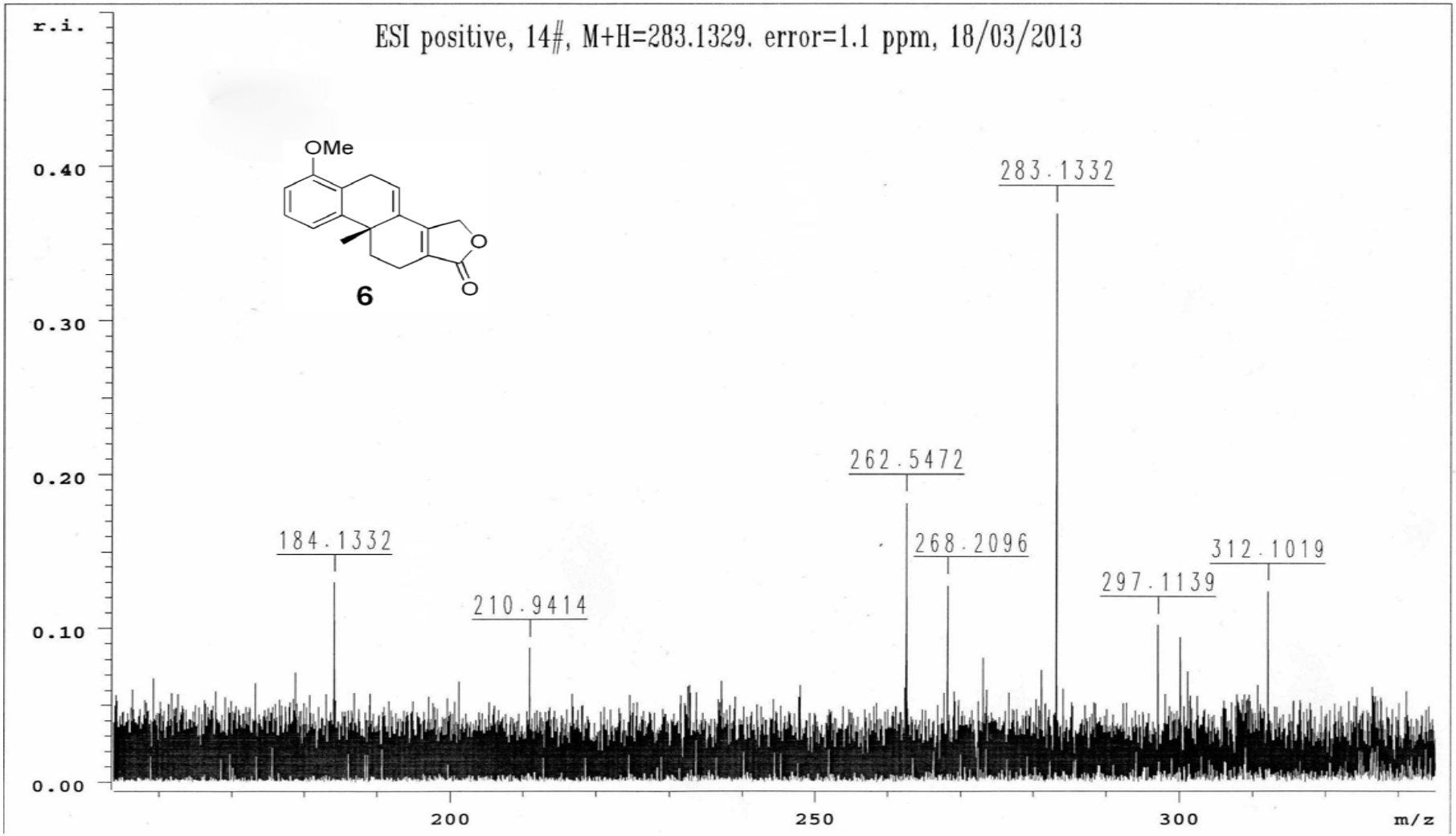
^{13}C NMR of *(R)-6-methoxy-9b-methyl-5,9b,10,11-tetrahydrophenanthro[1,2-c]furan-1(3H)- one (6).*



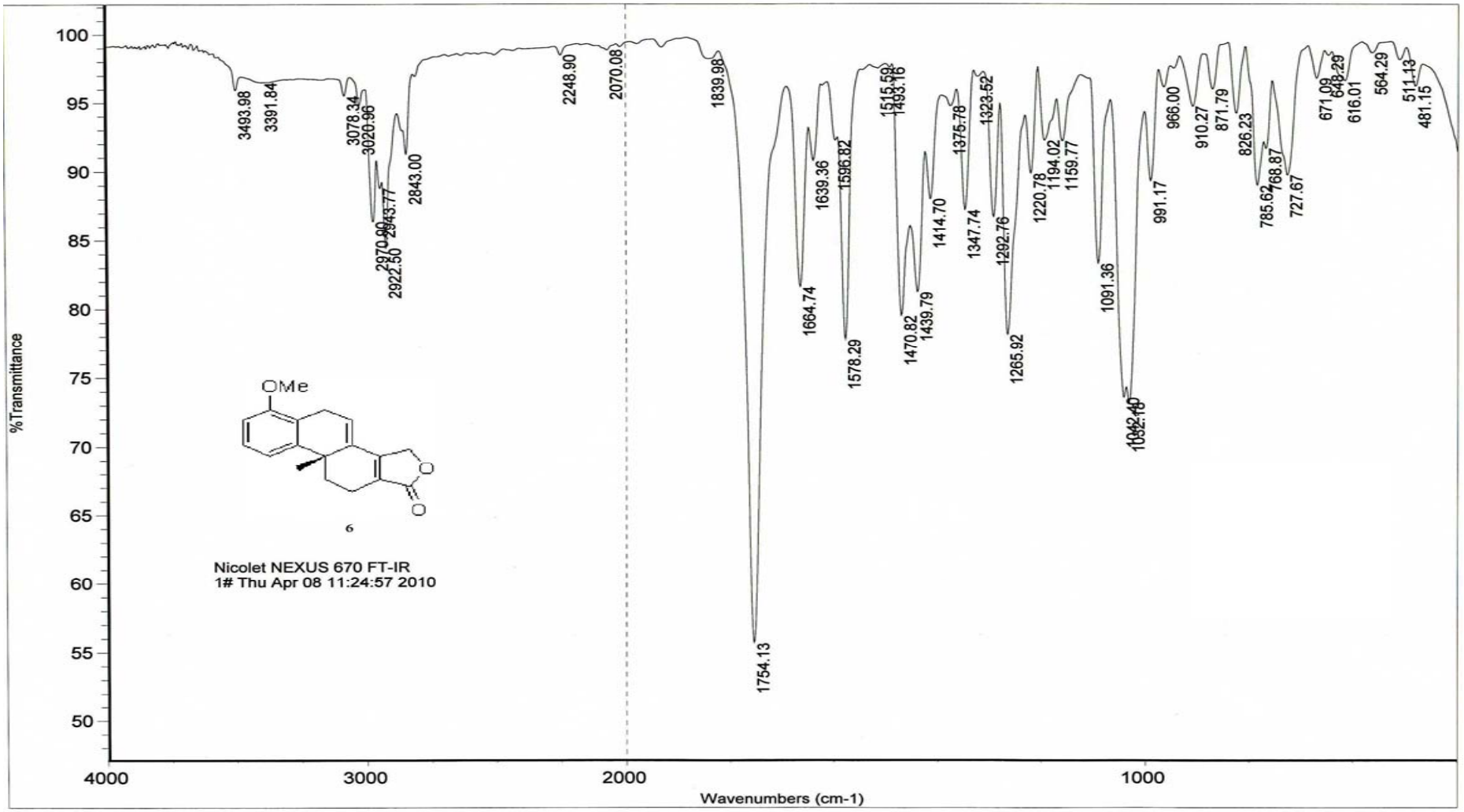
ESI-MS of *(R)-6-methoxy-9b-methyl-5,9b,10,11-tetrahydrophenanthro[1,2-c]furan-1(3H)- one (6).*



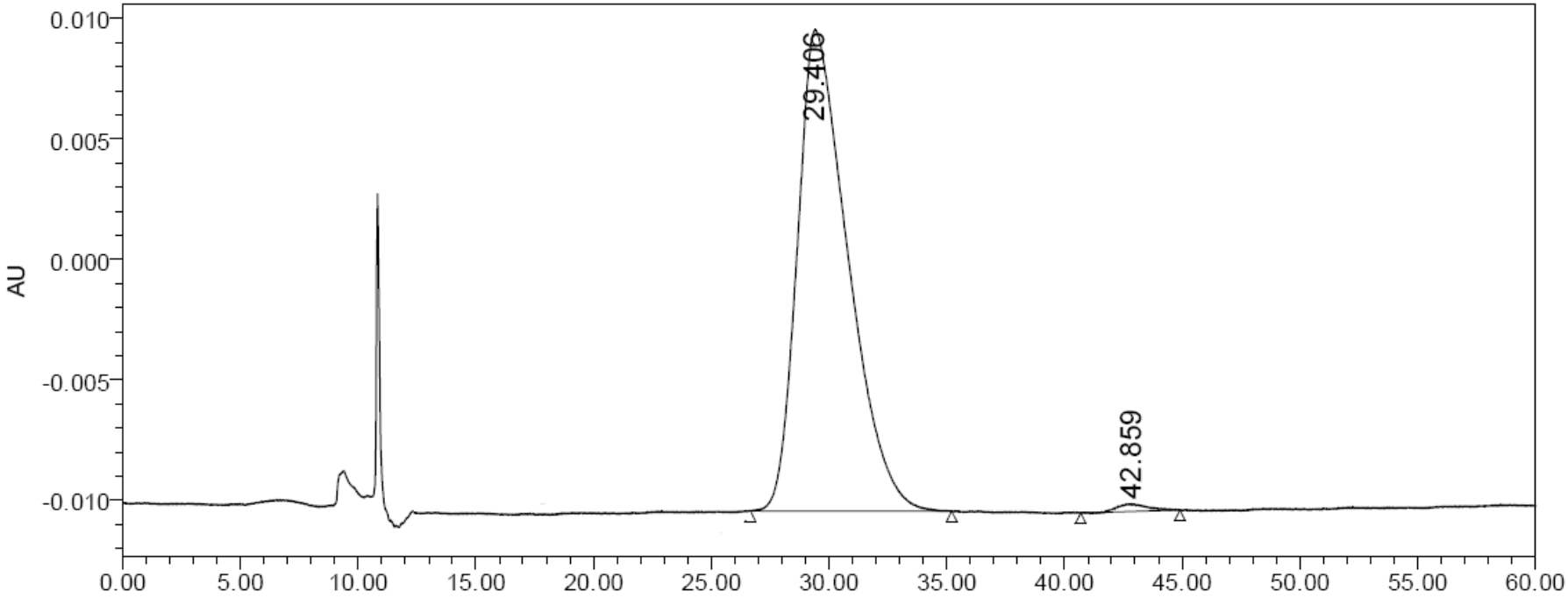
HRMS-ESI of *(R)-6-methoxy-9b-methyl-5,9b,10,11-tetrahydrophenanthro[1,2-c]furan-1(3H)- one (6).*



IR of *(R)-6-methoxy-9b-methyl-5,9b,10,11-tetrahydrophenanthro[1,2-c]furan-1(3H)- one (6).*

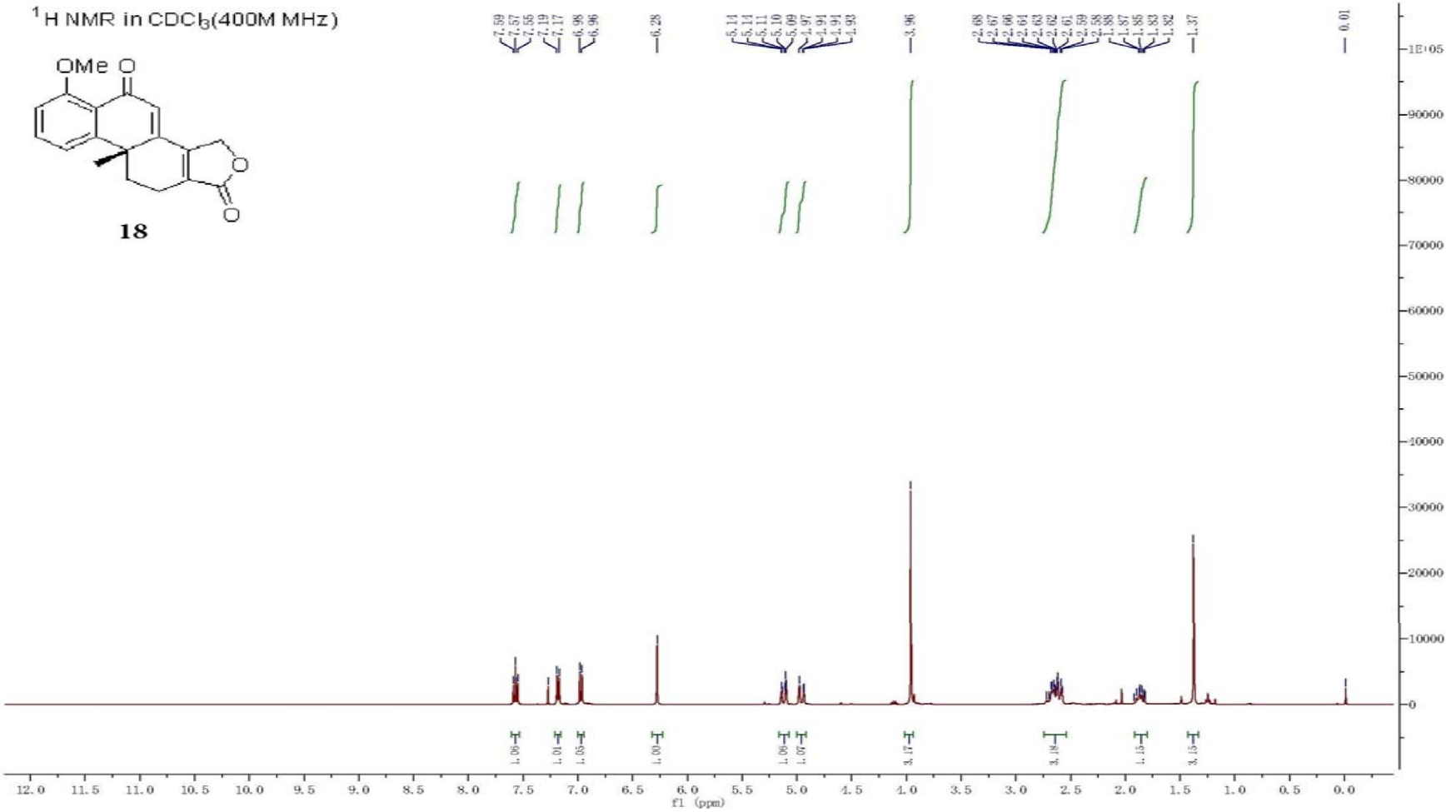


Chiral HPLC for ee value of *(R)-6-methoxy-9b-methyl-5,9b,10,11-tetrahydrophenanthro[1,2-c]furan-1(3H)- one (6)*.

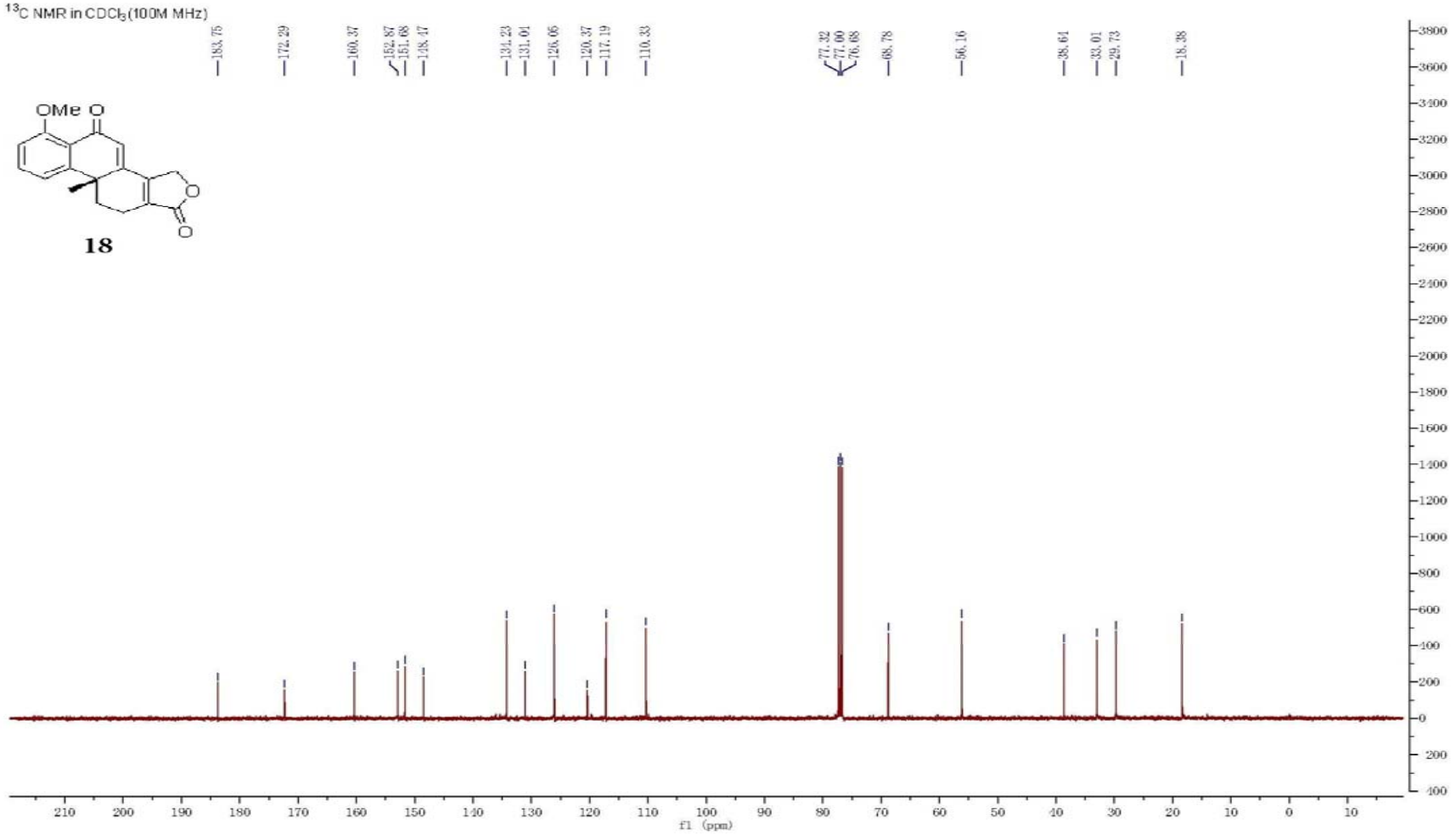


	channel	retenttion time(min)	area	%area	height
1	2998 (210-400)	29.406	2987779	99.04	20003
2	2998 (210-400)	42.859	29079	0.96	324

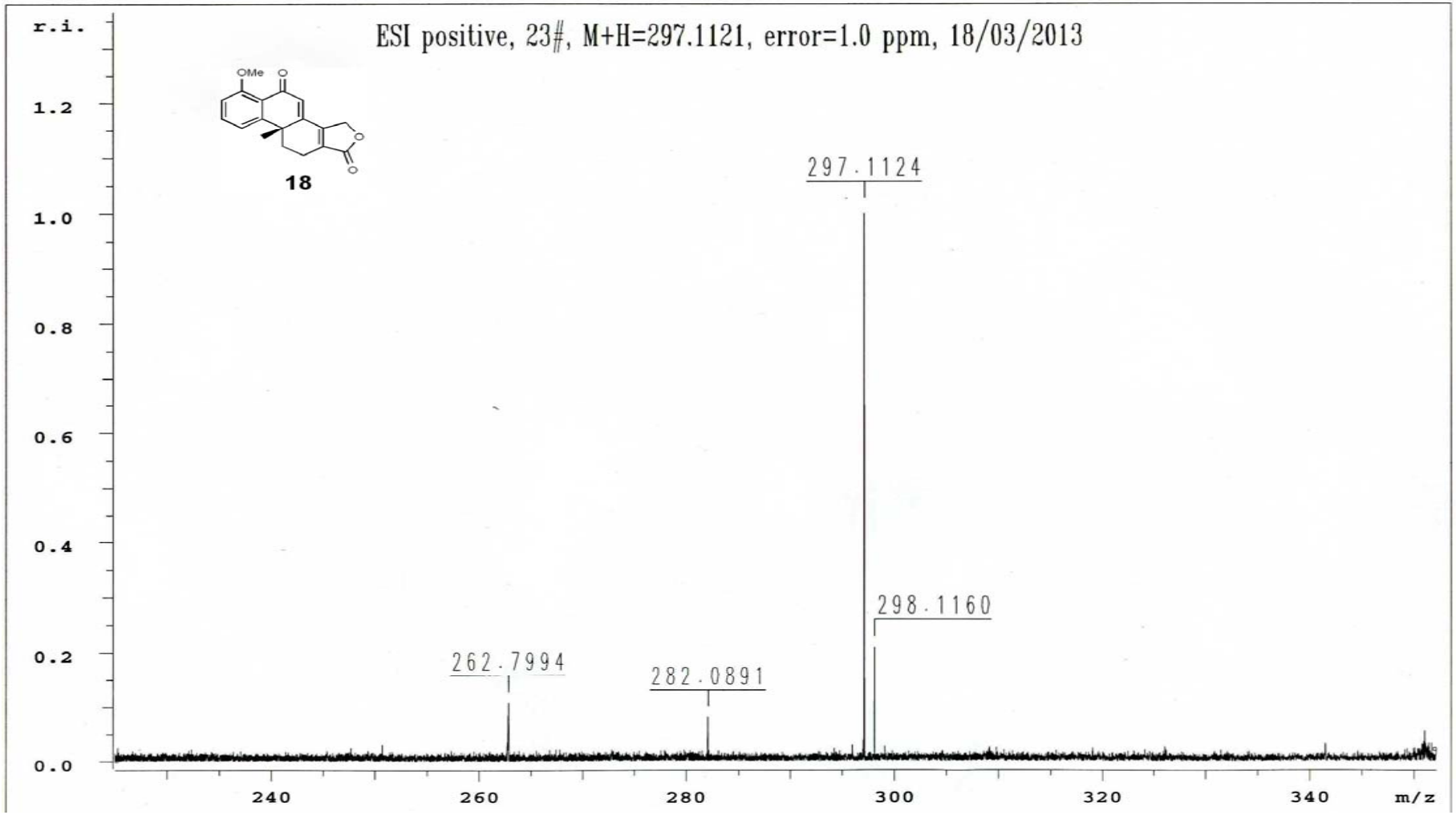
3.9. **^{1}H NMR of *(R)-6-methoxy-9b-methyl-10,11-dihydrophenanthro[1,2-c]furan-1,5(3H,9bH)- dione (18).***



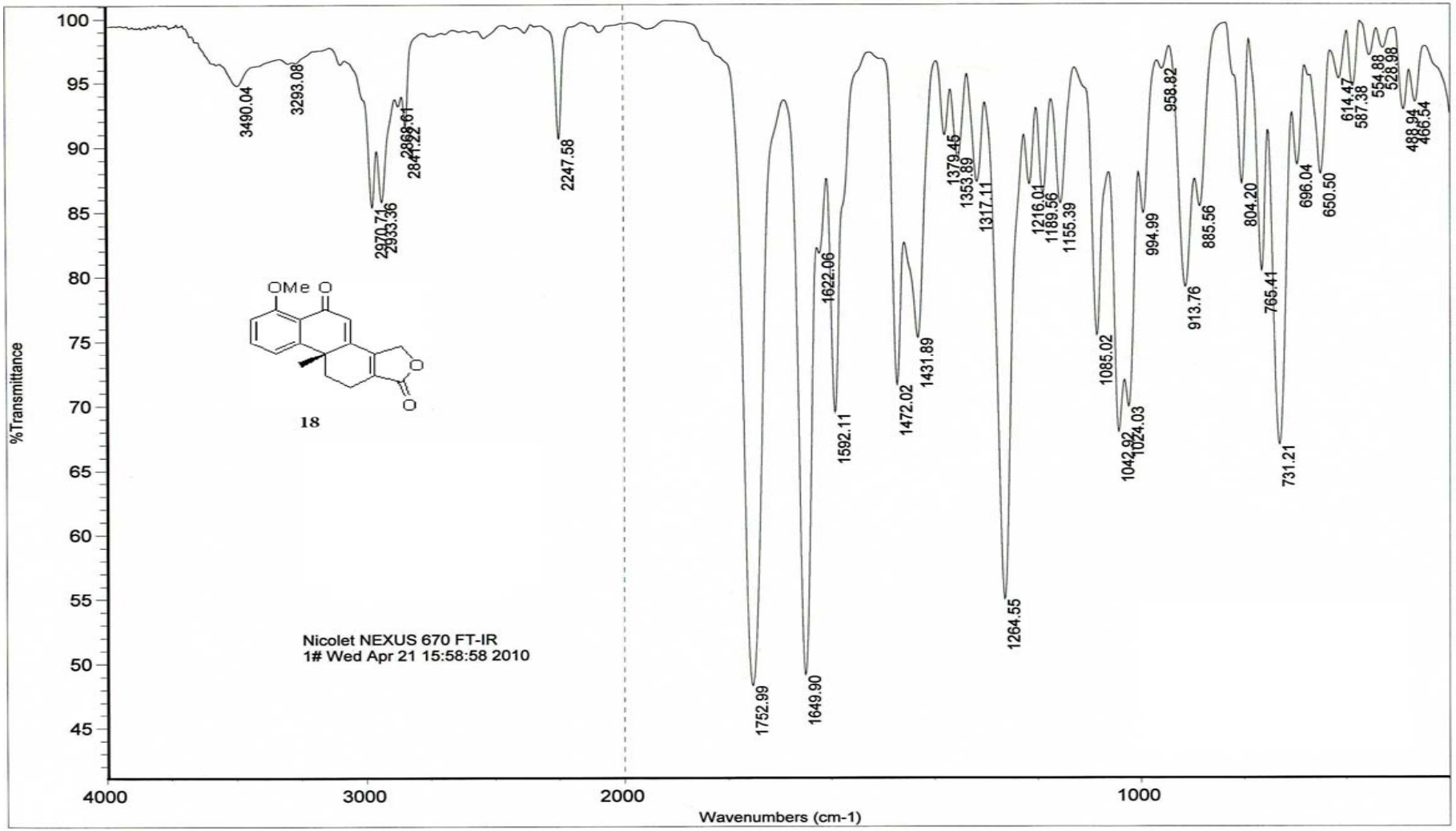
^{13}C NMR of *(R)-6-methoxy-9b-methyl-10,11-dihydrophenanthro[1,2-c]furan-1,5(3H,9bH)- dione (18).*



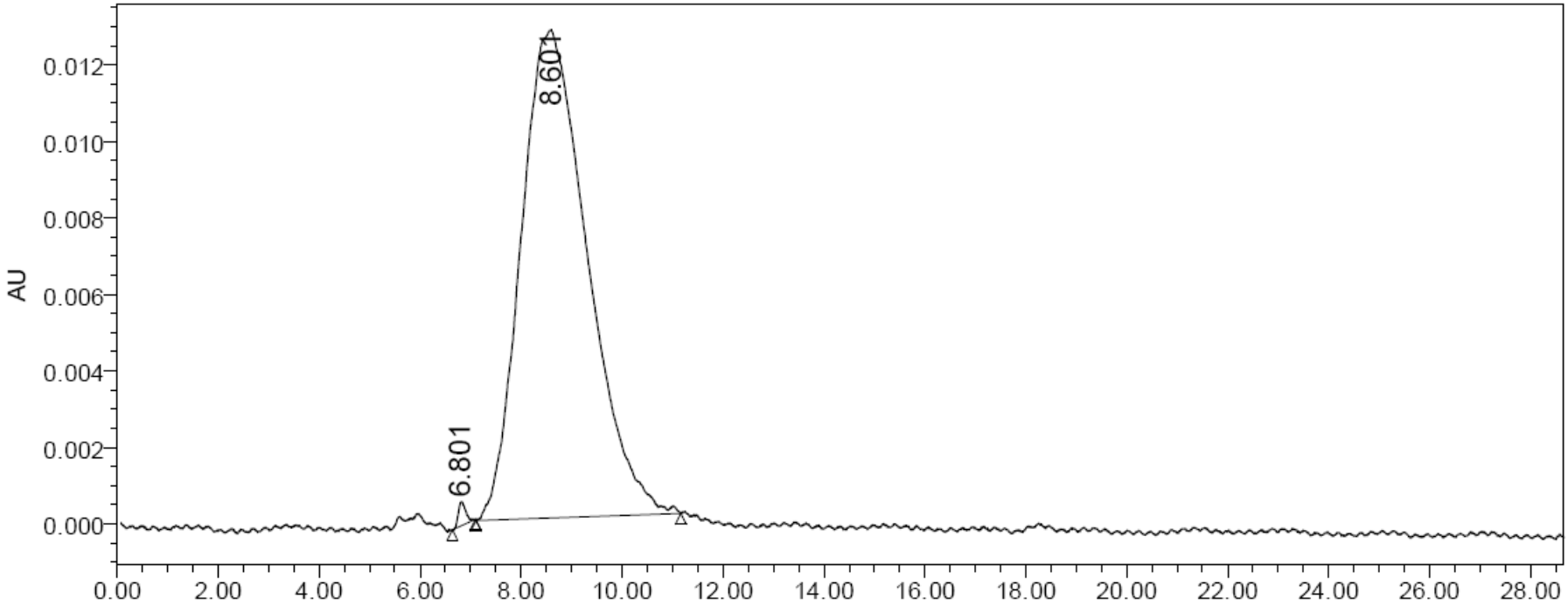
HRMS-ESI of *(R)-6-methoxy-9b-methyl-10,11-dihydrophenanthro[1,2-c]furan-1,5(3H,9bH)- dione (18).*



IR of *(R)-6-methoxy-9b-methyl-10,11-dihydrophenanthro[1,2-c]furan-1,5(3H,9bH)- dione (18).*

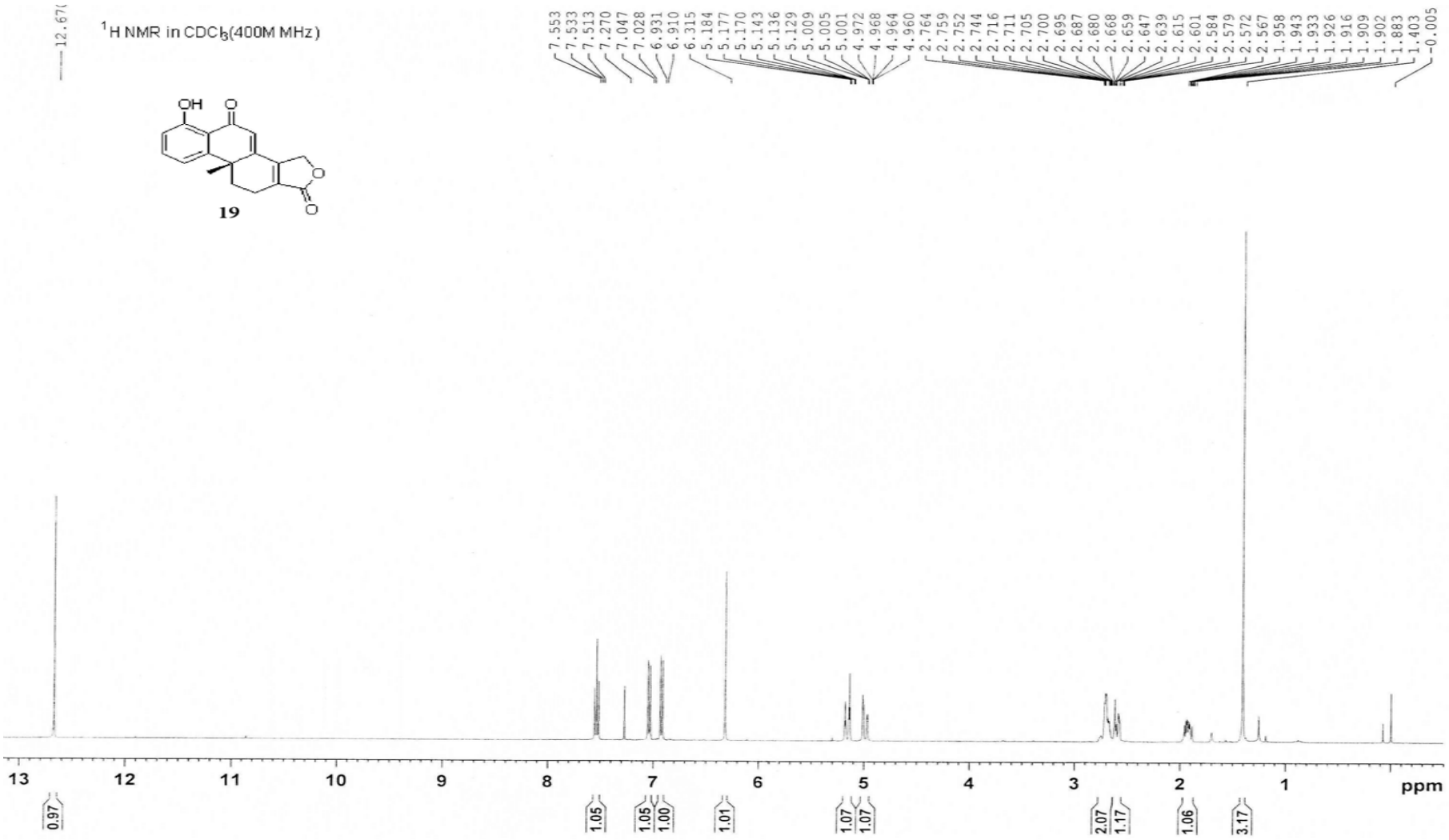


Chiral HPLC for ee value of *(R)-6-methoxy-9b-methyl-10,11-dihydrophenanthro[1,2-c]furan-1,5(3H,9bH)- dione (18).*

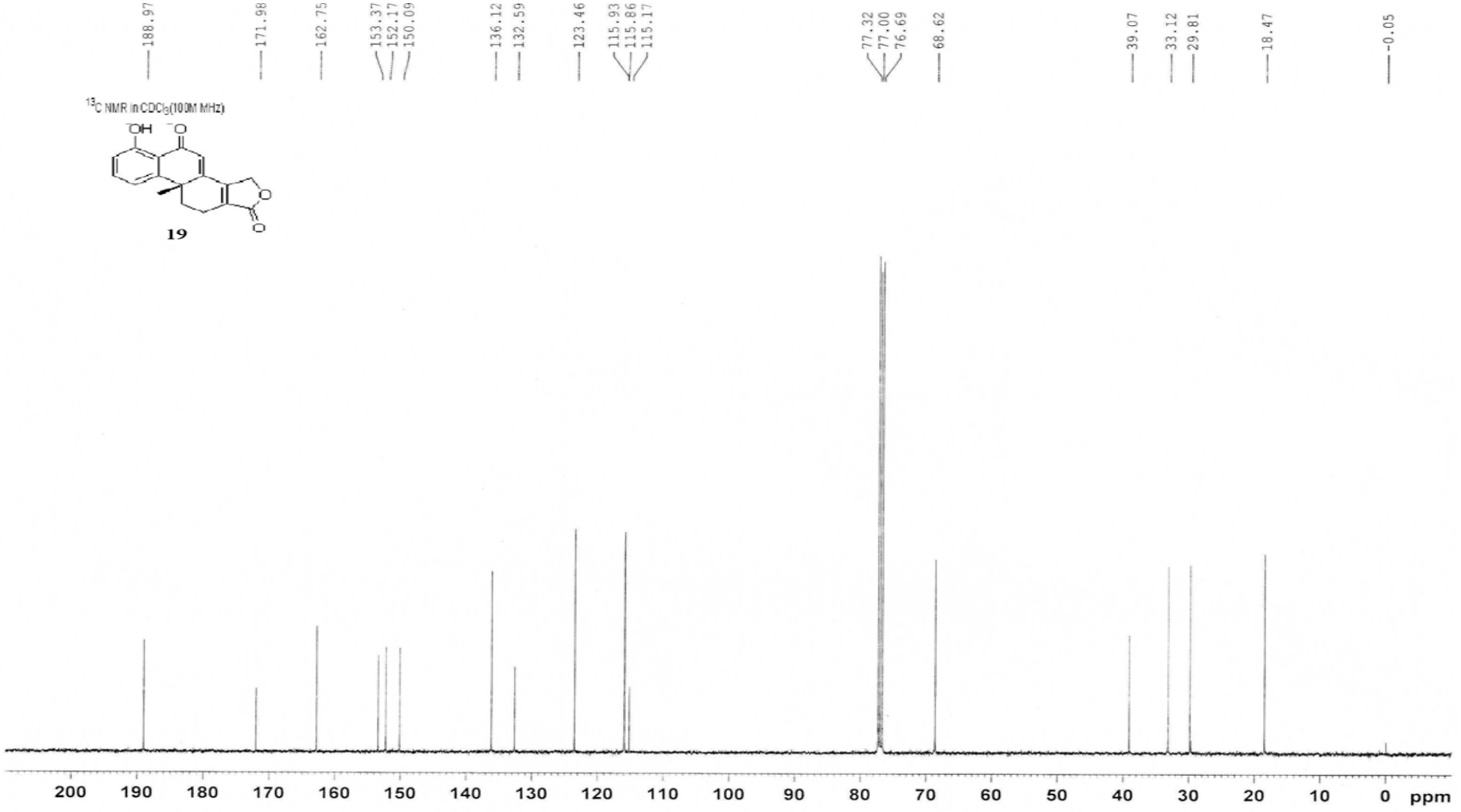


	channel	retenttion time(min)	area	%area	height
1	2998 (210-400)	6.801	6317	0.54	623
2	2998 (210-400)	8.601	1166112	99.46	12761

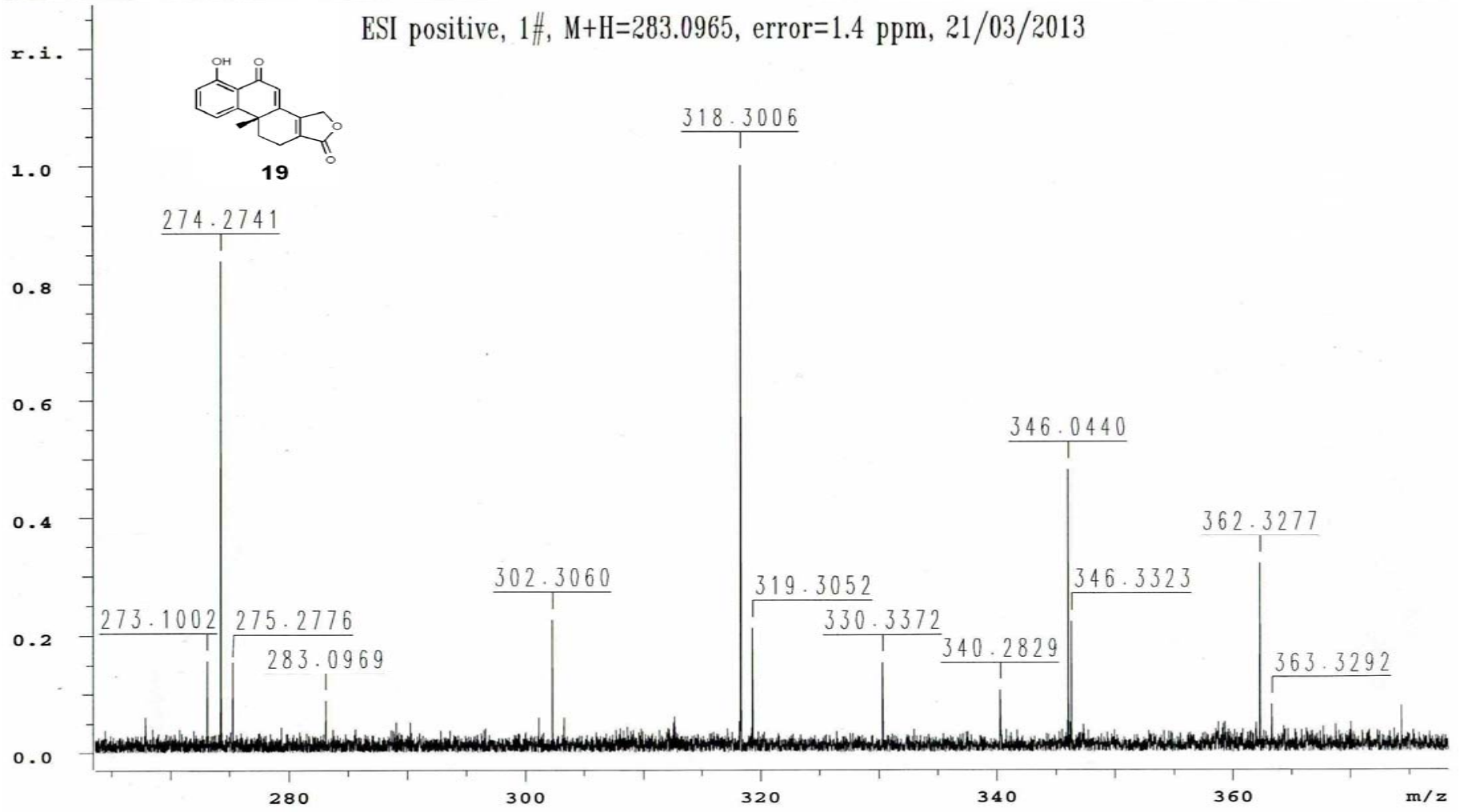
3.10. **^{1}H NMR of *(R)-6-hydroxy-9b-methyl-10,11-dihydrophenanthro[1,2-c]furan-1,5(3H,9bH)- dione (19).***



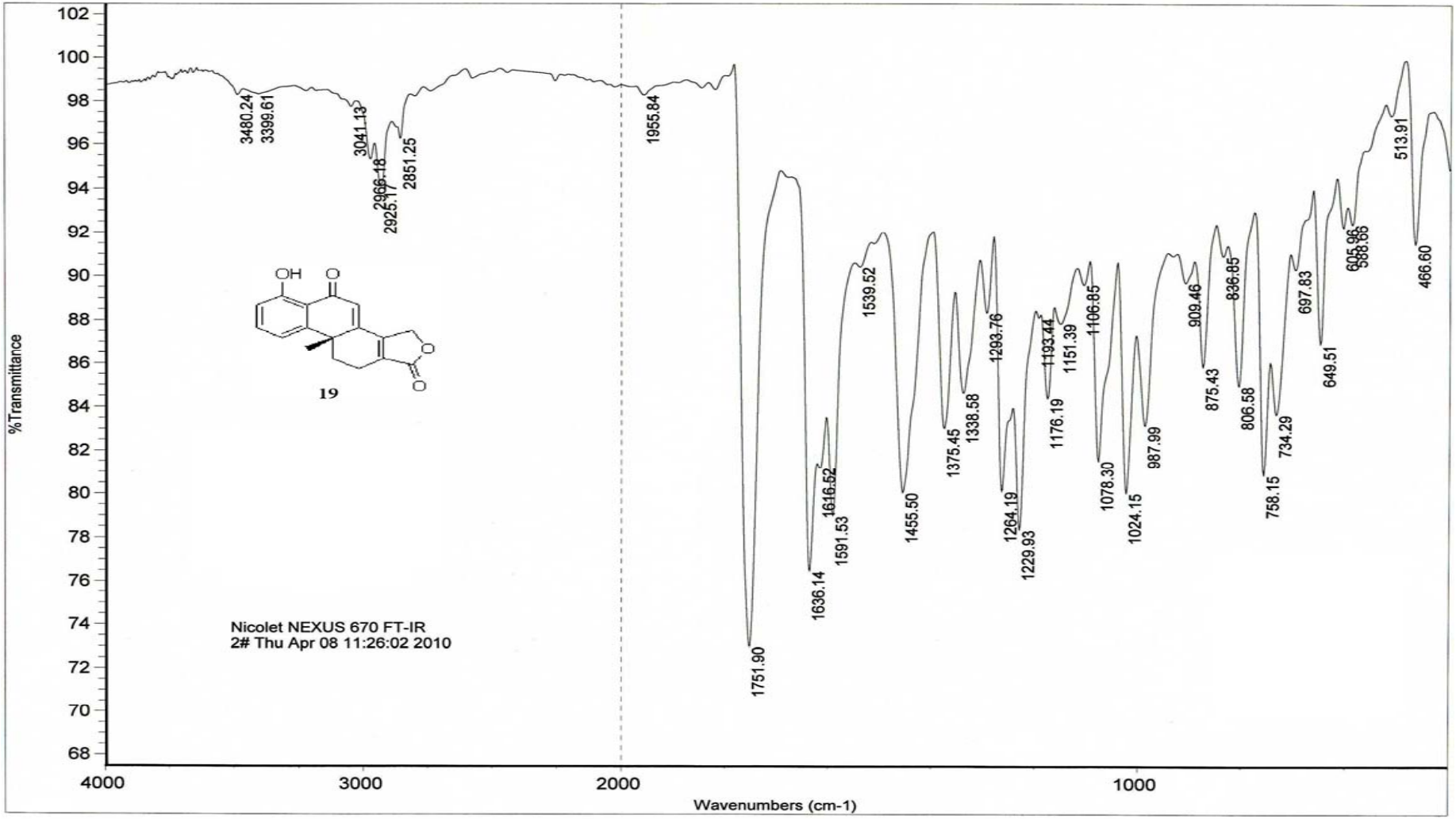
^{13}C NMR of *(R)-6-hydroxy-9b-methyl-10,11-dihydrophenanthro[1,2-c]furan-1,5(3H,9bH)- dione (19).*



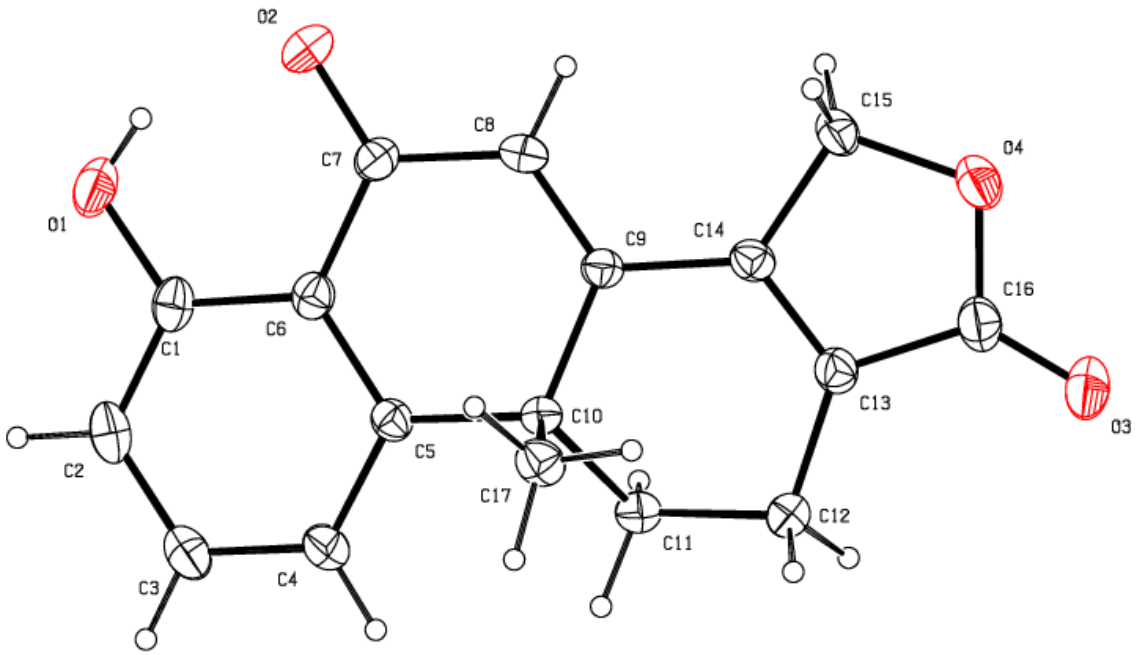
HRMS-ESI of *(R)-6-hydroxy-9b-methyl-10,11-dihydrophenanthro[1,2-c]furan-1,5(3H,9bH)- dione (19).*



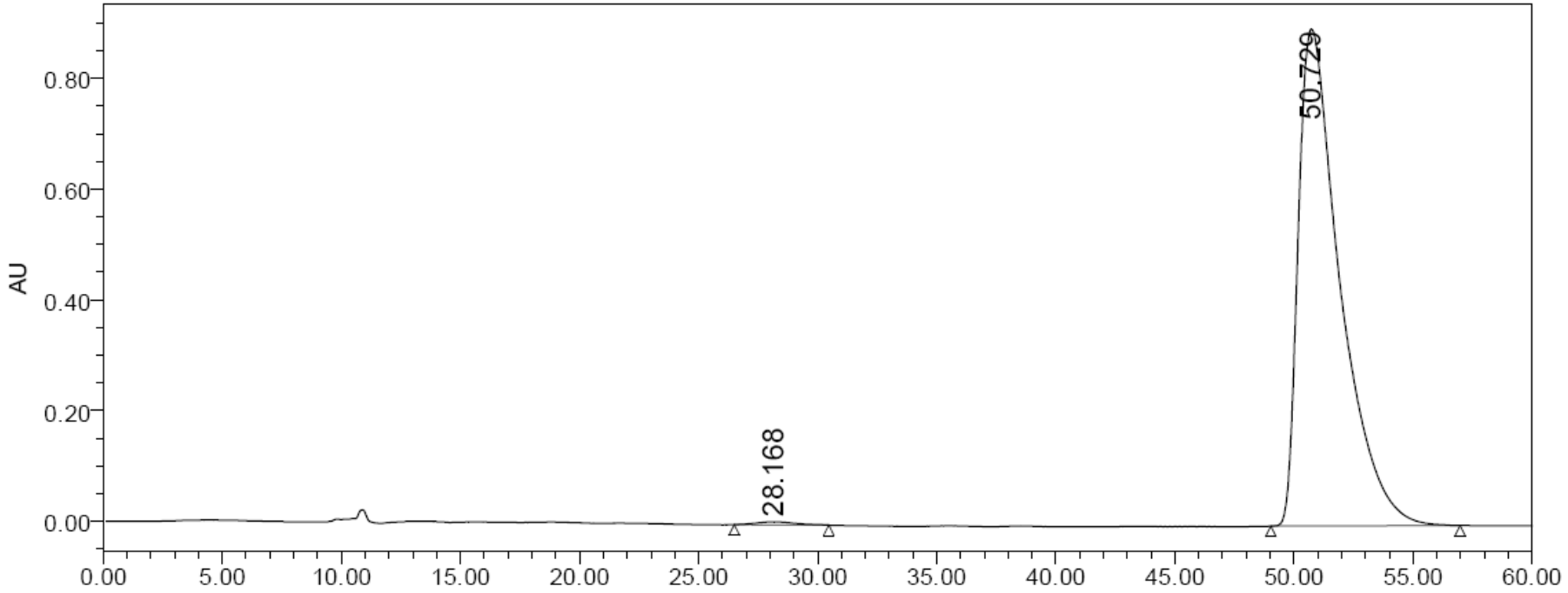
IR of *(R)-6-hydroxy-9b-methyl-10,11-dihydrophenanthro[1,2-c]furan-1,5(3H,9bH)- dione (19).*



X-ray structure of compound 19:

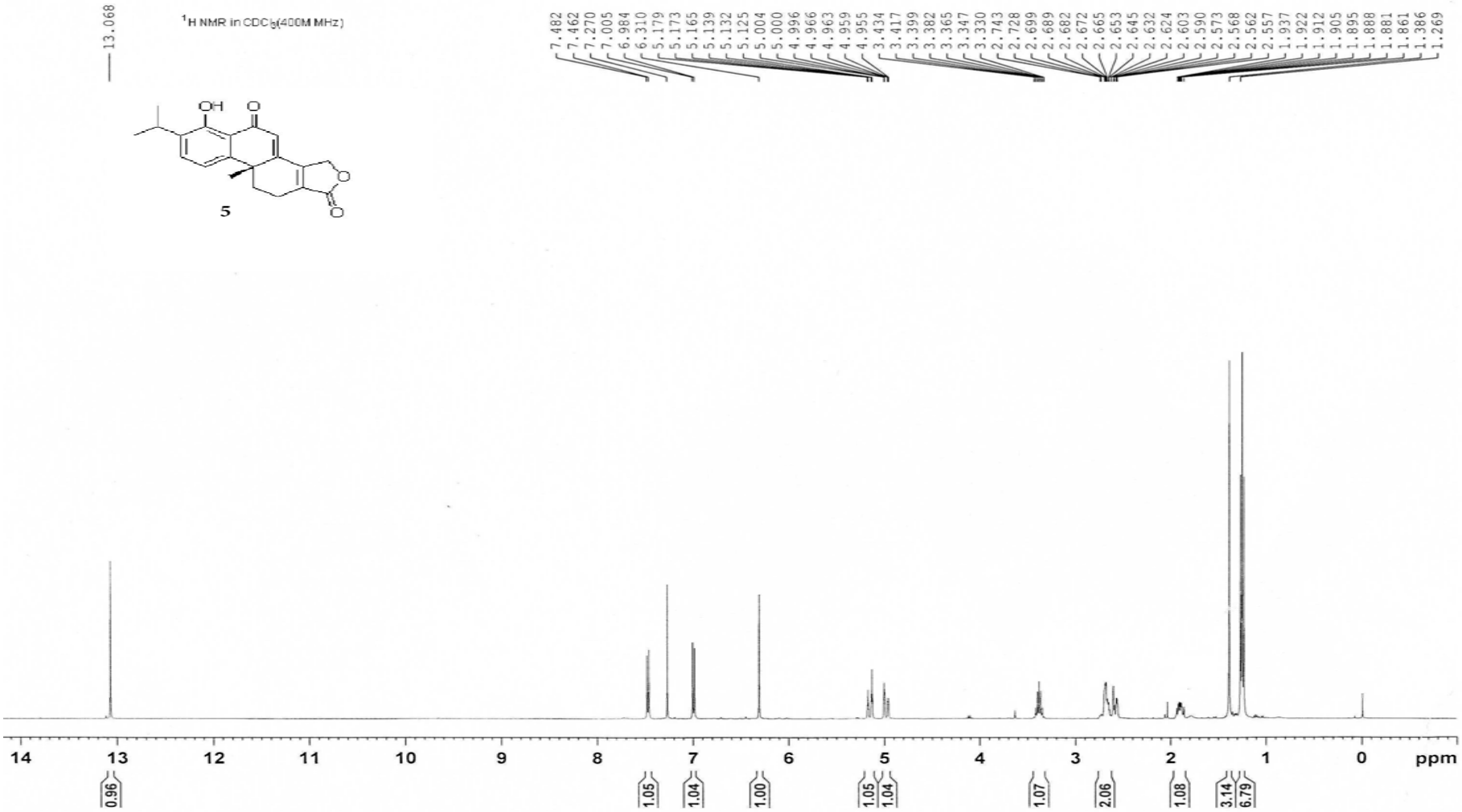


Chiral HPLC fro ee value of *(R)-6-hydroxy-9b-methyl-10,11-dihydrophenanthro[1,2-c]furan-1,5(3H,9bH)- dione (19).*

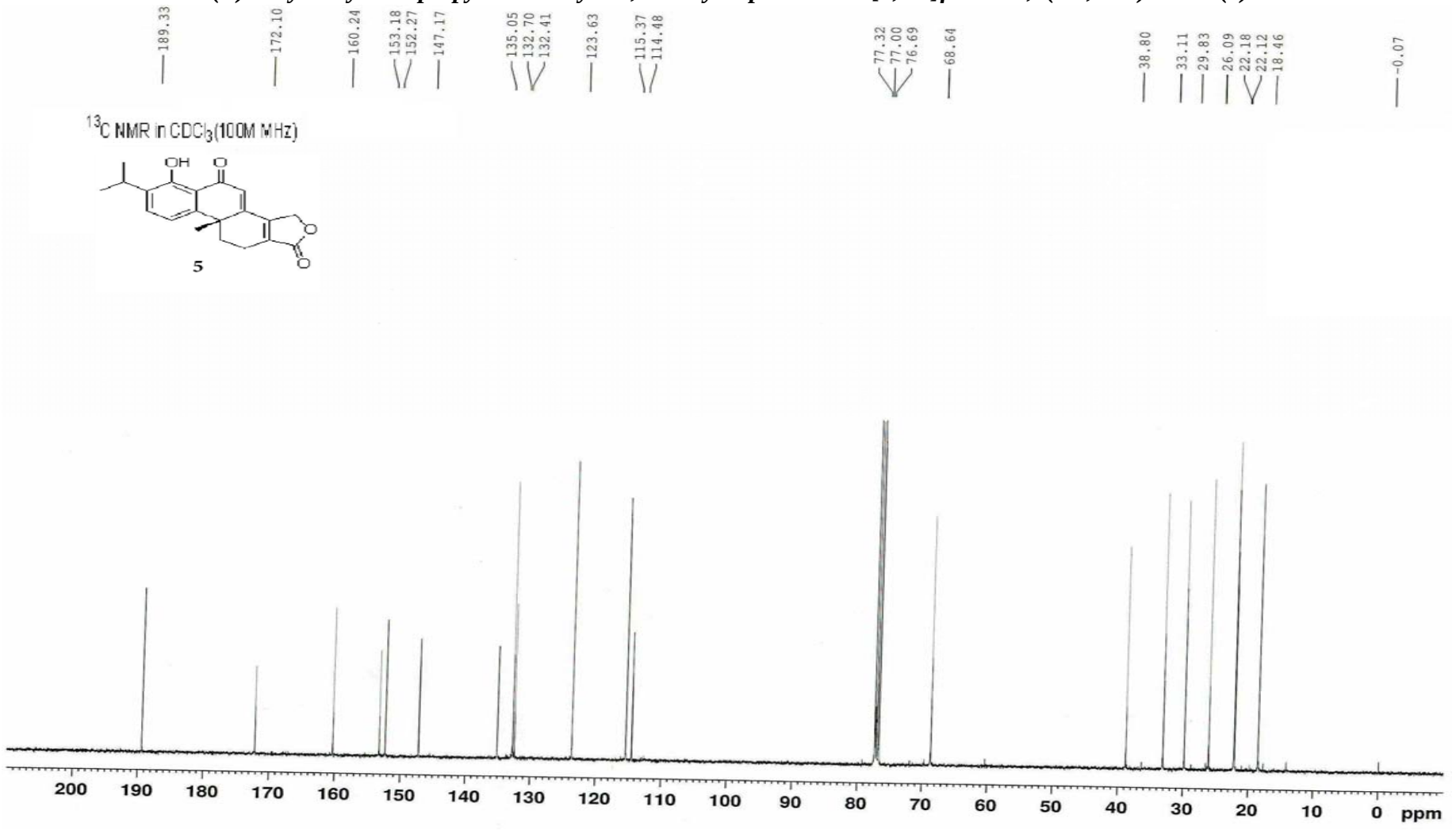


	channel	retenttion time(min)	area	%area	height
1	2998 (210-400)	28.168	634441	0.58	5765
2	2998 (210-400)	50.729	109232924	99.42	897220

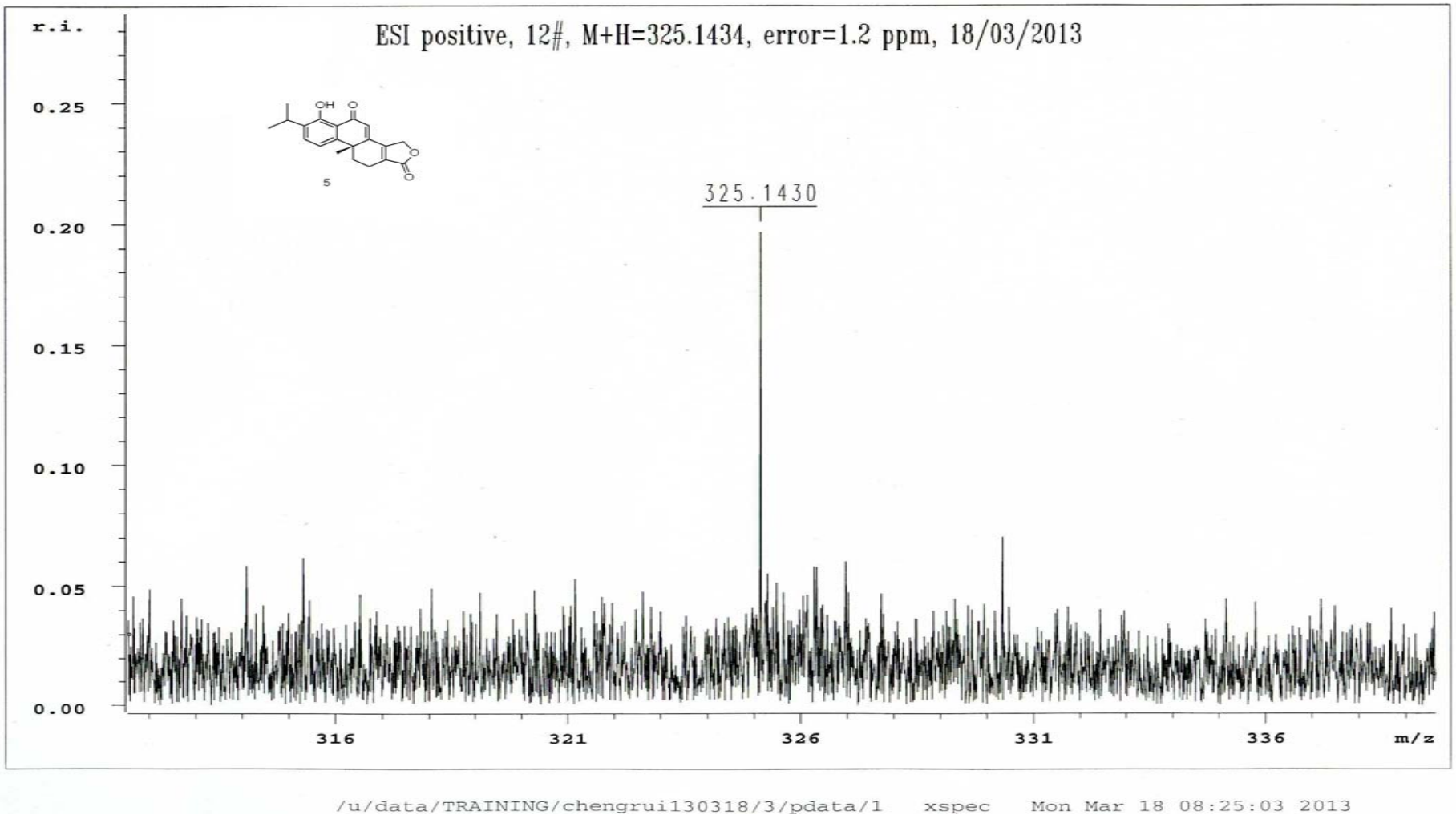
3.11. **^{1}H NMR of *(R)-6-hydroxy-7-isopropyl-9b-methyl-10,11-dihydrophenanthro[1,2-c]furan-1, 5(3H,9bH)-dione (5).***



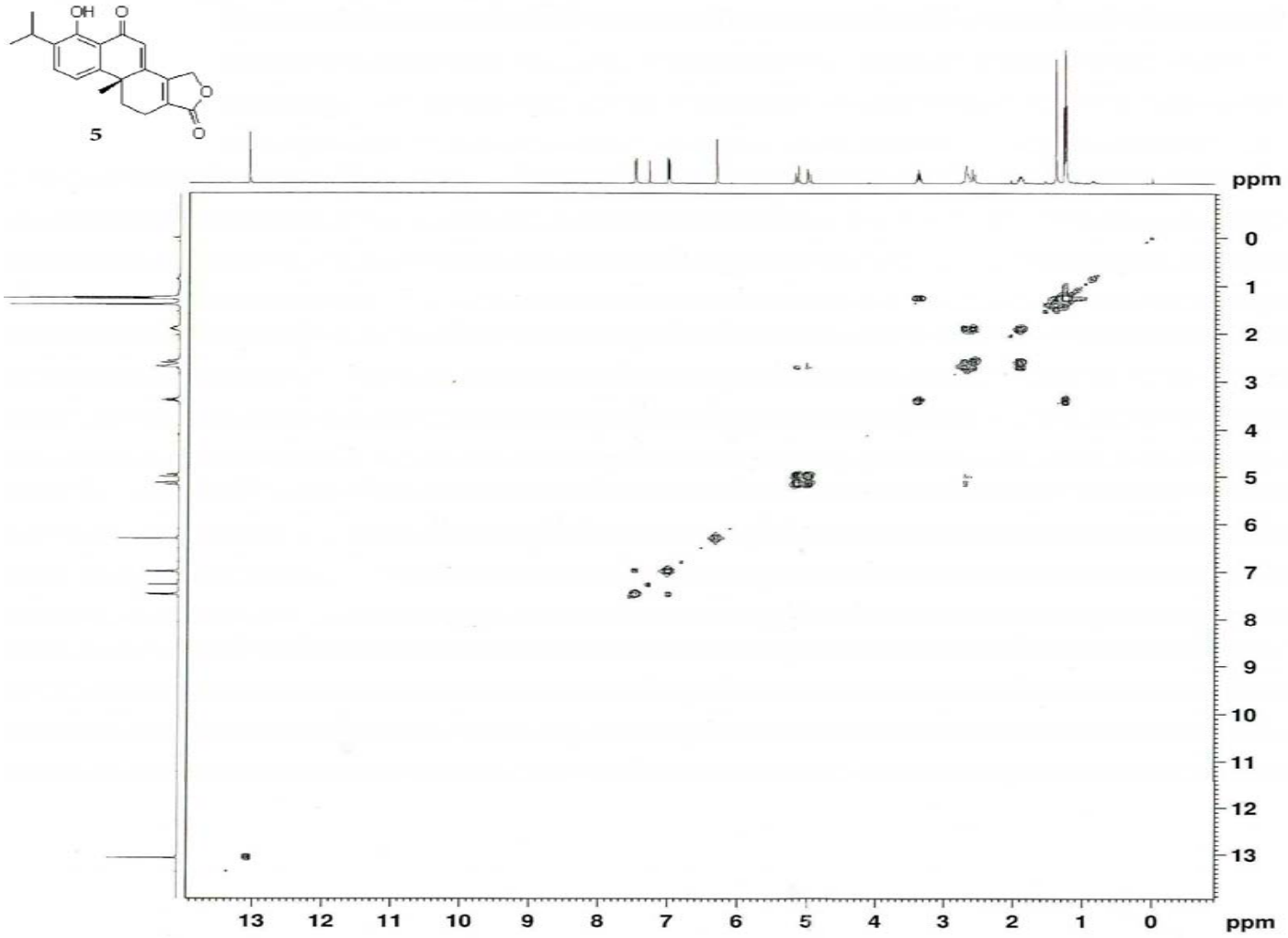
^{13}C NMR of *(R)-6-hydroxy-7-isopropyl-9b-methyl-10,11-dihydrophenanthro[1,2-c]furan- 1,5(3H,9bH)-dione (5).*



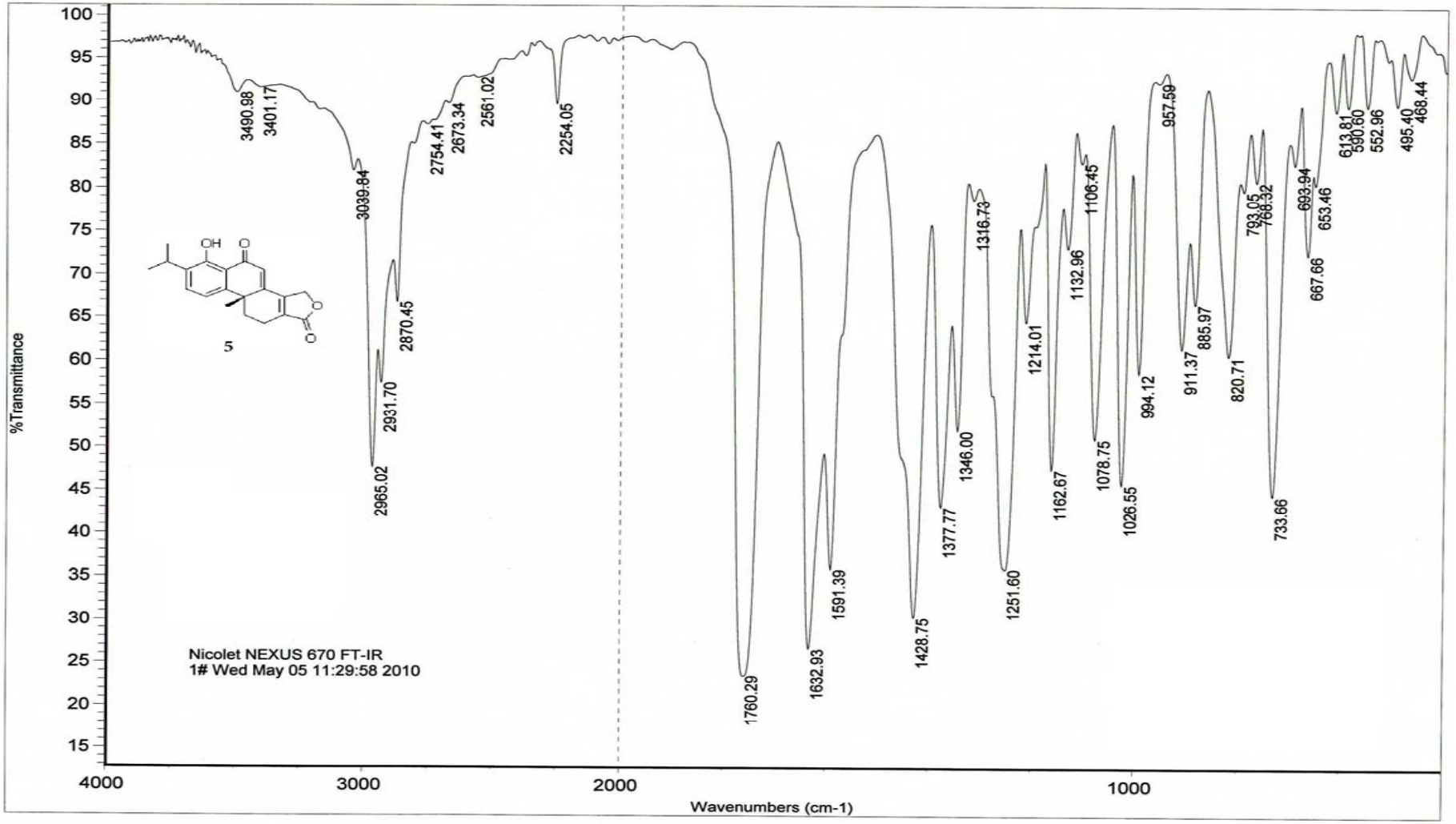
HRMS-ESI of (R)-6-hydroxy-7-isopropyl-9b-methyl-10,11-dihydrophenanthro[1,2-c]furan-1, 5(3H,9bH) -dione (5).



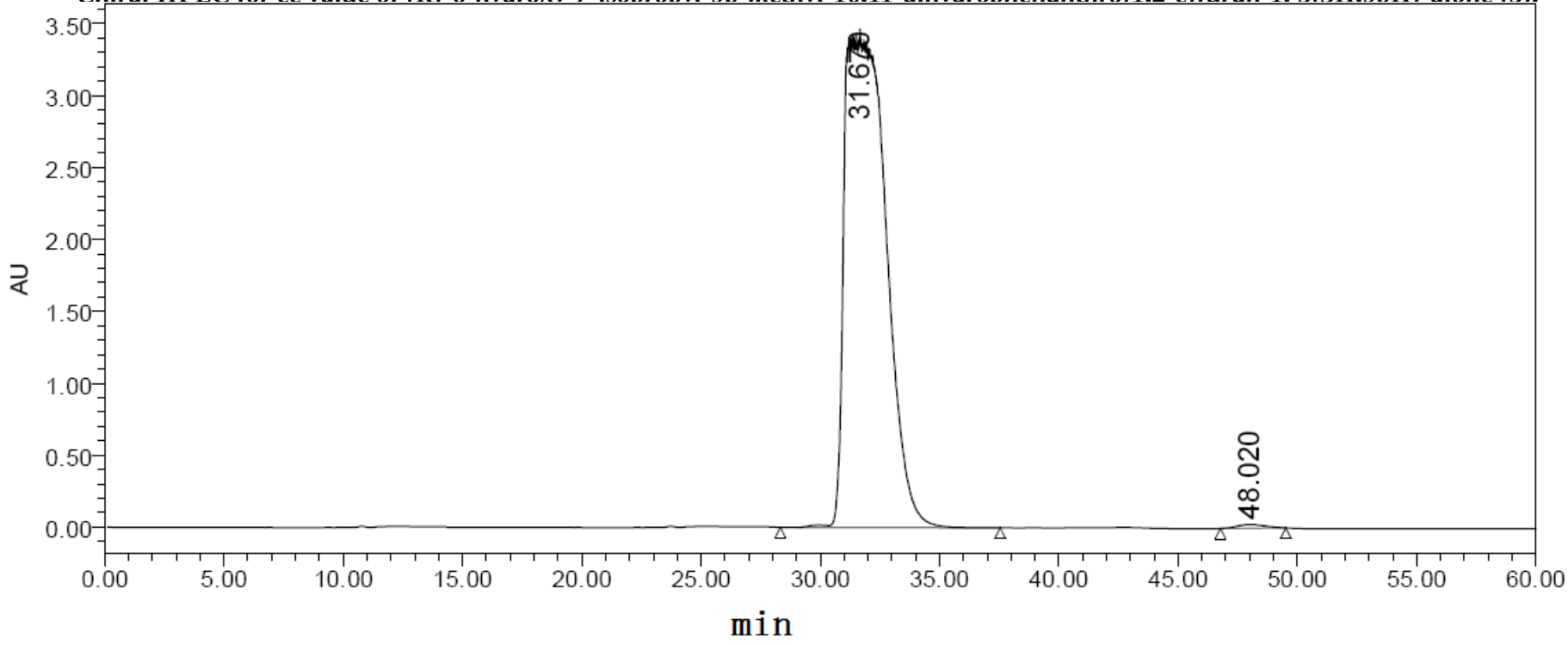
H-H COSY of (R)-6-hydroxy-7-isopropyl-9b-methyl-10,11-dihydrophenanthro[1,2-c]furan-1, 5(3H,9bH)-dione (5).



IR of (R)-6-hydroxy-7-isopropyl-9b-methyl-10,11-dihydrophenanthro[1,2-c]furan-1, 5(3H,9bH)-dione (5).

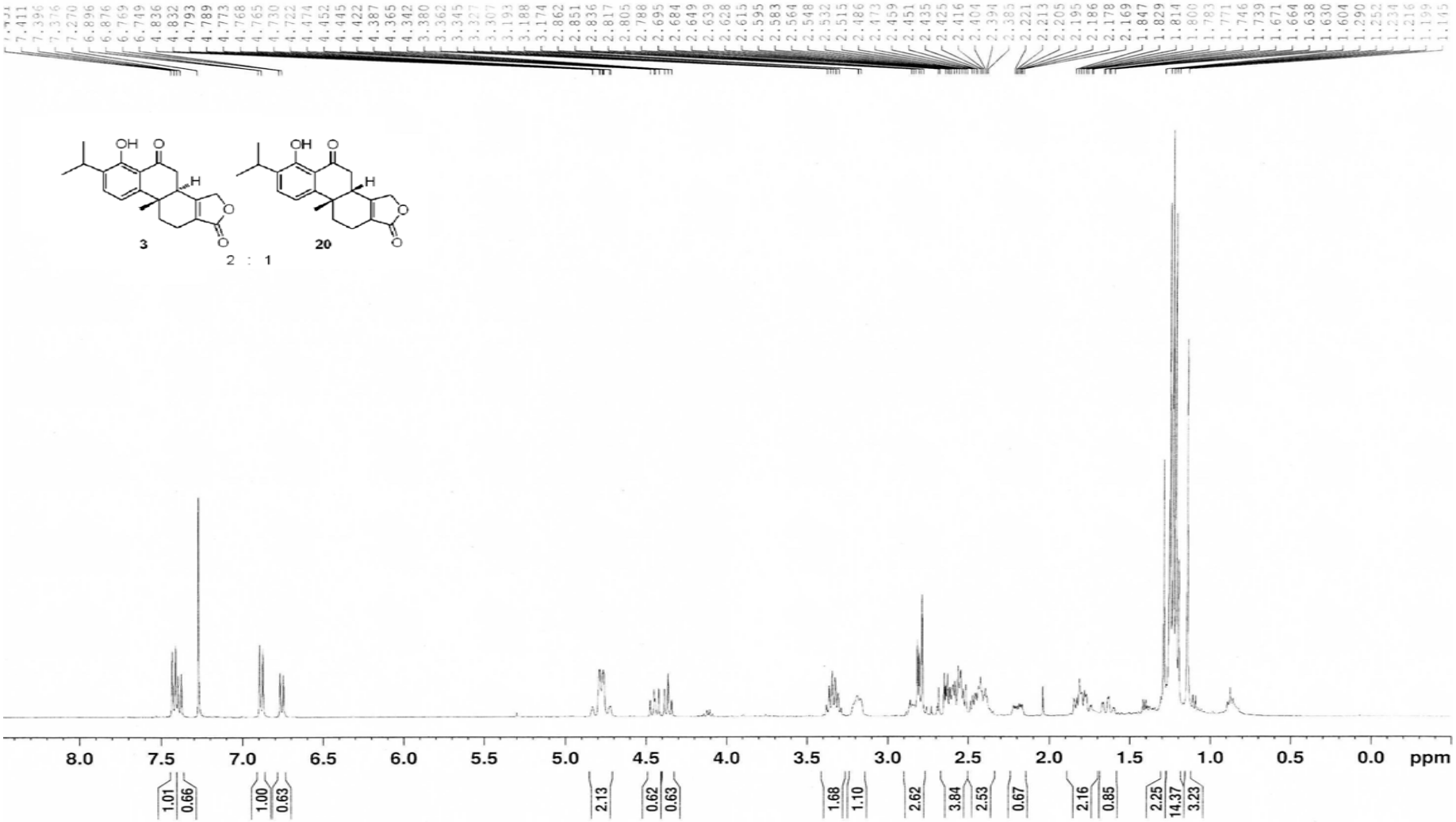


Chiral HPLC for ee value of (R)-6-hydroxy-7-isopropyl-9b-methyl-10,11-dihydrophenanthro[1,2-c]furan-1, 5(3H,9bH)-dione (5).

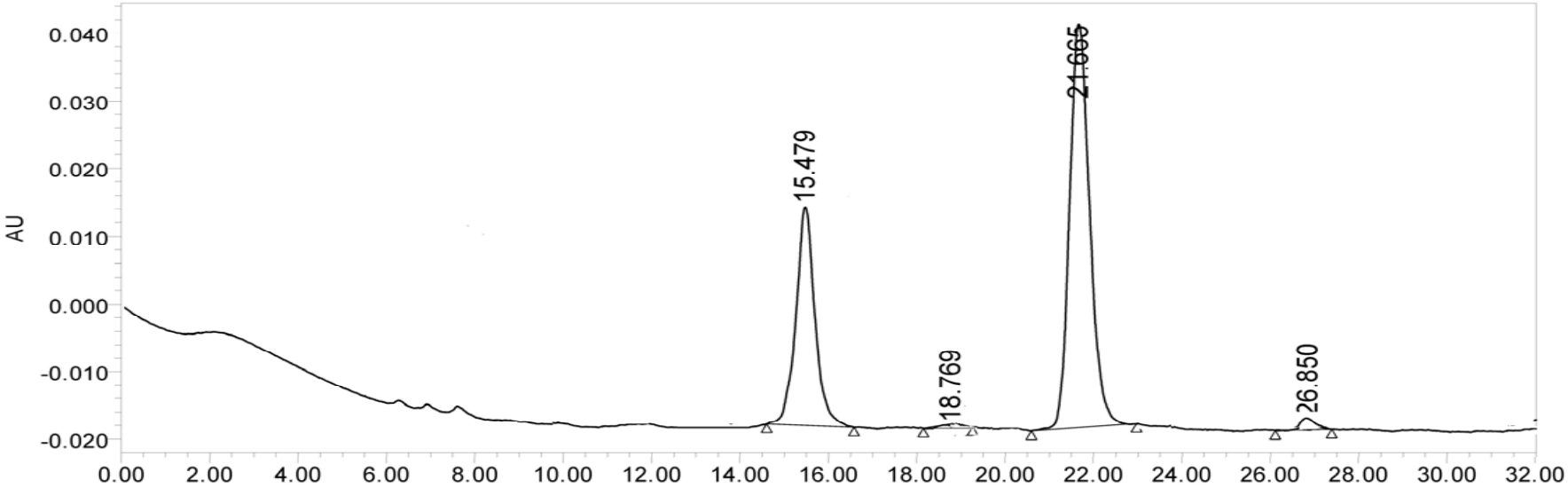


	channel	retenttion time(min)	area	%area	height
1	2998 (210-400)	31.670	415636609	99.52	3463472
2	2998 (210-400)	48.020	2008212	0.48	25573

3.12 **^{1}H NMR of the mixture of *4* and *20* prepared from Compound 5**

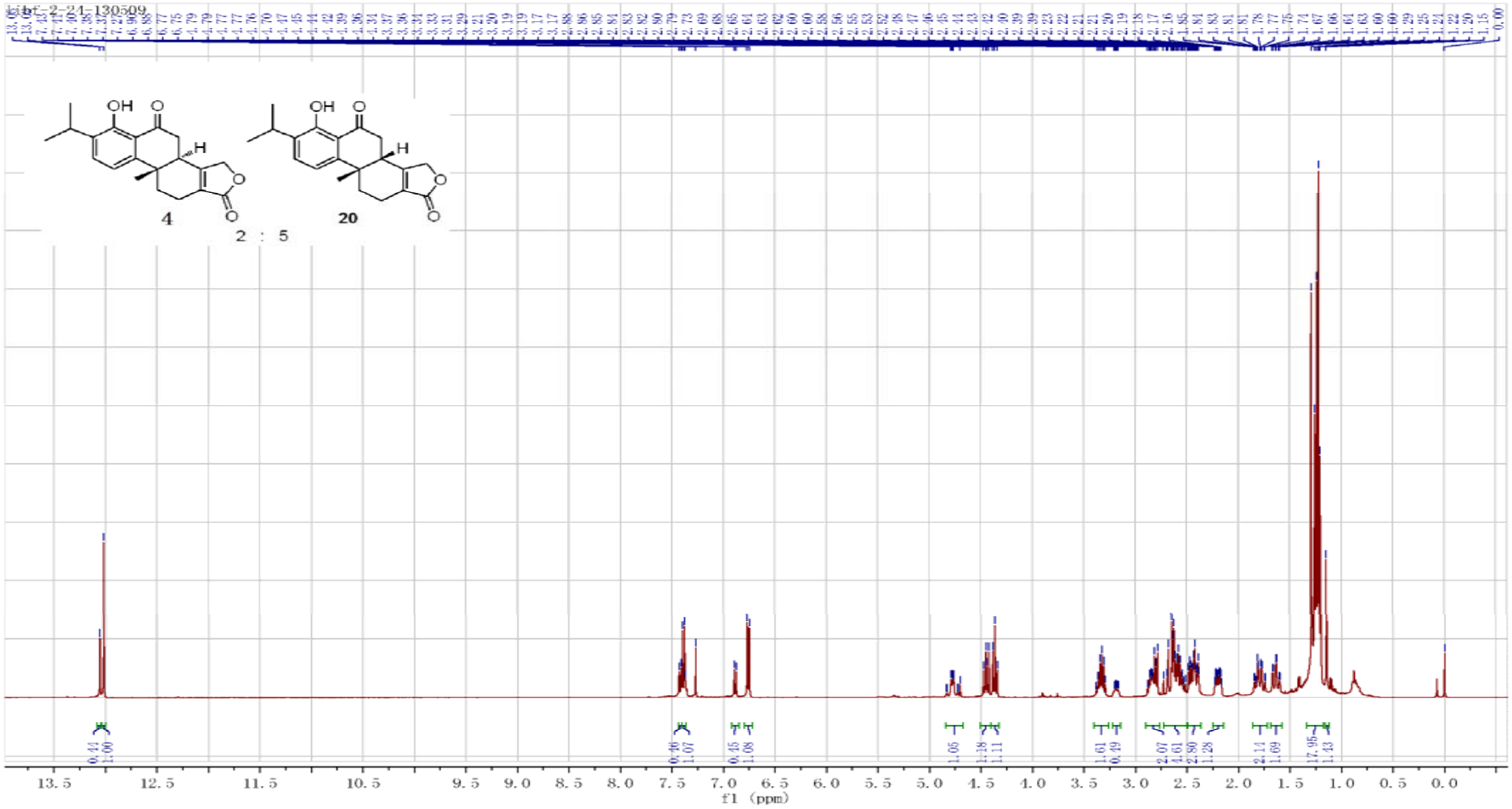


Chiral HPLC for ee and de value of the mixture of 4 and 20 prepared from Compound 5.

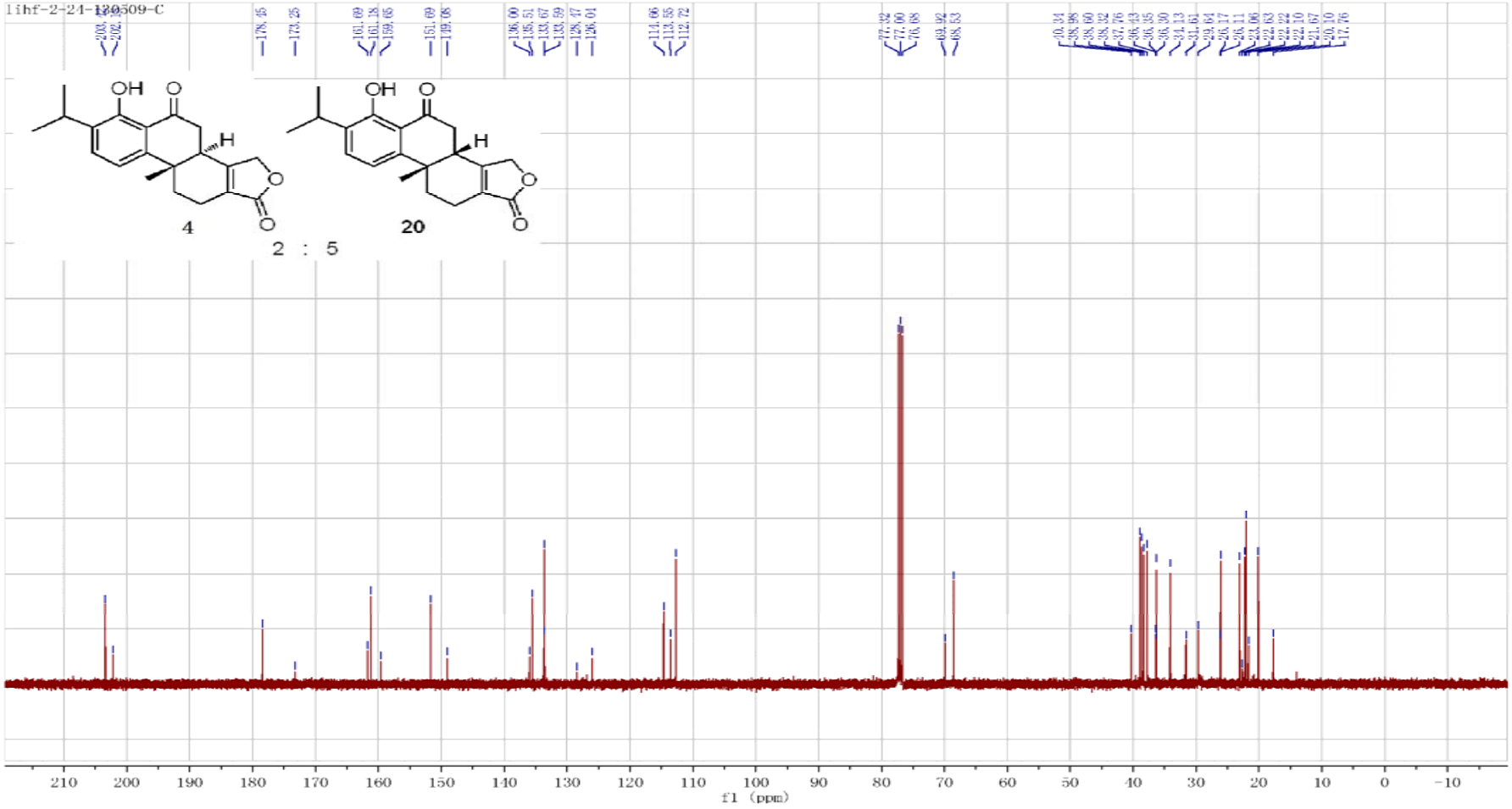


	channel	retenttion time(min)	area	%area	height
1	2998 (210-400)	15.479	971717	33.60	32284
2	2998 (210-400)	18.769	6495	0.22	332
3	2998 (210-400)	21.665	1895695	65.56	59681
4	2998 (210-400)	26.850	17849	0.62	579

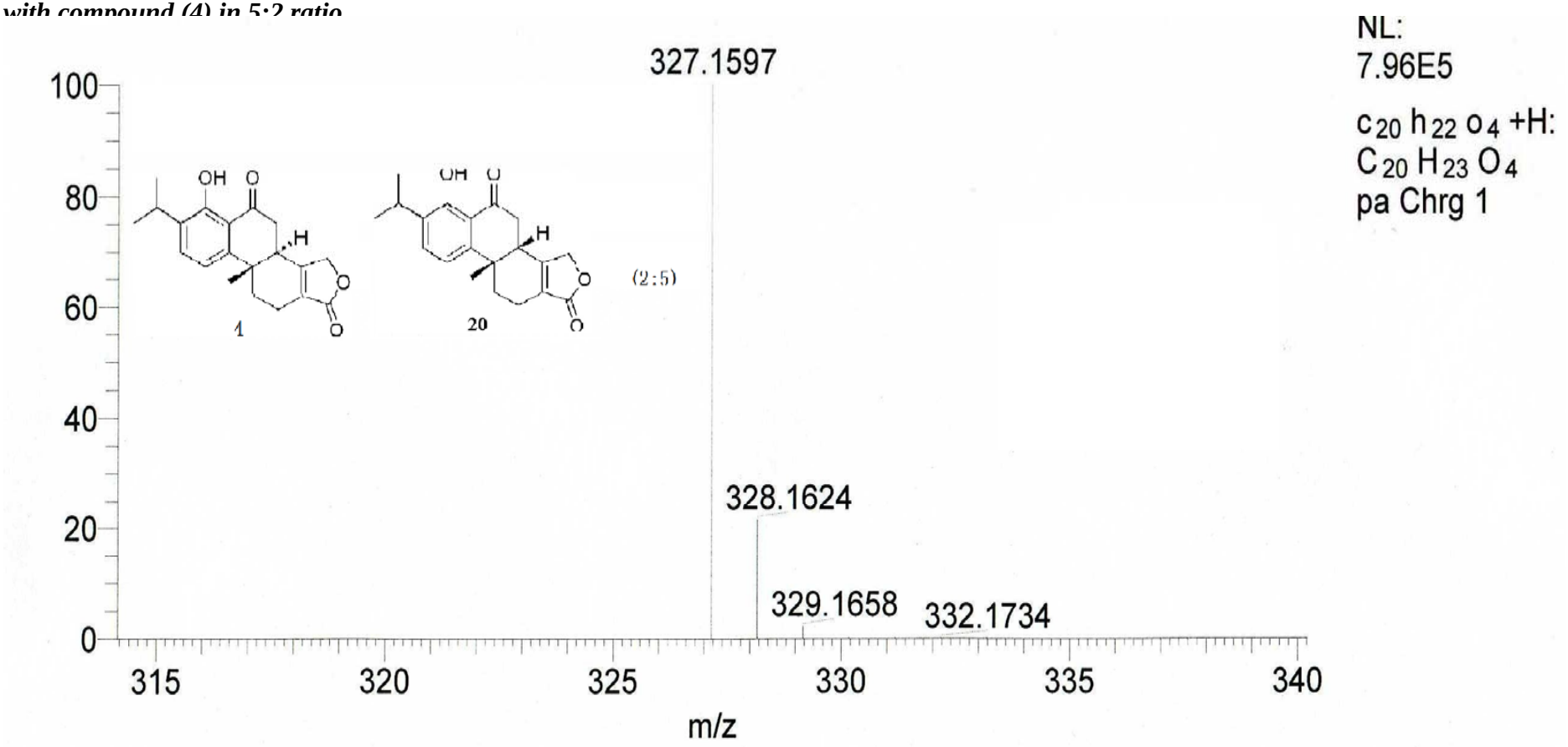
3.13. ^{1}H NMR of (3bS,9bS)-6-hydroxy-7-isopropyl-9b-methyl-3b,4,10,11-tetrahydrophenanthro[1,2-c]furan-1,5(3H,9bH)-dione (20) along with compound (4) in 5:2 ratio



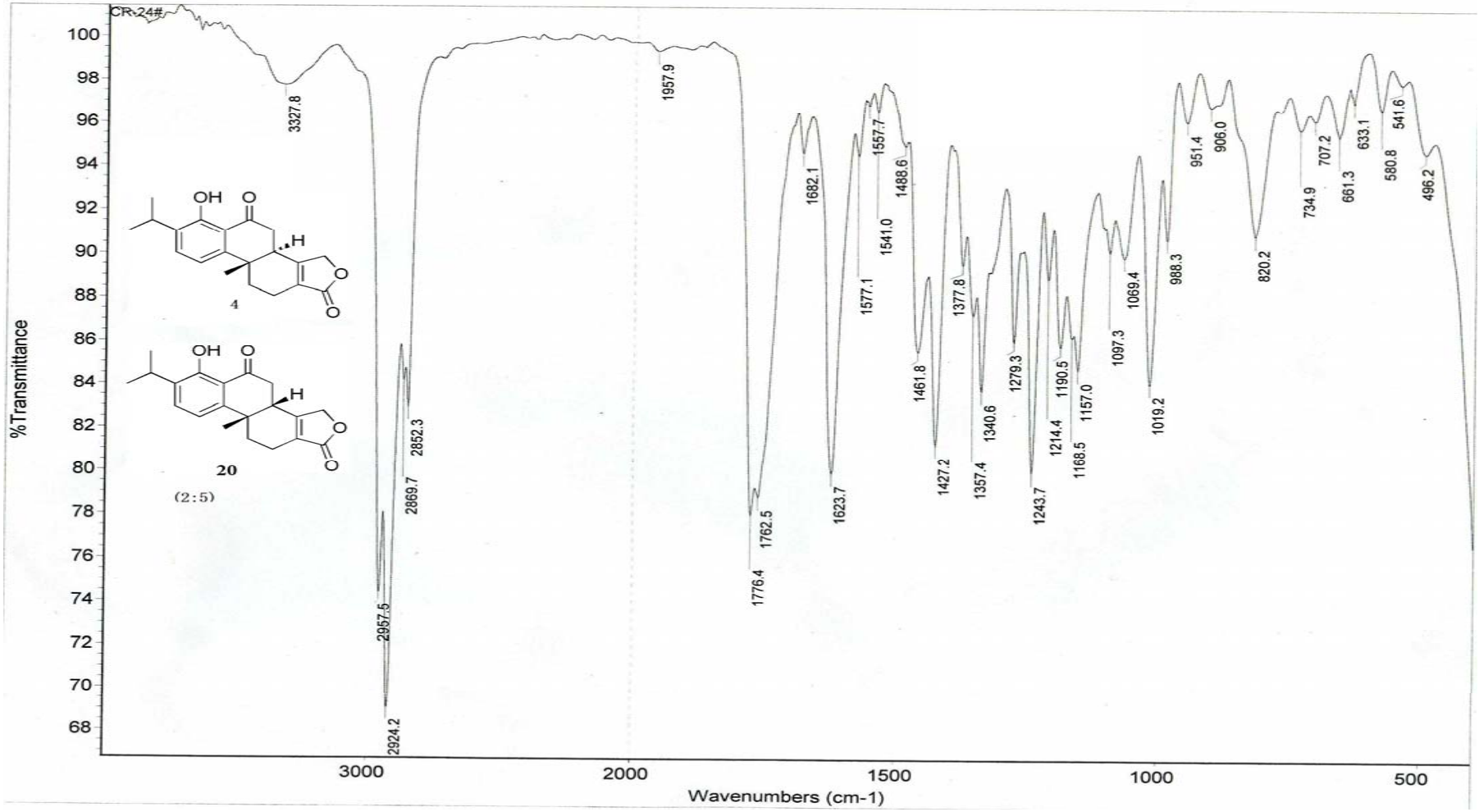
^{31}C NMR of (3bS,9bS)-6-hydroxy-7-isopropyl-9b-methyl-3b,4,10,11- tetrahydrophenanthro[1,2-c]furan -1,5(3H, 9bH)-dione (20) along with compound (4) in 5:2 ratio



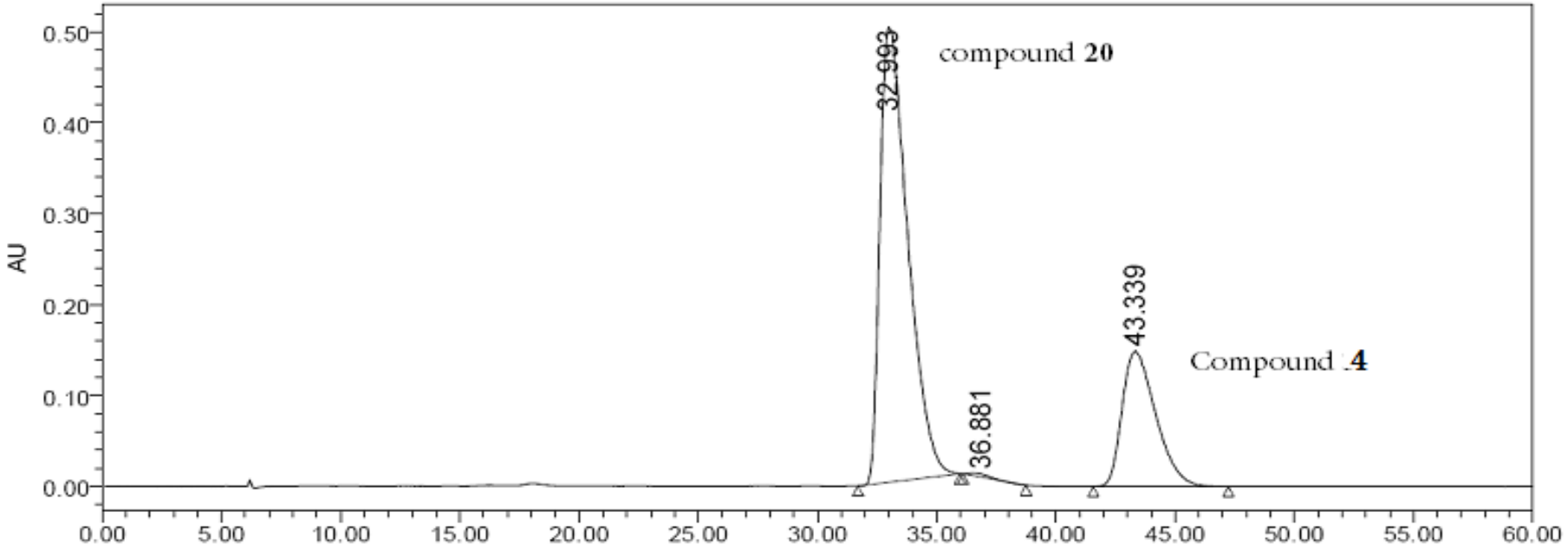
HR-MS of ((3bS,9bS)-6-hydroxy-7-isopropyl-9b-methyl-3b,4,10,11-tetrahydrophenanthro [1,2-c]furan -1,5(3H, 9bH)-dione (20) along with compound (4) in 5:2 ratio



IR of (3bS,9bS)-6-hydroxy-7-isopropyl-9b-methyl-3b,4,10,11-tetrahydrophenanthro [1,2-c]furan -1,5(3H, 9bH)-dione (20) along with compound (4) in 5:2 ratio

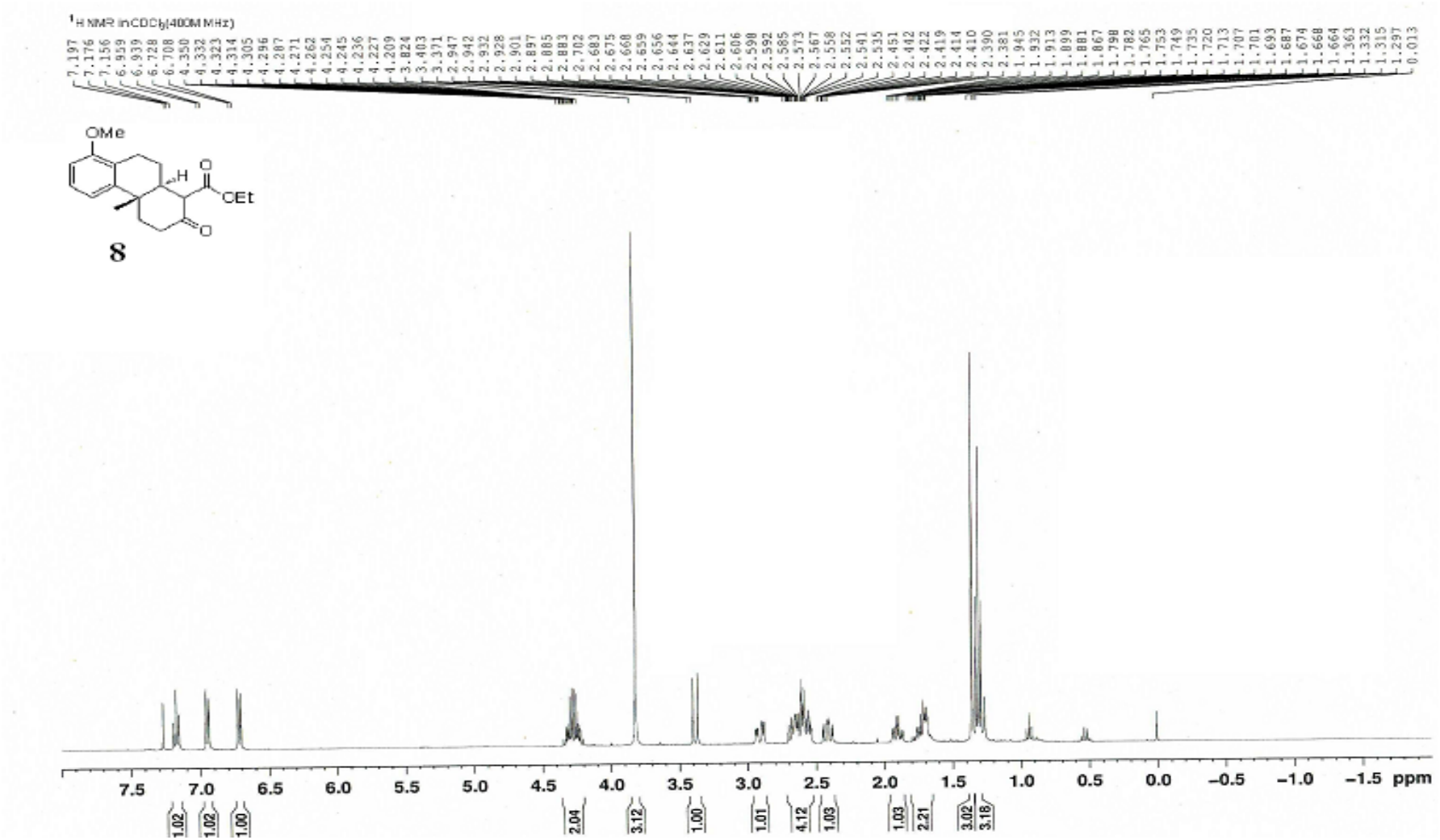


Chiral HPLC for ee value of (3bS,9bS)-6-hydroxy-7-isopropyl-9b-methyl-3b,4,10,11-tetrahydrophenanthro [1,2-c]furan -1,5(3H, 9bH)-dione (20) along with compound (4) in 5:2 ratio

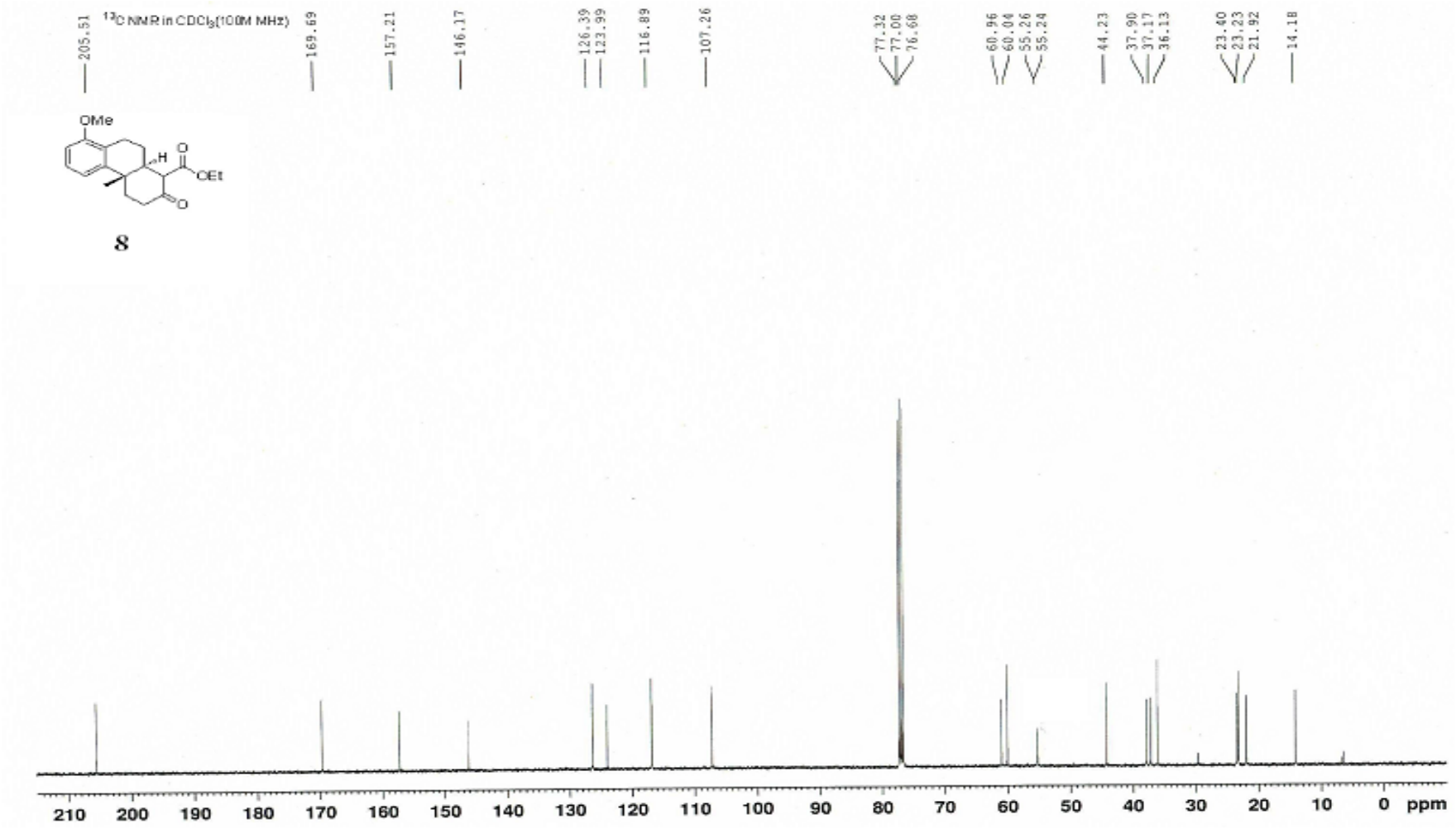


	channel	retenttion time(min)	area	%area	height
1	2998 (210-400)	32.993	40749295	73.37	500471
2	2998 (210-400)	36.881	1 199286	0.36	3331
3	2998 (210-400)	43.339	14591106	26.27	148858

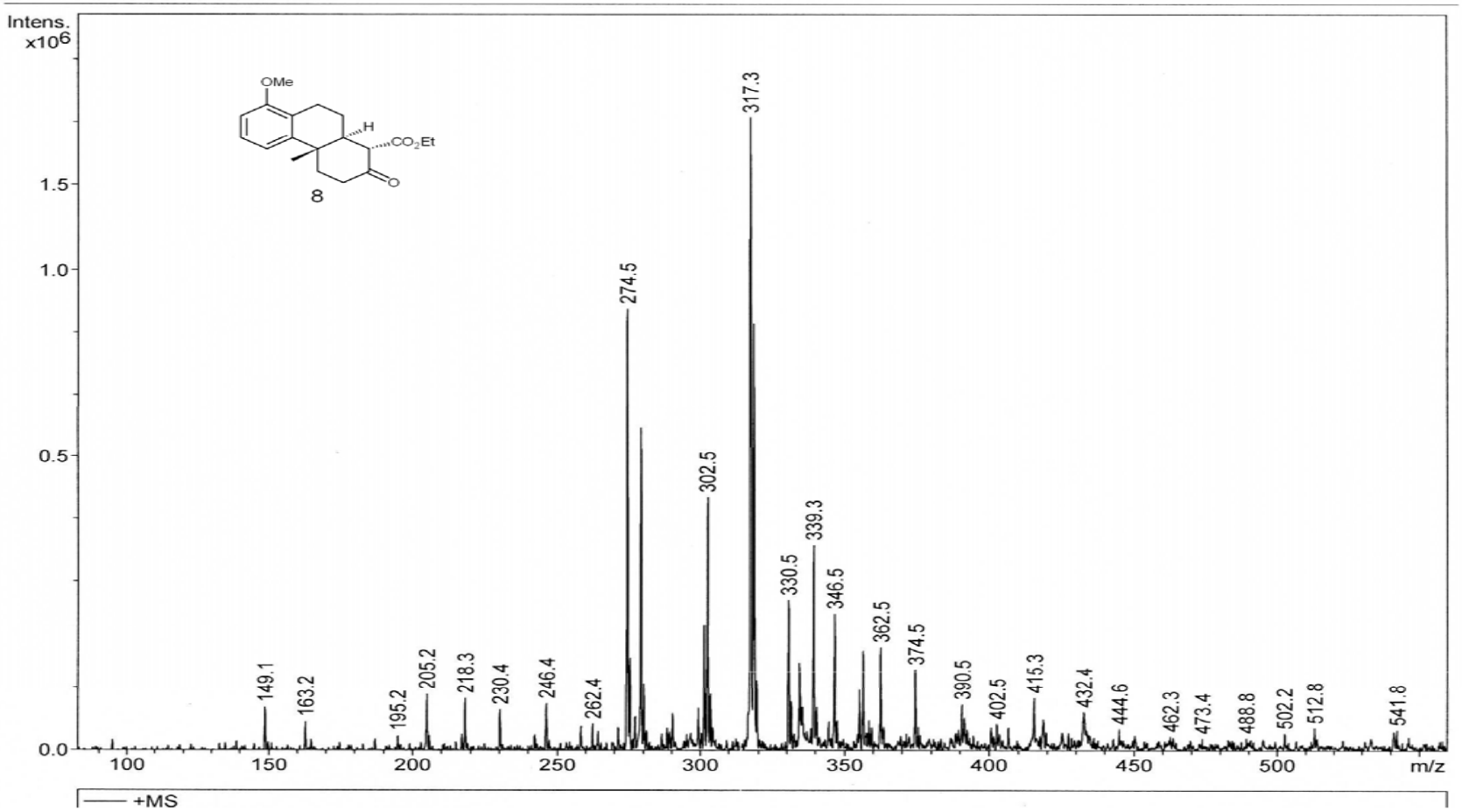
3.14. **^{1}H NMR of *(4aS,10aS)-ethyl 8-methoxy-4a-methyl-2-oxo-1,2,3,4,4a,9,10,10a- octahydrophenanthrene-1- carboxylate (8).***



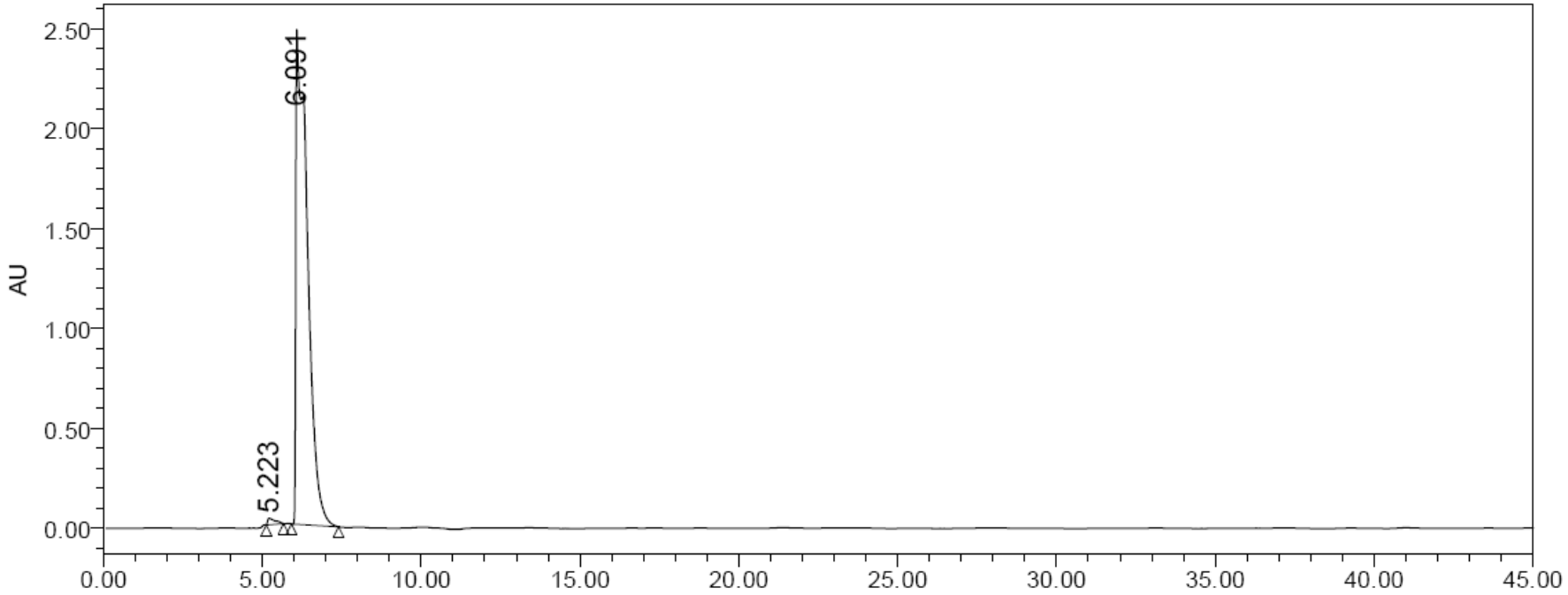
^{13}C NMR of *(4aS,10aS)-ethyl 8-methoxy-4a-methyl-2-oxo-1,2,3,4,4a,9,10,10a- octahydrophenanthrene-1- carboxylate (8).*



ESI-MS of *(4aS,10aS)-ethyl 8-methoxy-4a-methyl-2-oxo-1,2,3,4,4a,9,10,10a- octahydrophenanthrene-1- carboxylate (8).*

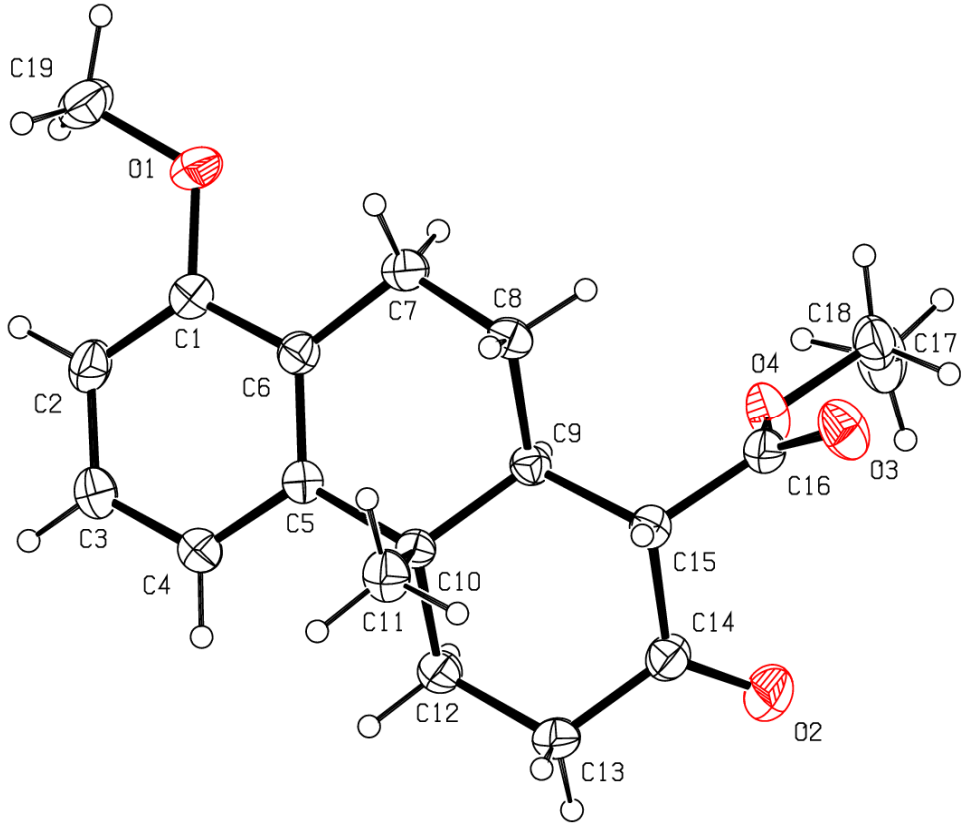


Chiral HPLC for ee value of *(4aS,10aS)-ethyl 8-methoxy-4a-methyl-2-oxo-1,2,3,4,4a,9,10,10a- octahydrophenanthrene-1-carboxylate (8).*

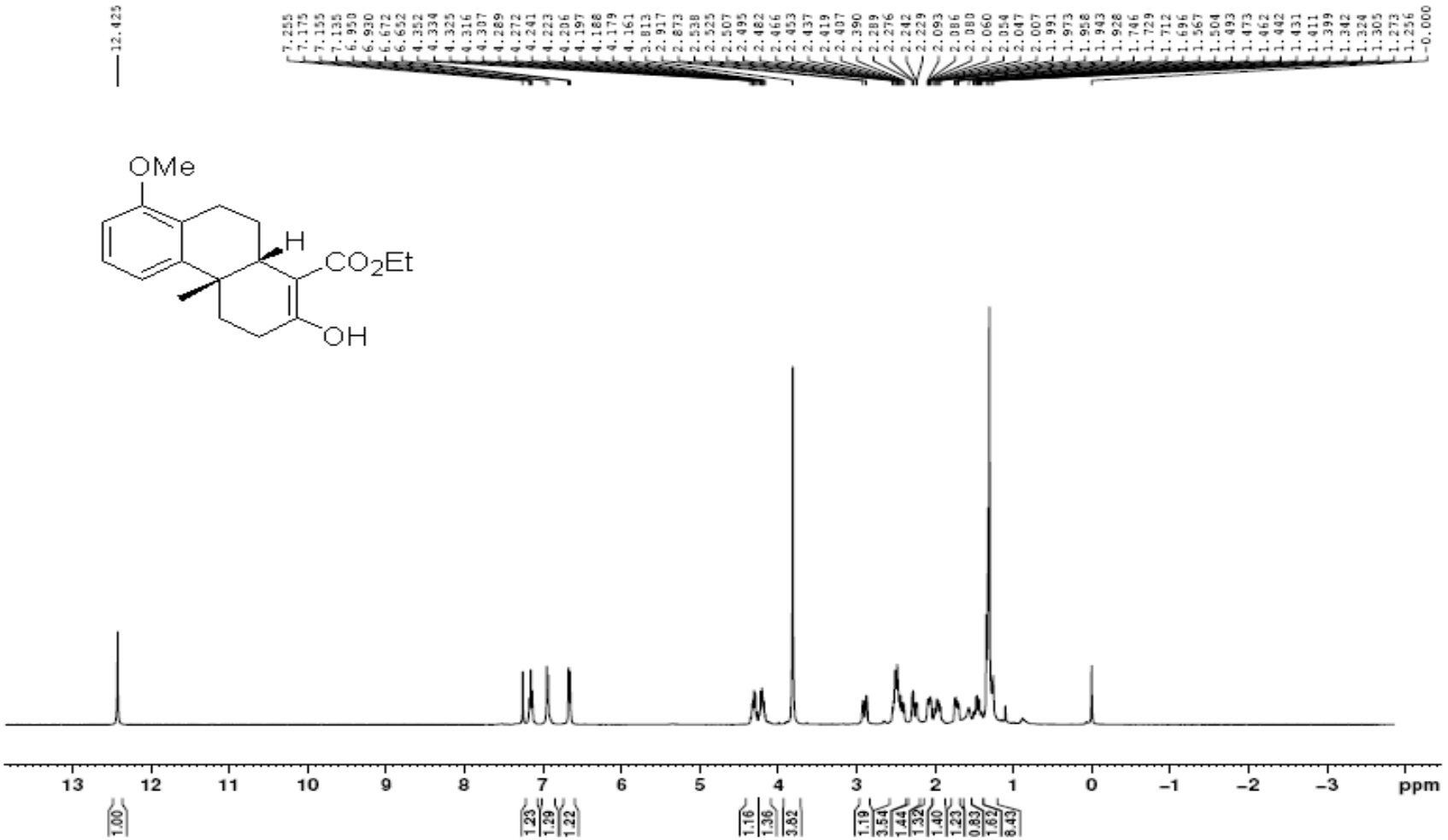


	channel	retenttion time(min)	area	%area	height
1	2998 (210-400)	5.223	545909	0.86	31931
2	2998 (210-400)	6.091	62670305	99.14	2475490

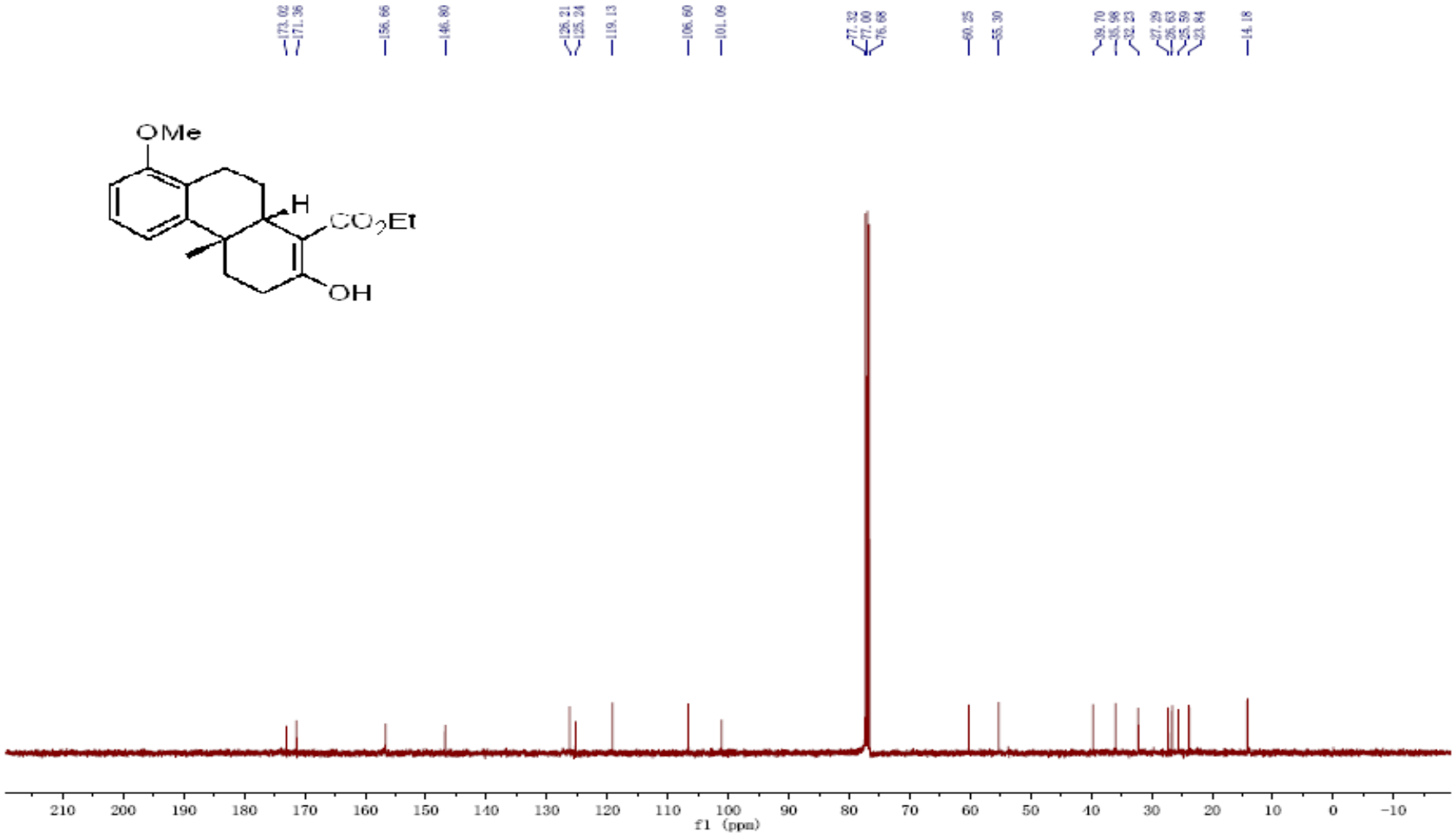
X-ray structure of compound 8:



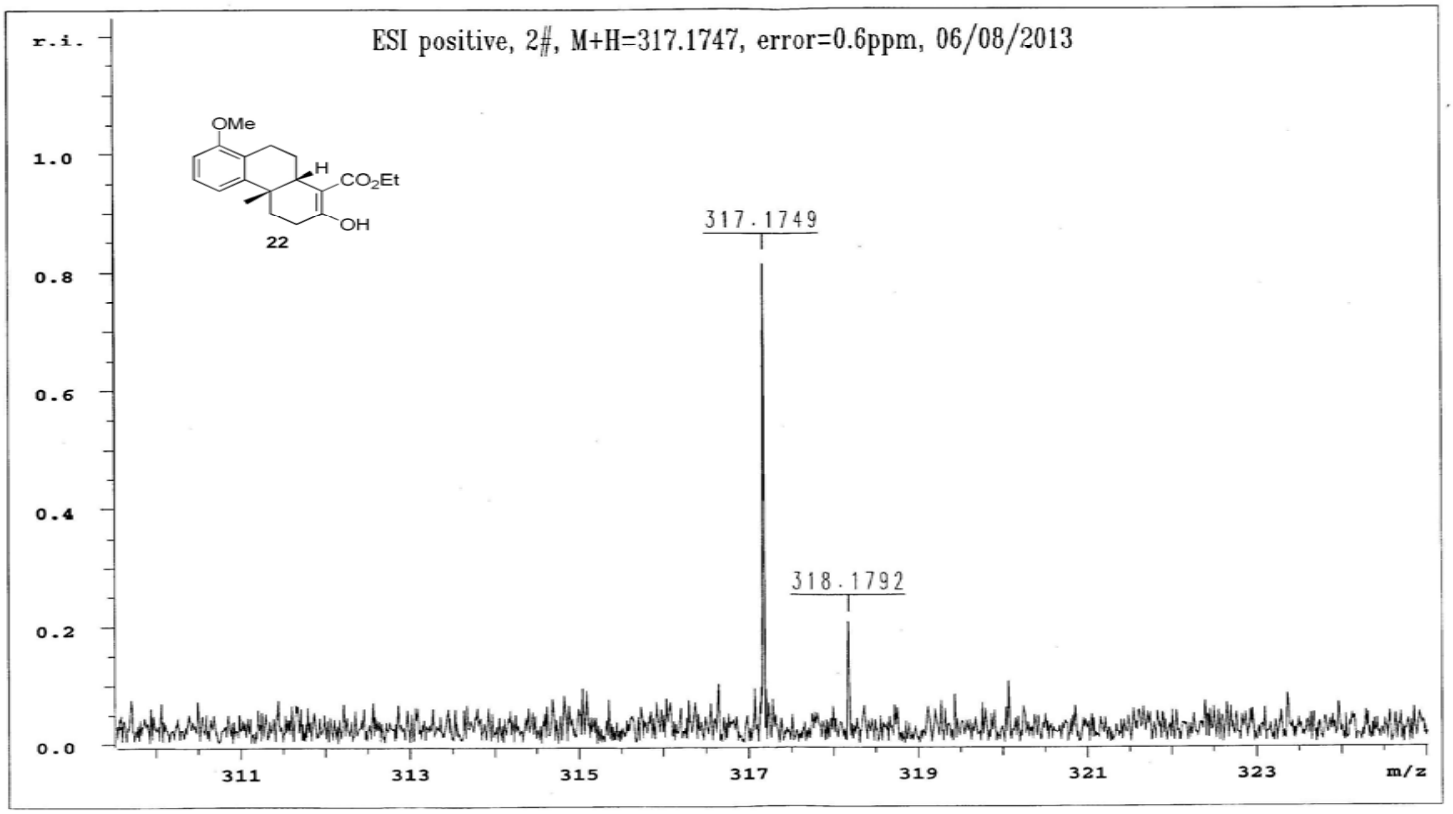
3.15. ^{1}H NMR of (4aS,10aR)-ethyl 2-hydroxy-8-methoxy-4a-methyl-3,4,4a,9,10,10a-hexahydro phenanthrene- 1-carboxylate (22)



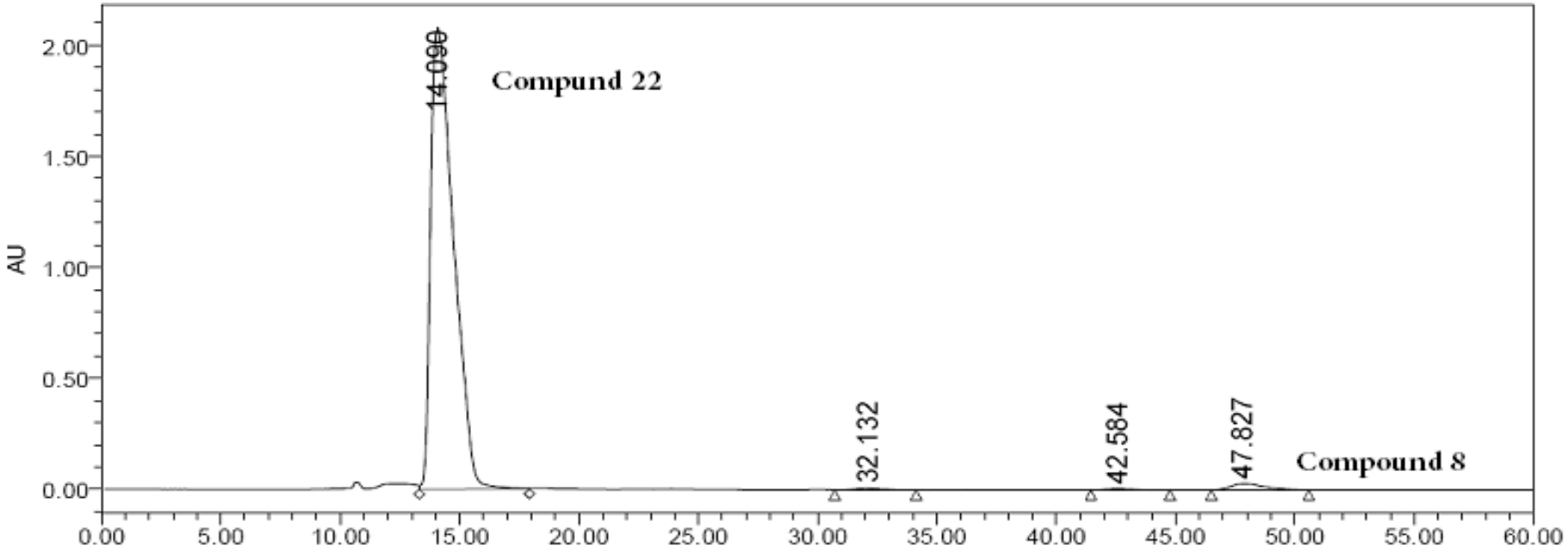
^{13}C NMR of (4aS,10aR)-ethyl 2-hydroxy-8-methoxy-4a-methyl-3,4,4a,9,10,10a-hexahydro phenanthrene- 1-carboxylate (22)



HRMS of (4aS,10aR)-ethyl 2-hydroxy-8-methoxy-4a-methyl-3,4,4a,9,10,10a-hexahydro phenanthrene-1-carboxylate (22)

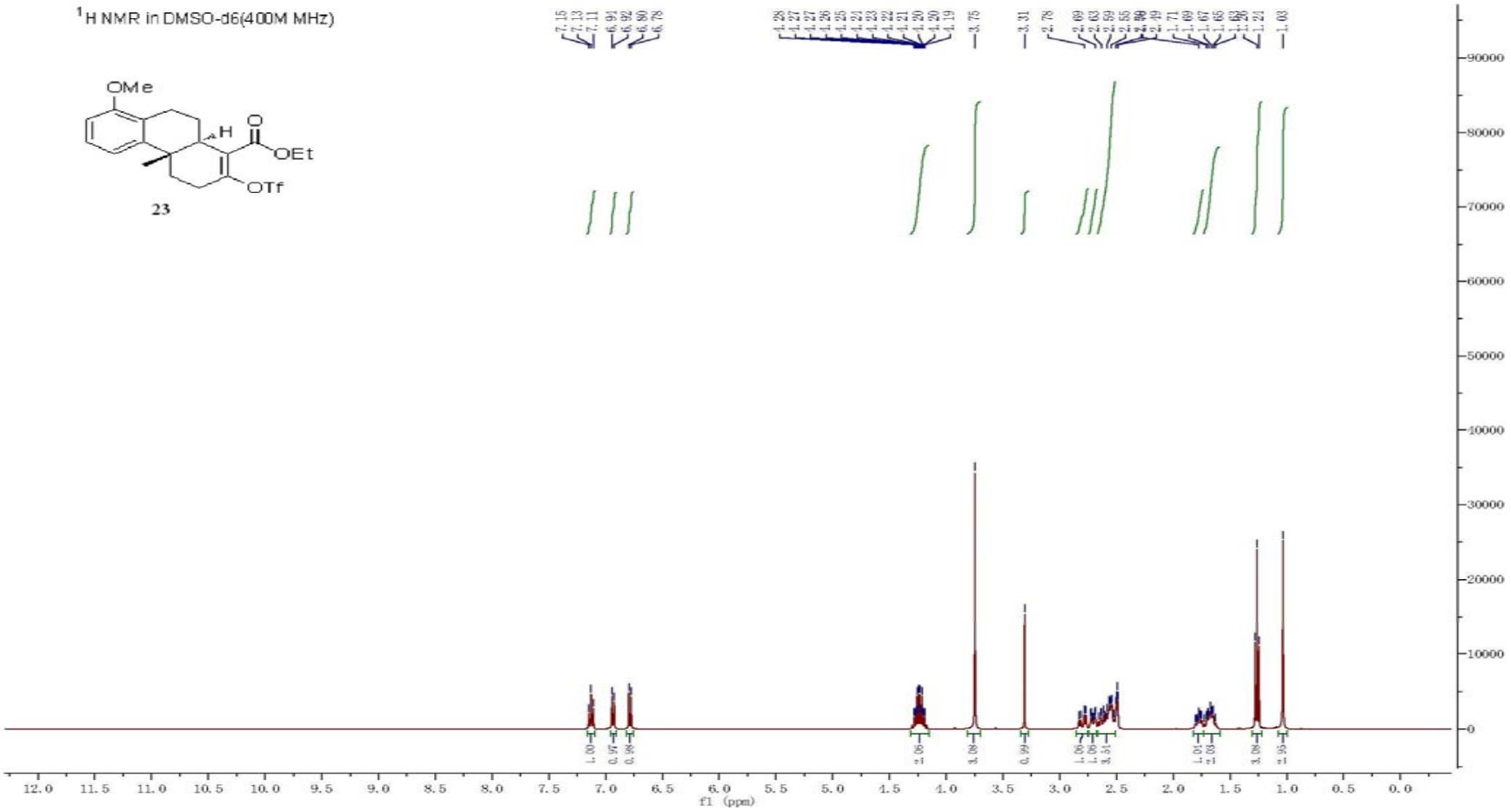


Chiral HPLC for ee value of (4aS,10aR)-ethyl 2-hydroxy-8-methoxy-4a-methyl-3,4,4a,9,10,10a-hexahydro phenanthrene-1 -carboxylate (22)

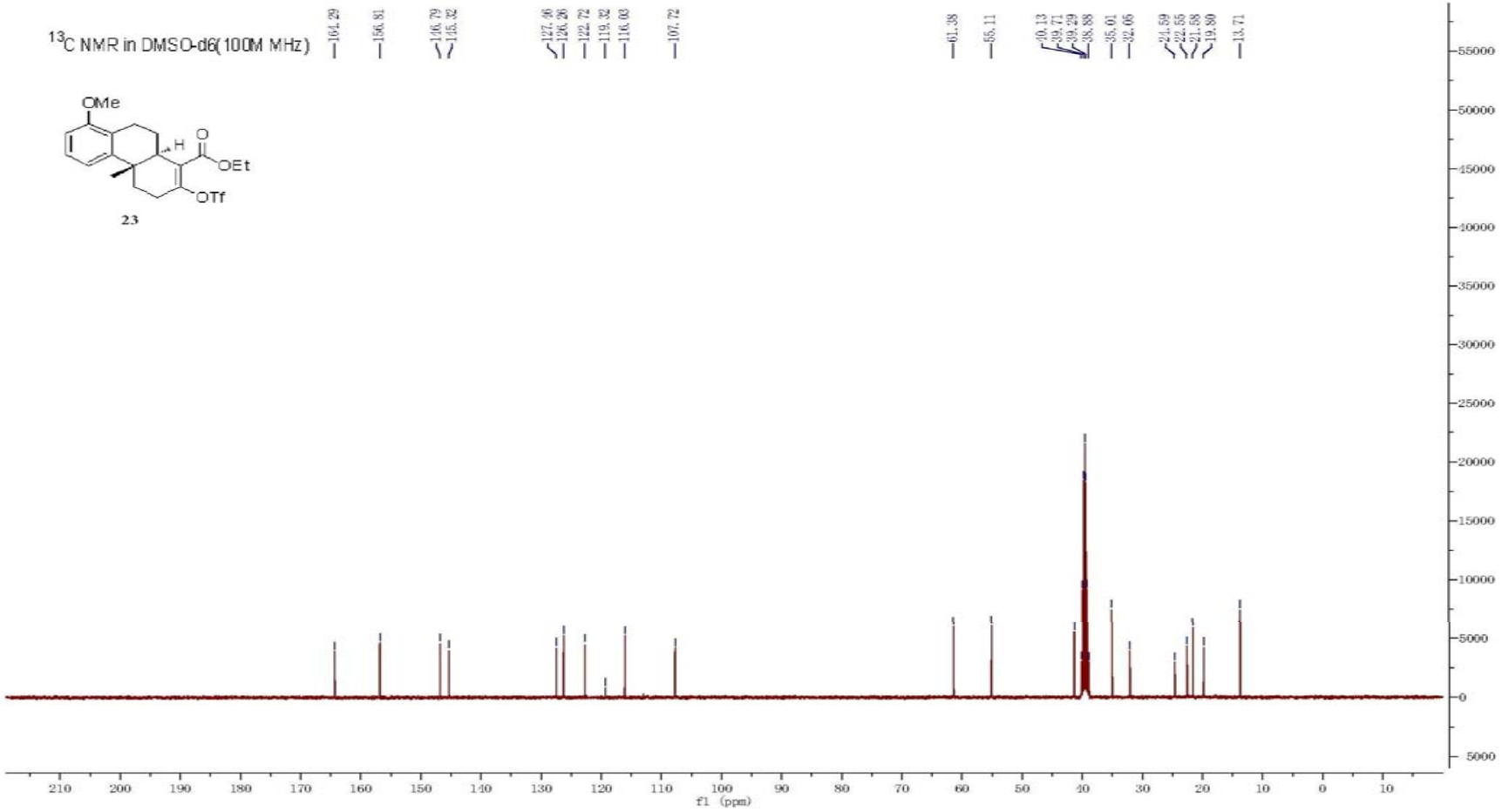


	channel	retenttion time(min)	area	%area	height
1	2998 (210-400)	14.090	139015140	97.56	2077666
2	2998 (210-400)	32.132	404780	0.28	5938
3	2998 (210-400)	42.584	401821	0.28	5039
4	2998 (210-400)	47.827	2676806	1.88	27622

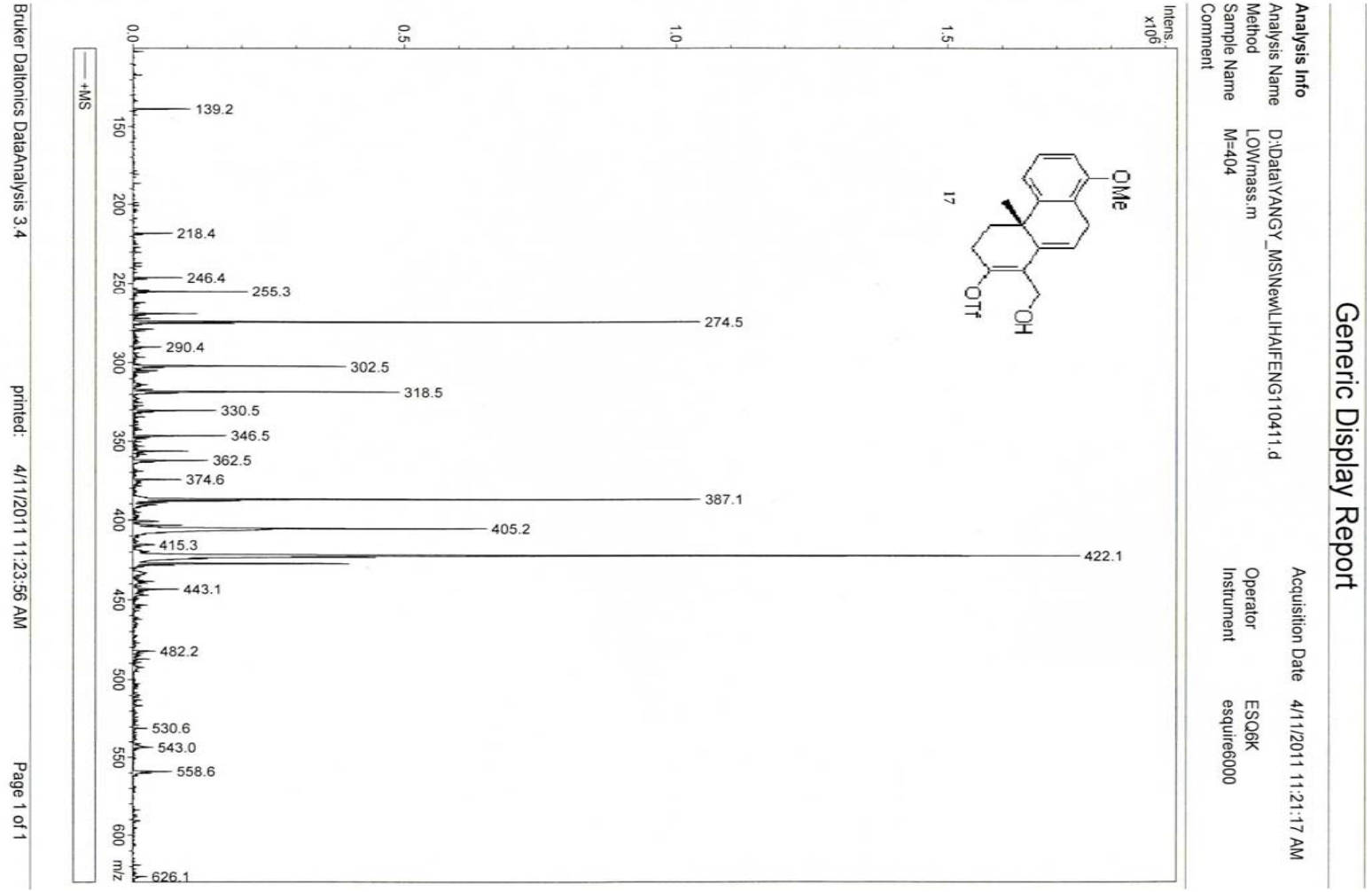
3.16. **^{1}H NMR of *(4aS,10aR)-ethyl 8-methoxy-4a-methyl-2-(((trifluoromethyl)sulfonyl)oxy)-3,4,4a,9,10,10a-hexahydrophenanthrene-1-carboxylate (23).***



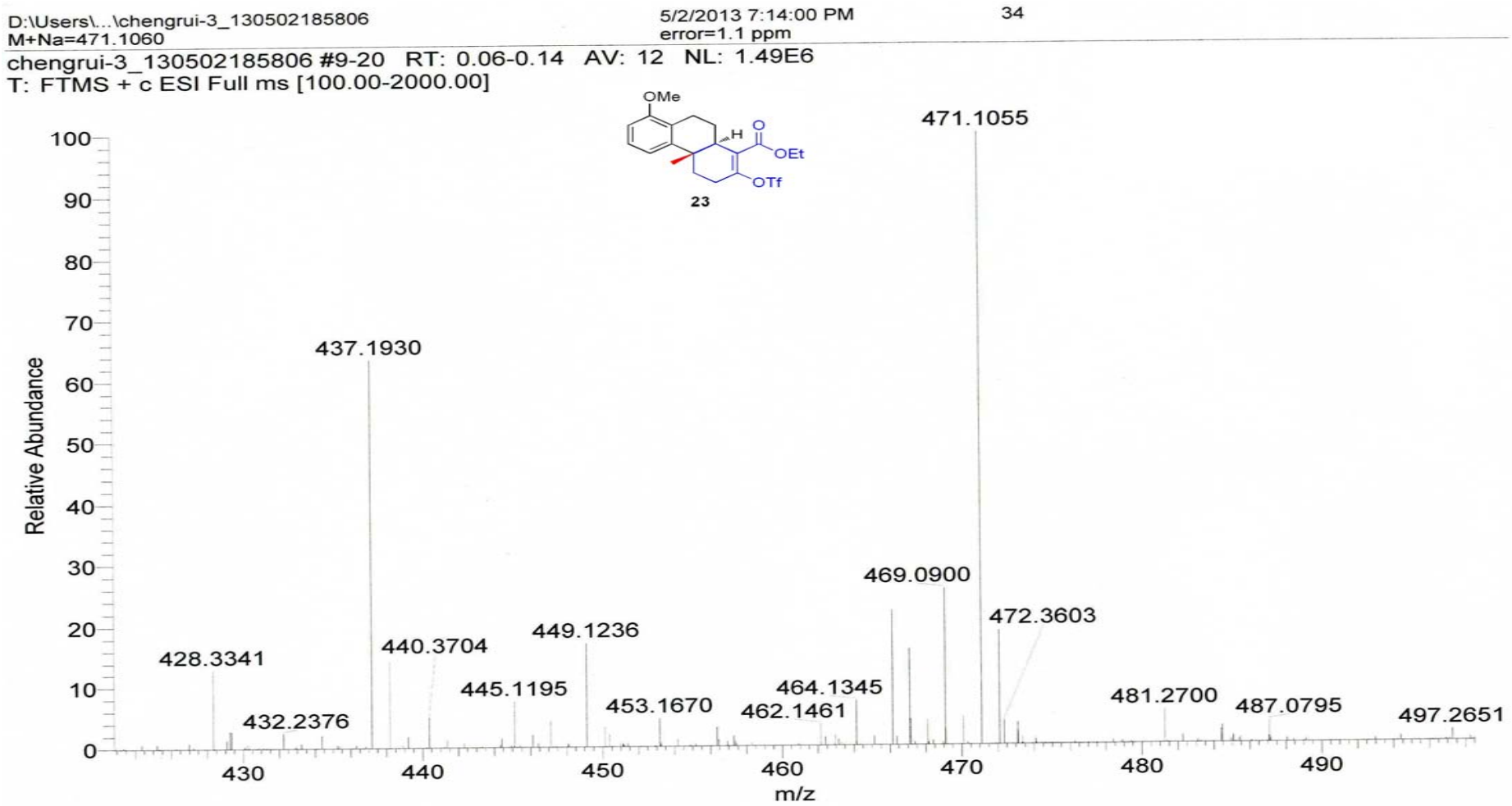
^{13}C NMR of *(4aS,10aR)-ethyl 8-methoxy-4a-methyl-2-(((trifluoromethyl)sulfonyl)oxy)- 3,4,4a,9,10,10a-hexahydrophenanthrene-1-carboxylate (23).*



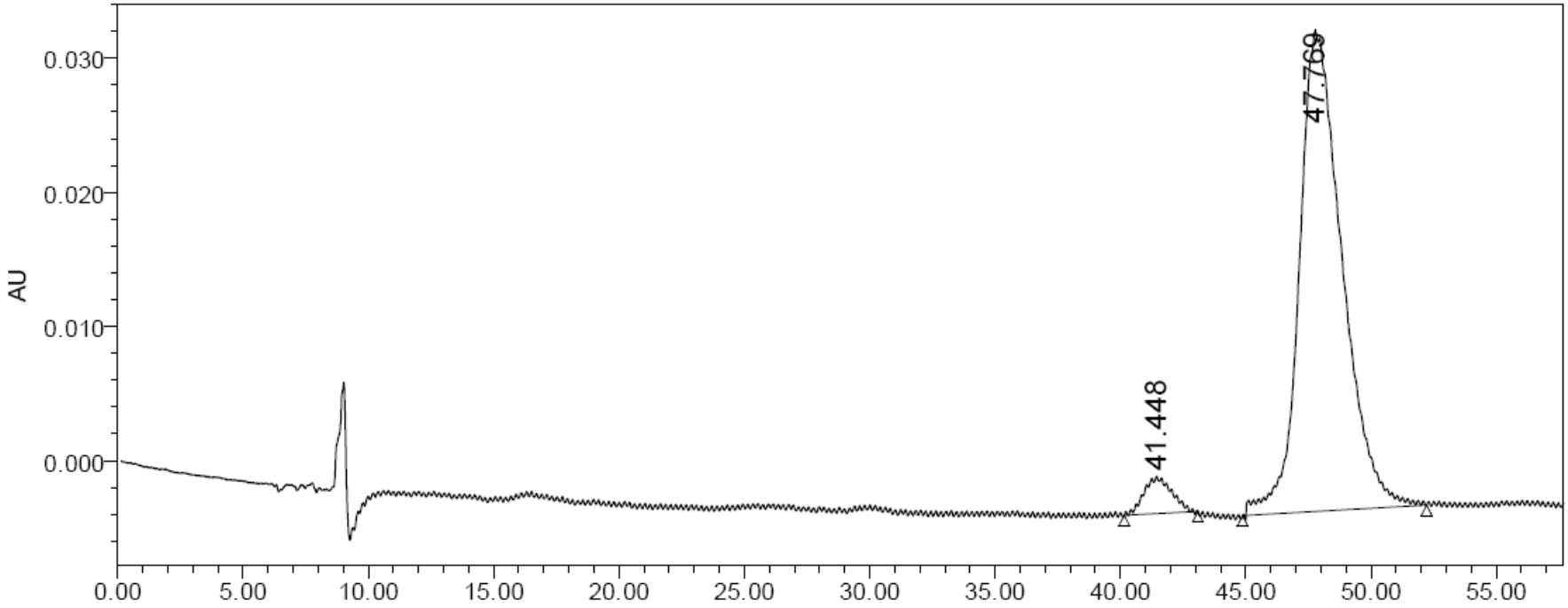
ESI-MS of *(4aS,10aR)-ethyl 8-methoxy-4a-methyl-2-(((trifluoromethyl)sulfonyl)oxy)-3,4,4a,9,10,10a-hexa-hydrophenanthrene-1-carboxylate (23).*



HR-MS of *(4aS,10aR)-ethyl 8-methoxy-4a-methyl-2-(((trifluoromethyl)sulfonyl)oxy)- 3,4,4a,9,10,10a-hexa- hydrophenanthrene-1-carboxylate (23).*

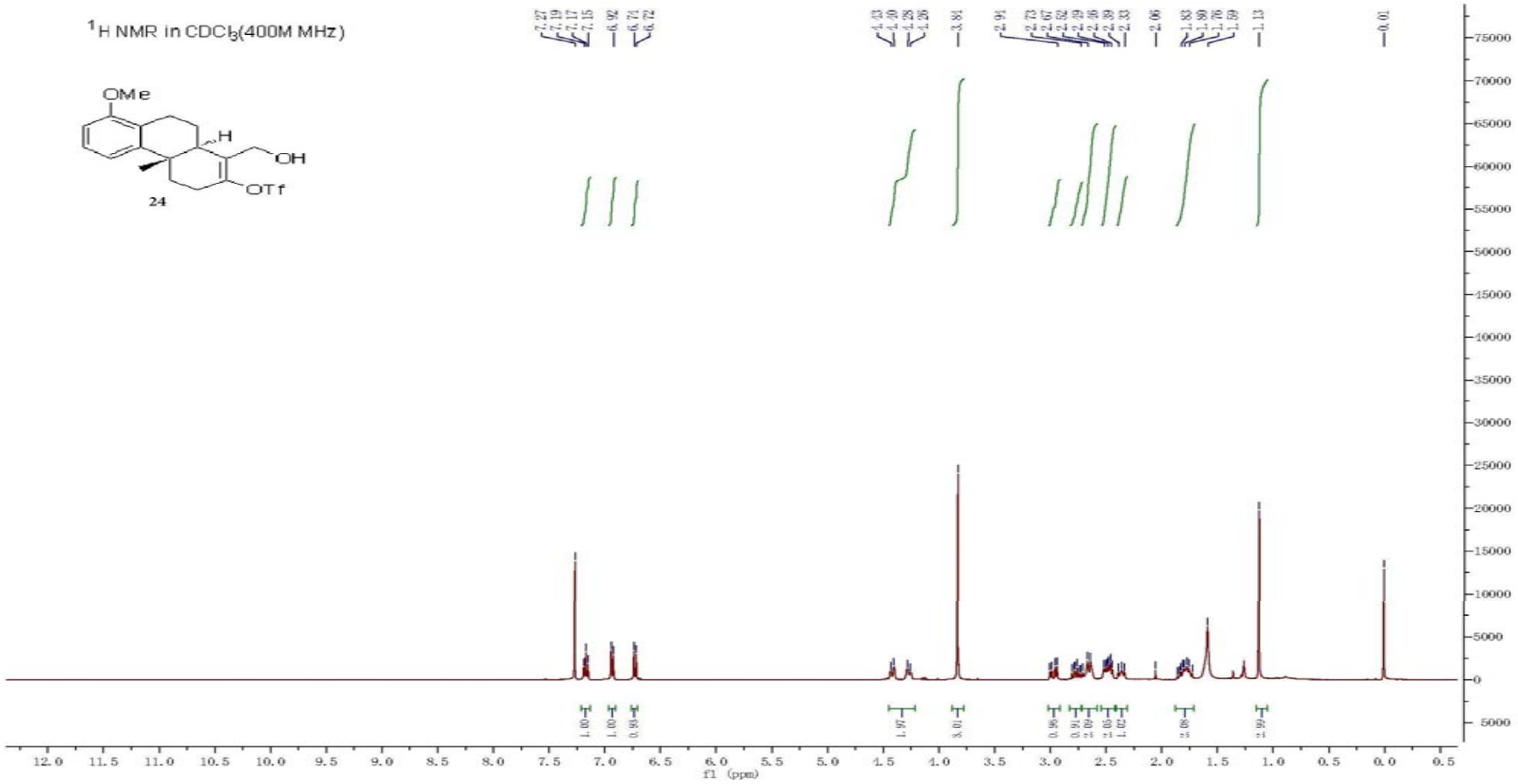


Chiral HPLC for ee value of *(4aS,10aR)-ethyl 8-methoxy-4a-methyl-2-(((trifluoromethyl)sulfonyl)oxy)- 3,4,4a,9,10,10a-hexa-hydrophenanthrene-1-carboxylate (23).*

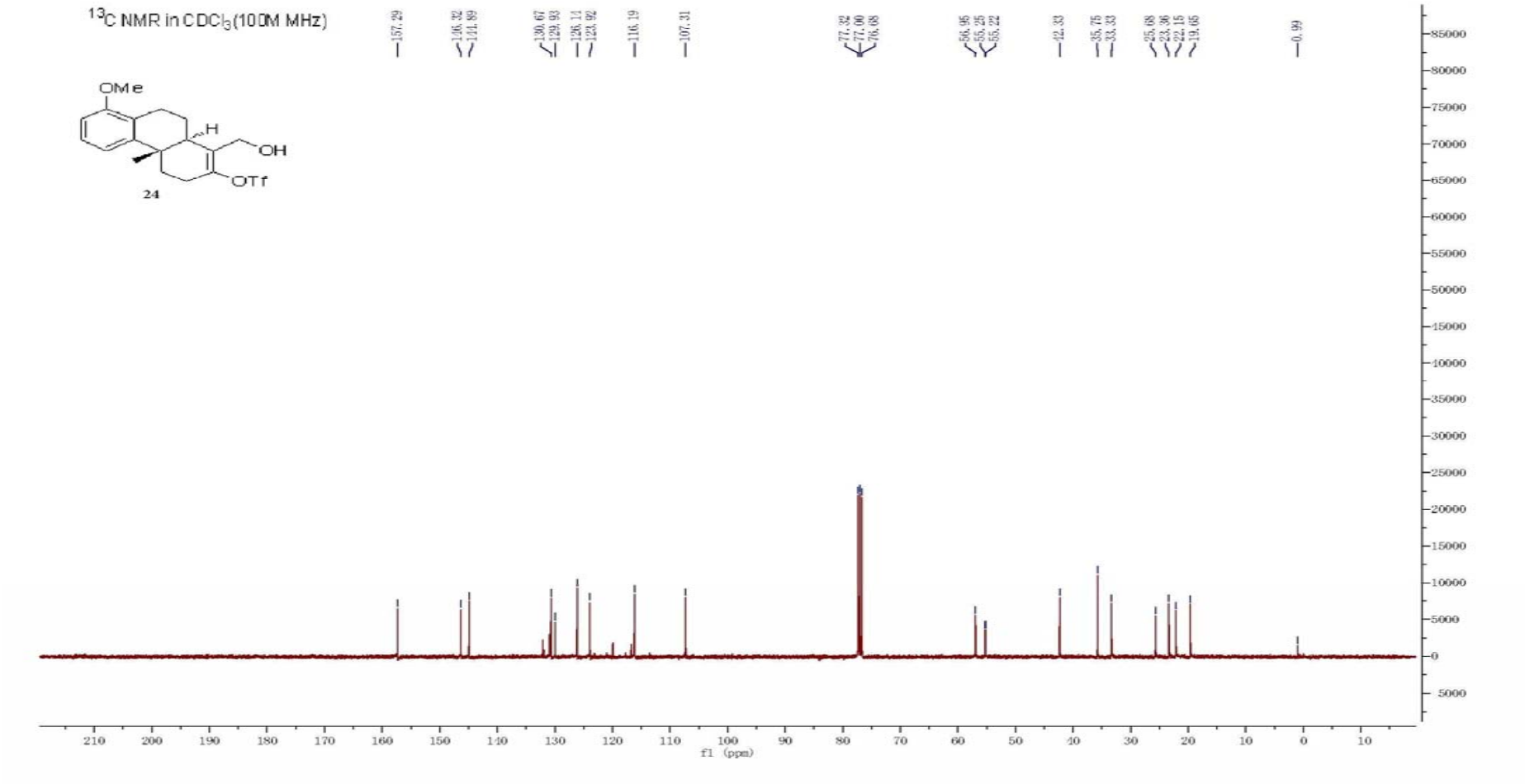


	channel	retenttion time(min)	area	%area	height
1	2998 (210-400)	41.448	208384	4.67	2762
2	2998 (210-400)	47.769	4249060	95.33	35857

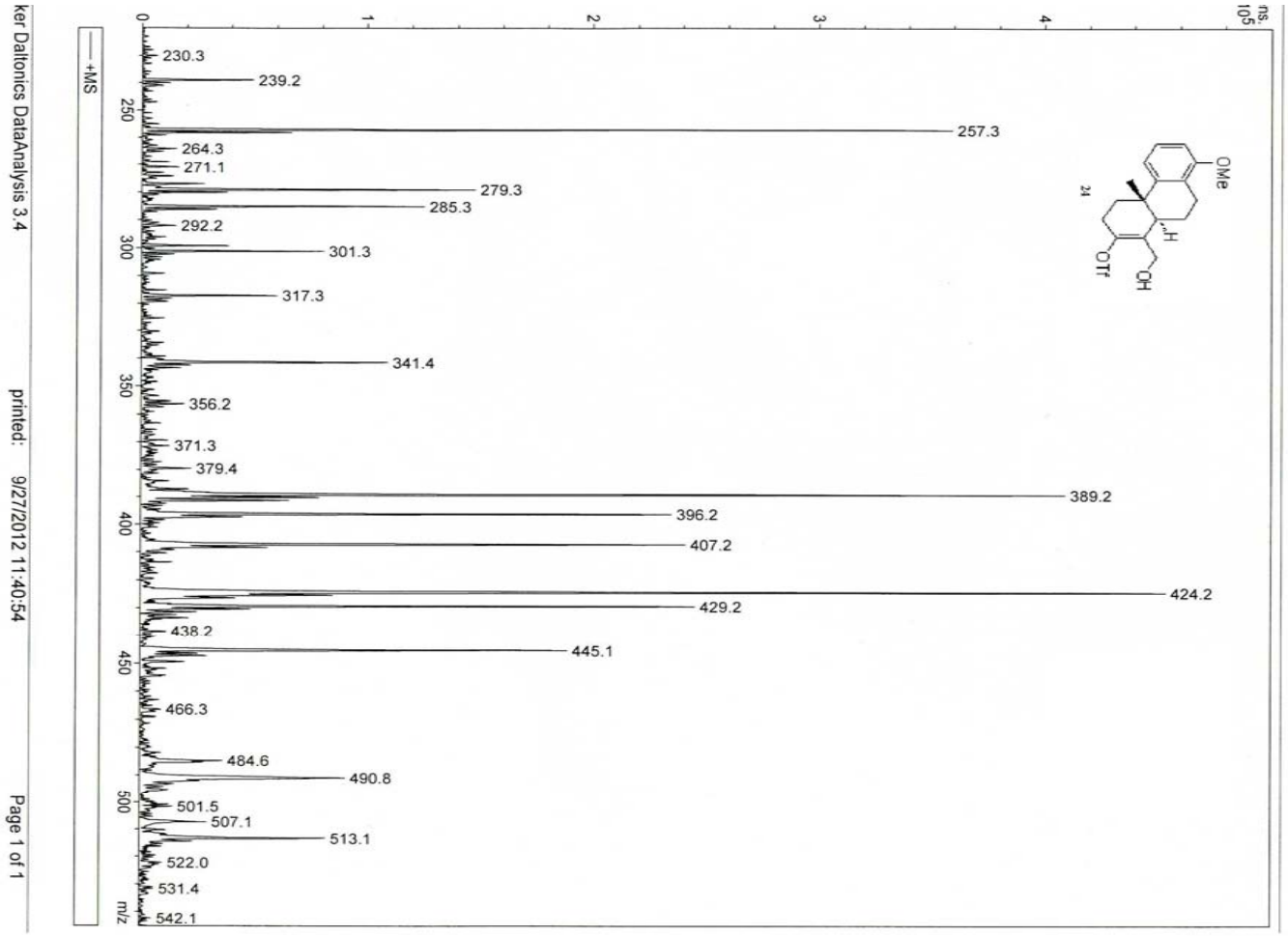
3.17. **^{1}H NMR of *(4aS,10aR)-1-(hydroxymethyl)-8-methoxy-4a-methyl-3,4,4a,9,10,10a-hexahydrophenanthren-2-yl trifluoromethanesulfonate (24).***



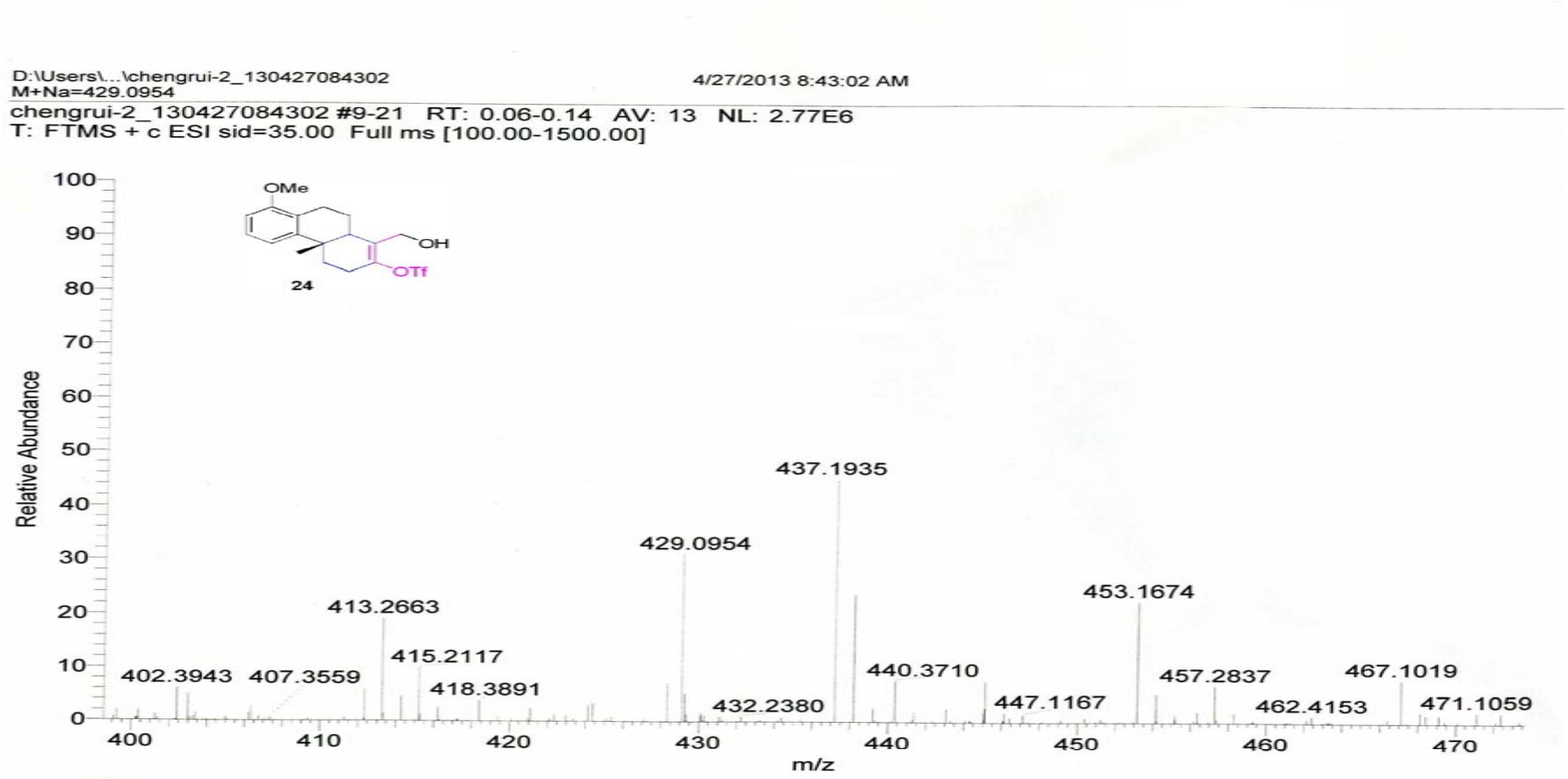
^{13}C NMR of *(4aS,10aR)-1-(hydroxymethyl)-8-methoxy-4a-methyl-3,4,4a,9,10,10a-hexahydrophenanthren-2-yl trifluoromethanesulfonate (24).*



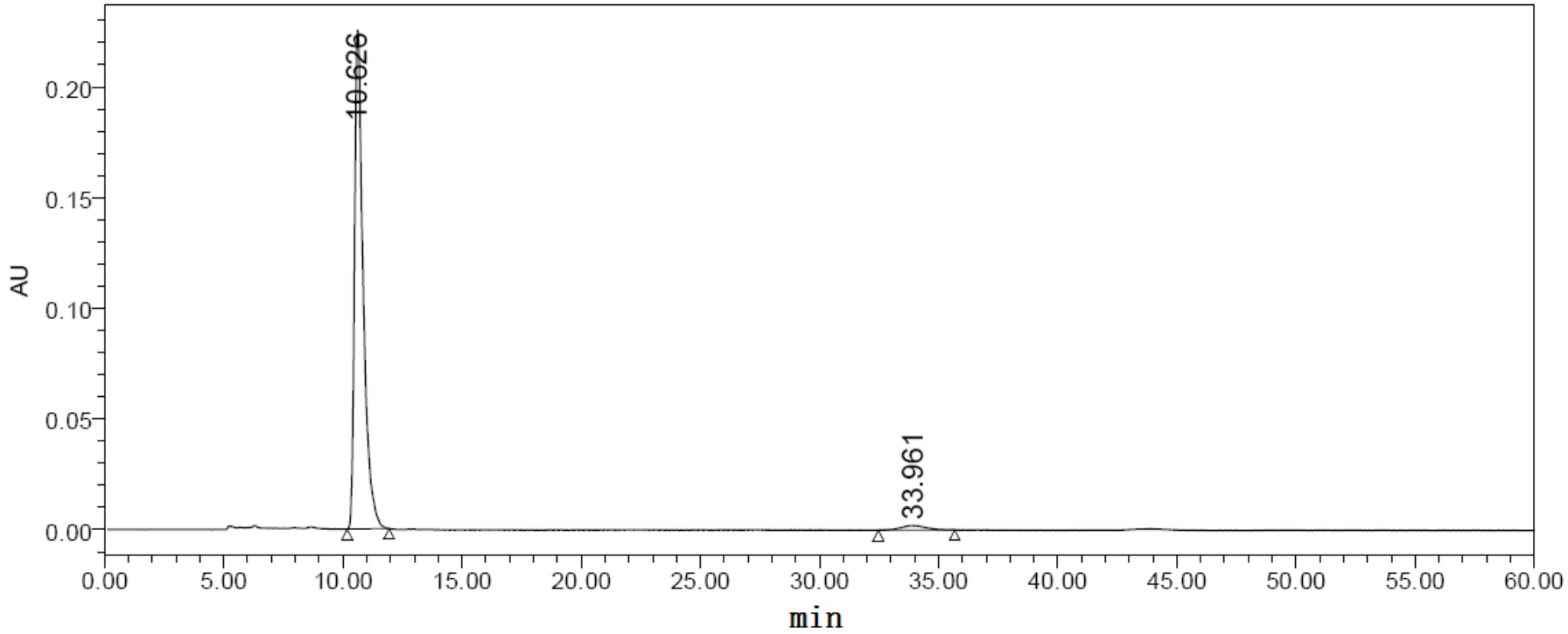
ESI-MS of *(4aS,10aR)-1-(hydroxymethyl)-8-methoxy-4a-methyl-3,4,4a,9,10,10a-hexahydrophenanthren-2-yl trifluoromethane sulfonate (24).*



HR-MS of *(4aS,10aR)-1-(hydroxymethyl)-8-methoxy-4a-methyl-3,4,4a,9,10,10a-hexahydrophenanthren-2-yl trifluoromethane sulfonate (24).*

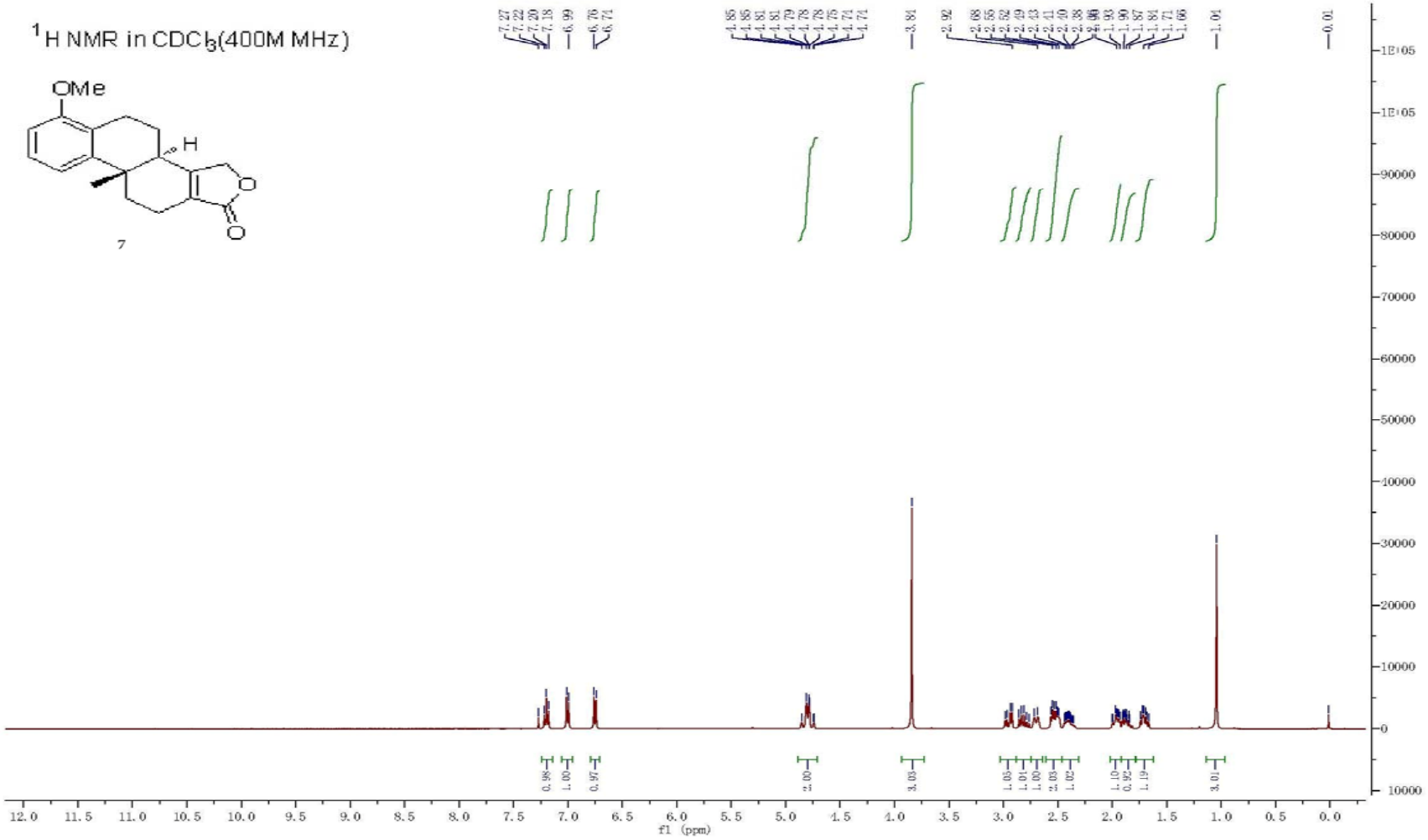


Chiral HPLC for ee value of *(4aS,10aR)-1-(hydroxymethyl)-8-methoxy-4a-methyl-3,4,4a,9,10,10a- hexahydrophenanthren-2-yl trifluoromethanesulfonate (24).*

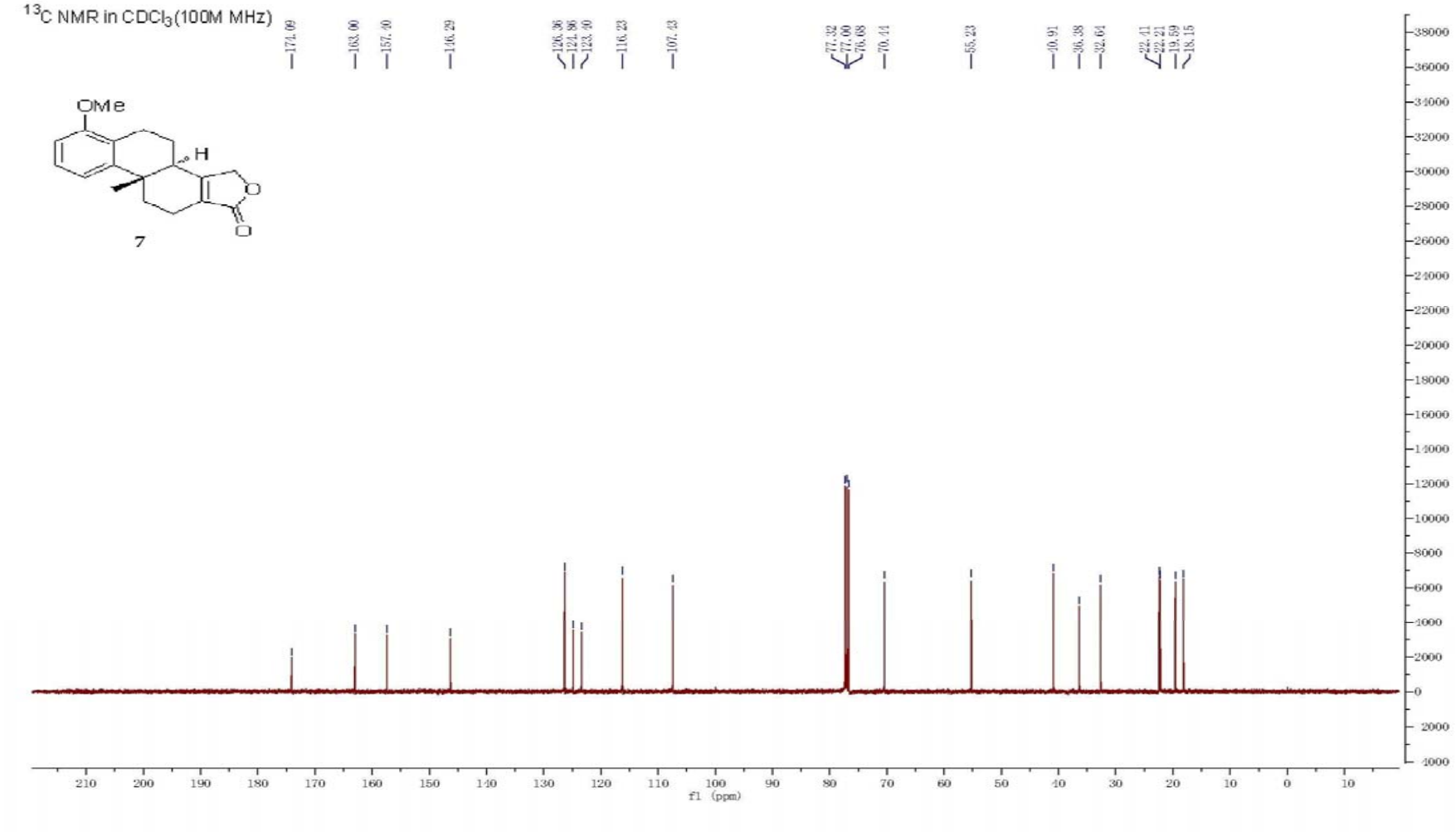


	channel	retenttion time(min)	area	%area	height
1	2998 (210-400)	10.626	5736849	97.59	225368
2	2998 (210-400)	33.961	141929	2.41	2044

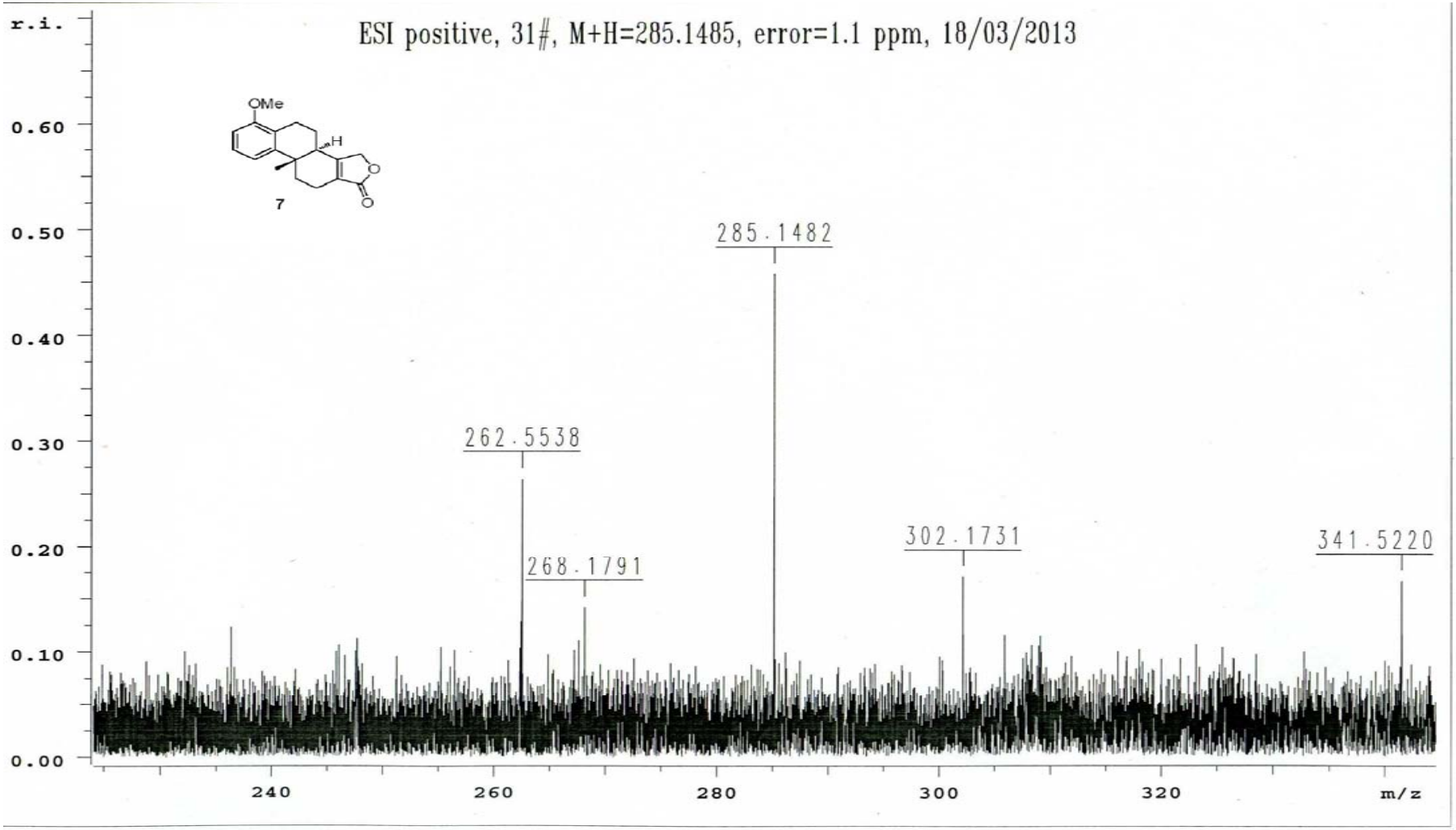
3.18. **^{1}H NMR of *(3bR,9bS)-6-methoxy-9b-methyl-3b,4,5,9b,10,11-hexahydrophenanthro[1,2- c]furan-1(3H)-one (7).***



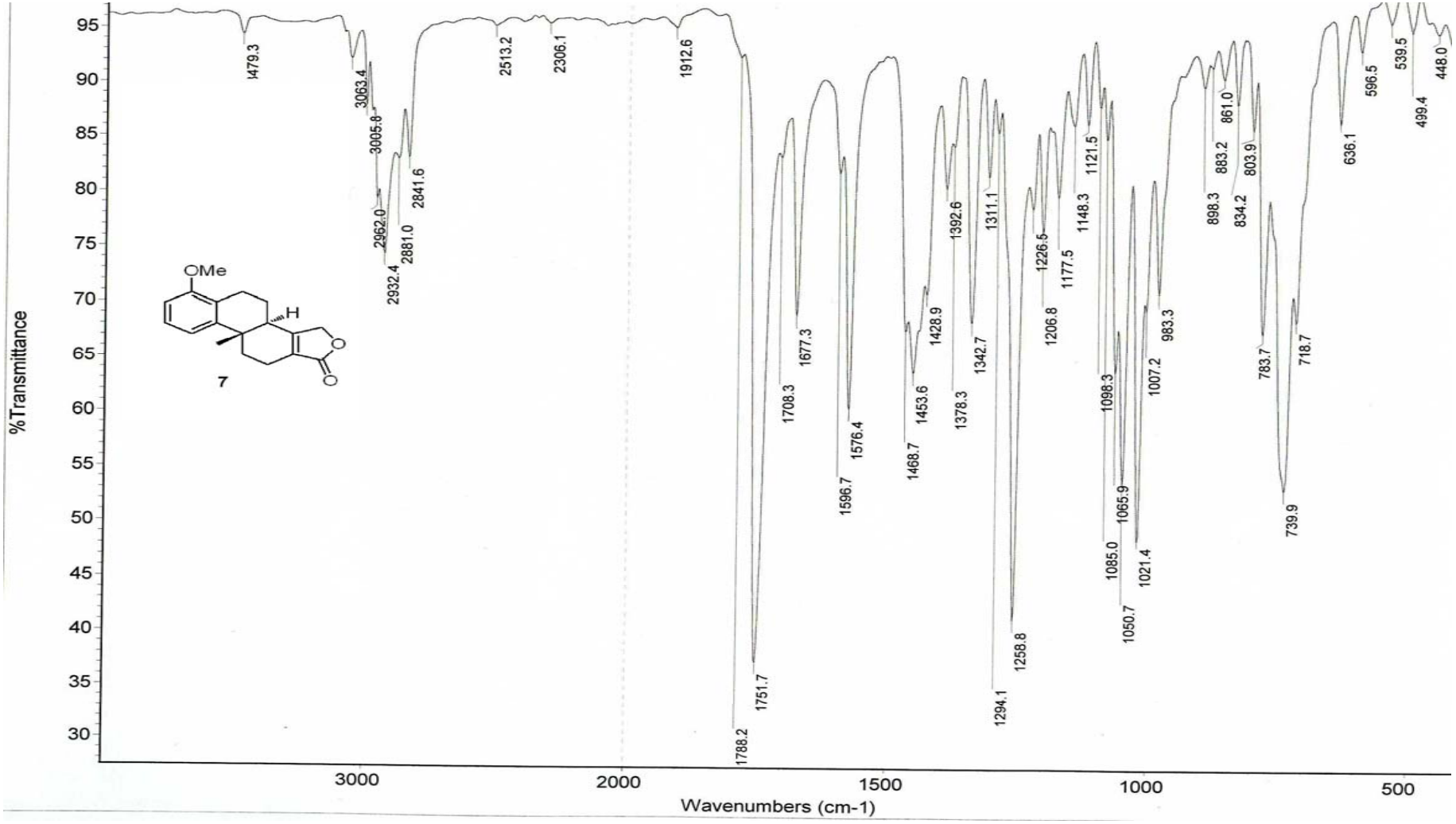
^{13}C NMR of *(3bR,9bS)-6-methoxy-9b-methyl-3b,4,5,9b,10,11-hexahydrophenanthro[1,2- c]furan-1(3H)-one (7).*



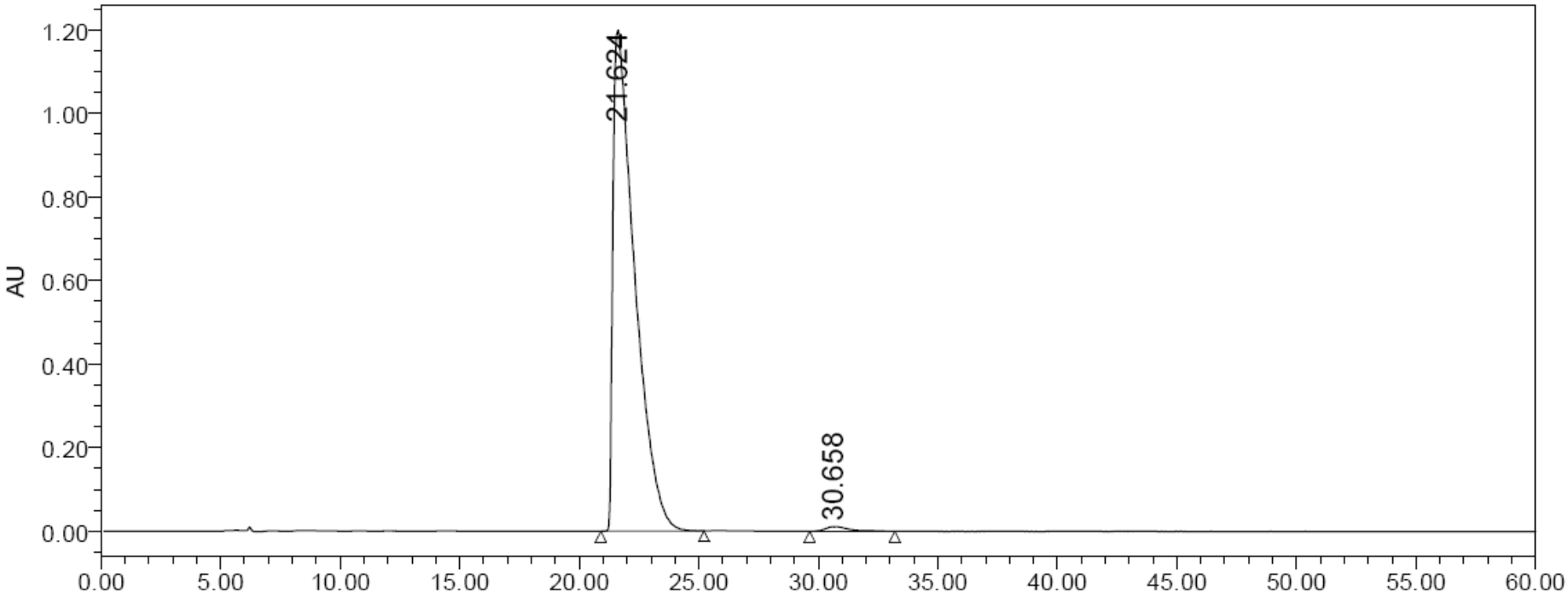
HRMS-ESI of *(3bR,9bS)-6-methoxy-9b-methyl-3b,4,5,9b,10,11-hexahydrophenanthro[1,2- c]furan-1(3H)-one (7).*



IR of *(3bR,9bS)-6-methoxy-9b-methyl-3b,4,5,9b,10,11-hexahydrophenanthro[1,2-c]furan -1(3H)-one (7).*

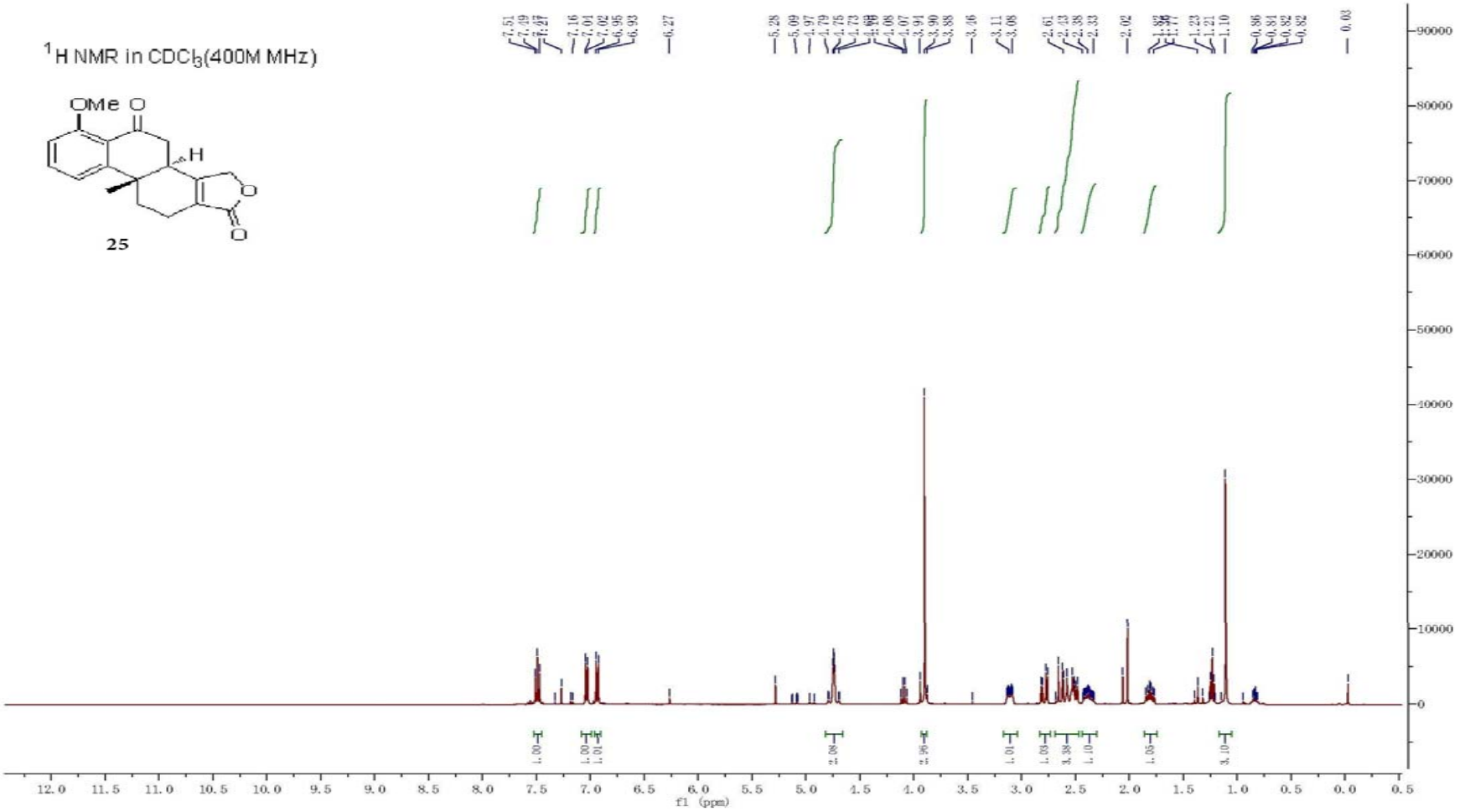


Chiral HPLC for ee value of *(3bR,9bS)-6-methoxy-9b-methyl-3b,4,5,9b,10,11-hexahydrophenanthro[1,2- c]furan-1(3H)-one (7).*

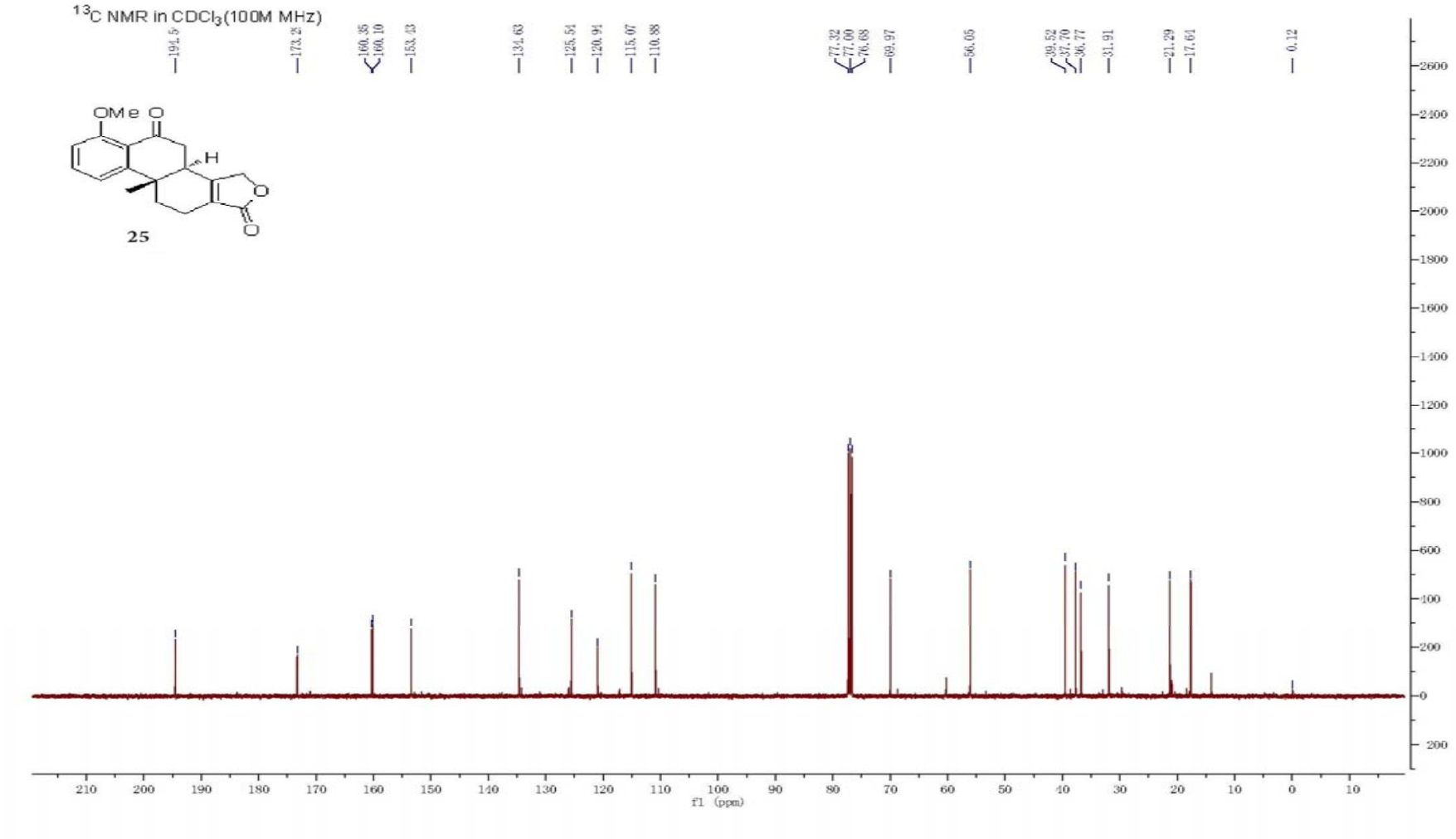


	channel	retenttion time(min)	area	%area	height
1	2998 (210-400)	21.624	75758082	99.07	1197556
2	2998 (210-400)	30.658	714985	0.93	10978

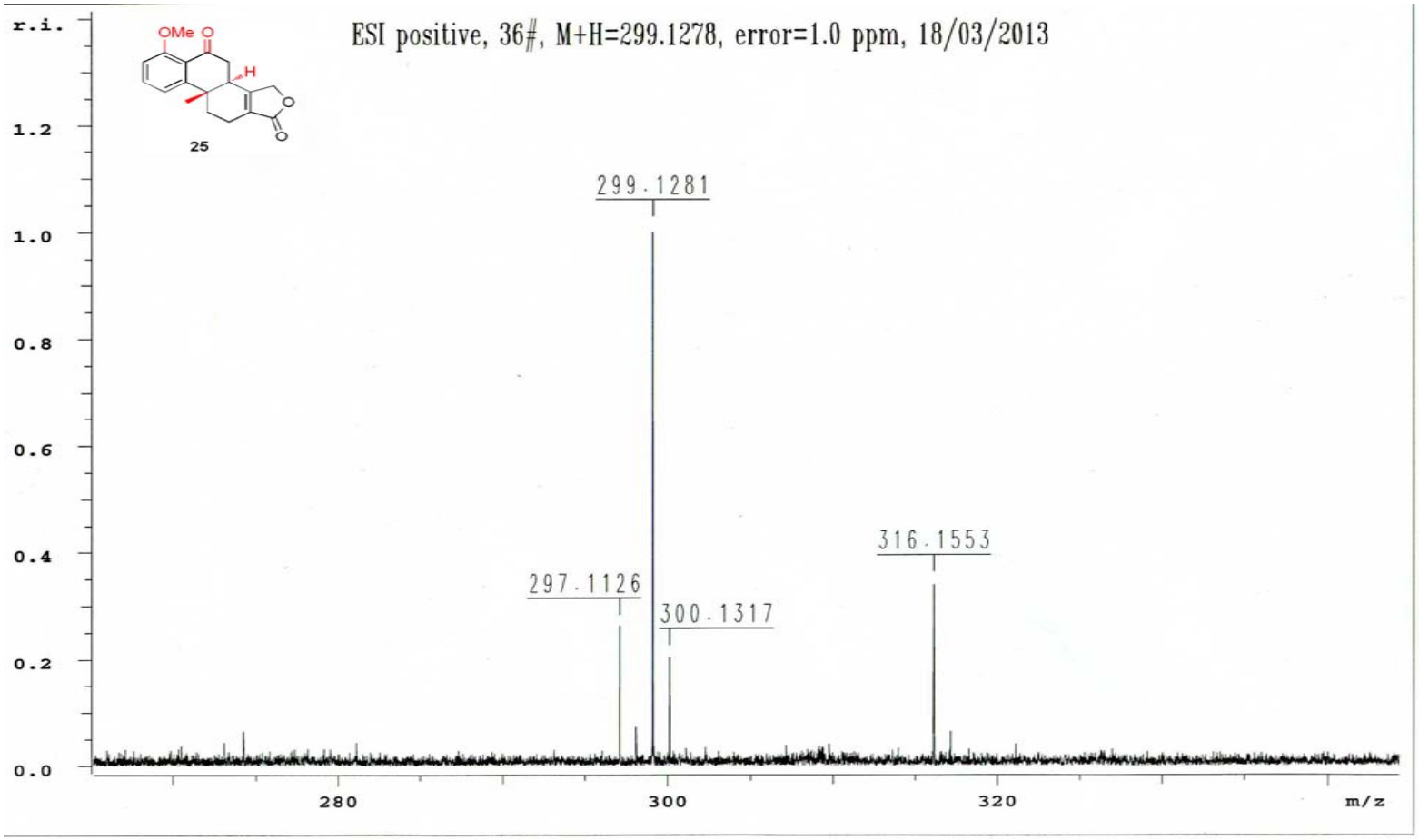
3.19. **^{1}H NMR of *(3bR,9bS)-6-methoxy-9b-methyl-3b,4,10,11-tetrahydrophenanthro[1,2-c]furan- 1,5(3H,9bH)-dione (25).***



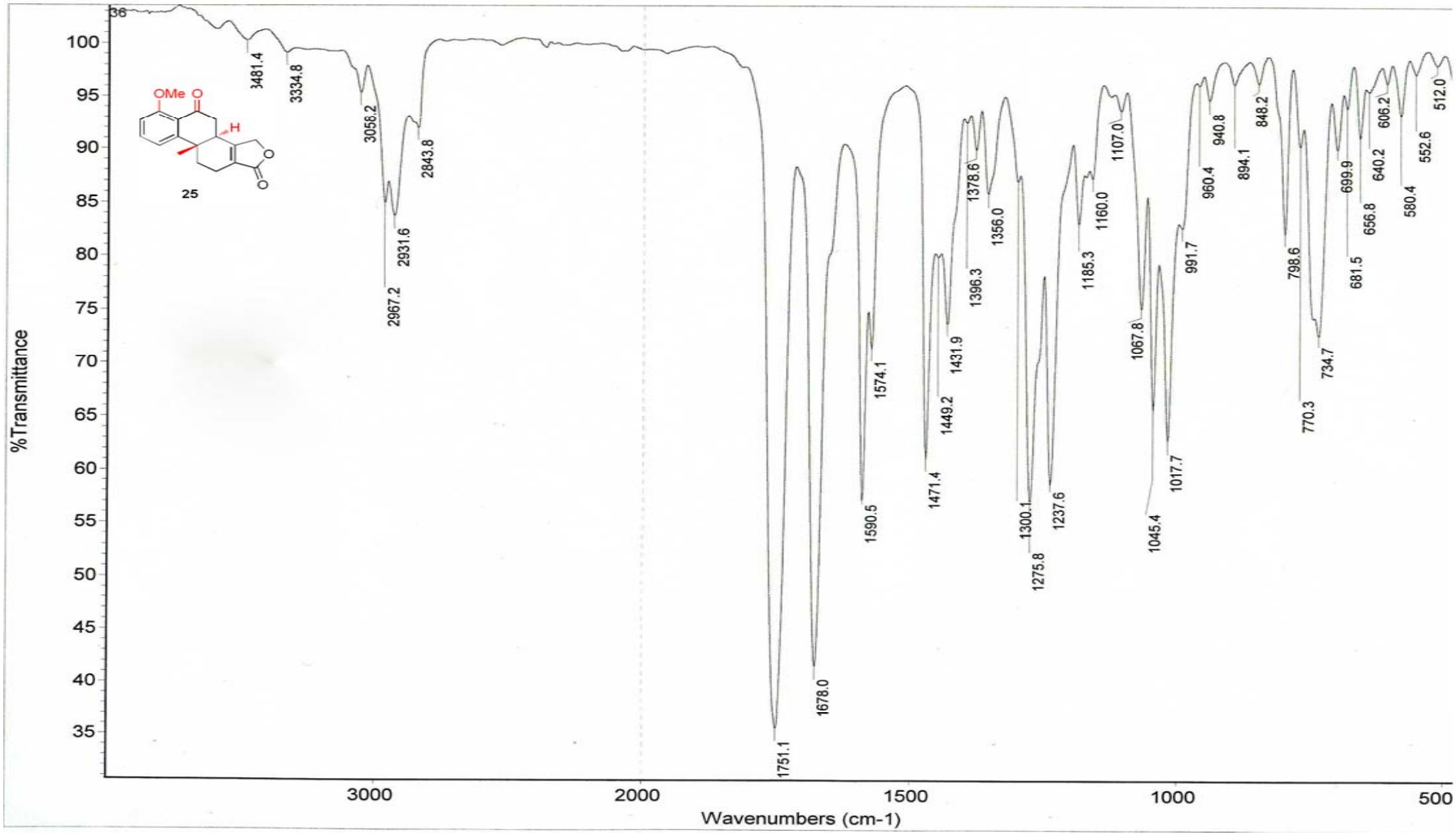
^{13}C NMR of *(3bR,9bS)-6-methoxy-9b-methyl-3b,4,10,11-tetrahydrophenanthro[1,2-c]furan- 1,5(3H,9bH)- dione (25).*



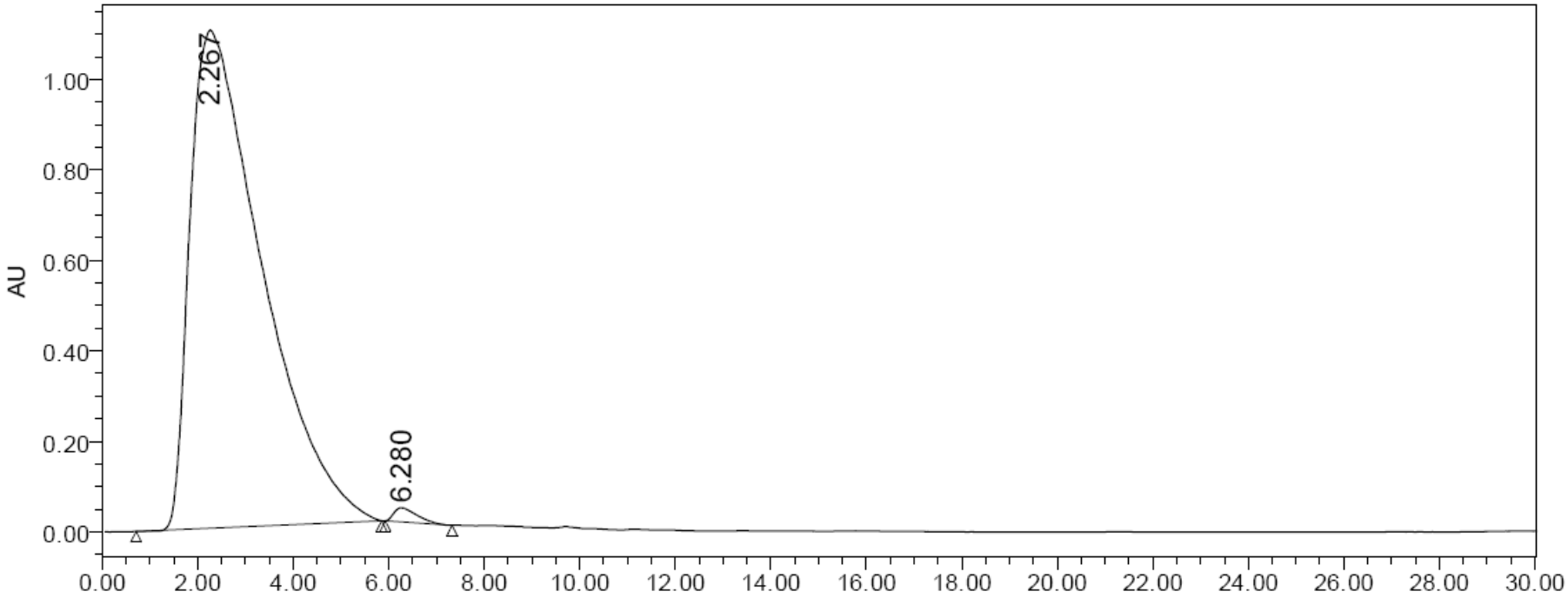
HRMS-ESI of *(3bR,9bS)-6-methoxy-9b-methyl-3b,4,10,11-tetrahydrophenanthro[1,2-c]furan- 1,5(3H,9bH)- dione (25).*



IR of *(3bR,9bS)-6-methoxy-9b-methyl-3b,4,10,11-tetrahydrophenanthro[1,2-c]furan- 1,5(3H,9bH)-dione (25).*

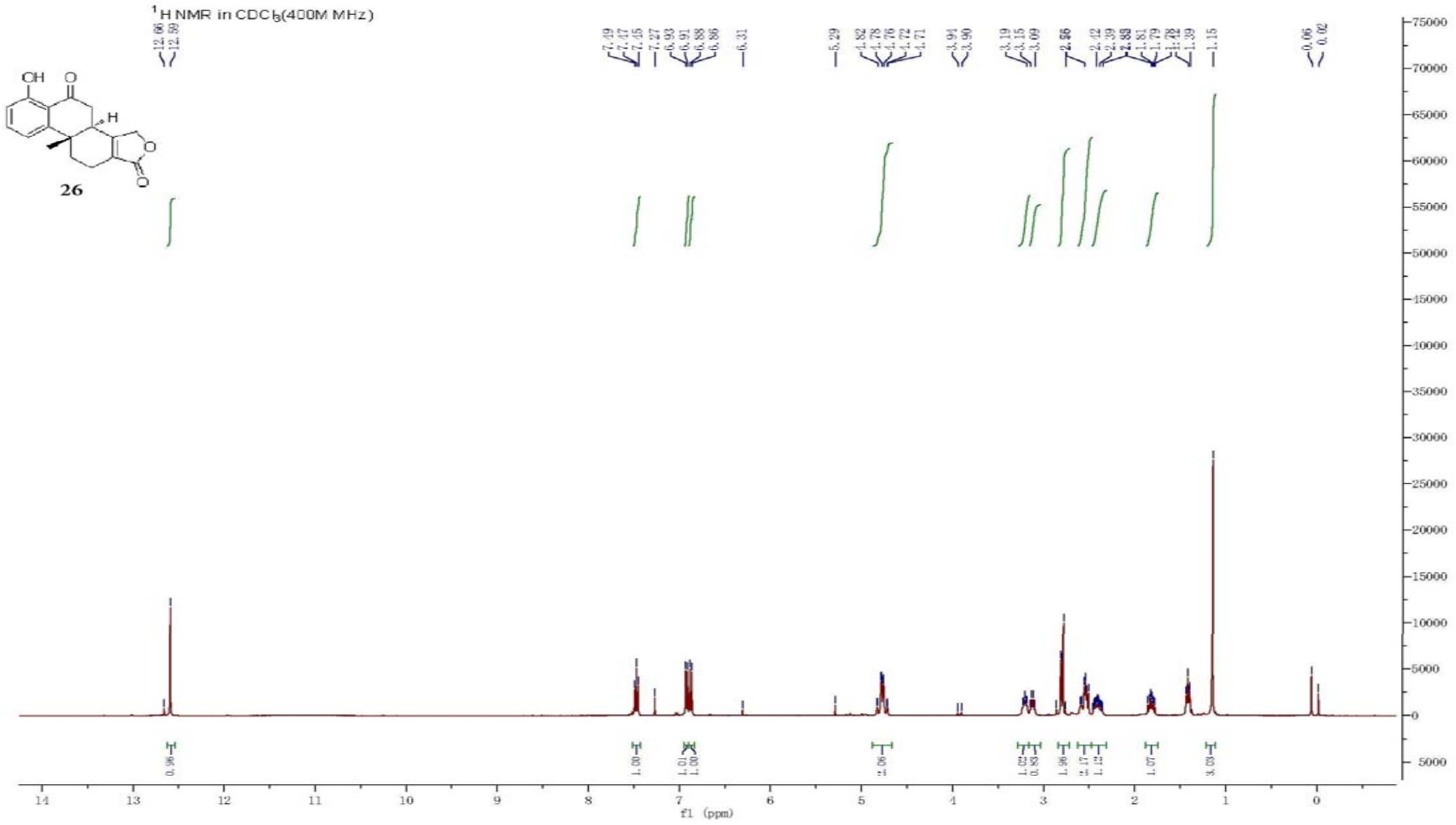


Chiral HPLC for ee value of *(3bR,9bS)-6-methoxy-9b-methyl-3b,4,10,11-tetrahydrophenanthro[1,2-c]furan- 1,5(3H,9bH)-dione (25)*.

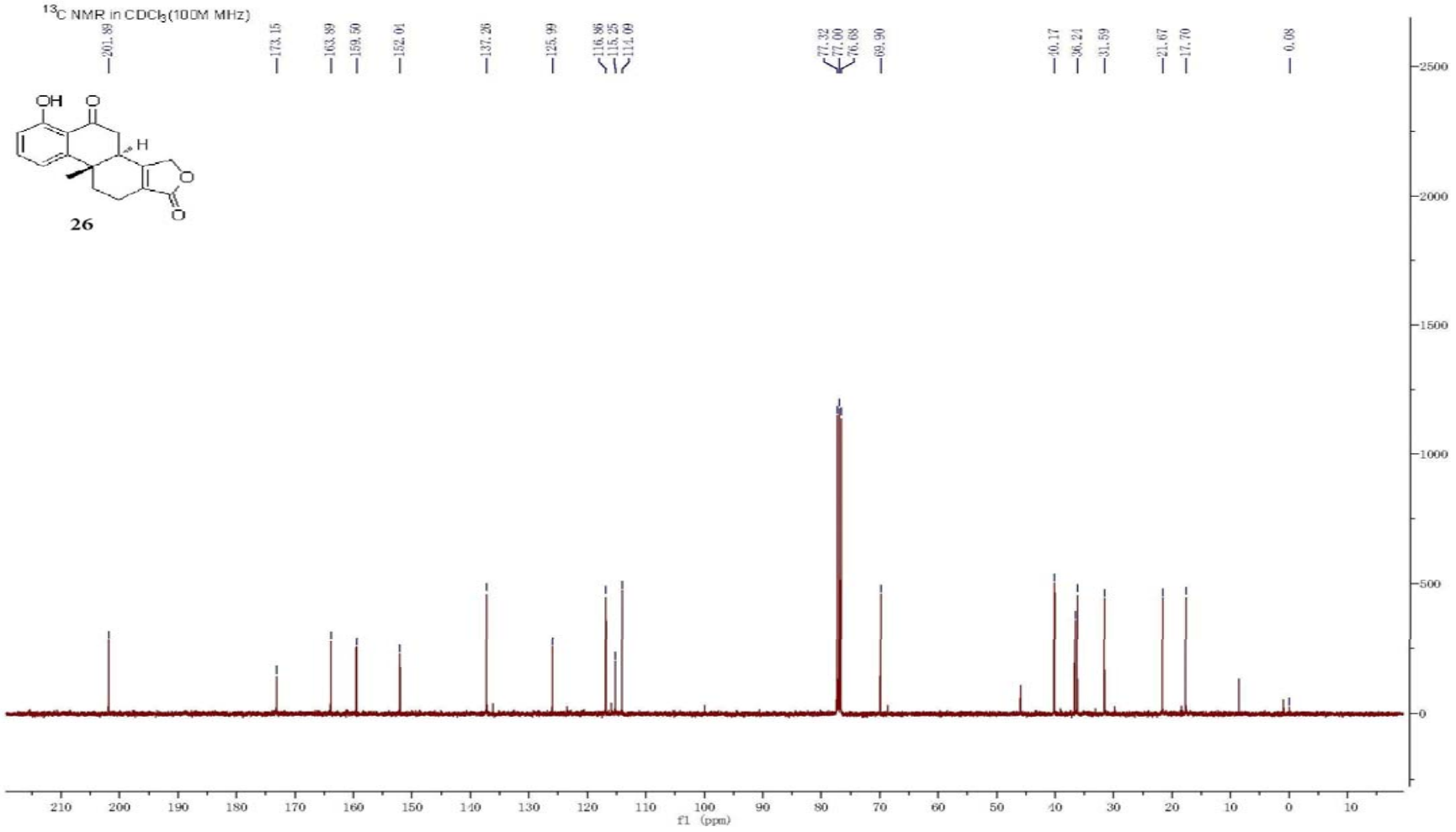


	channel	retenttion time(min)	area	%area	height
1	2998 (210-400)	2.267	115855315	99.10	1100880
2	2998 (210-400)	6.280	1052163	0.90	31304

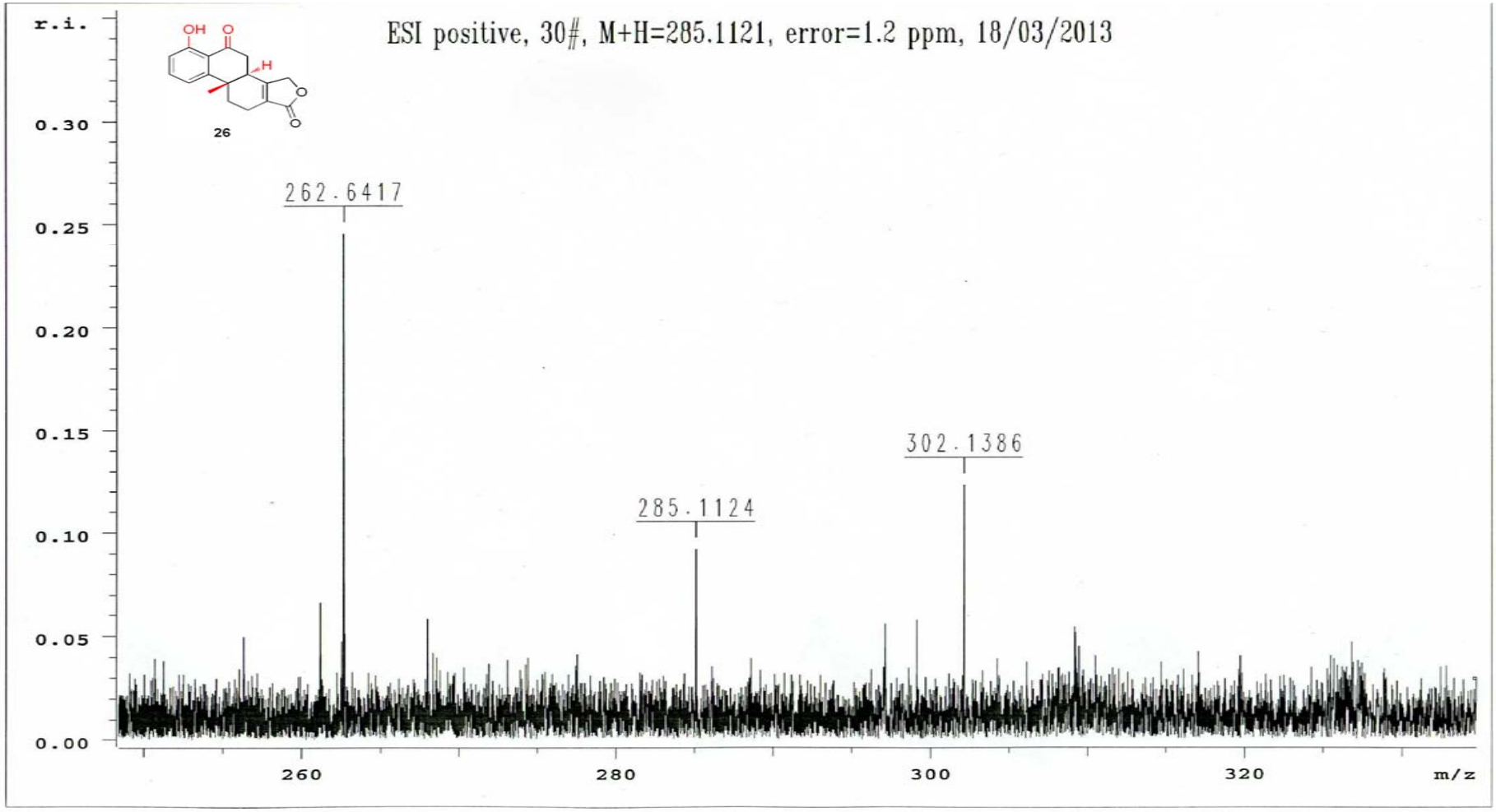
3.20. **^{1}H NMR of *(3bR,9bS)-6-hydroxy-9b-methyl-3b,4,10,11-tetrahydrophenanthro[1,2-c]furan-1,5(3H,9bH)-dione (26).***



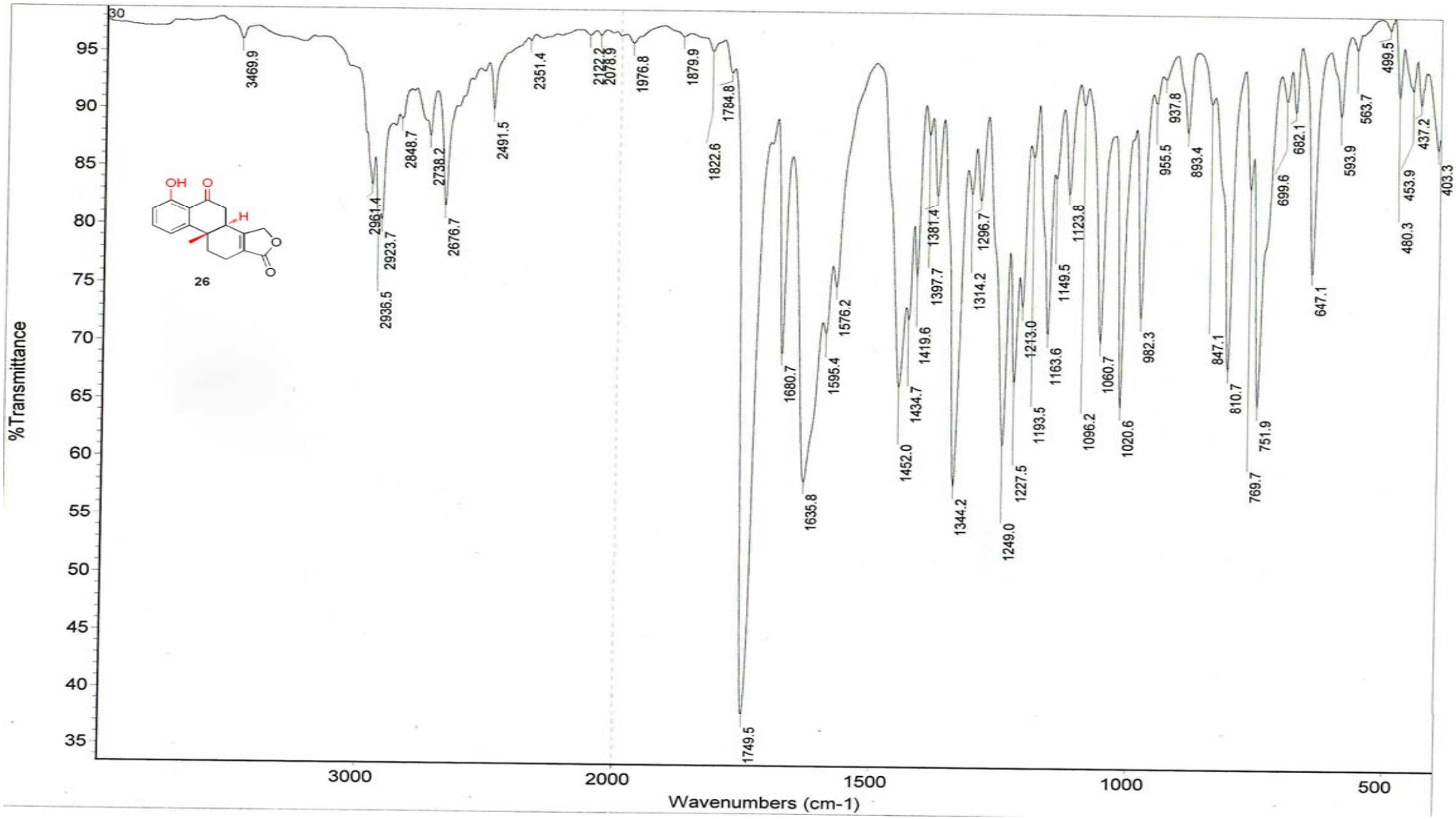
^{13}C NMR of *(3bR,9bS)-6-hydroxy-9b-methyl-3b,4,10,11-tetrahydrophenanthro[1,2-c]furan- 1,5(3H,9bH)-dione (26).*



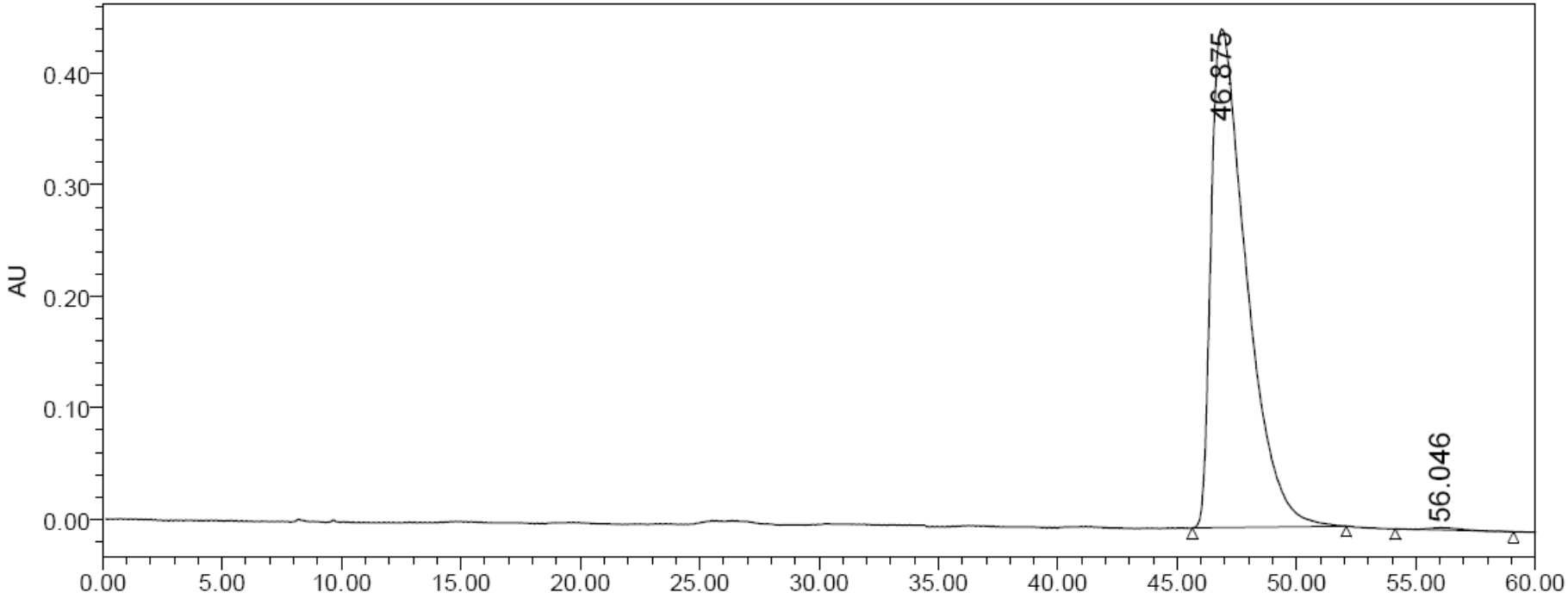
HRMS-ESI of *(3bR,9bS)-6-hydroxy-9b-methyl-3b,4,10,11-tetrahydrophenanthro[1,2-c]furan- 1,5(3H,9bH)-dione (26).*



IR of *(3bR,9bS)-6-hydroxy-9b-methyl-3b,4,10,11-tetrahydrophenanthro[1,2-c]furan- 1,5(3H,9bH)-dione (26).*

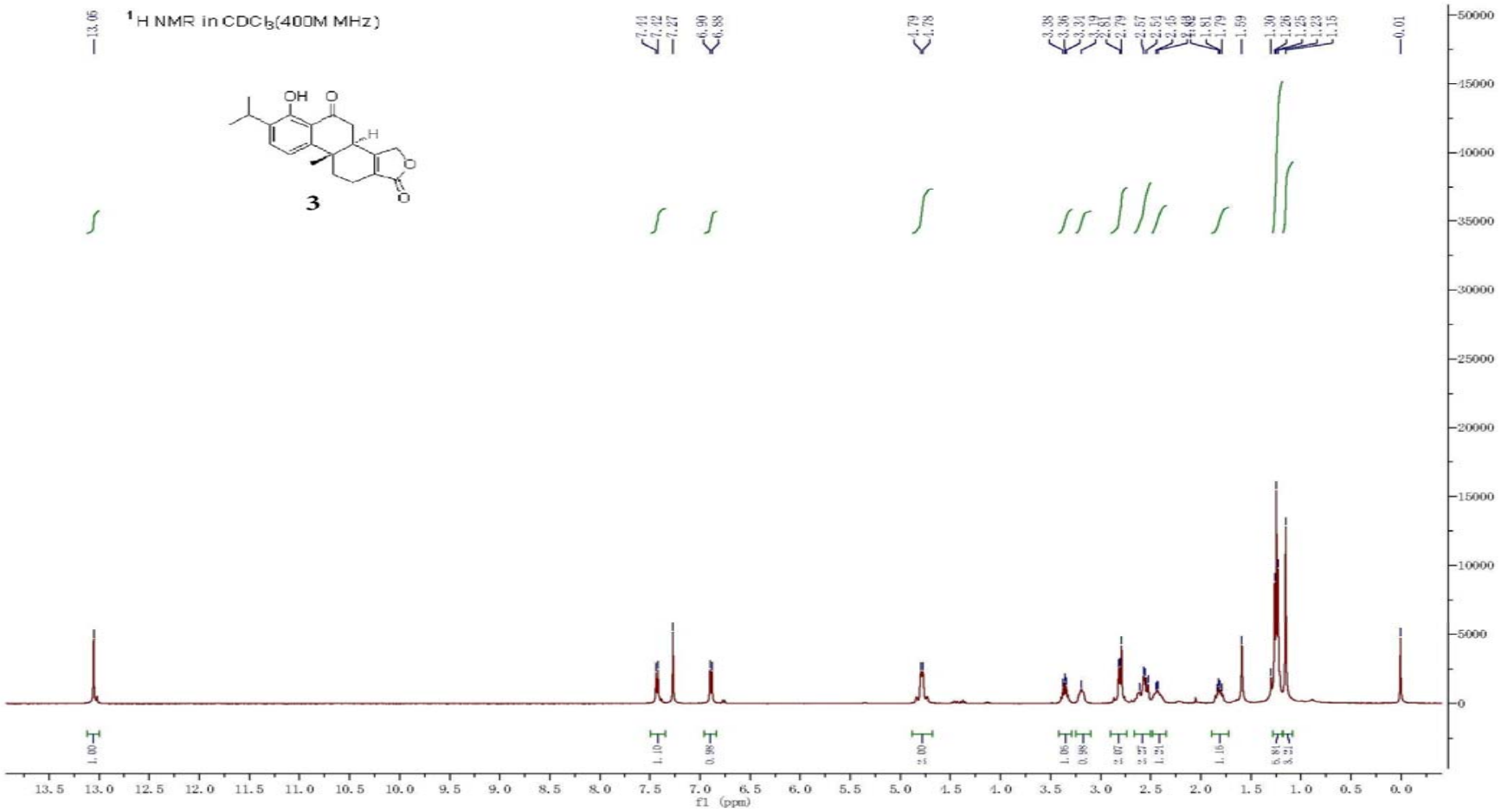


Chiral HPLC for ee value of *(3bR,9bS)-6-hydroxy-9b-methyl-3b,4,10,11-tetrahydrophenanthro[1,2-c]furan- 1,5(3H,9bH)-dione (26).*

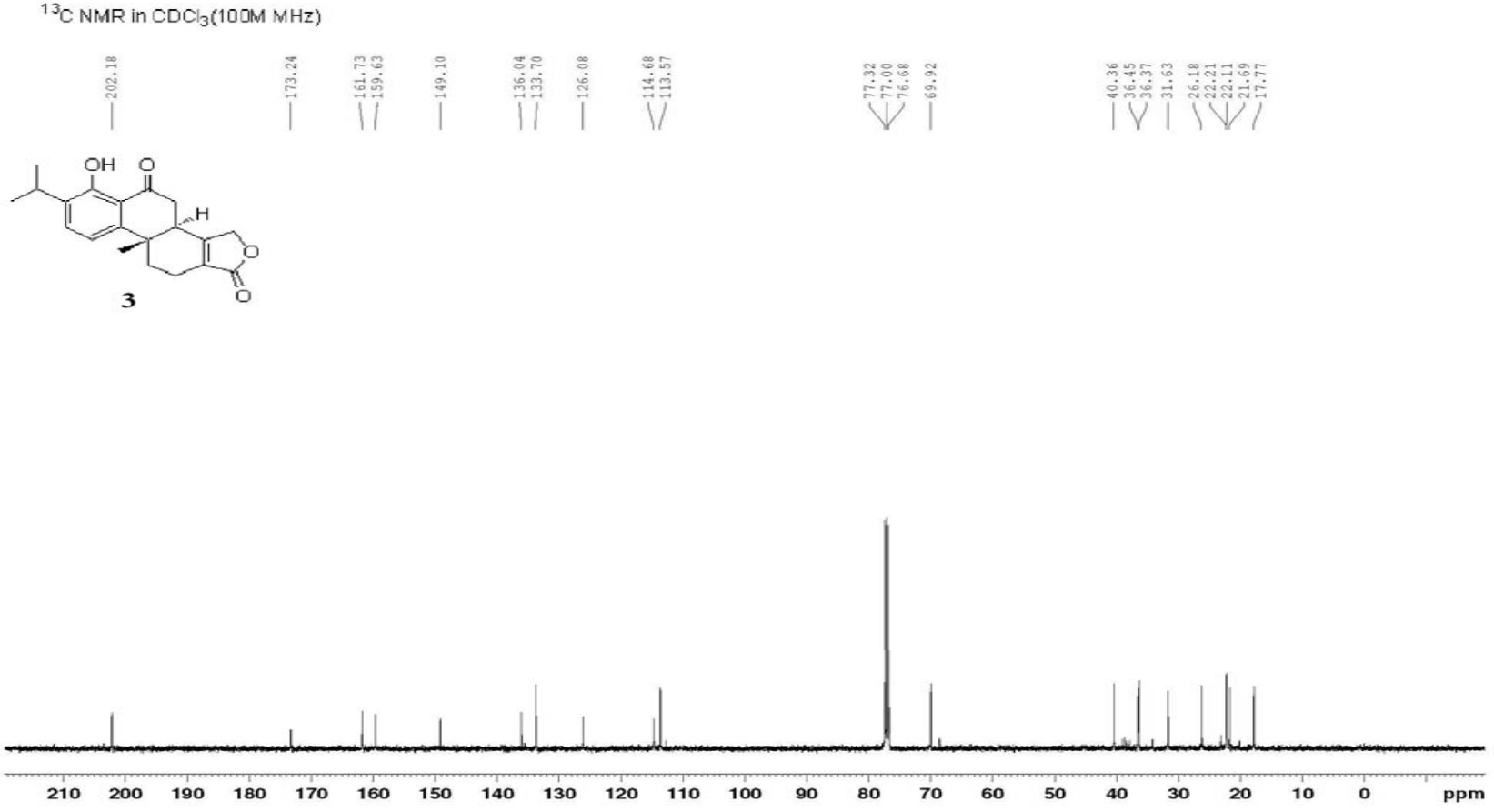


	channel	retenttion time(min)	area	%area	height
1	2998 (210-400)	46.875	146013716	99.55	446837
2	2998 (210-400)	56.046	205863	0.45	2173

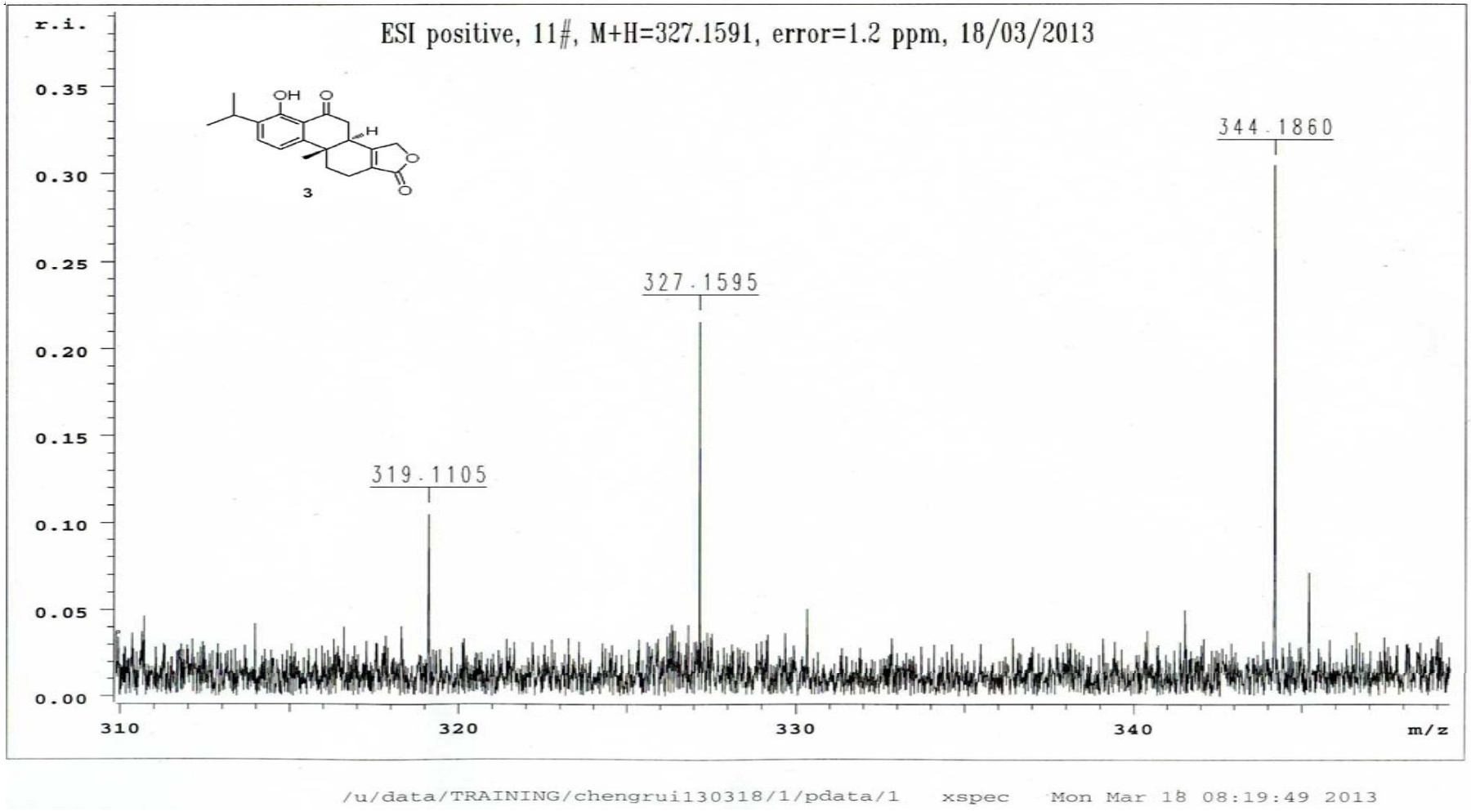
3.21. **^{1}H NMR of *(3bR,9bS)-6-hydroxy-7-isopropyl-9b-methyl-3b,4,10,11-tetrahydrophenanthro[1,2-c]furan-1,5(3H,9bH)-dione (4) prepared from Compound 26.***



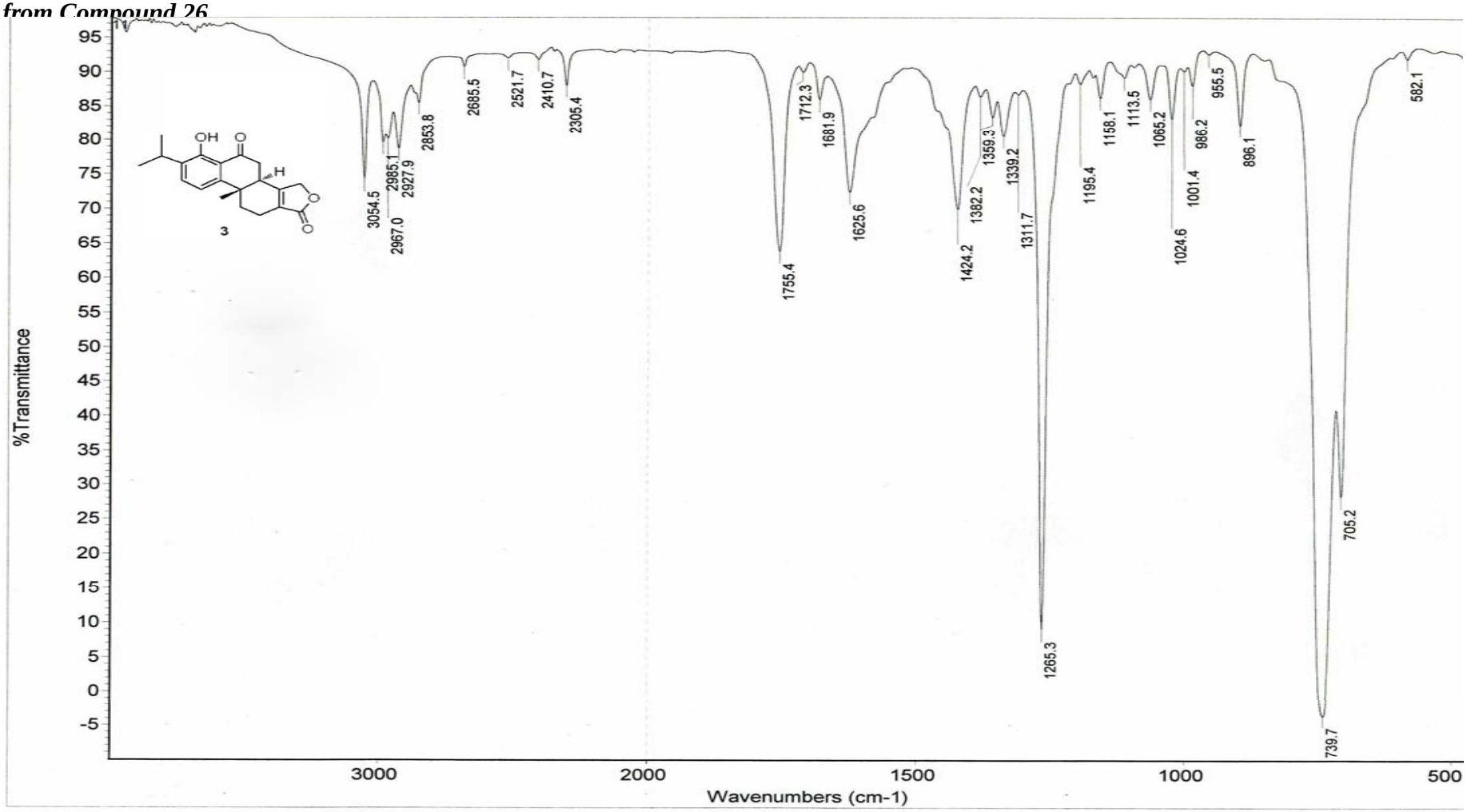
^{13}C NMR of *(3bR,9bS)-6-hydroxy-7-isopropyl-9b-methyl-3b,4,10,11-tetrahydrophenanthro[1,2-c]furan-1,5(3H,9bH)-dione (4) prepared from Compound 26.*



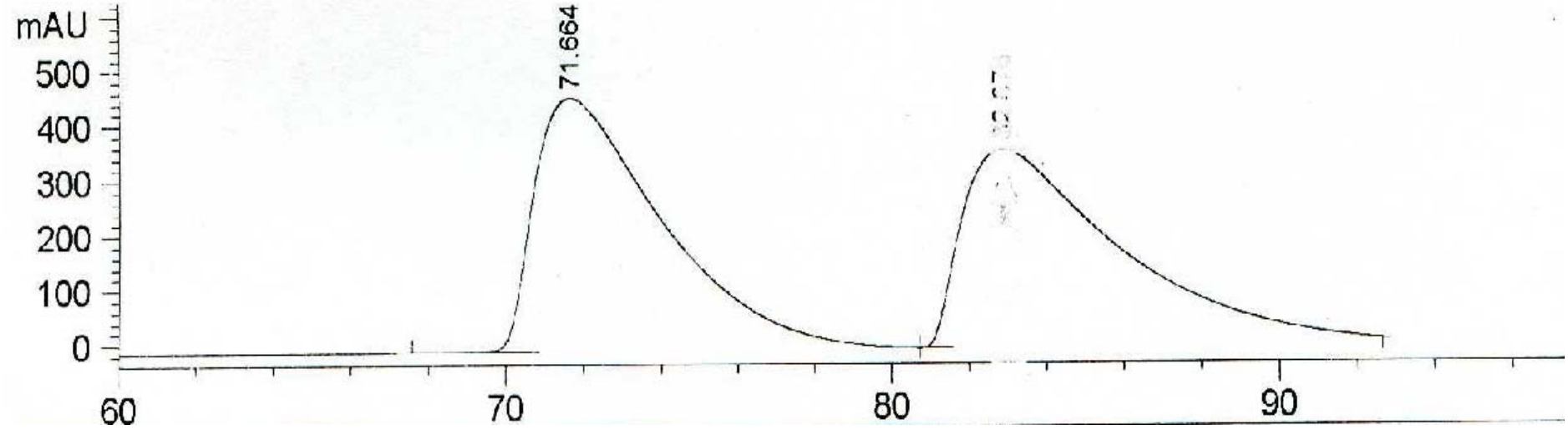
HRMS-ESI of *(3bR,9bS)-6-hydroxy-7-isopropyl-9b-methyl-3b,4,10,11-tetrahydrophenanthro [1,2- c]furan-1,5 (3H,9bH)-dione (4) prepared from Compound 26*



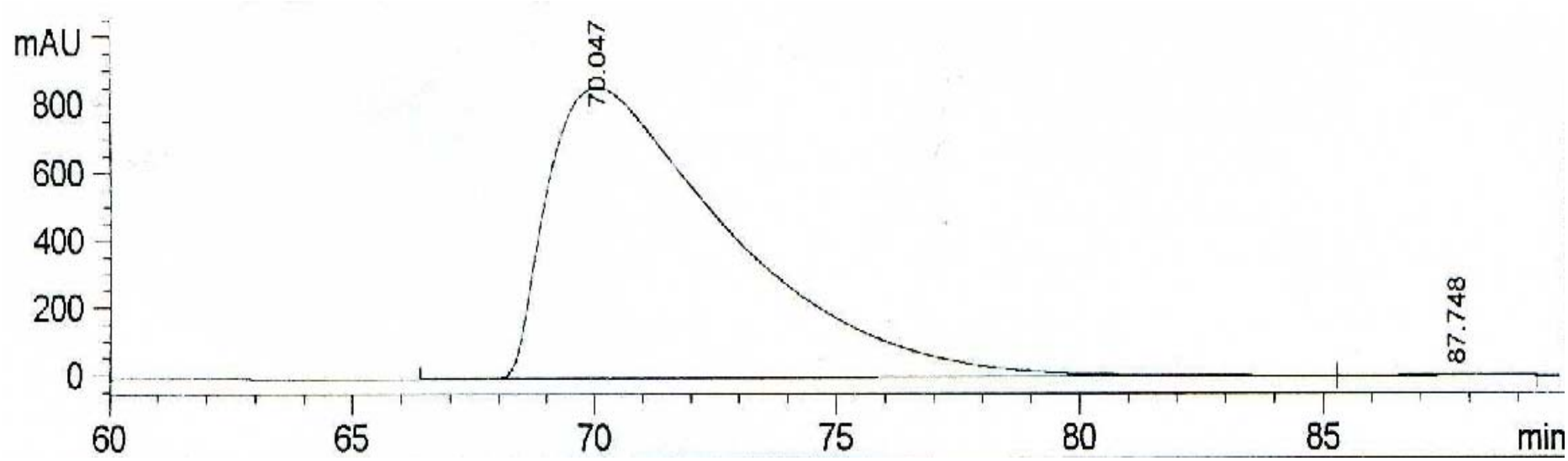
IR of *(3bR,9bS)-6-hydroxy-7-isopropyl-9b-methyl-3b,4,10,11-tetrahydrophenanthro [1,2-c] furan-1,5(3H, 9bH)-dione (4) prepared from Compound 26*



Chiral HPLC for ee value of *(3bR,9bS)-6-hydroxy-7-isopropyl-9b-methyl-3b,4,10,11-tetrahydrophenanthro [1,2-c] furan-1,5(3H, 9bH)-dione (4) prepared from Compound 26 or from 5 after recrystallization from CH_2Cl_2/Et_2O.*



	channel	retenttion time(min)	area	%area	height
1	2998 (210-400)	70.047	106360.348	51.77	460.589
2	2998 (210-400)	87.748	99089.132	48.23	358.408



	channel	retenttion time(min)	area	%area	height
1	2998 (210-400)	70.047	228263.125	99.81	860.961
2	2998 (210-400)	87.748	428.910	0.19	3.299