Electronic Supplementary Information

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Contents

1. General

Air and moisture sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of dry argon. Similarly sensitive liquids and solutions were transferred via syringe. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Organic solutions were concentrated using a Büchi rotary evaporator with a desktop vacuum pump. Analytical TLC was performed with 0.25 mm silica gel G plates with a 254 nm fluorescent indicator. The TLC plates were visualized by ultraviolet light and treatment with phosphomolybdic acid stain followed by gentle heating. Purification of products was accomplished by flash chromatography on silica gel or basic Al_2O_3 and the purified compounds showed a single spot by analytical TLC.

Tetrahydrofuran, diethyl ether, 1,2-dimethoxyethane and toluene were distilled from sodium and benzophenone prior to use. Dichloromethane, 1,2-dichloroethane and acetonitrile were distilled from CaH_2 prior to use. Synthetic reagents were purchased from Acros, Aldrich, and Alfa Aesar and used without further purification, unless otherwise indicated.

NMR spectra were measured on Bruker ARX 400 (^{1}H at 400 MHz, ^{13}C at 101 MHz) nuclear magnetic resonance spectrometers. ^{1}H-NMR spectra are reported relative to Me_4Si (0.00 ppm) or residual solvent signals (C_6D_6: 7.16 ppm). Data for ^{1}H-NMR spectra are reported as follows: chemical shift (ppm, s = singlet, br. = broad, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, dm = doublet of multiplet, ddd = doublet of doublet of doublets, tdd = triplet of doublet of doublets, m = multiplet), coupling constant (Hz), and integration. Data for ^{13}C-NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak ($CDCl_3$: 77.0 ppm, C_6D_6: 128.0 ppm). Infrared spectra were recorded on Bruker Tensor 27 fourier transform infrared spectrometer (FT-IR) and were reported in wavenumbers (cm^{-1}). High-resolution mass spectra (HRMS) were recorded on Bruker Apex IV FTMS mass spectrometer (ESI) and Micromass U.K. GCT GC–MS mass spectrometer (EI). Optical rotations were measured on a Perkin-Elmer 341 LC spectrometer. The enatiomeric excesses (ee) of the products were determined by chiral HPLC analysis using Dionex Ultimate 3000 instrument.

Abbreviations:

Ac = acetyl
AIBN = azodiisobutyronitrile
Bn = benzyl
Boc = *t*-butoxycarbonyl
ca = circa
CBS = Corey-Bakshi-Shibata reagent
COD = 1,5-cyclooctadiene
COE = cyclooctene
DCE = 1,2-dichloroethane
DCM = dichloromethane
DIAD = diisopropyl azodicarboxylate
dppp = 1,3-*bis*(diphenylphosphino)propane
dppm = *bis*(diphenylphosphino)methane
EA = ethyl acetate
MS = molecular sieve
PDC = pyridinium dichromate
PE = petroleum ether
TBDPS = *t*-butyldiphenylsilyl
TBS = *t*-butyldimethylsilyl
TBAF = *tert*-*n*-butylammonium fluoride
THF = tetrahydrofuran
THP = 2-tetrahydropyranyl

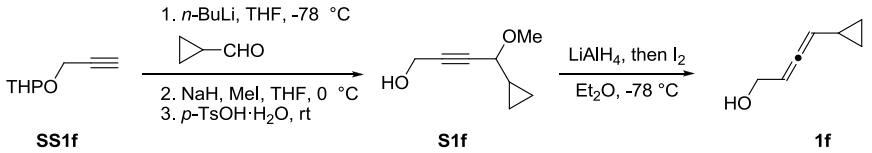
DMAP = *N*,*N*-4-dimethylaminopyridine
DME = 1,2-dimethoxyethane
DMF = *N*,*N*-dimethylformamide
TLC = thin layer chromatography
Ts = *p*-toluenesulfonyl

2. Experimental Procedures and Characterization Data

2.1 Synthesis of Substrates

Substrates **1a**,[1] **1b–d**,[2] **1e**,[3] **1j**,[2] **1o**[2] were synthesized according to the reported literature.

Substrate (1f)



SS1f **S1f** **1f**

To a solution of **SS1f**[4] (2.80 g, 20 mmol) in THF (40 mL) was added *n*-BuLi (2.5 M, 10 mL, 25 mmol) under an argon atmosphere at -78 ℃, and the resulting solution was stirred for 1 h at -78 ℃. Then cyclopropanecarboxaldehyde (2.10 g, 30 mmol) was added dropwise at -78 ℃, and the resulting mixture was stirred at room temperature until the disappearance of the starting material. After that, saturated aqueous NH_4Cl was added to quench the reaction, and the mixture was extracted with ether. The combined extract was washed with water and brine, dried over Na_2SO_4, and concentrated.

The crude product was dissolved in THF (40 mL) and NaH (60% purity, 1.20 g, 30 mmol) was added to it at 0 ℃. After stirred for 20 min, iodomethane (5.68 g, 40 mmol) was added and the reaction mixture was stirred for 1 h. After that, saturated aqueous NH_4Cl was added to quench the reaction, and the mixture was extracted with ether. The combined extract was washed with water and brine, dried over Na_2SO_4, and concentrated.

To a solution of the crude product in MeOH (30 mL) was added *p*-TsOH·H_2O (380 mg, 2 mmol) and the resulting solution was stirred for 6 h at room temperature. The solution was concentrated directly and the crude alcohol was purified by flash column chromatography (eluted with PE/EA, 5:1) to afford alcohol **S1f** (2.03 g, 72%, 3 steps).

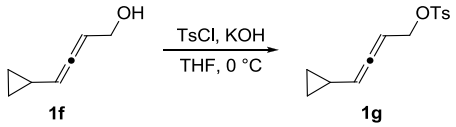
S1f: light yellow oil, TLC R_f = 0.32 (PE/EA, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.34–4.29 (m, 2H), 3.83–3.76 (m, 1H), 3.42 (d, J = 1.3 Hz, 3H), 2.23–1.98 (br, 1H), 1.25–1.15 (m, 1H), 0.59–0.52 (m, 2H), 0.48–0.39 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 84.3, 82.3, 74.5, 56.2, 50.9, 14.8, 3.2, 1.7. IR (KBr): υ 3383, 3008, 2937, 2827, 1729, 1645, 1580, 1449, 1320, 1083, 1022, 971, 897 cm^{-1}. HRMS (EI) calcd for $C_8H_{11}O_2$ ([M-H]$^+$): 139.0754. Found: 139.0754.

Lithium aluminum hydride (668 mg, 17.6 mmol) was added to diethyl ether (88 mL) and cooled to 0 ℃. Compound **S1f** (616 mg, 4.4 mmol) in ether (20 mL) was added dropwise, and the reaction mixture was stirred for 20 min at 0 ℃. The solution was cooled to -78 ℃, iodine was added (3.35 g, 13.2 mmol), and the mixture was stirred for 2 h. After warming to 0 ℃, saturated aqueous potassium sodium tartrate and saturated aqueous $Na_2S_2O_3$ were added and stirred overnight. The water layer was extracted twice with ether. Ether layers were combined and dried with anhydrous Na_2SO_4 and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with pentane/ether 3:1) to afford allene **1f** (429 mg, 89%).

1f: light yellow oil, TLC R_f = 0.47 (PE/EA, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.47–5.38 (m,

1H), 5.20–5.12 (m, 1H), 4.11 (dd, J = 5.7, 2.9 Hz, 2H), 1.53 (brs, 1H), 1.31–1.23 (m, 1H), 0.76–0.70 (m, 2H), 0.40–0.32 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 202.2, 98.6, 93.6, 60.6, 9.4, 6.8. IR (KBr): υ 3325, 3081, 3004, 2930, 2870, 1962, 1428, 1257, 1015 cm^{-1}. HRMS (EI) calcd for $C_7H_{10}O$ (M^+): 110.0726. Found: 110.0733.

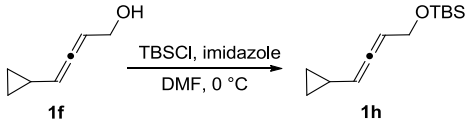
Substrate (1g)



To a solution of the **1f** (225 mg, 2 mmol) in THF (10 mL) was added TsCl (362 mg, 1.9 mmol) and KOH (1.12 g, 20 mmol) at 0 ℃. The resulting mixture was stirred for 2 h at 0 ℃ and then water was added to quench the reaction. The water layer was extracted twice with ether. The ether layers were combined and dried with anhydrous Na_2SO_4 and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 10:1) to afford product **1g** (326 mg, 60%)

1g: light yellow oil, TLC R_f = 0.54 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.3 Hz, 2H), 5.24 (td, J = 7.2, 1.0 Hz, 1H), 5.12–5.05 (m, 1H), 4.52 (dd, J = 7.2, 2.0 Hz, 2H), 2.45 (s, 3H), 1.26–1.16 (m, 1H), 0.75–0.67 (m, 2H), 0.37–0.28 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 205.9, 144.7, 133.5, 129.8, 127.9, 98.1, 87.4, 69.0, 21.6, 8.9, 6.9, 6.8. IR (KBr): υ 3080, 3005, 1964, 1598, 1453, 1364, 1180, 1097, 1021, 929 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{16}NaO_3S$ ($M+Na^+$): 287.0712. Found: 287.0710.

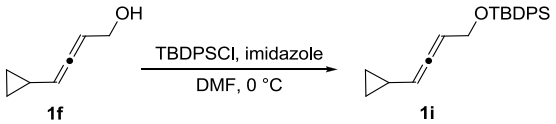
Substrate (1h)



To a solution of the **1f** (222 mg, 2 mmol) in DMF (10 mL) was added TBSCl (630 mg, 4.2 mmol) and imidazole (300 mg, 4.4 mmol) at 0 ℃. The resulting mixture was stirred for 1 h at 0 ℃ and then water was added to quench the reaction. The water layer was extracted twice with ether. The ether layers were combined and dried with anhydrous Na_2SO_4 and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE) to afford product **1h** (373 mg, 82%)

1h: colorless oil, TLC R_f = 0.88 (PE/EA, 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.34–5.26 (m, 1H), 5.06–4.99 (m, 1H), 4.19–4.14 (m, 2H), 1.30–1.22 (m, 1H), 0.91 (s, 9H), 0.72–0.66 (m, 2H), 0.38–0.32 (m, 2H), 0.08 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 202.8, 96.9, 93.5, 62.0, 25.9, 18.4, 9.5, 6.7, 6.6, -5.09, -5.11. IR (KBr): υ 3082, 2932, 2858, 1963, 1467, 1364, 1255, 1089, 839 cm^{-1}. HRMS (EI) calcd for $C_9H_{15}OSi$ ($[M-C(CH_3)_3]^+$): 167.0887. Found: 167.0894.

Substrate (1i)

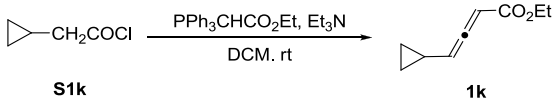


1f **1i**

To a solution of the **1f** (443 mg, 4 mmol) in DMF (25 mL) was added TBDPSCl (1.59 g, 5.8 mmol) and imidazole (546 mg, 8 mmol) at 0 ℃. The resulting mixture was stirred overnight and then water was added to quench the reaction. The water layer was extracted twice with ether. The ether layers were combined and dried with anhydrous Na_2SO_4 and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 100:1 then 30:1) to afford product **1i** (1.24 g, 89%).

1i: colorless oil, TLC R_f = 0.42 (PE). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73–7.66 (m, 4H), 7.45–7.35 (m, 6H), 5.36–5.29 (m, 1H), 5.03–4.97 (m, 1H), 4.20 (dd, J = 6.0, 2.7 Hz, 2H), 1.27–1.18 (m, 1H), 1.05 (s, 9H), 0.71–0.64 (m, 2H), 0.36–0.30 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 203.0, 135.6, 133.82, 133.81, 129.6, 127.6, 97.0, 93.2, 62.4, 26.8, 19.2, 9.5, 6.7, 6.6. IR (KBr): υ 3072, 3001, 2931, 2857, 1962, 1590, 1487, 1428, 1112 cm^{-1}. HRMS (EI) calcd for $C_{23}H_{28}OSi$ (M^+): 348.1904. Found: 348.1906.

Substrate (1k)

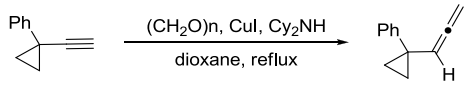


S1k **1k**

To a solution of (carbethoxymethylene)triphenylphosphorane (2.64 g, 7.6 mmol) in DCM (20 mL) was added Et_3N (773 mg, 7.6 mmol) and then a solution of **S1k**[5] (900 mg, 7.6 mmol) in 8mL DCM was added slowly in about 1 h. The reaction mixture was stirred overnight and concentrated. Pentane was added and then insoluble triphenylphosphine oxide was filtered off. The filtrate was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 20:1) to afford product **1k** (660 mg, 57%).

1k: colorless oil, TLC R_f = 0.52 (PE/EA, 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.65 (d, J = 6.1 Hz, 1H), 5.50 (dd, J = 7.5, 6.1 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 1.39–1.32 (m, 1H), 1.28 (t, J = 7.1 Hz, 3H), 0.82–0.77 (m, 2H), 0.51–0.43 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 212.5, 165.9, 100.0, 89.7, 60.8, 14.2, 8.4, 7.2, 6.9. IR (KBr): υ 3086, 2985, 1959, 1718, 1431, 1334, 1258, 1159, 1031 cm^{-1}. HRMS (EI) calcd for $C_9H_{12}O_2$ (M^+): 152.0832. Found: 152.0836.

Substrate (1l)



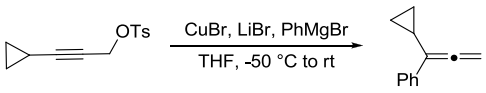
S1l **1l**

To a dried reaction tube was added CuI (244 mg, 1.28 mmol) and paraformaldehyde (193 mg, 6.43 mmol). Then the solution of alkyne **S1l**[6] (365 mg, 2.57 mmol) in dioxane (10 mL) and Cy_2NH (839 mg, 4.63 mmol) were added sequentially into this dried reaction tube equipped with a reflux condenser under an argon atmosphere and the resulting mixture was refluxed for 3 h. After

the disappearance of the starting material, the reaction mixture was cooled to room temperature and water was added to quench the reaction. The mixture was extracted with ether twice. The combined extract was washed with water and brine, dried over $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE) to afford product **1l** (256 mg, 64%).

1l: colorless oil, TLC R_f = 0.61 (PE). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33–7.25 (m, 4H), 7.21–7.15 (m, 1H), 5.44 (t, J = 6.6 Hz, 1H), 4.74 (d, J = 6.6 Hz, 2H), 1.10–1.06 (m, 2H), 1.05–1.00 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 207.6, 144.2, 128.2, 128.0, 126.1, 97.7, 77.4, 23.4, 15.7. IR (KBr): υ 3027, 3004, 1956, 1495, 1384, 1024, 849 cm^{-1}. HRMS (EI) calcd for $C_{12}H_{12}$ (M^+): 156.0934. Found: 156.0939.

Substrate (1m)

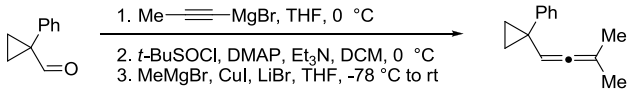


S1m **1m**

To a suspension of CuBr (860 mg, 6 mmol) and LiBr (521mg, 6 mmol) in THF (15 mL) was added PhMgBr (25%, 3.28 g, 6 mmol) at -50 ℃. The resulting mixture was stirred for 10 min and then a solution of **S1m**[7] (751 mg, 3 mmol) in THF (3 mL) was added dropwise. After stirred for 2 h at 0 ℃, buffer solution of NH_4Cl–NH_3 was added to quench the reaction, and the mixture was extracted with ether. The combined extract was washed with water and brine, dried over Na_2SO_4, and concentrated. The crude product was purified by flash column chromatography on basic Al_2O_3 (eluted with PE) to afford product **1m** (344 mg, 73%).

1m: colorless oil, TLC R_f = 0.76 (PE). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60–7.54 (m, 2H), 7.37–7.31 (m, 2H), 7.24–7.18 (m, 1H), 5.09 (d, J = 2.9 Hz, 2H), 1.60–1.53 (m, 1H), 0.91–0.84 (m, 2H), 0.58–0.52 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 207.8, 136.7, 128.3, 126.7, 126.2, 108.2, 79.2, 10.4, 6.8. The spectra are consistent with the literature reported[8].

Substrate (1n)



1n

To a solution of 1-phenylcyclopropanecarbaldehyde (440 mg, 3 mmol) in THF (3 mL) was added 1-propynylmagnesium bromide (0.5 M, 9 mL, 4.5 mmol) at 0 ℃, and the resulting solution was stirred for 3 h. Saturated aqueous NH_4Cl was added to quench the reaction, and the mixture was extracted with ether. The combined extract was washed with water and brine, dried over Na_2SO_4, and concentrated. The crude alcohol product was purified by flash column chromatography on silica gel (eluted with PE/EA 3:1) and used directly in the next step.

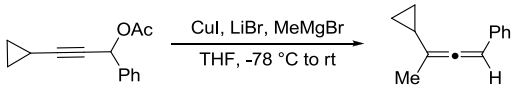
To a solution of the alcohol in DCM (30 mL) was added DMAP (41 mg, 0.34 mmol), Et_3N (610 mg, 6 mmol) and *t*-BuSOCl (849 mg, 6 mmol) in sequence and the resulting mixture was stirred for 90 min at 0 ℃. Water was added to quench the reaction, and the mixture was extracted with DCM. The combined extract was washed with brine, dried over Na_2SO_4, and concentrated.

The crude sulfinic ester was purified by flash column chromatography on silica gel (eluted with PE/EA 5:1).

To a suspension of CuI (1.14 g, 6 mmol) and LiBr (520 mg, 6 mmol) in THF (30 mL) was added MeMgBr (3 M, 2 mL, 6 mmol) at -78 ℃. The resulting mixture was stirred for 2 h and then a solution of the sulfinic ester in THF (5 mL) was added dropwise. After stirred for 3 h at room temperature, buffer solution of NH_4Cl–NH_3 was added to quench the reaction, and the mixture was extracted with ether. The combined extract was washed with brine, dried over Na_2SO_4, and concentrated. The crude product was purified by flash column chromatography on basic Al_2O_3 (eluted with PE) to afford product **1n** (146 mg, 26%, 3 steps).

1n: colorless oil, TLC R_f = 0.64 (PE). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32–7.25 (m, 4H), 7.19–7.13 (m, 1H), 5.27–5.21 (m, 1H), 1.63 (s, 3H), 1.62 (s, 3H), 1.06–1.02 (m, 2H), 0.97–0.93 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.8, 144.9, 128.0, 127.9, 125.8, 97.9, 96.6, 24.5, 20.6, 15.8. IR (KBr): υ 3080, 2909, 2856, 2712, 1963, 1602, 1496, 1447, 1217, 1018 cm^{-1}. HRMS (EI) calcd for $C_{14}H_{16}$ (M^+): 184.1246. Found: 184.1250.

Substrate (1p)

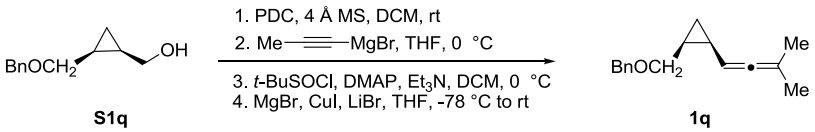


S1p **1p**

To a suspension of CuI (1.14 g, 6 mmol) and LiBr (520mg, 6 mmol) in THF (60 mL) was added MeMgBr (3 M, 2 mL, 6 mmol) at -78 ℃. The resulting mixture was stirred for 2 min and then a solution of **S1p**[9] (431 mg, 2 mmol) in THF (2 mL) was added dropwise at -78 ℃. After stirred for 1 h at room temperature, buffer solution of NH_4Cl–NH_3 was added to quench the reaction, and the mixture was extracted with ether. The combined extract was washed with brine, dried over Na_2SO_4, and concentrated. The crude product was purified by flash column chromatography on basic Al_2O_3 (eluted with PE) to afford product **1p** (304 mg, 89%).

1p: colorless oil, TLC R_f = 0.72 (PE). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.21 (m, 4H), 7.19–7.13 (m, 1H), 6.11–6.06 (m, 1H), 1.84 (d, J = 2.9 Hz, 3H), 1.31–1.22 (m, 1H), 0.72–0.64 (m, 2H), 0.49–0.44 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 202.1, 135.8, 128.5, 126.49, 126.47, 106.6, 95.1, 18.0, 13.7, 6.5, 6.0. IR (KBr): υ 3082, 3002, 2917, 2361, 1947, 1597, 1495, 1368, 1226, 1071 cm^{-1}. HRMS (EI) calcd for $C_{13}H_{14}$ (M^+): 170.1090. Found: 170.1093.

Substrate (1q)



S1q **1q**

To a solution of alcohol **S1q**[10] (573 mg, 3 mmol) in DCM (15 mL) was added PDC (1.69 g, 4.5 mmol) and 4 Å MS (1 g). The mixture was then stirred for 1 h at room temperature. The resulting mixture was purified by flash column chromatography on silica gel (eluted with PE/EA 20:1 then 10:1) to afford aldehyde.

To a solution of the aldehyde in THF (10 mL) was added 1-propynylmagnesium bromide

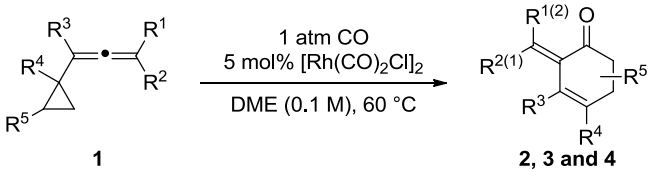
(0.5 M, 9 mL, 4.5 mmol) at 0 ℃, and the resulting solution was stirred for 3 h. Saturated aqueous NH_4Cl was added to quench the reaction, and the mixture was extracted with ether. The combined extract was washed with water and brine, dried over Na_2SO_4, and concentrated. The crude alcohol product was purified by flash column chromatography on silica gel (eluted with PE/EA 10:1 then 5:1) and used directly.

To a solution of the alcohol in DCM (30 mL) was added DMAP (37 mg, 0.3 mmol), Et_3N (607 mg, 6 mmol) and *t*-BuSOCl (840 mg, 6 mmol) in sequence and the resulting mixture was stirred until the disappearance of the substrate. Water was added to quench the reaction, and the mixture was extracted with DCM. The combined extract was washed with brine, dried over Na_2SO_4, and concentrated. The crude sulfinic ester was purified by flash column chromatography on silica gel (eluted with PE/EA 10:1 then 5:1).

To a suspension of CuI (1.71 g, 9 mmol) and LiBr (782 mg, 9 mmol) in THF (50 mL) was added MeMgBr (3 M, 3 mL, 9 mmol) at -78 ℃. The resulting mixture was stirred for 2 h and then a solution of the sulfinic ester in THF (5 mL) was added dropwise. After the consumption of the starting material, buffer solution of NH_4Cl–NH_3 was added to quench the reaction, and the mixture was extracted with ether. The combined extract was washed with brine, dried over Na_2SO_4, and concentrated. The crude product was purified by flash column chromatography on basic Al_2O_3 (eluted with PE) to afford product **1q** (387 mg, 57%, 4 steps).

1q: colorless oil, TLC R_f = 0.52 (PE/EA, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.24 (m, 5H), 5.05–4.94 (m, 1H), 4.53 (s, 2H), 3.52 (dd, *J* = 10.2, 6.2 Hz, 1H), 3.37 (dd, *J* = 10.2, 8.0 Hz, 1H), 1.68 (d, *J* = 2.8 Hz, 3H), 1.58 (d, *J* = 2.8 Hz, 3H), 1.49–1.41 (m, 1H), 1.35 – 1.27 (m, 1H), 0.90 – 0.82 (m, 1H), 0.32–0.26 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 202.8, 138.6, 128.3, 127.7, 127.5, 96.2, 87.7, 72.7, 69.9, 20.7, 20.5, 17.9, 15.0, 9.3. IR (KBr): υ 3066, 2980, 2909, 2855, 1973, 1732, 1450, 1369, 1093, 1029 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{20}NaO$ ($M+Na^+$): 251.1406. Found: 251.1403.

2.2 [5+1] Cycloaddition



1 **2, 3 and 4**

General procedure: $[Rh(CO)_2Cl]_2$ (5.8 mg, 0.015 mmol, 5 mol%) was dissolved in anhydrous solvent (DME, 2 mL) and bubbled with CO gas for 5 min at room temperature. Then a solution of substrate (0.3 mmol in 1 mL DME) was added slowly with the help of syringe pump (ca 1 h) at 60 ℃ under balloon pressured CO (1 atm). After addition of the substrate, the solution was continuously stirred for 1.5 h or 2 h at 60 ℃ under balloon pressured CO (1 atm). When TLC indicated the disappearance of the starting material, the reaction mixture was cooled to room temperature and concentrated. The crude mixture was submitted to flash column chromatography on silica gel to afford the corresponding product.

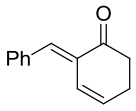
The *Z* or *E* configurations of **2a**, **2b**, **2o** & **3o** were assigned by comparing with the known compounds.

The configurations of **2b**, **2i** and **3i** were confirmed by NOESY.

The stereochemistry of **2c** and **2d** were assigned by analogy to the known compounds (**2a** and **2b)**. In these compounds, the chemical shifts of exocyclic vinyl H atom were around 7.5 ppm.

The stereochemistry of other compounds (**2e** & **3e**, **2h** & **3h**, **2j** & **3j**, **2p** & **3p**) were assigned by analogy to **2i** and **3i.** The chemical shifts of exocyclic vinyl H atom in *E* configuration products were in low field compared with the chemical shifts of exocyclic vinyl H atom in *Z* configuration products.

Product (2a)



2a

Reaction time: 2 h.

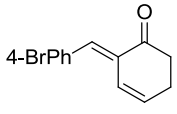
Run 1: 46.9 mg **1a** was converted to 45.0 mg **2a**, yield 81%.

Run 2: 47.3 mg **1a** was converted to 44.3 mg **2a**, yield 79%.

So the average yield of two runs was 80%.

2a: yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.35 (m, 5H), 7.35–7.30 (m, 1H), 6.95–6.89 (dm, J = 10.0 Hz, 1H), 6.20–6.10 (m, 1H), 2.70–2.65 (m, 2H), 2.62–2.56 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.2, 135.4, 132.0, 131.1, 131.0, 130.0, 128.6, 128.4, 125.2, 38.2, 24.6. The ^{1}H NMR and ^{13}C NMR spectra are consistent with the literature[11].

Product (2b)

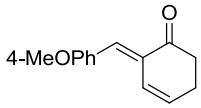


2b

Reaction time: 2 h.
Run 1: 70.3 mg **1b** was converted to 65.8 mg **2b**, yield 84%.
Run 2: 71.0 mg **1b** was converted to 69.8 mg **2b**, yield 88%.
So the average yield of two runs was 86%.

2b: light yellow solid, m.p. = 72–75 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.4 Hz, 2H), 7.33 (s, 1H), 7.29 (d, J = 8.4 Hz, 2H), 6.88– 6.82 (dm, J = 10.0 Hz, 1H), 6.23–6.15 (m, 1H), 2.70–2.65 (m, 2H), 2.63–2.56 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.9, 134.3, 131.8, 131.7, 131.5, 131.4, 130.5, 124.8, 122.7, 38.2, 24.6. The ^{1}H NMR and ^{13}C NMR spectra are consistent with the literature[12]

Product (2c)

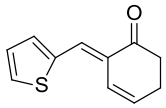


2c

Reaction time: 2 h.
Run 1: 55.4 mg **1c** was converted to 50.7 mg **2c**, yield 80%.
Run 2: 55.4 mg **1c** was converted to 49.0 mg **2c**, yield 77%.
So the average yield of two runs was 78%.

2c: light yellow oil, TLC R_f = 0.24 (PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.37 (m, 3H), 6.96–6.88 (m, 3H), 6.15–6.08 (m, 1H), 3.82 (s, 3H), 2.67–2.62 (m, 2H), 2.60–2.53 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.3, 160.0, 132.0, 131.8, 130.1, 129.6, 128.0, 125.4, 114.0, 55.3, 38.2, 24.4. IR (KBr): υ 2958, 2933, 2839, 1689, 1602, 1580, 1509, 1301, 1255 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{15}O_2$ ($M+H^+$): 215.1067. Found: 215.1066.

Product (2d)

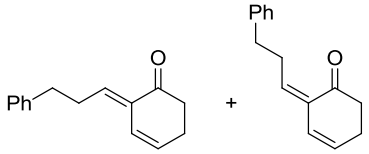


2d

Reaction time: 1.5 h.
Run 1: 49.6 mg **1d** was converted to 32.7 mg **2d**, yield 56%.
Run 2: 49.7 mg **1d** was converted to 33.0 mg **2d**, yield 57%.
So the average yield of two runs was 56%.

2d: yellow oil, TLC R_f = 0.12 (PE). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.52–7.48 (m, 1H), 7.36–7.32 (m, 1H), 7.18–7.12 (dm, J = 10.0 Hz, 1H), 7.12–7.07 (m, 1H), 6.27–6.20 (m, 1H), 2.69–2.64 (m, 2H), 2.63–2.57 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.6, 138.6, 133.6, 131.2, 123.0, 127.8, 127.6, 125.2, 124.4, 38.1, 24.5. IR (KBr): υ 3103, 2960, 2893, 2840, 2361, 1687, 1570, 1264, 1206, 1137 cm^{-1}. HRMS (ESI) calcd for $C_{11}H_{11}OS$ ($M+H^+$): 191.0525. Found: 191.0523.

Product (2e) and product (3e)



2e **3e**

Reaction time: 2 h.

Run 1: 56.2 mg **1e** was converted to 45.2 mg **2e** (yield 70%) and 12.9 mg **3e** (yield 20%)**.**

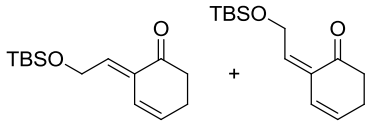
Run 2: 55.8 mg **1e** was converted to 44.6 mg **2e** (yield 69%) and 14.1 mg **3e** (yield 22%)**.**

So the average yield of **2e** was 70%. The average yield of **3e** was 21%.

2e: colorless oil, TLC R_f = 0.38 (PE/EA 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.24 (m, 2H), 7.22–7.15 (m, 3H), 6.59 (t, J = 7.8 Hz, 1H), 6.52–6.46 (dm, J = 10.0 Hz, 1H), 6.04–5.94 (m, 1H), 2.80–2.73 (m, 2H), 2.59–2.53 (m, 4H), 2.53–2.45 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.3, 141.0. 134.8, 132.2, 128.9, 128.4, 128.3, 126.0, 123.8, 38.1, 34.8, 29.2, 24.4. IR (KBr): υ 3379, 3027, 2927, 2845, 2360, 2338, 1697, 1633, 1592, 1495 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{16}NaO$ ($M+Na^+$): 235.1093. Found: 235.1090.

3e: colorless oil, TLC R_f = 0.56 (PE/EA 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.25 (m, 2H), 7.23–7.16 (m, 3H), 6.17 (d, J = 9.7 Hz, 1H), 5.85–5.73 (m, 2H), 2.98–2.89 (m, 2H), 2.75 (t, J = 7.6 Hz, 2H), 2.57–2.52 (m, 2H), 2.51–2.46 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 201.2, 141.4, 140.8, 133.0, 130.8, 128.5, 128.3, 126.5, 125.9, 40.4, 35.5, 30.8, 25.4. IR (KBr): υ 3084, 3061, 3027, 2925, 2848, 1695, 1599, 1495, 1452, 1370, 1122, 1011 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{16}NaO$ ($M+Na^+$): 235.1093. Found: 235.1090.

Product (2h) and product (3h)



2h **3h**

Reaction time: 2 h.

Run 1: 68.0 mg **1h** was converted to 48.9 mg **2h** and **3h** (yield 64%, E/Z = 5.1)**.**

Run 2: 68.8 mg **1h** was converted to 53.7 mg **2h** and **3h** (yield 69%, E/Z = 5.1)**.**

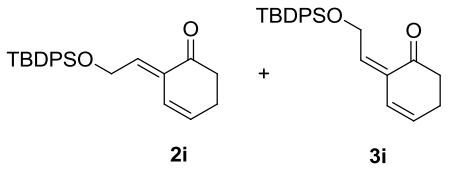
So the average yield of **2h** and **3h** was 66 %.

2h: colorless oil, TLC R_f = 0.41 (PE/EA 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.57–6.48 (m, 2H), 6.10–6.01 (m, 1H), 4.44 (d, J = 6.1 Hz, 2H), 2.62–2.57 (m, 2H), 2.56–2.50 (m, 2H), 0.91 (s, 9H), 0.08 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.0, 134.2, 130.9, 129.8, 123.9, 59.8, 38.2, 25.8, 24.5, 18.2, -5.3. IR (KBr): υ 3041, 2932, 2893, 2856, 1703, 1467, 1370, 1254, 1099, 839 cm^{-1}. HRMS (EI) calcd for $C_{14}H_{24}O_2Si$ (M^+): 252.1540. Found: 252.1548.

3h: colorless oil, TLC R_f = 0.62 (PE/EA 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.25 (d, J = 9.8 Hz, 1H), 5.94–5.86 (m, 2H), 4.70 (d, J = 4.7 Hz, 2H), 2.60–2.55 (m, 2H), 2.53–2.47 (m, 2H), 0.91 (s, 9H), 0.07 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.7, 143.6, 130.6, 129.8, 127.5, 62.5, 39.6,

25.9, 24.9, 18.3, -5.3. IR (KBr): υ 2955, 2931, 2895, 2857, 1697, 1469, 1364, 1255, 1100, 1051, 839 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{25}O_2Si$ ($[M+H]^+$): 252.1618. Found: 253.1621.

Product (2i) and product (3i)



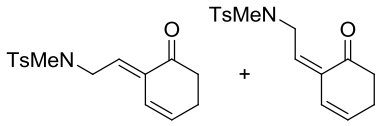
2i **3i**

Reaction time: 2 h.
Run 1: 105.0 mg **1i** was converted to 73.9 mg **2i** (yield 65%) and 13.6 mg **3i** (yield 12%).
Run 2: 104.5 mg **1i** was converted to 71.1 mg **2i** (yield 63%) and 12.4 mg **3i** (yield 11%).
So the average yield of **2i** was 64%. The average yield of **3i** was 12%.

2i: colorless oil, TLC R_f = 0.45 (PE/EA 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70–7.65 (m, 4H), 7.43–7.35 (m, 6H), 6.63 (t, J = 5.9 Hz, 1H), 6.35–6.29 (dm, J = 10.0 Hz, 1H), 5.94 (m, 1H), 4.44 (d, J = 5.9 Hz, 2H), 2.60–2.53 (m, 2H), 2.52–2.43 (m, 2H), 1.05 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.1, 135.5, 133.8, 133.2, 130.9, 129.7, 129.6, 127.7, 123.9, 60.6, 38.1, 26.7, 24.4, 19.1. IR (KBr): υ 3071, 2959, 2930, 2857, 1702, 1638, 1597, 1428, 1112, 1047 cm^{-1}. HRMS (ESI) calcd for $C_{24}H_{29}O_2Si$ ($M+H^+$): 377.1931. Found: 377.1940.

3i: colorless oil, TLC R_f = 0.58 (PE/EA 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68–7.63 (m, 4H), 7.42–7.33 (m, 6H), 6.23 (d, J = 9.2 Hz, 1H), 6.00 (t, J = 4.9 Hz, 1H), 5.90–5.84 (m, 1H), 4.78 (d, J = 4.9 Hz, 2H), 2.50–2.40 (m, 4H), 1.07 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.4, 143.0, 135.5, 133.6, 130.7, 129.7, 129.6, 127.6, 127.5, 63.4, 39.5, 26.9, 24.9, 19.2. IR (KBr): υ 3071, 2931, 2857, 1696, 1428, 1365, 1112, 702 cm^{-1}. HRMS (ESI) calcd for $C_{24}H_{29}O_2Si$ ($M+H^+$): 377.1931. Found: 377.1941.

Product (2j) and product (3j)



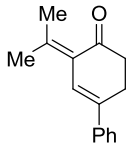
2j **3j**

Reaction time: 2 h.
Run 1: 83.2 mg **1j** was converted to 56.9 mg **2j** (yield 62%) and 14.3 mg **3j** (yield 16%).
Run 2: 83.0 mg **1j** was converted to 53.5 mg **2j** (yield 58%) and 12.7 mg **3j** (yield 14%).
So the average yield of **2j** was 60%. The average yield of **3j** was 15%.

2j: colorless oil, TLC R_f = 0.22 (PE/EA 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.3 Hz, 2H), 6.58–6.50 (dm, J = 10.0 Hz, 1H), 6.30 (dt, J = 7.1, 0.6 Hz, 1H), 6.17–6.10 (m, 1H), 3.88 (d, J = 7.1 Hz, 2H), 2.70 (s, 3H), 2.61–2.52 (m, 4H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.4, 143.6, 134.2, 134.1, 131.5, 129.7, 127.4, 127.1, 123.0, 46.7, 38.0, 34.8, 24.9, 21.4. IR (KBr): υ 3041, 2925, 1701, 1635, 1596, 1455, 1341, 1259, 1162 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{19}NNaO_3S$ ($M+Na^+$): 328.0978. Found: 328.0979.

3j: colorless oil, TLC R_f = 0.33 (PE/EA 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.3 Hz, 2H), 6.22 (d, J = 9.8 Hz, 1H), 5.98–5.91 (m, 1H), 5.80–5.74 (m, 1H), 4.18 (d, J = 6.1 Hz, 2H), 2.72 (s, 3H), 2.60–2.54 (m, 2H), 2.54–2.48 (m, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 201.0, 143.5, 136.4, 134.3, 133.8, 129.8, 129.7, 128.6, 127.5, 49.8, 39.9, 35.7, 25.2, 21.5. IR (KBr): υ 3032, 2923, 2852, 1694, 1598, 1456, 1344, 1162, 1090, 934 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{19}NNaO_3S$ ($M+Na^+$): 328.0978. Found: 328.0978.

Product (2n)

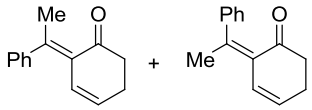


2n

Reaction time: 2 h.
Run 1: 55.4 mg **1n** was converted to 57.6 mg **2n**, yield 90%.
Run 2: 55.1 mg **1n** was converted to 57.8 mg **2n**, yield 91%.
So the average yield of **2n** was 90 %.

2n: colorless oil, TLC R_f = 0.44 (PE/EA 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.43 (m, 2H), 7.39–7.33 (m, 2H), 7.30–7.26 (m, 1H), 6.94 (s, 1H), 2.89 (t, J = 6.9 Hz, 2H), 2.70 (t, J = 6.9 Hz, 2H), 2.25 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 201.2, 145.8, 141.0, 135.6, 128.8, 128.5, 127.3, 125.2, 123.6, 40.5, 27.7, 23.8, 22.7. IR (KBr): υ 3055, 2905, 2846, 1690, 1585, 1442, 1370, 1296, 1188 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{17}O$ ($M+H^+$): 213.1274. Found: 213.1271.

Product (2o) and product (3o)



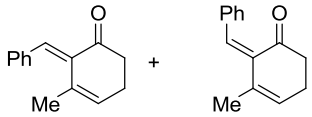
2o **3o**

Reaction time: 2 h.
Run 1: 51.1 mg **1o** was converted to 45.4 mg **2o** (yield 76%) and 6.4 mg **3o** (yield 11%)**.**
Run 2: 52.3 mg **1o** was converted to 43.0 mg **2o** (yield 71%) and 4.5 mg **3o** (yield 7%)**.**
So the average yield of **2o** was 74%. The average yield of **3o** was 9%.

2o: light yellow oil, TLC R_f = 0.53 (PE/EA 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.34 (m, 2H), 7.33–7.26 (m, 1H), 7.20–7.14 (m, 2H), 6.24–6.16 (m, 1H), 5.75–5.67 (m, 1H), 2.70–2.63 (m, 2H), 2.57–2.49 (m, *2*H), 2.43 (s, 3H). The ^{1}H NMR spectrum is consistent with the literature[11].

3o: yellow oil, TLC R_f = 0.32 (PE/EA 10:1). ^{1}H NMR (400 MHz, C_6D_6) δ 7.22–7.14 (m, 2H), 7.12–7.04 (m, 3H), 6.40 (dt, J = 10.0, 1.7 Hz, 1H), 5.61–5.53 (m, 1H), 2.31 (t, J = 6.8 Hz, 2H), 2.09–1.99 (m, 2H), 1.83 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6): δ 198.6, 144.6, 142.2, 131.2, 128.5, 128.2, 127.6, 127.2, 127.1, 40.8, 26.8, 21.8. IR (KBr): υ 3361, 3037, 2961, 2921, 2850, 2361, 2339, 1700, 1583, 1468, 1170 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{14}NaO$ ($M+Na^+$): 221.0937. Found: 221.0934.

Product (2p) and product (3p)



2p **3p**

Reaction time: 2 h.

Run 1: 51.1 mg **1p** was converted to 56.0 mg **2p** and **3p** (yield 94%, *E*/*Z* = 1.7)**.**

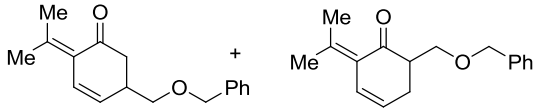
Run 2: 51.2 mg **1p** was converted to 55.6 mg **2p** and **3p** (yield 93%, *E*/*Z* = 1.7)**.**

So the average yield of **2p** and **3p** was 94 %.

2p and **3p** are hard to separate.

2p+3p: yellow oil, TLC R_f = 0.50 (PE/EA 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.39–7.26 (m, 5 + (5×0.6)H), 6.62 (s, 0.6H), 6.04–5.97 (m, 1H), 5.88–5.83 (m, 0.6H), 2.75–2.70 (m, 2×0.6H), 2.63–2.56 (m, 2×0.6H), 2.55–2.50 (m, 2H), 2.49–2.43 (m, 2H), 1.99 (dd, *J* = 3.0, 1.6 Hz, 3×0.6H), 1.63 (d, *J* = 1.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 202.8, 202.6 (**2p**), 136.7, 136.6 (**2p**), 136.0, 135.3 (**2p**), 135.1, 134.0 (**2p**), 133.2 (**2p**), 130.9, 130.2 (**2p**), 129.4 (**2p**), 129.2, 128.1 (**2p**), 128.0, 127.9, 127.8 (**2p**), 127.4, 40.8, 36.2 (**2p**), 26.6, 22.5 (**2p**), 21.0 (**2p**), 19.8. IR (KBr): υ 3368, 3056, 3024, 2959, 2926, 2851, 2360, 1691, 1628, 1586, 1445, 1176 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{14}NaO$ (M+Na$^+$): 221.0937. Found: 221.0934.

Product (2q) and product (4q)



2q **4q**

Reaction time: 2 h.

Run 1: 69.2 mg **1q** was converted to 64.7 mg **2q** and **4q** (yield 83%, **2q**/**4q** = 4.3)**.**

Run 2: 68.4 mg **1q** was converted to 59.4 mg **2q** and **4q** (yield 77%, **2q**/**4q** = 4.2)**.**

So the average yield of **2q** and **4q** was 80 %.

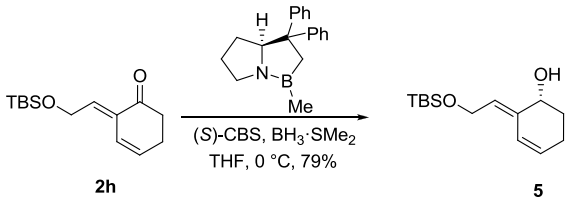
2q and **4q** can be separated by flash column chromatography.

2q: colorless oil, TLC R_f = 0.43 (PE/EA 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.26 (m, 5H), 6.60 (dd, *J* = 10.1, 1.8 Hz, 1H), 5.80 (dd, *J* = 10.1, 3.6 Hz, 1H), 4.52 (s, 2H), 3.48–3.38 (m, 2H), 2.99–2.84 (m, 1H), 2.63 (dd, *J* = 14.1, 6.0 Hz, 1H), 2.54 (dd, *J* = 14.1, 8.0 Hz, 1H), 2.18 (s, 3H), 1.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.8, 145.0, 138.1, 128.6, 128.3, 127.54, 127.50, 127.1, 127.0, 73.1, 73.0, 43.9, 37.9, 23.3, 22.4. IR (KBr): υ 3033, 2855, 1689, 1587, 1450, 1365, 1296, 1213, 1100 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{21}O_2$ (M+H$^+$): 257.1536. Found: 257.1534.

4q: colorless oil, TLC R_f = 0.60 (PE/EA 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.26 (m, 5H), 6.50 (dd, *J* = 10.1, 1.3 Hz, 1H), 5.82–5.74 (m, 1H), 4.53 (s, 2H), 3.87 (dd, *J* = 9.6, 5.7 Hz, 1H), 3.56 (dd, *J* = 9.6, 7.6 Hz, 1H), 2.98–2.89 (m, 1H), 2.78–2.67 (m, 1H), 2.37–2.25 (m, 1H), 2.12 (s, 3H), 1.90 (s, 3H) ^{13}C NMR (101 MHz, $CDCl_3$): δ 201.9, 143.8, 138.4, 129.4, 128.3, 127.6, 127.5, 126.2, 124.7, 73.2, 69.5, 49.4, 29.7, 23.1, 22.1. IR (KBr): υ 3035, 2918, 2857, 1688, 1629, 1589, 1446, 1369, 1293, 1155, 1099, 1035 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{21}O_2$ (M+H$^+$): 257.1536. Found: 257.1534.

2.3 Formal Synthesis of (–)-Galanthamine

(*R*,*E*)-2-(2-((*tert*-butyldimethylsilyl)oxy)ethylidene)cyclohex-3-en-1-ol (5)

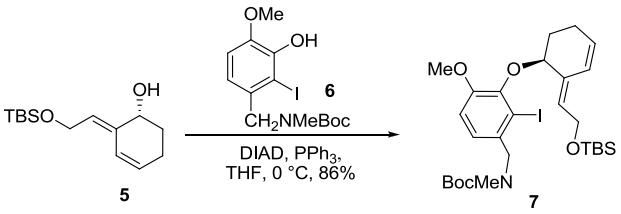


To a solution of (*S*)-CBS (1 M in toluene, 1.3 mL, 1.3 mmol) in THF (13 mL) was added BH_3•SMe_2 (2 M in THF, 1.3 mL, 2.6 mmol) at 0 ℃ and stirred for 5 min. Then a solution of ketone **2h** (324 mg, 1.3 mmol) in THF (13 mL) was added slowly and the reaction mixture was stirred for 10 min. When TLC indicated the disappearance of the starting material, the reaction was quenched by adding 2 mL CH_3OH. The mixture was concentrated and the crude product was purified by flash column chromatography (eluted with PE/EA, 5:1) to afford alcohol **5** (258 mg, 79%, ee 97%).

5: colorless oil, $[\alpha]_D$ = -32.5 °(c 1.78, $CHCl_3$, 20 ℃), ee = 97% (OD-H, hexane/^{i}PrOH = 95:1, 0.5 mL/min), TLC R_f = 0.29 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.28 (d, J = 10.1 Hz, 1H), 5.92–5.85 (m, 1H), 5.59 (t, J = 6.4 Hz, 1H), 4.40–4.30 (m, 2H), 4.27 (dd, J = 5.0, 5.0 Hz, 1H), 2.42–2.30 (m, 1H), 2.25–2.13 (m, 1H), 1.89–1.80 (m, 2H), 1.63 (br s, 1H), 0.91 (s, 9H), 0.08 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.7, 130.6, 125.5, 121.8, 70.3, 59.1, 30.3, 26.0, 22.6, 18.4, -5.09, -5.10. IR (KBr): υ 3379, 3034, 2956, 2857, 1652, 1468, 1254, 1103, 834 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{26}NaO_2Si$ ([M+Na]$^+$): 277.1594. Found: 277.1600.

The absolute configuration was further conformed by the $[\alpha]_D$ of the final compounds **10**, which has similar $[\alpha]_D$ as the literature reported[13].

***tert*-butyl (*S*,*E*)-(3-((2-(2-((tert-butyldimethylsilyl)oxy)ethylidene)cyclohex-3-en-1-yl)oxy) -2-iodo-4-methoxybenzyl)(methyl)carbamate (7)**



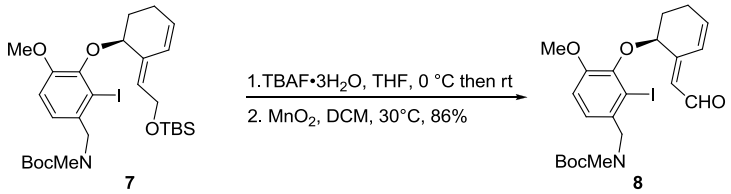
To a solution of alcohol **5** (74 mg, 0.29 mmol), phenol **6**[13] (149 mg, 0.38 mmol) and PPh_3 (153 mg, 0.58 mmol) in THF (2.5 mL) was added DIAD (117 mg, 0.58 mmol) under an argon atmosphere at 0 ℃. After 3 h, the mixture was concentrated and the crude product was purified by flash column chromatography (eluted with PE/EA, 5:1) to afford product **7** (158 mg, 86%).

7: colorless oil, $[\alpha]_D$ -9.2 °(c 1.2, $CHCl_3$, 20 ℃), TLC R_f = 0.66 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.87–6.72 (m, 2H), 6.27 (d, J = 10.1 Hz, 1H), 5.99–5.88 (m, 1H), 5.21 (br s, 1H), 4.99 (br s, 1H), 4.47–4.36 (m, 2H), 4.31 (dd, J = 13.7, 6.9 Hz, 1H), 4.15 (dd, J = 13.7, 5.4 Hz, 1H), 3.82 (s, 3H), 2.85–2.76 (m, 3H), 2.72–2.61 (m, 1H), 2.33–2.22 (m, 1H), 2.19–2.09 (m, 1H), 1.87–

1.76 (m, 1H), 1.53–1.39 (m, 9H), 0.84 (s, 9H), -0.01 (s, 3H), -0.03 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.0, 151.4, 146.0, 132.6, 131.7, 130.6, 128.7, 126.3&125.6, 122.5, 121.8, 112.2, 79.8, 79.6, 59.2, 57.6&56.6, 55.9, 34.0, 28.5 28.4, 25.9, 22.4, 18.3, -5.2. IR (KBr): υ 2954, 2931, 2857, 2248, 1700, 1588, 1476, 1391, 1254, 1143, 1031 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{45}INO_5Si$ ([M+H]$^+$): 630.2106. Found: 630.2104.

Note: NMR spectra exhibited broadening /doubling of peaks due to restricted rotation.

tert-butyl (_S_,_E_)-(2-iodo-4-methoxy-3-((2-(2-oxoethylidene)cyclohex-3-en-1-yl)oxy)benzyl) (methyl)carbamate (8)



7 **8**

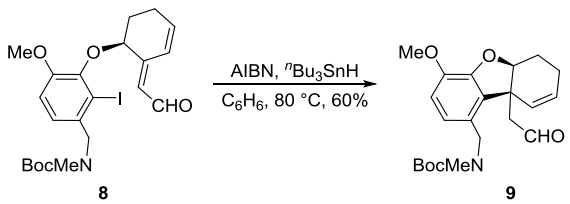
To a solution of **7** (400 mg, 0.65 mmol) in THF (7 mL) was added TBAF•3H$_2$O (401 mg, 1.3 mmol) at 0 ℃. Then the reaction mixture was stirred at rt for 3 h until the disappearance of the starting material. The mixture was concentrated and the crude product was purified by flash column chromatography (eluted with PE/EA, 3:1 then 1:1) to afford alcohol intermediate and used directly.

The alcohol intermediate was dissolved in DCM (16 mL) and activated MnO_2 (1.13 g, 13 mmol, heated at 100 ℃ for 4 h before using) was added. The suspension was stirred at 30 ℃ for 1 h and then filtered through a short silica gel eluting with EA. The filtrate was concentrated and the aldyhyde **8** (280 mg, 86%) was pure.

8: colorless oil, $[\alpha]_D$ -45.0 ° (c 1.0, $CHCl_3$, 20 ℃), TLC R_f = 0.45 (PE/EA, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.19 (d, J = 8.0 Hz, 1H), 7.12 (d, J = 10.0 Hz, 1H), 6.88 (d, J = 8.0 Hz, 1H), 6.91–6.78 (m, 1H), 6.41–6.32 (m, 1H), 6.05–5.89 (m, 1H), 5.08 (br s, 1H), 4.54–4.34 (m, 2H), 3.82 (s, 3H), 2.88–2.79 (m, 3H), 2.71–2.58 (m, 1H), 2.36–2.21 (m, 2H), 2.05–1.95 (m, 1H), 1.52–1.38 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 190.5, 155.8, 152.1, 151.1, 145.5, 138.8, 133.0, 124.0, 122.9, 122.4, 121.6, 112.4, 79.8, 78.8, 57.6&56.8, 56.0, 34.2, 28.43, 28.39, 24.0. IR (KBr): υ 2973, 2933, 1693, 1669, 1477, 1392, 1290, 1255, 1148, 1030 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{29}INO_5$ ([M+H]$^+$): 514.1085. Found: 514.1080.

Note: NMR spectra exhibited broadening /doubling of peaks due to restricted rotation.

tert-butyl (((5a_S_,9a_S_)-4-methoxy-9a-(2-oxoethyl)-5a,6,7,9a-tetrahydrodibenzo[_b_,_d_]furan-1-yl) methyl)(methyl)carbamate (9)



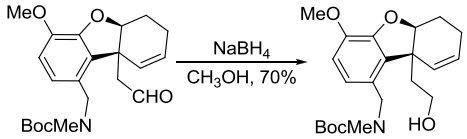
8 **9**

Aldehyde **8** (215 mg, 0.42 mmol) and AIBN (13.8 mg, 0.084 mmol) was dissolved in anhydrous C_6H_6 (5 mL) and bubbled with N_2 gas for 5 min at room temperature. Then a solution of $^nBu_3SnH$ in anhydrous C_6H_6 (3 mL) was added and the mixture was stirred at 80 ℃ for 3 h. The mixture was concentrated and the crude product was purified by flash column chromatography (eluted with PE/EA, 10:1 then 5:1) to afford product **9** (97.6 mg, 60%).

9: colorless oil, $[\alpha]_D$ -24.0 ° (c 0.5, $CHCl_3$, 20 ℃), TLC R_f = 0.47 (PE/EA, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.68 (s, 1H), 6.75 (d, J = 8.4 Hz, 1H), 6.62 (d, J = 8.4 Hz, 1H), 5.99–5.79 (m, 2H), 4.84 (br s, 1H), 4.54 (d, J = 15.2 Hz, 1H), 4.45 (d, J = 15.2 Hz, 1H), 3.87 (s, 3H), 2.99 (br s, 1H), 2.85–2.66 (m, 4H), 2.30–2.12 (m, 2H), 2.09–1.96 (m, 1H), 1.94–1.81 (m, 1H), 1.48 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.8, 155.8, 147.4, 144.4, 130.5, 128.8, 127.4, 125.4, 122.3&120.4, 111.3, 85.2, 79.9, 55.7, 50.0, 48.6, 47.8, 33.3, 28.3, 23.5, 19.6. IR (KBr): υ 2932, 2840, 1721, 1691, 1506, 1392, 1279, 1145, 1047 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{30}NO_5$ ($[M+H]^+$): 388.2118. Found: 388.2124.

Note: NMR spectra exhibited broadening /doubling of peaks due to restricted rotation.

***tert*-butyl (((5a*S*, 9a*S*)-9a-(2-hydroxyethyl)-4-methoxy-5a,6,7,9a-tetrahydrodibenzo[*b*,*d*]furan-1-yl)methyl)(methyl)carbamate (10)**



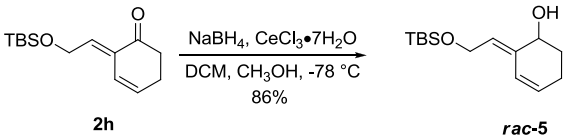
9 **10**

To a solution of aldehyde **9** (87 mg, 0.22 mmol) in CH_3OH (2.5 mL) was added $NaBH_4$ (12 mg, 0.32 mmol) at 0 ℃ and stirred for 10 min. The mixture was concentrated and the crude product was purified by flash column chromatography (eluted with PE/EA, 3:1 then 1:1) to afford alcohol product **10** (61.3 mg, 70%).

10: colorless oil, $[\alpha]_D$ -32.1 ° (c 0.53, $CHCl_3$, 20 ℃) (Lit[13]: –26.5, c 1.2, $CHCl_3$, 26 ℃), TLC R_f = 0.47 (PE/EA, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.72 (d, J = 8.4 Hz, 1H), 6.57 (d, J = 8.4 Hz, 1H), 5.90–5.84 (m, 1H), 5.81 (d, J = 10.3 Hz, 1H), 4.89–4.79 (m, 1H), 4.57 (d, J = 15.6 Hz, 1H), 4.43 (d, J = 15.6 Hz, 1H), 3.86 (s, 3H), 3.73–3.57 (m, 2H), 2.81 (s, 3H), 2.26–1.92 (m, 6H), 1.90–1.79 (m, 1H), 1.47 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.0, 147.4, 144.1, 131.2, 128.9, 128.2, 126.1, 120.2&119.4, 110.9, 85.3, 79.8, 77.0, 59.5, 55.7, 49.0, 48.5, 40.3, 33.9, 28.4, 24.4, 19.6. IR (KBr): υ 3441, 2933, 1691, 1504, 1395, 1279, 1147, 1044 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{32}NO_5$ ($[M+H]^+$): 390.2275. Found: 390.2285. Both the ^{1}H NMR and ^{13}C NMR spectra are consistent with the literature[13].

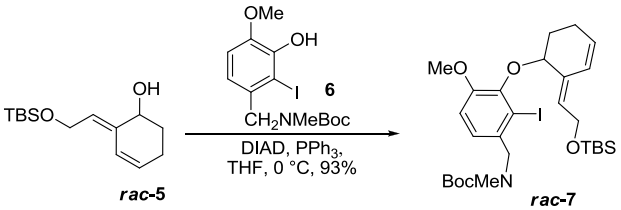
Note: NMR spectra exhibited broadening /doubling of peaks due to restricted rotation.

2.4 Synthesis of *rac*-11



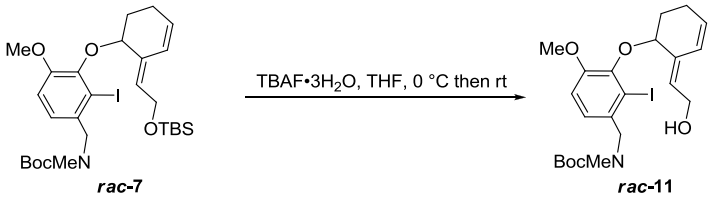
2h ***rac*-5**

To a solution of $CeCl_3•7H_2O$ (432 mg, 1.16 mmol) in CH_3OH (10 mL) was added **2h** (293 mg, 1.16 mmol) in DCM (3 mL) at -78 ℃ and stirred for 10 min. Then $NaBH_4$ (132 mg, 3.49 mmol) was added slowly and the reaction mixture was stirred for 2 h. When TLC indicated the disappearance of the starting material, the reaction was quenched by water and the product was extracted with ether twice. The combined extract was washed with brine, dried over Na_2SO_4. The crude product was purified by flash column chromatography (eluted with PE/EA, 5:1) to afford alcohol ***rac*-5** (254 mg, 86%).



***rac*-5** ***rac*-7**

The synthesis of ***rac*-7** follows the procedure described above, and similar yield could be achieved.



***rac*-7** ***rac*-11**

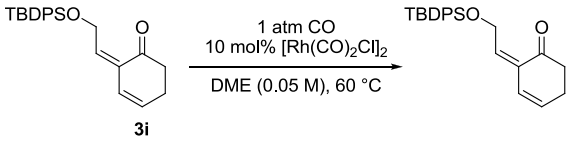
To a solution of ***rac*-7** (577 mg, 0.92 mmol) in THF (9 mL) was added $TBAF•3H_2O$ (592 mg, 1.88 mmol) at 0 ℃. Then the reaction mixture was stirred at rt for 3 h until the disappearance of the starting material. The mixture was concentrated and the crude product was purified by flash column chromatography (eluted with PE/EA, 3:1 then 1:1) to afford ***rac*-11** (324 mg, 69%).

***rac*-11:** colorless oil, TLC R_f = 0.33 (PE/EA, 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.87 (d, J = 8.5 Hz, 1H), 6.79 (d, J = 8.5 Hz, 1H), 6.36 (d, J = 10.0 Hz, 1H), 6.03–5.95 (m, 1H), 5.35–5.23 (m, 1H), 4.94 (br s, 1H), 4.50–4.34 (m, 2H), 4.23–4.14 (m, 2H), 3.83 (s, 3H), 2.83 (s, 3H), 2.71–2.59 (m, 1H), 2.35–2.26 (m, 1H), 2.22–2.10 (m, 1H), 1.87–1.77 (m, 1H), 1.66 (br s, 1H), 1.54–1.37 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.9, 151.4, 146.1, 133.9&133.5, 132.7, 131.3, 127.4&127.0, 122.3, 122.2&121.9, 112.7&112.5, 99.1&98.5, 79.9, 79.7, 57.9, 57.5&56.8, 56.1, 34.4&34.1, 28.34, 28.33, 22.4. IR (KBr): υ 3432, 2975, 2932, 1682, 1477, 1393, 1255, 1152, 1030, 877 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{31}INO_5$ ($[M+H]^+$): 516.1241. Found: 516.1249.

Note: NMR spectra exhibited broadening /doubling of peaks due to restricted rotation.

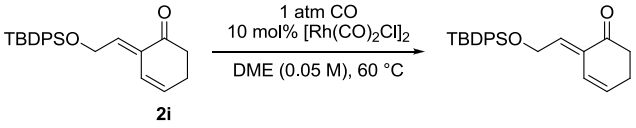
2.5 Isomerization Experiments for [5+1] Cycloadducts

Conditions A



3i

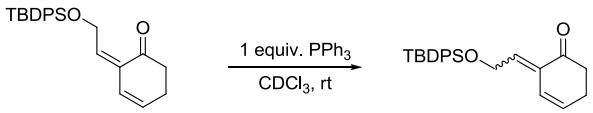
A solution of **3i** (9.9 mg, 0.026 mml) and $[Rh(CO)_2Cl]_2$ (1.0 mg, 2.6×10^{-3} mmol, 10 mol%) in anhydrous DME (0.05 M, 0.5 mL) was stirred under an CO atmosphere at 60 ℃ for 2 h, and the mixture was concentrated directly. No isomerization could be observed from the ^{1}H NMR.



2i

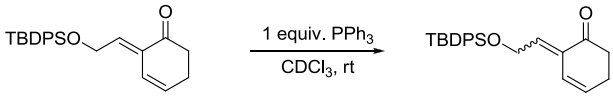
A solution of **2i** (9.9 mg, 0.026 mml) and $[Rh(CO)_2Cl]_2$ (1.0 mg, 2.6×10^{-3} mmol, 10 mol%) in anhydrous DME (0.05 M, 0.5 mL) was stirred under an CO atmosphere at 60 ℃ for 2 h, and the mixture was concentrated directly. No isomerization could be observed from the ^{1}H NMR.

Conditions B



3i *E*/*Z* = 3.6:1

A solution of **3i** (7.8 mg, 0.021 mml) and PPh_3 (5.4 mg, 0.021 mmol) in $CDCl_3$ (0.5 mL) was added to an NMR tube, and the reaction system was detected by ^{1}H NMR. After 36 h, the ^{1}H NMR showed that the ratio of **2i** and **3i** was 3.6:1.



2i *E*/*Z* = 3.6:1

A solution of **2i** (7.8 mg, 0.021 mml) and PPh_3 (5.4 mg, 0.021 mmol) in $CDCl_3$ (0.5 mL) was added to an NMR tube, and the reaction system was detected by ^{1}H NMR. After 36 h, the ^{1}H NMR showed that the ratio of **2i** and **3i** was 3.6:1.

2.6 References

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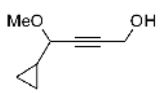
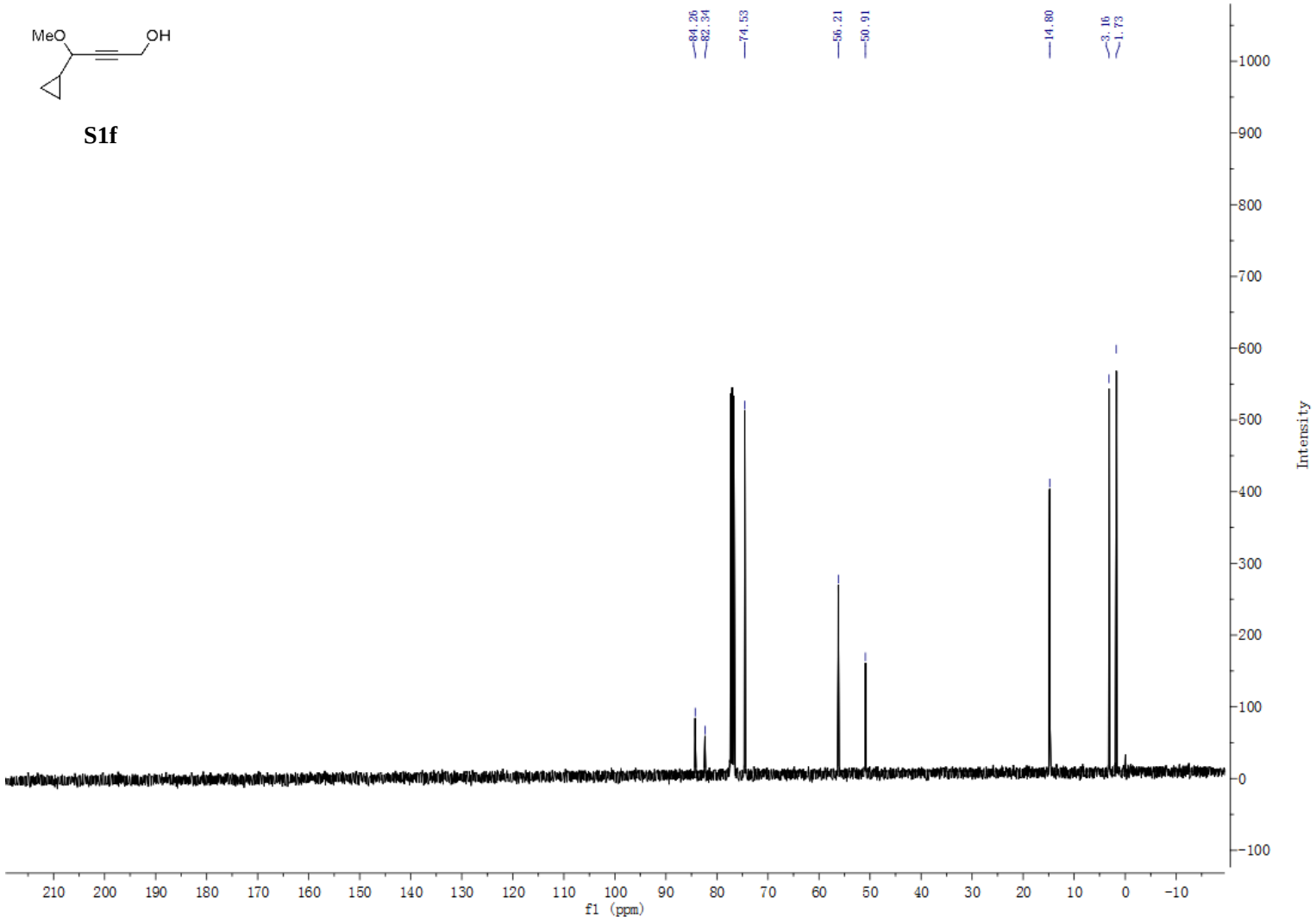
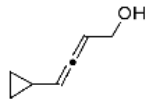
3. ^{1}H and ^{13}C-NMR Spectra



S1f

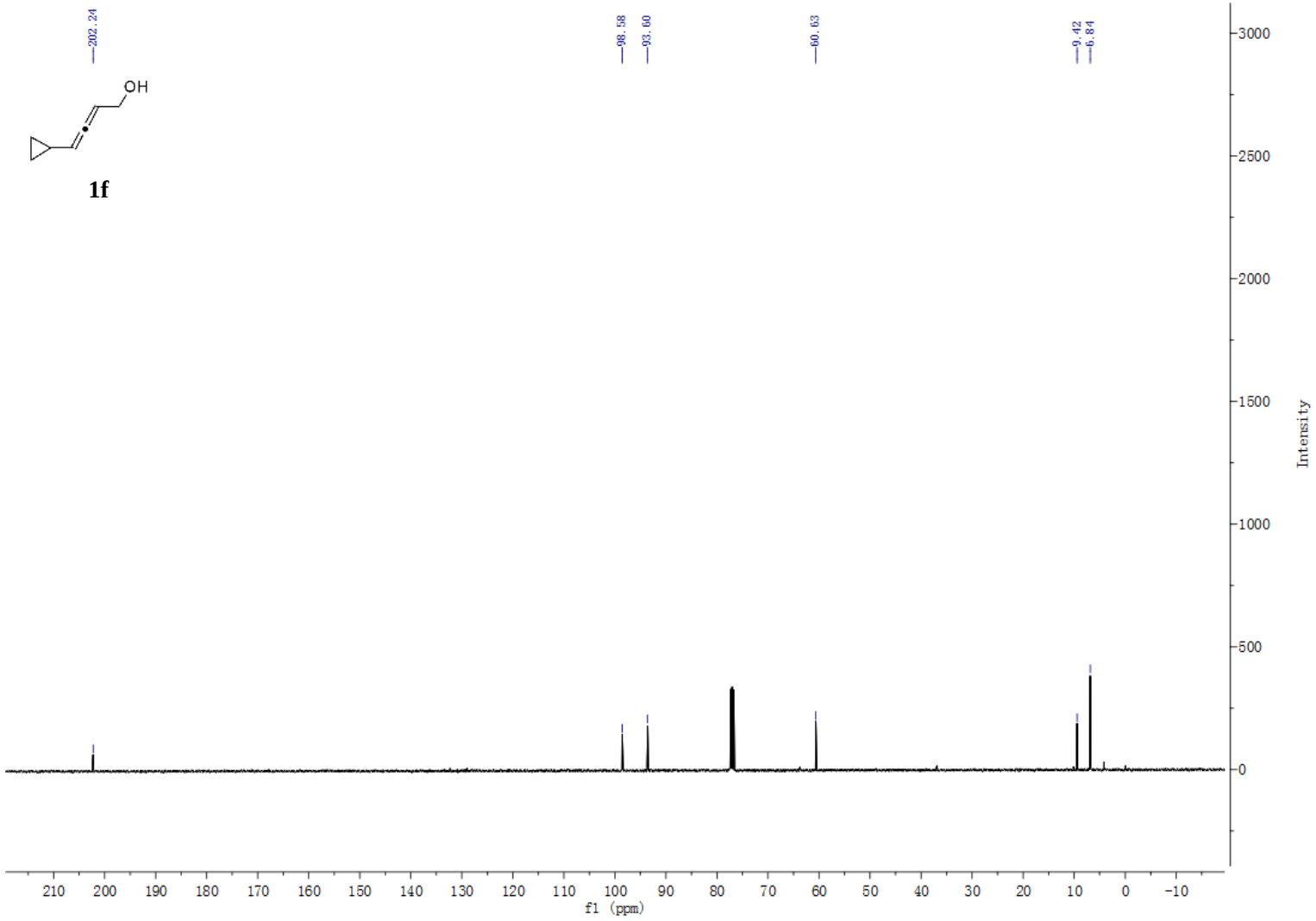


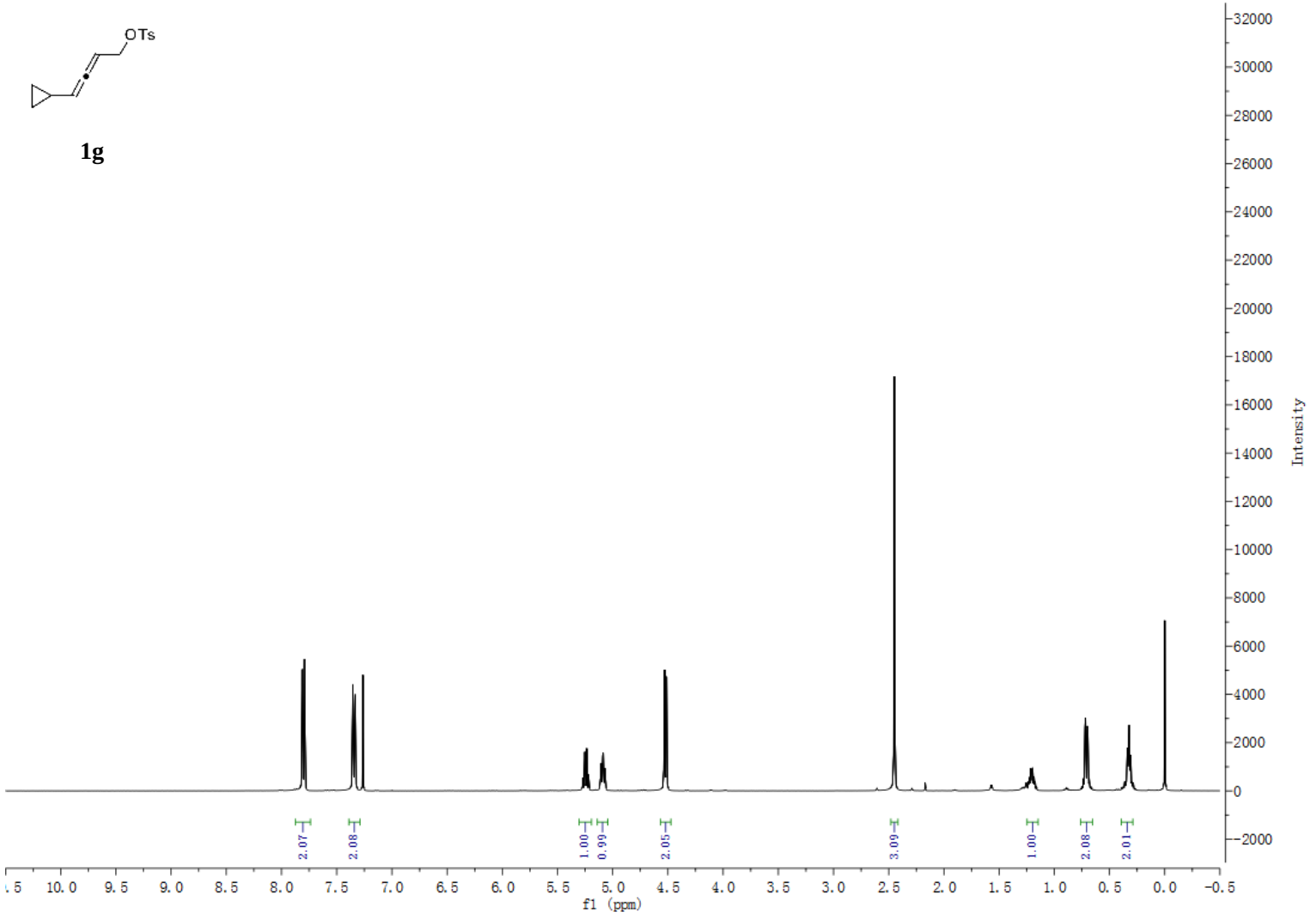
S1f


OH

1f

50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
Intensity
0.98
0.97
2.04
1.05
1.16
2.06
2.02
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
-0.5
f1 (ppm)


202.24
98.58
93.60
60.63
9.42
6.84
OH
1f
3000
2500
2000
1500
1000
500
0
Intensity
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)


OTs
1g
Intensity
f1 (ppm)
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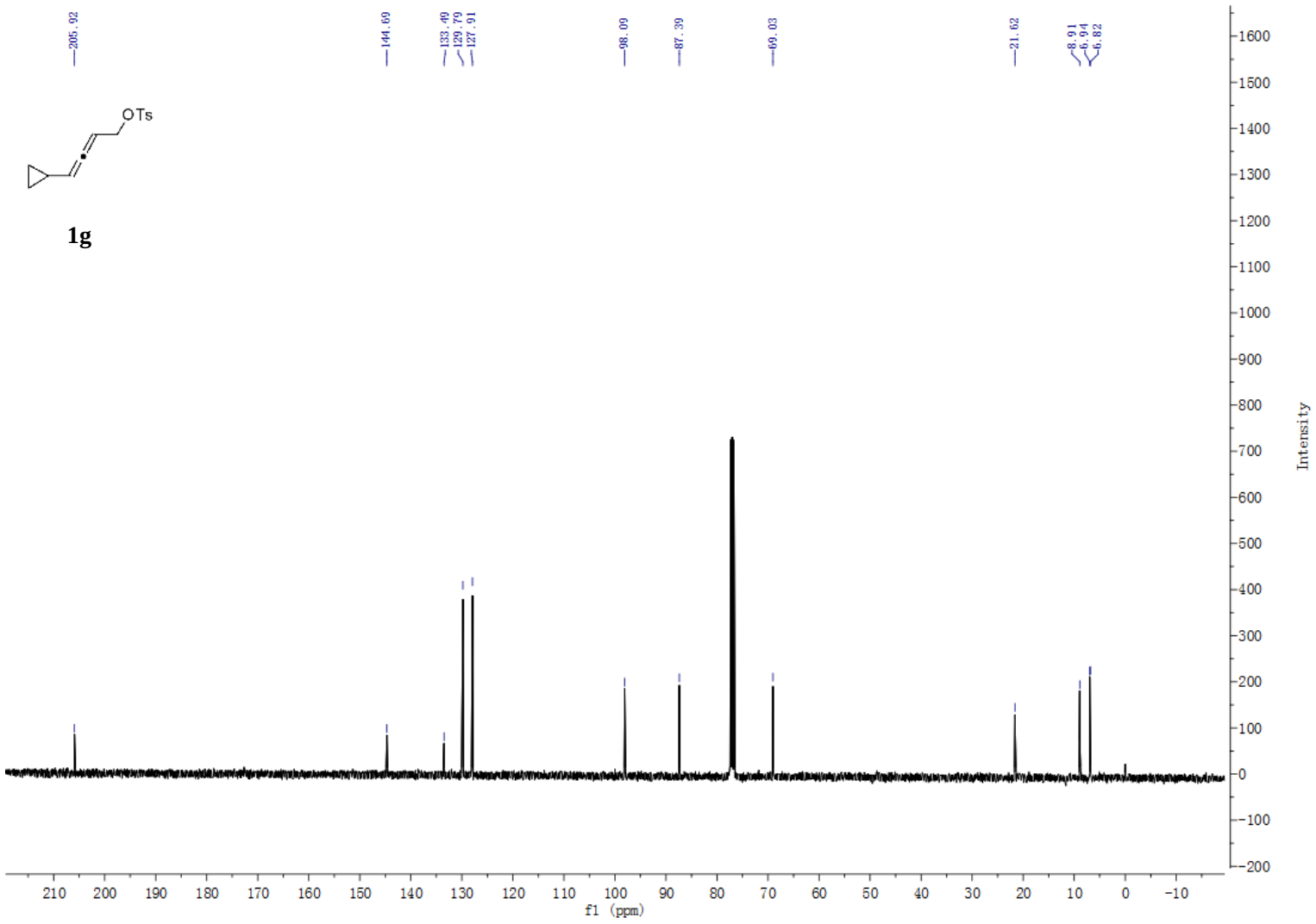
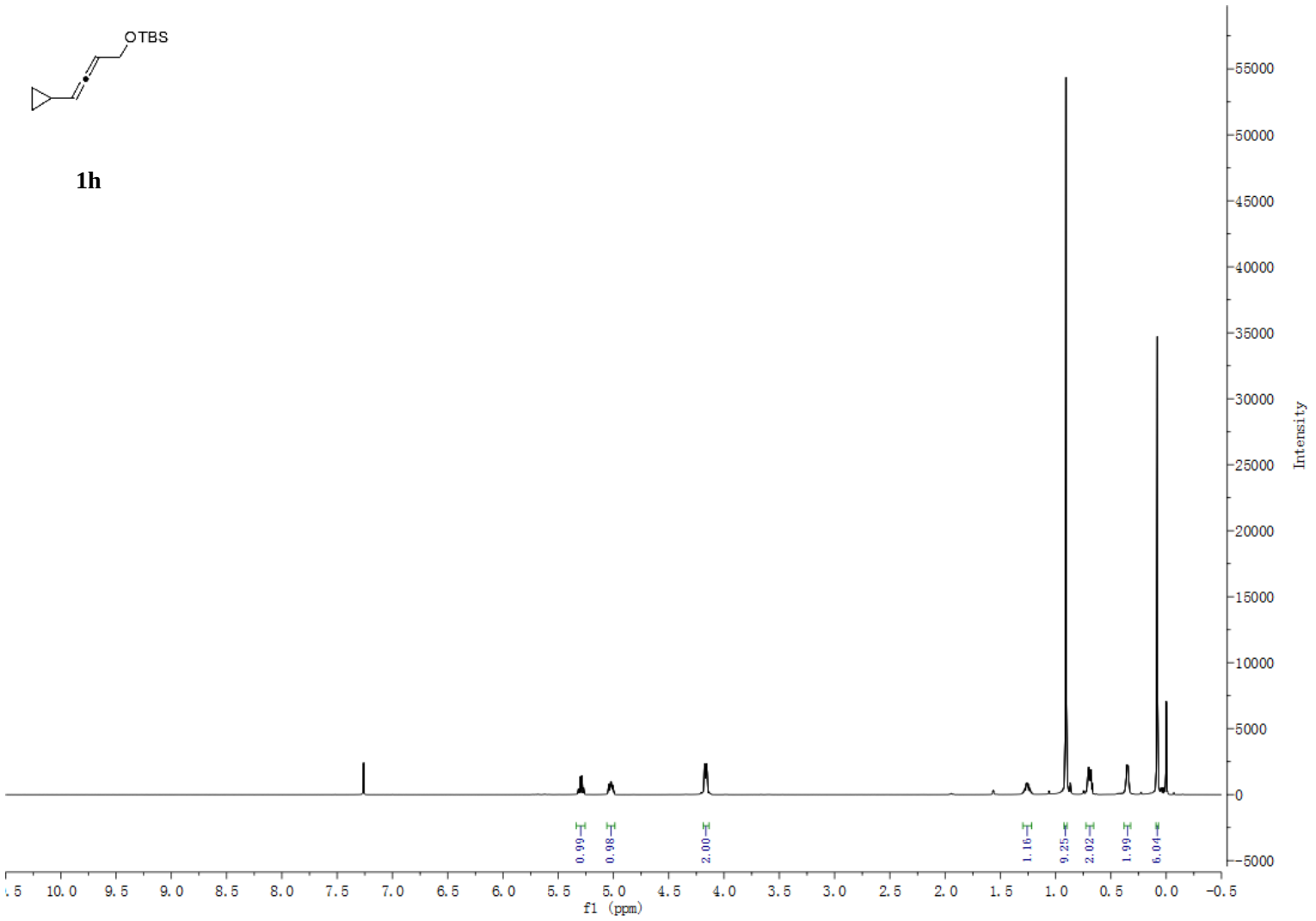
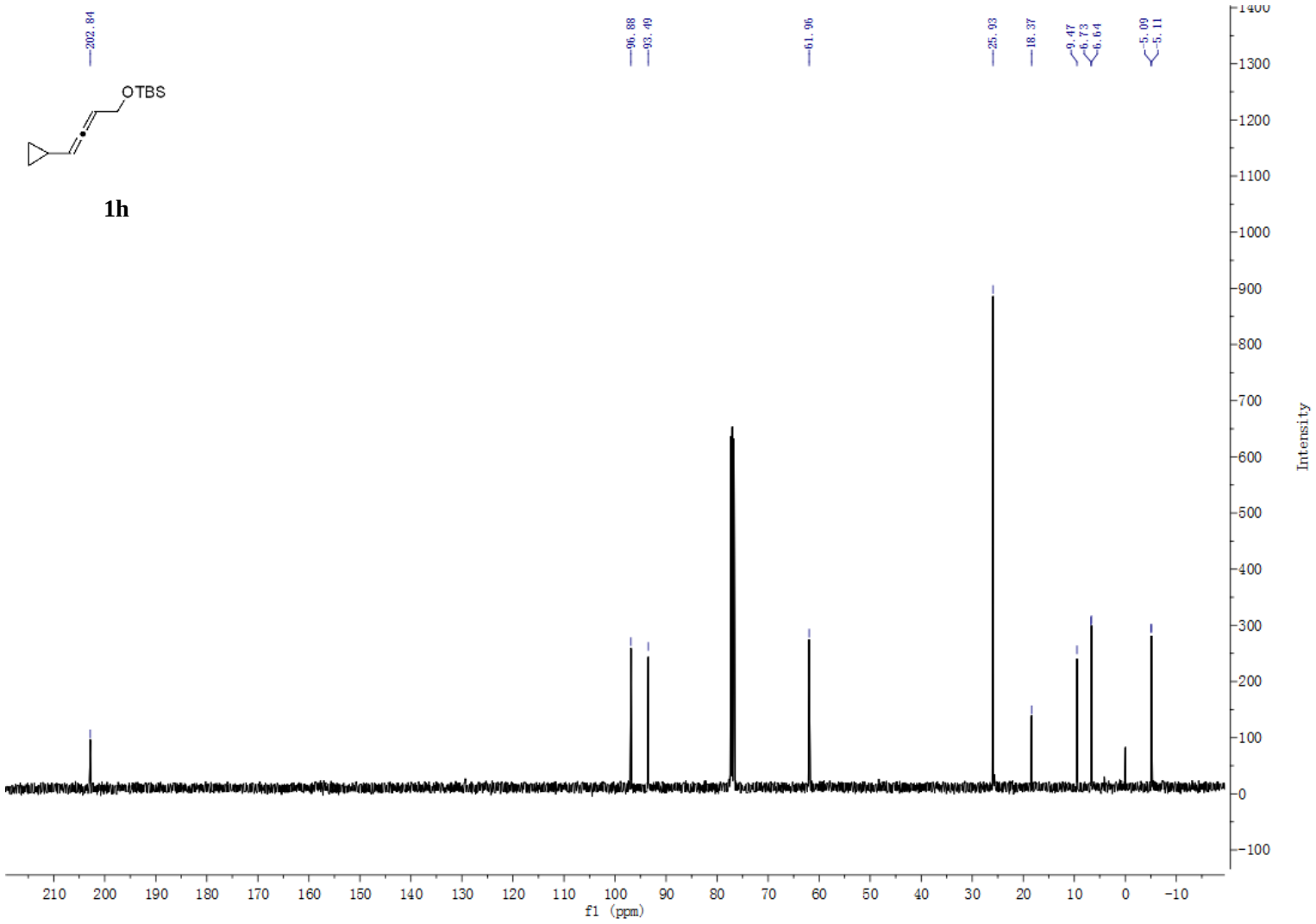
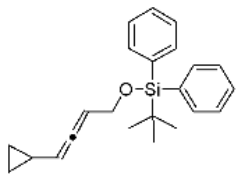
2.08
1.00
0.99
2.05
3.09
1.00
2.08
2.01

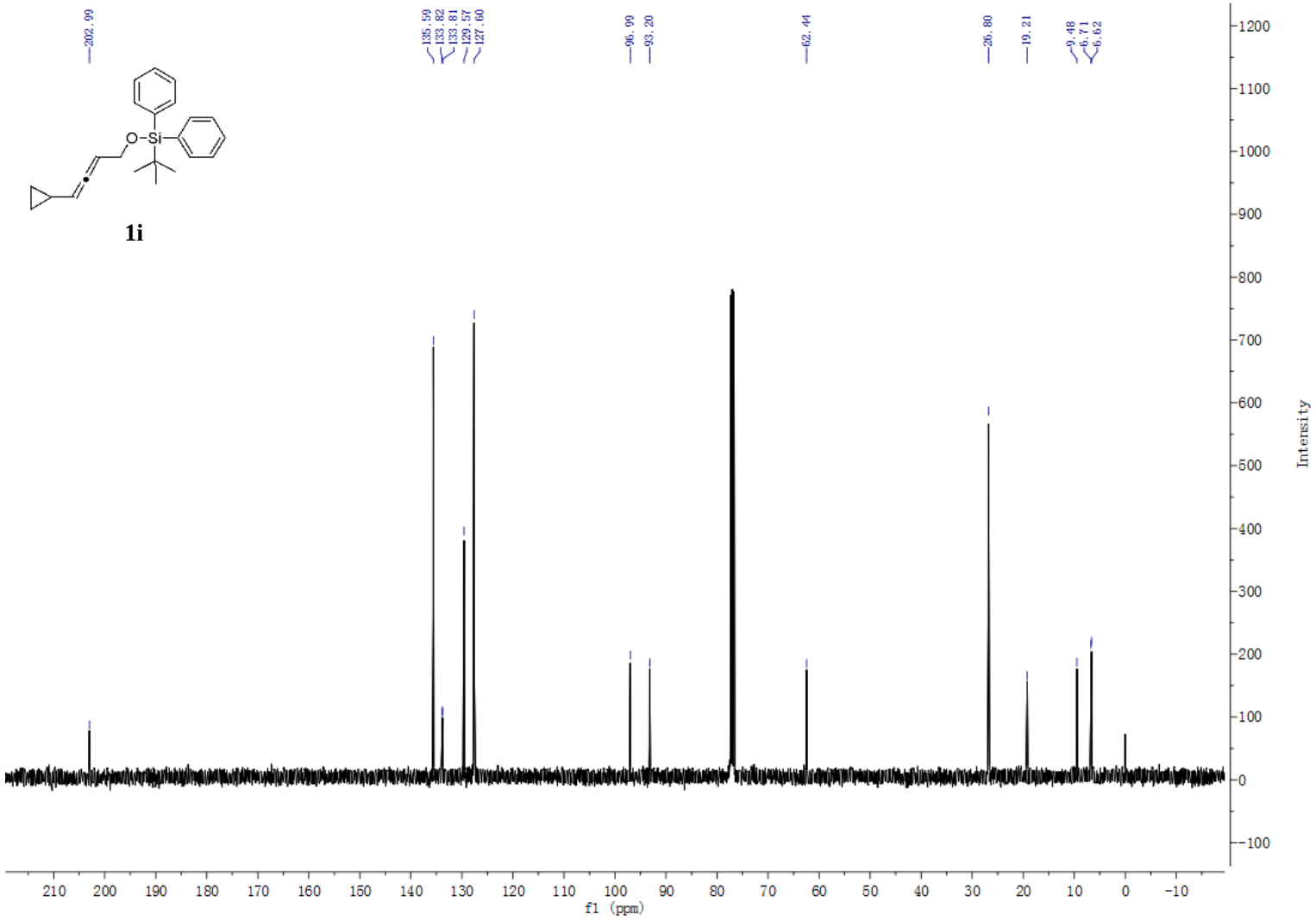

205.92
144.69
133.49
129.79
127.91
98.09
87.39
69.03
21.62
8.91
6.94
6.82
OTs
1g
Intensity
f1 (ppm)

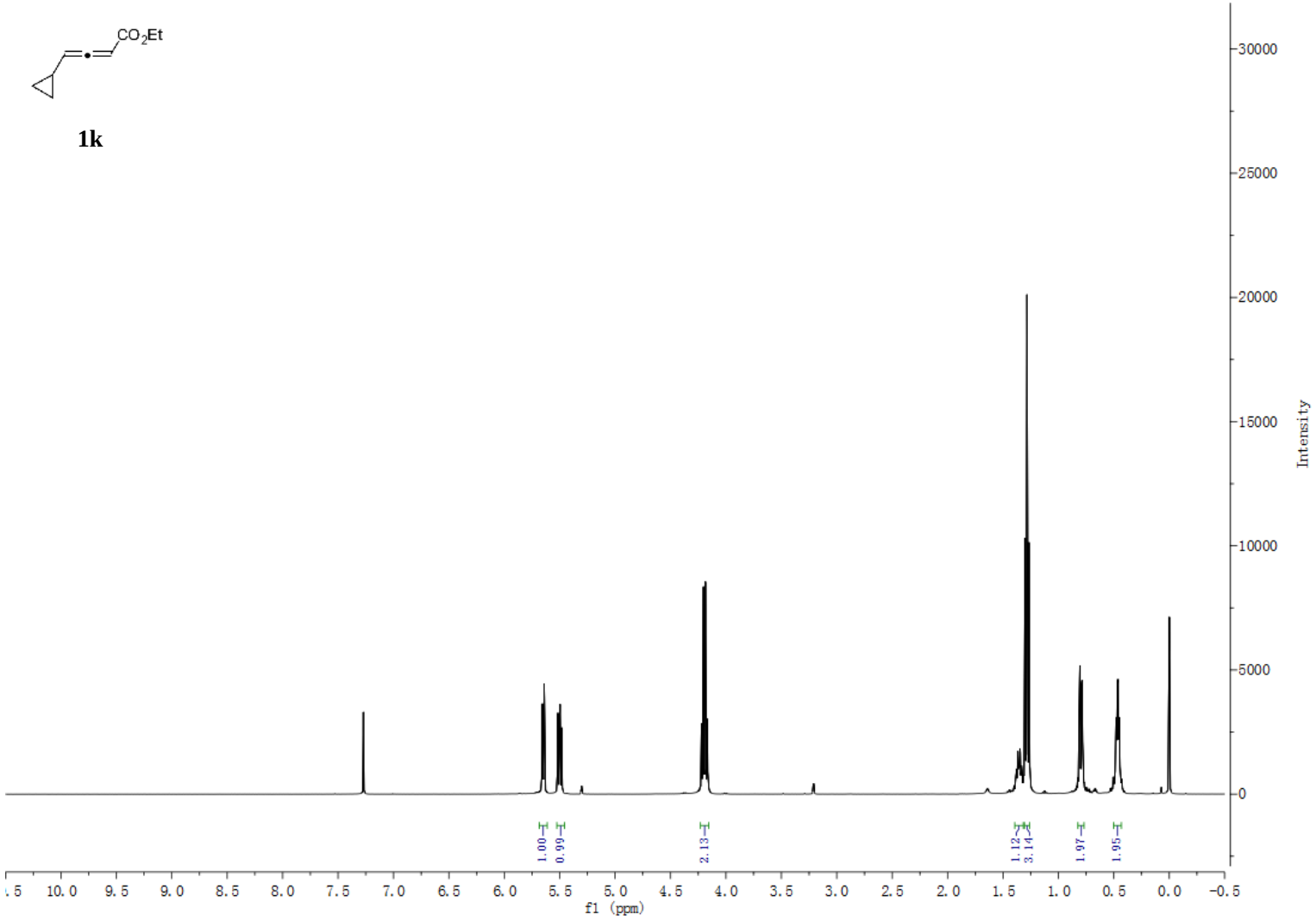

OTBS
1h
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
Intensity
0.99
0.98
2.00
1.16
9.25
2.02
1.99
6.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

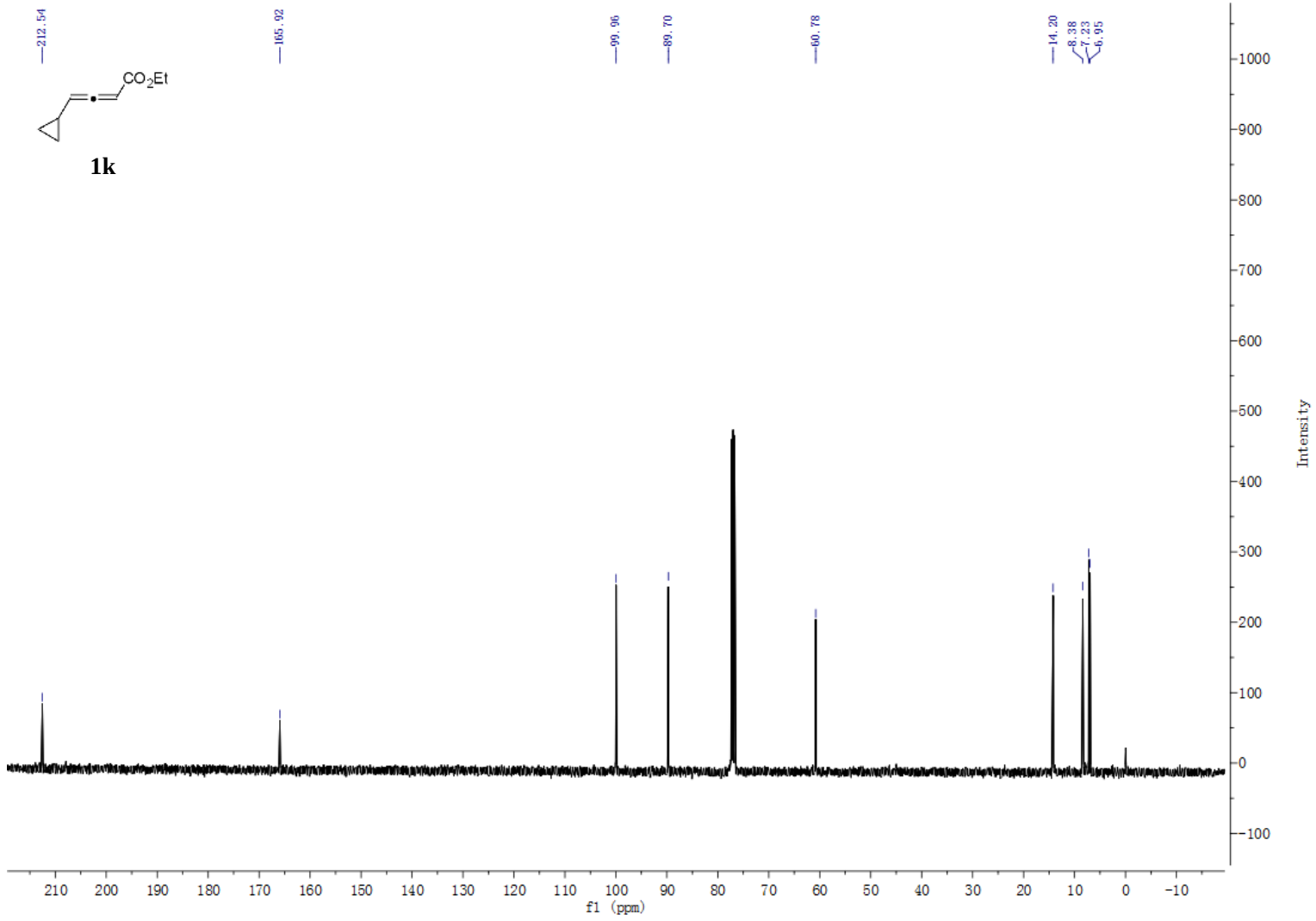

202.84
96.88
93.49
61.96
25.93
18.37
9.47
6.73
6.64
-5.09
-5.11
OTBS
1h
Intensity
f1 (ppm)

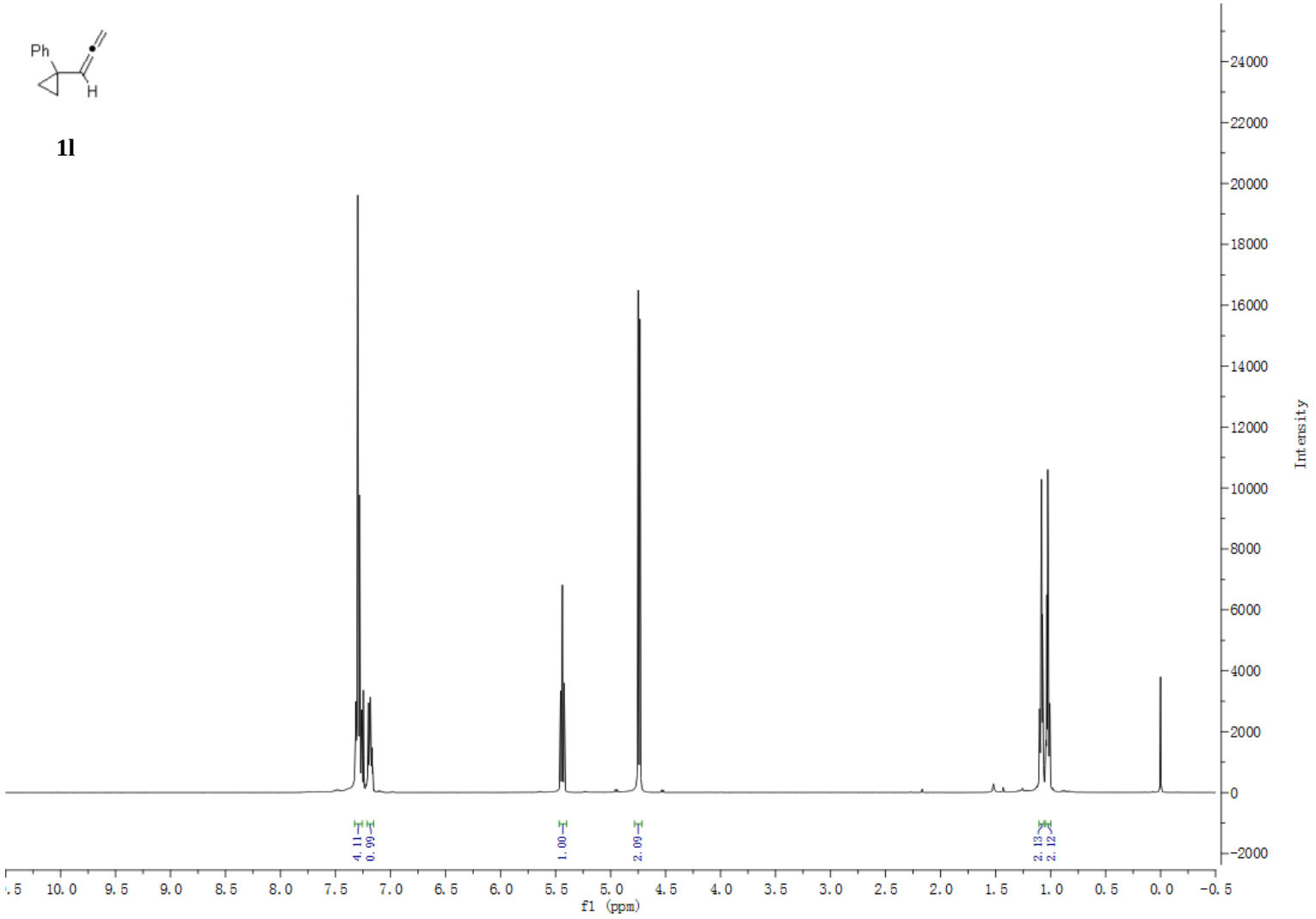


1i

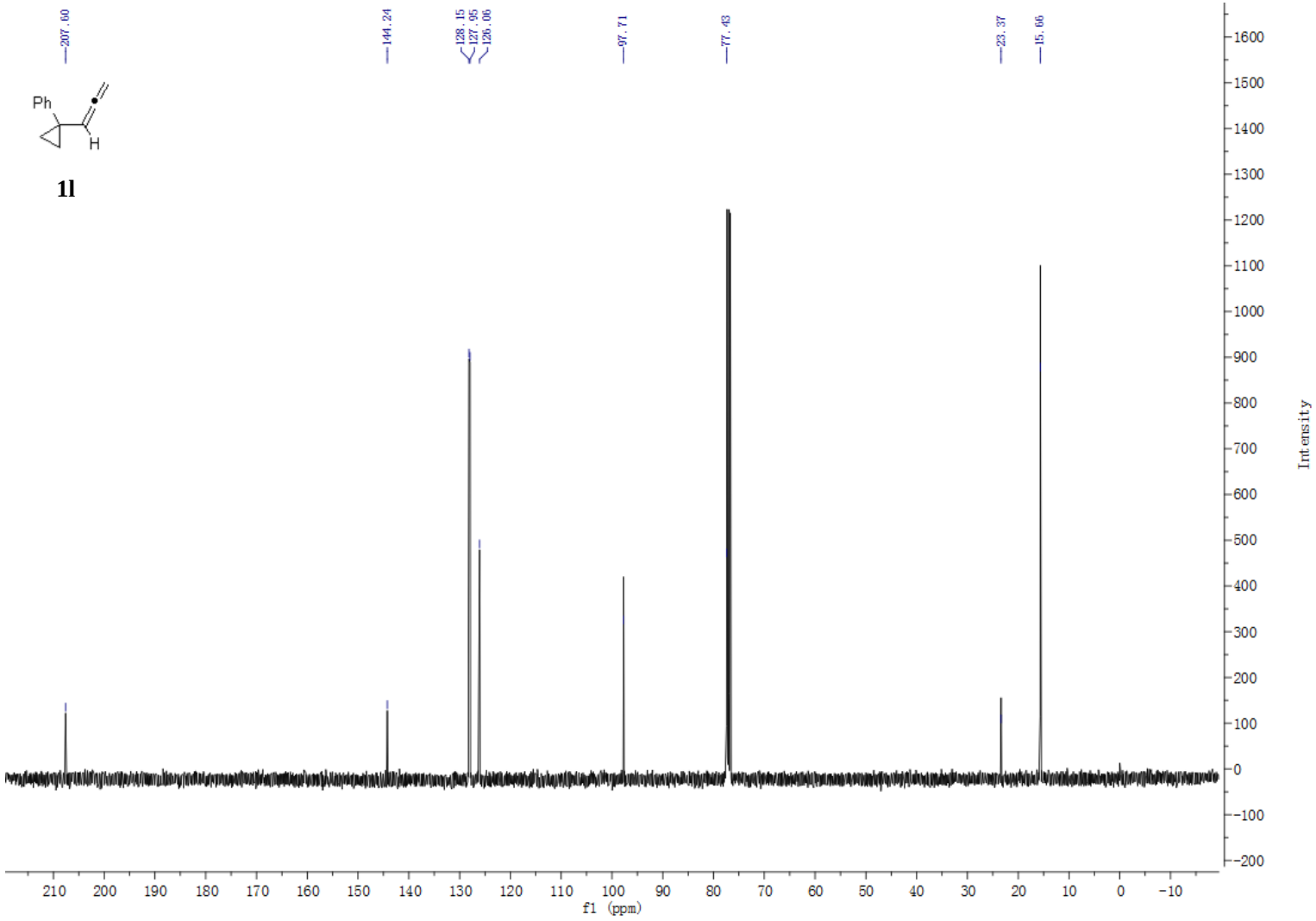

202.99
135.59
133.82
133.81
129.57
127.60
96.99
93.20
62.44
26.80
19.21
9.48
6.71
6.62
O-Si
1i
Intensity
f1 (ppm)

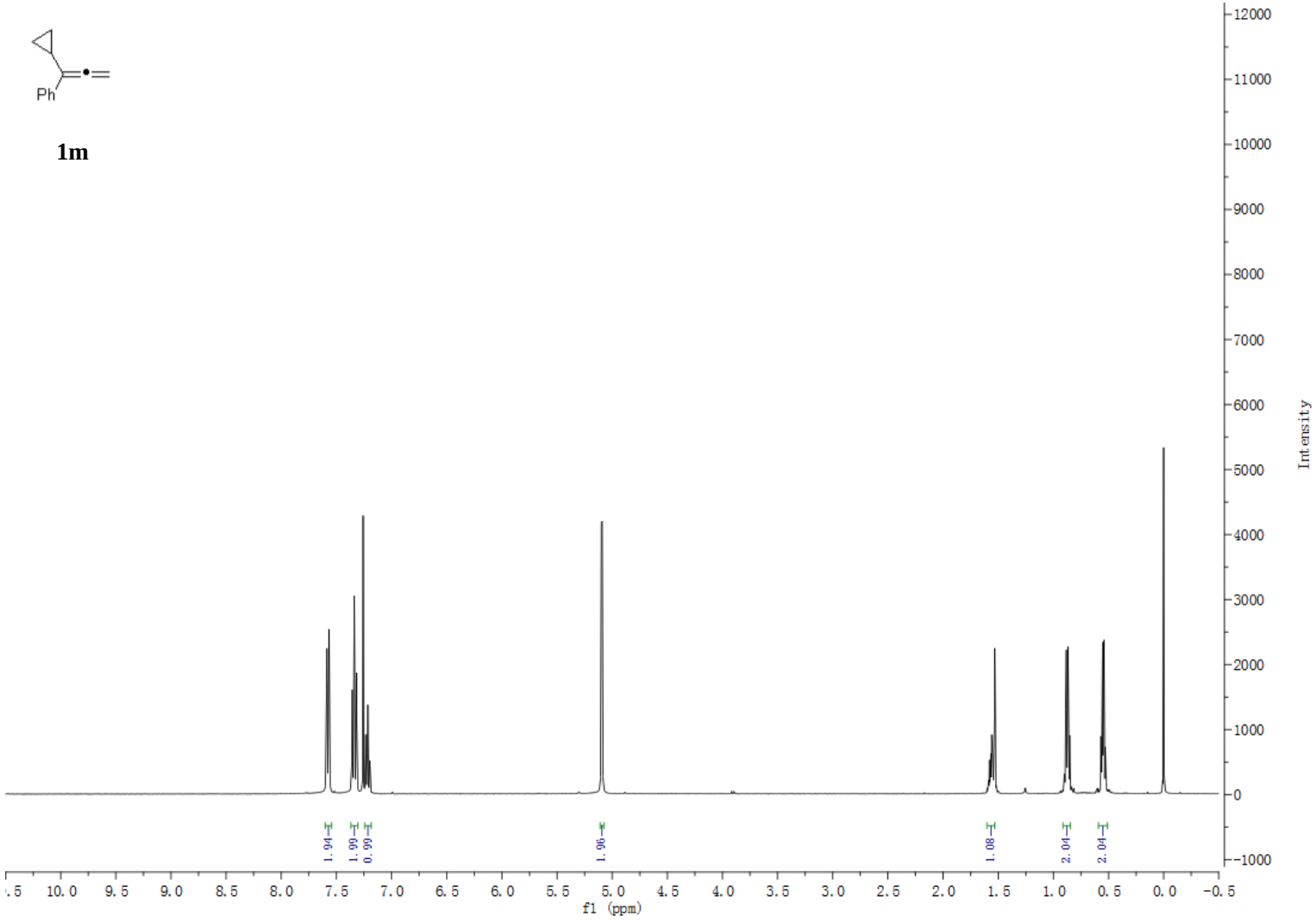

CO2Et
1k
30000
25000
20000
15000
10000
5000
0
Intensity
1.00
0.99
2.13
1.12
3.14
1.97
1.95
f1 (ppm)

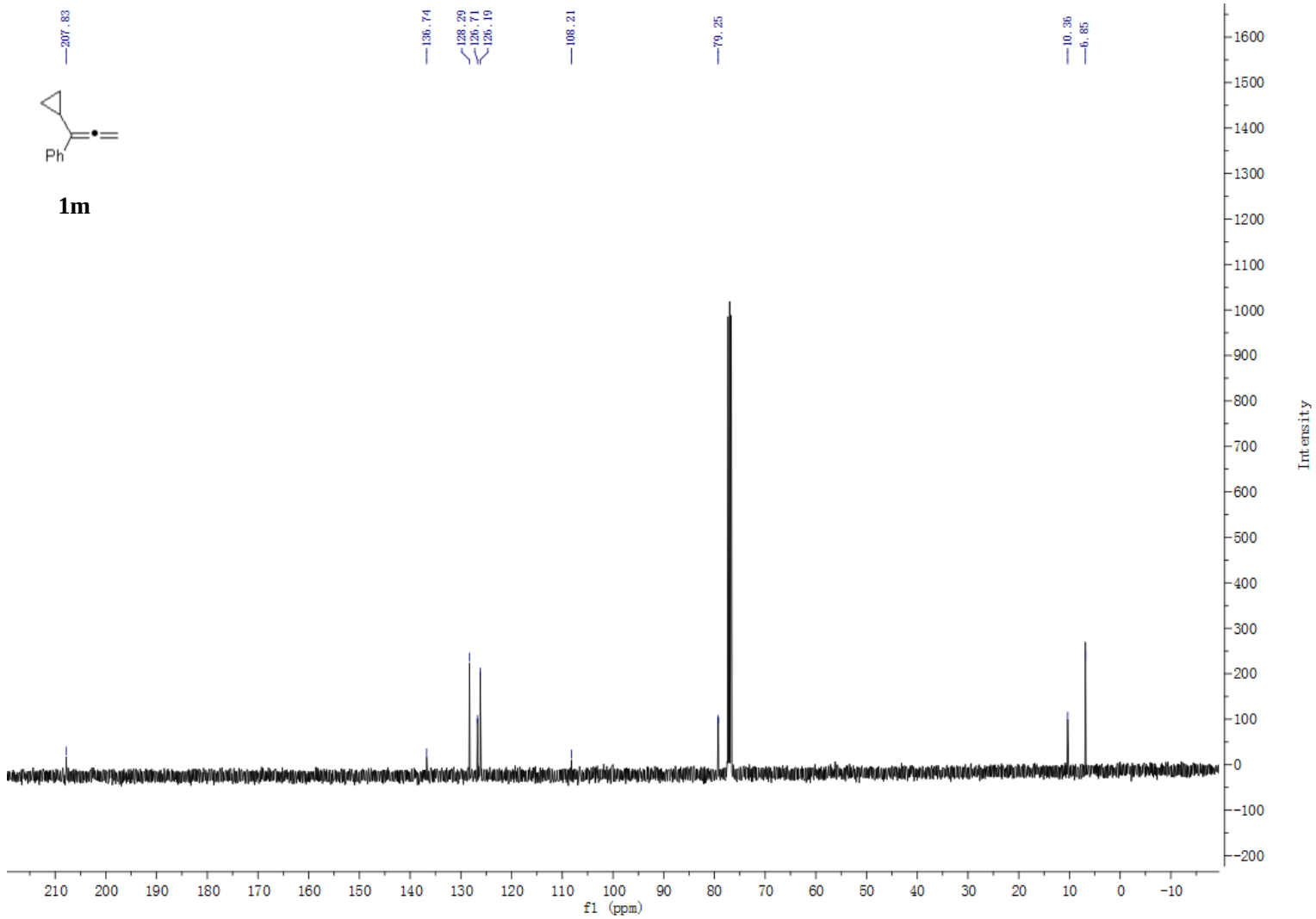

212.54
165.92
99.96
89.70
60.78
14.20
8.38
7.23
6.95
CO2Et
1k
Intensity
f1 (ppm)


Ph
H
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
Intensity
4.11
0.99
1.00
2.09
2.13
2.12
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
-0.5
f1 (ppm)

1l


207.60
144.24
128.15
127.95
126.06
97.71
77.43
23.37
15.66
Ph
H
1l
Intensity
f1 (ppm)


Ph
1m
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
Intensity
1.94
1.99
0.99
1.96
1.08
2.04
2.04
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
-0.5
f1 (ppm)


207.83
136.74
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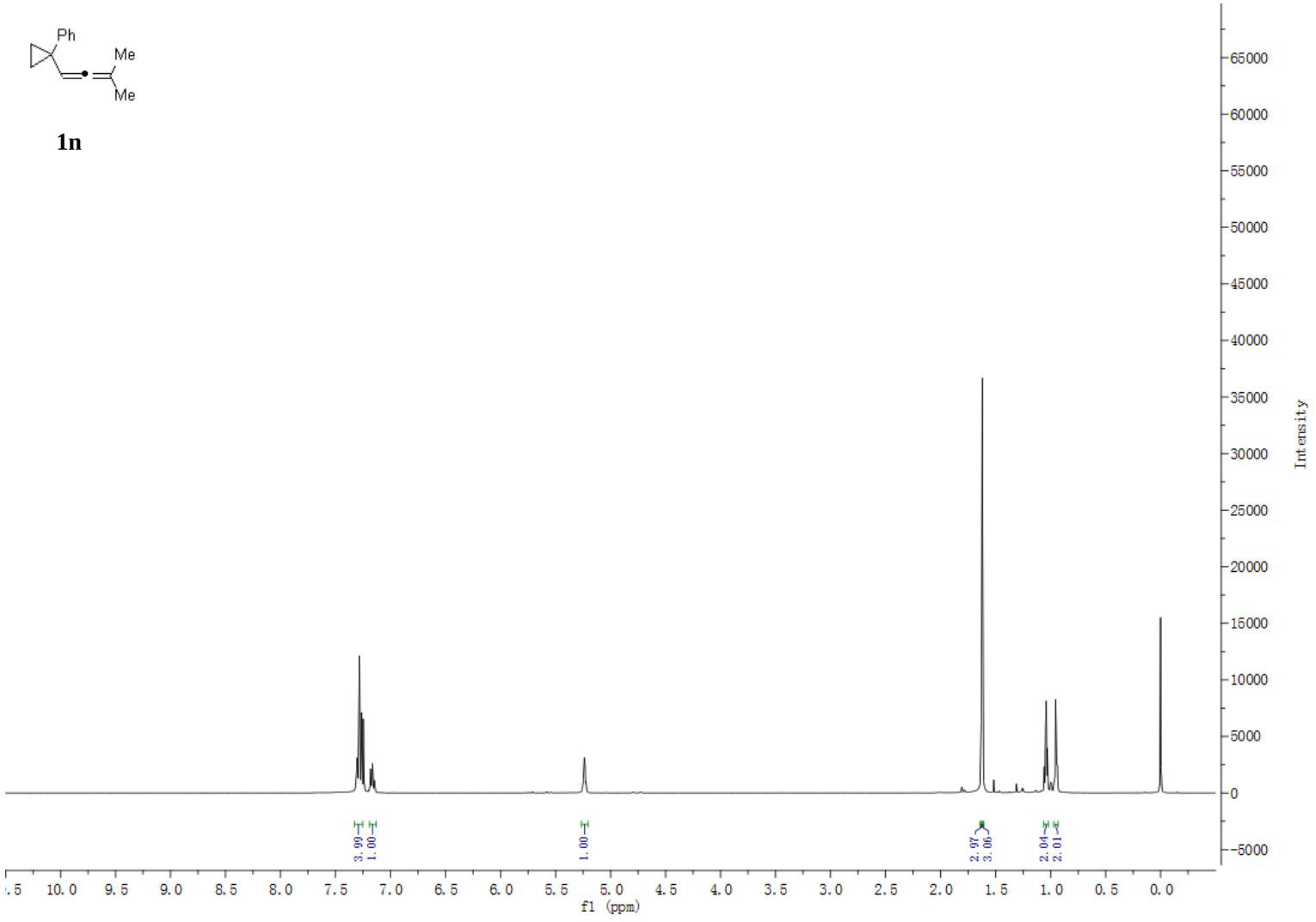
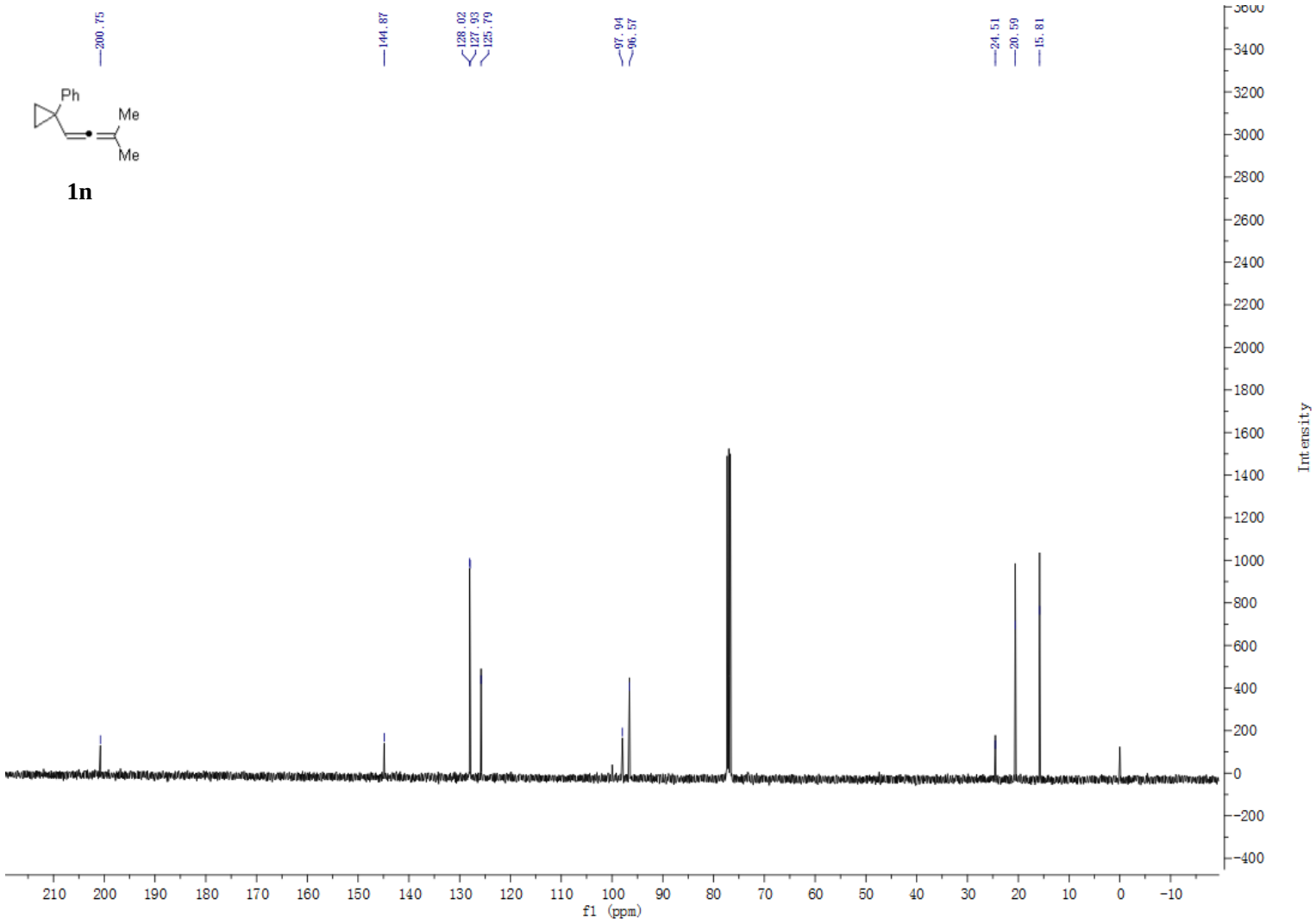
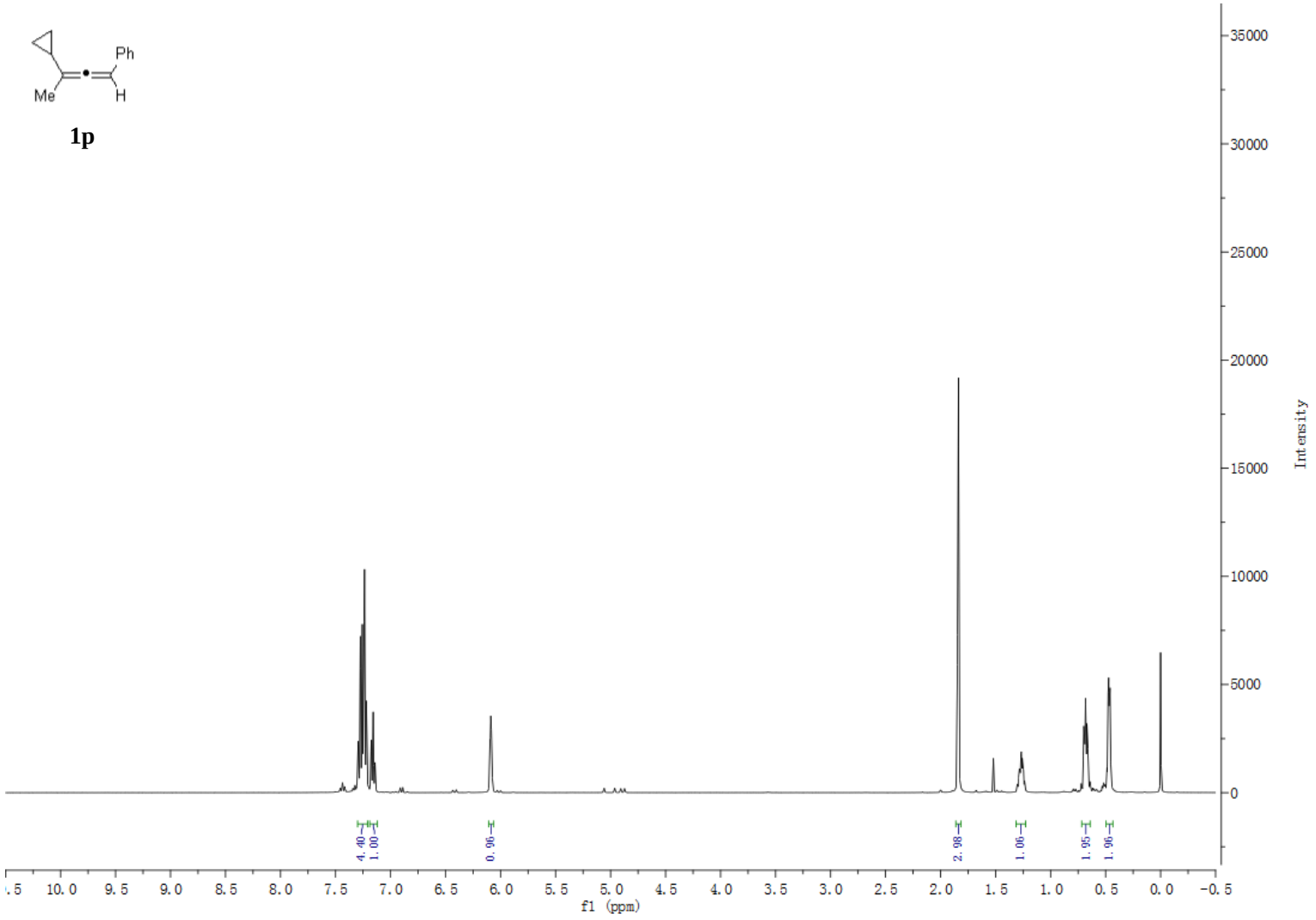
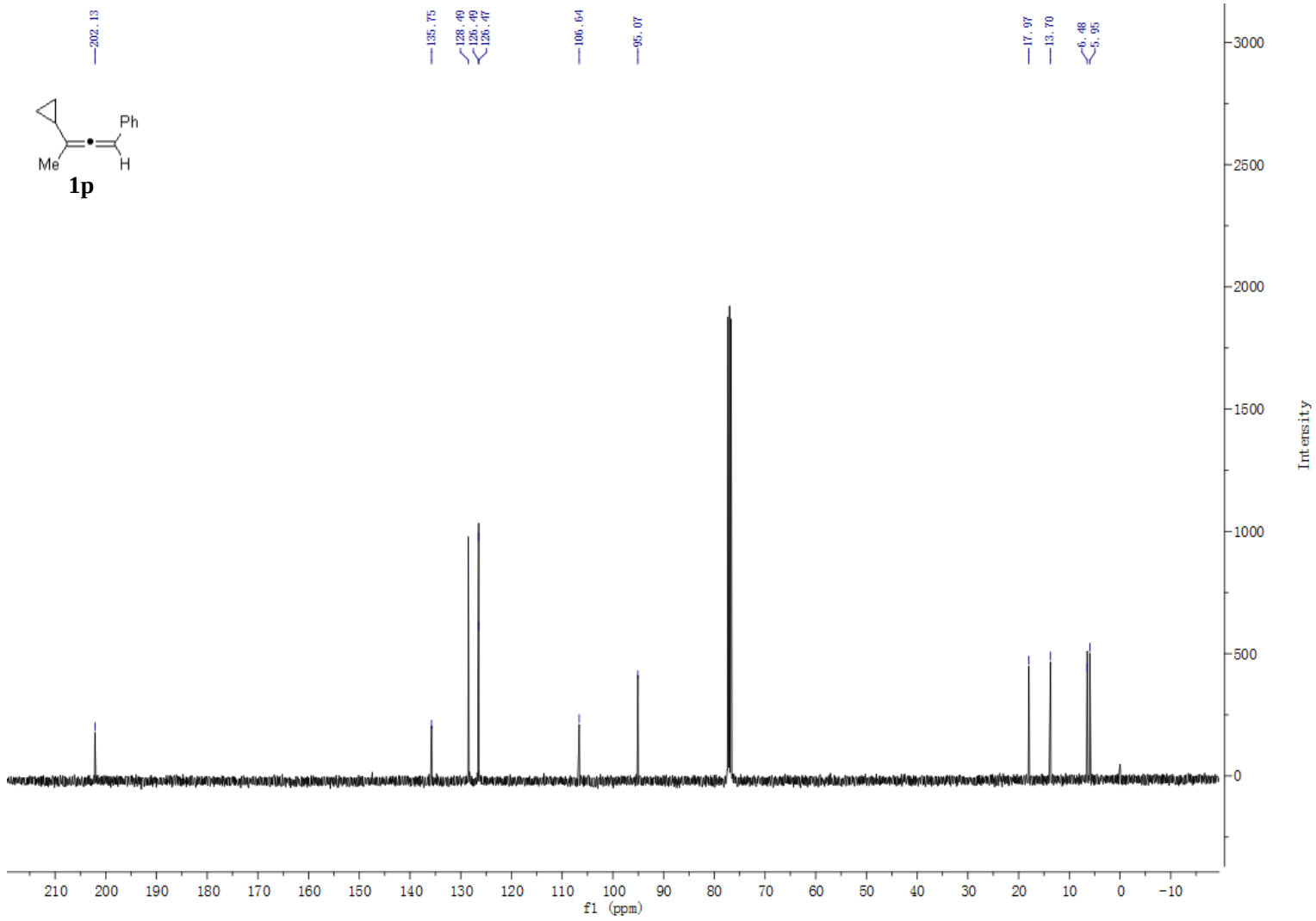
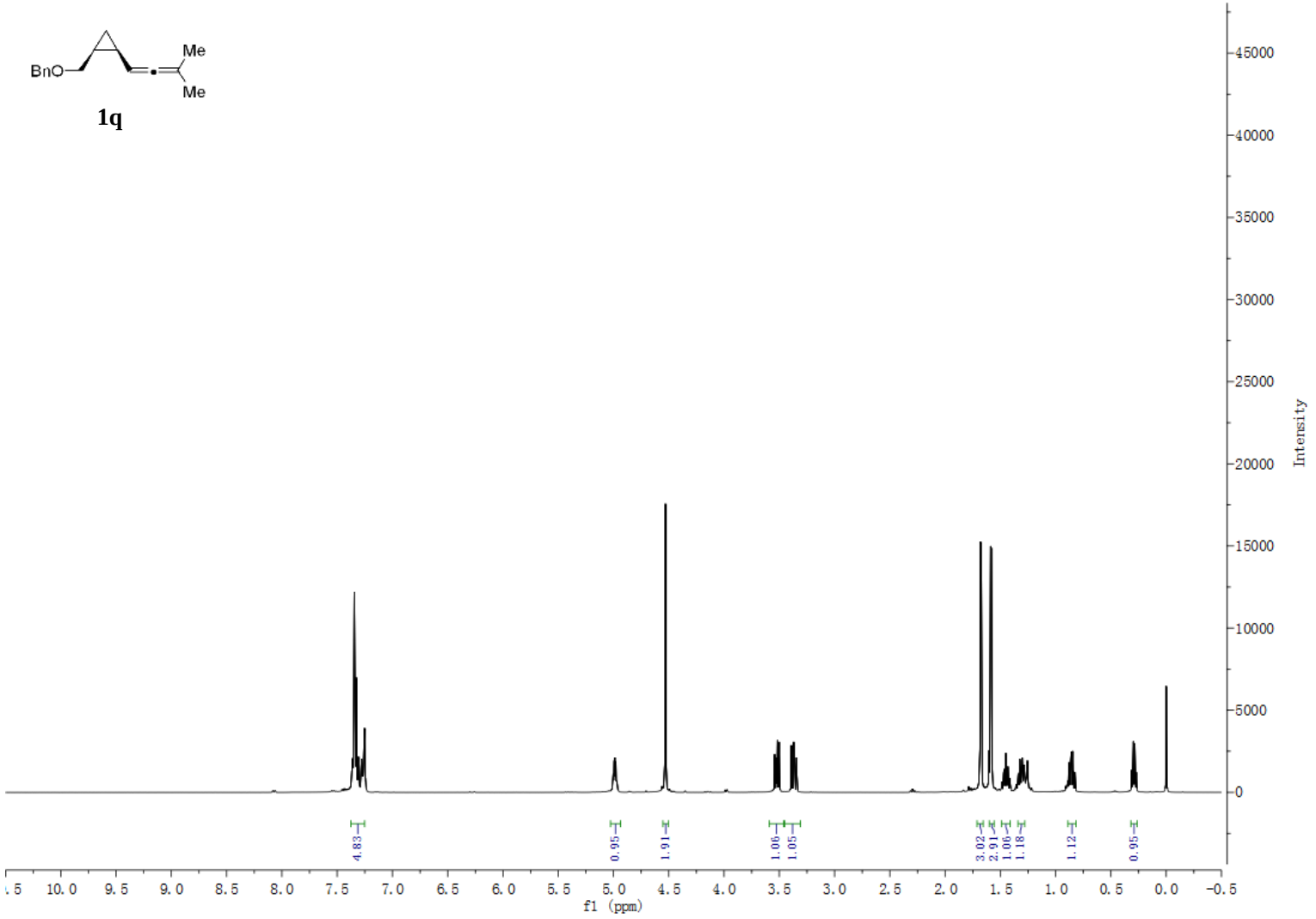
126.71
126.19
108.21
79.25
10.36
6.85
Ph
1m
Intensity
f1 (ppm)


Ph
Me
Me
1n
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
Intensity
3.99
1.00
1.00
2.97
3.06
2.04
2.01
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)


200.75
144.87
128.02
127.93
125.79
97.94
96.57
24.51
20.59
15.81
Ph
Me
Me
1n
Intensity
f1 (ppm)


Ph
Me
H
1p
35000
30000
25000
20000
15000
10000
5000
0
Intensity
4.40
1.00
0.96
2.98
1.06
1.95
1.96
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
-0.5
f1 (ppm)


202.13
135.75
128.49
126.49
126.47
106.64
95.07
17.97
13.70
6.48
5.95
Ph
Me
H
1p
3000
2500
2000
1500
1000
500
0
Intensity
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)


BnO
Me
Me
1q
Intensity
f1 (ppm)
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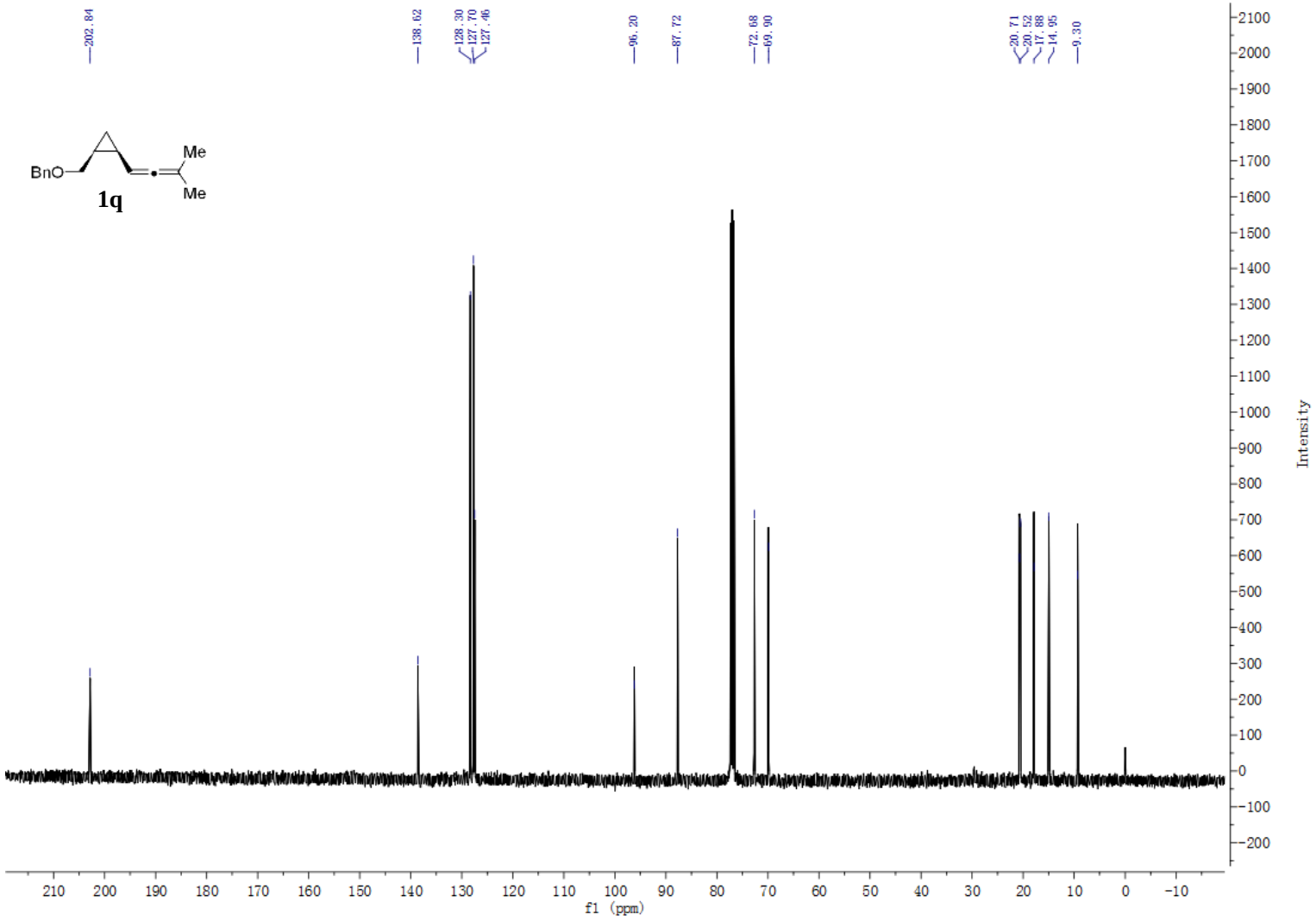
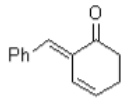
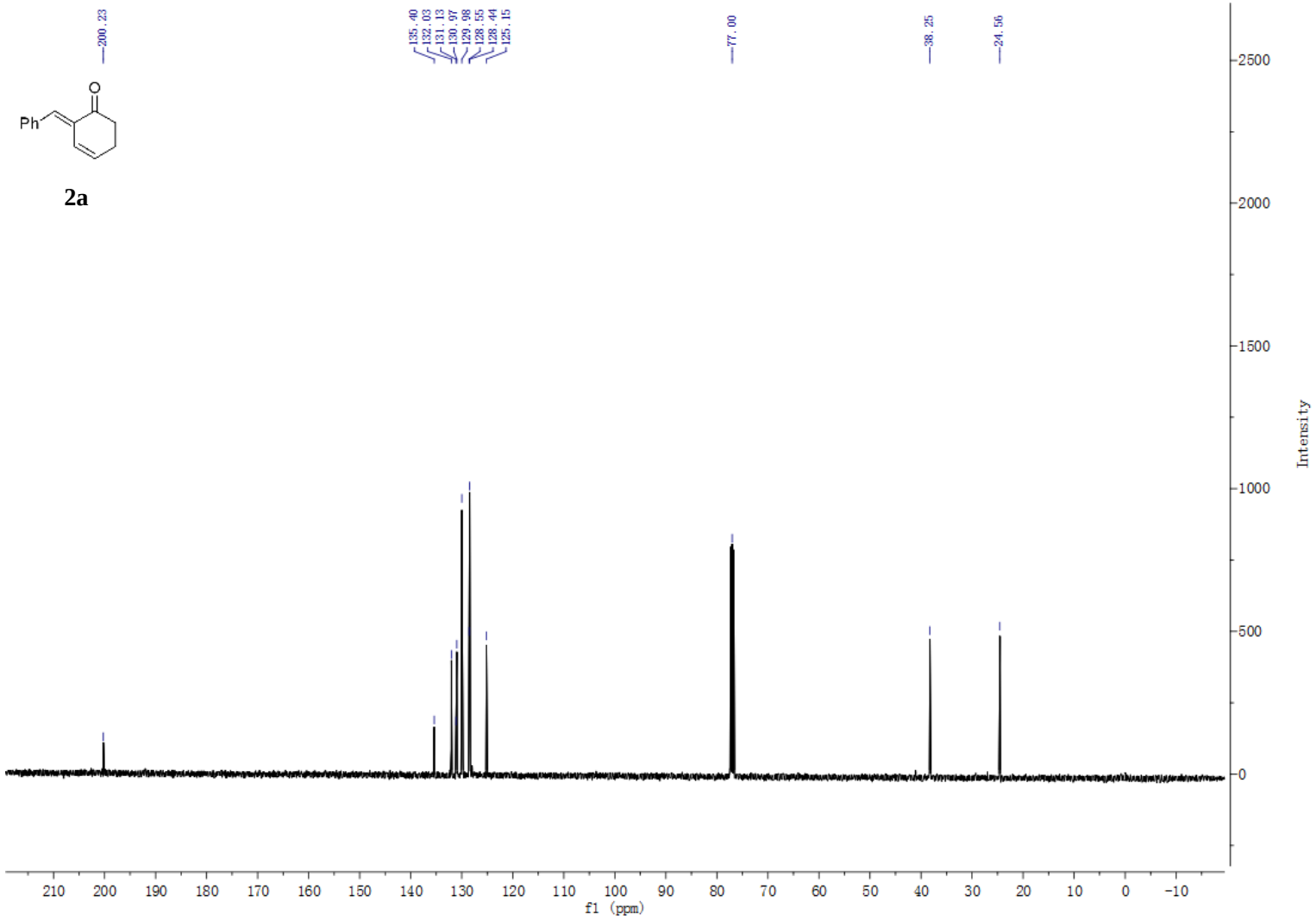
0.95
1.91
1.06
1.05
3.02
2.91
1.06
1.18
1.12
0.95


202.84
138.62
128.30
127.70
127.46
96.20
87.72
72.68
69.90
20.71
20.52
17.88
14.95
9.30
BnO
Me
Me
1q
Intensity
f1 (ppm)

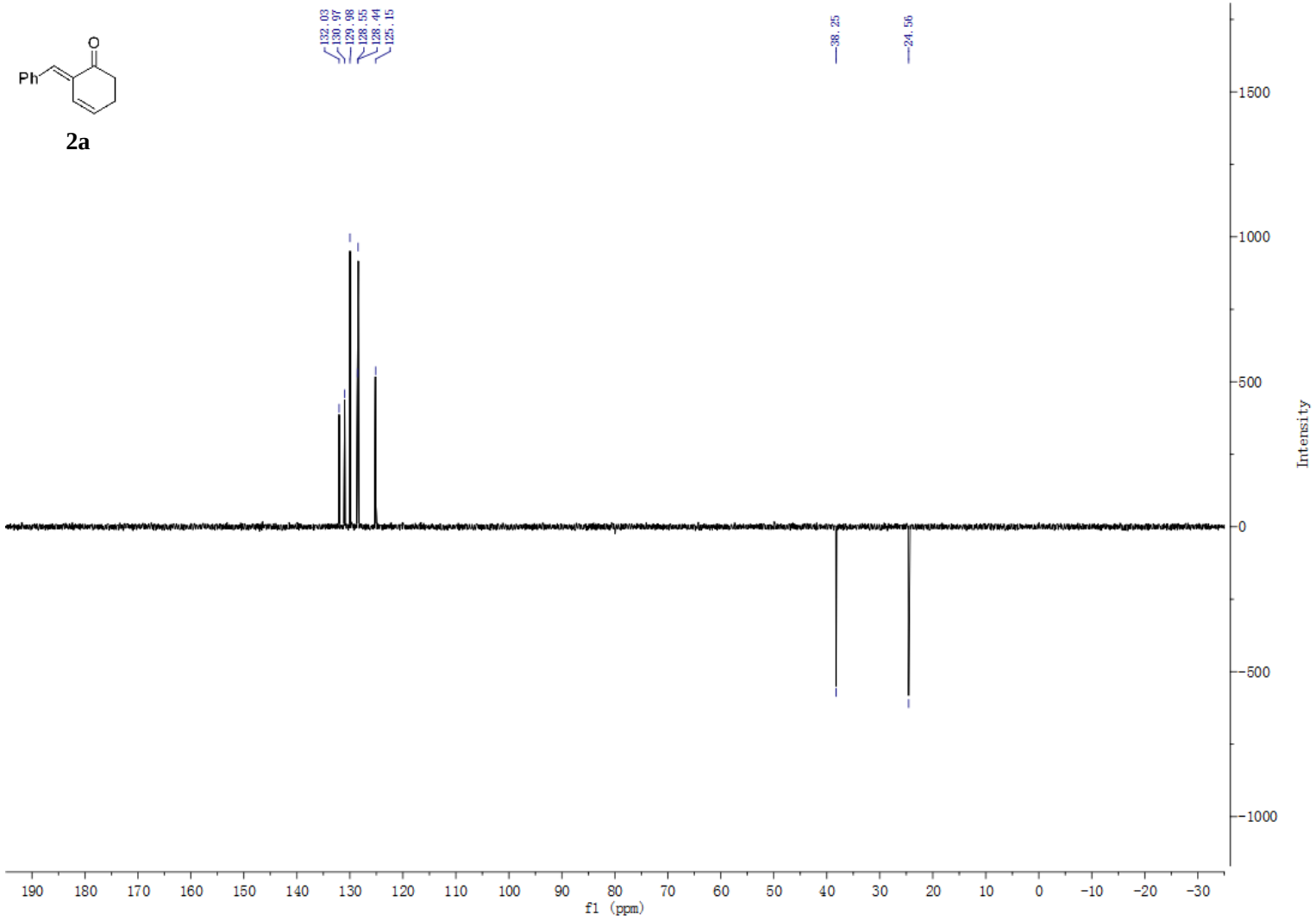

O
Ph

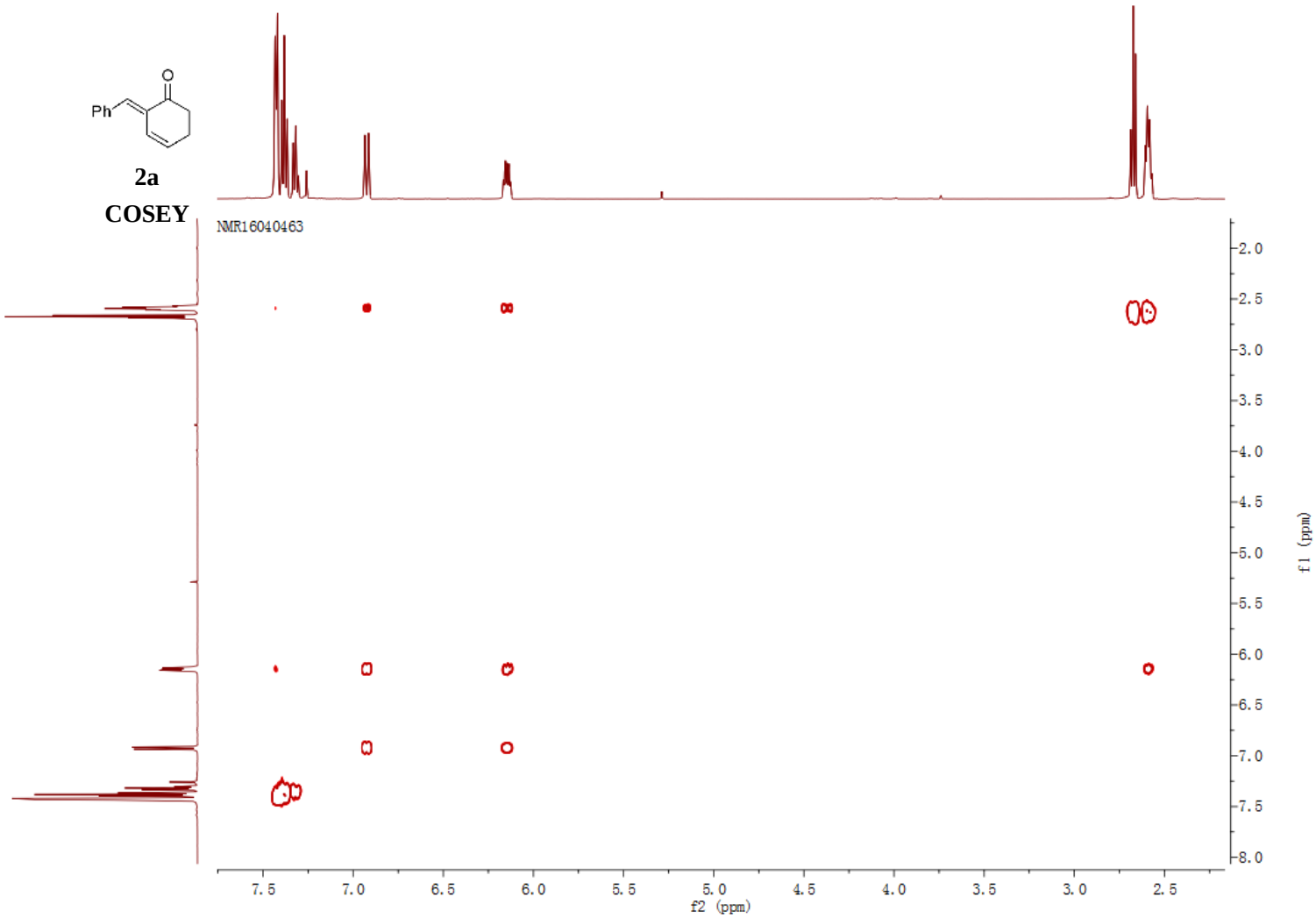
2a

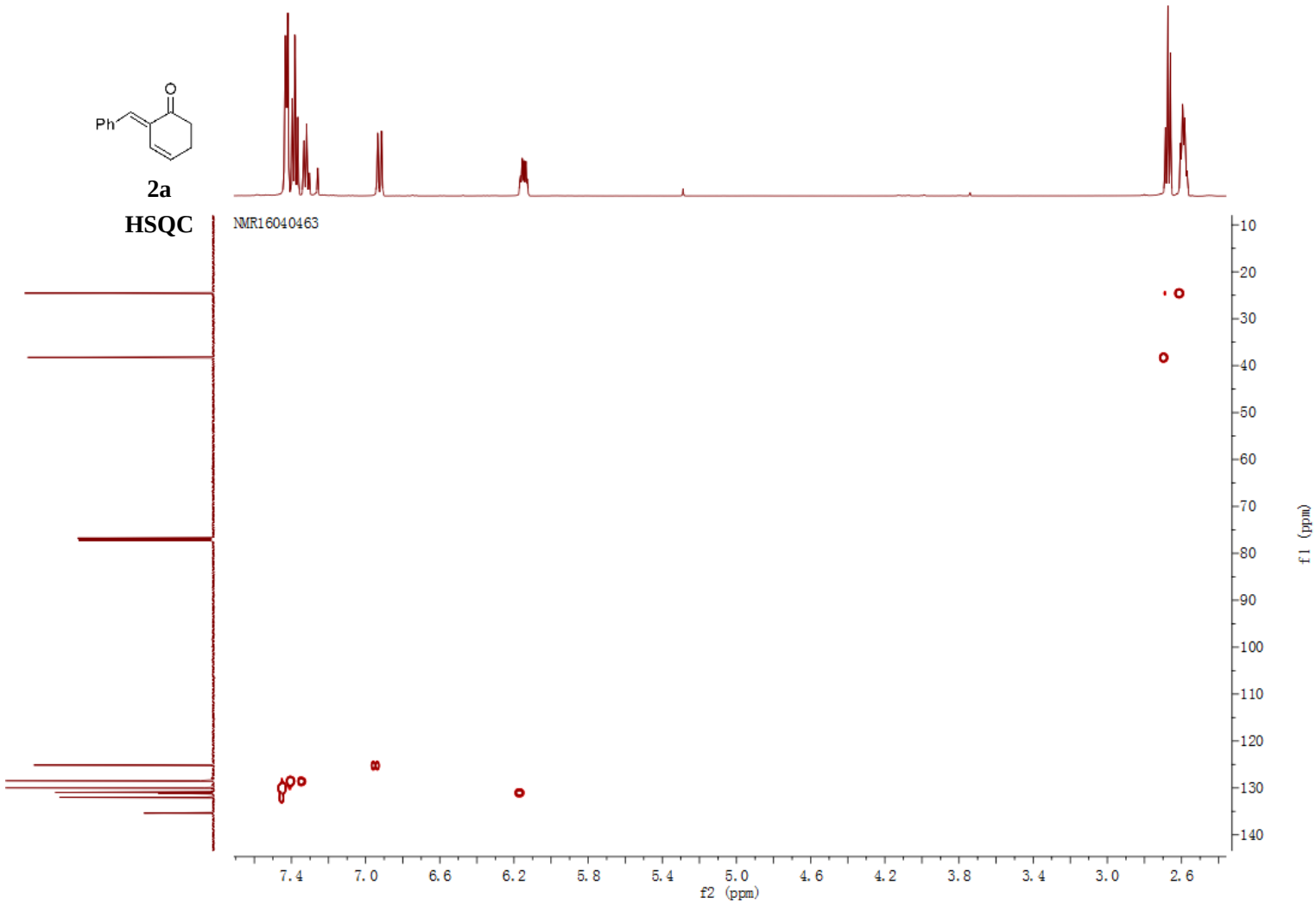
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
Intensity
4.93
1.06
0.99
0.97
2.07
2.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

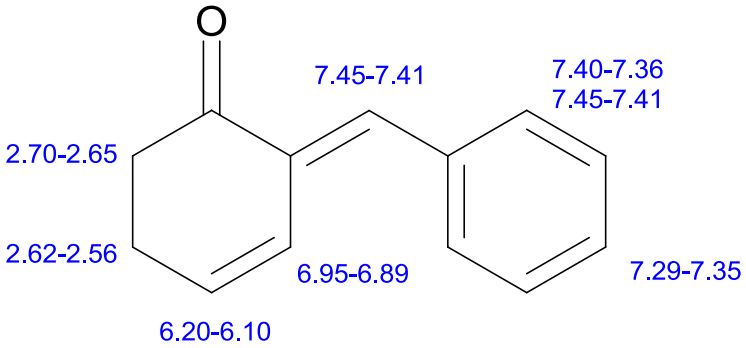

200.23
135.40
132.03
131.13
130.97
129.98
128.55
128.44
125.15
77.00
38.25
24.56
Ph
O
2500
2000
1500
1000
500
0
Intensity
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

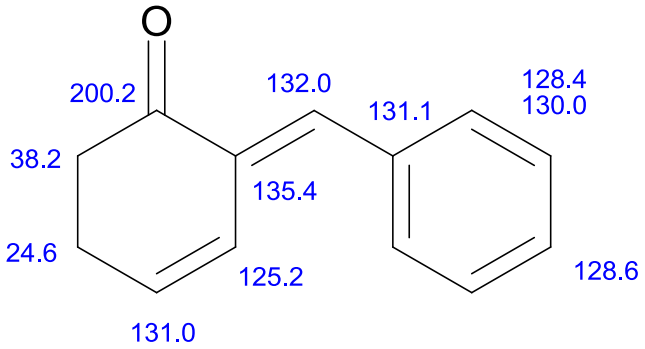
2a

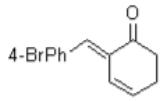

Ph
O
2a
132.03
130.97
129.98
128.55
128.44
125.15
38.25
24.56
1500
1000
500
0
-500
-1000
Intensity
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)


Ph
O
2a
COSEY
NMR16040463
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f2 (ppm)

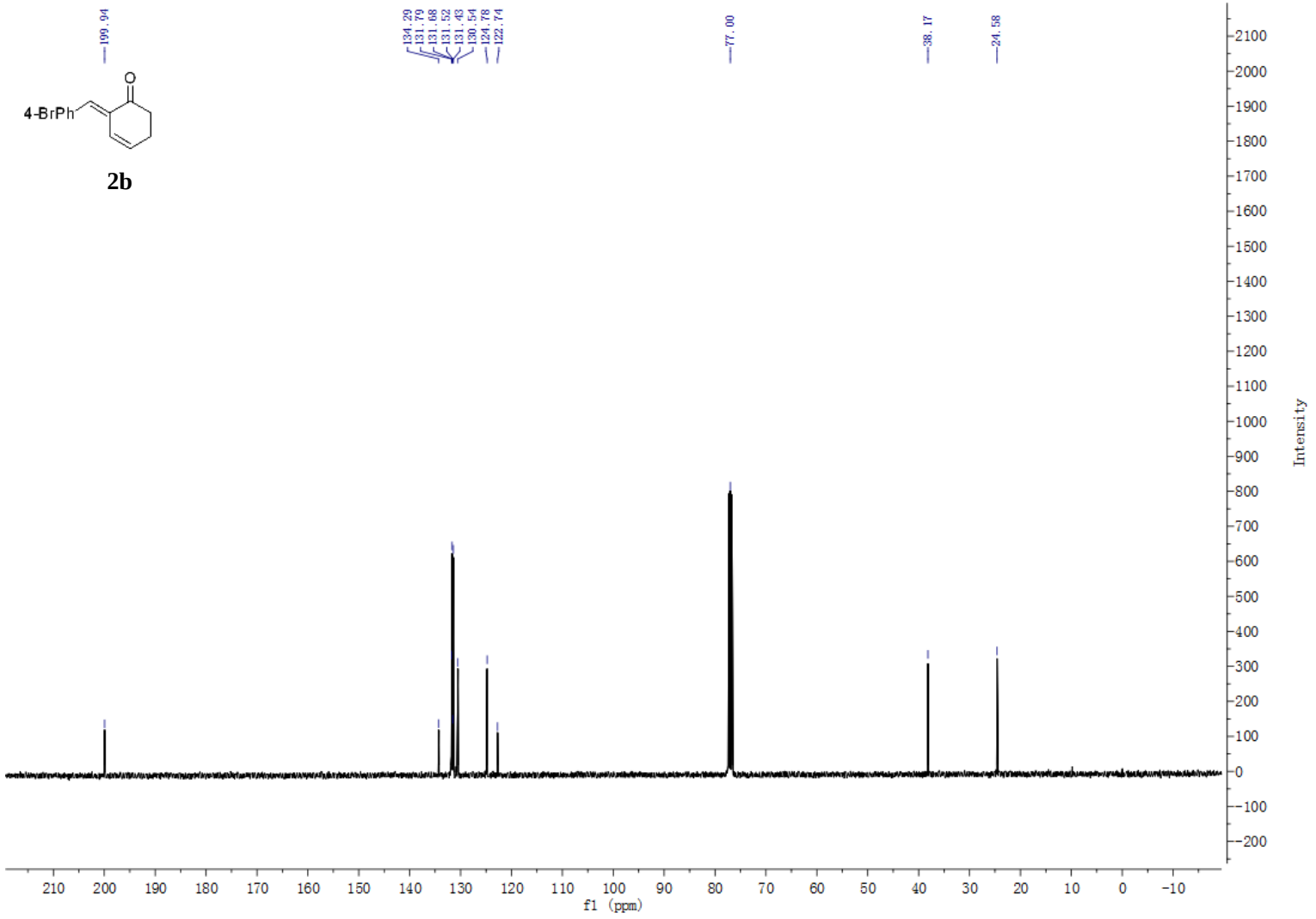

Ph
2a
HSQC
NMR16040463
f2 (ppm)
f1 (ppm)

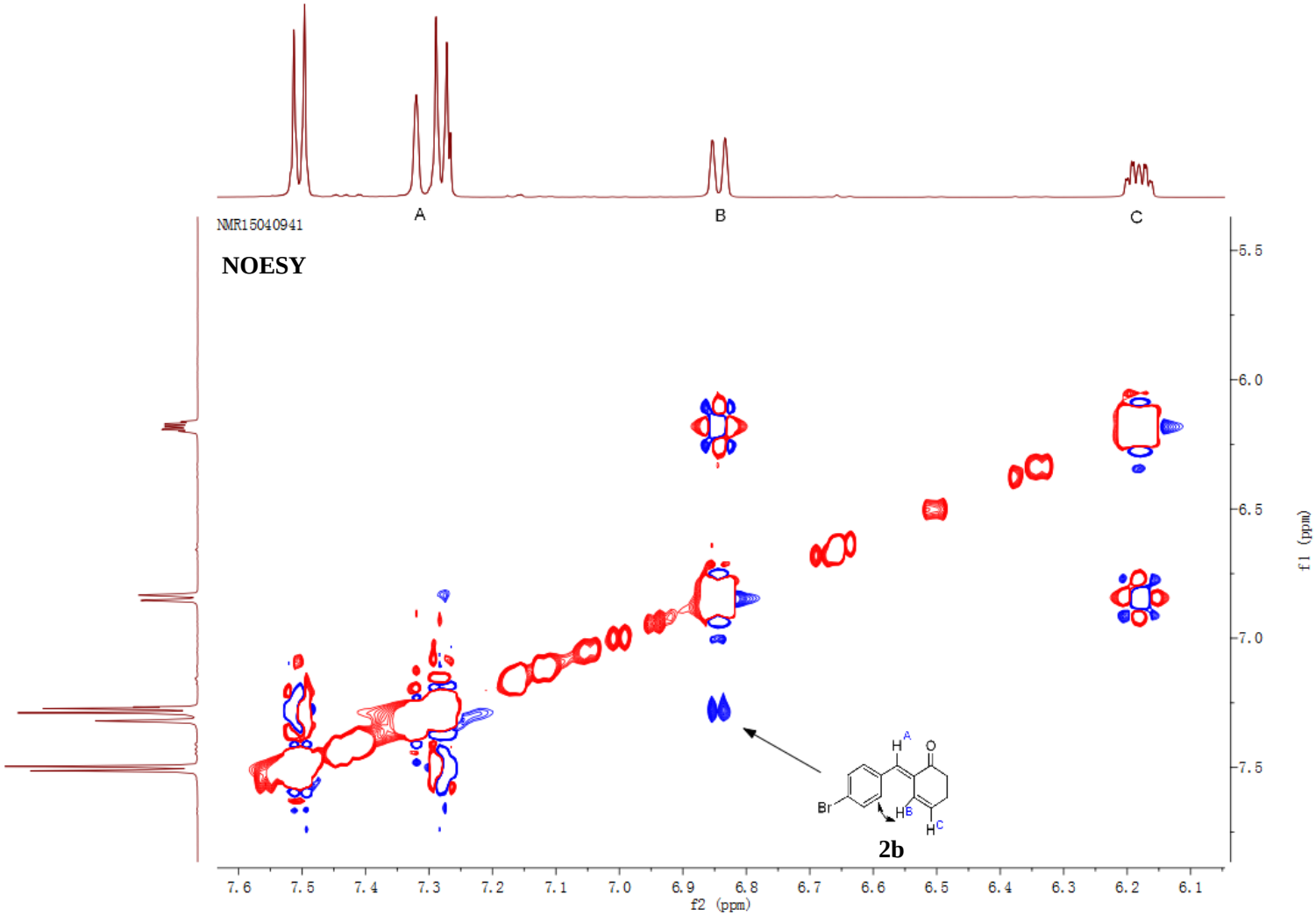

O
7.45-7.41
7.40-7.36
7.45-7.41
2.70-2.65
2.62-2.56
6.95-6.89
7.29-7.35
6.20-6.10

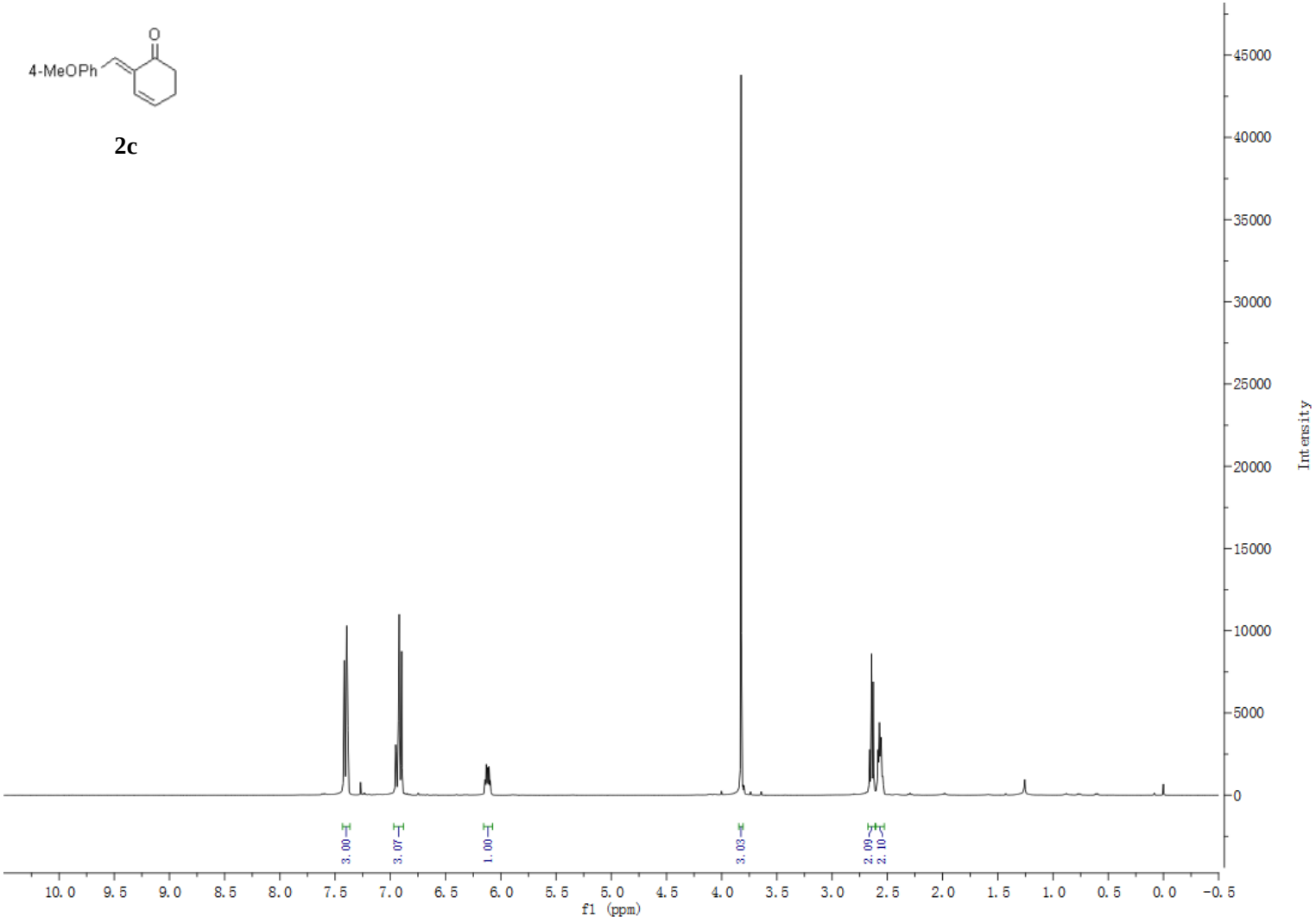

O
200.2
132.0
131.1
128.4
130.0
38.2
135.4
24.6
125.2
128.6
131.0

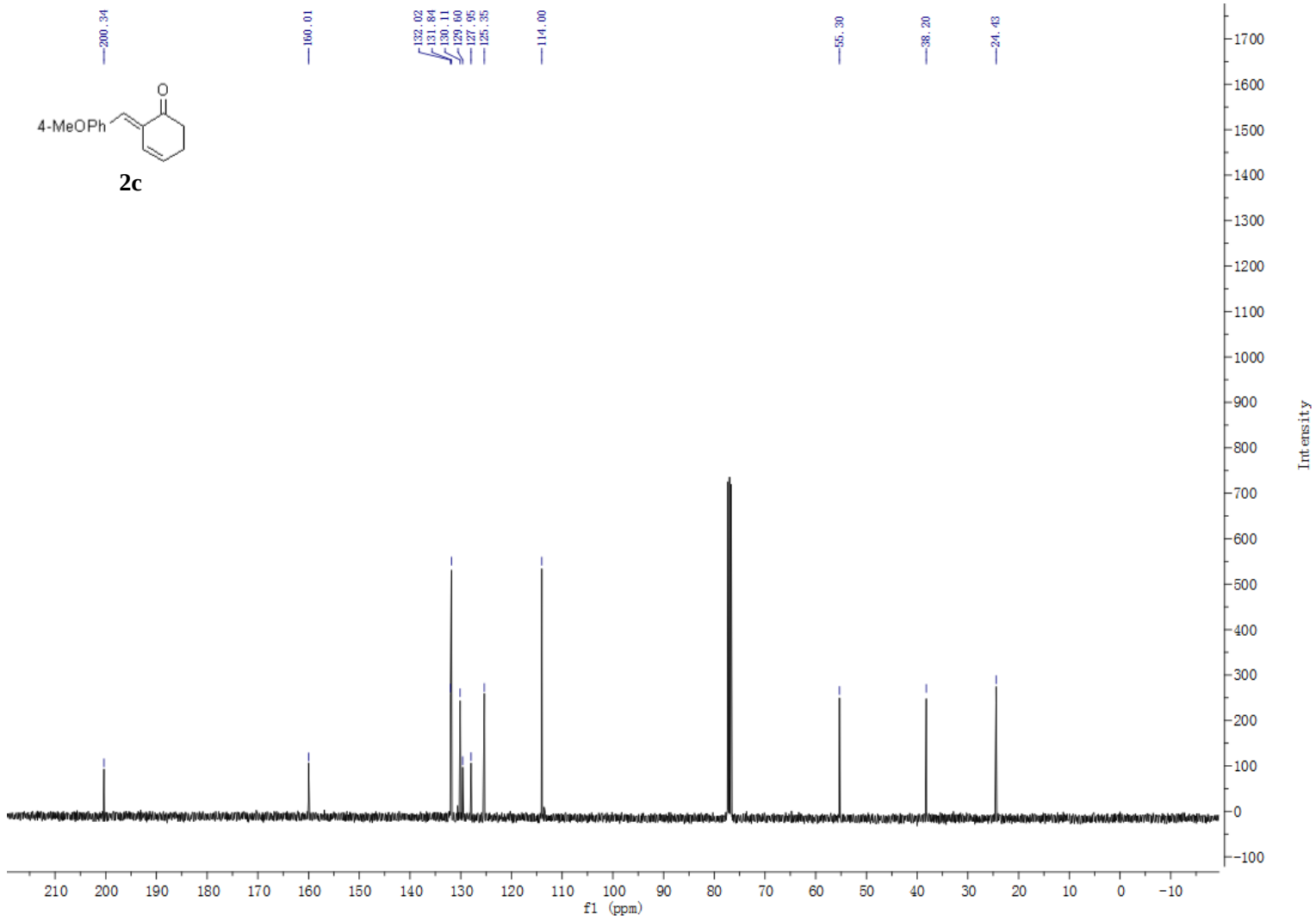


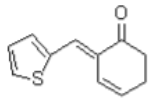
2b


199.94
134.29
131.79
131.68
131.52
131.43
130.54
124.78
122.74
77.00
38.17
24.58
4-BrPh
O
2b
Intensity
f1 (ppm)


NMR15040941
NOESY
A
B
C
f2 (ppm)
f1 (ppm)
Br
O
2b

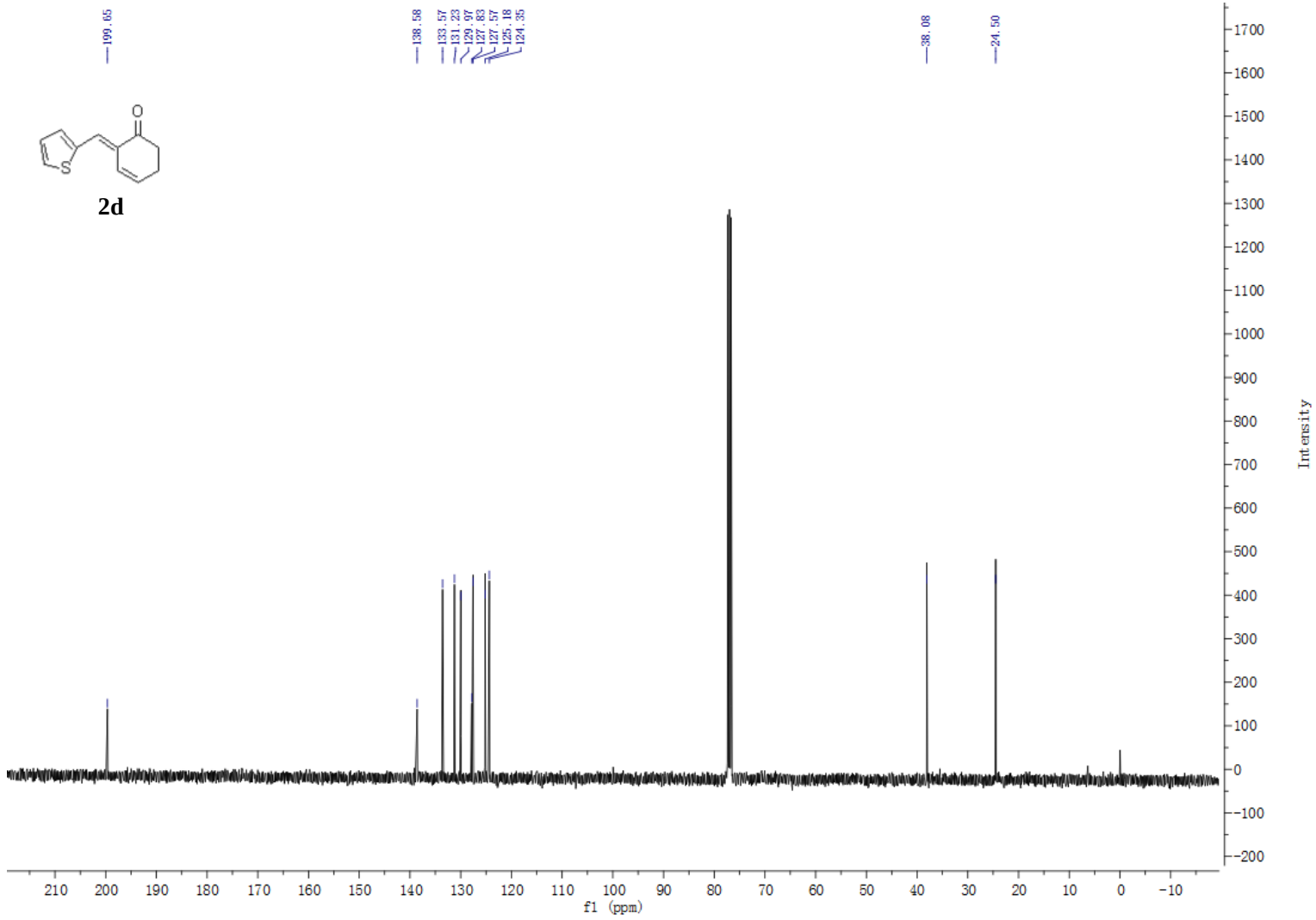

4-MeOPh
O
2c
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
Intensity
3.00
3.07
1.00
3.03
2.09
2.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

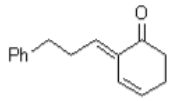

200.34
160.01
132.02
131.84
130.11
129.60
127.95
125.35
114.00
55.30
38.20
24.43
4-MeOPh
O
2c
Intensity
f1 (ppm)



2d

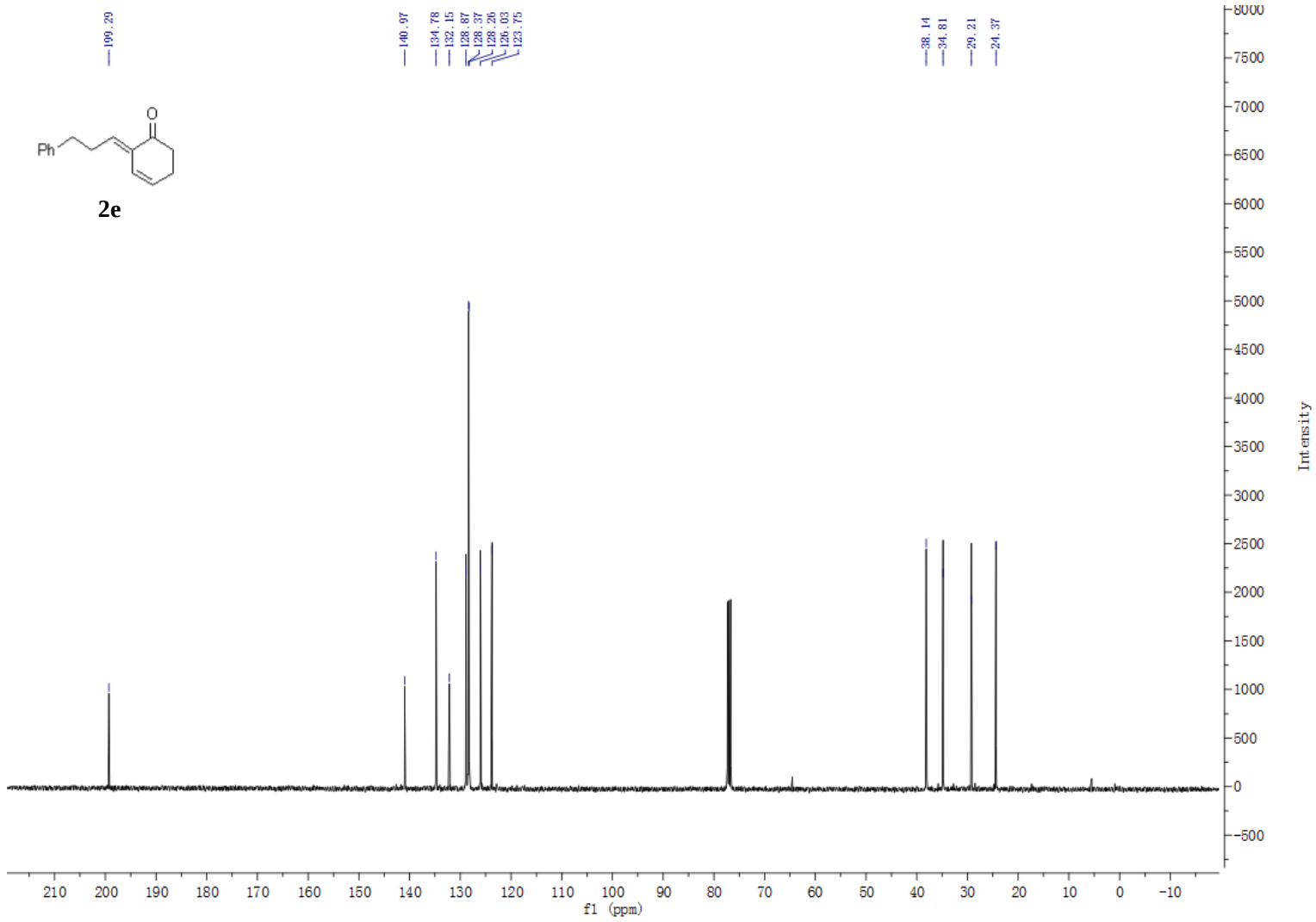
30000
25000
20000
15000
10000
5000
0
Intensity
0.98
0.95
1.02
1.03
1.01
1.00
2.08
2.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

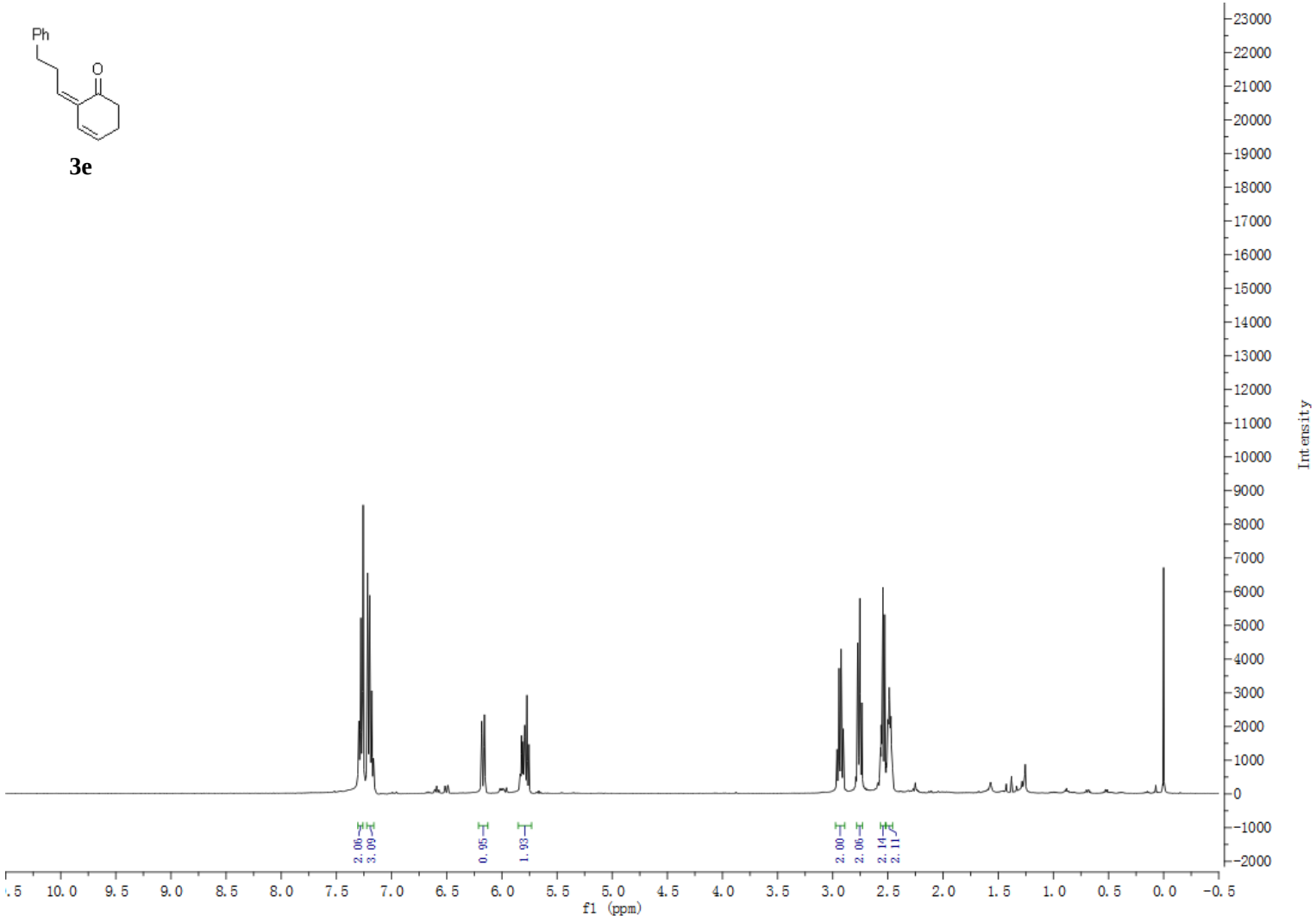

199.65
138.58
133.57
131.23
129.97
127.83
127.57
125.18
124.35
38.08
24.50
O
S
2d
Intensity
f1 (ppm)

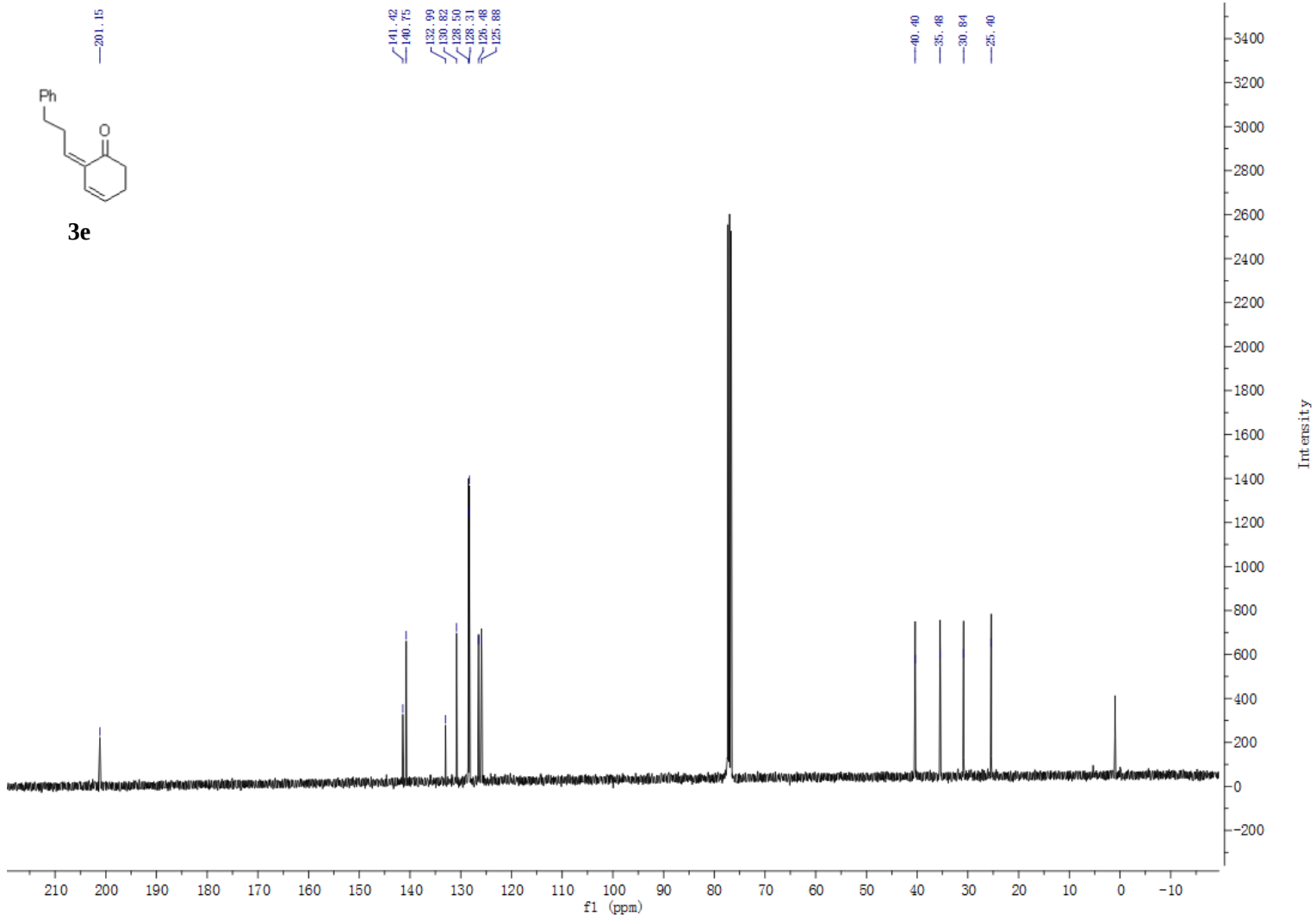

O
Ph

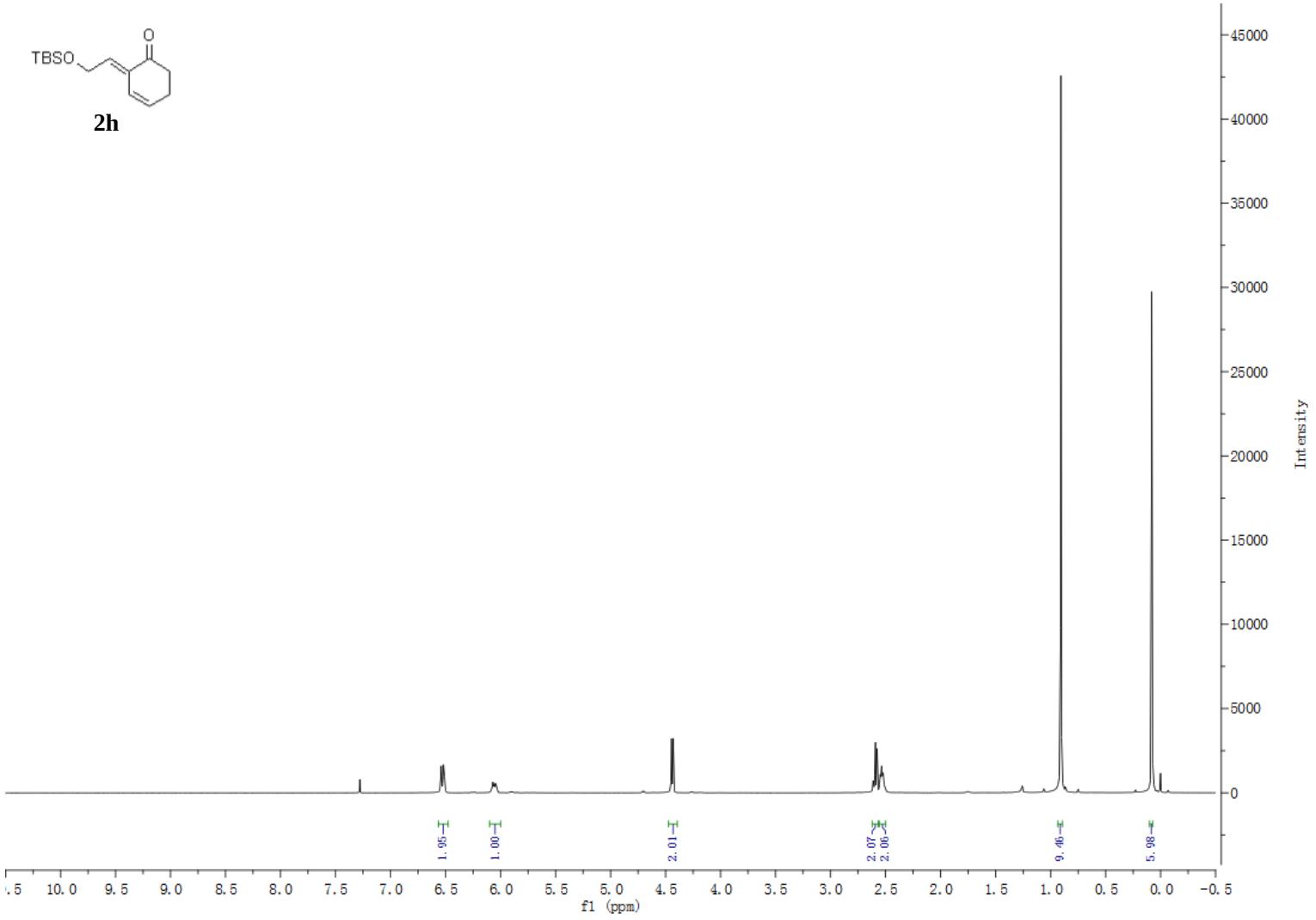
2e

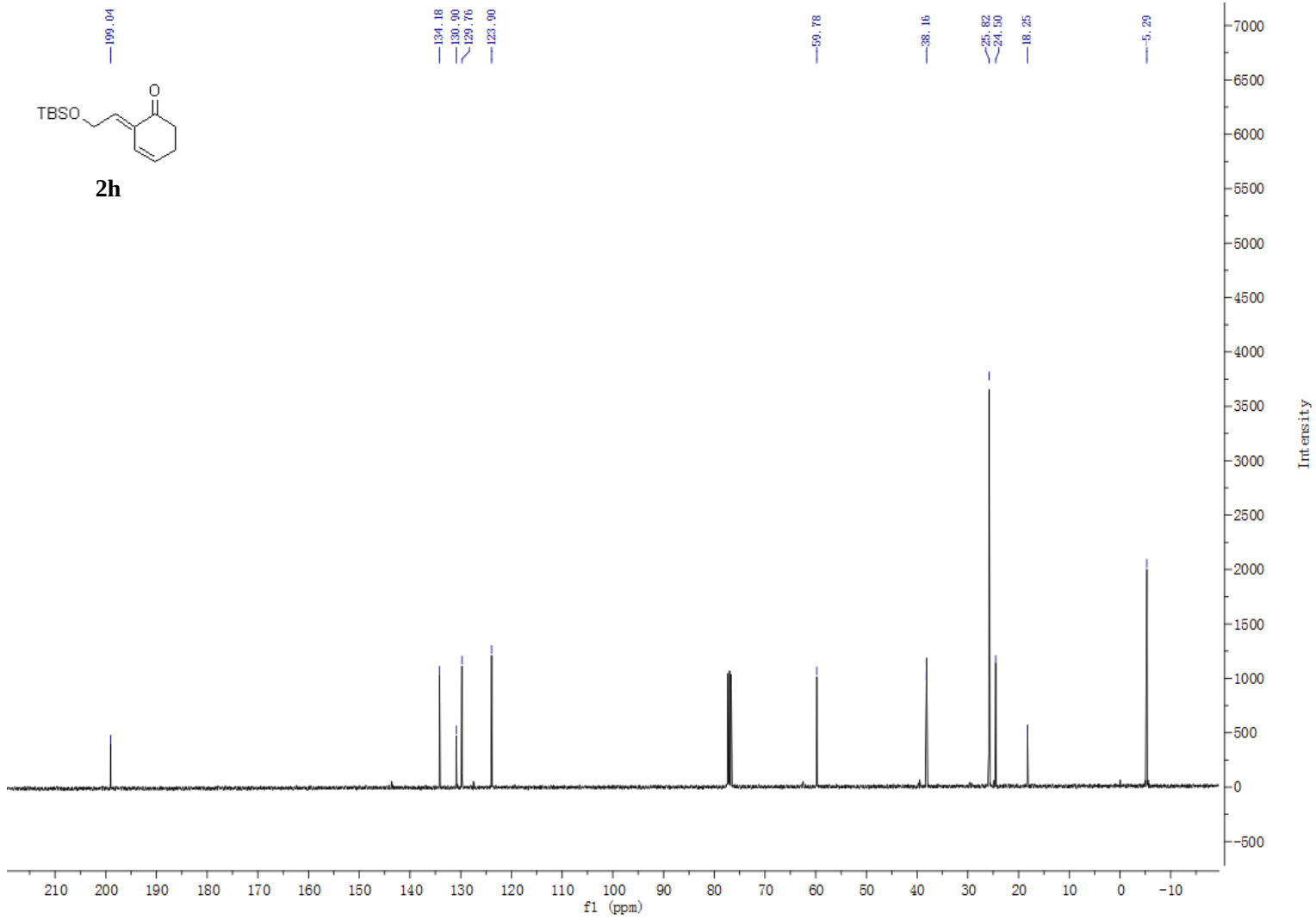
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
Intensity
2.00
2.95
0.99
1.00
1.00
2.09
3.96
2.20
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


199.29
140.97
134.78
132.15
128.87
128.37
128.26
126.03
123.75
38.14
34.81
29.21
24.37
O
Ph
2e
f1 (ppm)
Intensity

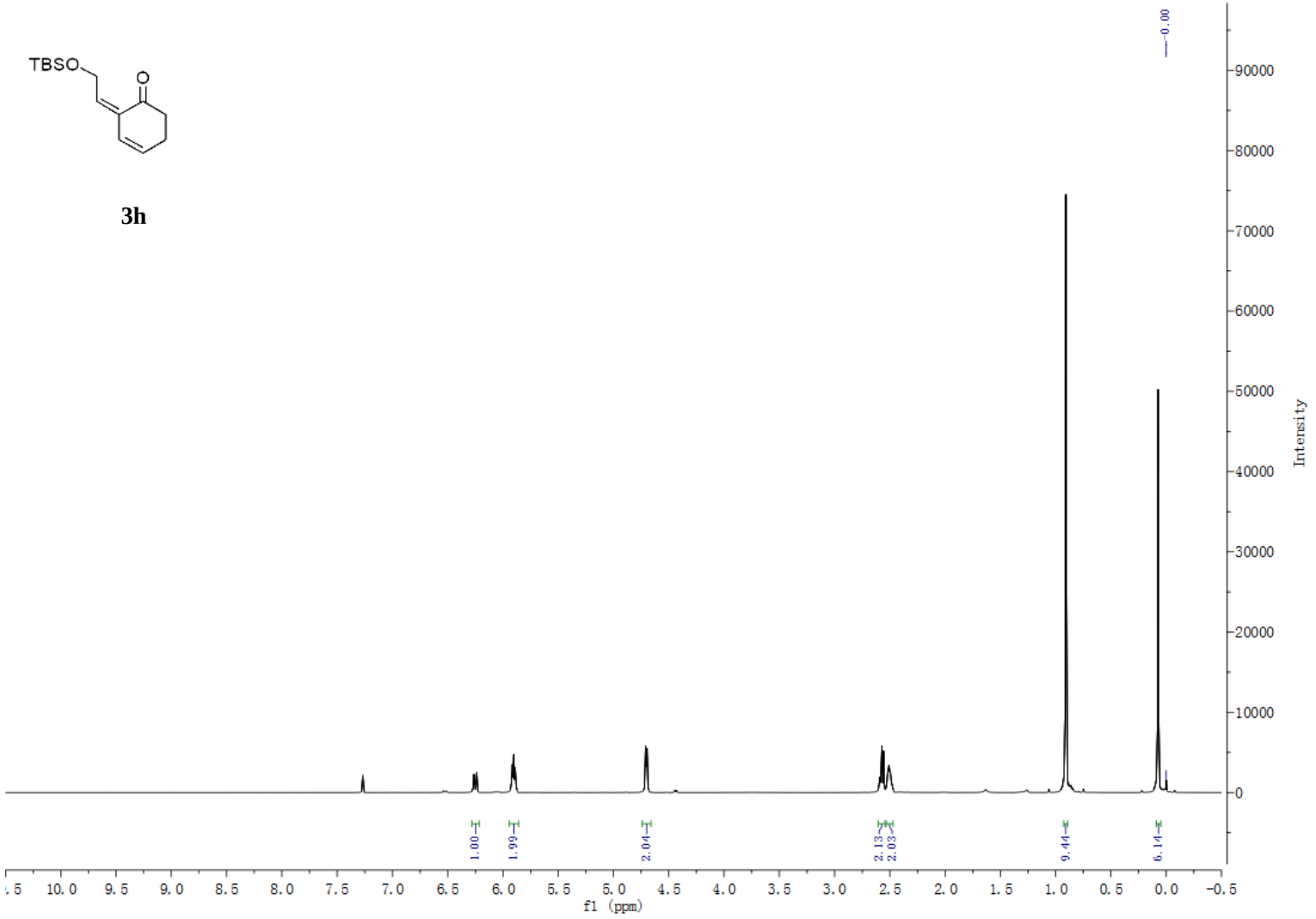

Ph
O
3e
2.06
3.09
0.95
1.93
2.00
2.06
2.14
2.11
f1 (ppm)
Intensity

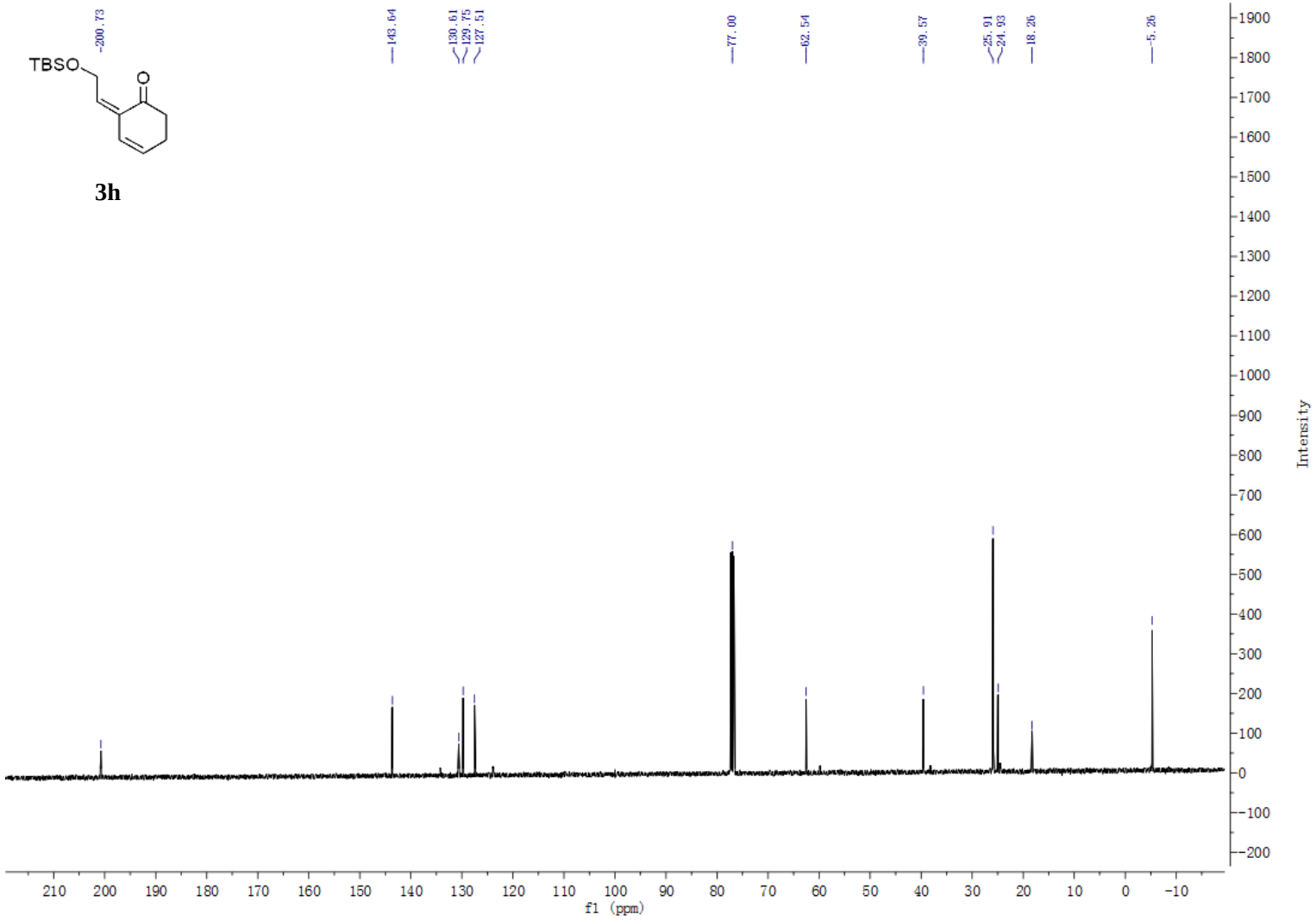

201.15
141.42
140.75
132.99
130.82
128.50
128.31
126.48
125.88
40.40
35.48
30.84
25.40
Ph
O
3e
f1 (ppm)
Intensity


TBSO
O
2h
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
Intensity
1.95
1.00
2.01
2.07
2.06
9.46
5.98
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
-0.5
f1 (ppm)

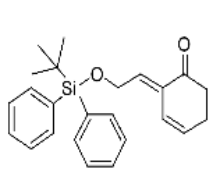

199.04
134.18
130.90
129.76
123.90
59.78
38.16
25.82
24.50
18.25
-5.29
TBSO
O
Intensity
f1 (ppm)

2h


TBSO
O
3h
0.00
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
Intensity
1.00
1.99
2.04
2.13
2.03
9.44
6.14
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
-0.5
f1 (ppm)

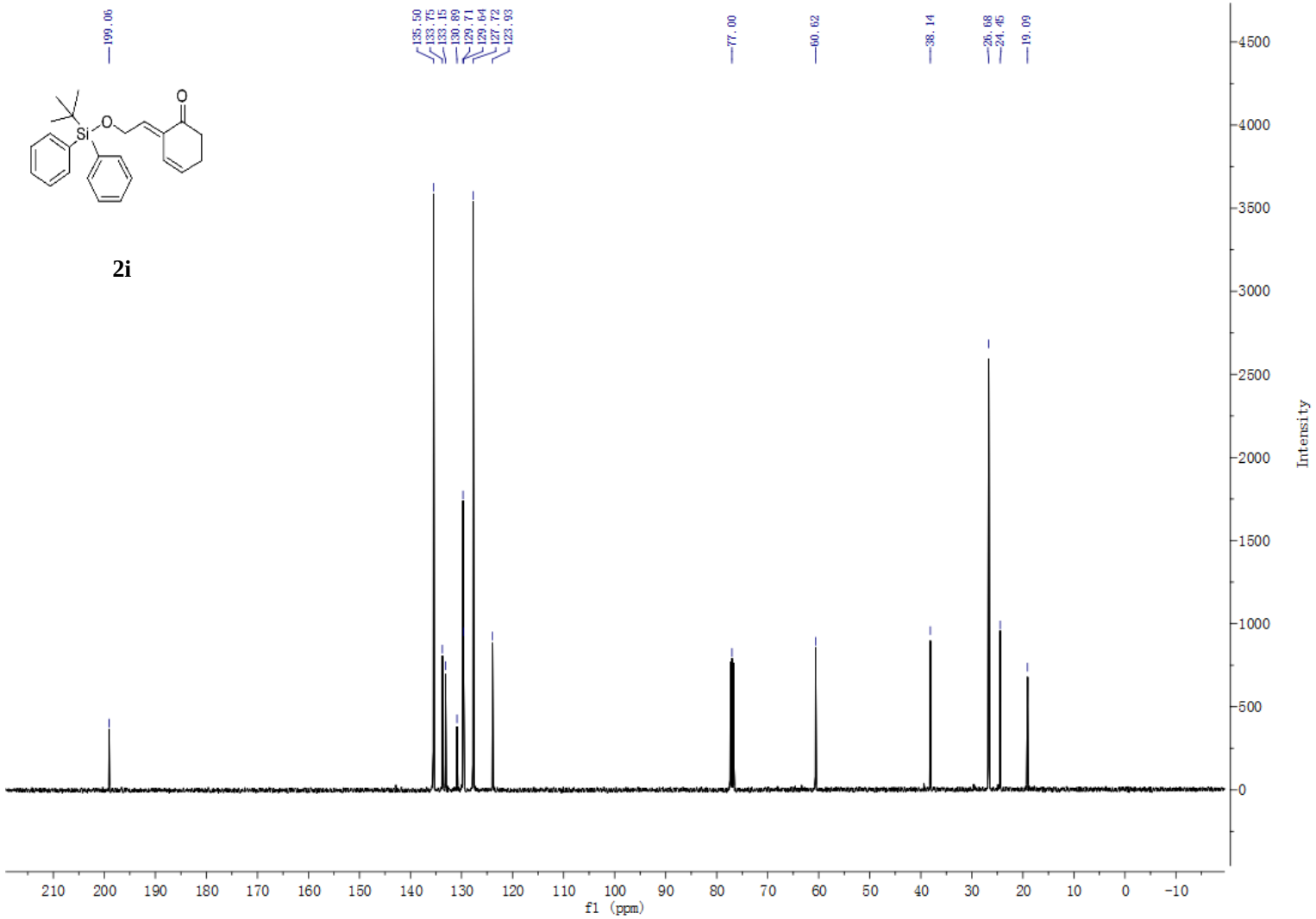

TBSO
O
200.73
143.64
130.61
129.75
127.51
77.00
62.54
39.57
25.91
24.93
18.26
-5.26
f1 (ppm)
Intensity

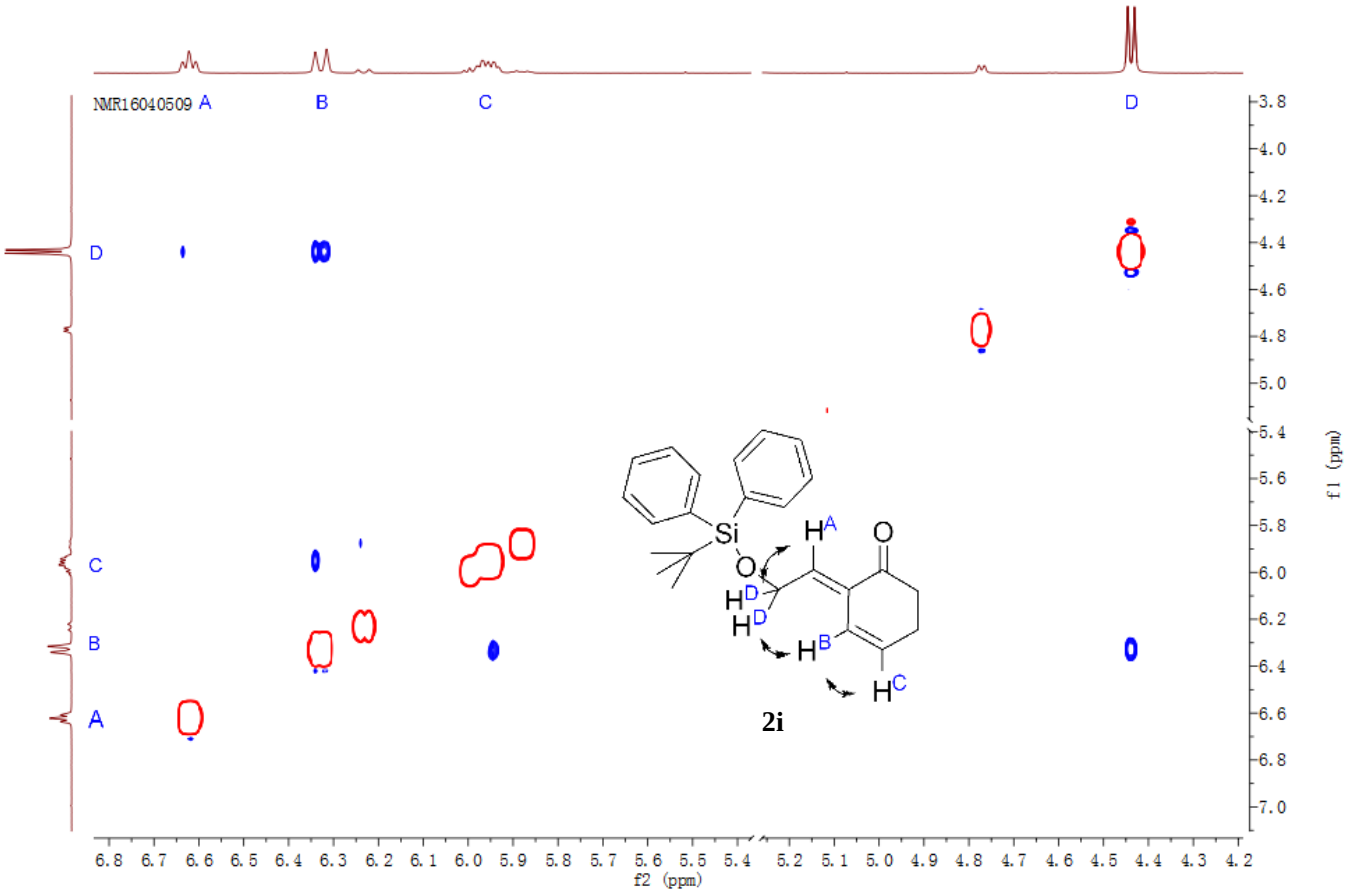
3h


Si
O
O

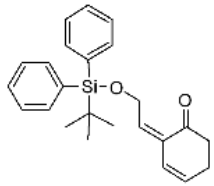
2i

-0.00 TMS
40000
35000
30000
25000
20000
15000
10000
5000
0
Intensity
4.20
6.34
1.00
1.04
1.04
2.07
2.09
2.08
9.39
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
-0.5
f1 (ppm)


199.06
135.50
133.75
133.15
130.89
129.71
129.64
127.72
123.93
77.00
60.62
38.14
26.68
24.45
19.09
Si
O
O
2i
Intensity
f1 (ppm)

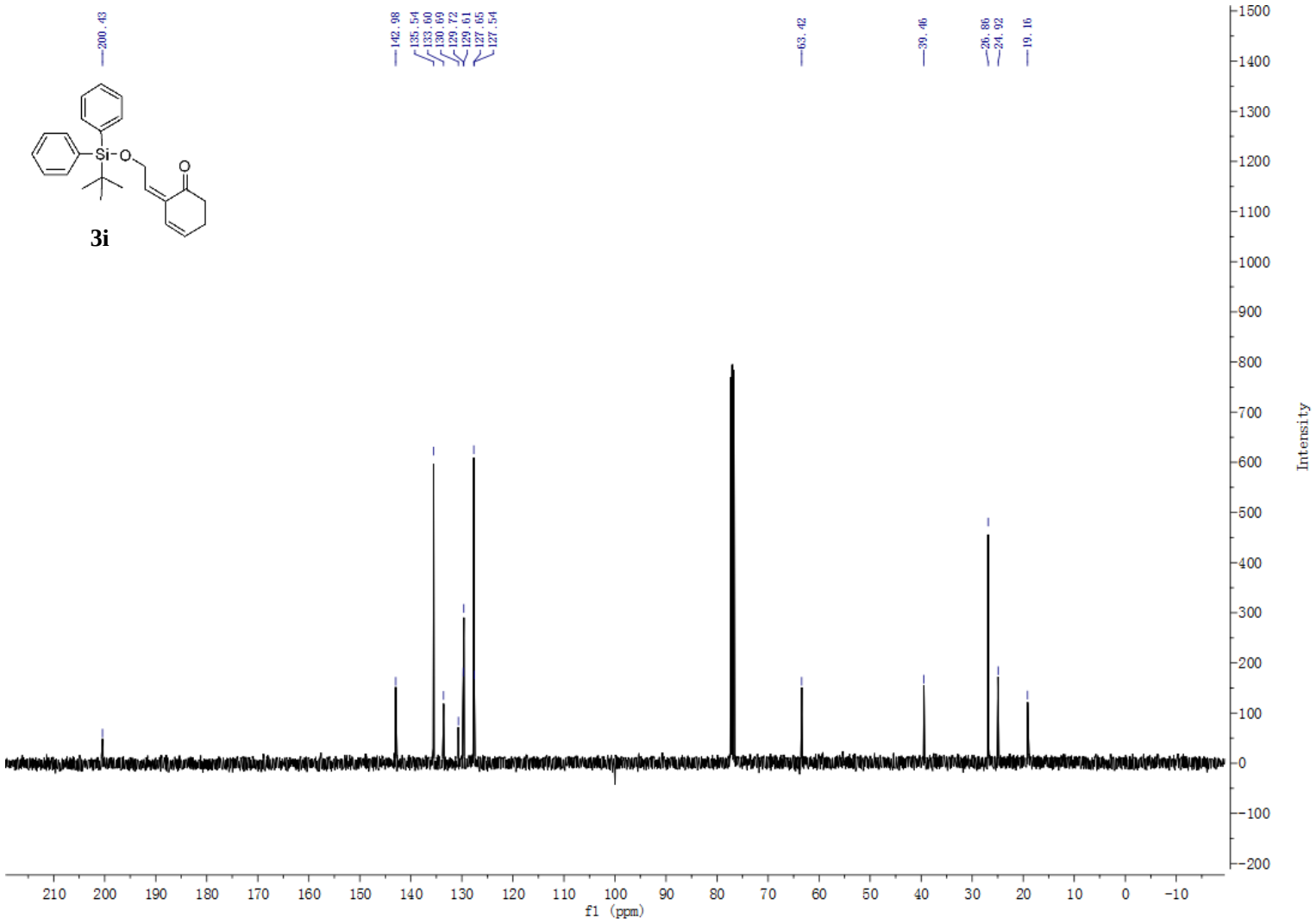


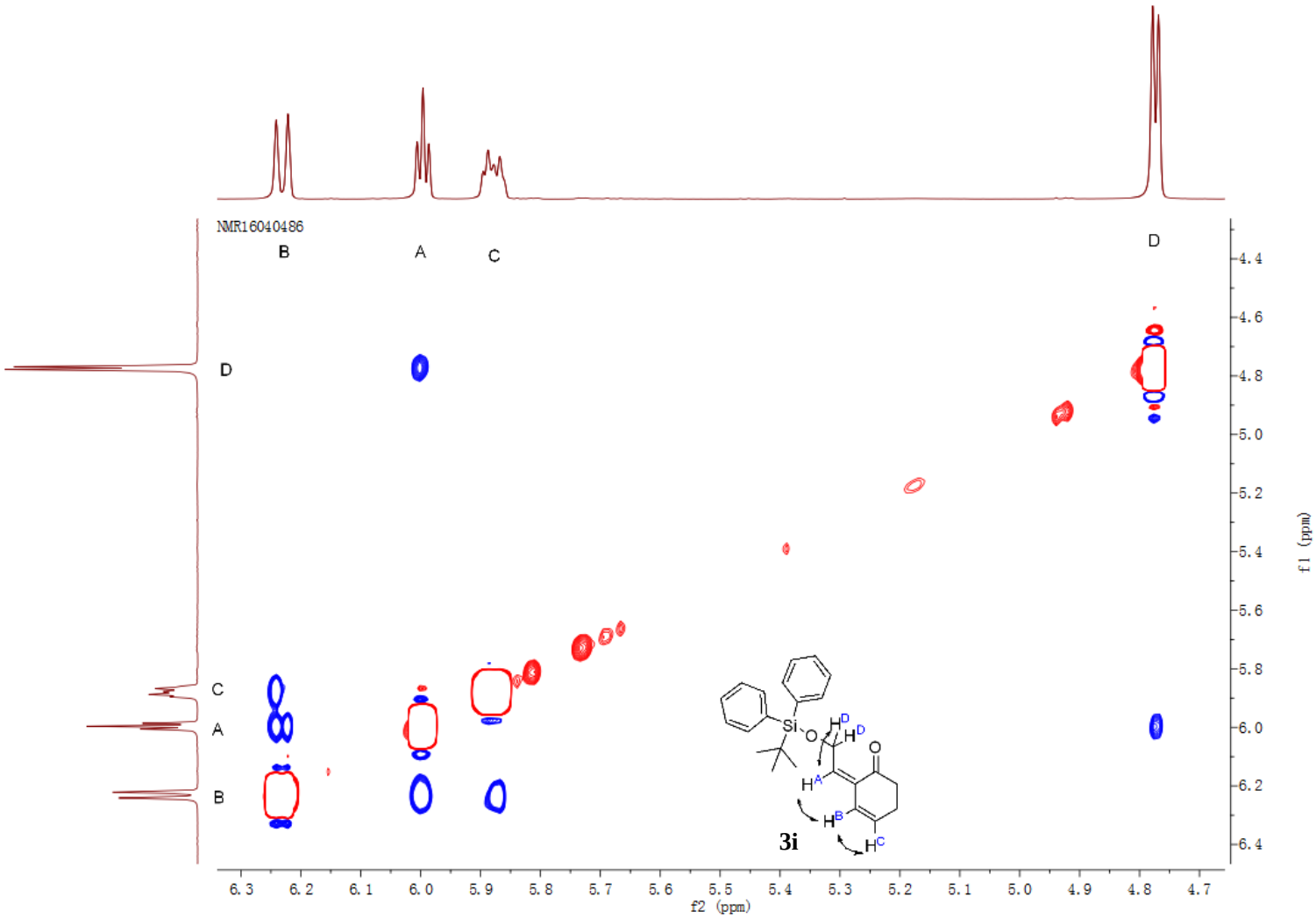
2i

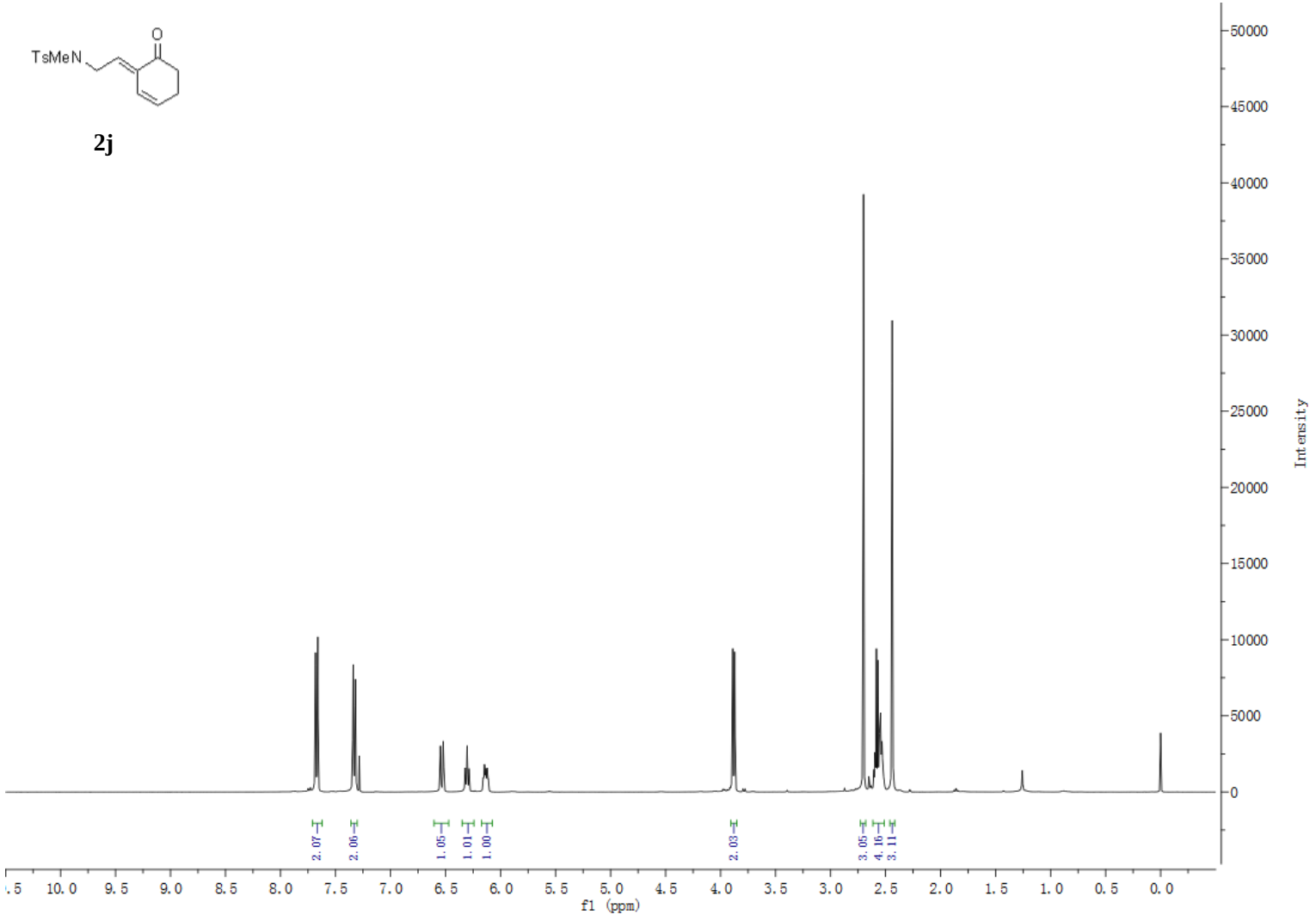

Si
O
O

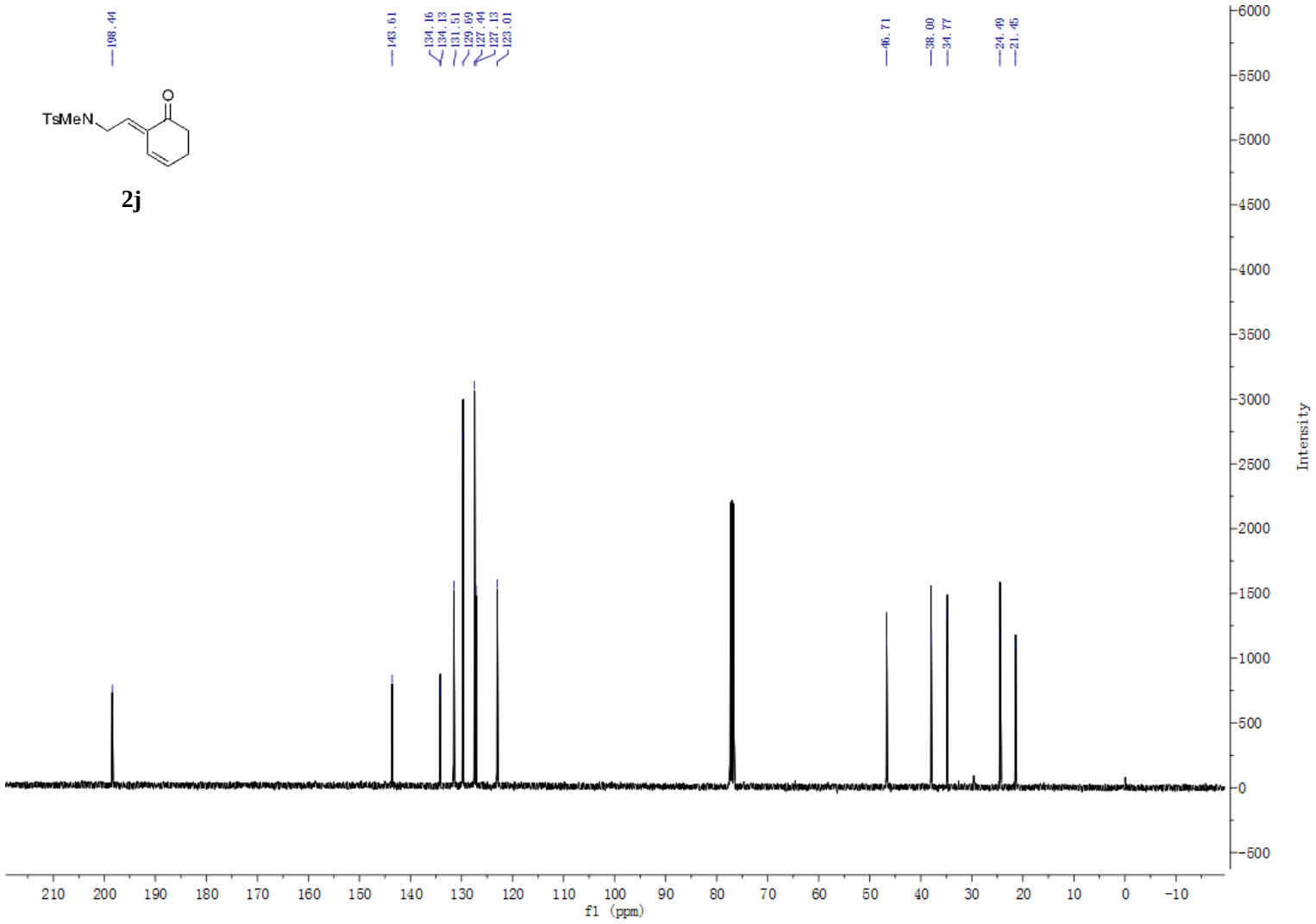
3i

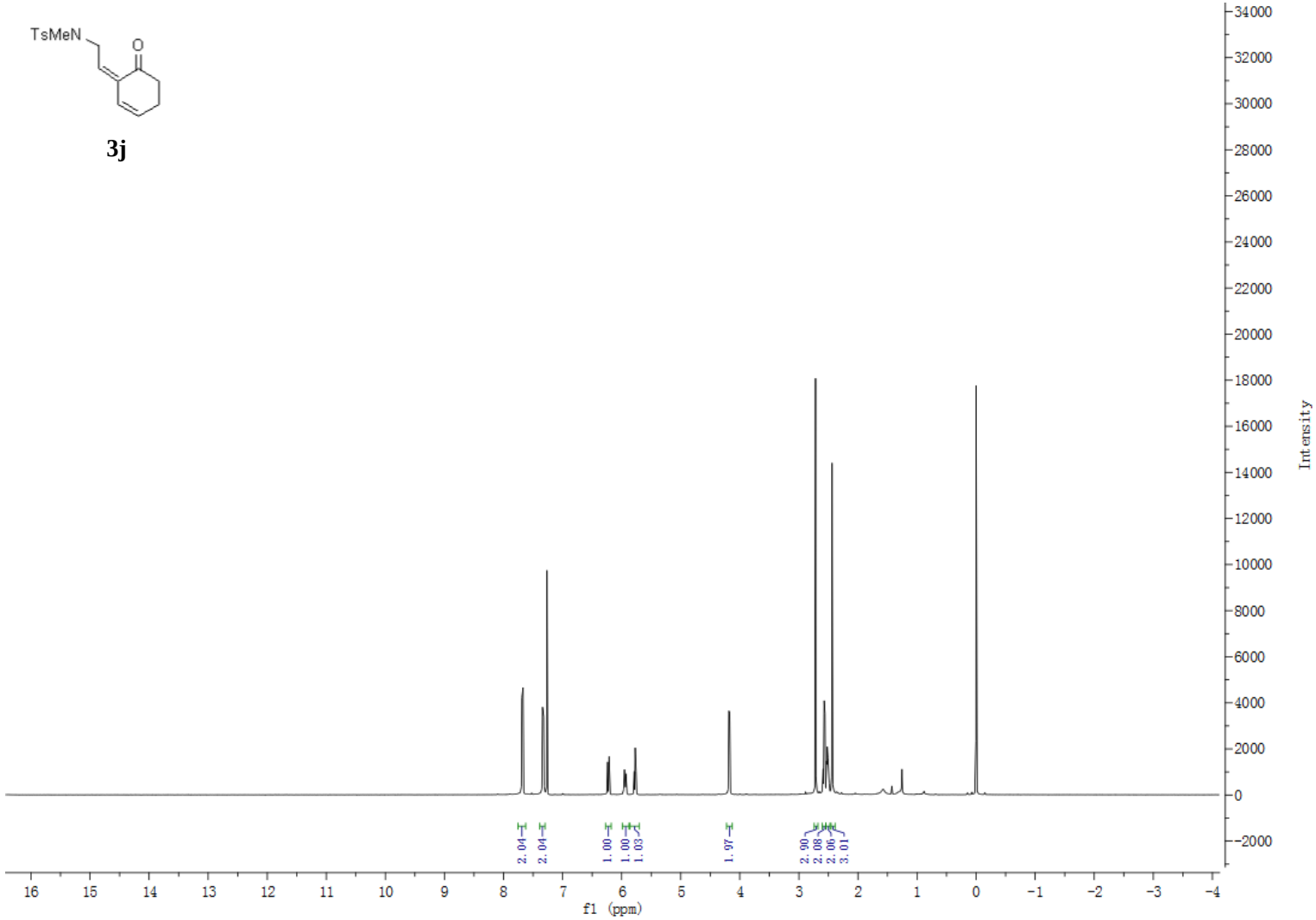
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
Intensity
4.04
6.33
1.00
1.02
1.03
2.01
4.10
9.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

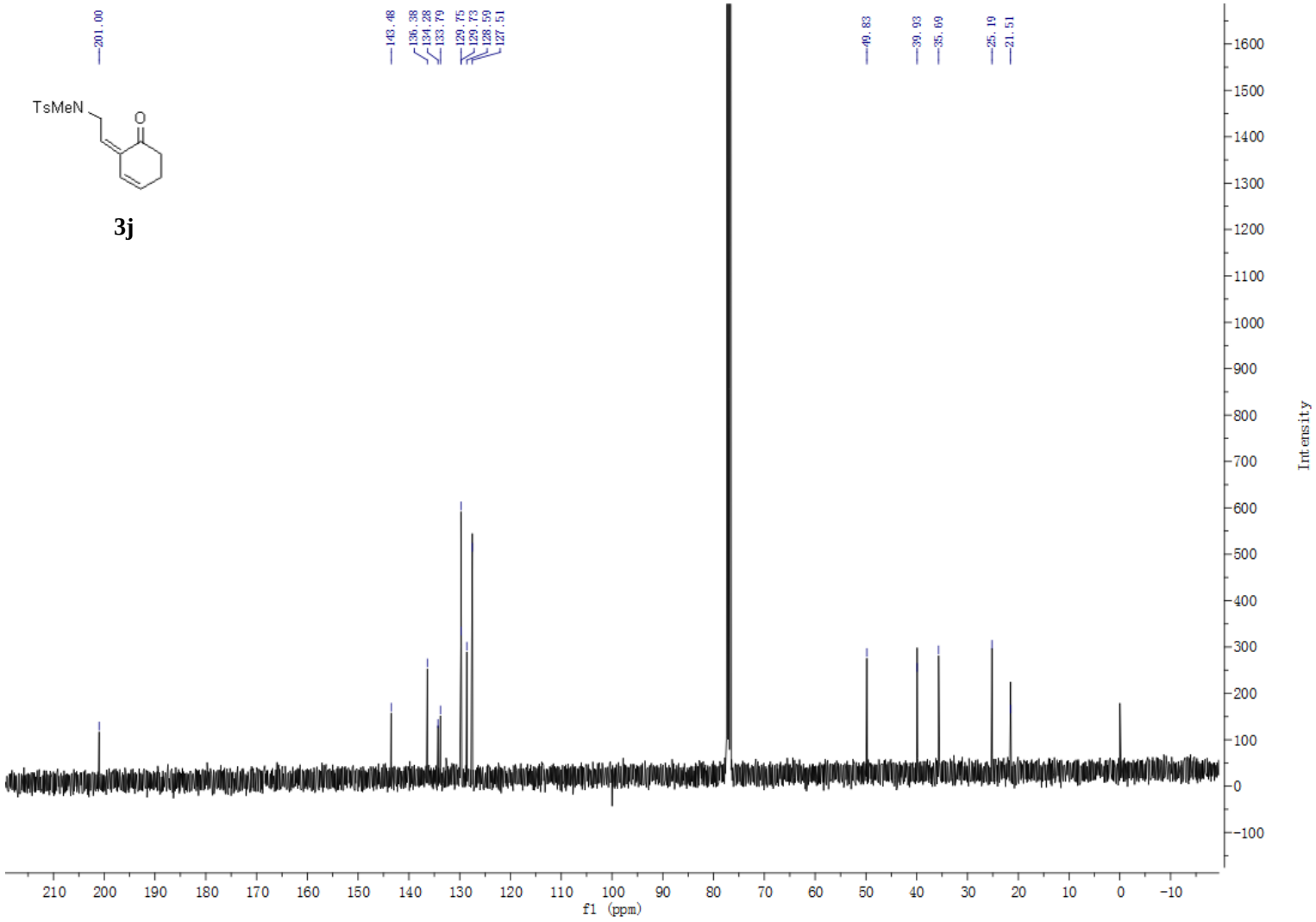

200.43
142.98
135.54
133.60
130.69
129.72
129.61
127.65
127.54
63.42
39.46
26.86
24.92
19.16
Si
O
O
3i
Intensity
f1 (ppm)


NMR16040486
B
A
C
D
D
C
A
B
f2 (ppm)
f1 (ppm)
3i

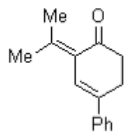

TsMeN
O
2j
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
Intensity
2.07
2.06
1.05
1.01
1.00
2.03
3.05
4.16
3.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


198.44
143.61
134.16
134.13
131.51
129.69
127.44
127.13
123.01
46.71
38.00
34.77
24.49
21.45
TsMeN
O
2j
Intensity
f1 (ppm)

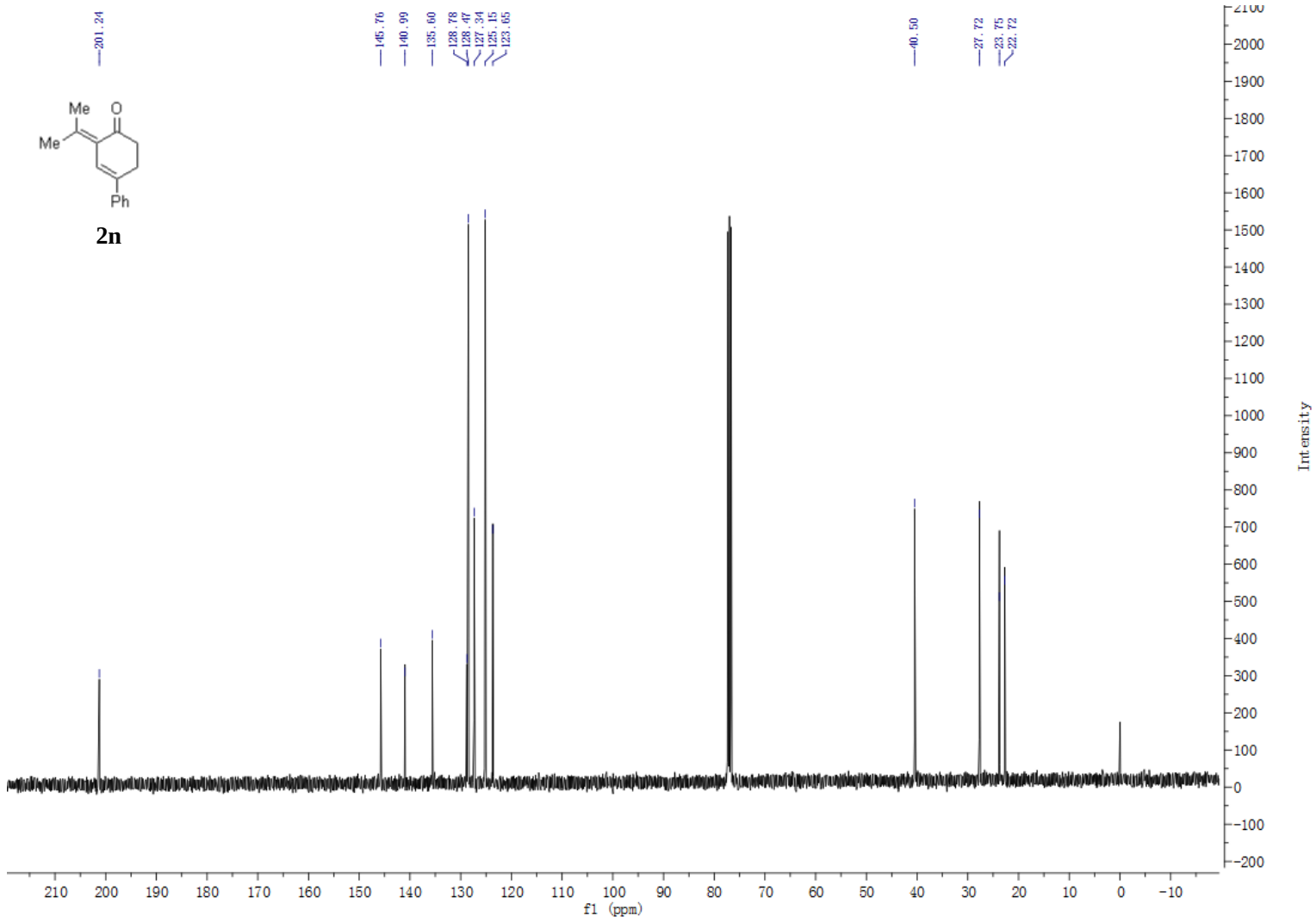

TsMeN
O
3j
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
Intensity
2.04
2.04
1.00
1.00
1.03
1.97
2.90
2.08
2.06
3.01
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

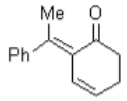

201.00
143.48
136.38
134.28
133.79
129.75
129.73
128.59
127.51
49.83
39.93
35.69
25.19
21.51
TsMeN
O
Intensity
f1 (ppm)

3j

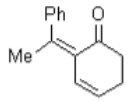


2n


201.24
145.76
140.99
135.60
128.78
128.47
127.34
125.15
123.65
40.50
27.72
23.75
22.72
Me
Me
O
Ph
2n
Intensity
f1 (ppm)

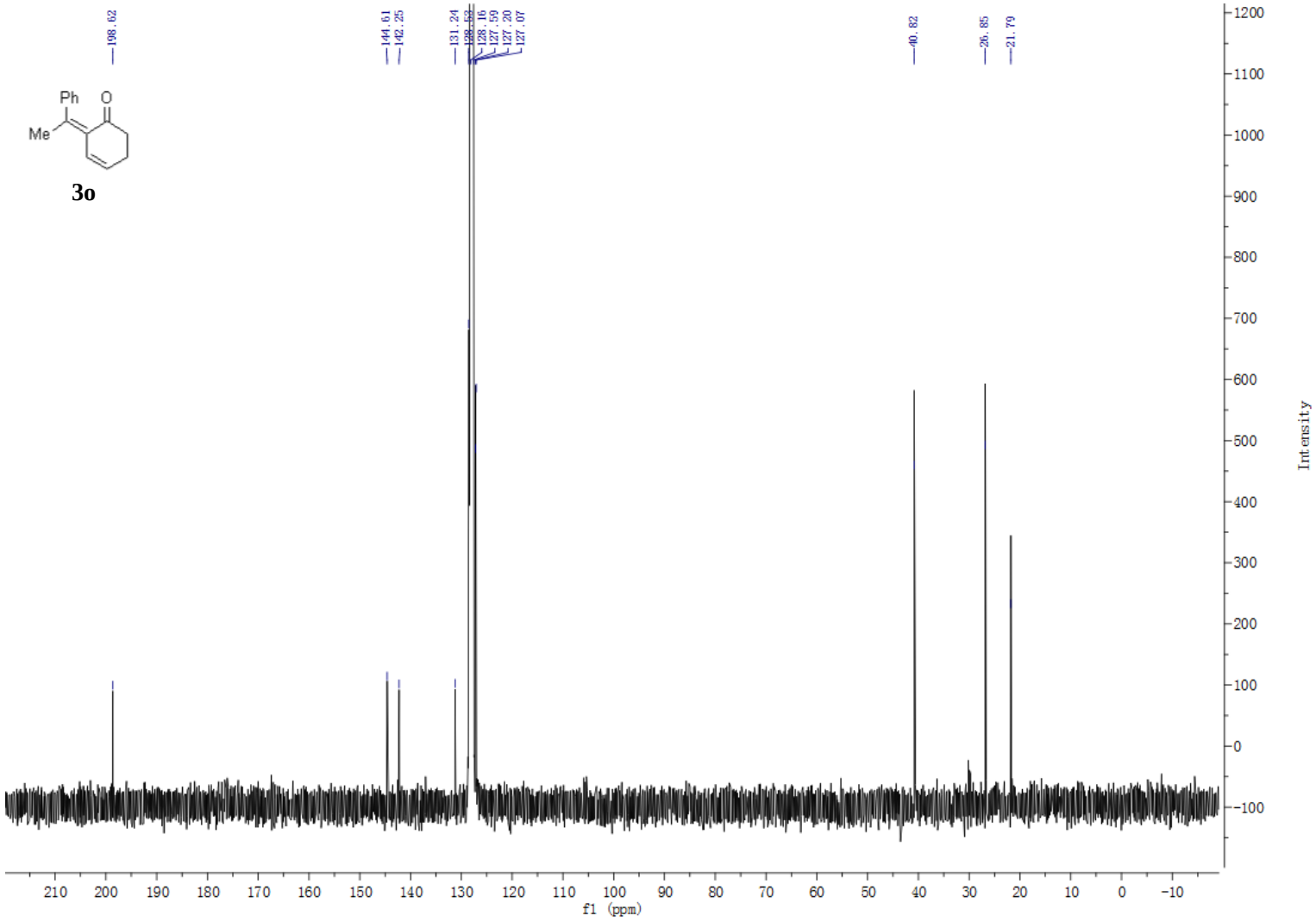


2o

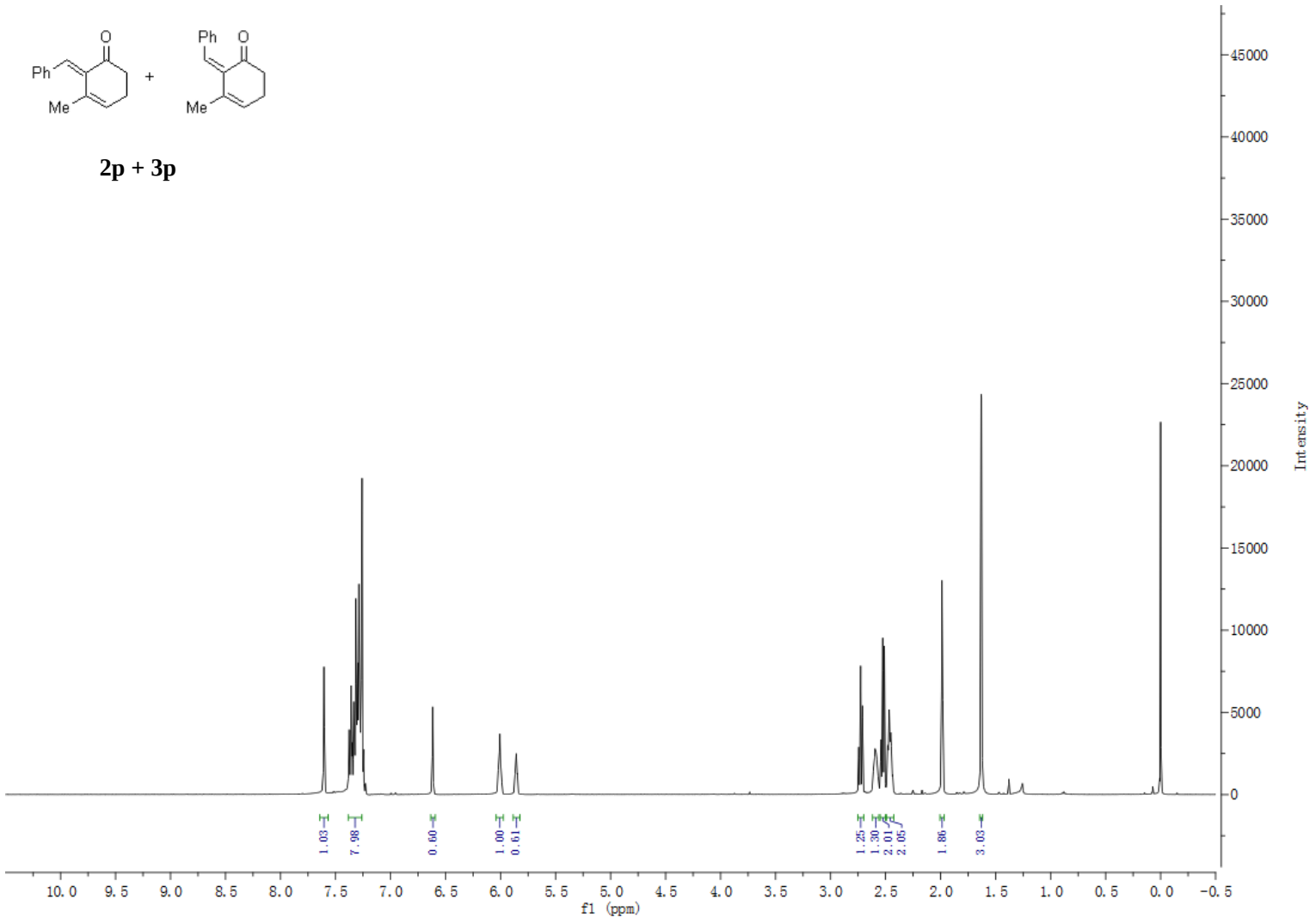

Ph
O
Me

3o

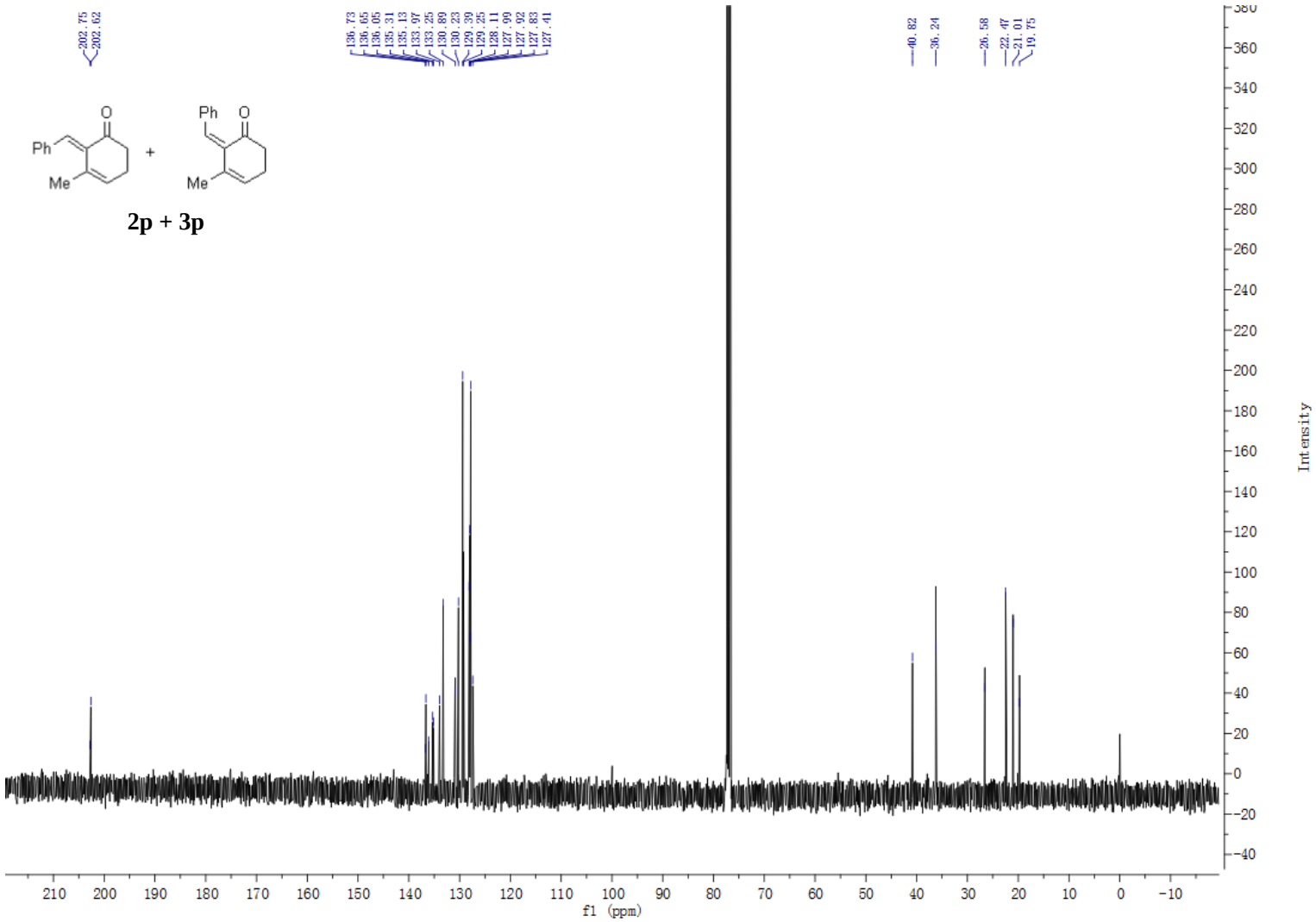
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
Intensity
2.13
2.92
0.96
0.99
2.00
2.07
2.89
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

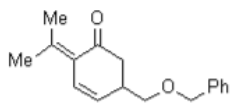

198.62
144.61
142.25
131.24
128.53
128.16
127.59
127.20
127.07
40.82
26.85
21.79
Ph
O
Me
Intensity
f1 (ppm)

3o


Ph
O
Me
+
Ph
O
Me
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
Intensity
1.03
7.98
0.60
1.00
0.61
1.25
1.30
2.01
2.05
1.86
3.03
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
-0.5
f1 (ppm)

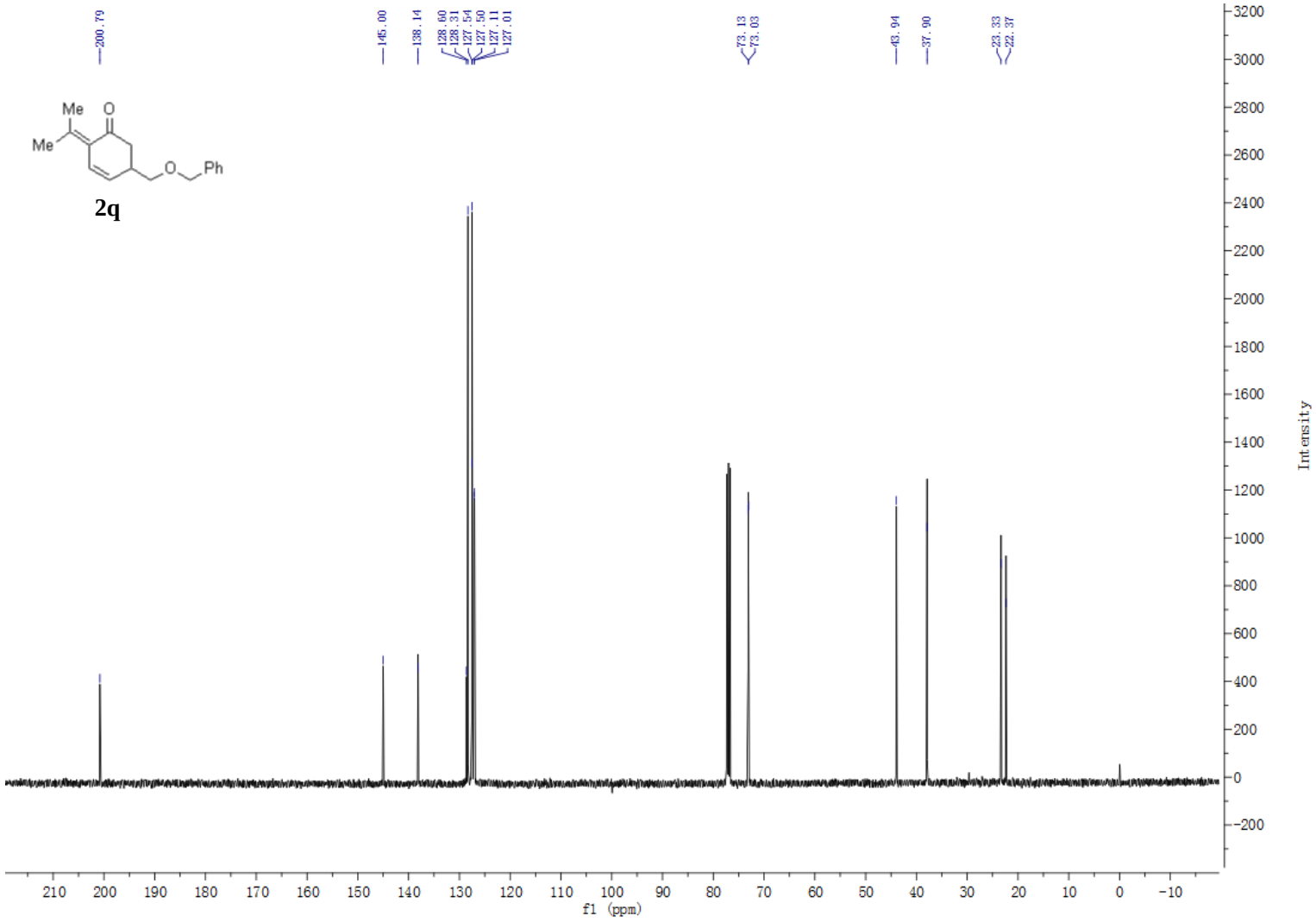
2p + 3p

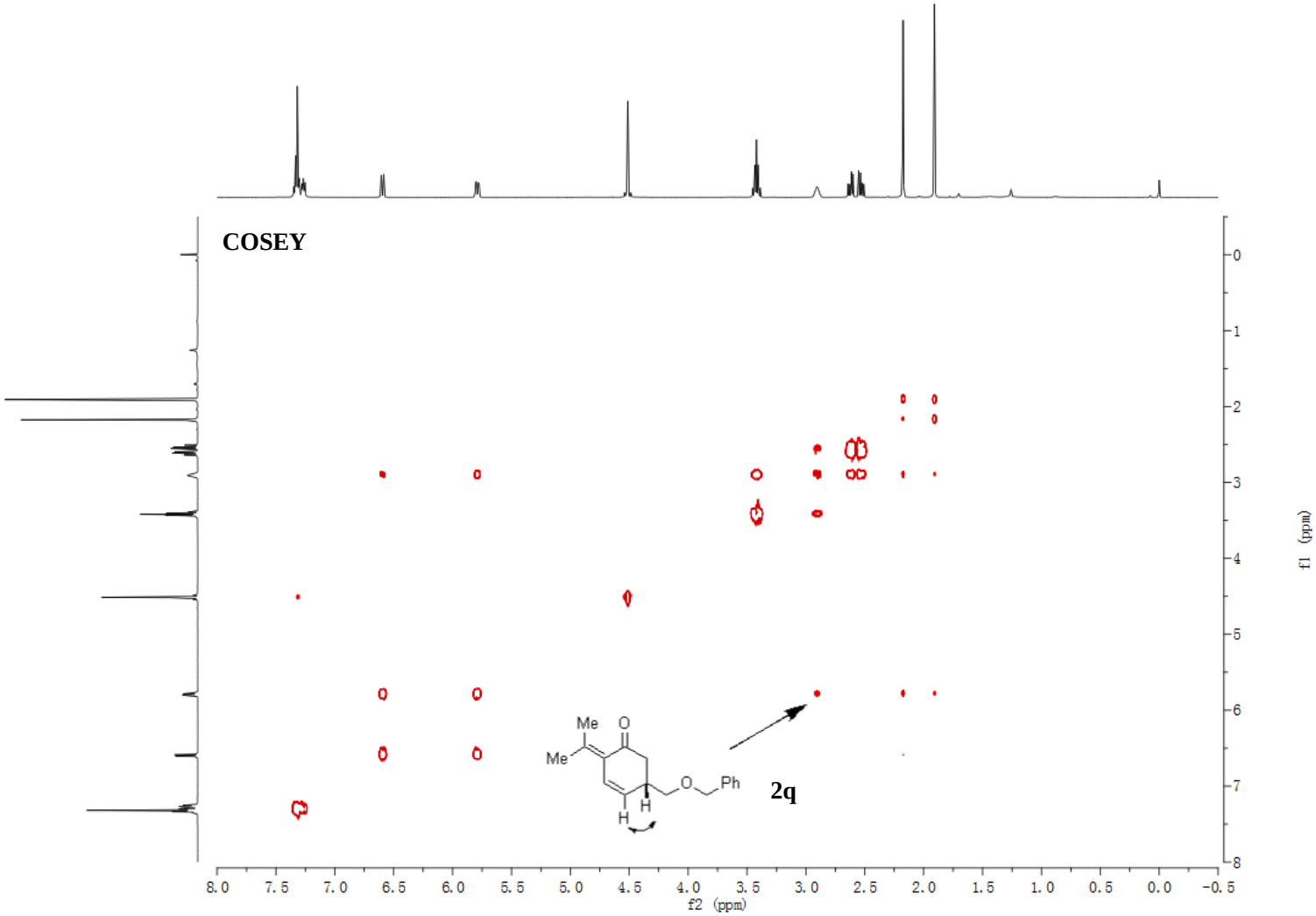

202.75
202.62
136.73
136.65
136.05
135.31
135.13
133.97
133.25
130.89
130.23
129.39
129.25
128.11
127.99
127.92
127.83
127.41
40.82
36.24
26.58
22.47
21.01
19.75
Ph
O
Me
+
Ph
O
Me
2p + 3p
Intensity
f1 (ppm)

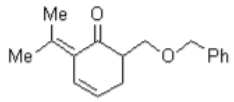

Me
O
Me
O
Ph

2q

50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
Intensity
4.73
1.00
1.00
2.00
1.96
1.02
1.02
1.01
2.92
2.89
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
-0.5
f1 (ppm)

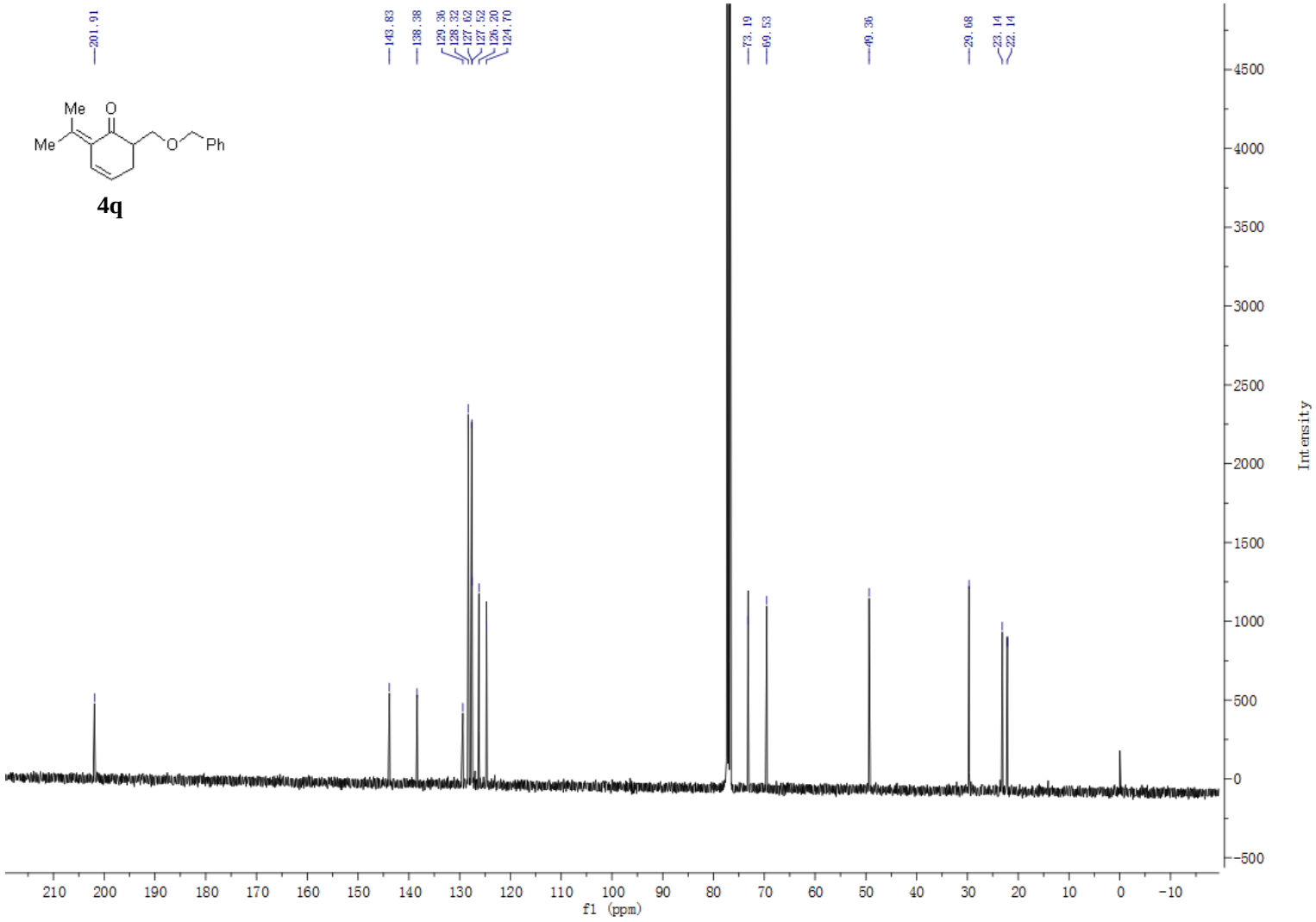

200.79
145.00
138.14
128.60
128.31
127.54
127.50
127.11
127.01
73.13
73.03
43.94
37.90
23.33
22.37
Me
O
Me
O
Ph
2q
Intensity
f1 (ppm)

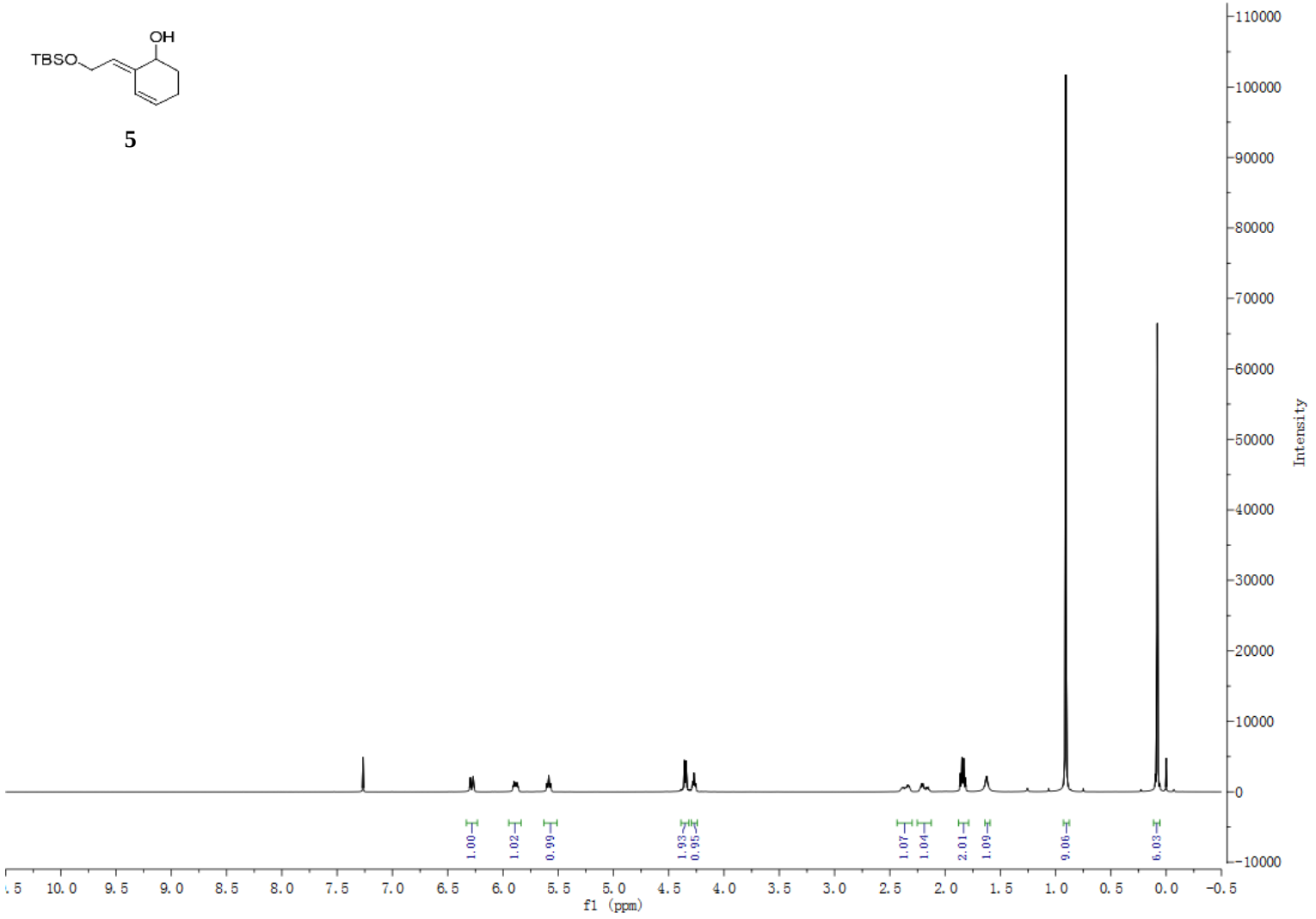

COSEY
Me
O
Me
O
Ph
H
H
2q
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)

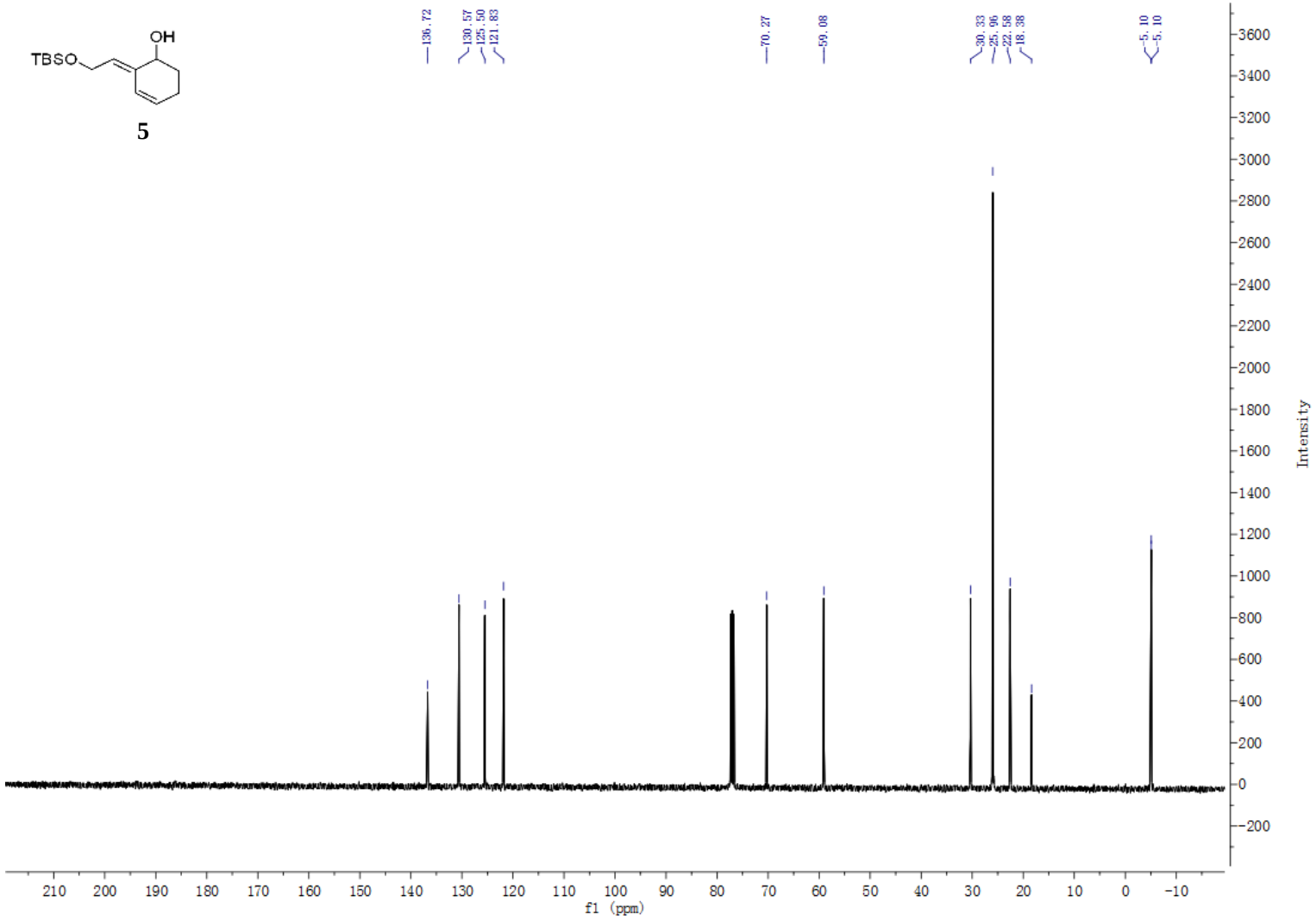

Me
O
Me
O
Ph

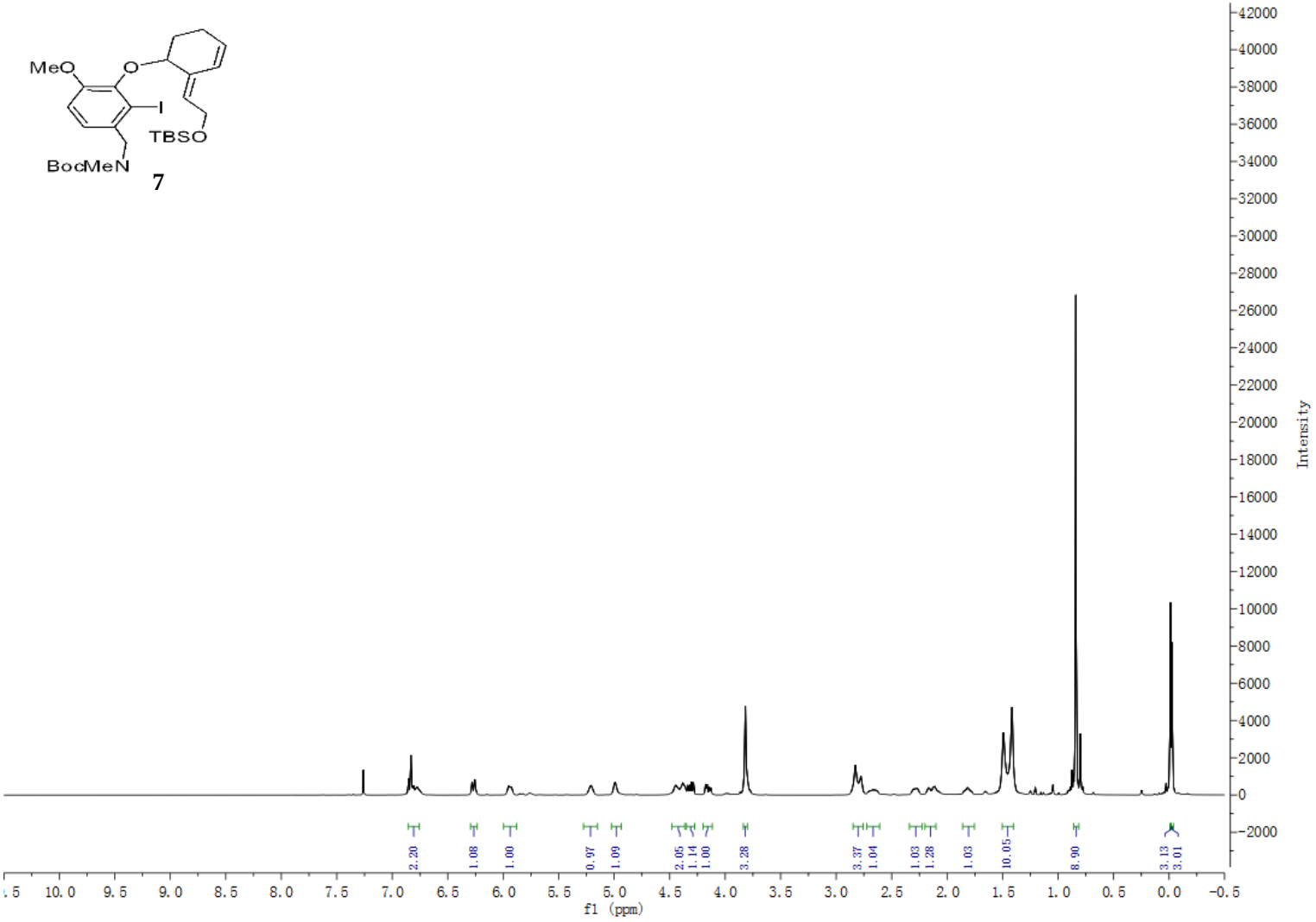
4q

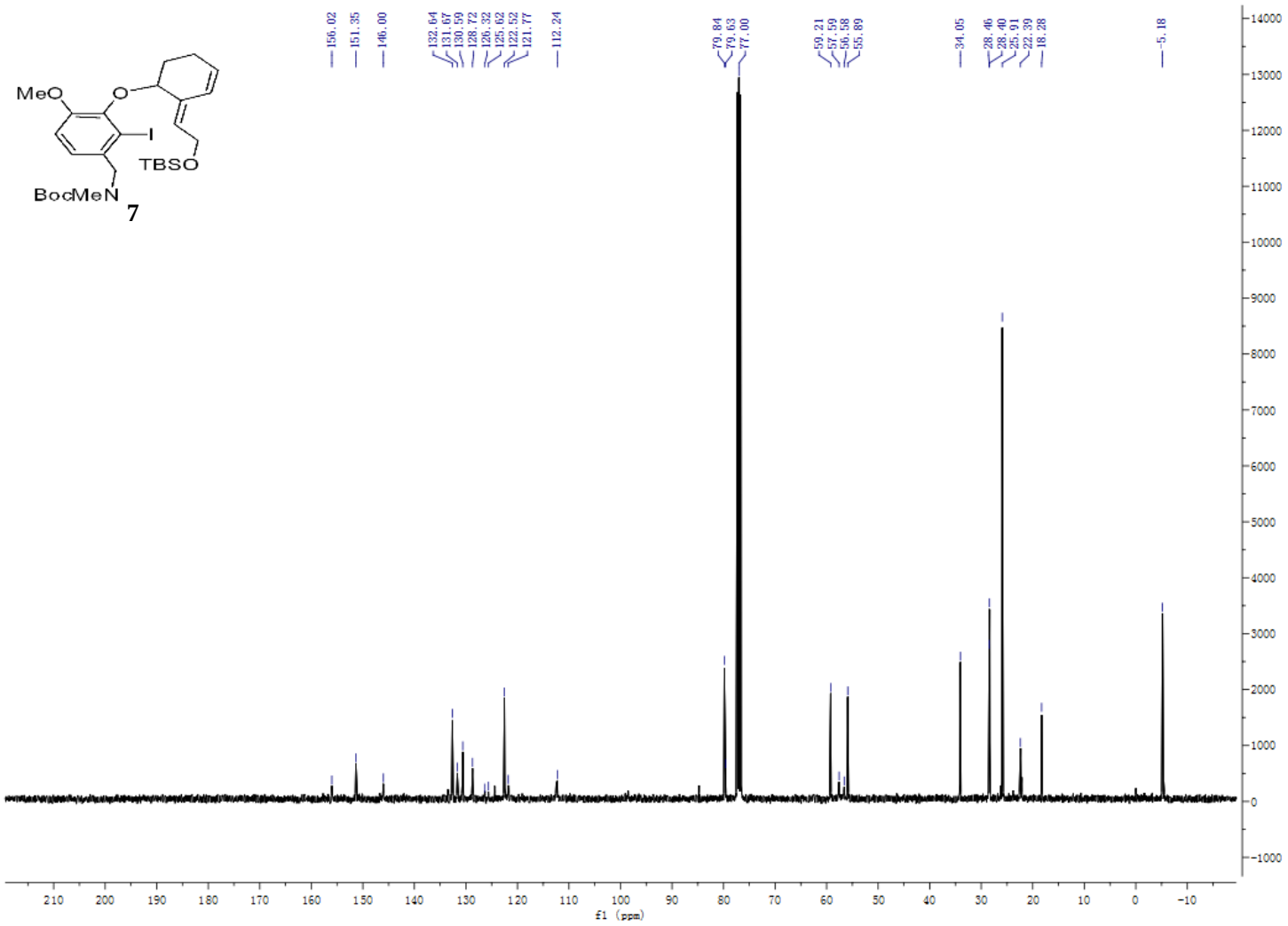
40000
35000
30000
25000
20000
15000
10000
5000
0
Intensity
4.87
0.96
0.96
2.00
1.03
1.01
1.00
1.03
1.09
2.96
2.91
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

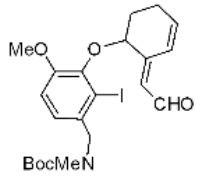

201.91
143.83
138.38
129.36
128.32
127.62
127.52
126.20
124.70
73.19
69.53
49.36
29.68
23.14
22.14
Me
O
Me
O
Ph
4q
Intensity
f1 (ppm)


OH
TBSO
5
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
Intensity
1.00
1.02
0.99
1.93
0.95
1.07
1.04
2.01
1.09
9.06
6.03
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
-0.5
f1 (ppm)


TBSO
OH
5
136.72
130.57
125.50
121.83
70.27
59.08
30.33
25.96
22.58
18.38
-5.10
-5.10
Intensity
f1 (ppm)

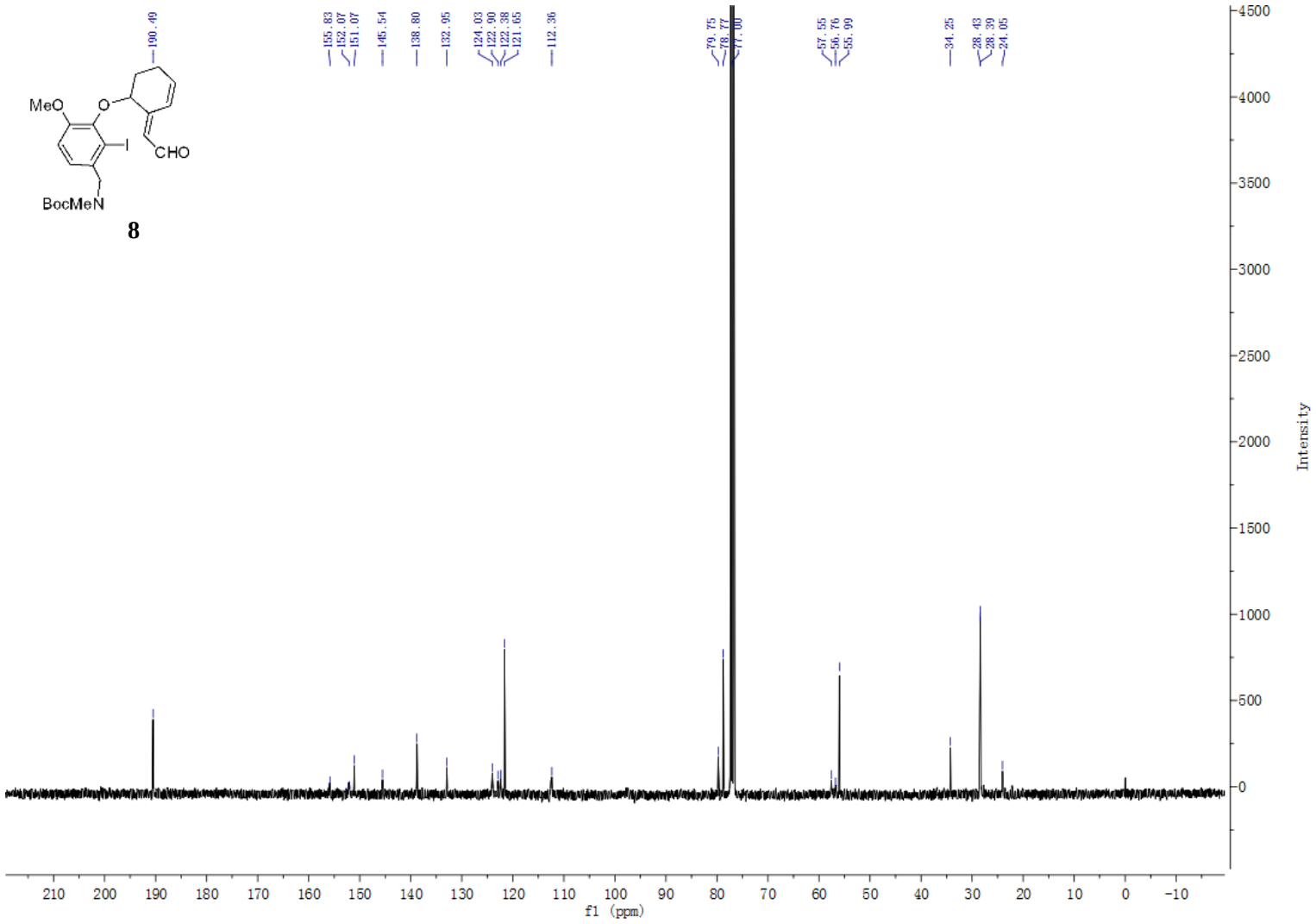

MeO
O
I
TBSO
BocMeN
7
Intensity
f1 (ppm)
2.20
1.08
1.00
0.97
1.09
2.05
1.14
1.00
3.28
3.37
1.04
1.03
1.28
1.03
10.05
8.90
3.13
3.01

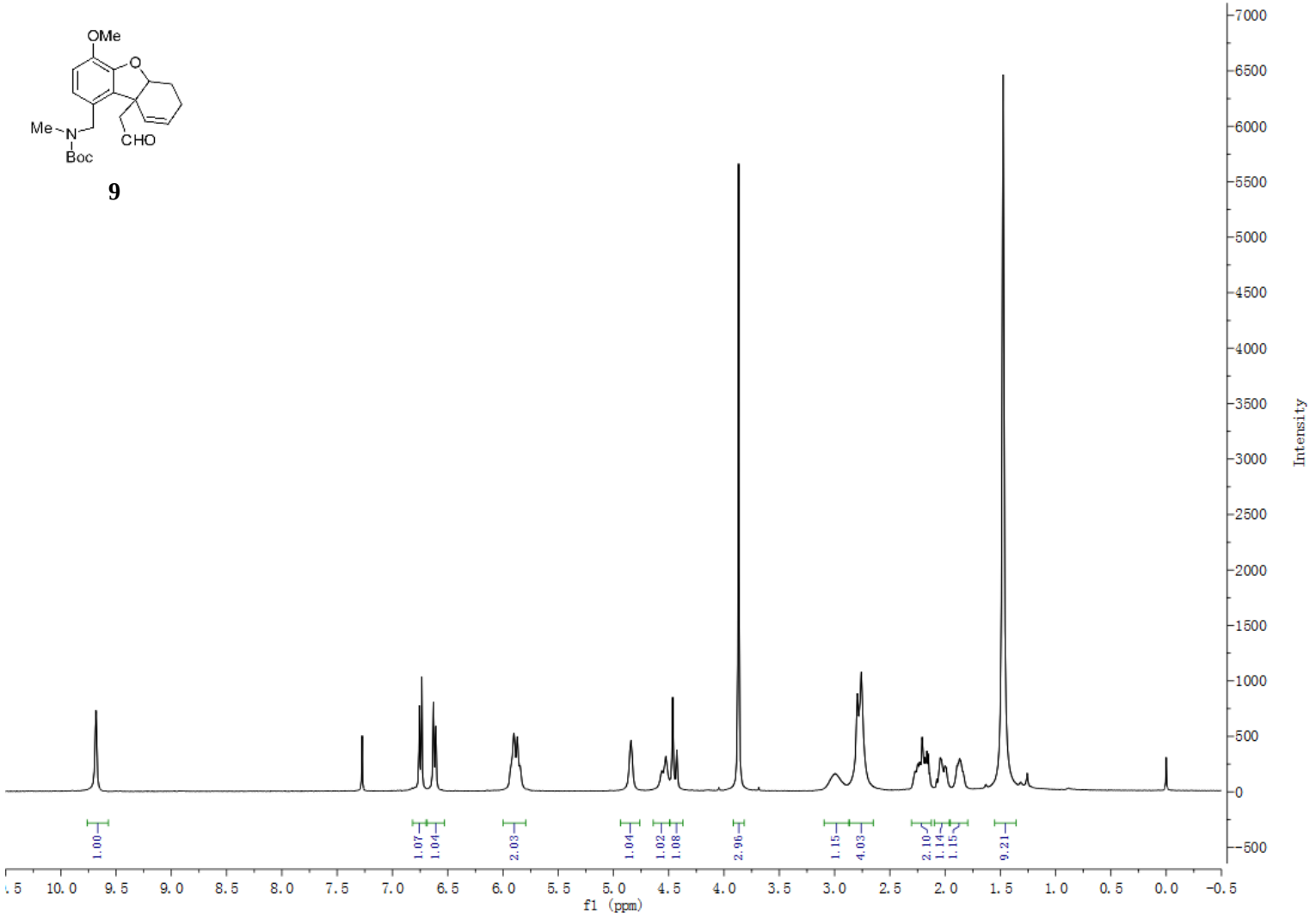

MeO
O
I
TBSO
BocMeN
7
156.02
151.35
146.00
132.64
131.67
130.59
128.72
126.32
125.62
122.52
121.77
112.24
79.84
79.63
77.00
59.21
57.59
56.58
55.89
34.05
28.46
28.40
25.91
22.39
18.28
-5.18
f1 (ppm)

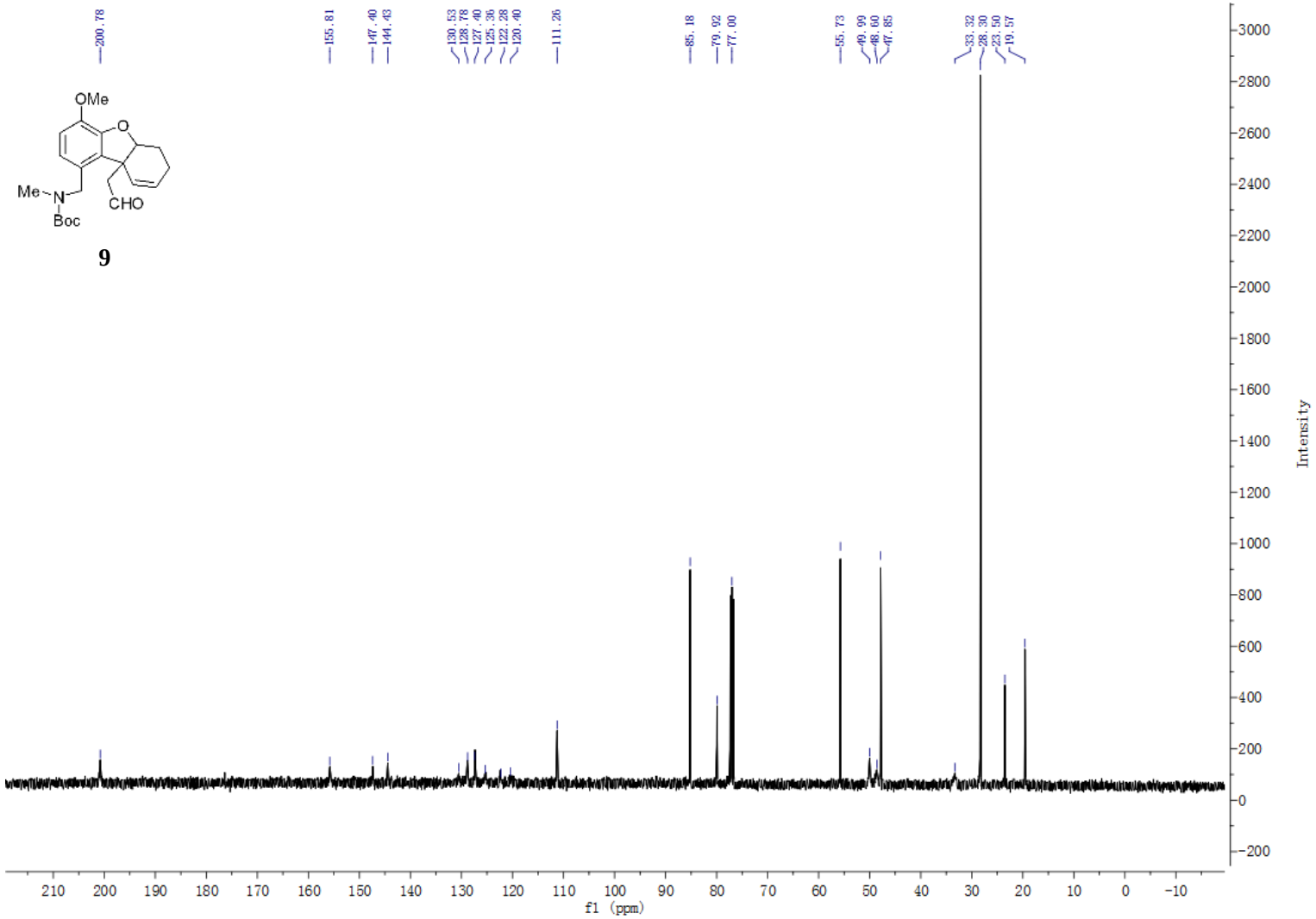

MeO
O
I
CHO
BocMeN

8

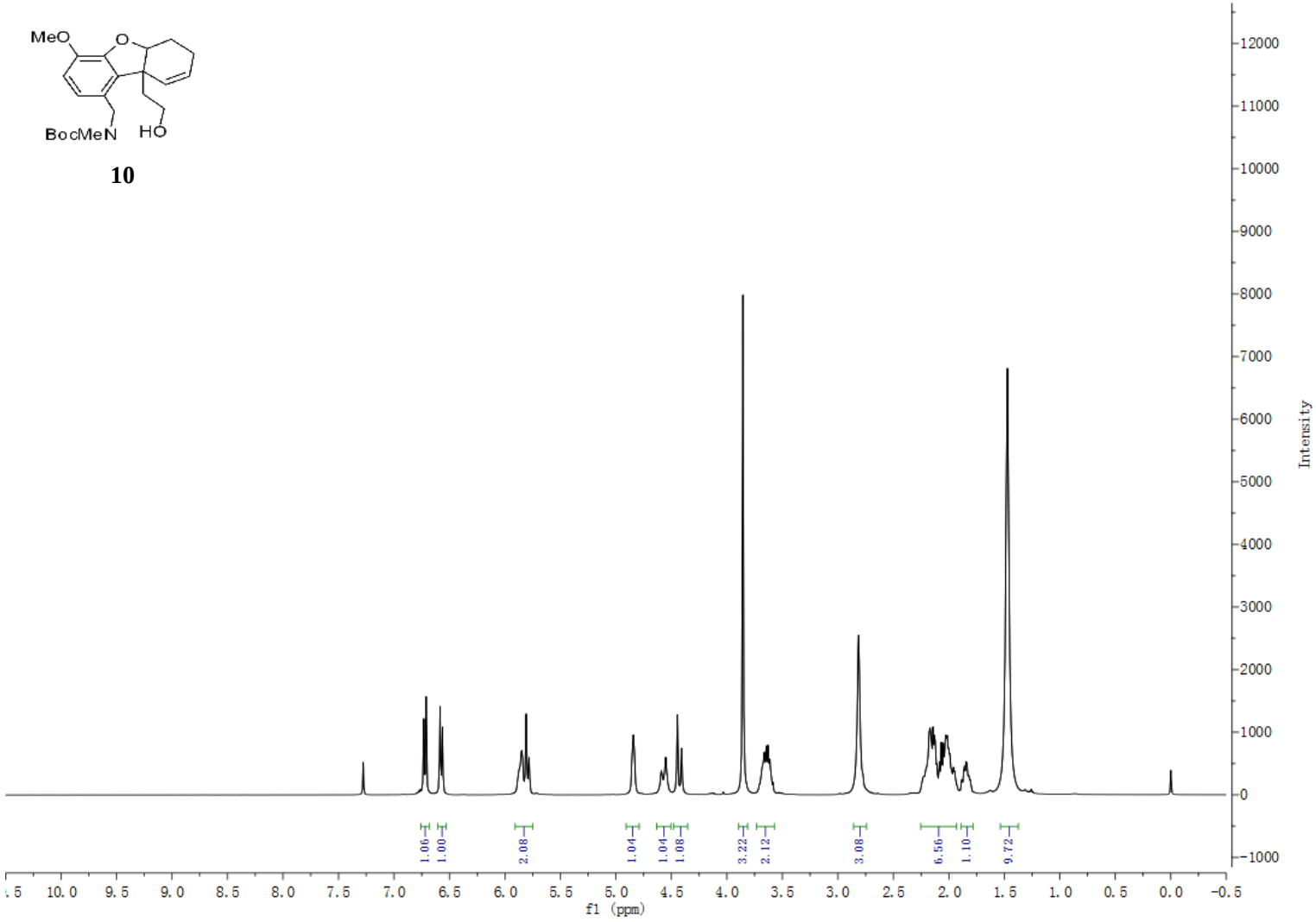
1.00
1.05
2.13
1.07
1.02
1.06
2.12
3.21
3.14
1.11
2.11
1.12
9.45
f1 (ppm)
Intensity


MeO
O
I
CHO
BocMeN
8
190.49
155.83
152.07
151.07
145.54
138.80
132.95
124.03
122.90
122.38
121.65
112.36
79.75
78.77
77.00
57.55
56.76
55.99
34.25
28.43
28.39
24.05
Intensity
f1 (ppm)

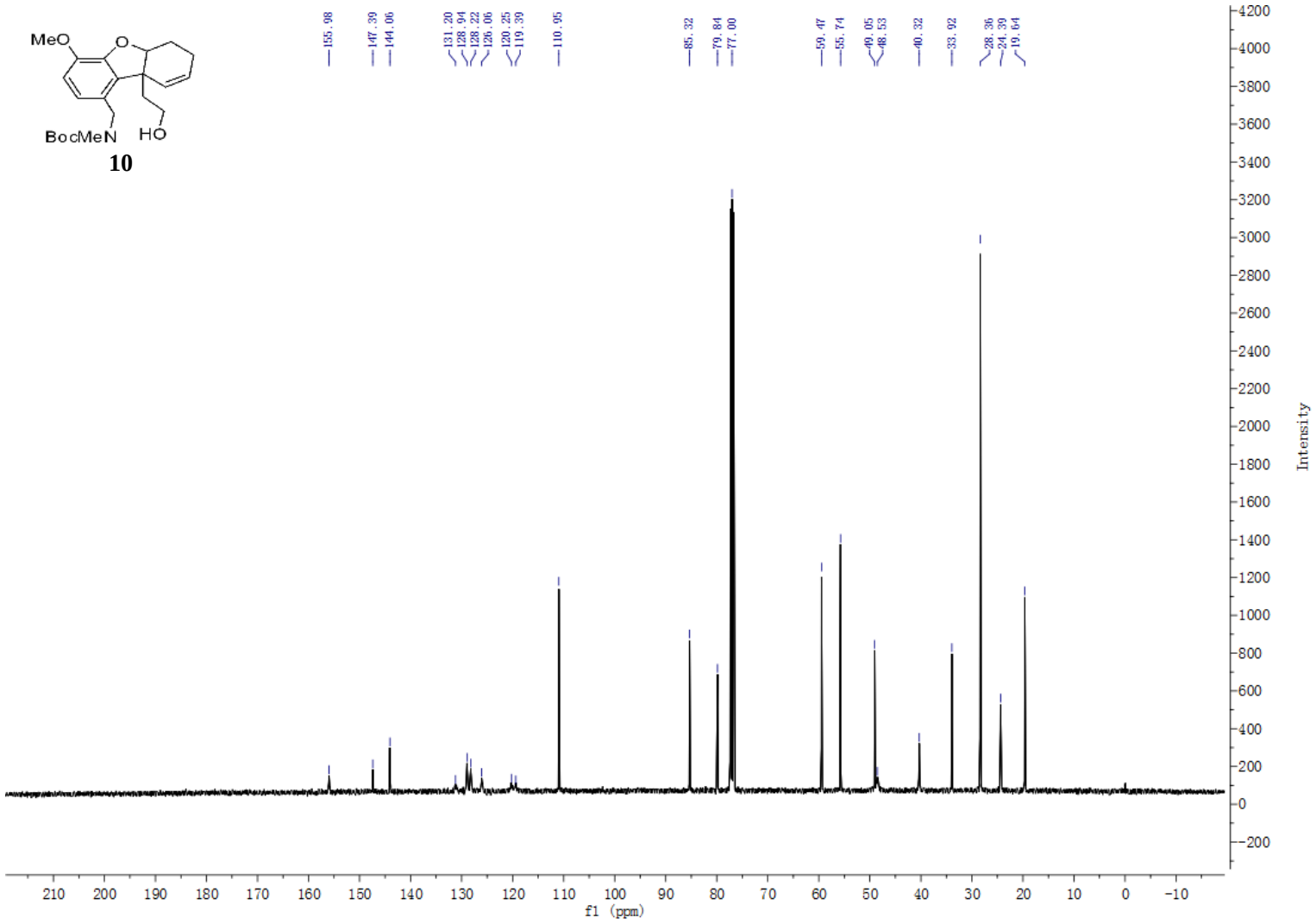

OMe
O
Me
N
Boc
CHO
9
Intensity
f1 (ppm)
1.00
1.07
1.04
2.03
1.04
1.02
1.08
2.96
1.15
4.03
2.10
1.14
1.15
9.21

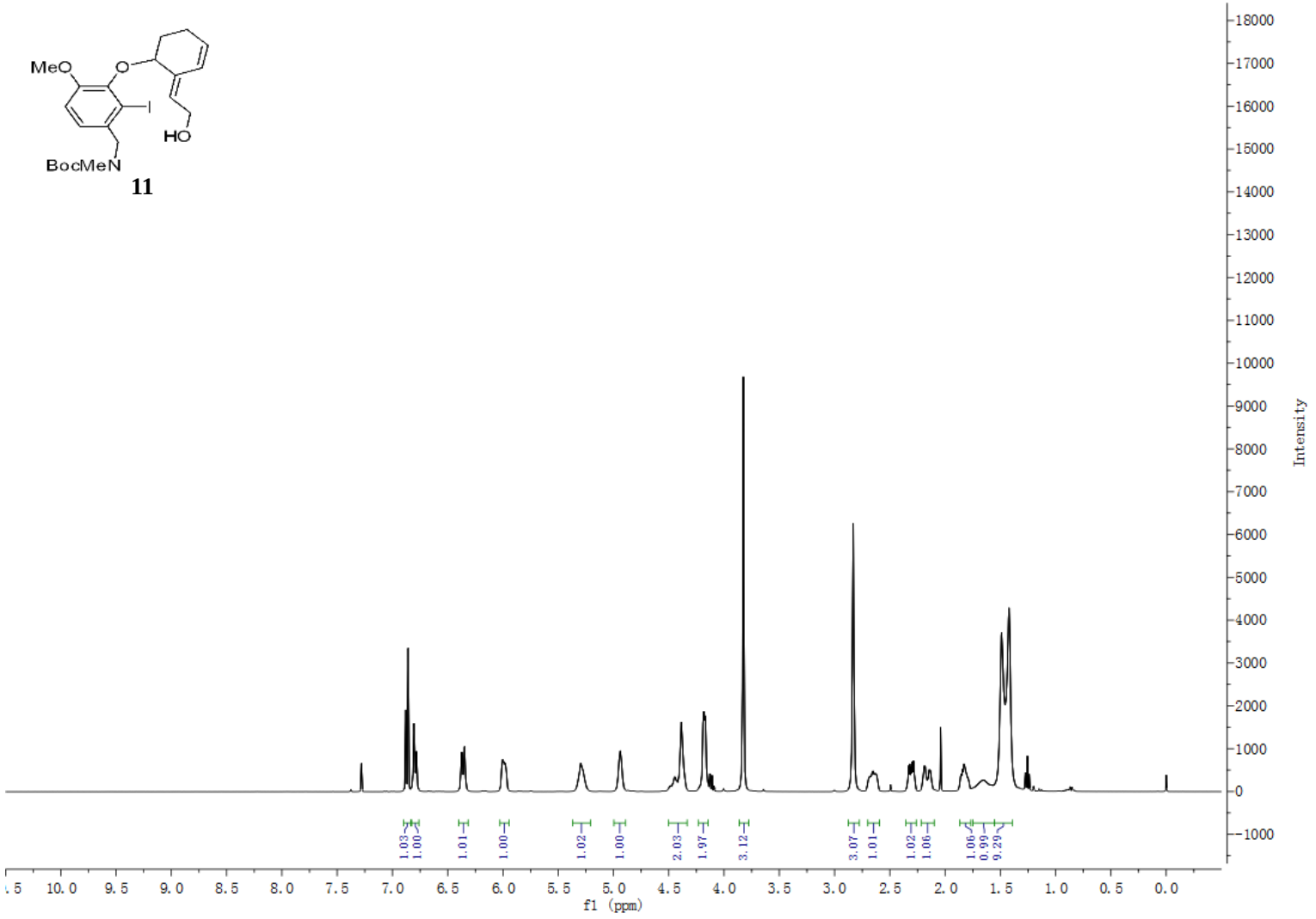

200.78
155.81
147.40
144.43
130.53
128.78
127.40
125.36
122.28
120.40
111.26
85.18
79.92
77.00
55.73
49.99
48.60
47.85
33.32
28.30
23.50
19.57
OMe
O
Me
N
Boc
CHO
Intensity
f1 (ppm)

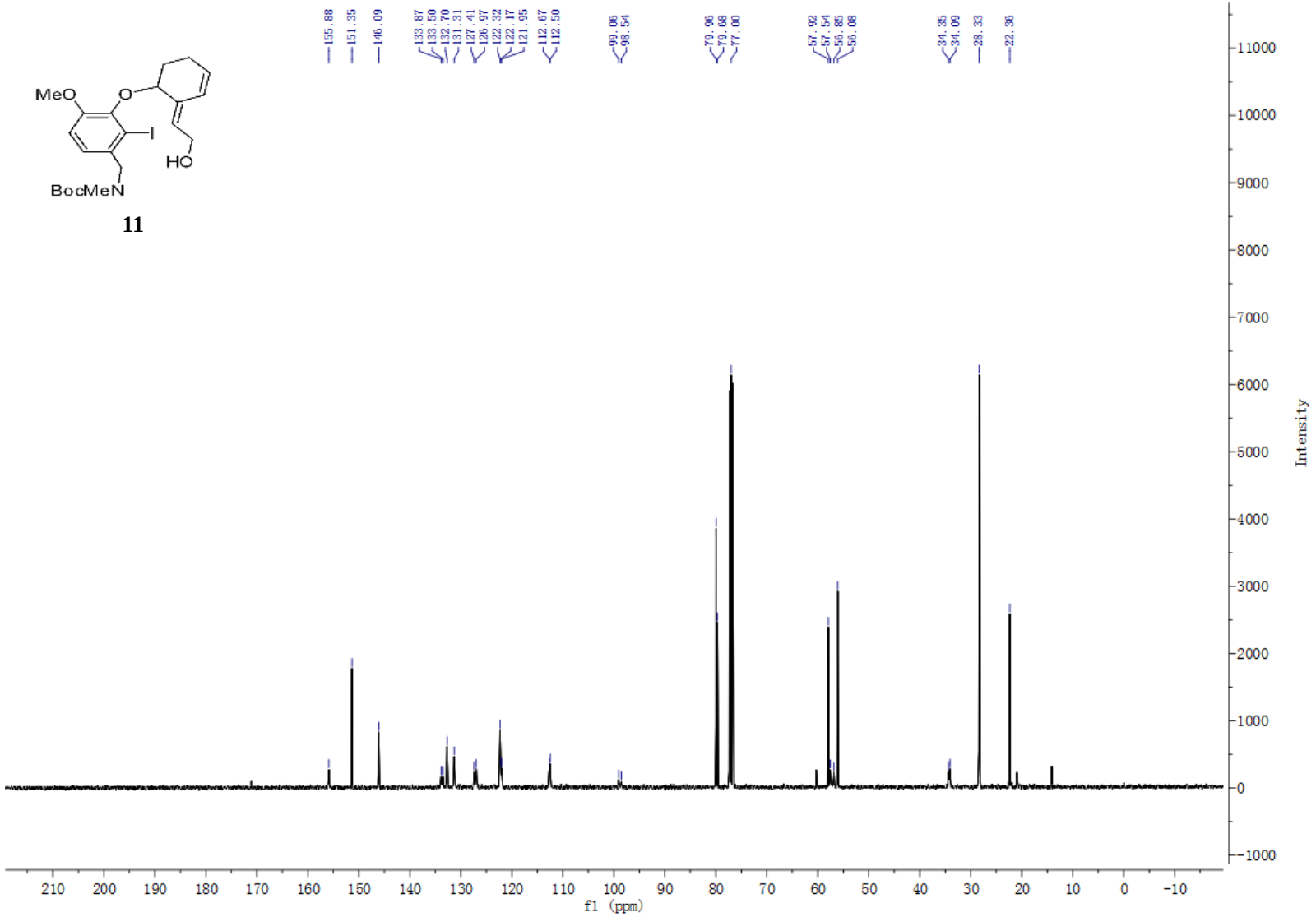
9


MeO
O
BocMeN
HO
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
Intensity
1.06
1.00
2.08
1.04
1.04
1.08
3.22
2.12
3.08
6.56
1.10
9.72
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
-0.5
f1 (ppm)

10


MeO
O
BocMeN
HO
10
155.98
147.39
144.06
131.20
128.94
128.22
126.06
120.25
119.39
110.95
85.32
79.84
77.00
59.47
55.74
49.05
48.53
40.32
33.92
28.36
24.39
19.64
Intensity
f1 (ppm)


MeO
O
I
HO
BocMeN
11
Intensity
f1 (ppm)

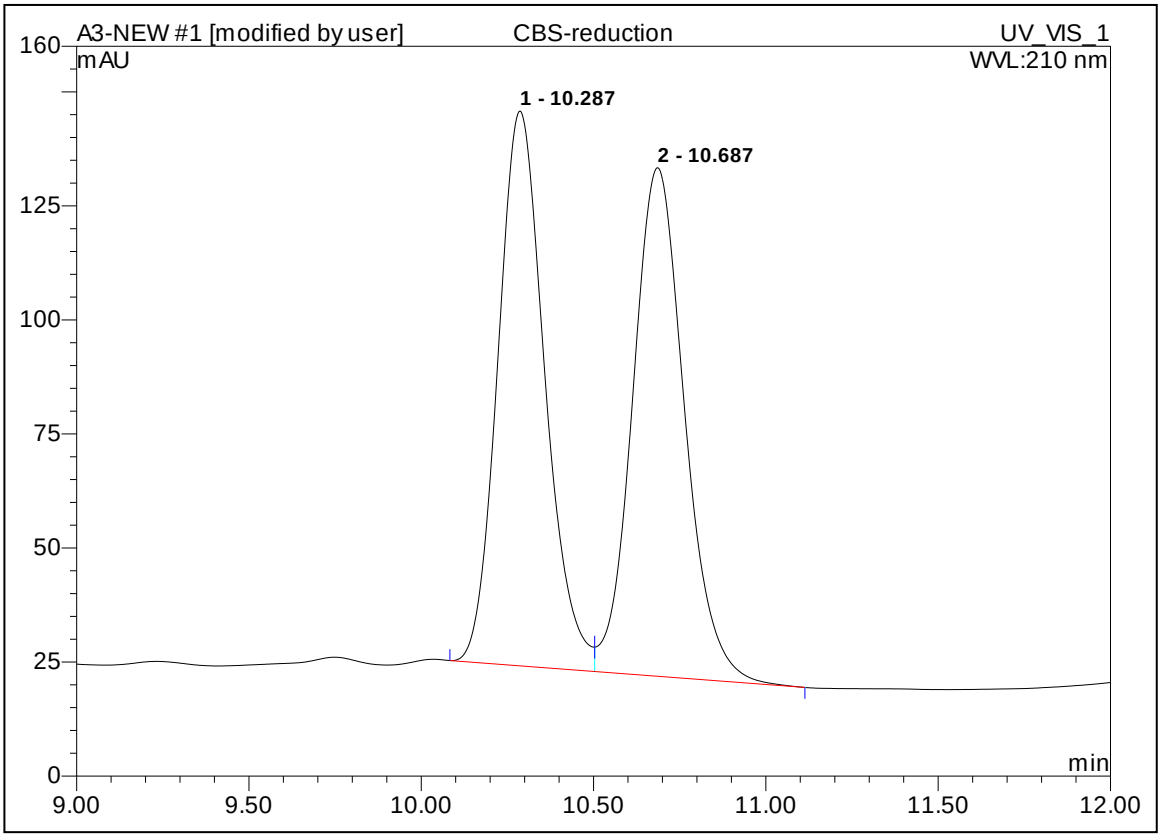

MeO
O
I
HO
BocMeN
155.88
151.35
146.09
133.87
133.50
132.70
131.31
127.41
126.97
122.32
122.17
121.95
112.67
112.50
99.06
98.54
79.96
79.68
77.00
57.92
57.54
56.85
56.08
34.35
34.09
28.33
22.36
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
Intensity
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

11

4. Copies of HPLC Profiles

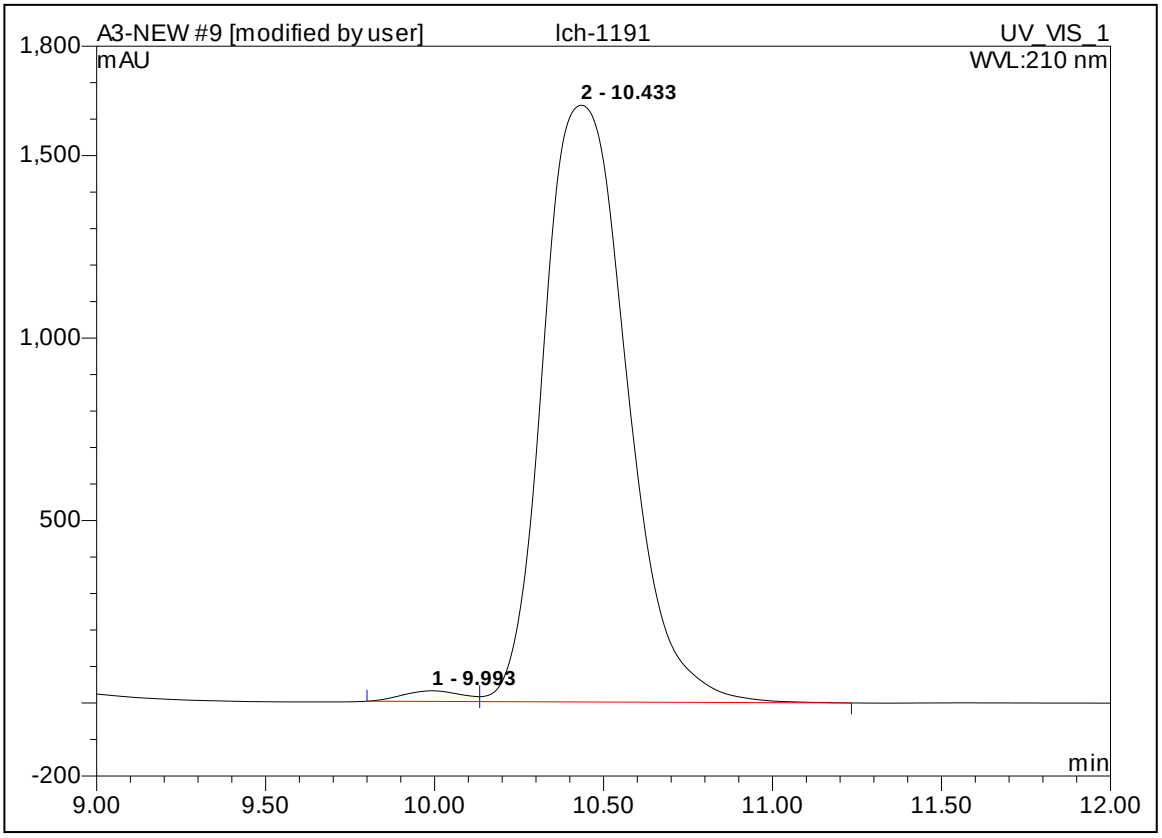
HPLC Conditions of *rac*-**5** and **5**: chiralcel OD-H column, hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min.

Sample Name:	**racemic**	*Injection Volume:*	**2.0**
Vial Number:	**1**	*Channel:*	**UV_VIS_1**
Sample Type:	**unknown**	*Wavelength:*	**210.0**
Control Program:	**test**	*Bandwidth:*	**4**
Quantif. Method:	**Method**	*Dilution Factor:*	**1.0000**
Recording Time:	**2016/3/30 17:18**	*Sample Weight:*	**1.0000**
Run Time (min):	**40.00**	*Sample Amount:*	**1.0000**



No.	Ret.Time min	Peak Name	Height mAU	Rel.Area %	Amount mg/l	Type
1	10.29	n.a.	121.660	49.68	n.a.	BM
2	10.69	n.a.	111.512	50.32	n.a.	MB
Total:			233.172	100.00	0.000	

Sample Name:	**lch-1191**	*Injection Volume:*	**2.0**
Vial Number:	**9**	*Channel:*	**UV_VIS_1**
Sample Type:	**unknown**	*Wavelength:*	**210.0**
Control Program:	**test**	*Bandwidth:*	**4**
Quantif. Method:	**Method**	*Dilution Factor:*	**1.0000**
Recording Time:	**2016/4/3 14:27**	*Sample Weight:*	**1.0000**
Run Time (min):	**15.00**	*Sample Amount:*	**1.0000**



No.	Ret.Time min	Peak Name	Height mAU	Rel.Area %	Amount mg/l	Type
1	9.99	n.a.	29.122	1.25	n.a.	BM *
2	10.43	n.a.	1635.258	98.75	n.a.	MB*
Total:			1664.379	100.00	0.000	