An Enyne Cycloisomerization/[5+1] Reaction Sequence to Synthesize Tetrahydroisoquinolinones from Enyne-Enes and CO

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I. General Information

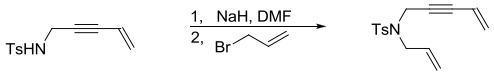
Air and moisture sensitive reactions were carried out in oven and flame-dried glassware sealed with rubber septa under a positive pressure of dry nitrogen or argon. Similarly, sensitive liquids and solutions were transferred via syringe. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Organic solutions were concentrated using a Büchi rotary evaporator with a desktop vacuum pump. DCE was superdry (water $\leq$ 30 ppm), which could be purchased from J&K. Synthetic reagents were purchased from J&K and Acros, and used without further purification, unless otherwise indicated. Analytical TLC was performed with 0.25 mm silica gel G plates with a 254 nm fluorescent indicator. The TLC plates were visualized by ultraviolet light and treatment with phosphomolybdic acid stain or $KMnO_4$ 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 100 MHz) and Bruker AVANCE III (^{1}H at 500 MHz, ^{13}C at 125 MHz) nuclear magnetic resonance spectrometers. Data for ^{1}H NMR spectra are reported as follows: chemical shift (ppm, referenced to residual solvent peak ($CDCl_3$ = δ 7.26 ppm, CD_2Cl_2 = δ 5.32 ppm; s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, ddt = doublet of doublet of triplets, dm = doublet of multiplet, m = multiplet), coupling constant (Hz), and integration. Data for ^{13}C NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak ($CDCl_3$ = δ 77.16 ppm, CD_2Cl_2 = δ 53.84 ppm). Infrared spectra were recorded on a Mettler-Toledo ReactIR iC10 system with a SiComp probe and are reported in wavenumbers (cm^{-1}). High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer (ESI or EI) with an FT-ICR analyzer.

Abbreviations:
Ar = argon
Bn = benzyl
Boc = *t*-butoxycarbonyl
DCE = 1,2-dichloroethane
DCM = dichloromethane
DIAD = diisopropyl azodiformate
DIBAL-H = diisobutyl aluminium hydride
DIPA = diisopropylamine
DMF = *N*, *N*-dimethylformamide
dppp = 1,3-bis(diphenylphosphino) propane
EA = ethyl acetate
IPr = 1,3-bis(2,6-diisopropylphenyl) imidazole-2-ylidene
JohnPhos = 2-(di-*t*-butylphosphino)biphenyl
MS = molecular sieve
N_2 = nitrogen
o-Ns = *o*-nitrobenzenesulfonyl
PE = petroleum ether
rt = room temperature
TBS = *t*-butyldimethylsilyl

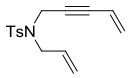
Tf = trifluoromethanesulfonyl
THF = tetrahydrofuran
TLC = thin layer chromatography
TMS = trimethylsilyl
Ts = *p*-toluenesulfonyl

II. Preparation of Substrates



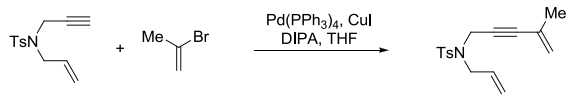
S1 **1a**

To a suspension of NaH (239.7 mg, 6.0 mmol, 60%) in DMF (20 mL) was added **S1**[1] (704.4 mg, 3.0 mmol) at 0 ºC. After stirred for 15 min, a solution of allyl bromide (0.51 mL, 6.0 mmol) in DMF (10 mL) was added at 0 ºC and the reaction mixture was stirred at the same temperature. The reaction was monitored by TLC and stirred for 1.5 h. Upon completion, saturated NH_4Cl solution was added to quench the reaction. The resulting mixture was extracted with ether (3×150 mL), and the combined organic phase was washed with brine, then dried over Na_2SO_4, then filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 50:1) to afford **1a** (804.7 mg, 98%).



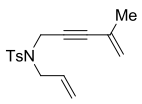
1a

Colorless oil, TLC R_f = 0.54 (EA/PE = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 5.80 – 5.67 (m, 1H), 5.56 – 5.43 (m, 1H), 5.40 – 5.19 (m, 4H), 4.19 (d, *J* = 1.5 Hz, 2H), 3.80 (d, *J* = 6.4 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 136.1, 132.2, 129.6, 127.9, 127.4, 120.0, 116.4, 84.4, 82.6, 49.3, 36.7, 21.6. IR (neat): 2923, 1349, 1162, 1092 cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{18}NO_2S$ ($[M+H]^+$): 276.1053, found 276.1049.



S2 **1b**

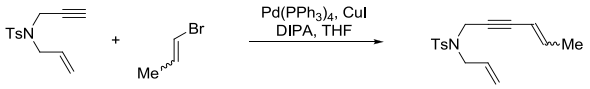
CuI (15.2 mg, 0.08 mmol) and $Pd(PPh_3)_4$ (34.8 mg, 0.03 mmol) were dissolved in DIPA (1.6 mL). 2-bromoprop-1-ene (483.2 mg, 4.0 mmol) was added to the resulting solution at 0 ºC. After stirred for 5 min, **S2**[2] (497.2 mg, 2.0 mmol) in DIPA (3.2 mL) and THF (2.0 mL) was added to the solution at 0 ºC. The reaction was gradually allowed to warm to room temperature overnight. The reaction was monitored by TLC and stirred for 16 h. Upon completion, 2M HCl solution (15 ml) was added to quench the reaction. The resulting mixture was extracted with ether (3×20 mL), and the combined organic phase was washed with brine, then dried over Na_2SO_4, then filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 50:1) to afford **1b** (183.6 mg, 32%).



1b

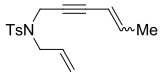
Yellow oil, TLC R_f = 0.50 (EA/PE = 1/5). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 5.76 (ddt, *J* = 16.9, 10.1, 6.4 Hz, 1H), 5.29 (dd, *J* = 16.9, 1.3 Hz, 1H), 5.23 (dd, *J* = 10.1, 1.3 Hz, 1H), 5.12 – 5.08 (m, 1H), 4.97 (s, 1H), 4.20 (s, 2H), 3.81 (d, *J* = 6.4 Hz, 2H), 2.40 (s, 3H), 1.66 – 1.62 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.5, 136.2, 132.2, 129.6, 127.9, 126.1, 122.1, 119.9, 87.0, 80.9, 49.3, 36.7, 23.1, 21.6. IR (neat): 2955, 2922, 1351, 1163,

1093 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{19}NaNO_2S$ ([M+Na]$^+$): 312.1029, found 312.1037.



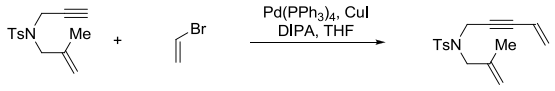
S2 **1c**

CuI (15.2 mg, 0.08 mmol) and $Pd(PPh_3)_4$ (34.9 mg, 0.03 mmol) were dissolved in DIPA (1.6 mL). 1-bromoprop-1-ene (cis- and trans- mixture, 487.1 mg, 4.0 mmol) was added to the resulting solution at 0 ºC. After stirred for 5 min, **S2**[2] (498.9 mg, 2.0 mmol) in DIPA (3.2 mL) and THF (2.0 mL) was added to the solution at 0 ºC. The reaction was gradually allowed to warm to room temperature overnight. The reaction was monitored by TLC and stirred for 16 h. Upon completion, 2M HCl solution (15 ml) was added to quench the reaction. The resulting mixture was extracted with ether (3×20 mL), and the combined organic phase was washed with brine, then dried over Na_2SO_4, then filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 50:1) to afford **1c** (203.3 mg, *Z/E* = 1/3.5, 35%).



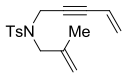
1c

Light yellow oil, TLC R_f = 0.53 (EA/PE = 1/5). **(*Z*)-1c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 5.91 – 5.69 (m, 2H), 5.32 – 5.17 (m, 3H), 4.17 (d, *J* = 1.3 Hz, 2H), 3.80 (d, *J* = 6.5 Hz, 2H), 2.42 (s, 3H), 1.71 (dd, *J* = 6.8, 1.7 Hz, 3H). **(*E*)-1c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H × 3.5), 7.27 (d, *J* = 8.3 Hz, 2H × 3.5), 5.91 – 5.69 (m, 2H × 3.5), 5.32 – 5.17 (m, 3H × 3.5), 4.25 (d, *J* = 1.6 Hz, 2H × 3.5), 3.83 (d, *J* = 6.4 Hz, 2H × 3.5), 2.40 (s, 3H × 3.5), 1.62 (dd, *J* = 6.8, 1.6 Hz, 3H × 3.5). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 143.4, 140.3, 138.9, 136.2, 136.1, 132.2, 129.5, 127.94, 127.87, 119.91, 119.88, 109.9, 109.3, 86.4, 84.4, 82.4, 80.0, 49.20, 49.19, 36.9, 36.8, 21.6, 18.7, 15.9. IR (neat): 1440, 1348, 1161, 1119, 1092, 1056 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{19}NaNO_2S$ ([M+Na]$^+$): 312.1029, found 312.1033.



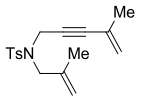
S3 **1d**

CuI (15.2 mg, 0.08 mmol) and $Pd(PPh_3)_4$ (35.0 mg, 0.03 mmol) were dissolved in DIPA (2 mL). bromoethene (4.0 mL, 1.0 M in THF) was added to the resulting solution at 0 ºC. After stirred for 5 min, **S3**[3] (524.6 mg, 2.0 mmol) in DIPA (8 mL) and THF (2 mL) was added to the solution at 0 ºC. The reaction was gradually allowed to warm to room temperature overnight. The reaction was monitored by TLC and stirred for 12 h. Upon completion, 2M HCl solution (30 ml) was added to quench the reaction. The resulting mixture was extracted with ether (3×15 mL), and the combined organic phase was washed with brine, then dried over Na_2SO_4, then filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 50:1) to afford **1d** (483.4 mg, 84%).



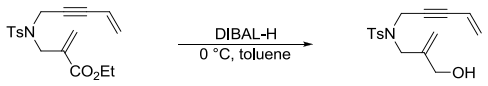
1d

Light yellow oil, TLC R_f = 0.65 (EA/PE = 1/5). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 5.47 (ddt, *J* = 17.3, 11.2, 1.7 Hz, 1H), 5.34 (dd, *J* = 11.2, 2.2 Hz, 1H), 5.28 (dd, *J* = 17.3, 2.2 Hz, 1H), 5.02 – 4.93 (m, 2H), 4.15 (d, *J* = 1.7 Hz, 2H), 3.71 (s, 2H), 2.41 (s, 3H), 1.77 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.5, 139.5, 136.2, 129.5, 128.0, 127.2, 116.4, 115.5, 84.1, 82.3, 52.8, 36.4, 21.6, 19.8. IR (neat): 2924, 1350, 1163, 1097 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{20}NO_2S$ ([M+H]$^+$): 290.1209, found 290.1214.



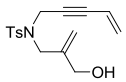
1e

1e[4] is a known substrate.



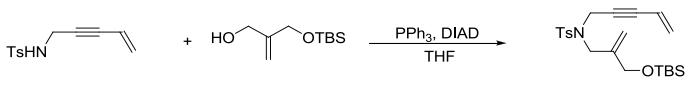
1h **1f**

To a solution of **1h** (526.1 mg, 1.51 mmol) (for the synthesis of **1h**, see below) in toluene (15 mL) was added DIBAL-H (3.8 mL, 1.0 M in hexane, 3.8 mmol) under Ar at 0 ºC. The reaction was gradually allowed to warm to room temperature, monitored by TLC, and stirred for 2 h. Upon completion, the reaction mixture was added saturated potassium sodium tartrate solution (30 mL) and stirred for further 30 min. The resulting mixture was extracted with ether (3×30 mL), and the combined organic phase was washed with brine, then dried over Na_2SO_4, then filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 3:1) to afford **1f** (346.5 mg, 75%).



1f

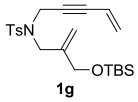
Colorless oil, TLC R_f = 0.49 (EA/PE = 1/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 5.50 (ddt, *J* = 17.2, 11.2, 1.8 Hz, 1H), 5.37 (dd, *J* = 11.2, 2.4 Hz, 1H), 5.32 (dd, *J* = 17.2, 2.4 Hz, 1H), 5.23 (s, 1H), 5.10 (s, 1H), 4.18 (s, 4H), 3.83 (s, 2H), 2.41 (s, 3H), 2.30 – 2.11 (br. s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 142.8, 135.7, 129.6, 128.0, 127.6, 116.3, 115.9, 84.6, 82.4, 63.5, 48.8, 36.7, 21.7. IR (neat): 2953, 2921, 1461, 1349, 1162, 1095 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{20}NO_3S$ ([M+H]$^+$): 306.1158, found 306.1161.



S1 **S4** **1g**

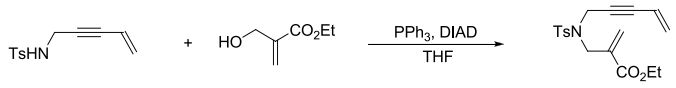
To a stirred solution of **S1**[1] (282.3 mg, 1.2 mmol) and PPh_3 (475.2 mg, 1.8 mmol) in THF (11 mL) was added DIAD (365.6 mg, 1.8 mmol) at 0 ºC. After stirring for 5 min, the solution was added **S4**[5]

(270.7 mg, 1.3 mmol) in THF (5 mL). The reaction was gradually allowed to warm to room temperature, monitored by TLC, and stirred for 3 h. Upon completion, the reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 50:1) to afford **1g** (466.2 mg, 93%).



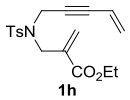
1g

Colorless oil, TLC R_f = 0.70 (EA/PE = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 5.47 (dd, *J* = 17.2, 11.2 Hz, 1H), 5.38 – 5.22 (m, 3H), 5.11 (s, 1H), 4.17 (s, 2H), 4.15 (s, 2H), 3.78 (s, 2H), 2.41 (s, 3H), 0.91 (s, 9H), 0.07 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 142.3, 135.9, 129.5, 128.0, 127.3, 116.4, 114.2, 84.6, 82.4, 63.7, 49.0, 36.6, 26.0, 21.6, 18.5, -5.3. IR (neat): 2953, 2928, 2856, 1463, 1351, 1257, 1094 cm^{-1}. HRMS (ESI): calcd. for $C_{22}H_{34}NO_3SSi$ ($[M+H]^+$): 420.2023, found 420.2030.



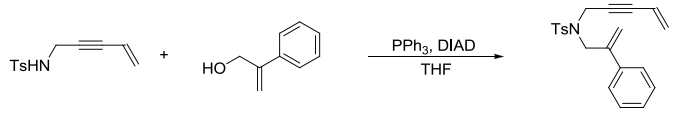
S1 **S5** **1h**

To a stirred solution of **S1**[1] (934.5 mg, 3.97 mmol), PPh_3 (1.5630 g, 5.96 mmol) in THF (39 mL) was added DIAD (1.2023 g, 5.95 mmol) at 0 ºC. After stirring for 5 min, the solution was added **S5**[6] (621.8 mg, 4.78 mmol) in THF (13 mL). The reaction was gradually allowed to warm to room temperature, monitored by TLC, and stirred for 3 h. Upon completion, the reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 20:1) to afford **1h** (1.1513 g, 83%).



1h

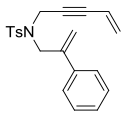
Yellow oil, TLC R_f = 0.42 (EA/PE = 1/5). ^{1}H NMR (400 MHz, CDCl3) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 6.39 (d, *J* = 1.0 Hz, 1H), 5.93 (d, *J* = 1.0 Hz, 1H), 5.56 – 5.42 (m, 1H), 5.39 – 5.28 (m, 2H), 4.26 – 4.18 (m, 4H), 4.07 (s, 2H), 2.41 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 143.7, 136.0, 135.3, 129.6, 127.9, 127.6, 127.4, 116.3, 84.6, 82.6, 61.2, 47.0, 37.8, 21.6, 14.3. IR (neat): 2956, 2924, 2852, 1721, 1352, 1163, 1094 cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{22}NO_4S$ ($[M+H]^+$): 348.1264, found 348.1271.



S1 **S6** **1i**

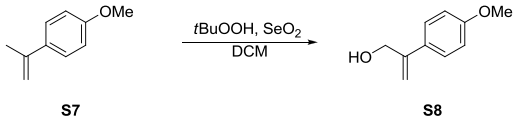
To a stirred solution of **S1**[1] (285.9 mg, 1.22 mmol), PPh_3 (479.1 mg, 1.83 mmol) in THF (12 mL) was added DIAD (369.4 mg, 1.83 mmol) at 0 ºC. After stirring for 5 min, the solution was added **S6**[7] (195.8 mg, 1.46 mmol) in THF (4 mL). The reaction was gradually allowed to warm to room

temperature, monitored by TLC, and stirred for 2 h. Upon completion, the reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 50:1) to afford **1i** (405.4 mg, 95%).

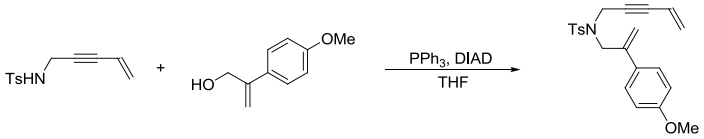


1i

Light yellow solid, TLC R_f = 0.58 (EA/PE = 1/5), m.p. = 113-116 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.73 (m, 2H), 7.57 – 7.52 (m, 2H), 7.38 – 7.29 (m, 5H), 5.58 (s, 1H), 5.52 – 5.42 (m, 1H), 5.38 – 5.24 (m, 3H), 4.24 (s, 2H), 4.09 (d, J = 1.7 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 141.5, 137.8, 135.6, 129.5, 128.6, 128.3, 128.1, 127.3, 126.5, 117.3, 116.3, 84.8, 82.3, 50.3, 36.4, 21.6. IR (neat): 2917, 2849, 1462, 1350, 1162, 1094 cm^{-1}. HRMS (ESI): calcd. for $C_{21}H_{22}NO_2S$ ([M+H]$^+$): 352.1366, found 352.1365.



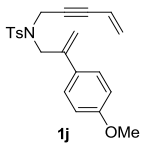
S7 **S8**



S1 **S8** **1j**

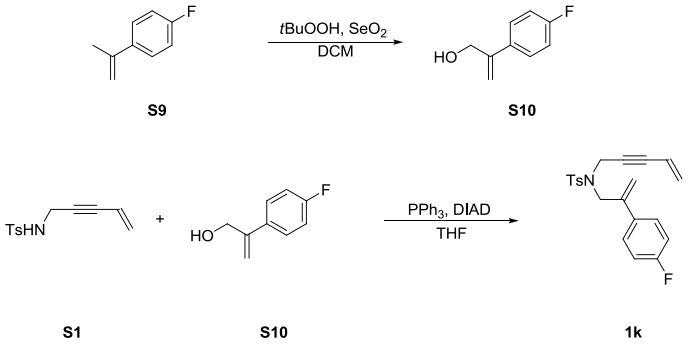
To a stirred solution of SeO_2 (7.70 g, 69.0 mmol) in DCM (30 mL) was added *t*BuOOH (8.90 g, 69.0 mmol, 70% solution in H_2O) at 0 ºC. After stirring for 10 min, the solution was added **S7**[8] (6.75 g, 46.0 mmol) in DCM (30 mL) at 0 ºC. After stirred for 1.5 h, the reaction was quenched by saturated $NaHCO_3$ (100 mL) at 0 ºC. The reaction mixture was extracted with DCM (3×100 mL) and the combined organic phase was dried over Na_2SO_4 and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 4:1) to afford **S8** (2.94 g, 48%). **S8**[9] is a known substrate.

To a stirred solution of **S1**[1] (235.8 mg, 1.0 mmol) and PPh_3 (394.1 mg, 1.5 mmol) in THF (10 mL) was added DIAD (305.4 mg, 1.5 mmol) at 0 ºC. After stirring for 5 min, the solution was added **S8** (172.4 mg, 1.0 mmol) in THF (4 mL). The reaction was gradually allowed to warm to room temperature, monitored by TLC, and stirred for 3 h. Upon completion, the reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 20:1) to afford **1j** (262.2 mg, 69%).



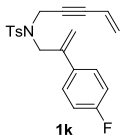
1j

Light yellow solid, TLC R_f = 0.40 (EA/PE = 1/5), m.p. = 162-163 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.54 – 7.48 (m, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 6.91 – 6.86 (m, 2H), 5.50 (s, 1H), 5.48 – 5.41 (m, 1H), 5.35 (dd, *J* = 11.2, 2.5 Hz, 1H), 5.26 (dd, *J* = 17.2, 2.5 Hz, 1H), 5.22 (d, *J* = 0.8 Hz, 1H), 4.21 (s, 2H), 4.07 (d, *J* = 1.5 Hz, 2H), 3.82 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 143.6, 140.6, 135.6, 130.1, 129.5, 128.2, 127.7, 127.3, 116.4, 115.7, 113.9, 84.7, 82.3, 55.4, 50.5, 36.3, 21.6. IR (neat): 2955, 2922, 1515, 1349, 1253, 1185, 1163, 1091 cm^{-1}. HRMS (ESI): calcd. for $C_{22}H_{24}NO_3S$ ([M+H]$^+$): 382.1471, found 382.1480.

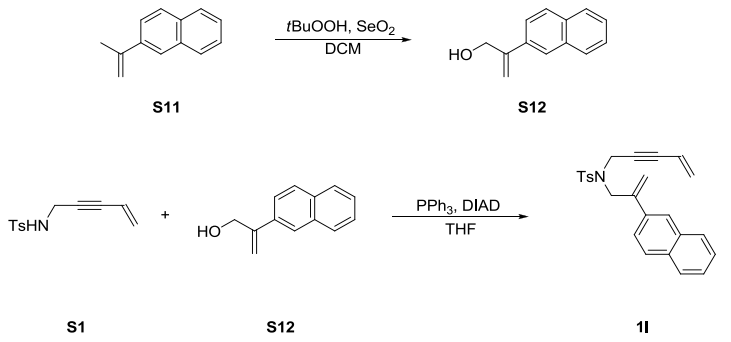


To a stirred solution of SeO_2 (735.2 mg, 6.6 mmol) in DCM (4 mL) was added *t*BuOOH (856.4 mg, 6.7 mmol, 70% solution in H_2O) at 0 ºC. After stirring for 10 min, the solution was added **S9**[8] (602.5 mg, 4.4 mmol) in DCM (4 mL) at 0 ºC. After stirred for 3 h at room temperature, the reaction was quenched by saturated $NaHCO_3$ at 0 ºC. The reaction mixture was extracted with DCM (3×10 mL) and the combined organic phase was washed with saturated Na_2SO_3, saturated $NaHCO_3$ and brine, then dried over Na_2SO_4, then filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 10:1) to afford **S10** (270.1 mg, 40%). **S10**[10] is a known substrate.

To a stirred solution of **S1**[1] (378.0 mg, 1.61 mmol) and PPh_3 (633.2 mg, 2.41 mmol) in THF (16 mL) was added DIAD (489.3 mg, 2.42 mmol) at 0 ºC. After stirring for 5 min, the solution was added **S10** (270.1 mg, 1.77 mmol) in THF (5 mL). The reaction was gradually allowed to warm to room temperature, monitored by TLC, and stirred for 7 h. Upon completion, the reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 50:1) to afford **1k** (521.7 mg, 88%).



White solid, TLC R_f = 0.60 (EA/PE = 1/5), m.p. = 97-98 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.60 – 7.47 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.10 – 6.95 (m, 2H), 5.52 (s, 1H), 5.51 – 5.40 (m, 1H), 5.39 – 5.32 (m, 1H), 5.32 – 5.22 (m, 2H), 4.21 (s, 2H), 4.07 (d, *J* = 1.4 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9 (d, *J* = 247.6 Hz), 143.7, 140.5, 135.6, 133.8 (d, *J* = 3.2 Hz), 129.6, 128.3 (d, *J* = 8.1 Hz), 128.5, 127.7, 117.3, 116.3, 115.5 (d, *J* = 21.5 Hz), 84.9, 82.2, 50.5, 36.4, 21.7. IR (neat): 2955, 2924, 2852, 1351, 1164, 1093 cm^{-1}. HRMS (ESI): calcd. for $C_{21}H_{21}FNO_2S$ ([M+H]$^+$): 370.1272, found 370.1275.

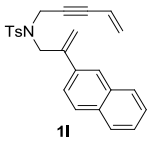


S11 **S12**

S1 **S12** **1l**

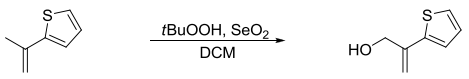
To a stirred solution of SeO_2 (1.5016 g, 13.5 mmol) in DCM (8 mL) was added *t*BuOOH (1.7453 g, 13.6 mmol, 70% solution in H_2O) at 0 ºC. After stirring for 10 min, the solution was added **S11**[8] (1.5179 g, 9.02 mmol) in DCM (8 mL) at 0 ºC. After stirred for 2 h at room temperature, the reaction was quenched by saturated $NaHCO_3$ (30 mL) at 0 ºC. The reaction mixture was extracted with DCM (3×20 mL) and the combined organic phase was washed with saturated Na_2SO_3, saturated $NaHCO_3$ and brine, then dried over Na_2SO_4, then filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 10:1) to afford **S12** (751.0 mg, 45%). **S12**[11] is a known substrate.

To a stirred solution of **S1**[1] (447.6 mg, 1.90 mmol) and PPh_3 (748.5 mg, 2.85 mmol) in THF (18 mL) was added DIAD (575.1 mg, 2.84 mmol) at 0 ºC. After stirring for 5 min, the solution was added **S12** (386.3 mg, 2.10 mmol) in THF (7 mL). The reaction was gradually allowed to warm to room temperature, monitored by TLC, and stirred for 3 h. Upon completion, the reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 20:1) to afford **1l** (729.9 mg, 96%).

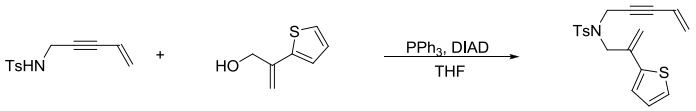


1l

Light yellow solid, TLC R_f = 0.46 (EA/PE = 1/5), m.p. = 146-149 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.93 – 7.72 (m, 5H), 7.66 (d, *J* = 8.6 Hz, 1H), 7.51 – 7.43 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.72 (s, 1H), 5.57 – 5.25 (m, 4H), 4.36 (s, 2H), 4.12 (s, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 141.5, 135.8, 135.1, 133.5, 133.3, 129.6, 128.7, 128.18, 128.15, 127.6, 127.4, 126.36, 126.35, 125.8, 124.5, 117.8, 116.4, 84.8, 82.5, 50.5, 36.6, 21.7. IR (neat): 2959, 2928, 2856, 1163, 1092 cm^{-1}. HRMS (ESI): calcd. for $C_{25}H_{24}NO_2S$ ($[M+H]^+$): 402.1522, found 402.1525.



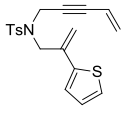
S13 **S14**



S1 **S14** **1m**

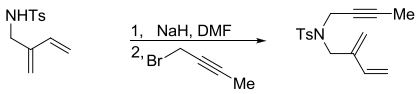
To a stirred solution of SeO_2 (3.3131 g, 29.9 mmol) in DCM (12 mL) was added *t*BuOOH (3.8445 g, 29.9 mmol, 70% solution in H_2O) at 0 ºC. After stirring for 10 min, the solution was added **S13**[12] (2.4706 g, 19.9 mmol) in DCM (12 mL) at 0 ºC. After stirred for 1 h, the reaction was quenched by saturated $NaHCO_3$ (40 mL) at 0 ºC. The reaction mixture was extracted with DCM (3×20 mL) and the combined organic phase was washed with saturated Na_2SO_3, saturated $NaHCO_3$ and brine, then dried over Na_2SO_4, then filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 10:1) to afford **S14** (408.7 mg, 15%). **S14**[12] is a known substrate.

To a stirred solution of **S1**[1] (492.1 mg, 2.09 mmol) and PPh_3 (822.9 mg, 3.14 mmol) in THF (20 mL) was added DIAD (635.0 mg, 3.14 mmol) at 0 ºC. After stirring for 5 min, the solution was added **S14** (352.4 mg, 2.51 mmol) in THF (7 mL). The reaction was gradually allowed to warm to room temperature, monitored by TLC, and stirred for 5 h. Upon completion, the reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 50:1) to afford **1m** (711.4 mg, 95%).



1m

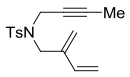
White solid, TLC R_f = 0.51 (EA/PE = 1/5), m.p. = 68-69 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 3.5 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 5.1 Hz, 1H), 7.05 – 6.97 (m, 1H), 5.59 (s, 1H), 5.46 (dd, *J* = 17.2, 11.2 Hz, 1H), 5.35 (dd, *J* = 11.2, 2.3 Hz, 1H), 5.26 (dd, *J* = 17.2, 2.3 Hz, 1H), 5.19 (s, 1H), 4.18 (s, 4H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 141.6, 135.6, 135.2, 129.6, 128.2, 128.0, 127.4, 125.7, 125.0, 116.3, 115.9, 85.0, 82.2, 50.6, 36.5, 21.7. IR (neat): 2952, 2922, 2854, 1351, 1163, 1094 cm^{-1}. HRMS (ESI): calcd. for $C_{19}H_{20}NO_2S_2$ ($[M+H]^+$): 358.0930, found 358.0939.



S15 **1o**

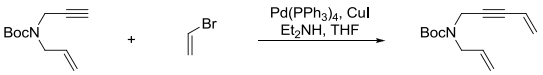
To a suspension of NaH (30.2 mg, 0.76 mmol, 60%) in DMF (1.0 mL) was added **S15**[13] (58.8 mg, 0.25 mmol) in DMF (1.5 mL) at 0 ºC. After stirred for 30 min, a solution of 1-bromobut-2-yne (60 uL, 0.67 mmol) was added at 0 ºC and the reaction mixture was allowed to warm to room

temperature. The reaction was monitored by TLC and stirred for 2 h. Upon completion, saturated NH_4Cl (2 mL) was added to quench the reaction. The resulting mixture was extracted with ether (3×10 mL) and the combined organic phase was washed with saturated NaCl, dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 20:1) to afford **1o** (56.4 mg, 79%).



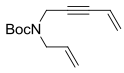
1o

Colorless oil, TLC R_f = 0.49 (EA/PE = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 6.35 (dd, *J* = 17.7, 11.1 Hz, 1H), 5.62 (d, *J* = 17.7 Hz, 1H), 5.23 (s, 1H), 5.22 (s, 1H), 5.17 (d, *J* = 11.1 Hz, 1H), 4.06 – 3.96 (m, 2H), 3.95 (s, 2H), 2.43 (s, 3H), 1.52 – 1.42 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 139.6, 135.82, 135.78, 129.2, 128.1, 119.8, 116.2, 81.9, 71.4, 47.8, 36.2, 21.5, 3.2. IR (neat): 1597, 1347, 1306, 1162, 1094 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{19}NaNO_2S$ ([M+Na]$^+$): 312.1029, found 312.1026.



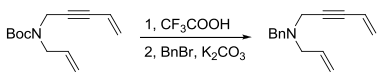
S16 **1p**

CuI (30.6 mg, 0.16 mmol) and $Pd(PPh_3)_4$ (69.2 mg, 0.06 mmol) were dissolved in Et_2NH (2.0 mL). **S16**[14] (783.0 mg, 4.0 mmol) in THF (6.0 mL) and bromoethene (8.0 mL, 1.0 M in THF) was added to the solution at 0 ºC. The reaction was gradually allowed to warm to room temperature, and was continued for another 13 h (TLC indicated that the reaction was completed). The reaction solution was then added to water (50 mL) at 0 ºC. The resulting mixture was extracted with ether (3×30 mL), and the combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 50:1) to afford **1p** (775.0 mg, 87%).



1p

Light yellow oil, TLC R_f = 0.53 (EA/PE = 1/10). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 5.85 – 5.74 (m, 2H), 5.61 (dd, *J* = 17.6, 2.2 Hz, 1H), 5.47 (dd, *J* = 11.1, 2.2 Hz, 1H), 5.20 – 5.12 (m, 2H), 4.12 (s, 2H), 3.91 (d, *J* = 5.7 Hz, 2H), 1.44 (s, 9H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 155.1, 134.0, 127.3, 117.2, 116.9, 86.3, 82.0, 80.3, 48.9, 36.4, 28.4. IR (neat): 2978, 2923, 1699, 1453, 1404, 1366, 1246, 1170, 1144, 920 cm^{-1}. HRMS (ESI): calcd. for $C_{13}H_{20}NO_2$ ([M+H]$^+$): 222.1489, found 222.1482.

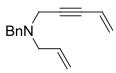


1p **1q**

1p (190.6 mg, 0.86 mmol) was dissolved in DCM (1.5 mL), then CF_3COOH (0.25 mL, 3.4 mmol) was added to the solution at 0 ºC. The reaction was gradually allowed to warm to room temperature. The reaction was monitored by TLC and stirred for 2 h. Upon completion, the reaction was quenched by saturated $NaHCO_3$ (10 mL). The resulting mixture was extracted with DCM (3×5 mL), and the

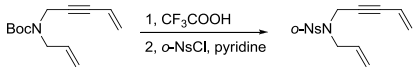
combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated. The crude product was used in the next step directly.

The crude product was dissolved in CH_3CN (4.0 mL), then K_2CO_3 (238.1 mg, 1.7 mmol) and BnBr (0.12 mL, 1.0 mmol) were added to the solution at room temperature. The reaction was monitored by TLC and stirred for 3 h at room temperature. Upon completion, the solution was added to water (40 mL). The resulting mixture was extracted with ether (3×20 mL), and the combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 50:1) to afford **1q** (115.8 mg, 64%).



1q

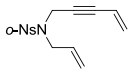
Colorless oil, TLC R_f = 0.68 (EA/PE = 1/5). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.38 – 7.29 (m, 4H), 7.29 – 7.21 (m, 1H), 5.97 – 5.80 (m, 2H), 5.64 (dd, *J* = 17.5, 2.1 Hz, 1H), 5.47 (dd, *J* = 11.1, 2.1 Hz, 1H), 5.28 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.17 (d, *J* = 10.1 Hz, 1H), 3.64 (s, 2H), 3.40 (d, *J* = 1.0 Hz, 2H), 3.18 (d, *J* = 6.3 Hz, 2H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 139.4, 136.3, 129.4, 128.6, 127.4, 126.8, 117.9, 117.5, 85.7, 84.5, 57.7, 57.0, 42.4. IR (neat): 3065, 3029, 2920, 2815, 1643, 1606, 1452, 1424, 1327, 1147, 1116, 973, 921 cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{18}N$ ($[M+H]^+$): 212.1434, found 212.1434.



1p **1r**

1p (216.3 mg, 0.98 mmol) was dissolved in DCM (2.0 mL), then CF_3COOH (0.29 mL, 3.9 mmol) was added to the solution at 0 ºC. The reaction was gradually allowed to warm to room temperature. The reaction was monitored by TLC and stirred for 2 h. Upon completion, the reaction was quenched by saturated $NaHCO_3$ (10 mL). The resulting mixture was extracted with DCM (3×10 mL), and the combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated. The crude product was used in the next step directly.

The crude product was dissolved in DCM (5.0 mL), then pyridine (0.16 mL, 2.0 mmol) and *o*-NsCl (326.0 mg, 1.5 mmol) were added to the solution at room temperature. The reaction was monitored by TLC and stirred for 3 h at room temperature. Upon completion, the solution was added to water (10 mL). The resulting mixture was extracted with DCM (3×10 mL), and the combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 5:1) to afford **1r** (119.9 mg, 40%).



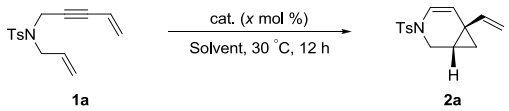
1r

Yellow oil, TLC R_f = 0.21 (EA/PE = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.03 (m, 1H), 7.73 – 7.60 (m, 3H), 5.79 – 5.67 (m, 1H), 5.65 – 5.55 (m, 1H), 5.49 – 5.39 (m, 2H), 5.31 (dd, *J* = 17.1, 1.0 Hz, 1H), 5.26 (dd, *J* = 10.1, 1.0 Hz, 1H), 4.25 (d, *J* = 1.3 Hz, 2H), 4.02 (d, *J* = 6.4 Hz, 2H). ^{13}C

NMR (100 MHz, $CDCl_3$) δ 148.3, 133.8, 133.0, 131.8, 131.7, 131.2, 128.0, 124.2, 120.4, 116.2, 84.4, 82.6, 49.7, 36.8. IR (neat): 3032, 3000, 2933, 1553, 1445, 1368, 1173, 1132, 1074, 936, 911 cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{15}N_2O_4S$ ($[M+H]^+$): 307.0747, found 307.0745.

III. Reaction Condition Screening

Table S1: Optimization of Au(I)-Catalyzed Cycloisomerization



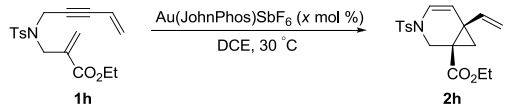
1a 2a

entry[a]	cat.	*x*	solvent	yield (%)[b]	conv. (%)[c]
1	$Au(PPh_3)SbF_6$	10	DCE	trace	100
2	$Au(IPr)SbF_6$	10	DCE	21	100
3	$Au(L)SbF_6$[d]	10	DCE	trace	100
4	$Au(JohnPhos)SbF_6$	10	DCE	52	100
5	Au(JohnPhos)OTf	10	DCE	56	96
6	$Au(JohnPhos)NTf_2$	10	DCE	52	97
7	$Au(JohnPhos)SbF_6$	10	DCM	43	97
8	$Au(JohnPhos)SbF_6$	10	THF	56	96
9	$Au(JohnPhos)SbF_6$	10	toluene	26	48
10	$Au(JohnPhos)SbF_6$	10	CH_3CN	N.R.	--
11	$Au(JohnPhos)SbF_6$	5	DCE	69	94
12	$Au(JohnPhos)MeCNSbF_6$[e]	5	DCE	56	92

[a] Conditions: 0.1 mmol **1a**, *x* mol % cat., solvent (0.05 M), 30 ºC, 12 h. [b] Isolated yield. [c] Based on recovered starting material. [d] L = tris(2,4-di-*t*-butylphenyl)phosphate. [e] Commercially available Echavarren's catalyst.

We also tested the Au(I)-catalyzed cycloisomerization using Boc, Bn, and *o*-Ns as the N-protecting groups (substrates **1p**, **1q** and **1r**), finding that no cyclopropanation took place (see Part IV).

Table S2: Optimization of Au(I)-Catalyzed Cycloisomerization of **1h**

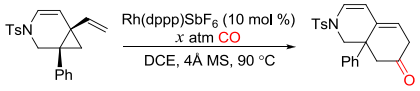


1h 2h

entry[a]	*x*	time (h)	yield (%)[b]	conv. (%)[c]
1	5	14	42	100
2	10	14	46	100

[a] Conditions: 0.1 mmol **1h**, *x* mol % cat., solvent (0.05 M), 30 ºC. [b] Isolated yield. [c] Based on recovered starting material.

Table S3: Optimization of Rh(I)-Catalyzed [5+1] Cycloaddition

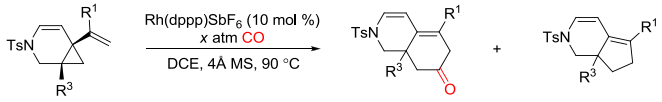


2i **3i**

entry[a]	*x*	Mole ratio of dppp to Rh	time (h)	yield (%)[b]
1	0.2	1.2	16	61
2	0.2	1.0	16	78
3[c]	0.2	1.0	16	58
4	0.1	1.0	16	39
5	1.0	1.0	12	74

[a] Conditions: 0.1 mmol **2i**, 10 mol % Rh(dppp)SbF_6, DCE (0.05 M), 0.08g 4Å MS, *x* atm CO, 90 °C. [b] Isolated yield. [c] Without 4Å MS.

Table S4: Test of CO Pressure on affecting the [5+1] Cycloaddition

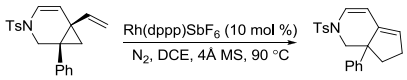


2 **3** **4**

entry[a]	R^1	R^3	*x*	time (h)	yield **3** (%)[b]	yield **4** (%)[b]	conv. (%)[c]
1	Me	H	0.2	12	56	29	100
2	Me	H	0.5	24	32	14	47
3	H	CH_2OH	0.2	3	40	36	100
4	H	CH_2OH	0.5	24	50	trace	/
5	H	CO_2Et	0.2	1	26	62	100
6	H	CO_2Et	0.5	24	trace	0	24

[a] Conditions: 0.1 mmol **2**, 10 mol % Rh(dppp)SbF_6, DCE (0.05 M), 0.08 g 4Å MS, *x* atm CO, 90 °C. [b] Isolated yield. [c] Based on recovered starting material.

Table S5: Optimization of Rh(I)-Catalyzed Rearrangement of VCPs

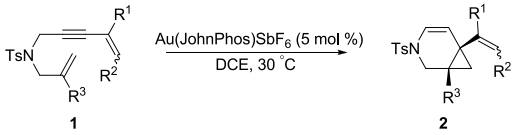


2i **4i**

entry[a]	Mole ratio of dppp to Rh	time (h)	yield (%)[b]
1	1.2	1	84
2	1.0	1	80

[a] Conditions: 0.1 mmol **2i**, 10 mol % Rh(dppp)SbF_6, DCE (0.05 M), 0.08g 4Å MS, 90 °C. [b] Isolated yield.

IV. General Procedure and Experimental Details of Au(I)-Catalyzed Cycloisomerization



General procedure A: (5 mol % catalyst)

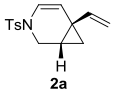
Preparation of solution of cationic Au(I) catalyst: Anhydrous DCE (2.0 mL) was added to a mixture of Au(JohnPhos)Cl (2.6 mg, 4.9 μmol) and $AgSbF_6$ (2.1 mg, 6.1 μmol) under argon. The mixture was stirred at room temperature for 30 min. The resulting suspension was left to stand until the formed AgCl precipitated. The supernatant was used in Au(I)-catalyzed cycloisomerization reactions as the catalyst precursor.

General procedure of Au(I)-catalyzed cycloisomerization: Under argon, the above $Au(I)^+$ solution (2.0 mL) was added to a flame-dried glassware containing **1** (0.1 mmol) at 30 ºC. The reaction was monitored by TLC. Upon completion, the reaction mixture was purified by flash column chromatography on silica gel to afford **2**.

General procedure B: (10 mol % catalyst)

Preparation of solution of cationic Au(I) catalyst: Anhydrous DCE (2.0 mL) was added to a mixture of Au(JohnPhos)Cl (5.3 mg, 10.0 μmol) and $AgSbF_6$ (4.1 mg, 11.9 μmol) under argon. The mixture was stirred at room temperature for 30 min. The resulting suspension was left to stand until the formed AgCl precipitated. The supernatant was used in Au(I)-catalyzed cycloisomerization reactions as the catalyst precursor.

General procedure of Au(I)-catalyzed cycloisomerization: Under argon, the above $Au(I)^+$ solution (2.0 mL) was added to a flame-dried glassware containing **1** (0.1 mmol) at 30 ºC. The reaction was monitored by TLC. Upon completion, the reaction mixture was purified by flash column chromatography on silica gel to afford **2**.



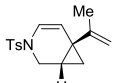
2a

Run 1: Following general procedure A, 27.4 mg **1a** was used, 12 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1), 18.6 mg **2a** was obtained in 68% yield and 1.1 mg **1a** was recovered.

Run 2: Following general procedure A, 27.9 mg **1a** was used, 12 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1), 19.5 mg **2a** was obtained in 70% yield and 2.1 mg **1a** was recovered.

Average yield: 69%.

Colorless oil, TLC R_f = 0.34 (EA/PE = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 6.41 (d, *J* = 8.3 Hz, 1H), 5.46 (d, *J* = 8.3 Hz, 1H), 5.43 (dd, *J* = 17.3, 10.6 Hz, 1H), 4.99 (d, *J* = 17.3 Hz, 1H), 4.93 (d, *J* = 10.6 Hz, 1H), 3.93 (d, *J* = 11.6 Hz, 1H), 3.03 (dd, *J* = 11.6, 2.7 Hz, 1H), 2.42 (s, 3H), 1.62 – 1.51 (m, 1H), 0.97 (dd, *J* = 8.6, 4.5 Hz, 1H), 0.85 – 0.78 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 141.8, 134.9, 129.9, 127.2, 121.4, 111.5, 111.4, 40.6, 27.7, 22.8, 21.7, 19.7. IR (neat): 2921, 1630, 1349, 1166, 1113, 1090, 1002 cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{18}NO_2S$ ($[M+H]^+$): 276.1053, found 276.1051.



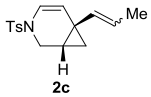
2b

Run 1: Following general procedure A, 28.2 mg **1b** was used, 12 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 20.9 mg **2b** was obtained in 74% yield and 2.5 mg **1b** was recovered.

Run 2: Following general procedure A, 28.4 mg **1b** was used, 12 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 21.5 mg **2b** was obtained in 76% yield and 2.8 mg **1b** was recovered.

Average yield: 75%.

Colorless oil, TLC R_f = 0.37 (EA/PE = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 6.39 (d, *J* = 8.3 Hz, 1H), 5.35 (d, *J* = 8.3 Hz, 1H), 4.77 – 4.74 (m, 1H), 4.73 – 4.69 (m, 1H), 3.92 (d, *J* = 11.7 Hz, 1H), 3.05 (dd, *J* = 11.7, 2.7 Hz, 1H), 2.43 (s, 3H), 1.66 (s, 3H), 1.60 – 1.55 (m, 1H), 1.05 (dd, *J* = 8.8, 4.5 Hz, 1H), 0.64 – 0.56 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 143.9, 135.1, 129.9, 127.2, 121.1, 113.7, 110.6, 40.8, 25.8, 23.2, 21.7, 20.6, 20.2. IR (neat): 2922, 1729, 1349, 1271, 1168, 1110, 1089, 1076, 1004 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{20}NO_2S$ ($[M+H]^+$): 290.1209, found 290.1212.



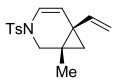
2c

Run 1: Following general procedure A, 28.4 mg **1c** was used, 12 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 24.8 mg **2c** was obtained in 87% yield, *Z/E* = 1/3.5.

Run 2: Following general procedure A, 29.6 mg **1c** was used, 12 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 26.5 mg **2c** was obtained in 90% yield, *Z/E* = 1/3.5.

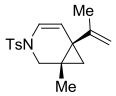
Average yield: 88%, *Z/E* = 1/3.5.

Colorless oil, TLC R_f = 0.41 (EA/PE = 1/10). **(*Z*)-2c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.41 – 6.33 (m, 1H), 5.54 – 5.34 (m, 2H), 5.10 (dd, *J* = 15.4, 1.0 Hz, 1H), 3.89 (d, *J* = 11.5 Hz, 1H), 3.03 (dd, *J* = 11.5, 2.6 Hz, 1H), 2.42 (s, 3H), 1.65 – 1.61 (m, 3H), 1.54 – 1.46 (m, 1H), 0.89 (dd, *J* = 8.6, 4.5 Hz, 1H), 0.74 – 0.68 (m, 1H). **(*E*)-2c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 2H × 3.5), 7.31 (d, *J* = 8.2 Hz, 2H × 3.5), 6.33 – 6.29 (m, 1H × 3.5), 5.54 – 5.34 (m, 2H × 3.5), 5.29 (d, *J* = 8.1 Hz, 1H × 3.5), 3.91 (d, *J* = 11.7 Hz, 1H × 3.5), 3.11 (dd, *J* = 11.7, 2.5 Hz, 1H × 3.5), 2.42 (s, 3H × 3.5), 1.65 – 1.61 (m, 3H × 3.5), 1.54 – 1.46 (m, 1H × 3.5), 0.83 (dd, *J* = 8.6, 4.3 Hz, 1H × 3.5), 0.74 – 0.68 (m, 1H × 3.5). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 143.8, 135.0, 134.8, 134.4, 132.7, 129.9, 128.8, 127.2, 127.1, 122.8, 121.0, 119.9, 116.0, 112.6, 40.8, 40.7, 27.3, 27.0, 22.43, 22.35, 21.67, 21.65, 18.7, 17.9, 16.5, 14.3. IR (neat): 1637, 1348, 1274, 1167, 1113, 1091, 1043, 1006 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{19}NaNO_2S$ ($[M+Na]^+$): 312.1029, found 312.1033.



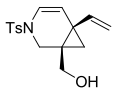
2d

Run 1: Following general procedure A, 29.4 mg **1d** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 27.1 mg **2d** was obtained in 92% yield.
Run 2: Following general procedure A, 29.0 mg **1d** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 26.8 mg **2d** was obtained in 92% yield.
Average yield: 92%.
Colorless oil, TLC R_f = 0.43 (EA/PE = 1/10). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 6.37 (d, *J* = 8.1 Hz, 1H), 5.60 (dd, *J* = 17.2, 10.6 Hz, 1H), 5.39 (d, *J* = 8.1 Hz, 1H), 5.12 – 5.03 (m, 2H), 3.83 (d, *J* = 11.5 Hz, 1H), 2.69 (d, *J* = 11.5 Hz, 1H), 2.42 (s, 3H), 1.09 (s, 3H), 0.99 (d, *J* = 4.6 Hz, 1H), 0.83 (d, *J* = 4.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.9, 138.7, 135.1, 129.9, 127.2, 121.2, 114.9, 113.4, 46.5, 32.7, 27.0, 25.3, 21.7, 18.1. IR (neat): 2920, 1351, 1272, 1170, 1112, 1003 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{20}NO_2S$ ([M+H]$^+$): 290.1209, found 290.1210.



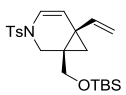
2e

Run 1: Following general procedure A, 29.7 mg **1e** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 29.5 mg **2e** was obtained in 99% yield.
Run 2: Following general procedure A, 30.7 mg **1e** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 29.1 mg **2e** was obtained in 95% yield.
Average yield: 97%.
2e is a known substrate[4].



2f

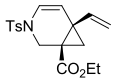
Run 1: Following general procedure A, 31.1 mg **1f** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 3:1), 21.0 mg **2f** was obtained in 68% yield.
Run 2: Following general procedure A, 30.7 mg **1f** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 3:1), 21.8 mg **2f** was obtained in 71% yield.
Average yield: 70%.
Colorless oil, TLC R_f =0.41 (EA/PE = 1/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 6.43 (d, *J* = 8.2 Hz, 1H), 5.74 (dd, *J* = 17.4, 10.4 Hz, 1H), 5.36 (d, *J* = 8.2 Hz, 1H), 5.25 – 5.11 (m, 2H), 3.96 (d, *J* = 11.4 Hz, 1H), 3.72 (d, *J* = 12.2 Hz, 1H), 3.52 (d, *J* = 12.2 Hz, 1H), 3.10 (d, *J* = 11.4 Hz, 1H), 2.42 (s, 3H), 1.58 – 1.38 (br. s, 1H), 1.14 (d, *J* = 4.9 Hz, 1H), 1.06 (d, *J* = 4.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 137.9, 134.8, 130.0, 127.3, 122.0, 116.7, 112.6, 65.5, 43.0, 38.6, 25.0, 24.7, 21.7. IR (neat): 2953, 2923, 2852, 1462, 1168, 1091, 1022 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{20}NO_3S$ ([M+H]$^+$): 306.1158, found 306.1166.



2g

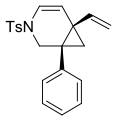
Run 1: Following general procedure A, 41.7 mg **1g** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 29.6 mg **2g** was obtained in 71% yield.

Run 2: Following general procedure A, 41.8 mg **1g** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 31.6 mg **2g** was obtained in 76% yield.
Average yield: 74%.
Colorless oil, TLC R_f = 0.50 (EA/PE = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 6.40 (d, *J* = 8.2 Hz, 1H), 5.67 (dd, *J* = 17.0, 10.7 Hz, 1H), 5.34 (d, *J* = 8.2 Hz, 1H), 5.16 – 5.08 (m, 1H), 5.08 – 5.00 (m, 1H), 3.93 (d, *J* = 11.6 Hz, 1H), 3.55 (d, *J* = 10.9 Hz, 1H), 3.48 (d, *J* = 10.9 Hz, 1H), 2.98 (d, *J* = 11.6 Hz, 1H), 2.42 (s, 3H), 0.95 (d, *J* = 4.9 Hz, 1H), 0.89 (d, *J* = 4.9 Hz, 1H), 0.84 (s, 9H), -0.01 (s, 3H), -0.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 137.8, 134.8, 129.9, 127.2, 121.5, 115.6, 113.5, 64.8, 43.4, 37.7, 25.9, 25.0, 24.2, 21.7, 18.3, -5.3. IR (neat): 2957, 2924, 2853, 1464, 1169, 1020 cm^{-1}. HRMS (ESI): calcd. for $C_{22}H_{34}NO_3SSi$ ($[M+H]^+$): 420.2023, found 420.2033.



2h

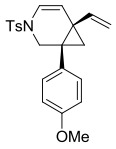
Run 1: Following general procedure A, 34.6 mg **1h** was used, 14 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1), 14.8 mg **2h** was obtained in 43% yield.
Run 2: Following general procedure A, 33.9 mg **1h** was used, 14 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1), 13.8 mg **2h** was obtained in 41% yield.
Average yield: 42%.
Colorless oil, TLC R_f = 0.30 (EA/PE = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 6.50 (d, *J* = 8.2 Hz, 1H), 5.74 (dd, *J* = 17.4, 10.7 Hz, 1H), 5.47 (d, *J* = 8.2 Hz, 1H), 5.17 (d, *J* = 17.4 Hz, 1H), 5.12 (d, *J* = 10.7 Hz, 1H), 4.18 – 4.07 (m, 2H), 4.02 (d, *J* = 12.2 Hz, 1H), 3.42 (d, *J* = 12.2 Hz, 1H), 2.43 (s, 3H), 1.81 (d, *J* = 4.9 Hz, 1H), 1.28 (d, *J* = 4.9 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 144.2, 136.6, 134.9, 130.1, 127.2, 123.6, 116.5, 112.2, 61.4, 42.1, 40.5, 28.8, 26.0, 21.7, 14.4. IR (neat): 2954, 2925, 1730, 1291, 1168, 1103 cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{22}NO_4S$ ($[M+H]^+$): 348.1264, found 348.1271.



2i

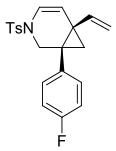
Run 1: Following general procedure A, 34.6 mg **1i** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 31.6 mg **2i** was obtained in 91% yield.
Run 2: Following general procedure A, 35.5 mg **1i** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 33.7 mg **2i** was obtained in 95% yield.
Average yield: 93%.
Light yellow solid, TLC R_f = 0.39 (EA/PE = 1/10), m.p. = 229-230 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.30 – 7.27 (m, 2H), 7.26 – 7.23 (m, 1H), 7.23 – 7.16 (m, 2H), 6.51 (d, *J* = 8.2 Hz, 1H), 5.66 (d, *J* = 8.2 Hz, 1H), 5.05 (dd, *J* = 16.1, 2.6 Hz, 1H), 5.01 – 4.93 (m, 1H), 4.89 (dd, *J* = 10.4, 2.6 Hz, 1H), 4.02 (d, *J* = 11.7 Hz, 1H), 2.99 (d, *J* = 11.7 Hz, 1H), 2.44 (s, 3H), 1.52 (d, *J* = 4.8 Hz, 1H), 1.41 (dd, *J* = 4.8, 0.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 139.9, 138.5, 135.0, 130.2, 130.0, 128.6, 127.5, 127.2, 122.0, 112.7, 112.4, 48.0,

42.4, 26.2, 25.8, 21.7. IR (neat): 2956, 2924, 2853, 1463, 1170, 1024 cm^{-1}. HRMS (ESI): calcd. for $C_{21}H_{22}NO_2S$ ($[M+H]^+$): 352.1366, found 352.1367.



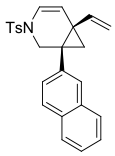
2j

Run 1: Following general procedure A, 38.4 mg **1j** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1), 32.4 mg **2j** was obtained in 84% yield.
Run 2: Following general procedure A, 37.9 mg **1j** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1), 33.4 mg **2j** was obtained in 88% yield.
Average yield: 86%.
Light yellow solid, TLC R_f = 0.28 (EA/PE = 1/10), m.p. = 197-198 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.15 – 7.08 (m, 2H), 6.87 – 6.74 (m, 2H), 6.49 (d, *J* = 8.2 Hz, 1H), 5.64 (d, *J* = 8.2 Hz, 1H), 5.04 (dd, *J* = 16.7, 2.3 Hz, 1H), 5.00 – 4.92 (m, 1H), 4.90 (dd, *J* = 10.1, 2.3 Hz, 1H), 3.99 (dd, *J* = 11.7, 0.7 Hz, 1H), 3.78 (s, 3H), 2.93 (d, *J* = 11.7 Hz, 1H), 2.43 (s, 3H), 1.50 (d, *J* = 4.8 Hz, 1H), 1.36 (dd, *J* = 4.8, 1.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 144.0, 140.1, 134.9, 131.2, 130.5, 130.0, 127.2, 121.9, 114.0, 112.5, 112.4, 55.4, 48.1, 41.8, 26.3, 25.8, 21.7. IR (neat): 2956, 2925, 2852, 1463, 1171, 1021 cm^{-1}. HRMS (ESI): calcd. for $C_{22}H_{24}NO_3S$ ($[M+H]^+$): 382.1471, found 382.1475.



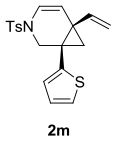
2k

Run 1: Following general procedure A, 36.4 mg **1k** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 30.4 mg **2k** was obtained in 84% yield.
Run 2: Following general procedure A, 36.9 mg **1k** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 30.7 mg **2k** was obtained in 83% yield.
Average yield: 84%.
Light yellow solid, TLC R_f = 0.37 (EA/PE = 1/10), m.p. = 209-210 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.20 – 7.11 (m, 2H), 7.04 – 6.91 (m, 2H), 6.50 (d, *J* = 8.2 Hz, 1H), 5.63 (d, *J* = 8.2 Hz, 1H), 5.13 – 4.98 (m, 1H), 4.98 – 4.84 (m, 2H), 3.99 (d, *J* = 11.7 Hz, 1H), 2.93 (d, *J* = 11.7 Hz, 1H), 2.44 (s, 3H), 1.51 (d, *J* = 4.8 Hz, 1H), 1.37 (d, *J* = 4.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1 (d, *J* = 246.5 Hz), 144.1, 139.7, 135.0, 134.3 (d, *J* = 3.2 Hz), 131.8 (d, *J* = 8.1 Hz), 130.0, 127.2, 122.1, 115.6 (d, *J* = 21.4 Hz), 113.1, 112.3, 48.1, 41.6, 26.3, 25.8, 21.7. IR (neat): 2925, 2854, 1731, 1286, 1170 cm^{-1}. HRMS (ESI): calcd. for $C_{21}H_{21}FNO_2S$ ($[M+H]^+$): 370.1272, found 370.1271.



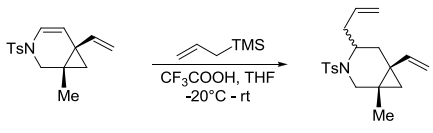
2l

Run 1: Following general procedure A, 40.8 mg **1l** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 34.4 mg **2l** was obtained in 84% yield.
Run 2: Following general procedure A, 40.3 mg **1l** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 34.2 mg **2l** was obtained in 85% yield.
Average yield: 84%.
White solid, TLC R_f = 0.33 (EA/PE = 1/10), m.p. = 223-225 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.73 (m, 3H), 7.70 (s, 1H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.51 – 7.43 (m, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.29 (dd, *J* = 8.5, 1.7 Hz, 1H), 6.55 (d, *J* = 8.3 Hz, 1H), 5.69 (d, *J* = 8.3 Hz, 1H), 5.09 (dd, *J* = 17.0, 1.5 Hz, 1H), 4.98 (dd, *J* = 17.0, 10.4 Hz, 1H), 4.88 (dd, *J* = 10.4, 1.5 Hz, 1H), 4.07 (dd, *J* = 11.7, 0.6 Hz, 1H), 3.09 (d, *J* = 11.7 Hz, 1H), 2.44 (s, 3H), 1.62 (d, *J* = 4.8 Hz, 1H), 1.57 – 1.53 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 139.8, 136.1, 134.9, 133.5, 132.7, 130.0, 129.1, 128.3, 128.0, 127.81, 127.77, 127.2, 126.4, 126.3, 122.1, 112.8, 112.2, 48.0, 42.4, 26.3, 25.9, 21.7. IR (neat): 2956, 2923, 2853, 1469, 1170 cm^{-1}. HRMS (ESI): calcd. for $C_{25}H_{24}NO_2S$ ([M+H]$^+$): 402.1522, found 402.1522.



2m

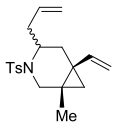
Run 1: Following general procedure A, 35.7 mg **1m** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 29.9 mg **2m** was obtained in 84% yield.
Run 2: Following general procedure A, 35.9 mg **1m** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 31.0 mg **2m** was obtained in 86% yield.
Average yield: 85%.
Light yellow solid, TLC R_f = 0.34 (EA/PE = 1/10), m.p. = 276-277 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.16 (dd, *J* = 5.1, 1.1 Hz, 1H), 6.92 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.84 (dd, *J* = 3.5, 1.1 Hz, 1H), 6.49 (d, *J* = 8.2 Hz, 1H), 5.59 (d, *J* = 8.2 Hz, 1H), 5.16 (dd, *J* = 17.3, 10.2 Hz, 1H), 5.07 (dd, *J* = 17.3, 1.5 Hz, 1H), 4.95 (dd, *J* = 10.2, 1.5 Hz, 1H), 4.11 (d, *J* = 11.6 Hz, 1H), 3.09 (d, *J* = 11.6 Hz, 1H), 2.44 (s, 3H), 1.56 (d, *J* = 5.1 Hz, 1H), 1.54 (d, *J* = 5.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 142.0, 138.6, 134.9, 130.1, 127.2, 127.0, 126.8, 124.9, 122.1, 113.9, 112.1, 47.5, 37.7, 27.7, 27.0, 21.7. IR (neat): 2925, 1345, 1164, 1089 cm^{-1}. HRMS (ESI): calcd. for $C_{19}H_{20}NO_2S_2$ ([M+H]$^+$): 358.0930, found 358.0938.



2d **2n**

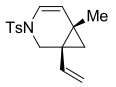
Following the reported procedure[15]: A solution of **2d** (171.7 mg, 0.59 mmol) in DCM (12 mL) was cooled to -20 ºC, and allyltrimethylsilane (560 μL, 3.5 mmol) and trifluoroacetic acid (180 μL, 2.4

mmol) were added to the solution. The reaction mixture was stirred at the same temperature for 2 h. The mixture was allowed to warm to room temperature and stirred for 2 h. Saturated $NaHCO_3$ solution (10 mL) was added, and the mixture was extracted with DCM (3×10 mL), and organic layer was washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated. The reaction mixture was purified by flash column chromatography on silica gel (eluted with PE/EA 50:1) to afford **2n** (159.9 mg, dr > 20/1, 81%).



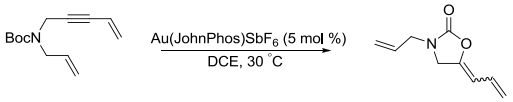
2n

Colorless oil, TLC R_f = 0.55 (EA/PE = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 5.66 (dd, *J* = 17.2, 10.6 Hz, 1H), 5.61 – 5.50 (m, 1H), 5.03 (dd, *J* = 10.6, 1.1 Hz, 1H), 5.02 – 4.98 (m, 1H), 4.97 – 4.95 (m, 1H), 4.93 (dd, *J* = 17.2, 1.1 Hz, 1H), 3.93 – 3.83 (m, 1H), 3.78 (d, *J* = 13.0 Hz, 1H), 2.88 (d, *J* = 13.0 Hz, 1H), 2.41 (s, 3H), 2.16 – 2.02 (m, 1H), 2.00 – 1.88 (m, 2H), 1.79 (dd, *J* = 14.5, 6.2 Hz, 1H), 1.02 (s, 3H), 0.64 (d, *J* = 4.9 Hz, 1H), 0.59 (d, *J* = 4.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 142.1, 138.0, 134.9, 129.8, 127.1, 117.9, 113.6, 50.8, 44.7, 35.8, 30.8, 23.6, 22.4, 21.7, 21.5, 18.7. IR (neat): 2923, 2851, 1342, 1286, 1163, 1091, 1040 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{26}NO_2S$ ($[M+H]^+$): 332.1679, found 332.1677.



2o

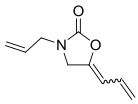
Run 1: Following general procedure B, 27.1 mg **1o** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 19.9 mg **2o** was obtained in 73% yield.
Run 2: Following general procedure B, 27.8 mg **1o** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 20.3 mg **2o** was obtained in 73% yield.
Average yield: 73%.
Colorless oil, TLC R_f = 0.48 (EA/PE = 1/10). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.64 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 6.32 – 6.27 (m, 1H), 5.72 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.23 (d, *J* = 8.0 Hz, 1H), 5.13 (dd, *J* = 10.8, 1.1 Hz, 1H), 5.05 (dd, *J* = 17.4, 1.1 Hz, 1H), 3.84 (d, *J* = 11.3 Hz, 1H), 2.91 (d, *J* = 11.3 Hz, 1H), 2.42 (s, 3H), 1.08 (s, 3H), 0.90 (d, *J* = 4.6 Hz, 1H), 0.78 (d, *J* = 4.6 Hz, 1H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 144.4, 137.3, 135.2, 130.2, 127.4, 121.1, 118.0, 115.6, 44.5, 36.9, 24.9, 21.7, 20.5, 19.2. IR (neat): 2929, 2854, 1353, 1168, 1127, 1097 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{20}NO_2S$ ($[M+H]^+$): 290.1209, found 290.1208.



1p **1p'** (point 1 and point 2)

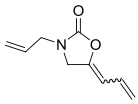
Run 1: Following general procedure A, 21.2 mg **1p** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 10:1), 5.2 mg **point 1** was obtained in 33% yield and 7.3 mg **point 2** was obtained in 46% yield.

Run 2: Following general procedure A, 22.1 mg **1p** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 10:1), 4.8 mg **point 1** was obtained in 29% yield and 8.2 mg **point 2** was obtained in 50% yield.
Average yield: 31% **point 1**, 48% **point 2**.



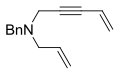
1p' (point 1)

Colorless oil, TLC R_f = 0.17 (EA/PE = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 – 6.54 (m, 1H), 5.82 – 5.70 (m, 1H), 5.33 – 5.21 (m, 3H), 5.13 (d, *J* = 17.1 Hz, 1H), 5.03 (d, *J* = 10.4 Hz, 1H), 4.15 (d, *J* = 0.7 Hz, 2H), 3.94 – 3.90 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 142.5, 131.3, 128.9, 119.9, 115.9, 104.3, 47.6, 46.6. IR (neat): 2919, 2849, 1789, 1689, 1646, 1478, 1438, 1413, 1305, 1258, 1056, 994, 972, 900 cm^{-1}. HRMS (ESI): calcd. for $C_9H_{12}NO_2$ ([M+H]$^+$): 166.0863, found 166.0861.



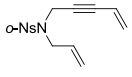
1p' (point 2)

Colorless oil, TLC R_f = 0.10 (EA/PE = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.04 (dd, *J* = 17.2, 11.0 Hz, 1H), 5.87 – 5.76 (m, 1H), 5.73 (d, *J* = 17.2 Hz, 1H), 5.30 – 5.20 (m, 3H), 5.05 (t, *J* = 3.3 Hz, 1H), 3.99 (d, *J* = 6.0 Hz, 2H), 3.86 (d, *J* = 3.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 147.9, 131.4, 128.0, 118.8, 116.3, 98.6, 51.3, 44.9. IR (neat): 2918, 1720, 1610, 1485, 1443, 1357, 1241, 1186, 1094, 991, 923 cm^{-1}. HRMS (ESI): calcd. for $C_9H_{12}NO_2$ ([M+H]$^+$): 166.0863, found 166.0860.



1q

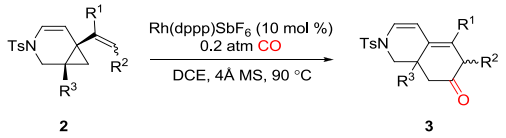
When **1q** was subjected to the Au(I)-catalyzed cycloisomerization, starting material was recovered (76%).



1r

When **1r** was subjected to the Au(I)-catalyzed cycloisomerization, starting material was recovered (67%) and some unidentified products were also found (judged by TLC).

V. General Procedure and Experimental Details of Rh(I)-Catalyzed [5+1] Cycloaddition



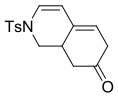
2 3

General procedure C:

Preparation of solution of cationic Rh(I) catalyst: Anhydrous DCE (2.0 mL) was added to a mixture of $[Rh(CO)_2Cl]_2$ (2.0 mg, 5.1 μmol), $AgSbF_6$ (4.1 mg, 11.9 μmol), and dppp (4.1 mg, 9.9 μmol) under nitrogen. The mixture was stirred at room temperature for 30 min. The resulting suspension was left to stand until the formed AgCl precipitated. The supernatant was used in Rh(I)-catalyzed [5+1] cycloaddition reactions as the catalyst precursor.

General procedure of Rh(I)-catalyzed [5+1] cycloaddition: Under nitrogen, the above $Rh(I)^+$ solution (2.0 mL) was added to a flame-dried glassware containing **2** (0.1 mmol) and the newly activated 4 Å molecular sieves (0.08 g) at rt. Then the reaction mixture was bubbled with a mixed gas of CO/N_2 (v/v = 1/4) for 10 min. The glassware was immersed into an oil bath at 90 ºC and reacted under the atmosphere pressure of the mixed gas of CO/N_2 (v/v = 1/4). The reaction was monitored by TLC. Upon completion, the reaction mixture was purified by flash column chromatography on silica gel to afford **3**.

(**Attention**: The present reaction is sensitive to solvent and very highly anhydrous DCE must be used. Molecular sieves also should be activated before the reaction. If the reaction system were not dry, VCP rearrangement products could be the major products.)



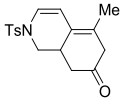
3a

Run 1: Following general procedure C, 27.4 mg **2a** was used, 20 h. After flash column chromatography on silica gel (eluted with PE/EA 3:1), 19.8 mg **3a** was obtained in 66% yield.

Run 2: Following general procedure C, 27.3 mg **2a** was used, 20 h. After flash column chromatography on silica gel (eluted with PE/EA 3:1), 19.4 mg **3a** was obtained in 64% yield.

Average yield: 65%.

Colorless oil, TLC R_f = 0.37 (EA/PE = 1/3). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 6.73 (d, *J* = 8.0 Hz, 1H), 5.53 (t, *J* = 6.4 Hz, 1H), 5.52 – 5.47 (m, 1H), 3.98 – 3.88 (m, 1H), 3.03 (d, *J* = 23.2 Hz, 1H), 2.90 (d, *J* = 23.2 Hz, 1H), 2.71 – 2.63 (m, 2H), 2.48 (dd, *J* = 14.3, 3.8 Hz, 1H), 2.43 (s, 3H), 2.17 – 2.07 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.2, 144.4, 134.9, 131.6, 130.2, 127.2, 125.7, 118.6, 109.6, 48.7, 42.3, 40.2, 33.8, 21.7. IR (neat): 2923, 1720, 1340, 1265, 1160, 1088 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{18}NO_3S$ ($[M+H]^+$): 304.1002, found 304.1005.



3b

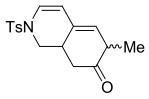
Run 1: Following general procedure C, 26.9 mg **2b** was used, 12 h. After flash column

chromatography on silica gel (eluted with PE/EA 20:1 then 3:1), 7.4 mg **4b** was obtained in 28% yield and 16.9 mg **3b** was obtained in 57% yield.

Run 2: Following general procedure C, 28.4 mg **2b** was used, 12 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1 then 3:1), 8.5 mg **4b** was obtained in 30% yield and 17.0 mg **3b** was obtained in 55% yield.

Average yield: 56% **3b**, 29% **4b**.

Colorless oil, TLC R_f = 0.34 (EA/PE = 1/3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 6.74 (d, *J* = 8.3 Hz, 1H), 5.74 (d, *J* = 8.3 Hz, 1H), 3.94 – 3.83 (m, 1H), 2.96 (d, *J* = 22.4 Hz, 1H), 2.80 (d, *J* = 22.4 Hz, 1H), 2.68 – 2.55 (m, 2H), 2.51 – 2.44 (m, 1H), 2.42 (s, 3H), 2.13 – 2.01 (m, 1H), 1.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.4, 144.3, 134.7, 130.1, 127.1, 125.2, 125.1, 124.4, 106.2, 49.0, 46.1, 42.7, 34.3, 21.7, 17.9. IR (neat): 2921, 1718, 1663, 1340, 1163, 1090 cm^{-1}. HRMS (ESI): calcd. for $C_{17}H_{20}NO_3S$ ($[M+H]^+$): 318.1158, found 318.1162.



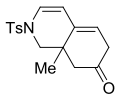
3c

Run 1: Following general procedure C, 27.9 mg **2c** was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA 3:1), 12.1 mg **3c** was obtained in 40% yield, dr = 1.4/1.

Run 2: Following general procedure C, 29.5 mg **2c** was used, 24 h. After flash column chromatography on silica gel (eluted with PE/EA 3:1), 14.4 mg **3c** was obtained in 44% yield, dr = 1.4/1.

Average yield: 42%, dr = 1.4/1.

Colorless oil, TLC R_f = 0.67 (EA/PE = 1/3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.64 (m, 2.8H + 2H), 7.32 (d, *J* = 8.2 Hz, 2.8H + 2H), 6.76 – 6.70 (m, 1.4H + 1H), 5.55 – 5.47 (m, 1.4H + 1H), 5.43 – 5.37 (m, 1.4H + 1H), 3.95 – 3.86 (m, 1.4H + 1H), 3.08 – 3.01 (m, 1.4H), 2.92 – 2.80 (m, 1H), 2.73 – 2.61 (m, 2.8H + 2H), 2.47 – 2.45 (m, 1H), 2.43 (s, 4.2H + 3H), 2.40 – 2.36 (m, 1.4H), 2.27 – 2.20 (m, 1.4H), 2.16 – 2.09 (m, 1H), 1.18 (d, *J* = 7.4 Hz, 3H), 1.11 (d, *J* = 7.2 Hz, 4.2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.1, 208.6, 144.39, 144.38, 134.82, 134.78, 130.8, 130.5, 130.2, 127.2, 127.1, 125.9, 125.8, 125.2, 109.6, 109.3, 48.9, 48.6, 44.2, 43.6, 42.4, 39.7, 34.9, 33.9, 21.7, 19.3, 15.3. IR (neat): 1717, 1353, 1235, 1186, 1168, 1101, 1030, 1008 cm^{-1}. HRMS (ESI): calcd. for $C_{17}H_{19}NaNO_3S$ ($[M+Na]^+$): 340.0978, found 340.0985.



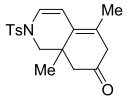
3d

Run 1: Following general procedure C, 29.2 mg **2d** was used, 12 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1 then 5:1), 4.8 mg **4d** was obtained in 16% yield and 24.1 mg **3d** was obtained in 75% yield.

Run 2: Following general procedure C, 28.8 mg **2d** was used, 12 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1 then 5:1), 2.4 mg **4d** was obtained in 8% yield and 24.0 mg **3d** was obtained in 76% yield.

Average yield: 76% **3d**, 12 % **4d**.

Yellow solid, TLC R_f = 0.39 (EA/PE = 1/3), m.p. = 141-143 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 6.73 (d, *J* = 8.1 Hz, 1H), 5.45 (d, *J* = 8.1 Hz, 1H), 5.41 (t, *J* = 3.9 Hz, 1H), 3.55 (d, *J* = 11.2 Hz, 1H), 3.02 (dd, *J* = 23.5, 3.9 Hz, 1H), 2.93 (dd, *J* = 23.5, 3.9 Hz, 1H), 2.68 (d, *J* = 11.2 Hz, 1H), 2.43 (s, 3H), 2.27 (s, 2H), 0.95 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.4, 144.4, 136.3, 135.0, 130.1, 127.2, 124.8, 117.1, 107.8, 54.2, 49.8, 40.1, 37.1, 23.2, 21.7. IR (neat): 1717, 1350, 1163, 1097, 1046, 1007 cm^{-1}. HRMS (ESI): calcd. for $C_{17}H_{20}NO_3S$ ($[M+H]^+$): 318.1158, found 318.1167.



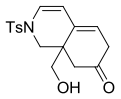
3e

Run 1: Following general procedure C, 29.8 mg **2e** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1 then 5:1), 19.2 mg **4e** was obtained in 64% yield and 11.2 mg **3e** was obtained in 34% yield.

Run 2: Following general procedure C, 30.7 mg **2e** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1 then 5:1), 20.4 mg **4e** was obtained in 66% yield and 11.0 mg **3e** was obtained in 33% yield.

Average yield: 34% **3e**, 65% **4e**.

Colorless oil, TLC R_f = 0.41 (EA/PE = 1/3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 6.74 (d, *J* = 8.3 Hz, 1H), 5.65 (d, *J* = 8.3 Hz, 1H), 3.52 (dd, *J* = 11.1, 1.1 Hz, 1H), 2.94 (d, *J* = 22.9 Hz, 1H), 2.85 (d, *J* = 22.9 Hz, 1H), 2.65 (d, *J* = 11.1 Hz, 1H), 2.42 (s, 3H), 2.24 (s, 2H), 1.70 (s, 3H), 0.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 144.3, 134.9, 130.1, 129.0, 127.2, 124.3, 123.4, 104.4, 54.5, 50.2, 45.9, 37.5, 23.2, 21.7, 17.9. IR (neat): 2920, 2851, 1659, 1341, 1162, 1037 cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{22}NO_3S$ ($[M+H]^+$): 332.1315, found 332.1324.



3f

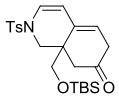
Run 1: Following general procedure C, 28.4 mg **2f** was used, 3 h. After flash column chromatography on silica gel (eluted with PE/EA 5:1 then 2:1), 11.3 mg **4f** was obtained in 40% yield and 12.0 mg **3f** was obtained in 39% yield.

Run 2: Following general procedure C, 32.9 mg **2f** was used, 3 h. After flash column chromatography on silica gel (eluted with PE/EA 5:1 then 2:1), 10.8 mg **4f** was obtained in 33% yield and 14.8 mg **3f** was obtained in 41% yield.

Average yield: 40% **3f**, 36% **4f**.

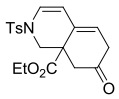
Colorless oil, TLC R_f = 0.15 (EA/PE = 1/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 6.70 (d, *J* = 8.0 Hz, 1H), 5.67 – 5.55 (m, 1H), 5.48 (d, *J* = 8.0 Hz, 1H), 3.85 (d, *J* = 11.6 Hz, 1H), 3.44 (d, *J* = 11.3 Hz, 1H), 3.32 (d, *J* = 11.3 Hz, 1H), 2.96 (s, 2H), 2.67 – 2.52 (m, 2H), 2.43 (s, 3H), 2.07 (d, *J* = 14.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.0, 144.6, 134.6, 131.9, 130.2, 127.2, 124.6, 120.5, 108.1, 64.5, 49.2, 45.1, 42.7, 40.1, 21.7. IR (neat): 2920,

2851, 1719, 1655, 1341, 1162, 1092 cm^{-1}. HRMS (ESI): calcd. for $C_{17}H_{20}NO_4S$ ($[M+H]^+$): 334.1108, found 334.1117.



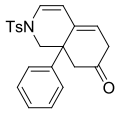
3g

Run 1: Following general procedure C, 41.5 mg **2g** was used, 16 h. After flash column chromatography on silica gel (eluted with PE/EA 5:1), 37.1 mg **3g** was obtained in 84% yield.
Run 2: Following general procedure C, 41.6 mg **2g** was used, 16 h. After flash column chromatography on silica gel (eluted with PE/EA 5:1), 37.5 mg **3g** was obtained in 84% yield.
Average yield: 84%.
Yellow solid, TLC R_f = 0.56 (EA/PE = 1/3), m.p. = 115-116 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 6.67 (d, *J* = 8.1 Hz, 1H), 5.59 (t, *J* = 3.8 Hz, 1H), 5.47 (d, *J* = 8.1 Hz, 1H), 3.80 (d, *J* = 11.4 Hz, 1H), 3.40 – 3.24 (m, 2H), 2.99 – 2.85 (m, 2H), 2.60 (d, *J* = 11.4 Hz, 1H), 2.52 (d, *J* = 14.9 Hz, 1H), 2.42 (s, 3H), 2.03 (d, *J* = 14.9 Hz, 1H), 0.82 (s, 9H), -0.05 (s, 3H), -0.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.3, 144.4, 134.7, 131.7, 130.1, 127.3, 124.3, 120.7, 108.2, 66.5, 49.8, 46.0, 42.6, 40.1, 26.0, 21.7, 18.5, -5.65, -5.70. IR (neat): 1718, 1344, 1253, 1167, 1091, 1043, 1005 cm^{-1}. HRMS (ESI): calcd. for $C_{23}H_{34}NO_4SSi$ ($[M+H]^+$): 448.1972, found 448.1984.



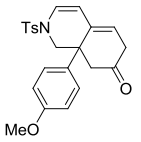
3h

Run 1: Following general procedure C, 32.5 mg **2h** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 10:1 then 3:1), 21.7 mg **4h** was obtained in 67% yield and 8.3 mg **3h** was obtained in 24% yield.
Run 2: Following general procedure C, 34.2 mg **2h** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 10:1 then 3:1), 19.2 mg **4h** was obtained in 56% yield and 10.0 mg **3h** was obtained in 27% yield.
Average yield: 26% **3h**, 62% **4h**.
Colorless oil, TLC R_f = 0.22 (EA/PE = 1/3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 6.74 (d, *J* = 8.2 Hz, 1H), 5.73 (t, *J* = 4.0 Hz, 1H), 5.53 (d, *J* = 8.2 Hz, 1H), 4.32 (d, *J* = 11.6 Hz, 1H), 4.09 – 3.94 (m, 2H), 3.08 (dd, *J* = 23.5, 4.0 Hz, 1H), 3.00 (dd, *J* = 23.5, 4.0 Hz, 1H), 2.70 (d, *J* = 11.6 Hz, 1H), 2.69 (d, *J* = 15.0 Hz, 1H), 2.43 (s, 3H), 2.25 (d, *J* = 15.0 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.9, 170.8, 144.4, 135.0, 130.2, 130.0, 127.3, 125.3, 121.4, 107.5, 62.2, 50.1, 47.5, 46.2, 39.7, 21.7, 14.0. IR (neat): 2924, 1727, 1346, 1252, 1164 cm^{-1}. HRMS (ESI): calcd. for $C_{19}H_{22}NO_5S$ ($[M+H]^+$): 376.1213, found 376.1224.



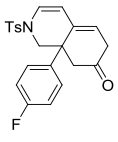
3i

Run 1: Following general procedure C, 35.0 mg **2i** was used, 16 h. After flash column chromatography on silica gel (eluted with PE/EA 3:1), 30.2 mg **3i** was obstained in 80% yield.
Run 2: Following general procedure C, 35.1 mg **2i** was used, 16 h. After flash column chromatography on silica gel (eluted with PE/EA 3:1), 29.0 mg **3i** was obstained in 77% yield.
Average yield: 78%.
Light yellow solid, TLC R_f = 0.29 (EA/PE = 1/3), m.p. = 81-86 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.3 Hz, 2H), 7.17 – 7.10 (m, 5H), 7.10 – 7.04 (m, 2H), 6.71 (d, *J* = 8.1 Hz, 1H), 5.86 – 5.75 (m, 1H), 5.68 (d, *J* = 8.1 Hz, 1H), 4.22 (d, *J* = 11.8 Hz, 1H), 3.09 (d, *J* = 11.8 Hz, 1H), 2.99 (dd, *J* = 23.5, 4.8 Hz, 1H), 2.84 – 2.71 (m, 2H), 2.53 (d, *J* = 14.2 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.4, 143.9, 139.1, 135.2, 134.6, 129.8 (CH), 128.9 (CH), 127.4 (CH), 126.9 (CH), 126.4 (CH), 126.0 (CH), 119.9 (CH), 108.5 (CH), 54.3 (CH_2), 50.8 (CH_2), 45.1, 40.1(CH_2), 21.6(CH_3). IR (neat): 1719, 1342, 1161, 1090 cm^{-1}. HRMS (ESI): calcd. for $C_{22}H_{21}NNaO_3S$ ([M+Na]$^+$): 402.1134, found 402.1143.



3j

Run 1: Following general procedure C, 38.3 mg **2j** was used, 14 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1 then 3:1), 4.4 mg **4j** was obtained in 11% yield and 32.1 mg **3j** was obtained in 78% yield.
Run 2: Following general procedure C, 37.8 mg **2j** was used, 14 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1 then 3:1), 4.0 mg **4j** was obtained in 11% yield and 30.7 mg **3j** was obtained in 76% yield.
Average yield: 77% **3j**, 11% **4j**.
White solid, TLC R_f = 0.20 (EA/PE = 1/3), m.p. = 65-70 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.62 (d, *J* = 8.7 Hz, 2H), 5.81 – 5.75 (m, 1H), 5.68 (d, *J* = 8.0 Hz, 1H), 4.15 (d, *J* = 11.9 Hz, 1H), 3.74 (s, 3H), 3.10 (d, *J* = 11.9 Hz, 1H), 2.98 (dd, *J* = 23.5, 4.7 Hz, 1H), 2.84 – 2.68 (m, 2H), 2.52 (d, *J* = 14.0 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.6, 158.8, 143.8, 135.5, 134.9, 130.9, 129.7, 127.5, 126.9, 125.9, 119.7, 114.2, 108.6, 55.2, 54.6, 50.8, 44.5, 40.1, 21.6. IR (neat): 1719, 1512, 1343, 1252, 1185, 1163 cm^{-1}. HRMS (ESI): calcd. for $C_{23}H_{23}NNaO_4S$ ([M+Na]$^+$): 432.1240, found 432.1249.

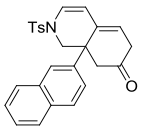


3k

Run 1: Following general procedure C, 37.1 mg **2k** was used, 12 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1 then 3:1), 9.9 mg **4k** was obtained in 27% yield and 28.0 mg **3k** was obtained in 70% yield.
Run 2: Following general procedure C, 36.5 mg **2k** was used, 12 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1 then 3:1), 8.2 mg **4k** was obtained in 22% yield and 27.7 mg **3k** was obtained in 70% yield.

Average yield: 70% **3k**, 24% **4k**.

White solid, TLC R_f = 0.27 (EA/PE = 1/3), m.p. = 66-70 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 7.06 – 6.94 (m, 2H), 6.85 – 6.69 (m, 3H), 5.85 – 5.77 (m, 1H), 5.69 (d, *J* = 8.0 Hz, 1H), 4.13 (d, *J* = 12.1 Hz, 1H), 3.15 (d, *J* = 12.1 Hz, 1H), 3.00 (dd, *J* = 23.5, 4.7 Hz, 1H), 2.79 – 2.71 (m, 2H), 2.55 (d, *J* = 14.1 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.0, 161.9 (d, *J* = 244.9 Hz), 143.9, 135.3, 134.7 (d, *J* = 3.2 Hz), 134.4, 129.7, 128.1 (d, *J* = 8.3 Hz), 126.7, 126.0, 120.0, 115.5 (d, *J* = 21.4 Hz), 108.2, 54.5, 50.5, 44.6, 40.0, 21.5. IR (neat): 1720, 1509, 1343, 1234, 1161, 1090 cm^{-1}. HRMS (ESI): calcd. for $C_{22}H_{20}FNNaO_3S$ ([M+Na]$^+$): 420.1040, found 420.1056.



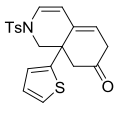
3l

Run 1: Following general procedure C, 40.5 mg **2l** was used, 14 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1 then 3:1), 9.6 mg **4l** was obtained in 24% yield and 30.2 mg **3l** was obtained in 70% yield.

Run 2: Following general procedure C, 40.8 mg **2l** was used, 14 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1 then 3:1), 12.7 mg **4l** was obtained in 31% yield and 28.7 mg **3l** was obtained in 66% yield.

Average yield: 68% **3l**, 28% **4l**.

Light yellow solid, TLC R_f = 0.24 (EA/PE = 1/3), m.p. = 187-189 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.69 (m, 1H), 7.63 – 7.54 (m, 2H), 7.49 – 7.39 (m, 2H), 7.35 (d, *J* = 1.4 Hz, 1H), 7.19 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.14 (d, *J* = 8.2 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 8.2 Hz, 2H), 5.97 – 5.86 (m, 1H), 5.80 (d, *J* = 8.0 Hz, 1H), 4.32 (d, *J* = 12.3 Hz, 1H), 3.31 (d, *J* = 12.3 Hz, 1H), 3.07 – 2.91 (m, 2H), 2.74 (dd, *J* = 23.6, 2.8 Hz, 1H), 2.62 (d, *J* = 14.3 Hz, 1H), 2.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.4, 143.5, 136.4, 135.5, 134.7, 133.2, 132.7, 129.3, 128.9, 128.2, 127.4, 126.4, 126.3, 126.2, 126.1, 126.0, 123.6, 120.2, 108.7, 54.8, 50.3, 45.2, 40.1, 21.5. IR (neat): 1720, 1345, 1163, 1107, 1090 cm^{-1}. HRMS (ESI): calcd. for $C_{26}H_{24}NO_3S$ ([M+H]$^+$): 430.1471, found 430.1474.



3m

Run 1: Following general procedure C, 35.4 mg **2m** was used, 12 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1 then 3:1), 10.0 mg **4m** was obtained in 28% yield and 22.5 mg **3m** was obtained in 59% yield.

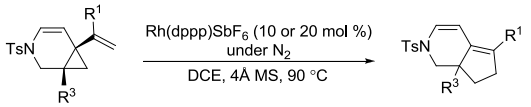
Run 2: Following general procedure C, 35.2 mg **2m** was used, 12 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1 then 3:1), 10.9 mg **4m** was obtained in 31% yield and 20.7 mg **3m** was obtained in 54% yield.

Average yield: 56% **3m**, 30% **4m**.

Colorless oil, TLC R_f = 0.30 (EA/PE = 1/3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.05 (dd, *J* = 5.1, 1.1 Hz, 1H), 6.80 – 6.70 (m, 2H), 6.69 (dd, *J* = 3.6, 1.1

Hz, 1H), 5.77 – 5.68 (m, 1H), 5.64 (d, *J* = 8.1 Hz, 1H), 4.13 (d, *J* = 11.7 Hz, 1H), 3.08 (d, *J* = 11.7 Hz, 1H), 3.06 – 2.96 (m, 1H), 2.91 (dd, *J* = 23.7, 3.0 Hz, 1H), 2.79 (d, *J* = 14.4 Hz, 1H), 2.56 (d, *J* = 14.4 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.8, 144.5, 144.0, 135.2, 134.8, 129.9, 127.1, 127.0, 125.6, 125.09, 125.07, 119.6, 107.9, 54.9, 51.6, 43.0, 39.9, 21.7. IR (neat): 1721, 1344, 1263, 1161, 1091, 1018 cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{19}NNaO_3S_2$ ($[M+Na]^+$): 408.0699, found 408.0710.

VI. General Procedure and Experimental Details of Rh(I)-Catalyzed Rearrangement of VCPs



2 **4**

General procedure D: (10 mol % catalyst)

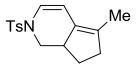
Preparation of solution of cationic Rh(I) catalyst: Anhydrous DCE (2.0 mL) was added to a mixture of $[Rh(CO)_2Cl]_2$ (2.0 mg, 5.1 μmol), $AgSbF_6$ (4.1 mg, 11.9 μmol), and dppp (5.0 mg, 12.1 μmol) under nitrogen. The mixture was stirred at room temperature for 30 min. The resulting suspension was left to stand until the formed AgCl precipitated. The supernatant was used in Rh(I)-catalyzed Rearrangement of VCPs as the catalyst precursor.

General procedure of Rh(I)-catalyzed Rearrangement of VCPs: Under nitrogen, the above $Rh(I)^+$ solution (2.0 mL) was added to a flame-dried glassware containing **2** (0.1 mmol) and the newly activated 4 Å molecular sieves (0.08 g) at rt. Then the glassware was immersed into an oil bath at 90 ºC. The reaction was monitored by TLC. Upon completion, the reaction mixture was purified by flash column chromatography on silica gel to afford **4**.

General procedure E: (20 mol % catalyst)

Preparation of solution of cationic Rh(I) catalyst: Anhydrous DCE (2.0 mL) was added to a mixture of $[Rh(CO)_2Cl]_2$ (3.9 mg, 10.0 μmol), $AgSbF_6$ (8.2 mg, 23.9 μmol), and dppp (9.9 mg, 24.0 μmol) under nitrogen. The mixture was stirred at room temperature for 30 min. The resulting suspension was left to stand until the formed AgCl precipitated. The supernatant was used in Rh(I)-catalyzed Rearrangement of VCPs as the catalyst precursor.

General procedure of Rh(I)-catalyzed Rearrangement of VCPs: Under nitrogen, the above $Rh(I)^+$ solution (2.0 mL) was added to a flame-dried glassware containing **2** (0.1 mmol) and the newly activated 4 Å molecular sieves (0.08 g) at rt. Then the glassware was immersed into an oil bath at 90 ºC. The reaction was monitored by TLC. Upon completion, the reaction mixture was purified by flash column chromatography on silica gel to afford **4**.



4b

Run 1: Following general procedure E, 27.6 mg **2b** was used, 3 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 16.4 mg **4b** was obtained in 59% yield.

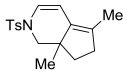
Run 2: Following general procedure E, 28.2 mg **2b** was used, 3 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 15.6 mg **4b** was obtained in 55% yield.

Average yield: 57%.

Colorless oil, TLC R_f = 0.38 (EA/PE = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 6.68 (d, *J* = 8.0 Hz, 1H), 5.63 (d, *J* = 8.0 Hz, 1H), 4.18 – 4.04 (m, 1H), 2.71 – 2.58 (m, 1H), 2.57 – 2.46 (m, 1H), 2.41 (s, 3H), 2.39 – 2.27 (m, 1H), 2.25 – 2.14 (m, 1H), 2.12 – 1.95 (m, 1H), 1.67 (s, 3H), 1.24 – 1.19 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 135.3, 132.6, 129.9, 128.8, 127.1, 124.7, 104.1, 50.5, 42.2, 37.4, 28.1, 21.7, 13.8. IR (neat): 2925, 1595, 1351, 1271, 1238, 1167, 1092 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{19}NaNO_2S$ ($[M+Na]^+$): 312.1029, found 312.1030.

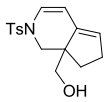
4d

Run 1: Following general procedure D, 29.9 mg **2d** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 26.1 mg **4d** was obtained in 87% yield.
Run 2: Following general procedure D, 28.7 mg **2d** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 26.1 mg **4d** was obtained in 91% yield.
Average yield: 89%.
Colorless oil, TLC R_f = 0.43 (EA/PE = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.65 (dm, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.69 (d, *J* = 8.1 Hz, 1H), 5.52 (d, *J* = 8.1 Hz, 1H), 5.34 – 5.25 (m, 1H), 3.85 (d, *J* = 10.9 Hz, 1H), 2.64 (d, *J* = 10.9 Hz, 1H), 2.53 – 2.44 (m, 1H), 2.41 (s, 3H), 2.30 – 2.22 (m, 1H), 1.81 – 1.75 (m, 1H), 1.53- 1.45 (m, 1H), 0.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 141.1, 135.4, 129.9, 127.1, 125.3, 120.9, 103.6, 55.7, 44.1, 37.3, 30.2, 21.7, 21.5. IR (neat): 2925, 2855, 1725, 1665, 1593, 1493, 1456, 1399, 1342, 1251, 1210, 1165, 1094, 1039, 978, 946 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{20}NO_2S$ ($[M+H]^+$): 290.1209, found 290.1212.



4e

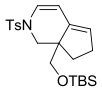
Run 1: Following general procedure D, 30.0 mg **2e** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 24.7 mg **4e** was obtained in 82% yield.
Run 2: Following general procedure D, 29.7 mg **2e** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 24.8 mg **4e** was obtained in 84% yield.
Average yield: 83%.
Colorless oil, TLC R_f = 0.45 (EA/PE = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 6.67 (d, *J* = 8.1 Hz, 1H), 5.52 (d, *J* = 8.1 Hz, 1H), 3.81 (d, *J* = 10.8 Hz, 1H), 2.58 (d, *J* = 10.8 Hz, 1H), 2.54 – 2.45 (m, 1H), 2.40 (s, 3H), 2.17 – 2.08 (m, 1H), 1.75 – 1.69 (m, 1H), 1.64 (s, 3H), 1.48 – 1.39 (m, 1H), 0.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 135.5, 133.4, 130.3, 129.8, 127.1, 123.9, 102.2, 55.9, 44.8, 36.2, 35.6, 21.6, 13.8. IR (neat): 2956, 2921, 2852, 1594, 1445, 1403, 1355, 1345, 1305, 1263, 1231, 1185, 1167, 1091, 1065, 1022, 1009, 962, 943 cm^{-1}. HRMS (ESI): calcd. for $C_{17}H_{22}NO_2S$ ($[M+H]^+$): 304.1366, found 304.1364.



4f

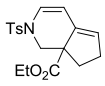
Run 1: Following general procedure D, 31.3 mg **2f** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 5:1), 27.8 mg **4f** was obtained in 89% yield.
Run 2: Following general procedure D, 31.6 mg **2f** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 5:1), 26.4 mg **4f** was obtained in 84% yield.
Average yield: 86%.
Colorless oil, TLC R_f = 0.48 (EA/PE = 1/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 6.70 (d, *J* = 8.1 Hz, 1H), 5.55 (d, *J* = 8.1 Hz, 1H), 5.51 – 5.42 (m, 1H),

4.19 (d, *J* = 11.5 Hz, 1H), 3.38 (dd, *J* = 11.3, 1.5 Hz, 1H), 3.20 (d, *J* = 11.3 Hz, 1H), 2.59 (d, *J* = 11.5 Hz, 1H), 2.51 – 2.45 (m, 2H), 2.43 (s, 3H), 2.35 – 2.23 (m, 1H), 2.24 – 2.14 (m, 1H), 1.44 – 1.30 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 136.9, 135.3, 130.0, 127.2, 125.3, 124.4, 103.8, 62.4, 50.20, 50.17, 32.0, 30.1, 21.7. IR (neat): 2924, 2855, 1345, 1165, 1101, 1034, 1020 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{20}NO_3S$ ([M+H]$^+$): 306.1158, found 306.1155.



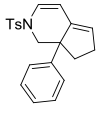
4g

Run 1: Following general procedure D, 41.9 mg **2g** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 37.2 mg **4g** was obtained in 89% yield.
Run 2: Following general procedure D, 42.2 mg **2g** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 37.5 mg **4g** was obtained in 89% yield.
Average yield: 89%.
White solid, TLC R_f = 0.51 (EA/PE = 1/10), m.p. = 115-117 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 6.66 (d, *J* = 8.1 Hz, 1H), 5.50 (d, *J* = 8.1 Hz, 1H), 5.43 – 5.39 (m, 1H), 4.28 (d, *J* = 10.8 Hz, 1H), 3.35 (dd, *J* = 9.7, 1.3 Hz, 1H), 3.13 (d, *J* = 9.7 Hz, 1H), 2.49 (d, *J* = 10.8 Hz, 1H), 2.46 – 2.36 (m, 1H), 2.41 (s, 3H), 2.28 – 2.16 (m, 2H), 1.36 – 1.25 (m, 1H), 0.89 (s, 9H), 0.03 (s, 3H), 0.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 137.0, 135.3, 129.9, 127.2, 125.6, 123.8, 103.6, 62.6, 50.5, 50.3, 32.4, 30.5, 26.0, 21.7, 18.4, -5.3, -5.5. IR (neat): 2954, 2928, 2856, 1638, 1590, 1462, 1397, 1364, 1351, 1276, 1249, 1198, 1169, 1104, 1086, 1021, 1013, 976, 938, 915 cm^{-1}. HRMS (ESI): calcd. for $C_{22}H_{34}NO_3SSi$ ([M+H]$^+$): 420.2023, found 420.2037.



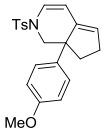
4h

Run 1: Following general procedure D, 37.3 mg **2h** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 10:1), 31.9 mg **4h** was obtained in 86% yield.
Run 2: Following general procedure D, 34.5 mg **2h** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 10:1), 28.2 mg **4h** was obtained in 82% yield.
Average yield: 84%.
Colorless oil, TLC R_f = 0.14 (EA/PE = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 6.71 (d, *J* = 8.2 Hz, 1H), 5.67 – 5.46 (m, 2H), 4.58 (d, *J* = 11.2 Hz, 1H), 4.04 – 3.95 (m, 2H), 2.70 (d, *J* = 11.2 Hz, 1H), 2.58 – 2.46 (m, 1H), 2.42 (s, 3H), 2.38 – 2.32 (m, 1H), 2.27 (dd, *J* = 12.9, 6.9 Hz, 1H), 1.75 – 1.63 (m, 1H), 1.18 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 144.0, 135.4, 135.2, 129.9, 127.2, 126.0, 125.7, 103.8, 61.3, 55.5, 52.1, 35.3, 31.2, 21.7, 14.2. IR (neat): 2926, 1727, 1346, 1236, 1164, 1021, 1007 cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{22}NO_4S$ ([M+H]$^+$): 348.1264, found 348.1264.



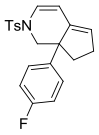
4i

Run 1: Following general procedure D, 35.7 mg **2i** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 31.1 mg **4i** was obtained in 87% yield.
Run 2: Following general procedure D, 35.4 mg **2i** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 29.2 mg **4i** was obtained in 82% yield.
Average yield: 84%.
White solid, TLC R_f = 0.54 (EA/PE = 1/5), m.p. = 150-153 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.18 – 7.09 (m, 7H), 6.65 (d, *J* = 8.0 Hz, 1H), 5.73 (d, *J* = 8.0 Hz, 1H), 5.70 (s, 1H), 4.55 (d, *J* = 11.5 Hz, 1H), 3.05 (d, *J* = 11.5 Hz, 1H), 2.38 (s, 3H), 2.29 – 2.19 (m, 2H), 2.14 – 2.03 (m, 1H), 1.94 – 1.83 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 142.5, 138.4, 135.5, 129.7, 128.2, 126.9, 126.6, 126.44, 126.36, 124.6, 104.1, 55.3, 52.8, 40.1, 30.2, 21.6. IR (neat): 3053, 3025, 2964, 2923, 2849, 1639, 1591, 1494, 1451, 1397, 1343, 1305, 1254, 1210, 1164, 1111, 1004, 972, 919 cm^{-1}. HRMS (ESI): calcd. for $C_{21}H_{22}NO_2S$ ($[M+H]^+$): 352.1366, found 352.1365.



4j

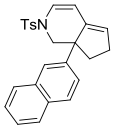
Run 1: Following general procedure D, 38.5 mg **2j** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1), 32.7 mg **4j** was obtained in 85% yield.
Run 2: Following general procedure D, 37.7 mg **2j** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1), 33.5 mg **4j** was obtained in 89% yield.
Average yield: 87%.
Colorless oil, TLC R_f = 0.24 (EA/PE = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 8.7 Hz, 2H), 6.66 (d, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 8.7 Hz, 2H), 5.72 (d, *J* = 8.0 Hz, 1H), 5.70 – 5.64 (m, 1H), 4.47 (d, *J* = 11.6 Hz, 1H), 3.76 (s, 3H), 3.05 (d, *J* = 11.6 Hz, 1H), 2.38 (s, 3H), 2.27 – 2.18 (m, 2H), 2.08 – 2.01 (m, 1H), 1.89 – 1.80 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 143.4, 138.6, 135.7, 134.4, 129.6, 127.7, 126.7, 126.3, 124.4, 113.5, 104.1, 55.6, 55.2, 52.1, 40.1, 30.1, 21.6. IR (neat): 2922, 2849, 1641, 1592, 1511, 1457, 1398, 1343, 1301, 1248, 1163, 1107, 1032, 1004, 971 cm^{-1}. HRMS (ESI): calcd. for $C_{22}H_{24}NO_3S$ ($[M+H]^+$): 382.1471, found 382.1473.



4k

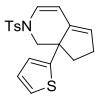
Run 1: Following general procedure D, 36.9 mg **2k** was used, 2 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1), 28.8 mg **4k** was obtained in 78% yield.
Run 2: Following general procedure D, 34.9 mg **2k** was used, 2 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1), 28.7 mg **4k** was obtained in 82% yield.
Average yield: 80%.
Colorless oil, TLC R_f = 0.40 (EA/PE = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 7.07 – 7.01 (m, 2H), 6.79 – 6.71 (m, 2H), 6.70 (d, *J* = 8.0 Hz, 1H), 5.73 (d, *J* = 8.0 Hz, 1H), 5.71 – 5.66 (m, 1H), 4.44 (d, *J* = 11.8 Hz, 1H), 3.09 (d, *J* = 11.8 Hz, 1H), 2.39 (s, 3H), 2.29 – 2.14 (m, 2H), 2.07 – 2.00 (m, 1H), 1.91 – 1.83 (m, 1H). ^{13}C NMR (100 MHz,

$CDCl_3$) δ 161.6 (d, *J* = 244.4 Hz), 143.7, 138.3, 138.1 (d, *J* = 3.0 Hz), 135.7, 129.7, 128.3 (d, *J* = 7.9 Hz), 126.8, 126.5, 124.8, 114.8 (d, *J* = 21.0 Hz), 103.9, 55.6, 52.3, 40.1, 30.1, 21.5. IR (neat): 2924, 2849, 1641, 1590, 1508, 1455, 1397, 1343, 1305, 1227, 1186, 1162, 1112, 1094, 1005, 972 cm^{-1}. HRMS (ESI): calcd. for $C_{21}H_{21}FNO_2S$ ($[M+H]^+$): 370.1272, found 370.1279.



4l

Run 1: Following general procedure D, 40.4 mg **2l** was used, 2 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1), 34.6 mg **4l** was obtained in 86% yield.
Run 2: Following general procedure D, 39.9 mg **2l** was used, 2 h. After flash column chromatography on silica gel (eluted with PE/EA 20:1), 34.5 mg **4l** was obtained in 86% yield.
Average yield: 86%.
White solid, TLC R_f = 0.38 (EA/PE = 1/10), m.p. = 63-66 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.72 (m, 1H), 7.64 – 7.60 (m, 1H), 7.56 (d, *J* = 8.6 Hz, 1H), 7.45 – 7.38 (m, 3H), 7.28 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.15 (d, *J* = 8.3 Hz, 2H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.65 (s, 1H), 6.63 (s, 1H), 5.86 (d, *J* = 8.0 Hz, 1H), 5.80 – 5.75 (m, 1H), 4.63 (d, *J* = 12.1 Hz, 1H), 3.27 (d, *J* = 12.1 Hz, 1H), 2.29 – 2.14 (m, 3H), 2.11 (s, 3H), 2.01 – 1.92 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 139.9, 138.3, 135.7, 133.1, 132.4, 129.1, 128.1, 128.0, 127.3, 126.4, 125.8, 125.7, 125.6, 125.1, 125.0, 104.3, 55.9, 53.1, 40.0, 30.2, 21.5. IR (neat): 3054, 2925, 2863, 1915, 1692, 1639, 1594, 1502, 1453, 1398, 1341, 1249, 1162, 1108, 1005, 972 cm^{-1}. HRMS (EI): calcd. for $C_{25}H_{23}NO_2S$ ($M^{\cdot+}$): 401.1444, found 401.1443.



4m

Run 1: Following general procedure D, 35.3 mg **2m** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 30.5 mg **4m** was obtained in 86% yield.
Run 2: Following general procedure D, 35.0 mg **2m** was used, 1 h. After flash column chromatography on silica gel (eluted with PE/EA 50:1), 28.6 mg **4m** was obtained in 82% yield.
Average yield: 84%.
Colorless oil, TLC R_f = 0.30 (EA/PE = 1/10). ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.04 (dd, *J* = 4.9, 1.3 Hz, 1H), 6.79 – 6.72 (m, 2H), 6.67 (d, *J* = 8.1 Hz, 1H), 5.67 (d, *J* = 8.1 Hz, 1H), 5.64 – 5.59 (m, 1H), 4.48 (d, *J* = 11.4 Hz, 1H), 3.01 (d, *J* = 11.4 Hz, 1H), 2.54 – 2.45 (m, 1H), 2.40 (s, 3H), 2.34 – 2.27 (m, 1H), 2.20 – 2.13 (m, 1H), 1.92 – 1.82 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 143.7, 139.1, 135.5, 129.8, 127.0, 126.7, 126.1, 124.0, 123.9, 123.6, 103.5, 55.6, 50.6, 40.5, 30.4, 21.7. IR (neat): 3091, 2924, 2850, 1641, 1592, 1493, 1454, 1398, 1345, 1303, 1255, 1201, 1165, 1108, 1002, 970, 918 cm^{-1}. HRMS (ESI): calcd. for $C_{19}H_{20}NO_2S_2$ ($[M+H]^+$): 358.0930, found 358.0937.

VII. General Procedure of One-pot Cycloisomerization/[5+1] Reaction Sequence

Preparation of solution of cationic Au(I) catalyst: Anhydrous DCE (1.0 mL) was added to a mixture of Au(JohnPhos)Cl (2.6 mg, 4.9 μmol) and $AgSbF_6$ (2.1 mg, 6.1 μmol) under nitrogen. The mixture was stirred at room temperature for 30 min. The resulting suspension was left to stand until the formed AgCl precipitated. The supernatant was used in Au(I)-catalyzed cycloisomerization reactions as the catalyst precursor.

Preparation of solution of cationic Rh(I) catalyst: Anhydrous DCE (1.0 mL) was added to a mixture of $[Rh(CO)_2Cl]_2$ (2.0 mg, 5.1 μmol), $AgSbF_6$ (4.1 mg, 11.9 μmol), and dppp (4.1 mg, 9.9 μmol) under nitrogen. The mixture was stirred at room temperature for 30 min. The resulting suspension was left to stand until the formed AgCl precipitated. The supernatant was used in Rh(I)-catalyzed [5+1] cycloaddition reactions as the catalyst precursor.

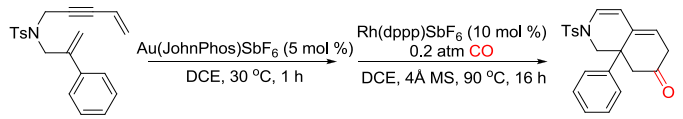
1i **3i**

One-pot Cycloisomerization/[5+1] Reaction Sequence: Under nitrogen, the above $Au(I)^+$ solution (1.0 mL) and $Rh(I)^+$ solution (1.0 mL) were added to a flame-dried glassware containing **1i** (0.1 mmol) at 30 ºC. The reaction was monitored by TLC and stirred for 1 h. Upon completion, the newly activated 4 Å molecular sieves (0.08 g) were added to the reaction mixture, then the reaction mixture was bubbled with a mixed gas of CO/N_2 (v/v = 1/4) for 10 min. The glassware was immersed into an oil bath at 90 ºC and reacted under the atmosphere pressure of the mixed gas of CO/N_2 (v/v = 1/4). The reaction was monitored by TLC and stirred for 16 h. Upon completion, the reaction mixture was purified by flash column chromatography on silica gel to afford **3i**.

Run 1: Following procedure, 34.6 mg **1i** was used. After flash column chromatography on silica gel (eluted with PE/EA 3:1), 25.5 mg **3i** was obtained in 68% yield.

Run 2: Following procedure, 35.0 mg **1i** was used. After flash column chromatography on silica gel (eluted with PE/EA 3:1), 27.2 mg **3i** was obtained in 72% yield.

Average yield: 70%.



1i **3i**

One-pot Cycloisomerization/[5+1] Reaction Sequence: Under nitrogen, the above $Au(I)^+$ solution (1.0 mL) was added to a flame-dried glassware containing **1i** (0.1 mmol) at 30 ºC. The reaction was monitored by TLC and stirred for 1 h. Upon completion, the above $Rh(I)^+$ solution (1.0 mL) and the newly activated 4 Å molecular sieves (0.08 g) were added to the reaction mixture. Then the reaction mixture was bubbled with a mixed gas of CO/N_2 (v/v = 1/4) for 10 min. The glassware was immersed into an oil bath at 90 ºC and reacted under the atmosphere pressure of the mixed gas of CO/N_2 (v/v = 1/4). The reaction was monitored by TLC and stirred for 16 h. Upon completion, the reaction mixture was purified by flash column chromatography on silica gel to afford **3i**.

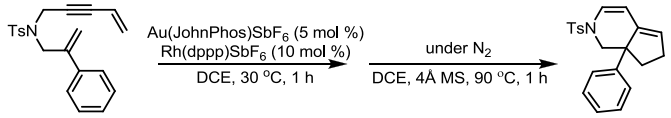
Run 1: Following procedure, 35.5 mg **1i** was used. After flash column chromatography on silica gel (eluted with PE/EA 3:1), 29.6 mg **3i** was obtained in 77% yield.

Run 2: Following procedure, 34.9 mg **1i** was used. After flash column chromatography on silica gel (eluted with PE/EA 3:1), 27.4 mg **3i** was obtained in 73% yield.
Average yield: 75%.

VIII. General Procedure of One-pot Cycloisomerization/Rearrangement Sequence

Preparation of solution of cationic Au(I) catalyst: Anhydrous DCE (1.0 mL) was added to a mixture of Au(JohnPhos)Cl (2.6 mg, 4.9 μmol) and $AgSbF_6$ (2.1 mg, 6.1 μmol) under nitrogen. The mixture was stirred at room temperature for 30 min. The resulting suspension was left to stand until the formed AgCl precipitated. The supernatant was used in Au(I)-catalyzed cycloisomerization reactions as the catalyst precursor.

Preparation of solution of cationic Rh(I) catalyst: Anhydrous DCE (1.0 mL) was added to a mixture of $[Rh(CO)_2Cl]_2$ (2.0 mg, 5.1 μmol), $AgSbF_6$ (4.1 mg, 11.9 μmol), and dppp (5.0 mg, 12.1 μmol) under nitrogen. The mixture was stirred at room temperature for 30 min. The resulting suspension was left to stand until the formed AgCl precipitated. The supernatant was used in Rh(I)-catalyzed [5+1] cycloaddition reactions as the catalyst precursor.



1i **4i**

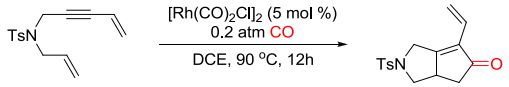
One-pot Cycloisomerization/[5+1] Reaction Sequence: Under nitrogen, the above $Au(I)^+$ solution (1.0 mL) and $Rh(I)^+$ solution (1.0 mL) were added to a flame-dried glassware containing **1i** (0.1 mmol) at 30 ºC. The reaction was stirred for 1 h (the cyclopropanation reaction was completed, as monitored by TLC). Then the newly activated 4 Å molecular sieves (0.08 g) were added to the reaction mixture and the glassware was immersed into an oil bath at 90 ºC. The reaction was stirred for 1 h (the vinyl-cyclopropane isomerization reaction was completed, as monitored by TLC). The reaction mixture was directly purified by flash column chromatography on silica gel to afford **4i**.

Run 1: Following procedure, 35.3 mg **1i** was used. After flash column chromatography on silica gel (eluted with PE/EA 20:1), 26.9 mg **4i** was obtained in 76% yield.

Run 2: Following procedure, 34.9 mg **1i** was used. After flash column chromatography on silica gel (eluted with PE/EA 20:1), 26.1 mg **4i** was obtained in 75% yield.

Average yield: 76%.

IX. General Procedure of Pauson-Khand Cycloaddition



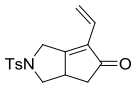
1a **5a**

Under argon, the solution of **1a** (0.1 mmol) in DCE (2.0 mL) was added to a flame-dried glassware containing $[Rh(CO)_2Cl]_2$ (2.0 mg, 5.0 μmol) at rt. Then the reaction mixture was bubbled with a mixed gas of CO/N_2 (v/v = 1/4) for 10 min. The glassware was immersed into an oil bath at 90 ºC and reacted under the atmosphere pressure of the mixed gas of CO/N_2 (v/v = 1/4). The reaction was monitored by TLC and stirred for 12 h. Upon completion, the reaction mixture was purified by flash column chromatography on silica gel to afford **5a**.

Run 1: Following procedure, 28.2 mg **1a** was used. After flash column chromatography on silica gel (eluted with PE/EA 3:1), 26.6 mg **5a** was obtained in 86% yield.

Run 2: Following procedure, 28.1 mg **1a** was used. After flash column chromatography on silica gel (eluted with PE/EA 3:1), 25.4 mg **5a** was obtained in 82% yield.

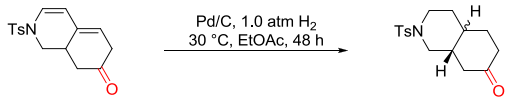
Average yield: 84%.



5a

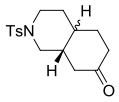
Colorless oil, TLC R_f = 0.41 (EA/PE = 1/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 6.29 (dd, *J* = 17.8, 11.3 Hz, 1H), 5.73 (d, *J* = 17.8 Hz, 1H), 5.44 (d, *J* = 11.3 Hz, 1H), 4.39 (d, *J* = 17.0 Hz, 1H), 4.10 – 3.96 (m, 2H), 3.20 – 2.98 (m, 1H), 2.64 (dd, *J* = 18.0, 6.5 Hz, 1H), 2.59 – 2.49 (m, 1H), 2.42 (s, 3H), 2.09 (dd, *J* = 18.0, 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.7, 171.5, 144.3, 134.0, 133.6, 130.1, 127.6, 124.9, 121.6, 52.4, 47.8, 42.1, 40.0, 21.7. IR (neat): 2923, 2853, 1711, 1344, 1306, 1289, 1261, 1220, 1161, 1092, 1047 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{18}NO_3S$ ($[M+H]^+$): 304.1002, found 304.0997.

X. General Procedure of Synthetic Transformation



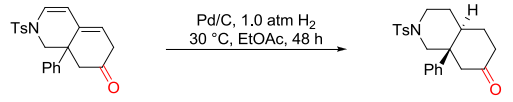
3a **6a**

The solution of **3a** (38.2 mg, 0.13 mmol) in EA (1.3 mL) was added to flame-dried glassware containing Pd/C (12.0 mg) at rt. Then the reaction mixture was bubbled with 1.0 atm H_2 (balloon) for 10 min. The glassware was immersed into an oil bath at 30 ºC and reacted under the 1.0 atm H_2 (balloon). The reaction was monitored by TLC and stirred for 48 h. Upon completion, the reaction mixture was purified by flash column chromatography on silica gel (eluted with PE/EA 3:1) to afford **6a** (26.0 mg, 67%, dr = 1.6/1).



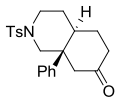
6a

Colorless oil, TLC R_f = 0.40 (EA/PE = 1/1). ^{1}H NMR (400 MHz, CDCl3) δ 7.67 – 7.56 (m, 3.2H + 2H), 7.35 – 7.28 (m, 3.2H + 2H), 3.87 (ddt, *J* = 11.6, 4.1, 2.0 Hz, 1.6H), 3.70 (ddd, *J* = 11.4, 3.8, 1.8 Hz, 1.6H), 3.56 – 3.42 (m, 1H), 3.13 (dd, *J* = 11.6, 4.4 Hz, 1H), 2.75 – 2.60 (m, 1.6H + 1H), 2.43 (s, 4.8H + 3H), 2.40 – 2.37 (m, 1.6H), 2.37 – 2.17 (m, 4.8H + 4H), 2.01 – 1.92 (m, 5H), 1.90 – 1.62 (m, 8H), 1.46 – 1.35 (m, 3.2H), 1.31 – 1.21 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.0, 209.0, 143.8, 133.3, 133.22, 129.83, 129.81, 127.72, 127.66, 51.7, 49.5, 46.5, 45.1, 44.6, 42.1, 41.2, 40.9, 39.4, 37.5, 37.1, 32.3, 32.0, 31.1, 29.0, 25.7, 21.6. IR (neat): 1715, 1340, 1306, 1164, 1092, 1014 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{22}NO_3S$ ([M+H]$^+$): 308.1315, found 308.1316.



3i **6i**

The solution of **3i** (47.2 mg, 0.12 mmol) in EA (1.2 mL) was added to flame-dried glassware containing Pd/C (14.0 mg) at rt. Then the reaction mixture was bubbled with 1.0 atm H_2 (balloon) for 10 min. The glassware was immersed into an oil bath at 30 ºC and reacted under the 1.0 atm H_2 (balloon). The reaction was monitored by TLC and stirred for 48 h. Upon completion, the reaction mixture was purified by flash column chromatography on silica gel (eluted with PE/EA 3:1) to afford **6i** (31.6 mg, 66%, dr > 20/1).

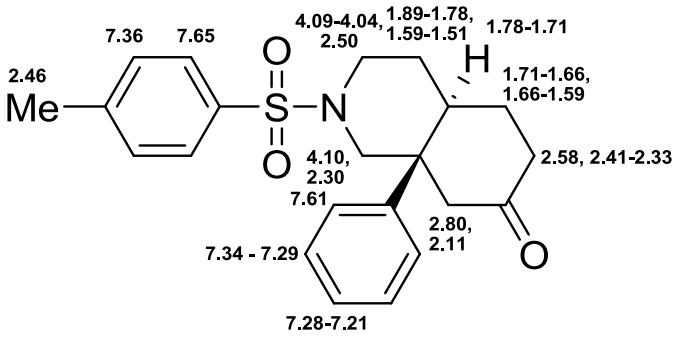


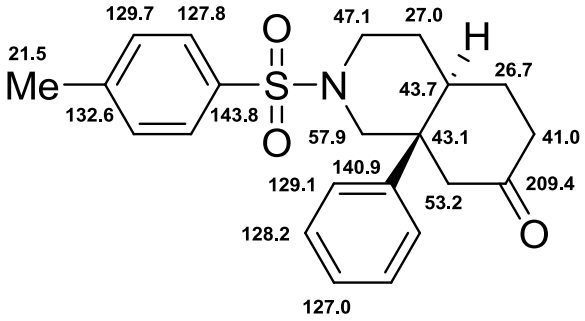
6i

Colorless oil, TLC R_f = 0.45 (EA/PE = 1/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.29 (m, 2H), 7.28 – 7.21 (m, 1H), 4.10 (d, *J* = 11.6 Hz, 1H), 4.09 – 4.04 (m, 1H), 2.80 (dd, *J* = 15.8, 1.3 Hz, 1H), 2.58 (dd, *J* = 16.9, 5.1 Hz, 1H), 2.50 (dd, *J* = 11.7, 3.1 Hz, 1H), 2.46 (s, 3H), 2.41 – 2.33 (m, 1H), 2.30 (d, *J* = 11.6 Hz, 1H),

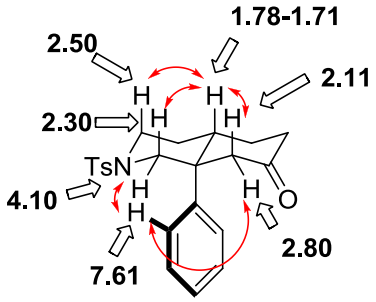
2.11 (d, *J* = 15.8 Hz, 1H), 1.89 – 1.78 (m, 1H), 1.78 – 1.71 (m, 1H), 1.71 – 1.66 (m, 1H), 1.66 – 1.59 (m, 1H), 1.59 – 1.51 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.4, 143.8, 140.9, 132.6, 129.7, 129.1, 128.2, 127.8, 127.0, 57.9, 53.2, 47.0, 43.7, 43.1, 41.0, 27.0, 26.7, 21.5. IR (neat): 2959, 2925, 1468, 1106, 1033, 1021 cm^{-1}. HRMS (ESI): calcd. for $C_{22}H_{26}NO_3S$ ([M+H]$^+$): 384.1628, found 384.1629.

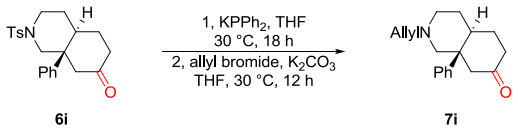
NMR analysis of **6i** by the DEPT and 2D NMR.





Determination of the stereostructure of **6i** by 2D NOESY.

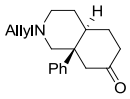




6i **7i**

Follow the reported procedure[16, 17]: To a solution of **6i** (40.0 mg, 0.1 mmol) in THF (1 mL) was added $KPPh_2$ (0.6 mL, 0.3 mmol, 0.5 M solution in THF) at 0 ºC. The solution was stirred for 18 h at 30 ºC. 1M HCl (0.5 mL) was added to the solution at 0 ºC and the temperature was raised to rt. The resulting mixture was stirred for 30 min, added with saturated aqueous $NaHCO_3$ (5 mL), extracted with DCM (3×10 mL), dried over Na_2SO_4, filtered, and concentrated. The crude amine was used without further purification. To the generated amine dissolved in THF (1 mL) was added

K_2CO_3 (55.0 mg, 0.4 mmol) and allyl bromide (0.035 mL, 0.4 mmol). The solution was stirred at 30 ºC for 12 h. Upon completion, The resulting mixture was quenched by water (10 mL) and extracted with ether (3×10 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 5:1) to afford **7i** (11.4 mg, 42%, dr > 20/1).



7i

Colorless oil, TLC R_f = 0.36 (EA/PE = 1/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.7 Hz, 2H), 7.32 – 7.23 (m, 2H), 7.22 – 7.16 (m, 1H), 5.94 – 5.78 (m, 1H), 5.15 (d, *J* = 17.5 Hz, 1H), 5.10 (d, *J* = 10.2 Hz, 1H), 3.15 (d, *J* = 11.0 Hz, 2H), 3.06 (dd, *J* = 13.5, 5.7 Hz, 1H), 2.92 (dd, *J* = 13.5, 6.6 Hz, 1H), 2.76 (d, *J* = 16.0 Hz, 1H), 2.57 (dd, *J* = 17.1, 5.2 Hz, 1H), 2.39 (ddd, *J* = 17.1, 12.1, 7.7 Hz, 1H), 2.25 – 2.09 (m, 2H), 2.01 (d, *J* = 11.3 Hz, 1H), 1.84 – 1.54 (m, 4H), 1.52 – 1.42 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.6, 143.4, 135.6, 130.0, 127.7, 126.5, 117.5, 66.6, 61.8, 54.8, 54.3, 44.7, 43.8, 41.4, 28.2, 26.9. IR (neat): 2939, 2793, 1708, 1498, 1462, 1152 cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{24}NO$ ($[M+H]^+$): 270.1852, found 270.1849.

XI. References

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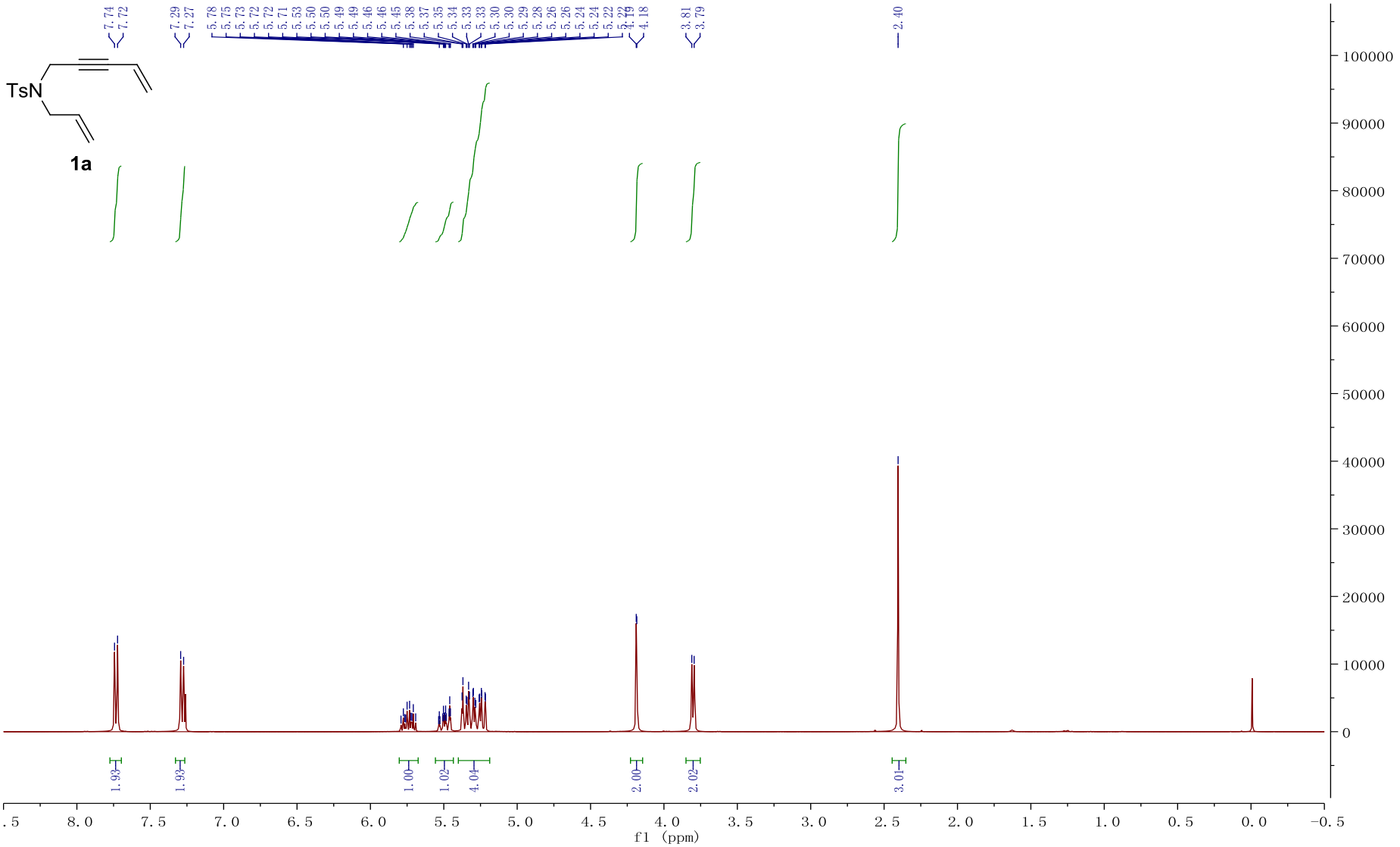
XII. NMR Spectra


TsN
1a
7.74
7.72
7.29
7.27
5.78
5.75
5.73
5.72
5.72
5.71
5.53
5.50
5.50
5.49
5.49
5.46
5.46
5.45
5.38
5.37
5.35
5.34
5.33
5.33
5.30
5.30
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5.28
5.26
5.26
5.24
5.24
5.22
4.18
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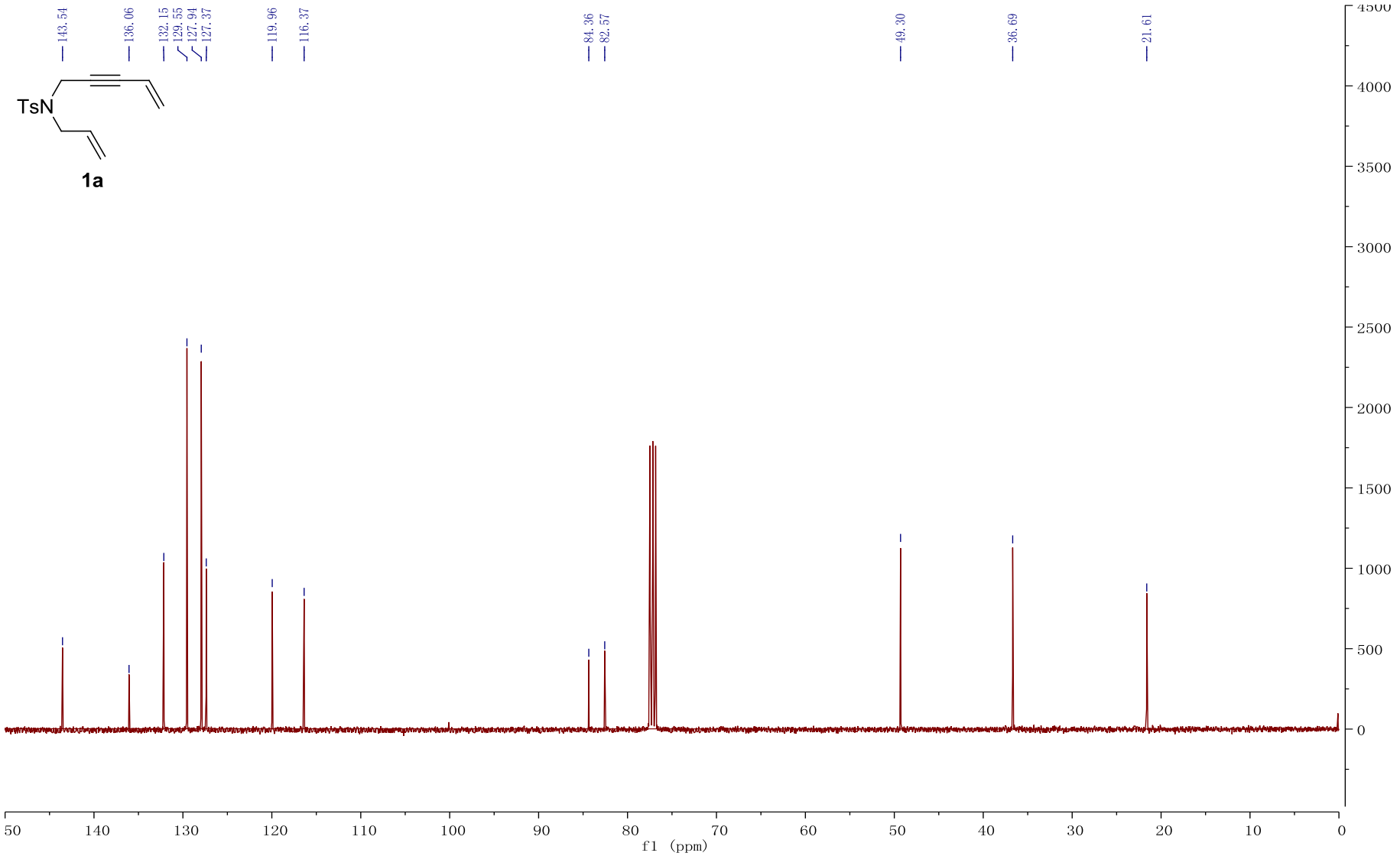
1.02
4.04
2.00
2.02
3.01
f1 (ppm)


143.54
136.06
132.15
129.55
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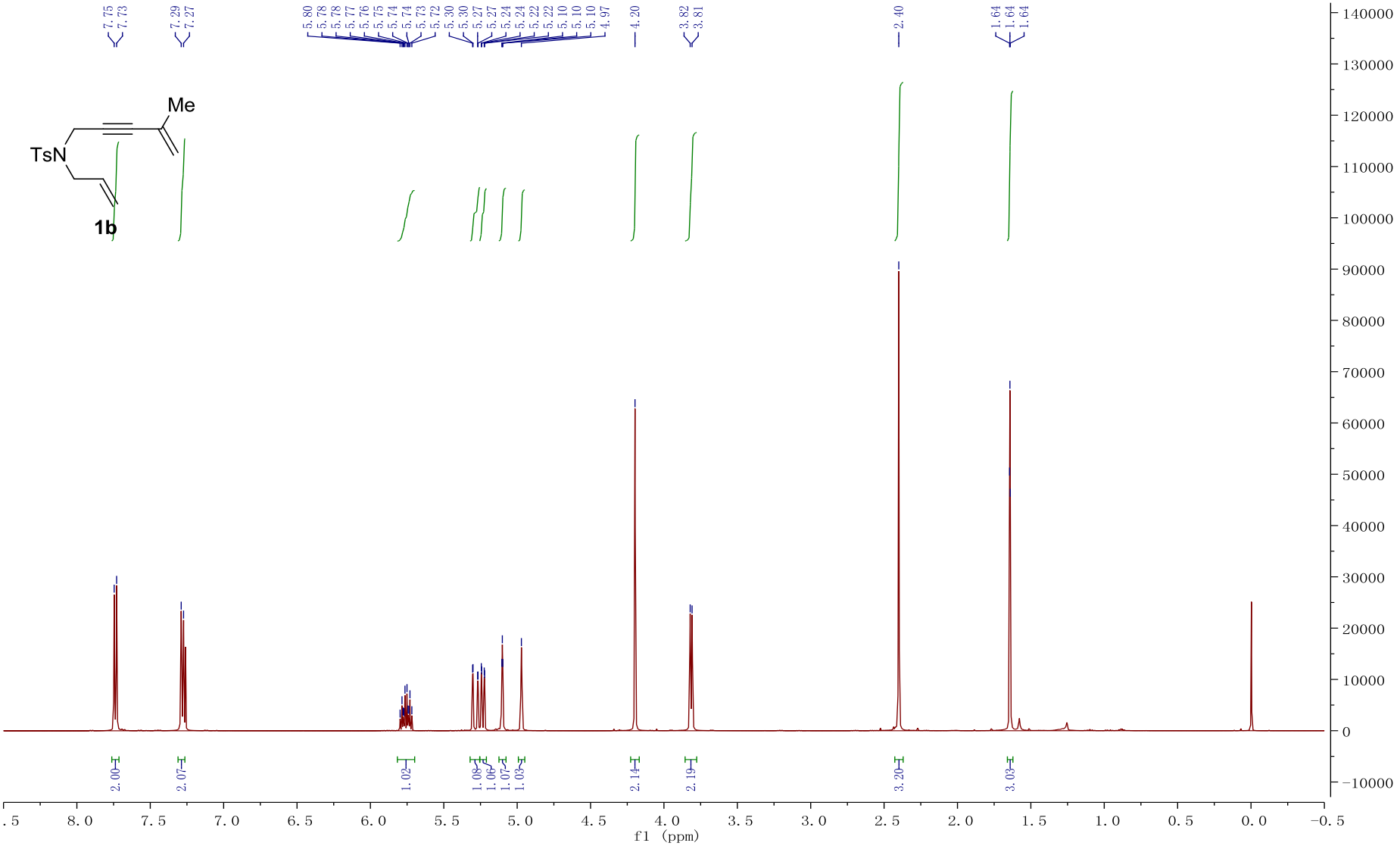
82.57
49.30
36.69
21.61
TsN
1a
4500
4000
3500
3000
2500
2000
1500
1000
500
0
50
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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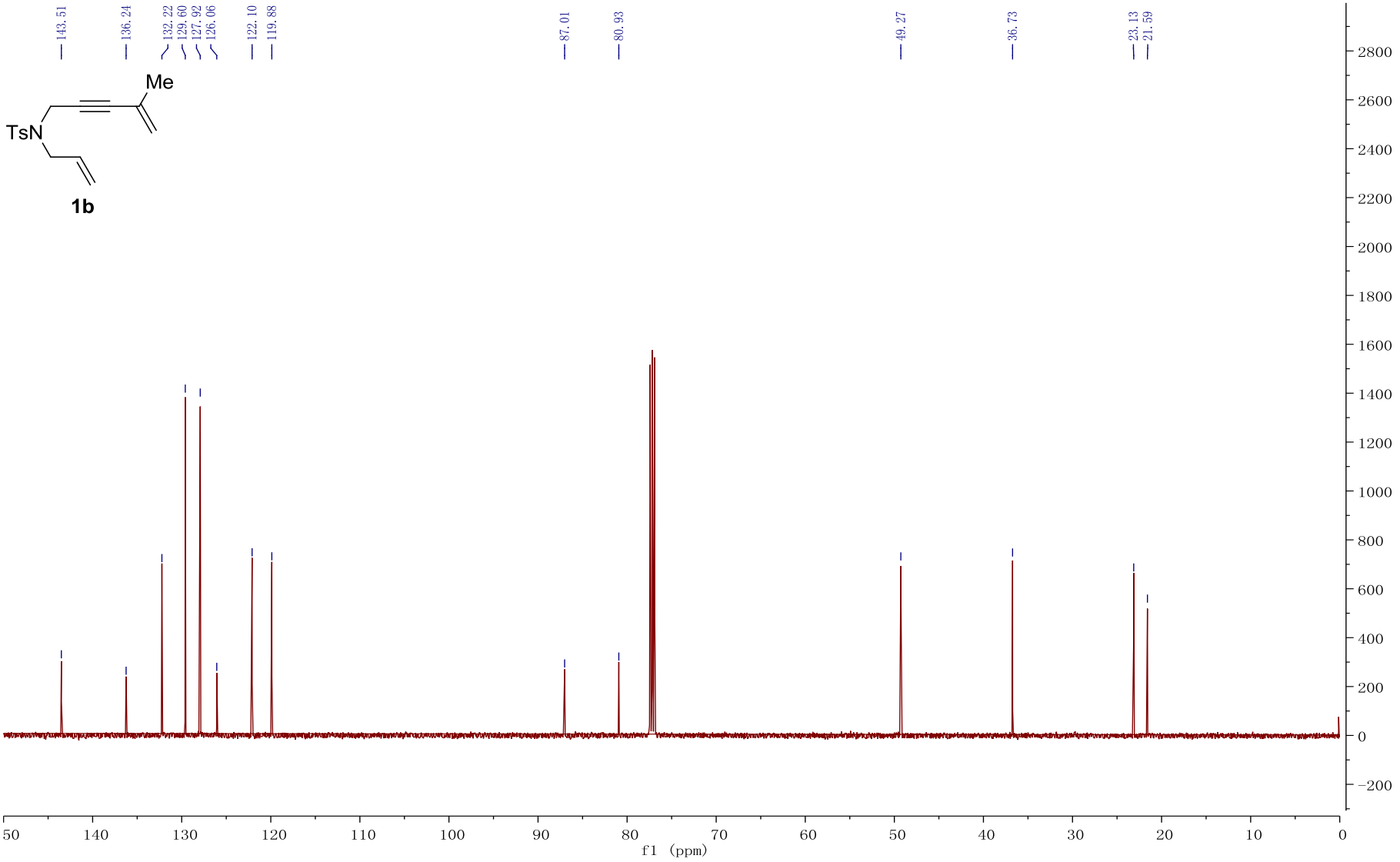
7.73
7.29
7.27
5.80
5.78
5.78
5.77
5.76
5.75
5.74
5.74
5.73
5.72
5.30
5.30
5.27
5.27
5.24
5.24
5.22
5.22
5.10
5.10
5.10
4.97
4.20
3.82
3.81
2.40
1.64
1.64
1.64
Me
TsN
1b
2.00
2.07
1.02
1.08
1.06
1.07
1.03
2.14
2.19
3.20
3.03
f1 (ppm)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136.24
132.22
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126.06
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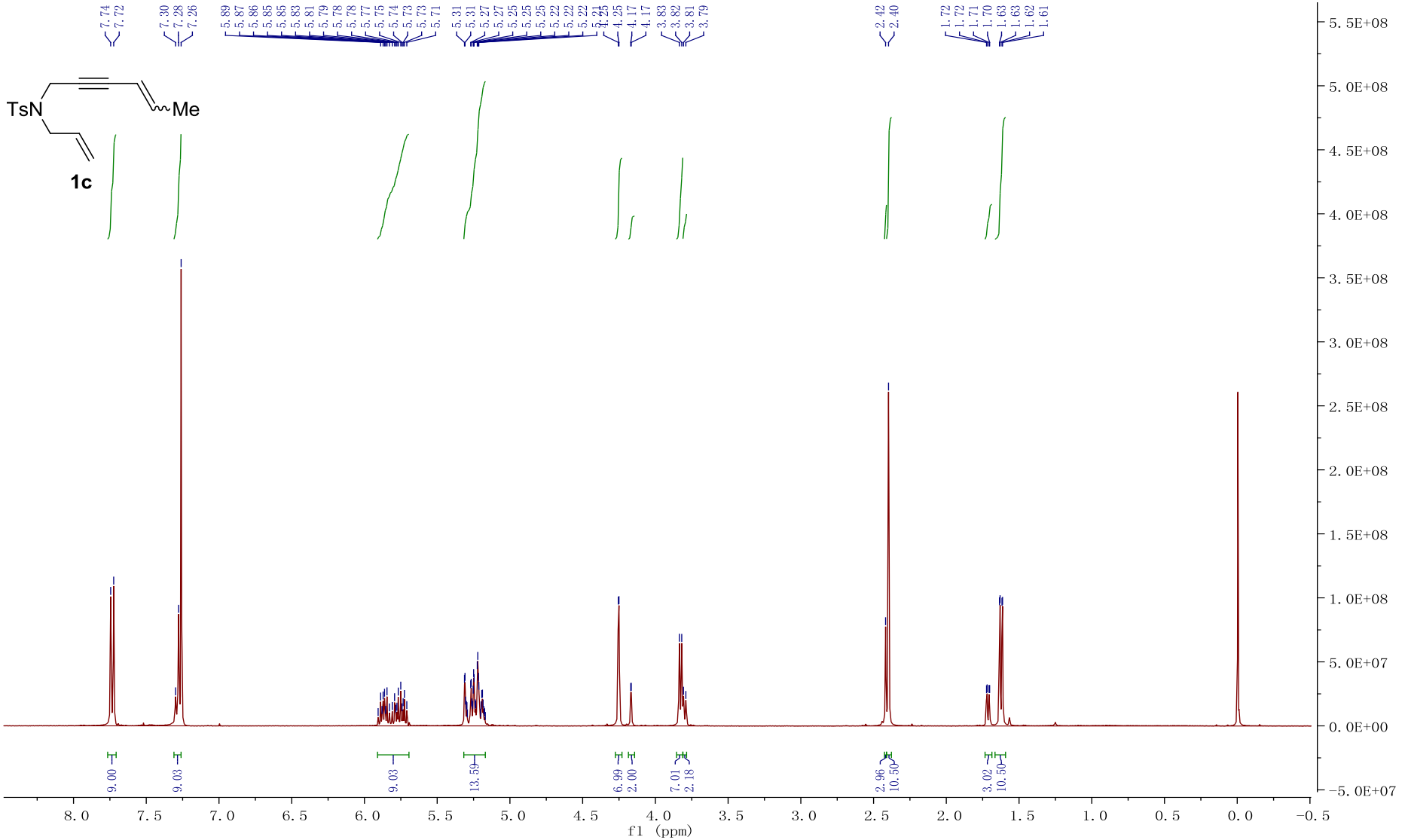
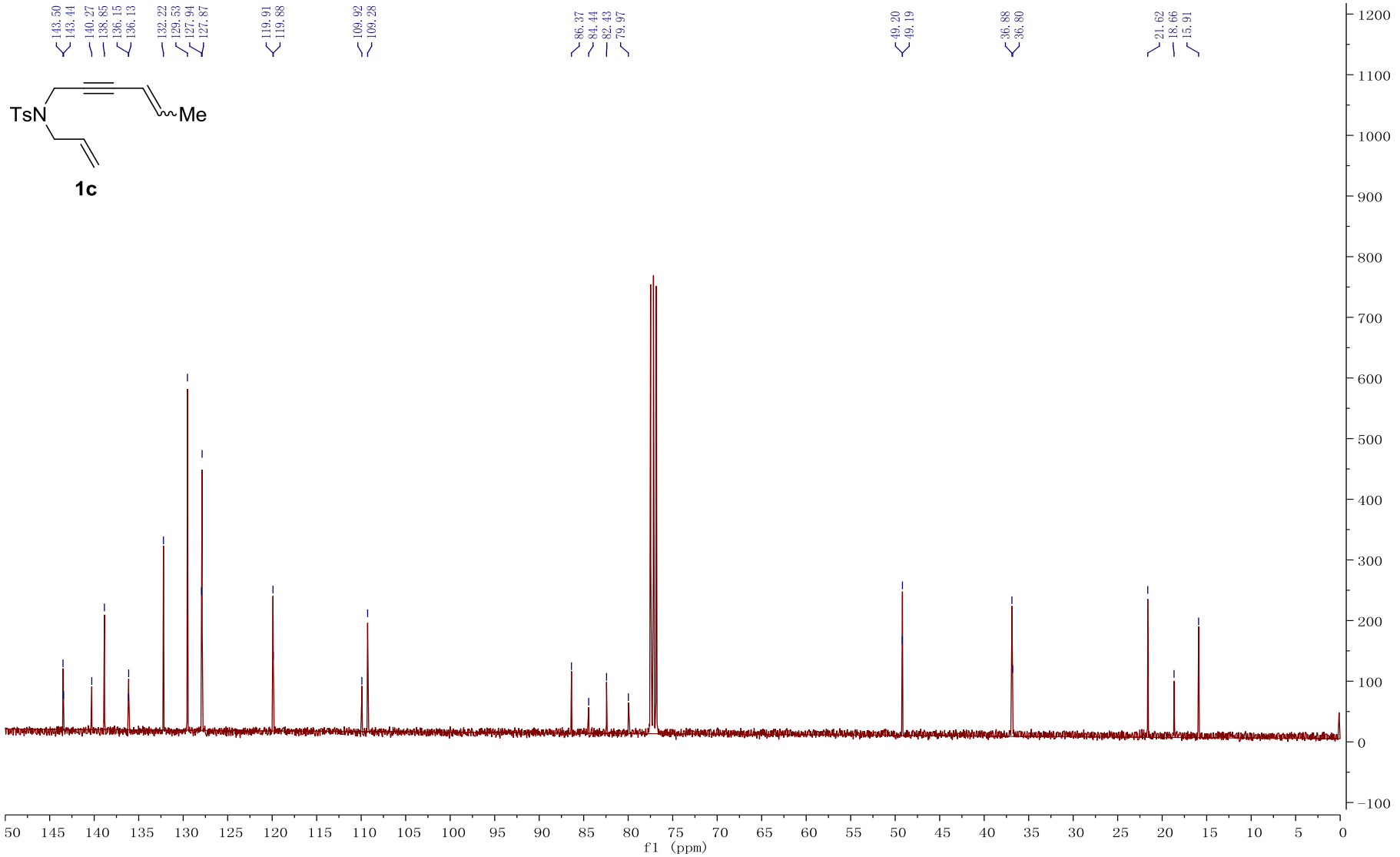
80.93
49.27
36.73
23.13
21.59
Me
TsN
1b
f1 (ppm)


TsN
Me
1c
f1 (ppm)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136.13
132.22
129.53
127.94
127.87
119.91
119.88
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109.28
86.37
84.44
82.43
79.97
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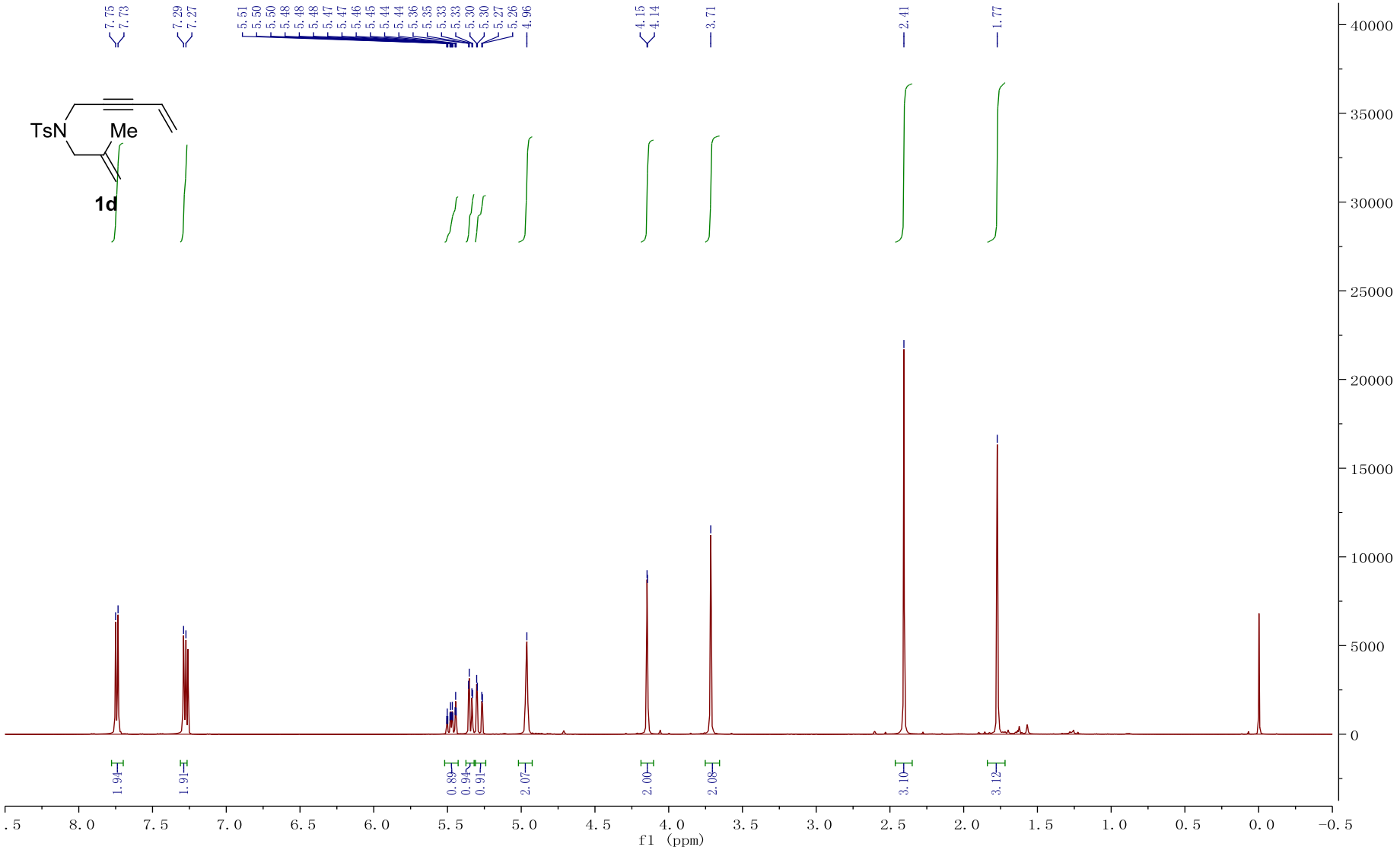
49.19
36.88
36.80
21.62
18.66
15.91
TsN
Me
1c
f1 (ppm)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7.73
7.29
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5.50
5.48
5.48
5.48
5.47
5.47
5.46
5.45
5.44
5.44
5.36
5.35
5.33
5.33
5.30
5.30
5.27
5.26
4.96
4.15
4.14
3.71
2.41
1.77
TsN
Me
1d
40000
35000
30000
25000
20000
15000
10000
5000
0
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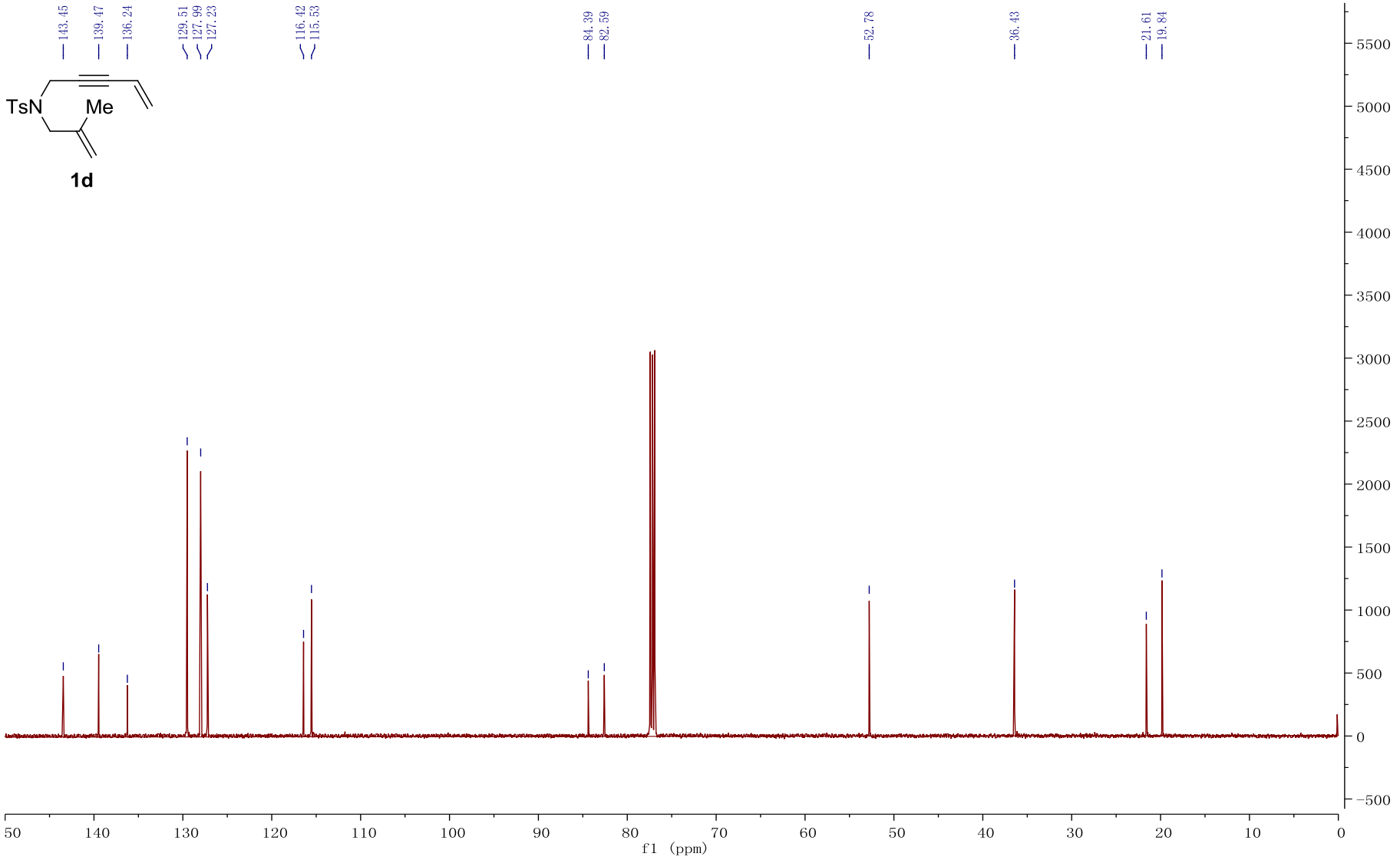
1.91
0.89
0.94
0.91
2.07
2.00
2.08
3.10
3.12
f1 (ppm)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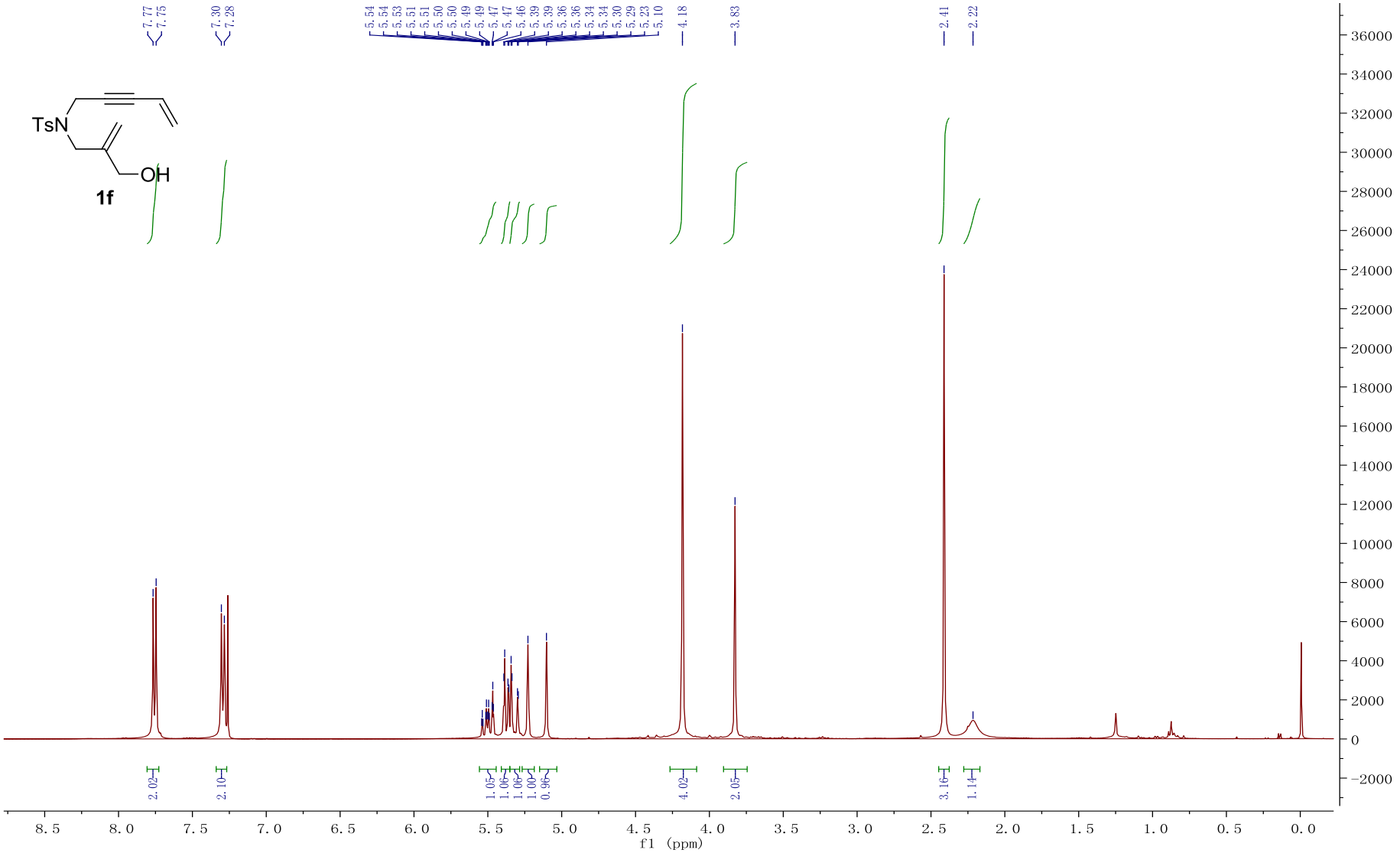
139.47
136.24
129.51
127.99
127.23
116.42
115.53
84.39
82.59
52.78
36.43
21.61
19.84
TsN
Me
1d
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
50
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.75
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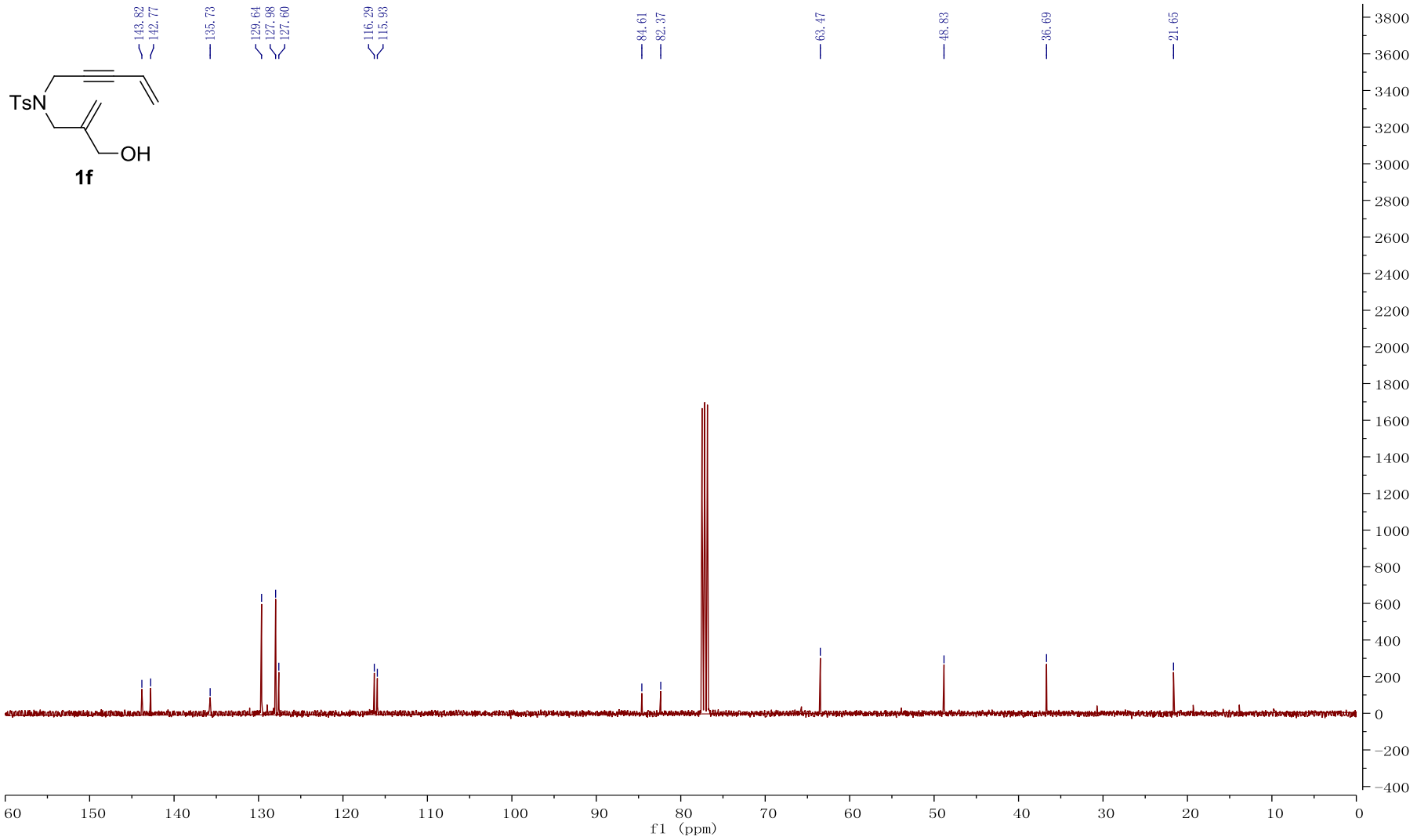
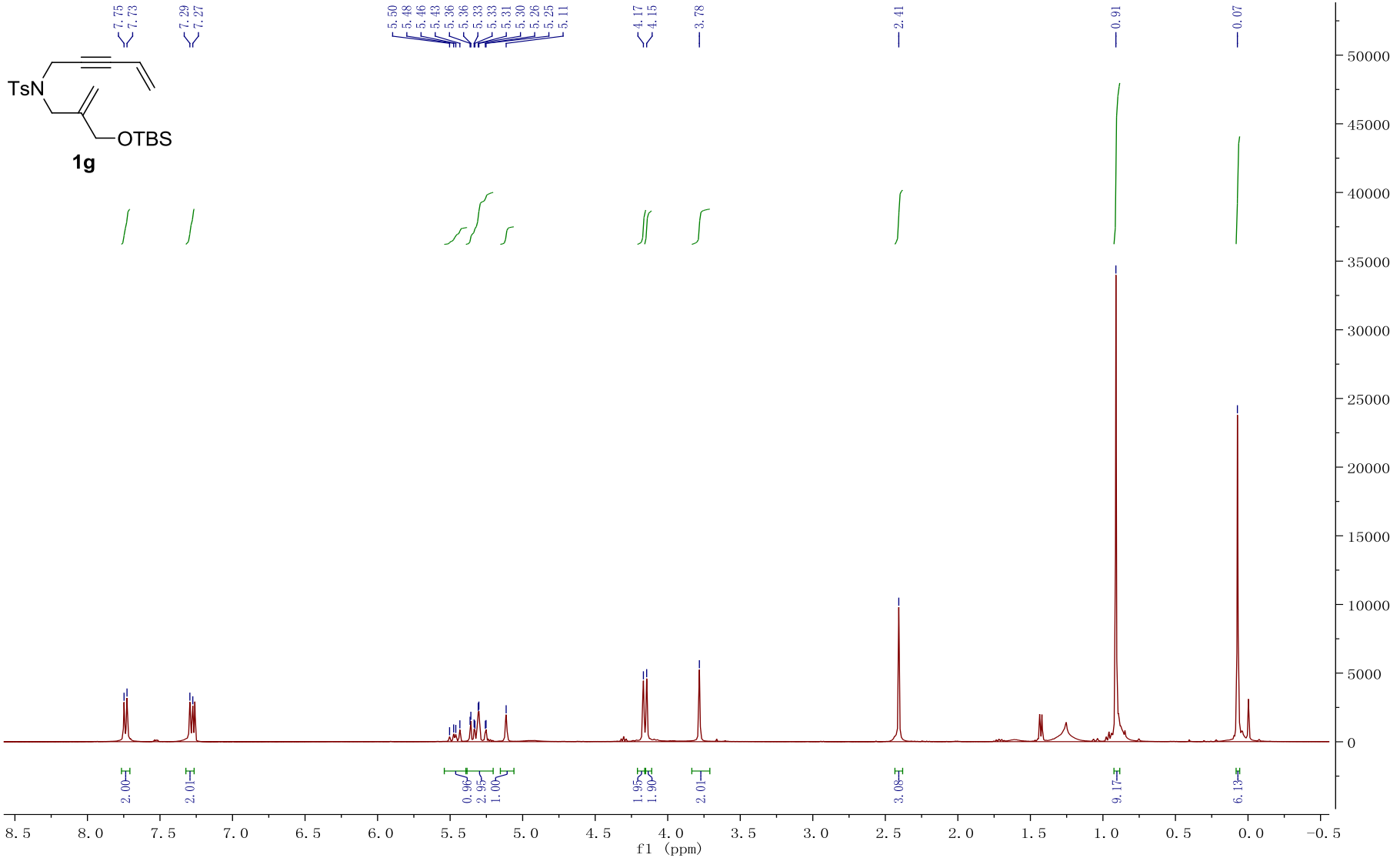
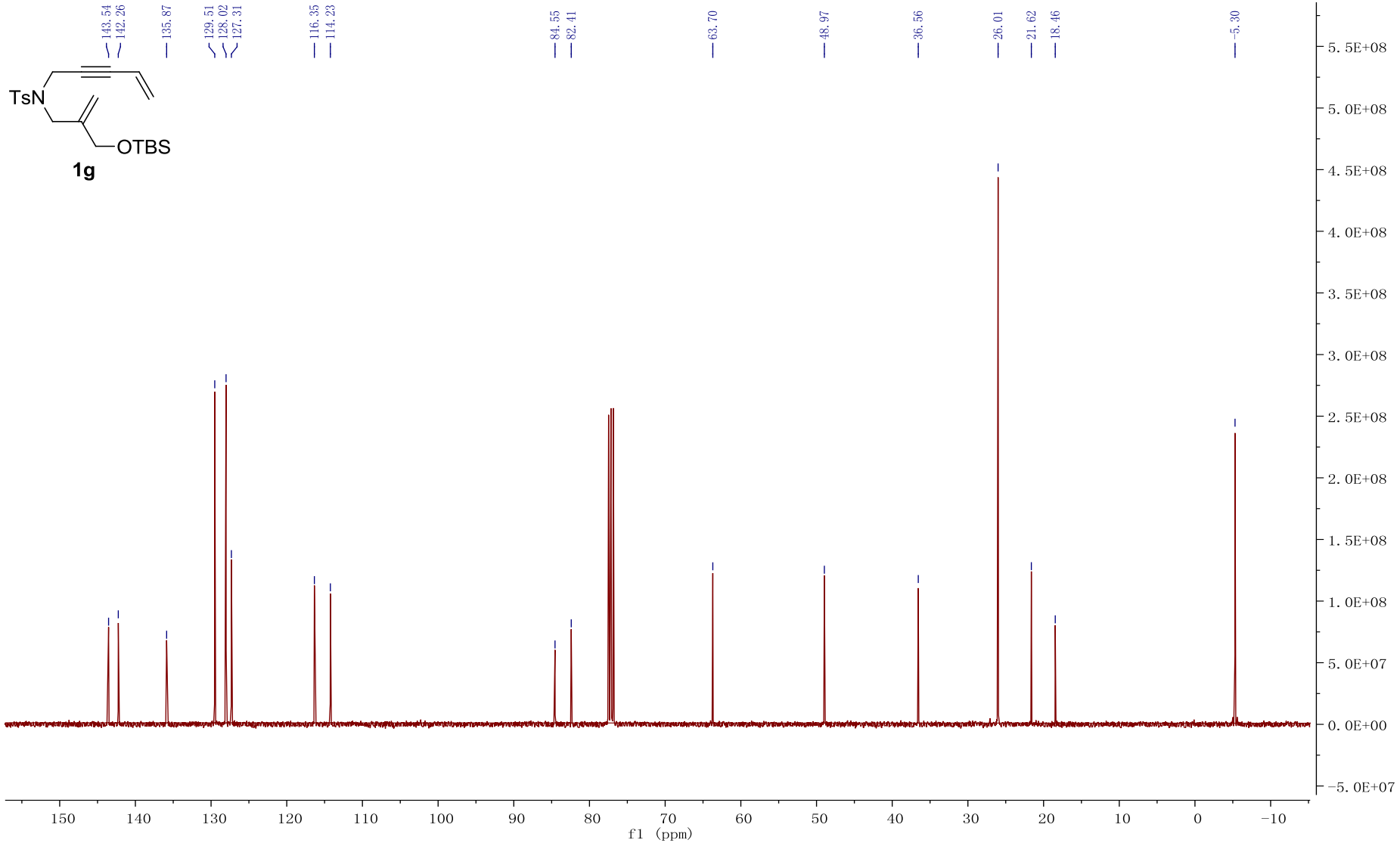
5.53
5.51
5.51
5.50
5.50
5.49
5.49
5.47
5.47
5.46
5.39
5.39
5.36
5.36
5.34
5.34
5.30
5.29
5.23
5.10
4.18
3.83
2.41
2.22
TsN
OH
1f
2.02
2.10
1.05
1.06
1.06
1.00
0.96
4.02
2.05
3.16
1.14
f1 (ppm)


143.82
142.77
135.73
129.64
127.98
127.60
116.29
115.93
84.61
82.37
63.47
48.83
36.69
21.65
TsN
OH
1f
f1 (ppm)


TsN
OTBS
1g
7.75
7.73
7.29
7.27
5.50
5.48
5.46
5.43
5.36
5.36
5.33
5.33
5.31
5.30
5.26
5.25
5.11
4.17
4.15
3.78
2.41
0.91
0.07
2.00
2.01
0.96
2.95
1.00
1.95
1.90
2.01
3.08
9.17
6.13
f1 (ppm)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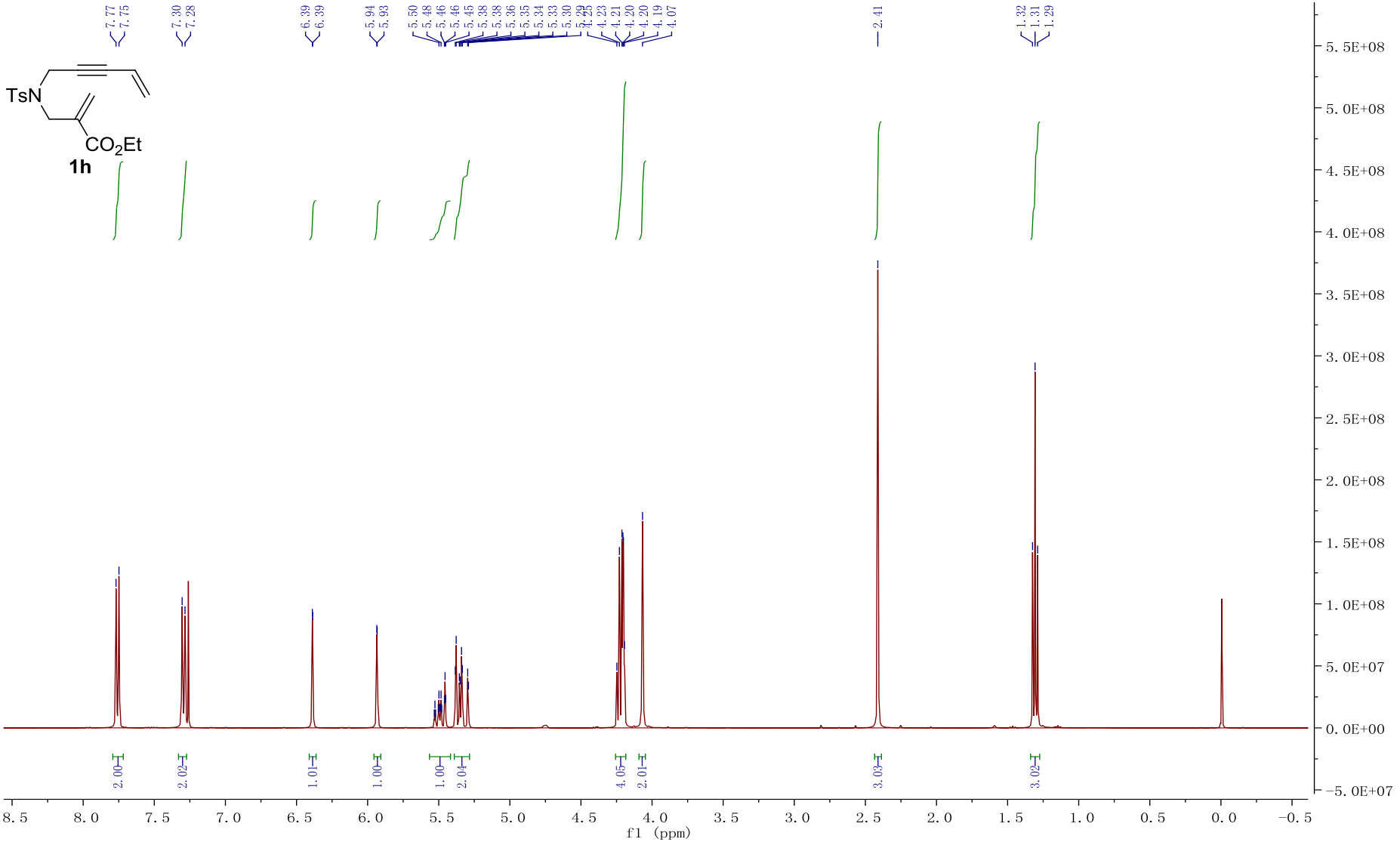
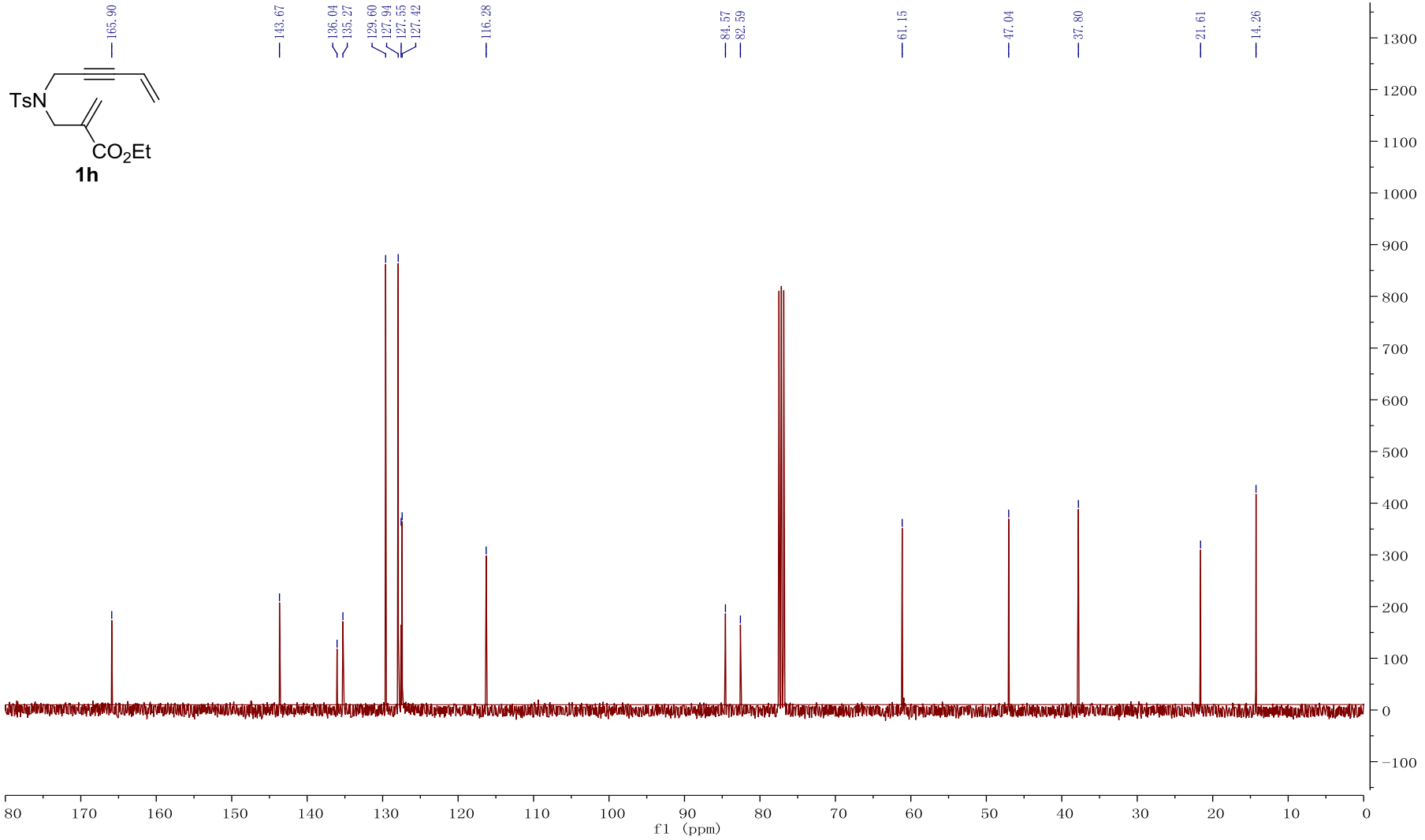
142.26
135.87
129.51
128.02
127.31
116.35
114.23
84.55
82.41
63.70
48.97
36.56
26.01
21.62
18.46
-5.30
TsN
OTBS
1g
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


TsN
CO2Et
1h
7.77
7.75
7.30
7.28
6.39
6.39
5.94
5.93
5.50
5.48
5.46
5.46
5.45
5.38
5.38
5.36
5.35
5.34
5.33
5.30
4.25
4.23
4.21
4.20
4.20
4.19
4.07
2.41
1.32
1.31
1.29
2.00
2.02
1.01
1.00
1.00
2.04
4.05
2.01
3.03
3.02
f1 (ppm)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143.67
136.04
135.27
129.60
127.94
127.55
127.42
116.28
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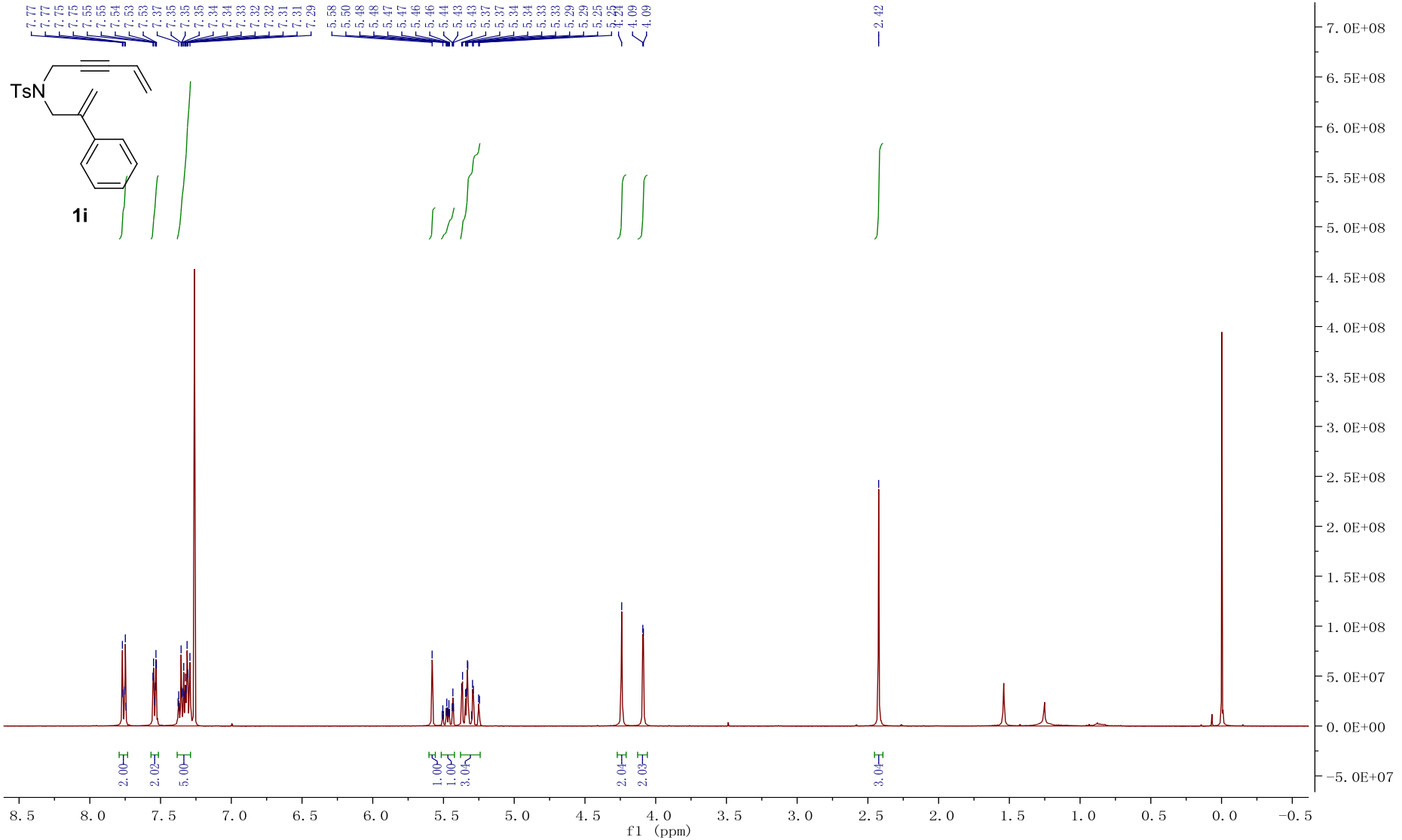
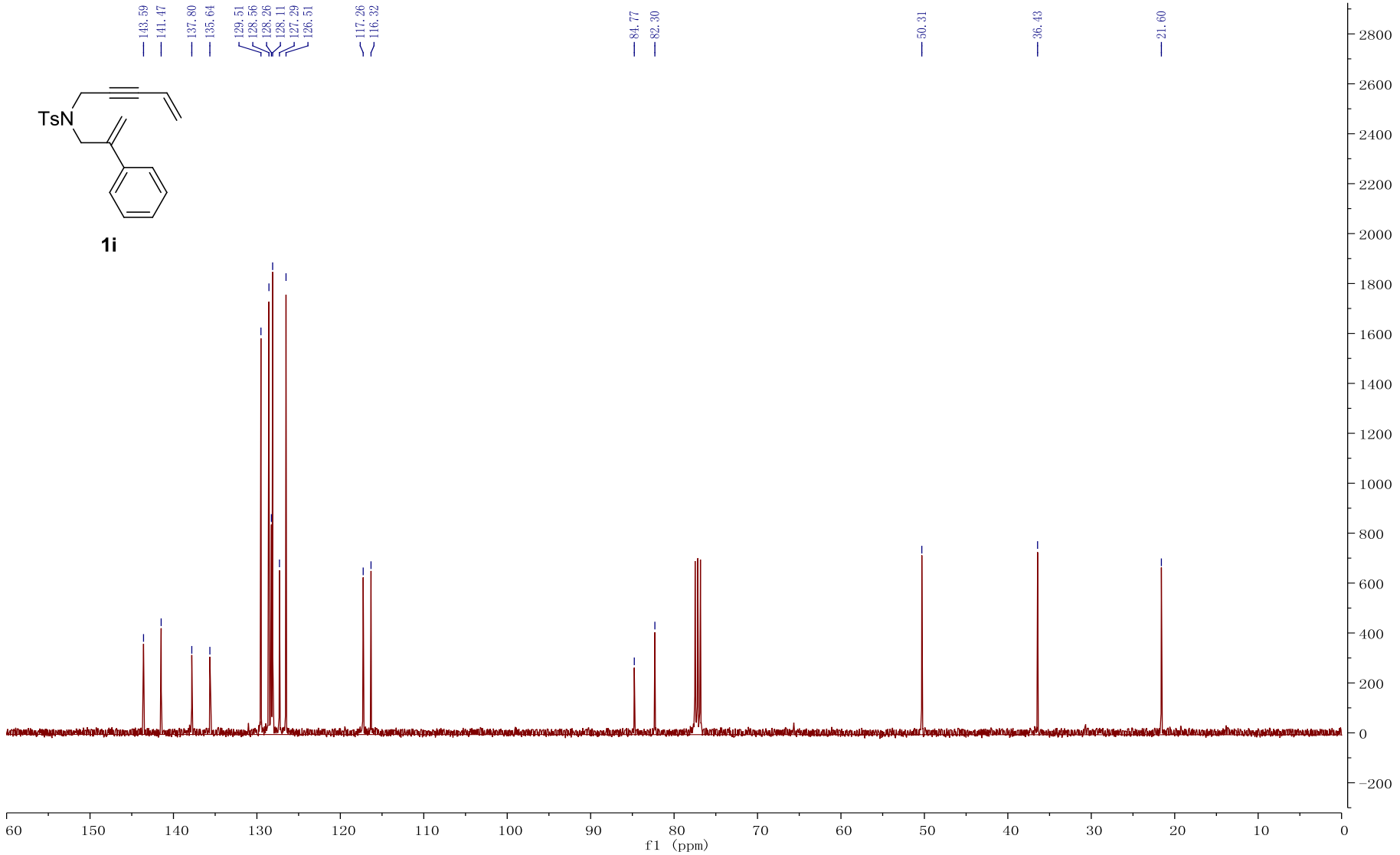
82.59
61.15
47.04
37.80
21.61
14.26
TsN
CO2Et
1h
f1 (ppm)


7.77
7.77
7.75
7.75
7.55
7.55
7.54
7.53
7.53
7.37
7.35
7.35
7.34
7.34
7.33
7.32
7.32
7.31
7.31
7.29
5.58
5.50
5.48
5.48
5.47
5.47
5.46
5.46
5.44
5.43
5.43
5.37
5.37
5.34
5.34
5.33
5.33
5.29
5.29
5.25
4.24
4.09
4.09
2.42
TsN
1i
2.00
2.02
5.00
1.00
1.00
3.04
2.04
2.03
3.04
7.0E+08
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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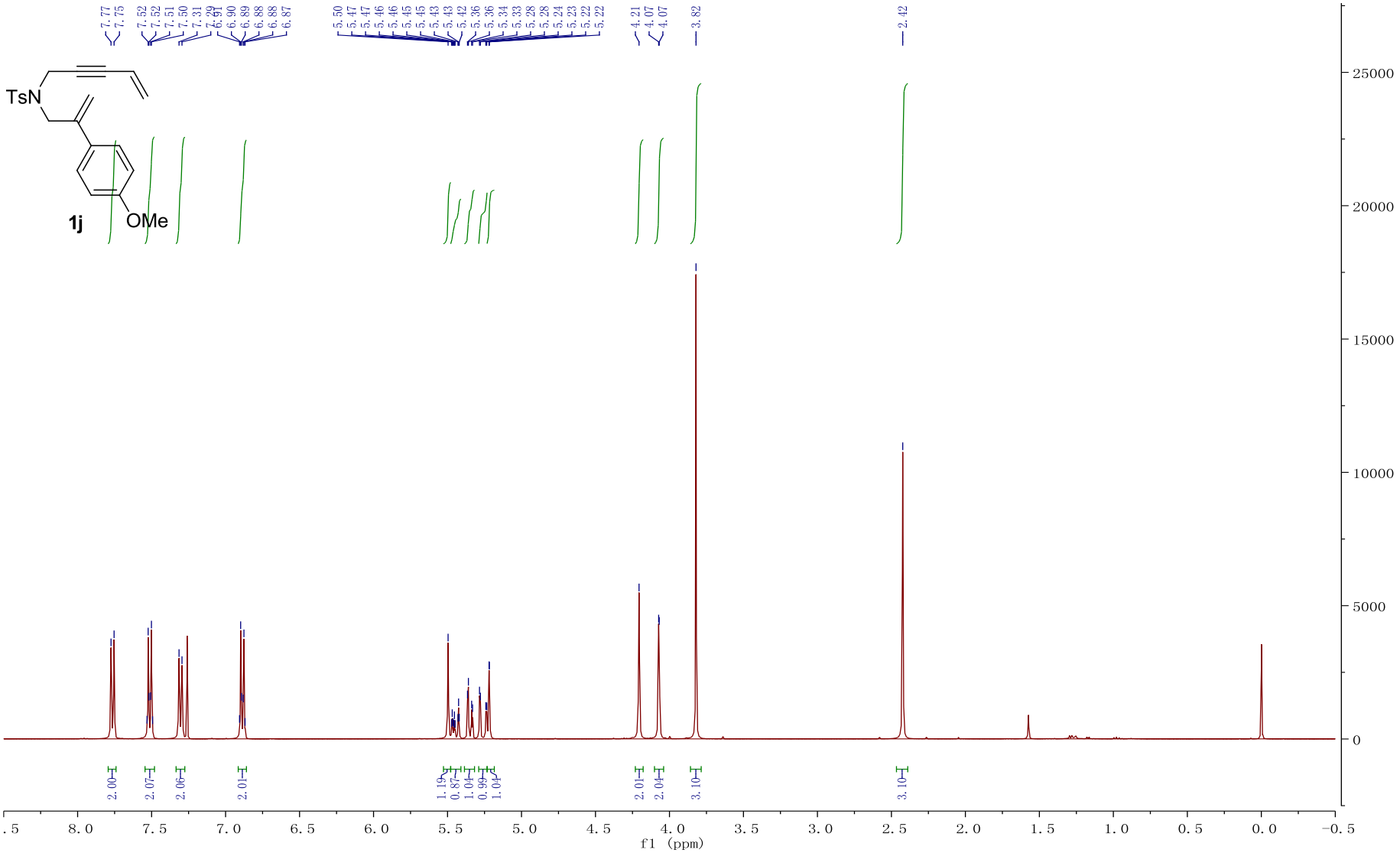
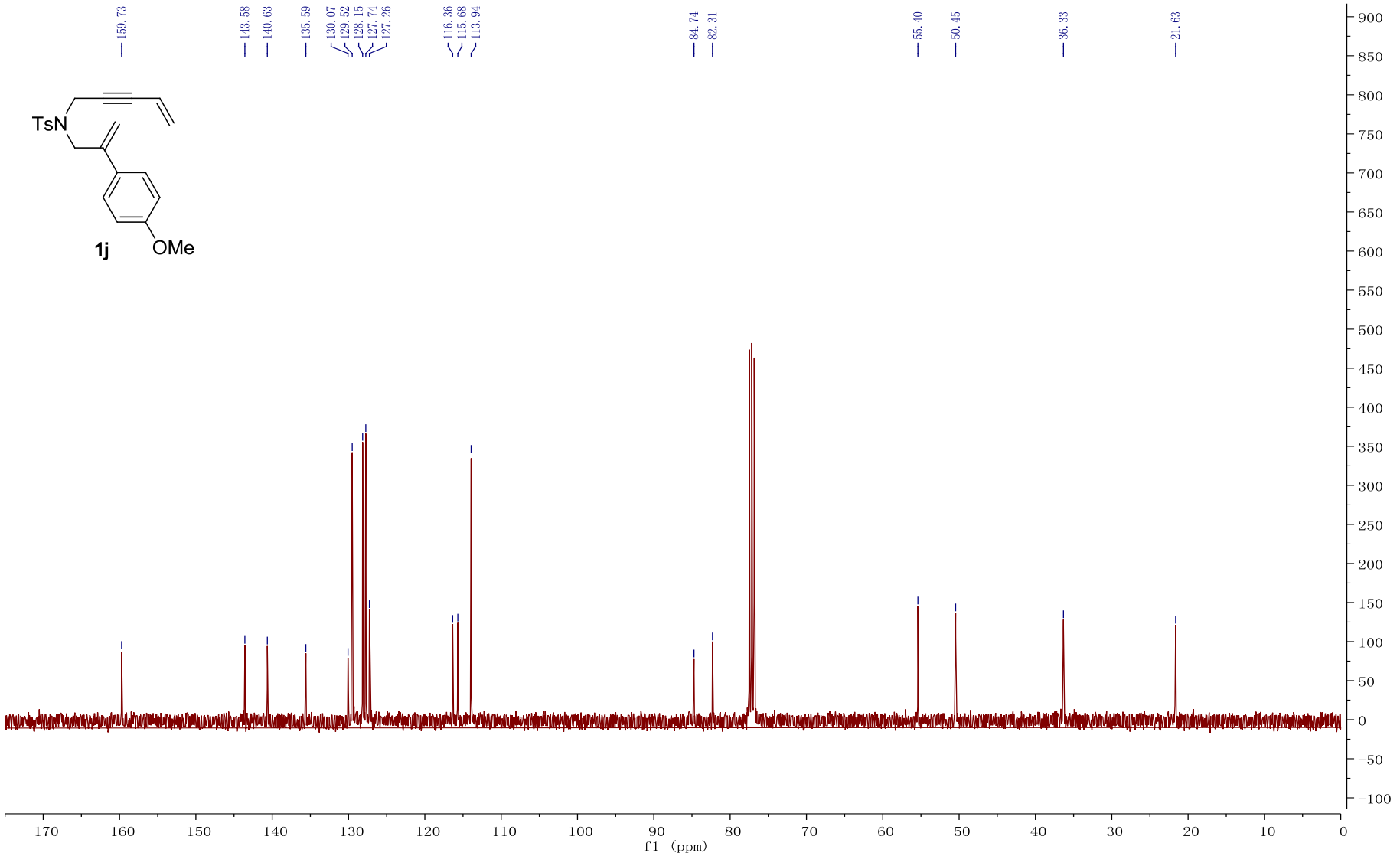
129.51
128.56
128.26
128.11
127.29
126.51
117.26
116.32
84.77
82.30
50.31
36.43
21.60
TsN
1i
f1 (ppm)


TsN
1j
OMe
7.77
7.75
7.52
7.52
7.51
7.50
7.31
7.29
6.91
6.90
6.89
6.88
6.88
6.87
5.50
5.47
5.47
5.46
5.46
5.45
5.45
5.43
5.43
5.42
5.36
5.36
5.34
5.33
5.28
5.24
5.23
5.22
5.22
4.21
4.07
4.07
3.82
2.42
2.00
2.07
2.06
2.01
1.19
0.87
1.04
0.99
1.04
2.01
2.04
3.10
3.10
25000
20000
15000
10000
5000
0
f1 (ppm)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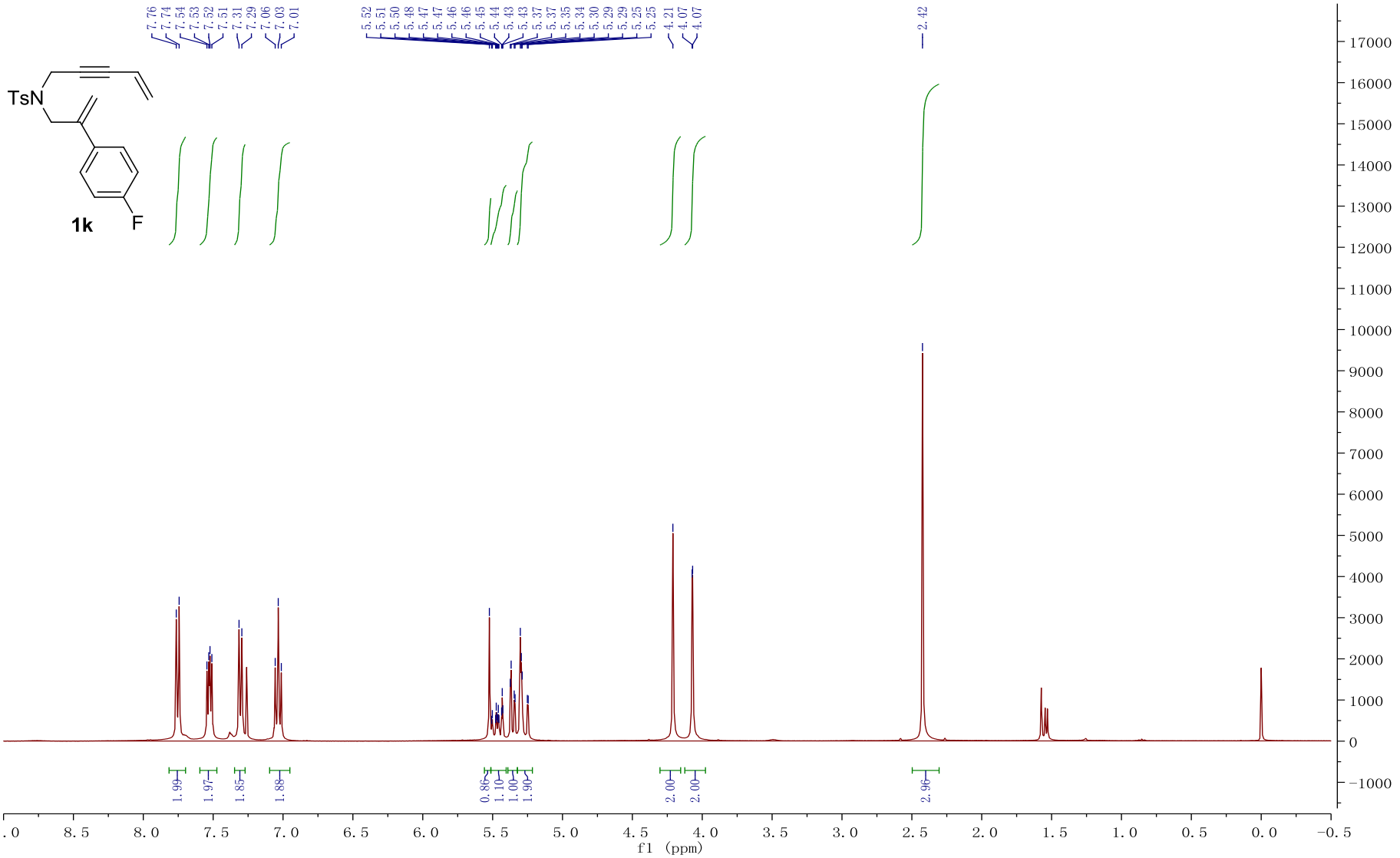
135.59
130.07
129.52
128.15
127.74
127.26
116.36
115.68
113.94
84.74
82.31
55.40
50.45
36.33
21.63
TsN
OMe
1j
f1 (ppm)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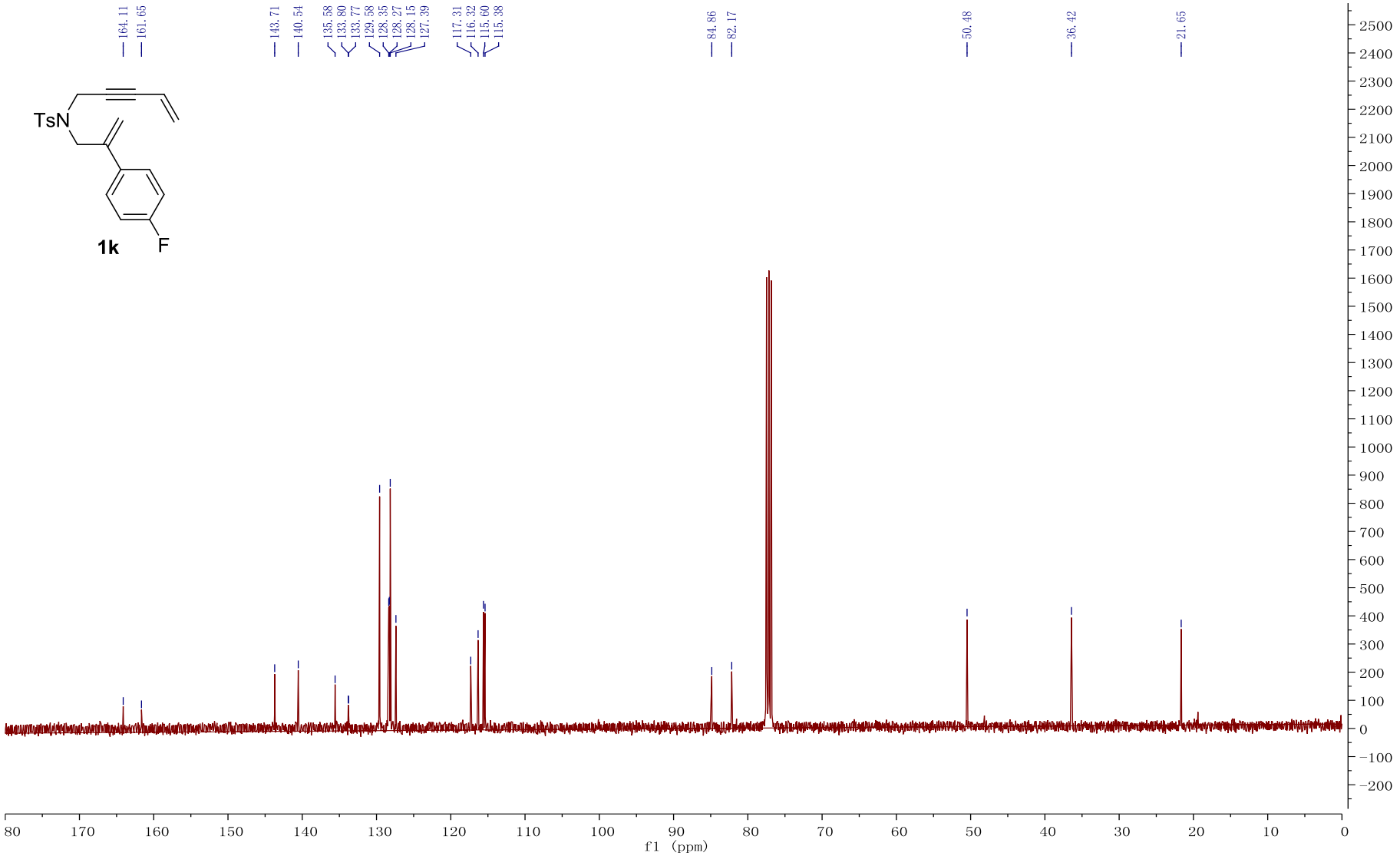
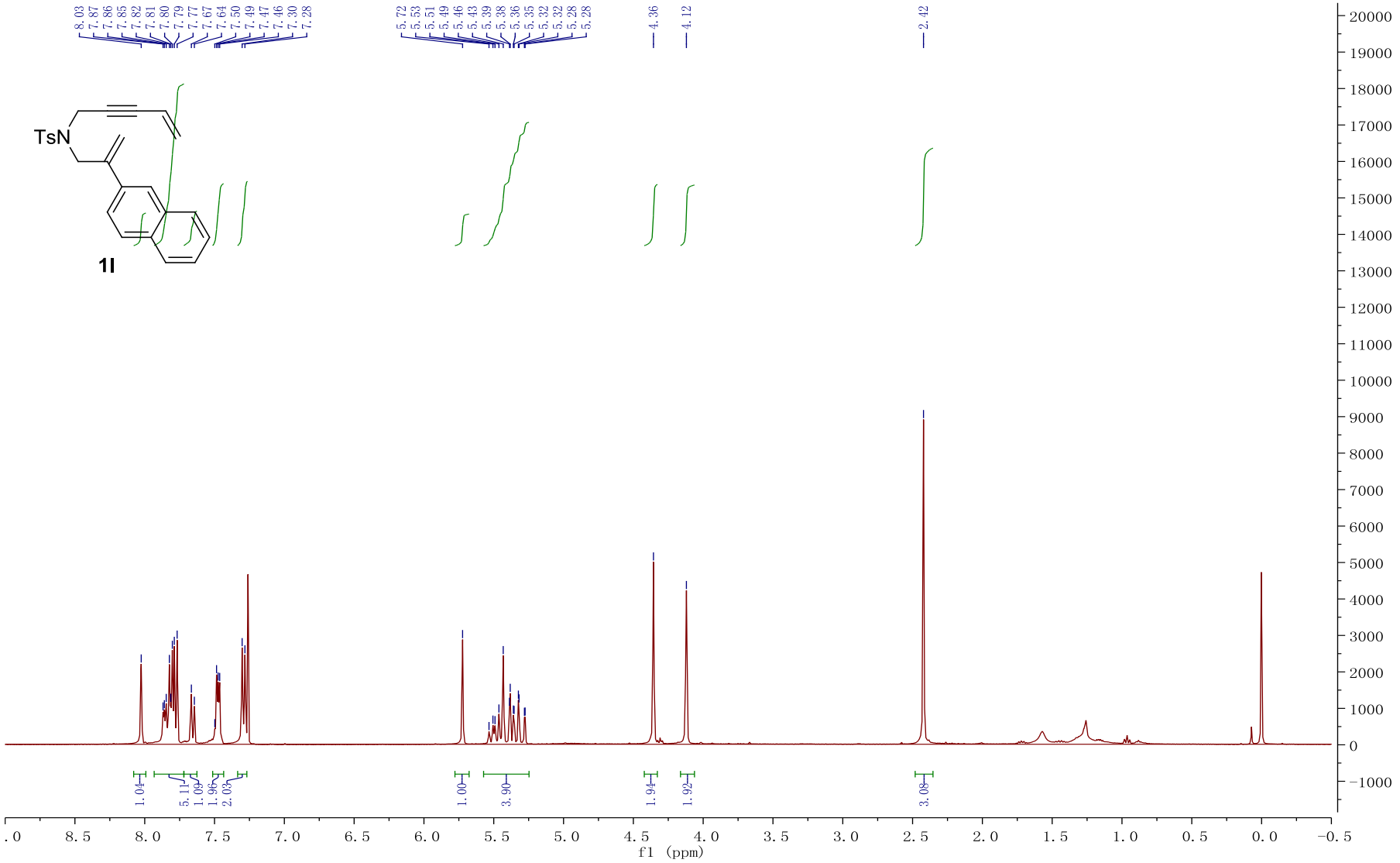
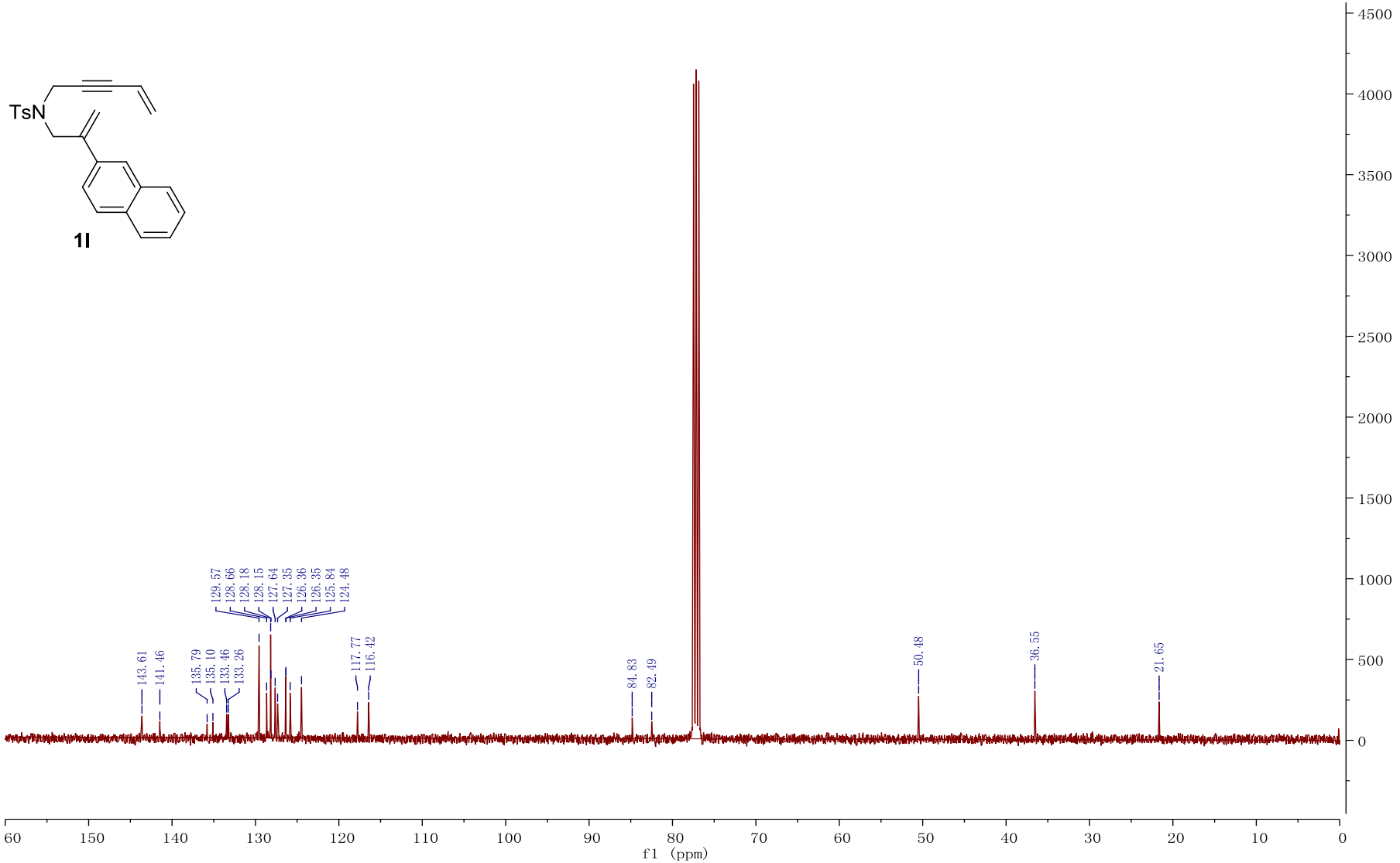
7.74
7.54
7.53
7.52
7.51
7.31
7.29
7.06
7.03
7.01
5.52
5.51
5.50
5.48
5.47
5.47
5.46
5.46
5.45
5.44
5.43
5.43
5.37
5.37
5.35
5.34
5.30
5.29
5.29
5.25
5.25
4.21
4.07
4.07
2.42
TsN
1k
F
1.99
1.97
1.85
1.88
0.86
1.10
1.00
1.90
2.00
2.00
2.96
f1 (ppm)


164.11
161.65
143.71
140.54
135.58
133.80
133.77
129.58
128.35
128.27
128.15
127.39
117.31
116.32
115.60
115.38
84.86
82.17
50.48
36.42
21.65
TsN
F
1k
f1 (ppm)


8.03
7.87
7.86
7.85
7.82
7.81
7.80
7.79
7.77
7.67
7.64
7.50
7.49
7.47
7.46
7.30
7.28
5.72
5.53
5.51
5.49
5.46
5.43
5.39
5.38
5.36
5.35
5.32
5.32
5.28
5.28
4.36
4.12
2.42
TsN
1l
1.04
5.11
1.09
1.96
2.03
1.00
3.90
1.94
1.92
3.08
f1 (ppm)


TsN
1l
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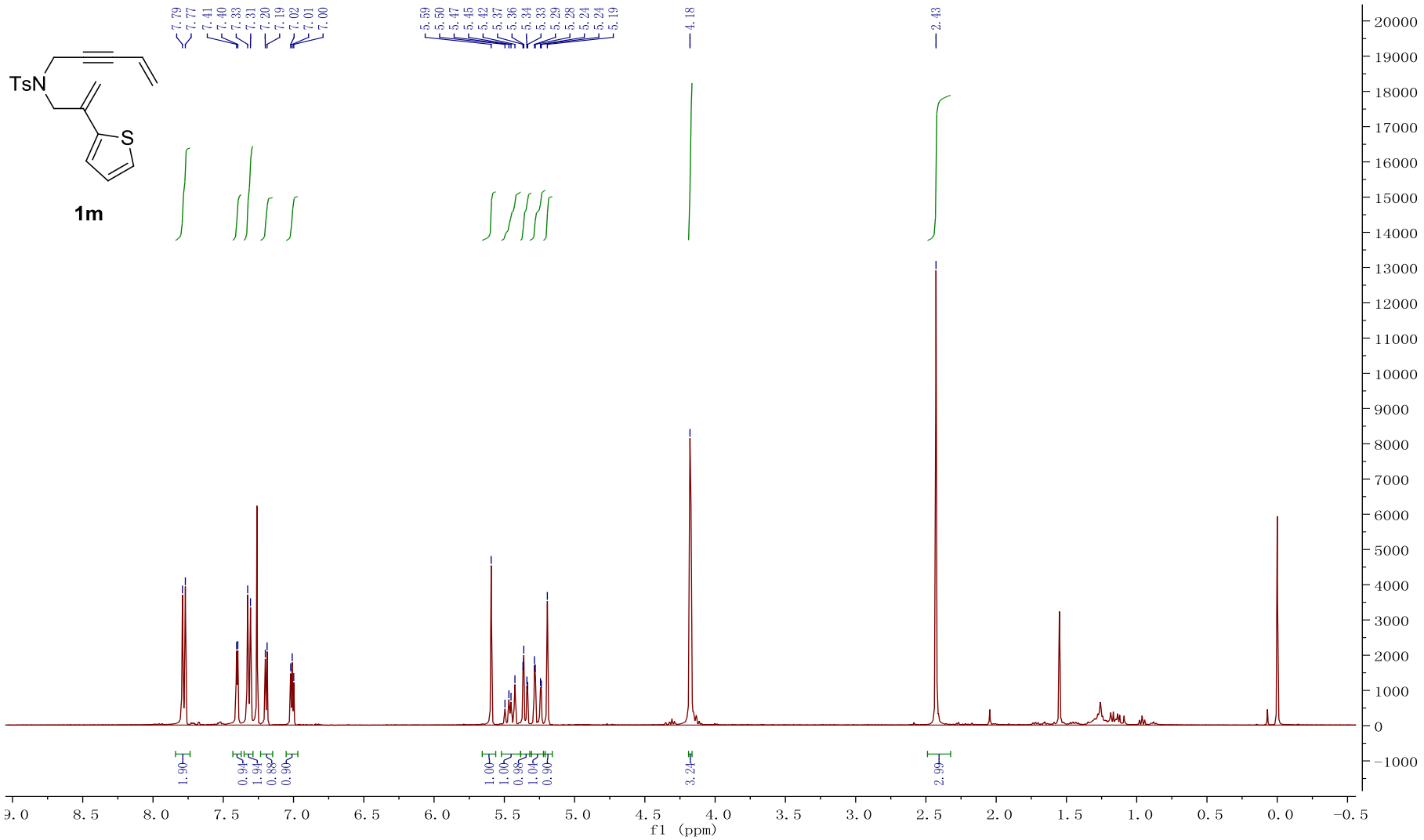
141.46
135.79
135.10
133.46
133.26
129.57
128.66
128.18
128.15
127.64
127.35
126.36
126.35
125.84
124.48
117.77
116.42
84.83
82.49
50.48
36.55
21.65
4500
4000
3500
3000
2500
2000
1500
1000
500
0
60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


TsN
S
1m
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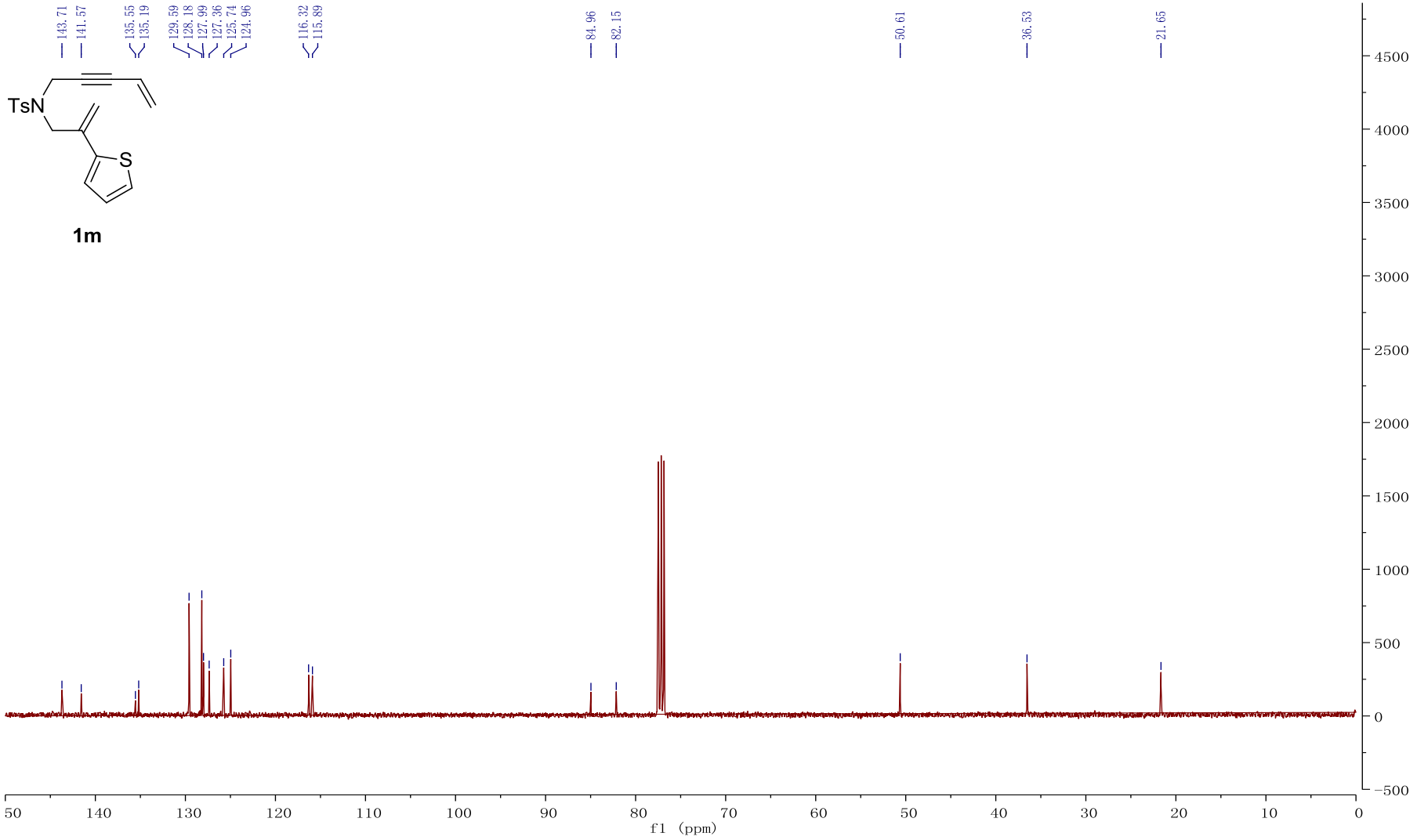
7.77
7.41
7.40
7.33
7.31
7.20
7.19
7.02
7.01
7.00
5.59
5.50
5.47
5.45
5.42
5.37
5.36
5.34
5.33
5.29
5.28
5.24
5.24
5.19
4.18
2.43
1.90
0.94
1.94
0.88
0.90
1.00
1.00
0.98
1.04
0.90
3.24
2.99
f1 (ppm)


143.71
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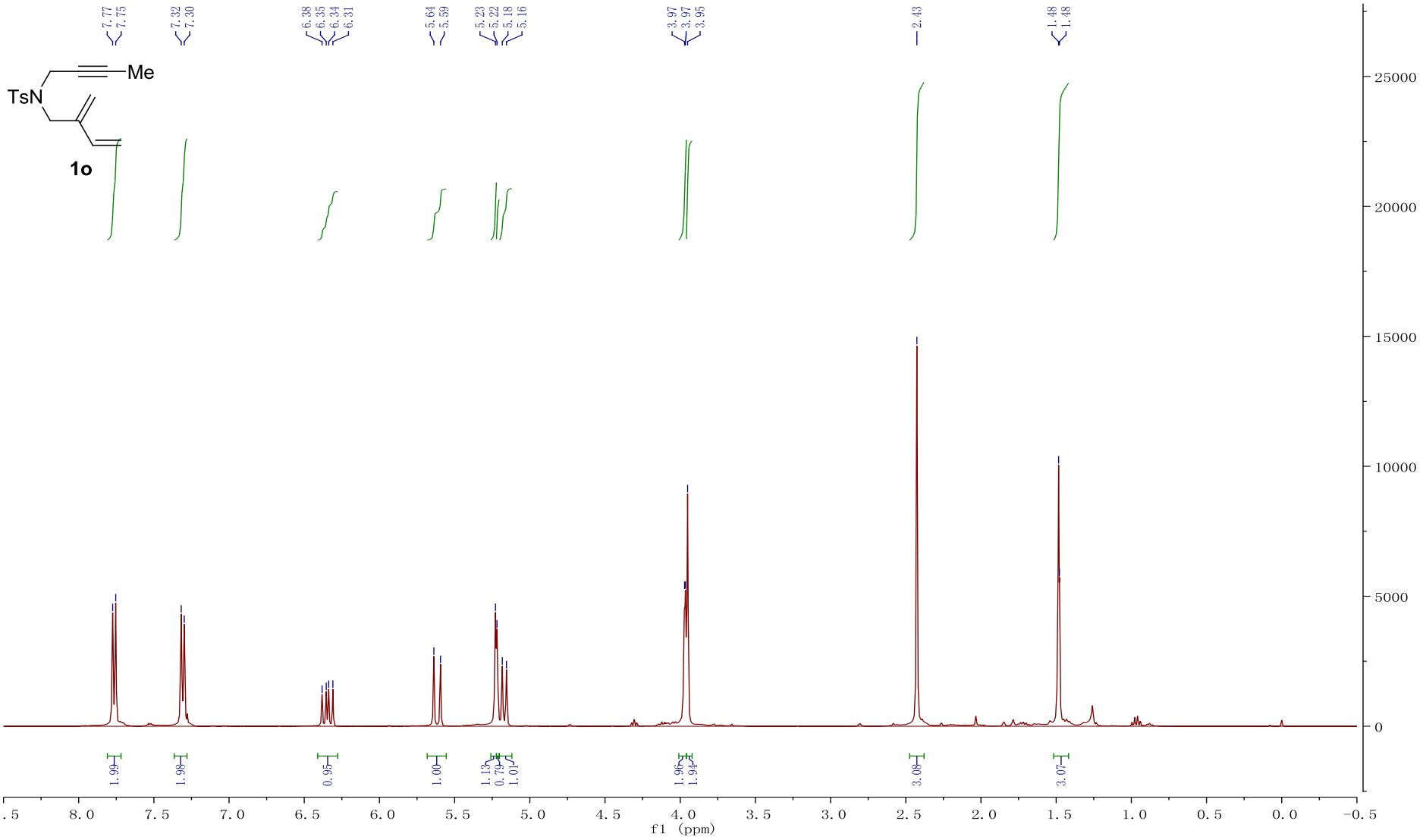
135.19
129.59
128.18
127.99
127.36
125.74
124.96
116.32
115.89
84.96
82.15
50.61
36.53
21.65
TsN
S
1m
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
50
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.77
7.75
7.32
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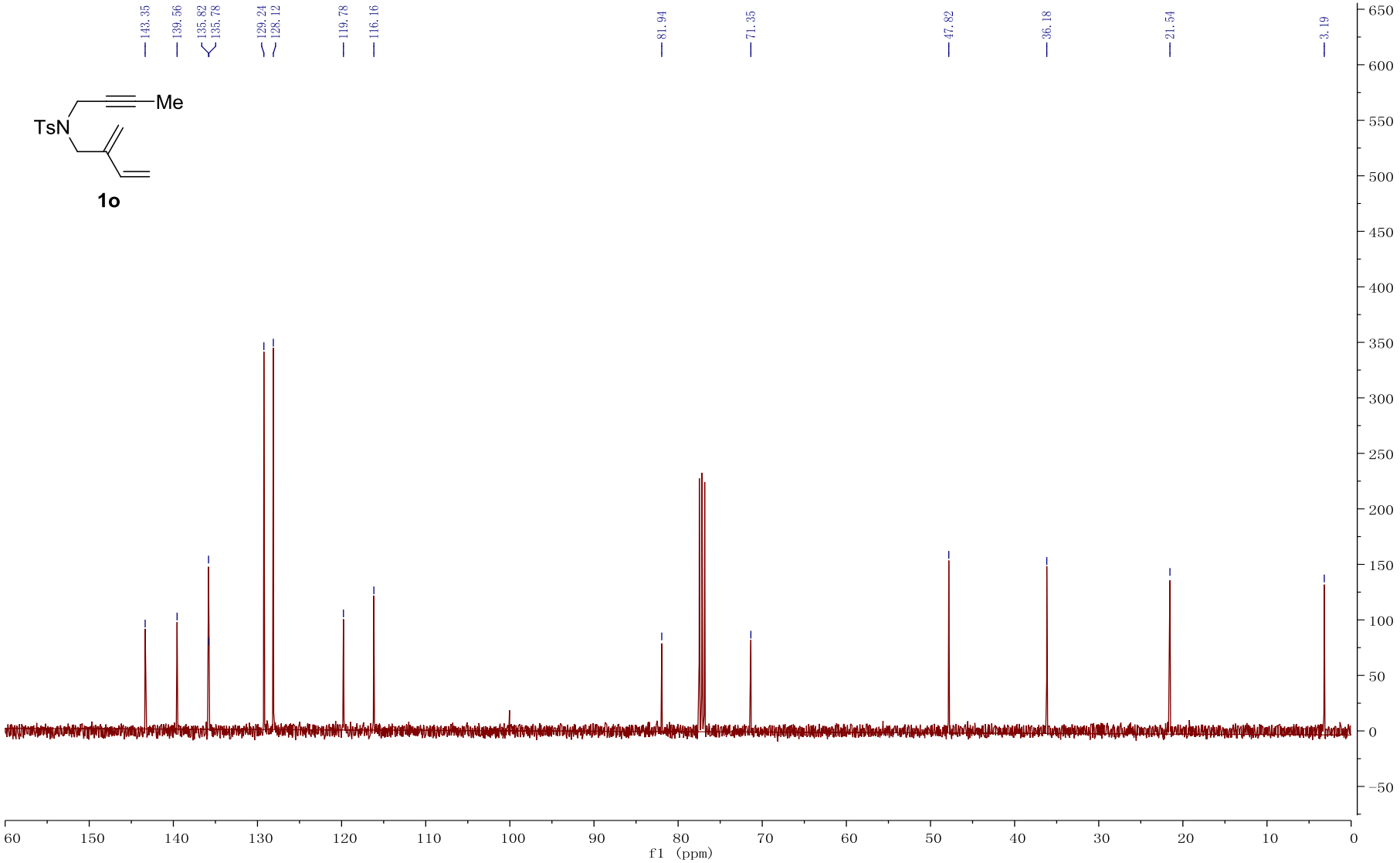
6.38
6.35
6.34
6.31
5.64
5.59
5.23
5.22
5.18
5.16
3.97
3.97
3.95
2.43
1.48
1.48
Me
TsN
1o
1.99
1.98
0.95
1.00
1.13
0.79
1.01
1.96
1.94
3.08
3.07
25000
20000
15000
10000
5000
0
f1 (ppm)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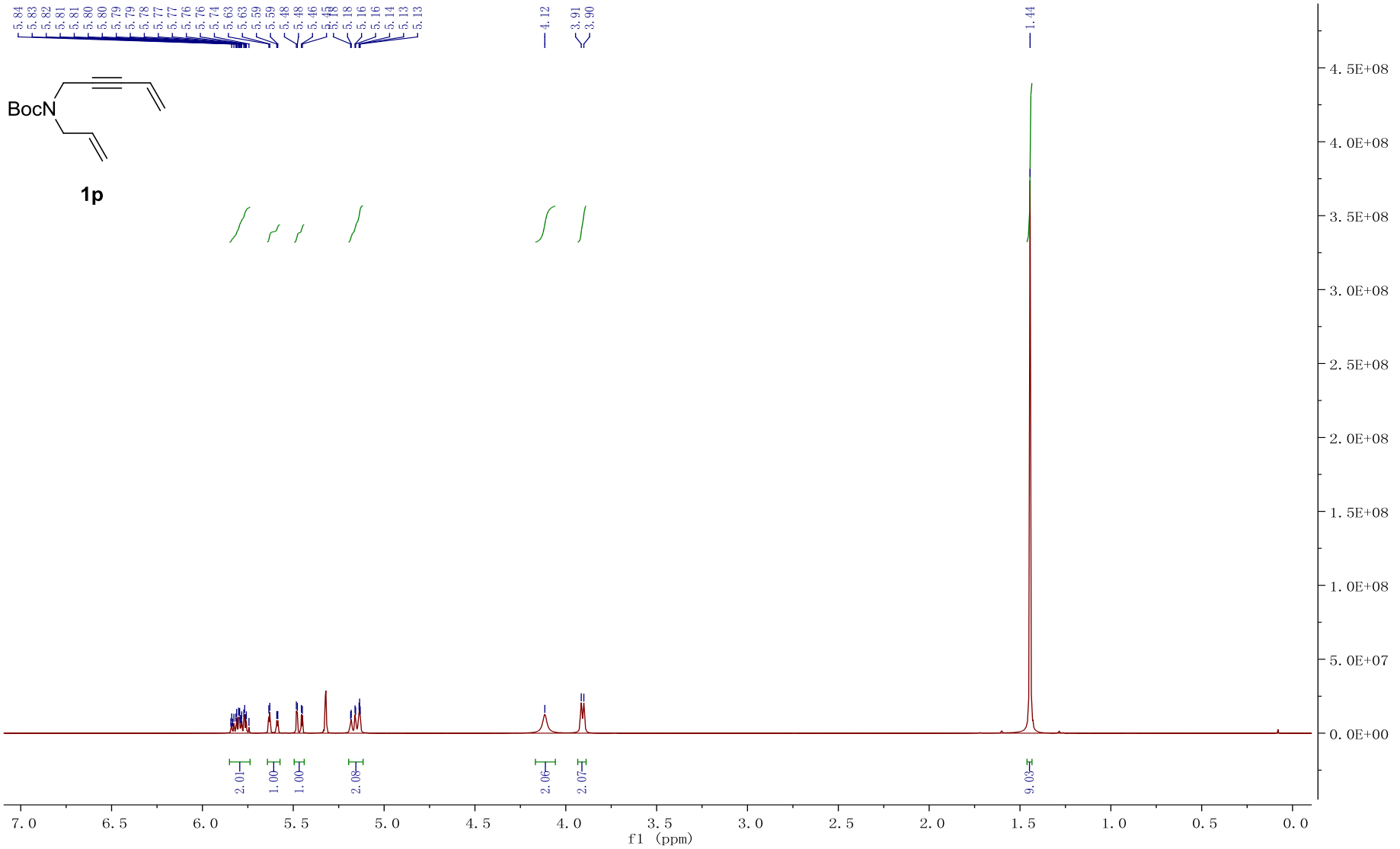
139.56
135.82
135.78
129.24
128.12
119.78
116.16
81.94
71.35
47.82
36.18
21.54
3.19
Me
TsN
1o
f1 (ppm)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5.79
5.79
5.78
5.77
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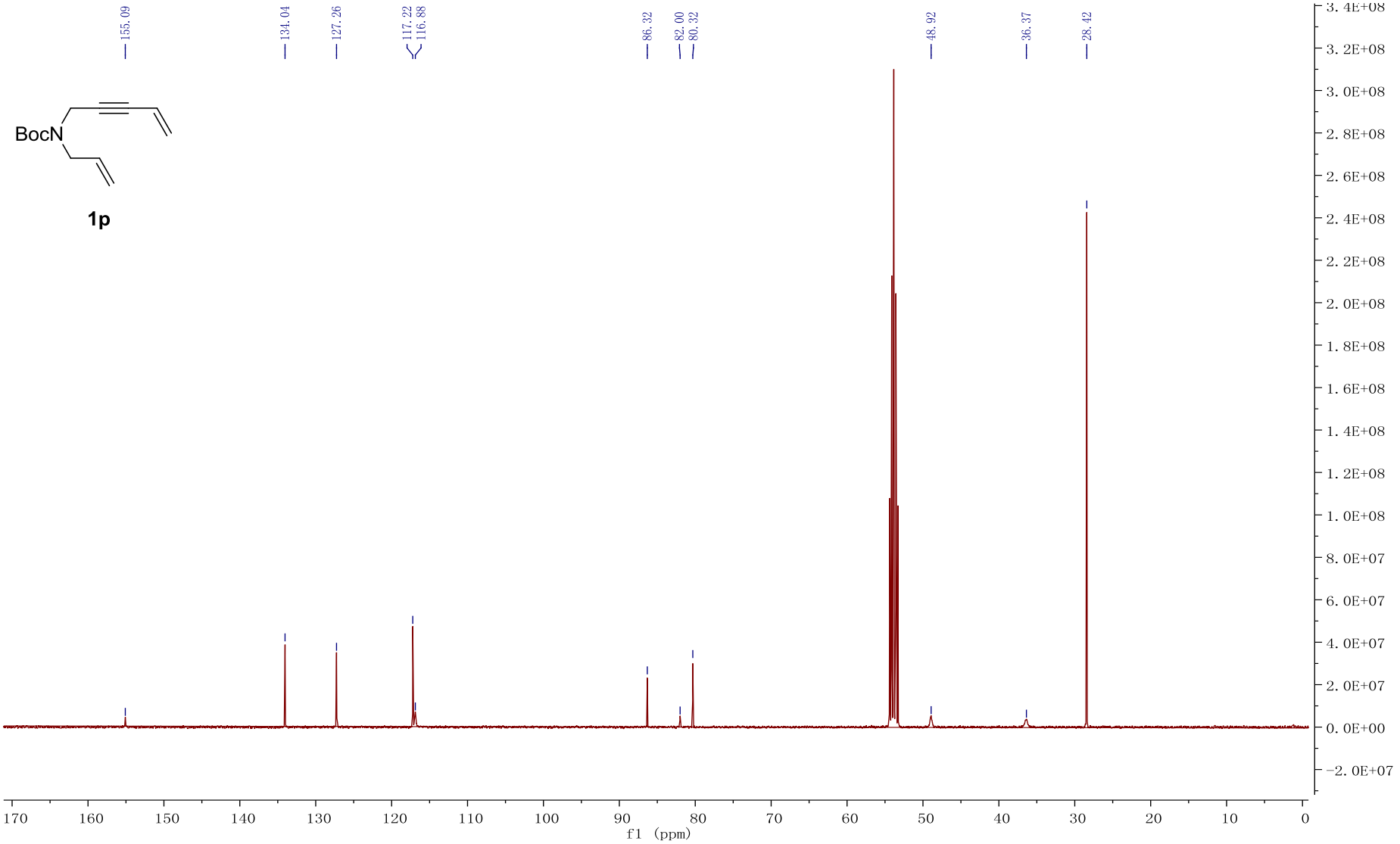
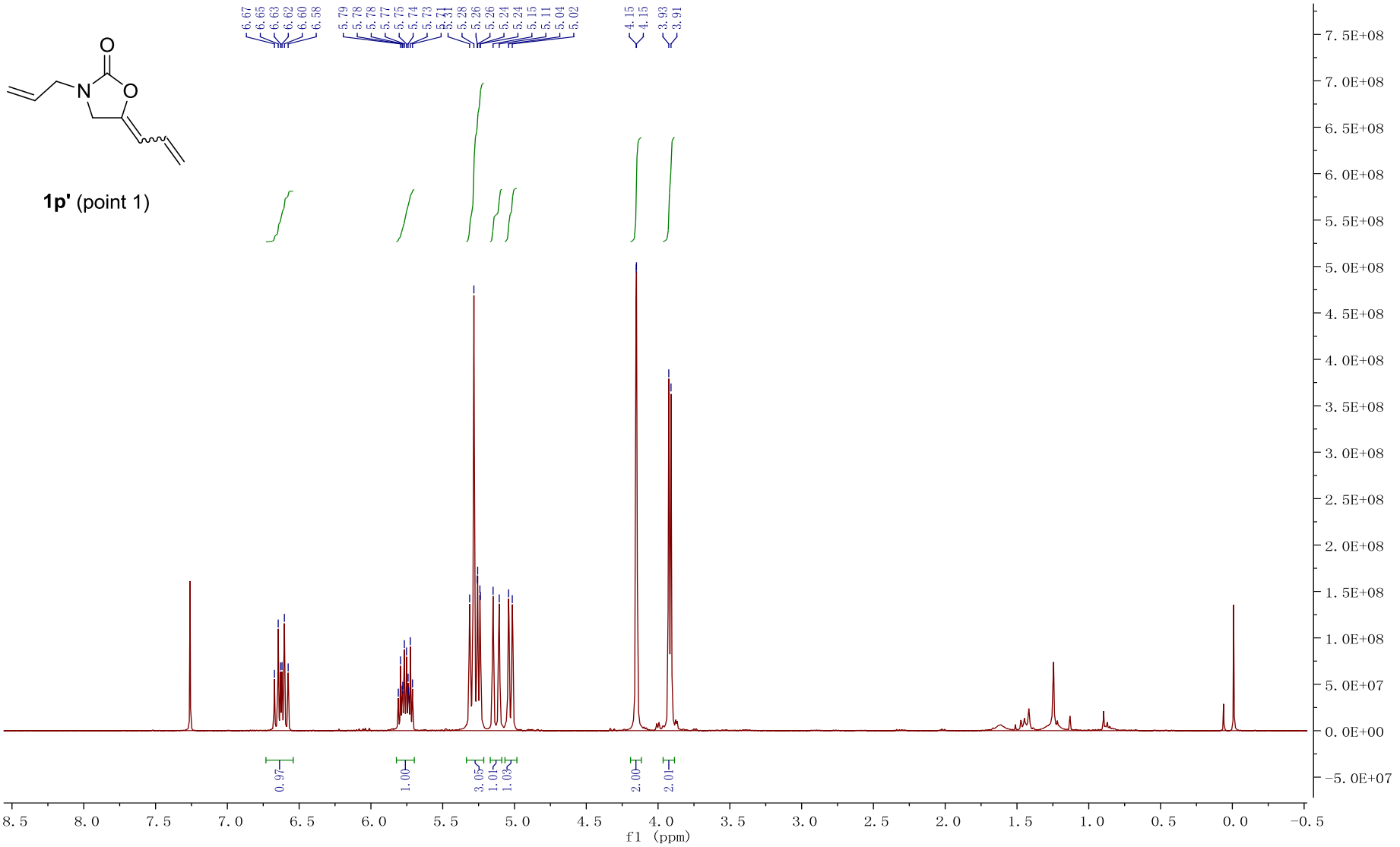
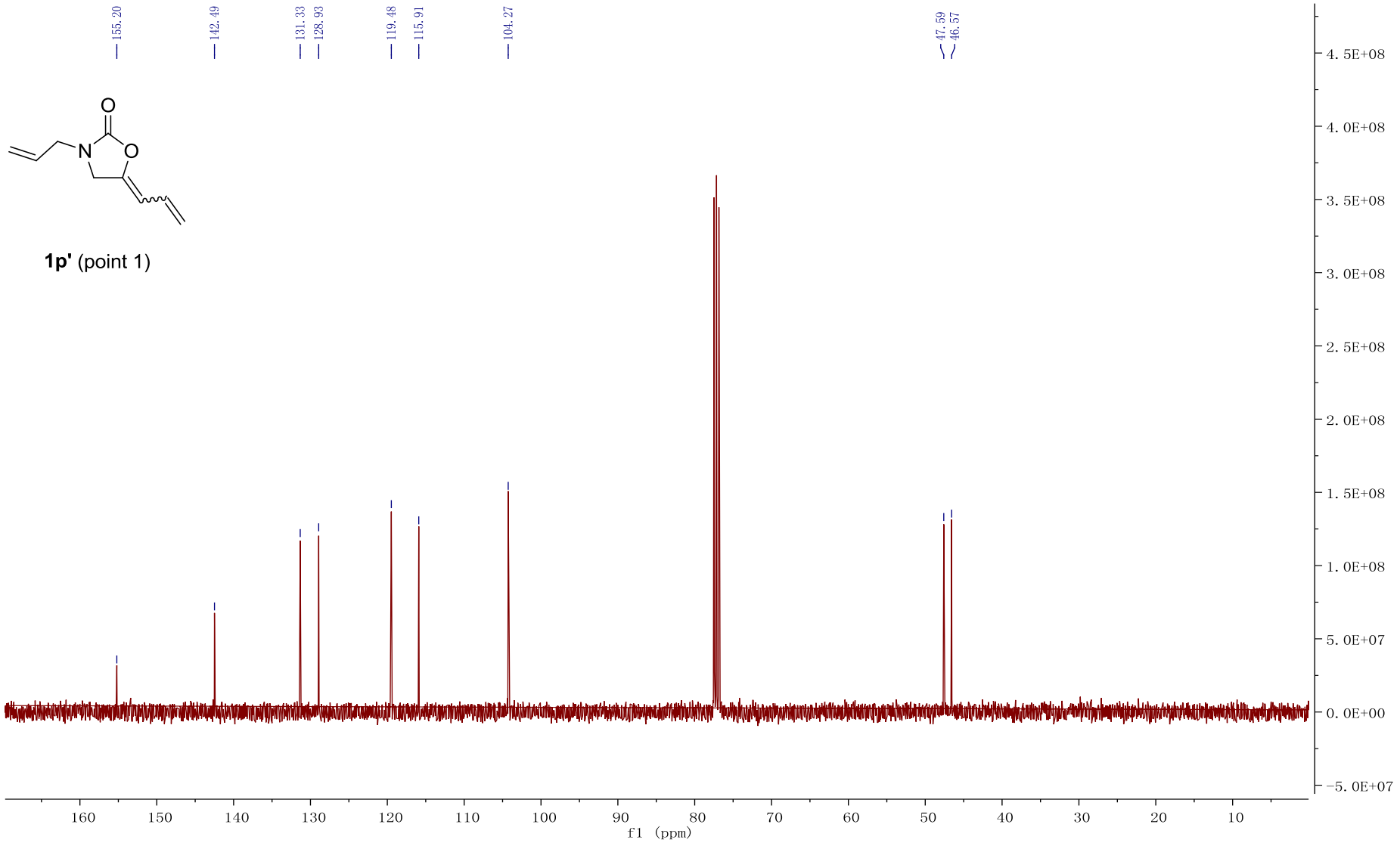
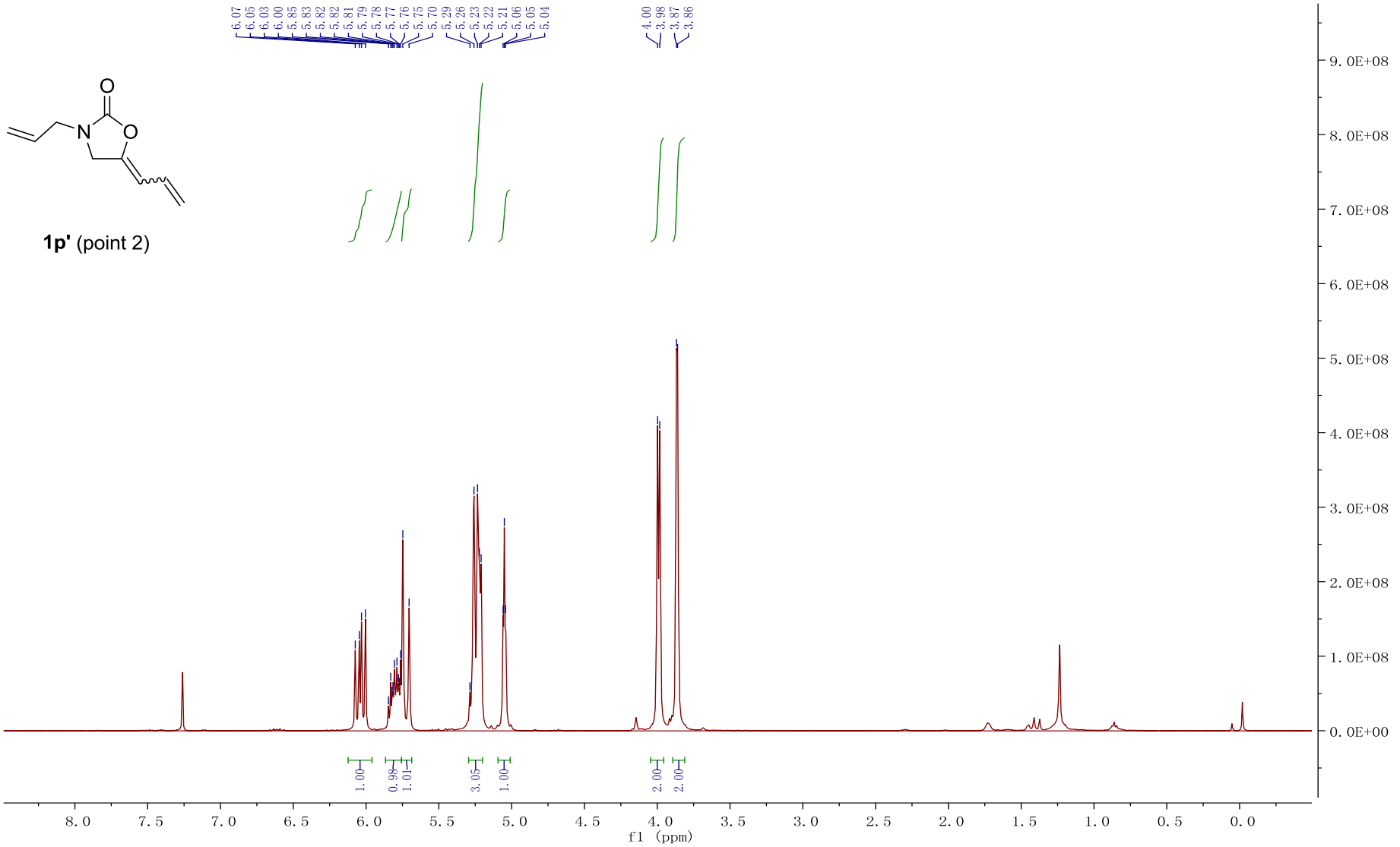
5.63
5.63
5.59
5.59
5.48
5.48
5.46
5.45
5.18
5.16
5.16
5.14
5.13
5.13
4.12
3.91
3.90
1.44
BocN
1p
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
2.01
1.00
1.00
2.08
2.06
2.07
9.03
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

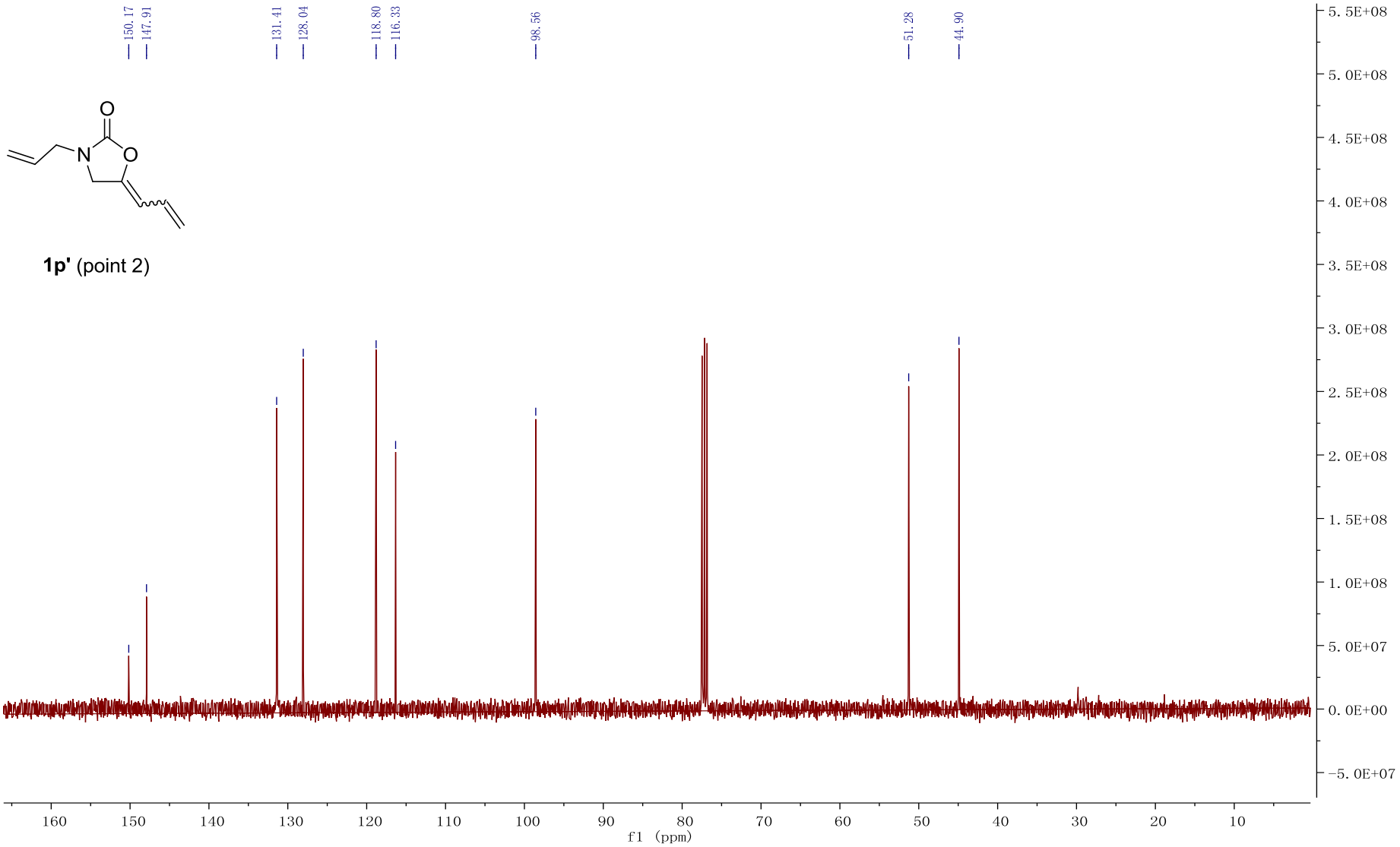

155.09
134.04
127.26
117.22
116.88
86.32
82.00
80.32
48.92
36.37
28.42
BocN
1p
f1 (ppm)

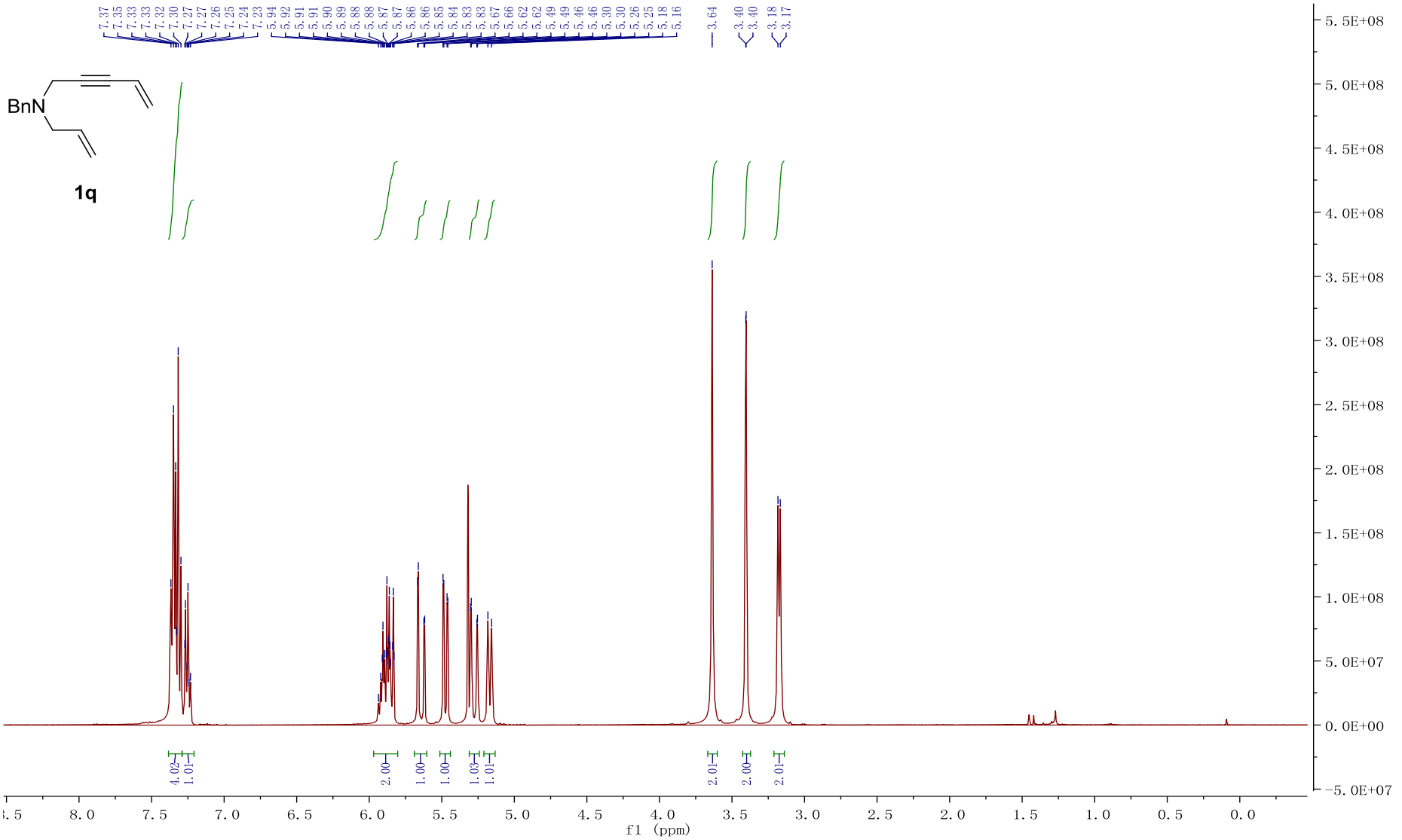

6.67
6.65
6.63
6.62
6.60
6.58
5.79
5.78
5.78
5.77
5.75
5.74
5.73
5.71
5.28
5.26
5.26
5.24
5.24
5.15
5.11
5.04
5.02
4.15
4.15
3.93
3.91
O
N
O
1p' (point 1)
0.97
1.00
3.05
1.01
1.03
2.00
2.01
7.5E+08
7.0E+08
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

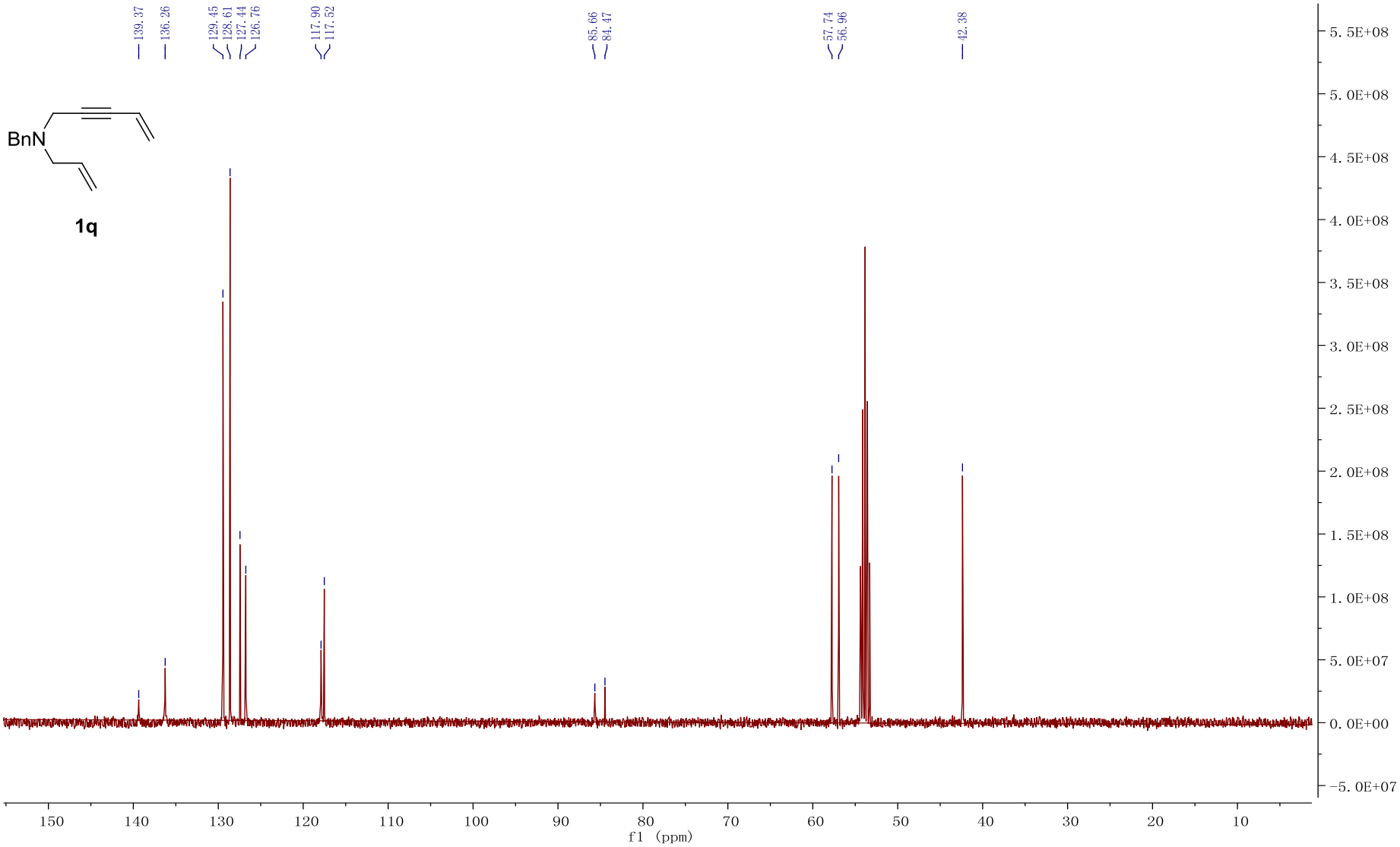

155.20
142.49
131.33
128.93
119.48
115.91
104.27
47.59
46.57
O
N
O
O
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

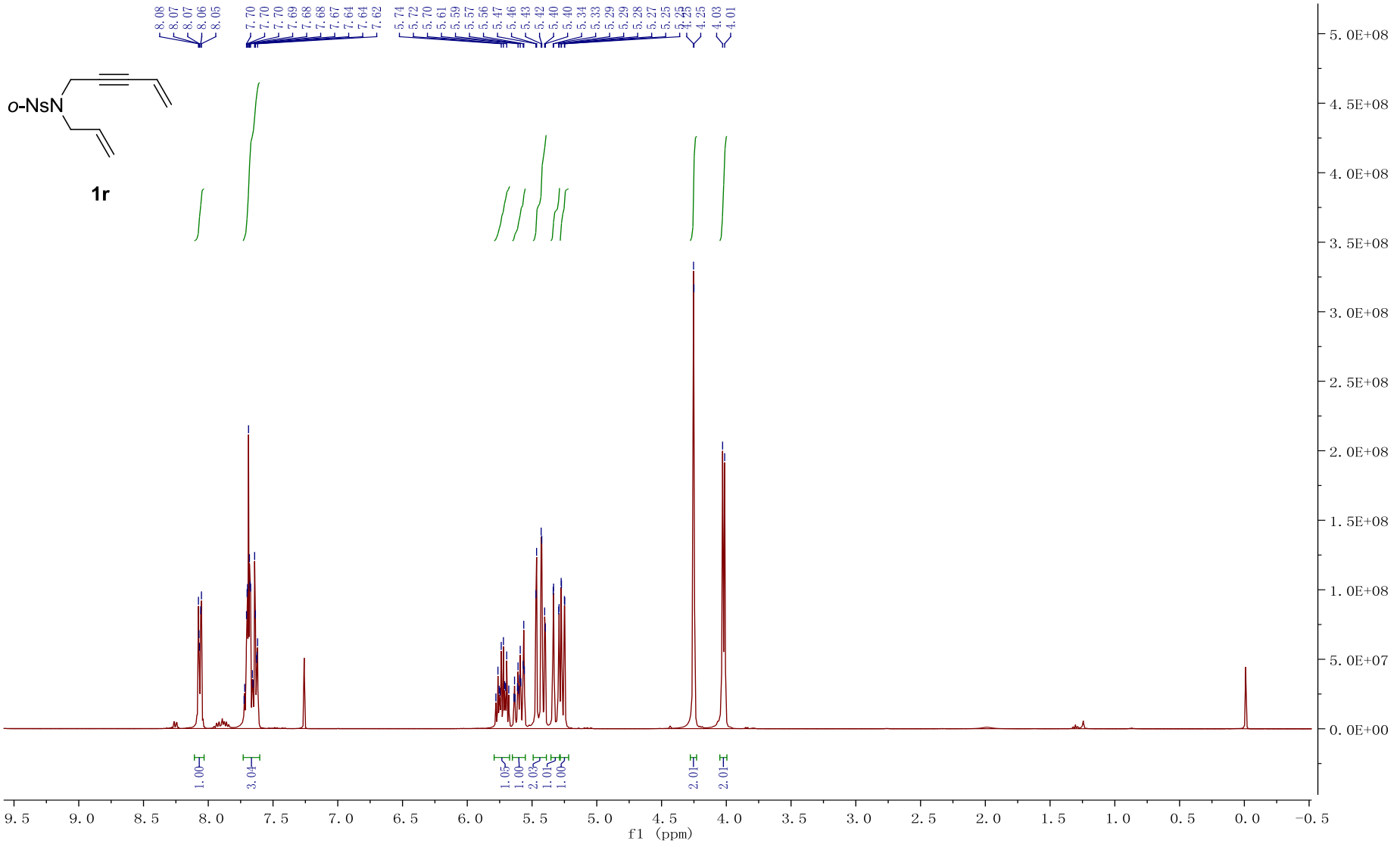
1p' (point 1)

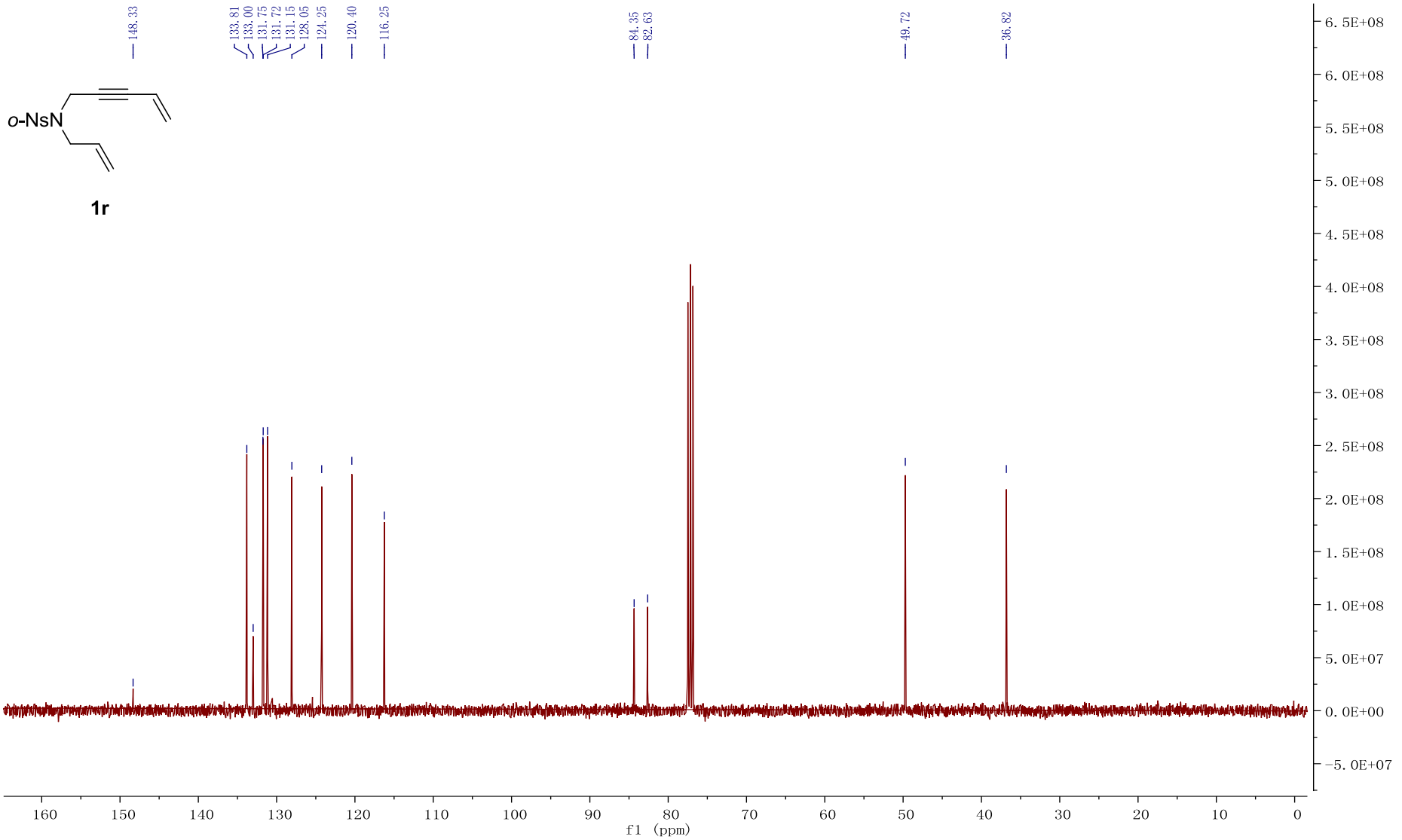

6.07
6.05
6.03
6.00
5.85
5.83
5.82
5.82
5.81
5.79
5.78
5.77
5.76
5.75
5.70
5.29
5.26
5.23
5.22
5.21
5.06
5.05
5.04
4.00
3.98
3.87
3.86
O
N
O
O
1p' (point 2)
9.0E+08
8.0E+08
7.0E+08
6.0E+08
5.0E+08
4.0E+08
3.0E+08
2.0E+08
1.0E+08
0.0E+00
1.00
0.98
1.01
3.05
1.00
2.00
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

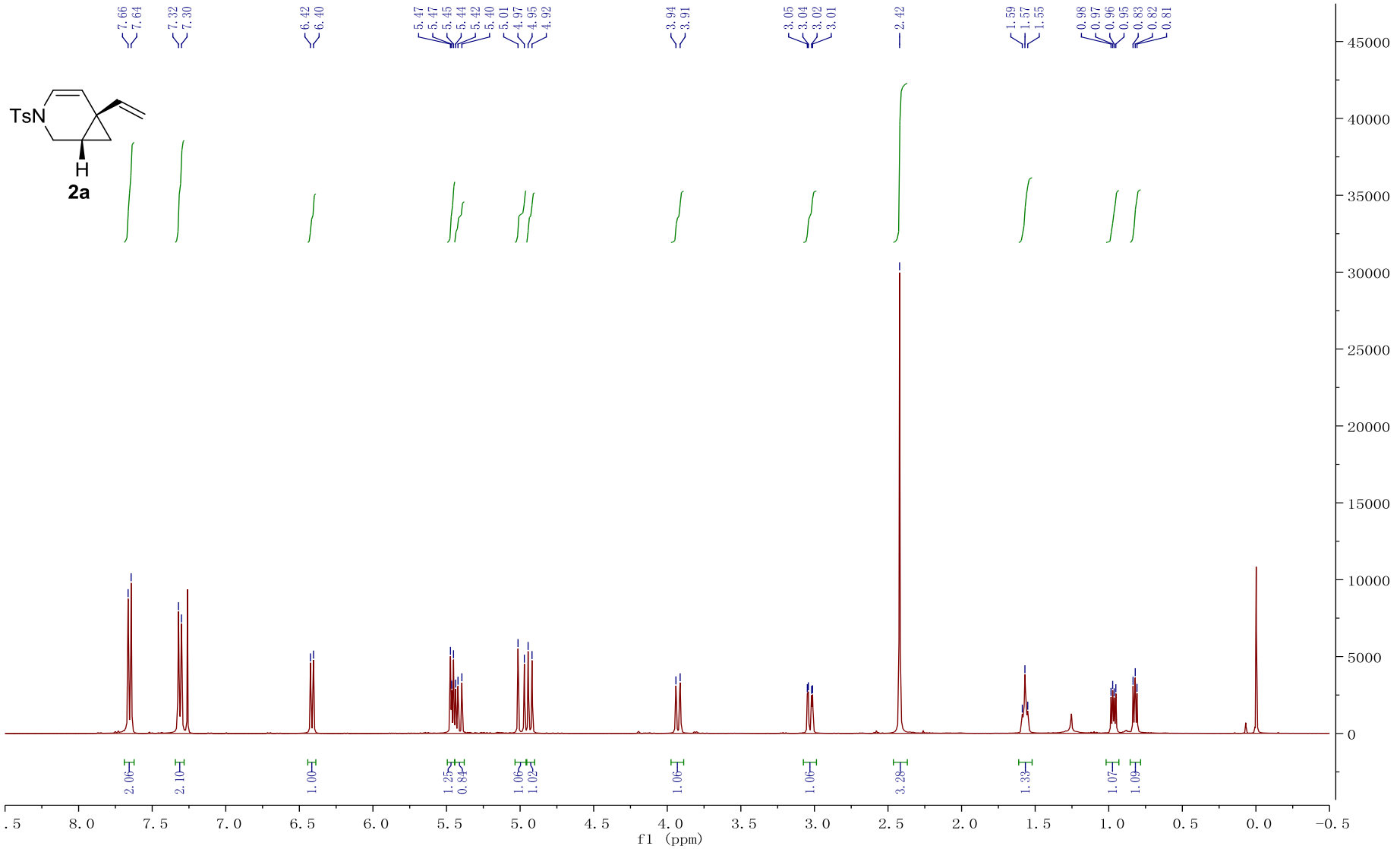

150.17
147.91
131.41
128.04
118.80
116.33
98.56
51.28
44.90
O
N
O
O
1p' (point 2)
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

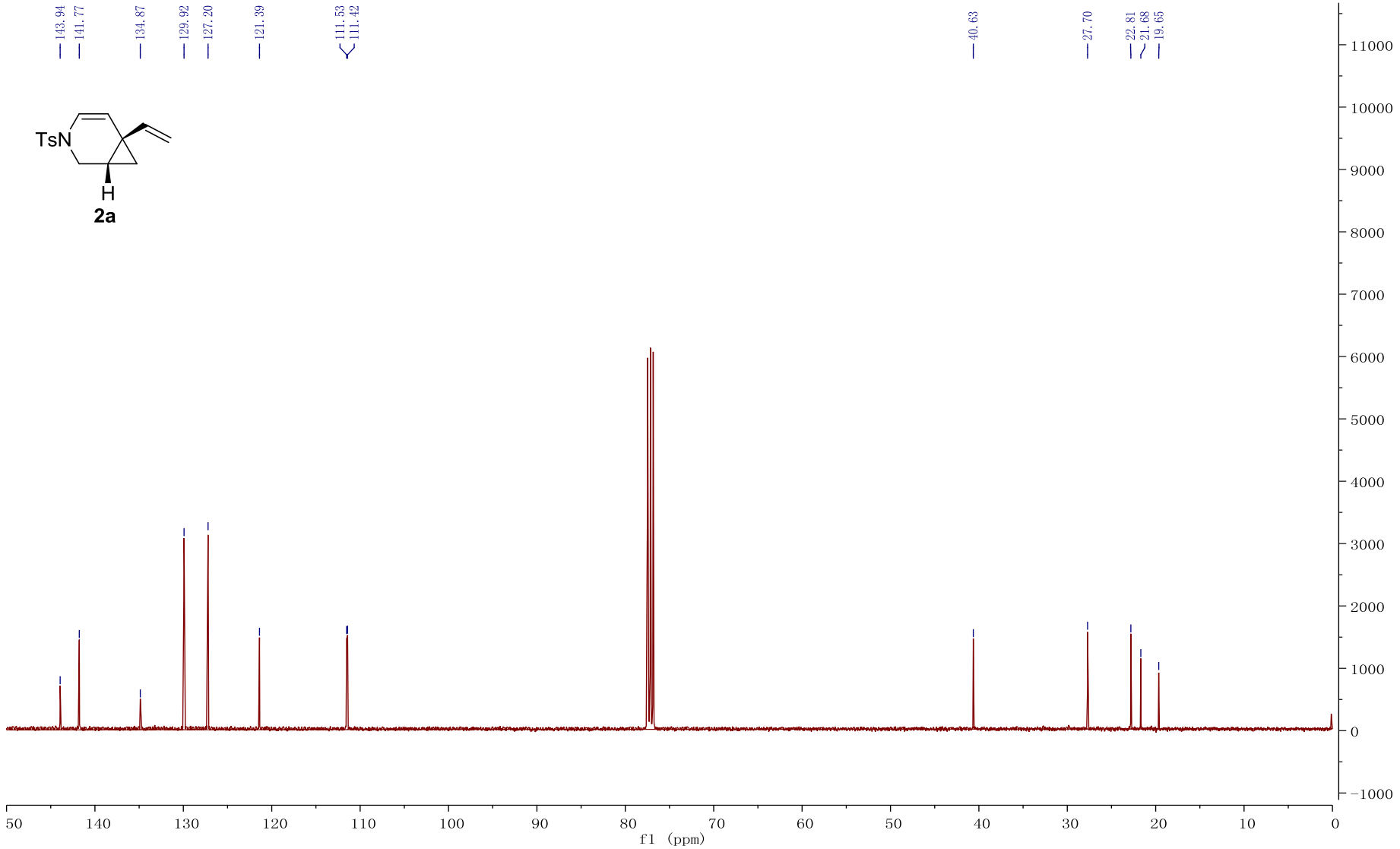

7.37
7.35
7.33
7.33
7.32
7.30
7.27
7.27
7.26
7.25
7.24
7.23
5.94
5.92
5.91
5.91
5.90
5.89
5.88
5.88
5.87
5.87
5.86
5.86
5.85
5.84
5.83
5.83
5.67
5.66
5.62
5.62
5.49
5.49
5.46
5.46
5.30
5.30
5.26
5.25
5.18
5.16
3.64
3.40
3.40
3.18
3.17
BnN
1q
4.02
1.01
2.00
1.00
1.00
1.03
1.01
2.01
2.00
2.01
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
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)

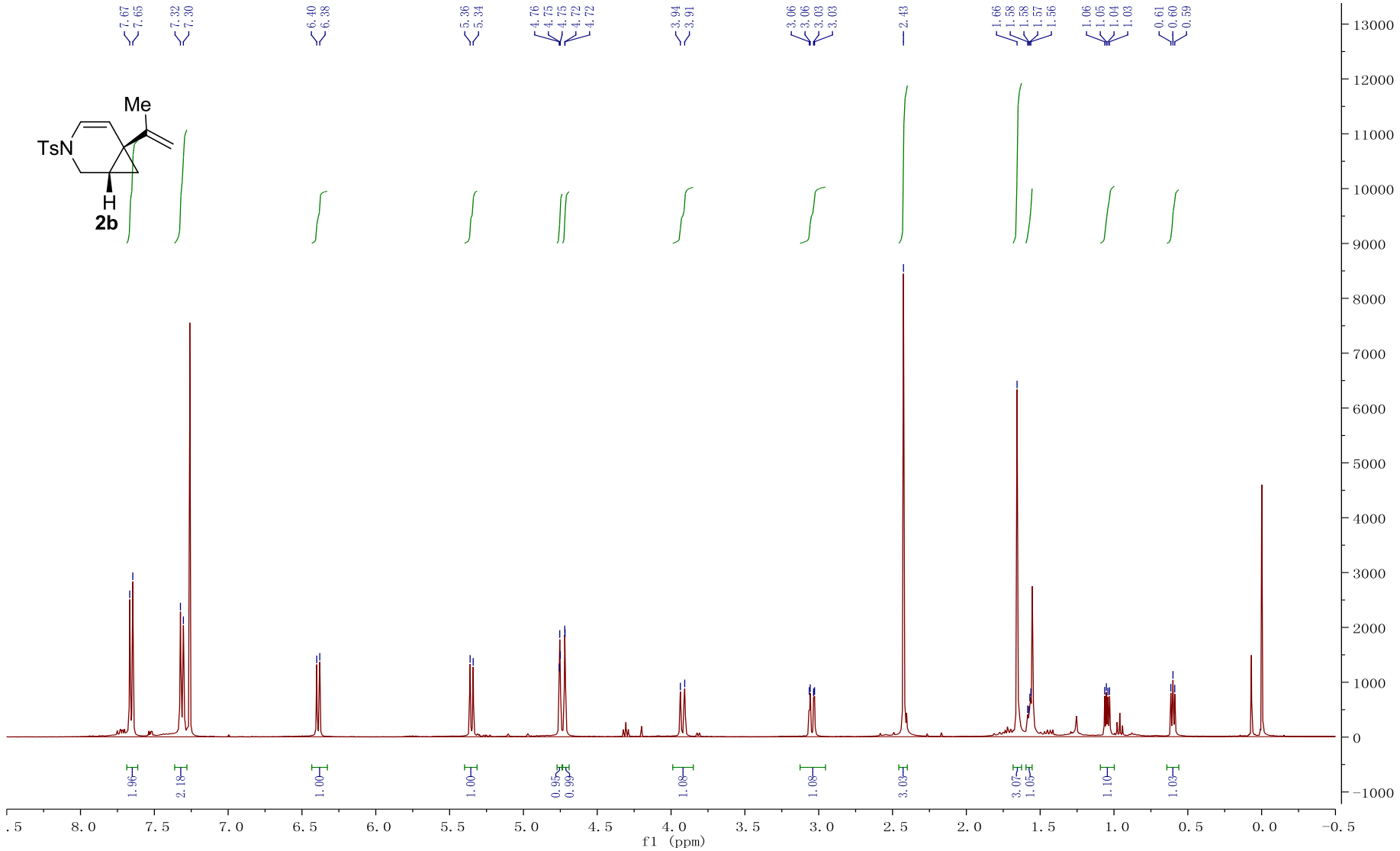

139.37
136.26
129.45
128.61
127.44
126.76
117.90
117.52
85.66
84.47
57.74
56.96
42.38
BnN
1q
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

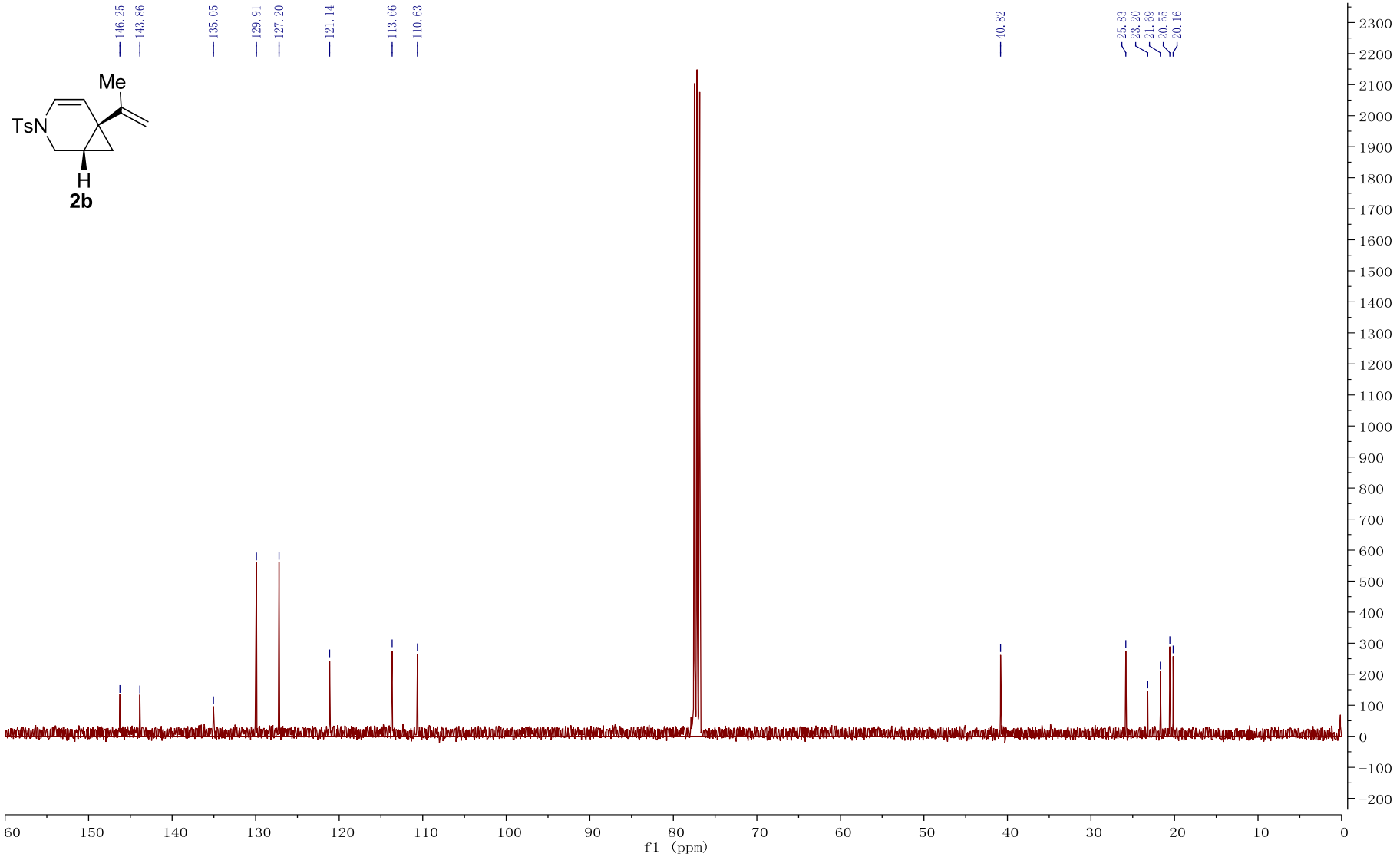

o-NsN
1r
f1 (ppm)

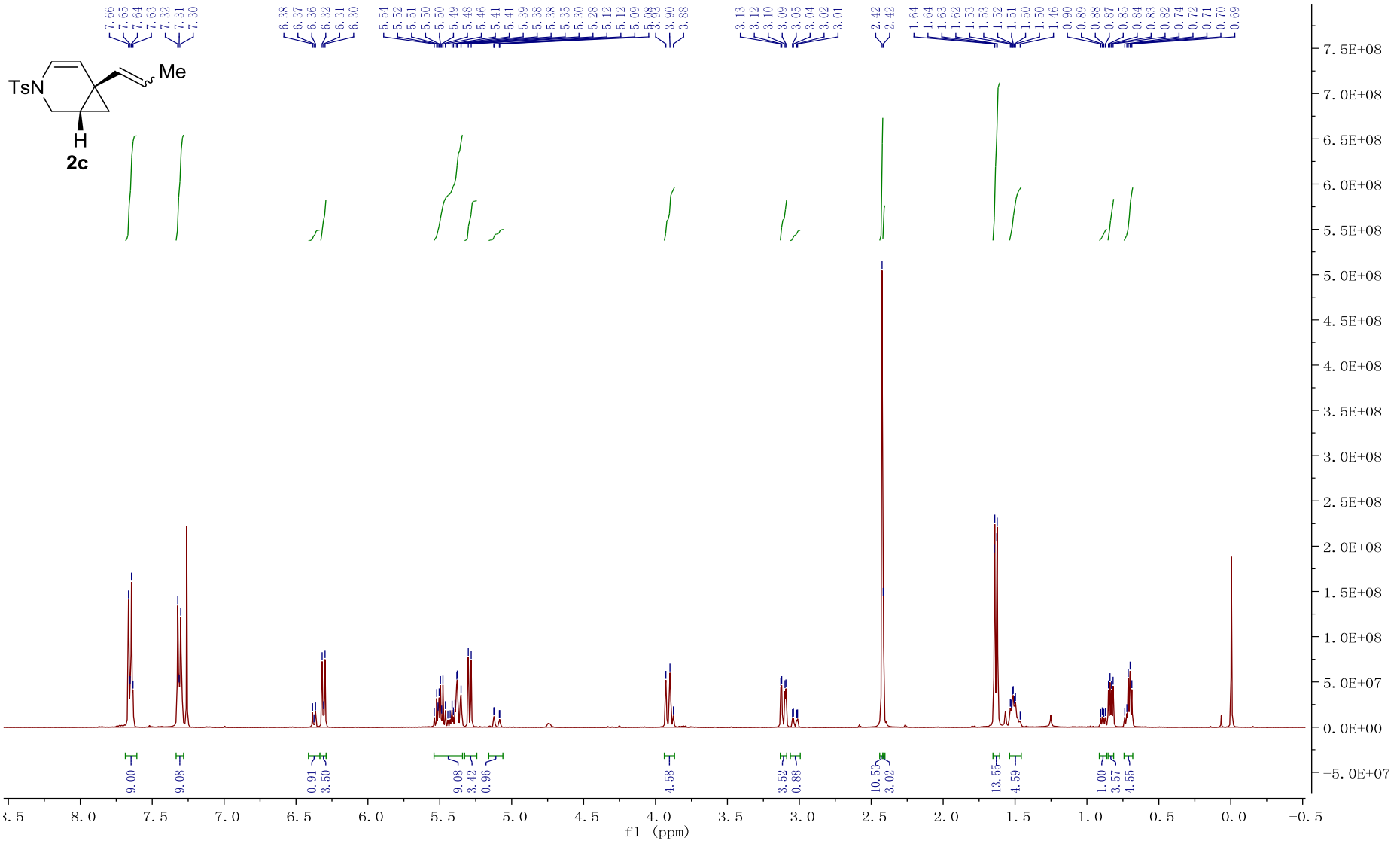

148.33
133.81
133.00
131.75
131.72
131.15
128.05
124.25
120.40
116.25
84.35
82.63
49.72
36.82
o-NsN
1r
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

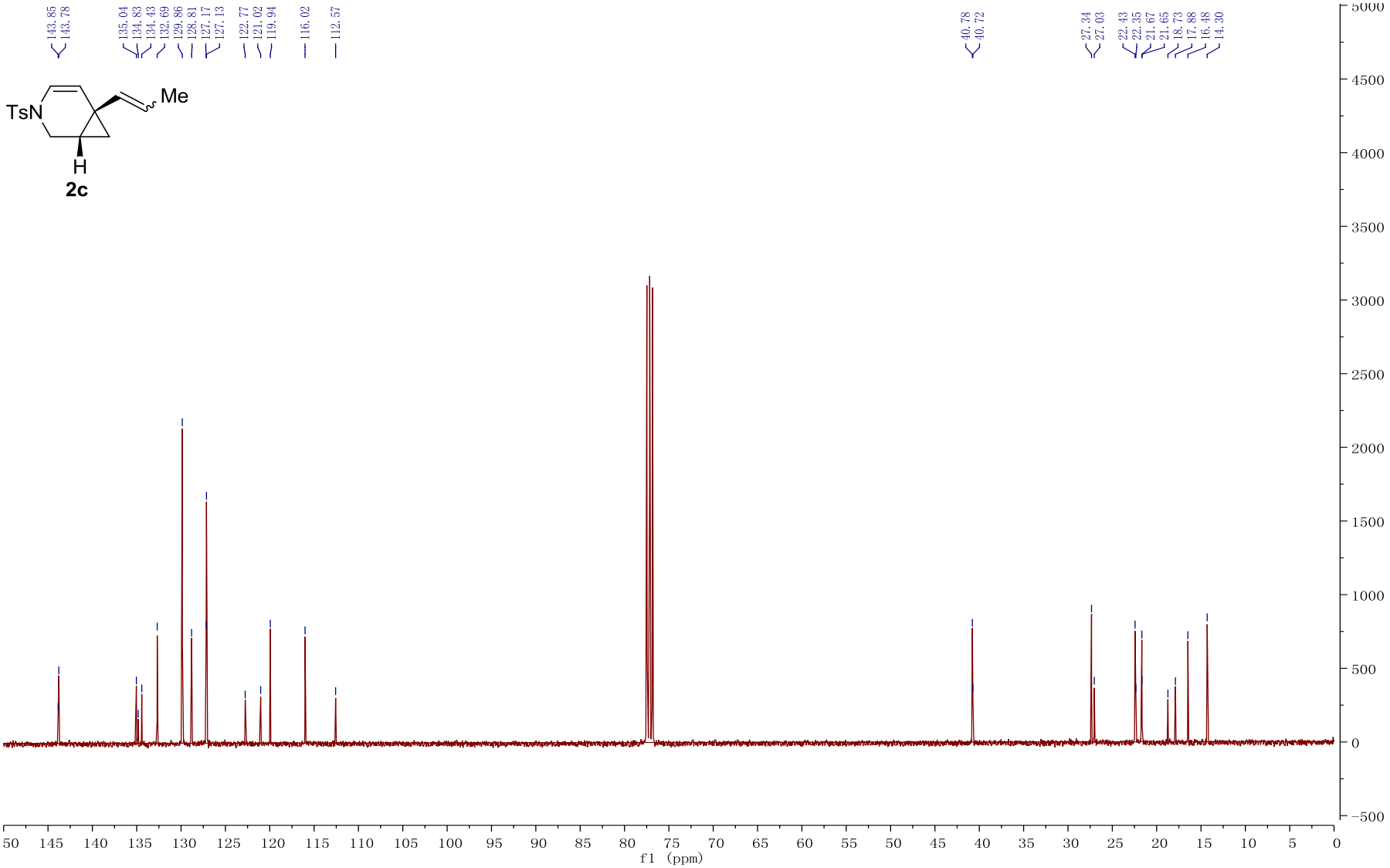

7.66
7.64
7.32
7.30
6.42
6.40
5.47
5.47
5.45
5.44
5.42
5.40
5.01
4.97
4.95
4.92
3.94
3.91
3.05
3.04
3.02
3.01
2.42
1.59
1.57
1.55
0.98
0.97
0.96
0.95
0.83
0.82
0.81
TsN
H
2a
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
2.06
2.10
1.00
1.25
0.84
1.06
1.02
1.06
1.06
3.28
1.33
1.07
1.09
f1 (ppm)

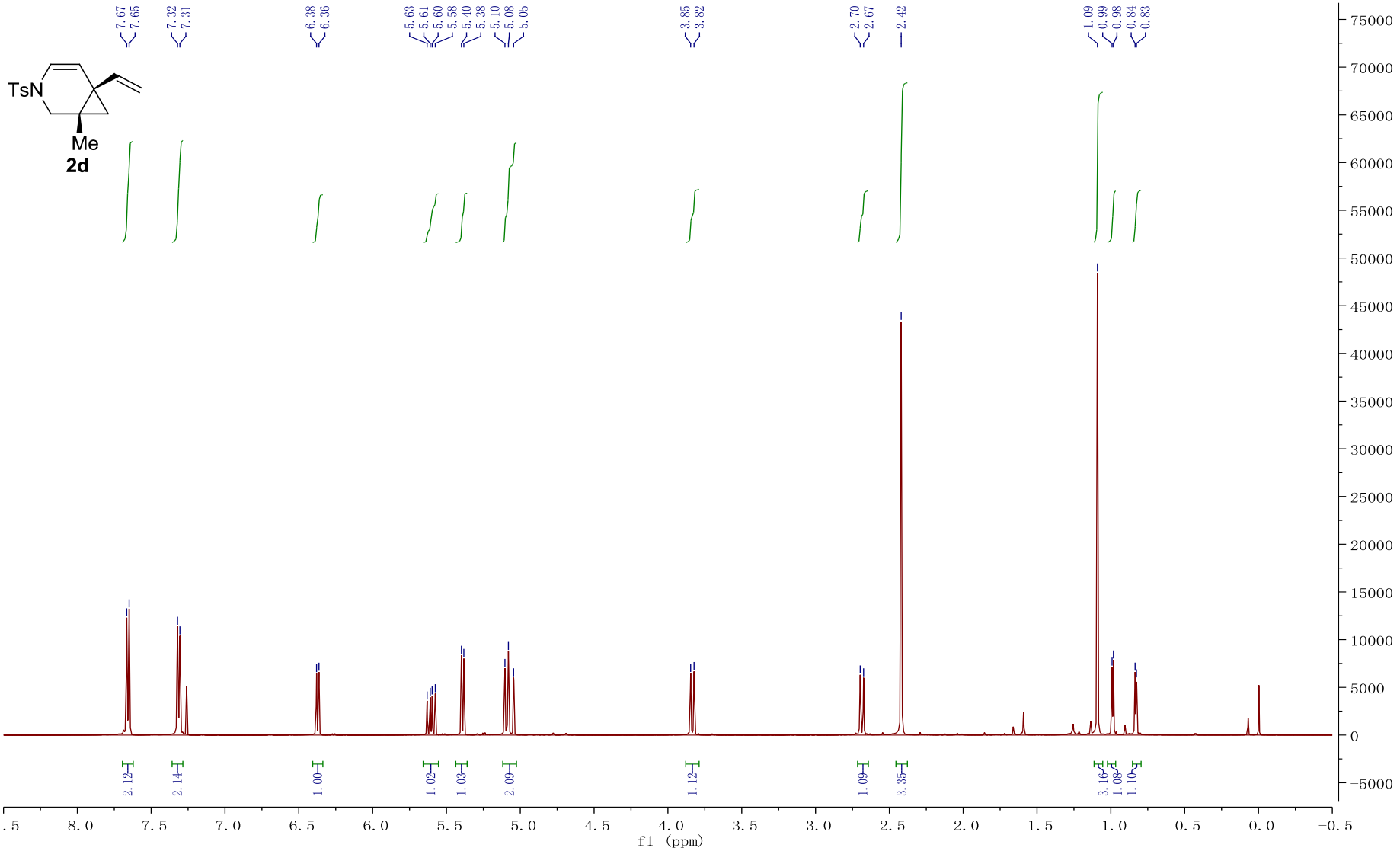

143.94
141.77
134.87
129.92
127.20
121.39
111.53
111.42
40.63
27.70
22.81
21.68
19.65
TsN
H
2a
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
50
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

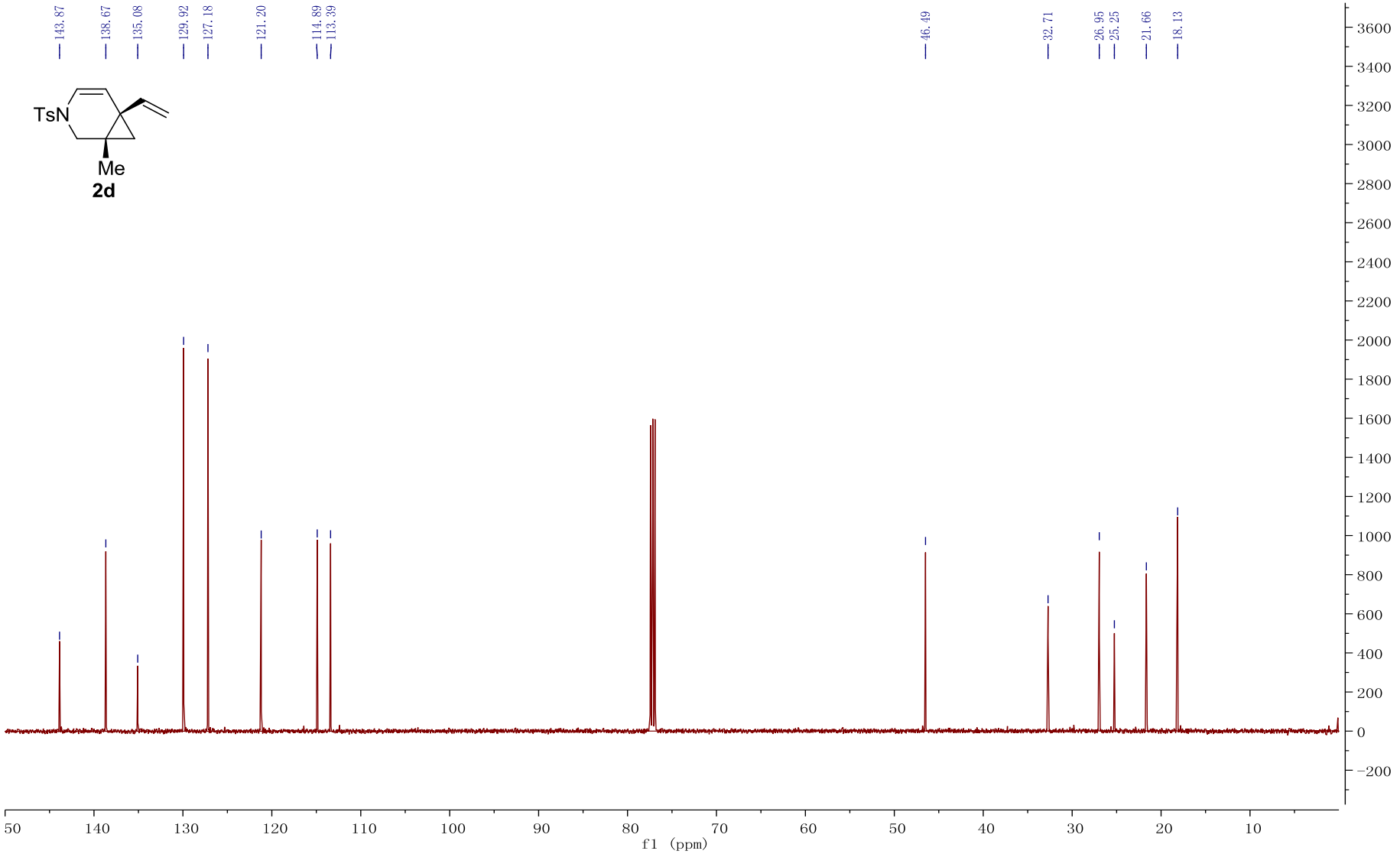

7.67
7.65
7.32
7.30
6.40
6.38
5.36
5.34
4.76
4.75
4.75
4.72
4.72
3.94
3.91
3.06
3.06
3.03
3.03
2.43
1.66
1.58
1.58
1.57
1.56
1.06
1.05
1.04
1.03
0.61
0.60
0.59
Me
TsN
H
2b
1.96
2.18
1.00
1.00
0.95
0.99
1.08
1.08
3.03
3.07
1.05
1.10
1.03
f1 (ppm)

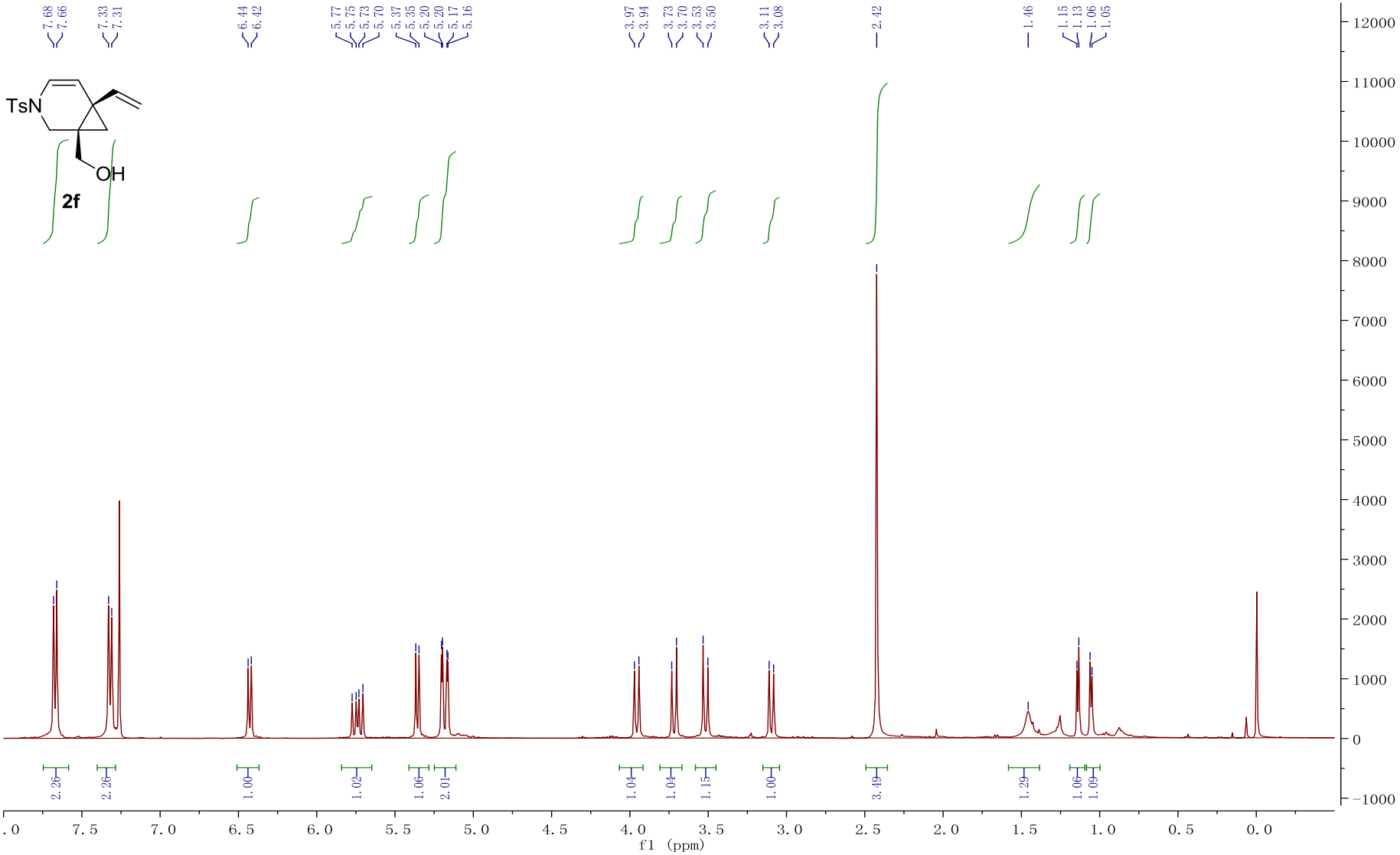

146.25
143.86
135.05
129.91
127.20
121.14
113.66
110.63
40.82
25.83
23.20
21.69
20.55
20.16
Me
TsN
H
2b
f1 (ppm)

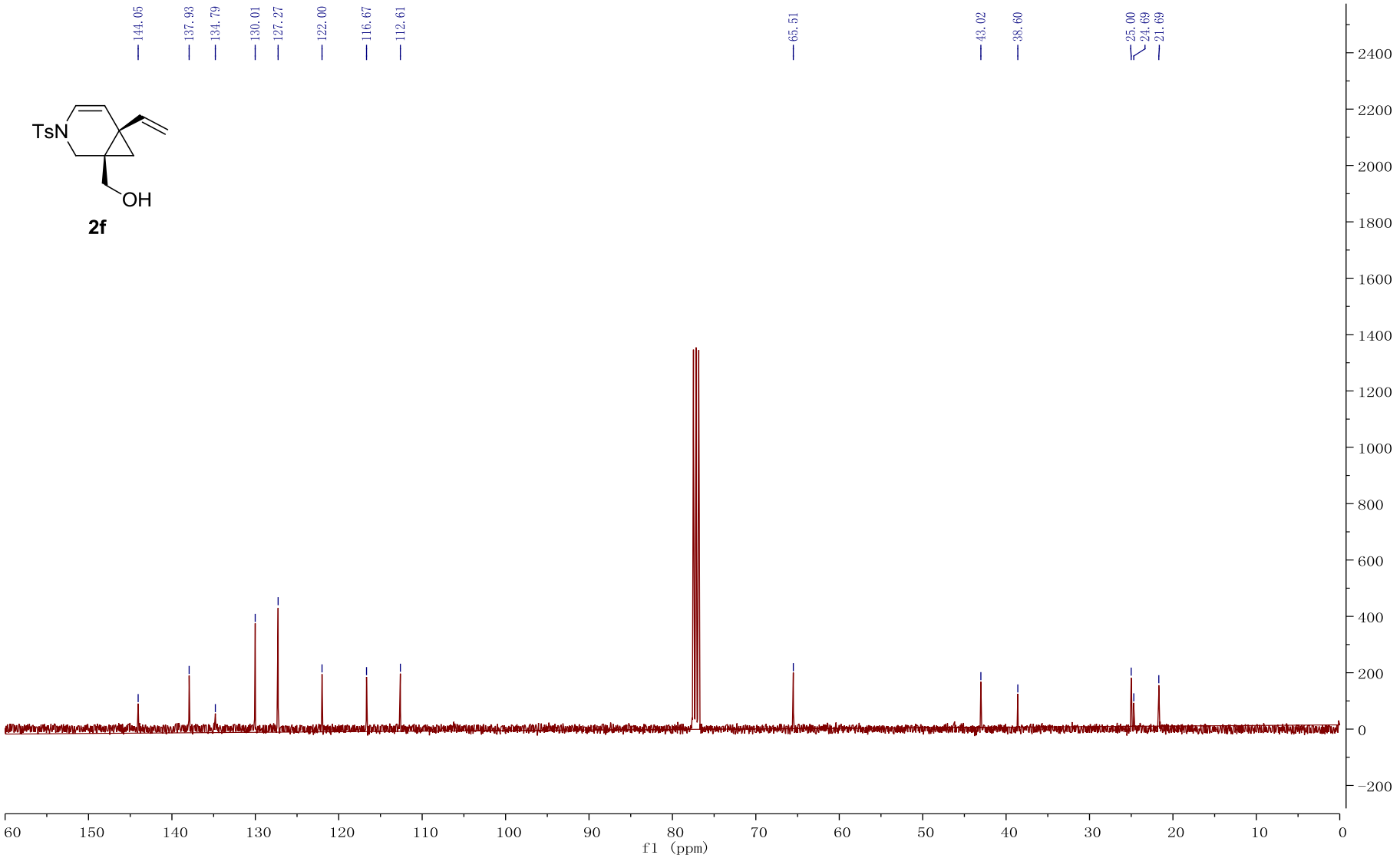

TsN
Me
H
2c
f1 (ppm)

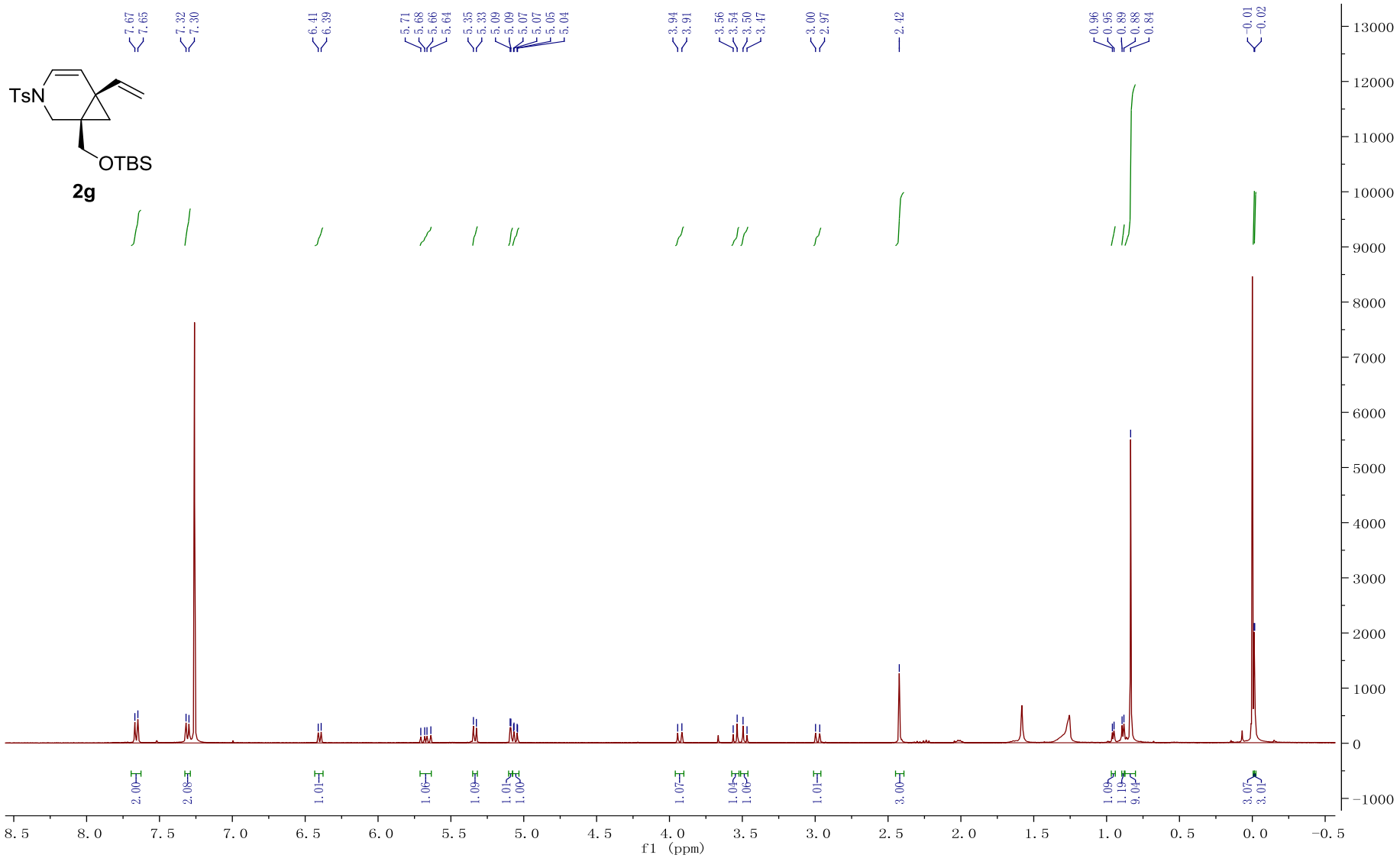

143.85
143.78
135.04
134.83
134.43
132.69
129.86
128.81
127.17
127.13
122.77
121.02
119.94
116.02
112.57
40.78
40.72
27.34
27.03
22.43
22.35
21.67
21.65
18.73
17.88
16.48
14.30
TsN
Me
H
2c
f1 (ppm)

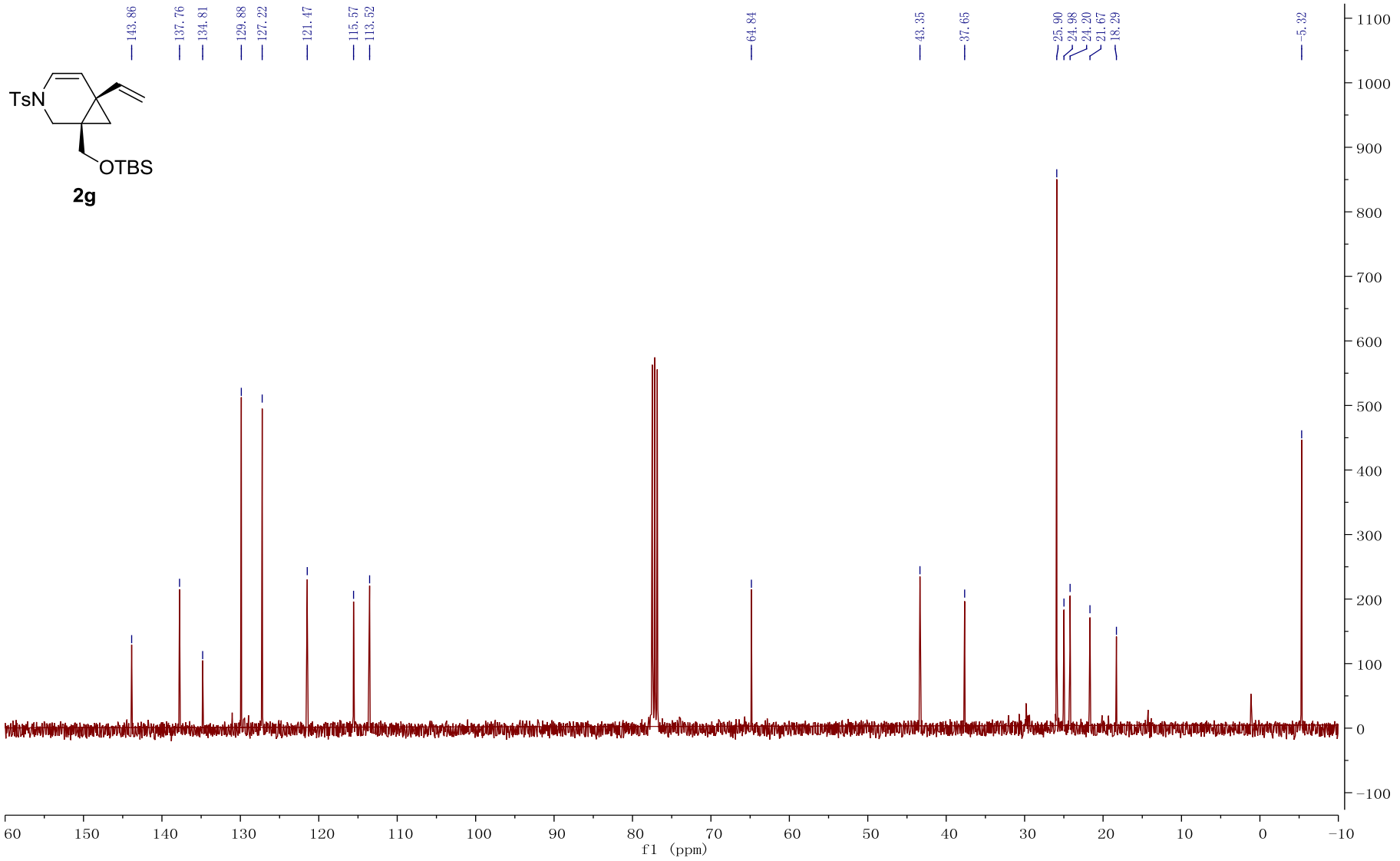

TsN
Me
2d
7.67
7.65
7.32
7.31
6.38
6.36
5.63
5.61
5.60
5.58
5.40
5.38
5.10
5.08
5.05
3.85
3.82
2.70
2.67
2.42
1.09
0.99
0.98
0.84
0.83
2.12
2.14
1.00
1.02
1.03
2.09
1.12
1.09
3.35
3.16
1.08
1.10
f1 (ppm)

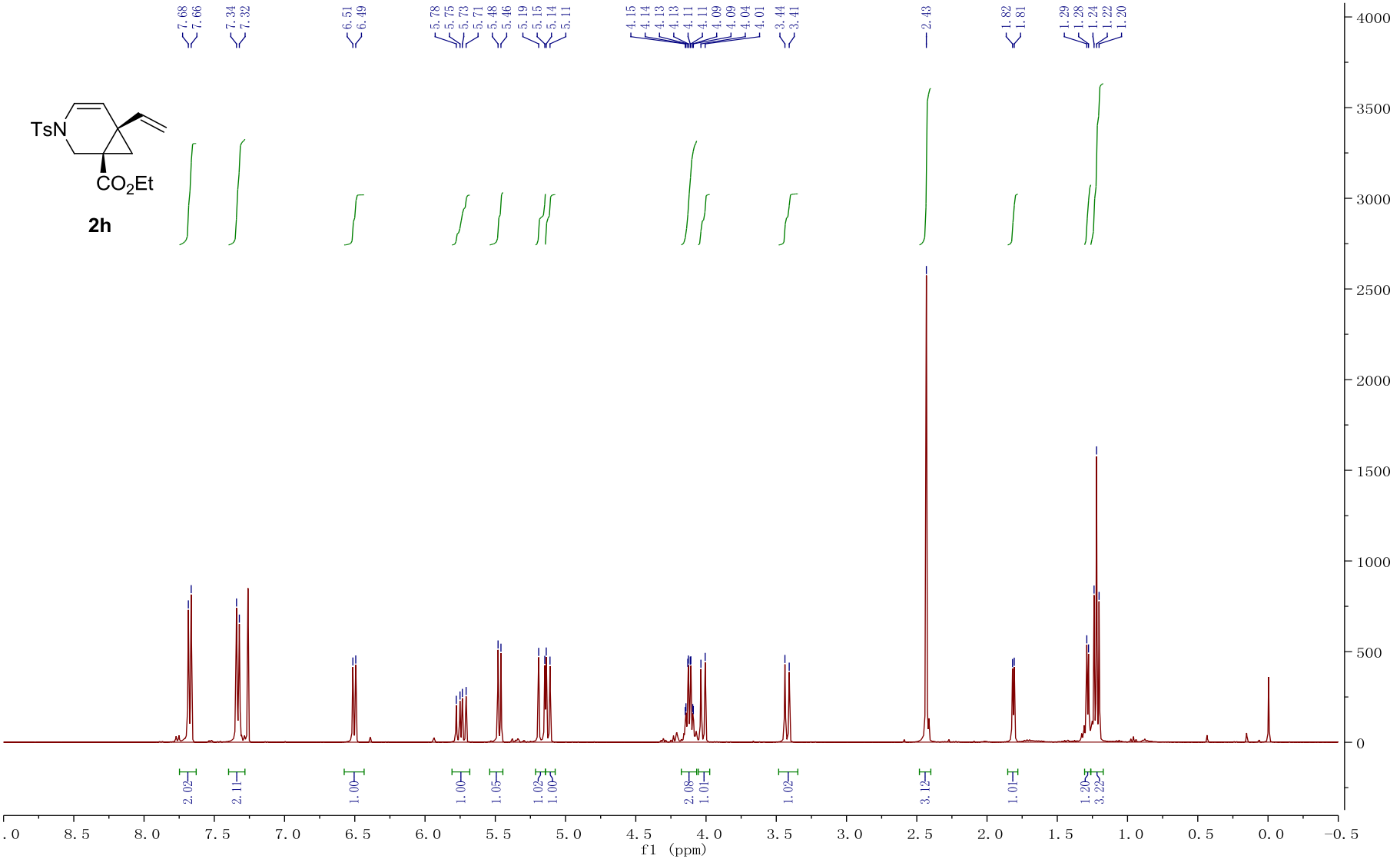

143.87
138.67
135.08
129.92
127.18
121.20
114.89
113.39
46.49
32.71
26.95
25.25
21.66
18.13
TsN
Me
2d
f1 (ppm)

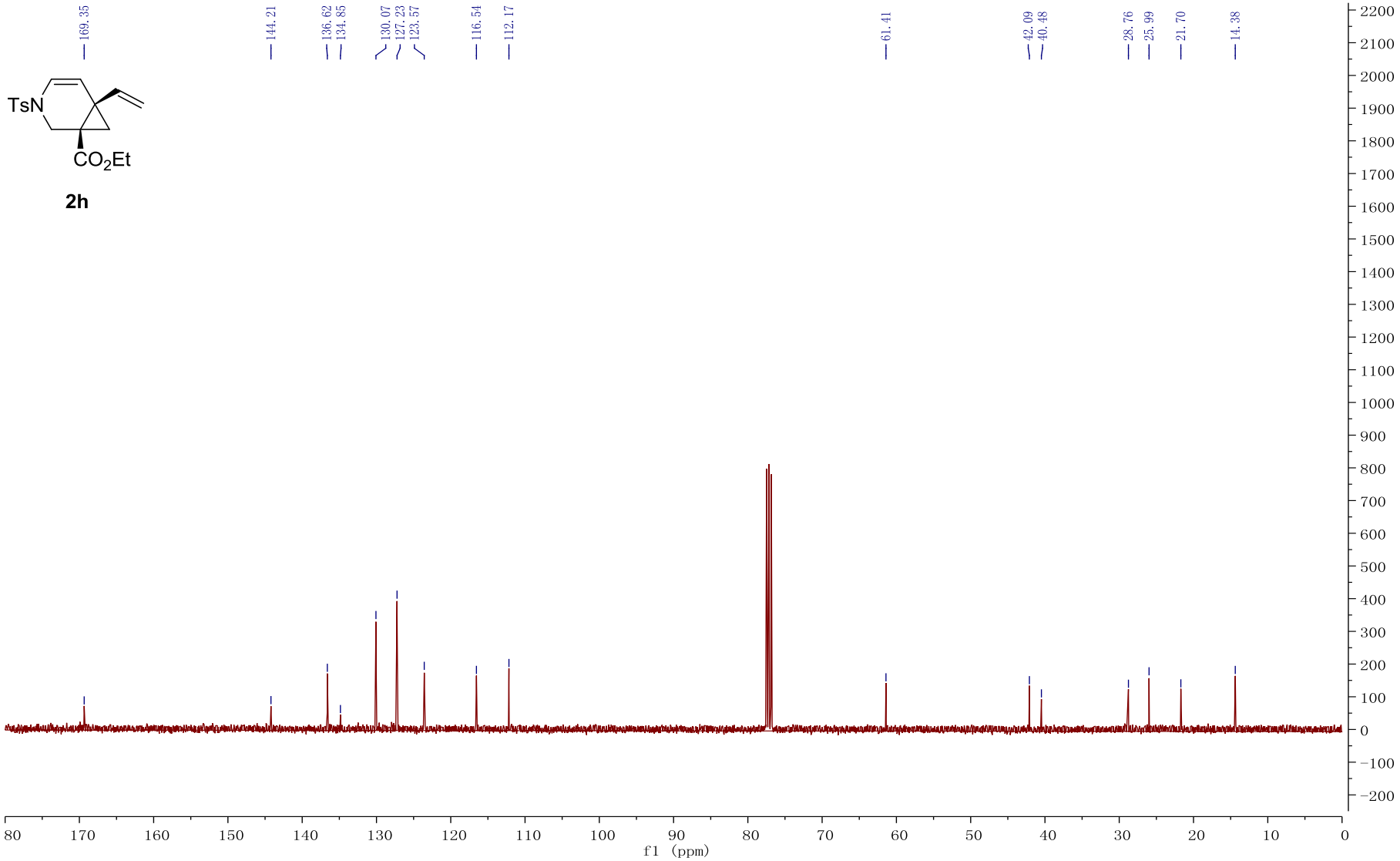

7.68
7.66
7.33
7.31
6.44
6.42
5.77
5.75
5.73
5.70
5.37
5.35
5.20
5.20
5.17
5.16
3.97
3.94
3.73
3.70
3.53
3.50
3.11
3.08
2.42
1.46
1.15
1.13
1.06
1.05
TsN
OH
2f
2.26
2.26
1.00
1.02
1.06
2.01
1.04
1.04
1.15
1.00
3.49
1.29
1.06
1.09
f1 (ppm)

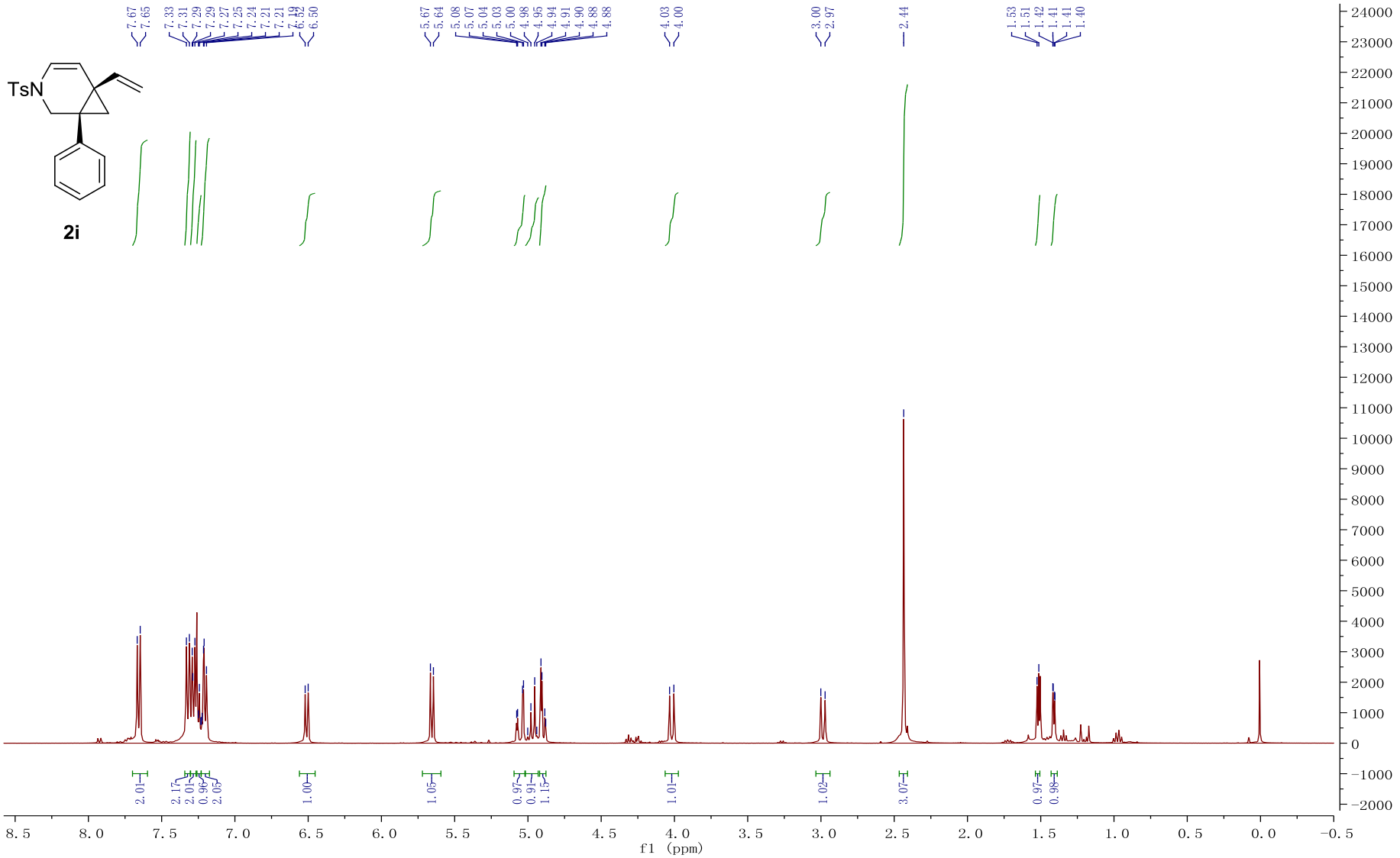

144.05
137.93
134.79
130.01
127.27
122.00
116.67
112.61
65.51
43.02
38.60
25.00
24.69
21.69
TsN
OH
2f
f1 (ppm)

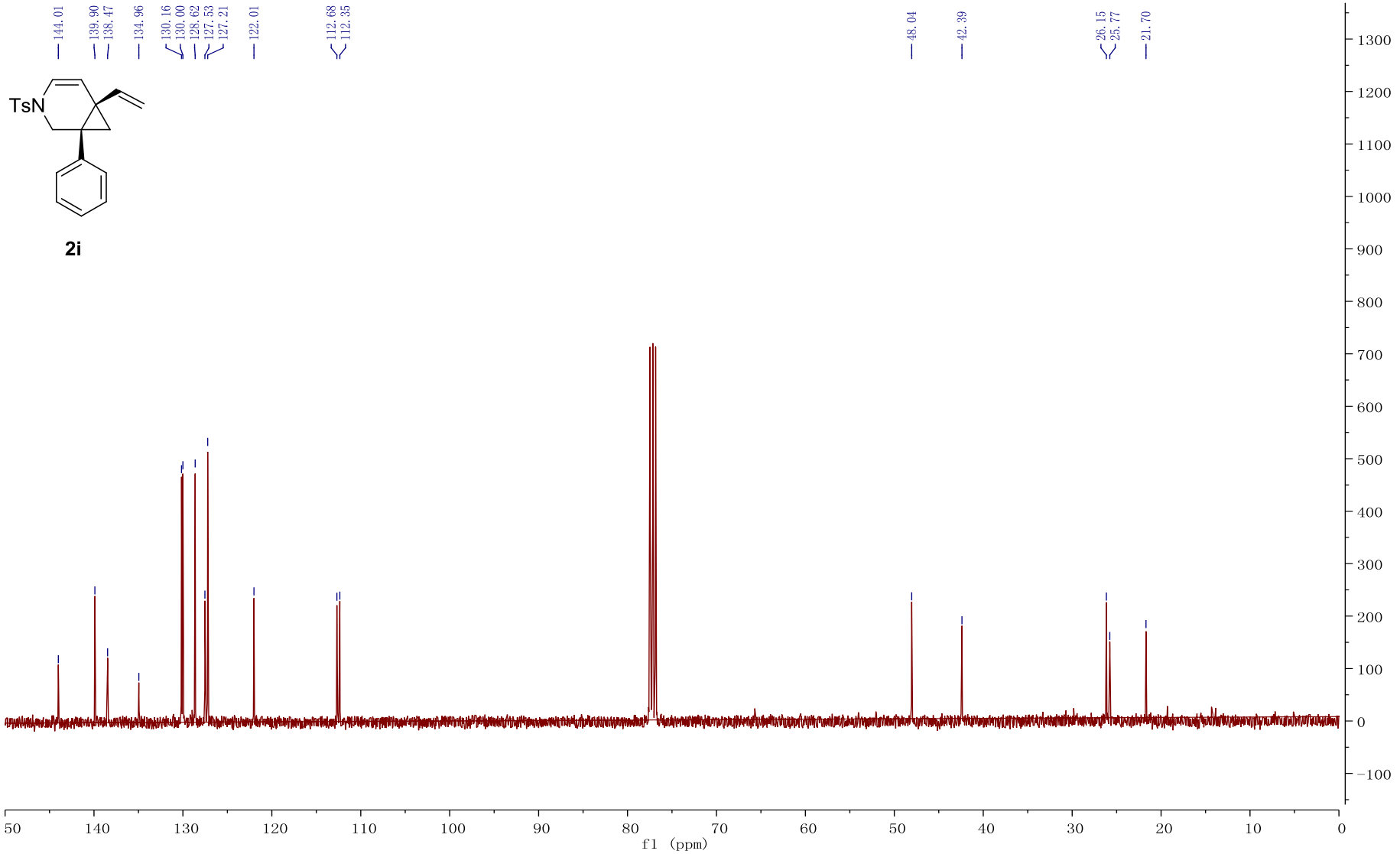

TsN
OTBS
2g
7.67
7.65
7.32
7.30
6.41
6.39
5.71
5.68
5.66
5.64
5.35
5.33
5.09
5.09
5.07
5.07
5.05
5.04
3.94
3.91
3.56
3.54
3.50
3.47
3.00
2.97
2.42
0.96
0.95
0.89
0.88
0.84
-0.01
-0.02
2.00
2.08
1.01
1.06
1.09
1.01
1.00
1.07
1.04
1.06
1.01
3.00
1.09
1.19
9.04
3.07
3.01
f1 (ppm)


143.86
137.76
134.81
129.88
127.22
121.47
115.57
113.52
64.84
43.35
37.65
25.90
24.98
24.20
21.67
18.29
-5.32
TsN
OTBS
2g
f1 (ppm)


TsN
CO2Et
2h
7.68
7.66
7.34
7.32
6.51
6.49
5.78
5.75
5.73
5.71
5.48
5.46
5.19
5.15
5.14
5.11
4.15
4.14
4.13
4.11
4.11
4.09
4.09
4.04
4.01
3.44
3.41
2.43
1.82
1.81
1.29
1.28
1.24
1.22
1.20
2.02
2.11
1.00
1.00
1.05
1.02
1.00
2.08
1.01
1.02
3.12
1.01
1.20
3.22
f1 (ppm)


169.35
144.21
136.62
134.85
130.07
127.23
123.57
116.54
112.17
61.41
42.09
40.48
28.76
25.99
21.70
14.38
TsN
CO2Et
2h
f1 (ppm)


TsN
2i
7.67
7.65
7.33
7.31
7.29
7.29
7.27
7.25
7.24
7.21
7.21
7.19
6.52
6.50
5.67
5.64
5.08
5.07
5.04
5.03
5.00
4.98
4.95
4.94
4.91
4.90
4.88
4.88
4.03
4.00
3.00
2.97
2.44
1.53
1.51
1.42
1.41
1.41
1.40
2.01
2.17
2.01
0.96
2.05
1.00
1.05
0.97
0.91
1.15
1.01
1.02
3.07
0.97
0.98
f1 (ppm)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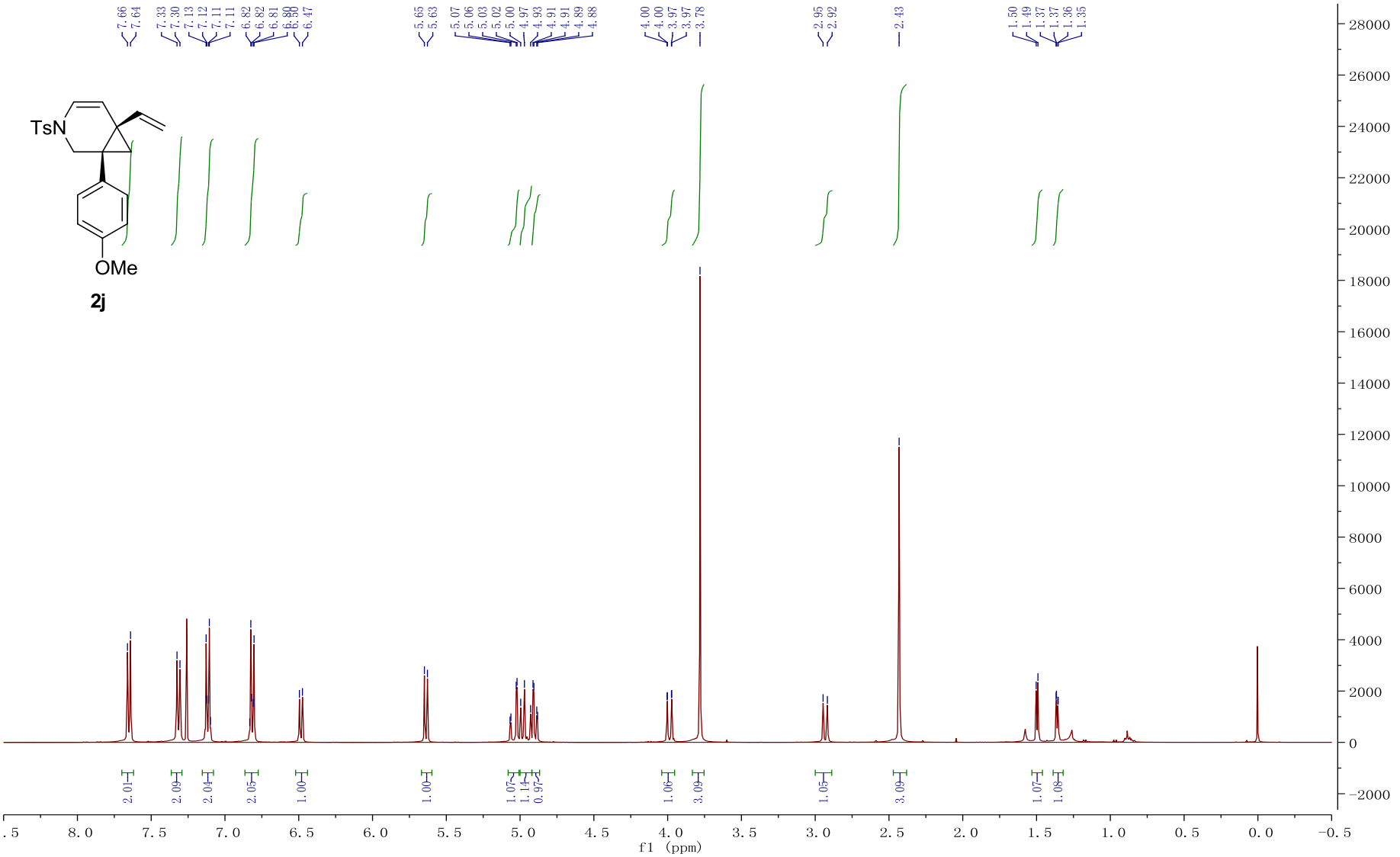
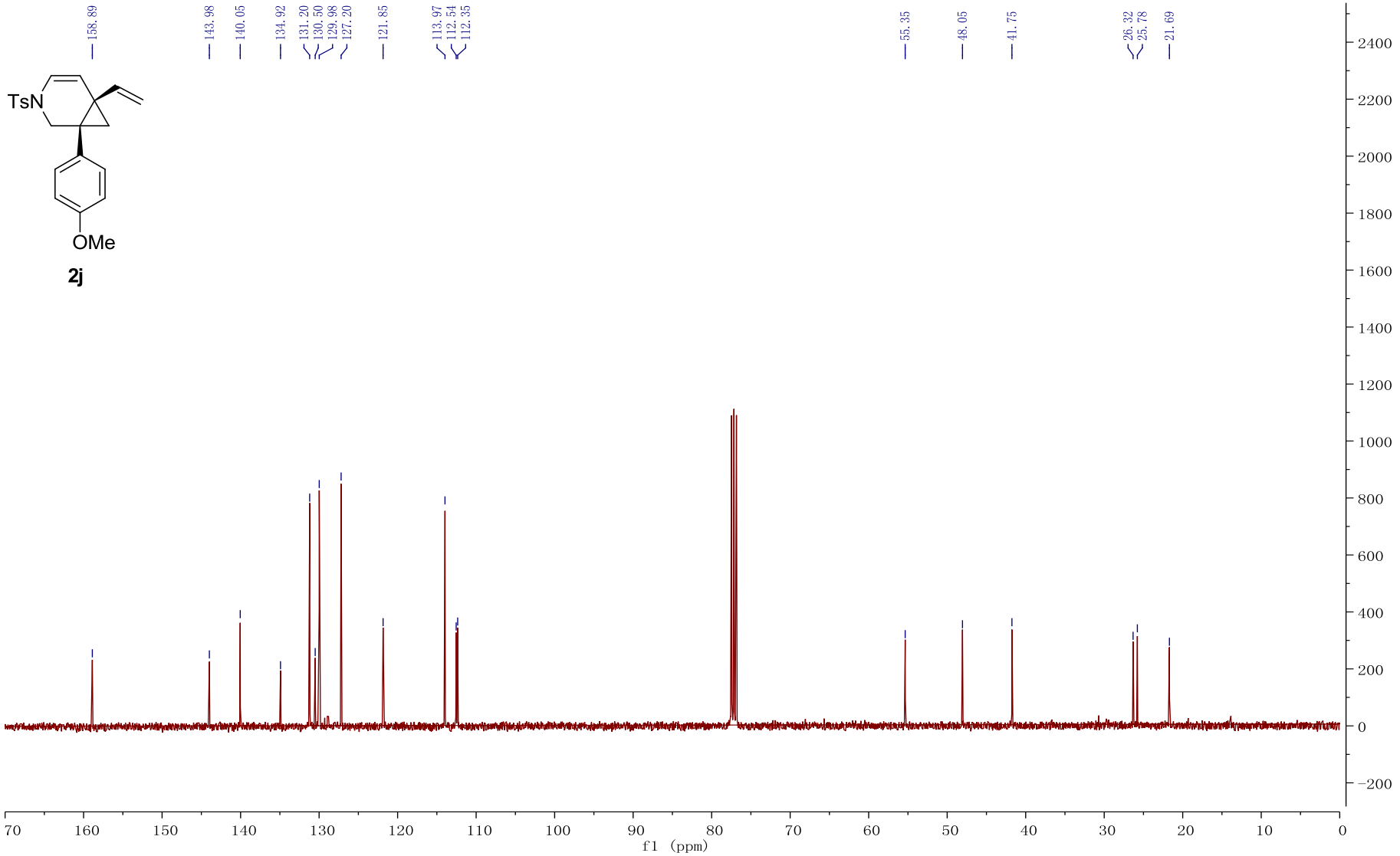
138.47
134.96
130.16
130.00
128.62
127.53
127.21
122.01
112.68
112.35
48.04
42.39
26.15
25.77
21.70
TsN
2i
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
50
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


TsN
OMe
2j
f1 (ppm)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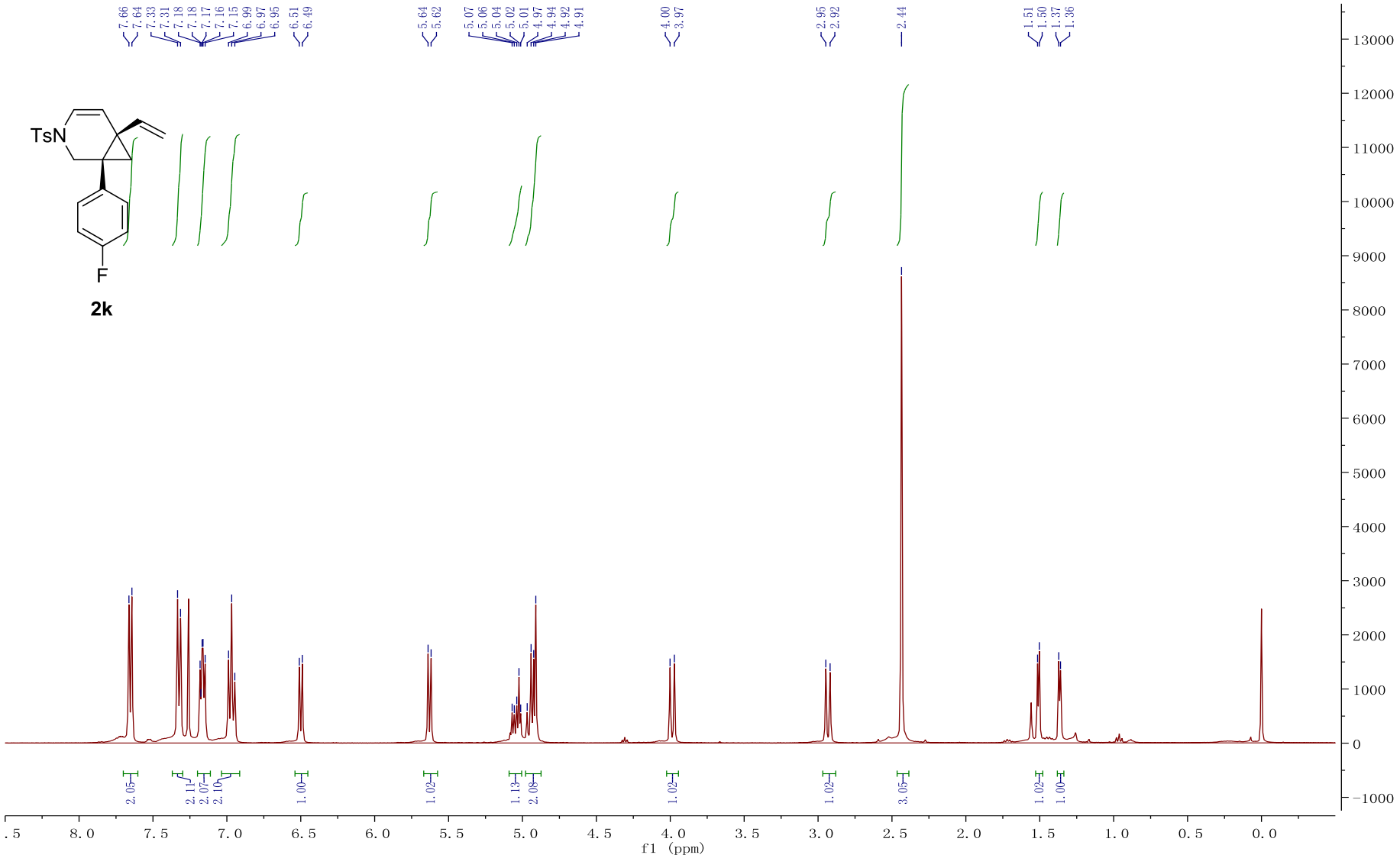
140.05
134.92
131.20
130.50
129.98
127.20
121.85
113.97
112.54
112.35
55.35
48.05
41.75
26.32
25.78
21.69
TsN
OMe
2j
f1 (ppm)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7.16
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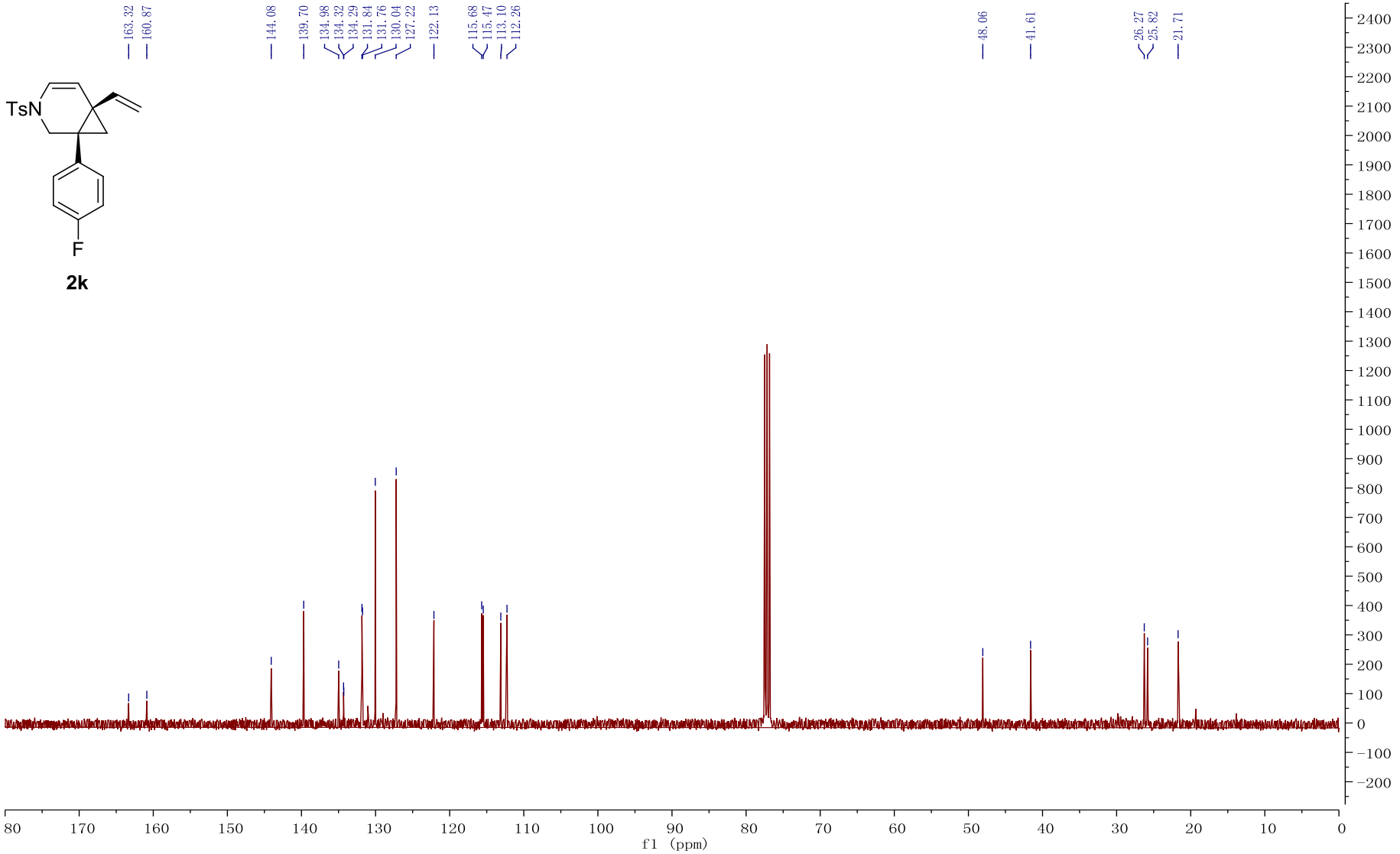
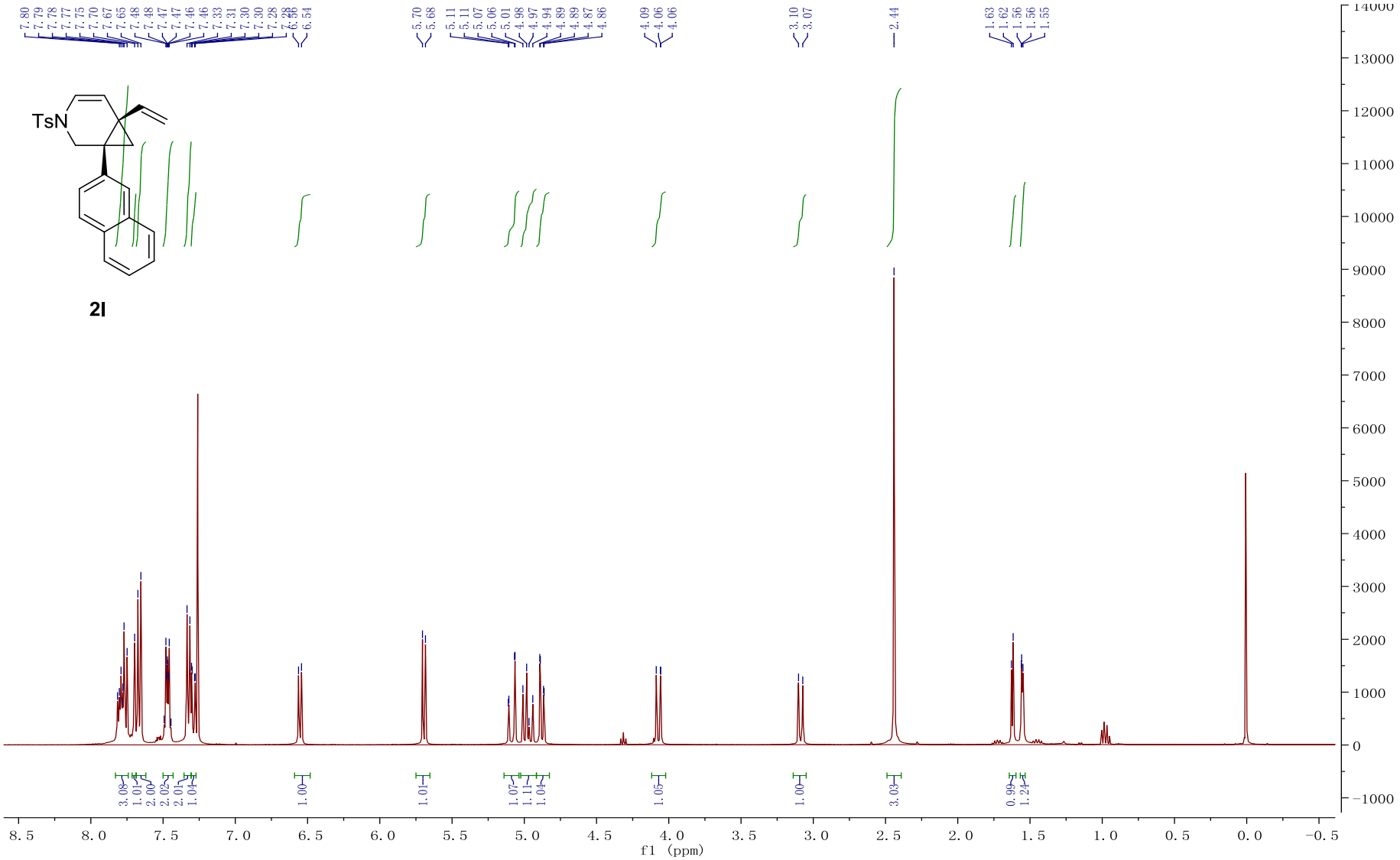
6.99
6.97
6.95
6.51
6.49
5.64
5.62
5.07
5.06
5.04
5.02
5.01
4.97
4.94
4.92
4.91
4.00
3.97
2.95
2.92
2.44
1.51
1.50
1.37
1.36
TsN
F
2k
2.05
2.11
2.07
2.10
1.00
1.02
1.13
2.08
1.02
1.02
3.05
1.02
1.00
f1 (ppm)


163.32
160.87
144.08
139.70
134.98
134.32
134.29
131.84
131.76
130.04
127.22
122.13
115.68
115.47
113.10
112.26
48.06
41.61
26.27
25.82
21.71
TsN
F
2k
f1 (ppm)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7.79
7.78
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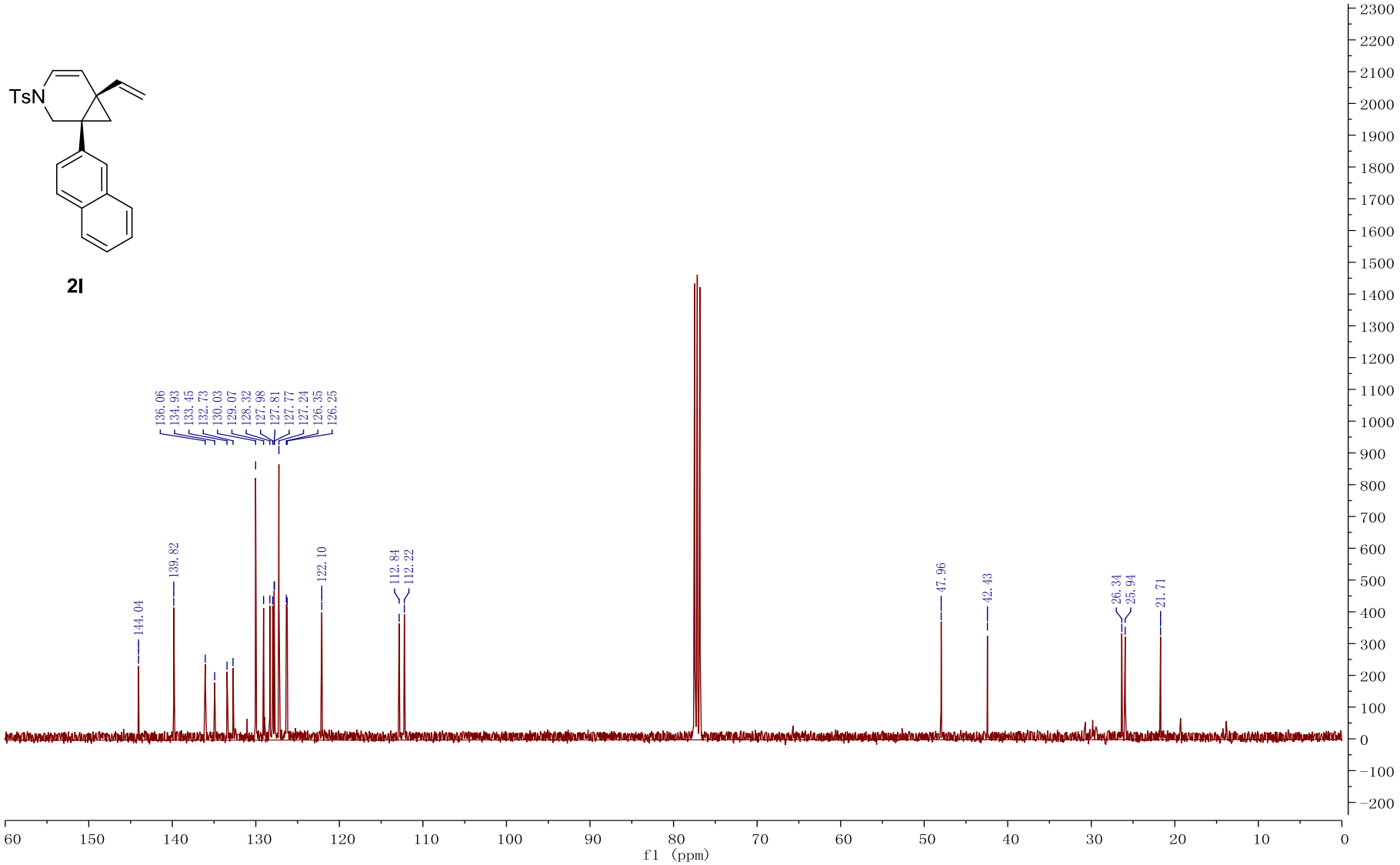
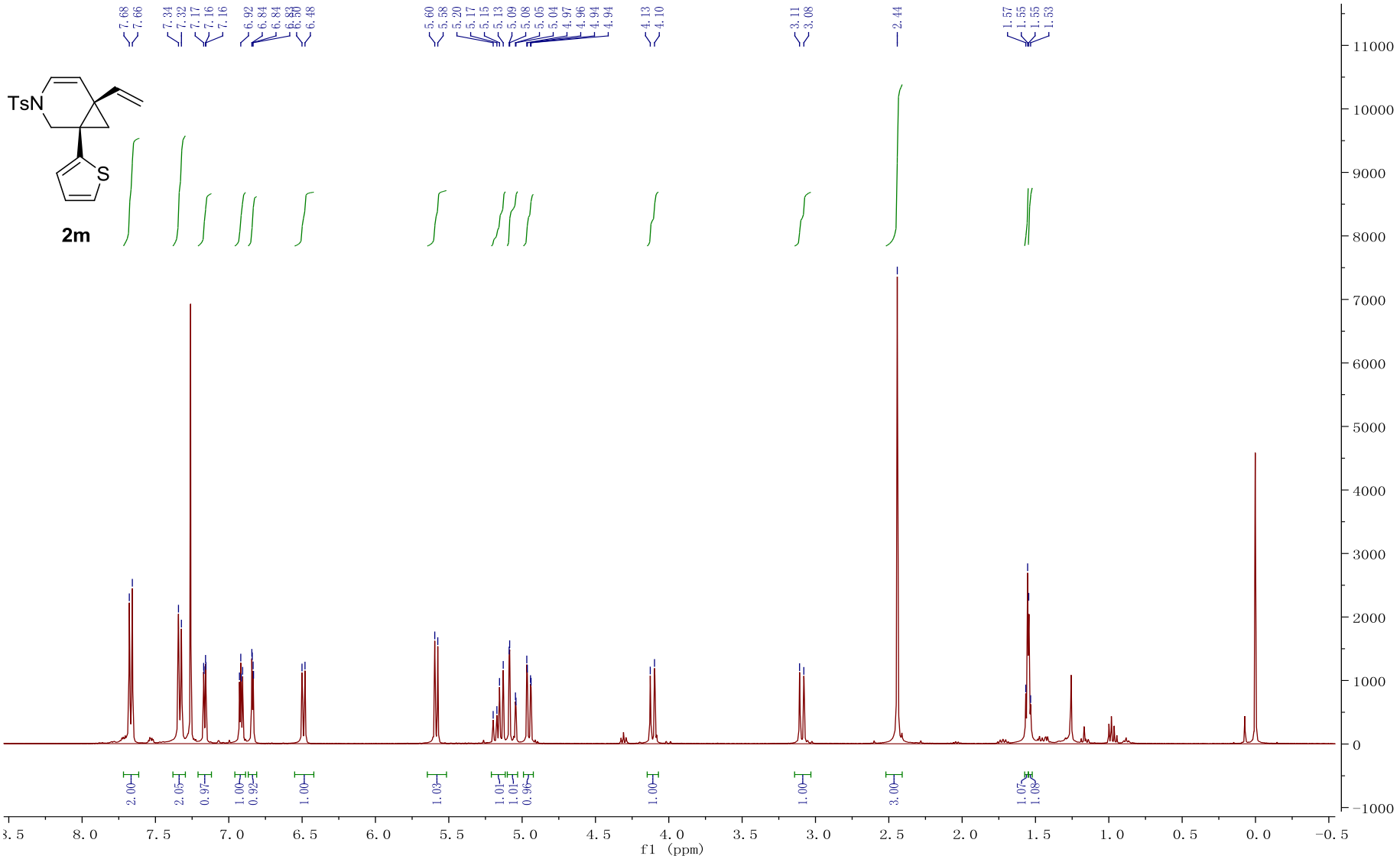
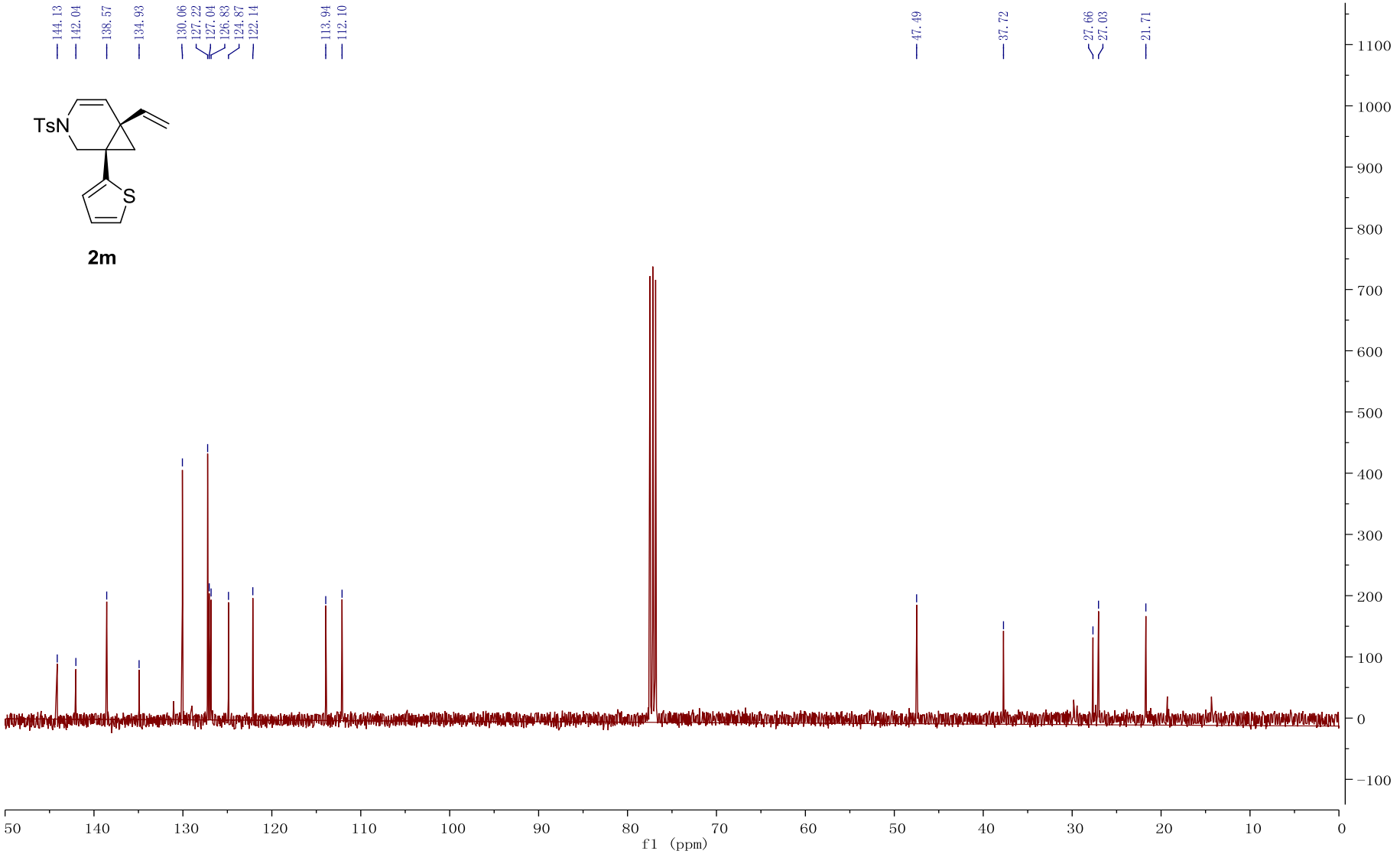
7.70
7.67
7.65
7.48
7.48
7.47
7.47
7.46
7.46
7.33
7.31
7.30
7.30
7.28
6.56
6.54
5.70
5.68
5.11
5.11
5.07
5.06
5.01
4.98
4.97
4.94
4.89
4.89
4.87
4.86
4.09
4.06
4.06
3.10
3.07
2.44
1.63
1.62
1.56
1.56
1.55
TsN
2l
3.08
1.01
2.00
2.02
2.01
1.04
1.00
1.01
1.07
1.11
1.04
1.05
1.00
3.03
0.99
1.24
f1 (ppm)


TsN
2l
136.06
134.93
133.45
132.73
130.03
129.07
128.32
127.98
127.81
127.77
127.24
126.35
126.25
144.04
139.82
122.10
112.84
112.22
47.96
42.43
26.34
25.94
21.71
f1 (ppm)


TsN
S
2m
7.68
7.66
7.34
7.32
7.17
7.16
7.16
6.92
6.84
6.84
6.50
6.48
5.60
5.58
5.20
5.17
5.15
5.13
5.09
5.08
5.05
5.04
4.97
4.96
4.94
4.94
4.13
4.10
3.11
3.08
2.44
1.57
1.55
1.55
1.53
2.00
2.05
0.97
1.00
0.92
1.00
1.03
1.01
1.01
0.96
1.00
1.00
3.00
1.07
1.08
f1 (ppm)


144.13
142.04
138.57
134.93
130.06
127.22
127.04
126.83
124.87
122.14
113.94
112.10
47.49
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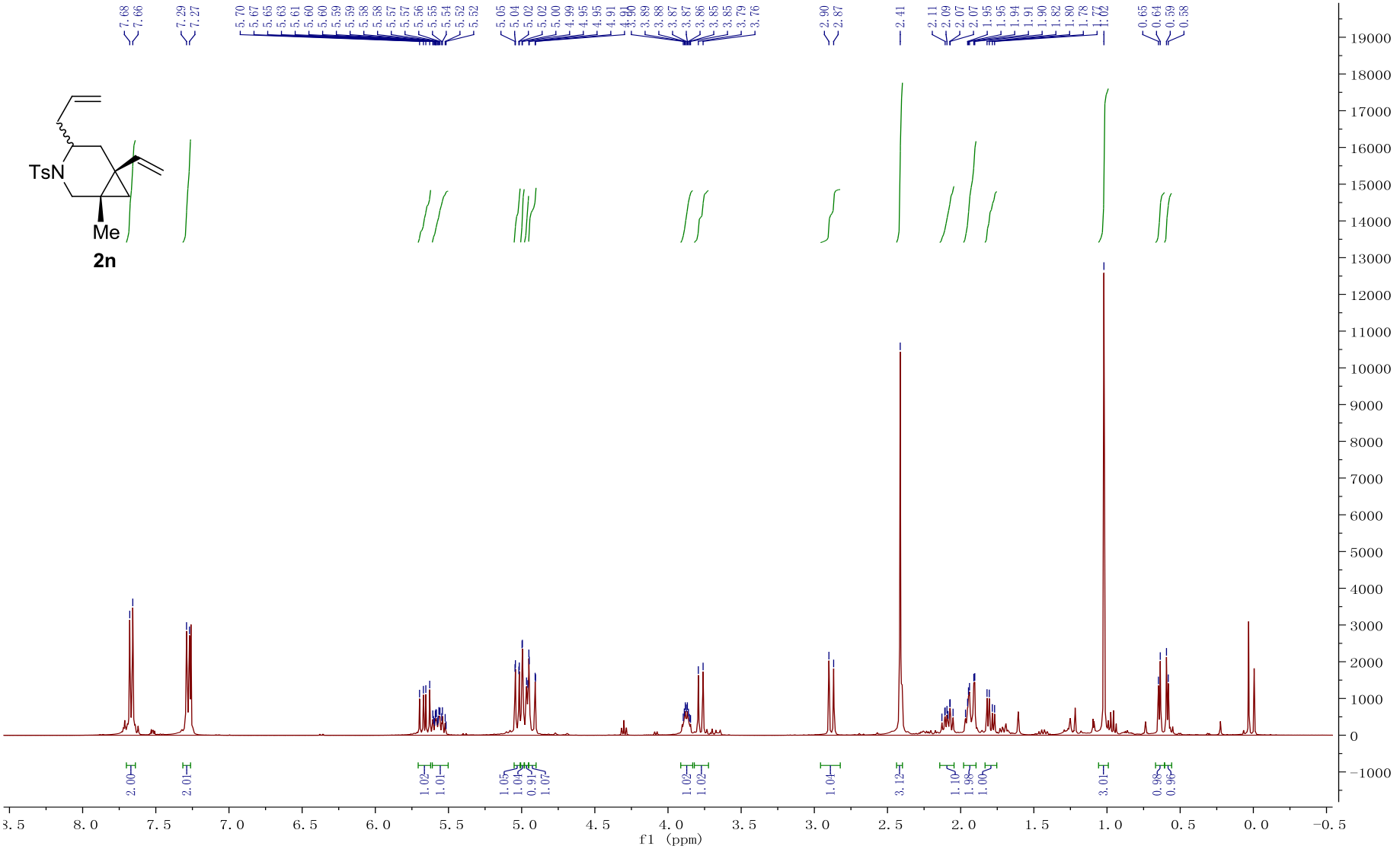
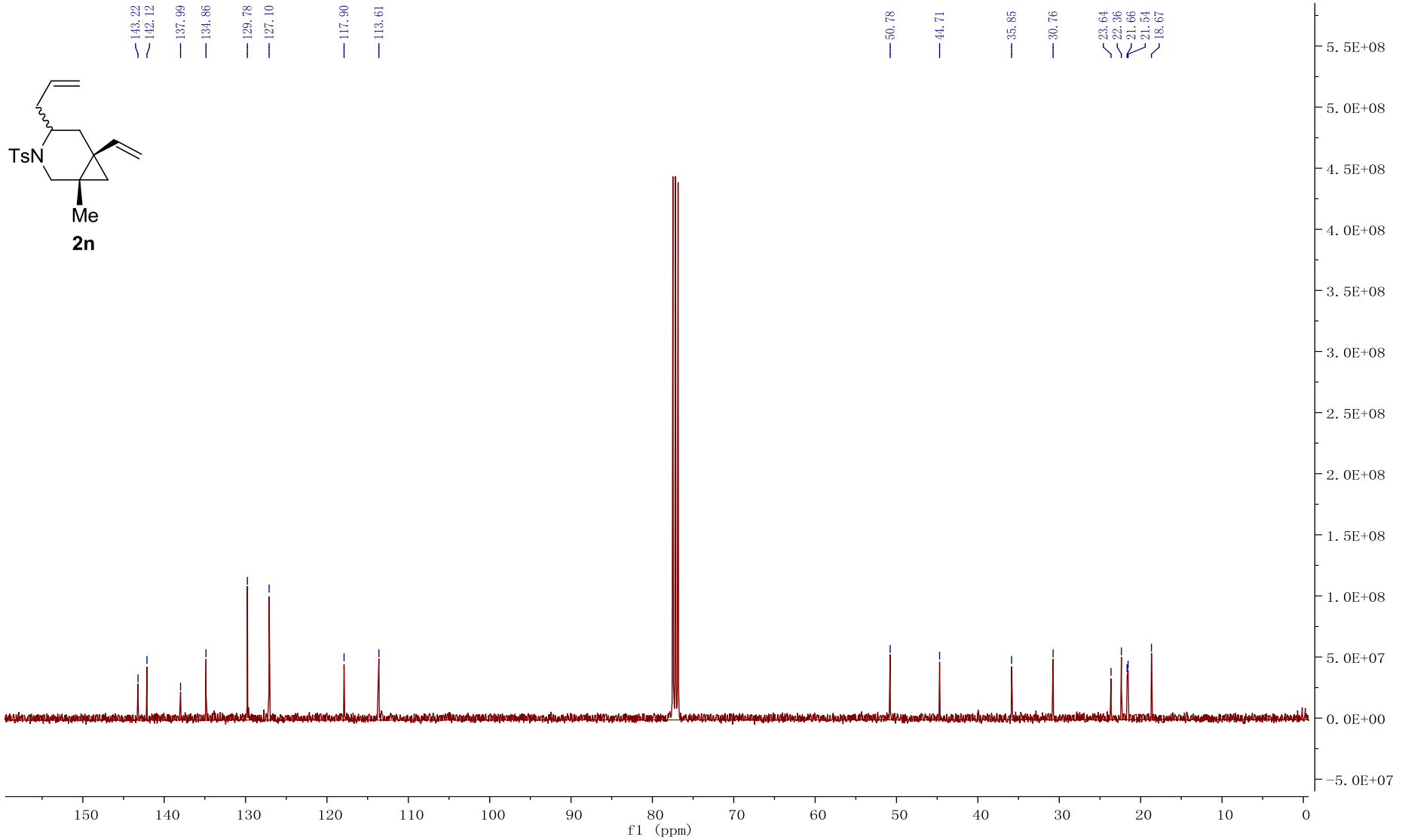
27.66
27.03
21.71
TsN
S
2m
f1 (ppm)


TsN
Me
2n
f1 (ppm)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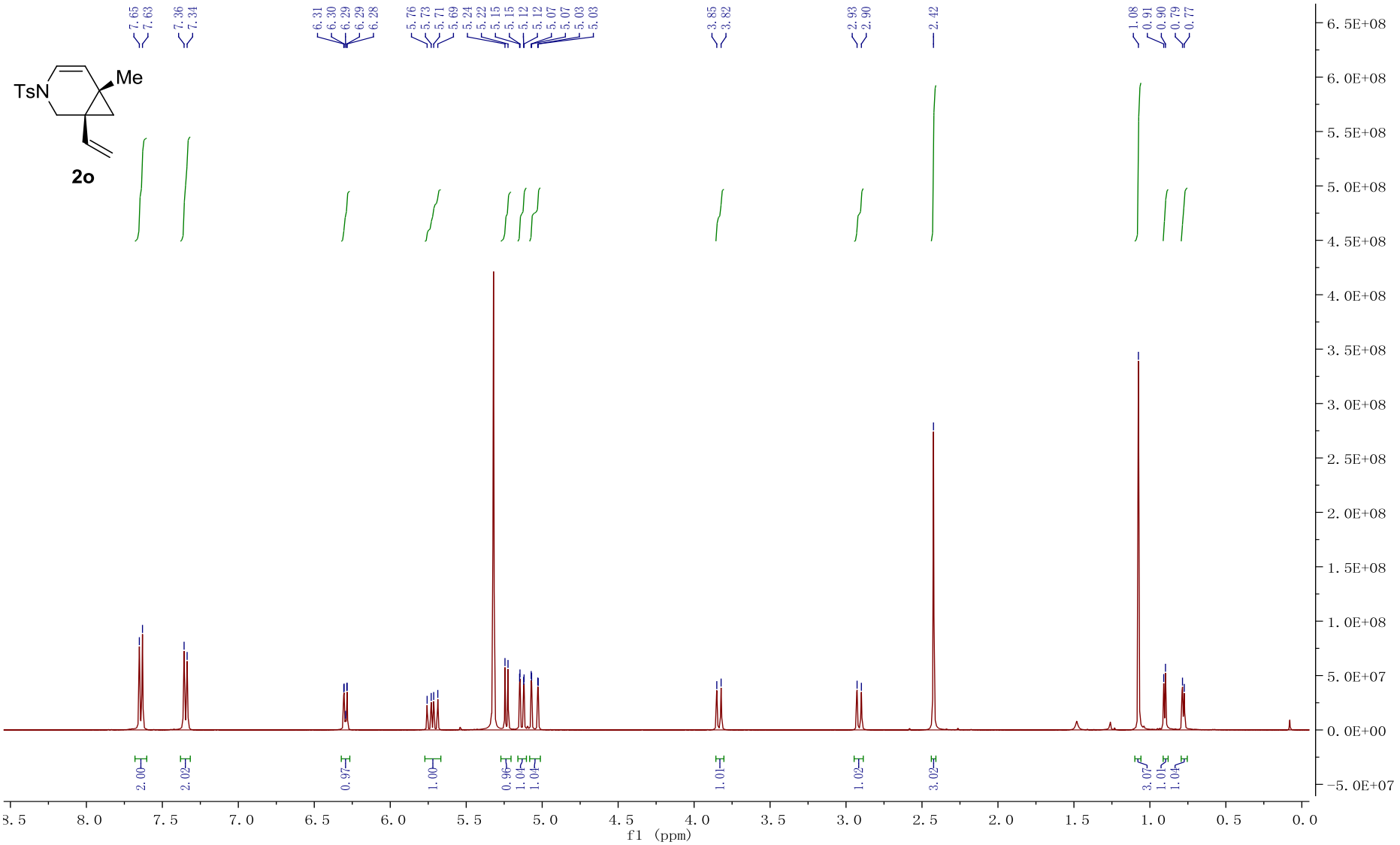
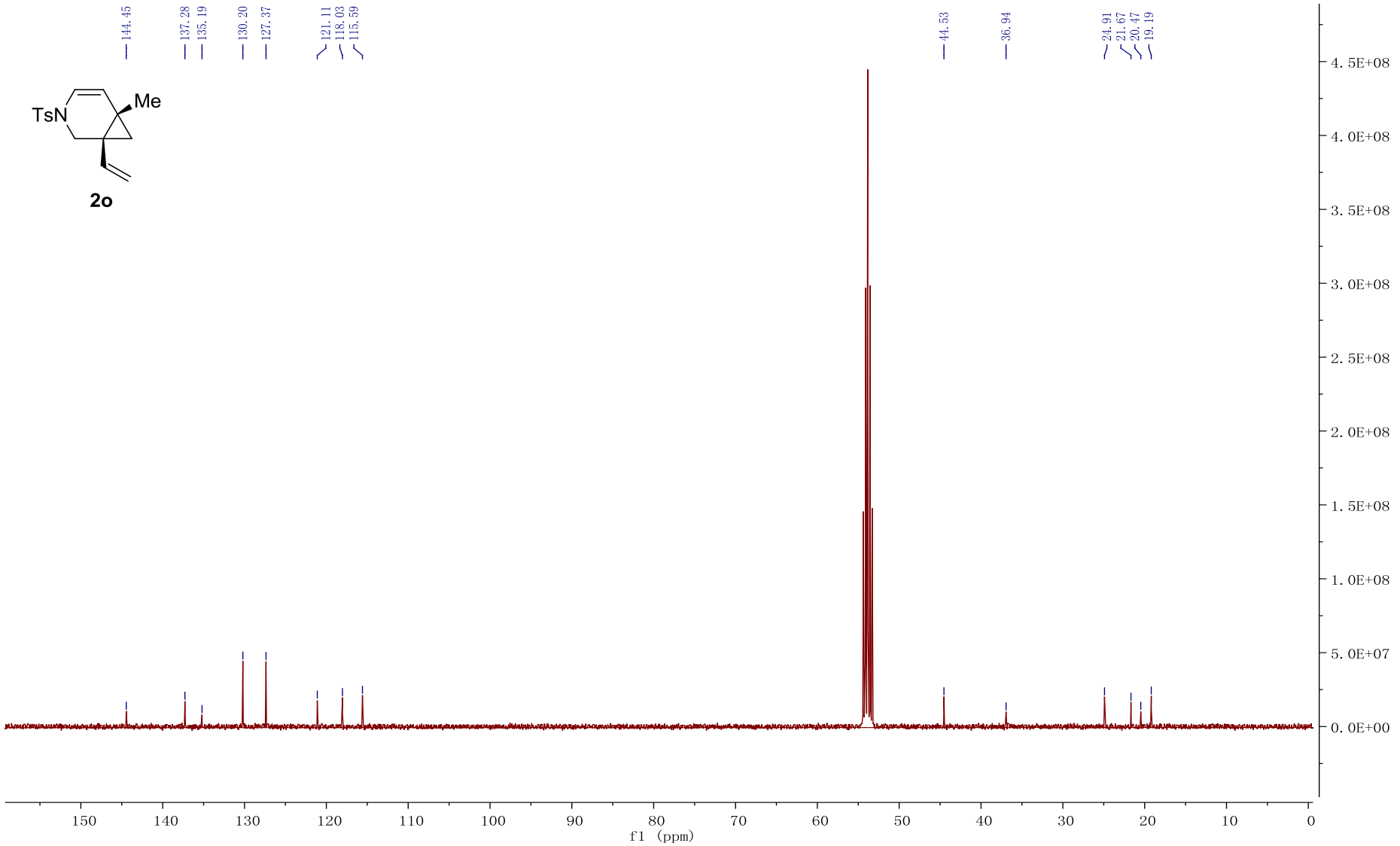
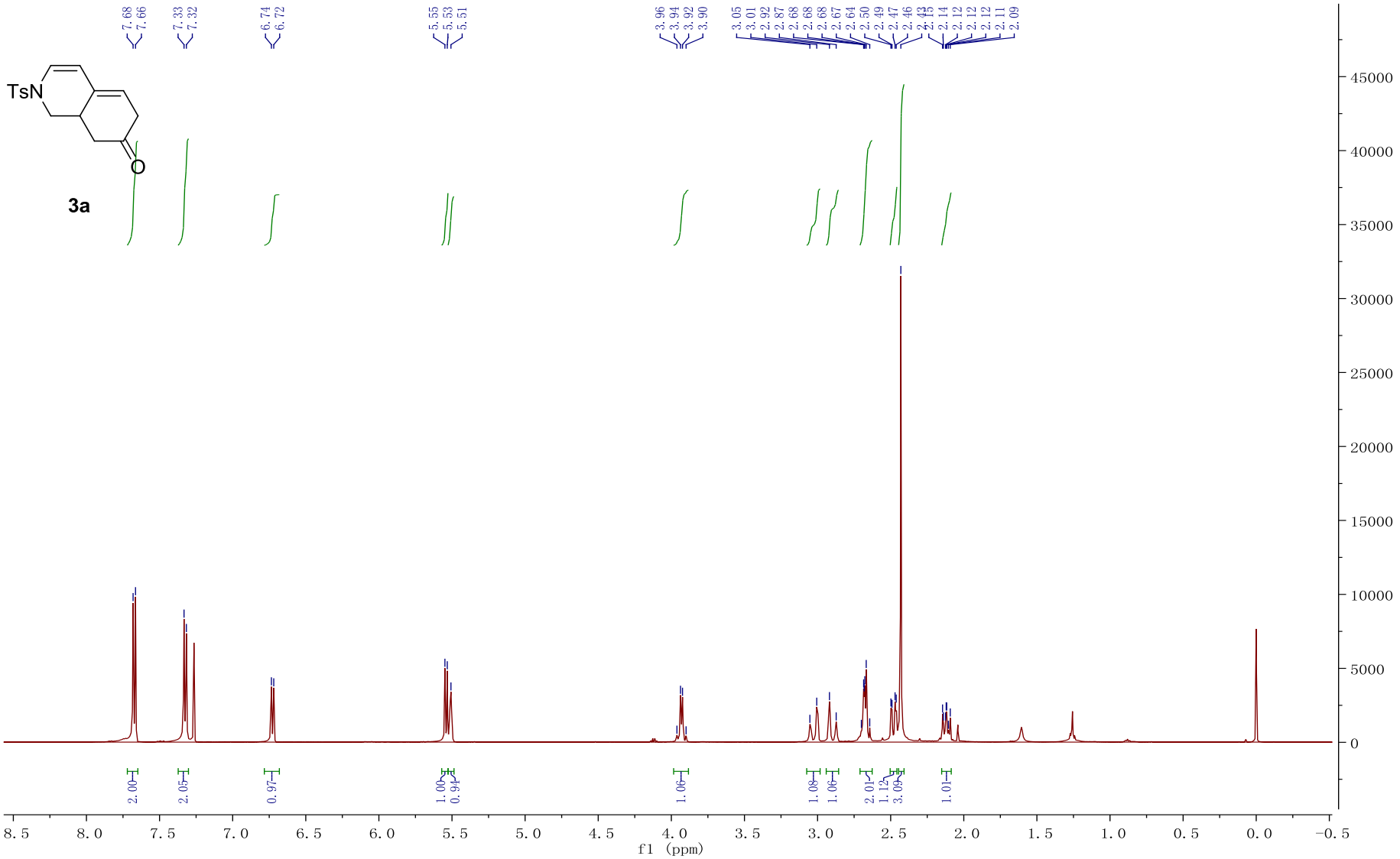
142.12
137.99
134.86
129.78
127.10
117.90
113.61
50.78
44.71
35.85
30.76
23.64
22.36
21.66
21.54
18.67
TsN
Me
2n
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


TsN
Me
2o
7.65
7.63
7.36
7.34
6.31
6.30
6.29
6.29
6.28
5.76
5.73
5.71
5.69
5.24
5.22
5.15
5.15
5.12
5.12
5.07
5.07
5.03
5.03
3.85
3.82
2.93
2.90
2.42
1.08
0.91
0.90
0.79
0.77
2.00
2.02
0.97
1.00
0.96
1.04
1.04
1.01
1.02
3.02
3.07
1.01
1.04
f1 (ppm)


144.45
137.28
135.19
130.20
127.37
121.11
118.03
115.59
44.53
36.94
24.91
21.67
20.47
19.19
TsN
Me
2o
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.66
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7.32
6.74
6.72
5.55
5.53
5.51
3.96
3.94
3.92
3.90
3.05
3.01
2.92
2.87
2.68
2.68
2.68
2.67
2.64
2.50
2.49
2.47
2.46
2.43
2.15
2.14
2.12
2.12
2.12
2.11
2.09
TsN
O
3a
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
2.00
2.05
0.97
1.00
0.94
1.06
1.08
1.06
2.01
1.12
3.09
1.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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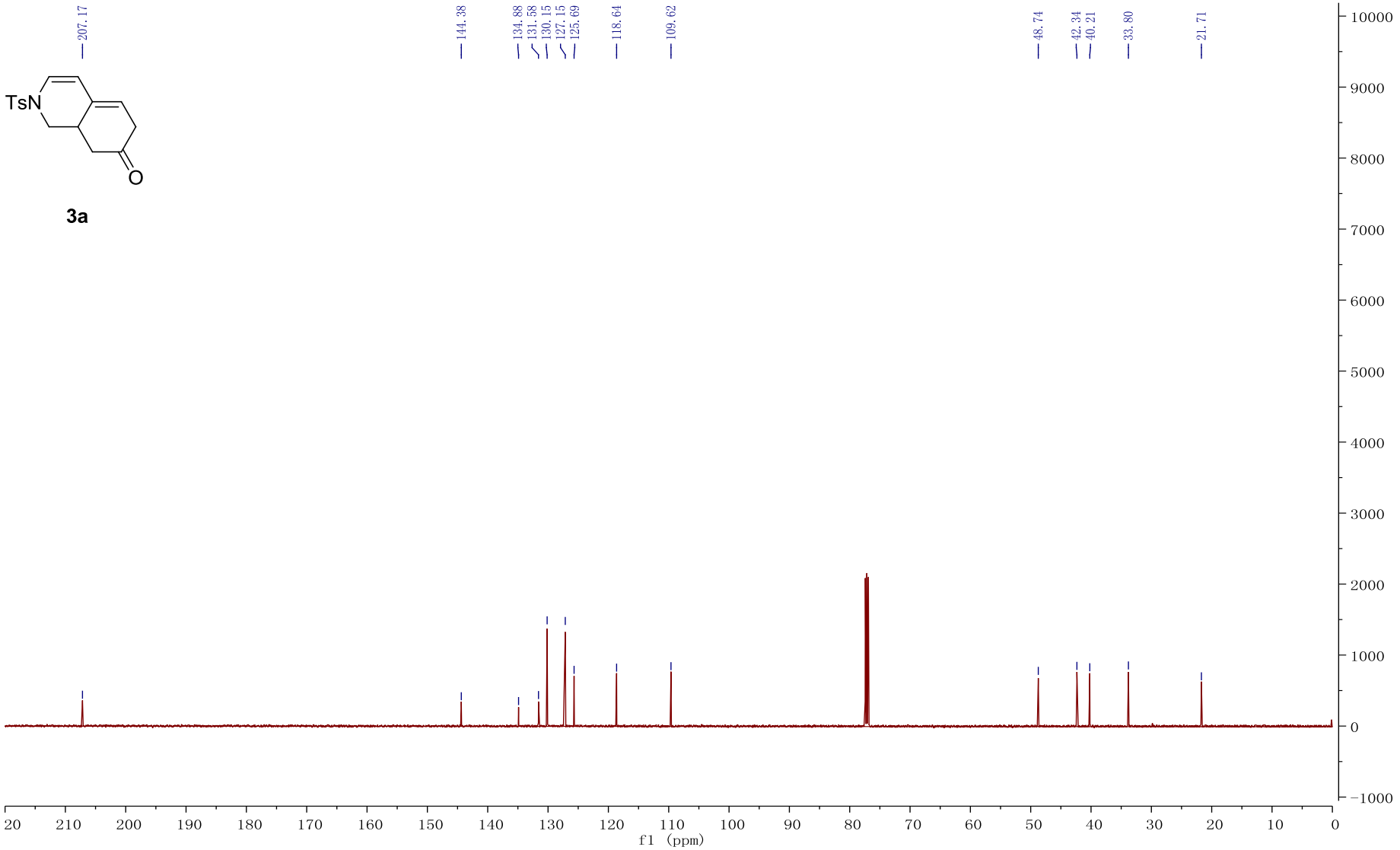
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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134.88
131.58
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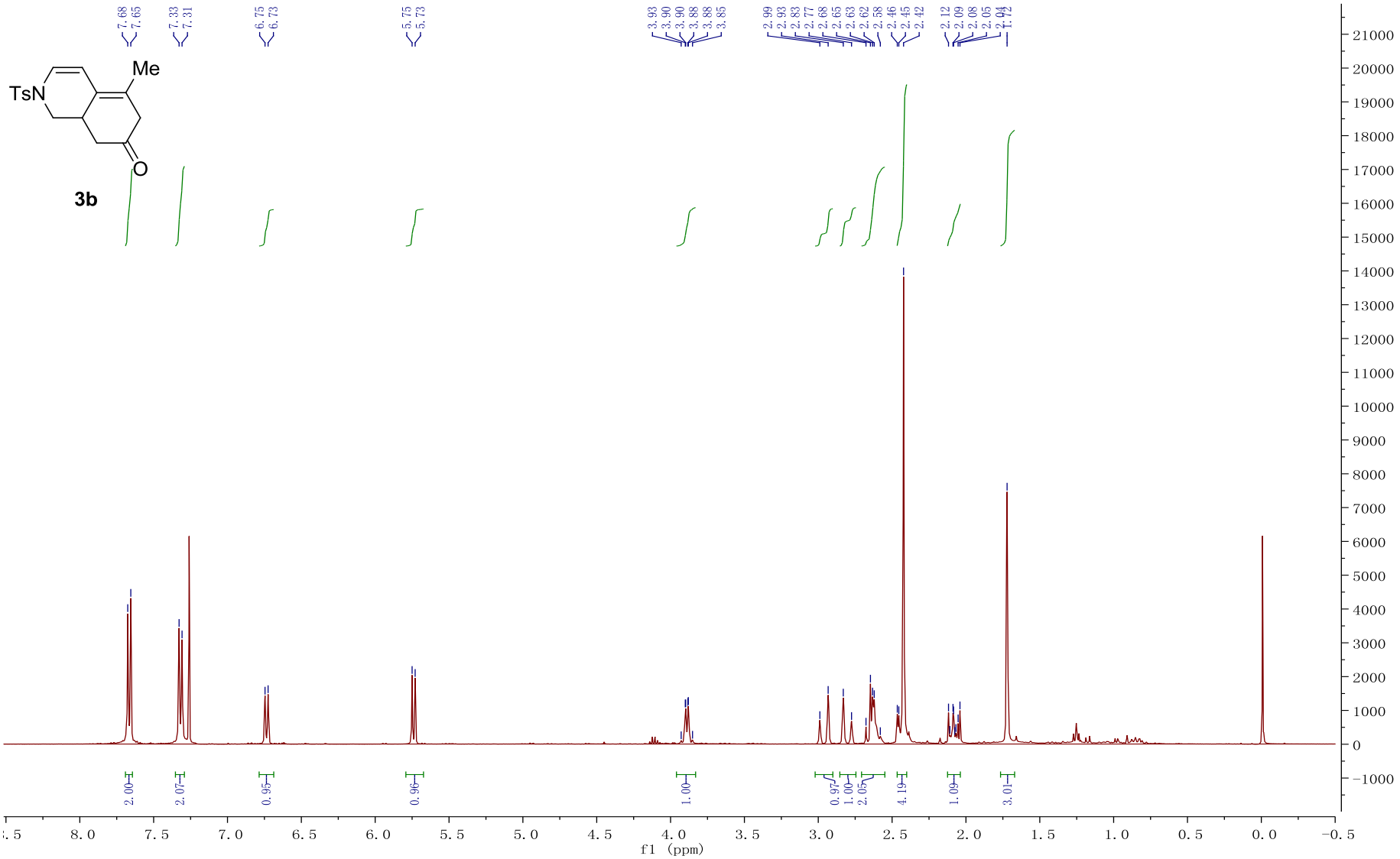
127.15
125.69
118.64
109.62
48.74
42.34
40.21
33.80
21.71
TsN
O
3a
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.65
7.33
7.31
6.75
6.73
5.75
5.73
3.93
3.90
3.90
3.88
3.88
3.85
2.99
2.93
2.83
2.77
2.68
2.65
2.63
2.62
2.58
2.46
2.45
2.42
2.12
2.09
2.08
2.05
2.04
1.74
Me
TsN
O
3b
2.00
2.07
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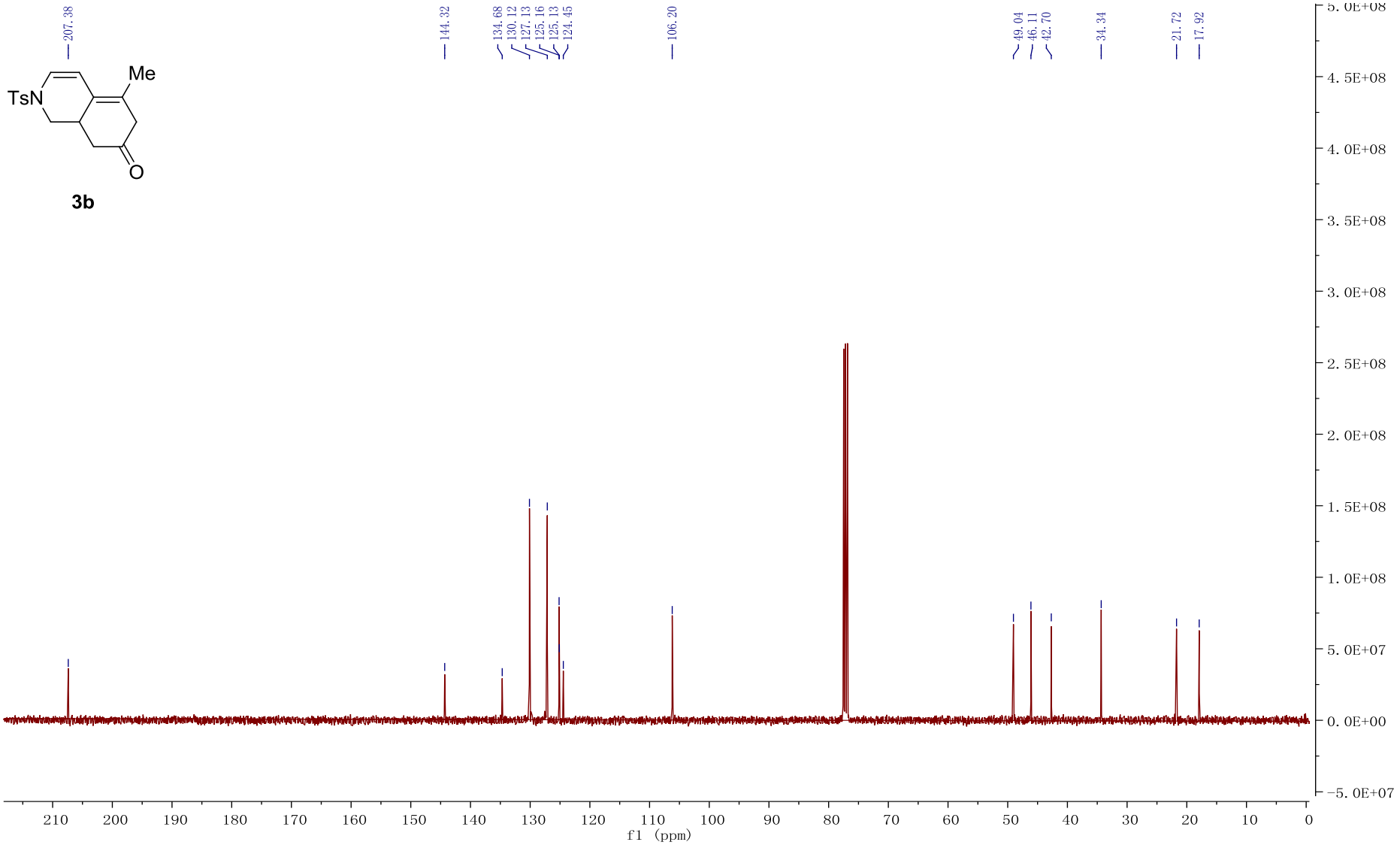
0.96
1.00
0.97
1.00
2.05
4.19
1.09
3.01
f1 (ppm)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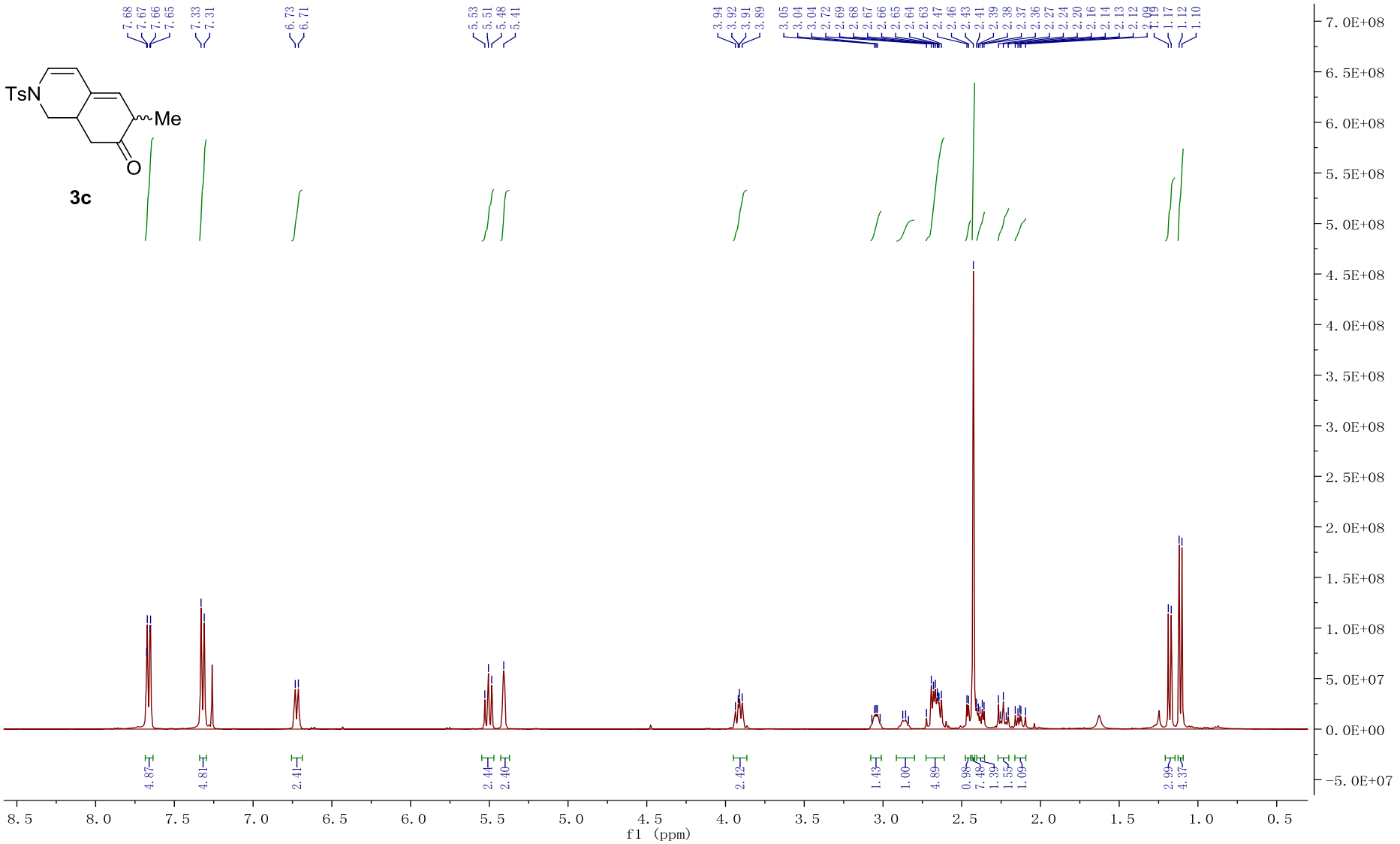
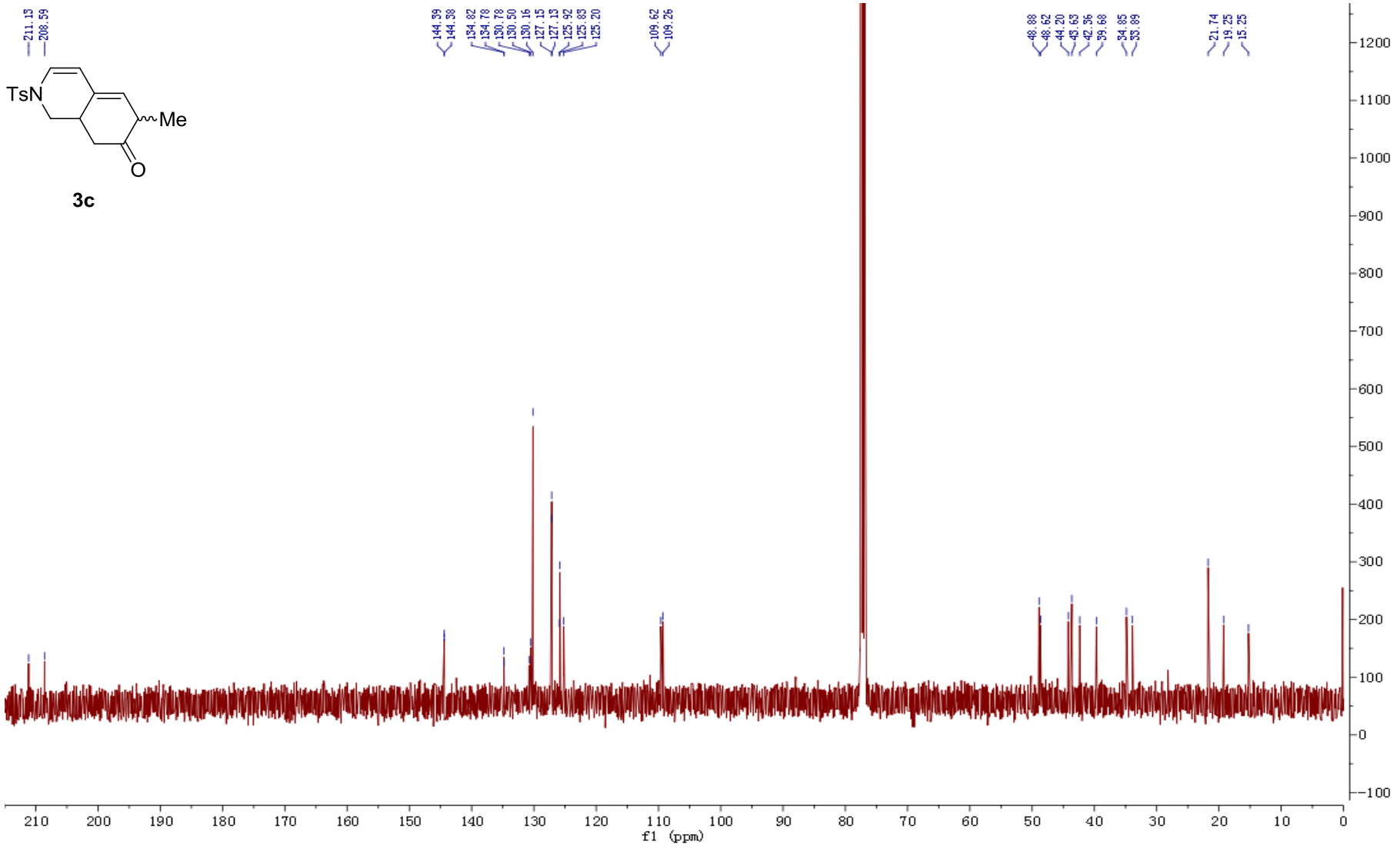
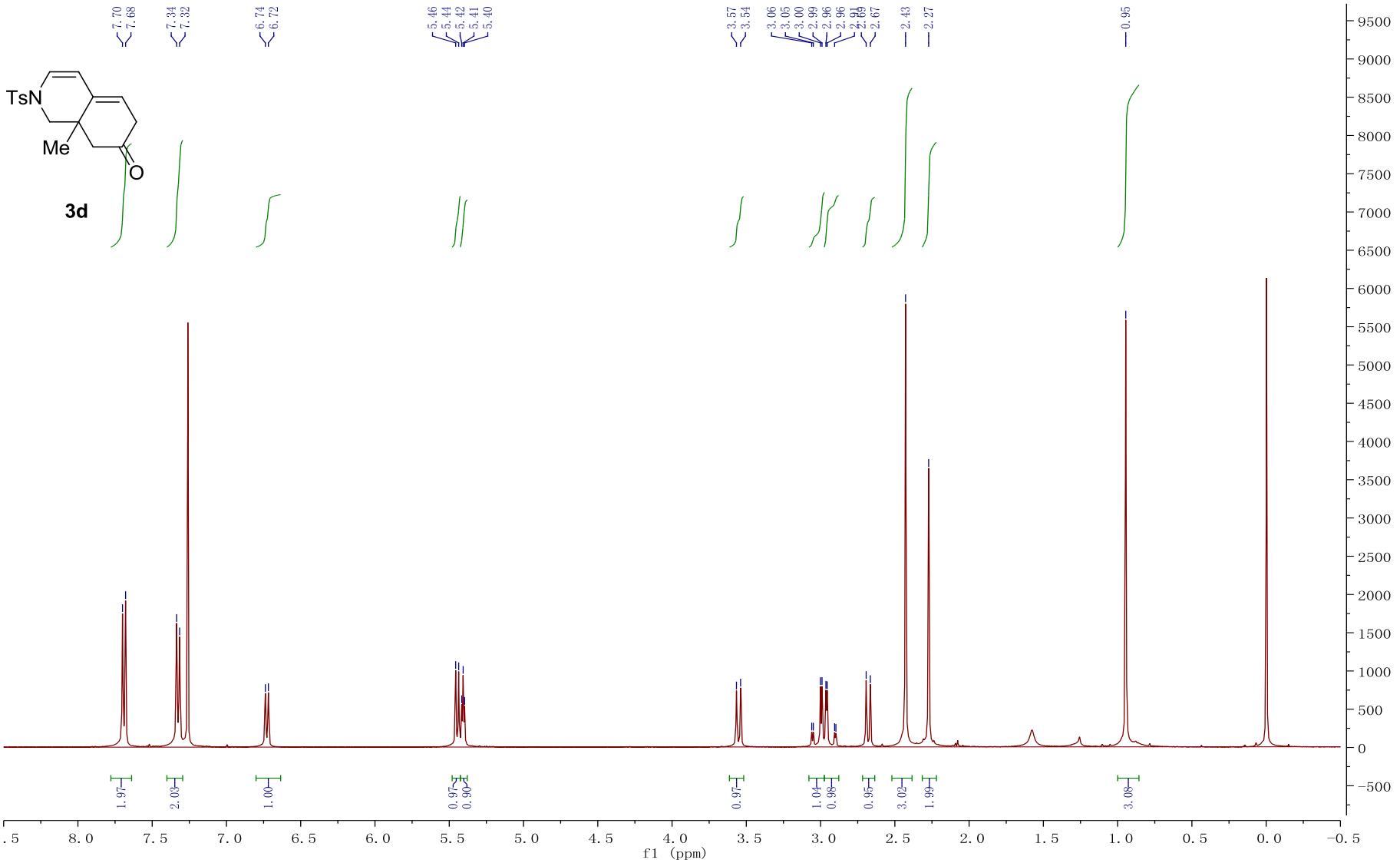
134.68
130.12
127.13
125.16
125.13
124.45
106.20
49.04
46.11
42.70
34.34
21.72
17.92
Me
TsN
O
3b
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


TsN
Me
O
3c
f1 (ppm)


211.13
208.59
144.59
144.38
134.82
134.78
130.78
130.50
130.16
127.15
127.13
125.92
125.83
125.20
109.62
109.26
48.88
48.62
44.20
43.63
42.36
39.68
34.85
33.89
21.74
19.25
15.25
TsN
Me
O
3c
f1 (ppm)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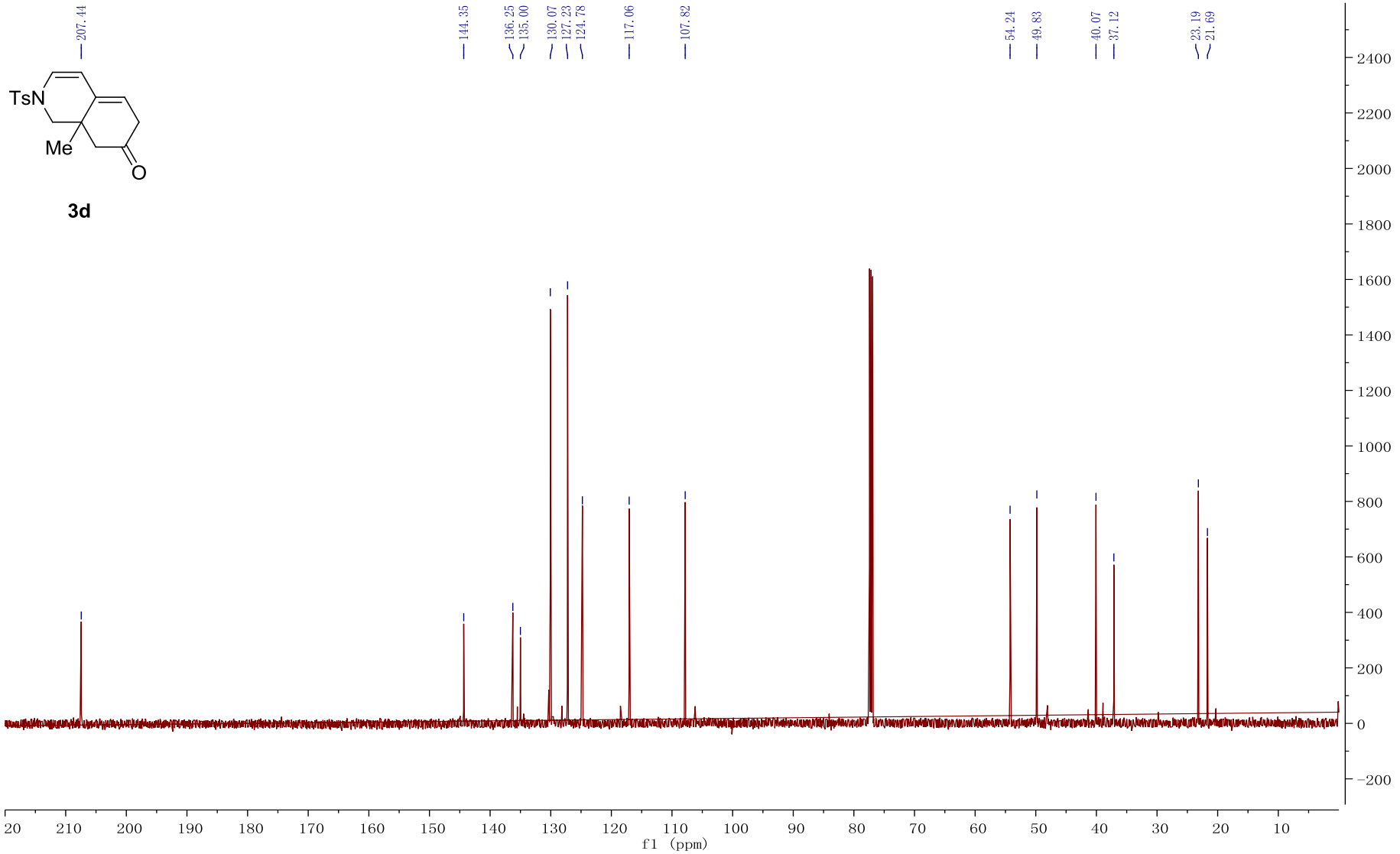
7.68
7.34
7.32
6.74
6.72
5.46
5.44
5.42
5.41
5.40
3.57
3.54
3.06
3.05
3.00
2.99
2.96
2.96
2.91
2.69
2.67
2.43
2.27
0.95
TsN
Me
O
3d
1.97
2.03
1.00
0.97
0.90
0.97
1.04
0.98
0.95
3.02
1.99
3.08
f1 (ppm)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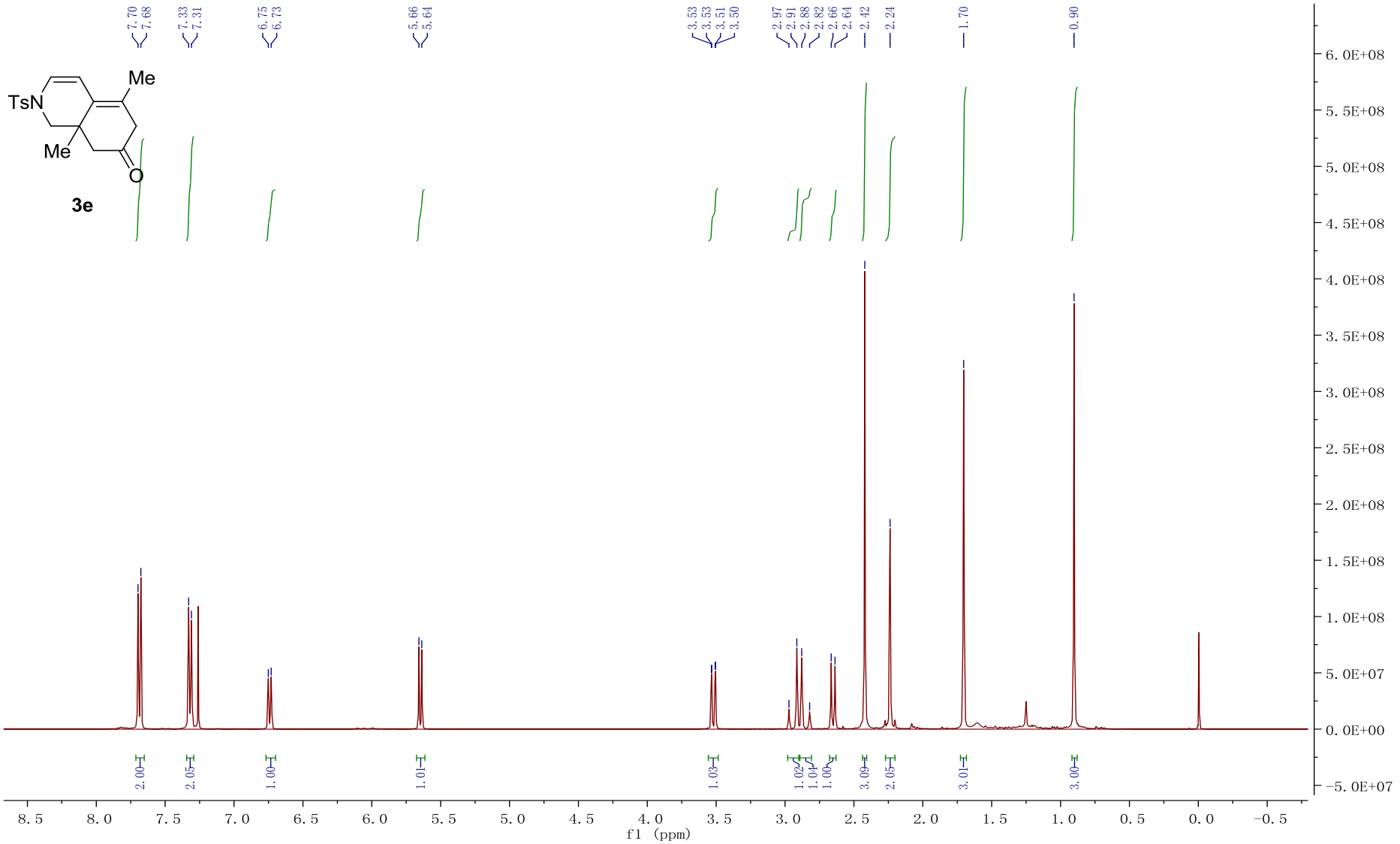
127.23
124.78
117.06
107.82
54.24
49.83
40.07
37.12
23.19
21.69
TsN
Me
O
3d
f1 (ppm)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6.73
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5.64
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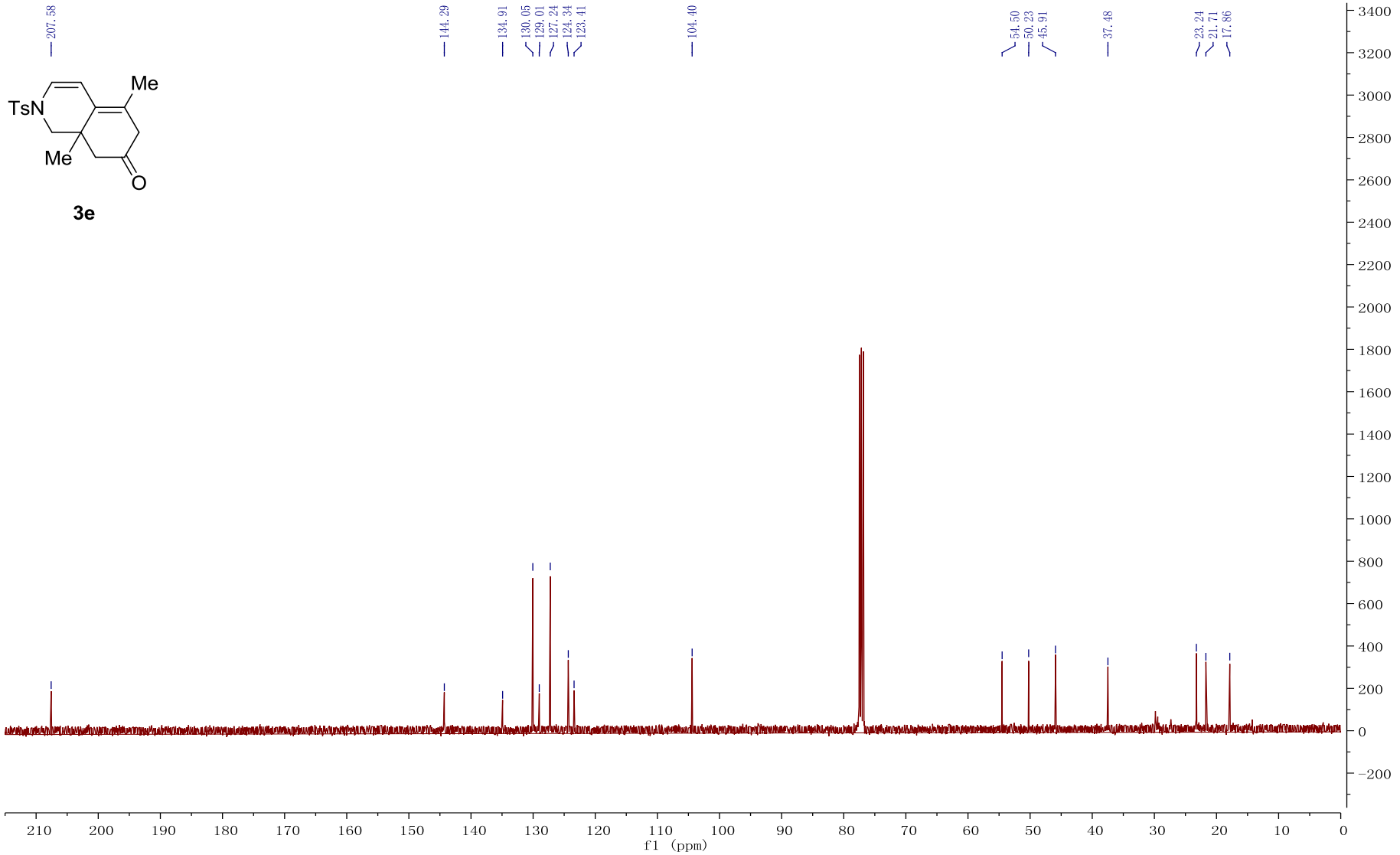
3.53
3.51
3.50
2.97
2.91
2.88
2.82
2.66
2.64
2.42
2.24
1.70
0.90
Me
TsN
Me
O
3e
2.00
2.05
1.00
1.01
1.03
1.02
1.04
1.00
3.09
2.05
3.01
3.00
f1 (ppm)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130.05
129.01
127.24
124.34
123.41
104.40
54.50
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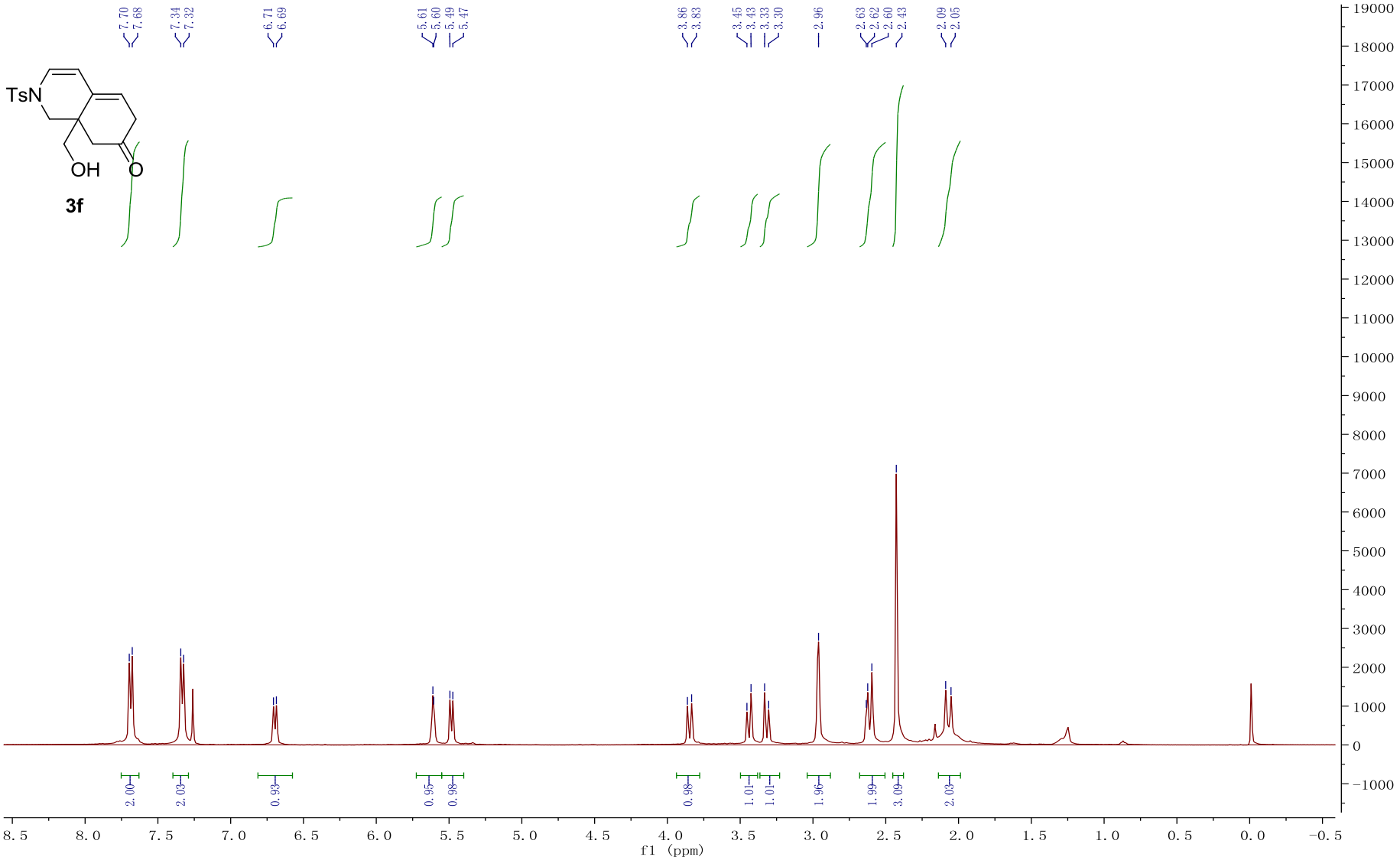
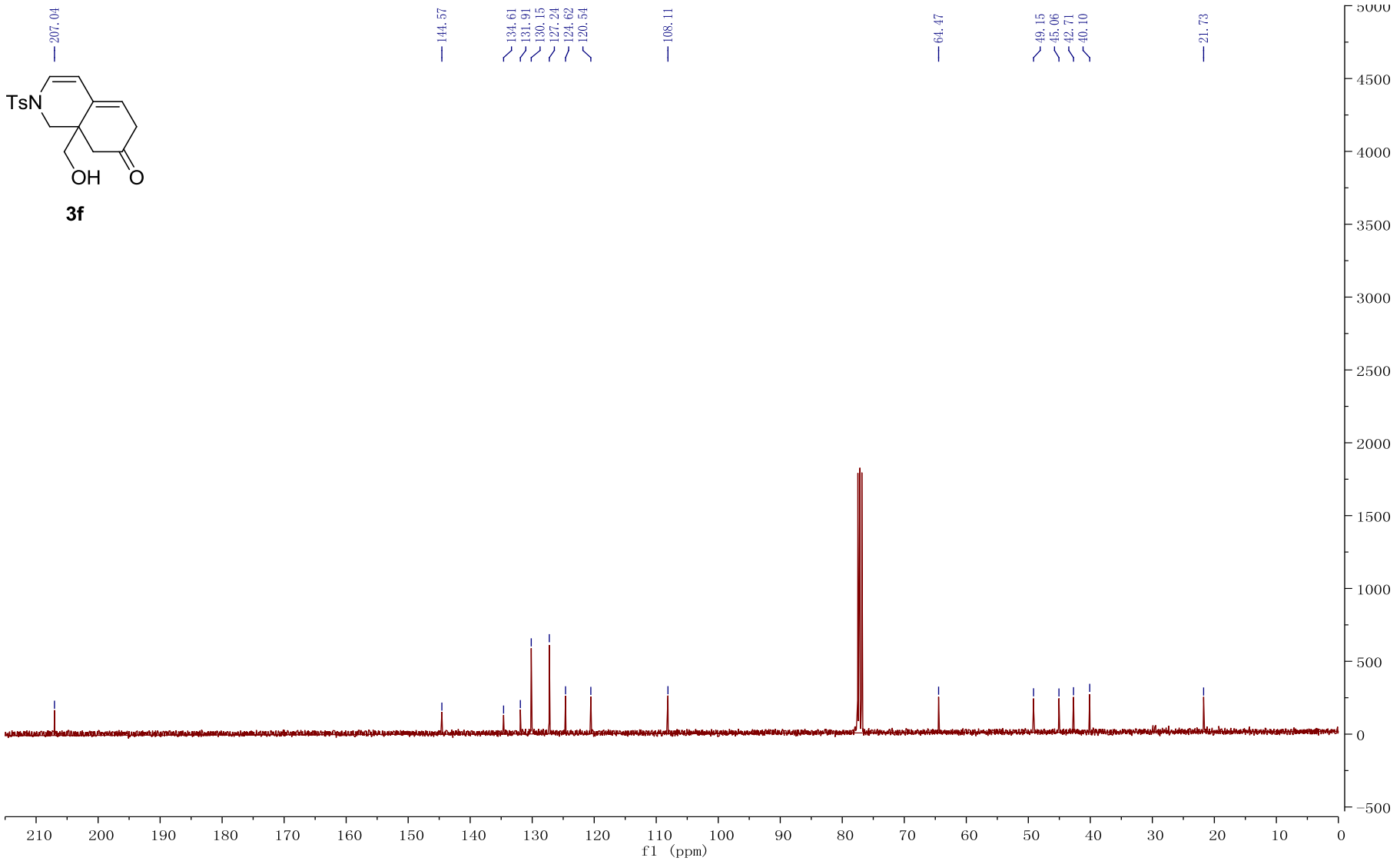
45.91
37.48
23.24
21.71
17.86
TsN
Me
Me
O
3e
f1 (ppm)


7.70
7.68
7.34
7.32
6.71
6.69
5.61
5.60
5.49
5.47
3.86
3.83
3.45
3.43
3.33
3.30
2.96
2.63
2.62
2.60
2.43
2.09
2.05
TsN
OH
O
3f
2.00
2.03
0.93
0.95
0.98
0.98
1.01
1.01
1.96
1.99
3.09
2.03
f1 (ppm)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131.91
130.15
127.24
124.62
120.54
108.11
64.47
49.15
45.06
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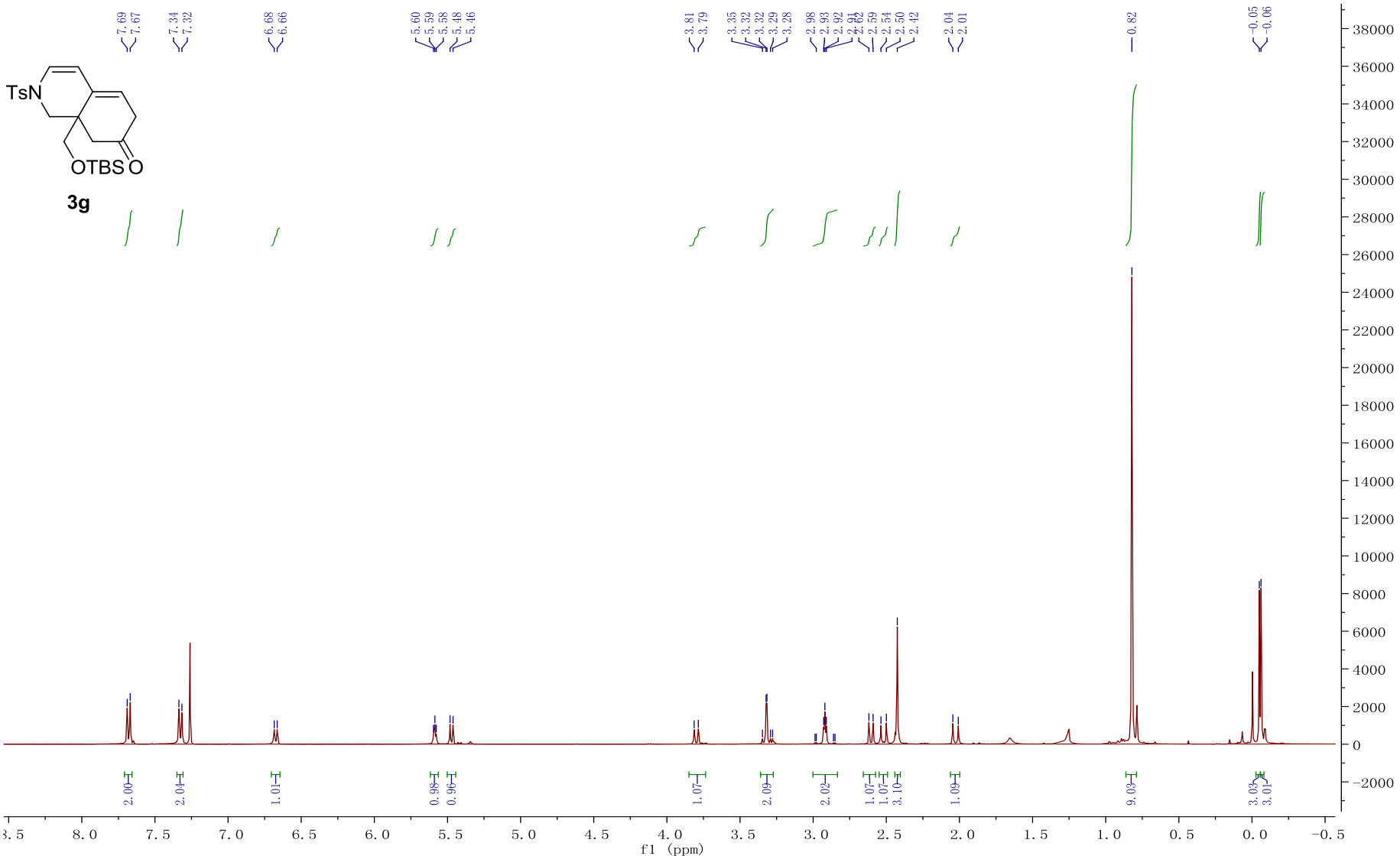
40.10
21.73
TsN
OH
O
3f
f1 (ppm)


TsN
OTBS
O
3g
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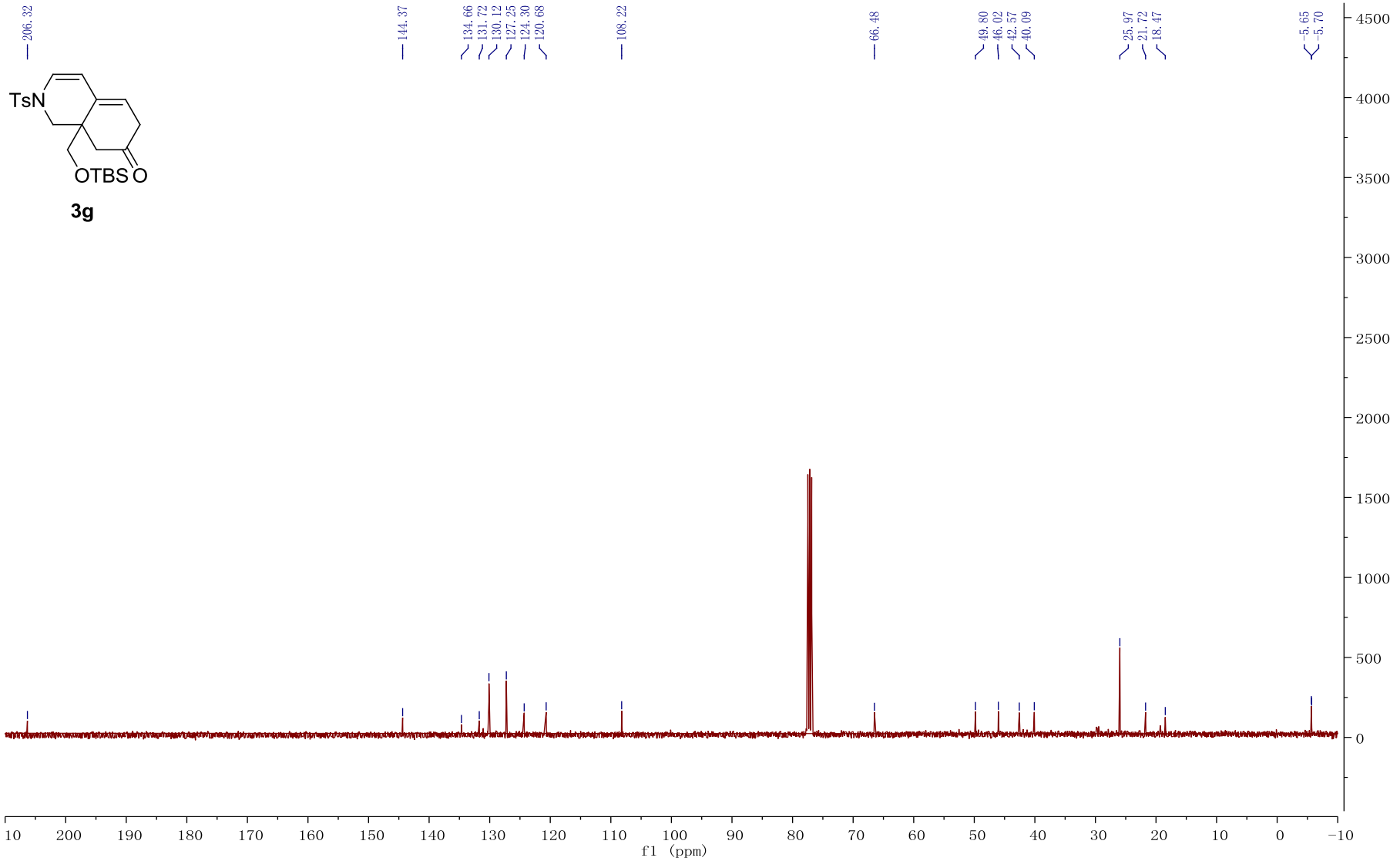
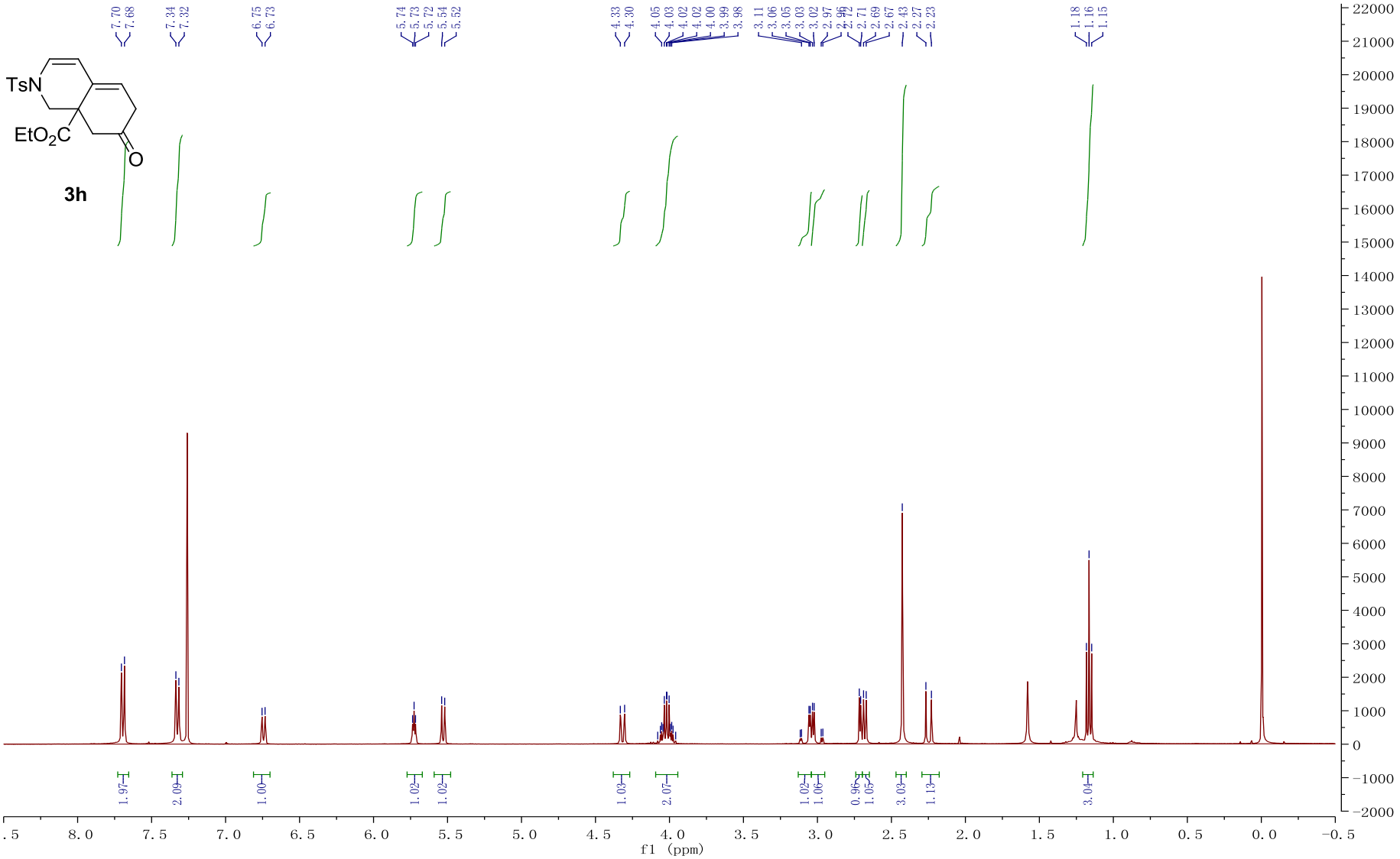
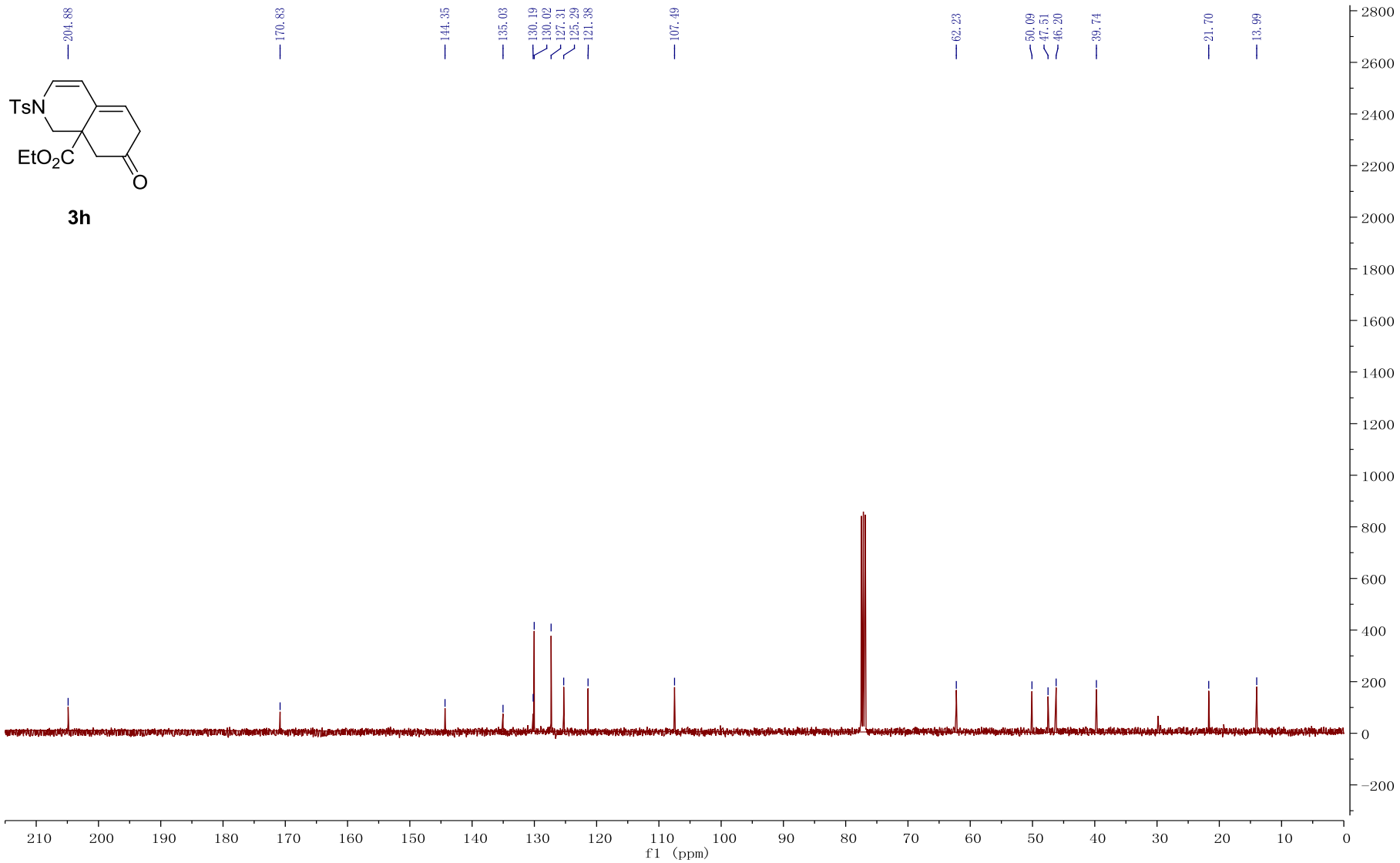
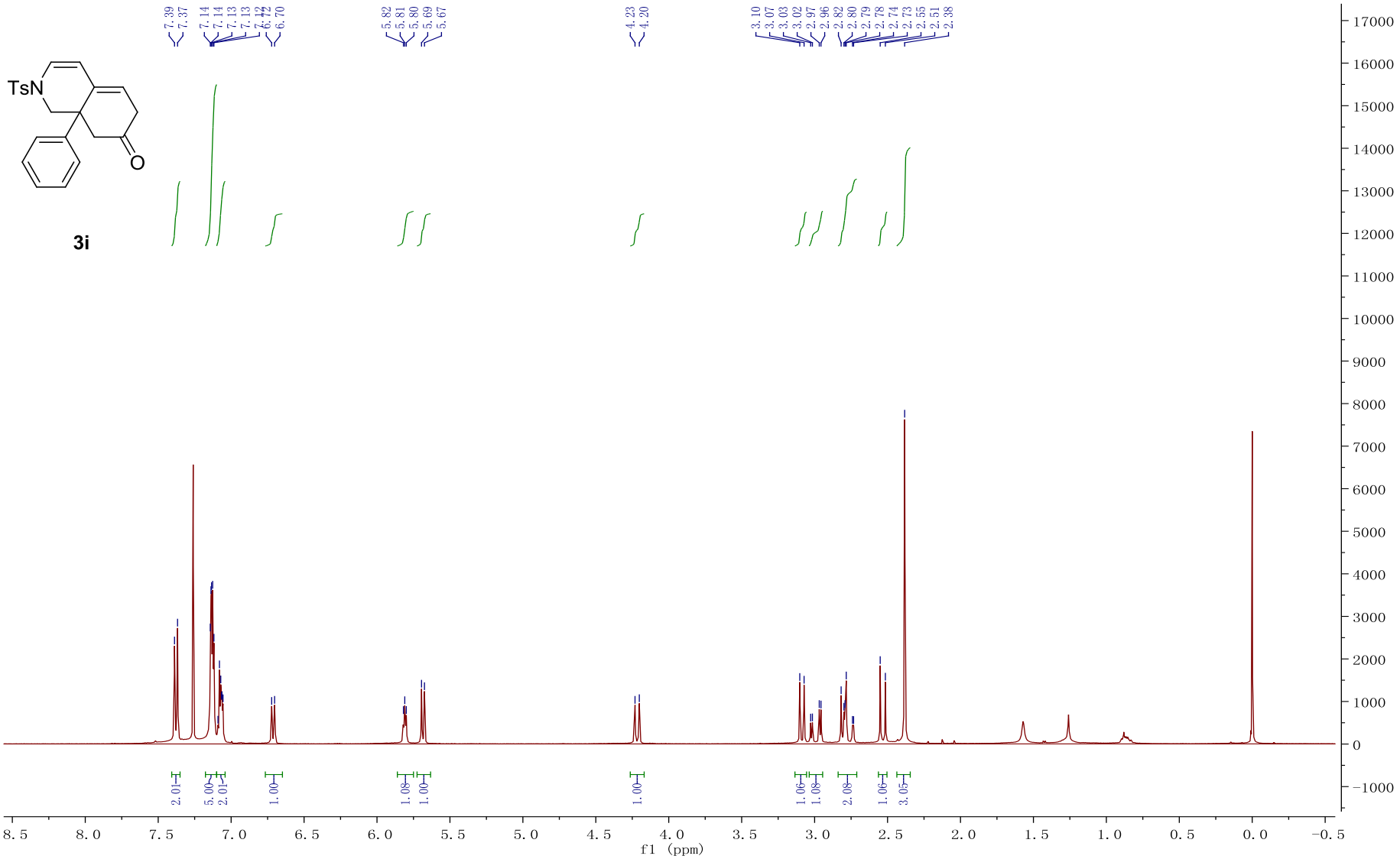
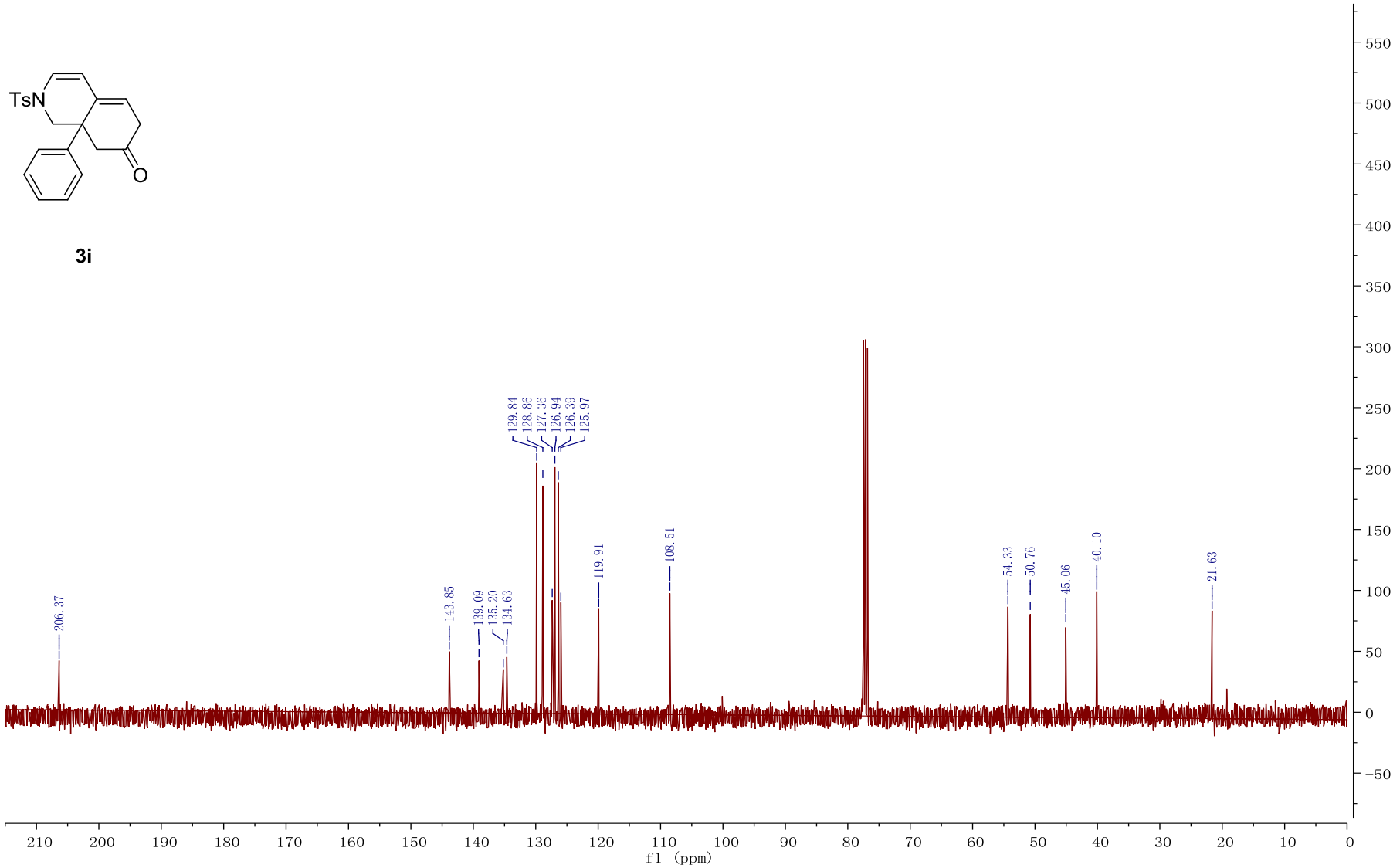
7.67
7.34
7.32
6.68
6.66
5.60
5.59
5.58
5.48
5.46
3.81
3.79
3.35
3.32
3.32
3.29
3.28
2.98
2.93
2.92
2.59
2.54
2.50
2.42
2.04
2.01
0.82
-0.05
-0.06
2.00
2.04
1.01
0.98
0.96
1.07
2.09
2.02
1.07
1.07
3.10
1.09
9.03
3.03
3.01
f1 (ppm)

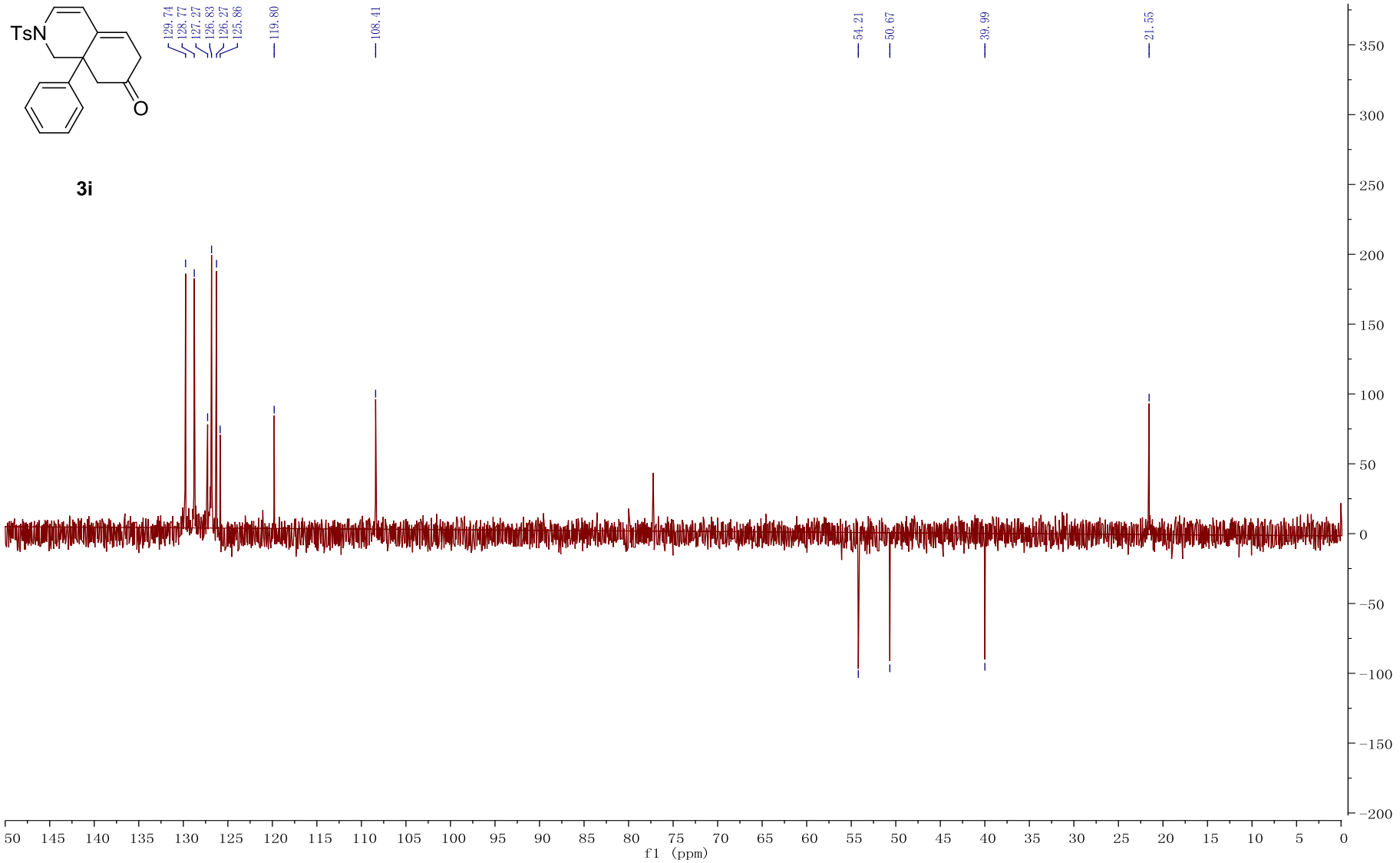

206.32
144.37
134.66
131.72
130.12
127.25
124.30
120.68
108.22
66.48
49.80
46.02
42.57
40.09
25.97
21.72
18.47
-5.65
-5.70
TsN
OTBS
O
3g
4500
4000
3500
3000
2500
2000
1500
1000
500
0
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

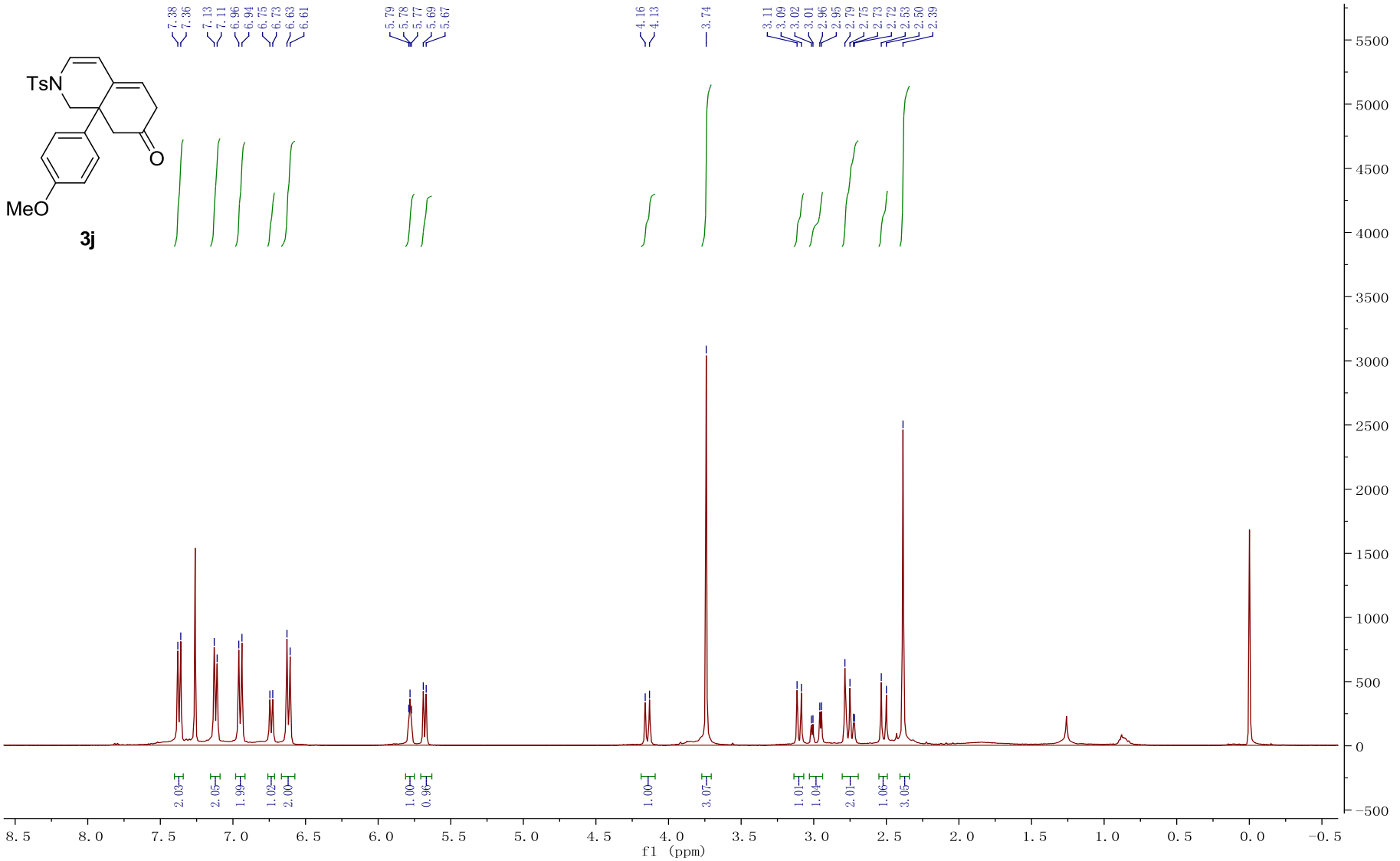

TsN
EtO2C
O
3h
7.70
7.68
7.34
7.32
6.75
6.73
5.74
5.73
5.72
5.54
5.52
4.33
4.30
4.05
4.03
4.02
4.00
3.99
3.98
3.11
3.06
3.05
3.03
3.02
2.97
2.71
2.69
2.67
2.43
2.27
2.23
1.18
1.16
1.15
1.97
2.09
1.00
1.02
1.02
1.03
2.07
1.02
1.06
0.96
1.05
3.03
1.13
3.04
f1 (ppm)

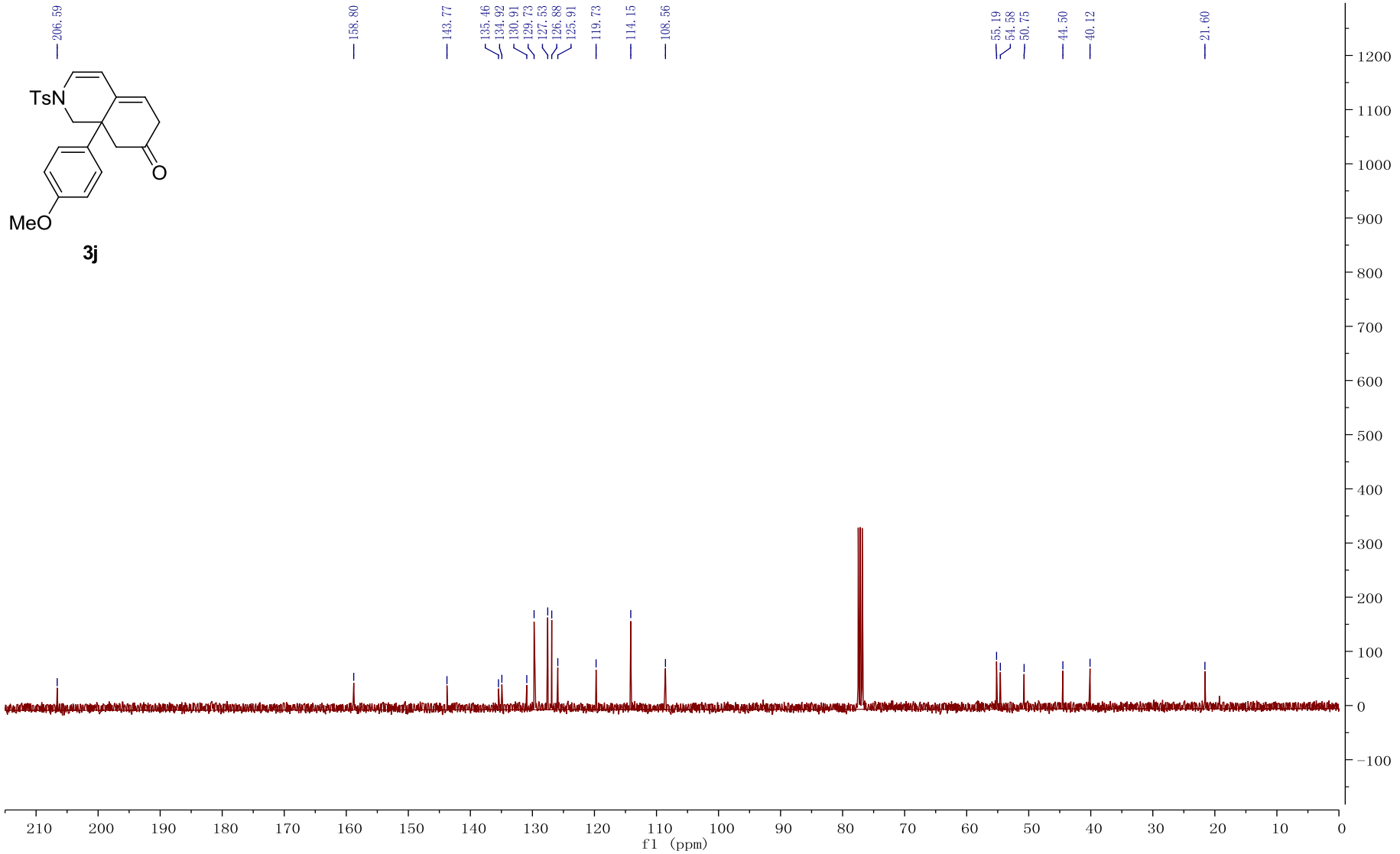

204.88
170.83
144.35
135.03
130.19
130.02
127.31
125.29
121.38
107.49
62.23
50.09
47.51
46.20
39.74
21.70
13.99
TsN
EtO2C
O
3h
f1 (ppm)

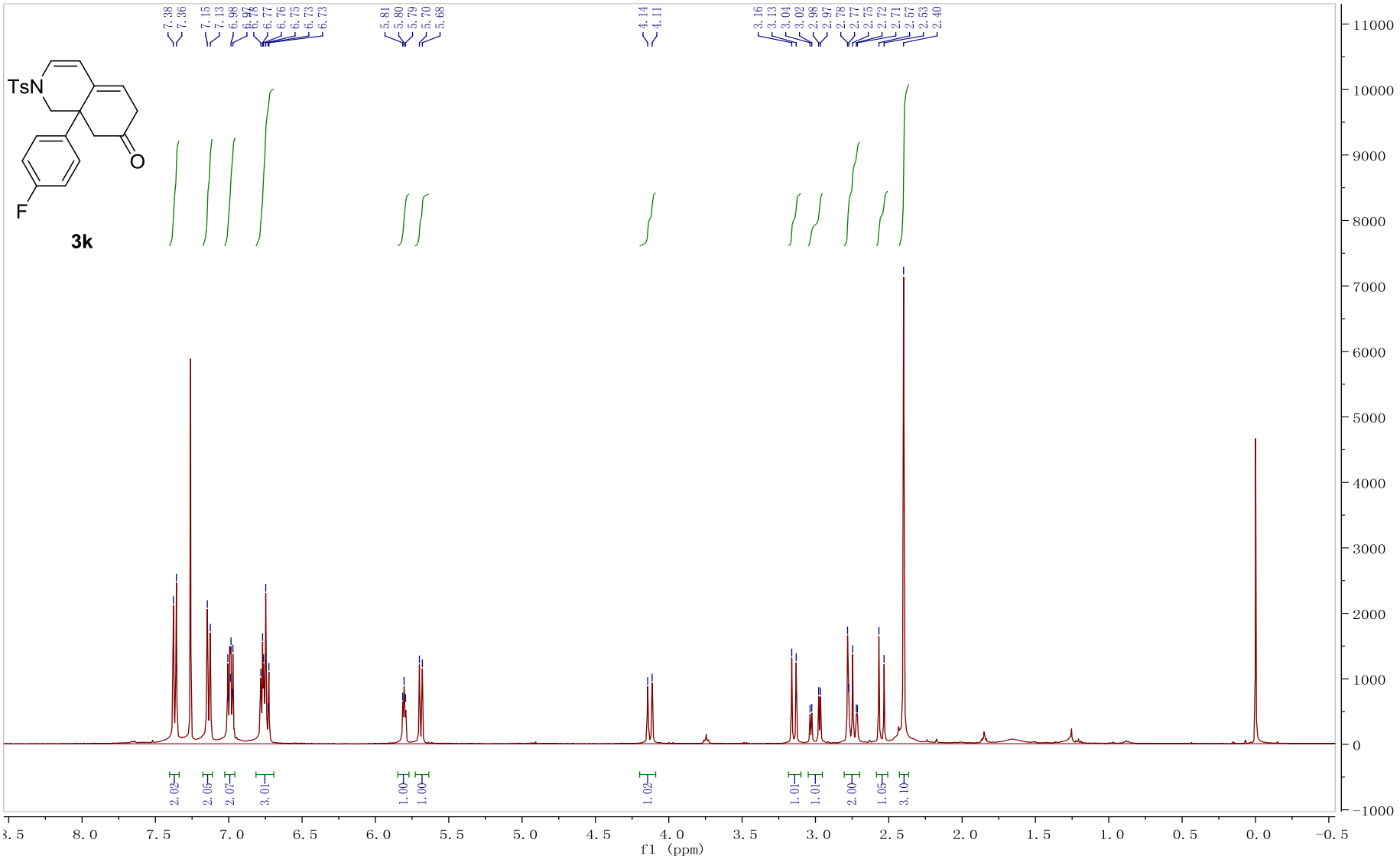

TsN
O
3i
7.39
7.37
7.14
7.14
7.13
7.13
6.72
6.70
5.82
5.81
5.80
5.69
5.67
4.23
4.20
3.10
3.07
3.03
3.02
2.97
2.96
2.82
2.80
2.79
2.78
2.74
2.73
2.55
2.51
2.38
2.01
5.00
2.01
1.00
1.08
1.00
1.00
1.06
1.08
2.08
1.06
3.05
f1 (ppm)

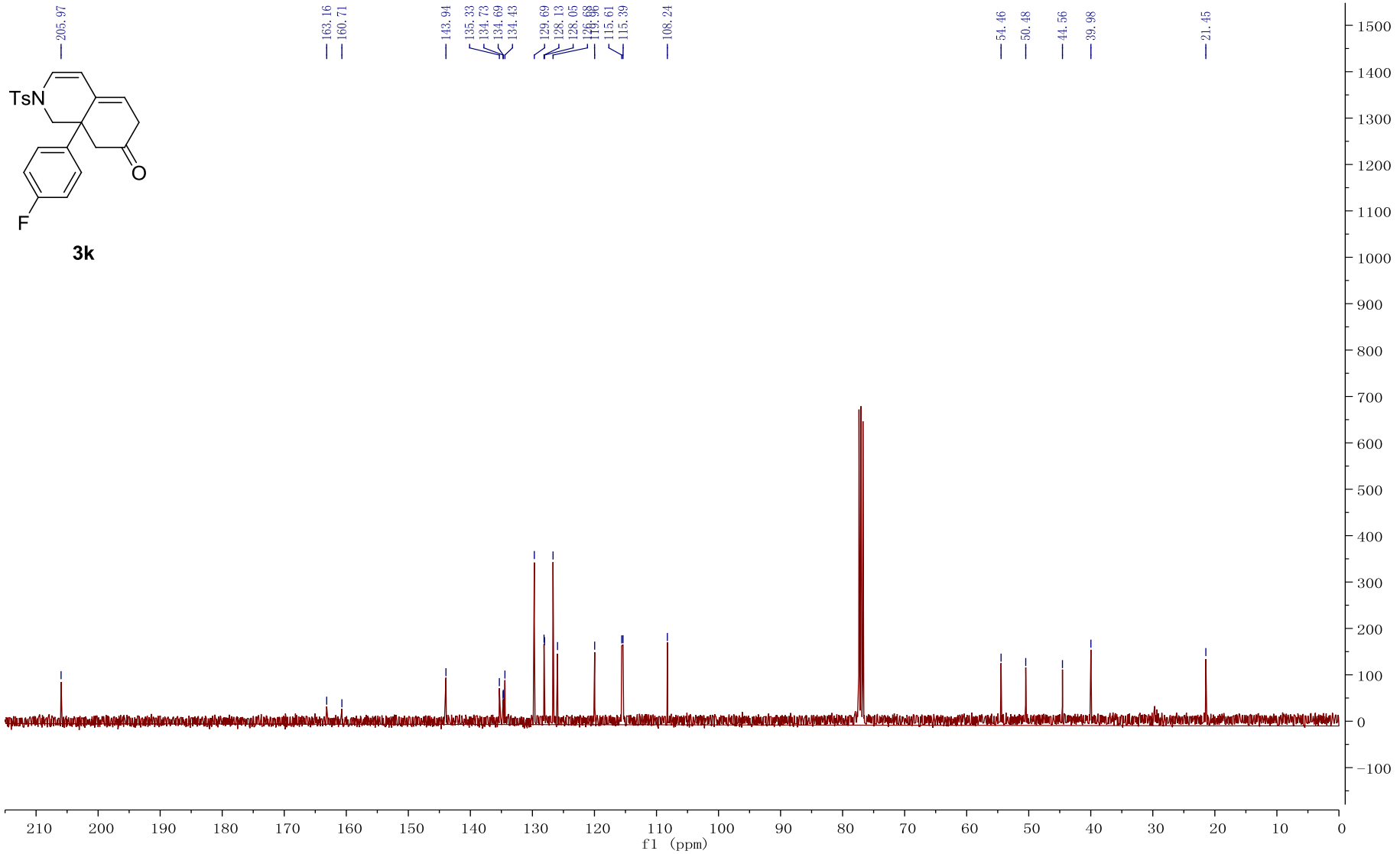

TsN
O
3i
206.37
143.85
139.09
135.20
134.63
129.84
128.86
127.36
126.94
126.39
125.97
119.91
108.51
54.33
50.76
45.06
40.10
21.63
f1 (ppm)

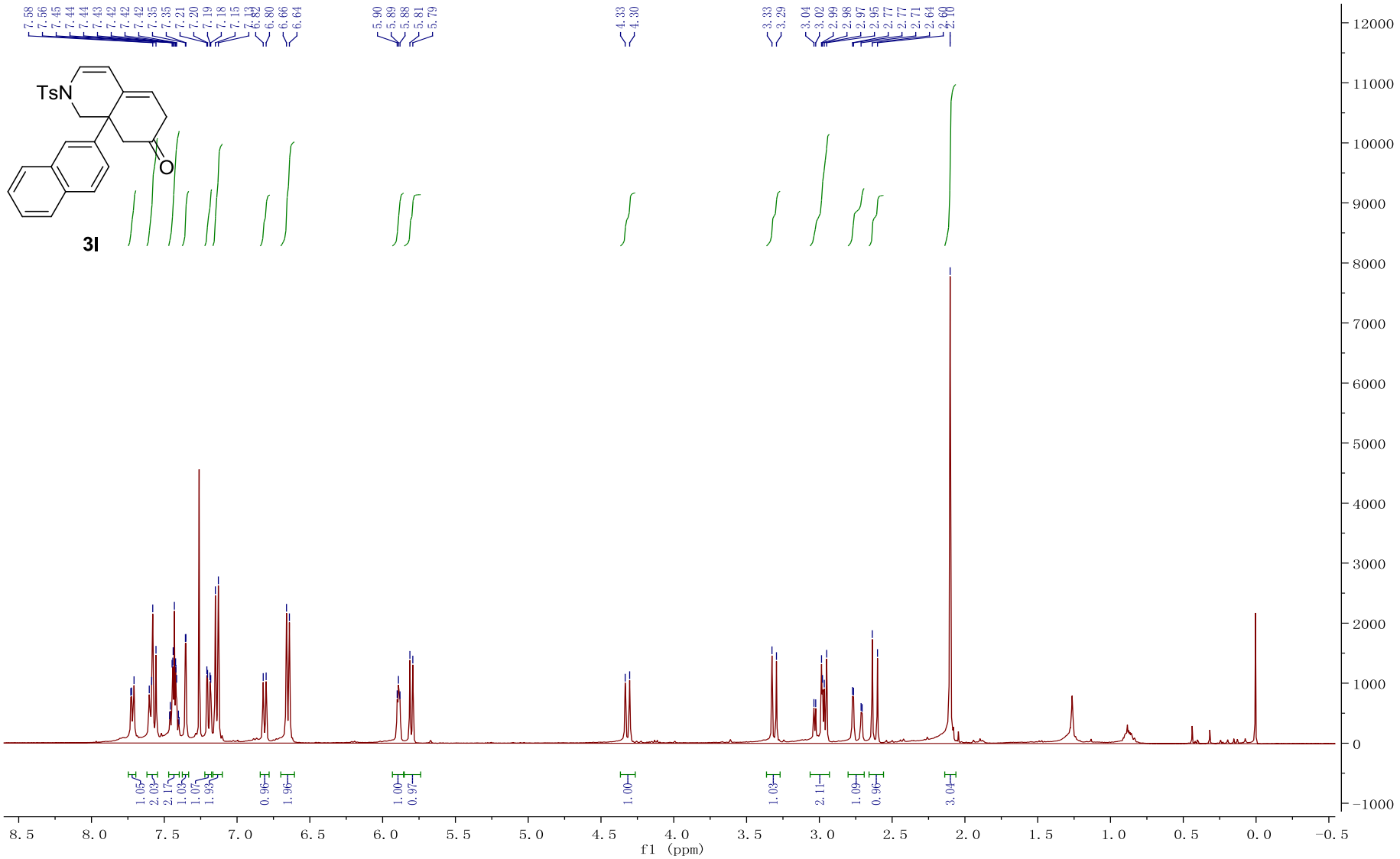

TsN
O
3i
129.74
128.77
127.27
126.83
126.27
125.86
119.80
108.41
54.21
50.67
39.99
21.55
f1 (ppm)

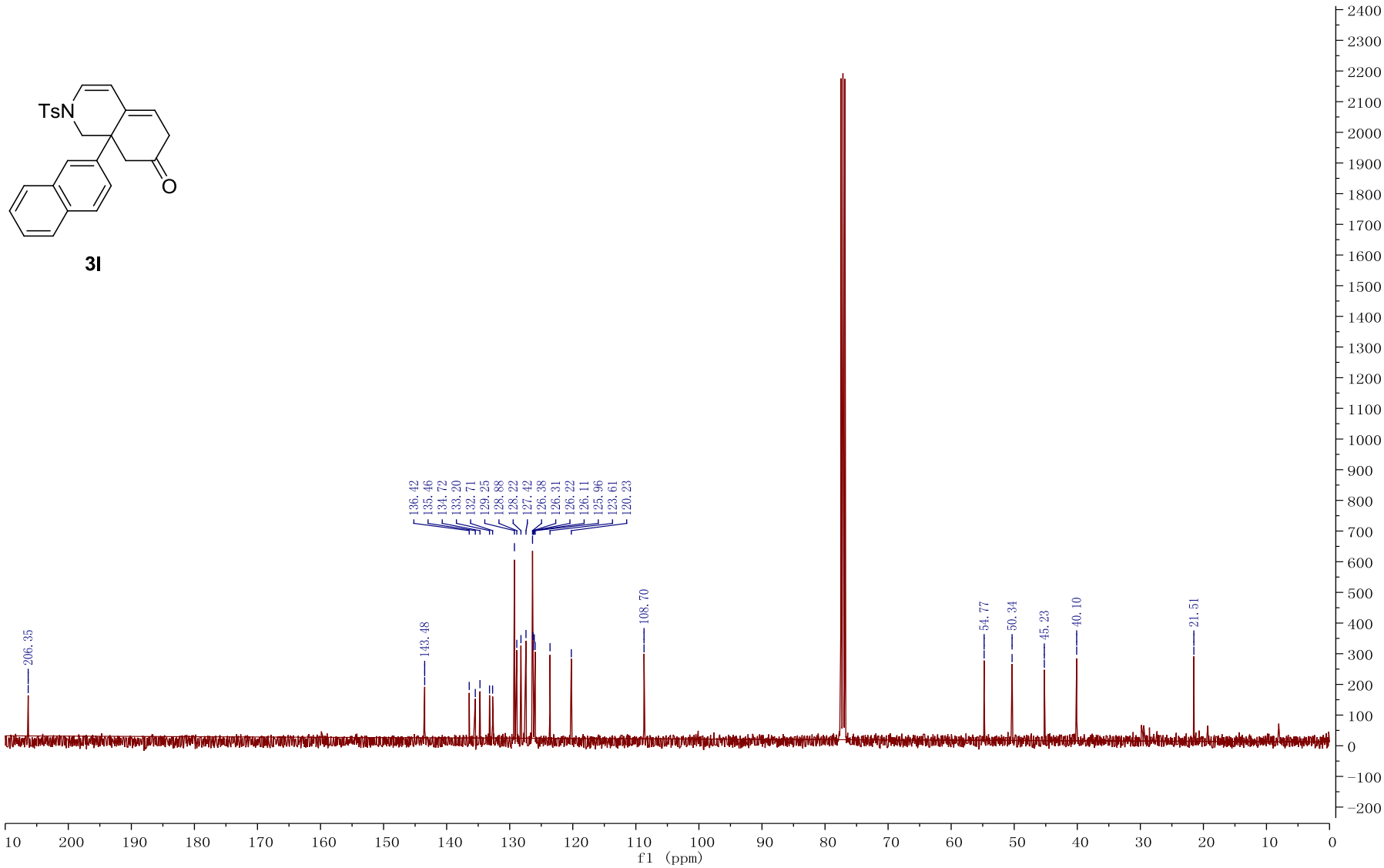

TsN
O
MeO
3j
7.38
7.36
7.13
7.11
6.96
6.94
6.75
6.73
6.63
6.61
5.79
5.78
5.77
5.69
5.67
4.16
4.13
3.74
3.11
3.09
3.02
3.01
2.96
2.95
2.79
2.75
2.73
2.72
2.53
2.50
2.39
2.03
2.05
1.99
1.02
2.00
1.00
0.96
1.00
3.07
1.01
1.04
2.01
1.06
3.05
f1 (ppm)

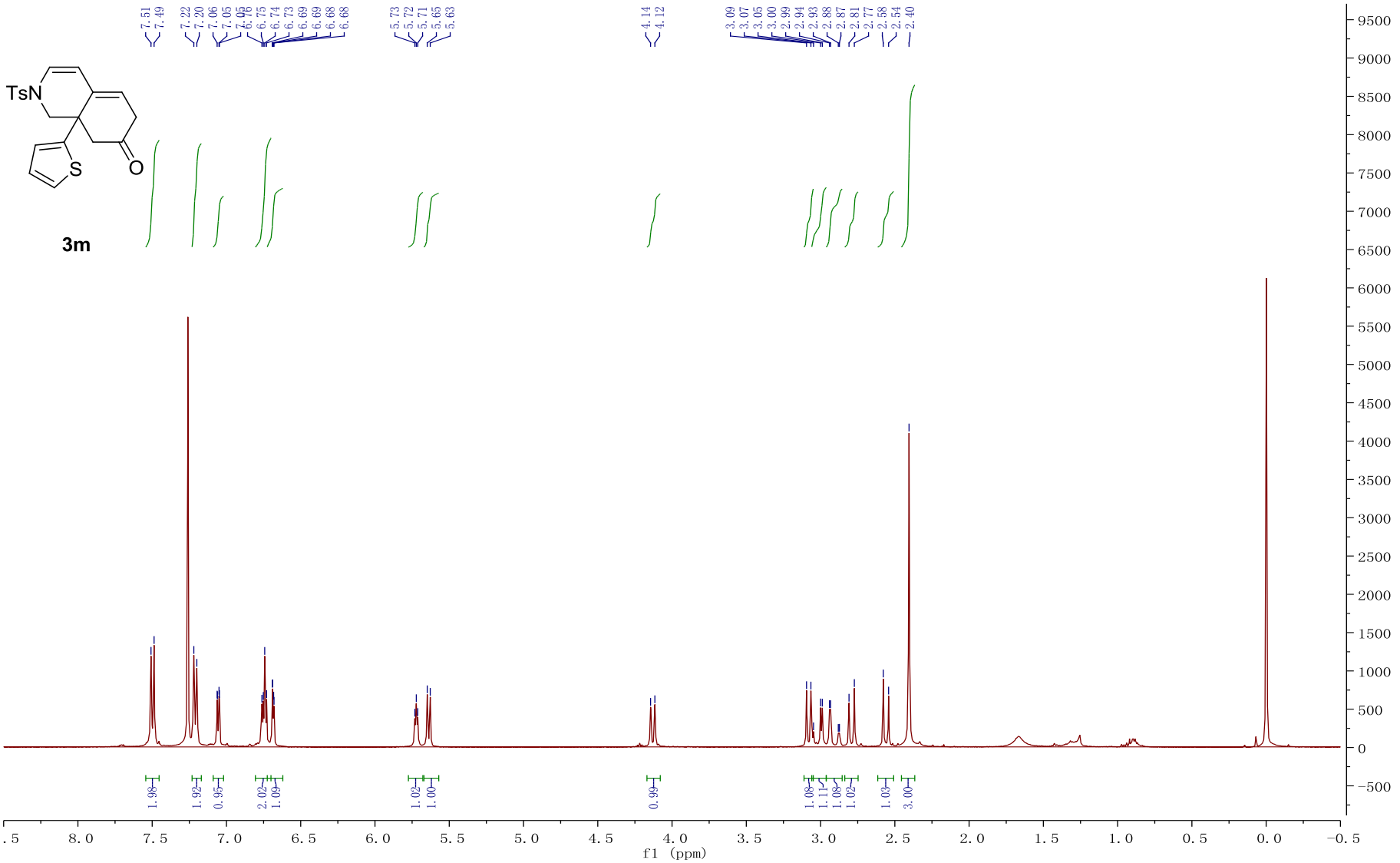

206.59
158.80
143.77
135.46
134.92
130.91
129.73
127.53
126.88
125.91
119.73
114.15
108.56
55.19
54.58
50.75
44.50
40.12
21.60
TsN
O
MeO
3j
f1 (ppm)

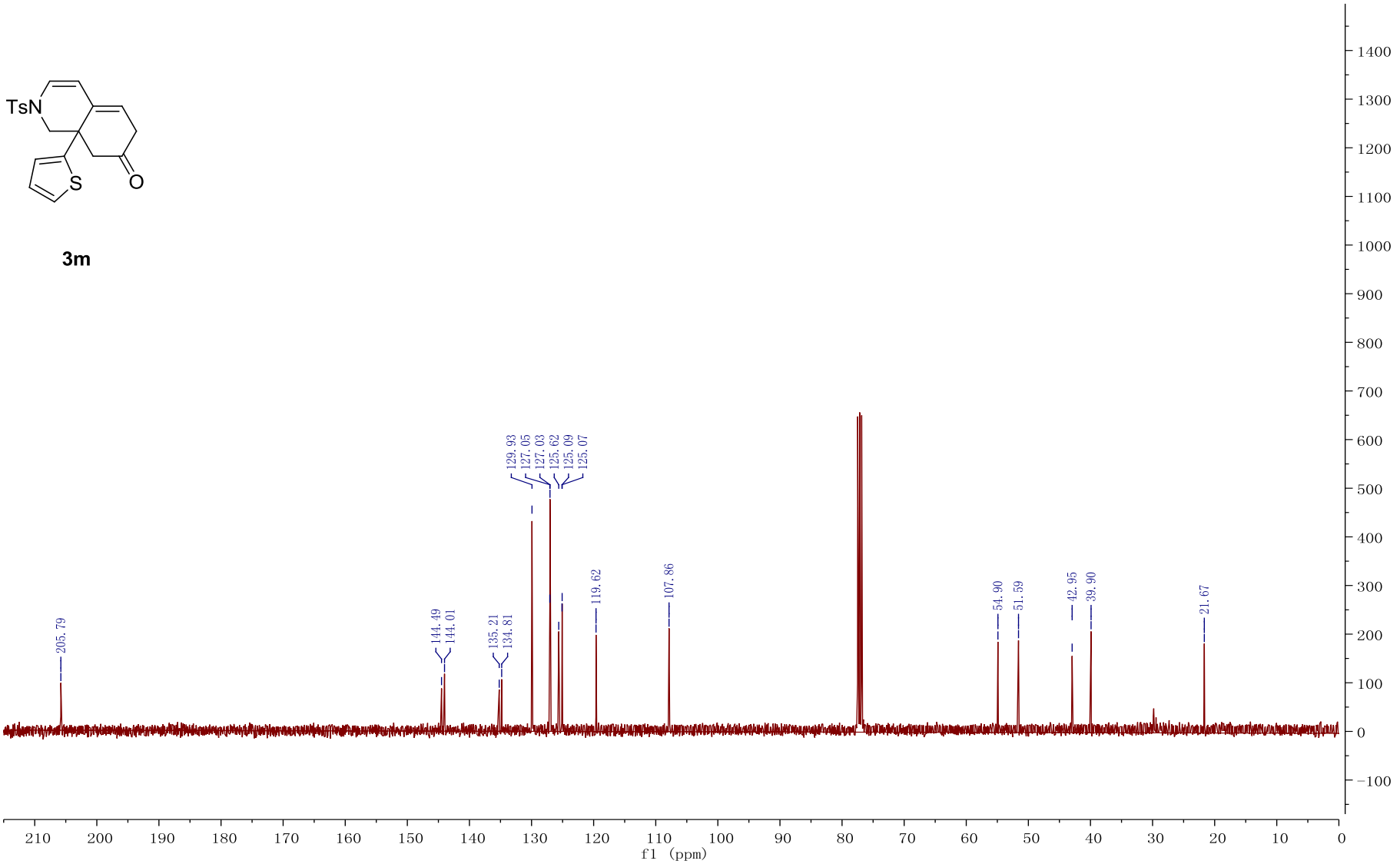

TsN
O
F
3k
7.38
7.36
7.15
7.13
6.98
6.97
6.78
6.77
6.76
6.75
6.73
6.73
5.81
5.80
5.79
5.70
5.68
4.14
4.11
3.16
3.13
3.04
3.02
2.98
2.97
2.78
2.77
2.75
2.72
2.71
2.57
2.53
2.40
2.02
2.05
2.07
3.01
1.00
1.00
1.02
1.01
1.01
2.00
1.05
3.10
f1 (ppm)

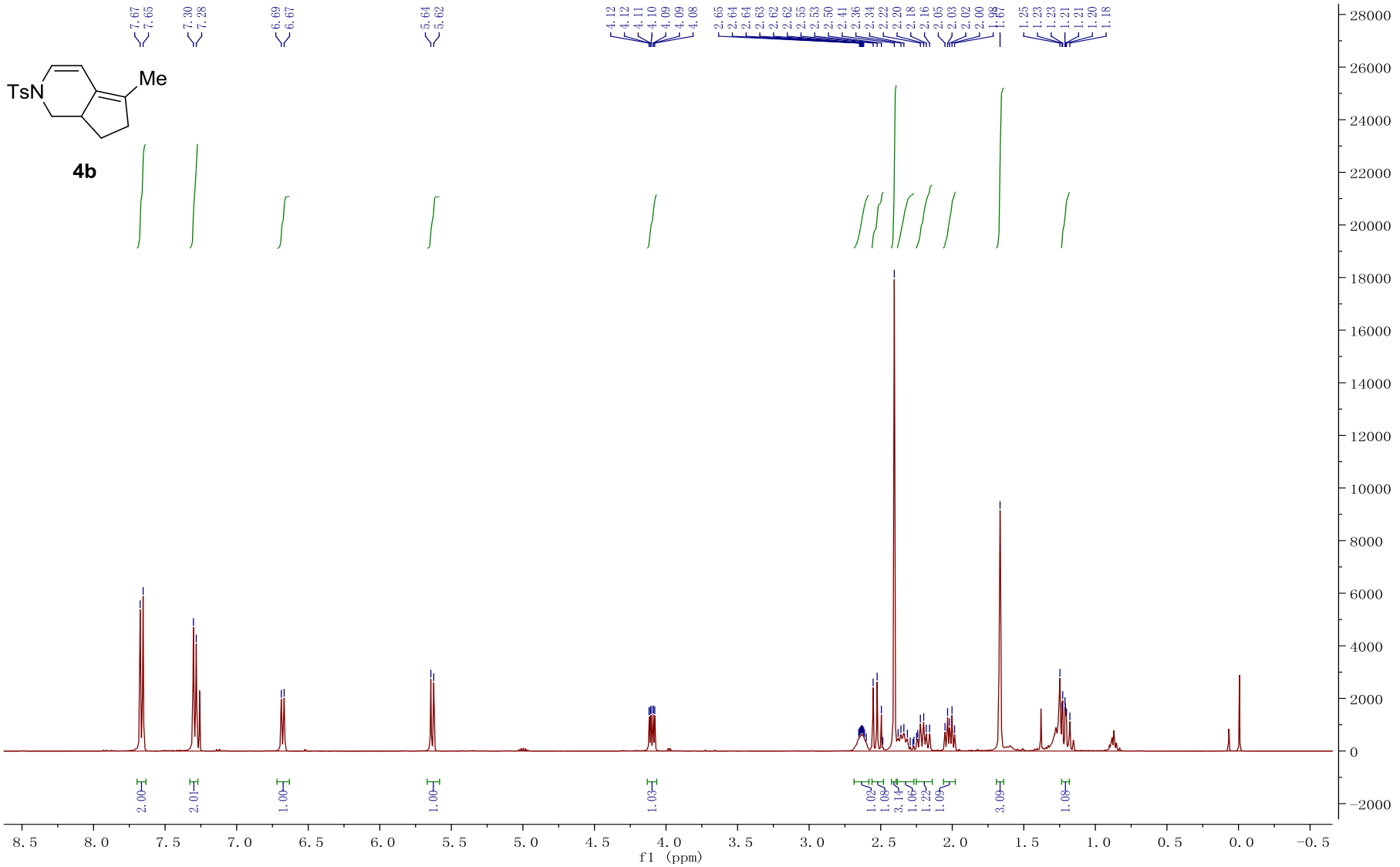

205.97
163.16
160.71
143.94
135.33
134.73
134.69
134.43
129.69
128.13
128.05
115.61
115.39
108.24
54.46
50.48
44.56
39.98
21.45
TsN
O
F
3k
f1 (ppm)

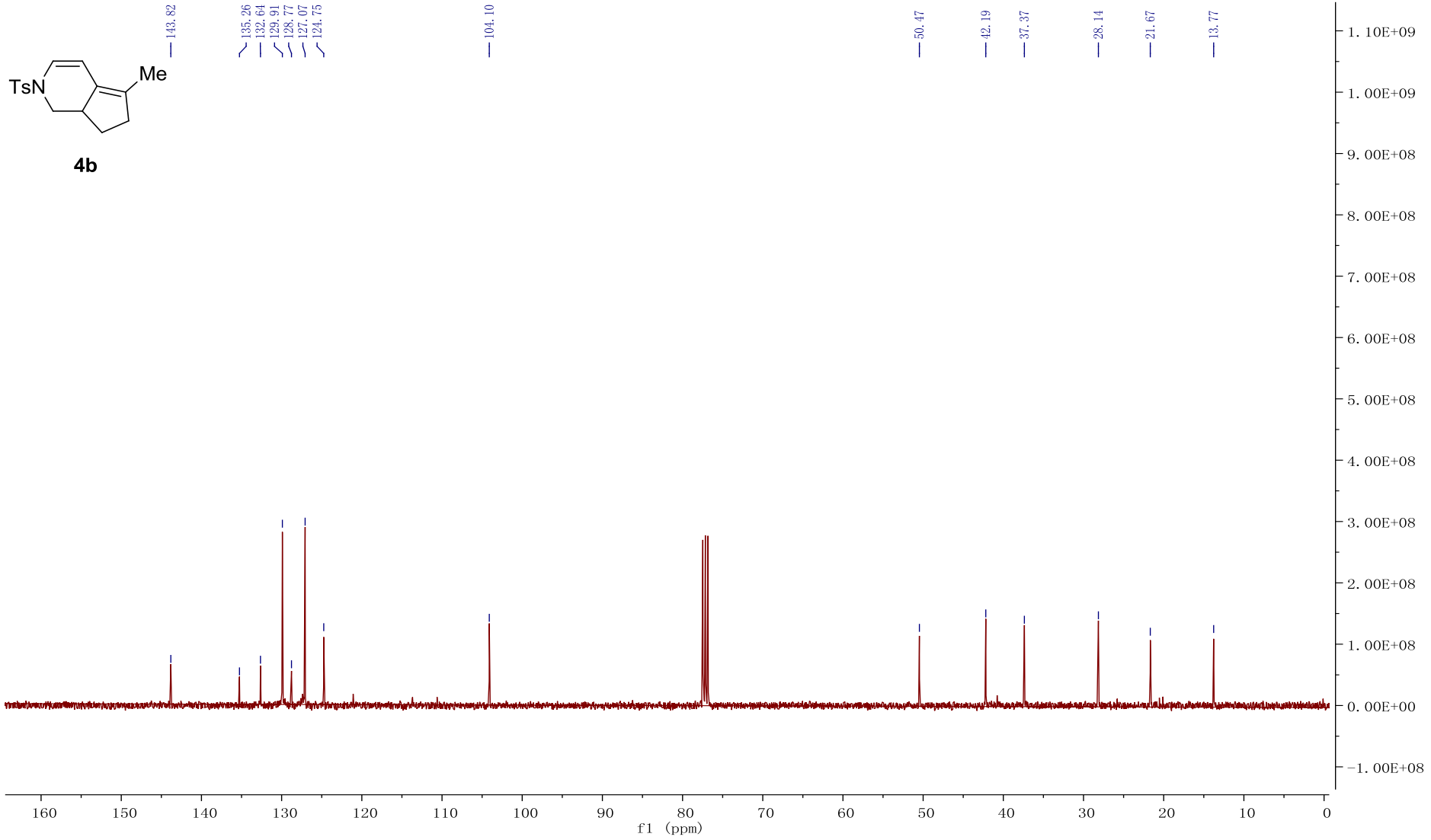

TsN
O
3l
7.58
7.56
7.45
7.44
7.44
7.43
7.42
7.42
7.42
7.35
7.35
7.21
7.20
7.19
7.18
7.15
7.13
6.82
6.80
6.66
6.64
5.90
5.89
5.88
5.81
5.79
4.33
4.30
3.33
3.29
3.04
3.02
2.99
2.98
2.97
2.95
2.77
2.77
2.71
2.64
2.60
2.10
1.05
2.03
2.17
1.03
1.07
1.93
0.96
1.96
1.00
0.97
1.00
1.03
2.11
1.09
0.96
3.04
f1 (ppm)

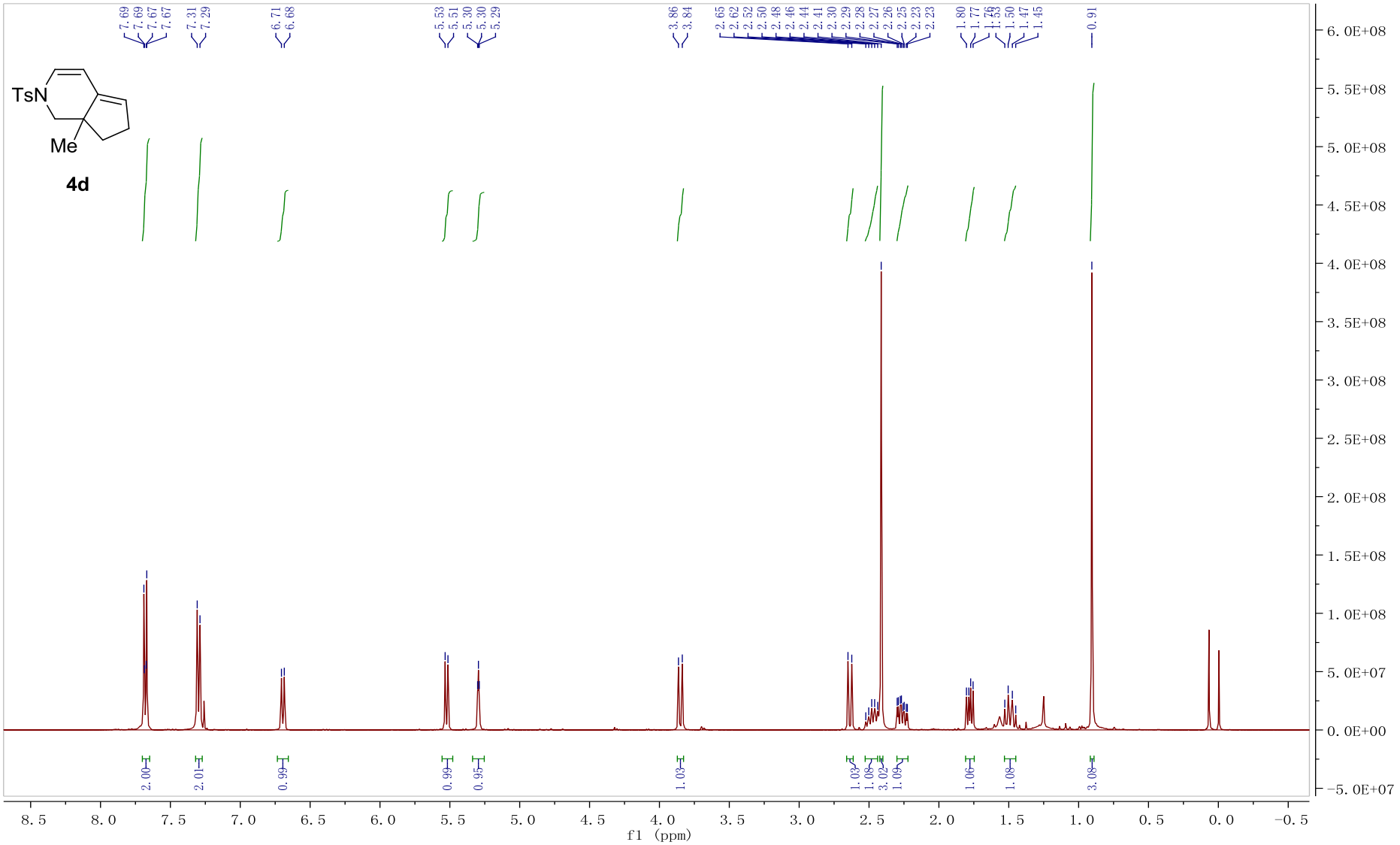

TsN
O
3l
206.35
143.48
136.42
135.46
134.72
133.20
132.71
129.25
128.88
128.22
127.42
126.38
126.31
126.22
126.11
125.96
123.61
120.23
108.70
54.77
50.34
45.23
40.10
21.51
f1 (ppm)

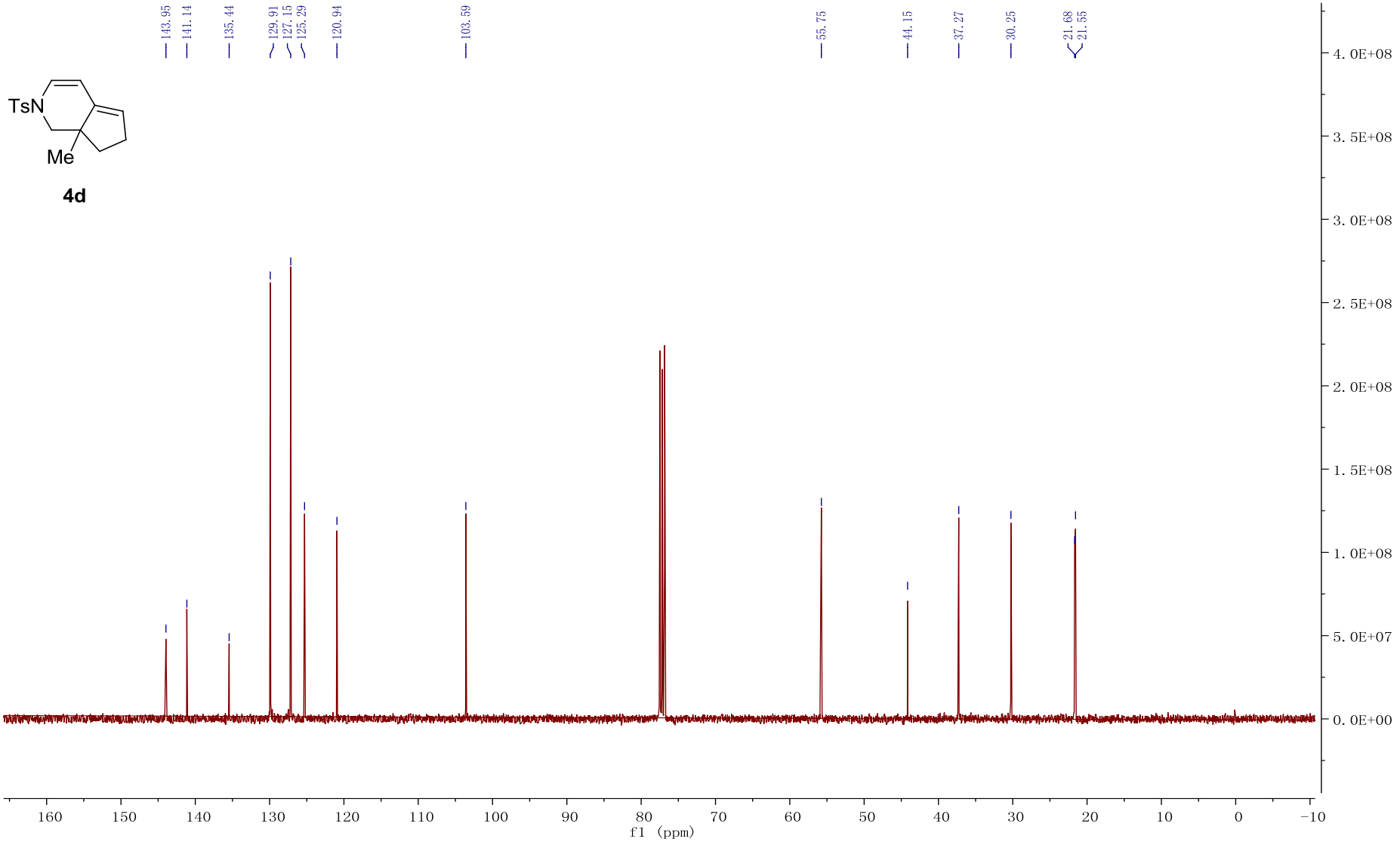

TsN
S
O
3m
7.51
7.49
7.22
7.20
7.06
7.05
6.75
6.74
6.73
6.69
6.68
5.73
5.72
5.71
5.65
5.63
4.14
4.12
3.09
3.07
3.05
3.00
2.99
2.94
2.93
2.88
2.87
2.81
2.77
2.58
2.54
2.40
1.98
1.92
0.95
2.02
1.09
1.02
1.00
0.99
1.08
1.11
1.08
1.02
1.03
3.00
f1 (ppm)

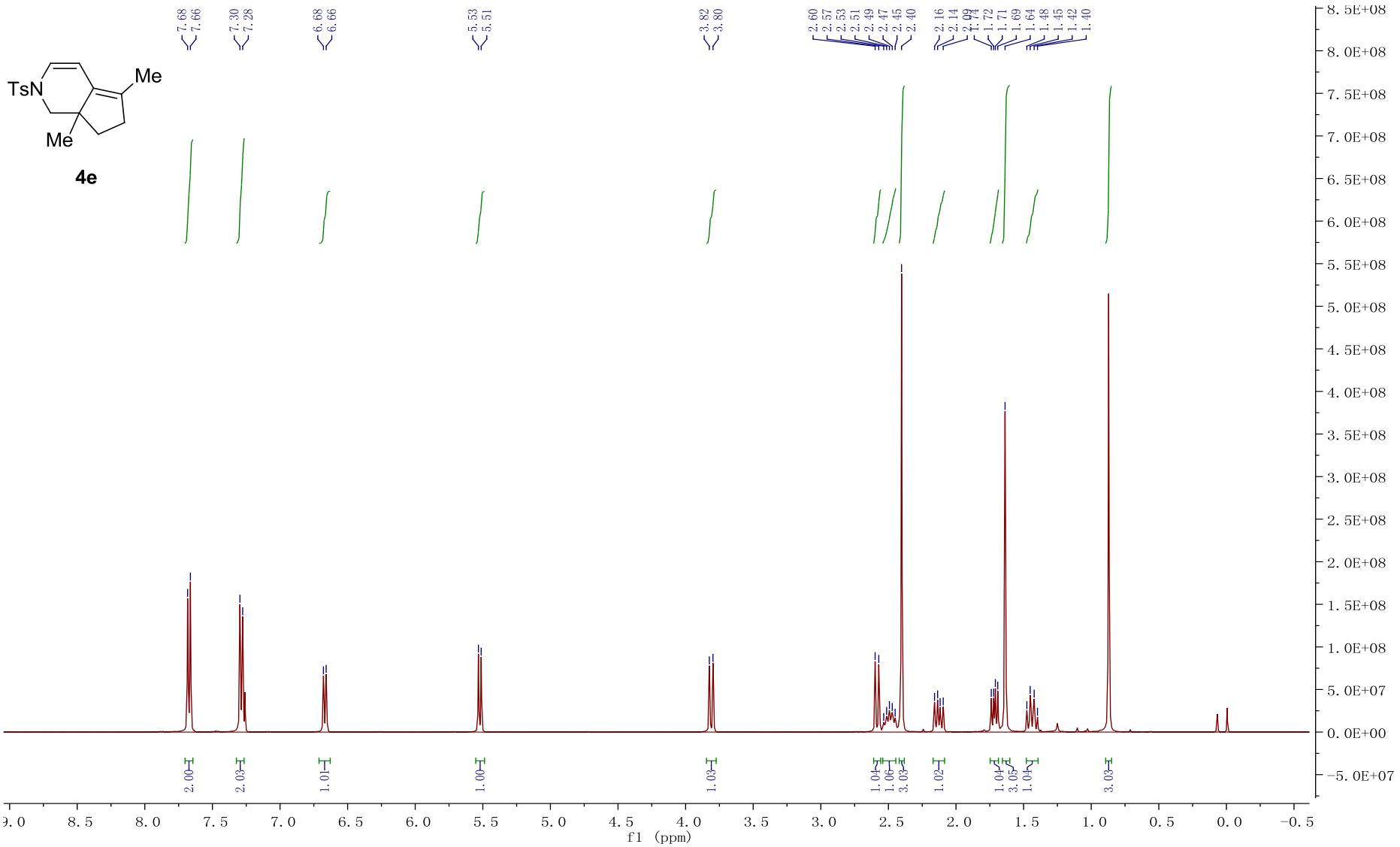

TsN
S
O
3m
205.79
144.49
144.01
135.21
134.81
129.93
127.05
127.03
125.62
125.09
125.07
119.62
107.86
54.90
51.59
42.95
39.90
21.67
f1 (ppm)

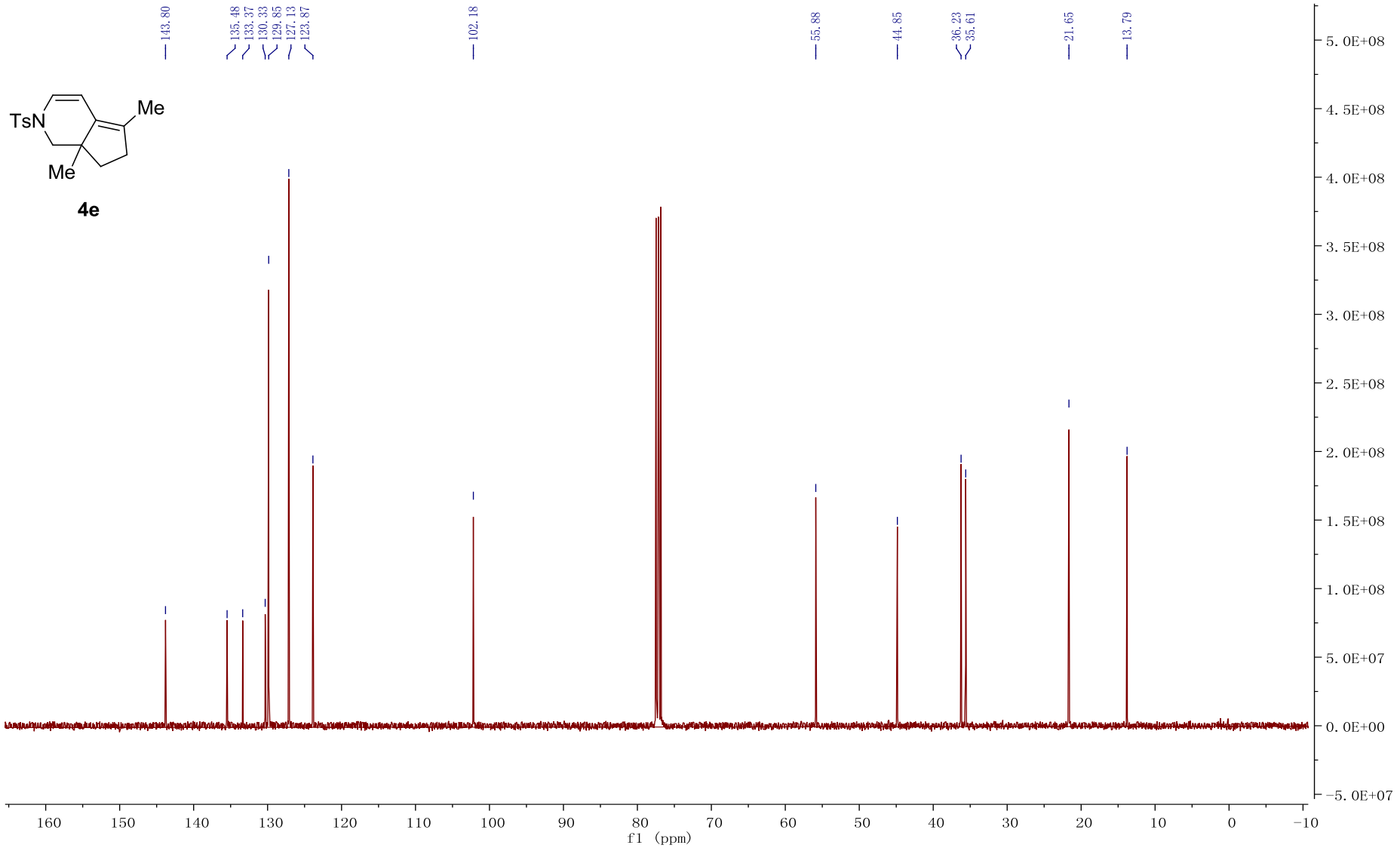

TsN
Me
4b
f1 (ppm)


143.82
135.26
132.64
129.91
128.77
127.07
124.75
104.10
50.47
42.19
37.37
28.14
21.67
13.77
TsN
Me
4b
1.10E+09
1.00E+09
9.00E+08
8.00E+08
7.00E+08
6.00E+08
5.00E+08
4.00E+08
3.00E+08
2.00E+08
1.00E+08
0.00E+00
-1.00E+08
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.69
7.69
7.67
7.67
7.31
7.29
6.71
6.68
5.53
5.51
5.30
5.30
5.29
3.86
3.84
2.65
2.62
2.52
2.50
2.48
2.46
2.44
2.41
2.30
2.29
2.28
2.27
2.26
2.25
2.23
2.23
1.80
1.77
1.53
1.50
1.47
1.45
0.91
TsN
Me
4d
2.00
2.01
0.99
0.99
0.95
1.03
1.03
1.08
3.02
1.09
1.06
1.08
3.08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


143.95
141.14
135.44
129.91
127.15
125.29
120.94
103.59
55.75
44.15
37.27
30.25
21.68
21.55
TsN
Me
4d
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


TsN
Me
Me
4e
7.68
7.66
7.30
7.28
6.68
6.66
5.53
5.51
3.82
3.80
2.60
2.57
2.53
2.51
2.49
2.47
2.45
2.40
2.16
2.14
1.74
1.72
1.71
1.69
1.64
1.48
1.45
1.42
1.40
2.00
2.03
1.01
1.00
1.03
1.04
1.06
3.03
1.02
1.04
3.05
1.04
3.03
f1 (ppm)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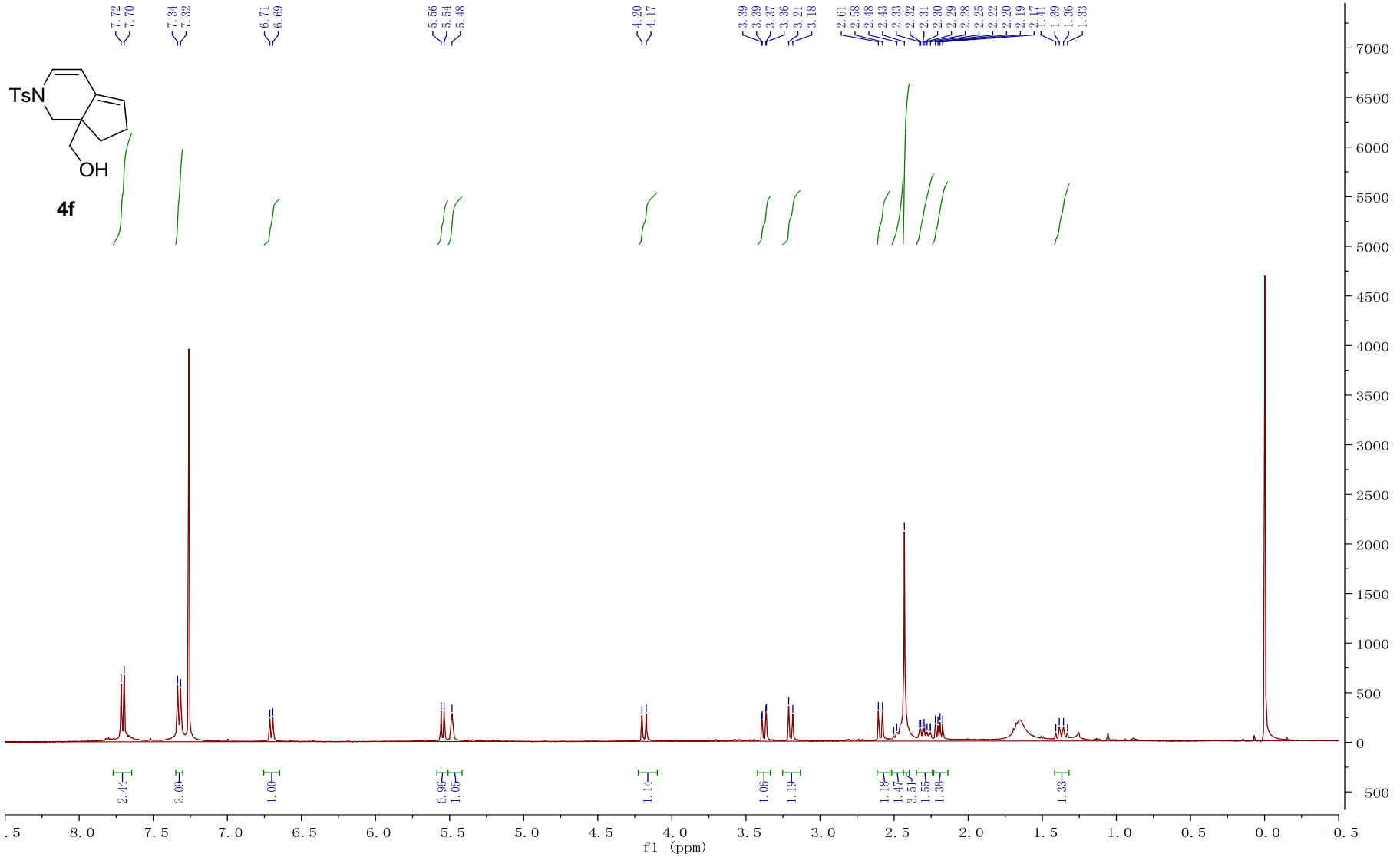
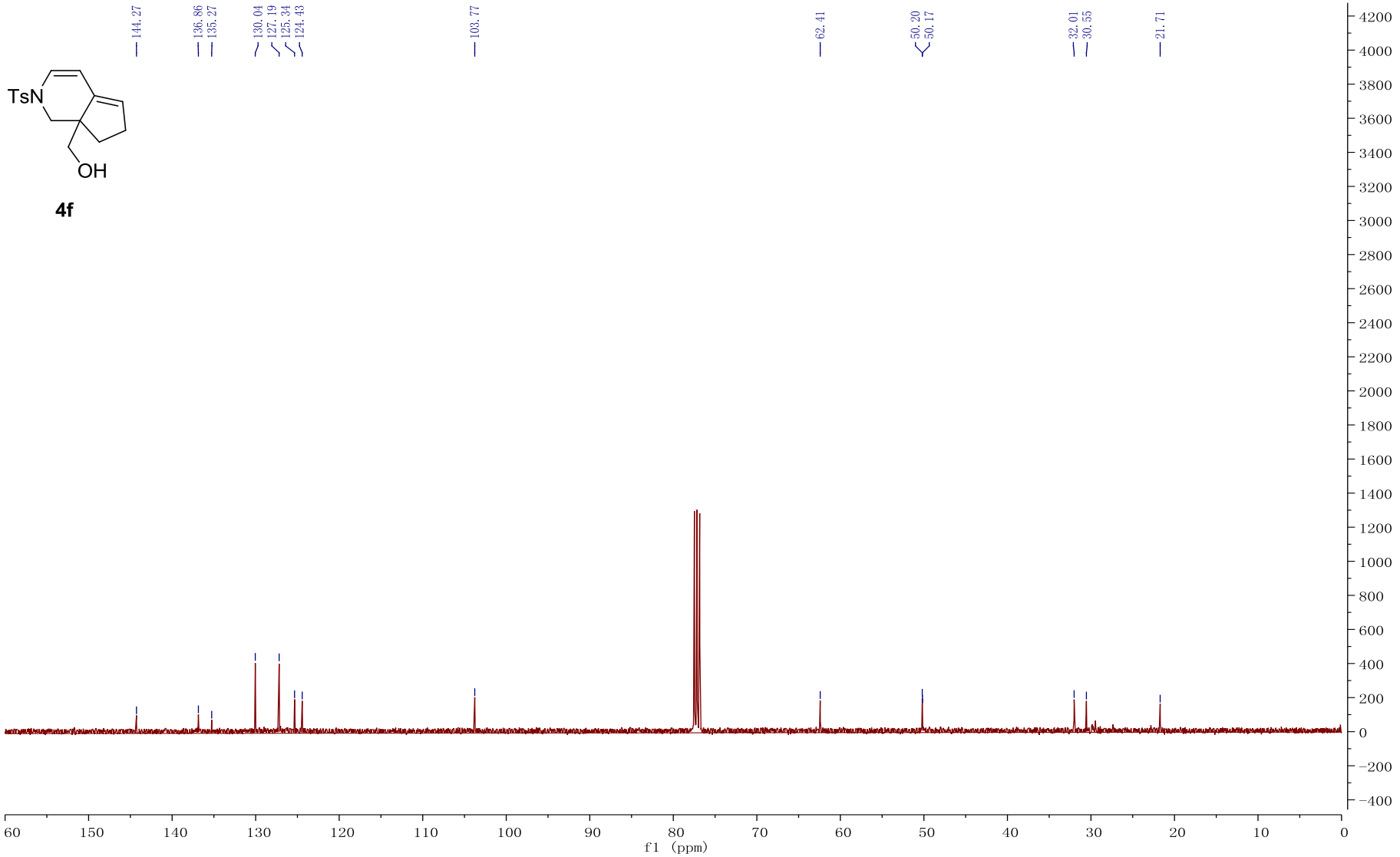
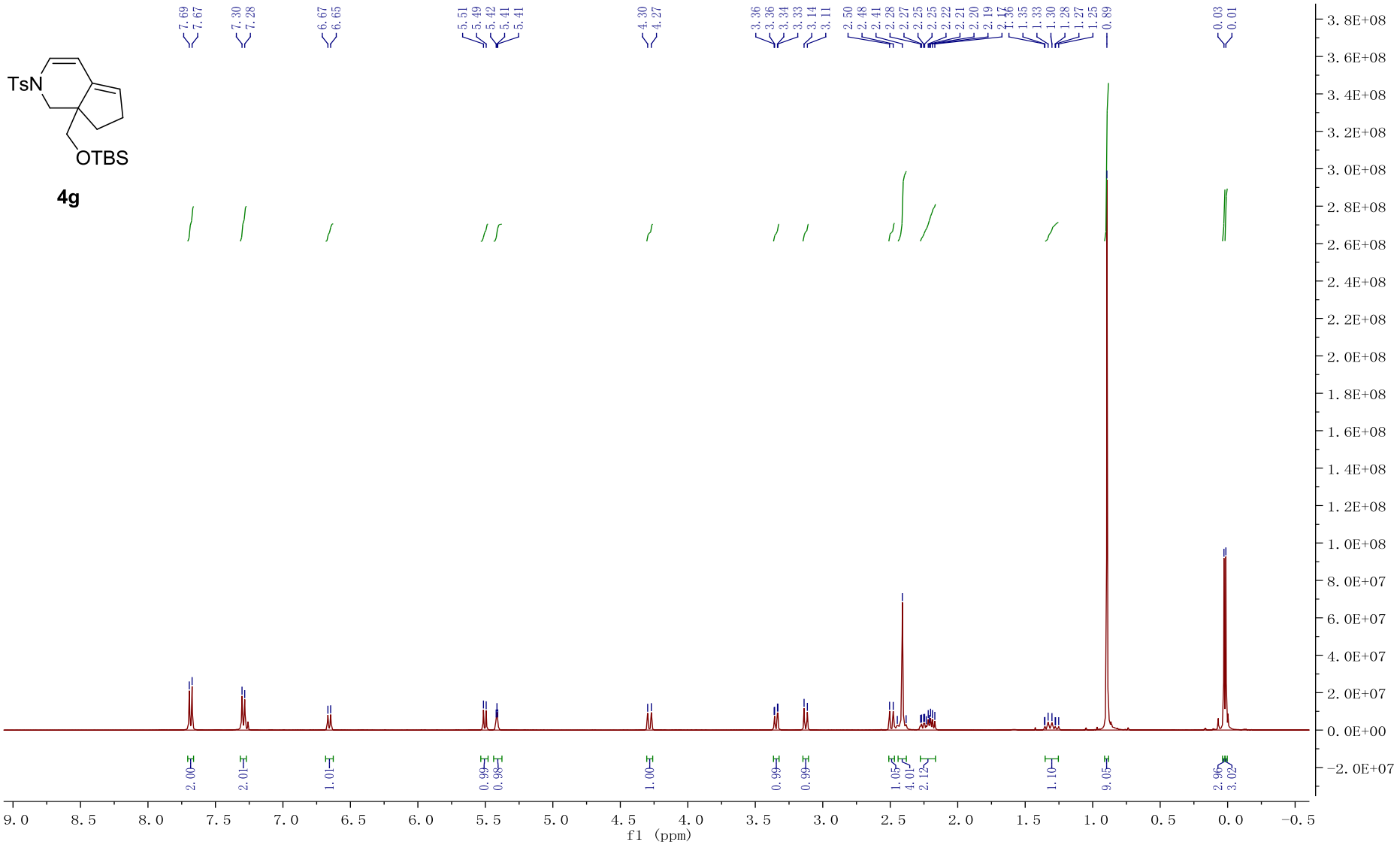
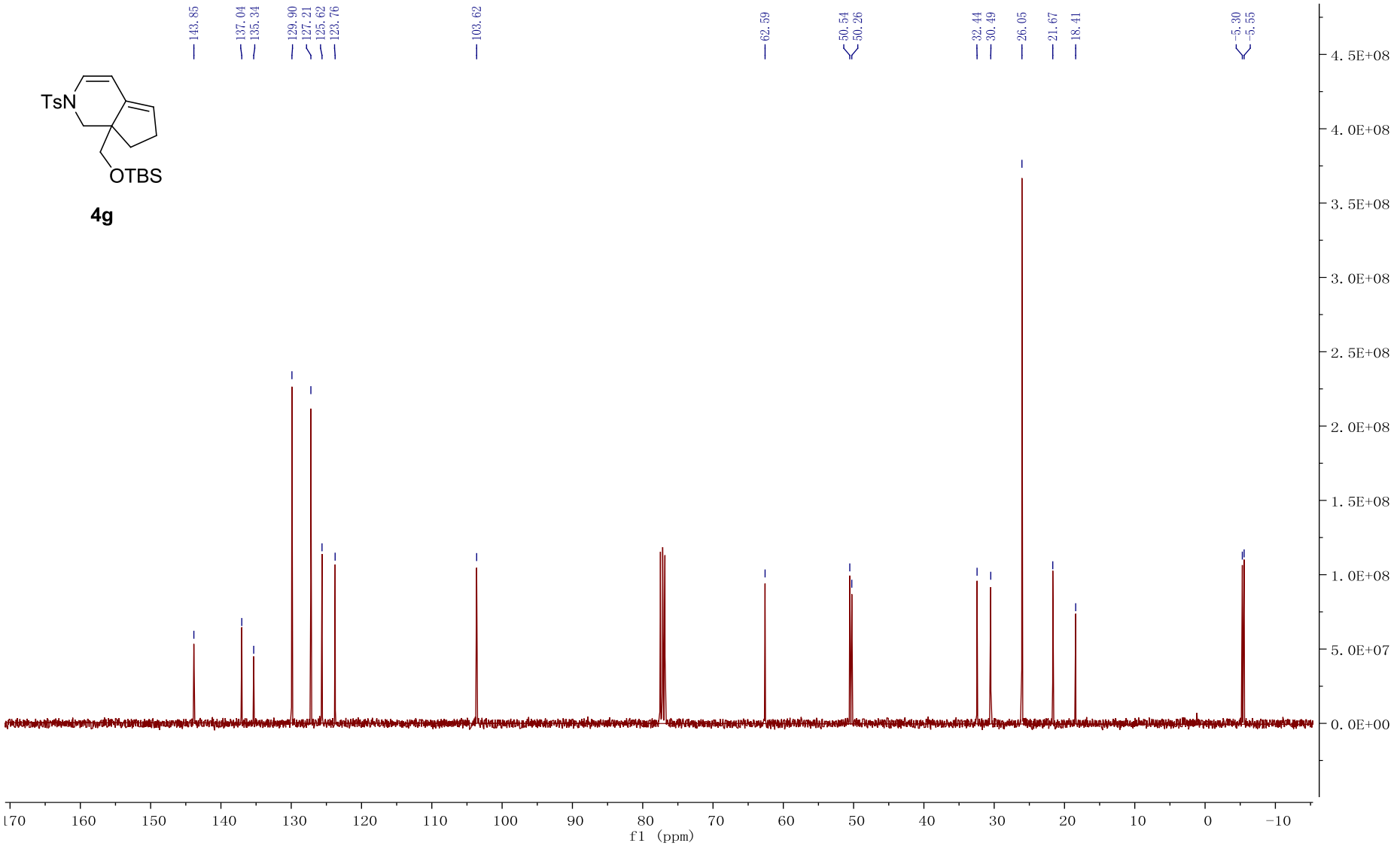
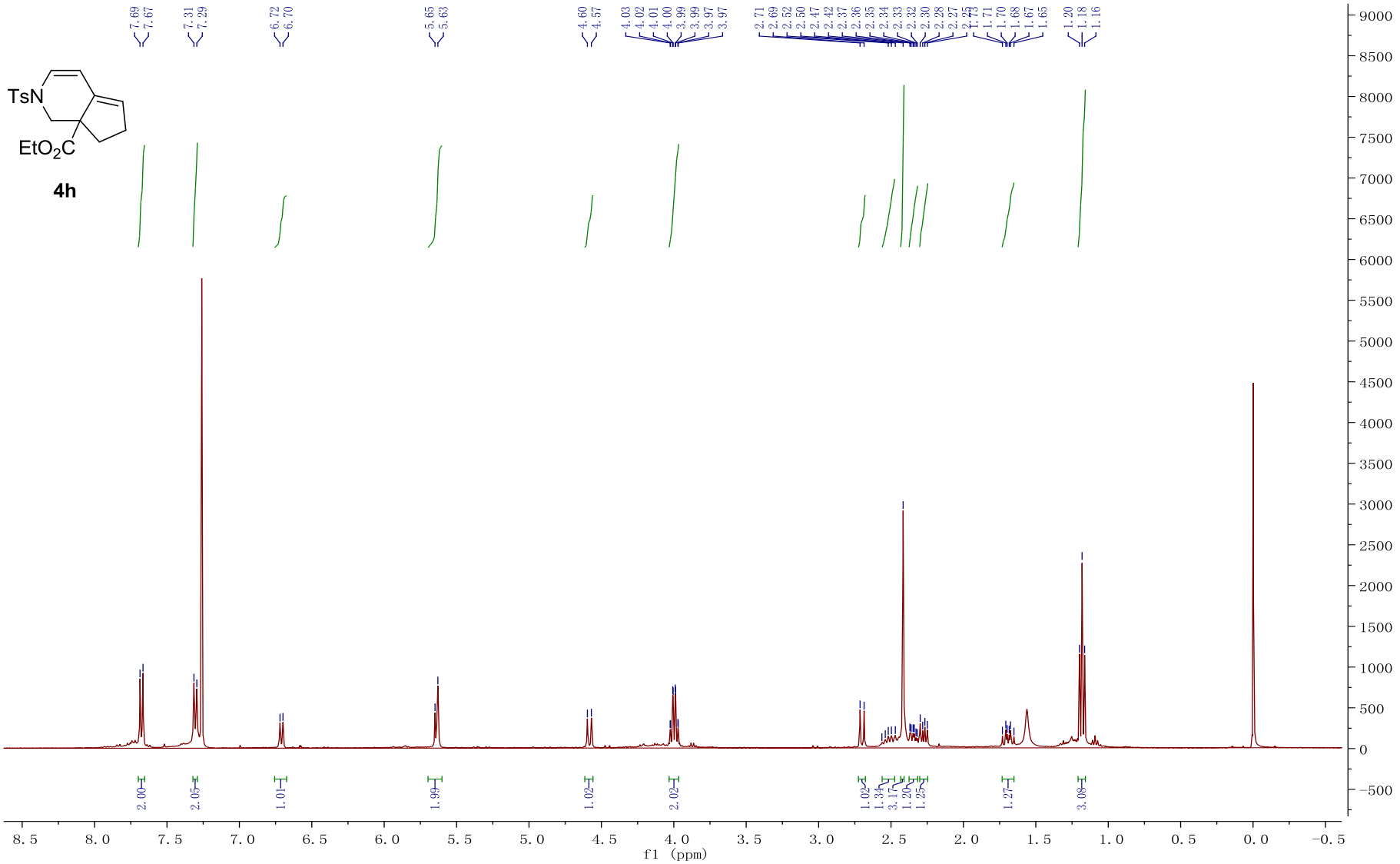
135.48
133.37
130.33
129.85
127.13
123.87
102.18
55.88
44.85
36.23
35.61
21.65
13.79
TsN
Me
Me
4e
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

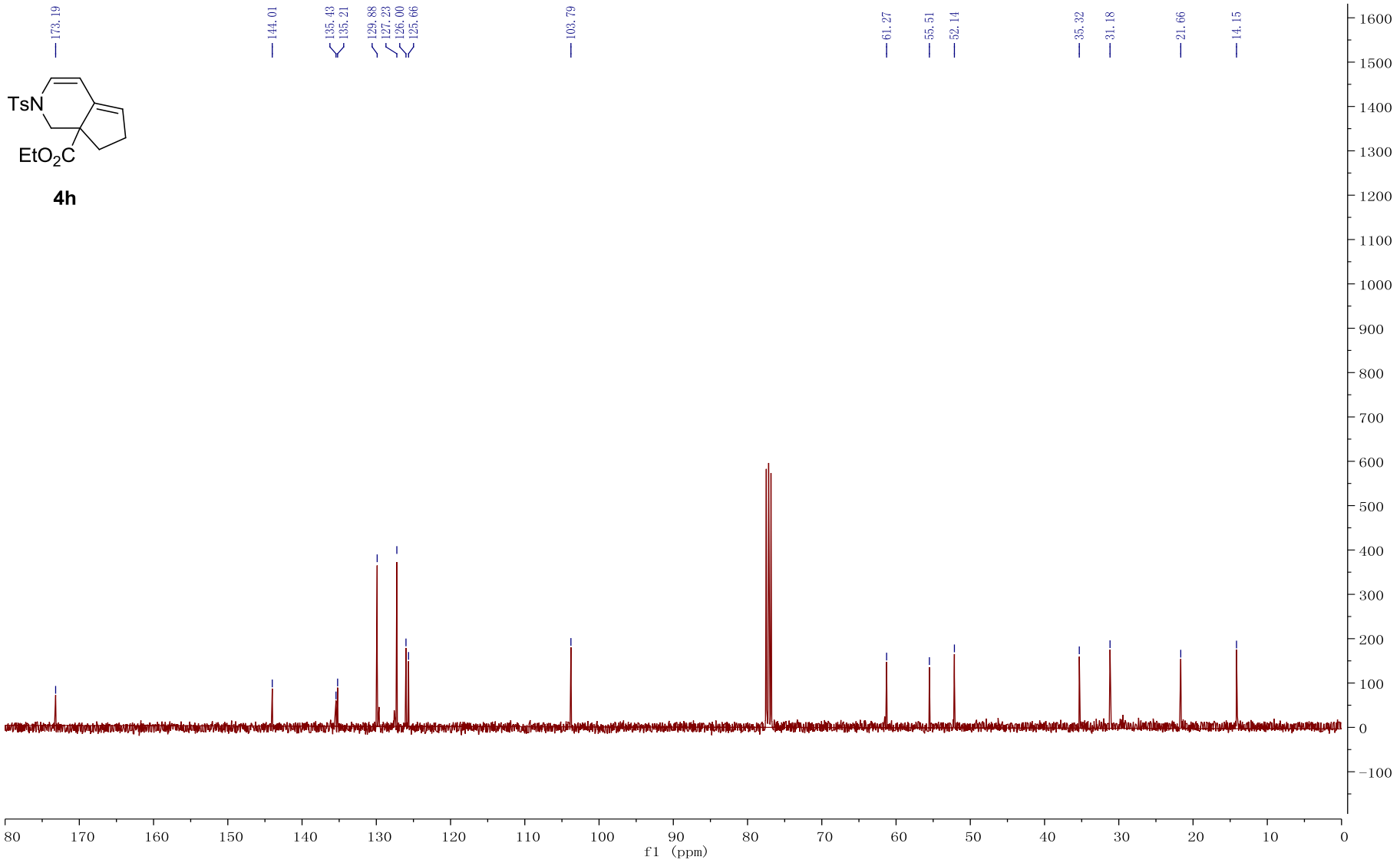

TsN
OH
4f
7.72
7.70
7.34
7.32
6.71
6.69
5.56
5.54
5.48
4.20
4.17
3.39
3.39
3.37
3.36
3.21
3.18
2.61
2.58
2.48
2.43
2.33
2.32
2.31
2.30
2.29
2.28
2.25
2.22
2.20
2.19
2.17
1.41
1.39
1.36
1.33
2.44
2.09
1.00
0.96
1.05
1.14
1.06
1.19
1.18
1.47
3.51
1.55
1.38
1.33
f1 (ppm)

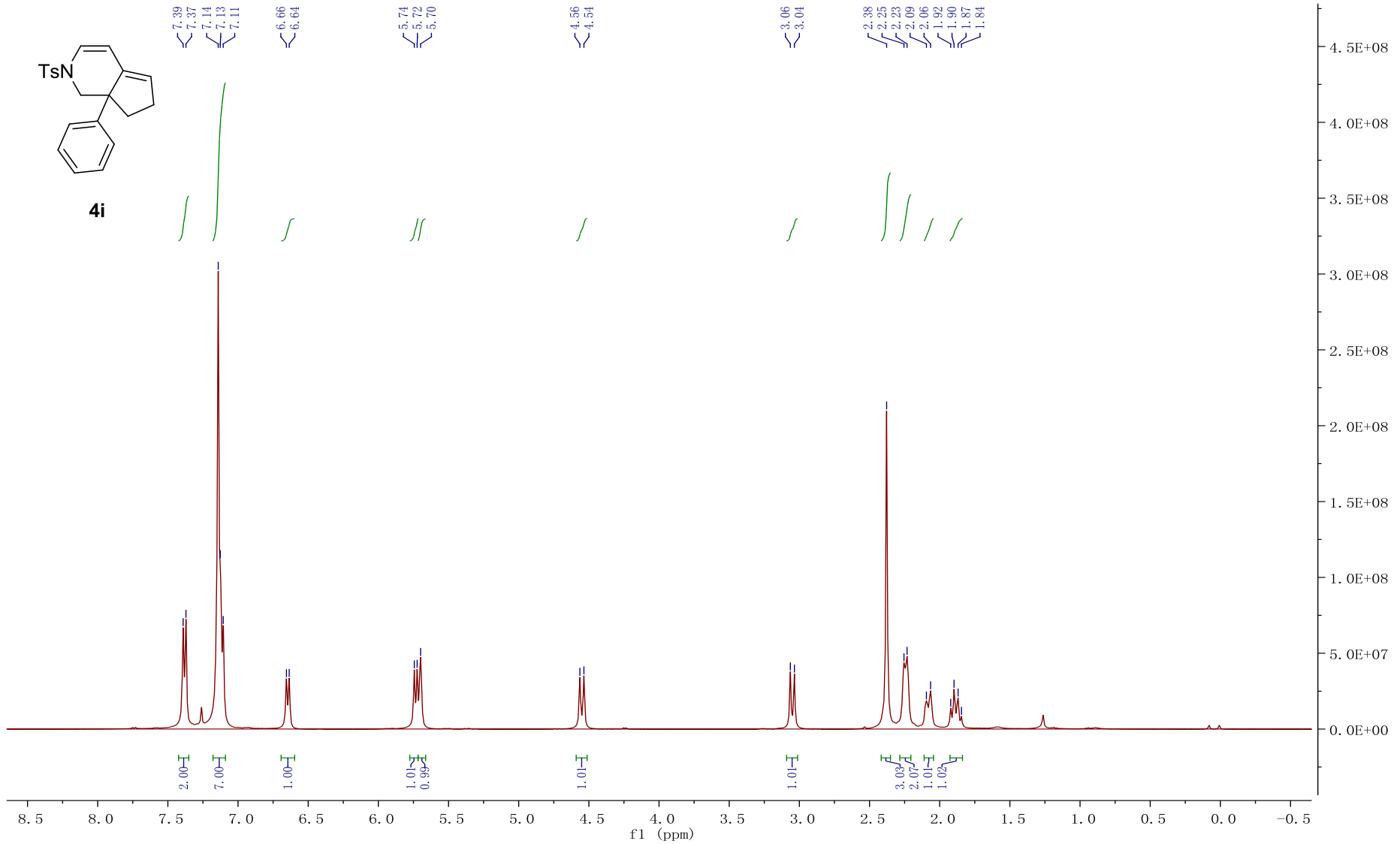

144.27
136.86
135.27
130.04
127.19
125.34
124.43
103.77
62.41
50.20
50.17
32.01
30.55
21.71
TsN
OH
4f
f1 (ppm)

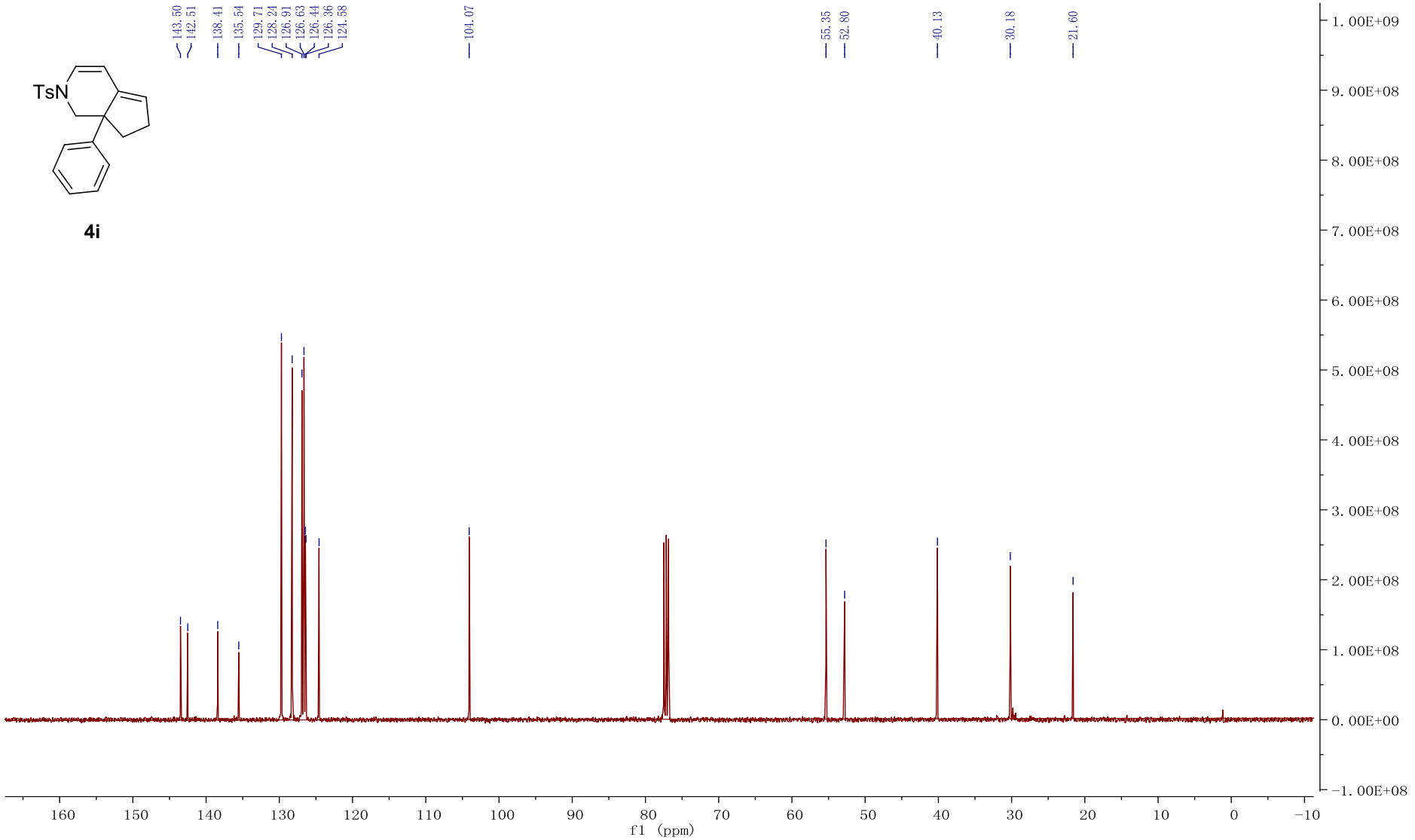

TsN
OTBS
4g
7.69
7.67
7.30
7.28
6.67
6.65
5.51
5.49
5.42
5.41
5.41
4.30
4.27
3.36
3.36
3.34
3.33
3.14
3.11
2.50
2.48
2.41
2.28
2.27
2.25
2.25
2.22
2.21
2.20
2.19
2.17
1.36
1.35
1.33
1.30
1.28
1.27
1.25
0.89
0.03
0.01
2.00
2.01
1.01
0.99
0.98
1.00
0.99
0.99
1.05
4.01
2.12
1.10
9.05
2.96
3.02
f1 (ppm)

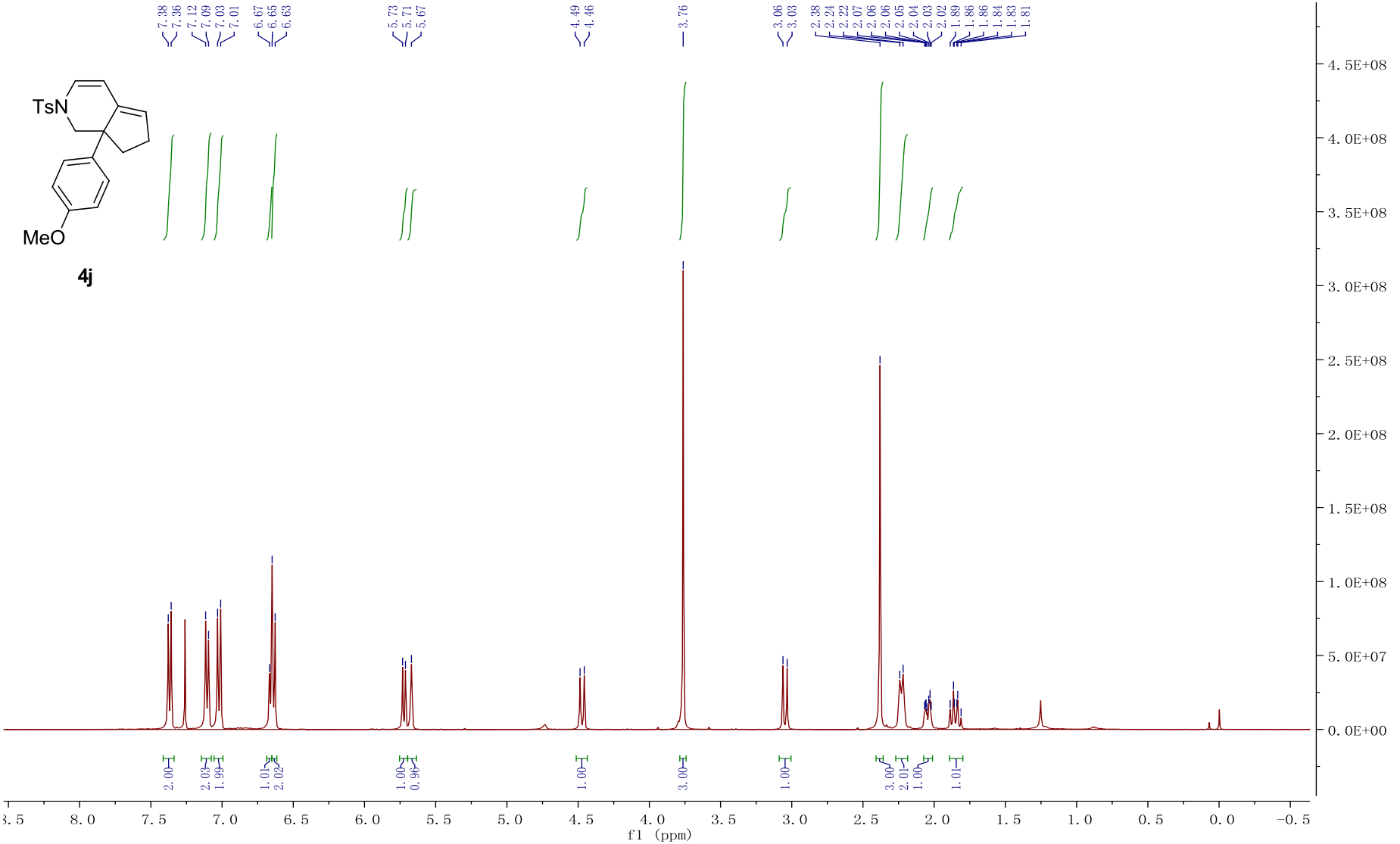

143.85
137.04
135.34
129.90
127.21
125.62
123.76
103.62
62.59
50.54
50.26
32.44
30.49
26.05
21.67
18.41
-5.30
-5.55
TsN
OTBS
4g
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

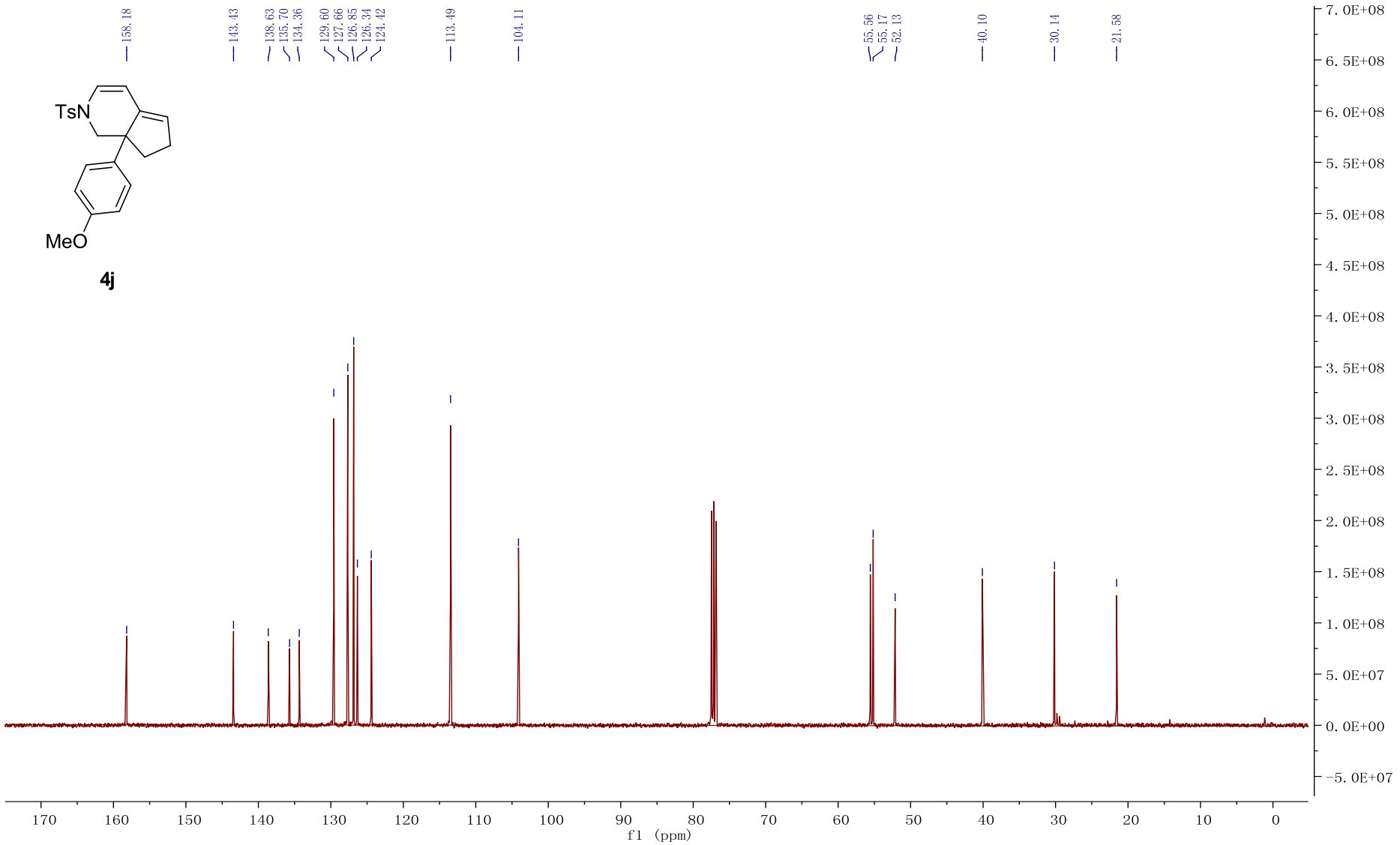

TsN
EtO2C
4h
f1 (ppm)

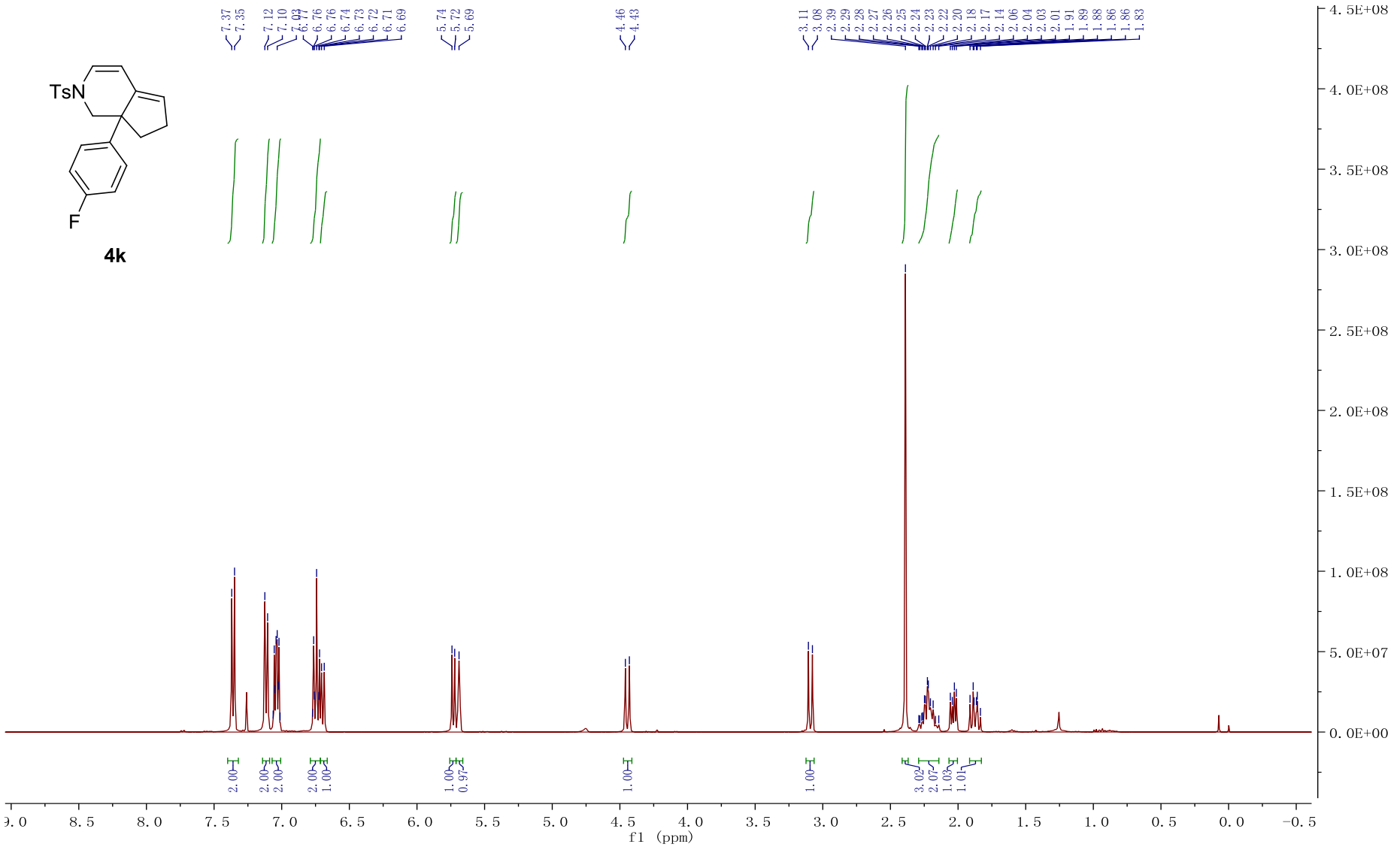

173.19
144.01
135.43
135.21
129.88
127.23
126.00
125.66
103.79
61.27
55.51
52.14
35.32
31.18
21.66
14.15
TsN
EtO2C
4h
f1 (ppm)

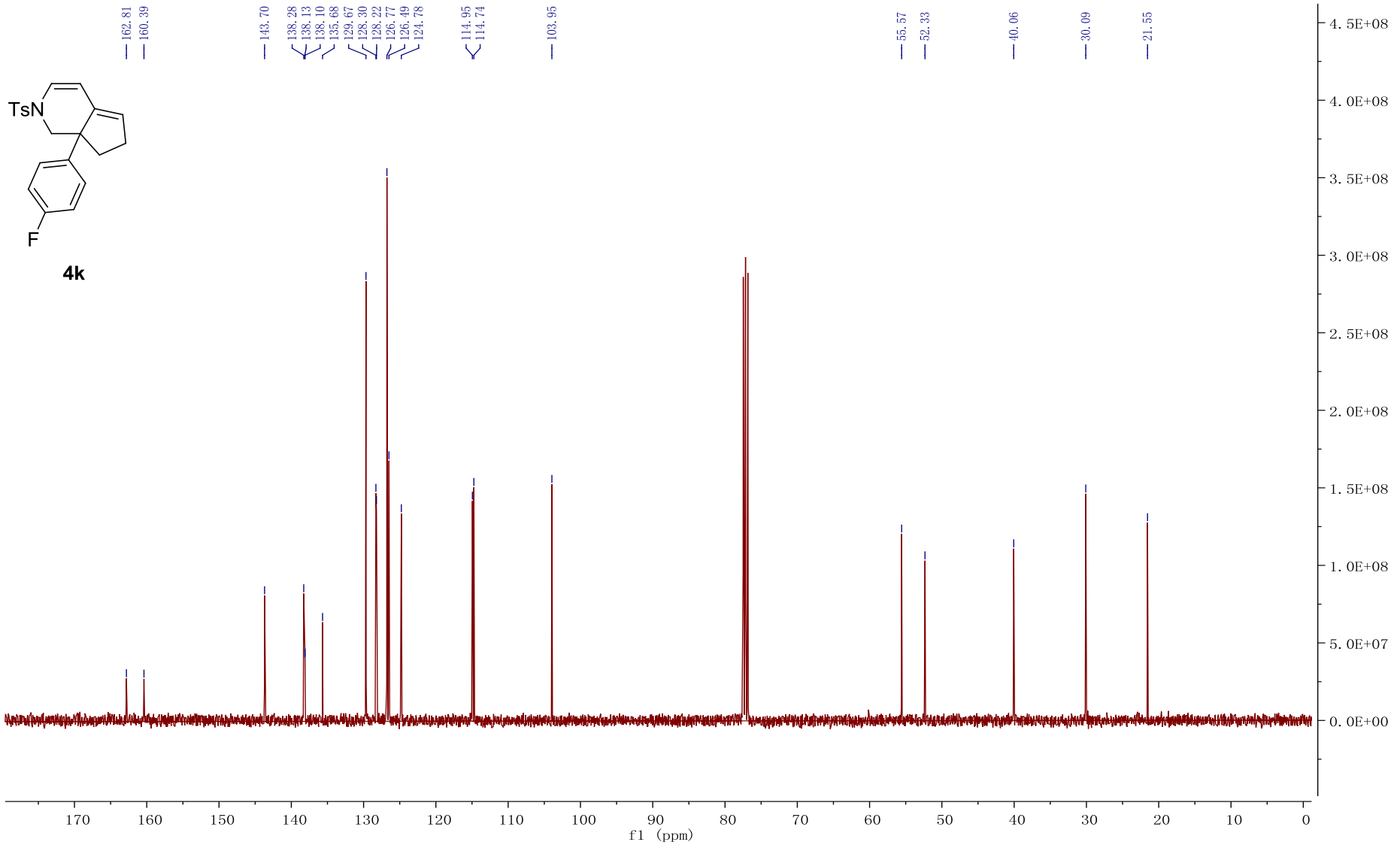

TsN
4i
7.39
7.37
7.14
7.13
7.11
6.66
6.64
5.74
5.72
5.70
4.56
4.54
3.06
3.04
2.38
2.25
2.23
2.09
2.06
1.92
1.90
1.87
1.84
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
2.00
7.00
1.00
1.01
0.99
1.01
1.01
3.03
2.07
1.01
1.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

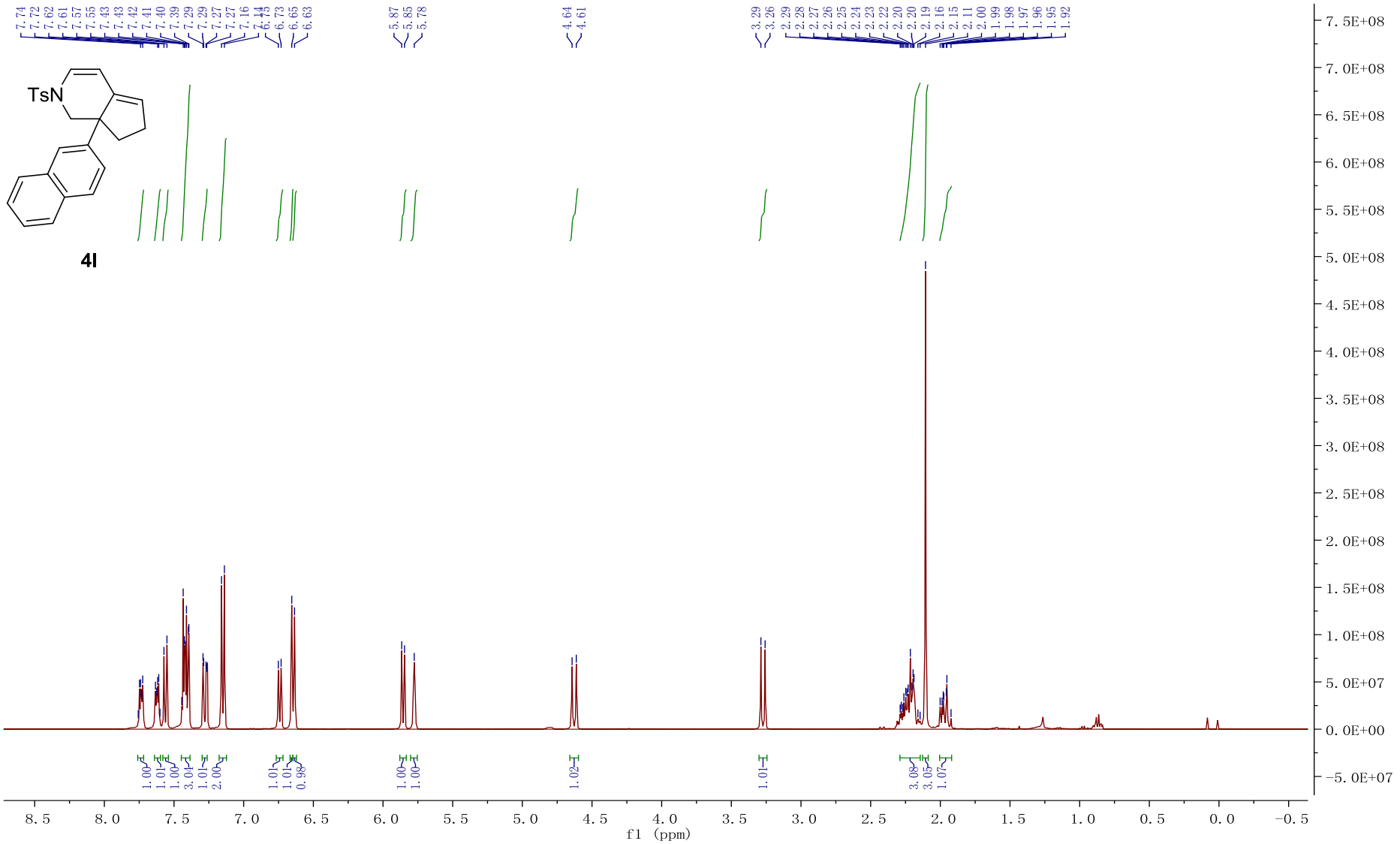

143.50
142.51
138.41
135.54
129.71
128.24
126.91
126.63
126.44
126.36
124.58
104.07
55.35
52.80
40.13
30.18
21.60
TsN
4i
1.00E+09
9.00E+08
8.00E+08
7.00E+08
6.00E+08
5.00E+08
4.00E+08
3.00E+08
2.00E+08
1.00E+08
0.00E+00
-1.00E+08
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

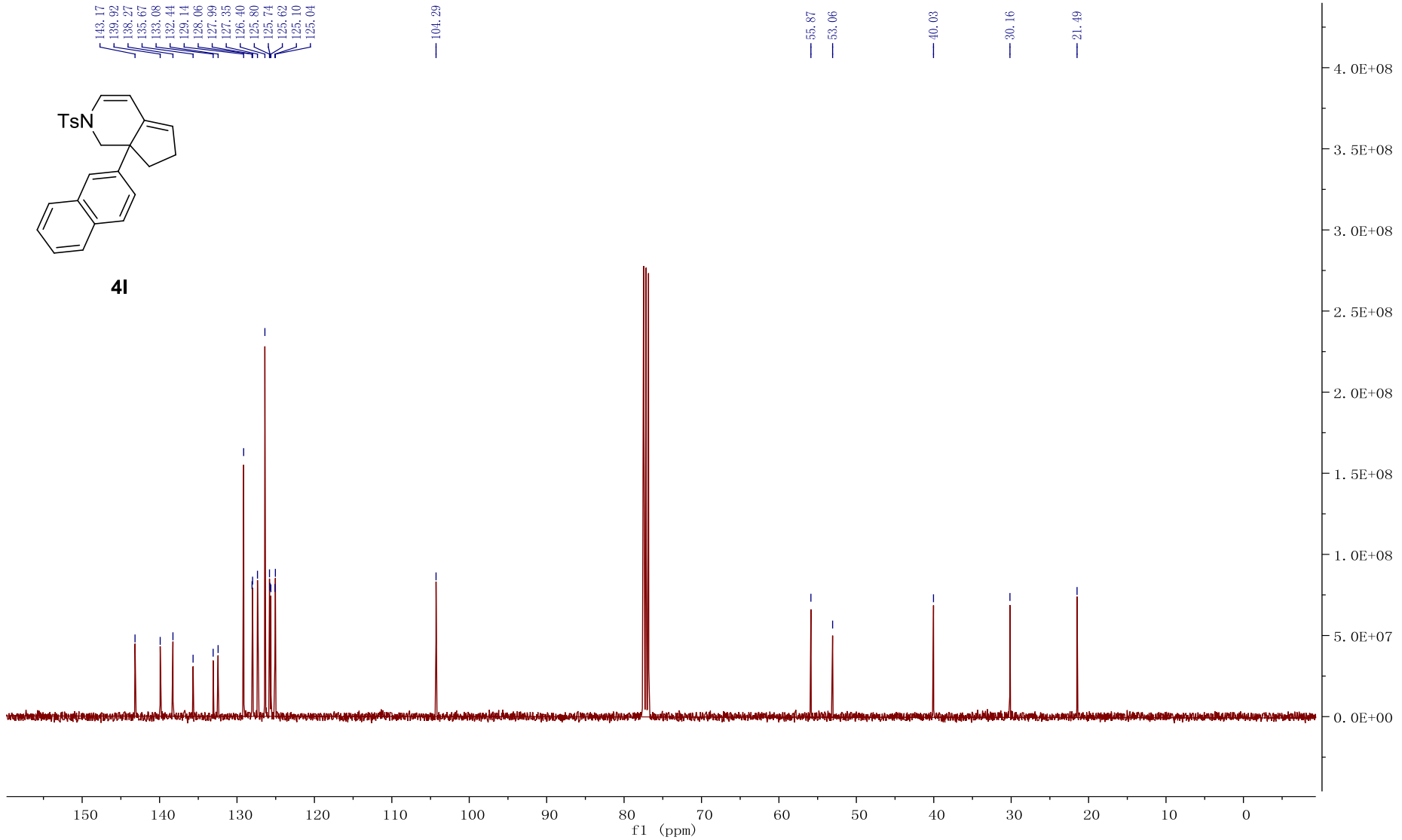

TsN
MeO
4j
7.38
7.36
7.12
7.09
7.03
7.01
6.67
6.65
6.63
5.73
5.71
5.67
4.49
4.46
3.76
3.06
3.03
2.38
2.24
2.22
2.07
2.06
2.06
2.05
2.04
2.03
2.02
1.89
1.86
1.86
1.84
1.83
1.81
2.00
2.03
1.99
1.01
2.02
1.00
0.96
1.00
3.00
1.00
3.00
2.01
1.00
1.01
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
f1 (ppm)

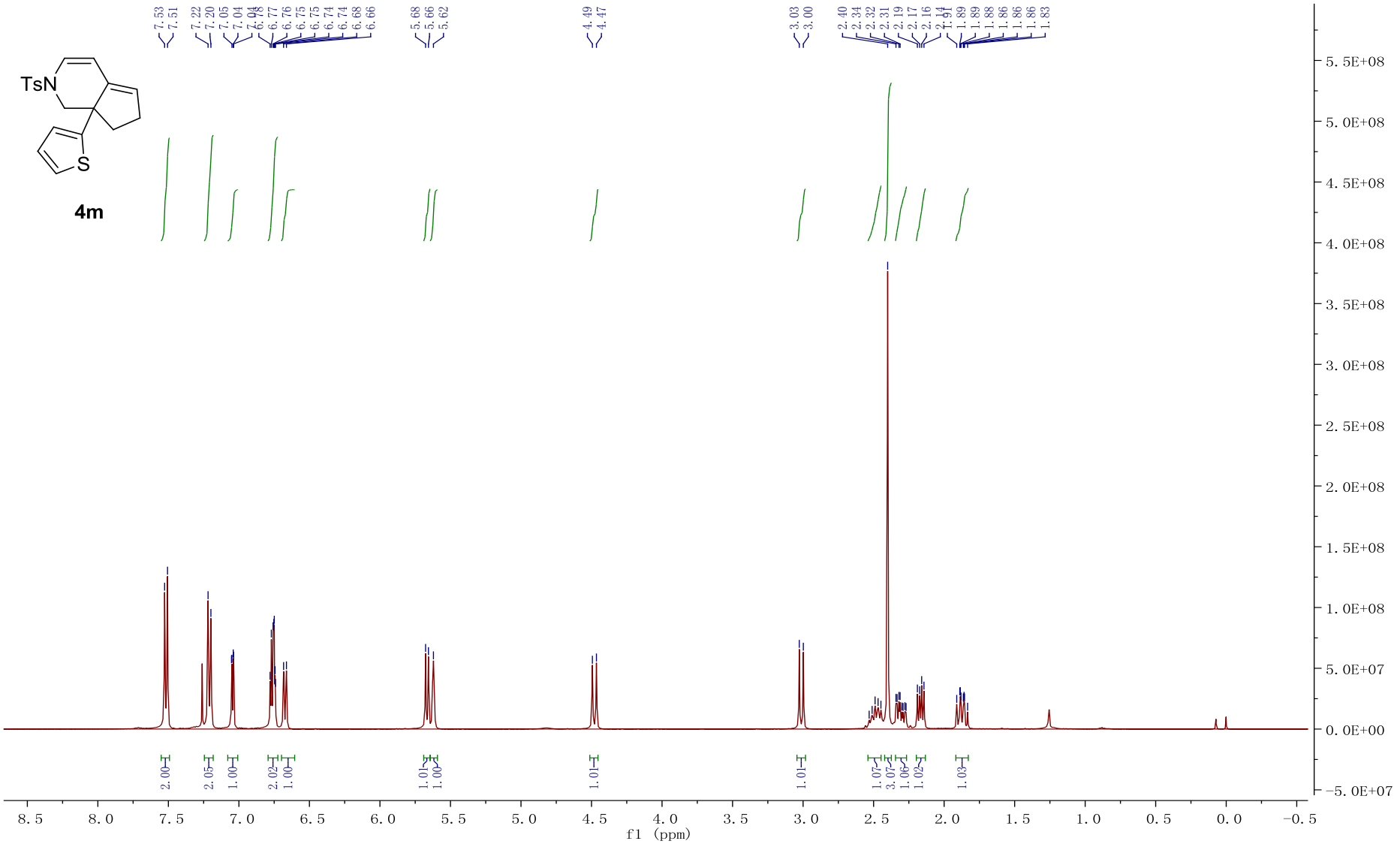

158.18
143.43
138.63
135.70
134.36
129.60
127.66
126.85
126.34
124.42
113.49
104.11
55.56
55.17
52.13
40.10
30.14
21.58
TsN
MeO
4j
7.0E+08
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

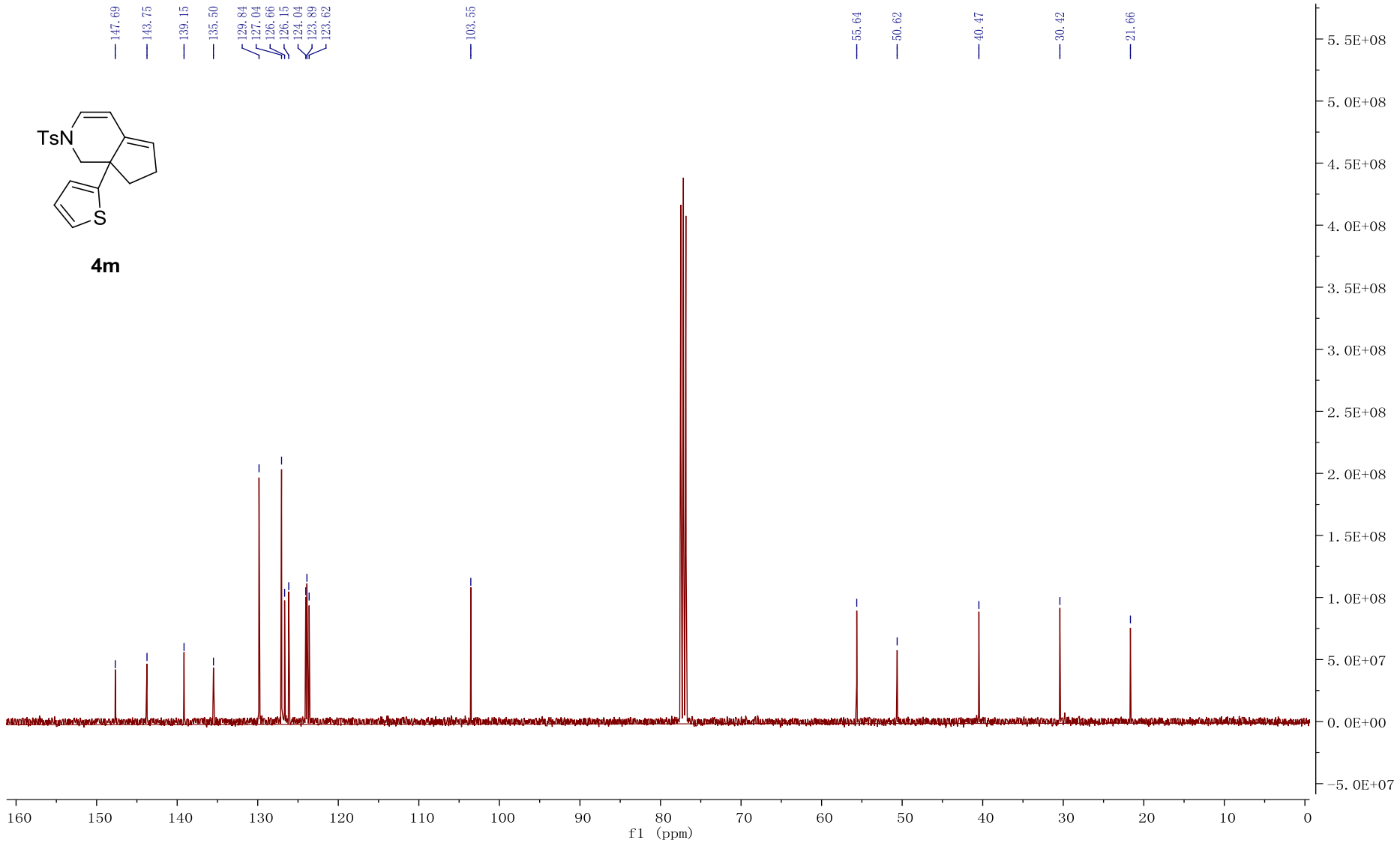

TsN
F
4k
7.37
7.35
7.12
7.10
6.76
6.74
6.73
6.72
6.71
6.69
5.74
5.72
5.69
4.46
4.43
3.11
3.08
2.39
2.29
2.28
2.27
2.26
2.25
2.24
2.23
2.22
2.20
2.18
2.17
2.14
2.06
2.04
2.03
2.01
1.91
1.89
1.88
1.86
1.86
1.83
2.00
2.00
2.00
2.00
1.00
1.00
0.97
1.00
1.00
3.02
2.07
1.03
1.01
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
f1 (ppm)

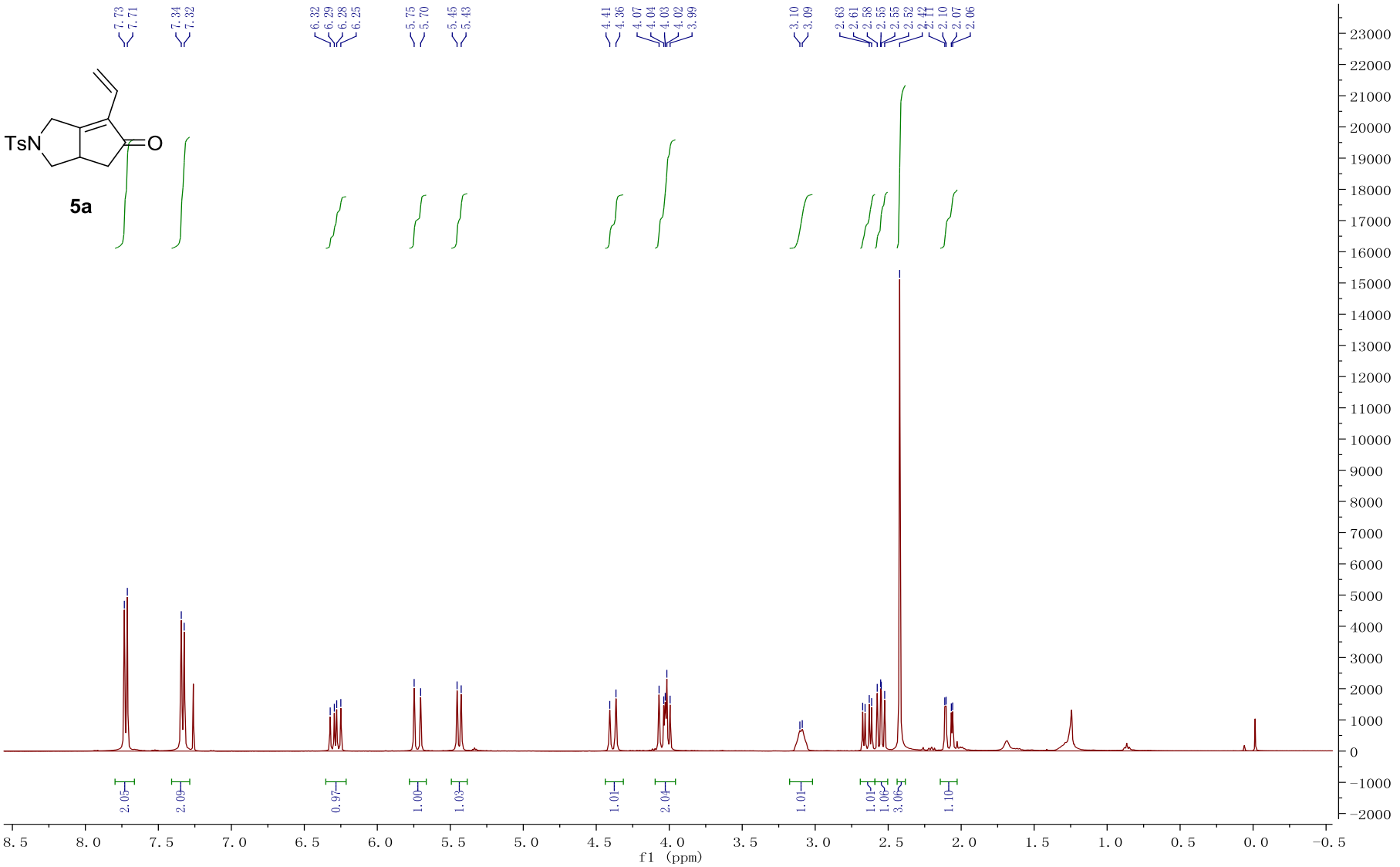

162.81
160.39
143.70
138.28
138.13
138.10
135.68
129.67
128.30
128.22
126.77
126.49
124.78
114.95
114.74
103.95
55.57
52.33
40.06
30.09
21.55
TsN
F
4k
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

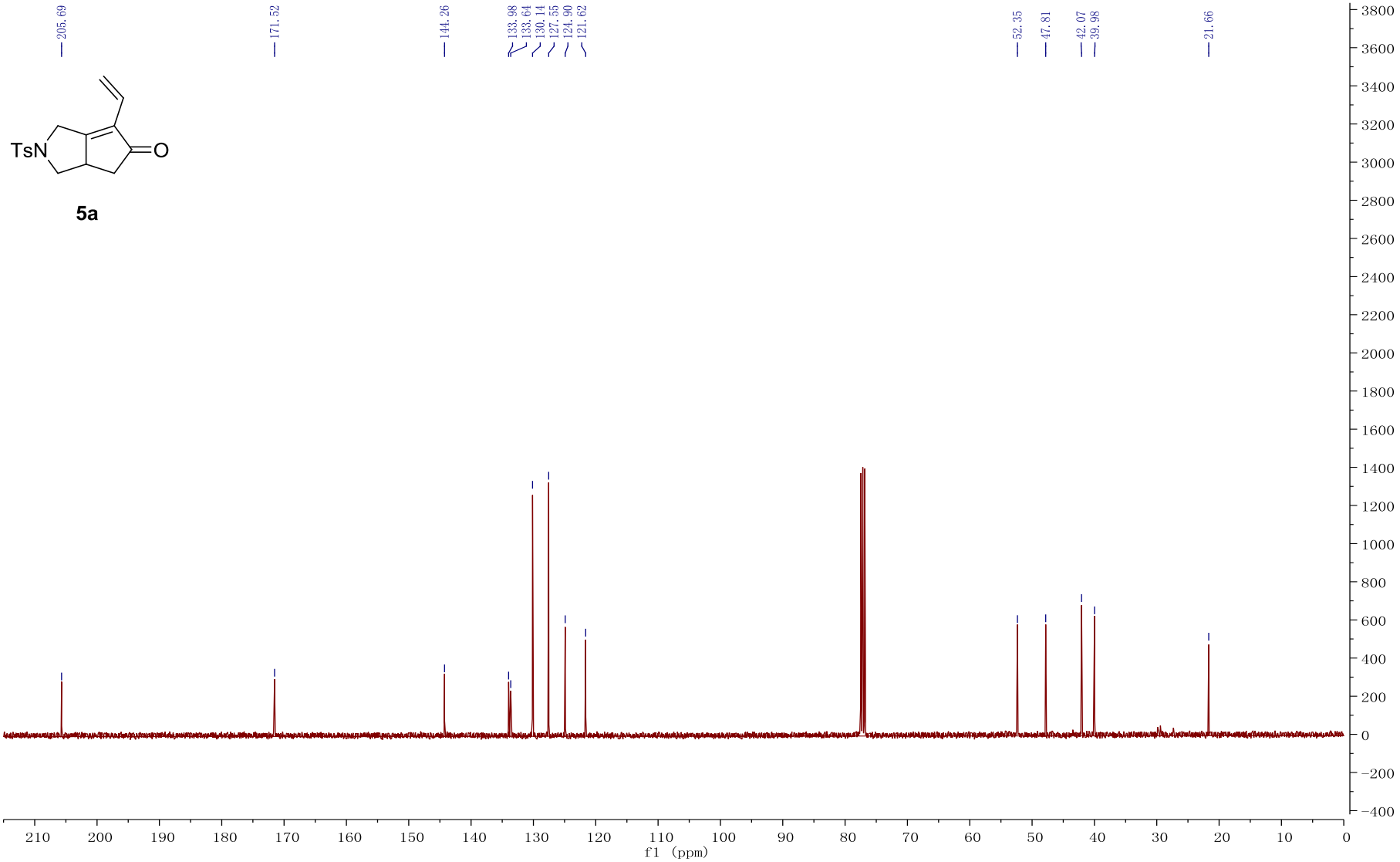

7.74
7.72
7.62
7.61
7.57
7.55
7.43
7.43
7.42
7.41
7.40
7.39
7.29
7.29
7.27
7.27
7.16
7.14
6.73
6.65
6.63
5.87
5.85
5.78
4.64
4.61
3.29
3.26
2.29
2.28
2.27
2.26
2.25
2.24
2.23
2.22
2.20
2.20
2.19
2.16
2.15
2.11
2.00
1.99
1.98
1.97
1.96
1.95
1.92
TsN
4l
1.00
1.01
1.00
3.04
1.01
2.00
1.01
1.01
0.98
1.00
1.00
1.02
1.01
3.08
3.05
1.07
f1 (ppm)

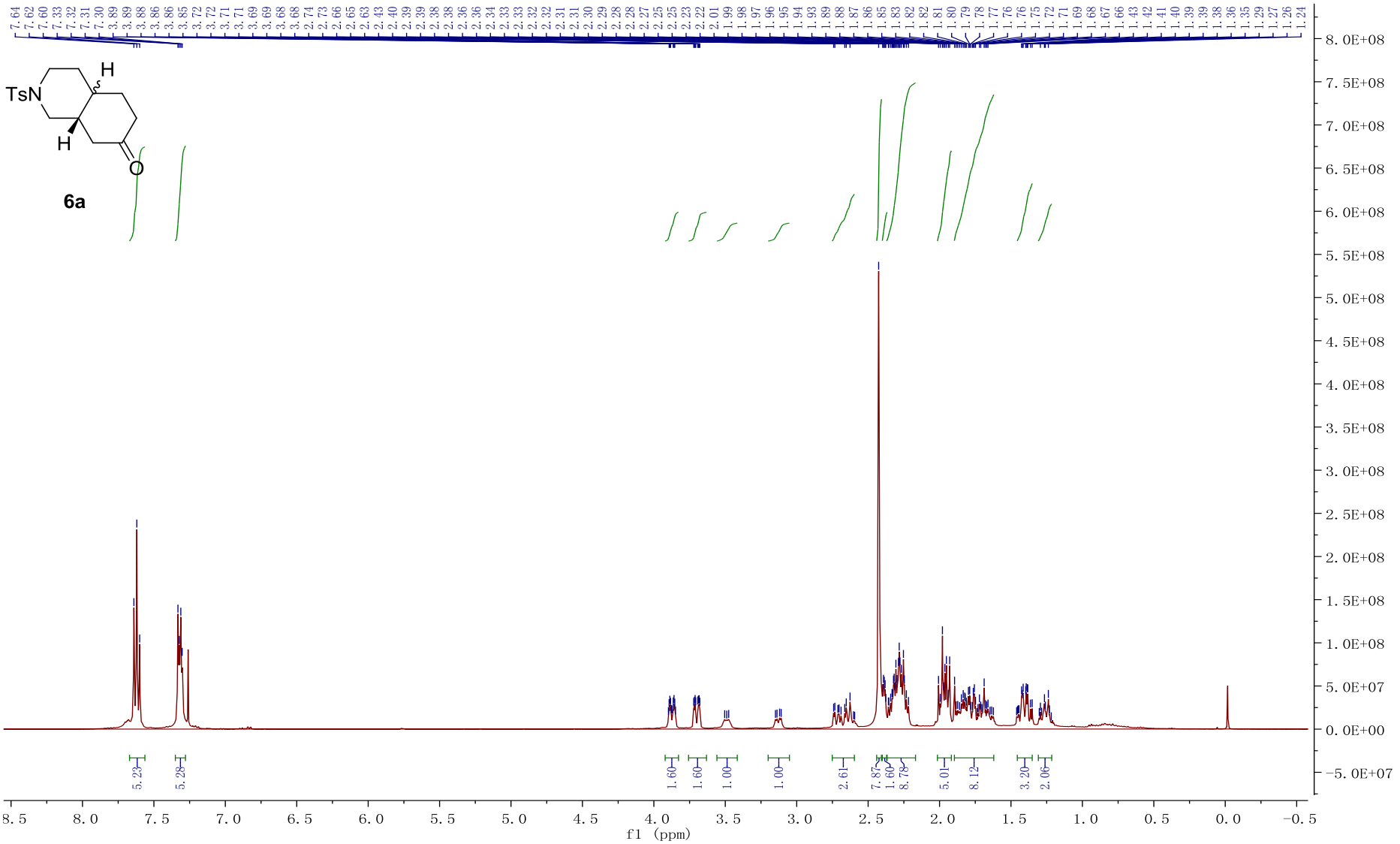

143.17
139.92
138.27
135.67
133.08
132.44
129.14
128.06
127.99
127.35
126.40
125.80
125.74
125.62
125.10
125.04
104.29
55.87
53.06
40.03
30.16
21.49
TsN
4l
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

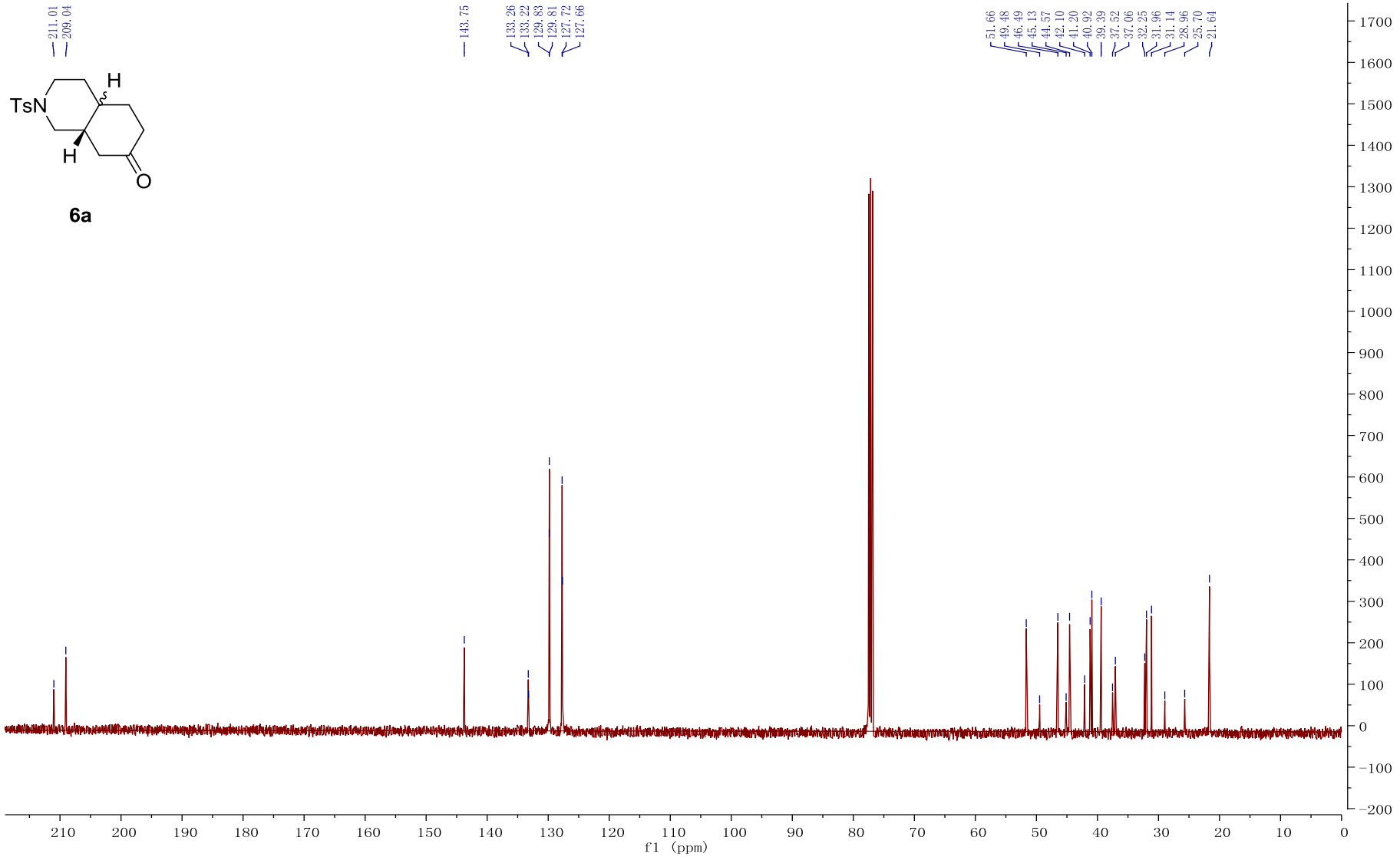

TsN
S
4m
7.53
7.51
7.22
7.20
7.05
7.04
6.78
6.77
6.76
6.75
6.75
6.74
6.74
6.68
6.66
5.68
5.66
5.62
4.49
4.47
3.03
3.00
2.40
2.34
2.32
2.31
2.19
2.17
2.16
1.89
1.89
1.88
1.86
1.86
1.86
1.83
2.00
2.05
1.00
2.02
1.00
1.01
1.00
1.01
1.07
3.07
1.06
1.02
1.03
f1 (ppm)

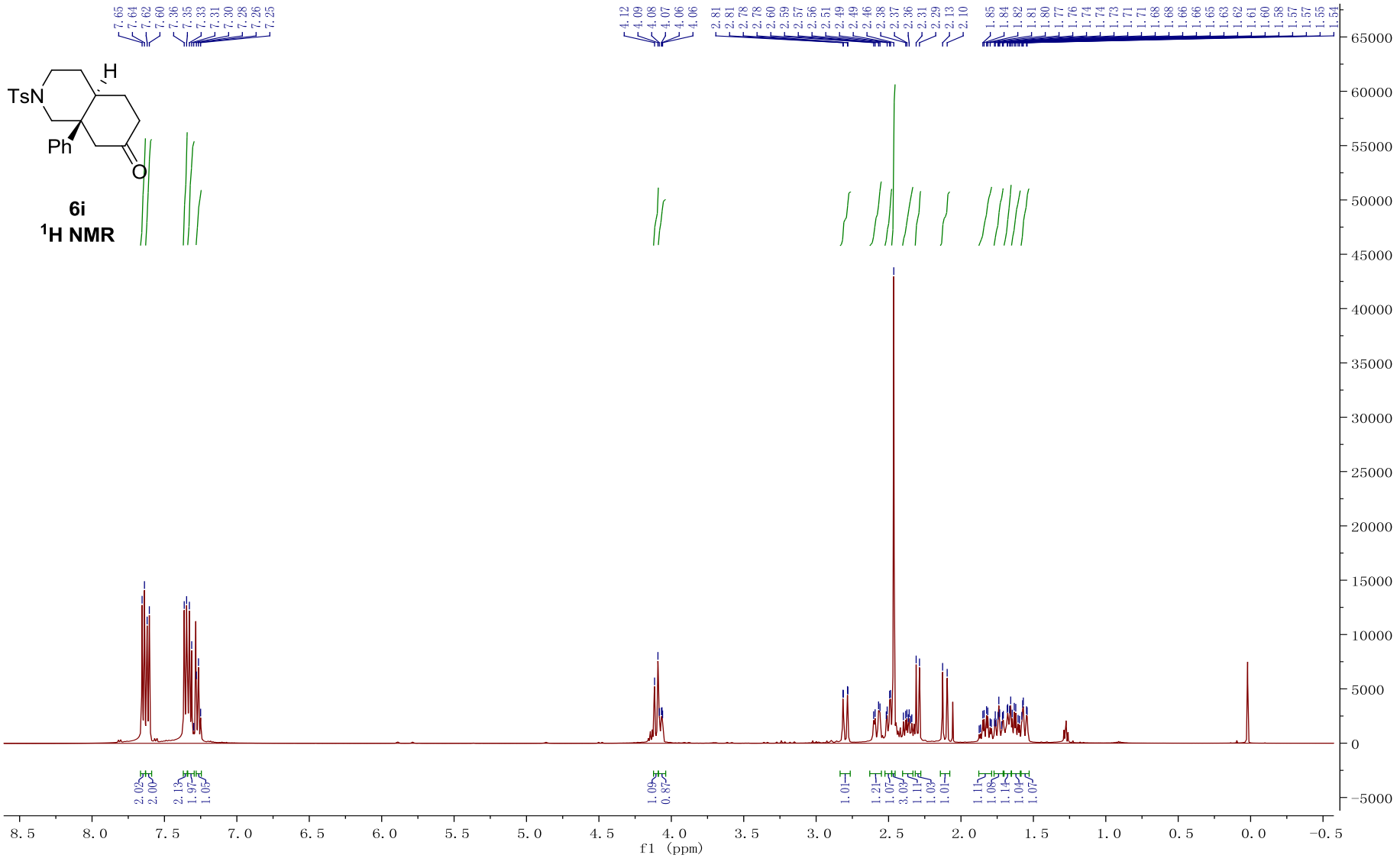

147.69
143.75
139.15
135.50
129.84
127.04
126.66
126.15
124.04
123.89
123.62
103.55
55.64
50.62
40.47
30.42
21.66
TsN
S
4m
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

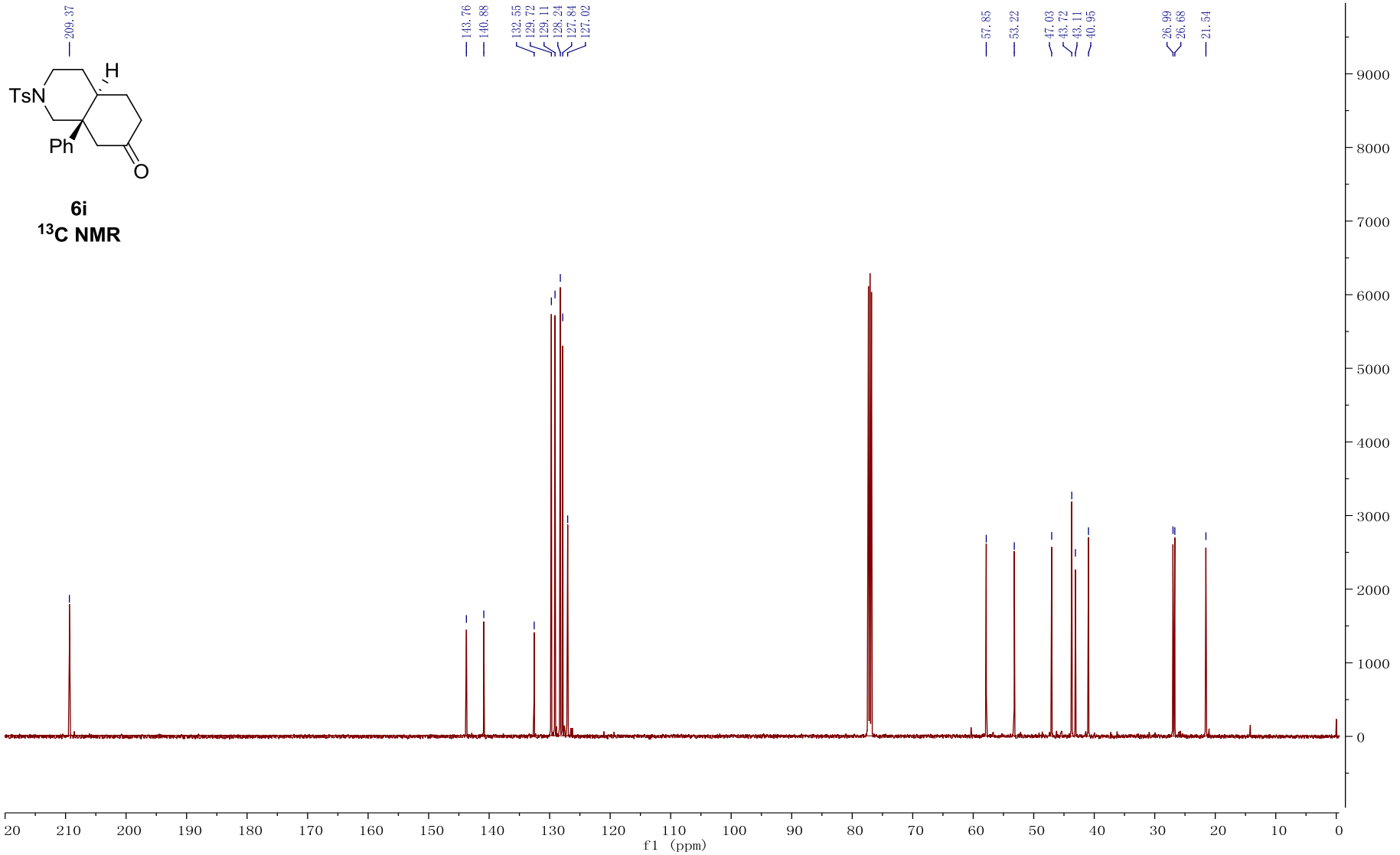

TsN
O
5a
7.73
7.71
7.34
7.32
6.32
6.29
6.28
6.25
5.75
5.70
5.45
5.43
4.41
4.36
4.07
4.04
4.03
4.02
3.99
3.10
3.09
2.63
2.61
2.58
2.55
2.52
2.42
2.10
2.07
2.06
2.05
2.09
0.97
1.00
1.03
1.01
2.04
1.01
1.01
1.00
3.06
1.10
f1 (ppm)

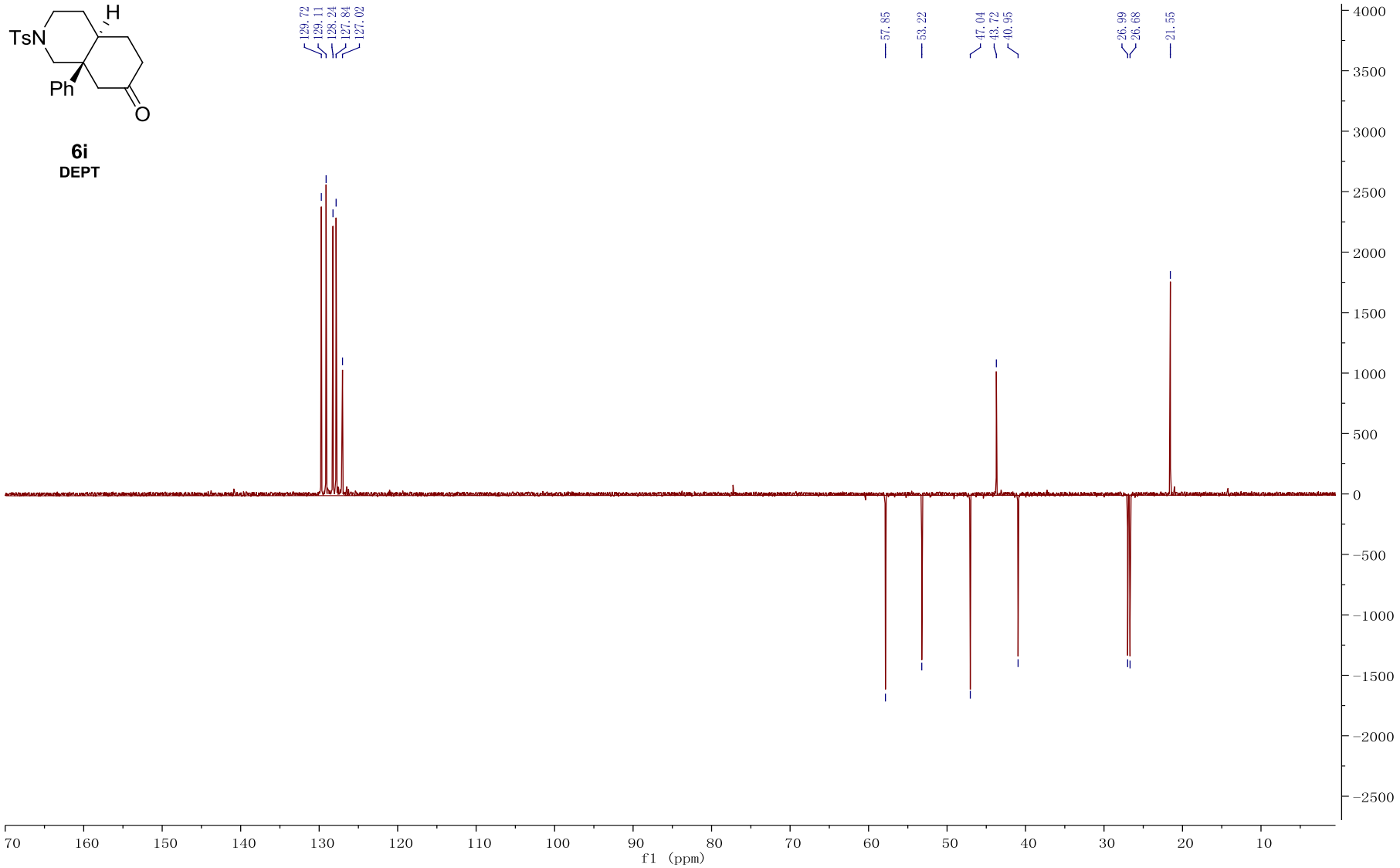

205.69
171.52
144.26
133.98
133.64
130.14
127.55
124.90
121.62
52.35
47.81
42.07
39.98
21.66
TsN
O
5a
f1 (ppm)

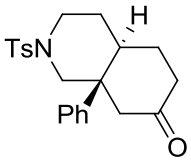

TsN
H
H
O
6a
f1 (ppm)


211.01
209.04
143.75
133.26
133.22
129.83
129.81
127.72
127.66
51.66
49.48
46.49
45.13
44.57
42.10
41.20
40.92
39.39
37.52
37.06
32.25
31.96
31.14
28.96
25.70
21.64
TsN
H
H
O
6a
f1 (ppm)


TsN
H
Ph
O
6i
1H NMR
f1 (ppm)

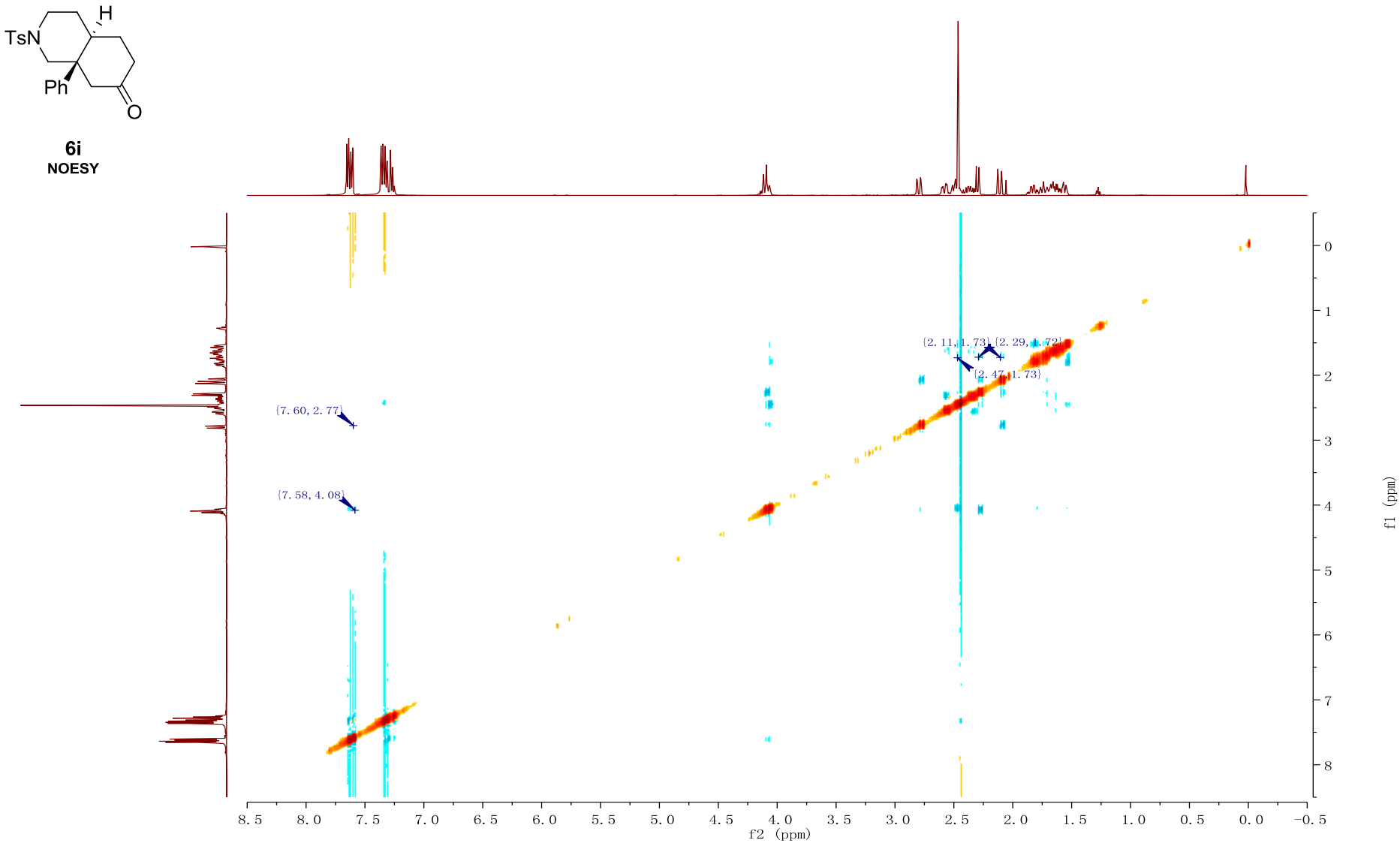

209.37
143.76
140.88
132.55
129.72
129.11
128.24
127.84
127.02
57.85
53.22
47.03
43.72
43.11
40.95
26.99
26.68
21.54
TsN
H
Ph
O
6i
13C NMR
f1 (ppm)

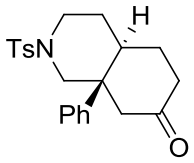

TsN
H
Ph
O
6i
DEPT
129.72
129.11
128.24
127.84
127.02
57.85
53.22
47.04
43.72
40.95
26.99
26.68
21.55
4000
3500
3000
2500
2000
1500
1000
500
0
−500
−1000
−1500
−2000
−2500
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


TsN
H
Ph
O

6i
COSY

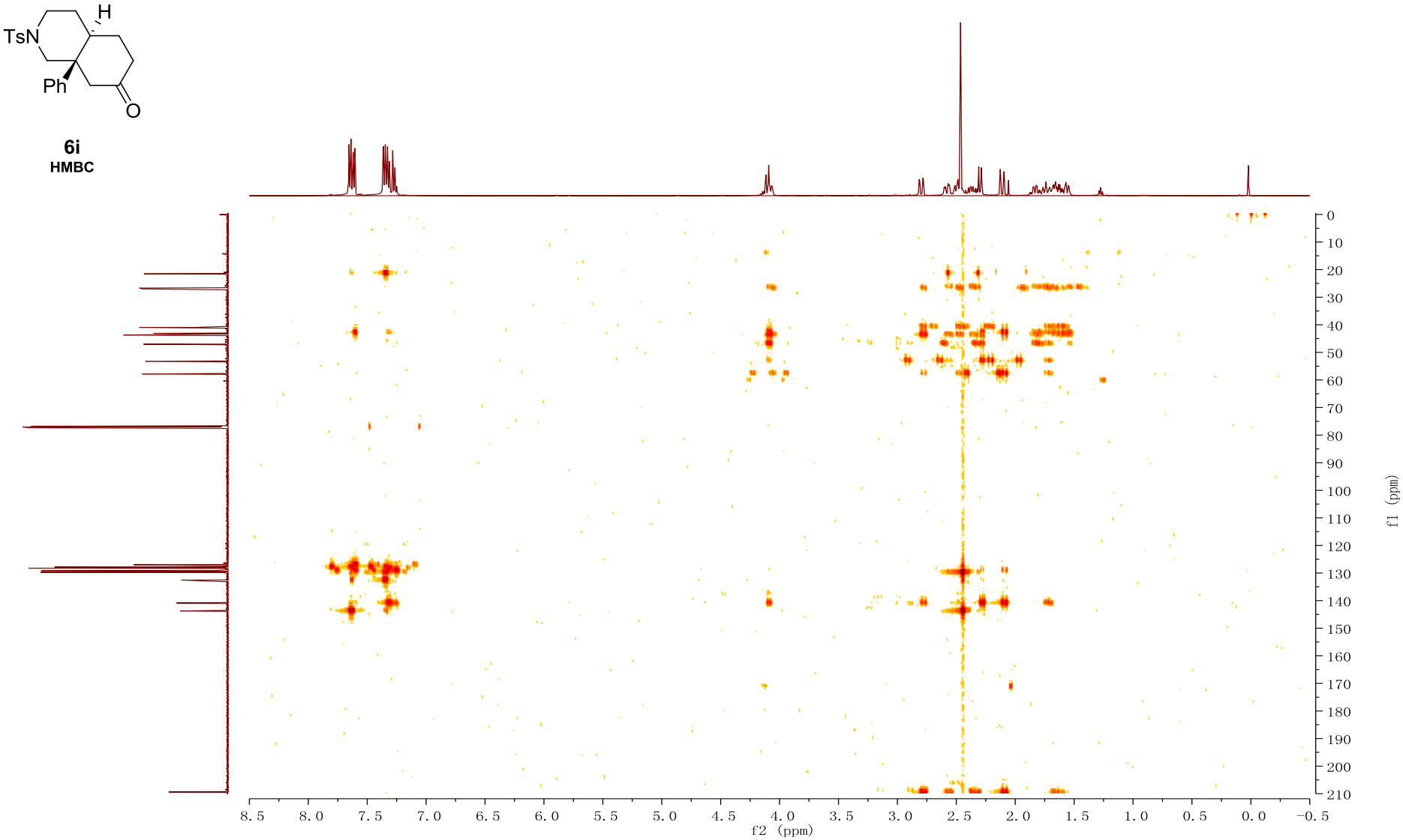
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)

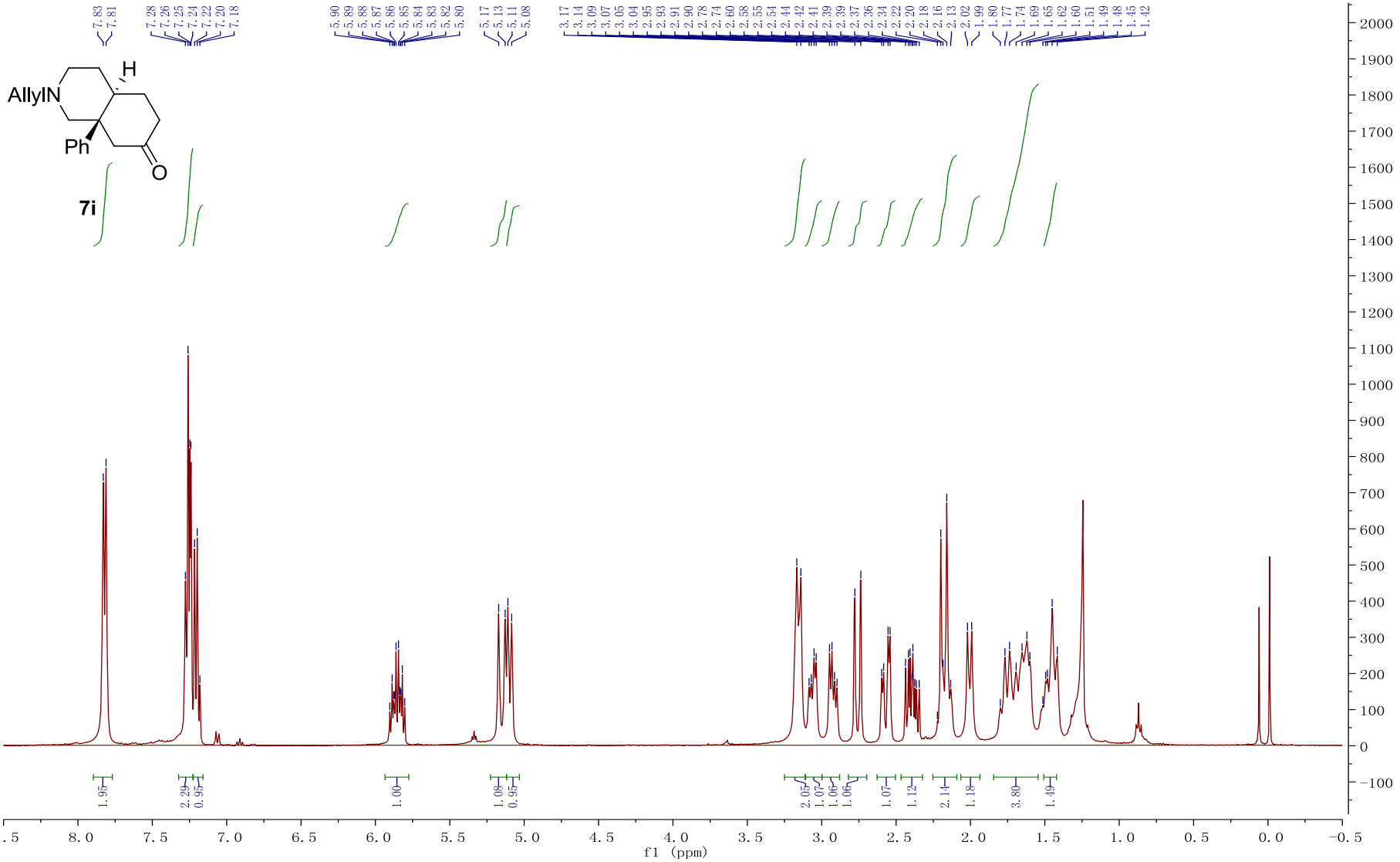

TsN
H
Ph
O
6i
NOESY
{7.60, 2.77}
{7.58, 4.08}
{2.11, 1.73}
{2.29, 1.72}
{2.47, 1.73}
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f2 (ppm)
0 1 2 3 4 5 6 7 8
f1 (ppm)

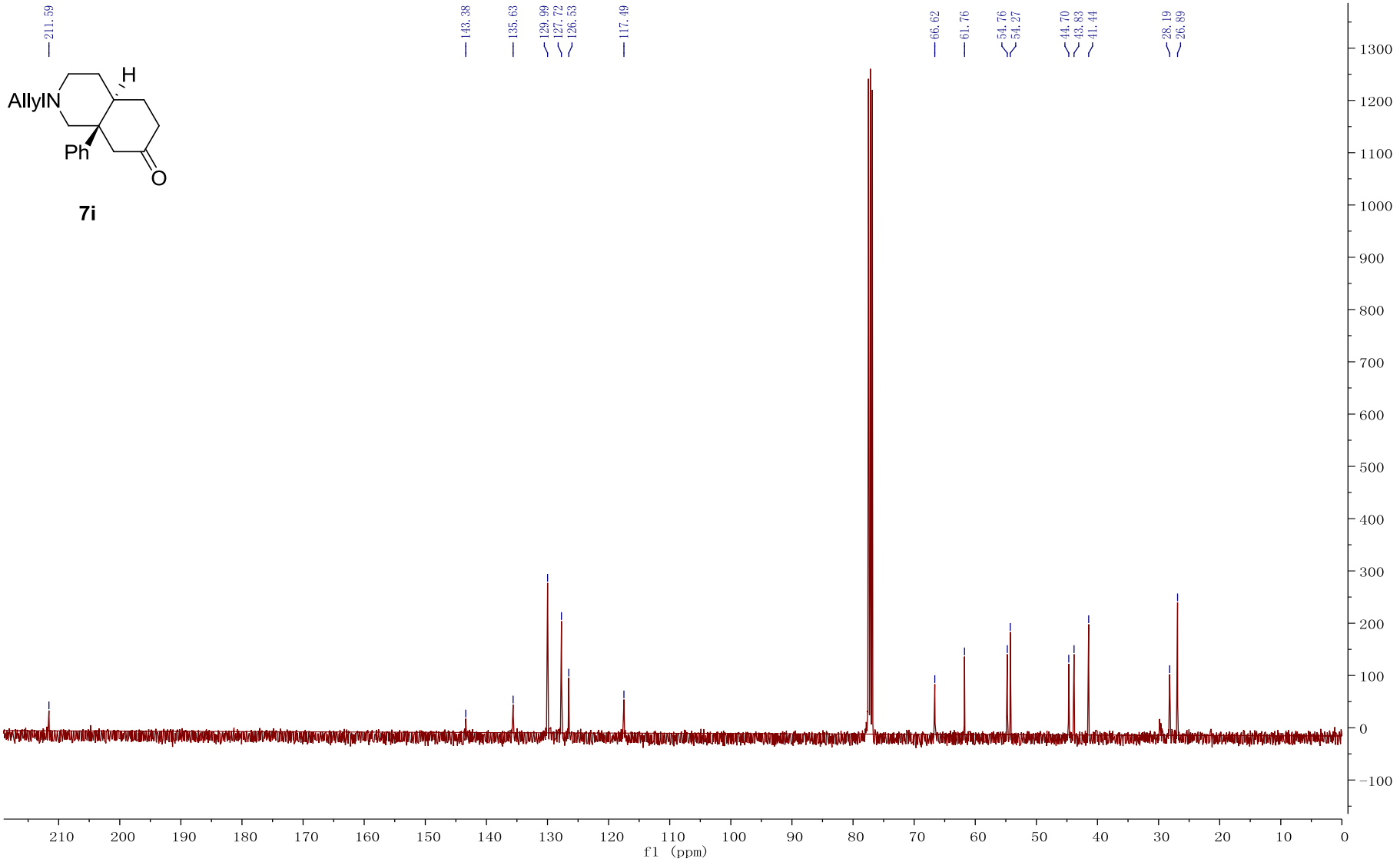

H
TsN
Ph
O

6i
HSQC

0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)


TsN
H
Ph
O
6i
HMBC
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f2 (ppm)
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210
f1 (ppm)


AllylN
H
Ph
O
7i
f1 (ppm)


211.59
143.38
135.63
129.99
127.72
126.53
117.49
66.62
61.76
54.76
54.27
44.70
43.83
41.44
28.19
26.89
AllylN
H
Ph
O
7i
f1 (ppm)