Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

Total Synthesis of (-)-8-*epi*-Chromazonarol Enabled by a Unique N_2H_4•H_2O Promoted Intramolecular *oxa*-Michael Cyclization Reaction

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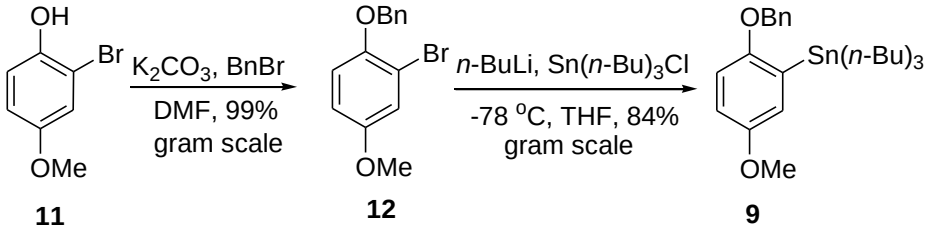
Contents

1. General Experimental Methods.

All reactions sensitive to air or moisture were carried out under argon atmosphere in dry and freshly distilled solvents under anhydrous conditions, unless otherwise noted. Column chromatography was performed on silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were obtained using 300 and 75MHz, 400 and 101MHz, or 600 and 150MHz NMR spectrometers respectively. Chemical shifts (δ) are given in ppm with reference to solvent signals [^{1}H NMR: $CDCl_3$ (7.26); ^{13}C NMR: $CDCl_3$ (77.0)]. The high resolution mass spectra (HRMS) were recorded on an FT-ICR mass spectrometer using electrospray ionization (ESI). Optical rotations were measured on a precision automated polarimeter. Melting points were measured on a melting point apparatus.

2. Experimental procedures and characterization dataof all synthetic new compounds

2.1 Preparation and spectra data of aryl stannane **9**



11 **12** **9**

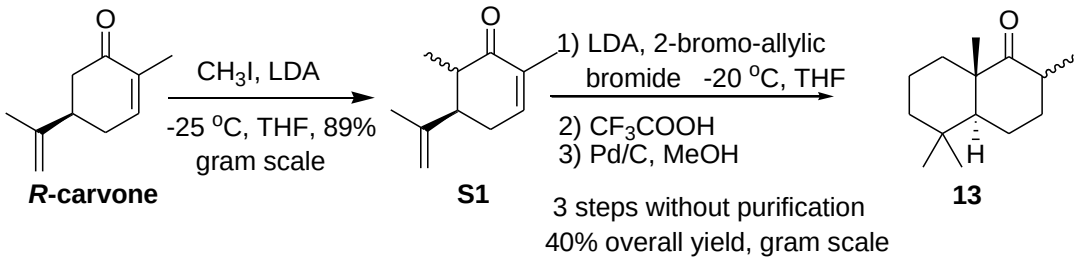
To a stirred solution phenol **11** (8.08 g, 40 mmol) in dry DMF (100 mL) was added K_2CO_3 (6.07 g, 44 mmol) and BnBr (5.2 mL, 44 mmol) at room temperature. The resulting mixture was then stirred at room temperature for 12 h. After it was completed, the reaction mixture was quenched with saturated NH_4Cl_{aq} (5 mL) and extracted with EtOAc (50 mL × 3). The combined organic extract was washed with saturated brine, dried over anhydrous Na_2SO_4, filtered, concentrated to give acrude residuewhich was further purified bycolumn chromatography on silica gel with

EtOAc/petroleum ether (1 : 50) as eluents to afford the corresponding known benzyl ether **12**[1] as yellow oil (11.53 g, 99%).

To a stirred solution of **12** (11.53 g**,** 39.5 mmol) in dry THF (100 mL) at -78 ℃ was added dropwise *n*-BuLi (2.5 M in *n*-hexane, 17.4 mL) under Ar. The resulting mixture was stirred at -78 ℃ for 3 h. Then (*n*-Bu)$_3$SnCl (11.8 mL, 43.4 mmol) was added and the mixture was allowed to react at -78℃ for another 1 h. After that, the cooling bath was removed and the mixture reacted at room temperature for 12 h. When the reaction was completed, it was quenched with saturated NH_4Cl_{aq} (50 mL) and extracted with EtOAc (80 mL × 3).The combined organic extract was washed with saturated brine, dried over anhydrous Na_2SO_4, filtered, concentrated to give a crude residue which was further purified by column chromatography on silica gel with EtOAc/petroleum (1 : 200) as eluents to afford the corresponding aryl stannane **9** as a colorless oil (16.72 g, 84%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.41 – 7.31 (m, 5H), 6.96 (t, *J* = 1.6 Hz, 1H), 6.79 – 6.75 (m, 2H), 4.97 (s, 2H), 3.77 (s, 3H), 1.50 – 1.37 (m, 6H), 1.31 – 1.19 (m, 6H), 1.04 – 0.90 (m, 6H), 0.83 (t, *J* = 7.3 Hz, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 157.2, 153.7, 137.4, 132.0, 128.3, 128.3, 127.7, 127.7, 127.6, 123.1, 113.2, 110.1, 70.4, 55.6, 29.1, 29.1, 29.1, 27.4, 27.4, 27.4, 13.7, 13.7, 13.7, 9.8, 9.8, 9.8 ppm. **HRMS(ESI)** : m/z $[M+H]^+$ calcd for $C_{26}H_{41}O_2Sn$: 505.2129, found : 505.2123.

2.2 Preparation and spectra data of bicyclic triflate **10**

2.2.1 The known bicyclic ketone **13** was prepared according to ref. 2



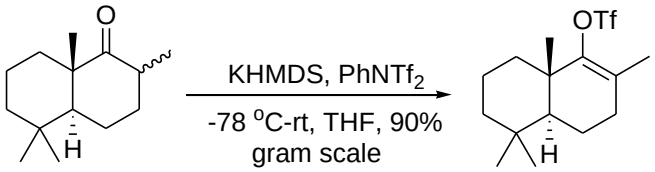
To a stirred solution of (*R*)-carvone (15.00 g, 100 mmol) in dry THF (30 mL) at -25 ℃ under Ar was added dropwise freshly prepared LDA (140 mmol in 70 mL dry THF). The resulting mixture was stirred at -25 ℃ for 2 h. Then it was added MeI (21.8 mL, 350 mmol) and allowed to react at -25 ℃ for 1 h. After that, the cooling bath was removed and the mixture reacted at room temperature for 12 h. When the reaction was completed, it was quenched with saturated NH_4Cl_{aq} (20 mL) and extracted with EtOAc (80 mL × 3).The combined organic extract was washed with saturated brine, dried over anhydrous Na_2SO_4, filtered, concentrated to give a crude residue which was further purified by column chromatography on silica gel with EtOAc/petroleum (1 : 200) as eluents to afford compound **S1** as yellow oil (14.62 g, 89%).

To a stirred solution of **S1** (6.30 g, 38.4 mmol) in dry THF (30 mL) at -20 ℃ under Ar was added dropwise freshly prepared LDA (57 mmol in 60 mL dry THF). The resulting mixture was stirred at -20 ℃ for 2 h, then it was added 2-bromo-allylic bromide (8 mL, 76.8 mmol) and allowed to react at -20 ℃ for 1 h. Then the cooling bath was removed and the mixture reacted at room temperature for 12 h. After the reaction was completed, it was quenched with saturated NH_4Cl_{aq} (20 mL) and extracted with EtOAc (80 mL × 3). The combined organic extract was washed with saturated brine, dried over anhydrous Na_2SO_4, filtered, concentrated to give a crude residue which was further treated with TFA (30 mL). After stirring for 3 days, it was quenched with saturated $NaHCO_{3aq}$ (40 mL) and extracted with EtOAc (40 mL × 3). The combined organic extract was washed with saturated brine, dried over anhydrous Na_2SO_4, filtered, concentrated to give a crude residue which was directly used in the subsequent hydrogenation reaction.

To a stirred solution of the obtained crude residue in 8 mL MeOH at autoclave,

Pd/C (10%, 1.50 g) was added. Then the autoclave was replaced with H_2 (20 atm) three times. Then the mixture was stirred at room temperature for 4 days. And the reaction mixture was filtered by celatom and concentrated to give acrude residue, which was further purified bycolumn chromatography on silica gel with EtOAc/petroleum (1 : 100) as eluents to afford compound **13** (3.20 g, 40% overall yields for 3 steps). The spectral data of compound **13** were in good agreement with that previously reported.[2]

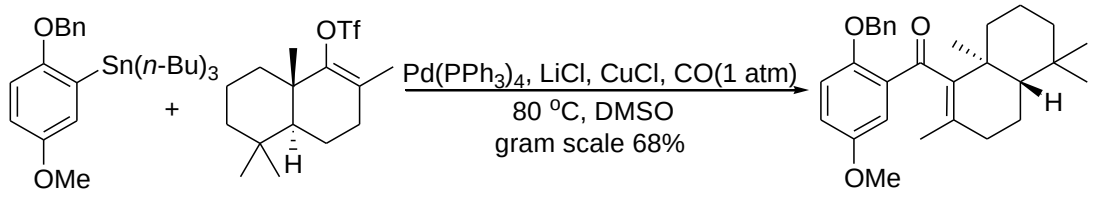
2.2.2 Preparation and spectra data of bicyclic triflate **10**



13 **10**

To a stirred solution of **13** (1.20 g, 5.8 mmol) in dry THF (25 mL) at -78 ℃ under Ar was added KHMDS (1 M, 14.4 mL, 14.4 mmol) dropwise. The resulting mixture was stirred at -78 ℃ for 2 h, then it was added the solution of $PhNTf_2$ (5.18 g, 14.4 mmol) in 20 mL dry THF. After it was complete, the reaction mixture was quenched with saturated NH_4Cl_{aq} (20 mL) and extracted with EtOAc (80 mL × 3). The organic extract was washed with saturated brine, dried over anhydrous Na_2SO_4, filtered, concentrated to give the crude residue, which was further purified by chromatography on silical gel with EtOAc/petroleum (1 : 200) to afford compound **10** as a colorless oil (1.77 g, 90%). $[a]_D^{27}$ = 38, (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 2.23 – 2.07 (m, 2H), 1.82 (d, J = 12.9, 1H), 1.74 – 1.69 (m, 4H), 1.60 – 1.52 (m, 2H), 1.49 – 1.42 (m, 2H), 1.28 – 1.17 (m, 3H), 1.14 (s, 3H), 0.90 (s, 3H), 0.86 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 152.0, 124.1, 117.1, 52.5, 41.2, 39.5, 34.7, 33.2, 33.1, 31.9, 21.4, 18.8, 18.3, 18.2, 17.5 ppm. **HRMS(ESI)** : m/z $[M+H]^+$ calcd for $C_{15}H_{24}F_3O_3S$: 341.1398, found : 341.1393.

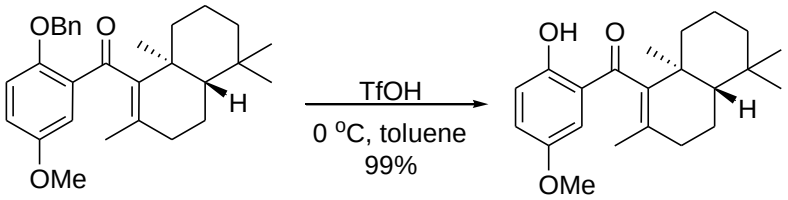
2.3 Preparation and spectra data of α, β-unsaturated aryl ketone **14**



9 **10** **14**

A dried vial (200 mL) with **9** (1.08 g, 2 mmol), **10** (680 mg, 2 mmol), $Pd(PPh_3)_4$ (1.15 g , 1 mmol), LiCl (504 mg, 12 mmol) and CuCl (980 mg,10 mmol) was added distilled DMSO (20 mL). Then it wasevacuated and refilled with carbon monoxide three times by using tee joint and balloon. The resulting mixture was heated to 80 ℃. After stirring for 8 h, the mixture was then cooled to 23 ℃ and filtered to remove the solid by celite and washed by EtOAc (200 mL). Then the organic phase was washed by water (100 mL) and saturated brine. The water layer was also washed by EtOAc (30 mL × 3) and the combined organic phase was dried over anhydrous Na_2SO_4, filtered, concentrated, and purified by silica gel with EtOAc/petroleum (1 : 100) to afford the corresponding ketene **14** as a white solid (588 mg, 68%). Mp: 85–88 ^oC. $[a]_D^{22}$ = 67, (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.38 – 7.23 (m, 6H), 6.92– 6.85 (m, 2H), 4.97 (s, 2H), 3.73 (s, 3H), 1.85 – 1.74 (m, 2H), 1.53 – 1.48 (m, 1H), 1.43 – 1.36 (m, 1H), 1.33 (s, 4H), 1.29 – 1.18 (m, 4H), 1.10 (s, 3H), 1.01 (m, 2H), 0.74 (s, 3H), 0.73 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 200.4, 153.2, 152.3, 145.3, 136.7, 130.3, 130.0, 128.5, 128.0, 128.0, 127.8, 127.8, 119.4, 115.8, 114.7, 71.2, 55.7, 49.9, 41.7, 37.9, 36.5, 33.1, 33.1, 32.1, 21.6, 21.1, 20.9, 18.6, 18.5 ppm. **HRMS(ESI)**: m/z $[M+H]^+$ calcd for $C_{29}H_{37}O_3$: 433.2743, found : 433.2733.

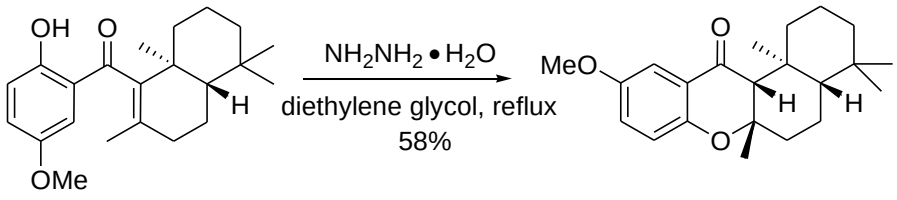
2.4 Preparation and spectra data of cyclization precursor 8



14 **8**

To a stirred solution of **14** (588 mg, 1.4 mmol) in dry toluene (7 mL) was added TfOH (0.37 mL, 4.2 mmol) at 0 ℃. The resulting mixture was then stirred at 0 ℃ for 5 min. After the reaction was complete, the reaction mixture was quenched with saturated $NaHCO_{3aq}$ (10 mL) and extracted with EtOAc (20 mL×3). The organic extract was washed with saturated brine, dried over dried Na_2SO_4, filtered, concentrated to give the crude residue, which was further purified by chromatography on silica gel with EtOAc/petroleum (1 : 50) to afford the phenol **8** as a yellow solid (460 mg,1.3 mmol, 99%). $[a]_D^{22}$ = 125, (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 12.05 (s, 1H), 7.09 (m, 2H), 6.94 – 6.91 (m, 1H), 3.77 (s, 3H), 2.23 – 2.17 (m, 2H), 1.83 – 1.78 (m,1H), 1.68– 1.53 (m, 3H), 1.45 (s, 3H), 1.40 – 1.33 (m, 3H), 1.30 (s, 3H), 1.19 – 1.10 (m, 2H), 0.94 (s, 3H), 0.88 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 207.6, 156.9, 151.6, 141.2, 131.2, 123.2, 120.7, 119.0, 116.6, 56.0, 50.5, 41.8, 38.3, 37.1, 33.3, 31.9, 21.5, 21.5, 21.3, 20.9, 18.6, 18.5 ppm. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{22}H_{31}O_3$: 343.2273, found : 343.2262.

2.5 Preparation and spectra data of tetracyclic ketone **7a** and **7a′**



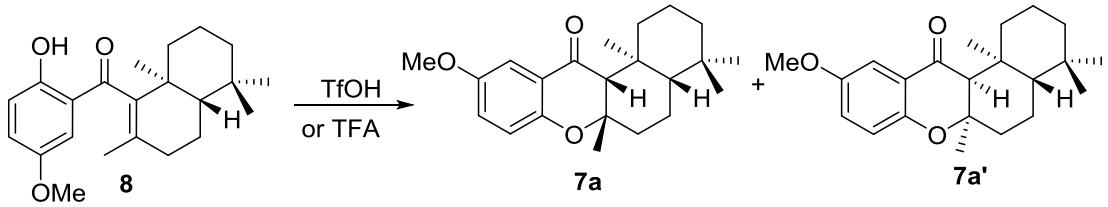
8 **7a**

2.5.1 Preparation and spectra data of tetracyclic ketone **7a**

To a stirred solution phenol of **8** (265 mg, 0.77 mmol) in dry diethylene glycol (5 mL) was added hydrazine hydrate (80%, 1.4 mL, 23 mmol). The resulting mixturewas

then heated to reflux. After the reaction was stirred for 12 h, the reaction mixture was quenched with saturated NH_4Cl_{aq} (5 mL). The mixture would be washed by 2 N HCl, then extracted with EtOAc (10 mL × 3). The organic extract was washed with saturated brine, dried over anhydrous Na_2SO_4, filtered, concentrated to give the crude residue, which was further purified by chromatography on silical gel with EtOAc/petroleum (1 : 50) to afford the ketone 7**a** as a white solid (153 mg,58%). Mp: 147 – 50 ^oC. $[a]_D^{23}$ = -69, (c = 1.0 , $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.29 (d, *J* = 3.2 Hz, 1H), 7.06 (dd, *J* = 9.0, 3.2 Hz, 1H), 6.83 (d, *J* = 9.0 Hz, 1H), 3.80 (s, 3H), 2.26 – 2.21 (m, 1H), 1.94 (s, 1H), 1.71– 1.65 (m, 3H), 1.60 – 1.52 (m, 2H), 1.47 – 1.40 (m, 3H), 1.25 – 1.18 (m, 6H), 0.92 (s, 3H), 0.90 (d, *J* = 2.2 Hz, 1H), 0.84 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 194.9, 154.7, 153.4, 124.6, 122.0, 119.3, 106.7, 80.0, 64.6, 55.7, 54.3, 41.6, 40.0, 39.9, 38.4, 33.8, 33.4, 26.5, 22.0, 18.4, 18.1, 15.2 ppm. **HRMS (ESI)** : m/z $[M+H]^+$ calcd for $C_{22}H_{31}O_3$: 343.2273, found : 343.2263.

2.5.2 Spectra data of **7a′**



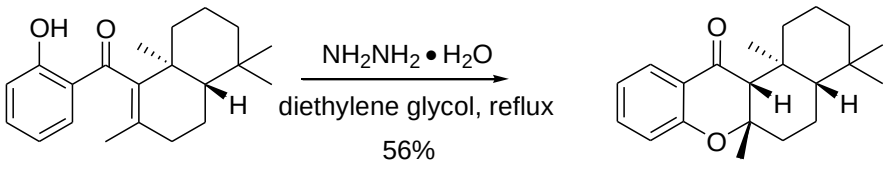
7a′and **7a** was obtained in 28% and 15% yields respectively as a 1:1 mixture when compound **8** was treated with TfOH or TFA in reflux toluene. **7a′**'s spectra data was shown as below. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.25 (d, J = 3.2 Hz, 1H), 7.08 (dd, *J* = 9.0, 3.2 Hz, 1H), 6.82 (d, *J* = 9.0 Hz, 1H), 3.81 (s, 3H), 2.17 (s, 1H), 2.15 – 2.12 (m, 1H), 1.98 – 1.92 (m, 1H), 1.81 – 1.78 (m, 1H), 1.71 (dd, *J* = 12.3, 6.3 Hz, 1H), 1.56 (d, *J* = 8.2 Hz, 2H), 1.54 – 1.46 (m, 2H), 1.34 – 1.29 (m, 2H), 1.27 (s, 3H), 1.19 (s, 3H), 0.92 (dd, *J* = 13.2, 3.3 Hz, 1H), 0.87 (s,3H), 0.80 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$)

δ = 195.0, 154.0, 153.4, 125.4, 119.7, 119.4, 106.7, 80.4, 63.8, 55.7, 44.0, 41.7, 37.9, 37.5, 33.7, 33.4, 31.8, 27.0, 26.8, 21.8, 18.9, 17.4.

2.6 Spectra data of **8b-8d** and cyclization products **7b-7d**

8b-8d was prepared in similar routs as **8** and treated by the standard cyclization conditions to afford **7b-7d**.

2.6.1 Spectra data of **8b** and **7b**



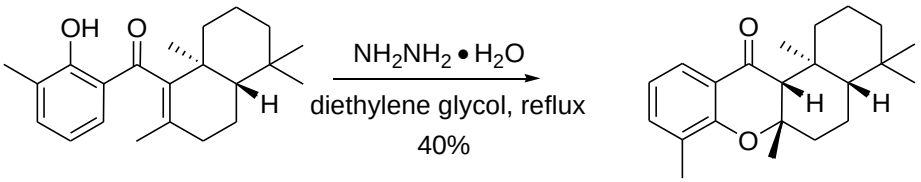
8b **7b**

Compound **8b**, white solid, Mp: 106 – 109 ^{o}C, $[a]_{D}^{27}$ = 165, (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 12.48 (s, 1H), 7.59 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.46 – 7.42 (m, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 6.87 (t, *J* = 7.5 Hz, 1H), 2.26 – 2.12 (m, 2H), 1.83 – 1.78 (m, 1H), 1.65 – 1.53 (m, 2H), 1.42 (s, 3H),1.40 – 1.33 (m, 4H), 1.31 (s, 3H), 1.20 – 1.10 (m, 2H), 0.95 (s, 3H), 0.88 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 208.0, 162.6, 141.3, 136.1, 133.3, 131.1, 121.1, 118.9, 118.3, 50.4, 41.8, 38.3, 37.1, 33.3, 33.3, 32.0, 21.5, 21.2, 20.9, 18.6, 18.5 ppm. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{21}H_{29}O_2$: 313.2168, found : 313.2162.

Compound **7b** was obtained in 56% yield, white solid, Mp: 90 – 93 ^{o}C, $[a]_{D}^{27}$ = -19, (c = 1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.84 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.45 – 7.40 (m, 1H), 6.97 – 6.92 (m, 1H), 6.89 (dd, *J* = 8.3, 0.9 Hz, 1H), 2.29- 2.23 (m, 1H), 1.97 (s, 1H), 1.77 – 1.60 (m, 3H), 1.61 – 1.51 (m, 2H), 1.48 – 1.39 (m, 3H), 1.24 (s, 3H),1.19 – 1.15 (m, 1H), 0.95 – 0.90 (m, 4H), 0.85 (s, 3H), 0.84 (s, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 194.8, 160.2, 135.5, 126.2, 122.5, 120.5, 118.1, 80.1,

64.8, 54.3, 41.7, 40.0, 40.0, 38.4, 33.8, 33.4, 26.6, 22.0, 18.4, 18.1, 15.3 ppm. **HRMS (ESI)**: m/z $[M+Na]^+$ calcd for $C_{21}H_{28}O_2Na$: 335.1987, found : 335.1982.

2.6.2 Spectra data of **8c** and **7c**

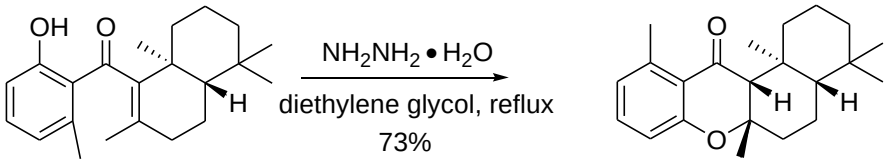


8c **7c**

Compound **8c**, oil, $[a]_D^{27}$ = 101, (c = 1.0, $CHCl_3$). **^{1}H NMR**(600 MHz, $CDCl_3$) δ = 12.78 (s, 1H), 7.44 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.31 (d, *J* = 7.2 Hz, 1H), 6.77 (t, *J* = 7.6 Hz, 1H), 2.27 (s, 3H), 2.21 – 2.13 (m, 2H), 1.81 – 1.78 (m, 1H), 1.64 – 1.53 (m, 2H), 1.45 – 1.40 (m, 4H), 1.37 – 1.32 (m, 2H), 1.31 (s, 3H), 1.18 – 1.09 (m, 2H), 0.93 (d, *J* = 15.0 Hz, 3H), 0.88 (s, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 208.2, 161.1, 141.5, 136.9, 131.0, 131.0, 127.2, 120.4, 118.1, 50.3, 41.8, 38.3, 37.1, 33.2, 32.5, 31.9, 21.5, 21.2, 20.9, 18.6, 18.5, 15.3 ppm.

Compound **7c** was obtained in 40% yield, white solid, Mp: 126 – 130 ^{o}C, $[a]_D^{27}$ = -13, (c = 1.0,$CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.69 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.29 (dd, *J* = 7.3, 0.8 Hz, 1H), 6.83 (t, *J* = 7.6 Hz, 1H), 2.32 – 2.27 (m, 1H), 2.21 (s, 3H), 1.95 (s, 1H), 1.82 – 1.73 (m, 1H),1.70 – 1.62 (m, 3H), 1.58 – 1.50 (m, 1H), 1.48 – 1.40 (m, 3H), 1.26 (s, 1H), 1.22 (s, 3H), 0.95 – 0.90 (m, 4H), 0.85 (s, 3H), 0.81 (s, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 195.2, 158.3, 136.2, 127.2, 123.7, 122.0, 119.8, 79.7, 64.6, 54.3, 41.7, 40.1, 38.4, 33.8, 33.4, 29.7, 26.8, 22.1, 18.5, 18.1, 15.7, 15.2 ppm. **HRMS (ESI)** : m/z $[M+Na]^+$ calcd for $C_{22}H_{30}O_2Na$: 349.2143, found : 349.2138.

2.6.3 Spectra data of **8d** and **7d**

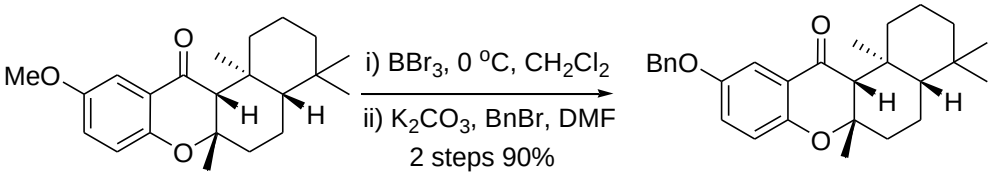


8d **7d**

Compound **8d**, oil, $[a]_D^{25}$ = 117, (c = 1.0, CH_2Cl_2). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 13.12 (s, 1H), 7.26 (t, *J* = 7.9 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 6.66 (d, *J* = 7.4 Hz, 1H), 2.49 (s, 3H), 2.20 (dd, *J* = 18.6, 6.6 Hz, 1H), 2.13 – 1.99 (m, 1H), 1.82 – 1.50 (m, 5H), 1.44 (s, 3H), 1.39 – 1.33 (m, 2H), 1.31 (s,3H), 1.19 (dd, *J* = 13.2, 3.3 Hz, 2H), 0.94 (s, 3H), 0.89 (s,3 H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 207.3, 163.9, 144.6, 140.3, 135.0, 131.9, 123.1, 122.3, 117.0, 50.0, 41.9, 38.7, 35.7, 33.4, 33.3, 32.2, 23.4, 22.7, 21.6, 20.9, 18.8, 18.5 ppm. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{22}H_{31}O_2$: 327.2324, found: 327.2319.

Compound **7d** was obtained in 73% yield, oil, $[a]_D^{25}$ = -32, (c = 1.0, CH_2Cl_2). **^{1}H NMR**(400 MHz, $CDCl_3$) δ = 7.26 (t, *J* = 8.0 Hz, 1H), 6.73 (t, *J* = 8.8Hz,2H), 2.62 (s, 3H), 2.22 (d, *J* = 14.1 Hz, 1H), 1.94 (s, 1H), 1.63 – 1.58 (m, 4H), 1.56 – 1.40 (m, 5H), 1.24 (s, 3H), 1.22 – 1.18 (m, 1H), 0.92 (s, 4H), 0.89 (s, 1H), 0.84 (s, 6H) ppm. **^{13}CNMR** (101 MHz, $CDCl_3$) δ = 196.6, 161.3, 141.0, 134.1, 123.9, 120.8, 116.0, 79.1, 66.2, 54.2, 41.7, 40.3, 39.9, 38.1, 33.8, 33.4, 26.5, 23.1, 22.0, 18.5, 18.2, 15.5 ppm. **HRMS (ESI)** : m/z $[M+H]^+$ calcd for $C_{22}H_{31}O_2$: 327.2324, found :327.2319.

2.7 Preparation and spectra data of benzyl ether **18**

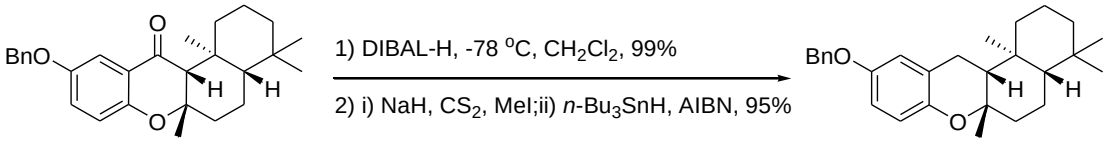


7a **18**

To a stirred solution of **7a** (153 mg, 0.45 mmol) in dry CH_2Cl_2 (5 mL) at 0 ℃ under Ar was added BBr_3 (0.087 mL, 0.90 mmol) dropwise. The resulting mixture

was allowed to warm to room temperature. After the reaction was stirred for 12 h, the reaction mixture was quenched with saturated $NaHCO_{3aq}$ (10 mL) and extracted with EtOAc (20 mL×3). The organic extract was washed with saturated brine, dried over dried Na_2SO_4, filtered, concentrated to give the crude residue, which was further treated with K_2CO_3 (124 mg, 0.90 mmol) and BnBr (0.11 mL, 0.90 mmol). The resulting mixture was then stirred at room temperature for 12 h. After the reaction was complete, the reaction mixture was quenched with saturated NH_4Cl_{aq} (5 mL) and extracted with EtOAc (10 mL × 3). The organic extract was washed with saturated brine, dried over Na_2SO_4, filtered, concentrated to give the crude residue, which was further purified by chromatography on silica gel with EtOAc/petroleum (1 : 50) to afford the corresponding compound **18** as a yellow solid (169 mg, 90%). Mp: 123–127 ^oC, $[a]_D^{24}$ = -69, (c = 1.0 , $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.44 – 7.31(m, 6H), 7.12 (dd, *J* = 9.0, 3.2 Hz, 1H), 6.83 (d, *J* = 9.0 Hz, 1H), 5.03 (s, 2H), 2.26 – 2.21 (m,1H), 1.94 (s, 1H), 1.75 – 1.64 (m, 3H), 1.62 – 1.51 (m, 2H), 1.49 – 1.41 (m, 3H),1.23 (s, 3H), 1.21 – 1.18 (m, 1H), 0.93 (s, 3H), 0.90 (d, *J* = 2.1 Hz, 1H), 0.85 (s, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 194.8, 154.9, 152.7, 136.8, 128.5, 128.5,128.0, 128.0, 127.7, 125.2, 122.1, 119.4, 108.2, 80.0, 70.6, 64.6, 54.3, 41.7, 40.1, 40.0, 38.5, 33.8, 33.4, 26.5, 22.0, 18.4, 18.1, 15.3 ppm. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{28}H_{35}O_3$: 419.2586, found : 419.2571.

2.8 Preparation and spectra data of compound **19**



18 **19**

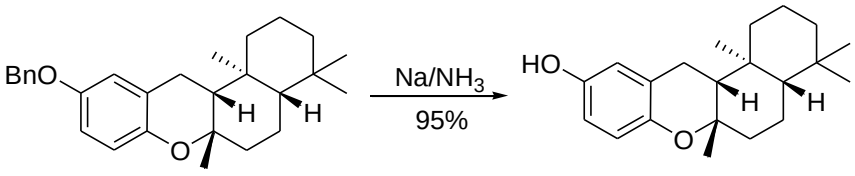
To a stirred solution of **18** (169 mg, 0.40 mmol) in dry CH_2Cl_2 (3 mL) at -78 ℃ under Ar was added DIBAL-H (1.5 M, 0.6 mL, 0.80 mmol) dropwise. The resulting mixture was stirred at -78℃ for 20 h. After the reaction was complete, the reaction mixture

was quenched with CH_3OH (0.1 mL) and the resulting mixture was added saturatedseignettesalt$_{aq}$.When the organic phase was clear, it was extracted with CH_2Cl_2 (20 mL×3).The organic extract was washed with saturated brine, dried over Na_2SO_4, filtered, concentrated to give the crude residue, which was further purified by chromatography on silica gel with EtOAc/petroleum (1 : 10) to afford the corresponding alcohol as a colorless oil (168 mg, 99%).

To a stirred solution of the obtained alcohol (168 mg,0.40 mmol) in dry THF (4 mL) at 0 ℃ under Ar was added NaH (60%, 48 mg, 1.20 mmol) in one portion. Carbon disulfide (0.24 mL, 4 mmol) was injected into the mixture by a syringe, then it was allowed to warm to room temperature and stir for another 0.5 h. Then the mixture was injected the iodomethane (0.25 mL, 4 mmol). After the reaction was complete, the reaction mixture was quenched with saturated NH_4Cl_{aq} (5 mL) and extracted with EtOAc (10 mL×3). The organic extract was washed with saturated brine, dried over dried Na_2SO_4, filtered, concentrated to give the crude residue, which was further to treat with *n*-Bu_3SnH (0.22 mL, 0.8 mmol) and AIBN(33 mg, 0.2 mmol) in dry toluene (3 mL). This resulting mixture was allowed to react at 80 ℃ for 8 h. After the reaction was complete, the reaction mixture was quenched with saturated NH_4Cl_{aq} (5 mL) and extracted with EtOAc (10 mL×3). The organic extract was washed with saturated brine, dried over dried Na_2SO_4, filtered, concentrated to give the crude residue, which was further purified by chromatography on silical gel with EtOAc/petroleum (1 : 50) to afford **19** as a white solid (152 mg, 95%). Mp: 124-128 ^oC. $[a]_D^{25}$= -32, (c =1.0 , $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.44 – 7.31 (m, 5H), 6.73 – 6.64 (m, 3H), 4.97 (s, 2H), 2.90 (dd, *J* = 18.0, 8.1 Hz, 1H), 2.73 (d, *J* = 18.1 Hz, 1H), 2.14–2.09 (m, 1H), 1.83 (d, *J* = 12.5 Hz, 1H), 1.59 – 1.54 (m, 3H), 1.46 – 1.39 (m, 3H), 1.34 – 1.26(m, 3H), 1.16 (s, 3H), 0.89 (s, 3H), 0.88 (s, 1H), 0.81 (s, 3H),

0.72 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 152.2, 148.8, 137.4, 128.5, 127.8,127.8, 127.6, 127.6, 123.4, 117.4, 114.4, 113.3, 75.3, 70.5, 55.3, 49.5, 41.9, 40.7, 40.0, 38.3, 33.7, 33.2, 27.2, 23.0, 21.9, 18.4, 18.2, 14.2 ppm. **HRMS (ESI)**: m/z $[M+Na]^+$ calcd for $C_{28}H_{36}O_2Na$: 427.2613, found : 427.2608.

2.9 Preparation and spectra data of 8-*epi*-chromazonarol **2**

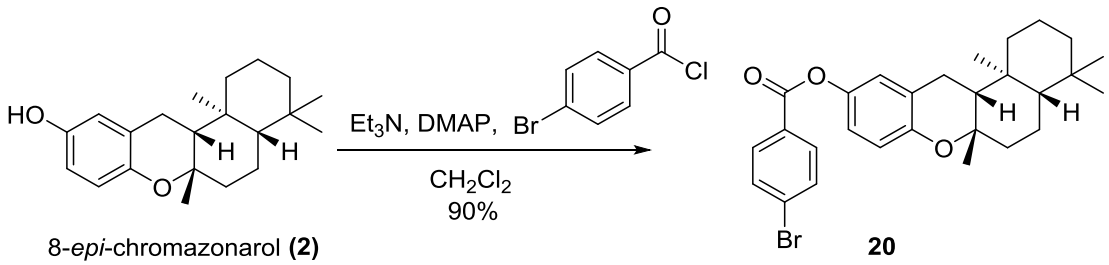


19 8-*epi*-chromazonarol **(2)**

To a stirred solution of freshly prepared liquid NH_3 (5 mL) in a two-necked bottle which was frozen by liquid nitrogen using a Dewar condenser at -78 ℃ was added cut Na (60%, 146 mg, 3.8 mmol) in one portion. Then the mixture had a blue color and it was allowed to add the solution of **19** (154 mg, 0.38 mmol) in dry THF (3 mL). After the mixture stirred for 10 min, the reaction was carefully quenched with solid NH_4Cl. After evaporation of ammonia, the residue was taken in water (1 mL) and extracted with EtOAc (10 mL×3). The organic extract was washed with saturated brine, dried over dried Na_2SO_4, filtered, concentrated to give the crude residue, which was further purified by chromatography on silica gel with EtOAc/petroleum (1 : 10) to afford **2** as a white solid (114 mg, 95%). Mp: 131-134 ^oC. $[a]_D^{25}$ = -30, (c = 1.0 , CCl_4). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 6.61 – 6.59 (m, 1H), 6.55 – 6.53 (m, 2H), 4.45 (s, 1H), 2.87 (dd, *J* = 18.0, 8.1 Hz, 1H), 2.70 (d, *J* = 18.0 Hz, 1H), 2.13 – 2.09 (m, 1H), 1.82 (d, *J* = 11.9 Hz, 1H), 1.64 – 1.60 (m, 2H), 1.58 – 1.52 (m, 3H), 1.43 – 1.39 (m, 2H), 1.29 – 1.26 (m, 2H), 1.15 (s, 3H), 0.90 (s, 3H),0.86 (dd, *J* = 13.0, 3.3 Hz, 1H), 0.82 (s, 3H), 0.72 (s, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 148.7, 148.6, 123.6, 117.6, 114.7, 113.8, 75.3, 55.3, 49.6, 41.9, 40.7, 40.1, 38.3, 33.7, 33.2, 27.1, 22.9, 21.9, 18.5, 18.3, 14.2 ppm. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{21}H_{31}O_2$:

315.2324, found : 315.2311.

2.10 Preparation and spectra data of ester **20**



8-*epi*-chromazonarol **(2)** **20**

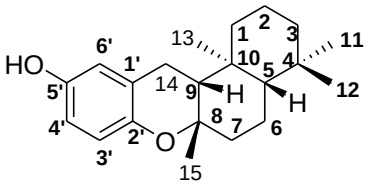
To a stirred solution phenol of **2** (16 mg, 0.05 mmol) in dry CH_2Cl_2 (0.5 mL) was added DMAP (1 mg, 0.005 mmol) and Et_3N (0.02 mL, 0.15 mmol) and 4-bromobenzoyl chloride (84 mg, 0.2 mmol). The resulting mixture was then stirred at room temperature for 15 min. After the reaction was complete, the reaction mixture was quenched with saturated NH_4Cl_{aq} (5 mL) and extracted with EtOAc (5 mL×3). The organic extract was washed with saturated brine, dried over dried Na_2SO_4, filtered, concentrated to give the crude residue, which was further purified by chromatography on silical gel with EtOAc/petroleum (1 : 50) to afford **25** as a white solid (22 mg, 90% yield). $[a]_D^{25}$= -44, (c = 1.0, CH_2Cl_2). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.05 – 7.98 (m, 2H), 7.69 – 7.62 (m, 2H), 6.89 – 6.85(m, 2H), 6.75 (d, *J* = 8.2 Hz, 1H), 2.95 (dd, *J* = 18.2, 8.0 Hz, 1H), 2.76 (d, *J* = 18.1 Hz, 1H), 2.17 – 2.13 (m, 1H), 1.82 (d, *J* = 12.3 Hz, 1H), 1.63 – 1.53 (m, 4H), 1.43 – 1.31 (m, 4H), 1.18 (s, 3H), 1.15 – 1.09 (m, 1H), 0.93 (s, 1H), 0.90 (s, 3H), 0.82 (s, 3H), 0.73 (s, 3H) ppm.**^{13}C NMR** (75 MHz, $CDCl_3$) δ = 164.8, 152.6, 143.5, 131.9, 131.6, 128.8, 128.6, 123.5, 121.0, 119.6, 117.7, 75.8, 55.3, 49.4, 41.9, 40.7, 40.0, 38.4, 33.7, 33.2, 27.3, 22.9, 21.9, 18.4, 18.3, 14.3 ppm. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{28}H_{34}BrO_3$: 497.1691, found : 497.1686.

2.11 Spectra data of Intermediate **17**

Compound **17** was obtained in 21% yield when the *oxa*-Michael cyclization

reaction was quenched in 1 h. **17**'s spectra data was shown as below. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.24 (d, *J* = 3.2 Hz, 1H), 7.02 (dd, *J* = 8.9, 3.2 Hz, 1H), 6.78 (d, *J* = 8.9 Hz, 1H), 3.78 (s, 3H), 2.71 (d, *J* = 11.5 Hz, 2H), 2.09 – 2.05 (m, 1H), 1.97 – 1.90 (m, 1H), 1.80 – 1.65 (m, 2H), 1.56 (s, 1H), 1.47 – 1.40 (m, 3H), 1.37 (s, 3H), 1.26 (s, 1H), 1.20 (dd, *J* = 13.8, 4.5 Hz, 1H), 1.14 (s, 3H), 1.01 – 0.95 (m, 2H), 0.91 (s, 3H), 0.86 (s, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 194.1, 153.4, 153.2, 124.0, 121.9, 118.9, 107.5, 82.8, 65.0, 55.7, 55.6, 41.9, 40.9, 39.8, 37.3, 33.6, 33.4, 21.7, 21.2, 19.4, 18.4, 15.6 ppm.

2.12 Comparison of the spectra data of synthetic (-)-8-epi-chromazonarol and those of natural product



8-*epi*-chromazonarol (**2**)

2.12.1 Comparisons of their ^{13}C NMR spectra data (ppm)

number	Synthetic 8-epi-chromazonarol	Natural 8-*epi*-chromazonarol	Δ
1	40.1	39.9	0.2
2	18.3	18.1	0.2
3	40.7	40.5	0.2
4	33.2	33.0	0.2
5	55.3	55.1	0.2
6	18.5	18.3	0.2
7	41.9	41.8	0.1
8	75.3	75.2	0.1
9	49.6	49.4	0.2
10	38.3	38.1	0.2
11	33.7	33.5	0.2
12	21.9	21.7	0.2
13	14.2	14.1	0.1
14	22.9	22.7	0.2
15	27.1	27.0	0.1
1'	123.6	123.3	0.3
2'	148.7	148.5	0.2
3'	117.6	117.3	0.3
4'	113.8	113.8	0
5'	148.6	148.2	0.4
6'	114.7	114.8	-0.1

2.12.2 Comparisons of their partial ^{1}H NMR spectra data (the isolation literature only reported partial of ^{1}H NMR spectra data of natural 8-*epi*-chromazonarol)

number	Synthetic 8-*epi*-chromazonarol	Natural 8-*epi*-chromazonarol	Δ
11	0.72(s, 3H)	0.72(s, 3H)	0
12	0.82(s, 3H)	0.82(s, 3H)	0
13	0.90(s, 3H)	0.90(s, 3H)	0
14	2.70(d, 1H$_{\alpha}$, J =18Hz); 2.87(dd,1H$_{ß}$, J =6Hz, 18Hz)	2.72(d, 1Hα, J = 17 Hz); 2.89(d,d, 1Hß, J =17.7Hz)	-0.02; -0.01
15	1.15(s, 3H)	1.16(s, 3H)	-0.01
3’	6.61-6.59(m, 1H)	6.57(m, 1H)	-0.03
4’	6.55(m, 1 H)	6.57(m, 1H)	-0.02
5’(-OH)	4.45(br, s, 1H)	4.75(br, s, 1H)	-0.3
6’	6.53(m,1H)	6.57(m,1H)	-0.04

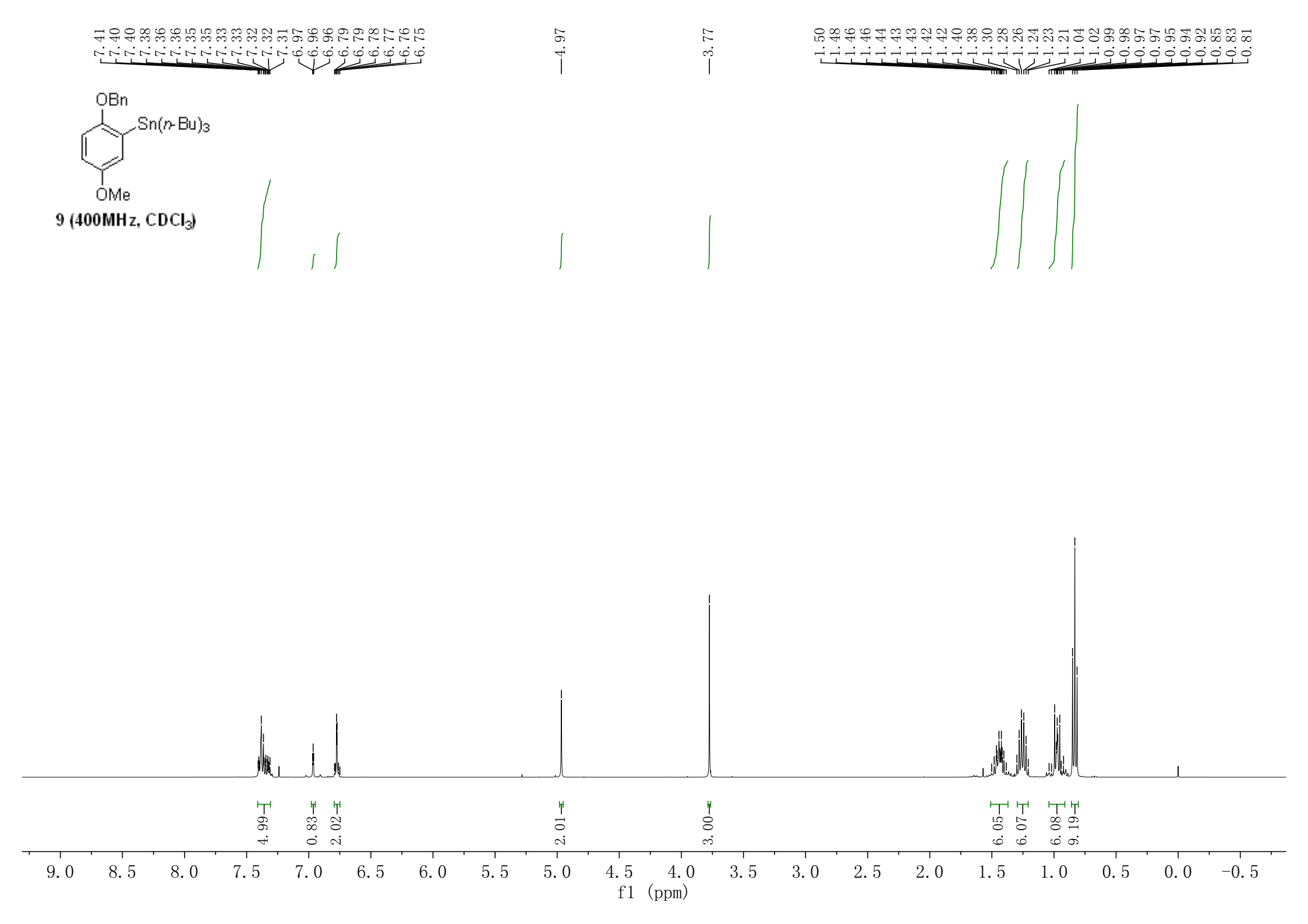
2.12.3 Comparisons of their physical data and MS data

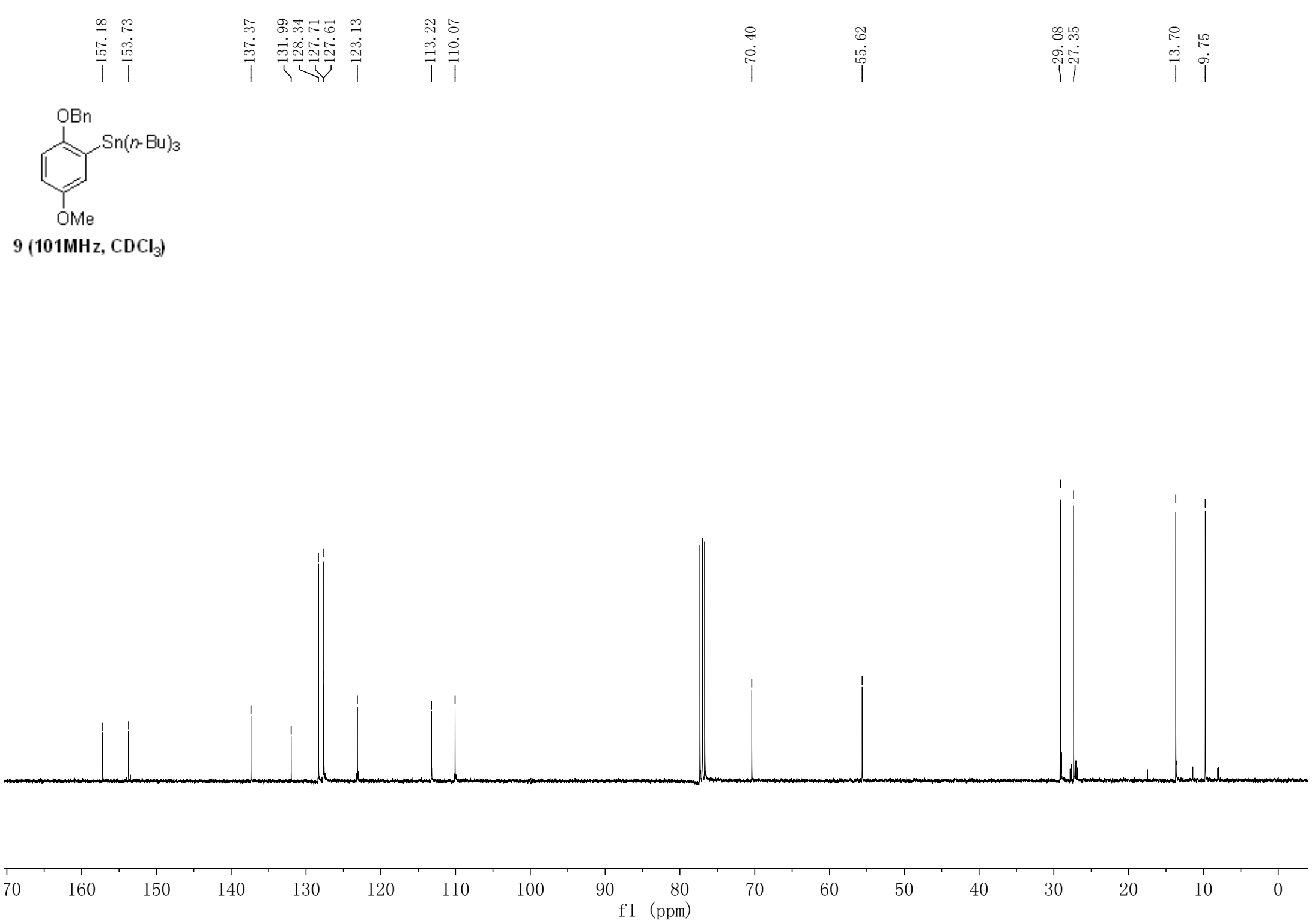
data	Synthetic 8-epi-chromazonarol	Natural 8-epi-chromazonarol
Mp	131-134^{o}C	132−134^{o}C
[a]$_{D}$	$[a]_{D}^{20}$= -30, (c = 1.0 , CCl_4)	-2, (c = 1.0, CCl_4)
MS	315.2311(M+H^{+})	314.2250

3. References

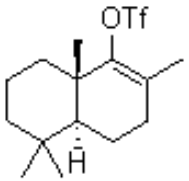
1. J. Oshita, Y. Noguchi, A. Watanabe, G. Sennari, S. Sato, T. Hirose, D. Oikawa, Y. Inahashi, M. Iwatsuki, A. Ishiyama, S. Õmura, Toshiaki Sunazuka, *Tetrahedron Lett.* 2016, **57**, 357.
2. J. P. Gesson, J. C. Jacquesy and B. Renoux, *Tetrahedron*, 1989, **45**, 5853.

4. NMR spectra of all synthetic new compounds.


7.41
7.40
7.40
7.38
7.36
7.36
7.35
7.35
7.33
7.33
7.32
7.32
7.31
6.97
6.96
6.96
6.79
6.79
6.78
6.77
6.76
6.75
4.97
3.77
1.50
1.48
1.46
1.46
1.44
1.43
1.43
1.42
1.42
1.40
1.38
1.30
1.28
1.26
1.24
1.23
1.21
1.04
1.02
0.99
0.98
0.97
0.97
0.95
0.94
0.92
0.85
0.83
0.81
OBn
Sn(n-Bu)3
OMe
9 (400MHz, CDCl3)
4.99
0.83
2.02
2.01
3.00
6.05
6.07
6.08
9.19
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

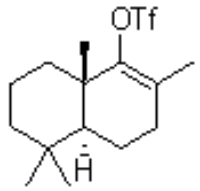

157.18
153.73
137.37
131.99
128.34
127.71
127.61
123.13
113.22
110.07
70.40
55.62
29.08
27.35
13.70
9.75
OBn
Sn(n-Bu)3
OMe
9 (101MHz, CDCl3)
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

化合物9



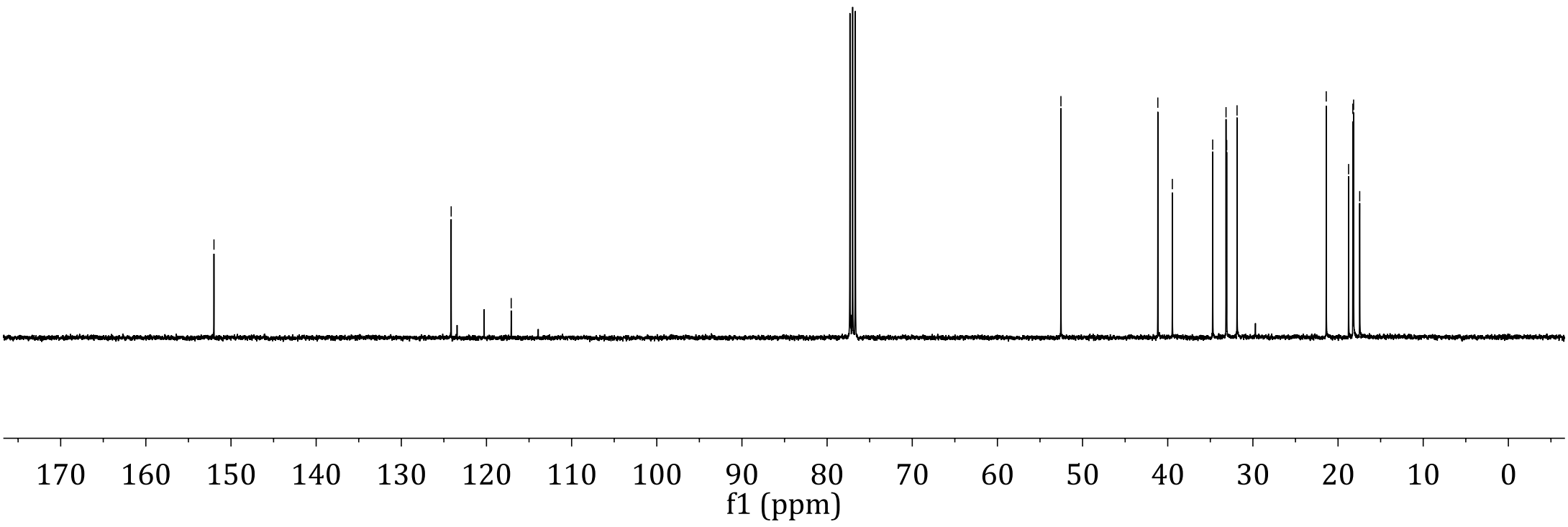
10 (400MHz, $CDCl_3$)

化合物9

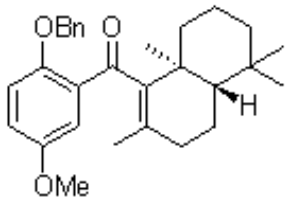


10 (101MHz, $CDCl_3$)

152.00
124.14
117.10
52.54
41.16
39.46
34.72
33.15
33.07
31.86
21.39
18.76
18.26
18.17
17.46



化合物1



14(400MHz, $CDCl_3$)

7.38 7.36 7.33 7.33 7.33 7.31 7.31 7.30 7.27 7.26 7.23 7.23 6.93 6.92 6.91 6.90 6.88 6.85

4.97 4.97

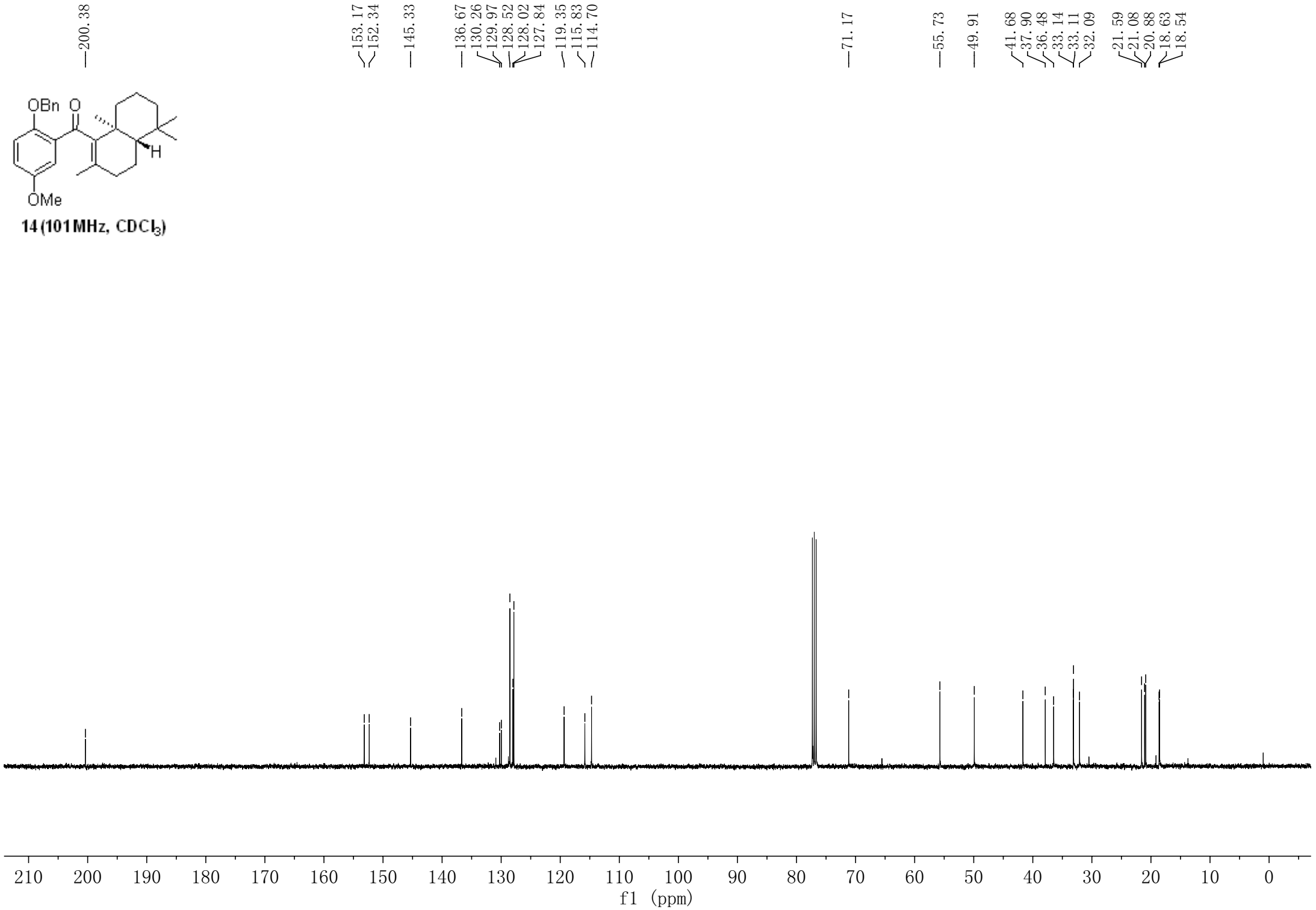
3.73

1.82 1.80 1.78 1.76 1.76 1.74 1.51 1.50 1.48 1.40 1.39 1.36 1.33 1.29 1.28 1.25 1.24 1.23 1.22 1.21 1.20 1.20 1.18 1.10 1.06 1.05 1.03 1.02 1.00 0.99 0.74

6.39 2.18 1.99 3.00 1.97 1.26 1.14 4.18 3.83 3.23 1.98 2.96 3.01

0.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0

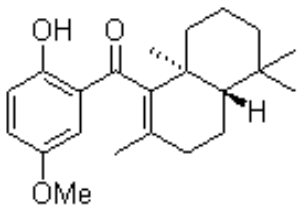
f1 (ppm)


200.38
153.17
152.34
145.33
136.67
130.26
129.97
128.52
128.02
127.84
119.35
115.83
114.70
71.17
55.73
49.91
41.68
37.90
36.48
33.14
33.11
32.09
21.59
21.08
20.88
18.63
18.54
OBn
O
H
OMe
14(101MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

化合物2

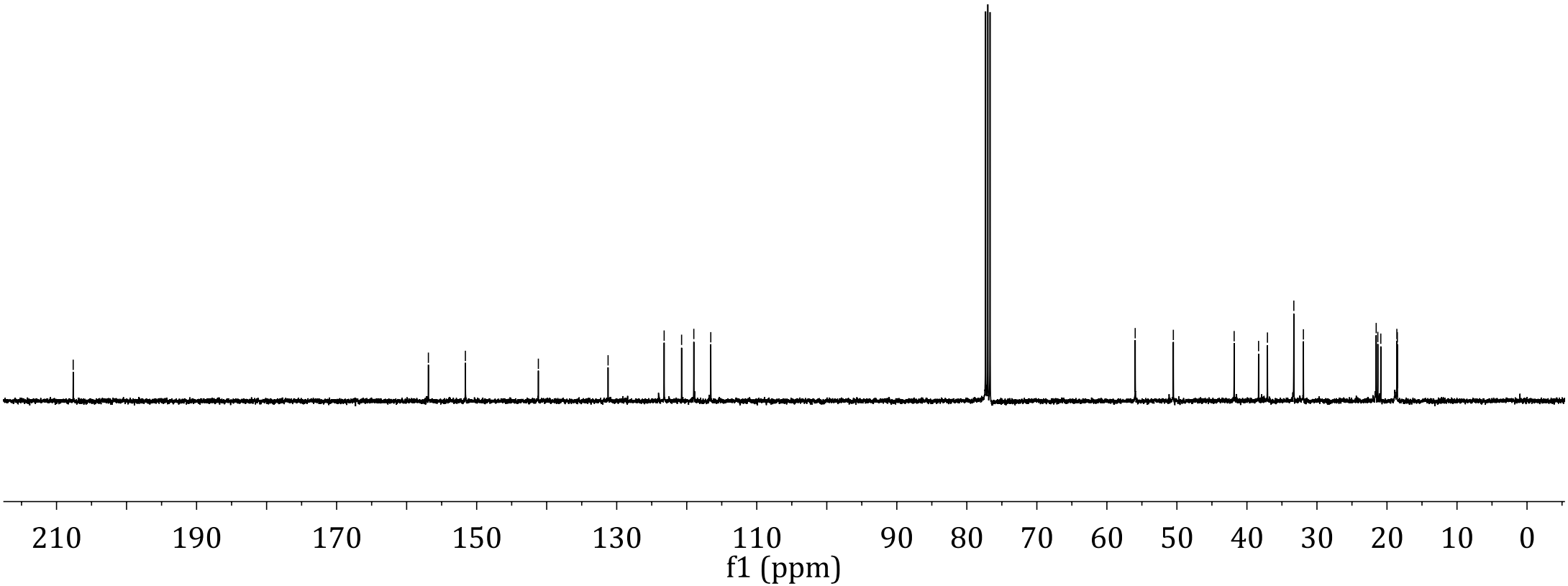
8(400MHz, $CDCl_3$)

化合物2

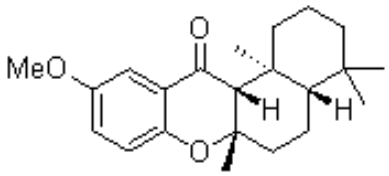


8(101MHz, $CDCl_3$)

207.62
156.89
151.61
141.19
131.23
123.23
120.73
118.99
116.57
55.96
50.51
41.82
38.34
37.07
33.30
31.93
21.54
21.31
20.88
18.59
18.52



化合物3



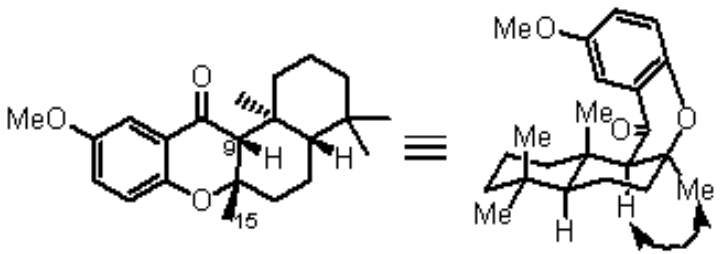
7a(400MHz, $CDCl_3$)

7.29 7.28 7.07 7.06 7.05 7.04 6.84 6.82 3.80 2.26 2.25 2.24 2.22 2.22 2.21 1.94 1.65 1.65 1.44 1.43 1.43 1.40 1.25 1.23 0.92 0.90 0.90 0.84

0.96 0.98 0.95 3.00 1.01 0.99 3.01 1.81 2.98 5.82 3.15 0.90 6.16

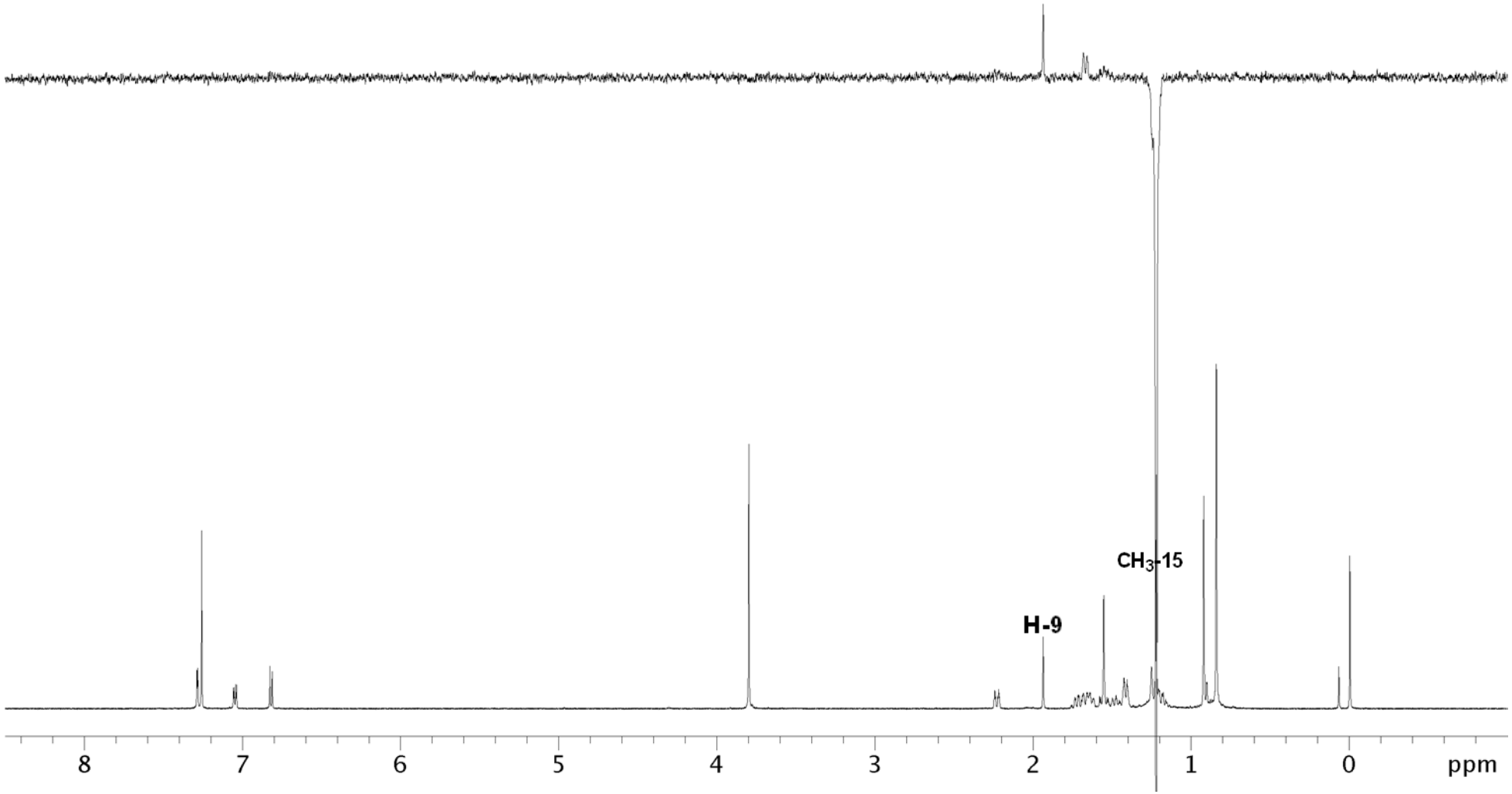
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

f1 (ppm)



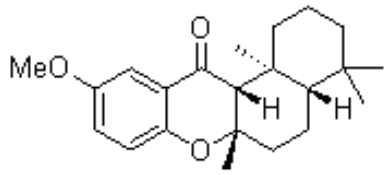
7 a(600MHz, $CDCl_3$)

NOE

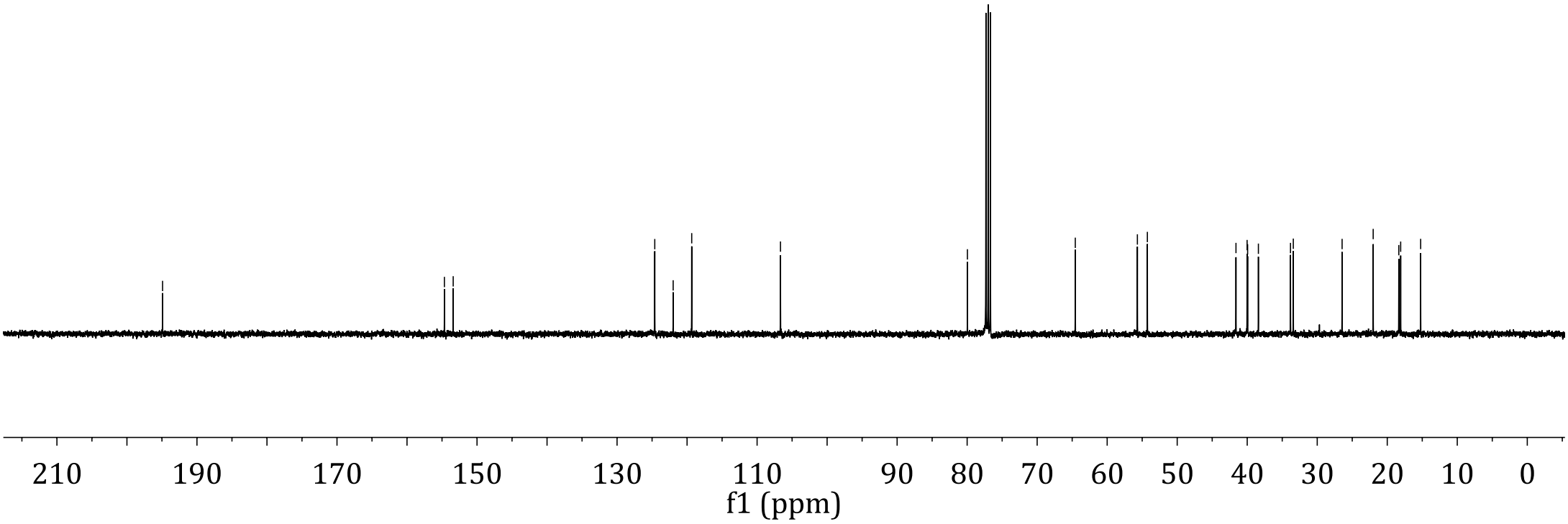


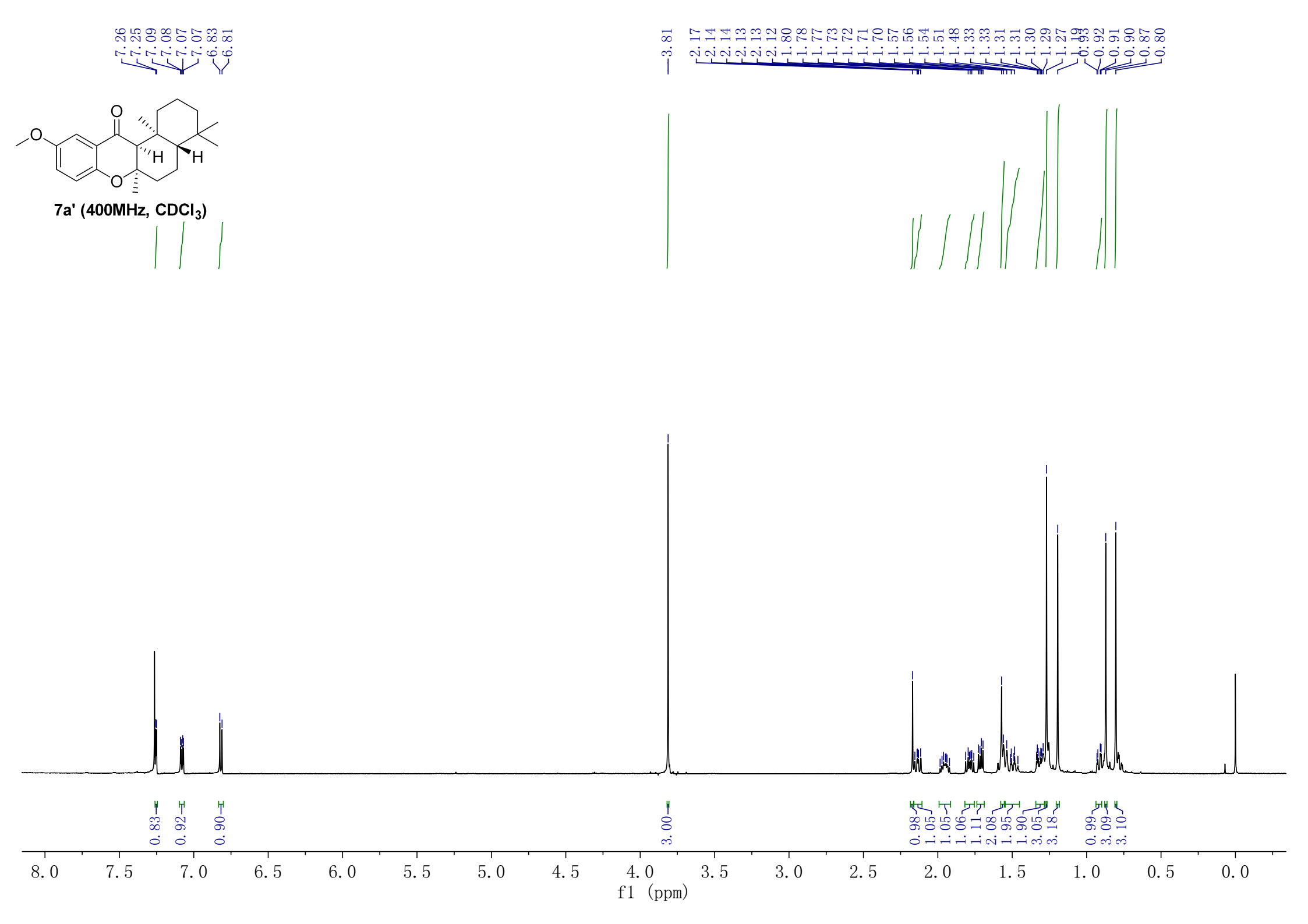
化合物3

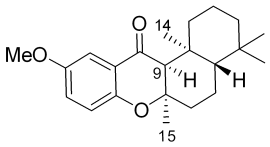
194.91
154.66
153.40
124.61
121.99
119.34
106.66
79.96
64.55
55.69
54.26
41.61
40.02
39.94
38.40
33.82
33.42
26.45
22.01
18.35
18.08
15.23



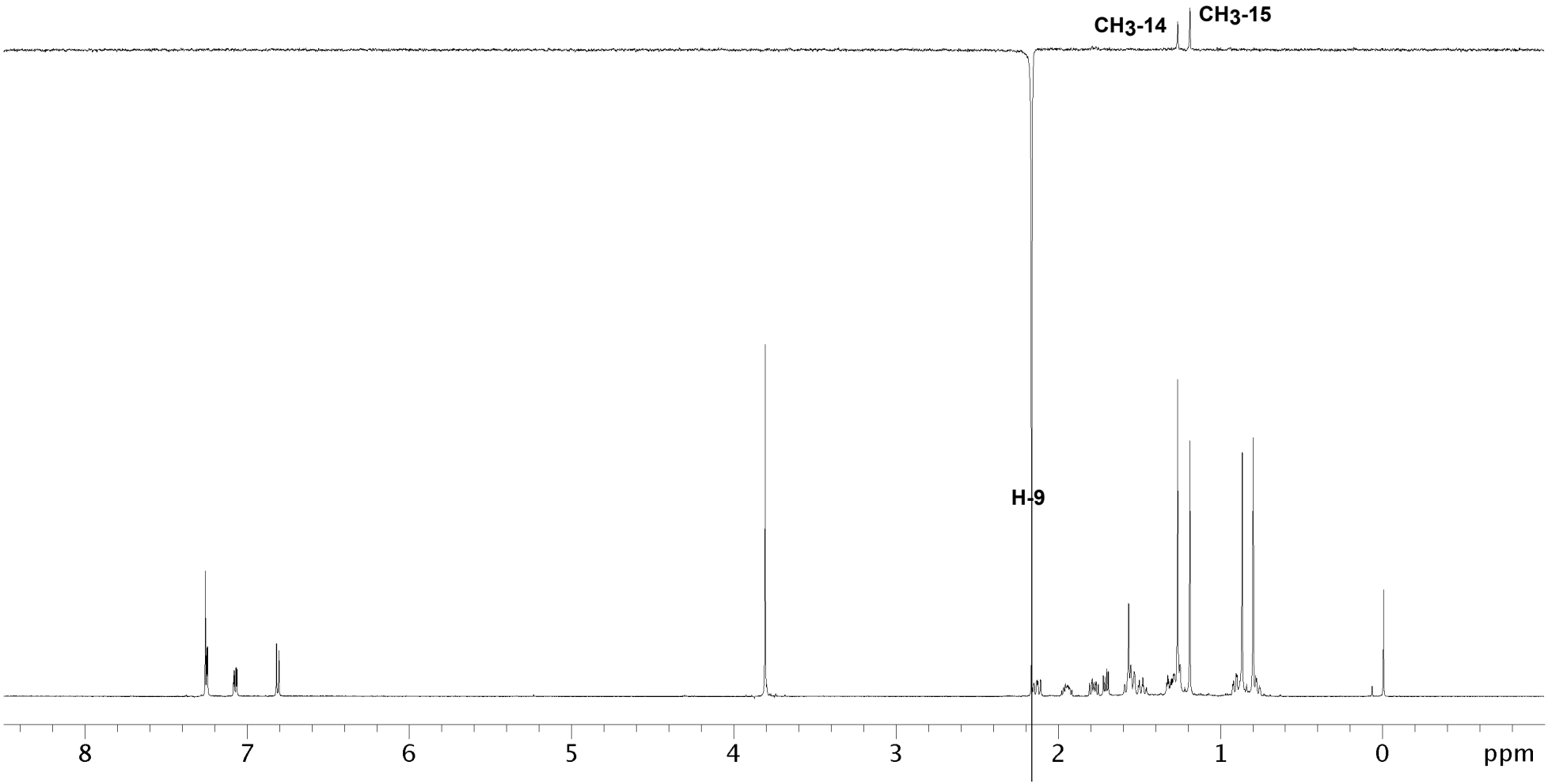
7a(101MHz, $CDCl_3$)

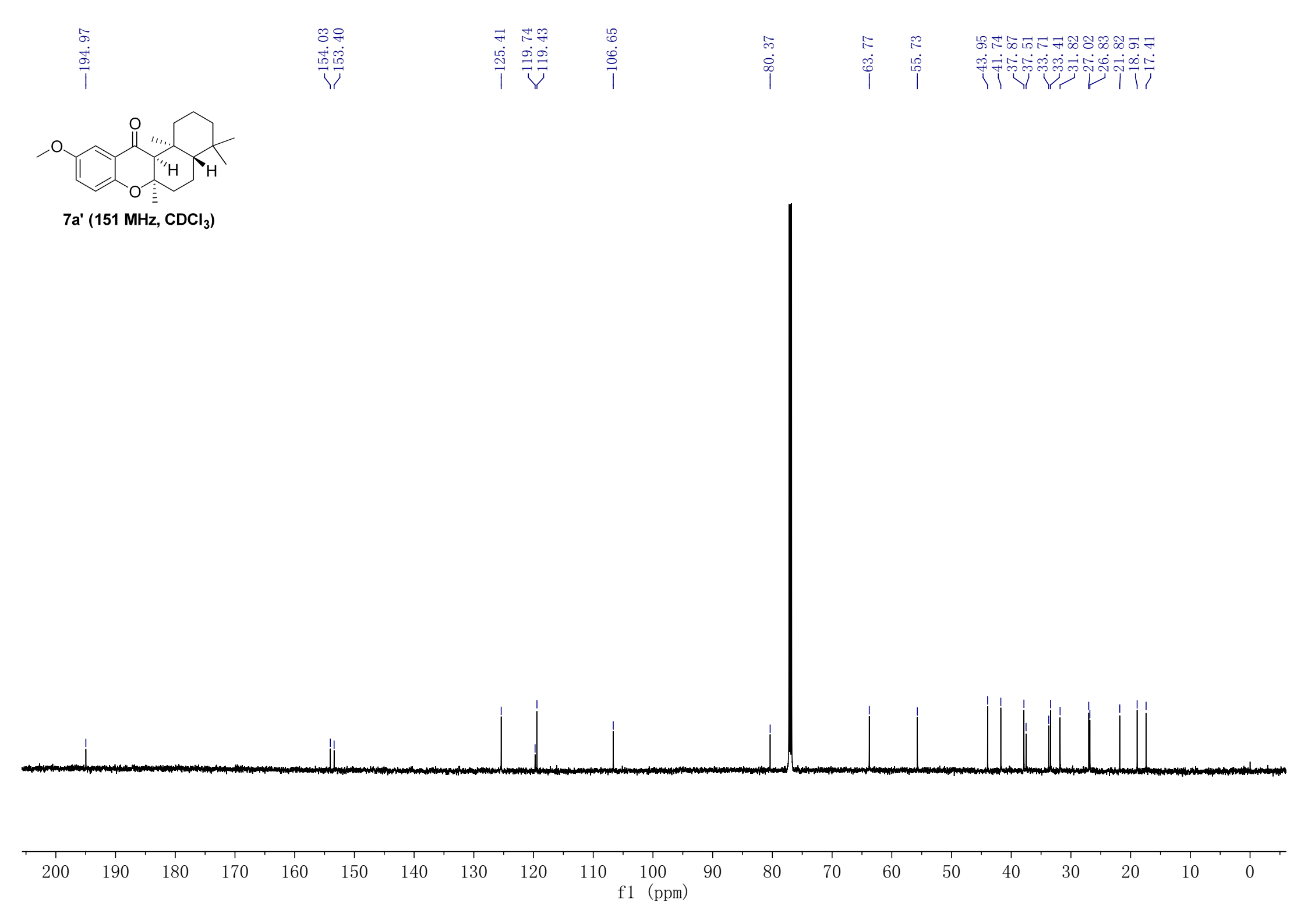



7.26
7.25
7.09
7.08
7.07
7.07
6.83
6.81
3.81
2.17
2.14
2.14
2.13
2.13
2.12
1.80
1.78
1.77
1.73
1.72
1.71
1.70
1.57
1.56
1.54
1.51
1.48
1.33
1.33
1.31
1.31
1.30
1.29
1.27
0.93
0.92
0.91
0.90
0.87
0.80
O
O
H
H
O
7a' (400MHz, CDCl3)
0.83
0.92
0.90
3.00
0.98
1.05
1.05
1.06
1.11
2.08
1.95
1.90
3.05
3.18
0.99
3.09
3.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

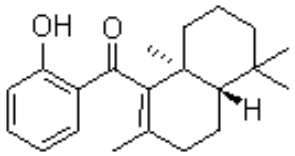


7a' (600MHz, $CDCl_3$)




194.97
154.03
153.40
125.41
119.74
119.43
106.65
80.37
63.77
55.73
43.95
41.74
37.87
37.51
33.71
33.41
31.82
27.02
26.83
21.82
18.91
17.41
O
O
H
H
O
7a' (151 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

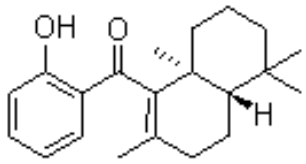
SP-180621-3



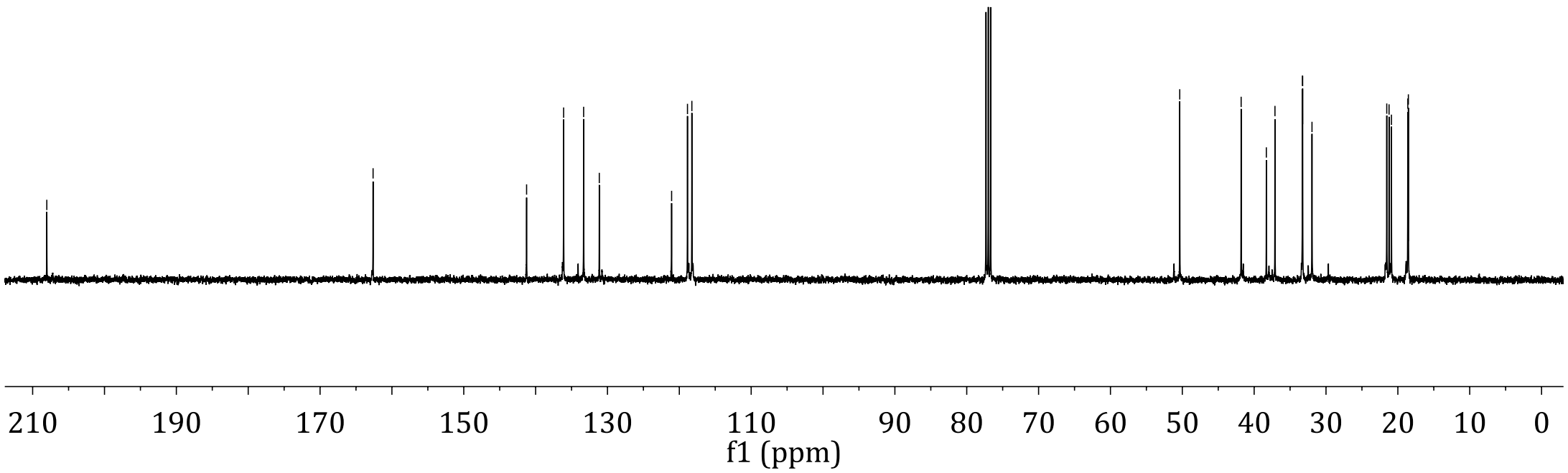
8b (400MHz, $CDCl_3$)

SP-180621-3

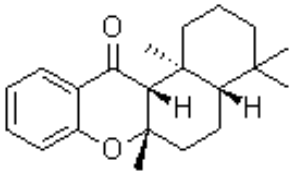
208.05
162.62
141.25
136.10
133.32
131.14
121.07
118.86
118.26
50.36
41.81
38.30
37.10
33.28
33.25
31.95
21.54
21.22
20.89
18.61
18.54



8b (101MHz, $CDCl_3$)



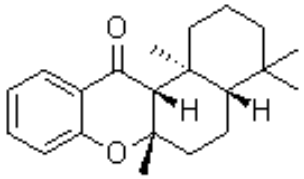
sp-0612-2-H
STANDARD 1H OBSERVE



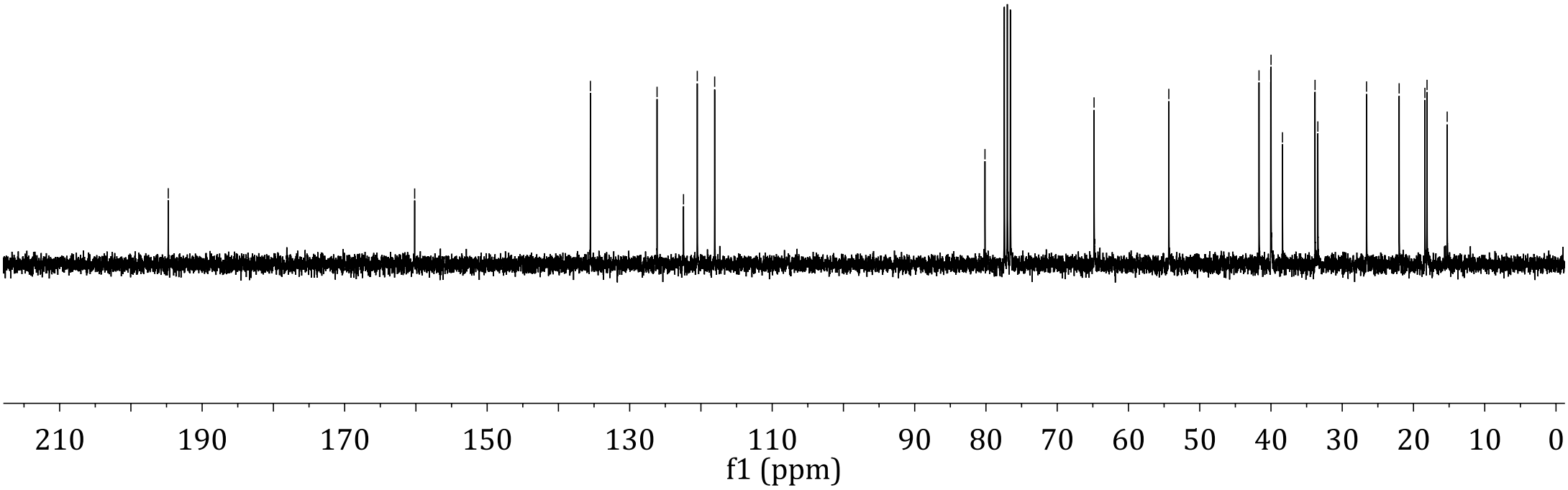
7b (300MHz, $CDCl_3$)

sp-0612-2-C
13C OBSERVE

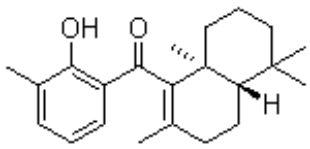
194.75
160.17
135.51
126.16
122.45
120.51
118.07
80.14
64.83
54.34
41.68
40.03
39.99
38.39
33.82
33.42
26.59
22.01
18.40
18.10
15.27



7b (75MHz, $CDCl_3$)



sp-0619-1-600-H
STANDARD FLUORINE PARAMETERS



8c (600M, $CDCl_3$)

12.75

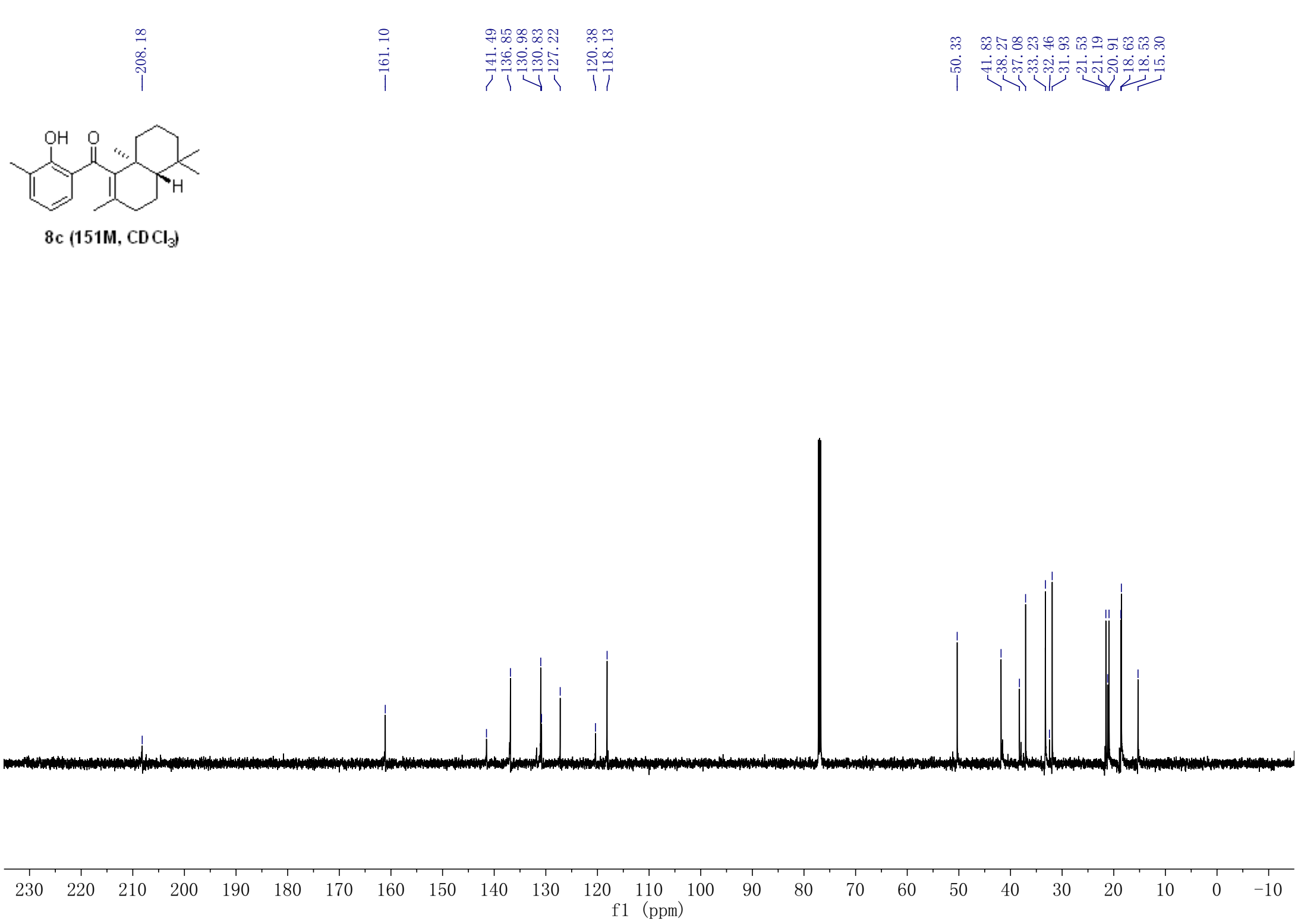
7.45 7.45 7.44 7.44 7.32 7.30 6.78 6.77 6.76

2.27 2.20 2.19 2.18 2.17 2.16 1.81 1.80 1.79 1.78 1.64 1.63 1.63 1.62 1.62 1.61 1.56 1.55 1.53 1.53 1.45 1.42 1.40 1.40 1.37 1.35 1.35 1.33 1.33 1.32 1.31 1.16 1.15 1.14 1.13 1.12 0.95 0.92

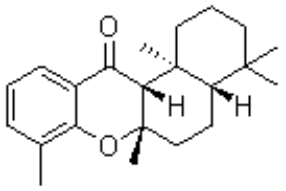
0.76 | 0.91 | 0.90 | 0.89 | 3.00 | 1.89 | 0.98 | 2.09 | 4.09 | 2.11 | 3.00 | 2.12 | 3.01 | 3.00

13.0 11.0 9.0 7.5 6.0 4.5 3.0 1.5 0.0

f1 (ppm)


208.18
161.10
141.49
136.85
130.98
130.83
127.22
120.38
118.13
50.33
41.83
38.27
37.08
33.23
32.46
31.93
21.53
21.19
20.91
18.63
18.53
15.30
OH
O
H
8c (151M, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

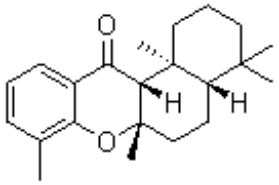
sp-180626-2-H
STANDARD 1H OBSERVE



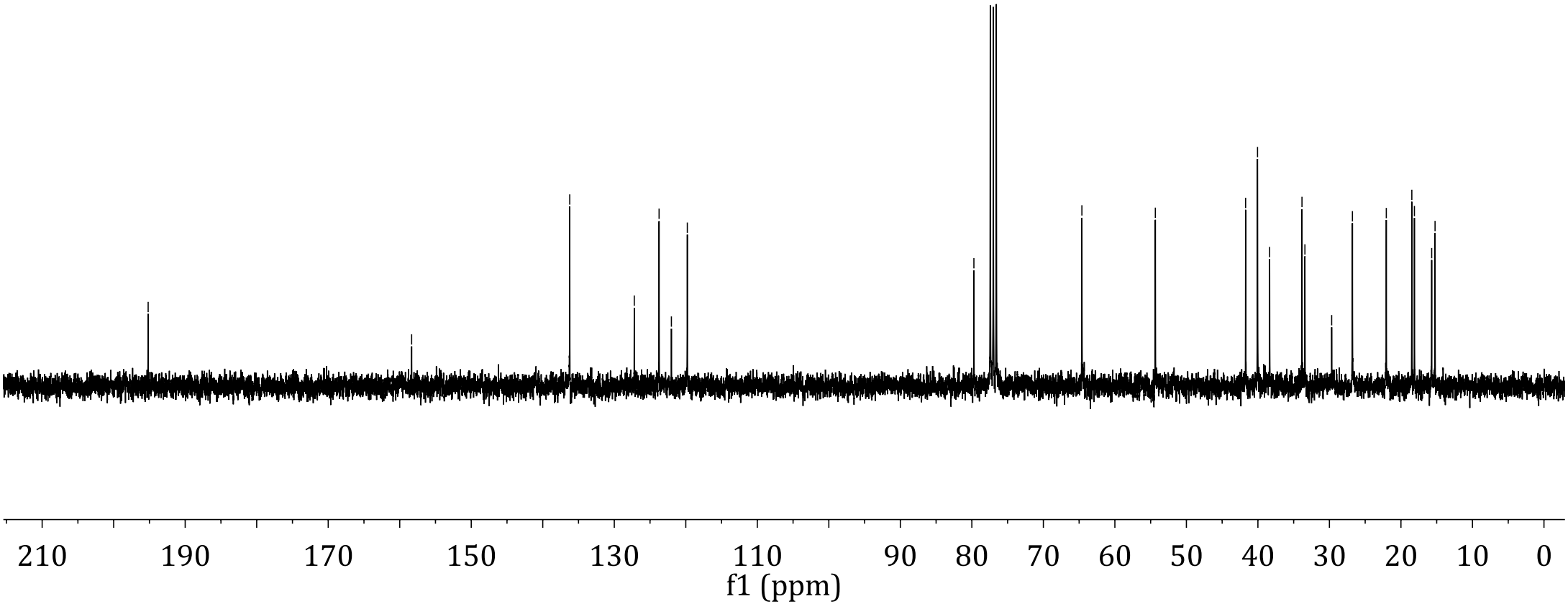
7c (300MHz, $CDCl_3$)

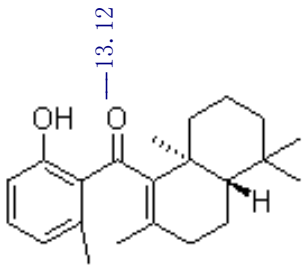
sp-180626-2-C
13C OBSERVE

195.18
158.33
136.23
127.20
123.73
122.01
119.79
79.71
64.61
54.34
41.72
40.05
38.36
33.84
33.43
29.69
26.78
22.05
18.48
18.12
15.70
15.23

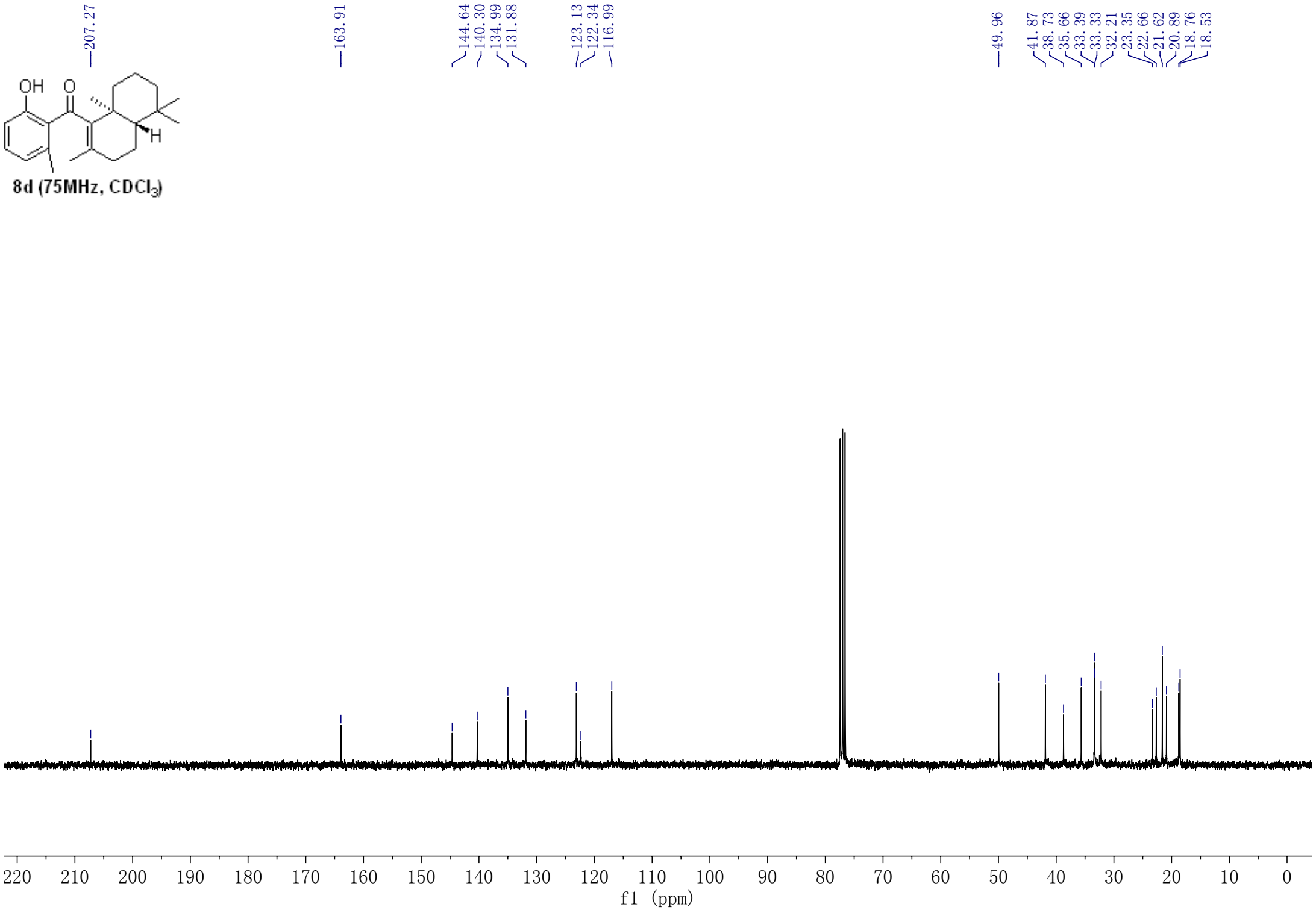


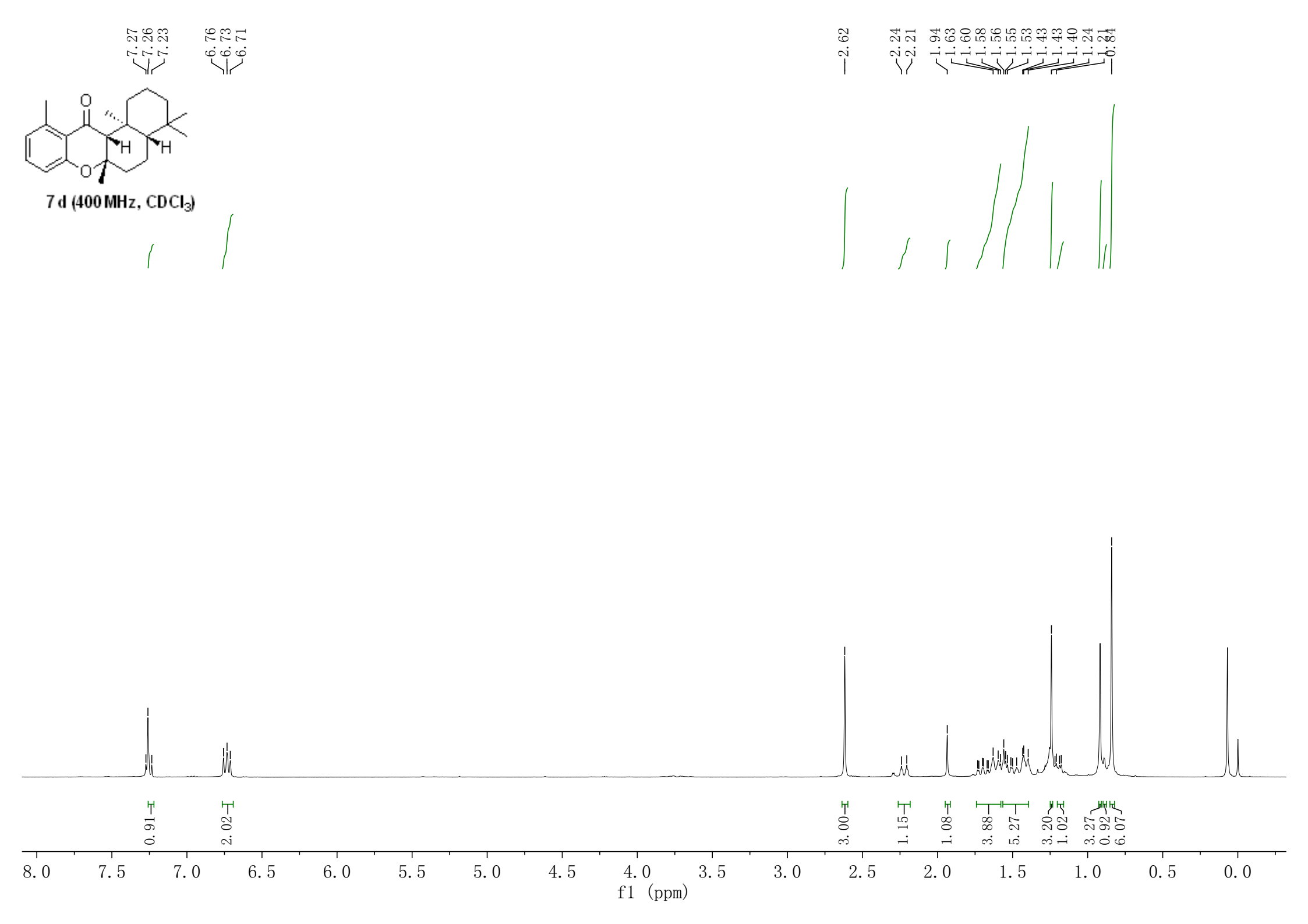
7c (75MHz, $CDCl_3$)

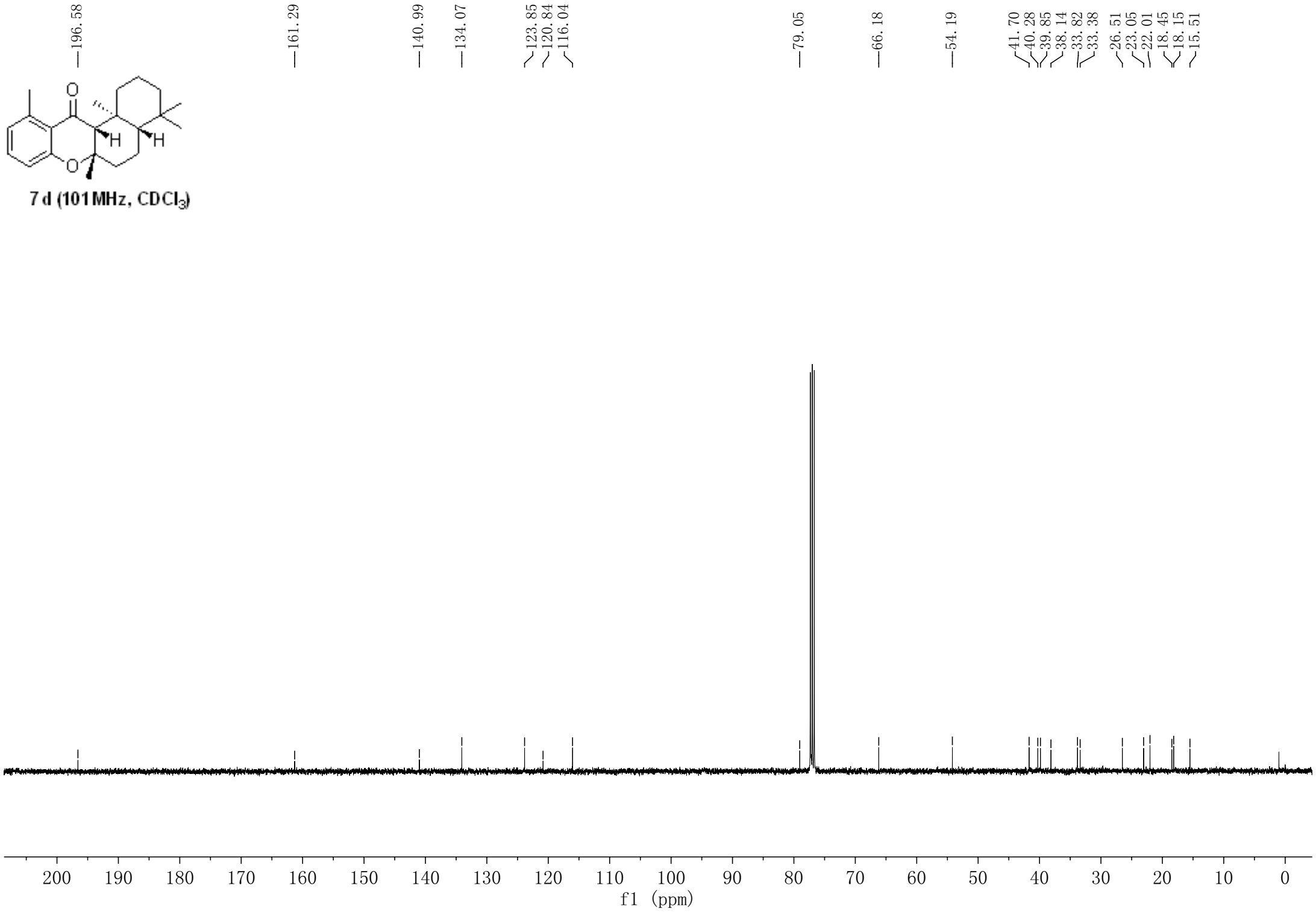


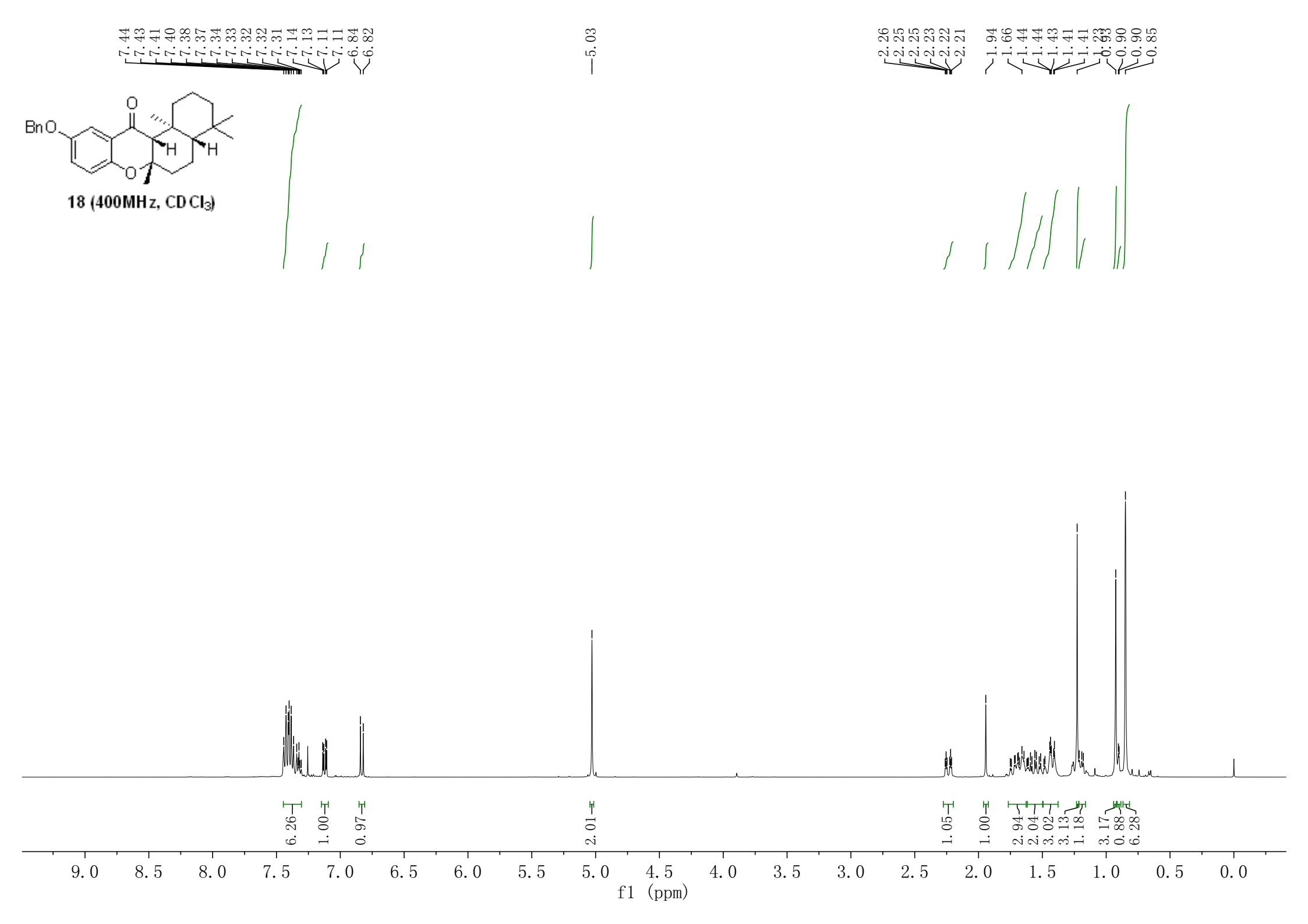


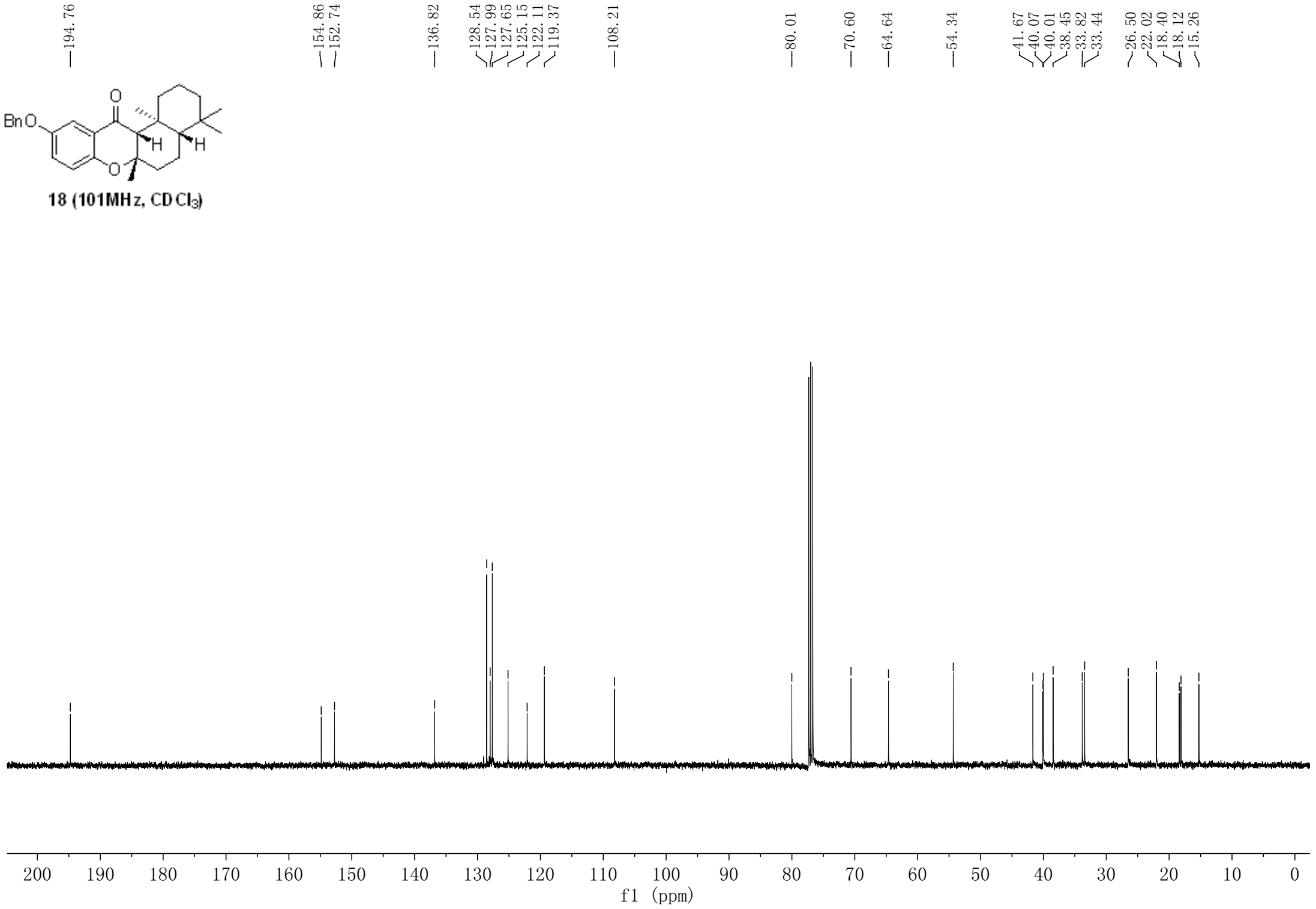
8d (300 MHz, $CDCl_3$)

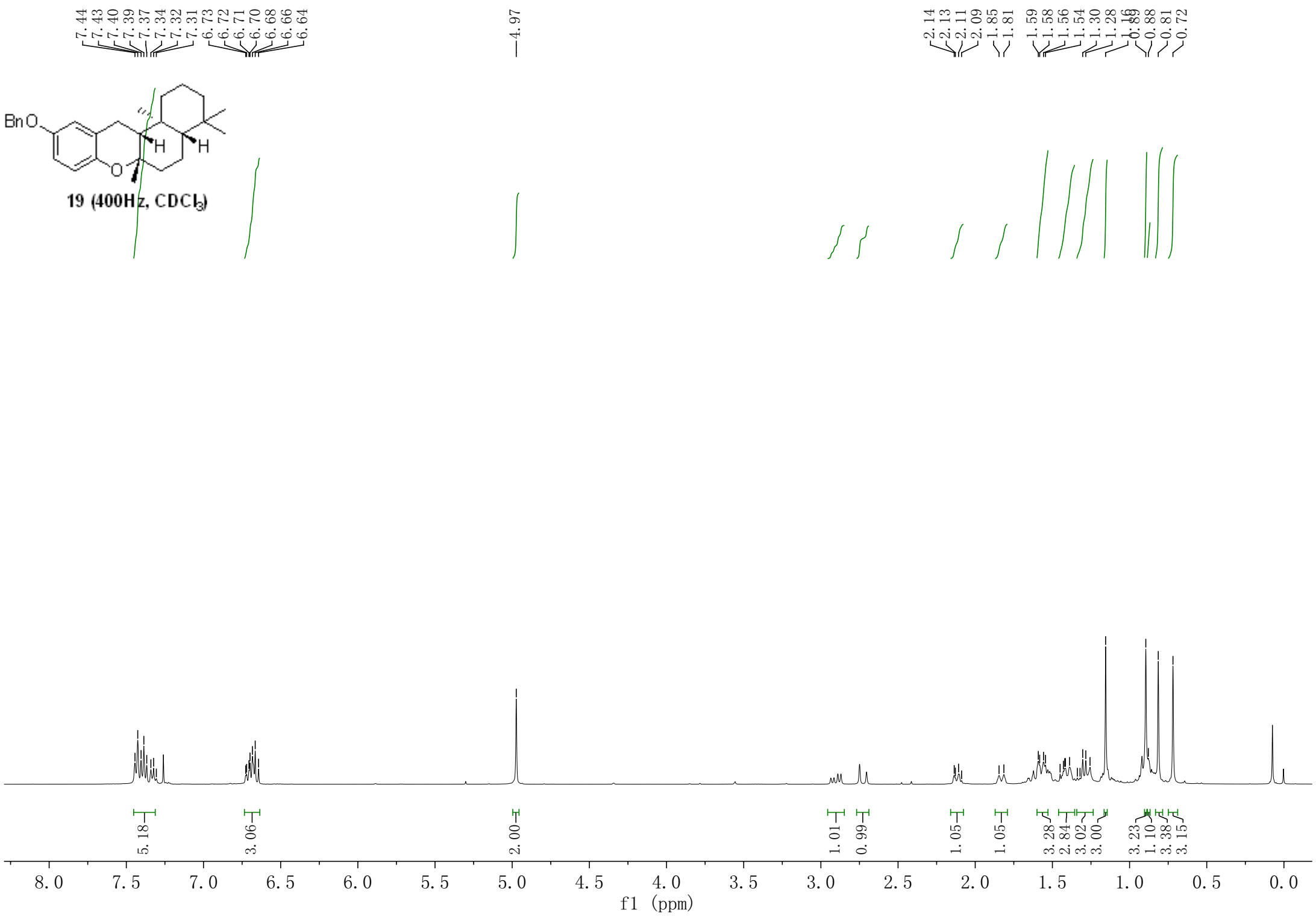

207.27
163.91
144.64
140.30
134.99
131.88
123.13
122.34
116.99
49.96
41.87
38.73
35.66
33.39
33.33
32.21
23.35
22.66
21.62
20.89
18.76
18.53
OH
O
H
8d (75MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.27
7.26
7.23
6.76
6.73
6.71
2.62
2.24
2.21
1.94
1.63
1.60
1.58
1.56
1.55
1.53
1.43
1.43
1.40
1.24
1.21
0.84
O
H
H
O
7 d (400 MHz, CDCl3)
0.91
2.02
3.00
1.15
1.08
3.88
5.27
3.20
1.02
3.27
0.92
6.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

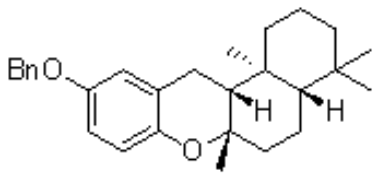

196.58
161.29
140.99
134.07
123.85
120.84
116.04
79.05
66.18
54.19
41.70
40.28
39.85
38.14
33.82
33.38
26.51
23.05
22.01
18.45
18.15
15.51
O
H
H
O
7 d (101MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.44
7.43
7.41
7.40
7.38
7.37
7.34
7.33
7.32
7.32
7.31
7.14
7.13
7.11
7.11
6.84
6.82
5.03
2.26
2.25
2.25
2.23
2.22
2.21
1.94
1.66
1.44
1.44
1.43
1.41
1.41
1.23
0.93
0.90
0.90
0.85
BnO
O
H
H
O
18 (400MHz, CDCl3)
6.26
1.00
0.97
2.01
1.05
1.00
2.94
2.04
3.02
3.13
1.18
3.17
0.88
6.28
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


194.76
154.86
152.74
136.82
128.54
127.99
127.65
125.15
122.11
119.37
108.21
80.01
70.60
64.64
54.34
41.67
40.07
40.01
38.45
33.82
33.44
26.50
22.02
18.40
18.12
15.26
BnO
O
H
H
O
18 (101MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

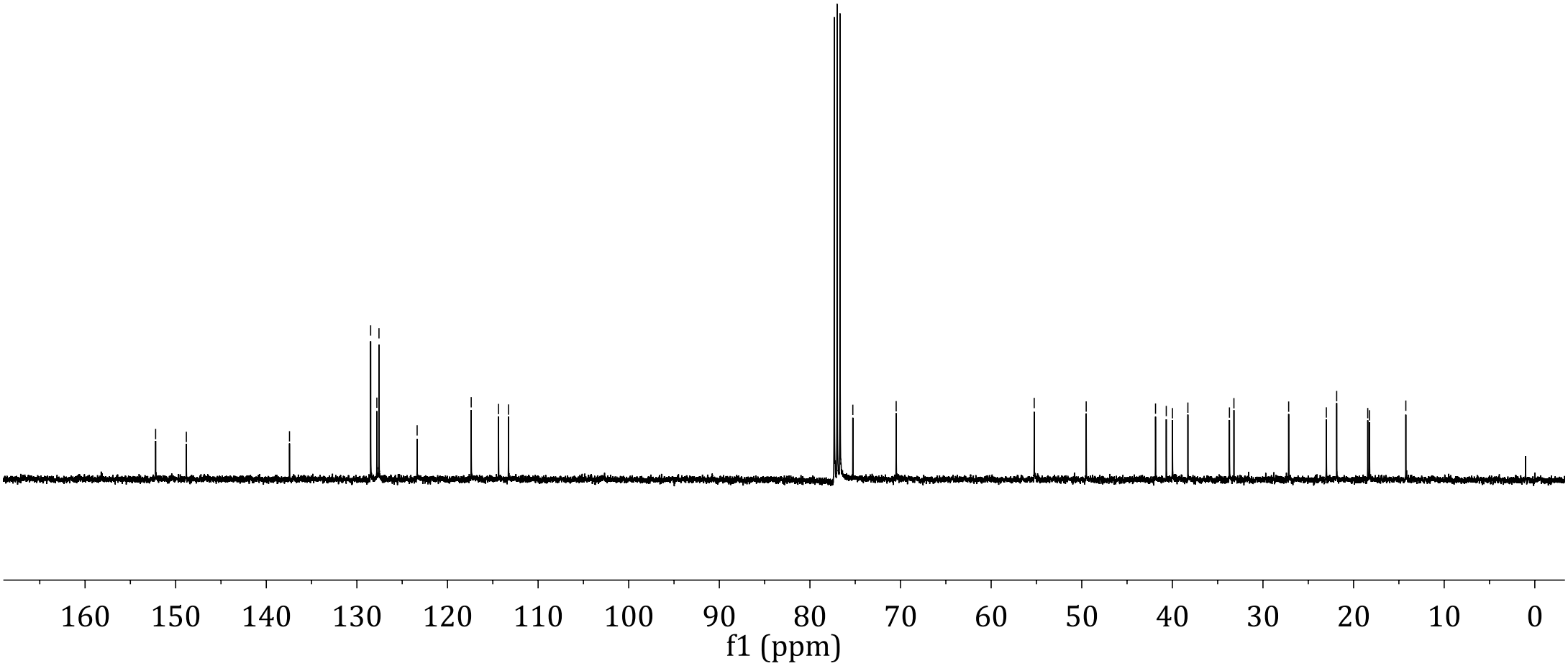

7.44
7.43
7.40
7.39
7.37
7.34
7.32
7.31
6.73
6.72
6.71
6.70
6.68
6.66
6.64
4.97
2.14
2.13
2.11
2.09
1.85
1.81
1.59
1.58
1.56
1.54
1.30
1.28
1.16
0.89
0.88
0.81
0.72
BnO
H
H
O
19 (400Hz, CDCl3)
5.18
3.06
2.00
1.01
0.99
1.05
1.05
3.28
2.84
3.02
3.00
3.23
1.10
3.38
3.15
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

化合物7

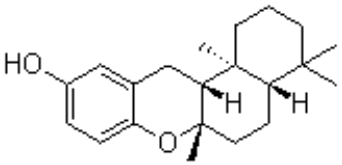


19 (101Hz, $CDCl_3$)

152.21
148.82
137.44
128.48
127.80
127.56
123.35
117.38
114.37
113.27
75.27
70.48
55.25
49.51
41.86
40.67
39.99
38.29
33.70
33.21
27.16
23.01
21.86
18.44
18.24
14.23



PROTON_01



8-*epi*-chromazonarol (2)
(600 MHz, $CDCl_3$)

6.60 6.59 6.59 6.55 6.54 6.53 — 4.44 — 2.89 2.88 2.86 2.85 2.71 2.68 2.13 2.12 2.12 2.10 1.64 1.58 1.56 1.55 1.53 1.29 1.27 1.15 0.89 0.87 0.87 0.85 0.85 0.81 0.72

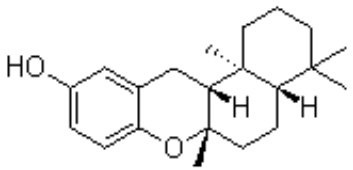
0.86 1.01 1.00 1.00 1.00 1.78 3.08 2.05 1.84 3.21 3.24 1.12 2.94 2.88

7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

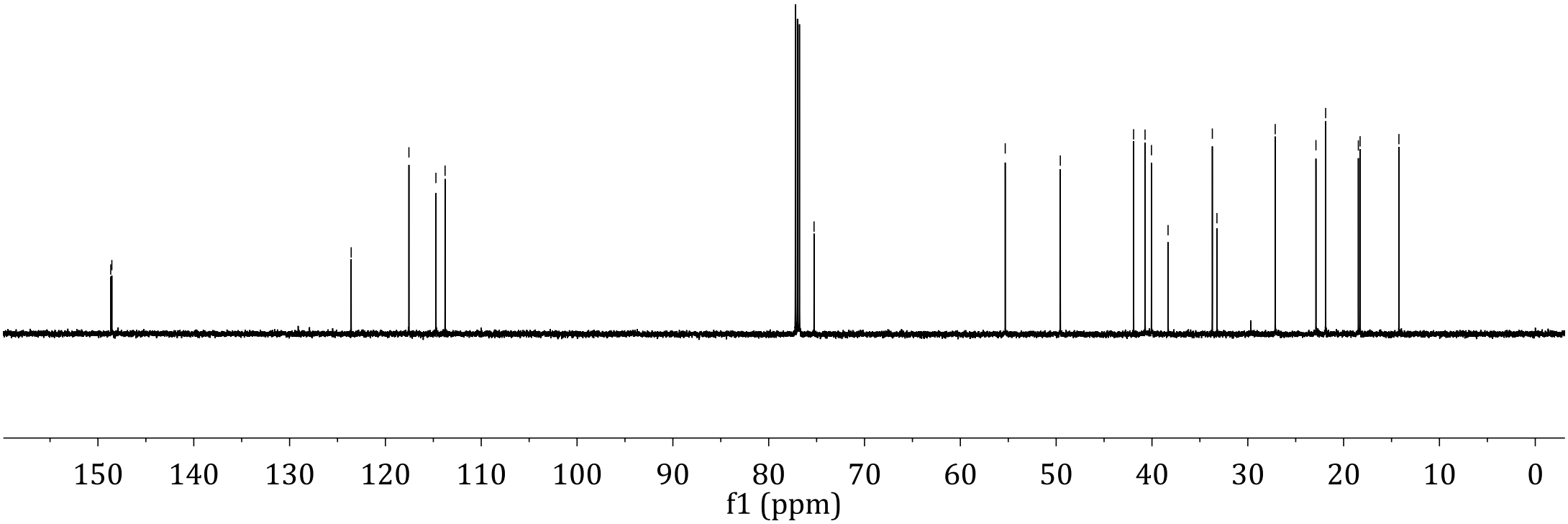
f1 (ppm)

CARBON_01

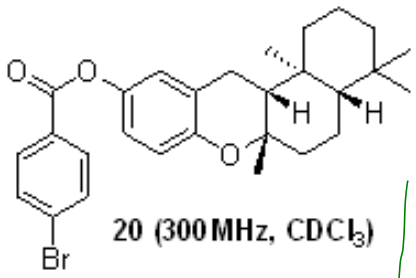
148.67
148.55
123.57
117.55
114.73
113.77
75.27
55.32
49.57
41.92
40.72
40.05
38.32
33.70
33.22
27.14
22.89
21.87
18.46
18.28
14.23



8-*epi*-chromazonarol **(2)**
(151MHz, $CDCl_3$)



sp-180330-TMdangjing-H
STANDARD 1H OBSERVE



20 (300 MHz, $CDCl_3$)

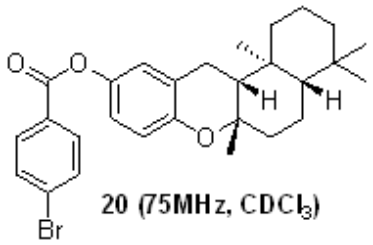
8.05 8.04 8.02 8.02 8.02 8.01 7.67 7.65 7.65 7.62 6.89 6.86 6.85 6.76 6.74

2.99 2.96 2.93 2.90 2.79 2.73 2.17 2.14 2.13 1.61 1.59 1.58 1.56 1.53 1.43 1.42 1.38 1.34 1.31 1.18 1.15 0.93 0.90 0.82

2.06 2.19 2.04 1.12 1.16 1.17 1.06 1.14 4.16 4.11 3.09 1.19 1.06 3.17 3.11 3.00

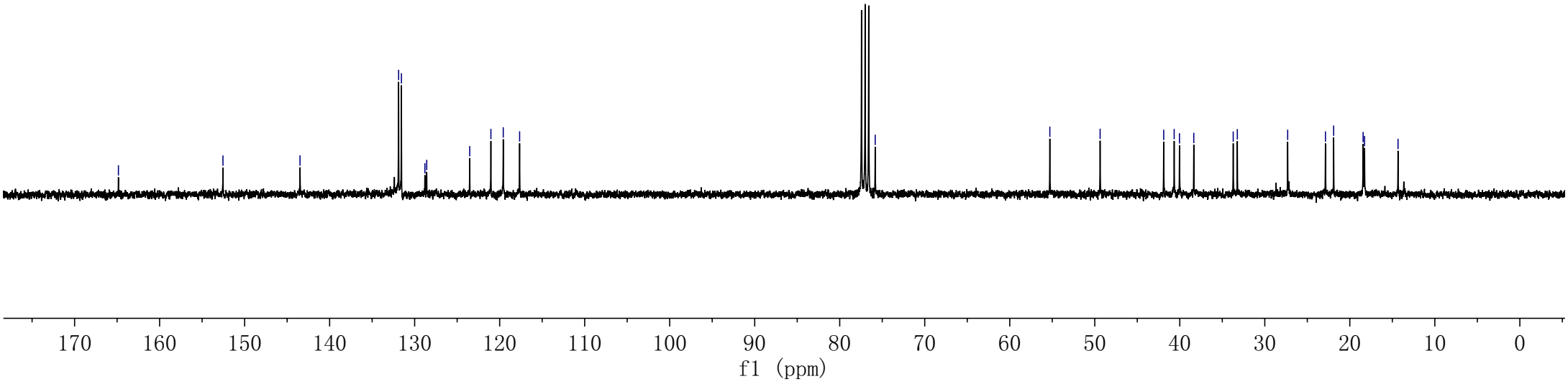
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

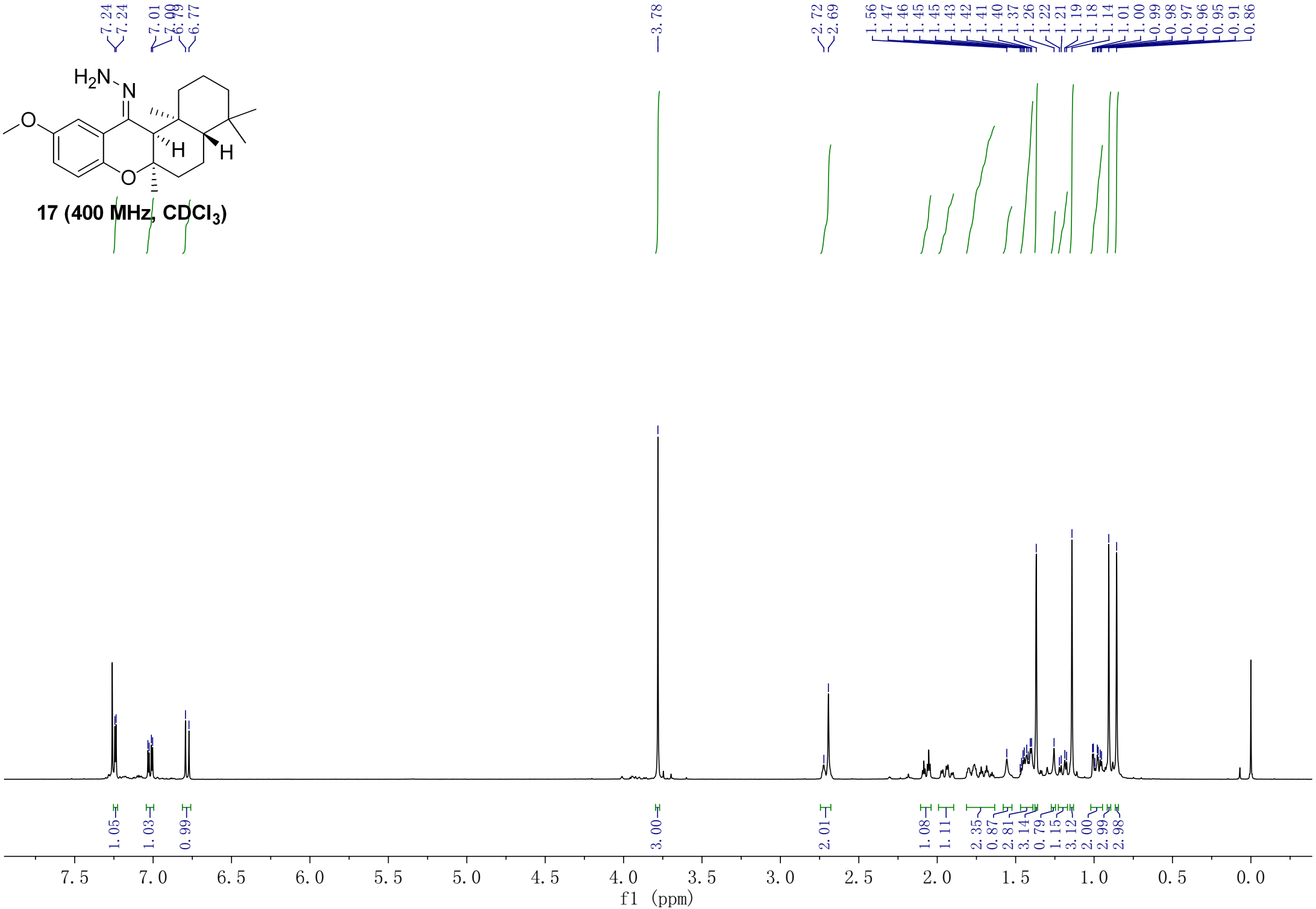
f1 (ppm)

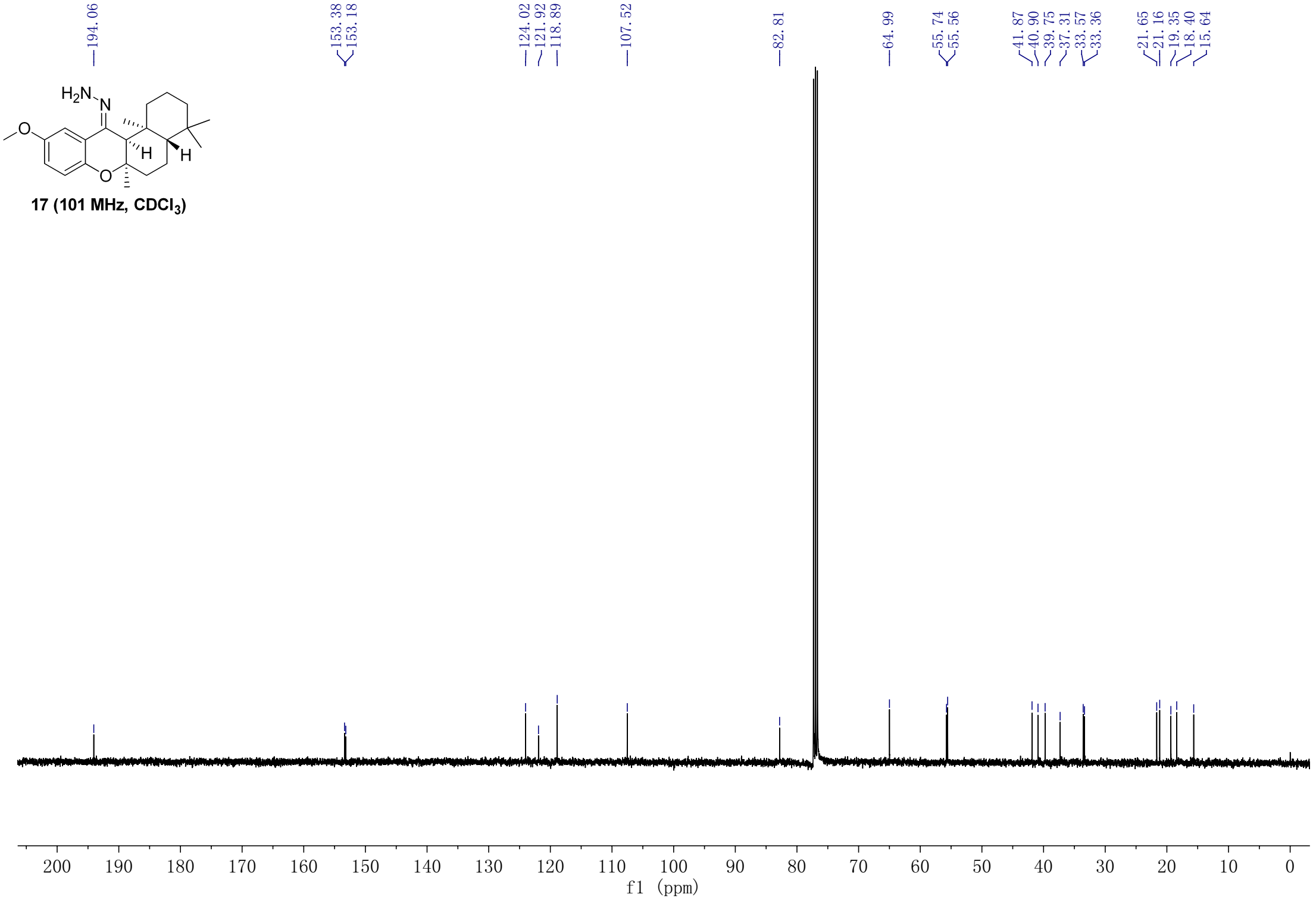


20 (75MHz, $CDCl_3$)

164.84
152.55
143.48
131.88
131.56
128.79
128.58
123.52
121.03
119.58
117.65
75.83
55.28
49.37
41.89
40.66
40.03
38.35
33.71
33.23
27.31
22.86
21.90
18.43
18.27
14.33




7.24
7.24
7.01
7.00
6.99
6.77
3.78
2.72
2.69
1.56
1.47
1.46
1.45
1.45
1.43
1.42
1.41
1.40
1.37
1.26
1.22
1.21
1.19
1.18
1.14
1.01
1.00
0.99
0.98
0.97
0.96
0.95
0.91
0.86
H2N
N
O
H
H
O
17 (400 MHz, CDCl3)
1.05
1.03
0.99
3.00
2.01
1.08
1.11
2.35
0.87
2.81
3.14
0.79
1.15
3.12
2.00
2.99
2.98
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


194.06
153.38
153.18
124.02
121.92
118.89
107.52
82.81
64.99
55.74
55.56
41.87
40.90
39.75
37.31
33.57
33.36
21.65
21.16
19.35
18.40
15.64
H2N
N
O
H
H
O
17 (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)