Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

Strategies towards *endo*-type B polycyclic polyprenylated acylphloroglucinols: total synthesis of *regio*-hyperibone L and (+)-*epi*-clusianone

Liping Wang, Xueying Wang, Guocai Zhang, Wenwei Fu, Hong Zhang, Hua Zhou, Hongxi Xu and Changwu Zheng

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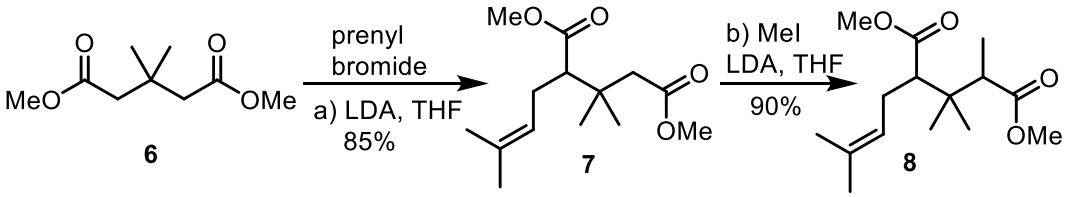
General Information

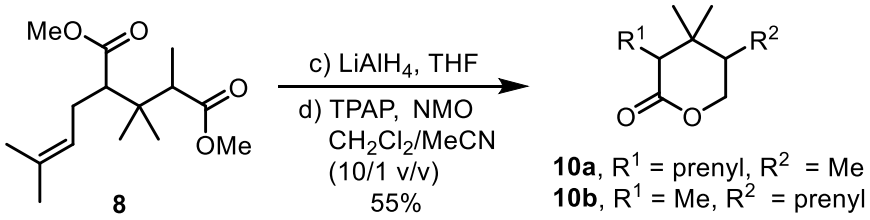
All glassware was dried with a hot air gun and all reactions were carried out under an atmosphere of dry N_2 unless otherwise stated. All reagents and dry solvents were used as received from the supplier. Melting points were performed using a Gallenkamp melting point apparatus and are uncorrected. IR spectra were carried out on either a neat oil or a solid using a Perkin-Elmer Spectrum 983G instrument. Wavelengths (ν) are reported in cm^{-1}. ^1H and ^{13}C NMR were performed on Bruker AV-400, AV-600 or Agilent 400 NMR spectrometers in $CDCl_3$, CD_3OD or DMSO-d_6. Chemical shifts (δ) are quoted in ppm, coupling constants (J) in Hz. All spectra are calibrated based on the solvent peak used unless otherwise stated. The following abbreviations apply: (br) broad, (s) singlet, (d) doublet, (t) triplet, (q) quartet and (m) multiplet. Mass spectrometry was performed on a SYNAPT G2-Si HDMS (Waters Corp., Manchester, UK). A Waters 2535 series machine equipped with an Xbridge C_{18} column (4.6 × 250 mm, 5 mm) was used for HPLC analysis, and a preparative Xbridge Prep C_{18} OBD column (19 × 250 mm, 5 mm) was used for the sample preparation. Flash column chromatography was performed using silica gel (300-400 mesh).

Procedures for total synthesis of *regio*-hyperibone L

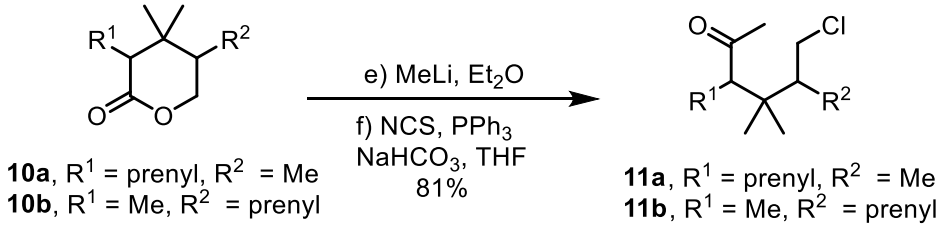


A 1.0 L of flame-dried flask at -78 °C was charged with compound **6** (57 g, 303 mmol) and THF (500 mL). A solution of lithium diisopropylamide (1.5 M in THF, 212 mL, 0.32 mol, 1.05 eq) was added dropwise. The solution was stirred for 30 min at -78 °C and then prenyl bromide (53 g, 0.32 mol, 1.05 eq) in THF (100 mL) was added dropwise. The reaction mixture was slowly warmed to rt and stirred at rt for 20 hours, and then quenched with saturated solution of NH_4Cl (100 mL) at 0 °C. The aqueous phase was extracted with AcOEt (3 × 200 mL), and the combined organic layers were dried over Na_2SO_4. Column chromatography (petroleum ether/ethyl acetate, 10:1) yielded esters **7** (65.8 g, 85 %) as yellow oils. ^1H NMR (400 MHz, $CDCl_3$) δ 4.96 (t, J = 7.3 Hz, 1H), 3.64 (s, 3H), 3.61 (s, 3H), 2.41 – 2.26 (m, 4H), 2.14 (dd, J = 12.7, 6.5 Hz, 1H), 1.64 (s, 3H), 1.58 (s, 3H), 1.07 (s, 3H), 1.06 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.0, 172.4, 133.8, 121.4, 55.2, 51.4, 51.2, 44.1, 35.3, 26.2, 25.9, 25.5, 25.1, 17.7. HRESIMS calcd for $C_{14}H_{24}NaO_4$ $[M + Na]^+$ 279.1567, found 279.1566.

According to the similar procedure above, product **8** (3:1 dr) was obtained from **7** (26 g) in 90% yield (24 g). ^1H NMR (400 MHz, $CDCl_3$) δ 4.97 - 4.93 (m, 1H), [3.65 (s), 3.62 (s)] (3H), 2.57 – 2.06 (m,4H), 1.65 (m, 3H), 1.61 - 1.58 (m, 3H), [1.14 (d, J = 7.0 Hz), 1.11 (d, J = 7.1 Hz)] (3H), [1.05 (s), 1.04 (s)] (3H), [0.97 (s), 0.95 (s)] (3H); ^{13}C NMR (100 MHz, $CDCl_3$) major: δ 175.7, 175.0, 133.6, 121.4, 53.6, 51.2, 51.0, 46.6, 37.8, 25.9, 25.8, 21.8, 20.9, 17.6, 12.3; minor: δ 175.8, 175.0, 133.7, 121.4, 52.8, 51.2, 51.0, 46.1, 37.3, 26.1, 25.8, 21.5, 21.4, 17.7, 12.7. HRESIMS calcd for $C_{15}H_{27}O_4$ $[M + H]^+$ 271.1904, found 271.1911.

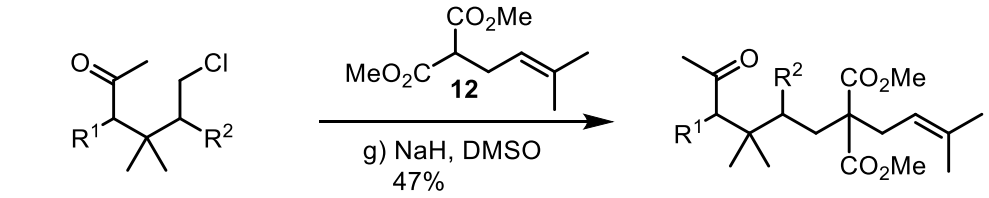


A solution of compounds **8** (13 g, 48 mmol) in dry THF (90 mL) was cooled to 0 °C. $LiAlH_4$ (3.73 g, 98 mmol) powder was then carefully added in small portions during 15 min under N_2. The resulting mixture was stirred for 3 h at room temperature, and then the reaction was slowly quenched with 3.75 mL of H_2O, 3 mL of 15% NaOH aq. and 11.25 mL of H_2O at 0 °C in sequence. The suspension was stirred at room temperature for 15 min, and anhydrous $MgSO_4$ was added. After stirring for 15 min, salts were filtered off through celite, and the residue was washed with AcOEt (3 × 30 mL). The combined organic layers were evaporated under reduced pressure to afford diols **9** (3:1 dr) as colorless oils in 85 % yield (8.7 g) without further purification. To a solution of the above diols **9** (10.8 g, 50 mmol) in dry CH_2Cl_2 (100 mL) and MeCN (10 mL) (v/v = 10:1) was added powdered molecular sieves (4 Å, 11 g) and 4-methylmorpholine *N*-oxide (17.7 g, 151 mmol). *tetra*-Propylammonium perruthenate was then added in small portions (0.88 g, 2.5 mmol) at 0 °C. The mixture was stirred at 0 °C for 4 h, filtered through silica and washed with AcOEt (3 × 50 mL). The filtrate was concentrated under reduced pressure. Flash column chromatography yielded **10a** and **10b** (6.88 g, 65 %) as a mixture of pale yellow oils (2.4:1.9:1:0.8 dr). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.27 – 4.96 (m, 1H), 4.25-3.83 (m, 2H), 2.39-1.70 (m, 4H), 1.64-1.54 (m, 6H), 1.19-0.76 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.6, 174.5, 174.2, 173.8, 134.0, 133.9, 132.6, 131.4, 124.4, 122.7, 121.7, 121.4, 71.3, 70.7, 70.1, 68.8, 53.9, 51.8, 47.3, 45.0, 44.6, 43.8, 38.8, 37.9, 36.1, 35.5, 35.4, 35.0, 26.2, 25.9, 25.8, 25.8, 25.7, 25.3, 25.0, 24.8, 24.6, 24.5, 23.3, 22.6, 17.8, 17.8, 17.8, 15.8, 15.8, 11.2, 11.1, 10.0. HRESIMS calcd for $C_{13}H_{23}O_2$ $[M + H]^+$ 211.1693, found 211.1688.

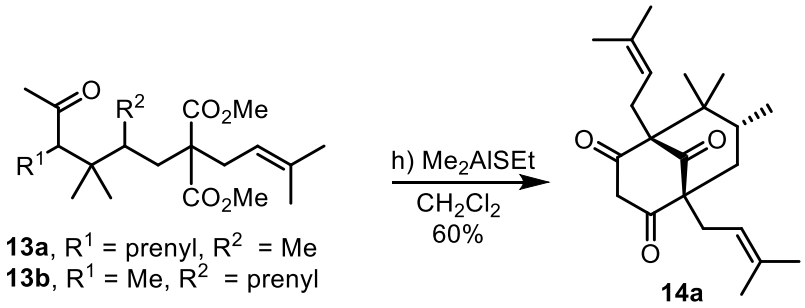


Mixtures of **10a** and **10b** (10.6 g, 50.4 mmol) were dissolved in 100 mL of Et_2O under N_2. The solution was brought to -78 °C, and then a solution of methyl lithium (1.6 M in Et_2O, 67.8 mL, 108.5 mmol) was added dropwise over 40 minutes. The reaction was stirred at that temperature for 7 hours, and then H_2O (40 mL) was added dropwise. The product was extracted with AcOEt (3 × 50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated. The crude product was obtained as a pale-yellow oil without further purification due to the instability. A solution of the above product in dry THF (200 mL) at - 30 °C was stirred for 15 min, sodium bicarbonate (7.1 g, 85.2 mmol), *N*-chlorosuccinimide (11.4 g, 85.2 mmol), and PPh_3 (22.3 g, 85.2 mmol) were successively added to the mixture. The mixture was then kept stirring at - 30 °C for 5 hours. The reaction was quenched by 30 mL of H_2O and extracted with CH_2Cl_2 (3 × 100 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, concentrated, and purified by flash chromatography on silica gel to give **11a** and **11b** as a mixture of yellow oils (10 g, 81 %, 3:1 dr). In this step, the major isomer was purified by prepared HPLC to give the pure product and verify the structure: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.01-4.96 (m, 1H), 3.77 (dd, J = 10.6, 2.9 Hz, 1H), 3.25 (dd, J = 10.6, 9.8 Hz, 1H), 2.72 (dd, J = 11.5, 3.0 Hz, 1H), 2.37-2.28 (m, 1H), 2.12 (s, 4H), 2.10-2.06 (m, 1H), 1.87-1.80 (m, 1H), 1.67 (s, 3H), 1.59 (s, 3H), 1.08

(d, J = 6.7 Hz, 3H), 0.94 (s, 3H), 0.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.1, 133.7, 121.6, 58.1, 48.1, 42.7, 38.9, 34.4, 26.5, 25.8, 21.4, 21.2, 17.6, 12.8. HRESIMS calcd for $C_{14}H_{26}ClO_5$ $[M + H]^+$ 245.1667, found 245.1674.

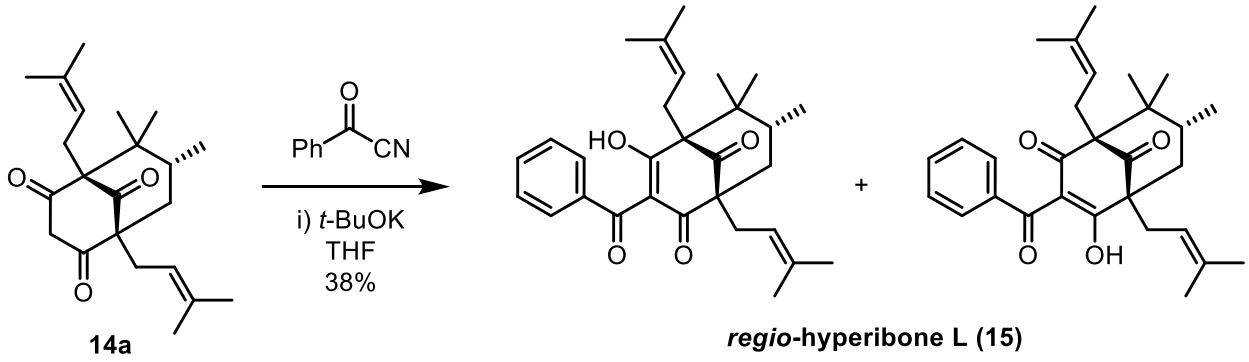


A 100 mL of round-bottomed flask was dried and charged with NaH (60% in mineral oil, 0.4 g, 10 mmol) and DMSO (10 mL) at 0 °C. Prenylated dimethyl malonate (2 g, 10 mol) was added dropwise at 0 °C. After 30 min, mixtures of compounds **11a** and **11b** (3 g, 12 mmol) in 10 mL of DMSO were added dropwise. Then the reaction was stirred at 80 °C for 12 h. After cooling to room temperature, the reaction was quenched with H_2O and extracted with AcOEt (3 × 20 mL). The organic layers were dried over Na_2SO_4 and purified via flash chromatography to give products **13a** and **13b** as a mixture of pale yellow oils (1.9 g, 47 %, >10:1 dr). ^{1}H NMR(400 MHz, $CDCl_3$) δ 5.07-4.91 (m, 2H), 3.74-3.58 (m, 6H), 2.72 (q, J = 7.1 Hz, 1H), 2.62 (d, J = 6.8 Hz, 1H), 2.19-2.05 (m, 3H), 2.06-1.93 (m, 1H), 1.86-1.70 (m, 2H), 1.69-1.51 (m, 3H), [1.67 (s), 1.63 (s), 1.59 (s), 1.56 (s), 1.54 (s)] (12H), 1.32-1.22 (m, 1H), 1.01-0.86 (m, 6H), 0.83-0.70 (m, 3H). ^{13}C NMR(100 MHz, $CDCl_3$) δ 213.71, 213.12, 172.92, 172.62, 172.52, 172.42, 168.00, 167.75, 167.53, 167.3, 135.75, 133.43, 132.70, 130.01, 129.92, 127.24, 126.61, 125.42, 123.23, 122.24, 117.91, 117.72, 79.43, 79.13, 78.64, 64.81, 64.62, 62.34, 58.47, 57.51, 57.31, 57.12, 53.91, 52.62, 52.50, 52.49, 52.46, 52.4, 52.3, 51.6, 50.94, 46.85, 40.80, 39.71, 39.42, 39.31, 36.13, 35.35, 35.12, 34.61, 34.33, 34.14, 32.04, 31.61, 31.29, 29.85, 29.36, 29.20, 28.61, 26.93, 26.13, 26.11, 25.99, 25.81, 25.77, 25.75, 25.55, 25.09, 24.89, 24.85, 24.71, 21.56, 21.32, 21.03, 18.14, 18.10, 18.06, 17.98, 17.84, 16.21, 15.63, 14.41, 13.47, 12.72, 10.83, 10.11. HRESIMS calcd for $C_{24}H_{41}O_5$ $[M + H]^+$ 409.2949, found 409.2958.



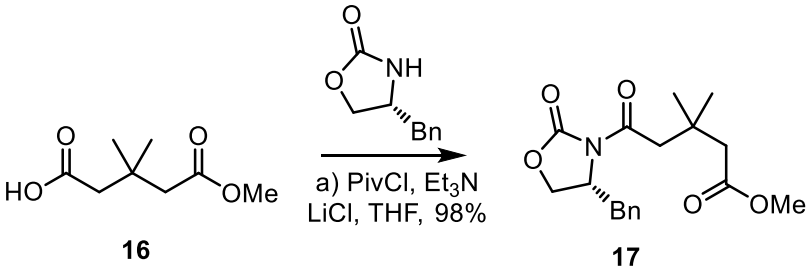
The ethanethiol (97 %, 0.15 mL, 2 mmol) was dissolved in 4 mL of CH_2Cl_2 under N_2. Trimethyl aluminium (1.0 M in heptane, 2 mL, 2 mmol) was added dropwise with emission of gas. The solution was stirred at room temperature for 0.5 h. Then the solvents were removed under vacuum (with a cold trap in liq. N_2) to give a white solid which was dissolved in 0.2 mL of dry heptane under N_2. The mixture of **13a** and **13b** (82 mg, 0.2 mmol) in 2 mL of CH_2Cl_2 was added dropwise and the reaction was stirred at 50 °C for 20 hours, quenched by H_2O after the solution was cooled to room temperature. 1 N HCl was added slowly into the white emulsion until the colloidal solution turned transparency and stirred for 10 min. The product was extracted from the aqueous layer extracted with CH_2Cl_2 (3 × 5 mL). The organic layer was dried over

Na_2SO_4 and purified via flash chromatography to give bicyclo[3.3.1]nonane product **14a** as a yellow oil (40 mg, 60 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.10 (t, J = 7.3 Hz, 1H), 4.98-4.84 (m, 1H), 3.59 (d, J = 16.9 Hz, 1H), 2.96 (d, J = 16.9 Hz, 1H), 2.64-2.44 (m, 4H), 2.27-2.22 (dd, J = 6.2, 13.9 Hz, 1H), 2.11-2.07 (dd, J = 2.1, 14.0 Hz, 1H), 1.67 – 1.52 (m, 13H), 1.20 (s, 3H), 0.96 (s, 3H), 0.86 (d, J = 7.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.7, 204.0, 202.7, 136.5, 135.9, 117.9, 117.6, 70.7, 64.5, 63.6, 51.9, 45.6, 40.2, 31.9, 27.2, 26.4, 26.2, 26.2, 23.4, 19.3, 18.1. HRESIMS calcd for $C_{22}H_{33}O_3$ $[M + H]^+$ 345.2430, found 345.2433.



The KO^{t}Bu (17 mg, 0.15 mmol) and compound **14a** (34 mg, 0.1 mmol) were dissolved in 2 mL of THF under N_2 and stirred at 0 °C for 15 min. After benzoyl cyanide (26 mg, 0.2 mmol) was added, the mixture was warmed up to room temperature and stirred for 2 hours. The reaction was quenched with saturated solution of NH_4Cl (5 mL). The product was extracted from the aqueous layer with AcOEt (3 × 10 mL). The organic layer was dried over Na_2SO_4, concentrated and purified via flash chromatography to yield *regio*-hyperibone L **15** (17 mg, 38 %) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.49 (m, 3H), 7.37 (t, J = 7.8 Hz, 2H), 5.31-4.74 (m, 2H), 2.77-2.28 (m, 4H), 2.23-1.96 (m, 2H), 1.89-1.51 (m, 13H), 1.26 (s, 3H), 1.06 (d, J = 19.0 Hz, 3H), 0.99 (d, J = 7.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.5, 197.5, 197.1, 197.0, 196.5, 194.7, 193.6, 136.8, 135.0, 132.9, 129.3, 129.3, 128.0, 120.3, 119.8, 119.0, 118.7, 116.3, 68.9, 65.8, 62.9, 61.1, 58.4, 48.6, 48.2, 45.1, 43.9, 40.1, 39.8, 31.4, 30.8, 29.8, 27.1, 26.9, 26.6, 26.3, 26.3, 26.2, 26.1, 25.9, 23.4, 22.8, 18.4, 18.3, 18.2. HRESIMS calcd for $C_{29}H_{37}O_4$ $[M+H]^+$ 449.2686, found 449.2693.

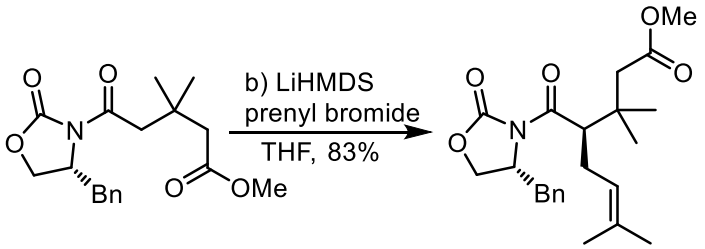
Asymmetric strategy for the total synthesis of PPAPs



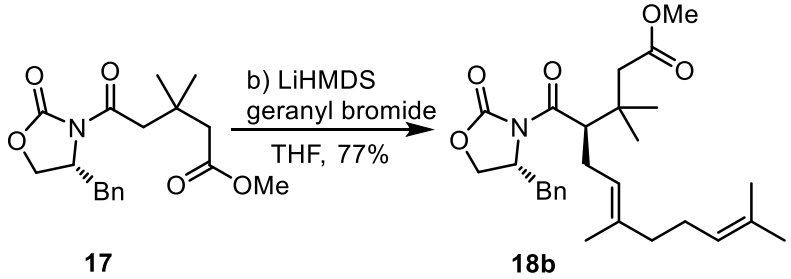
A mixture of commercial 3,3-dimethylpentanedioic acid (20 g, 124.9 mmol), $TsOH{\cdot}H_2O$ (2.4 g, 12.5 mmol), and methanol (5.1 mL, 124.9 mmol) in toluene (100 mL) was heated under reflux overnight in presence of a Dean-Stark. After completion, the resulting solution were concentrated under vacuum. The crude residue was applied onto a silica gel column to give the desired 5-methoxy-3,3-dimethyl-5-oxopentanoic acid **16** (19.6 g, 90 %) as a colorless oil. R_f = 0.5 (dichloromethane/methanol, 10:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.37 (br s, 1H), 3.63 (s, 3H), 2.43 (d, J = 12.1 Hz,

4H), 1.10 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.2, 172.6, 51.4, 45.0, 44.9, 32.5, 27.7; HRESIMS calcd for $C_8H_{14}NaO_4$ $[M + Na]^+$ 197.0784, found 197.0778.

To a solution of 5-methoxy-3,3-dimethyl-5-oxopentanoic acid **16** (19.6 g, 112.4 mmol) in THF (220 mL) was added Et_3N (46.8 mL, 337 mmol) and PivCl (16.6 mL, 135 mmol) at 0 °C. The resulting mixture was stirred at 0 °C for 1 h. The above suspension was added (*R*)-4-Benzyl-2-oxazolidinone (19.92 g, 112.4 mmol) and LiCl (4.76 g, 112.4 mmol) and the resulting suspension was warmed to room temperature and stirred overnight. The reaction mixture was quenched with saturated aqueous NH_4Cl solution and extracted with AcOEt (3 × 200 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. Column chromatography yielded product **17** (36.7 g, 98 %) as a colorless oil. $[\alpha]^{25}_D$ -40.43 (c = 0.61, $CHCl_3$); R_f = 0.3 (petroleum ether/ethyl acetate, 5:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 2H), 7.28 – 7.25 (m, 1H), 7.22 (d, *J* = 7.1 Hz, 2H), 4.71 – 4.66 (m, 1H), 4.18 – 4.12 (m, 2H), 3.65 (s, 3H), 3.30 (dd, *J* = 13.4, 3.2 Hz, 1H), 3.10 (dd, *J* = 29.3, 16.8 Hz, 2H), 2.75 (dd, *J* = 13.4, 9.8 Hz, 1H), 2.56 (d, *J* = 2.2 Hz, 2H), 1.18 (s, 3H), 1.17 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 171.7, 153.6, 135.5, 129.5, 129.1, 129.0, 127.4, 66.1, 55.4, 51.4, 44.7, 44.0, 38.1, 33.2, 28.2, 28.2; HRESIMS calcd for $C_{18}H_{23}NNaO_5$ $[M + Na]^+$ 356.1468, found 356.1472.

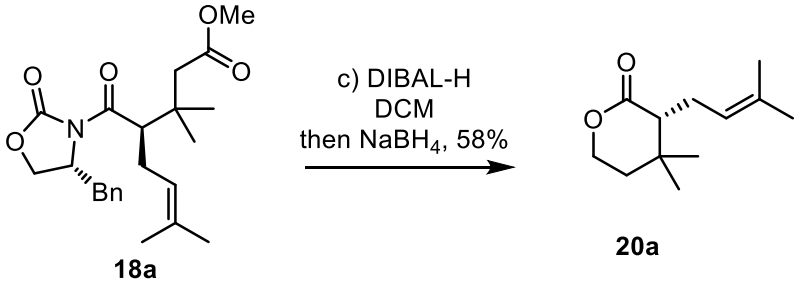


To a rapidly stirred mixture of **17** (10 g, 30 mmol) and THF (150 mL) at -78 °C was added lithium bis(trimethylsilyl)amide (1 M in THF, 31.5 mL, 31.5 mmol) dropwise under N_2. After stirring for 30 min at -78 °C, a solution of prenyl bromide (95%, 3.8 mL, 31.5 mmol) in 10 mL of THF was added dropwise. The reaction mixture was slowly warm to 0 °C and stirred at 0 °C for another 8 hours, and then quenched with saturated solution of NH_4Cl (150 mL). The aqueous phase was extracted with AcOEt (3 × 100 mL), and the combined organic layers were dried over Na_2SO_4. The product was purified via column chromatography with silica gel to yield **18a** (10 g, 83 %) as a colorless oil. R_f = 0.2 (petroleum ether/ethyl acetate, 10:1). $[\alpha]^{25}_D$ -48.16 (*c* = 6.47, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.31 (m, 2H), 7.28 – 7.25 (m, 1H), 7.22 (d, *J* = 6.9 Hz, 2H), 5.15 – 5.13 (m, 1H), 4.69 – 4.66 (m, 1H), 4.20 (dd, *J* = 11.6, 3.6 Hz, 1H), 4.11 – 4.07 (m, 2H), 3.66 (s, 3H), 3.18 (dd, *J* = 13.3, 3.2 Hz, 1H), 2.60 – 2.52 (m, 2H), 2.42 (dd, *J* = 38.2, 13.3 Hz, 2H), 2.23 (d, *J* = 13.3 Hz, 1H), 1.65 (s, 3H), 1.61 (s, 3H), 1.15 (s, 3H), 1.14 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.7, 172.4, 153.4, 135.7, 134.2, 129.5, 129.1, 127.4, 121.2, 65.5, 55.6, 51.5, 49.5, 44.3, 37.8, 36.3, 27.5, 26.0, 25.4, 25.2, 17.9. HRESIMS calcd for $C_{23}H_{31}NNaO_5$ $[M + Na]^+$ 424.2094, found 424.2103.



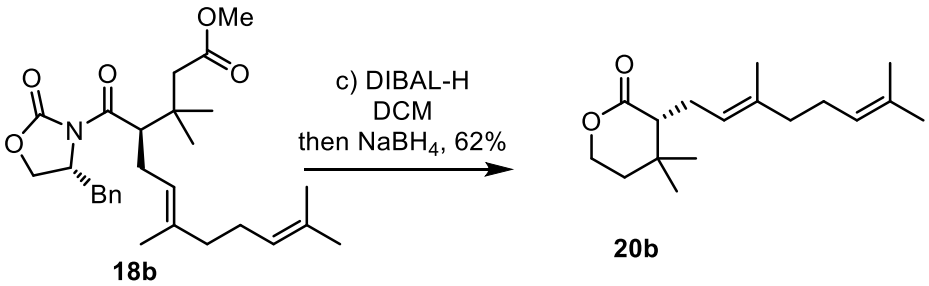
Compound **18b** were prepared according to the general procedure that used for **18a** with compound **17** (10 g, 30 mmol), lithium bis(trimethylsilyl)amide (1 M in THF, 31.5 mL, 31.5 mmol) and geranyl bromide (96%, 10.4 mL, 31.5

mmol). The residue was purified by column chromatography over silica gel yielding the desired product **18b** (11.4 g, 77 %) as a colorless oil. R_f = 0.3 (petroleum ether/ethyl acetate, 10:1). $[\alpha]^{25}_D$ -7.9 (*c* = 0.77, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 2H), 7.30 – 7.26 (m, 1H), 7.24 – 7.20 (m, 2H), 5.20 – 5.13 (m, 1H), 5.10 – 5.04 (m, 1H), 4.72 – 4.63 (m, 1H), 4.20 (dd, *J* = 11.5, 3.5 Hz, 1H), 4.13 – 4.05 (m, 2H), 3.67 (s, 3H), 3.25 (dd, *J* = 13.2, 3.3 Hz, 1H), 2.62 – 2.47 (m, 2H), 2.43 (dd, *J* = 23.6, 13.3 Hz, 2H), 2.26 (dt, *J* = 13.4, 4.3 Hz, 1H), 2.07 – 1.92 (m, 4H), 1.67 (s, 3H), 1.63 (s, 3H), 1.57 (s, 3H), 1.16 (s, 3H), 1.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 172.4, 153.4, 137.8, 135.8, 131.6, 129.5, 129.5, 129.1, 127.4, 124.2, 120.8, 65.5, 55.8, 51.5, 49.5, 44.3, 39.9, 37.9, 36.4, 27.4, 26.8, 25.8, 25.4, 25.2, 17.8, 16.2. HRESIMS calcd for $C_{28}H_{39}NNaO_5$ $[M + Na]^+$ 492.2720, found 492.2724.



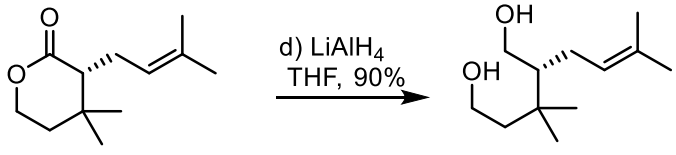
18a **20a**

To a solution of **18a** (10 g, 24.9 mmol) in dry CH_2Cl_2 (100 mL) at -78 °C was added diisobutylaluminium hydride (1.5 M in toluene, 33.2 mL, 49.8 mmol) dropwise under N_2. After stirring for 2 h at -78 °C. The reaction mixture was slowly warm to 0 °C and stirred at 0 °C for another 3 hours, and then the reaction was slowly quenched with 1 mL of H_2O, 1 mL of 15% NaOH aq. and 2.5 mL of H_2O at 0 °C in sequence. The suspension was stirred at room temperature for 15 min, and anhydrous $MgSO_4$ was added. After stirring for 15 min, salts were filtered off through celite, and the residue was washed with AcOEt (3 × 30 mL). The combined organic layers were evaporated under reduced pressure. The crude product was treated by $NaBH_4$ (0.5 eq) in MeOH at 0 °C for 0.5 h to yield **20a** (2.83 g, 58 %) as a colorless oil. R_f = 0.55 (petroleum ether/ethyl acetate, 10:1). $[\alpha]^{25}_D$ -19.22 (*c* = 0.67, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.22 (t, *J* = 6.7 Hz, 1H), 4.26 (t, *J* = 6.3 Hz, 2H), 2.40 – 2.29 (m, 1H), 2.22 – 2.14 (m, 2H), 1.76 –1.69 (m , 2H), 1.66 (s, 3H), 1.62 (s, 3H), 1.14 (s, 3H), 0.94 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 132.3, 123.3, 65.1, 51.7, 38.5, 33.4, 29.3, 25.8, 25.1, 24.2, 17.8. HRESIMS calcd for $C_{12}H_{21}O_2$ $[M + H]^+$ 197.1536, found 197.1541.



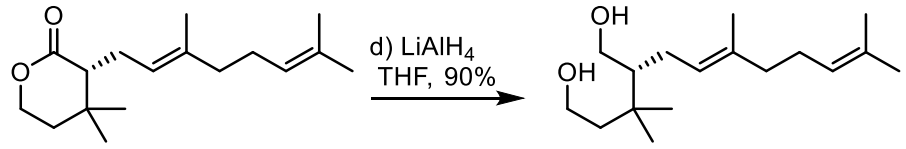
18b **20b**

Following the procedure for the synthesis of **20a**, **20b** was prepared as a colorless oil in 62% yield (3.98 g). R_f = 0.6 (petroleum ether/ethyl acetate, 10:1). $[\alpha]^{25}_D$ -20.41 (*c* = 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.25 (t, *J* = 6.7 Hz, 1H), 5.07 (t, *J* = 6.8 Hz, 1H), 4.28 (t, *J* = 6.3 Hz, 2H), 2.45 – 2.34 (m, 1H), 2.26 – 2.17 (m, 2H), 2.10 – 2.01 (m, 2H), 2.01 – 1.94 (m, 2H), 1.77 –1.70 (m , 2H), 1.66 (s, 3H), 1.63 (s, 3H), 1.58 (s, 3H),1.16 (s, 3H), 0.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 135.9, 131.5, 124.4, 123.3, 65.1, 51.8, 39.8, 38.5, 33.4, 29.4, 26.7, 25.8, 25.2, 24.3, 17.8, 16.2. HRESIMS calcd for $C_{17}H_{29}O_2$ $[M + H]^+$ 265.2162, found 265.2170.



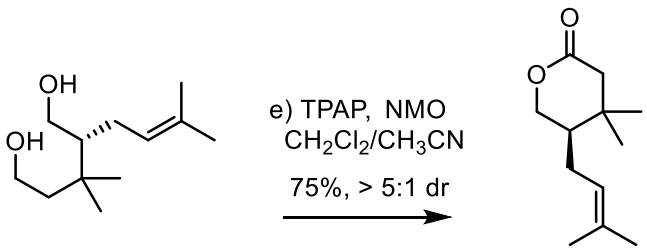
20a **21a**

Compound **21a** was prepared according to the general procedure that used for **9** with compound **20a** (1.96 g, 10 mmol), $LiAlH_4$ (1.14 g, 30 mmol) in THF. The residue was purified by column chromatography over silica gel to yield the desired product **21a** (1.8 g, 90 %) as a colorless oil. R_f = 0.4 (petroleum ether/ethyl acetate, 3:1). $[\alpha]^{25}_D$ 12.5 (*c* = 0.76, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.22 – 5.15 (t, *J* = 7.1 Hz, 1H), 3.76 – 3.62 (m, 3H), 3.55 (dd, *J* = 11.2, 4.8 Hz, 1H), 2.68 (d, *J* = 6.2 Hz, 2H), 2.09 (d, *J* = 14.4 Hz, 1H), 1.98 – 1.88 (m, 1H), 1.74 – 1.66 (m, 1H), 1.68 (s, 3H), 1.61 (s, 3H), 1.58 – 1.49 (m, 1H), 1.44 – 1.36 (m, 1H), 0.93 (s, 3H), 0.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.7, 124.5, 77.5, 77.2, 76.8, 63.4, 59.4, 49.9, 43.3, 34.8, 26.6, 26.2, 26.0, 25.5, 17.9. HRESIMS calcd for $C_{12}H_{25}O_2$ $[M + H]^+$ 201.1849, found 201.1857.



20b **21b**

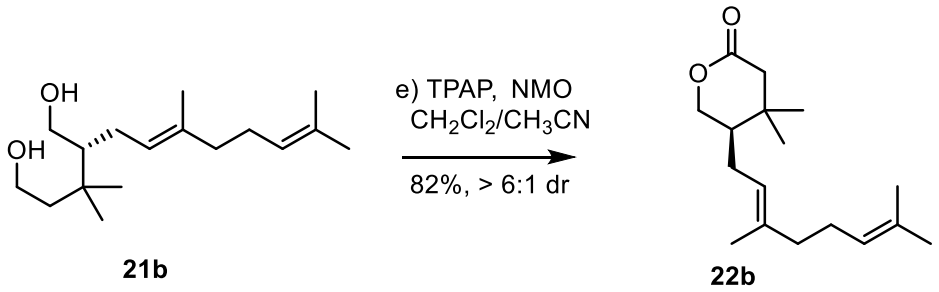
Compound **21b** was prepared according to the general procedure that used for **9** with compound **20b** (2.64 g, 10 mmol), $LiAlH_4$ (1.14 g, 30 mmol) in THF. The residue was purified by column chromatography over silica gel to yield the desired product **21b** (28 g, 90 %) as a colorless oil. R_f = 0.5 (petroleum ether/ethyl acetate, 3:1). $[\alpha]^{25}_D$ 12.52 (*c* = 1.07, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.20 (t, *J* = 6.9 Hz, 1H), 5.08 – 5.02 (m, 1H), 3.74 – 3.63 (m, 3H), 3.55 (dd, *J* = 11.2, 4.9 Hz, 1H), 2.58 (br s, 2H), 2.15 – 2.02 (m, 3H), 2.02 – 1.91 (m, 3H), 1.74 – 1.67 (m, 1H), 1.65 (s, 3H), 1.61 (s, 3H), 1.58 (s, 3H), 1.56 – 1.50 (m, 1H), 1.44 – 1.37 (m, 1H), 0.94 (s, 3H), 0.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.3, 131.7, 124.4, 124.2, 77.5, 77.2, 76.8, 63.5, 59.4, 49.9, 43.3, 39.9, 34.8, 26.6, 26.5, 26.2, 25.8, 25.6, 17.8, 16.2. HRESIMS calcd for $C_{17}H_{33}O_2$ $[M + H]^+$ 269.2475, found 269.2483.



21a **22a**

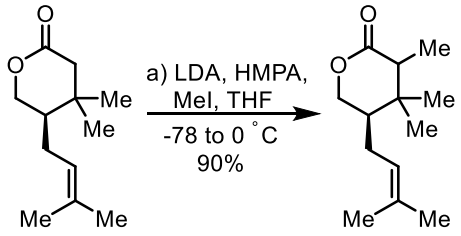
Compound **22a** were prepared according to the general procedure that used for **10a** with compound **21a** (1.8 g, 9 mmol)**,** molecular sieves (4 Å, 9 g), 4-methylmorpholine *N*-oxide (3.16 g, 27 mmol) and tetra-propylammonium perruthenate (316 mg, 0.9 mmol). The residue was purified by column chromatography over silica gel to yield the desired product **22a** (1.32 g, 75 %, > 5:1 dr) as a colorless oil. R_f = 0.55 (petroleum ether/ethyl acetate, 10:1). $[\alpha]^{25}_D$ 13.54 (*c* = 0.65, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.09 – 5.02 (m, 1H), 4.31 (dd, *J* = 11.7, 5.0 Hz, 1H), 3.99 (dd, *J* = 11.6,

10.4 Hz, 1H), 2.41 – 2.24 (m, 2H), 1.82 – 1.71 (m, 1H), 1.70 (s, 3H), 1.69 – 1.63 (m, 1H), 1.59 (s, 3H), 1.05 (s, 3H), 0.97 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 134.2, 121.4, 77.5, 77.2, 76.8, 70.7, 45.3, 43.4, 32.4, 28.8, 25.9, 24.8, 21.8, 17.9. HRESIMS calcd for $C_{12}H_{21}O_2$ $[M + H]^+$ 197.1536, found 197.1540.



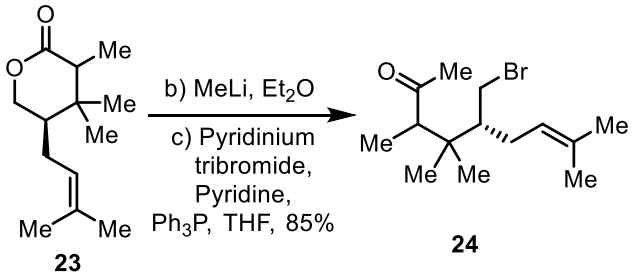
21b **22b**

Compound **22b** were prepared according to the general procedure that used for **10a** with compound **21b** (2.4 g, 9 mmol)**,** molecular sieves (4 Å, 9 g), 4-methylmorpholine *N*-oxide (3.16 g, 27 mmol) and tetra-propylammonium perruthenate (316 mg, 0.9 mmol). The residue was purified by column chromatography over silica gel to yield the desired product **22b** (1.95 g, 82 %, > 6:1 dr) as a colorless oil. R_f = 0.6 (petroleum ether/ethyl acetate, 10:1). $[\alpha]^{25}_D$ 16.91 (*c* = 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.10 – 5.01 (m, 2H), 4.31 (dd, *J* = 11.7, 5.0 Hz, 1H), 3.98 (dd, *J* = 11.7, 10.3 Hz, 1H), 2.43 – 2.25 (m, 2H), 2.26 – 2.18 (m, 1H), 2.11 – 2.04 (m, 2H), 2.03 – 1.97 (m, 2H), 1.84 – 1.68 (m, 2H), 1.67 (s, 3H), 1.59 (s, 3H), 1.06 (s, 3H), 0.98 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 137.7, 131.9, 124.1, 121.5, 77.5, 77.4, 77.2, 76.8, 70.7, 45.3, 43.4, 39.8, 32.5, 28.9, 26.6, 25.9, 24.7, 21.8, 17.8, 16.2. HRESIMS calcd for $C_{17}H_{29}O_2$ $[M + H]^+$ 265.2162, found 265.2169.



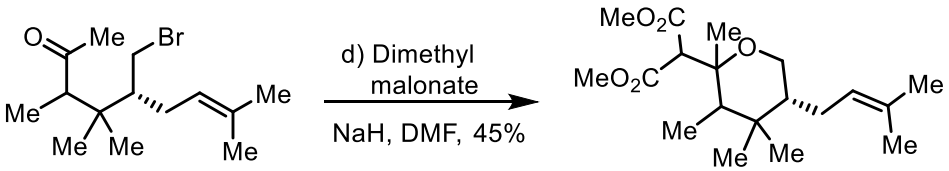
22a **23**

A 250 mL of flame-dried flask charged with compound **22a** (5 g, 25.5 mmol) and THF (50 mL) was cooled to -78 °C. A solution of lithium diisopropylamide (2 M in THF, 25 mL, 50 mmol) was added dropwise. The solution was stirred for 30 min at -78 °C and then iodomethane (5.4 g, 38 mmol) and HMPA (5 mL) in THF (10 mL) was added dropwise. The reaction mixture was slowly warm to 0 °C and stirred at 0 °C for another 5 hours, and then quenched with saturated solution of NH_4Cl (20 mL). The aqueous phase was extracted with AcOEt (3 × 40 mL), and the combined organic layers were dried over Na_2SO_4. Column chromatography yielded **23** (4.7 g, 90%, 1:1 dr) as pale yellow oils. R_f = 0.4 (petroleum ether/ethyl acetate, 5:1). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 5.11 – 4.99 (m, 1H), 4.33 – 4.18 (m, 1H), 4.02 – 3.87 (m, 1H), 2.40 – 2.08 (m, 2H), 1.89 – 1.59 (m, 8H), [1.17 (d, *J* = 7.1 Hz), 1.21 (d, *J* = 7.1 Hz)] (3H), [1.04 (s), 1.00 (s), 0.94 (s), 0.84 (s)] (6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.6, 174.2, 134.0, 133.8, 121.7, 121.4, 70.1, 68.7, 47.3, 45.0, 44.6, 43.8, 35.5, 35.0, 25.9, 25.8, 25.3, 25.0, 24.6, 23.3, 17.8, 17.8, 15.8, 11.1, 9.9. HRESIMS calcd for $C_{13}H_{23}O_2$ $[M + H]^+$ 211.1698, found 211.1696.



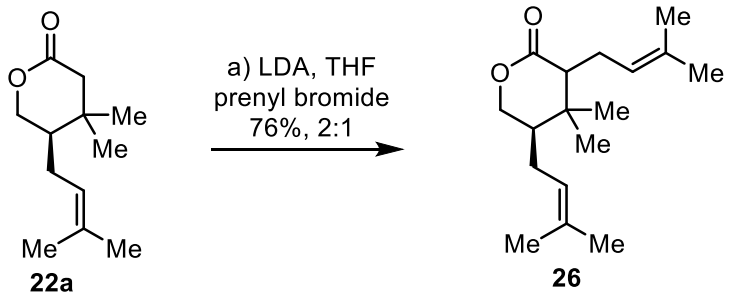
23 **24**

23 (2.0 g, 9.4 mmol) were dissolved in 50 mL of Et_2O under N_2. The solution was brought to -78 °C, and then a solution of methyl lithium (1.6 M in Et_2O, 12.5 mL, 20 mmol) was added dropwise over 20 minutes. The reaction was stirred at that temperature for 7 hours, and then H_2O (40 mL) was added dropwise. The product was extracted with AcOEt (3 × 20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated. The crude product was obtained as a pale-yellow oil without further purification due to the instability. PPh_3 (5 g, 19.2 mmol) and pyridinium tribromide (6.14 g, 19.2 mmol) in THF (48 mL) was stirred for 20 min, the above oil in THF (25 mL) and pyridine (3.1 mL, 38.4 mmol) was then added, mixture was heated for 30 min at 70 °C. After dilution in ethyl acetate, the organic phase was washed successively with a saturated $Na_2S_2O_3$ aqueous solution. The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, concentrated, and purified by flash chromatography on silica gel to give **24** as colorless oils (2.3 g, 85%, 1:1 dr). R*f* = 0.8 (petroleum ether/ethyl acetate, 10:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.12 – 5.03 (m, 1H), 3.43 – 3.28 (m, 1H), 3.23 – 3.08 (m, 1H), 2.56 – 2.39 (m, 1H), 2.24 – 2.02 (m, 2H), [1.77 (s), 1.73 (s)] (3H), 1.72 – 1.67 (m, 1H), [1.63 (s), 1.61 (s), 1.60 (s)] (6H), [1.91 (s), 1.88 (s), 1.87 (s), 1.86 (s)] (6H), [0.75 (d, *J* = 1.2 Hz), 0.74 (d, *J* = 1.2 Hz)] (3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 210.41, 210.39, 132.6, 132.3, 127.9, 127.7, 127.6, 123.4, 123.3, 51.4, 51.3, 46.7, 46.5, 39.1, 39.0, 35.6, 35.3, 31.4, 31.3, 27.4, 26.9, 25.6, 25.6, 21.7, 21.5, 21.3, 21.0, 17.8, 17.7, 11.9, 11.8. HRESIMS calcd for $C_{14}H_{26}BrO$ $[M + H]^+$ 289.1167, found 289.1176.



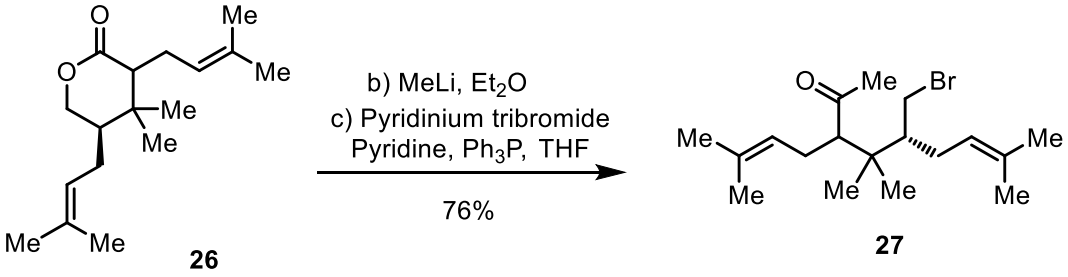
24 **25**

A 500 mL of round-bottomed flask was dried and charged with NaH (60% in mineral oil, 3.3 g, 84 mmol) and DMF (200 mL) at 0 °C. Dimethyl malonate (10.6 mL, 93 mol) added dropwise at 0 °C with stirred for 30 min at rt. Compounds **24** (2.6 g, 9.3 mmol) in 30 mL of DMF were added dropwise, following with TBAI (171 mg, 0.46 mmol). Then the reaction was stirred at 45 °C for 24 h. After cooling to room temperature, the reaction was quenched with H_2O and extracted with EtOAc (3 × 50 mL). The organic layers were dried over Na_2SO_4 and purified via flash chromatography to give products **25** as pale yellow oils (1.4 g, 45% yield, est. 1.5:1.5:1:1 dr). The mixture was purified by pre-HPLC to afford a pure compound as following. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 5.11 – 5.04 (m, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.65 – 3.58 (m, 2H), 3.32 (t, *J* = 11.7 Hz, 1H), 2.05 (dd, *J* = 14.6, 5.9 Hz, 1H), 1.85 (q, *J* = 7.2 Hz, 1H), 1.66 (d, *J* = 1.5 Hz, 3H), 1.56 (s, 3H), 1.55 (s, 3H), 1.55 – 1.51 (m, 1H), 1.45 – 1.41 (m, 1H), 1.41 (s, 3H), 0.97 (s, 3H), 0.88 – 0.83 (m, 6H).^{13}C NMR (151 MHz, $CDCl_3$) δ 167.8, 167.7, 132.4, 123.3, 78.8, 76.9, 61.8, 61.7, 52.3, 52.3, 46.3, 45.0, 35.6, 28.8, 25.7, 24.7, 17.7, 17.3, 16.0, 10.7. HRESIMS calcd for $C_{19}H_{33}O_5$ $[M + H]^+$ 341.2328, found 341.2326.



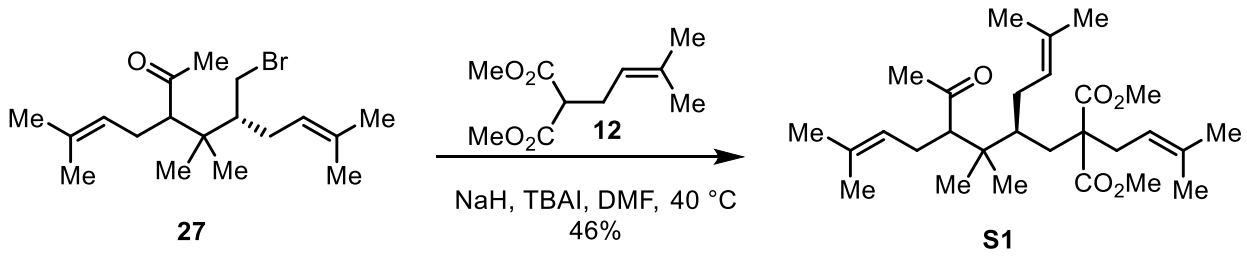
22a **26**

Compound **26** was prepared according to the general procedure that used for **23** with compound **22a** (0.6 g, 3.06 mmol), lithium diisopropylamide (2 M in THF, 1.6 mL, 3.21 mmol) and prenyl bromide (95%, 0.39 mL, 3.21 mmol). The residue was purified by column chromatography over silica gel to yield the desired product **26** (0.61 g, 76 %, 2:1) as a pale yellow oil. R_f = 0.6 (petroleum ether/ethyl acetate, 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.33 – 5.26 (m, 0.3H), 5.25 – 5.18 (m, 0.7H), 5.09 – 4.99 (m, 1H), 4.27 (dd, J = 11.8, 5.5 Hz, 0.3H), 4.17 (dd, J = 11.4, 4.3 Hz, 0.7H), 4.01 – 3.91 (m, 1H), 2.46 – 2.25 (m, 1.3H), 2.25 – 2.07 (m, 2.7H), 1.89 – 1.74 (m, 1.5H), 1.70 (s, 3H), 1.68 (s, 3H), 1.66 – 1.61 (m, 0.5H), 1.63 (s, 3H), [1.60 (s), 1.59 (s)] (3H), 1.11 (s, 1H), 1.02 (s, 2H), 0.96 (s, 2H), 0.86 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 174.3, 134.1, 132.7, 131.8, 124.3, 122.9, 121.8, 121.7, 69.7, 68.7, 53.6, 52.0, 45.07, 44.96, 36.7, 35.8, 26.9, 25.94, 25.90, 25.87, 25.7, 25.1, 24.9, 24.8, 24.4, 23.1, 18.0, 17.92, 17.90, 17.2. HRESIMS calcd for $C_{17}H_{29}O_2$ $[M + H]^+$ 265.2162, found 265.2170.

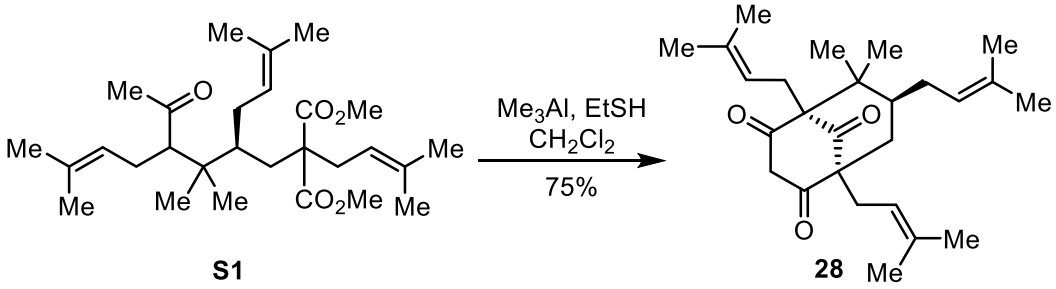


26 **27**

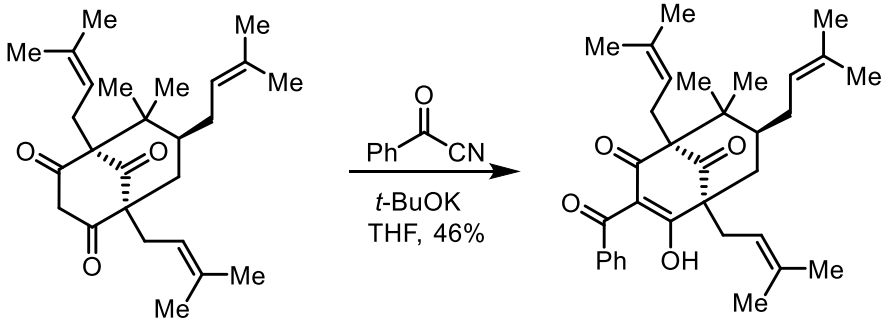
Compound **26** (40.5 g, 153.4 mmol) was dissolved in 150 mL of Et_2O under N_2. The solution was brought to -78 °C, and then a solution of methyl lithium (1.6 M in Et_2O, 240 mL, 383.6 mmol) was added dropwise over 40 minutes. The reaction was stirred at that temperature for 7 hours, and then H_2O (40 mL) was added dropwise. The product was extracted with AcOEt (3 × 30 mL). The combined organic layers were dried over Na_2SO_4 and concentrated. The crude product (42.1 g, 98 %) was obtained as a pale yellow solid without further purification due to the instability. R_f = 0.6 (petroleum ether/ethyl acetate, 10:1). PPh_3 (5 g, 19.2 mmol) and pyridinium tribromide (6.14 g, 19.2 mmol) in THF (48 mL) was stirred for 20 min. The above solid (2.7 g, 9.5 mL) in THF (25 mL) and pyridine (3.1 mL, 38.4 mmol) was then added. The mixture was heated for 30 min at 70 °C. After dilution in ethyl acetate, the organic phase was washed successively with a saturated $Na_2S_2O_3$ aqueous solution. The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, concentrated, and purified by flash chromatography on silica gel to give **27** as colorless oils (2.5 g, 77%, 2:1 dr). R*f* = 0.8 (petroleum ether/ethyl acetate, 10:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.16 – 5.04 (1H), 5.02 – 4.87 (1H), 3.63-3.55 (1H), 3.49 – 3.34 (1H), 2.84-2.76 (1H), 2.41 – 2.30 (1H), 2.30 – 2.16 (2H), 2.12-2.10 (3H), 2.08 – 1.97 (1H), 1.71 – 1.57 (13H), 1.06-0.95 (6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.4, 213.3, 148.2, 133.6, 133.5, 132.8, 129.4, 128.3, 123.1, 122.8, 121.7, 112.6, 77.2, 74.2, 58.2, 58.1, 56.9, 54.1, 51.5, 47.3, 47.0, 39.7, 39.6, 39.2, 37.1, 35.8, 35.1, 34.9, 34.9, 28.7, 28.1, 28.0, 27.6, 26.9, 26.9, 26.8, 26.5, 25.9, 25.8, 25.8, 25.4, 24.7, 22.7, 22.2, 22.1, 22.0, 21.5, 18.1, 18.1, 18.0, 17.7, 17.7, 16.2. HRESIMS calcd for $C_{18}H_{31}BrO$ $[M + H]^+$ 343.1637, found 343.1640.



A 500 mL of round-bottomed flask was dried and charged with NaH (60% in mineral oil, 3.3 g, 84 mmol) and DMF (200 mL) at 0 °C. **12** (18.6 g, 93 mol) was added dropwise at 0 °C. Then stirred for 30 min at rt. Compounds **27** (3.2 g, 9.3 mmol) in 30 mL of DMF were added dropwise, following with TBAI (171mg, 0.46 mmol). Then the reaction was stirred at 40 °C for 24 h. After cooling to room temperature, the reaction was quenched with H_2O and extracted with AcOEt (3 × 50 mL). The organic layers were dried over Na_2SO_4 and purified via flash chromatography to give products **S1** as pale yellow oils (2.0 g, 46 %, 2:1 dr). R_f = 0.5 (petroleum ether/ethyl acetate, 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.10 – 4.74 (m, 3H), 3.65 (s, 3H), 3.63 (s, 3H), 2.75 – 2.51 (m, 3H), 2.37 – 2.15 (m, 2H), 2.05 – 1.93 (m, 4H), 1.87 – 1.74 (m, 3H), 1.66 – 1.47 (m, 19H), [0.87 (s), 0.85 (s), 0.82 (s), 0.80 (s)] (6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.9, 213.4, 172.52, 172.45, 172.4, 135.63, 135.56, 133.2, 132.9, 130.1, 130.0, 125.2, 125.1, 122.3, 122.1, 117.8, 57.5, 57.3, 56.9, 56.4, 52.44, 52.36, 52.3, 40.06, 40.05, 39.91, 39.86, 35.3, 34.6, 34.0, 33.4, 31.8, 31.4, 30.0, 28.8, 27.2, 26.3, 26.1, 26.0, 25.92, 25.88, 25.8, 22.1, 21.5, 21.1, 18.2, 18.1, 18.0, 17.81, 17.78. HRESIMS calcd for $C_{28}H_{47}O_5$ $[M + H]^+$ 463.3418, found 463.3426.

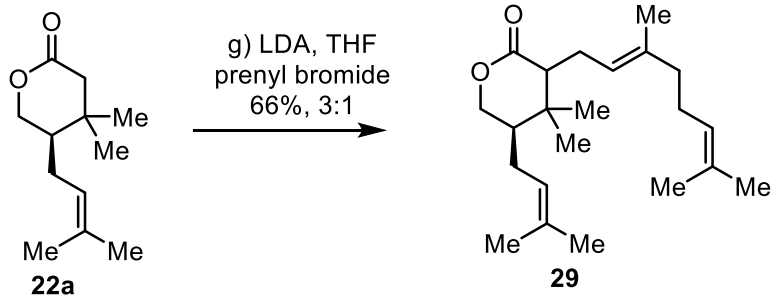


The ethanethiol (97 %, 40 μL, 0.5 mmol) was dissolved in 1 mL of CH_2Cl_2 under N_2. Trimethyl aluminium (1.0 M in heptane, 0.5 mL, 0.5 mmol) was added dropwise with emission of gas. The solution was stirred at room temperature for 0.5 h. Then the solvents were removed under vacuum (with a cold trap in liq. N_2) to give a white solid which was dissolved in 0.1 mL of dry heptane under N_2. The substrate **S1** (46 mg, 0.1 mmol) in 1 mL of CH_2Cl_2 was added dropwise and the reaction was stirred at 50 °C for 20 hours, quenched by H_2O after the solution was cooled to room temperature. 1 N HCl was added slowly into the white emulsion until the colloidal solution turned transparency and stirred for 10 min. The product was extracted from the aqueous layer extracted with CH_2Cl_2 (3 × 5 mL). The organic layer was dried over Na_2SO_4 and purified via flash chromatography to give bicyclo[3.3.1]nonane product **28** as a yellow oil (30 mg, 75 %). R_f = 0.15 (petroleum ether/ethyl acetate, 10:1). $[\alpha]^{20}_D$ = 36.85 (c = 8 g/l, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.11 (t, J = 7.4 Hz, 1H), 4.93 (t, J = 7.4 Hz, 1H), 4.86 (t, J = 6.8 Hz, 1H), 3.56 (d, J = 17.3 Hz, 1H), 2.96 (d, J = 17.3 Hz, 1H), 2.57 – 2.55 (m, 2H), 2.49 (d, J = 7.4 Hz, 2H), 2.19 – 2.15 (m, 2H), 2.04 (dd, J = 14.0, 5.7 Hz, 1H), 1.67 (s, 3H), 1.66 (s, 3H), 1.65 (s, 3H), 1.61 (s, 6H), 1.52 (s, 3H), 1.47-1.41 (m, 1H), 1.34 – 1.29 (m, 1H), 1.26 (s, 3H), 0.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.6, 203.0, 202.8, 136.6, 135.7, 133.8, 122.7, 118.2, 117.6, 70.3, 64.9, 62.7, 51.3, 46.5, 40.6, 31.3, 29.3, 27.3, 26.5, 26.20, 26.17, 26.0, 23.0, 18.11, 18.05, 18.0. HRESIMS calcd for $C_{26}H_{39}O_3$ $[M + H]^+$ 399.2894, found 399.2899.



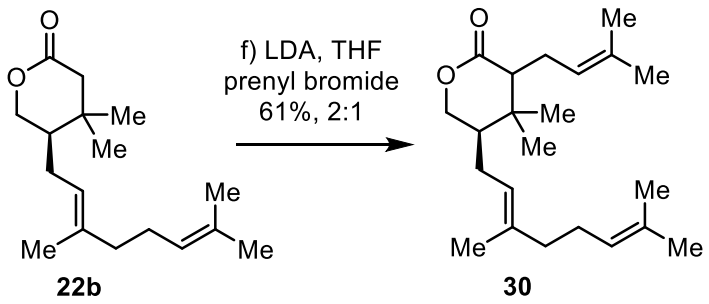
28 (+)-*epi*-clusianone (**3**)

The KO^{t}Bu (17 mg, 0.15 mmol), 4-dimethylaminopyridine (6 mg, 0.05 mmol) and compound **28** (20 mg, 0.05 mmol) were dissolved in 3 mL of THF under N_2 and stirred at 0 °C for 10 min. After benzoyl cyanide (13 mg, 0.1 mmol) was added, the mixture was warmed up to room temperature and stirred for 2 hours. The reaction was quenched with saturated solution of NH_4Cl (5 mL). The product was extracted from the aqueous layer with AcOEt (3 × 10 mL). The organic layer was dried over Na_2SO_4, concentrated and purified via flash chromatography to yield *epi*-clusianone (**3**) (11.5 mg, 46 %) as a white powder. R_f = 0.5 (petroleum ether/ethyl acetate, 10:1). $[\alpha]^{20}_D$ = 53 (c= 4 g/l, $CHCl_3$). All the other spectra are consistent with the literature[9] and our previous report.[10]



22a **29**

Compound **29** was prepared according to the general procedure that used for **23** with compound **22a** (0.6 g, 3.06 mmol), lithium diisopropylamide (2 M in THF, 1.6 mL, 3.21 mmol) and geranyl bromide (96%, 0.66 mL, 3.21 mmol). The residue was purified by column chromatography over silica gel to yield the desired product **29** (0.67 g, 66 %, 3:1) as a pale yellow oil. R_f = 0.65 (petroleum ether/ethyl acetate, 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.30 (t, J = 7.4 Hz, 0.3H), 5.23 (t, J = 7.0 Hz, 0.7H), 5.10 – 5.00 (m, 2H), 4.28 (dd, J = 11.8, 5.4 Hz, 0.3H), 4.17 (dd, J = 11.4, 4.3 Hz, 0.7H), 4.00 – 3.90 (m, 1H), 2.50 – 2.09 (m, 4H), 2.09 – 2.01 (m, 2H), 2.01 – 1.93 (m, 2H), 1.89 – 1.73 (m, 1.5H), 1.68 – 1.64 (m, 0.5H), [1.70 (s), 1.66 (s), 1.63 (s), 1.59 (s)] (15H), [1.11 (s), 1.03 (s), 0.96 (s), 0.87 (s)] (6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 174.2, 136.2, 135.2, 134.1, 131.5, 131.4, 124.5, 124.4, 124.3, 122.8, 121.8, 121.7, 69.7, 68.7, 53.6, 52.0, 45.1, 45.0, 39.9, 39.8, 36.7, 35.8, 26.9, 26.7, 25.93, 25.90, 25.83, 25.82, 25.7, 25.1, 24.9, 24.8, 24.3, 23.1, 18.0, 17.9, 17.8, 17.3, 16.2. HRESIMS calcd for $C_{22}H_{37}O_2$ $[M + H]^+$ 333.2788, found 333.2793.



Compound **30** was prepared according to the general procedure that used for **23** with compound **23b** (0.9 g, 3.4 mmol), lithium diisopropylamide (2 M in THF, 1.8 mL, 3.6 mmol) and prenyl bromide (95%, 0.44 mL, 3.6 mmol). The residue was purified by column chromatography over silica gel to yield the desired product **30** (0.69 g, 61 %, 2:1) as a pale yellow oil. R_f = 0.65 (petroleum ether/ethyl acetate, 10:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.30 – 5.26 (m, 0.4H), 5.20 (t, J = 6.9 Hz, 0.6H), 5.08 – 5.00 (m, 2H), 4.25 (dd, J = 11.8, 5.6 Hz, 0.4H), 4.14 (dd, J = 11.4, 4.3 Hz, 0.6H), 3.93 (q, J = 11.2 Hz, 1H), 2.43 – 2.09 (m, 4H), 2.08 – 2.01 (m, 2H), 2.01 – 1.95 (m, 2H), 1.87 – 1.78 (m, 1H), 1.78 – 1.72 (m, 0.5H), 1.66 – 1.59 (m, 0.5H), [1.66 (s), 1.62 (s), 1.57 (s), 1.56 (s)] (15H), 1.10 (s, 1H), 1.01 (s, 2H), 0.95 (s, 2H), 0.85 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.7, 174.1, 137.49, 137.48, 132.5, 131.7, 131.64, 131.58, 124.3, 124.08, 124.06, 122.9, 121.82, 121.81, 121.7, 69.6, 68.6, 53.5, 51.9, 45.0, 44.9, 39.78, 39.75, 36.6, 35.8, 26.8, 26.5, 25.80, 25.78, 25.75, 25.5, 25.0, 24.8, 24.7, 24.3, 23.0, 17.83, 17.80, 17.7, 17.2, 16.2, 16.1. HRESIMS calcd for $C_{22}H_{37}O_2$ $[M + H]^+$ 333.2788, found 333.2789.

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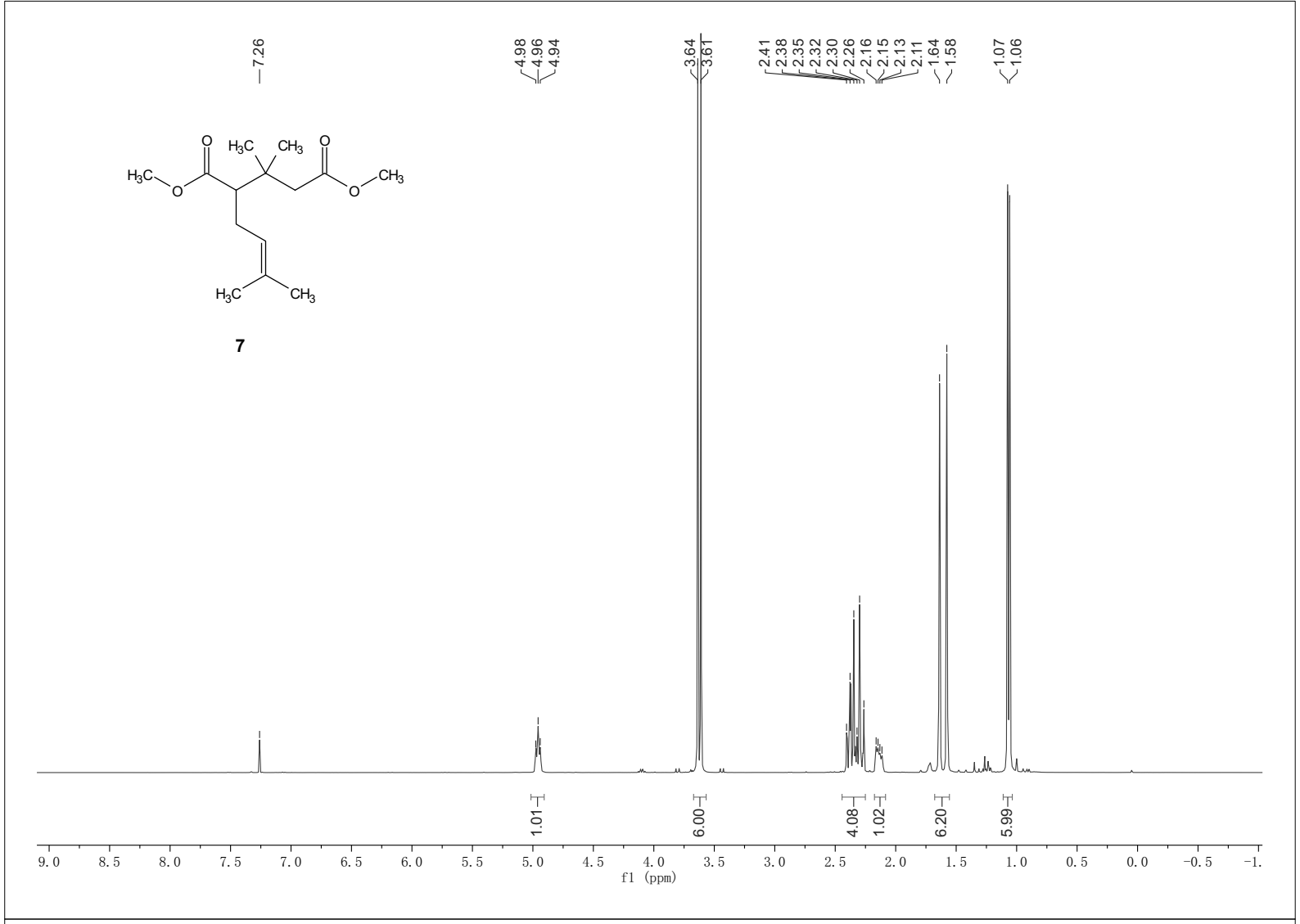
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4.96
4.94
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2.38
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2.32
2.30
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2.16
2.15
2.13
2.11
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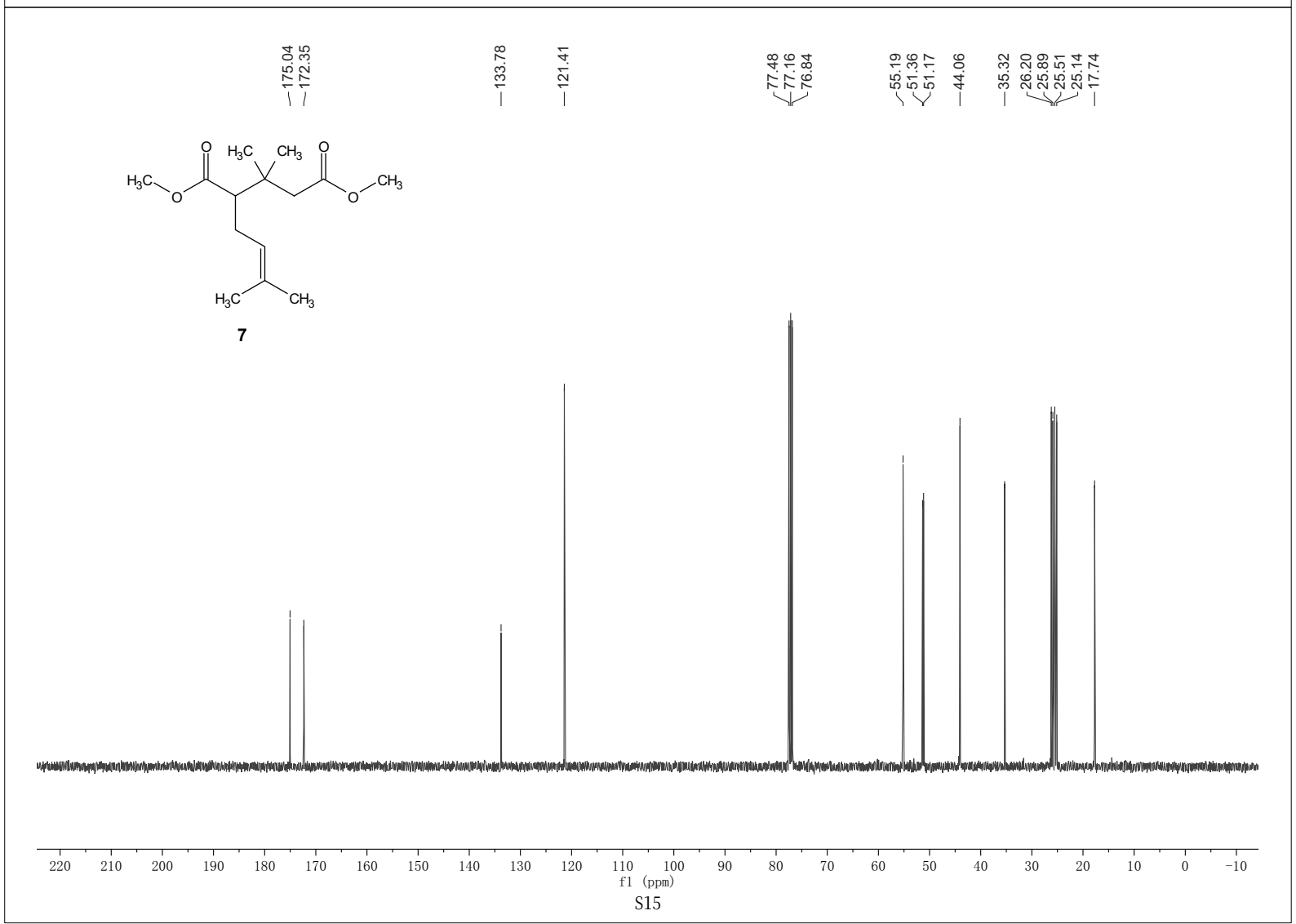
1.58
1.07
1.06
1.01
6.00
4.08
1.02
6.20
5.99
f1 (ppm)

7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25.51
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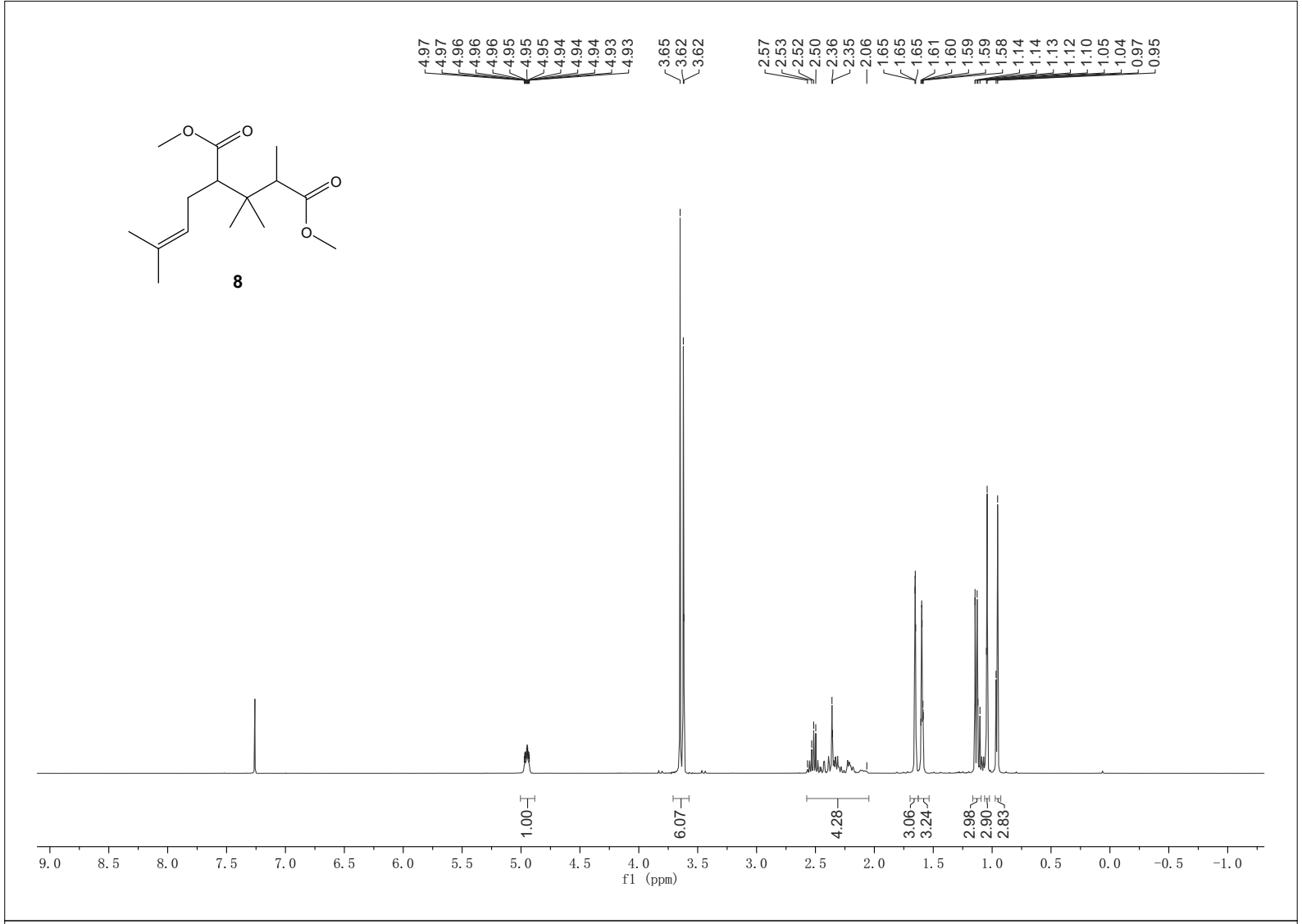
17.74
f1 (ppm)

7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2.57 2.53 2.52 2.50 2.36 2.35 2.06
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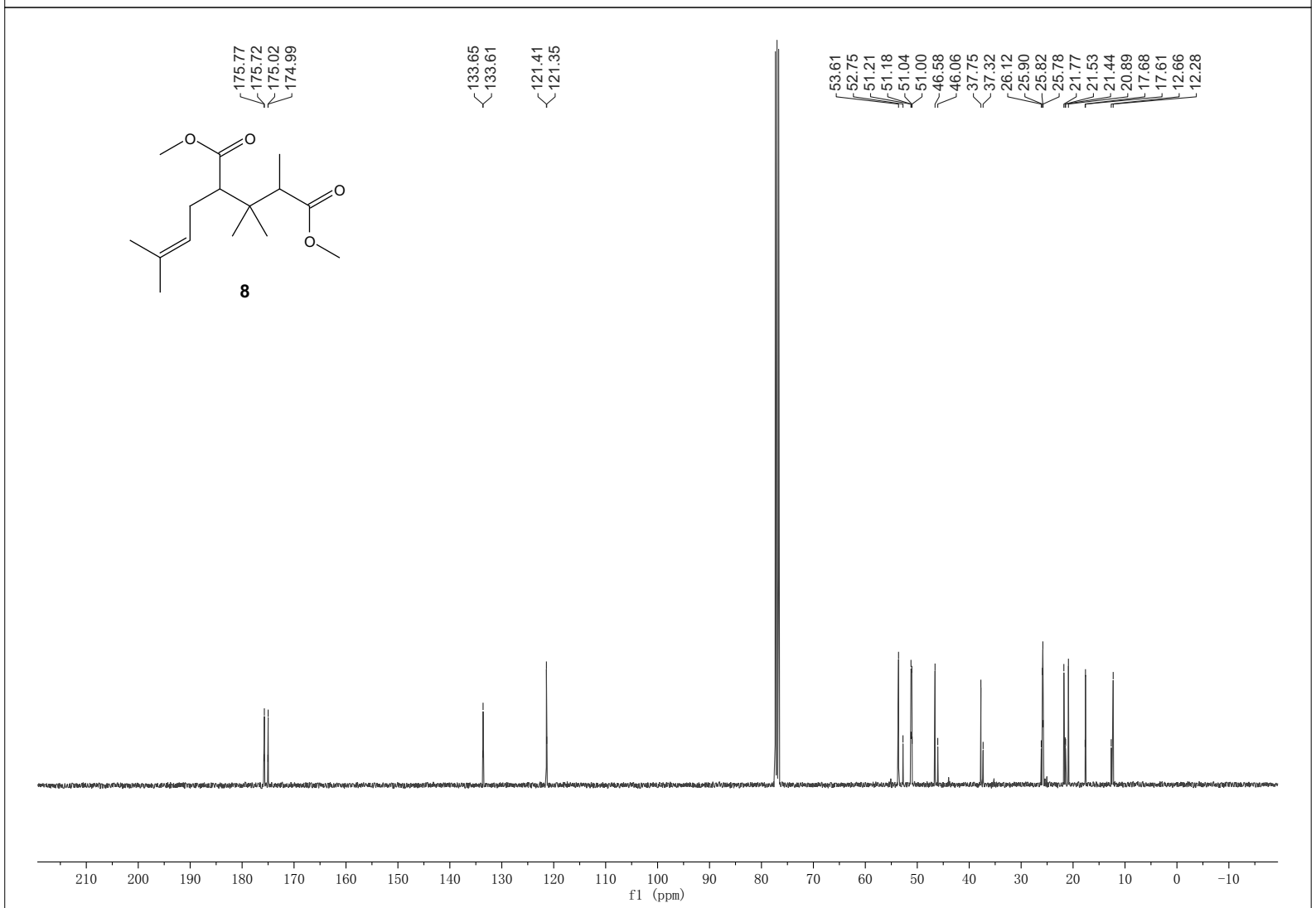
O
O
O
O
8
1.00
6.07
4.28
3.06
3.24
2.98
2.90
2.83
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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121.41 121.35
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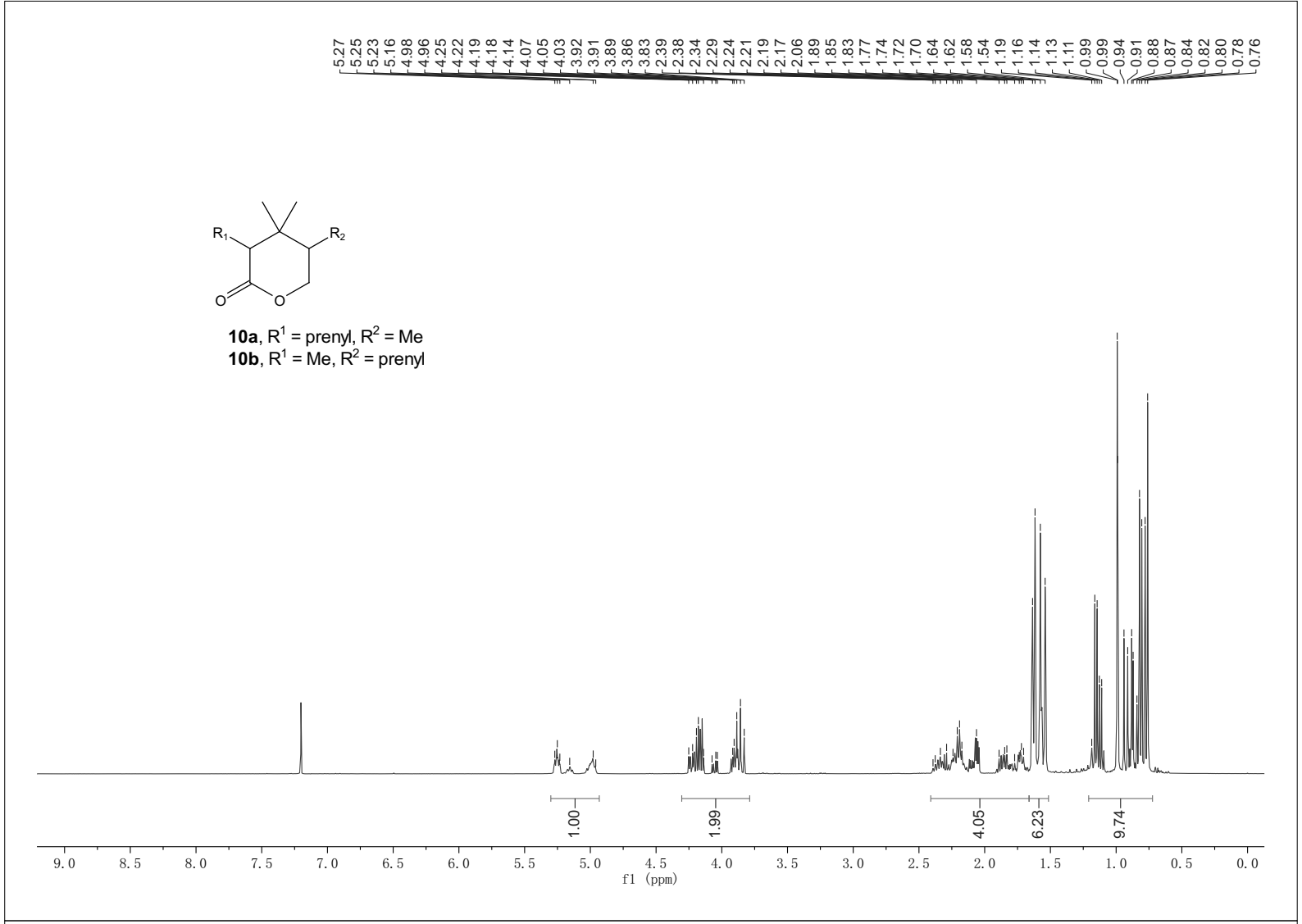
f1 (ppm)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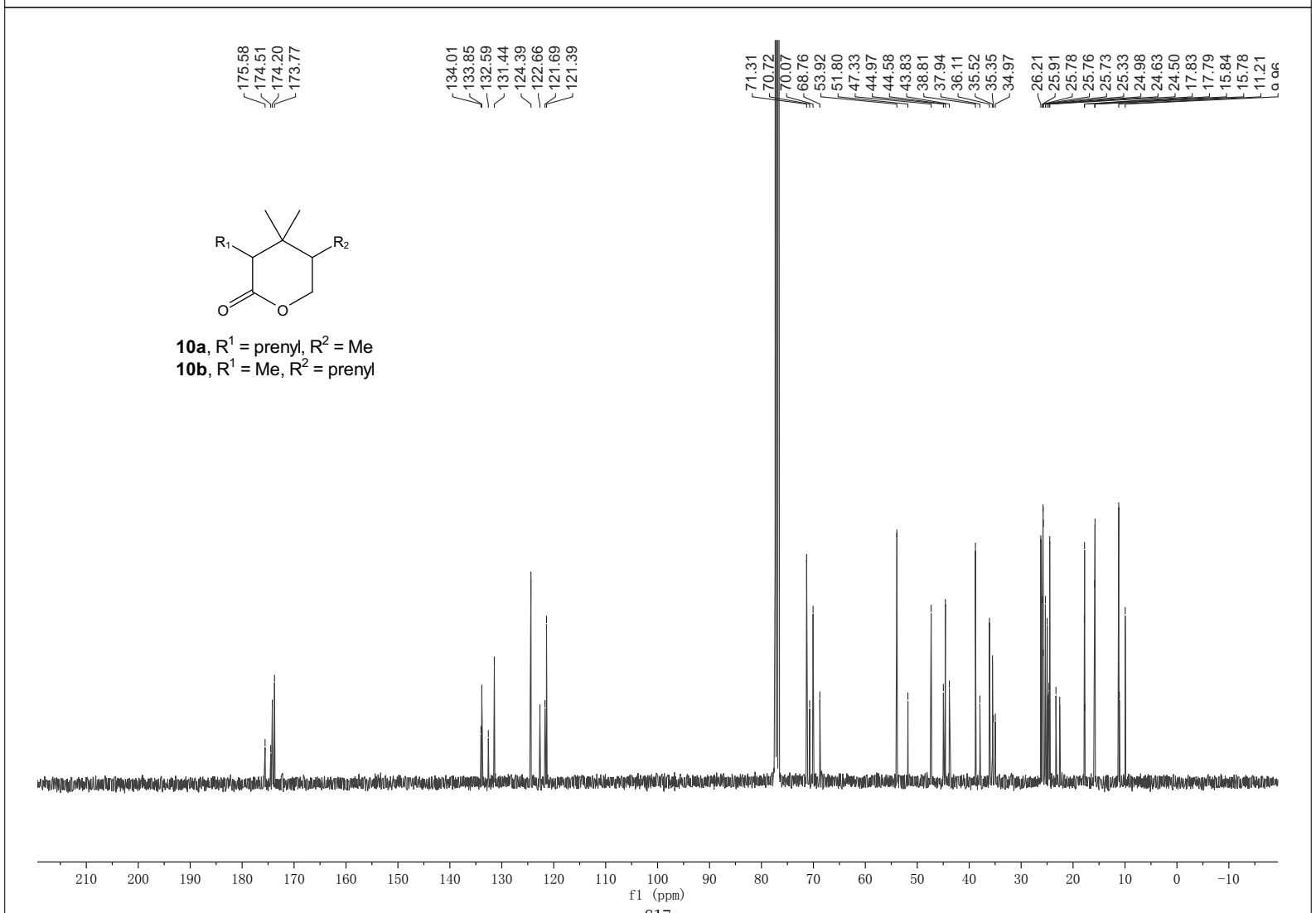
R1
R2
O
O
10a, R1 = prenyl, R2 = Me
10b, R1 = Me, R2 = prenyl
1.00
1.99
4.05
6.23
9.74
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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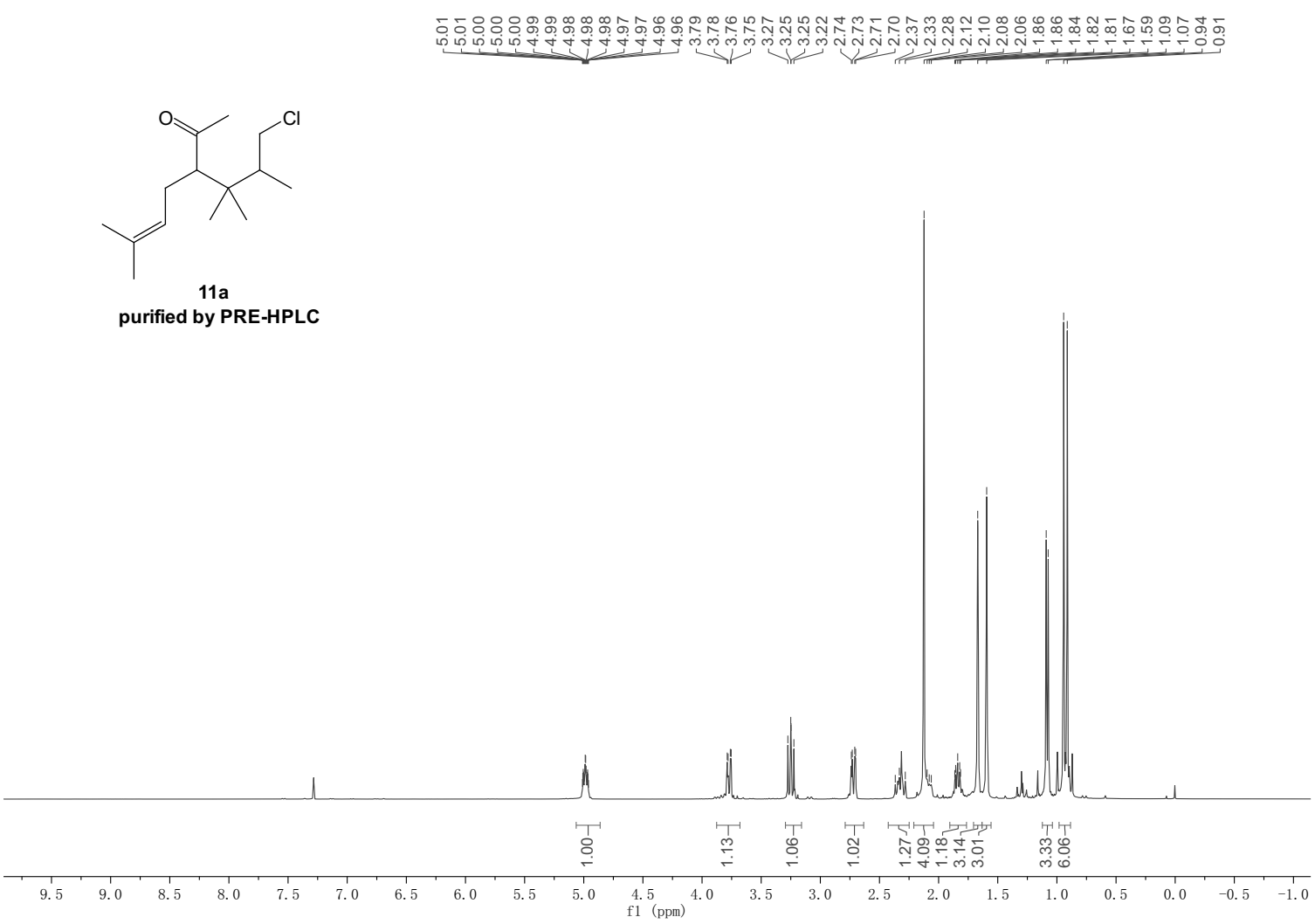
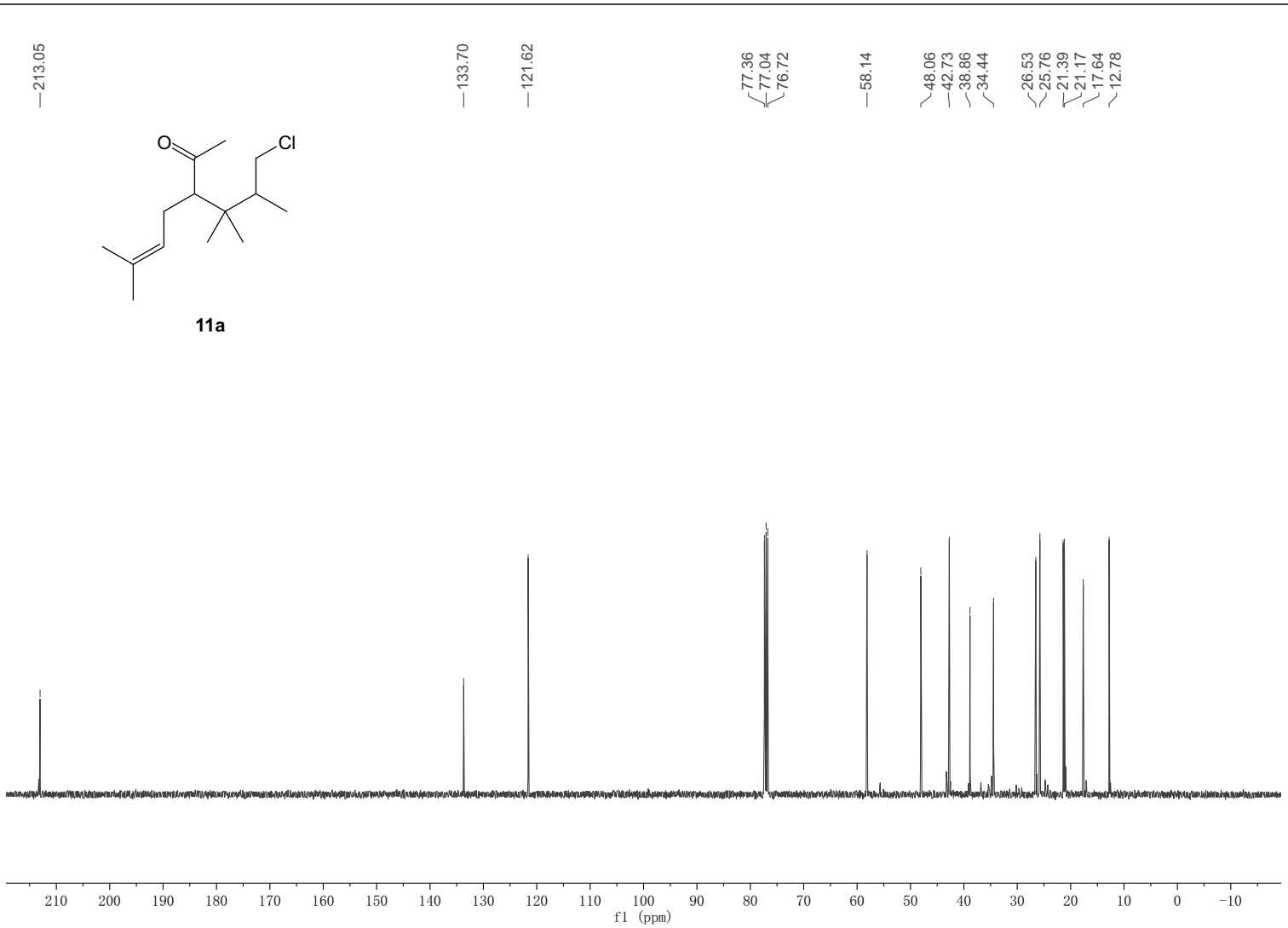
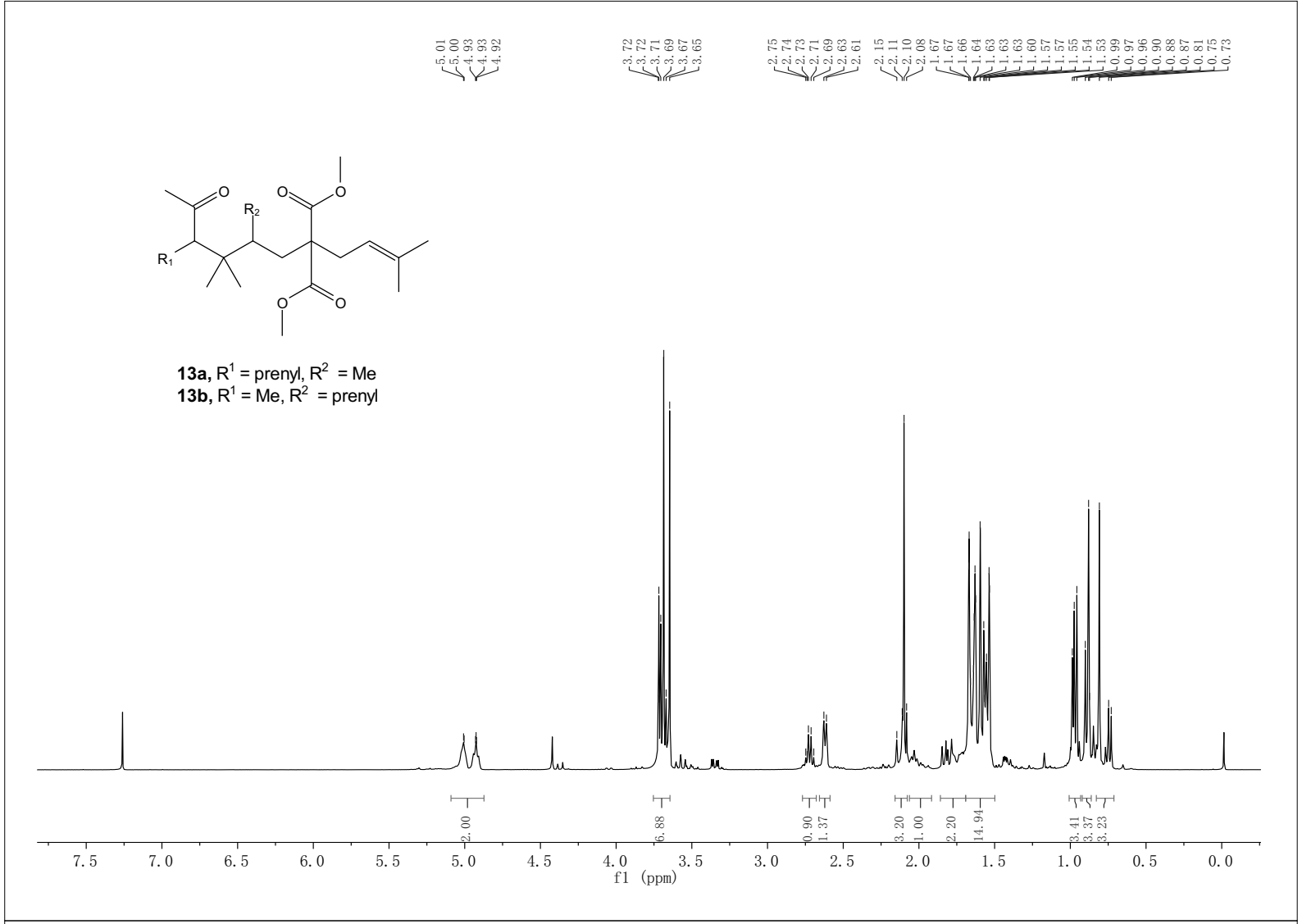
26.21 25.91 25.78 25.76 25.73 25.33 24.98 24.63 24.50 17.83 17.79 15.84 15.78 11.21
R1
R2
O
O
10a, R1 = prenyl, R2 = Me
10b, R1 = Me, R2 = prenyl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



11a
purified by PRE-HPLC



11a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1.63
1.63
1.63
1.60
1.57
1.57
1.55
1.54
1.53
0.99
0.97
0.96
0.90
0.88
0.87
0.81
0.75
0.73
O
O
O
R2
R1
O
O
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13b, R1 = Me, R2 = prenyl
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0.90
1.37
3.20
1.00
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3.37
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7.5
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6.0
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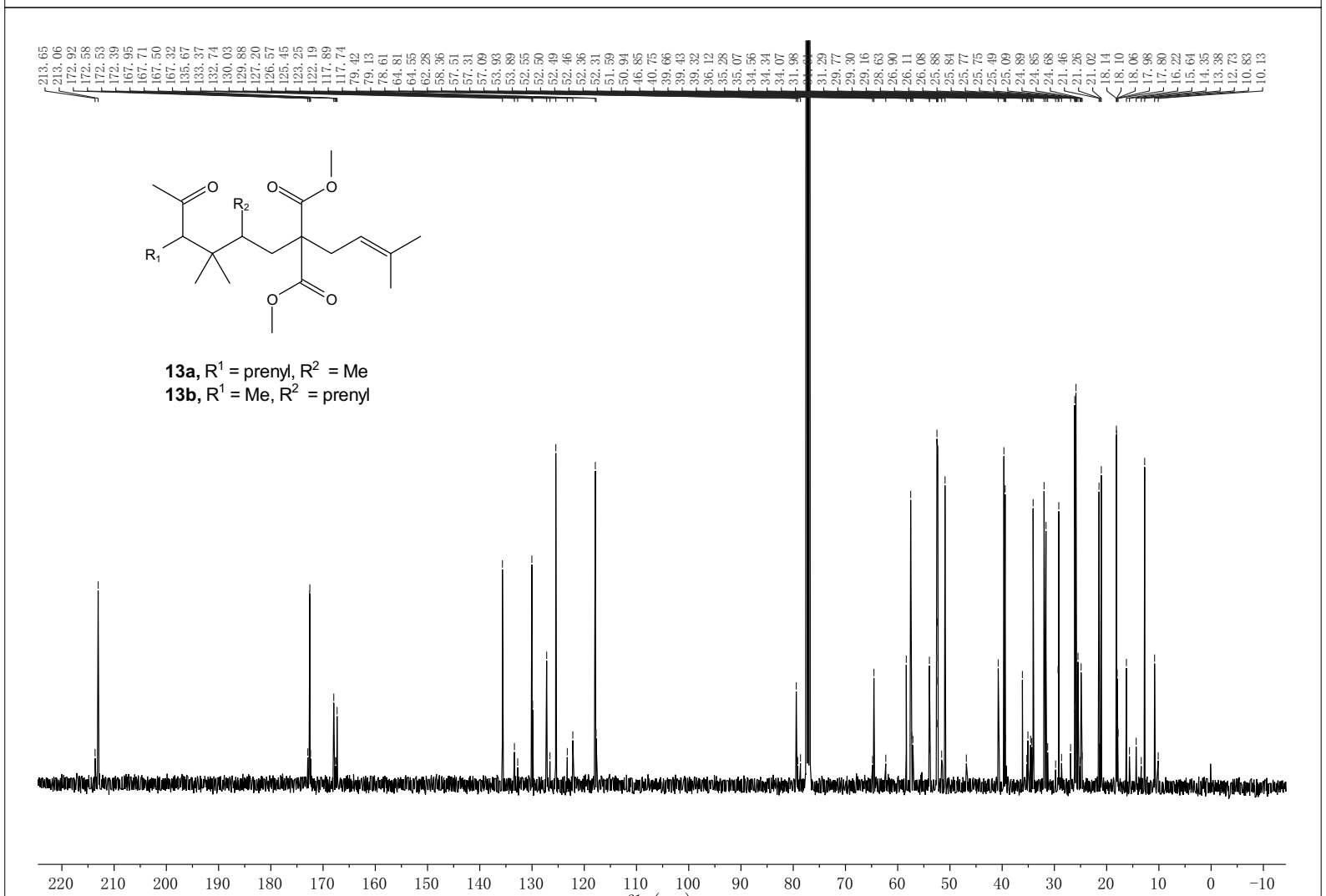
f1 (ppm)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130.03
129.88
127.20
126.57
125.45
123.25
122.19
117.89
117.74
79.42
79.13
78.61
64.81
64.55
62.28
58.36
57.51
57.31
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34.56
34.34
34.07
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31.29
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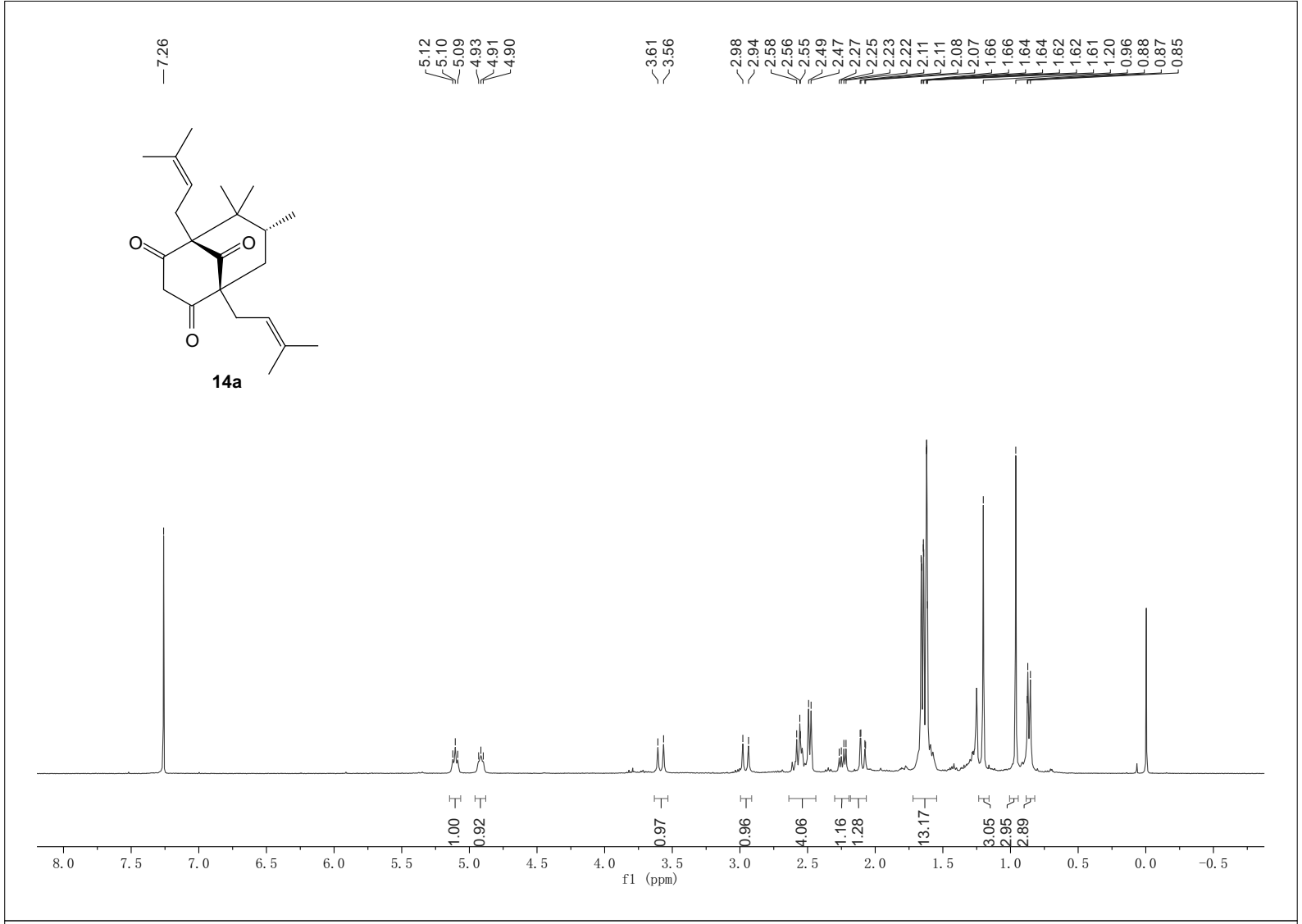
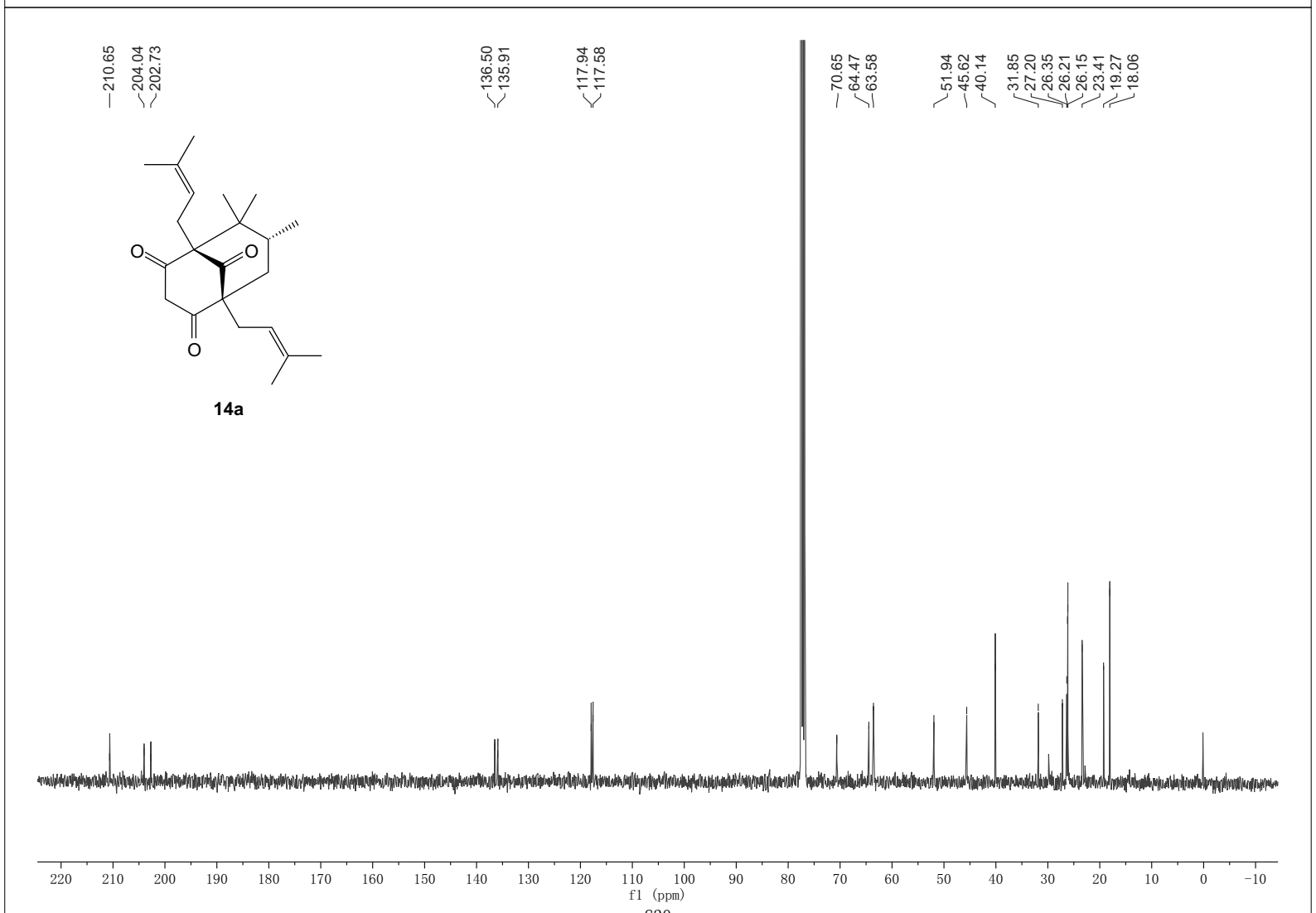
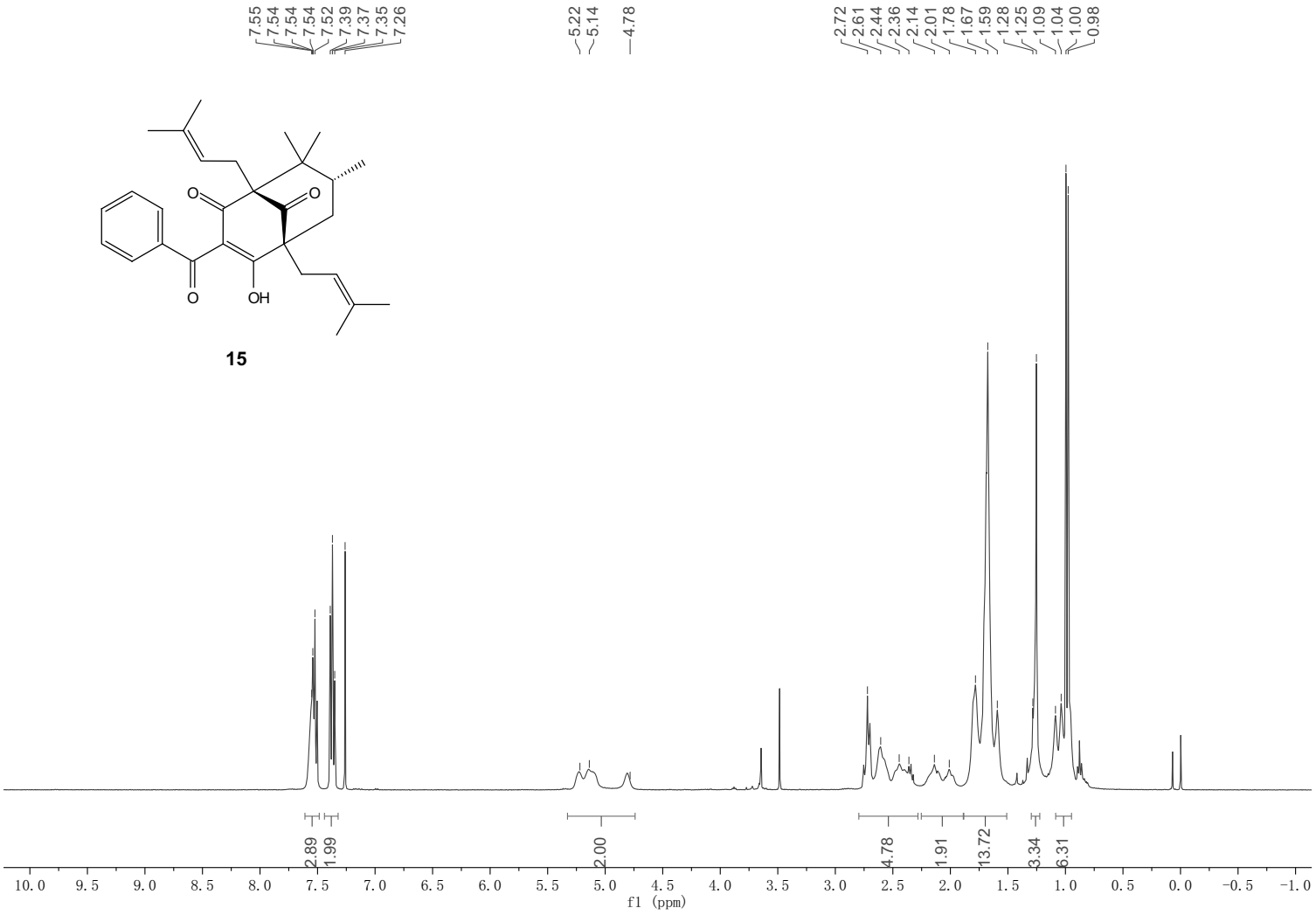
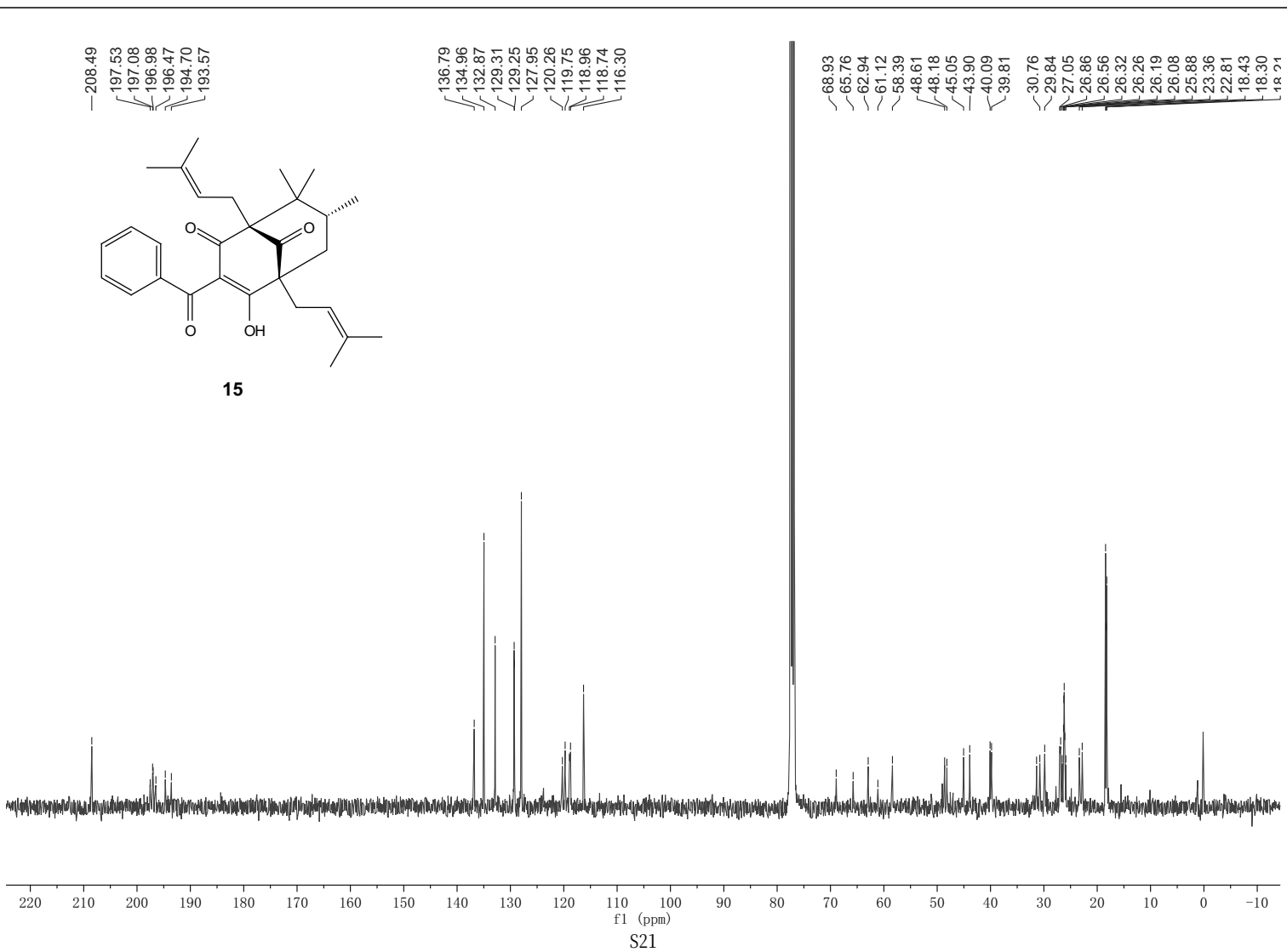
29.30
29.16
28.63
26.90
26.11
26.08
25.88
25.84
25.77
25.75
25.49
25.09
24.89
24.85
24.68
21.46
21.26
21.02
18.14
18.10
18.06
17.98
17.80
16.22
15.64
14.35
13.38
12.73
10.83
10.13
O
O
O
O
R2
R1
O
O
13a, R1 = prenyl, R2 = Me
13b, R1 = Me, R2 = prenyl
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.26
5.12
5.10
5.09
4.93
4.91
4.90
3.61
3.56
2.98
2.94
2.58
2.56
2.55
2.49
2.47
2.27
2.25
2.23
2.22
2.11
2.11
2.08
2.07
1.66
1.66
1.64
1.64
1.62
1.62
1.61
1.20
0.96
0.88
0.87
0.85
O
O
O
14a
1.00
0.92
0.97
0.96
4.06
1.16
1.28
13.17
3.05
2.95
2.89
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)

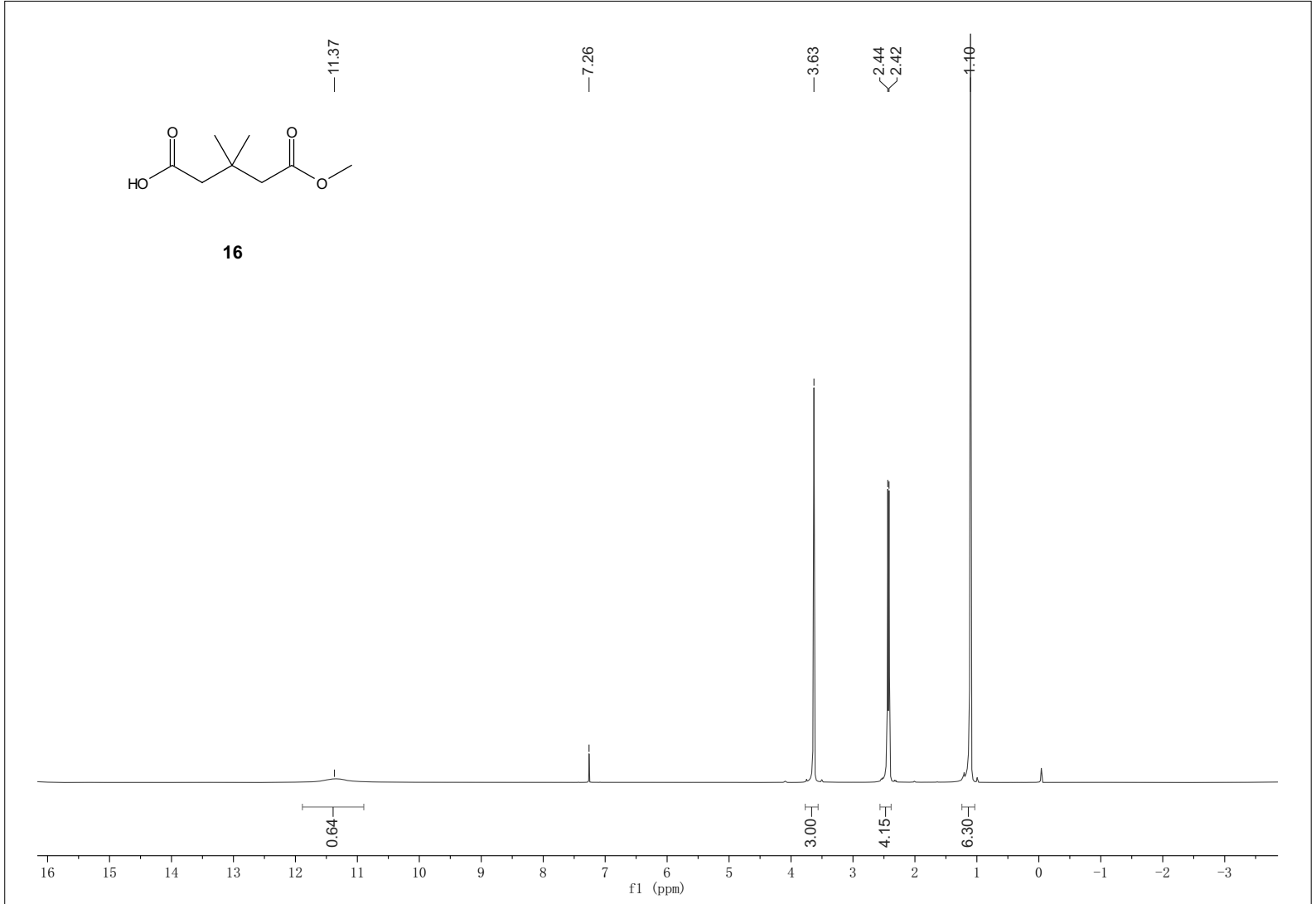

210.65
204.04
202.73
136.50
135.91
117.94
117.58
70.65
64.47
63.58
51.94
45.62
40.14
31.85
27.20
26.35
26.21
26.15
23.41
19.27
18.06
O
O
O
14a
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

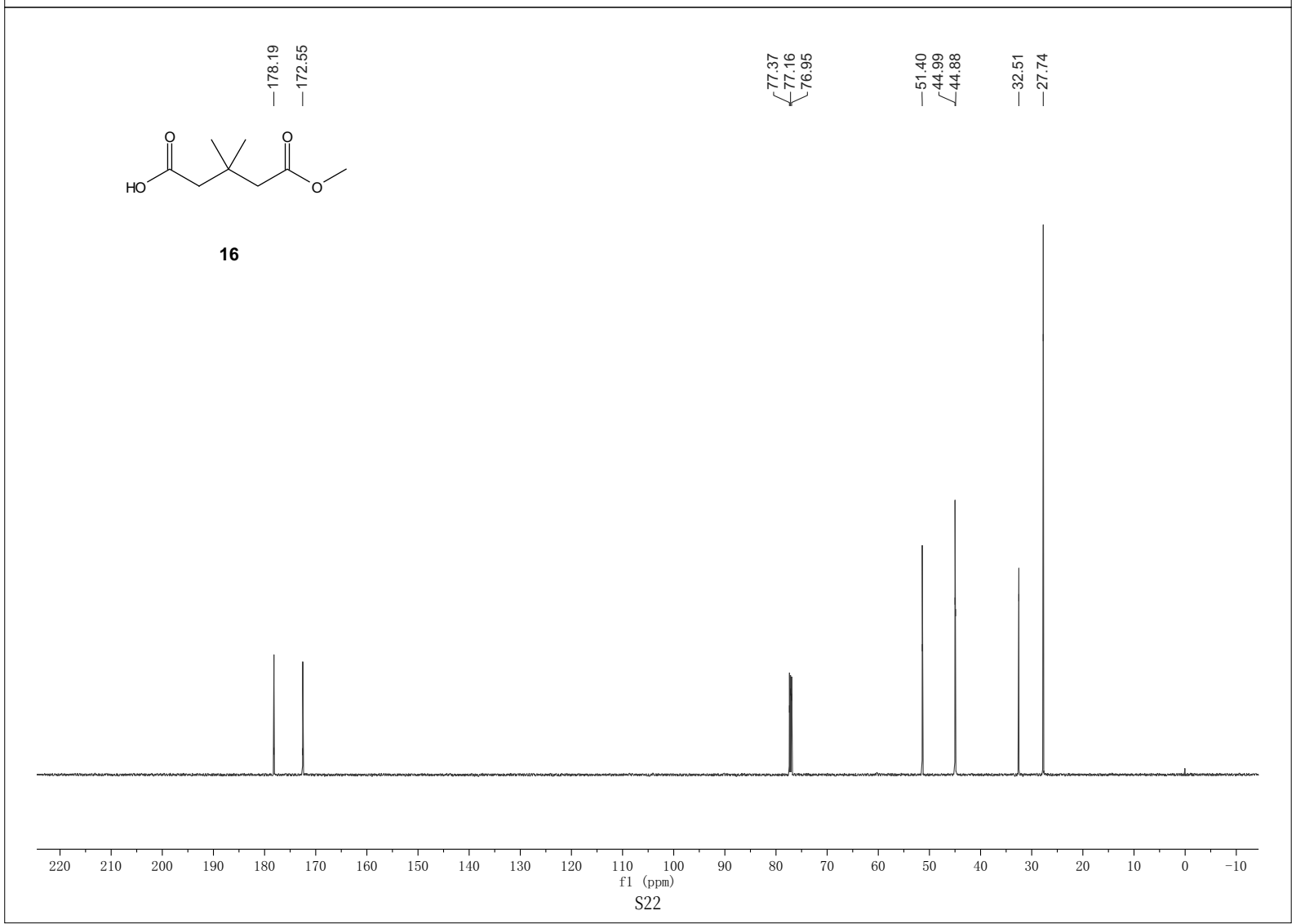

7.55
7.54
7.54
7.54
7.52
7.39
7.37
7.35
7.26
5.22
5.14
4.78
2.72
2.61
2.44
2.36
2.14
2.01
1.78
1.67
1.59
1.28
1.25
1.09
1.04
1.00
0.98
O
O
O
OH
2.89
1.99
2.00
4.78
1.91
13.72
3.34
6.31
f1 (ppm)

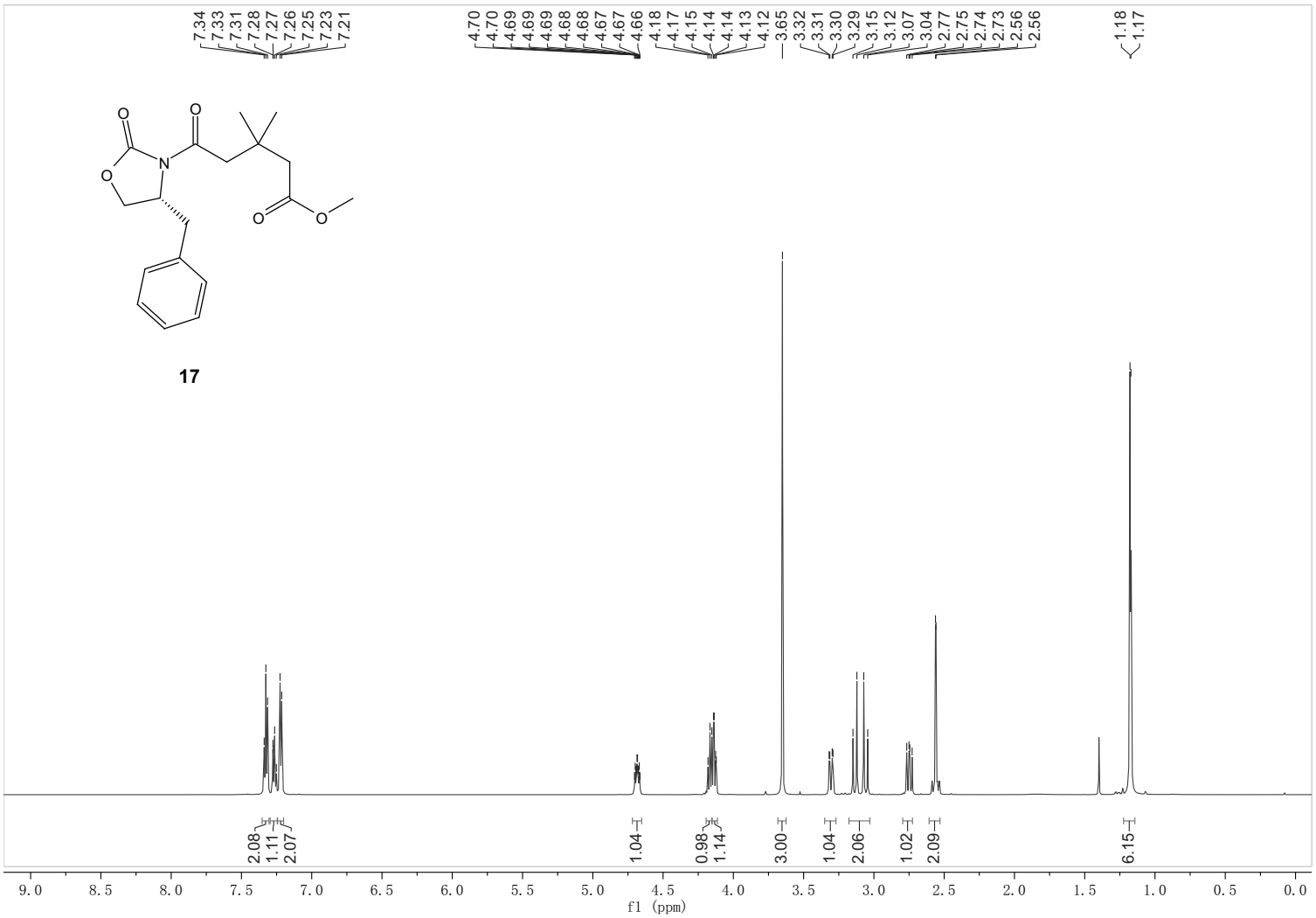
15

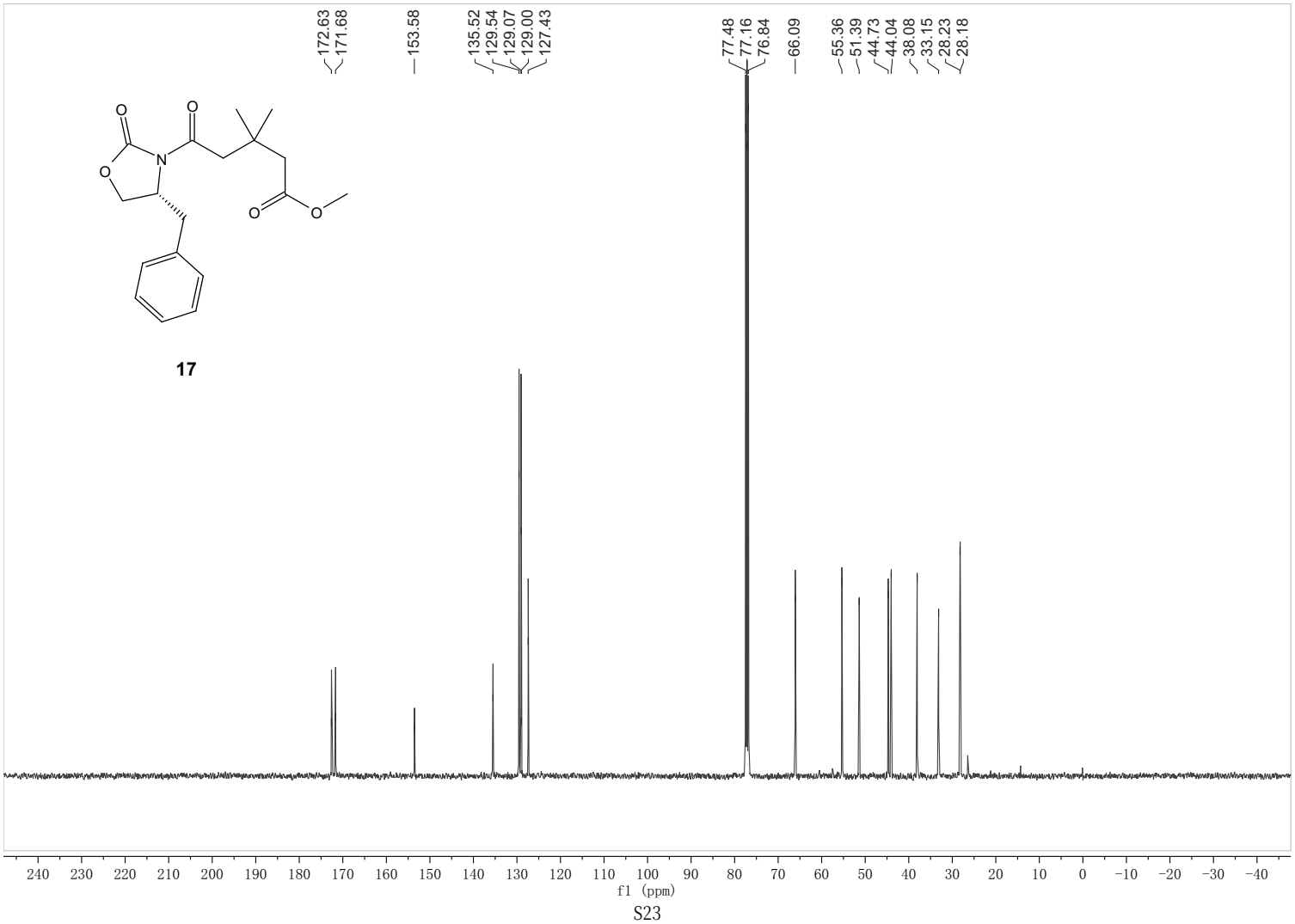

208.49
197.53
197.08
196.98
196.47
194.70
193.57
136.79
134.96
132.87
129.31
129.25
127.95
120.26
119.75
118.96
118.74
116.30
68.93
65.76
62.94
61.12
58.39
48.61
48.18
45.05
43.90
40.09
39.81
30.76
29.84
27.05
26.86
26.56
26.32
26.26
26.19
26.08
25.88
23.36
22.81
18.43
18.30
O
O
O
OH
f1 (ppm)

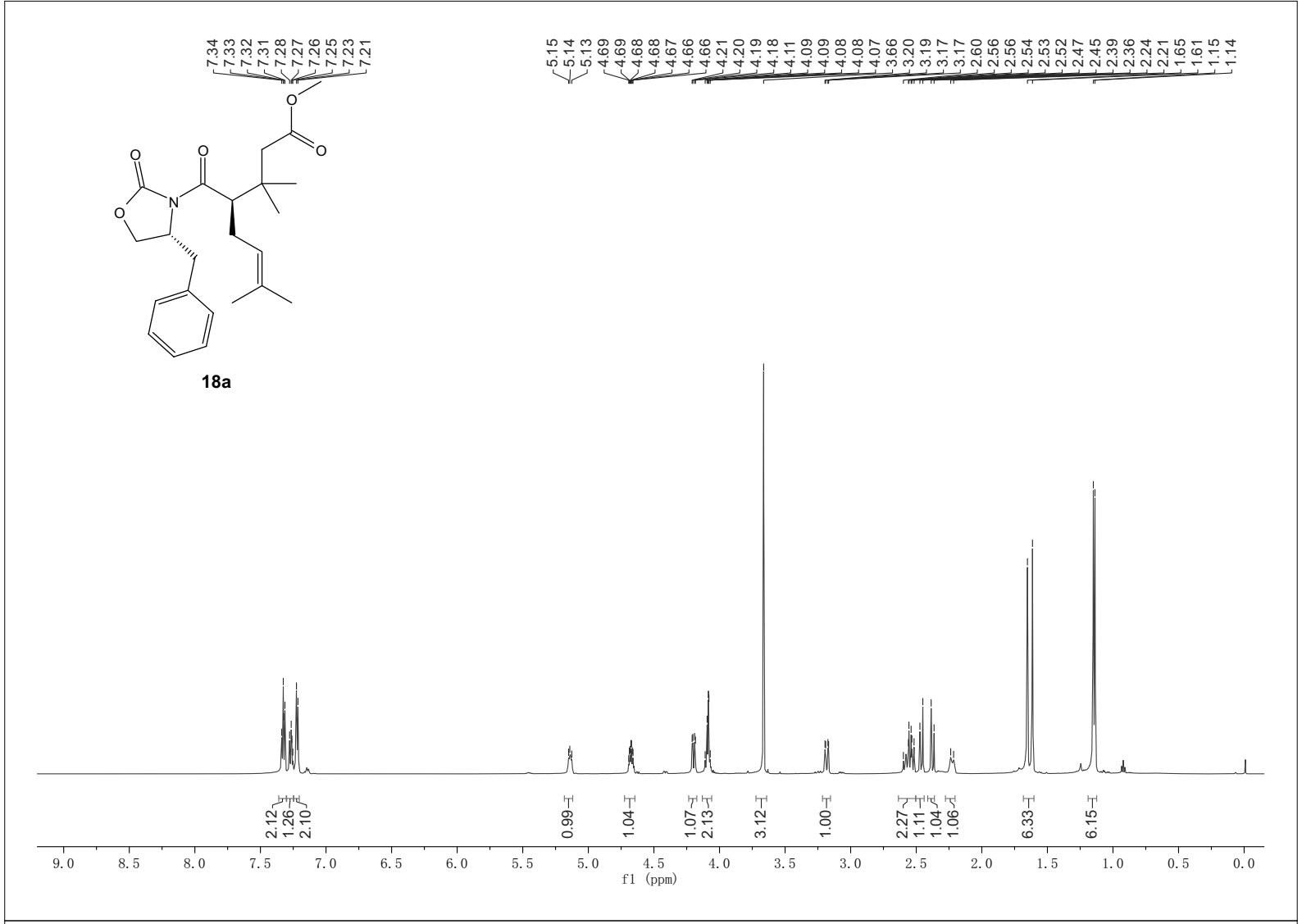
15

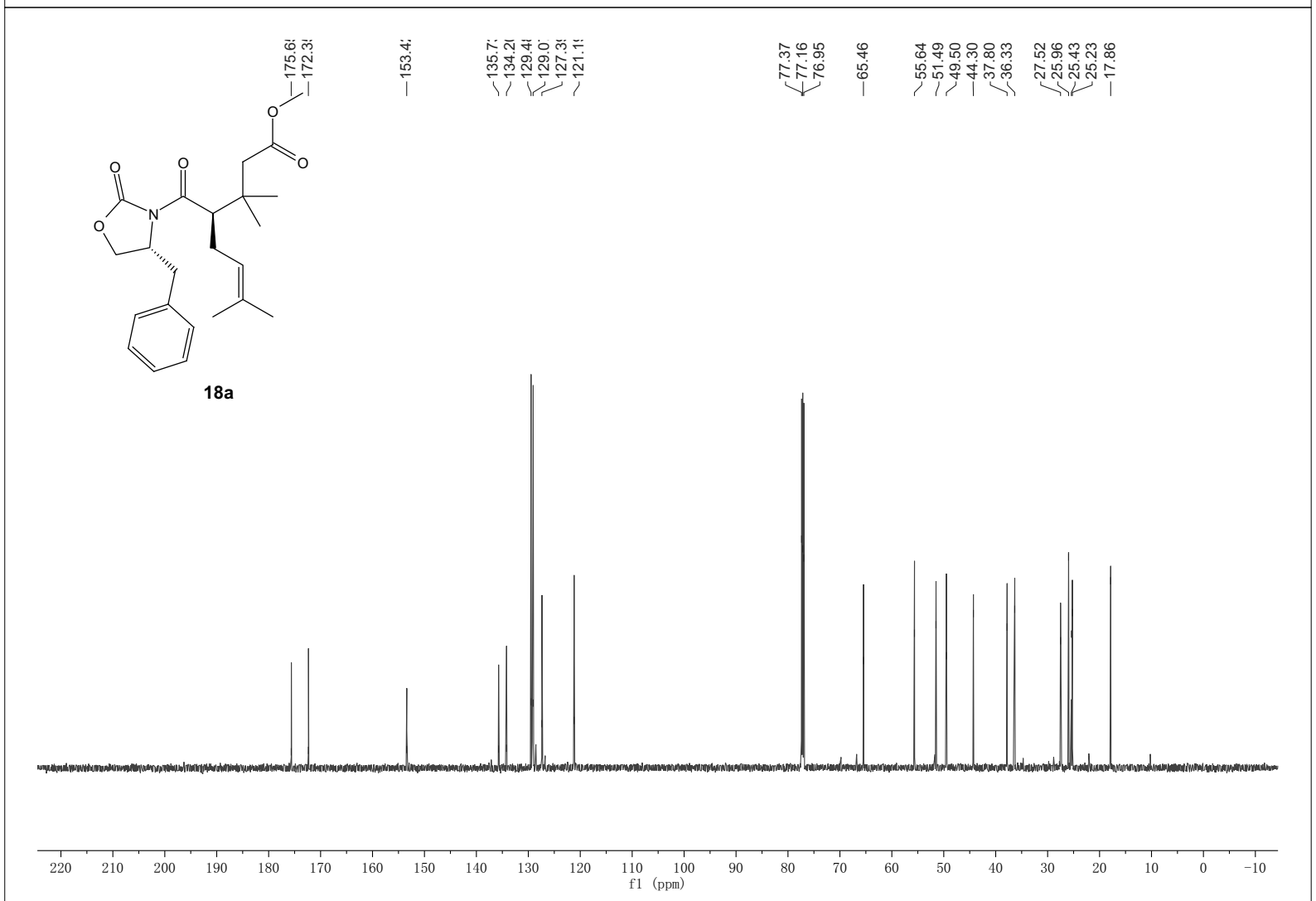

11.37
7.26
3.63
2.44
2.42
1.10
HO
O
O
O
16
0.64
3.00
4.15
6.30
f1 (ppm)

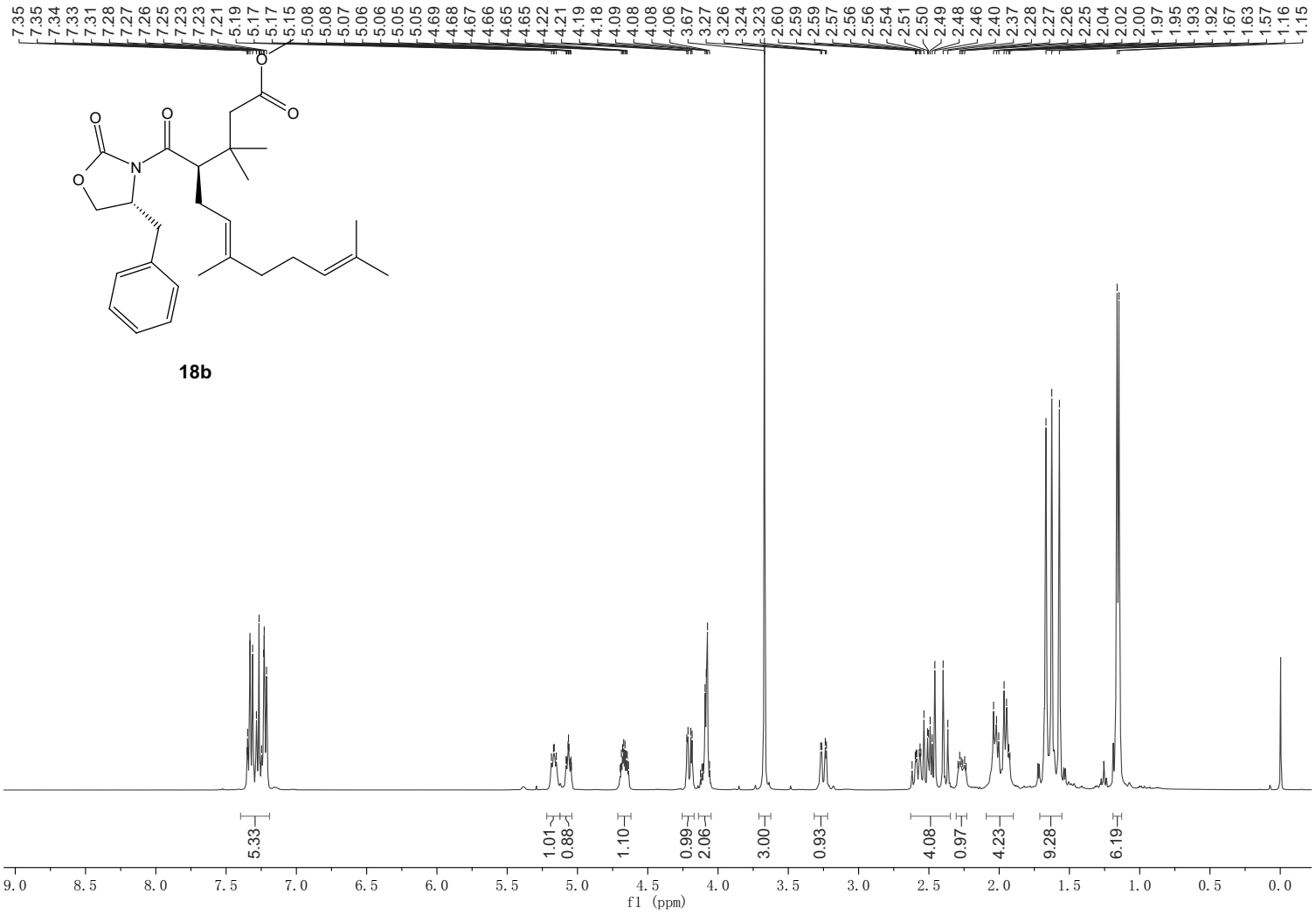

178.19
172.55
77.37
77.16
76.95
51.40
44.99
44.88
32.51
27.74
HO
O
O
O
16
f1 (ppm)


7.34
7.33
7.31
7.28
7.27
7.26
7.25
7.23
7.21
4.70
4.70
4.69
4.69
4.69
4.68
4.68
4.67
4.67
4.66
4.18
4.17
4.15
4.14
4.14
4.13
4.12
3.65
3.32
3.31
3.30
3.29
3.15
3.12
3.07
3.04
2.77
2.75
2.74
2.73
2.56
2.56
1.18
1.17
O
O
N
O
O
O
17
2.08
1.11
2.07
1.04
0.98
1.14
3.00
1.04
2.06
1.02
2.09
6.15
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)

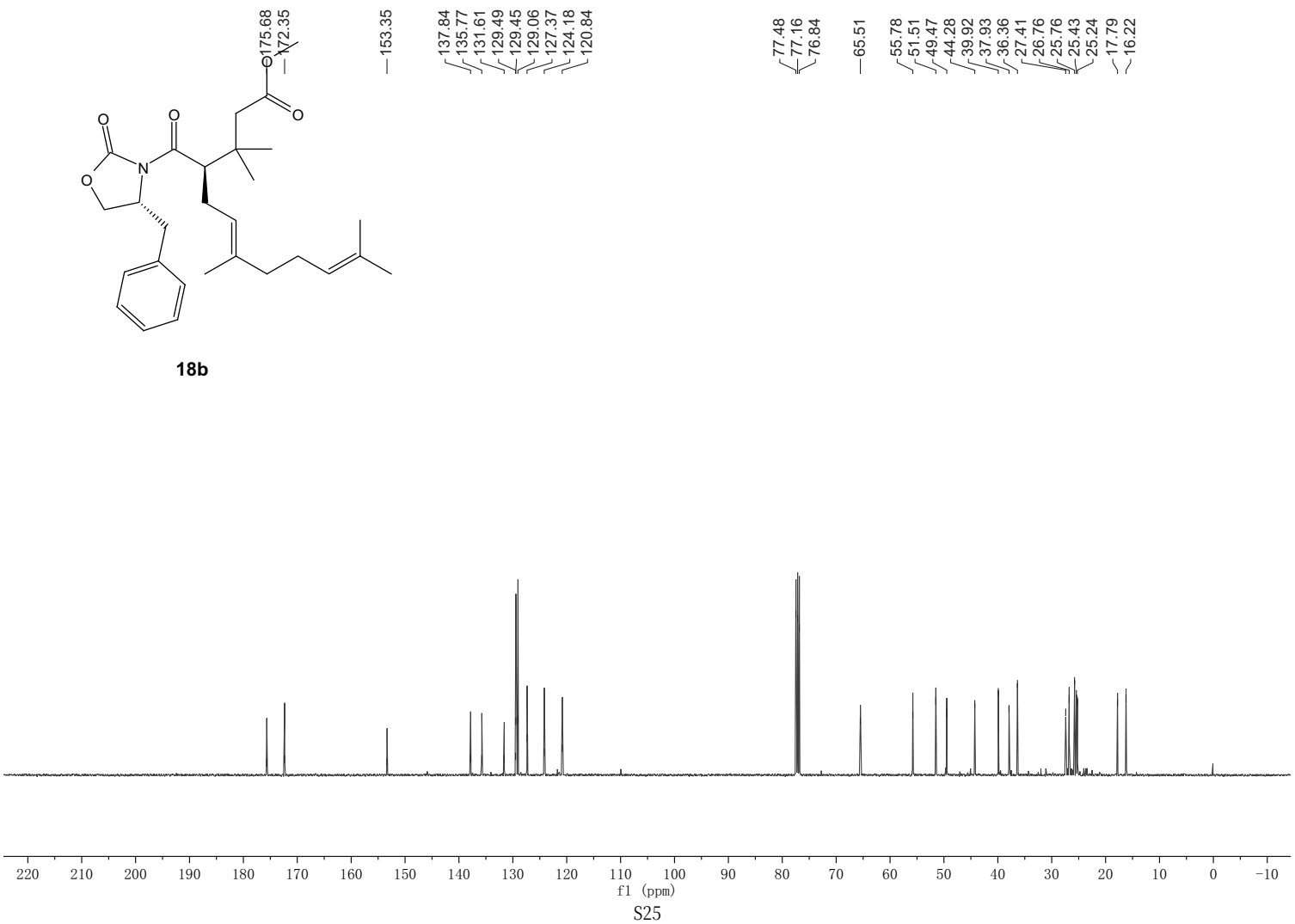

172.63
171.68
153.58
135.52
129.54
129.07
129.00
127.43
77.48
77.16
76.84
66.09
55.36
51.39
44.73
44.04
38.08
33.15
28.23
28.18
O
O
N
O
O
O
17
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)


7.34
7.33
7.32
7.31
7.28
7.27
7.26
7.25
7.23
7.21
5.15
5.14
5.13
4.69
4.69
4.68
4.68
4.67
4.66
4.66
4.21
4.20
4.19
4.18
4.11
4.09
4.09
4.08
4.08
4.07
3.66
3.20
3.19
3.17
3.17
2.60
2.56
2.56
2.54
2.53
2.52
2.47
2.45
2.39
2.36
2.24
2.21
1.65
1.61
1.15
1.14
O
O
O
O
N
O
18a
2.12
1.26
2.10
0.99
1.04
1.07
2.13
3.12
1.00
2.27
1.11
1.04
1.06
6.33
6.15
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)

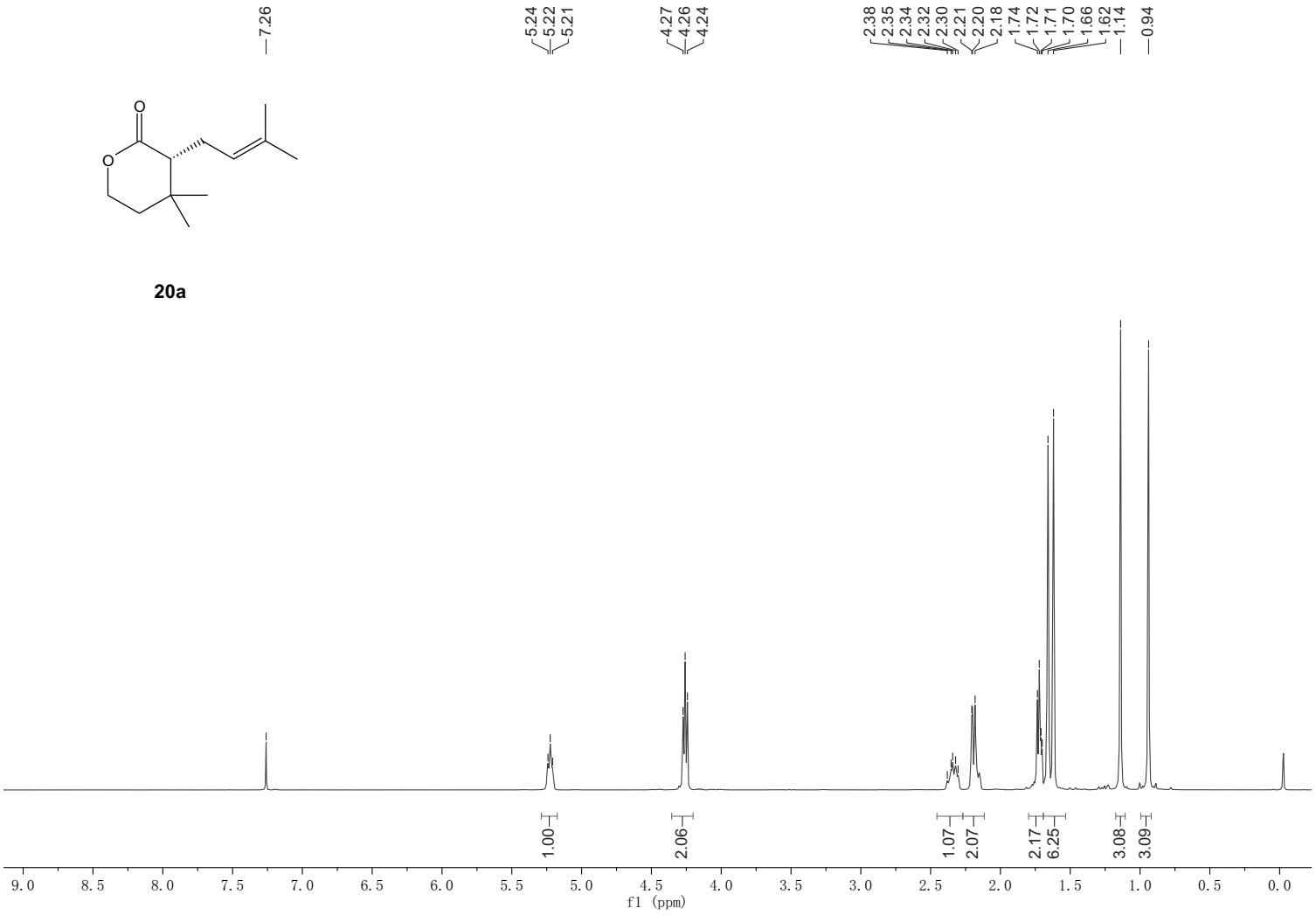

175.6
172.3
153.4
135.7
134.2
129.4
129.0
127.3
121.1
77.37
77.16
76.95
65.46
55.64
51.49
49.50
44.30
37.80
36.33
27.52
25.96
25.43
25.23
17.86
O
O
O
O
N
O
18a
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.35 7.35 7.34 7.33 7.31 7.28 7.27 7.26 7.25 7.23 7.23 7.21 5.19 5.17 5.17 5.15 5.08 5.08 5.07 5.06 5.05 5.05 4.69 4.68 4.67 4.66 4.65 4.65 4.22 4.21 4.19 4.18 4.09 4.08 4.08 4.06 3.67 3.27 3.26 3.24 3.23 2.60 2.59 2.59 2.57 2.56 2.56 2.54 2.51 2.50 2.49 2.48 2.46 2.40 2.37 2.28 2.27 2.26 2.25 2.04 2.02 2.00 1.97 1.95 1.93 1.92 1.67 1.63 1.57 1.16 1.15
5.33 1.01 0.88 1.10 0.99 2.06 3.00 0.93 4.08 0.97 4.23 9.28 6.19
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
f1 (ppm)

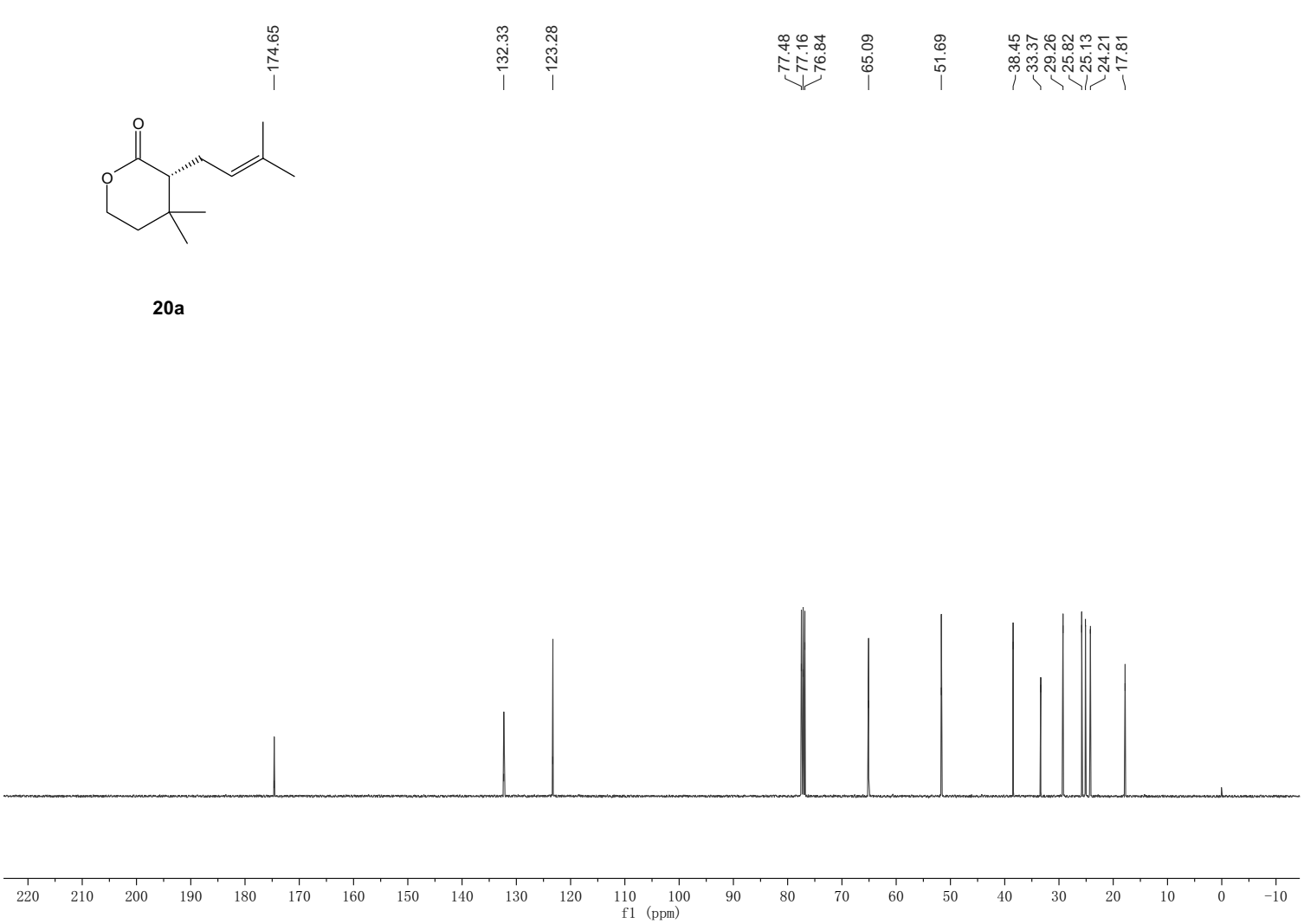
18b


175.68 172.35 153.35 137.84 135.77 131.61 129.49 129.45 129.06 127.37 124.18 120.84 77.48 77.16 76.84 65.51 55.78 51.51 49.47 44.28 39.92 37.93 36.36 27.41 26.76 25.76 25.43 25.24 17.79 16.22
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)

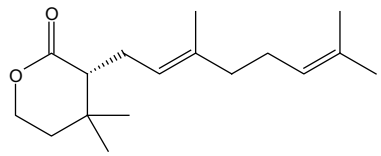
18b


7.26
5.24
5.22
5.21
4.27
4.26
4.24
2.38
2.35
2.34
2.32
2.30
2.21
2.20
2.18
1.74
1.72
1.71
1.70
1.66
1.62
1.14
0.94
O
O
1.00
2.06
1.07
2.07
2.17
6.25
3.08
3.09
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)

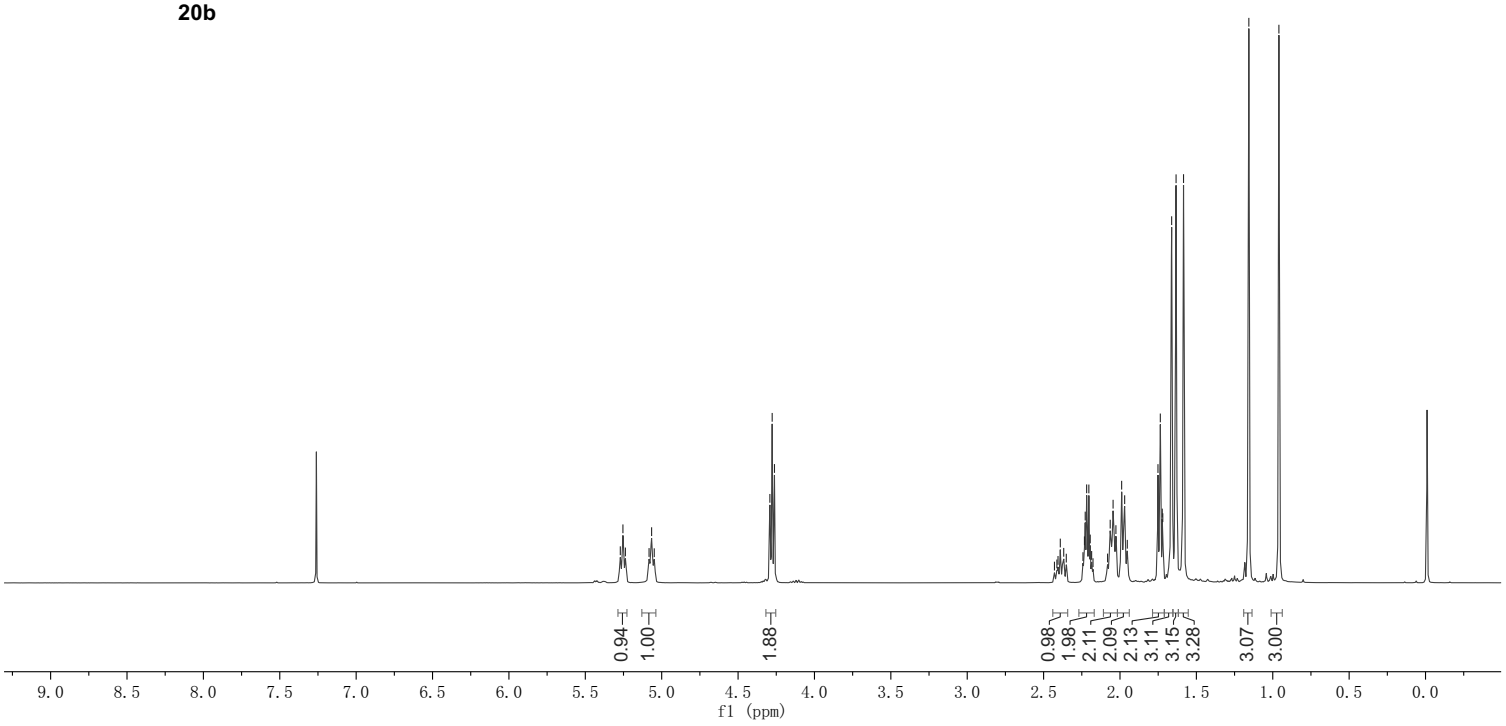
20a

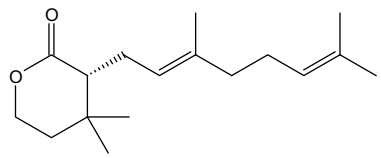

174.65
132.33
123.28
77.48
77.16
76.84
65.09
51.69
38.45
33.37
29.26
25.82
25.13
24.21
17.81
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

20a



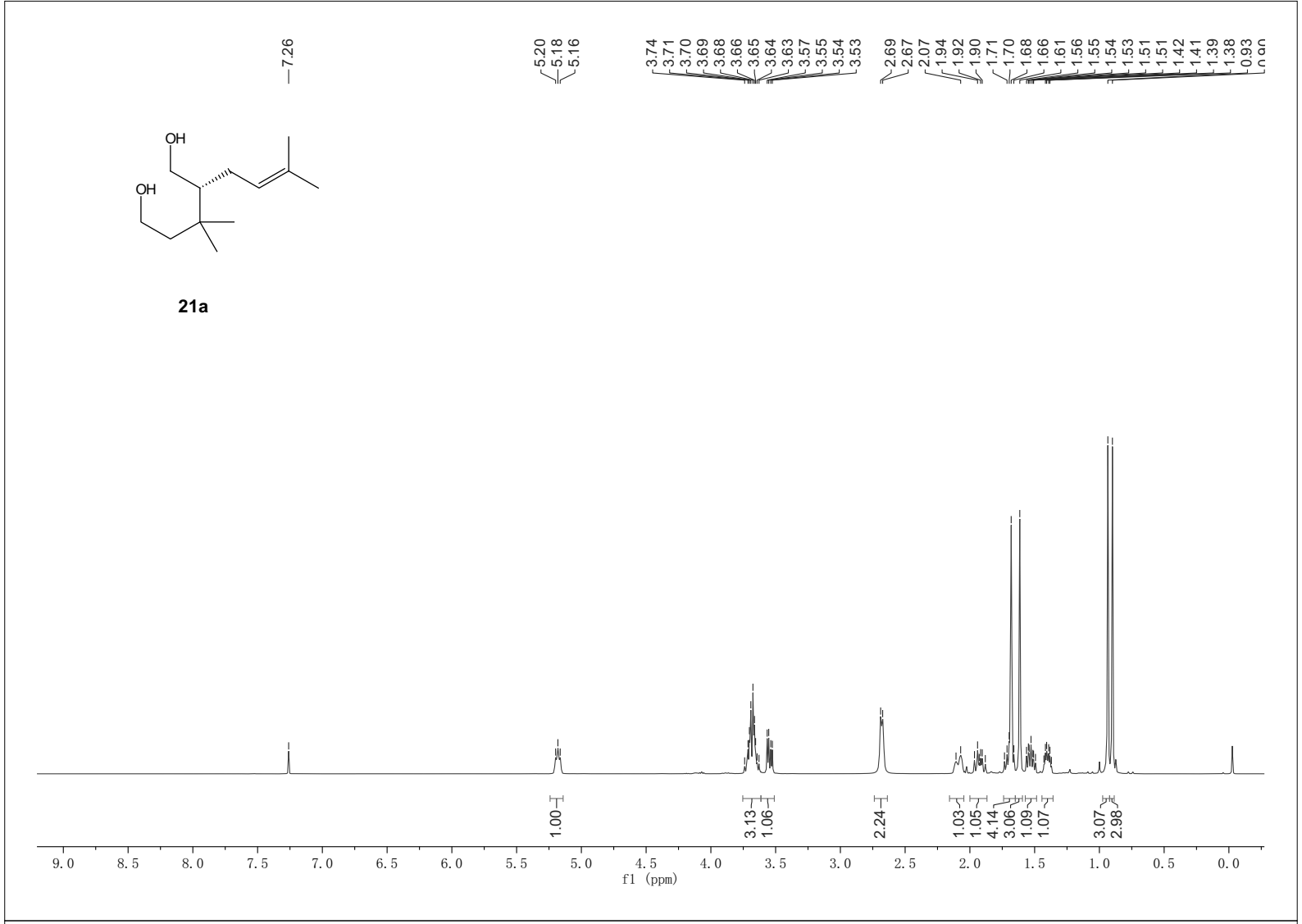
20b


5.27
5.25
5.24
5.08
5.07
5.05
4.29
4.28
4.26
2.43
2.41
2.41
2.39
2.37
2.35
2.24
2.23
2.23
2.22
2.20
2.19
2.19
2.18
2.08
2.06
2.05
2.03
1.99
1.97
1.95
1.75
1.74
1.72
1.72
1.66
1.63
1.58
1.16
0.96
0.94
1.00
1.88
0.98
1.98
2.11
2.09
2.13
3.11
3.15
3.28
3.07
3.00
f1 (ppm)

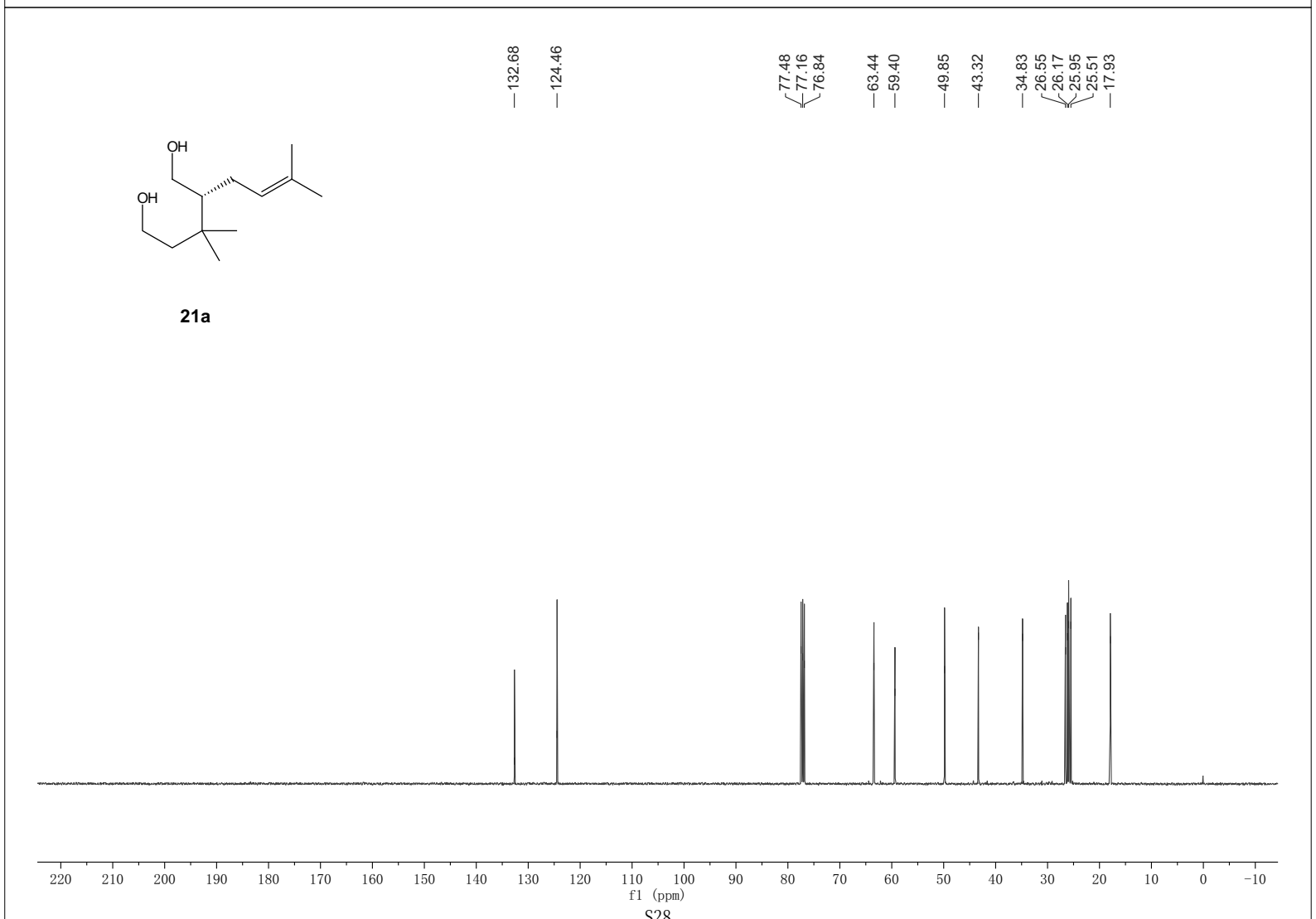


20b

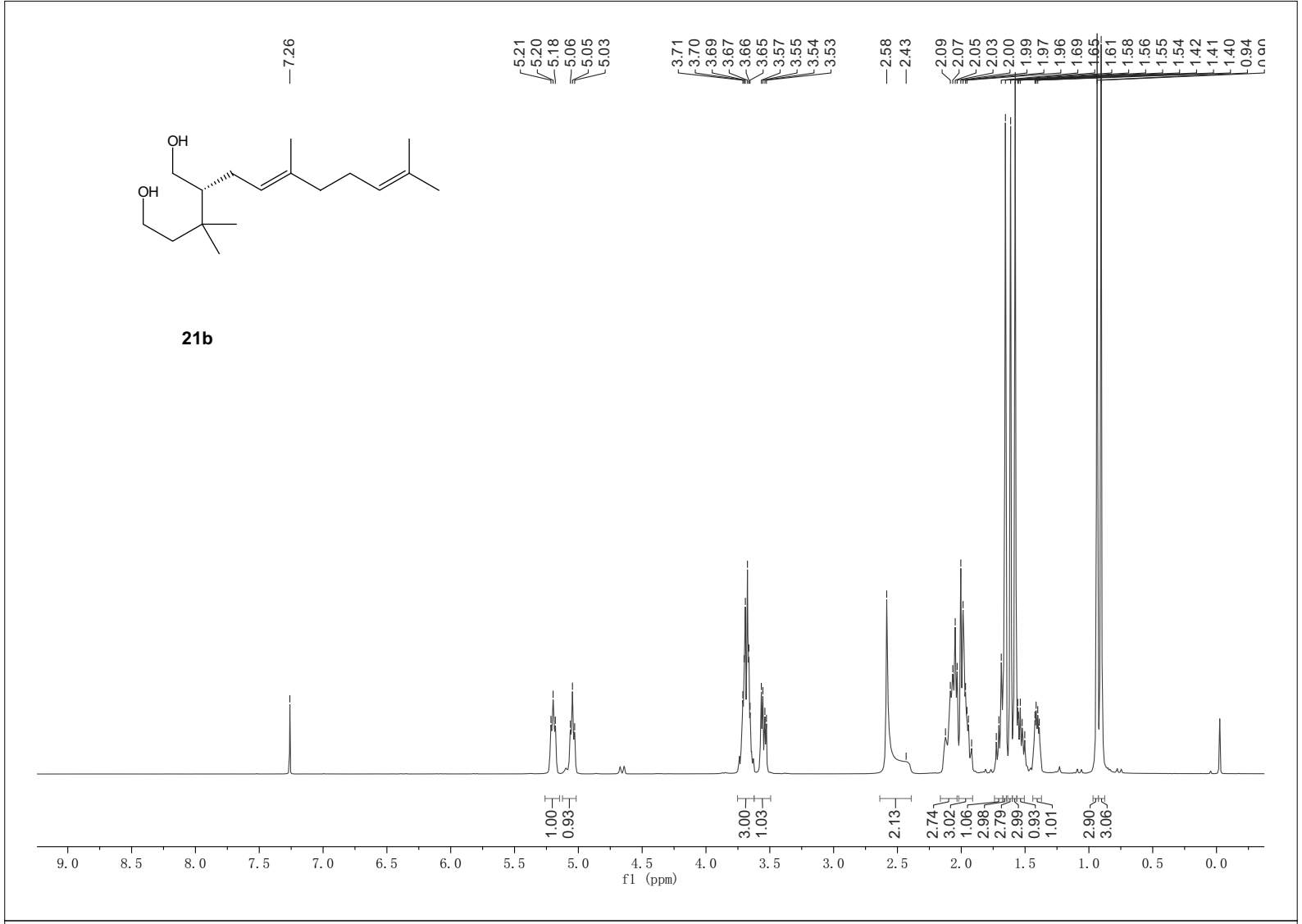
174.64
135.94
131.48
124.40
123.27
77.48
77.16
76.84
65.14
51.77
39.84
38.53
33.44
29.38
26.71
25.82
25.17
24.27
17.81
16.21
f1 (ppm)


7.26
5.20
5.18
5.16
3.74
3.71
3.70
3.69
3.68
3.66
3.65
3.64
3.63
3.57
3.55
3.54
3.53
2.69
2.67
2.07
1.94
1.92
1.90
1.71
1.70
1.68
1.66
1.61
1.56
1.55
1.54
1.53
1.51
1.51
1.42
1.41
1.39
1.38
0.93
OH
OH
1.00
3.13
1.06
2.24
1.03
1.05
4.14
3.06
1.09
1.07
3.07
2.98
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)

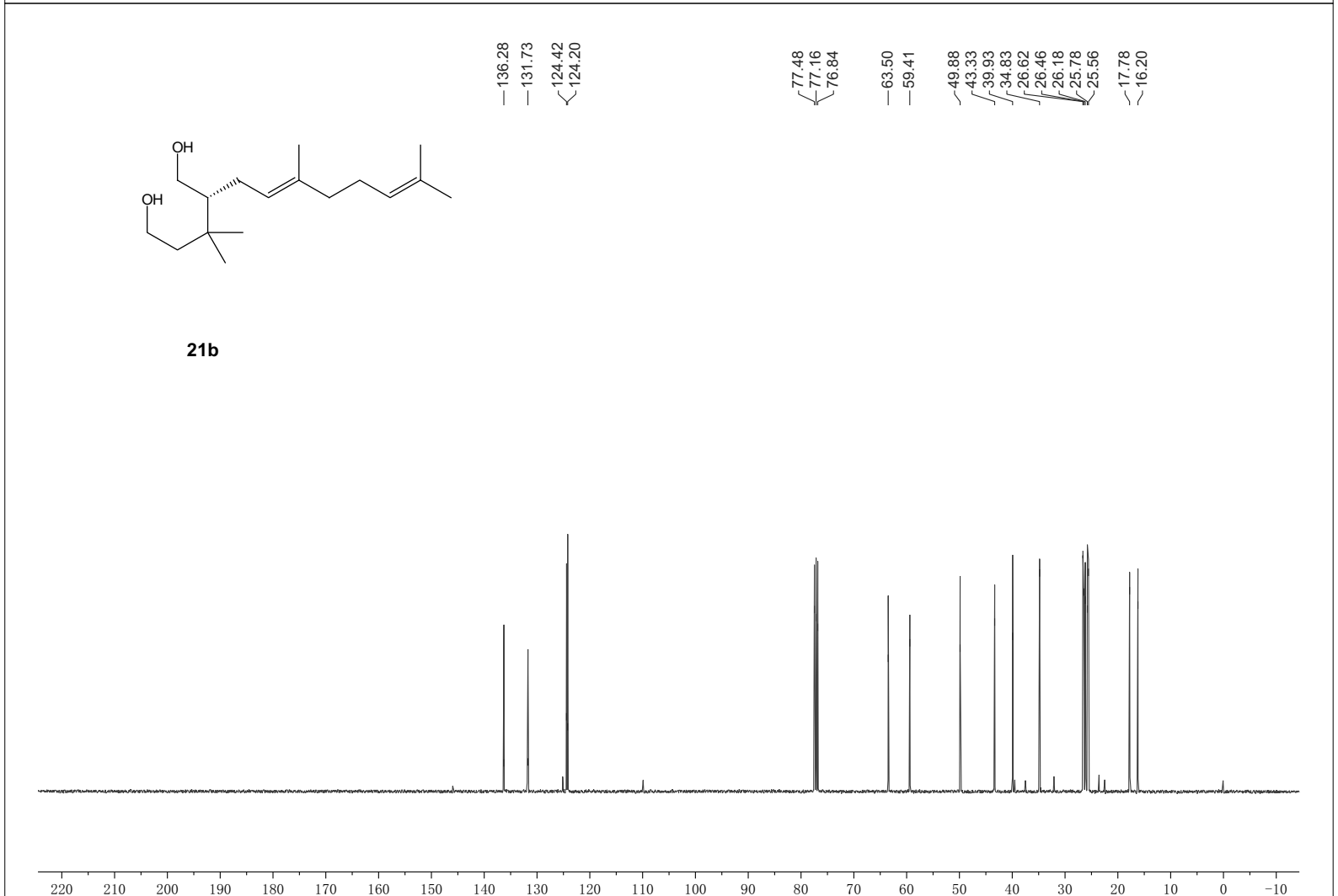
21a


132.68
124.46
77.48
77.16
76.84
63.44
59.40
49.85
43.32
34.83
26.55
26.17
25.95
25.51
17.93
OH
OH
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)

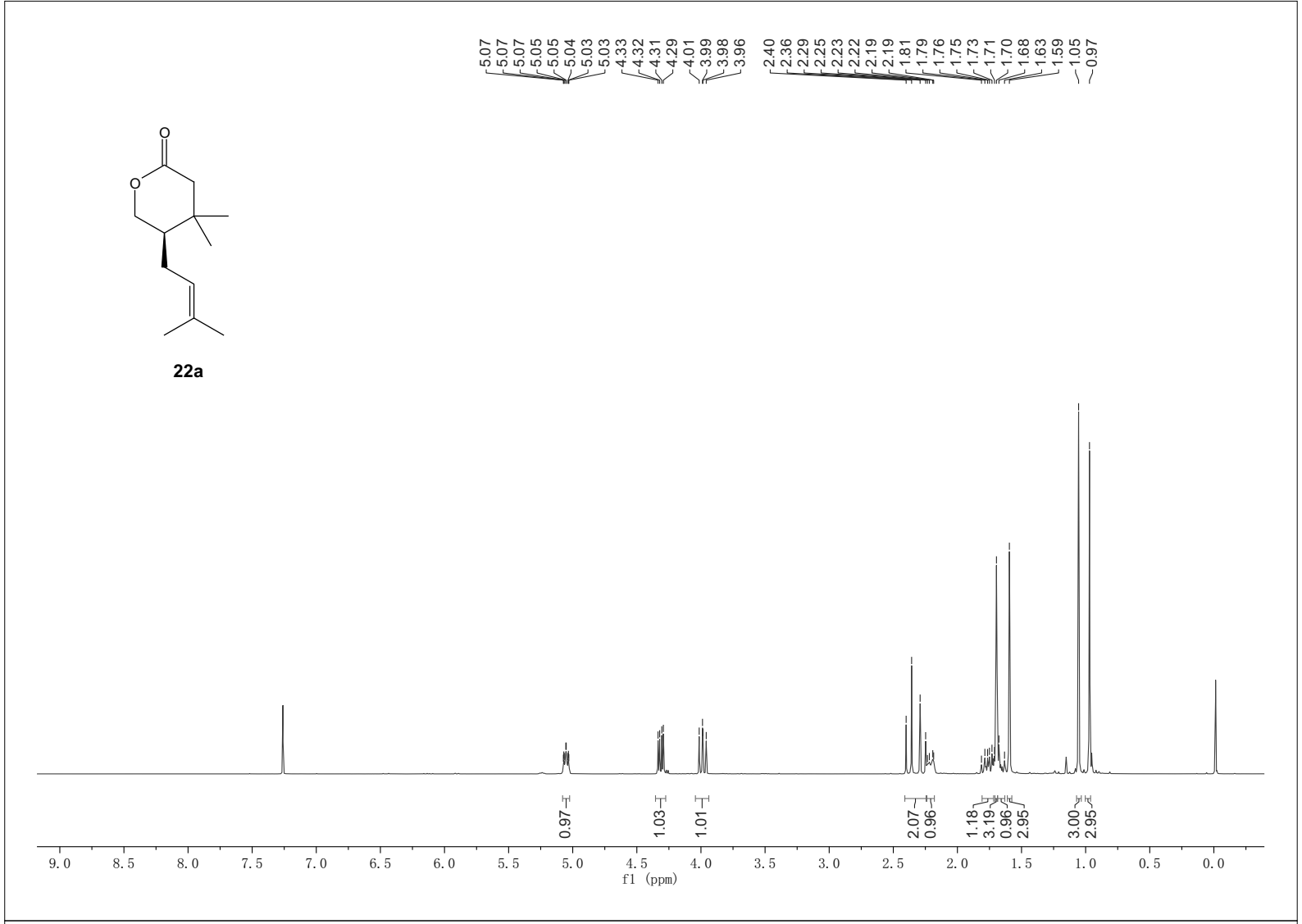
21a


7.26
5.21
5.20
5.18
5.06
5.05
5.03
3.71
3.70
3.69
3.67
3.66
3.65
3.57
3.55
3.54
3.53
2.58
2.43
2.09
2.07
2.05
2.03
2.00
1.99
1.97
1.96
1.69
1.65
1.61
1.58
1.56
1.55
1.54
1.42
1.41
1.40
0.94
OH
OH
1.00
0.93
3.00
1.03
2.13
2.74
3.02
1.06
2.98
2.79
2.99
0.93
1.01
2.90
3.06
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)

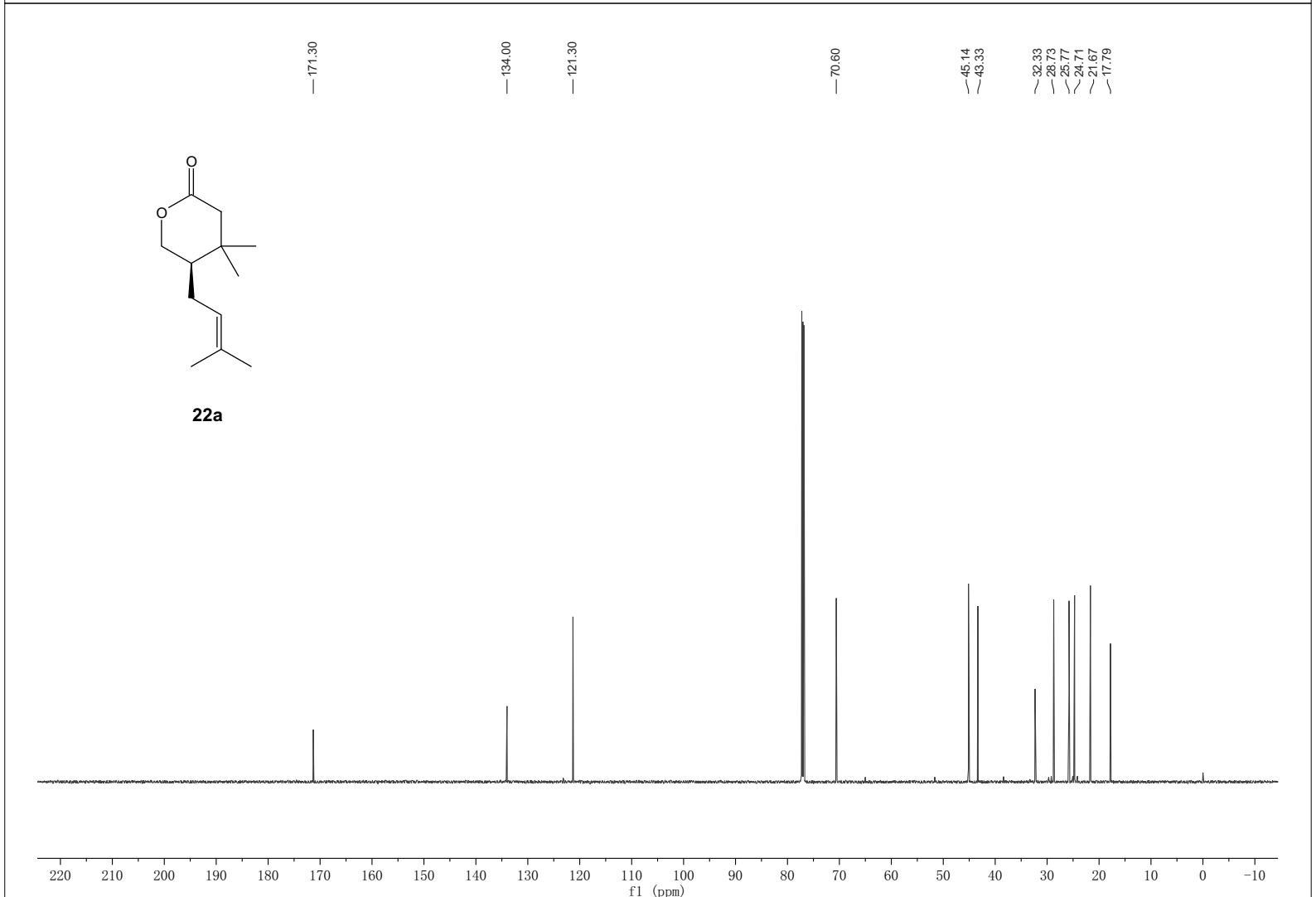
21b


136.28
131.73
124.42
124.20
77.48
77.16
76.84
63.50
59.41
49.88
43.33
39.93
34.83
26.62
26.46
26.18
25.78
25.56
17.78
16.20
OH
OH
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)

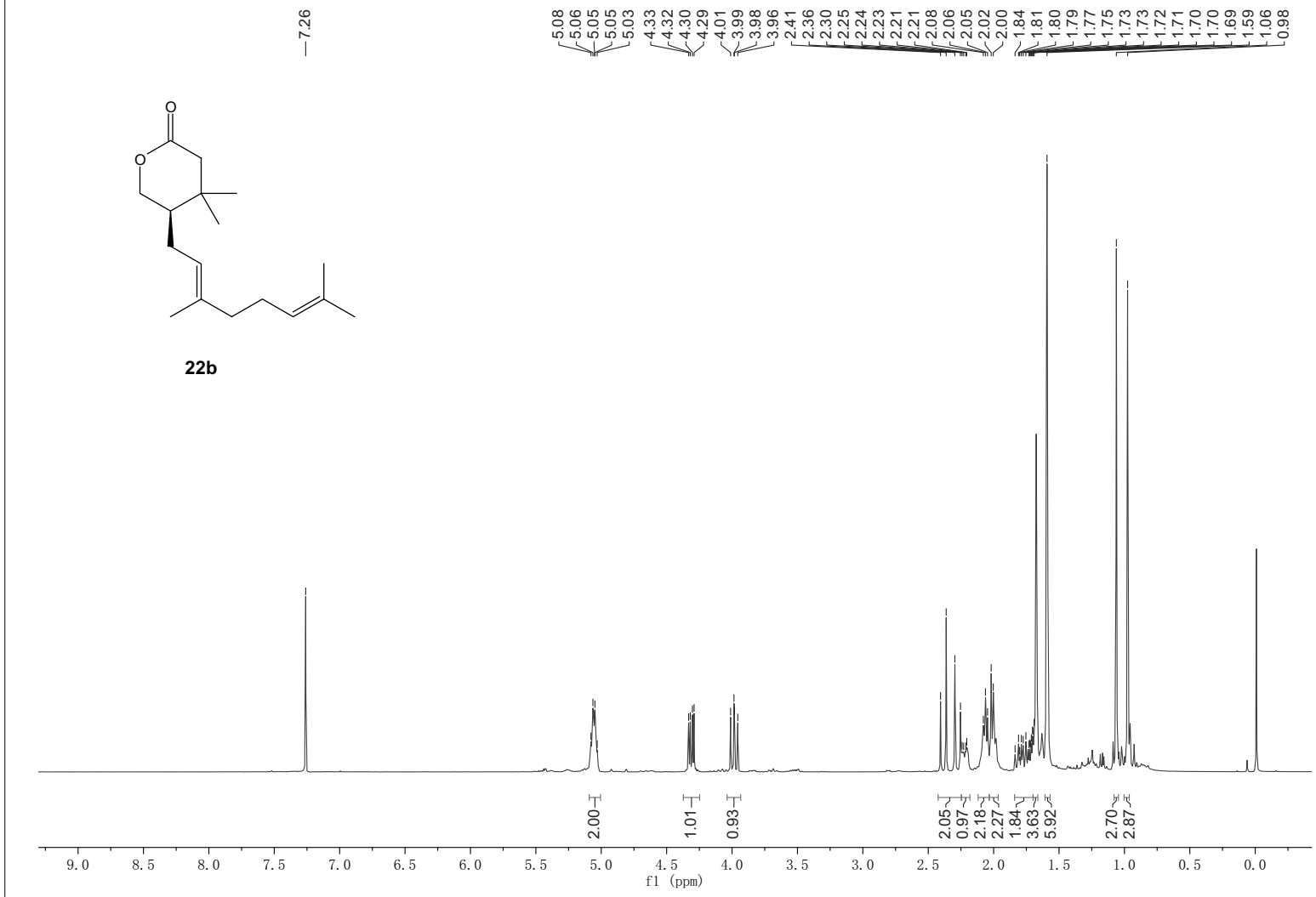
21b


5.07
5.07
5.07
5.05
5.05
5.04
5.03
5.03
4.33
4.32
4.31
4.29
4.01
3.99
3.98
3.96
2.40
2.36
2.29
2.25
2.23
2.22
2.19
2.19
1.81
1.79
1.76
1.75
1.73
1.71
1.70
1.68
1.63
1.59
1.05
0.97
O
O
0.97
1.03
1.01
2.07
0.96
1.18
3.19
0.96
2.95
3.00
2.95
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)

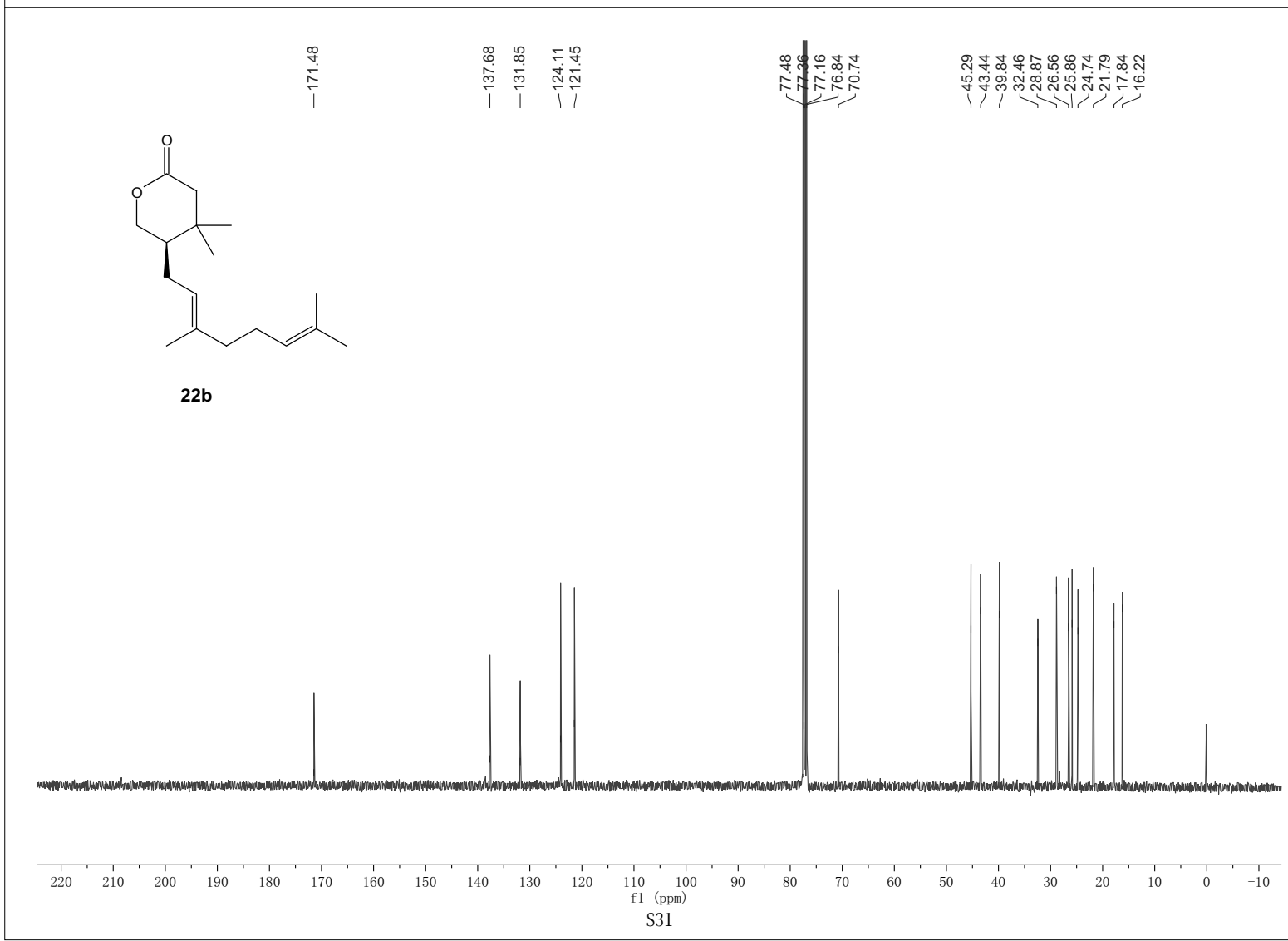
22a


171.30
134.00
121.30
70.60
45.14
43.33
32.33
28.73
25.77
24.71
21.67
17.79
O
O
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)

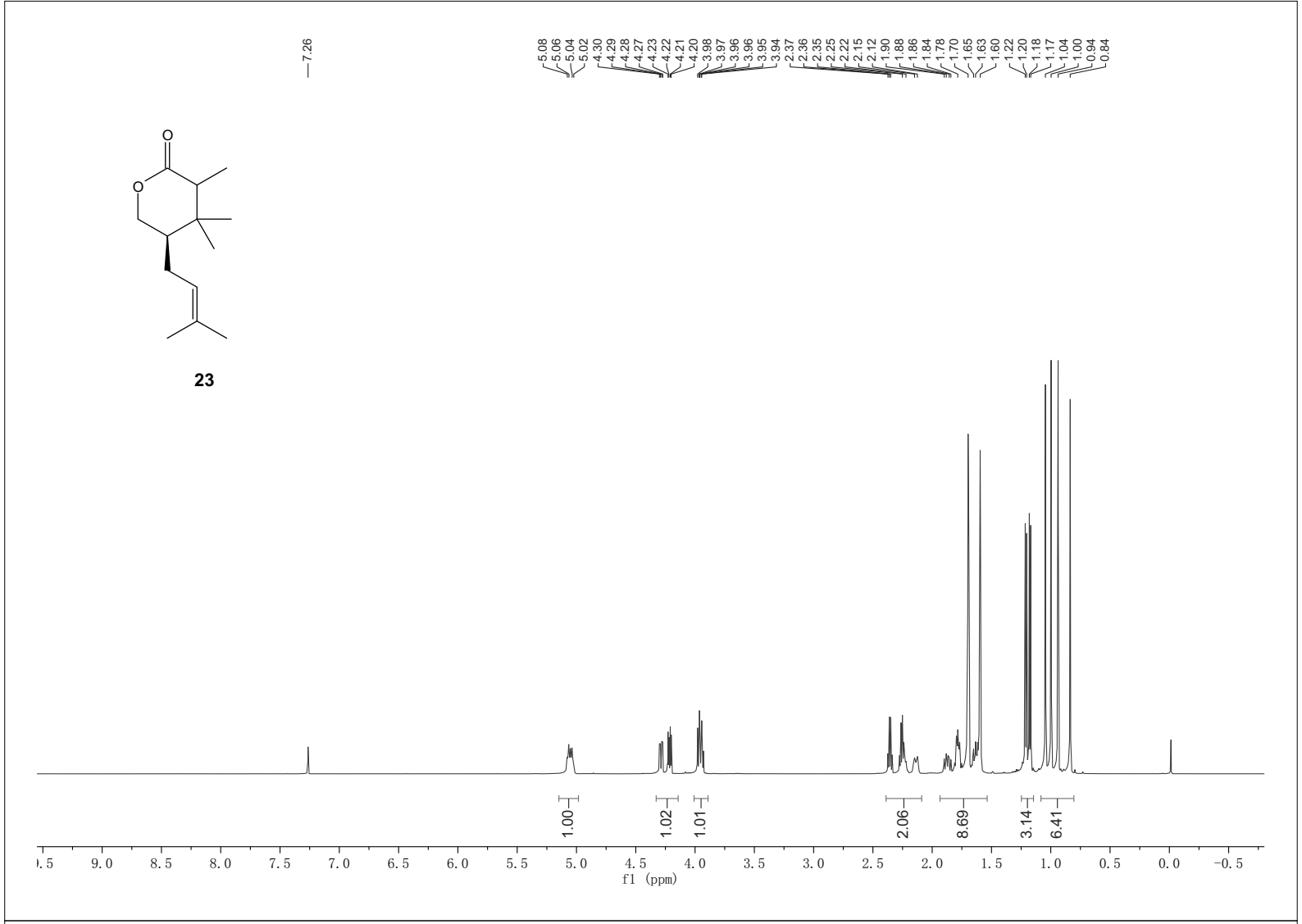
22a


7.26
5.08
5.06
5.05
5.05
5.03
4.33
4.32
4.30
4.29
4.01
3.99
3.98
3.96
2.41
2.36
2.30
2.25
2.24
2.23
2.21
2.21
2.08
2.06
2.05
2.02
2.00
1.84
1.81
1.80
1.79
1.77
1.75
1.73
1.73
1.72
1.71
1.70
1.70
1.69
1.59
1.06
0.98
O
O
2.00
1.01
0.93
2.05
0.97
2.18
2.27
1.84
3.63
5.92
2.70
2.87
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)

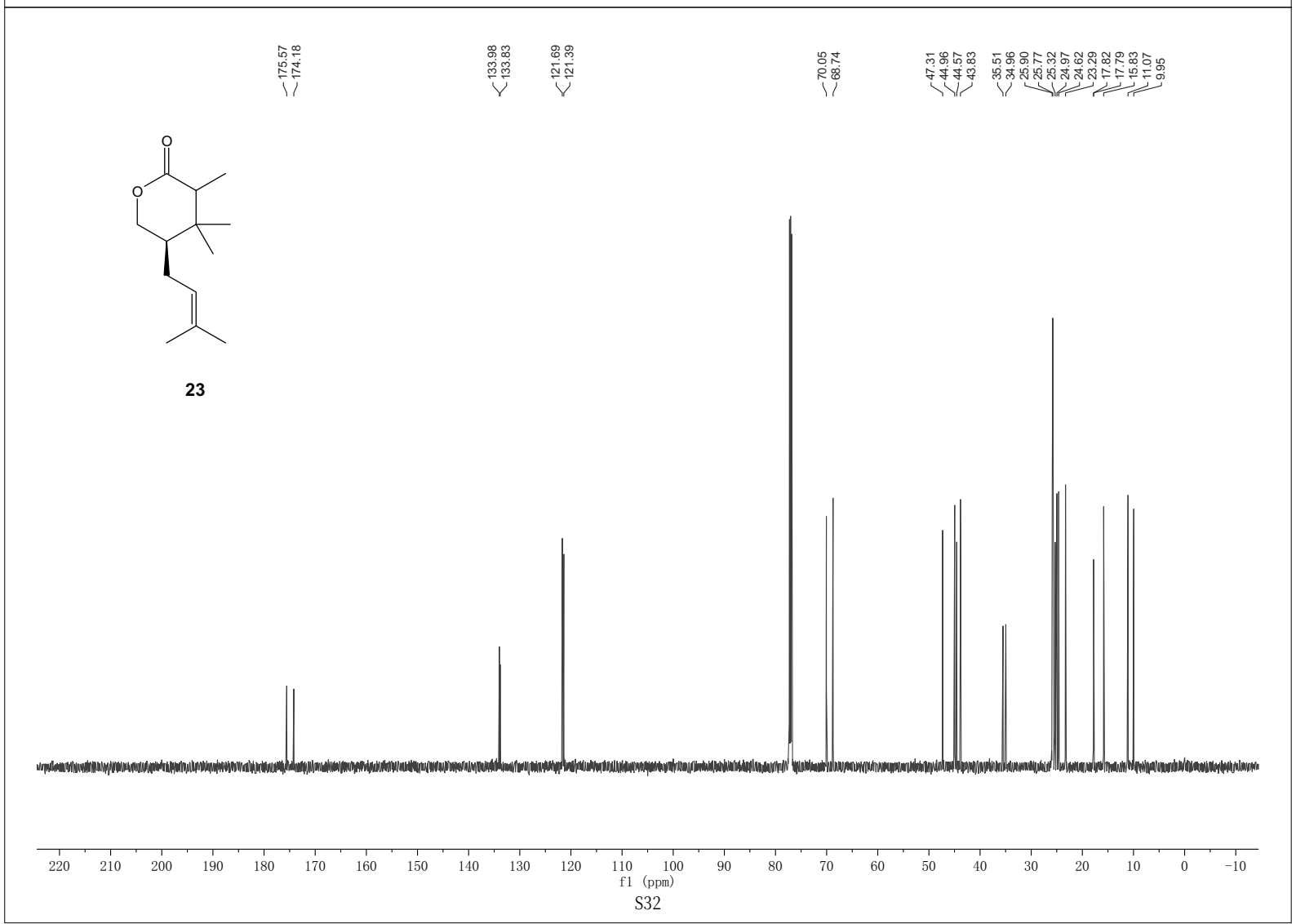
22b


171.48
137.68
131.85
124.11
121.45
77.48
77.36
77.16
76.84
70.74
45.29
43.44
39.84
32.46
28.87
26.56
25.86
24.74
21.79
17.84
16.22
O
O
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)

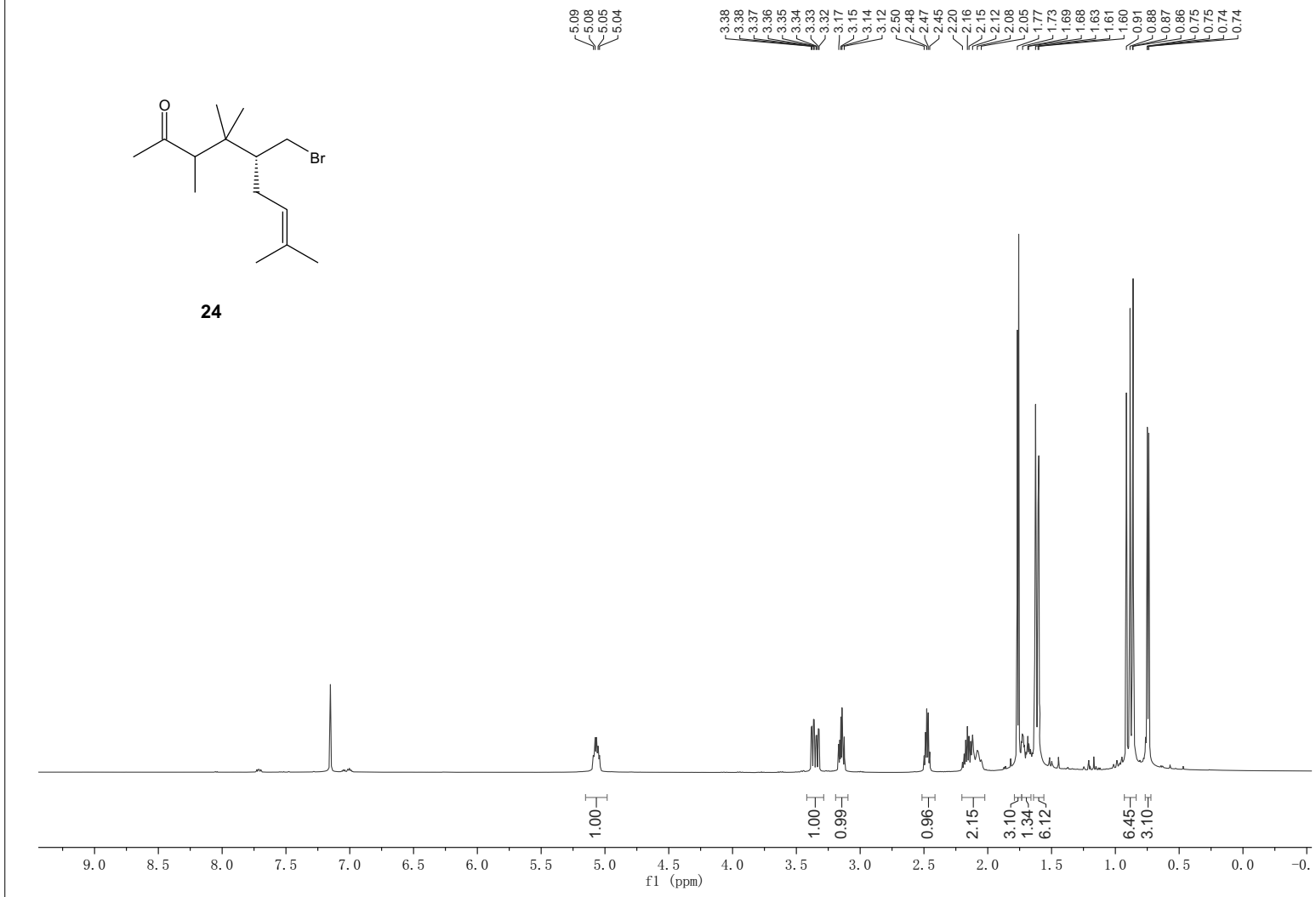
22b


7.26
5.08
5.06
5.04
5.02
4.30
4.29
4.28
4.27
4.23
4.22
4.21
4.20
3.98
3.97
3.96
3.96
3.95
3.94
2.37
2.36
2.35
2.25
2.22
2.15
2.12
1.90
1.88
1.86
1.84
1.78
1.70
1.65
1.63
1.60
1.22
1.20
1.18
1.17
1.04
1.00
0.94
0.84
O
O
1.00
1.02
1.01
2.06
8.69
3.14
6.41
f1 (ppm)

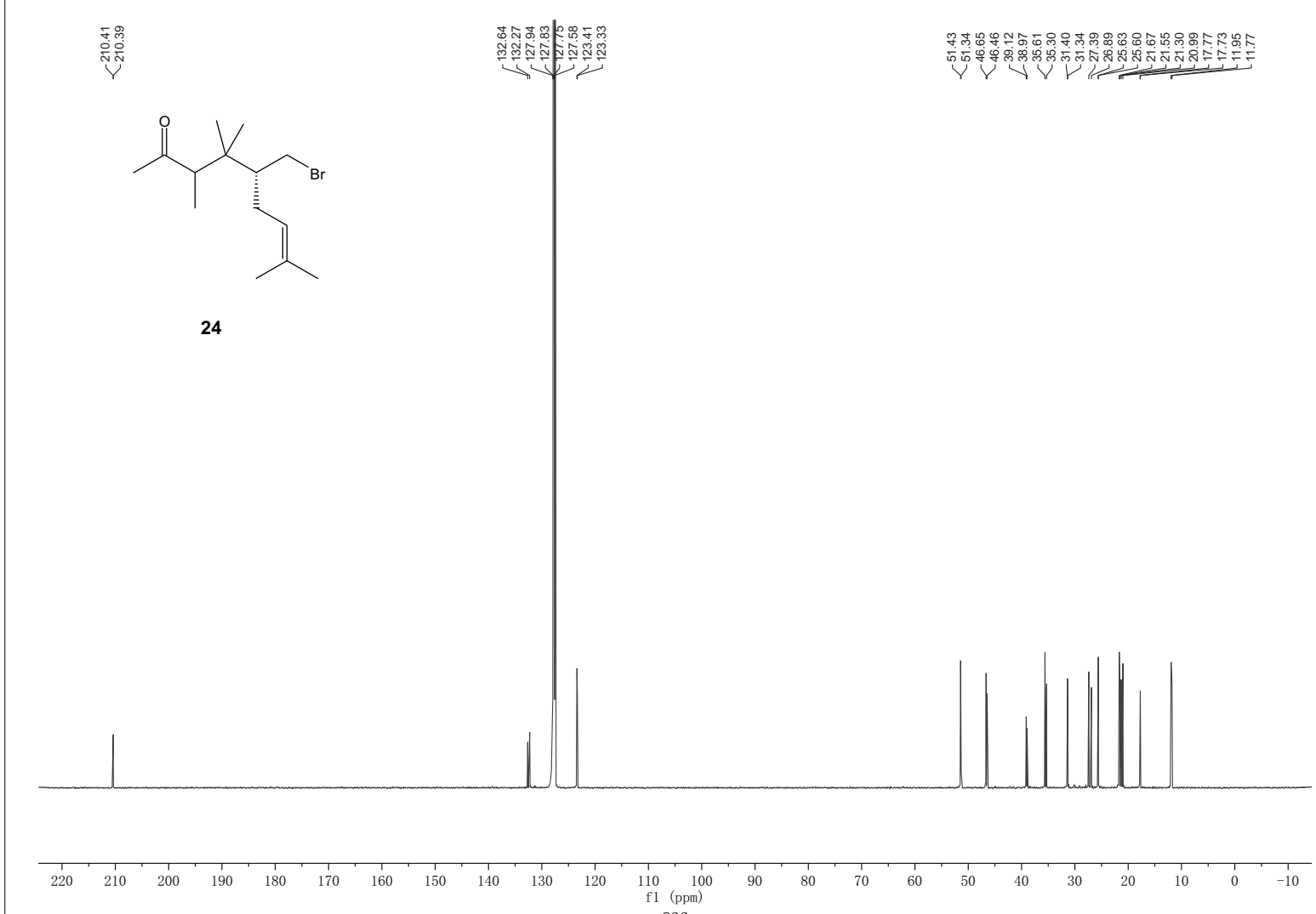
23


175.57
174.18
133.98
133.83
121.69
121.39
70.05
68.74
47.31
44.96
44.57
43.83
35.51
34.96
25.90
25.77
25.32
24.97
24.62
23.29
17.82
17.79
15.83
11.07
9.95
O
O
f1 (ppm)

23

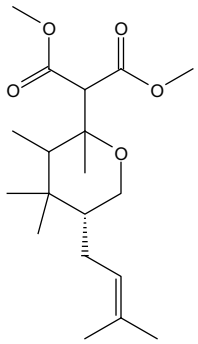

5.09
5.08
5.05
5.04
3.38
3.38
3.37
3.36
3.35
3.34
3.33
3.32
3.17
3.15
3.14
3.12
2.50
2.48
2.47
2.45
2.20
2.16
2.15
2.12
2.08
2.05
1.77
1.73
1.69
1.68
1.63
1.61
1.60
0.91
0.88
0.87
0.86
0.75
0.75
0.74
0.74
O
Br
1.00
1.00
0.99
0.96
2.15
3.10
1.34
6.12
6.45
3.10
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

24


210.41
210.39
132.64
132.27
127.94
127.83
127.75
127.58
123.41
123.33
51.43
51.34
46.65
46.46
39.12
38.97
35.61
35.30
31.40
31.34
27.39
26.89
25.63
25.60
21.67
21.55
21.30
20.99
17.77
17.73
11.95
11.77
O
Br
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)

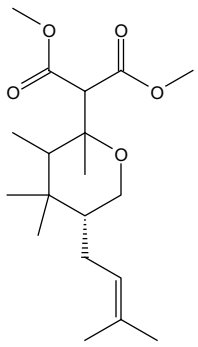
24

wxy-5-1-65-24.10.fid



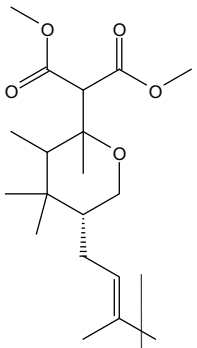
25

wxy-5-1-65-24/21



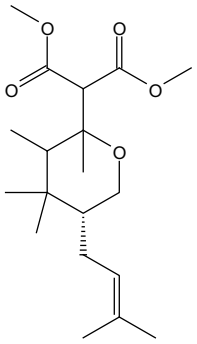
25

wxy-5-1-65-21/10

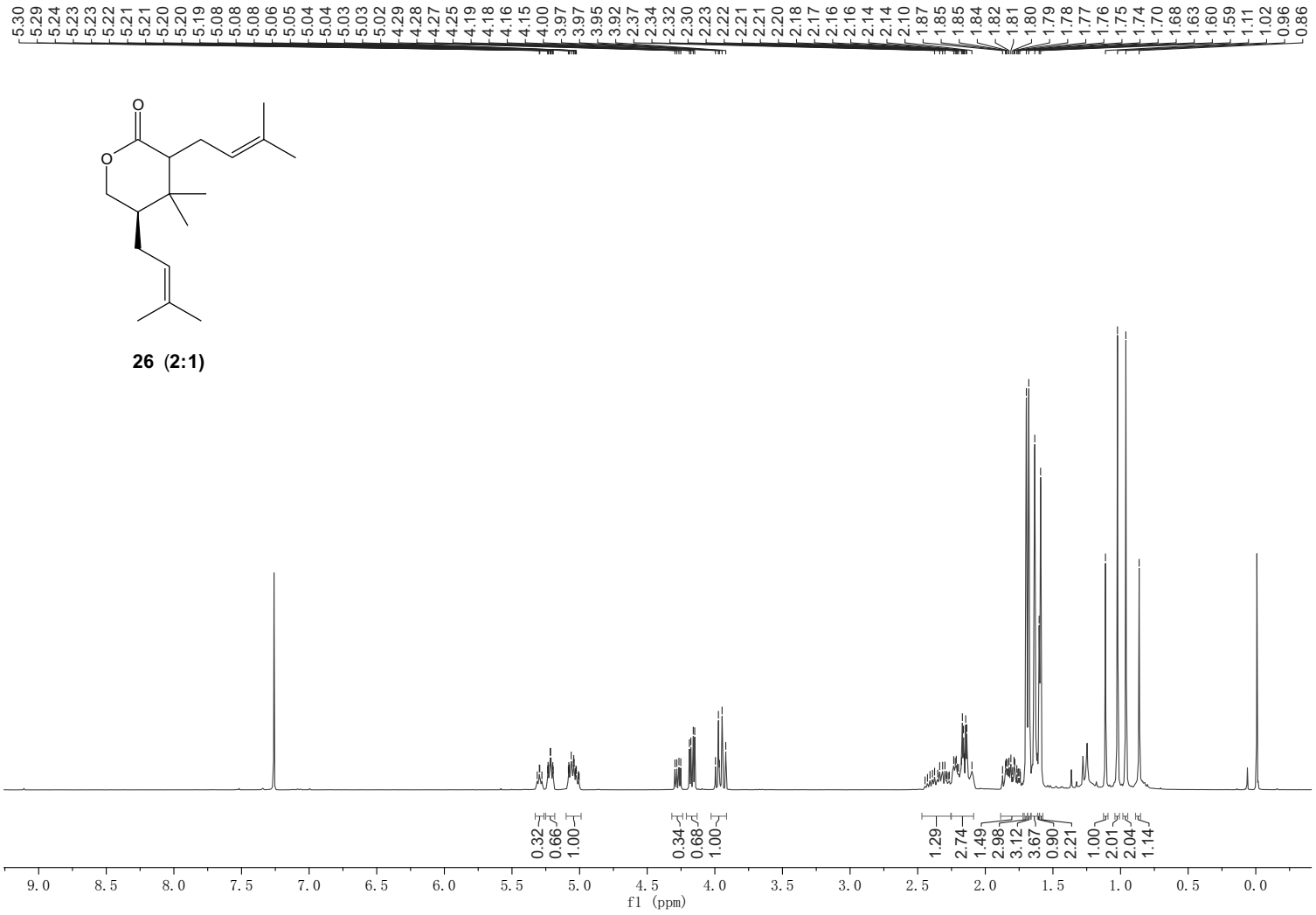


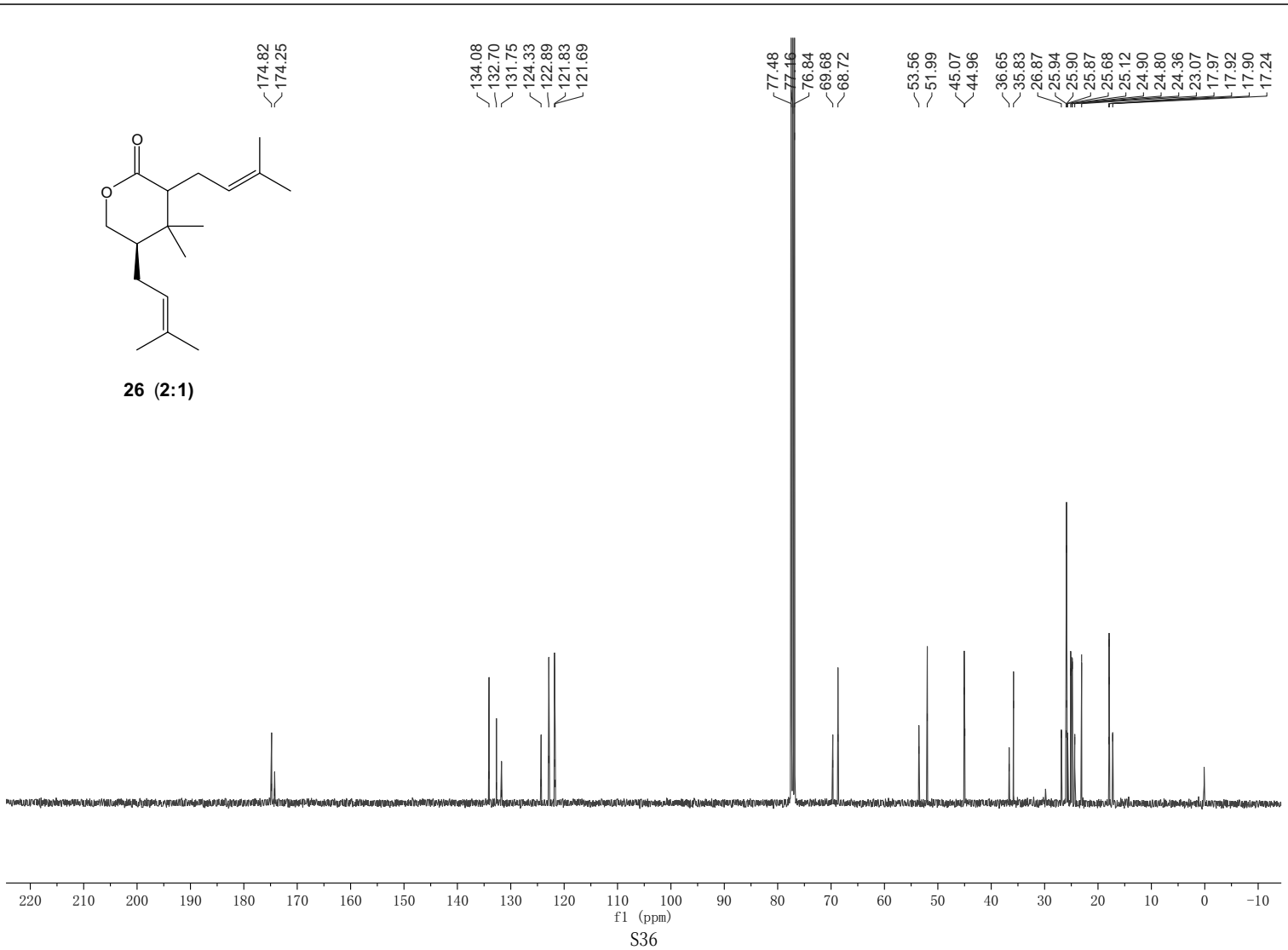
25'

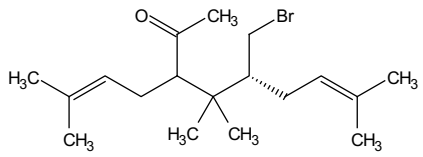
wxy-5-1-65-21/21



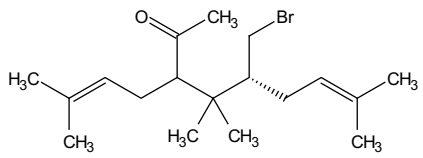
25'


5.30 5.29 5.24 5.23 5.23 5.22 5.21 5.21 5.20 5.20 5.19 5.08 5.08 5.06 5.05 5.04 5.04 5.03 5.03 5.02 4.29 4.28 4.27 4.25 4.19 4.18 4.16 4.15 4.00 3.97 3.95 3.92 2.37 2.34 2.32 2.30 2.23 2.22 2.21 2.21 2.20 2.18 2.17 2.16 2.16 2.14 2.14 2.10 1.87 1.85 1.85 1.84 1.82 1.81 1.80 1.79 1.78 1.77 1.76 1.75 1.74 1.70 1.68 1.63 1.60 1.59 1.11 1.02 0.96 0.86
O
O
26 (2:1)
0.32 0.66 1.00 0.34 0.68 1.00 1.29 2.74 1.49 2.98 3.12 3.67 0.90 2.21 1.00 2.01 2.04 1.14
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)

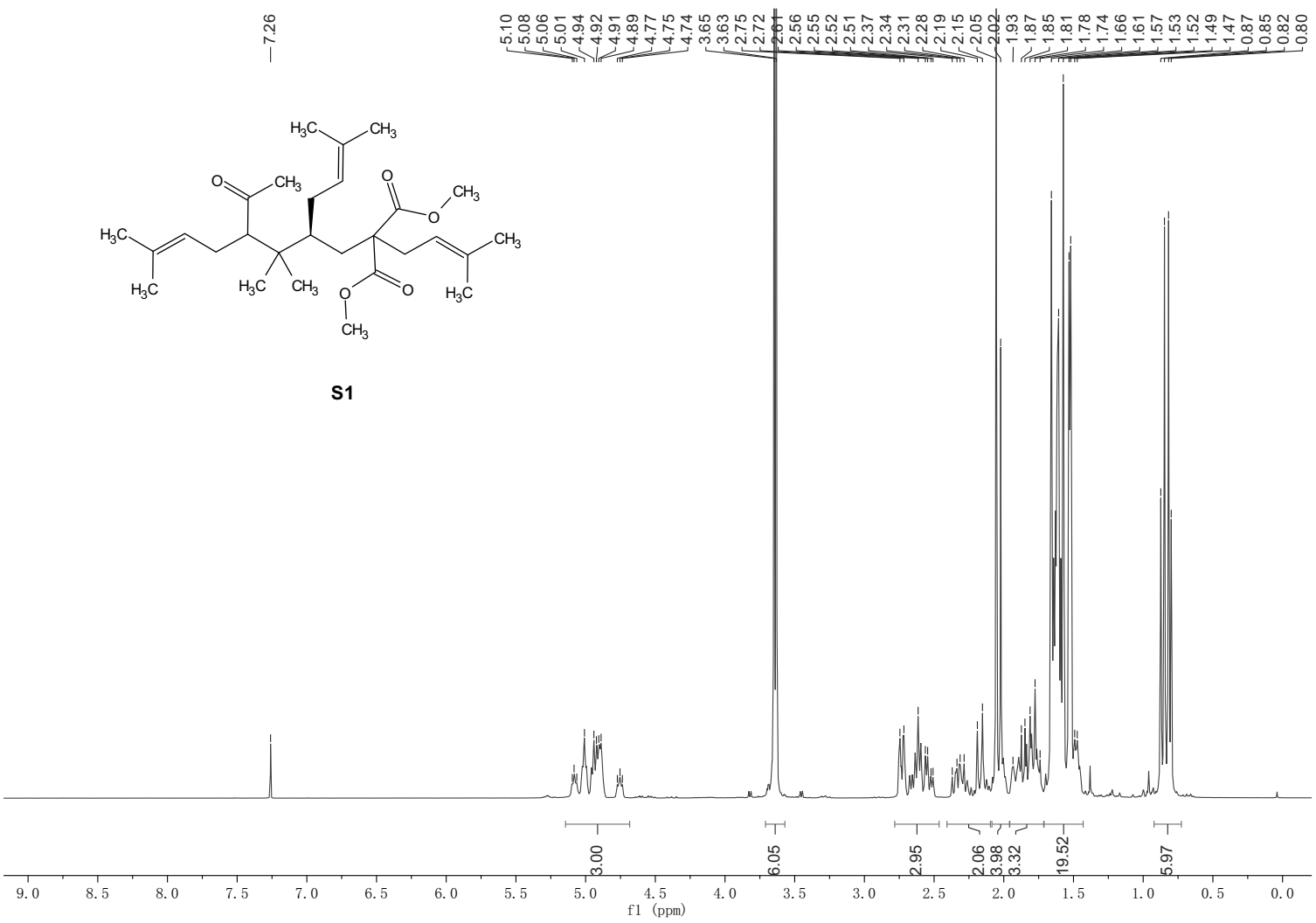

174.82 174.25 134.08 132.70 131.75 124.33 122.89 121.83 121.69 77.48 77.16 76.84 69.68 68.72 53.56 51.99 45.07 44.96 36.65 35.83 26.87 25.94 25.90 25.87 25.68 25.12 24.90 24.80 24.36 23.07 17.97 17.92 17.90 17.24
O
O
26 (2:1)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



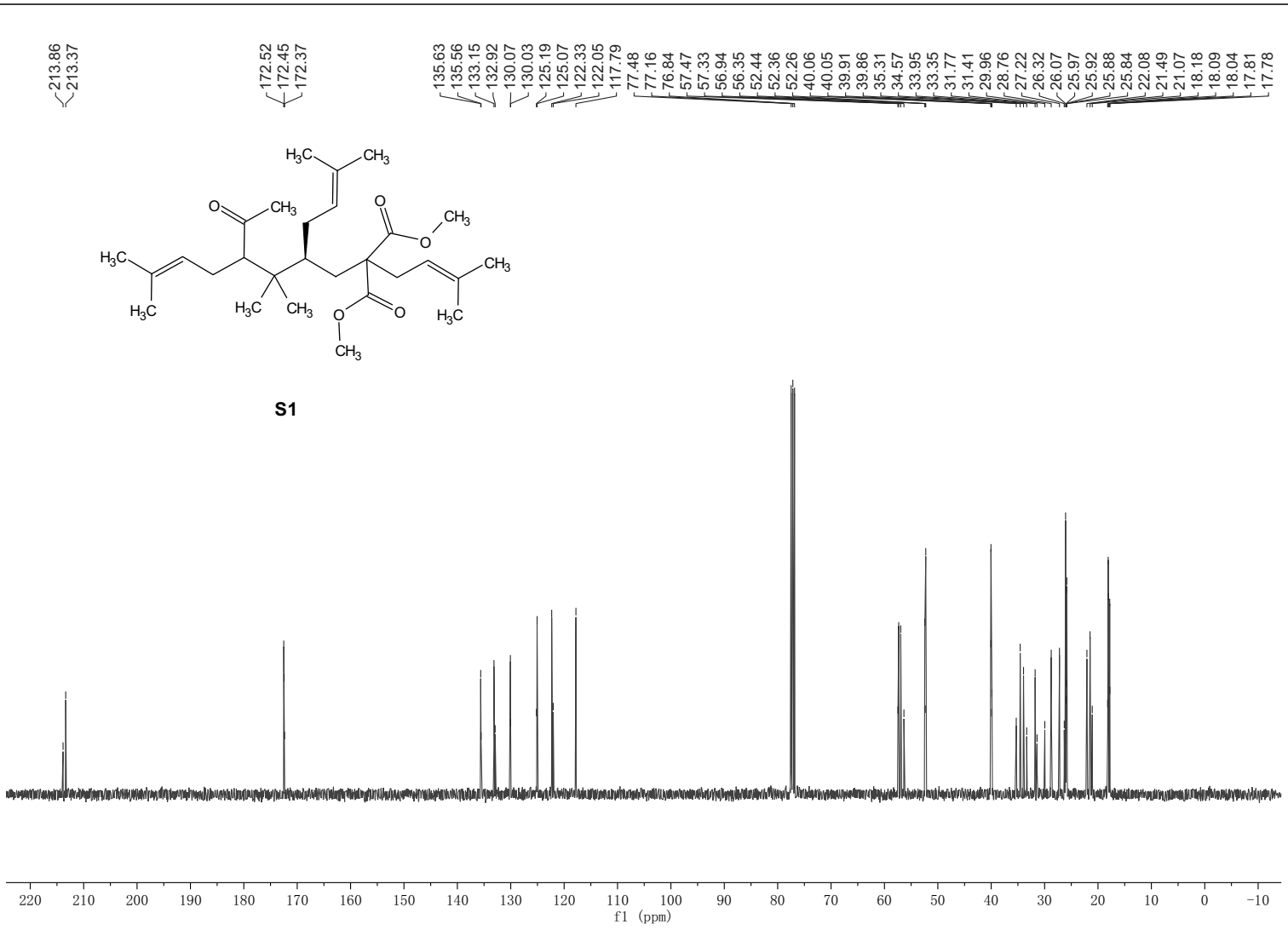
27 (2:1)



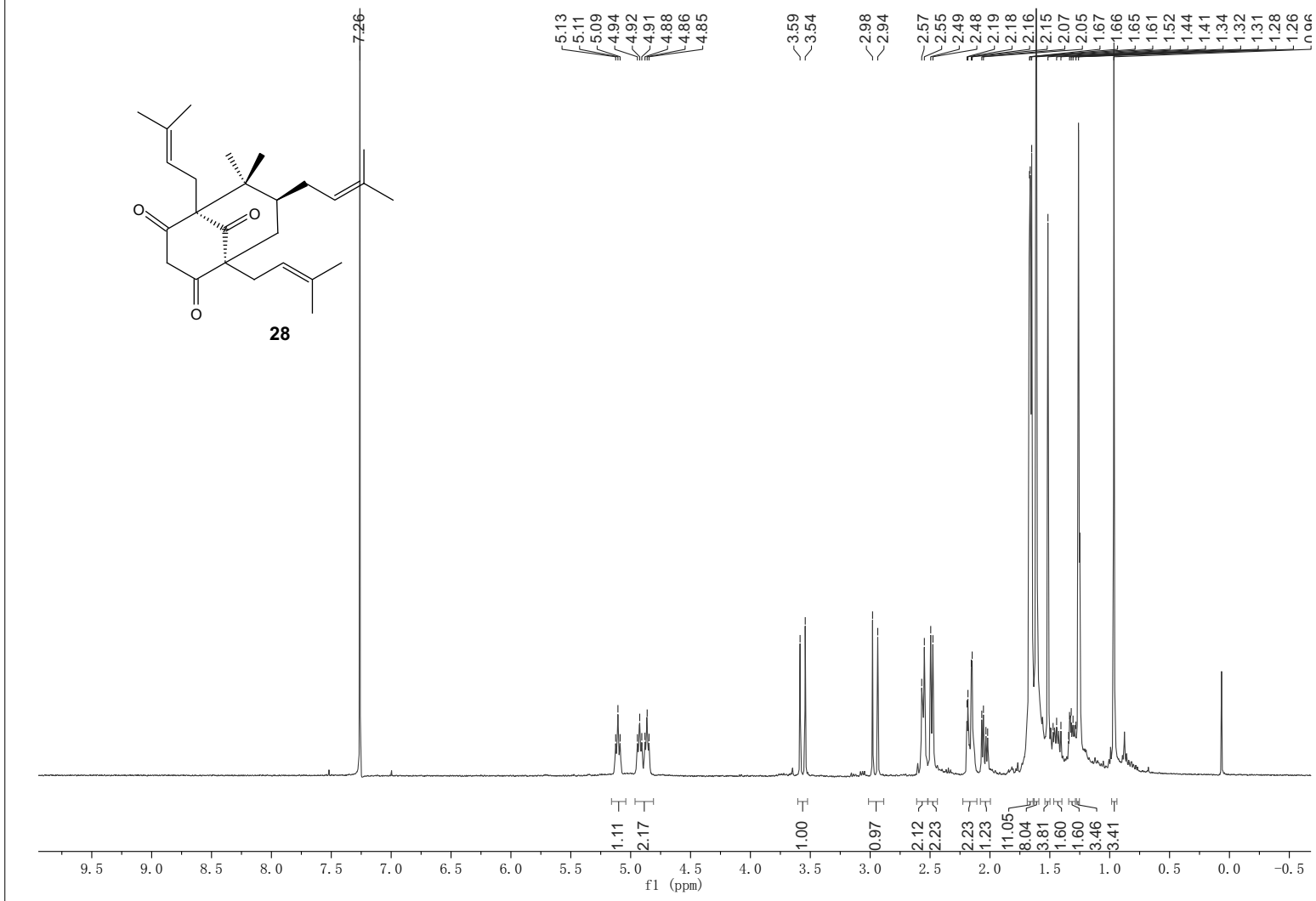
27 (2:1)


7.26
5.10
5.08
5.06
5.01
4.94
4.92
4.91
4.89
4.77
4.75
4.74
3.65
3.63
2.75
2.72
2.61
2.56
2.55
2.52
2.51
2.37
2.34
2.31
2.28
2.19
2.15
2.05
2.02
1.93
1.87
1.85
1.81
1.78
1.74
1.66
1.61
1.57
1.53
1.52
1.49
1.47
0.87
0.85
0.82
0.80
3.00
6.05
2.95
2.06
3.98
3.32
19.52
5.97
f1 (ppm)

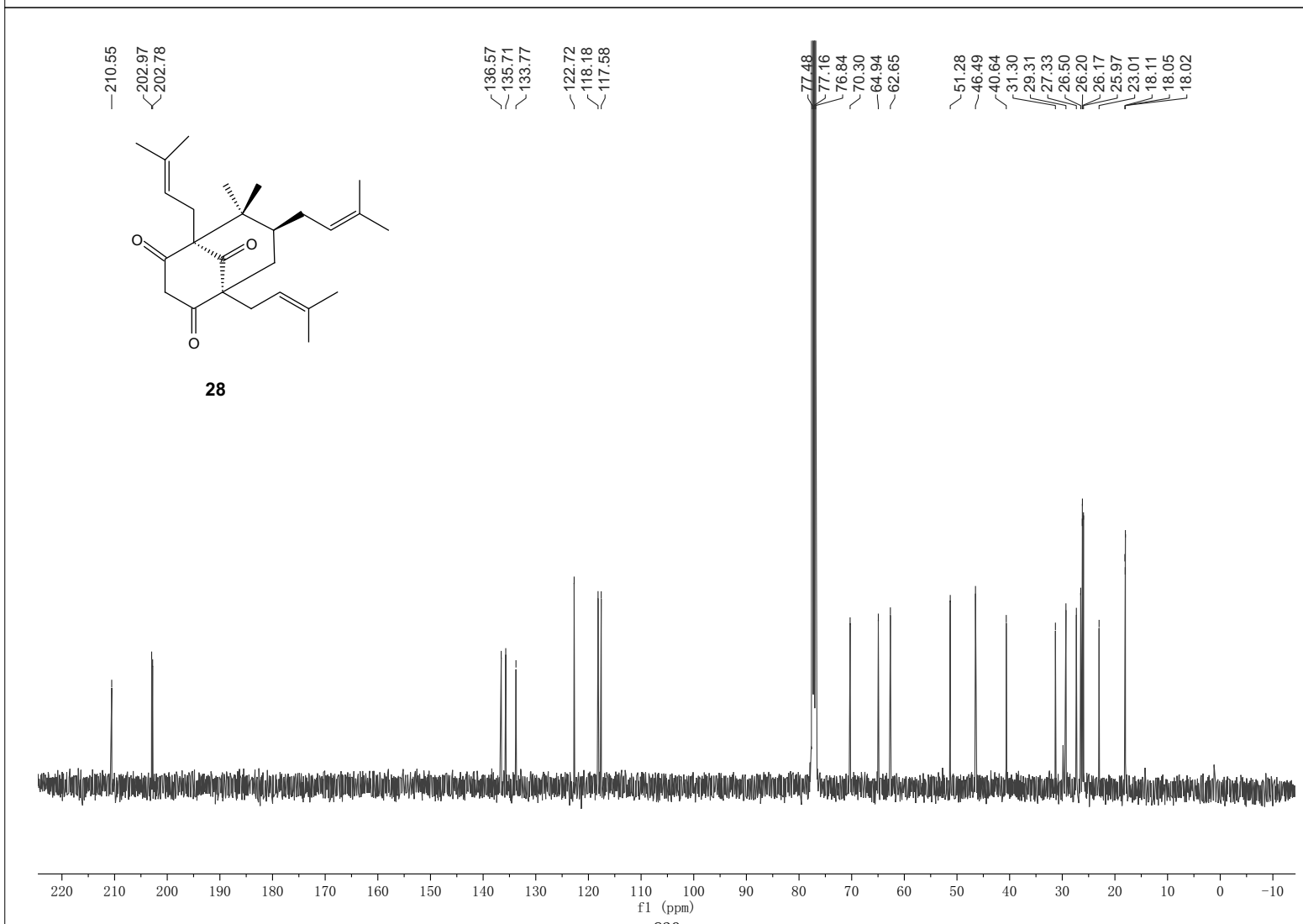
S1


213.86
213.37
172.52
172.45
172.37
135.63
135.56
133.15
132.92
130.07
130.03
125.19
125.07
122.33
122.05
117.79
77.48
77.16
76.84
57.47
57.33
56.94
56.35
52.44
52.36
52.26
40.06
40.05
39.91
39.86
35.31
34.57
33.95
33.35
31.77
31.41
29.96
28.76
27.22
26.32
26.07
25.97
25.92
25.88
25.84
22.08
21.49
21.07
18.18
18.09
18.04
17.81
17.78
f1 (ppm)

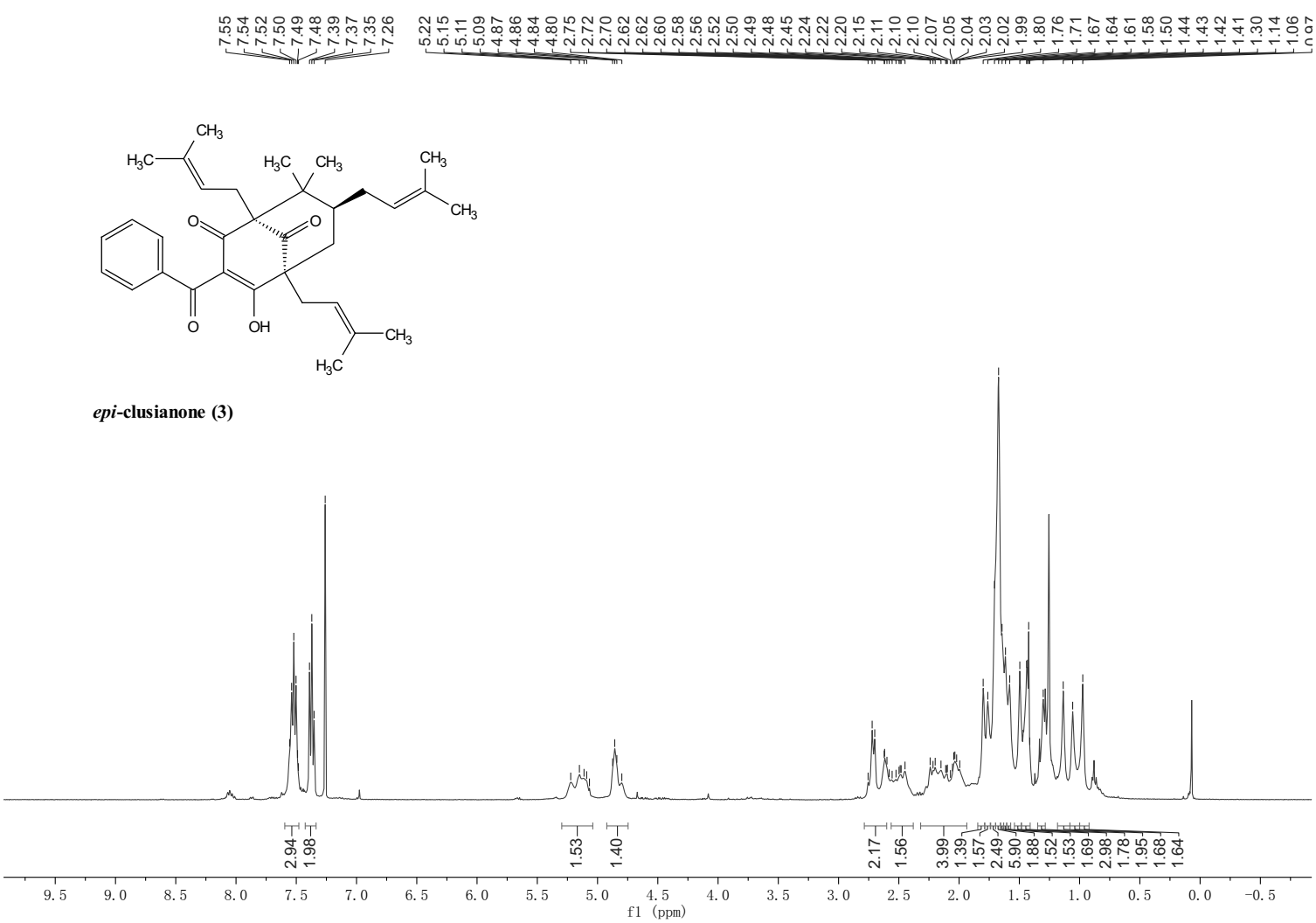
S1


7.26
5.13
5.11
5.09
4.94
4.92
4.91
4.88
4.86
4.85
3.59
3.54
2.98
2.94
2.57
2.55
2.49
2.48
2.19
2.18
2.16
2.15
2.07
2.05
1.67
1.66
1.65
1.61
1.52
1.44
1.41
1.34
1.32
1.31
1.28
1.26
1.11
2.17
1.00
0.97
2.12
2.23
2.23
1.23
11.05
8.04
3.81
1.60
1.60
3.46
3.41
f1 (ppm)

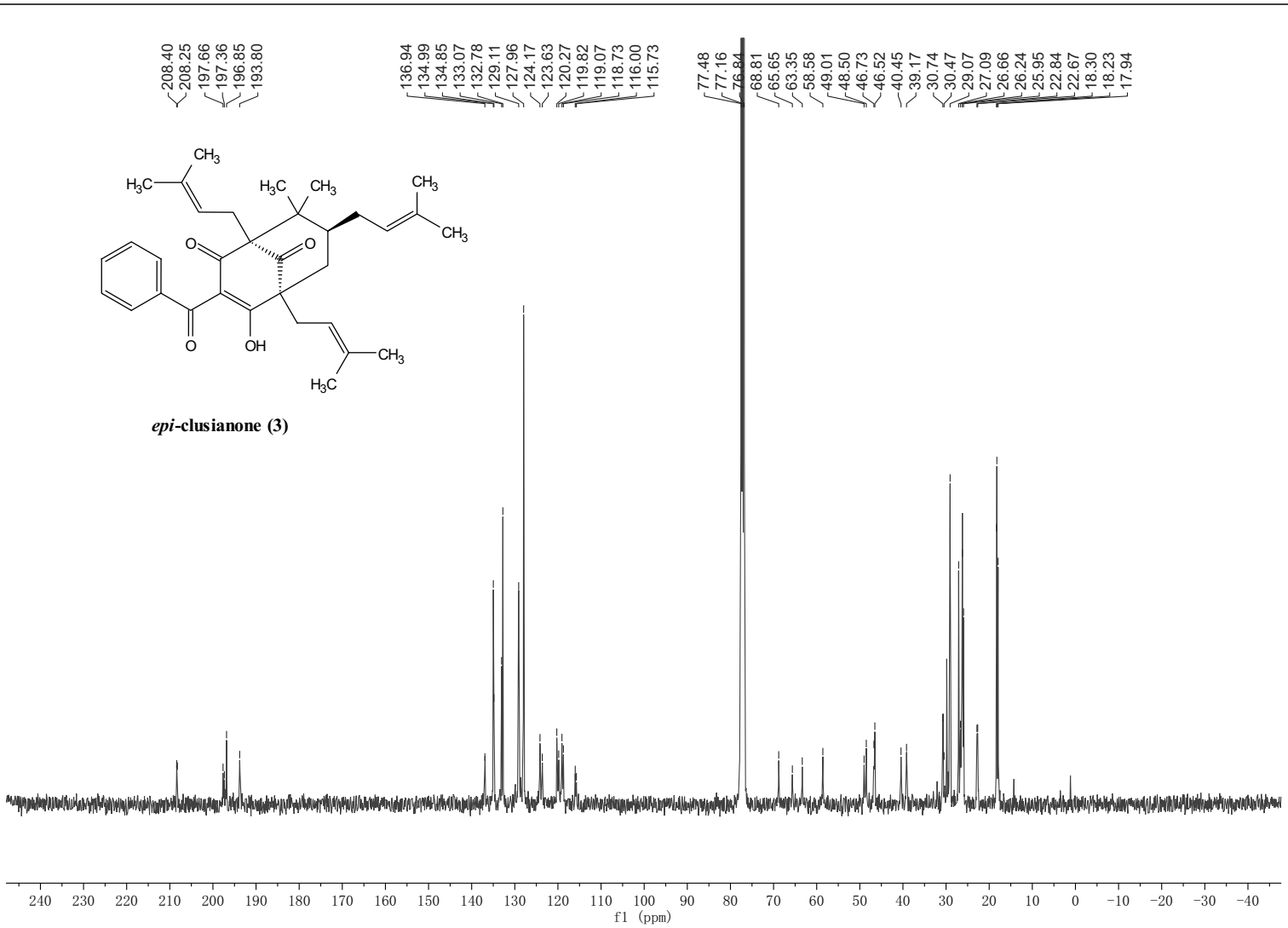
28


210.55
202.97
202.78
136.57
135.71
133.77
122.72
118.18
117.58
77.48
77.16
76.84
70.30
64.94
62.65
51.28
46.49
40.64
31.30
29.31
27.33
26.50
26.20
26.17
25.97
23.01
18.11
18.05
18.02
f1 (ppm)

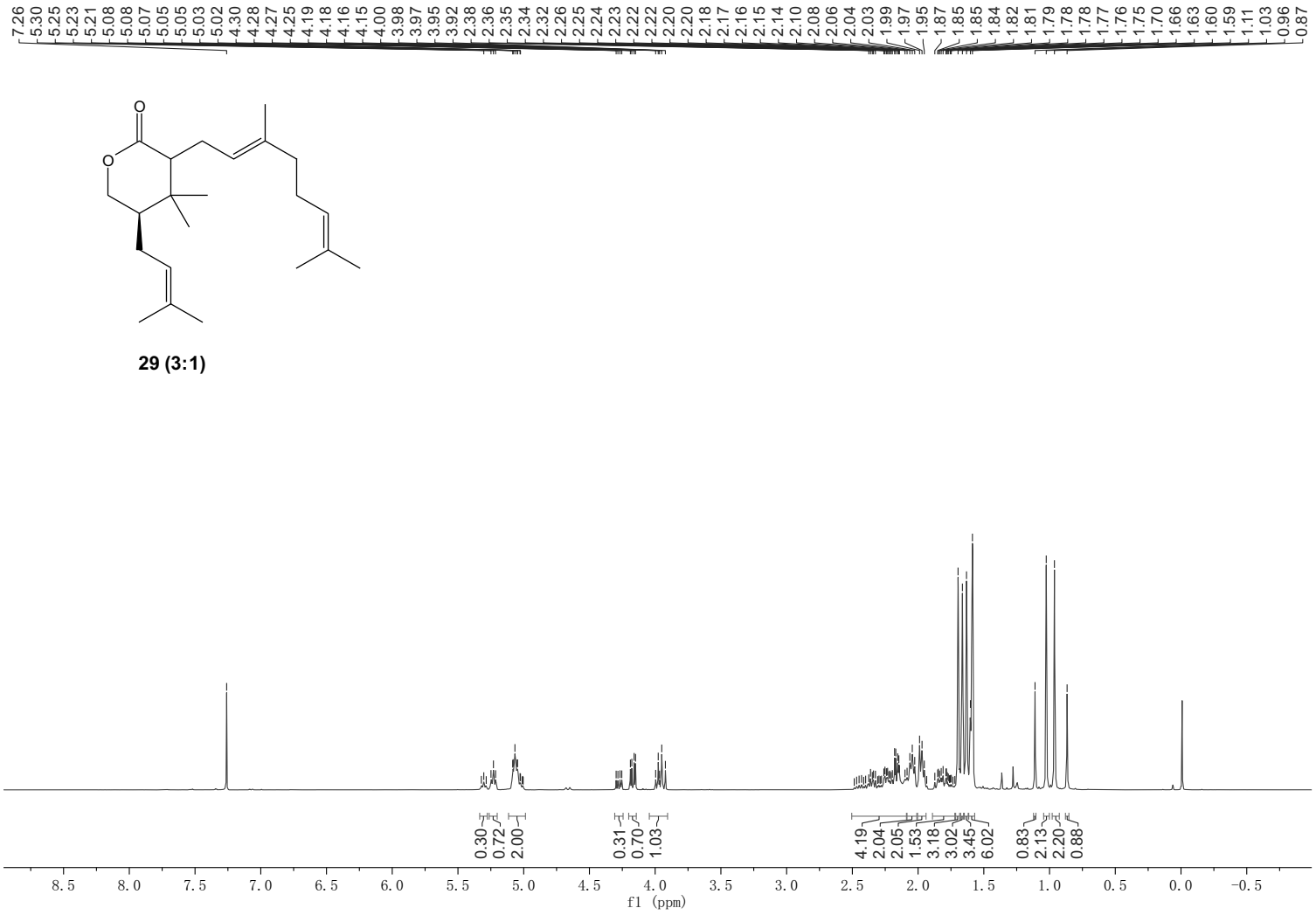
28

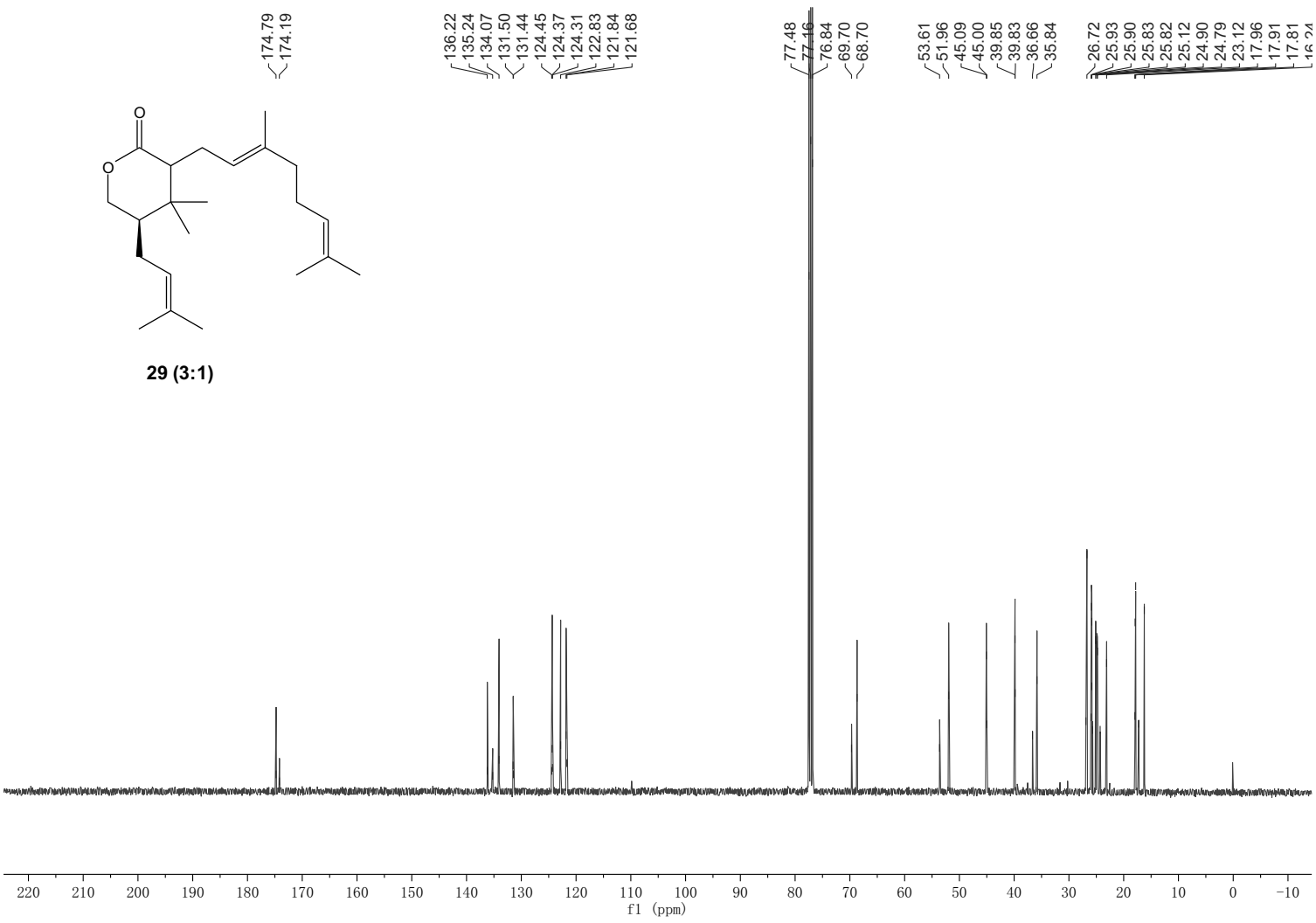


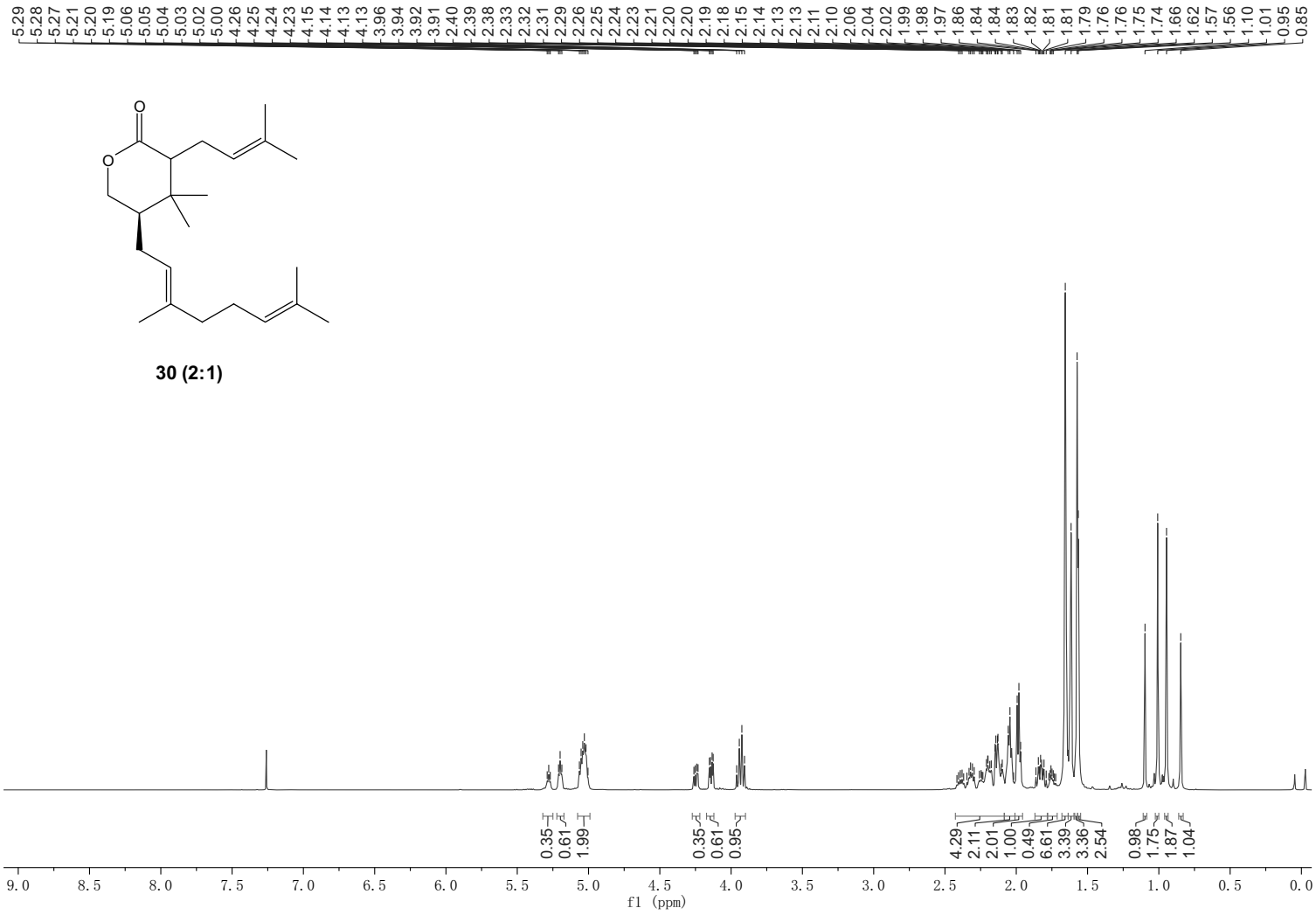
***epi*-clusianone (3)**



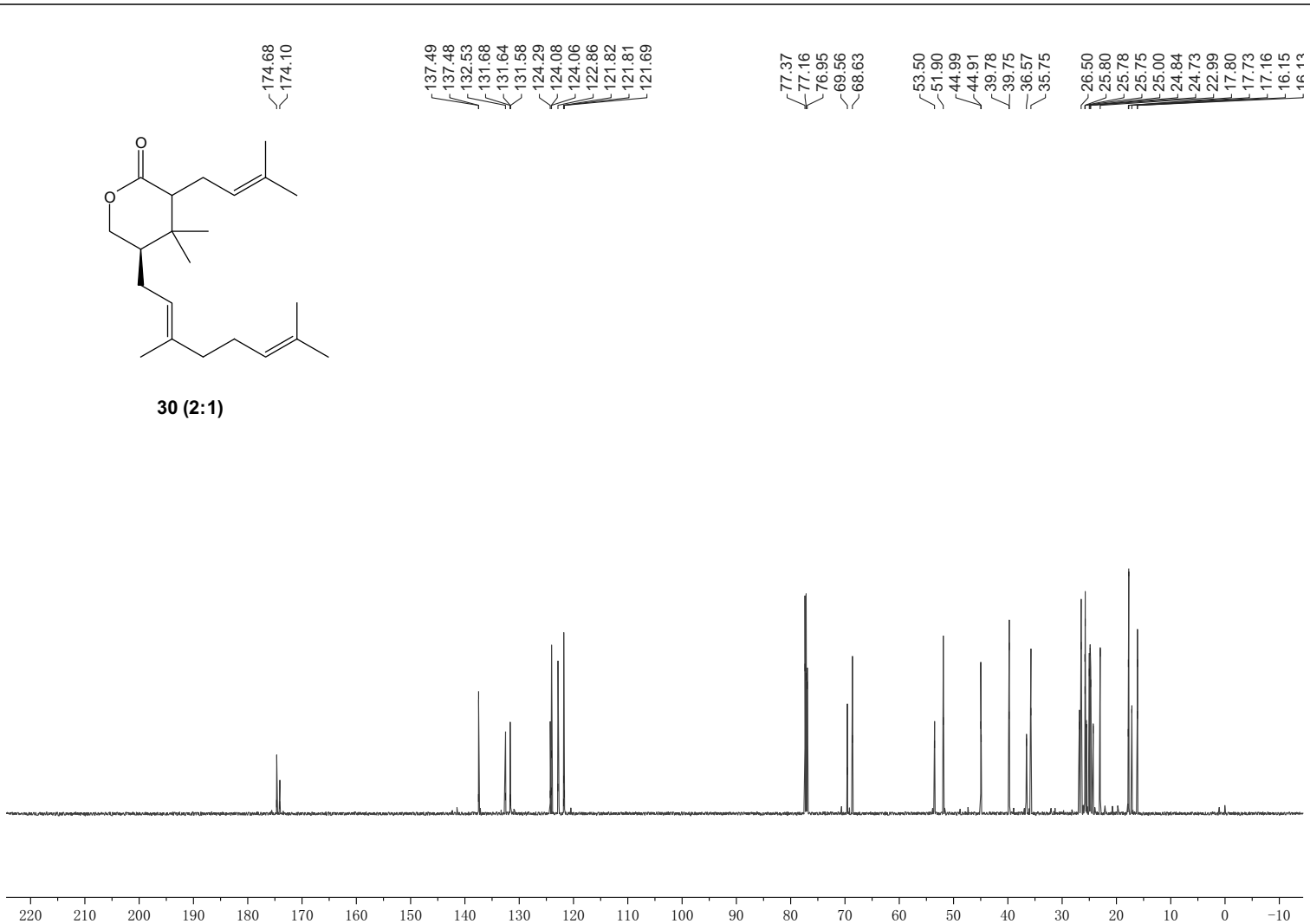
***epi*-clusianone (3)**


7.26 5.30 5.25 5.23 5.21 5.08 5.08 5.07 5.05 5.05 5.03 5.02 4.30 4.28 4.27 4.25 4.19 4.18 4.16 4.15 4.00 3.98 3.97 3.95 3.92 2.38 2.36 2.35 2.34 2.32 2.26 2.25 2.24 2.23 2.22 2.22 2.20 2.20 2.18 2.17 2.16 2.15 2.14 2.10 2.08 2.06 2.04 2.03 1.99 1.97 1.95 1.87 1.85 1.85 1.84 1.82 1.81 1.79 1.78 1.78 1.77 1.76 1.75 1.70 1.66 1.63 1.60 1.59 1.11 1.03 0.96 0.87
O
O
29 (3:1)
0.30 0.72 2.00 0.31 0.70 1.03 4.19 2.04 2.05 1.53 3.18 3.02 3.45 6.02 0.83 2.13 2.20 0.88
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)


174.79 174.19 136.22 135.24 134.07 131.50 131.44 124.45 124.37 124.31 122.83 121.84 121.68 77.48 77.16 76.84 69.70 68.70 53.61 51.96 45.09 45.00 39.85 39.83 36.66 35.84 26.72 25.93 25.90 25.83 25.82 25.12 24.90 24.79 23.12 17.96 17.91 17.81
O
O
29 (3:1)
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)


5.29 5.28 5.27 5.21 5.20 5.19 5.06 5.05 5.04 5.03 5.02 5.00 4.26 4.25 4.24 4.23 4.15 4.14 4.13 3.96 3.94 3.92 3.91 2.40 2.39 2.38 2.33 2.32 2.31 2.29 2.26 2.25 2.24 2.23 2.21 2.20 2.20 2.19 2.18 2.15 2.14 2.13 2.13 2.11 2.10 2.06 2.04 2.02 1.99 1.98 1.97 1.86 1.84 1.84 1.83 1.82 1.81 1.81 1.79 1.76 1.76 1.75 1.74 1.66 1.62 1.57 1.56 1.10 1.01 0.95 0.85
O
O
0.35 0.61 1.99 0.35 0.61 0.95 4.29 2.11 2.01 1.00 0.49 6.61 3.39 3.36 2.54 0.98 1.75 1.87 1.04
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)

30 (2:1)


174.68 174.10
137.49 137.48 132.53 131.68 131.64 131.58 124.29 124.08 124.06 122.86 121.82 121.81 121.69
77.37 77.16 76.95 69.56 68.63
53.50 51.90 44.99 44.91 39.78 39.75 36.57 35.75
26.50 25.80 25.78 25.75 25.00 24.84 24.73 22.99 17.80 17.73 17.16 16.15
O
O
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)

30 (2:1)