Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

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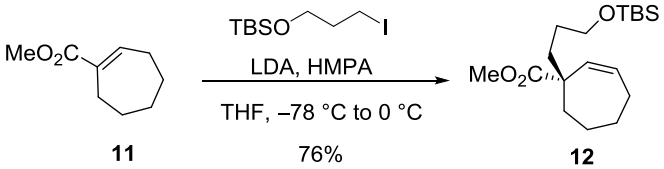
1. General Procedures:

Unless the reaction procedure states otherwise, all reactions were carried out under an atmosphere of argon or nitrogen in oven or flame-dried glassware, which was under positive pressure using balloon of argon or nitrogen. Air- or moisture-sensitive liquids and solutions were transferred via syringe. Reactions were monitored by thin layer chromatography (TLC) using pre-coated silica gel plates GF254 plates. TLC plates were visualized by exposure to ultraviolet light (UV), were stained by submersion in aqueous potassium permanganate solution ($KMnO_4$) or ceric ammonium molybdenate solution (CAM), iodine staining. Flash column chromatography was performed on silica gel (200–300 mesh, Qingdao Marine Chemical Factory, China). All chemicals were purchased from commercial vendors, unless otherwise referenced. Reagents obtained from Acros, Aldrich, J&K, TCI, and Aladdin were used without further purification. Anhydrous tetrahydrofuran (THF), diethyl ether (Et_2O) and toluene were freshly distilled from sodium/benzophenone. CH_2Cl_2, Et_3N, HMPA was dried by distillation over CaH_2. IR spectra were recorded on a Nicolet 200 SXV spectrometer; HRMS were obtained with a Bruker BioTOFQ mass spectrometer; Proton and carbon-13 nuclear magnetic resonance (^{1}H NMR, ^{13}C NMR) spectra were recorded on a Varian INOVA-400/54 spectrometer and Agilent Technologies 600/54 Premium Compact instrument and calibrated by using residual signals ($CDCl_3$: δ 7.26 for ^{1}H NMR, δ 77.00 for ^{13}C NMR). Data are presented as follows: chemical shift, multiplicity (s = singlet, bs = broad singlet, d = doublet, bd = broad doublet, t = triplet, dd = doublet of doublets, ddd = doublet of doublet of doublets, td = triplet of doublets, dt = doublet of triplets, m = multiplet and/or multiple resonances).

2. Experimental Procedures and Compound Characterization:

Preparation of Compound 12

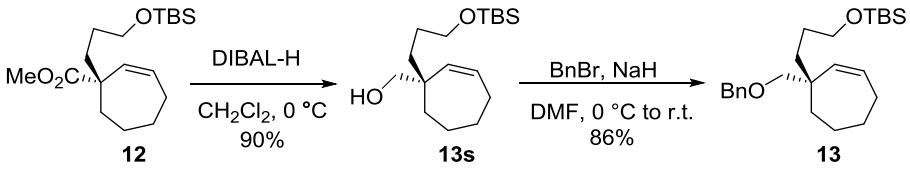


11 76% **12**

Deconjugate alkylation: To a solution of HMPA (8.7 g, 48.70 mmol) in THF (300 mL) was added LDA (21 mL, 2 M in THF) at −78 ºC dropwise over 10 min. After stirring for 30 min,

the reaction was added a solution of **11** (5 g, 32.46 mmol) and stirred for 30 min. Then iodide chain (11.7 g, 38.96 mmol) was added to the reaction, and stirring was continued for another 2 h. The reaction was quenched with *satd. aq.* NH_4Cl (100 mL) and extracted with EtOAc (3 × 110 mL). The combined organic phases were washed with brine (200 mL), dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography eluting with petroleum ether/ethyl acetate (150:1) to give **12** (8.1 g, 24.67 mmol, 76%) as yellow oil. **IR** (film, KBr) ν_{max}: 3453, 1689, 1141, 1110, 741, 702, cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.82 (dt, *J* = 11.7, 5.9 Hz, 1H), 5.62 (d, *J* = 11.7 Hz, 1H), 3.67 (s, 3H), 3.56 (t, *J* = 6.3 Hz, 2H), 2.08 (d, *J* = 10.0 Hz, 2H), 1.976 – 1.899 (m, 1H), 1.715 – 1.659 (m, 4H), 1.569 – 1.376 (m, 4H), 1.24 (s, 1H), 0.87 (s, 9H), 0.02 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.5, 133.7, 132.1, 63.2, 51.9, 51.7, 51.7, 36.6, 35.2, 28.1, 28.0, 26.9, 25.9, 25.9, 25.7, 18.3, –5.3, –5.3; **HRMS**: m/z calc'd for $C_{18}H_{35}O_3Si$ $[M+H]^+$ 327.2350, found 327.2355.

Preparation of Compound 13

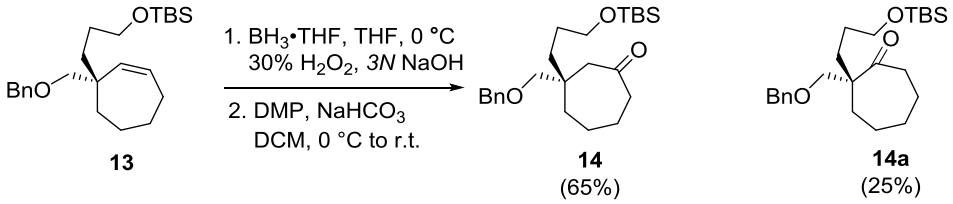


DIBAL-H Reduction: To a solution of **12** (8 g, 24.52 mmol) in CH_2Cl_2 (240 mL) was added DIBAL-H (24.5 mL, 1.5 M in toluene) dropwise at 0 ºC. After stirring for 1 h, the reaction was diluted with EtOAc (30 mL) and added Na_2SO_4•$10H_2O$ (39.5 g, 122.6 mmol) in turn. Stirring was continued for another 30 min, then the reaction was added anhydrous Na_2SO_4 (34.8 g, 245.2 mmol), stirred for additional 30 min, filtered through a celite pad and concentrated *in vacuo*. The residue was purified by silica gel column chromatography eluting with petroleum ether/ethyl acetate (30:1) to give **13s** (6.58 g, 22.07 mmol, 90%) as colorless oil. **IR** (film, KBr) ν_{max}: 3631, 3443, 2961, 1639, 1112, 711, 510 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.77 (dt, *J* = 11.8, 5.8 Hz, 1H), 5.37 (d, *J* = 11.9 Hz, 1H), 3.59 (t, *J* = 5.4 Hz, 2H), 3.43 (m, 2H), 2.14 (m, 2H), 1.75 (d, *J* = 10.7 Hz, 2H), 1.71 (m, 2H), 1.55 (dd, *J* = 10.7, 5.7 Hz, 4H), 1.51 (m, 2H), 1.47 (d, *J* = 7.8 Hz, 2H), 0.89 (s, 9H), 0.05 (s, 6H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 136.4, 131.7, 68.8, 63.9, 44.6, 33.1, 32.3, 28.3, 28.0, 28.0, 26.9, 25.9, 24.6, 18.3, –5.3; **HRMS**: m/z calc'd for $C_{17}H_{35}O_2Si$ $[M+H]^+$ 299.2401, found 299.2398.

Benzylation: A solution of **13s** (6.5 g, 21.80 mmol) in DMF (240 mL) was treated with NaH (2.6 g, 65.40 mmol, 60%) at 0 ºC. The reaction was allowed to warm to 25 ºC and stirred for 1

h at this temperature. After recooling to 0 ºC, benzyl bromide (BnBr, 4.1g, 23.98 mmol) was added dropwise over 5 min. Stirring was continued for 8 h at 25 ºC, until the reaction was quench with H_2O (100 mL), and extracted with EtOAc (3 × 100 mL). The combined organic phases were washed with brine (3 × 100 mL), dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (120:1) to give **13** (16.5 g, 18.75 mmol, 86%) as yellow oil. **IR** (film, KBr) ν_{max}: 3318, 3089, 1501, 1189, 720 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 4.3 Hz, 3H), 7.29 (dd, *J* = 8.8, 4.5 Hz, 2H), 5.73 (dt, *J* = 11.8, 5.9 Hz, 1H), 5.45 (d, *J* = 11.9 Hz, 1H), 4.53 (s, 2H), 3.59 (t, *J* = 6.1 Hz, 2H), 3.33 (d, *J* = 8.8 Hz, 1H), 3.22 (d, *J* = 8.8 Hz, 1H), 2.17 – 2.10 (m, 2H), 1.71 (dt, *J* = 11.1, 5.2 Hz, 2H), 1.64 – 1.59 (m, 2H), 1.58 (d, *J* = 4.5 Hz, 2H), 1.53 – 1.44 (m, 4H), 0.91 (s, 9H), 0.06 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.8, 137.2, 130.7, 128.2, 127.3, 76.1, 73.2, 64.0, 43.8, 33.5, 32.8, 28.4, 28.0, 27.4, 25.9, 24.7, 18.3, –5.2; **HRMS**: m/z calc'd for $C_{24}H_{41}O_2Si$ $[M+H]^+$ 389.2870, found 389.2795.

Preparation of Compound 14



13 | **14** (65%) | **14a** (25%)

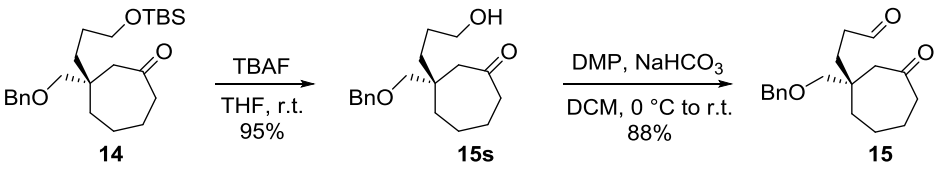
Hydroboration-oxidation: To a solution of **13** (7.1 g, 18.28 mmol) in THF (180 mL) was added BH_3•THF (36.6 mL, 1 M in THF) dropwise at 0 ºC. The resulting solution was stirred at this temperature until TLC analysis showed full conversion of the starting material. Then the reaction was added H_2O_2 (30%, 40 mL) and *aq.* NaOH (*3N*, 40 mL) slowly at 0 ºC. After stirring for 8 h, the reaction was quenched with *satd. aq.* NaS_2O_3 (60 mL) and extracted with EtOAc (3 × 50 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (15:1) to give crude alcohol as colorless oil (5.9 g 14.60 mmol), which was used for the next oxidation without further purification.

Dess-Martin oxidation: The crude oil obtained above was dissolved in CH_2Cl_2 (140 mL), and treated with $NaHCO_3$ (4.9 g, 58.40 mmol) and Dess-Martin periodinane (12.38 g, 29.20 mmol) at 0 ºC. The reaction was brought to room temperature and stirred for 1 h, then quenched with *satd. aq.* $Na_2S_2O_3$ (50 mL) at 0 ºC The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with brine (20

mL), dried over anhydrous Na_2SO_4 and evaporated *in vacuo*. The residue was purified by silica gel column chromatography eluting with petroleum ether/ethyl acetate (5:1) to give **14** (4.8 g, 11.88 mmol, 65% over 2 steps) and **14a** (1.85 g, 4.57 mmol, 25% over 2 steps) both as colorless oil. **IR** (film, KBr) ν_{max}: 3453, 3001, 1645, 1110, 709, 510 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.23 (m, 5H), 4.51 – 4.43 (m, 2H), 3.56 (ddt, *J* = 14.5, 10.2, 4.0 Hz, 2H), 3.20 (s, 2H), 2.62 – 2.48 (m, 2H), 2.41 (ddd, *J* = 13.0, 7.2, 4.9 Hz, 2H), 1.78 (dd, *J* = 14.3, 8.6 Hz, 2H), 1.69 (d, *J* = 14.4 Hz, 2H), 1.65 (d, *J* = 3.9 Hz, 2H), 1.48 – 1.33 (m, 4H), 0.89 (s, 9H), 0.05 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 213.8, 138.5, 128.2, 127.4, 76.2, 73.2, 63.6, 51.1, 43.9, 38.9, 37.2, 32.0, 26.5, 25.9, 24.0, 18.3, –5.3; **HRMS**: m/z calc'd for $C_{24}H_{41}O_3Si$ $[M+H]^+$ 405.2819, found 405.2821.

14a IR (film, KBr) ν_{max}: 3450, 3053, 1638, 1109, 709 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.30 (dq, *J* = 14.7, 7.7 Hz, 5H), 4.48 (s, 2H), 3.60 (d, *J* = 9.5 Hz, 1H), 3.54 (q, *J* = 6.2 Hz, 2H), 3.40 (d, *J* = 9.5 Hz, 1H), 2.64 (t, *J* = 11.0 Hz, 1H), 2.39 – 2.35 (m, 1H), 2.11 (dd, *J* = 14.7, 9.2 Hz, 1H), 1.77 – 1.73 (m, 1H), 1.70 (dd, *J* = 13.1, 8.3 Hz, 2H), 1.62 – 1.58 (m, 2H), 1.48 (dd, *J* = 17.3, 7.4 Hz, 4H), 1.30 (dt, *J* = 12.7, 5.4 Hz, 2H), 0.88 (s, 9H), 0.03 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 216.6, 138.5, 128.2, 127.3, 73.2, 71.4, 63.2, 54.6, 40.9, 32.2, 31.3, 30.7, 27.4, 26.5, 25.9, 24.2, 18.3, –5.3; **HRMS**: m/z calc'd for $C_{24}H_{41}O_3Si$ $[M+H]^+$ 405.2819, found 405.2818.

<u>Preparation of Compound 15</u>

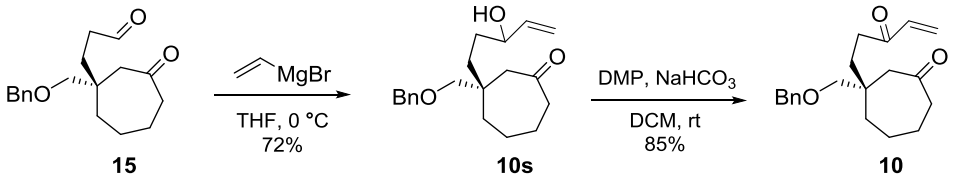


Desilylation: A solution of **14** (2.6 g, 6.57 mmol) in THF (60 mL) was treated with TBAF (4.1 g, 13.14 mmol). After stirring for 1 h at room temperature, the reaction mixture was quenched with H_2O (100 mL), extracted with EtOAc (3 × 50 mL). The combined organic phases were washed with brine (100 mL), dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (10:1) to give **15s** (1.81 g, 6.24 mmol, 95%) as colorless oil. **IR** (film, KBr) ν_{max}: 3445, 2961, 1724, 1631, 1427, 1112, 741, 698 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (m, 5H), 4.45 (d, *J* = 3.3 Hz, 2H), 3.55 (t, *J* = 5.5 Hz, 2H), 3.18 (s, 2H), 2.59 (d, *J* = 12.3 Hz, 1H), 2.46 (d, *J* = 12.2 Hz, 1H), 2.39 (dq, *J* = 8.8, 5.2, 4.8 Hz, 2H), 2.03 (s, 2H), 1.74 (ddd, *J* = 20.5, 12.2, 7.3 Hz, 4H), 1.66 – 1.62 (m, 2H), 1.42 (d, *J* = 10.9 Hz, 2H), 1.34 (d,

J = 8.2 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 214.01, 138.23, 128.2, 127.4, 76.0, 73.2, 63.1, 50.5, 43.9, 38.8, 37.4, 31.7, 26.2, 23.9; **HRMS**: m/z calc'd for $C_{18}H_{27}O_3$ $[M+H]^+$ 291.1955, found 291.1968.

Dess-Martin oxidation: Following the same procedure as described for the preparation of **14**, compound **15** (1.58 g, 5.49 mmol) as colorless oil was prepared from **15s** (1.8 g, 6.24 mmol) in 88% yield. **IR** (film, KBr) ν_{max}: 3443, 1731, 2705, 1631, 1421, 1100, 741, 703, 503, cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.68 (s, 1H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.31 – 7.25 (m, 3H), 4.46 – 4.40 (m, 2H), 3.15 (s, 2H), 2.56 (d, *J* = 12.2 Hz, 1H), 2.47 (d, *J* = 12.3 Hz, 1H), 2.41 (ddd, *J* = 25.1, 13.2, 7.8 Hz, 3H), 2.34 (dd, *J* = 13.1, 6.0 Hz, 1H), 1.79 (d, *J* = 6.7 Hz, 1H), 1.71 (ddd, *J* = 19.3, 14.8, 7.5 Hz, 3H), 1.67 – 1.58 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 213.0, 202.1, 138.0, 128.3, 127.5, 127.5, 75.4, 73.0, 49.8, 43.8, 38.5, 38.2, 37.5, 27.8, 23.9, 23.7; **HRMS**: m/z calc'd for $C_{18}H_{25}O_3$ $[M+H]^+$ 289.1798, found 289.1803.

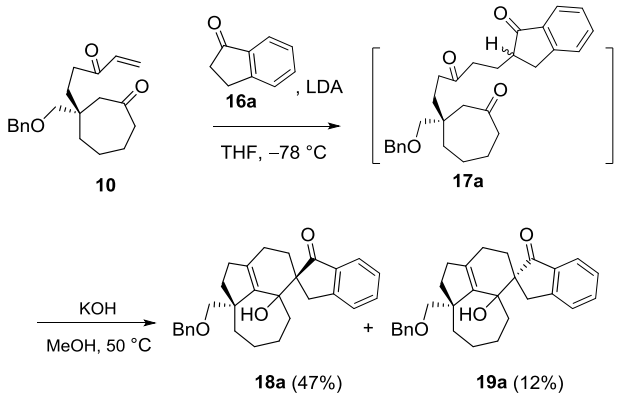
Preparation of Compound 10



Grignard Addition: To a solution of **15** (1.6 g, 5.55 mmol) in THF (55 mL) was added vinyl magnesium bromide (6.1 mL, 1 M in THF) dropwise at 0 ºC. The resulting solution was stirred at this temperature until TLC analysis showed full conversion of **15**. Then the reaction was quenched by addition of MeOH (10 mL) and *satd. aq.* sodium potassium tartrate (10 mL). The resulting mixture was vigorously stirred for 30 min. The organic layer was collected and the aqueous layer was extracted with EtOAc (3 × 50 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (3:1) to afford **10s** (1.26 g, 3.99 mmol, 72%) as colorless oil. **IR** (film, KBr) ν_{max}: 3560, 3291, 2935, 2861, 1731, 1452 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 5H), 5.85 – 5.78 (m, 1H), 5.21 (d, *J* = 17.2 Hz, 1H), 5.09 (d, *J* = 10.4 Hz, 1H), 4.50 – 4.43 (m, 2H), 4.00 (dt, *J* = 12.0, 5.6 Hz, 1H), 3.18 (s, 2H), 2.59 (dd, *J* = 12.3, 4.3 Hz, 1H), 2.47 (d, *J* = 12.4 Hz, 1H), 2.44 – 2.34 (m, 2H), 1.79 – 1.69 (m, 4H), 1.65 – 1.55 (m, 3H), 1.54 – 1.45 (m, 2H), 1.45 – 1.37 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 213.9, 213.9, 140.9, 138.3, 128.3, 127.5, 114.8, 75.9, 73.3, 73.2, 50.6, 50.5, 43.9, 38.8, 37.6, 37.5, 31.2, 31.1, 30.5, 30.4, 24.0, 23.9; **HRMS**: m/z calc'd for $C_{20}H_{29}O_3$ $[M+H]^+$ 317.2111, found 317.2111.

Dess-Martin oxidation: Following the same procedure as described for the preparation of **14**, compound **10** (1.04 g, 3.32 mmol) as colorless oil was prepared from **10s** (1.23 g, 3.90 mmol) in 85% yield. **IR** (film, KBr) ν_{max}: 3449, 2957, 1771, 1717, 1637, 1113, 702, 505 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 5H), 6.29 (dd, *J* = 17.7, 10.4 Hz, 1H), 6.16 (d, *J* = 16.9 Hz, 1H), 5.77 (d, *J* = 10.4 Hz, 1H), 4.45 (s, 2H), 3.18 (s, 2H), 2.61 – 2.57 (m, 1H), 2.52 (d, *J* = 21.2 Hz, 2H), 2.47 (dd, *J* = 6.4, 3.9 Hz, 1H), 2.41 (ddd, *J* = 12.8, 7.1, 4.7 Hz, 3H), 1.76 (d, *J* = 11.1 Hz, 2H), 1.68 (d, *J* = 5.7 Hz, 2H), 1.65 – 1.60 (m, 3H), 1.18 (d, *J* = 20.1 Hz, 1H), 0.90 (dq, *J* = 15.0, 7.4 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 213.3, 200.6, 138.2, 136.3, 128.3, 128.1, 127.6, 75.7, 73.2, 50.0, 43.9, 38.8, 37.9, 33.8, 30.2, 24.0, 23.9; **HRMS**: m/z calc'd for $C_{20}H_{27}O_3$ $[M+H]^+$ 315.1955, found 315.1963.

Preparation of Compound 18a and 19a



Michael/Double aldol reaction: To a solution of **16a** (253.7 mg, 1.92 mmol) in THF (6 mL) was added LDA (1.28 mL, 2 M in THF) dropwise at 0 ºC. After stirring for 30 min, the reaction was added a solution of **10** (200 mg, 0.64 mmol) in THF (4 mL) and stirred for another 1 h. The reaction was quenched by slow addition of *satd. aq.* NH_4Cl (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was roughly purified by flash eluting though a silica gel pad with Et_2O (20 mL). The filtrate was concentrated to afford unstable crude **17a** as yellow oil, which was redissolved in MeOH (8 mL) and treated with KOH (132 mg, 2.36 mmol). The reaction mixture was stirred for 8 h at 50 ºC, then quenched by addition of H_2O (3 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (9:1) to give **18a** (128.8 mg,0.30 mmol, 47%) and **19a** (32.9 mg, 0.077 mmol, 12%) both as colorless oil.

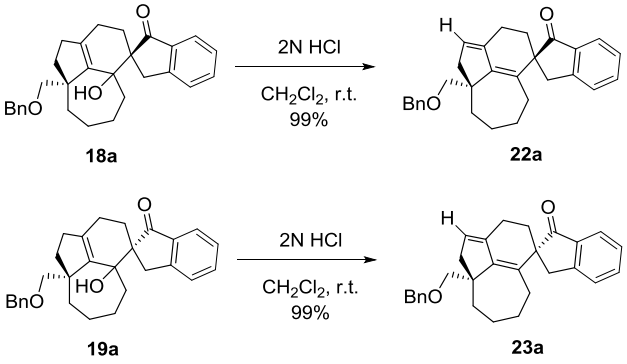
Because of the instability of crude **17a**, only the data of **^{1}H NMR** and **HRMS** have been

obtained. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.52 (s, 1H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.31 – 7.22 (m, 6H), 4.46 (d, *J* = 5.0 Hz, 1H), 4.44 – 4.37 (m, 1H), 3.34 – 3.22 (m, 2H), 3.18 (d, *J* = 7.5 Hz, 1H), 3.12 – 3.07 (m, 2H), 3.04 (s, 2H), 2.83 (dtd, *J* = 17.5, 9.1, 8.6, 5.4 Hz, 1H), 2.72 – 2.58 (m, 3H), 2.54 – 2.47 (m, 1H), 2.36 (dtd, *J* = 23.0, 11.3, 10.2, 4.2 Hz, 2H), 1.98 (ddd, *J* = 18.7, 11.8, 7.2 Hz, 2H), 1.86 (s, 2H), 1.74 (ddd, *J* = 14.5, 9.9, 6.0 Hz, 2H), 1.55 (m, 5H).; **HRMS**: m/z calc'd for $C_{29}H_{35}O_4$ $[M+H]^+$ 447.2530, found 447.2541.

18a IR (film, KBr) ν_{max}: 3631, 3426, 1736, 1634, 1320, 770, 712, 503 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.25 (dd, *J* = 6.9, 3.2 Hz, 2H), 7.19 – 7.12 (m, 3H), 5.43 (s, 1H), 4.68 (d, *J* = 11.2 Hz, 1H), 4.41 (d, *J* = 11.2 Hz, 1H), 3.72 (d, *J* = 8.0 Hz, 1H), 3.62 (d, *J* = 16.5 Hz, 1H), 3.39 (d, *J* = 8.1 Hz, 1H), 2.71 (d, *J* = 16.5 Hz, 1H), 2.45 (ddd, *J* = 17.0, 10.3, 7.4 Hz, 1H), 2.19 – 2.12 (m, 2H), 2.01 (d, *J* = 13.0 Hz, 3H), 1.75 – 1.67 (m, 3H), 1.42 (dq, *J* = 14.7, 7.1 Hz, 4H), 1.29 (s, 2H), 0.91 – 0.83 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 207.9, 152.8, 143.2, 137.3, 136.7, 136.6, 133.9, 128.2, 128.2, 127.6, 126.9, 126.3, 123.5, 77.3, 73.9, 73.7, 59.5, 54.6, 40.6, 38.1, 34.7, 34.4, 33.1, 30.9, 25.2, 23.9, 23.6; **HRMS**: m/z calc'd for $C_{29}H_{33}O_3$ $[M+H]^+$ 429.2424, found 429.2421.

19a IR (film, KBr) ν_{max}: 3619, 3413, 1724, 1633, 1315, 779, 503, cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.31 – 7.15 (m, 7H), 5.01 (s, 1H), 4.60 – 4.49 (m, 2H), 3.54 (d, *J* = 8.3 Hz, 1H), 3.30 (d, *J* = 8.3 Hz, 1H), 3.26 (d, *J* = 17.1 Hz, 1H), 2.85 (d, *J* = 17.1 Hz, 1H), 2.49 (d, *J* = 2.9 Hz, 1H), 2.47 – 2.43 (m, 1H), 2.37 (dd, *J* = 16.2, 8.3 Hz, 1H), 2.27 – 2.14 (m, 2H), 2.11 (d, *J* = 6.4 Hz, 1H), 1.95 (t, *J* = 12.8 Hz, 1H), 1.82 – 1.71 (m, 1H), 1.63 (d, *J* = 8.5 Hz, 2H), 1.42 (ddt, *J* = 20.6, 13.8, 7.6 Hz, 4H), 1.31 – 1.25 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 210.2, 153.5, 145.1, 138.3, 137.8, 136.7, 133.9, 128.5, 127.9, 127.6, 126.5, 125.2, 123.4, 77.6, 76.5, 74.0, 58.8, 54.3, 37.6, 35.1, 34.7, 33.0, 28.5, 25.6, 23.9, 23.7; **HRMS**: m/z calc'd for $C_{29}H_{33}O_3$ $[M+H]^+$ 429.2424, found 429.2430.

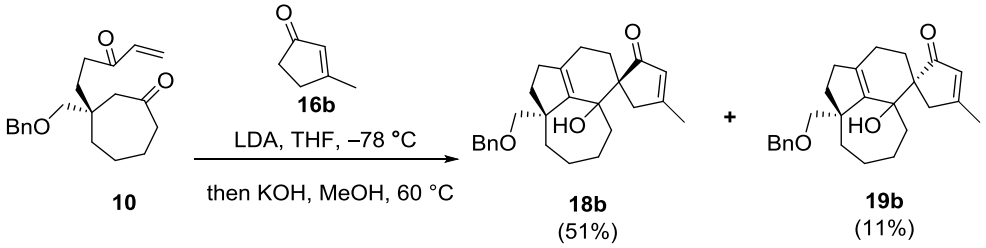
Preparation of Compound 22a and 23a



Elimination: A solution of **18a** (40 mg, 0.093 mmol) in CH_2Cl_2 (2 mL) was treated with *aq.* HCl (*2N*, 2 mL) at room temperature. The reaction mixture was stirred for 20 min, then quenched with *satd. aq.* $NaHCO_3$ (4 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3 × 3 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (3:1) to give **22a** (38.2 mg, 0.093 mmol) as colorless oil. **IR** (film, KBr) ν_{max}: 3689, 2921, 1731, 1680, 1538, 1364, 1221, 1006 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.6 Hz, 1H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.36 (p, *J* = 7.6 Hz, 5H), 7.29 – 7.26 (m, 1H), 5.54 (s, 1H), 4.57 (s, 2H), 3.81 (d, *J* = 9.1 Hz, 1H), 3.33 (d, *J* = 9.1 Hz, 1H), 3.09 (s, 2H), 2.79 (d, *J* = 17.7 Hz, 1H), 2.54 (d, *J* = 15.9 Hz, 1H), 2.43 – 2.33 (m, 1H), 2.26 (t, *J* = 14.7 Hz, 1H), 2.11 (t, *J* = 16.4 Hz, 2H), 1.73 (td, *J* = 17.3, 13.3, 4.1 Hz, 3H), 1.65 – 1.58 (m, 2H), 1.49 (dd, *J* = 8.2, 4.5 Hz, 1H), 1.46 – 1.42 (m, 1H), 1.34 (d, *J* = 6.3 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.5, 153.6, 147.8, 139.4, 139.1, 136.7, 134.7, 131.8, 128.2, 127.4, 127.28, 126.6, 125.8, 124.2, 73.2, 72.3, 56.4, 49.7, 44.5, 39.1, 34.8, 33.3, 31.8, 30.4, 26.7, 21.9; **HRMS**: m/z calc'd for $C_{29}H_{31}O_2$ $[M+H]^+$ 411.2319, found 411.2316.

Elimination: Following the same procedure as described for the preparation of **22a**, compound **23a** (15.3 mg,0.037 mmol) as yellow oil was prepared from **19a** (16 mg, 0.037 mmol) in 99% yield. **23a : IR** (film, KBr) ν_{max}: 3663, 2964, 1726, 1671, 1538, 1363, 1001, cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 7.4 Hz, 1H), 7.34 (d, *J* = 4.4 Hz, 4H), 7.28 (d, *J* = 4.4 Hz, 1H), 5.54 (s, 1H), 4.57 – 4.50 (m, 2H), 3.71 (d, *J* = 8.8 Hz, 1H), 3.21 (d, *J* = 8.8 Hz, 1H), 3.05 (q, *J* = 17.5 Hz, 2H), 2.69 (d, *J* = 17.4 Hz, 1H), 2.55 – 2.49 (m, 1H), 2.25 – 2.16 (m, 3H), 2.11 – 2.07 (m, 1H), 1.79 (td, *J* = 13.2, 4.2 Hz, 2H), 1.60 (d, *J* = 7.5 Hz, 2H), 1.51 – 1.48 (m, 2H), 1.27 (d, *J* = 18.2 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.2, 153.46, 147.8, 139.7, 138.9, 136.6, 134.7, 130.8, 128.2, 127.4, 127.3, 126.5, 125.8, 124.3, 73.2, 71.4, 56.6, 50.4, 44.1, 39.9, 34.7, 33.7, 31.4, 28.0, 26.9, 22.2; **HRMS**: m/z calc'd for $C_{29}H_{31}O_2$ $[M+H]^+$ 411.2319, found 411.2325.

<u>Preparation of Compound 18b and 19b</u>

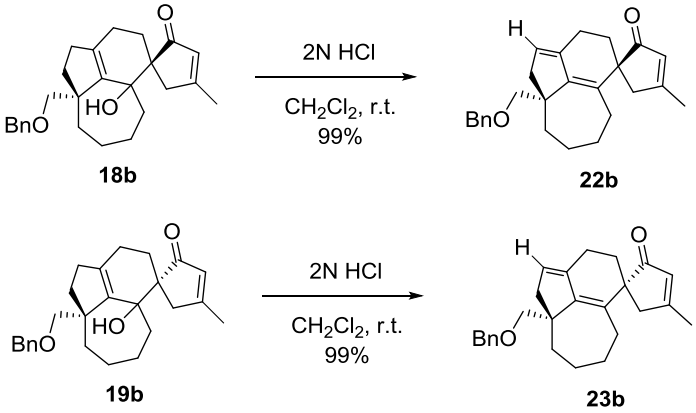


Michael/Double aldol reaction: Following the same procedure as described for the preparation of **18a** and **19a**, compound **18b** (128 mg, 0.326 mmol, 51%, colorless oil) and **19b** (27.6 mg, 0.070 mmol, 11%, colorless oil) were prepared from **10** (200 mg, 0.64 mmol)

18b IR (film, KBr) ν_{max}: 3443, 2933, 2359, 1735, 1211, 770 cm^{-1}; **^{1}H NMR** (600 MHz, MeOD) δ 7.38 – 7.26 (m, 5H), 5.76 (s, 1H), 4.60 – 4.55 (m, 2H), 3.60 (d, *J* = 8.4 Hz, 1H), 3.41 (d, *J* = 8.4 Hz, 1H), 2.61 (d, *J* = 18.6 Hz, 1H), 2.43 – 2.34 (m, 3H), 2.22 (ddd, *J* = 13.5, 10.7, 7.1 Hz, 1H), 2.16 – 2.10 (m, 2H), 2.09 – 2.05 (m, 1H), 1.95 (d, *J* = 12.9 Hz, 1H), 1.89 (s, 3H), 1.79 – 1.73 (m, 1H), 1.68 – 1.59 (m, 3H), 1.55 (dd, *J* = 12.8, 7.3 Hz, 1H), 1.46 (ddd, *J* = 19.8, 14.2, 6.6 Hz, 2H), 1.37 (td, *J* = 13.4, 4.0 Hz, 1H), 1.33 – 1.22 (m, 2H); **^{13}C NMR** (101 MHz, CD_3OD) δ 215.7, 180.4, 145.4, 140.0, 138.6, 131.0, 129.6, 129.1, 128.8, 78.8, 77.3, 75.0, 59.3, 55.6, 45.0, 38.3, 36.5, 35.7, 33.9, 29.6, 26.9, 24.7, 24.7, 19.2; **HRMS**: m/z calc'd for $C_{26}H_{33}O_3$ $[M+H]^+$ 393.2424, found 393.2421.

19b IR (film, KBr) ν_{max}: 3451, 2936, 2358, 1740, 1210 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.23 (m, 5H), 5.74 (s, 1H), 4.55 (d, *J* = 10.6 Hz, 1H), 4.39 (d, *J* = 10.7 Hz, 1H), 3.67 (d, *J* = 8.1 Hz, 1H), 3.40 (d, *J* = 8.2 Hz, 1H), 2.96 (d, *J* = 18.0 Hz, 1H), 2.45 – 2.36 (m, 1H), 2.18 (d, *J* = 18.1 Hz, 1H), 2.12 (d, *J* = 4.2 Hz, 3H), 2.08 – 1.97 (m, 4H), 1.86 (d, *J* = 13.0 Hz, 1H), 1.80 – 1.70 (m, 2H), 1.67 – 1.60 (m, 4H), 1.54 – 1.49 (m, 1H), 1.48 – 1.38 (m, 3H), 1.38 – 1.29 (m, 3H); **^{13}C NMR** (151 MHz, CD_3OD) δ 213.7, 178.9, 143.4, 138.8, 138.6, 129.5, 129.4, 128.9, 78.4, 75.6, 74.8, 59.4, 55.7, 45.9, 41.5, 35.6, 35.6, 33.9, 32.2, 26.4, 24.7, 24.6, 19.3; **HRMS**: m/z calc'd for $C_{26}H_{33}O_3$ $[M+H]^+$ 393.2424, found 393.2431.

<u>Preparation of Compound 22b and 23b</u>

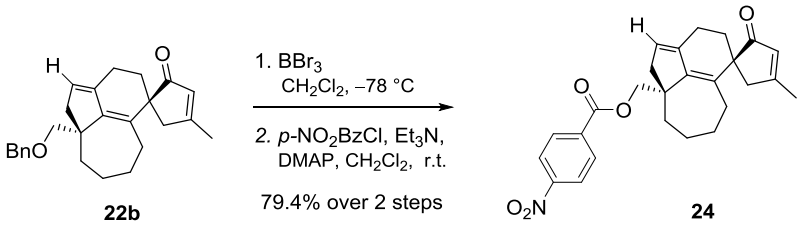


Elimination: Following the same procedure as described for the preparation of **22a**, compound **22b** (85.2 mg,0.228 mmol) as colorless yellow oil was prepared from **18b** (90 mg, 0.230 mmol) in 99% yield; compound **23b** (18.9 mg, 0.050 mmol) as colorless oil was prepared from **18b** (20 mg, 0.051 mmol) in 99% yield.

22b: IR (film, KBr) ν_{max}: 3310, 3003, 2369, 1737, 1631, 1210, 953, 770 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.17 (m, 4H), 5.94 (s, 1H), 5.49 (s, 1H), 4.56 – 4.48 (m, 2H), 3.68 (d, *J* = 8.8 Hz, 1H), 3.16 (d, *J* = 8.8 Hz, 1H), 2.65 (d, *J* = 17.1 Hz, 1H), 2.46 (q, *J* = 18.9 Hz, 3H), 2.18 (d, *J* = 13.6 Hz, 1H), 2.08 (d, *J* = 27.8 Hz, 6H), 1.76 (td, *J* = 14.4, 13.2, 4.5 Hz, 2H), 1.71 – 1.63 (m, 2H), 1.59 – 1.54 (m, 2H), 1.48 – 1.38 (m, 2H), 1.27 (dd, *J* = 9.8, 2.5 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 214.0, 177.2, 147.5, 139.8, 138.9, 130.5, 129.9, 128.2, 127.3, 126.9, 125.6, 73.6, 71.4, 55.6, 50.3, 47.0, 44.0, 34.6, 33.7, 30.4, 28.0, 26.9, 22.2, 19.5; **HRMS**: m/z calc'd for $C_{26}H_{31}O_2$ $[M+H]^+$ 375.2319, found 375.2323.

23b: IR (film, KBr) ν_{max}: 3310, 2368, 1725, 1639, 1212, 941, 772 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 5H), 5.93 (s, 1H), 5.49 (s, 1H), 4.57 – 4.51 (m, 2H), 3.77 (d, *J* = 9.1 Hz, 1H), 3.27 (d, *J* = 9.1 Hz, 1H), 2.76 (d, *J* = 17.7 Hz, 1H), 2.48 (s, 1H), 2.34 – 2.26 (m, 2H), 2.13 (s, 3H), 2.10 (s, 2H), 1.75 (d, *J* = 14.5 Hz, 2H), 1.65 (dt, *J* = 13.3, 6.7 Hz, 2H), 1.51 – 1.47 (m, 1H), 1.43 (dd, *J* = 8.8, 5.1 Hz, 1H), 1.30 (dd, *J* = 10.6, 3.8 Hz, 2H), 1.20 (s, 1H), 0.92 – 0.86 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 213.3, 177.3, 147.4, 139.5, 139.1, 131.6, 130.1, 128.2, 127.4, 127.2, 125.6, 73.1, 72.2, 55.51, 49.6, 46.3, 44.5, 34.8, 33.4, 30.9. 30.4, 26.7, 21.9, 19.5; **HRMS**: m/z calc'd for $C_{26}H_{31}O_2$ $[M+H]^+$ 375.2319, found 375.2318.

Preparation of Compound 24

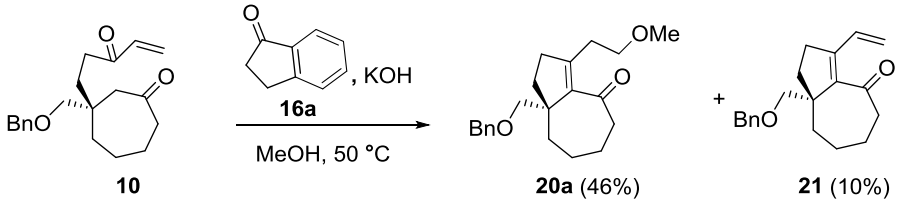


22b **24**

Debenzylation and following esterification: To a solution of **22b** (80 mg, 0.213 mmol) in CH_2Cl_2 (2 mL) was added BBr_3 (6.1 mL, 1 M in DCM) dropwise at –78 ºC. After stirring for 30 min, the reaction was quenched by addition of MeOH (2 mL) and diluting with brine (5 mL). The reaction was allowed to warm to room temperature, stirred for 30 min, and extracted with EtOAc (3 × 5 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 (2 mL), then Et_3N (0.1 mL, 0.70 mmol), 4-dimethylaminopyridine (4-DMAP, 8.6 mg, 0.07 mmol) and 4-nitrobenzoyl chloride (52 mg, 0.28 mmol) were added at 25 °C in turn. The mixture was stirred until TLC indicated complete consumption of the starting material (about 2 h). The reaction mixture was diluted with *satd. aq.* $NaHCO_3$ (3 mL) and CH_2Cl_2 (3 mL) and stirred for 30 min. The organic layer was collected and the aqueous layer was extracted with CH_2Cl_2 (3 × 3 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and

evaporated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (2:1) to give the ester **24** (59 mg, 0.137 mmol, 79.4% over 2 steps) as a yellow solid. **IR** (film, KBr) ν_{max}: 3688, 2925, 1732, 1683, 1530, 1359, 998 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 48.5, 8.6 Hz, 4H), 5.96 (s, 1H), 5.53 (s, 1H), 4.51 – 4.31 (m, 2H), 2.64 – 2.55 (m, 1H), 2.50 (d, *J* = 13.1 Hz, 2H), 2.40 – 2.25 (m, 3H), 2.13 (s, 3H), 2.08 – 1.99 (m, 2H), 1.86 (d, *J* = 12.8 Hz, 1H), 1.76 – 1.64 (m, 4H), 1.51 – 1.41 (m, 2H), 1.26 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 213.5, 177.5, 164.9, 150.5, 145.9, 140.3, 135.8, 132.3, 130.6, 130.0, 124.8, 123.6, 60.7, 55.6, 49.2, 46.8, 44.2, 34.8, 33.6, 30.3 27.7, 26.8, 22.2, 19.5; **HRMS**: m/z calc'd for $C_{26}H_{28}NO_5$ $[M+H]^+$ 434.1962, found 434.1979.

Preparation of Compound 20a and 21



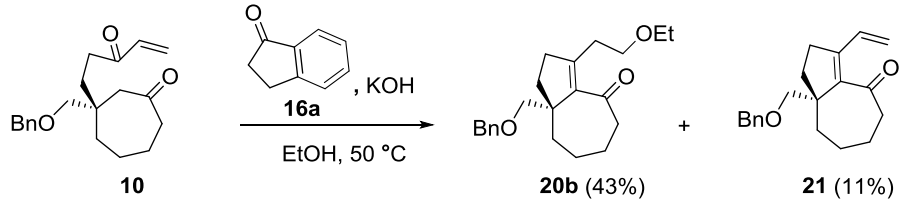
Michael/Aldol reaction: A solution of **10** (200 mg, 0.64 mmol) in MeOH (6 mL) was treated with KOH (179 mg, 3.20 mmol) at room temperature. The reaction was allowed to warm to 50 °C and stirred for 8 h. Then it was quenched with H_2O (5 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by silica gel column chromatography eluting with petroleum ether/ethyl acetate (12:1) to give **20a** (96.6 mg, 0.294 mmol, 46%) and **21** (18.9 mg, 0.064 mmol, 10%) as colorless oil.

20a IR (film, KBr) ν_{max}: 3446, 2933, 2363, 1737, 1220, 772 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (tt, *J* = 12.1, 6.0 Hz, 5H), 4.50 (s, 2H), 3.56 (d, *J* = 9.0 Hz, 1H), 3.47 (t, *J* = 6.6 Hz, 2H), 3.38 (d, *J* = 9.0 Hz, 1H), 3.30 (s, 3H), 2.75 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.64 – 2.56 (m, 1H), 2.44 (d, *J* = 6.3 Hz, 4H), 2.02 (dd, *J* = 14.3, 6.1 Hz, 2H), 1.76 (d, *J* = 11.6 Hz, 2H), 1.57 (ddd, *J* = 18.3, 9.7, 4.6 Hz, 4H), 1.53 – 1.44 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 204.6, 155.0, 142.5, 138.5, 128.3, 127.5, 73.8, 73.3, 70.9, 58.3, 53.7, 44.4, 36.9, 36.1, 34.9, 30.6, 25.4, 24.4; **HRMS**: m/z calc'd for $C_{21}H_{28}O_3$ $[M]^+$ 328.2033, found 328.2041.

21 IR (film, KBr) ν_{max}: 3446, 3059, 1737, 1631, 978, 692 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 5H), 7.09 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.49 – 5.32 (m, 2H), 4.55 – 4.46 (m, 2H), 3.57 (d, *J* = 9.0 Hz, 1H), 3.42 (d, *J* = 9.0 Hz, 1H), 2.59 (t, *J* = 7.4 Hz, 2H), 2.51 – 2.44 (m, 2H),

2.05 (dt, *J* = 15.4, 7.9 Hz, 2H), 1.83 – 1.74 (m, 2H), 1.64 (d, *J* = 7.2 Hz, 1H), 1.57 (s, 2H), 1.25 (s, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 204.8, 150.2, 143.8, 138.3, 132.2, 128.3, 127.6, 127.6, 120.6, 73.6, 73.4, 54.4, 44.3, 36.9, 35.6, 29.9, 25.3, 24.4; **HRMS**: m/z calc'd for $C_{20}H_{25}O_2$ $[M+H]^+$ 297.1849, found 297.1844.

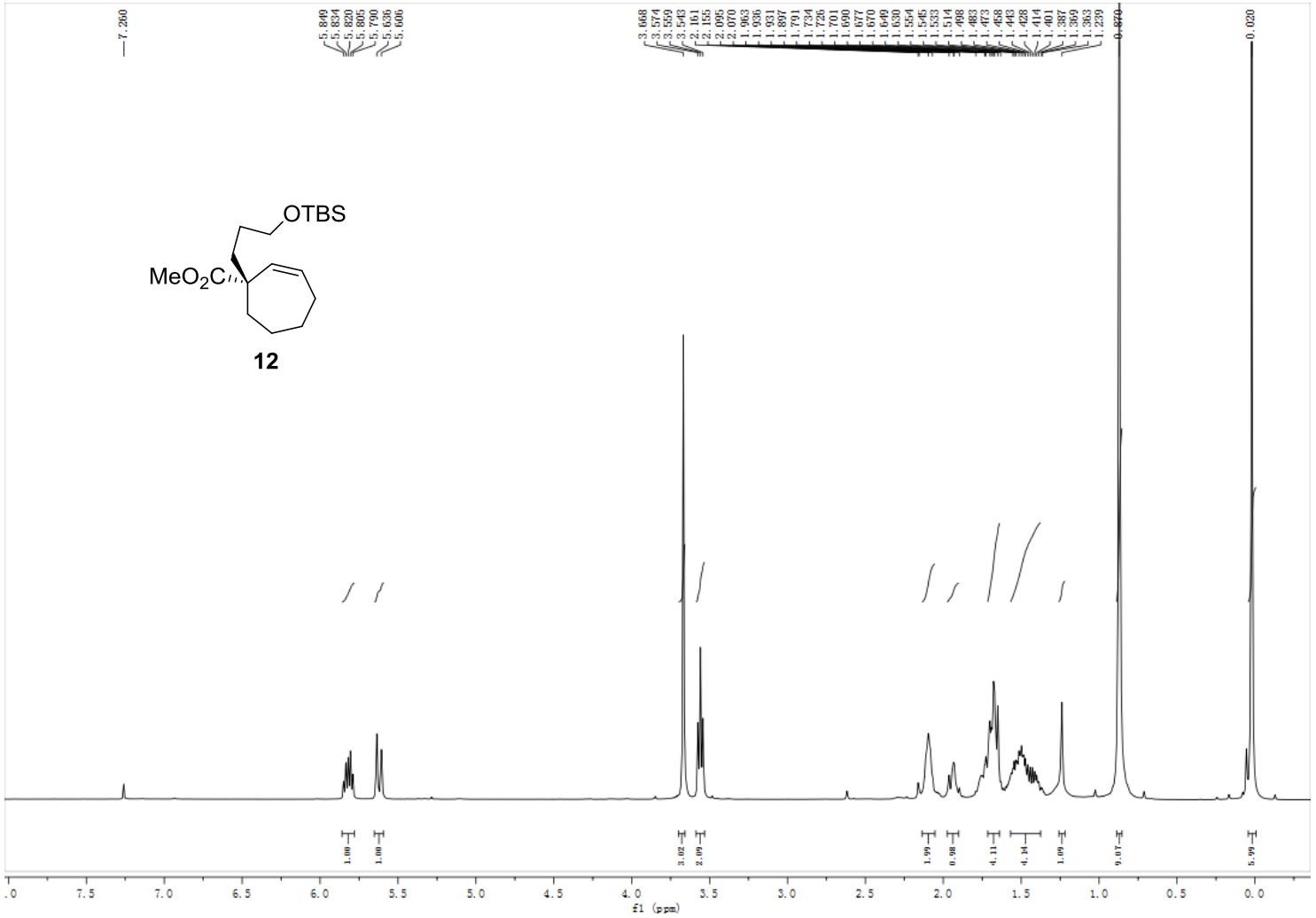
Preparation of Compound 20b and 21

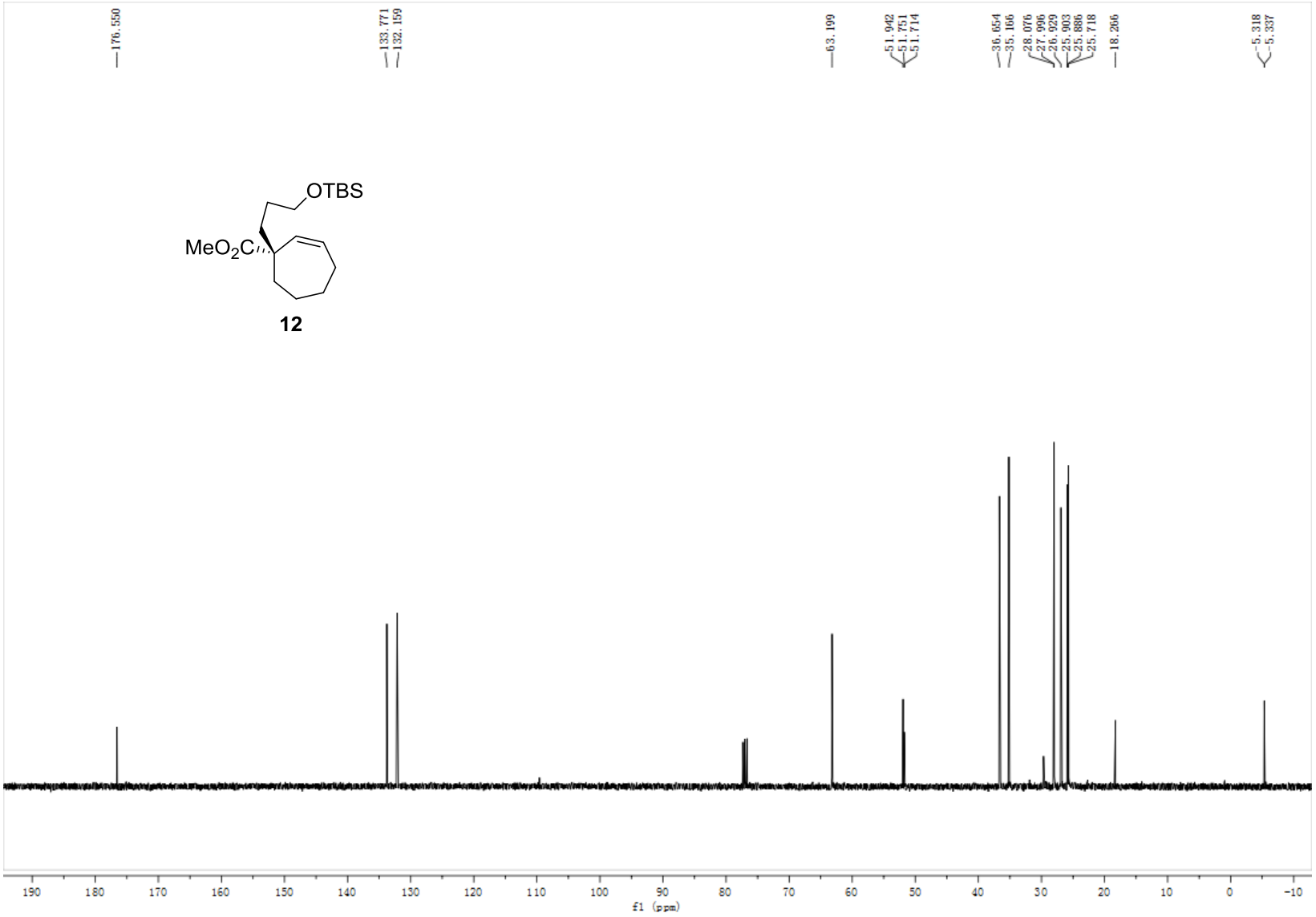


Michael/Aldol reaction: Following the same procedure as described for the preparation of **20a** and **21**, compound **20b** (47.1 mg,0.138 mmol, 43%, colorless oil) and **21** (10.4 mg,0.035 mmol, 11%, colorless oil) were prepared from **10** (100 mg, 0.32 mmol).

20b: IR (film, KBr) ν_{max}: 3456, 2939, 2401, 1738, 1212, 781 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 5H), 4.53 – 4.46 (m, 2H), 3.56 (d, *J* = 9.0 Hz, 1H), 3.51 (t, *J* = 6.6 Hz, 2H), 3.45 (dt, *J* = 14.1, 7.0 Hz, 2H), 3.38 (d, *J* = 9.0 Hz, 1H), 2.75 (dt, *J* = 13.7, 7.0 Hz, 1H), 2.59 (dt, *J* = 13.1, 6.1 Hz, 1H), 2.45 (tq, *J* = 24.1, 12.2, 9.6 Hz, 4H), 2.05 – 1.97 (m, 2H), 1.77 (t, *J* = 13.2 Hz, 2H), 1.62 (s, 2H), 1.50 (dd, *J* = 23.2, 9.9 Hz, 3H), 1.16 (t, *J* = 7.0 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 204.6, 155.2, 142.5, 138.5, 128.3, 127.5, 73.8, 73.3, 68.8, 65.9, 53.7, 44.4, 36.9, 36.1, 34.9, 30.9, 25.4, 24.4, 15.2; **HRMS**: m/z calc'd for $C_{22}H_{31}O_3$ $[M+H]^+$ 343.2268, found 343.2281.

3.Copies of ^{1}H- and ^{13}C-NMR spectra

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51.714
36.654
35.166
28.076
27.996
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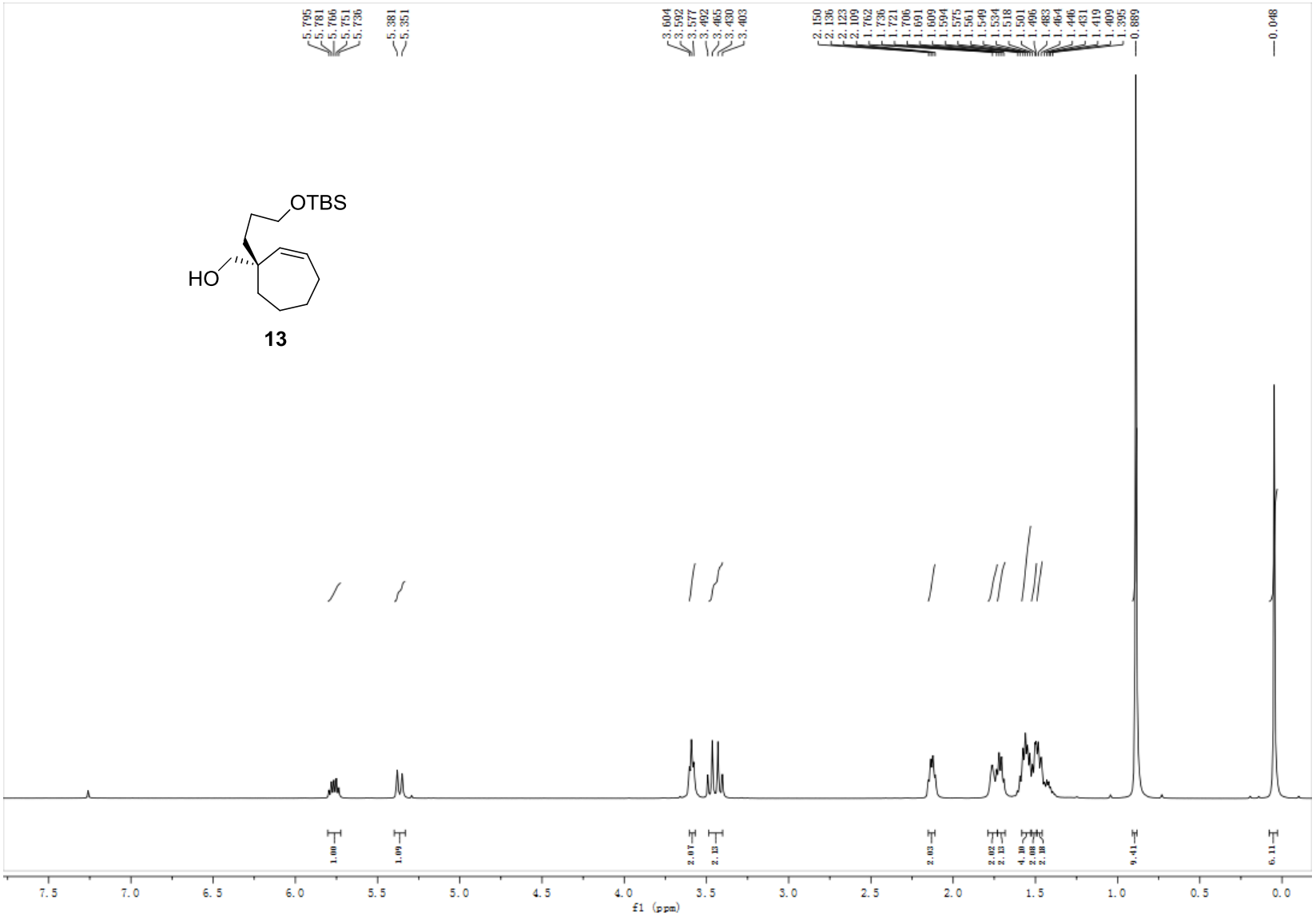
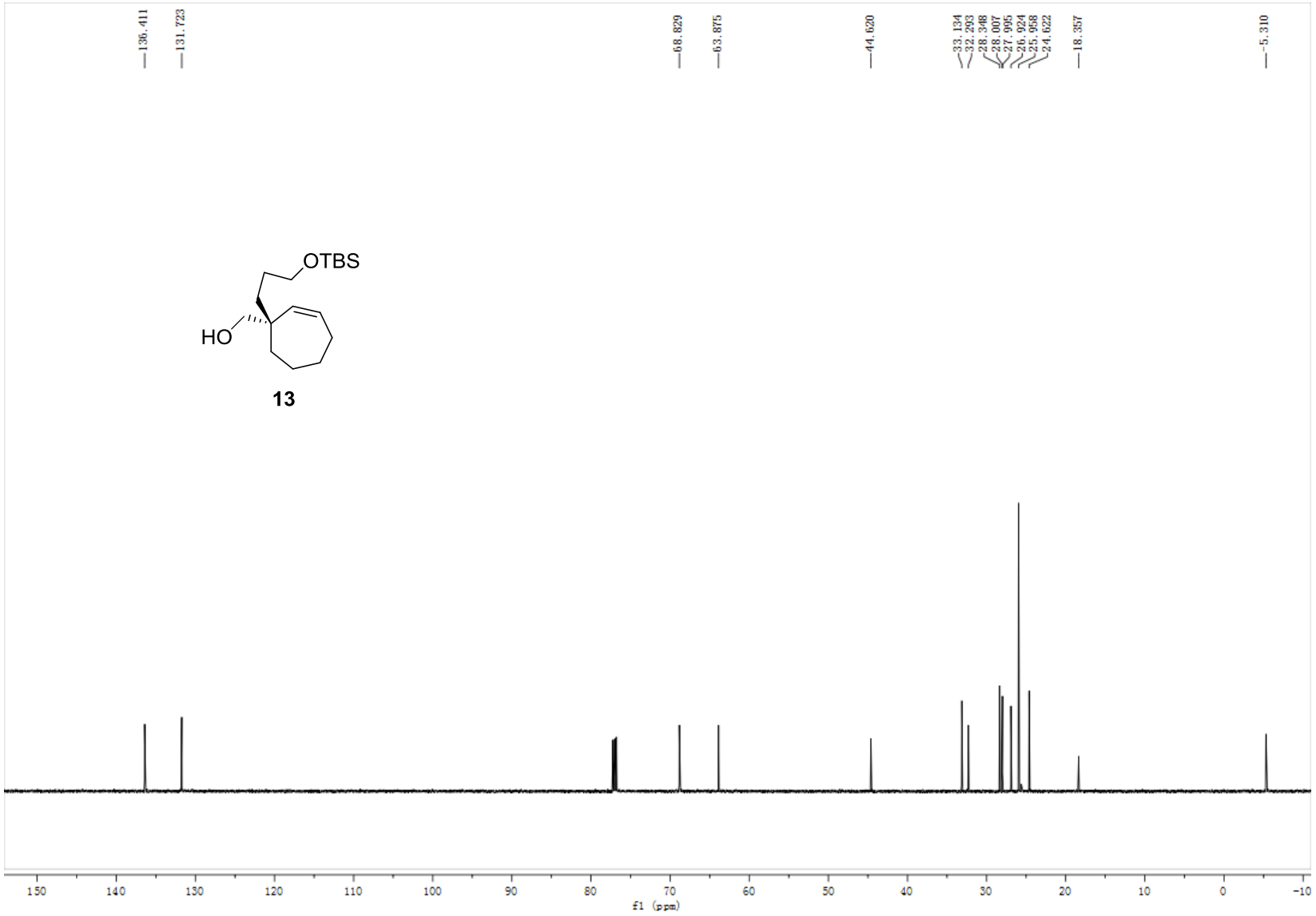
25.903
25.886
25.718
18.266
-5.318
-5.337
OTBS
MeO2C
12
f1 (ppm)


OTBS
HO
13
f1 (ppm)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68.829
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32.293
28.348
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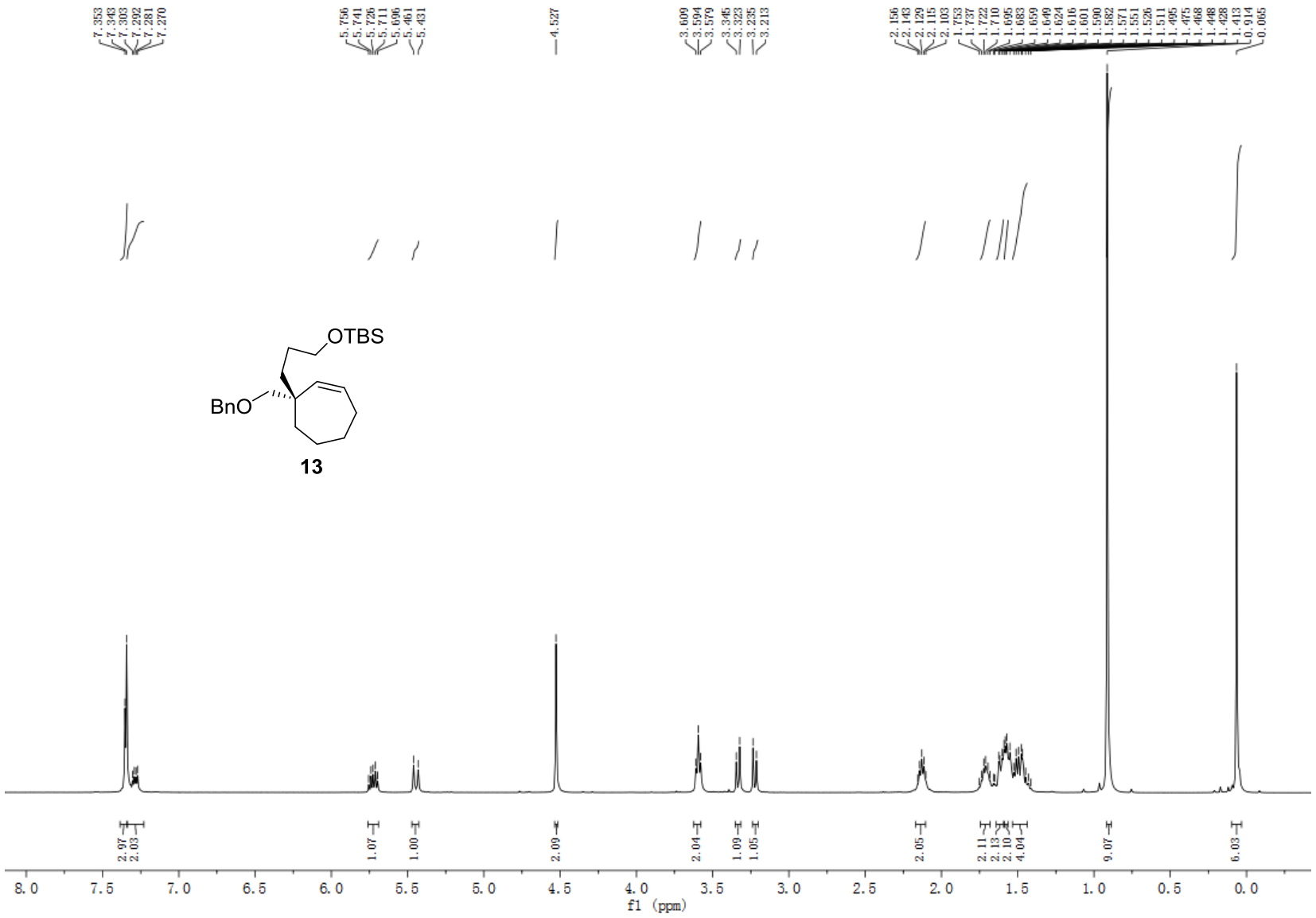
27.995
26.924
25.958
24.622
18.357
-5.310
OTBS
HO
13
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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5.461
5.431
4.527
3.609
3.594
3.579
3.345
3.323
3.235
3.213
2.156
2.143
2.129
2.115
2.103
1.753
1.737
1.722
1.710
1.695
1.683
1.659
1.649
1.624
1.616
1.601
1.590
1.582
1.571
1.551
1.526
1.511
1.495
1.475
1.468
1.448
1.428
1.413
0.914
0.065
OTBS
BnO
13
2.97
2.03
1.07
1.00
2.09
2.04
1.09
1.05
2.05
2.11
2.13
2.10
4.04
9.07
6.03
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
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1.0
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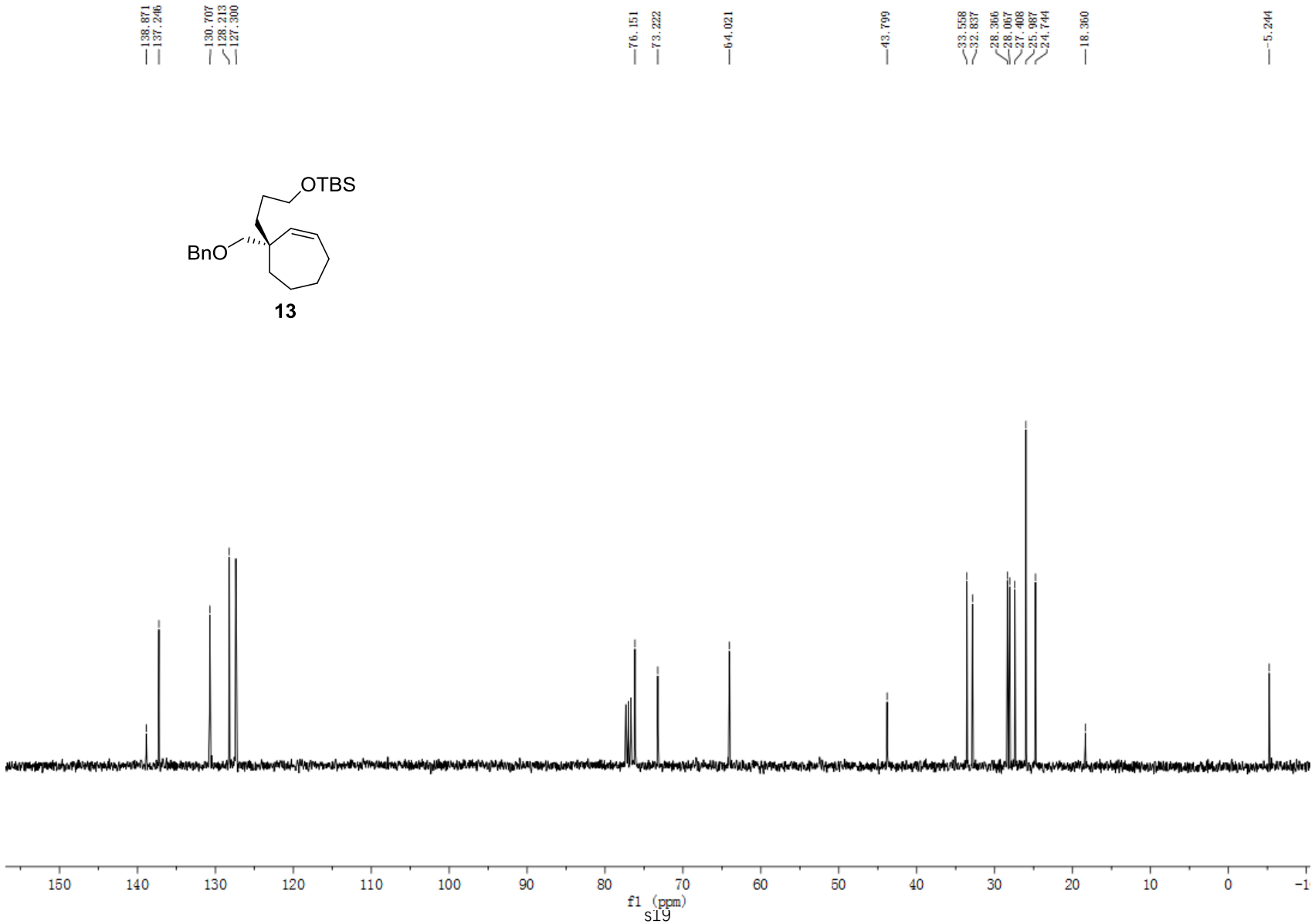
0.0
f1 (ppm)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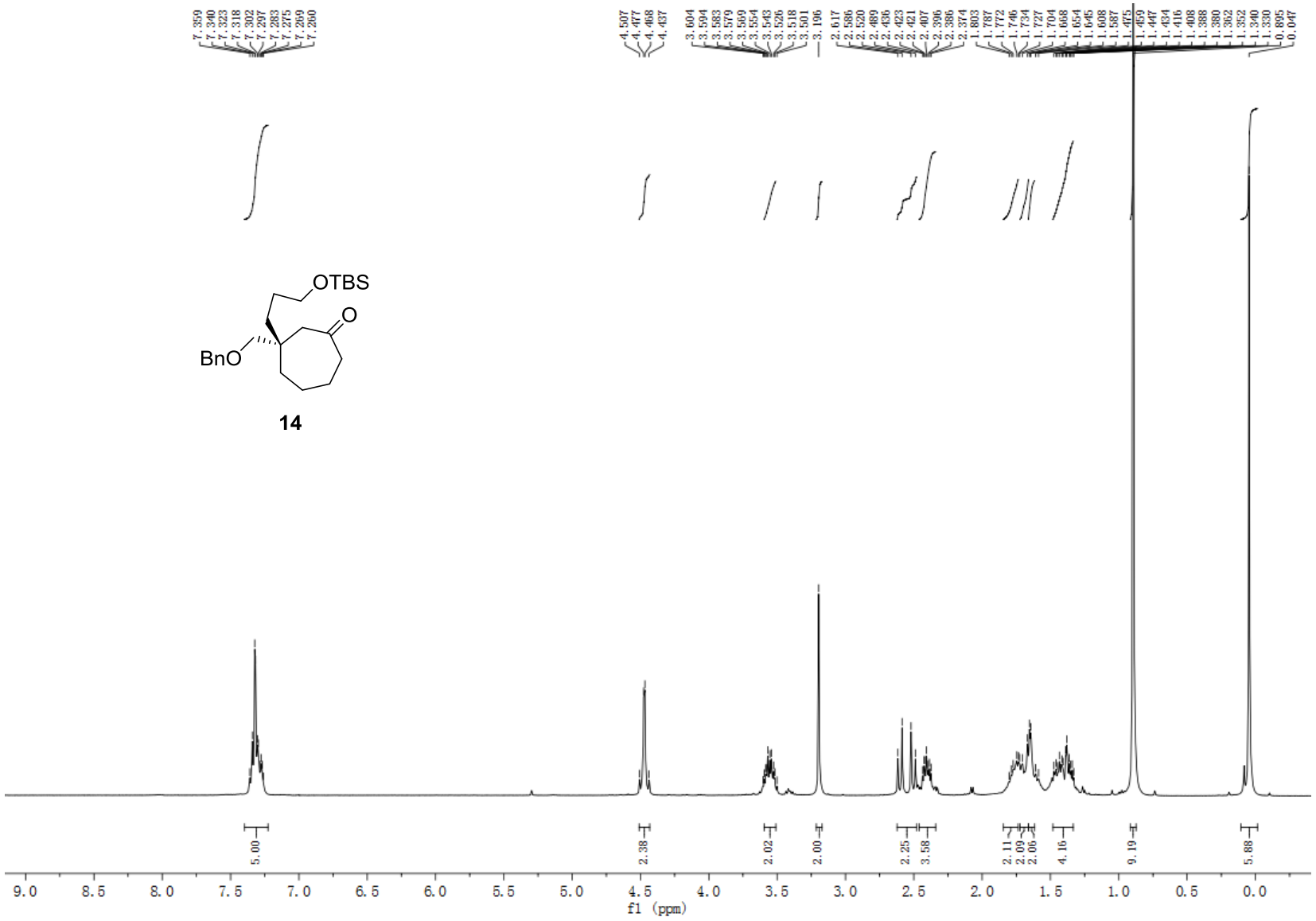
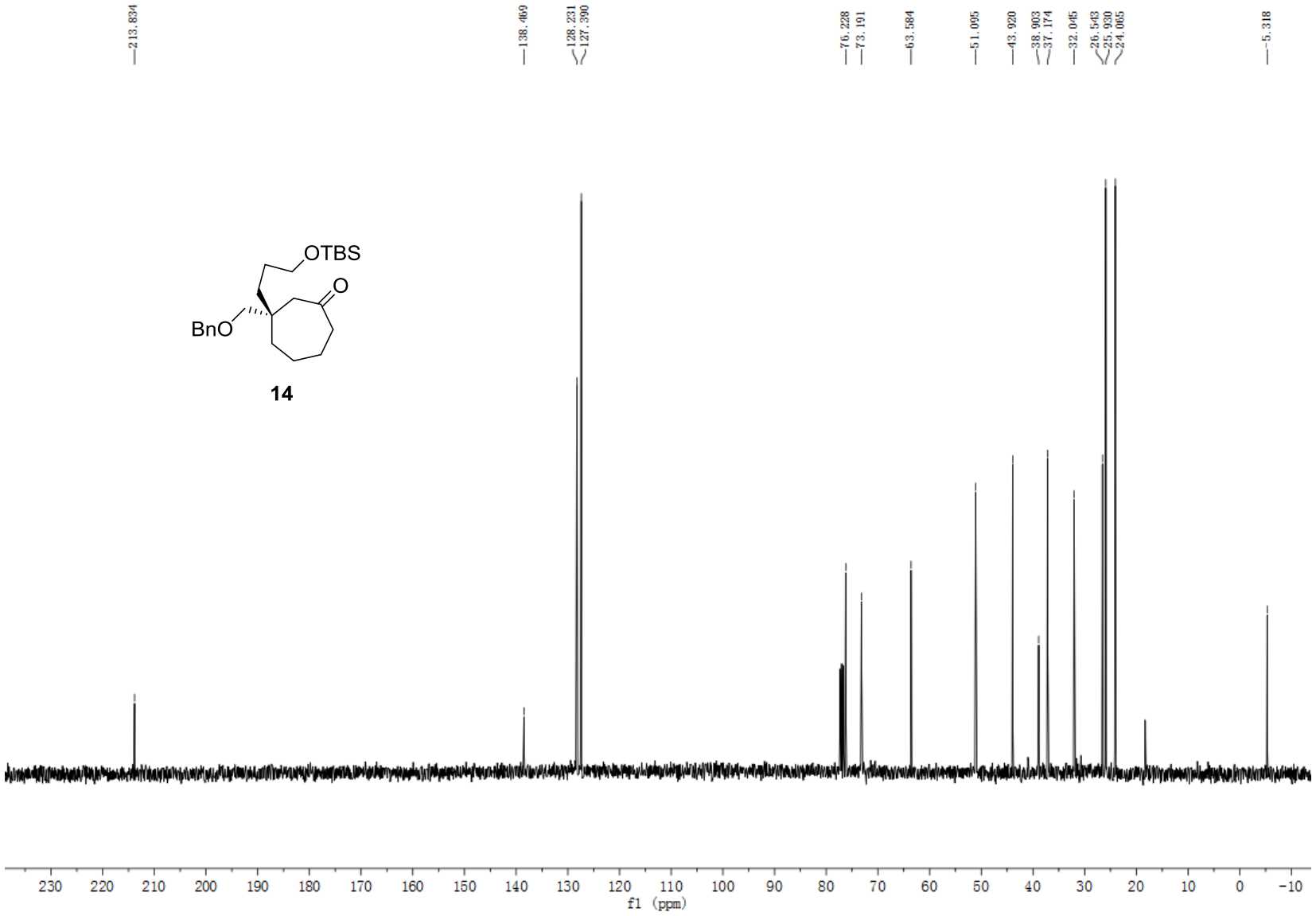
73.222
64.021
43.799
33.558
32.837
28.366
28.067
27.408
25.987
24.744
18.360
-5.244
OTBS
BnO
13
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


OTBS
O
BnO
14
f1 (ppm)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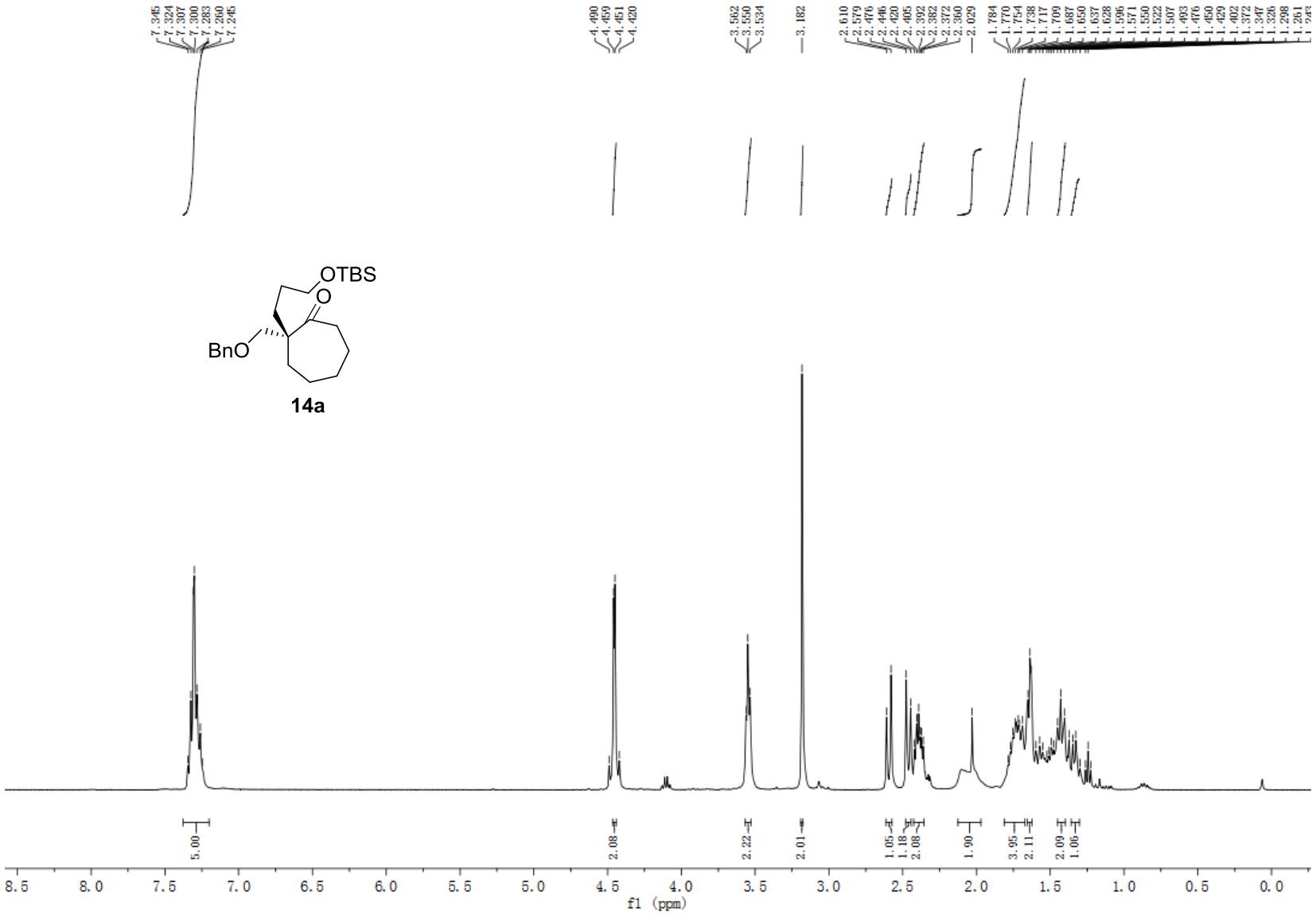
32.045
26.543
25.930
24.065
-5.318
OTBS
O
BnO
14
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.307
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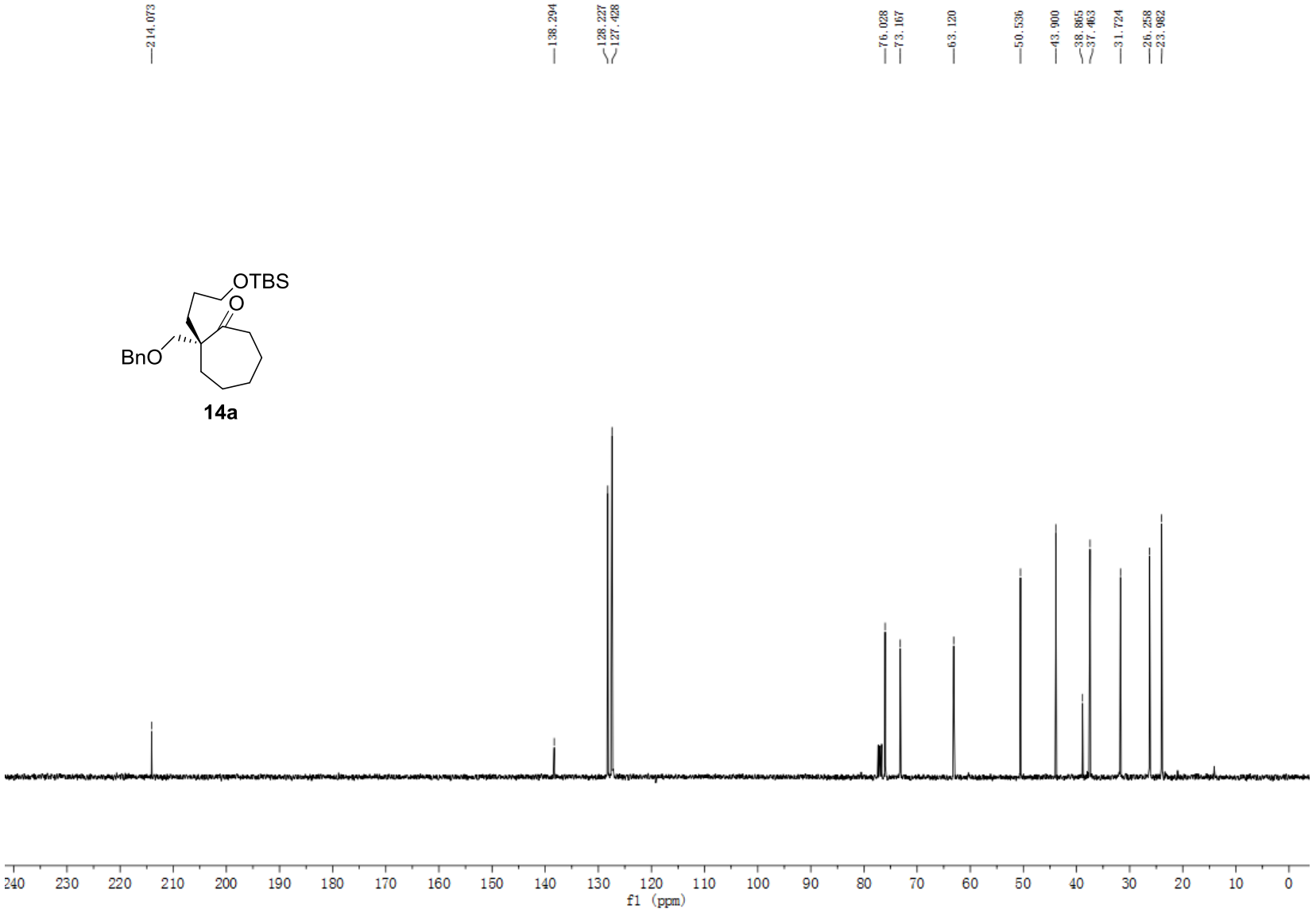
7.283
7.260
7.245
4.490
4.459
4.451
4.420
3.562
3.550
3.534
3.182
2.610
2.579
2.476
2.446
2.420
2.405
2.392
2.382
2.372
2.360
2.029
1.784
1.770
1.754
1.738
1.717
1.709
1.687
1.650
1.637
1.628
1.596
1.571
1.550
1.522
1.507
1.493
1.476
1.450
1.429
1.402
1.372
1.347
1.326
1.298
1.261
OTBS
O
BnO
14a
5.00
2.08
2.22
2.01
1.05
1.18
2.08
1.90
3.95
2.11
2.09
1.06
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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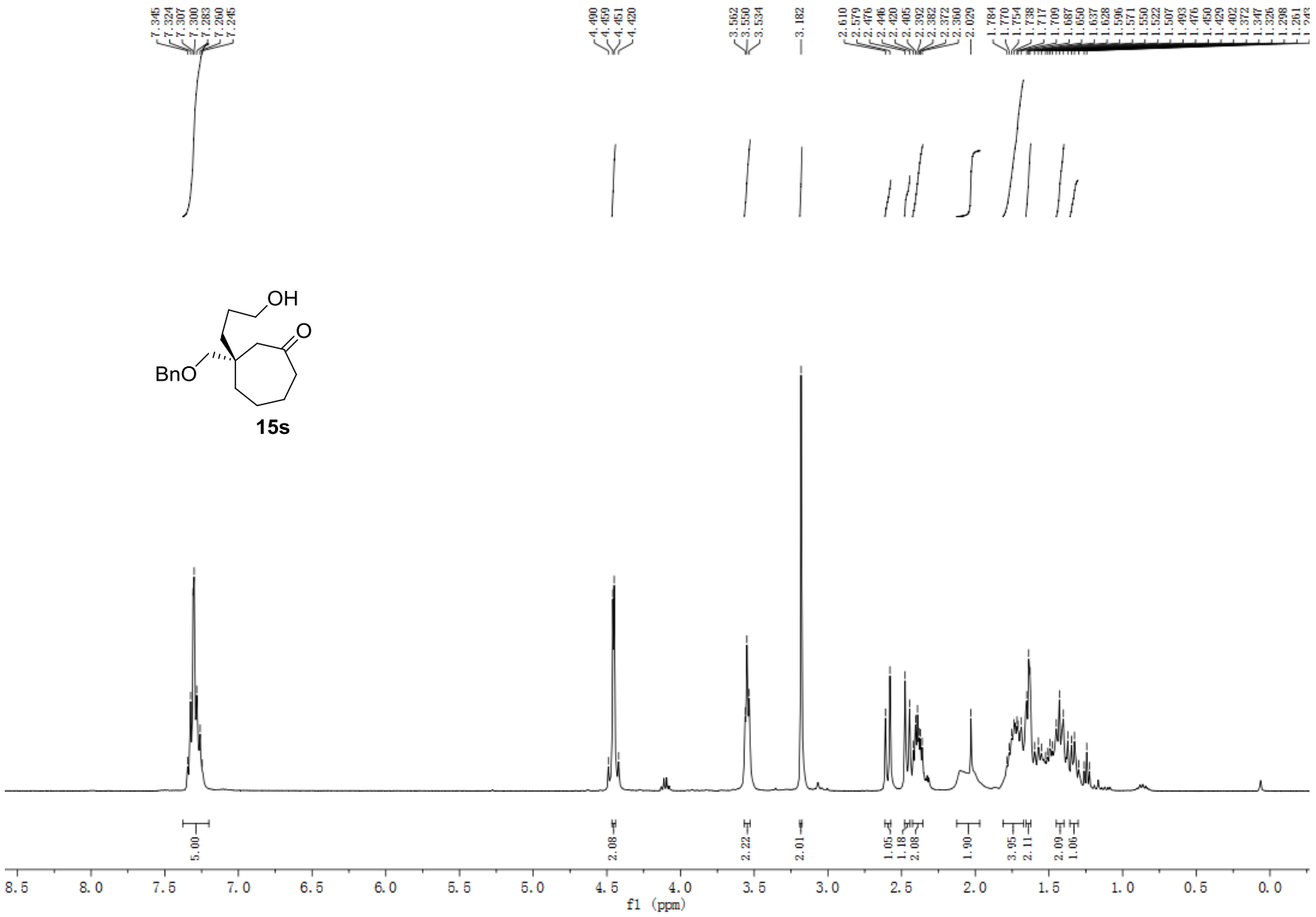
76.028
73.167
63.120
50.536
43.900
38.865
37.463
31.724
26.258
23.982
OTBS
O
BnO
14a
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.307
7.300
7.283
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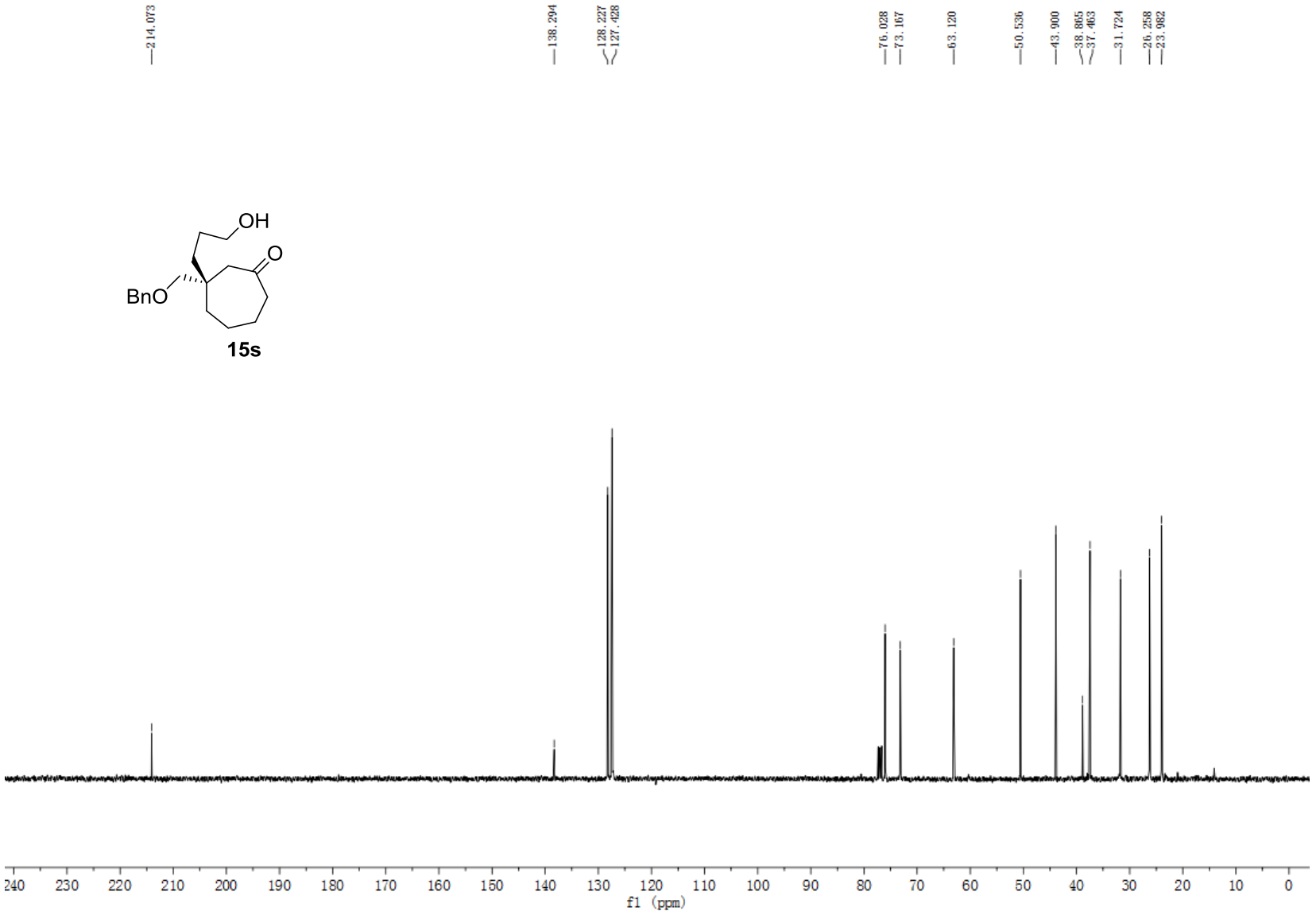
7.245
4.490
4.459
4.451
4.420
3.562
3.550
3.534
3.182
2.610
2.579
2.476
2.446
2.420
2.405
2.392
2.382
2.372
2.360
2.029
1.784
1.770
1.754
1.738
1.717
1.709
1.687
1.650
1.637
1.628
1.596
1.571
1.550
1.522
1.507
1.493
1.476
1.450
1.429
1.402
1.372
1.347
1.326
1.298
1.261
OH
O
BnO
15s
5.00
2.08
2.22
2.01
1.05
1.18
2.08
1.90
3.95
2.11
2.09
1.06
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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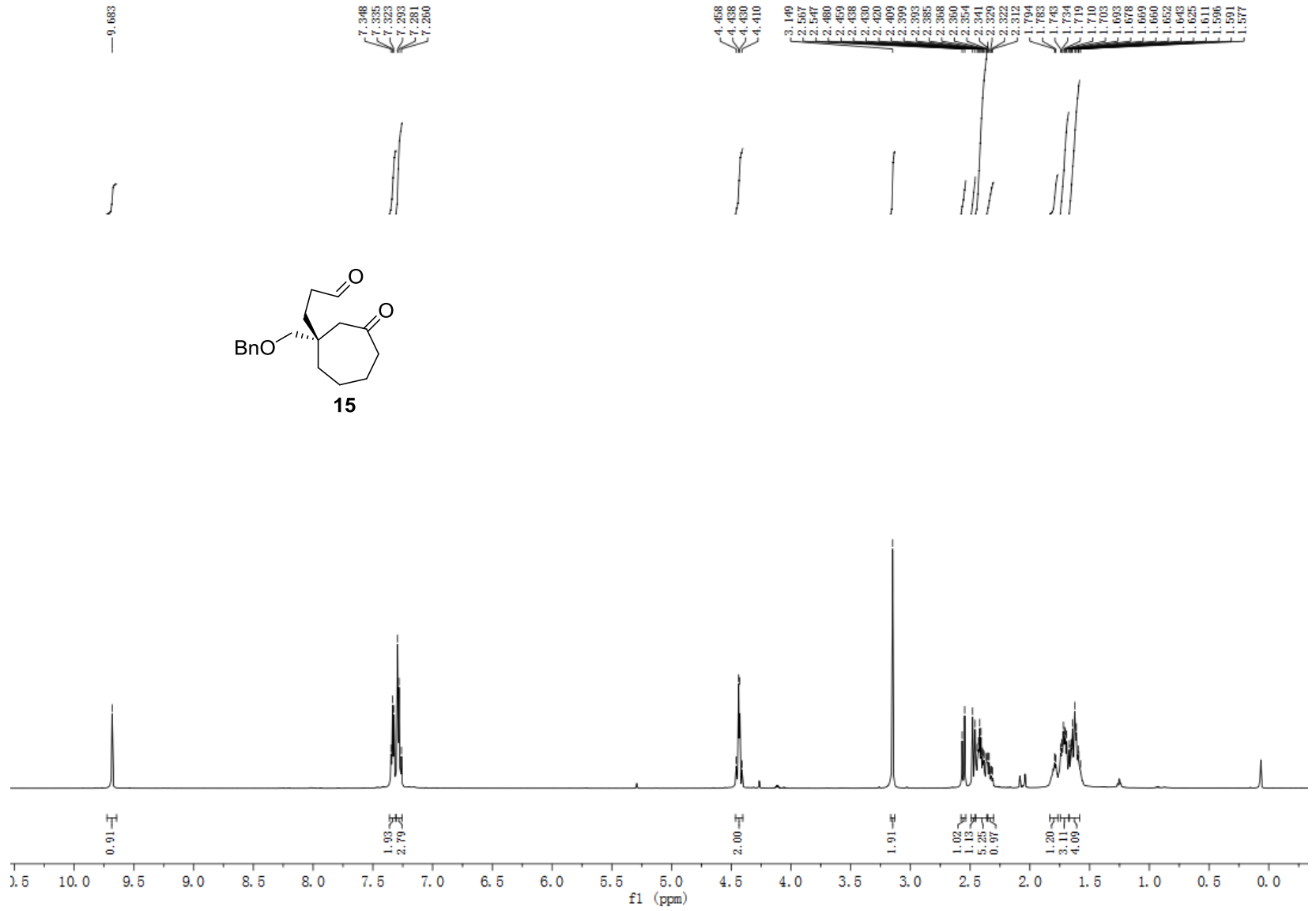
138.294
128.227
127.428
76.028
73.167
63.120
50.536
43.900
38.885
37.463
31.724
26.258
23.982
OH
O
BnO
15s
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.281
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4.458
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4.430
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2.567
2.547
2.480
2.459
2.438
2.430
2.420
2.409
2.399
2.393
2.385
2.368
2.360
2.354
2.341
2.329
2.322
2.312
1.794
1.783
1.743
1.734
1.719
1.710
1.703
1.693
1.678
1.669
1.660
1.652
1.643
1.625
1.611
1.596
1.591
1.577
O
O
BnO
15
0.91
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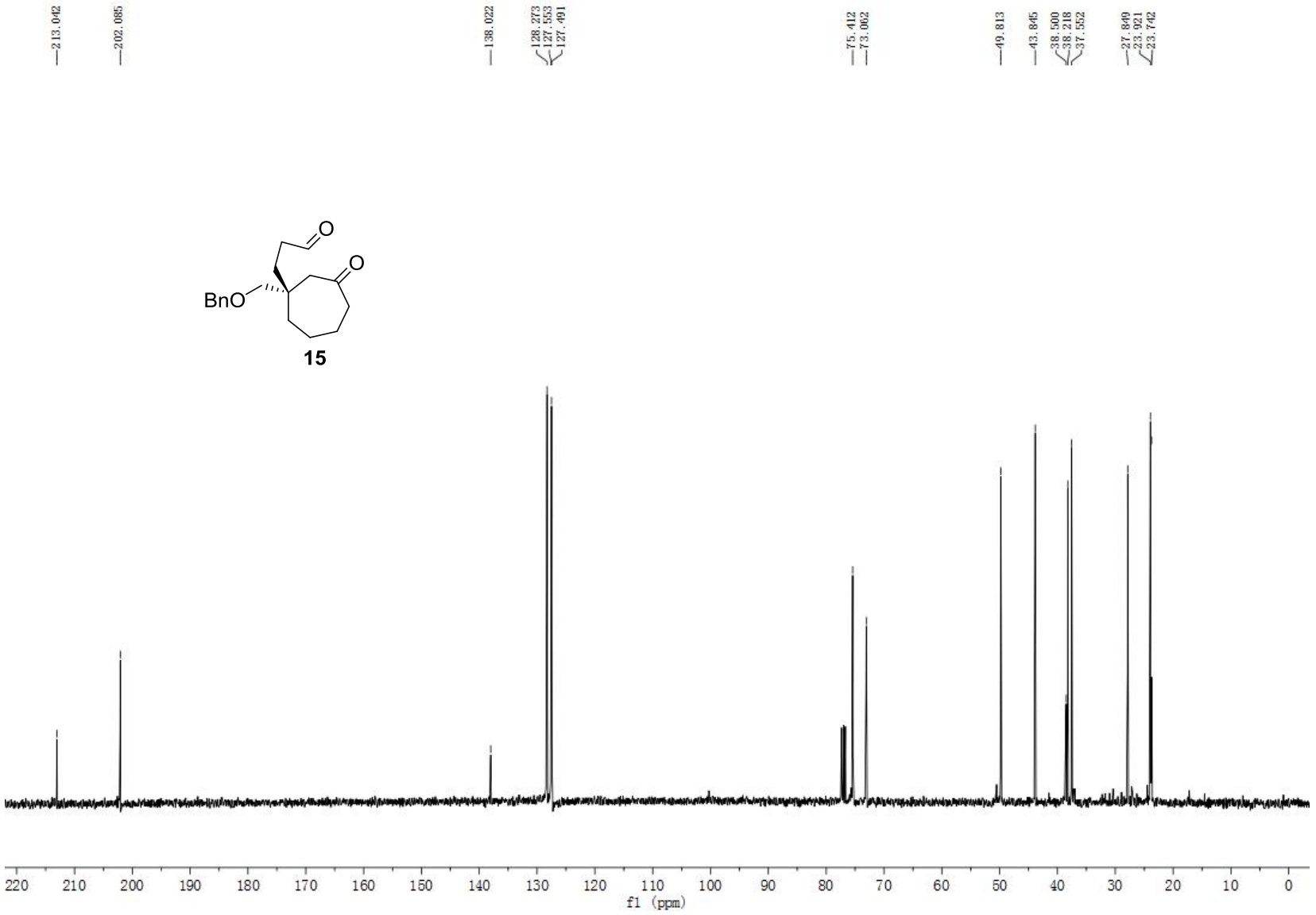
2.00
1.91
1.02
1.13
5.25
0.97
1.20
3.11
4.09
f1 (ppm)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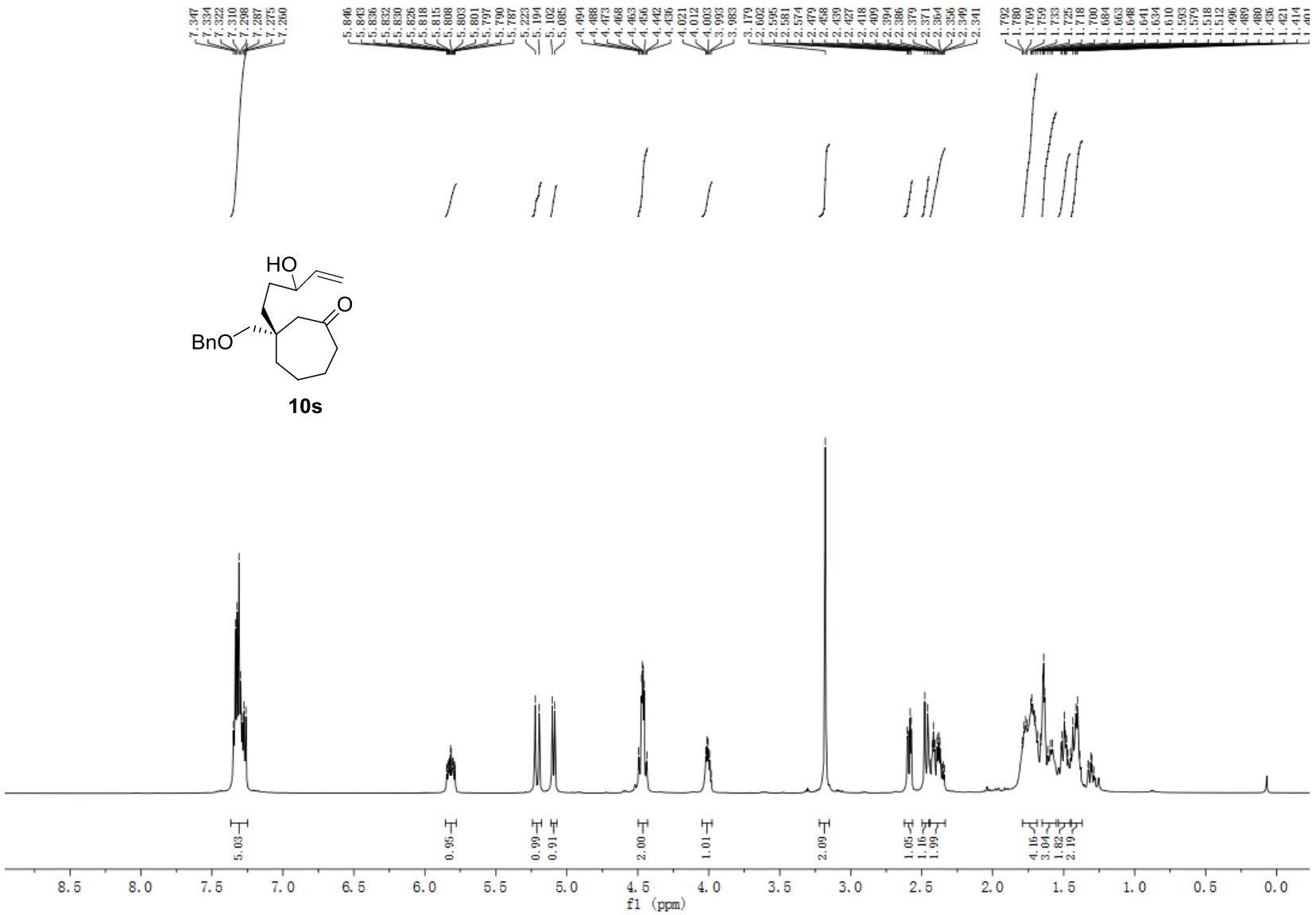
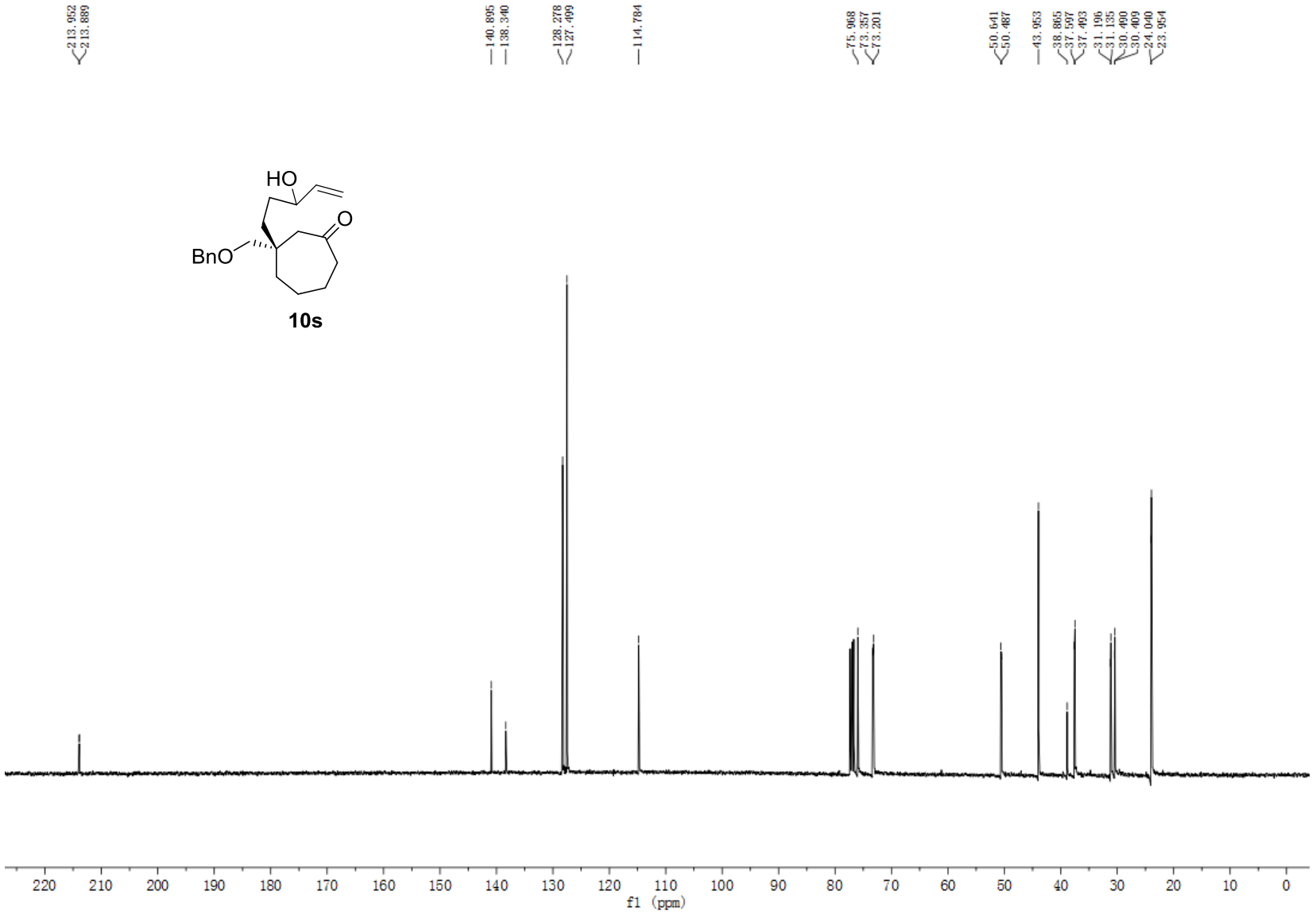
128.273
127.553
127.491
75.412
73.062
49.813
43.845
38.500
38.218
37.552
27.849
23.921
23.742
O
O
BnO
15
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HO
O
BnO
10s
f1 (ppm)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127.499
114.784
75.968
73.357
73.201
50.641
50.487
43.953
38.865
37.597
37.493
31.196
31.135
30.490
30.409
24.040
23.954
HO
O
BnO
10s
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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50
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30
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10
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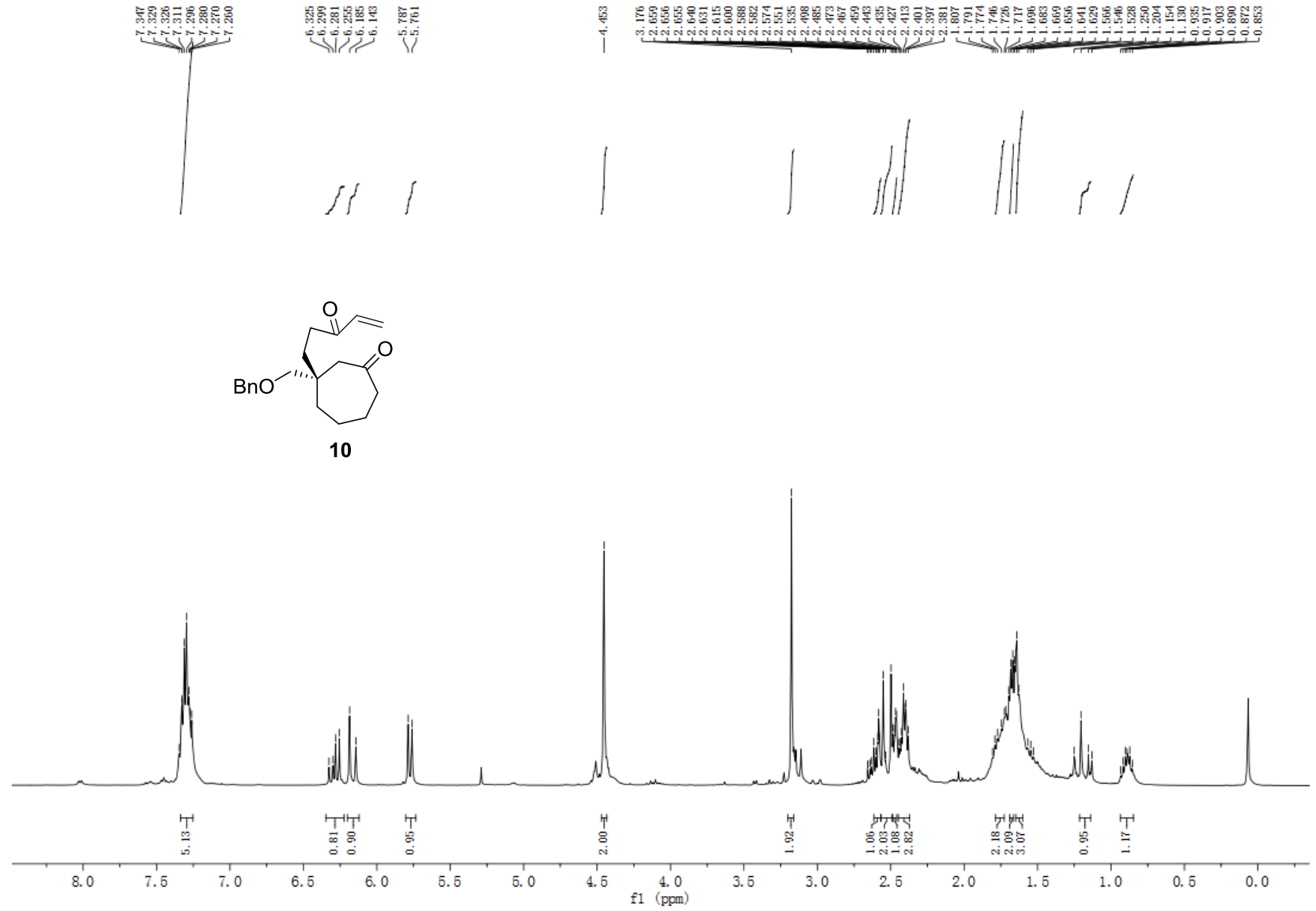
f1 (ppm)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2.640
2.631
2.615
2.600
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2.443
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2.427
2.413
2.401
2.397
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1.774
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1.726
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1.656
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1.629
1.566
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1.528
1.250
1.204
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1.130
0.935
0.917
0.903
0.890
0.872
0.853
O
O
BnO
10
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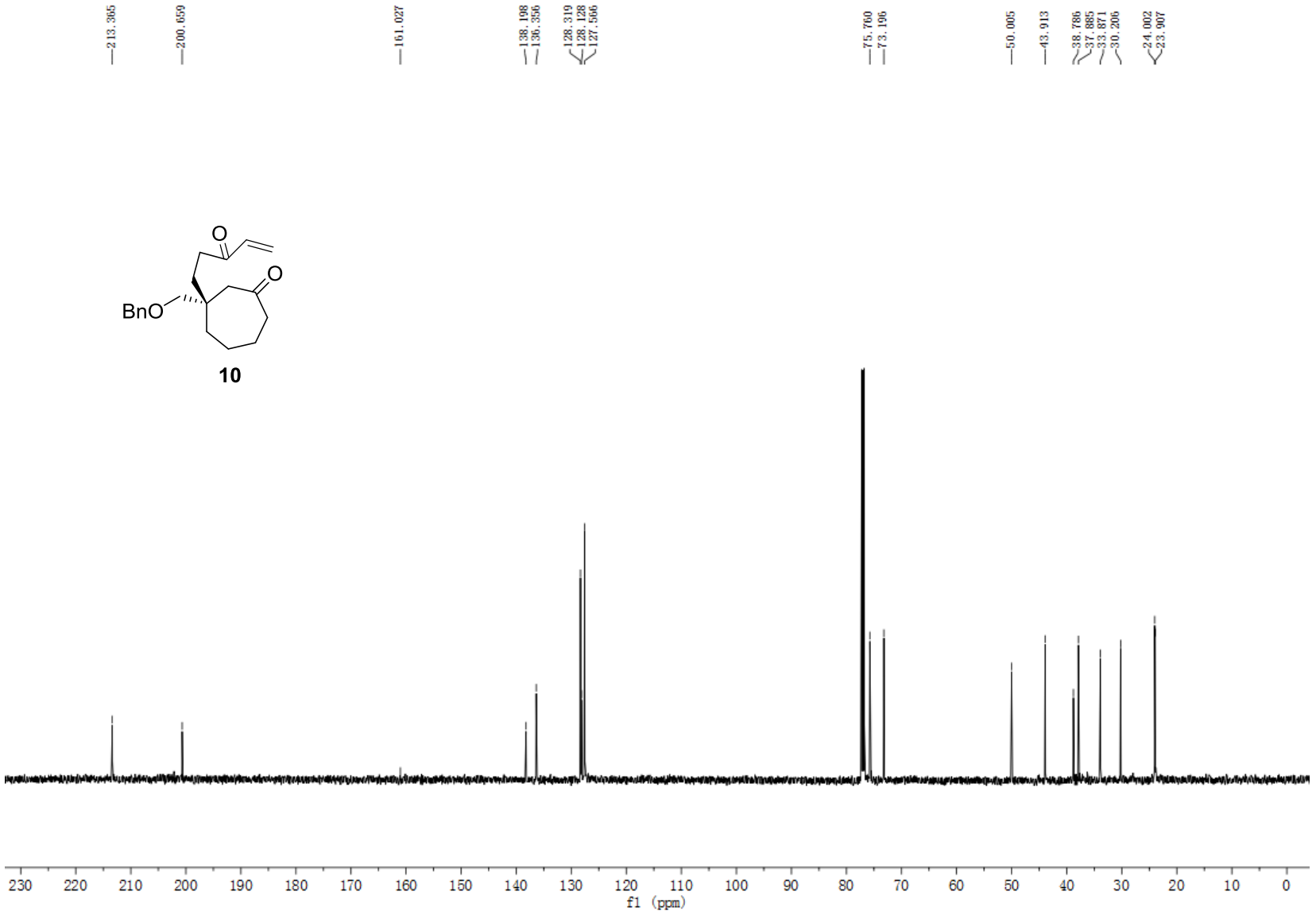
0.90
0.95
2.00
1.92
1.06
2.03
1.08
2.82
2.18
2.09
3.07
0.95
1.17
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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127.566
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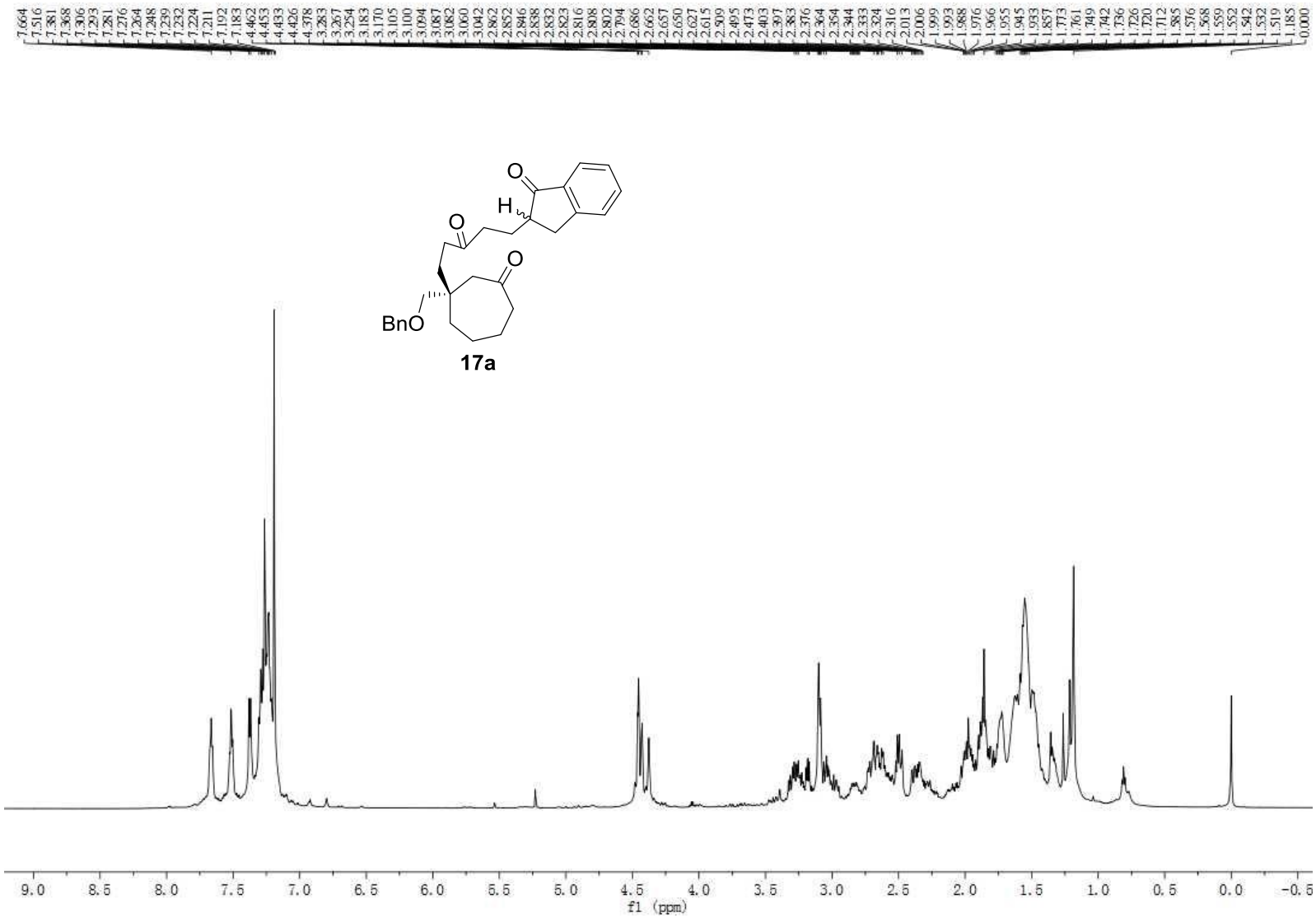
73.196
50.005
43.913
38.786
37.885
33.871
30.206
24.002
23.907
O
O
BnO
10
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.232
7.224
7.211
7.192
7.183
4.462
4.453
4.433
4.426
4.378
3.283
3.267
3.254
3.183
3.170
3.105
3.100
3.094
3.087
3.082
3.060
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2.838
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2.823
2.816
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2.376
2.364
2.354
2.344
2.333
2.324
2.316
2.013
2.006
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1.993
1.988
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1.955
1.945
1.933
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1.761
1.749
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1.736
1.726
1.720
1.712
1.585
1.576
1.568
1.559
1.552
1.542
1.532
1.519
1.185
0.000
O
H
O
O
BnO
17a
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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2.0
1.5
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0.5
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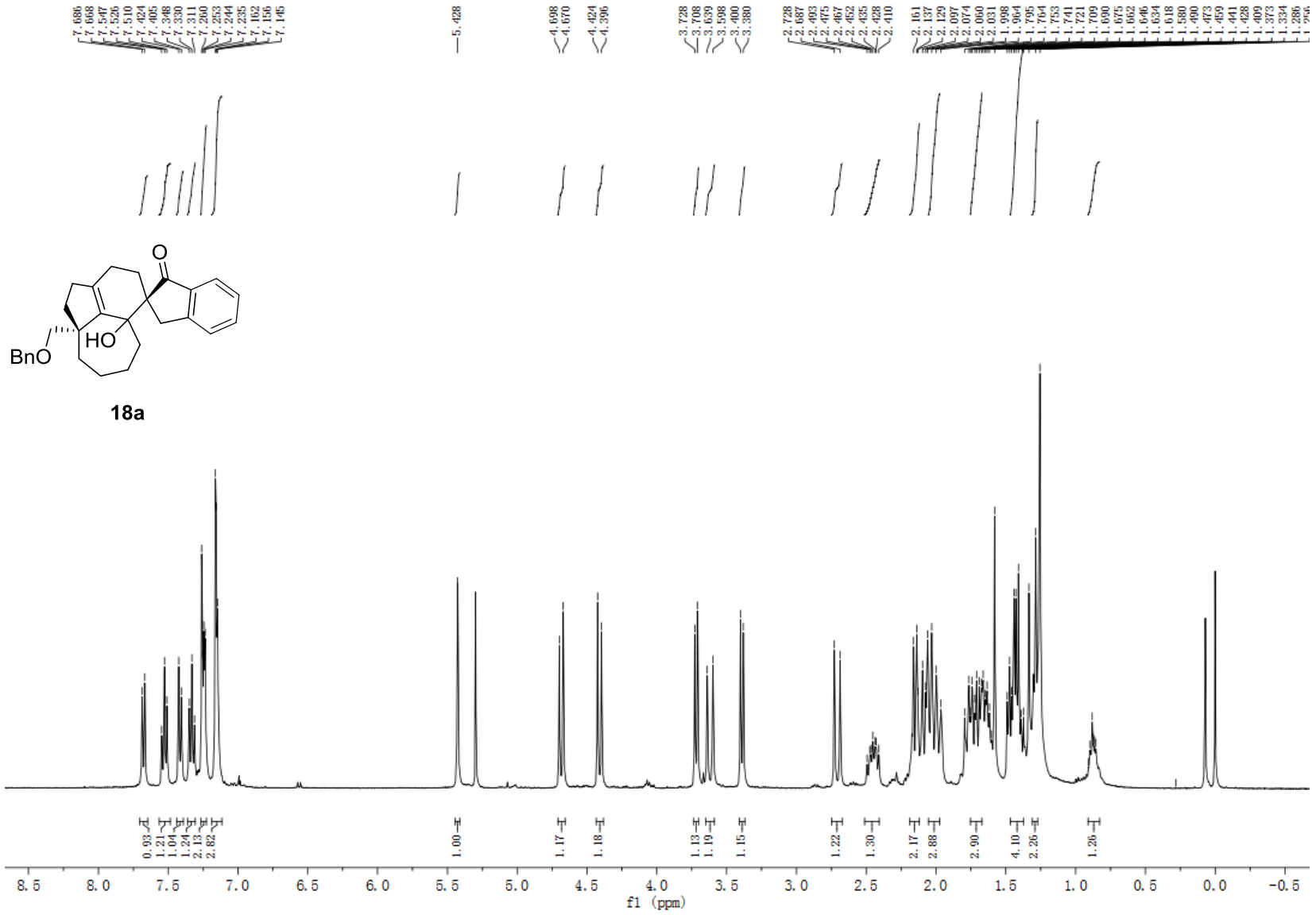
f1 (ppm)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3.708
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O
HO
BnO
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1.04
1.24
2.13
2.82
1.00
1.17
1.18
1.13
1.19
1.15
1.22
1.30
2.17
2.88
2.90
4.10
2.26
1.26
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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2.5
2.0
1.5
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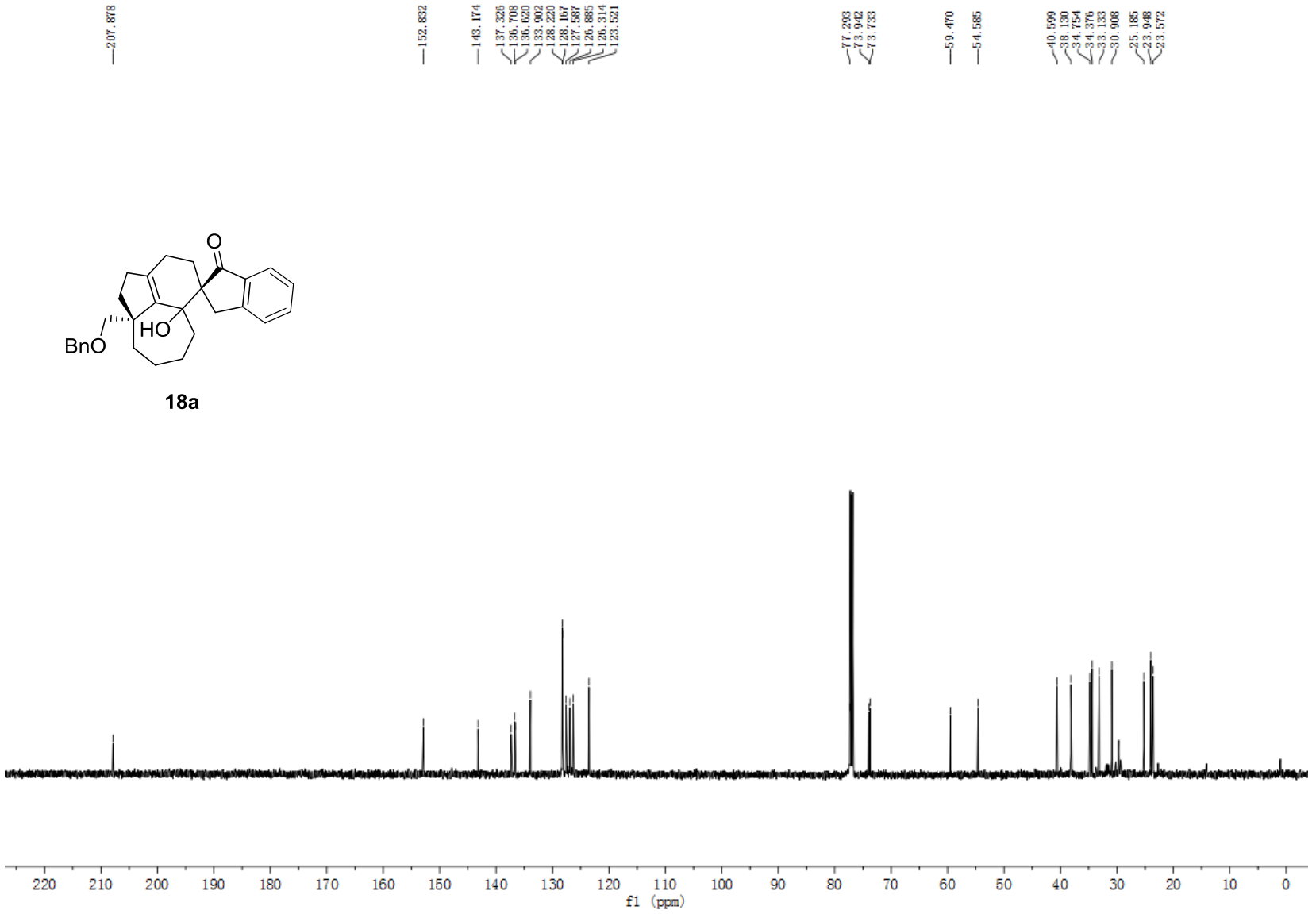
0.0
-0.5
f1 (ppm)

18a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123.521
77.293
73.942
73.733
59.470
54.585
40.599
38.130
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34.376
33.133
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25.185
23.948
23.572
O
HO
BnO
220
210
200
190
180
170
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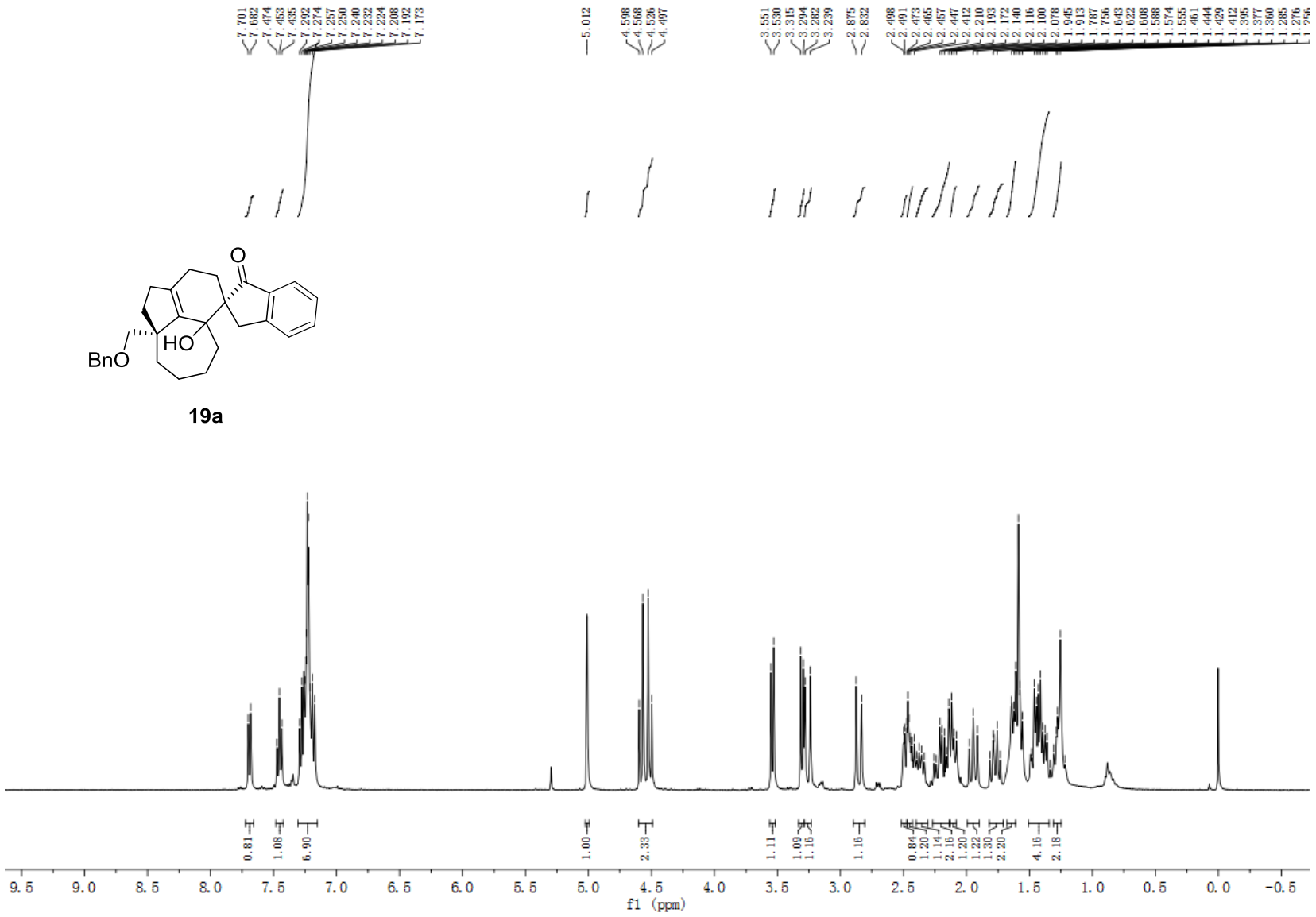
40
30
20
10
0
f1 (ppm)

18a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7.173
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4.598
4.568
4.526
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3.530
3.315
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1.588
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1.276
O
HO
BnO
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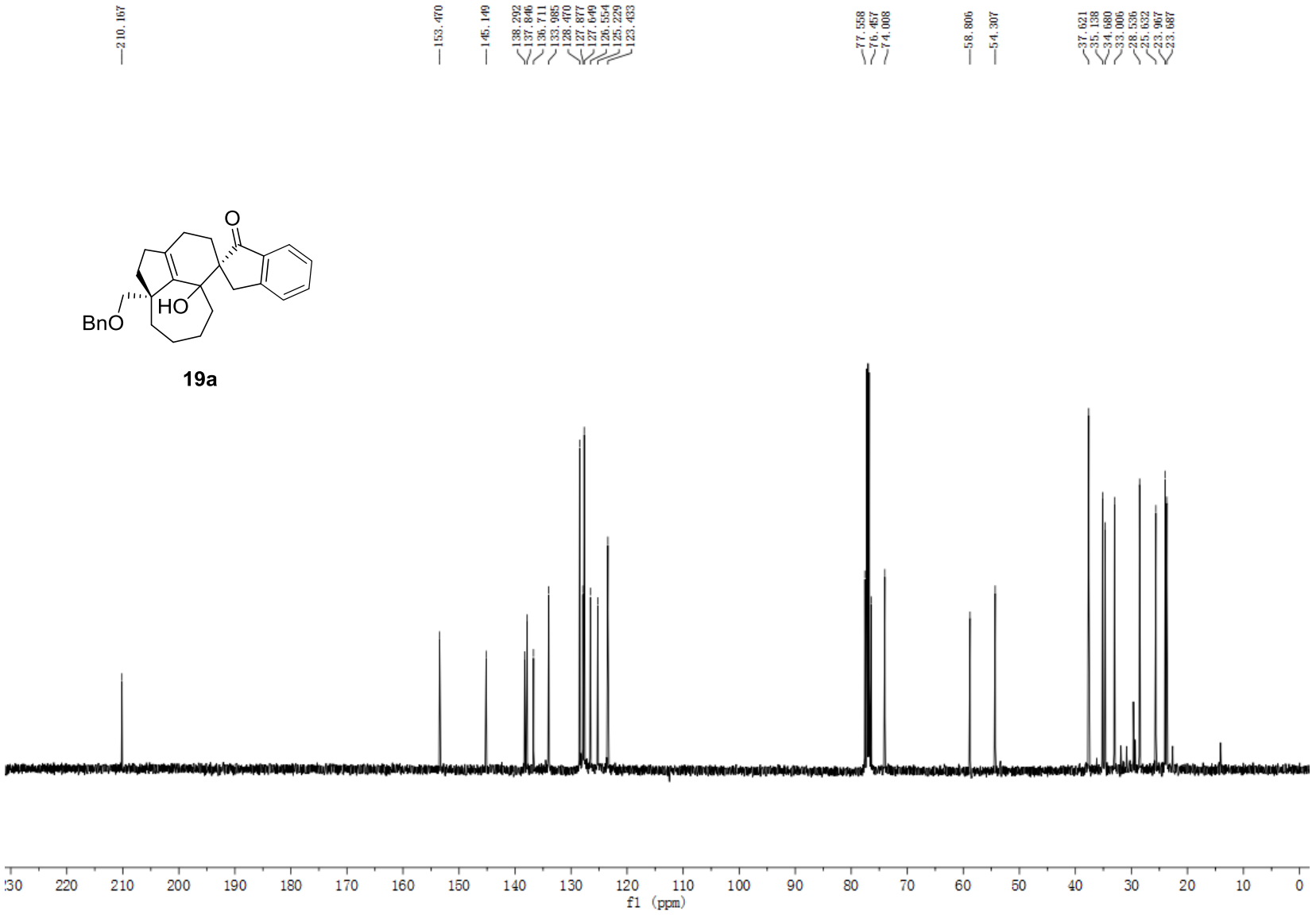
1.00
2.33
1.11
1.09
1.16
1.16
0.84
1.20
1.14
2.16
1.20
1.22
1.30
2.20
4.16
2.18
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

19a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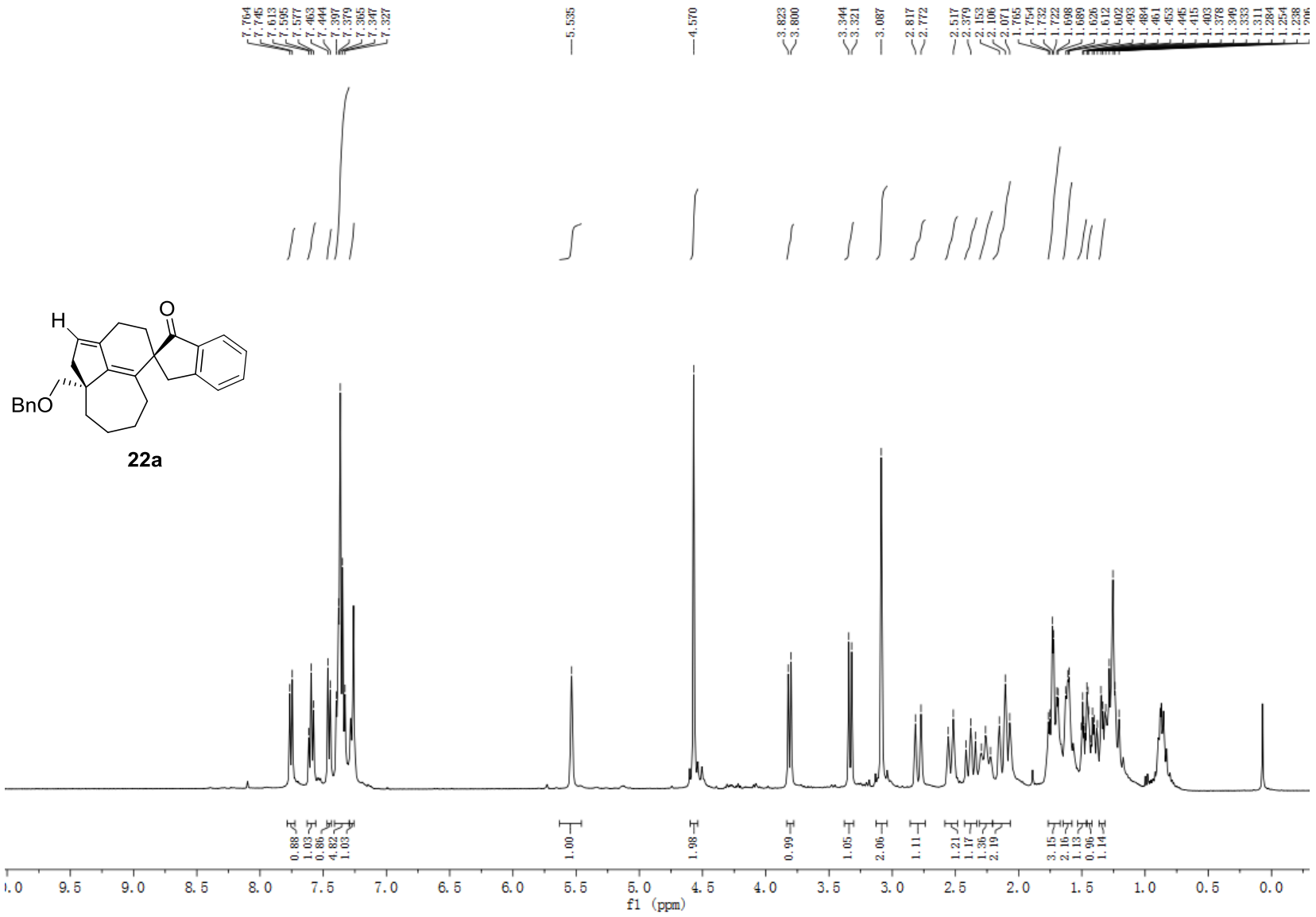
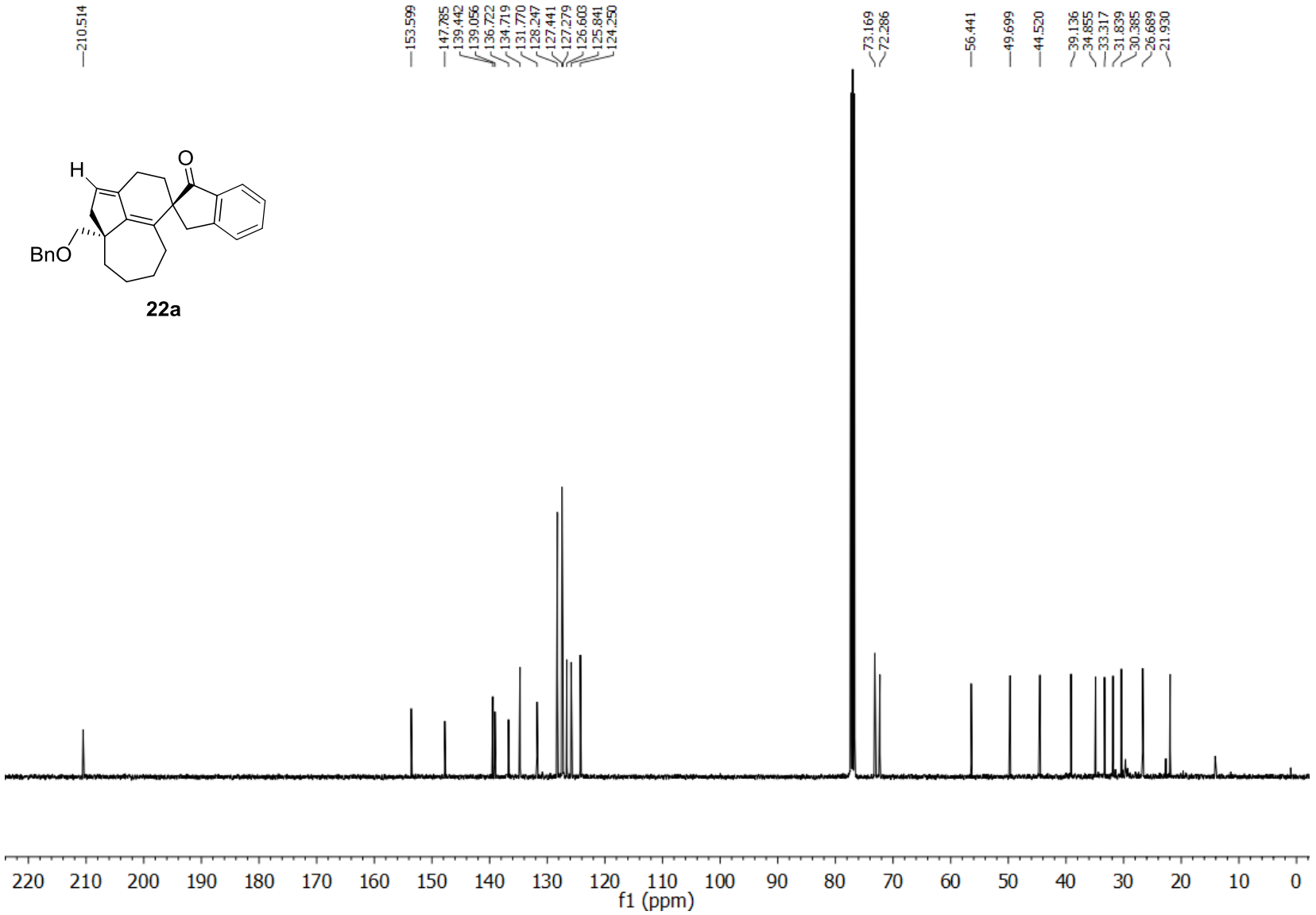
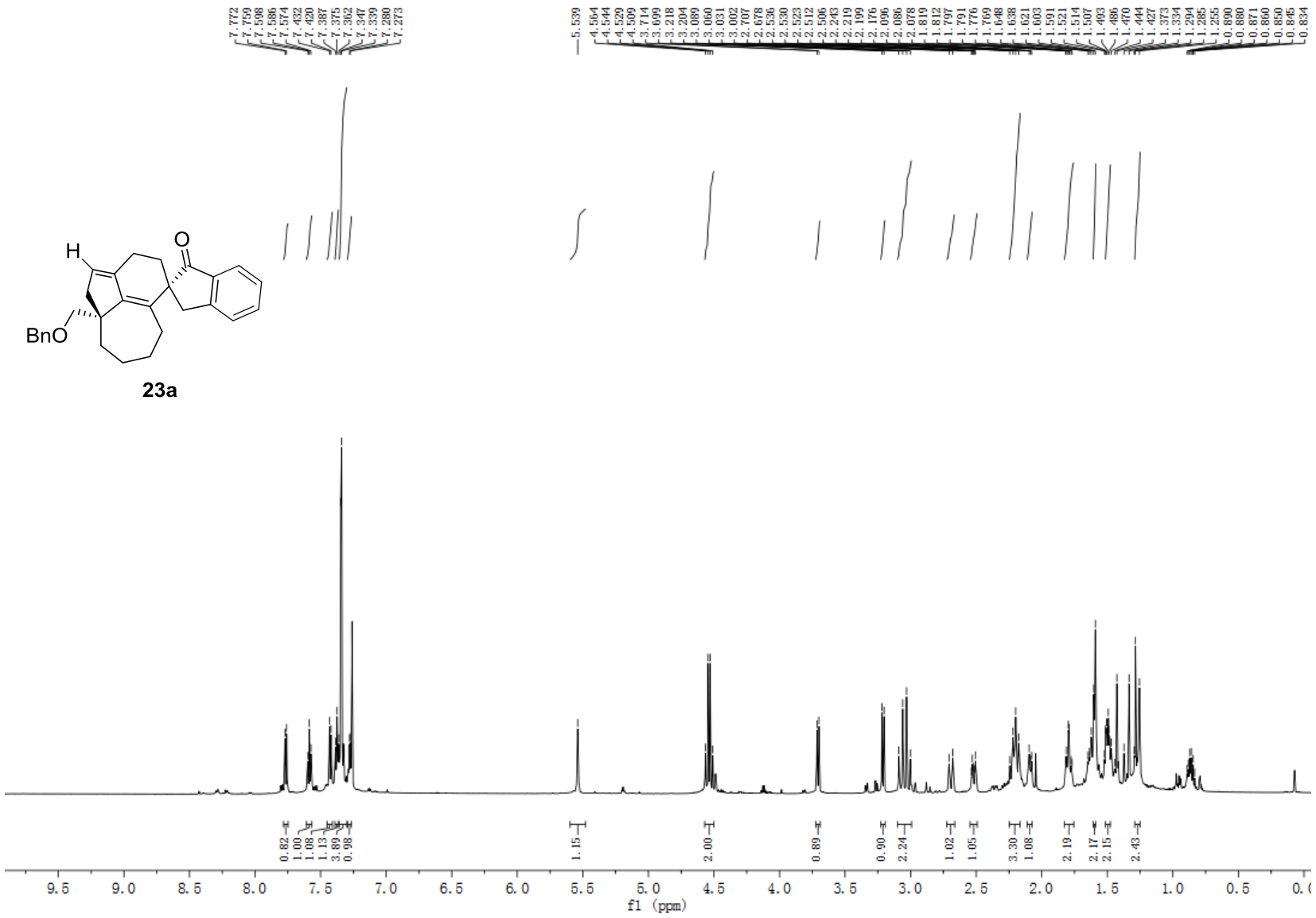
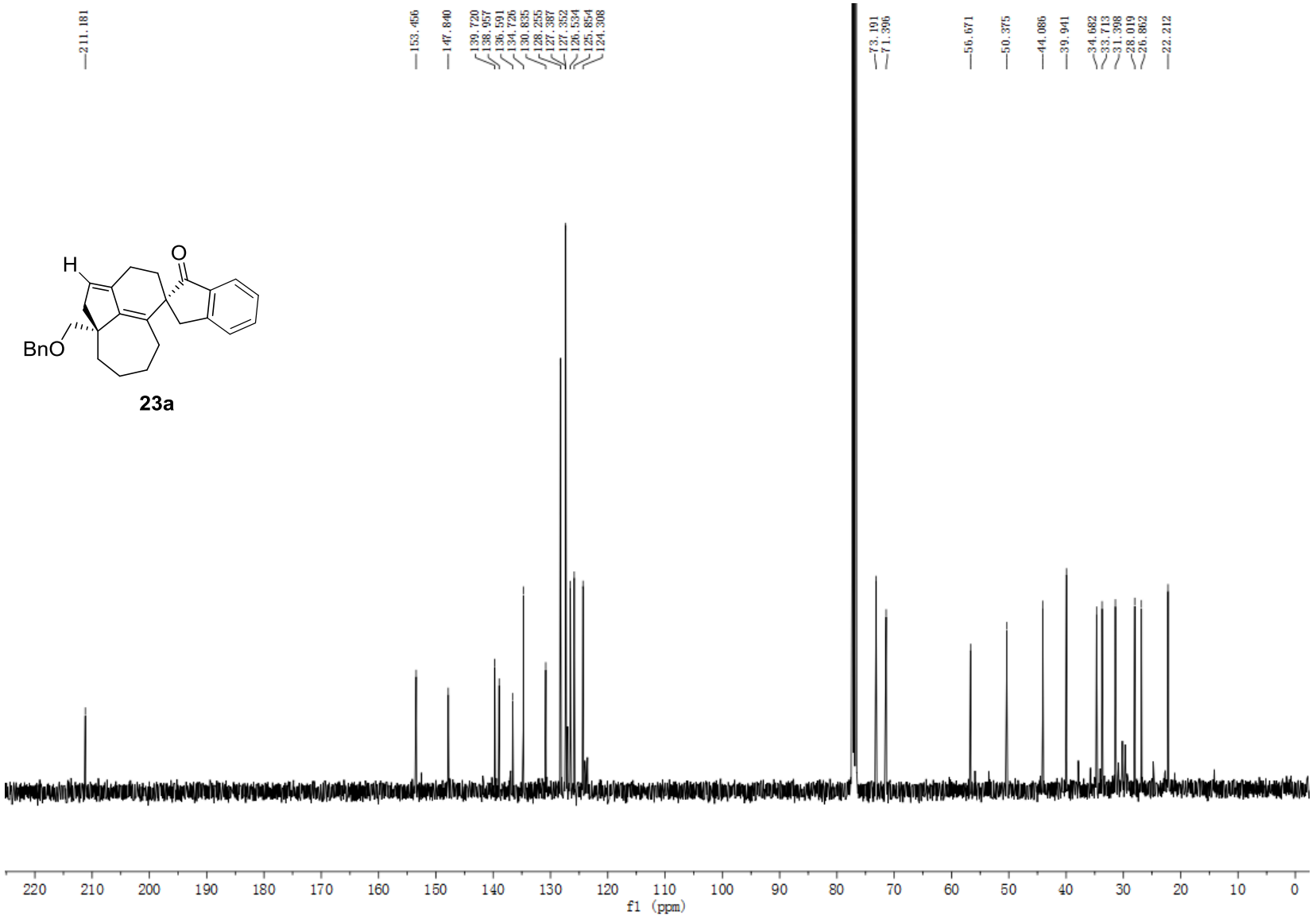
153.470
145.149
138.292
137.846
136.711
133.985
128.470
127.877
127.649
126.554
125.229
123.433
77.558
76.457
74.008
58.806
54.307
37.621
35.138
34.680
33.006
28.536
25.632
23.967
23.687
O
HO
BnO
19a
f1 (ppm)


7.764
7.745
7.613
7.595
7.577
7.463
7.444
7.397
7.379
7.365
7.347
7.327
5.535
4.570
3.823
3.800
3.344
3.321
3.087
2.817
2.772
2.517
2.379
2.153
2.106
2.071
1.765
1.754
1.732
1.722
1.698
1.689
1.626
1.612
1.602
1.493
1.484
1.461
1.453
1.445
1.415
1.403
1.378
1.349
1.333
1.311
1.284
1.254
1.238
H
O
BnO
22a
0.88
1.03
0.86
4.82
1.03
1.00
1.98
0.99
1.05
2.06
1.11
1.21
1.17
1.36
2.19
3.15
2.16
1.13
0.96
1.14
f1 (ppm)


210.514
153.599
147.785
139.442
139.056
136.722
134.719
131.770
128.247
127.441
127.279
126.603
125.841
124.250
73.169
72.286
56.441
49.699
44.520
39.136
34.855
33.317
31.839
30.385
26.689
21.930
H
O
BnO
22a
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)


H
O
BnO
23a
f1 (ppm)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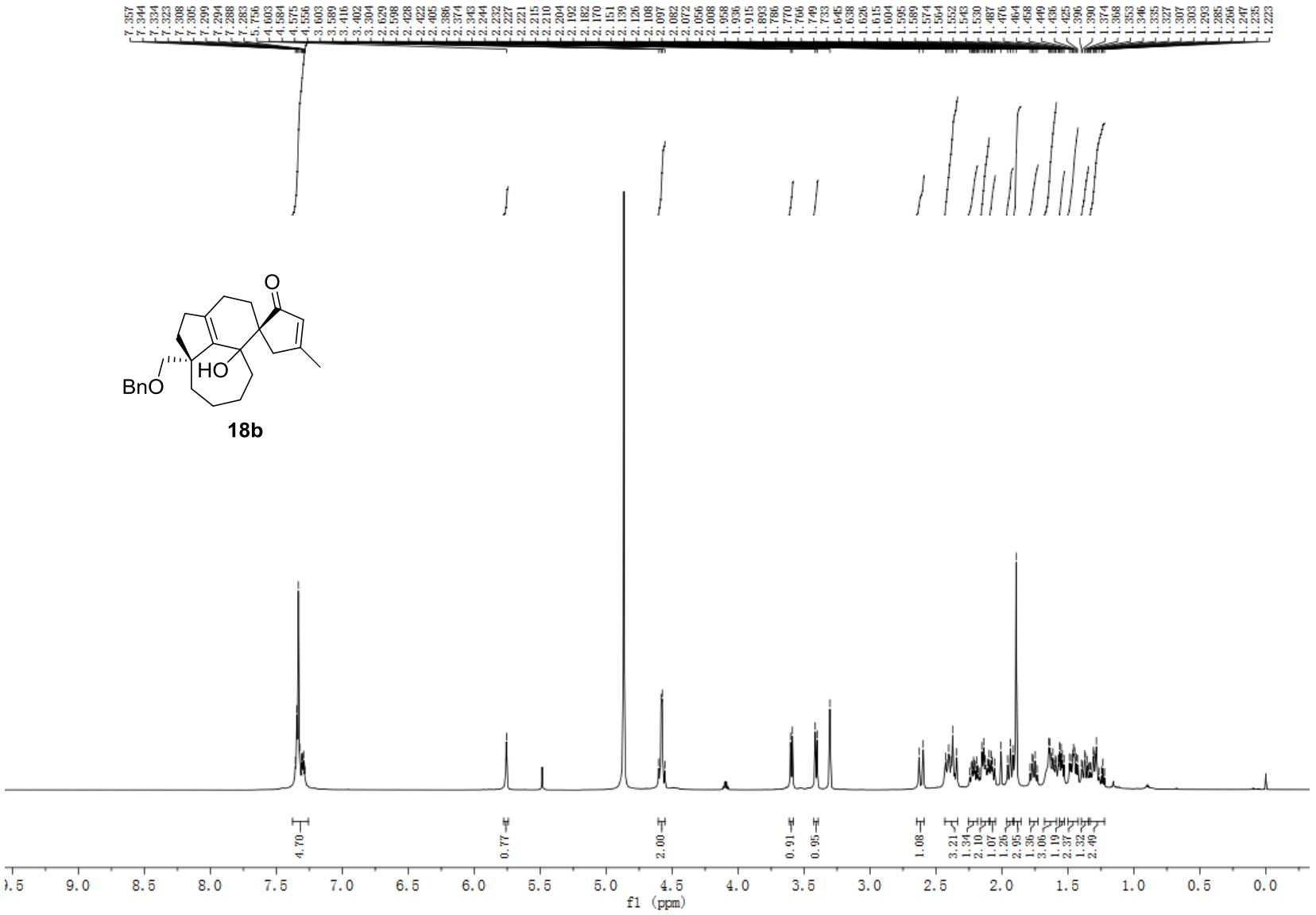
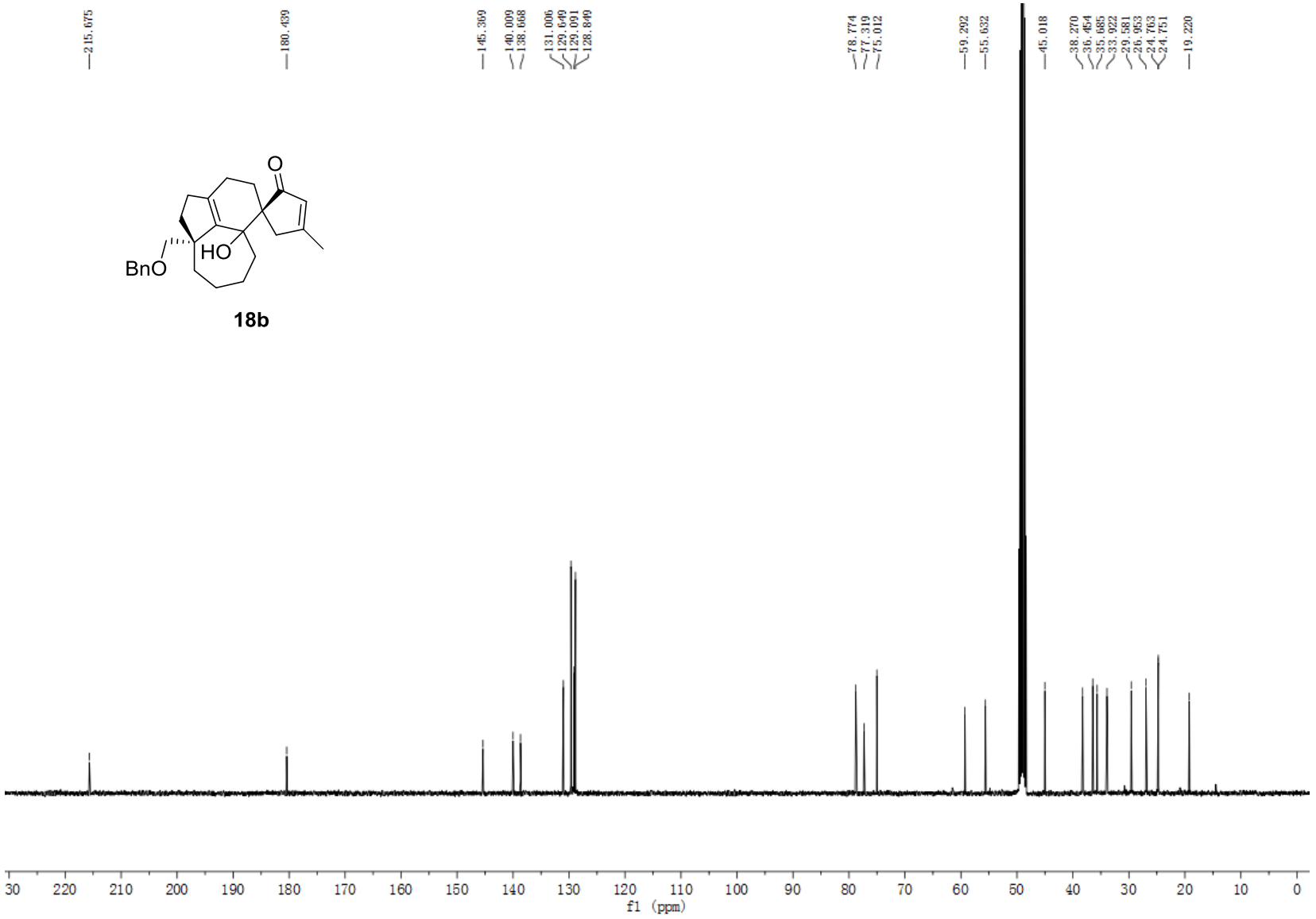
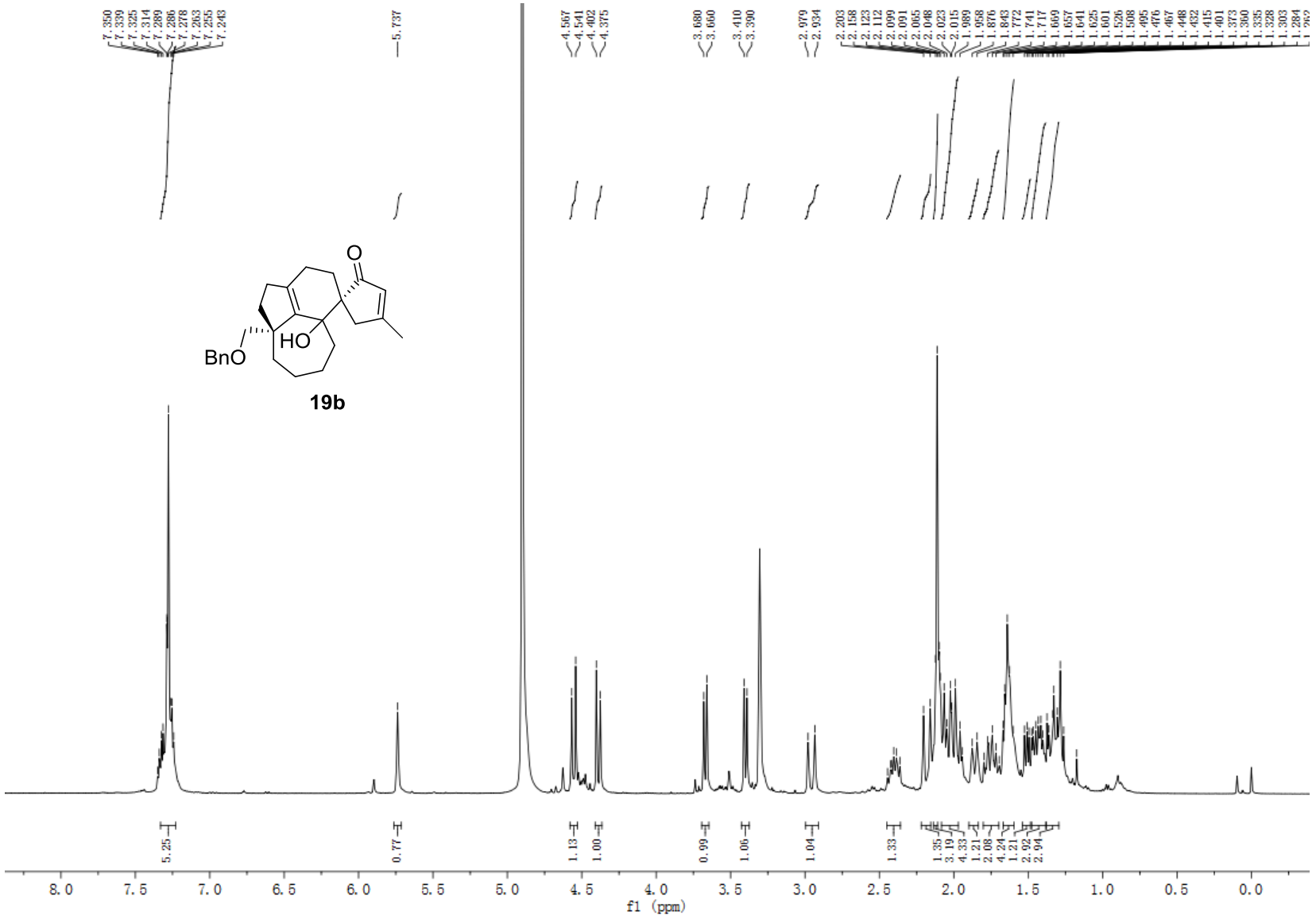
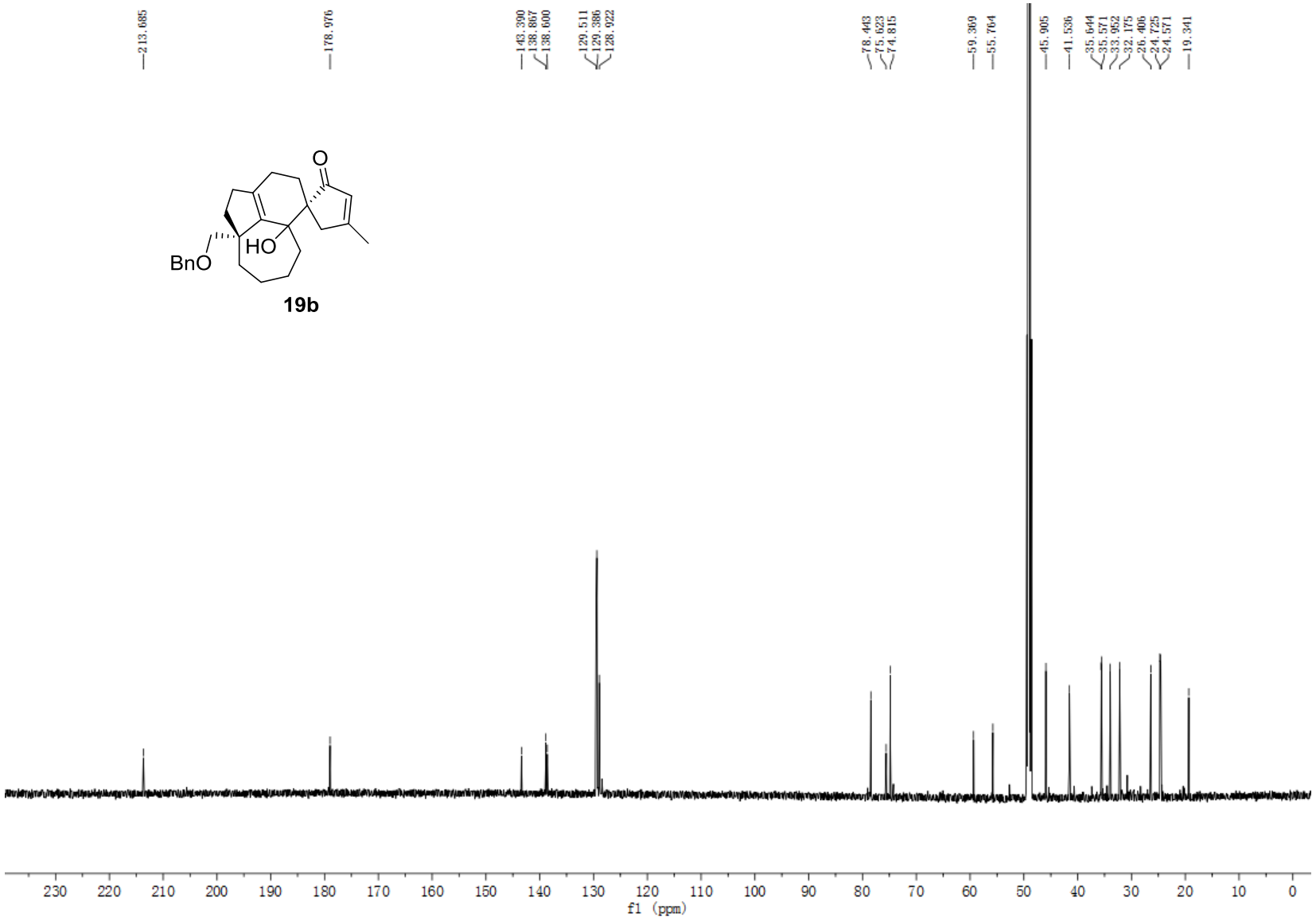
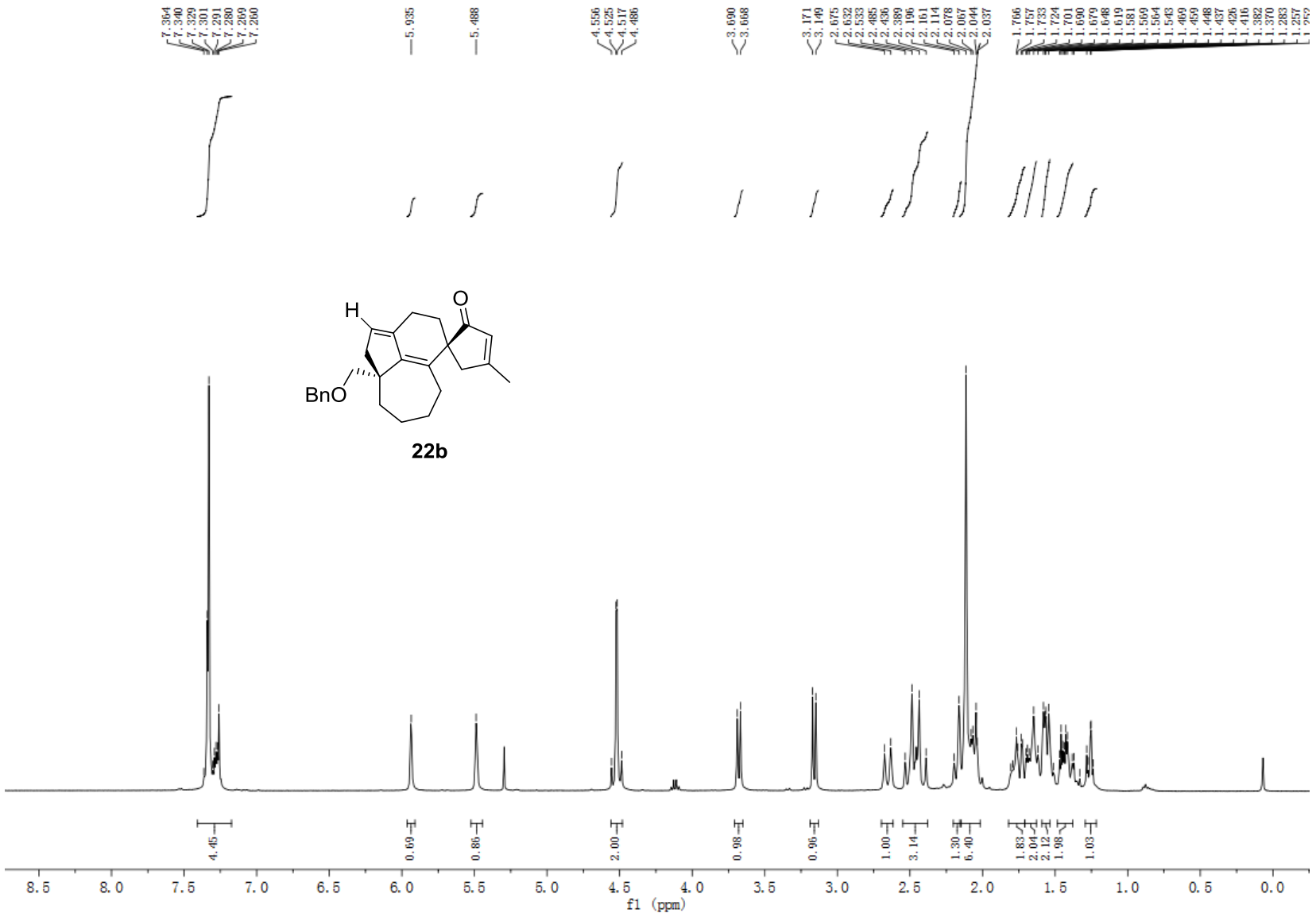
153.456
147.840
139.720
138.957
136.591
134.726
130.835
128.255
127.387
127.352
126.534
125.854
124.308
73.191
71.396
56.671
50.375
44.086
39.941
34.682
33.713
31.398
28.019
26.862
22.212
H
O
BnO
23a
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

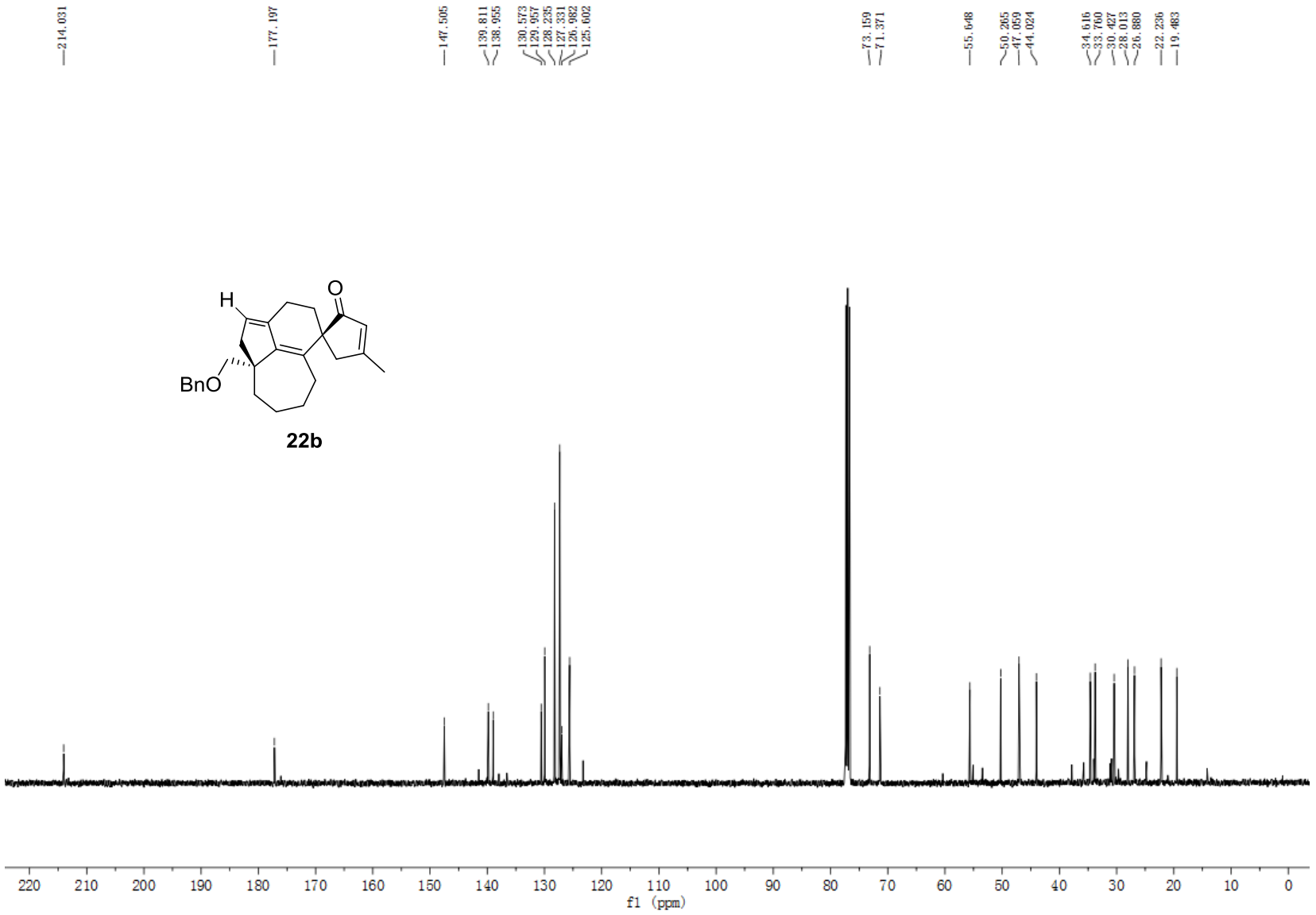

BnO
HO
O
18b
f1 (ppm)

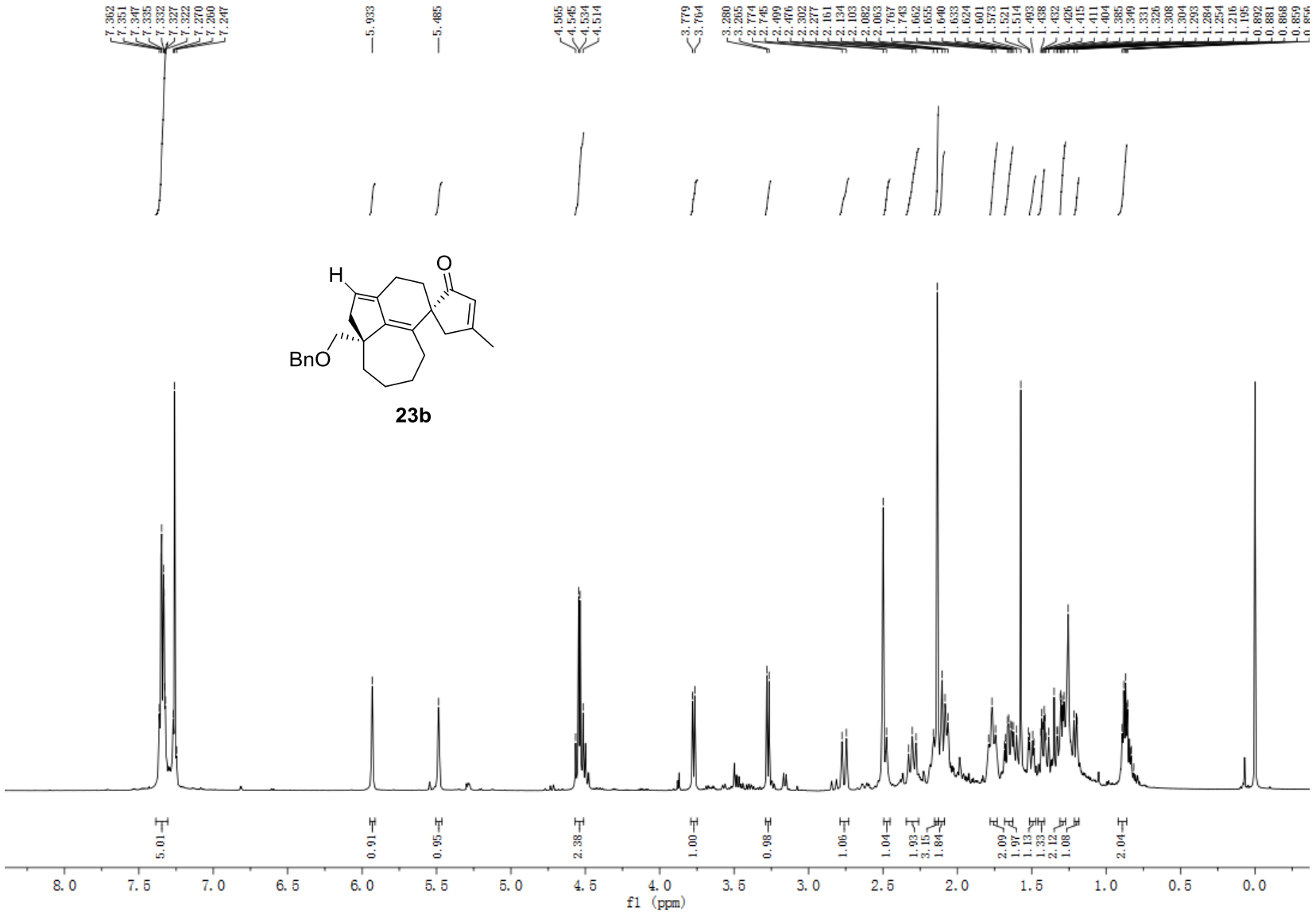

215.675
180.439
145.369
140.009
138.668
131.006
129.649
129.091
128.849
78.774
77.319
75.012
59.292
55.632
45.018
38.270
36.454
35.685
33.922
29.581
26.953
24.763
24.751
19.220
O
HO
BnO
18b
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
HO
BnO
19b
f1 (ppm)


213.685
178.976
143.390
138.867
138.600
129.511
129.386
128.922
78.443
75.623
74.815
59.369
55.764
45.905
41.536
35.644
35.571
33.952
32.175
26.406
24.725
24.571
19.341
O
HO
BnO
19b
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.364
7.340
7.329
7.301
7.291
7.280
7.269
7.260
5.935
5.488
4.556
4.525
4.517
4.486
3.690
3.668
3.171
3.149
2.675
2.632
2.533
2.485
2.436
2.389
2.196
2.161
2.114
2.078
2.067
2.044
2.037
1.766
1.757
1.733
1.724
1.701
1.690
1.679
1.648
1.619
1.581
1.569
1.564
1.543
1.469
1.459
1.448
1.437
1.426
1.416
1.382
1.370
1.283
1.257
H
O
BnO
22b
4.45
0.69
0.86
2.00
0.98
0.96
1.00
3.14
1.30
6.40
1.83
2.04
2.12
1.98
1.03
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)


214.031
177.197
147.505
139.811
138.955
130.573
129.957
128.235
127.331
126.982
125.602
73.159
71.371
55.648
50.265
47.059
44.024
34.616
33.760
30.427
28.013
26.880
22.236
19.483
H
O
BnO
22b
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)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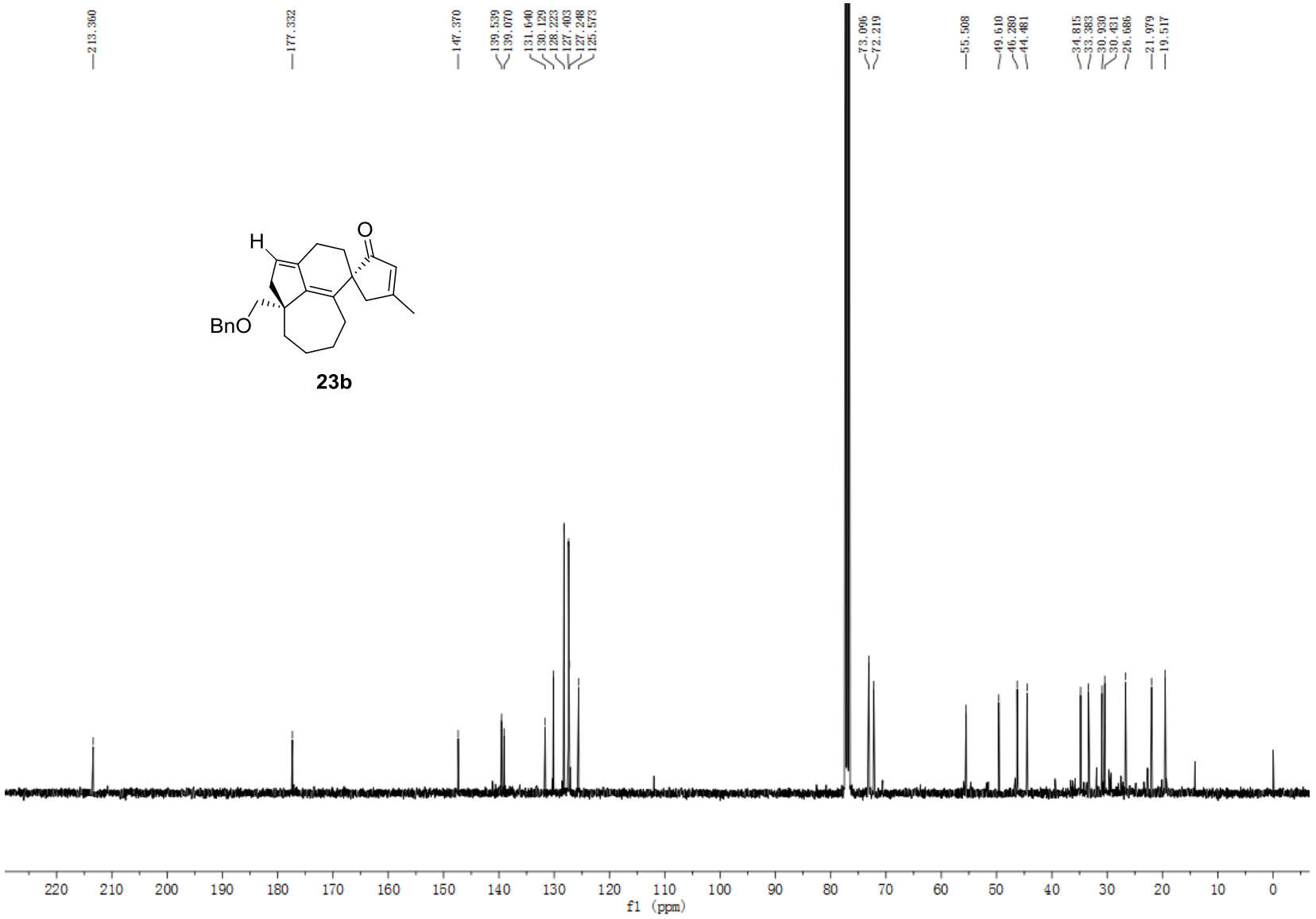
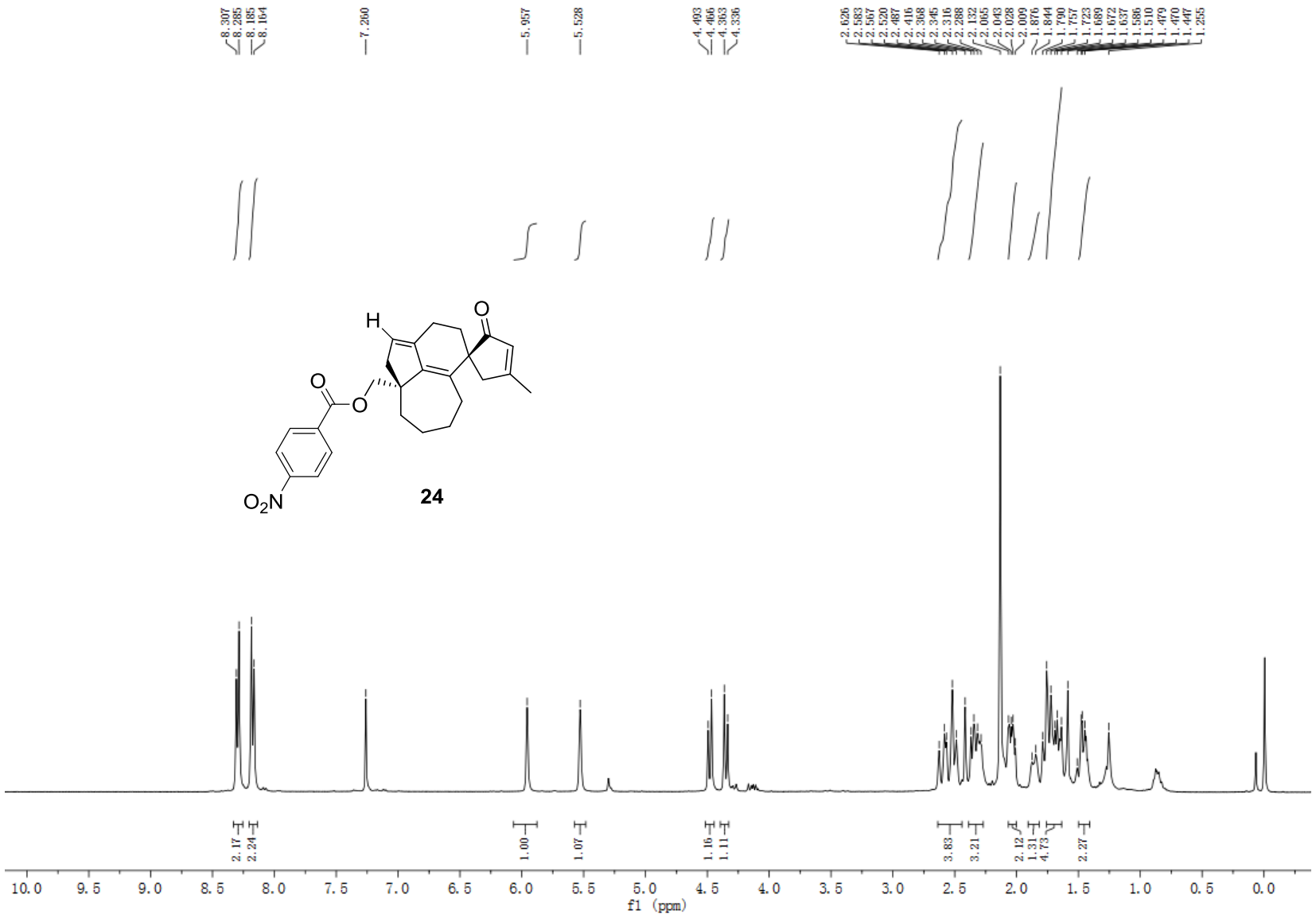
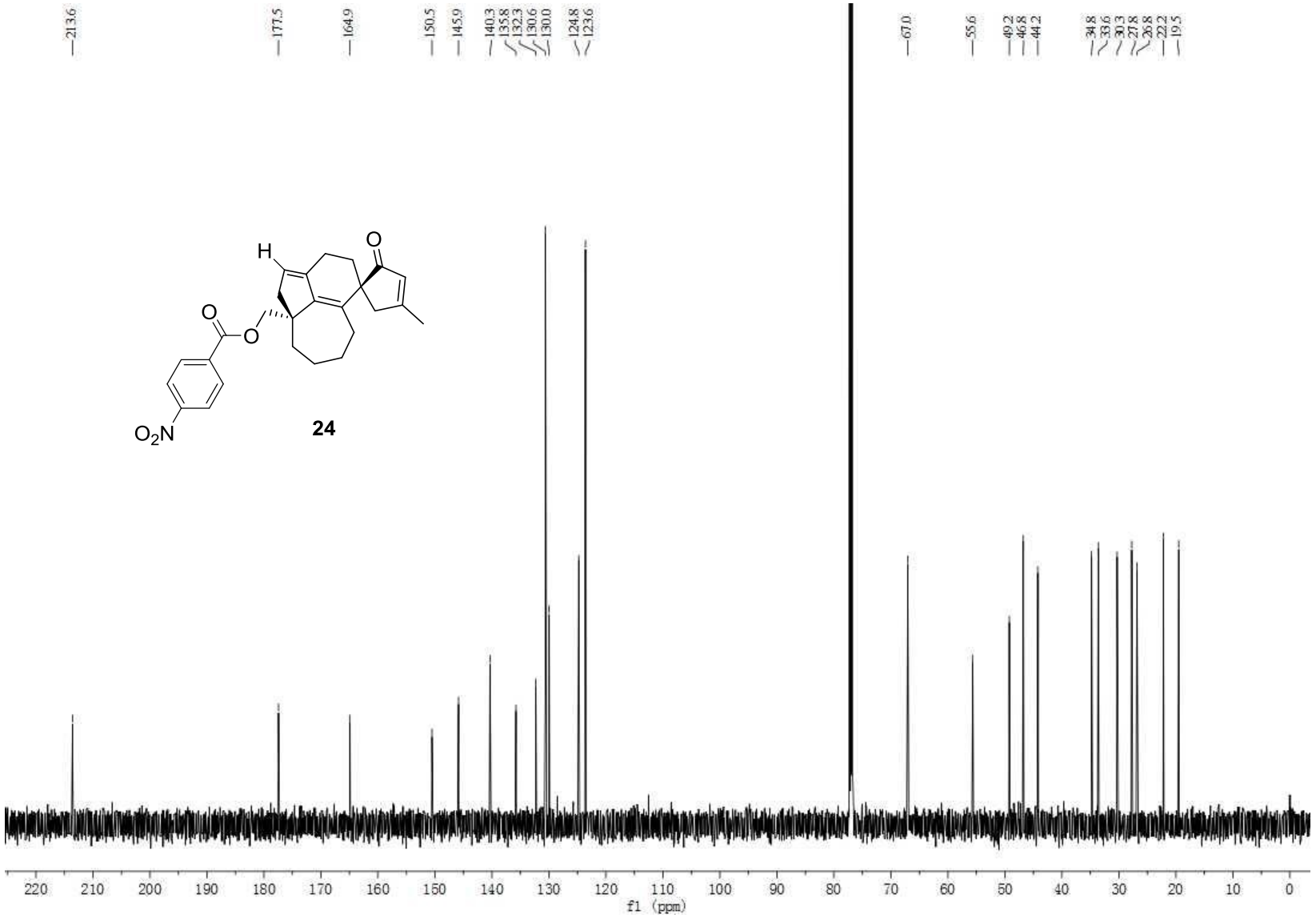
7.351
7.347
7.335
7.332
7.327
7.322
7.270
7.260
7.247
5.933
5.485
4.565
4.545
4.534
4.514
3.779
3.764
3.280
3.265
2.774
2.745
2.499
2.476
2.302
2.277
2.161
2.134
2.103
2.082
2.063
1.767
1.743
1.662
1.655
1.640
1.633
1.624
1.601
1.573
1.521
1.514
1.493
1.438
1.432
1.426
1.415
1.411
1.404
1.385
1.349
1.331
1.326
1.308
1.304
1.293
1.284
1.254
1.216
1.195
0.892
0.881
0.868
0.859
H
O
BnO
23b
5.01
0.91
0.95
2.38
1.00
0.98
1.06
1.04
1.93
3.15
1.84
2.09
1.97
1.13
1.33
2.12
1.08
2.04
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)


213.360
177.332
147.370
139.539
139.070
131.640
130.129
128.223
127.403
127.248
125.573
73.096
72.219
55.508
49.610
46.280
44.481
34.815
33.383
30.930
30.431
26.686
21.979
19.517
H
O
BnO
23b
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)


8.307
8.285
8.185
8.164
7.260
5.957
5.528
4.493
4.466
4.363
4.336
2.626
2.583
2.567
2.520
2.487
2.416
2.368
2.345
2.316
2.288
2.132
2.065
2.043
2.028
2.009
1.876
1.844
1.790
1.757
1.723
1.689
1.672
1.637
1.586
1.510
1.479
1.470
1.447
1.255
H
O
O
O
O_2N
24
2.17
2.24
1.00
1.07
1.16
1.11
3.83
3.21
2.12
1.31
4.73
2.27
10.0
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)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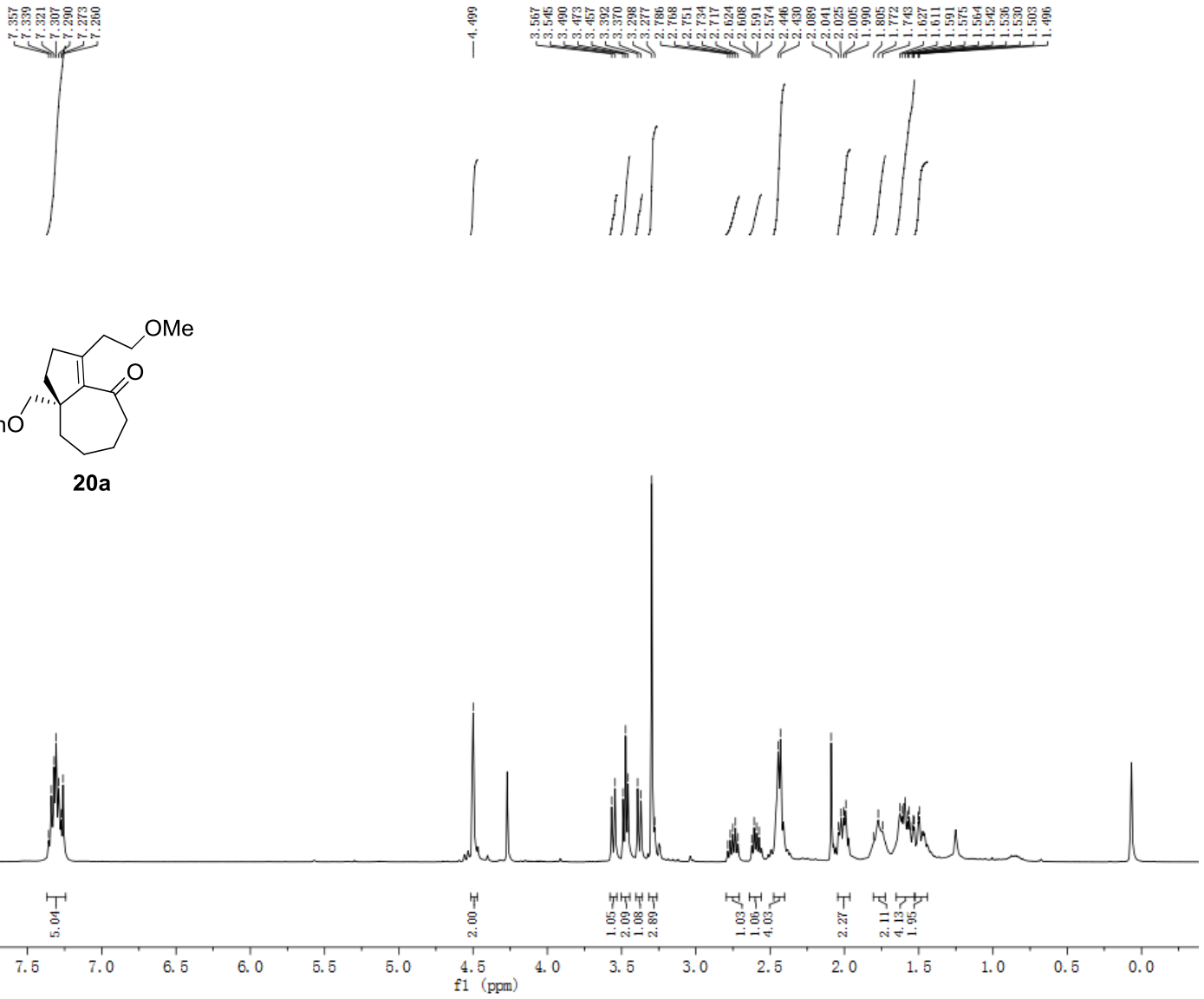
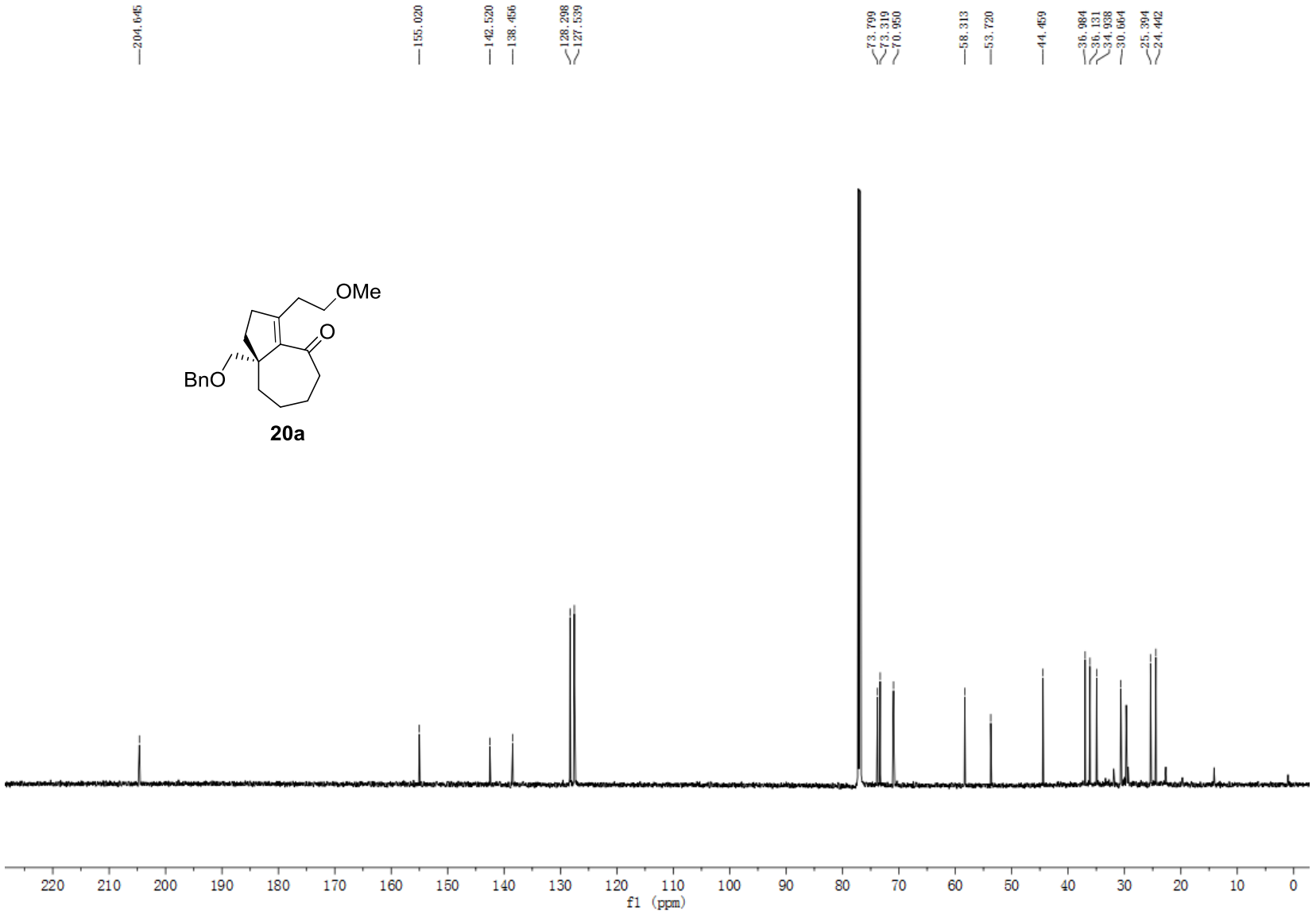
164.9
150.5
145.9
140.3
135.8
132.3
130.6
130.0
124.8
123.6
67.0
55.6
49.2
46.8
44.2
34.8
33.6
30.3
27.8
26.8
22.2
19.5
H
O
O
O
O_2N
24
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.357
7.339
7.321
7.307
7.290
7.273
7.260
4.499
3.567
3.545
3.490
3.473
3.457
3.392
3.370
3.298
3.277
2.786
2.768
2.751
2.734
2.717
2.624
2.608
2.591
2.574
2.446
2.430
2.089
2.041
2.025
2.005
1.990
1.805
1.772
1.743
1.627
1.611
1.591
1.575
1.564
1.542
1.536
1.530
1.503
1.496
OMe
O
BnO
5.04
2.00
1.05
2.09
1.08
2.89
1.03
1.06
4.03
2.27
2.11
4.13
1.95
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)

20a


204.645
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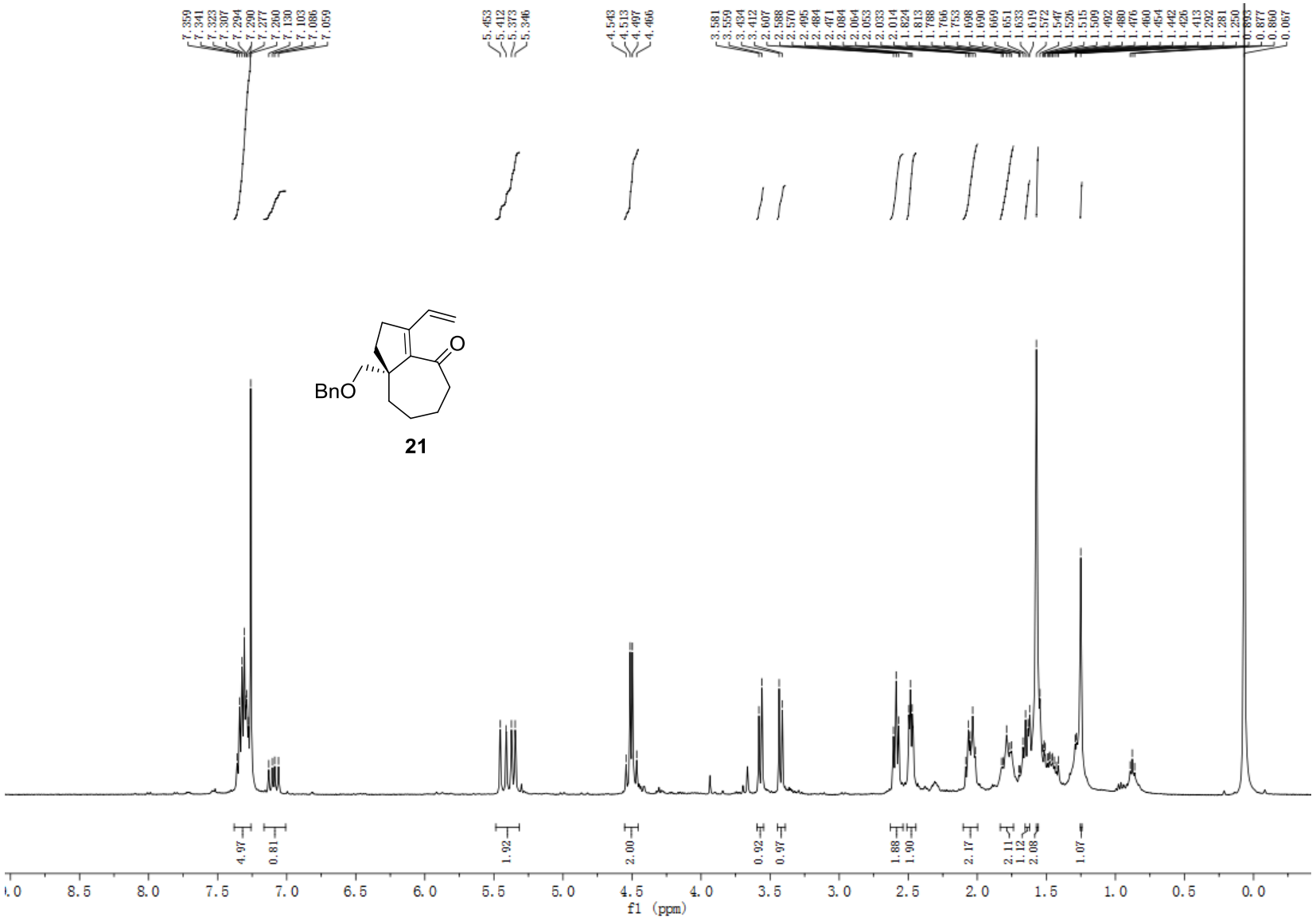
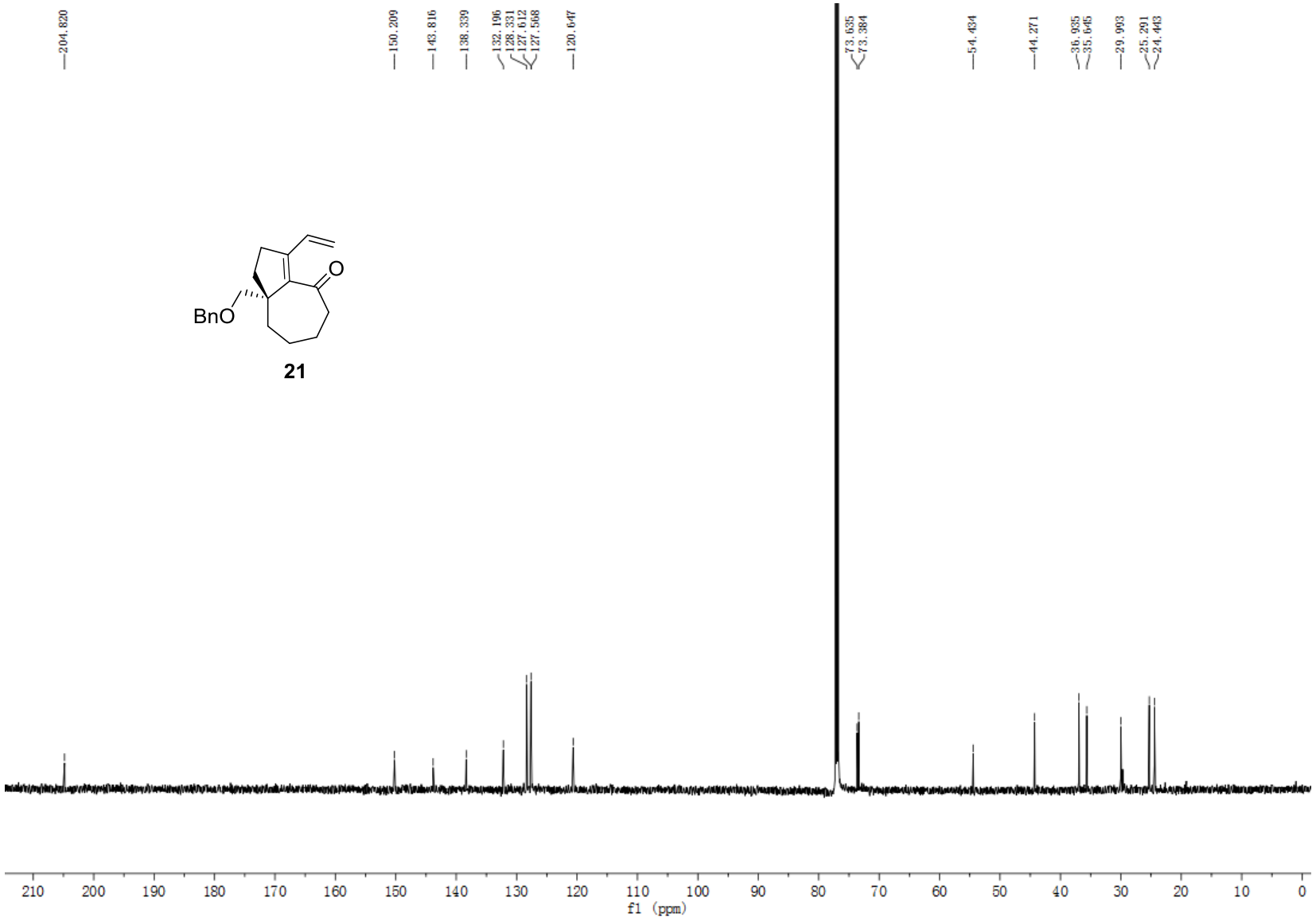
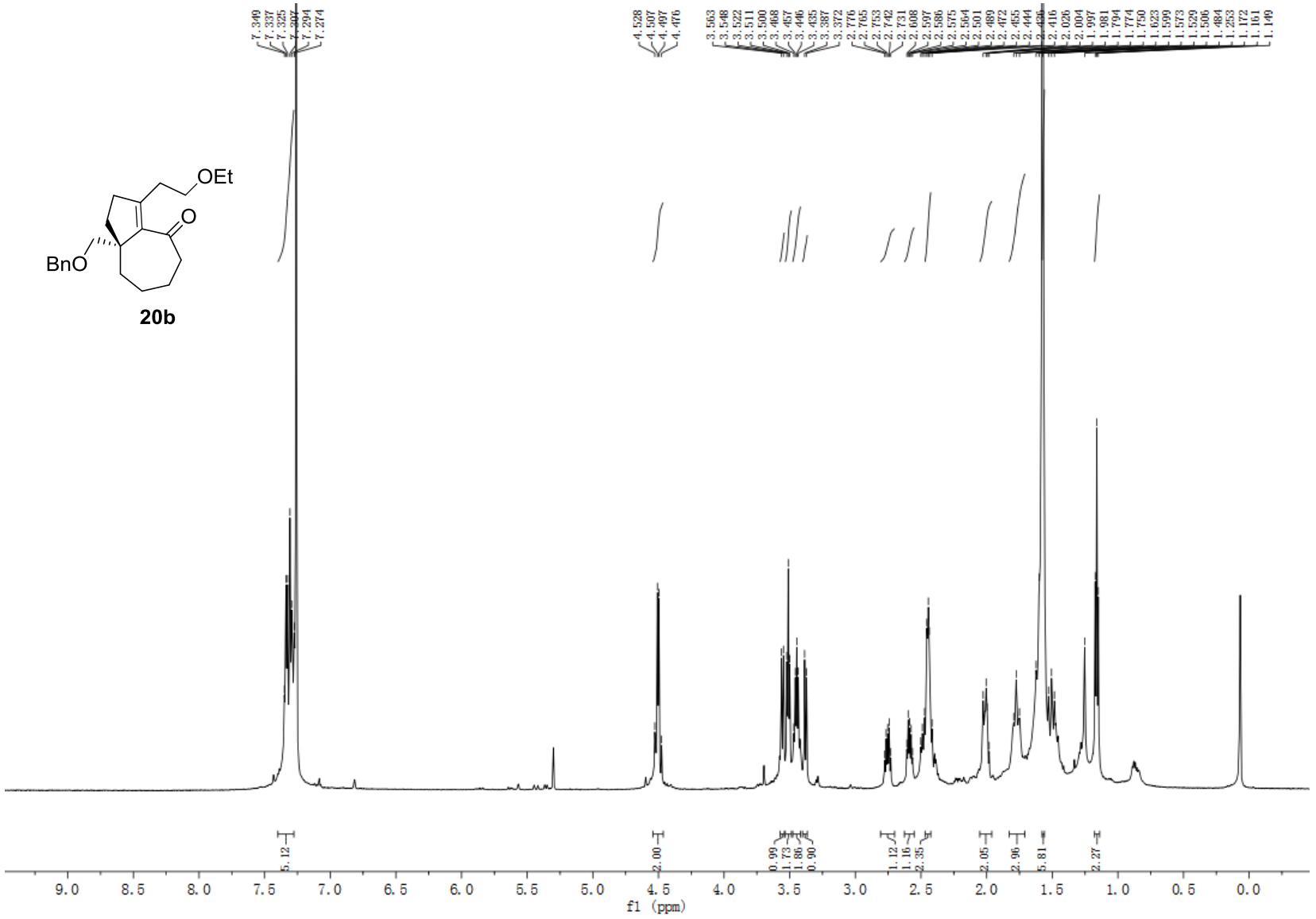
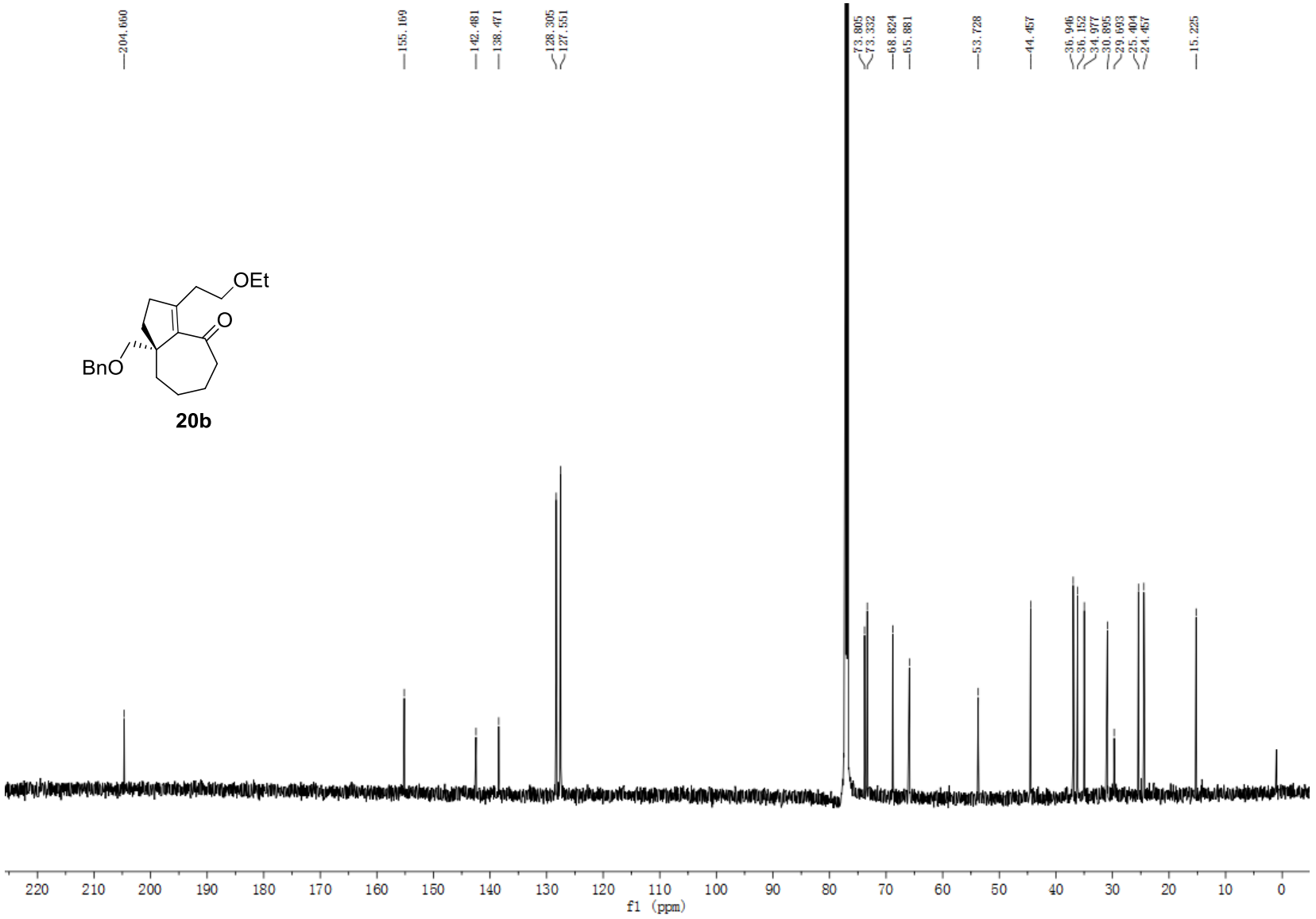
142.520
138.456
128.298
127.539
73.799
73.319
70.950
58.313
53.720
44.459
36.984
36.131
34.938
30.664
25.394
24.442
OMe
O
BnO
20a
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

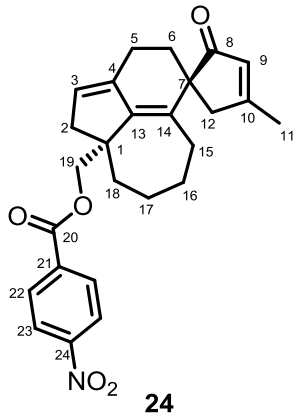

BnO
O
21
f1 (ppm)


204.820
150.209
143.816
138.339
132.196
128.331
127.612
127.568
120.647
73.635
73.384
54.434
44.271
36.935
35.645
29.993
25.291
24.443
BnO
O
21
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OEt
O
BnO
20b
f1 (ppm)


204.660
155.169
142.481
138.471
128.305
127.551
73.805
73.332
68.824
65.881
53.728
44.457
36.946
36.152
34.977
30.895
29.693
25.404
24.457
15.225
OEt
O
BnO
20b
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)

4. 2D-NMR spectra and their interpretations for compound 24



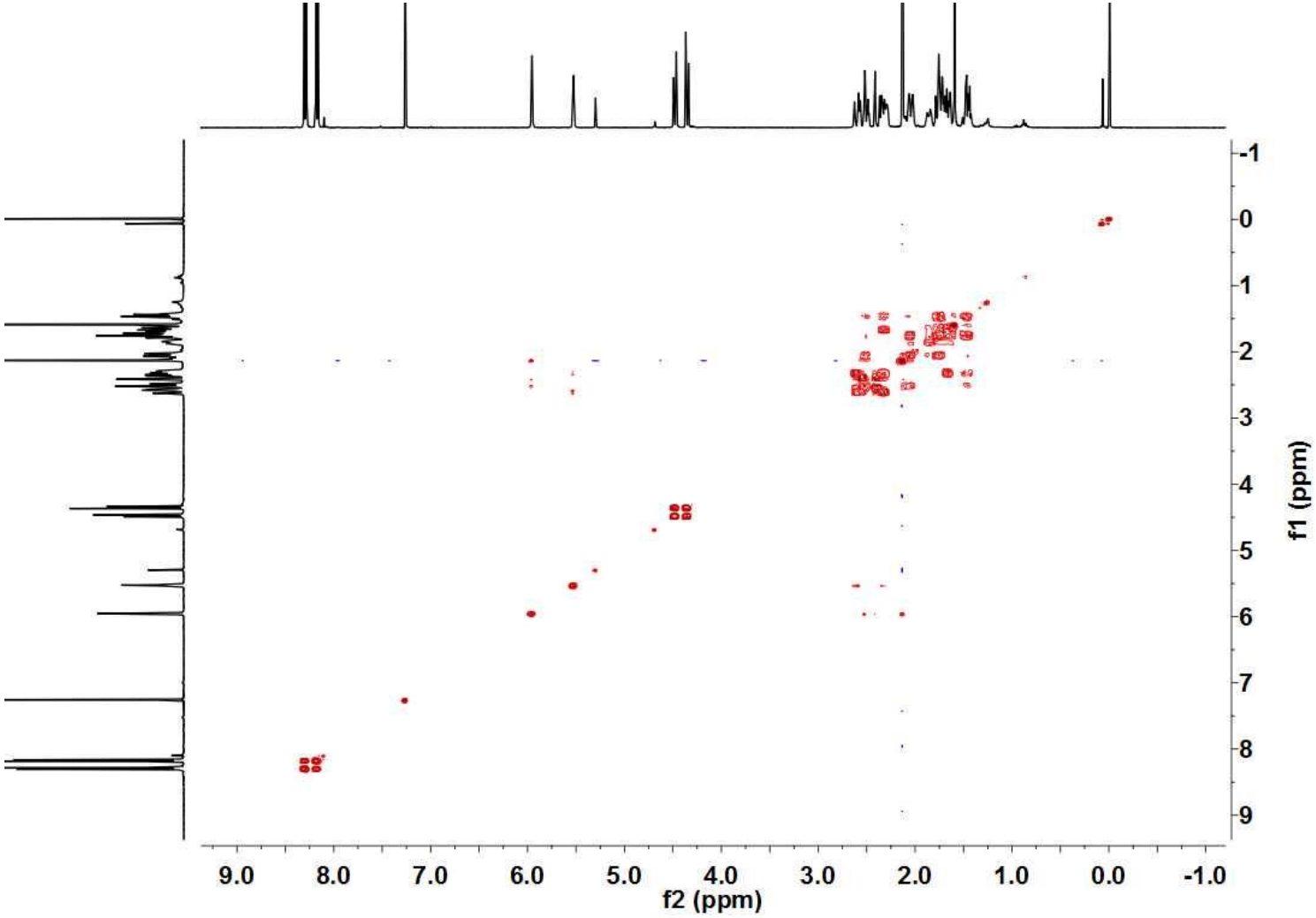
24

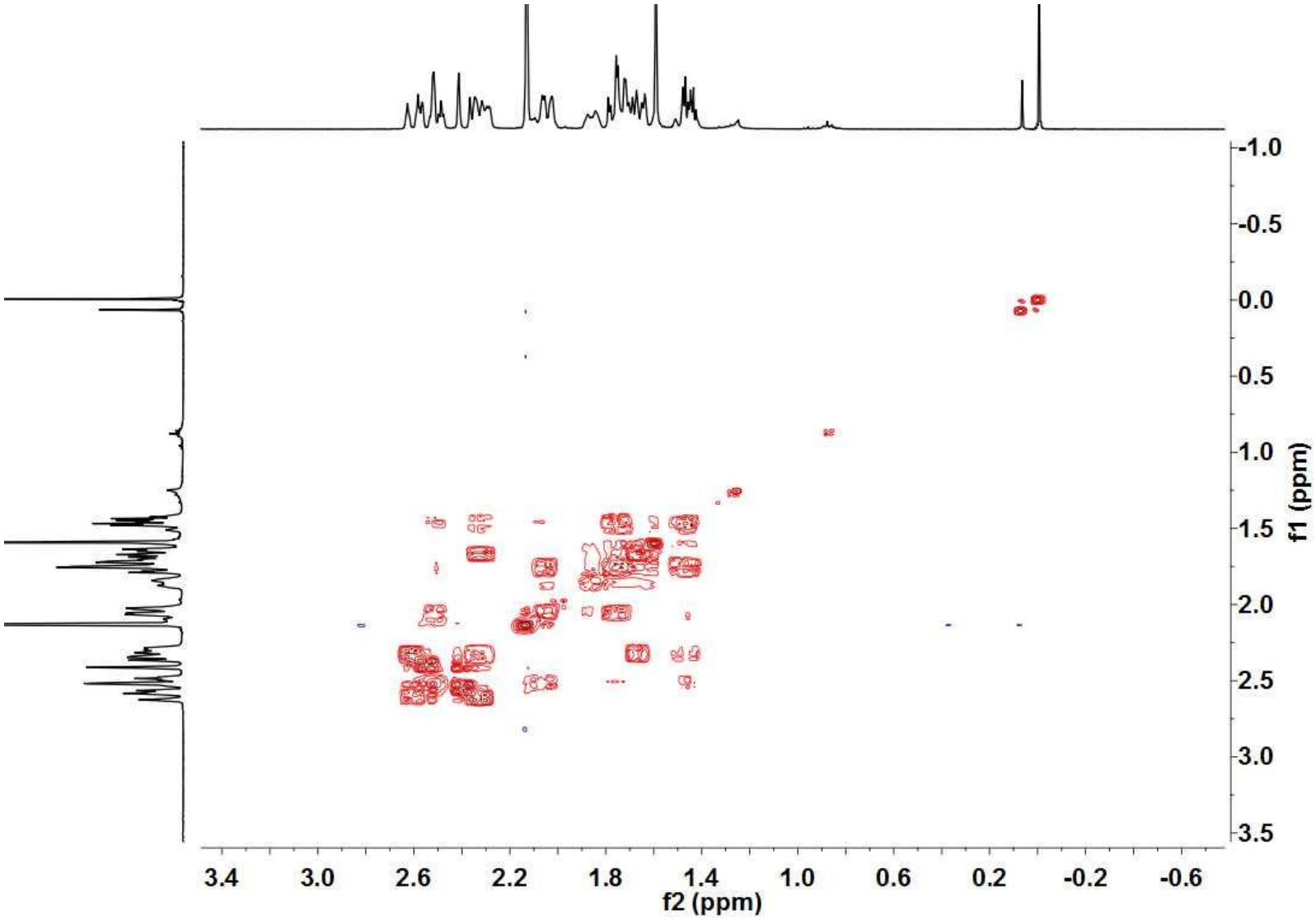
Table 1 The detailed interpretation of **2D NMR** spectra of **24**

Position	δ_C	δ_H	H-Hcosy	HMBC(H→C)
1	49.2 (C)			
2	44.2 (CH_2)	2.66 – 2.55 (m, 1 H) 2.37– 2.28 (m, 1 H)	H_3, H_{18}	C_3, C_4, C_5, C_{19}
3	124.8 (CH)	5.54 (s, 1 H)	H_2, H_5	C_1, C_2, C_{13}
4	140.3 (C)			
5	22.2 (CH_2)	2.57-2.46 (m, 1 H) 2.13-2.00 (m, 1 H)	H_6	C_1, C_6, C_7, C_{13}
6	27.7 (CH_2)	1.80-1.68 (m, 1 H) 1.54-1.40 (m, 1 H)	H_5, H_{12}	C_4, C_5, C_7, C_{12}
7	55.6 (C)			
8	213.5 (C)			
9	130.0 (CH)	5.96 (s, 1 H)	H_8	C_7, C_{10}, C_{11}, C_{12}

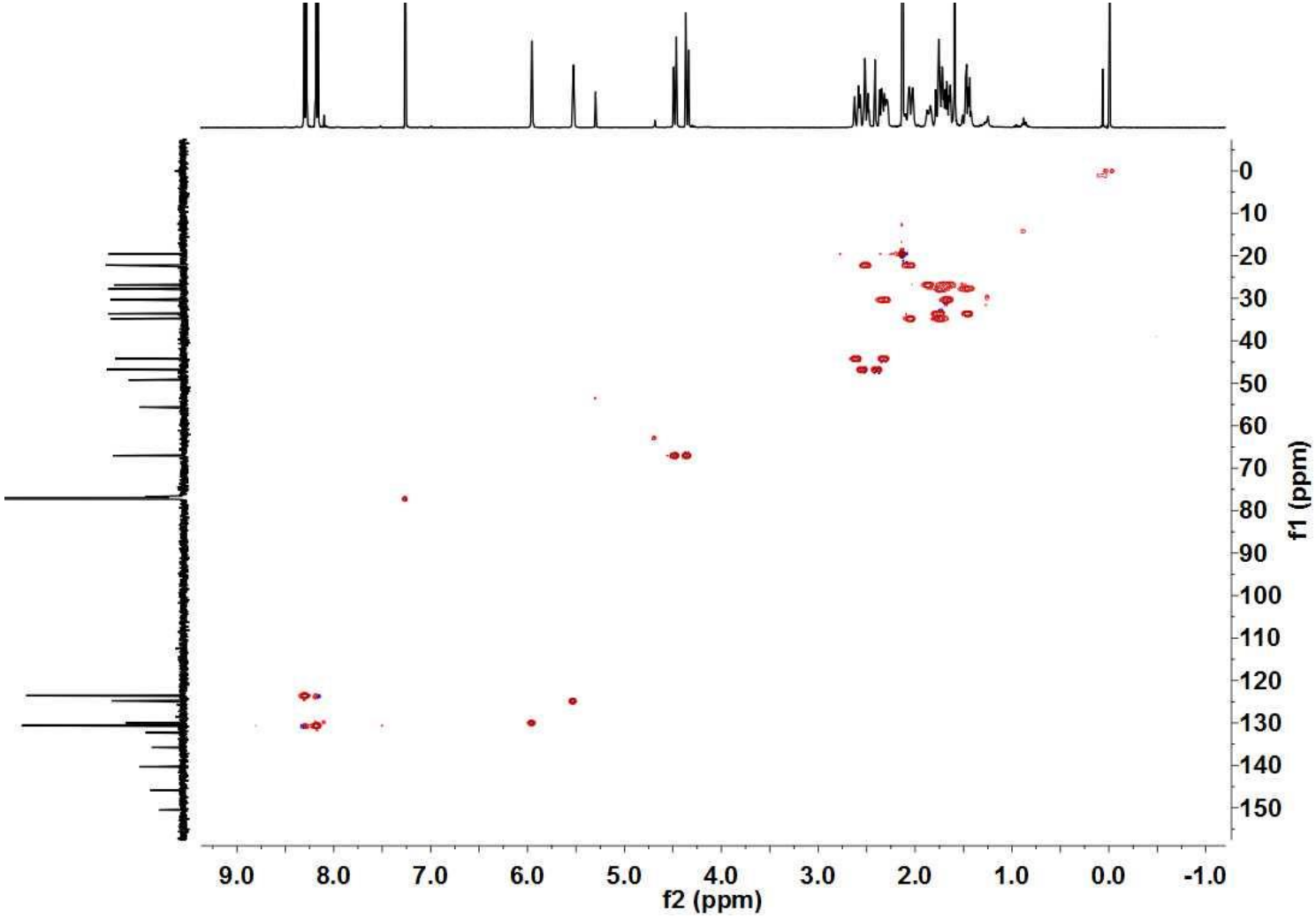
10	177.5 (C)			
11	19.5 (CH_3)	2.14 (s, 3 H)	H_{11}	C_9, C_{10}, C_{12}
12	46.8 (CH_2)	2.60-2.49 (m, 1 H) 2.45-2.35 (m, 1 H)	H_6, H_9, H_{11}	C_7, C_9, C_{11}
13	145.9 (C)			
14	132.3 (C)			
15	30.3 (CH_2)	2.40-2.26 (m, 1 H) 1.74-1.61 (m, 1 H)	H_{16}, H_{17}	C_{12}, C_{13}, C_{14}
16	33.6 (CH_2)	1.82-1.69 (m, 1 H) 1.51-1.41 (m, 1 H)	H_{15}, H_{17}, H_{18}	C_{13}, C_{14}
17	26.8 (CH_2)	1.93-1.81(m, 1 H) 1.78-1.58 (m, 1 H)	H_{15}, H_{16}, H_{18}	C_{14}
18	34.8 (CH_2)	2.11-2.00 (m, 1 H) 1.82-1.66 (m, 1 H)	H_{16}, H_{17}	C_1, C_{17}
19	67.0 (CH_2)	4.53-4.44 (d, *J* = 10.7 Hz, 1 H) 4.40-4.32 (d, *J* = 10.7 Hz, 1 H)		C_1, C_2, C_{13}, $C_{18,}$ C_{20}
20	164.9 (C)			
21	135.8 (C)			
22 (22*)	130.6 (CH)	8.25-8.14 (d, *J* = 8.7 Hz, 2 H)	H_{23} (H_{23*})	C_{20}, C_{21}, C_{23} (C_{23*})
23 (23*)	123.6 (CH)	8.35-8.26 (d, *J* = 8.7 Hz, 2 H)	H_{22} (H_{22*})	C_{20}, C_{21}, C_{22} (C_{22*})
24	150.5 (C)			

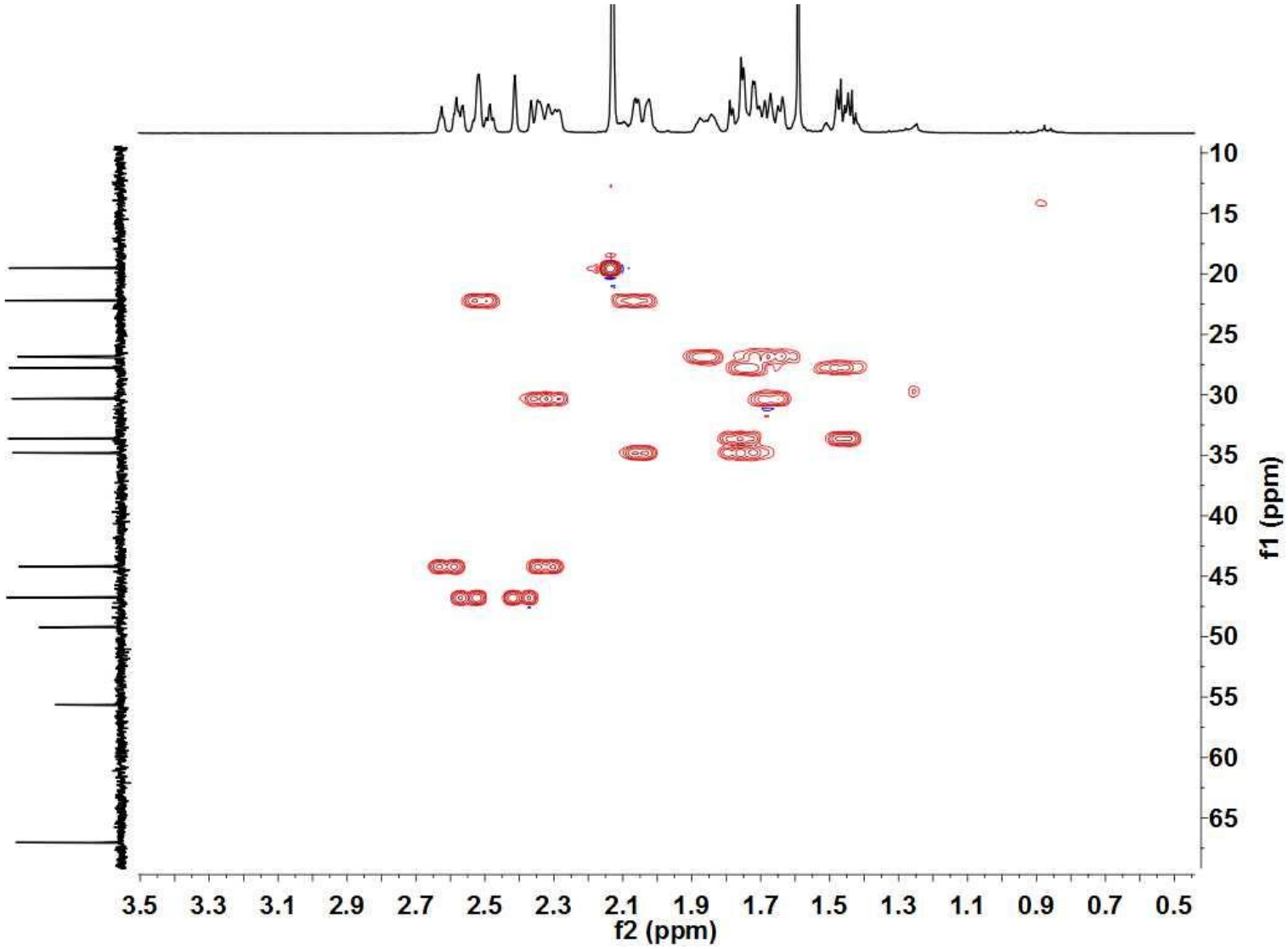
The copies of compound 24's ^{1}H-^{1}H COSY



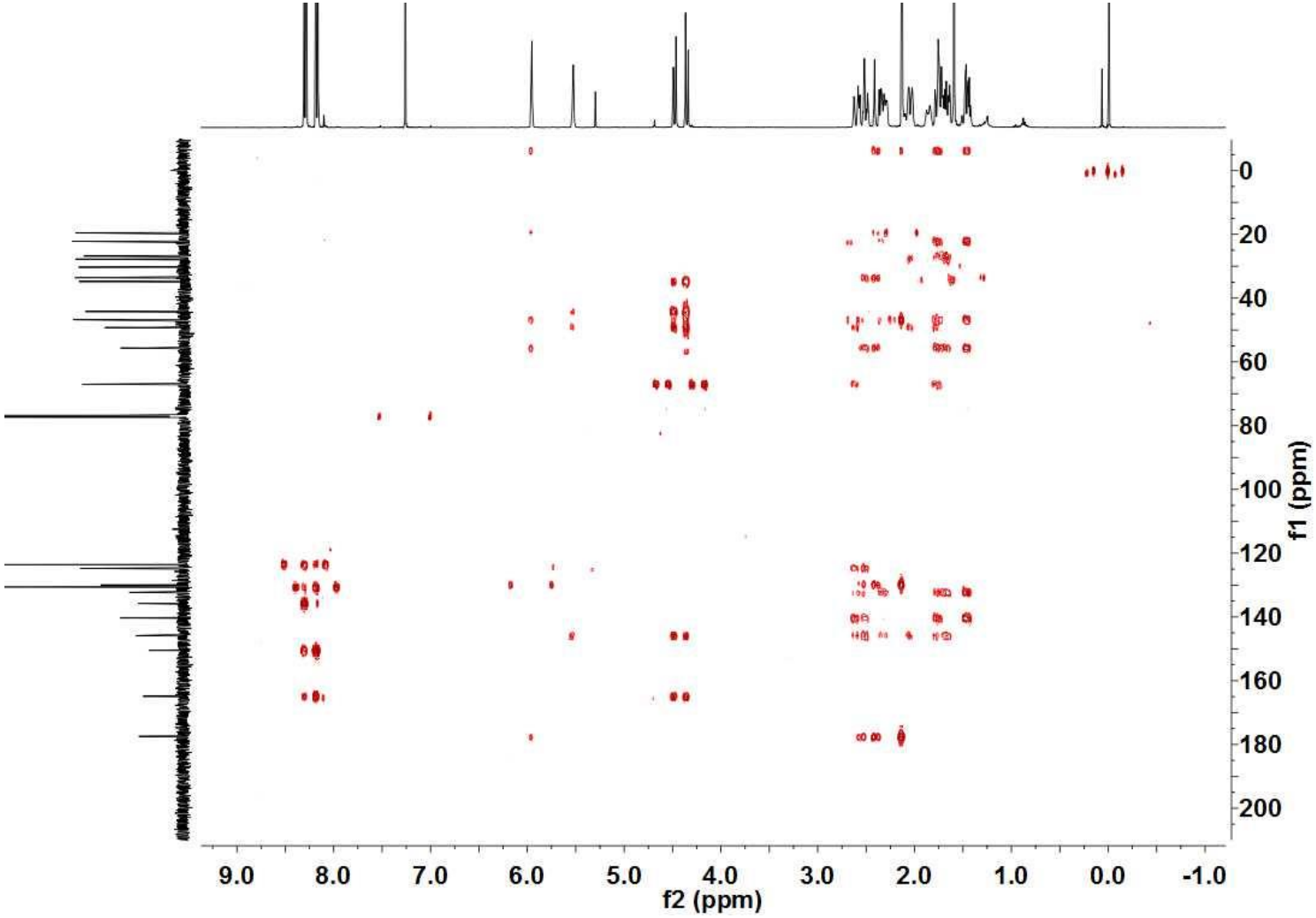

-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
f1 (ppm)
3.4
3.0
2.6
2.2
1.8
1.4
1.0
0.6
0.2
-0.2
-0.6
f2 (ppm)

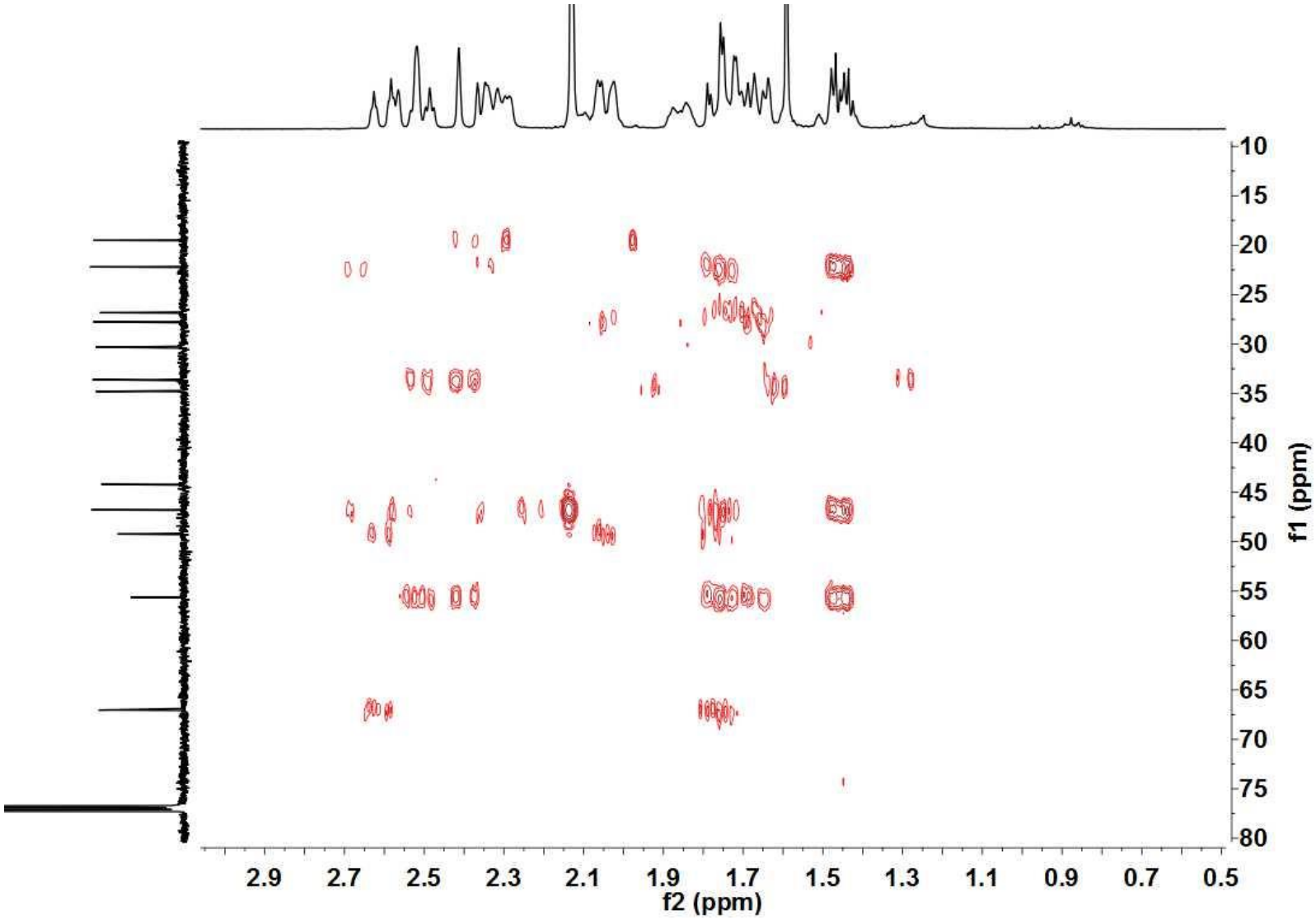
The copies of compound 24's HMQC

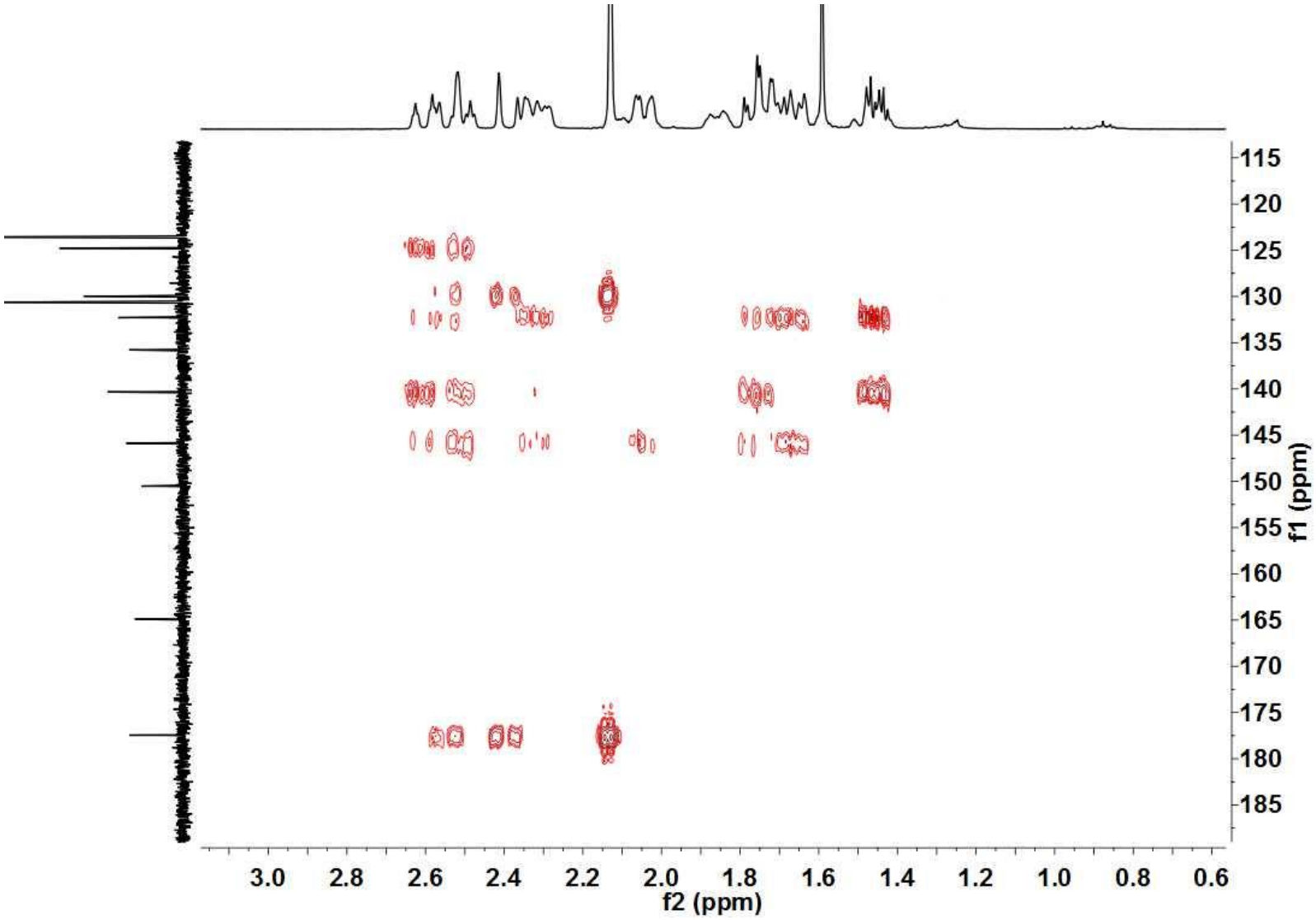



10
15
20
25
30
35
40
45
50
55
60
65
f1 (ppm)
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
1.5
1.3
1.1
0.9
0.7
0.5
f2 (ppm)

The copies of compound 24's HMBC




10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
f1 (ppm)
2.9
2.7
2.5
2.3
2.1
1.9
1.7
1.5
1.3
1.1
0.9
0.7
0.5
f2 (ppm)


115
120
125
130
135
140
145
150
155
160
165
170
175
180
185
f1 (ppm)
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
f2 (ppm)

The copy of compound 24's NOESY