Supporting Information

Gold(I)-Catalyzed Polycyclization of Linear Dienediynes to Seven-Membered Ring-Containing Polycycles via Tandem Cyclopropanation/ Cope Rearrangement/C–H Activation

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S1. General Information

Air and moisture sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of dry argon. Similarly sensitive liquids and solutions were transferred via syringe. Reactions were stirred using Teflon-coated magnetic stir bars. Organic solutions were concentrated using a Büchi rotary evaporator with a desktop vacuum pump. Tetrahydrofuran, Et_2O, and toluene were distilled from sodium prior to use. Dichloromethane was distilled from CaH_2 prior to use. Anhydrous 1,2-dichloroethane, acetone, and other synthetic reagents were purchased from Acros, Aldrich, and Alfa Aesar and used without further purification unless otherwise indicated. Analytical thin layer chromatography (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 then 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) or Bruker AVANCE 500 (^{1}H at 500 MHz, ^{13}C at 126 MHz) nuclear magnetic resonance spectrometers. Data for ^{1}H NMR spectra are reported as follows: chemical shift δ (ppm, referenced to Me_4Si; s = singlet, d = doublet, t = triplet, sept = septet, m = multiplet, br. = broad, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, ddd = doublet of doublet of doublets), coupling constant J (Hz), and integration. Data for ^{13}C NMR spectra are reported in terms of chemical shift δ (ppm) relative to residual solvent peak ($CDCl_3$: 77.0 ppm; CD_2Cl_2: 53.8 ppm). 2D NMR experiments were conducted on Bruker AVANCE 500 nuclear magnetic resonance spectrometer. Infrared spectra were recorded on an AVATAR 330 Fourier transform spectrometer (FT-IR) with an OMNI sampler and are reported in wavenumbers ν (cm^{-1}). High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer (ESI).

Abbreviations:

Ac = acetyl

Bn = benzyl

BrettPhos = 2-(dicyclohexylphosphino)-3,6-dimethoxy-2′,4′,6′-triisopropylbiphenyl

Bu = butyl

calcd. = calculated

DCM = dichloromethane

DCE = 1,2-dichloroethane

DEAD = diethyl azodicarboxylate

DIAD = diisopropyl azodicarboxylate

DIBAL = diisobutylaluminum hydride

DMAP = 4-dimethylaminopyridine

DMF = *N*,*N*-dimethylformamide

dr = diastereomeric ratio

EA = ethyl acetate

equiv. = equivalent

Et = ethyl

GC–MS = gas chromatography–mass spectrometry

IPr = 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene

*i*Pr = isopropyl

JohnPhos = 2-(di-*tert*-butylphosphino)biphenyl

Me = methyl

m.p. = melting point

MS = molecular sieve

NBS = *N*-bromosuccinimide

NMR = nuclear magnetic resonance

PE = petroleum ether

Ph = phenyl

Piv = pivaloyl

R_f = rate of flow

rt = room temperature

TBS = *tert*-butyldimethylsilyl

Tf = trifluoromethanesulfonyl

THF = tetrahydrofuran

TLC = thin layer chromatography

Ts = *para*-toluenesulfonyl

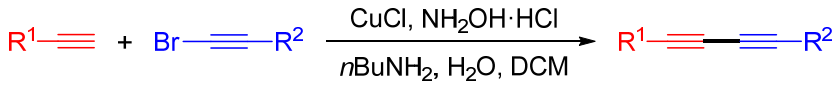
wt = weight

XPhos = 2-(dicyclohexylphosphino)-2′,4′,6′-triisopropylbiphenyl

S2. Experimental Procedures and Characterization Data

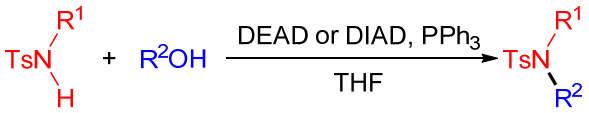
S2.1 Synthesis of Substrates

General Procedure A: Cadiot–Chodkiewicz Coupling

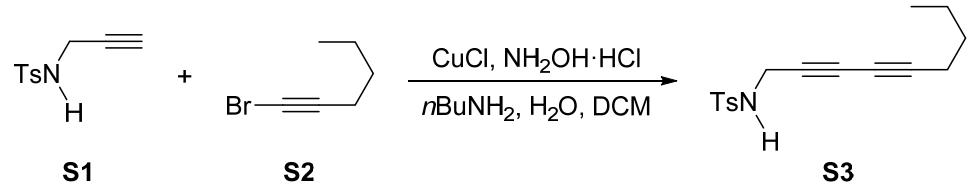


To a 30% (v/v) *n*BuNH$_2$ aqueous solution containing CuCl (0.5–1 equiv.) under argon at 0 °C was added NH$_2$OH·HCl until the blue color disappeared. A solution of terminal alkyne (0.5–2 equiv.) in DCM was then added, followed by the slow addition of a solution of bromoalkyne (1 equiv.) in DCM over 5 minutes. The reaction mixture was stirred for additional 10 minutes, quenched with aqueous ammonia and extracted with Et$_2$O for three times. The combined organic layers were washed with brine, dried over MgSO$_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to afford the diyne product.

General Procedure B: Mitsunobu Reaction

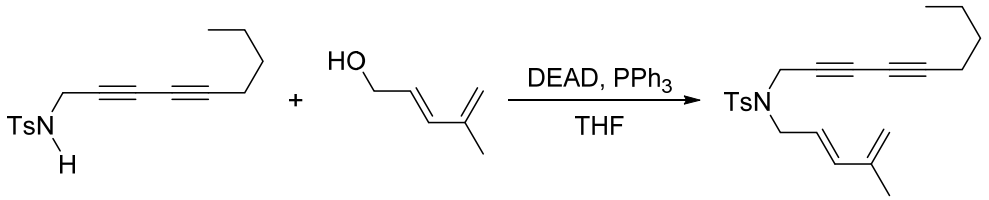


To a solution of tosylamide (1.0 equiv.) and PPh$_3$ (2.0 equiv.) in anhydrous THF under argon at 0 °C was added alcohol (1.1–1.5 equiv.), followed by the slow addition of DEAD or DIAD (2.2 equiv.). Then the mixture was allowed to warm to room temperature and stirred until TLC indicated the disappearance of the starting material. The solvent was then removed under reduced pressure, and the crude product was purified by column chromatography on silica gel to afford the product in generally good yield.



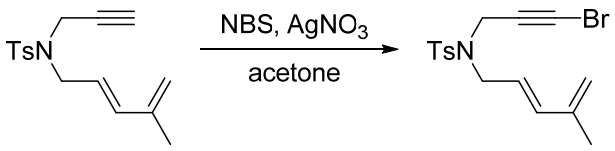
S1 **S2** **S3**

S3: Following the general procedure A, a solution of tosylamide **S1**[1] (1.03 g, 4.93 mmol) in DCM (6 mL), a solution of bromoalkyne **S2**[2] (1.62 g, 10.1 mmol) in DCM (5 mL), CuCl (504 mg, 5.09 mmol), and 30% *n*BuNH$_2$/H$_2$O (15 mL) were used. Purification of the crude product by column chromatography (PE/EA, 5/1) afforded **S3** (1.23 g, 4.26 mmol, 86%) as a light brown solid. m.p.: 68 °C; TLC (PE/EA, 3/1): R_f = 0.4; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 4.58–4.45 (br. s, 1H), 3.89 (d, J = 3.9 Hz, 2H), 2.43 (s, 3H), 2.23 (t, J = 6.9 Hz, 2H), 1.53–1.34 (m, 4H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.9, 136.5, 129.7, 127.4, 81.2, 70.0, 69.4, 64.1, 33.7, 30.1, 21.9, 21.5, 18.8, 13.5; IR (neat): ν 3375, 3155, 2932, 2361, 2254, 1794, 1600, 1384, 1163, 1094, 912, 742 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd. for $C_{16}H_{20}NO_2S$, 290.1209; found, 290.1215.



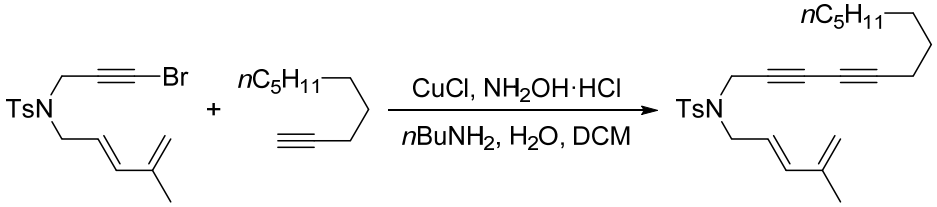
S3 **S4** **1a**

1a: Following the general procedure B, tosylamide **S3** (267 mg, 0.923 mmol), alcohol **S4**[3] (99 mg, 1.0 mmol), DEAD (360 mg, 2.07 mmol), PPh_3 (490 mg, 1.87 mmol), and THF (5.5 mL) were stirred at rt overnight. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **1a** (310 mg, 0.840 mmol, 91%) as a light yellow oil. TLC (PE/EA, 20/1): R_f = 0.4; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 6.29 (d, J = 15.6 Hz, 1H), 5.50 (dt, J = 15.5, 6.9 Hz, 1H), 4.99 (s, 1H), 4.97 (s, 1H), 4.11 (s, 2H), 3.85 (d, J = 6.8 Hz, 2H), 2.43 (s, 3H), 2.23 (t, J = 6.9 Hz, 2H), 1.80 (s, 3H), 1.54–1.34 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.6, 141.0, 137.7, 135.7, 129.5, 127.8, 122.9, 117.6, 80.4, 70.6, 68.5, 64.3, 48.7, 36.7, 30.2, 21.9, 21.5, 18.8, 18.4, 13.5; IR (neat): ν 2972, 2945, 2878, 2262, 1601, 1458, 1354, 1166, 1097 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd. for $C_{22}H_{28}NO_2S$, 370.1835; found, 370.1834.



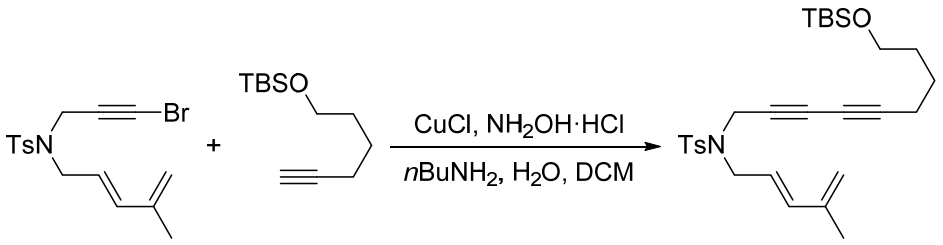
S5 **S6**

S6: NBS (876 mg, 4.92 mmol) and $AgNO_3$ (78 mg, 0.46 mmol) were added to a solution of tosylamide **S5**[4] (1.29 g, 4.46 mmol) in acetone (11 mL). The reaction mixture was stirred at room temperature for 2 hours, then quenched with saturated aqueous $Na_2S_2O_3$ solution. The aqueous layer was extracted with Et_2O for three times, washed with water, dried over $MgSO_4$, filtered, and concentrated. Purification of the crude product by column chromatography (PE/EA, 30/1) afforded **S6** (1.29 g, 3.51 mmol, 79%) as a white solid. m.p.: 73 °C; TLC (PE/EA, 20/1): R_f = 0.3; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 6.28 (d, J = 15.6 Hz, 1H), 5.52 (dt, J = 15.5, 6.8 Hz, 1H), 5.00 (s, 1H), 4.97 (s, 1H), 4.08 (s, 2H), 3.85 (d, J = 6.8 Hz, 2H), 2.44 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.7, 141.0, 137.7, 135.8, 129.5, 127.8, 122.9, 117.6, 73.1, 48.8, 44.9, 37.0, 21.5, 18.5; IR (neat): ν 2255, 1383, 1162, 908, 734 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd. for $C_{16}H_{19}BrNO_2S$, 368.0314; found, 368.0324.

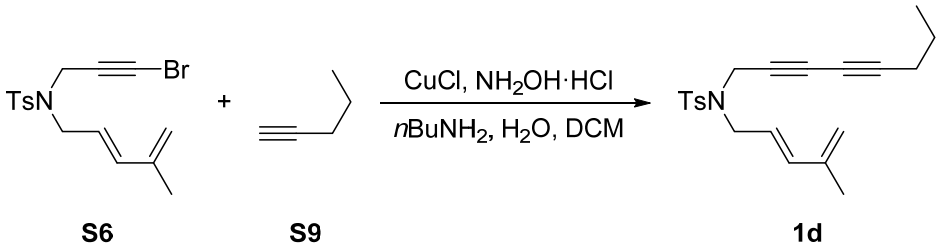


S6 **S7** **1b**

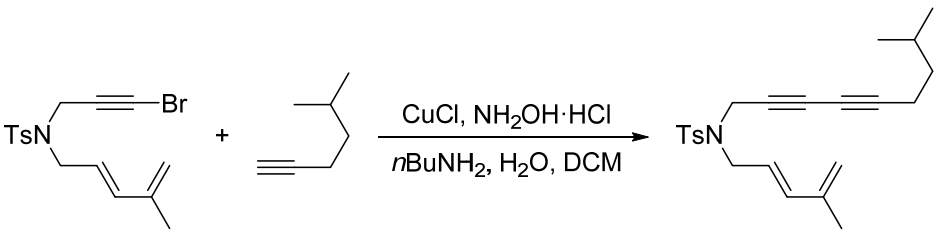
1b: Following the general procedure A, a solution of bromoalkyne **S6** (200 mg, 0.543 mmol) in DCM (2.0 mL), a solution of alkyne **S7** (150 mg, 1.09 mmol) in DCM (1.0 mL), CuCl (54.0 mg, 0.543 mmol), and 30% nBuNH$_2$/H$_2$O (2.0 mL) were used. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **1b** (155 mg, 0.364 mmol, 67%) as an orange oil. TLC (PE/EA, 5/1): R_f = 0.6; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 6.29 (d, J = 15.5 Hz, 1H), 5.50 (dt, J = 15.5, 6.8 Hz, 1H), 5.00 (s, 1H), 4.97 (s, 1H), 4.12 (s, 2H), 3.85 (d, J = 6.8 Hz, 2H), 2.43 (s, 3H), 2.22 (t, J = 7.0 Hz, 2H), 1.80 (s, 3H), 1.55–1.45 (m, 2H), 1.41–1.21 (m, 10H), 0.89 (t, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.6, 141.0, 137.7, 135.8, 129.5, 127.7, 122.9, 117.6, 80.5, 70.6, 68.5, 64.2, 48.7, 36.7, 31.8, 29.1, 29.0, 28.8, 28.2, 22.6, 21.5, 19.1, 18.4, 14.1; IR (neat): ν 2932, 2862, 2260, 1612, 1458, 1354, 1164 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd. for $C_{26}H_{36}NO_2S$, 426.2461; found, 426.2471.



1c: Following the general procedure A, a solution of bromoalkyne **S6** (153.6 mg, 0.417 mmol) in DCM (1.3 mL), a solution of alkyne **S8**[5] (179 mg, 0.843 mmol) in DCM (0.2 mL), CuCl (21.0 mg, 0.212 mmol), and 30% *n*BuNH$_2$/H$_2$O (1.7 mL) were used. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **1c** (123.5 mg, 0.247 mmol, 59%) as a pink oil. TLC (PE/EA, 10/1): R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 6.29 (d, J = 15.6 Hz, 1H), 5.50 (dt, J = 15.5, 6.8 Hz, 1H), 5.00 (s, 1H), 4.97 (s, 1H), 4.11 (s, 2H), 3.85 (d, J = 6.8 Hz, 2H), 3.62 (t, J = 5.8 Hz, 2H), 2.43 (s, 3H), 2.26 (t, J = 6.1 Hz, 2H), 1.80 (s, 3H), 1.62–1.54 (m, 4H), 0.90 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.6, 141.0, 137.7, 135.8, 129.5, 127.7, 122.9, 117.6, 80.2, 70.6, 68.6, 64.4, 62.4, 48.7, 36.7, 31.8, 25.9, 24.7, 21.5, 19.0, 18.4, 18.3, –5.4; IR (neat): ν 2927, 1731, 1635, 1352, 1258, 1229, 1163 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd. for $C_{28}H_{42}NO_3SSi$, 500.2649; found, 500.2649.

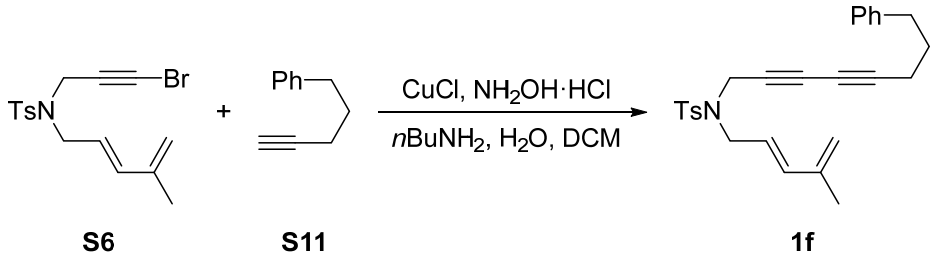


1d: Following the general procedure A, a solution of bromoalkyne **S6** (200 mg, 0.543 mmol) in DCM (1.7 mL), alkyne **S9** (74.0mg, 1.09 mmol), CuCl (26.0 mg, 0.263 mmol), and 30% *n*BuNH$_2$/H$_2$O (1.7 mL) were used. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **1d** (126.7 mg, 0.356 mmol, 66%) as a colorless oil. TLC (PE/EA, 10/1): R_f = 0.3; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 6.29 (d, J = 15.6 Hz, 1H), 5.51 (dt, J = 15.6, 6.8 Hz, 1H), 5.00 (s, 1H), 4.97 (s, 1H), 4.12 (s, 2H), 3.85 (d, J = 6.8 Hz, 2H), 2.43 (s, 3H), 2.21 (t, J = 7.0 Hz, 2H), 1.80 (s, 3H), 1.58–1.49 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.6, 141.0, 137.7, 135.8, 129.5, 127.8, 122.9, 117.6, 80.3, 70.6, 68.6, 64.4, 48.7, 36.7, 21.7, 21.5, 21.1, 18.4, 13.4; IR (neat): ν 2972, 2940, 2880, 2260, 1612, 1601, 1458, 1354, 1164, 1095 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd. for $C_{21}H_{26}NO_2S$, 356.1679; found, 356.1688.



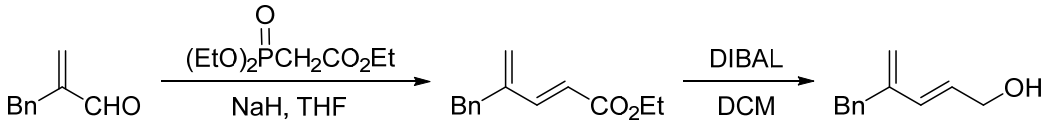
S6 **S10** **1e**

1e: Following the general procedure A, a solution of bromoalkyne **S6** (201 mg, 0.546 mmol) in DCM (2.0 mL), alkyne **S10** (94.0 mg, 0.977 mmol), CuCl (26.9 mg, 0.272 mmol), and 30% *n*BuNH$_2$/H$_2$O (1.7 mL) were used. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **1e** (163 mg, 0.425 mmol, 78%) as a pink oil. TLC (PE/EA, 10/1): R_f = 0.2; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 6.29 (d, J = 15.6 Hz, 1H), 5.50 (dt, J = 15.5, 6.9 Hz, 1H), 5.00 (s, 1H), 4.97 (s, 1H), 4.12 (s, 2H), 3.85 (d, J = 6.8 Hz, 2H), 2.43 (s, 3H), 2.24 (t, J = 7.4 Hz, 2H), 1.80 (s, 3H), 1.71–1.60 (m, 1H), 1.40 (q, J = 7.2 Hz, 2H), 0.90 (d, J = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.6, 141.0, 137.7, 135.7, 129.5, 127.7, 122.9, 117.6, 80.4, 70.6, 68.5, 64.2, 48.7, 37.0, 36.7, 27.1, 22.0, 21.5, 18.4, 17.1; IR (neat): ν 2964, 2940, 2877, 2262, 1614, 1601, 1456, 1352, 1164, 1097 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd. for $C_{23}H_{30}NO_2S$, 384.1992; found, 384.1986.



S6 **S11** **1f**

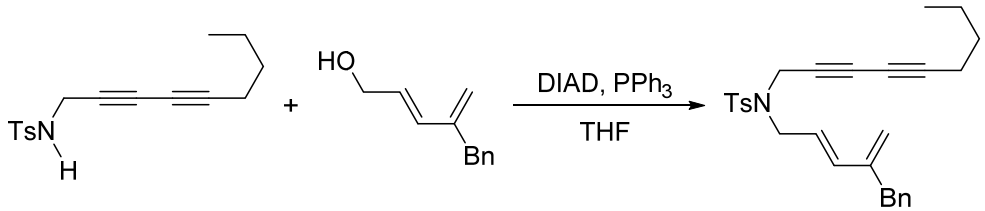
1f: Following the general procedure A, a solution of bromoalkyne **S6** (151 mg, 0.391 mmol) in DCM (1.3 mL), a solution of alkyne **S11** (113 mg, 0.784 mmol) in DCM (0.2 mL), CuCl (19.4 mg, 0.196 mmol), and 30% *n*BuNH$_2$/H$_2$O (1.7 mL) were used. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **1f** (112.4 mg, 0.260 mmol, 67%) as a colorless oil. TLC (PE/EA, 20/1): R_f = 0.4; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.2 Hz, 2H), 7.35–7.27 (m, 4H), 7.22 (d, J = 7.2 Hz, 1H), 7.17 (d, J = 7.3 Hz, 2H), 6.30 (d, J = 15.6 Hz, 1H), 5.51 (dt, J = 15.6, 6.8 Hz, 1H), 5.00 (s, 1H), 4.98 (s, 1H), 4.13 (s, 2H), 3.86 (d, J = 6.8 Hz, 2H), 2.70 (t, J = 7.5 Hz, 2H), 2.39 (s, 3H), 2.24 (t, J = 7.0 Hz, 2H), 1.87–1.77 (m, 2H), 1.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.6, 140.98, 140.96, 137.7, 135.7, 129.5, 128.43, 128.42, 127.7, 126.1, 122.8, 117.6, 79.8, 70.5, 68.8, 64.8, 48.7, 36.6, 34.6, 29.7, 21.5, 18.47, 18.45; IR (neat): ν 2955, 2871, 2266, 1605, 1458, 1352, 1166, 1100 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd. for $C_{27}H_{30}NO_2S$, 432.1992; found, 432.2001.



S12 **S13** **S14**

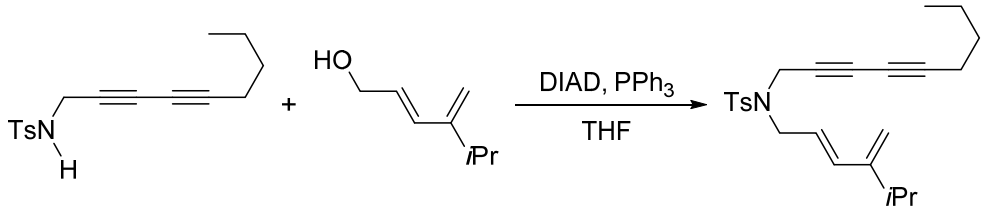
S13: To a stirred suspension of NaH (60 wt%, 0.75 g, 19 mmol) in THF (20 mL) was added a solution of triethyl phosphonoacetate (3.68 g, 16.4 mmol) in THF (10 mL) at 0 °C. After stirred for 30 minutes, a solution of aldehyde **S12**[6] (2.00 g, 13.7 mmol) in THF (10 mL) was added and the reaction mixture was stirred for additional one hour at 0 °C. Then the reaction was quenched with saturated aqueous NH_4Cl solution, extracted with Et_2O, washed with brine, dried over $MgSO_4$, filtered, and concentrated. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **S13** (1.64 g, 7.59 mmol, 55%) as a light yellow oil. TLC (PE/EA, 10/1): $R_f = 0.5$.

S14: To a stirred solution of ester **S13** (0.79 g, 3.7 mmol) in DCM (10 mL) was added DIBAL (in hexanes, 9.0 mL, 1.0 M, 9.0 mmol) at –78 °C. After stirred for 3 hours, the reaction mixture was allowed to warm to rt, quenched with MeOH (2 mL). Then saturated potassium sodium tartrate solution (50 mL) and Et_2O (50 mL) were added and the mixture was stirred until a clear organic phase was obtained. The aqueous layer was then extracted with Et_2O for three times and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. Purification of the crude product by column chromatography (PE/EA, 5/1) afforded **S14** (0.59 g, 3.4 mmol, 92%) as a colorless oil. TLC (PE/EA, 3/1): $R_f = 0.4$; ^1H NMR (400 MHz, $CDCl_3$): δ 7.31–7.24 (m, 2H), 7.20 (d, $J = 7.3$ Hz, 3H), 6.32 (d, $J = 15.8$ Hz, 1H), 5.85 (dt, $J = 15.8$, 5.8 Hz, 1H), 5.17 (s, 1H), 4.91 (s, 1H), 4.14 (d, $J = 5.8$ Hz, 2H), 3.55 (s, 2H), 1.64–1.50 (br. s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.2, 139.3, 132.7, 128.9, 128.8, 128.3, 126.1, 118.2, 63.5, 38.8; IR (neat): ν 2294, 2253, 1605, 1455, 1382, 1092, 908, 733 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd. for $C_{12}H_{15}O$, 175.1117; found, 175.1104.



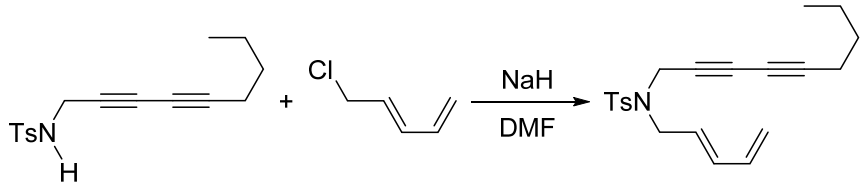
S3 **S14** **1g**

1g: Following the general procedure B, tosylamide **S3** (146 mg, 0.505 mmol), alcohol **S14** (130 mg, 0.747 mmol), DIAD (221 mg, 1.09 mmol), and PPh_3 (262 mg, 1.00 mmol) in THF (2.5 mL) were stirred at rt for 22 hours. Purification of the crude product by column chromatography (hexanes/EA, 50/1) afforded **1g** (206 mg, 0.462 mmol, 91%) as a light yellow oil. TLC (PE/EA, 3/1): R_f = 0.8; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 8.3 Hz, 2H), 7.33–7.24 (m, 4H), 7.20 (d, J = 7.1 Hz, 1H), 7.15 (d, J = 7.1 Hz, 2H), 6.26 (d, J = 15.7 Hz, 1H), 5.52 (dt, J = 15.7, 6.9 Hz, 1H), 5.15 (s, 1H), 4.93 (s, 1H), 3.94 (s, 2H), 3.79 (d, J = 6.8 Hz, 2H), 3.49 (s, 2H), 2.42 (s, 3H), 2.23 (t, J = 6.9 Hz, 2H), 1.53–1.34 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.0, 143.6, 139.0, 136.6, 135.6, 129.5, 128.7, 128.3, 127.7, 126.1, 123.5, 118.9, 80.4, 70.6, 68.5, 64.3, 48.8, 38.7, 36.5, 30.2, 21.8, 21.5, 18.8, 13.5; IR (neat): ν 3035, 2964, 2934, 2877, 2260, 1603, 1454, 1352, 1166, 1095, 1063 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd. for $C_{28}H_{32}NO_2S$, 446.2148; found, 446.2145.



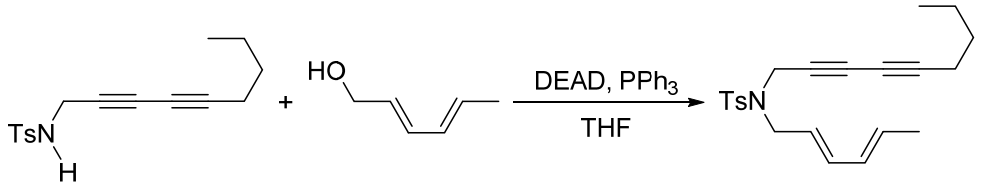
S3 **S15** **1h**

1h: Following the general procedure B, tosylamide **S3** (289 mg, 1.00 mmol), alcohol **S15**[7] (183 mg, 1.45 mmol), DIAD (446 mg, 2.21 mmol), and PPh_3 (525 mg, 2.00 mmol) in THF (5 mL) were stirred at rt for 28 hours. Purification of the crude product by column chromatography (hexanes/EA, 50/1) afforded **1h** (336 mg, 0.846 mmol, 85%) as a colorless oil. TLC (PE/EA, 5/1): R_f = 0.7; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 6.18 (d, J = 15.8 Hz, 1H), 5.59 (dt, J = 15.7, 6.9 Hz, 1H), 4.97 (s, 2H), 4.12 (s, 2H), 3.85 (d, J = 6.9 Hz, 2H), 2.55–2.44 (m, 1H), 2.43 (s, 3H), 2.23 (t, J = 6.9 Hz, 2H), 1.54–1.35 (m, 4H), 1.05 (d, J = 6.8 Hz, 6H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.7, 143.6, 137.1, 135.8, 129.5, 127.8, 121.7, 113.3, 80.4, 70.7, 68.6, 64.3, 49.1, 36.7, 30.2, 29.3, 22.1, 21.9, 21.5, 18.8, 13.5; IR (neat): ν 2966, 2938, 2877, 1655, 1560, 1460, 1352, 1166, 1097 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd. for $C_{24}H_{32}NO_2S$, 398.2148; found, 398.2159.



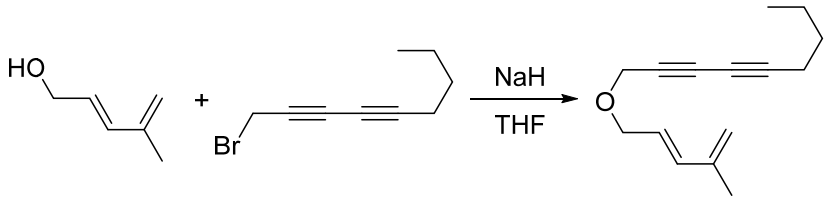
S3 **S16** **1i**

1i: To a stirred suspension of NaH (60 wt%, 48 mg, 1.2 mmol) in DMF (20 mL) was added tosylamide **S3** (289 mg, 1.00 mmol) in several portions at 0 °C. After one hour, a solution of chloride **S16**[8] (124 mg, 1.20 mmol) in DMF (5 mL) was added and the reaction mixture was allowed to warm to rt and stirred for additional 12 hours. Then the reaction mixture was quenched with water, extracted with Et_2O for three times. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. Purification of the crude product by column chromatography (hexanes/EA, 50/1) afforded **1i** (300 mg, 0.845 mmol, 84%) as a yellow oil. TLC (PE/EA, 5/1): R_f = 0.7; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 6.36–6.16 (m, 2H), 5.56 (dt, J = 14.8, 6.8 Hz, 1H), 5.22 (d, J = 16.4 Hz, 1H), 5.12 (d, J = 9.6 Hz, 1H), 4.11 (s, 2H), 3.82 (d, J = 6.9 Hz, 2H), 2.43 (s, 3H), 2.23 (t, J = 6.9 Hz, 2H), 1.53–1.35 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.6, 135.71, 135.67, 135.65, 129.5, 127.7, 126.8, 118.4, 80.4, 70.7, 68.4, 64.2, 48.3, 36.6, 30.2, 21.8, 21.5, 18.8, 13.5; IR (neat): ν 1600, 1350, 1162, 1092, 1005, 900 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd. for $C_{21}H_{26}NO_2S$, 356.1679; found, 356.1686.



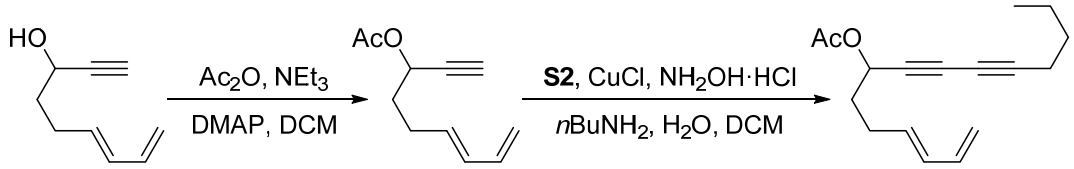
S3 **S17** **1j**

1j: Following the general procedure B, tosylamide **S3** (204 mg, 0.706 mmol), alcohol **S17** (83.1 mg, 0.846 mmol), DEAD (274 mg, 1.57 mmol), and PPh_3 (370 mg, 1.41 mmol) in THF (4.2 mL) were stirred at rt for 12 hours. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **1j** (188 mg, 0.509 mmol, 72%) as a colorless oil. TLC (PE/EA, 2/1): R_f = 0.7; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 6.17 (dd, J = 14.8, 10.4 Hz, 1H), 6.02 (ddd, J = 14.8, 10.4, 1.4 Hz, 1H), 5.71 (dq, J = 14.8, 6.8 Hz, 1H), 5.39 (dt, J = 15.2, 6.8 Hz, 1H), 4.10 (s, 2H), 3.78 (d, J = 7.0 Hz, 2H), 2.43 (s, 3H), 2.23 (t, J = 6.9 Hz, 2H), 1.75 (d, J = 6.6 Hz, 3H), 1.54–1.35 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.5, 135.7, 135.6, 131.0, 130.3, 129.5, 127.7, 123.3, 80.3, 70.6, 68.5, 64.3, 48.5, 36.4, 30.2, 21.8, 21.5, 18.8, 18.0, 13.5; IR (neat): ν 2924, 1385, 1168, 1093, 913, 714, 678, 549 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd. for $C_{22}H_{28}NO_2S$, 370.1835; found, 370.1845.



S4 **S18** **1k**

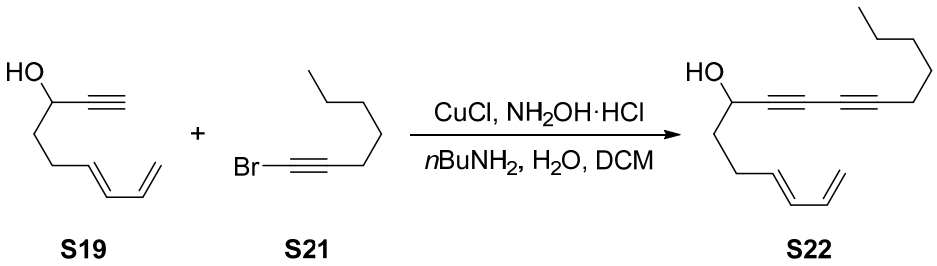
1k: To a stirred suspension of NaH (60 wt%, 90 mg, 2.3 mmol) in THF (2.5 mL) was added a solution of alcohol **S4**[3] (152 mg, 1.55 mmol) in THF (0.5 mL) at 0 °C. After 40 minutes, bromide **S18**[9] (380 mg, 1.91 mmol) was added and the reaction mixture was allowed to warm to rt and stirred for additional one hour. Then the reaction mixture was quenched with water, extracted with Et_2O for three times. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. Purification of the crude product by column chromatography (PE/EA, 50/1) afforded **1k** (281.4 mg, 1.30 mmol, 84%) as a yellow oil. TLC (PE/EA, 50/1): R_f = 0.8; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.36 (d, J = 15.7 Hz, 1H), 5.71 (dt, J = 15.7, 6.3 Hz, 1H), 5.00 (s, 2H), 4.20 (s, 2H), 4.13 (d, J = 6.3 Hz, 2H), 2.29 (t, J = 6.9 Hz, 2H), 1.85 (s, 3H), 1.55–1.48 (m, 2H), 1.47–1.37 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.2, 136.3, 124.9, 117.2, 81.2, 71.7, 71.4, 70.2, 64.5, 57.6, 30.1, 21.9, 18.9, 18.4, 13.4; IR (neat): ν 3413, 3004, 2144, 1715, 1422, 1362, 1222, 1092 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd. for $C_{15}H_{21}O$, 217.1587; found, 217.1585.



S19 **S20** **1l**

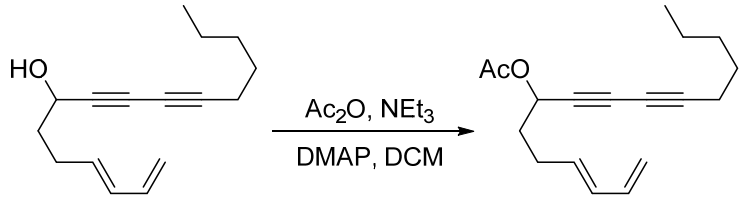
S20: To a stirred solution of alcohol **S19**[10] (3.57 mmol) in DCM (18 mL) was added NEt_3 (772 mg, 7.14 mmol), followed by DMAP (22 mg, 0.18 mmol) and Ac_2O (546 mg, 5.35 mmol) at 0 °C. After one hour, the reaction mixture was concentrated under reduced pressure. Purification of the crude product by column chromatography (*n*-pentane/Et_2O, 20/1) afforded a solution of **S20** (1.72 mmol, 48%) in *n*-pentane. TLC (PE/EA, 20/1): $R_f = 0.4$.

1l: Following the general procedure A, a solution of alkyne **S20** (1.72 mmol) in *n*-pentane, a solution of bromoalkyne **S2**[2] (70 wt%, 1.03 g, 4.50 mmol) in DCM (3.3 mL), CuCl (74.3 mg, 0.750 mmol), and 30% $nBuNH_2/H_2O$ (4.5 mL) were used. Purification of the crude product by column chromatography (PE/EA, 50/1) afforded **1l** (209 mg, 0.809 mmol, 47%) as a light yellow oil. TLC (PE/EA, 20/1): $R_f = 0.5$; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.29 (dt, J = 16.8, 10.4 Hz, 1H), 6.08 (dd, J = 15.2, 10.4 Hz, 1H), 5.59 (dt, J = 15.2, 6.8 Hz, 1H), 5.39 (t, J = 6.6 Hz, 1H), 5.11 (d, J = 16.8 Hz, 1H), 4.99 (d, J = 10.1 Hz, 1H), 2.32–2.21 (m, 4H), 2.07 (s, 3H), 1.87 (ddd, J = 9.3, 7.6, 1.9 Hz, 2H), 1.52 (ddd, J = 14.0, 9.3, 3.9 Hz, 2H), 1.46–1.37 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.7, 136.8, 132.7, 132.0, 115.6, 82.1, 72.3, 70.7, 64.2, 63.7, 34.0, 30.0, 27.9, 21.8, 20.8, 18.9, 13.4; IR (neat): ν 2957, 2940, 2258, 1746, 1371, 1225, 1020, 900 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{17}H_{22}O_2Na$, 281.1512; found, 281.1504.



S19 **S21** **S22**

S22: Following the general procedure A, a solution of alkyne **S19**[10] (274 mg, 2.01 mmol) in DCM (5 mL), a solution of bromoalkyne **S21**[11] (523 mg, 2.99 mmol) in DCM (5 mL), CuCl (198 mg, 2.00 mmol), and 30% *n*BuNH$_2$/H$_2$O (10 mL) were used. Purification of the crude product by column chromatography (PE/EA, 20/1→10/1) afforded **S22** (383 mg, 1.66 mmol, 83%) as a yellow oil. TLC (PE/EA, 5/1): R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.30 (dt, J = 16.8, 10.4 Hz, 1H), 6.10 (dd, J = 14.9, 10.6 Hz, 1H), 5.69 (dt, J = 14.9, 7.2 Hz, 1H), 5.11 (d, J = 16.8 Hz, 1H), 4.98 (d, J = 10.4 Hz, 1H), 4.43 (t, J = 6.5 Hz, 1H), 2.32–2.22 (m, 4H), 1.88–1.76 (m, 3H), 1.60–1.49 (m, 2H), 1.42–1.25 (m, 4H), 0.90 (t, J = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.0, 133.4, 132.0, 115.4, 82.0, 76.0, 70.3, 64.3, 62.3, 36.9, 31.0, 28.0, 27.8, 22.1, 19.2, 13.9; IR (neat): ν 3356, 2931, 2860, 2254, 1457, 1325, 1004 cm^{-1}.

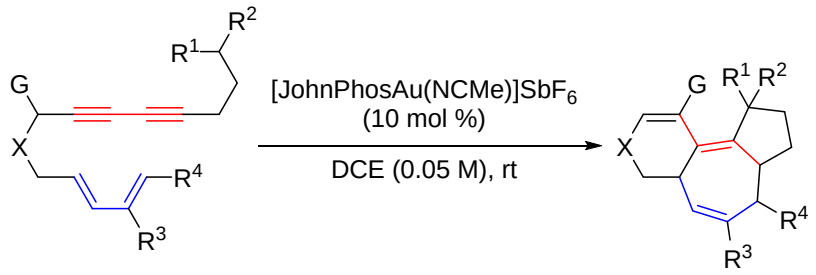


S22 **1m**

1m: To a stirred solution of alcohol **S22** (184 mg, 0.799 mmol) in DCM (4 mL) was added DMAP (11 mg, 0.090 mmol), followed by NEt_3 (164 mg, 1.62 mmol) and Ac_2O (132 mg, 1.29 mmol) at 0 °C. After one hour, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution and extracted with DCM for three times. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. Purification of the crude product by column chromatography (PE/EA, 50/1) afforded **1m** as a light yellow oil in quantitive yield. TLC (PE/EA, 20/1): R_f = 0.4; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.29 (dt, J = 16.8, 10.4 Hz, 1H), 6.08 (dd, J = 15.2, 10.4 Hz, 1H), 5.66 (dt, J = 15.2, 6.8 Hz, 1H), 5.39 (t, J = 6.6 Hz, 1H), 5.11 (d, J = 16.8 Hz, 1H), 4.99 (d, J = 10.4 Hz, 1H), 2.31–2.20 (m, 4H), 2.07 (s, 3H), 1.92–1.83 (m, 2H), 1.58–1.49 (m, 2H), 1.42–1.27 (m, 4H), 0.90 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.7, 136.9, 132.7, 132.1, 115.6, 82.2, 72.3, 70.7, 64.3, 63.8, 34.1, 30.9, 27.9, 27.7, 22.1, 20.9, 19.2, 13.9; IR (neat): ν 2933, 2861, 2257, 1747, 1457, 1371, 1224, 1021 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{18}H_{24}NaO_2$, 295.1669; found, 295.1669.

S2.2 Experimental Details for Gold(I)-Catalyzed Polycyclization

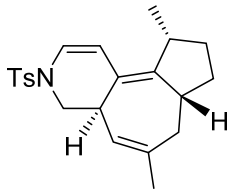
General procedure C: Gold(I)-Catalyzed Polycyclization



A solution of dienediyne and [JohnPhosAu(NCMe)]SbF_6 (10 mol %) in anhydrous DCE (0.05 M) was stirred under argon at rt until TLC indicated the disappearance of the starting material. The solvent was then removed under reduced pressure. The crude product was purified by column chromatography on silica gel to afford the polycyclization product.

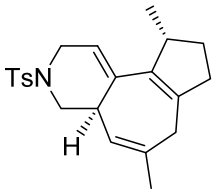
In all cases, only one of the two enantiomers of the racemic product is shown. Relative configurations of all other polycycles obtained were assigned by analog to that of compound **2a**, which was confirmed by X-ray crystallography. Detailed resonance assignments of all H and C atoms of **2a**, **3a**, and **2l** are given in Section S4. Diastereomeric ratio (dr) was determined by ^{1}H NMR analysis after column chromatography.

Attention: The present polycyclization reaction is very sensitive to water. When the solvent was not sufficiently dry, the polycyclization of **1a** gave a mixture of **2a**, **3a**, and one unidentified byproduct. It is suggested to keep all the substrates in the refrigerator (–20 °C) because some substrates are not stable at rt.



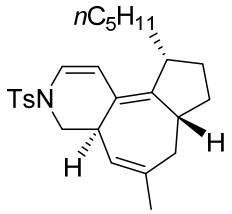
2a

2a: Following the general procedure C, substrate **1a** (31.4 mg, 0.0850 mmol) and [JohnPhosAu(NCMe)]SbF_6 (6.6 mg, 0.0085 mmol, 10 mol %) were stirred in anhydrous DCE (1.7 mL) at rt for 2 hours. Purification of the crude product by column chromatography (hexanes/EA, 20/1) afforded **2a** (24.8 mg, 0.0671 mmol, 79%, dr = 15:1) as a white solid. m.p.: 122–124 °C; TLC (PE/EA, 10/1): R_f = 0.4; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 6.53 (d, J = 8.3 Hz, 1H), 5.64 (d, J = 8.3 Hz, 1H), 4.95 (s, 1H), 3.79 (dd, J = 11.2, 4.3 Hz, 1H), 3.31–3.23 (br. d, 1H), 2.91–2.83 (m, 1H), 2.71–2.63 (m, 1H), 2.41 (s, 3H), 2.40–2.25 (m, 2H), 1.99 (d, J = 13.1 Hz, 1H), 1.75 (s, 3H), 1.74–1.67 (m, 1H), 1.63–1.50 (m, 1H), 1.45–1.35 (m, 2H), 1.03 (d, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 148.2, 143.7, 142.0, 134.8, 129.8, 127.1, 123.2, 122.0, 121.2, 111.0, 50.0, 43.1, 38.2, 37.7, 36.9, 32.3, 32.0, 25.5, 21.5, 21.0; IR (neat): ν 2958, 2932, 2871, 1611, 1460, 1352, 1171, 1097, 1056, 1017 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd. for $C_{22}H_{28}NO_2S$, 370.1835; found, 370.1838. The dr was determined by the integration of signals at 6.57 and 6.53 ppm in ^{1}H NMR.



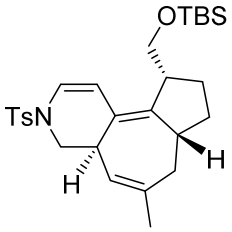
3a

3a: To a mixture of **1a** (40.7 mg, 0.110 mmol), JohnPhosAuCl (5.7 mg, 0.011 mmol), and AgOTf (3.3 mg, 0.013 mmol) was added DCM (2.2 mL) at rt. After 2 hours, the reaction mixture was concentrated under reduced pressure. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **3a** (28.2 mg, 0.0763 mmol, 69%, dr = 10:1) as a white solid. m.p.: 75–78 °C; TLC (PE/EA, 10/1): R_f = 0.3; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 5.63–5.58 (m, 1H), 5.37 (s, 1H), 3.95 (dd, J = 16.8, 4.3 Hz, 1H), 3.63 (d, J = 11.4 Hz, 1H), 3.34–3.24 (m, 7.4 Hz, 2H), 3.15–3.10 (br. s, 1H), 3.03–2.95 (br. s, 1H), 2.63 (dd, J = 11.5, 3.8 Hz, 1H), 2.60–2.45 (m, 2H), 2.43 (s, 3H), 2.26–2.17 (m, 1H), 2.06–1.97 (m, 1H), 1.75 (d, J = 0.7 Hz, 3H), 1.41–1.34 (m, 1H), 0.93 (d, J = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 143.5, 139.5, 135.9, 135.5, 133.2, 132.6, 129.6, 127.8, 126.2, 114.8, 47.5, 45.1, 40.4, 38.9, 38.2, 35.9, 30.3, 24.9, 21.5, 19.5; IR (neat): ν 2962, 2929, 2877, 1655, 1599, 1562, 1460, 1346, 1171, 1093 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd. for $C_{22}H_{28}NO_2S$, 370.1835; found, 370.1846. The dr was determined by the integration of signals at 5.60 and 5.45 ppm in ^{1}H NMR.



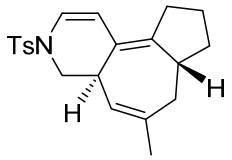
2b

2b: Following the general procedure C, substrate **1b** (72.7 mg, 0.171 mmol) and [JohnPhosAu(NCMe)]SbF_6 (13.4 mg, 0.0174 mmol, 10 mol %) were stirred in anhydrous DCE (3.4 mL) at rt for 2 hours. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **2b** (50.6 mg, 0.119 mmol, 70%, dr > 20:1) as a light yellow oil. TLC (PE/EA, 20/1): R_f = 0.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 6.54 (d, J = 8.3 Hz, 1H), 5.55 (d, J = 8.3 Hz, 1H), 4.95 (d, J = 1.0 Hz, 1H), 3.79 (ddd, J = 11.2, 4.4, 1.3 Hz, 1H), 3.32–3.22 (br. d, 1H), 2.66 (dd, J = 13.2, 11.3 Hz, 1H), 2.63–2.56 (m, 1H), 2.41 (s, 3H), 2.38–2.20 (m, 2H), 1.96 (d, J = 13.1 Hz, 1H), 1.75 (s, 3H), 1.73–1.66 (m, 1H), 1.54 (dd, J = 11.8, 5.4 Hz, 1H), 1.47–1.08 (m, 10H), 0.90 (t, J = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.1, 143.7, 142.0, 134.7, 129.7, 127.1, 123.2, 122.0, 121.0, 110.9, 50.0, 43.8, 42.7, 38.0, 37.0, 34.8, 32.2, 31.8, 28.8, 28.6, 25.5, 22.7, 21.5, 14.0; IR (neat): ν 2962, 2934, 2867, 2368, 1609, 1460, 1355, 1171, 1097, 1015 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd. for $C_{26}H_{36}NO_2S$, 426.2461; found, 426.2472.



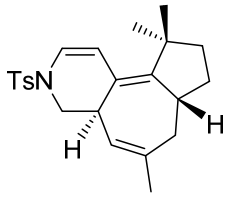
2c

2c: Following the general procedure C, substrate **1c** (70.0 mg, 0.140 mmol) and [JohnPhosAu(NCMe)]SbF_6 (11.0 mg, 0.0142 mmol, 10 mol %) were stirred in anhydrous DCE (2.8 mL) at rt for 4 hours. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **2c** (33.1 mg, 0.0662 mmol, 47%, dr = 7:1) as a colorless oil. TLC (PE/EA, 20/1): R_f = 0.6; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 6.54 (d, J = 8.0 Hz, 1H), 5.66 (d, J = 8.0 Hz, 1H), 4.95 (s, 1H), 3.79 (ddd, J = 11.1, 4.5, 1.2 Hz, 1H), 3.58 (dd, J = 10.2, 3.9 Hz, 1H), 3.35–3.26 (br. d, 1H), 3.21 (t, J = 10.2 Hz, 1H), 2.95–2.88 (m, 1H), 2.64 (dd, J = 13.2, 11.2 Hz, 1H), 2.41 (s, 3H), 2.36–2.22 (m, 2H), 1.97–1.91 (m, 1H), 1.87 (dd, J = 12.2, 5.5 Hz, 1H), 1.78–1.67 (m, 4H), 1.48–1.38 (m, 1H), 1.37–1.28 (m, 1H), 0.89 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.8, 143.0, 142.0, 134.6, 129.8, 127.1, 123.1, 122.5, 110.8, 64.0, 49.8, 46.9, 42.7, 37.9, 37.1, 31.9, 26.8, 26.0, 25.5, 21.5, 18.3, –5.22, –5.26; IR (neat): ν 2927, 2856, 1635, 1352, 1163, 1094 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd. for $C_{28}H_{41}NO_3SSi$, 500.2649; found, 500.2648. The dr was determined by the integration of signals at 6.54 and 6.50 ppm in ^{1}H NMR.



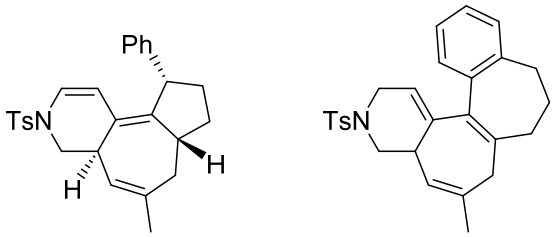
2d

2d: Following the general procedure C, substrate **1d** (67.0 mg, 0.188 mmol) and [JohnPhosAu(NCMe)]SbF_6 (14.1 mg, 0.0183 mmol, 10 mol %) were stirred in anhydrous DCE (3.6 mL) at rt for 24 hours. Purification of the crude product by column chromatography (PE/EA, 30/1) afforded a mixture of **2d** and an unidentified byproduct (10.0 mg, 24% combined isolated yield based on recovered **1d**, dr of **2d** > 20:1, the ratio of **2d** to the byproduct was 6:1, as determined by the integration of signals at 6.56 and 6.29 ppm in ^{1}H NMR) as a colorless oil, with 25.5 mg of **1d** recovered. TLC (PE/EA, 20/1): R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 6.56 (d, J = 8.3 Hz, 1H), 5.54 (d, J = 8.3 Hz, 1H), 4.98 (d, J = 1.4 Hz, 1H), 3.81 (ddd, J = 11.4, 4.8, 1.3 Hz, 1H), 3.28–3.18 (br. d, 1H), 2.67 (dd, J = 13.2, 11.4 Hz, 1H), 2.47–2.15 (m, 7H), 2.00–1.93 (m, 1H), 1.85–1.66 (m, 5H), 1.49–1.32 (m, 1H), 1.21–1.10 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.7, 142.2, 141.8, 134.7, 129.8, 127.1, 123.8, 122.3, 121.4, 110.3, 49.5, 42.4, 36.7, 35.3, 34.9, 31.9, 24.7, 22.9, 21.5; IR (neat): ν 2924, 2858, 1635, 1361, 1168, 913, 746 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd. for $C_{21}H_{26}NO_2S$, 356.1679; found, 356.1688.



2e

2e: Following the general procedure C, substrate **1e** (49.6 mg, 0.129 mmol) and [JohnPhosAu(NCMe)]SbF_6 (10.1 mg, 0.0131 mmol, 10 mol %) were stirred in anhydrous DCE (2.6 mL) at rt for 3 hours. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **2e** (27.6 mg, 0.0720 mmol, 56%, dr > 20:1) as a white solid. m.p.: 112–115 °C; TLC (PE/EA, 20/1): R_f = 0.4; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 6.51 (d, J = 8.5 Hz, 1H), 5.89 (d, J = 8.5 Hz, 1H), 4.91 (s, 1H), 3.76 (dd, J = 11.4, 4.6 Hz, 1H), 3.32–3.23 (br. d, 1H), 2.71 (t, J = 12.3 Hz, 1H), 2.41 (s, 3H), 2.40–2.31 (m, 2H), 1.90 (d, J = 12.1 Hz, 1H), 1.74 (s, 3H), 1.61 (dt, J = 10.8, 5.6 Hz, 1H), 1.46–1.25 (m, 3H), 1.24 (s, 3H), 1.21 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 149.9, 143.7, 142.4, 134.8, 129.8, 127.1, 123.4, 122.1, 121.6, 110.3, 49.9, 44.6, 44.3, 43.7, 37.6, 36.4, 32.3, 30.1, 28.0, 24.4, 21.5; IR (neat): ν 2966, 2938, 2870, 1627, 1601, 1355, 1173, 1097, 1048 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd. for $C_{23}H_{30}NO_2S$, 384.1992; found, 384.2003.

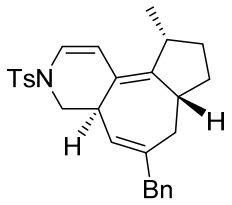


2f **4f**

2f + **4f**: Following the general procedure C, substrate **1f** (59.3 mg, 0.137 mmol) and [JohnPhosAu(NCMe)]SbF_6 (10.7 mg, 0.0139 mmol, 10 mol %) were stirred in anhydrous DCE (2.8 mL) at rt for 14 hours. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **2f** (17.5 mg, 0.0405 mmol, 30%, dr > 20:1) as a white solid, with **4f** (23.4 mg, 0.0542 mmol, 39%) as a white solid.

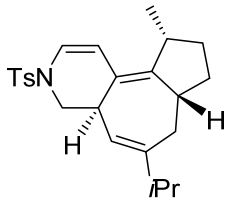
2f: m.p.: 69–72 °C; TLC (PE/EA, 20/1): R_f = 0.5; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (d, J = 8.1 Hz, 2H), 7.30–7.22 (m, 4H), 7.19–7.13 (m, 1H), 7.06 (d, J = 7.5 Hz, 2H), 6.29 (d, J = 8.3 Hz, 1H), 5.12 (d, J = 8.3 Hz, 1H), 5.01 (s, 1H), 4.01 (d, J = 8.2 Hz, 1H), 3.81 (dd, J = 11.3, 4.3 Hz, 1H), 3.40–3.31 (br. d, 1H), 2.73–2.66 (m, 1H), 2.62 (t, J = 12.3 Hz, 1H), 2.51–2.43 (m, 1H), 2.41 (s, 3H), 2.06 (d, J = 13.4 Hz, 1H), 1.96–1.87 (m, 1H), 1.81 (s, 3H), 1.64 (dt, J = 11.9, 6.1 Hz, 1H), 1.60–1.52(m, 1H), 1.45–1.32 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 146.8, 143.7, 143.6, 142.1, 134.6, 129.7, 128.3, 127.7, 127.1, 125.7, 123.9, 123.3, 122.6, 111.2, 50.1, 49.7, 43.4, 37.0, 36.3, 34.8, 31.6, 25.5, 21.5; IR (neat): ν 2932, 2871, 1601, 1452, 1355, 1171 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd. for $C_{27}H_{30}NO_2S$, 432.1992; found, 432.1996.

4f: m.p.: 95 °C; TLC (PE/EA, 20/1): R_f = 0.3; ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.57 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 7.06–6.99 (m, 3H), 6.93–6.89 (m, 1H), 5.60–5.56 (m, 1H), 4.88 (dd, J = 4.2, 2.6 Hz, 1H), 3.73 (dd, J = 17.0, 4.5 Hz, 1H), 3.61 (d, J = 11.4 Hz, 1H), 3.52 (d, J = 19.7 Hz, 1H), 3.39–3.34 (br. s, 1H), 3.07 (dd, J = 16.8, 2.0 Hz, 1H), 2.68 (d, J = 19.9 Hz, 1H), 2.55 (dd, J = 11.4, 3.3 Hz, 1H), 2.45–2.37 (m, 2H), 2.35 (s, 3H), 2.08–1.98 (m, 1H), 1.88–1.79 (m, 1H), 1.73 (s, 3H), 1.68–1.61 (m, 2H); ^{13}C NMR (126 MHz, CD_2Cl_2): δ 144.2, 141.72, 141.69, 137.4, 135.8, 135.6, 135.4, 133.5, 130.1, 129.8, 128.4, 128.2, 127.2, 127.0, 125.8, 118.9, 47.9, 45.6, 41.8, 38.9, 35.2, 33.1, 31.9, 24.8, 21.7; IR (neat): ν 2944, 2862, 1601, 1460, 1350, 1171, 1093 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd. for $C_{27}H_{30}NO_2S$, 432.1992; found, 432.1996.



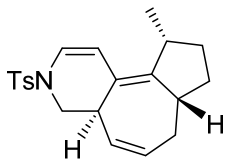
2g

2g: Following the general procedure C, substrate **1g** (77.7 mg, 0.174 mmol) and [JohnPhosAu(NCMe)]SbF_6 (13.5 mg, 0.0175 mmol, 10 mol %) were stirred in anhydrous DCE (3.5 mL) at rt for 12 hours. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **2g** (59.9 mg, 0.134 mmol, 77%, dr = 12:1) as a white solid. m.p.: 164–166 °C; TLC (PE/EA, 20/1): R_f = 0.4; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 8.2 Hz, 2H), 7.33–7.24 (m, 4H), 7.23–7.17 (m, 1H), 7.14 (d, J = 7.0 Hz, 2H), 6.53 (d, J = 8.4 Hz, 1H), 5.63 (d, J = 8.4 Hz, 1H), 5.04 (s, 1H), 3.83 (ddd, J = 11.2, 4.4, 1.2 Hz, 1H), 3.42–3.33 (m, 1H), 3.32 (s, 2H), 2.89–2.79 (m, 1H), 2.69 (dd, J = 12.9, 11.3 Hz, 1H), 2.41 (s, 3H), 2.31–2.22 (m, 1H), 2.20–2.07 (m, 1H), 2.05–1.97 (m, 1H), 1.61–1.43 (m, 2H), 1.38–1.28 (m, 2H), 1.00 (d, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.3, 144.5, 143.7, 139.1, 134.7, 129.8, 129.0, 128.3, 127.1, 126.2, 124.9, 122.1, 120.9, 110.9, 50.0, 45.8, 43.4, 37.7, 37.2, 36.5, 32.2, 31.8, 21.5, 20.9; IR (neat): ν 2955, 2869, 2365, 1607, 1354, 1171, 1097, 1046 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd. for $C_{28}H_{32}NO_2S$, 446.2148; found, 446.2141. The dr was determined by the integration of signals at 5.63 and 5.59 ppm in ^{1}H NMR.



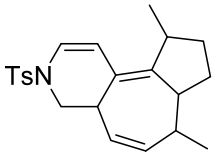
2h

2h: Following the general procedure C, substrate **1h** (75.1 mg, 0.189 mmol) and [JohnPhosAu(NCMe)]SbF_6 (15.8 mg, 0.0205 mmol, 11 mol %) were stirred in anhydrous DCE (3.8 mL) at rt for 6 hours. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **2h** (70.7 mg, 0.178 mmol, 94%, dr = 10:1) as a white solid. m.p.: 51–53 °C; TLC (PE/EA, 20/1): R_f = 0.4; ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.58 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 6.41 (d, J = 8.3 Hz, 1H), 5.57 (d, J = 8.3 Hz, 1H), 4.85 (s, 1H), 3.72 (ddd, J = 11.1, 4.5, 1.1 Hz, 1H), 3.27–3.17 (br. d, 1H), 2.81–2.72 (m, 1H), 2.55 (dd, J = 13.1, 11.3 Hz, 1H), 2.33 (s, 3H), 2.23–2.02 (m, 4H), 1.67–1.60 (m, 1H), 1.51–1.40 (m, 1H), 1.39–1.25 (m, 2H), 0.94 (d, J = 7.1 Hz, 3H), 0.883 (d, J = 6.8 Hz, 3H), 0.879 (d, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2): δ 151.6, 148.9, 144.5, 135.0, 130.2, 127.5, 122.3, 121.4, 120.8, 111.7, 50.6, 44.6, 38.1, 37.34, 37.26, 35.0, 32.7, 32.2, 21.7, 21.19, 21.13, 21.10; IR (neat): ν 2966, 2875, 2365, 1355, 1171, 1043 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd. for $C_{24}H_{32}NO_2S$, 398.2148; found, 398.2155. The dr was determined by the integration of signals at 5.64 and 5.59 ppm in ^{1}H NMR.



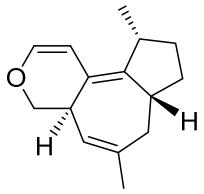
2i

2i: Following the general procedure C, substrate **1i** (87.2 mg, 0.245 mmol) and [JohnPhosAu(NCMe)]SbF_6 (18.9 mg, 0.0245 mmol, 10 mol %) were stirred in anhydrous DCE (4.9 mL) at rt for 11 hours. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **2i** (75.5 mg, 0.212 mmol, 87%, dr = 8:1) as a colorless oil. TLC (PE/EA, 20/1): R_f = 0.4; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 6.53 (d, J = 8.4 Hz, 1H), 6.02–5.92 (m, 1H), 5.65 (d, J = 8.4 Hz, 1H), 5.30–5.21 (m, 1H), 3.85 (ddd, J = 11.2, 4.0, 1.2 Hz, 1H), 3.30–3.21 (br. d, 1H), 2.95–2.84 (m, 1H), 2.74 (dd, J = 13.1, 11.3 Hz, 1H), 2.41 (s, 3H), 2.37–2.10 (m, 3H), 1.78–1.67 (m, 1H), 1.61–1.53 (m, 1H), 1.49–1.34 (m, 2H), 1.03 (d, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.6, 143.8, 134.7, 133.2, 129.8, 129.6, 127.1, 122.0, 120.5, 110.8, 49.9, 43.8, 37.9, 37.8, 32.8, 32.1, 31.7, 21.5, 20.8; IR (neat): ν 2930, 1598, 1455, 1355, 1167, 1092, 982 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd. for $C_{21}H_{26}NO_2S$, 356.1679; found, 356.1680. The dr was determined by the integration of signals at 5.65 and 5.60 ppm in ^{1}H NMR.



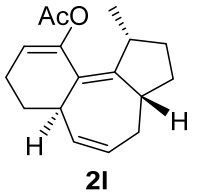
2j

2j: Following the general procedure C, substrate **1j** (44.2 mg, 0.120 mmol) and [JohnPhosAu(NCMe)]SbF_6 (9.3 mg, 0.012 mmol, 10 mol %) were stirred in anhydrous DCE (2.5 mL) at rt for 10 minutes. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **2j** (29.6 mg, 0.0801 mmol, 67%, dr = 3:1) as a white solid. m.p.: 112–115 °C; TLC (PE/EA, 20/1): R_f = 0.4; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 6.53 (d, J = 8.4 Hz, 1H), 5.66 (d, J = 8.4 Hz, 1H), 5.64–5.57 (m, 1H), 5.15 (dt, J = 11.0, 2.5 Hz, 1H), 3.84 (ddd, J = 11.3, 4.4, 1.3 Hz, 1H), 3.32–3.20 (br. d, 1H), 2.93–2.83 (m, 1H), 2.70 (dd, J = 13.1, 11.3 Hz, 1H), 2.41 (s, 3H), 2.40–2.33 (m, 1H), 2.19–2.09 (m, 1H), 1.76 (ddd, J = 11.3, 7.2, 3.4 Hz, 1H), 1.52–1.33 (m, 3H), 1.08–0.99 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ147.8, 143.8, 141.6, 134.7, 129.8, 127.2, 127.1, 122.1, 120.6, 111.1, 49.7, 49.2, 37.8, 37.03, 36.94, 31.6, 29.2, 21.5, 20.8, 19.8; IR (neat): ν 2962, 2932, 2871, 1601, 1355, 1171, 1098, 1031 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd. for $C_{22}H_{28}NO_2S$, 370.1835; found, 370.1840. The dr was determined by the integration of signals at 6.57 and 6.53 ppm in ^{1}H NMR.



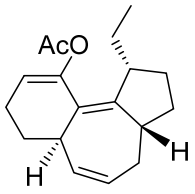
2k

2k: Following the general procedure C, substrate **1k** (42.0 mg, 0.194 mmol) and [JohnPhosAu(NCMe)]SbF_6 (14.3 mg, 0.0185 mmol, 10 mol %) were stirred in anhydrous DCE (3.7 mL) at rt for 30 minutes. Purification of the crude product by column chromatography (PE/EA, 100/1→50/1) afforded **2k** (31.0 mg, 0.143 mmol, 74%, dr > 20:1) as a colorless oil. TLC (*n*-hexane): R_f = 0.4; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.37 (d, J = 6.1 Hz, 1H), 5.46 (d, J = 6.1 Hz, 1H), 4.93 (s, 1H), 4.05 (dd, J = 10.0, 4.6 Hz, 1H), 3.65 (dd, J = 12.7, 10.4 Hz, 1H), 3.52–3.40 (br. d, 1H), 2.95–2.85 (m, 1H), 2.47 (t, J = 12.2 Hz, 1H), 2.40–2.27 (m, 1H), 2.03 (d, J = 13.1 Hz, 1H), 1.79 (s, 3H), 1.75–1.68 (m, 1H), 1.66–1.55 (m, 1H), 1.46–1.34 (m, 2H), 1.06 (d, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.5, 142.6, 142.2, 121.8, 121.1, 105.5, 71.2, 42.8, 38.2, 37.4, 37.2, 32.4, 32.1, 25.3, 20.9; IR (neat): ν 2957, 2868, 2254, 1711, 1607, 1458, 1383, 1255, 1090, 908, 733 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd. for $C_{15}H_{21}O$, 217.1587; found, 217.1588.



2l

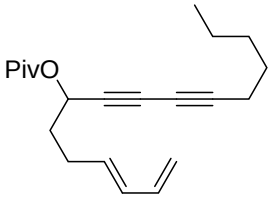
2l: Following the general procedure C, substrate **1l** (95.9 mg, 0.371 mmol), [JohnPhosAu(NCMe)]SbF_6 (57.3 mg, 0.0742 mmol, 20 mol %), and 4 Å MS were stirred in anhydrous DCE (7.4 mL) at rt for 4.5 hours. Purification of the crude product by column chromatography (*n*-hexane/EA, 100/1→50/1) afforded a mixture of **2l** and two unidentified byproducts (63.9 mg, 66% combined isolated yield, the ratio was 20:2:1, as determined by GC–MS. The molecular weight of the unidentified byproducts is the same as that of **2l**) as a light yellow oil. TLC (PE/EA, 50:1): R_f = 0.3; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.75 (ddd, J = 10.6, 6.6, 3.0 Hz, 1H), 5.39 (ddd, J = 11.5, 4.2, 2.6 Hz, 1H), 5.23 (t, J = 4.0 Hz, 1H), 3.15–3.07 (br. d, 1H), 2.96–2.88 (m, 1H), 2.63–2.52 (m, 1H), 2.35–2.18 (m, 4H), 2.17 (s, 3H), 1.96–1.86 (m, 1H), 1.86–1.76 (m, 1H), 1.72–1.39 (m, 4H), 1.01 (d, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.5, 149.2, 148.2, 133.0, 128.3, 124.5, 115.2, 44.5, 43.8, 39.7, 34.2, 32.8, 31.3, 30.6, 24.7, 21.7, 21.5; IR (neat): ν 2934, 2864, 1758, 1432, 1367, 1207, 1146, 1091, 1010 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{17}H_{22}O_2Na$, 281.1512; found, 281.1513.



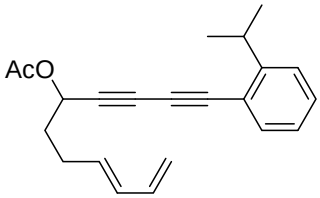
2m

2m: Following the general procedure C, substrate **1m** (42.2 mg, 0.155 mmol), [JohnPhosAu(NCMe)]SbF_6 (23.9 mg, 0.0310 mmol, 20 mol %), and 4 Å MS were stirred in anhydrous DCE (2.9 mL) at rt for 4 hours. Purification of the crude product by column chromatography (PE/EA, 50/1) afforded a mixture of **2m** and three assuming byproducts (32.0 mg, 76% combined isolated yield, the ratio was 27:2:2:1, as determined by GC–MS) as a colorless oil. TLC (PE/EA, 20:1): R_f = 0.4; ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.73–5.65 (m, 1H), 5.39–5.30 (m, 1H), 5.13 (t, J = 3.7 Hz, 1H), 3.06–2.97 (br. d, 1H), 2.55–2.43 (m, 2H), 2.25–2.06 (m, 4H), 2.03 (s, 3H), 1.88–1.79 (m, 1H), 1.73–1.65 (m, 1H), 1.60–1.50 (m, 2H), 1.39–1.29 (m, 2H), 1.25–1.13 (m, 2H), 0.85 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2): δ 169.9, 149.5, 149.0, 133.4, 128.9, 125.4, 115.7, 48.0, 44.7, 43.9, 33.9, 31.6, 31.0, 28.4, 27.7, 25.0, 21.4, 13.2; IR (neat): ν 2929, 2869, 1759, 1660, 1460, 1367, 1209, 1146, 1012 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{18}H_{24}NaO_2$, 295.1669; found, 295.1674.

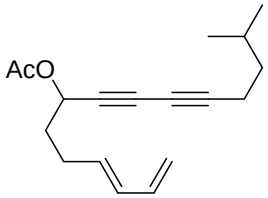
S2.3 Unsuccessful Substrates 1n–u for Gold(I)-Catalyzed Polycyclization



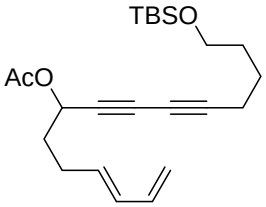
1n



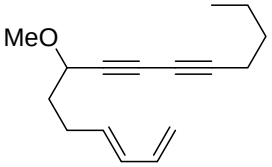
1o



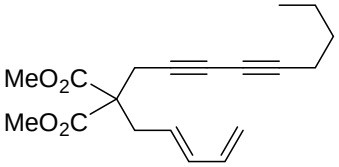
1p



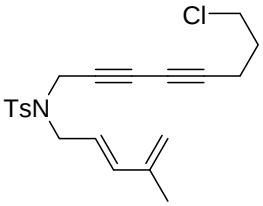
1q



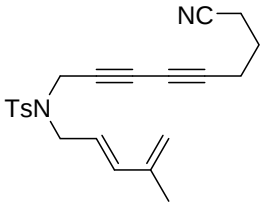
1r



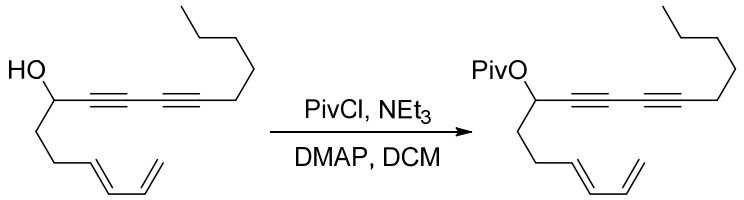
1s



1t

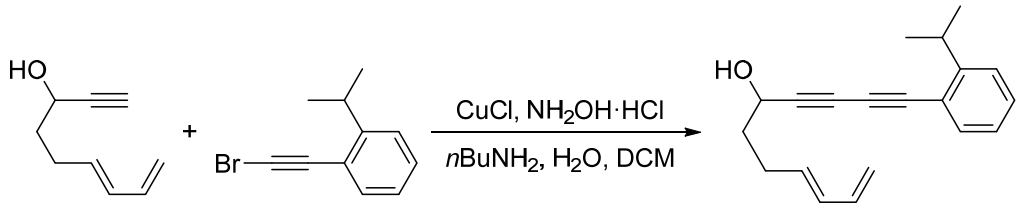


1u



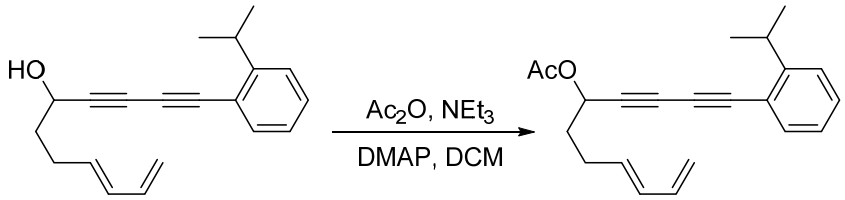
S22 **1n**

1n: To a stirred solution of alcohol **S22** (184 mg, 0.799 mmol) in DCM (4 mL) was added DMAP (10 mg, 0.082 mmol), followed by NEt_3 (161 mg, 1.59 mmol) and PivCl (143 mg, 1.19 mmol) at 0 °C. After 45 minutes, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution and extracted with Et_2O for four times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated. Purification of the crude product by column chromatography (*n*-pentane/Et_2O, 50/1) afforded **1n** (251 mg, 0.798 mmol) as a colorless oil in quantitive yield. TLC (PE/EA, 20/1): R_f = 0.6; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.29 (dt, J = 17.2, 10.0 Hz, 1H), 6.07 (dd, J = 15.2, 10.6 Hz, 1H), 5.67 (dt, J = 15.2, 6.8 Hz, 1H), 5.38 (t, J = 6.4 Hz, 1H), 5.11 (d, J = 17.2 Hz, 1H), 4.99 (d, J = 10.0 Hz, 1H), 2.32–2.19 (m, 4H), 1.93–1.83 (m, 2H), 1.58–1.49 (m, 2H), 1.41–1.24 (m, 4H), 1.21 (s, 9H), 0.90 (t, J = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 177.1, 136.9, 132.8, 132.0, 115.6, 81.9, 72.6, 70.4, 64.4, 63.5, 38.8, 34.1, 31.0, 28.0, 27.8, 27.0, 22.1, 19.2, 13.9; IR (neat): ν 2959, 2934, 2873, 2257, 1737, 1480, 1277, 1141, 1003 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd. for $C_{21}H_{31}O_2$, 315.2319; found, 315.2321.



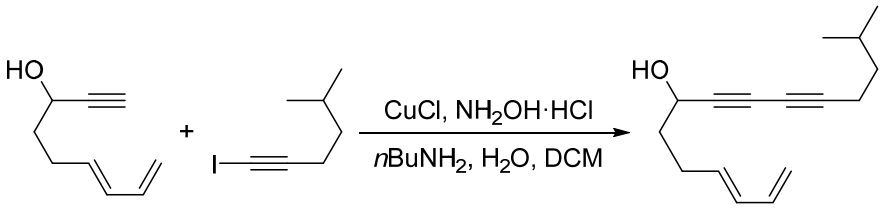
S19 **S23** **S24**

S24: Following the general procedure A, a solution of alcohol **S19**[10] (136 mg, 1.00 mmol) in DCM (5 mL), a solution of bromoalkyne **S23**[12] (320 mg, 1.43 mmol) in DCM (5 mL), CuCl (99 mg, 1.0 mmol), and 30% *n*$BuNH_2$/H_2O (10 mL) were used. Purification of the crude product by column chromatography (PE/EA, 10/1) afforded **S24** (251 mg, 0.902 mmol, 90%) as a yellow oil. TLC (PE/EA, 5/1): R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J = 7.7 Hz, 1H), 7.36–7.24 (m, 2H), 7.13 (t, J = 7.4 Hz, 1H), 6.31 (dt, J = 16.8, 10.4 Hz, 1H), 6.13 (dd, J = 15.2, 10.6 Hz, 1H), 5.72 (dd, J = 15.2, 6.8 Hz, 1H), 5.12 (d, J = 16.8 Hz, 1H), 4.99 (d, J = 10.0 Hz, 1H), 4.55 (t, J = 6.5 Hz, 1H), 3.49–3.36 (m, 1H), 2.38–2.27 (m, 2H), 1.98–1.84 (m, 3H), 1.26 (d, J = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.2, 136.9, 133.5, 133.3, 132.1, 129.6, 125.6, 125.1, 120.2, 115.5, 83.4, 77.7, 76.4, 70.1, 62.5, 36.8, 31.7, 28.1, 23.2; IR (neat): ν 3346, 2963, 2869, 2236, 1653, 1602, 1483, 1446, 1364, 1004 cm^{-1}; HRMS (ESI): $[M+H–H_2O]^+$ calcd. for $C_{20}H_{21}$, 261.1638; found, 261.1642.



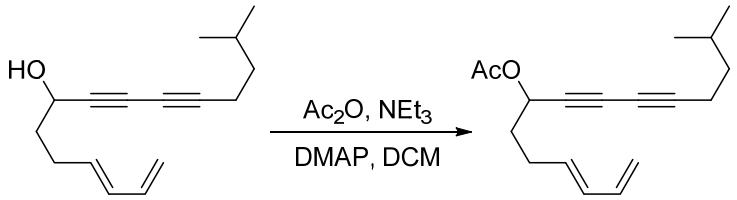
S24 **1o**

1o: To a stirred solution of alcohol **S24** (230 mg, 0.826 mmol) in DCM (4 mL) was added DMAP (10 mg, 0.082 mmol), followed by NEt_3 (171 mg, 1.69 mmol) and Ac_2O (130 mg, 1.27 mmol) at 0 °C. After one hour, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution and extracted with DCM for three times. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. Purification of the crude product by column chromatography (PE/EA, 50/1) afforded **1o** as a light yellow oil in quantitive yield. TLC (PE/EA, 20/1): R_f = 0.5; ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.39 (d, J = 7.7 Hz, 1H), 7.27 (t, J = 7.6 Hz, 1H), 7.21 (d, J = 7.8 Hz, 1H), 7.07 (t, J = 7.4 Hz, 1H), 6.24 (dt, J = 17.0, 10.2 Hz, 1H), 6.04 (dd, J = 15.2, 10.4 Hz, 1H), 5.63 (dd, J = 15.2, 6.8 Hz, 1H), 5.37 (t, J = 6.6 Hz, 1H), 5.04 (d, J = 17.0 Hz, 1H), 4.91 (d, J = 10.1 Hz, 1H), 3.32 (sept, J = 6.9 Hz, 1H), 2.24–2.15 (m, 2H), 2.00 (s, 3H), 1.90–1.81 (m, 2H), 1.17 (d, J = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, CD_2Cl_2): δ 170.1, 152.8, 137.4, 134.0, 133.3, 132.5, 130.3, 126.1, 125.6, 120.3, 115.8, 80.5, 78.0, 76.6, 70.3, 64.1, 34.4, 32.2, 28.4, 23.4, 21.1; IR (neat): ν 2963, 2927, 2237, 1745, 1371, 1227, 1021 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{22}H_{24}NaO_2$, 343.1669; found, 343.1670.



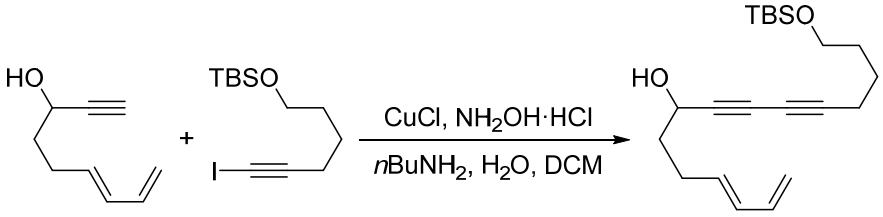
S19 **S25** **S26**

S26: Following the general procedure A, a solution of alcohol **S19**[10] (450 mg, 35 wt% in Et_2O, 1.16 mmol) in DCM (3.2 mL), a solution of iodoalkyne **S25**[13] (1.0 g, 46 wt% in Et_2O, 2.0 mmol), CuCl (58 mg, 0.59 mmol), and 30% nBuNH$_2$/H_2O (3.6 mL) were used. Purification of the crude product by column chromatography (PE/EA, 20/1→10/1) afforded **S26** (163.2 mg, 0.709 mmol, 61%) as a light yellow oil. TLC (PE/EA, 3/1): R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.30 (dt, J = 17.0, 10.4 Hz, 1H), 6.10 (dd, J = 15.2, 10.6 Hz, 1H), 5.69 (dd, J = 15.2, 6.8 Hz, 1H), 5.11 (d, J = 17.0 Hz, 1H), 4.98 (d, J = 10.1 Hz, 1H), 4.42 (t, J = 6.5 Hz, 1H), 2.33–2.22 (m, 4H), 2.09–1.92 (br. s, 1H), 1.87–1.77 (m, 2H), 1.74–1.63 (m, 1H), 1.48–1.39 (m, 2H), 0.90 (d, J = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.9, 133.4, 131.9, 115.4, 81.9, 76.0, 70.3, 64.2, 62.2, 36.90, 36.85, 28.0, 27.1, 22.0, 17.2; IR (neat): ν 3339, 2957, 2932, 2870, 2254, 1468, 1386, 1368, 1317, 1004 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{16}H_{22}NaO$, 253.1563; found, 253.1558.



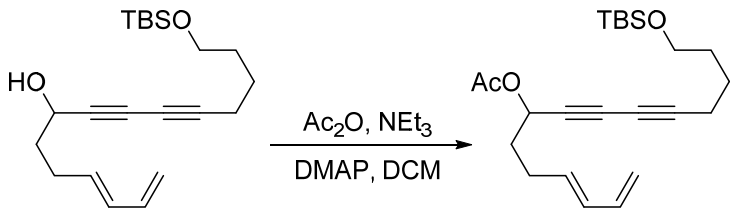
S26 **1p**

1p: To a stirred solution of alcohol **S26** (251.7 mg, 1.09 mmol) in DCM (5.4 mL) was added DMAP (6.7 mg, 0.055 mmol), followed by NEt_3 (221 mg, 2.18 mmol) and Ac_2O (167 mg, 1.63 mmol) at 0 °C. After one hour, the reaction mixture was concentrated under reduced pressure. Purification of the crude product by column chromatography (PE/EA, 50/1→20/1) afforded **1p** (288.0 mg, 1.06 mmol, 97%) as a light yellow oil. TLC (PE/EA, 20/1): R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.29 (dt, J = 16.8, 10.2 Hz, 1H), 6.08 (dd, J = 15.0, 10.4 Hz, 1H), 5.66 (dd, J = 15.0, 7.2 Hz, 1H), 5.39 (t, J = 6.6 Hz, 1H), 5.11 (d, J = 16.8 Hz, 1H), 4.99 (d, J = 10.2 Hz, 1H), 2.32–2.19 (m, 4H), 2.07 (s, 3H), 1.91–1.83 (m, 2H), 1.74–1.63 (m, 1H), 1.42 (q, J = 7.2 Hz, 2H), 0.89 (d, J = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.7, 136.8, 132.7, 132.1, 115.6, 82.1, 72.3, 70.7, 64.2, 63.8, 36.8, 34.1, 27.9, 27.1, 22.0, 20.9, 17.2; IR (neat): ν 2957, 2934, 2870, 1746, 1370, 1224, 1020, 1005 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{18}H_{24}NaO_2$, 295.1669; found, 295.1662.



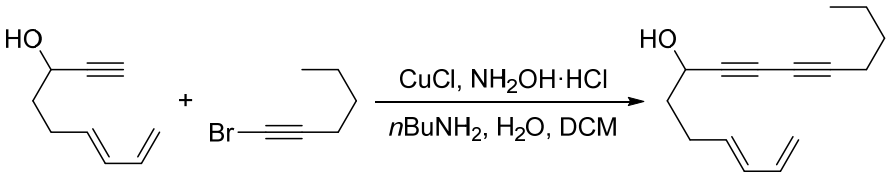
S19 **S27** **S28**

S28: Following the general procedure A, a solution of alkyne **S19**[10] (230 mg, 88 wt% in Et_2O, 1.49 mmol) in DCM (4.0 mL), a solution of iodoalkyne **S27**[14] (962 mg, 2.84 mmol) in DCM (3.8 mL), CuCl (141 mg, 1.42 mmol), and 30% nBuNH$_2$/H_2O (8.7 mL) were used. Purification of the crude product by column chromatography (PE/EA, 20/1→10/1) afforded **S28** (322.8 mg, 0.932 mmol, 63%) as a light yellow oil. TLC (PE/EA, 5/1): R_f = 0.6; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.30 (dt, J = 16.8, 10.4 Hz, 1H), 6.10 (dd, J = 15.2, 10.6 Hz, 1H), 5.69 (dd, J = 15.2, 6.8 Hz, 1H), 5.11 (d, J = 16.8 Hz, 1H), 4.98 (d, J = 10.1 Hz, 1H), 4.46–4.39 (m, 1H), 3.67–3.59 (m, 2H), 2.37–2.22 (m, 4H), 2.06–2.00 (br. s, 1H), 1.86–1.78 (m, 2H), 1.66–1.55 (m, 4H), 0.89 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.9, 133.4, 131.9, 115.4, 81.7, 76.1, 70.2, 64.5, 62.4, 62.2, 36.9, 31.8, 28.0, 25.9, 24.6, 19.1, 18.3, –5.4; IR (neat): ν 3387, 2930, 2858, 2254, 1472, 1389, 1361, 1256, 1106, 1004 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{21}H_{34}NaO_2Si$, 369.2220; found, 369.2225.



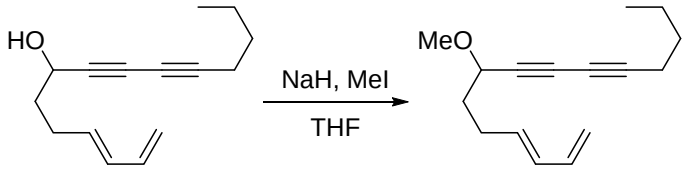
S28 **1q**

1q: To a stirred solution of alcohol **S28** (200 mg, 0.578 mmol) in DCM (2.9 mL) was added DMAP (3.5 mg, 0.029 mmol), followed by NEt_3 (117 mg, 1.16 mmol) and Ac_2O (88.5 mg, 0.867 mmol) at 0 °C. After one hour, the reaction mixture was concentrated under reduced pressure. Purification of the crude product by column chromatography (PE/EA, 50/1→20/1) afforded **1q** (217 mg, 0.558 mmol, 97%) as a colorless oil. TLC (PE/EA, 10/1): R_f = 0.6; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.29 (dt, J = 17.2, 10.0 Hz, 1H), 6.08 (dd, J = 15.0, 10.4 Hz, 1H), 5.66 (dd, J = 15.0, 7.2 Hz, 1H), 5.39 (t, J = 6.5 Hz, 1H), 5.11 (d, J = 17.2 Hz, 1H), 4.99 (d, J = 10.1 Hz, 1H), 3.65–3.59 (br. d, 2H), 2.35–2.28 (m, 2H), 2.28–2.20 (m, 2H), 2.07 (s, 3H), 1.92–1.83 (m, 2H), 1.65–1.57 (m, 4H), 0.89 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.7, 136.8, 132.7, 132.1, 115.6, 81.9, 72.4, 70.7, 64.4, 63.8, 62.4, 34.0, 31.8, 27.9, 25.9, 24.6, 20.9, 19.0, 18.3, –5.4; IR (neat): ν 2930, 2857, 1747, 1371, 1224, 1106, 1005 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{23}H_{36}NaO_3Si$, 411.2326; found, 411.2325.



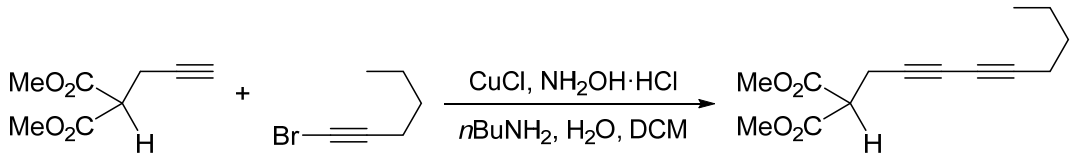
S19 **S2** **S29**

S29: Following the general procedure A, a solution of alcohol **S19**[10] (203 mg, 90 wt% in Et_2O, 1.34 mmol) in DCM (4.0 mL), a solution of bromoalkyne **S2**[2] (630 mg, 70 wt% in Et_2O, 2.74 mmol) in DCM (3.3 mL), CuCl (133 mg, 1.34 mmol), and 30% nBuNH$_2$/H$_2$O (8.1 mL) were used. Purification of the crude product by column chromatography (PE/EA, 20/1→10/1) afforded **S29** (241 mg, 1.12 mmol, 84%) as a yellow oil. TLC (PE/EA, 5/1): R_f = 0.6; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.30 (dt, J = 17.0, 10.4 Hz, 1H), 6.10 (dd, J = 15.0, 10.8 Hz, 1H), 5.69 (dd, J = 15.0, 6.8 Hz, 1H), 5.11 (d, J = 17.0 Hz, 1H), 4.98 (d, J = 10.4 Hz, 1H), 4.48–4.38 (m, 1H), 2.35–2.20 (m, 4H), 2.13–2.01 (br. s, 1H), 1.88–1.76 (m, 2H), 1.59–1.37 (m, 4H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.9, 133.4, 131.9, 115.4, 81.9, 76.0, 70.2, 64.3, 62.2, 36.8, 30.1, 28.0, 21.9, 18.9, 13.5; IR (neat): ν 3358, 2958, 2932, 2873, 2254, 1427, 1300, 1059, 1004 cm^{-1}.



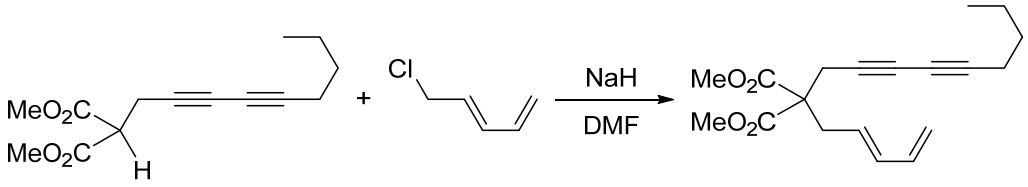
S29 **1r**

1r: To a stirred suspension of NaH (217 mg, 60 wt%, 5.4 mmol) in THF (2.0 mL) was added a solution of **S29** (241 mg, 1.11 mmol) in THF (2.0 mL) at 0 °C. After 30 minutes, MeI (0.1 mL, 1.6 mmol) was added and the reaction mixture was stirred for another 50 minutes. Then the reaction mixture was quenched with saturated aqueous NH_4Cl solution and extracted with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. Purification of the crude product by column chromatography (PE/EA, 50/1) afforded **1r** (227 mg, 0.984 mmol, 89%) as a light yellow oil. TLC (PE/EA, 10/1): R_f = 0.9; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.30 (dt, J = 17.0, 10.4 Hz, 1H), 6.08 (dd, J = 15.1, 10.6 Hz, 1H), 5.67 (dd, J = 15.1, 6.8 Hz, 1H), 5.10 (d, J = 17.0 Hz, 1H), 4.97 (d, J = 10.1 Hz, 1H), 3.98 (t, J = 6.5 Hz, 1H), 3.39 (s, 3H), 2.33–2.19 (m, 4H), 1.88–1.73 (m, 2H), 1.57–1.38 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.0, 133.6, 131.8, 115.2, 81.2, 74.4, 71.1, 70.9, 64.4, 56.6, 34.9, 30.2, 28.1, 21.9, 18.9, 13.5; IR (neat): ν 2934, 2874, 2823, 2253, 1465, 1338, 1106, 1004 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd. for $C_{16}H_{23}O$, 231.1743; found, 231.1750.



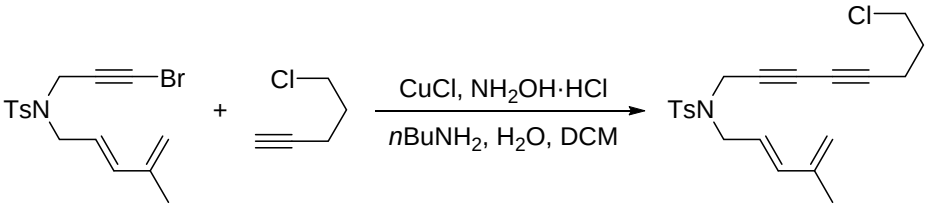
S30 **S2** **S31**

S31: Following the general procedure A, a solution of alkyne **S30**[15] (696 mg, 4.09 mmol) in DCM (5 mL), a solution of bromoalkyne **S2**[2] (1.42 g, 70 wt%, 6.2 mmol) in DCM (4 mL), CuCl (203 mg, 2.05 mmol), and 30% nBuNH$_2$/H$_2$O (15 mL) were used. Purification of the crude product by column chromatography (PE/EA, 50/1→20/1→10/1→5/1) afforded **S31** (706 mg, 2.82 mmol, 69%) as a colorless oil. TLC (PE/EA, 10/1): R_f = 0.3; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.77 (s, 6H), 3.60 (t, J = 7.6 Hz, 1H), 2.86 (d, J = 7.6 Hz, 2H), 2.24 (t, J = 6.9 Hz, 2H), 1.55–1.35 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.0, 78.8, 72.0, 67.3, 64.8, 52.8, 50.7, 30.2, 21.9, 19.3, 18.8, 13.4; IR (neat): ν 2958, 2874, 2260, 1741, 1436, 1344, 1281, 1241, 1157, 1070, 1030 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{14}H_{18}NaO_4$, 273.1097; found, 273.1100.



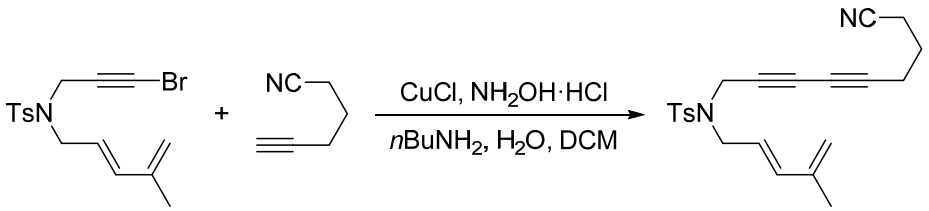
S31 **S16** **1s**

1s: To a stirred solution of diyne **S31** (201 mg, 0.80 mmol) in DMF (5 mL) was added NaH (48 mg, 60 wt%, 1.2 mmol) at 0 °C. After one hour, chloride **S16**[8] (162 mg, 71 wt%, 1.12 mmol) was added and the reaction mixture was allowed to warm to rt and stirred for additional two hours. Then the reaction mixture was quenched with saturated aqueous NH_4Cl solution, extracted with Et_2O for four times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated. Purification of the crude product by column chromatography (PE/EA, 20/1→10/1) afforded **1s** (194 mg, 0.61 mmol, 76%) as a colorless oil. TLC (PE/EA, 10/1): R_f = 0.4; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.33–6.21 (m, 1H), 6.21–6.11 (m, 1H), 5.47 (dt, J = 14.8, 7.6 Hz, 1H), 5.16 (d, J = 16.8 Hz, 1H), 5.04 (d, J = 10.0 Hz, 1H), 3.74 (s, 6H), 2.87 (s, 2H), 2.82 (d, J = 7.6 Hz, 2H), 2.25 (t, J = 6.9 Hz, 2H), 1.55–1.35 (m, 4H), 0.91 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.9, 136.4, 135.7, 126.9, 116.9, 78.7, 71.0, 68.4, 64.9, 57.2, 52.9, 35.6, 30.2, 23.7, 21.9, 18.9, 13.5; IR (neat): ν 2956, 2934, 2874, 2259, 1740, 1653, 1603, 1436, 1286, 1271, 1210, 1165, 1068, 1030, 1006 cm^{-1}; HRMS (ESI): $[M+Na]^+$ calcd. for $C_{19}H_{24}NaO_4$, 339.1567; found, 339.1565.



S6 **S32** **1t**

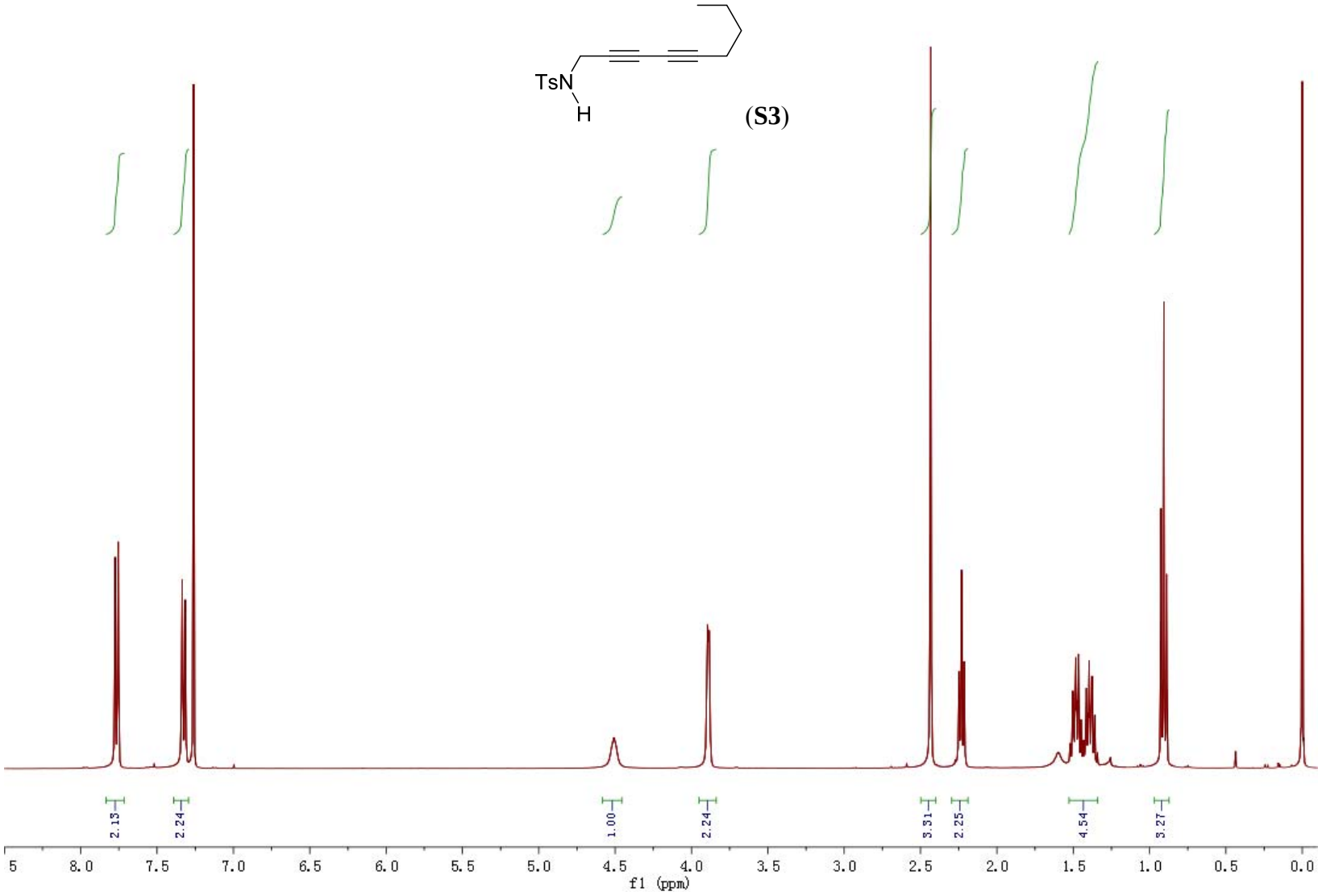
1t: Following the general procedure A, a solution of bromoalkyne **S6** (200 mg, 0.543 mmol) in DCM (1.0 mL), alkyne **S32** (111 mg, 1.08 mmol) in DCM (0.2 mL), CuCl (26.9 mg, 0.272 mmol), and 30% nBuNH$_2$/H$_2$O (1.7 mL) were used. Purification of the crude product by column chromatography (PE/EA, 20/1) afforded **1t** (160.3 mg, 0.411 mmol, 76%) as a light yellow oil. TLC (PE/EA, 20/1): R_f = 0.2; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 6.29 (d, J = 15.6 Hz, 1H), 5.50 (dt, J = 15.5, 6.8 Hz, 1H), 5.00 (s, 1H), 4.97 (s, 1H), 4.12 (s, 2H), 3.85 (d, J = 6.8 Hz, 2H), 3.61 (t, J = 6.3 Hz, 2H), 2.47–2.41 (m, 2H), 2.44 (s, 3H), 1.96 (p, J = 6.6 Hz, 2H), 1.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.7, 141.0, 137.7, 135.7, 129.5, 127.7, 122.8, 117.6, 78.1, 70.2, 69.2, 65.3, 48.7, 43.2, 36.6, 30.8, 21.5, 18.4, 16.6; IR (neat): ν 2922, 2258, 1610, 1598, 1441, 1348, 1162, 1093, 1060 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd. for $C_{21}H_{25}ClNO_2S$, 390.1289; found, 390.1289.

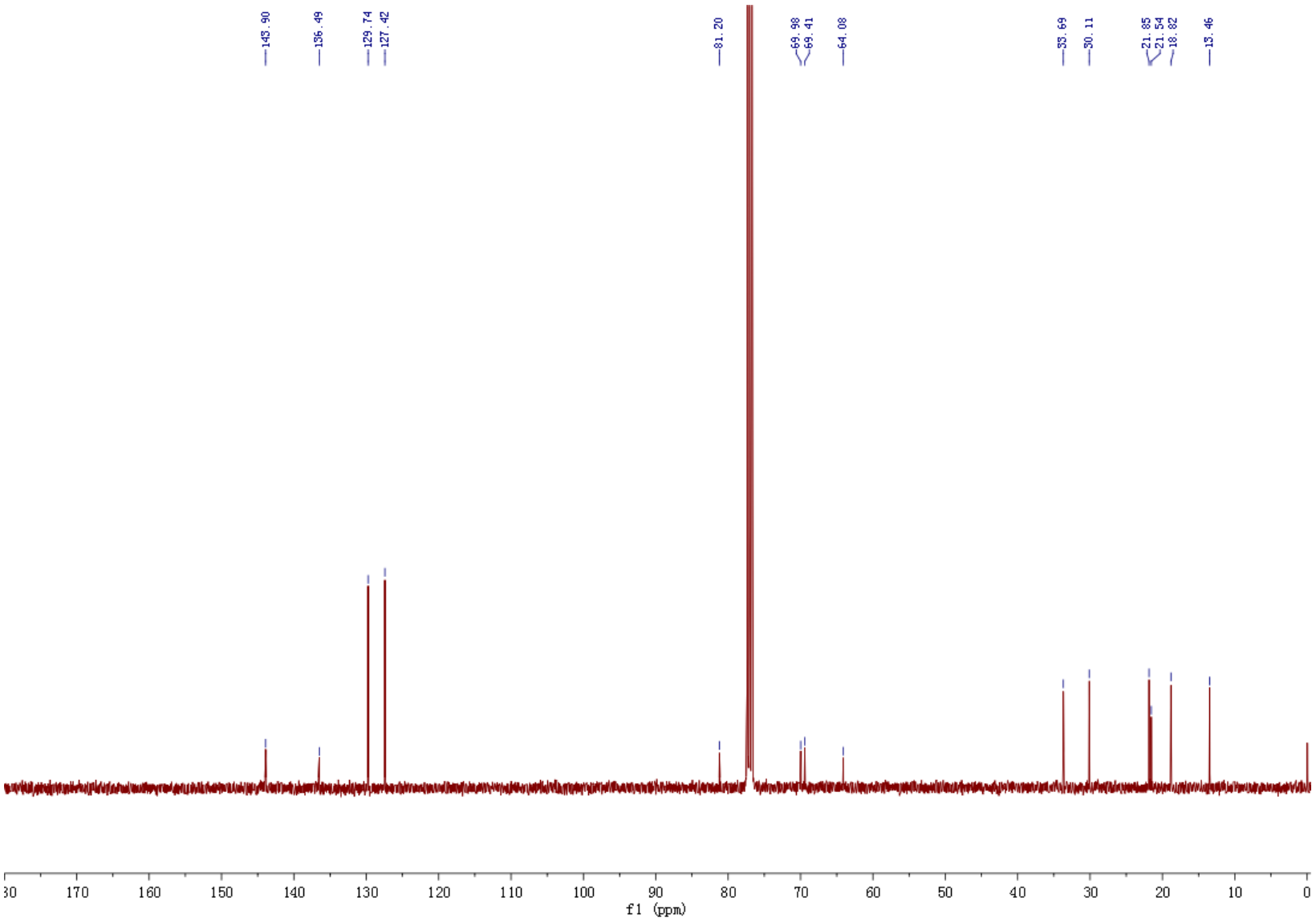


S6 **S33** **1u**

1u: Following the general procedure A, a solution of bromoalkyne **S6** (199 mg, 0.540 mmol) in DCM (1.0 mL), alkyne **S33** (102 mg, 1.10 mmol) in DCM (0.6 mL), CuCl (28 mg, 0.28 mmol), and 30% *n*$BuNH_2$/H_2O (2.2 mL) were used. Purification of the crude product by column chromatography (PE/EA, 5/1) afforded **1u** (118.6 mg, 0.312 mmol, 58%) as a colorless oil. TLC (PE/EA, 2/1): R_f = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 6.28 (d, J = 15.6 Hz, 1H), 5.49 (dt, J = 15.5, 6.8 Hz, 1H), 5.01 (s, 1H), 4.98 (s, 1H), 4.12 (s, 2H), 3.86 (d, J = 6.8 Hz, 2H), 2.53–2.40 (m, 4H), 2.44 (s, 3H), 1.87 (p, J = 6.9 Hz, 2H), 1.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.7, 140.9, 137.8, 135.8, 129.5, 127.7, 122.7, 118.6, 117.7, 76.9, 69.92, 69.87, 66.1, 48.8, 36.6, 24.1, 21.5, 18.4, 18.2, 16.1; IR (neat): ν 2944, 2250, 1598, 1428, 1348, 1162, 1093 cm^{-1}; HRMS (ESI): $[M+H]^+$ calcd. for $C_{22}H_{25}N_2O_2S$, 381.1631; found, 381.1630.

S3. ^{1}H and ^{13}C NMR Spectra of All New Compounds

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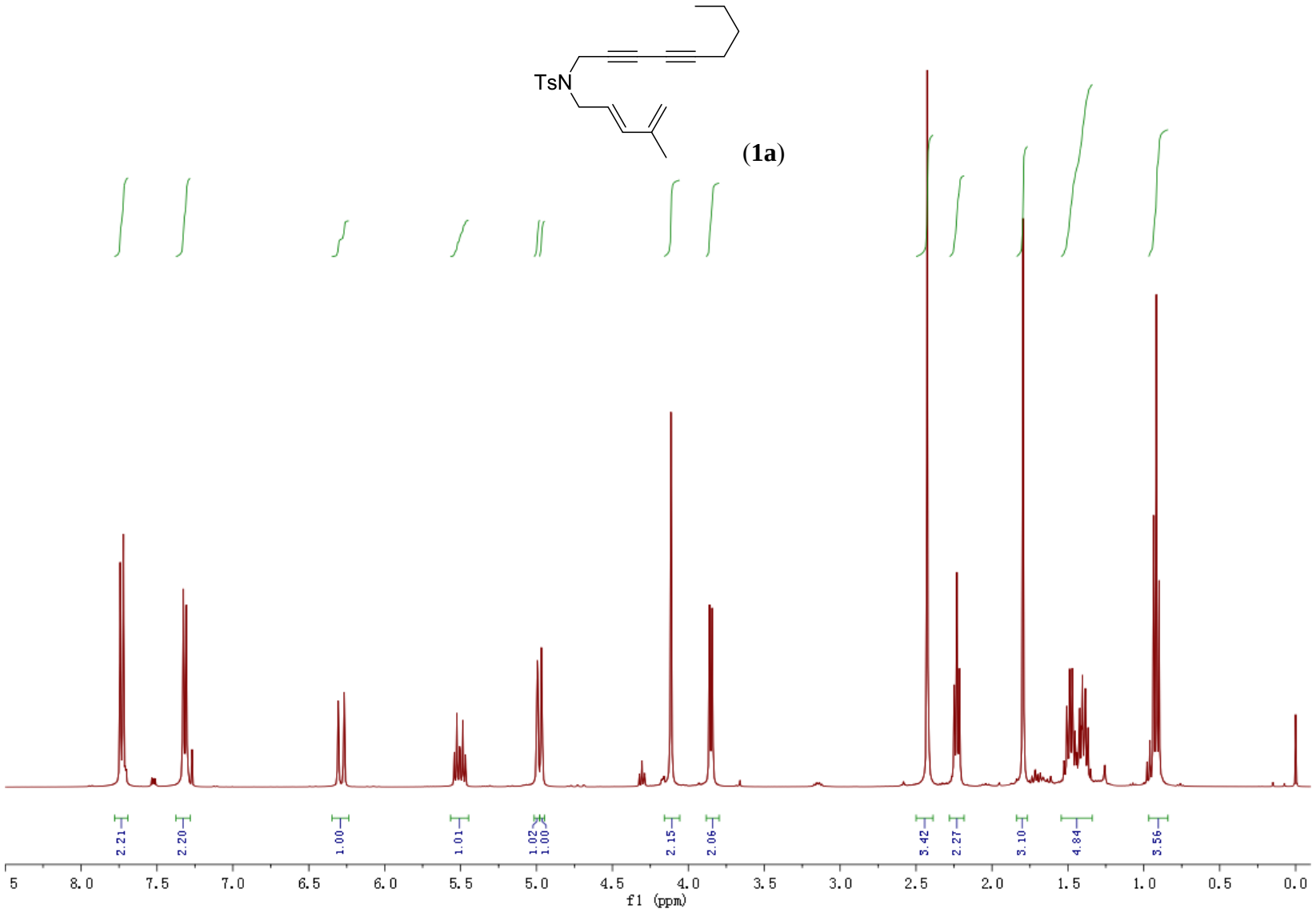
f1 (ppm)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5
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7.5
7.0
6.5
6.0
5.5
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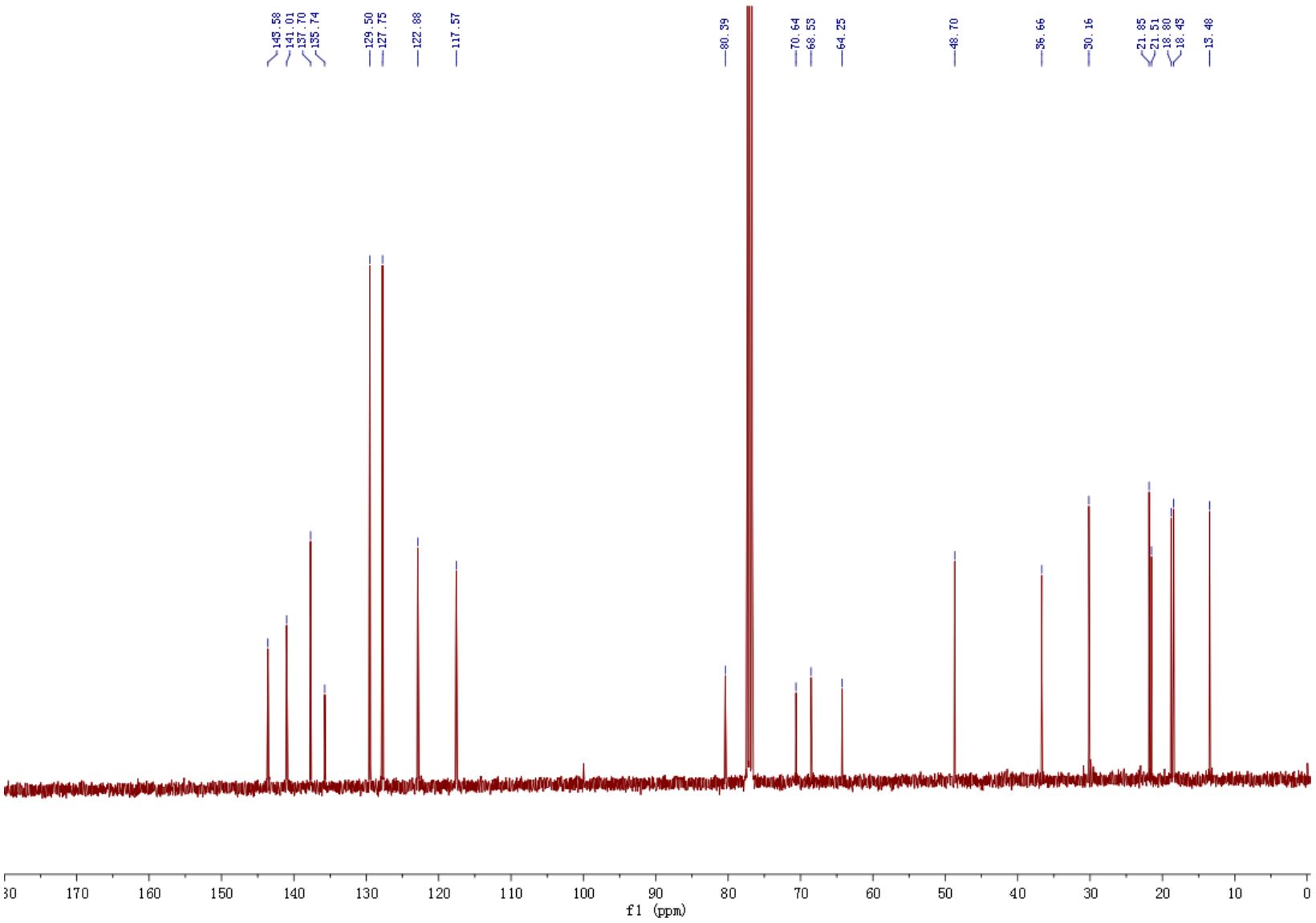
f1 (ppm)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21.51
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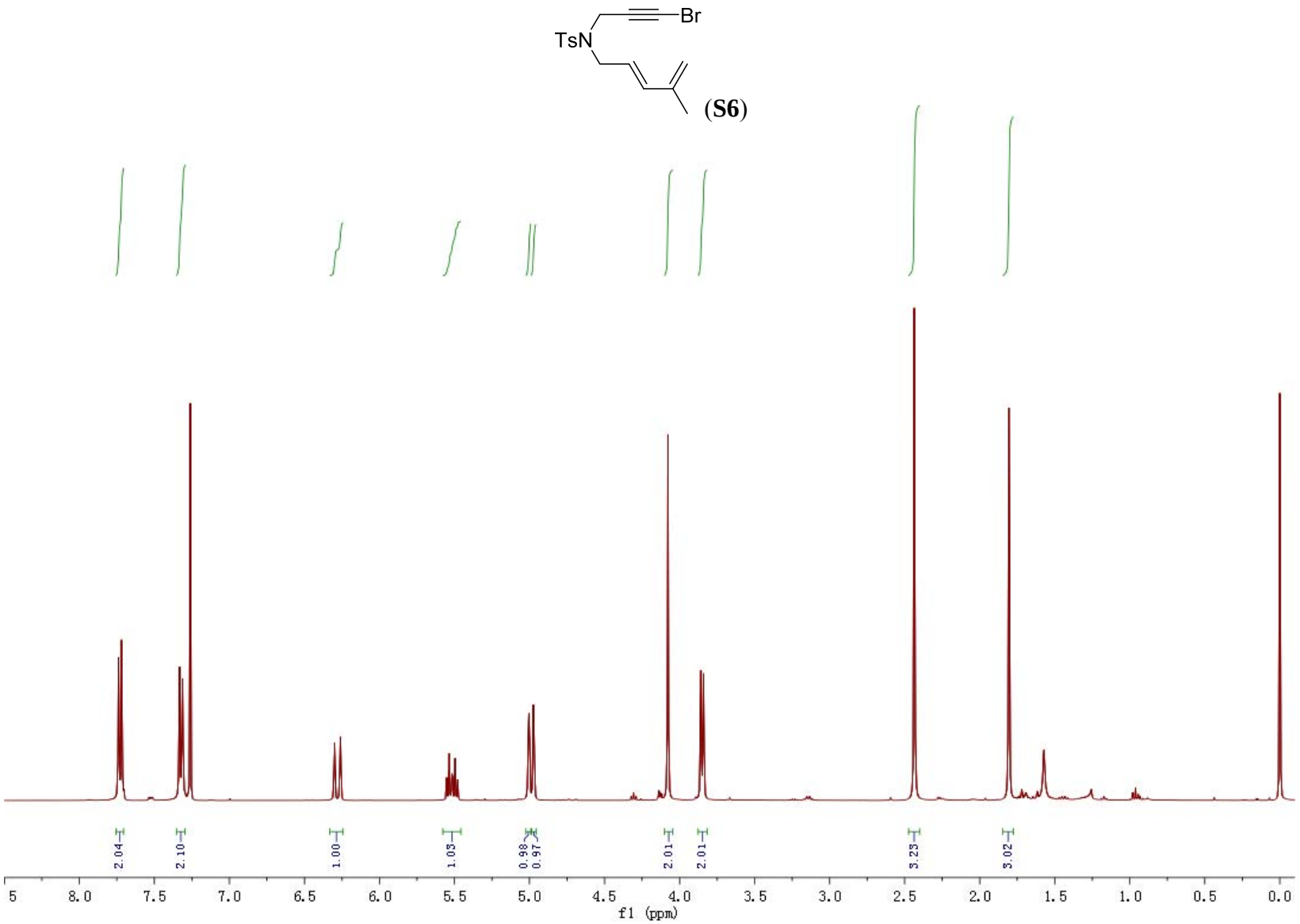
13.48
f1 (ppm)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6.5
6.0
5.5
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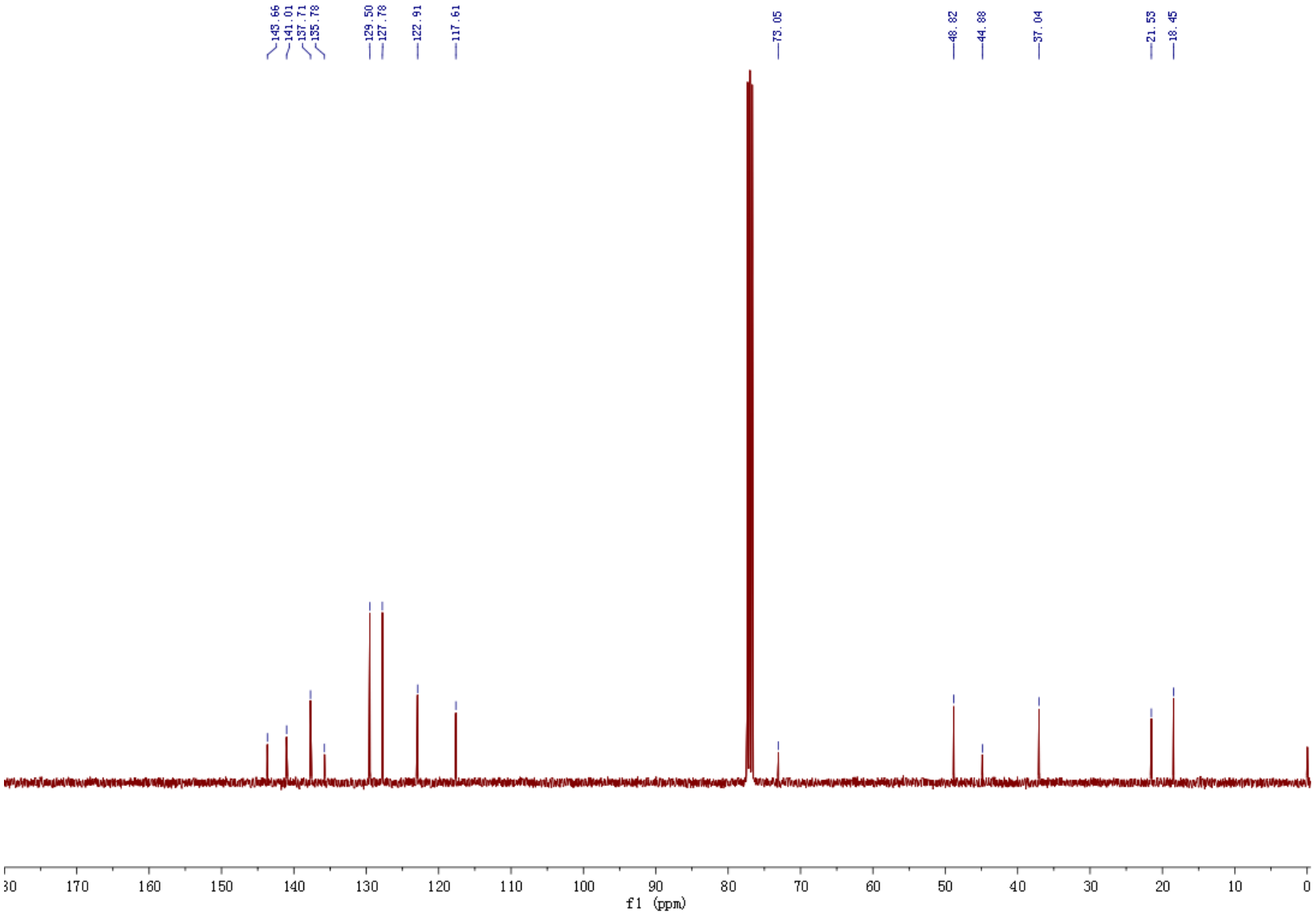
f1 (ppm)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37.04
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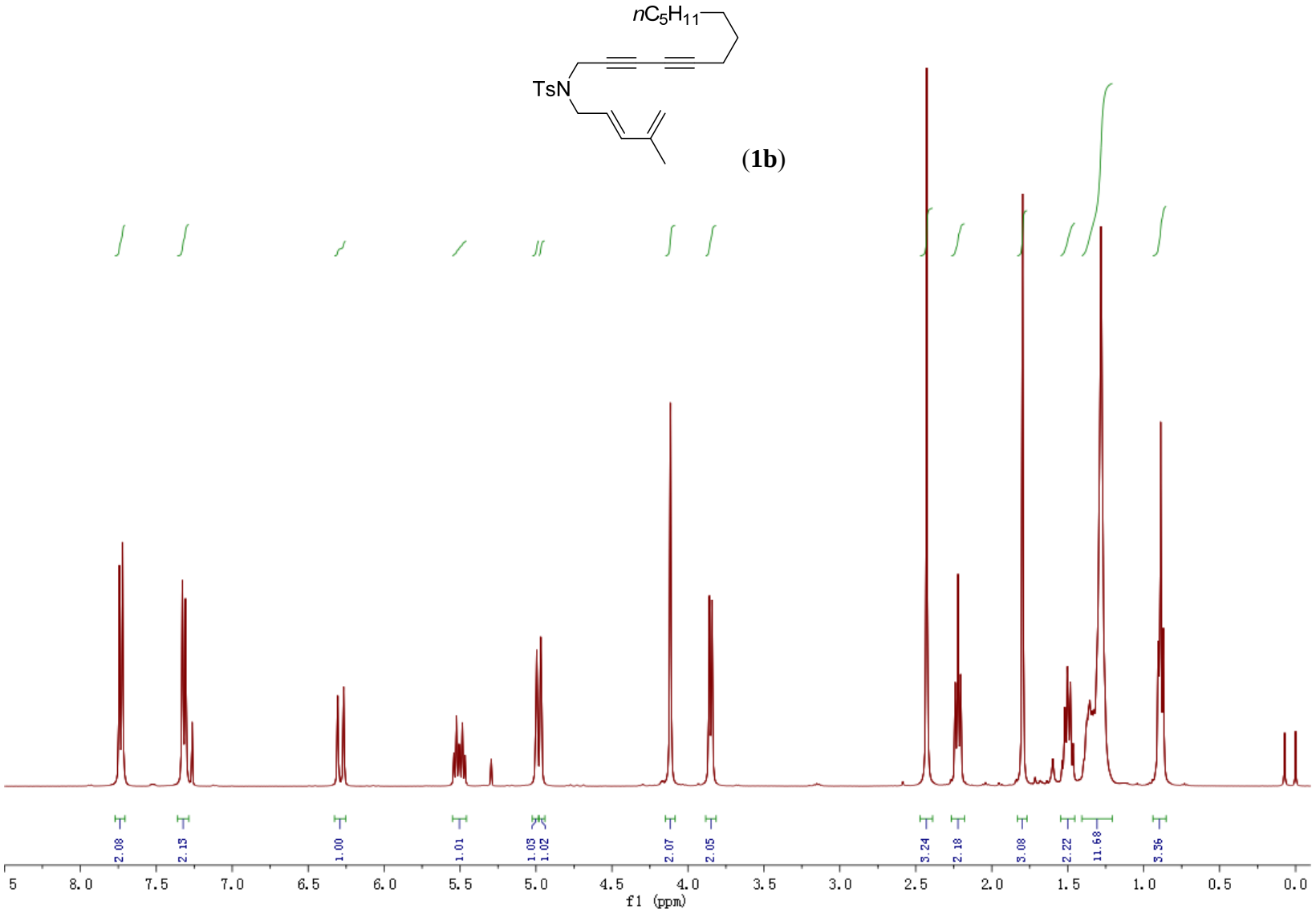
f1 (ppm)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3.08
2.22
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3.36
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7.0
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6.0
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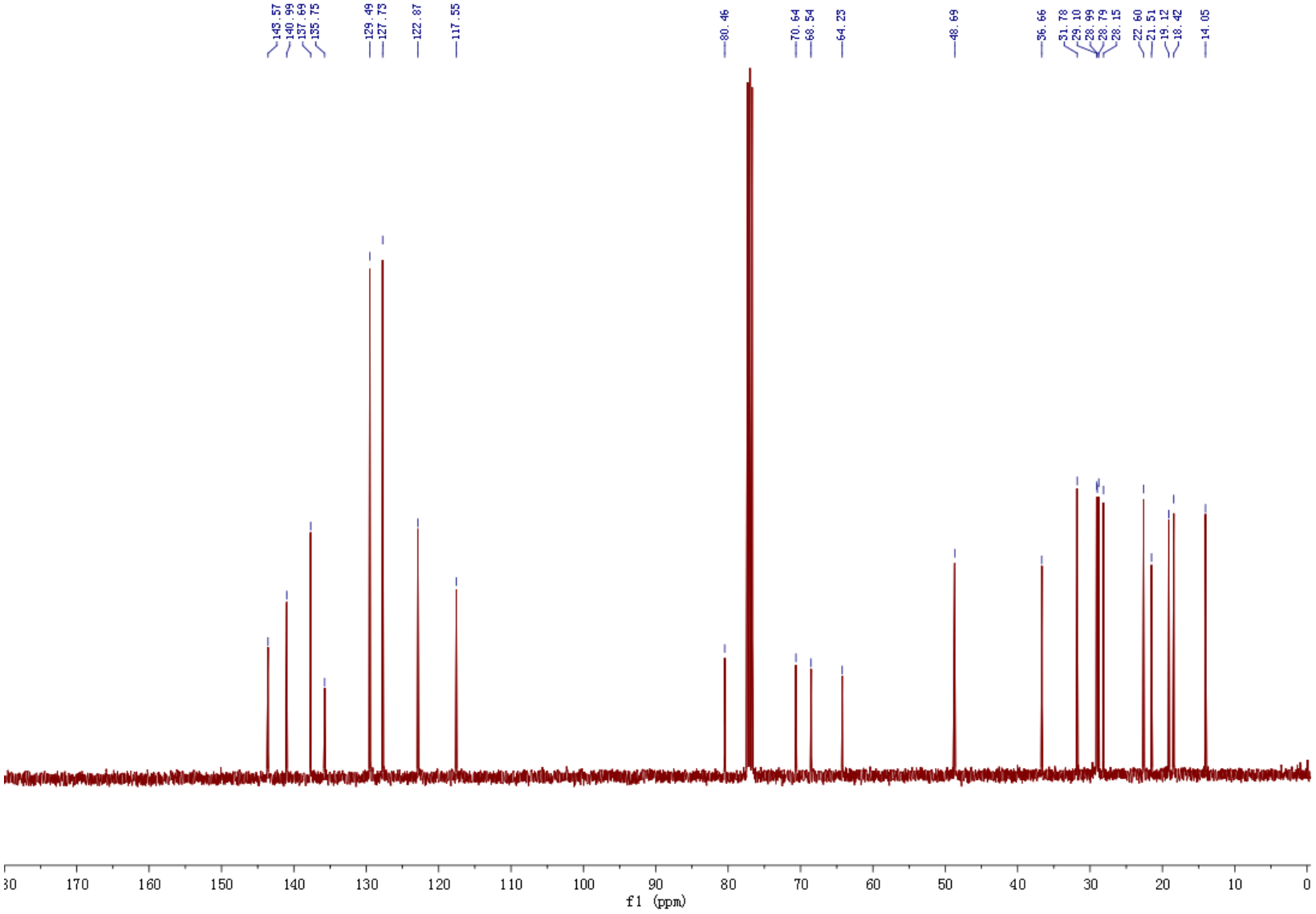
f1 (ppm)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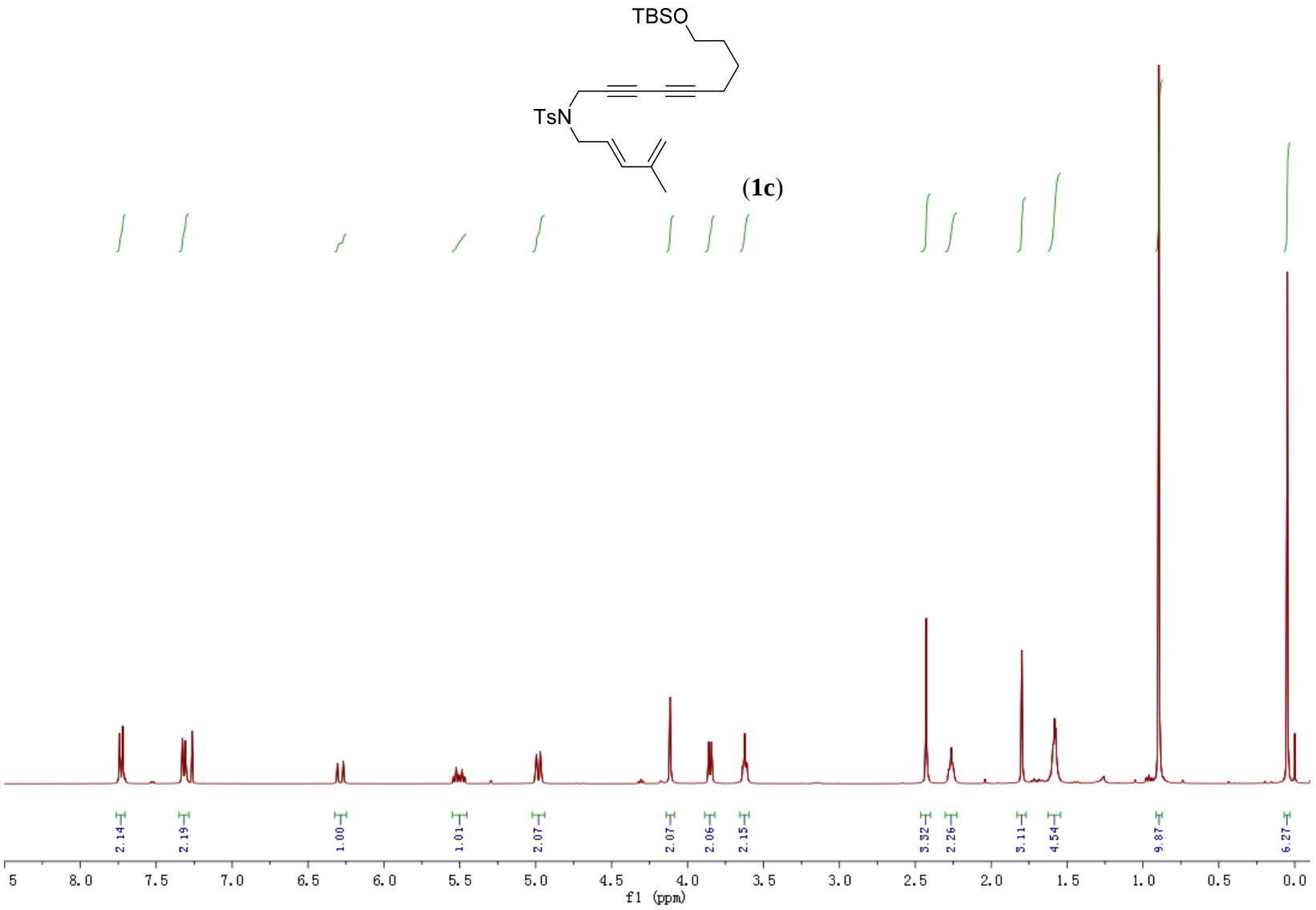
f1 (ppm)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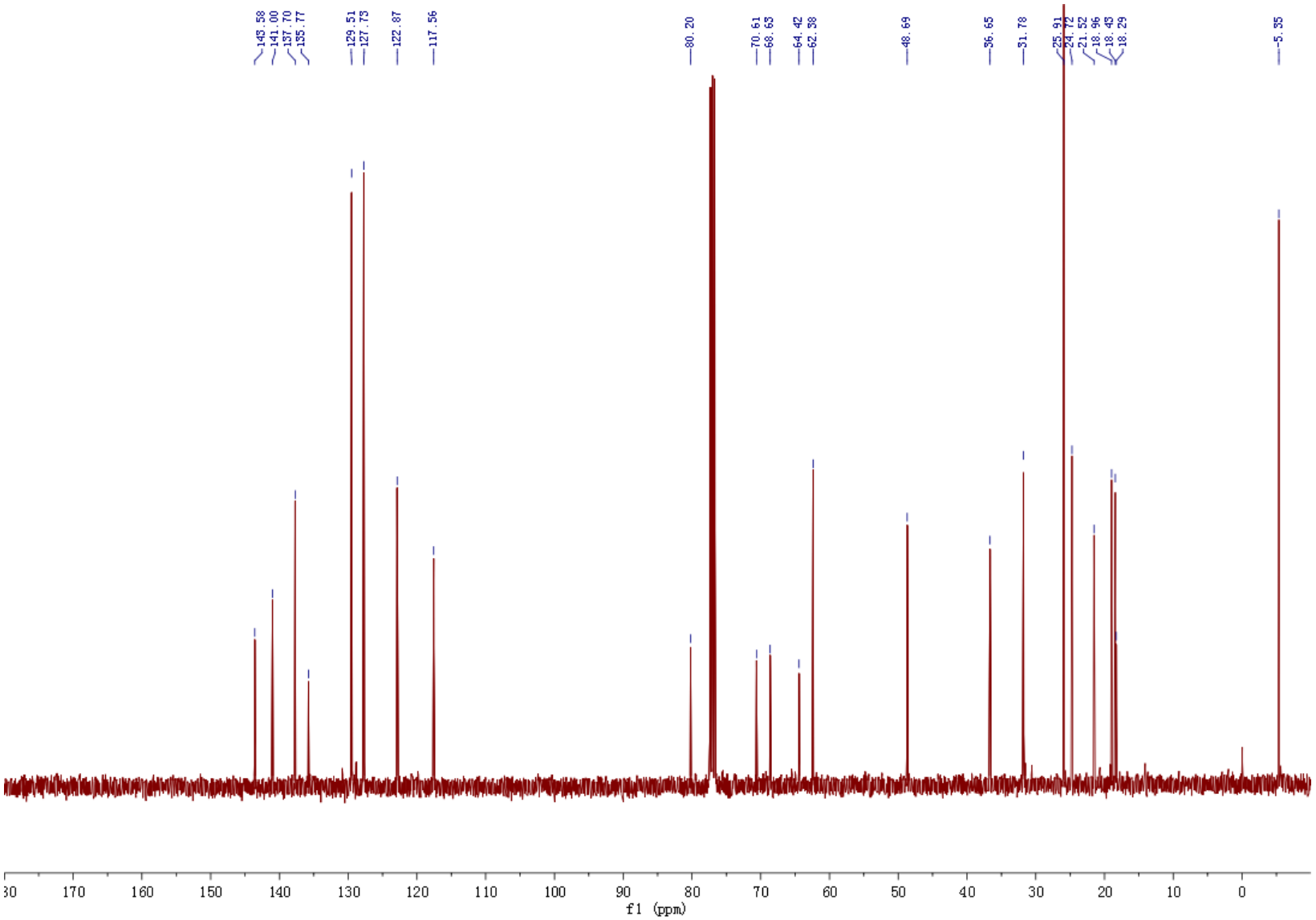
f1 (ppm)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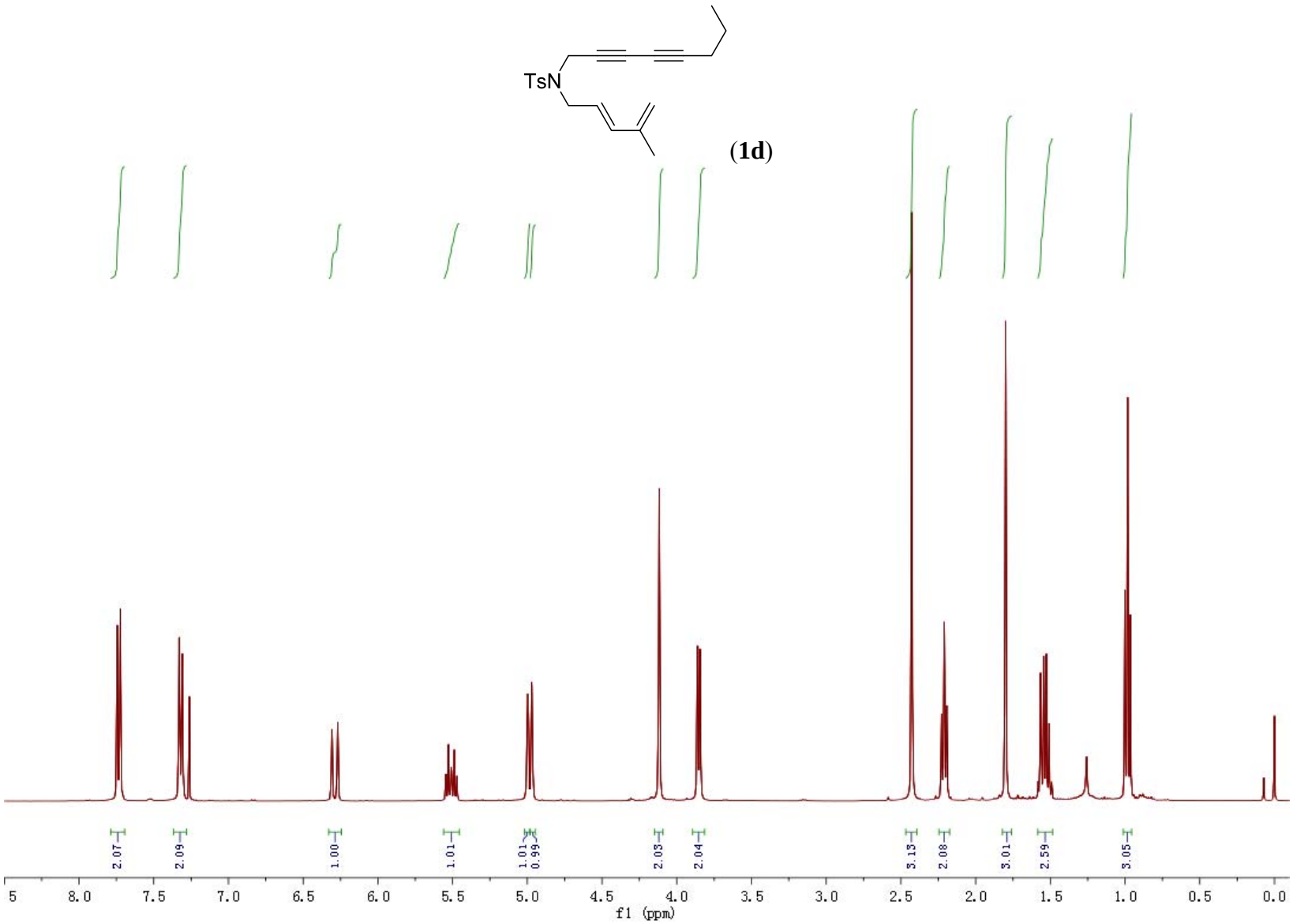
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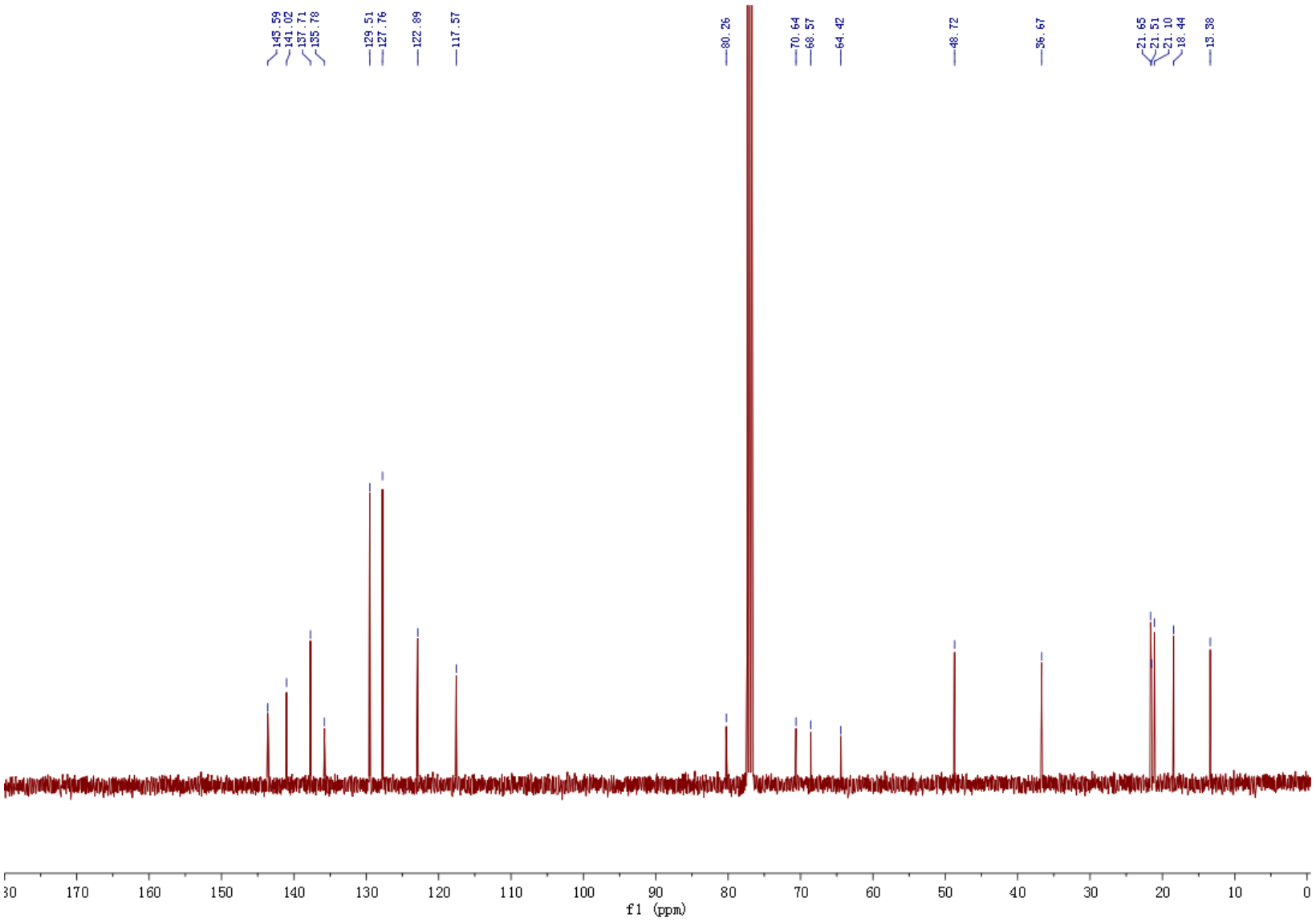
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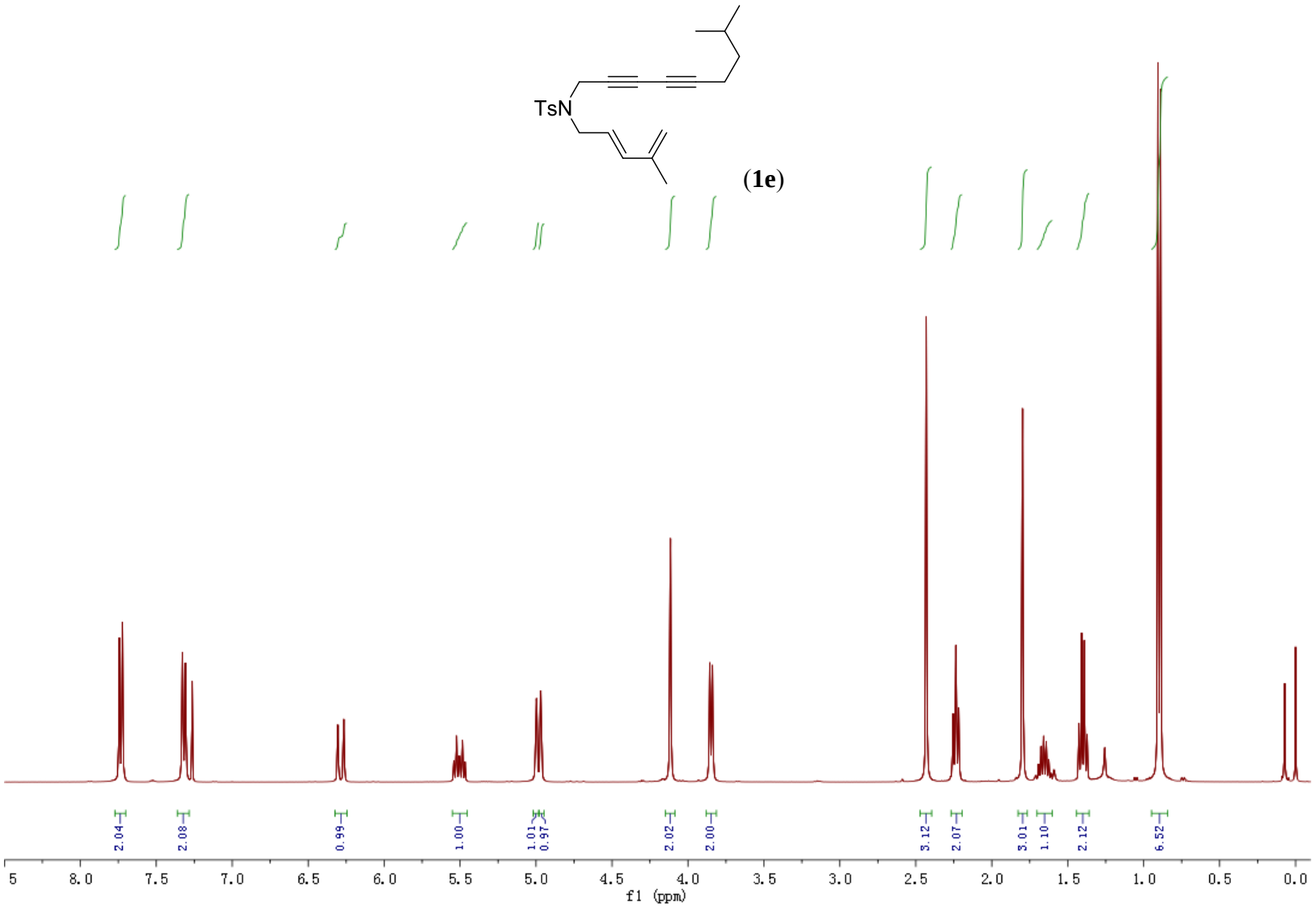
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6.0
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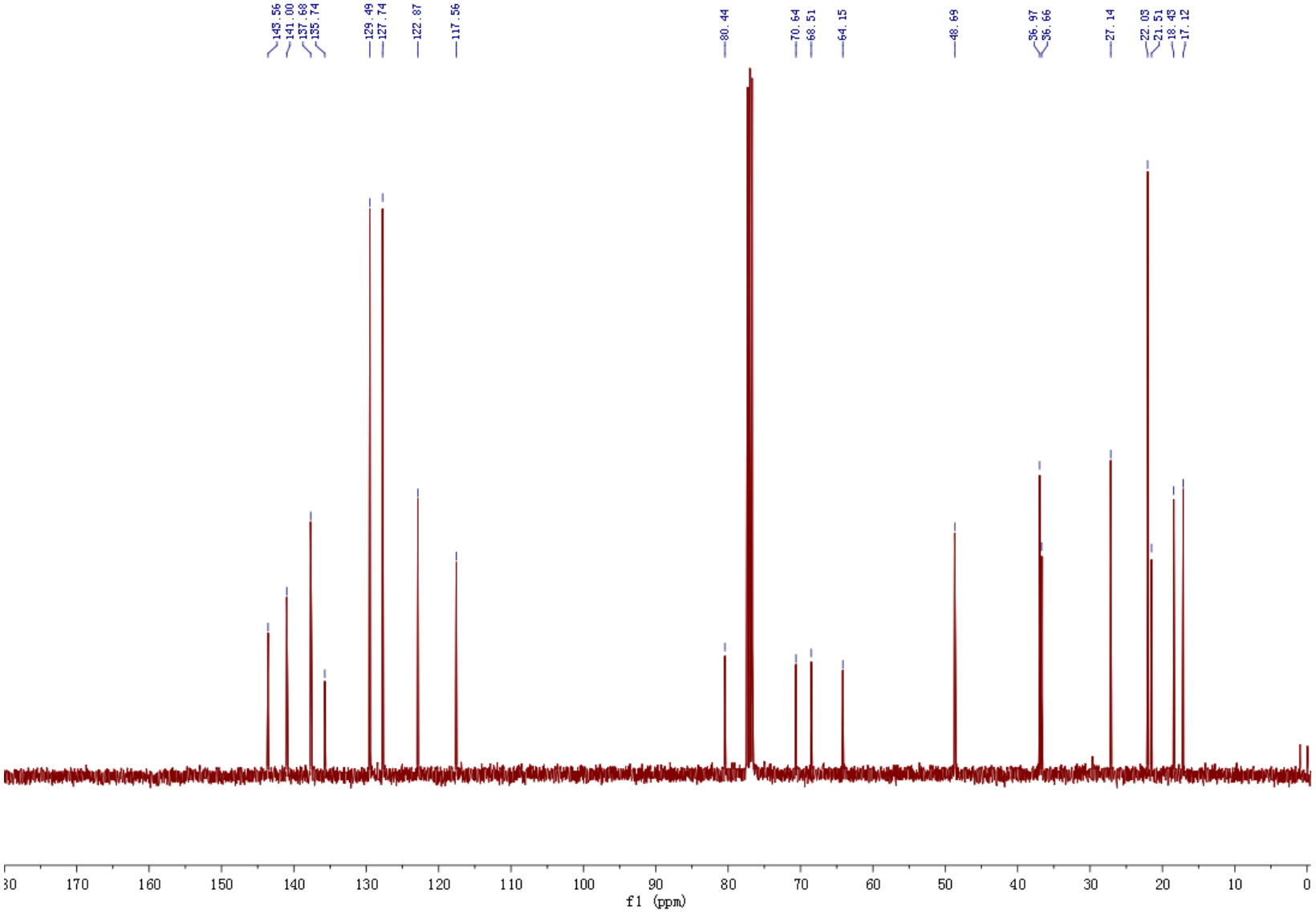
f1 (ppm)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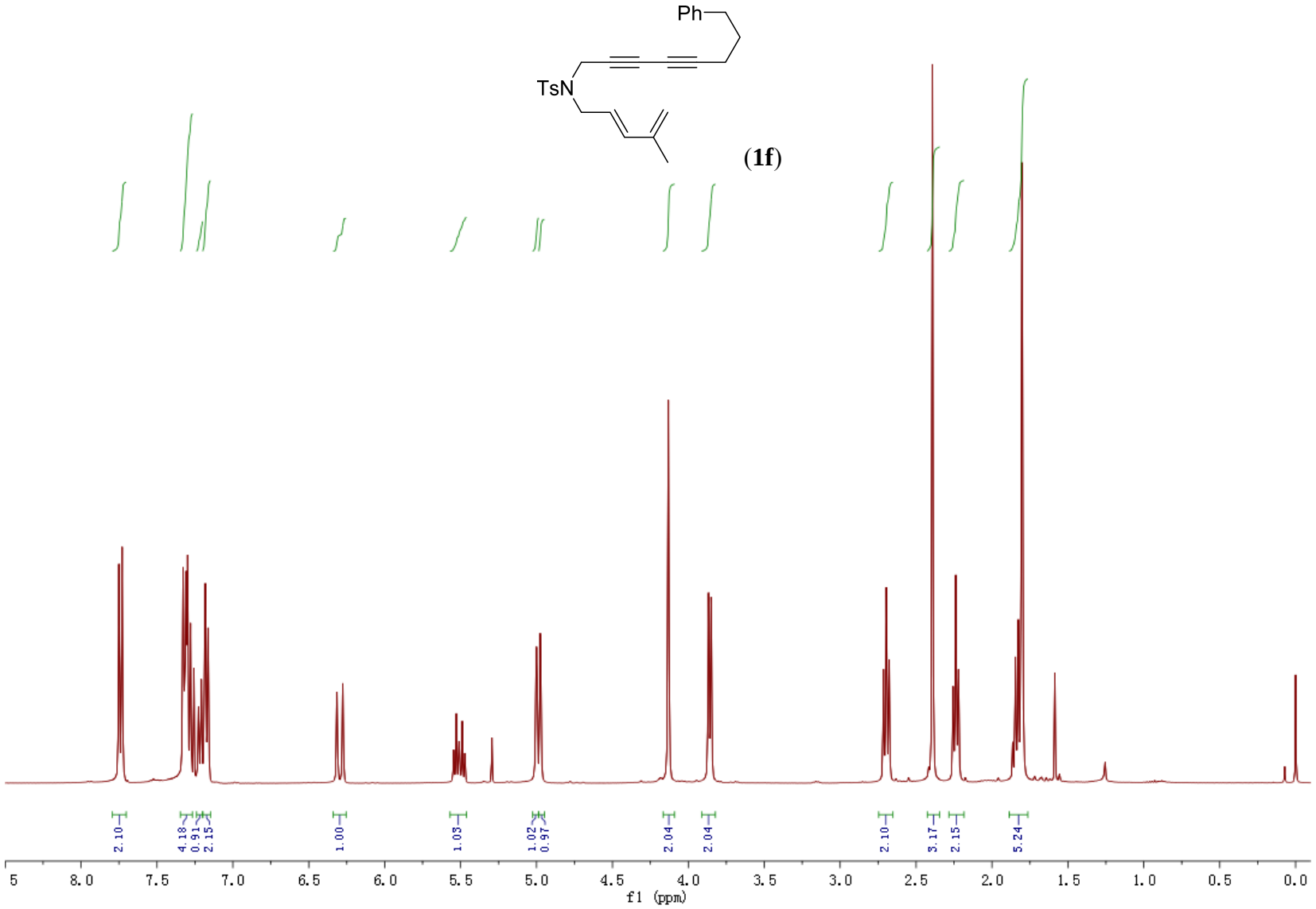
f1 (ppm)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2.04
2.10
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5
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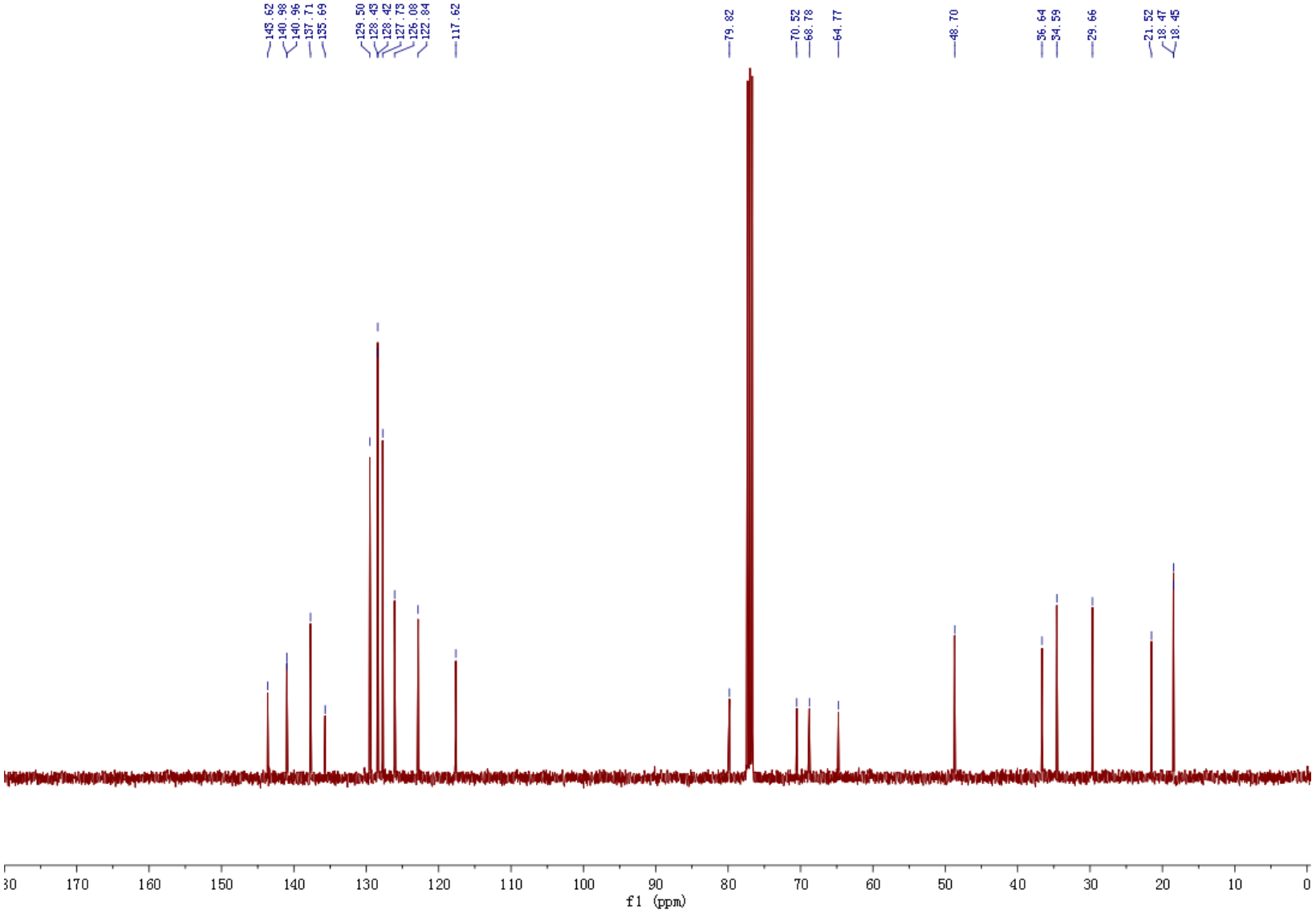
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18.47
18.45
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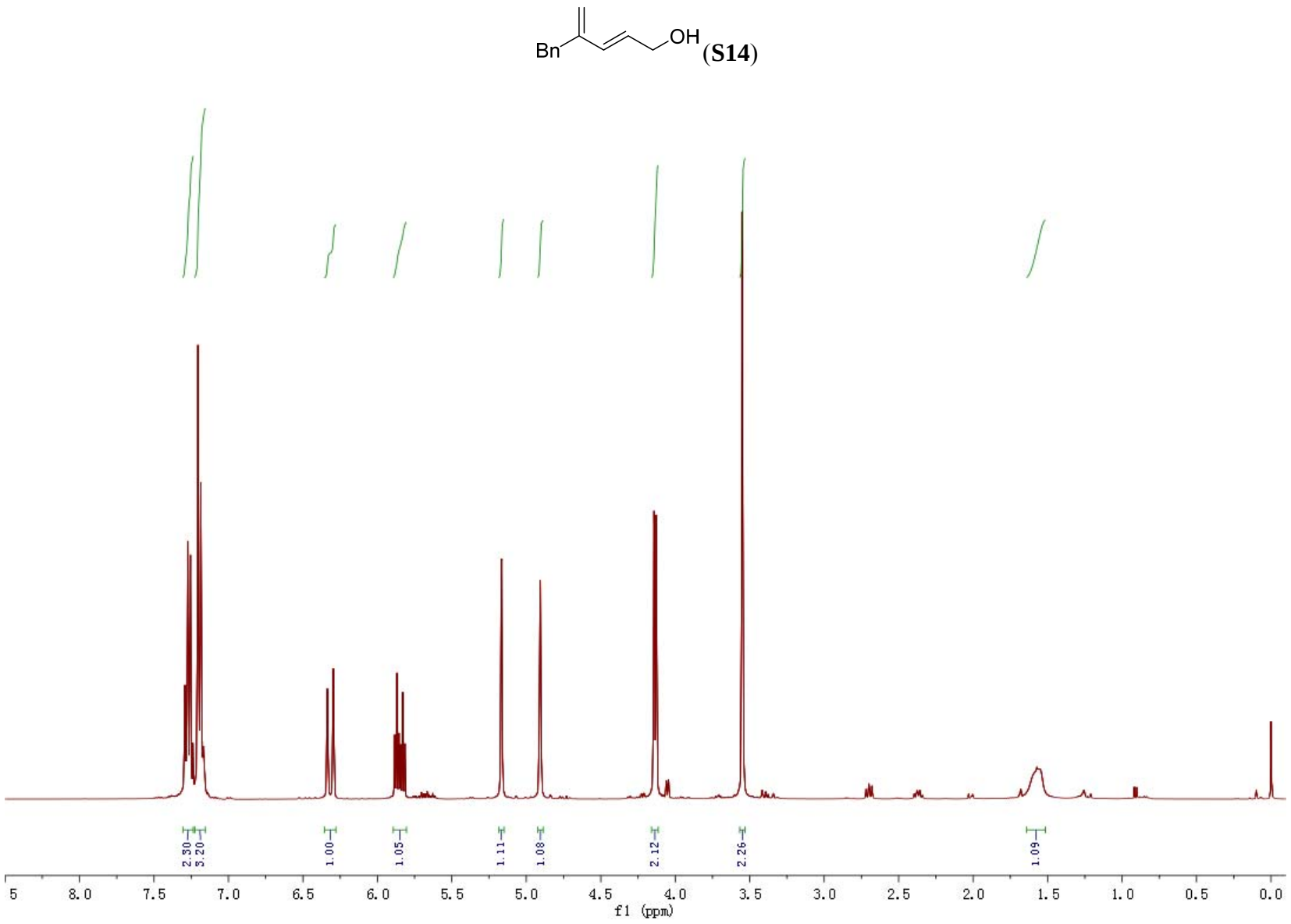
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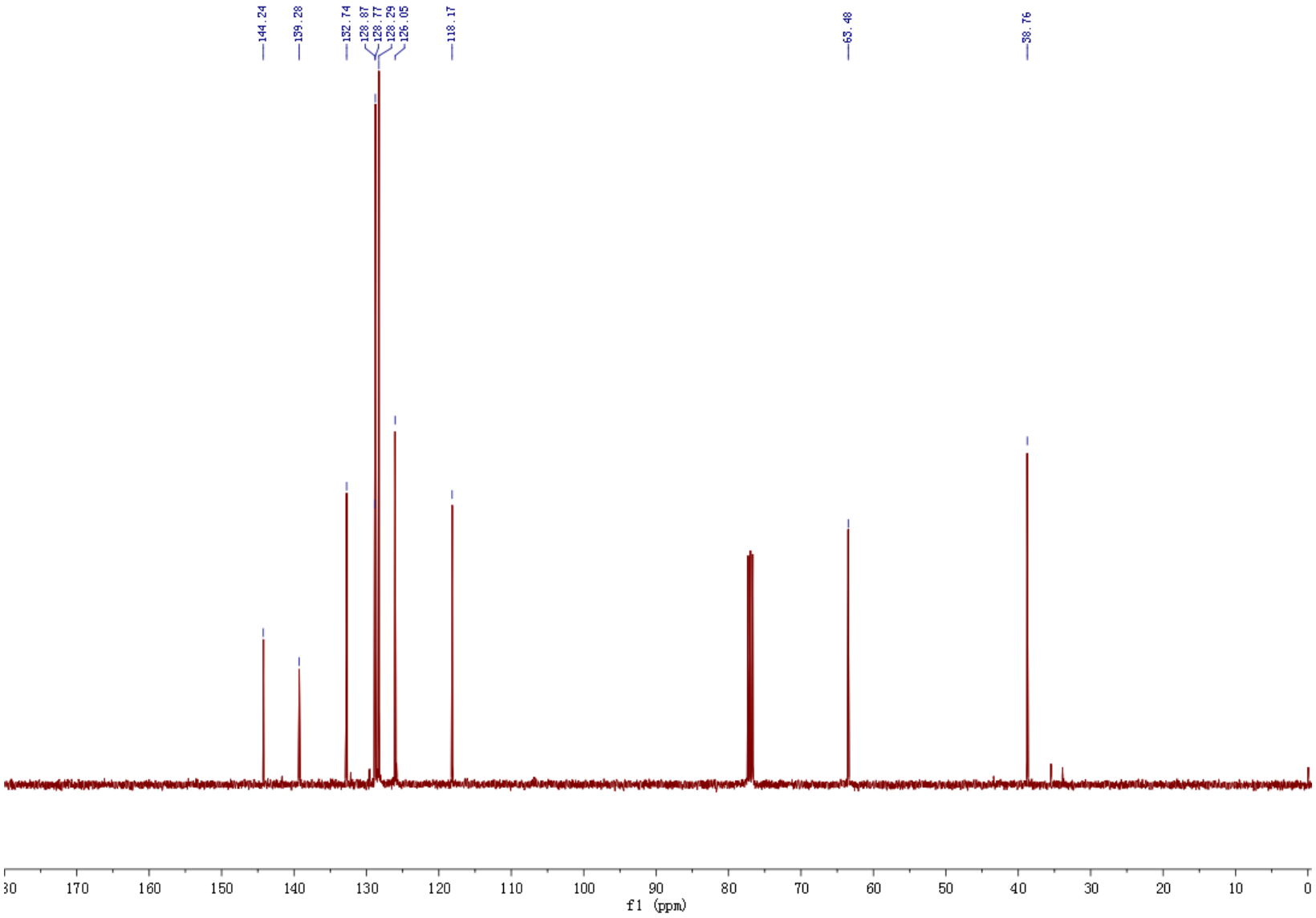
0.0
f1 (ppm)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90
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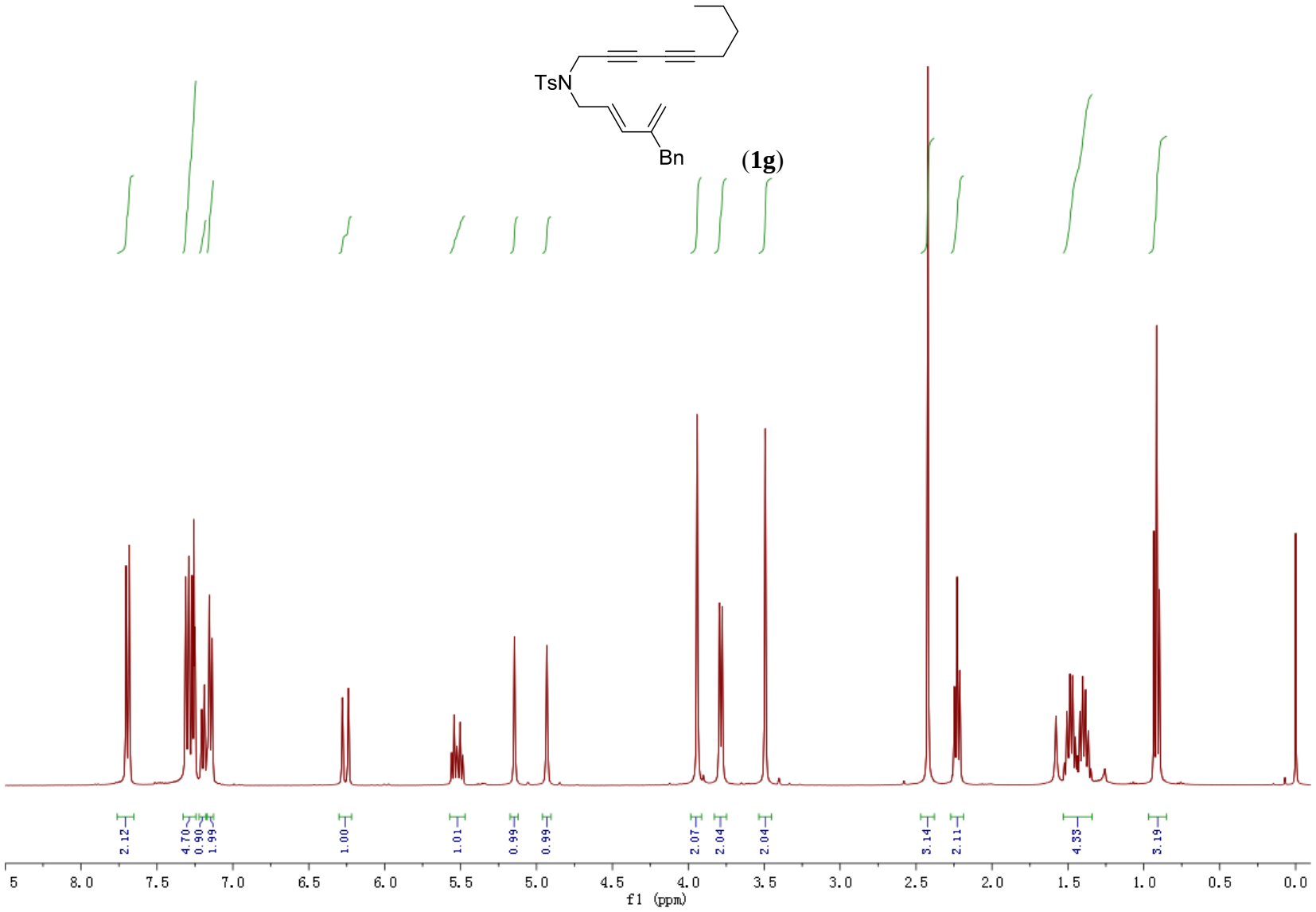
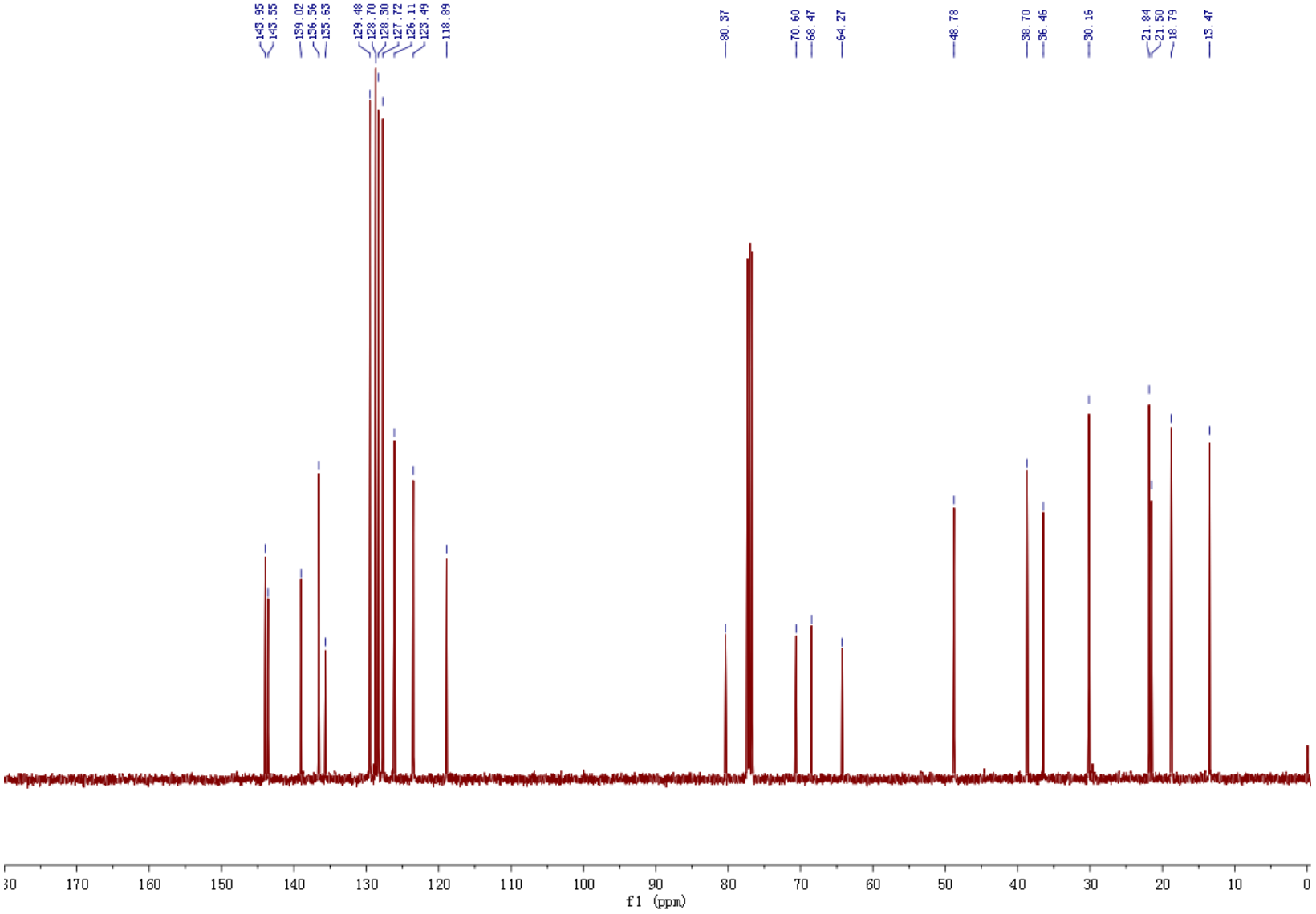
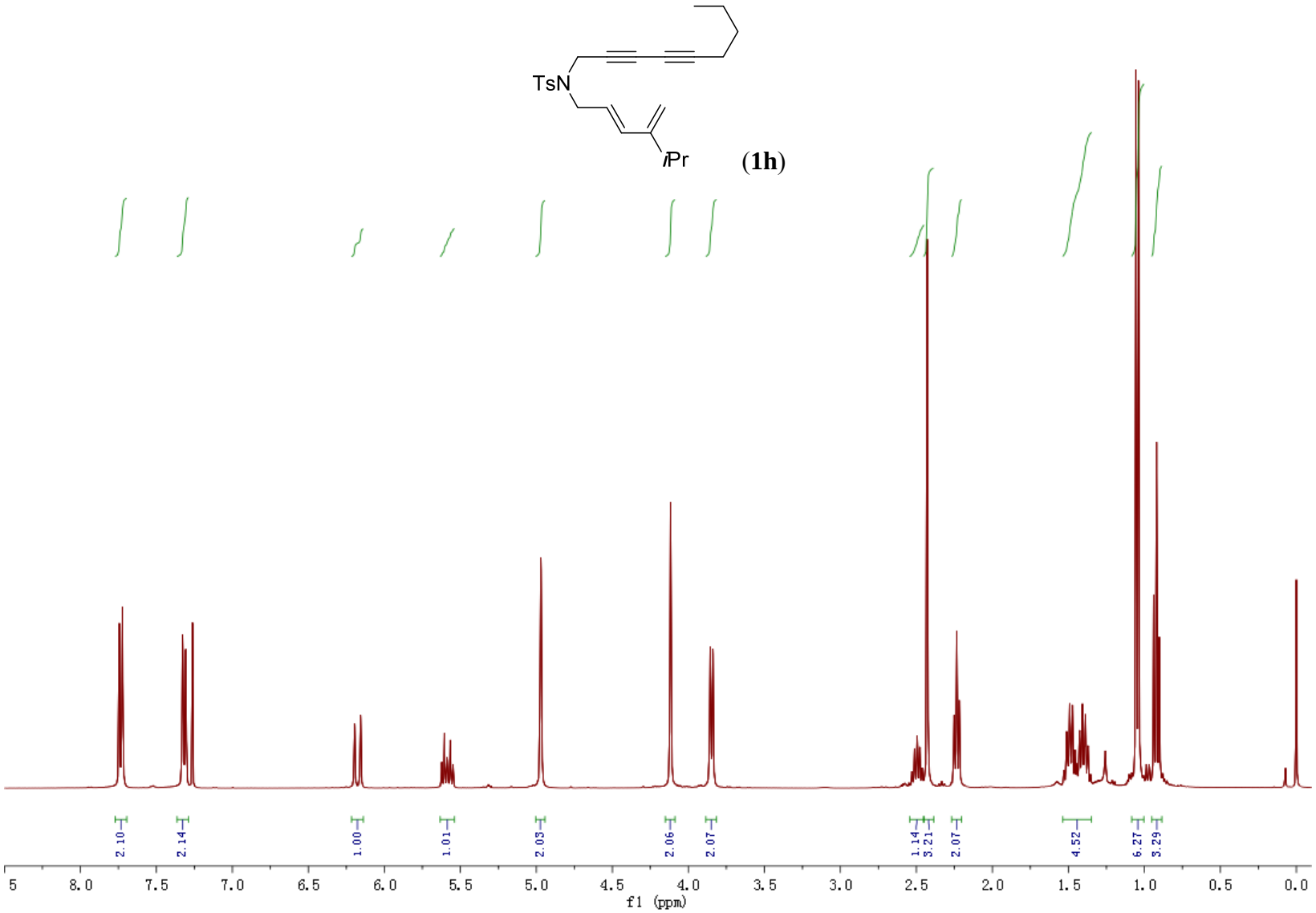
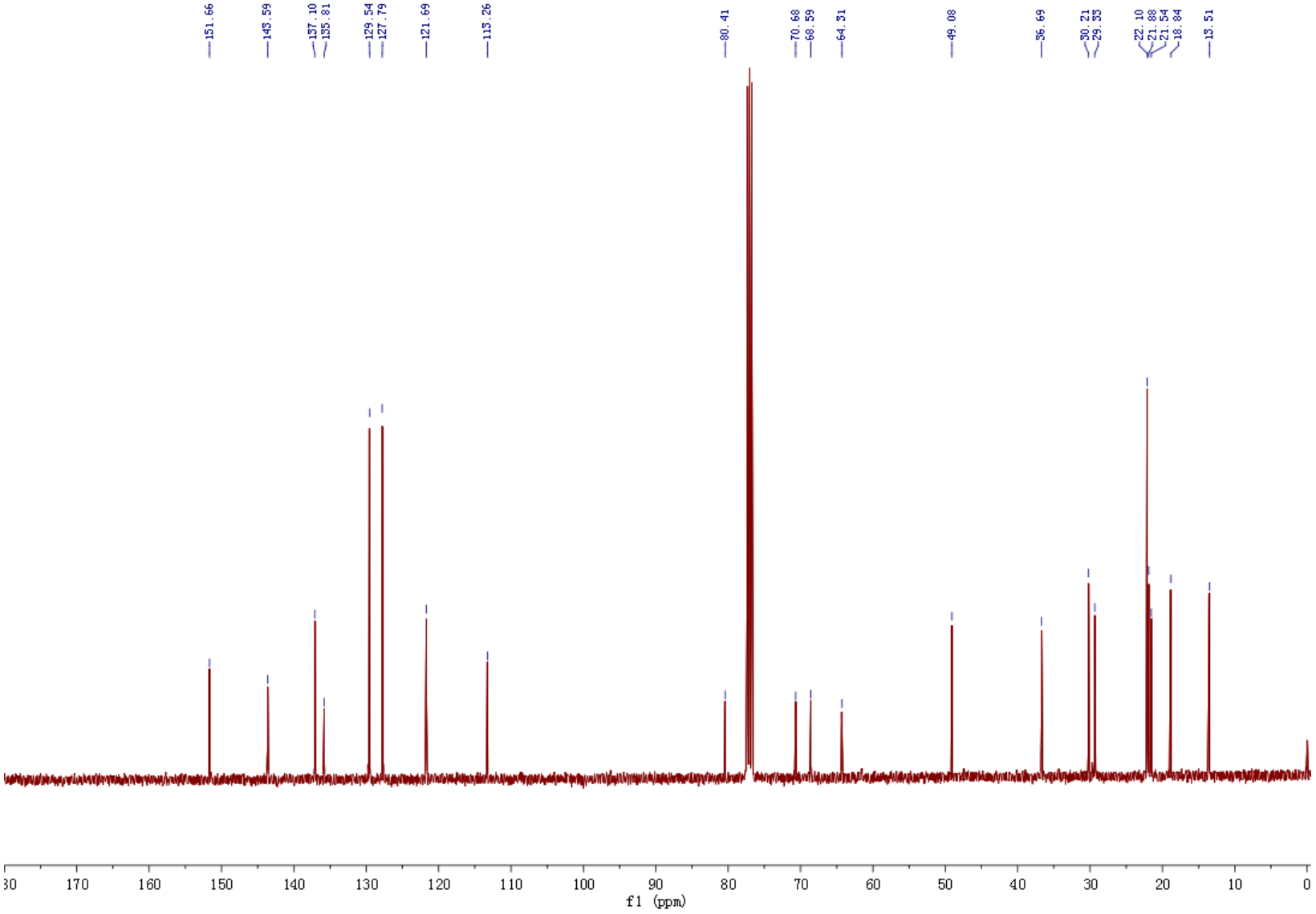
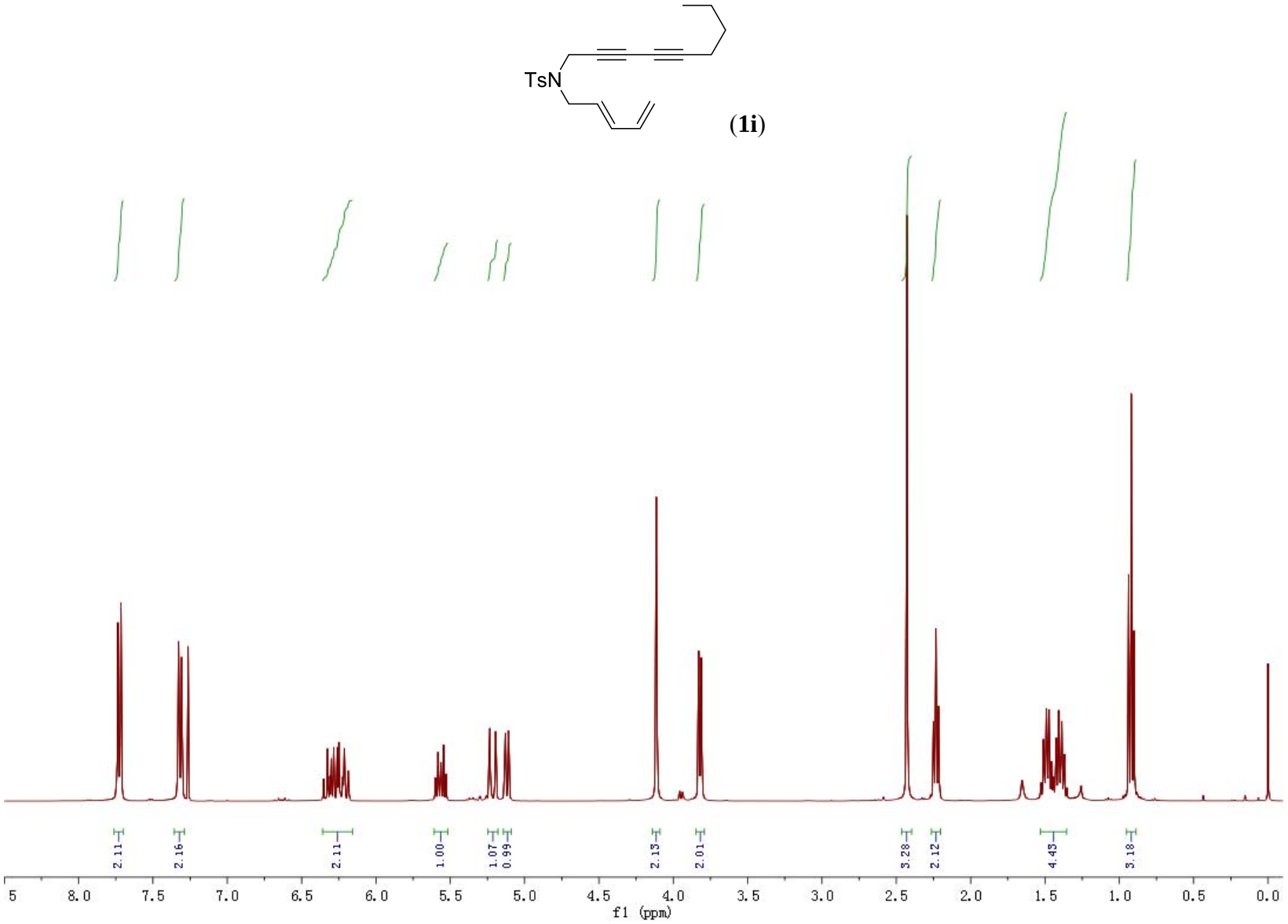
70
60
50
40
30
20
10
0
f1 (ppm)


TsN
Bn
(1g)
2.12
4.70
0.90
1.99
1.00
1.01
0.99
0.99
2.07
2.04
2.04
3.14
2.11
4.33
3.19
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)

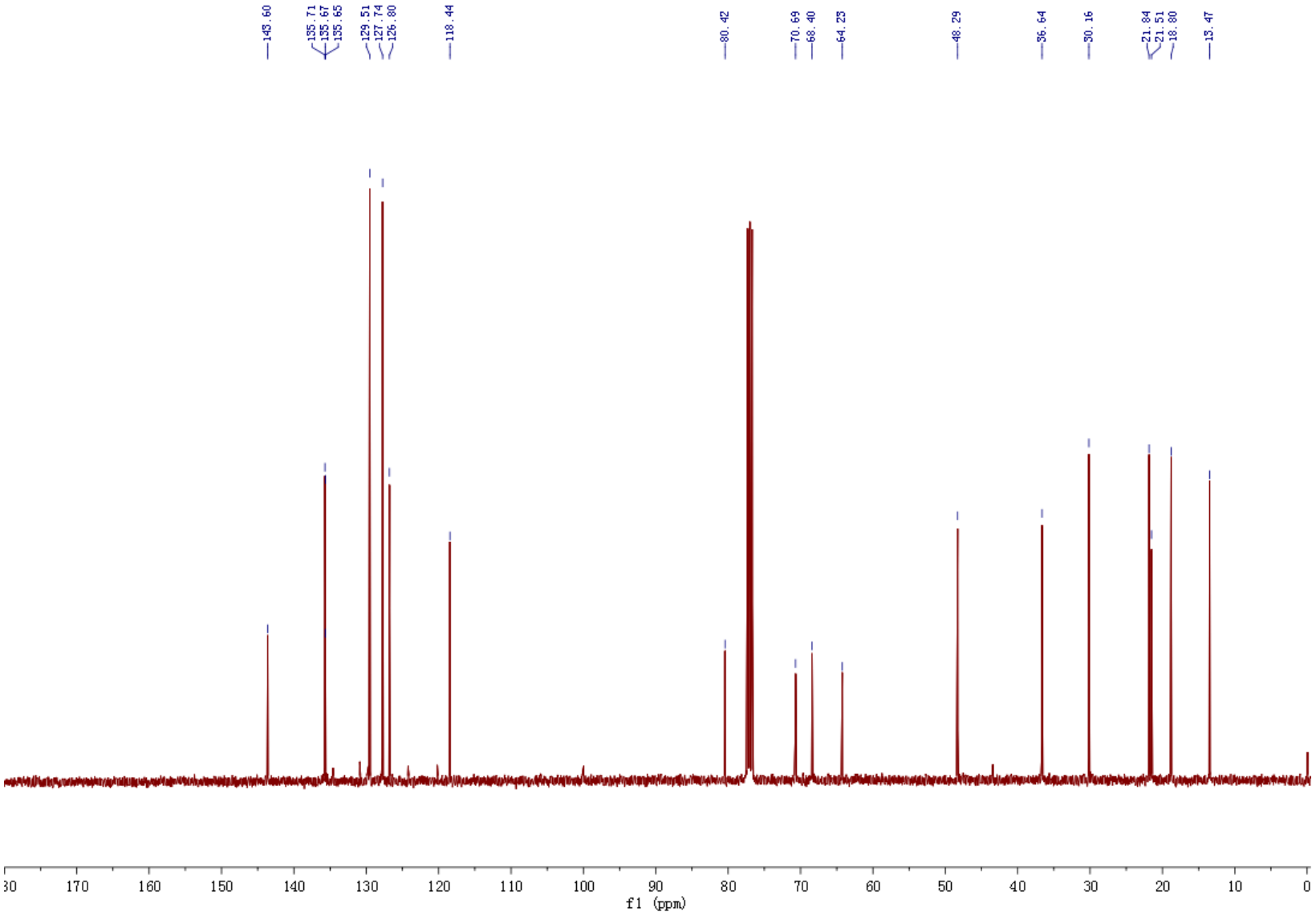

143.95
143.55
139.02
136.56
135.63
129.48
128.70
128.30
127.72
126.11
123.49
118.89
80.37
70.60
68.47
64.27
48.78
38.70
36.46
30.16
21.84
21.50
18.79
13.47
f1 (ppm)

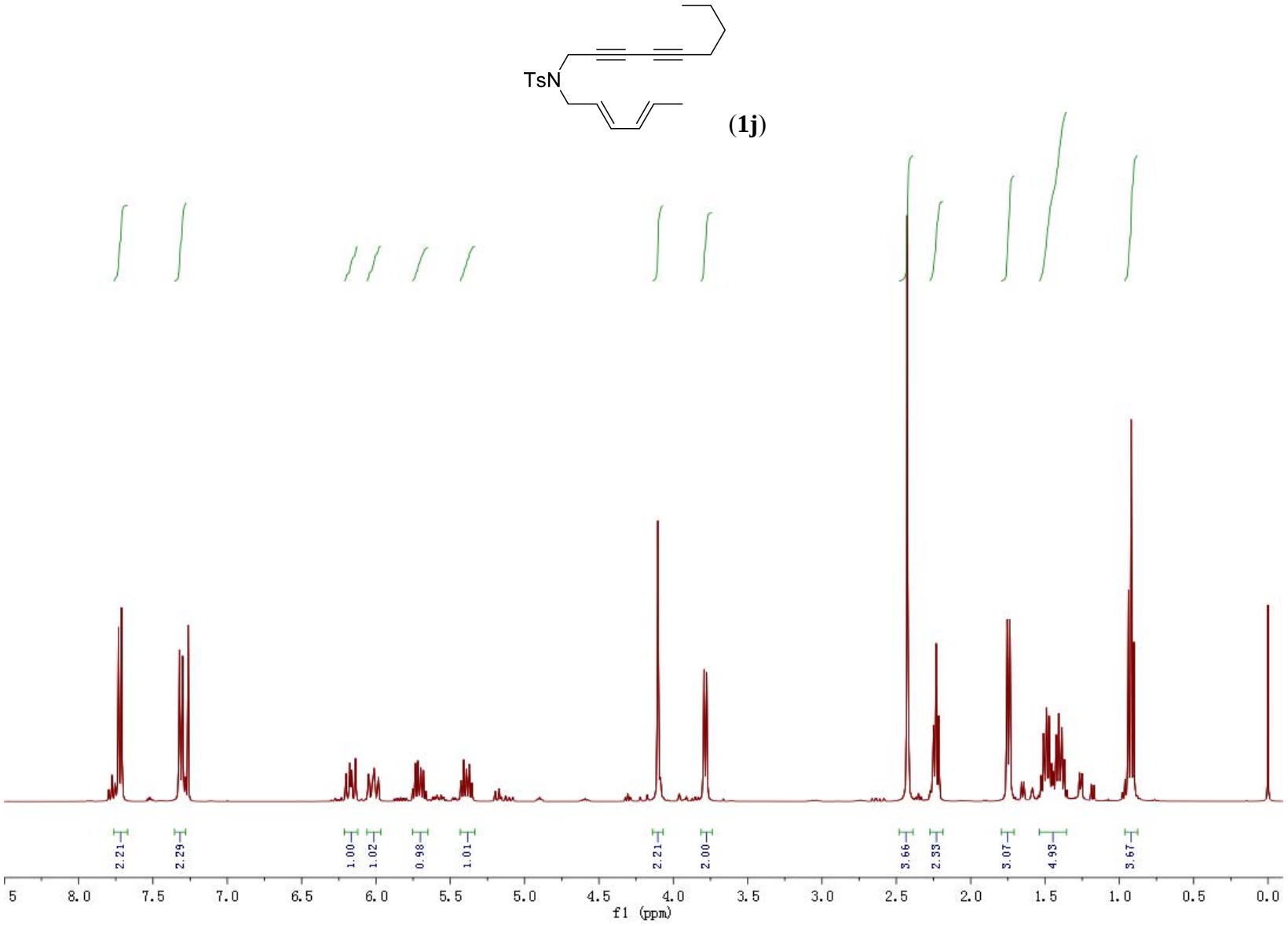

TsN
iPr
(1h)
2.10
2.14
1.00
1.01
2.03
2.06
2.07
1.14
3.21
2.07
4.52
6.27
3.29
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


151.66
143.59
137.10
135.81
129.54
127.79
121.69
113.26
80.41
70.68
68.59
64.31
49.08
36.69
30.21
29.53
22.10
21.88
21.54
18.84
13.51
f1 (ppm)

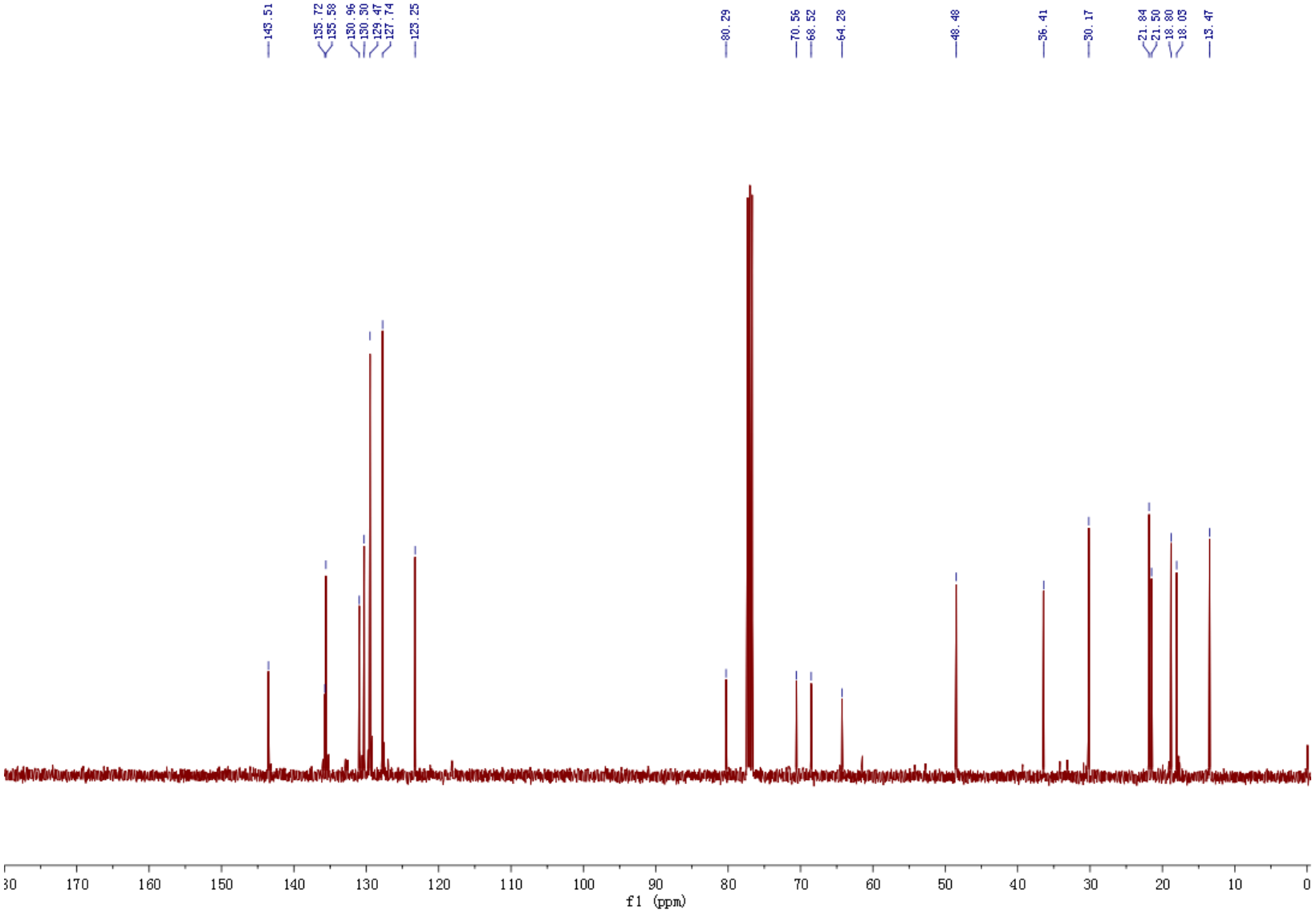


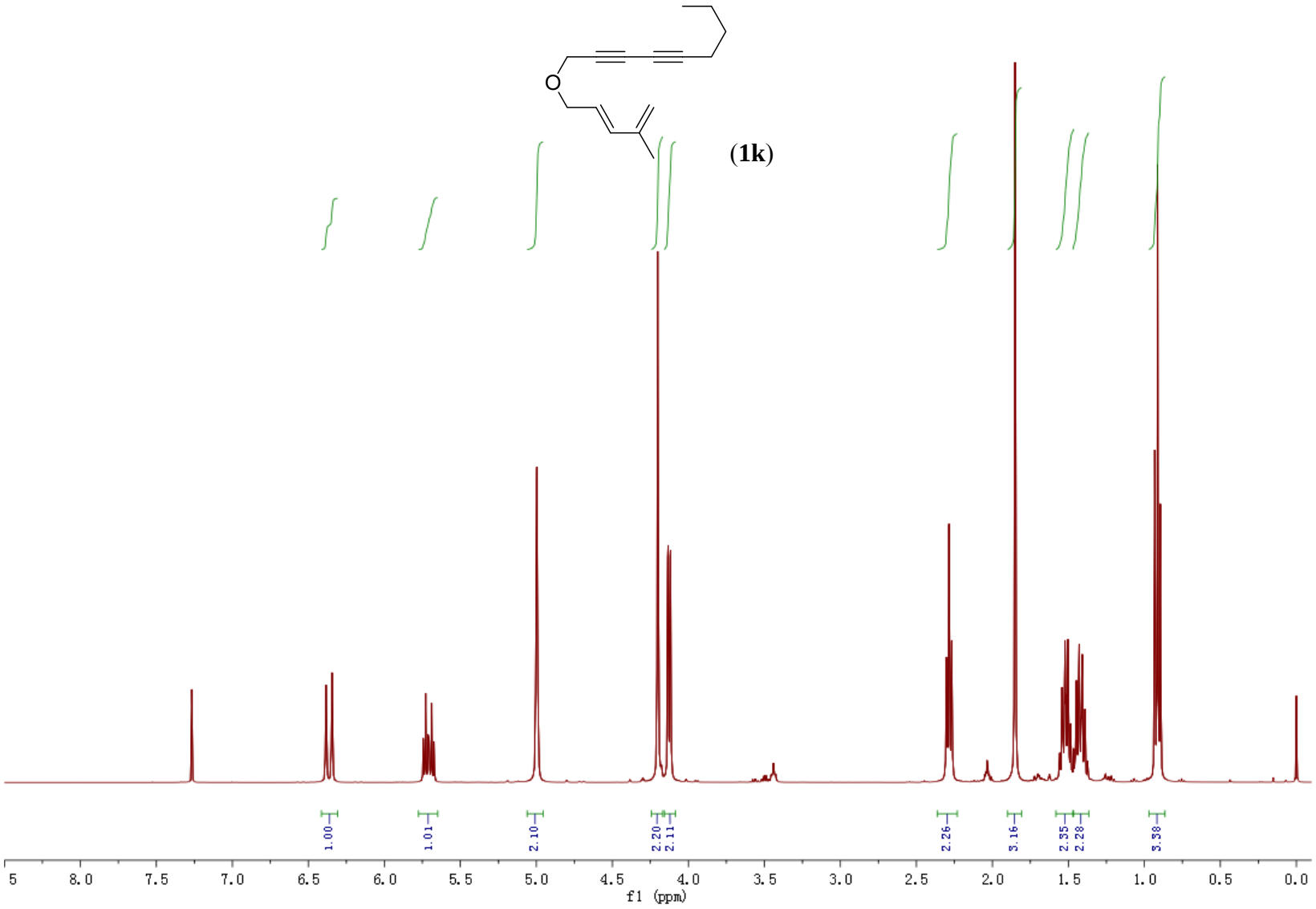
(1i)

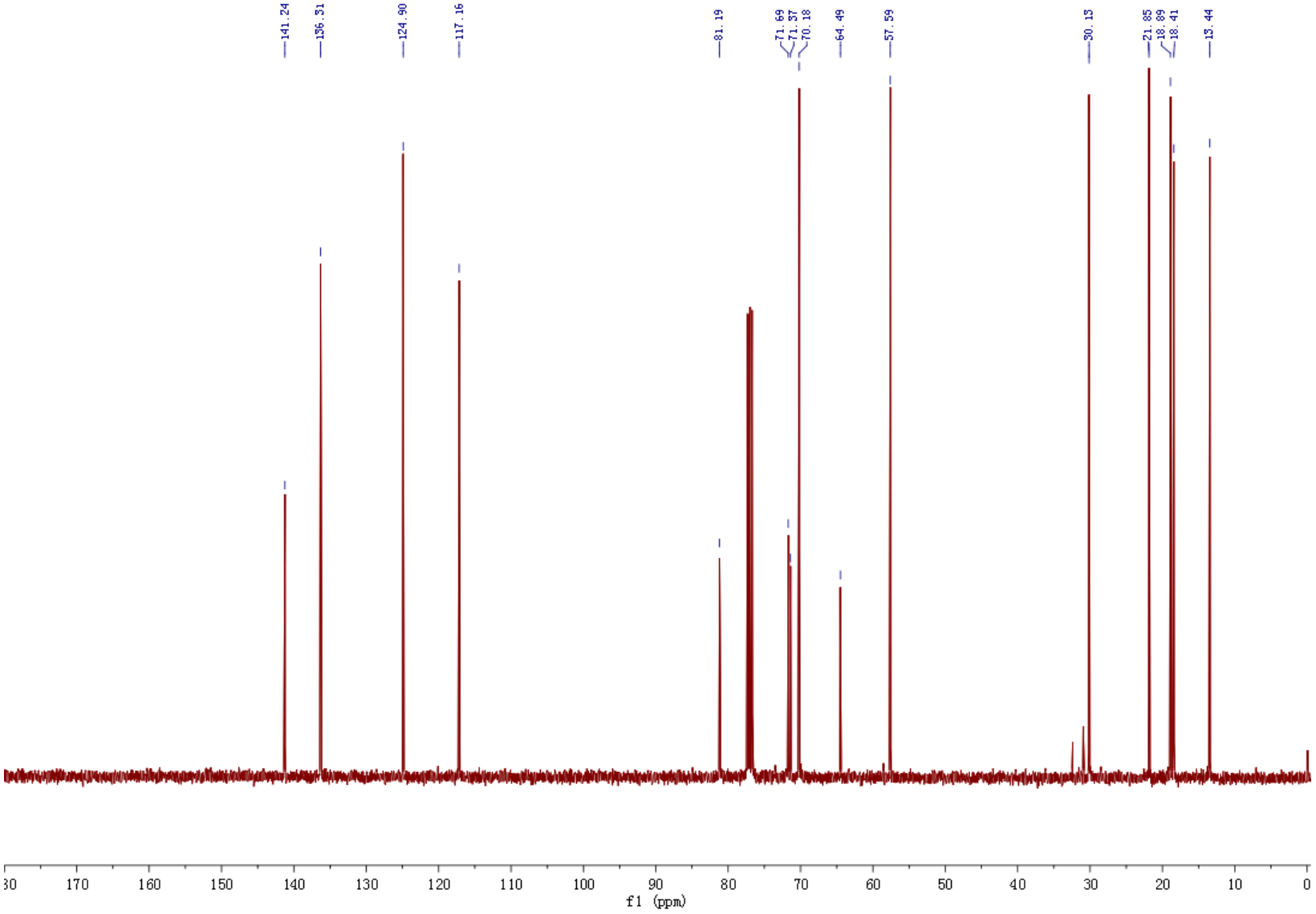

143.60
135.71
135.67
135.65
129.51
127.74
126.80
118.44
80.42
70.69
68.40
64.23
48.29
36.64
30.16
21.84
21.51
18.80
13.47
f1 (ppm)

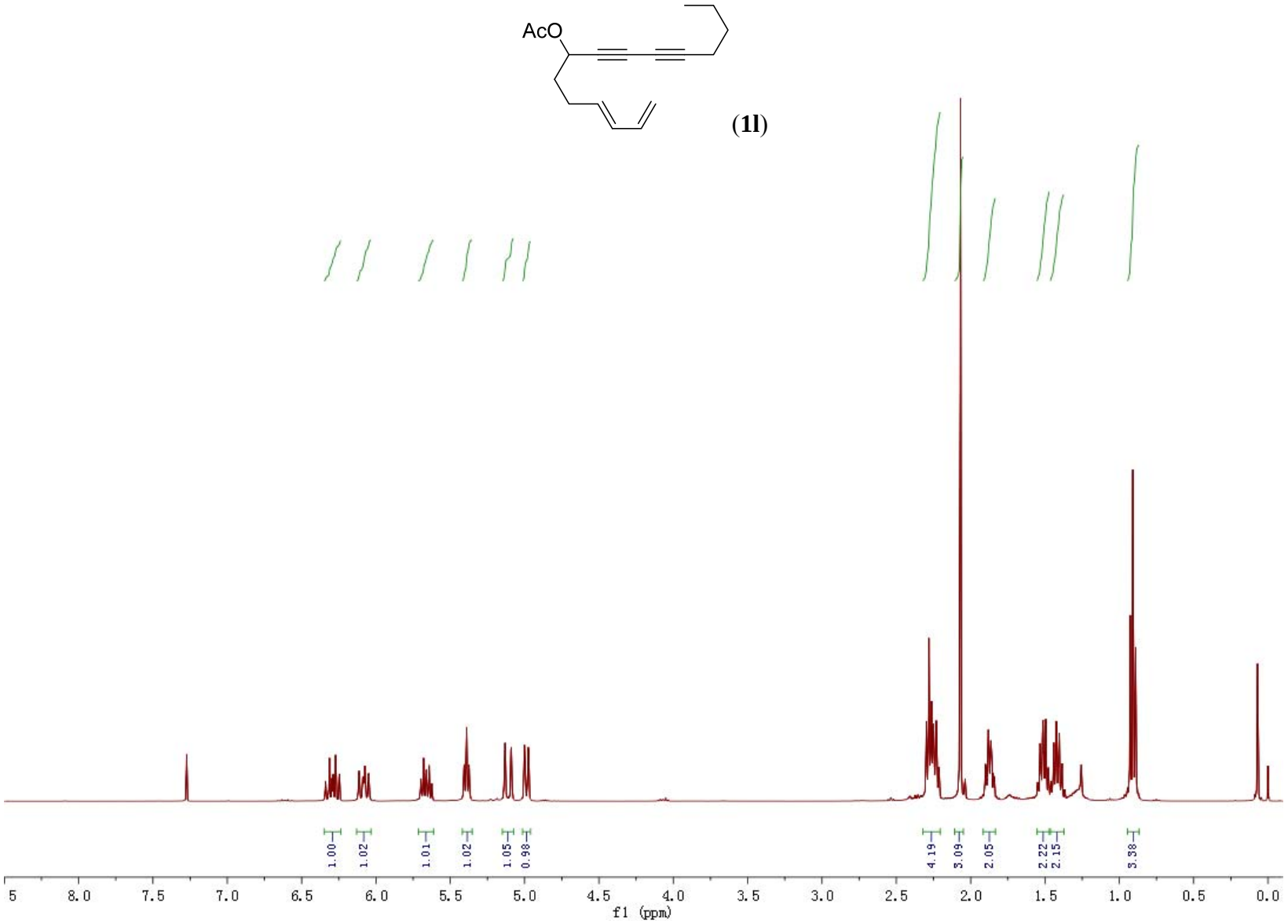

TsN
2.21
2.29
1.00
1.02
0.98
1.01
2.21
2.00
3.66
2.33
3.07
4.93
3.67
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

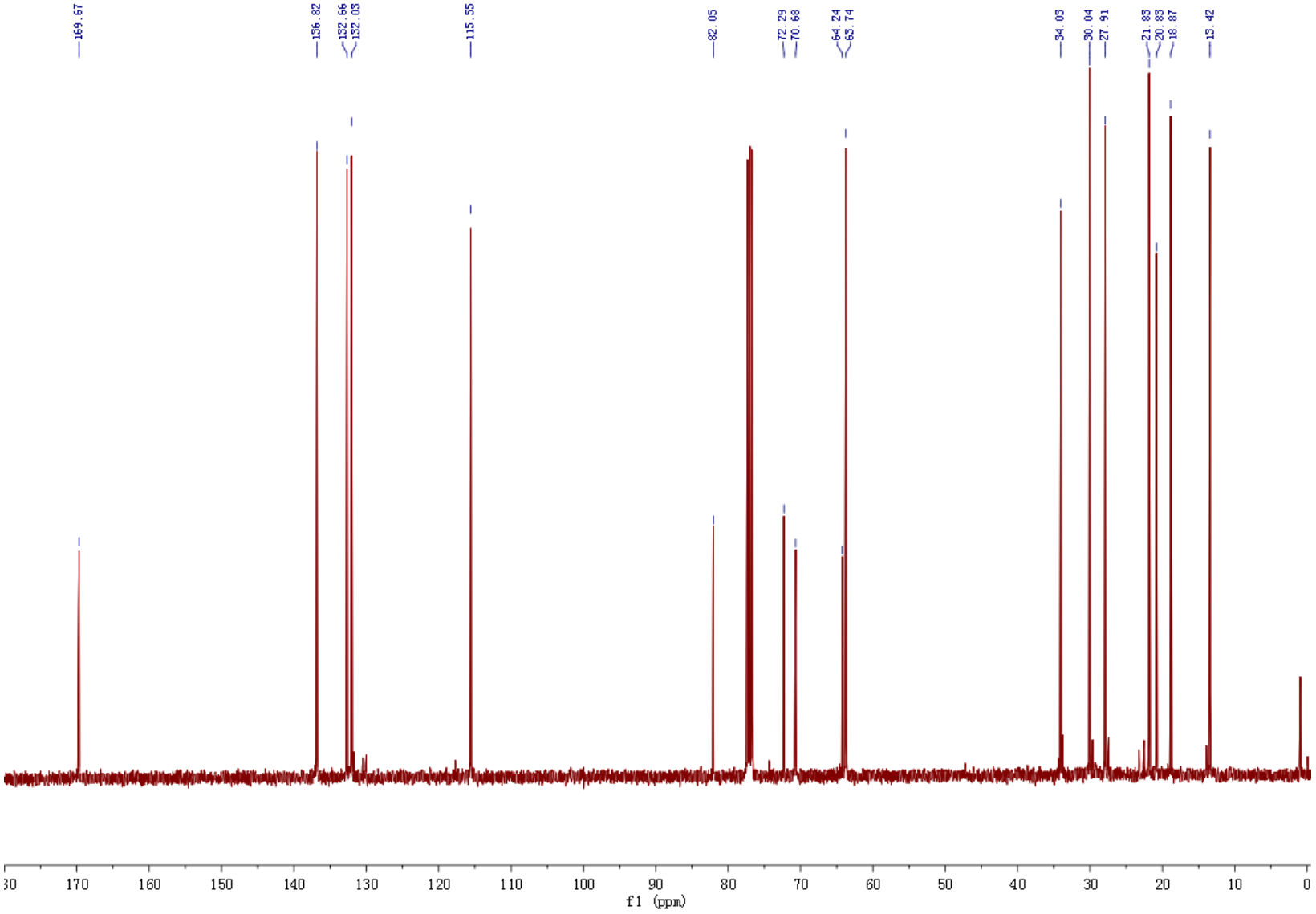
(1j)

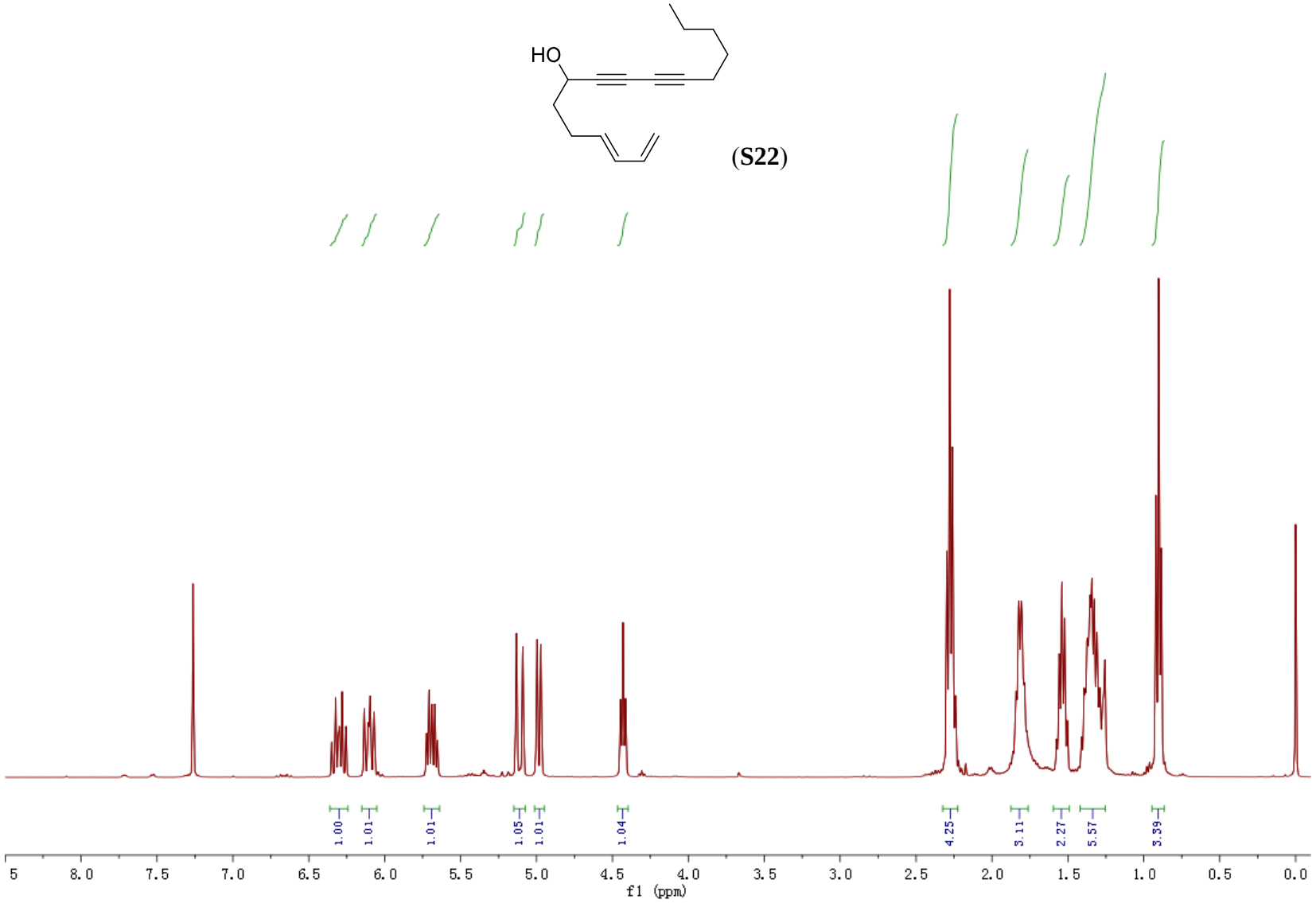

143.51
135.72
135.58
130.96
130.30
129.47
127.74
123.25
80.29
70.56
68.52
64.28
48.48
36.41
30.17
21.84
21.50
18.80
18.08
13.47
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

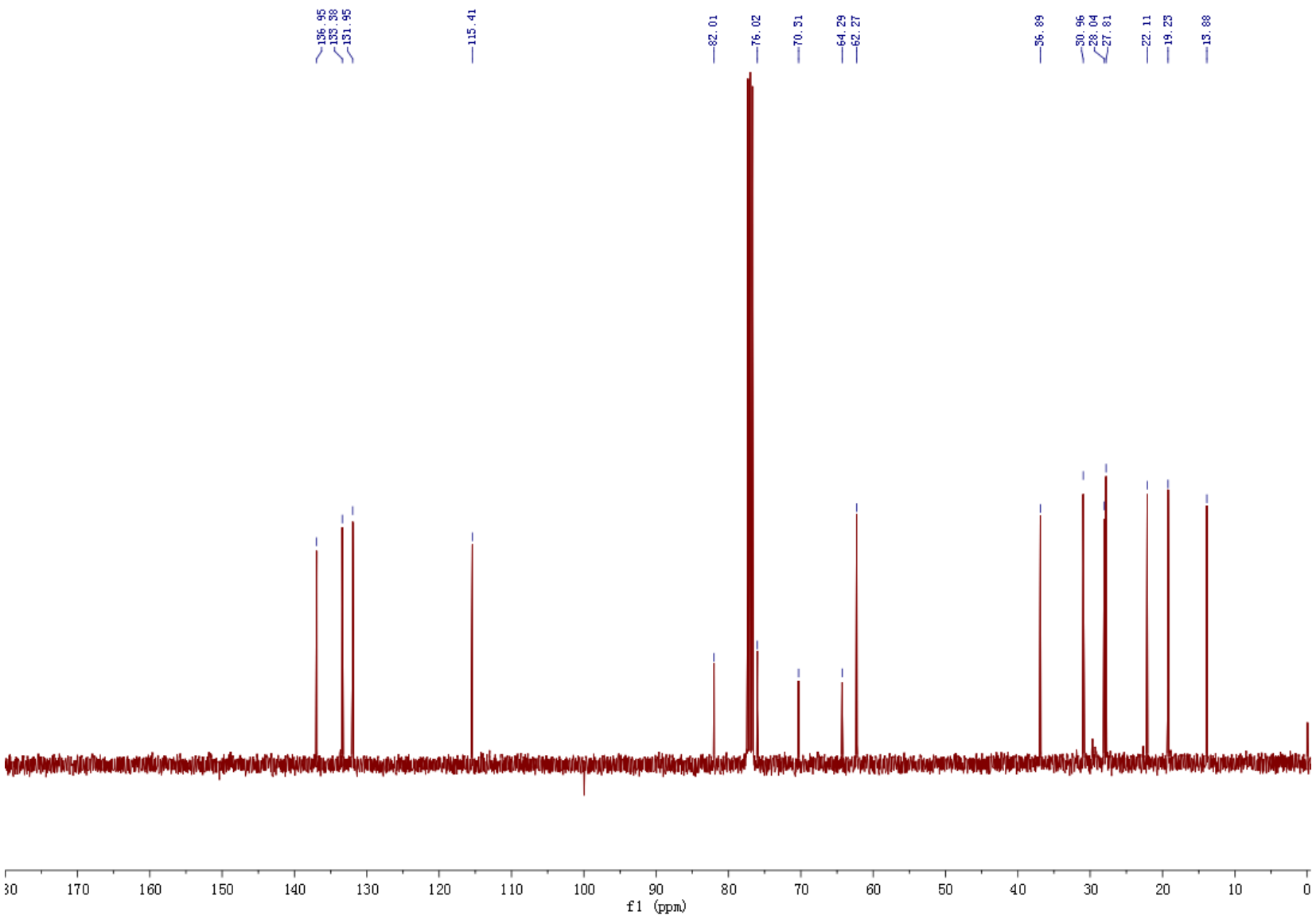

(1k)
1.00
1.01
2.10
2.20
2.11
2.26
3.16
2.35
2.28
3.38
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

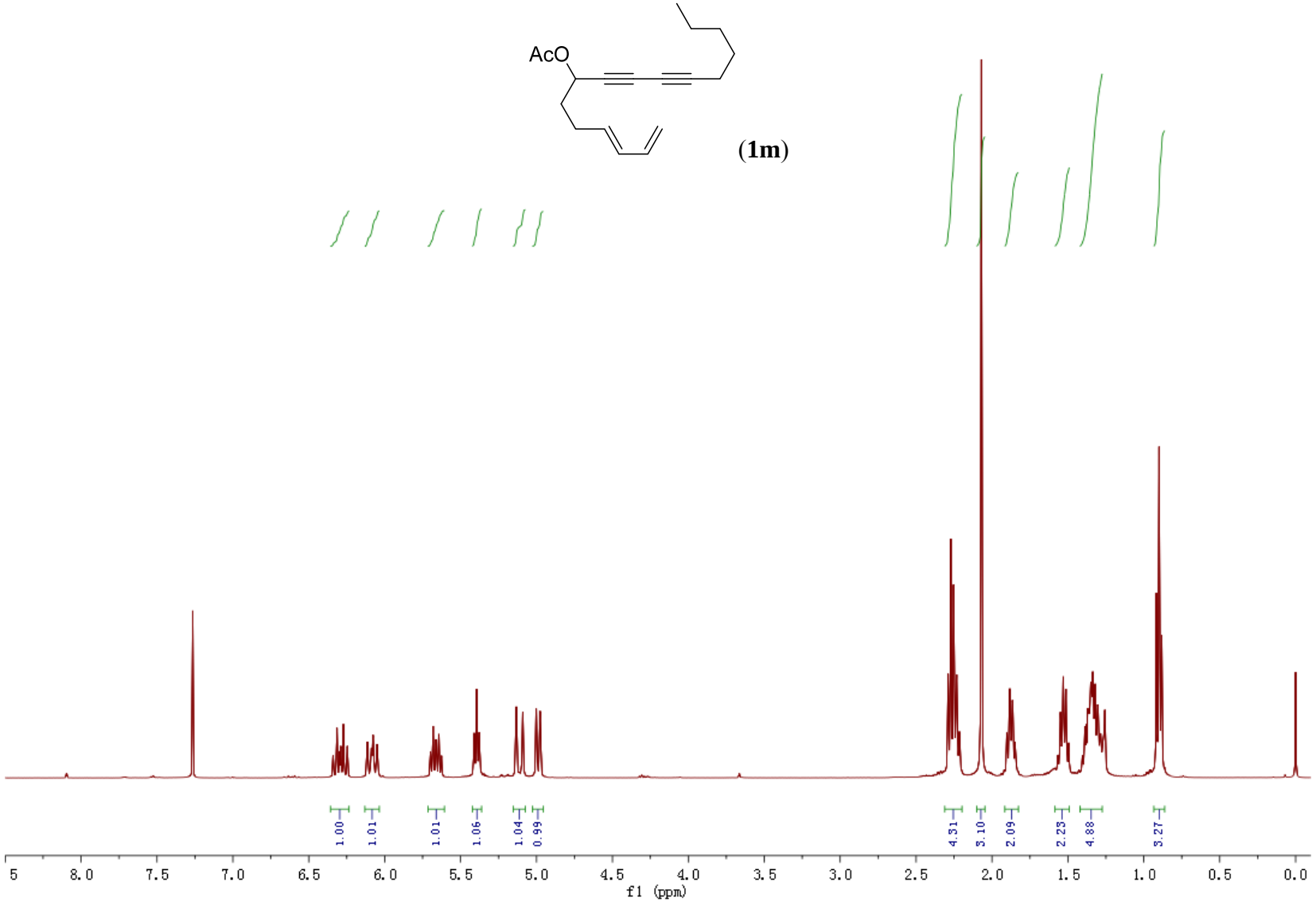

141.24
136.31
124.90
117.16
81.19
71.69
71.37
70.18
64.49
57.59
30.13
21.85
18.89
18.41
13.44
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

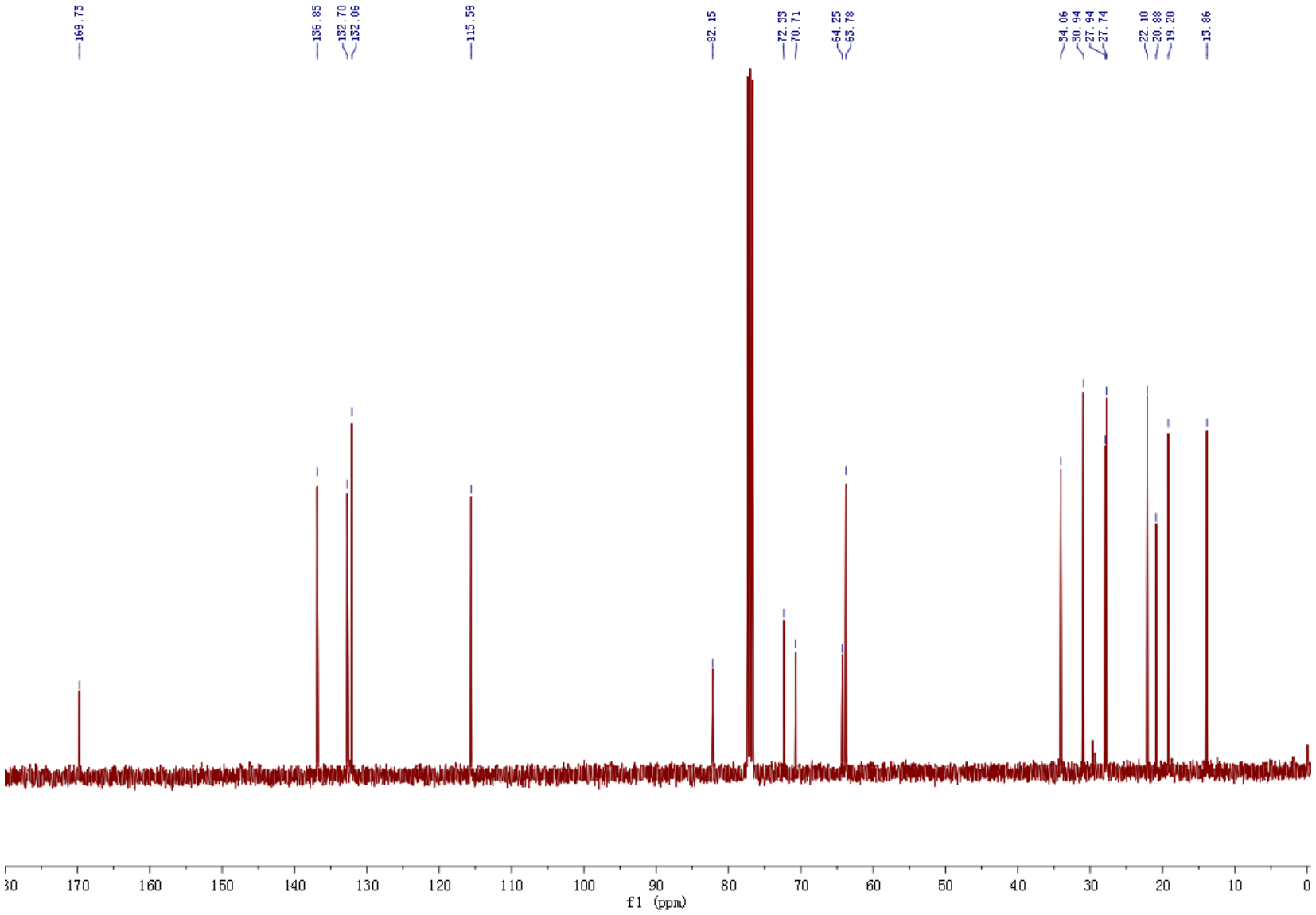

AcO
(1l)
1.00
1.02
1.01
1.02
1.05
0.98
4.19
3.09
2.05
2.22
2.15
3.38
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

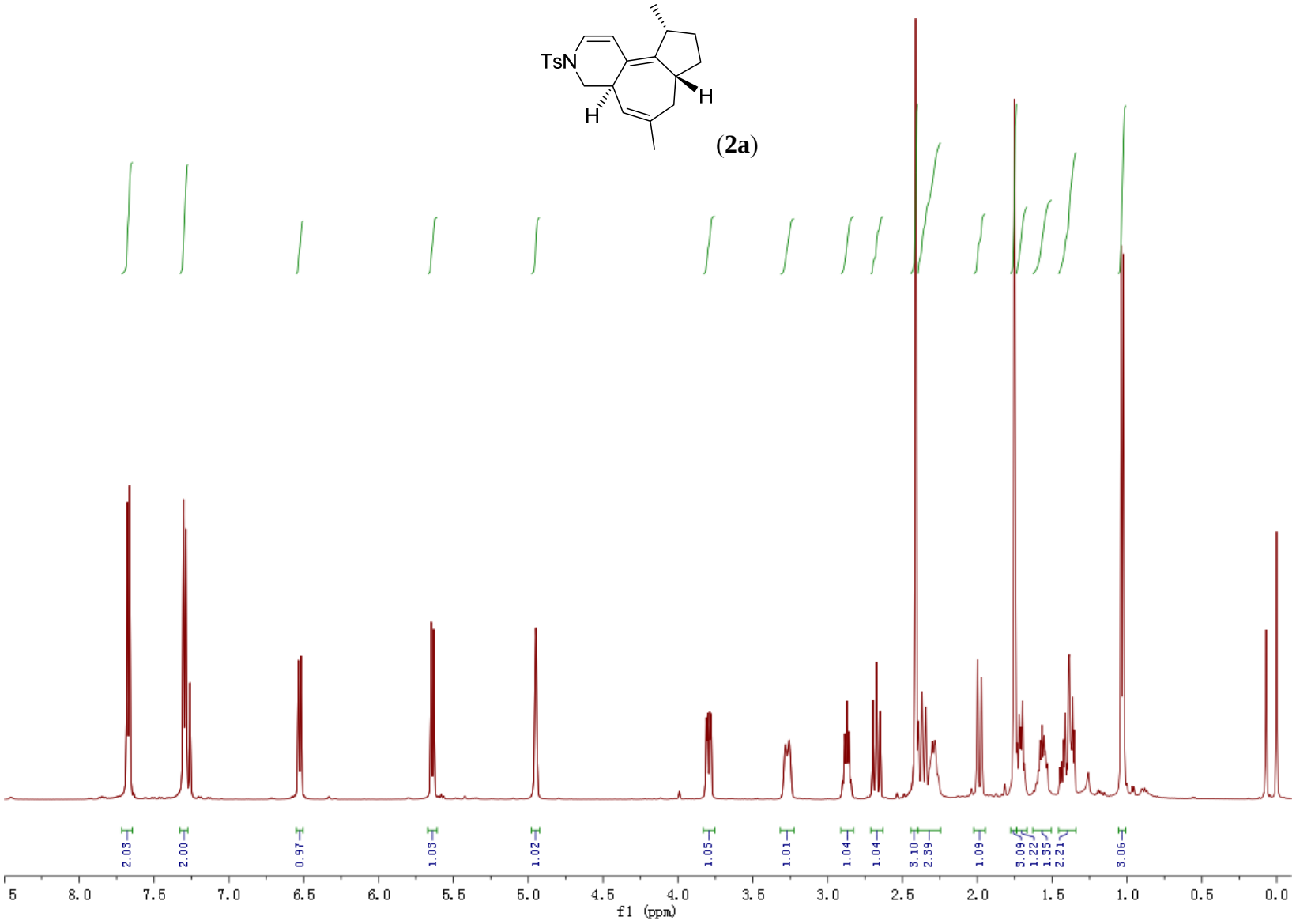

169.67
136.82
132.66
132.03
115.55
82.05
72.29
70.68
64.24
63.74
34.03
30.04
27.91
21.83
20.83
18.87
13.42
f1 (ppm)

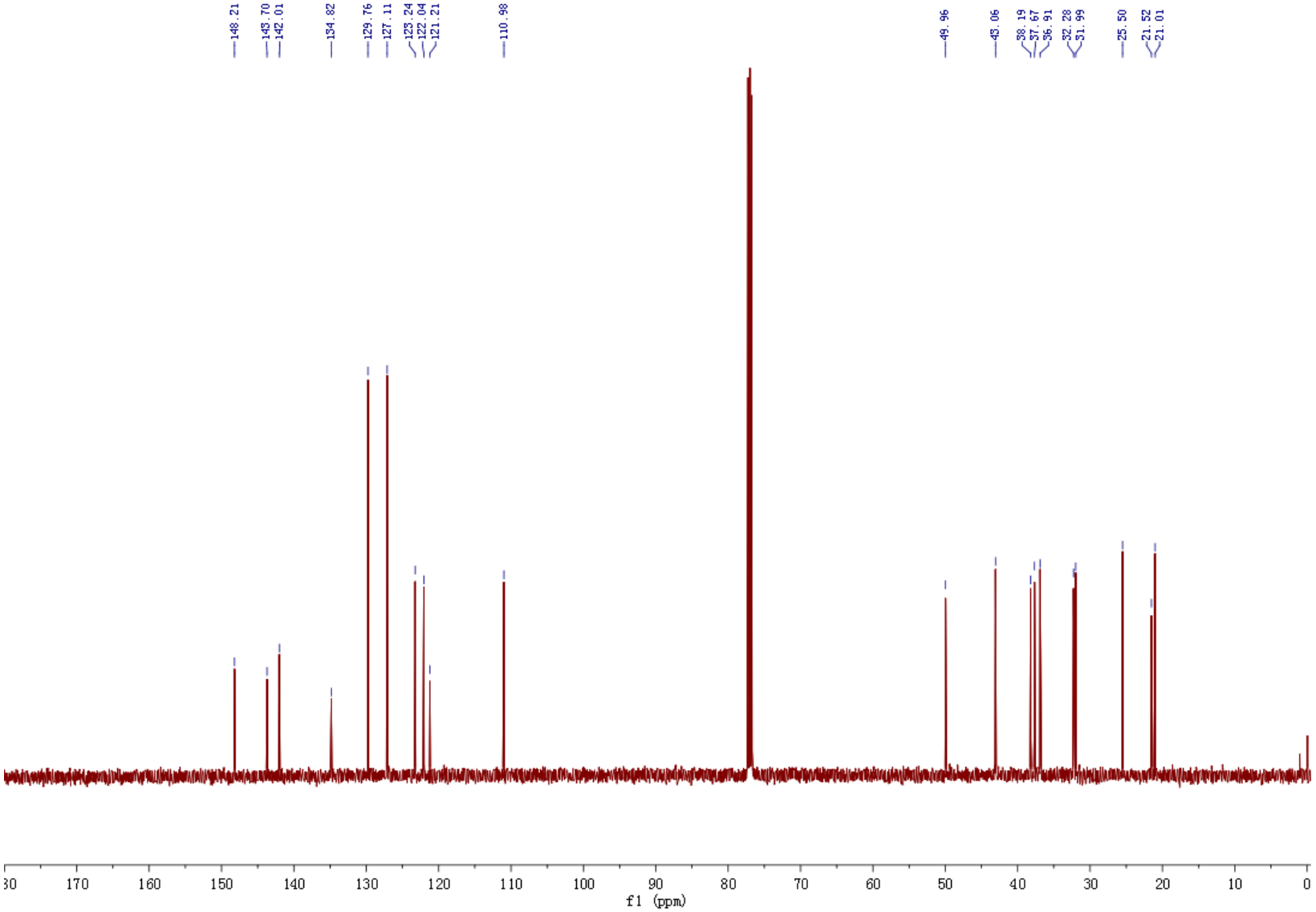

HO
(S22)
1.00
1.01
1.01
1.05
1.01
1.04
4.25
3.11
2.27
5.57
3.39
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

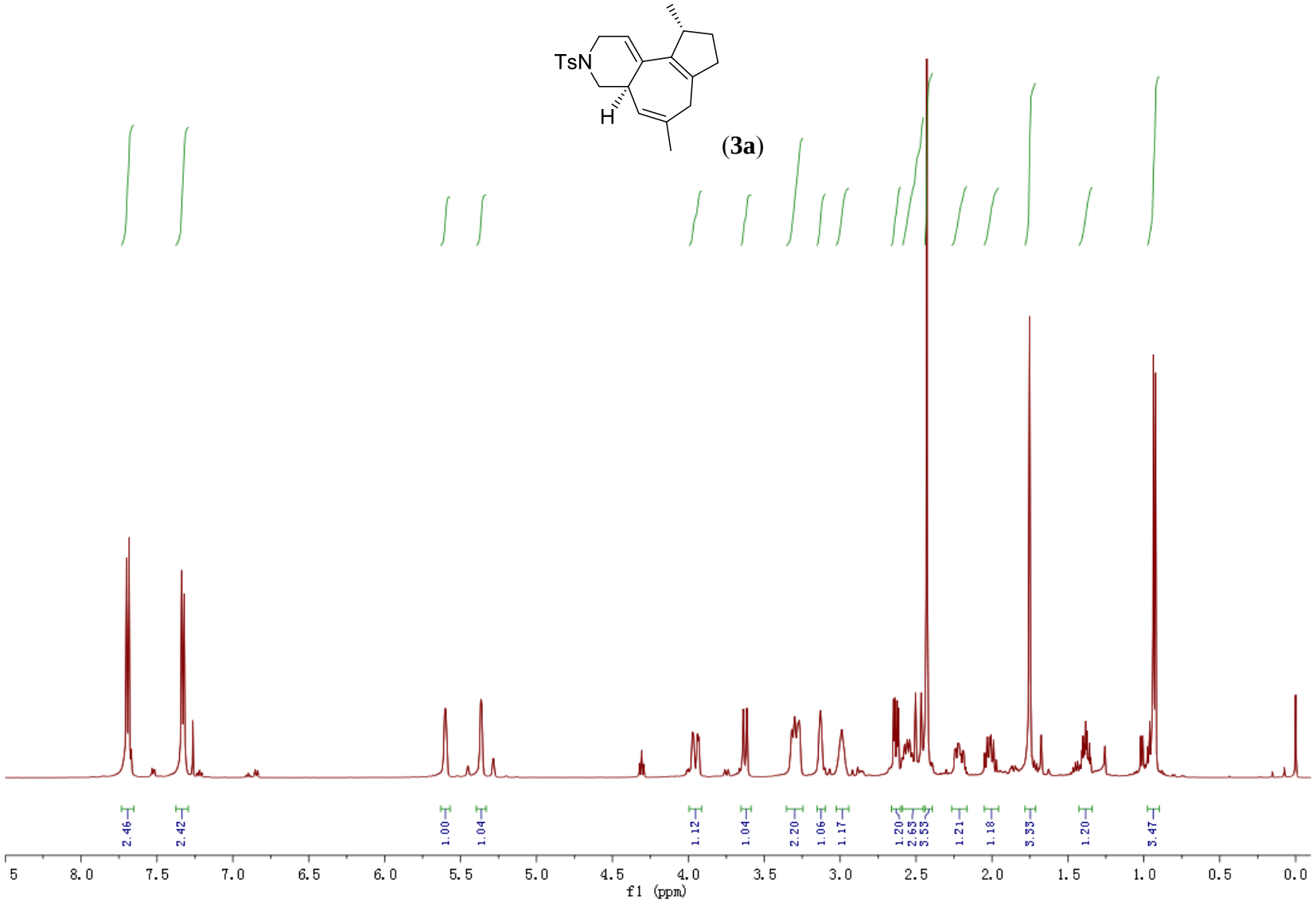

186.95
153.38
131.95
115.41
82.01
76.02
70.31
64.29
62.27
36.89
30.96
28.04
27.81
22.11
19.23
13.88
f1 (ppm)

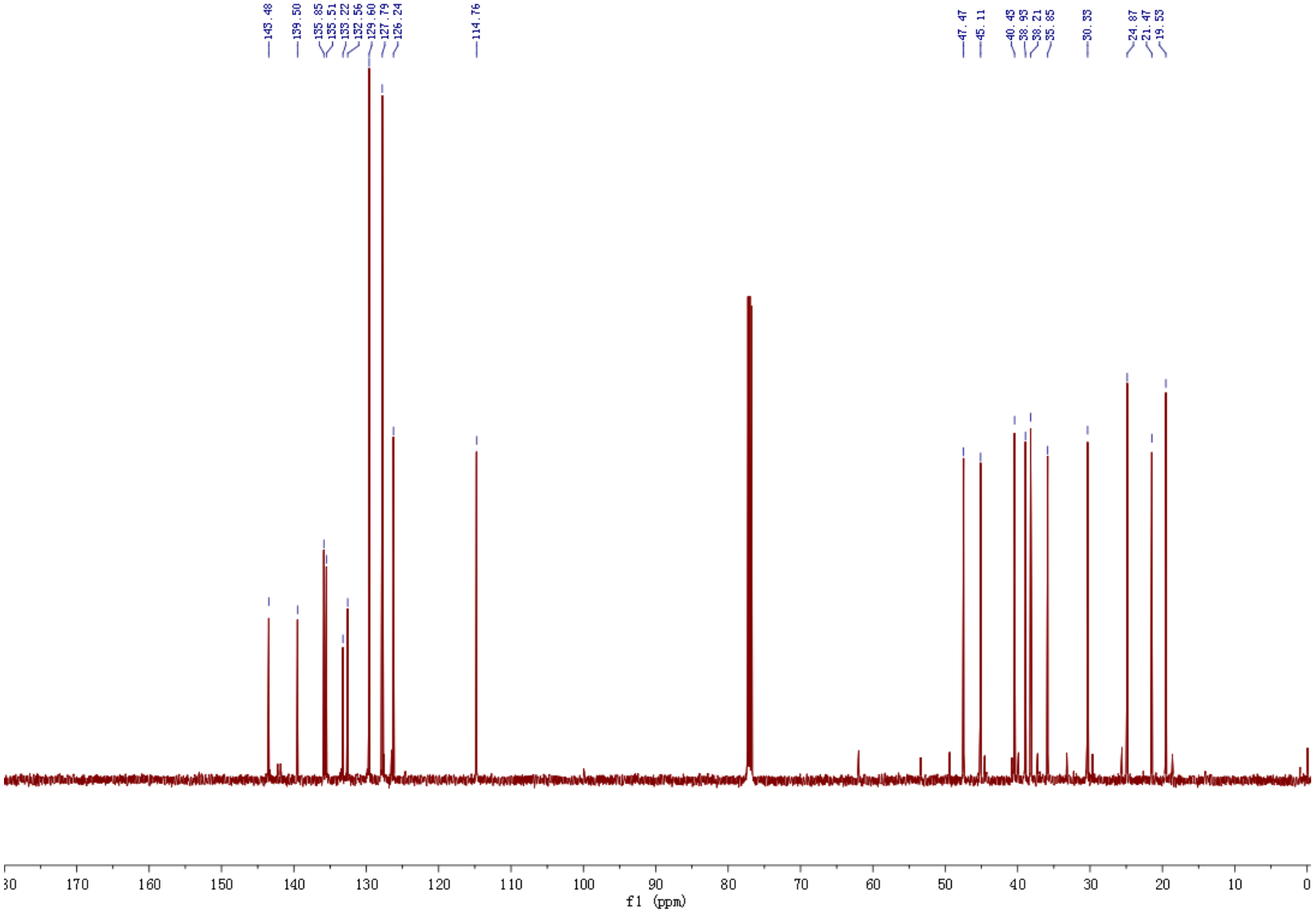

AcO
(1m)
1.00
1.01
1.01
1.06
1.04
0.99
4.31
3.10
2.09
2.23
4.88
3.27
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

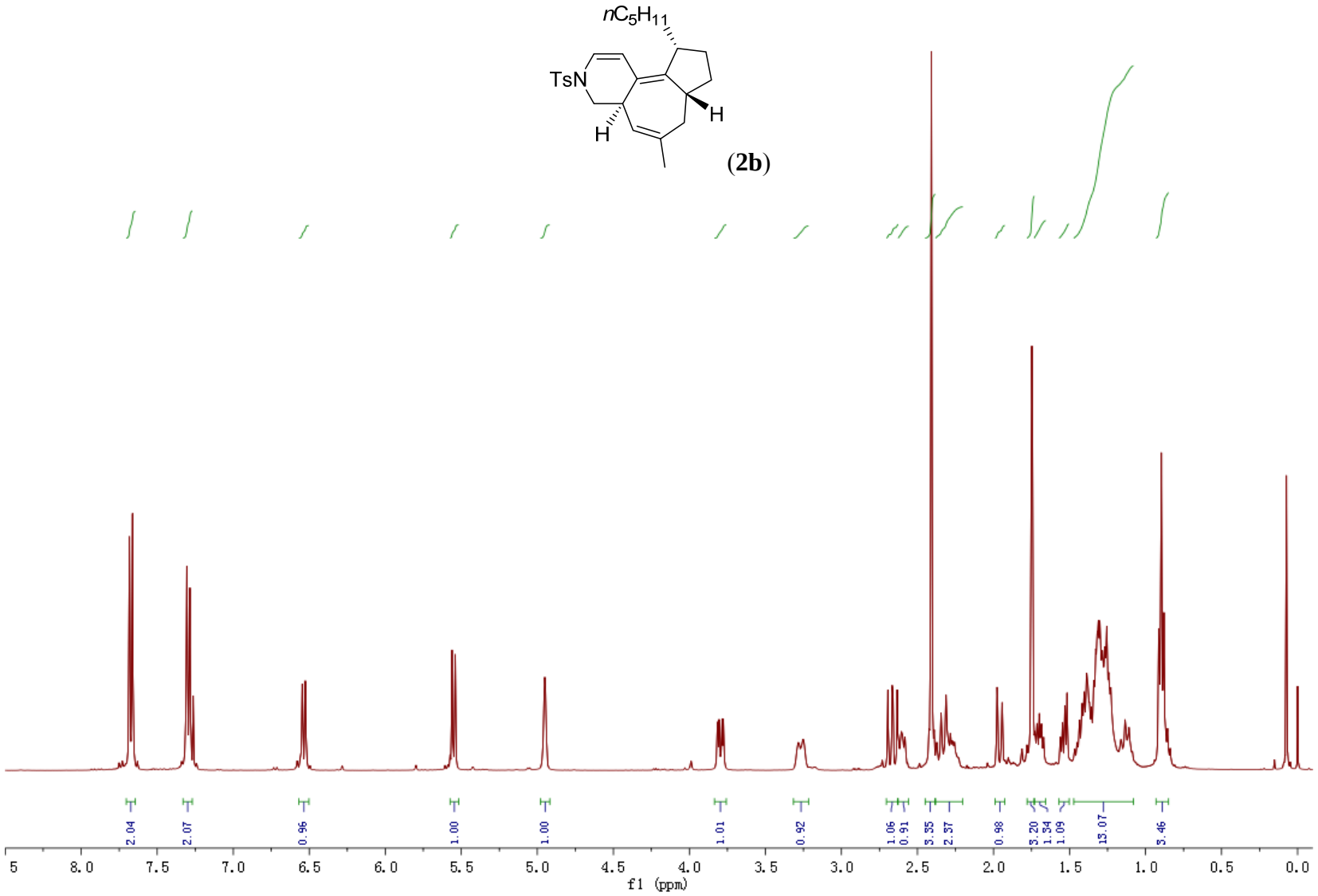

169.73
136.85
132.70
132.06
115.59
82.15
72.33
70.71
64.25
63.78
34.06
30.94
27.94
27.74
22.10
20.88
19.20
13.86
f1 (ppm)

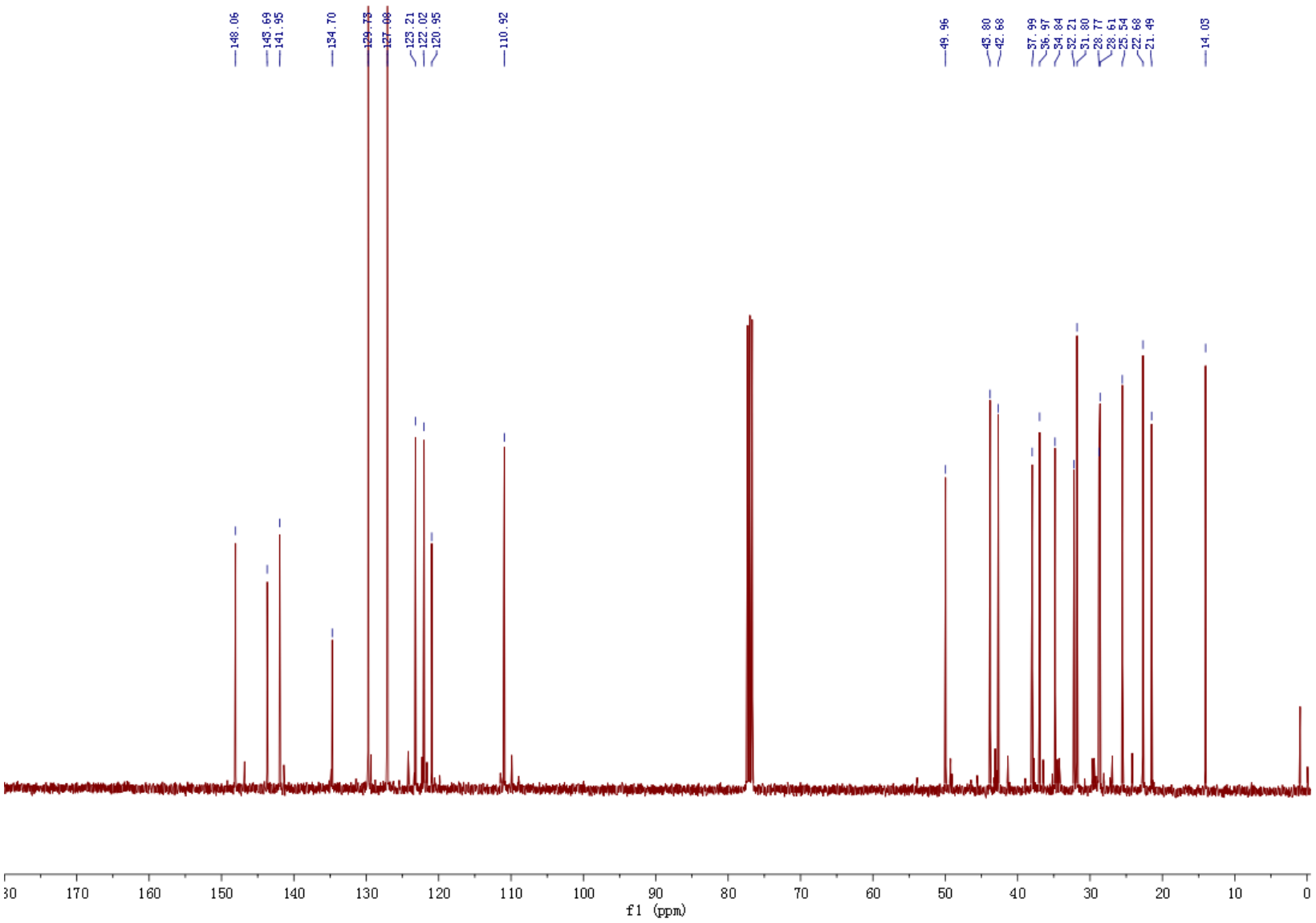

TsN
H
H
(2a)
2.03
2.00
0.97
1.03
1.02
1.05
1.01
1.04
1.04
3.10
2.39
1.09
3.09
1.22
1.35
2.21
3.06
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

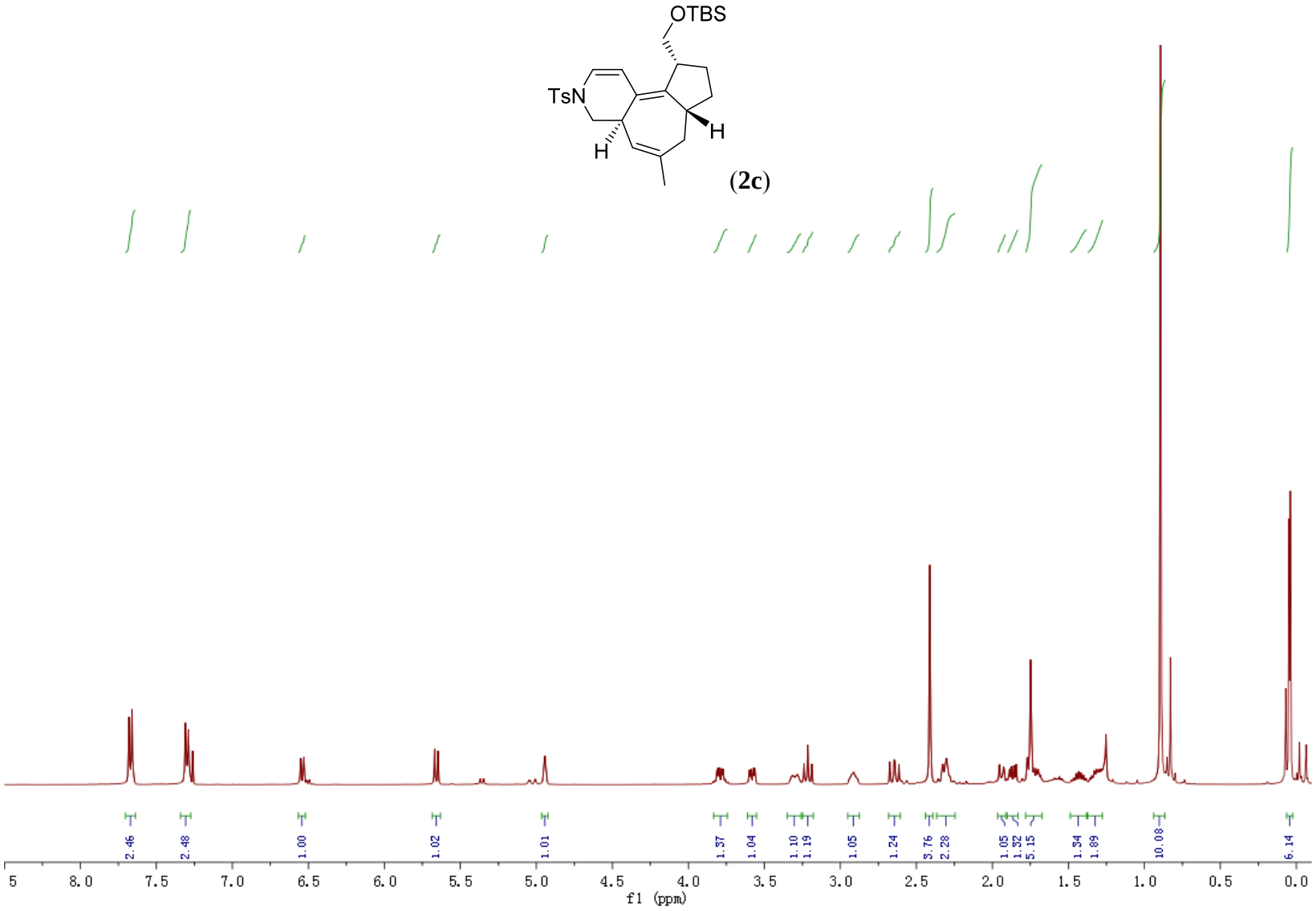

148.21
143.70
142.01
134.82
129.76
127.11
123.24
122.04
121.21
110.98
49.96
45.06
38.19
37.67
36.91
32.28
31.99
25.50
21.52
21.01
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

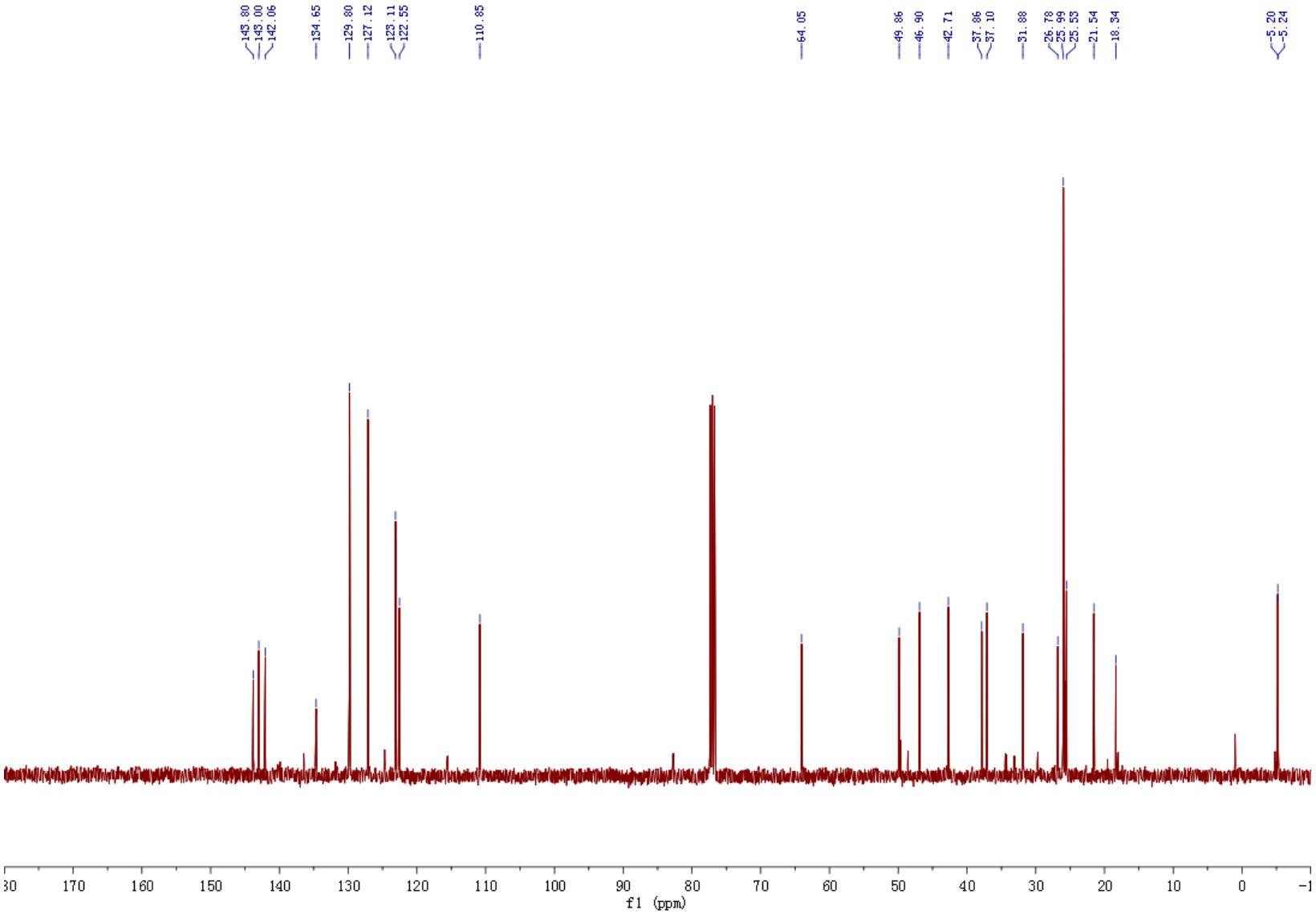

TsN
H
(3a)
2.46
2.42
1.00
1.04
1.12
1.04
2.20
1.06
1.17
1.20
2.63
3.55
1.21
1.18
3.33
1.20
3.47
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

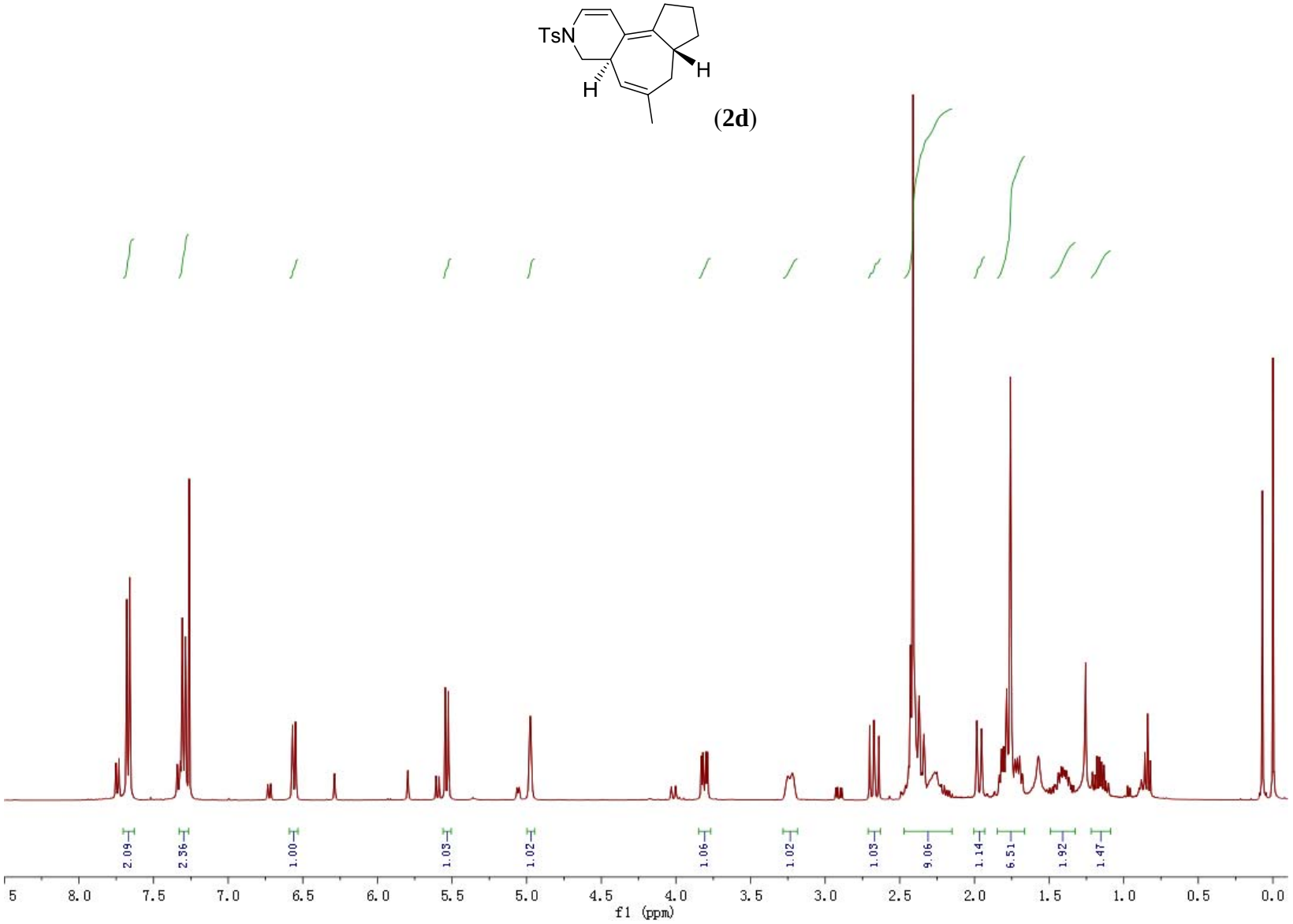

143.48
139.50
135.85
135.51
133.22
132.56
129.60
127.79
126.24
114.76
47.47
45.11
40.45
38.93
38.21
35.85
30.33
24.87
21.47
19.53
f1 (ppm)


nC5H11
TsN
H
H
(2b)
2.04
2.07
0.96
1.00
1.00
1.01
0.92
1.06
0.91
3.35
2.37
0.98
3.20
1.34
1.09
13.07
3.46
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)

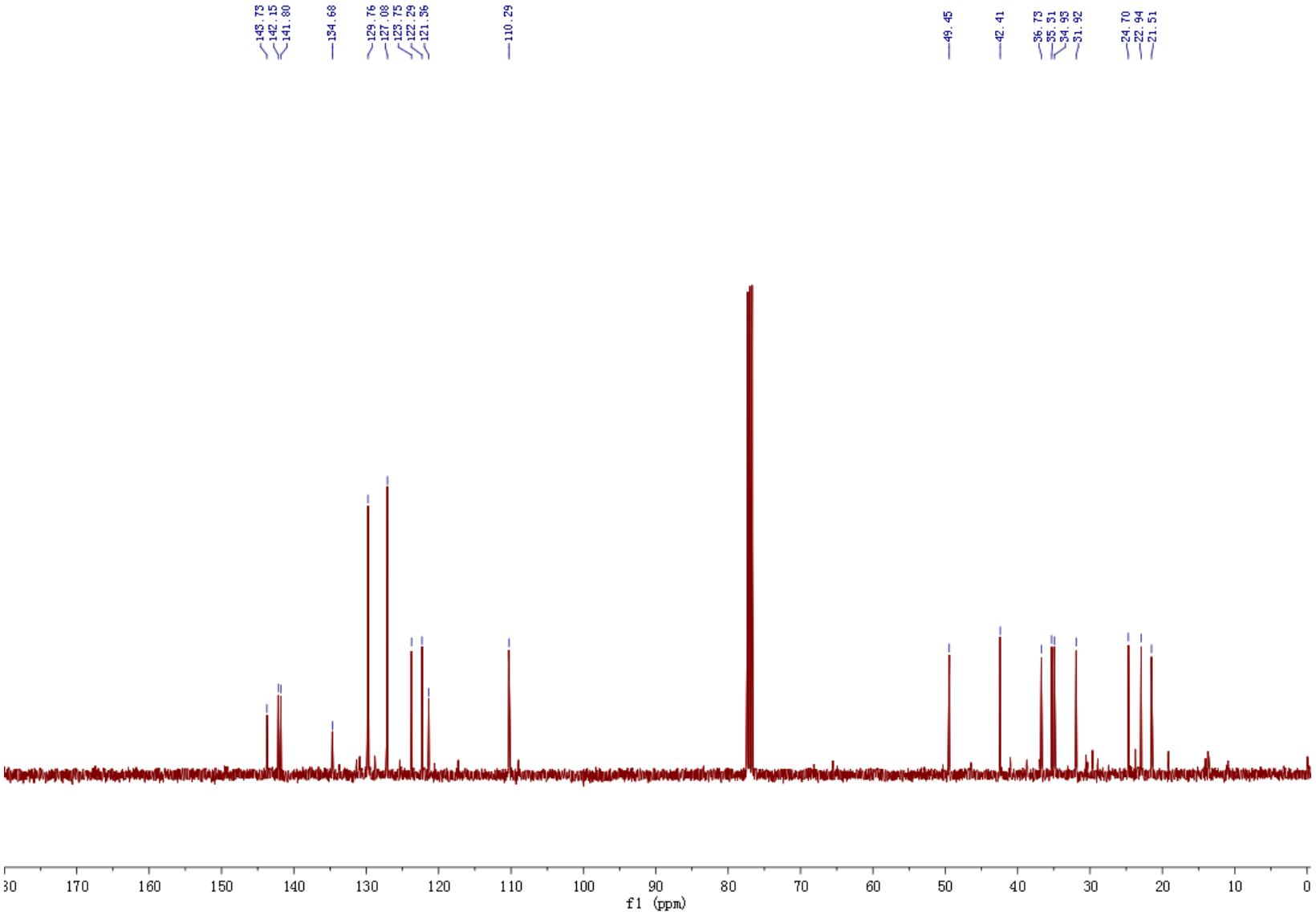

148.06
143.69
141.95
134.70
129.78
127.00
123.21
122.02
120.95
110.92
49.96
43.80
42.68
37.99
36.97
34.84
32.21
31.80
28.77
28.61
25.54
22.68
21.49
14.03
f1 (ppm)

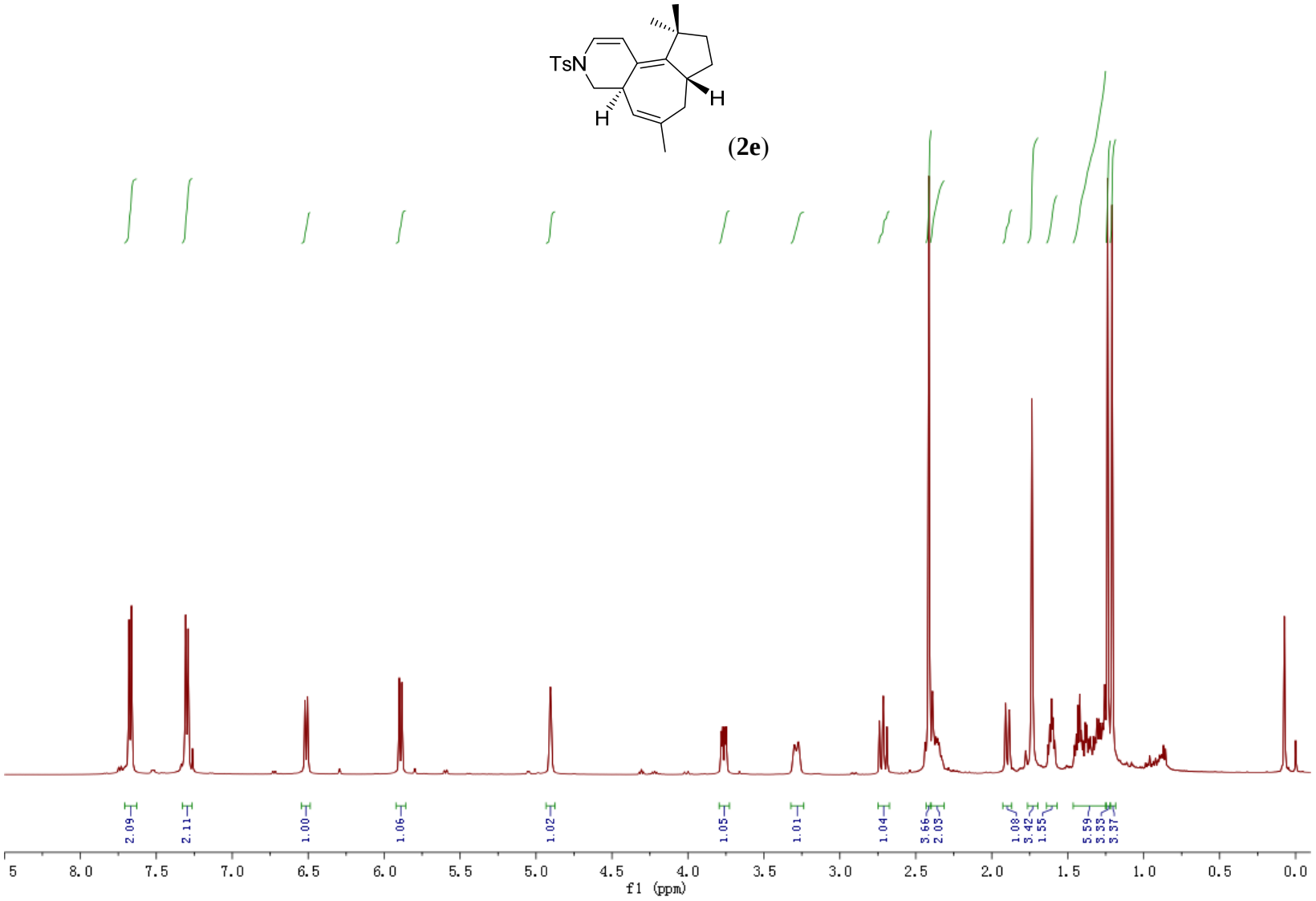

OTBS
TsN
H
H
(2c)
2.46
2.48
1.00
1.02
1.01
1.37
1.04
1.10
1.19
1.05
1.24
3.76
2.28
1.05
1.32
5.15
1.34
1.89
10.08
6.14
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

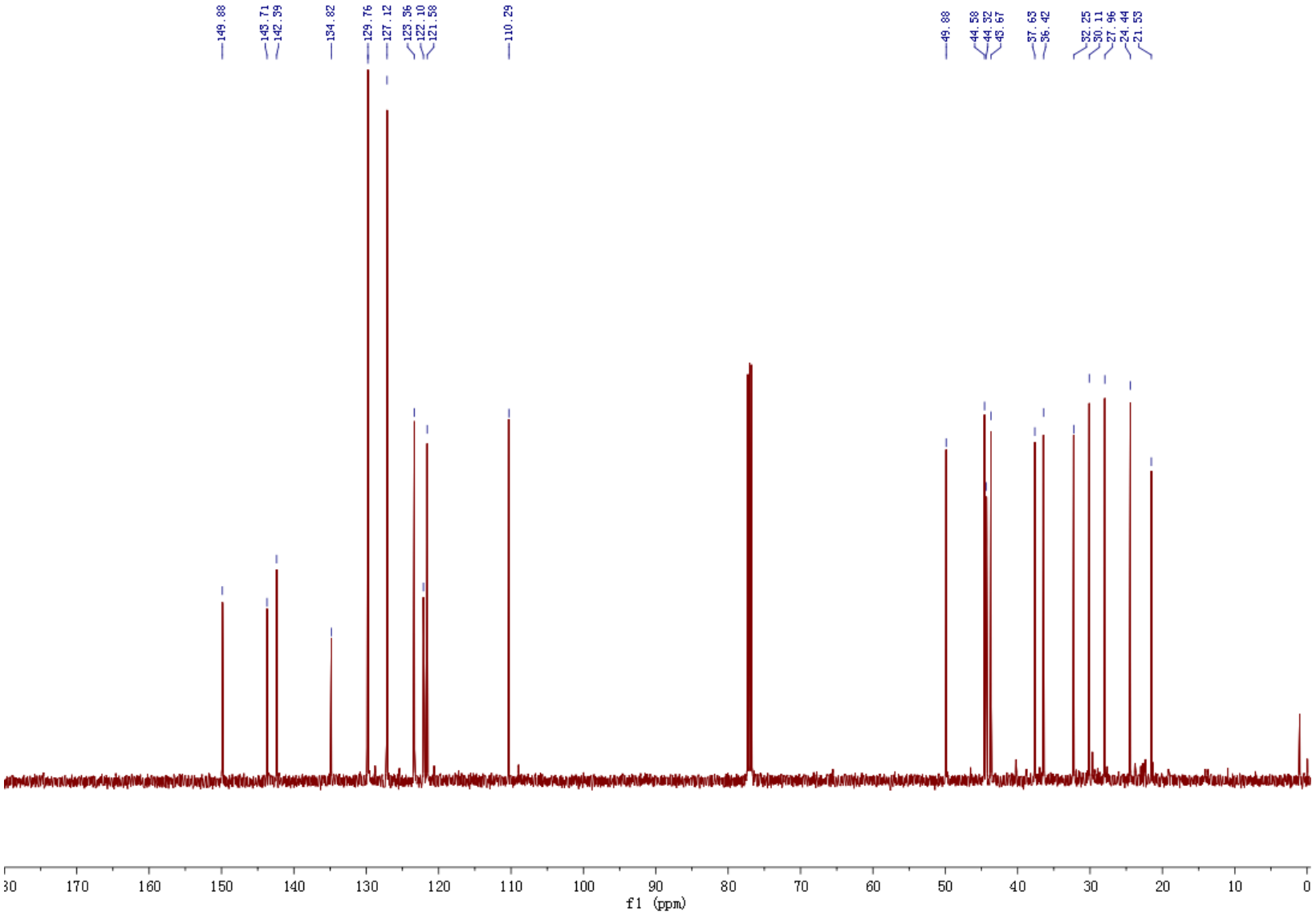

143.80
143.00
142.06
134.65
129.80
127.12
123.11
122.55
110.85
64.05
49.86
46.90
42.71
37.86
37.10
31.88
26.78
25.99
25.53
21.54
18.34
-5.20
-5.24
f1 (ppm)

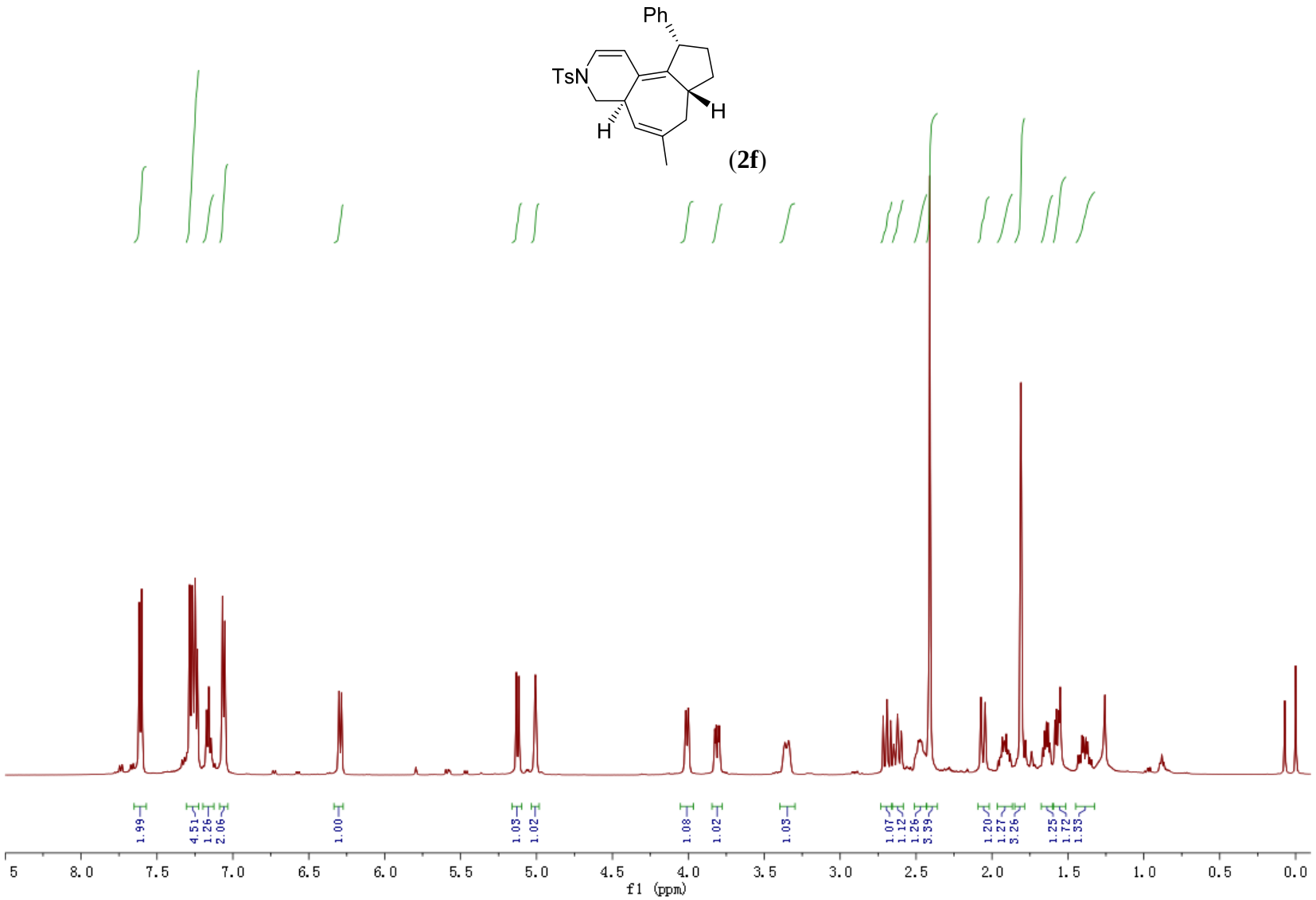

TsN
H
H
2.09
2.36
1.00
1.03
1.02
1.06
1.02
1.03
9.06
1.14
6.51
1.92
1.47
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

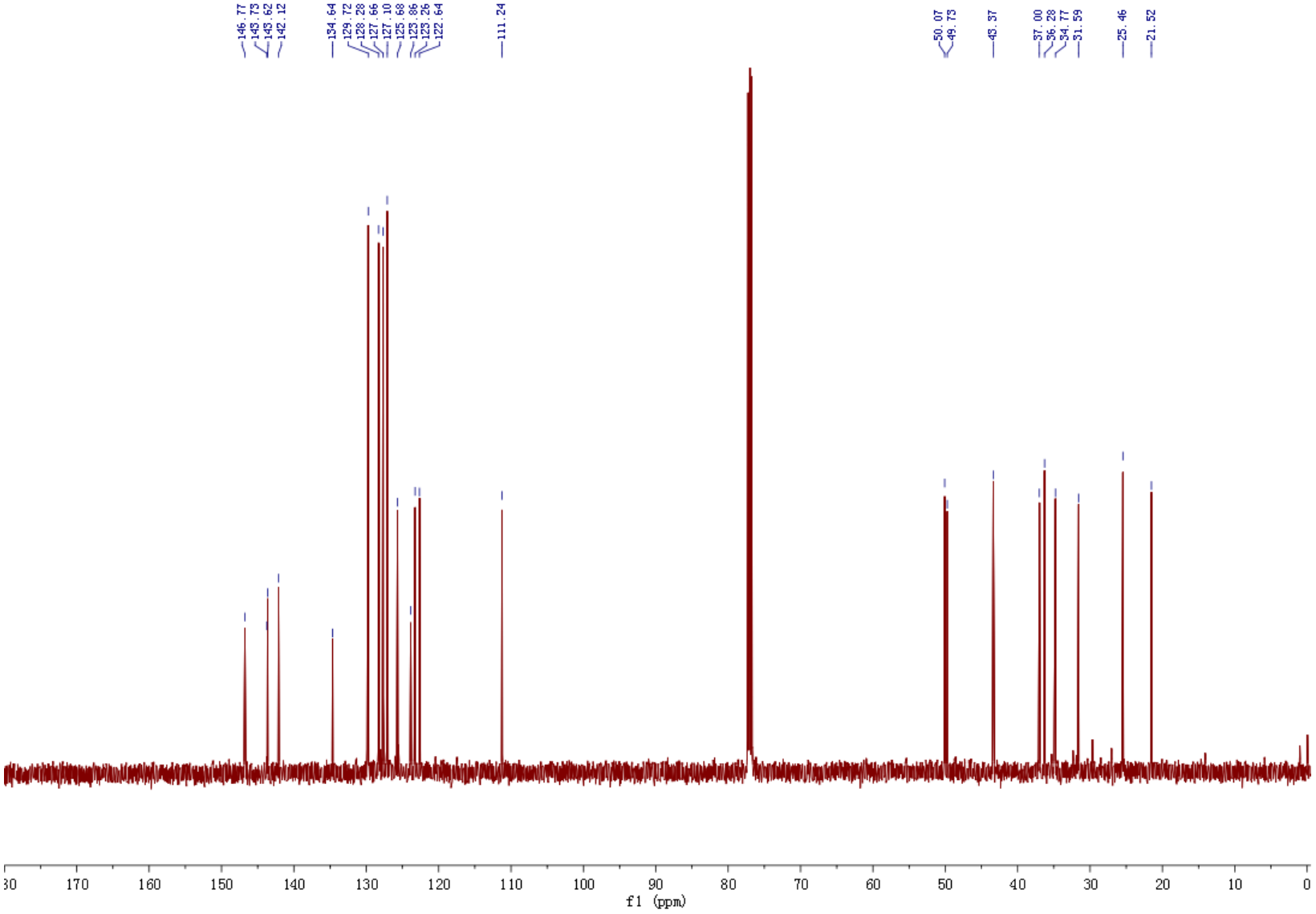
(**2d**)

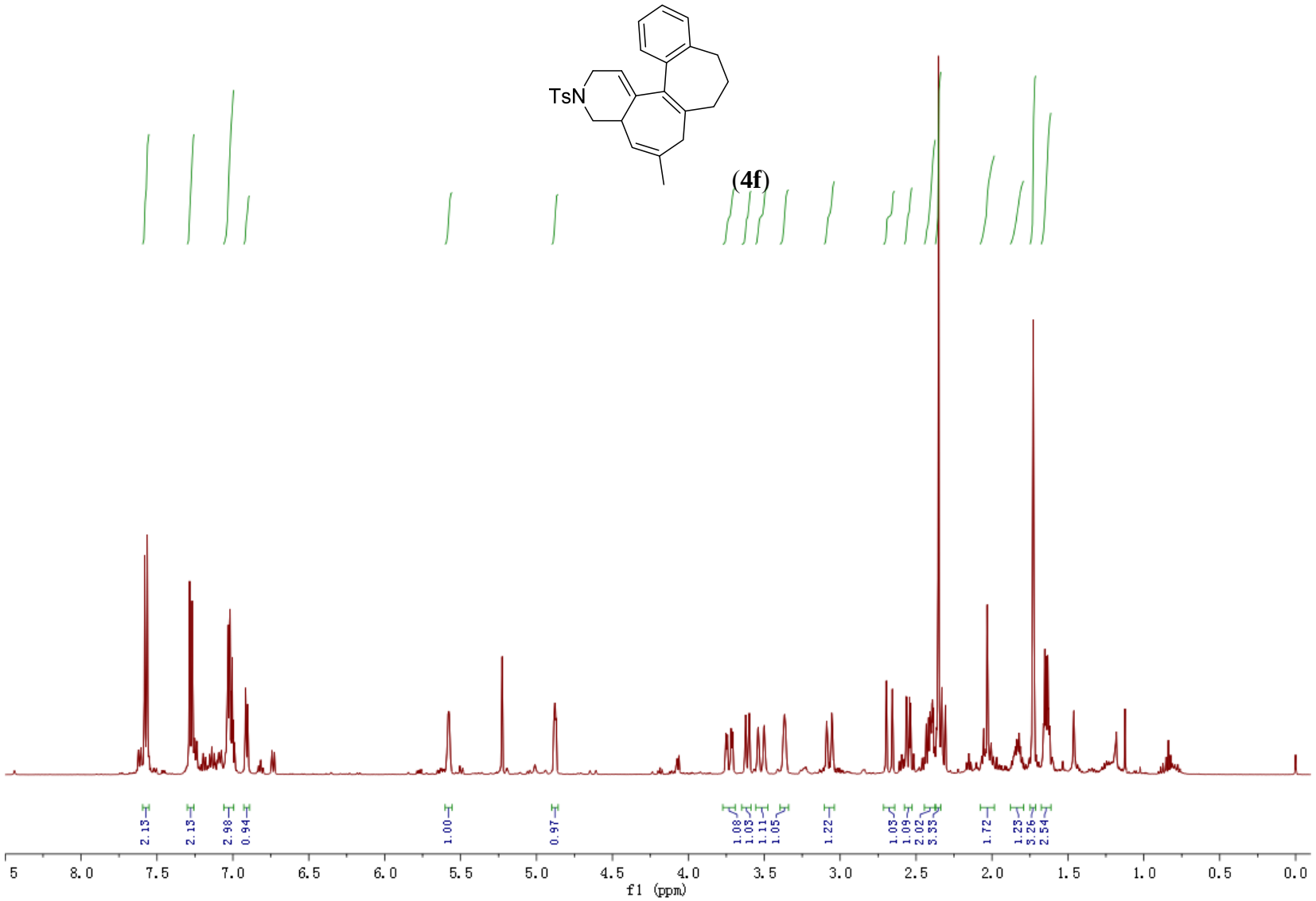

143.73
142.15
141.80
134.68
129.76
127.08
123.75
122.29
121.36
110.29
49.45
42.41
56.73
55.31
34.93
31.92
24.70
22.94
21.51
f1 (ppm)

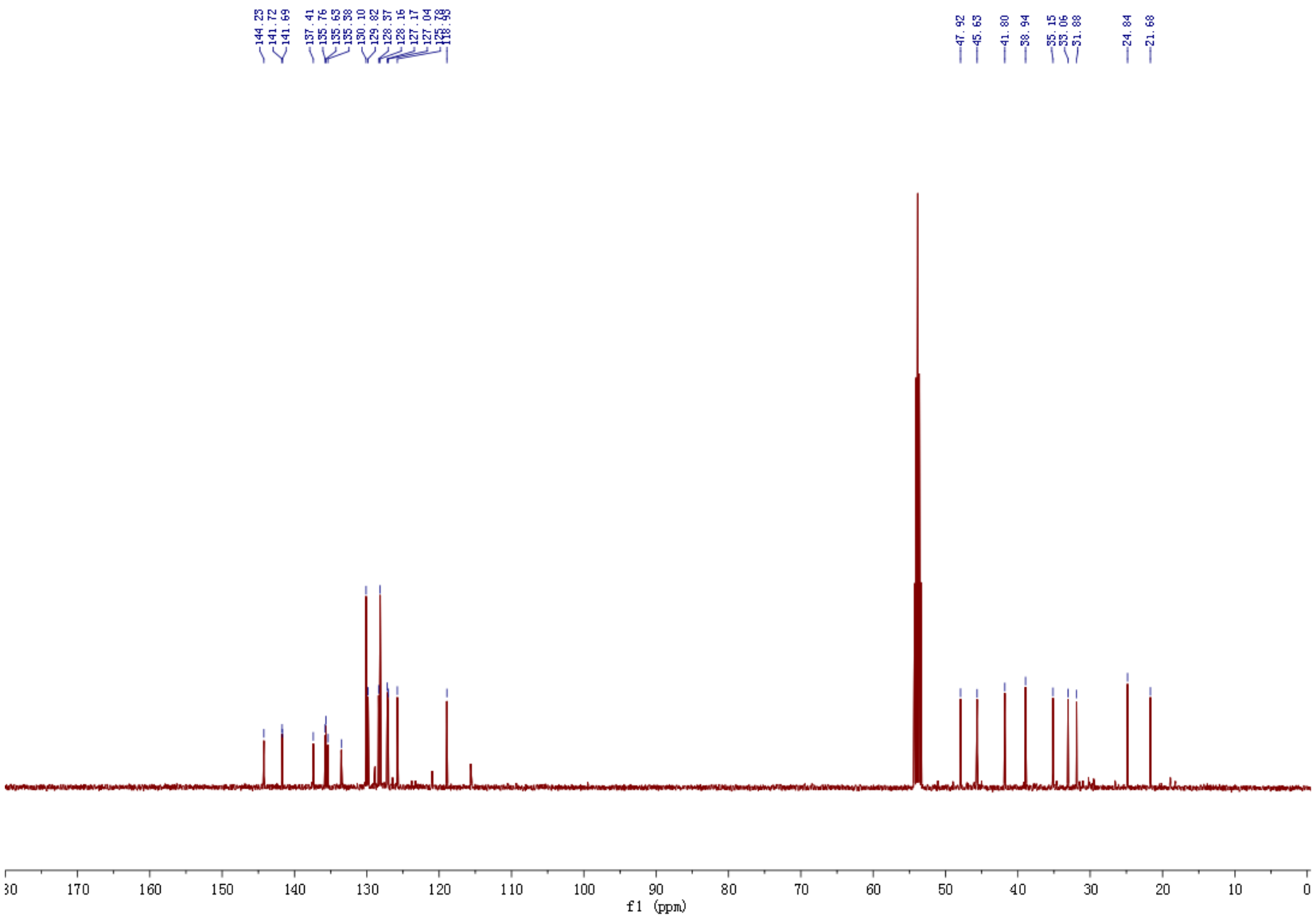

TsN
H
H
(2e)
2.09
2.11
1.00
1.06
1.02
1.05
1.01
1.04
3.66
2.03
1.08
3.42
1.55
5.59
3.33
3.37
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

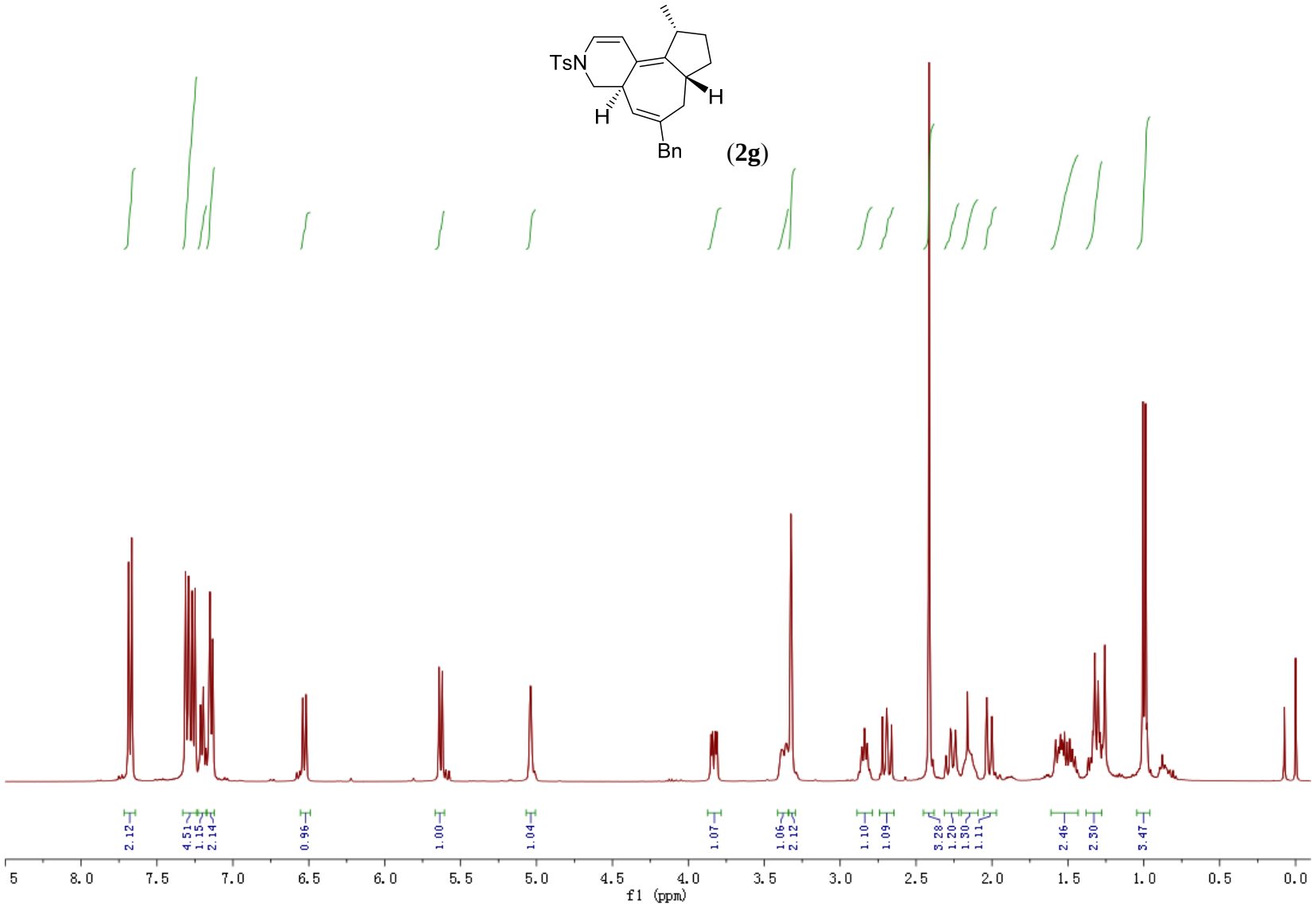

149.88
145.71
142.39
134.82
129.76
127.12
123.36
122.10
121.58
110.29
49.88
44.58
44.32
43.67
37.63
36.42
32.25
30.11
27.96
24.44
21.53
f1 (ppm)

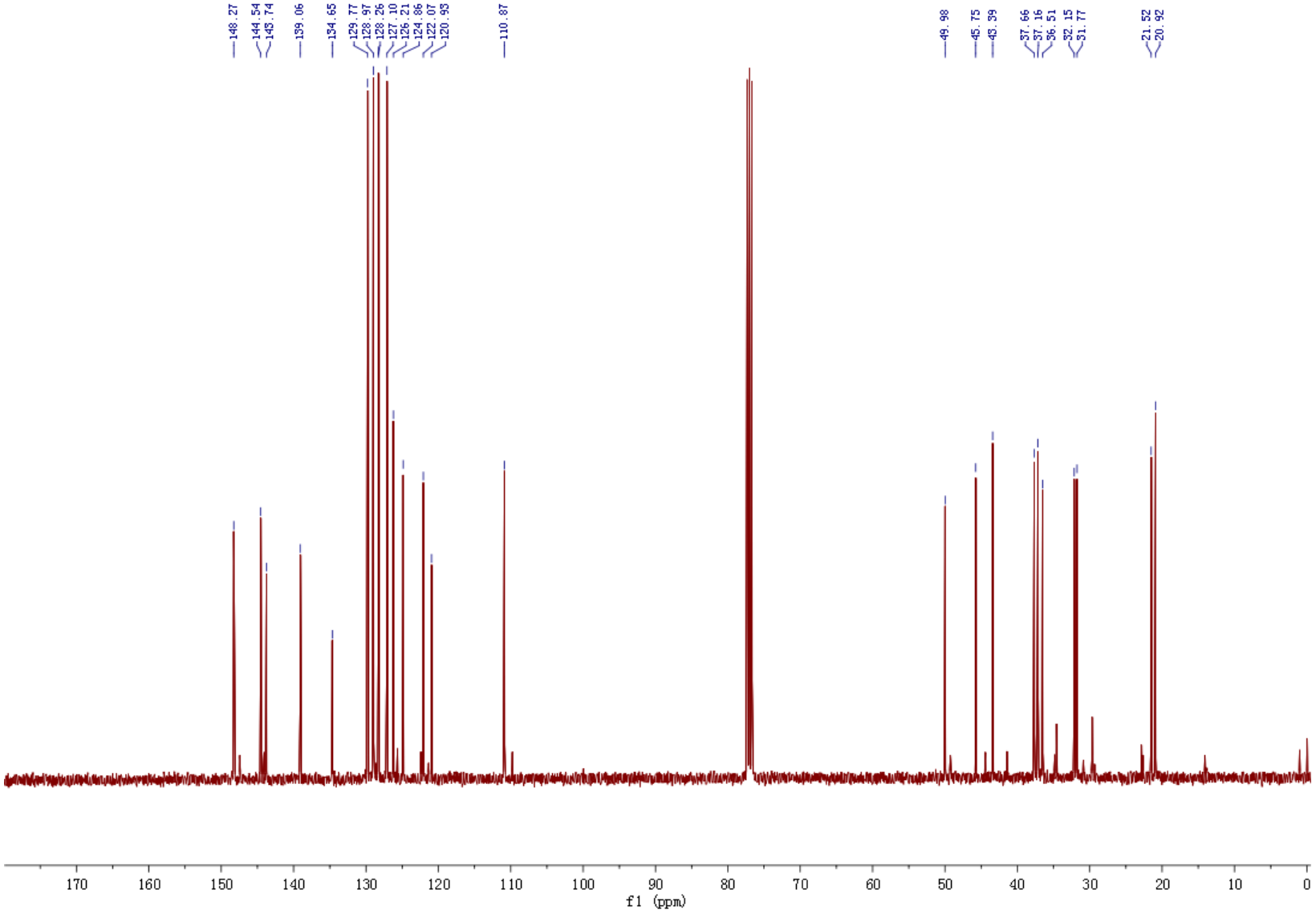

Ph
TsN
H
H
(2f)
1.99
4.51
1.26
2.06
1.00
1.03
1.02
1.08
1.02
1.03
1.07
1.12
1.26
3.39
1.20
1.27
3.26
1.25
1.72
1.33
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

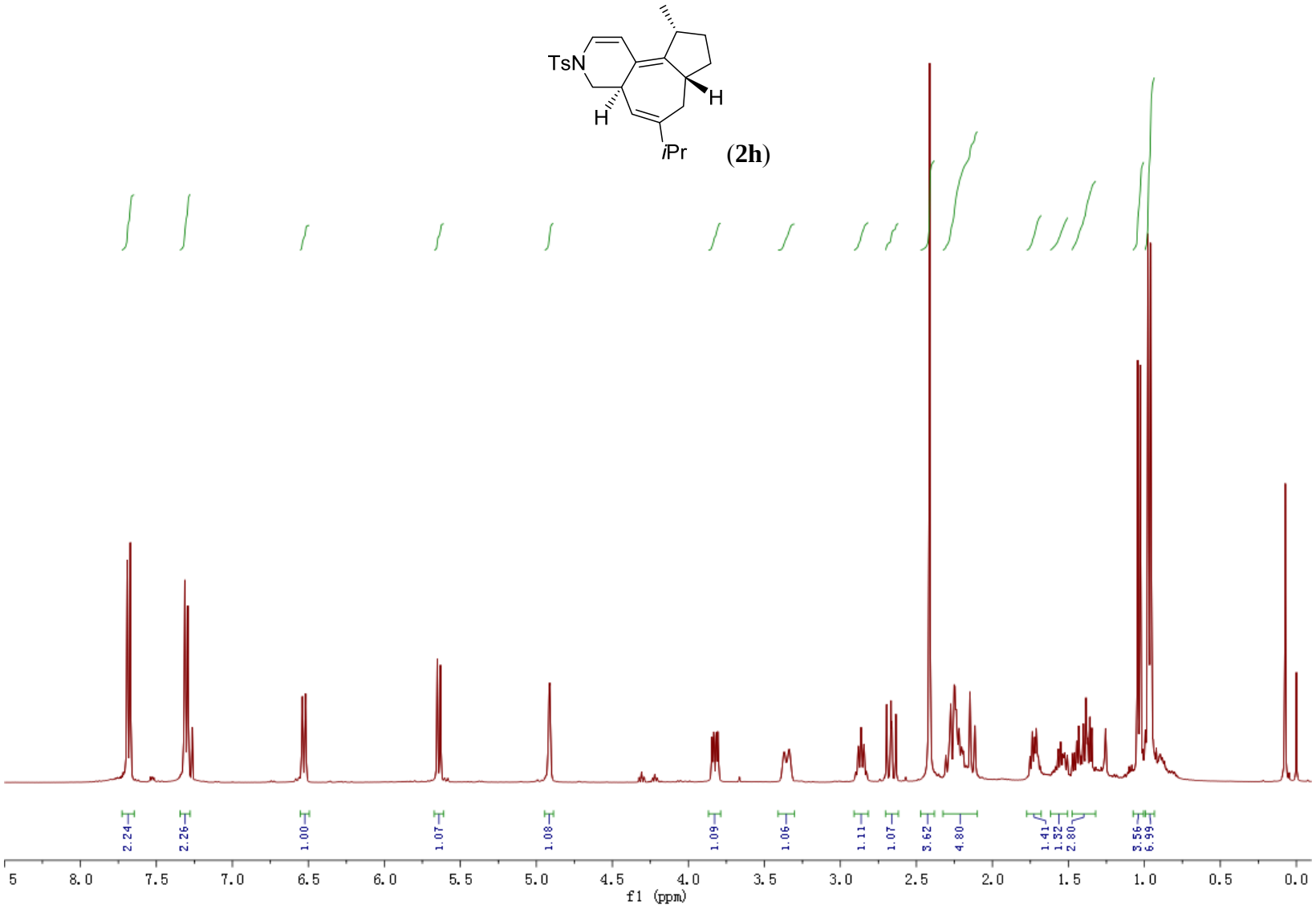

146.77
143.73
143.62
142.12
134.64
129.72
128.28
127.66
127.10
125.68
123.86
123.26
122.64
111.24
50.07
49.73
43.37
37.00
36.28
34.77
31.59
25.46
21.52
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

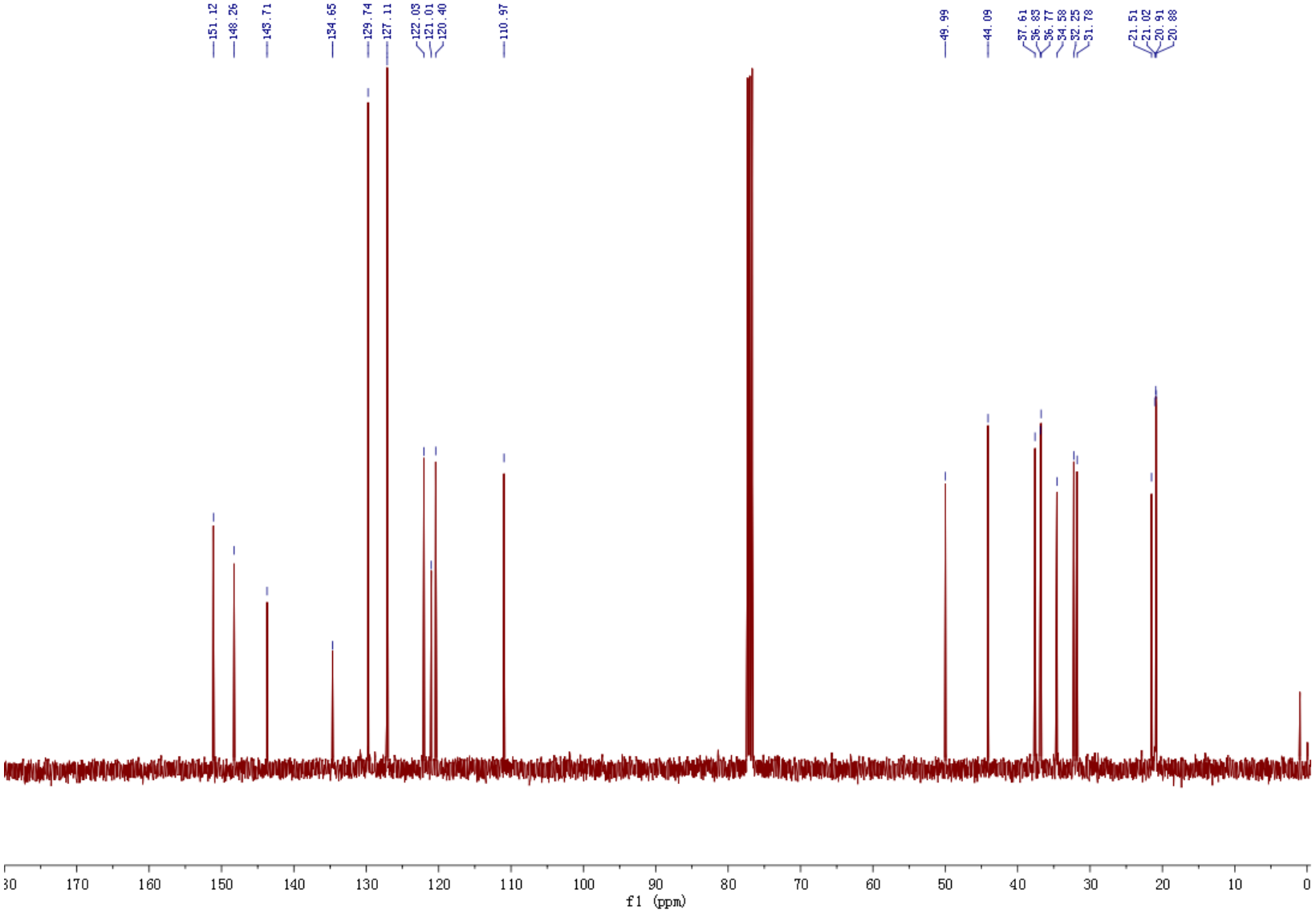

TsN
(4f)
2.13
2.13
2.98
0.94
1.00
0.97
1.08
1.03
1.11
1.05
1.22
1.03
1.09
2.02
3.33
1.72
1.23
3.26
2.54
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

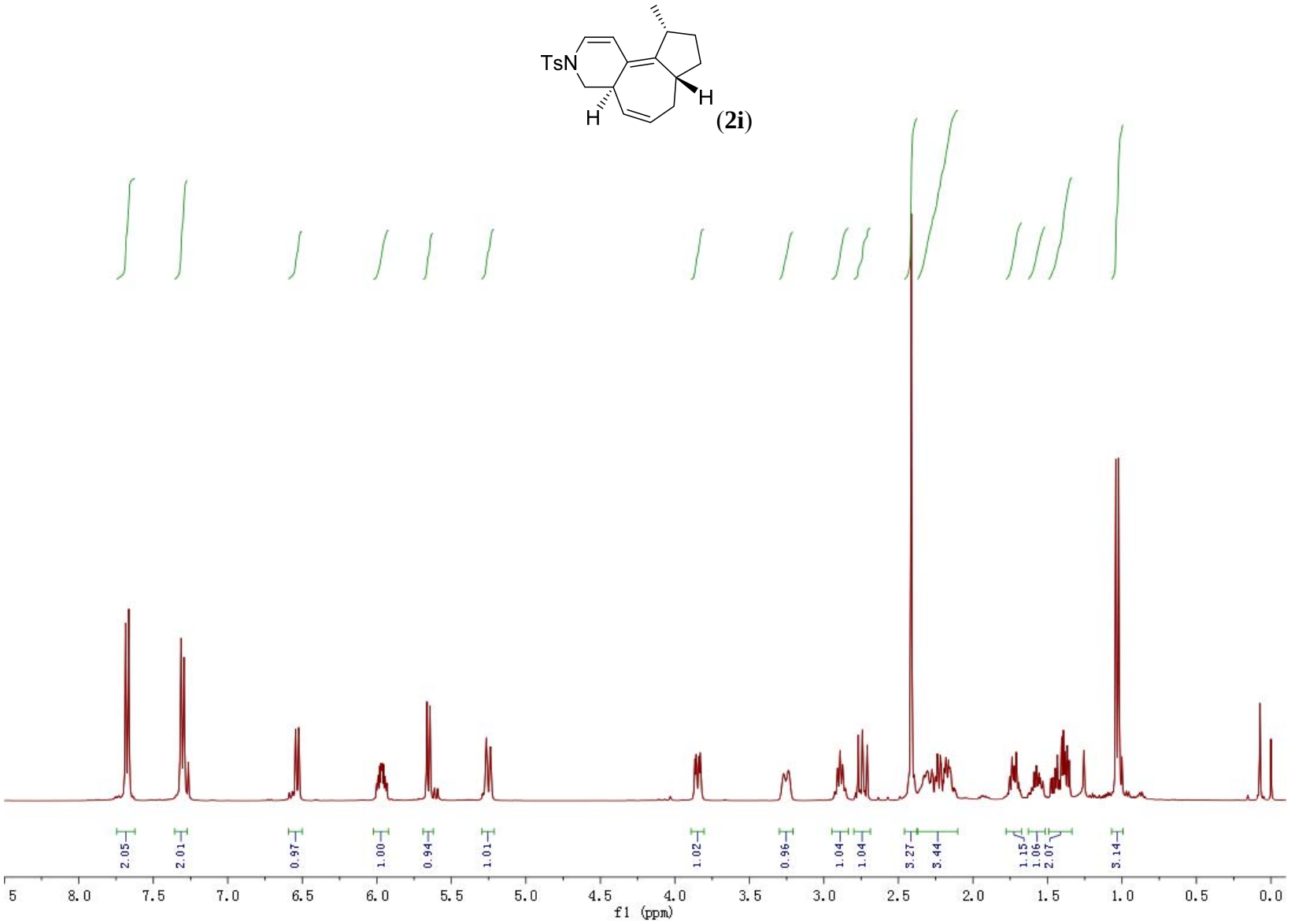

144.23
141.72
141.69
137.41
135.76
135.63
135.38
130.10
129.82
128.37
128.16
127.17
127.04
118.93
47.92
45.63
41.80
38.94
35.15
33.06
31.88
24.84
21.68
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

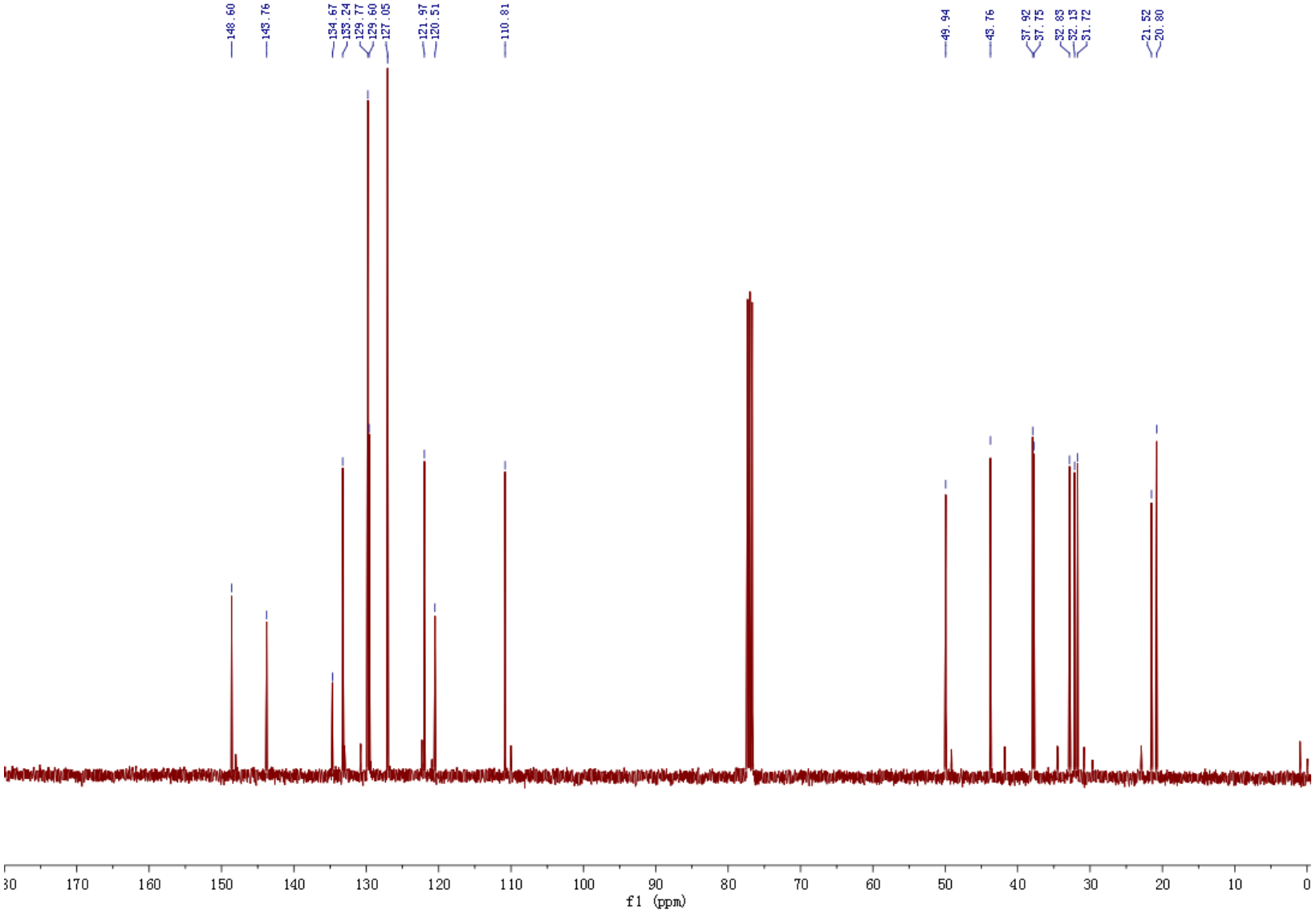

TsN
H
H
Bn
(2g)
2.12
4.51
1.15
2.14
0.96
1.00
1.04
1.07
1.06
2.12
1.10
1.09
3.28
1.20
1.30
1.11
2.46
2.30
3.47
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

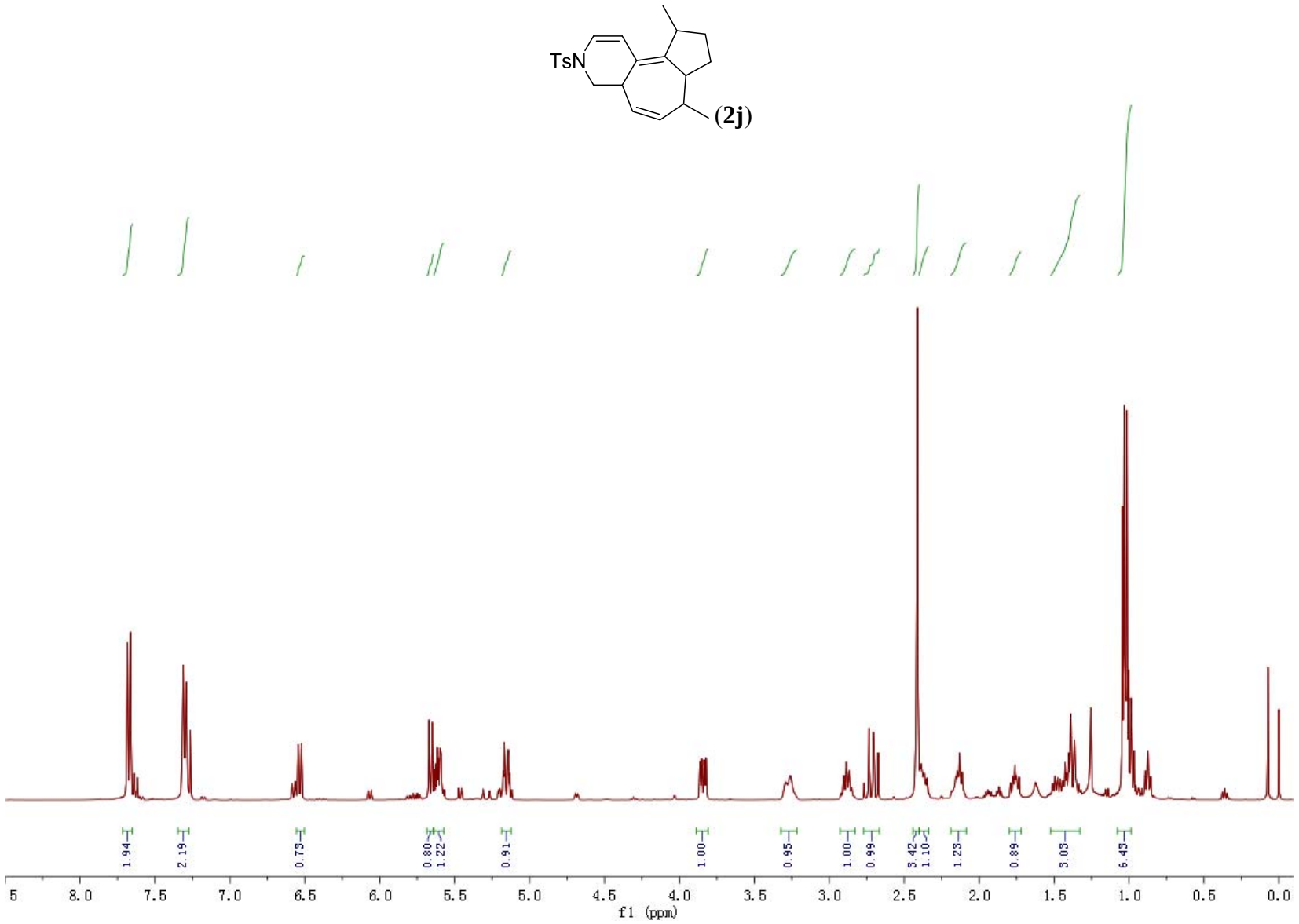

148.27
144.54
143.74
139.06
134.65
129.77
128.97
128.26
127.10
126.21
124.86
122.07
120.93
110.87
49.98
45.75
45.39
37.66
37.16
36.51
32.15
31.77
21.52
20.92
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

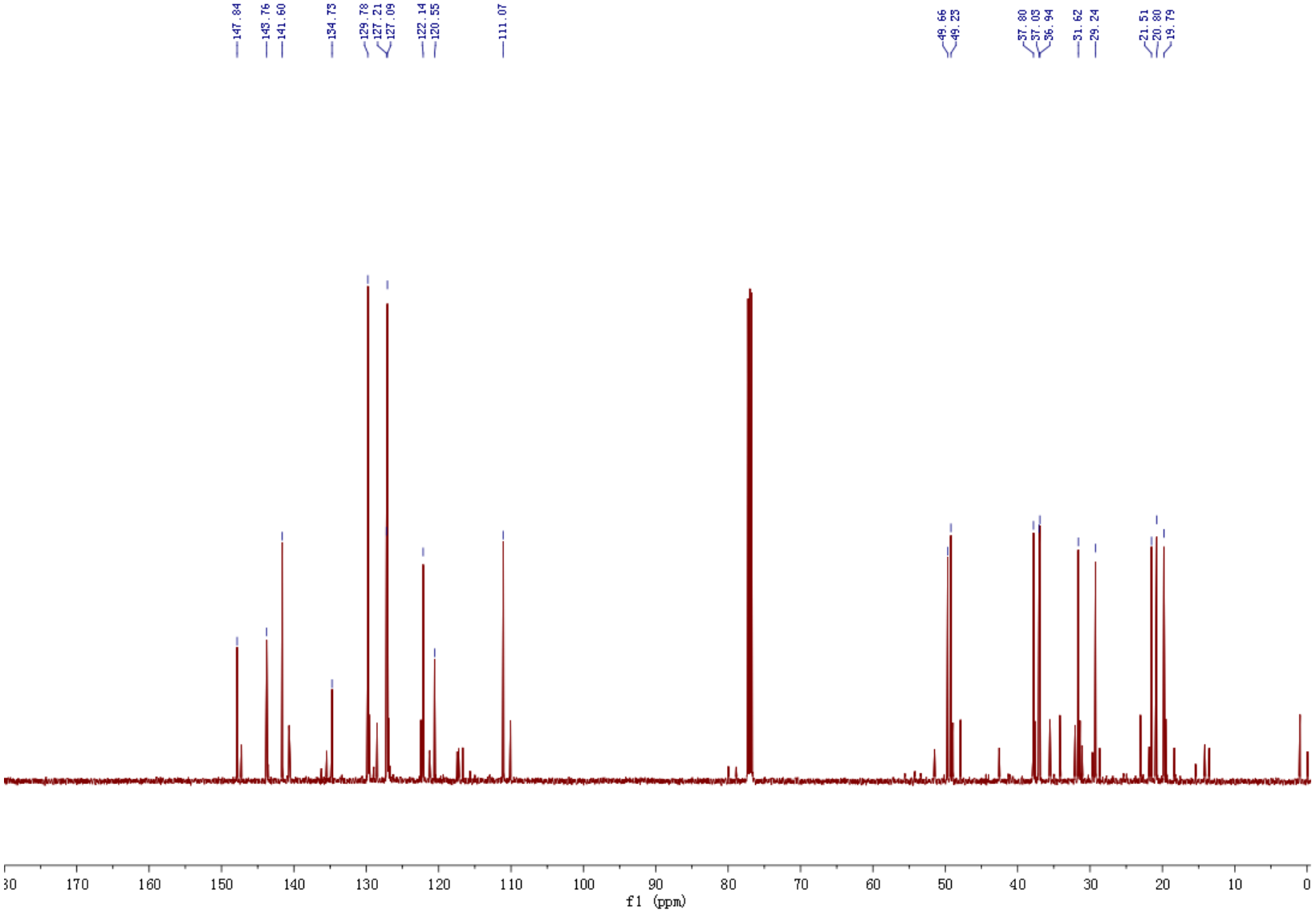

TsN
H
H
iPr
(2h)
2.24
2.26
1.00
1.07
1.08
1.09
1.06
1.11
1.07
3.62
4.80
1.41
1.32
2.80
3.56
6.99
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

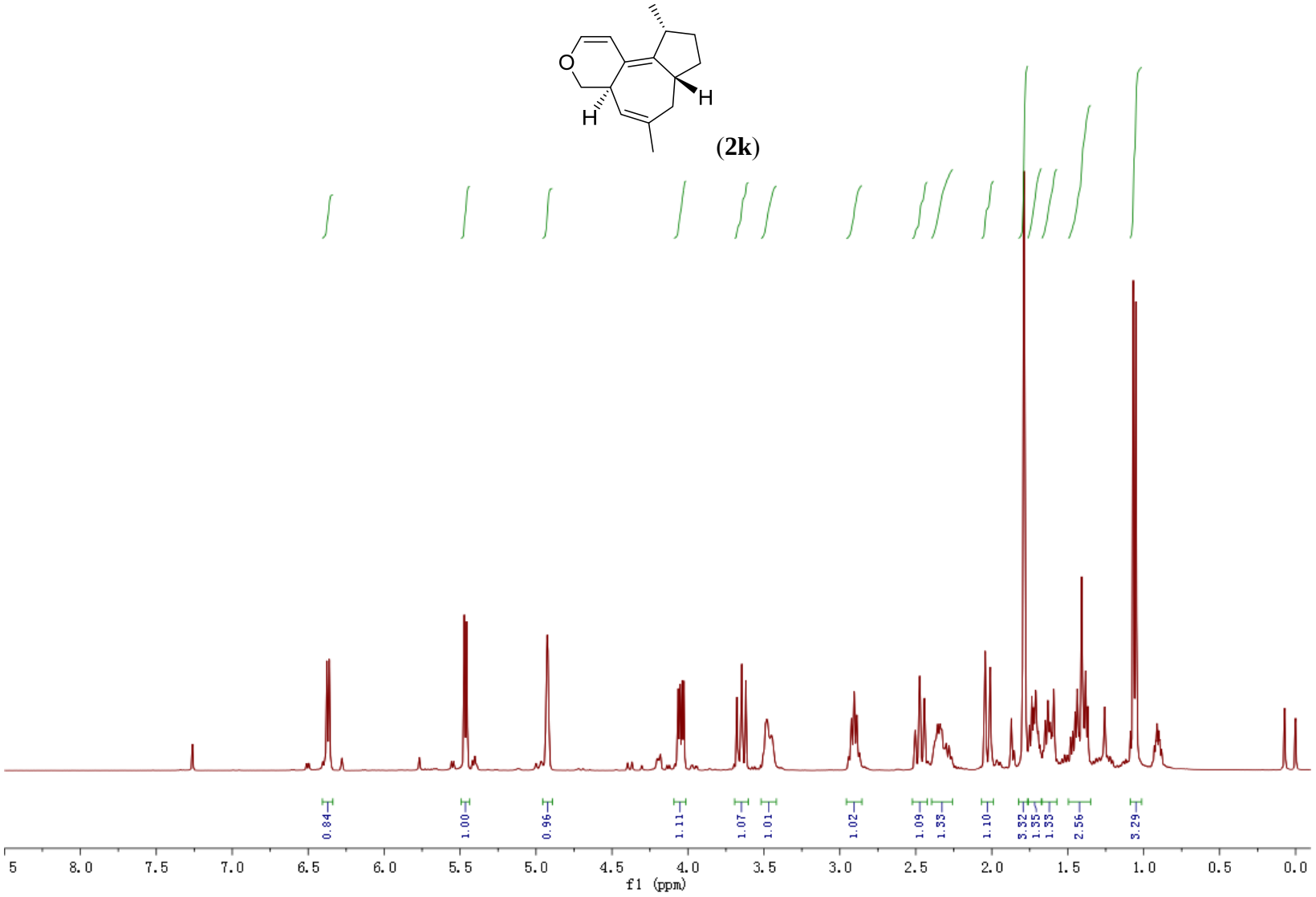

151.12
148.26
143.71
134.65
129.74
127.11
122.03
121.01
120.40
110.97
49.99
44.09
37.61
36.83
36.77
34.58
32.25
31.78
21.51
21.02
20.91
20.88
f1 (ppm)

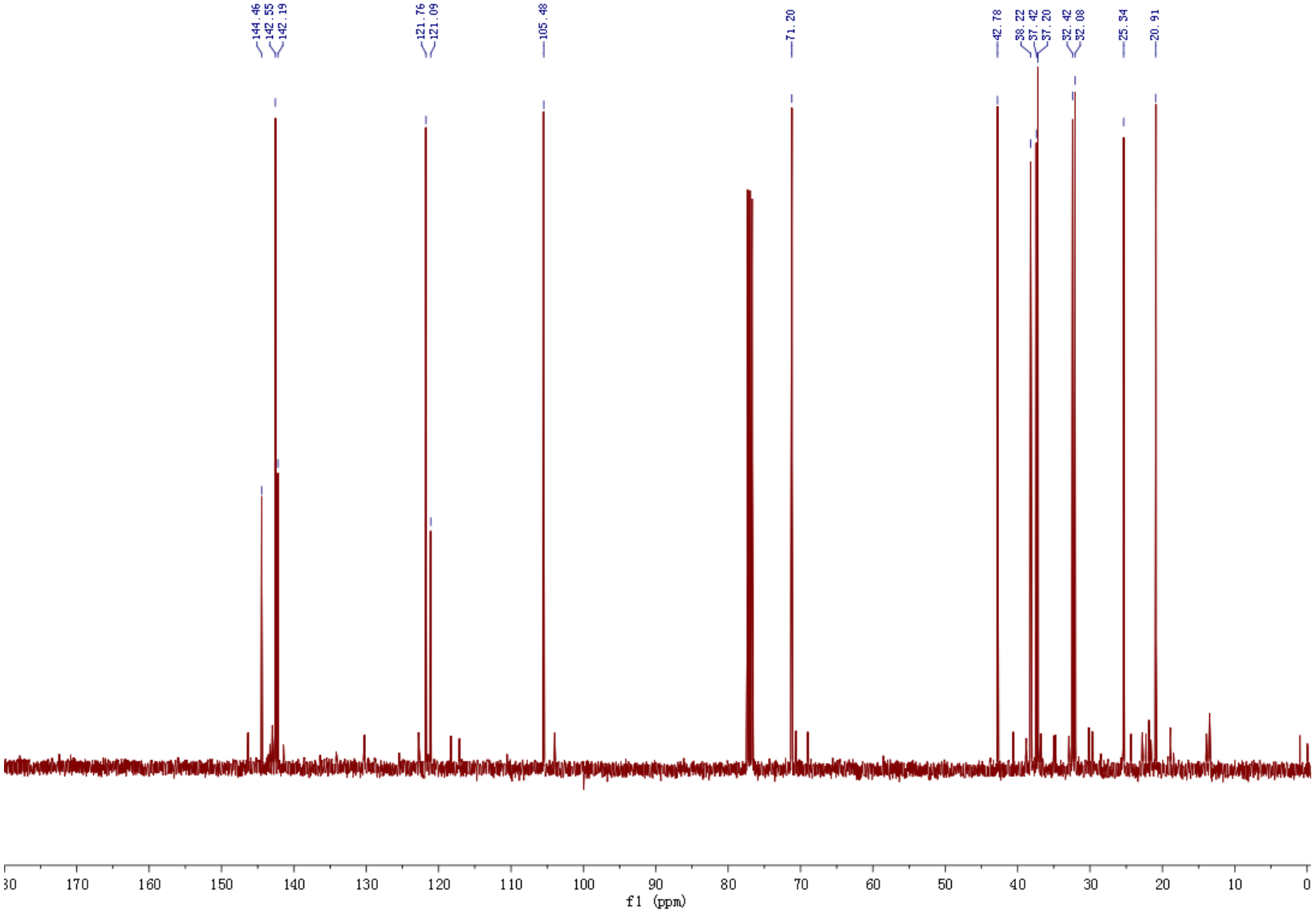

TsN
H
H
(2i)
2.05
2.01
0.97
1.00
0.94
1.01
1.02
0.96
1.04
1.04
3.27
3.44
1.15
1.06
2.07
3.14
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

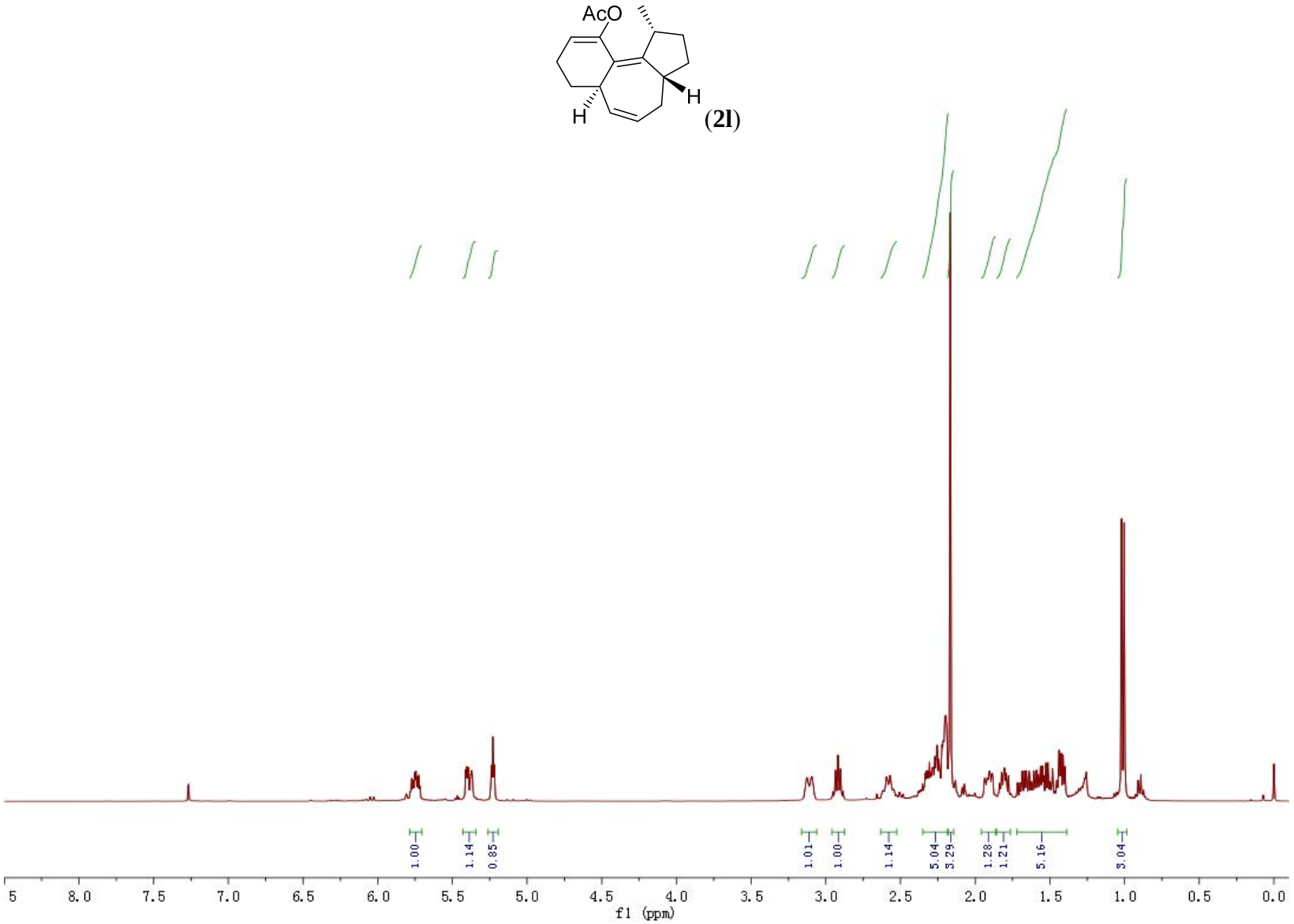

148.60
143.76
134.67
133.24
129.77
129.60
127.05
121.97
120.51
110.81
49.94
43.76
37.92
37.75
32.83
32.13
31.72
21.52
20.80
f1 (ppm)

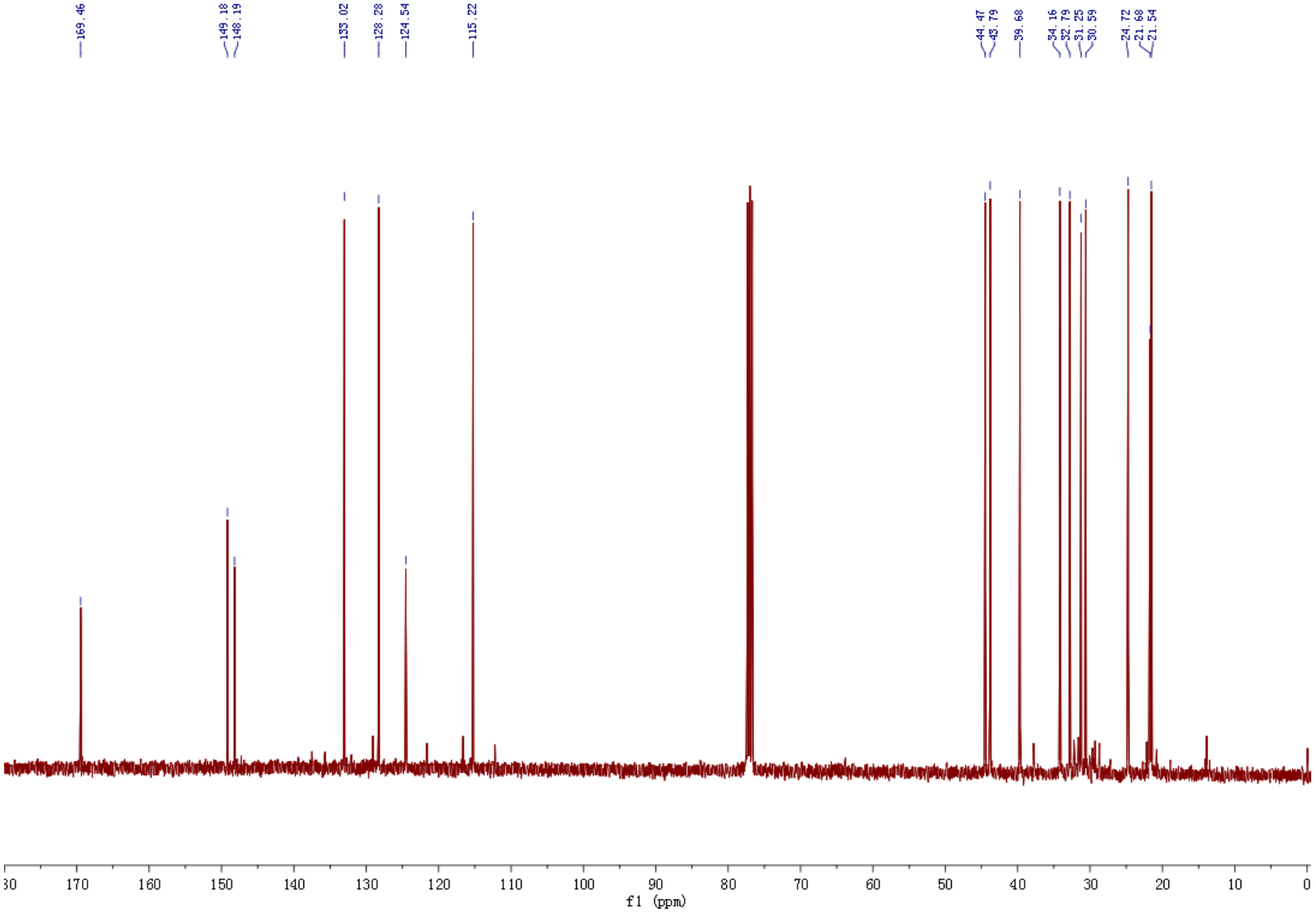

TsN
(2j)
1.94
2.19
0.73
0.80
1.22
0.91
1.00
0.95
1.00
0.99
3.42
1.10
1.23
0.89
3.03
6.43
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

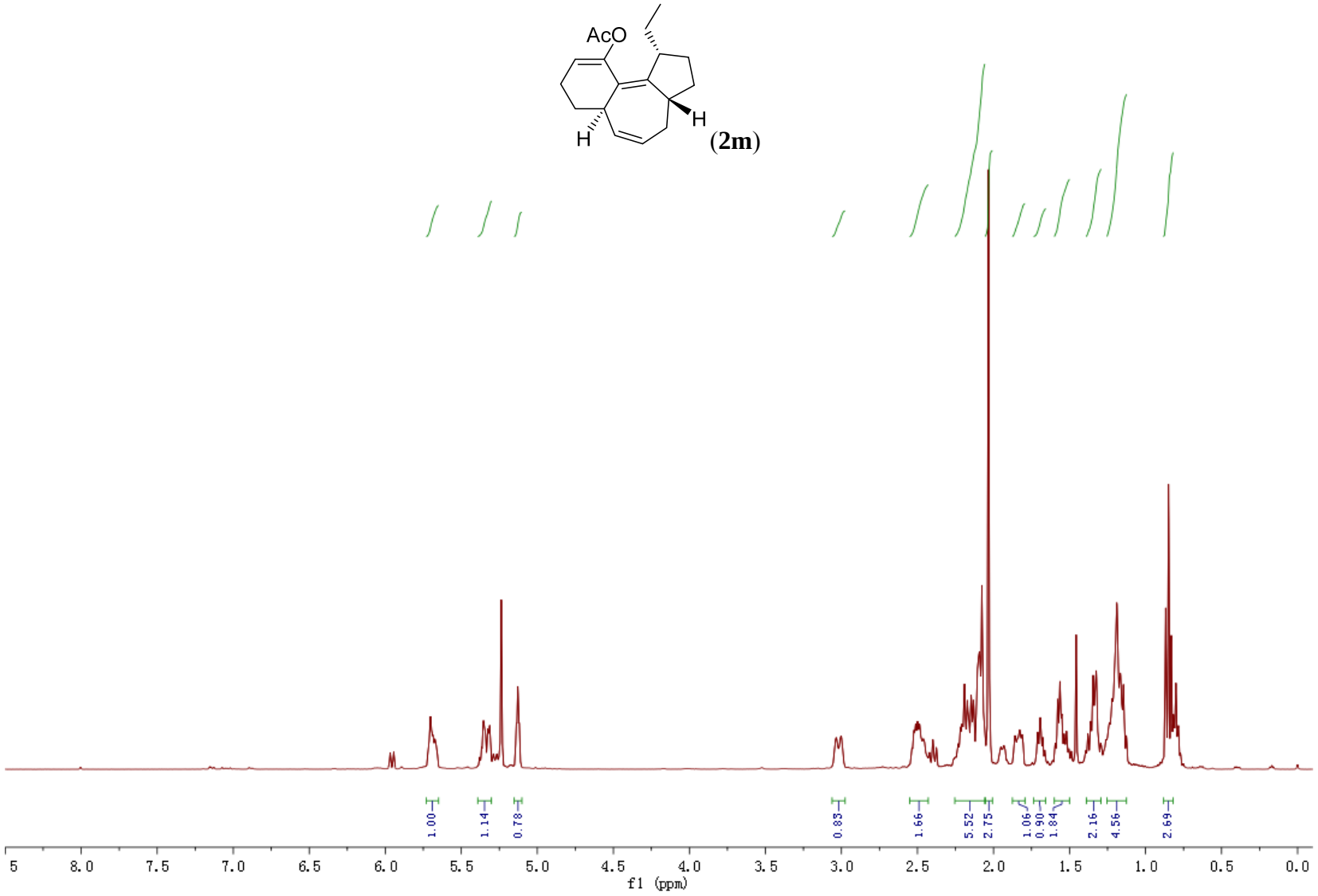

147.84
143.76
141.60
134.73
129.78
127.21
127.09
122.14
120.55
111.07
49.66
49.23
37.80
37.03
36.94
31.62
29.24
21.51
20.80
19.79
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

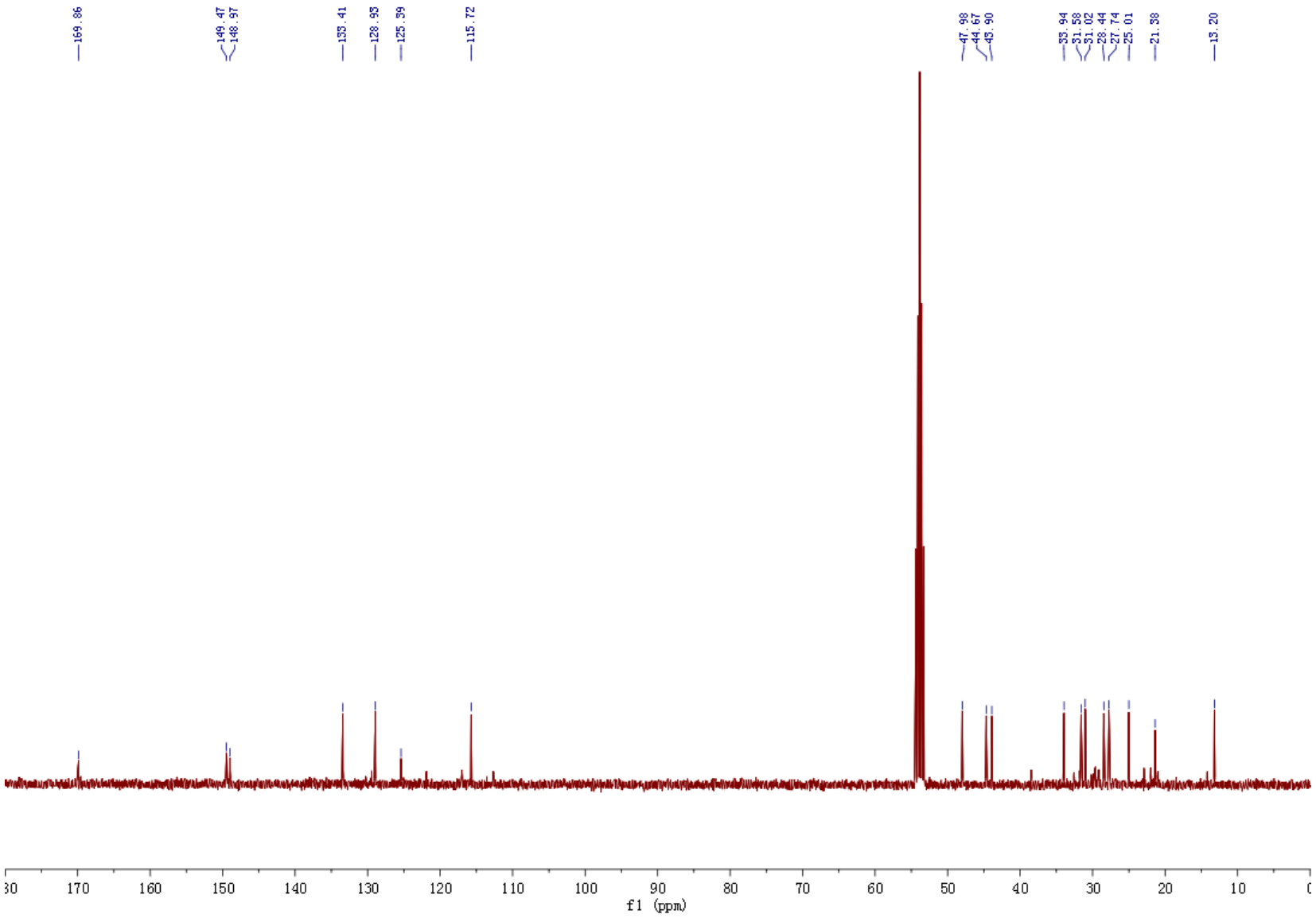

O
H
H
(2k)
0.84
1.00
0.96
1.11
1.07
1.01
1.02
1.09
1.33
1.10
3.32
1.35
1.33
2.56
3.29
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

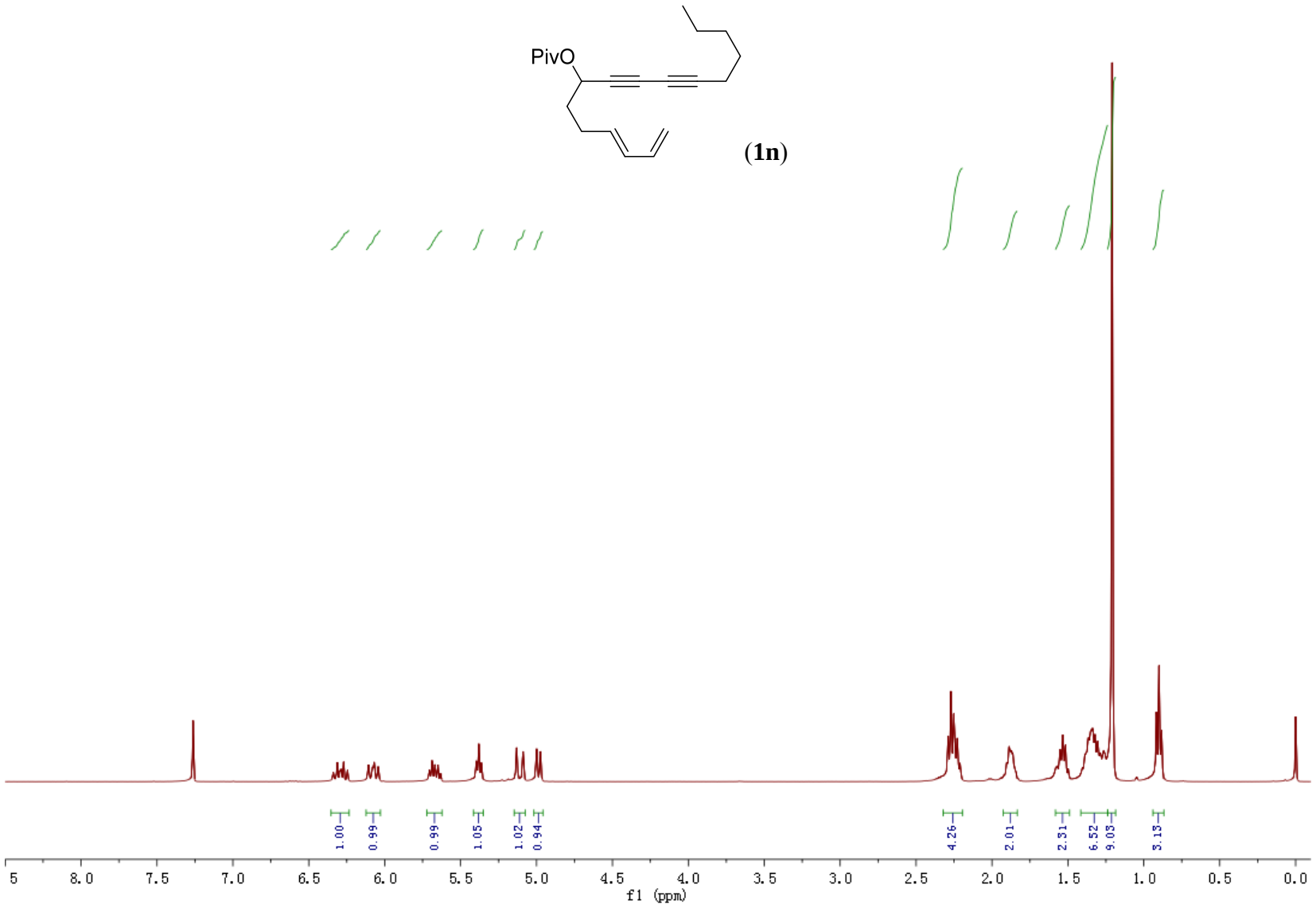

144.46
142.55
142.19
121.76
121.09
105.48
71.20
42.78
38.22
37.42
37.20
32.42
32.08
25.34
20.91
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


AcO
H
H
(2l)
1.00
1.14
0.85
1.01
1.00
1.14
5.04
3.29
1.28
1.21
5.16
3.04
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)

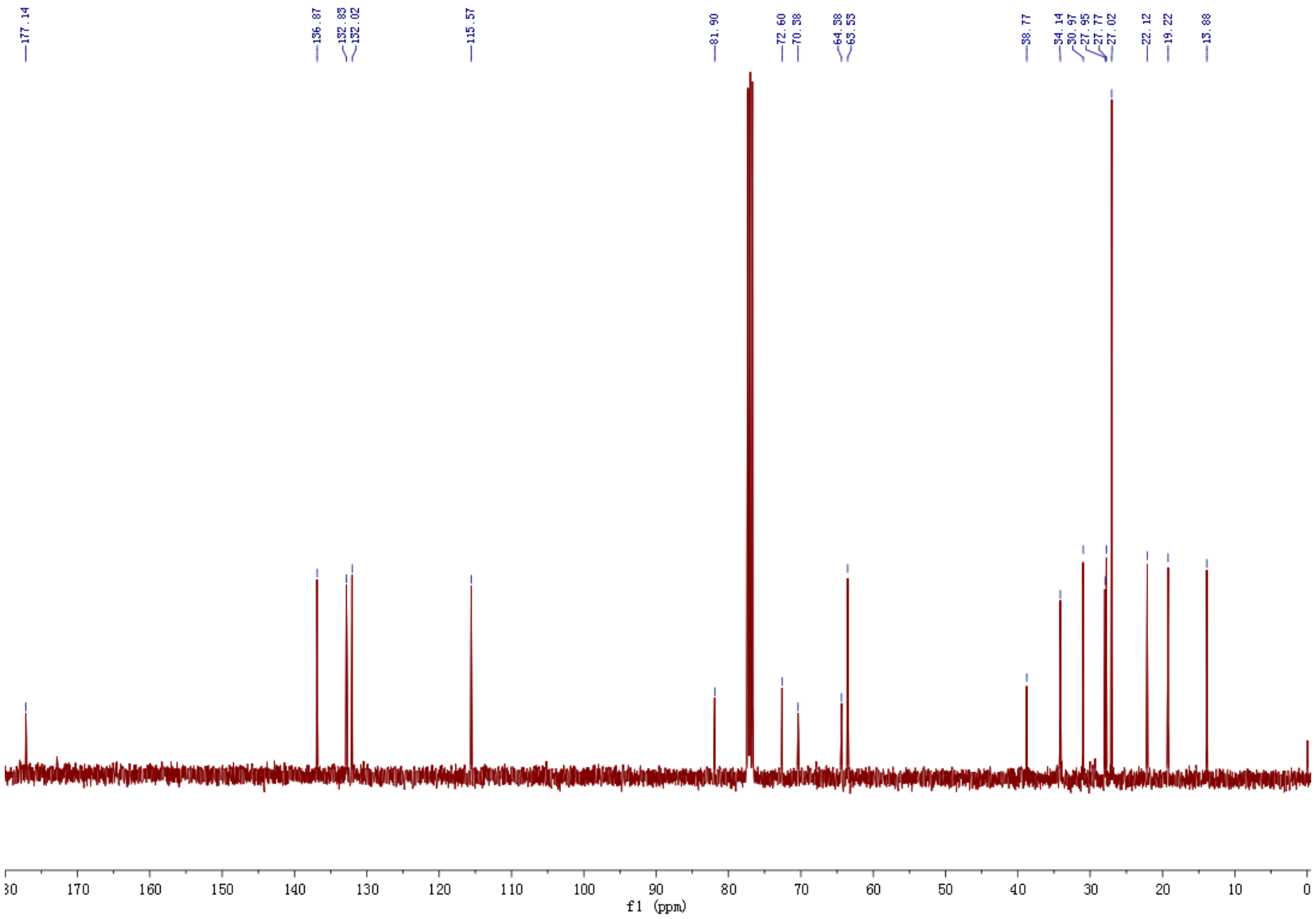

169.46
149.18
148.19
135.02
128.28
124.54
115.22
44.47
43.79
39.68
34.16
32.79
31.25
30.59
24.72
21.68
21.54
f1 (ppm)

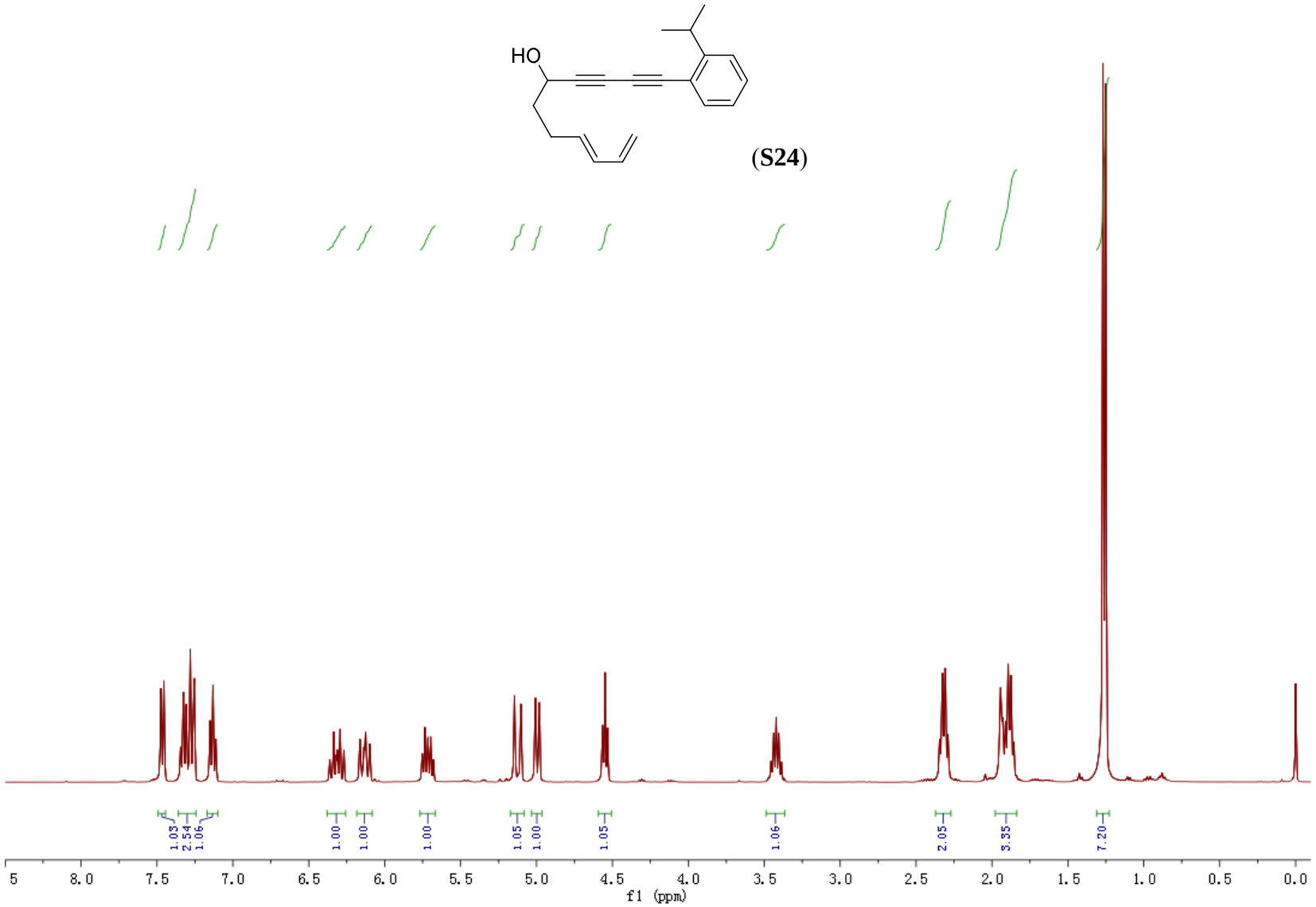

AcO
H
H
(2m)
1.00
1.14
0.78
0.83
1.66
5.52
2.75
1.06
0.90
1.84
2.16
4.56
2.69
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

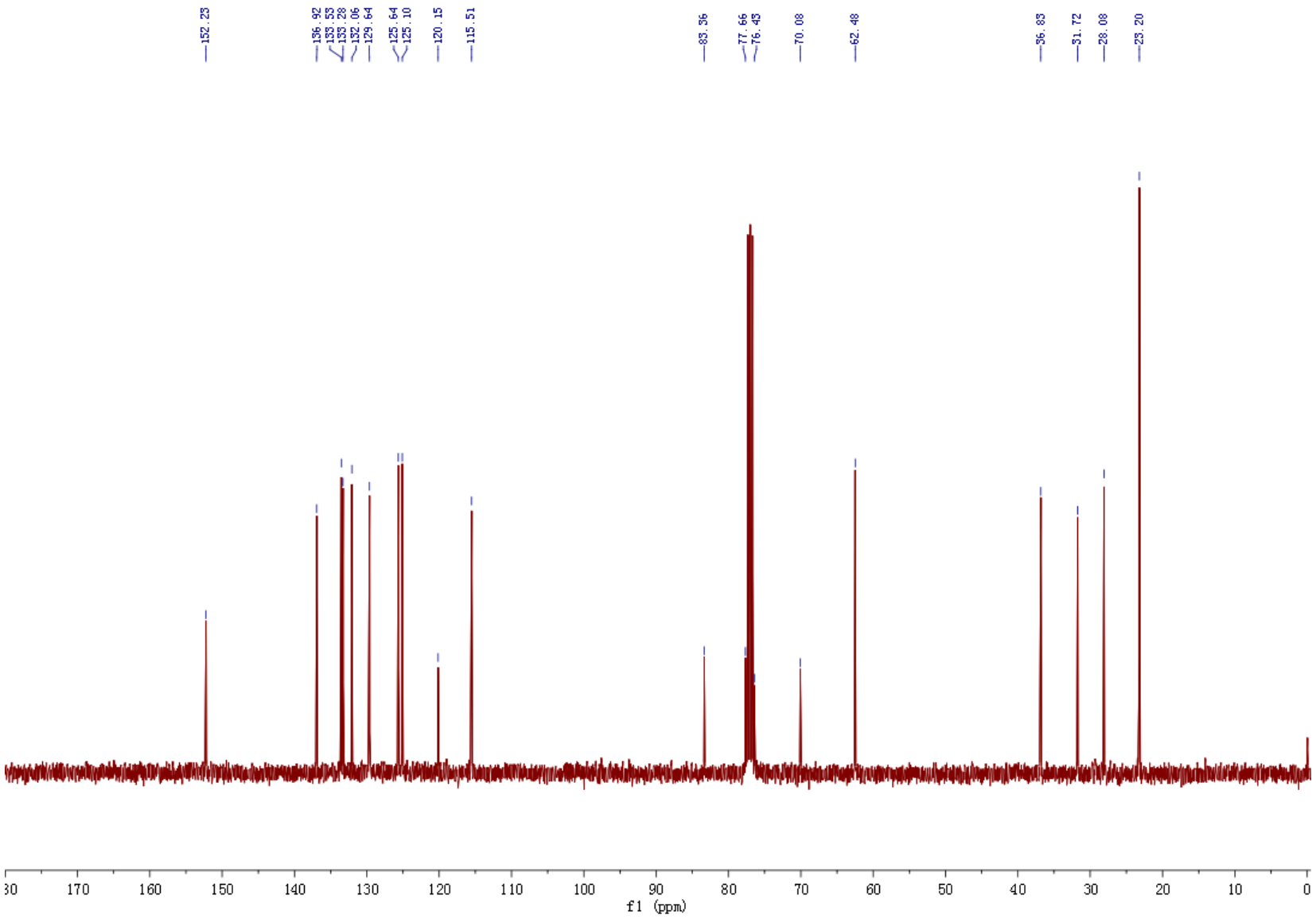

169.86
149.47
148.97
133.41
128.93
125.39
115.72
47.98
44.67
43.90
33.94
31.58
31.02
28.44
27.74
25.01
21.38
13.20
f1 (ppm)

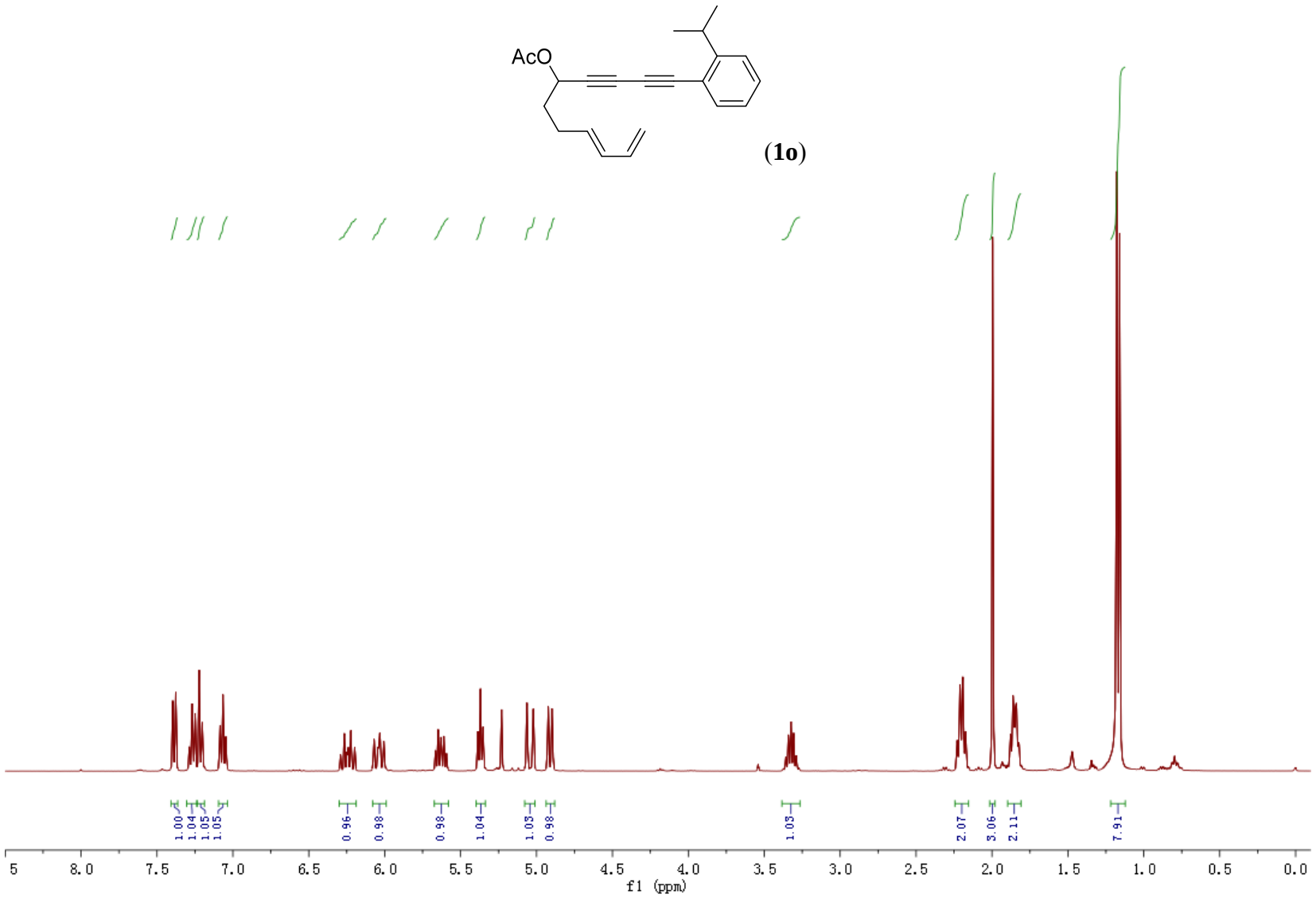

PivO
1.00
0.99
0.99
1.05
1.02
0.94
4.26
2.01
2.31
6.52
9.03
3.13
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

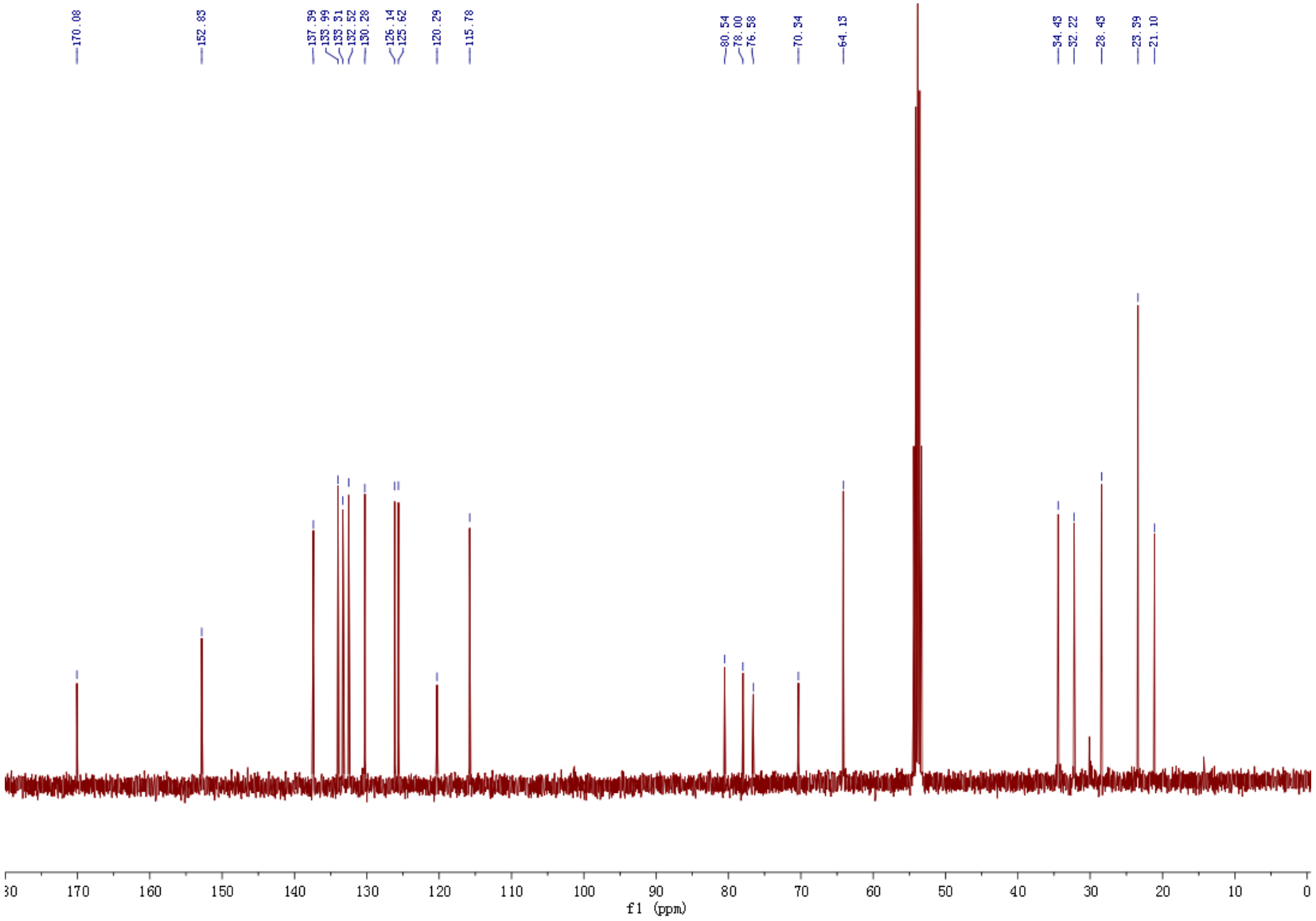
(1n)

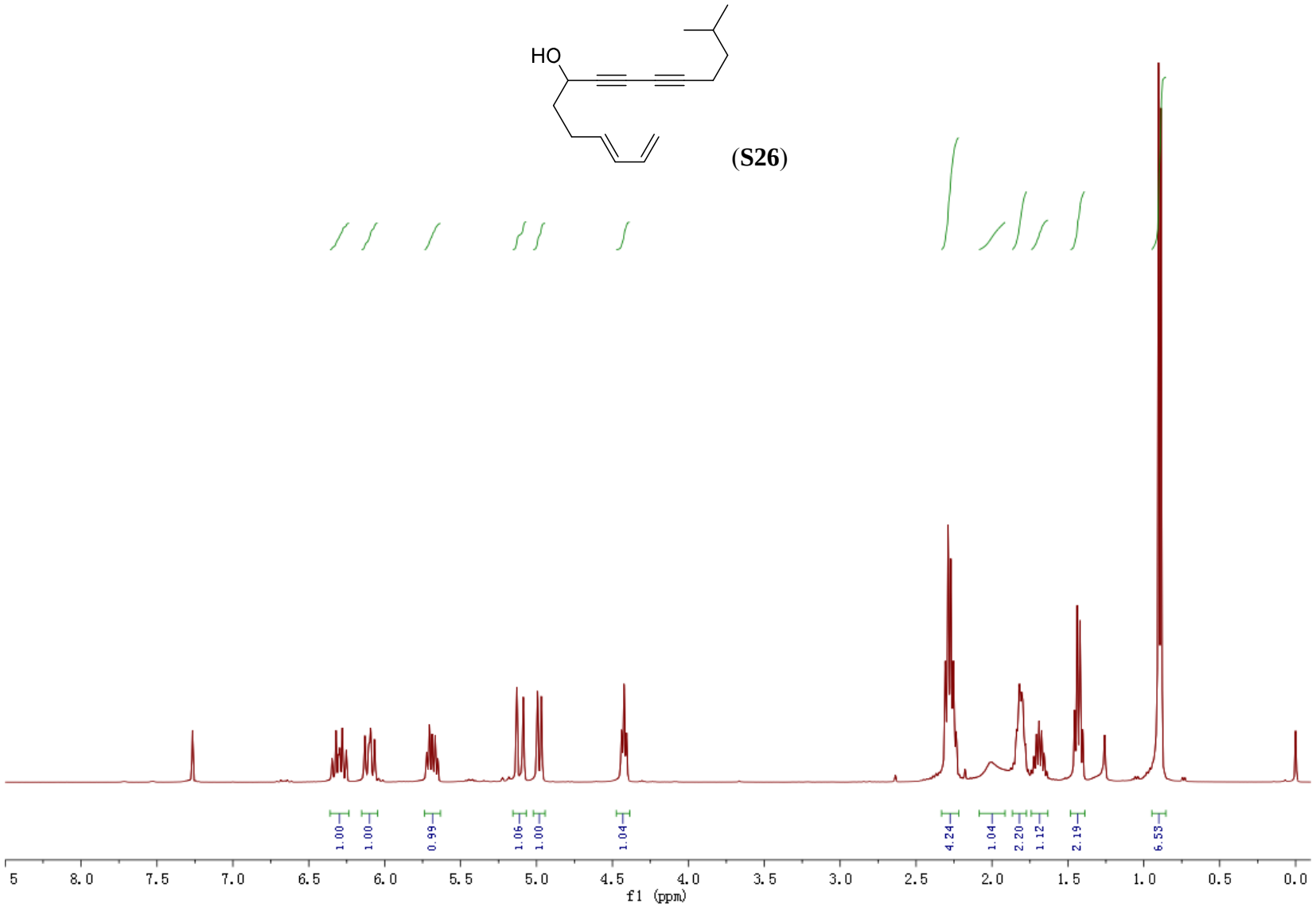

177.14
136.87
132.83
132.02
115.57
81.90
72.60
70.38
64.38
63.53
38.77
34.14
30.97
27.95
27.77
27.02
22.12
19.22
13.88
f1 (ppm)

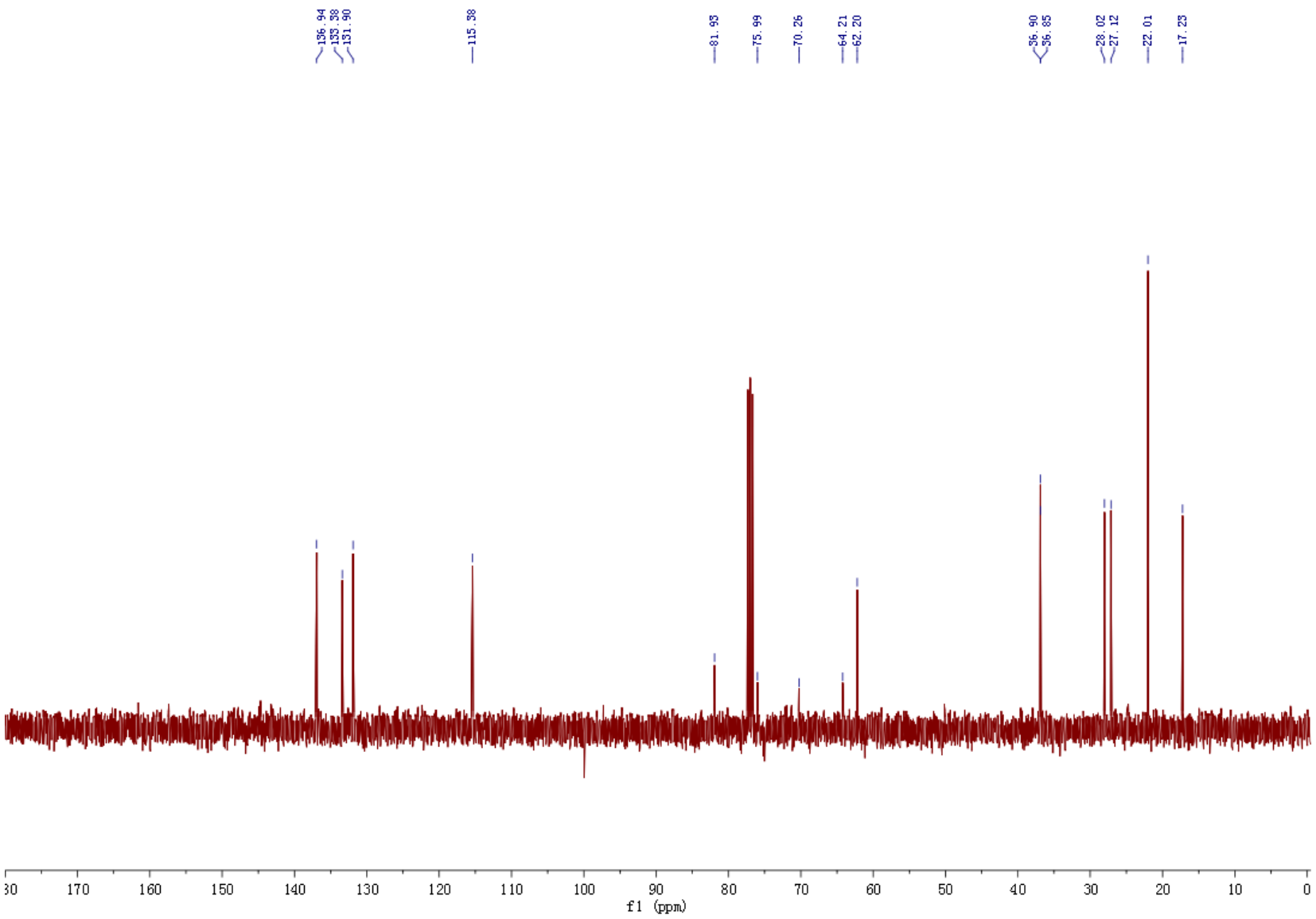

HO
(S24)
1.03
2.54
1.06
1.00
1.00
1.00
1.05
1.00
1.05
1.06
2.05
3.35
7.20
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

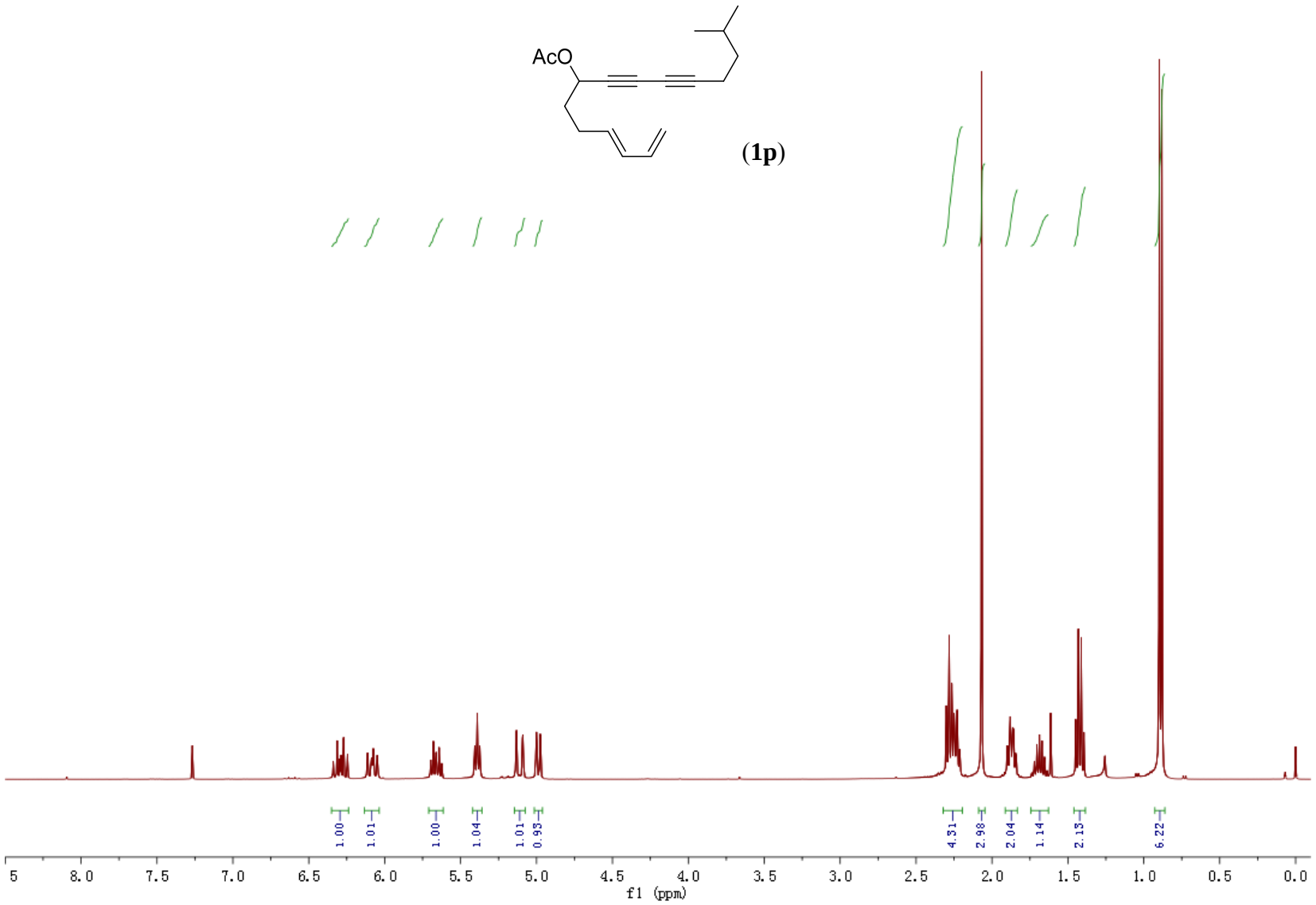

152.23
136.92
133.53
133.28
132.06
129.64
125.64
125.10
120.15
115.51
83.36
77.66
76.43
70.08
62.48
36.83
31.72
28.08
23.20
f1 (ppm)

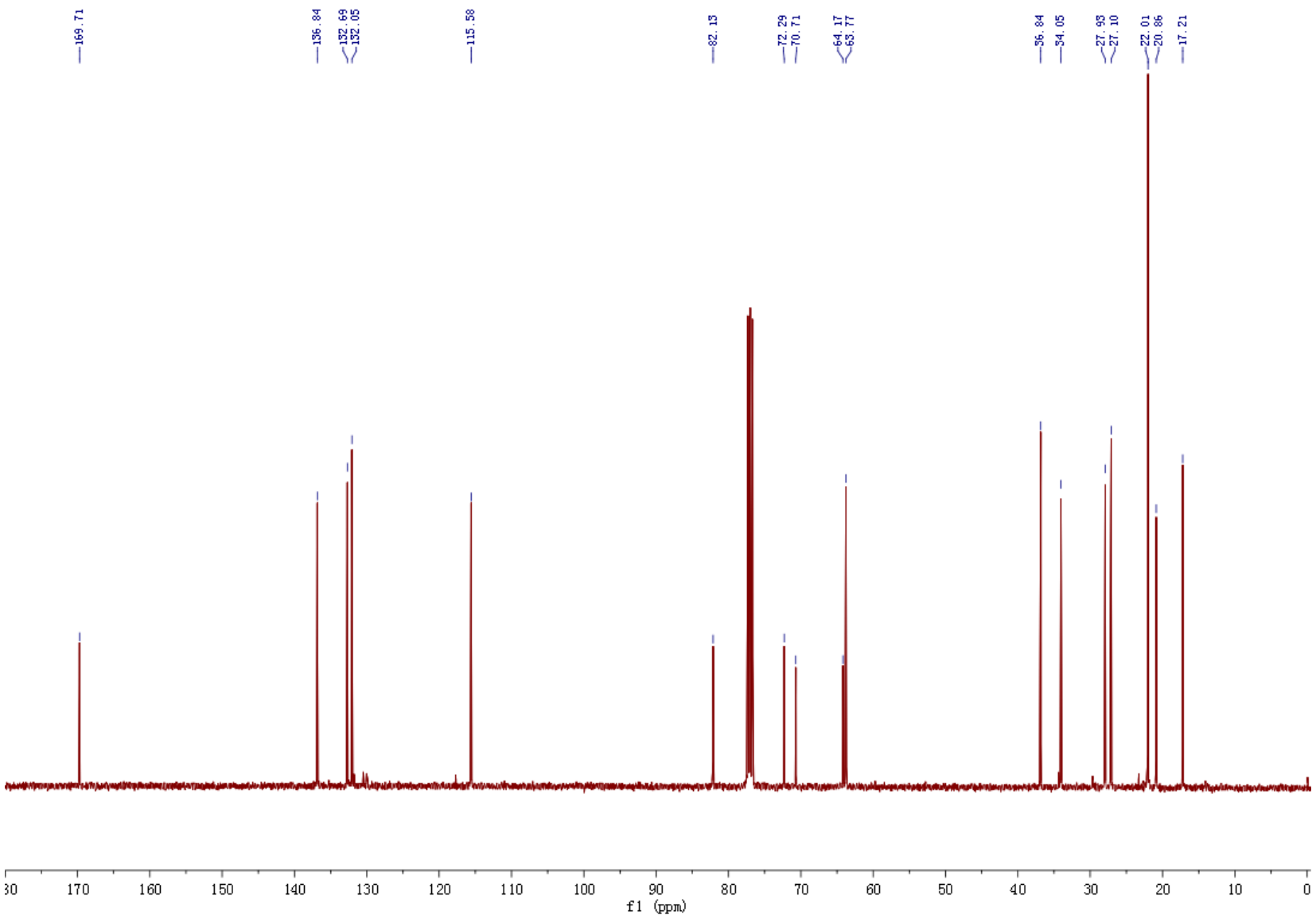

AcO
(1o)
1.00
1.04
1.05
1.05
0.96
0.98
0.98
1.04
1.03
0.98
1.03
2.07
3.06
2.11
7.91
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

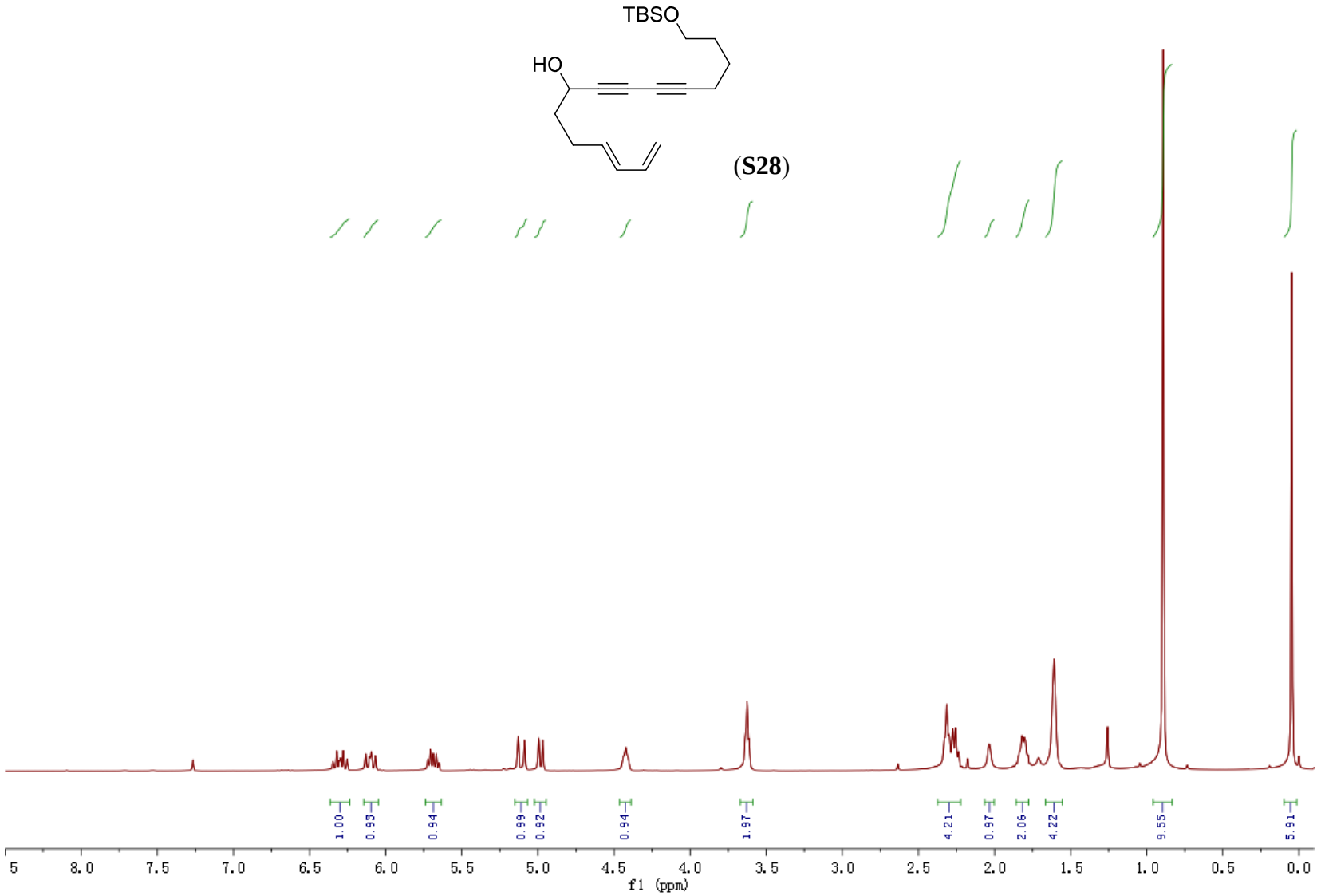

170.08
152.83
137.39
133.99
133.31
132.52
130.28
126.14
125.62
120.29
115.78
80.54
78.00
76.58
70.34
64.13
34.45
32.22
28.43
23.39
21.10
f1 (ppm)

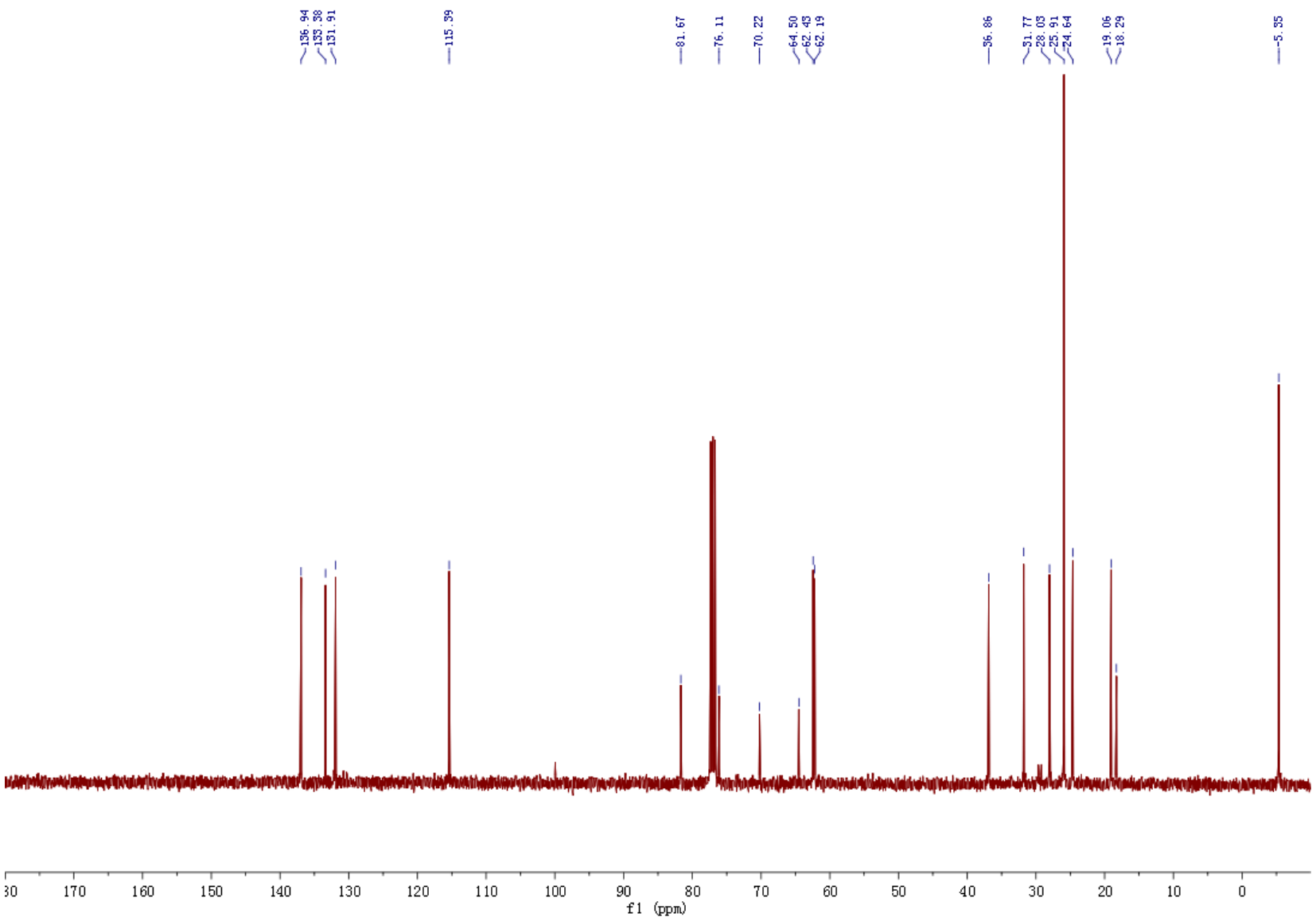

HO
(S26)
1.00
1.00
0.99
1.06
1.00
1.04
4.24
1.04
2.20
1.12
2.19
6.53
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

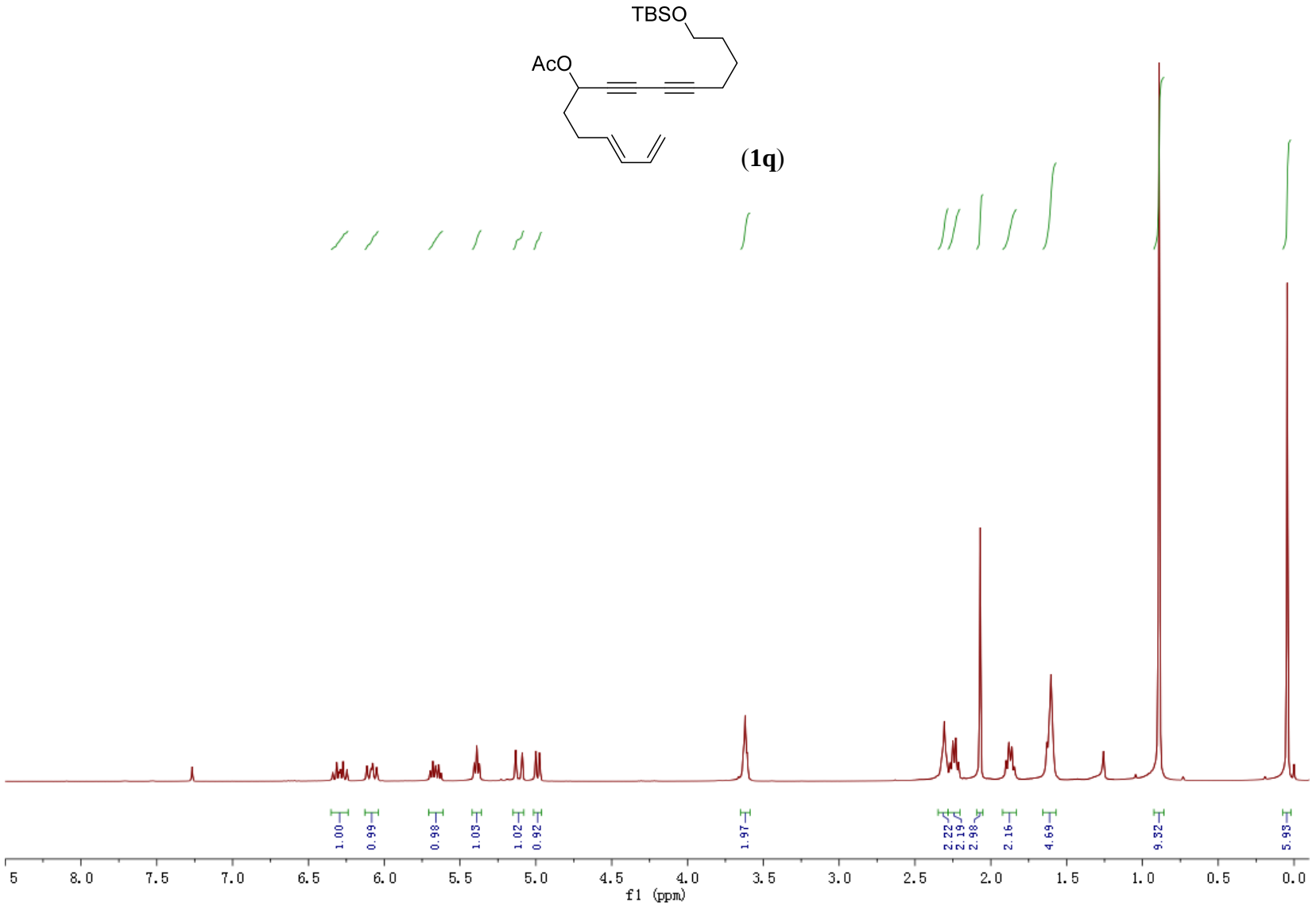

186.94
155.38
131.90
115.38
81.93
75.99
70.26
64.21
62.20
36.90
36.85
28.02
27.12
22.01
17.25
f1 (ppm)

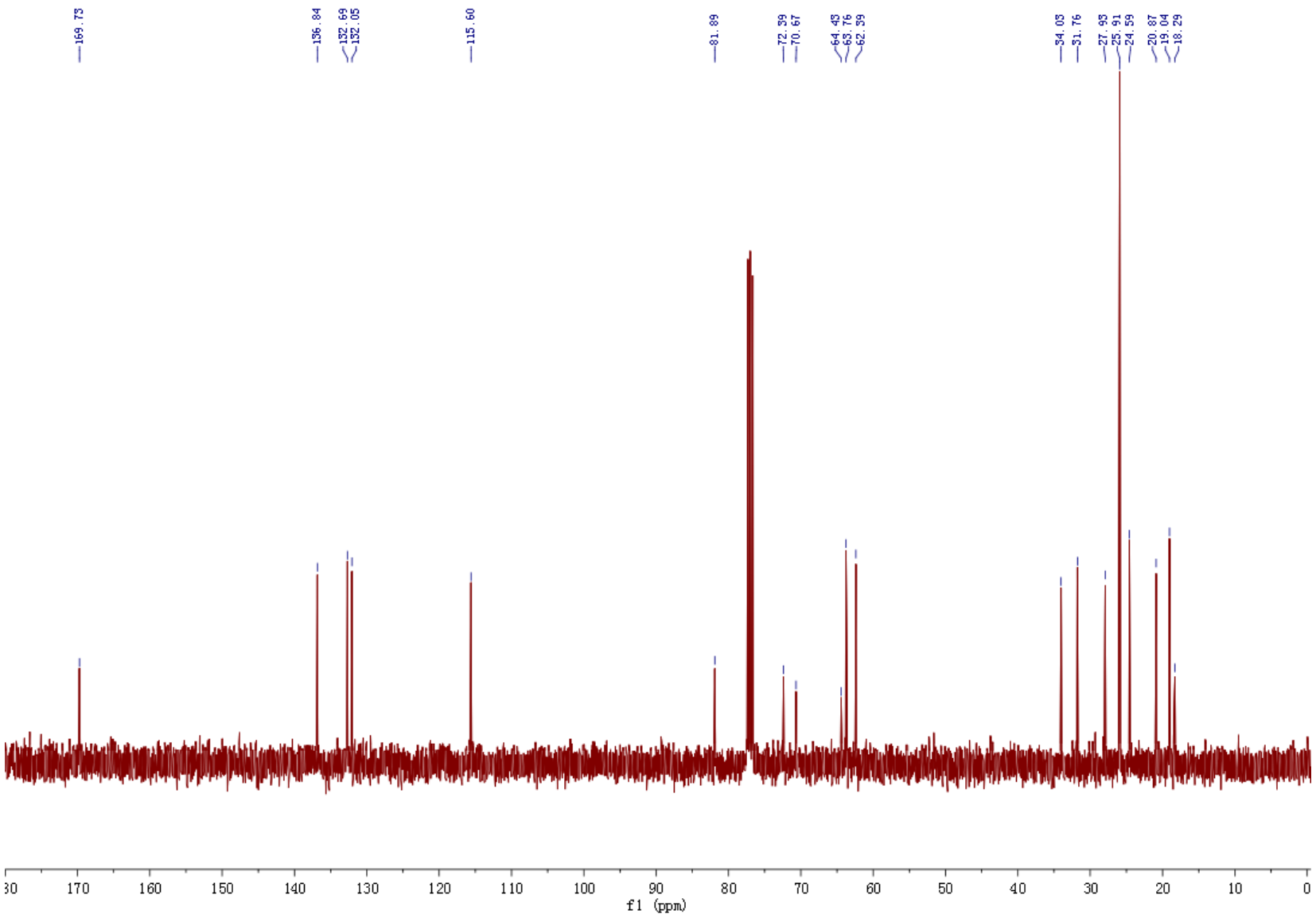

AcO
(1p)
1.00
1.01
1.00
1.04
1.01
0.93
4.31
2.98
2.04
1.14
2.13
6.22
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

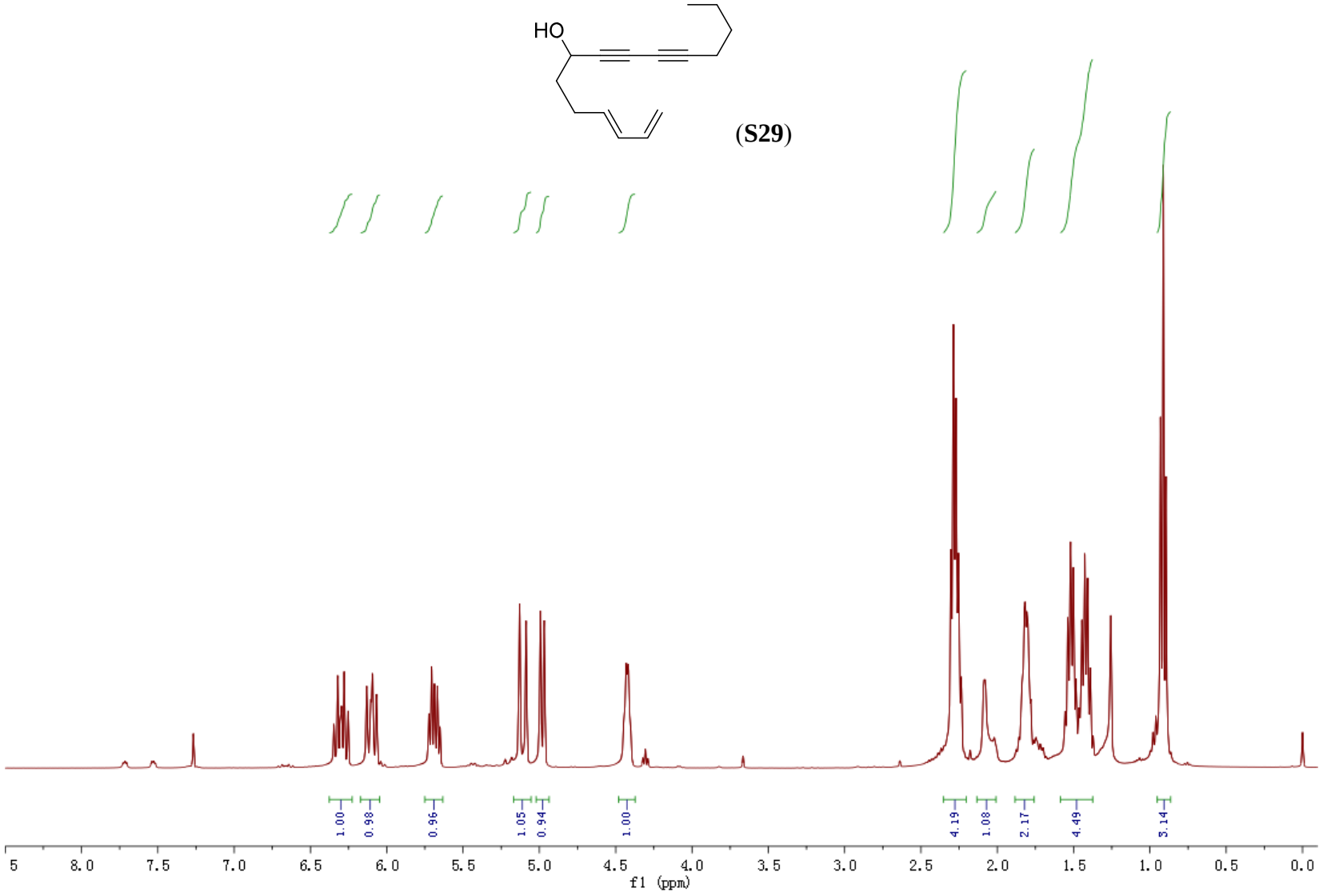

169.71
136.84
132.69
132.05
115.58
82.13
72.29
70.71
64.17
63.77
36.84
34.05
27.93
27.10
22.01
20.86
17.21
f1 (ppm)

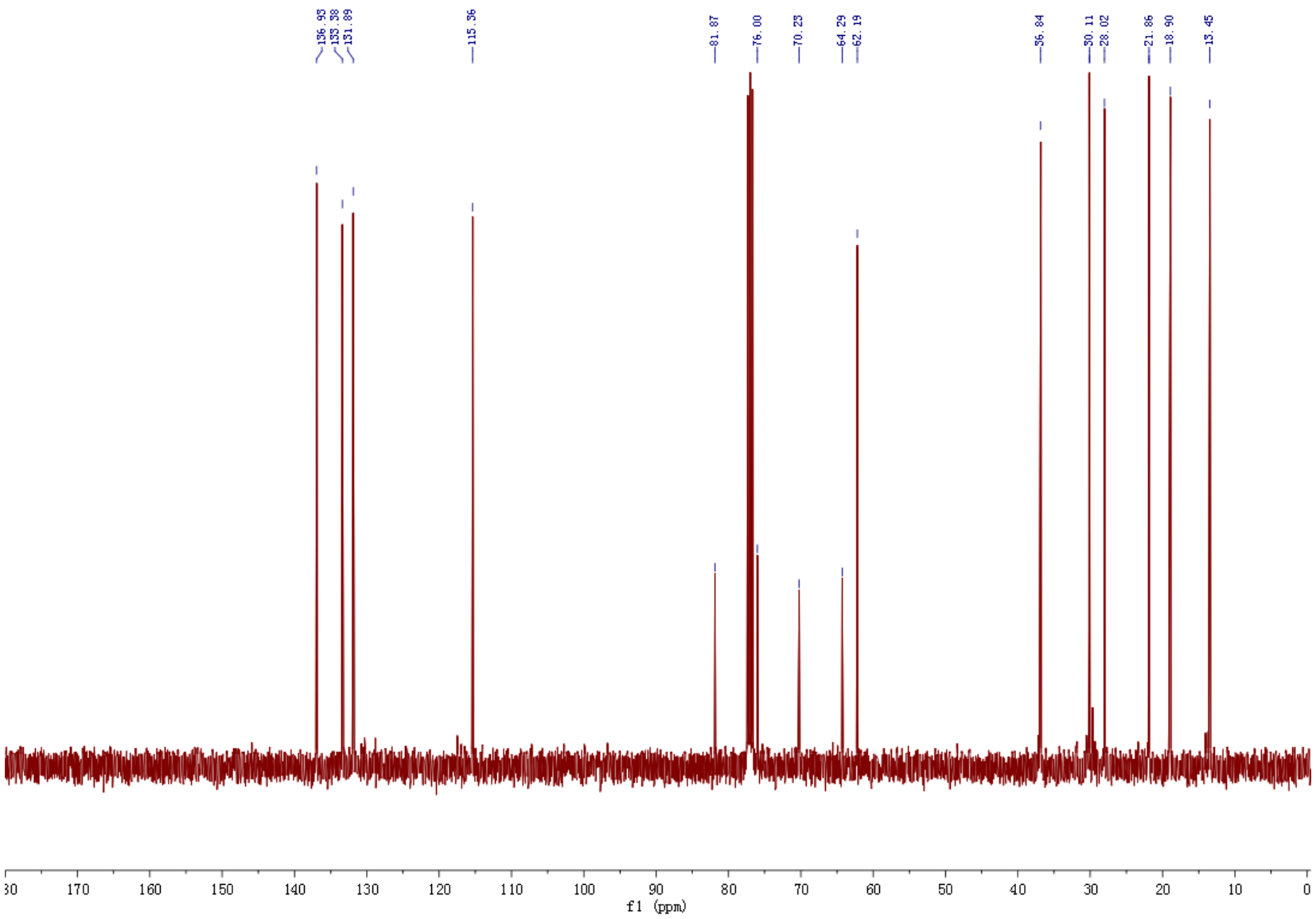

TBSO
HO
(S28)
1.00
0.93
0.94
0.99
0.92
0.94
1.97
4.21
0.97
2.06
4.22
9.55
5.91
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

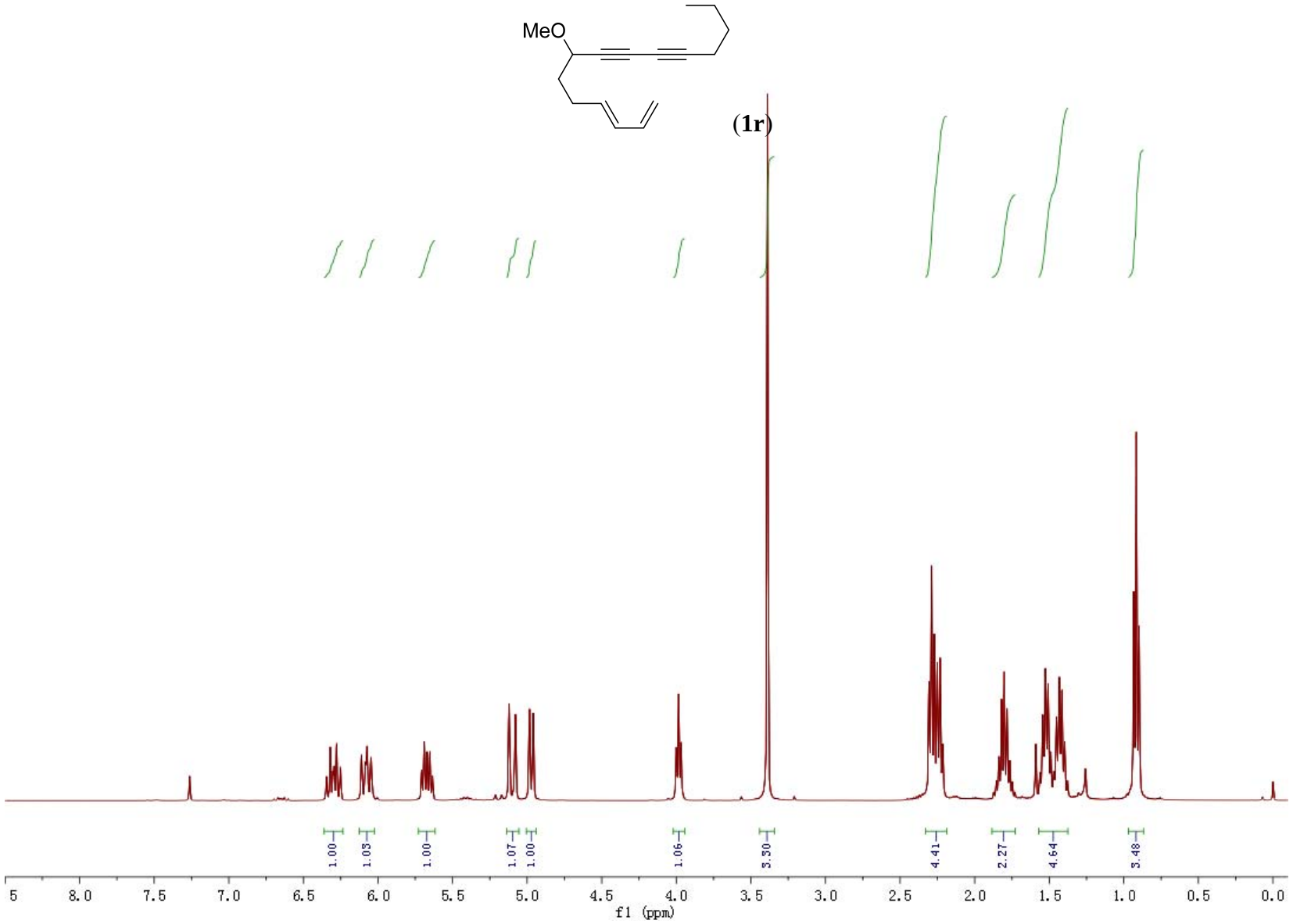

136.94
133.38
131.91
115.39
81.67
76.11
70.22
64.50
62.43
62.19
36.86
31.77
28.03
25.91
24.64
19.06
18.29
-5.35
f1 (ppm)

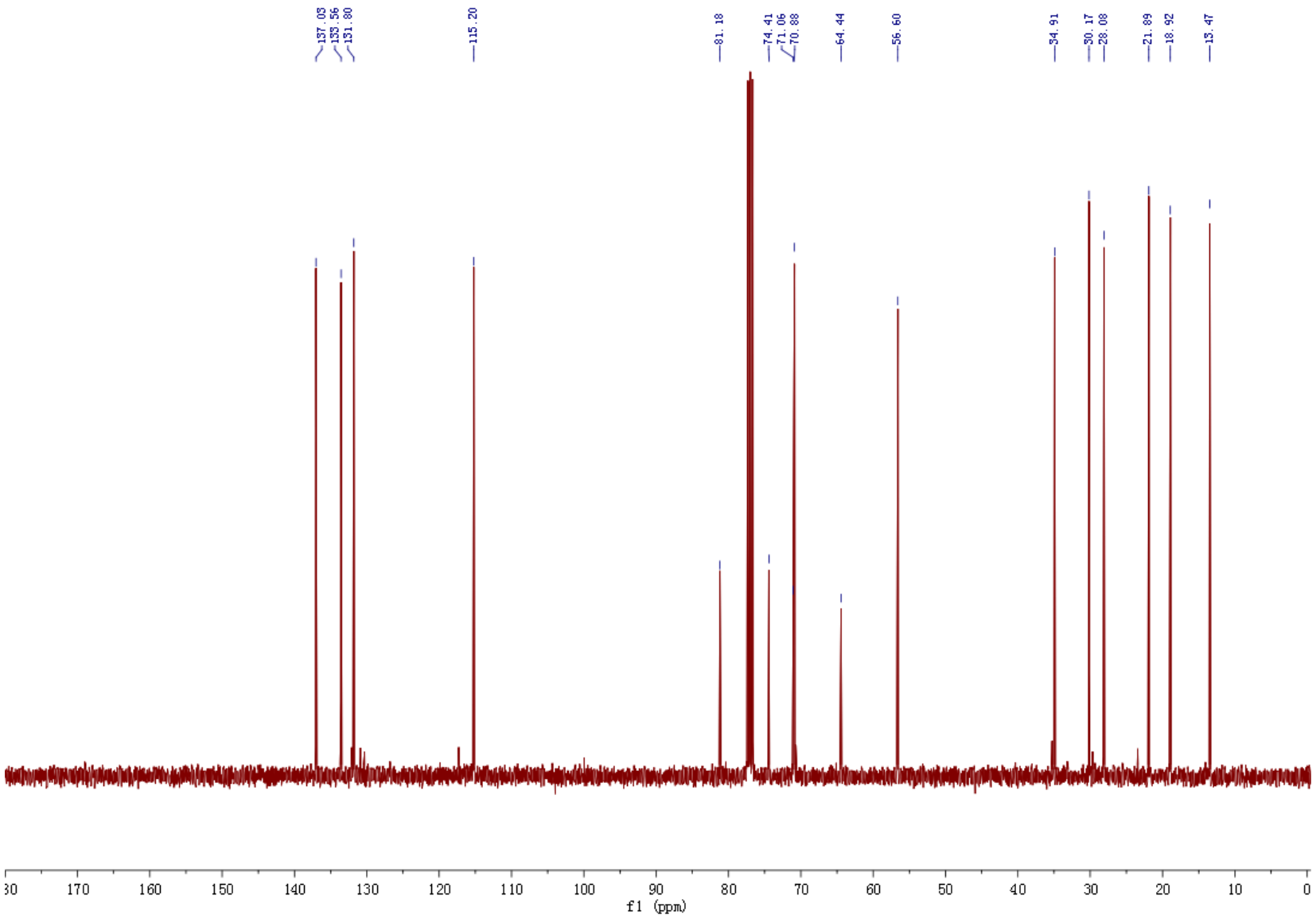

TBSO
AcO
(1q)
1.00
0.99
0.98
1.03
1.02
0.92
1.97
2.22
2.19
2.98
2.16
4.69
9.32
5.93
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

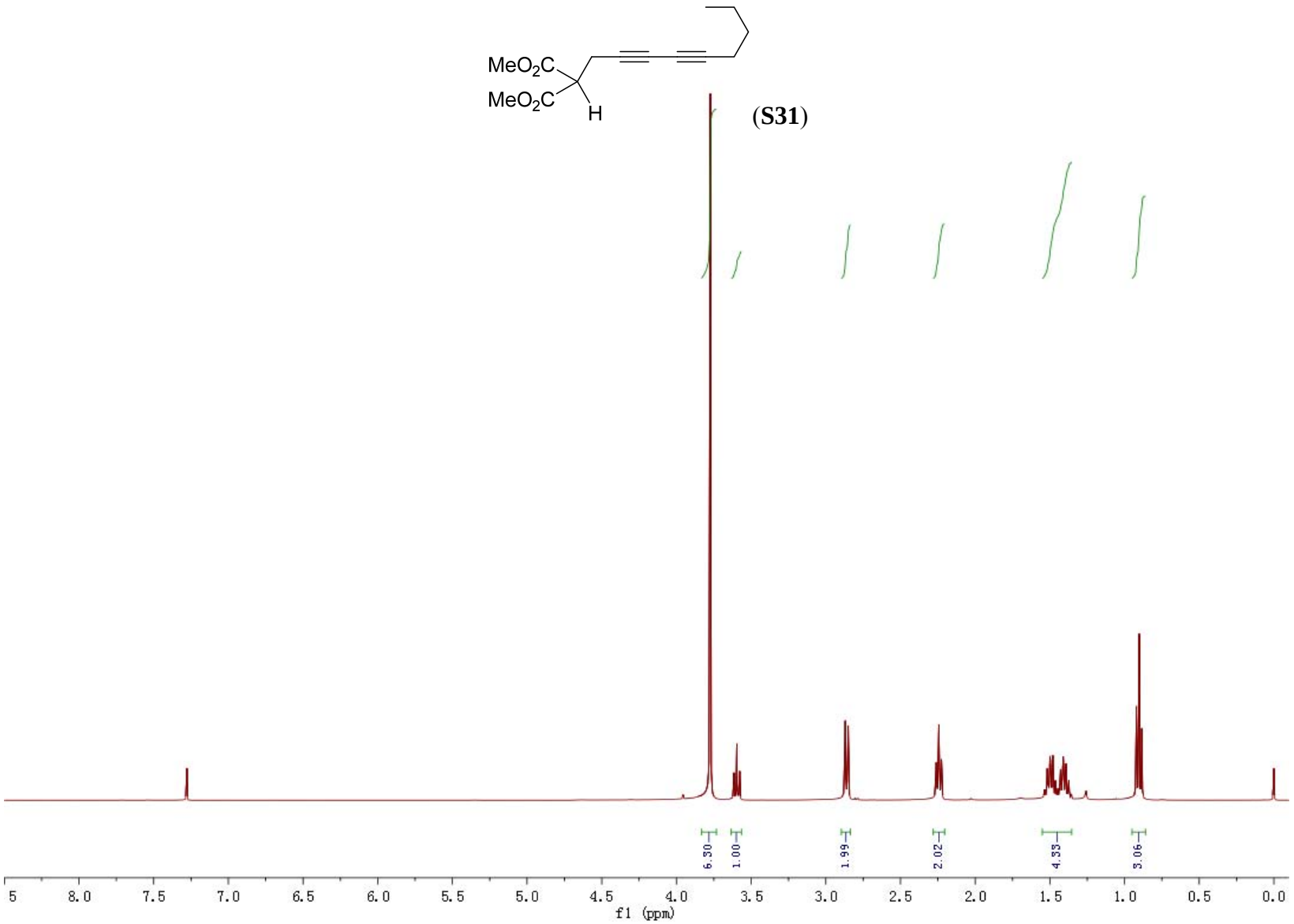

169.73
136.84
132.69
132.05
115.60
81.89
72.39
70.67
64.45
63.76
62.39
34.03
31.76
27.93
25.91
24.59
20.87
19.04
18.29
f1 (ppm)

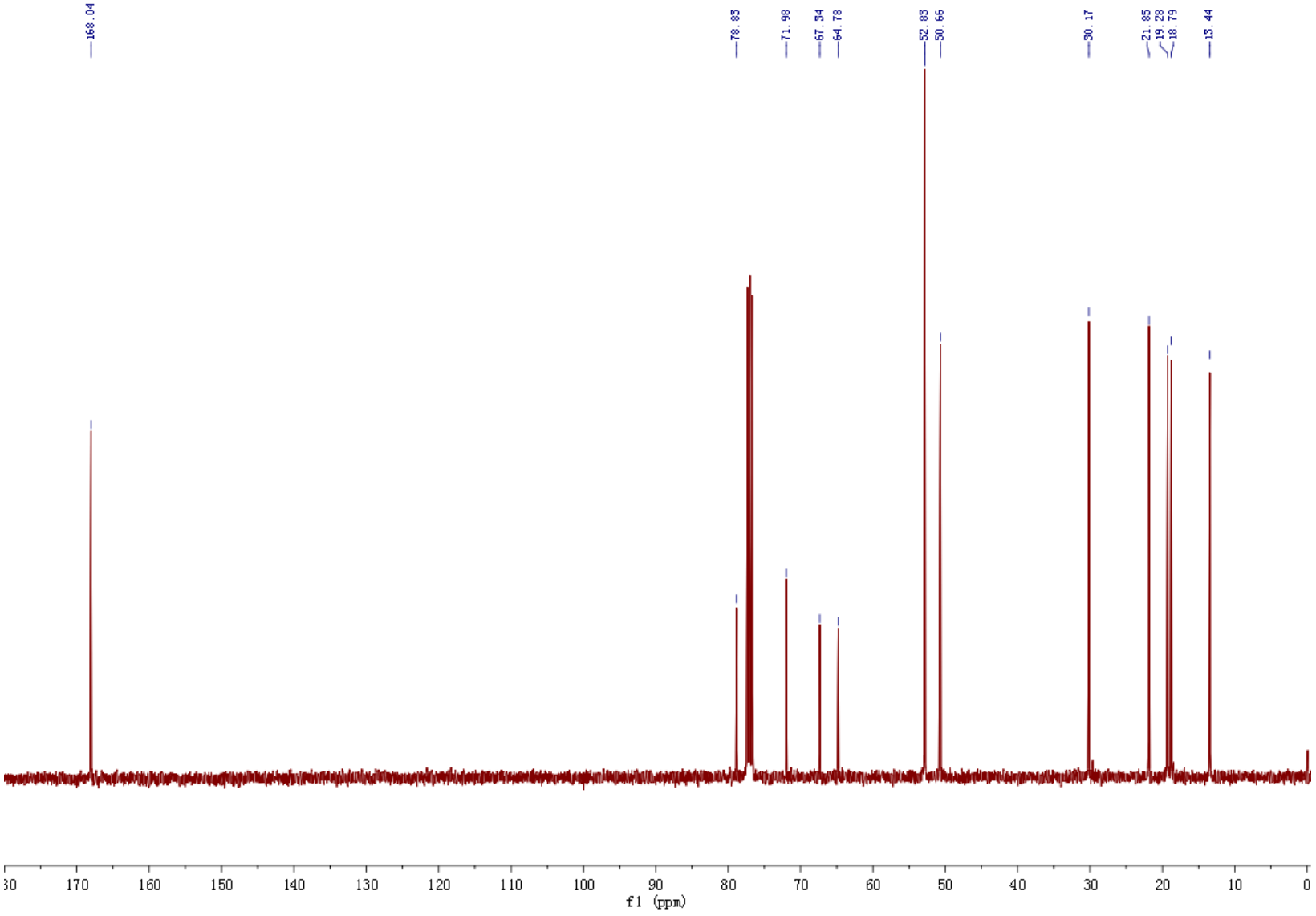

HO
(S29)
1.00
0.98
0.96
1.05
0.94
1.00
4.19
1.08
2.17
4.49
3.14
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

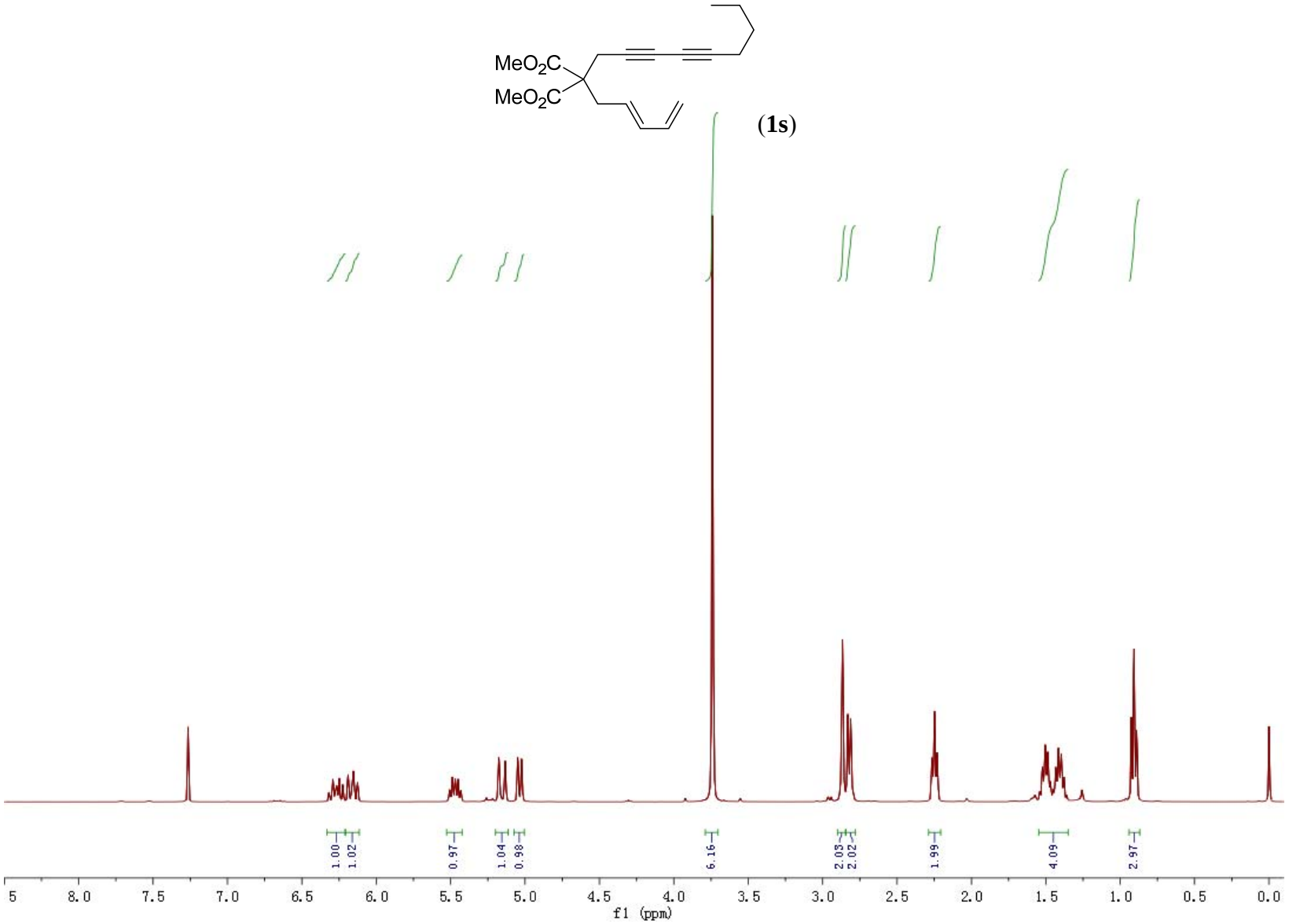

186.93
155.38
131.89
115.36
81.87
76.00
70.23
64.29
62.19
36.84
30.11
28.02
21.86
18.90
13.45
f1 (ppm)

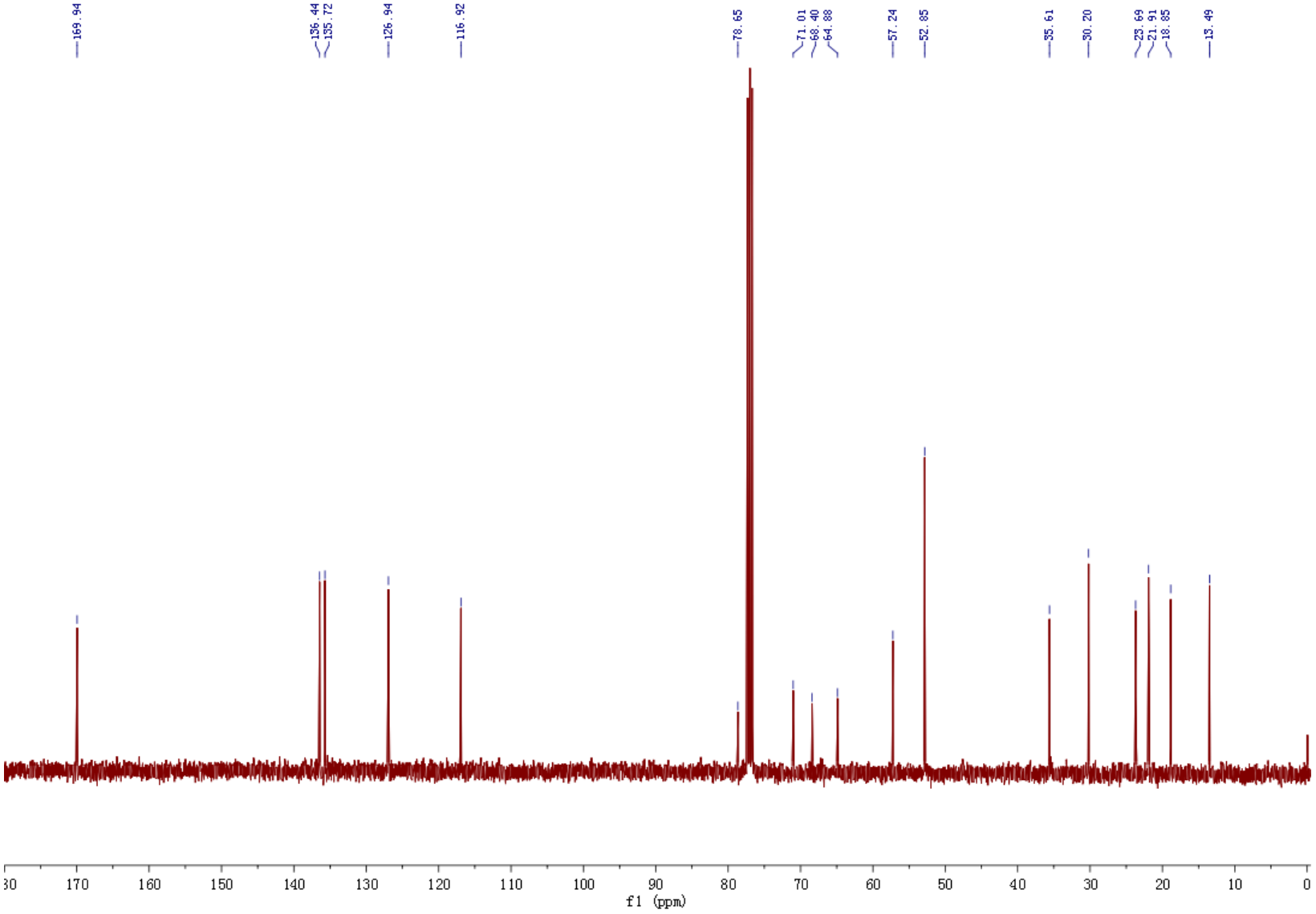

MeO
(1r)
1.00
1.03
1.00
1.07
1.00
1.06
3.30
4.41
2.27
4.64
3.48
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

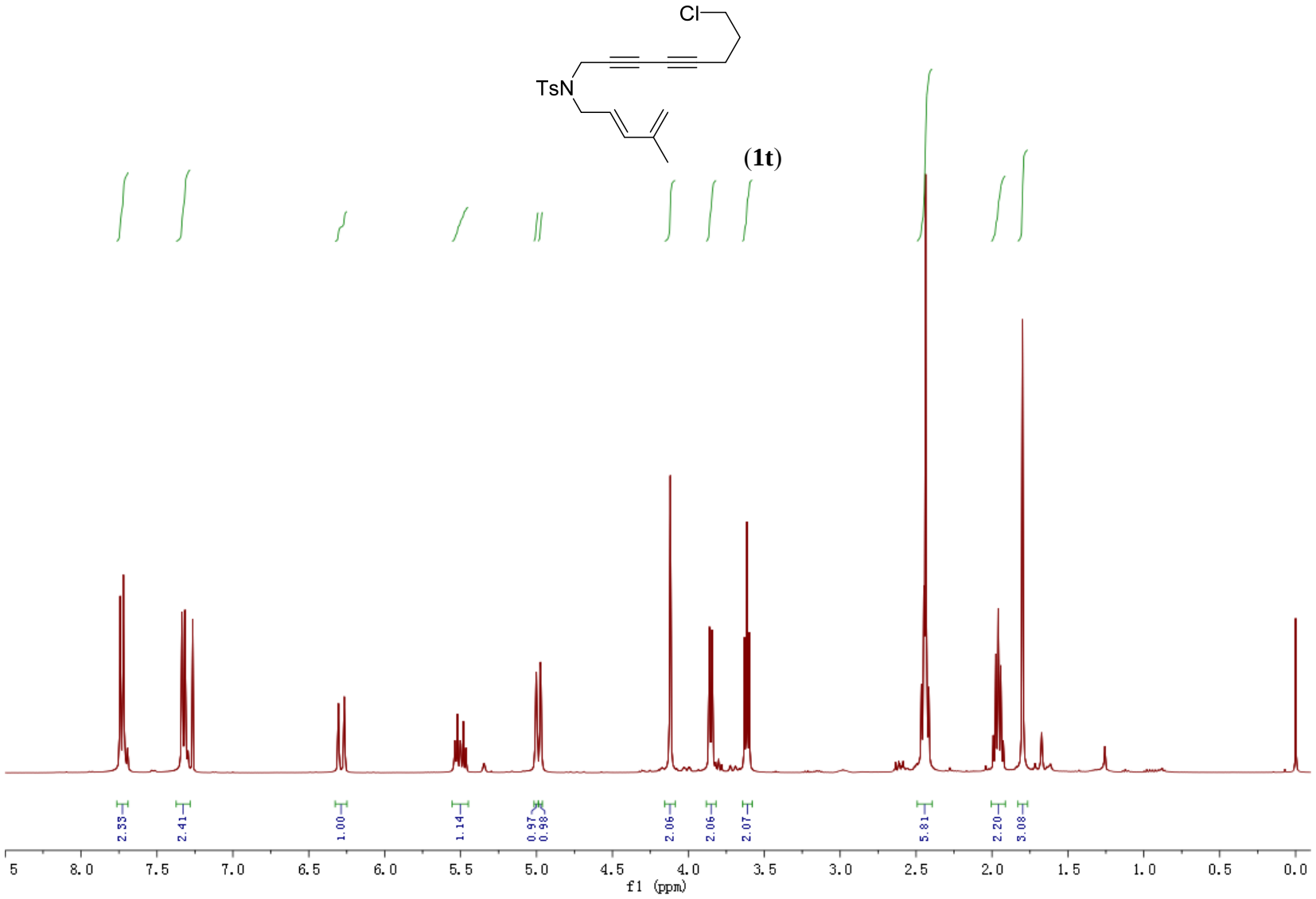

137.03
133.56
131.80
115.20
81.18
74.41
71.06
70.88
64.44
56.60
34.91
30.17
28.08
21.89
18.92
13.47
f1 (ppm)

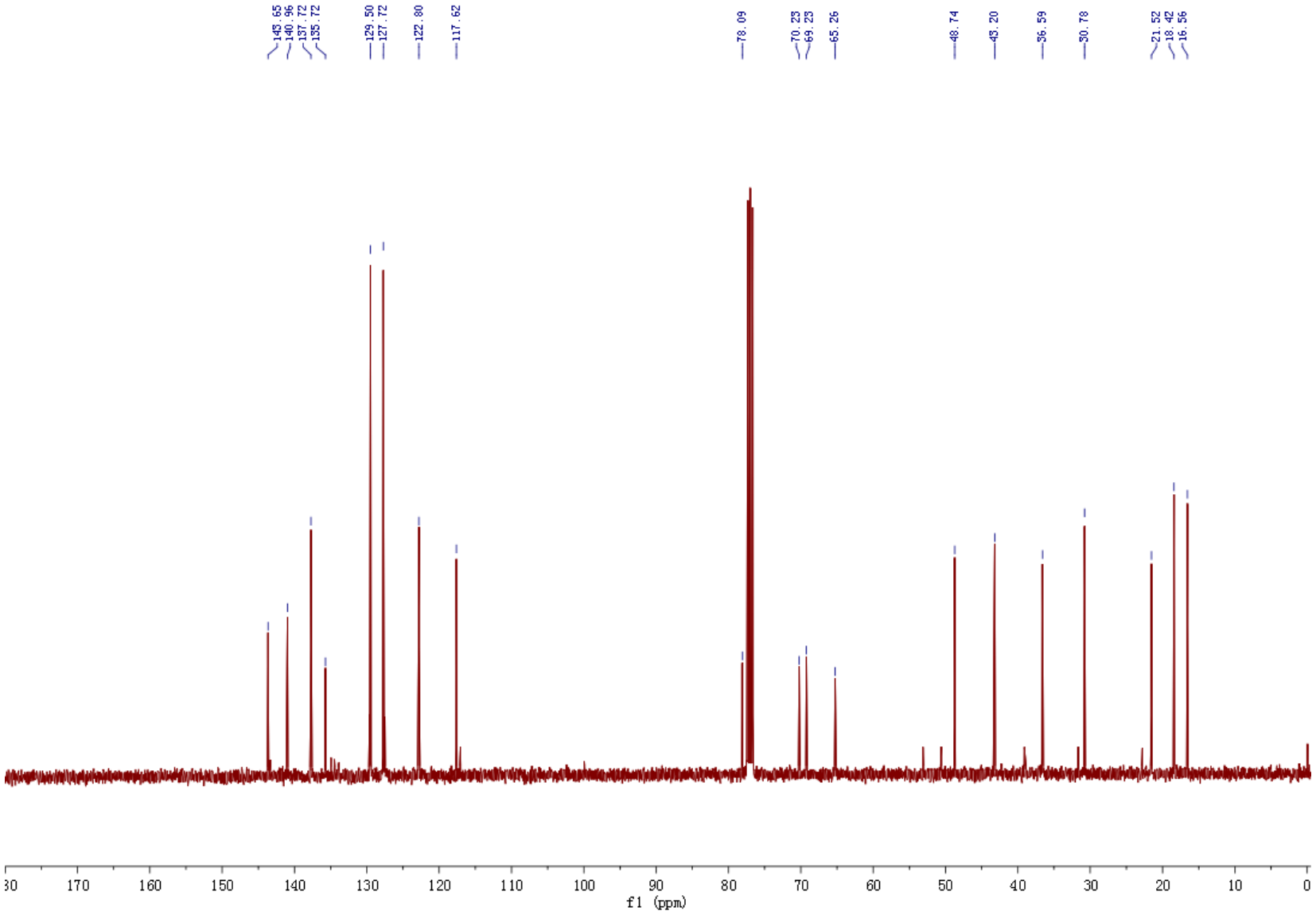

MeO2C
MeO2C
H
(S31)
6.30
1.00
1.99
2.02
4.33
3.06
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

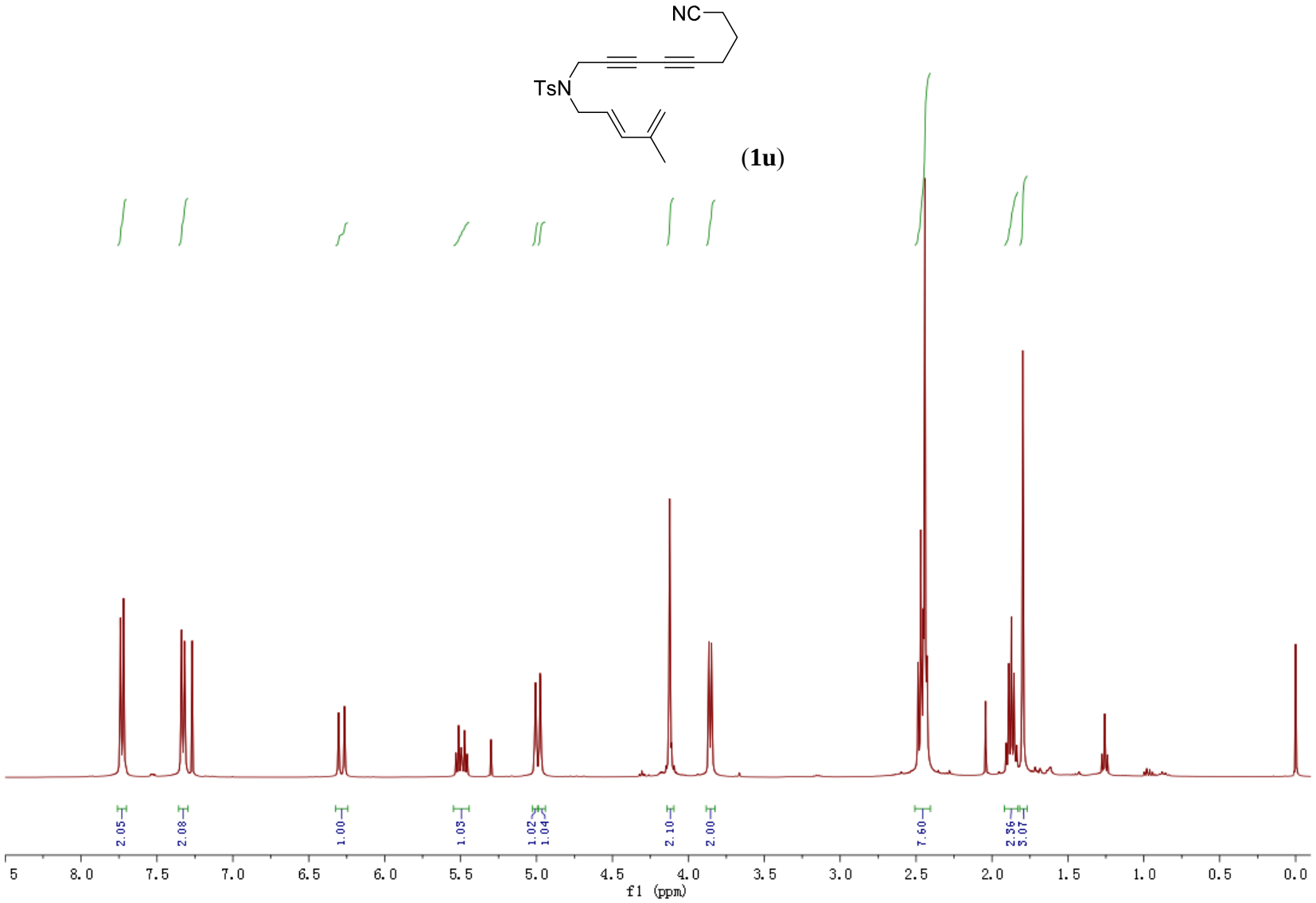

168.04
78.83
71.98
67.34
64.78
52.83
50.66
30.17
21.85
19.28
18.79
13.44
f1 (ppm)

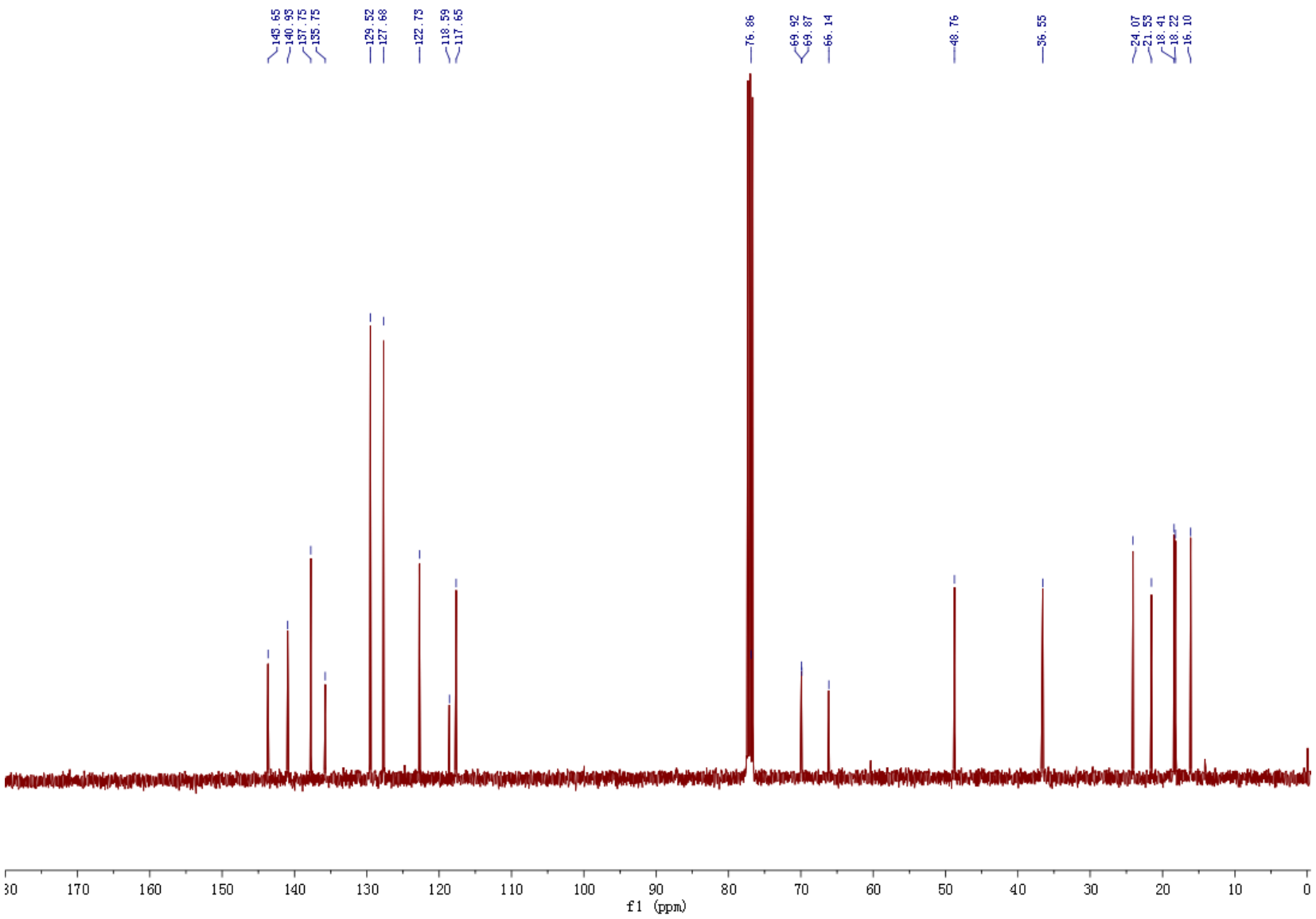

MeO2C
MeO2C
(1s)
1.00
1.02
0.97
1.04
0.98
6.16
2.03
2.02
1.99
4.09
2.97
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


169.94
136.44
135.72
126.94
116.92
78.65
71.01
68.40
64.88
57.24
52.85
55.61
30.20
23.69
21.91
18.85
13.49
f1 (ppm)


Cl
TsN
(1t)
2.33
2.41
1.00
1.14
0.97
0.98
2.06
2.06
2.07
5.81
2.20
3.08
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)

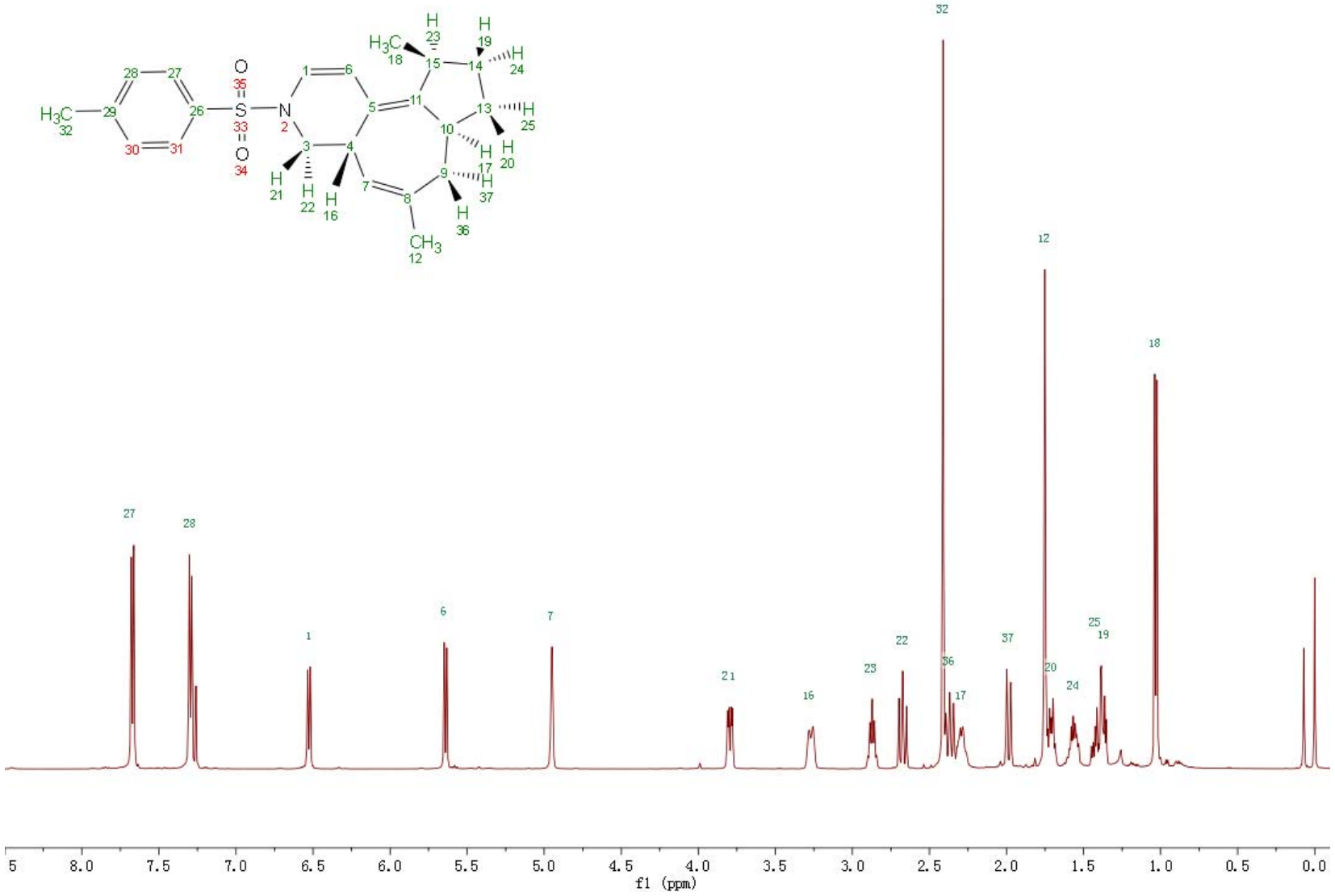

148.65
140.96
137.72
135.72
129.50
127.72
122.80
117.62
78.09
70.23
69.23
65.26
48.74
43.20
36.59
30.78
21.52
18.42
16.56
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

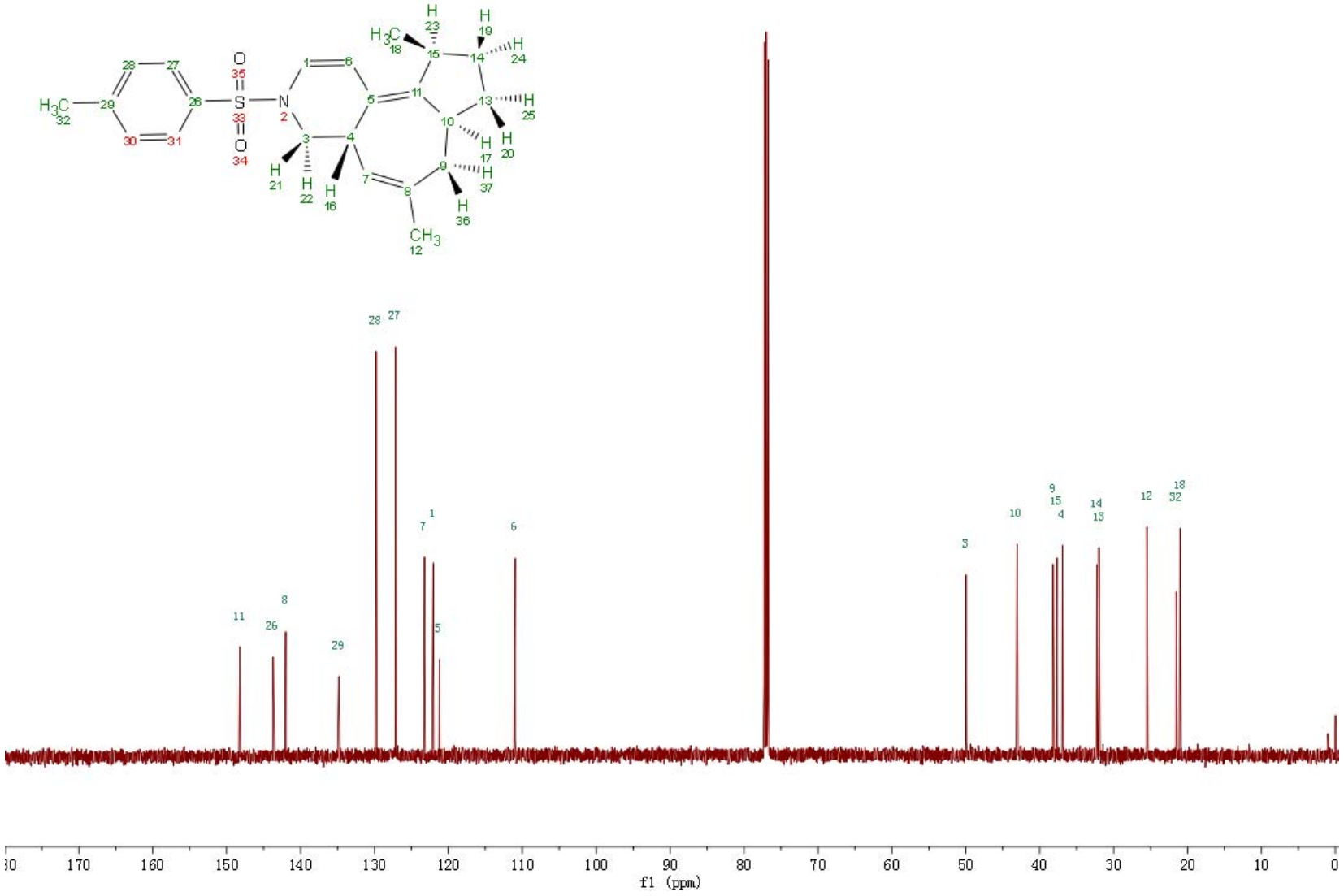

NC
TsN
(1u)
2.05
2.08
1.00
1.03
1.02
1.04
2.10
2.00
7.60
2.36
3.07
5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


143.65
140.93
137.75
135.75
129.52
127.68
122.73
118.59
117.65
76.86
69.92
69.87
66.14
48.76
36.55
24.07
21.55
18.41
18.22
16.10
f1 (ppm)

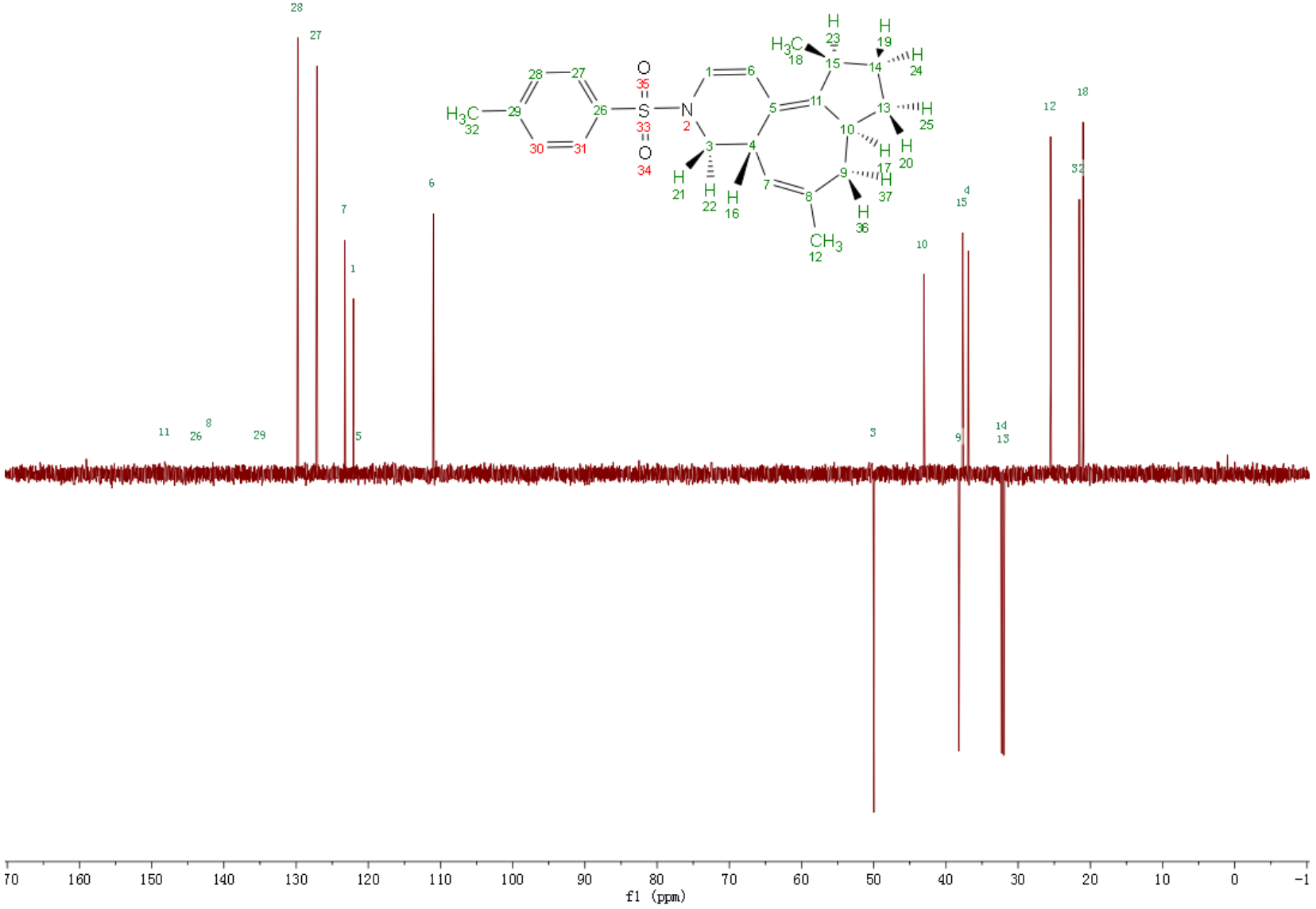
S4. 2D NMR Spectra of Representative New Compounds

2a

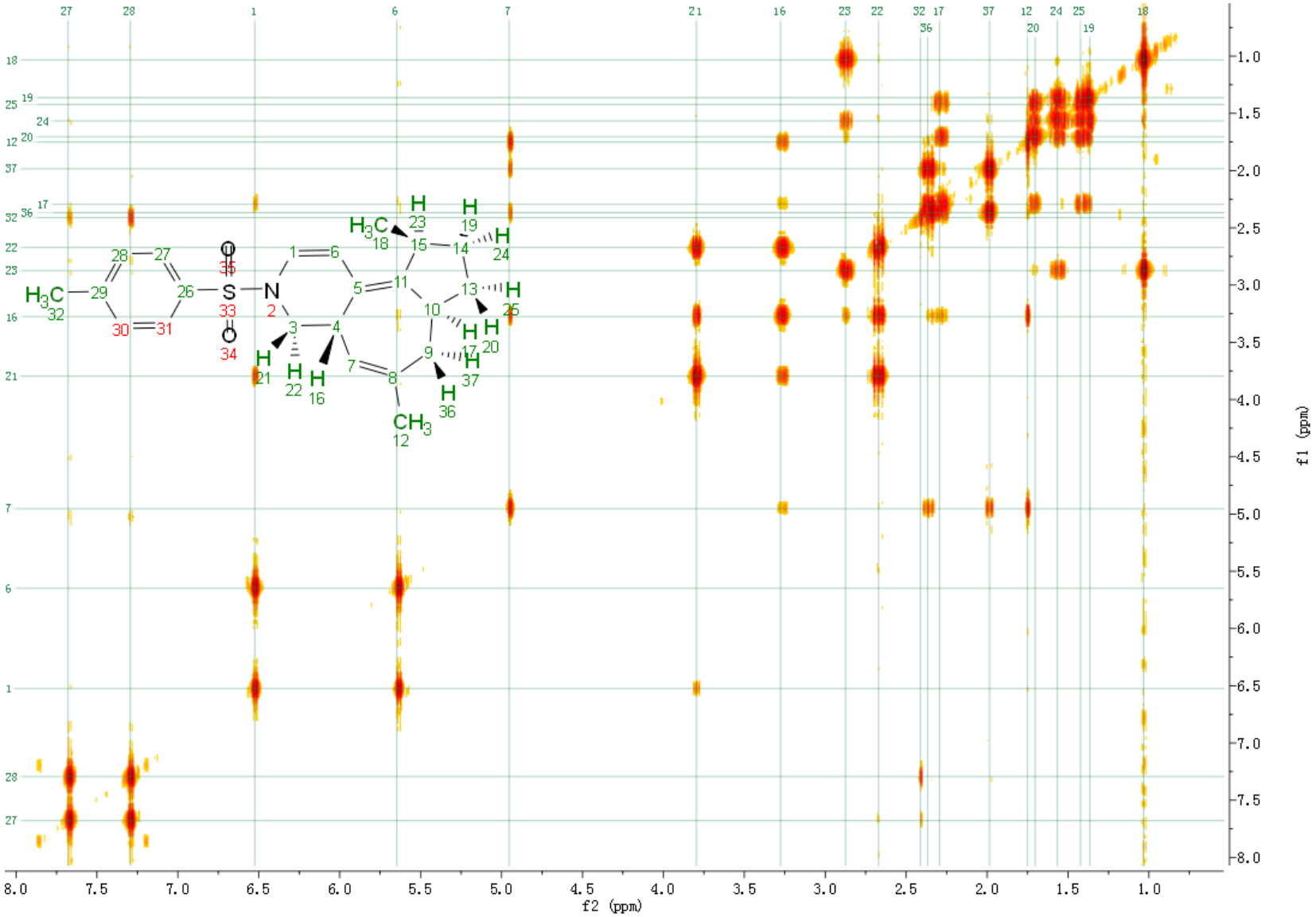



f1 (ppm)

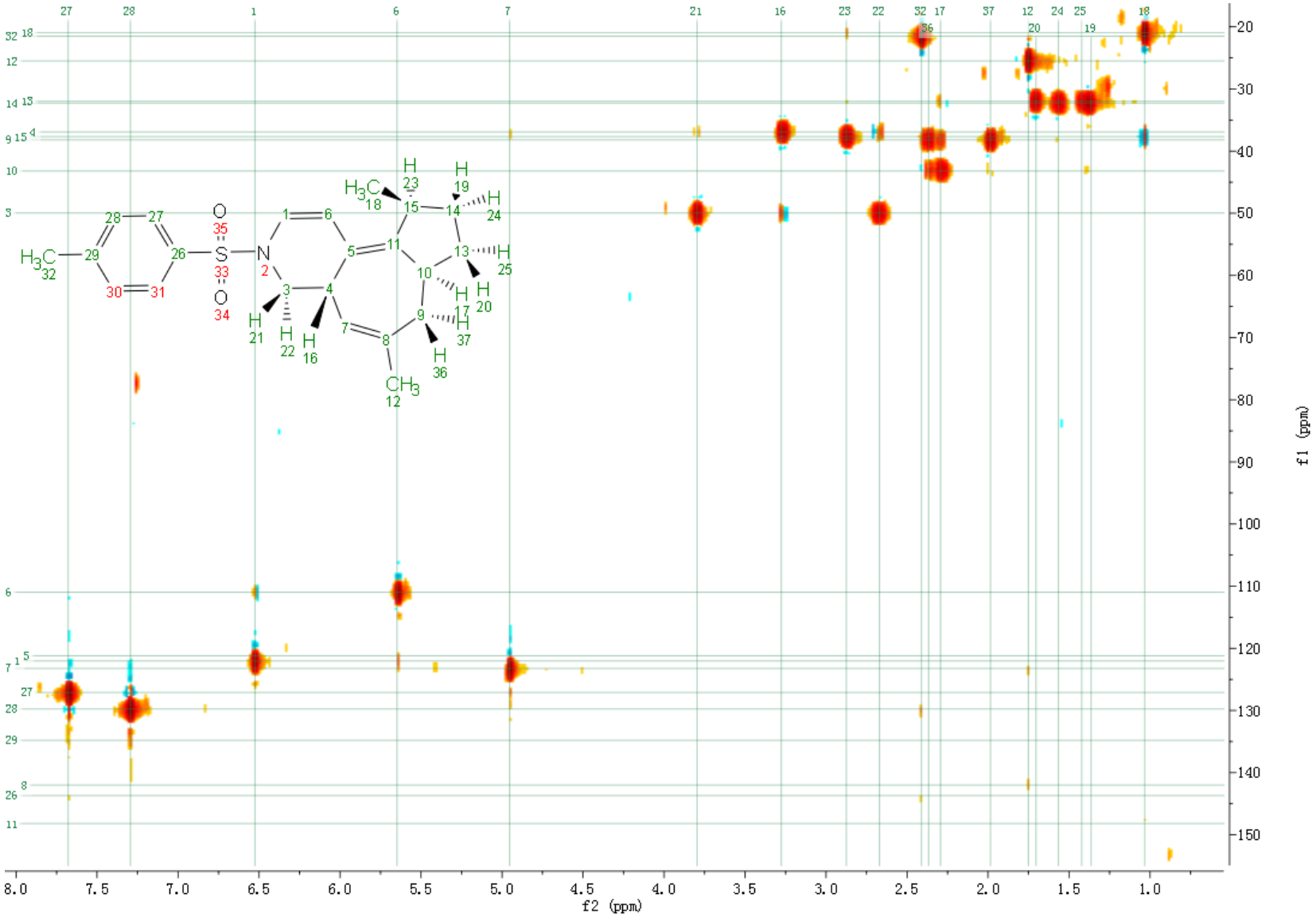
DEPT



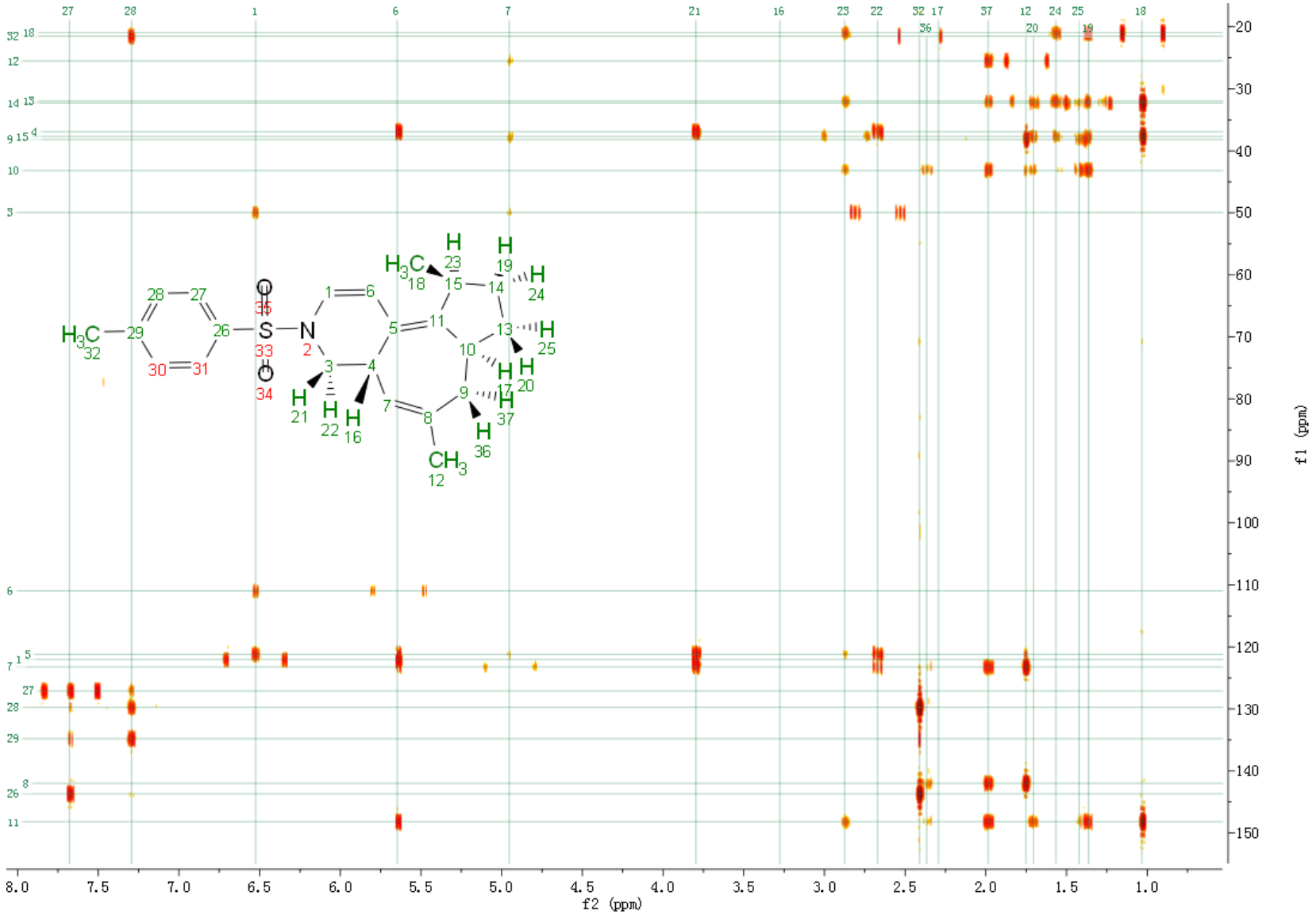
COSY



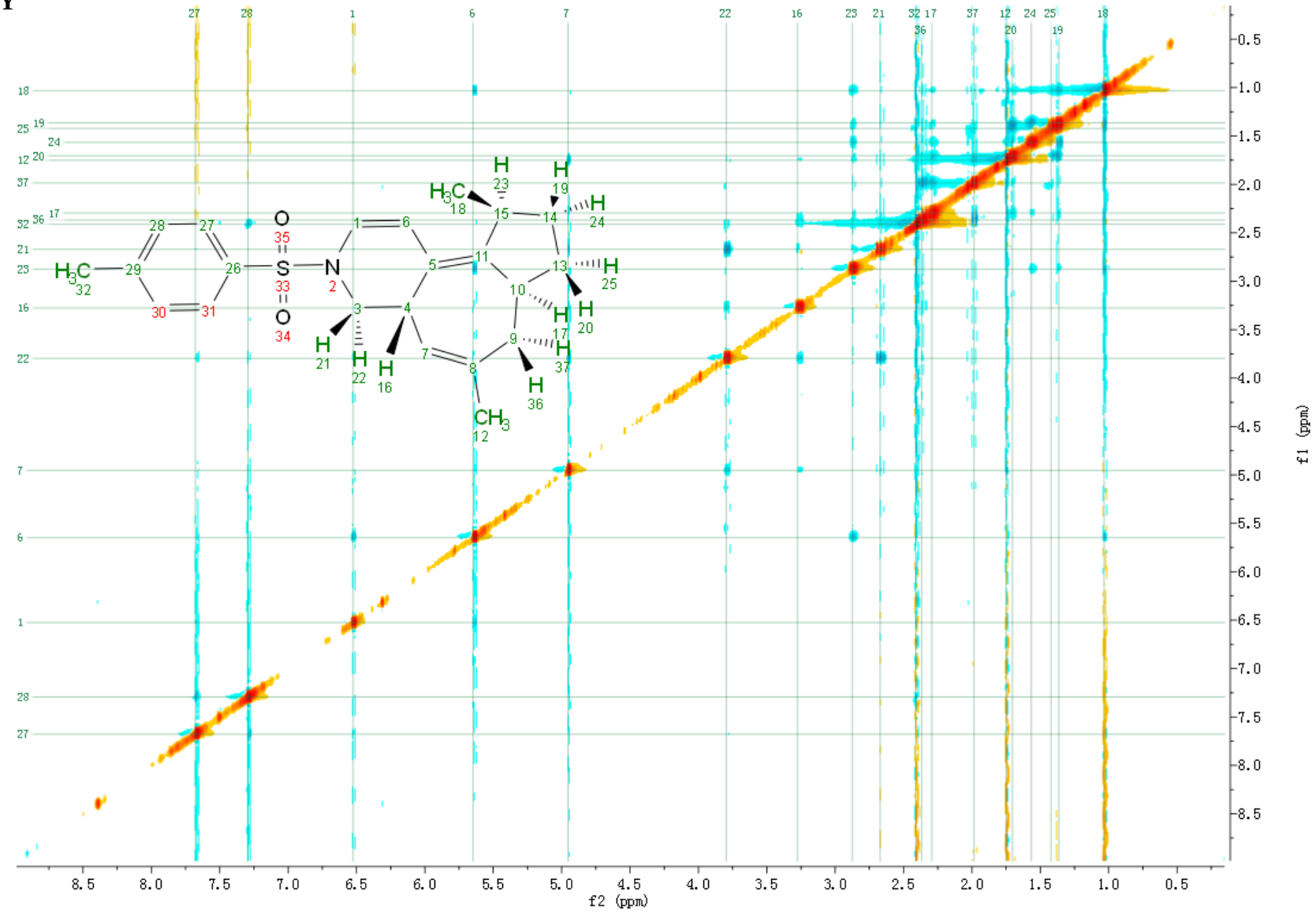
HSQC



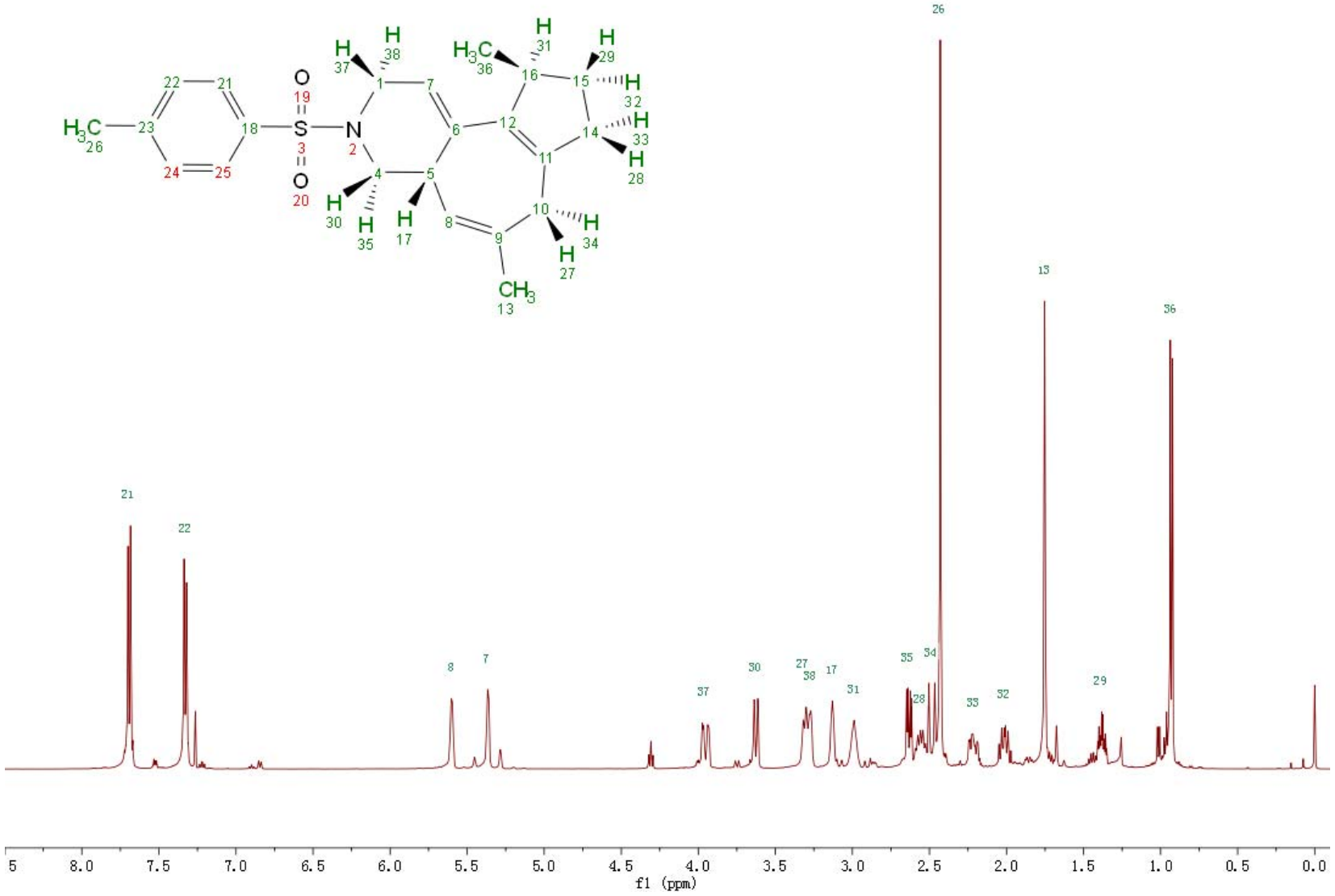
HMBC

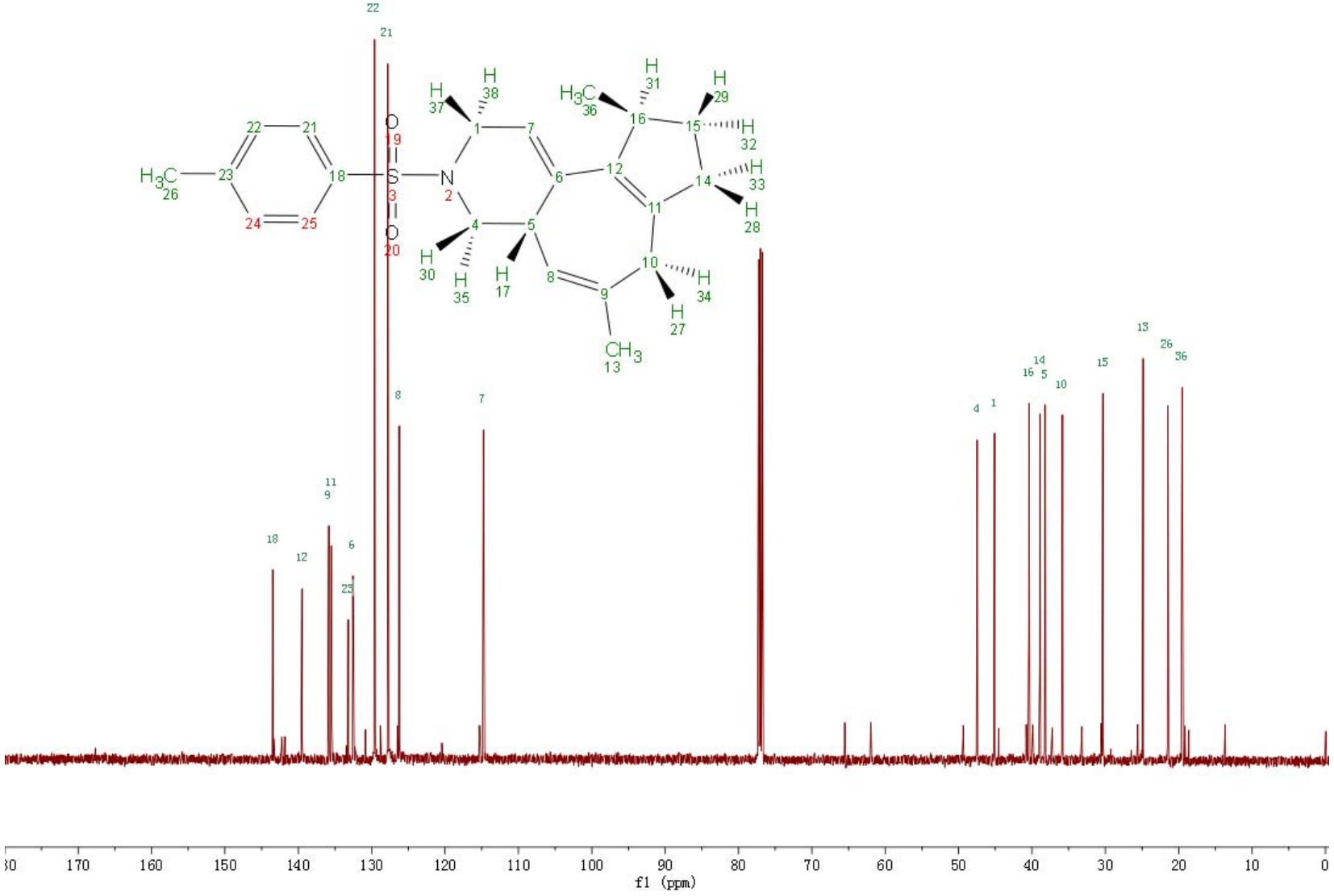


NOESY

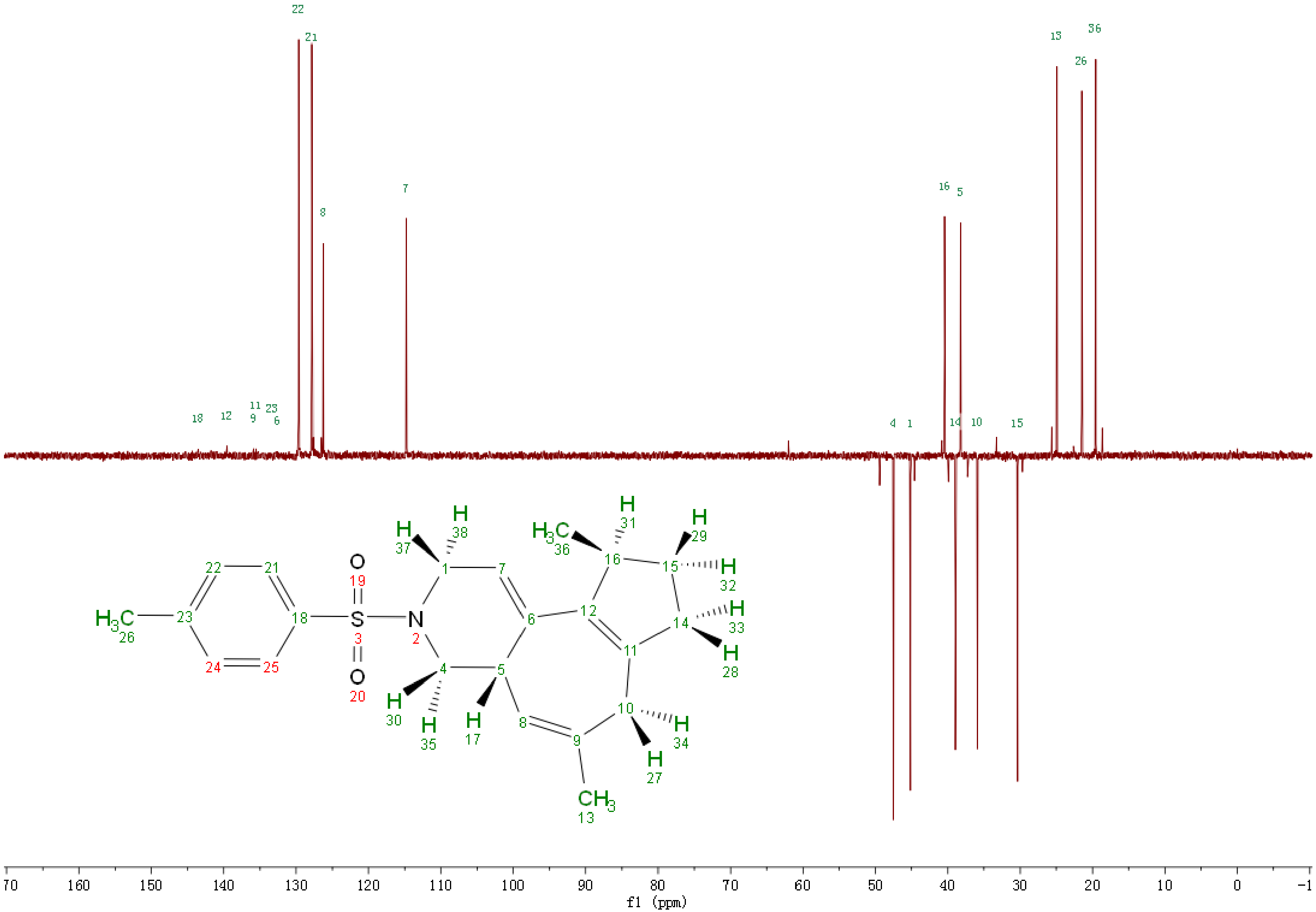


3a

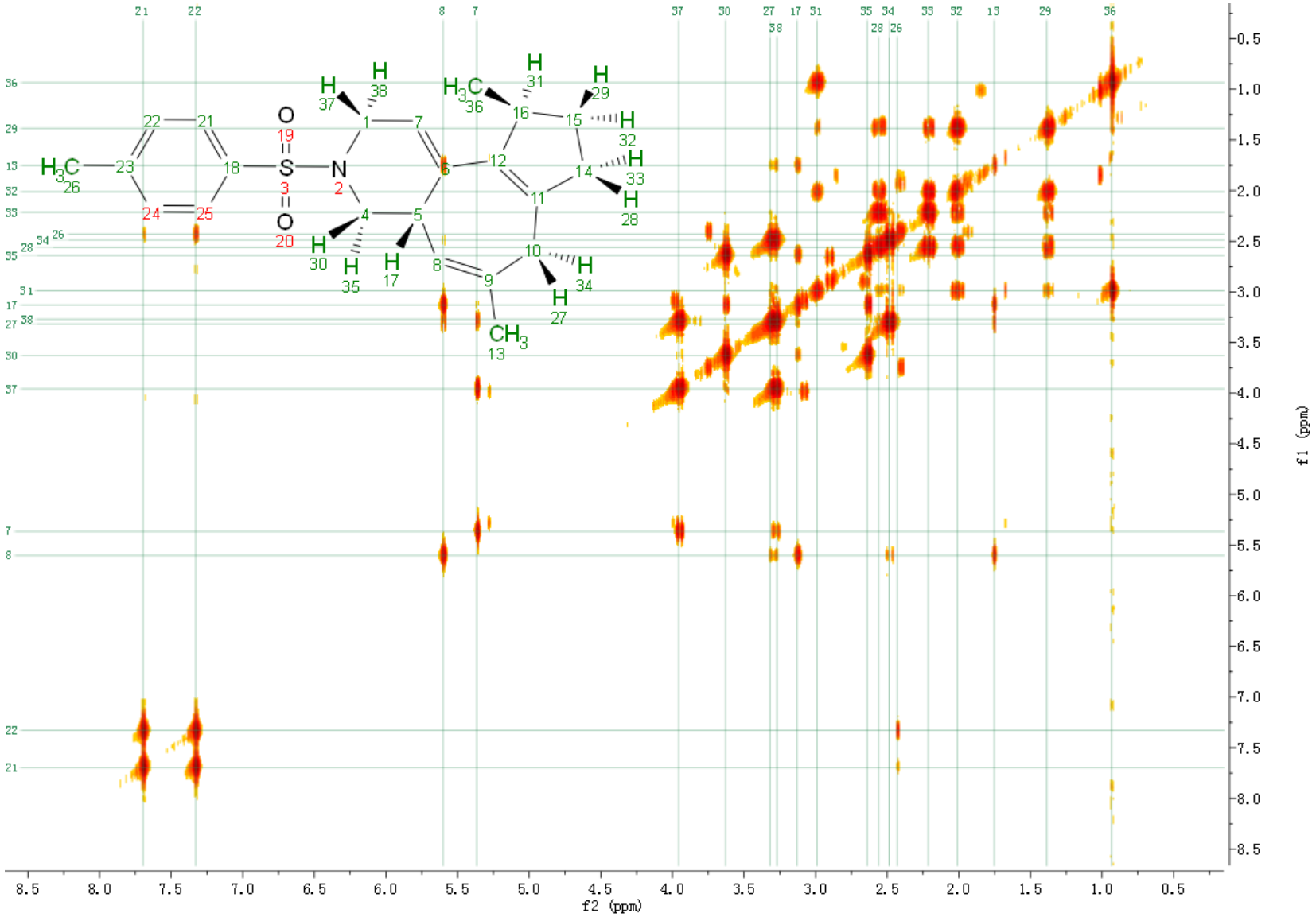



f1 (ppm)

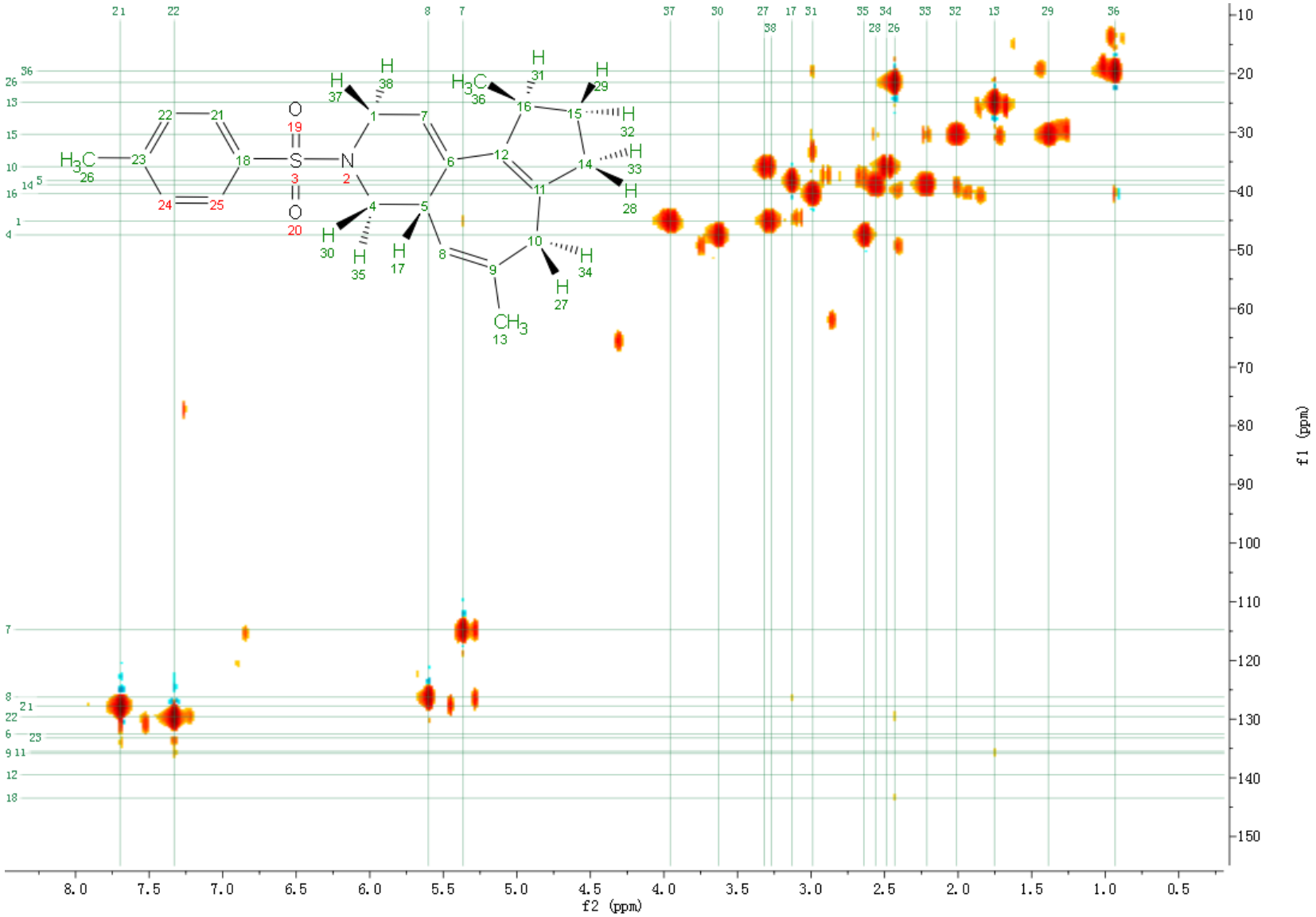
DEPT


22
21
8
7
18
12
11
9
23
6
4
1
16
5
14
10
15
13
26
36
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

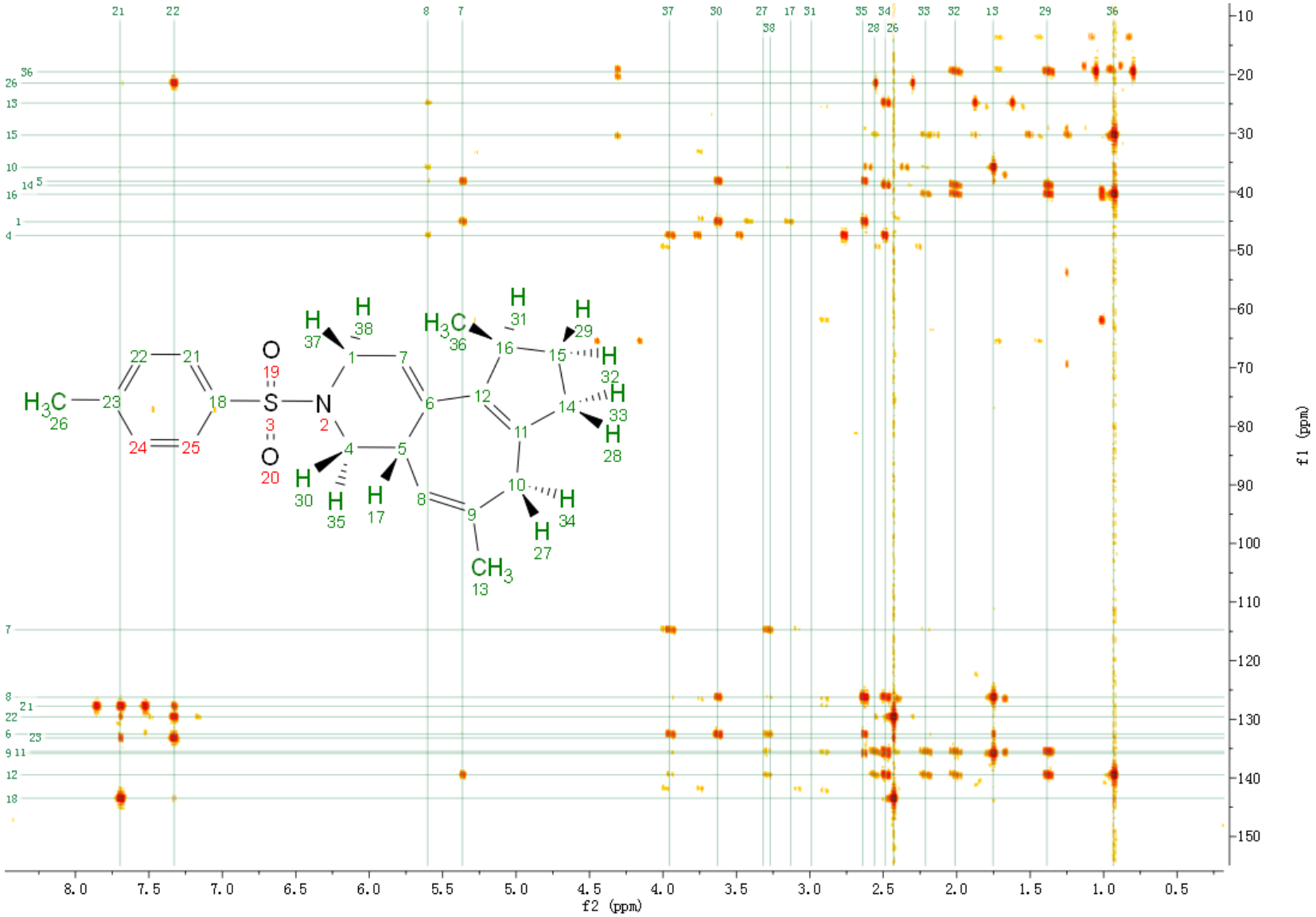
COSY



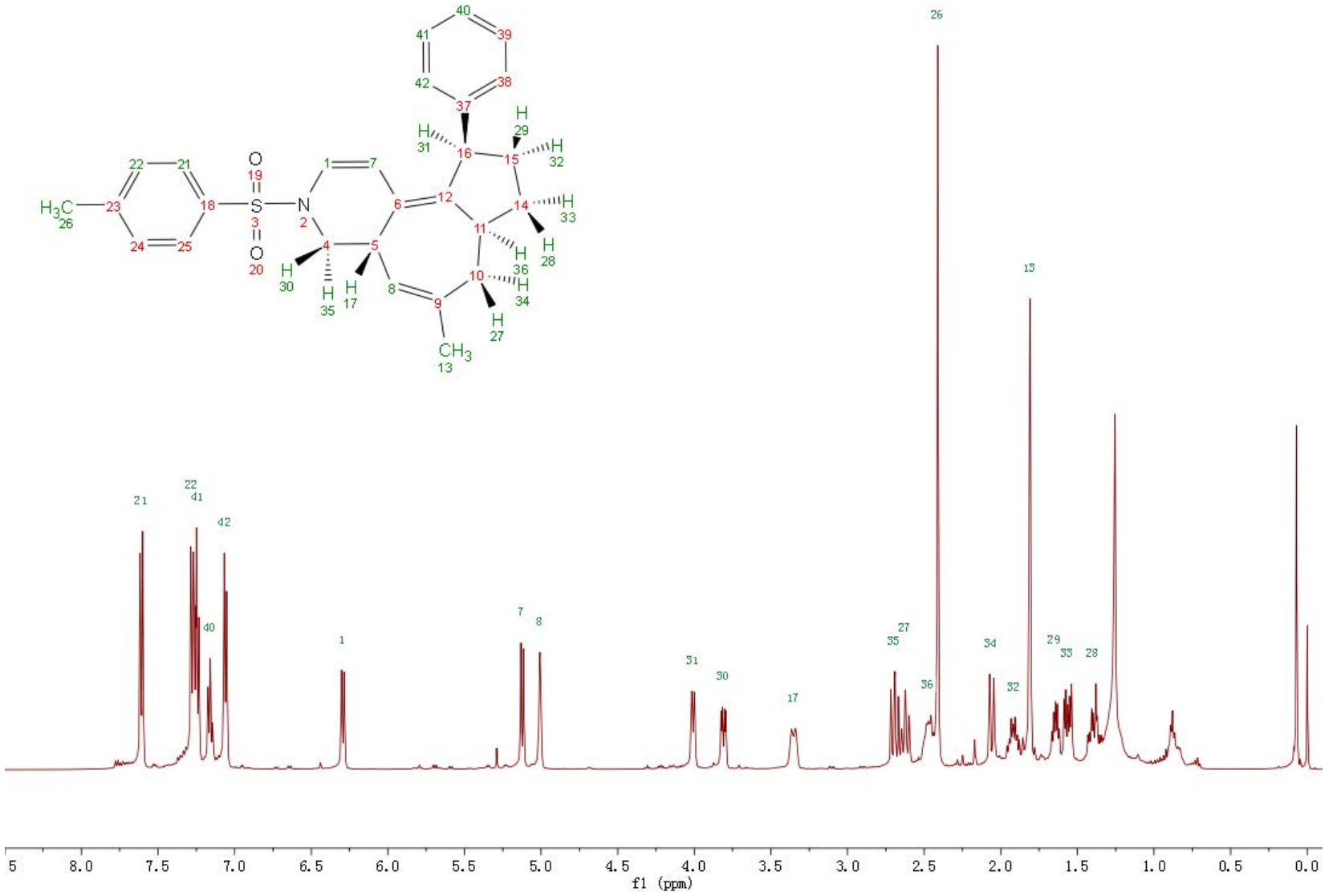
HSQC



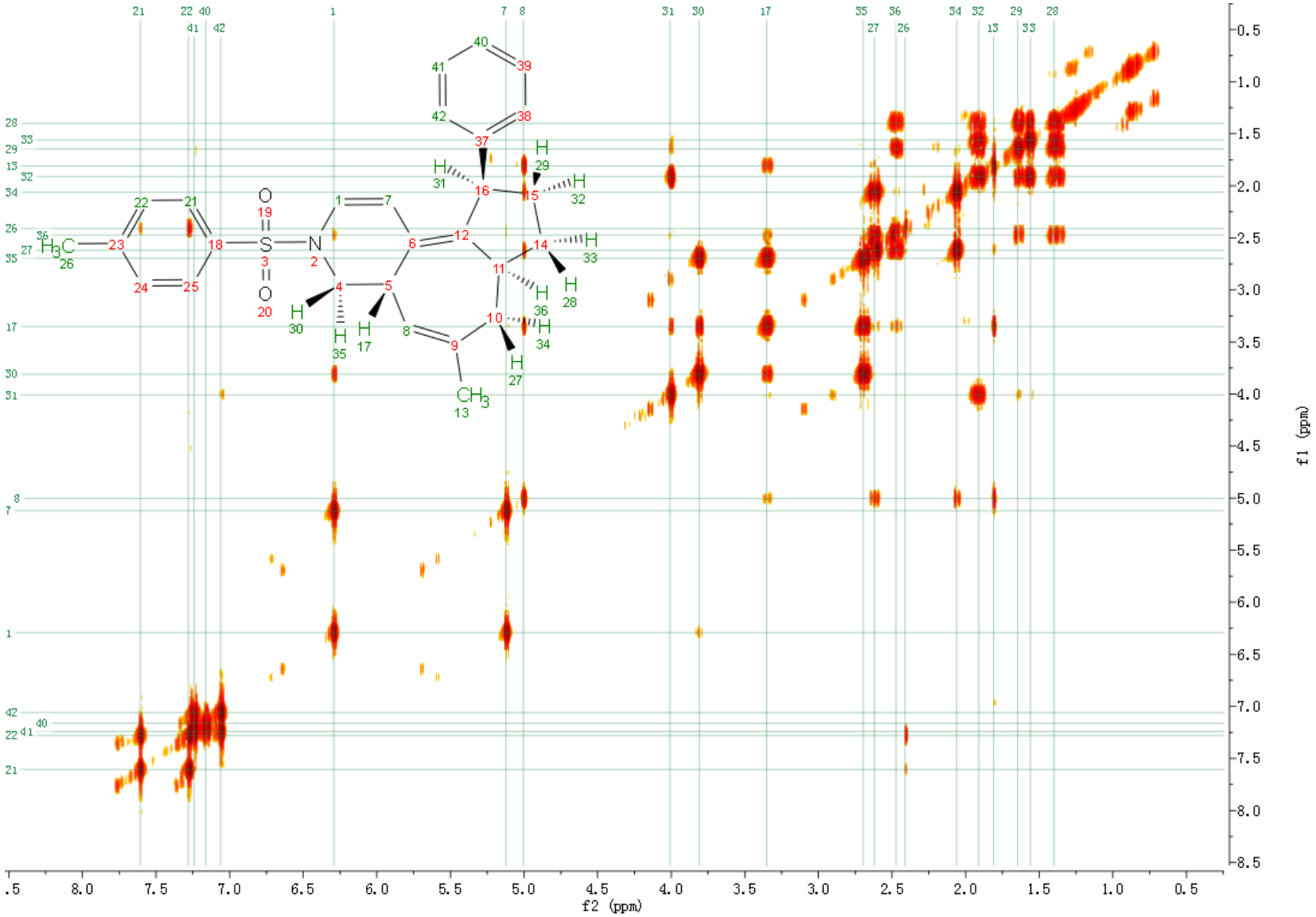
HMBC



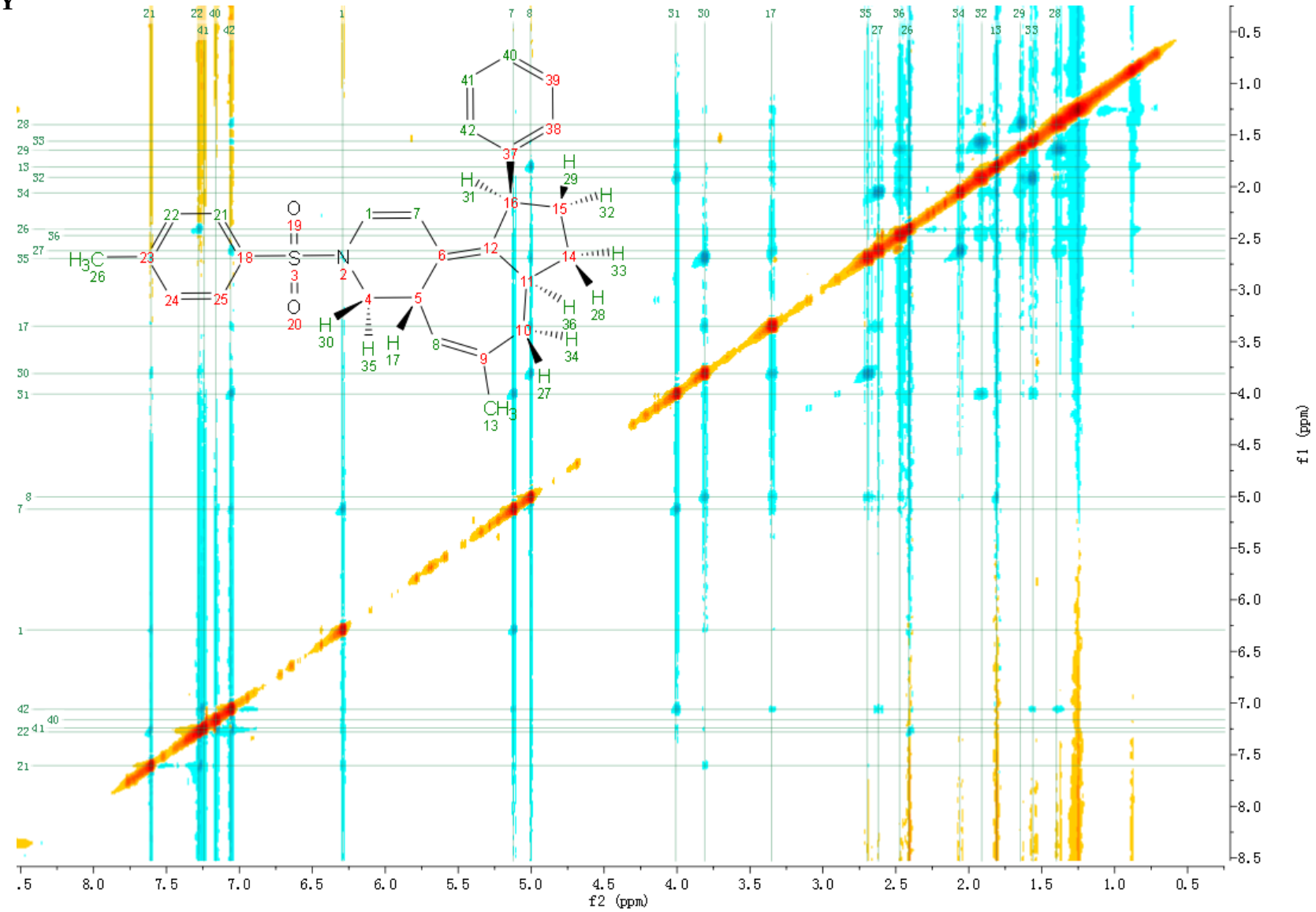
2f



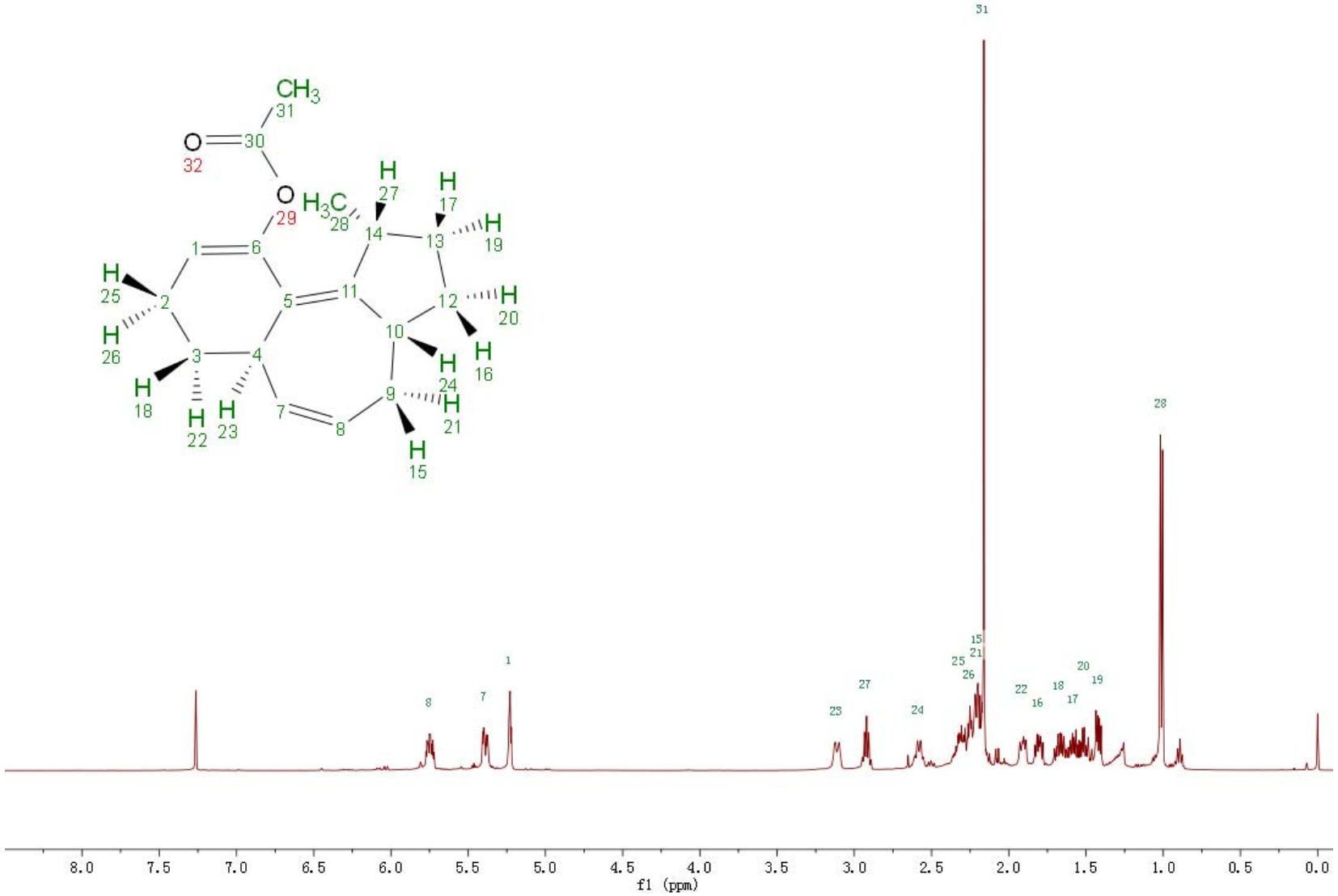
COSY

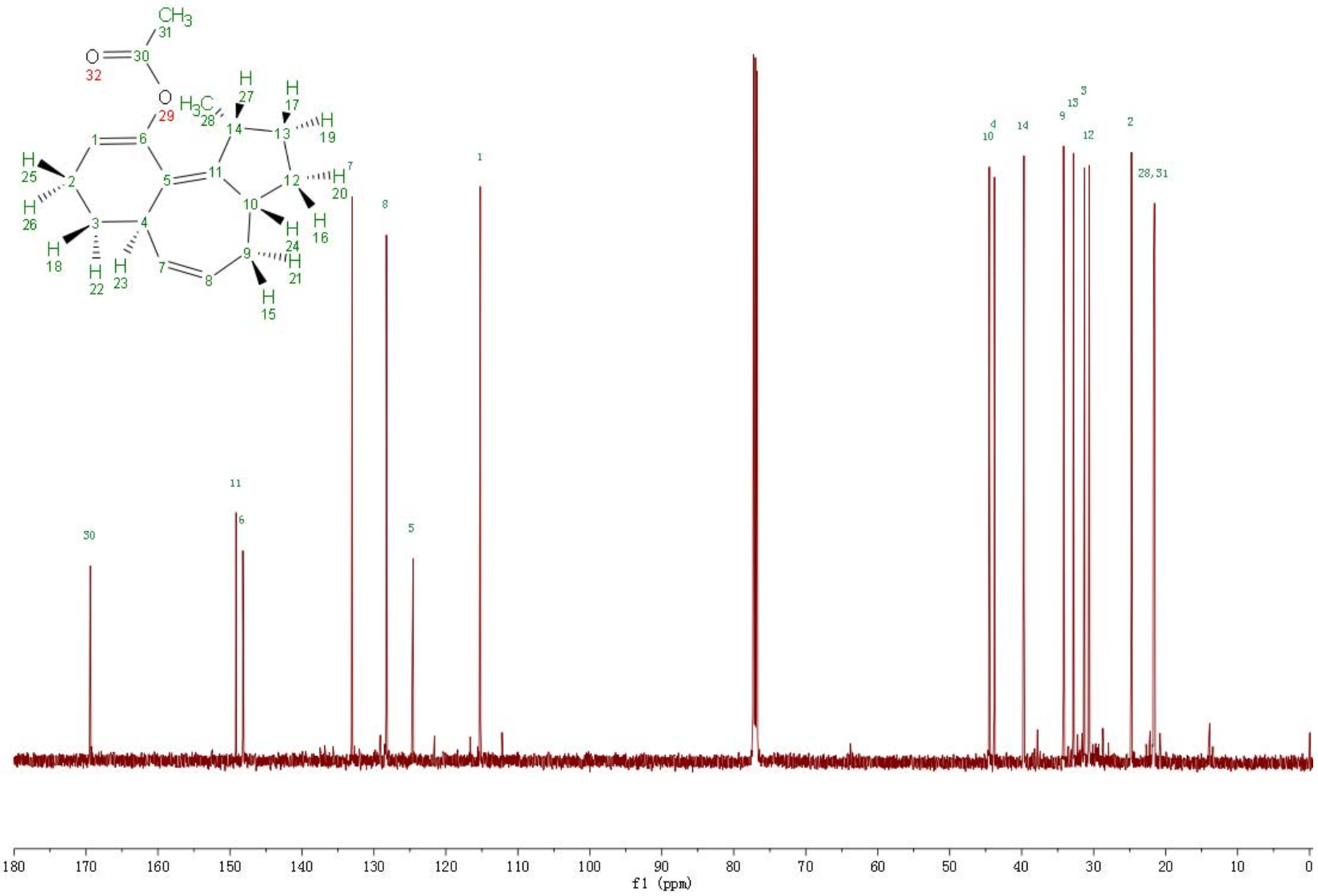


NOESY

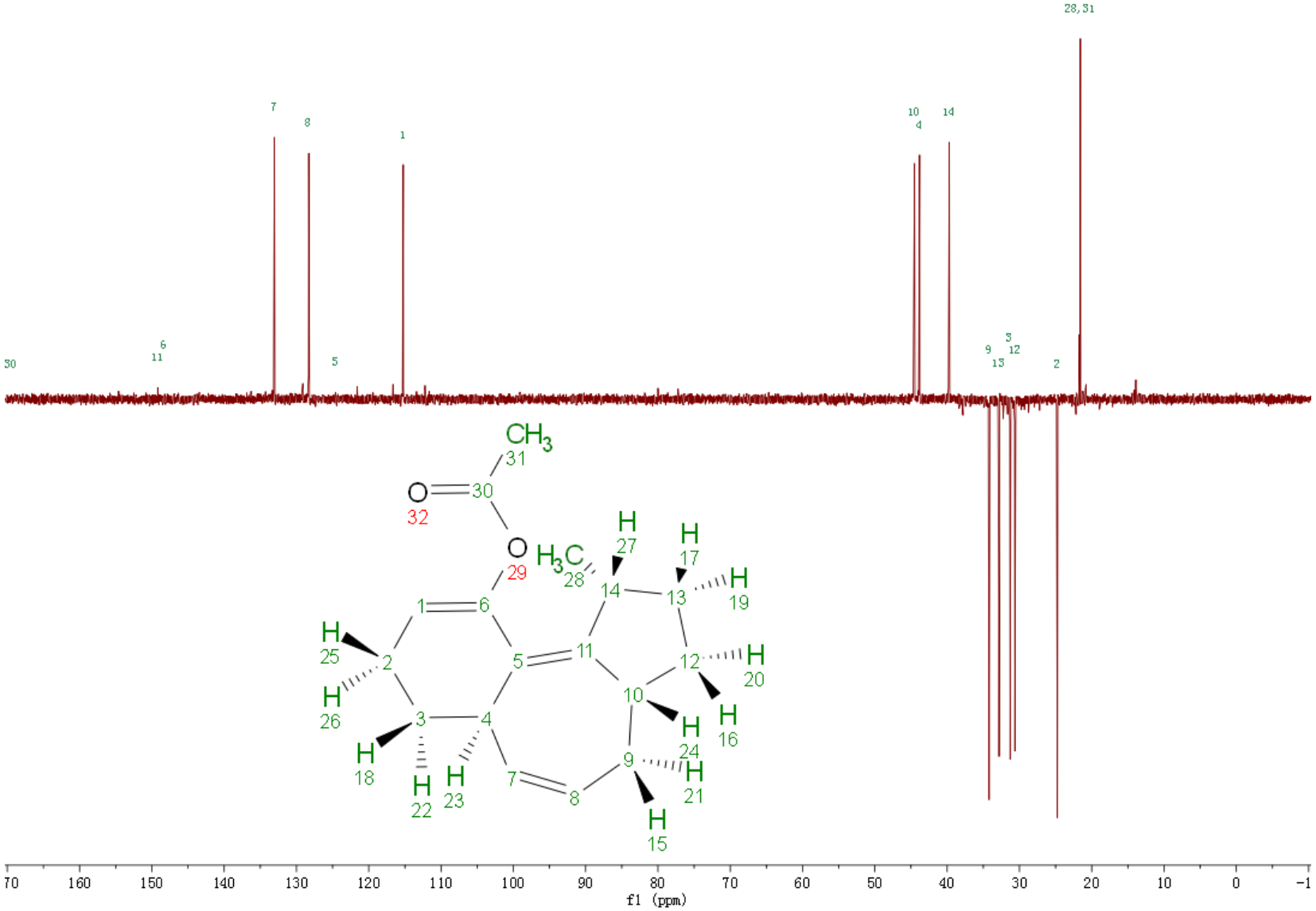


2l

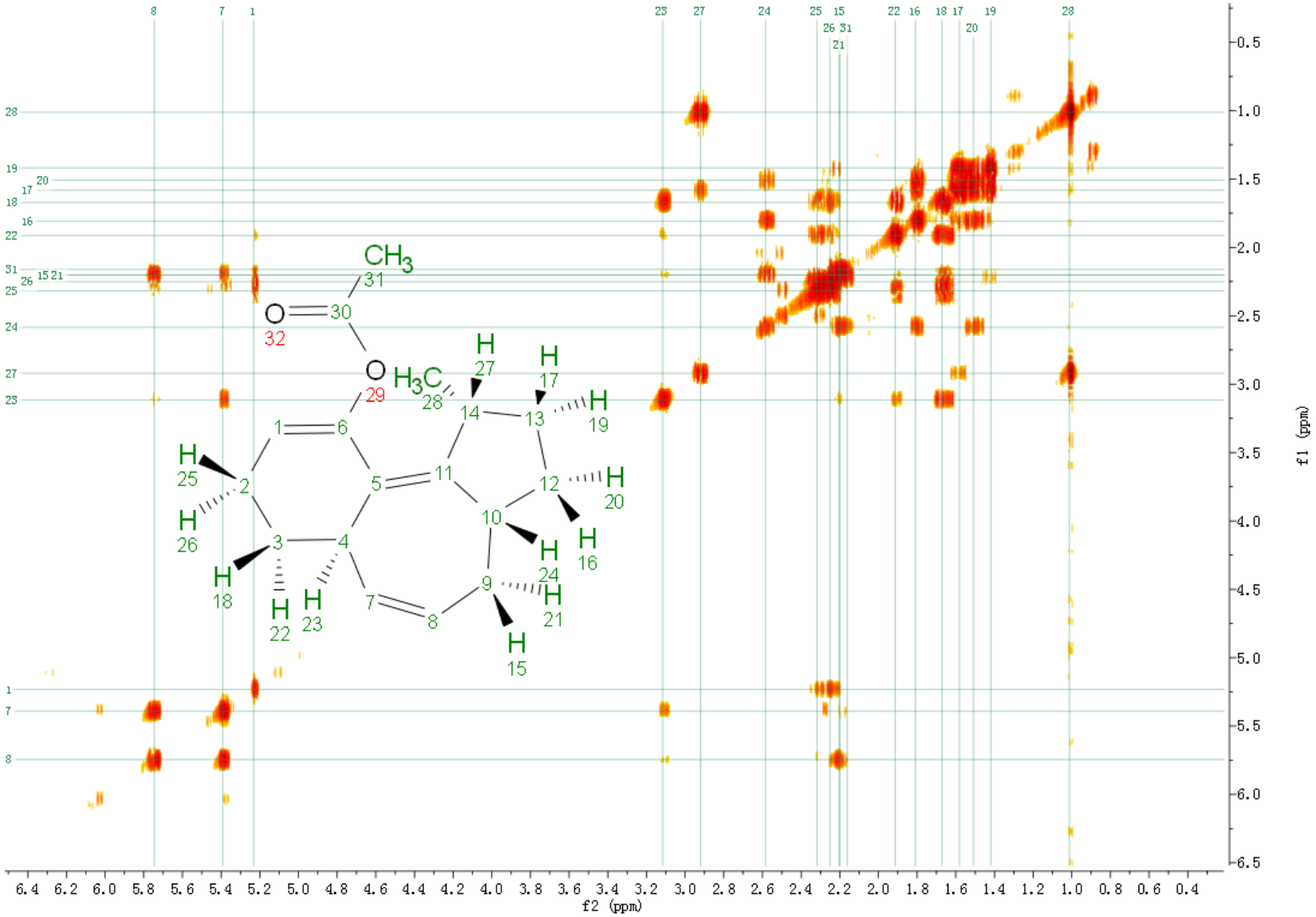

CH3
31
O
30
32
O
29
H3C
28
H
27
H
17
H
19
H
25
H
26
H
18
H
22
H
23
H
15
H
24
H
21
H
16
H
20
1
2
3
4
5
6
7
8
9
10
11
12
13
14
31
28
1
8
7
23
27
24
15
21
25
26
22
16
18
17
20
19
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


CH3
31
O
30
32
O
29
H3C
28
H
27
H
17
H
19
14
13
1
6
H
25
2
5
11
12
H
20
7
H
26
3
4
10
H
16
H
24
H
18
9
H
21
H
22
H
23
7
8
H
15
1
8
5
11
6
30
4
10
14
9
13
3
12
2
28, 31
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

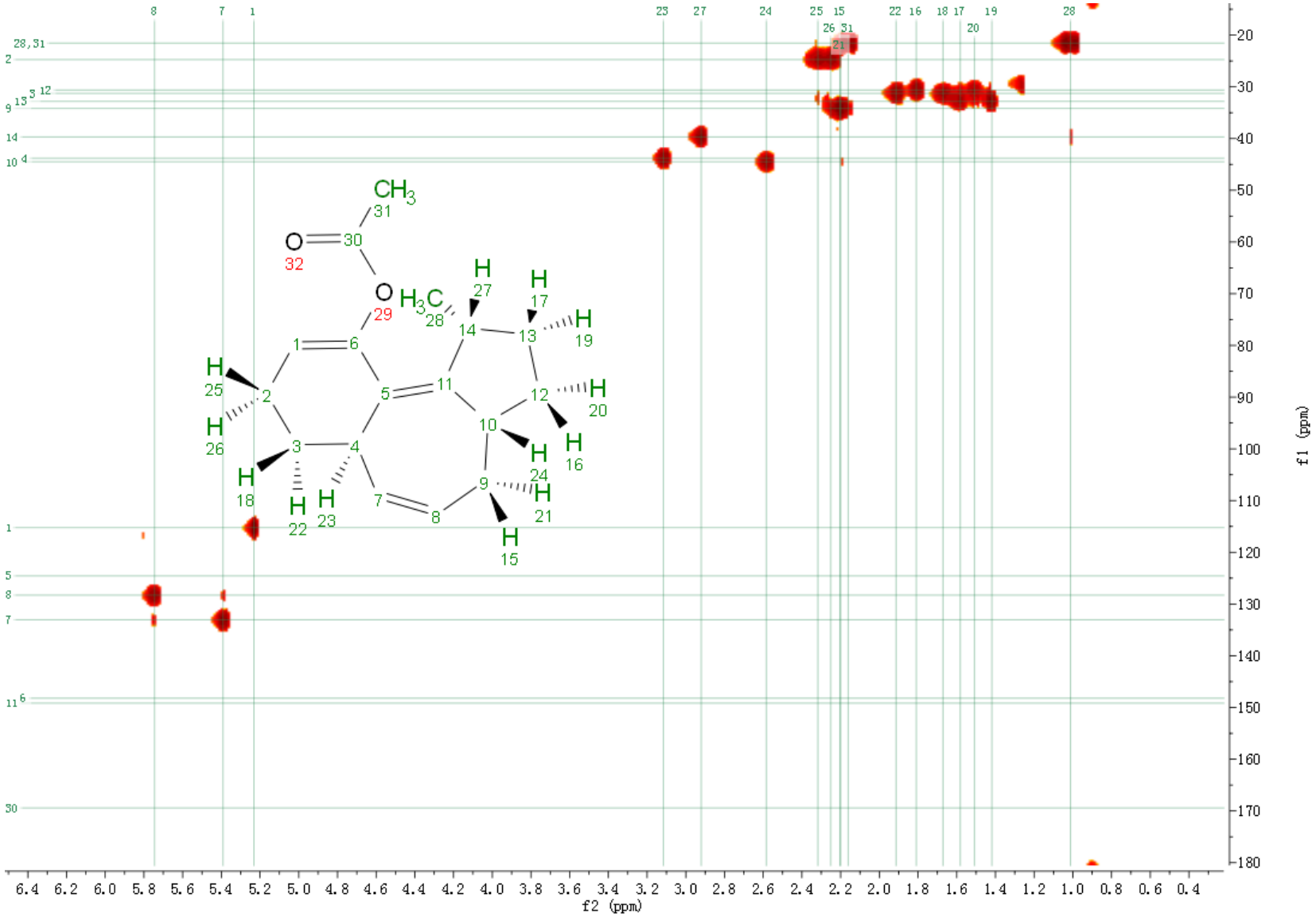
DEPT


28,31
7
8
1
10
4
14
30
6
11
5
9
3
12
13
2
CH3
31
O
30
32
O
29
H3C
28
H
27
H
17
H
19
14
13
1
6
H
25
2
5
11
12
H
20
H
26
10
H
16
3
4
H
24
H
18
9
H
21
H
22
H
23
7
8
H
15
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

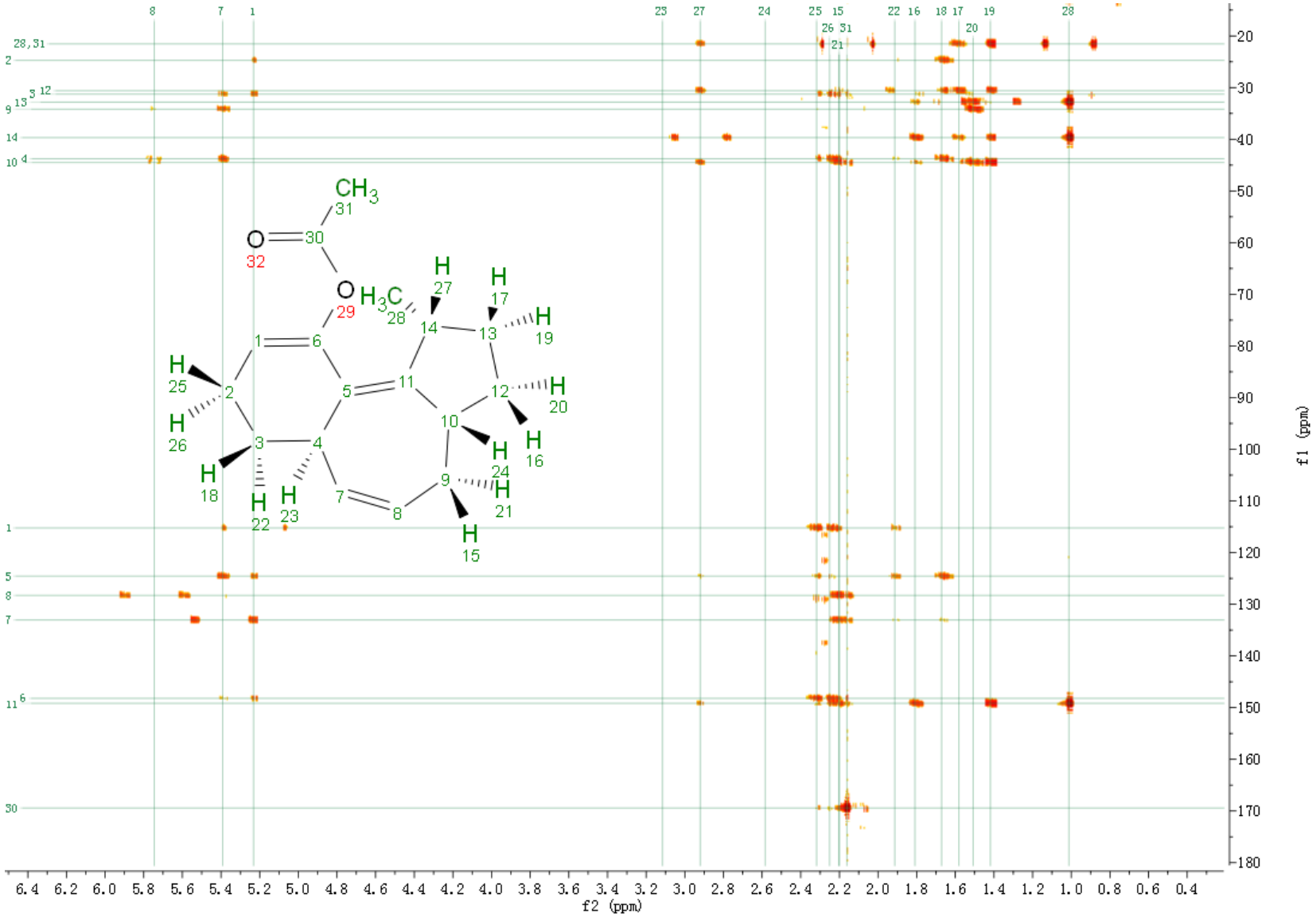
COSY


f2 (ppm)
f1 (ppm)
CH3
31
O
30
32
O
29
H3C
28
H
27
H
17
H
19
H
25
H
26
H
18
H
22
H
23
H
24
H
16
H
20
H
21
H
15

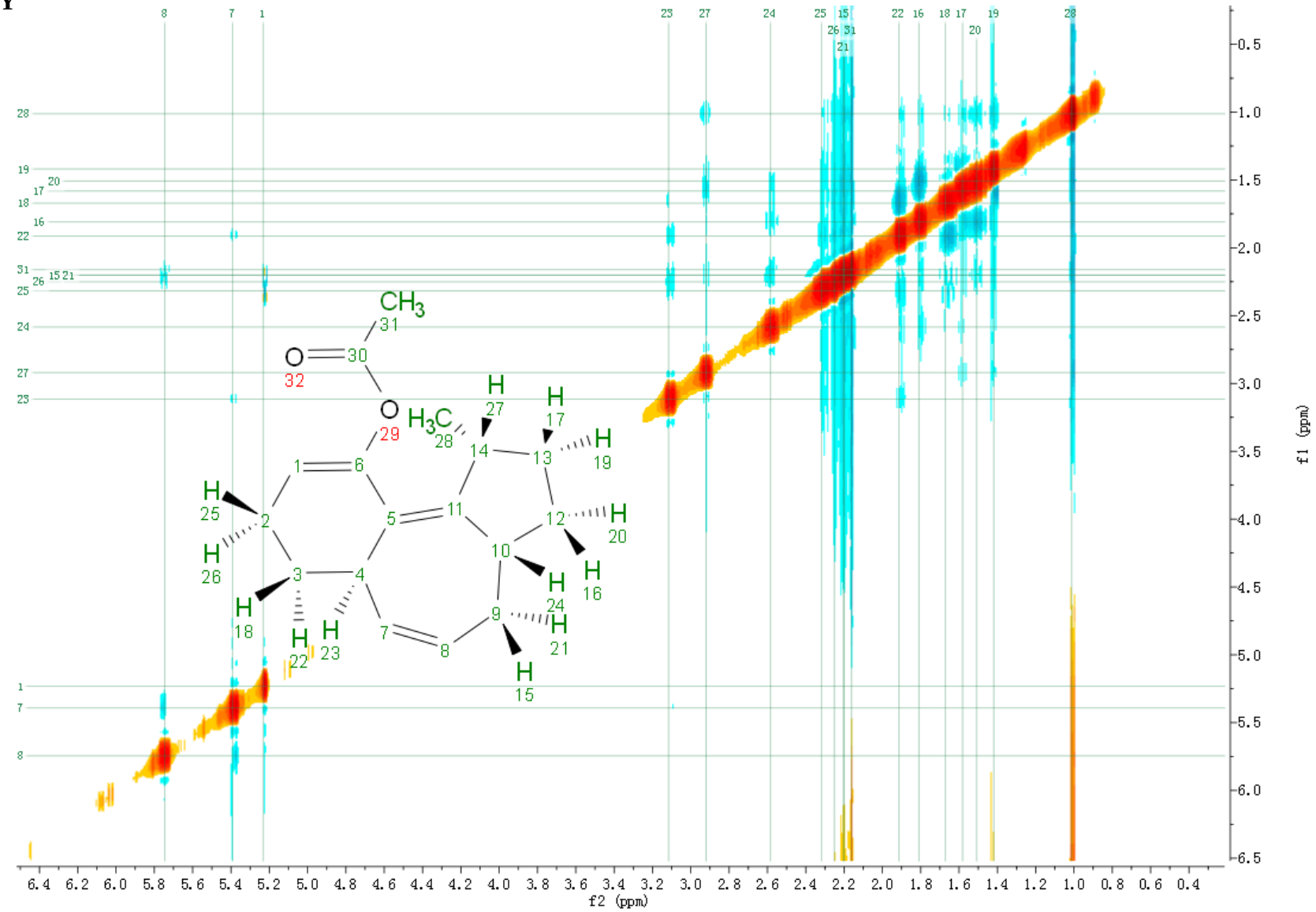
HSQC


f2 (ppm)
f1 (ppm)
CH3
31
O
30
32
O
29
H3C
28
H
27
H
17
H
19
H
20
H
16
H
24
H
21
H
15
H
18
H
22
H
23
H
25
H
26

HMBC



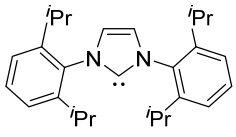
NOESY


f2 (ppm)
f1 (ppm)
CH3
31
O
30
32
O
29
H3C
28
H
27
H
17
H
19
H
25
H
26
H
18
H
22
H
23
H
24
H
16
H
21
H
15
H
20

References

1. Achard, T.; Lepronier, A.; Gimbert, Y.; Clavier, H.; Giordano, L.; Tenaglia, A.; Buono, G. *Angew. Chem., Int. Ed.* **2011**, *50*, 3552.
2. Niggemann, M.; Jelonek, A.; Biber, N.; Wuchrer, M.; Plietker, B. *J. Org. Chem.* **2008**, *73*, 7028.
3. Laird, T.; Ollis, W. D.; Sutherland, I. O. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2033.
4. Kim, S. M.; Parka, J. H.; Chung, Y. K. *Chem. Commun.* **2011**, *47*, 6719.
5. Negishi, E.; Pour, M.; Cederbaum, F. E.; Kotora, M. *Tetrahedron* **1998**, *54*, 7057.
6. Erkkilä, A.; Pihko, P. M. *J. Org. Chem.* **2006**, *71*, 2538.
7. Wender, P. A.; Christy, J. P. *J. Am. Chem. Soc.* **2006**, *128*, 5354.
8. Maruyama, K.; Nagai, N.; Naruta, Y. *J. Org. Chem.* **1986**, *51*, 5083.
9. Domnin, I. N.; Remizova, L. A. *Russ. J. Org. Chem.* **2009**, *45*, 1123.
10. Roush, W. R.; Peseckis, S. M. *J. Am. Chem. Soc.* **1981**, *103*, 6696.
11. Maleczka, R. E., Jr.; Terrell, L. R.; Clark, D. H.; Whitehead, S. L.; Gallagher, W. P.; Terstiege, I. *J. Org. Chem.* **1999**, *64*, 5958.
12. Tobisu, M.; Nakai, H.; Chatani, N. *J. Org. Chem.* **2009**, *74*, 5471.
13. Ochiai, M.; Tsuchimoto, Y.; Hayashi, T. *Tetrahedron Lett.* **2003**, *44*, 5381.
14. Piers, E.; Coish, P. D. G. *Synthesis* **2001**, *2001*, 251.
15. Llerena, D.; Buisine, O.; Aubert, C.; Malacria, M. *Tetrahedron* **1998**, *54*, 9373.

Structures of Ligands Used



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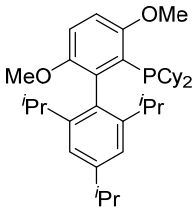
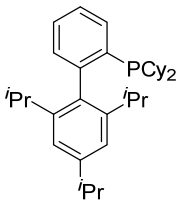


BrettPhos



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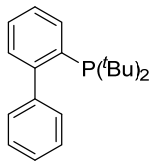

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