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Supporting Information

Rh^{I}-Catalyzed Intramolecular [3+2] Cycloaddition of 1-Allene-vinylcyclopropanes

Cheng-Hang Liu, Feng Li, Yuan Yuan, Meng Dou, and Zhi-Xiang Yu*[a]

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Supporting Information

for

Rh(I)-catalyzed intramolecular [3+2] cycloaddition reaction of 1-allene-vinylcyclopropanes

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Content

1. General Information

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 and the purified compounds showed a single spot by analytical TLC. Purification of products was accomplished by flash chromatography on silica gel, and the purified compounds showed a single spot by analytical TLC.

Tetrahydrofuran (THF) and toluene were distilled from sodium and benzophenone prior to use. Dioxane, 1,2-dichloroethane (DCE) and 1,2-dimethoxyethane (DME) (SuperDry, with molecular sieves) were purchased from J&K and used directly. Synthetic reagents were purchased from Acros, Aldrich, and Alfa Aesar and used without further purification, unless otherwise indicated.

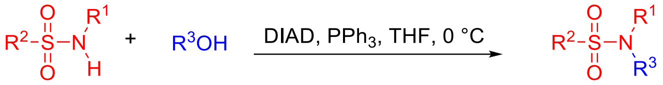
NMR spectra were measured on Bruker ARX 400 (^{1}H at 400 MHz, ^{13}C at 101 MHz) nuclear magnetic resonance spectrometers. ^{1}H-NMR spectra are reported relative to Me$_4$Si (0.00 ppm) and C$_6$D$_6$ (7.16 ppm). Data for ^{1}H-NMR spectra are reported as follows: chemical shift (ppm, s = singlet, brs = broad singlet, 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$_6$D$_6$: 128.0 ppm). ^{13}C signals are analyzed as follows: (+) = CH3/CH, (−) = CH2, quaternary carbons and other carbons with no attached protons are not marked. The assignment resulted from DEPT-135°. High-resolution mass spectra (HRMS) were recorded on Bruker Apex IV FTMS mass spectrometer (ESI).

Abbreviations:

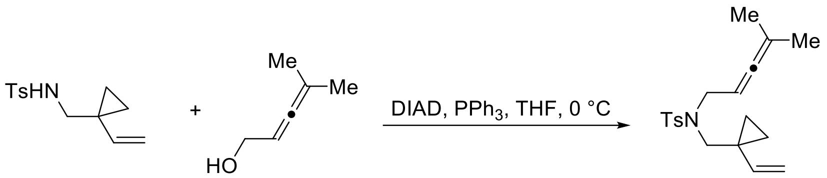
Ac = acetyl
9-BBN = 9-borabicyclo[3.3.1]nonane
Bs = *p*-bromobenzenesulfonyl
COD = 1,5-cyclooctadiene
DCE = 1,2-dichloroethane
DCM = dichloromethane
DIAD = diisopropyl azodicarboxylate
DMAP = *N*,*N*-4-dimethylaminopyridine
DMP = Dess-Martin periodinane
EA = ethyl acetate
MS = molecular sieve
Ms = methylsulfonyl
m-CPBA = meta chloroperbenzoic acid
m.p. = melting point
NBD = norbornadiene
PDC = pyridinium dichromate
PE = petroleum ether
THF = tetrahydrofuran
TLC = thin layer chromatography
Ts = *p*-toluenesulfonyl

2. Synthesis of substrates 1a−1k

General procedure A: Mitsunobu Reaction



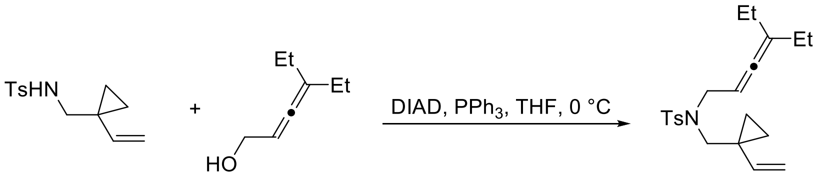
To a stirred solution of alcohol, sulfonamide, and PPh_3 in anhydrous THF was added DIAD at 0 ºC under N_2. Then the mixture was allowed to warm to room temperature and stirred until TLC indicated the disappearance of the starting material. The reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA) to afford product **1a–g, 1j, 1k**, **7** and **13**.



V1a **A1a** **1a**

Following the general procedure A, sulfonamide **V1a**[1] (1.04 g, 4.1 mmol), alcohol **A1a**[2] (432 mg, 4.4 mmol), DIAD (1.62 g, 8.0 mmol), PPh_3 (2.1 g, 8.0 mmol), and THF (20 mL) were stirred at rt for 13 h. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **1a** (805 mg, 59%) as a light yellow solid.

1a: m.p. = 78–79 °C, TLC R_f = 0.53 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 5.92 (dd, J = 17.3, 10.6 Hz, 1H), 4.95 (dd, J = 17.3, 0.9 Hz, 1H), 4.89 (dd, J = 10.6, 0.9 Hz, 1H), 4.65–4.51 (m, 1H), 3.94 (d, J = 6.8 Hz, 2H), 3.30 (s, 2H), 2.41 (s, 3H), 1.63 (d, J = 2.8 Hz, 6H), 0.72–0.66 (m, 2H), 0.66–0.61 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 203.0, 142.9, 140.4 (+), 138.0, 129.6 (+), 127.2 (+), 112.1 (–), 96.6, 84.0 (+), 51.8 (–), 46.0 (–), 21.5 (+), 20.7 (+), 20.3, 12.7 (–). HRMS (ESI) calcd for $C_{19}H_{26}NO_2S$ (M+H$^+$): 332.1679. Found: 332.1677.

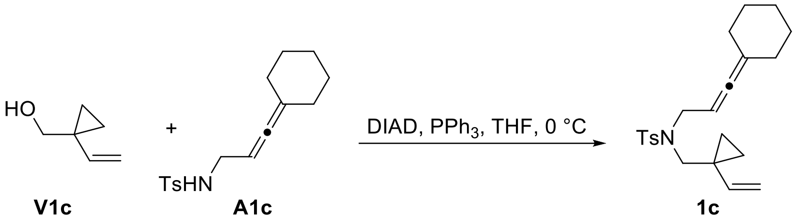


V1a **A1b** **1b**

Following the general procedure A, sulfonamide **V1a** (256 mg, 1.0 mmol), alcohol **A1b**[3] (139 mg, 1.1 mmol), DIAD (404 mg, 2.0 mmol), PPh_3 (525 mg, 2.0 mmol), and THF (5 mL) were stirred at rt for 7 h. Purification of the crude product by column chromatography (PE/EA, 50/1) afforded **1b** (177 mg, 48%) as a yellow oil.

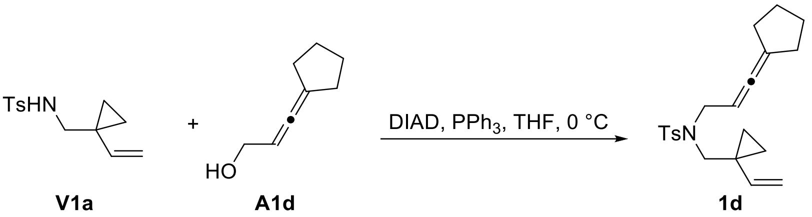
1b: TLC R_f = 0.62 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 8.3 Hz, 2H), 5.92 (dd, J = 17.3, 10.6 Hz, 1H), 4.93 (dd, J = 17.3, 1.1 Hz, 1H), 4.89 (dd, J = 10.6, 1.1 Hz, 1H), 4.84–4.76 (m, 1H), 3.96 (d, J = 6.8 Hz, 2H), 3.32 (s, 2H), 2.41 (s, 3H), 1.99–1.87 (m, 4H), 0.95 (t, J = 7.4 Hz, 6H), 0.69–0.67 (m, 2H), 0.67–0.64 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 201.5, 142.9, 140.4 (+), 138.1, 129.5 (+), 127.2 (+), 112.1 (–), 109.4, 87.7 (+), 51.9 (–), 46.5 (–), 25.4 (–), 21.5 (+), 20.9, 12.7 (–), 12.3 (+). HRMS (ESI) calcd for $C_{21}H_{30}NO_2S$ (M+H$^+$):

360.1992. Found: 360.1984.



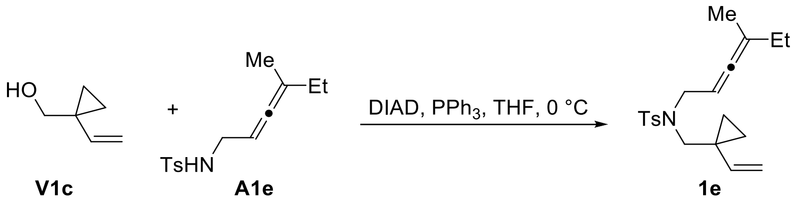
Following the general procedure A, sulfonamide **A1c**[4] (320 mg, 1.1 mmol), (1-vinylcyclopropyl)methanol **V1c**[5] (98 mg, 1.0 mmol), DIAD (404 mg, 2.0 mmol), PPh_3 (524 mg, 2.0 mmol), and THF (5 mL) were stirred at rt for 14 h. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **1c** (287 mg, 77%) as a colorless oil.

1c: TLC R_f = 0.61 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 5.93 (dd, J = 17.3, 10.6 Hz, 1H), 4.94 (dd, J = 17.3, 0.9 Hz, 1H), 4.89 (dd, J = 10.6, 0.9 Hz, 1H), 4.60–4.51 (m, 1H), 3.96 (d, J = 6.8 Hz, 2H), 3.30 (s, 2H), 2.41 (s, 3H), 2.08–1.98 (m, 4H), 1.60–1.47 (m, 6H), 0.71–0.67 (m, 2H), 0.67–0.62 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.9, 142.9, 140.4 (+), 138.1, 129.6 (+), 127.2 (+), 112.0 (–), 103.6, 83.7 (+), 51.7 (–), 46.2 (–), 31.2 (–), 27.0 (–), 25.9 (–), 21.5 (+), 20.7, 12.8 (–). HRMS (ESI) calcd for $C_{22}H_{30}NO_2S$ (M+H$^+$): 372.1992. Found: 372.1991.



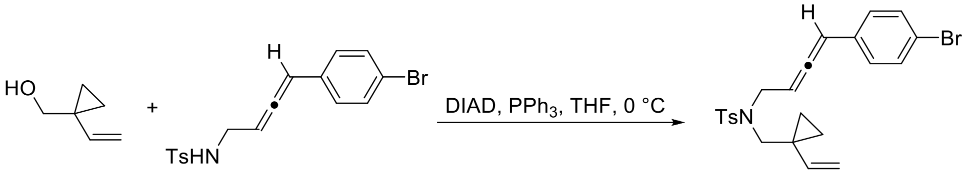
Following the general procedure A, sulfonamide **V1a** (402 mg, 1.6 mmol), alcohol **A1d**[6] (191 mg, 1.5 mmol), DIAD (607 mg, 3.0 mmol), PPh_3 (787 mg, 3.0 mmol), and THF (7.5 mL) were stirred at rt for 19 h. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **1d** (239 mg, 44%) as a white solid.

1d: m.p. = 62–64 °C, TLC R_f = 0.57 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 8.3 Hz, 2H), 5.92 (dd, J = 17.3, 10.7 Hz, 1H), 4.95 (dd, J = 17.3, 1.0 Hz, 1H), 4.90 (dd, J = 10.7, 1.0 Hz, 1H), 4.69–4.60 (m, 1H), 3.97 (d, J = 6.8 Hz, 2H), 3.29 (s, 2H), 2.41 (s, 3H), 2.33–2.23 (m, 4H), 1.69–1.60 (m, 4H), 0.73–0.66 (m, 2H), 0.66–0.60 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.5, 142.9, 140.4 (+), 138.0, 129.5 (+), 127.2 (+), 112.0 (–), 105.1, 86.2 (+), 51.8 (–), 46.1 (–), 31.1 (–), 26.9 (–), 21.5 (+), 20.6, 12.8 (–). HRMS (ESI) calcd for $C_{21}H_{28}NO_2S$ (M+H$^+$): 358.1835. Found: 358.1825.



Following the general procedure A, sulfonamide **A1e**[7] (292 mg, 1.1 mmol), (1-vinylcyclopropyl)methanol **V1c** (101 mg, 1.0 mmol), DIAD (404 mg, 2.0 mmol), PPh$_3$ (524 mg, 2.0 mmol), and THF (5 mL) were stirred at rt for 14 h. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **1e** (244 mg, 68%) as a light yellow solid.

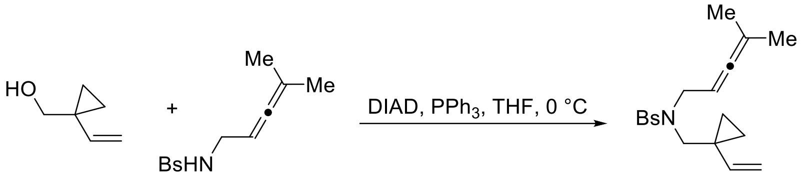
1e: m.p. = 28–30 °C, TLC R_f = 0.55 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.71 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 5.92 (dd, J = 17.3, 10.6 Hz, 1H), 4.94 (dd, J = 17.3, 0.8 Hz, 1H), 4.89 (dd, J = 10.6, 0.8 Hz, 1H), 4.72–4.63 (m, 1H), 4.01 (dd, J = 15.8, 6.3 Hz, 1H), 3.89 (dd, J = 15.8, 7.4 Hz, 1H), 3.38 (d, J = 14.0 Hz, 1H), 3.24 (d, J = 14.0 Hz, 1H), 2.41 (s, 3H), 1.94–1.85 (m, 2H), 1.63 (d, J = 2.8 Hz, 3H), 0.95 (t, J = 7.4 Hz, 3H), 0.72–0.60 (m, 4H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 202.2, 142.9, 140.4 (+), 138.0, 129.5 (+), 127.2 (+), 112.1 (–), 102.7, 85.7 (+), 51.9 (–), 46.2 (–), 26.9 (–), 21.5 (+), 20.8, 18.7 (+), 12.9 (–), 12.6 (–), 12.2 (+). HRMS (ESI) calcd for C$_{20}$H$_{28}$NO$_2$S (M+H$^+$): 346.1835. Found: 346.1835.



V1c **A1f** **1f**

Following the general procedure A, sulfonamide **A1f**[8] (416 mg, 1.1 mmol), (1-vinylcyclopropyl)methanol **V1c** (101 mg, 1.0 mmol), DIAD (404 mg, 2.0 mmol), PPh$_3$ (524 mg, 2.0 mmol), and THF (5 mL) were stirred at rt for 5 h. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **1f** (355 mg, 75%) as a colorless oil.

1f: TLC R_f = 0.78 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.71 (d, J = 8.3 Hz, 2H), 7.40 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.05 (d, J = 8.4 Hz, 2H), 6.05–5.98 (m, 1H), 5.86 (dd, J = 17.3, 10.7 Hz, 1H), 5.36–5.27 (m, 1H), 4.94 (dd, J = 17.3, 0.8 Hz, 1H), 4.89 (dd, J = 10.7, 0.8 Hz, 1H), 4.14 (ddd, J = 16.1, 6.4, 2.6 Hz, 1H), 4.03 (ddd, J = 16.1, 6.9, 2.4 Hz, 1H), 3.29 (s, 2H), 2.42 (s, 3H), 0.72–0.64 (m, 2H), 0.63–0.54 (m, 2H) ^{13}C NMR (101 MHz, CDCl$_3$): δ 205.8, 143.2, 140.1 (+), 137.6, 132.6, 131.7 (+), 129.6 (+), 128.4 (+), 127.3 (+), 120.9, 112.4 (–), 95.2 (+), 91.0 (+), 52.6 (–), 45.2 (–), 21.5 (+), 20.7, 12.9 (–), 12.8 (–). HRMS (ESI) calcd for C$_{23}$H$_{25}$BrNO$_2$S (M+H$^+$): 458.0784. Found: 458.0774.

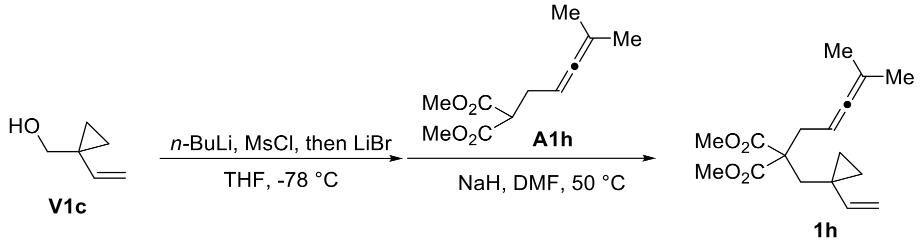


V1c **A1g** **1g**

Following the general procedure A, sulfonamide **A1g**[9] (507 mg, 1.6 mmol), (1-vinylcyclopropyl)methanol **V1c** (150 mg, 1.5 mmol), DIAD (607 mg, 3.0 mmol), PPh$_3$ (787 mg, 3.0 mmol), and THF (7.5 mL) were stirred at rt for 6 h. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **1g** (484 mg, 80%) as a white solid.

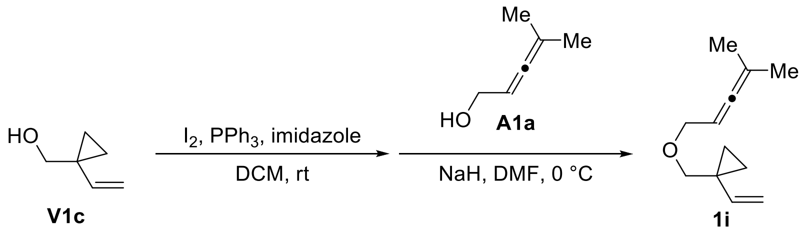
1g: m.p. = 48–50 °C, TLC R_f = 0.54 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.69 (d, J = 8.7 Hz, 2H), 7.62 (d, J = 8.7 Hz, 2H), 5.90 (dd, J = 17.3, 10.6 Hz, 1H), 4.98–4.88 (m, 2H), 4.64–4.53 (m, 1H), 3.95 (d, J = 6.7 Hz, 2H), 3.30 (s, 2H), 1.63 (d, J = 2.9 Hz, 6H), 0.72–0.67 (m, 2H), 0.67–0.61 (m, 2H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 203.2, 140.2, 140.1 (+), 132.2 (+), 128.7 (+), 127.2, 112.5 (–), 97.0, 83.8 (+), 52.0 (–), 46.0 (–), 20.7, 20.4 (+), 12.7 (–). HRMS (ESI) calcd for

$C_{18}H_{23}BrNO_2S$ (M+H$^+$): 396.0627. Found: 396.0627.



To a stirred solution of (1-vinylcyclopropyl)methanol **V1c** (150 mg, 1.5 mmol) in anhydrous THF (7 mL) was added *n*-BuLi (1.6 M, 1.2 mL, 1.92 mmol) at -78 ºC under N_2. The mixture was then stirred for 15 min at -78 ºC and MsCl (206 mg, 1.8 mmol) was added. After 5 min, LiBr (651 mg, 7.5 mmol) was added and the mixture was stirred for another 20 min at -78 ºC. The solution of bromide product was used in the next step directly. To a stirred solution of **A1h**[9] (245 mg, 1.15 mmol) in DMF (5 mL) was added NaH (92 mg, 60% purity, 2.3 mmol) at 0 ºC under N_2. After 30 min, the above THF solution of bromide was added at -78 ºC and the reaction mixture was stirred for 43 h at 50 ºC. After the completion of this transformation, 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 $MgSO_4$, and concentrated. After removing the solvent, the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 50:1) to afford **1h** (141 mg, 42% for 2steps) as a yellow oil.

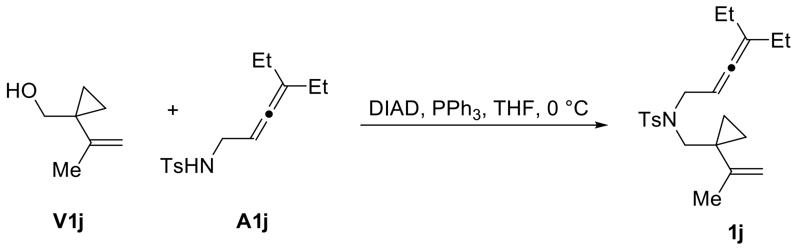
1h: TLC R_f = 0.26 (PE/EA, 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.94 (dd, *J* = 17.4, 10.1 Hz, 1H), 4.85–4.82 (m, 1H), 4.81–4.79 (m, 1H), 4.79–4.74 (m, 1H), 3.68 (s, 6H), 2.72 (d, *J* = 7.4 Hz, 2H), 2.16 (s, 2H), 1.65 (d, *J* = 2.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 203.6, 171.6, 141.5 (+), 111.8 (–), 95.3, 83.4 (+), 57.9, 52.1 (+), 39.2 (–), 32.5 (–), 20.5 (+), 20.0, 13.3 (–). HRMS (ESI) calcd for $C_{17}H_{25}O_4$ (M+H$^+$): 293.1747. Found: 293.1746.



To a stirred solution of **V1c** (474 mg, 4.83 mmol), PPh_3 (1.52 g, 5.80 mmol) and imidazole (411 mg, 6.04 mmol) in anhydrous DCM (10 mL) was added I_2 (1.84 g, 7.25 mmol) slowly and the resulting mixture was stirred for 1 hour in dark. Saturated aqueous $Na_2S_2O_3$ was added to quench the reaction. The layers were separated, and the aqueous layers were extracted with ether. The combined organic layer was dried over $MgSO_4$ and concentrated. The crude product was used directly without further purification.

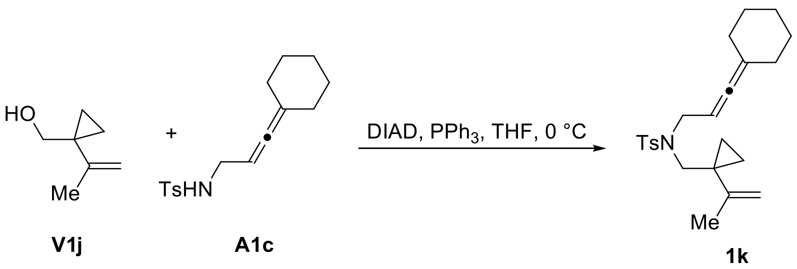
To a solution of **A1a** (474 mg, 4.83 mol) in DMF (10 mL) was added NaH (60% purity, 290 mg, 7.25 mmol) and stirred at rt for 10 min. Then a solution of the above iodide in DMF (1 mL) was added and the reaction mixture was stirred for 21 h. Saturated aqueous NH_4Cl was added to quench the reaction, and the mixture was extracted with ether. The combined extract was washed with water and brine, dried over Na_2SO_4, and concentrated. After removing the solvent, the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 200:1, then 50:1) to afford **1i** (327 mg, 38%, 2 steps) as a light yellow oil.

1i: TLC R_f = 0.51 (PE/EA, 50:1). ^{1}H NMR (400 MHz, C_6D_6): δ 5.70 (dd, J = 17.4, 10.7 Hz, 1H), 5.20–5.12 (m, 1H), 5.13 (dd, J = 17.4, 1.3 Hz, 1H), 4.98 (dd, J = 10.7, 1.4 Hz, 1H), 3.95 (d, J = 6.6 Hz, 2H), 3.39 (s, 2H), 1.56 (d, J=2.9 Hz, 6H), 0.69–0.64 (m, 2H), 0.56–0.50 (m, 2H). ^{13}C NMR (101 MHz, C_6D_6): δ 203.0, 142.3 (+), 111.2 (–), 95.8, 87.4(+), 74.1 (–), 69.3 (–), 22.7, 20.4(+), 12.5 (–). HRMS (ESI) calcd for $C_{12}H_{19}O$ (M+H$^+$): 179.1430. Found: 179.1426.



Following the general procedure A, sulfonamide **A1j**[9] (309 mg, 1.1 mmol), alcohol **V1j**[5] (113 mg, 1.0 mmol), DIAD (408 mg, 2.0 mmol), PPh_3 (520 mg, 2.0 mmol), and THF (5 mL) were stirred at rt for 6 h. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **1j** (127 mg, 34%) as a colorless oil.

1j: TLC R_f = 0.56 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 8.3 Hz, 2H), 4.83–4.75 (m, 3H), 3.95 (d, J = 6.8 Hz, 2H), 3.30 (s, 2H), 2.41 (s, 3H), 1.98–1.88 (m, 4H), 1.77 (s, 3H), 0.95 (t, J = 7.4 Hz, 6H), 0.63–0.58 (m, 2H), 0.58–0.52 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 201.5, 145.7, 142.9, 138.3, 129.4 (+), 127.3 (+), 113.4 (–), 109.2, 87.6 (+), 50.7 (–), 46.1 (–), 25.5, 25.4 (–), 21.5 (+), 20.5 (+), 12.3 (+), 10.8 (–). HRMS (ESI) calcd for $C_{22}H_{32}NO_2S$ (M+H$^+$): 374.2148. Found: 374.2142.

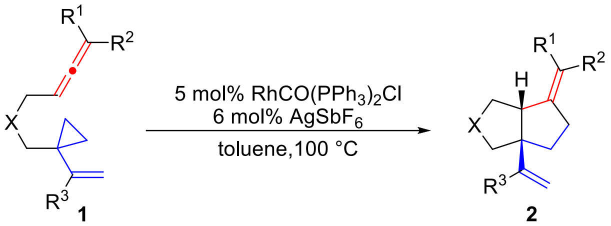


Following the general procedure A, sulfonamide **A1c** (233 mg, 0.8 mmol), alcohol **V1j** (80 mg, 0.7 mmol), DIAD (303 mg, 1.5 mmol), PPh_3 (393 mg, 1.5 mmol), and THF (5 mL) were stirred at rt for 9 h. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **1k** (206 mg, 74%) as a yellow oil.

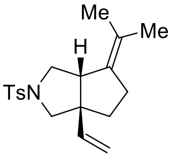
1k: TLC R_f = 0.78 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 8.3 Hz, 2H), 4.82–4.76 (m, 2H), 4.61–4.51 (m, 1H), 3.94 (d, J = 6.9 Hz, 2H), 3.28 (s, 2H), 2.41 (s, 3H), 2.08–2.00 (m, 4H), 1.79 (s, 3H), 1.59–1.47 (m, 6H), 0.64–0.58 (m, 2H), 0.57–0.51 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.9, 145.7, 142.8, 138.3, 129.5 (+), 127.3 (+), 113.3 (–), 103.5, 83.6 (+), 50.5 (–), 46.0 (–), 31.2 (–), 27.0 (–), 25.9 (–), 25.4, 21.5 (+), 20.5 (+), 10.8 (–). HRMS (ESI) calcd for $C_{23}H_{32}NO_2S$ (M+H$^+$): 386.2148. Found: 386.2145.

3. Rh-catalyzed [3+2] cycloaddition reaction

General procedure B: Rh-catalyzed [3+2] cycloaddition reaction



To a mixture of $Rh(CO)(PPh_3)_2Cl$ (3.5 mg, 5 mol%) and $AgSbF_6$ (2.1 mg, 6 mol%) was added toluene (1 mL) and stirred at room temperature under argon for 5 min. Then a solution of substrate (**1a–g, 1j**, **1k** or **7,** 0.1 mmol) in toluene (1 mL) was added slowly by syringe pump (ca 1 h) at 100 °C. After addition of the substrate, the solution was continuously stirred for 3 h at 100 °C. The reaction mixture was cooled to room temperature and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA) to afford the corresponding [3+2] cycloadduct **2a–g, 2j**, **2k** or **8**.

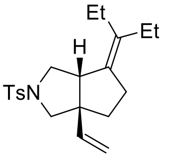


2a

Following the general procedure B, 32.9 mg **1a** was converted to 29.1 mg **2a** (run 1, 88%) and 32.7 mg **1a** was converted to 29.9 mg **2a** (run 2, 91%). So the average yield of two runs was 90%. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **2a** as a colorless oil.

2a: TLC $R_f = 0.46$ (PE/EA, 5:1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, $J = 8.2$ Hz, 2H), 7.33 (d, $J = 8.2$ Hz, 2H), 5.77 (dd, $J = 17.4, 10.8$ Hz, 1H), 4.97 (dd, $J = 10.8, 0.6$ Hz, 1H), 4.95 (dd, $J = 17.4, 0.6$ Hz, 1H), 3.56–3.49 (m, 1H), 3.25 (d, $J = 9.8$ Hz, 1H), 3.14 (d, $J = 9.8$ Hz, 1H), 3.02 (dd, $J = 9.7, 6.2$ Hz, 1H), 2.92–2.86 (m, 1H), 2.44 (s, 3H), 2.29–2.20 (m, 2H), 1.78–1.69 (m, 1H), 1.64–1.59 (m, 1H), 1.57 (s, 3H), 1.55 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.4, 141.4 (+), 136.1, 133.2, 129.5 (+), 127.6 (+), 125.0, 112.7 (–), 56.7 (–), 56.0, 53.3 (–), 51.3 (+), 34.0 (–), 29.2 (–), 21.5 (+), 21.3 (+), 21.0 (+). HRMS (ESI) calcd for $C_{19}H_{26}NO_2S$ ($M+H^+$): 332.1679. Found: 332.1677.

Product **2a** can also be prepared in large scale. 664 mg **1a** was converted to 611 mg **2a** (92%) using 2.5 mol% $Rh(CO)(PPh_3)_2Cl$ (35 mg) and 3 mol% $AgSbF_6$ (21 mg) in 40 mL toluene.

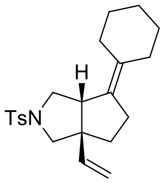


2b

Following the general procedure B, 35.6 mg **1b** was converted to 33.1 mg **2b** (run 1, 93%) and 35.9 mg **1b** was converted to 31.5 mg **2b** (run 2, 88%). So the average yield of two runs was 90%. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **2b** as a white solid.

2b: m.p. = 68–71 °C, TLC R_f = 0.54 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.71 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 5.77 (dd, J = 17.4, 10.8 Hz, 1H), 4.97 (dd, J = 10.8, 0.6 Hz, 1H), 4.94 (dd, J = 17.4, 0.6 Hz, 1H), 3.60–3.53 (m, 1H), 3.27 (d, J = 9.7 Hz, 1H), 3.14 (d, J = 9.7 Hz, 1H), 2.99–2.88 (m, 2H), 2.44 (s, 3H), 2.31–2.23 (m, 2H), 1.97–1.89 (m, 4H), 1.77–1.68 (m, 1H), 1.62–1.53 (m, 1H), 0.92 (t, J = 6.2 Hz, 3H), 0.89 (t, J = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 143.4, 141.2 (+), 137.0, 135.3, 133.4, 129.6 (+), 127.6 (+), 112.7 (–), 56.7 (–), 55.7, 53.6 (–), 50.7 (+), 33.7 (–), 28.4 (–), 25.6 (–), 24.7 (–), 21.5 (+), 13.1 (+), 12.4 (+). HRMS (ESI) calcd for $C_{21}H_{30}NO_2S$ (M+H$^+$): 360.1992. Found: 360.1983.

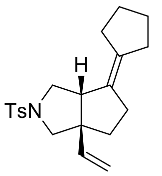
Product **2b** can also be prepared in large scale. 948 mg **2a** was converted to 842 mg **2b** (89%) using 2.5 mol% Rh(CO)(PPh$_3$)$_2$Cl (45 mg) and 3 mol% AgSbF$_6$ (27 mg) in 50 mL toluene.



2c

Following the general procedure B, 39.1 mg **1c** was converted to 33.5 mg **2c** (run 1, 86%) and 38.9 mg **1c** was converted to 35.0 mg **2c** (run 2, 90%). So the average yield of two runs was 88%. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **2c** as a white solid.

2c: m.p. = 82–85 °C, TLC R_f = 0.50 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.70 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 5.78 (dd, J = 17.4, 10.8 Hz, 1H), 4.97 (dd, J = 10.8, 0.6 Hz, 1H), 4.95 (dd, J = 17.4, 0.6 Hz, 1H), 3.56–3.49 (m, 1H), 3.25 (d, J = 9.7 Hz, 1H), 3.13 (d, J = 9.7 Hz, 1H), 2.99 (dd, J = 9.6, 6.3 Hz, 1H), 2.95–2.88 (m, 1H), 2.44 (s, 3H), 2.31–2.22 (m, 2H), 2.03–1.93 (m, 4H), 1.77– 1.69 (m, 1H), 1.65–1.57 (m, 1H), 1.53–1.41 (m, 6H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 143.3, 141.4 (+), 133.31, 133.30, 132.8, 129.6 (+), 127.6 (+), 112.7 (–), 56.6 (–), 55.7, 53.8 (–), 50.6 (+), 33.8 (–), 32.2 (–), 31.6 (–), 28.4 (–), 27.9 (–), 27.5 (–), 26.5 (–), 21.5 (+). HRMS (ESI) calcd for $C_{22}H_{30}NO_2S$ (M+H$^+$): 372.1992. Found: 372.1991.

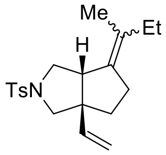


2d

Following the general procedure B, 35.9 mg **1d** was converted to 29.6 mg **2d** (run 1, 82%) and 35.2 mg **1d** was converted to 28.0 mg **2d** (run 2, 80%). So the average yield of two runs was 81%. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **2d** as a coloeless oil.

2d: TLC R_f = 0.48 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.70 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 5.79 (dd, J = 17.3, 10.8 Hz, 1H), 4.99–4.92 (m, 2H), 3.49–3.42 (m, 1H), 3.22 (d, J = 9.8 Hz, 1H), 3.14 (d, J = 9.8 Hz, 1H), 3.17–3.09 (m, 1H), 2.80–2.73 (m, 1H), 2.44 (s, 3H), 2.21–2.13 (m, 2H), 2.10–1.96 (m, 4H), 1.78–1.70 (m, 1H), 1.70–1.55 (m, 5H). ^{13}C NMR (101

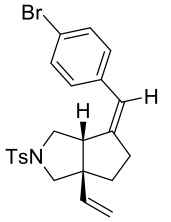
MHz, $CDCl_3$): δ 143.3, 141.7 (+), 136.4, 133.2, 132.5, 129.5 (+), 127.7 (+), 112.5 (–), 56.5 (–), 56.4, 52.6 (–), 52.1 (+), 34.3 (–), 31.3 (–), 31.1 (–), 29.9 (–), 26.9 (–), 26.5 (–), 21.5 (+). HRMS (ESI) calcd for $C_{21}H_{28}NO_2S$ (M+H$^+$): 358.1835. Found: 358.1828.



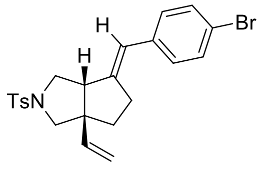
2e

Following the general procedure B, 34.7 mg **1e** was converted to 30.7 mg **2e** (run 1, 88%) and 33.8 mg **1e** was converted to 29.8 mg **2e** (run 2, 88%). So the average yield of two runs was 88%. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **2e** as a colorless oil. The ratio of two isomers was 1.2:1. The two isomers were inseparable and the configuration of them was not determined.

2e: TLC R_f = 0.40 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 5.83–5.71 (m, 1H), 5.01–4.90 (m, 2H), 3.59–3.49 (m, 1H), 3.29–3.22 (m, 1H), 3.18–3.10 (m, 1H), 3.05–2.84 (m, 2H), 2.44 (s, 3H), 2.32–2.18 (m, 2H), 1.96–1.86 (m, 2H), 1.78–1.68 (m, 1H), 1.66–1.57 (m, 1H), 1.56–1.51 (m, 3H), 0.96 – 0.86 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.4, 143.3, 141.4 (+), 141.2 (+), 135.8, 135.3, 133.4, 133.2, 130.9, 130.8, 129.6 (+), 129.5 (+), 127.7 (+), 127.6 (+), 112.8 (–), 112.7 (–), 56.7 (–), 56.6 (–), 55.9, 55.9, 53.5 (–), 53.4 (–), 51.2 (+), 50.8 (+), 34.0 (–), 33.7 (–), 29.2 (–), 28.5 (–), 28.1 (–), 21.5 (+), 18.5 (+), 17.9 (+), 12.8 (+), 12.1 (+). HRMS (ESI) calcd for $C_{20}H_{28}NO_2S$ (M+H$^+$): 346.1835. Found: 346.1836.



***Z*-2f**
(major)



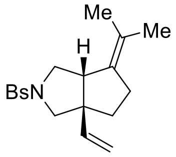
***E*-2f**
(minor)

Following the general procedure B, 45.8 mg **1f** was converted to 34.1 mg **2f** (run 1, 74%) and 46.1 mg **1f** was converted to 36.5 mg **2f** (run 2, 79%). So the average yield of two runs was 76%. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **2f**. The *Z*:*E* ratio of two isomers was 3.2:1. Pure ***Z*-2f** could be achieved by recrystallization from EA/PE, and ***E*-2f** was enriched in the mother liquor. The configuration of **Z-2f** was confirmed by NOSEY.

***Z*-2f:** white solid. m.p. = 113–114 °C, TLC R_f = 0.68 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 7.01 (d, J = 8.2 Hz, 2H), 6.26 (s, 1H), 5.80 (dd, J = 17.4, 10.8 Hz, 1H), 5.02–4.92 (m, 2H), 3.55–3.47 (m, 1H), 3.28 (d, J = 9.8 Hz, 1H), 3.19–3.13 (m, 1H), 3.13 (d, J = 9.8 Hz, 1H), 3.09 (dd, J = 9.5, 5.7 Hz, 1H), 2.63–2.47 (m, 2H), 2.45 (s, 3H), 1.84–1.76 (m, 1H), 1.74–1.66 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.7, 143.6, 141.2 (+), 136.1, 132.7, 131.6 (+), 129.6 (+), 129.4 (+), 127.8 (+), 122.7 (+), 120.4, 113.0 (–), 57.2 (–), 56.9, 53.0 (–), 50.6 (+), 34.2 (–), 33.3 (–), 21.6 (+). HRMS (ESI) calcd for $C_{23}H_{25}BrNO_2S$ (M+H$^+$): 458.0784. Found: 458.0783.

***E*-2f:** colorless oil. TLC R_f = 0.68 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 8.1

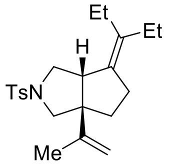
Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 8.2 Hz, 2H), 5.82 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.18 (s, 1H), 4.94–4.82 (m, 2H), 3.32–3.20 (m, 2H), 3.20–3.02 (m, 4H), 2.82–2.74 (m, 1H), 2.51–2.41 (m, 1H), 2.45 (s, 3H), 2.41–2.32 (m, 1H). ^{13}C NMR (126 MHz, CDCl$_3$): *δ* 143.5, 142.3, 142.0 (+), 137.6, 132.6, 131.5 (+), 130.6 (+), 129.6 (+), 127.9 (+), 125.9 (+), 120.1, 112.2 (–), 58.2 (–), 56.2 (+), 55.3, 50.2 (–), 42.9 (–), 35.5 (–), 21.6 (+). HRMS (ESI) calcd for $C_{23}H_{25}BrNO_2S$ (M+H$^+$): 458.0784. Found: 458.0780.



2g

Following the general procedure B, 39.9 mg **1g** was converted to 36.5 mg **2g** (run 1, 91%) and 39.9 mg **1g** was converted to 34.9 mg **2g** (run 2, 87%). So the average yield of two runs was 89%. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **2g** as a white solid.

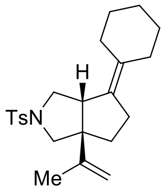
2g: m.p. = 101–104 °C, TLC *R*$_f$ = 0.49 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CDCl$_3$): *δ* 7.71–7.64 (m, 4H), 5.78 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.03–4.92 (m, 2H), 3.59–3.49 (m, 1H), 3.25 (d, *J* = 9.8 Hz, 1H), 3.16 (d, *J* = 9.8 Hz, 1H), 3.03 (dd, *J* = 9.7, 6.2 Hz, 1H), 2.96–2.87 (m, 1H), 2.30–2.20 (m, 2H), 1.81–1.71 (m, 1H), 1.65–1.59 (m, 1H), 1.58–1.54 (m, 6H). ^{13}C NMR (101 MHz, CDCl$_3$): *δ* 141.1 (+), 135.8, 135.4, 132.2 (+), 129.0 (+), 127.6, 125.3, 113.0 (–), 56.6 (–), 56.1, 53.3 (–), 51.2 (+), 34.0 (–), 29.2 (–), 21.4 (+), 21.1 (+). HRMS (ESI) calcd for $C_{18}H_{23}BrNO_2S$ (M+H$^+$): 396.0627. Found: 396.0626.



2j

Following the general procedure B, 37.3 mg **1j** was converted to 32.1 mg **2j** (run 1, 86%) and 37.5 mg **1j** was converted to 32.1 mg **2j** (run 2, 86%). So the average yield of two runs was 86%. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **2j** as a colorless oil.

2j: TLC *R*$_f$ = 0.50 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CDCl$_3$): *δ* 7.70 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 4.70 (s, 1H), 4.58 (s, 1H), 3.59–3.52 (m, 1H), 3.39 (d, *J* = 9.5 Hz, 1H), 3.14–3.05 (m, 1H), 3.08 (d, *J* = 9.5 Hz, 1H), 2.99 (dd, *J* = 9.4, 7.1 Hz, 1H), 2.44 (s, 3H), 2.29–2.15 (m, 2H), 2.00–1.88 (m, 4H), 1.78–1.70 (m, 1H), 1.68 (s, 3H), 1.61–1.53 (m, 1H), 0.93 (t, *J* = 7.6 Hz, 3H), 0.89 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): *δ* 146.4, 143.3, 136.3, 135.8, 133.4, 129.6 (+), 127.6 (+), 110.1 (–), 58.4, 56.4 (–), 54.0 (–), 48.7 (+), 33.3 (–), 28.0 (–), 25.6 (–), 24.7 (–), 21.5 (+), 20.4 (+), 13.1 (+), 12.3 (+). HRMS (ESI) calcd for $C_{22}H_{32}NO_2S$ (M+H$^+$): 374.2148. Found: 374.2145.

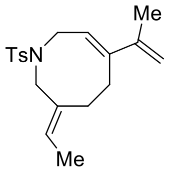


2k

Following the general procedure B, 38.7 mg **1k** was converted to 31.6 mg **2k** (run 1, 82%) and 38.7 mg **1k** was converted to 31.0 mg **2k** (run 2, 80%). So the average yield of two runs was 81%. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **2k** as a colorless oil.

2k: TLC R_f = 0.70 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.70 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 4.73–4.68 (m, 1H), 4.60 (s, 1H), 3.56–3.48 (m, 1H), 3.36 (d, J = 9.6 Hz, 1H), 3.14–3.08 (m, 1H), 3.08 (d, J = 9.6 Hz, 1H), 3.01 (dd, J = 9.5, 6.5 Hz, 1H), 2.44 (s, 3H), 2.29–2.15 (m, 2H), 2.05–1.94 (m, 4H), 1.78–1.71 (m, 1H), 1.70–1.65 (m, 3H), 1.62–1.55 (m, 1H), 1.53– 1.43 (m, 6H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 146.5, 143.3, 133.4, 133.2, 132.7, 129.6 (+), 127.6 (+), 110.1 (–), 58.4, 56.5 (–), 54.1 (–), 48.4 (+), 33.5 (–), 32.2 (–), 31.6 (–), 28.0 (–), 27.9 (–), 27.5 (–), 26.6 (–), 21.5 (+), 20.4 (+). HRMS (ESI) calcd for $C_{23}H_{32}NO_2S$ (M+H$^+$): 386.2148. Found: 386.2140.

4. Byproducts 4a, 5a and 6

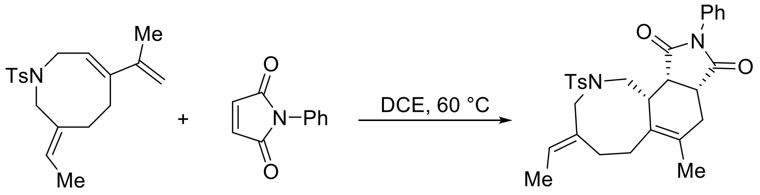


4a

When using $[Rh(C_2H_4)_2Cl]_2$, $[Rh(NBD)Cl]_2$ or $[Rh(COE)Cl]_2$ as catalyst, compound **4a** can be generated as the major product.

To a mixture of $[Rh(COE)Cl]_2$ (14.5 mg, 5 mol%) and substrate **1a** (134 mg, 0.40 mmol) was added toluene (8 mL) and stirred at 100 °C for 6 h. The reaction mixture was cooled to room temperature and concentrated. The crude product was purified by careful flash column chromatography on silica gel (eluted with PE/EA, 50:1) to afford the compound **4a** (36.1 mg, 27%) as a colorless oil.

4a: TLC R_f = 0.49 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 5.61 (q, J = 6.8 Hz, 1H), 5.35 (t, J = 7.1 Hz, 1H), 5.07 (s, 1H), 4.91 (s, 1H), 3.86 (d, J = 7.1 Hz, 2H), 3.60 (s, 2H), 2.65–2.58 (m, 2H), 2.43 (s, 3H), 2.31–2.22 (m, 2H), 1.71 (s, 3H), 1.55 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.2, 143.1, 143.0, 136.5, 134.4, 129.6 (+), 128.5 (+), 127.1 (+), 120.0 (+), 112.2 (–), 53.9 (–), 45.3 (–), 29.6 (–), 25.4 (–), 21.4 (+), 20.8 (+), 13.3 (+). HRMS (ESI) calcd for $C_{19}H_{26}NO_2S$ (M+H$^+$): 332.1679. Found: 32.1678.

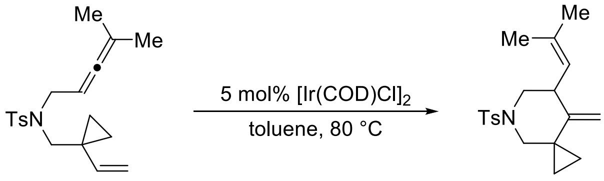


4a

6 CCDC(1825181)

A mixture of compound **4a** (36.1 mg, 0.11 mmol) and 1-phenyl-1*H*-pyrrole-2,5-dione (26.4 mg, 0.15 mmol) in DCE (2 mL) was heated in 60 ºC. After 9 h, the solution was concentrated and the crude product was purified by column chromatography (PE/EA, 10/1 then 5:1) to afford **6** (32.5 mg, 59%) as a white solid (CCDC: 1825181).

6: m.p. = 179–180 °C, TLC R_f = 0.44 (PE/EA, 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, J = 8.2 Hz, 2H), 7.50–7.38 (m, 3H), 7.25 (d, J = 8.2 Hz, 2H), 7.20–7.14 (m, 2H), 5.43 (q, J = 6.5 Hz, 1H), 4.16 (d, J = 13.9 Hz, 1H), 3.59–3.43 (m, 1H), 3.24–3.07 (m, 4H), 2.86–2.63 (m, 3H), 2.62–2.49 (m, 2H), 2.42 (s, 3H), 2.19–2.06 (m, 1H), 1.96–1.88 (m, 1H), 1.87 (s, 3H), 1.66 (dd, J = 6.5, 1.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 178.8, 177.3, 143.3, 137.0, 135.6, 132.2, 131.7, 129.7 (+), 129.3, 129.1 (+), 128.7 (+), 126.9 (+), 126.3 (+), 122.6 (+), 56.6 (–), 46.6 (–), 43.4 (+), 39.0 (+), 38.4 (+), 31.4 (–), 29.0 (–), 27.2 (–), 21.5 (+), 19.5 (+), 13.4 (+). HRMS (ESI) calcd for $C_{29}H_{33}N_2O_4S$ (M+H$^+$): 505.2156. Found: 505.2160.



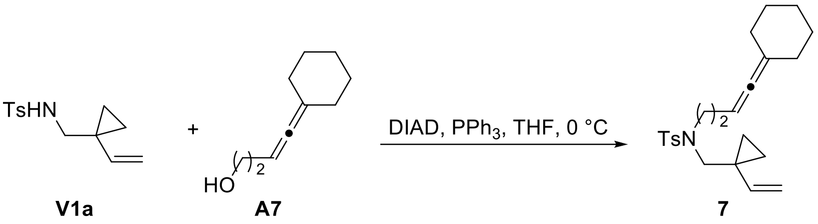
1a

5a

When using [Ir(COD)Cl]$_2$ (3.4 mg, 5 mol%) as catalyst, 33.0 mg **1a** was converted to 11.3 mg **5a** (34%). Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **5a** as a colorless oil.

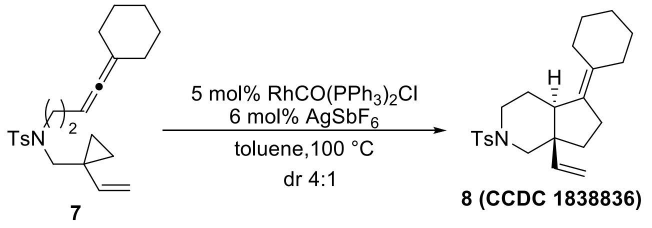
5a: TLC R_f = 0.35 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.65 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 5.76 (dd, J = 7.1, 3.8 Hz, 1H), 4.89 (s, 1H), 4.86 (s, 1H), 4.16–4.04 (m, 2H), 3.74 (dd, J = 16.8, 3.7 Hz, 1H), 2.42 (s, 3H), 2.16 (d, J = 11.9 Hz, 1H), 1.87–1.77 (m, 1H), 1.83 (s, 3H), 1.26 (d, J = 7.1 Hz, 3H), 0.49–0.33 (m, 4H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 147.6, 143.9, 143.1, 135.4, 129.6 (+), 127.2 (+), 122.1 (+), 111.8 (–), 53.8 (–), 44.7 (–), 43.2 (+), 21.9 (+), 21.5 (+), 21.3, 16.5 (+), 14.8 (–), 11.7 (–). HRMS (ESI) calcd for $C_{19}H_{26}NO_2S$ (M+H$^+$): 332.1679. Found: 332.1673.

5. Other reactions



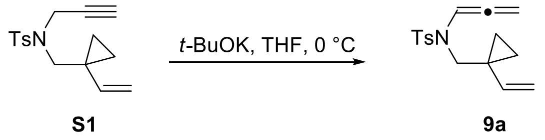
Following the general procedure A, sulfonamide **V1a** (248 mg, 1.0 mmol), alcohol **A7**[10] (183 mg, 1.2 mmol), DIAD (405 mg, 2.0 mmol), PPh$_3$ (525 mg, 2.0 mmol), and THF (5 mL) were stirred at rt for 16 h. Purification of the crude product by column chromatography (PE/EA, 50/1 then 20/1) afforded **7** (197 mg, 52%) as a colorless oil.

7: TLC R_f = 0.56 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CDCl$_3$): δ7.68 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 5.86 (dd, J = 17.3, 10.7 Hz, 1H), 4.99 (dd, J = 17.3, 0.8 Hz, 1H), 4.92 (dd, J = 10.7, 0.8 Hz, 1H), 4.89–4.83 (m, 1H), 3.26–3.15 (m, 4H), 2.42 (s, 3H), 2.20–2.13 (m, 2H), 2.10–2.00 (m, 4H), 1.63–1.46 (m, 6H), 0.75–0.68 (m, 2H), 0.64–0.58 (m, 2H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 198.8, 142.9, 140.4 (+), 137.2, 129.5 (+), 127.1 (+), 112.3 (–), 103.1, 85.2 (+), 54.4 (–), 47.6 (–), 31.6 (–), 27.8 (–), 27.4 (–), 26.1 (–), 21.5 (+), 21.0, 13.2 (–). HRMS (ESI) calcd for $C_{23}H_{32}NO_2S$ (M+H$^+$): 386.2148. Found: 386.2141.



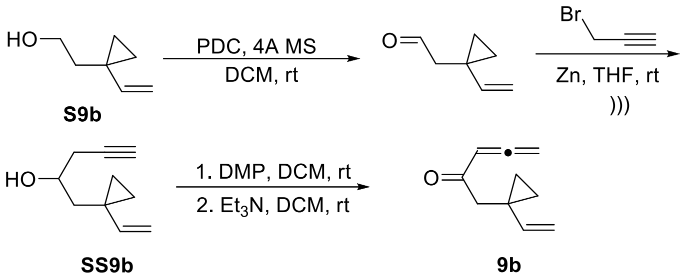
Following the general procedure B, 38.6 mg **7** was converted to 25.4 mg **8** (run 1, 66%) and 38.4 mg **7** was converted to 25.4 mg **8** (run 2, 66%). So the average yield of two runs was 66%. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **8**. The *trans*/*cis* ratio of two isomers was 3.2:1. Pure major product ***trans*-8** could be achieved by recrystallization from PE, and the structure was further confirmed by XRD (CCDC: 1838836).

***trans*-8:** TLC R_f = 0.47 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.64 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 5.76 (dd, J = 17.8, 11.2 Hz, 1H), 5.30 (dd, J = 17.8, 1.0 Hz, 1H), 5.21 (dd, J = 11.2, 1.0 Hz, 1H), 4.11–4.04 (m, 1H), 3.90–3.82 (m, 1H), 2.43 (s, 3H), 2.40–2.29 (m, 1H), 2.28–2.15 (m, 4H), 2.13–2.01 (m, 3H), 2.00–1.87 (m, 3H), 1.66 (dd, J = 11.4, 8.4 Hz, 1H), 1.54–1.38 (m, 6H), 1.28–1.18 (m, 1H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 143.2, 138.7 (+), 133.4, 132.4, 129.5 (+), 129.1, 127.6 (+), 115.9 (–), 55.7 (–), 51.7 (+), 47.1, 46.7 (–), 34.1 (–), 32.8 (–), 29.7 (–), 28.5 (–), 27.8 (–), 27.7 (–), 26.8 (–), 26.6 (–), 21.5 (+). HRMS (ESI) calcd for $C_{23}H_{32}NO_2S$ (M+H$^+$): 386.2148. Found: 386.2146.



A mixture of **S1**[5] (292 mg, 1.0 mmol) and *t*-BuOK (34.2 mg, 0.3 mmol) in THF (3 mL) was stirred at 0 ºC under N_2. Then the mixture was allowed to warm to rt. After 20 h, the reaction mixture was filtered through a short silica gel eluting with Et_2O. The solution was concentrated and the crude product was purified by column chromatography (PE/EA, 20/1) to afford **9a** as a light yellow solid.

9a: m.p. = 57–60 °C, TLC R_f = 0.68 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.3 Hz, 2H), 6.74 (t, J = 6.2 Hz, 1H), 5.88 (dd, J = 17.3, 10.7 Hz, 1H), 5.26 (d, J = 6.2 Hz, 2H), 4.89 (dd, J = 10.7, 1.1 Hz, 1H), 4.85 (dd, J = 17.3, 1.1 Hz, 1H), 3.26 (s, 2H), 2.43 (s, 3H), 0.82 (dd, J = 6.5, 4.4 Hz, 2H), 0.63 (dd, J = 6.5, 4.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 202.4, 143.7, 141.2 (+), 135.2, 129.6 (+), 127.3 (+), 111.5 (–), 101.1 (+), 87.8 (–), 50.8 (–), 21.6 (+), 21.1, 12.3 (–). HRMS (ESI) calcd for $C_{16}H_{20}NO_2S$ (M+H$^+$): 290.1209. Found: 290.1212.

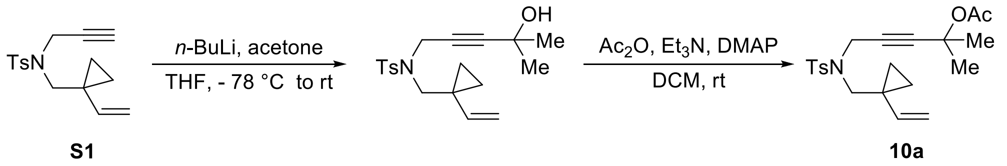


S9b[11] (510 mg 4.55 mmol) was dissolved in DCM (9 mL), then PDC (1.71 g, 4.55 mmol) and 4 Å MS (2.68 g) were added successively. The resulting mixture was stirred for 2 h at rt. After the accomplishment of the oxidation reaction, the mixture was filtered and the filtrate was concentrated.

To a solution of the above crude aldehyde product in THF (18 mL) was added propargyl bromide (80% in toluene, 1.28 g, 8.60 mmol), Zn powder (1.49 g, 22.78 mmol) and 1,2-diiodoethane (1.29 g, 4.58 mmol). The resulting mixture was stirred under ultrasonic wave for 1 h. After that, saturated aqueous NH_4Cl was added to quench the reaction, and 10% HCl aqueous solution was added to dissolve the precipitate. The mixture was extracted with ether and the combined extract was washed with water and brine, dried over Na_2SO_4, and concentrated. The crude product was purified by column chromatography (PE/EA, 10/1 then 5:1) to afford **SS9b** (354 mg, 52%, 2 steps) as a light yellow oil.

To a solution of the above alcohol product **SS9b** in DCM (18 mL) was added DMP (1.98 g, 4.66 mmol) and the mixture was stirred for 13 h. Et_2O/water was added to dilute the reaction mixture and saturated aqueous Na_2SO_3 was added to quench the reaction. The mixture was extracted with ether, dried over Na_2SO_4, and concentrated. The crude product was purified by column chromatography (PE/EA, 10/1). Then the crude product was dissolved in DCE (3 mL) and Et_3N (23 mg, 0.23 mmol) was added. The mixture was stirred for 1 h at rt. The solution was concentrated directly and crude product was purified by column chromatography (PE/EA, 10/1) to afford **9b** (232 mg, 66%, 2 steps) as a colorless oil.

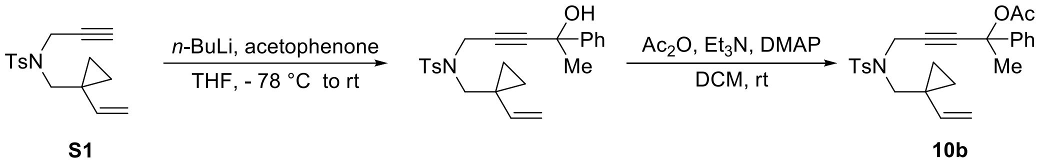
9b: TLC R_f = 0.50 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.84 (t, J = 6.5 Hz, 1H), 5.57 (dd, J = 17.3, 10.6 Hz, 1H), 5.25 (d, J = 6.5 Hz, 2H), 4.89 (dd, J = 10.6, 0.7 Hz, 1H), 4.84 (dd, J = 17.3, 0.7 Hz, 1H), 2.75 (s, 2H), 0.75–0.72 (m, 2H), 0.72–0.69 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 216.6, 198.7, 143.2 (+), 110.7 (–), 97.0 (+), 79.5 (–), 44.7 (–), 19.3, 13.9 (–). HRMS (ESI) calcd for $C_{10}H_{13}O$ (M+H$^+$): 149.0961. Found: 149.0960.



To a stirred solution of **S1** (290 mg, 1.0 mmol) in anhydrous THF (5 ml) was added *n*-BuLi in hexane (1.6 M, 0.7 ml, 1.12 mmol) at -78 °C. After stirring for 30 min at this temperature, acetone (174 mg, 3 mmol) was added to the reaction mixture in dropwise. After the addition finishing, the reaction was allowed to warm to room temperature and stirred for 2 h. The reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (PE/EA, 5:1 then 1:1) to yield alcohol intermediate which was used directly in the next step.

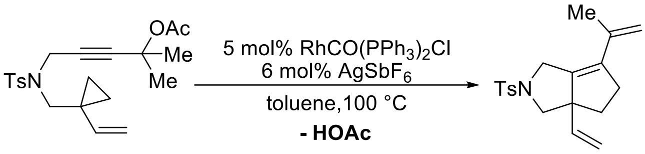
To a stirred solution of the above alcohol in DCM (7.5 ml) was added Ac_2O (512 mg, 5.0 mmol), Et_3N (1.01 g, 10.0 mmol) and DMAP (12.9 mg, 0.1 mmol) at room temperature and stirred for 15 h. The reaction mixture was concentrated and the residue was purified by flash column chromatography (PE/EA, 10:1) to afford **10a** (274 mg, 70% for 2 steps) as a colorless oil.

10a: TLC R_f = 0.58 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 5.81 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.13 (dd, *J* = 17.4, 1.0 Hz, 1H), 4.96 (dd, *J* = 10.8, 1.0 Hz, 1H), 4.26 (s, 2H), 3.26 (s, 2H), 2.40 (s, 3H), 1.92 (s, 3H), 1.33 (s, 6H), 0.78–0.72 (m, 2H), 0.72–0.66 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.9, 143.1, 140.2 (+), 136.1, 129.4 (+), 127.8 (+), 112.2 (–), 87.2, 76.0, 71.2, 51.2 (–), 35.8 (–), 28.5 (+), 21.7 (+), 21.4 (+), 19.4, 12.6 (–). HRMS (ESI) calcd for $C_{21}H_{31}N_2O_4S$ (M+NH_4^+): 407.1999. Found: 407.1991.



Following the synthetic procedure of **10a**, **S1** (286 mg, 1 mmol) and acetophenone (240 mg, 2 mmol) were converted to product **10b** (298 mg, 67%) as a light yellow oil. **10b** was not stable and should be used as soon as possible.

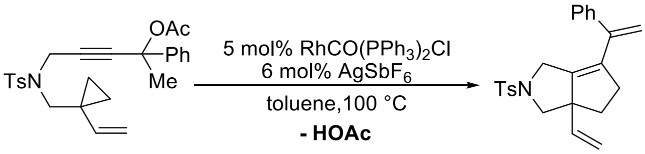
10b: TLC R_f = 0.52 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.30–7.19 (m, 7H), 5.84 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.13 (dd, *J* = 17.4, 0.9 Hz, 1H), 4.97 (dd, *J* = 10.8, 0.9 Hz, 1H), 4.45–4.35 (m, 2H), 3.33 (d, *J* = 13.2 Hz, 1H), 3.25 (d, *J* = 13.2 Hz, 1H), 2.32 (s, 3H), 1.98 (s, 3H), 1.56 (s, 3H), 0.78–0.72 (m, 2H), 0.72–0.65 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.2, 143.2, 142.0, 140.2 (+), 136.1, 129.5 (+), 128.2 (+), 127.8 (+), 127.7 (+), 124.6 (+), 112.3 (–), 85.6, 80.2, 75.2, 51.4 (–), 35.9 (–), 31.4 (+), 21.6 (+), 21.5 (+), 19.5, 12.7 (–), 12.6 (–). HRMS (ESI) calcd for $C_{26}H_{33}N_2O_4S$ (M+NH_4^+): 469.2156. Found: 469.2156.



10a **11a**

To a mixture of Rh(CO)(PPh$_3$)$_2$Cl (3.5 mg, 5 mol%) and AgSbF$_6$ (2.1 mg, 6 mol%) was added toluene (1 mL) and stirred at room temperature under argon for 5 min. Then a solution of substrate (**10a**, 0.1 mmol) in toluene (1 mL) was added slowly with the help of syringe pump (ca 1 h) at 100 °C. After addition of the substrate, the solution was continuously stirred for 1 h at 100 °C. The reaction mixture was cooled to room temperature and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA, 20:1) to afford the **11a**. 39.0 mg **10a** was converted to 26.4 mg **11a** (run 1, 80%) and 38.5 mg **1i** was converted to 24.7 mg **2i** (run 2, 76%). So the average yield of two runs was 78%.

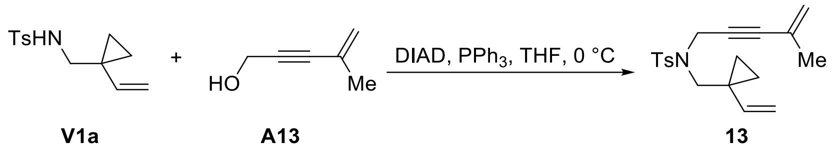
11a: colorless oil. TLC R_f = 0.46 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.71 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.3 Hz, 2H), 5.74 (dd, J = 17.3, 10.4 Hz, 1H), 4.98–4.88 (m, 3H), 4.86 (s, 1H), 4.06–3.96 (m, 2H), 3.66 (d, J = 9.0 Hz, 1H), 2.79 (d, J = 9.0 Hz, 1H), 2.80–2.70 (m, 1H), 2.66–2.57 (m, 1H), 2.43 (s, 3H), 1.95–1.89 (m, 1H), 1.88 (s, 3H), 1.73–1.64 (m, 1H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 143.4, 140.6, 139.0, 138.9 (+), 134.9, 134.2, 129.6 (+), 127.4 (+), 115.1 (–), 112.6 (–), 62.2, 57.1 (–), 46.6 (–), 36.7 (–), 34.5 (–), 21.8 (+), 21.5 (+). HRMS (ESI) calcd for $C_{19}H_{24}NO_2S$ (M+H$^+$): 330.1522. Found: 330.1517.



10b **11b**

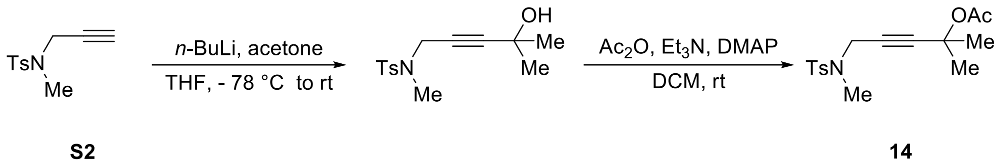
Following the synthetic procedure of **11a**, 45.3 mg **10b** was converted to 16.0 mg **11b** (run 1, 41%) and 45.2 mg **10b** was converted to 15.2 mg **11b** (run 2, 39%). So the average yield of two runs was 40%. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **10b** as a colorless oil.

11b: TLC R_f = 0.65 (PE/EA, 5:1). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.51 (d, J = 8.2 Hz, 2H), 7.37–7.30 (m, 3H), 7.27 (d, J = 8.2 Hz, 2H), 7.14–7.06 (m, 2H), 5.79 (dd, J = 17.3, 10.4 Hz, 1H), 5.19 (s, 1H), 5.16 (s, 1H), 5.04–4.94 (m, 2H), 3.63 (d, J = 9.0 Hz, 1H), 3.33 (dd, J = 15.0, 2.9 Hz, 1H), 2.93 (d, J = 14.4 Hz, 1H), 2.89–2.81 (m, 1H), 2.72 (d, J = 9.0 Hz, 1H), 2.72–2.64 (m, 1H), 2.43 (s, 3H), 1.97 (dd, J = 12.2, 6.5 Hz, 1H), 1.74 (ddd, J = 12.2, 10.7, 8.8 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 144.9, 143.2, 142.9, 141.1, 139.1 (+), 134.2, 134.0, 129.5 (+), 128.2 (+), 127.8 (+), 127.7 (+), 127.4 (+), 116.3 (–), 112.8 (–), 62.0, 57.6 (–), 46.1 (–), 36.9 (–), 34.8 (–), 21.5 (+). HRMS (ESI) calcd for $C_{24}H_{26}NO_2S$ (M+H$^+$): 392.1679. Found: 392.1670.



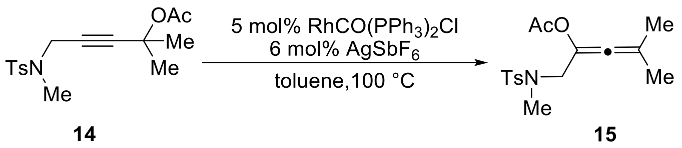
Following the general procedure A, **V1a** (152 mg, 0.6 mmol), **A13**[12] (79 mg, 0.8 mmol), DIAD (246 mg, 1.2 mmol), PPh_3 (315 mg, 1.2 mmol), and THF (3 mL) were stirred at rt for 5 h. Purification of the crude product by column chromatography (PE/EA, 50/1) afforded **13** (109 mg, 55%) as a white solid.

13: m.p. = 79–81 °C, TLC R_f = 0.48 (PE/EA, 5:1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 8.3 Hz, 2H), 5.82 (dd, J = 17.4, 10.8 Hz, 1H), 5.13 (dd, J = 17.4, 0.9 Hz, 1H), 5.10–5.05 (m, 1H), 4.98 (dd, J = 10.8, 0.9 Hz, 1H), 4.91 (s, 1H), 4.34 (s, 2H), 3.22 (s, 2H), 2.39 (s, 3H), 1.63–1.59 (m, 3H), 0.72 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.2, 140.0 (+), 135.8, 129.4 (+), 127.8 (+), 125.8, 121.9 (–), 112.4 (–), 87.2, 80.8, 51.6 (–), 36.3 (–), 23.0 (+), 21.4 (+), 19.6, 12.8 (–). HRMS (ESI) calcd for $C_{19}H_{24}NO_2S$ (M+H$^+$): 330.1522. Found: 330.1522.



Following the synthetic procedure of **10a**, sulfonamide **S2**[13] (449 mg, 2 mmol) and acetone (1.16 g, 20 mmol) were converted to product **14** (419 mg, 64%) as a white solid.

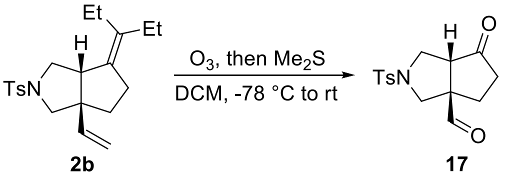
14: m.p. = 102–104 °C, TLC R_f = 0.33 (PE/EA, 5:1). ^1H NMR (400 MHz, C_6D_6): δ 7.66 (d, J = 8.3 Hz, 2H), 6.79 (d, J = 8.3 Hz, 2H), 3.80 (s, 2H), 2.62 (s, 3H), 1.90 (s, 3H), 1.59 (s, 3H), 1.34 (s, 6H). ^{13}C NMR (101 MHz, C_6D_6): δ 168.3, 142.7, 135.6, 129.5 (+), 128.3 (+), 87.1, 77.5, 71.3, 39.9 (–), 34.1 (+), 28.7 (+), 21.3 (+), 21.0 (+). HRMS (ESI) calcd for $C_{16}H_{25}N_2O_4S$ (M+NH$_4^+$): 341.1530. Found: 341.1527.



To a mixture of $Rh(CO)(PPh_3)_2Cl$ (3.5 mg, 5 mol%) and $AgSbF_6$ (2.1 mg, 6 mol%) was added toluene (1 mL) and stirred at room temperature under argon for 5 min. Then a solution of **14** in toluene (1 mL) was added slowly with the help of syringe pump (ca 1 h) at 100 °C. After addition of the substrate, the solution was continuously stirred for 1 h at 100 °C. The reaction mixture was cooled to room temperature and concentrated. The crude product was purified by flash column chromatography on silica gel (PE/EA, 20:1 then 10:1) to afford the corresponding product **15** (8.4 mg, 26%) as a colorless oil.

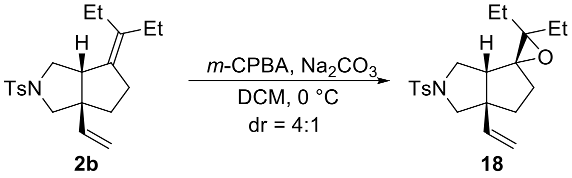
15: TLC R_f = 0.42 (PE/EA, 5:1). ^1H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.3 Hz, 2H), 3.74 (s, 2H), 2.76 (s, 3H), 2.42 (s, 3H), 2.11 (s, 3H), 1.78 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 193.3, 168.9, 143.3, 135.0, 129.6 (+), 127.4 (+), 114.1, 109.3, 51.6 (–), 34.2 (+), 21.5 (+), 21.2 (+), 20.9 (+). HRMS (ESI) calcd for $C_{16}H_{22}NO_4S$ (M+H$^+$): 324.1264. Found: 324.1261.

6. Derivations of 1a and 2a



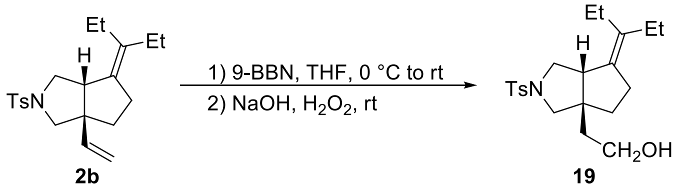
A solution of **2b** (186 mg, 0.52 mmol) in 5 mL of DCM was ozonized at -78 ℃ until TLC indicated complete consumption of the starting material. Excess ozone was purged with a stream of dry N_2 and Me_2S (0.5 mL) was added. The mixture was warmed to room temperature and stirred for 2 h. The reaction was concentrated, and the residue was purified by flash column chromatography on silica gel (PE/EA = 1:2) to afford **17** (81.4 mg, 51%) as a colorless oil.

17: TLC R_f = 0.50 (PE/EA, 1:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.57 (s, 1H), 7.68 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 8.3 Hz, 2H), 3.65 (dd, J = 10.1, 2.2 Hz, 1H), 3.60 (d, J = 10.5 Hz, 1H), 3.27 (d, J = 10.5 Hz, 1H), 3.10 (dd, J = 10.1, 8.4 Hz, 1H), 2.86 (dd, J = 8.4, 2.2 Hz, 1H), 2.45 (s, 3H), 2.52–2.34 (m, 3H), 2.06–1.95 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 214.2, 198.3, 144.3, 131.6, 129.8 (+), 127.8 (+), 60.9, 52.8 (–), 52.0 (+), 50.1 (–), 36.7 (–), 25.9 (–), 21.5 (+). HRMS (ESI) calcd for $C_{15}H_{18}NO_4S$ (M+H$^+$): 308.0951. Found: 308.0951.



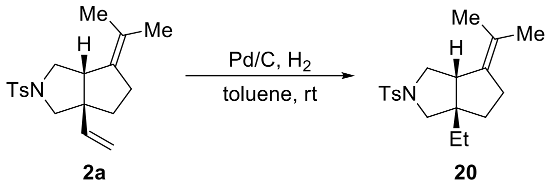
m-CPBA (20.9 mg, 0.12 mmol) and Na_2CO_3 (20 mg, 0.20 mmol) was added to a solution of **2b** (36.3 mg, 0.10 mmol) in DCM (3.0 mL). The reaction mixture was stirred at 0 ℃ for 2 h. The mixture was concentrated directly and the residue was purified by flash column chromatography on silica gel (PE/EA = 10:1) to afford **18** (28.9 mg, 76% yield) as a colorless oil. The ratio of two isomers was 4:1. The two isomers were inseparable.

Major isomer of 18: TLC R_f = 0.37 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 5.92 (dd, J = 17.4, 10.7 Hz, 1H), 5.09 (d, J = 17.4 Hz, 1H), 5.04 (d, J = 10.7 Hz, 1H), 3.50–3.41 (m, 1H), 3.26 (d, J = 9.6 Hz, 1H), 3.11 (d, J = 9.6 Hz, 1H), 3.05 (dd, J = 10.2, 7.1 Hz, 1H), 2.45 (s, 3H), 2.22 (dd, J = 9.6, 7.1 Hz, 1H), 2.17–2.09 (m, 1H), 2.03–1.95 (m, 1H), 1.78–1.63 (m, 4H), 1.32–1.23 (m, 2H), 0.98 (t, J = 7.6 Hz, 3H), 0.91 (t, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.7, 141.0 (+), 132.6, 129.7 (+), 127.7 (+), 113.2 (–), 76.6, 66.8, 57.6 (–), 55.6, 53.2 (+), 50.9 (–), 33.9 (–), 29.7 (–), 24.5 (–), 24.2 (–), 21.5 (+), 9.5 (+), 8.8 (+). HRMS (ESI) calcd for $C_{21}H_{30}NO_3S$ (M+H$^+$): 376.1941. Found: 376.1945.



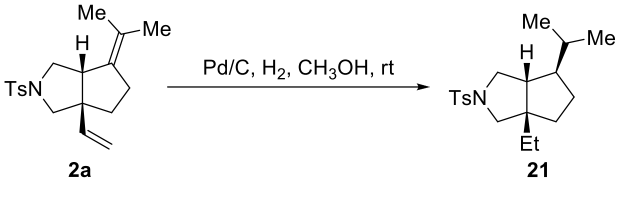
A solution of compound **2b** (119 mg, 0.33 mmol) in THF (6.5 mL), 9- BBN (0.5 M) in THF (3.4 mL, 1.70 mmol) was added at 0 °C. The ice bath was removed after 5 min and the reaction mixture was stirred at room temperature for 8 h. Then NaOH (3.4 mL, 3 M) and 30% H_2O_2 (5.0 mL) were added sequentially to the solution at 0 °C. The reaction mixture was stirred for 2 h, then diluted with diethyl ether, and washed with water and brine and dried over anhydrous Na_2SO_4. The solvent was removed and the residue was purified by flash column chromatography on silica gel (PE/EA = 3:1) to afford **19** (105 mg, 85% yield) as a white solid.

19: m.p. = 101–104 °C, TLC R_f = 0.50 (PE/EA, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 3.74–3.59 (m, 2H), 3.54 (t, *J* = 8.5 Hz, 1H), 3.19 –3.08 (m, 2H), 2.87 –2.73 (m, 2H), 2.44 (s, 3H), 2.30–2.18 (m, 2H), 1.98–1.87 (m, 4H), 1.70–1.55 (m, 3H), 1.52 –1.40 (m, 2H), 0.92 (t, *J* = 5.8 Hz, 3H), 0.88 (t, *J* = 5.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.4, 137.2, 135.4, 133.1, 129.6 (+), 127.6 (+), 60.0 (–), 57.2 (–), 53.6 (–), 52.2, 51.7 (+), 40.0 (–), 33.3 (–), 28.1 (–), 25.5 (–), 24.7 (–), 21.5 (+), 13.2 (+), 12.5 (+). HRMS (ESI) calcd for $C_{21}H_{32}NO_3S$ (M+H$^+$): 378.2097. Found: 378.2097.



Compound **2a** (33.7 mg, 0.10 mmol) was dissolved in toluene (4 mL) and Pd/C (10%, 10.6 mg, 0.01 mmol) was added to it and the reaction mixture was stirred at room temperature under a balloon pressure of hydrogen gas for 90 min. The mixture was filtered through Celite by washing with EA and followed by removal of the solvent and column chromatography through silica gel (PE/EA 10:1) to afford the product **20** (31.1 mg, 92%) as a colorless oil.

20: TLC R_f = 0.46 (PE/EA, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 3.54–3.45 (m, 1H), 3.06 (s, 2H), 2.94 (dd, *J* = 9.6, 6.1 Hz, 1H), 2.74–2.64 (m, 1H), 2.44 (s, 3H), 2.29–2.11 (m, 2H), 1.56 (s, 3H), 1.55 (s, 3H), 1.53–1.26 (m, 4H), 0.81 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.2, 136.7, 133.2, 129.4 (+), 127.6 (+), 124.5, 56.7 (–), 54.4, 53.7 (–), 51.5 (+), 33.3 (–), 30.2 (–), 29.0 (–), 21.5 (+), 21.2 (+), 21.0 (+), 9.6 (+). HRMS (ESI) calcd for $C_{19}H_{28}NO_2S$ (M+H$^+$): 334.1835. Found: 334.1841.



Compound **2a** (33.5 mg, 0.10 mmol) was dissolved in CH_3OH (4 mL) and Pd/C (10%, 12.1 mg, 0.01 mmol) was added to it and the reaction mixture was stirred at room temperature under a balloon pressure of hydrogen gas for 3 h. The mixture was filtered through Celite by washing with EA and followed by removal of the solvent and column chromatography through silica gel (PE/EA 10:1) to afford the product **21** (33.3 mg, 98%) as a colorless oil. The ratio of two isomers was 10:1.

21: TLC R_f = 0.33 (PE/EA, 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ7.68 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 3.14 (dd, *J* = 9.4, 1.9 Hz, 1H), 3.09 (d, *J* = 9.2 Hz, 1H), 2.86 (dd, *J* = 9.4, 7.6 Hz, 1H), 2.52 (d, *J* = 9.2 Hz, 1H), 2.44 (s, 3H), 1.80–1.65 (m, 3H), 1.56 – 1.46 (m, 1H), 1.43–1.30 (m, 3H), 1.25–1.15 (m, 2H), 0.86 (d, *J* = 6.3 Hz, 3H), 0.84 (d, *J* = 6.3 Hz, 3H), 0.77 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 143.4, 132.1, 129.4 (+), 128.0 (+), 58.2 (–), 54.6 (+), 54.6 (–), 54.5, 53.0 (+), 35.6 (–), 33.0 (+), 31.4 (–), 30.2 (–), 21.6 (+), 21.5 (+), 20.7 (+), 9.7 (+). HRMS (ESI) calcd for $C_{19}H_{30}NO_2S$ (M+H$^+$): 336.1992. Found: 336.1991.

7. References

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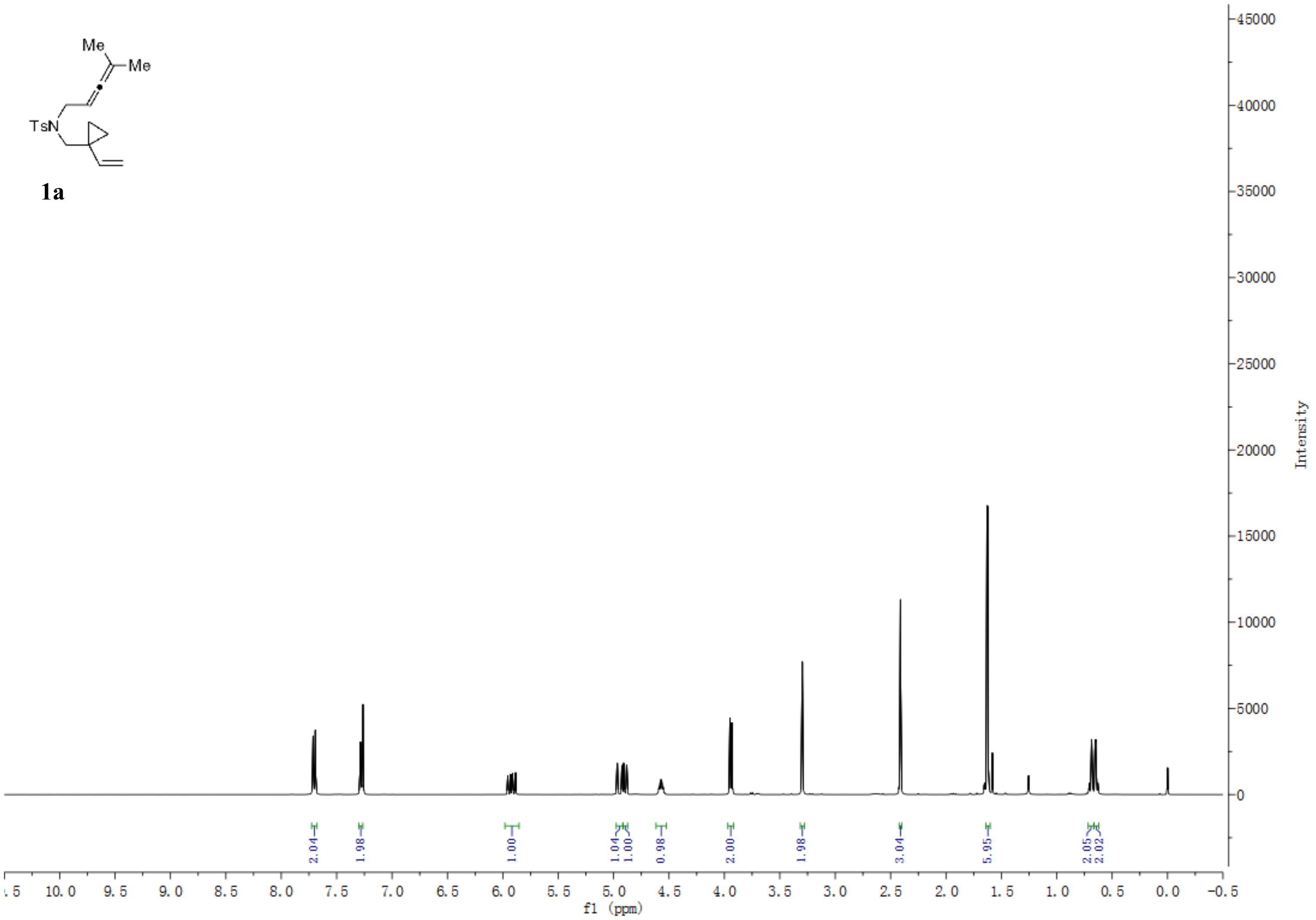
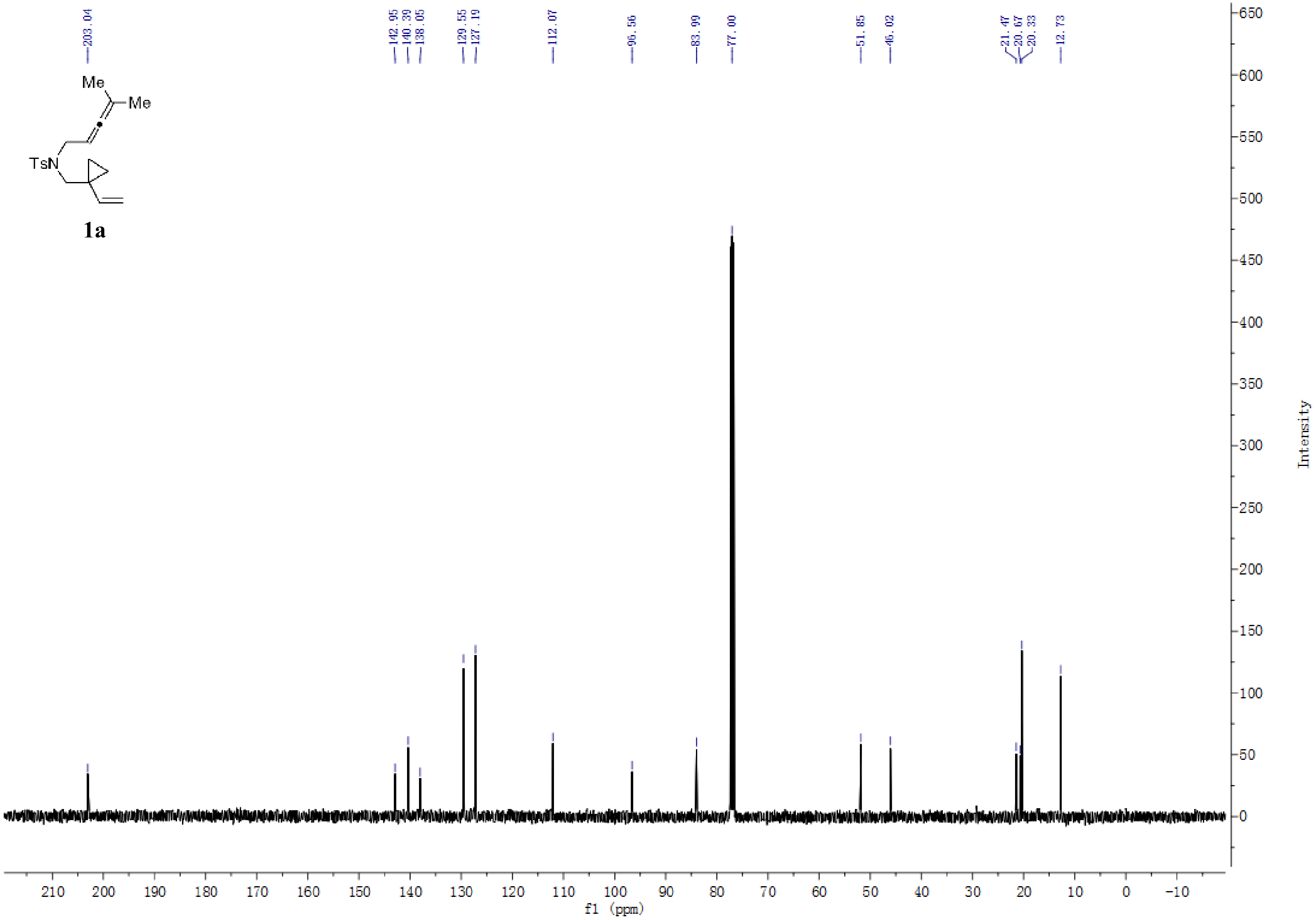
13. Wang, Q.; Jiang, Y.; Sun, R.; Tang, X.-Y.; Shi, M. *Chem. Eur. J.* **2016,** *22,* 14739.

8. Spectra of new compounds



1a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21.47
20.67
20.33
12.73
Me
Me
TsN
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200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
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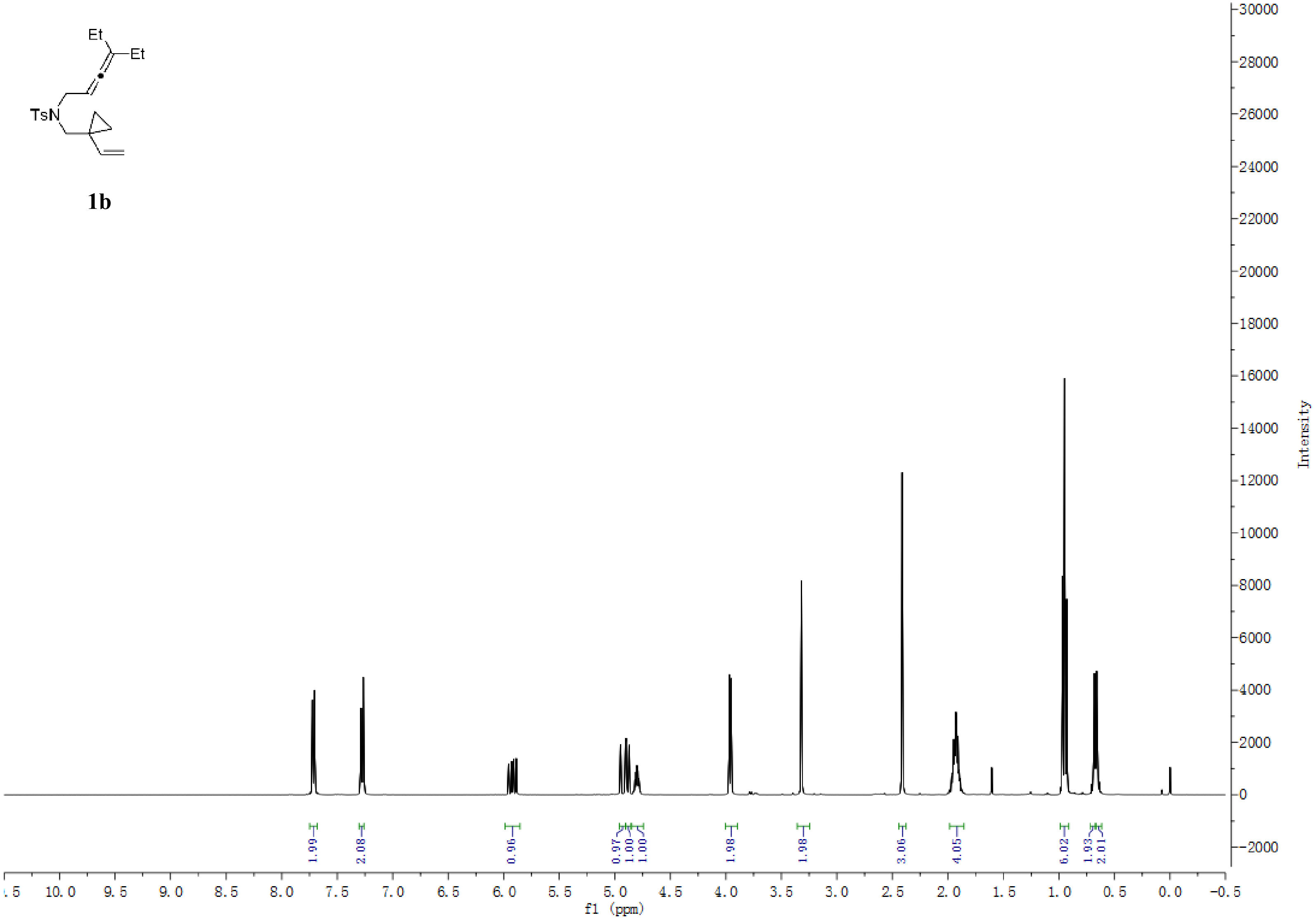
550
500
450
400
350
300
250
200
150
100
50
0
Intensity

1a


Et
Et
TsN

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6.5
6.0
5.5
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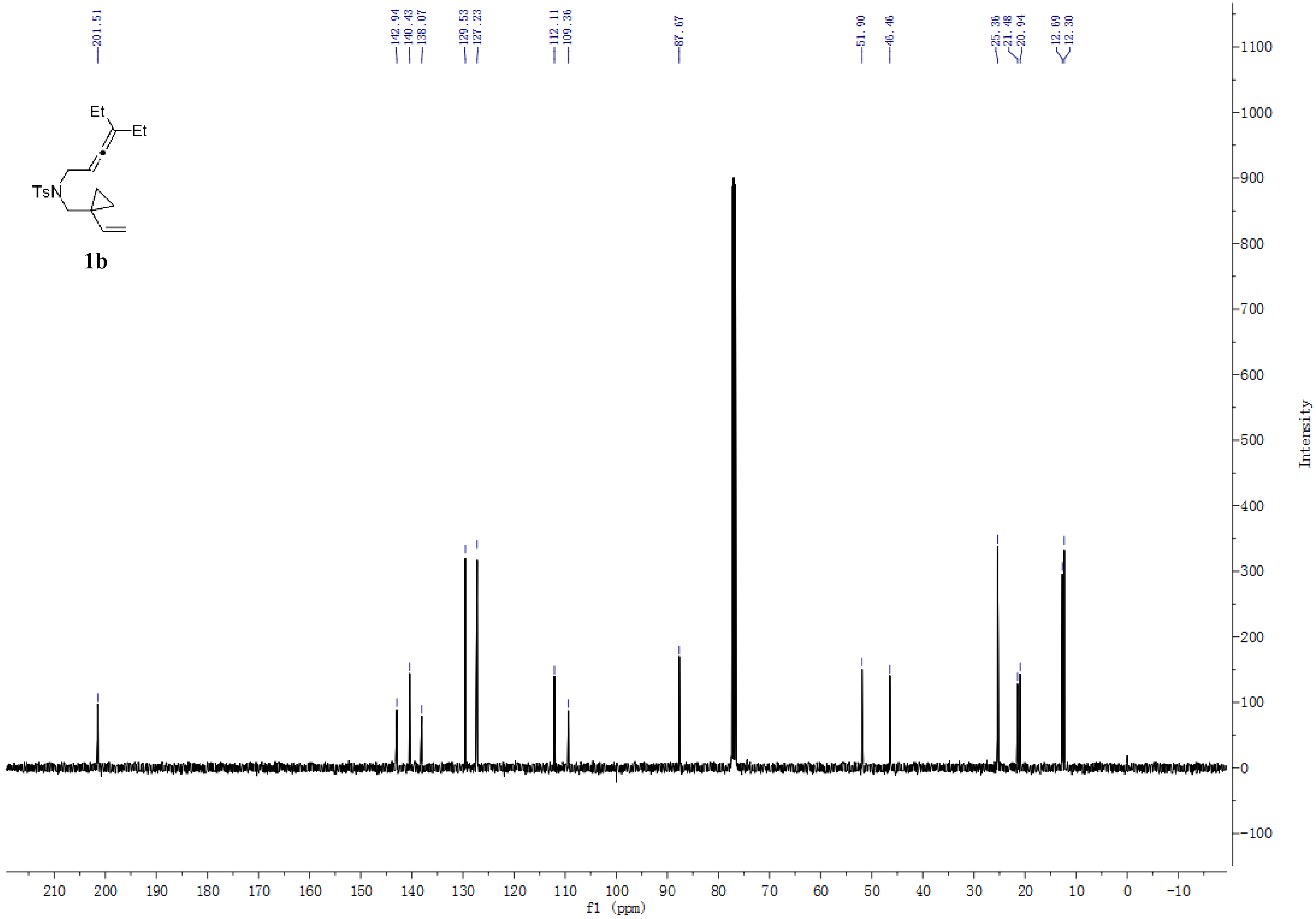
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Et
TsN
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20
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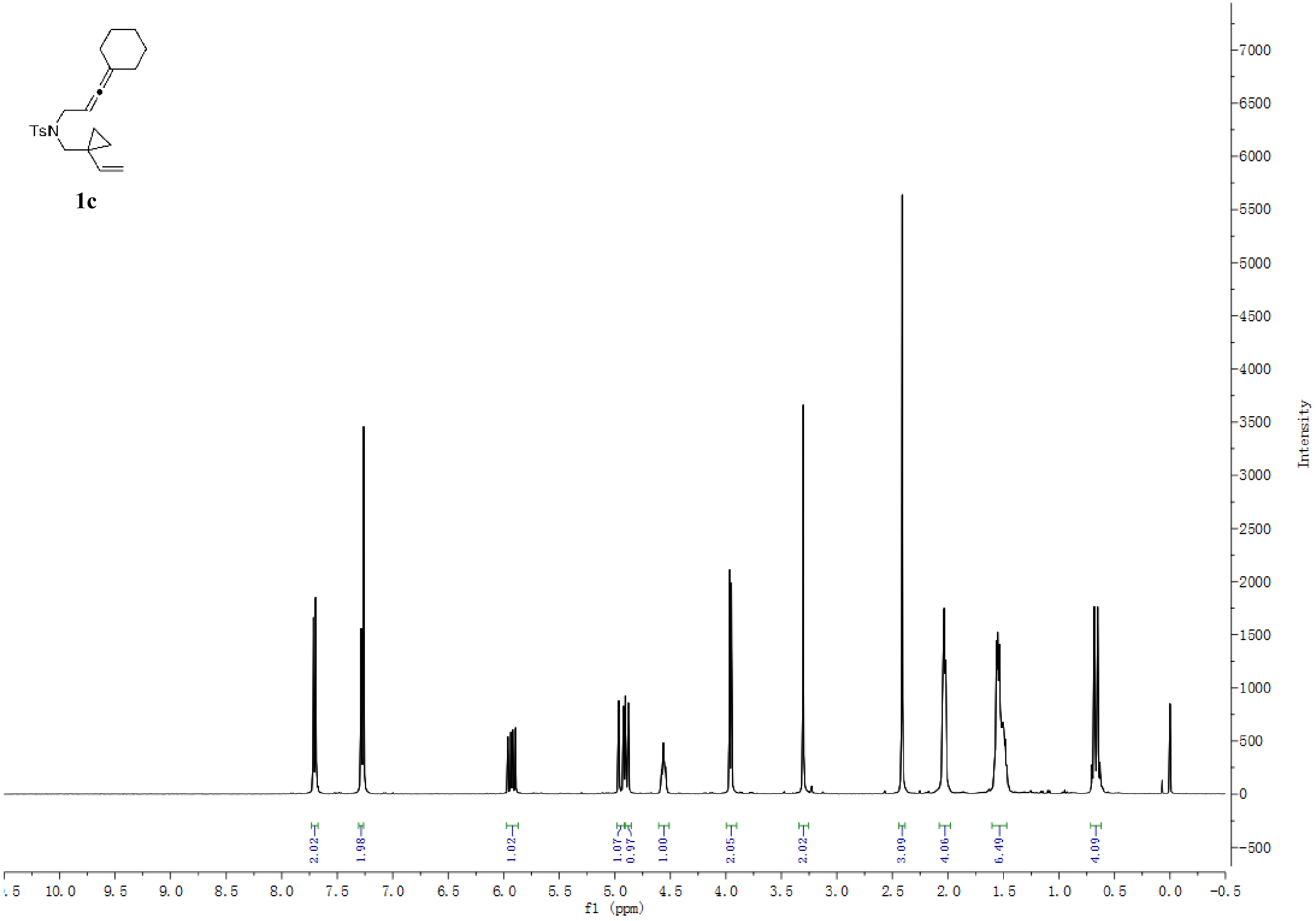
Intensity

1b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f1 (ppm)
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0
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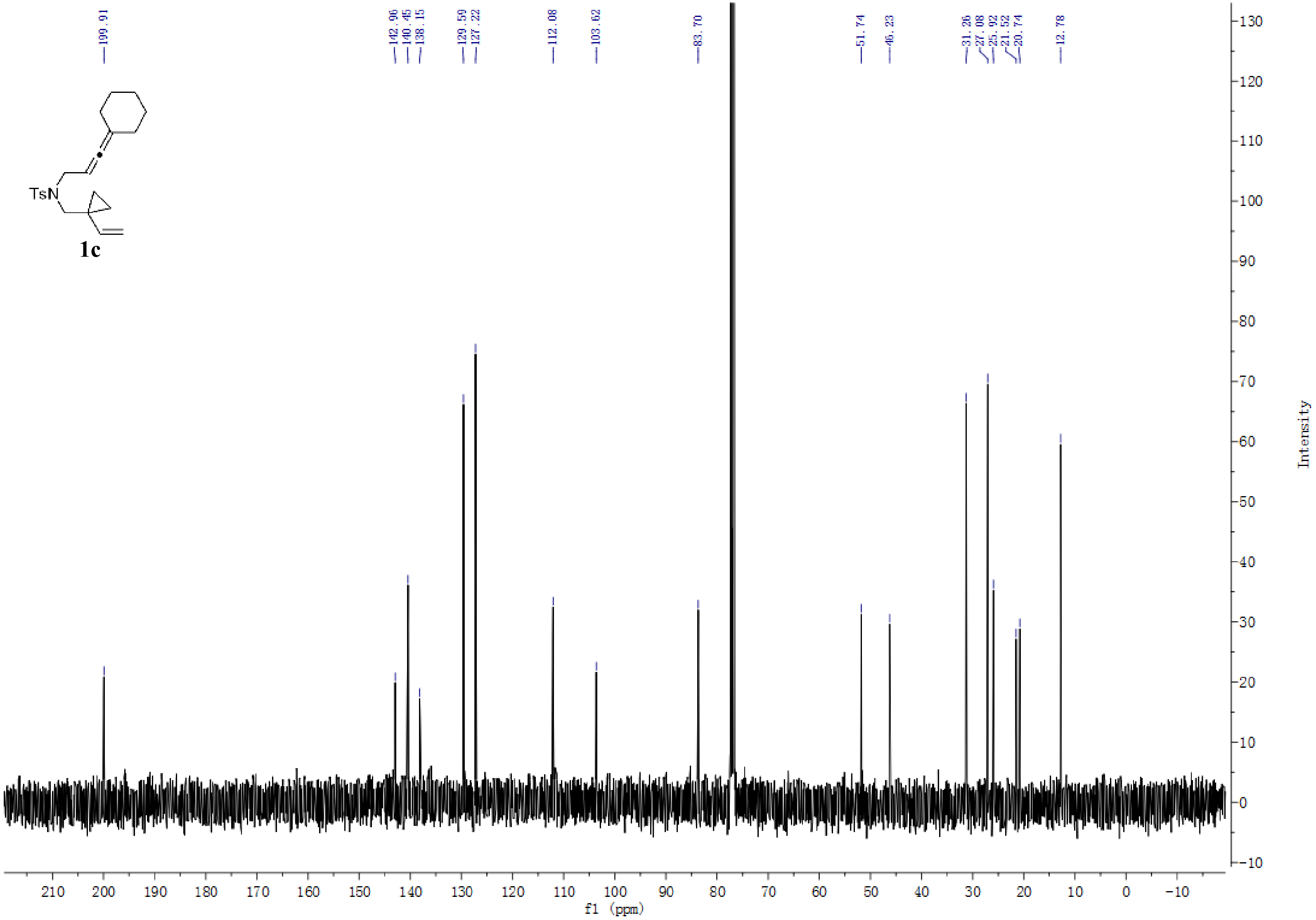
Intensity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1c
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200
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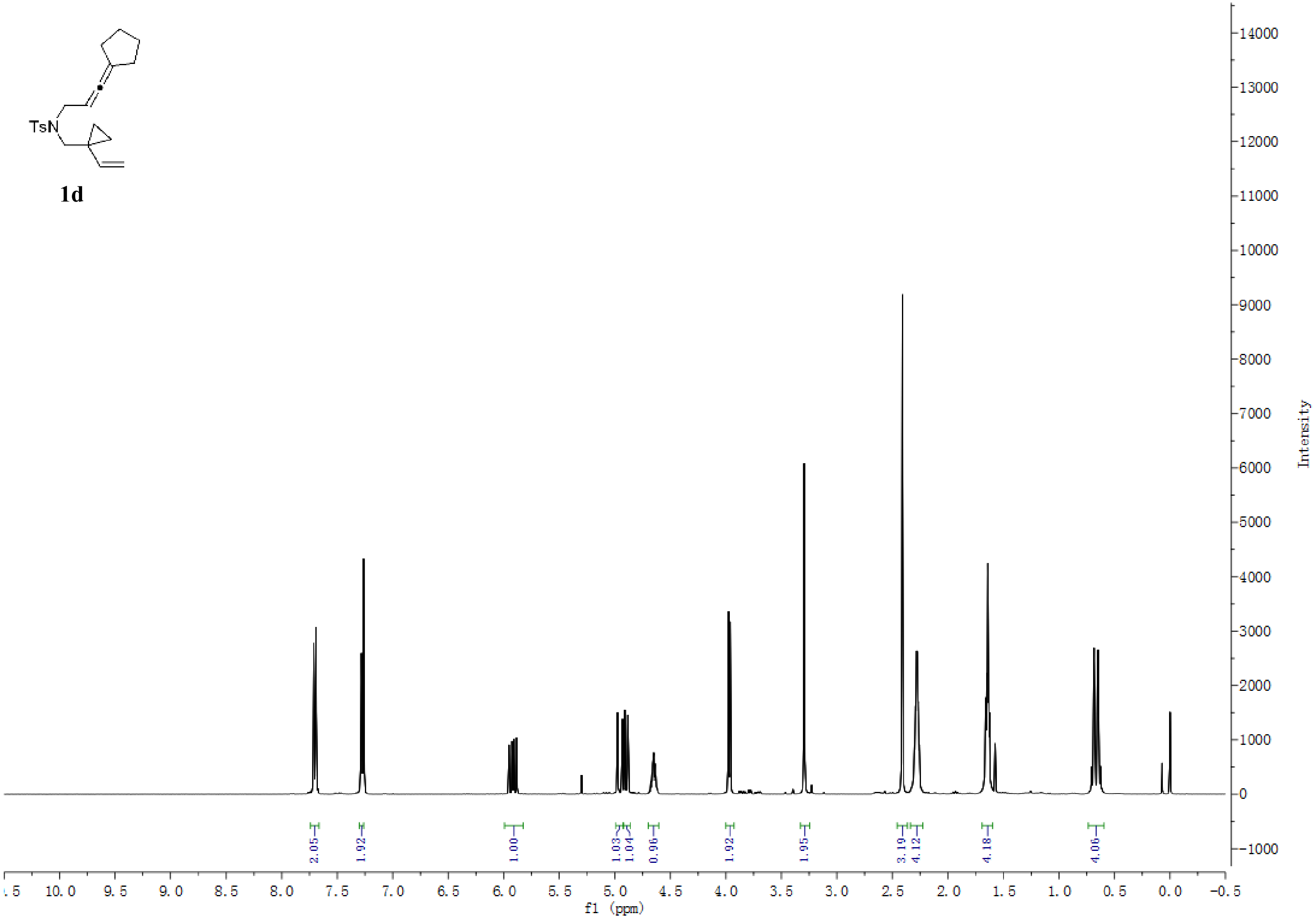
Intensity



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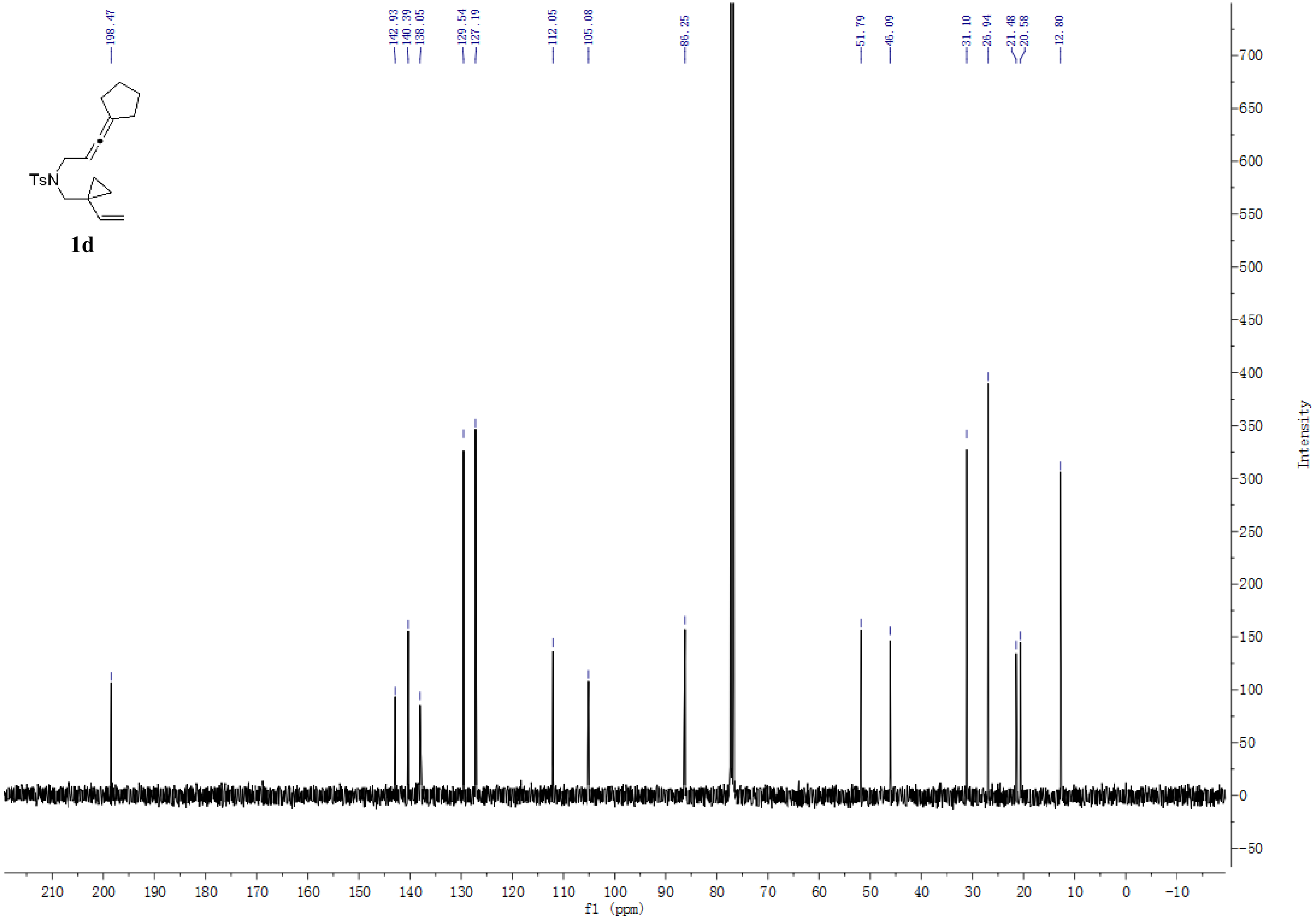
Intensity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1d
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200
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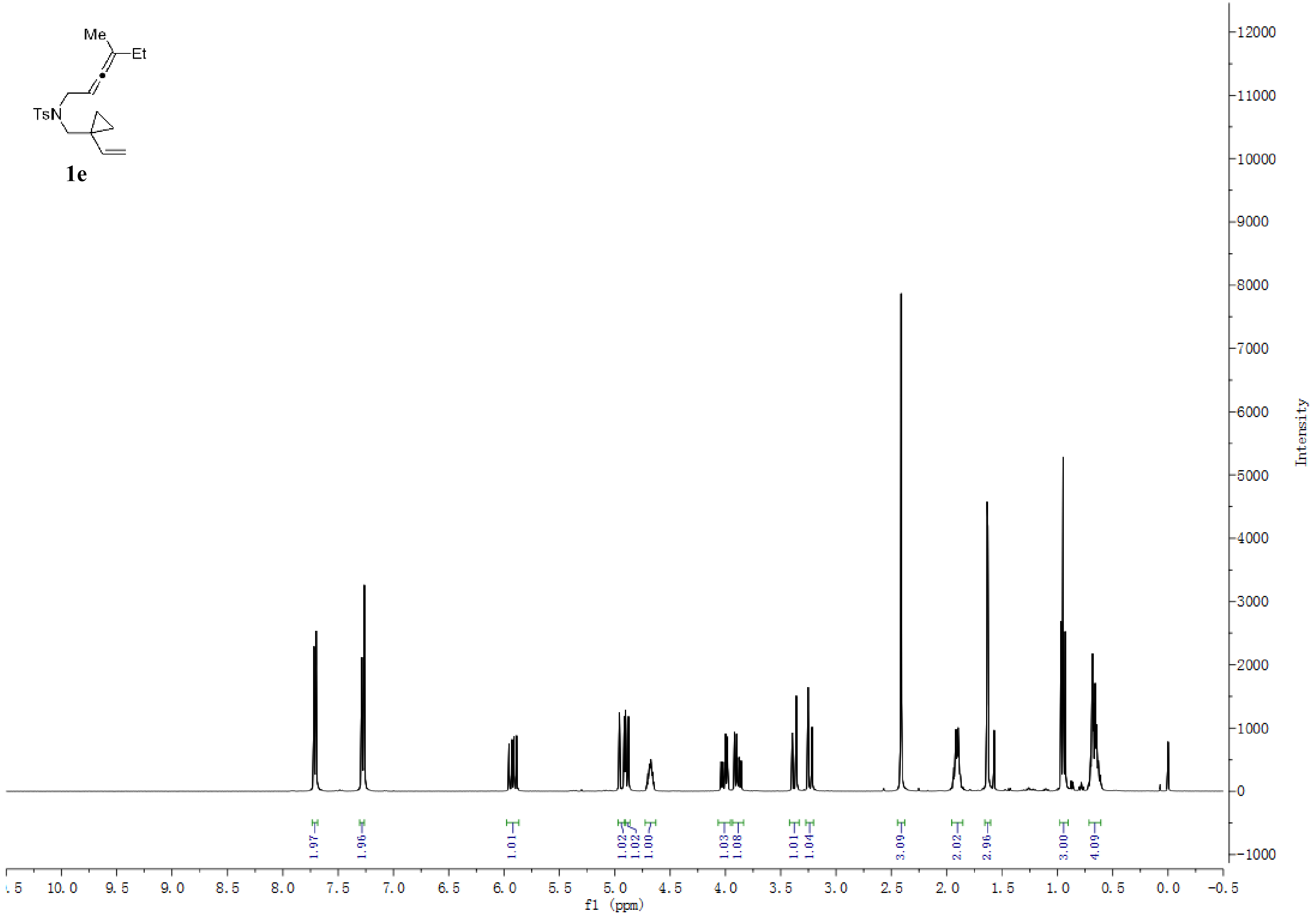
Intensity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Intensity
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1.01
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1.00
1.03
1.08
1.01
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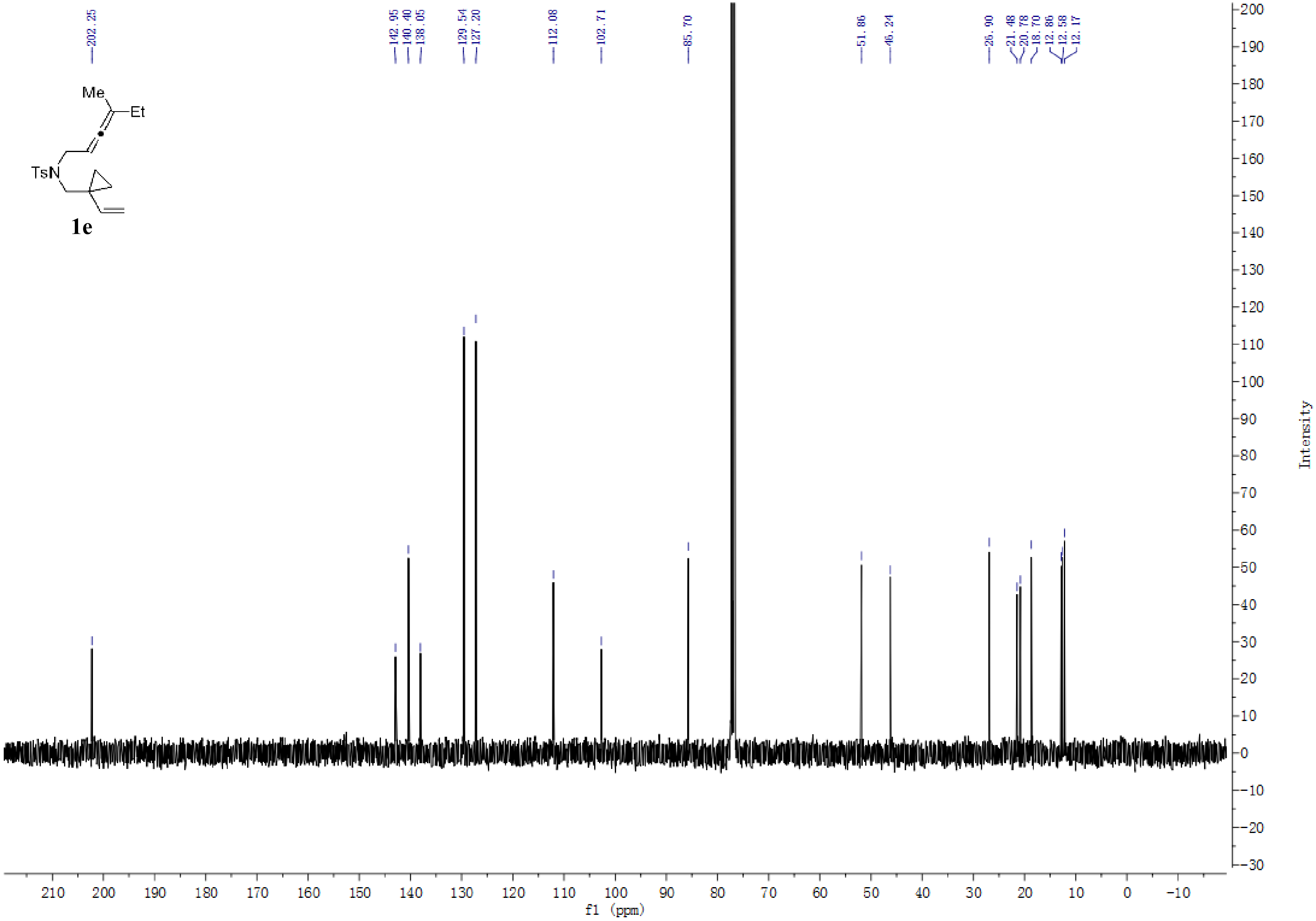
f1 (ppm)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Et
TsN
1e
f1 (ppm)
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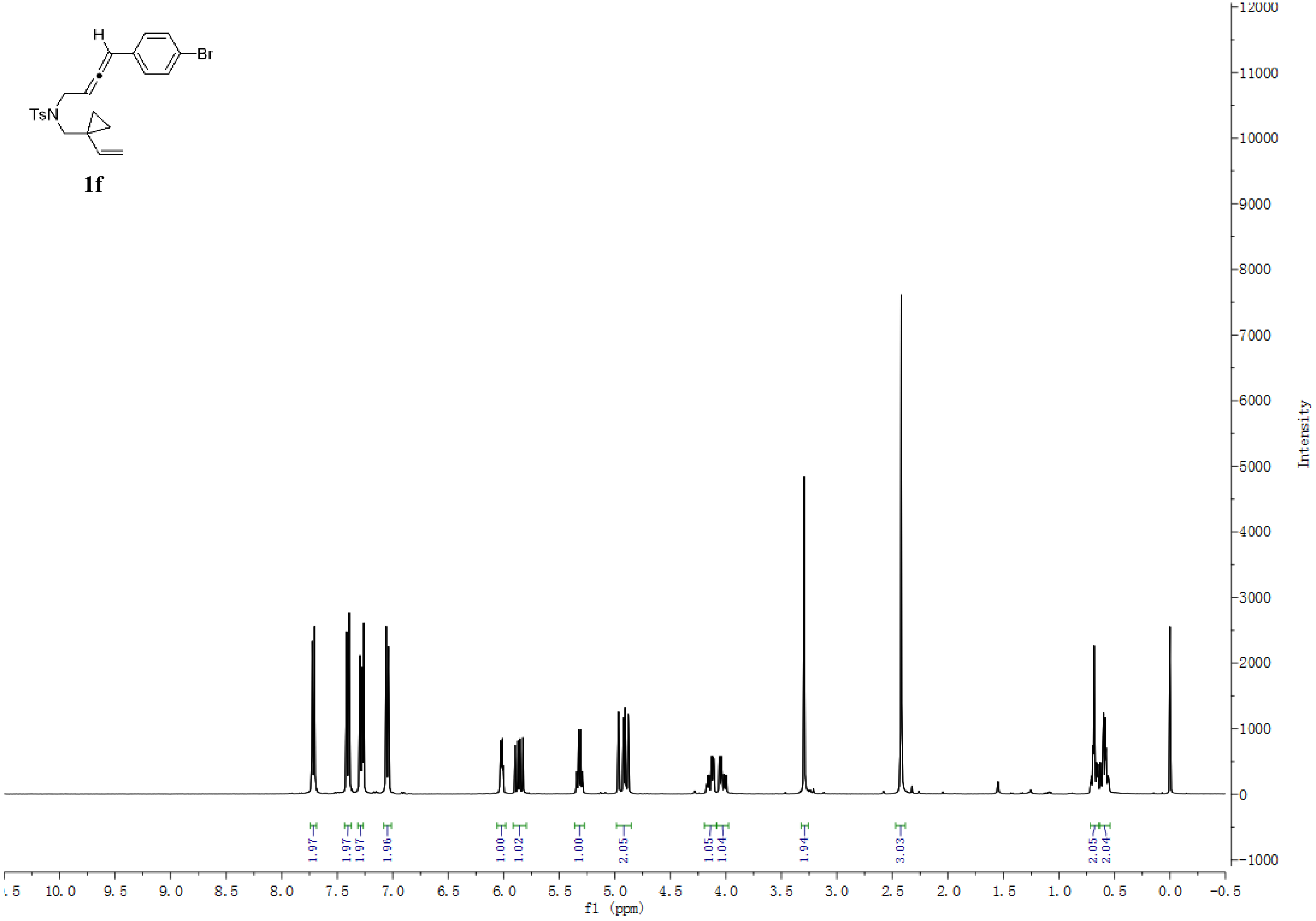

1f

H
Br
TsN
Intensity
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10000
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1.97
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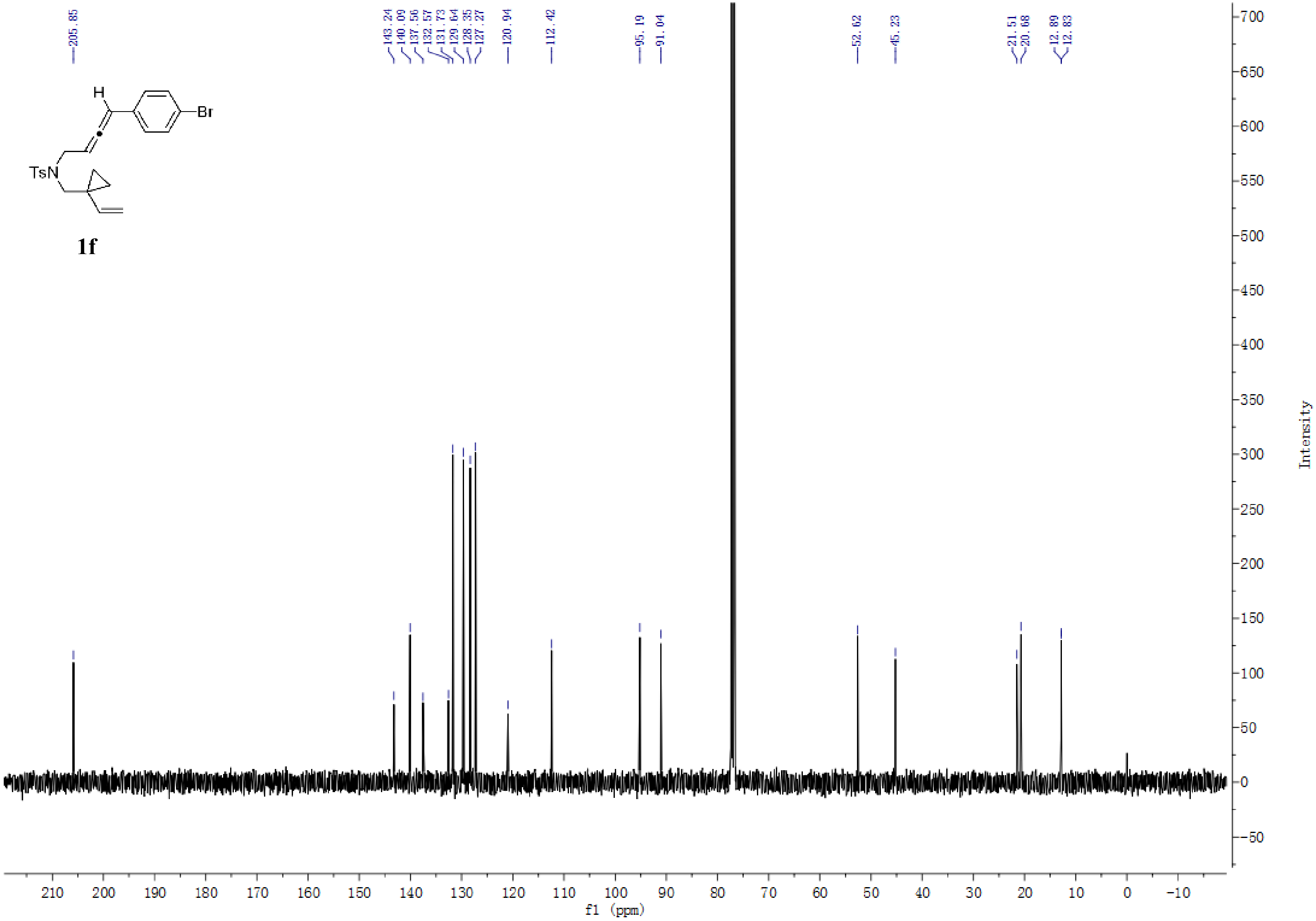
−0.5
f1 (ppm)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H
Br
TsN
1f
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650
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Intensity
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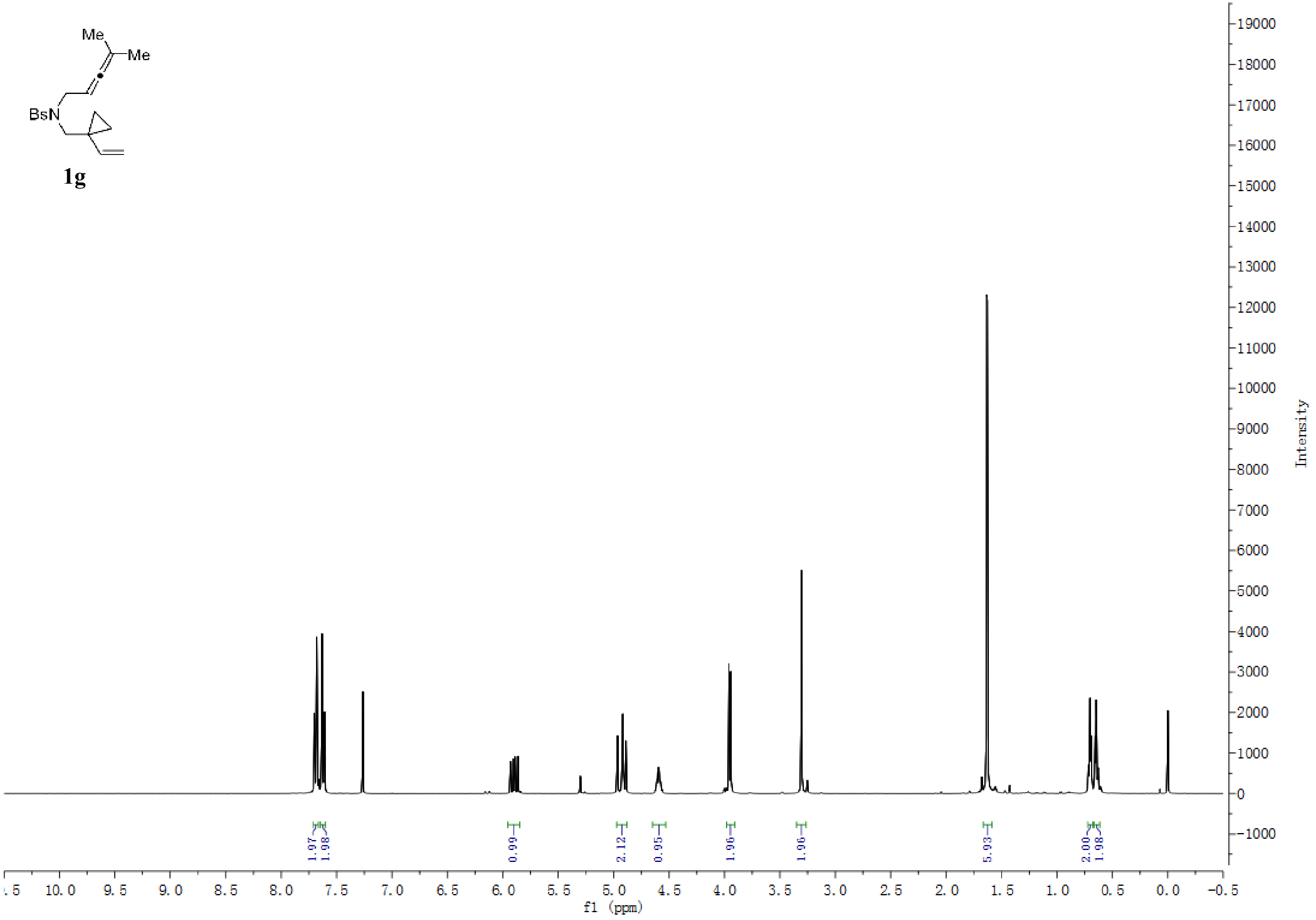
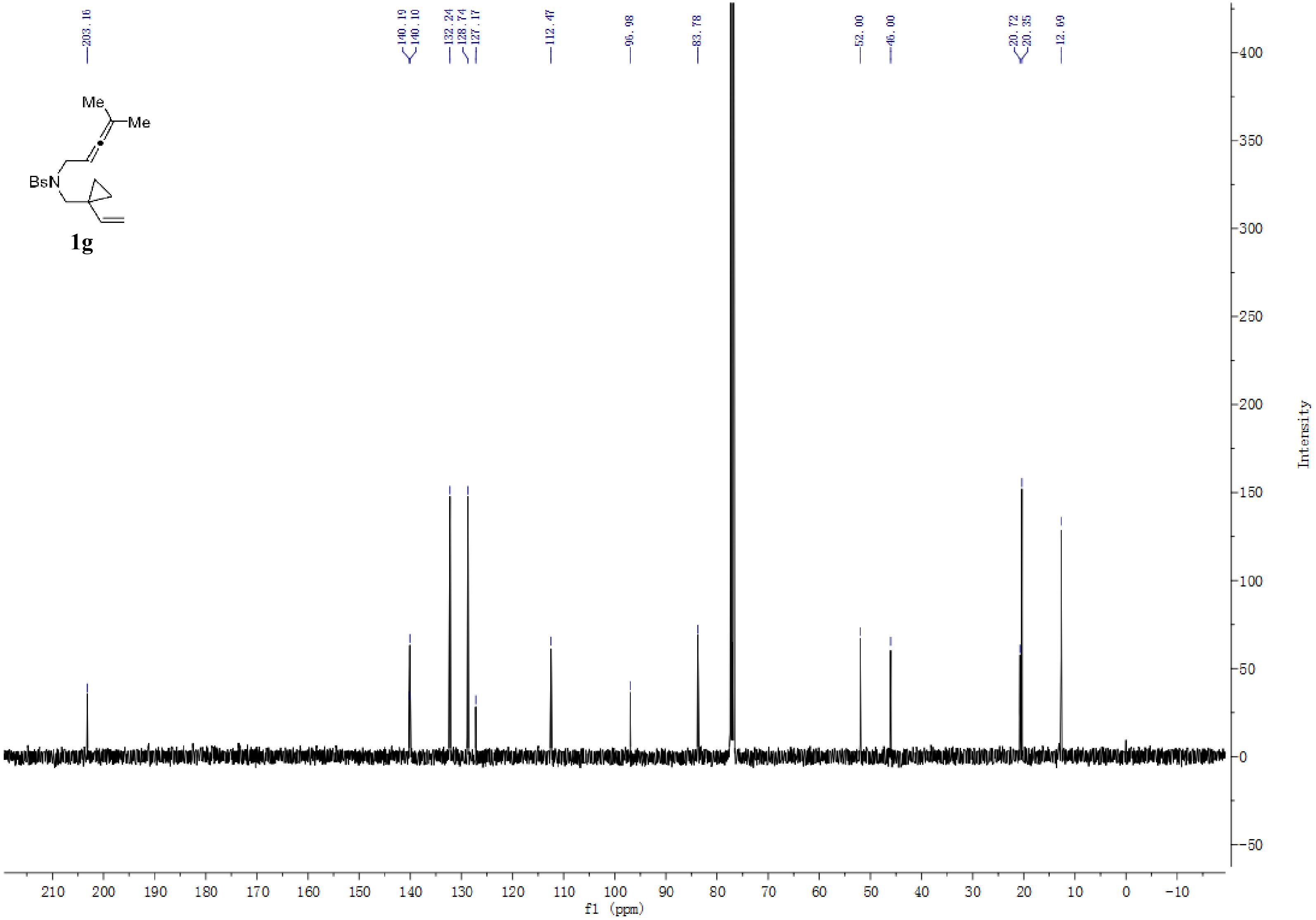
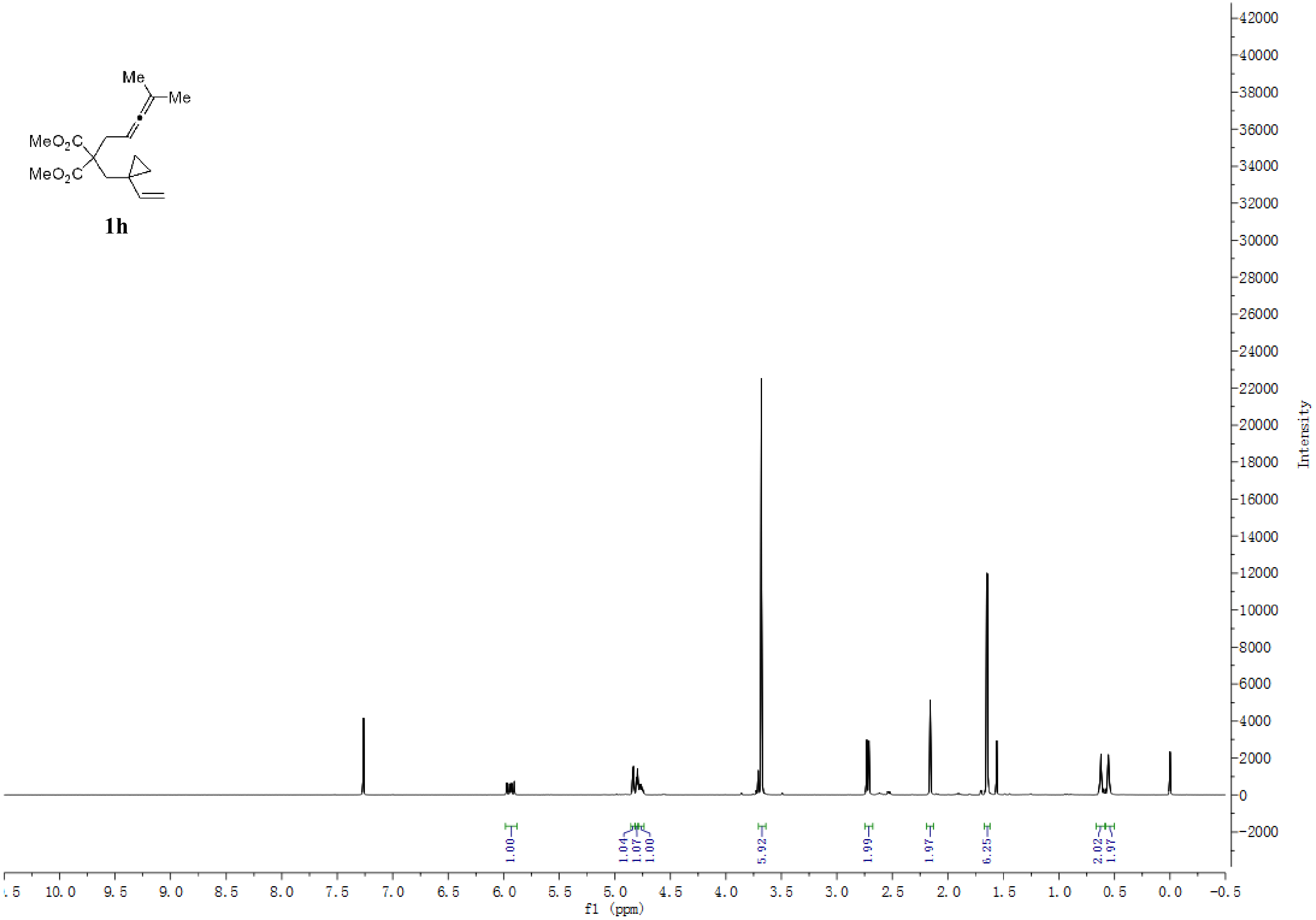
-10
f1 (ppm)


Me
Me
BsN
1g
1.97
1.98
0.99
2.12
0.95
1.96
1.96
5.93
2.00
1.98
.5
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)
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
Intensity



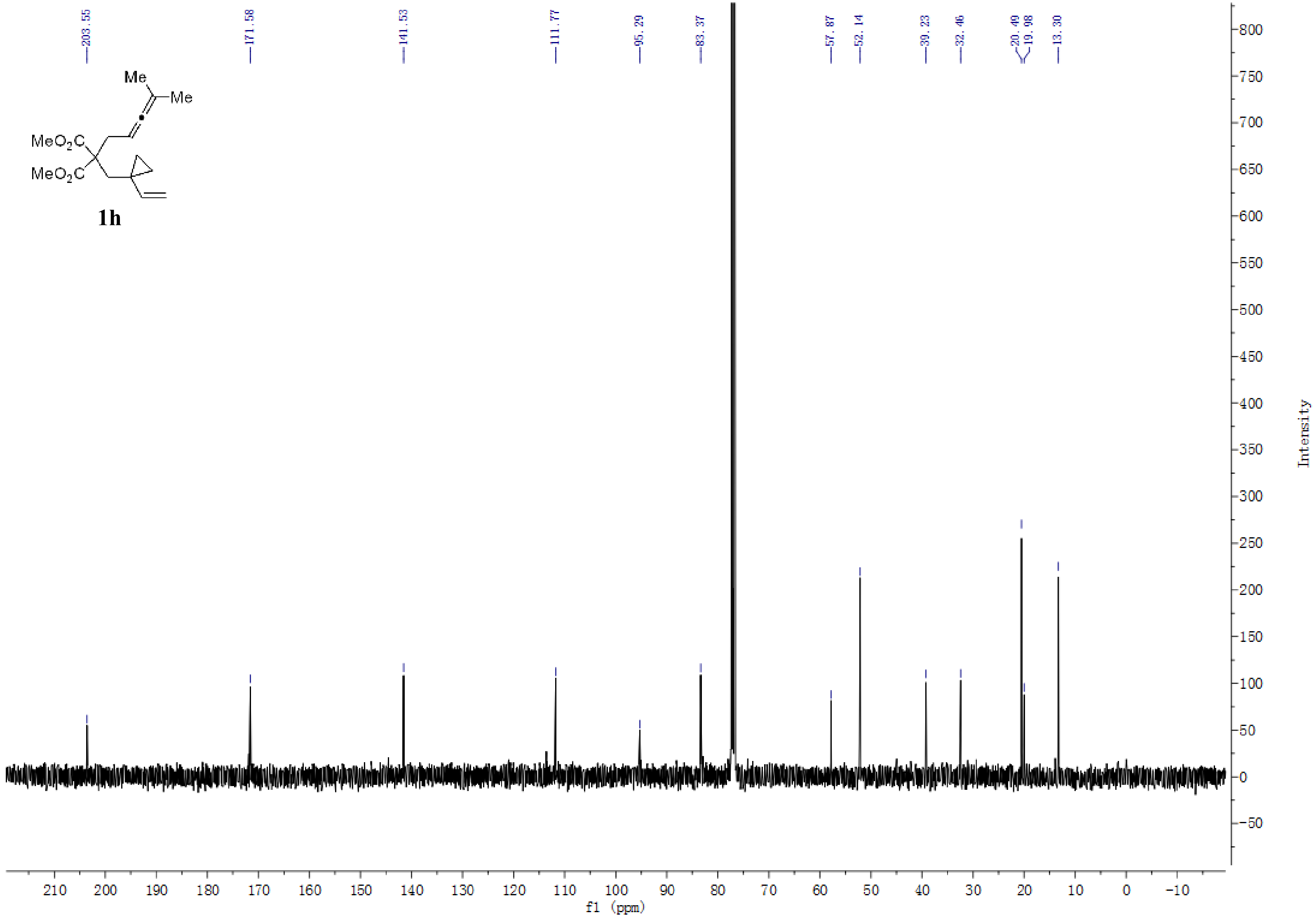
1g

203.16
140.19
140.10
132.24
128.74
127.17
112.47
96.98
83.78
52.00
46.00
20.72
20.35
12.69
Me
Me
BsN
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)
400
350
300
250
200
150
100
50
0
-50
Intensity


Me
Me
MeO2C
MeO2C

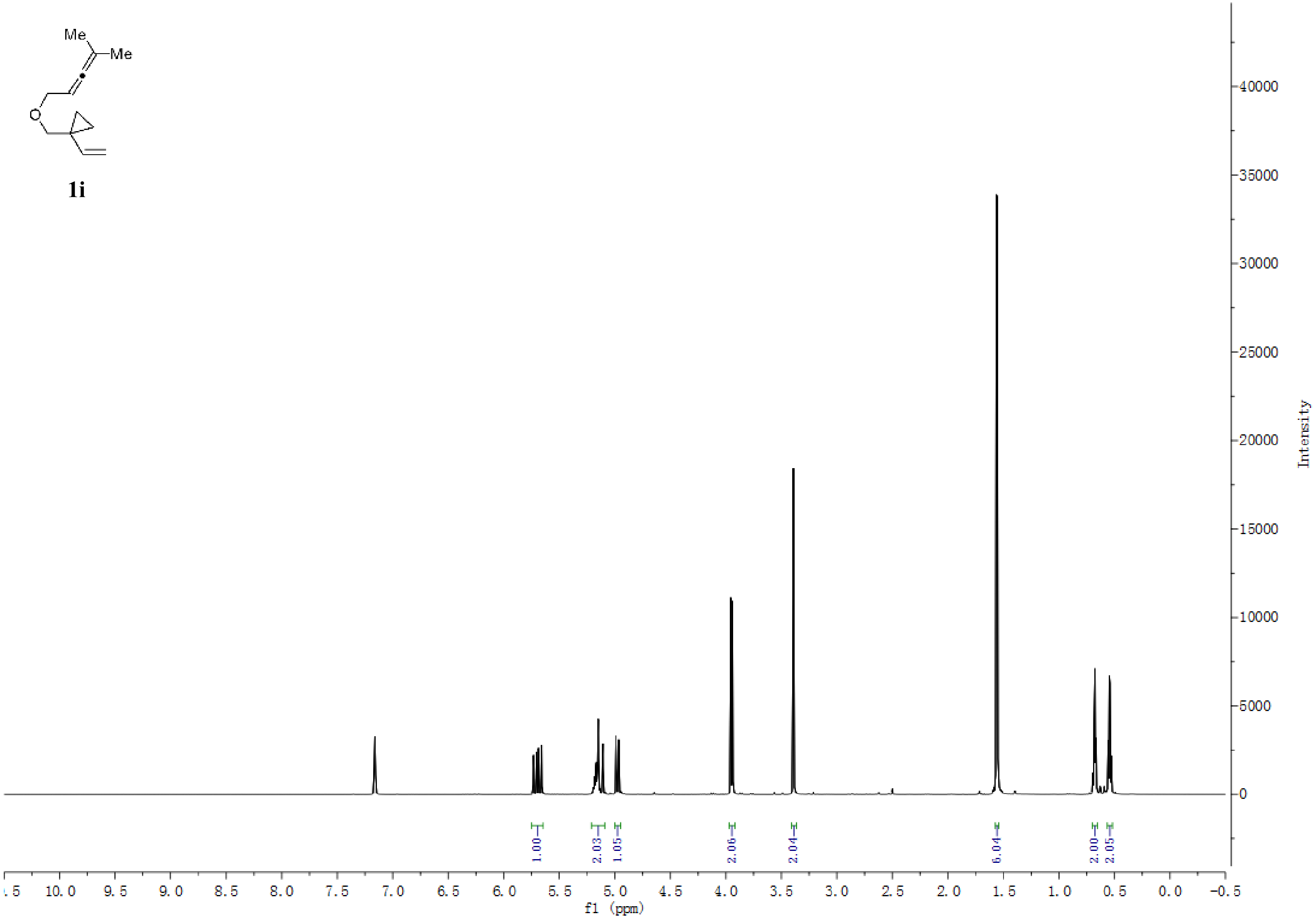
1h

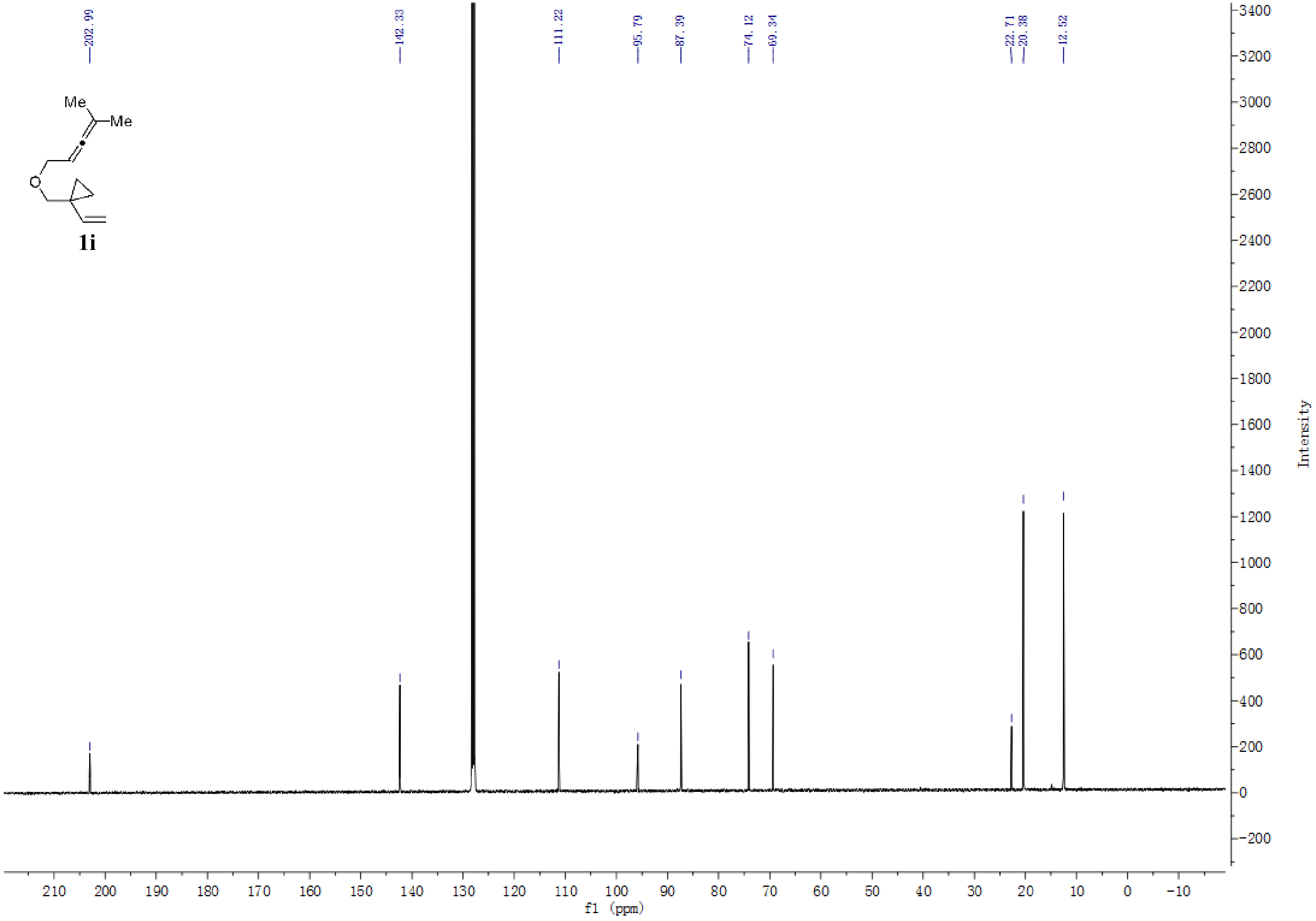
42000
40000
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
Intensity
1.00
1.04
1.07
1.00
5.92
1.99
1.97
6.25
2.02
1.97
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

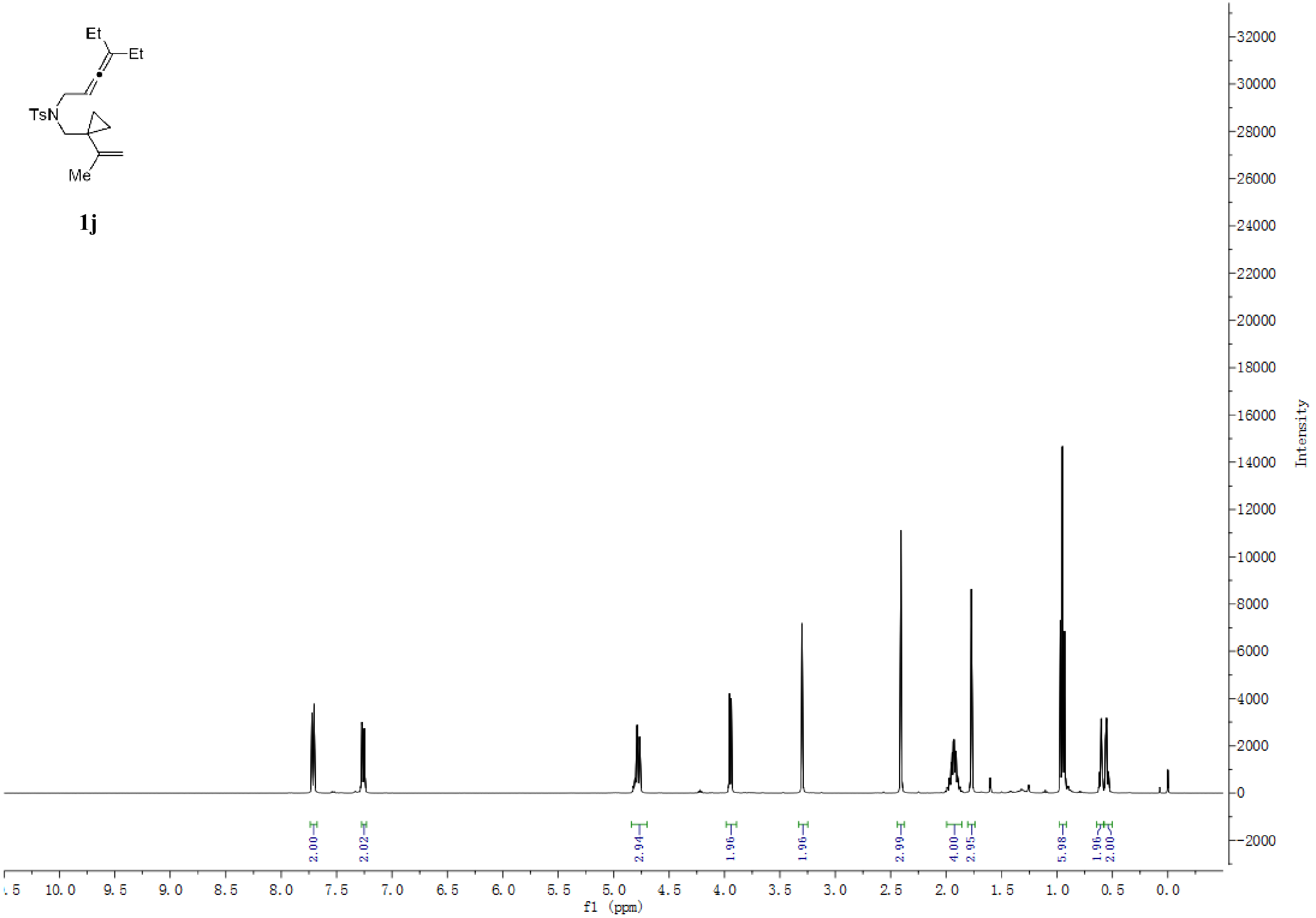

203.55
171.58
141.53
111.77
95.29
83.37
57.87
52.14
39.23
32.46
20.49
19.98
13.30
Me
Me
MeO_2C
MeO_2C
1h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
Intensity

Me
Me
O

1i

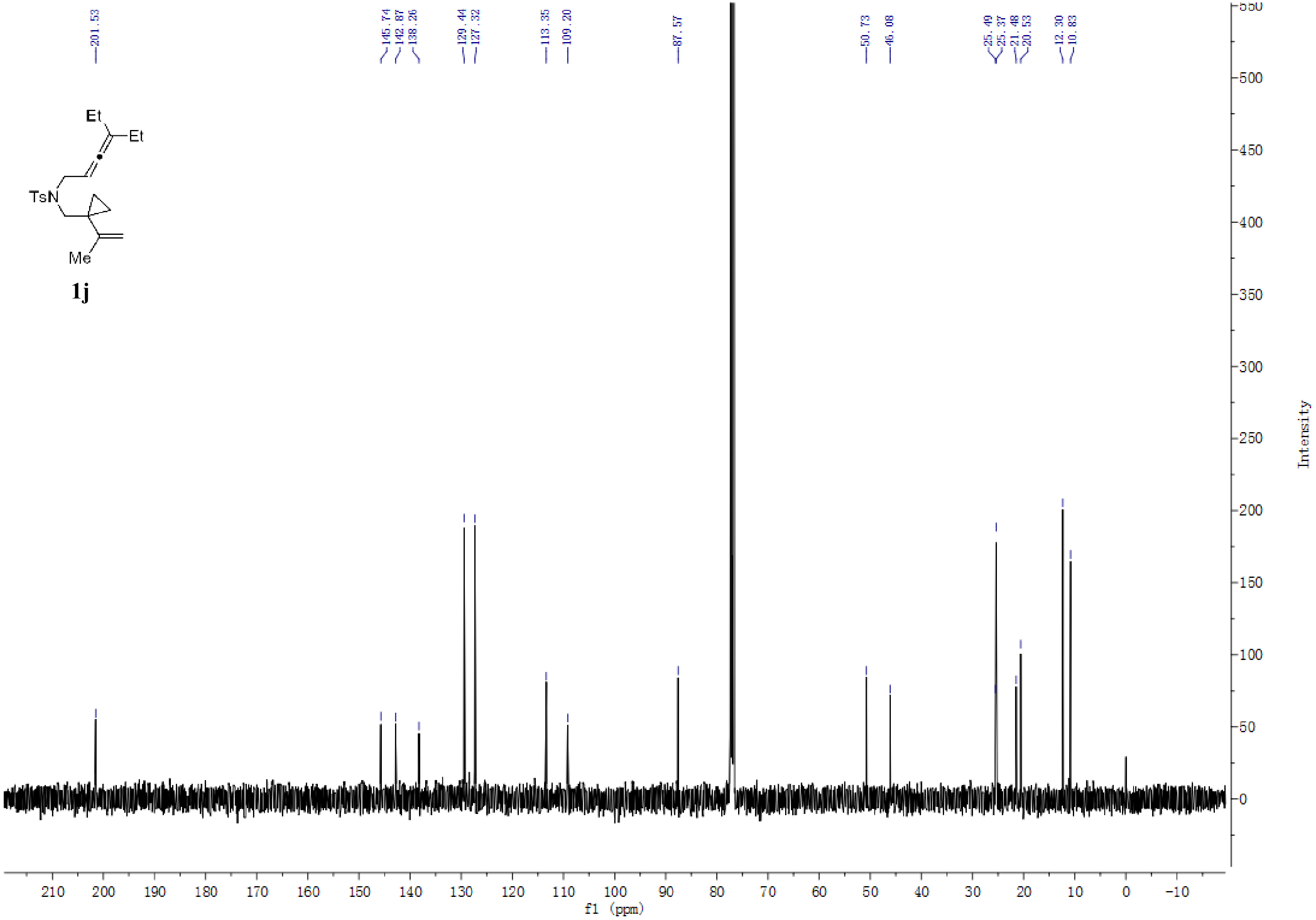

40000
35000
30000
25000
20000
15000
10000
5000
0
Intensity
1.00
2.03
1.05
2.06
2.04
6.04
2.00
2.05
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


202.99
142.33
111.22
95.79
87.39
74.12
69.34
22.71
20.38
12.52
Me
Me
O
1i
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
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)



1j

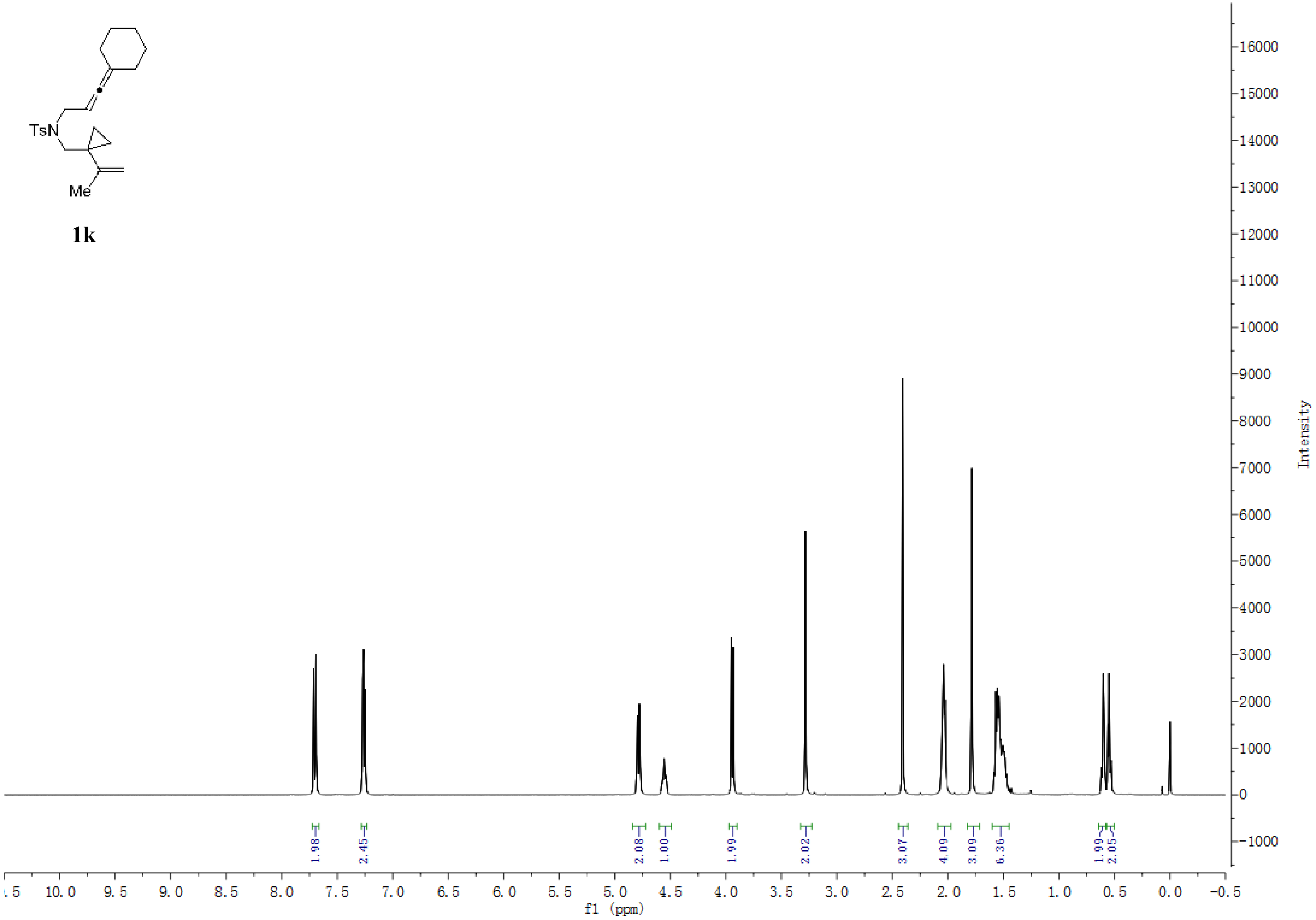
Et
Et
TsN
Me
2.00
2.02
2.94
1.96
1.96
2.99
4.00
2.95
5.98
1.96
2.00
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
Intensity

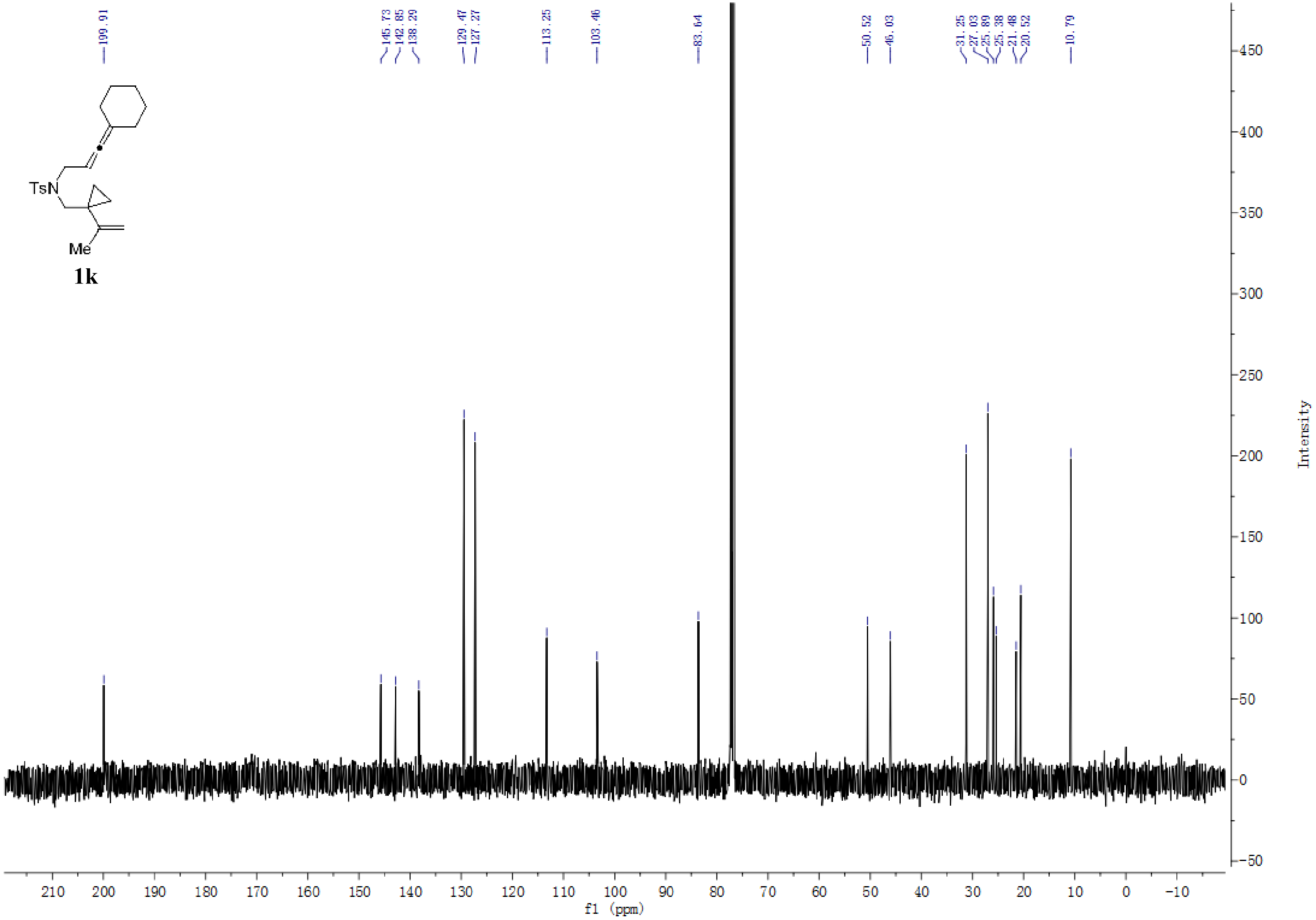

201.53
145.74
142.87
138.26
129.44
127.32
113.35
109.20
87.57
50.73
46.08
25.49
25.37
21.48
20.53
12.30
10.83
Et
Et
TsN
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)
550
500
450
400
350
300
250
200
150
100
50
0
Intensity

1j

TsN
Me

1k

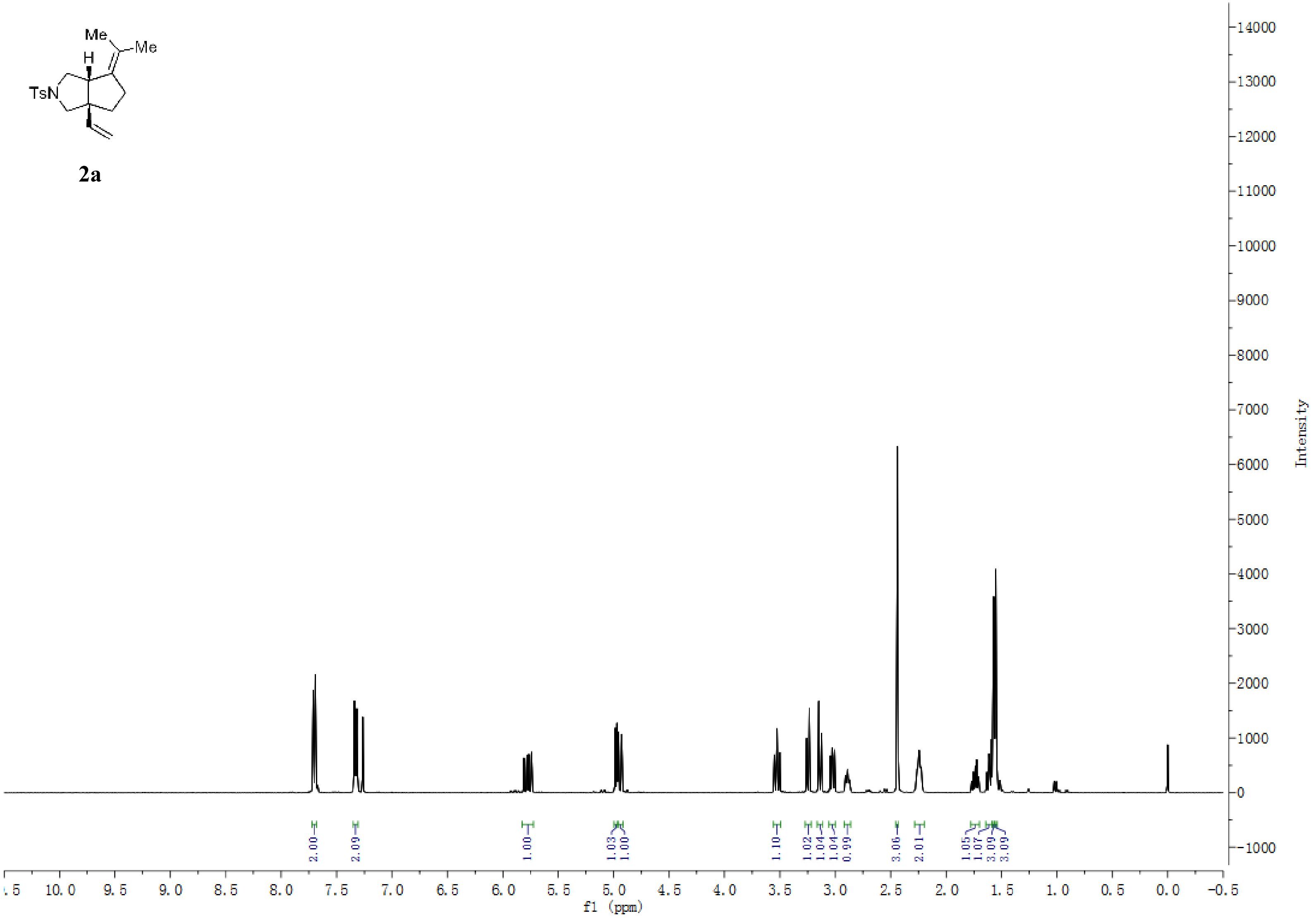

16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
Intensity
1.98
2.45
2.08
1.00
1.99
2.02
3.07
4.09
3.09
6.36
1.99
2.05
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

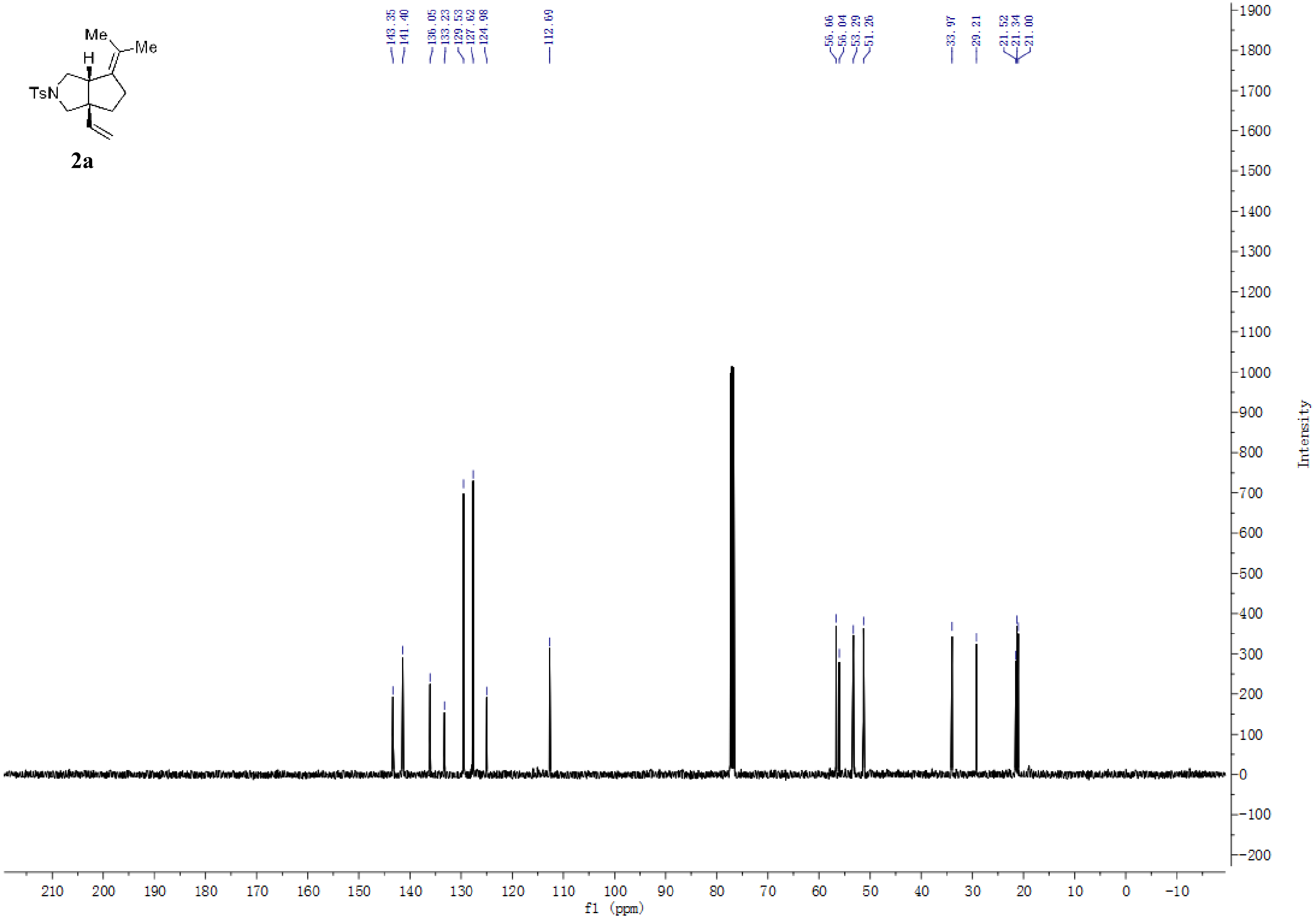

199.91
145.73
142.85
138.29
129.47
127.27
113.25
103.46
83.64
50.52
46.03
31.25
27.03
25.89
25.38
21.48
20.52
10.79
TsN
Me
f1 (ppm)
Intensity
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
450 400 350 300 250 200 150 100 50 0 -50

1k

Me
Me
H
TsN

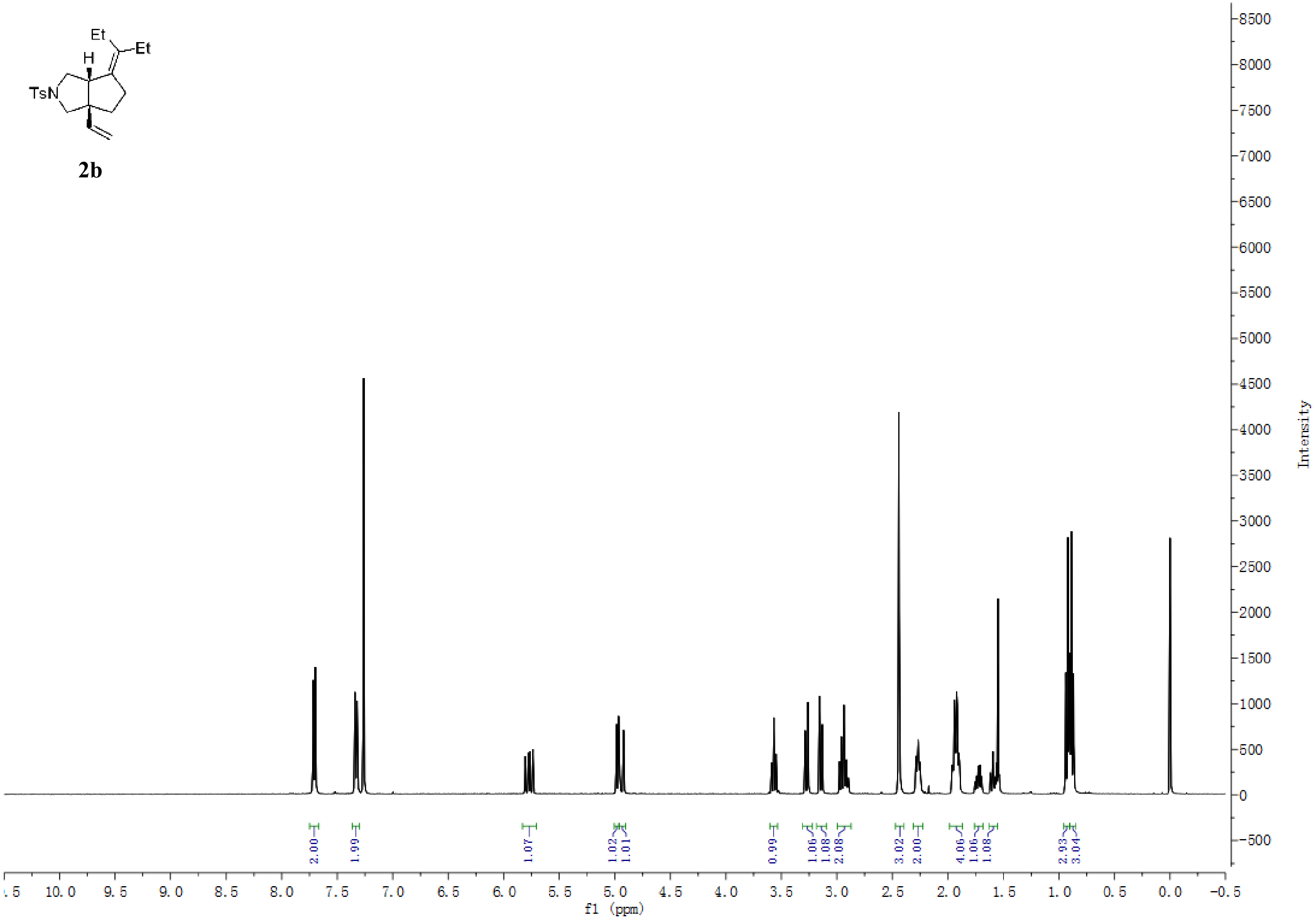
2a


14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
Intensity
2.00
2.09
1.00
1.03
1.00
1.10
1.02
1.04
1.04
0.99
3.06
2.01
1.05
1.07
3.09
3.09
.5
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)

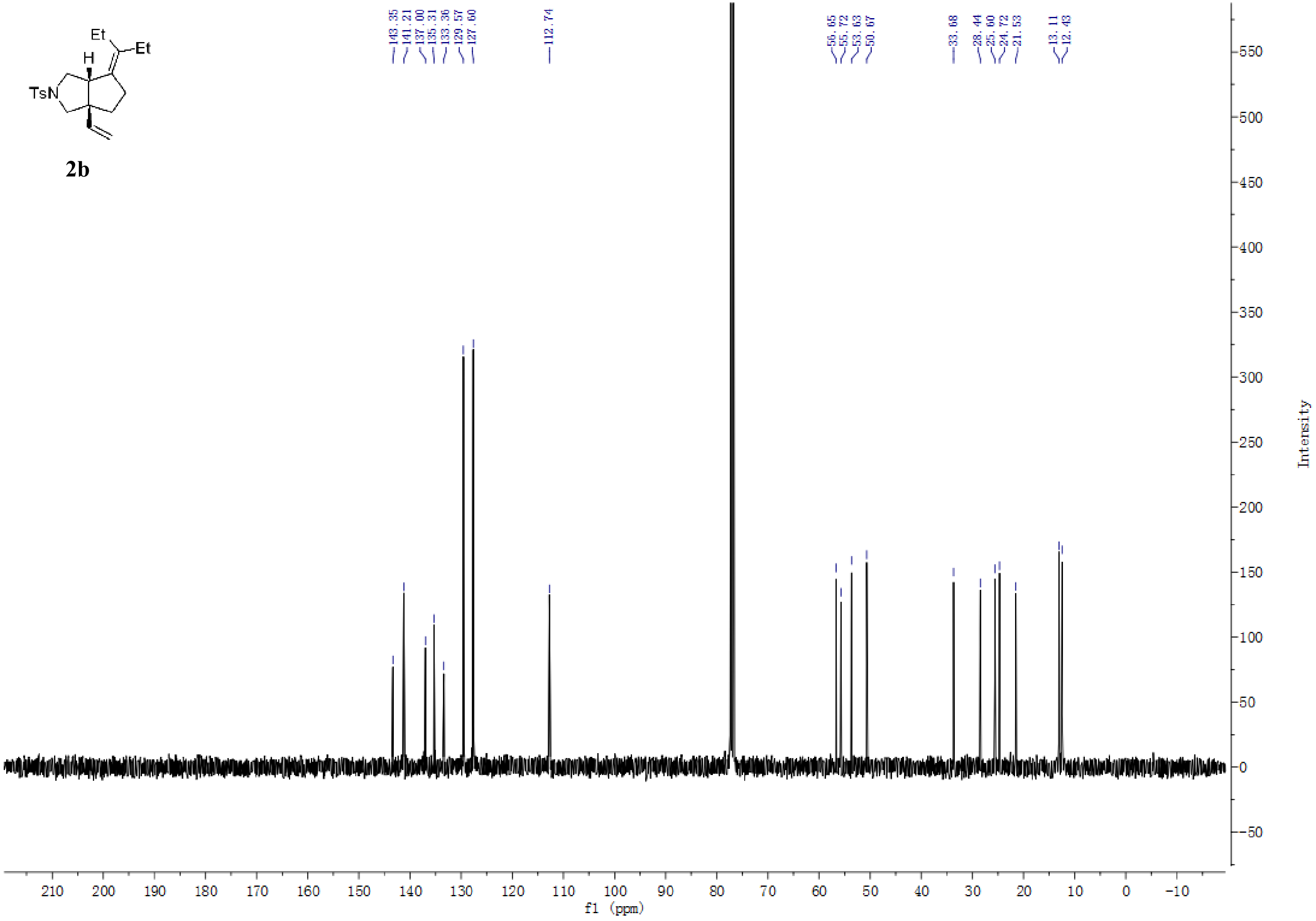

Me
Me
H
TsN

2a

143.35
141.40
136.05
133.23
129.53
127.62
124.98
112.69
56.66
56.04
53.29
51.26
33.97
29.21
21.52
21.34
21.00
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)
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
Intensity

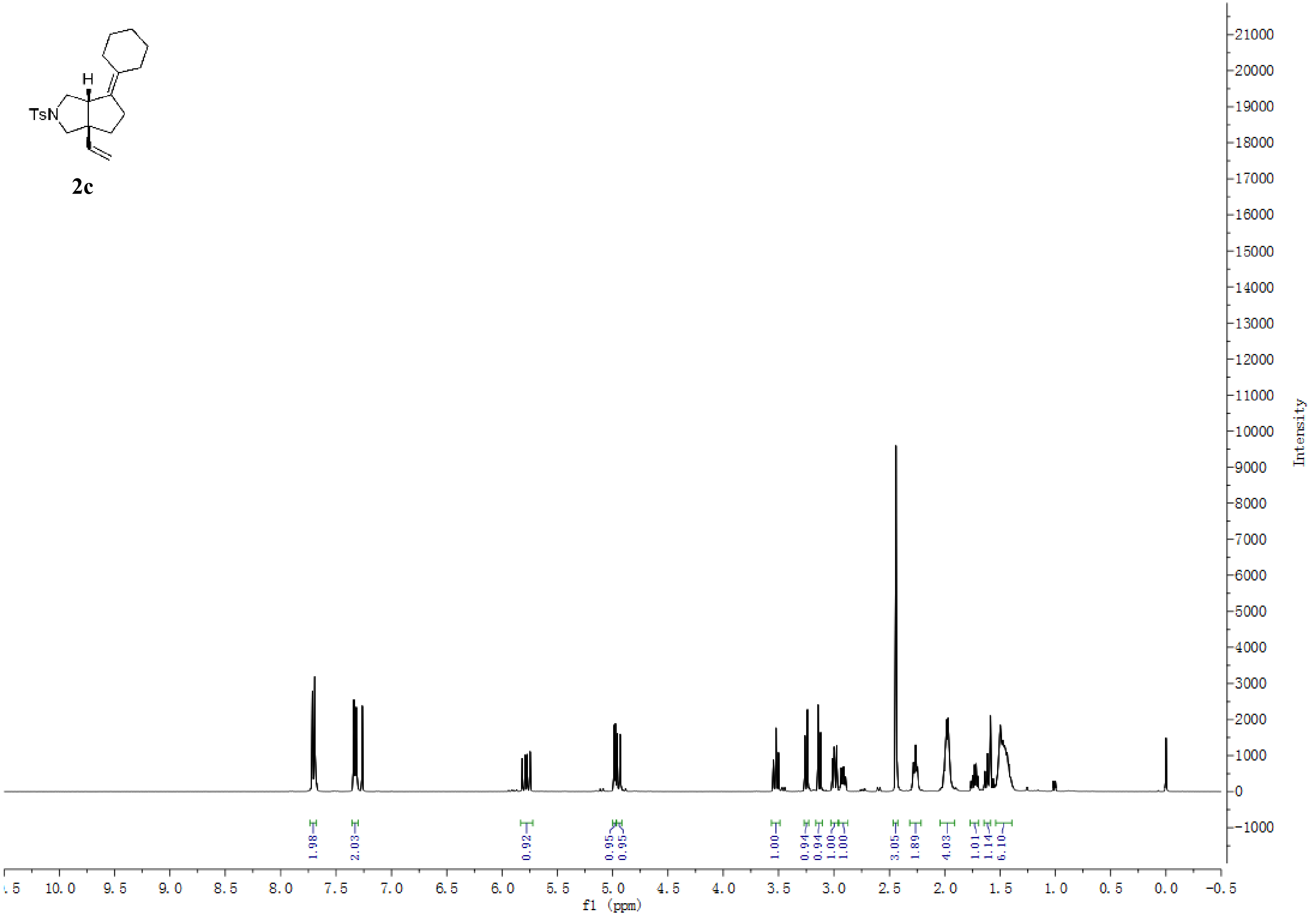

2b

Et
Et
H
TsN
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
Intensity
2.00
1.99
1.07
1.02
1.01
0.99
1.06
1.08
2.08
3.02
2.00
4.06
1.06
1.08
2.93
3.04
.5
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)


Et
Et
H
TsN

2b

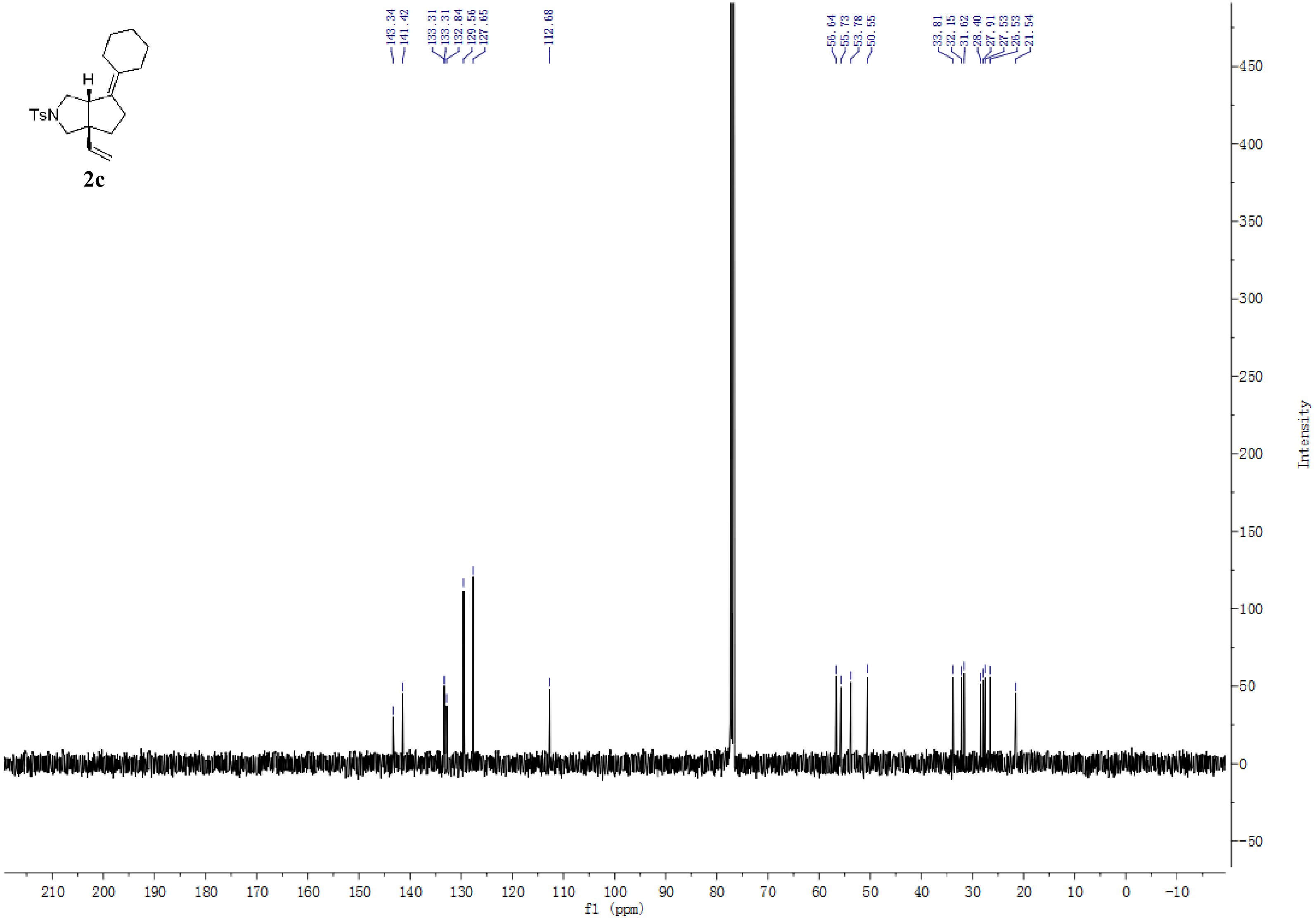
143.35
141.21
137.00
135.31
133.36
129.57
127.60
112.74
56.65
55.72
53.63
50.67
33.68
28.44
25.60
24.72
21.53
13.11
12.43
550
500
450
400
350
300
250
200
150
100
50
0
-50
Intensity
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

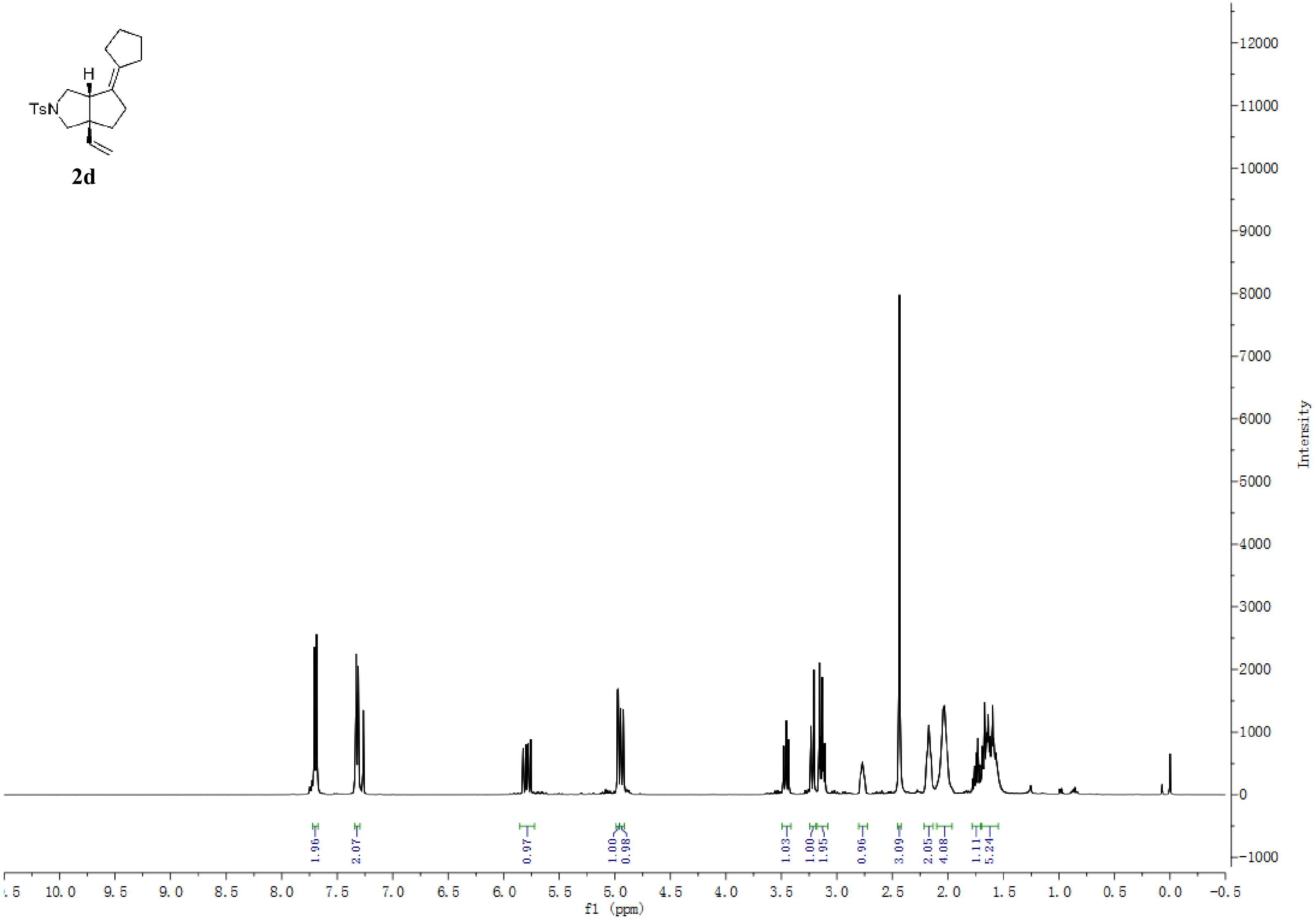

TsN
H
1.98
2.03
0.92
0.95
0.95
1.00
0.94
0.94
1.00
1.00
3.05
1.89
4.03
1.01
1.14
6.10
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
Intensity

2c

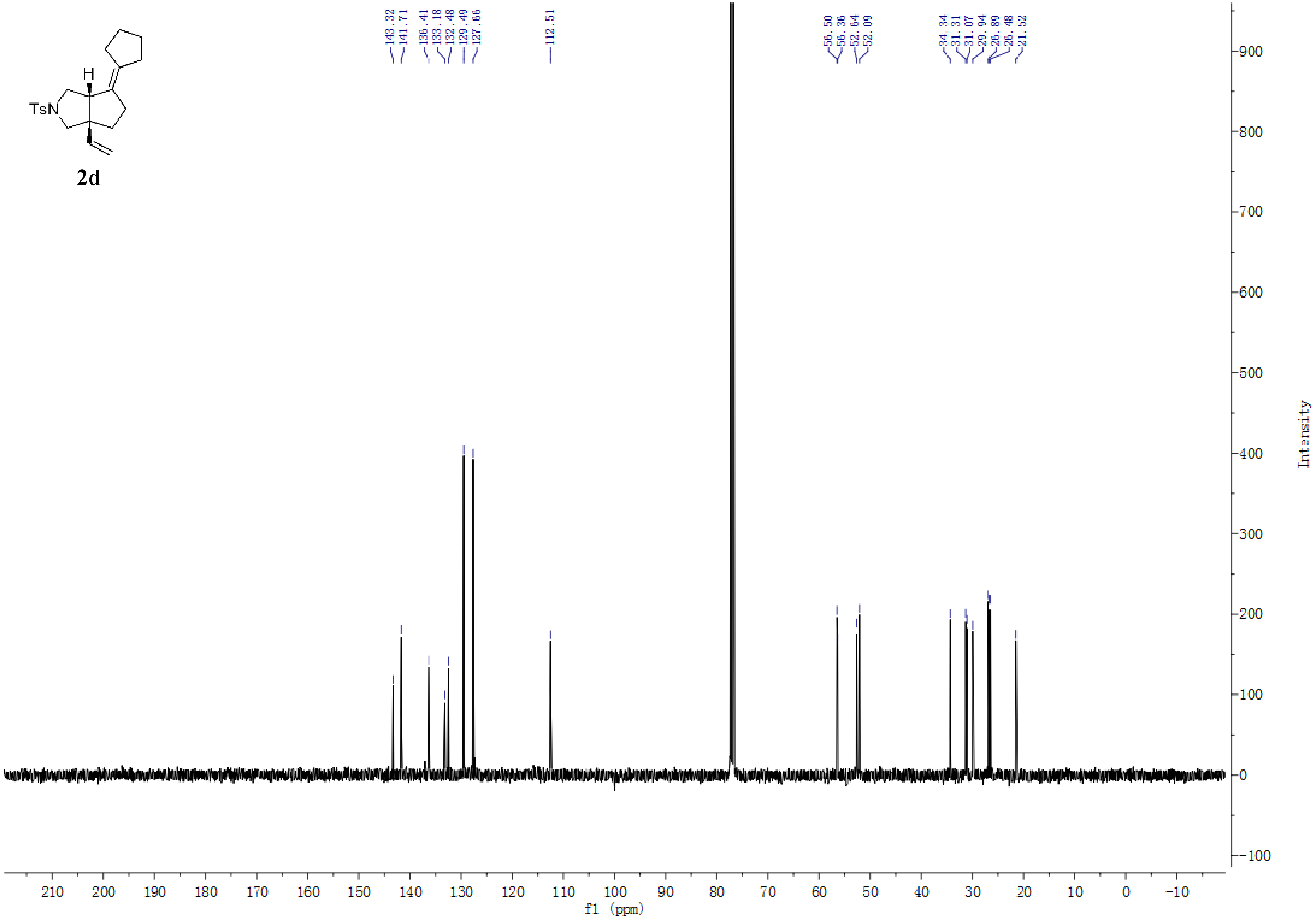
H
TsN

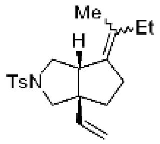
2c


143.34
141.42
133.31
133.31
132.84
129.56
127.65
112.68
56.64
55.73
53.78
50.55
33.81
32.15
31.62
28.40
27.91
27.53
26.53
21.54
450
400
350
300
250
200
150
100
50
0
-50
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)

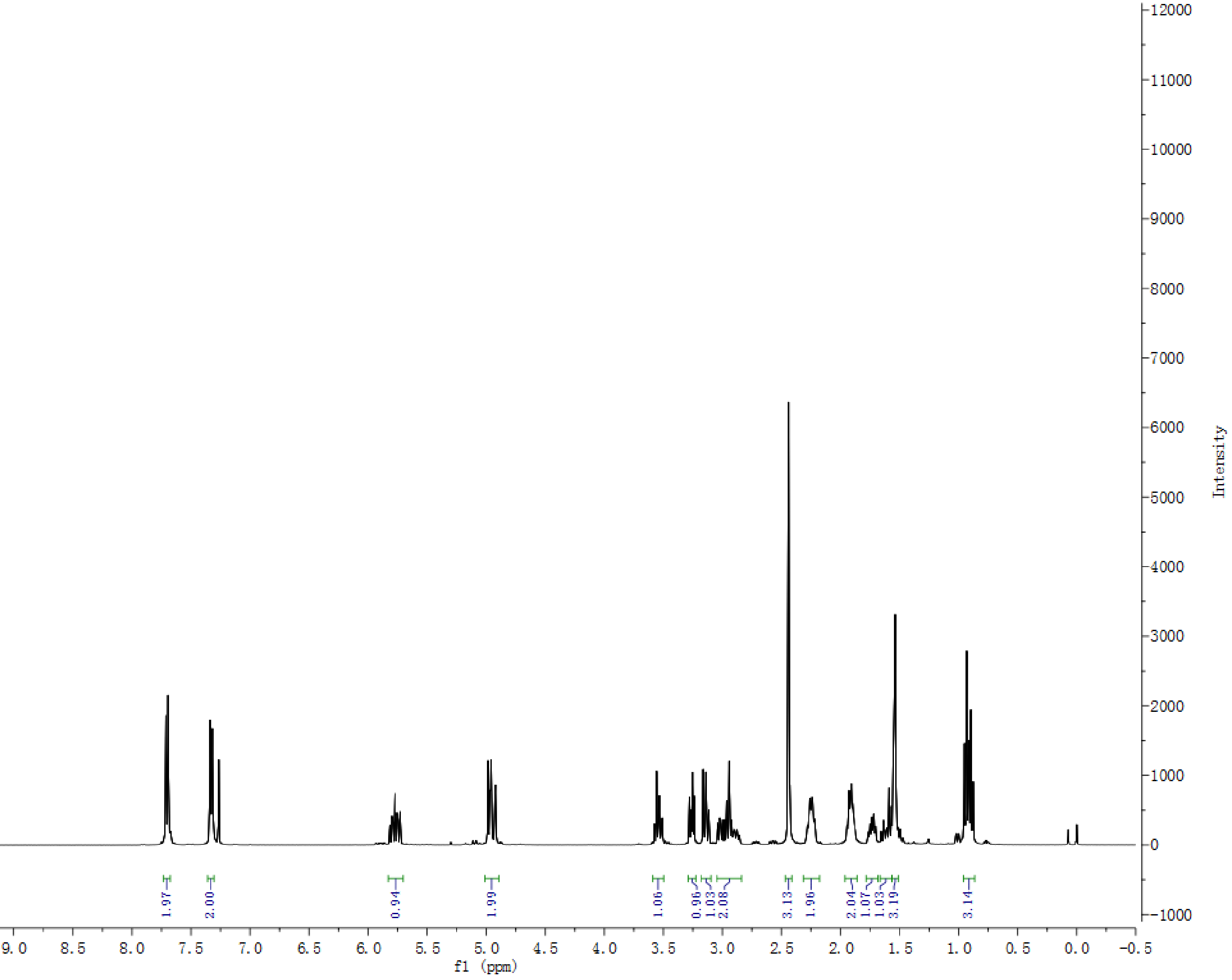


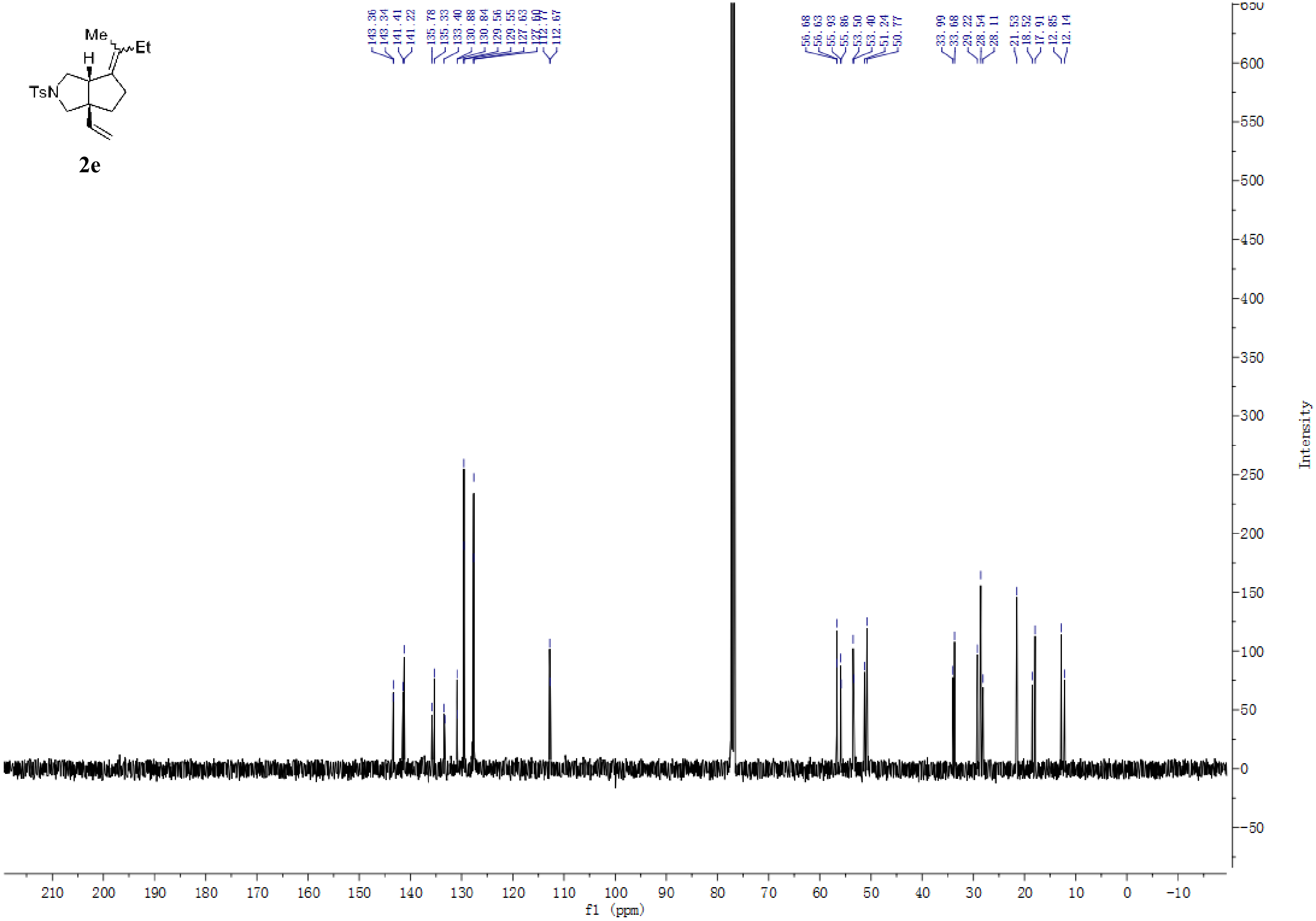
TsN
H
2d
1.96
2.07
0.97
1.00
0.98
1.03
1.00
1.95
0.96
3.09
2.05
4.08
1.11
5.24
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
Intensity

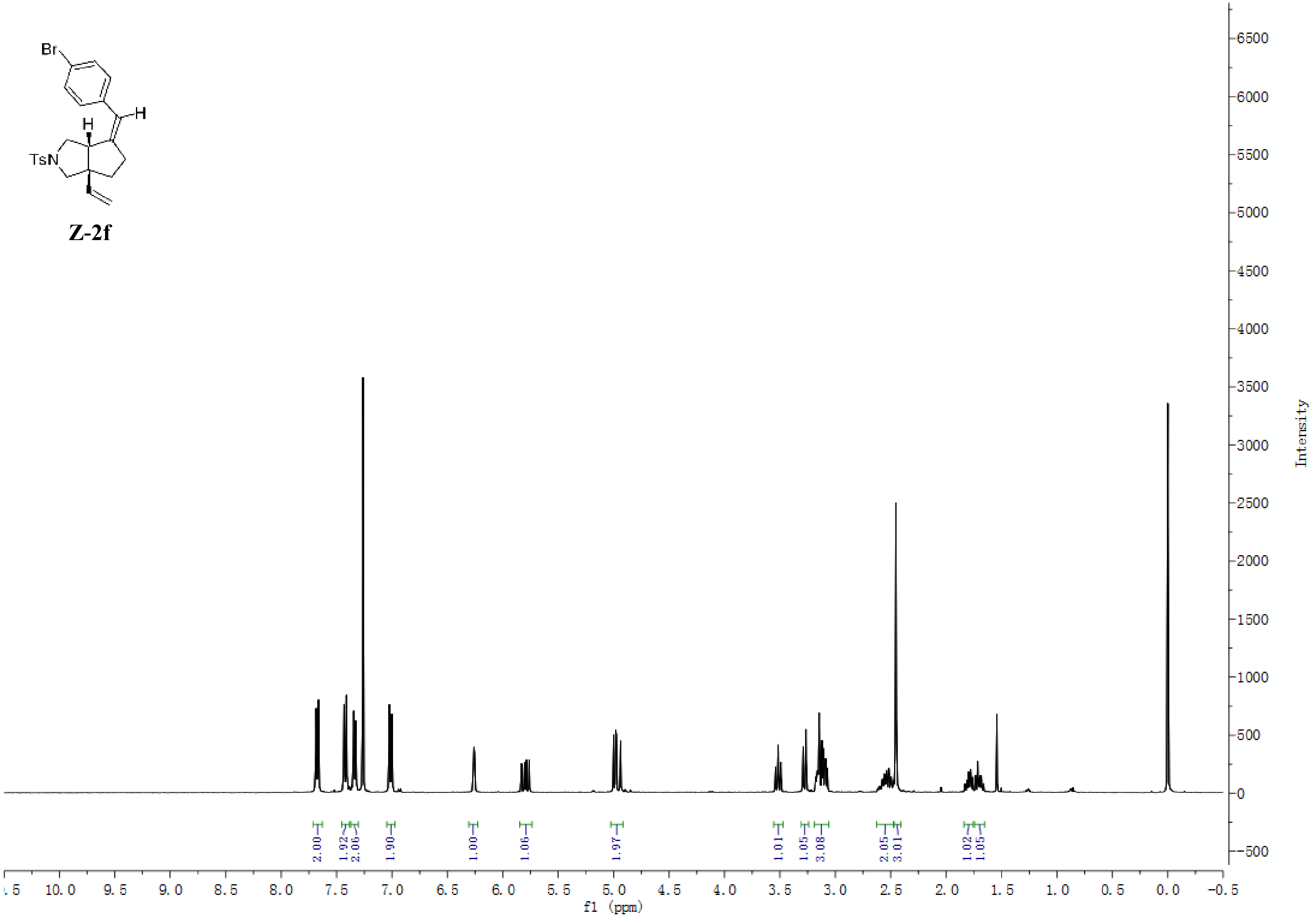

TsN
H
2d
143.32
141.71
136.41
133.18
132.48
129.49
127.66
112.51
56.50
56.36
52.64
52.09
34.34
31.31
31.07
29.94
26.89
26.48
21.52
900
800
700
600
500
400
300
200
100
0
−100
Intensity
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


Me
Et
H
TsN

2e


12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
Intensity
1.97
2.00
0.94
1.99
1.06
0.96
1.03
2.08
3.13
1.96
2.04
1.07
1.03
3.19
3.14
.5
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)

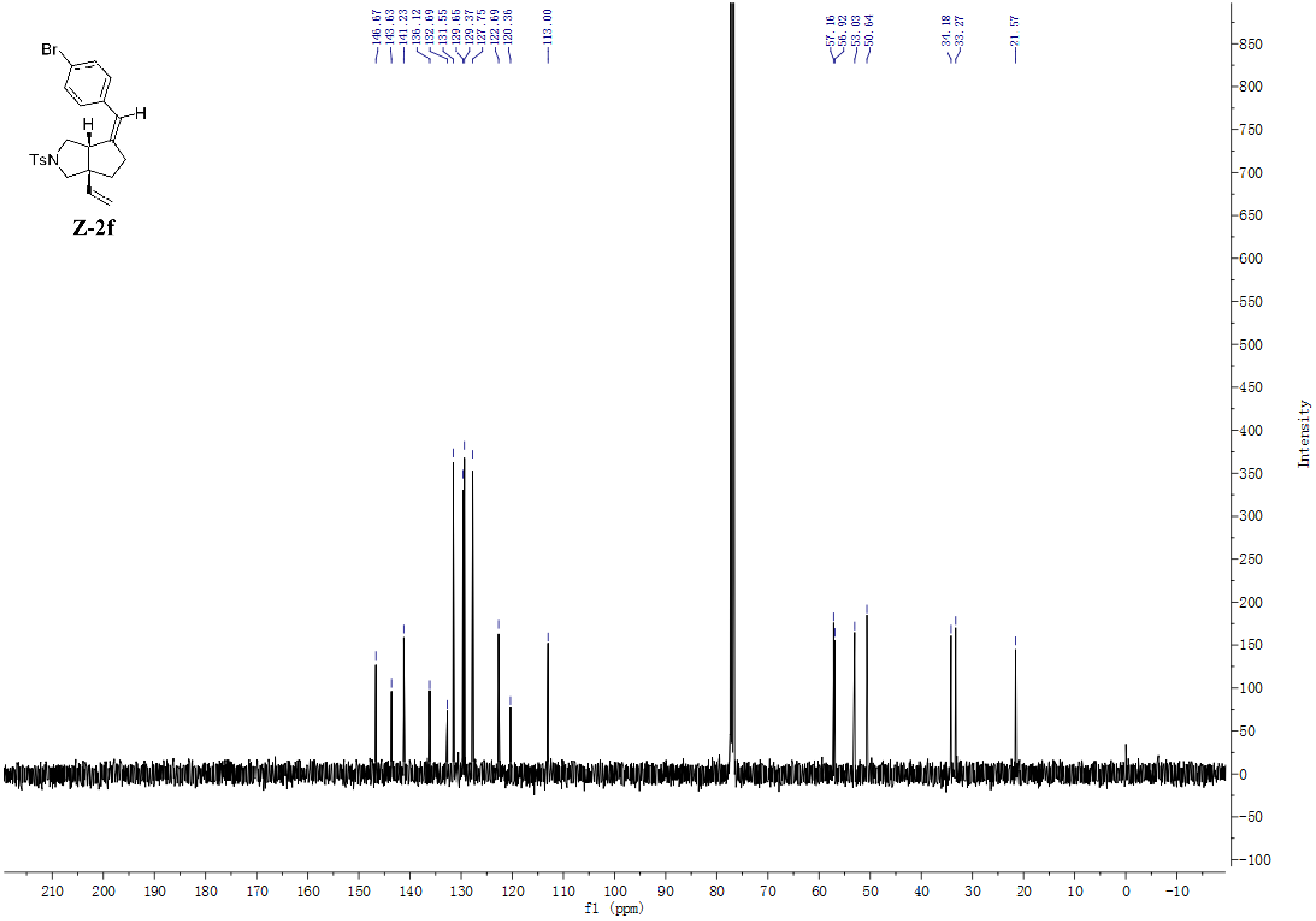

Me
Et
H
TsN
2e
143.36
143.34
141.41
141.22
135.78
135.33
133.40
130.88
130.84
129.56
129.55
127.63
127.60
112.77
112.67
56.68
56.63
55.93
55.86
53.50
53.40
51.24
50.77
33.99
33.68
29.22
28.54
28.11
21.53
18.52
17.91
12.85
12.14
650
600
550
500
450
400
350
300
250
200
150
100
50
0
−50
Intensity
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

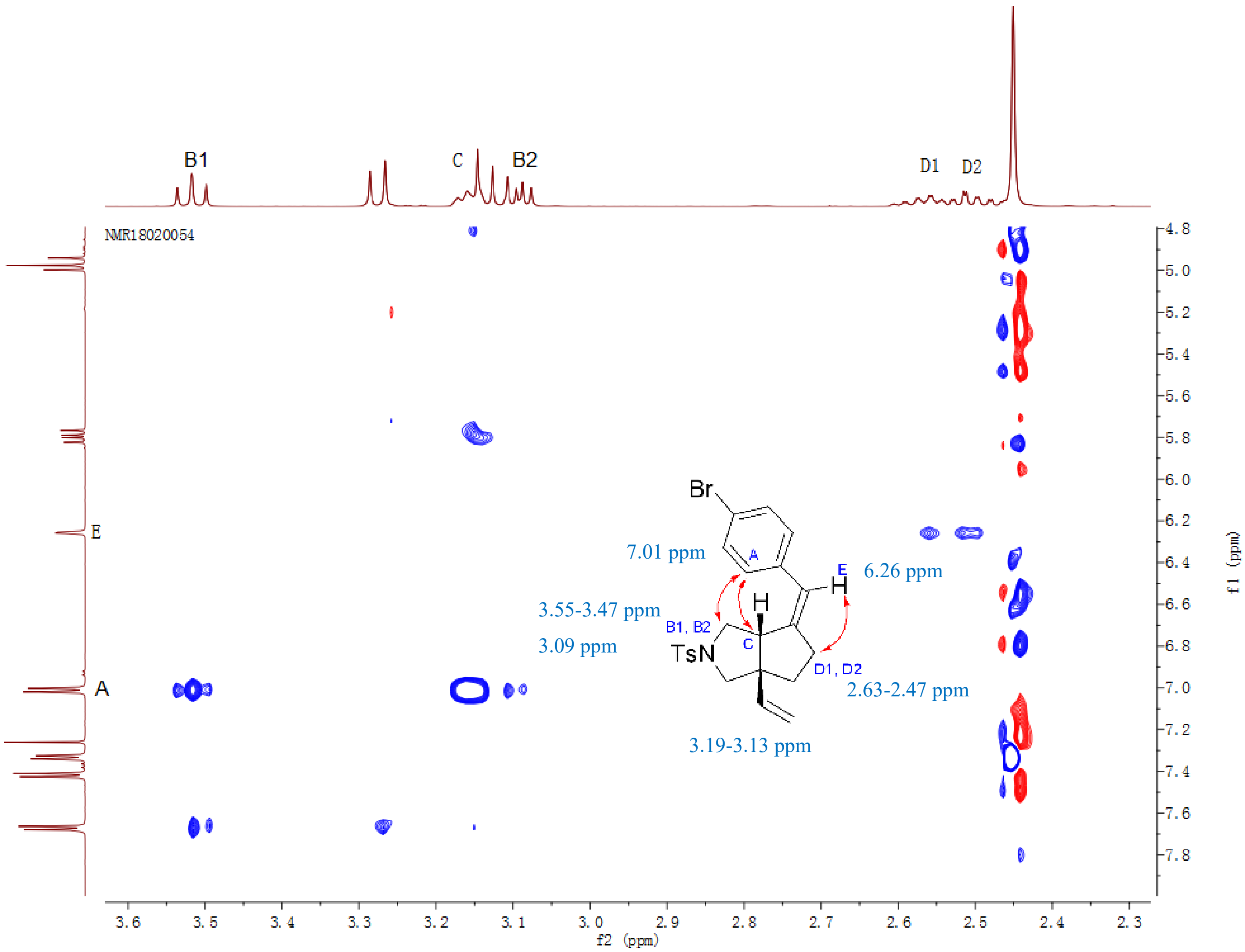

Z-2f

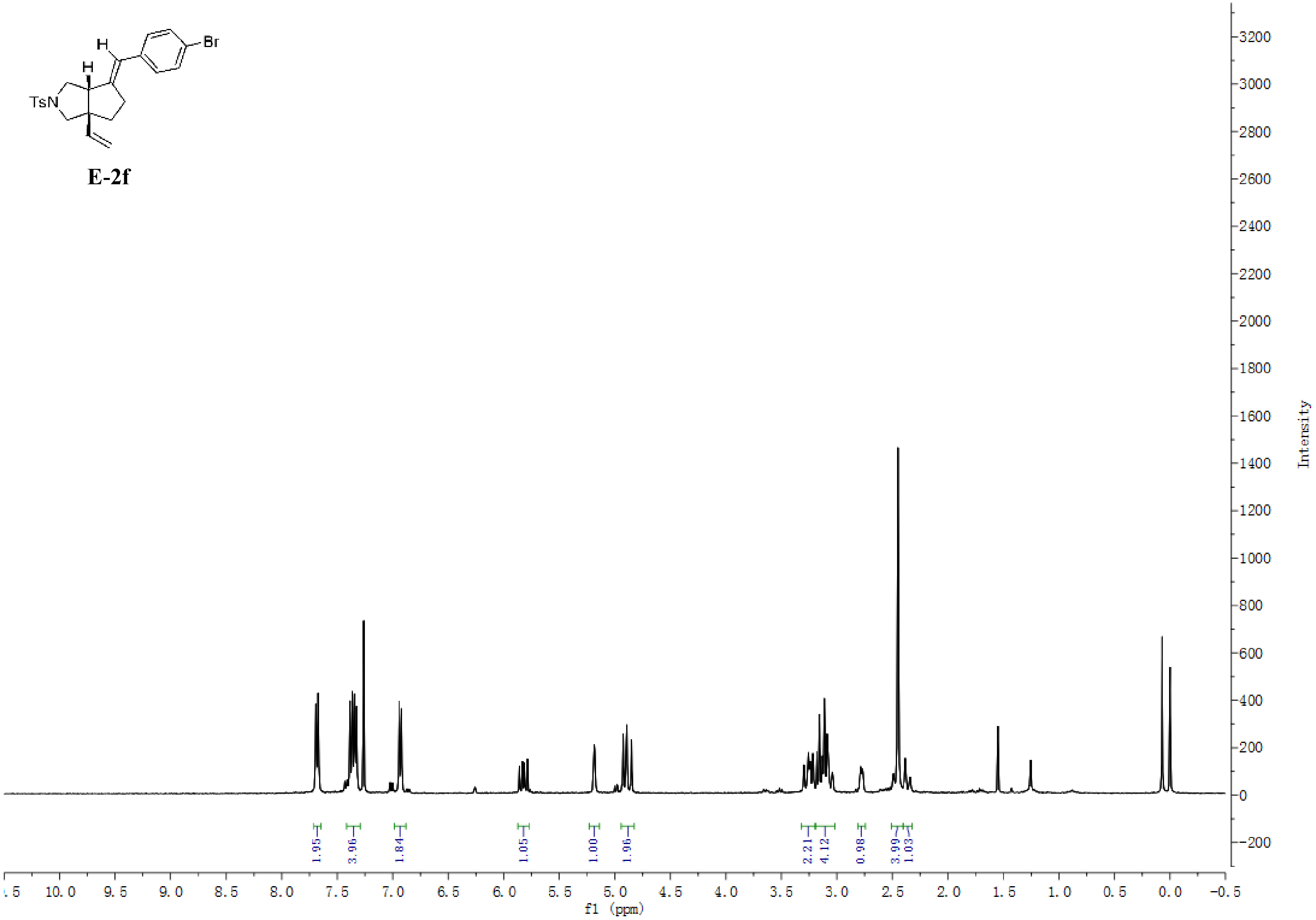
Br
H
H
TsN
2.00
1.92
2.06
1.90
1.00
1.06
1.97
1.01
1.05
3.08
2.05
3.01
1.02
1.05
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
Intensity

Br
H
H
TsN

Z-2f


146.67
143.63
141.23
136.12
132.69
131.55
129.65
129.37
127.75
122.69
120.36
113.00
57.16
56.92
53.03
50.64
34.18
33.27
21.57
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
-100
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)

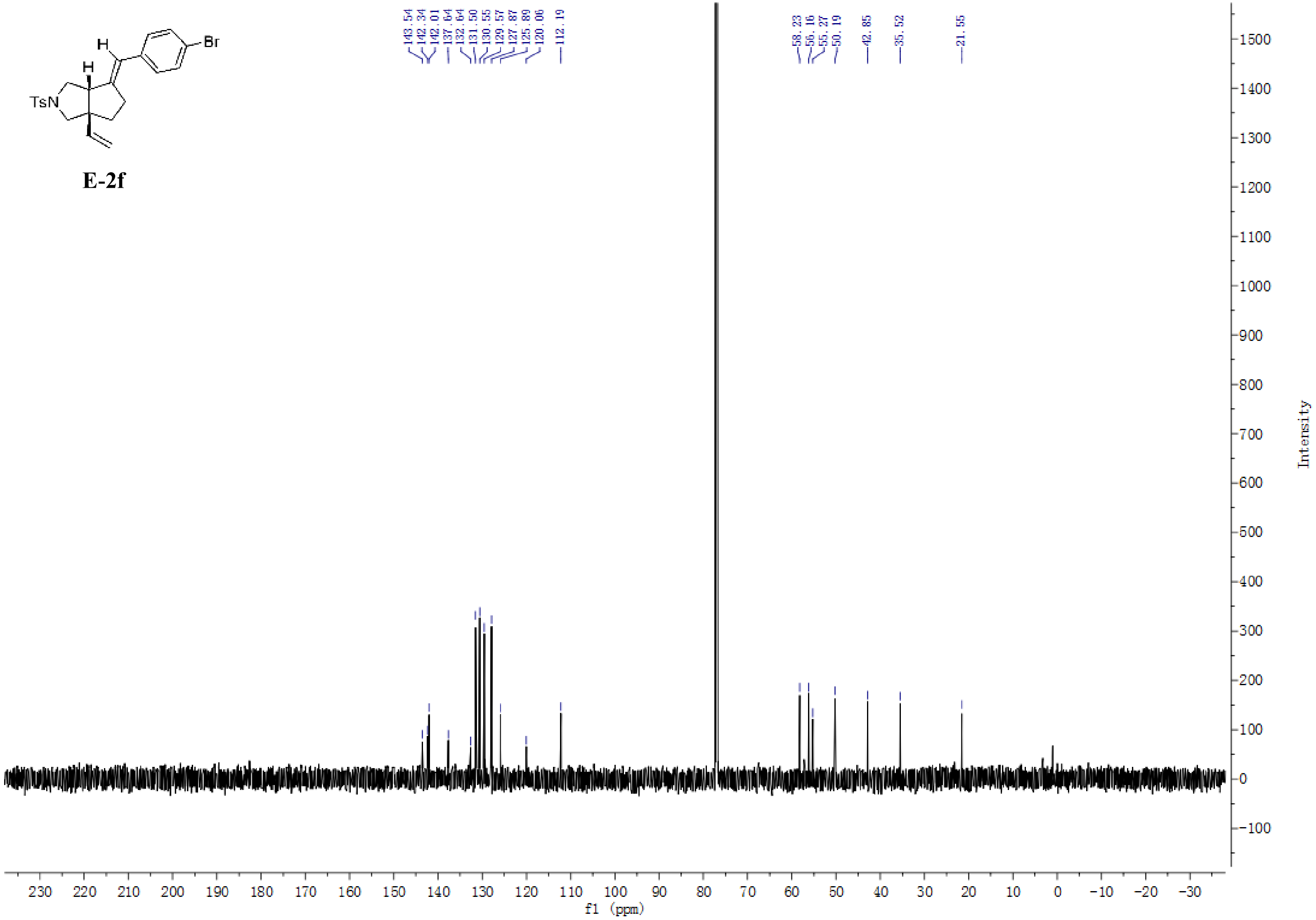

B1
C
B2
D1
D2
NMR18020054
E
A
Br
A
E
H
H
TsN
B1, B2
C
D1, D2
7.01 ppm
6.26 ppm
3.55-3.47 ppm
3.09 ppm
2.63-2.47 ppm
3.19-3.13 ppm
3.6
3.5
3.4
3.3
3.2
3.1
3.0
2.9
2.8
2.7
2.6
2.5
2.4
2.3
f2 (ppm)
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.2
6.4
6.6
6.8
7.0
7.2
7.4
7.6
7.8
f1 (ppm)

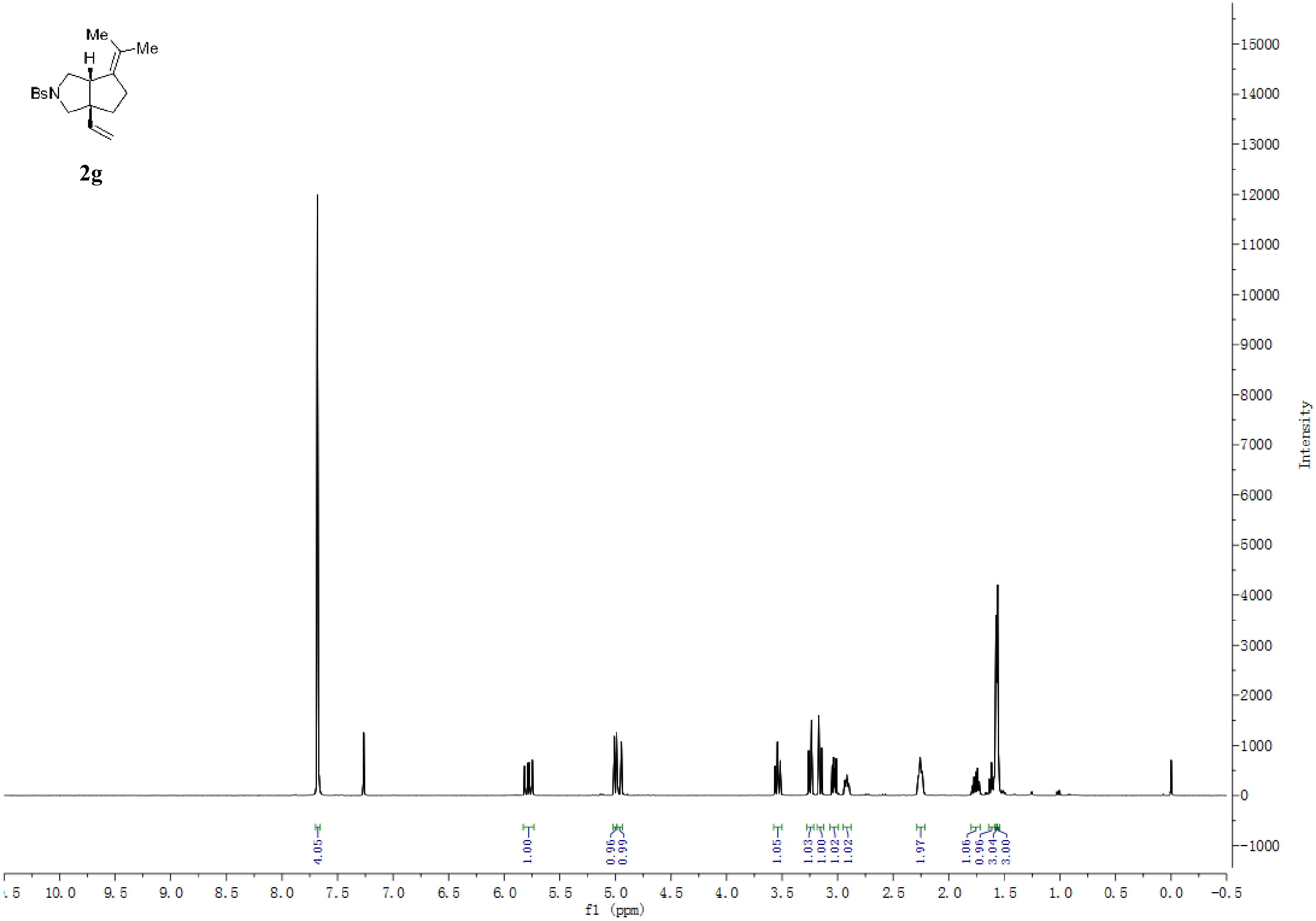

H
H
TsN
Br
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
Intensity
1.95
3.96
1.84
1.05
1.00
1.96
2.21
4.12
0.98
3.99
1.03
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

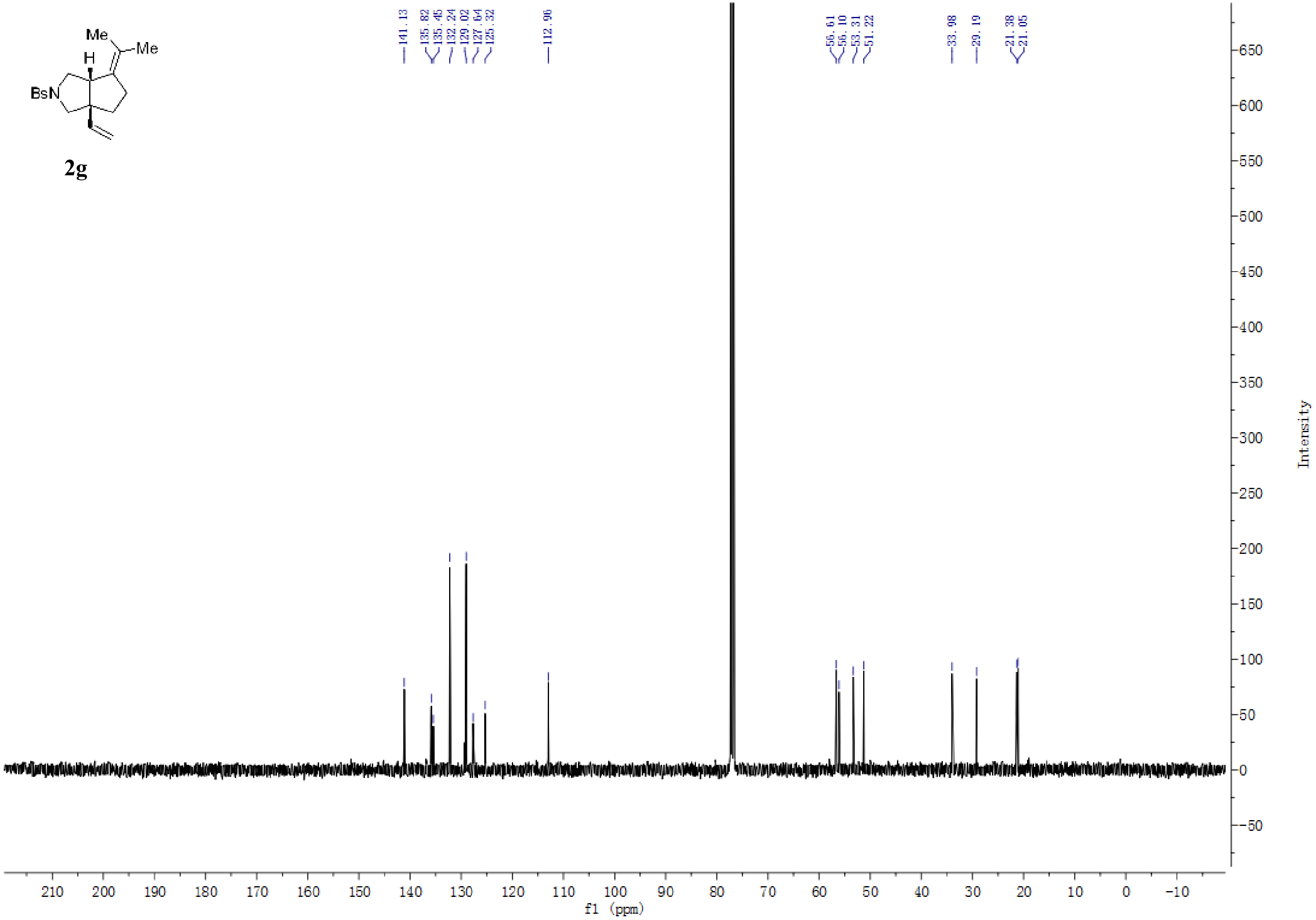
E-2f

H
H
Br
TsN

E-2f

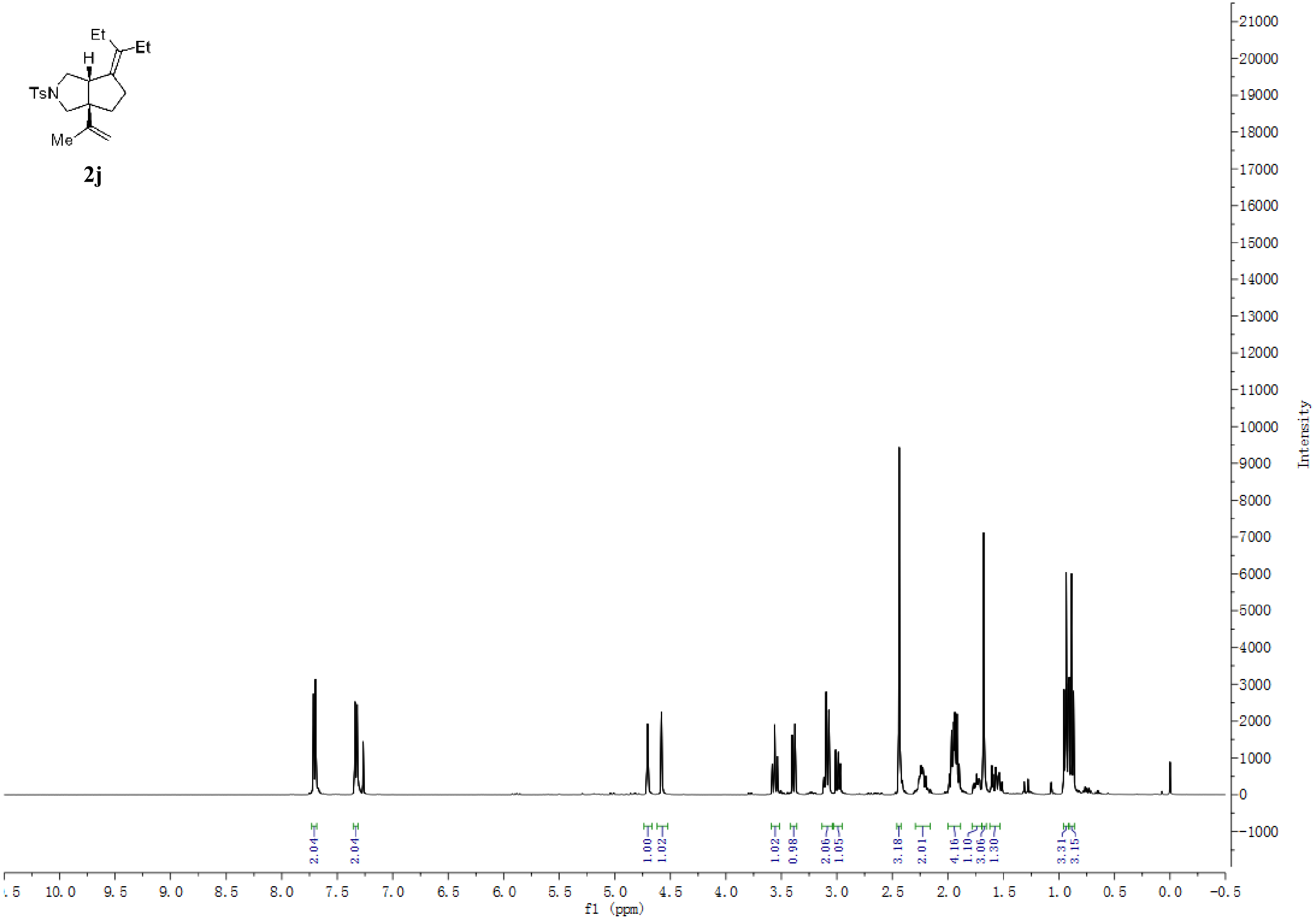

143.54
142.34
142.01
137.64
132.64
131.50
130.55
129.57
127.87
125.89
120.06
112.19
58.23
56.16
55.27
50.19
42.85
35.52
21.55
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
Intensity
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
f1 (ppm)


Me
Me
H
BsN
2g
4.05
1.00
0.96
0.99
1.05
1.03
1.00
1.02
1.02
1.97
1.06
0.96
3.04
3.00
.5
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)
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
Intensity


Me
Me
H
BsN

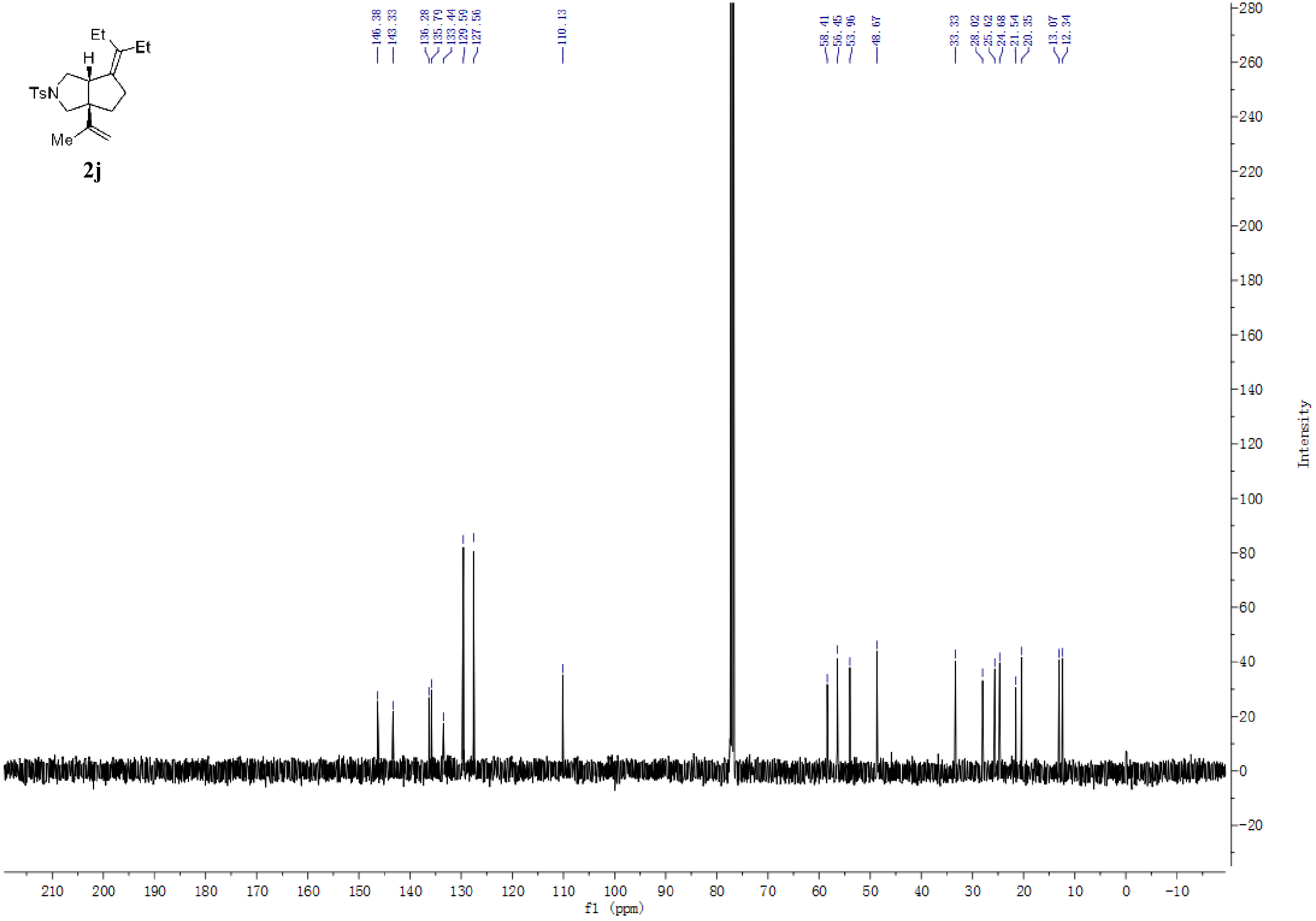
2g

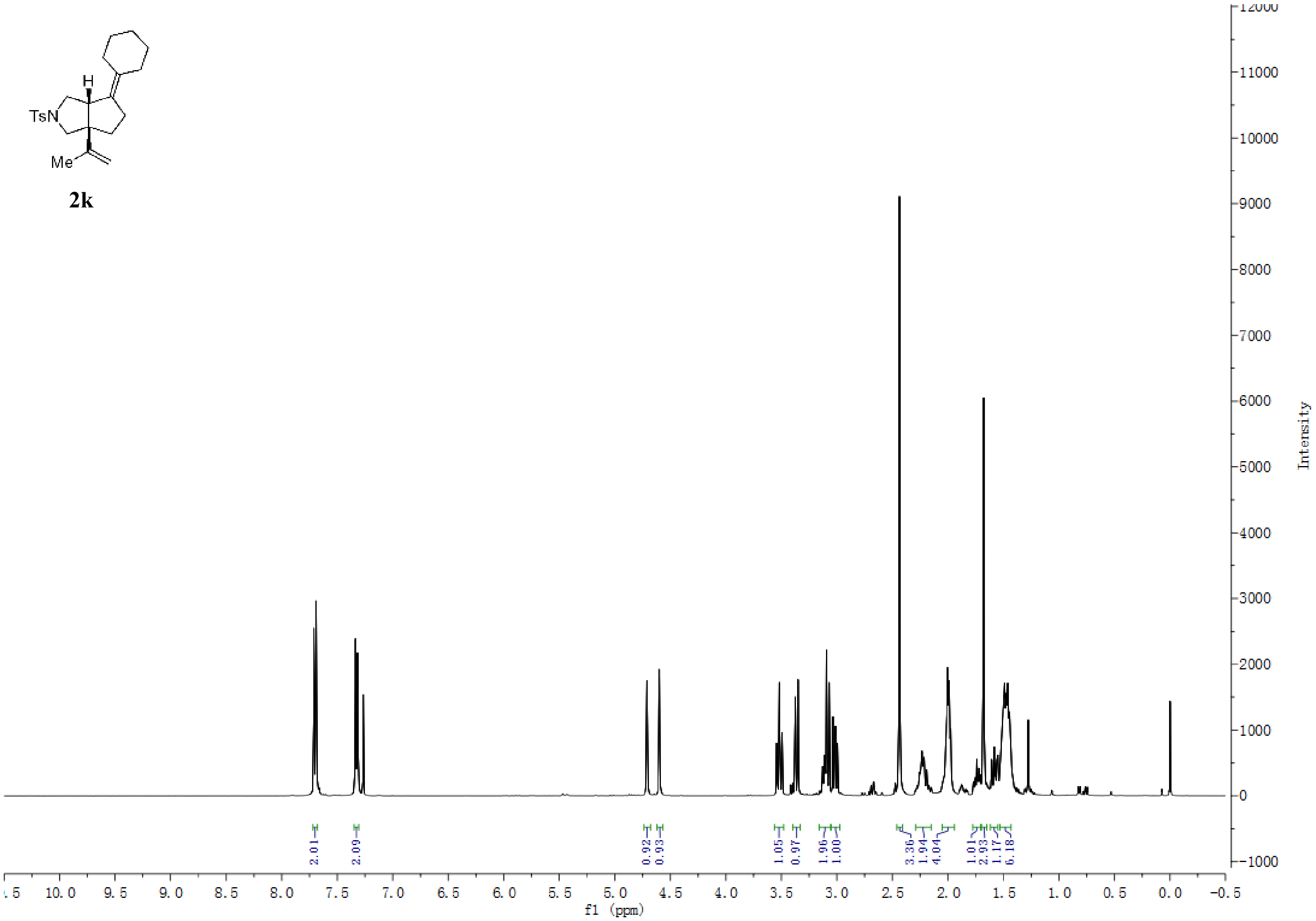
141.13
135.82
135.45
132.24
129.02
127.64
125.32
112.96
56.61
56.10
53.31
51.22
33.98
29.19
21.38
21.05
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
Intensity



2j

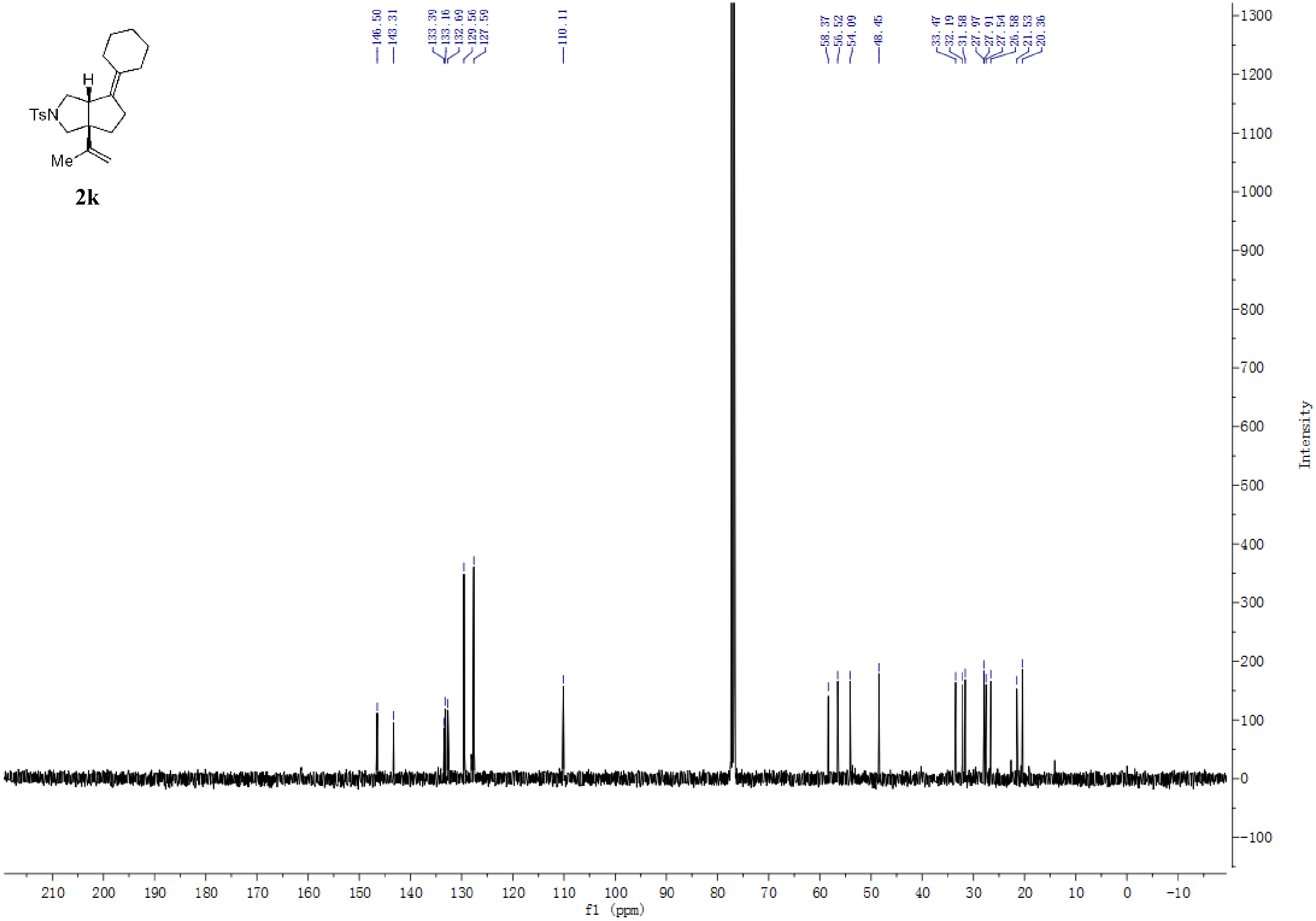
Et
Et
H
TsN
Me
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
Intensity
2.04
2.04
1.00
1.02
1.02
0.98
2.06
1.05
3.18
2.01
4.16
1.10
3.06
1.30
3.31
3.15
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


Et
Et
H
TsN
Me
2j
146.38
143.33
136.28
135.79
133.44
129.59
127.56
110.13
58.41
56.45
53.96
48.67
33.33
28.02
25.62
24.68
21.54
20.35
13.07
12.34
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)
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
Intensity


TsN
H
Me

2k

2.01
2.09
0.92
0.93
1.05
0.97
1.96
1.00
3.36
1.94
4.04
1.01
2.93
1.17
6.18
.5
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)
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
Intensity

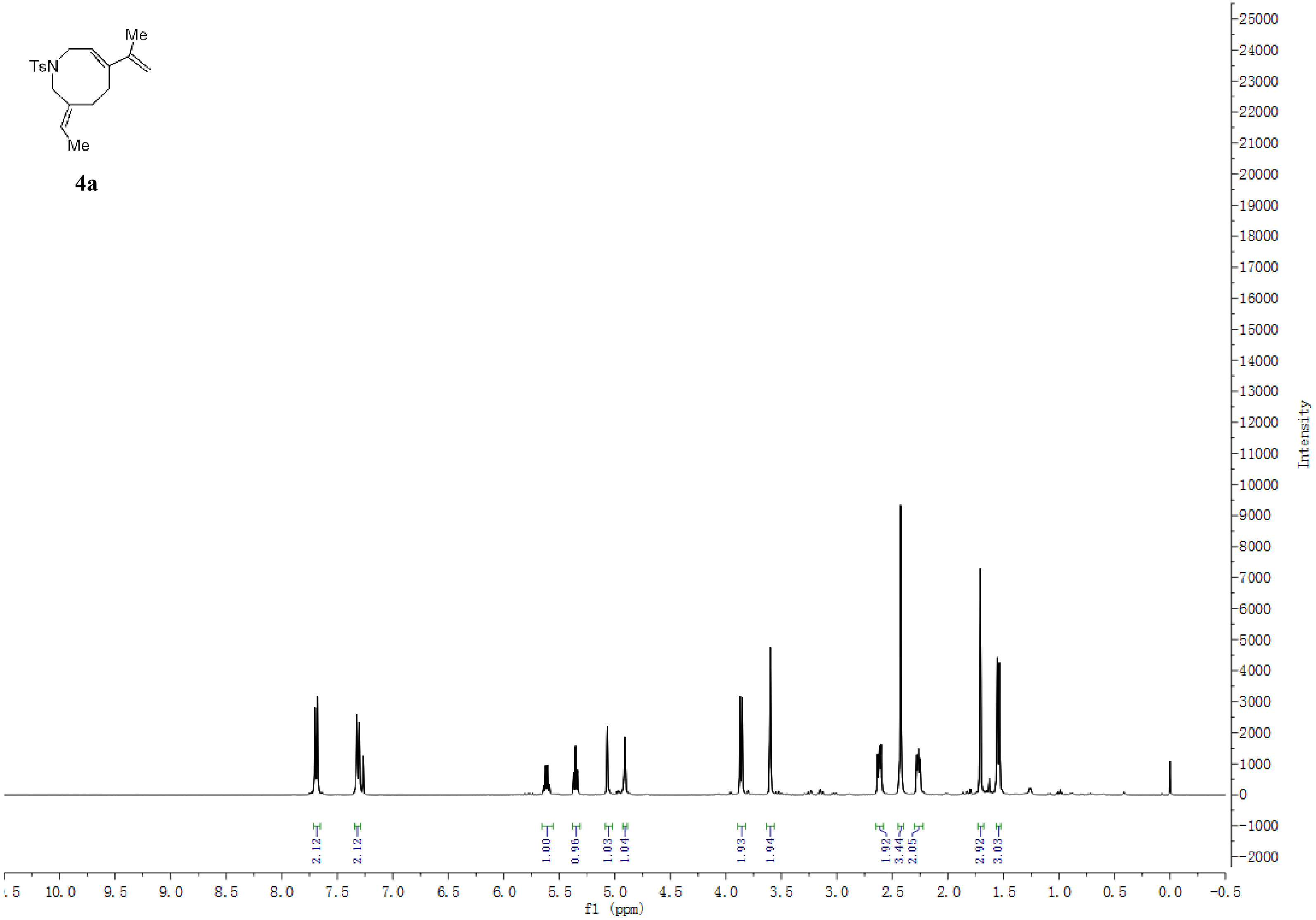


2k

TsN
H
Me
146.50
143.31
133.39
133.16
132.69
129.56
127.59
110.11
58.37
56.52
54.09
48.45
33.47
32.19
31.58
27.97
27.91
27.54
26.58
21.53
20.36
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
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)

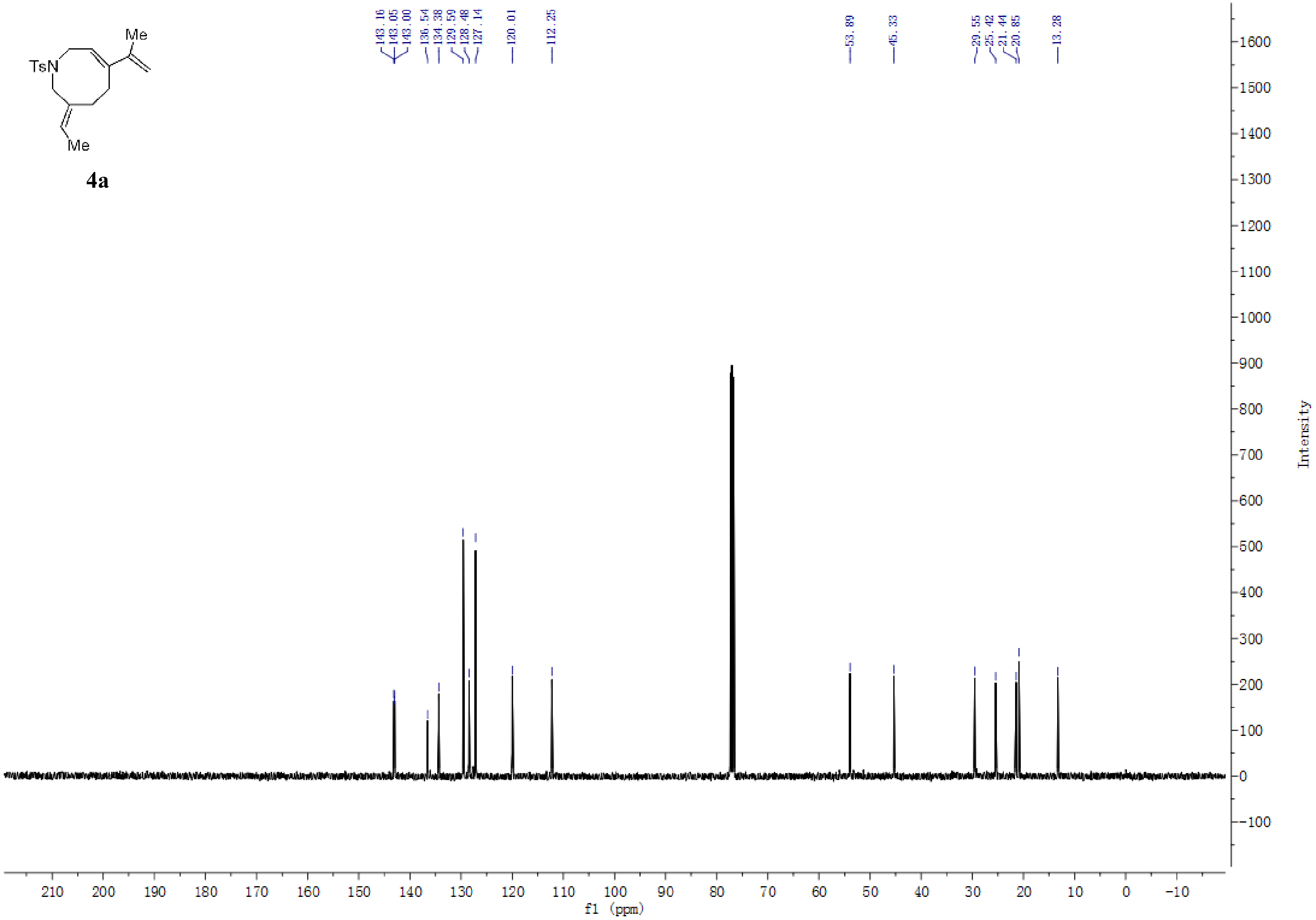
Me
TsN
Me

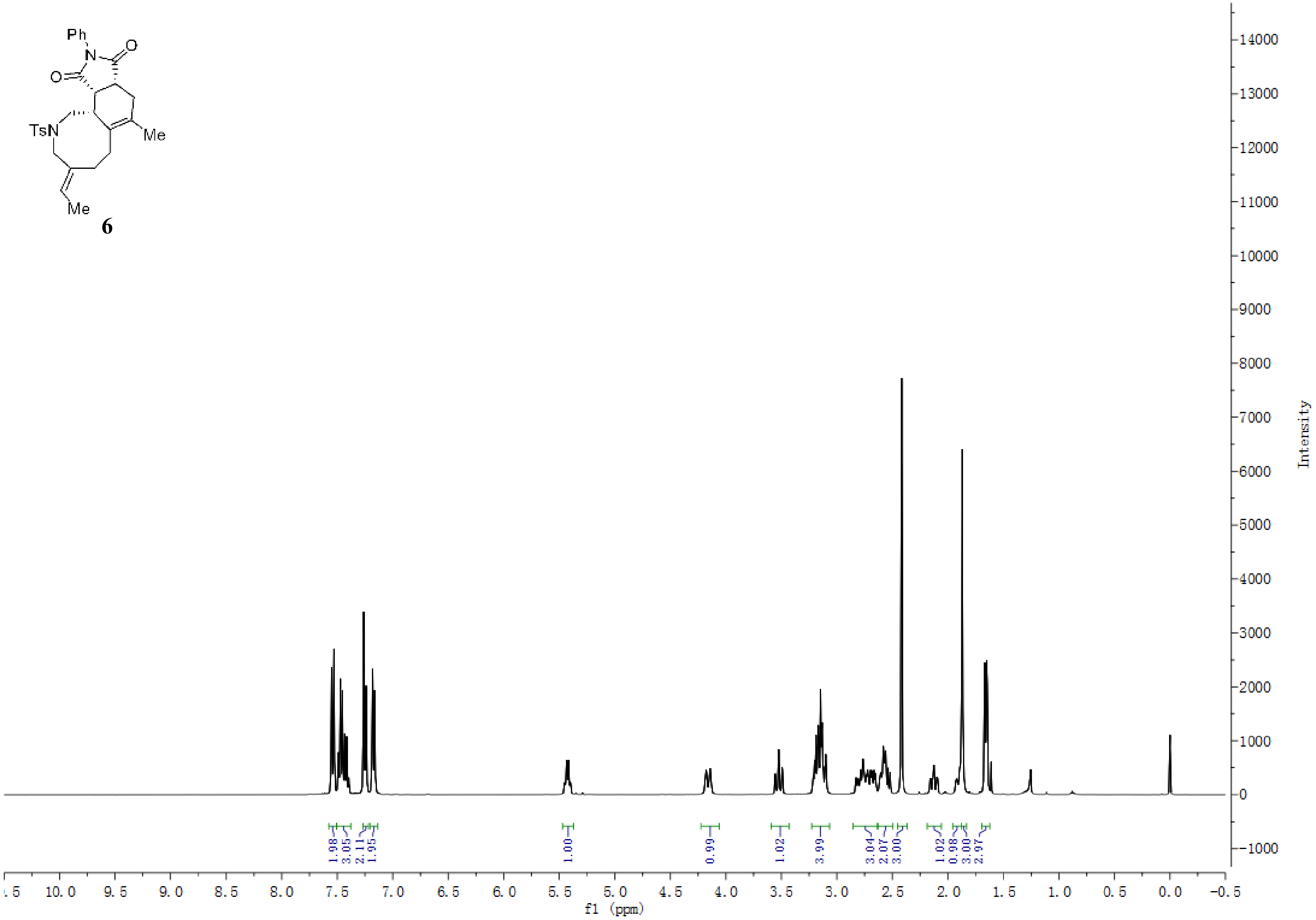
4a


2.12
2.12
1.00
0.96
1.03
1.04
1.93
1.94
1.92
3.44
2.05
2.92
3.03
.5
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)
25000
24000
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
Intensity

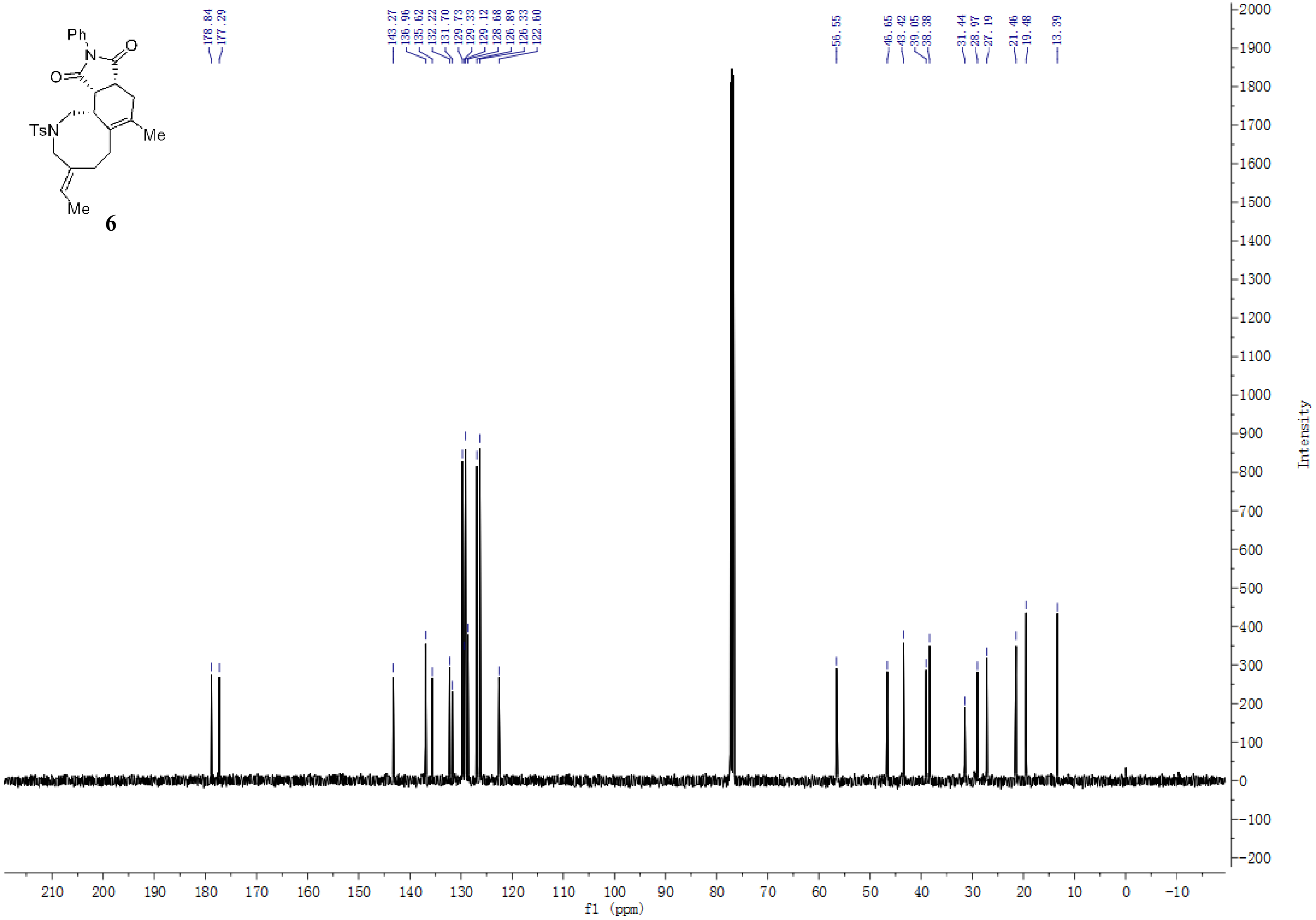
Me
TsN
Me

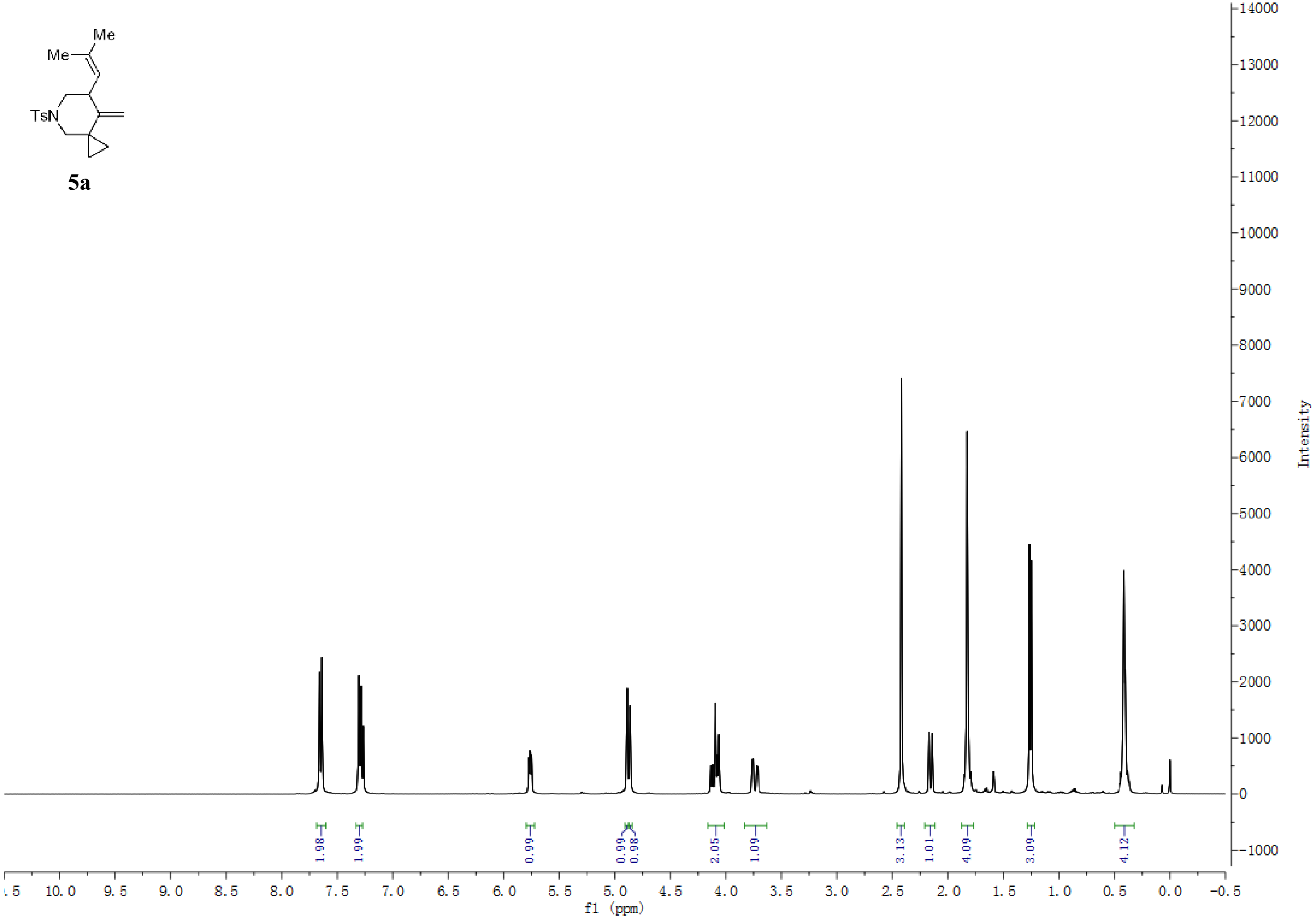
4a


143.16
143.05
143.00
136.54
134.38
129.59
128.48
127.14
120.01
112.25
53.89
45.33
29.55
25.42
21.44
20.85
13.28
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
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)


Ph
N
O
O
TsN
Me
Me
1.98
3.05
2.11
1.95
1.00
0.99
1.02
3.99
3.04
2.07
3.00
1.02
0.98
3.00
2.97
.5
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)
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
Intensity

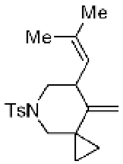
6


Ph
N
O
O
TsN
Me
Me
6
178.84
177.29
143.27
136.96
135.62
132.22
131.70
129.73
129.33
129.12
128.68
126.89
126.33
122.60
56.55
46.65
43.42
39.05
38.38
31.44
28.97
27.19
21.46
19.48
13.39
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
−200
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)

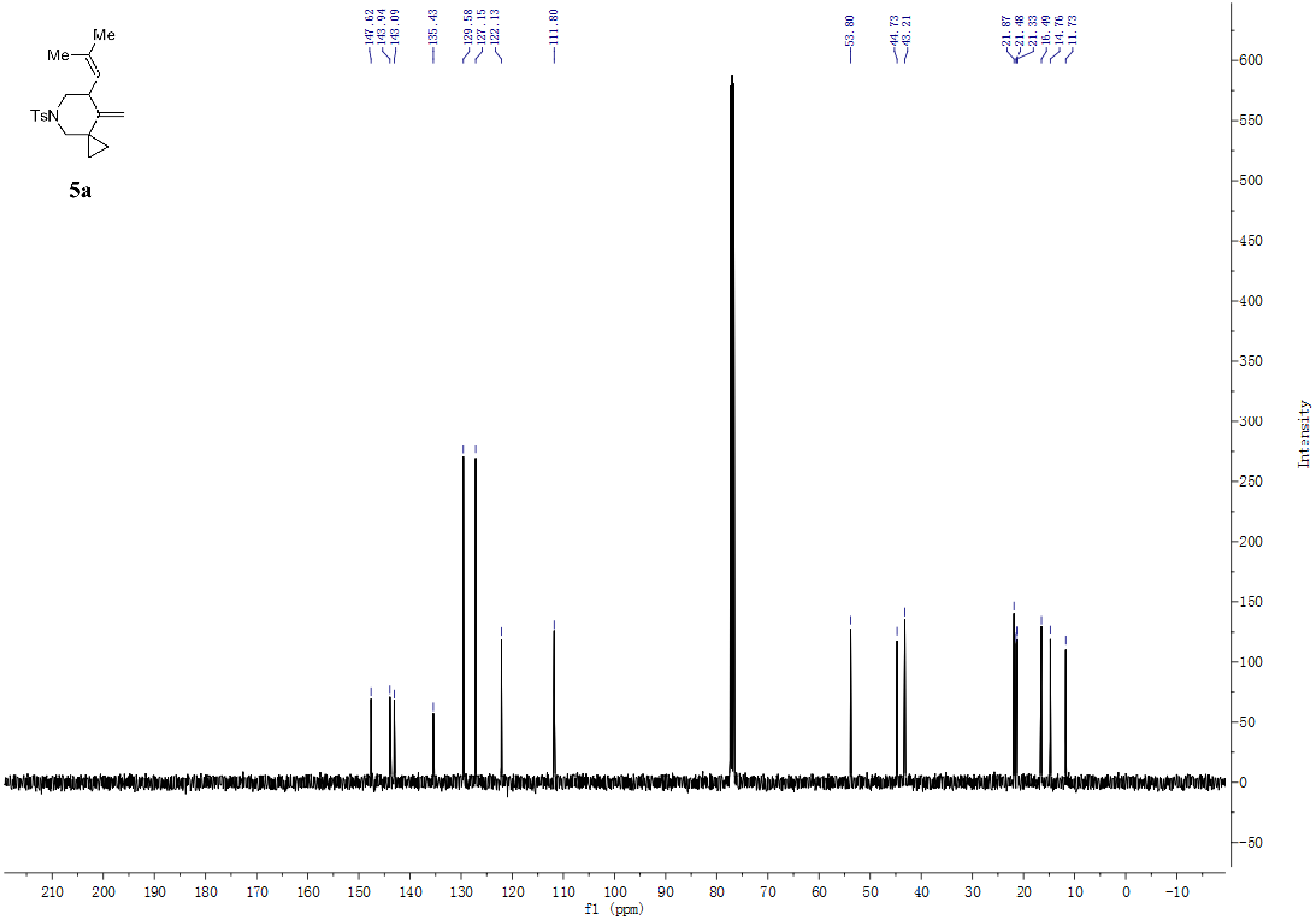


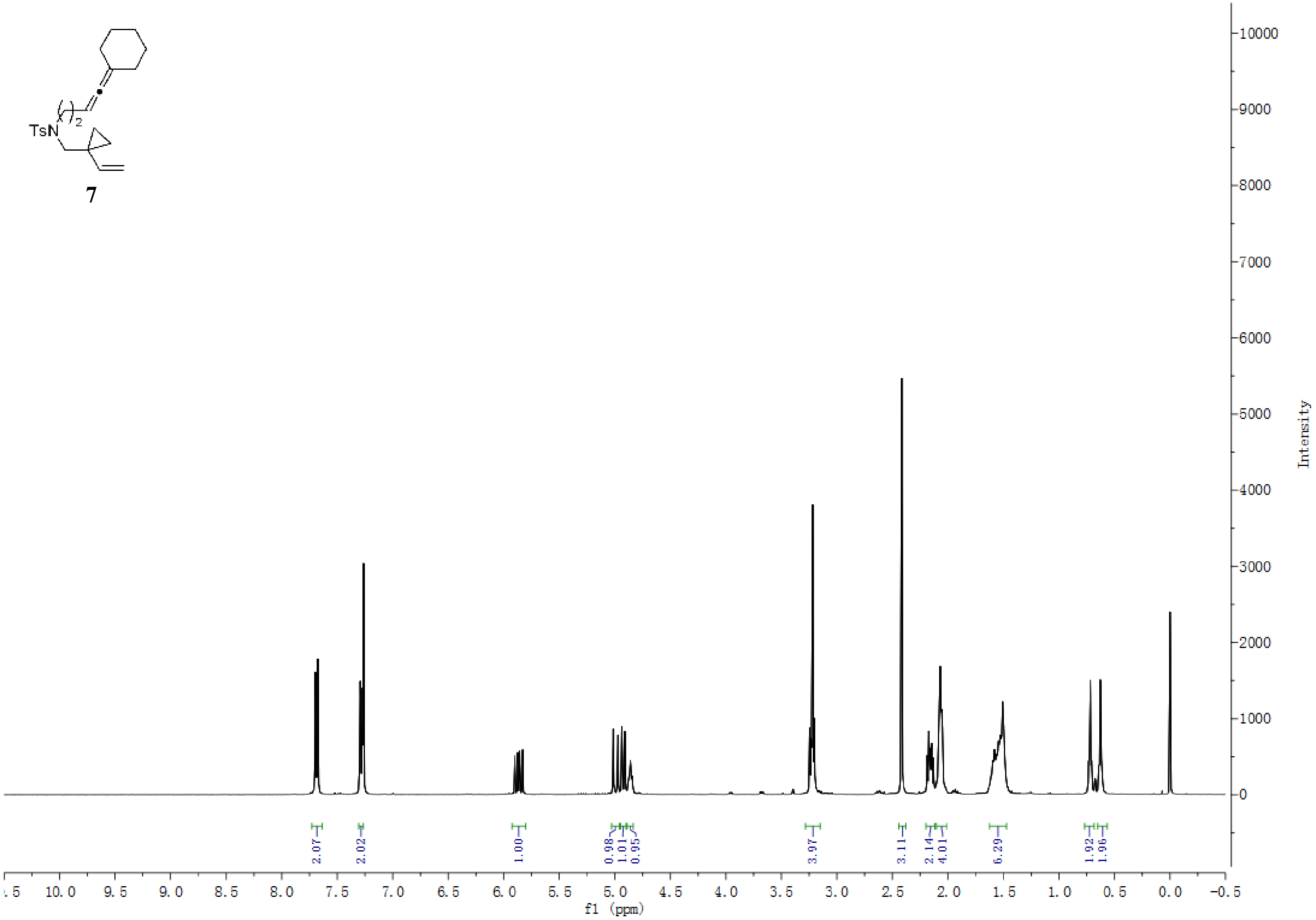
5a

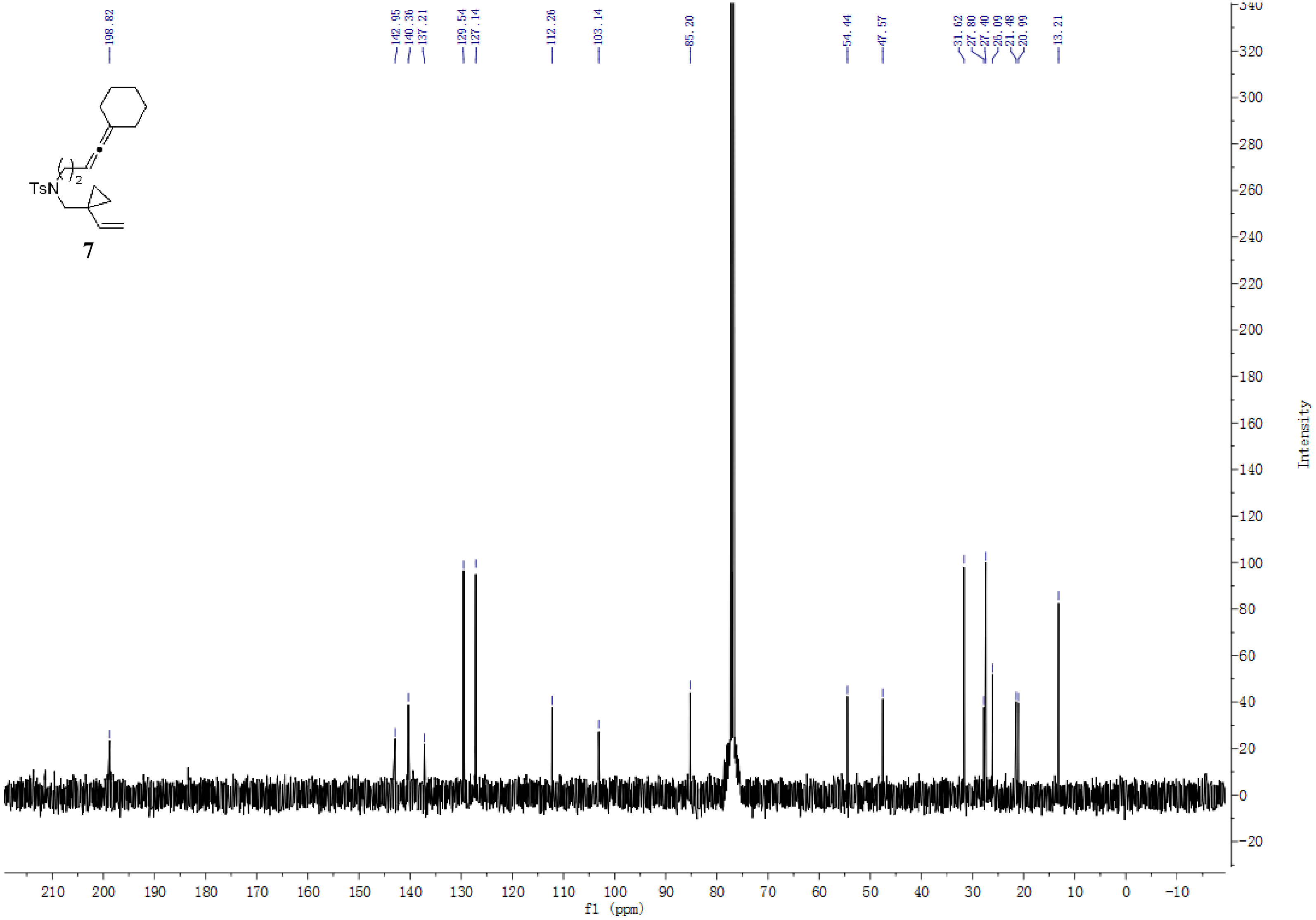
Me
Me
TsN
1.98
1.99
0.99
0.99
0.98
2.05
1.09
3.13
1.01
4.09
3.09
4.12
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
Intensity

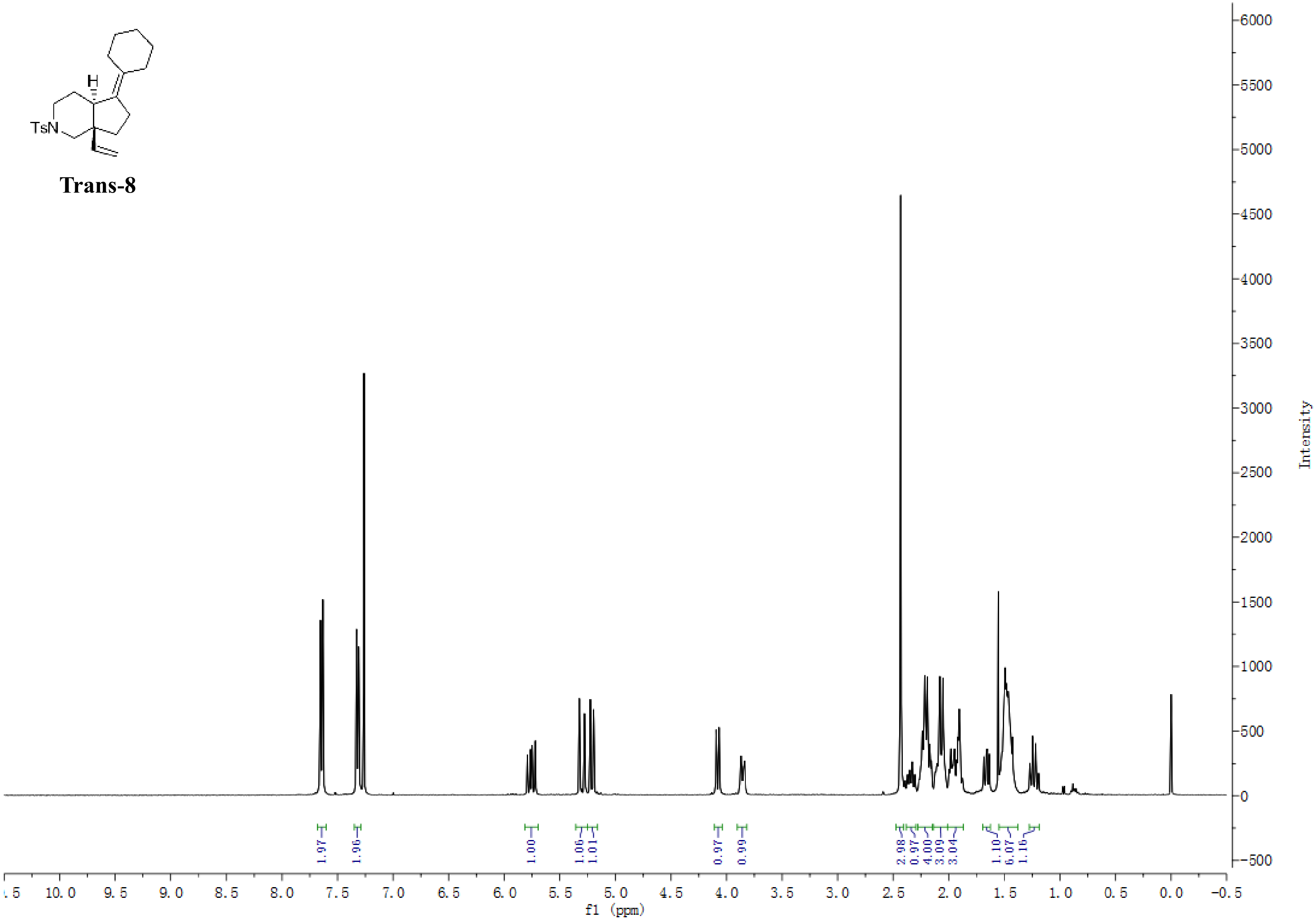

Me
Me
TsN

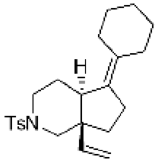
5a


147.62
143.94
143.09
135.43
129.58
127.15
122.13
111.80
53.80
44.73
43.21
21.87
21.48
21.33
16.49
14.76
11.73
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
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)

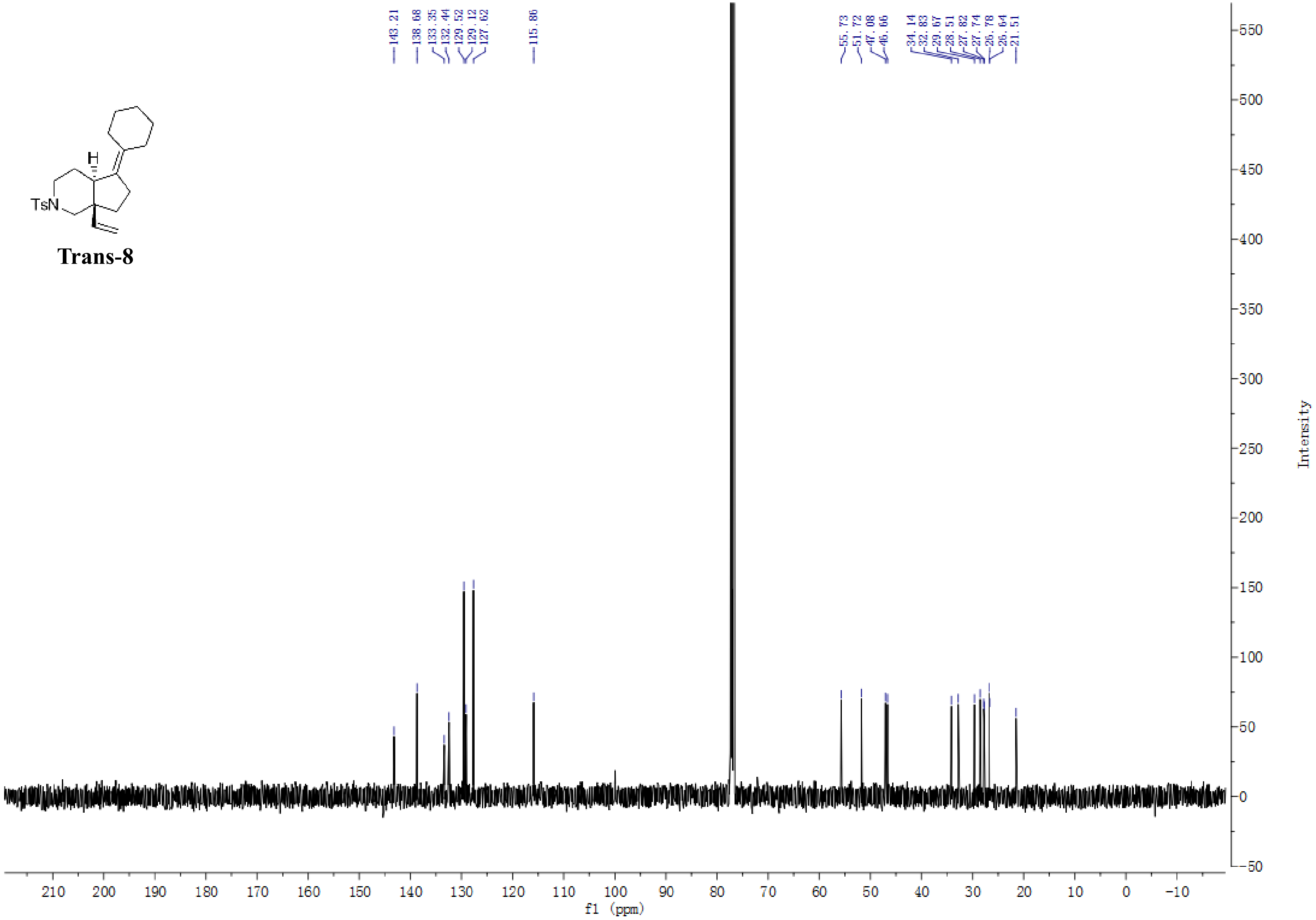

TsN
2
7
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
Intensity
2.07
2.02
1.00
0.98
1.01
0.95
3.97
3.11
2.14
4.01
6.29
1.92
1.96
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

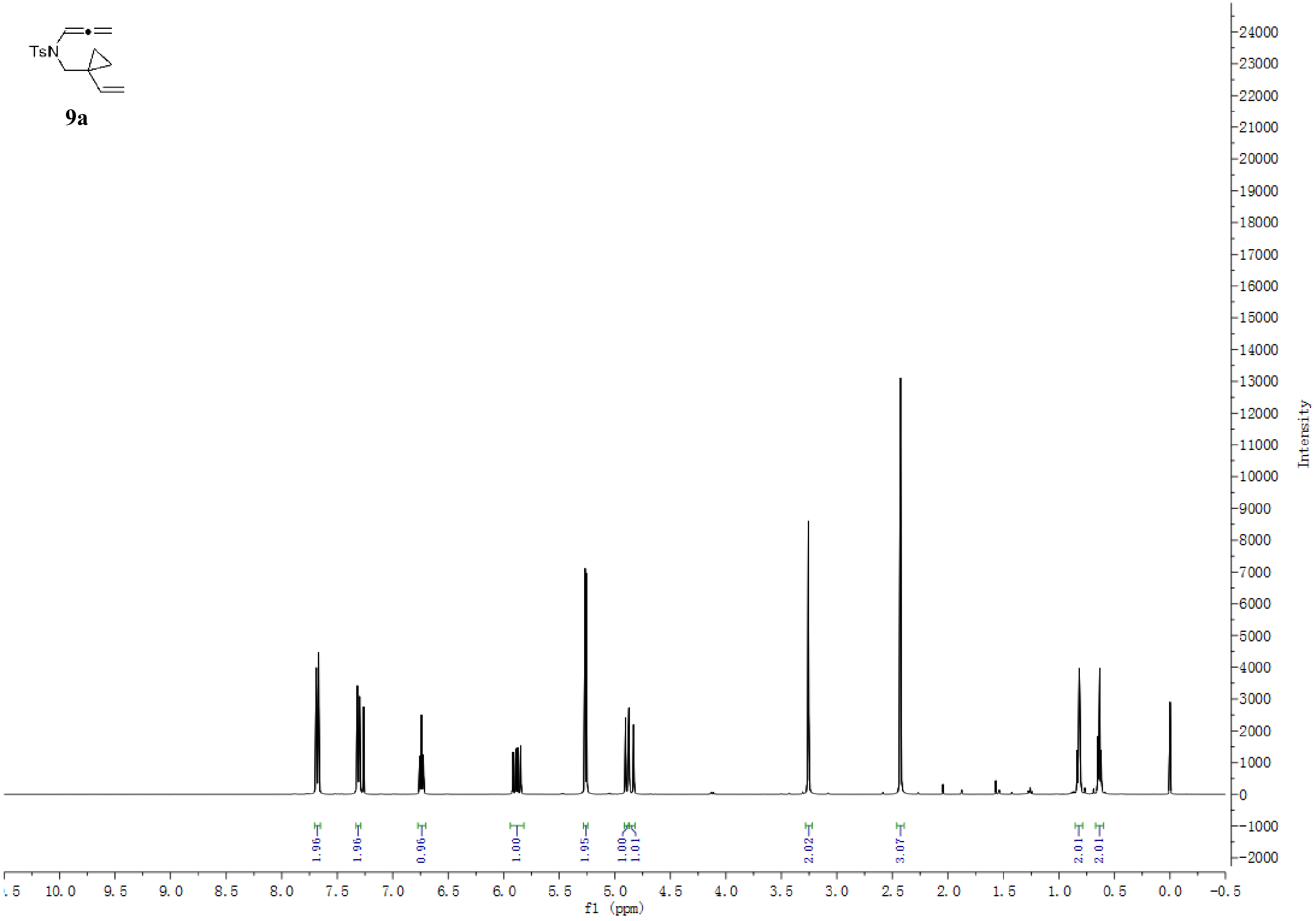

198.82
142.95
140.36
137.21
129.54
127.14
112.26
103.14
85.20
54.44
47.57
31.62
27.80
27.40
26.09
21.48
20.99
13.21
TsN
2
7
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
Intensity
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

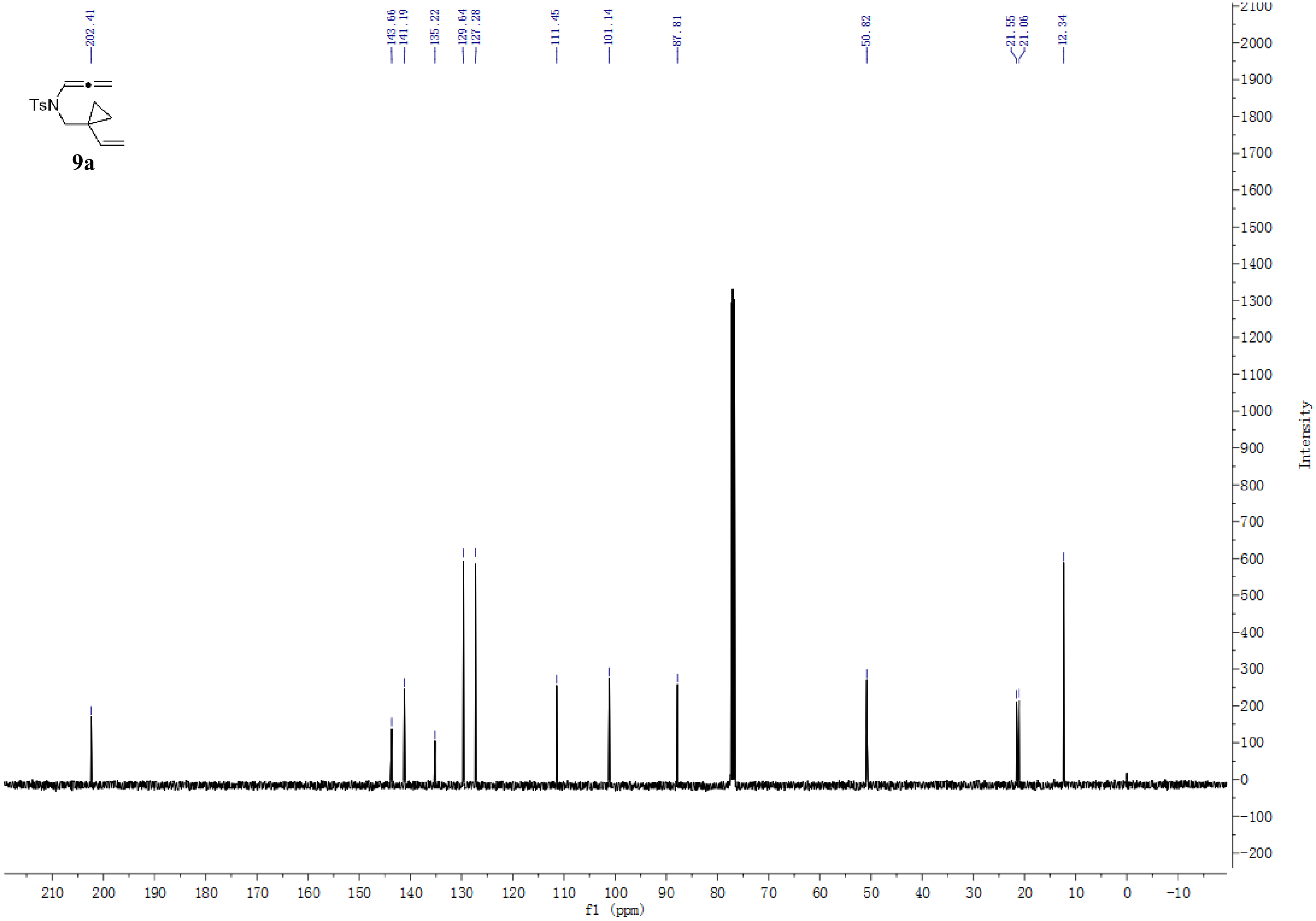

TsN
H
Trans-8
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
Intensity
1.97
1.96
1.00
1.06
1.01
0.97
0.99
2.98
0.97
4.00
3.09
3.04
1.10
6.07
1.16
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

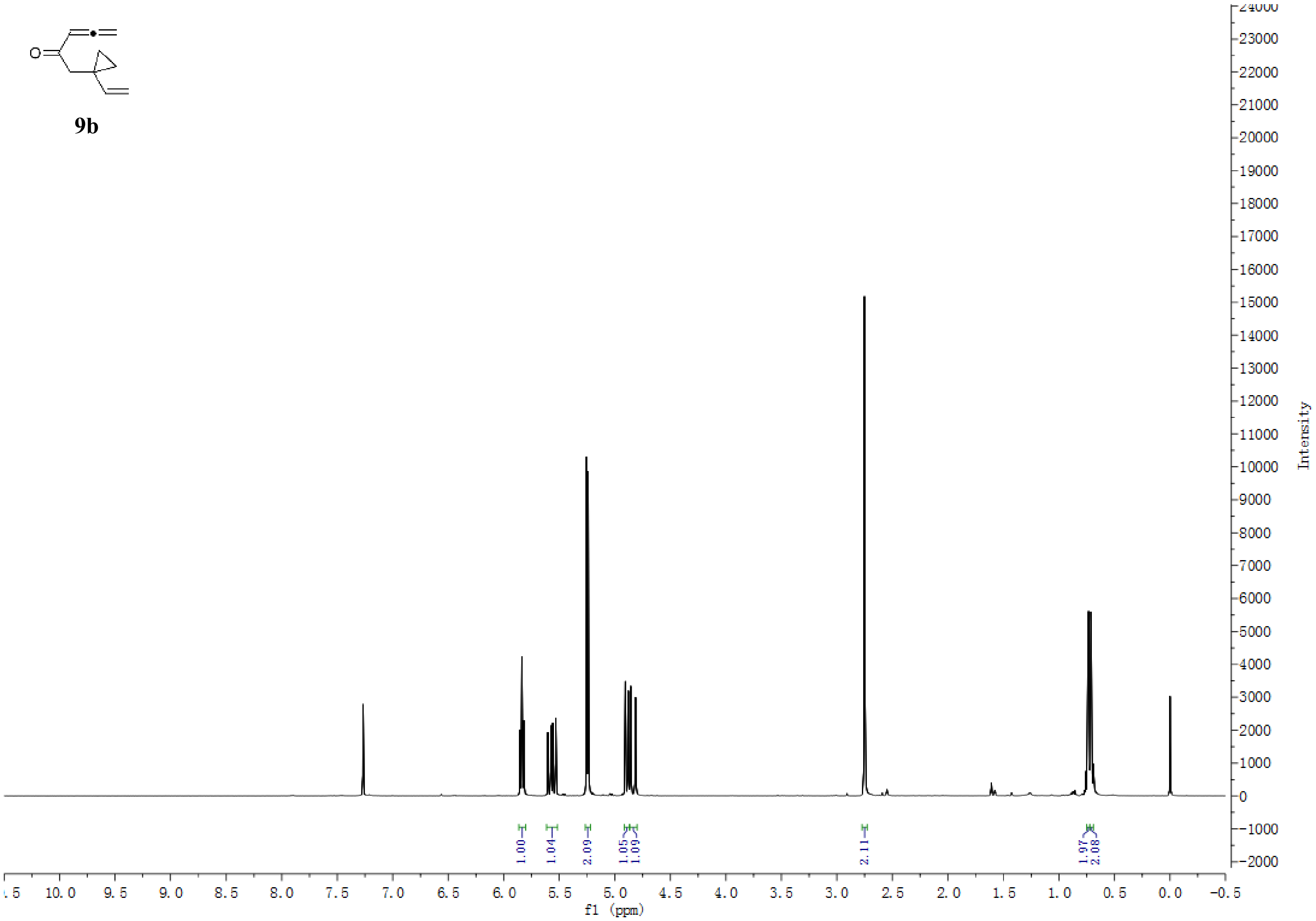

H
TsN

Trans-8

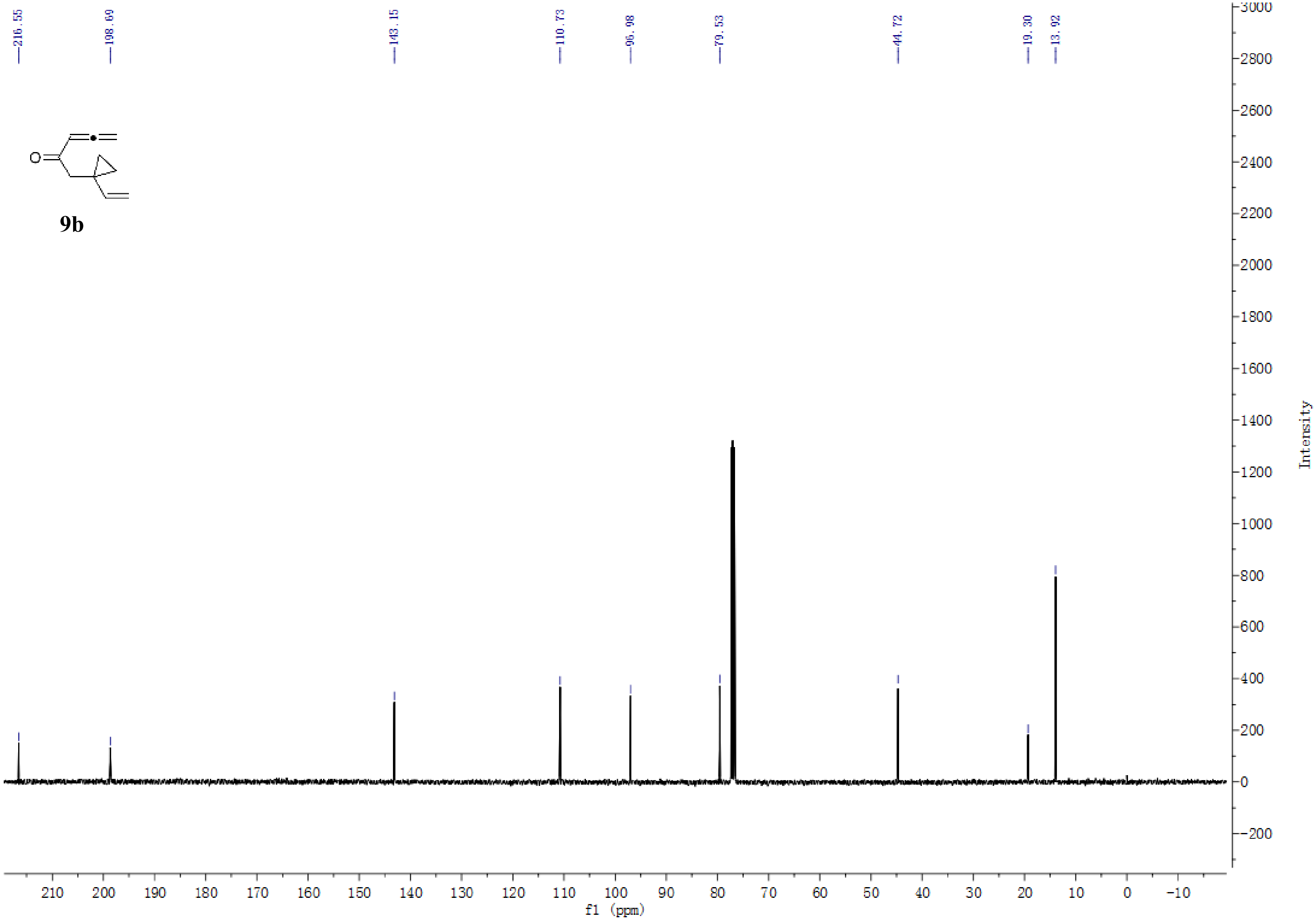

143.21
138.68
133.35
132.44
129.52
129.12
127.62
115.86
55.73
51.72
47.08
46.66
34.14
32.83
29.67
28.51
27.82
27.74
26.78
26.64
21.51
550
500
450
400
350
300
250
200
150
100
50
0
-50
Intensity
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


TsN
9a
1.96
1.96
0.96
1.00
1.95
1.00
1.01
2.02
3.07
2.01
2.01
.5
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)
24000
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
Intensity

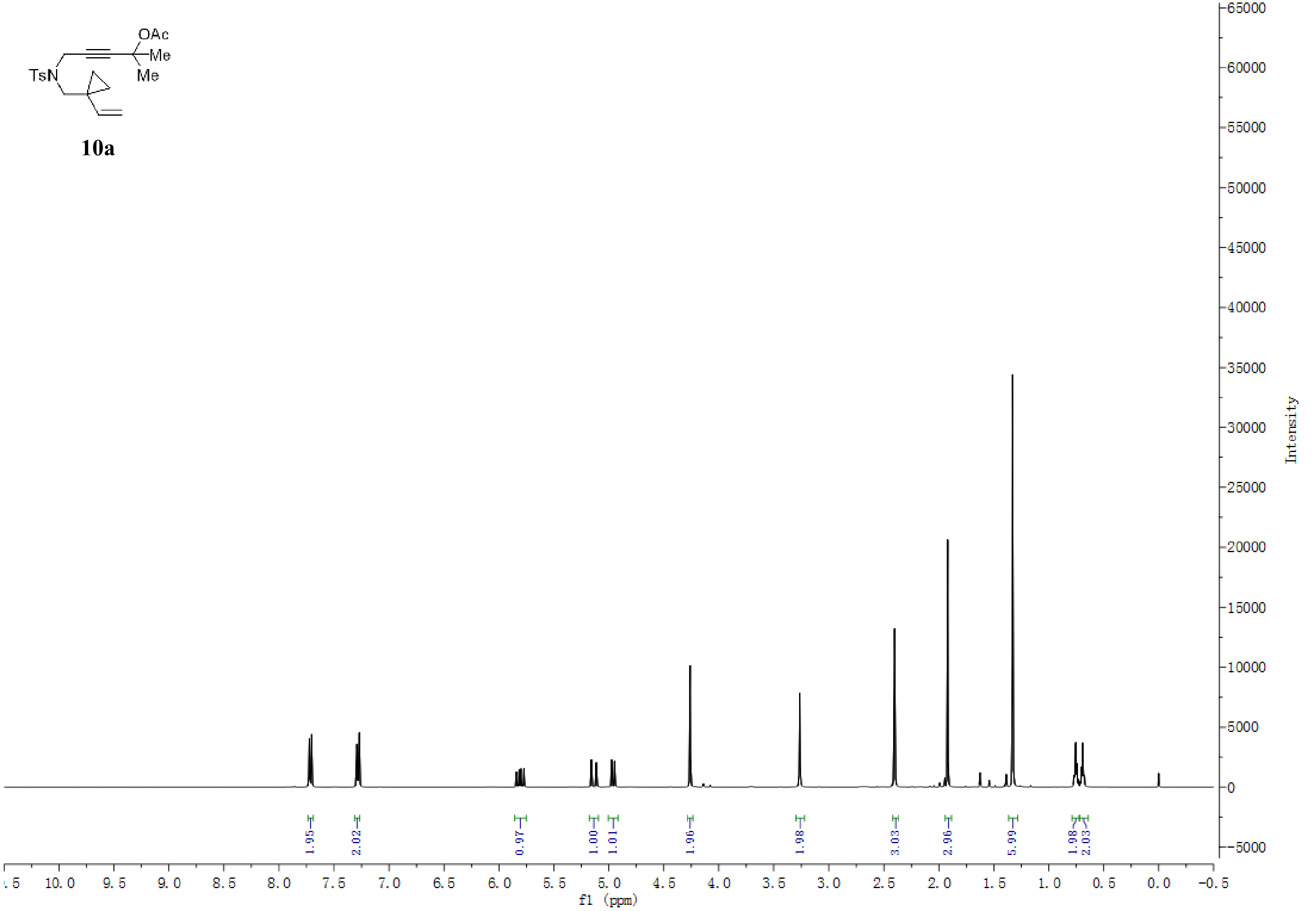

202.41
143.66
141.19
135.22
129.64
127.28
111.45
101.14
87.81
50.82
21.55
21.06
12.34
TsN
9a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
Intensity



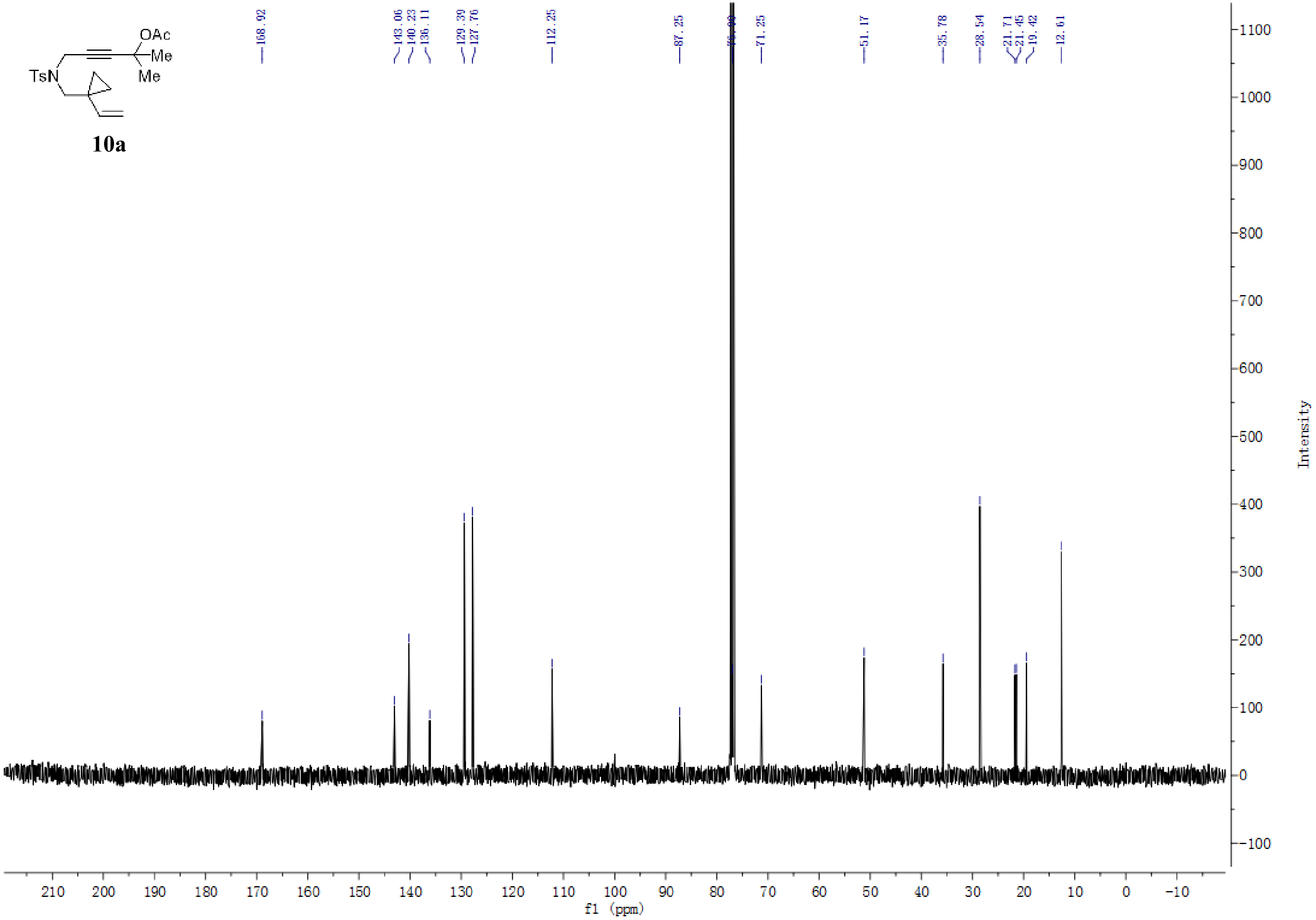
9b
1.00
1.04
2.09
1.05
1.09
2.11
1.97
2.08
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
24000
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
Intensity

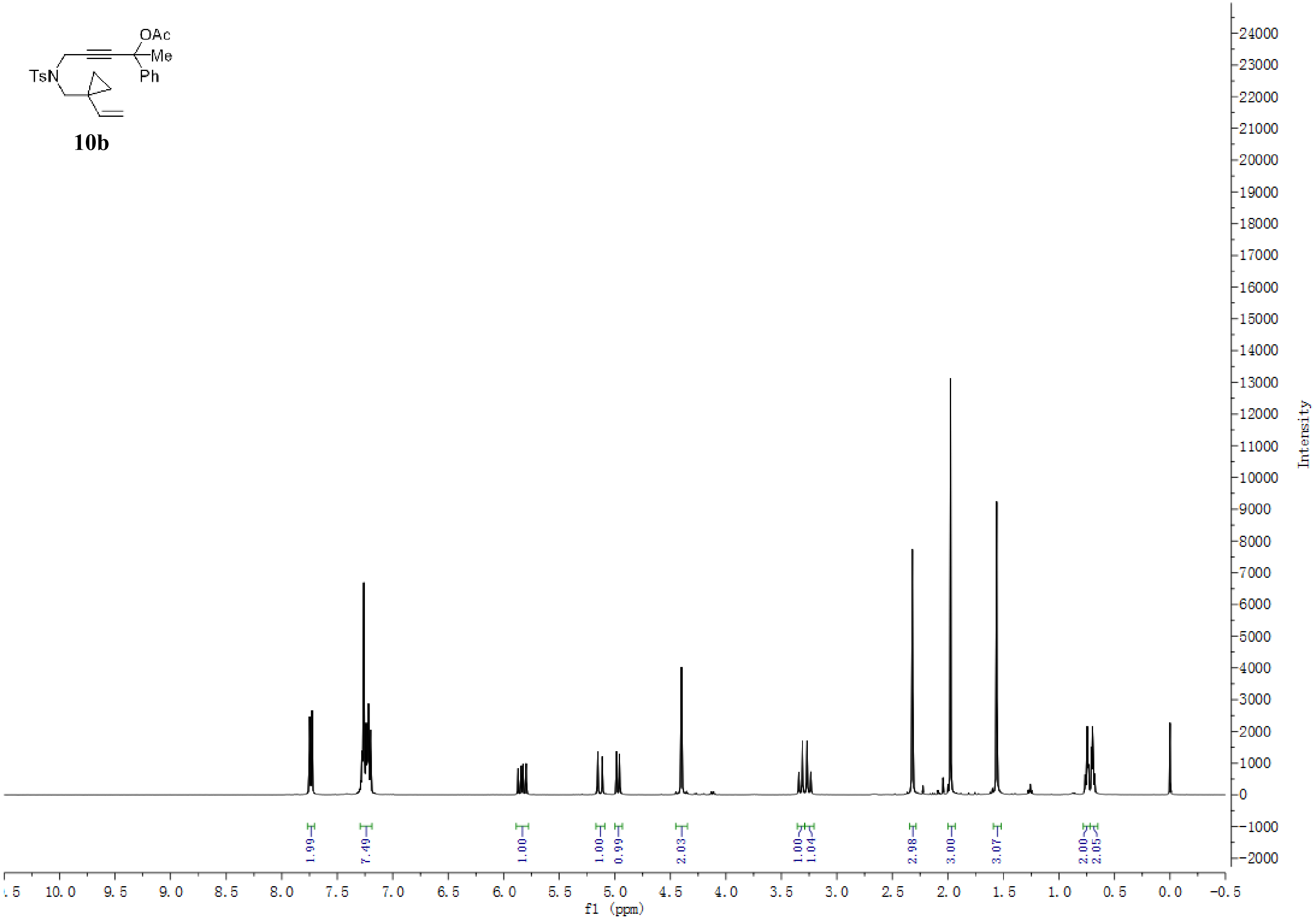

216.55
198.69
143.15
110.73
96.98
79.53
44.72
19.30
13.92
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
Intensity
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

9b

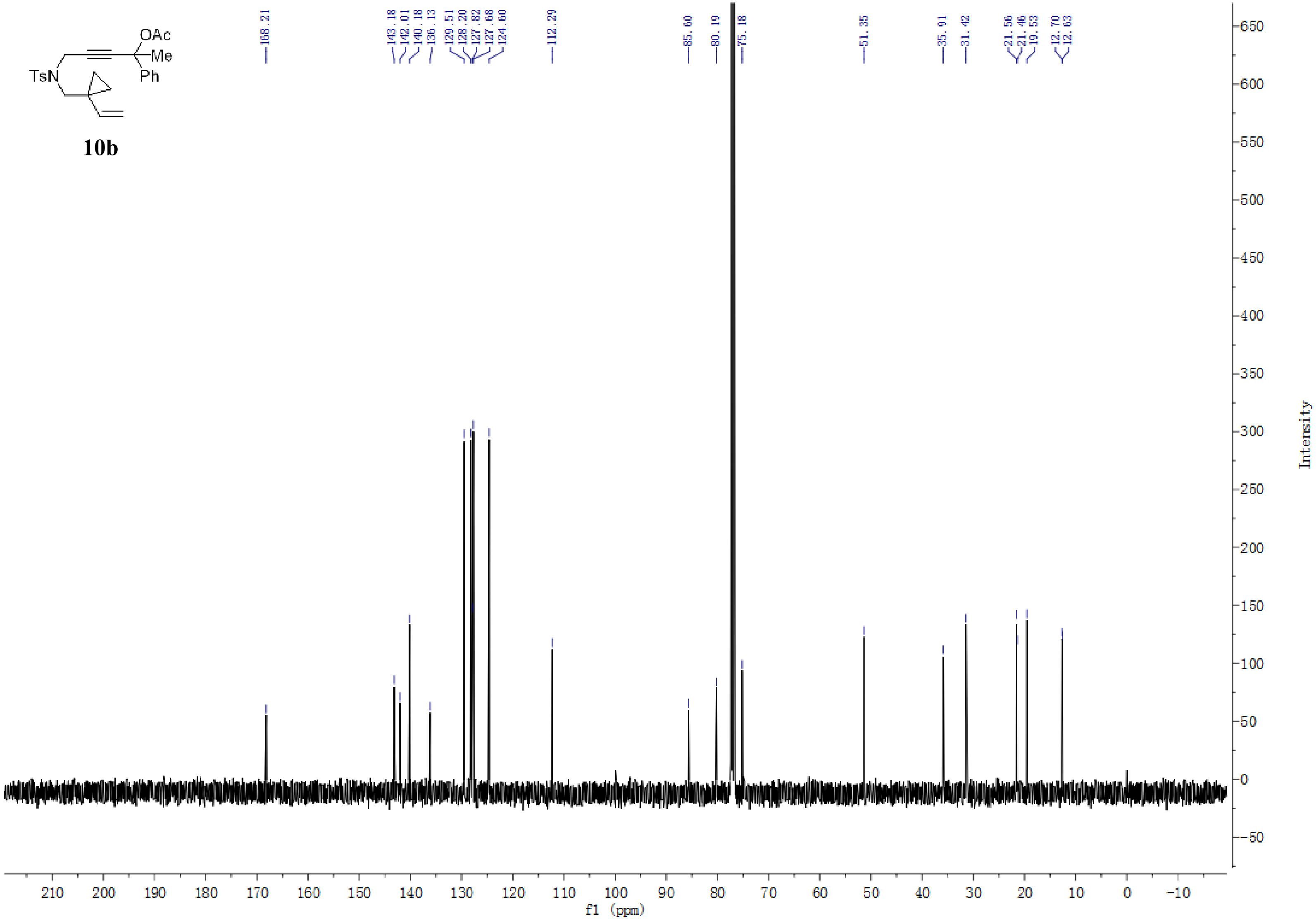

OAc
Me
Me
TsN
1.95
2.02
0.97
1.00
1.01
1.96
1.98
3.03
2.96
5.99
1.98
2.03
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
Intensity

10a


OAc
Me
Me
TsN
10a
168.92
143.06
140.23
136.11
129.39
127.76
112.25
87.25
71.25
51.17
35.78
28.54
21.71
21.45
19.42
12.61
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
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)

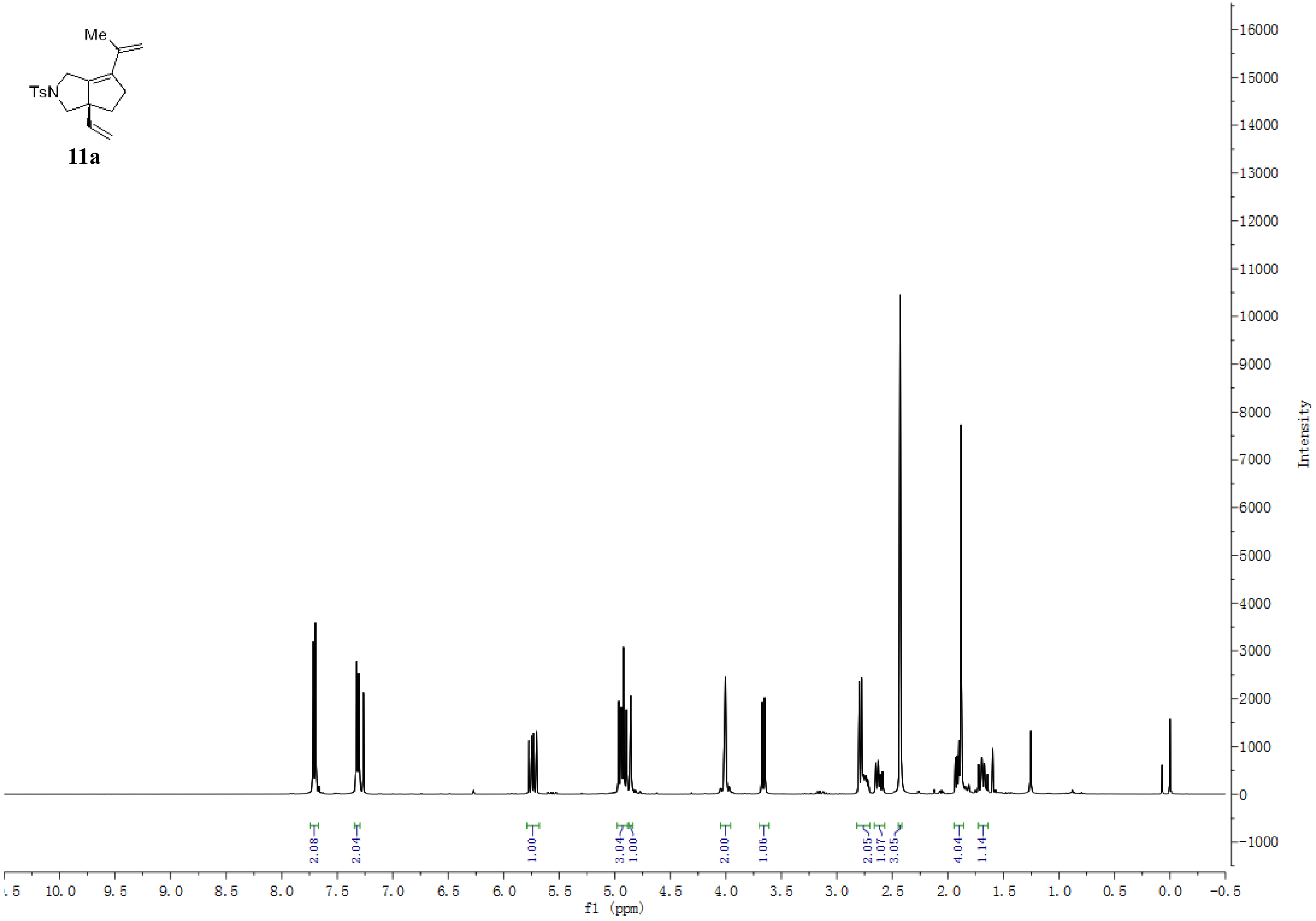

OAc
Me
Ph
TsN
24000
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
−2000
Intensity
1.99
7.49
1.00
1.00
0.99
2.03
1.00
1.04
2.98
3.00
3.07
2.00
2.05
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

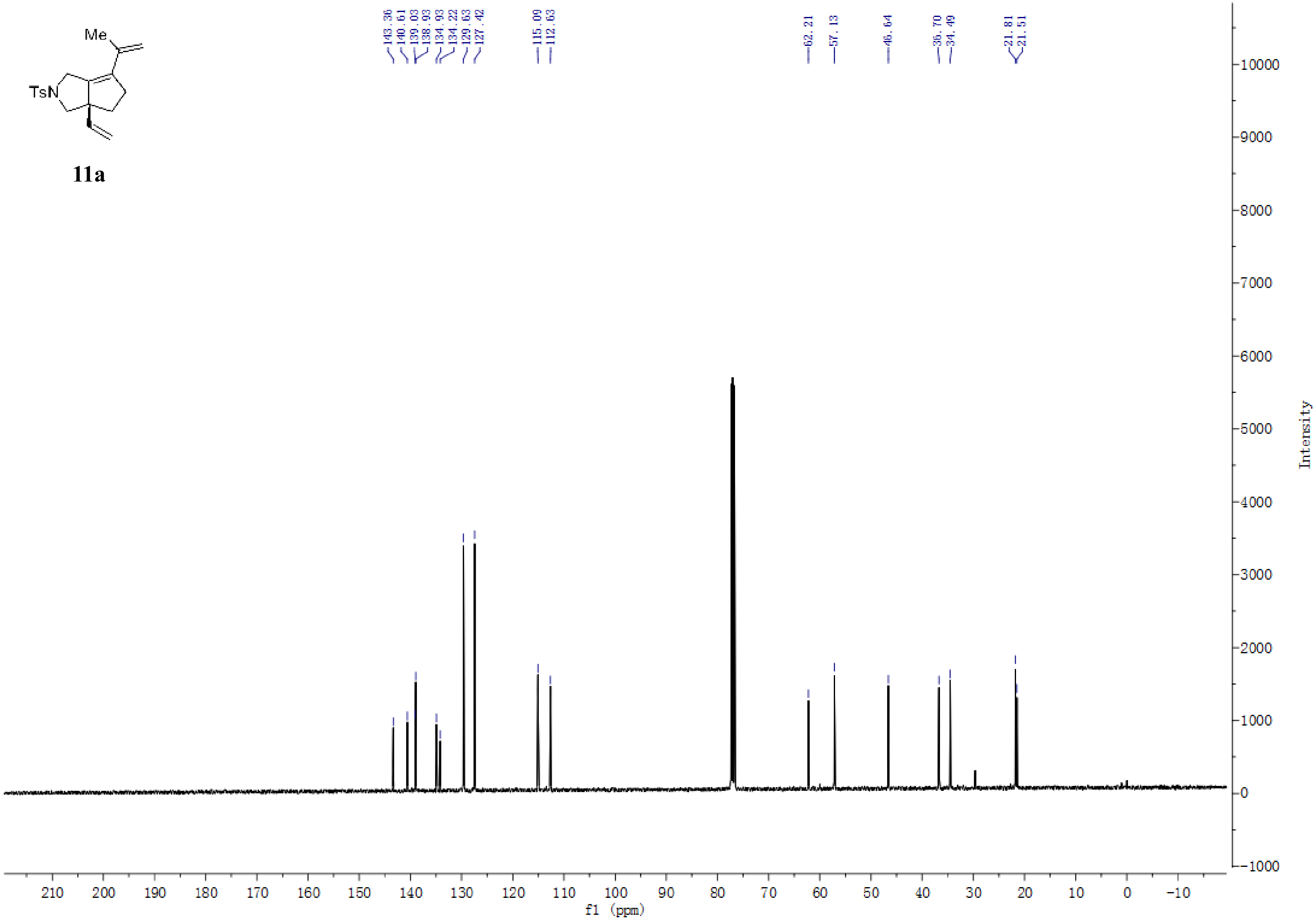
10b



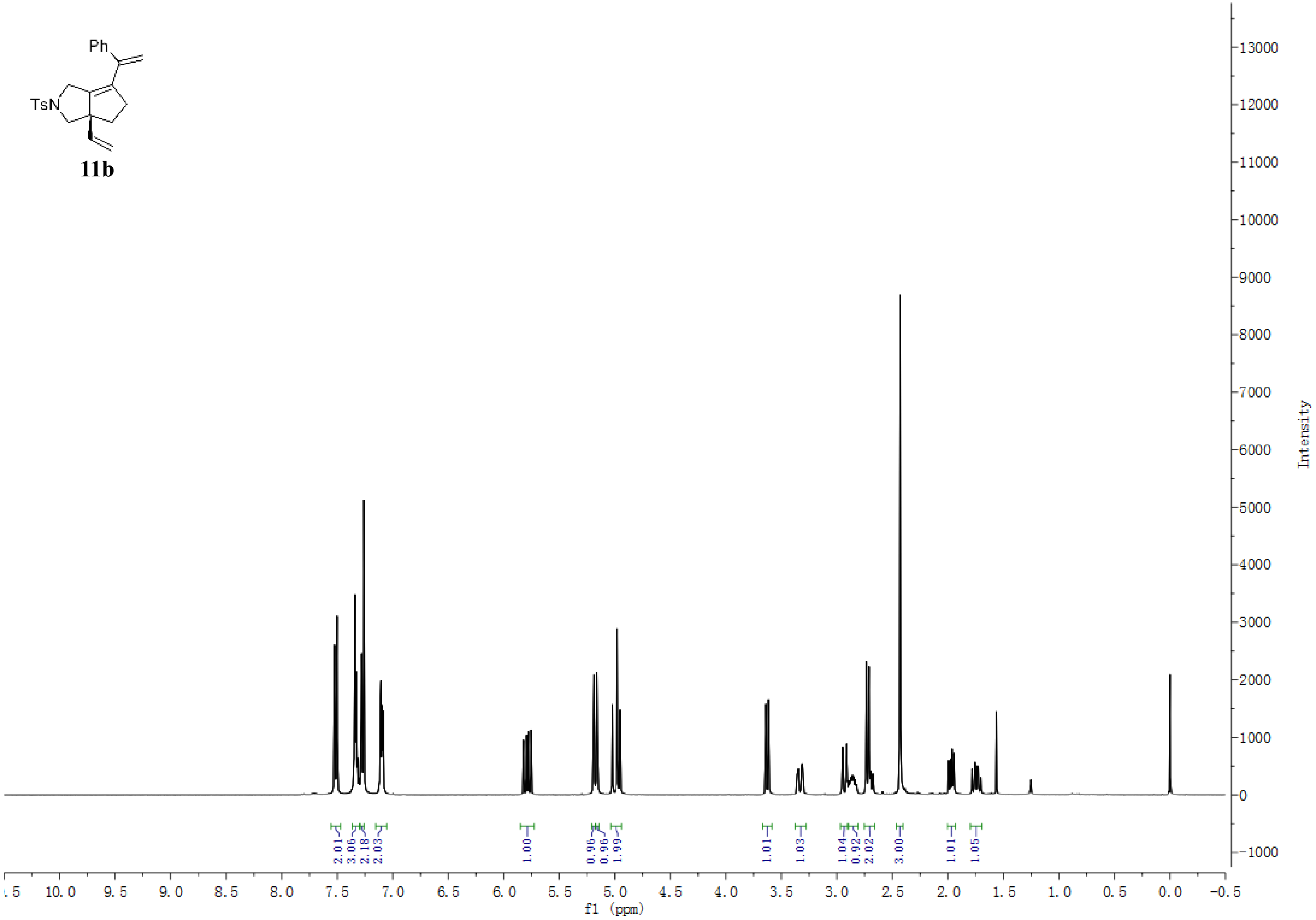
10b

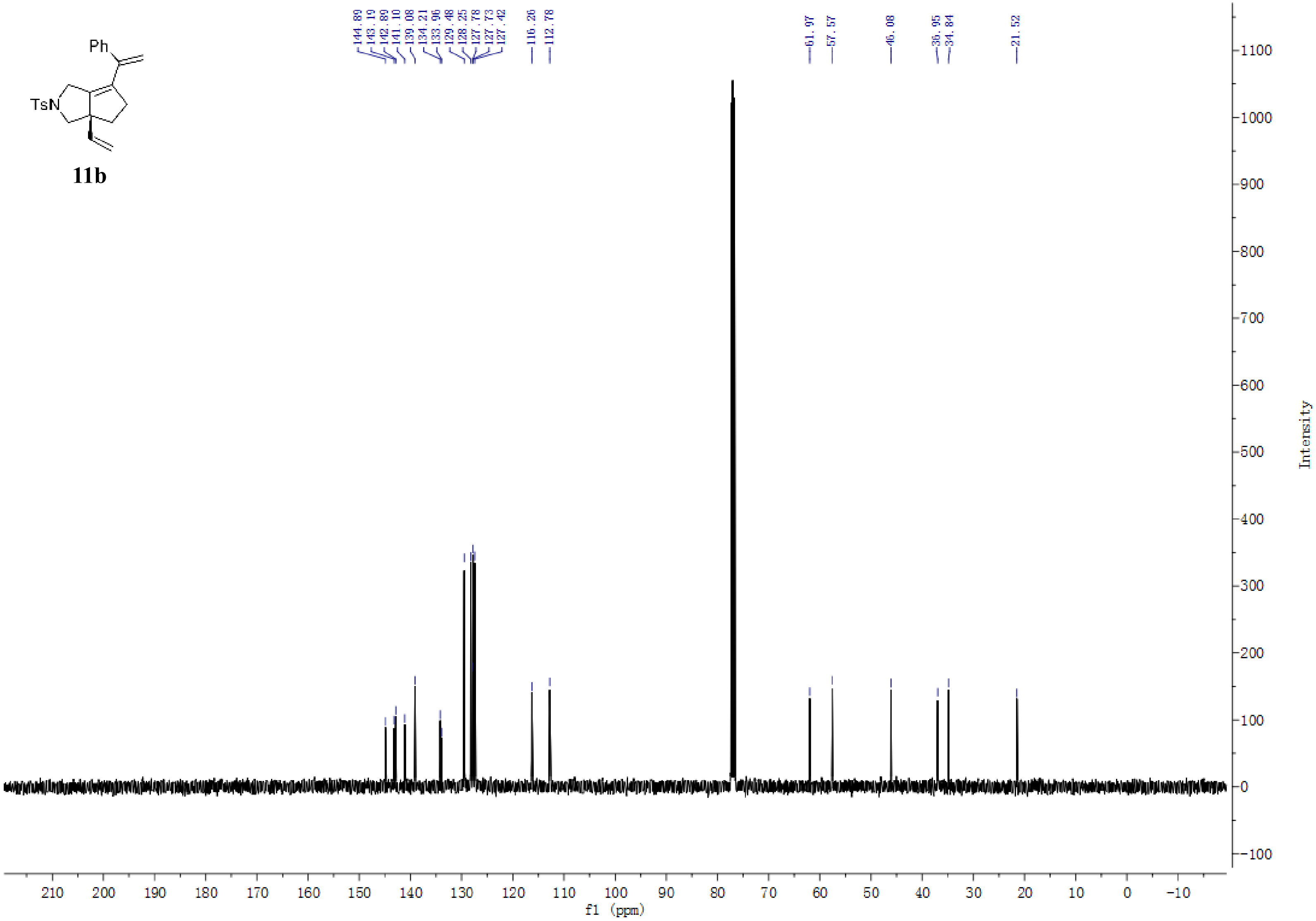
OAc
Me
Ph
TsN
168.21
143.18
142.01
140.18
136.13
129.51
128.20
127.82
127.68
124.60
112.29
85.60
80.19
75.18
51.35
35.91
31.42
21.56
21.46
19.53
12.70
12.63
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
Intensity
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Me
TsN
11a
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
Intensity
2.08
2.04
1.00
3.04
1.00
2.00
1.06
2.05
1.07
3.05
4.04
1.14
.5
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)

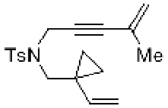

11a

Me
TsN
143.36
140.61
139.03
138.93
134.93
134.22
129.63
127.42
115.09
112.63
62.21
57.13
46.64
36.70
34.49
21.81
21.51
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)

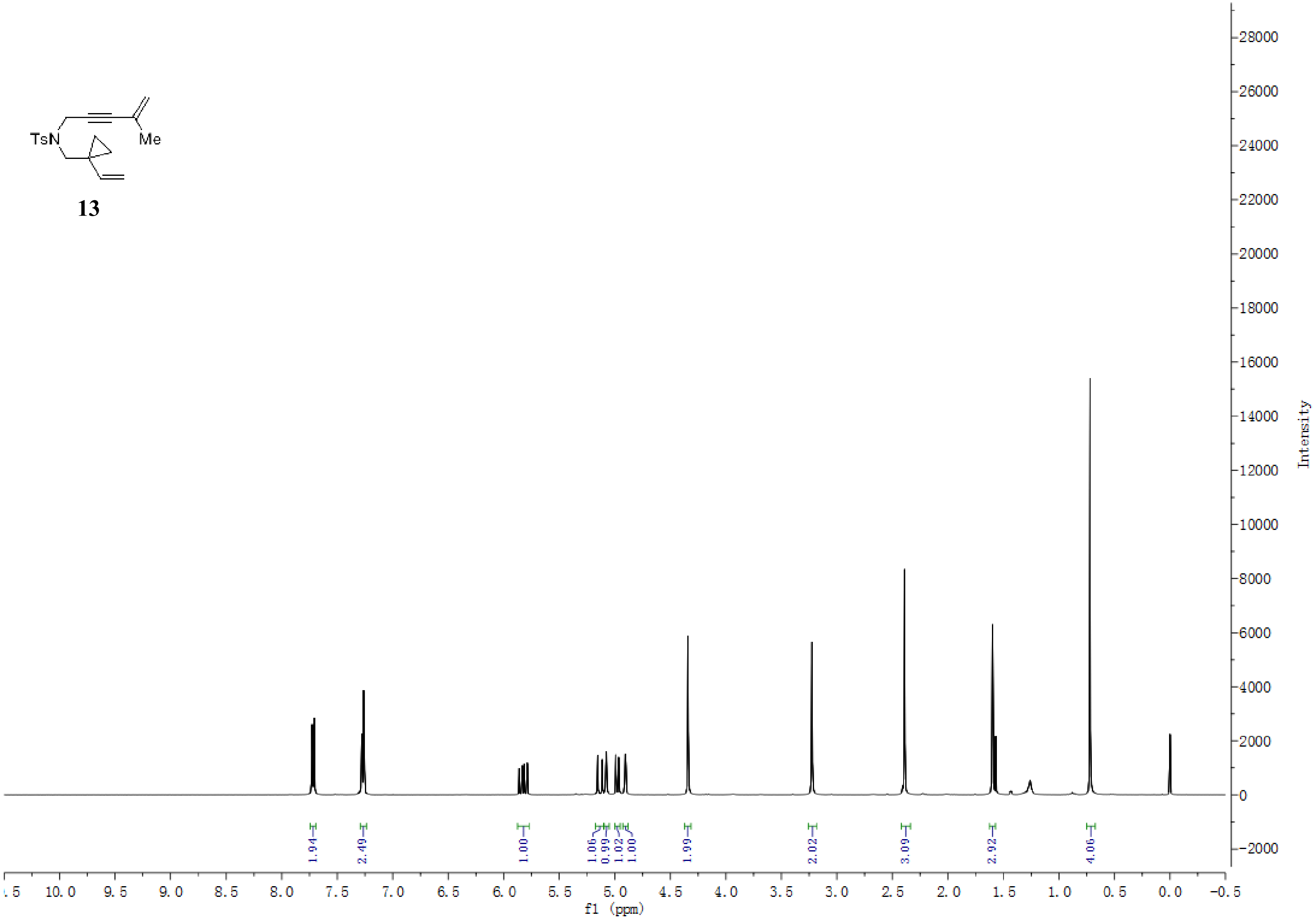

Ph
TsN
11b
2.01
3.06
2.18
2.03
1.00
0.96
0.96
1.99
1.01
1.03
1.04
0.92
2.02
3.00
1.01
1.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
Intensity

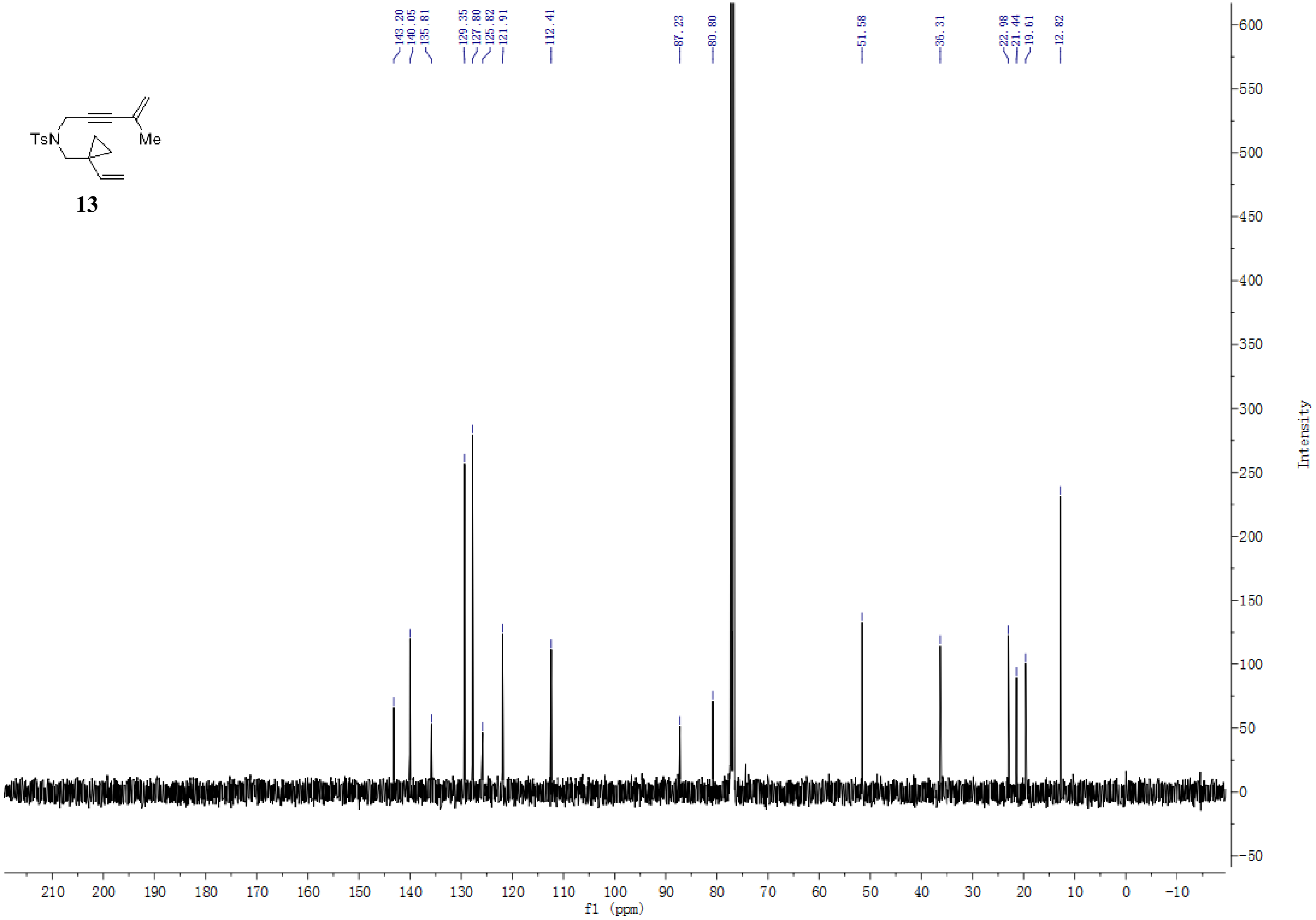

Ph
TsN
144.89
143.19
142.89
141.10
139.08
134.21
133.96
129.48
128.25
127.78
127.73
127.42
116.26
112.78
61.97
57.57
46.08
36.95
34.84
21.52
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
Intensity
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

11b


TsN
Me

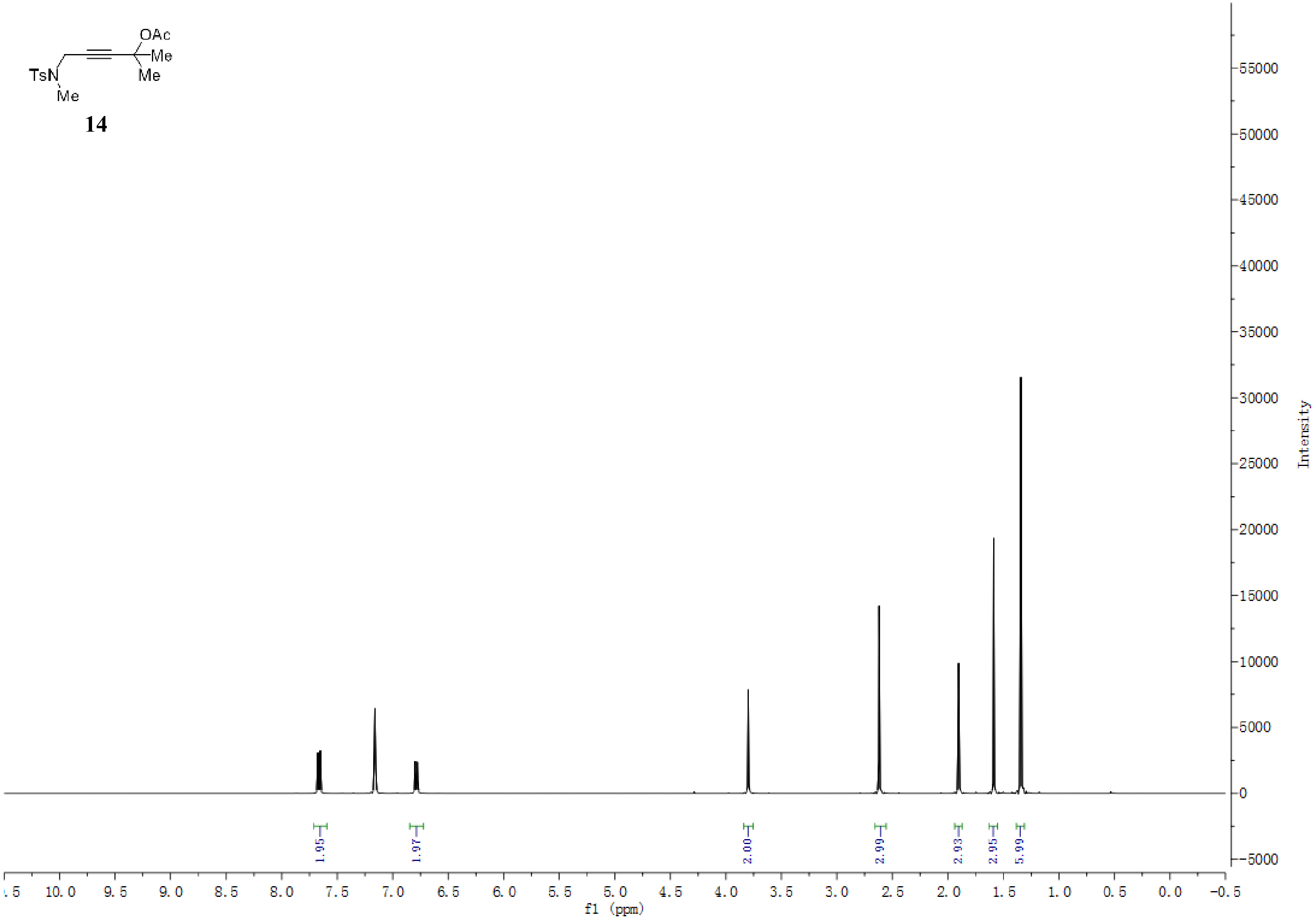
13


1.94
2.49
1.00
1.06
0.99
1.02
1.00
1.99
2.02
3.09
2.92
4.06
.5
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)
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
Intensity

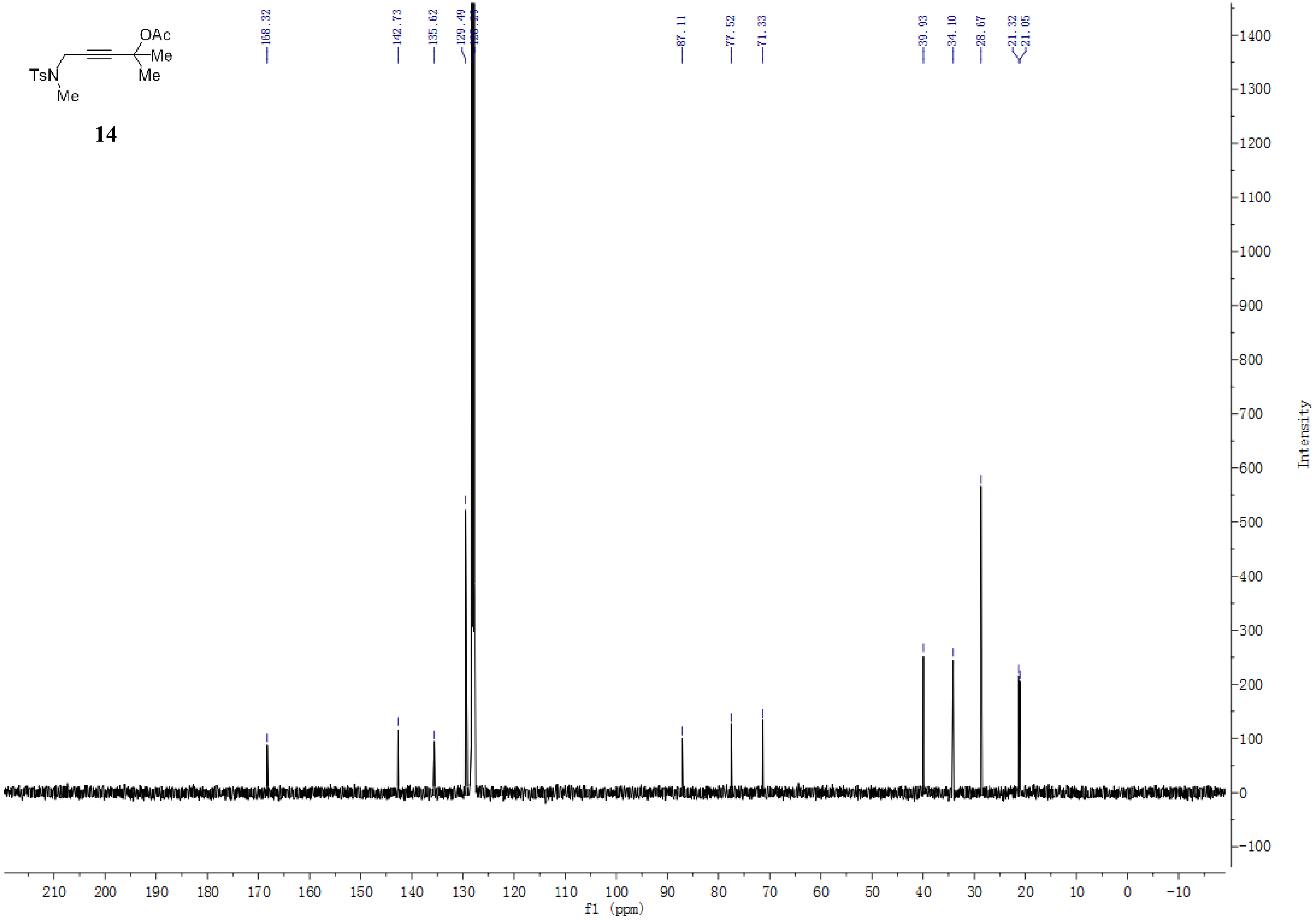

TsN
Me

13

143.20
140.05
135.81
129.35
127.80
125.82
121.91
112.41
87.23
80.80
51.58
36.31
22.98
21.44
19.61
12.82
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)
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
Intensity


14

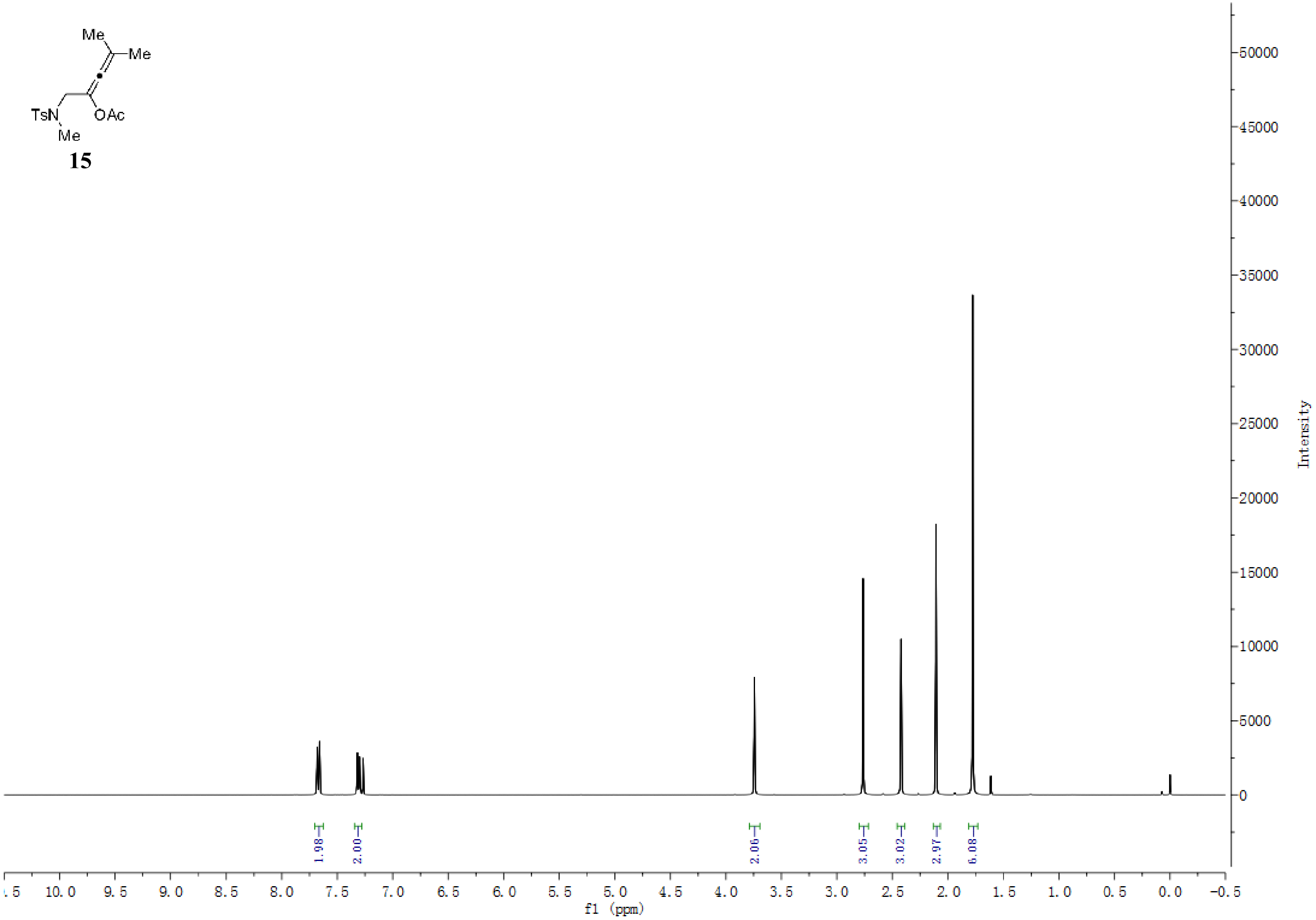
OAc
Me
Me
TsN
Me
1.95
1.97
2.00
2.99
2.93
2.95
5.99
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
Intensity

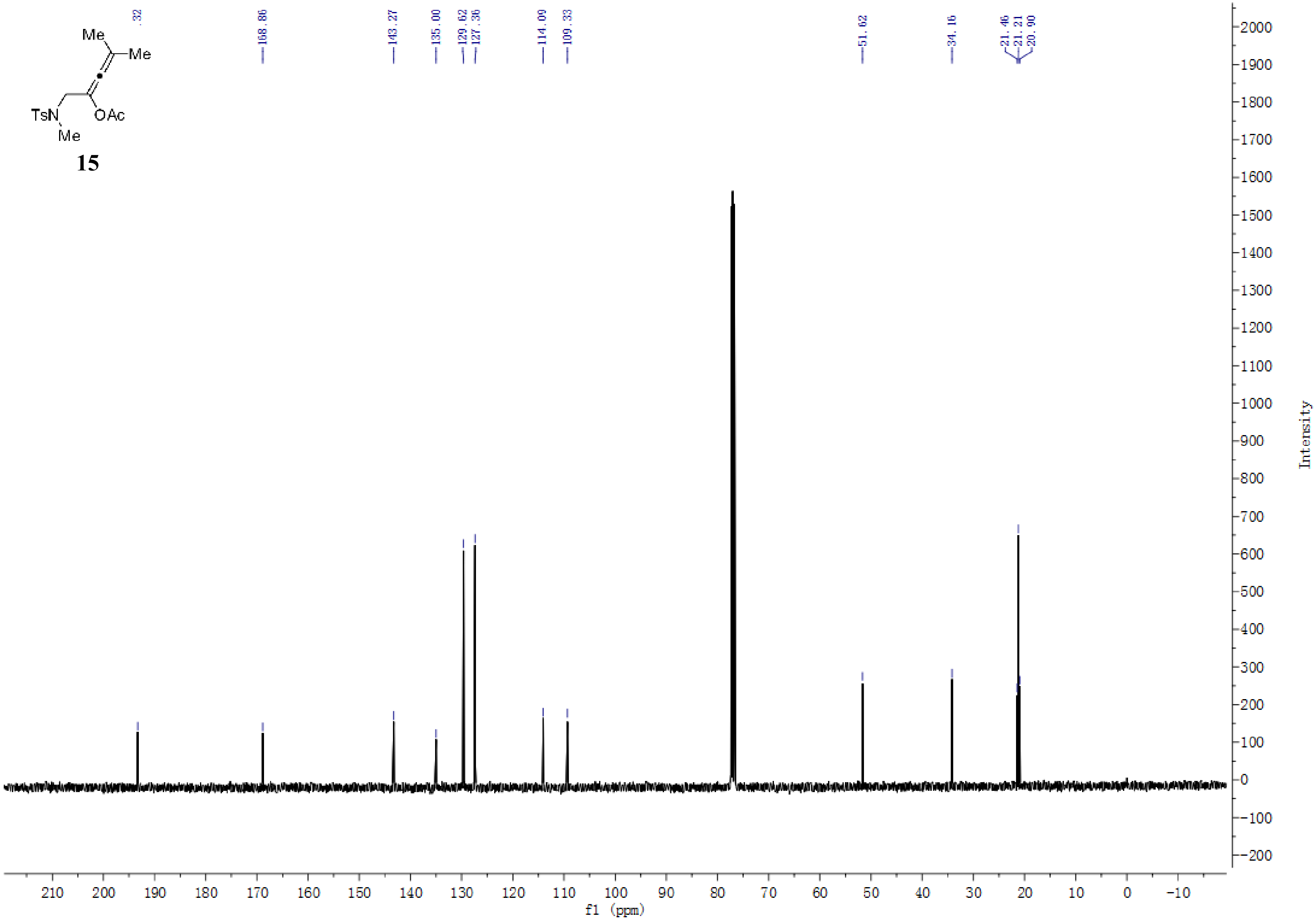

OAc
Me
Me
TsN
Me
168.32
142.73
135.62
129.49
87.11
77.52
71.33
39.93
34.10
28.67
21.32
21.05
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
Intensity

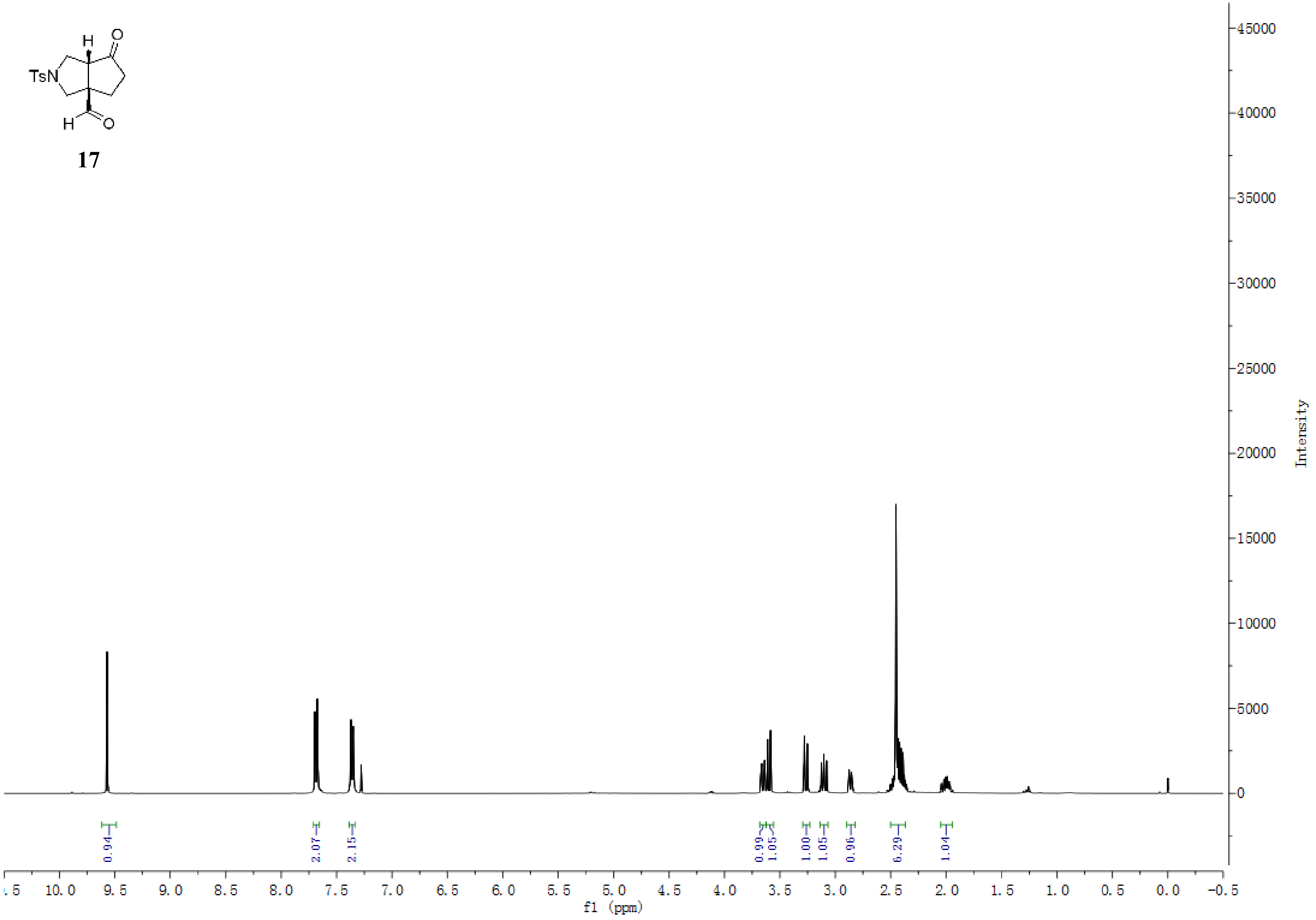
14

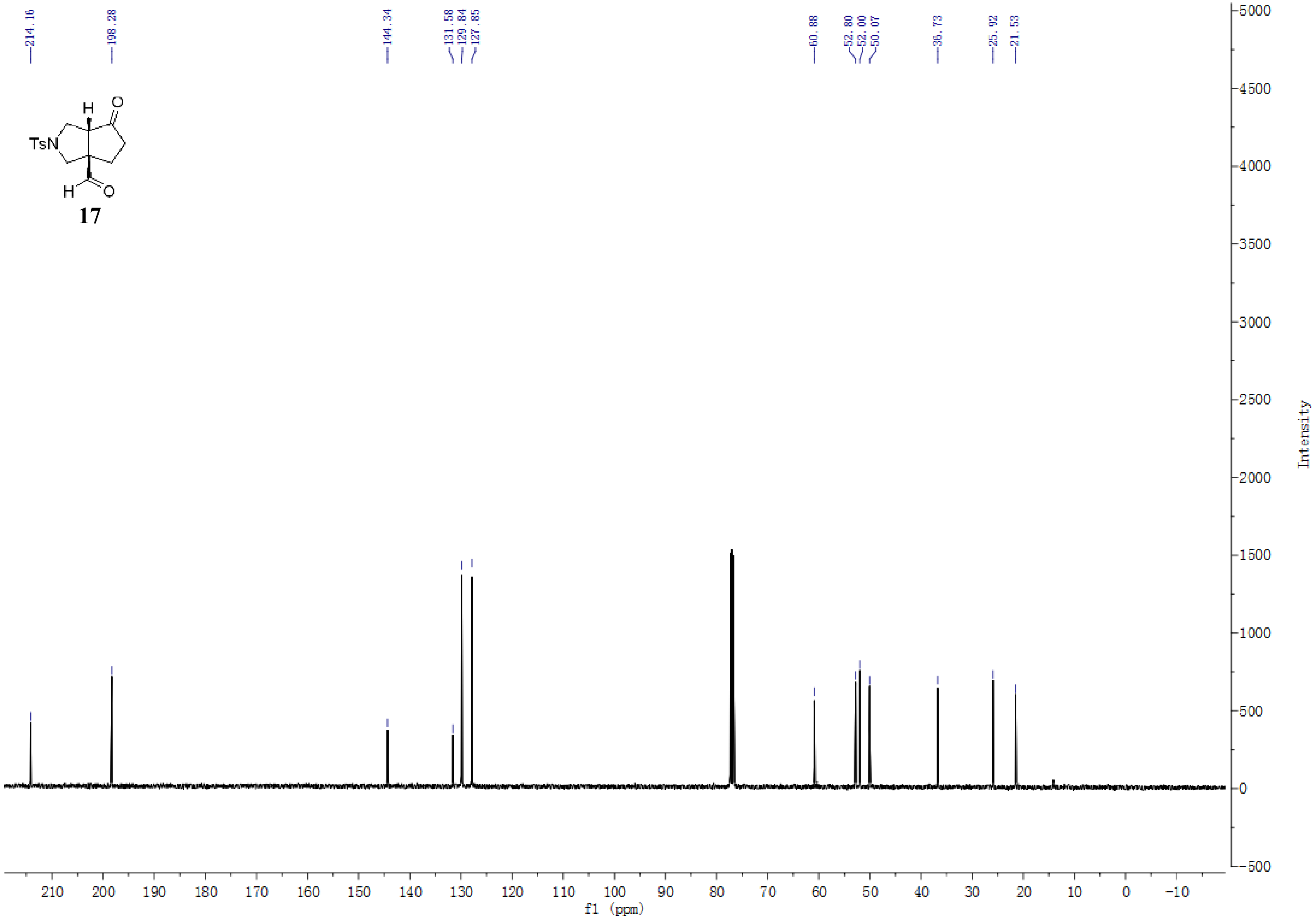
Me
Me
TsN
OAc
Me

15

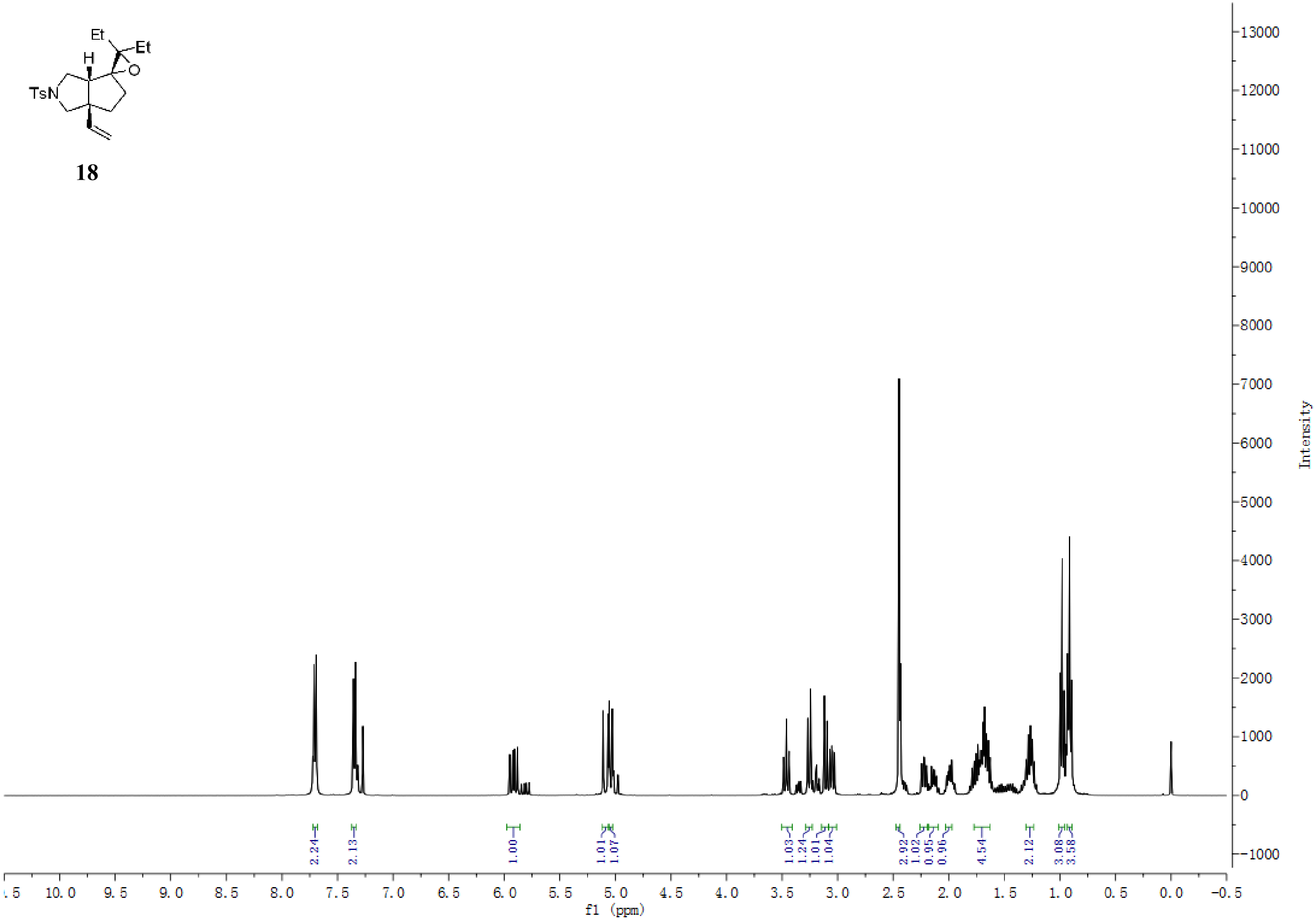

1.98
2.00
2.06
3.05
3.02
2.97
6.08
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
Intensity


Me
Me
TsN
OAc
Me
15
.32
168.86
143.27
135.00
129.62
127.36
114.09
109.33
51.62
34.16
21.46
21.21
20.90
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)
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
Intensity


TsN
H
O
H
O
17
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
Intensity
0.94
2.07
2.15
0.99
1.05
1.00
1.05
0.96
6.29
1.04
.5
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)

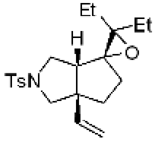

214.16
198.28
144.34
131.58
129.84
127.85
60.88
52.80
52.00
50.07
36.73
25.92
21.53
H
O
TsN
H
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500
Intensity

17

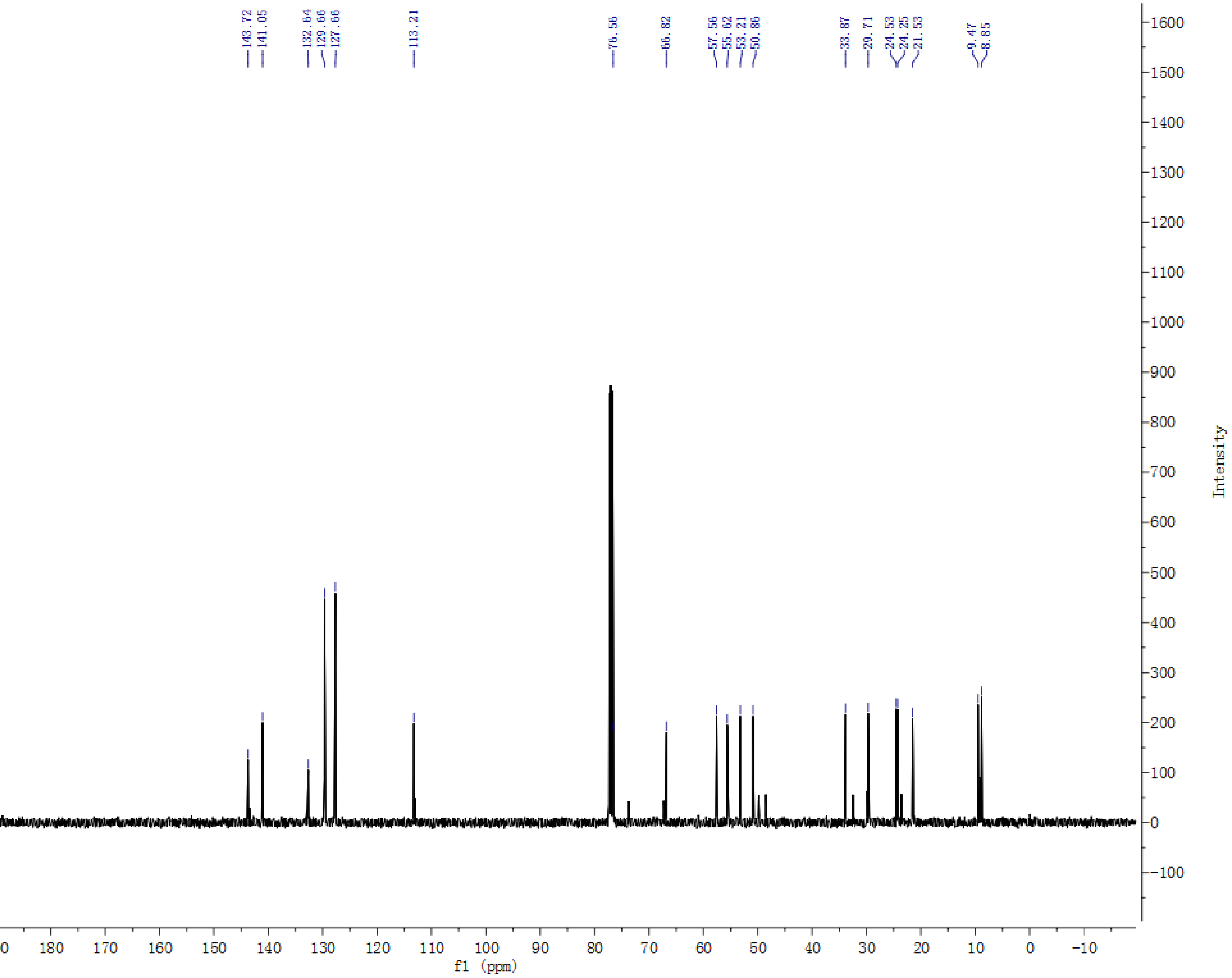


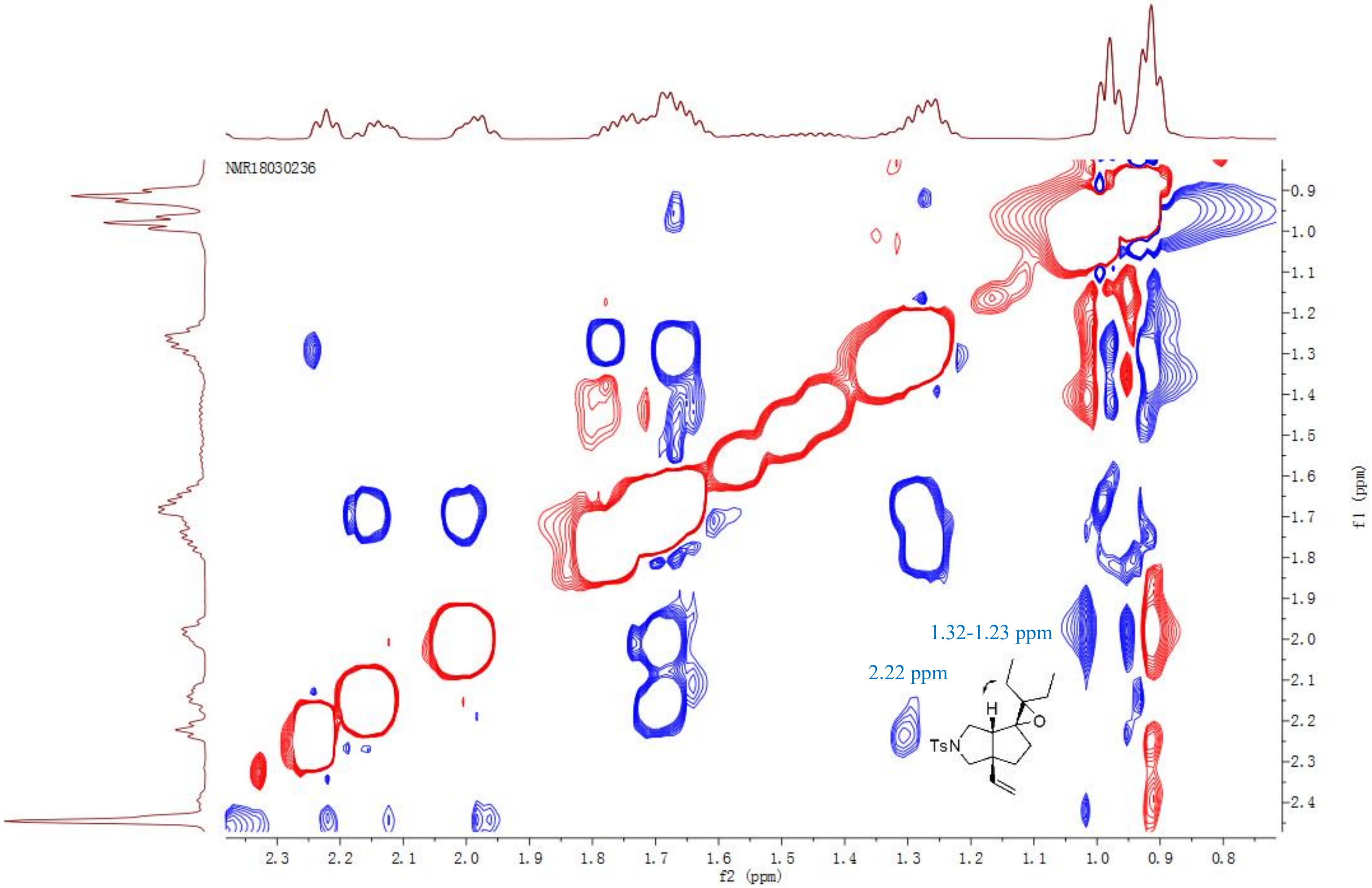
18

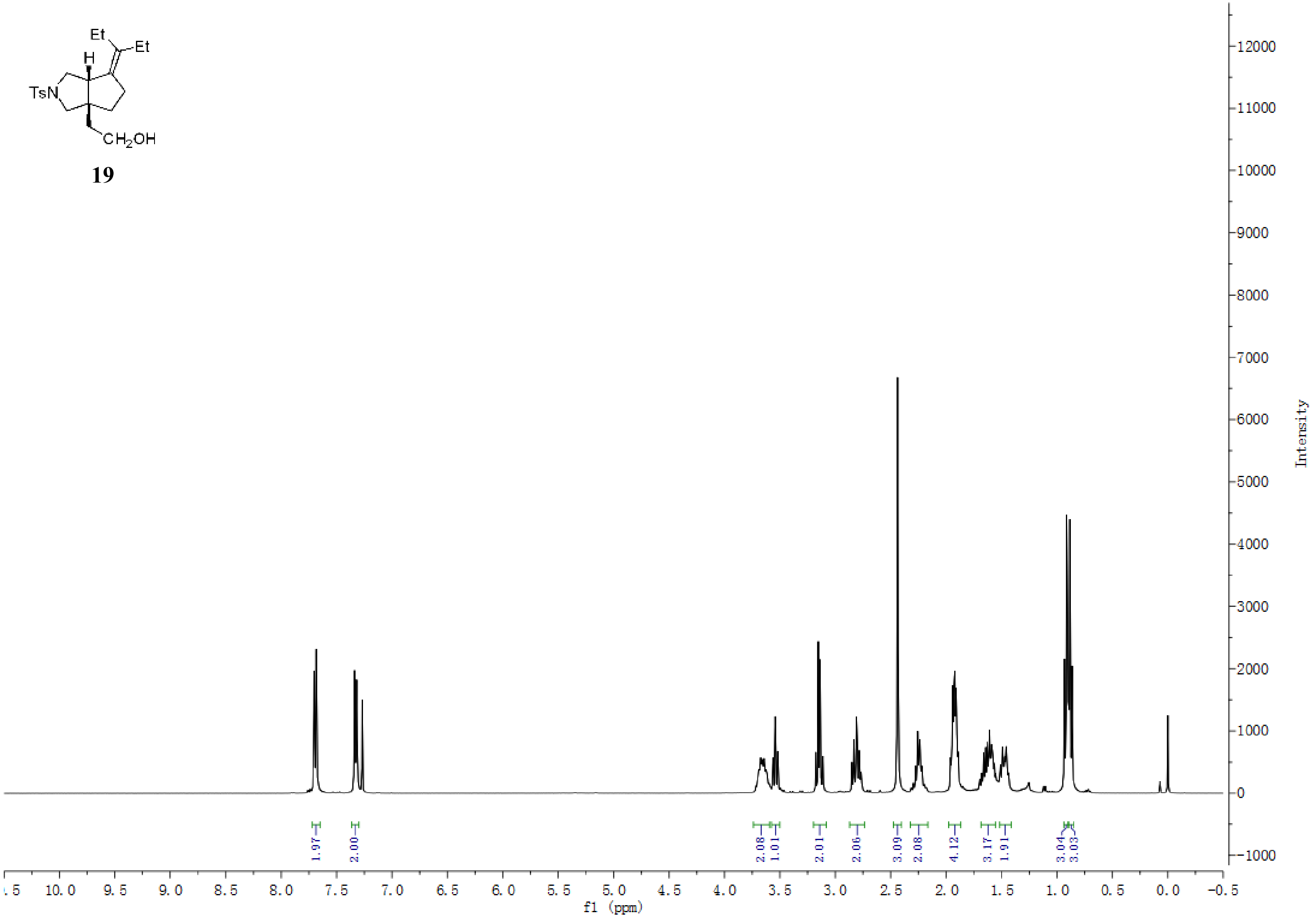
Et
Et
H
O
TsN
2.24
2.13
1.00
1.01
1.07
1.03
1.24
1.01
1.04
2.92
1.02
0.95
0.96
4.54
2.12
3.08
3.58
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
Intensity


Et
Et
H
O
TsN

18

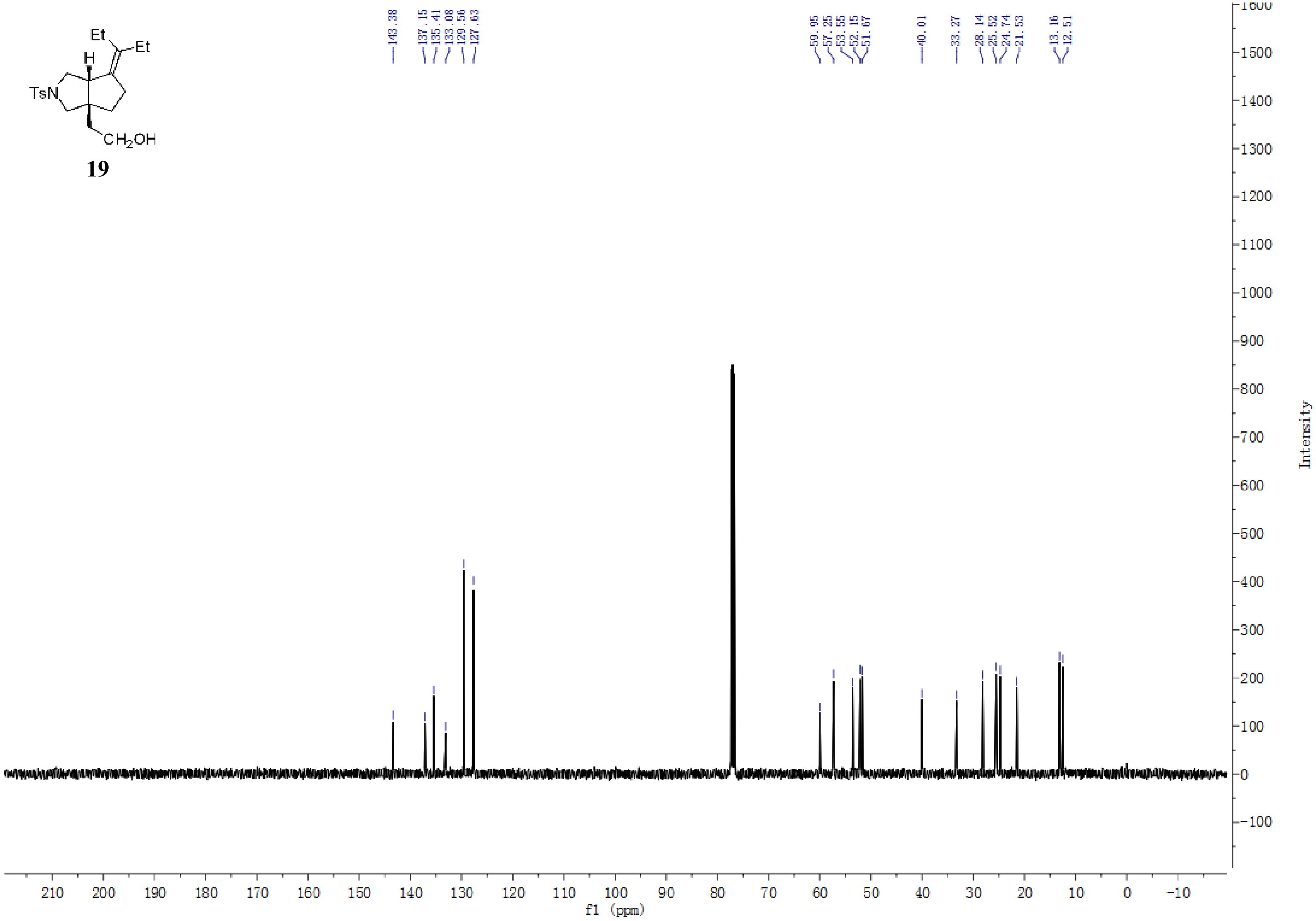

143.72
141.05
132.64
129.66
127.66
113.21
76.56
66.82
57.56
55.62
53.21
50.86
33.87
29.71
24.53
24.25
21.53
9.47
8.85
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
Intensity
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

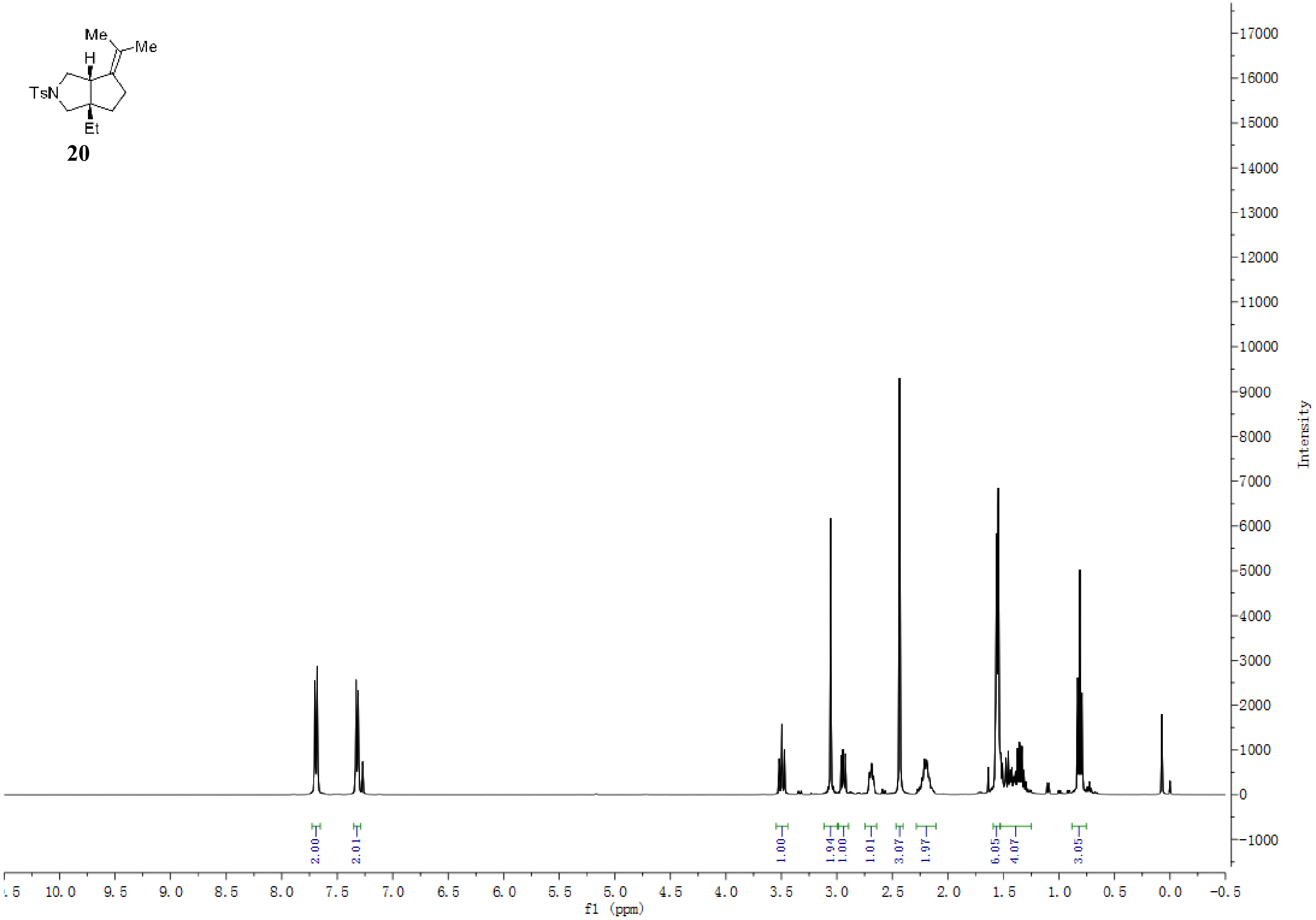

NMR18030236
1.32-1.23 ppm
2.22 ppm
H
TsN
O
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
f2 (ppm)
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
f1 (ppm)



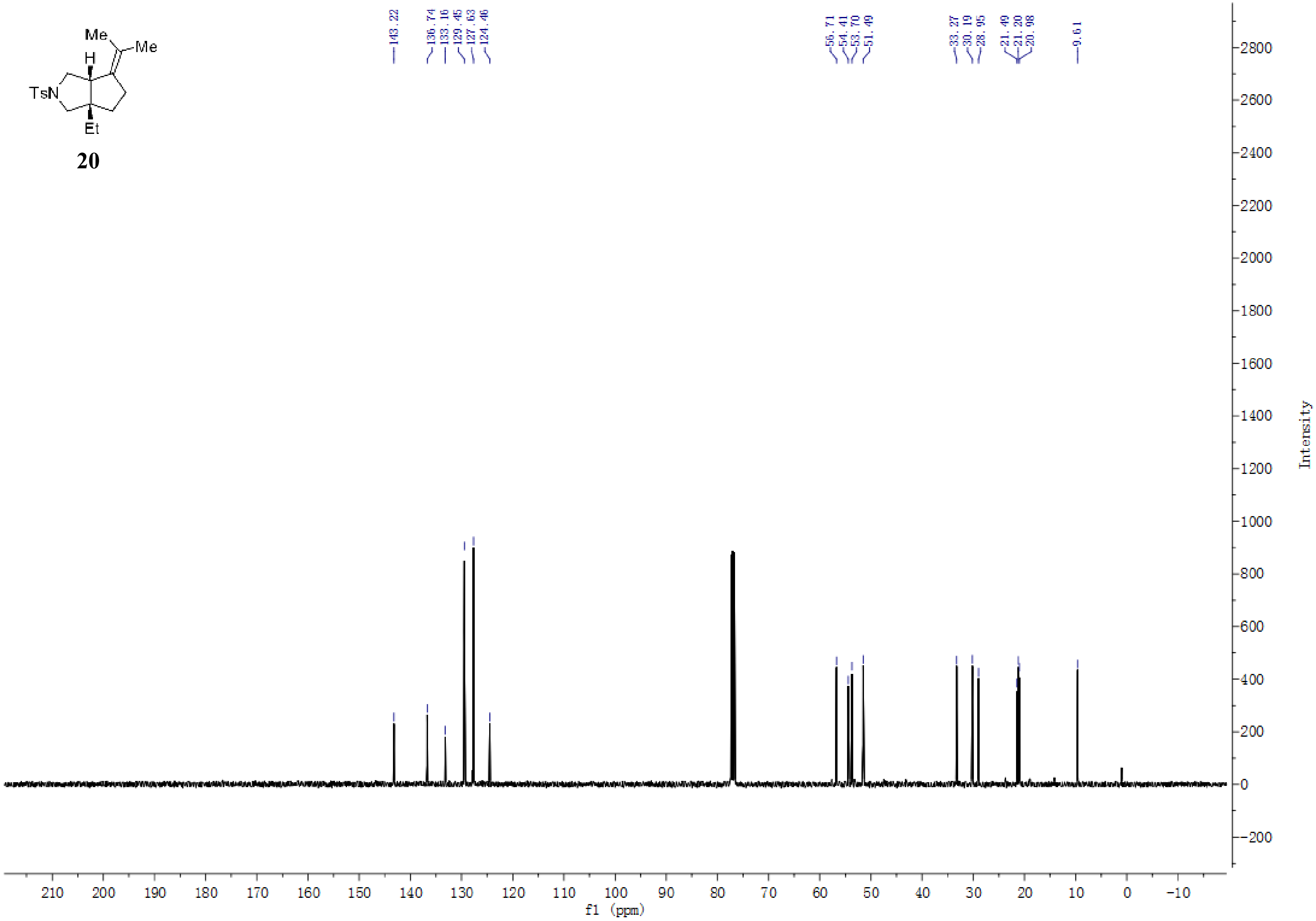
Et
Et
H
TsN
CH2OH
1.97
2.00
2.08
1.01
2.01
2.06
3.09
2.08
4.12
3.17
1.91
3.04
3.03
.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
Intensity

19

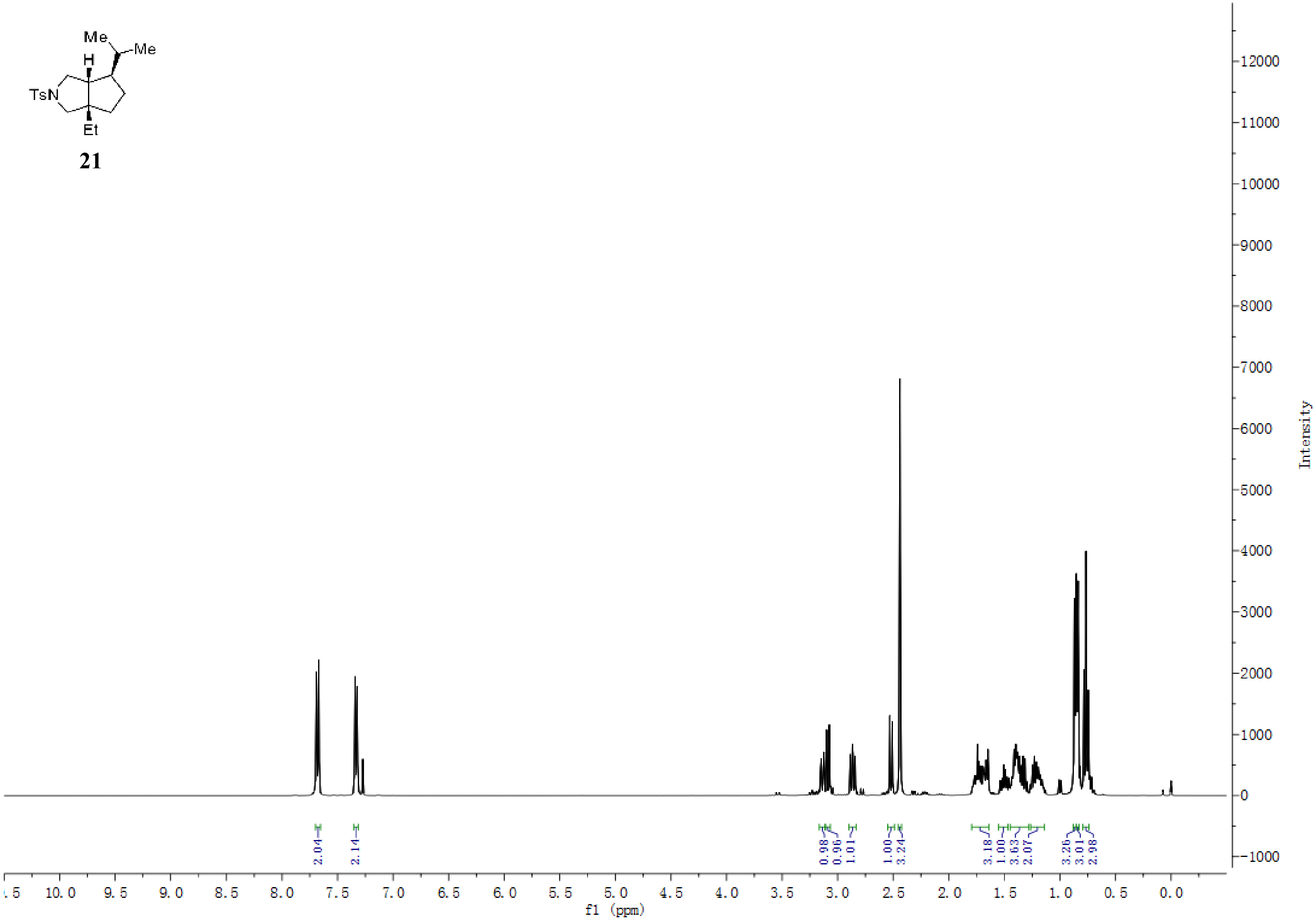

Et
Et
H
TsN
CH2OH
19
143.38
137.15
135.41
133.08
129.56
127.63
59.95
57.25
53.55
52.15
51.67
40.01
33.27
28.14
25.52
24.74
21.53
13.16
12.51
f1 (ppm)
Intensity


20

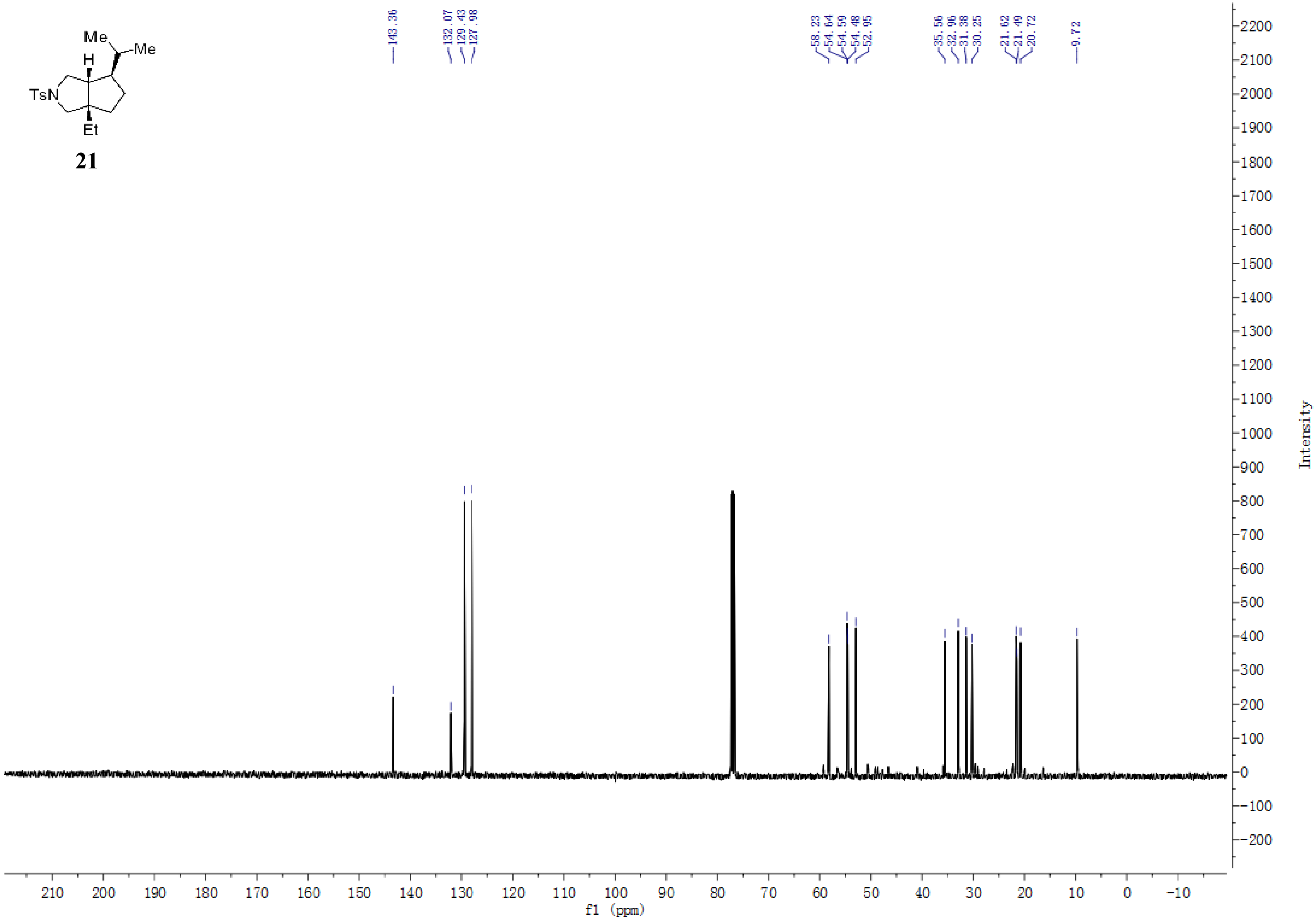
Me
Me
H
TsN
Et
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
Intensity
2.00
2.01
1.00
1.94
1.00
1.01
3.07
1.97
6.05
4.07
3.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


Me
Me
H
TsN
Et
143.22
136.74
133.16
129.45
127.63
124.46
56.71
54.41
53.70
51.49
33.27
30.19
28.95
21.49
21.20
20.98
9.61
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200
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)

20

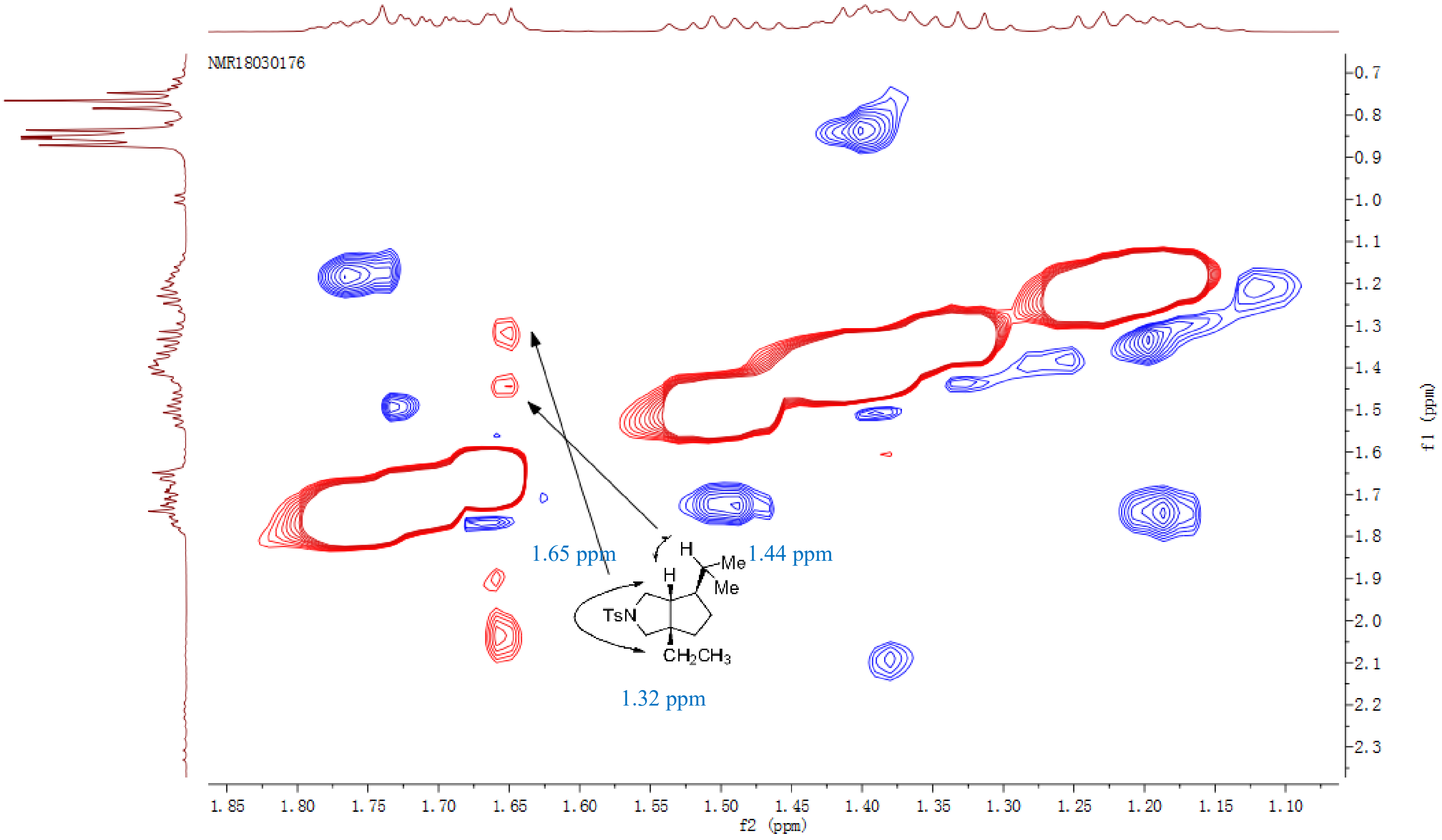

Me
Me
H
TsN
Et
2.04
2.14
0.98
0.96
1.01
1.00
3.24
3.18
1.00
3.63
2.07
3.26
3.01
2.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
Intensity

21



21

Me
Me
H
TsN
Et
143.36
132.07
129.43
127.98
58.23
54.64
54.59
54.48
52.95
35.56
32.96
31.38
30.25
21.62
21.49
20.72
9.72
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
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)


NMR18030176
1.65 ppm
1.44 ppm
1.32 ppm
H
H
Me
Me
TsN
CH2CH3
1.85
1.80
1.75
1.70
1.65
1.60
1.55
1.50
1.45
1.40
1.35
1.30
1.25
1.20
1.15
1.10
f2 (ppm)
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
f1 (ppm)