Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

Rhodium-Catalyzed [4+2+1] Cycloaddition of In Situ Generated Ene/Yne-Ene-Allenes and CO

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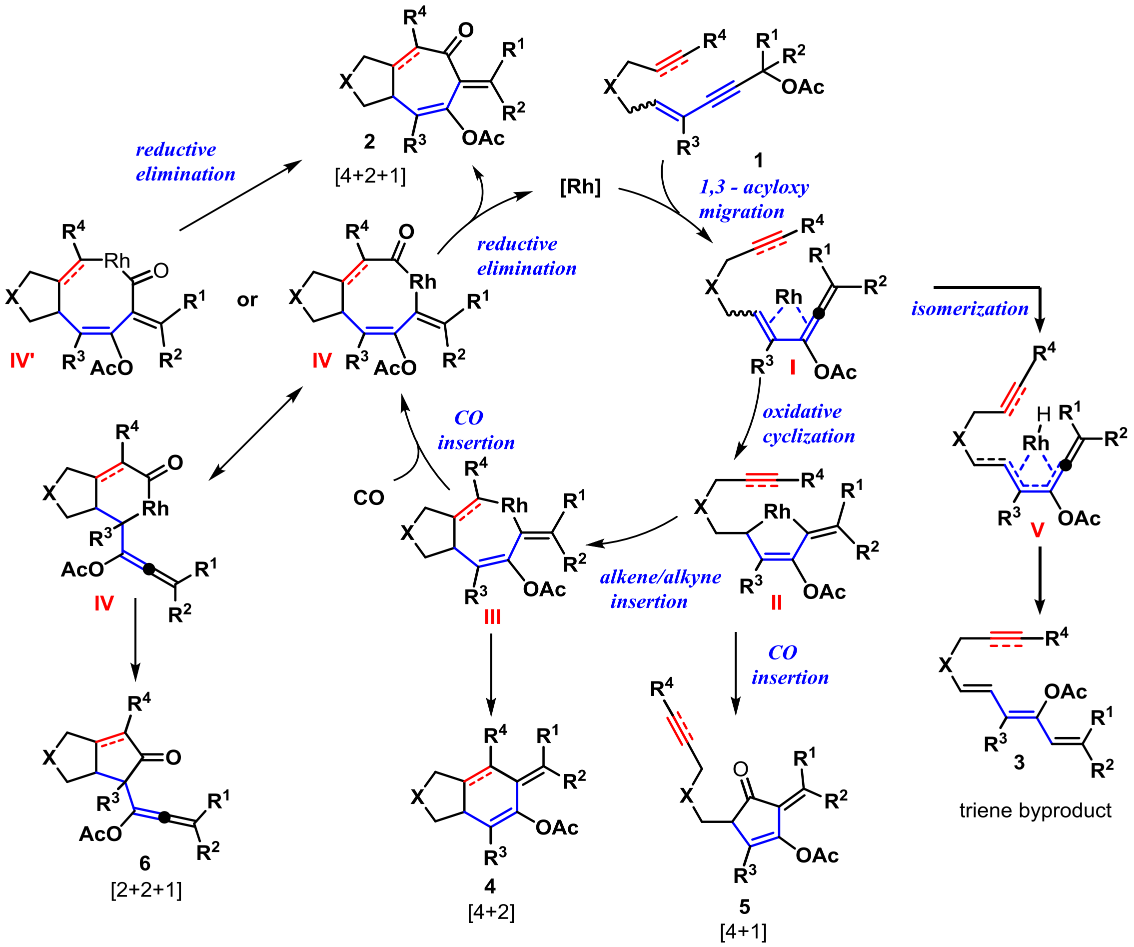
1. Proposed mechanism and the possible competing reactions



Scheme S1

2. General information

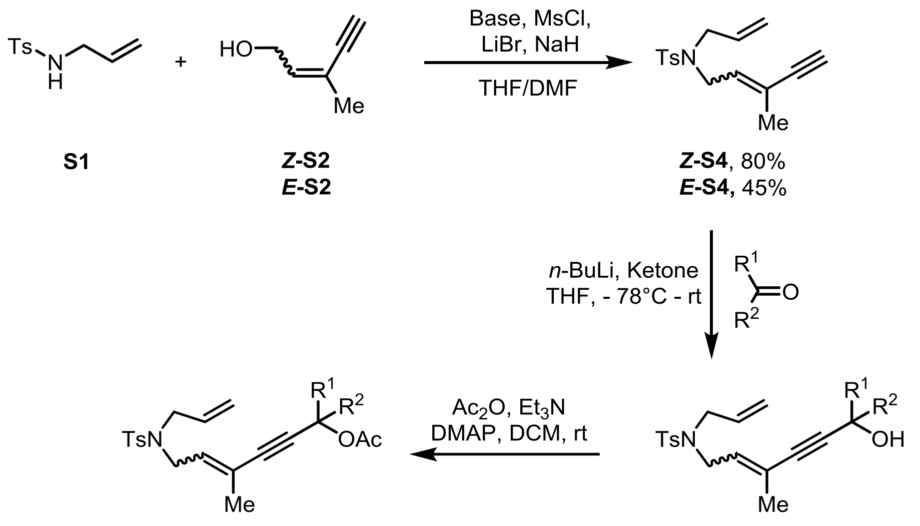
Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Organic solutions were concentrated using a Büchi or Eyela rotary evaporator with a desktop vacuum pump. Super-dried DCE and synthetic reagents were purchased from J&K, Energy, Acros, Aldrich, and Alfa Aesar, **especially $[Rh(CO)_2Cl]_2$ catalysts from Acros**, **$[Rh(COD)Cl]_2$ from J&K**, and used without further purification, unless otherwise indicated. 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 show a single spot by analytical TLC.

NMR spectra were measured on Bruker ARX 400 (^{1}H at 400 MHz, ^{13}C at 101 MHz) and 500 (^{1}H at 500 MHz, ^{13}C at 125 MHz) nuclear magnetic resonance spectrometers. Data for ^{1}H-NMR spectra are reported as follows: chemical shift (ppm, referenced to residual solvent peak (CD_2Cl_2: 5.32 ppm, $CDCl_3$: 7.26 ppm); s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, ddt = doublet of doublet of triplets, 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 (CD_2Cl_2: 54.0 ppm, $CDCl_3$: 77.2 ppm). High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer (ESI).

Abbreviations:
Ac = acetyl
COD = 1,5-cyclooctadiene
COE = Cyclooctene
DCE = 1,2-dichloroethane
DCM = dichloromethane
DMAP = *N,N*-4-dimethylaminopyridine
DME = 1,2-dimethoxyethane
DMF = *N*, *N*-dimethylformamide
EA = ethyl acetate
HMPA = hexamethylphosphoric acid triamide
Ms = mesyl (methanesulfonyl)
NBD = norbornadiene
PE = petroleum ether
TBAF = tetra-*N*-butylammonium fluoride
TBS = *t*-butyldimethylsilyl
THF = tetrahydrofuran
Ts = 4-toluenesulfonyl.

3. Substrates preparations

Preparation of substrates *Z, E*-1a, *Z, E*-1b, *Z, E*-1f, *Z, E*-1g, and *Z*-1e



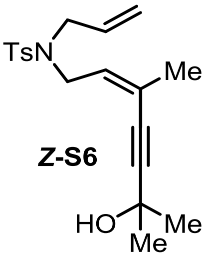
***Z*-1a**, $R^1 = R^2$ = Me, R^3 = Me, 75%
***E*-1a**, $R^1 = R^2$ = Me, R^3 = Me, 89%
***Z*-1b**, $R^1 = R^2$ = Et, R^3 = Me, 70%
***E*-1b**, $R^1 = R^2$ = Et, R^3 = Me, 64%
***Z*-1e**, R^1 = Me, R^2 = H, R^3 = Me, 73%

***Z*-S6**, $R^1 = R^2$ = Me, R^3 = Me, 41%
***E*-S6**, $R^1 = R^2$ = Me, R^3 = Me, 50%
***Z*-S7**, $R^1 = R^2$ = Et, R^3 = Me, 33%
***E*-S7**, $R^1 = R^2$ = Et, R^3 = Me, 80%
S10, R^1 = Me, R^2 = H, R^3 = Me, 64%

Preparation of substrate *Z*-1a

To a stirred solution of alcohol ***Z*-S2** (1.0 g, 10.4 mmol) in THF at -78 °C (20 mL), *n*-BuLi (7.2 mL, 1.6 M in hexanes) was added carefully in 3 minutes under N_2 atmosphere. MsCl (1.3 g, 11.4 mmol) was added after 10 minutes. The mixture was warmed to room temperature to react for 30 minutes. LiBr (4.52 g, 52 mmol) was added to the above solution at 0 °C and then stirred at room temperature for 1 h. The reaction mixture was then transferred with pipette to tosyl amine **S1** (2.42 g, 11.4 mmol) solution at 0 °C that was previously depronated by NaH (832 mg, 60%, 20.8 mmol) in DMF (50 mL) for 1 h. The reaction was stirred for 16 h at room temperature. Then, 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 = 10 / 1) to yield ***Z*-S4**[1] (R_f: 0.60 (PE / EA = 3 / 1), 2.4 g, Yield = 80 %) as a yellow oil.

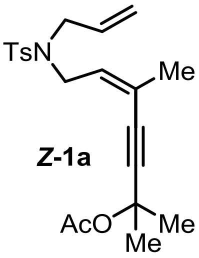
To a stirred solution of ***Z*-S4** (964.1mg, 3.3 mmol) in anhydrous THF (20 mL) was added *n*-BuLi in hexanes (1.6 M, 5 mL, 8 mmol) at -78 °C. After stirring for 30 min at this temperature, acetone (744 mg, 10 mmol) was added to the reaction mixture in dropwise. After the addition finished, the reaction was allowed to warm to room temperature and stirred for 16 h. After the reaction was complete, 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 = 3 / 1) to yield ***Z*-S6** (R_f: 0.33 (PE / EA = 3 / 1), 470.3 mg, Yield = 41 %) as a yellow oil.



***Z*-S6**

***Z*-S6**: yellow oil, TLC *Rf* = 0.33 (PE / EA = 3 / 1).
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.68 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 5.68 (ddt, *J* = 17.1, 10.1, 6.2 Hz, 1H), 5.51 (tq, *J* = 7.0, 1.4 Hz, 1H), 5.18 (dd, *J* = 17.1, 1.2 Hz, 1H), 5.13 (dd, *J* = 10.1, 1.2 Hz, 1H), 3.94 (d, *J* = 7.0 Hz, 2H), 3.74 (d, *J* = 6.2 Hz, 2H), 2.42 (s, 3H), 2.24 (brs, 1H), 1.78 (d, *J* = 1.4 Hz, 3H), 1.48 (s, 6H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 144.0, 137.7, 133.6, 131.5, 130.2, 127.7, 122.7, 118.8, 100.1, 80.4, 65.8, 50.5, 47.3, 31.8, 23.3, 21.8. HRMS (ESI) m/z calcd. for $C_{19}H_{29}N_2O_3S$ $(M+NH_4)^+$: 365.1893, found 365.1890.

To a stirred solution of ***Z*-S6** (470.3 mg, 1.35 mmol) in DCM (10 mL) was added Ac_2O (691 mg, 6.8 mmol), Et_3N (1.37 g, 13.5 mmol) and DMAP (16.5 mg, 0.1 mmol) at room temperature. After stirring for 24 h, the reaction was complete. The reaction mixture was concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 5 / 1) to yield ***Z*-1a** (R*f*: 0.56 (PE / EA = 3 / 1), 395.4 mg, Yield = 75 %) as a yellow oil.



***Z*-1a**

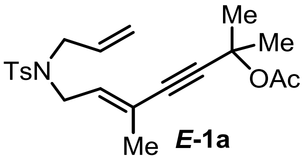
***Z*-1a**: yellow oil, TLC *Rf* = 0.56 (PE / EA = 3 / 1)
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 5.69 (ddt, *J* = 17.1, 10.1, 6.2 Hz, 1H), 5.51 (tq, *J* = 7.1, 1.5 Hz, 1H), 5.17 (dd, *J* = 17.1, 1.4 Hz, 1H), 5.11 (dd, *J* = 10.1, 1.4 Hz, 1H), 3.94 (d, *J* = 7.1 Hz, 2H), 3.73 (d, *J* = 6.2 Hz, 2H), 2.42 (s, 3H), 1.94 (s, 3H), 1.76 (d, *J* = 1.5 Hz, 3H), 1.62 (s, 6H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.5, 143.9, 137.8, 133.7, 132.4, 130.2, 127.7, 122.3, 118.6, 96.2, 82.3, 72.5, 50.6, 47.6, 29.3, 23.1, 22.2, 21.8. HRMS (ESI) m/z calcd. for $C_{21}H_{31}N_2O_4S$ $(M+NH_4)^+$: 407.1999, found 407.1995.

Preparation of substrate *E*-1a

To a stirred solution of alcohol ***E*-S2**[2] (1.46 g, w% = 76%, 11.6 mmol) in THF at 0 °C (20 mL), Et_3N (1.41 g, 13.9 mmol) was added under N_2 atmosphere. MsCl (1.35 g, 11.8 mmol) was added carefully in 3 minutes. The mixture was warmed to room temperature to react for 4.5 h. LiBr (3.11 g, 35.8 mmol) was added to the above solution at 0 °C and then stirred at room temperature for 30 minutes. The reaction mixture was then transferred with pipette to tosyl amine **S1** (2.45 g, 11.6 mmol) solution at 0 °C that was previously depronated by NaH (700.3 mg, 60%, 17.5 mmol) in DMF (50 mL) for 1 h. The reaction was stirred for 21 h at room temperature. Then, 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 = 10 / 1) to yield ***E*-S4**[1] (R*f*: 0.57 (PE / EA = 3 / 1), 1.51 g, Yield = 45 %) as a yellow oil.

To a stirred solution of ***E*-S4** (510.2 mg, 1.8 mmol) in anhydrous THF (30 mL) was added *n*-BuLi in hexanes (2.4 M, 1.0 mL, 2.4 mmol) at -78 °C. After stirring for 30 min at this temperature, acetone (0.3 mL, 3.5 mmol) was added to the reaction mixture in dropwise. After the addition finished, the reaction was allowed to warm to room temperature and stirred for 18 h. After the reaction was complete, 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 = 3 / 1) to yield ***E*-S6** (R*f*: 0.33 (PE / EA = 3 / 1), 303.4 mg, Yield = 50 %) as a yellow oil.

To a stirred solution of ***E*-S6** (283.4 mg, 0.8 mmol) in DCM (15 mL) was added Ac_2O (259.5 mg, 2.5 mmol), Et_3N (505.3 mg, 5.0 mmol) and DMAP (9.9 mg, 0.08 mmol) at room temperature. After stirring for 13 h, the reaction was complete. The reaction mixture was concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 5 / 1) to yield ***E*-1a** (R*f*: 0.46 (PE / EA = 3 / 1), 284.3 mg, Yield = 89 %) as a yellow oil.



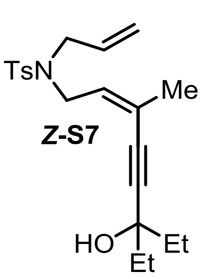
***E*-1a**

***E*-1a**: yellow oil, TLC R_f = 0.46 (PE / EA = 3 / 1)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.67 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 5.70 – 5.60 (m, 1H), 5.61 – 5.56 (m, 1H), 5.20 – 5.13 (m, 2H), 3.82 (d, *J* = 7.0 Hz, 2H), 3.76 (d, *J* = 6.4 Hz, 2H), 2.43 (s, 3H), 1.98 (s, 3H), 1.73 (d, *J* = 1.4 Hz, 3H), 1.63 (s, 6H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.6, 144.1, 137.7, 133.5, 132.1, 130.3, 127.7, 121.7, 119.3, 89.2, 86.0, 72.7, 50.6, 44.8, 29.3, 22.3, 21.8, 17.7. HRMS (ESI) m/z calcd. for $C_{21}H_{31}N_2O_4S$ $(M+NH_4)^+$: 407.1999, found 407.1999.

Preparation of substrate *Z*-1b

To a stirred solution of ***Z*-S4** (591.8 mg, 2.0 mmol) in anhydrous THF (20 mL) was added *n*-BuLi in hexanes (1.6 M, 3.6 mL, 5.8 mmol) at -78 °C. After stirring for 30 min at this temperature, 3-pentanone (0.8 mL, 4.8 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 16 h. Then 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 = 3 / 1) to yield ***Z*-S7** (R*f*: 0.45 (PE / EA = 3 / 1), 253.7 mg, Yield = 33 %) as a yellow oil.

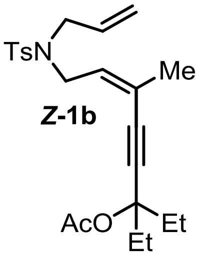


***Z*-S7**

***Z*-S7**: yellow oil, TLC *Rf*: 0.45 (PE / EA = 3 / 1)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.68 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 5.67 (ddt, *J* = 17.1, 10.1, 6.2 Hz, 1H), 5.50 (tq, *J* = 6.9, 1.5 Hz, 1H), 5.16 (dd, *J* = 17.1, 1.4 Hz, 1H), 5.12 (dd, *J* = 10.1, 1.4 Hz, 1H), 3.95 (d, *J* = 6.9 Hz, 2H), 3.73 (d, *J* = 6.2 Hz, 2H), 2.43 (s, 3H), 2.03 (brs, 1H), 1.79 (d, *J* = 1.5 Hz, 3H), 1.63 (qd, *J* = 7.4, 4.3 Hz, 4H), 0.97 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 144.0, 137.6, 133.7, 131.5, 130.2, 127.7, 122.7, 118.7, 98.2, 82.7, 72.8, 50.6, 47.7, 34.9, 23.5, 21.8, 9.0. HRMS (ESI) m/z calcd. for $C_{21}H_{33}N_2O_3S$ $(M+NH_4)^+$: 393.2206, found 393.2213.

To a stirred solution of ***Z*-S7** (211.3 mg, 0.6 mmol) in DCM (10 mL) was added Ac_2O (172.3 mg, 1.7 mmol), Et_3N (341.6 mg, 3.4 mmol) and DMAP (6.9 mg, 0.06 mmol) at room temperature. After stirring for 24 h, the reaction was complete. The reaction mixture was concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 5 / 1) to yield ***Z*-1b** (R*f*: 0.59 (PE / EA = 3 / 1), 165.6 mg, Yield = 70 %) as a yellow oil.



***Z*-1b**

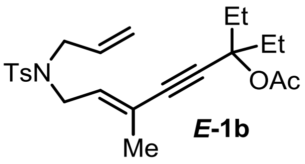
***Z*-1b:** yellow oil, TLC, R*f*: 0.59 (PE / EA = 3 / 1)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.69 (ddt, *J* = 17.1, 10.1, 6.2 Hz, 1H), 5.52 (tq, *J* = 7.0, 1.4 Hz, 1H), 5.16 (dd, *J* = 17.1, 1.5 Hz, 1H), 5.10 (dd, *J* = 10.1, 1.5 Hz, 1H), 3.97 (d, *J* = 7.0 Hz, 2H), 3.73 (d, *J* = 6.2 Hz, 2H), 2.42 (s, 3H), 2.03 – 1.95 (m, 2H), 1.95 (s, 3H), 1.94 – 1.82 (m, 2H), 1.79 (d, *J* = 1.4 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.4, 143.9, 137.7, 133.7, 132.3, 130.2, 127.7, 122.3, 118.6, 94.8, 84.2, 80.3, 50.7, 47.9, 31.3, 23.3, 22.1, 21.8, 8.7. HRMS (ESI) m/z calcd. for $C_{23}H_{35}N_2O_4S$ $(M+NH_4)^+$: 435.2312, found 435.2310.

Preparation of substrate *E*-1b

To a stirred solution of ***E*-S4** (404.8 mg, 1.4 mmol) in anhydrous THF (10 mL) was added *n*-BuLi in hexanes (2.4 M, 0.8 mL, 1.9 mmol) at -78 °C. After stirring for 30 min at this temperature, 3-pentanone (0.3 mL, 3.5 mmol) was added to the reaction mixture in dropwise. After the addition finished, the reaction was allowed to warm to room temperature and stirred for 12 h. After the reaction was complete, 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 = 3 / 1) to yield ***E*-S7** (R_f: 0.17 (PE / EA = 5 / 1), 421.5 mg, Yield = 80 %) as a yellow oil.

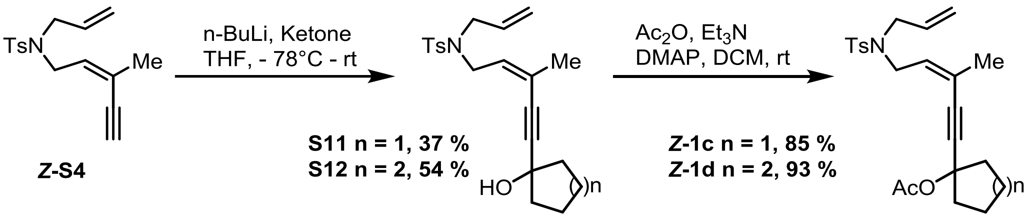
To a stirred solution of ***E*-S7** (357.4 mg, 1.0 mmol) in DCM (10 mL) was added Ac_2O (0.27 mL, 2.9 mmol), Et_3N (0.79 mL, 5.7 mmol) and DMAP (5 mg, 0.04 mmol) at room temperature. After stirring for 13 h, the reaction was complete. The reaction mixture was concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 20 / 1) to yield ***E*-1a** (R_f: 0.50, PE / EA = 5 / 1), 255.4 mg, Yield = 64 %) as a yellow oil.



***E*-1b**

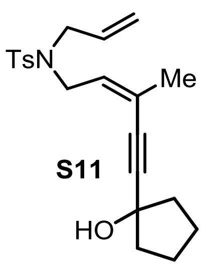
***E*-1b**: yellow oil, TLC R_f = 0.50 (PE / EA = 5 / 1)
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.67 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 5.66 (ddt, J = 16.7, 10.3, 6.3 Hz, 1H), 5.57 (tq, J = 7.0, 1.5 Hz, 1H), 5.20 – 5.14 (m, 2H), 3.83 (d, J = 7.0 Hz, 2H), 3.76 (d, J = 6.3 Hz, 2H), 2.42 (s, 3H), 2.06 – 1.93 (m, 2H), 1.99 (s, 3H), 1.92 – 1.82 (m, 2H), 1.75 (d, J = 1.5 Hz, 3H), 0.94 (t, J = 7.4 Hz, 6H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.6, 144.1, 137.8, 133.5, 131.9, 130.3, 127.7, 121.9, 119.2, 88.1, 87.6, 80.5, 50.6, 44.9, 31.3, 22.2, 21.8, 17.8, 8.7. HRMS (ESI) m/z calcd. for $C_{23}H_{35}N_2O_4S$ $(M+NH_4)^+$: 435.2312, found 435.2312.

Preparation of substrates *Z*-1c and *Z*-1d



Preparation of substrate *Z*-1c

To a stirred solution of ***Z*-S4** (586.2 mg, 2.0 mmol) in anhydrous THF (20 mL) was added *n*-BuLi in hexanes (1.6 M, 2.5 mL, 4.0 mmol) at -78 °C. After stirring for 30 min at this temperature, cyclopentanone (1.0 mL, 11.3 mmol) was added to the reaction mixture dropwise. After the addition was completed, the reaction was allowed to warm to room temperature and stirred for 16 h. After the reaction was completed, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 3 / 1) to yield **S11** (R_f: 0.34 (PE / EA = 3 / 1), 274.3 mg, Yield = 37 %) as a yellow oil.

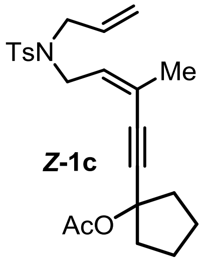


S11

S11: yellow oil, TLC *R_f*: 0.34 (PE / EA = 3 / 1)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.68 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 5.68 (ddt, *J* = 17.2, 10.1, 6.2 Hz, 1H), 5.50 (tq, *J* = 6.9, 1.4 Hz, 1H), 5.18 (dd, *J* = 17.2, 1.5 Hz, 1H), 5.13 (dd, *J* = 10.1, 1.4 Hz, 1H), 3.93 (d, *J* = 6.9 Hz, 2H), 3.74 (dd, *J* = 6.2, 1.4 Hz, 2H), 2.43 (s, 3H), 1.99 – 1.93 (brs, 1H), 1.94 – 1.85 (m, 4H), 1.85 – 1.74 (m, 2H), 1.79 (d, *J* = 1.4 Hz, 3H), 1.76 – 1.64 (m, 2H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 144.0, 137.7, 133.6, 131.4, 130.2, 127.7, 122.9, 118.8, 99.2, 81.4, 75.1, 50.5, 47.4, 43.0, 24.0, 23.3, 21.8. HRMS (ESI) m/z calcd. for $C_{21}H_{31}N_2O_3S$ $(M+NH_4)^+$: 391.2050, found 391.2050.

To a stirred solution of **S11** (274.3 mg, 0.7 mmol) in DCM (10 mL) was added Ac_2O (225 mg, 2.2 mmol), Et_3N (446 mg, 4.4 mmol) and DMAP (9 mg, 0.07 mmol) at room temperature. After stirring for 24 h, the reaction was completed. The reaction mixture was concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 5 / 1) to yield ***Z*-1c** (R_f: 0.64 (PE / EA = 3 / 1), 260.9 mg, Yield = 85 %) as a colorless oil.



***Z*-1c**

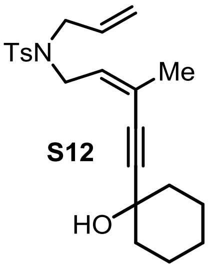
***Z*-1c:** colorless oil, TLC *R_f*: 0.64 (PE / EA = 3 / 1)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 5.70 (ddt, *J* = 17.2, 10.1, 6.2 Hz, 1H), 5.50 (tq, *J* = 7.1, 1.4 Hz, 1H), 5.17 (dd, *J* = 17.2, 1.4 Hz, 1H), 5.11 (dd, *J* = 10.1, 1.4 Hz, 1H), 3.93 (d, *J* = 7.1 Hz, 2H), 3.73 (d, *J* = 6.2 Hz, 2H), 2.42 (s, 3H), 2.23 – 2.12 (m, 2H), 2.11 – 2.02 (m, 2H), 1.94 (s, 3H), 1.76 (d, *J* = 1.4 Hz, 3H), 1.76 – 1.66 (m, 4H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.7, 143.9, 137.7, 133.7, 132.1, 130.2, 127.7, 122.4, 118.6, 95.8, 82.9, 81.1, 50.6, 47.7, 40.9, 23.8, 23.1, 22.0, 21.8. HRMS (ESI) m/z calcd. for $C_{23}H_{33}N_2O_4S$ $(M+NH_4)^+$: 433.2156, found 433.2153.

Preparation of substrate *Z*-1d

To a stirred solution of ***Z*-S4** (589.9 mg, 2.0 mmol) in anhydrous THF (20 mL) was added *n*-BuLi in hexanes (1.6 M, 1.4 mL, 2.2 mmol) at -78 °C. After stirring for 30 min at this temperature, cyclohexanone (0.2 mL, 2.0 mmol) was added to the reaction mixture dropwise.

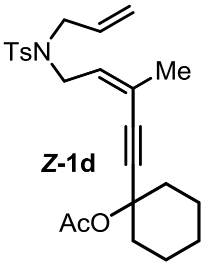
After the addition was completed, the reaction was allowed to warm to room temperature and stirred for 16 h. After the reaction was completed, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 3 / 1) to yield **S12** (R*f*: 0.31 (PE / EA = 3 / 1), 430.5 mg, Yield = 54 %) as a yellow oil.



S12

S12: yellow oil, TLC *Rf*: 0.31 (PE / EA = 3 / 1)
^1H NMR (400 MHz, CD_2Cl_2) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 5.68 (ddt, *J* = 16.8, 10.1, 6.2 Hz, 1H), 5.51 (tq, *J* = 6.6, 1.5 Hz, 1H), 5.18 (dd, *J* = 16.8, 1.5 Hz, 1H), 5.12 (dd, *J* = 10.1, 1.5 Hz, 1H), 3.96 (d, *J* = 6.6 Hz, 2H), 3.74 (d, *J* = 6.2 Hz, 2H), 2.48 (s, 1H), 2.42 (s, 3H), 1.88 – 1.81 (m, 2H), 1.79 (d, *J* = 1.5 Hz, 3H), 1.70 – 1.60 (m, 2H), 1.59 – 1.41 (m, 5H), 1.29 – 1.18 (m, 1H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 144.0, 137.6, 133.6, 131.4, 130.2, 127.7, 122.7, 118.8, 99.4, 82.4, 69.3, 50.6, 47.7, 40.5, 25.7, 23.9, 23.4, 21.8. HRMS (ESI) m/z calcd. for $C_{22}H_{33}N_2O_3S$ $(M+NH_4)^+$: 405.2206, found 405.2213.

To a stirred solution of **S12** (310.1 mg, 0.8 mmol) in DCM (10 mL) was added Ac_2O (264.6 mg, 2.6 mmol), Et_3N (493.7 mg, 4.9 mmol) and DMAP (9.8 mg, 0.08 mmol) at room temperature. After stirring for 24 h, the reaction was completed. The reaction mixture was concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 5 / 1) to yield ***Z*-1d** (R*f*: 0.54 (PE / EA = 3 / 1), 319.1 mg, Yield = 93 %) as a yellow oil.



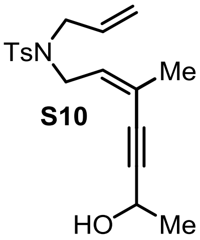
***Z*-1d**

***Z*-1d:** yellow oil, TLC *Rf*: 0.54 (PE / EA = 3 / 1)
^1H NMR (400 MHz, CD_2Cl_2) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 5.69 (ddt, *J* = 16.7, 10.1, 6.2 Hz, 1H), 5.51 (tq, *J* = 7.0, 1.5 Hz, 1H), 5.17 (dd, *J* = 16.7, 1.4 Hz, 1H), 5.10 (dd, *J* = 10.1, 1.4 Hz, 1H), 3.95 (d, *J* = 7.0 Hz, 2H), 3.73 (d, *J* = 6.2 Hz, 2H), 2.42 (s, 3H), 2.11 – 2.00 (m, 2H), 1.95 (s, 3H), 1.86 – 1.76 (m, 2H), 1.78 (d, *J* = 1.5 Hz, 3H), 1.65 – 1.42 (m, 5H), 1.39 – 1.24 (m, 1H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.3, 143.9, 137.7, 133.7, 132.2, 130.2, 127.7, 122.3,

118.6, 95.4, 84.4, 76.0, 50.7, 47.9, 37.5, 25.7, 23.22, 23.20, 22.2, 21.8. HRMS (ESI) m/z calcd. for $C_{24}H_{35}N_2O_4S$ $(M+NH_4)^+$: 447.2312, found 447.2313.

Preparation of substrate ***Z*-1e**

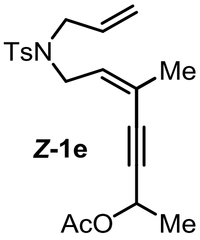
To a stirred solution of ***Z*-S4** (582.1 mg, 2.0 mmol) in anhydrous THF (20 mL) was added *n*-BuLi in hexanes (1.6 M, 2.5 mL, 4.0 mmol) at -78 °C. After stirring for 30 min at this temperature, acetaldehyde (0.8 mL, 14.2 mmol) was added to the reaction mixture in dropwise. After the addition finished, the reaction was allowed to warm to room temperature and stirred for 16 h. Then 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 = 3 / 1) to yield **S10** (R_f: 0.33 (PE / EA = 3 / 1), 428.5 mg, Yield = 64 %) as a yellow oil.



S10

S10: yellow oil, TLC R_f: 0.33 (PE / EA = 3 / 1)
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.68 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 5.67 (ddt, *J* = 16.5, 10.1, 6.6 Hz, 1H), 5.52 (tq, *J* = 6.5, 1.4 Hz, 1H), 5.18 (dd, *J* = 16.5, 1.4 Hz, 1H), 5.13 (dd, *J* = 10.1, 1.4 Hz, 1H), 4.61 (q, *J* = 6.6 Hz, 1H), 3.93 (d, *J* = 6.5 Hz, 2H), 3.75 (d, *J* = 6.6 Hz, 2H), 2.42 (s, 3H), 2.12 (brs, 1H), 1.79 (d, *J* = 1.4 Hz, 3H), 1.41 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 144.0, 137.7, 133.6, 131.9, 130.2, 127.7, 122.5, 118.9, 97.4, 82.1, 59.0, 50.5, 47.3, 24.8, 23.3, 21.8. HRMS (ESI) m/z calcd. for $C_{18}H_{27}N_2O_3S$ $(M+NH_4)^+$: 351.1737, found 351.1740.

To a stirred solution of **S10** (428.5 mg, 1.3 mmol) in DCM (10 mL) was added Ac_2O (656 mg, 6.4 mmol), Et_3N (1.3 g, 12.9 mmol) and DMAP (31.4 mg, 0.25 mmol) at room temperature. After stirring for 24 h, the reaction was complete. The reaction mixture was concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 5 / 1) to yield ***Z*-1e** (R_f: 0.57 (PE / EA = 3 / 1), 353.1 mg, Yield = 73 %) as a yellow oil.

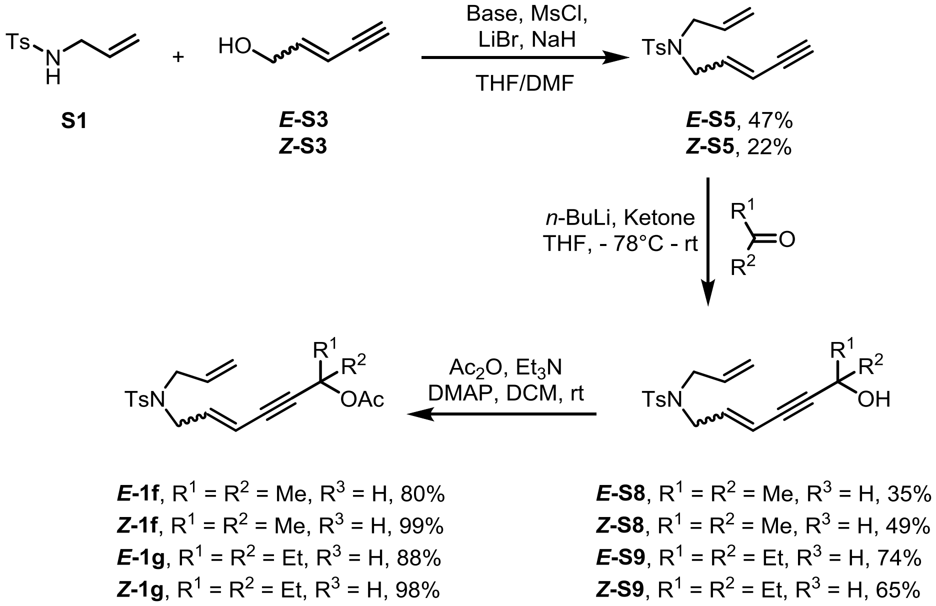


***Z*-1e**

***Z*-1e:** yellow oil, TLC R_f: 0.57 (PE / EA = 3 / 1)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.68 (ddt, *J* = 16.7, 10.1, 6.2 Hz, 1H), 5.55 (tq, *J* = 7.2, 1.4 Hz, 1H), 5.51 (q, *J* = 6.7 Hz, 1H), 5.18 (dd, *J* = 16.7, 1.4 Hz, 1H), 5.13 (dd, *J* = 10.1, 1.4 Hz, 1H), 3.92 (d, *J* = 7.2 Hz, 2H), 3.74 (d, *J* = 6.2, Hz, 2H), 2.42 (s, 3H), 2.01 (s, 3H), 1.78 (d, *J* = 1.4 Hz, 3H), 1.45 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 170.1, 144.0, 137.8, 133.5, 133.0, 130.2, 127.7, 121.9, 118.9, 93.5, 82.8, 61.0, 50.6, 47.4, 23.1, 21.8, 21.7, 21.3. HRMS (ESI) m/z calcd. for $C_{20}H_{29}N_2O_4S$ $(M+NH_4)^+$: 393.1843, found 393.1835.

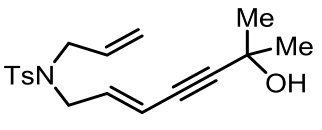
Preparation of substrate ***E, Z*-1f, *E, Z*-1g,**



Preparation of substrate ***E*-1f**

To a stirred solution of alcohol ***E*-S3** (337.0 mg, 4.1 mmol) in THF at -78 °C (20 mL), *n*-BuLi (2.8 mL, 1.6 M in hexanes, 4.5 mmol) was added carefully in 3 minutes under N_2 atmosphere. MsCl (517.2 mg, 4.5 mmol) was added after 10 minutes. The mixture was warmed to room temperature to react for 30 minutes. LiBr (1.8 g, 21 mmol) was added to the above solution at 0 °C and then stirred at room temperature for 1 h. The reaction mixture was then transferred with pipette to tosyl amine **S1** (953.6 mg, 4.5 mmol) solution at 0 °C that was previously depronated by NaH (246.3 mg, 60%, 6.2 mmol) in DMF (50 mL) for ***Z*-1h**. The reaction was stirred for 16 h at room temperature. Then, 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 = 10 / 1) to yield ***E*-S5**[1] (R*f*: 0.36 (PE / EA = 3 / 1), 535.1 mg, Yield = 47 %) as a yellow oil.

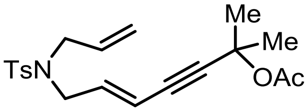
To a stirred solution of ***E*-S5** (394.5 mg, 1.4 mmol) in anhydrous THF (20 mL) was added *n*-BuLi in hexanes (1.6 M, 1.8 mL, 2.9 mmol) at -78 °C. After stirring for 30 min at this temperature, acetone (0.2 mL, 2.9 mmol) was added to the reaction mixture in dropwise. After the addition finished, the reaction was allowed to warm to room temperature and stirred for 16 h. Then 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 = 3 / 1) to yield ***E*-S8** (R*f*: 0.24 (PE / EA = 3 / 1), 168.1 mg, Yield = 35 %) as a yellow oil.



***E*-S8**

***E*-S8**: yellow oil, TLC *R**f*: 0.24 (PE / EA = 3 / 1)
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.67 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 5.86 (dt, *J* = 15.8, 6.4 Hz, 1H), 5.69 – 5.52 (m, 2H), 5.20 – 5.15 (m, 1H), 5.15 – 5.12 (m, 1H), 3.79 (dd, *J* = 6.4, 1.5 Hz, 2H), 3.76 (d, *J* = 6.4 Hz, 2H), 2.43 (s, 3H), 2.00 (s, 1H), 1.48 (s, 6H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 144.2, 138.1, 137.6, 133.2, 130.3, 127.7, 119.5, 113.6, 95.6, 79.8, 65.8, 50.5, 48.9, 31.7, 21.8. HRMS (ESI) m/z calcd. for $C_{18}H_{27}N_2O_3S$ $(M+NH_4)^+$: 351.1737, found 351.1737.

To a stirred solution of ***E*-S8** (168.1 mg, 0.5 mmol) in DCM (10 mL) was added Ac_2O (154.4 mg, 1.5 mmol), Et_3N (306.9 mg, 3.0 mmol) and DMAP (6.2 mg, 0.05 mmol) at room temperature. After stirring for 24 h, the reaction was complete. The reaction mixture was concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 5 / 1) to yield ***E*-1f** (R*f*: 0.56 (PE / EA = 3 / 1), 157.2 mg, Yield = 80 %) as a yellow oil.



***E*-1f**

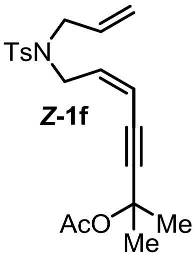
***E*-1f:** yellow oil, TLC *R**f*: 0.56 (PE / EA = 3 / 1)
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 5.92 (dt, *J* = 15.9, 6.4 Hz, 1H), 5.69 – 5.58 (m, 2H), 5.22 – 5.16 (m, 2H), 3.83 (dd, *J* = 6.4, 1.6 Hz, 2H), 3.80 (d, *J* = 6.5 Hz, 2H), 2.47 (s, 3H), 2.02 (s, 3H), 1.67 (s, 6H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.6, 144.2, 138.5, 137.6, 133.1, 130.3, 127.7, 119.5, 113.3, 91.9, 81.7, 72.6, 50.5, 48.9, 29.3, 22.2, 21.8. HRMS (ESI) m/z calcd. for $C_{20}H_{29}N_2O_4S$ $(M+NH_4)^+$: 393.1842, found 393.1842.

Preparation of substrate *Z*-1f

To a stirred solution of alcohol ***Z*-S3** (1.2 g, w% = 70%, 10.2 mmol) in THF at 0 °C (20 mL), Et_3N (1.26 g, 12.4 mmol) was added under N_2 atmosphere. MsCl (1.18 g, 10.3 mmol) was added carefully in 3 minutes. The mixture was warmed to room temperature to react for 30 minutes. LiBr (2.69 g, 31.0 mmol) was added to the above solution at 0 °C and then stirred at room temperature for 30 minutes. The reaction mixture was then transferred with pipette to tosyl amine **S1** (2.16 g, 10.2 mmol) solution at 0 °C that was previously deprotonated by NaH (663.0 mg, 60%, 16.6 mmol) in DMF (40 mL) for 30 minutes. The reaction was stirred for 19 h at room temperature. Then, 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 = 10 / 1) to yield ***Z*-S5**[1] (R*f*: 0.61 (PE / EA = 3 / 1), 629.5 mg, Yield = 22 %) as a yellow oil.

To a stirred solution of ***Z*-S5** (312.0 mg, 1.1 mmol) in anhydrous THF (20 mL) was added *n*-BuLi in hexanes (2.4 M, 0.6 mL, 1.6 mmol) at -78 °C. After stirring for 30 min at this temperature, acetone (0.16 mL, 2.2 mmol) was added to the reaction mixture in dropwise. After the addition finished, the reaction was allowed to warm to room temperature and stirred for 18 h. After the reaction was complete, 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 = 3 / 1) to yield ***Z*-S8** (R*f*: 0.30 (PE / EA = 3 / 1), 185.0 mg, Yield = 49 %) as a yellow oil.

To a stirred solution of ***Z*-S8** (175.0 mg, 0.5 mmol) in DCM (10 mL) was added Ac_2O (171.8 mg, 1.7 mmol), Et_3N (319.1 mg, 3.2 mmol) and DMAP (6.4 mg, 0.05 mmol) at room temperature. After stirring for 13 h, the reaction was complete. The reaction mixture was concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 5 / 1) to yield ***Z*-1f** (R*f*: 0.50 (PE / EA = 3 / 1), 196.5 mg, Yield = 99 %) as a yellow oil.

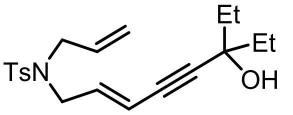


***Z*-1f**

***Z*-1f**: yellow oil, TLC R_f = 0.50 (PE / EA = 3 / 1)
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 5.76 (dt, *J* = 10.6, 6.8 Hz, 1H), 5.75 – 5.62 (m, 1H), 5.58 (d, *J* = 10.6 Hz, 1H), 5.19 (dd, *J* = 17.1, 1.5 Hz, 1H), 5.14 (dd, *J* = 10.2, 1.5 Hz, 1H), 4.00 (d, *J* = 6.8 Hz, 2H), 3.75 (d, *J* = 6.4 Hz, 2H), 2.43 (s, 3H), 1.95 (s, 3H), 1.62 (s, 6H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.6, 144.1, 138.6, 137.6, 133.3, 130.3, 127.7, 119.1, 112.4, 97.2, 79.8, 72.5, 50.8, 46.9, 29.2, 22.2, 21.8. HRMS (ESI) m/z calcd. for $C_{20}H_{29}N_2O_4S$ $(M+NH_4)^+$: 393.1842, found 393.1843.

Preparation of substrate *E*-1g

To a stirred solution of ***E*-S5** (500.0 mg, 1.8 mmol) in anhydrous THF (20 mL) was added *n*-BuLi in hexanes (1.6 M, 1.4 mL, 2.2 mmol) at -78 °C. After stirring for 30 min at this temperature, 3-pentanone (0.4 mL, 3.6 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 16 h. After the reaction was complete, 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 = 3 / 1) to yield ***E*-S9** (R*f*: 0.33 (PE / EA = 3 / 1), 483.0 mg, Yield = 74 %) as a yellow oil.

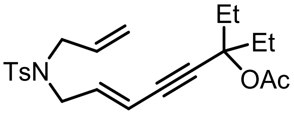


***E*-S9**

***E*-S9:** yellow oil, TLC *R_f*: 0.33 (PE / EA = 3 / 1)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 5.85 (dt, *J* = 15.9, 6.4 Hz, 1H), 5.69 – 5.54 (m, 2H), 5.20 – 5.16 (m, 1H), 5.15 – 5.11 (m, 1H), 3.80 (dd, *J* = 6.4, 1.4 Hz, 2H), 3.77 (d, *J* = 6.4 Hz, 2H), 2.43 (s, 3H), 1.91 (s, 1H), 1.69 – 1.62 (m, 2H), 1.67 – 1.60 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 144.2, 138.0, 137.7, 133.2, 130.3, 127.7, 119.5, 113.6, 93.5, 82.1, 72.8, 50.5, 48.9, 34.9, 21.8, 8.9. HRMS (ESI) m/z calcd. for $C_{20}H_{31}N_2O_3S$ $(M+NH_4)^+$: 379.2054, found 379.2050.

To a stirred solution of ***E*-S9** (206.6 mg, 0.6 mmol) in DCM (10 mL) was added Ac_2O (175 mg, 1.7 mmol), Et_3N (347 mg, 3.4 mmol) and DMAP (10.0 mg, 0.06 mmol) at room temperature. After stirring for 24 h, the reaction was complete. The reaction mixture was concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 5 / 1) to yield ***E*-1g** (R_f: 0.52 (PE / EA = 3 / 1), 202.0 mg, Yield = 88 %) as a yellow oil.



***E*-1g**

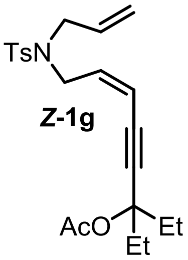
***E*-1g:** yellow oil, TLC R_f: 0.52 (PE / EA = 3 / 1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.87 (dt, *J* = 15.8, 6.4 Hz, 1H), 5.61 (dd, *J* = 15.8, 1.5 Hz, 1H), 5.64 – 5.49 (m, 1H), 5.18 – 5.08 (m, 2H), 3.80 (dd, *J* = 6.6, 1.6 Hz, 2H), 3.78 (d, *J* = 6.4 Hz, 2H), 2.41 (s, 3H), 2.01 (s, 3H), 2.08 – 1.94 (m, 2H), 1.95 – 1.81 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 143.4, 137.6, 137.2, 132.4, 129.7, 127.2, 119.4, 113.2, 89.6, 83.2, 80.1, 49.7, 48.2, 30.7, 21.9, 21.5, 8.4. HRMS (ESI) m/z calcd. for $C_{22}H_{33}N_2O_4S$ $(M+NH_4)^+$: 421.2156, found 421.2148.

Preparation of substrate *Z*-1g

To a stirred solution of ***Z*-S5** (278.8 mg, 1.0 mmol) in anhydrous THF (10 mL) was added *n*-BuLi in hexanes (2.4 M, 0.6 mL, 1.6 mmol) at -78 °C. After stirring for 30 min at this temperature, 3-pentanone (0.2 mL, 2.0 mmol) was added to the reaction mixture in dropwise. After the addition finished, the reaction was allowed to warm to room temperature and stirred for 12 h. After the reaction was complete, 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 = 10 / 1) to yield ***Z*-S9** (R_f: 0.25 (PE / EA = 5 / 1), 234.2 mg, Yield = 65 %) as a yellow oil.

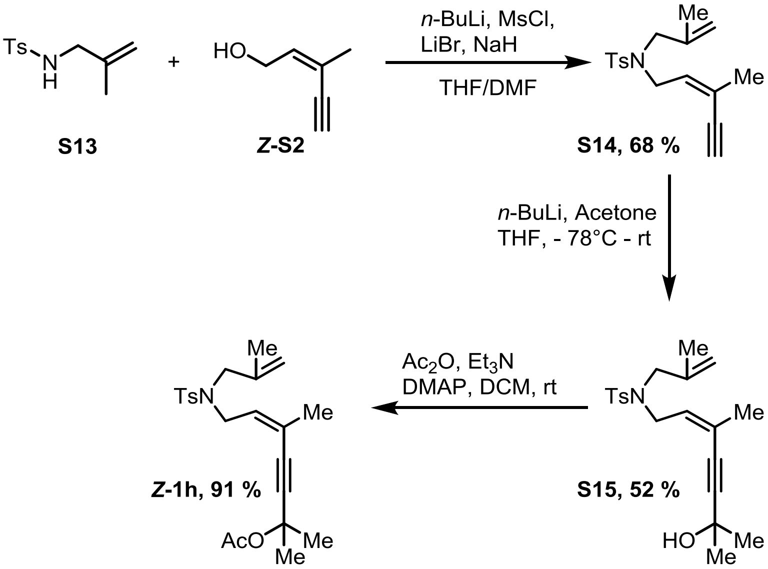
To a stirred solution of ***Z*-S9** (204.7 mg, 0.6 mmol) in DCM (10 mL) was added Ac_2O (0.16 mL, 1.7 mmol), Et_3N (0.46 mL, 3.3 mmol) and DMAP (5.0 mg, 0.01 mmol) at room temperature. After stirring for 36 h, the reaction was complete. The reaction mixture was concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 20 / 1) to yield ***Z*-1g** (R_f: 0.50 (PE / EA = 5 / 1), 216.4 mg, Yield = 98 %) as a yellow oil.



***Z*-1g**

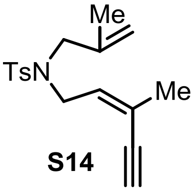
***Z*-1g**: yellow oil, TLC R_f = 0.50 (PE / EA = 5 / 1)
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.81 – 5.70 (m, 1H), 5.66 (dt, *J* = 10.4, 6.4 Hz, 1H), 5.61 (dt, *J* = 10.4, 1.6 Hz, 1H), 5.18 (dd, *J* = 17.1, 1.5 Hz, 1H), 5.12 (dd, *J* = 10.1, 1.4 Hz, 1H), 4.02 (dd, *J* = 6.4, 1.6 Hz, 2H), 3.74 (d, *J* = 6.3 Hz, 2H), 2.43 (s, 3H), 2.03 – 1.91 (m, 2H), 1.96 (s, 3H), 1.92 – 1.82 (m, 2H), 0.92 (t, *J* = 7.5 Hz, 6H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.5, 144.1, 138.5, 137.5, 133.3, 130.3, 127.7, 119.1, 112.5, 95.9, 81.6, 80.2, 50.8, 47.1, 31.2, 22.1, 21.8, 8.7. HRMS (ESI) m/z calcd. for $C_{22}H_{33}N_2O_4S$ $(M+NH_4)^+$: 421.2156, found 421.2154.

Preparation of substrate *Z*-1h



To a stirred solution of alcohol ***Z*-S2** (514.1 mg, 5.4 mmol) in THF(10 mL) at -78 °C, *n*-BuLi (3.5 mL, 1.6 M in hexanes) was added carefully in 3 minutes under N_2 atmosphere. MsCl (850.4 mg, 7.1 mmol) was added subsequentely after the solution was stirred for additional 10 minutes.

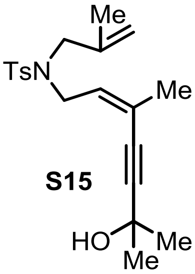
The mixture was warmed to room temperature to react for 30 minutes. LiBr (2.26 g, 26 mmol) was added at 0 °C and then stirred at room temperature for 1 h. The mixture was transferred with pipette to tosyl amine **S13**[3] (1.06 g, 4.7 mmol) solution at 0 °C that was previously deprotonated by NaH (259.7 mg, 60%, 6.5 mmol) in DMF (20 mL) for ***Z*-1h**. The reaction was stirred for 16 h at room temperature. After the reaction was completed, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 10 / 1) to yield **S14** (R_f: 0.55 (PE / EA = 3 / 1), 966.1 mg, Yield = 68 %) as a yellow oil.



S14

S14: yellow oil, TLC R_f: 0.55 (PE / EA = 3 / 1)
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 5.55 (tq, *J* = 7.0, 1.2 Hz, 1H), 4.90 (s, 1H), 4.87 (s, 1H), 3.93 (d, *J* = 7.0 Hz, 2H), 3.65 (s, 2H), 3.18 (s, 1H), 2.43 (s, 3H), 1.77 (d, *J* = 1.2 Hz, 3H), 1.70 (s, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 144.0, 141.0, 137.6, 133.8, 130.2, 127.8, 121.3, 114.4, 83.0, 82.0, 54.3, 47.6, 23.2, 21.8, 20.2. HRMS (ESI) m/z calcd. for $C_{17}H_{25}N_2O_2S$ $(M+NH_4)^+$: 321.1631, found 321.1630.

To a stirred solution of **S14** (303.9 mg, 1.0 mmol) in anhydrous THF (10 mL) was added *n*-BuLi in hexanes (1.6 M, 1.3 mL, 2.0 mmol) at -78 °C. After stirring for 30 min at this temperature, acetone (0.3 mL, 4.0 mmol) was added to the reaction mixture dropwise. After the addition was completed, the reaction was allowed to warm to room temperature and stirred for 16 h. After the reaction was completed, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 3 / 1) to yield **S15** (R_f: 0.34 (PE / EA = 3 / 1), 189.0 mg, Yield = 52 %) as a yellow oil.

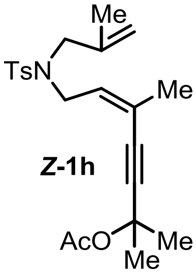


S15

S15: yellow oil, TLC R_f: 0.34 (PE / EA = 3 / 1)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 5.42 (tq, *J* = 7.0, 1.5 Hz, 1H), 4.90 (s, 1H), 4.87 (s, 1H), 3.92 (d, *J* = 7.0 Hz, 2H), 3.64 (s, 2H), 2.42 (s, 3H), 2.09 (brs, 1H), 1.73 (d, *J* = 1.5 Hz, 3H), 1.70 (s, 3H), 1.48 (s, 6H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 144.0, 141.1, 137.5, 131.3, 130.14, 130.13, 122.5, 114.2, 100.1, 80.2, 65.7, 53.9, 47.5, 31.8, 23.2, 21.8, 20.2. HRMS (ESI) m/z calcd. for $C_{20}H_{31}N_2O_3S$ $(M+NH_4)^+$: 379.2050, found 379.2048.

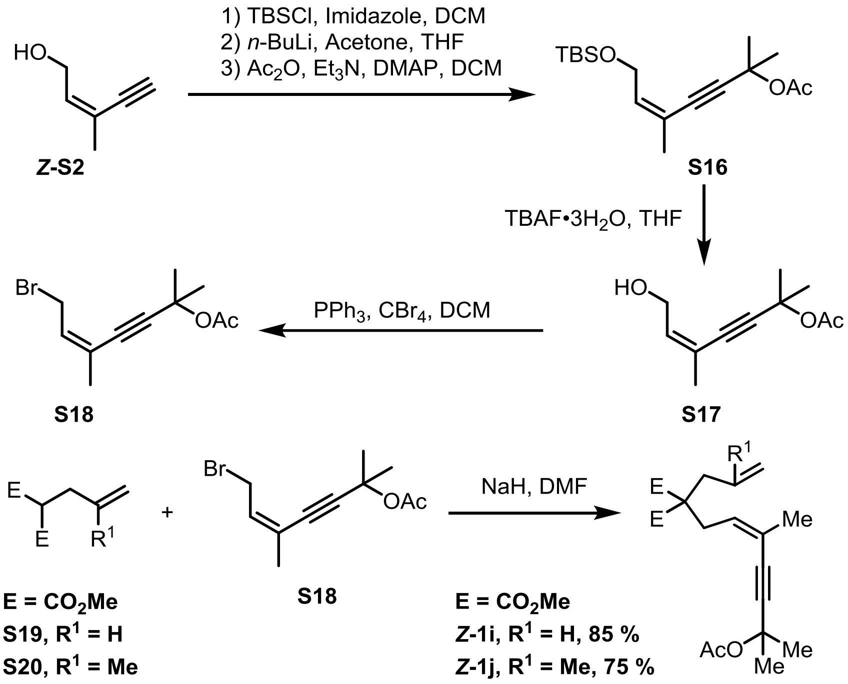
To a stirred solution of **S15** (160.6 mg, 0.4 mmol) in DCM (10 mL) was added Ac_2O (233.7 mg, 2.3 mmol), Et_3N (726 mg, 7.2 mmol) and DMAP (10 mg, 0.08 mmol) at room temperature. After stirring for 24 h, the reaction was completed. The reaction mixture was concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 5 / 1) to yield ***Z*-1h** (R_f: 0.67 (PE / EA = 3 / 1), 163.2 mg, Yield = 91 %) as a colorless oil.



***Z*-1h**

***Z*-1h:** colorless oil, TLC R_f: 0.67 (PE / EA = 3 / 1)
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 5.43 (tq, *J* = 7.1, 1.5 Hz, 1H), 4.89 (s, 1H), 4.87 (s, 1H), 3.91 (d, *J* = 7.1 Hz, 2H), 3.64 (s, 2H), 2.42 (s, 3H), 1.95 (s, 3H), 1.72 (d, *J* = 1.5 Hz, 3H), 1.71 (s, 3H), 1.62 (s, 6H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.5, 143.9, 141.0, 137.7, 132.1, 130.1, 127.7, 122.0, 114.1, 96.2, 82.2, 72.5, 54.1, 47.8, 29.3, 23.1, 22.2, 21.8, 20.2. HRMS (ESI) m/z calcd. for $C_{22}H_{23}N_2O_4S$ $(M+NH_4)^+$: 421.2156, found 421.2144.

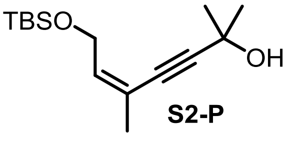
Preparation of substrates *Z*-1i and *Z*-1j



Preparation of substrate *Z*-1i

To a stirred suspension of imidazole (7.1 g, 104 mmol) in CH_2Cl_2 (50 mL) was added commercially available alcohol ***Z*-S2** (5.0 g, 52 mmol) in CH_2Cl_2 (10 mL) at 0 °C. TBSCl (9.5 g, 63.0 mmol) in CH_2Cl_2 (10 mL) was then added to the above solution. The reaction mixture was allowed to warm to room temperature and stirred for 16 h. After the reaction was completed, the reaction mixture was quenched with water (50 mL) and extracted with Et_2O (3 × 50 mL). The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 10 / 1) to yield pure TBS-protected alcohol 5.0 g[5] **.**

To a stirred solution of above TBS-protected alcohol (2.0 g, 9.5 mmol) in anhydrous THF (20 mL) was added *n*-BuLi in hexanes (1.6 M, 8.9 mL, 14.3 mmol) at -78 °C. After stirring for 30 min at -78 °C, acetone (1.4 mL, 19.0 mmol) was added to the reaction mixture dropwise. After the addition was completed, the reaction was allowed to warm to room temperature and stirred for 16 h. Then the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 10 / 1 to 5 / 1) to yield tertiary alcohol ***Z*-S2-P** (R_f: 0.22 (PE / EA = 3 / 1), 1.75 g, Yield = 69 %) as a colorless oil.

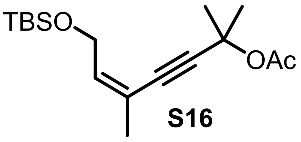


S2-P

***Z*-S2-P:** colorless oil, TLC R_f: 0.22 (PE / EA = 10 / 1)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 5.76 (tq, *J* = 6.5, 1.5 Hz, 1H), 4.31 (d, *J* = 6.5 Hz, 2H), 2.11 (s, 1H), 1.84 (d, *J* = 1.5 Hz, 3H), 1.52 (s, 6H), 0.90 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 137.2, 118.9, 99.4, 80.7, 65.9, 62.6, 31.9, 26.3, 23.4, 18.8, -4.8. HRMS (ESI) m/z calcd. for $C_{15}H_{32}NO_2Si$ $(M+NH_4)^+$: 286.2197, found 286.2198.

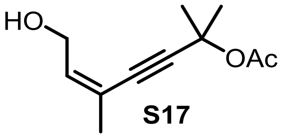
To a stirred solution of the above alcohol intermediate (1.63 g, 6.0 mmol) in DCM (20 mL) was added Ac_2O (1.88 g, 18.0 mmol), Et_3N (3.7 g, 36.0 mmol) and DMAP (76 mg, 0.6 mmol) at room temperature. After stirring for 24 h, the reaction was completed. The reaction mixture was concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 10 / 1) to yield **S16** (R_f: 0.71 (PE / EA = 3 / 1), 1.7274 g, Yield = 92 %) as a colorless oil.



S16

S16: colorless oil, TLC R_f: 0.71 (PE / EA = 3 / 1)
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.76 (tq, *J* = 6.5, 1.4 Hz, 1H), 4.33 (d, *J* = 6.5 Hz, 2H), 2.01 (s, 3H), 1.83 (d, *J* = 1.4 Hz, 3H), 1.67 (s, 6H), 0.90 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 137.3, 118.3, 95.0, 82.5, 72.5, 62.4, 29.2, 26.1, 22.9, 22.1, 18.5, -5.0. HRMS (ESI) m/z calcd. for $C_{17}H_{34}NO_3Si$ $(M+NH_4)^+$: 328.2302, found 328.2292.

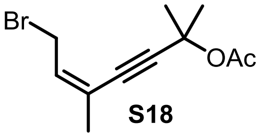
To a stirred solution of **S16** (1.29 g, 4.2 mmol) in THF (10 mL) was added TBAF (1.58 g, 5.0 mmol) in THF (10 mL) at room temperature. The reaction mixture was stirred for 2 h at room temperature. It was then quenched with saturated NH_4Cl and was extracted with Et_2O. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 1 / 1) to yield **S17** (R_f: 0.28 (PE / EA = 3 / 1), 752.6 mg, 92%) as a colorless oil.



S17

S17: colorless oil, TLC R_f: 0.28 (PE / EA = 3 / 1)
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 (tq, *J* = 6.7, 1.3 Hz, 1H), 4.22 (d, *J* = 6.7 Hz, 2H), 2.51 (s, 1H), 1.99 (s, 3H), 1.81 (d, *J* = 1.3 Hz, 3H), 1.64 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 136.7, 120.3, 95.0, 82.5, 72.4, 60.9, 29.1, 22.9, 22.0. HRMS (ESI) m/z calcd. for $C_{11}H_{20}NO_3$ $(M+NH_4)^+$: 214.1438, found 214.1439.

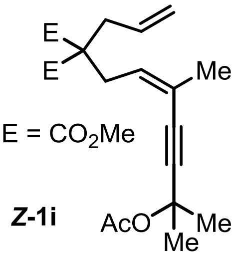
To a stirred solution of alcohol **S17** (524.6 mg, 2.67 mmol) in CH_2Cl_2 (15 mL) was added CBr_4 (1.17 g, 3.48 mmol) and PPh_3 (1.05 g, 4.01 mmol) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C and then concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 20 / 1) to yield **S18** (R*f*: 0.67 (PE / EA = 5 / 1), 645.5 mg, 93%) as a yellow oil.



S18

S18: colorless oil, TLC *R*$_f$: 0.67 (PE / EA = 5 / 1)
^{1}H NMR (400 MHz, CD_2Cl_2) δ 5.93 (tq, *J* = 8.2, 1.6 Hz, 1H), 4.16 (dq, *J* = 8.2, 0.9 Hz, 2H), 2.00 (s, 3H), 1.87 (dt, *J* = 1.6, 0.9 Hz, 3H), 1.68 (s, 6H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.7, 132.9, 123.9, 98.0, 81.6, 72.5, 30.9, 29.3, 23.1, 22.2. HRMS (ESI) m/z calcd. for $C_{11}H_{19}BrNO_2$ $(M+NH_4)^+$: 276.0594, found 276.0588.

To a stirred suspension of NaH (69.5 mg, 60%, 1.74 mmol, 60% in mineral oil) in HPLC grade DMF (5 mL) was added **S19** (298.9 mg, 1.74 mmol) in DMF (10 mL) at 0 °C. The reaction mixture was stirred for 30 min at this temperature. Then the mixture was cooled to 0 °C, the bromide **S18** (292.9 mg, 1.13 mmol) in DMF (5mL) was added dropwise. The reaction mixture was stirred 1 h at room temperature, and was then quenched with saturated aqueous NH_4Cl (20 mL), and extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated in *vacuo*. The residue was purified by flash column chromatography (R*f*: 0.32 (PE / EA = 5 / 1), PE / EA = 10 / 1) to give substrate ***Z*-1i** (336.4 mg, 85 %) as a colorless oil.

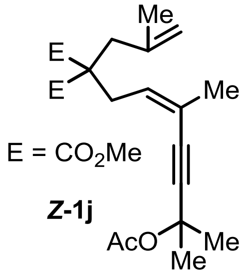


***Z*-1i**

***Z*-1i**: colorless oil, TLC *R*$_f$: 0.32 (PE / EA = 5 / 1)
^{1}H NMR (400 MHz, CD_2Cl_2) δ 5.74 (ddt, *J* = 16.9, 10.2, 7.5 Hz, 1H), 5.50 (dq, *J* = 7.5, 1.3 Hz, 1H), 5.14 – 5.02 (m, 2H), 3.68 (s, 6H), 2.79 (d, *J* = 7.5 Hz, 2H), 2.57 (d, *J* = 7.5 Hz, 2H), 1.99 (s, 3H), 1.81 (d, *J* = 1.3 Hz, 3H), 1.67 (s, 6H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 171.6, 169.6, 133.4, 131.8, 121.9, 119.2, 95.2, 83.2, 72.8, 58.3, 52.8, 37.9, 34.4, 29.4, 23.4, 22.2. HRMS (ESI) m/z calcd. for $C_{19}H_{30}NO_6$ $(M+NH_4)^+$: 368.2068, found 368.2056.

Preparation of substrate *Z*-1j

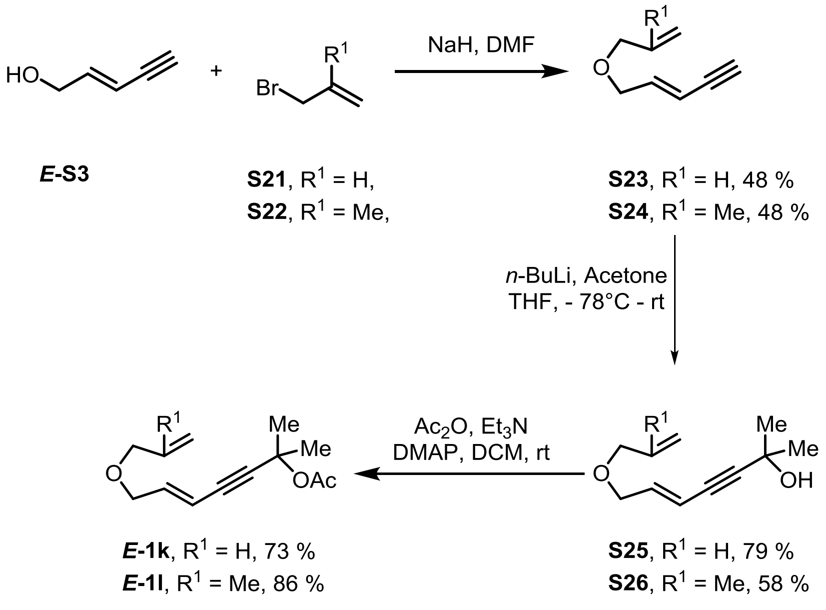
To a stirred suspension of NaH (74.7 mg, 1.9 mmol, 60% in mineral oil) in HPLC grade DMF (5 mL) was added **S20** (315.8 mg, 1.7 mmol) in THF (10 mL) at 0 °C. The reaction mixture was stirred for 30 min at this temperature. Then the mixture was cooled to 0 °C, and the bromide **S18** (352.6 mg, 1.4 mmol) in DMF (5mL) was added dropwise. The reaction mixture was stirred 1 h at room temperature, then was quenched with saturated aqueous NH_4Cl solution (20 mL), and extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated in *vacuo*. The residue was purified by flash column chromatography (PE / EA = 10 / 1) to give substrate ***Z*-1j** (R_f: 0.41 (PE / EA = 10 / 1), 372.6 mg, 75 %) as a colorless oil.



***Z*-1j**

***Z*-1j:** colorless oil, TLC R_f: 0.41 (PE / EA = 10 / 1)
^{1}H NMR (400 MHz, CD_2Cl_2) δ 5.55 (td, *J* = 7.5, 1.4 Hz, 1H), 4.86 (t, *J* = 1.8 Hz, 1H), 4.74 (s, 1H), 3.67 (s, 6H), 2.80 (dq, *J* = 7.5, 1.4 Hz, 2H), 2.66 (d, *J* = 1.8 Hz, 2H), 1.98 (s, 3H), 1.79 (d, *J* = 1.4 Hz, 3H), 1.66 (s, 6H), 1.65 (s, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 172.0, 169.5, 141.2, 132.2, 121.4, 116.1, 95.1, 83.1, 72.7, 57.7, 52.8, 41.4, 34.6, 29.4, 23.6, 23.3, 22.2. HRMS (ESI) m/z calcd. for $C_{20}H_{32}NO_6$ $(M+NH_4)^+$: 382.2224, found 382.2219.

Preparation of substrates *E*-1k and *E*-1l



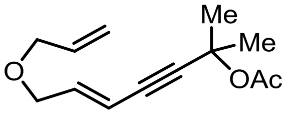
Preparation of substrate *E*-1k

To a stirred suspension of NaH (354.8 mg, 8.9 mmol, 60% in mineral oil) in anhydrous THF (5 mL) was added commercially available alcohol ***E*-S3** (660.2 mg, 8.0 mmol) in THF (15 mL) at 0 °C. The reaction mixture stirred for 5 min. The solution of bromide **S21** (992.0 mg, 8.2 mmol) in THF (5 mL) was added to the above reaction. The reaction mixture was heated to 50 °C for 16 h. It was then quenched with saturated aqueous NH_4Cl (30 mL) and extracted with Et_2O (3 × 20 mL).

The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 40 / 1) to give the ether **S23** (R_f: 0.57 (PE / EA = 10 / 1), 475.1 mg, 48%) as a yellow oil.

To a stirred solution of **S23** (475.1 mg, 3.9 mmol) in anhydrous THF (20 mL) was added *n*-BuLi in hexanes (1.6 M, 2.7 mL, 4.3 mmol) at -78 °C. After stirring for 30 min at -78 °C, acetone (0.4 mL, 4.3 mmol) was added to the reaction mixture dropwise. After the addition was completed, the reaction was allowed to warm to room temperature and stirred for 16 h. After the reaction was completed, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic layers were 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) to yield **S25** (R_f: 0.43 (PE / EA = 3 / 1), 550.6 mg, Yield = 79 %) as a colorless oil

To a stirred solution of **S25** (550.6 mg, 3.1 mmol) in DCM (10 mL) was added Ac_2O (936 mg, 9.2 mmol), Et_3N (1.85g, 18.3 mmol) and DMAP (37 mg, 0.3 mmol) at room temperature. After stirring for 24 h, the reaction was completed. The reaction mixture was concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 10 / 1) to yield ***E*-1k** (R_f: 0.77 (PE / EA = 3 / 1), 497.9 mg, Yield = 73 %) as a colorless oil.



***E*-1k**

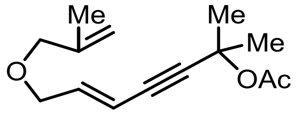
***E*-1k**: yellow oil, TLC R_f: 0.77 (PE / EA = 3 / 1)
^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.14 (dt, *J* = 16.2, 5.3 Hz, 1H), 5.89 (ddt, *J* = 17.2, 10.6, 5.5 Hz, 1H), 5.73 (dt, *J* = 16.2, 1.8 Hz, 1H), 5.25 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.15 (dd, *J* = 10.6, 1.6 Hz, 1H), 3.99 (dd, *J* = 5.3, 1.8 Hz, 2H), 3.95 (d, *J* = 5.5 Hz, 2H), 1.97 (s, 3H), 1.64 (s, 6H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.7, 140.7, 135.3, 117.0, 111.0, 91.4, 82.3, 72.7, 71.7, 70.1, 29.3, 22.3. HRMS (ESI) m/z calcd. for $C_{13}H_{22}NO_3$ $(M+NH_4)^+$: 240.1594, found 240.1591.

Preparation of substrate *E*-1l

To a stirred suspension of NaH (359.1 mg, 9.0 mmol, 60% in mineral oil) in anhydrous THF (5 mL) was added commercially available alcohol ***E*-S3** (487.8 mg, 5.9 mmol) in THF (15 mL) at 0 °C. The reaction mixture stirred for 5 min. The solution of commercially available bromide **S22** (1.0 g, 7.4 mmol) in THF (5 mL) was added to the above reaction. The reaction mixture was heated to 50 °C for 16 h, and was then quenched with saturated aqueous NH_4Cl solution (30 mL) and extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 40 / 1) to give the ether **S24** (R_f: 0.57 (PE / EA = 10 / 1), 401.1 mg, 48%) as a yellow oil.

To a stirred solution of **S24** (401.1 mg, 3.0 mmol) in anhydrous THF (20 mL) was added *n*-BuLi in hexanes (1.6 M, 1.93 mL, 3.1 mmol) at -78 °C. After stirring for 30 min at -78 °C, acetone (0.4 mL, 5.9 mmol) was added to the reaction mixture dropwise. After the addition was completed, the reaction was allowed to warm to room temperature and stirred for 16 h. Then the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with Et_2O. The combined organic layers were 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) to yield **S26** (R*f*: 0.48 (PE / EA = 3 / 1), 333.5 mg, Yield = 58 %) as a yellow oil

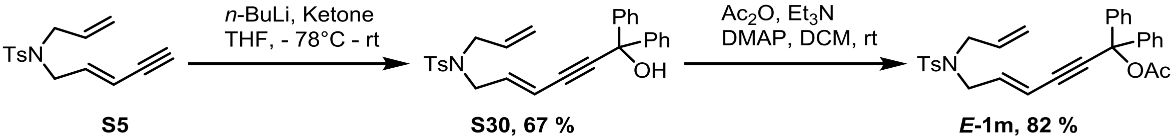
To a stirred solution of **S26** (203.5 mg, 1.1 mmol) in DCM (10 mL) was added Ac_2O (321 mg, 3.1 mmol), Et_3N (636 mg, 6.3 mmol) and DMAP (12.8 mg, 0.1 mmol) at room temperature. After stirring for 24 h, the reaction was completed. The reaction mixture was concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 10 / 1) to yield ***E*-1l** (R*f*: 0.42 (PE / EA = 3 / 1), 212.3 mg, Yield = 86 %) as a yellow oil.



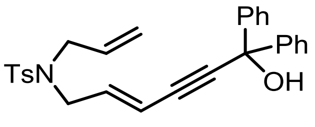
***E*-1l**

***E*-1l**: yellow oil, TLC R_f = 0.42 (PE / EA = 3 / 1)
^1H NMR (400 MHz, $CDCl_3$) δ 6.17 (dt, *J* = 16.0, 5.4 Hz, 1H), 5.76 (dt, *J* = 16.0, 1.7 Hz, 1H), 4.95 (s, 1H), 4.88 (s, 1H), 3.98 (dd, *J* = 5.4, 1.7 Hz, 2H), 3.86 (s, 2H), 2.01 (s, 3H), 1.72 (s, 3H), 1.66 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 142.1, 140.1, 112.3, 111.0, 90.8, 82.1, 74.3, 72.5, 69.5, 29.1, 22.1, 19.6. HRMS (ESI) m/z calcd. for $C_{14}H_{24}NO_3$ $(M+NH_4)^+$: 254.1751, found 254.1750.

Preparation of substrate *E*-1m



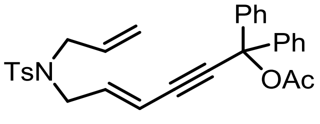
To a stirred solution of ***E*-S5** (336.9 mg, 1.2 mmol) in anhydrous THF (20 mL) was added *n*-BuLi in hexanes (1.6 M, 1.2 mL, 1.8 mmol) at -78 °C. After stirring for 30 min at this temperature, benzophenone (344 mg, 1.8 mmol) was added to the reaction mixture in dropwise. After the addition finishing, the reaction was allowed to warm to room temperature and stirred for 16 h. After the reaction was complete, the reaction mixture was quenched with saturated aqueous NH_4Cl solution 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 = 3 / 1) to yield **S30** (R*f*: 0.34 (PE / EA = 3 / 1), 376.3 mg, Yield = 67 %) as a yellow oil.



S30

S30: yellow oil, TLC R_f = 0.34 (PE / EA = 3 / 1)
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.62 – 7.58 (m, 2H), 7.58 – 7.56 (m, 2H), 7.37 – 7.32 (m, 4H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.31 – 7.26 (m, 2H), 6.03 (dt, *J* = 15.9, 6.3 Hz, 1H), 5.76 (dt, *J* = 15.9, 1.6 Hz, 1H), 5.62 (ddt, *J* = 17.1, 9.8, 6.4 Hz, 1H), 5.23 – 5.17 (m, 1H), 5.17 – 5.14 (m, 1H), 3.85 (dd, *J* = 6.3, 1.6 Hz, 2H), 3.80 (d, *J* = 6.4 Hz, 2H), 3.01 (s, 1H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 145.6, 144.2, 139.3, 137.6, 133.1, 130.3, 128.8, 128.2, 127.7, 126.4, 119.6, 113.0, 93.0, 85.1, 75.1, 50.6, 48.9, 21.8. HRMS (ESI) m/z calcd. for $C_{28}H_{31}N_2O_3S$ $(M+NH_4)^+$: 475.2050, found 475.2047.

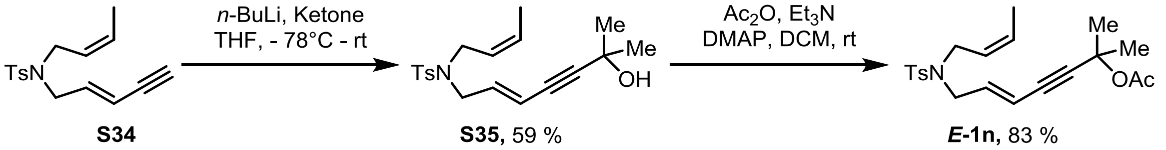
To a stirred solution of **S30** (376.3 mg, 0.8 mmol) in DCM (10 mL) was added Ac_2O (252 mg, 2.5 mmol), Et_3N (500 mg, 4.9 mmol) and DMAP (10 mg, 0.08 mmol) at room temperature. After stirring for 24 h, the reaction was complete. The reaction mixture was concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 5 / 1) to yield ***E*-1m** (R_f: 0.28 (PE / EA = 3 / 1), 337.9 mg, Yield = 82 %) as a yellow oil.



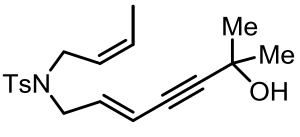
***E*-1m**

***E*-1m:** yellow oil, TLC R_f = 0.28 (PE / EA = 3 / 1)
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.72 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 1.7 Hz, 2H), 7.53 – 7.49 (m, 2H), 7.40 – 7.33 (m, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.33 – 7.28 (m, 4H), 6.07 (dt, *J* = 15.9, 6.2 Hz, 1H), 5.80 (dt, *J* = 15.9, 1.6 Hz, 1H), 5.64 (ddt, *J* = 17.6, 9.8, 6.4 Hz, 1H), 5.23 – 5.19 (m, 1H), 5.18 – 5.16 (m, 1H), 3.87 (dd, *J* = 6.2, 1.6 Hz, 2H), 3.82 (d, *J* = 6.4 Hz, 2H), 2.43 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 168.6, 144.2, 143.2, 139.6, 137.6, 133.1, 130.3, 128.8, 128.4, 127.7, 126.5, 119.6, 112.9, 89.3, 87.4, 79.9, 50.6, 48.8, 22.2, 21.8. HRMS (ESI) m/z calcd. for $C_{30}H_{33}N_2O_4S$ $(M+NH_4)^+$: 517.2156, found 517.2152.

Preparation of substrate *E*-1n



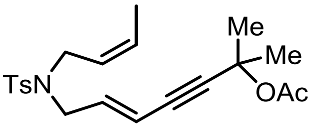
To a stirred solution of **S34**[1] (373.2 mg, 1.3 mmol) in anhydrous THF (20 mL) was added *n*-BuLi in hexanes (1.6 M, 1.2 mL, 1.8 mmol) at -78 °C. After stirring for 30 min at this temperature, acetone (0.2 mL, 2.6 mmol) was added to the reaction mixture in dropwise. After the addition finishing, the reaction was allowed to warm to room temperature and stirred for 22 h. After the reaction was complete, the reaction mixture was quenched with saturated aqueous NH_4Cl solution 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 = 3 / 1) to yield **S35** (R*f*: 0.20 (PE / EA = 3 / 1), 262.9 mg, Yield = 59 %) as a yellow oil.



S35

S35: yellow oil, TLC R_f = 0.20 (PE / EA = 3 / 1)
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.55 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 5.78 (dt, *J* = 15.8, 6.4 Hz, 1H), 5.56 – 5.42 (m, 1H), 5.49 (dt, *J* = 15.7, 1.5 Hz, 1H), 5.07 (dtq, *J* = 10.7, 7.0, 1.8 Hz, 1H), 3.68 (d, *J* = 6.8 Hz, 2H), 3.65 (dd, *J* = 6.4, 1.5 Hz, 2H), 2.30 (s, 3H), 1.98 (brs, 1H), 1.46 (dd, *J* = 7.0, 1.8 Hz, 3H), 1.36 (s, 6H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 144.1, 138.4, 137.7, 130.3, 129.5, 127.7, 124.9, 113.3, 95.5, 79.8, 65.8, 49.1, 44.2, 31.7, 21.8, 13.3. HRMS (ESI) m/z calcd. for $C_{19}H_{29}N_2O_3S$ $(M+NH_4)^+$: 365.1893, found 364.9076.

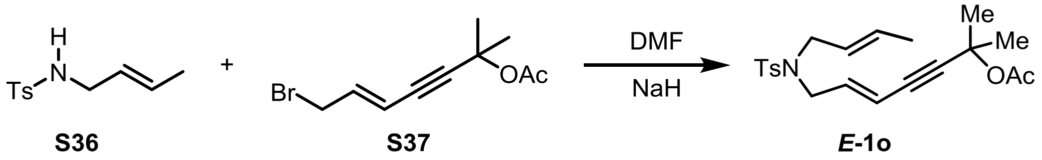
To a stirred solution of **S35** (262.9 mg, 0.76 mmol) in DCM (10 mL) was added Ac_2O (228.9 mg, 2.2 mmol), Et_3N (483.8 mg, 4.8 mmol) and DMAP (9.2 mg, 0.07 mmol) at room temperature. After stirring for 24 h, the reaction was complete. The reaction mixture was concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 5 / 1) to yield ***E*-1n** (R*f*: 0.63 (PE / EA = 5 / 1), 244.9 mg, Yield = 83 %) as a yellow oil.



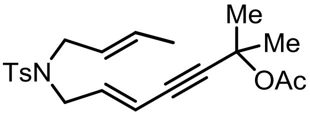
***E*-1n**

***E*-1n:** yellow oil, TLC R_f = 0.63 (PE / EA = 5 / 1)
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 5.92 (dt, *J* = 15.8, 6.3 Hz, 1H), 5.63 (dt, *J* = 15.8, 1.6 Hz, 1H), 5.66 – 5.57 (m, 1H), 5.20 (dtq, *J* = 10.7, 7.0, 1.8 Hz, 1H), 3.81 (d, *J* = 6.6 Hz, 2H), 3.76 (dd, *J* = 6.3, 1.6 Hz, 2H), 2.43 (s, 3H), 1.98 (s, 3H), 1.63 (s, 6H), 1.61 – 1.57 (m, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.6, 144.1, 138.8, 137.6, 130.3, 129.5, 127.7, 124.9, 113.1, 91.9, 81.8, 72.6, 49.1, 44.3, 29.3, 22.2, 21.8, 13.2. HRMS (ESI) m/z calcd. for $C_{21}H_{31}N_2O_4S$ $(M+NH_4)^+$: 407.1999, found 407.1991.

Preparation of substrate *E*-1o



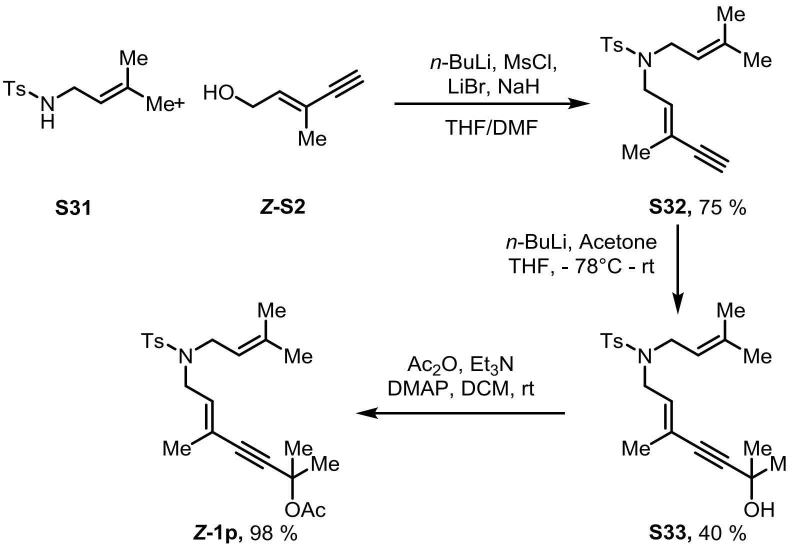
To a stirred suspension of NaH (79.5 mg, 2.0 mmol, 60% in mineral oil) in HPLC grade DMF (5 mL) was added **S36**[1] (318.7 mg, 1.4 mmol) in DMF (10 mL) at 0 °C. The reaction mixture was stirred for 30 min at this temperature. Then the mixture was cooled to 0 °C, the bromide **S37**[6] (292.7 mg, 1.2 mmol) in DMF (5mL) was added dropwise. The reaction mixture was stirred 1.5 h at room temperature, then was quenched with saturated aqueous NH_4Cl (20 mL), and extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated in *vacuo*. The residue was purified by flash column chromatography (R_f: 0.56 (PE / EA = 5 / 1), PE / EA = 5 / 1) to give substrate ***E*-1o** (290.9 mg, 56 %) as a yellow oil.



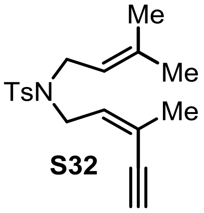
***E*-1o**

***E*-1o:** yellow oil, TLC R_f = 0.56 (PE / EA = 5 / 1)
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 5.88 (dt, *J* = 15.8, 6.4 Hz, 1H), 5.60 (dt, *J* = 15.8, 1.5 Hz, 1H), 5.63 – 5.52 (m, 1H), 5.21 (dtq, *J* = 15.2, 6.8, 1.7 Hz, 1H), 3.77 (dd, *J* = 6.4, 1.5 Hz, 2H), 3.69 (d, *J* = 6.8 Hz, 2H), 2.43 (s, 3H), 1.98 (s, 3H), 1.63 (s, 6H), 1.63 – 1.61 (m, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.6, 144.0, 138.8, 137.8, 131.6, 130.2, 127.7, 125.6, 113.1, 91.8, 81.8, 72.6, 49.8, 48.5, 29.3, 22.2, 21.8, 17.9. HRMS (ESI) m/z calcd. for $C_{21}H_{31}N_2O_4S$ $(M+NH_4)^+$: 407.1999, found 407.1998.

Preparation of substrate *Z*-1p



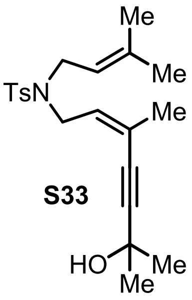
To a stirred solution of alcohol ***Z*-S2** (442.5 mg, 4.6 mmol) in THF at -78 °C (20 mL), *n*-BuLi (3.2 mL, 1.6 M in hexanes, 5.0 mmol) was added carefully in 3 minutes under N_2 atmosphere. MsCl (526.5 mg, 4.6 mmol) was added after the solution was stirred for additional 10 minutes. The mixture was warmed to room temperature to react for 30 minutes. LiBr (1.2 g, 12.5 mmol) was added to the above solution at 0 °C and then stirred at room temperature for 1 h. The reaction mixture was then transferred with pipette to tosyl amine **S31**[7] (1.0 g, 4.2 mmol) solution at 0 °C that was previously depronated by NaH (334.2 mg, 60%, 8.4 mmol) in DMF (50 mL) for ***Z*-1h**. The reaction was stirred for 16 h at room temperature. Then, 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 = 10 / 1) to yield **S32** (R_f: 0.57 (PE / EA = 3 / 1), 995.7 mg, Yield = 75 %) as a colorless oil.



S32

S32: colorless oil, TLC R_f = 0.57 (PE / EA = 3 / 1)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 5.68 – 5.59 (m, 1H), 5.06 – 4.96 (m, 1H), 3.96 (d, *J* = 6.9 Hz, 2H), 3.75 (d, *J* = 7.1 Hz, 2H), 3.10 (s, 1H), 2.41 (s, 3H), 1.81 (d, *J* = 1.5 Hz, 3H), 1.64 (d, *J* = 1.4 Hz, 3H), 1.58 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 137.3, 137.0, 134.4, 129.6, 127.3, 120.6, 119.0, 82.5, 81.7, 46.9, 45.4, 25.9, 23.0, 21.6, 17.9. HRMS (ESI) m/z calcd. for $C_{18}H_{27}N_2O_2S$ $(M+H)^+$: 318.1522, found 318.1523.

To a stirred solution of **S32** (464.2mg, 1.5 mmol) in anhydrous THF (20 mL) was added *n*-BuLi in hexanes (1.6 M, 3.0 mL, 4.8 mmol) at -78 °C. After stirring for 30 min at this temperature, acetone (0.5 mL, 6.7 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 16 h. Then 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 = 3 / 1) to yield **S33** (R_f: 0.41 (PE / EA = 3 / 1), 217.4 mg, Yield = 40 %) as a yellow oil.

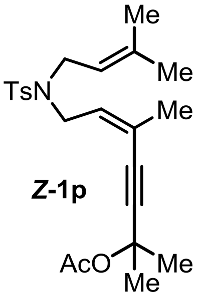


S33

S33: yellow oil, TLC R_f = 0.41 (PE / EA = 3 / 1)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.66 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 5.50 (tq, *J* = 6.9, 1.6 Hz, 1H), 5.07 – 4.97 (m, 1H), 3.92 (d, *J* = 6.0 Hz, 2H), 3.73 (d, *J* = 6.9 Hz, 2H), 2.42 (s, 3H), 2.10 (brs, 1H), 1.78 (d, *J* = 1.6 Hz, 3H), 1.66 (s, 3H), 1.60 (s, 3H), 1.48 (s, 6H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 143.8, 137.8, 137.3, 132.2, 130.1, 127.7, 122.1, 119.5, 100.1, 80.4, 65.8, 47.3, 45.7, 31.8, 26.1, 23.3, 21.8, 18.1. HRMS (ESI) m/z calcd. for $C_{21}H_{33}N_2O_3S$ $(M+NH_4)^+$: 393.2206, found 393.2210.

To a stirred solution of **S33** (184.3 mg, 0.5 mmol) in DCM (10 mL) was added Ac_2O (150 mg, 1.5 mmol), Et_3N (300 mg, 3.0 mmol) and DMAP (6.0 mg, 0.005 mmol) at room temperature. After stirring for 24 h, the reaction was complete. The reaction mixture was concentrated under vacuum. The residue was purified by flash column chromatography (PE / EA = 5 / 1) to yield ***Z*-1p** (R_f: 0.60 (PE / EA = 3 / 1), 201.3 mg, Yield = 98 %) as a yellow oil.

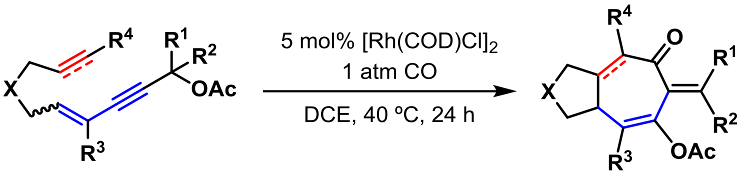


***Z*-1p**

***Z*-1p:** yellow oil, TLC R_f = 0.60 (PE / EA = 3 / 1)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.51 (tq, *J* = 6.8, 1.4 Hz, 1H), 5.09 – 4.99 (m, 1H), 3.93 (d, *J* = 6.8 Hz, 2H), 3.72 (d, *J* = 7.0 Hz, 2H), 2.42 (s, 3H), 1.94 (s, 3H), 1.77 (d, *J* = 1.4 Hz, 3H), 1.65 (d, *J* = 1.5 Hz, 3H), 1.62 (s, 6H), 1.60 (s, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.5, 143.7, 137.8, 137.1, 133.1, 130.0, 127.7, 121.6, 119.6, 96.2, 82.3, 72.5, 47.6, 45.8, 29.3, 26.0, 23.1, 22.2, 21.8, 18.0. HRMS (ESI) m/z calcd. for $C_{23}H_{35}N_2O_4S$ $(M+NH_4)^+$: 435.2312, found 435.2306.

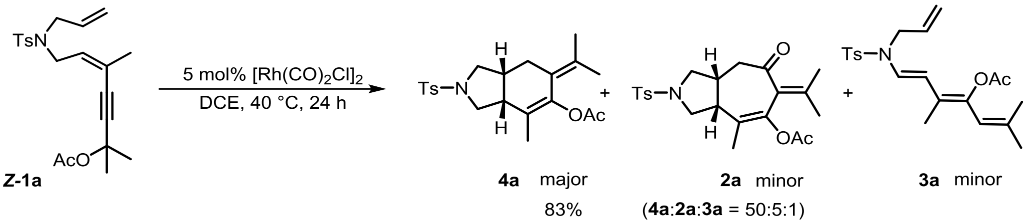
4. General procedure and byproducts of [4+2+1] cycloaddition



General procedure for ene/yne-ene-propargyl ester substrates: A solution of substrate **1** (0.1 mmol) in super-dried DCE (2.0 mL, 0.05 M) was added to [Rh(COD)Cl]$_2$ (2.5 mg, 5 mol%, except that 10 mol% was used for substrate ***Z*-1e**) in a reaction tube. 1 atm CO was bubbled to the solution for 3 minutes and then put the reaction tube in the oil bath at 40 ºC for all substrates (except for ***E*-1a**, ***E*-1b** at 60 °C, and ***Z*-1e** at 75 °C) with the balloon pressure of CO. After 24 h, the reaction mixture was cooled to room temperature and concentrated. The crude mixture was submitted to flash column chromatography on silica gel to afford the corresponding [4+2+1] cycloadduct **2**.

All the reactions reported have been repeated for at least two times and the desired [4+2+1] cycloadducts were isolated and characterized. Other byproducts, such as triene byproducts **3** and [4+2] **4** can sometimes be detected by TLC but were not isolated, because we were concentrated on developing a method to synthesize [4+2+1] products.

We also found that, the [4+2] cycloadduct **4a** could be obtained with high yield using [Rh(CO)$_2$Cl]$_2$ as catalyst under the atmosphere of N$_2$.

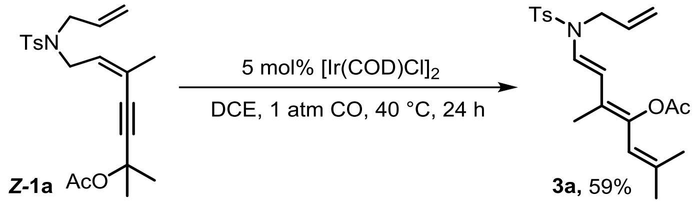


A solution of substrates ***Z*-1a** (0.1 mmol, 39.1 mg) in super-dried DCE (2.0 mL, 0.05 M) was added to [Rh(CO)$_2$Cl]$_2$ (0.05 eq, 2.1 mg) in reaction tube. Put the reaction tube in the oil bath under 40 °C. After 24 h, the reaction mixture was cooled to room temperature and concentrated. Crude ^{1}H-NMR showed that, [4+2] cycloadduct **4a** was the major product and the ration of **4a**: **2a**: **3a** is 50:5:1. The crude mixture was submitted to flash column chromatography with PE/EA = 3:1 on silica gel to afford the corresponding product **4a** as light yellow oil (32.5 mg, 83%).

4a: yellow oil, TLC R_f: 0.32 (PE / EA = 3 / 1)

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.66 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 3.63 – 3.52 (m, 1H), 3.49 – 3.37 (m, 1H), 3.01 – 2.93 (m, 1H), 2.90 – 2.79 (m, 1H), 2.78 – 2.69 (m, 1H), 2.46 – 2.40 (m, 1H), 2.43 (s, 3H), 2.29 – 2.21 (m, 1H), 2.10 (s, 3H), 1.74 (s, 3H), 1.69 – 1.58 (m, 1H), 1.65 (s, 3H), 1.48 (s, 3H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 168.6, 144.2, 143.6, 133.9, 130.2, 130.1, 128.1, 128.0, 122.6, 52.7, 44.0, 37.5, 31.8, 30.2, 22.5, 22.4, 21.8, 20.8, 15.4. HRMS (ESI) m/z calcd. for $C_{21}H_{31}N_2O_4S$ $(M+NH_4)^+$: 407.1999, found 407.2004.

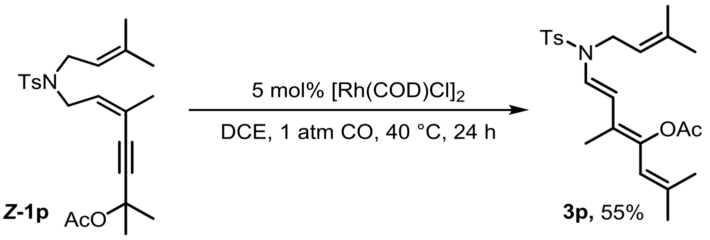
While using [Ir(COD)Cl]$_2$ instead of Rh catalyst, the triene byproduct **3a** could be achieved in 59% yield.



A solution of substrates (0.1 mmol, 38.9 mg) in super-dried DCE (2 mL, 0.05 M) was added to [Ir(COD)Cl]$_2$ (0.05 eq, 3.4 mg) in reaction tube. 1 atm CO was bubbled to the solution for 3 minutes and then put the reaction tube in the oil bath with the balloon pressure of CO. After 24 h, the reaction mixture was cooled to room temperature and concentrated. The crude mixture was submitted to flash column chromatography on silica gel to afford **3a** (23.1 mg, 59%).

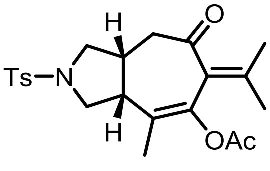
3a: yellow oil, TLC R_f: 0.62 (PE / EA = 3 / 1)
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 6.91 (d, *J* = 14.5 Hz, 1H), 5.70 – 5.65 (m, 1H), 5.62 (d, *J* = 14.5 Hz, 1H), 5.65 – 5.59 (m, 1H), 5.19 (dd, *J* = 9.2, 1.4 Hz, 1H), 5.17 – 5.14 (m, 1H), 4.06 – 3.98 (m, 2H), 2.42 (s, 3H), 2.12 (s, 3H), 1.76 (d, *J* = 1.5 Hz, 3H), 1.72 (d, *J* = 1.2 Hz, 3H), 1.63 (d, *J* = 1.3 Hz, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.4, 144.8, 142.7, 140.4, 136.5, 132.9, 130.4, 127.4, 127.2, 122.0, 118.2, 117.9, 110.7, 49.0, 26.4, 21.8, 21.0, 20.4, 12.0. HRMS (ESI) m/z calcd. for $C_{21}H_{31}N_2O_4S$ $(M+NH_4)^+$: 407.1999, found 407.2005.

For substrate ***Z*-1p**, no [4+2+1] cycloadduct was observed under the optimized reaction conditions. Instead, but triene byproduct **3p** could be delivered in a moderate yield.



Following the general procedure, 42.0 mg ***Z*-1p** was converted to 33.0 mg **3p**, yield 55 %.
Reaction time: 24 h, reaction temperature: 40 ℃, eluted with PE / EA = 3 / 1
3p: yellow oil, TLC R_f : 0.57 (PE / EA = 3 / 1)
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.55 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 6.82 (d, *J* = 14.4 Hz, 1H), 5.60 (q, *J* = 1.4 Hz, 1H), 5.46 (d, *J* = 14.4 Hz, 1H), 4.87 – 4.78 (m, 1H), 3.92 (d, *J* = 5.3 Hz, 2H), 2.33 (s, 3H), 2.04 (s, 3H), 1.67 (s, 3H), 1.64 (s, 3H), 1.59 – 1.55 (m, 6H), 1.55 (s, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.4, 144.6, 142.4, 140.1, 136.7, 136.1, 130.3, 127.4, 127.3, 122.1, 119.7, 118.0, 109.9, 44.8, 26.5, 25.8, 21.8, 21.0, 20.3, 18.2, 12.1. HRMS (ESI) m/z calcd. for $C_{23}H_{35}N_2O_4S$ $(M+NH_4)^+$: 435.2312, found 435.2313.

5. Products of [4+2+1] cycloaddition



2a

Reaction of ***Z*-1a**

Reaction time: 24 h, reaction temperature: 40 °C, eluted with PE / EA = 3 / 1

Run 1: 39.1 mg ***Z*-1a** was converted to 33.1 mg **2a**, yield 79 %. Run 2: 38.8 mg ***Z*-1a** was converted to 33.5 mg **2a**, yield 81 %.

In the third run, we isolated both the [4+2+1] cycloadduct **2a** and triene byproduct **3a**. 38.4 mg ***Z*-1a** was converted to 31.9 mg **2a** (yield 77 %) and 3.5 mg **3a** (yield 9%). So the average yield of three runs was 79 %.

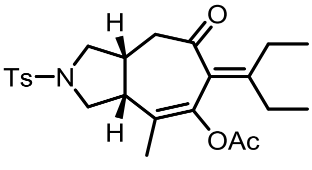
Reaction of ***E*-1a**

Reaction time: 24 h, reaction temperature: 60 °C, eluted with PE / EA = 3 / 1

Run 1: 39.1 mg ***E*-1a** was converted to 37.1 mg **2a**, yield 88 %. Run 2: 39.3 mg ***E*-1a** was converted to 37.3 mg **2a**, yield 88 %. So the average yield of two runs was 88%.

2a: yellow solid, m. p.: 161-162 ℃, TLC R_f: 0.1 (PE / EA = 3 / 1)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.64 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 3.57 - 3.47 (m, 2H), 3.05 – 2.83 (m, 2H), 2.72 – 2.49 (m, 4H), 2.43 (s, 3H), 2.06 (s, 3H), 1.80 (s, 3H), 1.69 (s, 3H), 1.67 (s, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 199.5, 169.6, 153.7, 144.5, 142.1, 133.0, 132.0, 130.3, 128.3, 124.6, 53.4, 51.9, 43.5, 43.3, 39.2, 24.8, 22.5, 21.8, 20.7, 16.3. HRMS (ESI) m/z calcd. for $C_{22}H_{31}N_2O_5S$ $(M+NH_4)^+$: 435.1948, found 435.1953.



2b

Reaction of ***Z*-1b**

Reaction time: 24 h, reaction temperature: 40 ℃, eluted with PE / EA = 3 / 1

Run 1: 42.4 mg **Z-1b** was converted to 29.6 mg **2b**, yield 65%. Run 2: 42.1 mg **Z-1b** was converted to 27.7 mg **2b**, yield 62 %. So the average yield of two runs was 63 %.

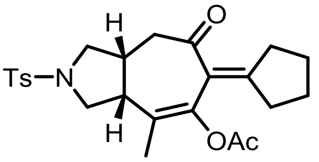
Reaction of ***E*-1b**

Reaction time: 24 h, reaction temperature: 60 ℃, eluted with PE / EA = 3 / 1

Run 1: 41.7 mg ***E*-1b** was converted to 34.9 mg **2b**, yield 78%. Run 2: 41.7 mg ***E*-1b** was converted to 36.1 mg **2b**, yield 81 %. So the average yield of two runs was 79 %

2b: white solid, m. p.: 159 – 160 ℃, TLC *Rf* : 0.28 (PE / EA = 3 / 1)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.66 (d, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 2H), 3.51 (dd, *J* = 10.0, 7.5 Hz, 1H), 3.46 (dd, *J* = 10.0, 7.5 Hz, 1H), 3.28 – 3.06 (m, 1H), 3.03 – 2.92 (m, 1H), 2.81 – 2.71 (m, 1H), 2.71 – 2.61 (m, 1H), 2.57 – 2.47 (m, 1H), 2.43 (s, 3H), 2.47 – 2.33 (m, 2H), 2.22 – 2.08 (m, 2H), 2.07 (s, 3H), 2.08 – 1.97 (m, 1H), 1.63 (s, 3H), 0.98 (t, *J* = 7.5 Hz, 3H), 0.92 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 199.5, 169.5, 163.7, 144.5, 141.8, 133.7, 131.1, 130.3, 128.1, 123.7, 53.7, 50.8, 43.9, 43.2, 39.4, 28.9, 25.8, 21.8, 21.0, 15.3, 13.5, 12.6. HRMS (ESI) m/z calcd. for $C_{24}H_{35}N_2O_5S$ $(M+NH_4)^+$: 463.2261, found 463.2260.



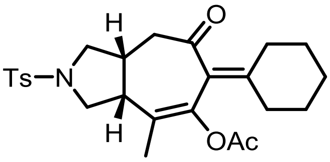
2c

Reaction time: 24 h, reaction temperature: 40 ℃, eluted with PE / EA = 3 / 1

Run 1: 42.0 mg ***Z*-1c** was converted to 18.7 mg **2c**, yield 42 %. Run 2: 42.2 mg ***Z*-1c** was converted to 17.8 mg **2c**, yield 42 %. So the average yield of two runs was 42 %.

2c : colorless oil, TLC *Rf* : 0.18 (PE / EA = 3 / 1)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 3.49 (dd, *J* = 10.0, 7.5 Hz, 1H), 3.35 (dd, *J* = 10.0, 7.5 Hz, 1H), 3.16 – 3.02 (m, 1H), 3.01 – 2.91 (m, 1H), 2.77 – 2.67 (m, 2H), 2.67 – 2.63 (m, 2H), 2.61 – 2.54 (m, 1H), 2.43 (s, 3H), 2.40 – 2.35 (m, 1H), 2.34 – 2.27 (m, 2H), 2.08 (s, 3H), 1.69 (s, 3H), 1.67 – 1.48 (m, 4H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 198.2, 169.5, 169.0, 144.4, 143.0, 133.4, 130.2, 128.2, 127.7, 123.9, 53.0, 51.4, 43.6, 42.9, 41.1, 36.1, 35.2, 26.7, 26.0, 21.8, 20.6, 15.9. HRMS (ESI) m/z calcd. for $C_{24}H_{33}N_2O_5S$ $(M+NH_4)^+$: 461.2105, found 461.2108.



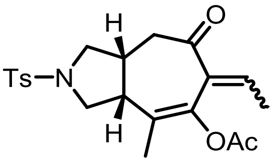
2d

Reaction time: 24 h, reaction temperature: 40 ℃, eluted with PE / EA = 3 / 1

Run 1: 42.3 mg ***Z*-1d** was converted to 31.3 mg **2d**, yield 70 %. Run 2: 42.9 mg ***Z*-1d** was converted to 31.8 mg **2d**, yield 70 %. So the average yield of two runs was 70 %.

2d : colorless oil, TLC *Rf* : 0.17 (PE / EA = 3 / 1)

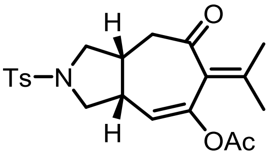
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 3.63 – 3.49 (m, 2H), 3.15 – 2.79 (m, 2H), 2.72 – 2.48 (m, 4H), 2.44 (s, 3H), 2.19 – 2.09 (m, 1H), 2.05 (s, 3H), 2.00 – 1.74 (m, 2H), 1.65 (s, 3H), 1.62 – 1.37 (m, 7H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 199.7, 170.8, 169.0, 158.6, 143.9, 140.9, 132.9, 129.8, 129.0, 127.7, 53.1, 51.1, 43.1, 43.0, 38.1, 33.8, 30.3, 28.6, 28.3, 26.1, 21.3, 20.3, 14.0. HRMS (ESI) m/z calcd. for $C_{25}H_{35}N_2O_5S$ $(M+NH_4)^+$: 475.2261, found 475.2263.



2e

Reaction time: 24 h, reaction temperature: 75 ℃, catalyst loading: 10 mol%
Eluted with PE / EA = 3 / 1
Run 1: 37.6 mg ***Z*-1e** was converted to 17.4 mg **2e**, yield 43 %. Run 2: 36.9 mg ***Z*-1e** was converted to 17.6 mg **2e**, yield 44 %. So the average yield of two runs was 44 %. The ratio of two regioisomer is 2.5 : 1.

2e : colorless oil, TLC R_f : 0.14 (PE / EA = 3 / 1)
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.59 (d, J = 8.2 Hz, 2.0 H), 7.58 (d, J = 8.3 Hz, 5.0 H), 7.27 (d, J = 8.0 Hz, 7.0 H), 6.61 (q, J = 7.4 Hz, 2.5 H), 6.13 (q, J = 7.5 Hz, 1.0 H), 3.49 – 3.39 (m, 3.5 H), 3.32 – 3.23 (m, 3.5 H), 3.23 – 3.15 (m, 3.5 H), 2.95 – 2.81 (m, 5.0 H), 2.78 – 2.64 (m, 5.0 H), 2.50 – 2.38 (m, 7.5 H), 2.37 – 2.33 (m, 10.5 H), 2.06 (s, 3H), 2.02 (s, 7.5 H), 1.89 (d, J = 7.5 Hz, 3.0 H), 1.68 (d, J = 7.5 Hz, 7.5 H), 1.62 (s, 7.5 H), 1.58 (s, 3.0 H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 199.8, 197.0, 169.44, 169.39, 144.5, 144.4, 142.2, 141.6, 141.0, 140.8, 136.9, 136.5, 133.8, 133.6, 130.29, 130.27, 128.04, 128.00, 125.7, 122.9, 53.2, 53.0, 51.3, 43.7, 42.9, 42.4, 42.0, 41.6, 40.9, 22.9, 21.8, 21.0, 20.5, 16.3, 16.2, 15.9, 15.2. HRMS (ESI) m/z calcd. for $C_{21}H_{29}N_2O_5S$ $(M+NH_4)^+$: 421.1792, found 421.1792.



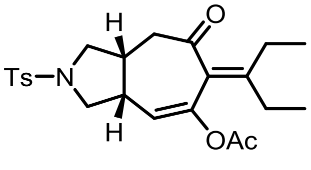
2f

Reaction of ***E*-1f**
Reaction time: 24 h, reaction temperature: 40 ℃, eluted with PE / EA = 3 / 1
Run 1: 38.6 mg ***E*-1f** was converted to 29.3 mg **2f**, yield 71 %. Run 2: 38.7 mg ***E*-1f** was converted to 28.4 mg **2f**, yield 68 %. So the average yield of two runs was 70 %.

Reaction of ***Z*-1f**
Reaction time: 24 h, reaction temperature: 40 ℃, eluted with PE / EA = 3 / 1
Run 1: 37.0 mg ***Z*-1f** was converted to 24.4 mg **2f**, yield 61 %. Run 2: 37.4 mg ***Z*-1f** was converted to 25.9 mg **2f**, yield 64 %. So the average yield of two runs was 62 %

2f: yellow oil, TLC R_f : 0.18 (PE / EA = 3 / 1)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.67 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 5.26 (d, *J* = 5.1 Hz, 1H), 3.54 – 3.42 (m, 2H), 3.04 – 2.92 (m, 2H), 2.83 (dd, *J* = 13.7, 10.7 Hz, 1H), 2.73 (dd, *J* = 10.0, 7.7 Hz, 1H), 2.64 – 2.49 (m, 1H), 2.44 (s, 3H), 2.34 (dd, *J* = 13.7, 4.1 Hz, 1H), 2.04 (s, 3H), 1.99 (s, 3H), 1.82 (s, 3H).; ^{13}C NMR (101 MHz, CD_2Cl_2) δ 198.9, 169.8, 155.1, 147.8, 144.5, 133.2, 131.1, 130.3, 128.2, 118.6, 53.51, 53.46, 44.1, 40.1, 37.8, 25.1, 23.1, 21.8, 20.7. HRMS (ESI) m/z calcd. for $C_{21}H_{29}N_2O_5S$ $(M+NH_4)^+$: 421.1792, found 421.1791.



2g

Reaction of ***E*-1g**

Reaction time: 24 h, reaction temperature: 40 ℃, eluted with PE / EA = 3 / 1

Run 1: 37.6 mg ***E*-1g** was converted to 30.9 mg **2g**, yield 77 %. Run 2: 37.5 mg ***E*-1g** was converted to
29.4 mg **2g**, yield 73 %. So the average yield of two runs was 75 %.

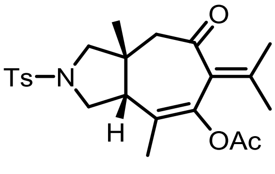
Reaction of ***Z*-1g**

Reaction time: 24 h, reaction temperature: 40 ℃, eluted with PE / EA = 3 / 1

Run 1: 40.3 mg ***Z*-1g** was converted to 31.3 mg **2g**, yield 73 %. Run 2: 40.3 mg ***Z*-1g** was converted to 31.2 mg **2g**, yield 72 %. So the average yield of two runs was 72 %.

2g: yellow oil, TLC *R$_f$* : 0.28 (PE / EA = 3 / 1)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.67 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 5.22 (d, *J* = 4.8 Hz, 1H), 3.55 – 3.44 (m, 2H), 3.04 (dd, *J* = 10.0, 6.2 Hz, 1H), 2.99 – 2.92 (m, 1H), 2.86 (dd, *J* = 14.1, 11.5 Hz, 1H), 2.78 (dd, *J* = 10.0, 7.3 Hz, 1H), 2.59 – 2.45 (m, 2H), 2.44 (s, 3H), 2.33 – 2.07 (m, 4H), 2.05 (s, 3H), 1.00 (t, *J* = 7.5 Hz, 3H), 0.96 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 199.0, 169.8, 165.1, 147.6, 144.5, 133.4, 130.3, 130.2, 128.1, 118.3, 54.3, 53.2, 44.4, 39.7, 38.2, 28.9, 25.9, 21.8, 21.1, 13.6, 12.8. HRMS (ESI) m/z calcd. for $C_{23}H_{33}N_2O_5S$ $(M+NH_4)^+$: 449.2105, found 449.2107.



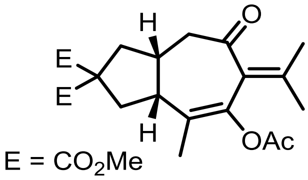
2h

Reaction time: 24 h, reaction temperature: 40 ℃, eluted with PE / EA = 3 / 1

Run 1: 42.6 mg ***Z*-1h** was converted to 19.4 mg **2g**, yield 43 %. Run 2: 43.3 mg ***Z*-1h** was converted to 20.9 mg **2h**, yield 45 %. So the average yield of two runs was 44 %.

2h: colorless oil, TLC *R$_f$* : 0.21 (PE / EA = 3 / 1)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.63 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 3.45 (dd, *J* = 9.8, 8.2 Hz, 1H), 3.1 – 2.9 (m, 1H), 3.03 (d, *J* = 9.7 Hz, 1H), 2.75 (d, *J* = 9.7 Hz, 1H), 2.70 – 2.53 (m, 2H), 2.59 (dd, *J* = 8.2, 5.8 Hz, 1H), 2.43 (s, 3H), 2.07 (s, 3H), 1.87 (s, 3H), 1.74 (s, 3H), 1.66 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.2, 169.2, 155.5, 143.8, 142.7, 131.0, 129.7, 127.9, 124.6, 58.9, 51.3, 51.0, 49.7, 46.4, 29.8, 28.6, 25.3, 22.9, 21.6, 20.4. HRMS (ESI) m/z calcd. for $C_{23}H_{30}NO_5S$ $(M+H)^+$: 432.1840, found 432.1827.



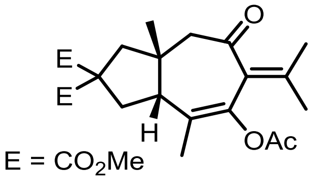
2i

Reaction time: 24 h, reaction temperature: 40 ℃, eluted with PE / EA = 5 / 1

Run 1: 35.2 mg ***Z*-1i** was converted to 36.5 mg **2i**, yield 96 %. Run 2: 35.5 mg ***Z*-1i** was converted to 34.7 mg **2i**, yield 91 %. So the average yield of two runs was 94 %.

2i: colorless oil, TLC R_f : 0.30 (PE / EA = 3 / 1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.72 (s, 3H), 3.67 (s, 3H), 2.89 – 2.75 (m, 2H), 2.69 – 2.53 (m, 3H), 2.52 – 2.45 (m, 1H), 2.07 (s, 3H), 2.05 (s, 3H), 2.12 – 2.01 (m, 1H), 1.82 (s, 3H), 1.78 – 1.69 (m, 1H), 1.72 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.4, 172.3, 171.9, 169.2, 151.5, 140.8, 132.6, 127.1, 59.4, 52.9, 52.8, 44.3, 43.2, 40.0, 39.2, 37.7, 24.3, 22.1, 20.5, 17.6. HRMS (ESI) m/z calcd. for $C_{20}H_{30}NO_7$ $(M+NH_4)^+$: 396.2017, found 396.2020.



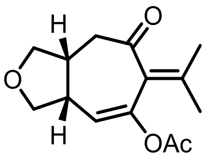
2j

Reaction time: 12 h, reaction temperature: 60 ℃, eluted with PE / EA = 5 / 1

Run 1: 37.8 mg ***Z*-1j** was converted to 33.8 mg **2j**, yield 83 %. Run 2: 39.5 mg ***Z*-1j** was converted to 36.4 mg **2j**, yield 86 %. So the average yield of two runs was 85 %.

2j: white solid, m. p. : 110 – 111 ℃, TLC R_f : 0.33 (PE / EA = 3 / 1)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.72 (s, 3H), 3.64 (s, 3H), 3.01 (d, *J* = 13.2 Hz, 1H), 2.63 (ddd, *J* = 13.2, 7.6, 1.7 Hz, 1H), 2.44 (dd, *J* = 11.7, 7.6 Hz, 1H), 2.30 – 2.25 (m, 1H), 2.25 – 2.22 (m, 1H), 2.17 – 2.09 (m, 1H), 2.13 (s, 3H), 2.09 (s, 3H), 2.10 – 2.00 (m, 1H), 1.85 (s, 3H), 1.77 (s, 3H), 1.02 (s, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 200.4, 173.0, 172.3, 169.7, 154.3, 142.2, 132.5, 127.3, 59.4, 54.8, 53.2, 53.1, 52.6, 46.3, 46.0, 39.9, 32.6, 25.4, 23.0, 20.8, 19.5. HRMS (ESI) m/z calcd. for $C_{21}H_{29}O_7$ $(M+H)^+$: 393.1908, found 393.1901.



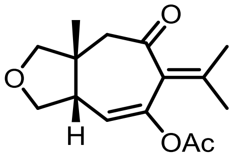
2k

Reaction time: 24 h, reaction temperature: 40 ℃, eluted with PE / EA = 5 / 1.

Run 1: 22.5 mg ***E*-1k** was converted to 21.6 mg **2k**, yield 85 %. Run 2: 22.6 mg ***E*-1k** was converted to 21.3 mg **2k**, yield 84 %. So the average yield of two runs was 85 %.

2k: colorless oil, TLC R_f : 0.22 (PE / EA = 3 / 1)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 5.46 (d, J = 4.7 Hz, 1H), 4.07 – 3.94 (m, 2H), 3.57 (dd, J = 8.7, 6.5 Hz, 1H), 3.32 (dd, J = 8.6, 7.3 Hz, 1H), 3.09 – 2.96 (m, 2H), 2.69 – 2.54 (m, 1H), 2.39 (dd, J = 13.7, 3.6 Hz, 1H), 2.11 (s, 3H), 2.07 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 199.5, 170.1, 154.2, 147.7, 131.5, 119.2, 74.5, 74.0, 43.9, 41.0, 38.8, 25.1, 23.0, 20.8. HRMS (ESI) m/z calcd. for $C_{14}H_{22}NO_4$ $(M+NH_4)^+$: 268.1543, found 268.1542.



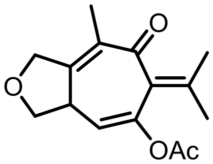
2l

Reaction time: 24 h, reaction temperature: 40 ℃, eluted with PE / EA = 5 / 1.

Run 1: 27.1 mg ***E*-1l** was converted to 22.1 mg **2l**, yield 73 %. Run 2: 28.2 mg ***E*-1l** was converted to 21.5 mg **2l**, yield 68 %. So the average yield of two runs was 71 %.

2l: yellow solid, m. p.: 89 – 90 ℃ TLC R_f : 0.24 (PE / EA = 3 / 1)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 5.49 (d, J = 5.3 Hz, 1H), 4.14 (dd, J = 8.9, 7.6 Hz, 1H), 3.62 (dd, J = 8.9, 5.3 Hz, 1H), 3.51 (d, J = 8.4 Hz, 1H), 3.42 (d, J = 8.4 Hz, 1H), 3.11 (d, J = 13.1 Hz, 1H), 2.59 (ddd, J = 7.6, 5.3, 5.3 Hz, 1H), 2.32 (d, J = 13.1 Hz, 1H), 2.16 (s, 3H), 2.07 (s, 3H), 1.90 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 198.8, 170.2, 155.0, 148.3, 131.4, 121.0, 80.5, 75.0, 50.6, 47.9, 45.7, 27.0, 25.3, 23.1, 20.8. HRMS (ESI) m/z calcd. for $C_{15}H_{21}O_4$ $(M+H)^+$: 265.1434, found 265.1429.



2q

Reaction time: 24 h, reaction temperature: 40 ℃, eluted with PE / EA = 5 : 1

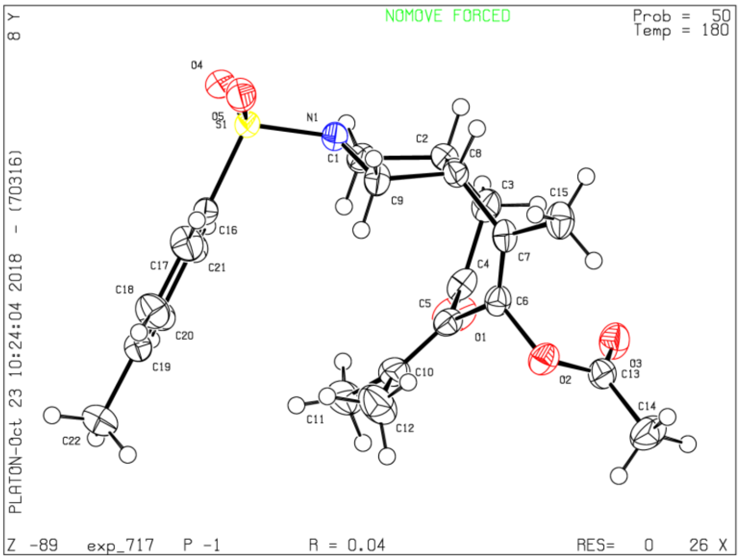
Run 1: 25.5 mg ***E*-1q** was converted to 15.4 mg **2q**, yield 53 %. Run 2: 27.1 mg ***E*-1q** was converted to 14.7 mg **2q**, yield 48 %. So the average yield of two runs was 51 %.

2q : yellow oil, TLC *R_f* : 0.31 (PE / EA = 3:1)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 5.58 (d, *J* = 3.1 Hz, 1H), 4.53 (d, *J* = 15.8 Hz, 1H), 4.45 (d, *J* = 15.8 Hz, 1H), 4.38 – 4.29 (m, 1H), 3.77 – 3.61 (m, 2H), 2.06 (s, 3H), 1.87 (s, 3H), 1.86 (s, 3H), 1.76 – 1.71 (m, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 189.0, 169.5, 158.8, 148.2, 147.0, 135.1, 128.7, 117.5, 74.4, 72.7, 41.3, 23.2, 22.0, 21.0, 14.3. HRMS (ESI) m/z calcd. for $C_{15}H_{19}O_4$ $(M+H)^+$: 263.1278, found 263.1273.

6. Discussions of stereochemistry of [4+2+1] cycloadducts

For the standard product **2a**, the X-ray crystal structure shows the H atoms on the fused carbon atoms are *cis*-configuration.



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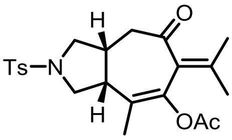


2a CCDC 1874821

Table 1 Crystal data and structure refinement for exp_717.

Identification code	exp_717
Empirical formula	$C_{22}H_{27}NO_5S$
Formula weight	417.50
Temperature/K	179.9(2)
Crystal system	triclinic
Space group	P-1
a/Å	8.6028(3)
b/Å	11.7142(3)
c/Å	12.4375(3)
α/°	107.884(2)
β/°	98.631(2)
γ/°	111.291(3)
Volume/Å^3	1061.95(6)
Z	2
ρ_{calc}g/cm^3	1.306
μ/mm^{-1}	0.185
F(000)	444.0
Crystal size/mm^3	0.15 × 0.1 × 0.1
Radiation	Mo Kα (λ = 0.71073)

2Θ range for data collection/°	7.252 to 52.044
Index ranges	$-10 \leq h \leq 10$, $-14 \leq k \leq 14$, $-15 \leq l \leq 14$
Reflections collected	13450
Independent reflections	4170 [R_{int} = 0.0272, R_{sigma} = 0.0252]
Data/restraints/parameters	4170/0/267
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0373, wR_2 = 0.1016
Final R indexes [all data]	R_1 = 0.0418, wR_2 = 0.1047
Largest diff. peak/hole / e Å^{-3}	0.29/-0.34

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for exp_717. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ}tensor.

Atom	***x***	***y***	***z***	**U(eq)**
C1	8572.6(19)	4627.7(14)	6356.6(13)	30.7(3)
C2	7806.8(19)	3102.1(14)	5918.7(13)	29.8(3)
C3	6069(2)	2369.7(15)	4944.9(13)	33.4(3)
C4	4650.9(19)	2779.9(14)	5218.2(13)	31.5(3)
C5	4412.1(18)	2947.4(14)	6409.7(13)	27.9(3)
C6	4701.2(19)	1991.0(13)	6879.0(12)	27.6(3)
C7	6163.2(19)	1866.7(13)	7151.8(12)	27.9(3)
C8	7856.2(19)	2812.5(13)	7073.7(13)	28.9(3)
C9	8689(2)	4203.6(14)	8089.6(13)	31.1(3)
C10	3973(2)	3891.5(15)	7022.3(15)	35.7(3)
C11	3595(3)	4840.3(19)	6567(2)	51.4(5)
C12	3883(3)	4105(2)	8260.1(18)	55.0(5)
C13	2011.0(19)	77.1(14)	5997.4(14)	31.3(3)
C14	497(2)	-818.2(18)	6248.0(18)	45.8(4)
C15	6262(2)	811.7(15)	7572.5(14)	36.3(4)
C16	9549.0(17)	7344.0(13)	8836.7(13)	26.8(3)
C17	9444(2)	7609.8(16)	9982.6(14)	36.3(3)
C18	8387(2)	8199.0(16)	10356.8(14)	38.5(4)
C19	7406.2(19)	8509.7(14)	9602.5(14)	31.8(3)
C20	7483(2)	8198.1(15)	8446.6(14)	33.7(3)
C21	8550(2)	7619.3(14)	8055.5(13)	30.4(3)
C22	6268(2)	9166.7(18)	10019.4(17)	46.1(4)
N1	9710.6(15)	5050.4(11)	7546.5(11)	29.7(3)
O1	3764.6(16)	2962.6(14)	4490.5(11)	48.5(3)
O2	3159.2(13)	1104.2(10)	7010.7(9)	32.4(2)

O3	2248.1(15)	-72.4(11)	5046.3(10)	39.3(3)
O4	11695.0(14)	7202.5(11)	7595.2(11)	42.3(3)
O5	12025.6(14)	6686.5(11)	9387.3(11)	43.6(3)
S1	10934.8(4)	6630.1(3)	8361.9(3)	31.38(12)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for exp_717. The Anisotropic displacement factor exponent takes the form: -2π^2[h^{2}a*^{2}U$_{11}$+2hka*b*U$_{12}$+⋯].

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
C1	29.9(7)	28.7(7)	32.1(8)	11.7(6)	10.9(6)	10.7(6)
C2	29.3(7)	26.9(7)	31.6(7)	7.3(6)	12.0(6)	12.8(6)
C3	35.6(8)	31.1(7)	25.6(7)	7.6(6)	9.6(6)	8.8(6)
C4	26.8(7)	30.4(7)	30.4(8)	13.9(6)	4.4(6)	5.1(6)
C5	24.0(7)	28.8(7)	31.5(7)	14.8(6)	7.7(6)	9.8(6)
C6	31.4(7)	23.9(7)	25.4(7)	10.6(6)	9.8(6)	8.8(6)
C7	33.4(7)	21.0(6)	23.6(7)	6.2(5)	3.8(6)	9.8(6)
C8	28.4(7)	23.0(7)	33.6(8)	8.7(6)	5.5(6)	12.8(6)
C9	32.0(8)	23.7(7)	30.8(7)	8.8(6)	2.8(6)	9.2(6)
C10	32.7(8)	33.9(8)	48.1(9)	20.9(7)	18.2(7)	15.9(7)
C11	52.3(11)	46.3(10)	78.4(14)	36.1(10)	29.8(10)	31.6(9)
C12	75.9(14)	51.3(11)	56.9(12)	23.9(9)	39.3(11)	38(1)
C13	31.0(7)	26.3(7)	41.5(9)	17.7(6)	9.6(6)	14.1(6)
C14	35.7(9)	43.6(9)	61.8(11)	30.4(9)	16.3(8)	12.2(7)
C15	41.5(9)	28.1(7)	34.8(8)	12.7(6)	2.8(7)	13.4(7)
C16	22.8(7)	20.7(6)	33.7(7)	8.6(6)	5.7(6)	8.8(5)
C17	40.2(9)	37.6(8)	31.4(8)	13.3(7)	3.3(7)	20.2(7)
C18	47.7(9)	41.1(9)	29.9(8)	13.0(7)	14.8(7)	22.1(7)
C19	31.5(7)	26.1(7)	38.7(8)	11.8(6)	13.8(6)	13.0(6)
C20	37.5(8)	34.4(8)	38.9(8)	18.9(7)	11.8(7)	21.9(7)
C21	36.9(8)	29.8(7)	31.2(7)	15.4(6)	14.0(6)	17.2(6)
C22	45.2(10)	45.0(9)	54.6(11)	15.2(8)	23.5(8)	26.8(8)
N1	25.3(6)	23.0(6)	36.0(7)	8.1(5)	5.7(5)	9.6(5)
O1	40.0(6)	67.2(8)	43.5(7)	34.5(6)	8.3(5)	19.6(6)
O2	33.5(5)	32.3(5)	31.5(5)	16.4(4)	12.4(4)	10.2(4)
O3	42.6(6)	31.9(6)	34.9(6)	9.6(5)	11.3(5)	10.2(5)
O4	32.6(6)	29.9(5)	63.7(8)	15.2(5)	23.7(6)	11.8(5)
O5	28.3(6)	31.3(6)	55.6(7)	4.5(5)	-6.1(5)	13.9(5)
S1	21.22(19)	21.90(19)	44.1(2)	6.92(16)	5.62(15)	8.61(14)

Table 4 Bond Lengths for exp_717.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**

C1	C2	1.5375(19)	C10	C12	1.501(2)
C1	N1	1.4687(19)	C13	C14	1.491(2)
C2	C3	1.525(2)	C13	O2	1.3578(19)
C2	C8	1.572(2)	C13	O3	1.2011(19)
C3	C4	1.511(2)	C16	C17	1.387(2)
C4	C5	1.490(2)	C16	C21	1.389(2)
C4	O1	1.2152(19)	C16	S1	1.7610(14)
C5	C6	1.4893(19)	C17	C18	1.380(2)
C5	C10	1.349(2)	C18	C19	1.386(2)
C6	C7	1.324(2)	C19	C20	1.389(2)
C6	O2	1.4264(17)	C19	C22	1.508(2)
C7	C8	1.515(2)	C20	C21	1.387(2)
C7	C15	1.506(2)	N1	S1	1.6351(12)
C8	C9	1.5432(19)	O4	S1	1.4311(12)
C9	N1	1.4730(19)	O5	S1	1.4338(12)
C10	C11	1.502(2)			

Table 5 Bond Angles for exp_717.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	C1	C2	101.77(12)	O2	C13	C14	110.82(14)
C1	C2	C8	104.85(11)	O3	C13	C14	126.31(15)
C3	C2	C1	113.97(13)	O3	C13	O2	122.85(13)
C3	C2	C8	117.33(12)	C17	C16	C21	120.47(13)
C4	C3	C2	115.82(12)	C17	C16	S1	119.77(11)
C5	C4	C3	116.77(12)	C21	C16	S1	119.75(11)
O1	C4	C3	120.69(14)	C18	C17	C16	119.42(14)
O1	C4	C5	122.54(14)	C17	C18	C19	121.21(14)
C6	C5	C4	114.79(12)	C18	C19	C20	118.65(13)
C10	C5	C4	122.91(13)	C18	C19	C22	121.01(14)
C10	C5	C6	122.30(13)	C20	C19	C22	120.34(14)
C7	C6	C5	128.17(13)	C21	C20	C19	121.09(14)
C7	C6	O2	118.63(12)	C20	C21	C16	119.10(14)
O2	C6	C5	113.18(12)	C1	N1	C9	106.17(11)
C6	C7	C8	121.00(13)	C1	N1	S1	120.61(10)
C6	C7	C15	122.87(13)	C9	N1	S1	118.64(10)
C15	C7	C8	116.12(13)	C13	O2	C6	115.49(11)
C7	C8	C2	117.60(12)	N1	S1	C16	107.46(6)
C7	C8	C9	113.40(12)	O4	S1	C16	108.40(7)
C9	C8	C2	104.46(11)	O4	S1	N1	106.15(7)
N1	C9	C8	102.02(11)	O4	S1	O5	120.35(7)

C5	C10	C11	124.30(15)	O5	S1	C16	107.54(7)
C5	C10	C12	121.56(15)	O5	S1	N1	106.31(7)
C12	C10	C11	114.11(15)				

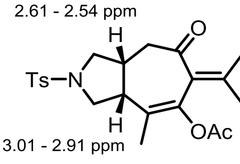
Table 6 Torsion Angles for exp_717.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C2	C3	C4	-53.87(17)	C9	N1	S1	C16	-61.58(12)
C1	C2	C8	C7	125.49(13)	C9	N1	S1	O4	-177.41(10)
C1	C2	C8	C9	-1.22(15)	C9	N1	S1	O5	53.34(12)
C1	N1	S1	C16	72.20(12)	C10	C5	C6	C7	-115.93(18)
C1	N1	S1	O4	-43.63(12)	C10	C5	C6	O2	65.47(18)
C1	N1	S1	O5	-172.89(11)	C14	C13	O2	C6	177.24(12)
C2	C1	N1	C9	-45.04(13)	C15	C7	C8	C2	133.59(13)
C2	C1	N1	S1	176.25(9)	C15	C7	C8	C9	-104.18(14)
C2	C3	C4	C5	-44.58(18)	C16	C17	C18	C19	1.1(2)
C2	C3	C4	O1	135.26(15)	C17	C16	C21	C20	1.8(2)
C2	C8	C9	N1	-24.86(14)	C17	C16	S1	N1	102.67(13)
C3	C2	C8	C7	-2.10(18)	C17	C16	S1	O4	-143.00(12)
C3	C2	C8	C9	-128.81(13)	C17	C16	S1	O5	-11.42(14)
C3	C4	C5	C6	-35.63(17)	C17	C18	C19	C20	1.0(2)
C3	C4	C5	C10	144.22(15)	C17	C18	C19	C22	-179.34(15)
C4	C5	C6	C7	63.91(19)	C18	C19	C20	C21	-1.7(2)
C4	C5	C6	O2	-114.69(13)	C19	C20	C21	C16	0.3(2)
C4	C5	C10	C11	2.8(2)	C21	C16	C17	C18	-2.5(2)
C4	C5	C10	C12	-175.01(15)	C21	C16	S1	N1	-76.42(13)
C5	C6	C7	C8	3.8(2)	C21	C16	S1	O4	37.91(13)
C5	C6	C7	C15	-177.28(14)	C21	C16	S1	O5	169.49(11)
C5	C6	O2	C13	77.84(15)	C22	C19	C20	C21	178.63(15)
C6	C5	C10	C11	-177.34(15)	N1	C1	C2	C3	156.52(12)
C6	C5	C10	C12	4.8(2)	N1	C1	C2	C8	26.90(14)
C6	C7	C8	C2	-47.41(18)	O1	C4	C5	C6	144.54(15)
C6	C7	C8	C9	74.83(17)	O1	C4	C5	C10	-35.6(2)
C7	C6	O2	C13	-100.90(15)	O2	C6	C7	C8	-177.69(11)
C7	C8	C9	N1	-154.13(12)	O2	C6	C7	C15	1.3(2)
C8	C2	C3	C4	69.19(17)	O3	C13	O2	C6	-1.3(2)
C8	C9	N1	C1	44.29(13)	S1	C16	C17	C18	178.44(12)
C8	C9	N1	S1	-176.02(9)	S1	C16	C21	C20	-179.14(11)

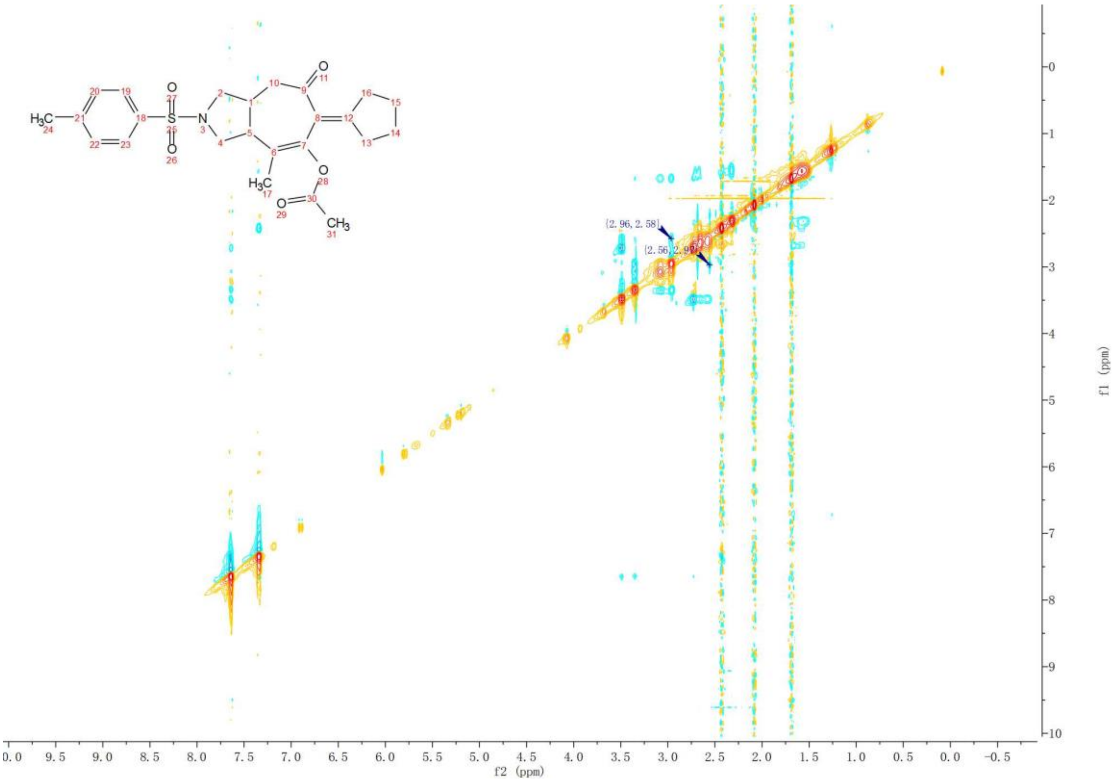
Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for exp_717.

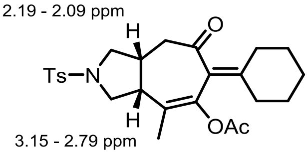
Atom	***x***	***y***	***z***	**U(eq)**
H1A	9234	4950	5860	37
H1B	7665	4932	6386	37
H2	8640	2840	5577	36
H3A	6277	2503	4238	40
H3B	5642	1424	4766	40
H8	8684	2425	7138	35
H9A	7805	4469	8323	37
H9B	9434	4230	8773	37
H11A	4149	4927	5963	77
H11B	4038	5696	7204	77
H11C	2357	4505	6244	77
H12A	4248	3526	8518	82
H12B	2705	3912	8277	82
H12C	4638	5015	8776	82
H14A	-325	-1512	5518	69
H14B	-58	-313	6648	69
H14C	899	-1206	6740	69
H15A	6900	1219	8397	54
H15B	6847	368	7131	54
H15C	5103	176	7457	54
H17	10080	7393	10495	44
H18	8332	8391	11129	46
H20	6807	8380	7926	40
H21	8597	7418	7281	36
H22A	5436	8617	10296	69
H22B	5662	9281	9376	69
H22C	6982	10021	10651	69

For products **2c** and **2d**, the NOESY shows the 2 H atoms on the fused carbon atoms are *cis*-configuration. The reason why we wanted to characterize **2c** and **2d** in NOESY is about the considerations that the large cyclic substitution groups can whether effect the fused ring's configuration.

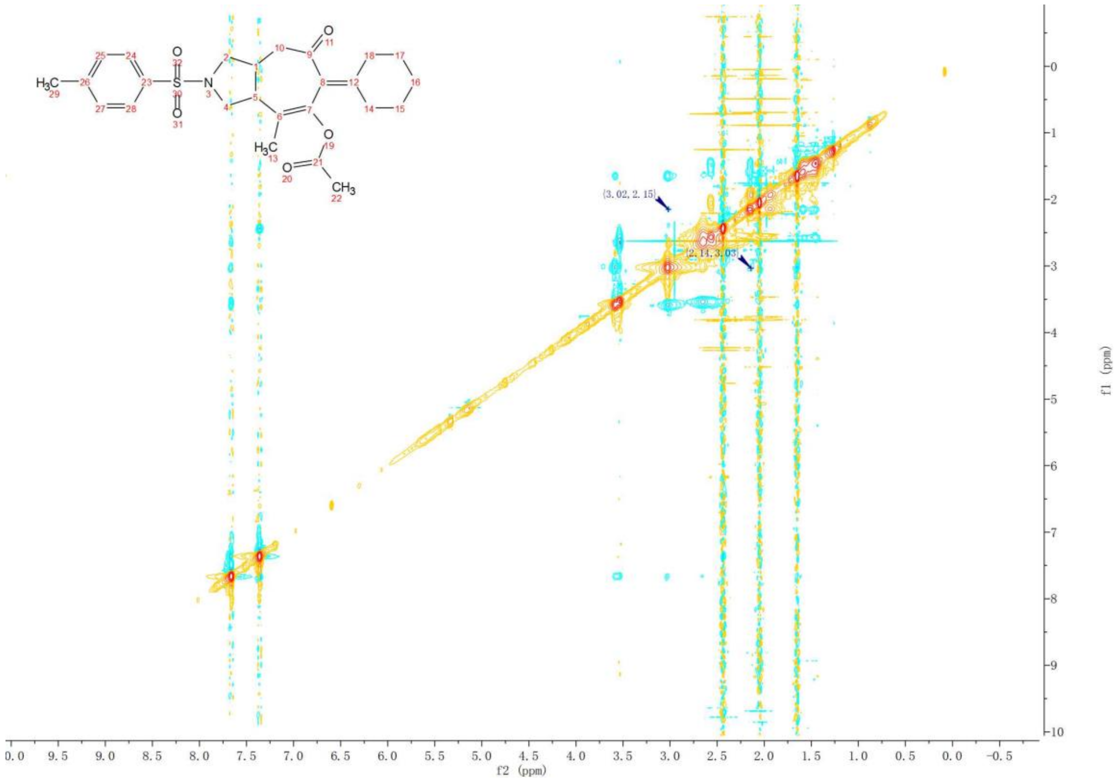


2c

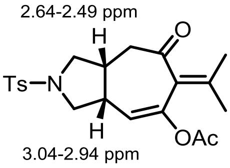



2.19 - 2.09 ppm
H
O
Ts
N
H
3.15 - 2.79 ppm
OAc

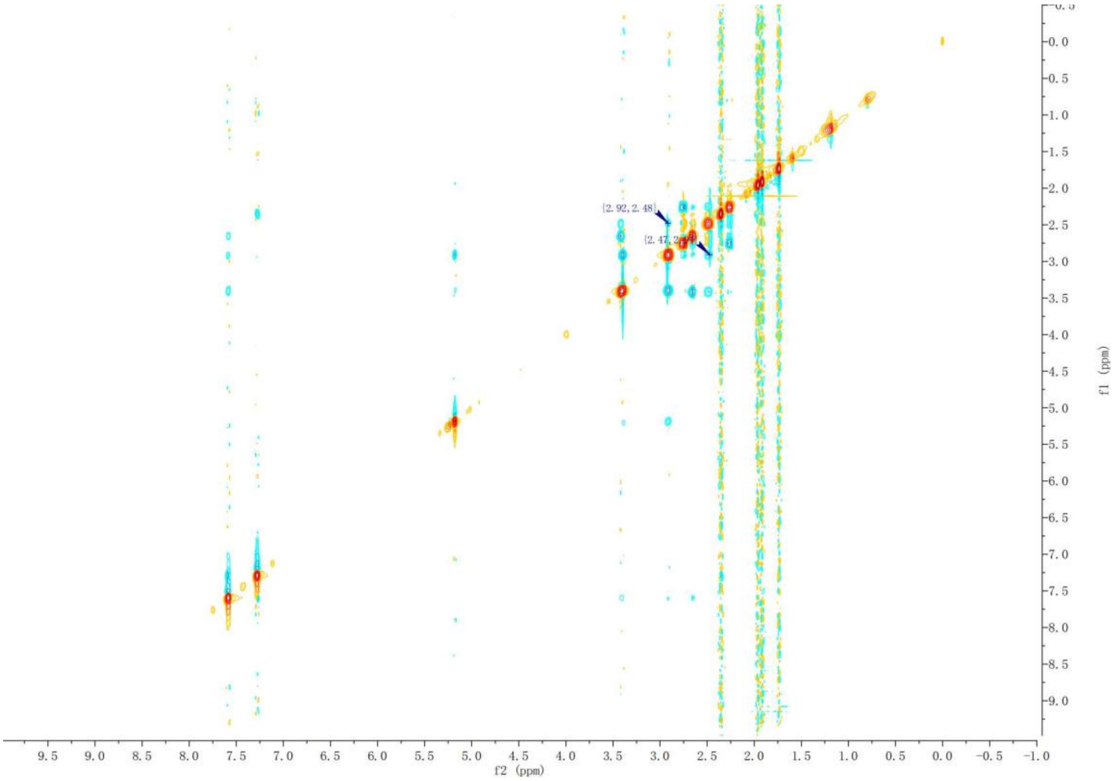
2d


H3C
O
S
O
N
O
H3C
O
CH3
(3.02, 2.15)
(2.14, 3.03)
f2 (ppm)
f1 (ppm)
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
0
1
2
3
4
5
6
7
8
9
10

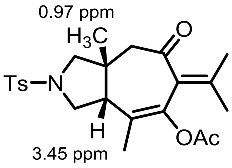
For products **2f**, the NOESY shows the two H atoms on the fused carbon atoms are *cis*-configuration.



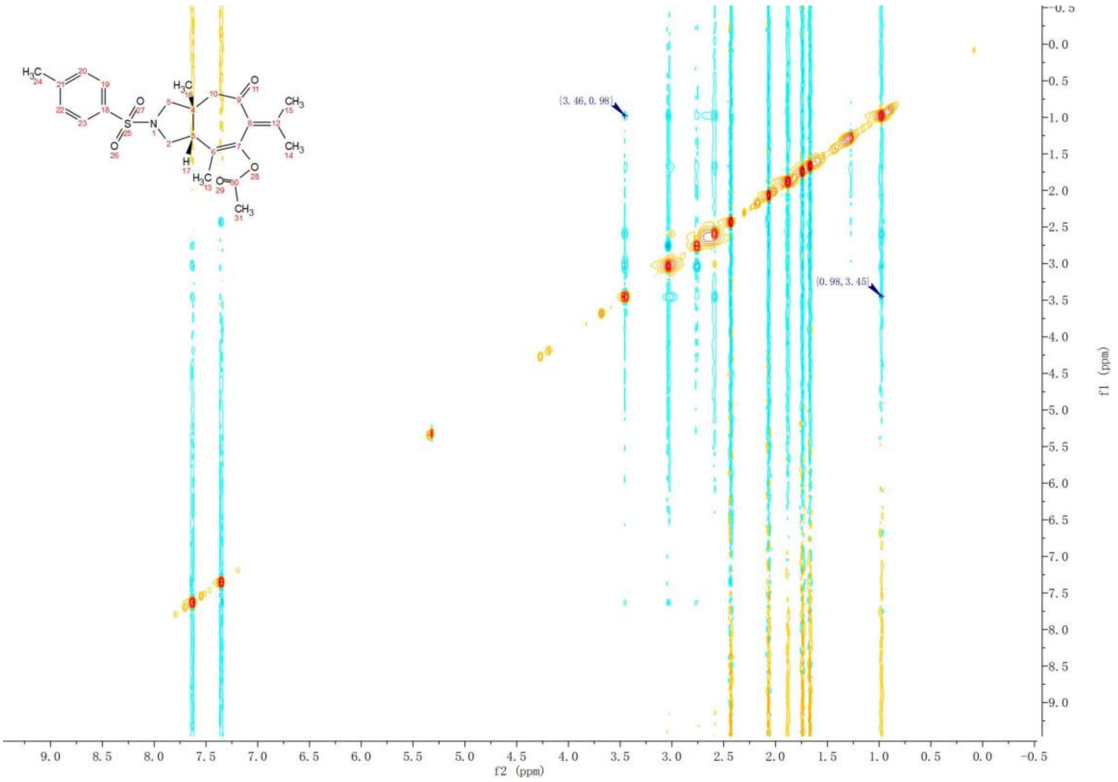
2f

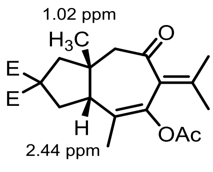


For products **2h** and **2j**, the NOESY shows the methyl and H atom on the fused carbon atoms are *cis*-configuration.

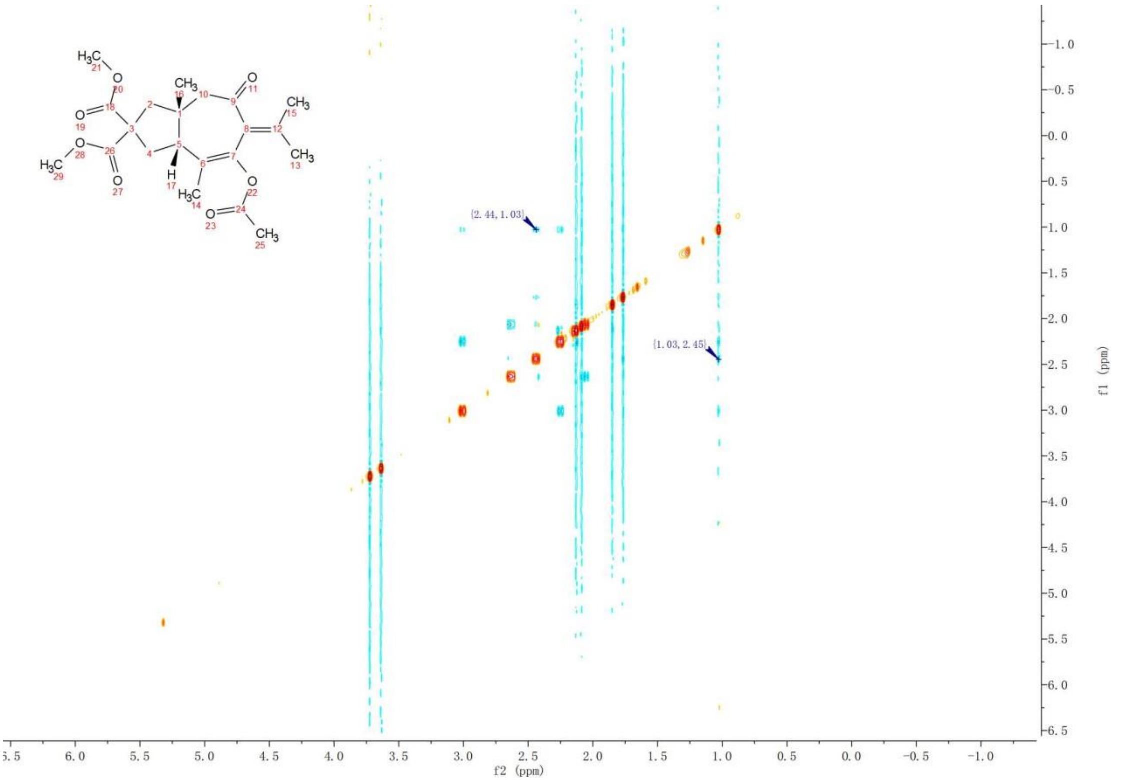


2h

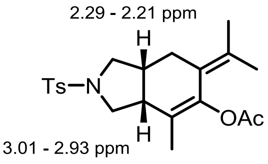



1.02 ppm
H$_3$C
O
E
E
H
OAc
2.44 ppm

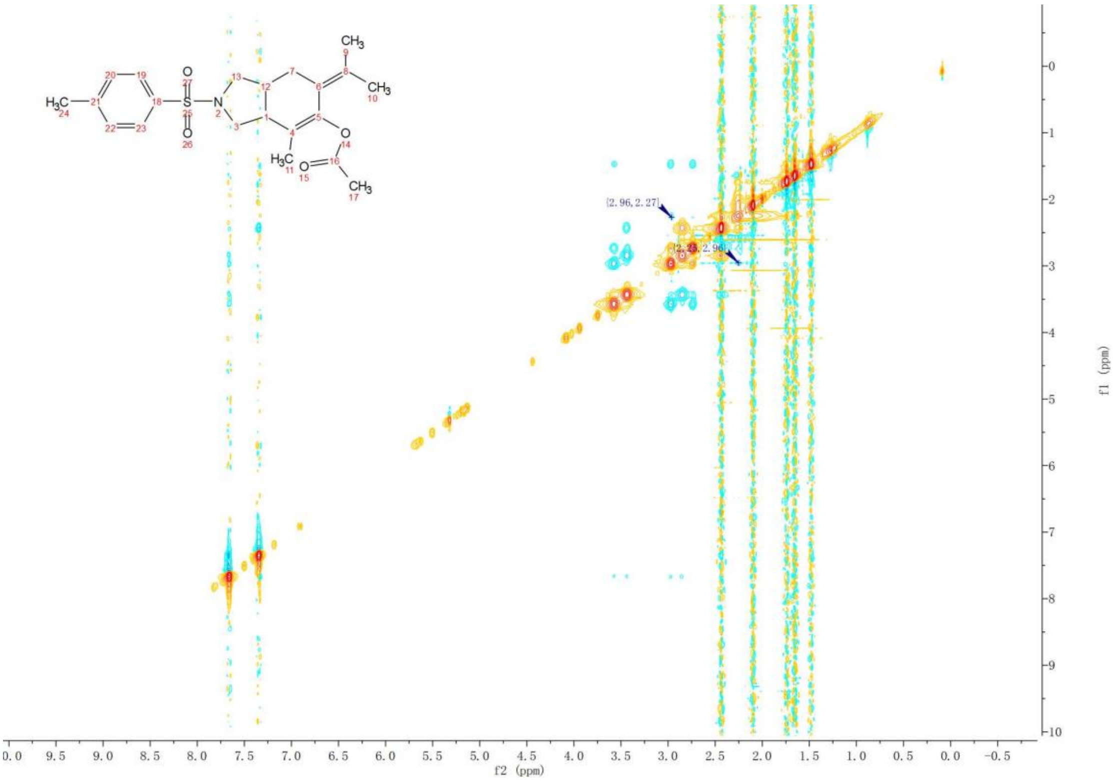
E = CO$_2$Me **2j**


[2.44, 1.03]
[1.03, 2.45]
f2 (ppm)
f1 (ppm)
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

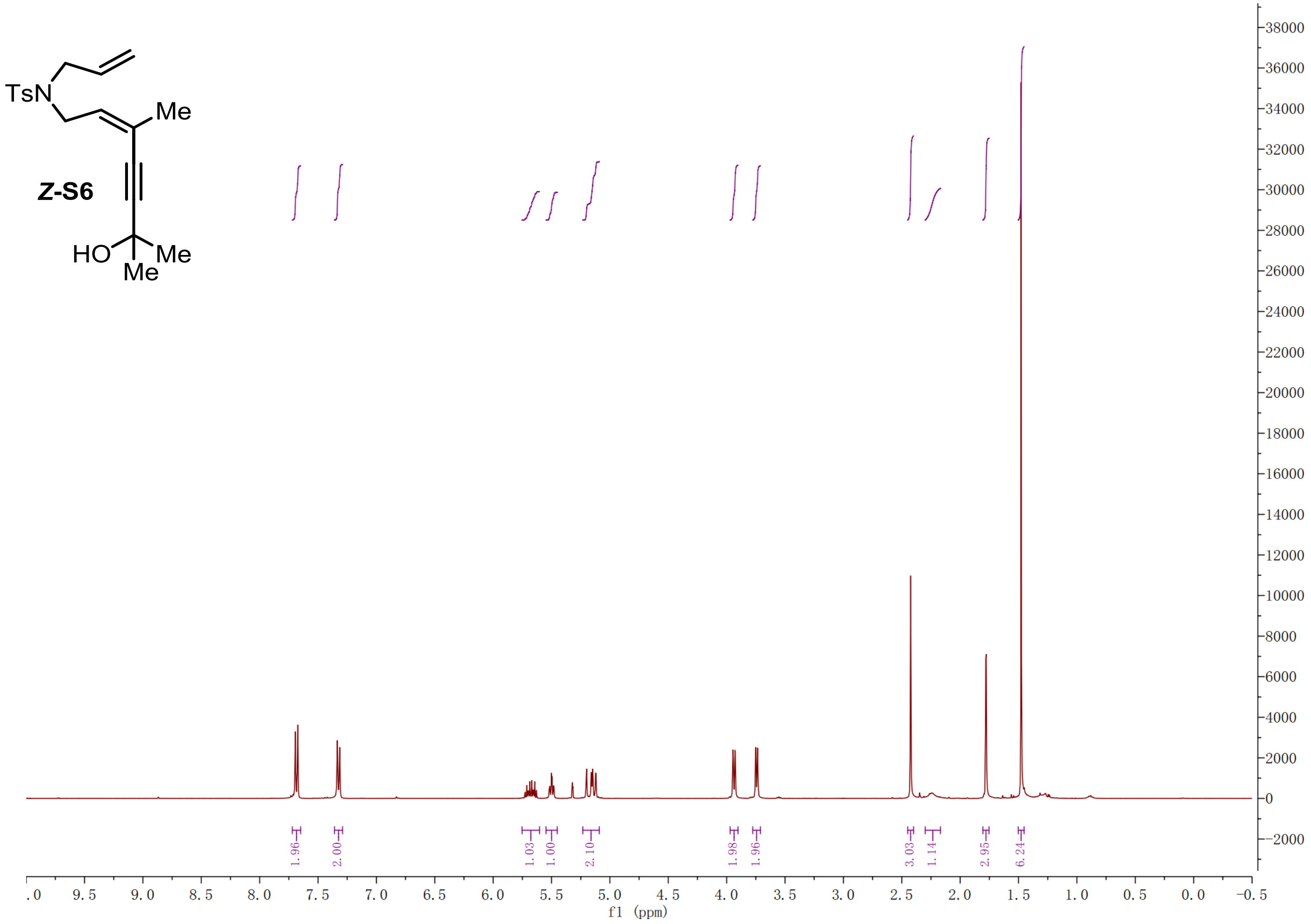
For products **4a**, the NOESY shows the 2H atoms on the fused carbon atoms are *cis*-configuration.

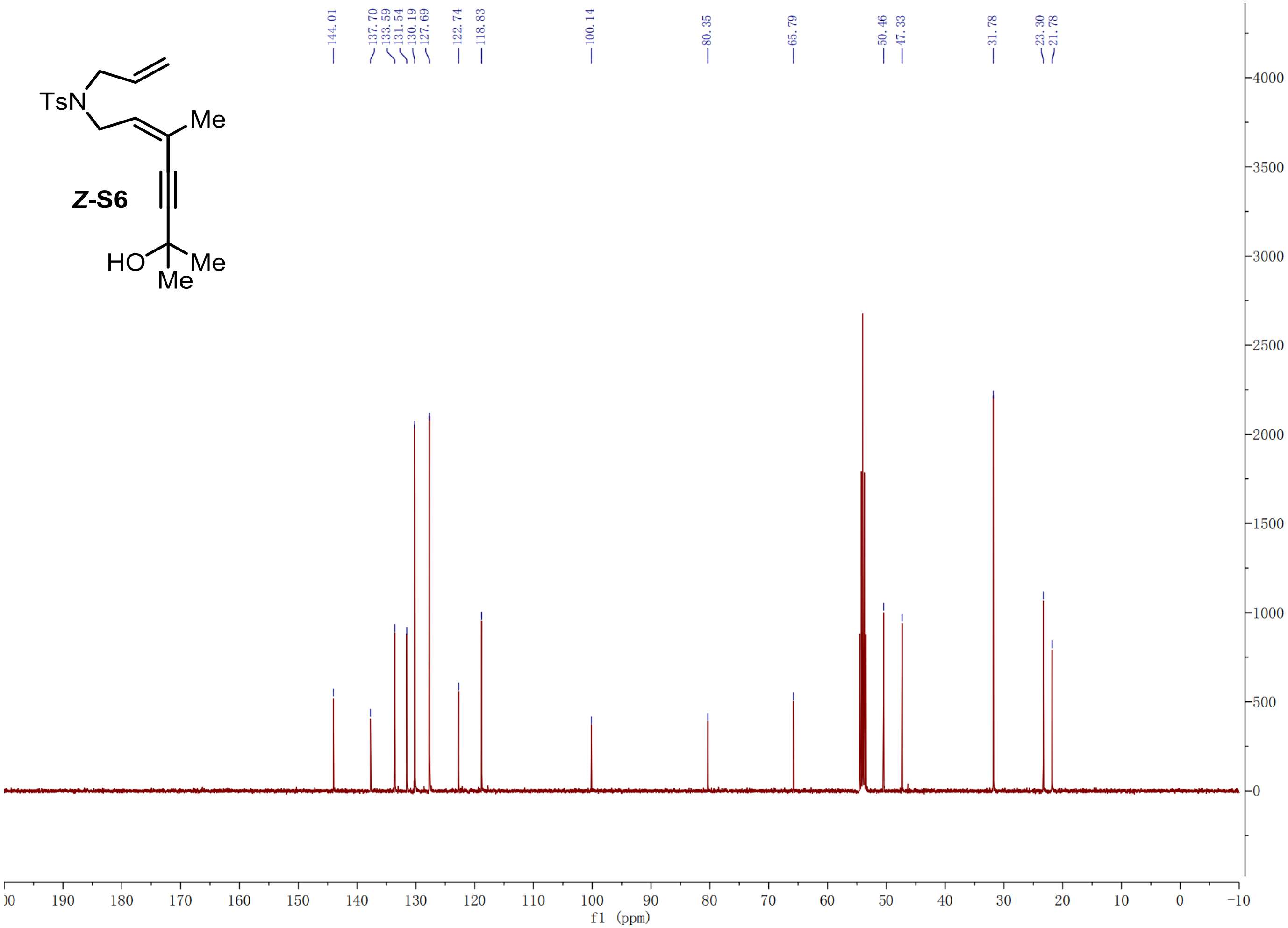


4a



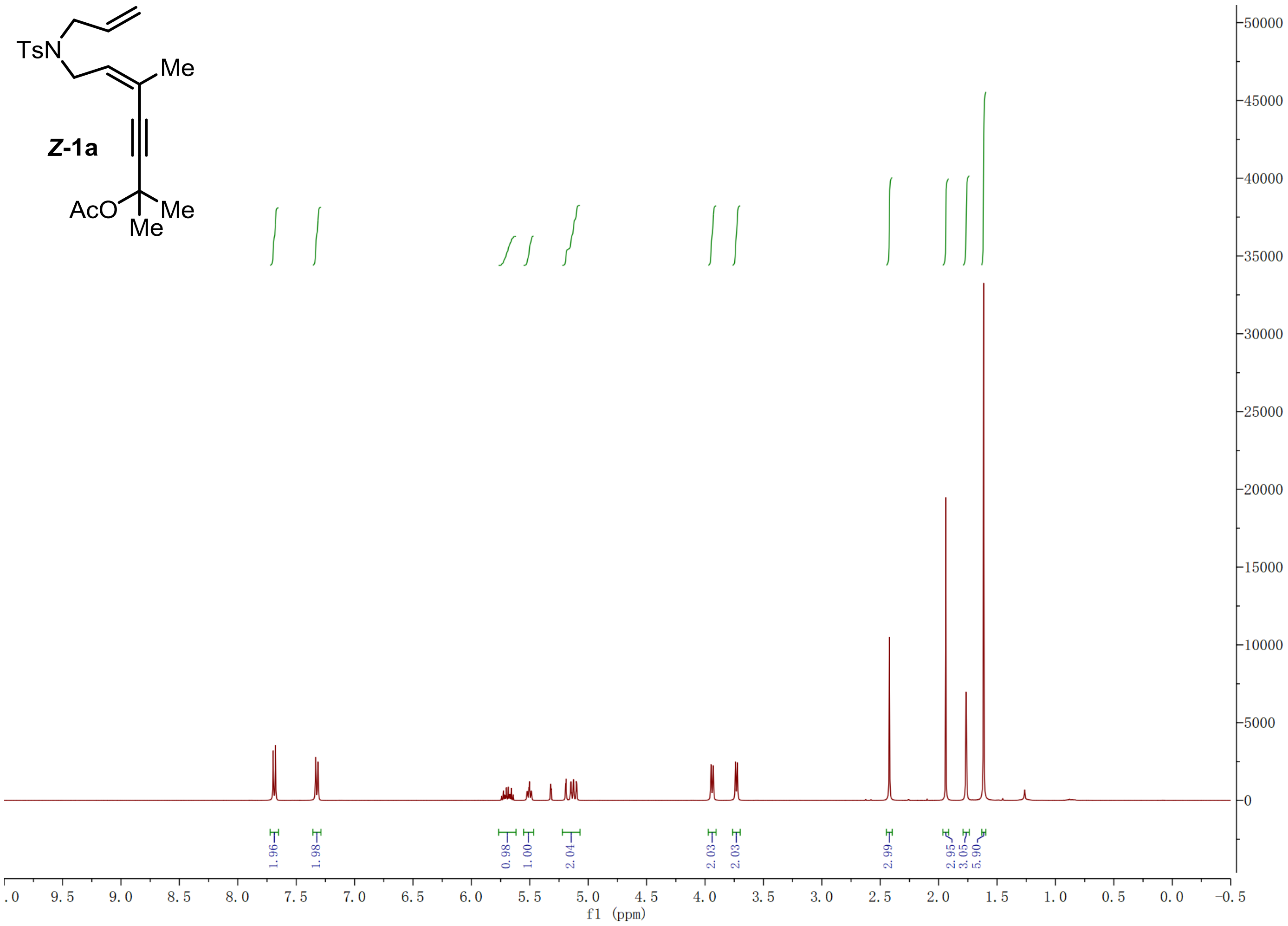
7. NMR spectra of new compounds

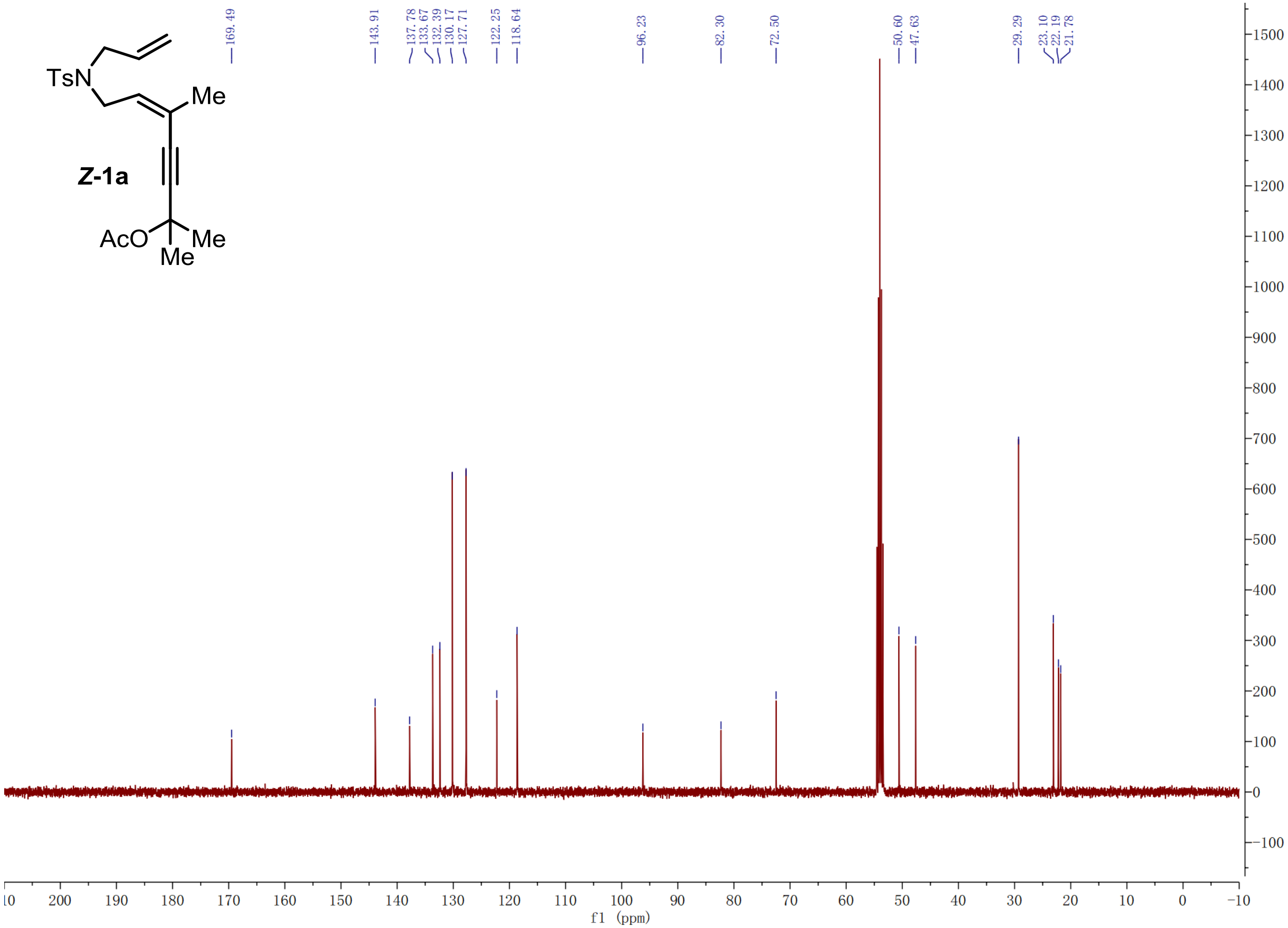


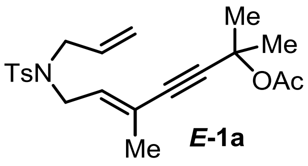


Z-S6

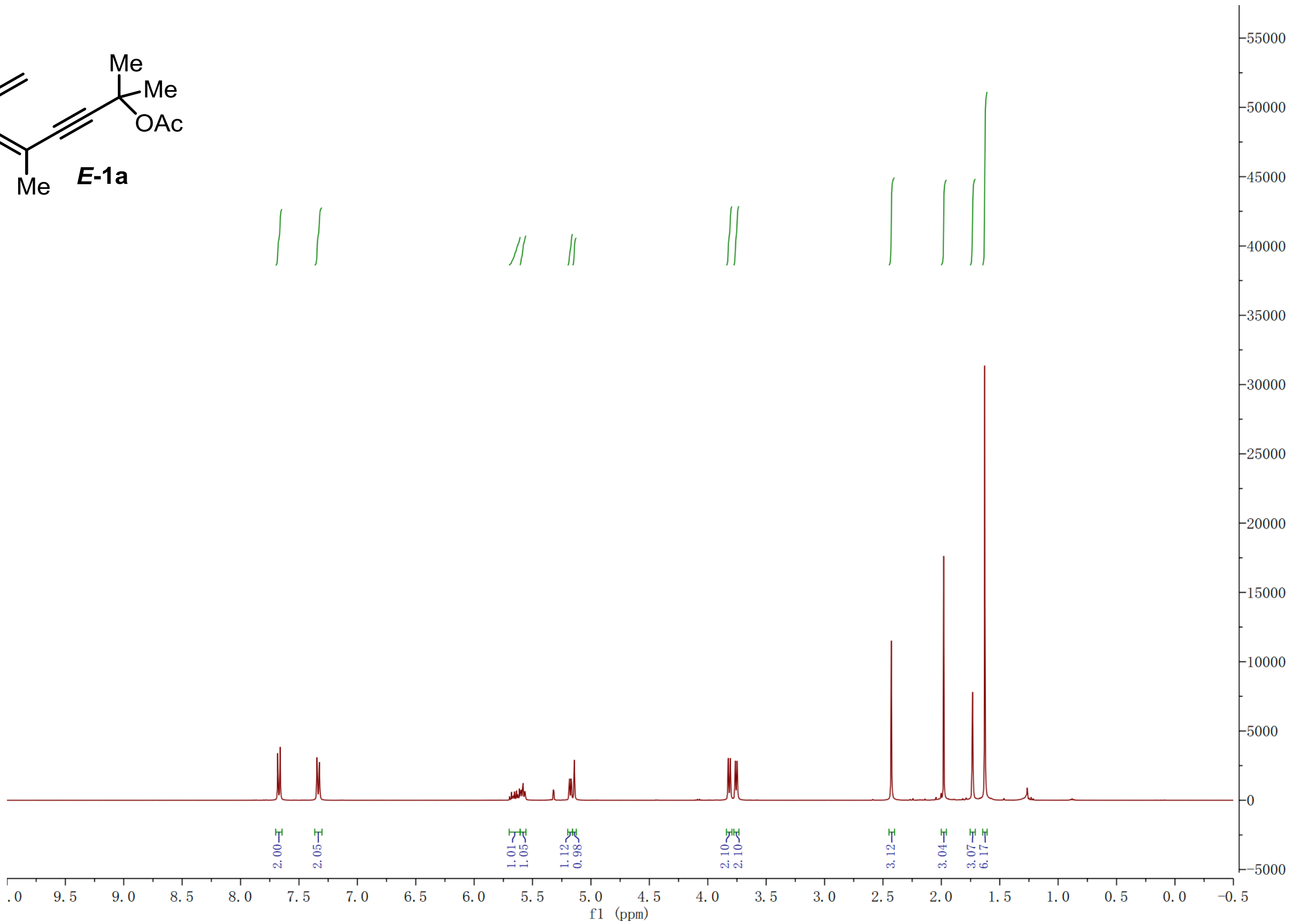
TsN
Me
HO
Me
Me
144.01
137.70
133.59
131.54
130.19
127.69
122.74
118.83
100.14
80.35
65.79
50.46
47.33
31.78
23.30
21.78
4000
3500
3000
2500
2000
1500
1000
500
0
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

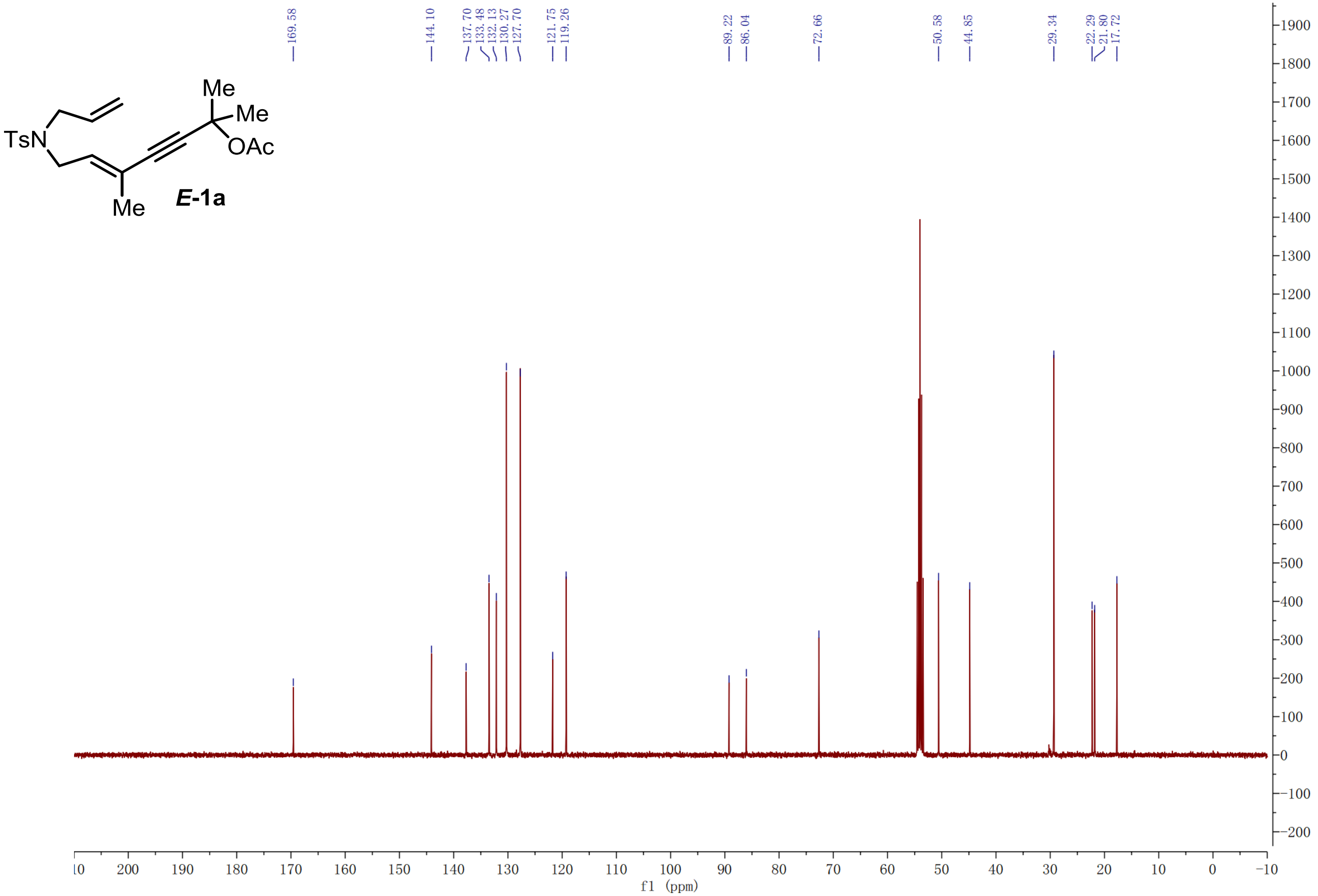

TsN
Me
Z-1a
AcO
Me
Me
1.96
1.98
0.98
1.00
2.04
2.03
2.03
2.99
2.95
3.05
5.90
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0

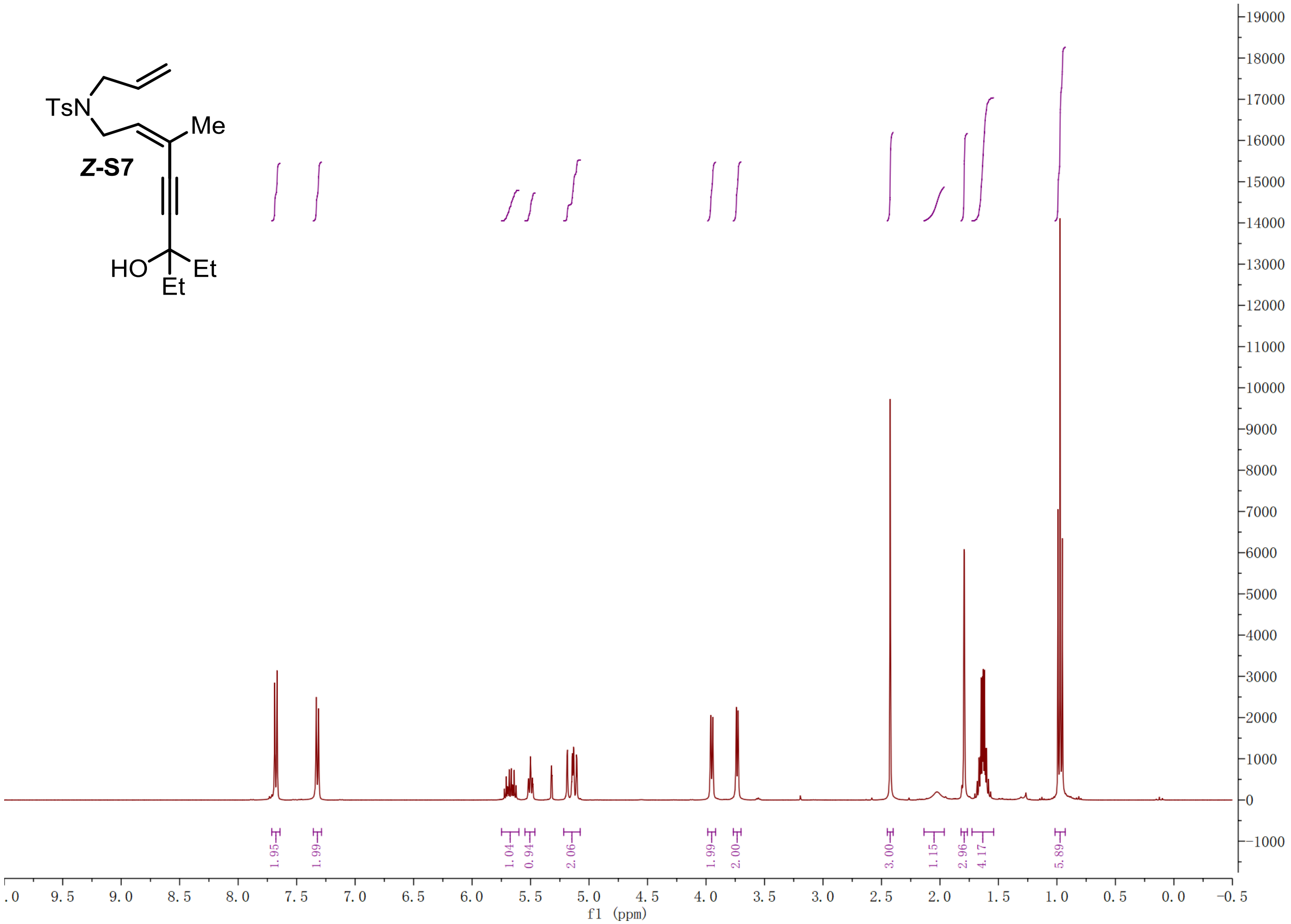

Z-1a
TsN
Me
AcO
Me
Me
169.49
143.91
137.78
133.67
132.39
130.17
127.71
122.25
118.64
96.23
82.30
72.50
50.60
47.63
29.29
23.10
22.19
21.78
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

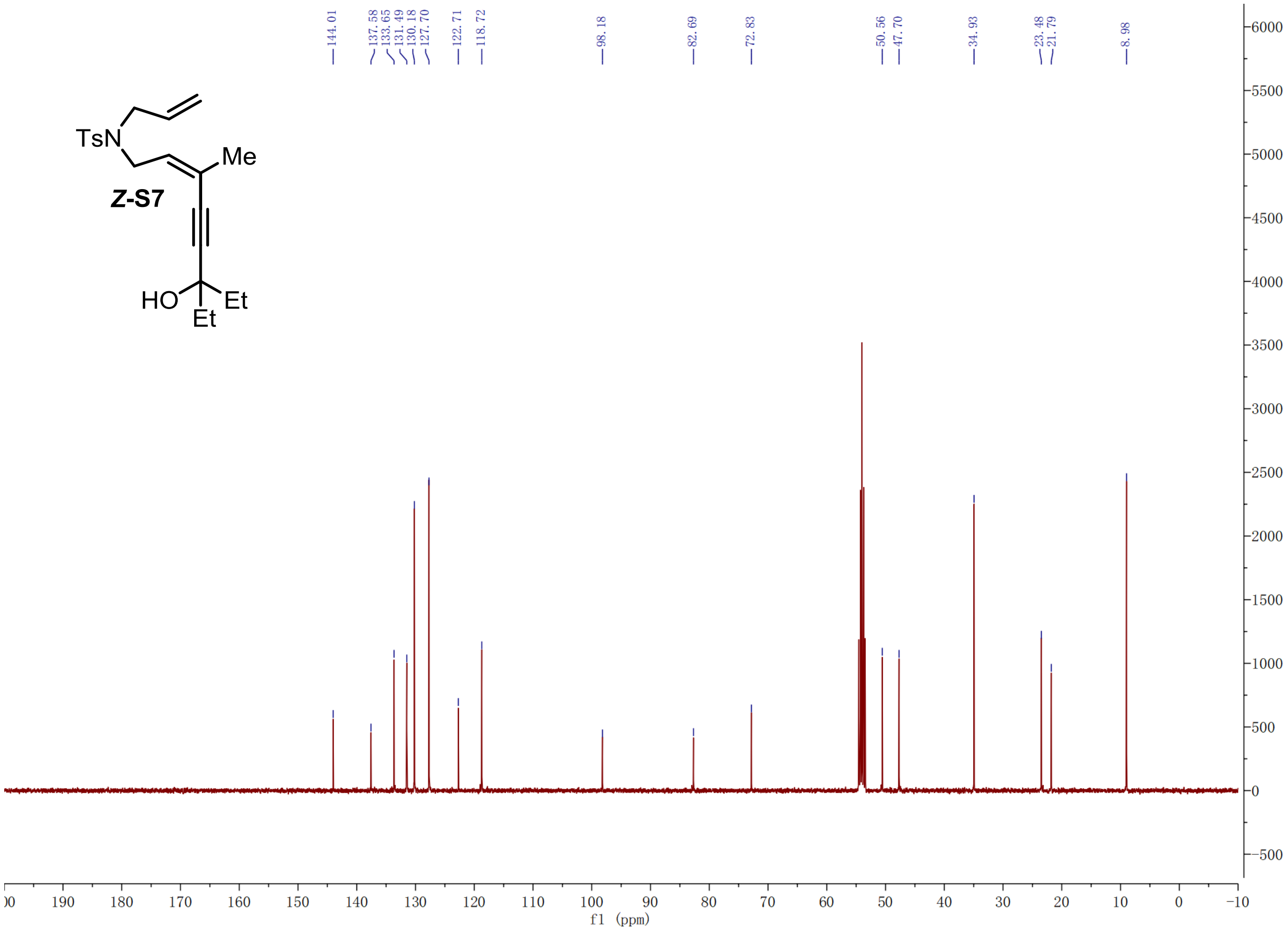

TsN
Me
Me
OAc
Me

***E*-1a**

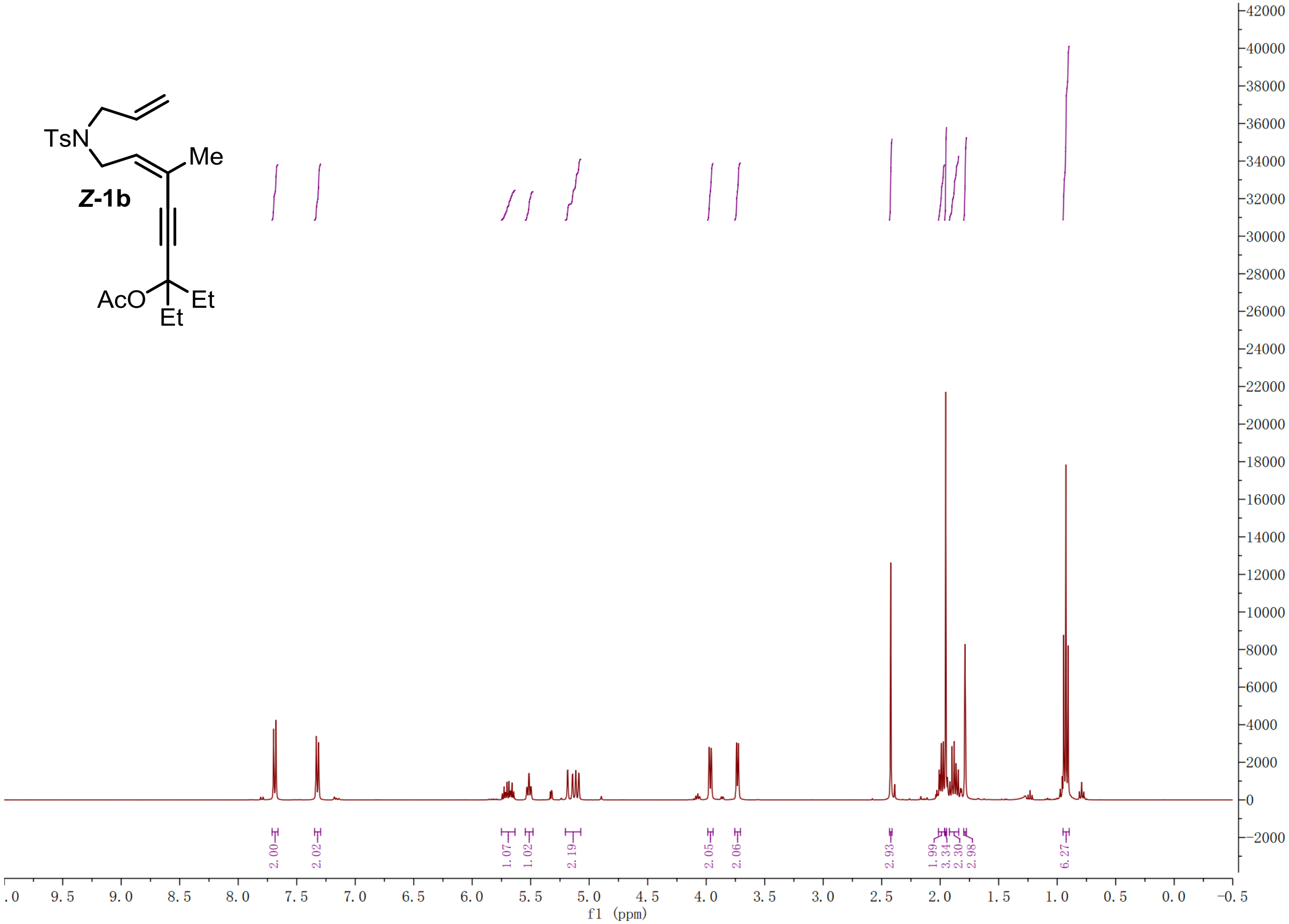

55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
−5000
2.00
2.05
1.01
1.05
1.12
0.98
2.10
2.10
3.12
3.04
3.07
6.17
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

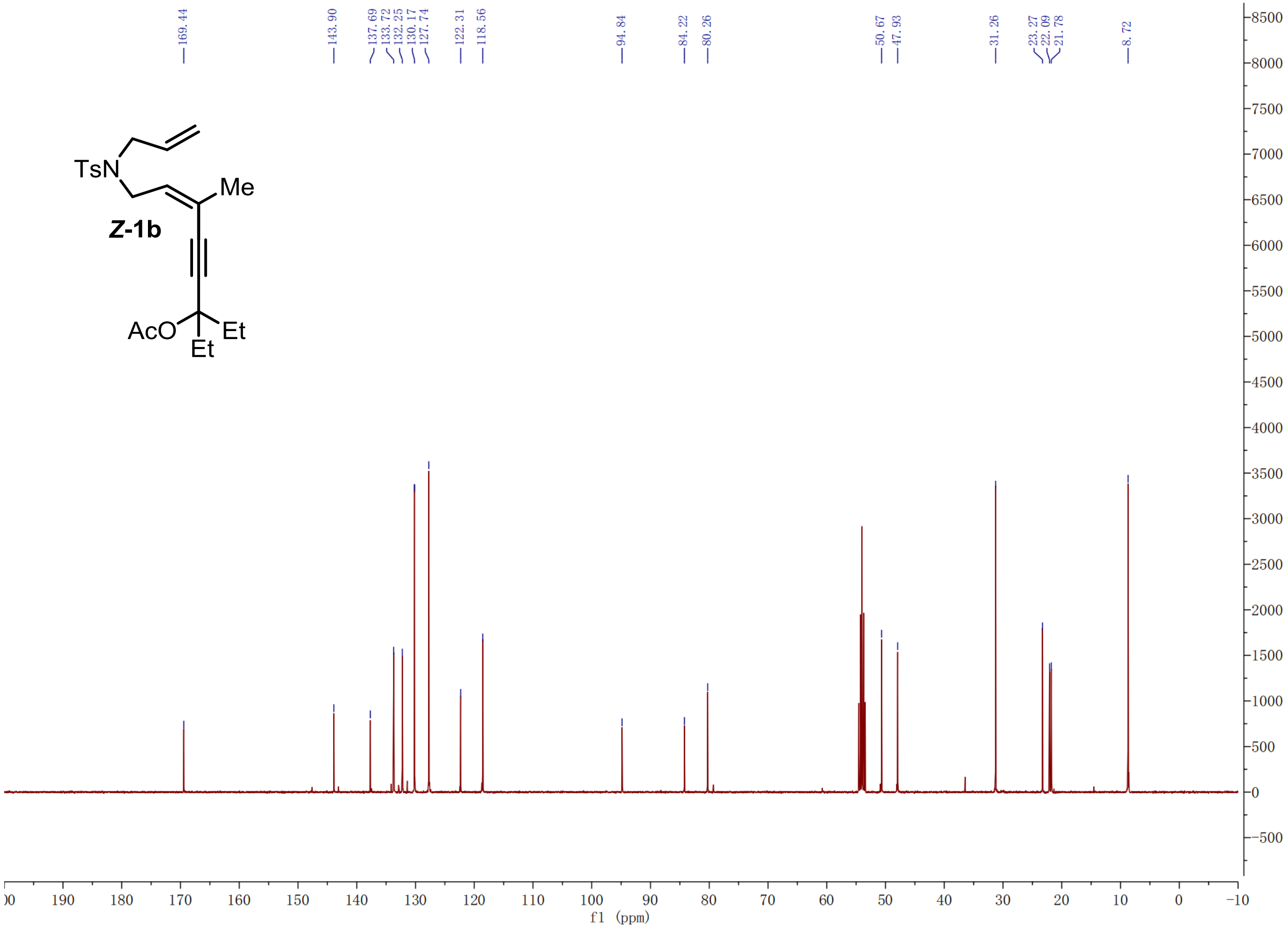
169.58
144.10
137.70
133.48
132.13
130.27
127.70
121.75
119.26
89.22
86.04
72.66
50.58
44.85
29.34
22.29
21.80
17.72
TsN
Me
Me
OAc
Me
E-1a
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
−200
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


TsN
Me
Z-S7
HO
Et
Et
1.95
1.99
1.04
0.94
2.06
1.99
2.00
3.00
1.15
2.96
4.17
5.89
.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

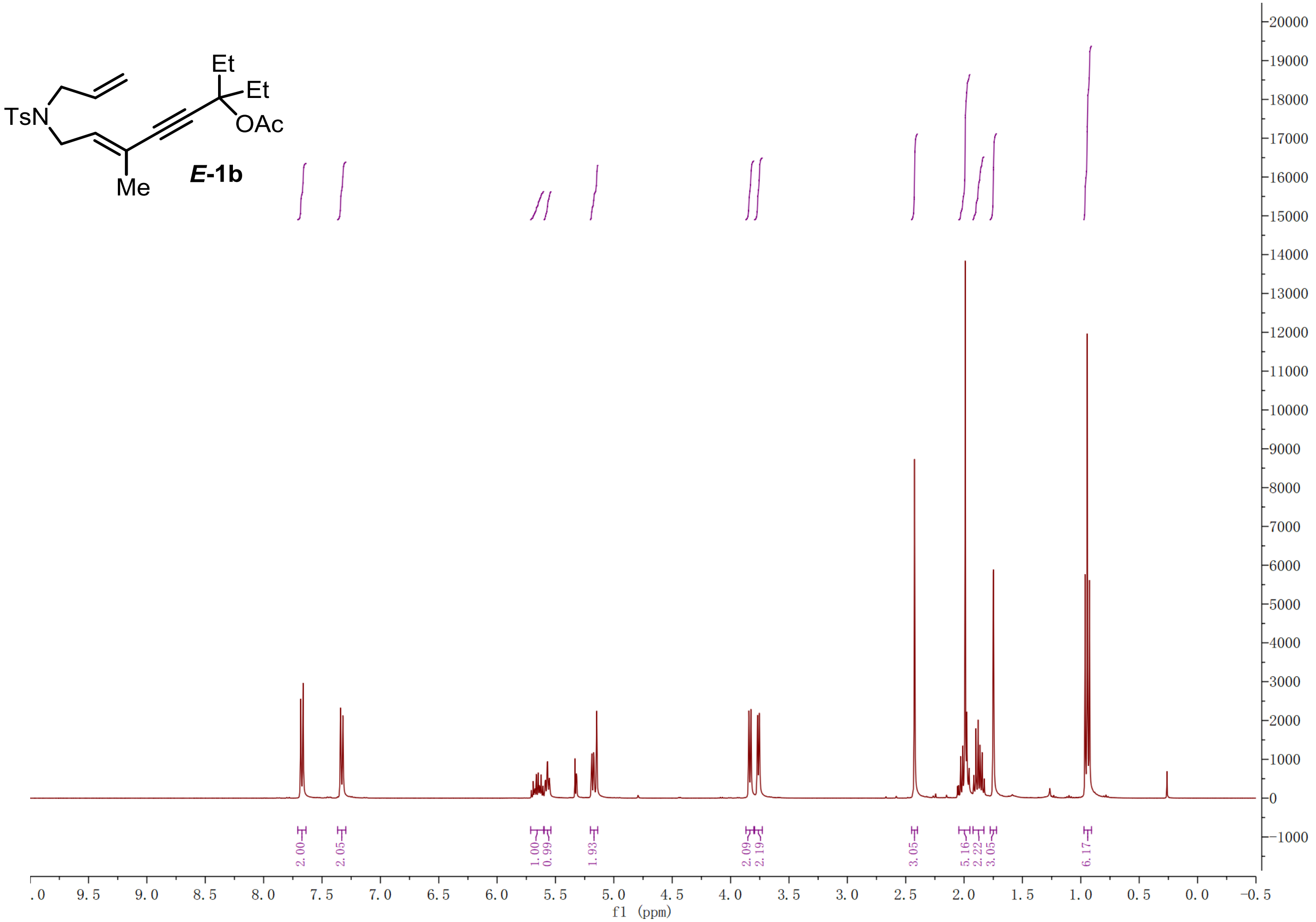

Z-S7

TsN
Me
HO
Et
Et
144.01
137.58
133.65
131.49
130.18
127.70
122.71
118.72
98.18
82.69
72.83
50.56
47.70
34.93
23.48
21.79
8.98
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


TsN
Me
Z-1b
AcO
Et
Et
42000
40000
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
2.00
2.02
1.07
1.02
2.19
2.05
2.06
2.93
1.99
3.34
2.30
2.98
6.27
.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)

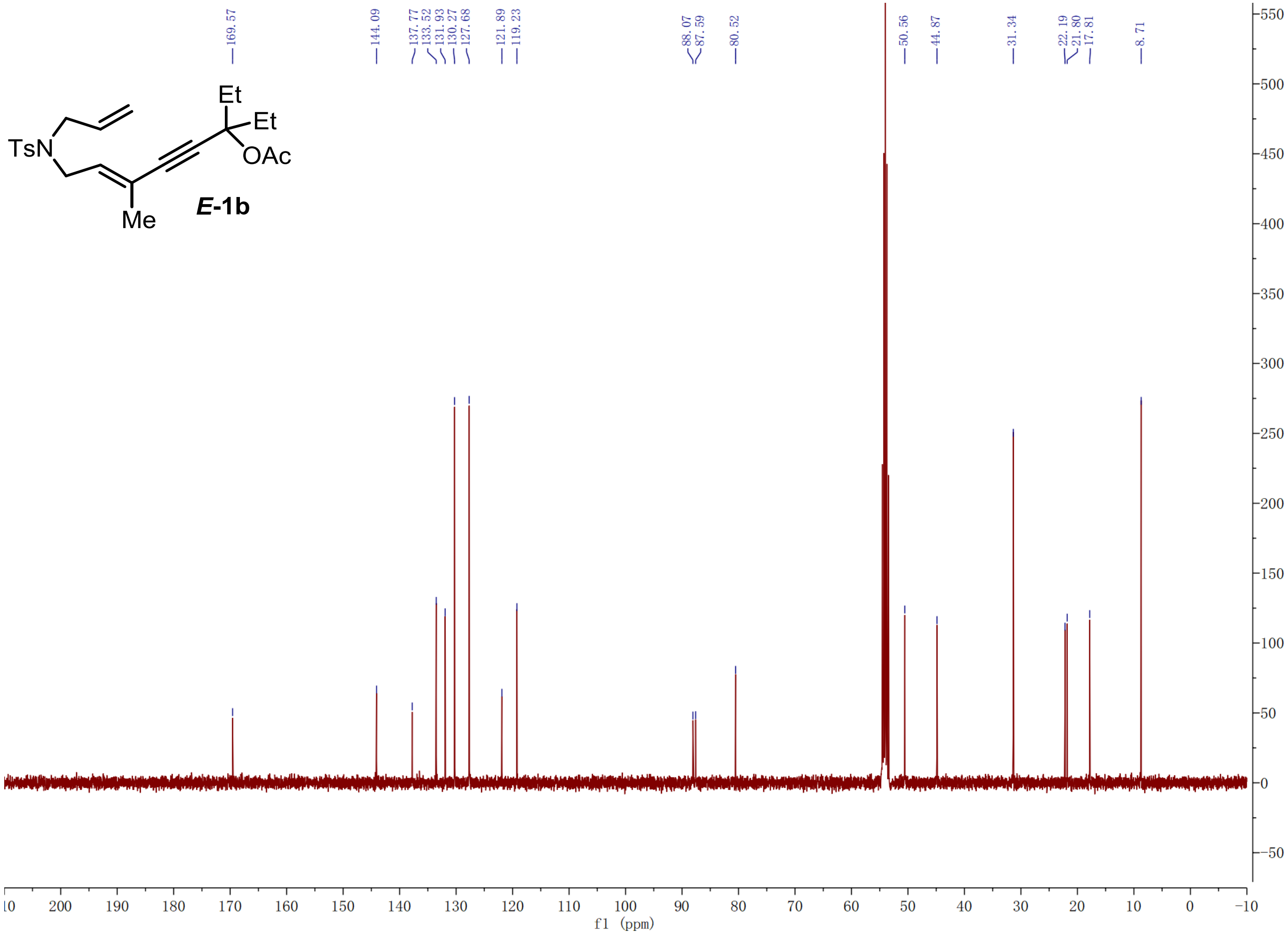

169.44
143.90
137.69
133.72
132.25
130.17
127.74
122.31
118.56
94.84
84.22
80.26
50.67
47.93
31.26
23.27
22.09
21.78
8.72
TsN
Me
AcO
Et
Et
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

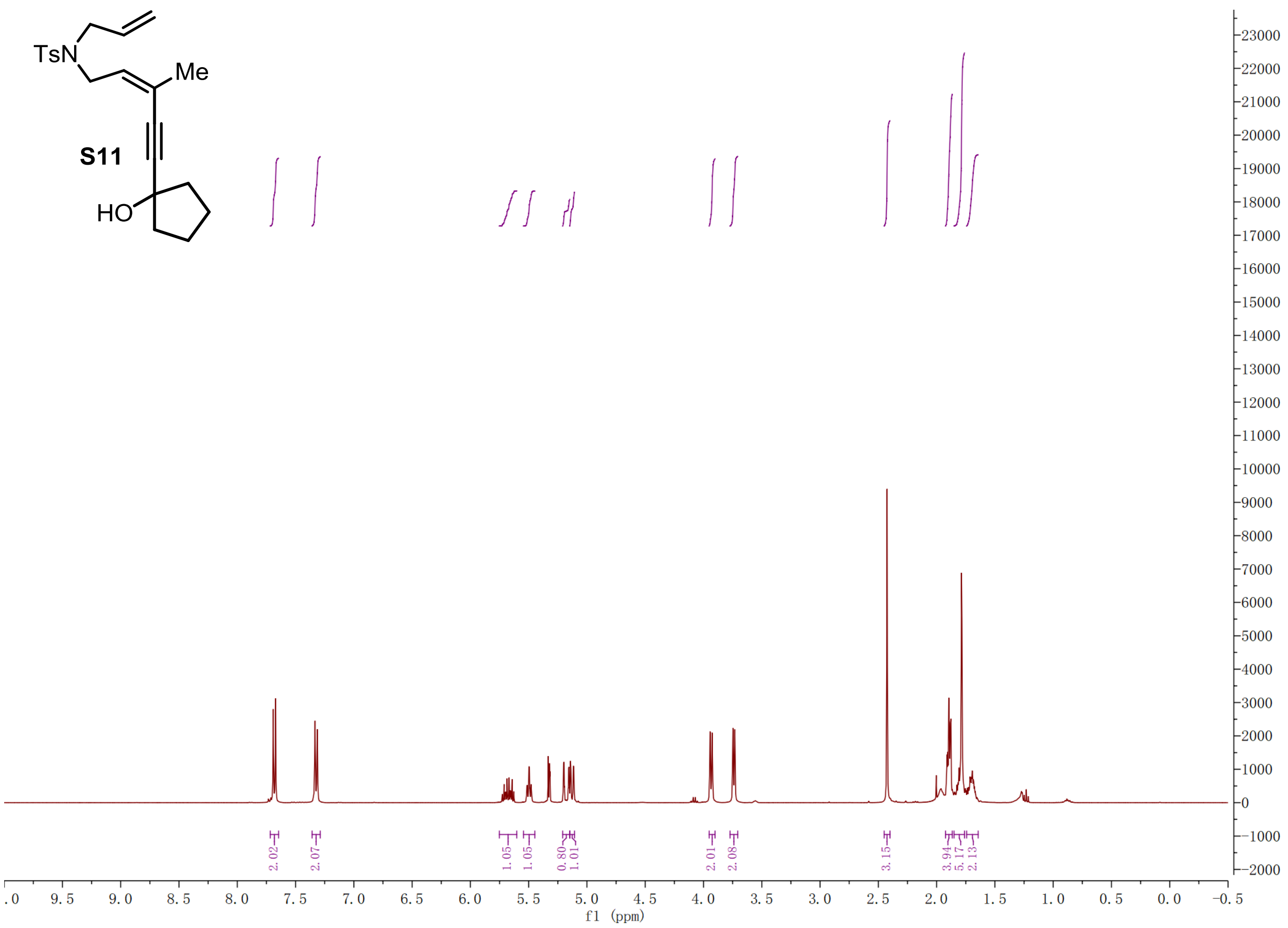
***Z*-1b**



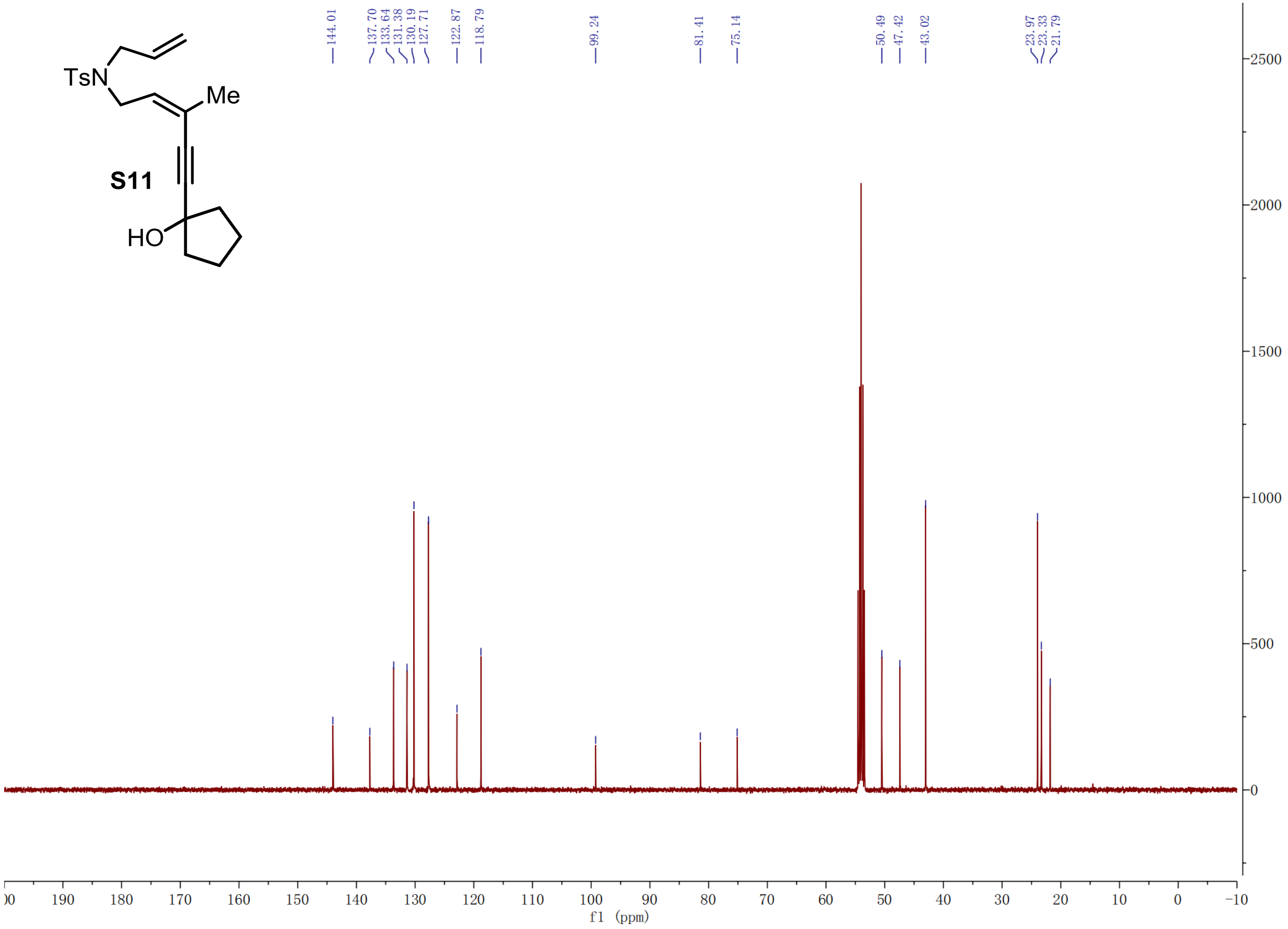
TsN
Et
Et
OAc
Me
2.00
2.05
1.00
0.99
1.93
2.09
2.19
3.05
5.16
2.22
3.05
6.17
f1 (ppm)
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

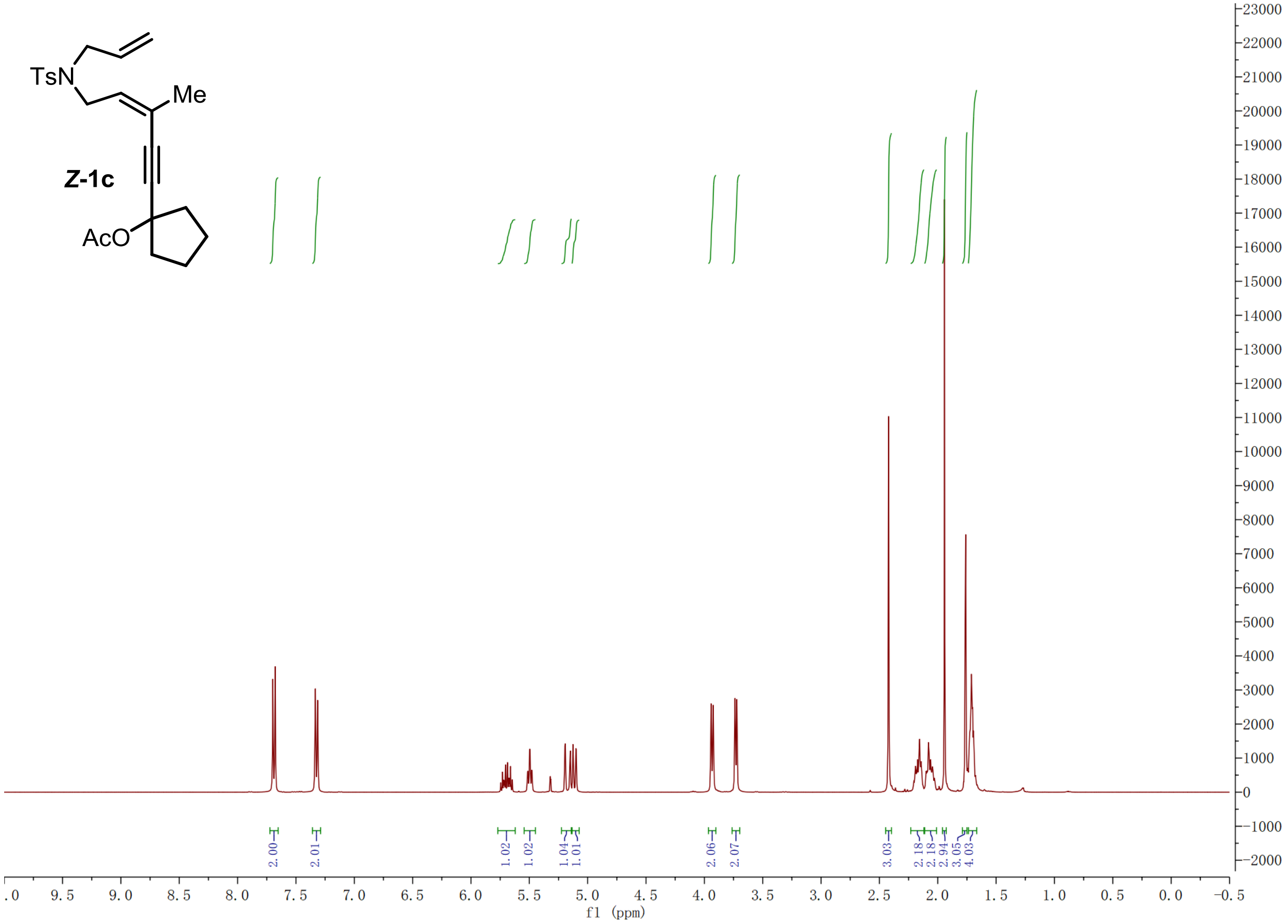
***E*-1b**

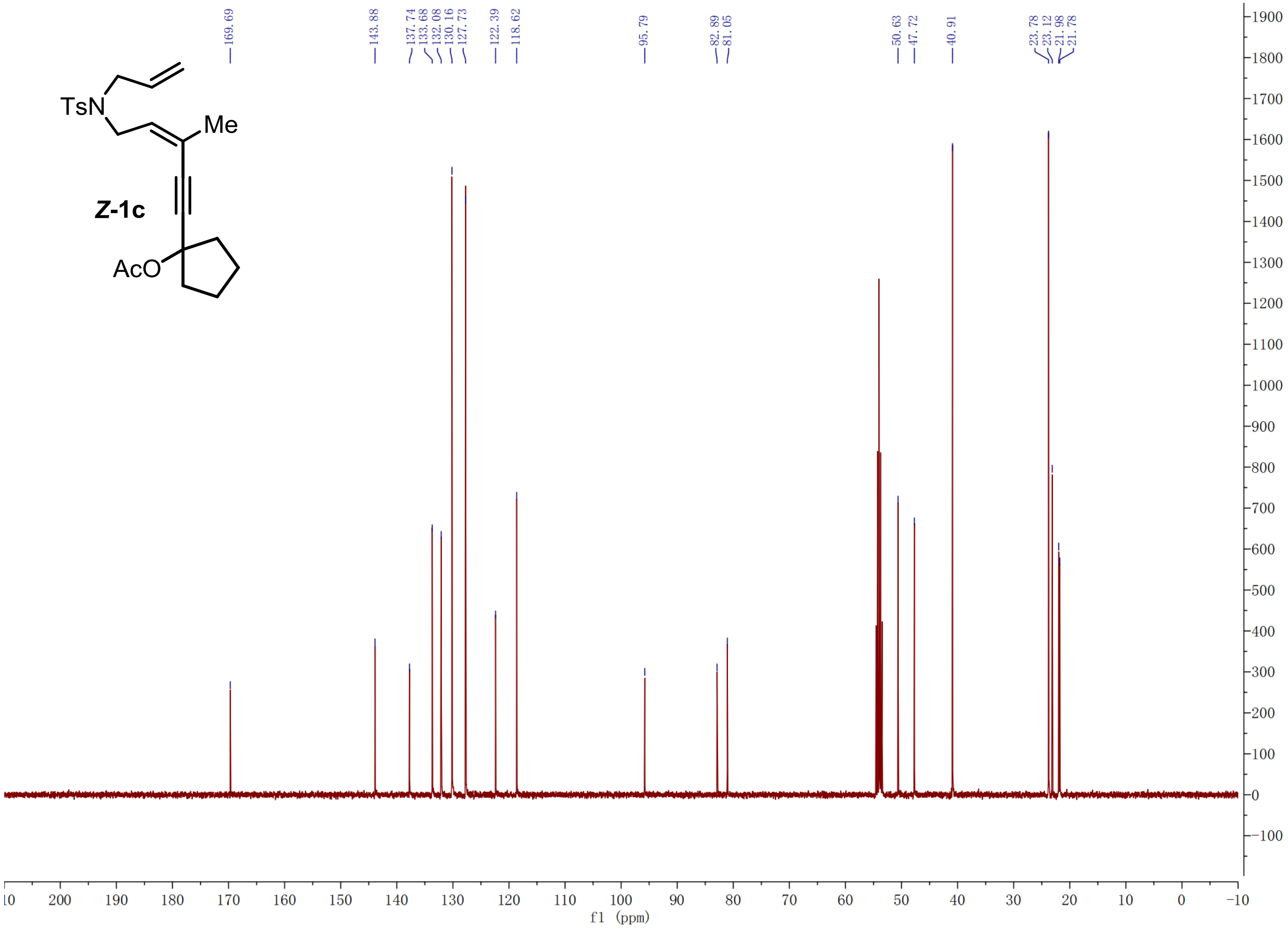

TsN
Et
Et
OAc
Me
E-1b
169.57
144.09
137.77
133.52
131.93
130.27
127.68
121.89
119.23
88.07
87.59
80.52
50.56
44.87
31.34
22.19
21.80
17.81
8.71
550
500
450
400
350
300
250
200
150
100
50
0
−50
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

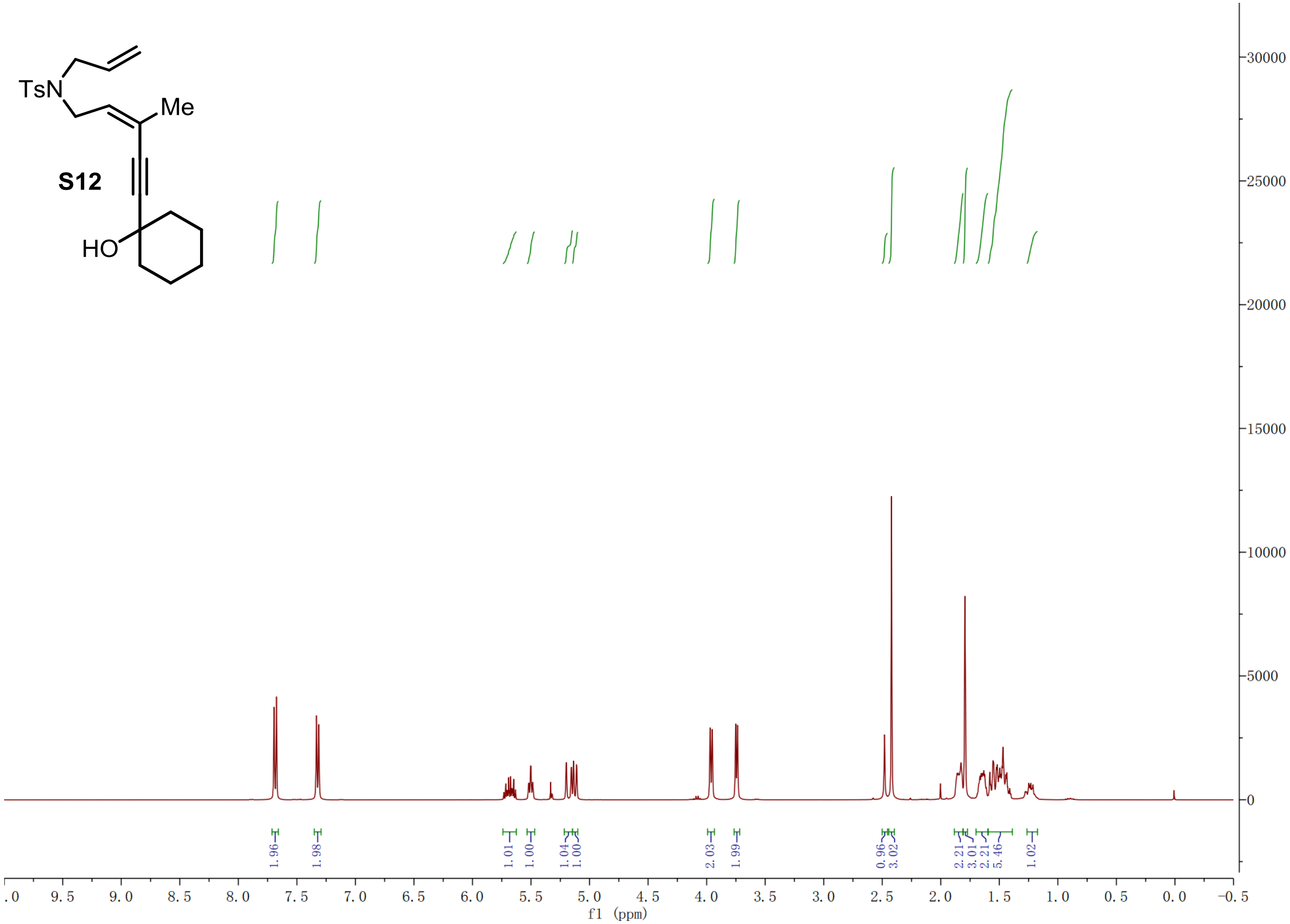

TsN
Me
HO
2.02
2.07
1.05
1.05
0.80
1.01
2.01
2.08
3.15
3.94
5.17
2.13
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

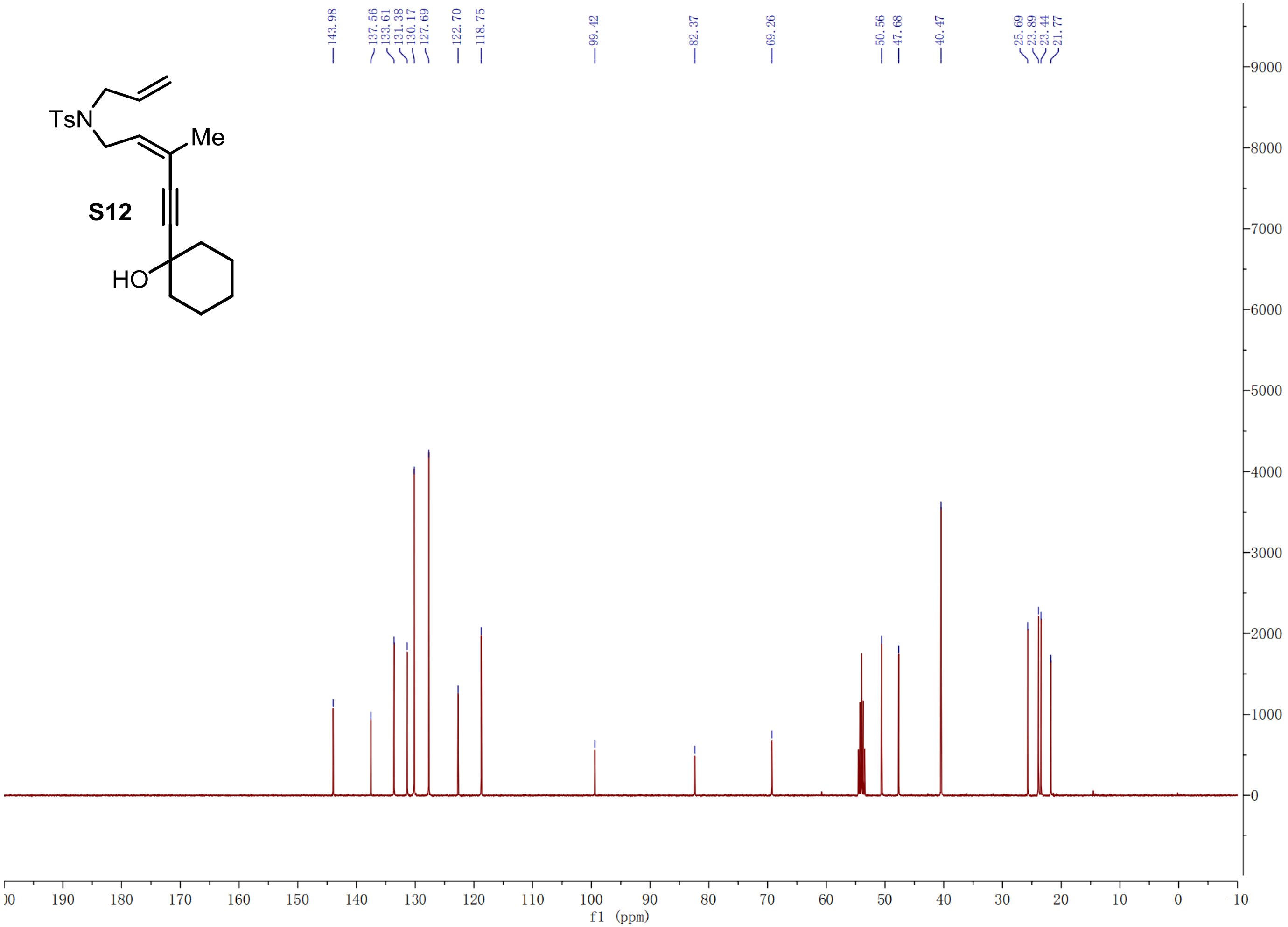
S11

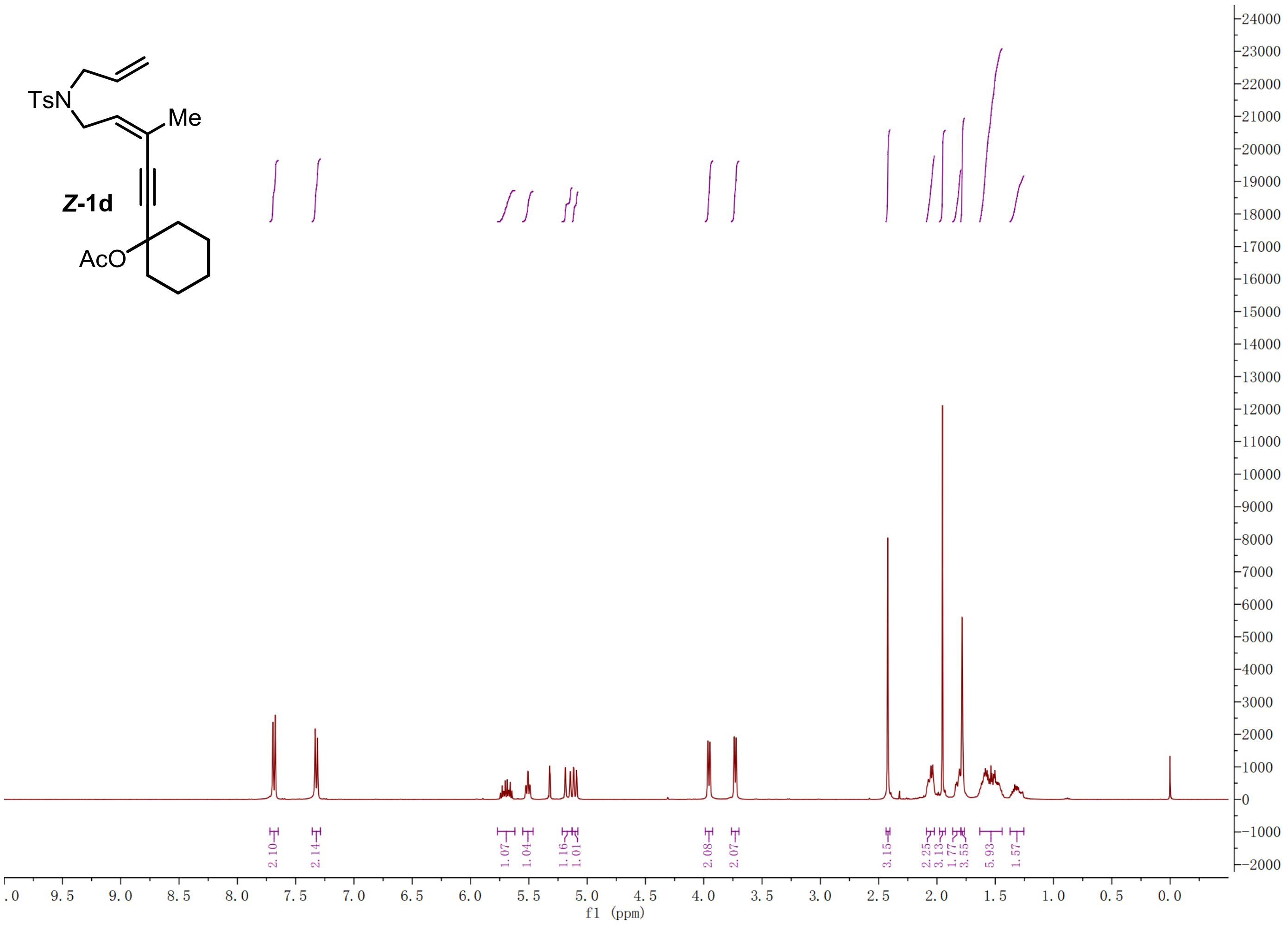

TsN
Me
S11
HO
144.01
137.70
133.64
131.38
130.19
127.71
122.87
118.79
99.24
81.41
75.14
50.49
47.42
43.02
23.97
23.33
21.79
2500
2000
1500
1000
500
0
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


TsN
Me
Z-1c
AcO
2.00
2.01
1.02
1.02
1.04
1.01
2.06
2.07
3.03
2.18
2.18
2.94
3.05
4.03
.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)
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

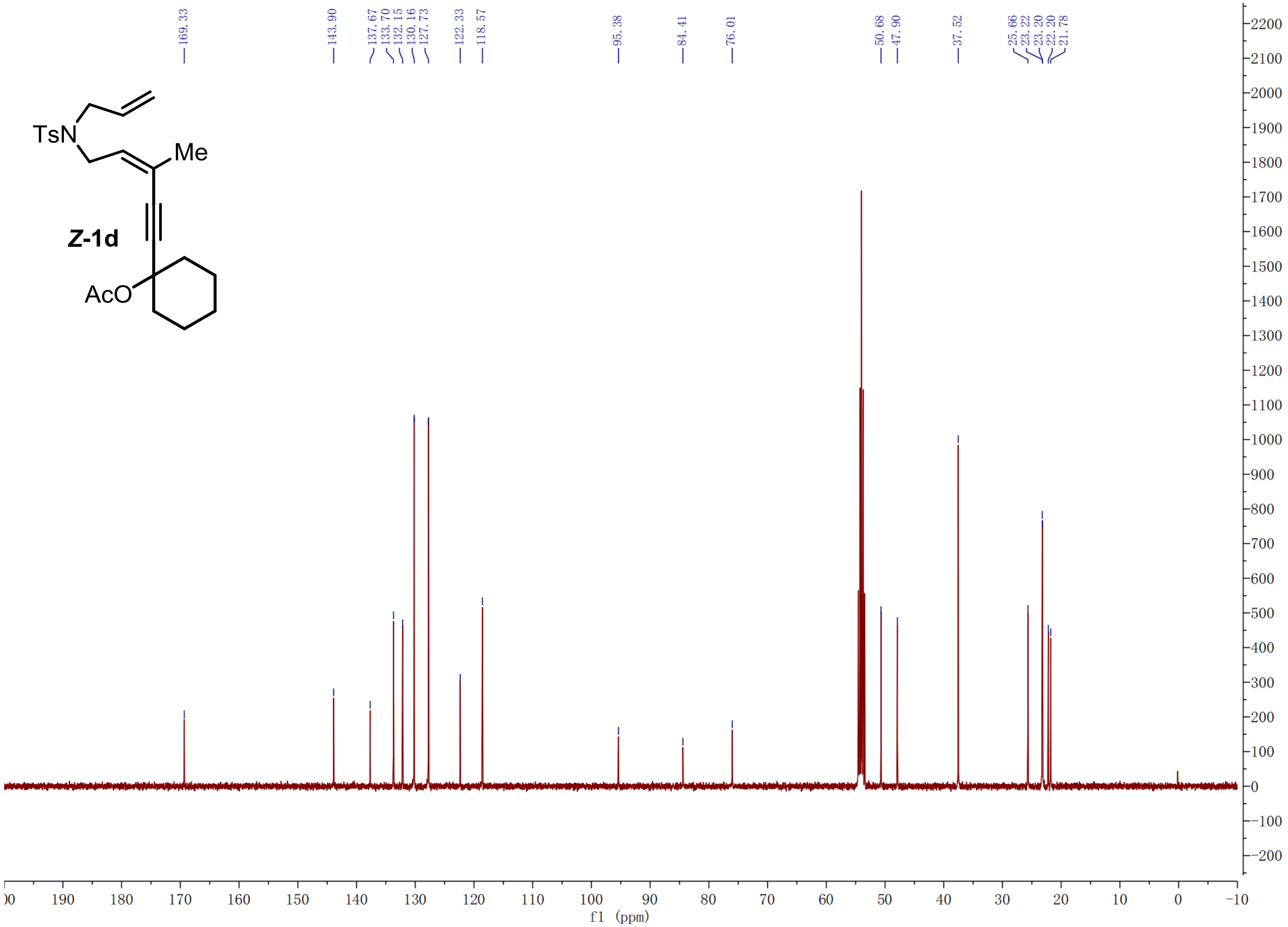

169.69
143.88
137.74
133.68
132.08
130.16
127.73
122.39
118.62
95.79
82.89
81.05
50.63
47.72
40.91
23.78
23.12
21.98
21.78
TsN
Me
Z-1c
AcO
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

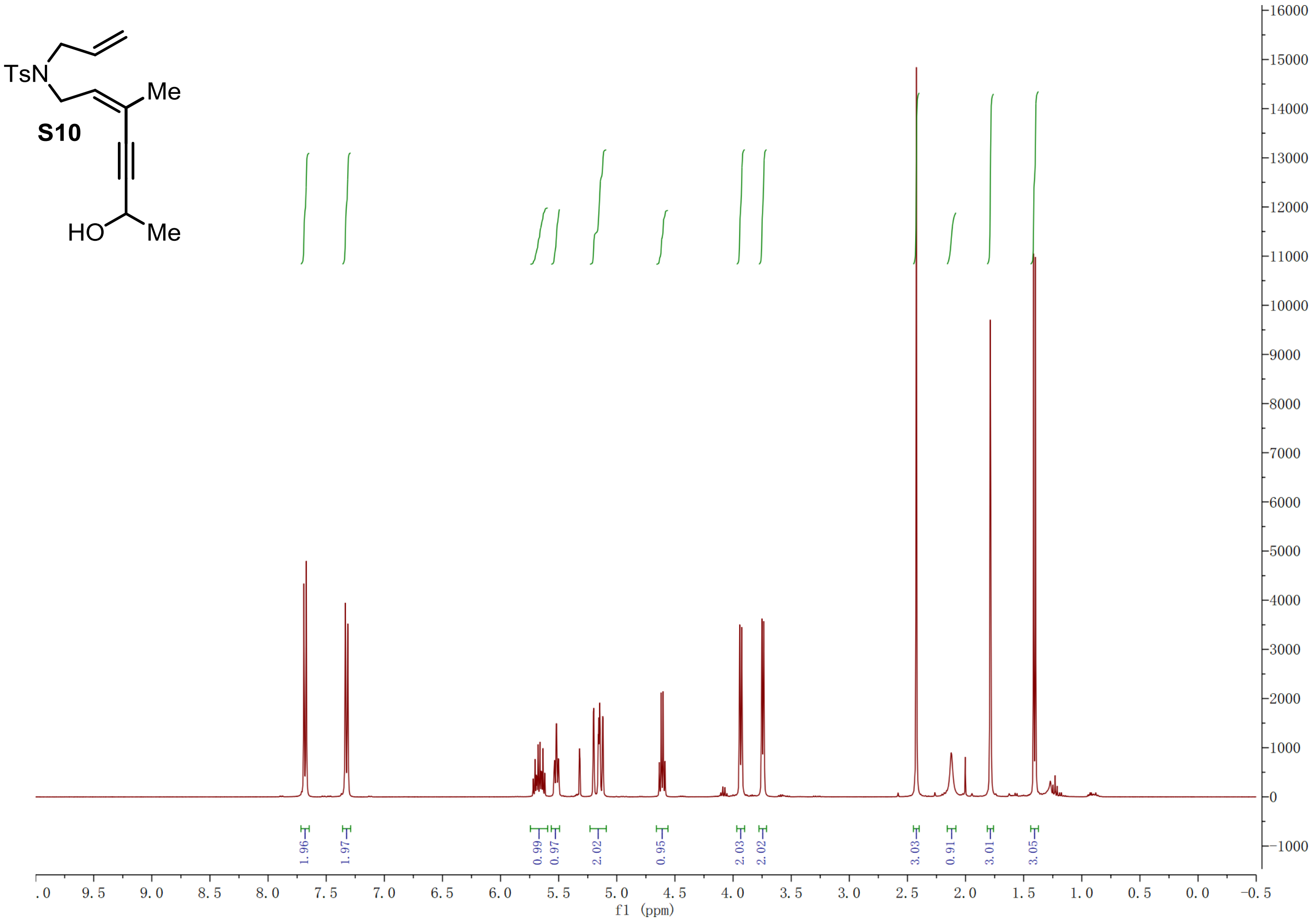

TsN
Me
S12
HO
30000
25000
20000
15000
10000
5000
0
1.96
1.98
1.01
1.00
1.04
1.00
2.03
1.99
0.96
3.02
2.21
3.01
2.21
5.46
1.02
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

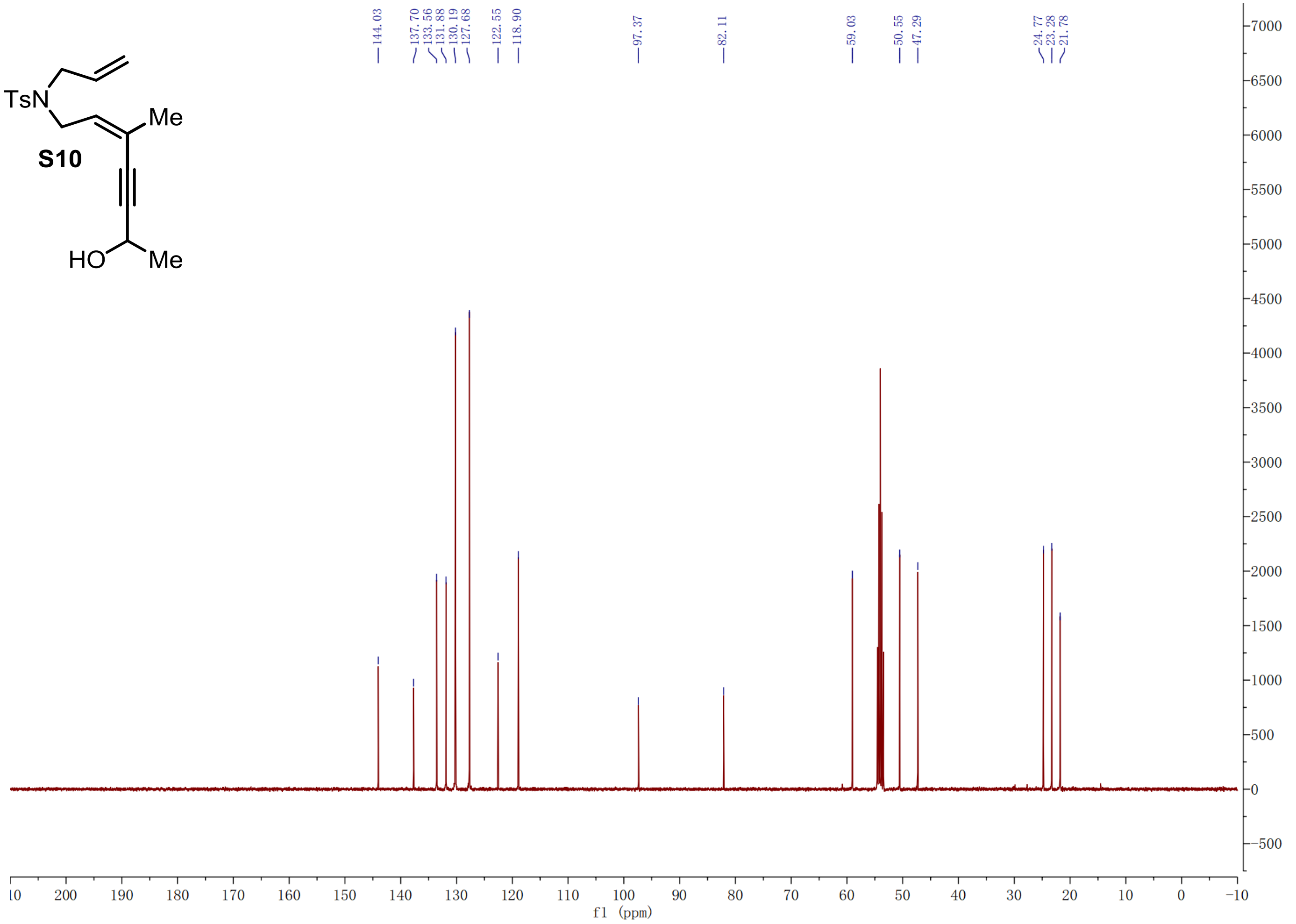

143.98
137.56
133.61
131.38
130.17
127.69
122.70
118.75
99.42
82.37
69.26
50.56
47.68
40.47
25.69
23.89
23.44
21.77
TsN
Me
S12
HO
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



TsN
Me
AcO
Z-1d
2.10
2.14
1.07
1.04
1.16
1.01
2.08
2.07
3.15
2.25
3.13
1.77
3.55
5.93
1.57
.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)
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

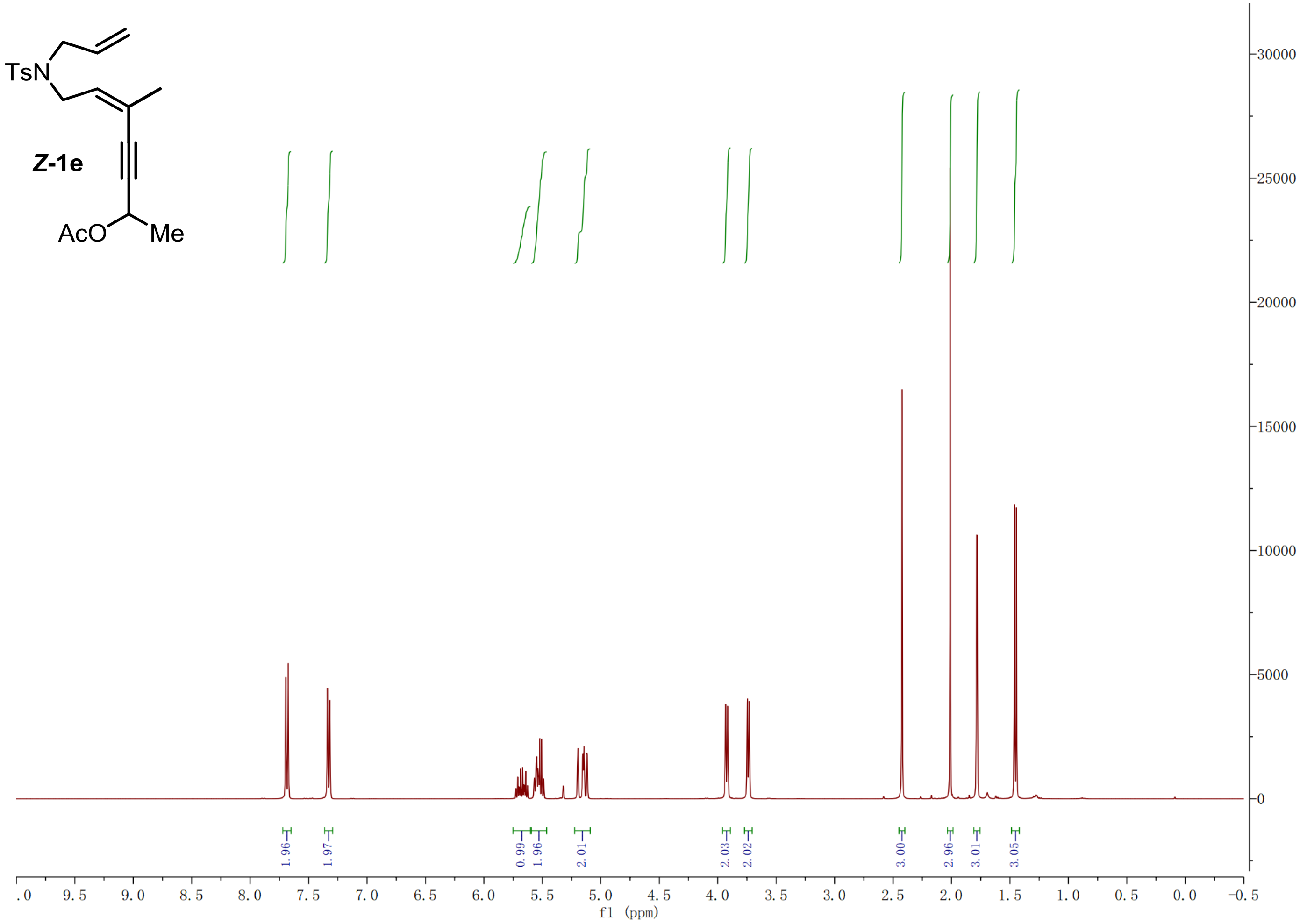

169.33
143.90
137.67
133.70
132.15
130.16
127.73
122.33
118.57
95.38
84.41
76.01
50.68
47.90
37.52
25.66
23.22
23.20
22.20
21.78
TsN
Me
Z-1d
AcO
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
−200
)0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

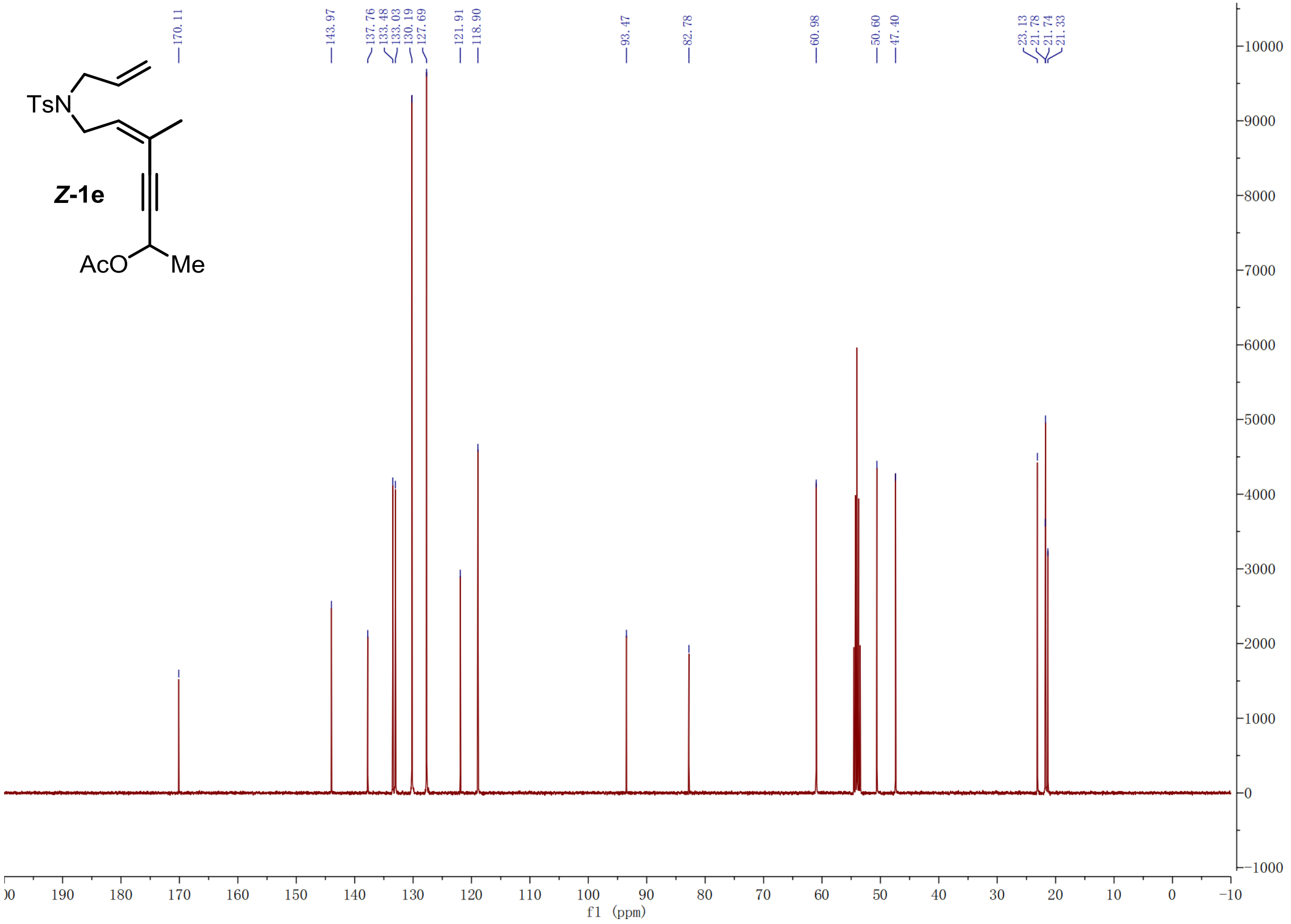

TsN
Me
S10
HO
Me
1.96
1.97
0.99
0.97
2.02
0.95
2.03
2.02
3.03
0.91
3.01
3.05
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



S10

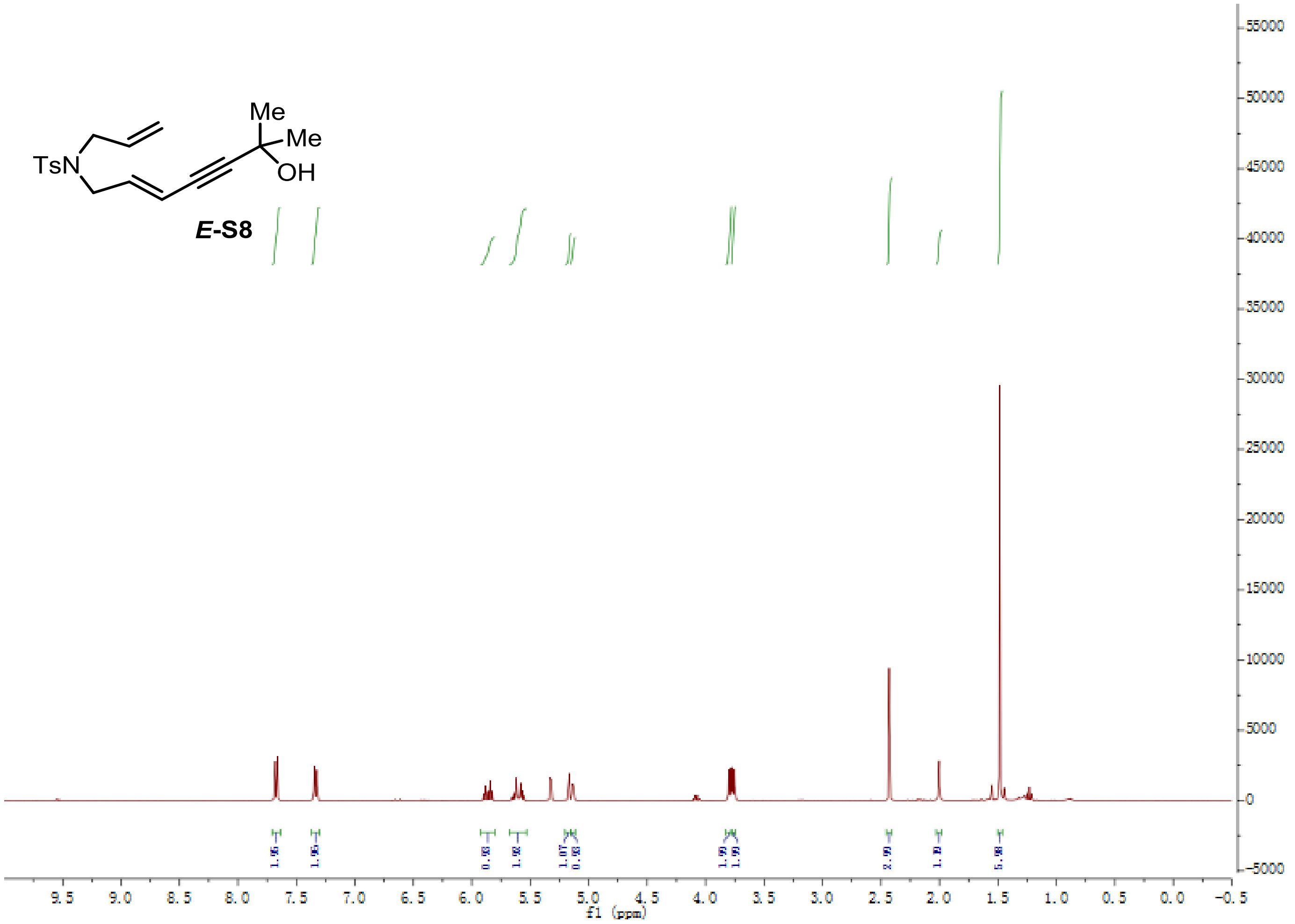
TsN
Me
HO
Me
144.03
137.70
133.56
131.88
130.19
127.68
122.55
118.90
97.37
82.11
59.03
50.55
47.29
24.77
23.28
21.78
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

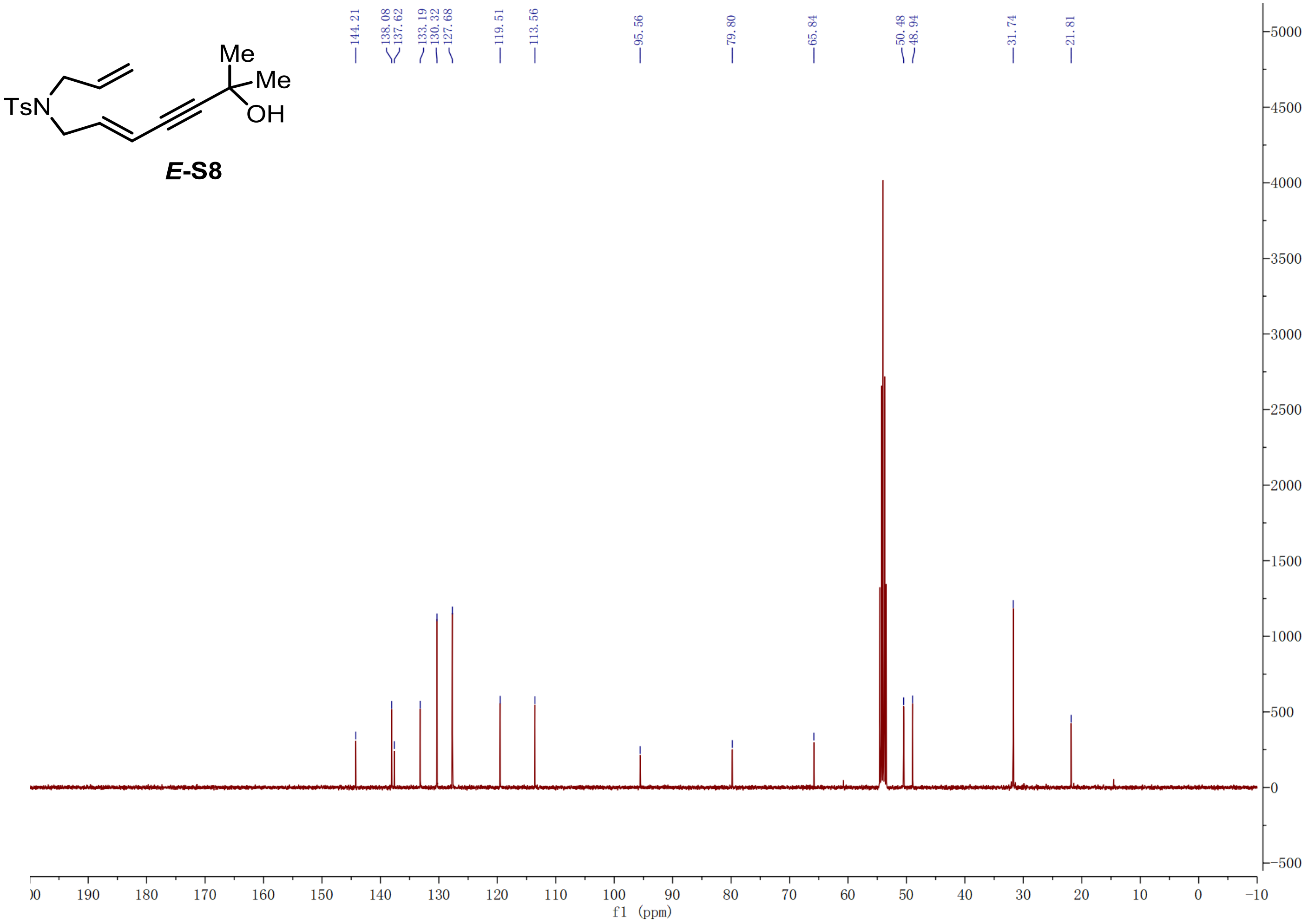

TsN
Z-1e
AcO
Me
1.96
1.97
0.99
1.96
2.01
2.03
2.02
3.00
2.96
3.01
3.05
30000
25000
20000
15000
10000
5000
0
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



Z-1e

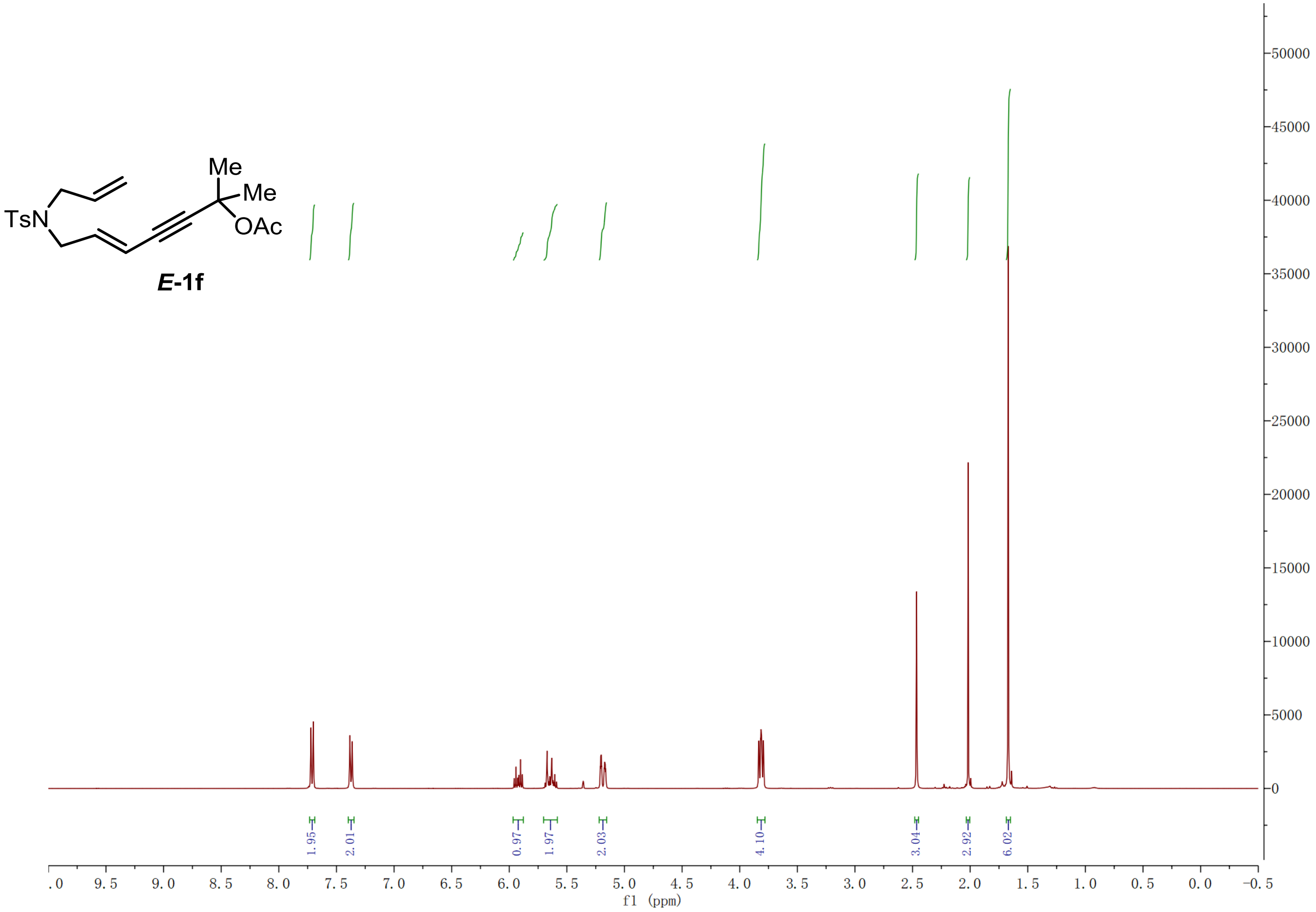
TsN
AcO
Me
170.11
143.97
137.76
133.48
133.03
130.19
127.69
121.91
118.90
93.47
82.78
60.98
50.60
47.40
23.13
21.78
21.74
21.33
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


TsN
Me
Me
OH
E-S8
1.95
1.95
0.93
1.92
1.07
0.93
1.99
1.99
2.99
1.10
5.98
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
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)

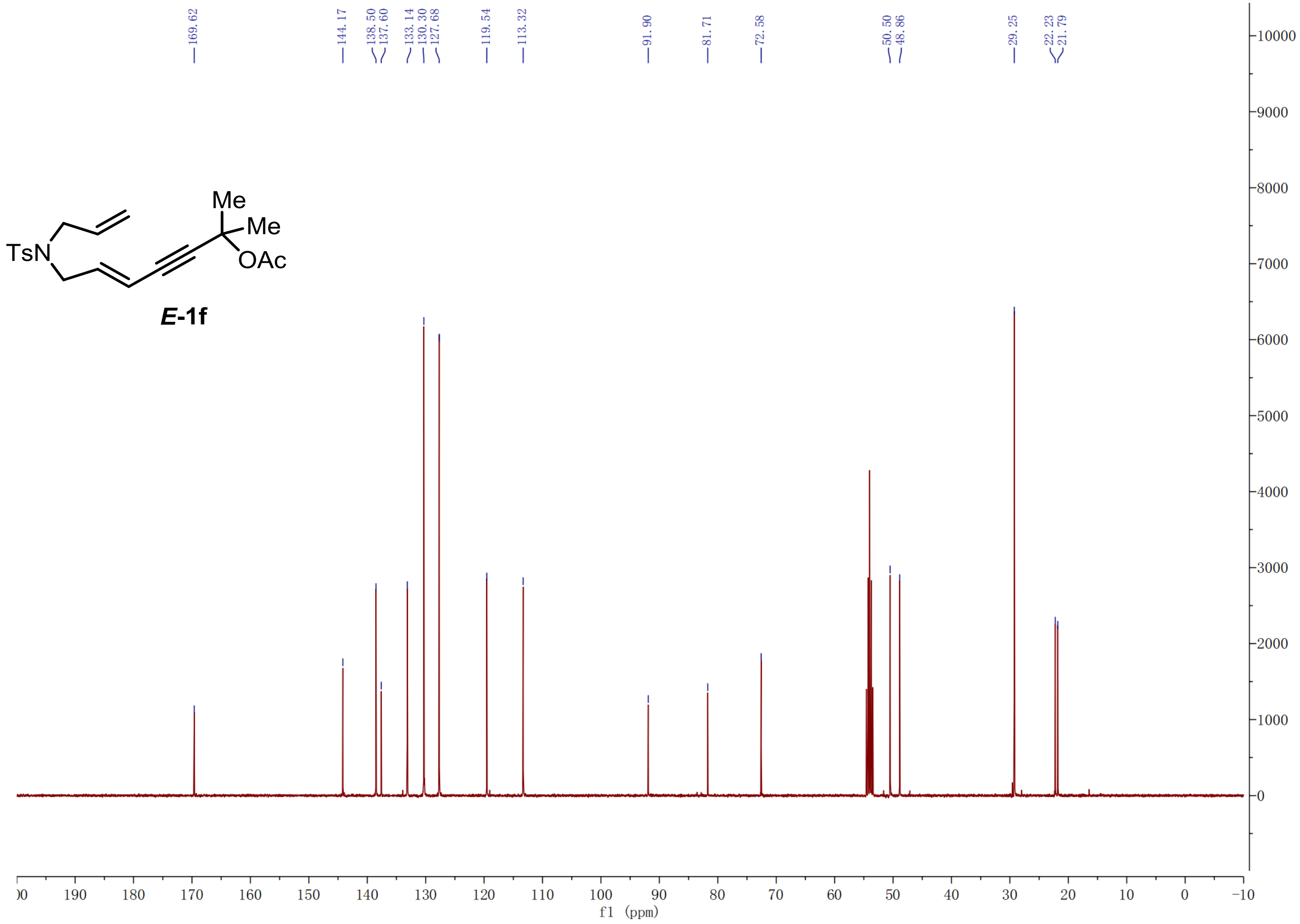

Me
Me
TsN
OH

***E*-S8**

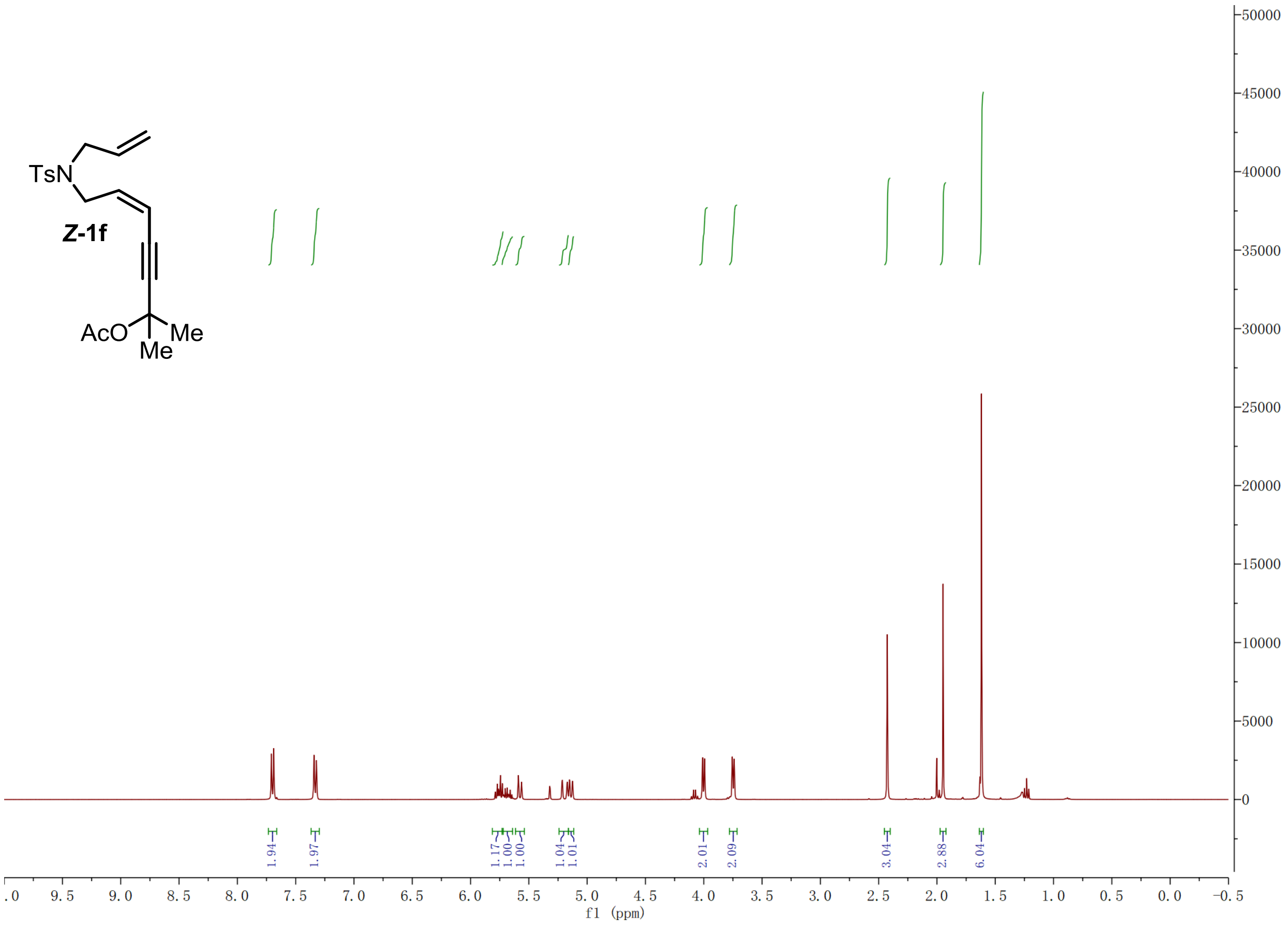
144.21
138.08
137.62
133.19
130.32
127.68
119.51
113.56
95.56
79.80
65.84
50.48
48.94
31.74
21.81
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

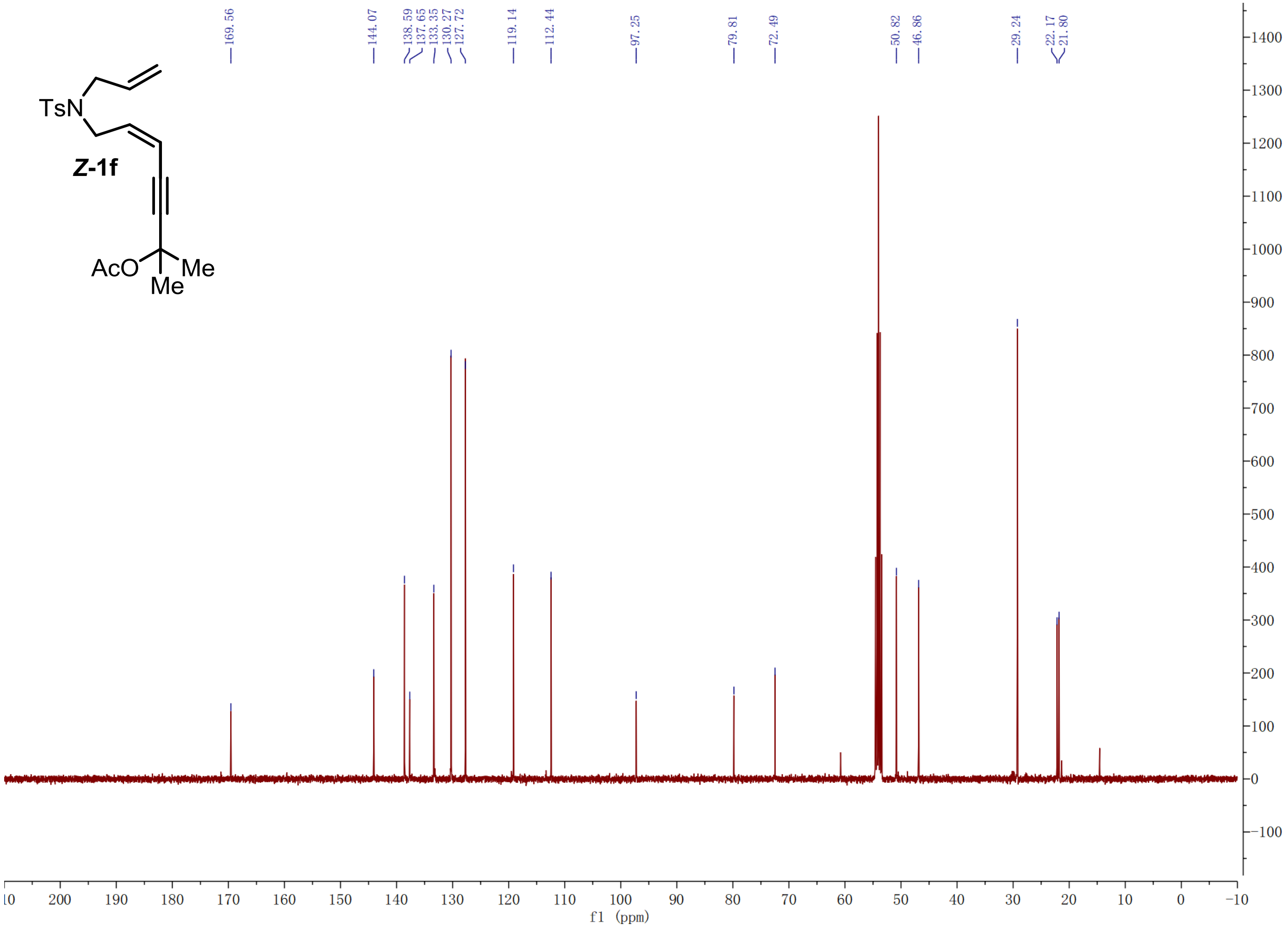

Me
Me
TsN
OAc
1.95
2.01
0.97
1.97
2.03
4.10
3.04
2.92
6.02
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

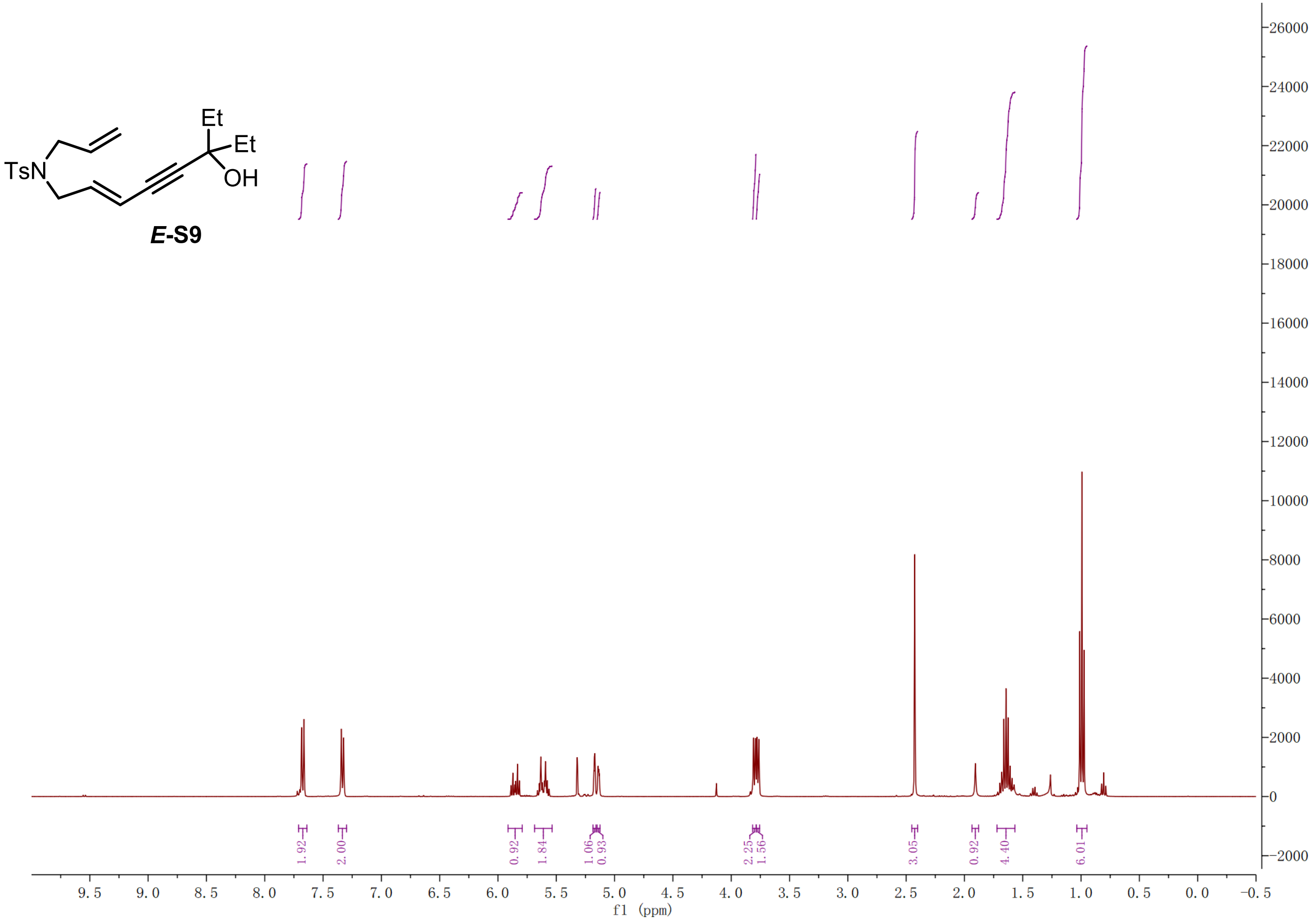
***E*-1f**


169.62
144.17
138.50
137.60
133.14
130.30
127.68
119.54
113.32
91.90
81.71
72.58
50.50
48.86
29.25
22.23
21.79
TsN
Me
Me
OAc
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

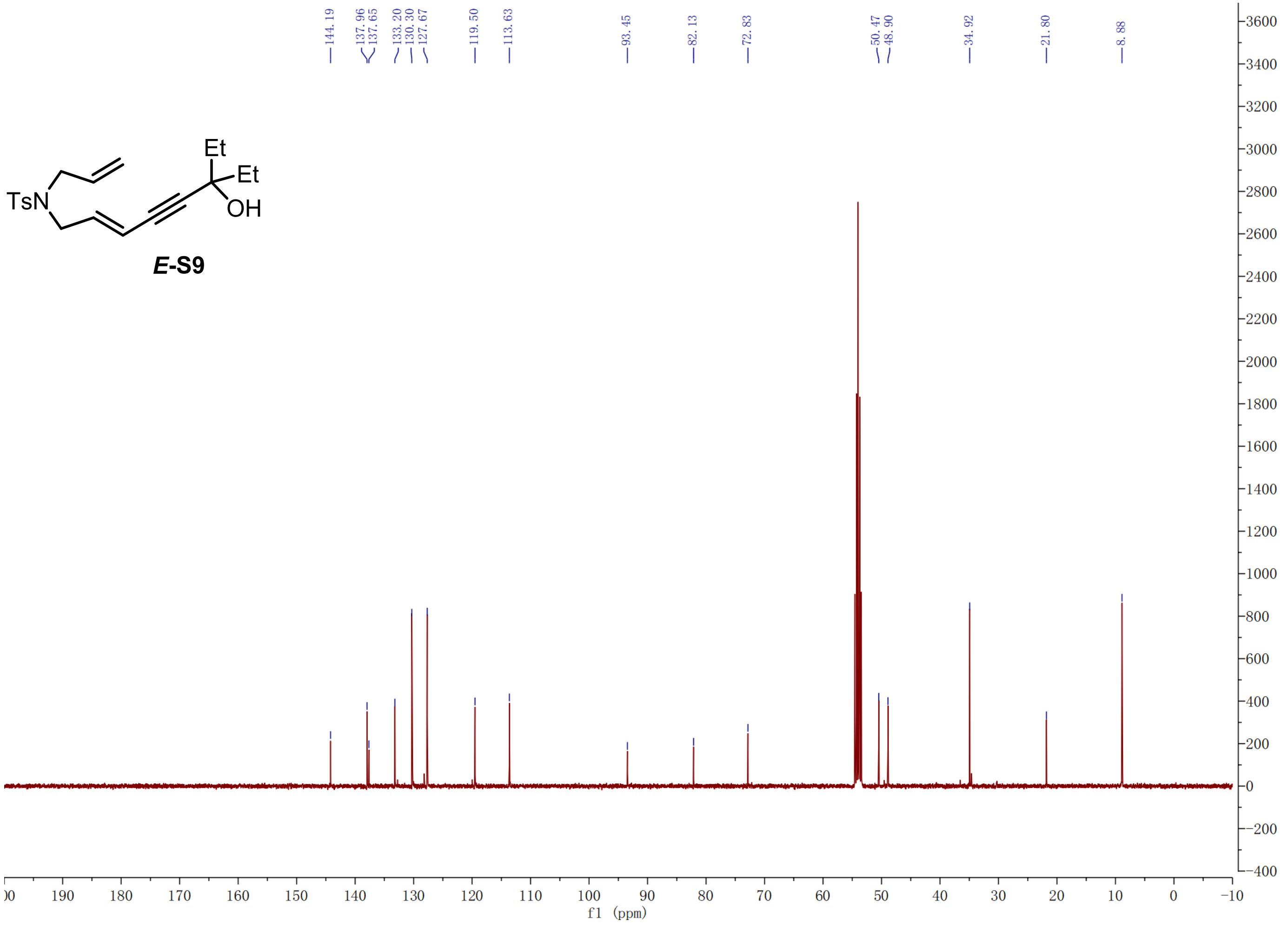
***E*-1f**


TsN
Z-1f
AcO
Me
Me
1.94
1.97
1.17
1.00
1.00
1.04
1.01
2.01
2.09
3.04
2.88
6.04
.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

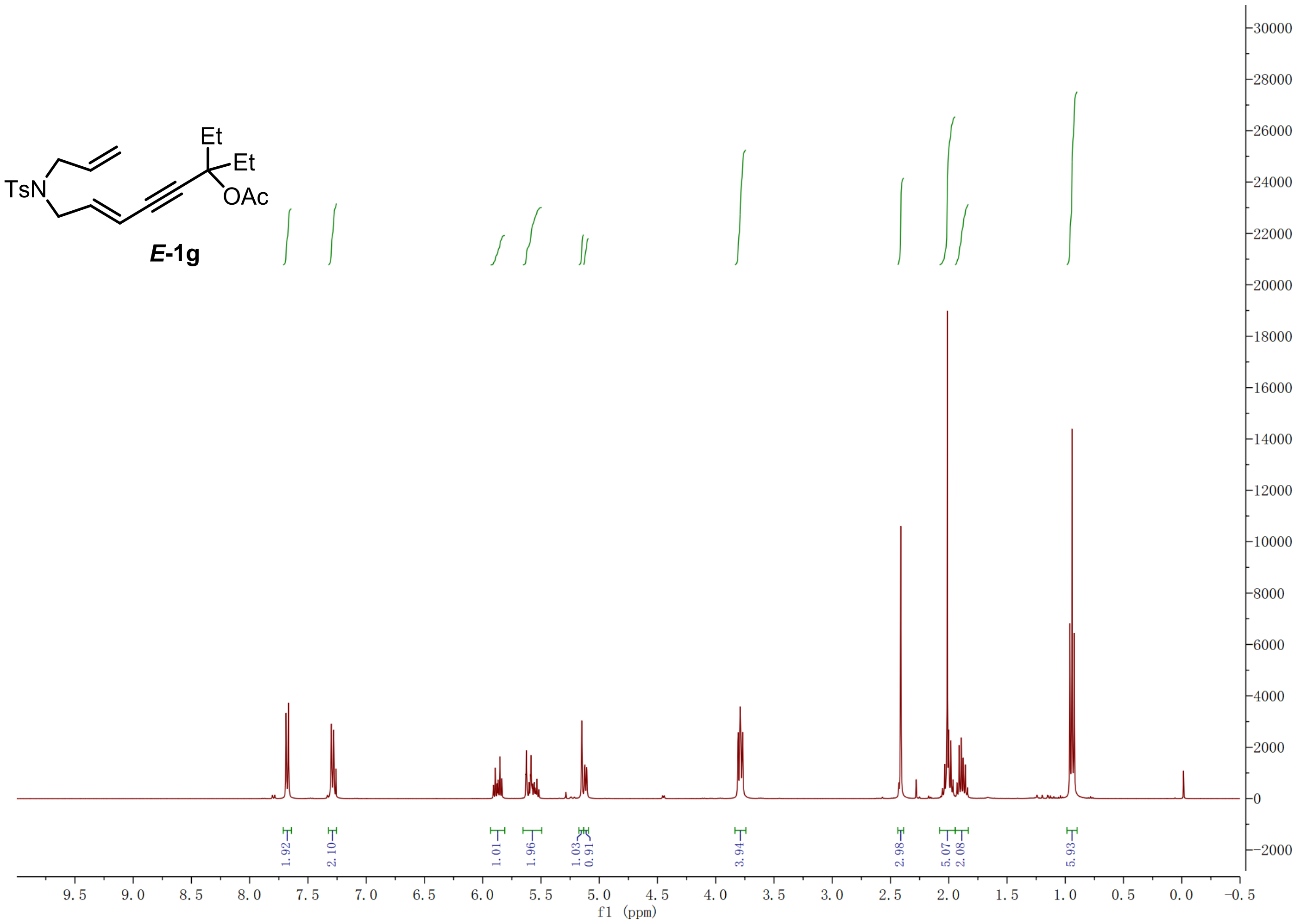

Z-1f
TsN
AcO
Me
Me
169.56
144.07
138.59
137.65
133.35
130.27
127.72
119.14
112.44
97.25
79.81
72.49
50.82
46.86
29.24
22.17
21.80
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


***E*-S9**

TsN
Et
Et
OH
1.92
2.00
0.92
1.84
1.06
0.93
2.25
1.56
3.05
0.92
4.40
6.01
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)
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000

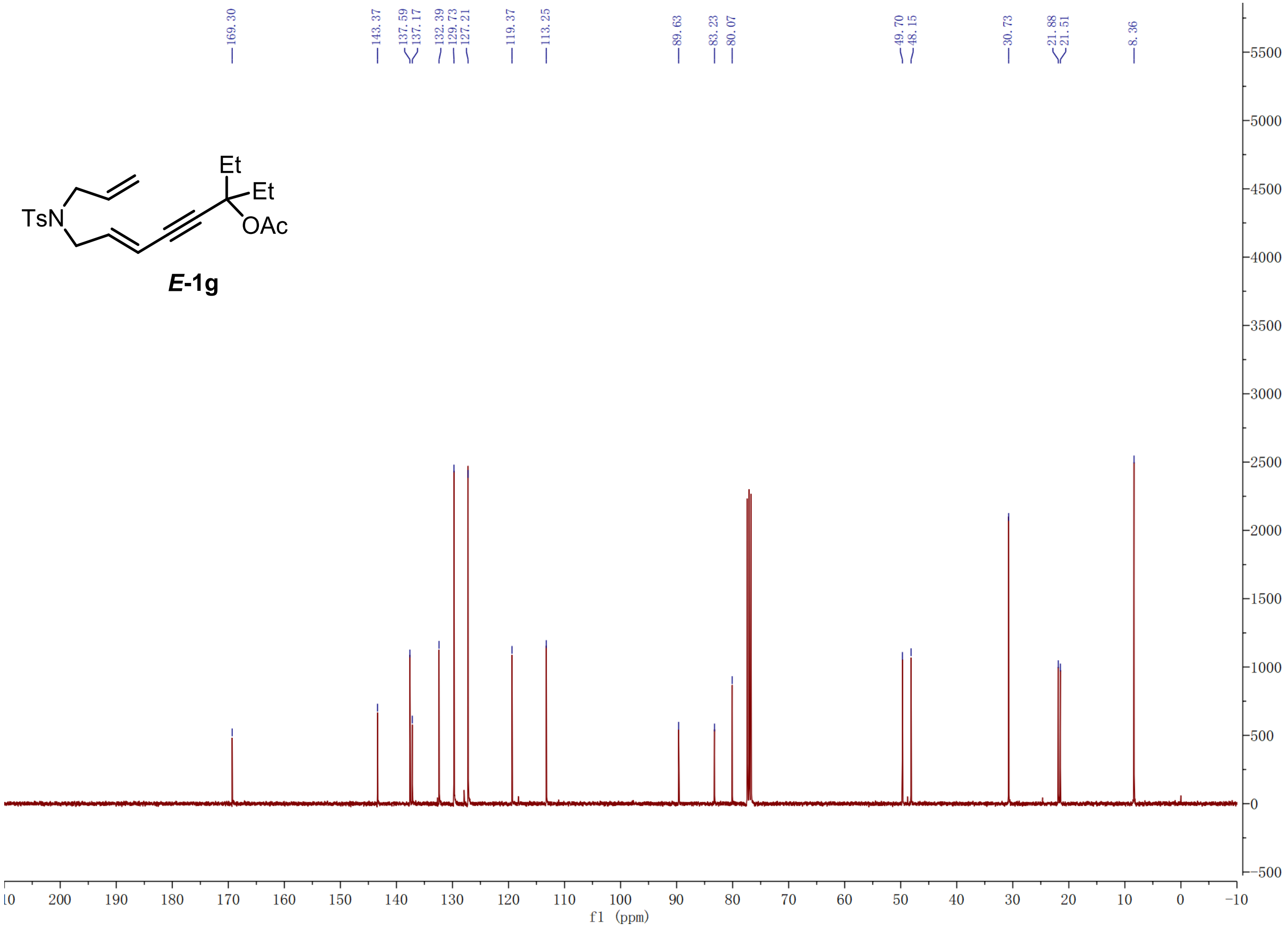

TsN
Et
Et
OH
144.19
137.96
137.65
133.20
130.30
127.67
119.50
113.63
93.45
82.13
72.83
50.47
48.90
34.92
21.80
8.88
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

***E*-S9**



E-1g

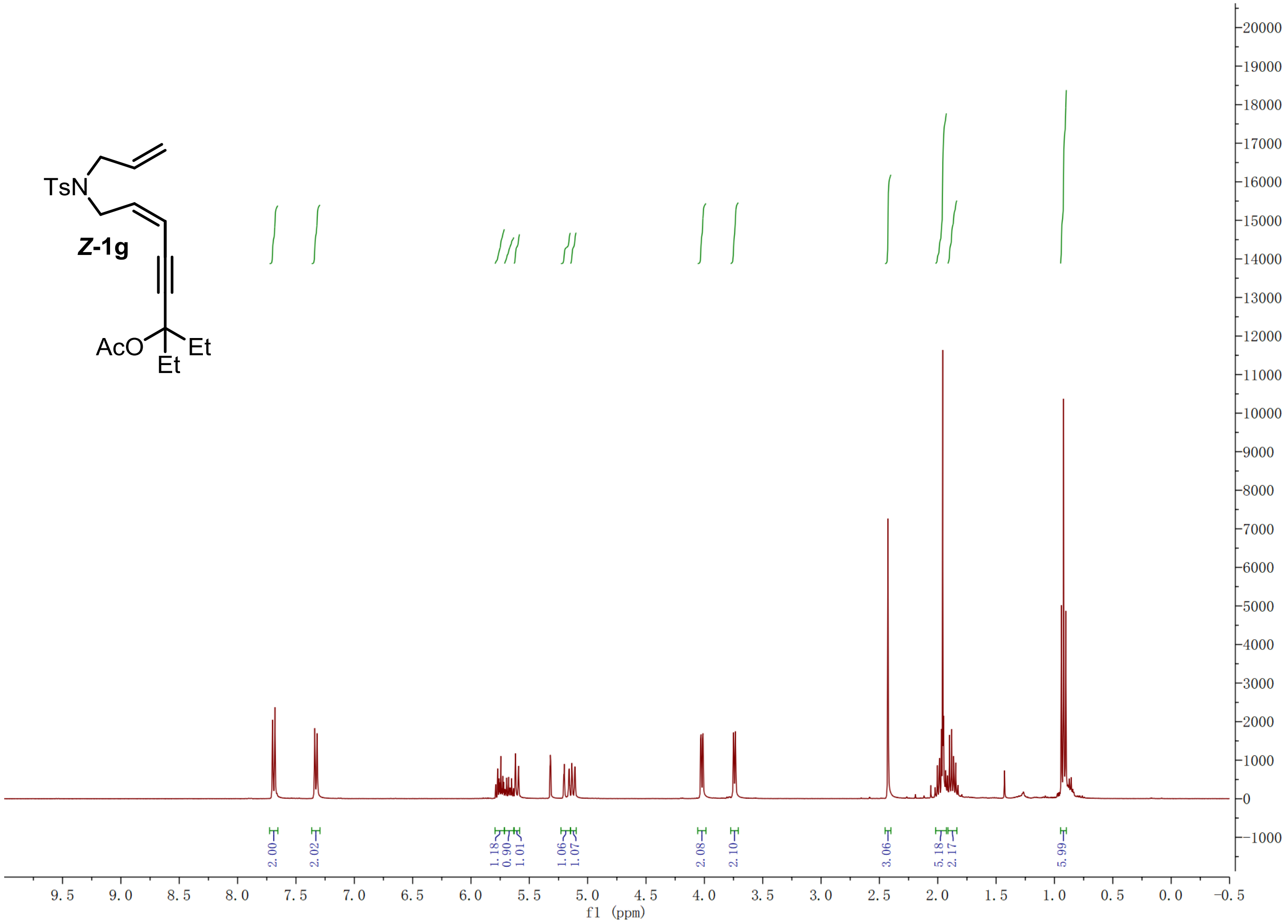
TsN
Et
Et
OAc
1.92
2.10
1.01
1.96
1.03
0.91
3.94
2.98
5.07
2.08
5.93
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000

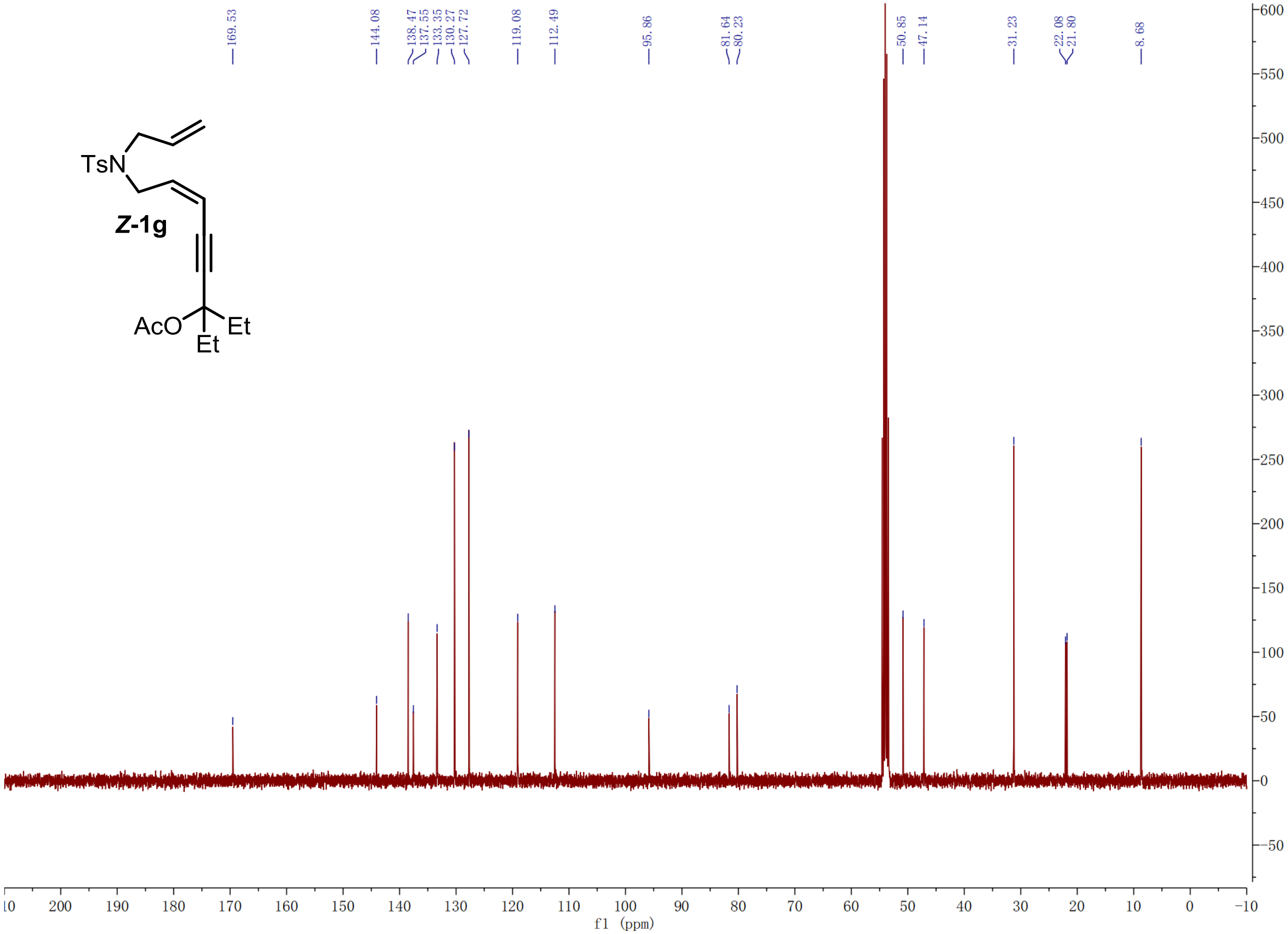

169.30
143.37
137.59
137.17
132.39
129.73
127.21
119.37
113.25
89.63
83.23
80.07
49.70
48.15
30.73
21.88
21.51
8.36
TsN
Et
Et
OAc
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

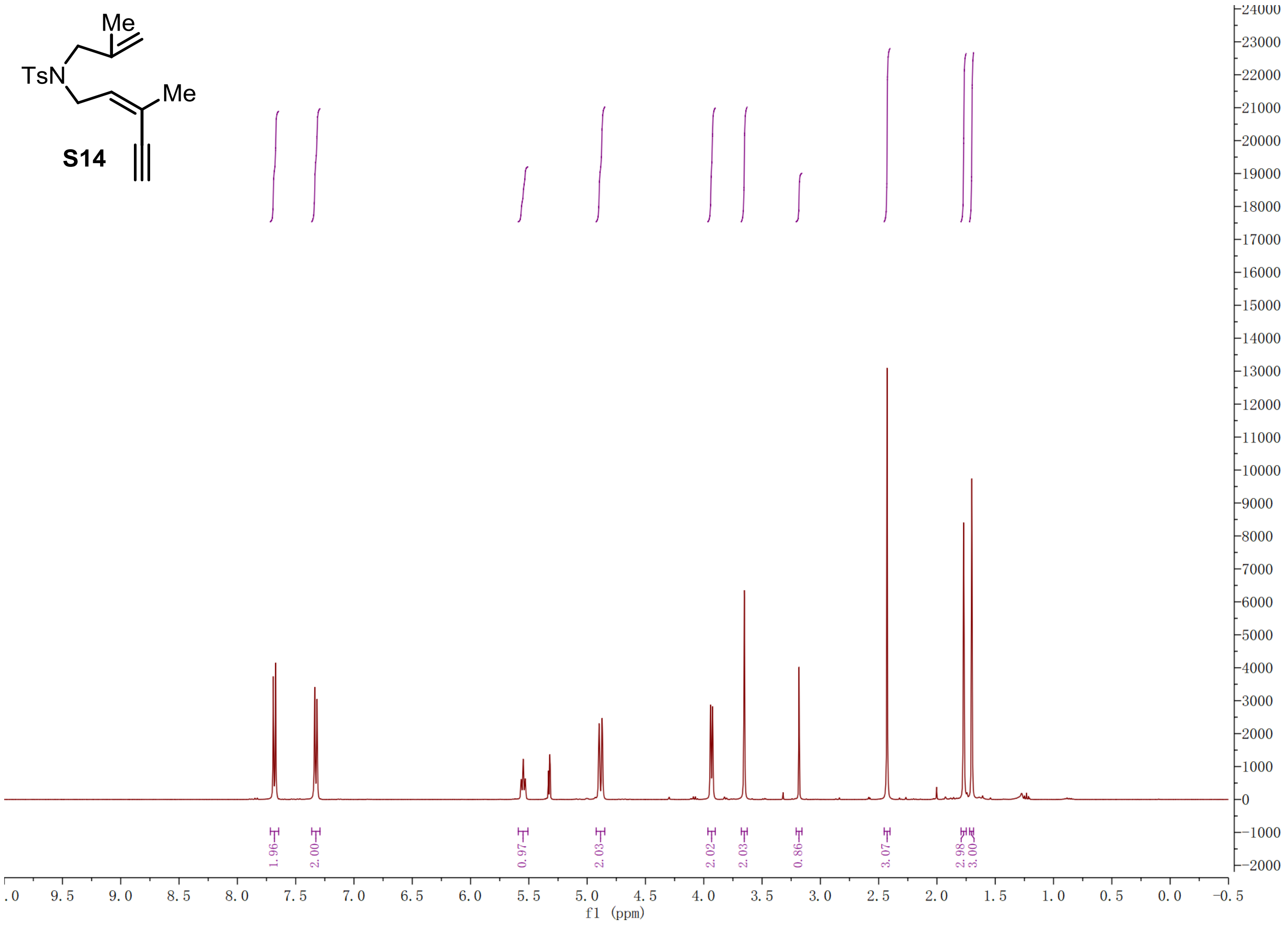
***E*-1g**

TsN
AcO
Et
Et

Z-1g


2.00
2.02
1.18
0.90
1.01
1.06
1.07
2.08
2.10
3.06
5.18
2.17
5.99
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)
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

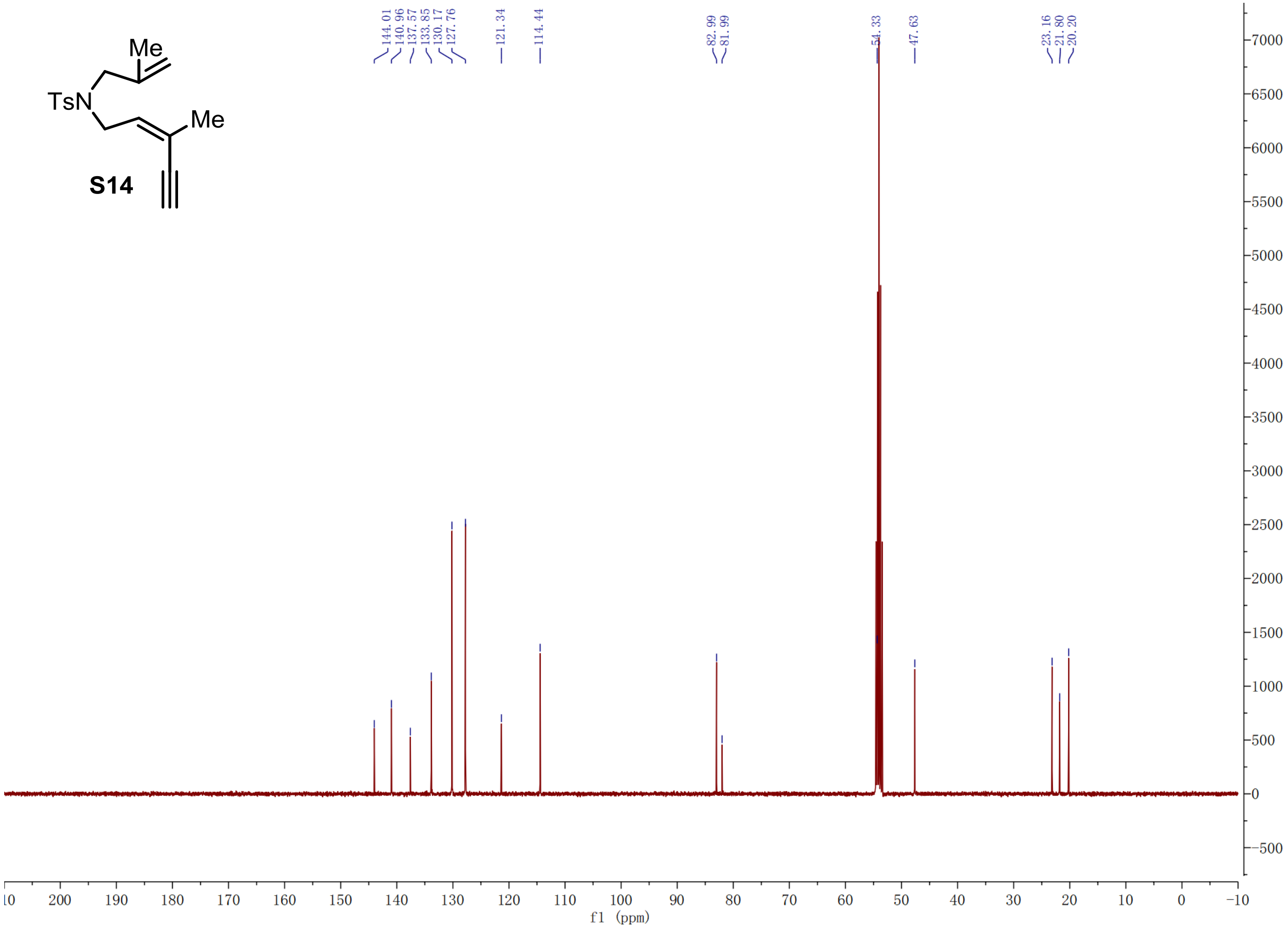

169.53
144.08
138.47
137.55
133.35
130.27
127.72
119.08
112.49
95.86
81.64
80.23
50.85
47.14
31.23
22.08
21.80
8.68
TsN
Z-1g
AcO
Et
Et
600
550
500
450
400
350
300
250
200
150
100
50
0
−50
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

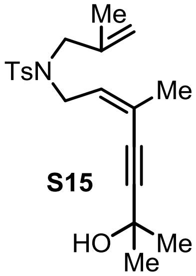

S14

Me
TsN
Me
1.96
2.00
0.97
2.03
2.02
2.03
0.86
3.07
2.98
3.00
.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

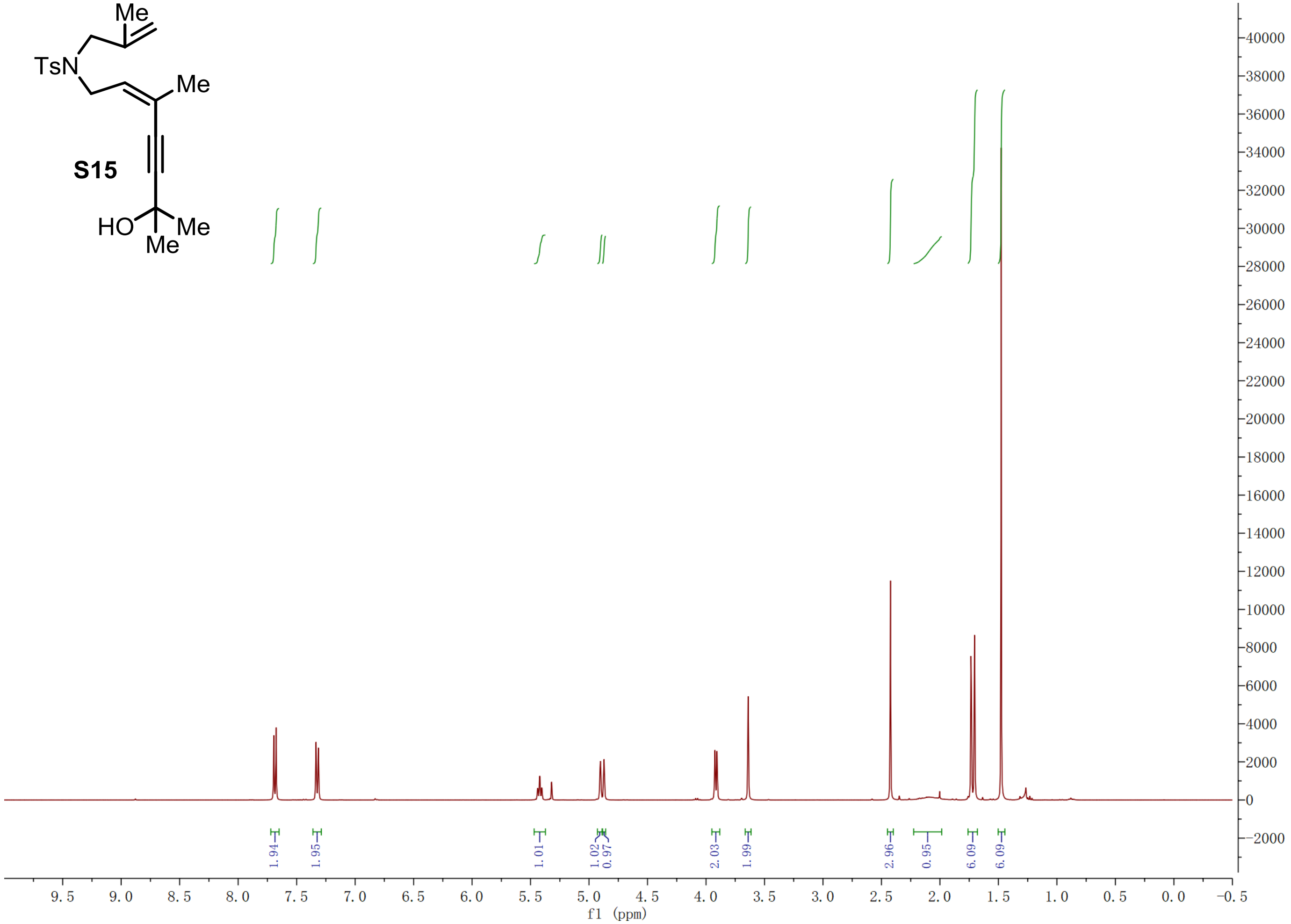
Me
TsN
Me

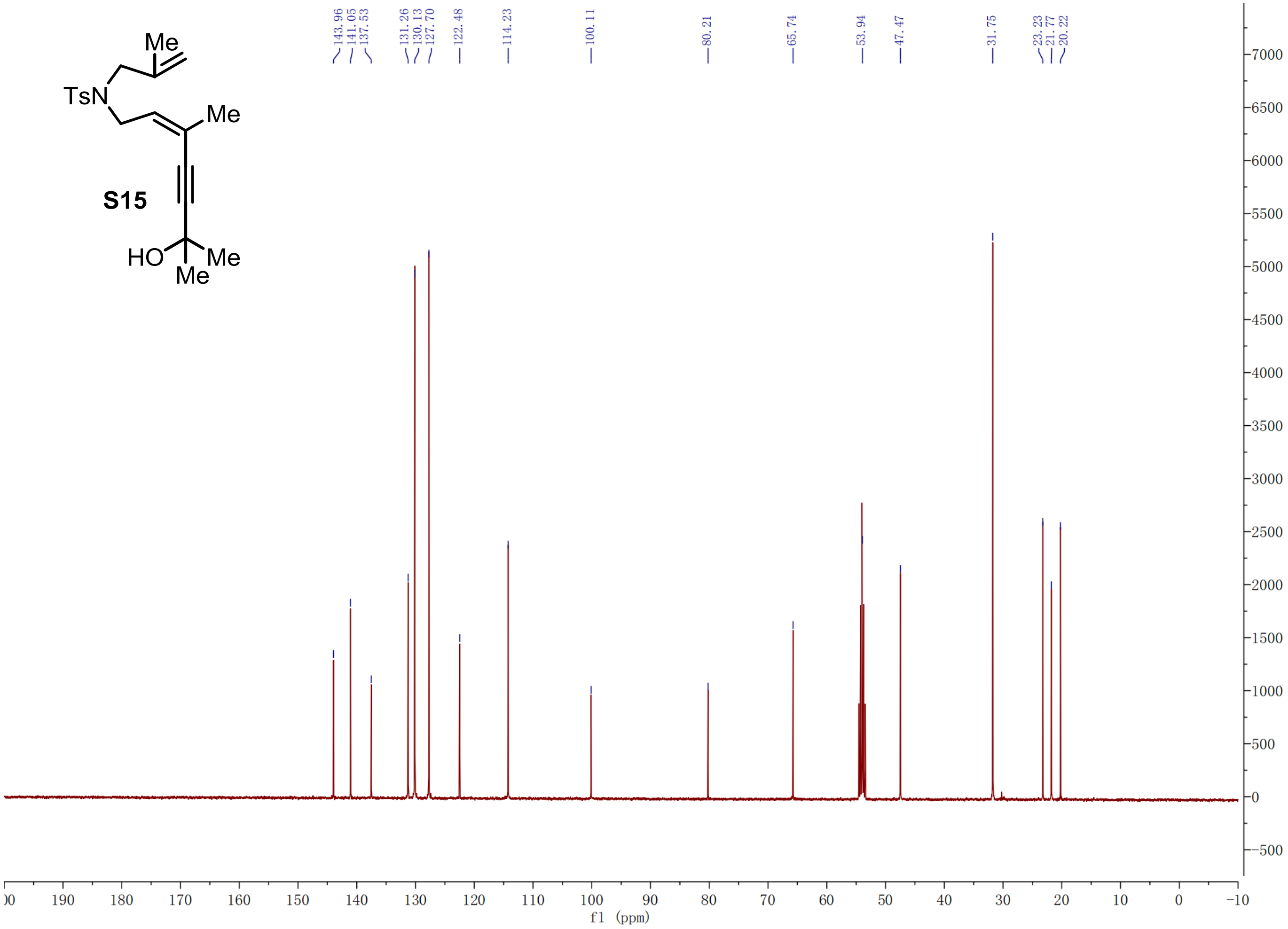
S14

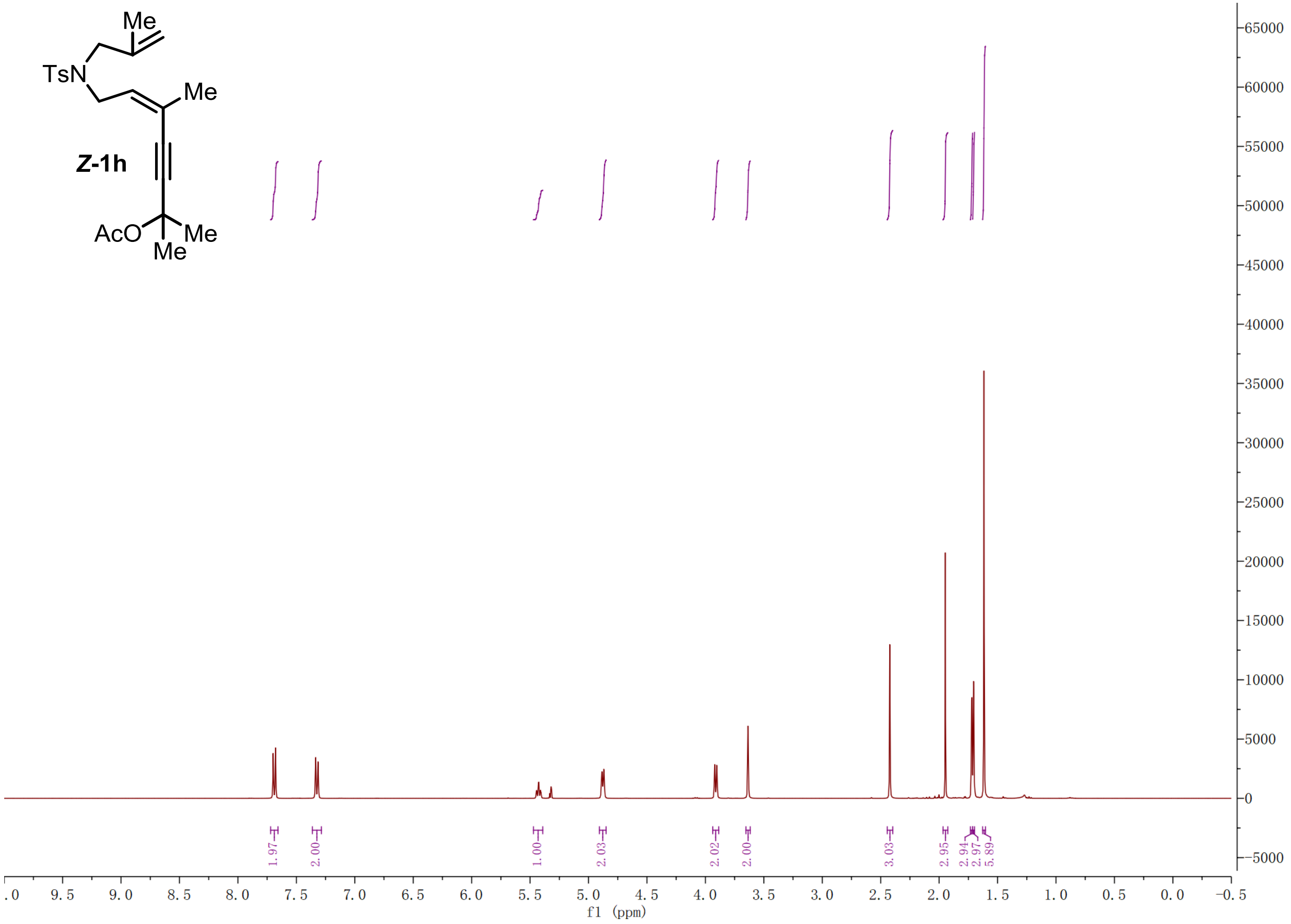

144.01
140.96
137.57
133.85
130.17
127.76
121.34
114.44
82.99
81.99
54.33
47.63
23.16
21.80
20.20
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

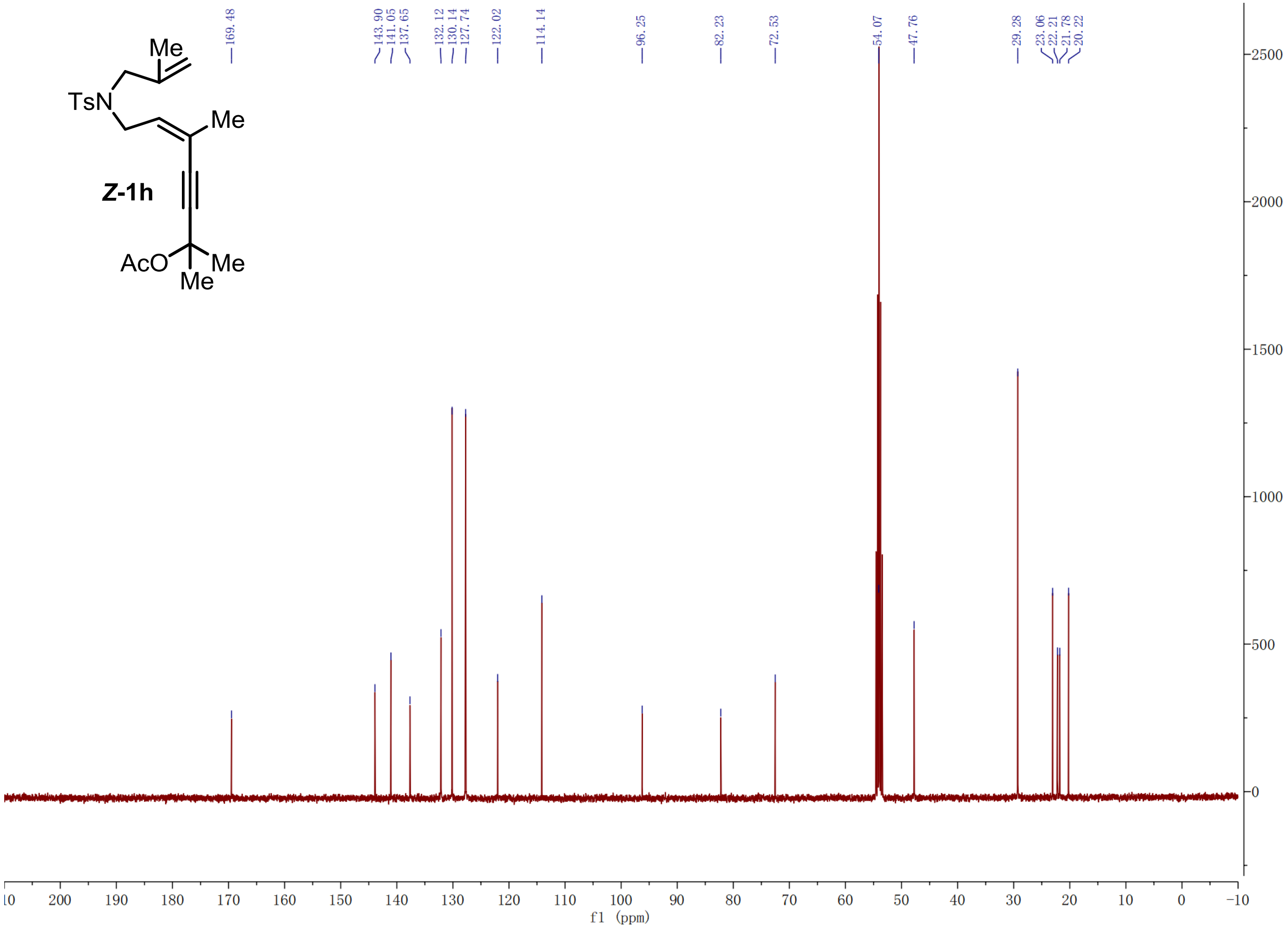

Me
TsN
Me
HO
Me
Me

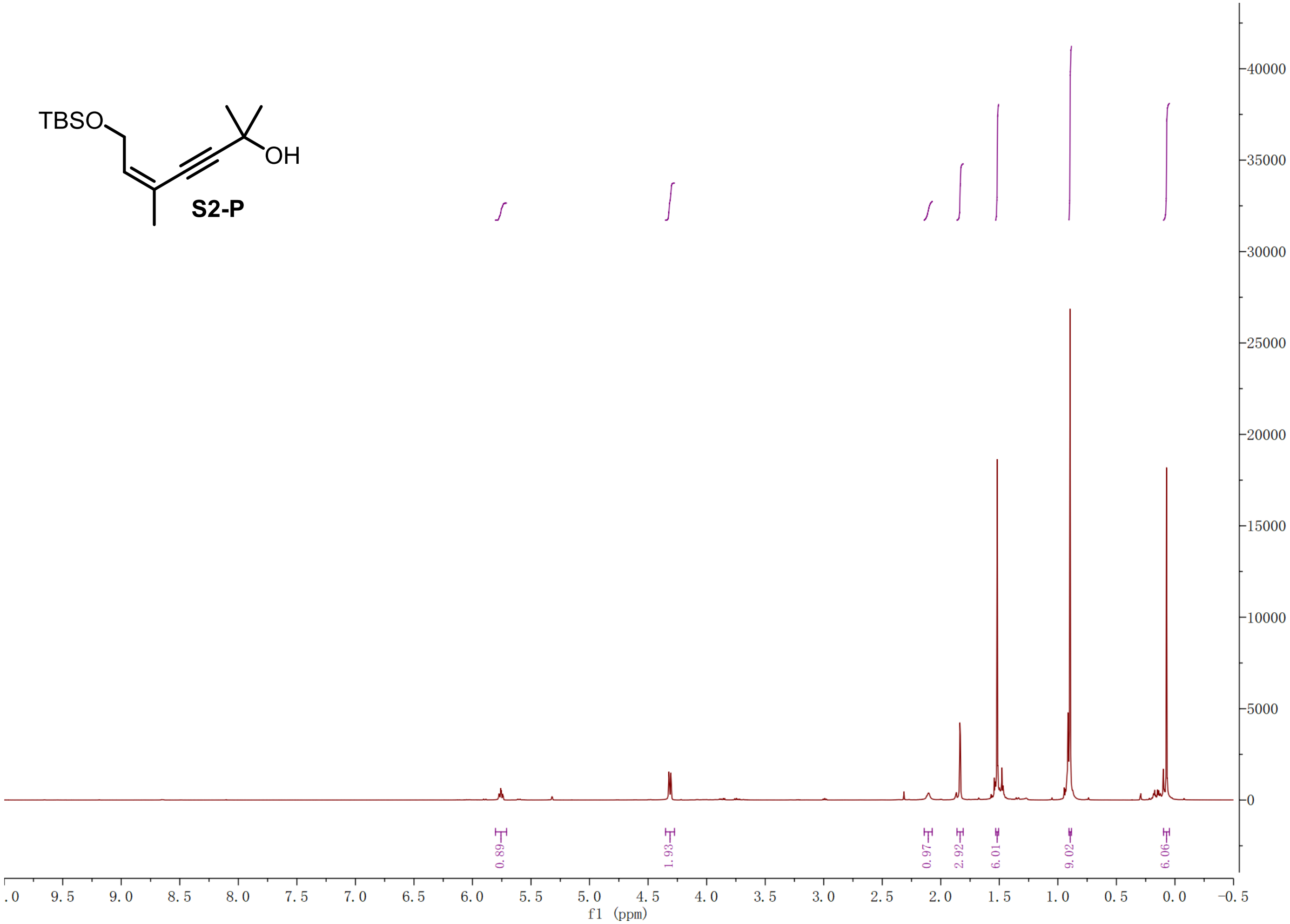
S15

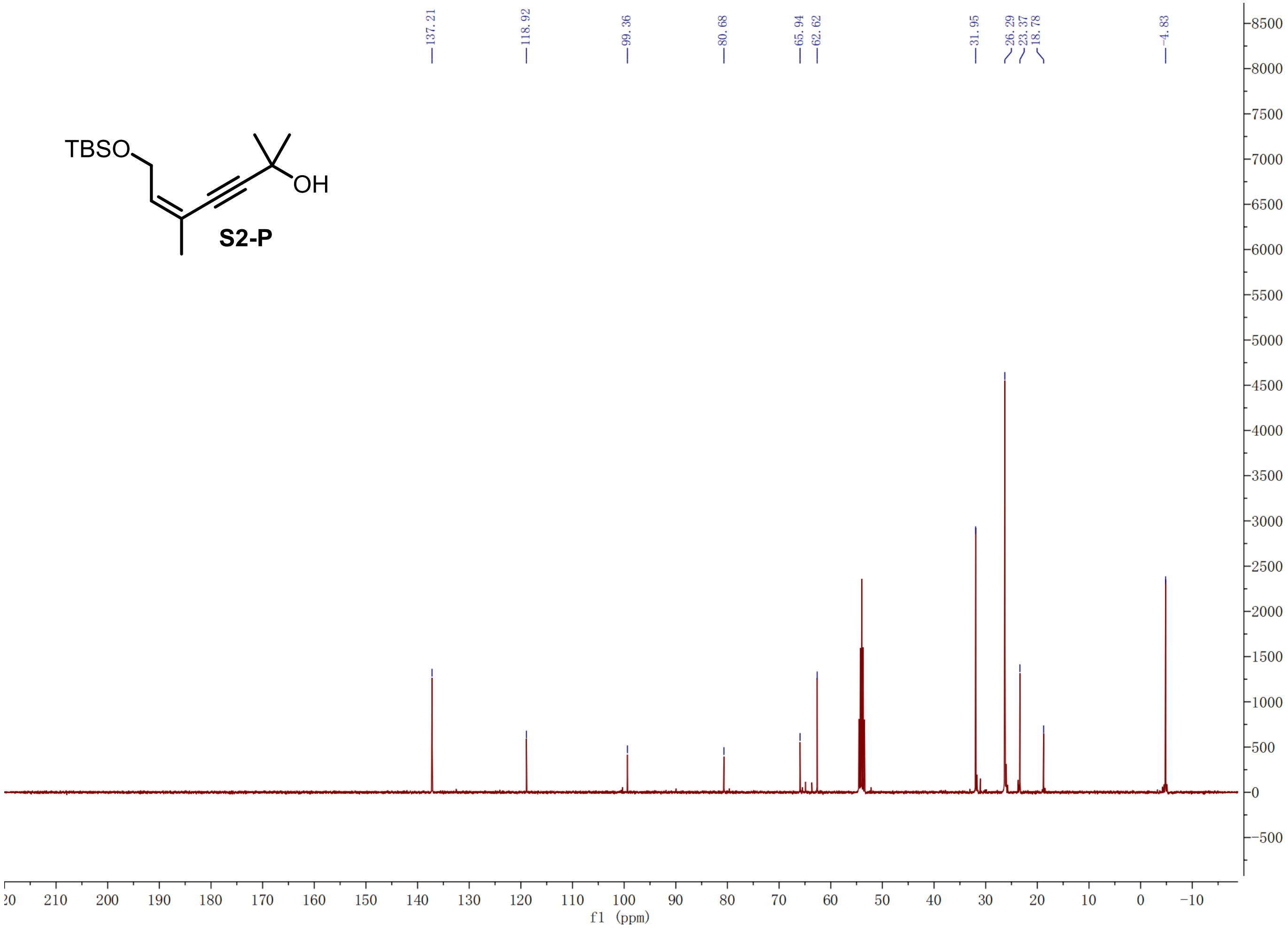

1.94
1.95
1.01
1.02
0.97
2.03
1.99
2.96
0.95
6.09
6.09
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
40000
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000

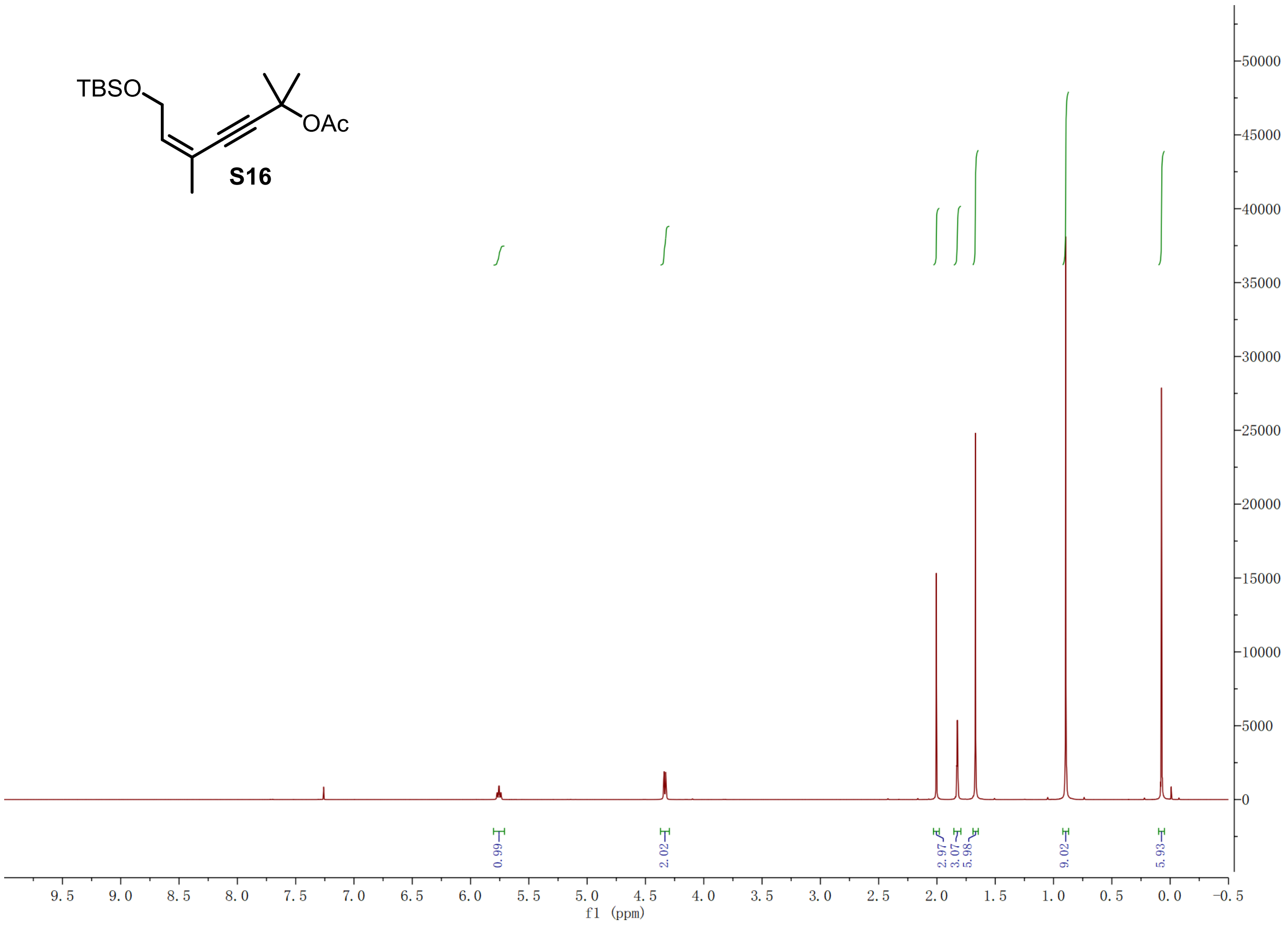

TsN
Me
Me
S15
HO
Me
Me
143.96
141.05
137.53
131.26
130.13
127.70
122.48
114.23
100.11
80.21
65.74
53.94
47.47
31.75
23.23
21.77
20.22
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

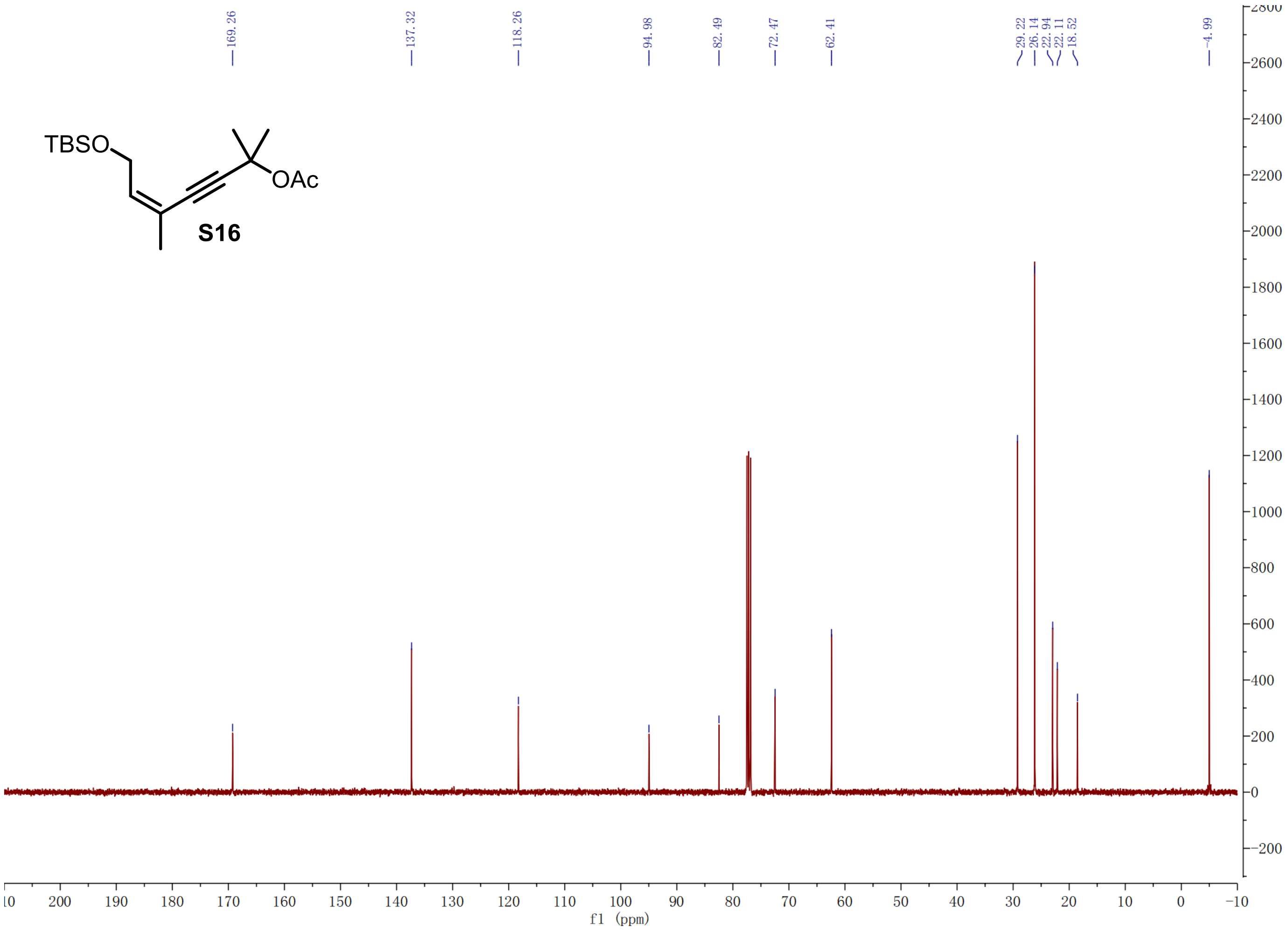

Z-1h
Me
TsN
Me
AcO
Me
Me
1.97
2.00
1.00
2.03
2.02
2.00
3.03
2.95
2.94
2.97
5.89
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000

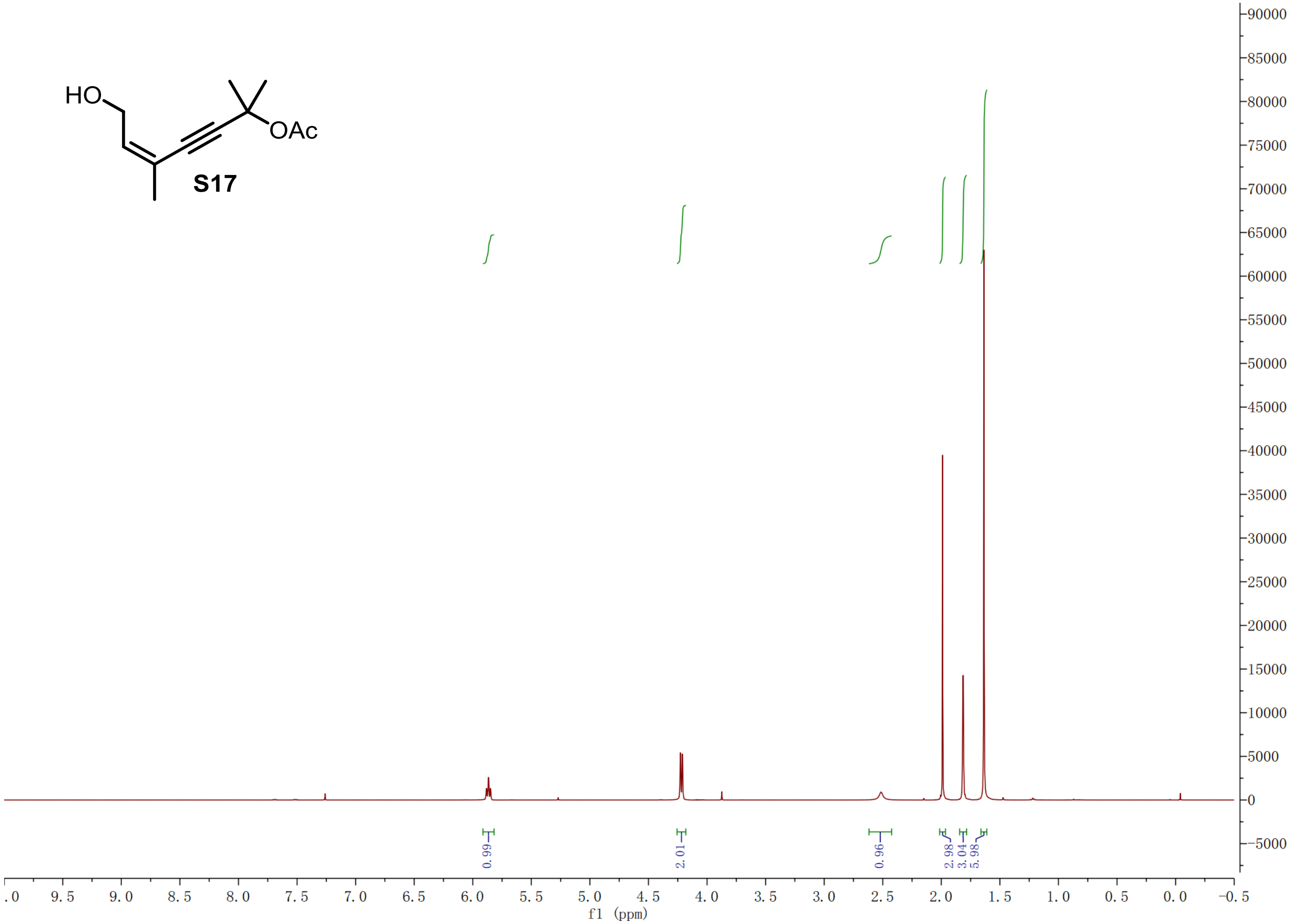

Me
TsN
Me
Z-1h
AcO
Me
Me
169.48
143.90
141.05
137.65
132.12
130.14
127.74
122.02
114.14
96.25
82.23
72.53
54.07
47.76
29.28
23.06
22.21
21.78
20.22
2500
2000
1500
1000
500
0
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

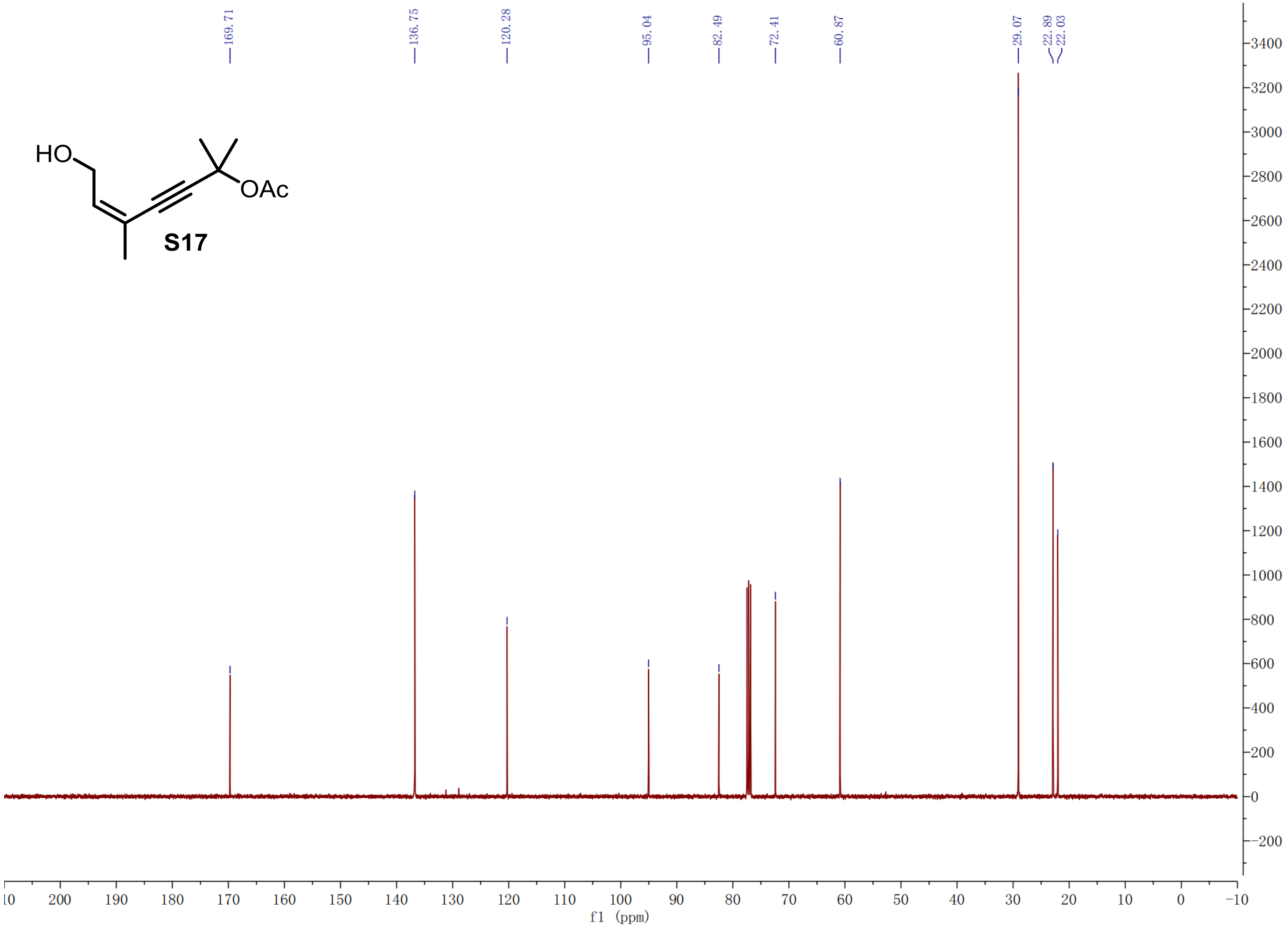

TBSO
OH
S2-P
0.89
1.93
0.97
2.92
6.01
9.02
6.06
40000
35000
30000
25000
20000
15000
10000
5000
0
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

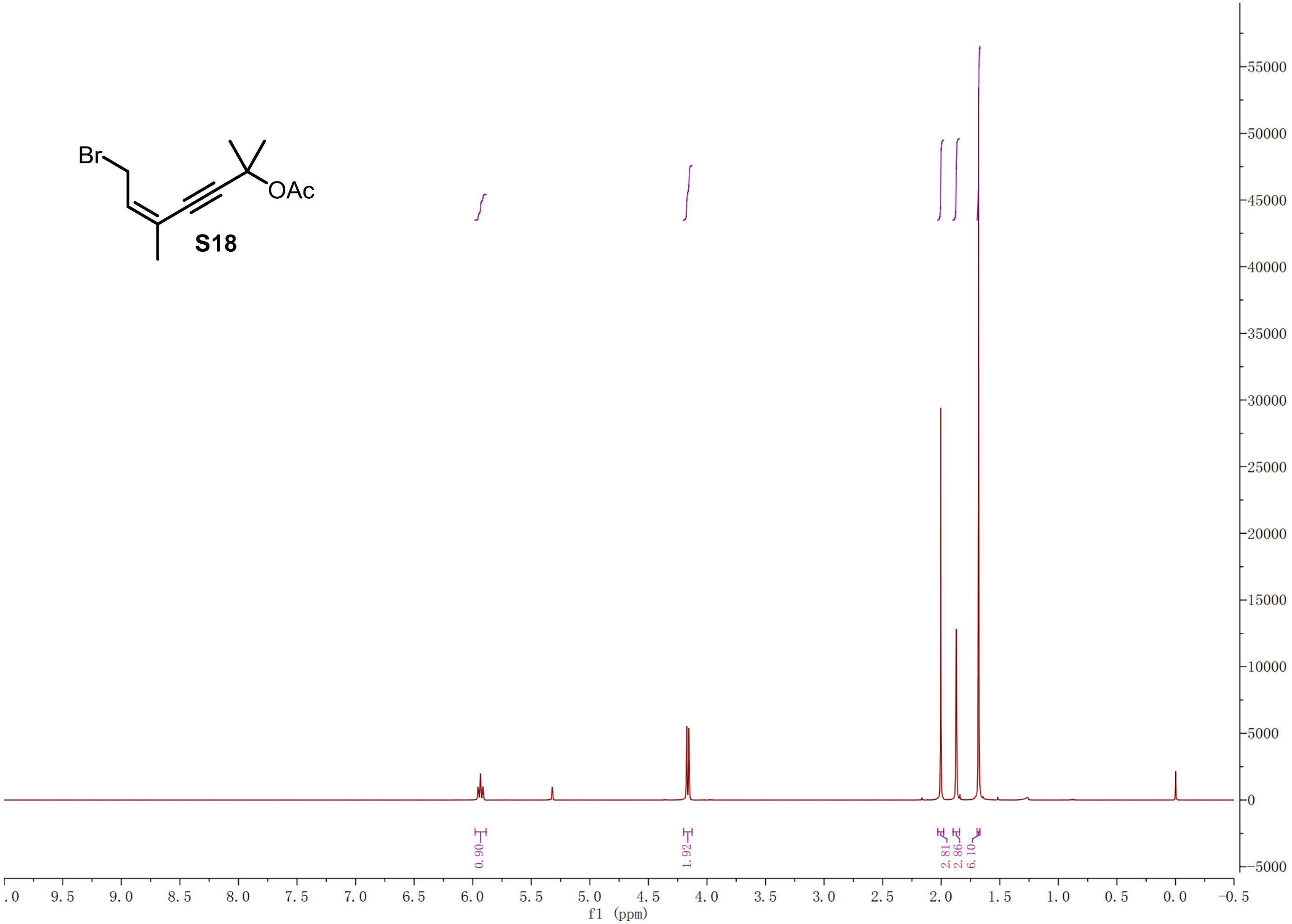

137.21
118.92
99.36
80.68
65.94
62.62
31.95
26.29
23.37
18.78
-4.83
TBSO
OH
S2-P
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


TBSO
OAc
S16
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
0.99
2.02
2.97
3.07
5.98
9.02
5.93
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)

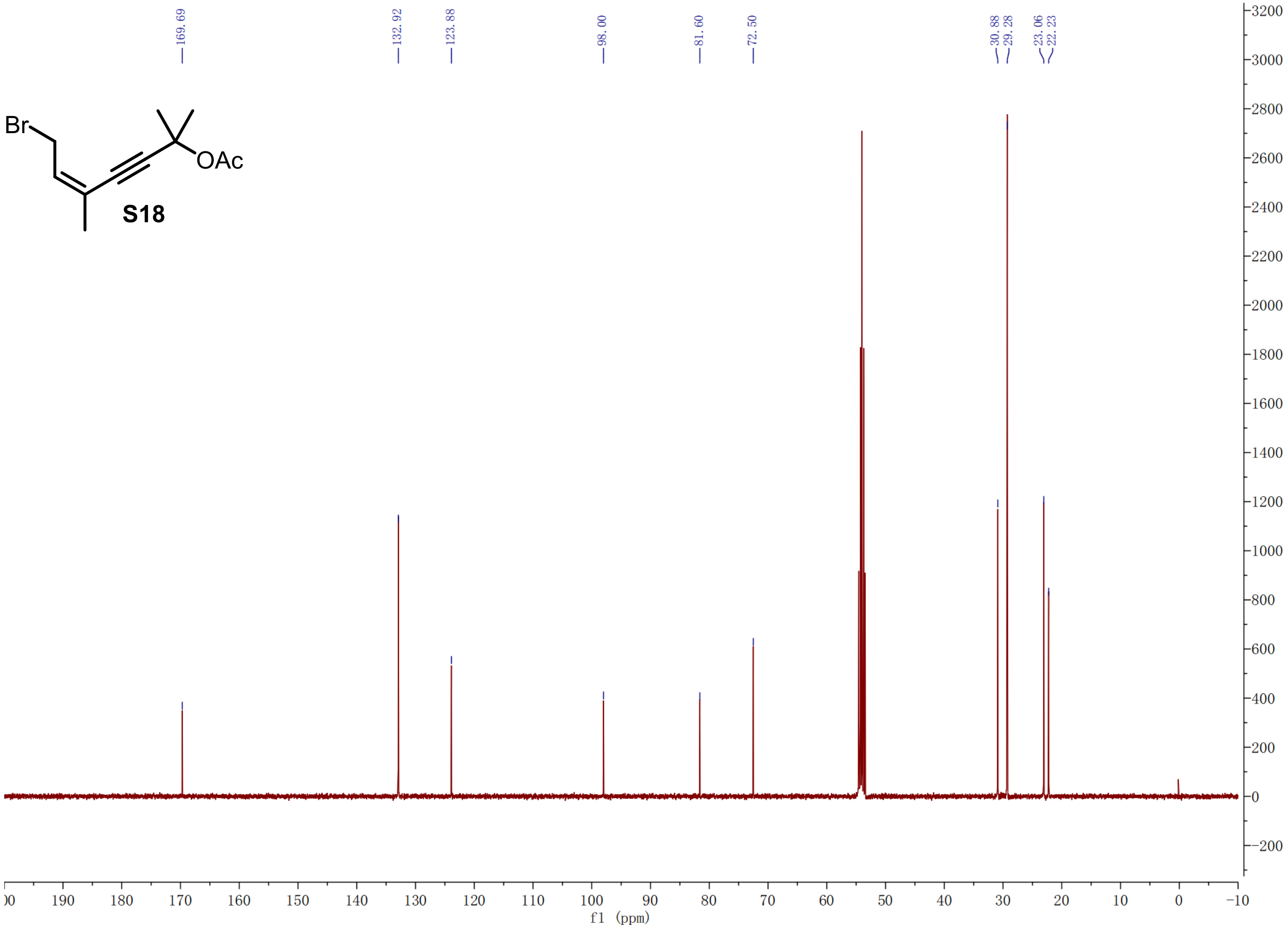

169.26
137.32
118.26
94.98
82.49
72.47
62.41
29.22
26.14
22.94
22.11
18.52
-4.99
TBSO
OAc
S16
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

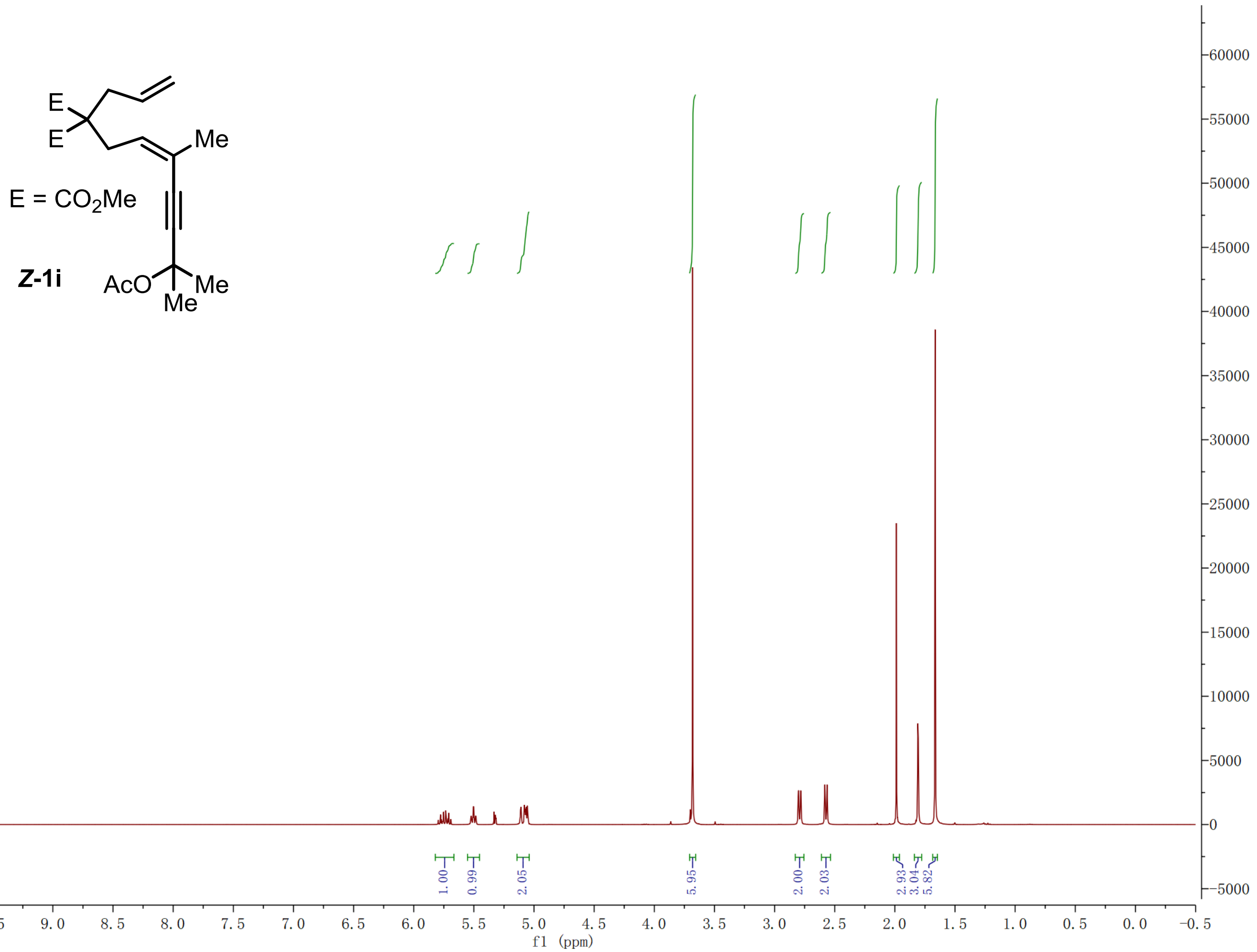

HO
OAc
S17
0.99
2.01
0.96
2.98
3.04
5.98
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
90000
85000
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000

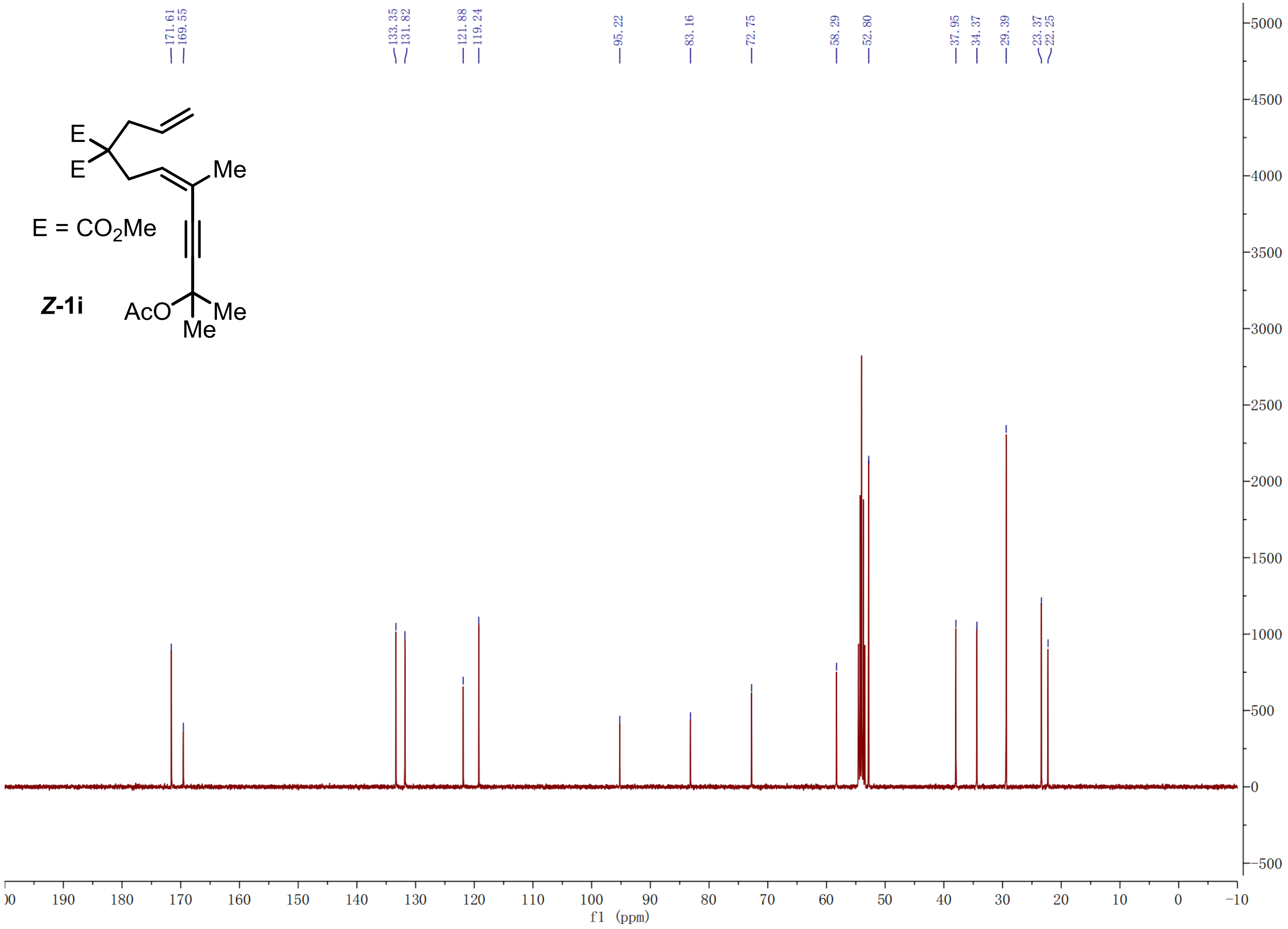

169.71
136.75
120.28
95.04
82.49
72.41
60.87
29.07
22.89
22.03
HO
OAc
S17
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

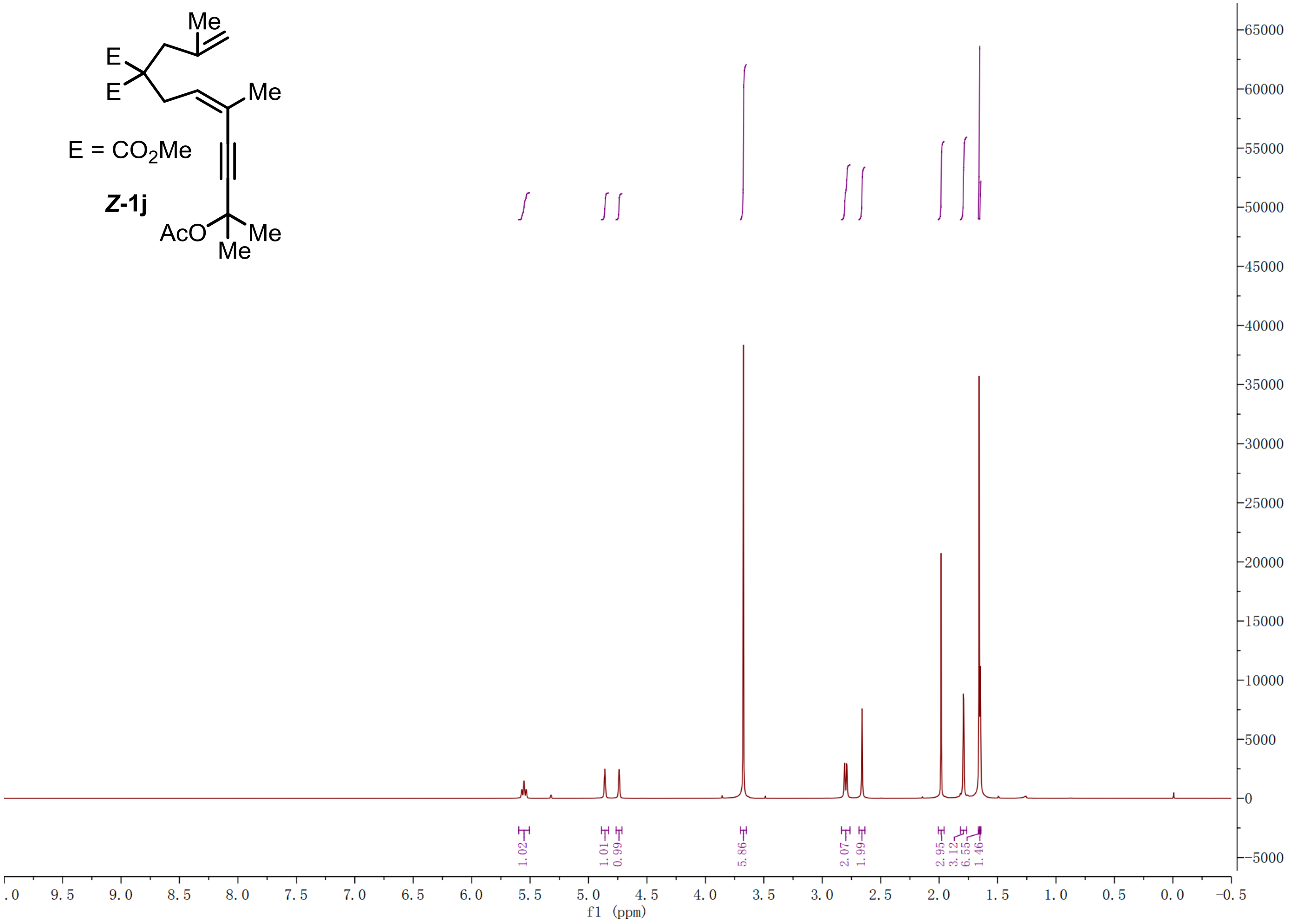

Br
OAc
0.90
1.92
2.81
2.86
6.10
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

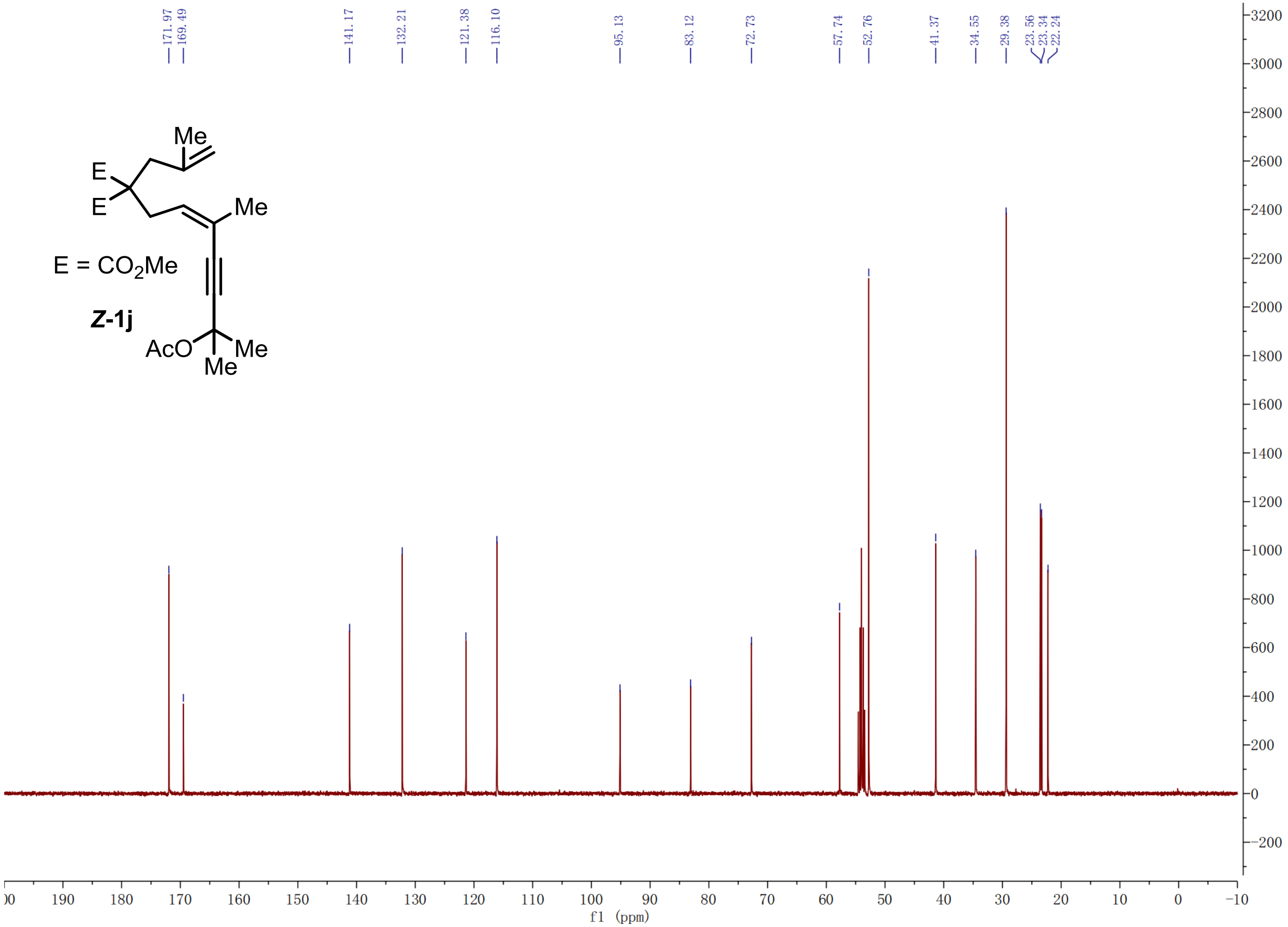
S18


169.69
132.92
123.88
98.00
81.60
72.50
30.88
29.28
23.06
22.23
Br
OAc
S18
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200
)0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


E
E
Me
E = CO2Me
Z-1i
AcO
Me
Me
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
1.00
0.99
2.05
5.95
2.00
2.03
2.93
3.04
5.82
.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)

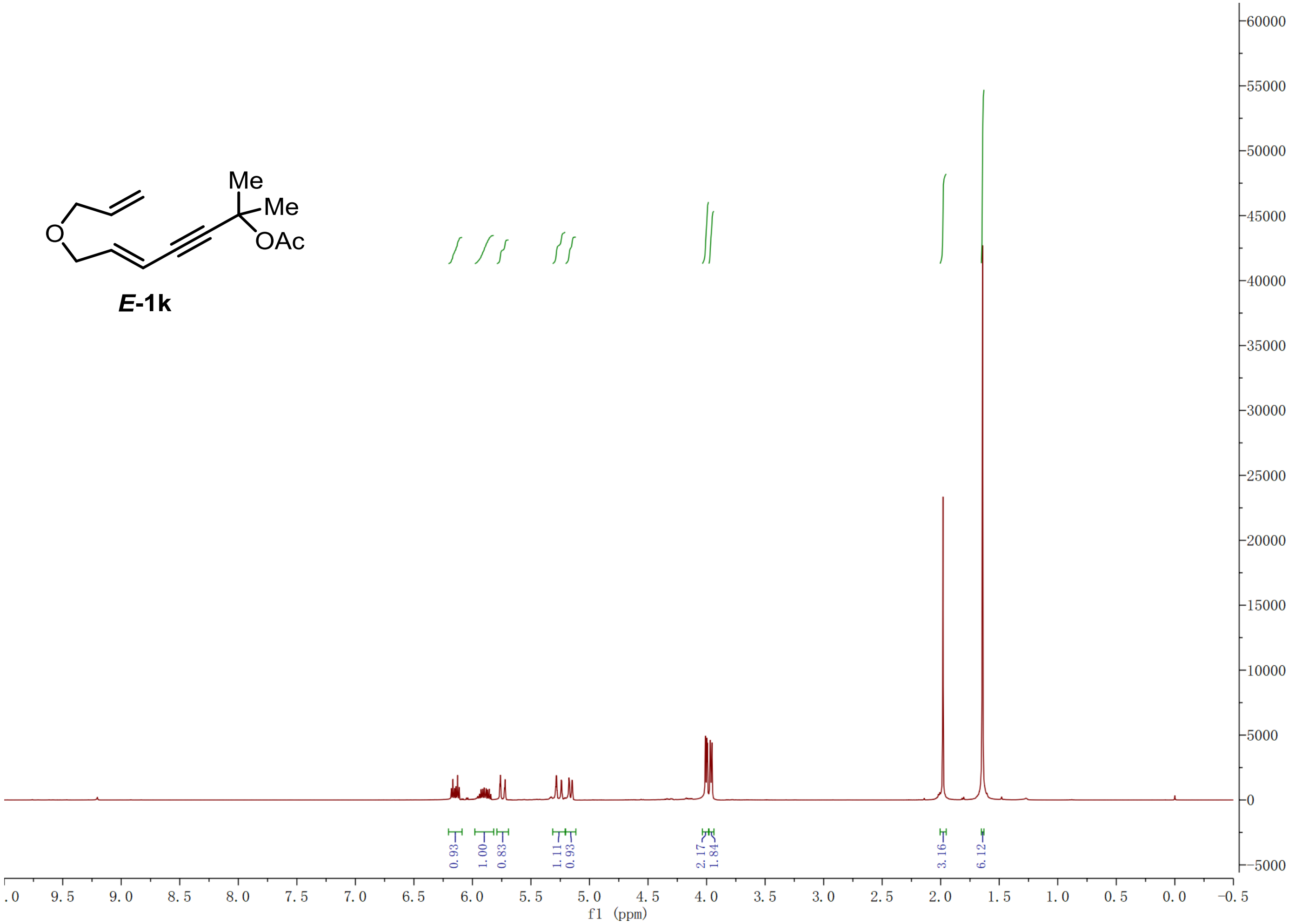

171.61
169.55
133.35
131.82
121.88
119.24
95.22
83.16
72.75
58.29
52.80
37.95
34.37
29.39
23.37
22.25
E
E
Me
E = CO$_2$Me
Z-1i
AcO
Me
Me
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
)0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

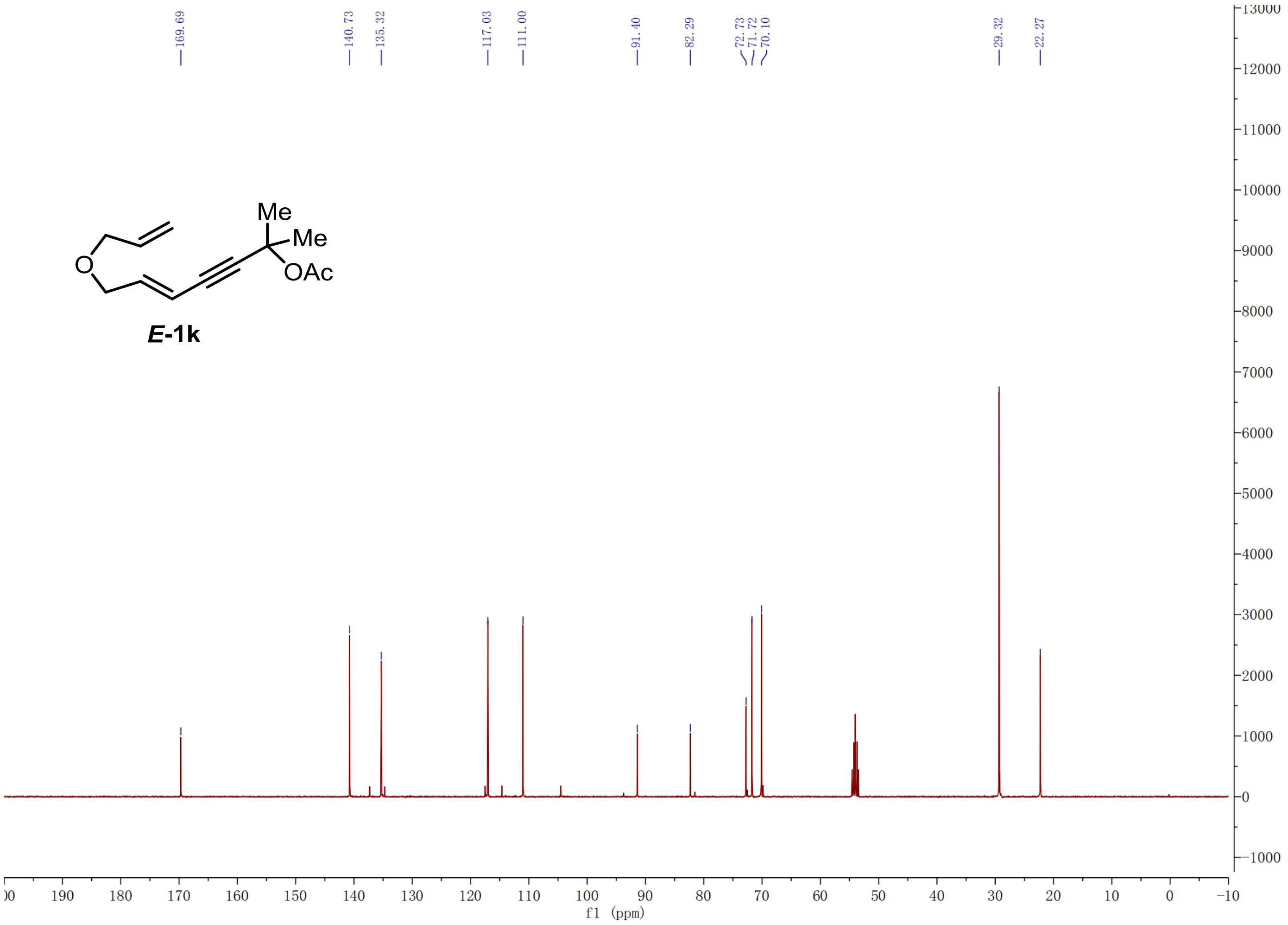

Me
E
E
Me
E = CO$_2$Me
Z-1j
AcO
Me
Me
1.02
1.01
0.99
5.86
2.07
1.99
2.95
3.12
6.55
1.46
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
−5000
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

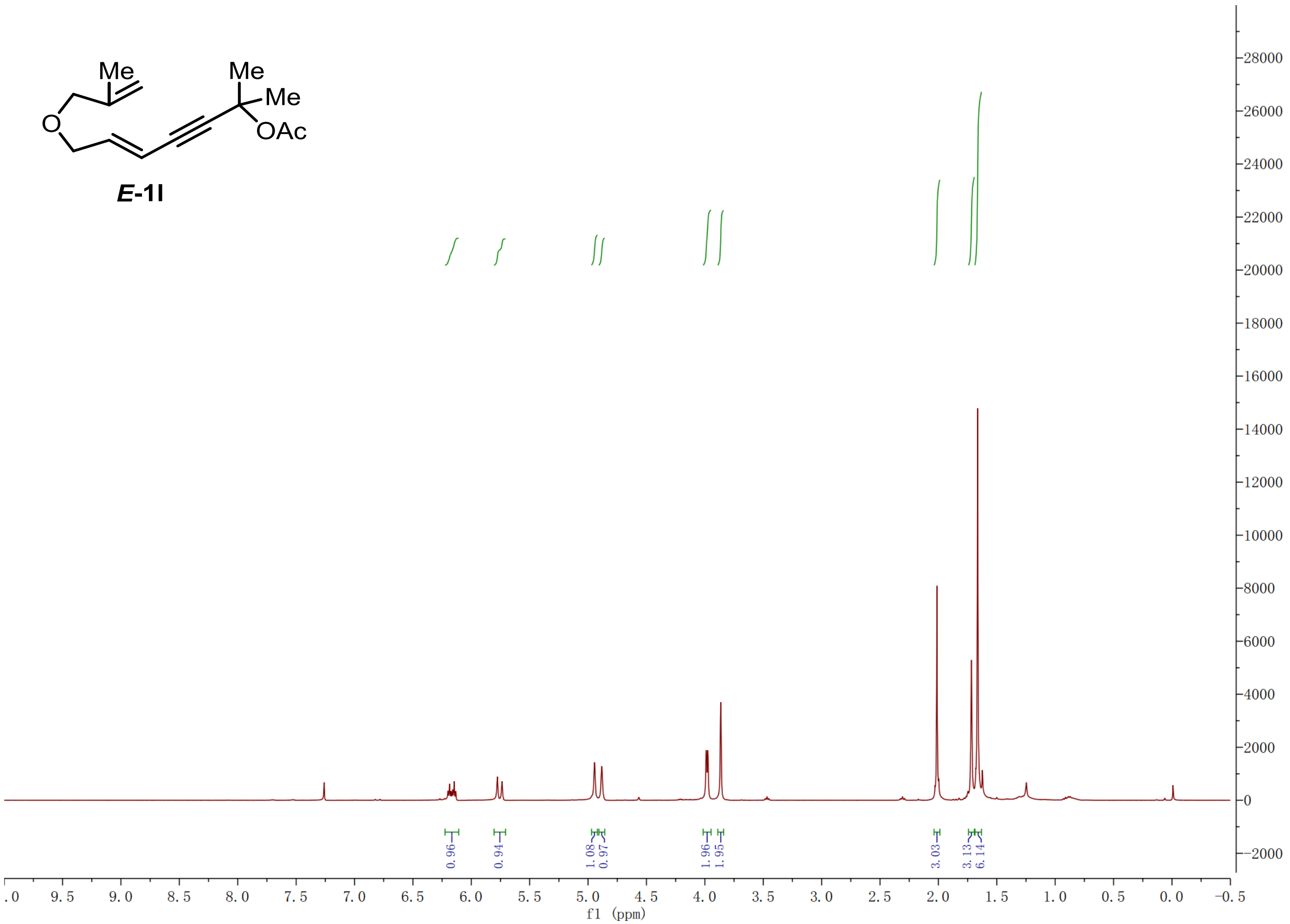

E = CO$_2$Me

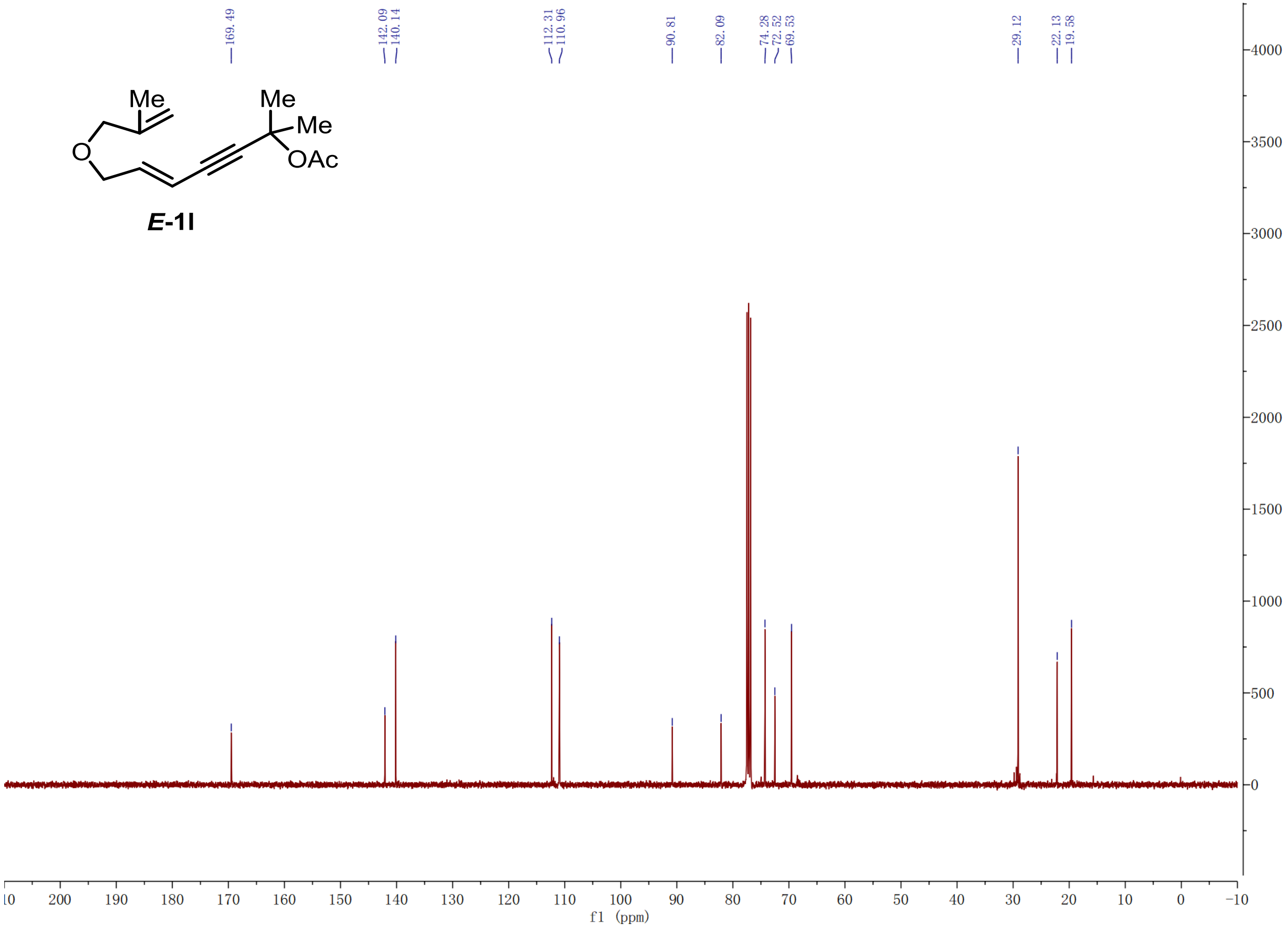
***Z*-1j**

171.97
169.49
141.17
132.21
121.38
116.10
95.13
83.12
72.73
57.74
52.76
41.37
34.55
29.38
23.56
23.34
22.24
Me
E
E
Me
AcO
Me
Me
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


Me
Me
OAc
O
E-1k
0.93
1.00
0.83
1.11
0.93
2.17
1.84
3.16
6.12
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
−5000
.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)

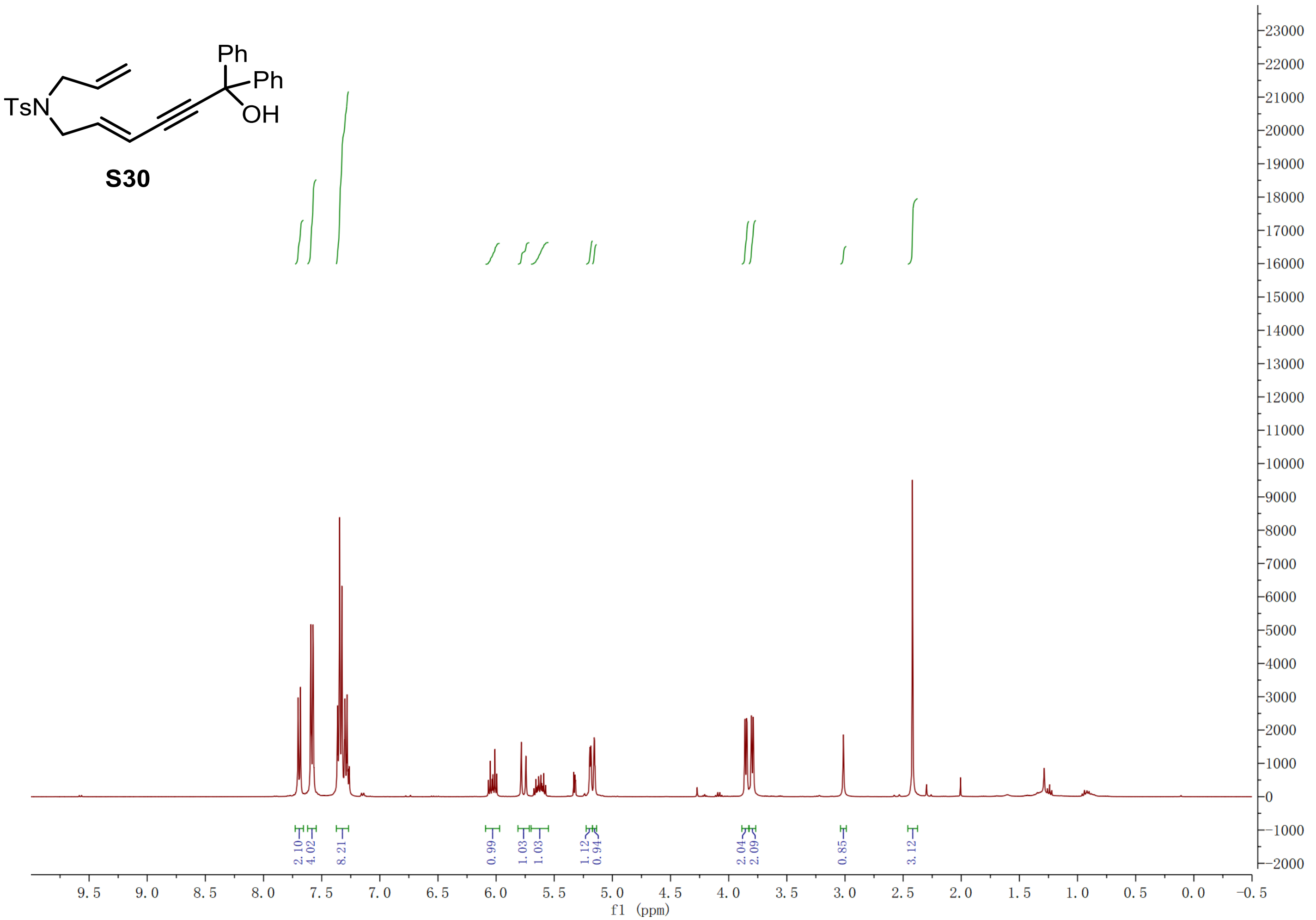

169.69
140.73
135.32
117.03
111.00
91.40
82.29
72.73
71.72
70.10
29.32
22.27
Me
Me
O
OAc
E-1k
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Me
Me
Me
O
OAc
E-1l
0.96
0.94
1.08
0.97
1.96
1.95
3.03
3.13
6.14
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
.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*-1l**

169.49
142.09
140.14
112.31
110.96
90.81
82.09
74.28
72.52
69.53
29.12
22.13
19.58
Me
Me
Me
O
OAc
4000
3500
3000
2500
2000
1500
1000
500
0
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

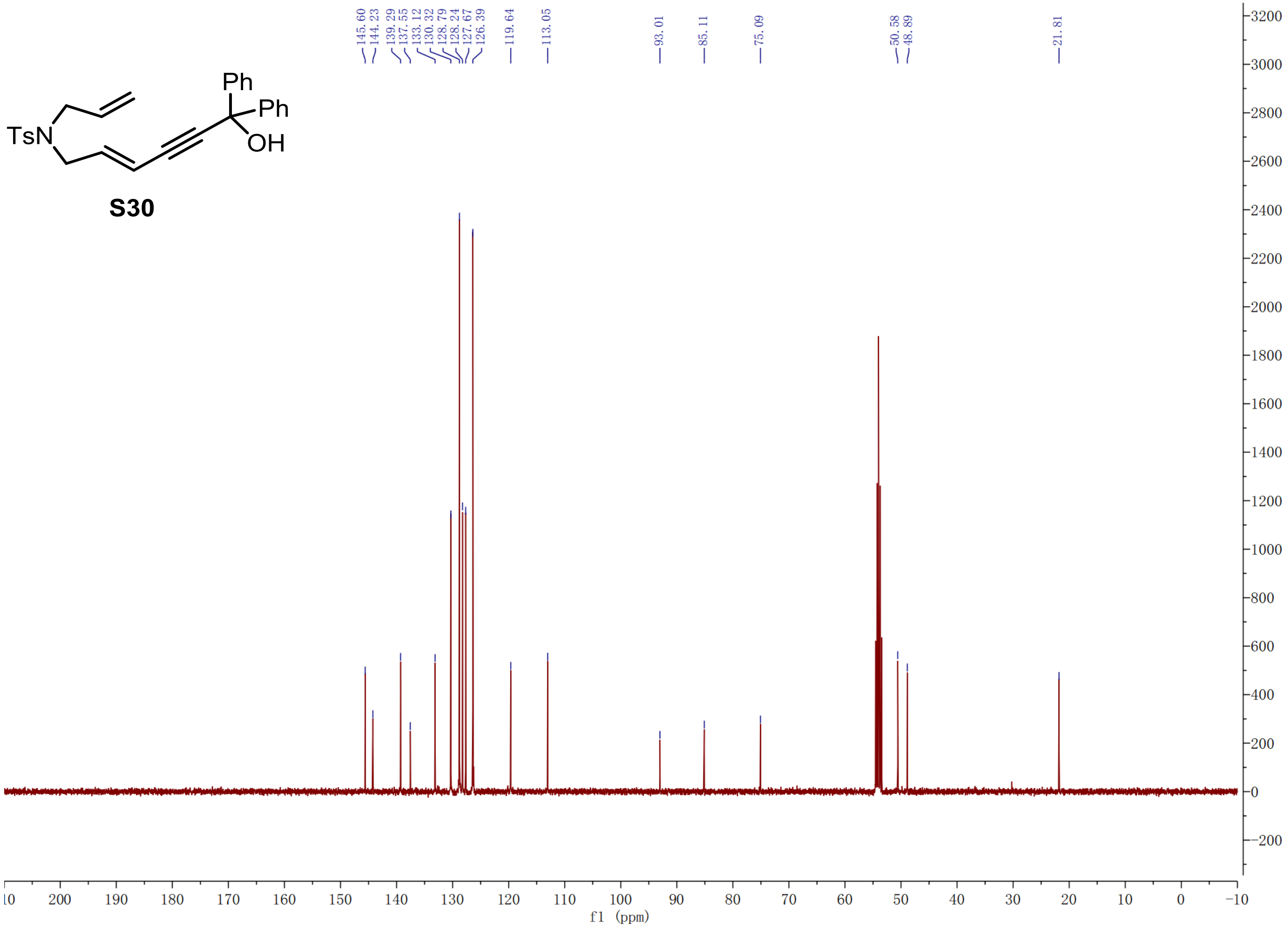

TsN
Ph
Ph
OH

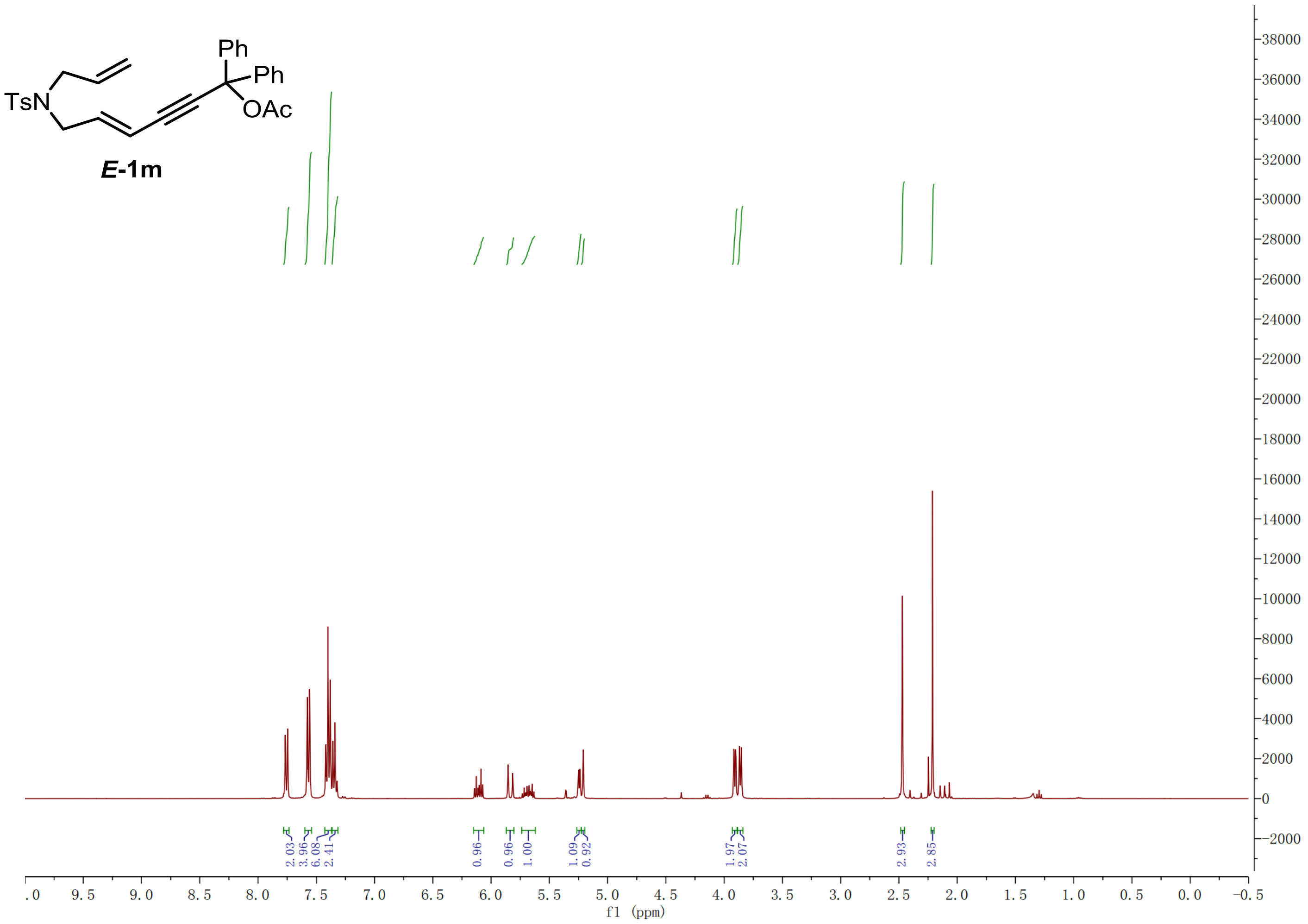
S30

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
2.10
4.02
8.21
0.99
1.03
1.03
1.12
0.94
2.04
2.09
0.85
3.12
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)

Ph
Ph
TsN
OH

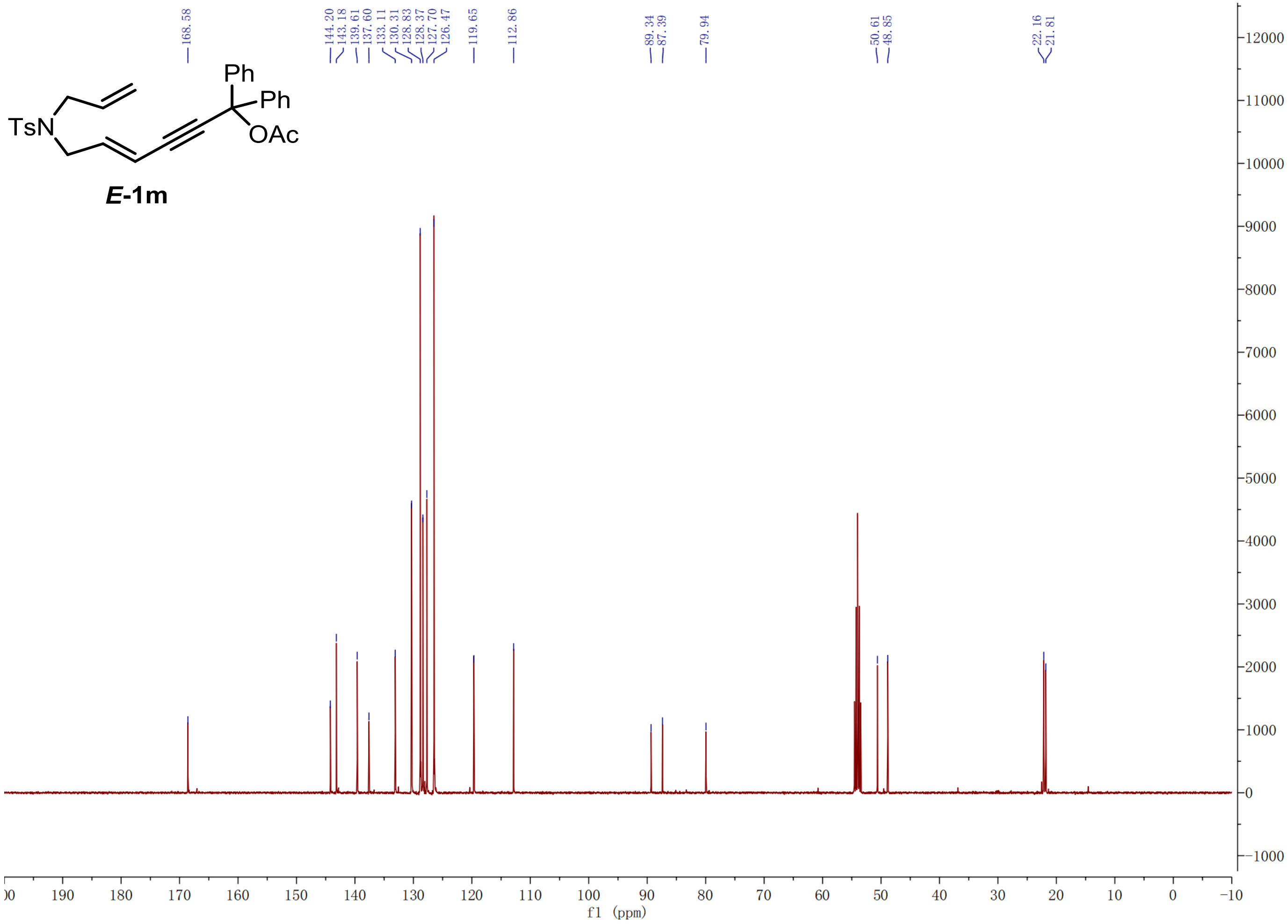
S30


145.60
144.23
139.29
137.55
133.12
130.32
128.79
128.24
127.67
126.39
119.64
113.05
93.01
85.11
75.09
50.58
48.89
21.81
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

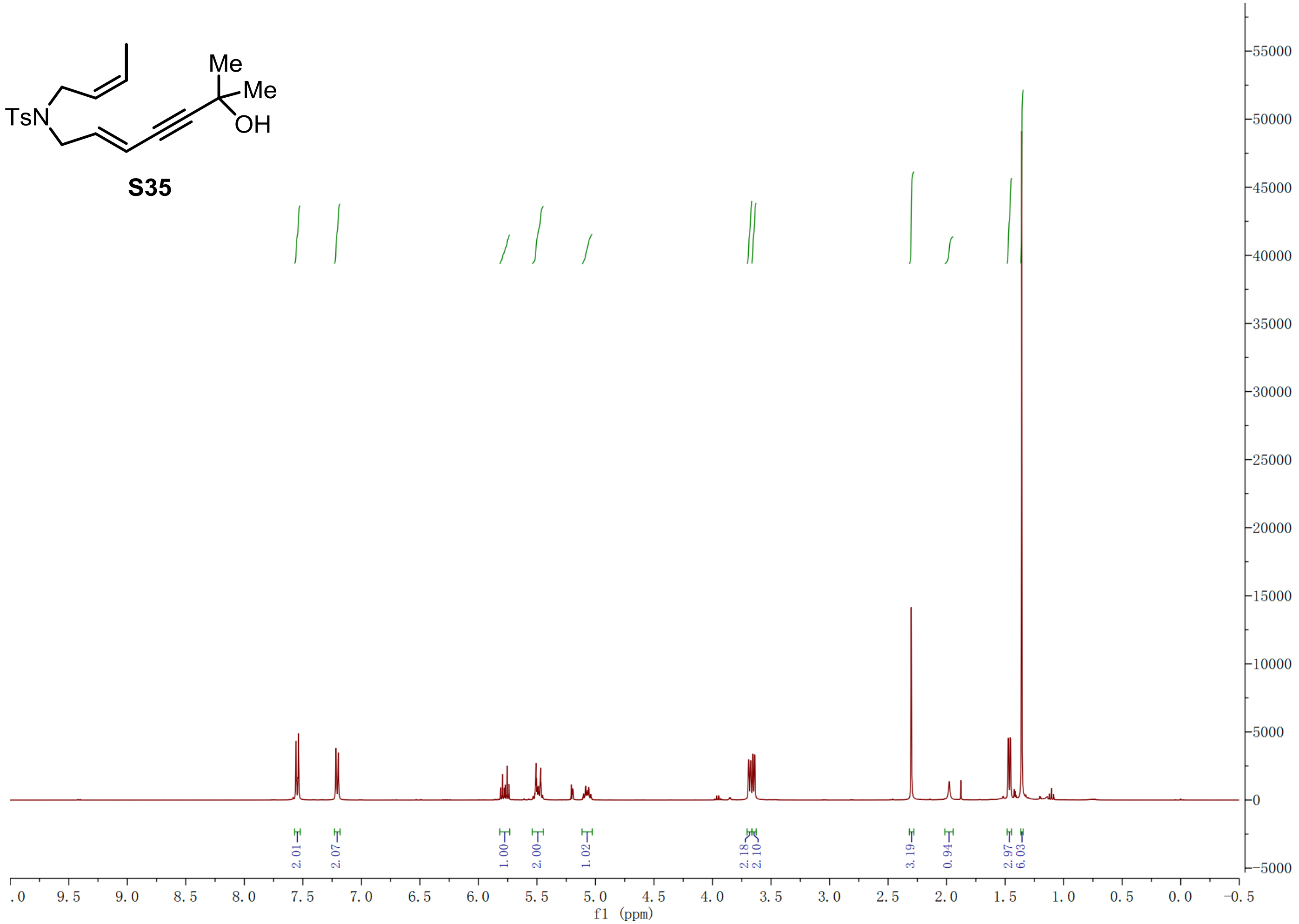


TsN
Ph
Ph
OAc
2.03
3.96
6.08
2.41
0.96
0.96
1.00
1.09
0.92
1.97
2.07
2.93
2.85
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000

***E*-1m**


E-1m

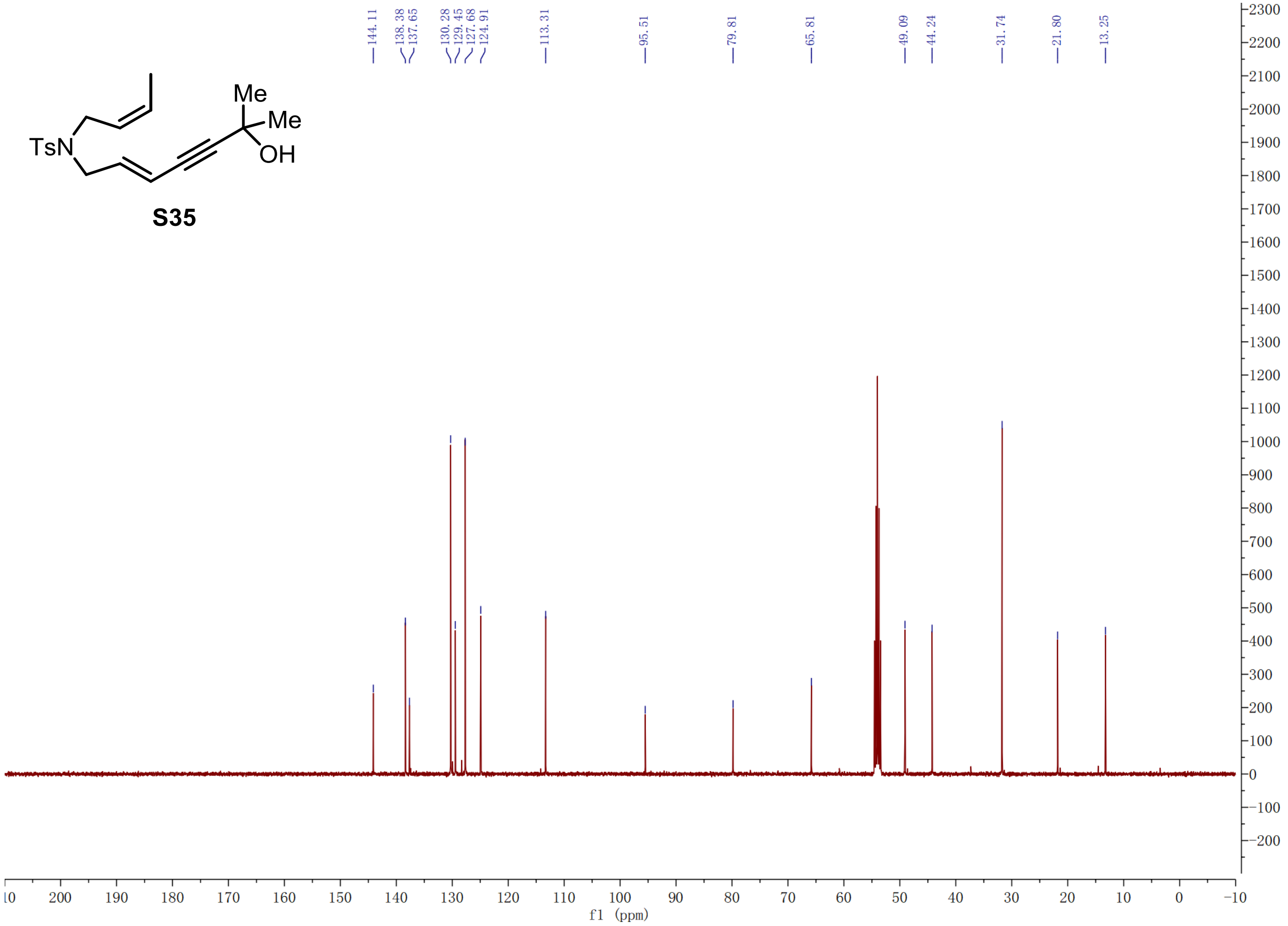
168.58
144.20
143.18
139.61
137.60
133.11
130.31
128.83
128.37
127.70
126.47
119.65
112.86
89.34
87.39
79.94
50.61
48.85
22.16
21.81
TsN
Ph
Ph
OAc
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

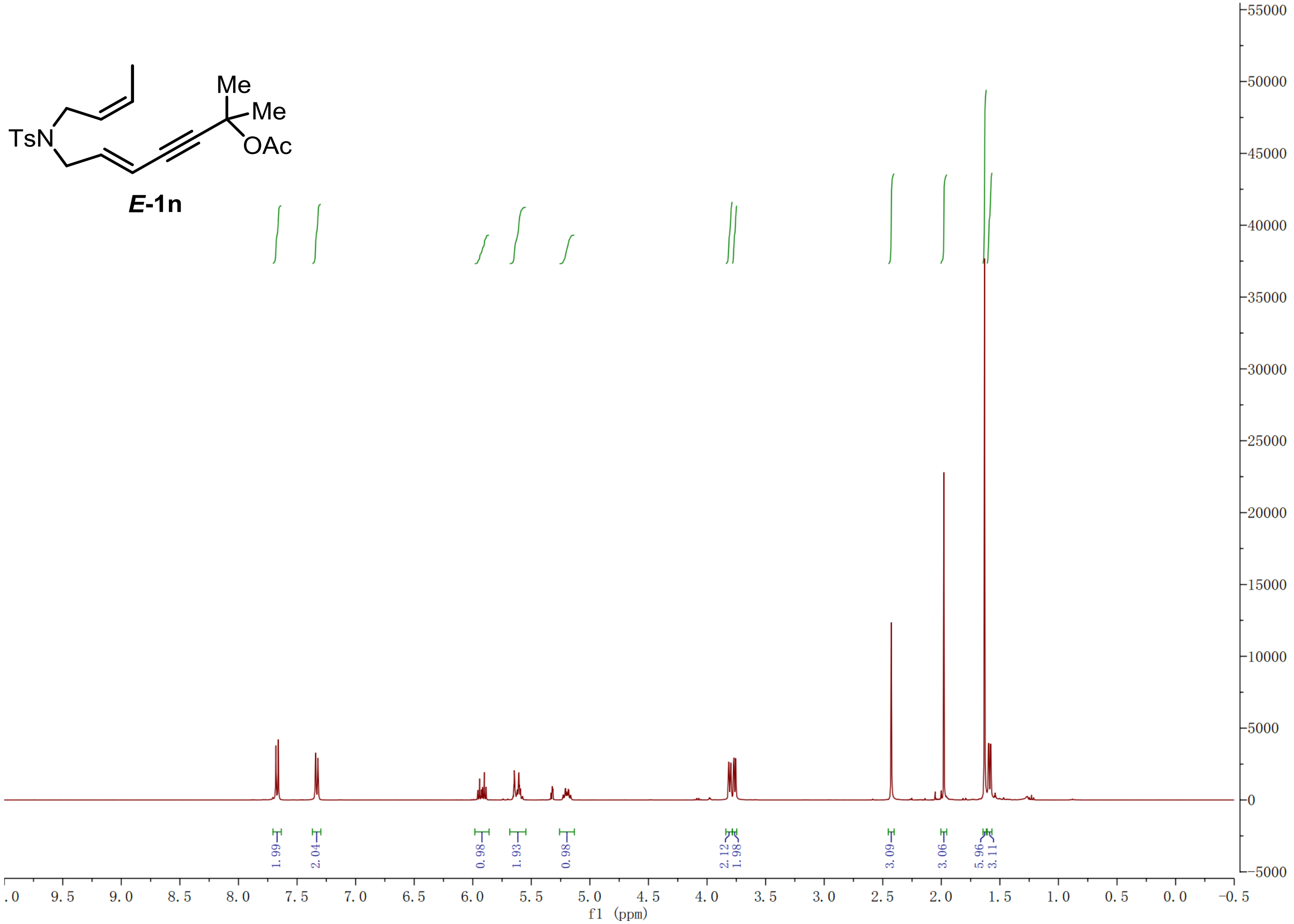

Me
Me
TsN
OH
2.01
2.07
1.00
2.00
1.02
2.18
2.10
3.19
0.94
2.97
6.03
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
−5000
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

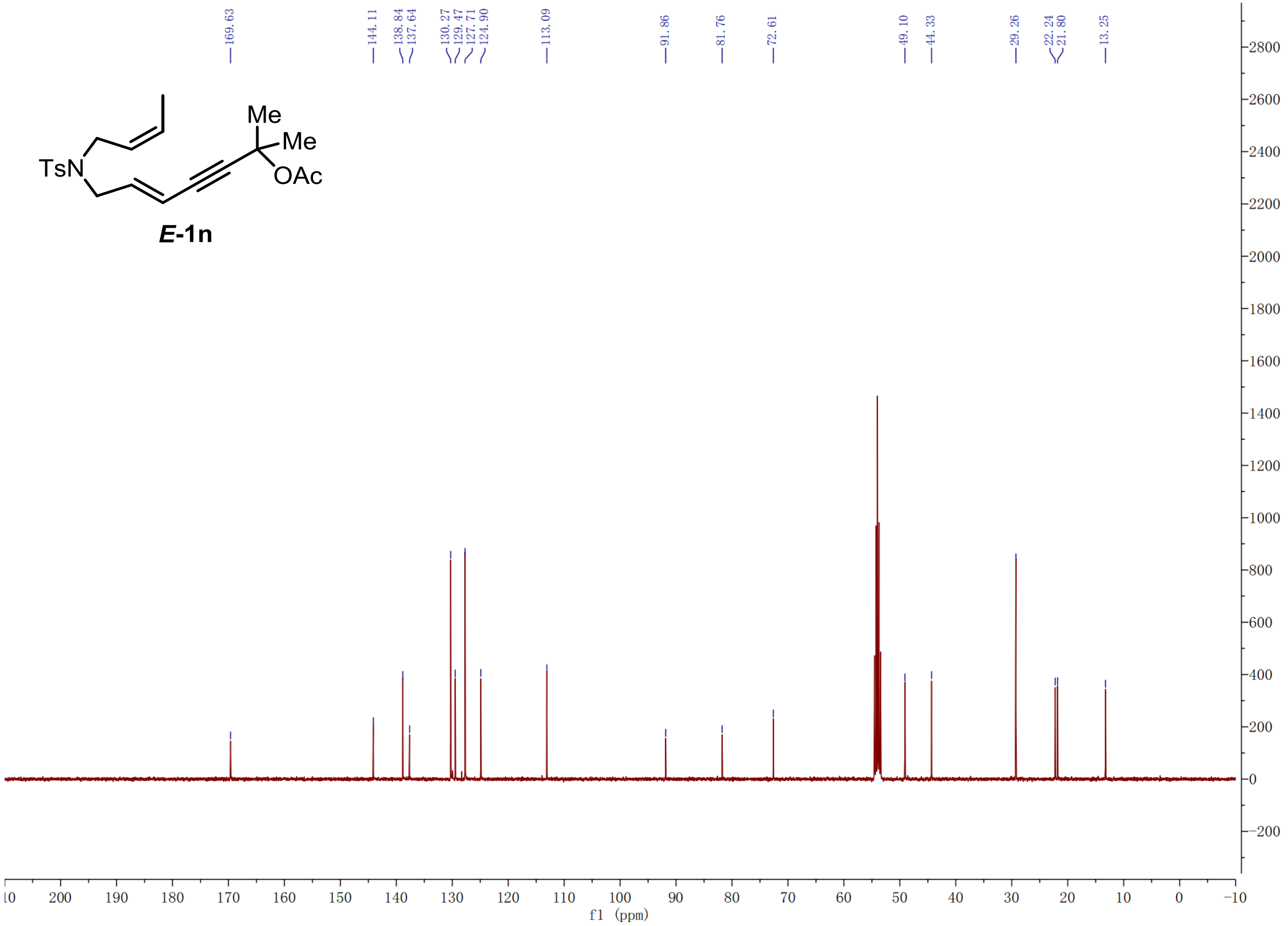
S35

Me
Me
OH
TsN

S35

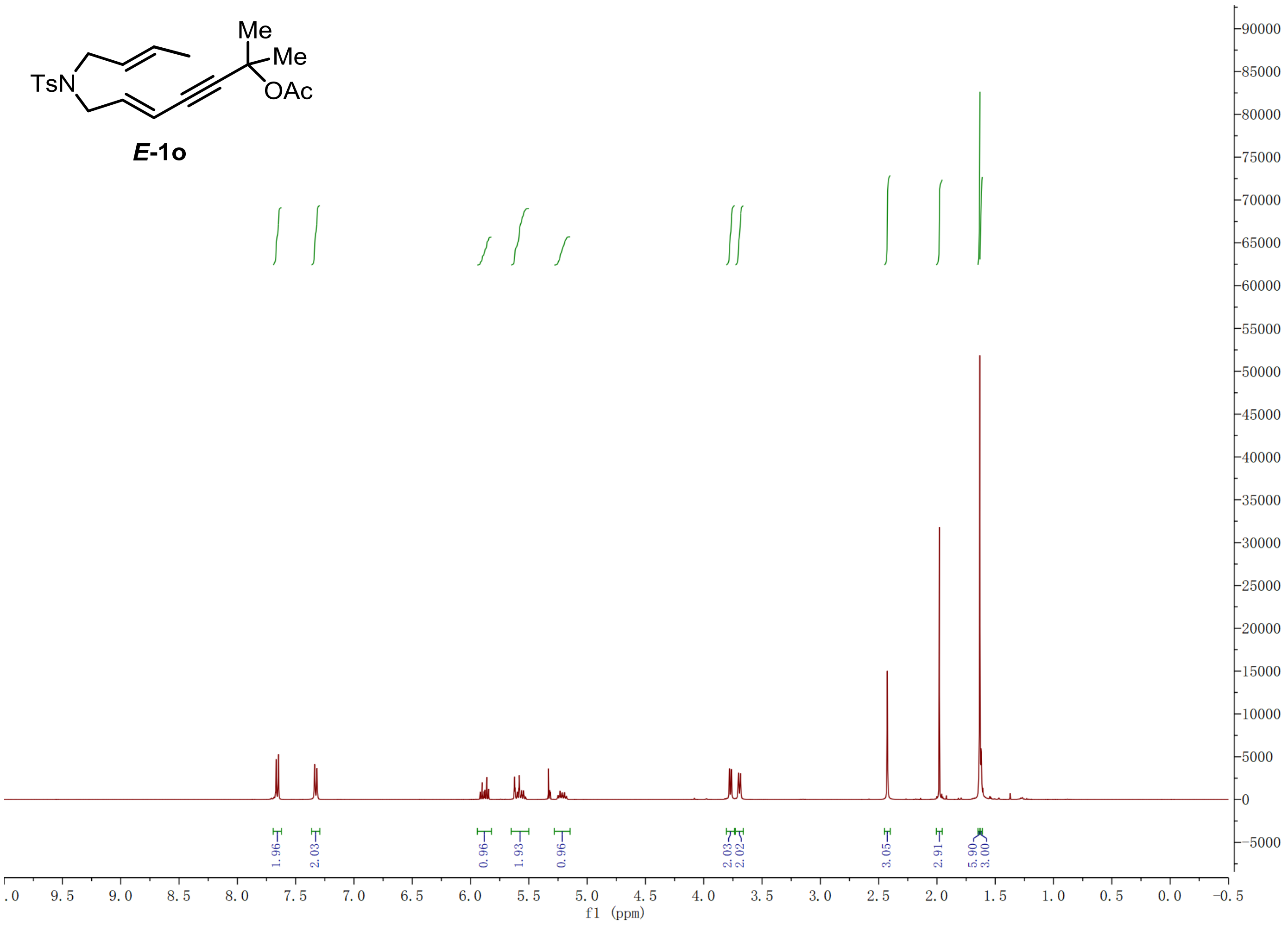

144.11
138.38
137.65
130.28
129.45
127.68
124.91
113.31
95.51
79.81
65.81
49.09
44.24
31.74
21.80
13.25
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


TsN
Me
Me
OAc
E-1n
1.99
2.04
0.98
1.93
0.98
2.12
1.98
3.09
3.06
5.96
3.11
.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

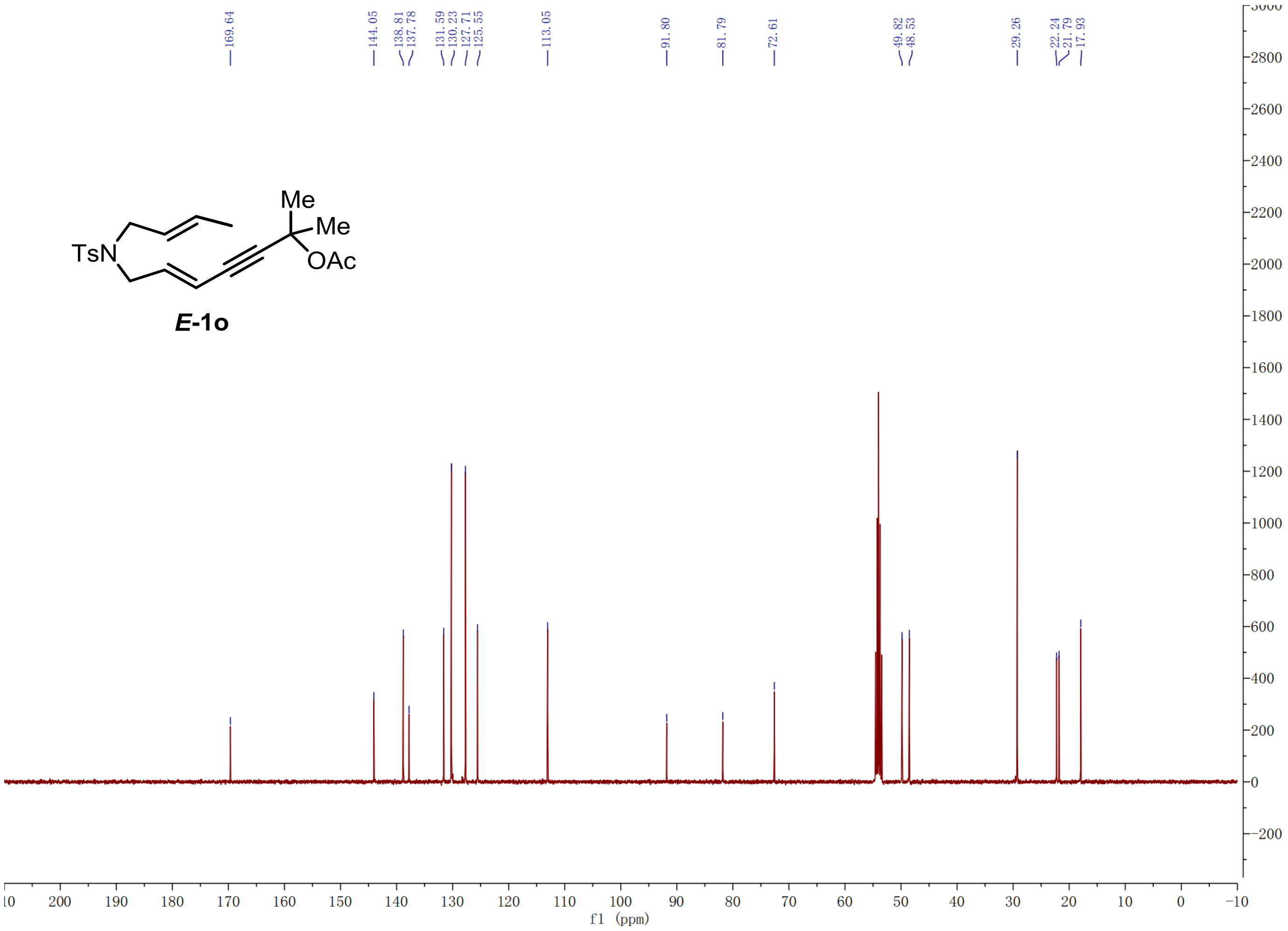


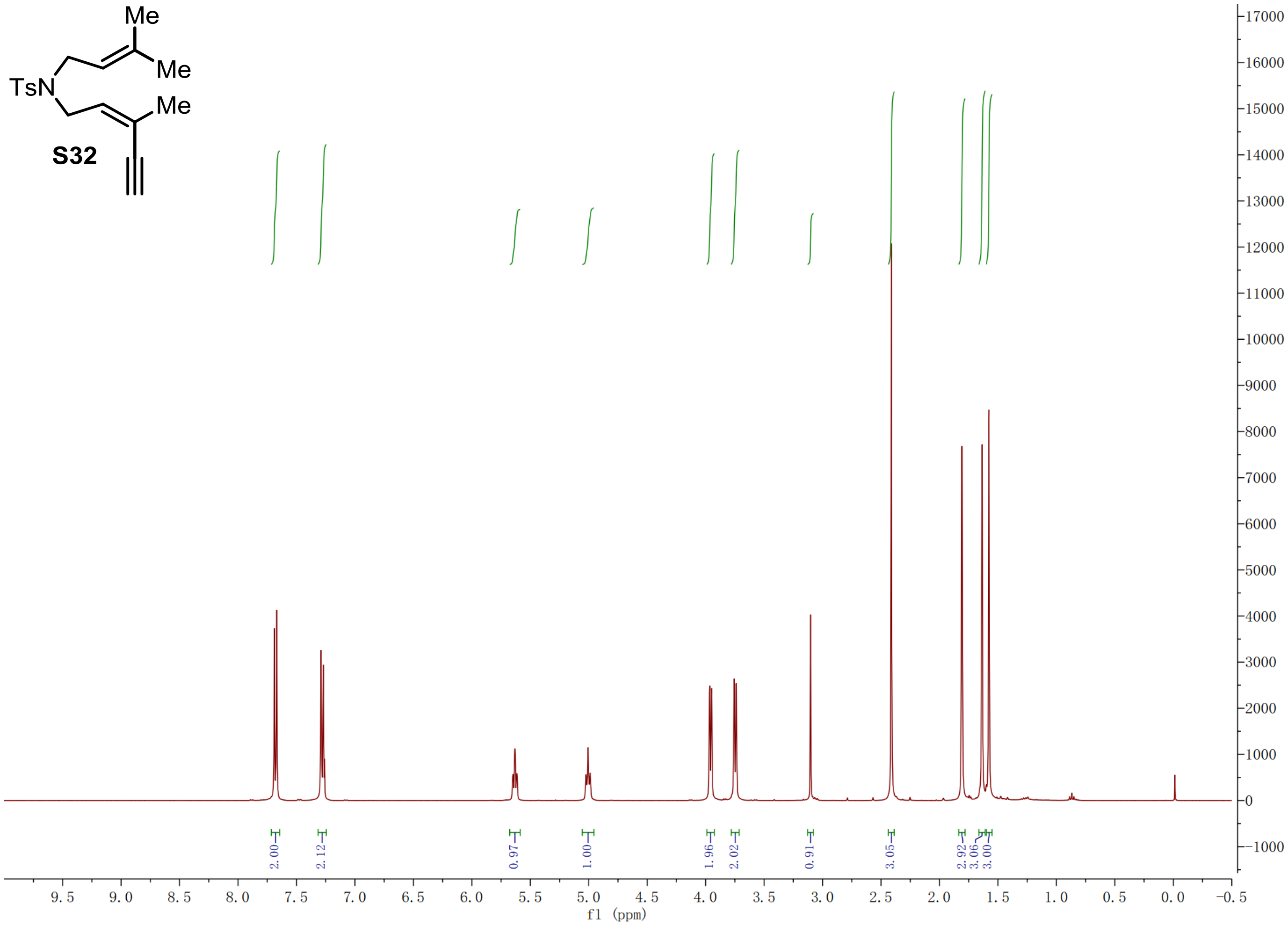
E-1n

169.63
144.11
138.84
137.64
130.27
129.47
127.71
124.90
113.09
91.86
81.76
72.61
49.10
44.33
29.26
22.24
21.80
13.25
TsN
Me
Me
OAc
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


***E*-1o**

TsN
Me
Me
OAc
1.96
2.03
0.96
1.93
0.96
2.03
2.02
3.05
2.91
5.90
3.00
.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)
90000
85000
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
−5000

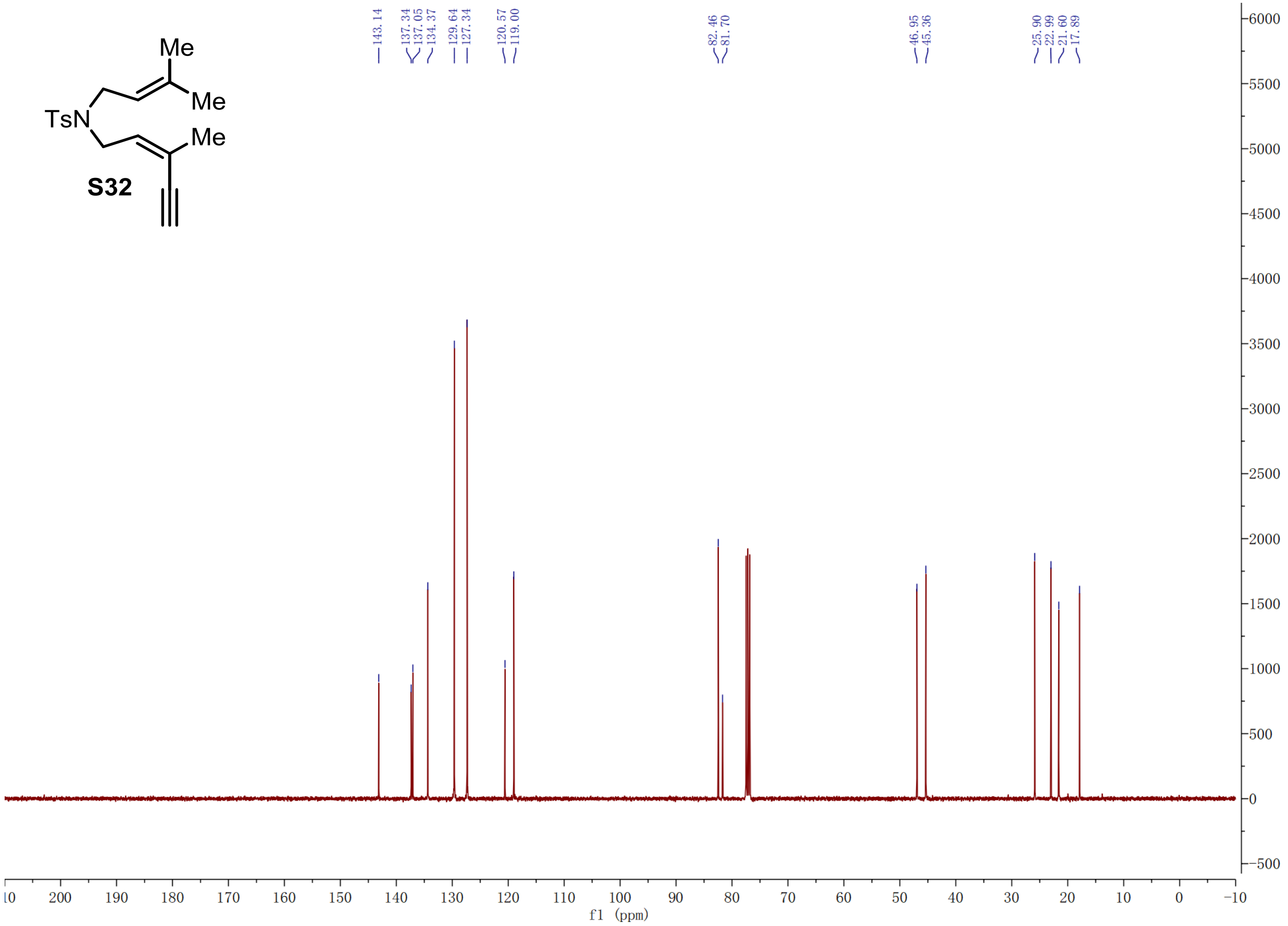

169.64
144.05
138.81
137.78
131.59
130.23
127.71
125.55
113.05
91.80
81.79
72.61
49.82
48.53
29.26
22.24
21.79
17.93
TsN
Me
Me
OAc
E-1o
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

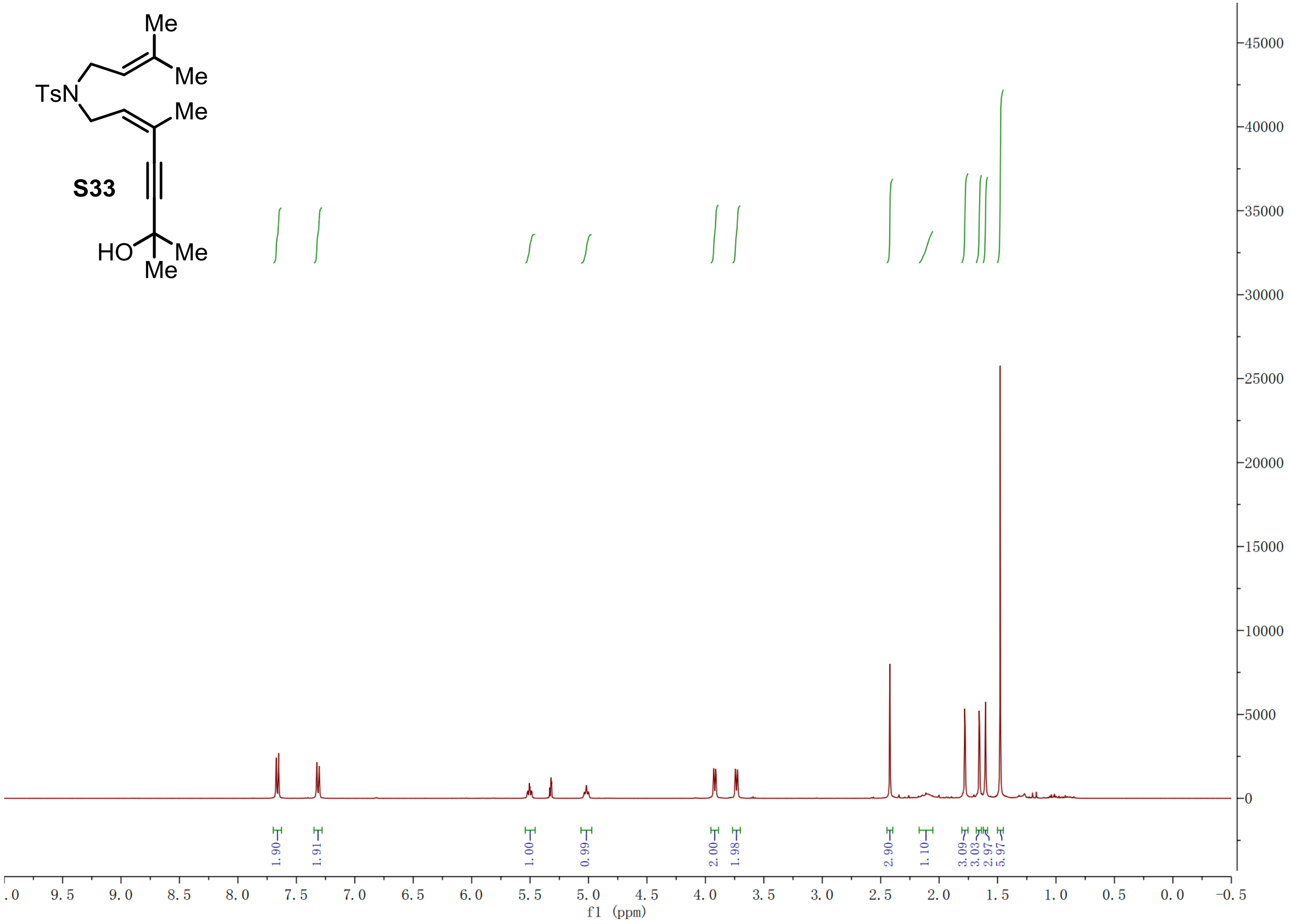

S32

Me
Me
TsN
Me
2.00
2.12
0.97
1.00
1.96
2.02
0.91
3.05
2.92
3.06
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

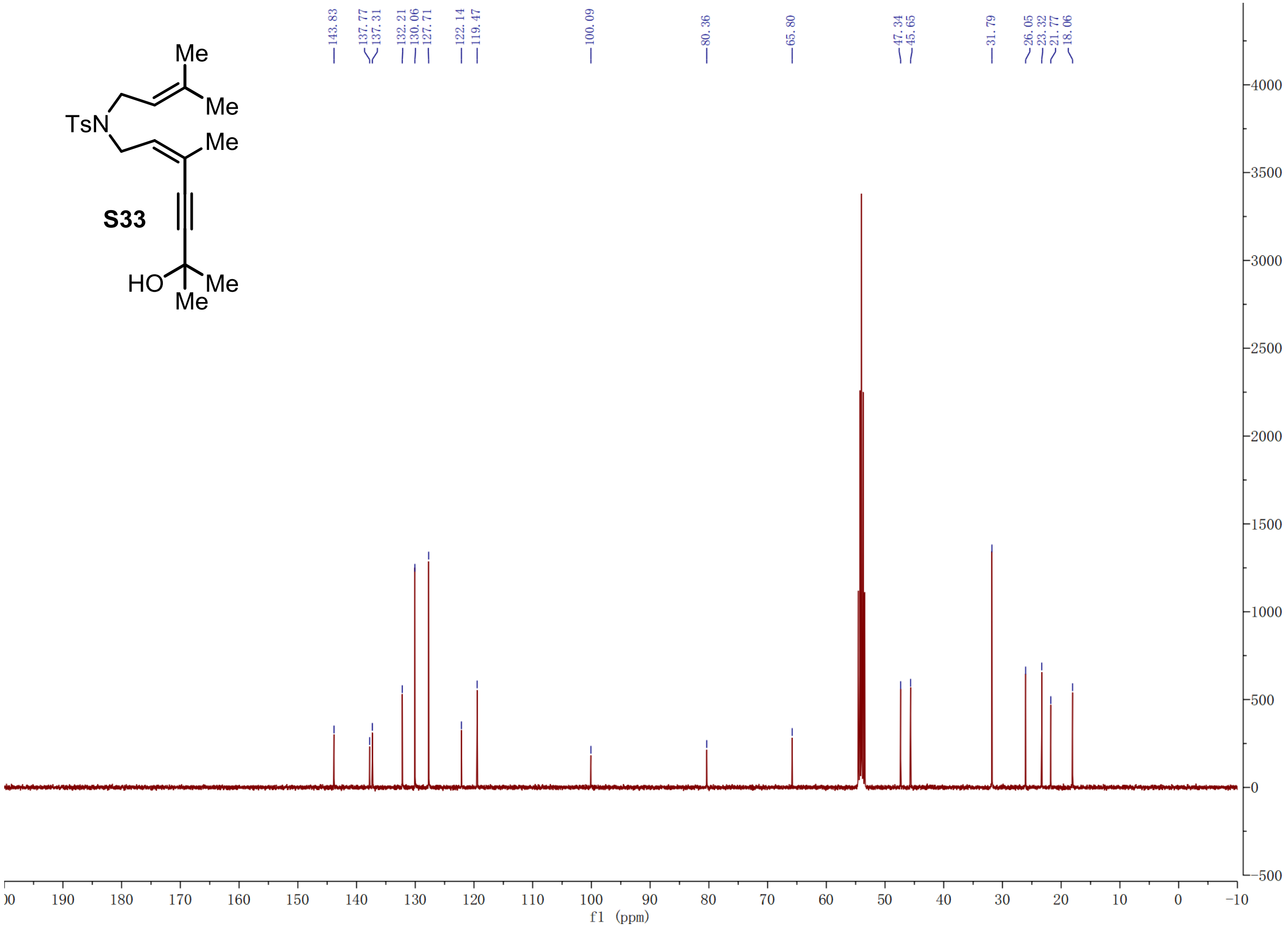
Me
Me
TsN
Me

S32

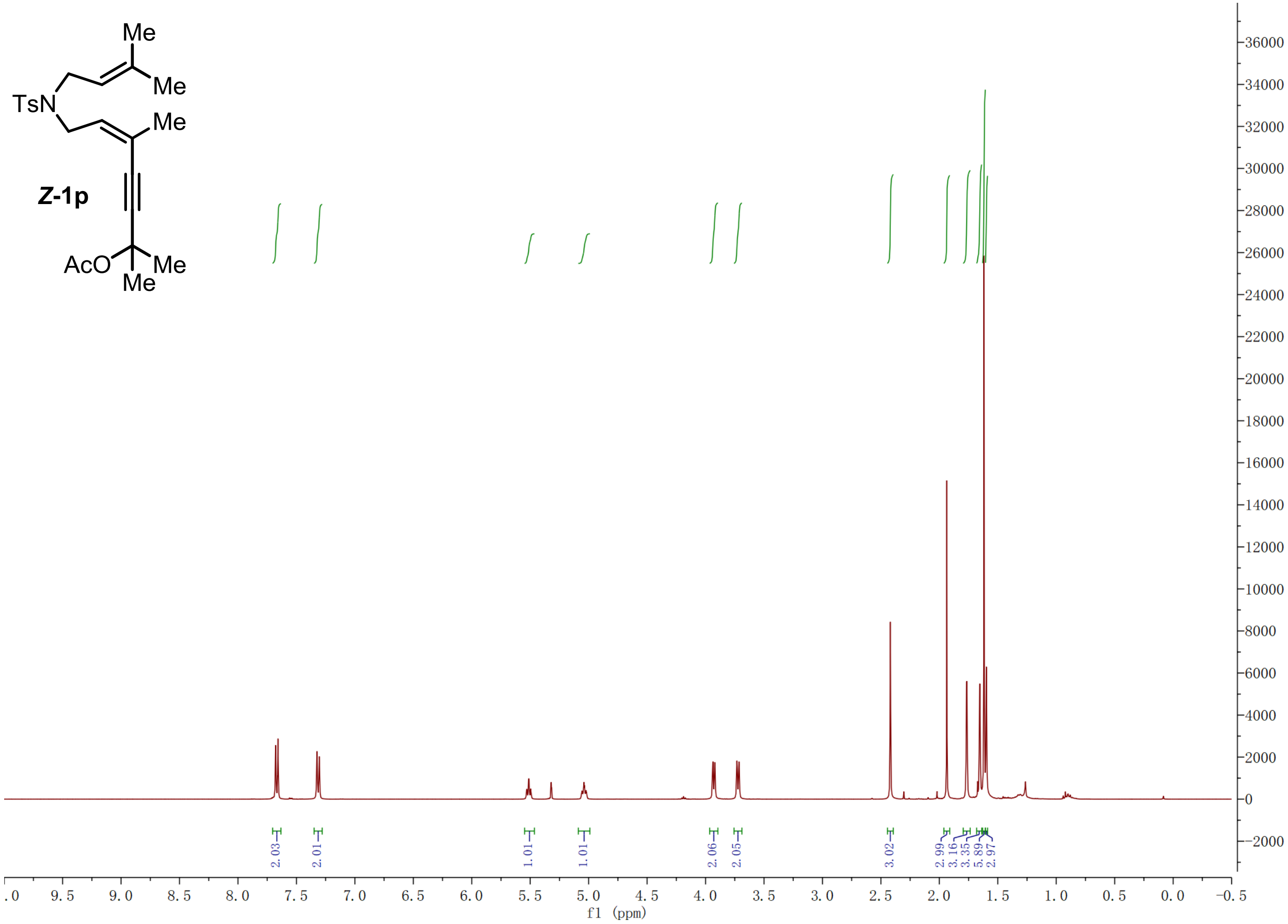

143.14
137.34
137.05
134.37
129.64
127.34
120.57
119.00
82.46
81.70
46.95
45.36
25.90
22.99
21.60
17.89
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


Me
Me
TsN
Me
HO
Me
Me
1.90
1.91
1.00
0.99
2.00
1.98
2.90
1.10
3.09
3.03
2.97
5.97
.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)
45000
40000
35000
30000
25000
20000
15000
10000
5000
0

S33

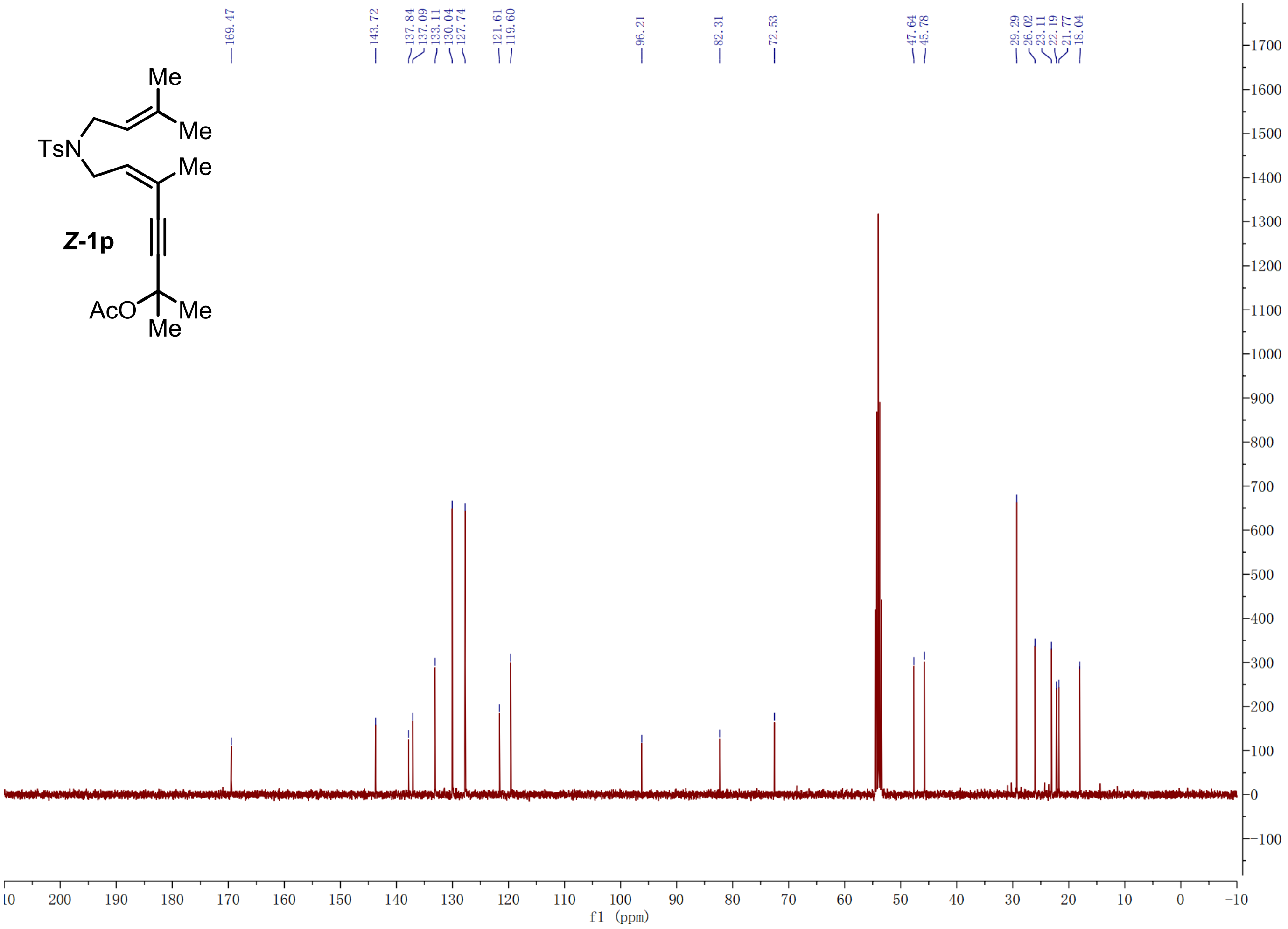

S33

143.83
137.77
137.31
132.21
130.06
127.71
122.14
119.47
100.09
80.36
65.80
47.34
45.65
31.79
26.05
23.32
21.77
18.06
TsN
Me
Me
Me
HO
Me
Me
4000
3500
3000
2500
2000
1500
1000
500
0
-500
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Z-1p

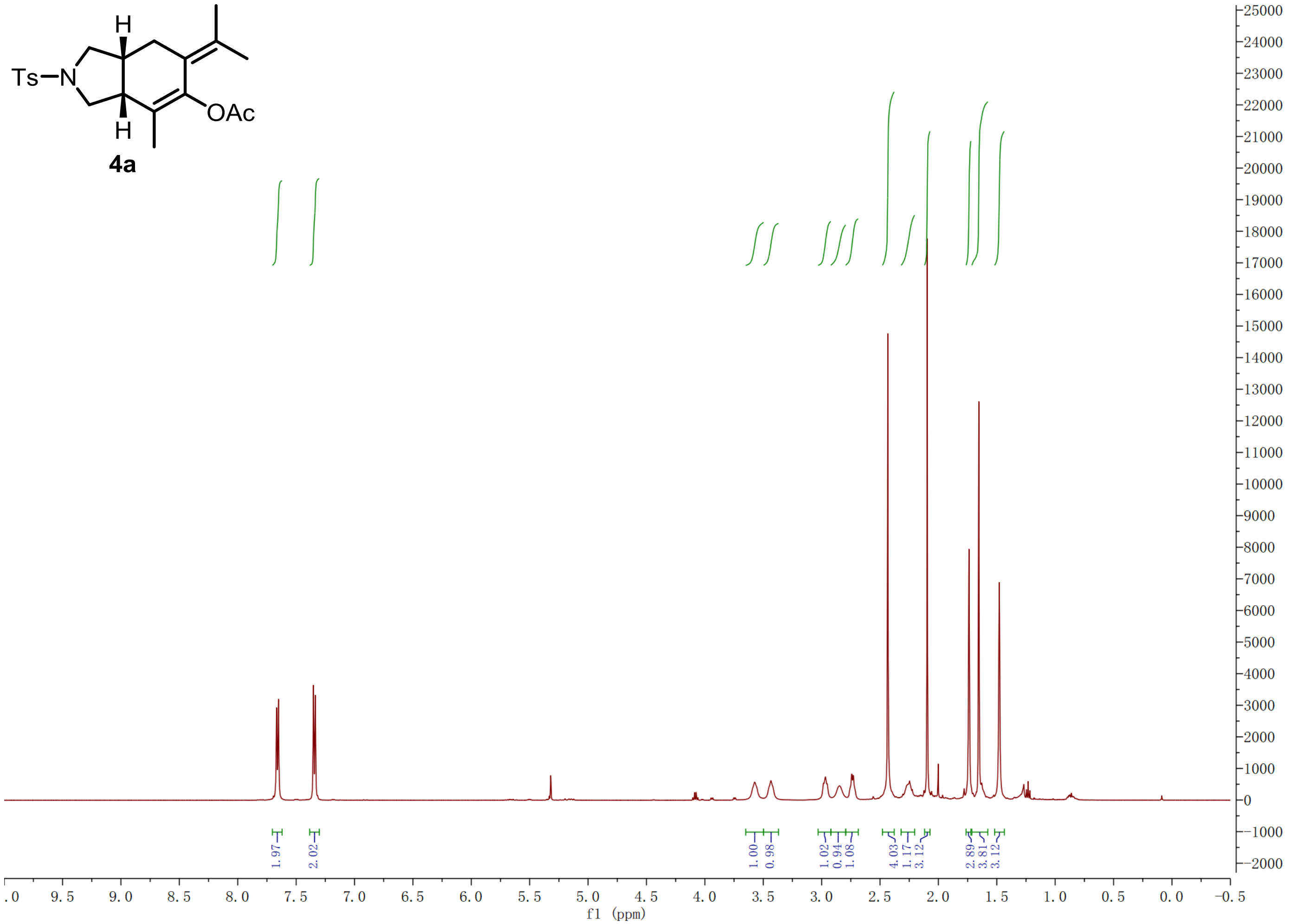
TsN
Me
Me
Me
AcO
Me
Me
2.03
2.01
1.01
1.01
2.06
2.05
3.02
2.99
3.16
3.35
5.89
2.97
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000

S



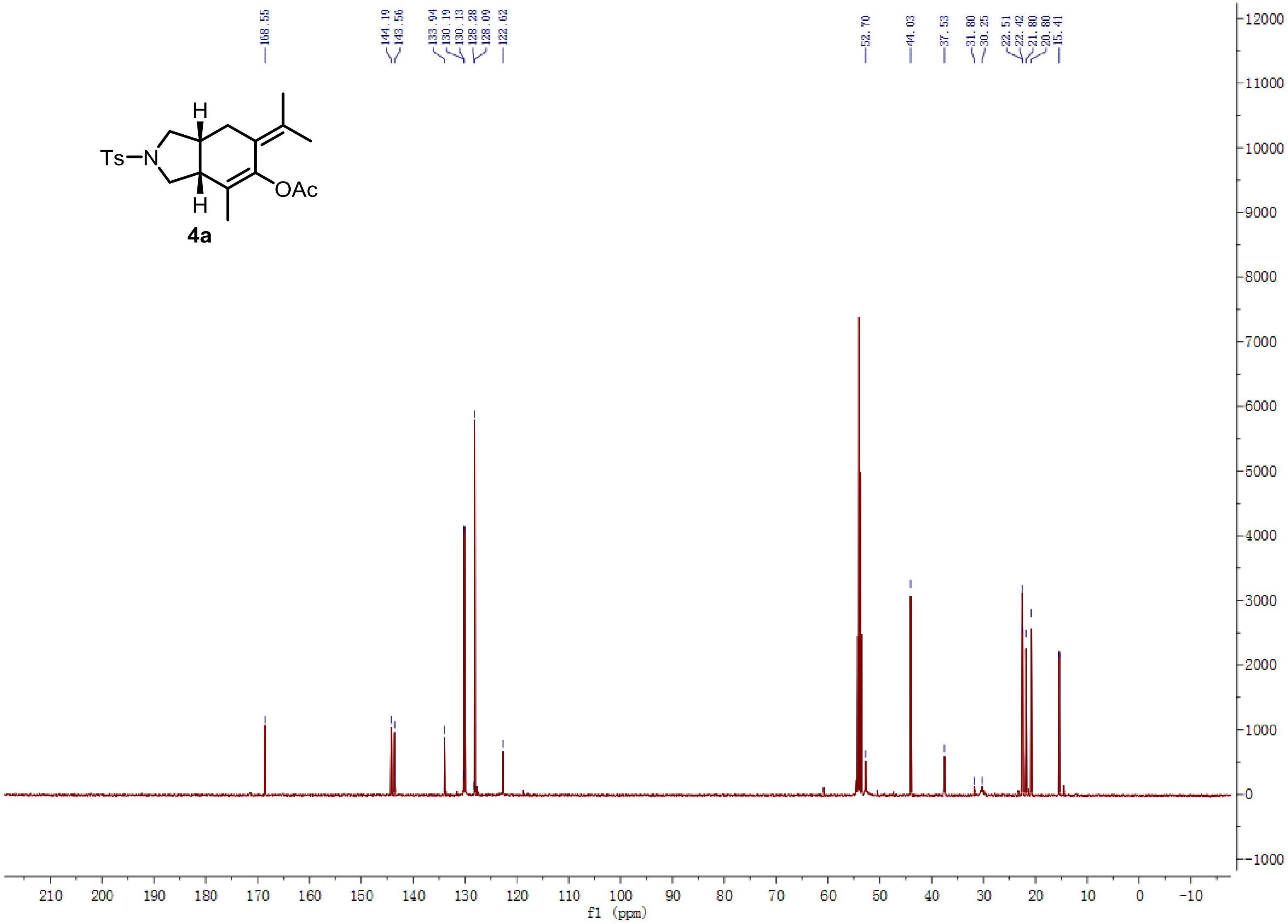
Me
Me
TsN
Me
AcO
Me
Me
169.47
143.72
137.84
137.09
133.11
130.04
127.74
121.61
119.60
96.21
82.31
72.53
47.64
45.78
29.29
26.02
23.11
22.19
21.77
18.04
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

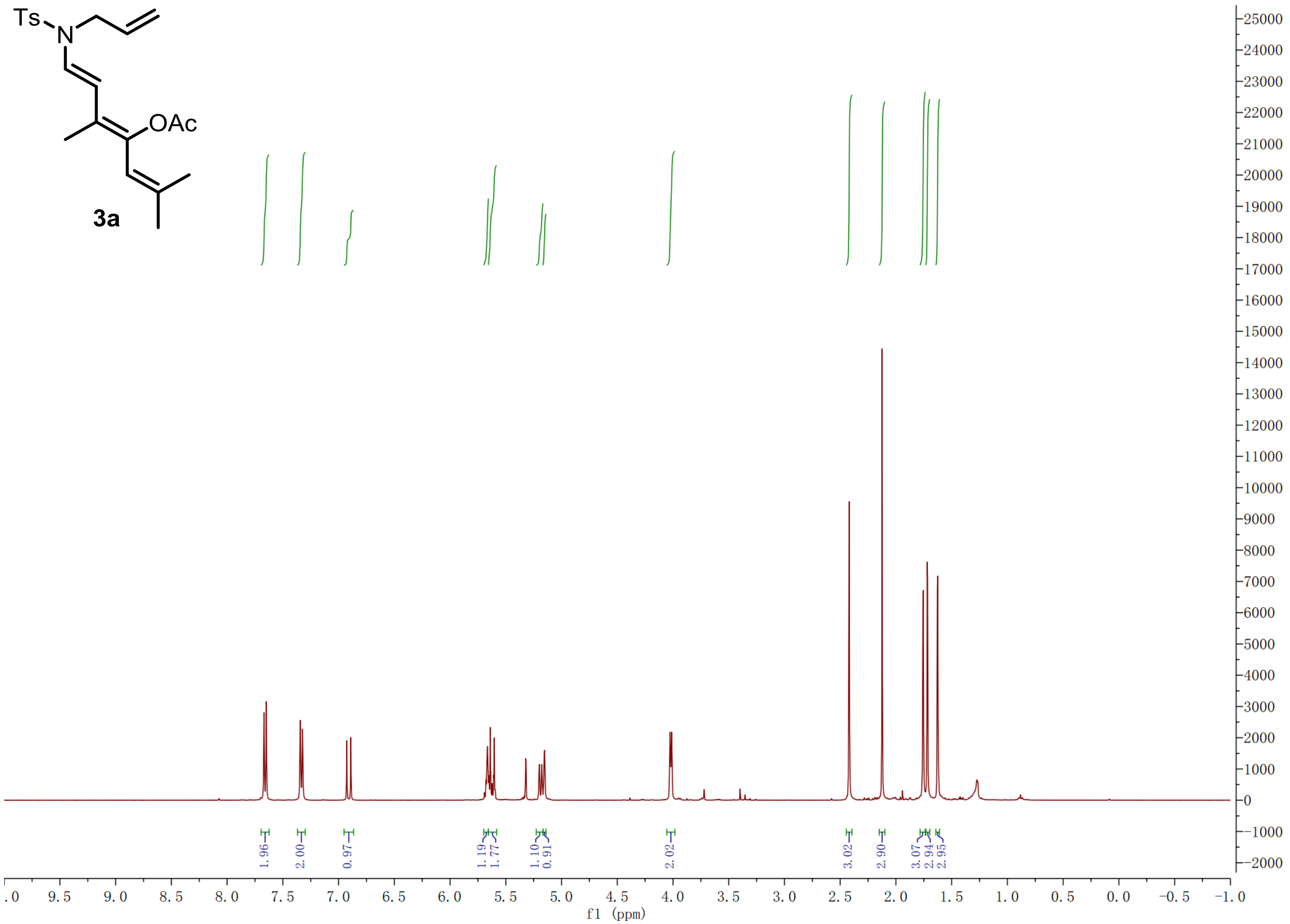
***Z*-1p**



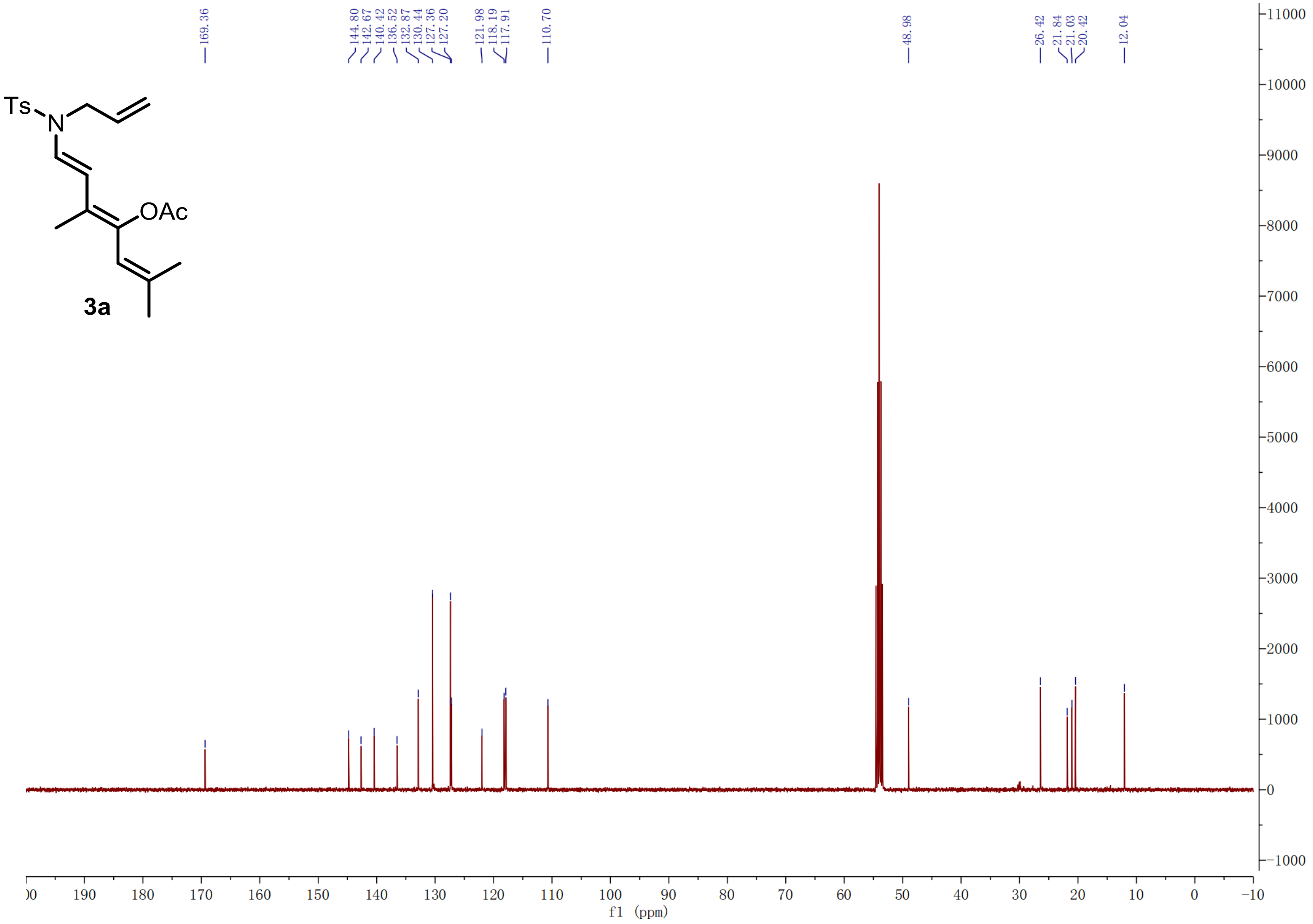
4a

Ts
N
H
H
OAc
1.97
2.02
1.00
0.98
1.02
0.94
1.08
4.03
1.17
3.12
2.89
3.81
3.12
.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


168.55
144.19
143.56
133.94
130.19
130.13
128.28
128.09
122.62
52.70
44.03
37.53
31.80
30.25
22.51
22.42
21.80
20.80
15.41
H
Ts
N
H
OAc
4a
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
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)

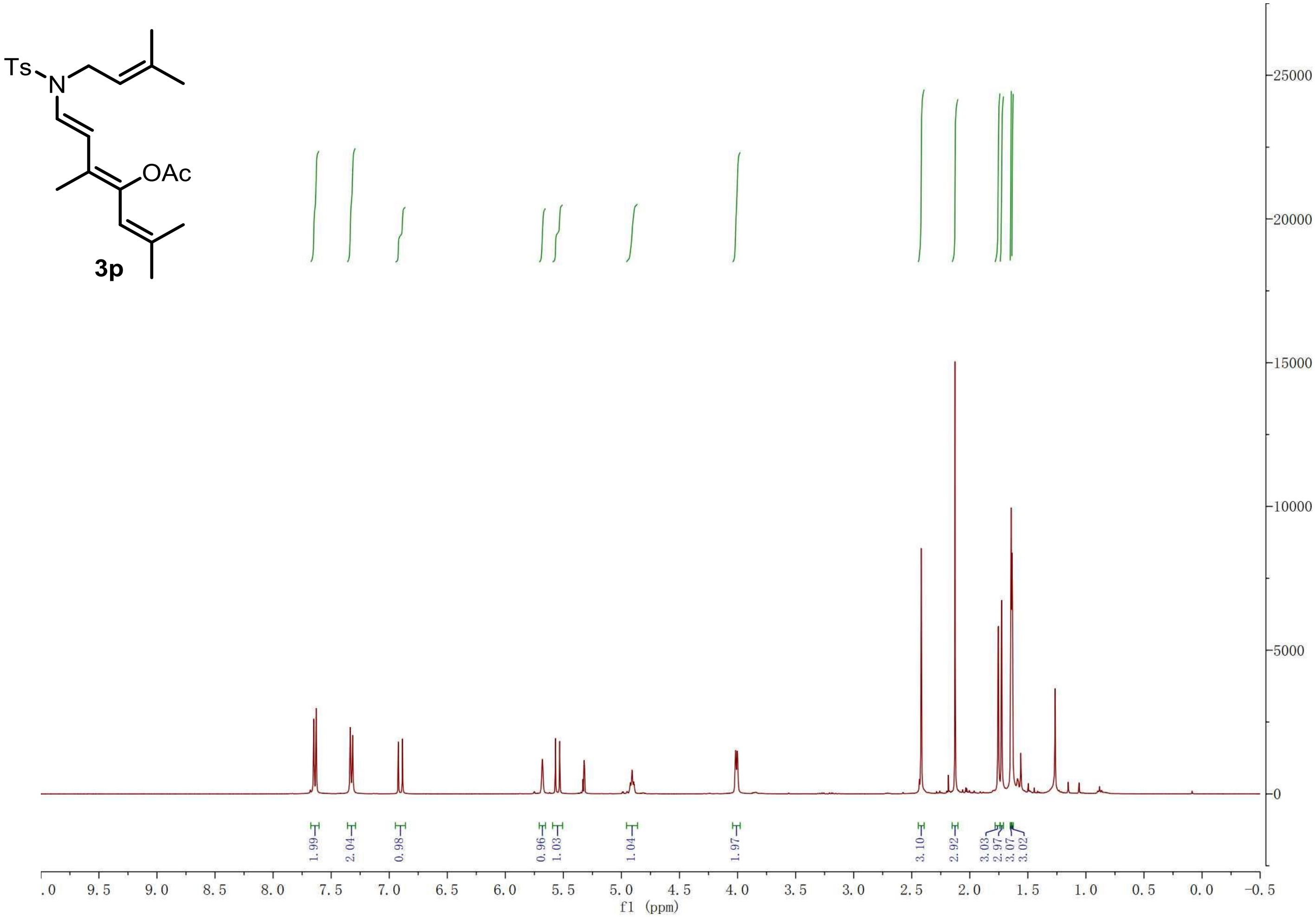

Ts
N
OAc
1.96
2.00
0.97
1.19
1.77
1.10
0.91
2.02
3.02
2.90
3.07
2.94
2.95
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)
25000
24000
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000

3a



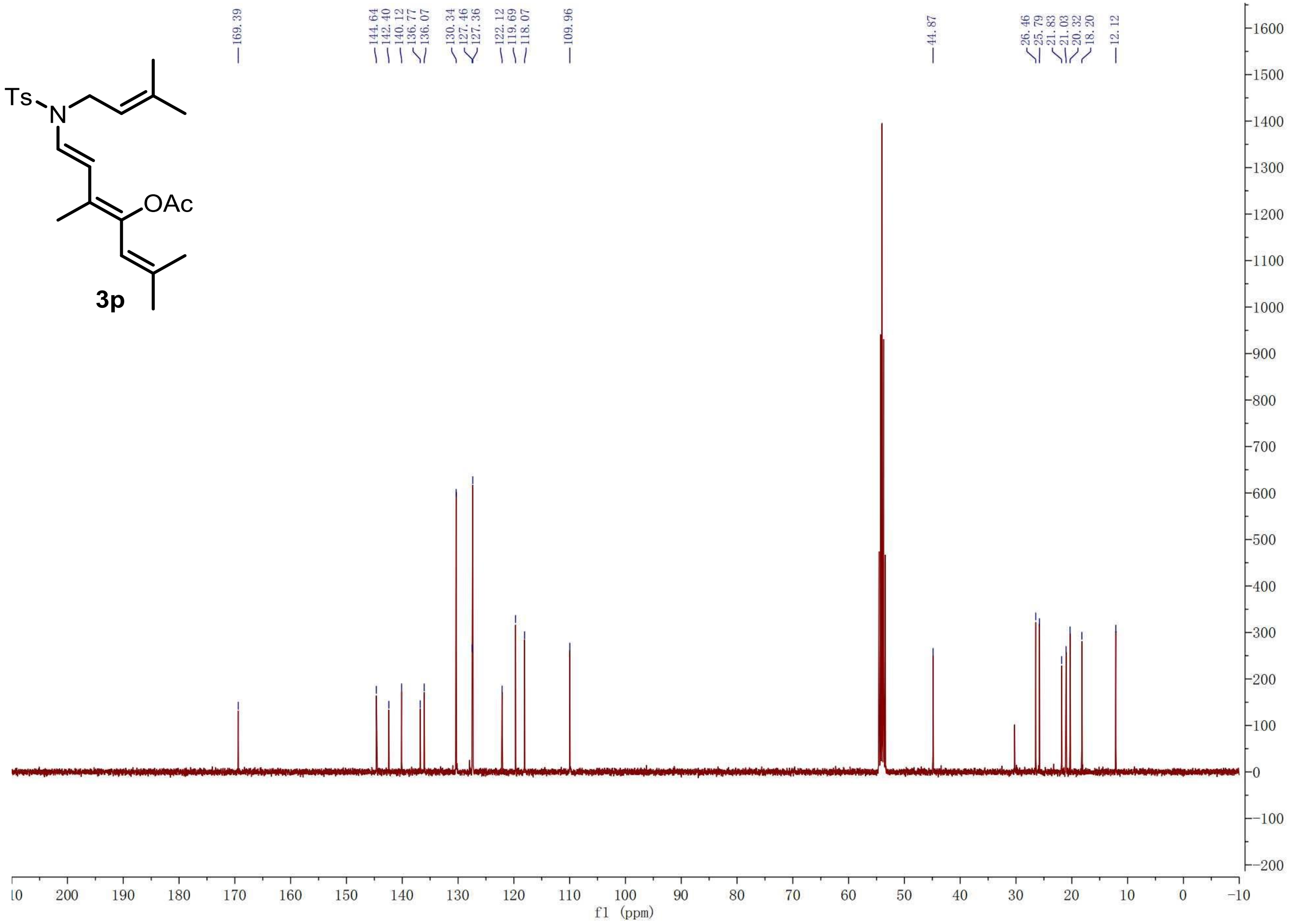
3a

169.36
144.80
142.67
140.42
136.52
132.87
130.44
127.36
127.20
121.98
118.19
117.91
110.70
48.98
26.42
21.84
21.03
20.42
12.04
Ts
N
OAc
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

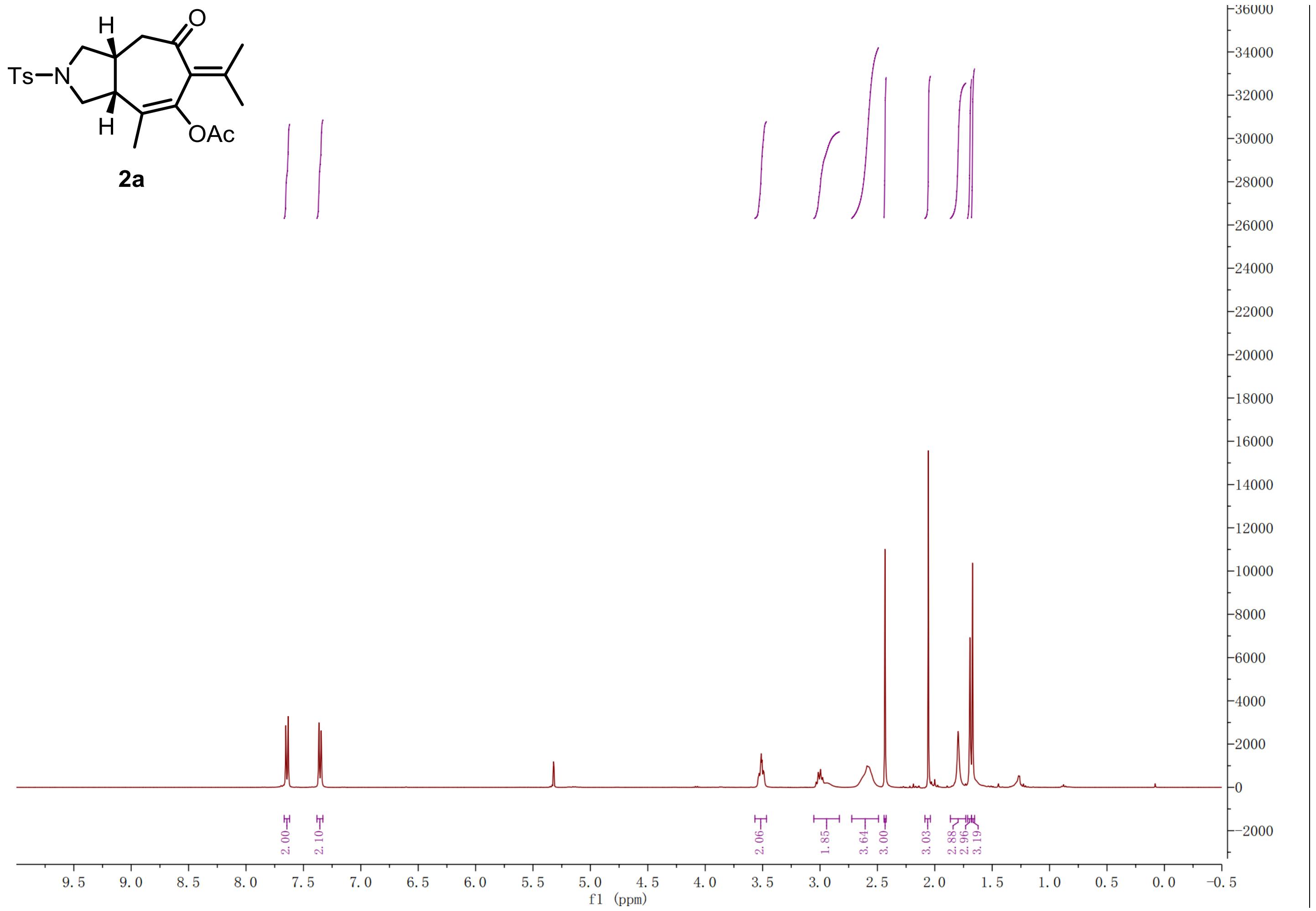

Ts
N
OAc

3p

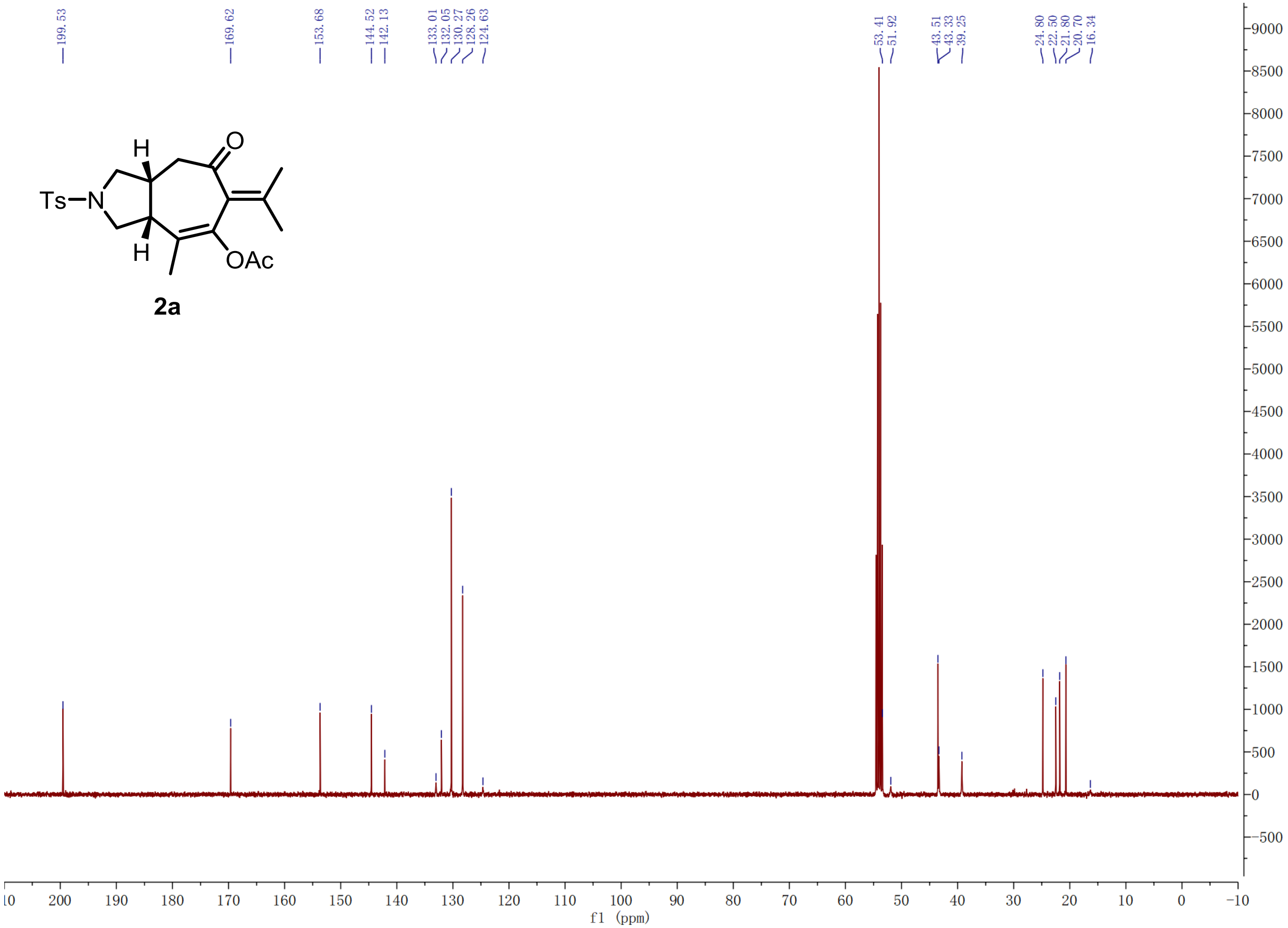
1.99
2.04
0.98
0.96
1.03
1.04
1.97
3.10
2.92
3.03
2.97
3.07
3.02
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
25000
20000
15000
10000
5000
0

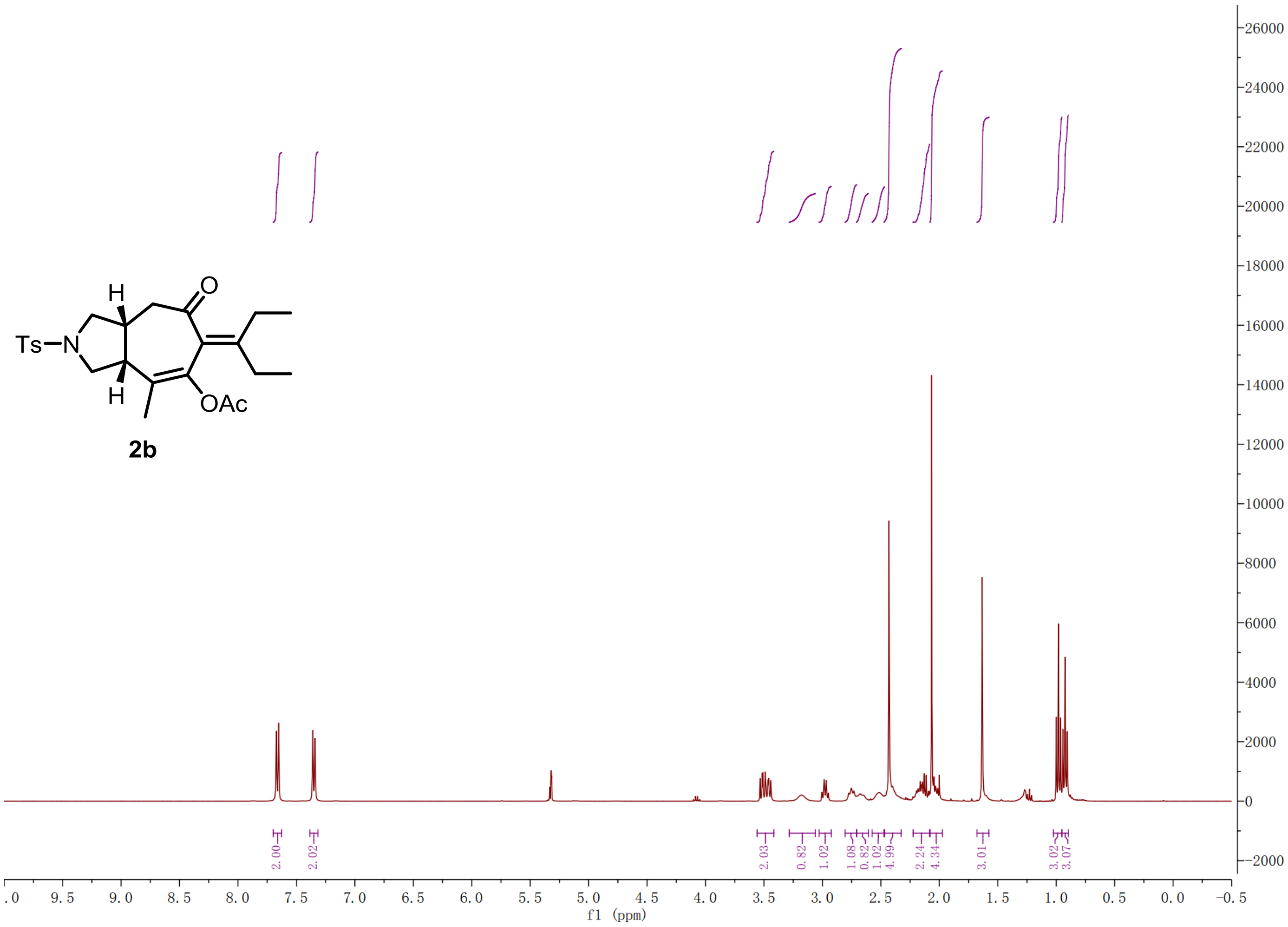


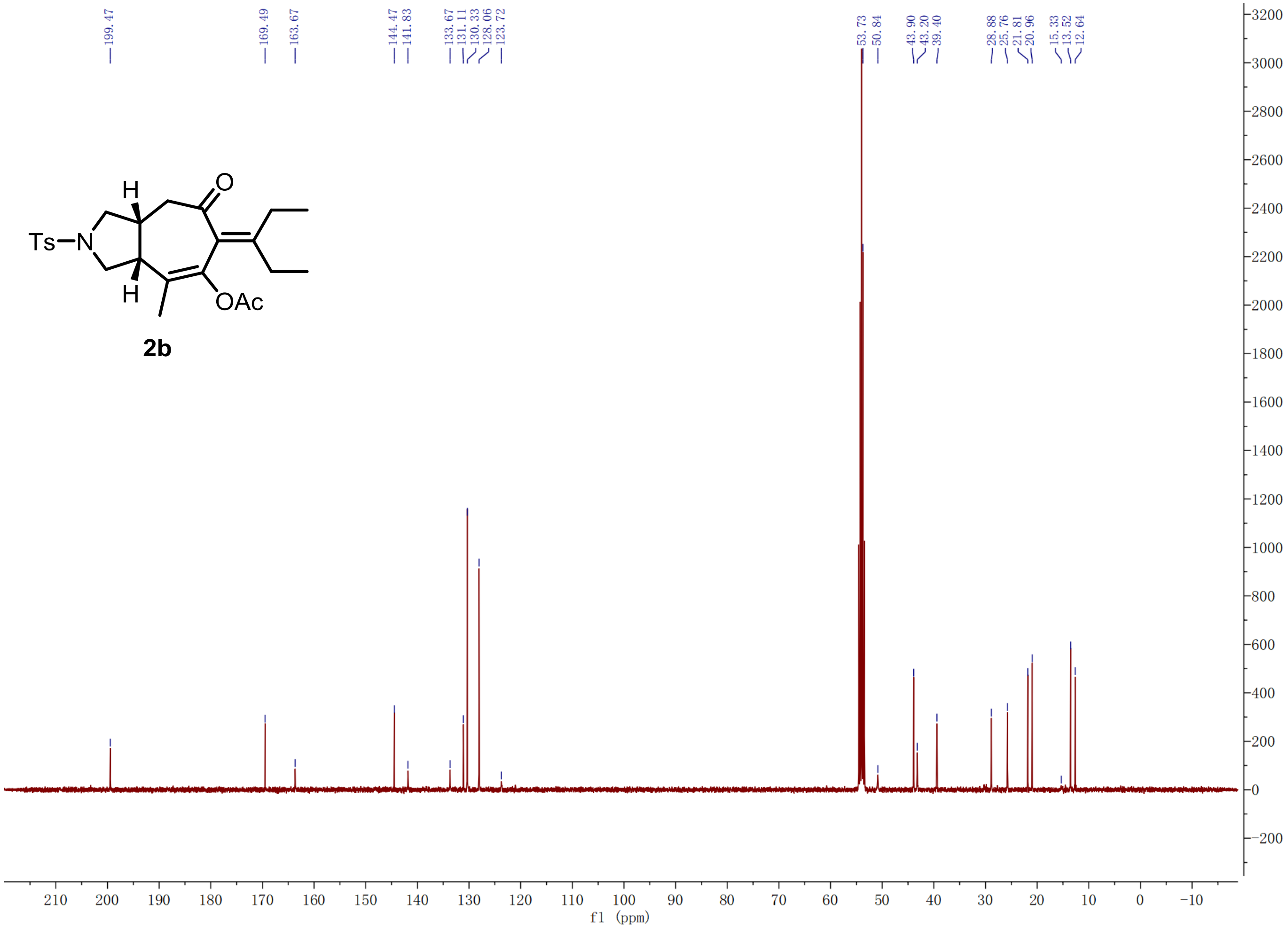
169.39
144.64
142.40
140.12
136.77
136.07
130.34
127.46
127.36
122.12
119.69
118.07
109.96
44.87
26.46
25.79
21.83
21.03
20.32
18.20
12.12
Ts
N
OAc
3p
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



2a
Ts
N
H
H
O
OAc
2.00
2.10
2.06
1.85
3.64
3.00
3.03
2.88
2.96
3.19
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)
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
−2000

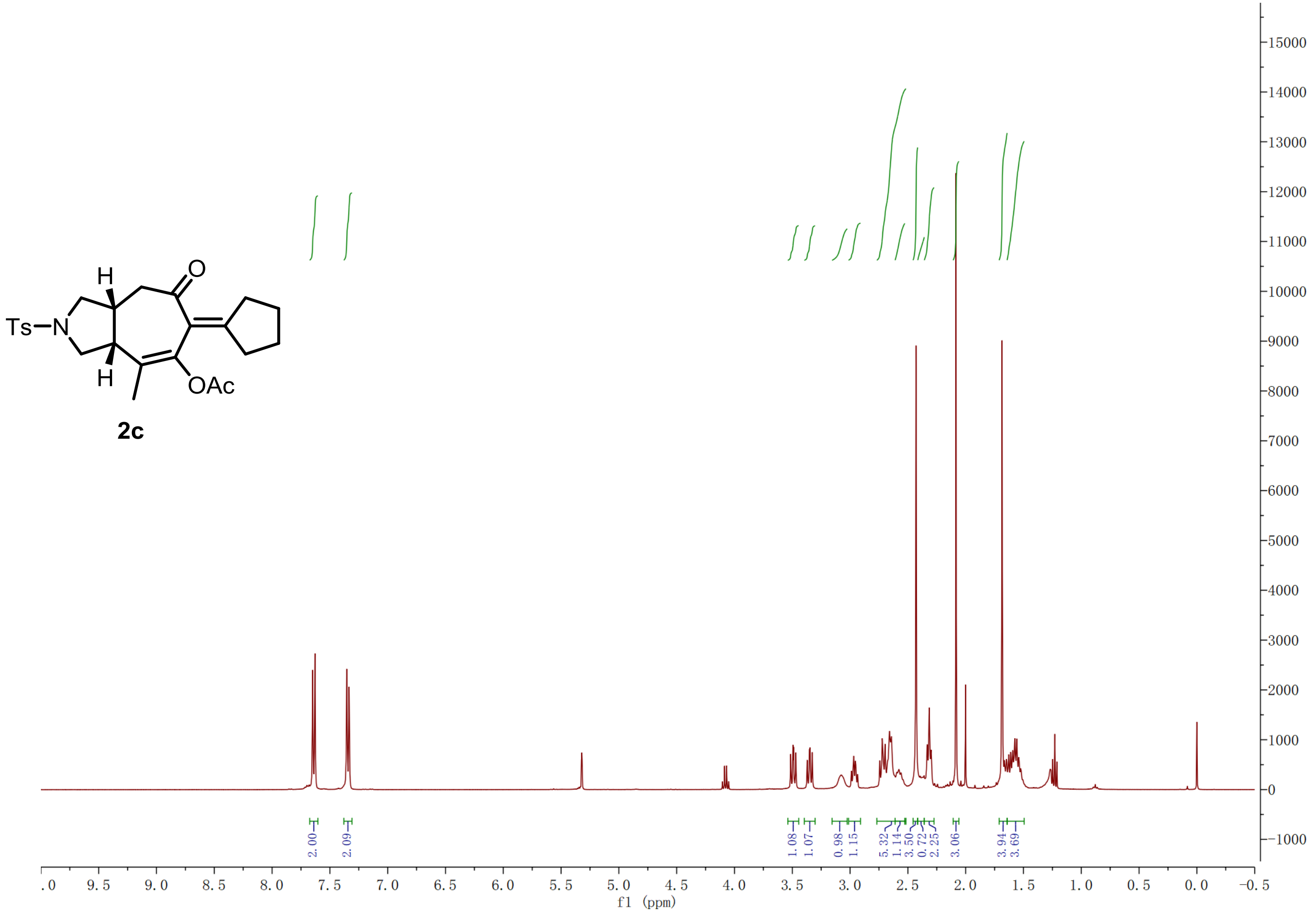

199.53
169.62
153.68
144.52
142.13
133.01
132.05
130.27
128.26
124.63
53.41
51.92
43.51
43.33
39.25
24.80
22.50
21.80
20.70
16.34
Ts
N
H
H
O
OAc
2a
9000
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


Ts
N
H
H
O
OAc
2b
2.00
2.02
2.03
0.82
1.02
1.08
0.82
1.02
4.99
2.24
4.34
3.01
3.02
3.07
.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)
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000

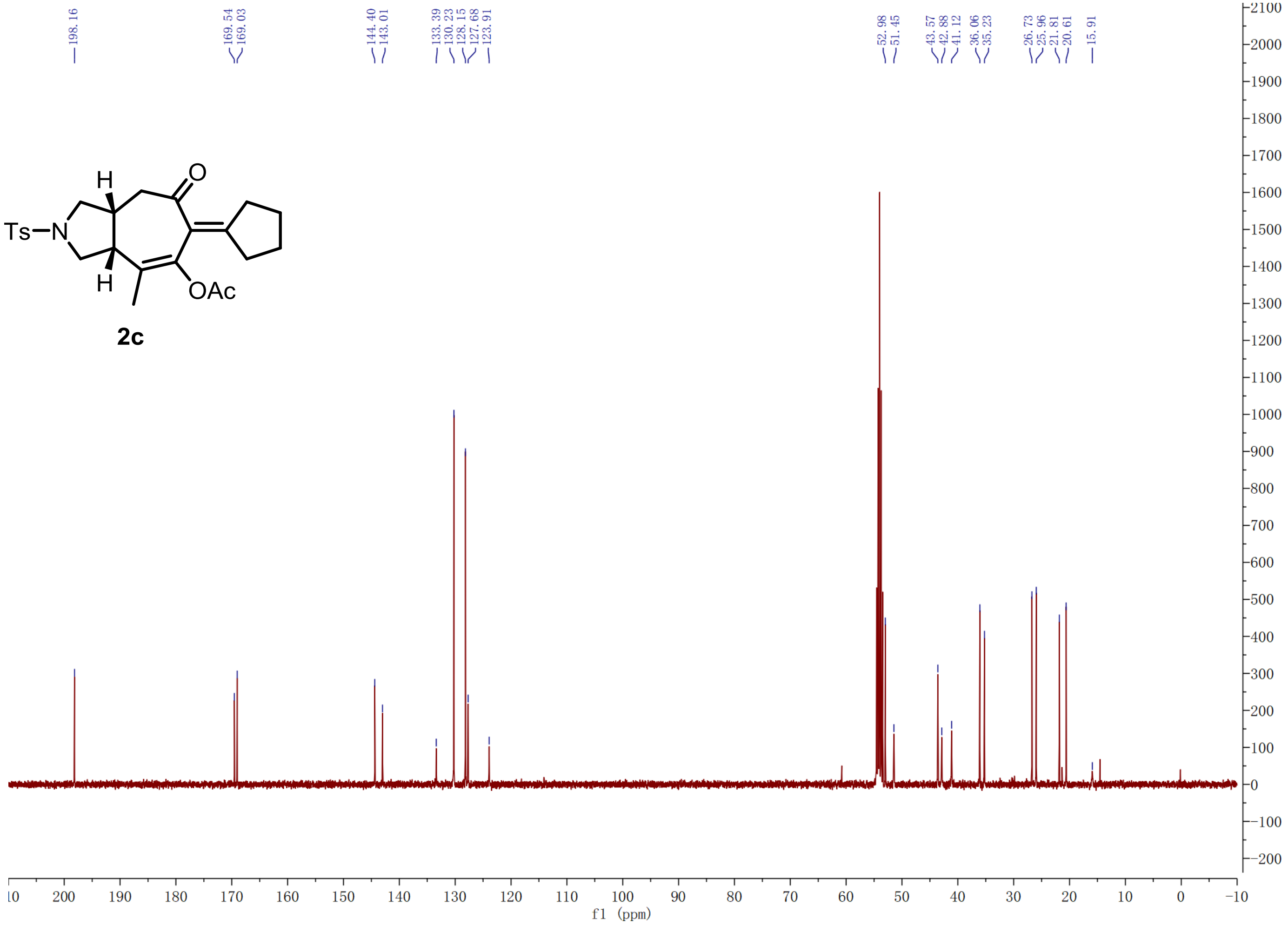


199.47
169.49
163.67
144.47
141.83
133.67
131.11
130.33
128.06
123.72
53.73
50.84
43.90
43.20
39.40
28.88
25.76
21.81
20.96
15.33
13.52
12.64
Ts
N
H
H
O
OAc
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

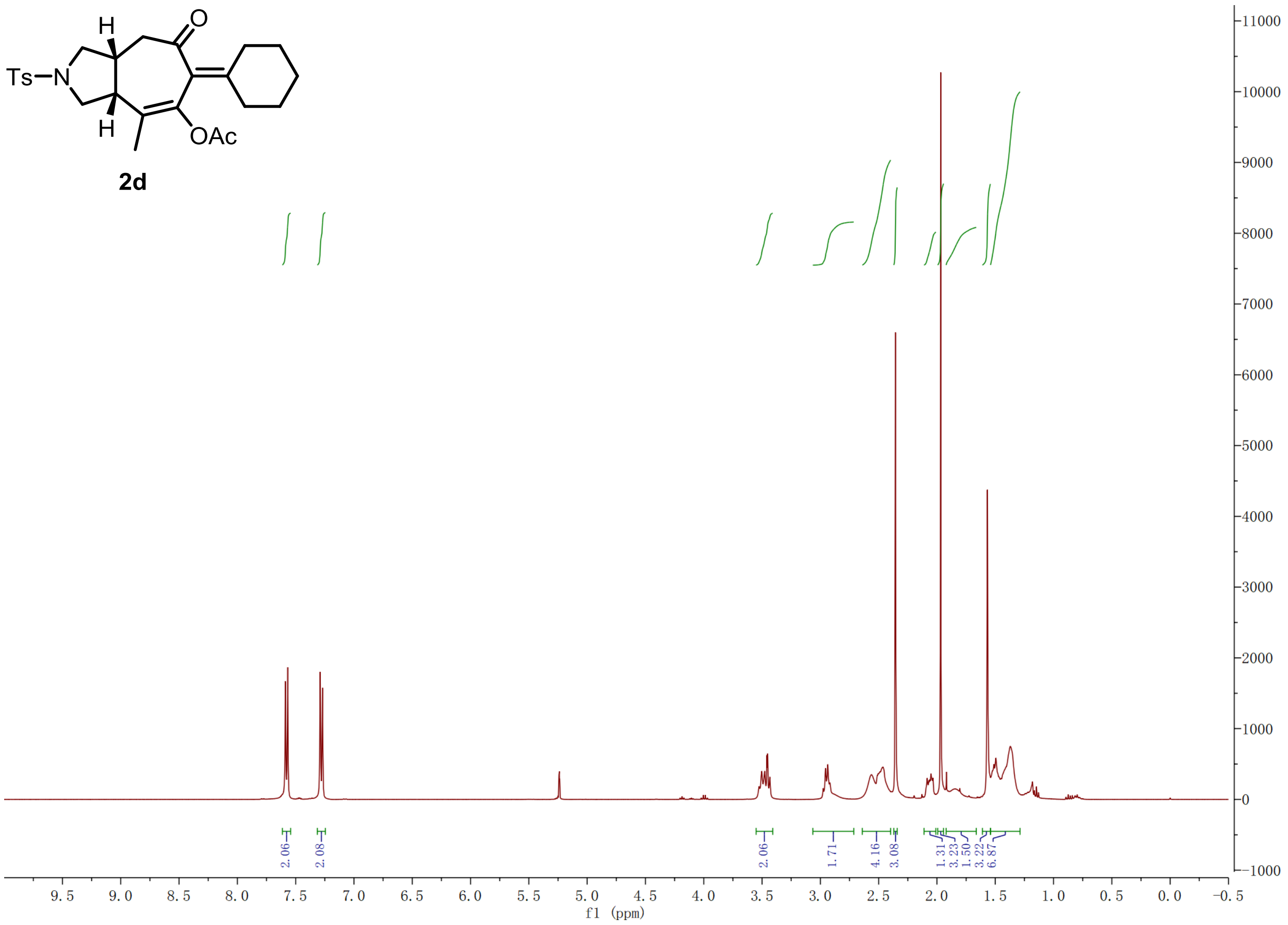
2b


Ts
N
H
H
O
OAc
2.00
2.09
1.08
1.07
0.98
1.15
5.32
1.14
3.50
0.72
2.25
3.06
3.94
3.69
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
.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)

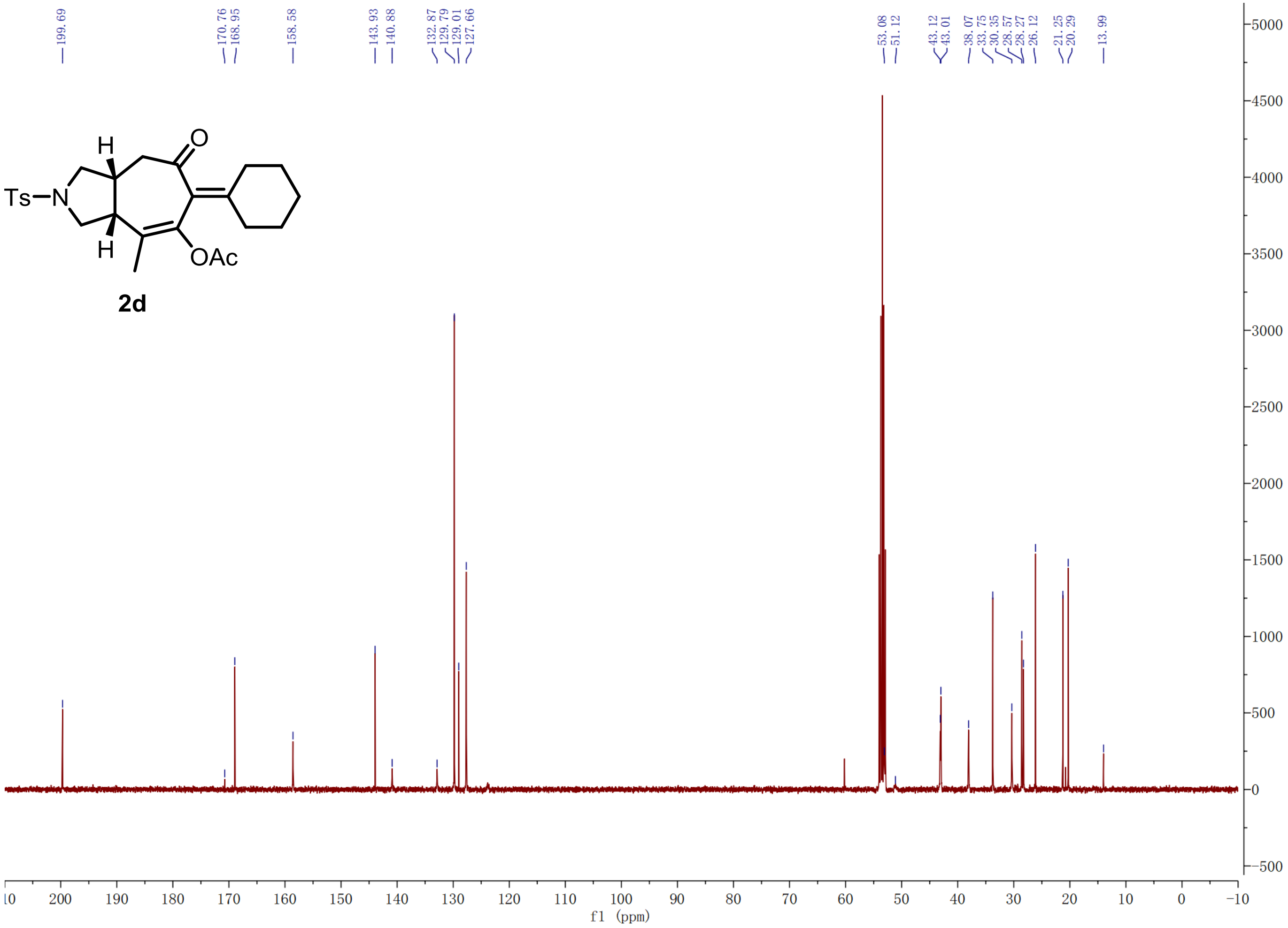
2c

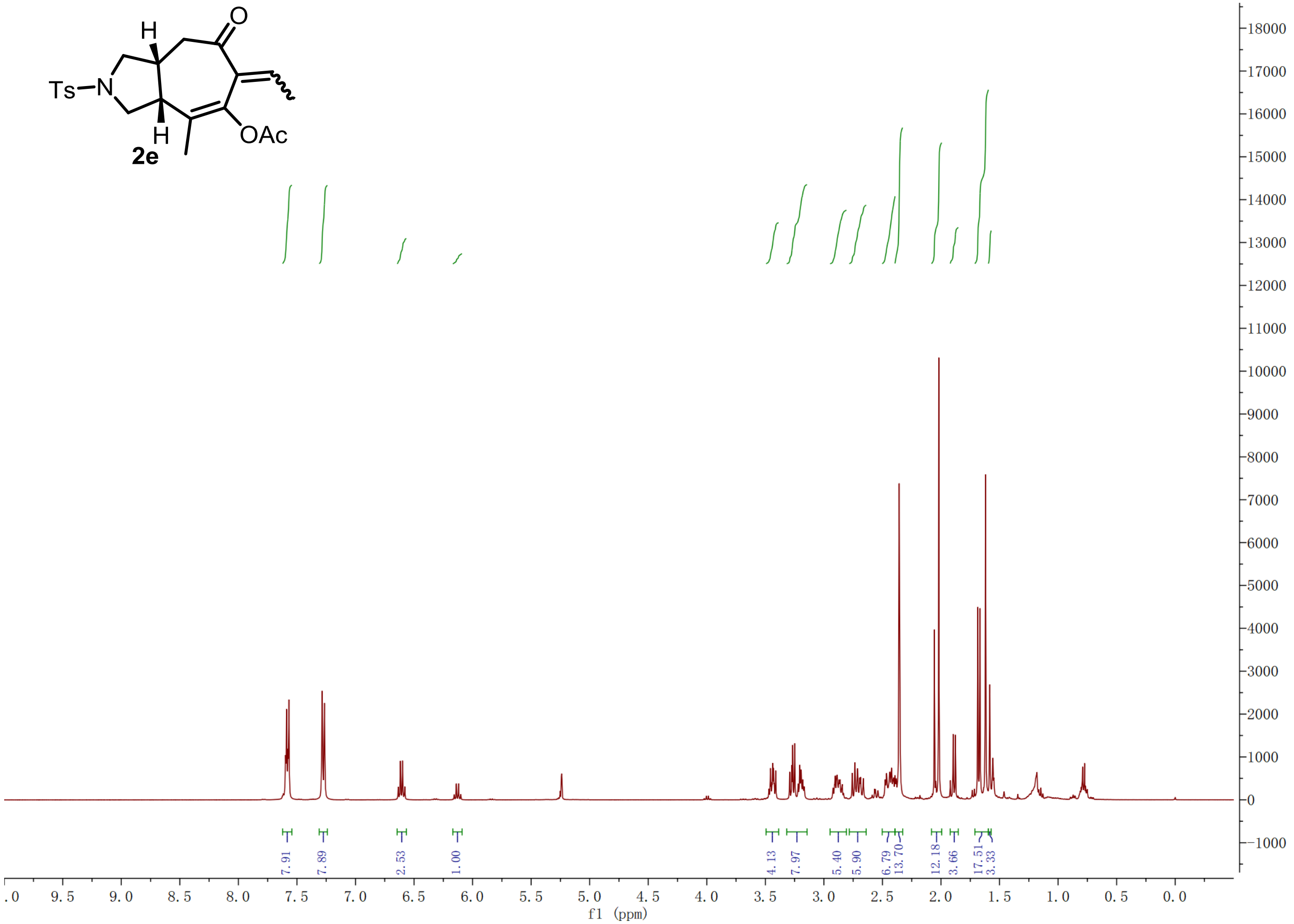

198.16
169.54
169.03
144.40
143.01
133.39
130.23
128.15
127.68
123.91
52.98
51.45
43.57
42.88
41.12
36.06
35.23
26.73
25.96
21.81
20.61
15.91
Ts
N
H
H
O
OAc
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200

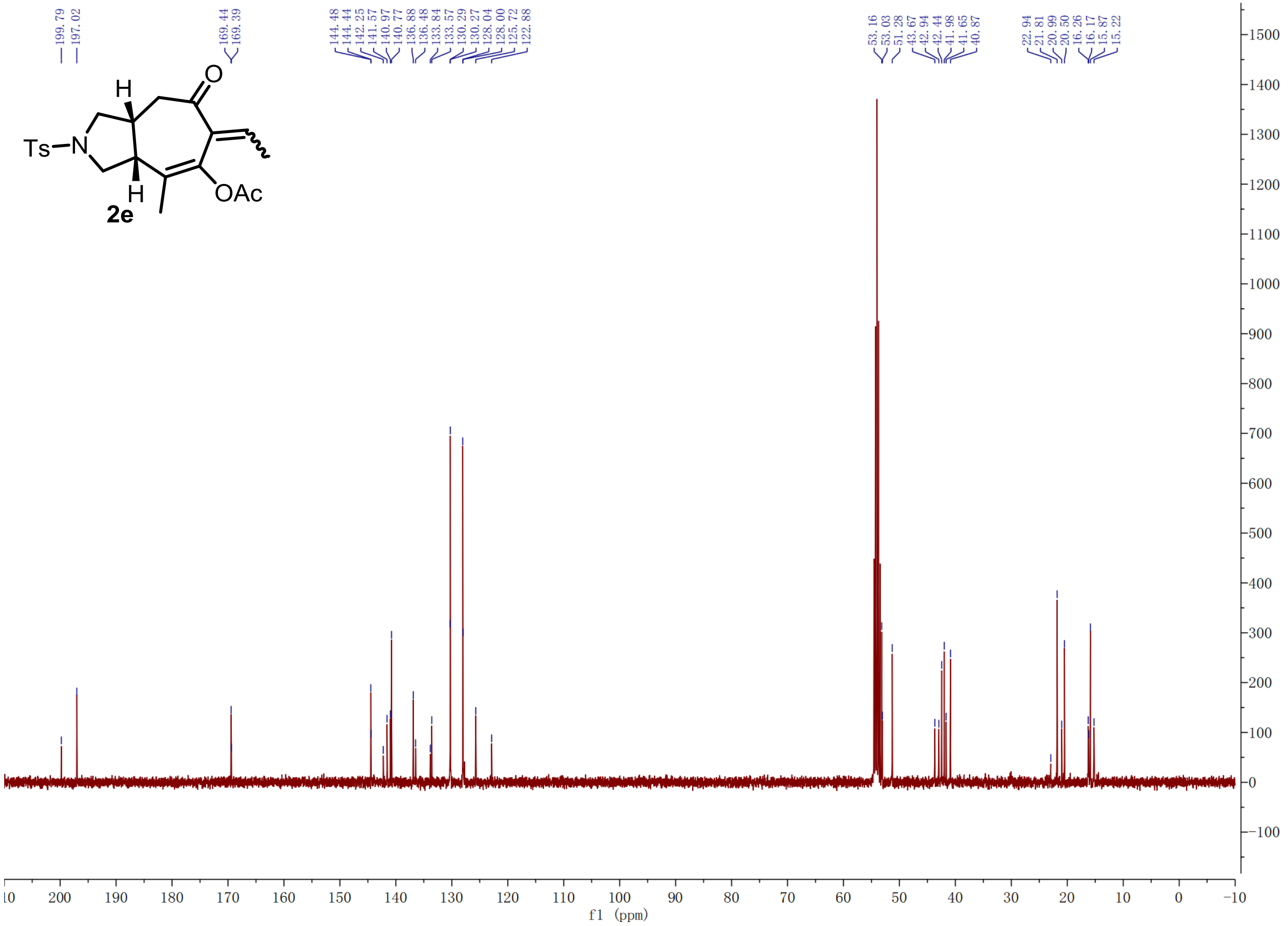
2c

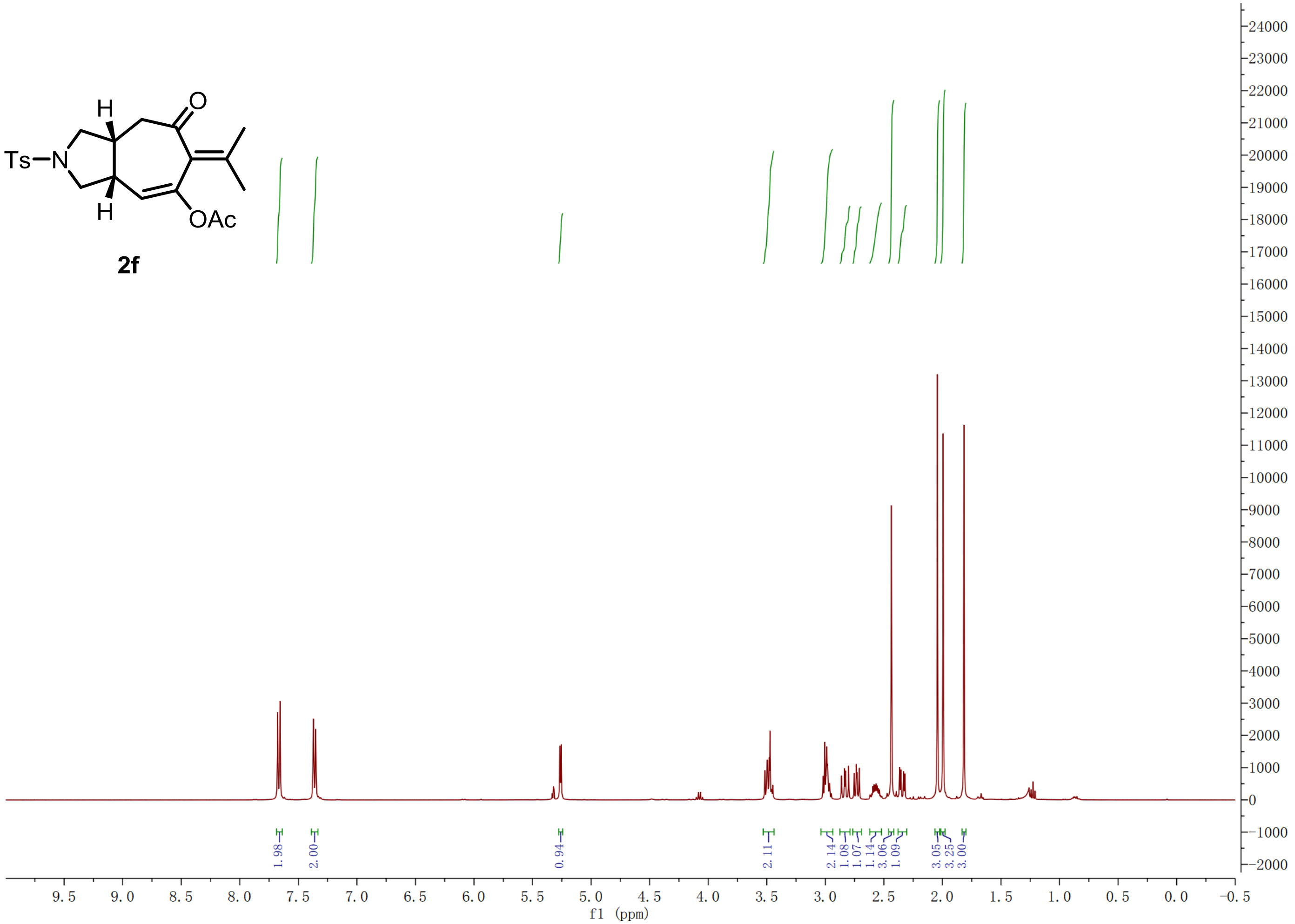

Ts
N
H
H
O
OAc
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
2.06
2.08
2.06
1.71
4.16
3.08
1.31
3.23
1.50
3.22
6.87
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

2d

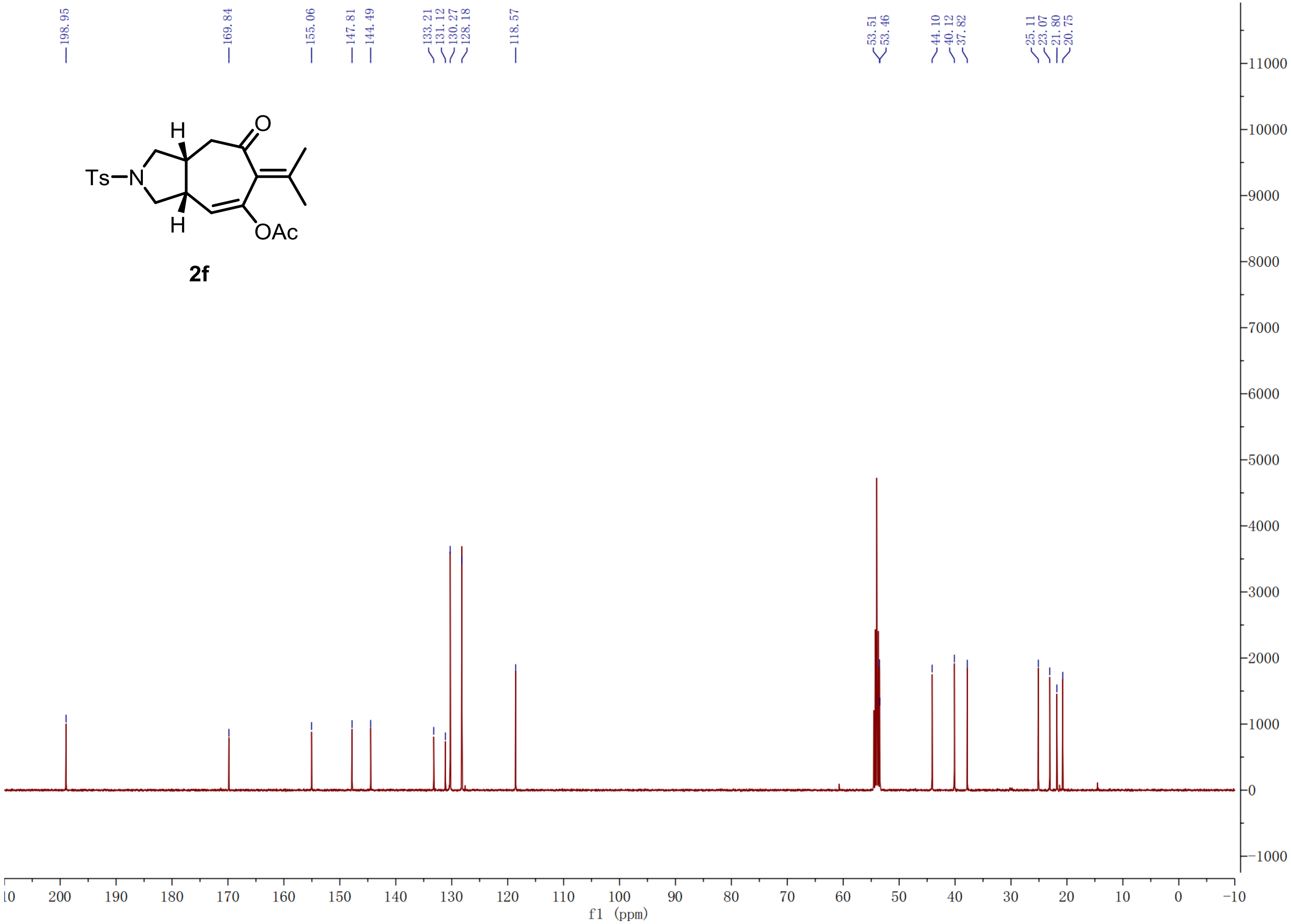

199.69
170.76
168.95
158.58
143.93
140.88
132.87
129.79
129.01
127.66
53.08
51.12
43.12
43.01
38.07
33.75
30.35
28.57
28.27
26.12
21.25
20.29
13.99
Ts
N
H
H
O
OAc
2d
f1 (ppm)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

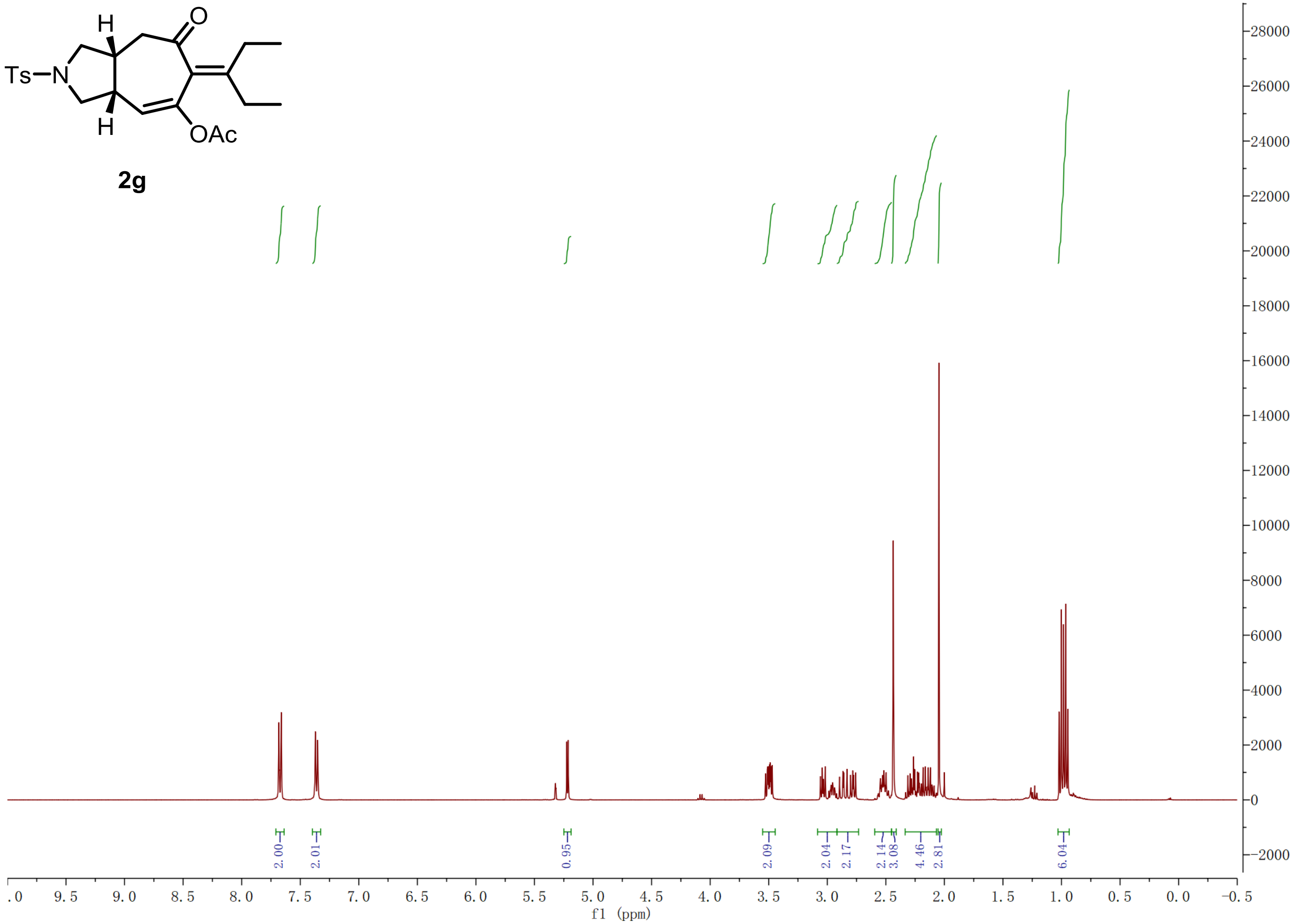

Ts
N
H
H
O
OAc
2e
7.91
7.89
2.53
1.00
4.13
7.97
5.40
5.90
6.79
13.70
12.18
3.66
17.51
3.33
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

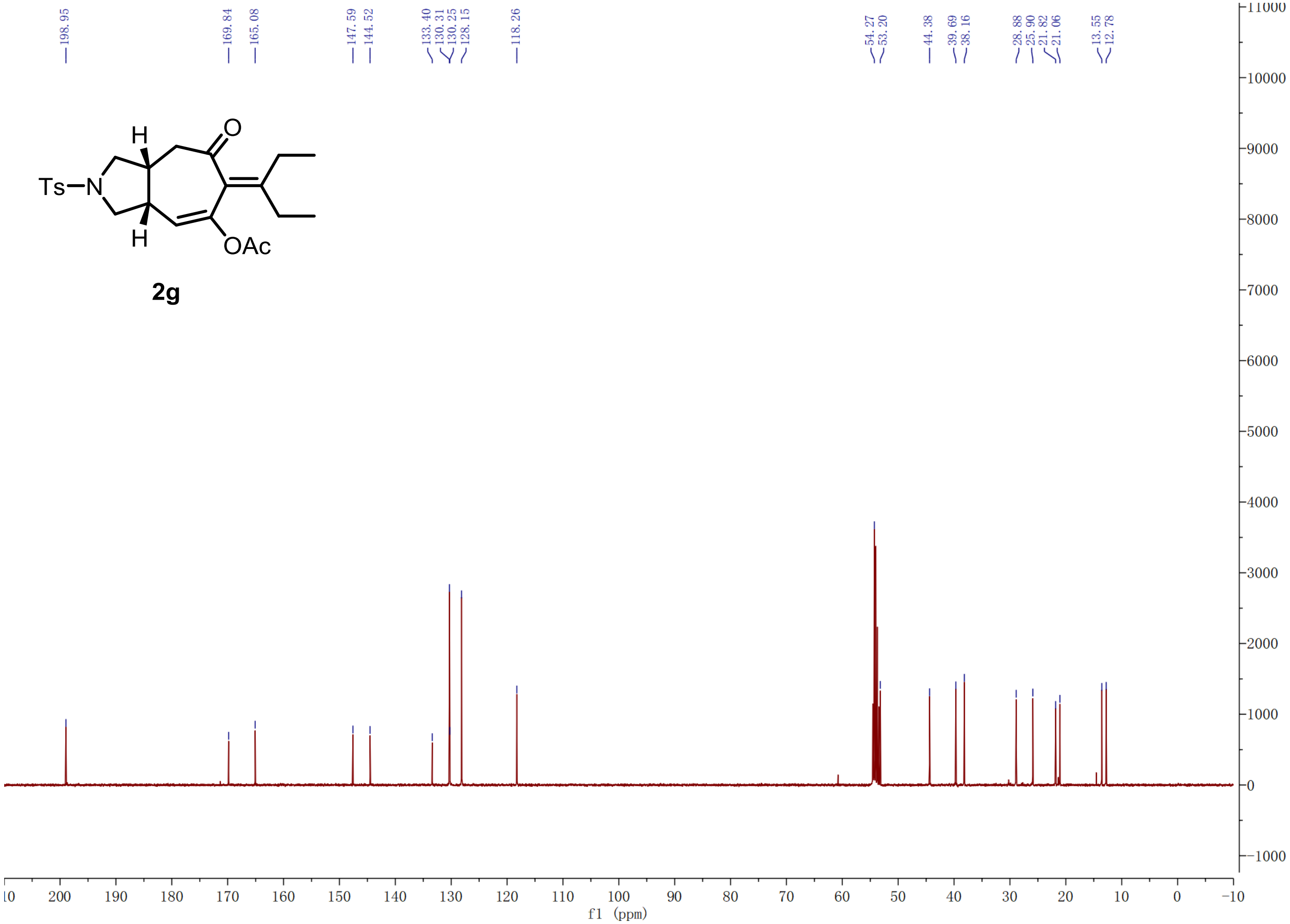

199.79
197.02
169.44
169.39
144.48
144.44
142.25
141.57
140.97
140.77
136.88
136.48
133.84
133.57
130.29
130.27
128.04
128.00
125.72
122.88
53.16
53.03
51.28
43.67
42.94
42.44
41.98
41.65
40.87
22.94
21.81
20.99
20.50
16.26
16.17
15.87
15.22
Ts
N
H
H
O
OAc
2e
f1 (ppm)


Ts
N
H
H
O
OAc
1.98
2.00
0.94
2.11
2.14
1.08
1.07
1.14
3.06
1.09
3.05
3.25
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-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

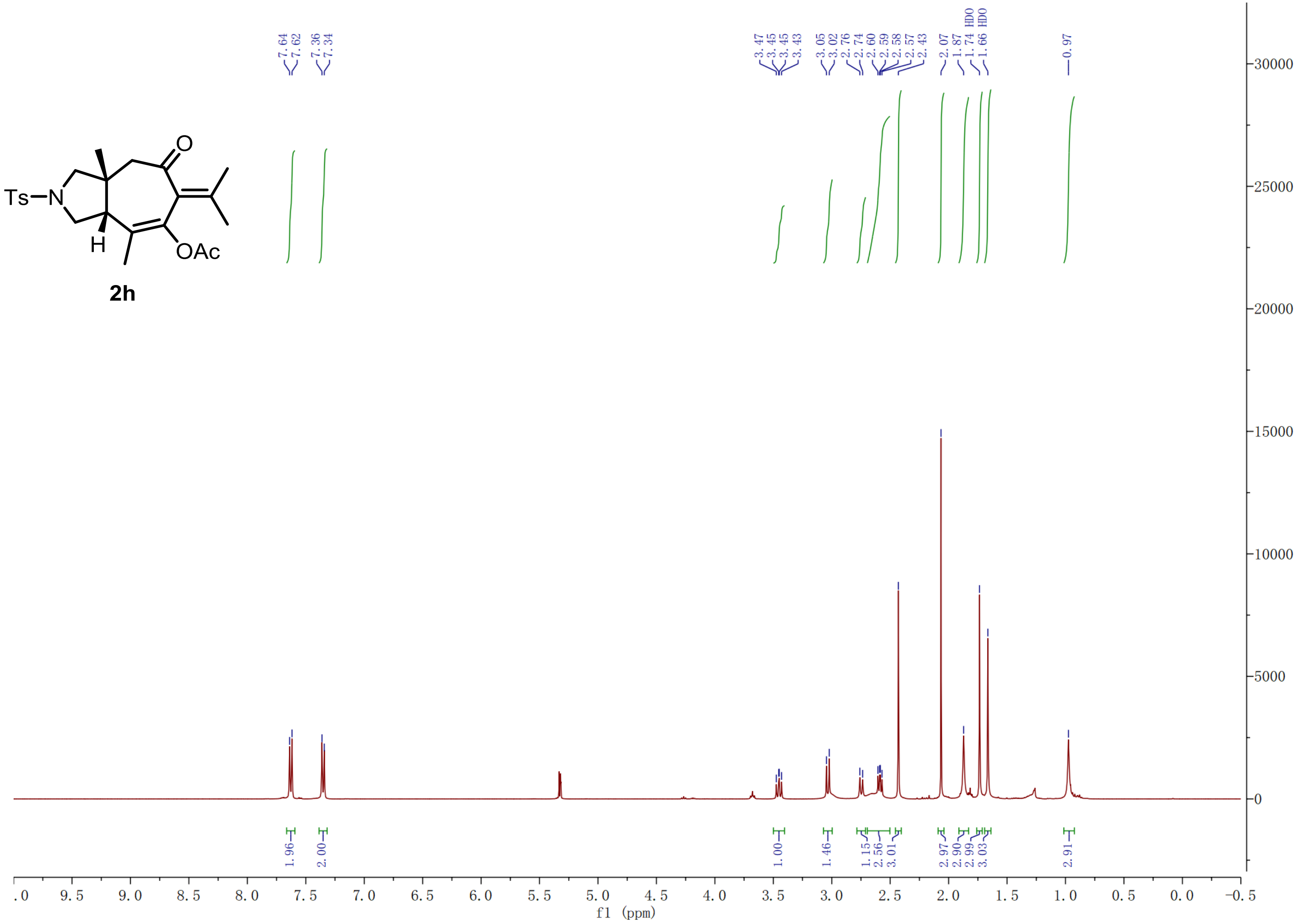
2f


198.95
169.84
155.06
147.81
144.49
133.21
131.12
130.27
128.18
118.57
53.51
53.46
44.10
40.12
37.82
25.11
23.07
21.80
20.75
Ts
N
H
H
O
OAc
2f
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

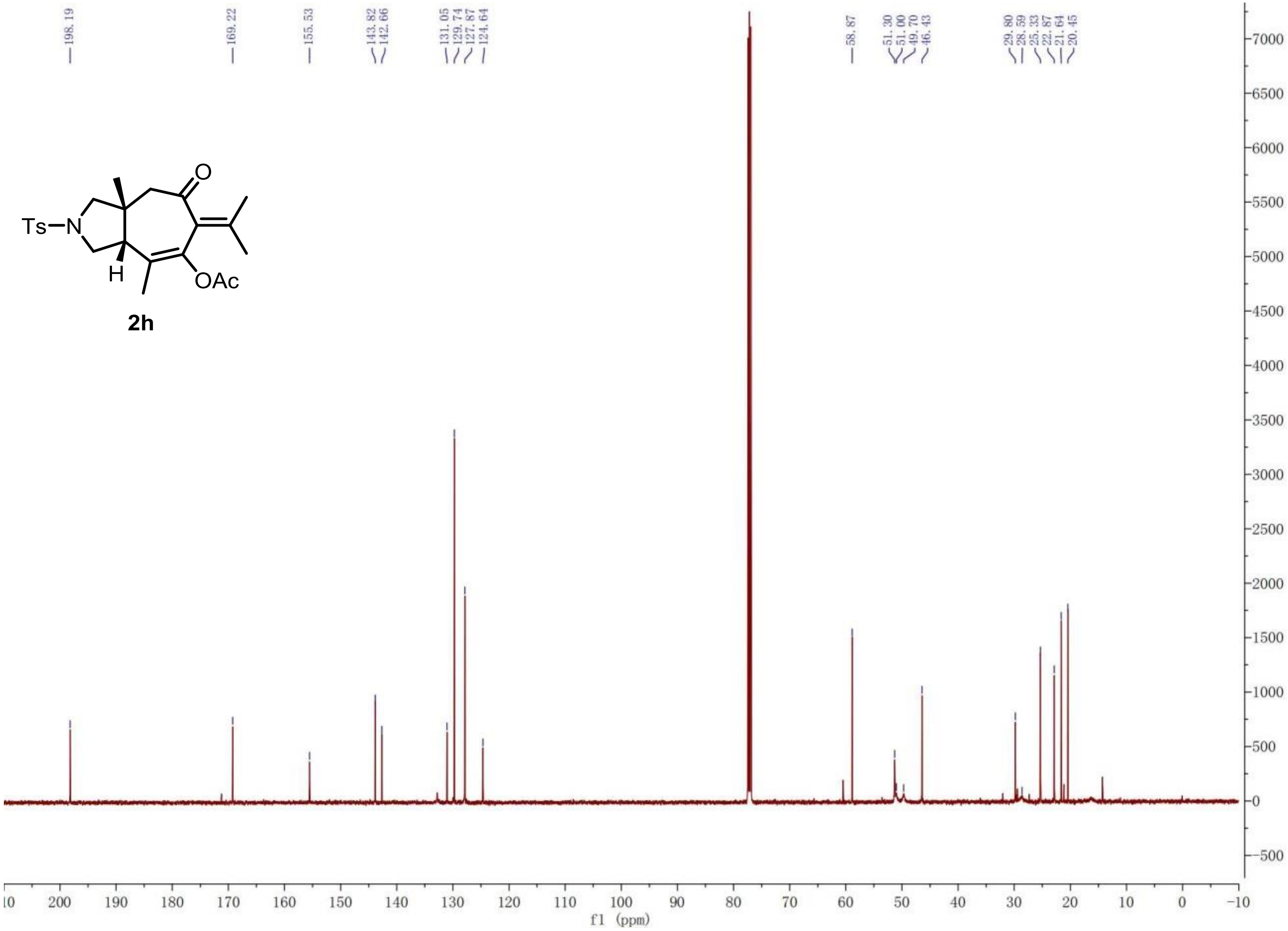

Ts
N
H
H
O
OAc
2g
2.00
2.01
0.95
2.09
2.04
2.17
2.14
3.08
4.46
2.81
6.04
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

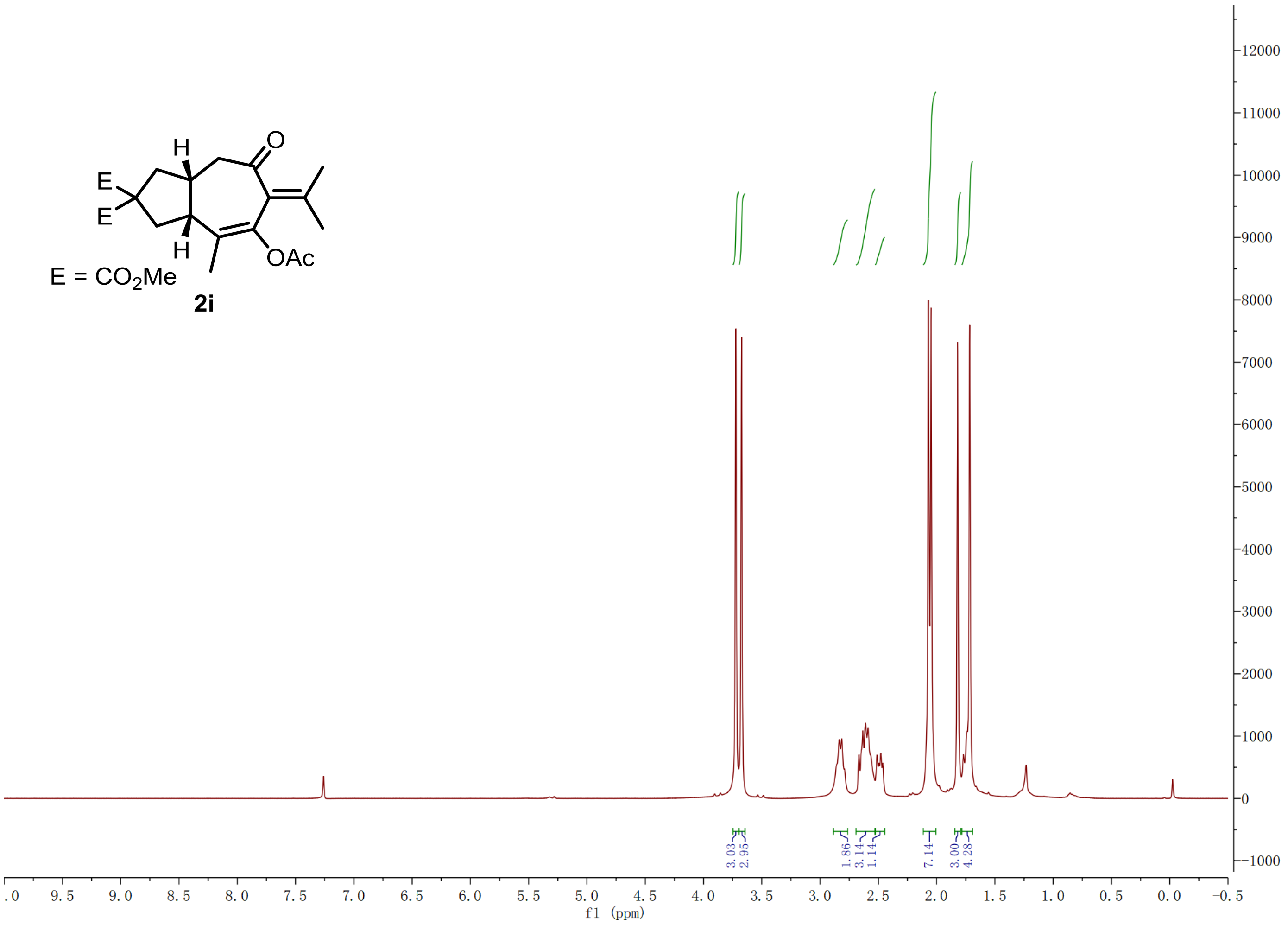

2g

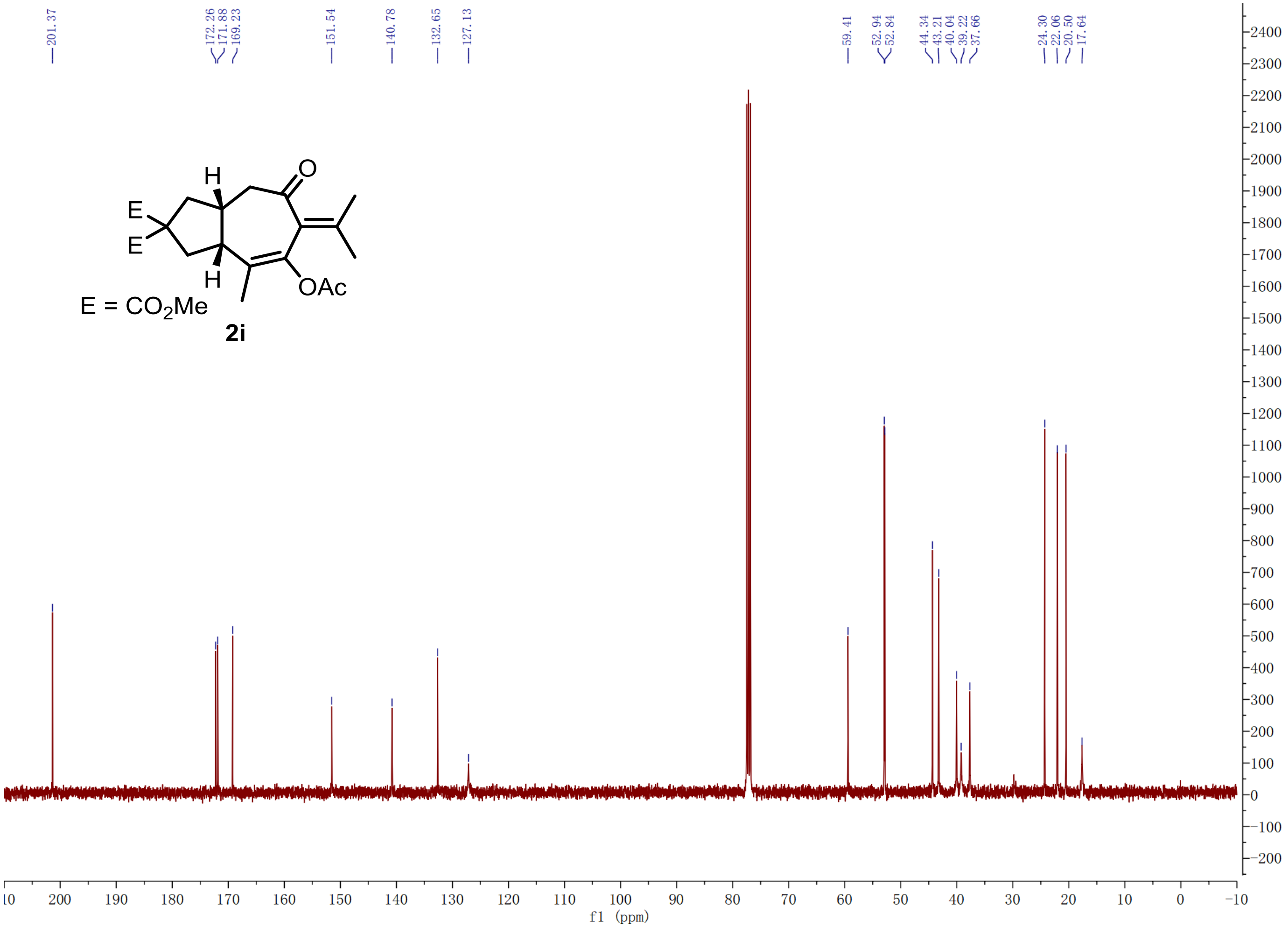
198.95
169.84
165.08
147.59
144.52
133.40
130.31
130.25
128.15
118.26
54.27
53.20
44.38
39.69
38.16
28.88
25.90
21.82
21.06
13.55
12.78
Ts
N
H
H
O
OAc
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Ts
N
H
O
OAc
7.64
7.62
7.36
7.34
3.47
3.45
3.45
3.43
3.05
3.02
2.76
2.74
2.60
2.59
2.58
2.57
2.43
2.07
1.87
1.74 HDO
1.66 HDO
0.97
1.96
2.00
1.00
1.46
1.15
2.56
3.01
2.97
2.90
2.99
3.03
2.91
30000
25000
20000
15000
10000
5000
0
.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)

2h


198.19
169.22
155.53
143.82
142.66
131.05
129.74
127.87
124.64
58.87
51.30
51.00
49.70
46.43
29.80
28.59
25.33
22.87
21.64
20.45
Ts
N
O
H
OAc
2h
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


E
E
H
H
O
OAc
E = CO₂Me
2i
3.03
2.95
1.86
3.14
1.14
7.14
3.00
4.28
.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

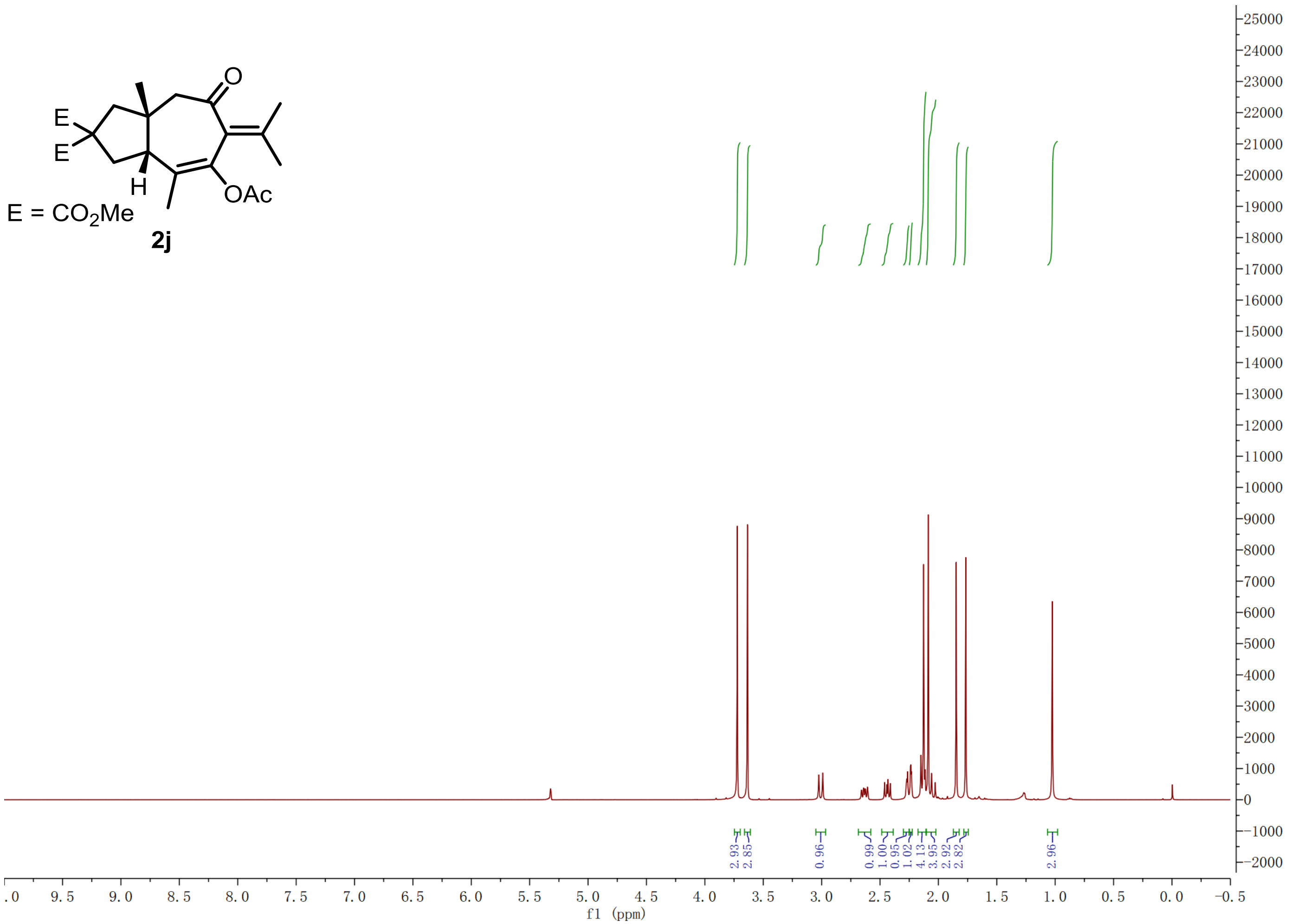

201.37
172.26
171.88
169.23
151.54
140.78
132.65
127.13
59.41
52.94
52.84
44.34
43.21
40.04
39.22
37.66
24.30
22.06
20.50
17.64
H
O
E
E
H
OAc
E = CO$_2$Me
f1 (ppm)

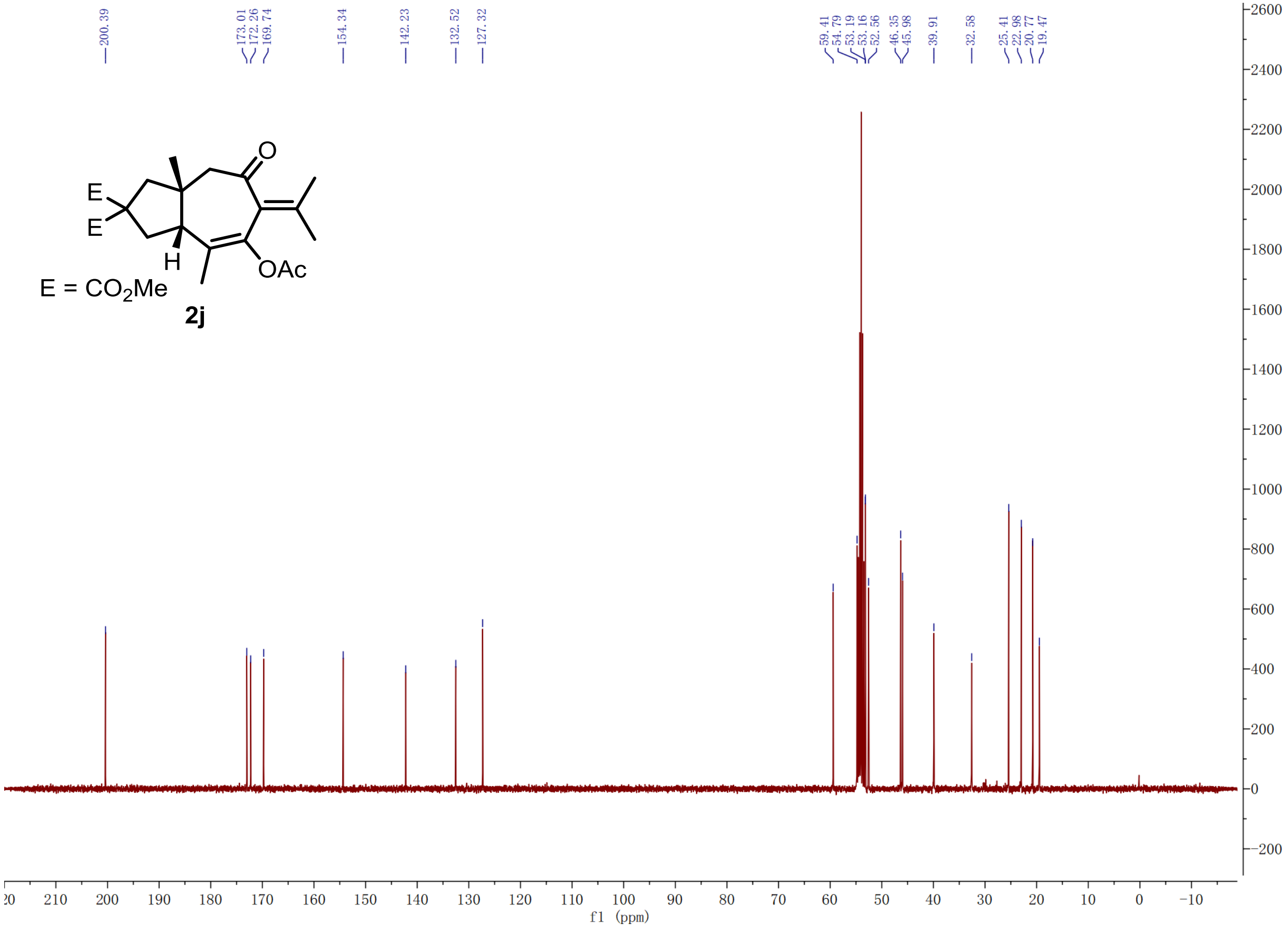
2i

O
E
E
H
OAc

E = CO_2Me

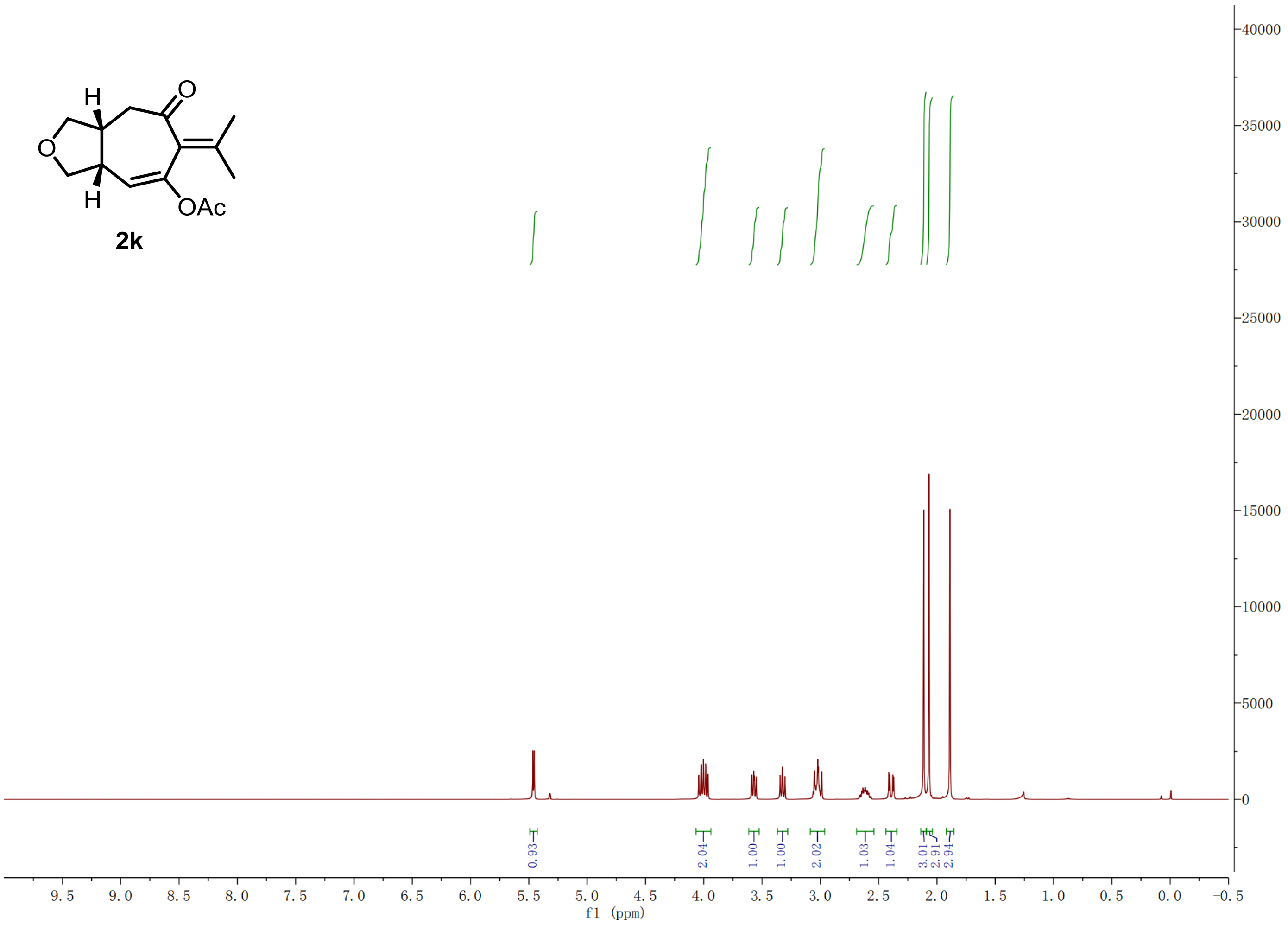
2j

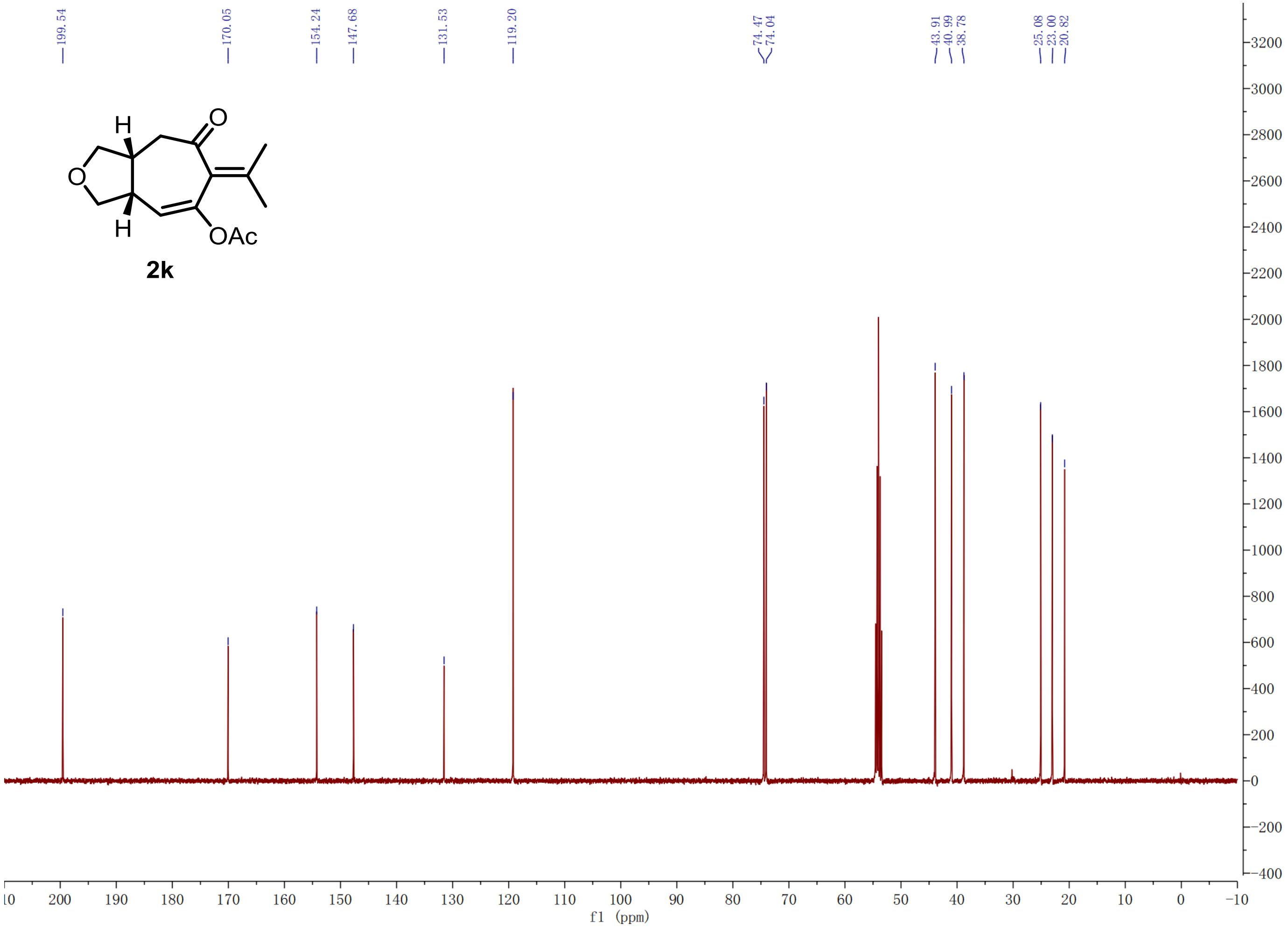

25000
24000
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
2.93
2.85
0.96
0.99
1.00
0.95
1.02
4.13
3.95
2.92
2.82
2.96
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

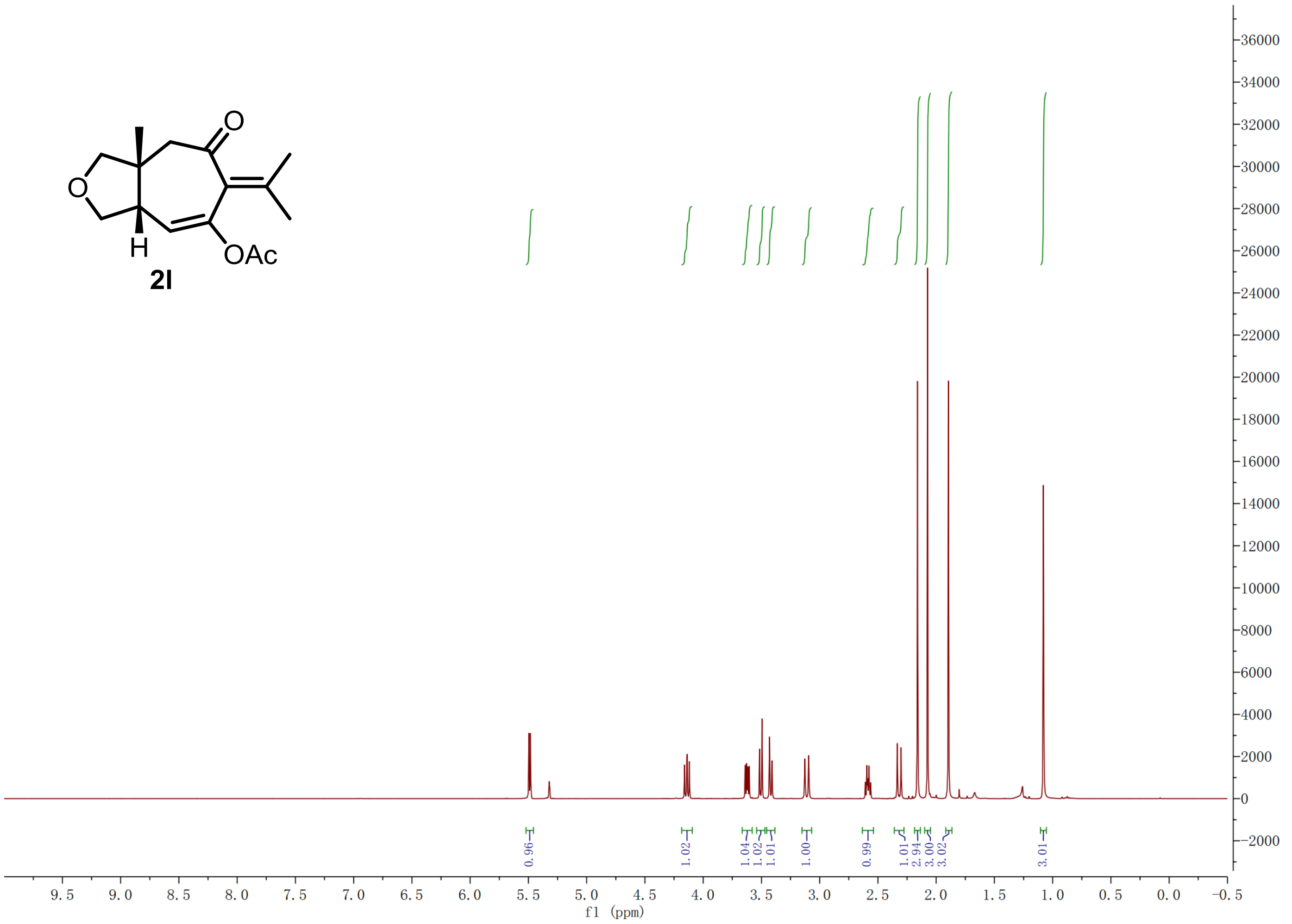

200.39
173.01
172.26
169.74
154.34
142.23
132.52
127.32
59.41
54.79
53.19
53.16
52.56
46.35
45.98
39.91
32.58
25.41
22.98
20.77
19.47
E
E
H
O
OAc
E = CO2Me
2j
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

H
O
O
H
OAc

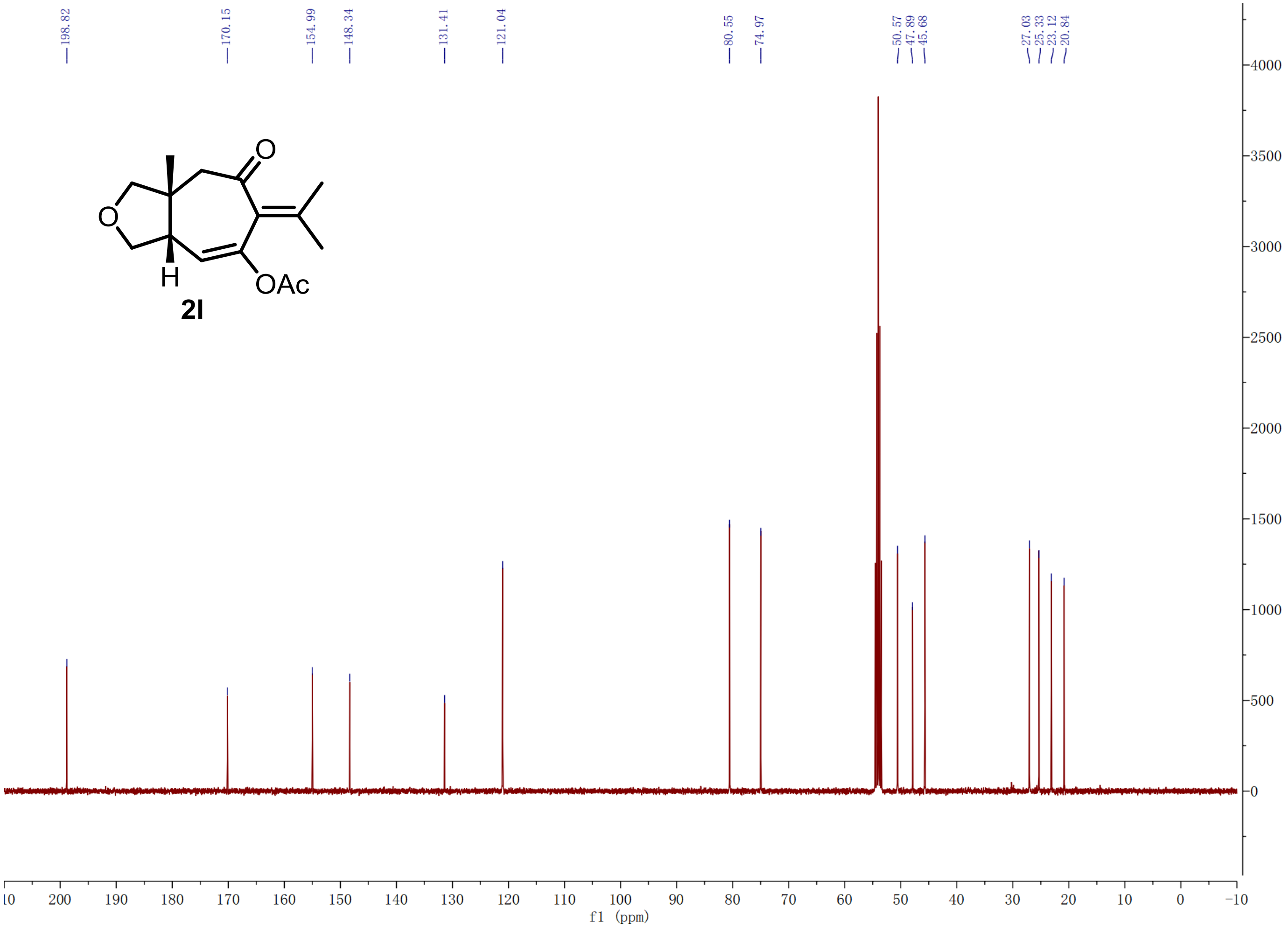
2k

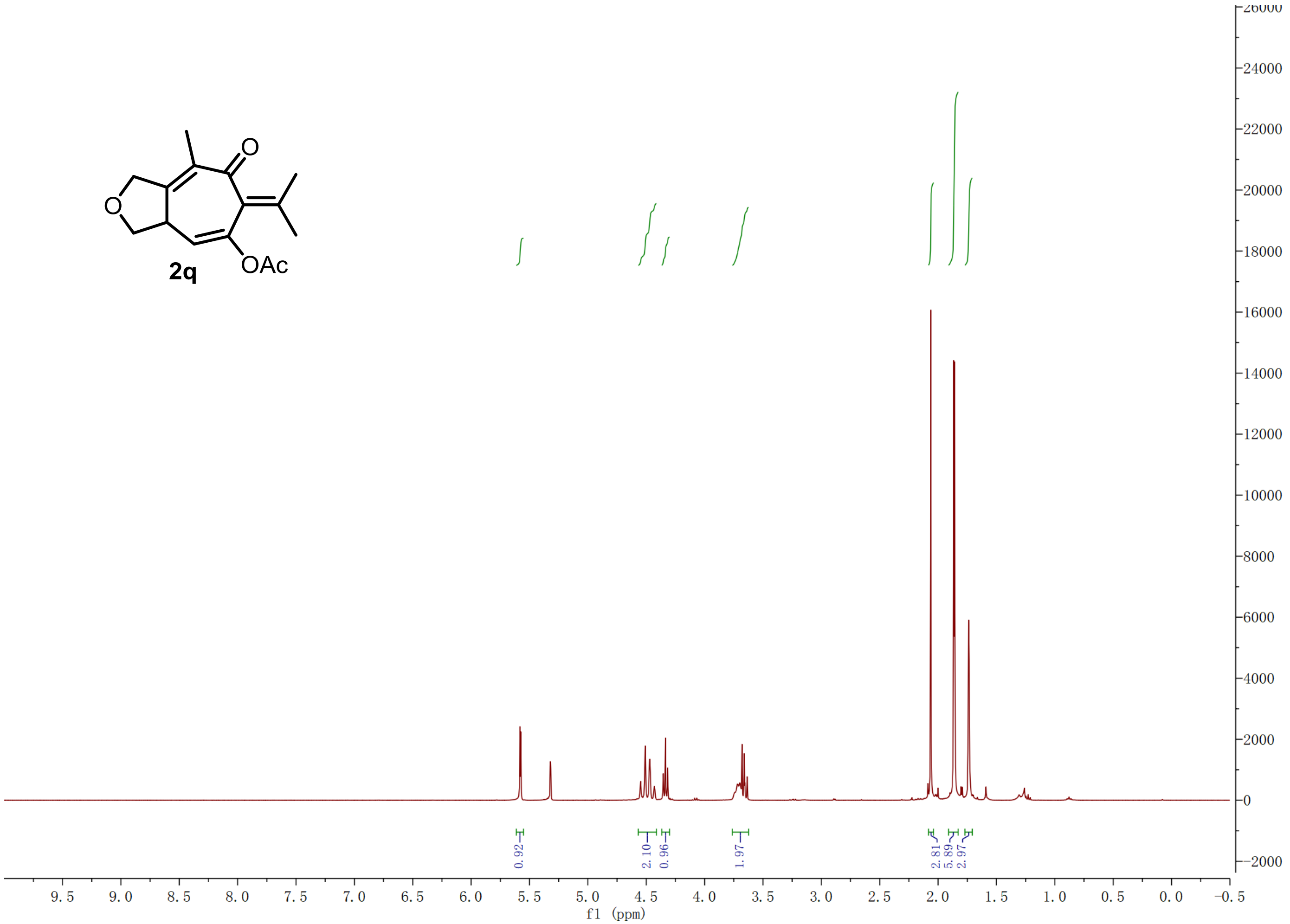

40000
35000
30000
25000
20000
15000
10000
5000
0
0.93
2.04
1.00
1.00
2.02
1.03
1.04
3.01
2.91
2.94
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

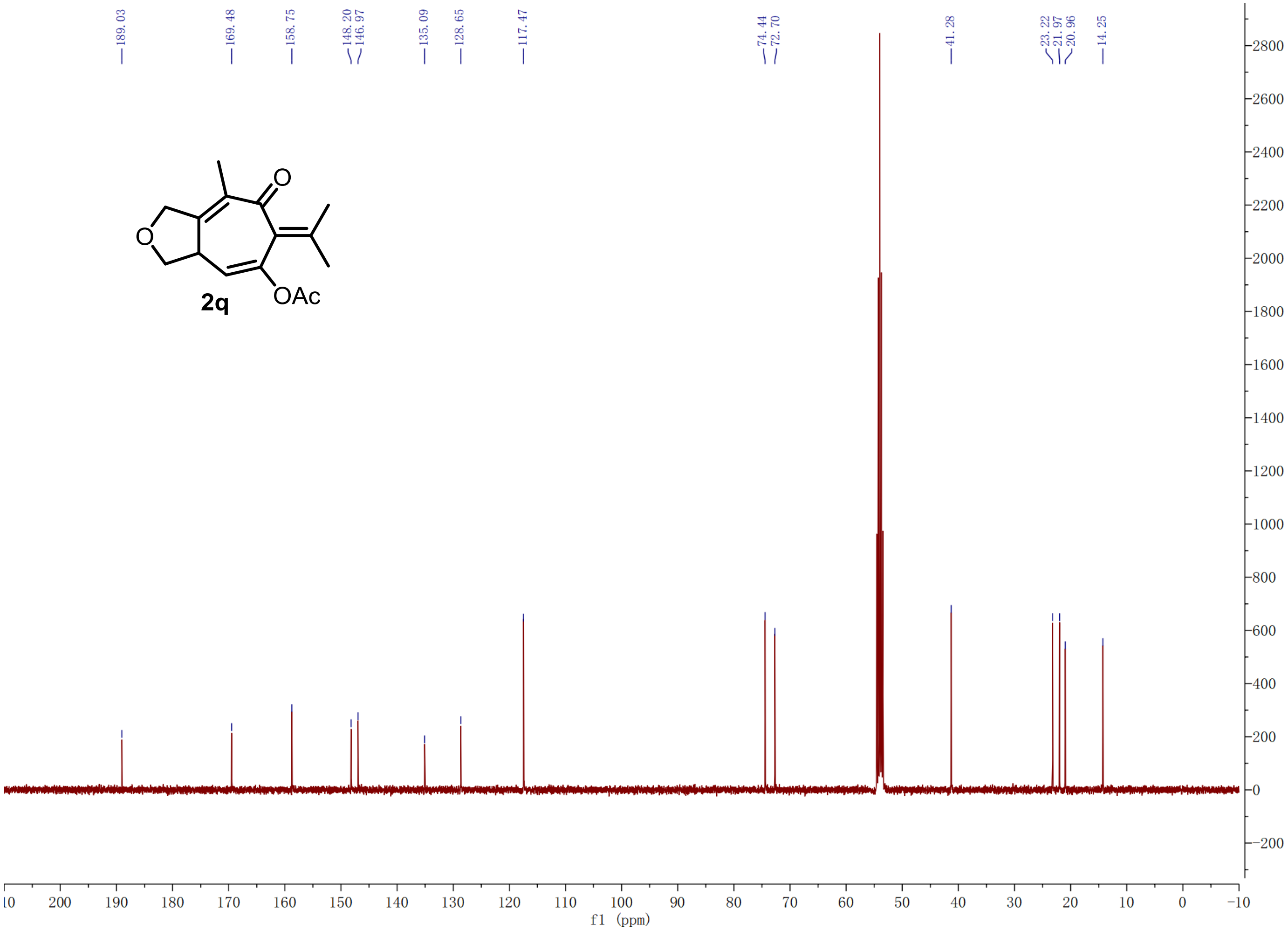

199.54
170.05
154.24
147.68
131.53
119.20
74.47
74.04
43.91
40.99
38.78
25.08
23.00
20.82
H
H
O
O
OAc
2k
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


2l

O
OAc
H
0.96
1.02
1.04
1.02
1.01
1.00
0.99
1.01
2.94
3.00
3.02
3.01
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)
36000 34000 32000 30000 28000 26000 24000 22000 20000 18000 16000 14000 12000 10000 8000 6000 4000 2000 0 -2000


198.82
170.15
154.99
148.34
131.41
121.04
80.55
74.97
50.57
47.89
45.68
27.03
25.33
23.12
20.84
O
O
OAc
H
2l
4000
3500
3000
2500
2000
1500
1000
500
0
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


O
OAc
2q
0.92
2.10
0.96
1.97
2.81
5.89
2.97
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
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)


2q

189.03
169.48
158.75
148.20
146.97
135.09
128.65
117.47
74.44
72.70
41.28
23.22
21.97
20.96
14.25
O
O
OAc
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

8. References

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