Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

(3+2)-Annulation of 1,3-*N*,*Si*-tetraorganosilane Reagents $TsHNCH_2SiBnR^1R^2$ with Benzyne for Efficient Synthesis of 3-Silaindolines

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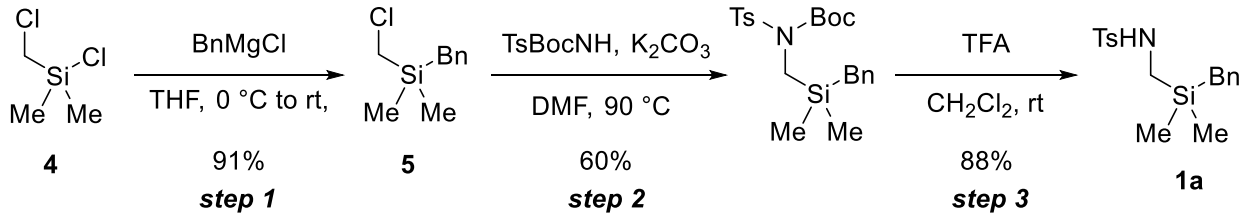
1. General Information

Commercial reagents were used without any purification. Chloro(chloromethyl)dimethylsilane, Benzylmagnesium chloride, Cs_2CO_3 and 18-crown-6 were purchased from Adamas-*beta*, *tert*-butyl tosylcarbamate was purchased from Energy Chemicals. Other reagents were used as purchased from J&K, Aldrich, Adamas-*beta*, Alfa Aesar or Energy Chemicals reagent suppliers. Aryne precursors were purchased for those are commercially available, or were prepared according to literatures for those are known compounds, or were synthesized as new compounds. DMF and CH_2Cl_2 were distilled from CaH_2. Toluene, DME and THF were distilled from sodium. Inert atmosphere techniques were carried out through Schlenk system and Standard Glovebox (purchased from Vigor Gas Purification Technologies (Suzhou) Co. Ltd.). Reactions were monitored by TLC which was performed on glass-backed silica plates and visualized using UV, $KMnO_4$ stains. Column chromatography was performed using silica gel (200-300 mesh or 300-400 mesh, purchased from Yantai Jiangyou Silica Gel Development Co. Ltd.) eluting with EtOAc/petroleum ether. Melting point were recorded at WRX-4 Melting-point Apparatus (purchased from Shanghai Yice Apparatus & Equipments Co. Lit.). ^{1}H NMR spectra were recorded at 400 MHz (Varian and Bruker) or 600 MHz (Agilent), ^{13}C NMR spectra were recorded at 100 MHz (Bruker) and 150 MHz (Agilent), and ^{29}Si NMR spectra were recorded at 400 MHz (Bruker) using $CDCl_3$ (except where noted) with TMS or residual solvent as standard. Infrared spectra were obtained using PerkinElmer Spectrum Two FTIR Spectrometer. High-resolution mass spectral analyses performed on Sciex Q-TOF or ThermoFisherScienti Orbitrap in positive or negative mode. X-ray diffraction experiment was carried out on Xcalibur E and the data obtained was deposited at the Cambridge Crystallographic Data Centre. Enantiomeric excess was determined by HPLC (Agilent Technologies: 1260 Infinity II) analysis on chiral column. Specific optical rotation was measured on Chiralpak® AS-H column. All spectral data obtained for new compounds are reported here.

2. Synthesis of 1,3-N, Si-Reagent 1

N-((benzyldimethylsilyl)methyl)-4-methylbenzenesulfonamide **(1a)**



Step 1: To a solution of chloro(chloromethyl)dimethylsilane **4** (5.00 g, 34.94 mmol) in anhydrous THF (50 mL) at 0 °C under argon atmosphere was added benzylmagnesium chloride (40.89 mL of 1 M solution in THF, 40.89 mmol) dropwise over 1 h. Care was taken to maintain the temperature below 10 °C until all the reagents were added. After addition was completed, the reaction mixture was warmed up to room temperature and stirred overnight before quenching with sat. aq. NH_4Cl and extracting with Et_2O (3 × 50 mL). The combined organic layers were washed with sat. aq. NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (eluent: petroleum ether) to give the product benzyl(chloromethyl)-dimethyllsilane **5** as a colorless oil (6.32 g, 91%).

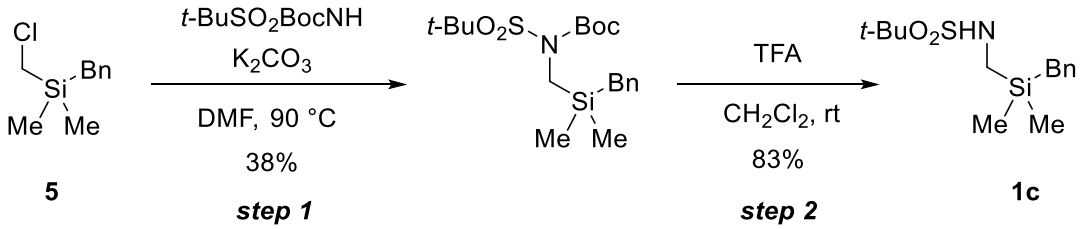
Step 2: To a suspension of TsBocNH (12.94 g, 47.69 mmol, 1.5 equiv.) and K_2CO_3 (6.59 g, 47.69 mmol, 1.5 equiv.) in DMF (60 mL) was added benzyl(chloromethyl)dimethylsilane **5** (6.32 g, 31.80 mmol) at room temperature. The resulting mixture was stirred at 90 °C for 6 h. The reaction was cooled to room temperature and quenched by sat. aq. NH_4Cl. The mixture was extracted with EtOAc (3 × 50 mL). The combined organic phases were washed with sat. aq. NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (eluent: EtOAc/ petroleum ether = 1/10) to give the product *tert*-butyl ((benzyldimethylsilyl)methyl)(tosyl)carbamate as a white solid (8.27 g, 60%).

Step 3: To a solution of *tert*-butyl ((benzyldimethylsilyl)methyl)(tosyl)carbamate (8.27 g, 19.07 mmol) in CH_2Cl_2 (80 mL) was added TFA (21.75 g, 190.71 mmol, 10.0 equiv.) dropwise at room temperature. The reaction was stirred at room temperature for 1 h before quenching with sat. aq. $NaHCO_3$ and stirring at room temperature for additional 10 min. The resulting mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were washed with sat. aq. NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (EtOAc/ petroleum ether = 1/10) to give the product **1a** as a white solid (5.6 g, 88%).

- R_f = 0.5 (EtOAc/Petroleum Ether = 1/4).
- mp: 113.5 – 115.6 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 2H), 7.09 (t, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 7.2 Hz, 2H), 4.12 (t, *J* = 6.0 Hz, 1H), 2.44 (s, 3H), 2.28 (d, *J* = 6.0 Hz, 2H), 2.12 (s, 2H), 0.04 (s, 6H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 138.6, 135.3, 129.6, 128.6, 127.9, 127.5, 124.6, 30.8, 24.0, 21.5, -4.7.
- ^{29}Si NMR (400 MHz, $CDCl_3$) δ -1.94.

- IR (neat) cm^{-1} 3272, 3006, 1321, 1275, 1260, 1160, 849, 750.
- HRMS calcd for $C_{17}H_{24}NO_2SSi$ $(M+H)^+$: 334.1292, found 334.1292.

N-((benzyldimethylsilyl)methyl)-2-methylpropane-2-sulfonamide **(1c)**



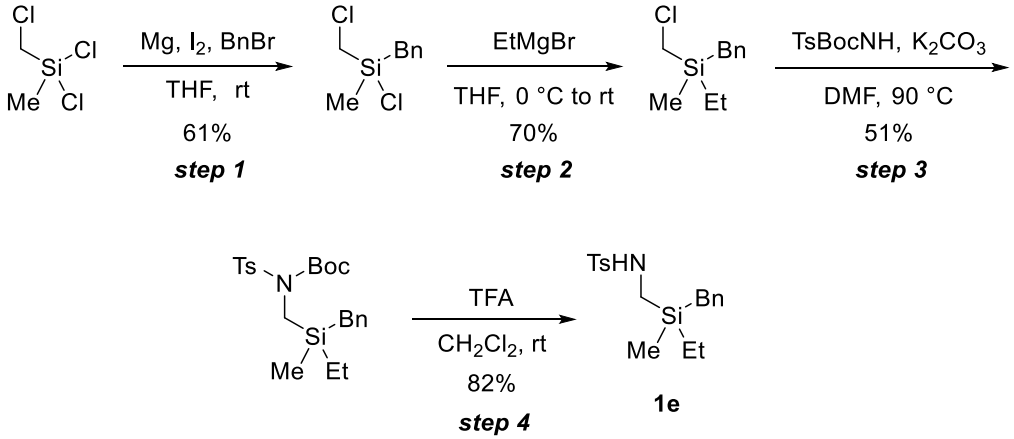
1c was prepared according to the last two steps used for preparation of **1a**.

Step 1: Benzyl(chloromethyl)dimethylsilane **5** (1.90 g, 9.56 mmol), *t*-$BuSO_2BocNH$ (3.40 g, 14.34 mmol, 1.5 equiv.) and K_2CO_3 (1.98 g, 14.34 mmol, 1.5 equiv.) in DMF (20 mL) at 90 °C for 3 h gave *tert*-butyl ((benzyldimethylsilyl)methyl)(*tert*-butylsulfonyl)carbamate as a pale yellow oil (1.45 g, 38%).

Step 2: *Tert*-butyl ((benzyldimethylsilyl)methyl)(*tert*-butylsulfonyl)carbamate (1.45 g, 3.63 mmol), TFA (4.14 g, 36.28 mmol, 10.0 equiv.) in CH_2Cl_2 (15 mL) at room temperature for 1 h afforded **1c** as a white solid (905 mg, 83%).

- mp: 60.4 – 62.0 °C.
- R_f = 0.6 (EtOAc/Petroleum Ether = 1/5).
- ^1H NMR (400 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.6 Hz, 2H), 7.00 (t, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 2H), 3.37 (d, *J* = 6.0 Hz, 1H), 2.57 (d, *J* = 6.0 Hz, 2H), 2.08 (s, 2H), 1.25 (s, 9H), 0.00 (s, 6H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 128.6, 127.9, 124.6, 60.3, 33.2, 24.5, 24.2, -4.7.
- IR (neat) cm^{-1} 3291, 3024, 2956, 1738, 1599, 1493, 1298, 1248, 1056, 825.
- HRMS calcd for $C_{14}H_{26}NO_2SSi$ $(M+Na)^+$: 322.1267, found 322.1257.

N-((benzyl(ethyl)(methyl)silyl)methyl)-4-methylbenzenesulfonamide **(1e)**



Step 1: To a suspension of magnesium (1.10 g, 45.08 mmol, 3.0 equiv.) and a grain of I_2 in anhydrous THF (5 mL) was added a small amount (about 20 drops) solution of the benzyl bromide in THF by syringe at room temperature under argon atmosphere. The reaction was initiated and heated to reflux with addition the rest of the benzyl bromide solution (2.57 g, 15.03 mmol, 1.0 equiv. in 20 mL THF)

dropwise over 30 min. The resulting mixture was stirred at room temperature for additional 1 h. The resulting Grignard reagent solution, which was separated from residual magnesium turnings by decantation, was added dropwise within 90 min to a solution of dichloro(chloromethyl)(methyl)silane (2.46 g, 5.01 mmol, 1.0 equiv.) in anhydrous THF (20 mL) at 0 °C under argon atmosphere. After addition was completed, the reaction mixture was warmed up to room temperature and stirred for 24 h. The reaction mixture was concentrated under reduced pressure, causing a precipitation. The precipitate was separated by decantation and washed with *n*-hexane (3 × 30 ml), and all organic solutions were combined. The solvent was removed as described above, and the crude product was isolated by distillation *in vacuo* (b.p.: 70 °C/0.8mmHg) to afford the benzylchloro(chloromethyl)-(methyl)silane as a colorless oil (2.01 g, 61%).

1e was then prepared from benzylchloro(chloromethyl)(methyl)silane according to the procedure as that used for **1a**.

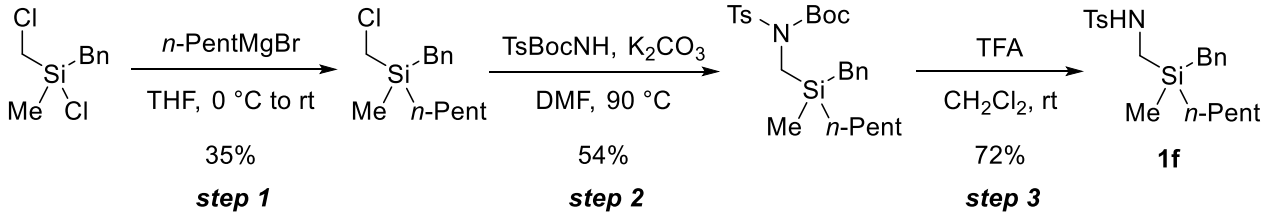
Step 2: Benzylchloro(chloromethyl)(methyl)silane (2.01 g, 9.12 mmol), ethylmagnesium bromide (10.04 mL, 1 M in THF, 1.1equiv.) in anhydrous THF (20 mL) at room temperature under argon overnight afforded benzyl(chloromethyl)(ethyl)(methyl)silane as a colorless oil (1.36 g, 70%).

Step 3: Benzyl(chloromethyl)(ethyl)(methyl)silane (1.36 g, 6.39 mmol), TsBocNH (2.60 g, 9.59 mmol, 1.5 equiv.), K_2CO_3 (1.32 g, 9.59 mmol, 1.5 equiv.) in DMF (10 mL) at 90 °C for 6 h gave *tert*-butyl ((benzyl(ethyl)(methyl)silyl)methyl)(tosyl)carbamate as a colorless oil (1.46 g, 51%).

Step 4: *Tert*-butyl ((benzyl(ethyl)(methyl)silyl)methyl)(tosyl)carbamate (1.46 g, 3.26 mmol), TFA (3.72 g, 32.61 mmol, 10.0 equiv.) in CH_2Cl_2 (15 mL) at room temperature for 1 h afforded **1e** as white solid (927 mg, 82%).

- R_f = 0.5 (EtOAc/Petroleum Ether = 1/4).
- mp : 92.0 – 94.0 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 7.6 Hz, 2H), 7.09 (t, *J* = 7.2 Hz, 1H), 6.90 (d, *J* = 7.2 Hz, 2H), 3.84 (t, *J* = 6.4 Hz, 1H), 2.45 (s, 3H), 2.28 (d, *J* = 6.0 Hz, 2H), 2.11 (s, 2H), 0.90 (t, *J* = 8.0 Hz, 3H), 0.56 (q, *J* = 8.0 Hz, 2H), 0.01 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 138.7, 135.2, 129.6, 128.6, 127.8, 127.5, 124.5, 29.3, 22.4, 21.5, 6.9, 3.9, -6.9.
- IR (neat) cm^{-1} 3273, 2955, 1958, 1492, 1451, 1320, 1275, 1260, 1158, 1055, 750.
- HRMS calcd for $C_{18}H_{25}NNaO_2SSi$ $(M+Na)^+$: 370.1267, found 370.1263.

N-((benzyl(methyl)(pentyl)silyl)methyl)-4-methylbenzenesulfonamide **(1f)**



1f was prepared according to the procedure as that used for **1a**.

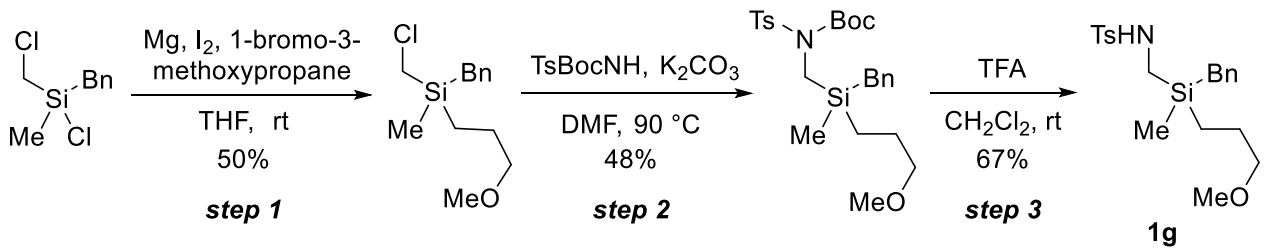
Step 1: Benzylchloro(chloromethyl)(methyl)silane (2.00 g, 9.12 mmol), pentylmagnesium bromide (10.04 mL, 1.0 M in THF, 1.1 equiv.) in anhydrous THF (20 mL) at room temperature under argon atmosphere overnight gave benzyl(chloromethyl)(methyl)(pentyl)silane as colorless oil (816 mg, 35%).

Step 2: Benzyl(chloromethyl)(methyl)(pentyl)silane (816 mg, 3.20 mmol), TsBocNH (1.30 g, 4.8 mmol, 1.5 equiv.), K_2CO_3 (663 mg, 4.80 mmol, 1.5equiv.) in DMF (10 mL) at 90 °C for 6 h gave the *tert*-butyl ((benzyl(methyl)(pentyl)silyl)methyl)(tosyl)carbamate as a colorless oil (848 mg, 54%).

Step 3: *Tert*-butyl ((benzyl(methyl)(pentyl)silyl)methyl)(tosyl)carbamate (848 mg, 1.78 mmol), TFA (2.03 g, 17.83 mmol, 10.0 equiv.) in CH_2Cl_2 (10 mL) at room temperature for 1 h afforded **1f** as white solid (500 mg, 72%).

- R_f = 0.6 (EtOAc/Petroleum Ether = 1/4).
- mp: 90.2 – 95.6 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 7.6 Hz, 2H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 7.2 Hz, 2H), 3.89 (t, *J* = 6.0 Hz, 1H), 2.44 (s, 3H), 2.28 (d, *J* = 6.0 Hz, 2H), 2.11 (s, 2H), 1.40 – 1.10 (m, 6H), 0.86 (t, *J* = 6.4 Hz, 3H), 0.54 (t, *J* = 4.8 Hz, 2H), 0.01 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 138.7, 135.2, 129.6, 128.6, 127.8, 127.5, 124.6, 35.6, 29.7, 22.9, 22.8, 22.2, 21.5, 13.9, 12.0, -6.4.
- IR (neat) cm^{-1} 3277, 2922, 1452, 1323, 1275, 1260, 1159, 750.
- HRMS calcd for $C_{21}H_{32}NO_2SSi$ $(M+H)^+$: 390.1918, found 390.1915.

N-((benzyl(3-methoxypropyl)(methyl)silyl)methyl)-4-methylbenzenesulfonamide **(1g)**



Step 1: To a suspension of magnesium (665 mg, 27.37 mmol, 3.0 equiv.) and a grain of I_2 in anhydrous THF (7 mL) was added a small amount (about 20 drops) solution of the 1-bromo-3-methoxypropane in THF by syringe at room temperature under argon atmosphere. The reaction was initiated and heated to reflux with addition the rest of the 1-bromo-3-methoxypropane solution (1.54 g, 10.04 mmol, 1.1 equiv. in 14 mL THF) dropwise over 30 min. The resulting mixture was stirred at room temperature for additional 1 h. The resulting Grignard reagent solution, which was separated from residual magnesium turnings by decantation, was added dropwise within 90 min to a solution of dichloro(chloromethyl)(methyl)silane (2.00 g, 9.12 mmol, 1.0 equiv.) in anhydrous THF (20 mL) at 0 °C under argon atmosphere. After addition was completed, the reaction mixture was warmed up to room temperature and stirred for 24 h before quenching with sat. aq. NH_4Cl and extracting with Et_2O (3 × 30 mL). The combined organic layers were washed with sat. aq. NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel flash column

chromatography (eluent: EtOAc/petroleum ether = 1/20) to give the product benzyl(chloromethyl)(3-methoxypropyl)(methyl)silane as colorless oil (1.17 g, 50%).

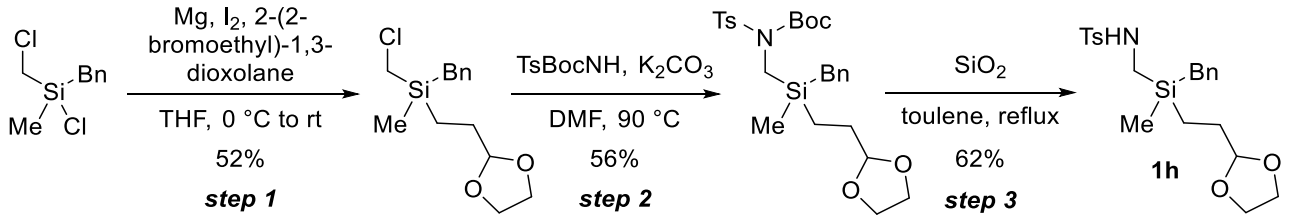
1g was prepared from benzyl(chloromethyl)(3-methoxypropyl)(methyl)silane according to the procedure as that used for **1a**.

Step 2: Benzyl(chloromethyl)(3-methoxypropyl)(methyl)silane (1.17 g, 4.55 mmol), TsBocNH (1.85 g, 6.83 mmol, 1.5 equiv.), K_2CO_3 (944 mg, 6.83 mmol, 1.5 equiv.) in DMF (10 mL) at 90 °C for 6 h gave the *tert*-butyl ((benzyl(3-methoxypropyl)(methyl)silyl)methyl)(tosyl)carbamate as colorless oil (1.07 g, 48%).

Step 3: *Tert*-butyl ((benzyl(3-methoxypropyl)(methyl)silyl)methyl)(tosyl)carbamate (1.07 g, 2.24 mmol), TFA (2.55 g, 22.40 mmol, 10.0 equiv.) in CH_2Cl_2 (10 mL) at room temperature for 1 h afforded **1g** as white solid (588 mg, 67%).

- R_f = 0.2 (EtOAc/Petroleum Ether = 1/4).
- mp: 94.5 – 99.2 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 2H), 7.09 (t, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 7.2 Hz, 2H), 4.37 (t, *J* = 6.0 Hz, 1H), 3.33 (s, 3H), 3.30 (t, *J* = 6.4 Hz, 2H), 2.44 (s, 3H), 2.34 – 2.21 (m, 2H), 2.12 (dd, *J* = 17.2, 14.0 Hz, 2H), 1.64 – 1.38 (m, 2H), 0.80 – 0.46 (m, 2H), 0.00 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 138.6, 135.3, 129.5, 128.6, 127.9, 127.5, 124.6, 74.8, 58.5, 29.6, 23.3, 22.8, 21.5, 8.4, -6.3.
- IR (neat) cm^{-1} 3278, 2925, 1598, 1493, 1451, 1322, 1260, 1275, 1159, 1094, 750.
- HRMS calcd for $C_{20}H_{30}NO_3SSi$ $(M+H)^+$: 392.1710, found 392.1715.

N-(((2-(1,3-dioxolan-2-yl)ethyl)(benzyl)(methyl)silyl)methyl)-4-methylbenzenesulfonamide **(1h)**



1h was prepared according to the procedure as that used for **1g**.

Step 1: Magnesium (665 mg, 27.37 mmol, 3.0 equiv.), a grain of I_2, 2-(2-Bromoethyl)-1,3-dioxolane (1.82 g, 10.04 mmol, 1.1 equiv.), benzylchloro(chloromethyl)(methyl)silane (2.00 g, 9.12 mmol, 1.0 equiv.) in anhydrous THF at room temperature for 24 h gave (2-(1,3-dioxolan-2-yl)ethyl)benzyl)-(chloromethyl)(methyl)silane as a colorless oil (1.35 g, 52%).

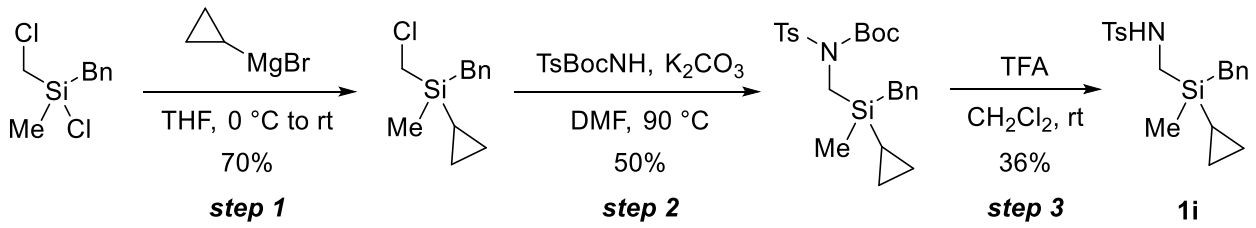
Step 2: (2-(1,3-Dioxolan-2-yl)ethyl)benzyl)(chloromethyl)(methyl)silane (1.35 g, 4.74 mmol), TsBocNH (1.93 g, 7.11 mmol, 1.5 equiv.), K_2CO_3 (983 mg, 7.11 mmol, 1.5 equiv.) in DMF (10 mL) at 90 °C for 6 h gave *tert*-butyl (((2-(1,3-dioxolan-2-yl)ethyl)(benzyl)(methyl)silyl)methyl)tosyl)-carbamate as a colorless oil (1.38 g, 56%).

Step 3: To a solution of *tert*-butyl (((2-(1,3-dioxolan-2-yl)ethyl)(benzyl)(methyl)silyl)methyl)(tosyl)-carbamate (1.38 g, 2.66 mmol) in toluene (10 mL) was added SiO_2 (1.60 g, 26.55 mmol, 10.0 equiv.).

The reaction mixture was refluxed at 130 °C for 2 h. After the reaction was completed, the mixture was concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (eluent: EtOAc/petroleum ether = 1/4) to give the product **1h** as a white solid (688 mg, 62%).

- R_f = 0.2 (EtOAc/Petroleum Ether = 1/4).
- mp: 79.4 – 83.7 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 7.1 Hz, 2H), 4.78 (t, *J* = 4.4 Hz, 1H), 4.30 (t, *J* = 6.2 Hz, 1H), 4.14 – 3.91 (m, 2H), 3.90 – 3.75 (m, 2H), 2.44 (s, 3H), 2.35 – 2.22 (m, 2H), 2.13 (dd, *J* = 17.2, 14.0 Hz, 2H), 1.68 – 1.53 (m, 2H), 0.78 – 0.60 (m, 2H), 0.01 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 138.4, 135.3, 129.5, 128.6, 127.9, 127.5, 124.6, 105.2, 64.9, 29.5, 27.3, 22.7, 21.5, 5.4, -6.3.
- IR (neat) cm^{-1} 1275, 750.
- HRMS calcd for $C_{21}H_{29}NNaO_4SSi$ $(M+Na)^+$: 442.1478, found 442.1477.

N-((benzyl(cyclopropyl)(methyl)silyl)methyl)-4-methylbenzenesulfonamide **(1i)**



1i was prepared according to the procedure as that used for **1e**.

Step 1: Benzylchloro(chloromethyl)(methyl)silane (2.00 g, 9.12 mmol), cyclopropylmagnesium bromide (10.04 mL, 1.0 M in THF, 1.1 equiv.) in anhydrous THF (20 mL) at room temperature under argon atmosphere overnight gave benzyl(chloromethyl)(cyclopropyl)(methyl)silane as colorless oil (1.43 g, 70%).

Step 2: Benzyl(chloromethyl)(cyclopropyl)(methyl)silane (1.43 g, 6.36 mmol), K_2CO_3 (1.32 g, 9.54 mmol, 1.5 equiv.), TsBocNH (2.59 g, 9.54 mmol, 1.5 equiv.) in DMF (14 mL) at 90 °C for 6 h gave *tert*-butyl ((benzyl(cyclopropyl)(methyl)silyl)methyl)(tosyl)carbamate as a colorless oil (1.46 g, 50%).

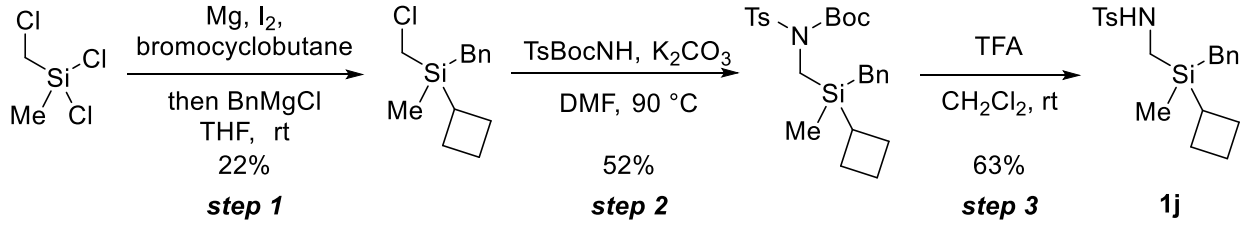
Step 3: *Tert*-butyl ((benzyl(cyclopropyl)(methyl)silyl)methyl)(tosyl)carbamate (1.46 g, 3.18 mmol), TFA (3.62 g, 31.76 mmol, 10.0 equiv.) in CH_2Cl_2 (15 mL) at room temperature for 1 h afforded **1i** as white solid (410 mg, 36%).

- R_f = 0.7 (EtOAc/Petroleum Ether = 1/4).
- mp: 105.9 – 111.9 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 2H), 7.09 (t, *J* = 7.2 Hz, 1H), 6.94 (d, *J* = 7.2 Hz, 2H), 3.92 (t, *J* = 6.4 Hz, 1H), 2.45 (s, 3H), 2.36 – 2.19 (m, 2H), 2.12 (dd, *J* = 16.8, 14.0 Hz, 2H), 0.84 – 0.44 (m, 2H), 0.29 – 0.13 (m, 2H), -0.15 (s, 3H), -0.46 (tt, *J* = 9.6, 6.8 Hz, 1H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 138.5, 135.3, 129.6, 128.5, 128.0, 127.5, 124.6, 29.8, 22.5,

21.5, 1.2, 1.2, -8.2, -8.4.

- IR (neat) cm^{-1} 3275, 3063, 2999, 1598, 1492, 1410, 1320, 1252, 1158, 1093.
- HRMS calcd for $C_{19}H_{26}NO_2SSi$ $(M+H)^+$: 360.1448, found 360.1449.

N-((benzyl(cyclobutyl)(methyl)silyl)methyl)-4-methylbenzenesulfonamide **(1j)**



Step 1: To a suspension of magnesium (540 mg, 22.22 mmol, 1.5 equiv.) and a grain of I_2 in anhydrous THF (7 mL) was added a small amount (about 20 drops) solution of the bromocyclobutane in THF by syringe at ambient temperature under argon atmosphere. The reaction was initiated and heated to reflux with addition the rest of the bromocyclobutane solution (2.00 g, 14.81 mmol, 1.0 equiv. in 14 mL THF) dropwise over 30 min. The resulting mixture was stirred at room temperature for additional 1 h. The resulting Grignard reagent solution, which was separated from residual magnesium turnings by decantation, was added dropwise within 90 min to a solution of dichloro(chloromethyl)(methyl)silane (2.42 g, 14.81 mmol, 1.0 equiv.) at 0 °C under argon. After addition was completed, the reaction mixture was warmed up to room temperature and stirred for 24 h. Then the reaction system was cooled to 0 °C. To the mixture was added benzylmagnesium chloride (17.33 mL, 1.0 M in THF, 1.17 equiv.) dropwise over 1 h. After addition was completed, the reaction mixture was warmed up to room temperature and stirred for 24 h before quenching with sat. aq. NH_4Cl and extracting with Et_2O (3 × 30 mL). The combined organic layers were washed with sat. aq. NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (eluent: petroleum ether) to give the product benzyl(chloromethyl)(cyclobutyl)(methyl)silane as a colorless oil (780 mg, 22%).

1j was prepared from benzyl(chloromethyl)(cyclobutyl)(methyl)silane according to the procedure as that used for **1a**.

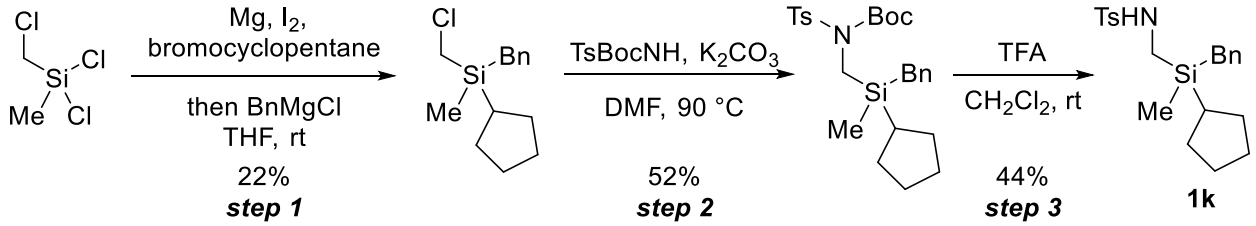
Step 2: Benzyl(chloromethyl)(cyclobutyl)(methyl)silane (780 mg, 3.27 mmol), TsBocNH (1.33 g, 4.90 mmol, 1.5 equiv.), K_2CO_3 (677 mg, 4.90 mmol, 1.5 equiv.) in DMF (10 mL) at 90 °C for 6 h gave *tert*-butyl ((benzyl(cyclobutyl)(methyl)silyl)methyl)(tosyl)carbamate as a colorless oil (805 mg, 52%).

Step 3: *Tert*-butyl ((benzyl(cyclobutyl)(methyl)silyl)methyl)(tosyl)carbamate (805 mg, 1.70 mmol), TFA (1.94 g, 17.01 mmol, 10.0 equiv.) in CH_2Cl_2 (10 mL) at room temperature for 1 h afforded **1j** as a white solid (400 mg, 63%).

- R_f = 0.5 (EtOAc/Petroleum Ether = 1/4).
- mp: 91.3 – 95.3 °C.
- ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.16 (t, *J* = 7.6 Hz, 2H), 7.08 (t, *J* = 7.2 Hz, 1H), 6.88 (d, *J* = 7.2 Hz, 2H), 3.86 (t, *J* = 6.0 Hz, 1H), 2.45 (s, 3H), 2.35 – 2.21 (m, 2H), 2.19 – 2.12 (m, 1H), 2.10 (s, 2H), 2.06 – 1.98 (m, 2H), 1.95 – 1.74 (m, 4H), 0.05 (s, 3H).

- ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 138.7, 135.2, 129.6, 128.6, 127.8, 127.5, 124.5, 28.7, 23.1, 23.0, 21.5, 21.5, 19.0, -8.3.
- IR (neat) cm^{-1} 3278, 3024, 2931, 2861, 1598,1492, 1320, 1159, 1093, 1055.
- HRMS calcd for $C_{20}H_{28}NO_2SSi$ $(M+H)^+$: 374.1605, found 374.1605.

N-((benzyl(cyclopentyl)(methyl)silyl)methyl)-4-methylbenzenesulfonamide **(1k)**



1k was prepared according to the procedure as that used for **1j**.

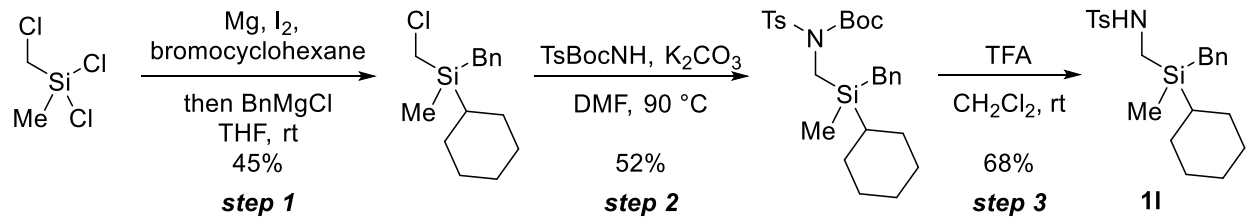
Step 1: Magnesium (538 mg, 22.14 mmol, 1.5 equiv.), a grain of I_2, bromocyclopentane (2.20 g, 14.76 mmol, 1.0 equiv.), dichloro(chloromethyl)(methyl)silane (2.41 g, 14.76 mmol, 1.0 equiv.), benzyl-magnesium chloride (17.27 mL, 1 M in THF, 1.17 equiv.) in anhydrous THF (40 mL) at room temperature under argon atmosphere overnight gave benzyl(chloromethyl)(cyclopentyl)(methyl)-silane as a colorless oil (820 mg, 22%).

Step 2: Benzyl(chloromethyl)(cyclopentyl)(methyl)silane (820 mg, 3.24 mmol), TsBocNH (1.32 g, 4.86 mmol, 1.5 equiv.), K_2CO_3 (672 mg, 4.86 mmol, 1.5 equiv.) in DMF (10 mL) at 90 °C for 6 h gave *tert*-butyl ((benzyl(cyclopentyl)(methyl)silyl)methyl)(tosyl)carbamate as a colorless oil (821 mg, 52%).

Step 3: *Tert*-butyl ((benzyl(cyclopentyl)(methyl)silyl)methyl)(tosyl)carbamate (821 mg, 1.68 mmol), TFA (1.92 g, 16.83 mmol, 10.0 equiv.) in CH_2Cl_2 (10 mL) at room temperature for 1 h afforded **1k** as a white solid (287 mg, 44%).

- R_f = 0.5 (EtOAc/Petroleum Ether = 1/4).
- mp: 125.9 – 128.3°C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.17 (t, J = 7.2 Hz, 2H), 7.09 (t, J = 7.2 Hz, 1H), 6.91 (d, J = 7.2 Hz, 2H), 3.72 (t, J = 6.4 Hz, 1H), 2.45 (s, 3H), 2.35 – 2.26 (m, 2H), 2.18 – 2.06 (m, 2H), 1.79 – 1.61 (m, 2H), 1.58 – 1.45 (m, 4H), 1.37 – 1.13 (m, 2H), 1.02 - 0.91 (m, 1H), -0.02 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 138.8, 135.2, 129.5, 128.6, 127.9, 127.5, 124.6, 29.3, 27.8, 27.7, 26.9, 26.9, 22.5, 22.1, 21.5, -8.0.
- IR (neat) cm^{-1} 3279, 3024, 2948, 2861, 1598, 1493, 1321, 1157, 1093.
- HRMS calcd for $C_{21}H_{30}NO_2SSi$ $(M+H)^+$: 388.1761, found 388.1762.

N-((benzyl(cyclohexyl)(methyl)silyl)methyl)-4-methylbenzenesulfonamide **(1l)**



1l was prepared according to the procedure as that used for **1j**.

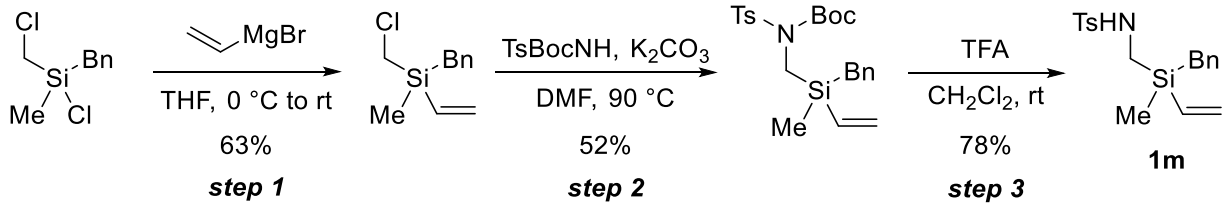
Step 1: Magnesium (548 mg, 22.54 mmol, 1.5 equiv.), a grain of I_2, bromocyclohexane (2.45 g, 15.03 mmol, 1.0 equiv.), dichloro(chloromethyl)(methyl)silane (2.46 g, 15.03 mmol, 1.0 equiv.), benzylmagnesium chloride (17.58 mL, 1.0 M in THF, 1.17 equiv.) in anhydrous THF (40 mL) at room temperature under argon atmosphere overnight gave benzyl(chloromethyl)(cyclohexyl)(methyl)silane as a colorless oil (1.79 g, 45%).

Step 2: Benzyl(chloromethyl)(cyclohexyl)(methyl)silane (1.79 g, 6.71 mmol), K_2CO_3 (1.39 g, 10.06 mmol, 1.5 equiv.), TsBocNH (2.73 g, 10.06 mmol, 1.5 equiv.) in DMF (20 mL) at 90 ^oC for 6 h gave *tert*-butyl ((benzyl(cyclohexyl)(methyl)silyl)methyl)(tosyl)carbamate as a colorless oil (1.75 g, 52%).

Step 3: *Tert*-butyl ((benzyl(cyclohexyl)(methyl)silyl)methyl)(tosyl)carbamate (1.75 g, 3.49 mmol), TFA (3.98 g, 34.88 mmol, 10.0 equiv.) in CH_2Cl_2 (20 mL) at room temperature for 1 h afforded **1l** as a white solid (959 mg, 68%).

- R_f = 0.6 (EtOAc/Petroleum Ether = 1/4).
- mp: 97.7 – 102.0^oC.
- ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 7.6 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 2H), 7.10 (t, *J* = 7.2 Hz, 1H), 6.89 (d, *J* = 7.2 Hz, 2H), 3.58 (t, *J* = 6.4 Hz, 1H), 2.45 (s, 3H), 2.33 – 2.16 (m, 2H), 2.10 (dd, *J* = 20.4, 14.0 Hz, 2H), 1.75 – 1.66 (m, 3H), 1.65 – 1.57 (m, 2H), 1.26 – 1.14 (m, 3H), 1.12 – 1.01 (m, 2H), 0.86 – 0.67 (m, 1H), -0.04 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 138.8, 135.2, 129.5, 128.6, 127.9, 127.5, 124.6, 28.4, 27.7, 27.7, 27.1, 26.6, 23.0, 21.5, 21.0, -8.2.
- IR (neat) cm^{-1} 3278, 2918, 2846, 1598, 1493, 1446, 1321, 1157, 1091.
- HRMS calcd for $C_{22}H_{31}NNaO_2SSi$ $(M+Na)^+$: 424.1737, found 424.1737.

N-((benzyl(methyl)(vinyl)silyl)methyl)-4-methylbenzenesulfonamide **(1m)**



1m was prepared according to the procedure as that used for **1e**.

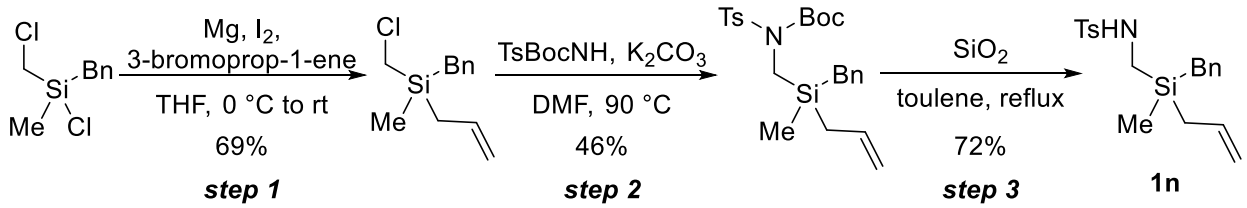
Step 1: Benzylchloro(chloromethyl)(methyl)silane (2.00 g, 9.12 mmol), vinylmagnesium bromide (10.04 mL, 1.0 M in THF, 1.0 equiv.) in anhydrous THF (20 mL) at room temperature under argon atmosphere overnight gave benzyl(chloromethyl)(methyl)(vinyl)silane as colorless oil (1.21 g, 63%).

Step 2: Benzyl(chloromethyl)(methyl)(vinyl)silane (1.21 g, 5.74 mmol), K_2CO_3 (1.19 g, 8.61 mmol, 1.5 equiv.), TsBocNH (2.34 g, 8.61 mmol, 1.5 equiv.) in DMF (12 mL) at 90 ^oC for 6 h gave *tert*-butyl ((benzyl(methyl)(vinyl)silyl)methyl)(tosyl)carbamate as a colorless oil (1.32 g, 52%).

Step 3: *Tert*-butyl ((benzyl(methyl)(vinyl)silyl)methyl)(tosyl)carbamate (1.32 g, 3.96 mmol), TFA (3.38 g, 39.62 mmol, 10.0 equiv.) in CH_2Cl_2 (15 mL) at room temperature for 1 h afforded **1m** as white solid (800 mg, 78%).

- R_f = 0.7 (EtOAc/Petroleum Ether = 1/4).
- mp: 107.6 – 110.1 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 2H), 7.09 (t, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 2H), 6.14 – 5.94 (m, 2H), 5.73 (dd, *J* = 19.6, 4.0 Hz, 1H), 4.02 (t, *J* = 6.0 Hz, 1H), 2.44 (s, 3H), 2.40 – 2.27 (m, 2H), 2.20 (dd, *J* = 18.4, 14.0 Hz, 2H), 0.09 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 138.0, 135.6, 135.2, 133.5, 129.6, 128.5, 128.1, 127.5, 124.7, 29.5, 22.4, 21.5, -6.7.
- IR (neat) cm^{-1} 3271, 3025, 2956, 2891, 1597, 1406, 1351, 1153, 812.
- HRMS calcd for $C_{18}H_{24}NO_2SSi$ $(M+H)^+$: 346.1292, found 346.1292.

N-((allyl(benzyl)(methyl)silyl)methyl)-4-methylbenzenesulfonamide **(1n)**



1n was prepared according to the procedure as that used for **1h**.

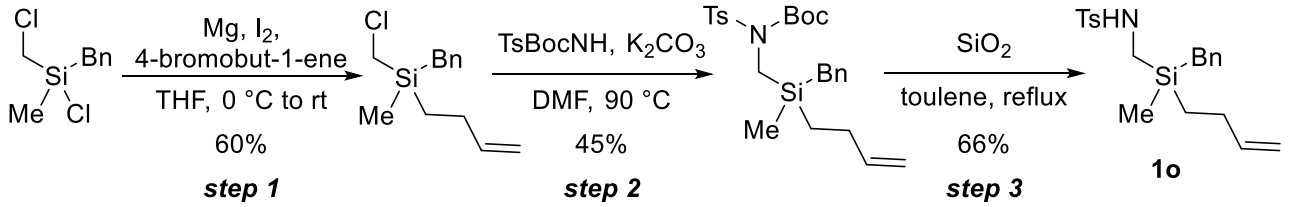
Step 1: Magnesium (547 mg, 22.50 mmol, 1.5 equiv.), a grain of I_2, 3-bromoprop-1-ene (1.81 g, 15.00 mmol, 1.0 equiv.), benzylchloro(chloromethyl)(methyl)silane (3.29 g, 15.00 mmol, 1.0 equiv.) in anhydrous THF at room temperature for 24 h gave allyl(benzyl)(chloromethyl)(methyl)silane as colorless oil (2.33 g, 69%).

Step 2: Allyl(benzyl)(chloromethyl)(methyl)silane (2.33 g, 10.36 mmol), TsBocNH (4.22 g, 15.55 mmol, 1.5 equiv.), K_2CO_3 (2.15 g, 15.55 mmol, 1.5 equiv.) in DMF (20 mL) at 90 °C for 6 h gave *tert*-butyl ((allyl(benzyl)(methyl)silyl)methyl)(tosyl)carbamate as a colorless oil (2.19 g, 46%).

Step 3: *Tert*-butyl ((allyl(benzyl)(methyl)silyl)methyl)(tosyl)carbamate (2.19 g, 4.76 mmol), SiO_2 (2.86 g, 47.64 mmol, 10.0 equiv.) in toluene (20 mL) refluxed for 2 h afforded **1n** as a white solid (1.25 g, 72%).

- R_f = 0.5 (EtOAc/Petroleum Ether = 1/4).
- mp: 75.5 – 79.5 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 2H), 7.10 (t, *J* = 7.2 Hz, 1H), 6.92 (d, *J* = 7.2 Hz, 2H), 5.94 – 5.52 (m, 1H), 5.24 – 4.69 (m, 2H), 4.13 (t, *J* = 6.0 Hz, 1H), 2.44 (s, 3H), 2.31 (d, *J* = 6.0 Hz, 2H), 2.15 (dd, *J* = 16.8, 14 Hz, 2H), 1.59 (d, *J* = 8.0 Hz, 2H), 0.03 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 138.2, 135.2, 133.3, 129.6, 128.6, 127.9, 127.5, 124.7, 114.7, 29.4, 22.2, 21.5, 20.0, -6.7.
- IR (neat) cm^{-1} 3271, 2890, 1598, 1492, 1449, 1316, 1242, 1155, 1054.
- HRMS calcd for $C_{19}H_{25}NNaO_2SSi$ $(M+Na)^+$: 382.1267, found 382.1266.

N-((benzyl(but-3-en-1-yl)(methyl)silyl)methyl)-4-methylbenzenesulfonamide **(1o)**



1o was prepared according to the procedure as that used for **1h**.

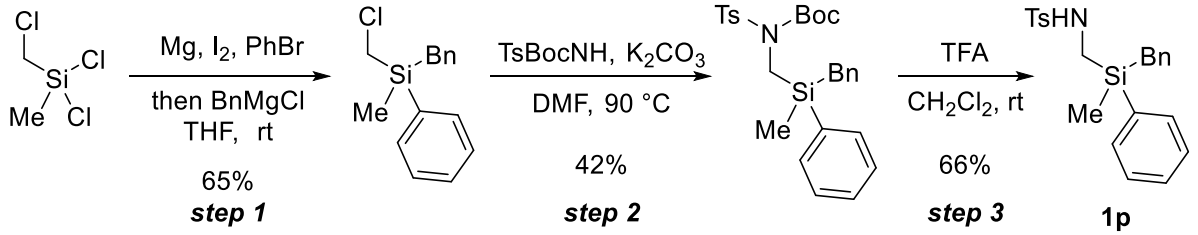
Step 1: Magnesium (540 mg, 22.22 mmol, 1.5 equiv.), a grain of I_2, 4-bromobut-1-ene (2.00 g, 14.81 mmol, 1.0 equiv.), benzylchloro(chloromethyl)(methyl)silane (3.25 g, 14.81 mmol, 1.0 equiv.) in anhydrous THF at room temperature for 24 h gave benzyl(but-3-en-1-yl)(chloromethyl)(methyl)-silane as colorless oil (2.12 g, 60%).

Step 2: Benzyl(but-3-en-1-yl)(chloromethyl)(methyl)silane (2.12 g, 8.88 mmol), TsBocNH (3.61 g, 13.31 mmol, 1.5 equiv.), K_2CO_3 (1.84 g, 13.31 mmol, 1.5 equiv.) in DMF (20 mL) at 90 °C for 6 h gave *tert*-butyl ((benzyl(but-3-en-1-yl)(methyl)silyl)methyl)(tosyl)carbamate as a colorless oil (1.89 g, 45%).

Step 3: *Tert*-butyl ((benzyl(but-3-en-1-yl)(methyl)silyl)methyl)(tosyl)carbamate (1.89 g, 3.99 mmol), SiO_2 (2.40 g, 39.90 mmol, 10.0 equiv.) in toluene (20 mL) refluxed for 2 h afforded **1o** as a white solid (984.0 mg, 66%).

- R_f = 0.7 (EtOAc/Petroleum Ether = 1/4).
- mp: 88.9 – 94.6 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 2H), 7.09 (t, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 7.2 Hz, 2H), 5.92 – 5.68 (m, 1H), 5.05 – 4.81 (m, 2H), 3.90 (t, *J* = 6.0 Hz, 1H), 2.45 (s, 3H), 2.29 (d, *J* = 6.4 Hz, 2H), 2.13 (s, 2H), 2.08 – 1.89 (m, 2H), 0.91 – 0.43 (m, 2H), 0.03 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 140.5, 138.5, 135.2, 129.6, 128.6, 127.9, 127.5, 124.7, 113.6, 29.7, 27.3, 22.8, 21.5, 11.2, -6.3.
- IR (neat) cm^{-1} 3277, 3025, 2917, 1639, 1598, 1493, 1409, 1320, 1157, 1093, 812.
- HRMS calcd for $C_{20}H_{28}NO_2SSi$ $(M+H)^+$: 374.1605, found 374.1606.

N-((benzyl(methyl)(phenyl)silyl)methyl)-4-methylbenzenesulfonamide **(1p)**



1p was prepared according to the procedure as that used for **1j**.

Step 1: Magnesium (548 mg, 22.55 mmol, 1.5 equiv.), a grain of I_2, bromobenzene (2.36 g, 15.03 mmol, 1.0 equiv.), dichloro(chloromethyl)(methyl)silane (2.46 g, 15.03 mmol, 1.0 equiv.), benzylmagnesium chloride (17.59 mL, 1 M in THF, 1.17 equiv.) in anhydrous THF (40 mL) at room

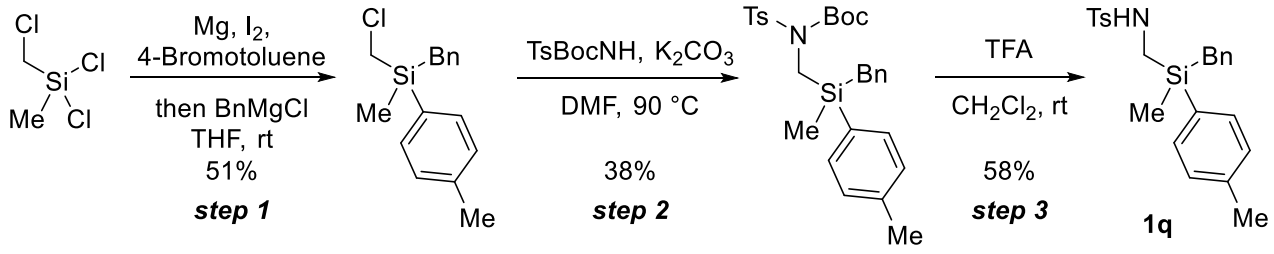
temperature under argon atmosphere overnight gave benzyl(chloromethyl)(methyl)(phenyl)silane as a colorless oil (2.55 g, 65%).

Step 2: Benzyl(chloromethyl)(methyl)(phenyl)silane (2.55 g, 9.78 mmol), TsBocNH (3.98 g, 14.66 mmol, 1.5 equiv.), K_2CO_3 (2.03 g, 14.66 mmol, 1.5 equiv.) in DMF (25 mL) at 90 °C for 6 h gave *tert*-butyl ((benzyl(methyl)(phenyl)silyl)methyl)(tosyl)carbamate as a colorless oil (2.04 g, 42%).

Step 3: *Tert*-butyl ((benzyl(methyl)(phenyl)silyl)methyl)(tosyl)carbamate (2.04 g, 4.12 mmol), TFA (4.69 g, 41.15 mmol, 10.0 equiv.) in CH_2Cl_2 (20 mL) at room temperature for 1 h afforded **1p** as a white solid (1.07 g, 66%).

- R_f = 0.6 (EtOAc/Petroleum Ether = 1/4).
- mp: 111.6 – 113.7 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.45 – 7.32 (m, 5H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 2H), 7.10 (t, *J* = 7.2 Hz, 1H), 6.90 (d, *J* = 7.2 Hz, 2H), 3.87 (t, *J* = 6.4 Hz, 1H), 2.61 – 2.46 (m, 2H), 2.45 (s, 3H), 2.38 (dd, *J* = 26.4,14.0 Hz, 2H), 0.28 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 137.8, 135.1, 134.0, 133.6, 130.1, 129.6, 128.5, 128.3, 128.2, 127.5, 124.8, 29.7, 22.6, 21.5, -6.4.
- IR (neat) cm^{-1} 3277, 3024, 2922, 1598, 1492, 1450, 1320, 1113, 1092.
- HRMS calcd for $C_{22}H_{25}NNaO_2SSi$ $(M+Na)^+$: 418.1267, found 418.1267.

N-((benzyl(methyl)(p-tolyl)silyl)methyl)-4-methylbenzenesulfonamide **(1q)**



1q was prepared according to the procedure as that used for **1j**.

Step 1: Magnesium (546 mg, 22.45 mmol, 1.5 equiv.), a grain of I_2, 4-Bromotoluene (2.56 g, 14.97 mmol, 1.0 equiv.), dichloro(chloromethyl)(methyl)silane (2.45 g, 14.97 mmol, 1.0 equiv.), benzylmagnesium chloride (17.51 mL, 1 M in THF, 1.17 equiv.) in anhydrous THF (40 mL) at room temperature under argon atmosphere overnight gave benzyl(chloromethyl)(methyl)(*p*-tolyl)silane as a colorless oil (2.11 g, 51%).

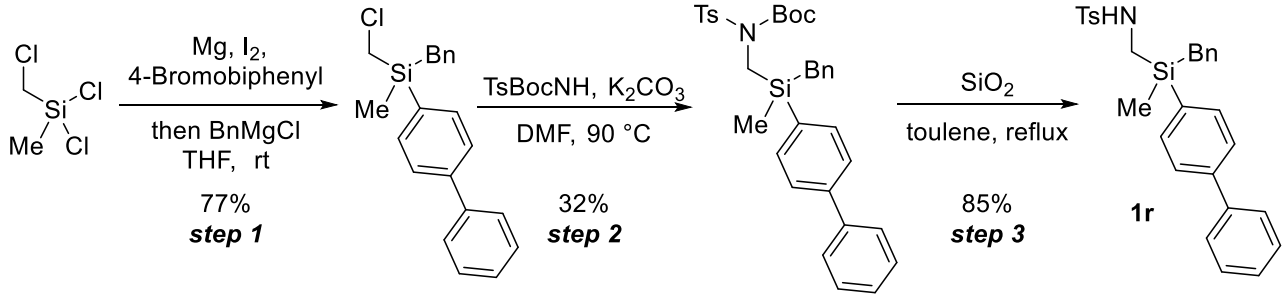
Step 2: Benzyl(chloromethyl)(methyl)(*p*-tolyl)silane (2.11 g, 7.68 mmol), TsBocNH (2.50 g, 9.21 mmol, 1.5 equiv.), K_2CO_3 (1.27 g, 9.21 mmol, 1.5 equiv.) in DMF (20 mL) at 90 °C for 6 h gave *tert*-butyl ((benzyl(methyl)(*p*-tolyl)silyl)methyl)(tosyl)carbamate as a colorless oil (1.48 g, 38%).

Step 3: *Tert*-butyl ((benzyl(methyl)(*p*-tolyl)silyl)methyl)(tosyl)carbamate (1.48 g, 2.90 mmol), TFA (3.31 g, 29.03 mmol, 10.0 equiv.) in CH_2Cl_2 (15 mL) at room temperature for 1 h afforded **1q** as a white solid (690 mg, 58%).

- R_f = 0.6 (EtOAc/Petroleum Ether = 1/4).
- mp: 120.6 – 122.9 °C.

- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.20 – 7.13 (m, 4H), 7.09 (t, *J* = 7.2 Hz, 1H), 6.90 (d, *J* = 7.2 Hz, 2H), 3.78 (t, *J* = 6.0 Hz, 1H), 2.52 – 2.30 (m, 10H), 0.25 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 140.2, 137.9, 135.1, 134.0, 129.8, 129.5, 129.1, 128.5, 128.2, 127.5, 124.7, 29.8, 22.7, 21.5, 21.5, -6.4.
- IR (neat) cm^{-1} 3277, 3024, 2920, 1599, 1493, 1449, 1320, 1250, 1157, 1093.
- HRMS calcd for $C_{23}H_{27}NNaO_2SSi$ $(M+Na)^+$: 432.1424, found 432.1424.

N-(([1,1'-biphenyl]-4-yl(benzyl)(methyl)silyl)methyl)-4-methylbenzenesulfonamide **(1r)**



1r was prepared according to the procedure as that used for **1j** and **1h**.

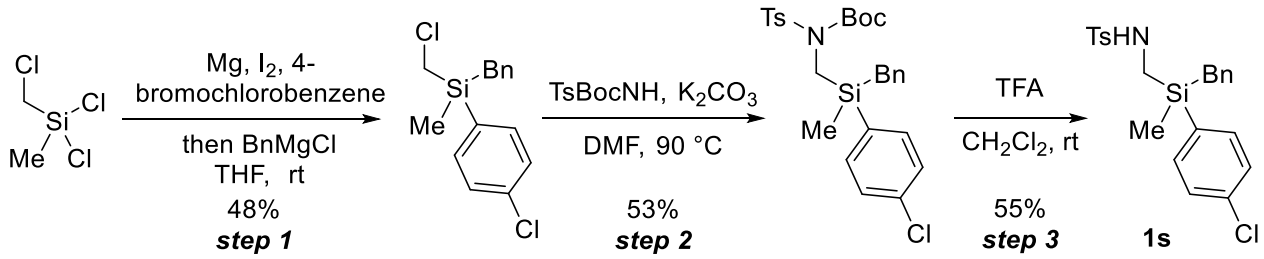
Step 1: Magnesium (547 mg, 22.52 mmol, 1.5 equiv.), a grain of I_2, 4-Bromobiphenyl (3.50 g, 15.01 mmol, 1.0 equiv.), dichloro(chloromethyl)(methyl)silane (2.45 g, 15.01 mmol, 1.0 equiv.) and benzylmagnesium chloride (17.57 mL, 1.0 M in THF, 1.17 equiv.) in anhydrous THF at room temperature for 24 h gave [1,1'-biphenyl]-4-yl(benzyl)(chloromethyl)(methyl)silane as a white solid (3.93 g, 77%).

Step 2: [1,1'-biphenyl]-4-yl(benzyl)(chloromethyl)(methyl)silane (3.93 g, 11.66 mmol), TsBocNH (4.75 g, 17.50 mmol, 1.5 equiv.), K_2CO_3 (2.42 g, 17.50 mmol, 1.5 equiv.) in DMF (40 mL) at 90 °C for 6 h gave *tert*-butyl (([1,1'-biphenyl]-4-yl(benzyl)(methyl)silyl)methyl)(tosyl)carbamate as a white solid (2.14 g, 32%).

Step 3: *Tert*-butyl (([1,1'-biphenyl]-4-yl(benzyl)(methyl)silyl)methyl)(tosyl)carbamate (2.14 g, 3.74 mmol), SiO_2 (2.25 g, 37.43 mmol, 10.0 equiv.) in toluene (20 mL) refluxed for 2 h afforded **1r** as white solid (1.52 g, 85%).

- R_f = 0.5 (EtOAc/Petroleum Ether = 1/4).
- mp: 93.1 – 97.4 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.59 (t, *J* = 7.6 Hz, 4H), 7.50 – 7.43 (m, 4H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 2H), 7.11 (t, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 2H), 3.87 (t, *J* = 6.0 Hz, 1H), 2.59 – 2.46 (m, 2H), 2.48 - 2.33 (m, 5H), 0.31 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 142.9, 140.6, 137.8, 135.1, 134.5, 132.2, 129.6, 128.9, 128.6, 128.2, 127.7, 127.5, 127.1, 126.9, 124.8, 29.8, 22.7, 21.5, -6.3.
- IR (neat) cm^{-1} 3281, 3025, 2922, 1597, 1492, 1320, 1158, 1117, 1092, 813.
- HRMS calcd for $C_{28}H_{29}NNaO_2SSi$ $(M+Na)^+$: 494.1580, found 494.1597.

N-((benzyl(4-chlorophenyl)(methyl)silyl)methyl)-4-methylbenzenesulfonamide **(1s)**



1s was prepared according to the procedure as that used for **1j**.

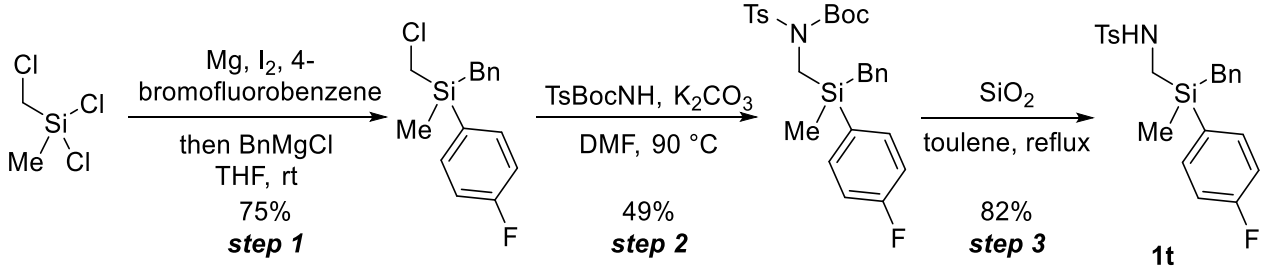
Step 1: Magnesium (547 mg, 22.49 mmol, 1.5 equiv.), a grain of I_2, 4-Bromochlorobenzene (2.87 g, 14.99 mmol, 1.0 equiv.), dichloro(chloromethyl)(methyl)silane (2.45 g, 14.99 mmol, 1.0 equiv.), benzylmagnesium chloride (17.54 mL, 1 M in THF, 1.17 equiv.) in anhydrous THF (40 mL) at room temperature under argon atmosphere overnight to give benzyl(chloromethyl)(4-chlorophenyl)-(methyl)silane as a colorless oil (2.12 g, 48%).

Step 2: Benzyl(chloromethyl)(4-chlorophenyl)(methyl)silane (2.12 g, 9.09 mmol), TsBocNH (3.70 g, 13.64 mmol, 1.5 equiv.) and K_2CO_3 (1.88 g, 13.64 mmol, 1.5 equiv.) in DMF (20 mL) at 90 °C for 6 h gave *tert*-butyl ((benzyl(4-chlorophenyl)(methyl)silyl)methyl)(tosyl)carbamate as a colorless oil (2.55 g, 53%).

Step 3: *Tert*-butyl ((benzyl(4-chlorophenyl)(methyl)silyl)methyl)(tosyl)carbamate (2.55 g, 4.81 mmol) and TFA (5.48 g, 48.1 mmol, 10.0 equiv.) in CH_2Cl_2 (25 mL) at room temperature for 1 h afforded **1s** as a white solid (1.14 g, 55%).

- R_f = 0.6 (EtOAc/Petroleum Ether = 1/4).
- mp: 127.4 – 130.2 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.35 – 7.26 (m, 6H), 7.16 (t, *J* = 7.2 Hz, 2H), 7.10 (t, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 6.8 Hz, 2H), 3.81 (t, *J* = 6.4 Hz, 1H), 2.55 – 2.46 (m, 2H), 2.45 (s, 3H), 2.38 (dd, *J* = 22.8, 14.0 Hz, 2H), 0.28 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 137.4, 136.6, 135.3, 135.1, 131.9, 129.6, 128.6, 128.5, 128.2, 127.5, 124.9, 29.7, 22.7, 21.5, -6.4.
- IR (neat) cm^{-1} 3277, 3060, 2923, 1598, 1576, 1491, 1321, 1242, 1158, 1084.
- HRMS calcd for $C_{22}H_{25}ClNO_2SSi$ $(M+Na)^+$: 452.0878, found 452.0879.

N-((benzyl(4-fluorophenyl)(methyl)silyl)methyl)-4-methylbenzenesulfonamide **(1t)**



1t was prepared according to the procedure as that used for **1r**.

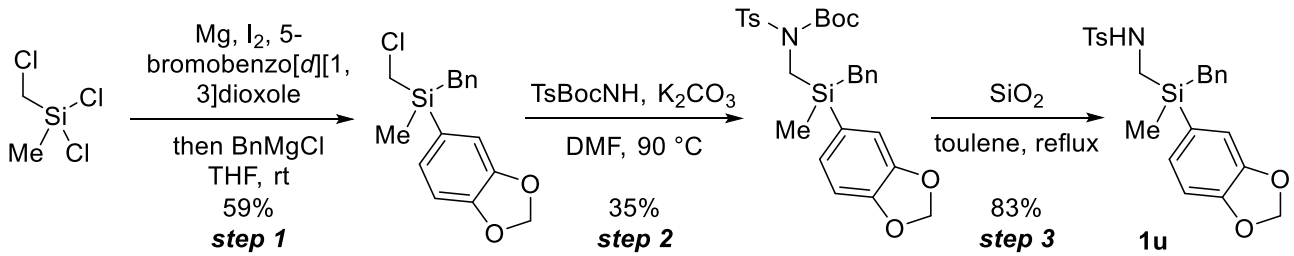
Step 1: Magnesium (542 mg, 22.29 mmol, 1.5 equiv.), a grain of I_2, 4-Bromofluorobenzene (2.60 g, 14.86 mmol, 1.0 equiv.), dichloro(chloromethyl)(methyl)silane (2.43 g, 14.86 mmol, 1.0 equiv.) and benzylmagnesium chloride (17.38 mL, 1.0 M in THF, 1.17 equiv.) in anhydrous THF at room temperature for 24 h gave benzyl(chloromethyl)(4-fluorophenyl)(methyl)silane as colorless oil (3.09 g, 75%).

Step 2: Benzyl(chloromethyl)(4-fluorophenyl)(methyl)silane (3.09 g, 11.08 mmol), TsBocNH (4.51 g, 16.62 mmol, 1.5 equiv.), K_2CO_3 (2.30 g, 16.62 mmol, 1.5 equiv.) in DMF (30 mL) at 90 °C for 6 h gave *tert*-butyl ((benzyl(4-fluorophenyl)(methyl)silyl)methyl)(tosyl)carbamate as a colorless oil (2.80 g, 49%).

Step 3: *Tert*-butyl ((benzyl(4-fluorophenyl)(methyl)silyl)methyl)(tosyl)carbamate (2.80 g, 5.45 mmol) and SiO_2 (3.27 g, 54.51 mmol, 10.0 equiv.) in toluene (30 mL) refluxed for 2 h afforded **1t** as white solid (1.85 g, 82%).

- R_f = 0.6 (EtOAc/Petroleum Ether = 1/4).
- mp: 103.2 – 106.2 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.34 (dd, *J* = 8.4, 6.2 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.04 (t, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 7.1 Hz, 2H), 3.88 (t, *J* = 6.2 Hz, 1H), 2.49 (dd, *J* = 6.2, 1.8 Hz,2H), 2.45 (s, 3H), 2.37 (dd, *J* = 23.6, 14.0 Hz, 2H), 0.27 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2 (d, *J* = 250.2 Hz), 143.5, 137.6, 136.1, 136.0, 135.1, 129.6, 129.1 (d, *J* = 3.9 Hz), 128.6, 128.2, 127.5, 124.9, 115.6, 115.4, 29.8, 22.8, 21.5, -6.3.
- IR (neat) cm^{-1} 3277, 1588, 1497, 1451, 1322, 1160, 1105, 814.
- HRMS calcd for $C_{22}H_{24}FNNaO_2SSi$ $(M+Na)^+$: 436.1173, found 436.1171.

N-((benzo[d][1,3]dioxol-5-yl(benzyl)(methyl)silyl)methyl)-4-methylbenzenesulfonamide **(1u)**



1u was prepared according to the procedure as that used for **1r**.

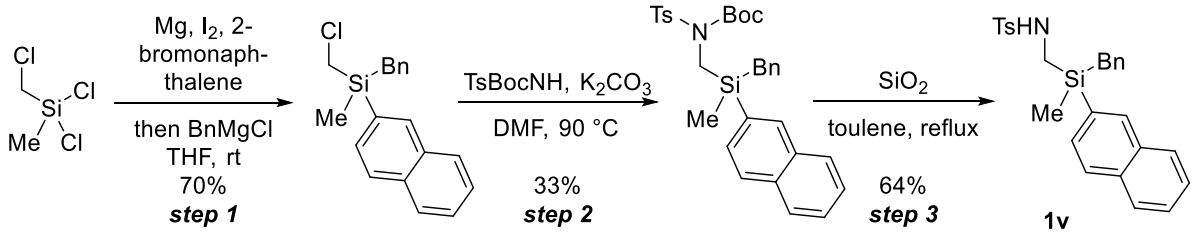
Step 1: Magnesium (544 mg, 22.39 mmol, 1.5 equiv.), a grain of I_2, 5-bromobenzo[*d*][1,3]dioxole (3.00 g, 14.92 mmol, 1.0 equiv.), dichloro(chloromethyl)(methyl)silane (2.44 g, 14.92 mmol, 1.0 equiv.) and benzylmagnesium chloride (17.46 mL, 1.0 M in THF, 1.17 equiv.) in anhydrous THF (40 mL) at room temperature for 24 h gave benzo[*d*][1,3]dioxol-5-yl(benzyl)(chloromethyl)(methyl)-silane as a colorless oil (2.68 g, 59%).

Step 2: Benzo[*d*][1,3]dioxol-5-yl(benzyl)(chloromethyl)(methyl)silane (2.68 g, 8.79 mmol), TsBocNH (3.58 g, 13.19 mmol, 1.5 equiv.) and K_2CO_3 (1.82 g, 13.19 mmol, 1.5 equiv.) in DMF (30 mL) at 90 °C for 6 h gave *tert*-butyl ((benzo[*d*][1,3]dioxol-5-yl(benzyl)(methyl)silyl)methyl)(tosyl)-carbamate as a colorless oil (1.66 g, 35%).

Step 3: *Tert*-butyl ((benzo[*d*][1,3]dioxol-5-yl(benzyl)(methyl)silyl)methyl)(tosyl)carbamate (1.66 g, 3.08 mmol) and SiO_2 (3.51 g, 30.76 mmol, 10.0 equiv.) in toluene (15 mL) refluxed for 2 h afforded **1u** as white solid (1.12 g, 83%).

- R_f = 0.4 (EtOAc/Petroleum Ether = 1/4).
- mp: 146.7 – 149.1 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 2H), 7.09 (t, *J* = 7.2 Hz, 1H), 6.89 (d, *J* = 7.2 Hz, 2H), 6.86 – 6.80 (m, 2H), 6.78 (s, 1H), 5.97 (s, 2H), 3.80 (t, *J* = 6.0 Hz, 1H), 2.50 – 2.40 (m, 5H), 2.35 (dd, *J* = 24.0,14.0 Hz, 2H), 0.24 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 147.8, 143.4, 137.8, 135.1, 129.6, 128.6, 128.3, 128.2, 127.5, 126.2, 124.8, 113.1, 109.0, 100.8, 29.8, 22.9, 21.5, -6.2.
- IR (neat) cm^{-1} 3277, 3023, 2891, 1598, 1483, 1417, 1320, 1233, 1157, 751.
- HRMS calcd for $C_{23}H_{25}NNaO_4SSi$ $(M+Na)^+$: 462.1166, found 462.1166.

N-((benzyl(methyl)(naphthalen-2-yl)silyl)methyl)-4-methylbenzenesulfonamide **(1v)**



1v was prepared according to the procedure as that used for **1r**.

Step 1: Magnesium (528 mg, 21.73 mmol, 1.5 equiv.), a grain of I_2, 2-bromonaph-thalene (3.00 g, 14.49 mmol, 1.0 equiv.), dichloro(chloromethyl)(methyl)silane (2.37 g, 14.49 mmol, 1.0 equiv.) and benzylmagnesium chloride (16.95 mL, 1.0 M in THF, 1.17 equiv.) in anhydrous THF (40 mL) at room temperature for 24 h gave benzyl(chloromethyl)(methyl)(naphthalen-2-yl)silane as a white solid (3.15 g, 70%).

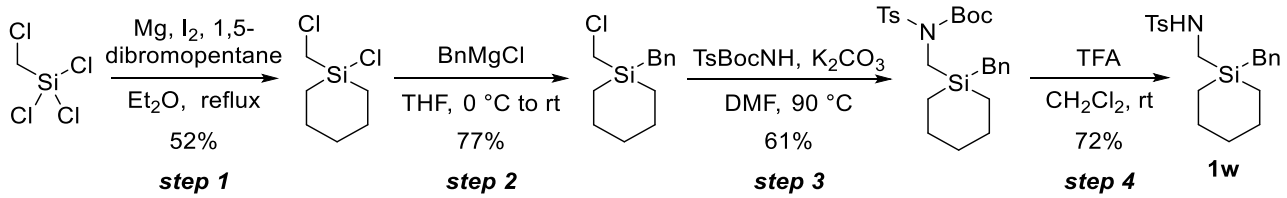
Step 2: Benzyl(chloromethyl)(methyl)(naphthalen-2-yl)silane (3.15 g, 10.13 mmol), TsBocNH (4.12 g, 15.20 mmol, 1.5 equiv.) and K_2CO_3 (2.10 g, 15.20 mmol, 1.5 equiv.) in DMF (30 mL) at 90 °C for 6 h gave *tert*-butyl ((benzyl(methyl)(naphthalen-2-yl)silyl)methyl)(tosyl)carbamate as a white solid (1.82 g, 33%).

Step 3: *Tert*-butyl ((benzyl(methyl)(naphthalen-2-yl)silyl)methyl)(tosyl)carbamate (1.82 g, 3.33 mmol) and SiO_2 (3.80 g, 33.35 mmol, 10.0 equiv.) in toluene (20 mL) refluxed for 2 h afforded **1v** as white solid (954 mg, 64%).

- R_f = 0.6 (EtOAc/Petroleum Ether = 1/4).
- mp: 107.6 – 113.0 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.85 – 7.76 (m, 3H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.59 – 7.47 (m, 2H), 7.41 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.26 (d, *J* = 7.2 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 2H), 7.10 (t, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 6.8 Hz, 2H), 3.94 (t, *J* = 6.0 Hz, 1H), 2.66 – 2.54 (m, 2H), 2.50 (dd, *J* = 34.4, 14.0 Hz, 2H), 2.43 (s, 3H), 0.37 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 137.8, 135.2, 135.1, 134.0, 132.8, 130.9, 129.6, 129.5, 128.6, 128.2, 128.1, 127.7, 127.6, 127.5, 127.0, 126.3, 124.8, 29.8, 22.7, 21.5, -6.4.

- IR (neat) cm^{-1} 3276, 3053, 2922, 1598, 1493, 1321, 1158, 1088, 812.
- HRMS calcd for $C_{26}H_{27}NNaO_2SSi$ $(M+Na)^+$: 468.1424, found 468.1396.

N-((1-benzylsilinan-1-yl)methyl)-4-methylbenzenesulfonamide **(1w)**



Step 1: 1-chloro-1-(chloromethyl)silinane was prepared according to literature[1]. To a suspension of magnesium (2.55 g, 105.03 mmol, 3.0 equiv.) and a grain of I_2 in anhydrous Et_2O (7 mL) was added a small amount (about 20 drops) solution of the 1,5-dibromopentane in Et_2O by syringe at ambient temperature under argon atmosphere. The reaction was initiated and heated to reflux with addition the rest of the 1,5-dibromopentane solution (8.05 g, 35.01 mmol, 1.0 equiv. in 20 mL Et_2O) dropwise over 30 min. The resulting mixture was refluxed for additional 1 h then cooled to room temperature within 1 h. The resulting Grignard reagent solution, which was separated from residual magnesium turnings by decantation, was added dropwise within 90 min to a solution of trichloro(chloromethyl)silane (6.44 g, 35.01 mmol, 1.0 equiv.) in anhydrous Et_2O (20 mL) under argon atmosphere. After addition was completed, the mixture was stirred for 24 h at room temperature. The reaction was concentrated under reduced pressure, causing a precipitation. The precipitate was separated by decantation and washed with *n*-hexane (3 × 30 ml), and all organic solutions were combined. The solvent was removed as described above, and the crude product was isolated by distillation in vacuo (b.p.: 80 °C/ 0.8mmHg) to afford the 1-chloro-1-(chloromethyl)silinane as a colorless oil (3.36 g, 52%).

1w was prepared from 1-chloro-1-(chloromethyl)silinane according to the procedure as that used for **1a**.

Step 2: 1-chloro-1-(chloromethyl)silinane (3.36 g, 18.35 mmol), benzylmagnesium chloride (21.46 mL, 1.0 M in THF, 1.17 equiv.) in anhydrous THF (30 mL) at room temperature under argon overnight gave 1-benzyl-1-(chloromethyl)silinane as a colorless oil (3.37 g, 77%).

Step 3: 1-benzyl-1-(chloromethyl)silinane (3.37 g, 14.11 mmol), TsBocNH (5.74 g, 21.17 mmol, 1.5 equiv.), K_2CO_3 (2.93 g, 21.17 mmol, 1.5 equiv.) in DMF (30 mL) at 90 °C for 6 h gave *tert*-butyl ((1-benzylsilinan-1-yl)methyl)(tosyl)carbamate as a colorless oil (4.07 g, 61%),

Step 4: *Tert*-butyl ((1-benzylsilinan-1-yl)methyl)(tosyl)carbamate (4.07 g, 8.59 mmol), TFA (9.80 g, 85.92 mmol, 10.0 equiv.) in CH_2Cl_2 (40 mL) at room temperature for 1 h afforded **1w** as a white solid (2.31 g, 72%).

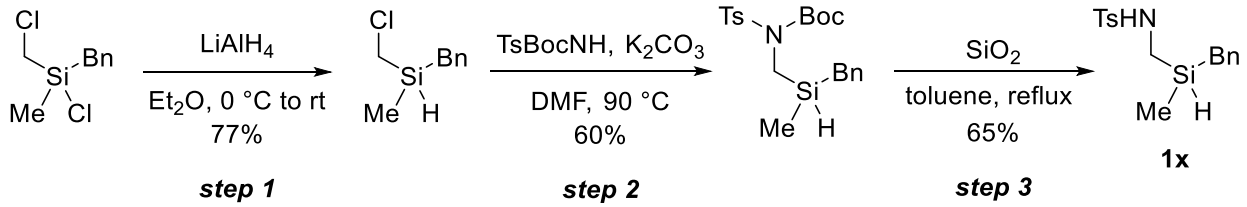
- R_f = 0.6 (EtOAc/Petroleum Ether = 1/4).
- mp: 101.3 – 105.3 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 7.6 Hz, 2H), 7.10 (t, *J* = 7.2 Hz, 1H), 6.90 (d, *J* = 7.2 Hz, 2H), 3.83 (t, *J* = 6.0 Hz, 1H), 2.45 (s, 3H),

1. J. O. Daiß, C. Burschka, R. Tacke, *J. Organomet. Chem.* **2005**, *690*, 678.

2.32 (d, J = 6.4 Hz, 2H), 2.15 (s, 2H), 1.78 – 1.50 (m, 4H), 1.45 – 1.25 (m, 2H), 0.64 (t, J = 6.8 Hz, 4H).

- ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 138.6, 135.3, 129.5, 128.6, 127.8, 127.5, 124.6, 29.4, 28.4, 23.9, 21.8, 21.5, 9.6.
- IR (neat) cm^{-1} 3276, 2914, 2851, 1598, 1493, 1321, 1158, 1093.
- HRMS calcd for $C_{20}H_{28}NO_2SSi$ $(M+H)^+$: 374.1605, found 374.1606.

N-((benzyl(methyl)silyl)methyl)-4-methylbenzenesulfonamide **(1x)**



Step 1: To a solution of dichloro(chloromethyl)(methyl)silane (1.00 g, 4.56 mmol, 1.0 equiv.) in anhydrous Et_2O (10 mL) at 0 ºC under argon atmosphere was added $LiAlH_4$ (1.37 mL, 1 M in THF, 0.3 equiv.) dropwise. The reaction was warmed up to room temperature and stirred for 1 h before quenching with 1M HCl and extracting with Et_2O (3 × 10 mL). The combined organic layers were washed with sat. aq. NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (eluent: EtOAc/petroleum ether = 1/60) to give the product benzyl(chloromethyl)(methyl)silane (650 mg, 77%).

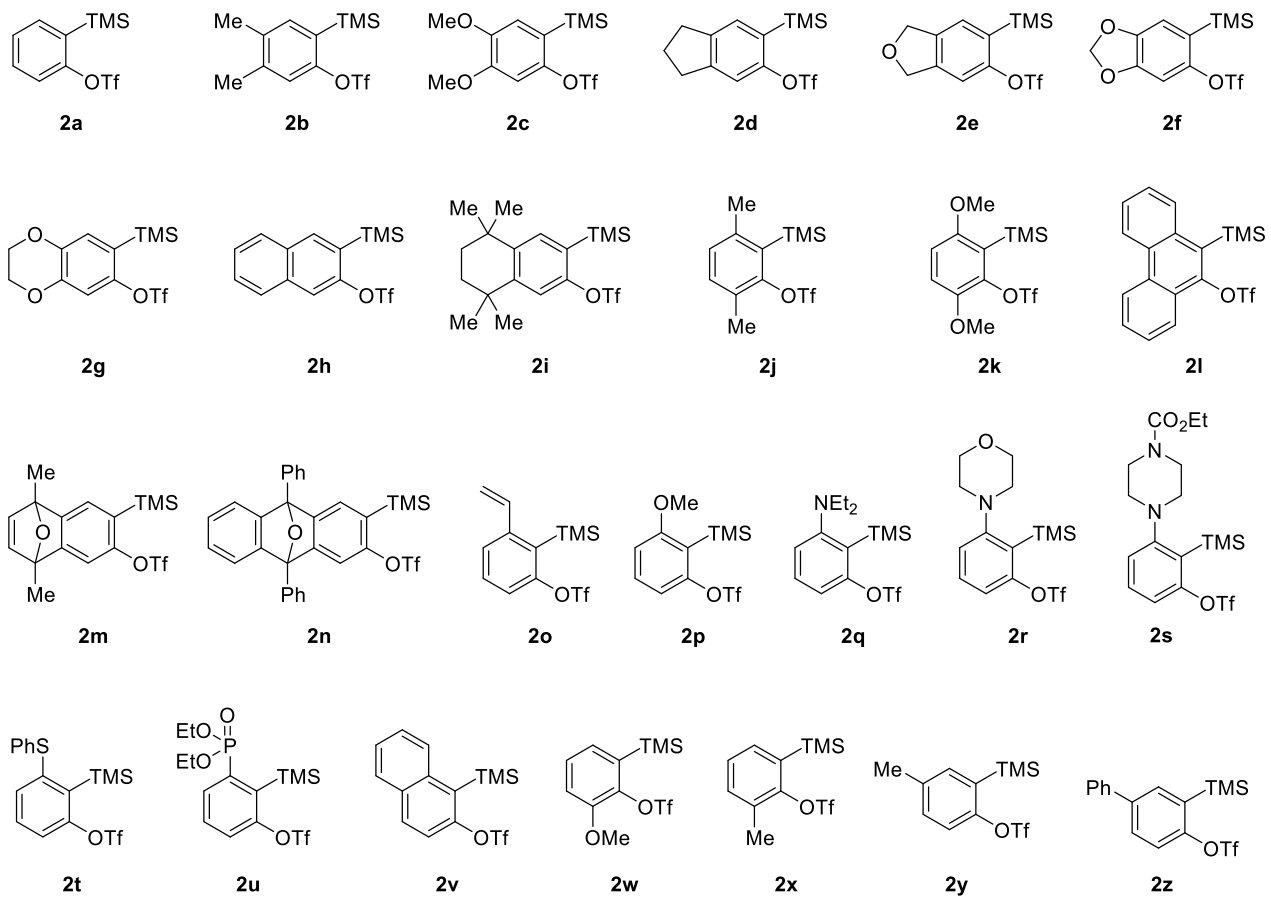
1x was prepared from benzyl(chloromethyl)(methyl)silane according to the procedure as that used for **1h**.

Step 2: Benzyl(chloromethyl)(methyl)silane (650 mg, 3.52 mmol), TsBocNH (1.15 g, 4.22 mmol, 1.2 equiv.) and K_2CO_3 (584 mg, 4.22 mmol, 1.2 equiv.) in DMF (5 mL) at 90 ºC for 6 h gave *tert*-butyl ((benzyl(methyl)silyl)methyl)(tosyl)carbamate as a color less oil (888 mg, 60%).

Step 3: *Tert*-butyl ((benzyl(methyl)silyl)methyl)(tosyl)carbamate (888 mg, 2.12 mmol) and SiO_2 (1.27 g, 21.16 mmol, 10.0 equiv.) in toluene (10 mL) refluxed for 2 h afforded **1x** as a white solid (439 mg, 65%).

- R_f = 0.5 (EtOAc/Petroleum Ether = 1/4).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.20 (t, J = 7.6 Hz, 2H), 7.11 (t, J = 7.2 Hz, 1H), 6.97 (d, J = 7.2 Hz, 2H), 4.07 (t, J = 6.0 Hz, 1H), 3.95 (h, J = 3.2 Hz, 1H), 2.44 (s, 3H), 2.41 – 2.32 (m, 2H), 2.28 – 2.11 (m, 2H), 0.11 (d, J = 3.7 Hz, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 138.1, 135.3, 129.6, 128.7, 128.0, 127.5, 124.9, 28.8, 21.5, 21.1, -7.6.
- HRMS calcd for $C_{16}H_{22}NO_2SSi$ $(M+H)^+$: 320.1135, found 320.1134.

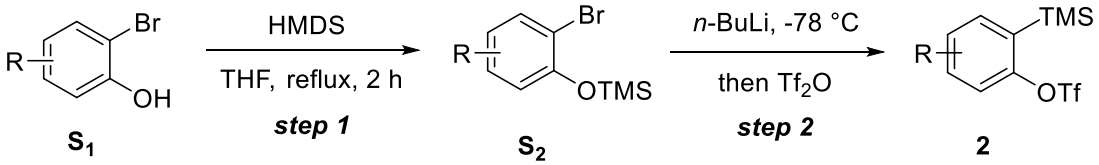
3. Synthesis of Aryne Precursors 2



- commercially available benzyne precursor:
  2a.
- known benzyne precursors:
  2b, **2c**, **2d**, **2f**, **2h**, **2j**, **2k**, **2l**, **2m**, **2n**, **2p**, **2q**, **2r**, **2t**, **2u**, **2v**, **2w**, **2x**, **2y**, **2z**.
- new benzyne precursors:
  2e, **2g**, **2i**, **2o**, **2s**.

General Method A:

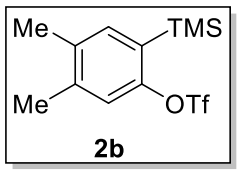
General Method A was used for preparation of known benzyne precursors **2b**, **2c**, **2d**, **2f**, **2h**, **2j**, **2l**, **2p**, **2v**, **2w**, **2x**, **2y**, **2z**. and new benzyne precursors **2e**, **2g**, **2i**.



Step 1: To a solution of *o*-bromophenol **S1** (11.00 mmol) in anhydrous THF (20 mL) was added HMDS (22.00 mmol, 2.0 equiv.) under argon atmosphere. The reaction mixture was refluxed for 2 h. After cooling to room temperature, the crude product **S2** was obtained by removing the solvent *in vacuo* and used for the next step without further purification.

Step 2: To a solution of the crude product **S2** in anhydrous THF (30 mL) was added *n*-BuLi (12.10 mmol, 2.4 M in hexane, 1.1 equiv.) dropwise under argon atmosphere at -78 ºC. The mixture was stirred for 1 h at -78 ºC before adding Tf_2O (13.20 mmol, 1.2 equiv.). The reaction was stirred for additional 1 h before quenching with sat. aq. $NaHCO_3$ at -78 °C. Then the aqueous layer was extracted with Et_2O (3 × 30 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography to afford aryne precursors **2**.

4,5-dimethyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **(2b)**

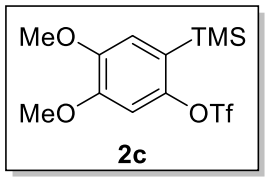


2b

2b was prepared according to General Method A, and the NMR spectral data are in accordance with the reported data[2].

- a colorless oil, 1.90 g, 53%.
- R_f = 0.8 (Petroleum Ether).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (s, 1H), 7.09 (s, 1H), 2.28 (s, 3H), 2.26 (s, 3H), 0.34 (s, 9H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 140.3, 137.0, 136.0, 129.1, 120.5, 118.5 (q, J = 317.9 Hz), 19.9, 19.1, -0.7.

4,5-dimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **(2c)**

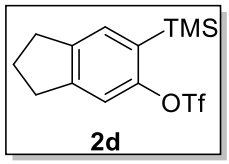


2c

2c was prepared according to General Method A, and the NMR spectral data are in accordance with the reported data[2].

- a colorless oil, 1.18 g, 30%.
- R_f = 0.6 (EtOAc/Petroleum Ether = 1/20).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (s, 1H), 6.85 (s, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 0.35 (s, 9H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 148.2, 147.9, 123.1, 118.5 (q, J = 317.9 Hz), 116.6, 104.2, 104.2, 104.2, 104.2, 56.1, 56.1, -0.7.

6-(trimethylsilyl)-2,3-dihydro-1H-inden-5-yl trifluoromethanesulfonate **(2d)**



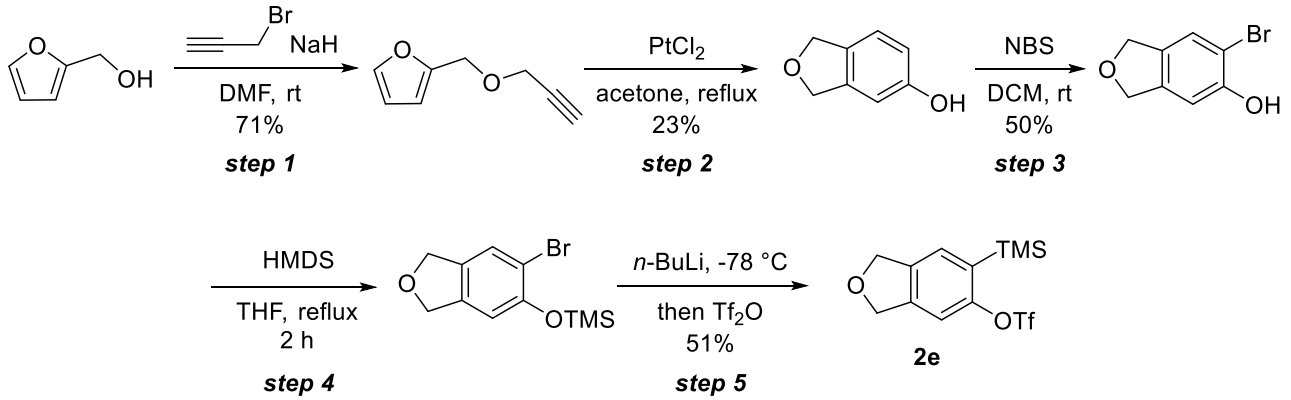
2d

2d was prepared according to General Method A, and the NMR spectral data are in accordance with the reported data[2].

- a colorless oil, 1.68 g, 45%.
- R_f = 0.8 (Petroleum Ether).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.21 (s, 1H), 2.94 (m, 4H), 2.14 (m, 2H), 0.38 (s, 9H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 148.3, 143.6, 131.3, 129.5, 118.5 (q, J = 318.1 Hz), 115.7, 33.1, 32.1, 25.7, -0.7.

6-(trimethylsilyl)-1,3-dihydroisobenzofuran-5-yl trifluoromethanesulfonate **(2e)**

2. H. F. Jiang, Z. Yu, W. F. Xiong, J. H. Cen, L. Wang, R. X. Cheng, *Org. Lett*. **2019**, *21*, 345.



Step 1: 2-((prop-2-yn-1-yloxy)methyl)furan was prepared according to the literature[3]. To a suspension of NaH (1.44 g, 35.88 mmol; 60% in mineral oil) in DMF (40 mL) at 0°C was added furfuryl alcohol (3.20 g, 32.62 mmol) dropwise. After being stirred for 10 min, propargyl bromide (4.27 g, 35.88 mmol, 1.1 equiv.) was added and the mixture was stirred for 4 h at room temperature before quenching with H_2O and extracting with Et_2O (3 × 30 mL). The combined organic layers were washed with sat. aq. NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (eluent: EtOAc/petroleum ether = 1/20) to give the product 2-((prop-2-yn-1-yloxy)methyl)furan as a colorless oil (3.14 g, 71%).

Step 2: 1,3-dihydroisobenzofuran-5-ol was prepared according to the literature[3]. To a solution of 2-((prop-2-yn-1-yloxy)methyl)furan (3.14 g, 23.06 mmol) in acetone (30 mL) was added $PtCl_2$ (306 mg, 1.15 mmol, 5 mol%). The reaction mixture was stirred for 16 h under reflux. The solvent was evaporated and the crude product was purified by silica gel flash column chromatography (eluent: EtOAc/petroleum ether = 1/10) to yield 1,3-dihydroisobenzofuran-5-ol as a pale yellow solid (722 mg, 23 %).

Step 3: To a solution of 1,3-dihydroisobenzofuran-5-ol (722 mg, 5.30 mmol) in AcOH (8 mL) was added a solution of bromine (243 μL, 4.74 mmol, 0.9 equiv.) in AcOH (3 mL) dropwise at 0 °C. The reaction mixture was stirred for 30 min at this temperature before quenching with H_2O and extracting with EtOAc (3 × 20 mL). The combined organic layers were washed with sat. aq. NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (eluent: EtOAc/petroleum ether = 1/8) to give 6-bromo-1,3-dihydroisobenzofuran-5-ol as a colorless oil (570 mg, 50%).

2e was prepared from 6-bromo-1,3-dihydroisobenzofuran-5-ol according to the General Method A.

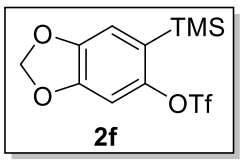
Step 4 and 5: 6-bromo-1,3-dihydroisobenzofuran-5-ol (570 mg, 2.65 mmol), HMDS (855 mg, 5.30 mmol, 2.0 equiv.) refluxed for 2 h; *n*-BuLi (1.21 mL, 2.4 M in hexane, 1.0 equiv.) and Tf_2O (898 mg, 3.18 mmol, 1.2 equiv) in anhydrous THF at -78 °C for 4 h gave **2e** as a colorless oil (460 mg, 51%).

- R_f = 0.5 (EtOAc/Petroleum Ether = 1/10).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.22 (s, 1H), 5.11 (d, J = 2.4 Hz, 4H), 0.37 (s, 9H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 143.2, 138.5, 131.6, 128.2, 118.4 (q, J = 318.1 Hz), 112.6, 112.6, 73.2, 73.0, -0.8.
- IR (neat) cm^{-1} 2958, 2858, 1472, 1417, 1357, 1257, 1205, 1138, 974.

3. B. Martín-Matute, C. Nevado, D. Cárdenas, A. M. Echavarren, *J. Am. Chem. Soc.* **2003**, *125*, 5757.

- HRMS calcd for $C_{12}H_{14}F_3O_4SSi$ $(M-H)^+$: 339.0329, found 339.0326.

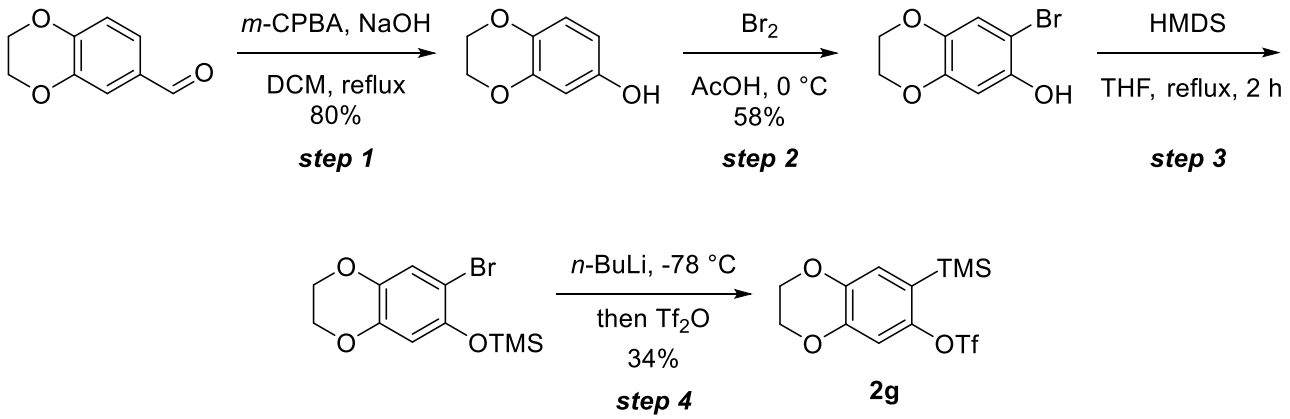
6-(trimethylsilyl)benzo[d][1,3]dioxol-5-yl trifluoromethanesulfonate **(2f)**



2f was prepared according to the General Method A, and the NMR spectral data are in accordance with the reported data[2].

- a colorless oil, 1.77 g, 47%.
- R_f = 0.5 (EtOAc/Petroleum Ether = 1/10).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (s, 1H), 6.84 (s, 1H), 6.03 (s, 2H), 0.33 (s, 9H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 148.6, 146.9, 124.9, 118.5 (q, J = 318.1 Hz), 113.2, 102.4, 102.3, 102.3, -0.7.

7-(trimethylsilyl)-2,3-dihydrobenzo[b][1,4]dioxin-6-yl trifluoromethanesulfonate **(2g)**



Step 1: 6-hydroxy-1,4-benzodioxane was prepared according to the literature[4]. A solution of 1,4-benzodioxan-6-carboxaldehyde (5.00 g, 30.46 mmol) in CH_2Cl_2 (50 mL) and meta-chloroperoxybenzoic acid (7.88 g, 45.69 mmol, 1.5 equiv.) was heated to 50 °C for 16 h before quenching with sat. aq. $NaHCO_3$ and extracting with CH_2Cl_2 (3 × 40 mL). The combined organic layers were concentrated *in vacuo*. The residue was subsequently dissolved in methanol (20 mL), and NaOH (1.46 g, 36.55 mmol) was added to the solution. The resulting mixture was stirred for 2 h, The solution was acidified to pH 7 (1 M HCl) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with sat. aq. NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (eluent: EtOAc/petroleum ether = 1/8) to 6-hydroxy-1,4-benzodioxane as a colorless oil (3.75 g, 80%).

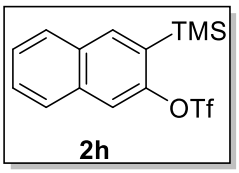
Step 2: To a solution of 6-hydroxy-1,4-benzodioxane (3.75 g, 24.61 mmol) in AcOH (35 mL) was added a solution of bromine (1.13 mL, 22.03 mmol, 0.9 equiv.) in AcOH (5 mL) dropwise at 0 °C and the reaction mixture was stirred for 1 h at this temperature before quenching with H_2O and extracting with EtOAc (3 × 50 mL). The combined organic layers were washed with sat. aq. NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (eluent: EtOAc/petroleum ether = 1/8) to give 7-bromo-2,3-dihydrobenzo[*b*][1,4]dioxin-6-ol as a colorless oil (3.29 g, 58%).

4. I. Engelbrecht, J. P. Petzer, A. Petzer, *Bioorg. Med. Chem. Lett.* **2015**, *25*, 1896.

Step 3 and 4: **2g** was prepared according to the General Method A. 7-bromo-2,3-dihydrobenzo[*b*][1,4]dioxin-6-ol (2.54 g, 11.00 mmol), HMDS (3.55 g, 22.00 mmol, 2.0 equiv.) refluxed for 2 h, then *n*-BuLi (6.54 mL, 2.4 M in hexane, 1.0 equiv) and Tf_2O (4.83 g, 13.20 mmol, 1.2 equiv) in anhydrous THF at -78 °C for 4 h gave **2g** as a colorless oil (1.73 g, 34%).

- R_f = 0.4 (EtOAc/Petroleum Ether = 1/20).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (s, 1H), 6.88 (s, 1H), 4.27 (s, 4H), 0.32 (s, 9H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 144.8, 142.7, 124.7, 123.6, 118.4 (q, J = 318.0 Hz), 109.4, 109.4, 109.4, 64.5, 64.2, -0.8.
- IR (neat) cm^{-1} 2965, 1610, 1577, 1486, 1415, 1297, 1204, 1138, 1063, 978.
- HRMS calcd for $C_{12}H_{14}F_3O_5SSi$ $(M-H)^-$: 355.0289, found 355.0290.

3-(trimethylsilyl)naphthalen-2-yl trifluoromethanesulfonate **(2h)**

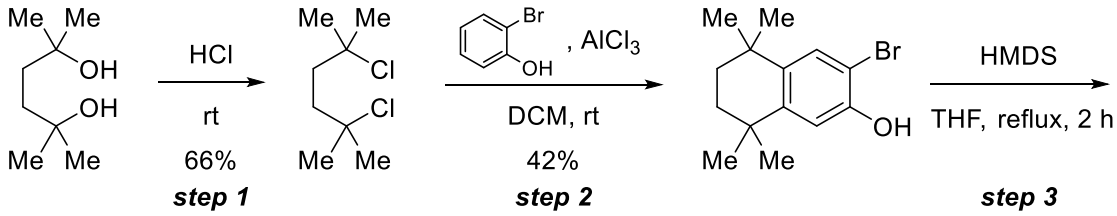


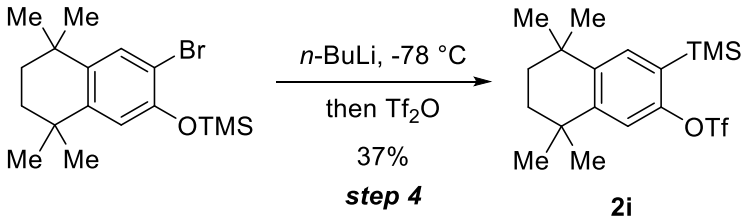
2h

2h was prepared according to the General Method A, and the NMR spectral data are in accordance with the reported data[2].

- a pale yellow oil, 1.57 g, 41%.
- R_f = 0.6 (Petroleum Ether).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.92 – 7.82 (m, 2H), 7.82 (s, 1H), 7.65 – 7.51 (m, 2H), 0.46 (s, 9H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 137.5, 134.1, 131.8, 131.0, 127.9, 127.8, 127.7, 126.9, 118.6 (q, J = 318.2 Hz), 116.5, 113.8, -0.8.

5,5,8,8-tetramethyl-3-(trimethylsilyl)-5,6,7,8-tetrahydronaphthalen-2-yl trifluoromethanesulfonate **(2i)**





Step 1: 2,5-dichloro-2,5-dimethylhexane was prepared according to the literature [5]. 2,5-dimethylhexane-2,5-diol (5.00 g, 34.19 mmol) was dissolved in concentrated hydrochloric acid (50 mL). The white slurry was shaken and stirred for 17 h. The white solid was collected by suction filtration and rinsed with 500 mL of H_2O. The solid was dissolved in 200 mL of CH_2Cl_2, the small water layer was removed. The organic layers were dried over Na_2SO_4 and concentrated under reduced

5. N. Lamei, A. Foroumadi, S. Emami, M. Amini, A. Shafiee, *Chin. J. Chem.* **2010**, *28*, 1951.

pressure. The white crystalline solid was dried *in vacuo* for 30 min to provide the product 2,5-dichloro-2,5-dimethylhexane (4.13 g, 66%).

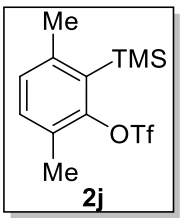
Step 2: 3-bromo-5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalen-2-ol was prepared according to the literature[6]. To a solution of 2,5-dichloro-2,5-dimethylhexane (4.13 g, 28.24 mmol) in anhydrous CH_2Cl_2 (40 mL) under argon was added 2-bromophenol (7.33 g, 42.36 mmol) and $AlCl_3$ (376 mg, 2.82 mmol). The reaction was stirred overnight at room temperature before quenching with H_2O and extracting with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with sat. aq. NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (eluent: EtOAc/petroleum ether = 1/100) to give 3-bromo-5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalen-2-ol as a brown solid (3.36 g, 42%).

2i was prepared from 3-bromo-5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalen-2-ol according to the General Method A.

Step 3 and 4: 3-bromo-5,5,8,8-tetramethyl-5,6,7,8-tetrahydronaphthalen-2-ol (3.12 g, 11.00 mmol), HMDS (3.55 g, 22.00 mmol, 2.0 equiv.) refluxed for 2 h, then *n*-BuLi (5.04 mL, 2.4 M in hexane, 1.0 equiv) and Tf_2O (3.72 g, 13.20 mmol, 1.2 equiv) in anhydrous THF at -78 °C for 4 h gave **2i** as a white solid (1.66 g, 37%).

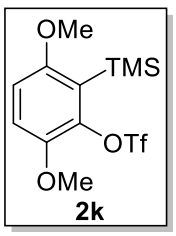
- R_f = 0.4 (EtOAc/Petroleum Ether = 1/20).
- mp: 50.6 – 55.2 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ7.43 (s, 1H), 7.21 (s, 1H), 1.69 (s, 4H), 1.28 (s, 6H), 1.27 (s, 6H), 0.35 (s, 9H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 149.5, 144.6, 135.2, 129.4, 119.2 (q, J = 318.2 Hz), 117.8, 114.4, 35.4, 35.3, 35.1, 34.7, 32.4, 32.1, -0.1.
- IR (neat) cm^{-1} 2961, 1419, 1275, 1260, 1208, 1142, 1090, 971.
- HRMS calcd for $C_{18}H_{28}F_3O_3SSi$ $(M+H)^+$: 409.1475, found 409.1473.

<u>3,6-dimethyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate</u> **(2j)**



2j was prepared according to the General Method A, and the NMR spectral data are in accordance with the reported data[7].

- a colorless oil, 1.83 g, 51%.
- R_f = 0.8 (Petroleum Ether).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, J = 7.6 Hz, 1H), 7.08 (d, J = 8.0 Hz, 1H), 2.47 (s, 3H), 2.32 (s, 3H), 0.44 (s, 9H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 144.3, 133.3, 132.9, 130.5, 128.7, 118.6 (q, J = 317.6 Hz), 23.3, 16.8, 1.7.



<u>3,6-dimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate</u> **(2k)**

2k was prepared according to the literature, and the NMR spectral data are in accordance with the reported data[8].

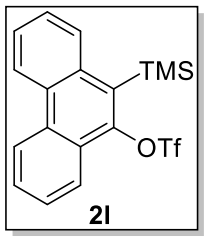
6. V. Nahoum, E. Perez, P. Germain, F. Rodriguez-Barrios, F.Manzo, S. Kammerer, G. Lemaire, O. Hirsch, C. A. Royer, H. Gronemeyer, *Proc. Natl. Acad. Sci. U. S. A.***2007**, *104*, 17323.

7. Y. Wang, A. D. Stretton, M. C. Mcconnell, P. A. Wood, S. Parsons, J. B. Henry, A. R. Mount, T. H. Galow, *J. Am. Chem. Soc.* **2007**, *129*, 13193.

8. J. George, J. S. Ward, M. S. Sherburn, *Org. Lett.* **2019**, *21*, 7529.

- a white solid, 2.05 g, 52%.
- R_f = 0.6 (EtOAc/Petroleum Ether = 1/20).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (d, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 0.38 (s, *J* = 1.0 Hz, 9H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 145.1, 142.6, 123.9, 118.9 (q, *J* = 319.2 Hz), 114.1, 109.9, 56.1, 55.8, 0.7.

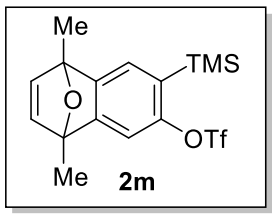
10-(trimethylsilyl)phenanthren-9-yl trifluoromethanesulfonate **(2l)**



2l was prepared according to the General Method A, and the NMR spectral data are in accordance with the reported data[9].

- a brown solid, 2.45 g, 56%.
- R_f = 0.3 (Petroleum Ether).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (m, *J* = 8.4, 1.5 Hz, 2H), 8.25 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.15 (d, *J* = 6.8 Hz, 1H), 7.83 – 7.60 (m, 4H), 0.64 (s, 9H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 134.6, 132.7, 130.5, 130.0, 129.7, 128.4, 127.3, 127.1, 126.6, 125.8, 123.3, 122.7, 122.2, 118.7 (q, *J* = 320.5 Hz), 2.2.

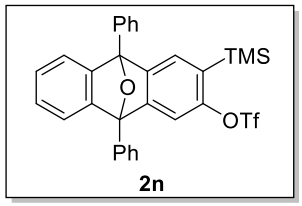
1,4-dimethyl-7-(trimethylsilyl)-1,4-dihydro-1,4-epoxynaphthalen-6-yl trifluoromethanesulfonate **(2m)**



2m was prepared according to the literature, and the NMR spectral data are in accordance with the reported data[10].

- a white solid, 600 mg, 79%.
- R_f = 0.3 (EtOAc/Petroleum Ether = 1/10).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (s, 1H), 7.08 (s, 1H), 6.78 (q, *J* = 5.2 Hz, 2H), 1.90 (s, 3H), 1.87 (s, 3H), 0.34 (s, 9H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 152.4, 151.6, 146.9, 146.3, 127.9, 124.1, 118.4 (q, *J* = 319.5 Hz), 111.1, 88.6, 88.5, 15.1, 15.0, -0.7.

9,10-diphenyl-3-(trimethylsilyl)-9,10-dihydro-9,10-epoxyanthracen-2-yl trifluoromethanesulfonate **(2n)**



2n was prepared according to the literature, and the NMR spectral data are in accordance with the reported data[11].

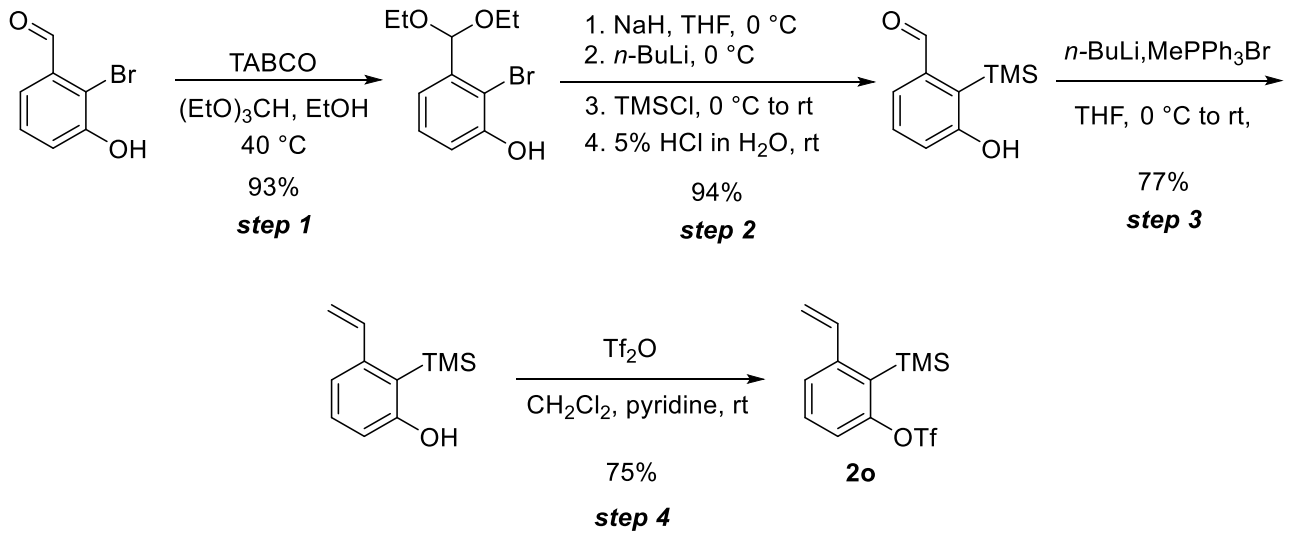
- a colorless oil, 690 mg, 63%.
- R_f = 0.8 (EtOAc/Petroleum Ether = 1/10).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ7.95 – 7.85 (m, 4H), 7.73 – 7.55 (m, 4H), 7.57 – 7.48 (m, 2H), 7.45 (s, 1H), 7.44 – 7.34 (m, 2H), 7.33 (s, 1H), 7.23 – 7.00 (m, 2H), 0.30 (s, 9H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 152.8, 149.7, 149.4, 149.3, 134.2, 133.9, 129.6, 129.0, 128.9, 128.7, 128.6, 126.6, 126.6, 126.5, 126.3, 126.2, 120.9, 120.6, 118.4 (q, *J* = 320.0 Hz)112.8, 90.5, 90.4, -0.9.

2-(trimethylsilyl)-3-vinylphenyl trifluoromethanesulfonate **(2o)**

9. P. Diego, P. Dolores, G. Enrique, C. Luis, *Org. Lett.* **1999**, *1*, 1555.

10. T. Ikawa, S. Masuda, A. Takagi, S. Akai, *Chem. Sci.* **2016**, *7*, 5206.

11. a) T. Kitamura, K. Gondo, J. Oyamada, *J. Am. Chem. Soc.* **2017**, *139*, 8416. b) X.-K. Yang, G. C. Tsui, *Chem. Sci.*, **2018**,*9*, 8871.



Step 1: To a solution of 2-bromo-3-hydroxy benzaldehyde (7.00 g, 34.82 mmol, 1.0 equiv.) in EtOH (80 mL) was added TABCO (1.43 g, 3.48 mmol, 0.1 equiv.) and $(EtO)_3CH$ (25.80 g, 174.11 mmol, 5.0 equiv.). The reaction was stirred overnight at 40 ºC before quenching with sat. aq. $NaHCO_3$ (30 mL) and extracting with CH_2Cl_2 (50 mL x 3). The combined organic layers were washed with sat. aq. NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (eluent: EtOAc/ petroleum ether = 1/10) on triethylamine-buffered silica gel afforded 2-bromo-3-(diethoxymethyl) phenol as a pale yellow oil (9.00 g, 93% yield).

Step 2: 3-hydroxy-2-(trimethylsilyl)benzaldehyde was prepared according to the literature [12]. To a solution of NaH (785 mg, 19.63 mmol, 1.2 equiv.) in THF (30 mL) at 0 ºC was added a solution of 2-bromo-3-(diethoxymethyl) phenol (4.50 g, 16.36 mmol, 1.0 equiv.) in THF (10 mL). After being stirred for 1 h at 0 ºC, *n*-BuLi (8.18 mL, 2.4 M in hexane, 1.2 equiv.) was added dropwise. After stirring 40 min at 0 ºC, TMSCl (5.33 g, 49.07 mmol, 3 equiv.) was then added. After the addition was complete, the reaction mixture was warmed to room temperature over 2 h. After being stirred for 2 h, 20 mL of 5 % aqueous HCl was added. A saturated aqueous $NaHCO_3$ (50 mL) solution was added after 12 h, and the resulting mixture extracted with Et_2O (50 mL × 3). The combined organic layers were washed with sat. aq. NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (eluent: EtOAc/ petroleum ether = 1/5) afforded 3-hydroxy-2-(trimethylsilyl)benzaldehyde as a pale yellow solid (3.00 g, 94% yield).

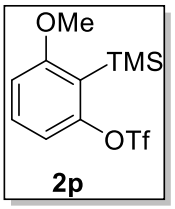
Step 3: To a solution of 3-hydroxy-2-(trimethylsilyl)benzaldehyde (3.00 g, 15.44 mmol) in THF (30 mL) was added *n*-BuLi (9.65 mL, 2.4 M in hexane, 1.5 equiv.) dropwise under Ar at 0 ºC. After stirring 30 min, methyltriphenylphosphonium bromide (8.27 g, 23.16 mmol, 1.5 equiv.) was added dropwise and the mixture was stirred at room temperature for 5 hours before quenching with H_2O and extracted with Et_2O (50 mL × 3). The combined organic layers were washed with sat. aq. NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (eluent: EtOAc/ petroleum ether = 1/10) to give 2-(trimethylsilyl)-3-vinylphenol as a pale colorless oil (2.28 g, 77% yield).

Step 4: To a solution of the resulting 2-(trimethylsilyl)-3-vinylphenol (2.28 g, 11.85 mmol) in CH_2Cl_2

(10 mL) at 0 ºC was added pyridine (2.81 g, 35.56 mmol, 3.0 equiv.) and Tf_2O (5.02 g, 17.78 mmol, 1.5 equiv.) dropwise. The reaction was stirred 1h at room temperature before quenching with sat. aq. NH_4Cl (30 mL) and extracting with CH_2Cl_2 (30 mL× 3).The combined organic layers were washed with sat. aq. NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (eluent: Petroleum ether) afforded **2o** as a pale yellow oil (2.89 g, 75% yield).

- R_f = 0.3 (Petroleum Ether).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 5.2 Hz, 1H), 7.39 (t, *J* = 5.2 Hz, 1H), 7.23 (d, *J* = 5.6 Hz, 1H), 7.05 (dd, *J* = 11.6, 7.2 Hz, 1H), 5.60 (d, *J* = 11.6 Hz, 1H), 5.36 (d, *J* = 7.2 Hz, 1H), 0.44 (s, 9H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 147.5, 138.0, 130.7, 126.3, 119.1, 119.1, 118.6 (q, *J* = 320.6 Hz), 117.2, 1.9.
- IR (neat) cm^{-1} 3008, 2989, 1550, 1416, 1275, 1240, 1163, 919, 841, 820, 764, 726.
- HRMS calcd for $C_{12}H_{16}F_3O_3SSi$ $(M+H)^+$: 325.0536, found 325.0536.

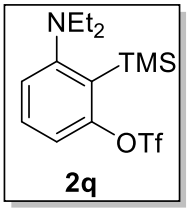
3-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **(2p)**



2p was prepared according to the General Method A, and the NMR spectral data are in accordance with the reported data[2].

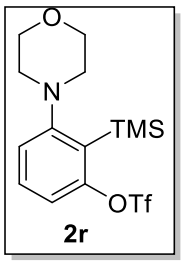
- a colorless oil, 1.51 g, 33%.
- R_f = 0.9 (EtOAc/Petroleum Ether = 1/10).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (t, *J* = 8.4 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 3.83 (s, 3H), 0.37 (s, 9H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 154.7, 131.6, 120.8, 118.6 (q, *J* = 318.8 Hz), 112.8, 109.5, 55.6, 0.7

3-(diethylamino)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **(2q)**



2q was prepared according to the literature, and the NMR spectral data are in accordance with the reported data[12].

- a colorless oil, 482 mg, 66%.
- R_f = 0.9 (Petroleum Ether).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 8.4 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 3.02 (q, *J* = 7.2 Hz, 4H), 0.98 (t, *J* = 7.2 Hz, 6H), 0.40 (s, 9H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 155.9, 130.5, 130.0, 122.3, 118.6 (q, *J* = 318.4 Hz), 115.2, 48.3, 11.1, 1.7.
- IR (neat) cm^{-1} 2977, 1592, 1555, 1461, 1275, 1259, 1205, 1138, 1052, 877.
- HRMS calcd for $C_{14}H_{22}F_3NO_3SSi$ $(M+H)^+$: 370.1115, found 370.1113.



3-morpholino-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **(2r)**

2r was prepared according to the literature, and the NMR spectral data are in accordance with the reported data[13].

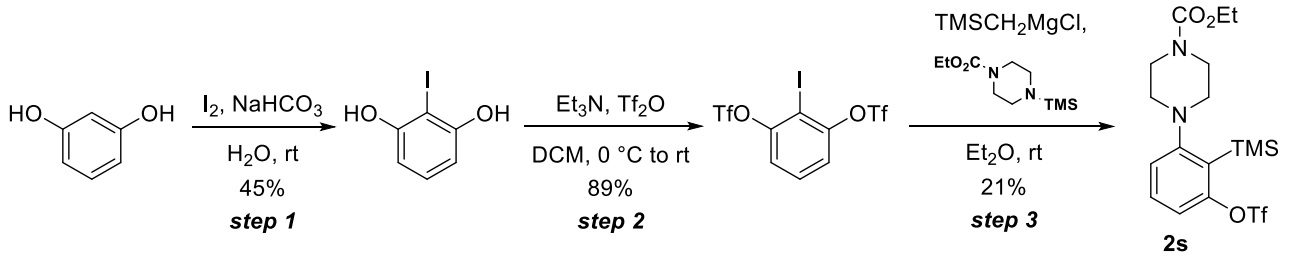
- a colorless oil, 473 mg, 27%.
- R_f = 0.3 (EtOAc/Petroleum Ether = 1/20).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (t, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H),

12. S. Yoshida, Y. Nakamura, K. Uchida, Y. Hazama, T. Hosoya, *Org. Lett.* **2016**, *18*, 6212.

7.16 (d, J = 8.4 Hz, 1H), 3.85 (s, 4H), 2.88 (s, 4H), 0.41 (s, 9H).

- ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 154.8, 131.6, 131.4, 122.4, 118.6 (q, J = 318.7 Hz), 118.2, 66.8, 54.6, 2.0.
- IR (neat) cm^{-1} 2856, 1592, 1442, 1416, 1259, 1205, 1138, 1114, 1105, 965.
- HRMS calcd for $C_{14}H_{20}F_3NO_4SSi$ $(M+H)^+$: 384.0907, found 384.0909.

ethyl 4-(3-(((trifluoromethyl)sulfonyl)oxy)-2-(trimethylsilyl)phenyl)piperazine-1-carboxylate **(2s)**



Step 1: 2-iodobenzene-1,3-diol was prepared according to the literature[13]. To a solution of resorcinol (5.00 g, 45.41 mmol) in H_2O (50 mL) at 0 ºC were added I_2 (12.56 g, 49.50 mmol, 1.09 equiv.) and $NaHCO_3$ (5.44 g, 50.86 mmol, 1.12 equiv.). Once the addition was completed, the reaction was warmed to room temperature and stirred for 16 h. The remaining iodine was quenched with sat. aq. Na_2SO_3. The mixture was extracted with EtOAc (3 × 50 mL). The combined organic layers were concentrated under reduced pressure, The crude residue was purified by silica gel flash column chromatography (eluent: EtOAc/petroleum ether = 1/5) to give 2-iodobenzene-1,3-diol as a white solid (4.82 g, 45%).

Step 2: 1,3-bis(triflyloxy)-2-iodobenzene was prepared according to the literature[14]. To a solution of 2-iodobenzene-1,3-diol (4.82 g, 20.42 mmol) in anhydrous CH_2Cl_2 (50 mL) at 0 ºC under argon were added Et_3N (4.55 g, 44.93 mmol, 2.2 equiv.) and Tf_2O (12.68 g, 44.93 mmol, 2.2 equiv.). The reaction was warmed to room temperature and stirred for 2 h before quenching with H_2O and extracting with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with sat. aq. NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (eluent: petroleum ether) to give 1,3-bis(triflyloxy)-2-iodobenzene as a pale yellow solid (9.08 g, 89%).

Step 3: To a solution of 1,3-bis(triflyloxy)-2-iodobenzene (1.00 g, 2.00 mmol) and ethyl 4-(trimethylsilyl)piperazine-1-carboxylate[15] (691 mg, 3.00 mmol, 1.5 equiv. in Et_2O 10 mL) was slowly added (trimethylsilyl)methylmagnesium chloride (2.60 mL, 1.0 M in Et_2O, 1.3 equiv.) at room temperature. After stirring for 1 h at the same temperature, the reaction was quenched with sat. aq. NH_4Cl and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with sat. aq. NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (eluent: EtOAc/petroleum ether = 1/ 20) to give **2s** as a pale yellow oil (191 mg, 21%).

- R_f = 0.1 (EtOAc/Petroleum Ether = 1/20).

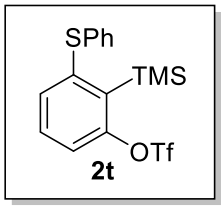
13. S. Meyer, J. Hfliger, M. Schfer, J. J. Molloy, C. G. Daniliuc, R. Gilmour, *Angew. Chem. Int. Ed.* **2021**, *60*, 6430.

14. L. Deng, M.-Q. Chen, G.-B. Dong, *J. Am. Chem. Soc.* **2018**, *140*, 9652.

15. S. H. Kim, B. H. Jin, J. H. Ahn, S. H. Park, S. Y. Choi, D. H. Kim, WO2018105920A1. 2018.

- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (t, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 4.11 (s, 2H), 3.14 (s, 2H), 2.84 (s, 4H), 1.28 (t, *J* = 7.2 Hz, 3H), 0.41 (s, 9H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 155.6, 154.7, 131.6, 131.3, 123.4, 120.2, 118.4, 118.6 (q, *J* = 318.8 Hz), 61.5, 54.1, 43.5, 14.7, 2.0.
- IR (neat) cm^{-1} 2987, 1698, 1592, 1555, 1417, 1311, 1276, 1259, 1243, 1206.
- HRMS calcd for $C_{17}H_{26}F_3N_2O_5SSi$ $(M+H)^+$: 455.1278, found 455.1277.

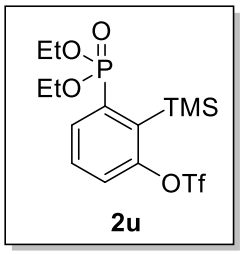
3-(phenylthio)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **(2t)**



2t was prepared according to the literature, and the NMR spectral data are in accordance with the reported data[16].

- a colorless oil, 1.14 g, 69%.
- R_f = 0.6 (Petroleum ether).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.06 (m, 8H), 0.53 (s, 9H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 145.6, 136.7, 135.2, 133.2, 130.9, 130.4, 129.4, 127.1, 119.2, 118.6 (q, *J* = 320.8 Hz), 2.1.

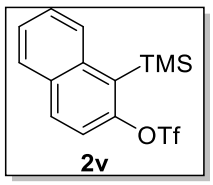
3-(diethoxyphosphoryl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **(2u)**



2u was prepared according to the literature, and the NMR spectral data are in accordance with the reported data[17].

- a colorless oil, 2.10 g, 53%.
- R_f = 0.2 (EtOAc/ petroleum ether = 1/5).
- ^{1}H NMR (400 MHz, $CDCl_3$) 7.92 (dd, *J* = 8.8, 4.8 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.46 (t, *J* = 6.4 Hz, 1H), 4.51 – 3.81 (m, 4H), 1.34 (t, *J* = 4.8 Hz, 6H), 0.51 (s, 9H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 155.4, 138.5, 138.4, 138.2, 137.0, 133.1, 133.1, 130.3, 130.2, 123.8, 118.5 (q, *J* = 320.4 Hz), 62.4, 16.2, 2.2.

1-(trimethylsilyl)naphthalen-2-yl trifluoromethanesulfonate **(2v)**



2v was prepared according to the General Method A, and the NMR spectral data are in accordance with the reported data[2].

- a colorless oil, 1.38 g, 36%.
- R_f = 0.5 (Petroleum Ether).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.4 Hz, 1H), 7.91 (m, 2H), 7.57 (m, 2H), 7.42 (d, *J* = 8.8 Hz, 1H), 0.61 (s, 9H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 137.5, 132.4, 132.4, 129.3, 129.0, 128.8, 126.7, 126.3, 119.1, 118.7 (q, *J* = 318.7 Hz), 2.2.

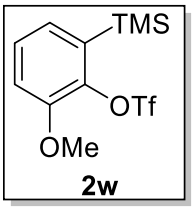
2-methoxy-6-(trimethylsilyl)phenyl trifluoromethanesulfonate **(2w)**

2w was prepared according to the General Method A, and the NMR spectral data are in accordance with the reported data[18].

16. Y. Nakamura, Y. Miyata, K. Uchida, S. Yoshida, T. Hosoya, *Org. Lett.* **2019**, *21*, 5252.

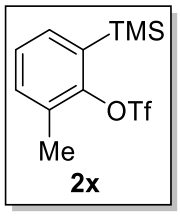
17. B. M. Bembenek, M. M. S. Petersen, J. A. Lilly, A. L. Haugen, N. J. Jiter, A. J. Johnson, E. E. Ripp, S. A. Winchell, A. N. Harvat, C. McNulty, S. A. Thein, A. M. Grieger, B. J. Lyle, G. L. Mraz, A. M. Stitgen, S. Foss, M. L. Schmid, J. D. Scanlon, P. H. Willoughby, *J. Org. Chem*. **2021**, *86*, 10724.

18. J. R. Shi, L. G. Li, C. H Shan, Z. H. Chen, L. Dai, M. Tan, Y. Lan, Y. Li, *J. Am. Chem. Soc.* **2021**, *143*, 10530.



- a colorless oil, 2.24 g, 62%.
- R_f = 0.2 (Petroleum Ether).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 3.86 (s, 3H), 0.38 (s, 9H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 143.8, 135.7, 129.2, 127.4, 119.5 (q, *J* = 319.4 Hz), 56.2, 0.1.

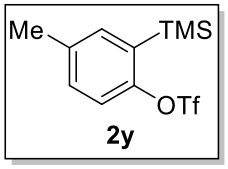
2-methyl-6-(trimethylsilyl)phenyl trifluoromethanesulfonate **(2x)**



2x was prepared according to the General Method A, and the NMR spectral data are in accordance with the reported data[2].

- a colorless oil, 1.48 g, 43%.
- R_f = 0.8 (Petroleum Ether).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 7.22 (s, 2H), 2.37 (s, 3H), 0.37 (s, 9H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 137.2, 136.7, 132.2, 131.7, 119.3, 118.5 (q, *J* = 317.9 Hz), 20.8, -0.8.

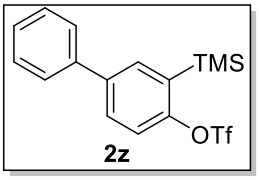
4-methyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **(2y)**



2y was prepared according to the General Method A, and the NMR spectral data are in accordance with the reported data[19].

- a colorless oil, 719 mg, 21%.
- R_f = 0.8 (Petroleum Ether).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 7.22 (s, 2H), 2.37 (s, 3H), 0.37 (s, 9H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 137.2, 136.7, 132.2, 131.7, 118.5 (q, *J* = 318.1 Hz) 119.3, 20.8, -0.8.

3-(trimethylsilyl)-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate **(2z)**

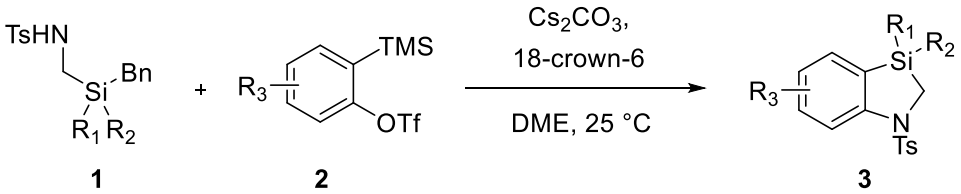


2z was prepared according to the General Method A, and the NMR spectral data are in accordance with the reported data[2].

- a colorless oil, 1.85 g, 45%.
- R_f = 0.7 (Petroleum Ether).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 2.4 Hz, 1H), 7.62 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.55 (d, *J* = 7.2 Hz, 2H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.41 (m, 2H), 0.42 (s, 9H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 140.7, 139.9, 135.1, 133.1, 130.1, 129.1, 128.0, 127.4, 119.9, 118.7 (q, *J* = 317.9 Hz), -0.7.

19. T. Y. Zhang, C. Liu, C. Chen, J. X. Liu, H. Y. Xiang, W. Jiang, T. M. Ding, S.-Y. Zhang, *Org. Lett.* **2018**, *20*, 220.

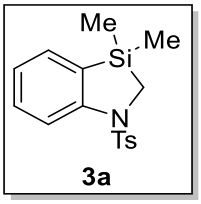
4. Synthesis of 3-Silaindoline 3



General Method B:

A mixture of 1,3-N, Si-reagent **1** (100 mg, 1.0 equiv.), aryne precursor **2** (2.5 equiv.), Cs_2CO_3 (2.5 equiv.) and 18-crown-6 (2.5 equiv.) in DME (1.5 mL) was stirred at 25 °C for 10 h under argon atmosphere. After the reaction was completed, the mixture was quenched wtih H_2O and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with sat. aq. NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography to afford silaindoline **3**.

3,3-dimethyl-1-tosyl-2,3-dihydro-1H-benzo[d][1,3]azasilole **(3a)**



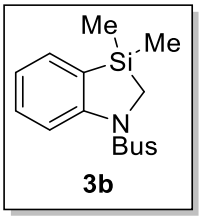
3a was prepared according to General Method B. **1a** (100 mg, 0.30 mmol), **2a** (223 mg, 0.75 mmol, 2.5 equiv.), Cs_2CO_3 (244 mg, 0.75 mmol, 2.5 equiv.) and 18-crown-6 (198 mg, 0.75 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3a** as a white solid (84 mg, 88%).

Gram-scale synthesis: 1a (2.00 g, 6 mmol), **2a** (4.47 g, 15.00 mmol, 2.5 equiv.), Cs_2CO_3 (4.88 g, 15.00 mmol, 2.5 equiv.) and 18-crown-6 (3.96 g, 15.00 mmol, 2.5 equiv.) in DME (30 mL) at 25 °C for 10 h afforded **3a** as a white solid (1.47 g, 77%).

Generation from 1b: 1b (100 mg, 0.34 mmol), **2a** (255 mg, 0.85 mmol, 2.5 equiv.), Cs_2CO_3 (279 mg, 0.85 mmol, 2.5 equiv.) and 18-crown-6 (226 mg, 0.85 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3a** as a white solid (21 mg, 19%).

- R_f = 0.4 (EtOAc/Petroleum Ether = 1/10).
- mp: 121.2 – 127.6 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.33 (dd, *J* = 7.2, 0.8 Hz, 1H), 7.28 (ddd, *J* = 8.6, 7.6, 1.6 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.96 (t, *J* = 7.6 Hz, 1H), 3.12 (s, 2H), 2.31 (s, 3H), 0.16 (s, 6H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 143.6, 135.2, 132.7, 131.1, 129.5, 127.1, 127.0, 122.9, 117.0, 38.4, 21.5, -2.2.
- ^{29}Si NMR (400 MHz, $CDCl_3$) δ -4.54.
- IR (neat) cm^{-1} 1441, 1349, 1260, 1165, 1091, 816, 751.
- HRMS calcd for $C_{16}H_{20}NO_2SSi$ $(M+H)^+$: 318.0979, found 318.0979.

1-(tert-butylsulfonyl)-3,3-dimethyl-2,3-dihydro-1H-benzo[d][1,3]azasilole **(3b)**



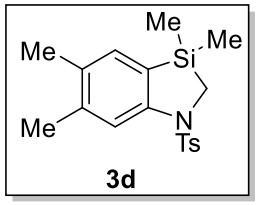
3b was prepared according to General Method B. **1c** (100 mg, 0.33 mmol), **2a** (249 mg, 0.83 mmol, 2.5 equiv.), Cs_2CO_3 (272 mg, 0.83 mmol, 2.5 equiv.) and 18-crown-6 (221 mg, 0.83 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3b** as a pale yellow oil (43 mg, 48%).

- R_f = 0.4 (EtOAc/Petroleum Ether = 1/10).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 1H), 7.43 (dd, *J* = 7.2, 1.6

Hz, 1H), 7.29 (ddd, *J* = 8.8, 7.2, 1.6 Hz, 1H), 6.99 (t, *J* = 7.2 Hz, 1H), 3.33 (s, 2H), 1.46 (s, 9H), 0.40 (s, 6H).

- ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 132.6, 130.9, 125.8, 122.1, 116.8, 64.0, 40.8, 25.3, -2.0.
- IR (neat) cm^{-1} 2923, 1658, 1607, 1586, 1459, 1328, 1130, 1025.
- HRMS calcd for $C_{13}H_{21}NNaO_2SSi$ $(M+Na)^+$: 306.0954, found 306.0951.

3,3,5,6-tetramethyl-1-tosyl-2,3-dihydro-1H-benzo[d][1,3]azasilole **(3d)**



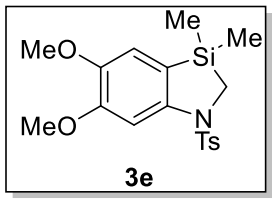
3d

3d was prepared according to General Method B. **1a** (100 mg, 0.30 mmol), **2b** (245 mg, 0.75 mmol, 2.5 equiv.), Cs_2CO_3 (244 mg, 0.75 mmol, 2.5 equiv.) and 18-crown-6 (198 mg, 0.75 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3d** as a white solid (87 mg, 84%).

- R_f = 0.3 (EtOAc/Petroleum Ether = 1/10).
- mp: 119.7 – 125.1 °C.

- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.14 (s, 1H), 3.14 (s, 2H), 2.36 (s, 3H), 2.28 (s, 3H), 2.20 (s, 3H), 0.18 (s, 6H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 143.4, 140.1, 135.1, 133.3, 131.4, 129.4, 127.1, 124.1, 118.3, 38.6, 21.4, 20.6, 19.0, -2.1.
- IR (neat) cm^{-1} 2920, 1599, 1450, 1386, 1346, 1249, 1163, 1090, 1049, 1000.
- HRMS calcd for $C_{18}H_{24}NO_2SSi$ $(M+H)^+$: 346.1292, found 346.1290.

5,6-dimethoxy-3,3-dimethyl-1-tosyl-2,3-dihydro-1H-benzo[d][1,3]azasilole **(3e)**



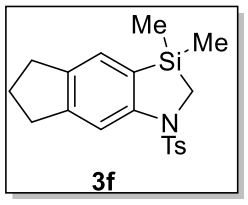
3e

3e was prepared according to General Method B. **1a** (100 mg, 0.30 mmol), **2c** (269 mg, 0.75 mmol, 2.5 equiv.), Cs_2CO_3 (244 mg, 0.75 mmol, 2.5 equiv.) and 18-crown-6 (198 mg, 0.75 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3e** as a white solid (78 mg, 69%).

- R_f = 0.3 (EtOAc/Petroleum Ether = 1/4).
- mp: 170.2 – 175.1 °C.

- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.78 (s, 1H), 3.93 (s, 3H), 3.85 (s, 3H), 3.13 (s, 2H), 2.36 (s, 3H), 0.11 (s, 6H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 145.7, 144.8, 143.6, 134.7, 129.4, 127.2, 117.7, 113.2, 102.6, 56.0, 55.9, 39.0, 21.4, -1.9.
- IR (neat) cm^{-1} 2956, 1595, 1588, 1491, 1463, 1443, 1386, 1343, 1243, 1162, 1090.
- HRMS calcd for $C_{18}H_{24}NO_4SSi$ $(M+H)^+$: 378.1190, found 378.1191.

3,3-dimethyl-1-tosyl-1,2,3,5,6,7-hexahydroindeno[5,6-d][1,3]azasilole **(3f)**



3f

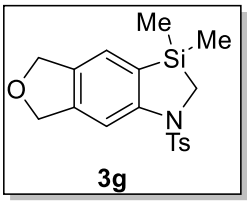
3f was prepared according to General Method B. **1a** (100 mg, 0.30 mmol), **2d** (254 mg, 0.75 mmol, 2.5 equiv.), Cs_2CO_3 (244 mg, 0.75 mmol, 2.5 equiv.) and 18-crown-6 (198 mg, 0.75 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3f** as a white solid (84 mg, 75%).

- R_f = 0.4 (EtOAc/Petroleum Ether = 1/10).
- mp: 108.5 – 113.1 °C.

- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.12 – 7.05 (m, 3H), 3.06 (s, 2H), 2.78 (t, *J* = 7.2 Hz, 2H), 2.69 (t, *J* = 7.2 Hz, 2H), 2.23 (s, 3H), 1.94 (p, *J* = 7.2 Hz, 2H), 0.05 (s, 6H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 148.4, 143.4, 139.1, 135.2, 129.4, 127.8, 127.1, 124.8, 113.5, 39.0, 33.3, 31.7, 25.6, 21.4, -2.1.

- IR (neat) cm^{-1} 2938, 2855, 1461, 1436, 1398, 1345, 1305, 1250, 1140, 1090.
- HRMS calcd for $C_{19}H_{24}NO_2SSi$ $(M+H)^+$: 358.1292, found 358.1290.

3,3-dimethyl-1-tosyl-2,3,5,7-tetrahydro-1H-isobenzofuro[5,6-d][1,3]azasilole **(3g)**

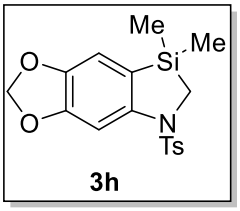


3g

3g was prepared according to General Method B. **1a** (100 mg, 0.30 mmol), **2e** (255 mg, 0.75 mmol, 2.5 equiv.), Cs_2CO_3 (244 mg, 0.75 mmol, 2.5 equiv.) and 18-crown-6 (198 mg, 0.75 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3g** as a white solid (70 mg, 65%).

- R_f = 0.1 (EtOAc/Petroleum Ether = 1/10).
- mp: 150.7 – 153.2 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.25 (s, 2H), 7.22 (d, *J* = 3.6 Hz, 1H), 5.08 (s, 2H), 5.03 (s, 2H), 3.21 (s, 2H), 2.37 (s, 3H), 0.20 (s, 6H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 143.7, 143.4, 135.0, 134.1, 129.6, 127.1, 126.7, 124.7, 110.0, 73.6, 72.8, 39.1, 21.5, -2.1.
- IR (neat) cm^{-1} 2850, 1615, 1406, 1347, 1275, 1162, 1132, 1090, 1057.
- HRMS calcd for $C_{18}H_{22}NO_3SSi$ $(M+H)^+$: 360.1084, found 360.1079.

7,7-dimethyl-5-tosyl-6,7-dihydro-5H-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,3]azasilole **(3h)**

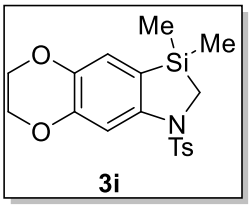


3h

3h was prepared according to General Method B. **1a** (100 mg, 0.30 mmol), **2f** (257 mg, 0.75 mmol, 2.5 equiv.), Cs_2CO_3 (244 mg, 0.75 mmol, 2.5 equiv.) and 18-crown-6 (198 mg, 0.75 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3h** as a pale yellow solid (70 mg, 74%).

- R_f = 0.2 (EtOAc/Petroleum Ether = 1/10).
- mp: 152.4 – 156.1 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.54 (s, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.71 (s, 1H), 5.95 (s, 2H), 3.15 (s, 2H), 2.37 (s, 3H), 0.10 (s, 6H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 145.5, 144.2, 143.6, 134.7, 129.5, 127.2, 119.2, 109.9, 101.5, 100.8, 39.3, 21.5, -2.0.
- IR (neat) cm^{-1} 2906, 1599, 1503, 1467, 1435, 1392, 1257, 1159, 1121, 1089, 1036.
- HRMS calcd for $C_{17}H_{19}NNaO_4SSi$ $(M+Na)^+$: 384.0696, found 384.0695.

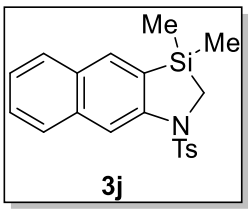
3,3-dimethyl-1-tosyl-2,3,6,7-tetrahydro-1H-[1,4]dioxino[2',3':4,5]benzo[1,2-d][1,3]azasilole **(3i)**



3i

3i was prepared according to General Method B. **1a** (100 mg, 0.30 mmol), **2g** (267 mg, 0.75 mmol, 2.5 equiv.), Cs_2CO_3 (244 mg, 0.75 mmol, 2.5 equiv.) and 18-crown-6 (198 mg, 0.75 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3i** as a pale yellow solid (55 mg, 49%).

- R_f = 0.1 (EtOAc/Petroleum Ether = 1/10).
- mp: 112.0 – 117.1 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.49 (s, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 6.82 (s, 1H), 4.27 – 4.18 (m, 4H), 3.13 (s, 2H), 2.37 (s, 3H), 0.14 (s, 6H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 144.3, 143.5, 140.0, 134.9, 129.5, 127.2, 119.9, 119.4, 106.9, 64.5, 64.1, 38.9, 21.5, -2.1.
- IR (neat) cm^{-1} 2925, 1598, 1568, 1473, 1407, 1345, 1242, 1162, 1090, 1069, 1001.
- HRMS calcd for $C_{18}H_{22}NO_4SSi$ $(M+H)^+$: 376.1033, found 376.1033.



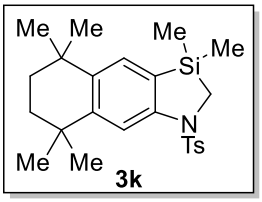
3j

3,3-dimethyl-1-tosyl-2,3-dihydro-1H-naphtho[2,3-d][1,3]azasilole **(3j)**

3j was prepared according to General Method B. **1a** (100 mg, 0.30 mmol), **2h** (261 mg, 0.75 mmol, 2.5 equiv.), Cs_2CO_3 (244 mg, 0.75 mmol, 2.5 equiv.) and 18-crown-6 (198 mg, 0.75 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3j** as a white solid (49 mg, 45%).

- R_f = 0.4 (EtOAc/Petroleum Ether = 1/10).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.90 (s, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 3H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 3.28 (s, 2H), 2.34 (s, 3H), 0.30 (s, 6H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 143.7, 135.3, 135.2, 133.7, 129.9, 129.5, 128.4, 128.0, 127.5, 127.2, 127.0, 124.7, 112.9, 38.7, 21.5, -2.3.
- IR (neat) cm^{-1} 3052, 2957, 2850, 1591, 1440, 1345, 1263, 1162, 1144, 1089, 1041.
- HRMS calcd for $C_{20}H_{22}NO_2SSi$ $(M+H)^+$: 368.1135, found 368.1133.

3,3,5,5,8,8-hexamethyl-1-tosyl-2,3,5,6,7,8-hexahydro-1H-naphtho[2,3-d][1,3]azasilole **(3k)**

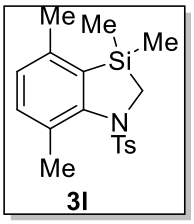


3k

3k was prepared according to General Method B. **1a** (100 mg, 0.30 mmol), **2i** (306 mg, 0.75 mmol, 2.5 equiv.), Cs_2CO_3 (244 mg, 0.75 mmol, 2.5 equiv.) and 18-crown-6 (198 mg, 0.75 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3k** as a white solid (46 mg, 36%).

- R_f = 0.5 (EtOAc/Petroleum Ether = 1/10).
- mp: 197.4 – 201.8 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.30 (s, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 3.17 (s, 2H), 2.37 (s, 3H), 1.85 – 1.61 (m, 4H), 1.30 (s, 6H), 1.23 (s, 6H), 0.25 (s, 6H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 147.7, 143.4, 139.4, 135.5, 130.7, 129.4, 127.3, 124.0, 114.2, 38.6, 35.1, 35.0, 34.9, 33.8, 31.9, 31.8, 21.5, -2.0.
- IR (neat) cm^{-1} 2956, 2859, 1599, 1472, 1345, 1250, 1056, 1091, 1020, 994.
- HRMS calcd for $C_{24}H_{34}NO_2SSi$ $(M+H)^+$: 428.2074, found 428.2072.

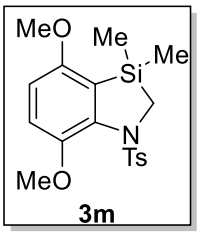
3,3,4,7-tetramethyl-1-tosyl-2,3-dihydro-1H-benzo[d][1,3]azasilole **(3l)**



3l

3l was prepared according to General Method B. **1a** (100 mg, 0.30 mmol), **2j** (244 mg, 0.75 mmol, 2.5 equiv.), Cs_2CO_3 (244 mg, 0.75 mmol, 2.5 equiv.) and 18-crown-6 (198 mg, 0.75 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3l** as a white solid (89 mg, 86%).

- R_f = 0.3 (EtOAc/Petroleum Ether = 1/10).
- mp: 98.4 – 103.2 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 3H), 6.95 (d, *J* = 7.6 Hz, 1H), 3.11 (s, 2H), 2.54 (s, 3H), 2.38 (s, 3H), 2.28 (s, 3H), -0.10 (s, 6H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 143.6, 139.8, 134.7, 133.9, 133.3, 131.5, 129.3, 128.5, 126.9, 40.3, 21.7, 21.4, 20.6, -2.8.
- IR (neat) cm^{-1} 2922, 1598, 1468, 1348, 1234, 1158, 1089, 1037, 1004.
- HRMS calcd for $C_{18}H_{24}NO_2SSi$ $(M+H)^+$: 346.1292, found 346.1295.

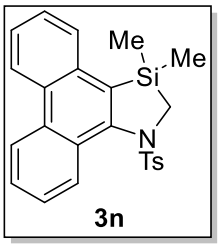


4,7-dimethoxy-3,3-dimethyl-1-tosyl-2,3-dihydro-1H-benzo[d][1,3]azasilole **(3m)**

3m was prepared according to General Method B. **1a** (100 mg, 0.30 mmol), **2k** (268 mg, 0.75 mmol, 2.5 equiv.), Cs_2CO_3 (244 mg, 0.75 mmol, 2.5 equiv.) and 18-crown-6 (198 mg, 0.75 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3m** as a pale yellow solid (70 mg, 62%).

- R_f = 0.2 (EtOAc/Petroleum Ether = 1/10).
- mp: 168.5 – 172.1 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 7.2 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.56 (d, *J* = 8.4 Hz, 1H), 3.75 (s, 3H), 3.63 (s, 3H), 3.37 (s, 2H), 2.41 (s, 3H), 0.26 (s, 6H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 146.7, 142.6, 140.3, 138.9, 129.1, 127.0, 121.2, 116.8, 107.0, 56.2, 55.7, 41.5, 21.5, -3.2.
- IR (neat) cm^{-1} 2955, 2835, 1583, 1481, 1462, 1389, 1331, 1274, 1255, 1153, 1081.
- HRMS calcd for $C_{18}H_{24}NO_4SSi$ $(M+H)^+$: 378.1190, found 378.1194.

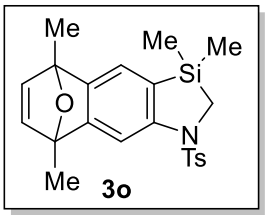
3,3-dimethyl-1-tosyl-2,3-dihydro-1H-phenanthro[9,10-d][1,3]azasilole **(3n)**



3n was prepared according to General Method B. **1a** (100 mg, 0.30 mmol), **2l** (299 mg, 0.75 mmol, 2.5 equiv.), Cs_2CO_3 (244 mg, 0.75 mmol, 2.5 equiv.) and 18-crown-6 (198 mg, 0.75 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3n** as a pale solid (79 mg, 63%).

- R_f = 0.2 (EtOAc/Petroleum Ether = 1/10).
- mp: 180.4 – 184.9 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (t, *J* = 8.0 Hz, 2H), 8.66 (d, *J* = 8.0 Hz, 1H), 7.75 – 7.69 (m, 1H), 7.70 – 7.61 (m, 2H), 7.60 – 7.52 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 3.39 (s, 2H), 2.35 (s, 3H), -0.02 (s, 6H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 144.0, 135.9, 133.5, 132.8, 129.8, 129.7, 129.4, 129.1, 128.7, 128.4, 128.3, 127.8, 126.9, 126.3, 125.6, 123.4, 122.3, 40.9, 21.4, -2.1.
- IR (neat) cm^{-1} 2923, 1597, 1491, 1447, 1350, 1162, 1088, 987.
- HRMS calcd for $C_{24}H_{24}NO_2SSi$ $(M+H)^+$: 418.1292, found 418.1292.

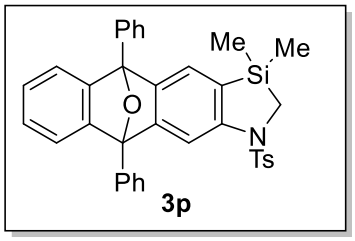
3,3,5,8-tetramethyl-1-tosyl-2,3,5,8-tetrahydro-1H-5,8-epoxynaphtho[2,3-d][1,3]azasilole **(3o)**



3o was prepared according to General Method B. **1a** (100 mg, 0.30 mmol), **2m** (294 mg, 0.75 mmol, 2.5 equiv.), Cs_2CO_3 (244 mg, 0.75 mmol, 2.5 equiv.) and 18-crown-6 (198 mg, 0.75 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3o** as a white solid (82 mg, 67%).

- R_f = 0.4 (EtOAc/ petroleum ether = 1/4).
- mp : 147.6 – 150.3 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.05 (s, 1H), 6.75 (s, 2H), 3.47 – 2.97 (m, 2H), 2.37 (s, 3H), 1.89 (s, 3H), 1.86 (s, 3H), 0.17 (s, 3H), 0.12 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 148.5, 147.2, 146.7, 146.0, 143.6, 135.0, 129.5, 127.1, 122.2, 120.9, 109.8, 88.7, 88.2, 39.2, 21.4, 15.2, 15.2, -2.0, -2.1.
- IR (neat) cm^{-1} 3006, 2982, 1449, 1389, 1275, 1260, 764, 750, 708.
- HRMS calcd for $C_{22}H_{26}NO_3SSi$ $(M+H)^+$: 312.1397, found 312.1392.

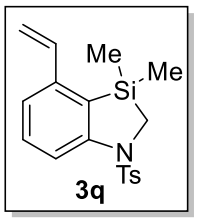
3,3-dimethyl-5,10-diphenyl-1-tosyl-2,3,5,10-tetrahydro-1H-5,10-epoxyanthra[2,3-d][1,3]azasilole **(3p)**



3p was prepared according to General Method B. **1a** (100 mg, 0.30 mmol), **2n** (425 mg, 0.75 mmol, 2.5 equiv.), Cs_2CO_3 (244 mg, 0.75 mmol, 2.5 equiv.) and 18-crown-6 (198 mg, 0.75 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3p** as a white solid (103 mg, 59%).

- R_f = 0.3 (EtOAc/ petroleum ether = 1/4).
- mp : 233.6 – 235.8 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.87 (m, 4H), 7.84 (s, 1H), 7.69 – 7.45 (m, 8H), 7.43 – 7.30 (m, 2H), 7.26 (s, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.07 – 7.03 (m, 2H), 3.42 – 2.83 (m, 2H), 2.32 (s, 3H), 0.23 (s, 3H), 0.12 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 150.5, 149.4, 148.7, 144.5, 143.7, 135.1, 135.0, 134.6, 129.5, 128.8, 128.7, 128.4, 128.1, 127.2, 126.9, 126.4, 125.9, 125.9, 123.3, 123.2, 120.7, 120.0, 110.4, 90.6, 90.1, 39.2, 21.4, -2.0, -2.1.
- IR (neat) cm^{-1} 2163, 2154, 2018, 1981, 1275, 1260, 1165, 764, 749, 705, 575.
- HRMS calcd for $C_{36}H_{32}NO_3SSi$ $(M+H)^+$: 586.1867, found 586.1863.

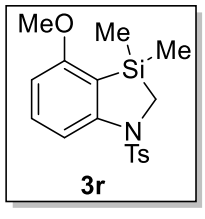
3,3-dimethyl-1-tosyl-4-vinyl-2,3-dihydro-1H-benzo[d][1,3]azasilole **(3q)**



3q was prepared according to General Method B. **1a** (100 mg, 0.30 mmol), **2o** (243 mg, 0.75 mmol, 2.5 equiv.), Cs_2CO_3 (244 mg, 0.75 mmol, 2.5 equiv.) and 18-crown-6 (198 mg, 0.75 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3q** as a pale yellow oil (59 mg, 57%).

- R_f = 0.3 (EtOAc/Petroleum Ether = 1/10).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.24 – 7.20 (m, 2H), 6.62 (dd, *J* = 17.2, 10.8 Hz, 1H), 5.70 (d, *J* = 17.2 Hz, 1H), 5.28 (d, *J* = 10.8 Hz, 1H), 3.18 (s, 2H), 2.37 (s, 3H), 0.28 (s, 6H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 143.7, 143.2, 136.8, 135.2, 131.7, 129.6, 127.1, 126.4, 118.9, 116.2, 115.8, 38.3, 21.5, -1.7.
- IR (neat) cm^{-1} 3004, 2994, 1561, 1440, 1345, 1275, 1260, 1183, 1089, 808, 764, 749.
- HRMS calcd for $C_{18}H_{22}NO_2SSi$ $(M+H)^+$: 344.1135, found 344.1134.

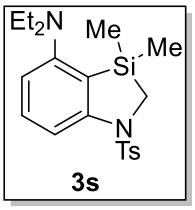
4-methoxy-3,3-dimethyl-1-tosyl-2,3-dihydro-1H-benzo[d][1,3]azasilole **(3r)**



3r was prepared according to General Method B. **1a** (100 mg, 0.30 mmol), **2p** or **2w** (246 mg, 0.75 mmol, 2.5 equiv.), Cs_2CO_3 (244 mg, 0.75 mmol, 2.5 equiv.) and 18-crown-6 (198 mg, 0.75 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3r** as a white solid (64 mg, 62% or 60 mg, 58%).

- R_f = 0.4 (EtOAc/Petroleum Ether = 1/10).
- mp: 93.6 – 99.6 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.29 (t, *J* = 8.4 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.46 (d, *J* = 8.0 Hz, 1H), 3.76 (s, 3H), 3.13 (s, 2H), 2.36 (s, 3H), 0.25 (s, 6H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 151.5, 143.5, 135.3, 133.3, 129.5, 127.1, 114.1, 109.8, 103.9, 55.2, 38.9, 21.5, -2.5.
- IR (neat) cm^{-1} 2959, 1587, 1461, 1344, 1249, 1160, 1119, 1079, 1032, 981.

- HRMS calcd for $C_{17}H_{22}NO_3SSi$ $(M+H)^+$: 348.1084, found 348.1084.

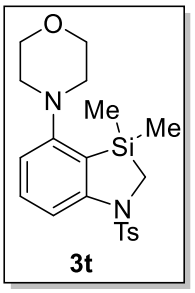


N,N-diethyl-3,3-dimethyl-1-tosyl-2,3-dihydro-1H-benzo[d][1,3]azasilol-4-amine **(3s)**

3s was prepared according to General Method B. **1a** (100 mg, 0.30 mmol), **2q** (277 mg, 0.75 mmol, 2.5 equiv.), Cs_2CO_3 (244 mg, 0.75 mmol, 2.5 equiv.) and 18-crown-6 (198 mg, 0.75 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3s** as a pale yellow solid (100 mg, 89%).

- R_f = 0.3 (EtOAc/Petroleum Ether = 1/10).
- mp: 91.7 – 97.4 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.27 (t, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.77 (d, *J* = 7.6 Hz, 1H), 3.10 (s, 2H), 2.91 (q, *J* = 7.2 Hz, 4H), 2.37 (s, 3H), 0.95 (t, *J* = 7.2 Hz, 6H), 0.24 (s, 6H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 151.4, 143.4, 135.5, 132.1, 129.4, 127.2, 125.7, 116.6, 113.1, 48.4, 38.9, 21.5, 12.6, -1.7.
- IR (neat) cm^{-1} 2969, 2929, 1597, 1571, 1455, 1345, 1247, 1160, 1089, 1040.
- HRMS calcd for $C_{20}H_{29}N_2O_2SSi$ $(M+H)^+$: 389.1714, found 389.1712.

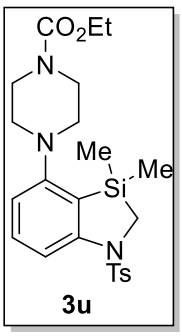
4-(3,3-dimethyl-1-tosyl-2,3-dihydro-1H-benzo[d][1,3]azasilol-4-yl)morpholine **(3t)**



3t was prepared according to General Method B. **1a** (100 mg, 0.30 mmol), **2r** (288 mg, 0.75 mmol, 2.5 equiv.), Cs_2CO_3 (244 mg, 0.75 mmol, 2.5 equiv.) and 18-crown-6 (198 mg, 0.75 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3t** as a white solid (70 mg, 58%).

- R_f = 0.2 (EtOAc/Petroleum Ether = 1/10).
- mp: 186.5 – 190.5 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.80 (d, *J* = 7.6 Hz, 1H), 3.78 (t, *J* = 4.4 Hz, 4H), 3.13 (s, 2H), 2.87 (t, *J* = 4.4 Hz, 4H), 2.38 (s, 3H), 0.28 (s, 6H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 151.4, 143.6, 135.4, 132.8, 129.5, 127.2, 124.2, 114.7, 113.7, 67.4, 53.8, 38.7, 21.5, -1.7.
- IR (neat) cm^{-1} 2956, 2851, 1572, 1450, 1346, 1292, 1163, 1070.
- HRMS calcd for $C_{20}H_{27}N_2O_3SSi$ $(M+H)^+$: 403.1506, found 403.1506.

ethyl 4-(3,3-dimethyl-1-tosyl-2,3-dihydro-1H-benzo[d][1,3]azasilol-4-yl)piperazine-1-carboxylate **(3u)**



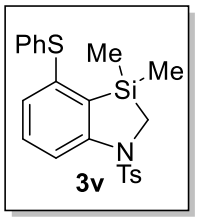
3u was prepared according to General Method B. **1a** (100 mg, 0.30 mmol), **2s** (341 mg, 0.75 mmol, 2.5 equiv.), Cs_2CO_3 (244 mg, 0.75 mmol, 2.5 equiv.) and 18-crown-6 (198 mg, 0.75 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3u** as a pale yellow solid (102 mg, 72%).

- R_f = 0.3 (EtOAc/Petroleum Ether = 1/4).
- mp: 152.3 – 155.1 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.75 (d, *J* = 7.6 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.55 (t, *J* = 4.4 Hz, 4H), 3.13 (s, 2H), 2.82 (t, *J* = 4.4 Hz, 4H), 2.38 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H), 0.27 (s, 6H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 155.6, 151.5, 143.6, 135.4, 132.8, 129.5, 127.2, 124.3,

114.8, 113.9, 61.5, 53.3, 44.2, 38.7, 21.5, 14.7, -1.7.

- IR (neat) cm^{-1} 2955, 1697, 1573, 1429, 1347, 1243, 1163, 1090, 1062, 1006.
- HRMS calcd for $C_{23}H_{32}N_3O_4SSi$ $(M+H)^+$: 474.1877, found 474.1874.

3,3-dimethyl-4-(phenylthio)-1-tosyl-2,3-dihydro-1H-benzo[d][1,3]azasilole **(3v)**

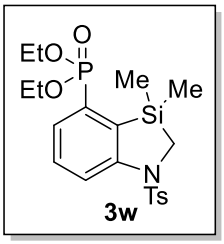


3v

3v was prepared according to General Method B. **1b** (100 mg, 0.30 mmol), **2t** (305 mg, 0.75 mmol, 2.5 equiv.), Cs_2CO_3 (244 mg, 0.75 mmol, 2.5 equiv.) and 18-crown-6 (198 mg, 0.75 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3v** as a pale yellow oil (73 mg, 57%).

- R_f = 0.4 (EtOAc/Petroleum Ether = 1/10).
- ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.19 (m, 5H), 7.19 – 7.11 (m, 3H), 6.88 (d, *J* = 7.2 Hz, 1H), 3.13 (s, 2H), 2.35 (s, 3H), 0.22 (s, 6H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 143.8, 140.6, 136.4, 135.1, 132.4, 130.9, 129.7, 129.6, 129.1, 127.1, 126.8, 126.7, 116.0, 38.4, 21.5, -2.2.
- IR (neat) cm^{-1} 2921, 2152, 2017, 1980, 1569, 1438, 1275, 1260, 1165, 764, 750.
- HRMS calcd for $C_{22}H_{24}NO_2S_2Si$ $(M+H)^+$: 426.1012, found 426.1009.

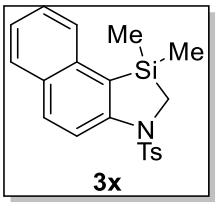
diethyl (3,3-dimethyl-1-tosyl-2,3-dihydro-1H-benzo[d][1,3]azasilol-4-yl)phosphonate **(3w)**



3w

3w was prepared according to General Method B. **1b** (100 mg, 0.30 mmol), **2u** (326 mg, 0.75 mmol, 2.5 equiv.), Cs_2CO_3 (244 mg, 0.75 mmol, 2.5 equiv.) and 18-crown-6 (198 mg, 0.75 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3w** as a pale yellow oil (60 mg, 44%).

- R_f = 0.2 (EtOAc/Petroleum Ether = 1/4).
- ^1H NMR (400 MHz, $CDCl_3$) δ 8.1 (d, *J* = 8.4 Hz, 1H), 7.7 (d, *J* = 8.4 Hz, 2H), 7.5 – 7.3 (m, 2H), 7.2 (d, *J* = 8.0 Hz, 4H), 4.2 – 3.8 (m, 4H), 3.1 (s, 2H), 2.4 (s, 3H), 1.3 (t, *J* = 7.2 Hz, 6H), 0.4 (s, 6H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1 (d, *J* = 22.5 Hz), 143.8, 135.2, 133.4 (d, *J* = 156.1 Hz), 132.3 (d, *J* = 10.7 Hz), 131.2 (d, *J* = 15.5 Hz), 129.6, 127.1, 125.9 (d, *J* = 10.6 Hz), 120.3 (d, *J* = 3.3 Hz), 62.0, 62.0, 39.5, 21.5, 16.3, 16.2, -1.1.
- IR (neat) cm^{-1} 3004, 2987, 1571, 1446, 1348,1275, 1260, 1160, 1020, 764, 749.
- HRMS calcd for $C_{20}H_{29}NO_5PSSi$ $(M+H)^+$: 454.1268, found 454.1263.



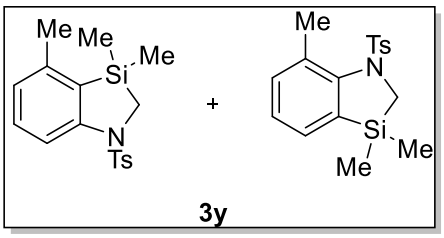
3x

1,1-dimethyl-3-tosyl-2,3-dihydro-1H-naphtho[1,2-d][1,3]azasilole **(3x)**

3x was prepared according to General Method B. **1a** (100 mg, 0.30 mmol), **2v** (261 mg, 0.75 mmol, 2.5 equiv.), Cs_2CO_3 (244 mg, 0.75 mmol, 2.5 equiv.) and 18-crown-6 (198 mg, 0.75 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3x** as a pale yellow solid (98 mg, 89%).

- R_f = 0.3 (EtOAc/Petroleum Ether = 1/10).
- ^1H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 9.2 Hz, 1H), 7.85 (d, *J* = 9.2 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 3.28 (s, 2H), 2.34 (s, 3H), 0.37 (s, 6H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 143.7, 136.4, 134.9, 132.1, 130.1, 129.5, 128.5, 127.1, 127.0, 124.6, 122.4, 118.0, 38.9, 21.4, -1.7.
- IR (neat) cm^{-1} 2961, 1619, 1585, 1503, 1452, 1341, 1275, 1258, 1159, 1088, 1008.
- HRMS calcd for $C_{20}H_{22}NO_2SSi$ $(M+H)^+$: 368.1135, found 368.1133.

3,3,4-trimethyl-1-tosyl-2,3-dihydro-1H-benzo[d][1,3]azasilole and 3,3,7-trimethyl-1-tosyl-2,3-dihydro-1H-benzo[d][1,3]azasilole **(3y)**

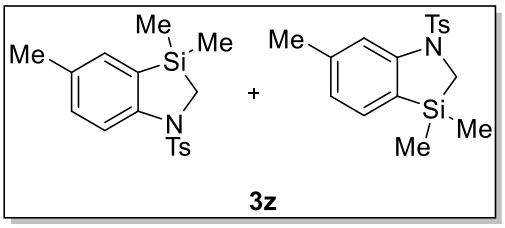


3y

3y was prepared according to General Method B. **1a** (100 mg, 0.3 mmol), **2x** (234 mg, 0.75 mmol, 2.5 equiv.), Cs_2CO_3 (244 mg, 0.75 mmol, 2.5 equiv.) and 18-crown-6 (198 mg, 0.75 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3y** as a white solid (72 mg, 73%, *rr* = 3:1).

- R_f = 0.2 (EtOAc/Petroleum Ether = 1/10).
- mp: 86.3 – 89.1 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.4 Hz, 3H), 7.60 (d, *J* = 8.4 Hz, 6H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.21 – 7.18 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 9H), 7.12 (d, *J* = 8.4 Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 1H), 6.74 (d, *J* = 7.2 Hz, 3H), 3.10 (s, 6H), 3.09 (s, 2H), 2.52 (s, 3H), 2.32 (s, 3H), 2.30 (s, 9H), 2.26 (s, 9H), 0.21 (s, 18H), -0.22 (s, 6H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 149.2, 143.7, 143.5, 143.4, 135.2, 134.7, 134.5, 134.2, 133.6, 131.6, 129.5, 129.4, 129.3, 128.5, 127.1, 126.1, 126.1, 123.6, 114.2, 40.6, 38.2, 22.3, 21.4, 21.4, 21.0, -2.3, -2.6.
- IR (neat) cm^{-1} 2965, 2918, 1578, 1454, 1345, 1251, 1160, 1089, 1041, 968.
- HRMS calcd for $C_{17}H_{22}NO_2SSi$ $(M+H)^+$: 332.1135, found 332.1130.

3,3,5-trimethyl-1-tosyl-2,3-dihydro-1H-benzo[d][1,3]azasilole and 3,3,6-trimethyl-1-tosyl-2,3-dihydro-1H-benzo[d][1,3]azasilole **(3z)**

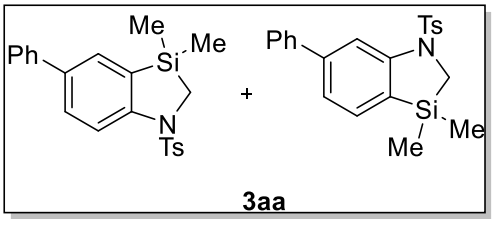


3z

3z was prepared according to General Method C. **1a** (100 mg, 0.30 mmol), **2y** (234 mg, 0.75 mmol, 2.5 equiv.), Cs_2CO_3 (244 mg, 0.75 mmol, 2.5 equiv.) and 18-crown-6 (198 mg, 0.75 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3z** as a white solid (78 mg, 79%, *rr* = 1.25:1).

- R_f = 0.3 (EtOAc/Petroleum Ether = 1/10).
- mp: 83.9 – 87.4 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.8 Hz, 0.85H), 7.78 (d, *J* = 17.6 Hz, 1H), 7.66 (t, *J* = 8.4 Hz, 3.7H), 7.28 (d, *J* = 7.2 Hz, 0.85H), 7.25 -7.20 (m, 3.7H), 7.19 – 7.12 (m, 1.85H), 6.86 (d, *J* = 7.6 Hz, 1H), 3.17 (s, 2H), 3.16 (s, 1.7H), 2.37 (s, 6H), 2.36 (s, 2.55H), 2.28 (s, 2.55H), 0.20 (s, 6H), 0.19 (s, 5.1H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 147.9, 143.5, 143.5, 141.5, 135.2, 135.0, 132.9, 132.4, 132.3, 131.9, 129.5, 129.4, 127.1, 127.1, 127.1, 124.1, 123.6, 117.6, 117.0, 38.7, 38.5, 22.0, 21.4, 21.4, 20.5, -2.1, -2.2.
- IR (neat) cm^{-1} 2965, 2918, 1598, 1461, 1398, 1347, 1258, 1164, 1145, 1090.
- HRMS calcd for $C_{17}H_{22}NO_2SSi$ $(M+H)^+$: 332.1135, found 332.1133.

3,3-dimethyl-5-phenyl-1-tosyl-2,3-dihydro-1H-benzo[d][1,3]azasilole and 3,3-dimethyl-6-phenyl-1-tosyl-2,3-dihydro-1H-benzo[d][1,3]azasilole **(3aa)**



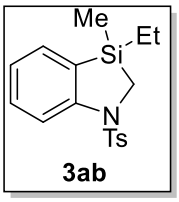
3aa

3aa was prepared according to General Method C. **1a** (100 mg, 0.30 mmol), **2z** (281 mg, 0.75 mmol, 2.5 equiv.), Cs_2CO_3 (244 mg, 0.75 mmol, 2.5 equiv.) and 18-crown-6

(198 mg, 0.75 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3aa** as a pale yellow oil (80 mg, 68%, *rr* = 1.5:1).

- R_f = 0.4 (EtOAc/Petroleum Ether = 1/10).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 1.5 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 0.67H), 7.74 – 7.68 (m, 3.33H), 7.63 – 7.61 (m, 1.33H), 7.60 (s, 2H), 7.56 (s, 1H), 7.54 (s, 0.67H), 7.53 – 7.42 (m, 3.33H), 7.41 (s, 0.77H), 7.40 - 7.38 (m, 1H), 7.36 - 7.30 (m, 1H), 7.32 – 7.27 (m, 0.77H), 7.26 – 7.20 (m, 3.33H), 3.24 (s, 2H), 3.22 (s, 1.33H), 2.36 (s, 2H), 2.35 (s, 3H), 0.26 (s, 4H), 0.25 (s, 6H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 150.1, 144.8, 144.3, 141.5, 141.0, 136.4, 135.8, 135.7, 133.5, 131.7, 130.7, 130.2, 130.2, 129.4, 129.3, 128.2, 128.2, 127.9, 127.7, 127.7, 127.6, 127.3, 126.3, 122.7, 117.7, 116.2, 39.4, 39.2, 22.1, 22.1, -1.5, -1.6.
- IR (neat) cm^{-1} 3060, 2965, 1594, 1465, 1390, 1346, 1250, 1161, 1089, 1071.
- HRMS calcd for $C_{22}H_{24}NO_2SSi$ $(M+H)^+$: 394.1292, found 394.1292.

3-ethyl-3-methyl-1-tosyl-2,3-dihydro-1H-benzo[d][1,3]azasilole **(3ab)**

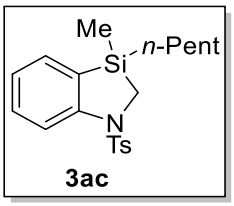


3ab

3ab was prepared according to General Method B. **1e** (100 mg, 0.29 mmol), **2a** (215 mg, 0.72 mmol, 2.5 equiv.), Cs_2CO_3 (234 mg, 0.72 mmol, 2.5 equiv.) and 18-crown-6 (190 mg, 0.72 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3ab** as a pale yellow oil (74 mg, 78%).

- R_f = 0.3 (EtOAc/Petroleum Ether = 1/10).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.38 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.34 (ddd, *J* = 8.6, 7.2, 1.6 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.01 (t, *J* = 7.2 Hz, 1H), 3.17 (dd, *J* = 45.6, 14.8 Hz, 2H), 2.36 (s, 3H), 0.86 (t, *J* = 8.4 Hz, 3H), 0.68 (q, *J* = 8.0 Hz, 2H), 0.21 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 143.6, 135.3, 132.9, 131.2, 129.5, 127.1, 125.9, 122.8, 116.8, 36.8, 21.4, 6.9, 6.2, -4.3.
- IR (neat) cm^{-1} 2955, 1586, 1459, 1346, 1162, 1135, 1089, 938.
- HRMS calcd for $C_{17}H_{22}NO_2SSi$ $(M+H)^+$: 354.0954, found 354.0954.

3-methyl-3-pentyl-1-tosyl-2,3-dihydro-1H-benzo[d][1,3]azasilole **(3ac)**

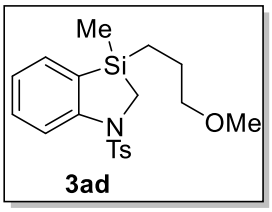


3ac

3z was prepared according to General Method B. **1f** (100 mg, 0.25 mmol), **2a** (191 mg, 0.64 mmol, 2.5 equiv.), Cs_2CO_3 (209 mg, 0.64 mmol, 2.5 equiv.) and 18-crown-6 (169 mg, 0.64 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3ac** as a pale yellow oil (82 mg, 86%).

- R_f = 0.5 (EtOAc/Petroleum Ether = 1/10).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.01 (t, *J* = 7.2 Hz, 1H), 3.16 (dd, *J* = 35.2, 14.4 Hz, 2H), 2.36 (s, 3H), 1.26 – 1.15 (m, 6H), 0.81 (t, *J* = 6.8 Hz, 3H), 0.68 – 0.55 (m, 2H), 0.21 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 143.6, 135.2, 132.9, 131.1, 129.5, 127.1, 126.3, 122.8, 116.9, 37.2, 35.3, 23.0, 22.1, 21.5, 14.2, 13.9, -3.8.
- IR (neat) cm^{-1} 2956, 2921, 1586, 1460, 1439, 1348, 1260, 1164, 1135, 1090, 1026.
- HRMS calcd for $C_{20}H_{28}NO_2SSi$ $(M+H)^+$: 374.1605, found 374.1603.

3-(3-methoxypropyl)-3-methyl-1-tosyl-2,3-dihydro-1H-benzo[d][1,3]azasilole **(3ad)**

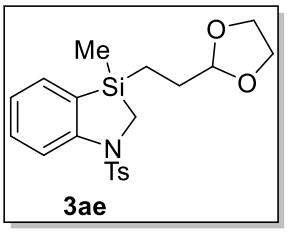


3ad

3ad was prepared according to General Method B. **1g** (100 mg, 0.26 mmol), **2a** (190 mg, 0.64 mmol, 2.5 equiv.), Cs_2CO_3 (208 mg, 0.64 mmol, 2.5 equiv.) and 18-crown-6 (168 mg, 0.64 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3ad** as a pale yellow oil (76 mg, 79%).

- R_f = 0.2 (EtOAc/Petroleum Ether = 1/10).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.37 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.33 (ddd, *J* = 8.8, 7.6, 1.6 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.00 (td, *J* = 7.2, 0.8 Hz, 1H), 3.28 (s, 3H), 3.16 (dd, *J* = 37.2, 14.4 Hz, 2H), 3.20 – 3.01 (m, 2H), 2.36 (s, 3H), 1.57 – 1.40 (m, 2H), 0.78 – 0.55 (m, 2H), 0.22 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 143.6, 135.2, 132.9, 131.1, 129.5, 127.1, 126.5, 122.8, 116.9, 74.5, 58.5, 37.4, 23.6, 21.5, 11.0, -3.8.
- IR (neat) cm^{-1} 2929, 2882, 1586, 1460, 1439, 1346, 1275, 1260, 1162, 1067, 1027.
- HRMS calcd for $C_{19}H_{26}NO_3SSi$ $(M+H)^+$: 376.1397, found 376.1396.

3-(2-(1,3-dioxolan-2-yl)ethyl)-3-methyl-1-tosyl-2,3-dihydro-1H-benzo[d][1,3]azasilole **(3ae)**

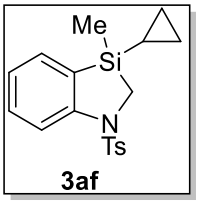


3ae

3ae was prepared according to General Method B. **1h** (100 mg, 0.24 mmol), **2a** (177 mg, 0.60 mmol, 2.5 equiv.), Cs_2CO_3 (194 mg, 0.60 mmol, 2.5 equiv.) and 18-crown-6 (157 mg, 0.60 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3ae** as a pale yellow oil (77 mg, 80%).

- R_f = 0.4 (EtOAc/Petroleum Ether = 1/4).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 6.8 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.00 (t, *J* = 7.2 Hz, 1H), 4.73 (t, *J* = 4.4 Hz, 1H), 4.03 – 3.71 (m, 4H), 3.17 (dd, *J* = 31.2, 14.8 Hz, 2H), 2.36 (s, 3H), 1.64 – 1.40 (m, 2H), 0.78 (t, *J* = 8.4 Hz, 2H), 0.23 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 143.7, 135.1, 133.0, 131.2, 129.5, 127.1, 126.1, 122.9, 116.9, 104.9, 65.0, 64.9, 37.4, 27.5, 21.5, 7.9, -3.8.
- IR (neat) cm^{-1} 2920, 1586, 1460, 1439, 1345, 1261, 1162, 1132, 1068, 1028.
- HRMS calcd for $C_{20}H_{26}NO_4SSi$ $(M+H)^+$: 404.1346, found 404.1345.

3-cyclopropyl-3-methyl-1-tosyl-2,3-dihydro-1H-benzo[d][1,3]azasilole **(3af)**

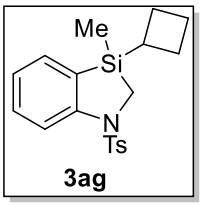


3af

3af was prepared according to General Method B. **1i** (100 mg, 0.28 mmol), **2a** (207 mg, 0.69 mmol, 2.5 equiv.), Cs_2CO_3 (226 mg, 0.69 mmol, 2.5 equiv.) and 18-crown-6 (184 mg, 0.69 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3af** as a pale yellow oil (64 mg, 67%).

- R_f = 0.3 (EtOAc/Petroleum Ether = 1/10).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.43 – 7.28 (m, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.00 (t, *J* = 7.2 Hz, 1H), 3.17 (dd, *J* = 56.0, 14.4 Hz, 2H), 2.36 (s, 3H), 0.75 – 0.49 (m, 2H), 0.27 – 0.20 (m, 1H), 0.16 (s, 3H), 0.09 – 0.01 (m, 1H), -0.37 (tt, *J* = 9.6, 6.8 Hz, 1H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 143.6, 135.2, 133.1, 131.3, 129.5, 127.1, 125.1, 122.7, 116.8, 37.2, 21.5, 1.6, 1.3, -5.2, -6.8.
- IR (neat) cm^{-1} 3005, 2933, 1586, 1438, 1346, 1260, 1161, 1089, 1028, 940.
- HRMS calcd for $C_{18}H_{21}NNaO_2SSi$ $(M+Na)^+$: 366.0954, found 366.0953.

3-cyclobutyl-3-methyl-1-tosyl-2,3-dihydro-1H-benzo[d][1,3]azasilole **(3ag)**

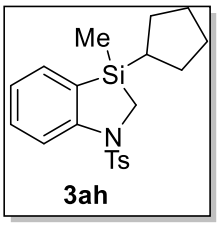


3ag

3ag was prepared according to General Method B. **1j** (100 mg, 0.27 mmol), **2a** (195 mg, 0.67 mmol, 2.5 equiv.), Cs_2CO_3 (218 mg, 0.67 mmol, 2.5 equiv.) and 18-crown-6 (177 mg, 0.67 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3ag** as a pale yellow oil (78 mg, 81%).

- R_f = 0.4 (EtOAc/Petroleum Ether = 1/10).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 7.2 Hz, 1H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.01 (t, *J* = 7.2 Hz, 1H), 3.17 (d, *J* = 55.6, 14.4 Hz, 2H), 2.36 (s, 3H), 2.14 – 1.99 (m, 3H), 1.98 – 1.81 (m, 3H), 1.78 – 1.66 (m, 1H), 0.22 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 143.6, 135.2, 133.1, 131.2, 129.5, 127.1, 125.4, 122.7, 116.6, 76.7, 36.2, 23.0, 22.7, 21.5, 20.2, -5.6.
- IR (neat) cm^{-1} 2963, 2860, 1585, 1492, 1460, 1438, 1346, 1274, 1261, 1162, 1089.
- HRMS calcd for $C_{19}H_{24}NO_2SSi$ $(M+H)^+$: 358.1291, found 358.1292.

3-cyclopentyl-3-methyl-1-tosyl-2,3-dihydro-1H-benzo[d][1,3]azasilole **(3ah)**

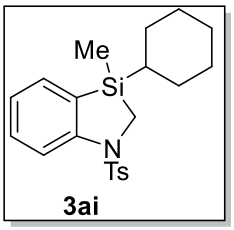


3ah

3ah was prepared according to General Method B. **1k** (100 mg, 0.26 mmol), **2a** (192 mg, 0.65 mmol, 2.5 equiv.), Cs_2CO_3 (210 mg, 0.65 mmol, 2.5 equiv.) and 18-crown-6 (170 mg, 0.65 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3ah** as a pale yellow oil (82 mg, 85%).

- R_f = 0.4 (EtOAc/Petroleum Ether = 1/10).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.0 Hz,2H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.00 (t, *J* = 7.2 Hz, 1H), 3.15 (dd, *J* = 50.8, 14.4 Hz, 2H), 2.36 (s, 3H), 1.75 – 1.60 (m, 2H), 1.55 – 1.39 (m, 4H), 1.25 – 1.08 (m, 2H), 1.05 – 0.90 (m, 1H), 0.21 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 143.6, 135.2, 133.1, 131.1, 129.5, 127.1, 125.8, 122.7, 116.7, 36.6, 27.8, 27.7, 26.8, 24.0, 21.4, -5.1.
- IR (neat) cm^{-1} 2947, 2861, 1585, 1439, 1347, 1260, 1163, 1068, 1026, 940.
- HRMS calcd for $C_{20}H_{26}NO_2SSi$ $(M+H)^+$: 372.1448, found 372.1447.

3-cyclohexyl-3-methyl-1-tosyl-2,3-dihydro-1H-benzo[d][1,3]azasilole **(3ai)**

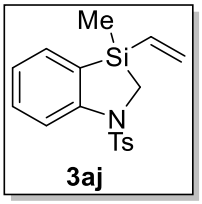


3ai

3ai was prepared according to General Method B. **1l** (100 mg, 0.25 mmol), **2a** (186 mg, 0.62 mmol, 2.5 equiv.), Cs_2CO_3 (203 mg, 0.62 mmol, 2.5 equiv.) and 18-crown-6 (164 mg, 0.62 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3ai** as a pale yellow oil (85 mg, 88%).

- R_f = 0.4 (EtOAc/Petroleum Ether = 1/10).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.45 – 7.29 (m, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.00 (t, *J* = 7.2 Hz, 1H), 3.15 (dd, *J* = 94.0, 14.4 Hz, 2H), 2.36 (s, 3H), 1.75 – 1.58 (m, 2H), 1.57 – 1.50 (m, 2H), 1.50 – 1.44 (m, 2H), 1.20 – 1.05 (m, 2H), 1.03 – 0.85 (m, 2H), 0.77 – 0.60 (m, 1H), 0.19 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 143.6, 135.1, 133.2, 131.1, 129.5, 127.1, 125.5, 122.7, 116.9, 35.9, 27.5, 27.5, 26.9, 26.7, 26.4, 24.5, 21.5, -6.1.
- IR (neat) cm^{-1} 2918, 1439, 1348, 1275, 1261, 1163, 1068, 1025, 940.
- HRMS calcd for $C_{21}H_{28}NO_2SSi$ $(M+H)^+$: 386.1605, found 386.1605.

3-methyl-1-tosyl-3-vinyl-2,3-dihydro-1H-benzo[d][1,3]azasilole **(3aj)**

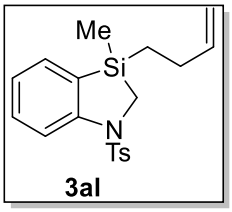


3aj

3aj was prepared according to General Method B. **1m** (100 mg, 0.29 mmol), **2a** (216 mg, 0.72 mmol, 2.5 equiv.), Cs_2CO_3 (236 mg, 0.72 mmol, 2.5 equiv.) and 18-crown-6 (191 mg, 0.72 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3aj** as a pale yellow oil (76 mg, 80%).

- R_f = 0.3 (EtOAc/Petroleum Ether = 1/10).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.35 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.02 (t, *J* = 7.2 Hz, 1H), 6.23 – 5.87 (m, 2H), 5.70 (dd, *J* = 19.6, 4.4 Hz, 1H), 3.22 (dd, *J* = 24.4, 14.4 Hz, 2H), 2.37 (s, 3H), 0.31 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 143.7, 136.1, 135.2, 133.5, 133.2, 131.4, 129.5, 127.1, 125.2, 123.0, 117.1, 37.6, 21.4, -4.7.
- IR (neat) cm^{-1} 1586, 1493, 1460, 1345, 1161, 1089.
- HRMS calcd for $C_{17}H_{20}NO_2SSi$ $(M+H)^+$: 339.0979, found 339.0978.

3-(but-3-en-1-yl)-3-methyl-1-tosyl-2,3-dihydro-1H-benzo[d][1,3]azasilole **(3al)**

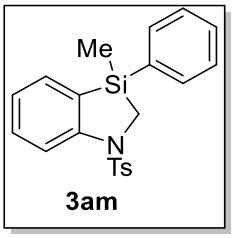


3al

3al was prepared according to General Method B. **1o** (100 mg, 0.27 mmol), **2a** (199 mg, 0.67 mmol, 2.5 equiv.), Cs_2CO_3 (218 mg, 0.67 mmol, 2.5 equiv.) and 18-crown-6 (177 mg, 0.67 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3al** as a pale yellow oil (83 mg, 86%).

- R_f = 0.3 (EtOAc/Petroleum Ether = 1/10).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.42 – 7.31 (m, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.02 (t, *J* = 7.2 Hz, 1H), 5.73 (ddt, *J* = 16.6, 10.0, 6.4 Hz, 1H), 5.21 – 4.53 (m, 2H), 3.49 – 2.74 (m, 2H), 2.36 (s, 3H), 2.03 – 1.84 (m, 2H), 0.96 - 0.57 (m, 2H), 0.23 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 143.7, 140.0, 135.0, 133.0, 131.2, 129.5, 127.1, 125.9, 122.9, 117.0, 113.8, 37.2, 27.3, 21.5, 13.4, -3.8.
- IR (neat) cm^{-1} 2922, 1586, 1459, 1439, 1347, 1248, 1163, 1089, 1026, 941.
- HRMS calcd for $C_{19}H_{24}NO_2SSi$ $(M+H)^+$: 358.1292, found 358.1290.

3-methyl-3-phenyl-1-tosyl-2,3-dihydro-1H-benzo[d][1,3]azasilole **(3am)**

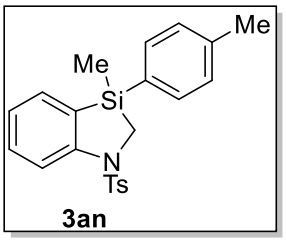


3am

3am was prepared according to General Method B. **1p** (100 mg, 0.25 mmol), **2a** (188 mg, 0.63 mmol, 2.5 equiv.), Cs_2CO_3 (206 mg, 0.63 mmol, 2.5 equiv.) and 18-crown-6 (167 mg, 0.63 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3am** as a pale yellow oil (52 mg, 54%).

- R_f = 0.3 (EtOAc/Petroleum Ether = 1/10).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.45 – 7.33 (m, 3H), 7.32 – 7.22 (m, 4H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.04 (t, *J* = 7.2 Hz, 1H), 3.48 – 3.24 (dd, *J* = 24.0, 14.8 Hz, 2H), 2.38 (s, 3H), 0.55 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 143.7, 135.0, 134.2, 133.9, 133.4, 131.6, 130.1, 129.6, 128.1, 127.1, 125.1, 123.2, 117.1, 38.4, 21.5, -4.5.
- IR (neat) cm^{-1} 1734, 1586, 1460, 1439, 1348, 1260, 1163, 1026.
- HRMS calcd for $C_{21}H_{22}NO_2SSi$ $(M+H)^+$: 380.1135, found 380.1135.

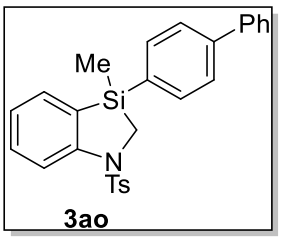
3-methyl-3-(p-tolyl)-1-tosyl-2,3-dihydro-1H-benzo[d][1,3]azasilole **(3an)**



3an was prepared according to General Method B. **1q** (100 mg, 0.24 mmol), **2a** (182 mg, 0.61 mmol, 2.5 equiv.), Cs_2CO_3 (199 mg, 0.61 mmol, 2.5 equiv.) and 18-crown-6 (161 mg, 0.61 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3an** as a pale yellow oil (60 mg, 62%).

- R_f = 0.4 (EtOAc/Petroleum Ether = 1/10).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 7.2 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.6 Hz, 2H), 7.10 (d, *J* = 7.6 Hz, 2H), 7.03 (t, *J* = 7.2 Hz, 1H), 3.33 (dd, *J* = 19.2, 14.8 Hz, 2H), 2.38 (s, 3H), 2.33 (s, 3H), 0.52 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 143.6, 140.3, 135.0, 134.3, 133.4, 131.5, 130.2, 129.5, 128.9, 127.2, 125.4, 123.1, 117.1, 38.5, 21.5, -4.4.
- IR (neat) cm^{-1} 2926, 1586, 1460, 1438, 1347, 1262, 1163, 1089.
- HRMS calcd for $C_{22}H_{24}NO_2SSi$ $(M+H)^+$: 394.1292, found 394.1292.

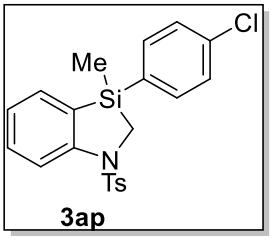
3-([1,1'-biphenyl]-4-yl)-3-methyl-1-tosyl-2,3-dihydro-1H-benzo[d][1,3]azasilole **(3ao)**



3ao was prepared according to General Method B. **1r** (100 mg, 0.21 mmol), **2a** (158 mg, 0.53 mmol, 2.5 equiv.), Cs_2CO_3 (173 mg, 0.53 mmol, 2.5 equiv.) and 18-crown-6 (140 mg, 0.53 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3ao** as a pale yellow oil (67 mg, 69%).

- R_f = 0.2 (EtOAc/Petroleum Ether = 1/10).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.8 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.43 (dt, *J* = 14.4, 7.6 Hz, 4H), 7.38 (d, *J* = 7.2 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.06 (t, *J* = 7.2 Hz, 1H), 3.39 (dd, *J* = 27.6, 14.8 Hz, 2H), 2.37 (s, 3H), 0.58 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 143.7, 143.0, 140.6, 135.0, 134.8, 133.4, 132.5, 131.6, 129.6, 128.9, 127.7, 127.2, 127.1, 126.8, 125.1, 123.2, 117.1, 38.5, 21.5, -4.4.
- IR (neat) cm^{-1} 3060, 2929, 1595, 1492, 1443, 1346, 1167, 1089, 1064, 1024.
- HRMS calcd for $C_{27}H_{26}NO_2SSi$ $(M+H)^+$: 456.1448, found 456.1448.

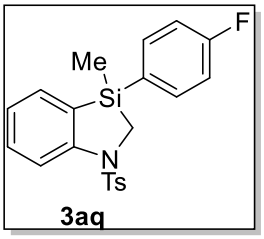
3-(4-chlorophenyl)-3-methyl-1-tosyl-2,3-dihydro-1H-benzo[d][1,3]azasilole **(3ap)**



3ap was prepared according to General Method B. **1s** (100 mg, 0.22 mmol), **2a** (173 mg, 0.58 mmol, 2.5 equiv.), Cs_2CO_3 (189 mg, 0.58 mmol, 2.5 equiv.) and 18-crown-6 (154 mg, 0.58 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3ap** as a colorless oil (36 mg, 37%).

- R_f = 0.3 (EtOAc/Petroleum Ether = 1/10).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.8 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 8.4 Hz, 1H), 7.37 (d, *J* = 6.8 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.05 (t, *J* = 7.2 Hz, 1H), 3.33 (dd, *J* = 21.2, 14.8 Hz, 2H), 2.38 (s, 3H), 0.55 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 143.8, 136.6, 135.5, 134.9, 133.3, 132.3, 131.8, 129.5, 128.3, 127.1, 124.6, 123.4, 117.4, 38.4, 21.5, -4.6.
- IR (neat) cm^{-1} 2919, 1734, 1580, 1460, 1438, 1347, 1259, 1163, 1136, 1085, 1044.
- HRMS calcd for $C_{21}H_{21}ClNO_2SSi$ $(M+H)^+$: 414.0745, found 414.0744.

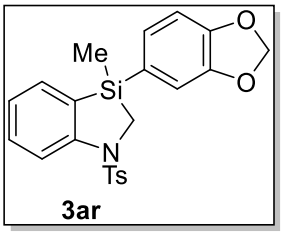
3-(4-fluorophenyl)-3-methyl-1-tosyl-2,3-dihydro-1H-benzo[d][1,3]azasilole **(3aq)**



3aq was prepared according to General Method B. **1t** (100 mg, 0.24 mmol), **2a** (180 mg, 0.60 mmol, 2.5 equiv.), Cs_2CO_3 (197 mg, 0.60 mmol, 2.5 equiv.) and 18-crown-6 (160 mg, 0.60 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3aq** as a pale yellow oil (43 mg, 45%).

- R_f = 0.2 (EtOAc/Petroleum Ether = 1/10).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 8.4 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.23 – 7.13 (m, 4H), 7.05 (t, *J* = 7.2 Hz, 1H), 6.97 (t, *J* = 8.8 Hz, 2H), 3.33 (dd, *J* = 21.2, 14.8 Hz, 2H), 2.38 (s, 3H), 0.55 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3 (d, *J* = 248.9 Hz), 151.0, 143.8, 136.4, 136.3, 135.0, 133.3, 131.7, 129.6, 129.5, 127.1, 124.9, 123.3, 117.3, 115.5, 115.3, 76.7, 38.5, 21.5, -4.4.
- IR (neat) cm^{-1} 2921, 1585, 1497, 1438, 1346, 1305, 1260, 1161, 1089, 1025, 939.
- HRMS calcd for $C_{21}H_{21}FNO_2SSi$ $(M+H)^+$: 398.1041, found 398.1041.

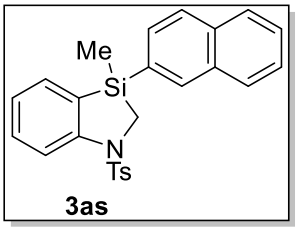
3-(benzo[d][1,3]dioxol-5-yl)-3-methyl-1-tosyl-2,3-dihydro-1H-benzo[d][1,3]azasilole **(3ar)**



3ar was prepared according to General Method B. **1u** (100 mg, 0.23 mmol), **2a** (169 mg, 0.57 mmol, 2.5 equiv.), Cs_2CO_3 (185 mg, 0.57 mmol, 2.5 equiv.) and 18-crown-6 (150 mg, 0.57 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3ar** as a pale yellow solid (69 mg, 71%).

- R_f = 0.1 (EtOAc/Petroleum Ether = 1/10).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.52 – 7.31 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.76 (s, 2H), 6.56 (s, 1H), 5.92 (d, *J* = 4.0 Hz, 2H), 3.30 (dd, *J* = 16.4, 14.8 Hz, 2H), 2.37 (s, 3H), 0.51 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 149.4, 147.7, 143.8, 134.9, 133.3, 131.6, 129.6, 128.8, 127.1, 126.7, 125.2, 123.2, 117.2, 113.4, 108.8, 100.8, 38.5, 21.5, -4.3.
- IR (neat) cm^{-1} 3054, 2921, 1585, 1482, 1439, 1267, 1233, 1089.
- HRMS calcd for $C_{22}H_{22}NO_4SSi$ $(M+H)^+$: 424.1033, found 424.1033.

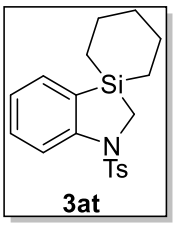
3-methyl-3-(naphthalen-2-yl)-1-tosyl-2,3-dihydro-1H-benzo[d][1,3]azasilole **(3as)**



3as was prepared according to General Method B. **1v** (100 mg, 0.22 mmol), **2a** (167 mg, 0.56 mmol, 2.5 equiv.), Cs_2CO_3 (183 mg, 0.56 mmol, 2.5 equiv.) and 18-crown-6 (148 mg, 0.56 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3as** as a pale yellow oil (45 mg, 47%).

- R_f = 0.2 (EtOAc/Petroleum Ether = 1/10).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.8 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.77 (s, 1H), 7.75 – 7.69 (m, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.55 – 7.46 (m, 2H), 7.47 – 7.39 (m, 2H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.06 (t, *J* = 7.2 Hz, 1H), 3.42 (dd, *J* = 29.6,14.8 Hz, 2H), 2.29 (s, 3H), 0.64 (s, 3H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 143.7, 135.5, 135.0, 134.0, 133.5, 132.7, 131.7, 131.3, 129.6, 129.5, 128.1, 127.7, 127.5, 127.1, 127.1, 126.3, 125.2, 123.3, 117.3, 38.5, 21.4, -4.3.
- IR (neat) cm^{-1} 3056, 2926, 1586, 1439, 1346, 1250, 1156, 1136, 1086, 1023.
- HRMS calcd for $C_{25}H_{24}NO_2SSi$ $(M+H)^+$: 430.1292, found 430.1292.

1-tosyl-1,2-dihydrospiro[benzo[d][1,3]azasilole-3,1'-silinane] **(3at)**

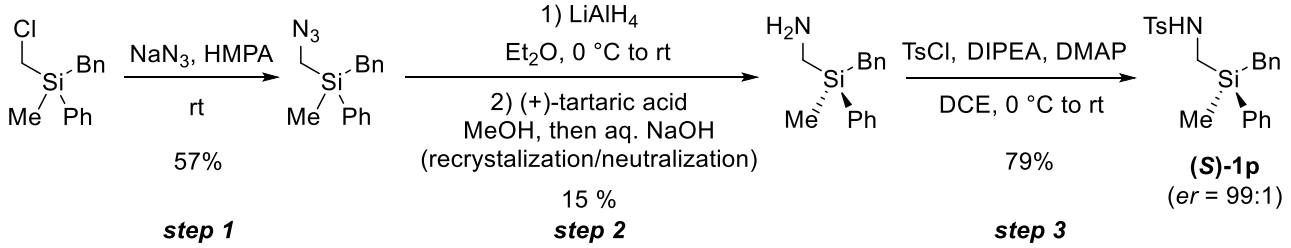


3at

3at was prepared according to General Method B. **1w** (100 mg, 0.27 mmol), **2a** (200 mg, 0.67 mmol, 2.5 equiv.), Cs_2CO_3 (218 mg, 0.67 mmol, 2.5 equiv.) and 18-crown-6 (177 mg, 0.67 mmol, 2.5 equiv.) in DME (1.5 mL) at 25 °C for 10 h afforded **3at** as a colorless oil (57 mg, 60%).

- R_f = 0.4 (EtOAc/Petroleum Ether = 1/10).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 2H), 7.01 (t, *J* = 7.2 Hz, 1H), 3.21 (s, 2H), 2.36 (s, 3H), 1.99 – 1.78 (m, 2H), 1.75 – 1.62 (m, 2H), 1.56 – 1.40 (m, 2H), 1.01 – 0.58 (m, 4H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 143.6, 135.2, 133.3, 131.3, 129.5, 127.1, 126.1, 122.8, 116.9, 36.7, 29.2, 24.9, 21.5, 12.2.
- IR (neat) cm^{-1} 2917, 2849, 1586, 1460, 1439, 1346, 1161, 1134, 1090, 1027.
- HRMS calcd for $C_{19}H_{24}NO_2SSi$ $(M+H)^+$: 358.1292, found 358.1290.

5. Enantioselective Synthesis of 1,3-N, Si-Reagent (*S*)-1p.



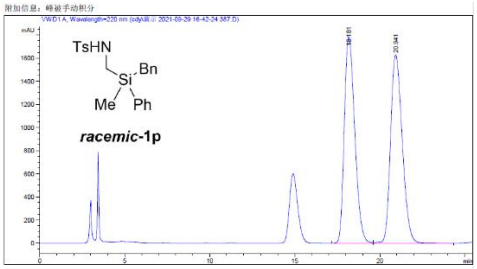
Step 1: To a solution of benzyl(chloromethyl)(methyl)(phenyl)silane (5.00 g, 19.17 mmol) in HMPA (30 mL) was added sodium azide (1.37 g, 21.09 mmol, 1.1 equiv.). The reaction was stirred for 5 h at room temperature before quenching with H_2O and extracting with EtOAc (3 × 50 mL). The combined organic layers were washed with sat. aq. NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (eluent: petroleum ether) to give (azidomethyl)(benzyl)(methyl)(phenyl)silane as a colorless oil (2.91 g, 57%).

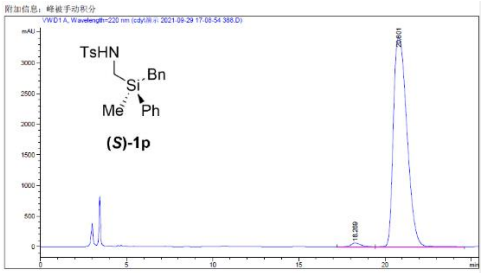
Step 2: To a solution of (azidomethyl)(benzyl)(methyl)(phenyl)silane (2.91 g, 10.84 mmol) in anhydrous Et_2O (30 mL) was added $LiAlH_4$ (13.01 mL, 1.0 M in THF, 1.2 equiv.) dropwise at 0 °C under argon atmosphere. The reaction was warmed up to room temperature and stirred for 30 min before quenching with sat. aq. potassium sodium tartrate solution and extracting with EtOAc (3 × 50 mL). The combined organic layers were washed with sat. aq. NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (eluent/ methanol/CH_2Cl_2 = 1/20) to give (benzyl(methyl)(phenyl)silyl)methanamine as a colorless oil (2.00 g, 76%).

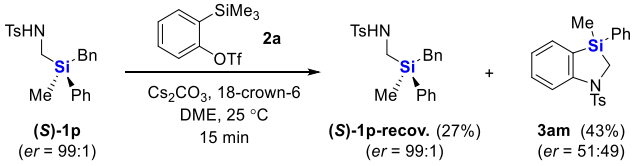
To a solution of (+)-tartaric acid (1.24 g, 8.28 mmol, 1.0 equiv.) in methanol (90 mL) was added a solution of (benzyl(methyl)(phenyl)silyl)methanamine (2.00 g, 8.28 mmol) in methanol (3 mL). A white crystalline precipitate appeared immediately. The flask was then allowed to stand overnight at room temperature. The crystallin precipitate was filtered off, washed with a small amount of cooled methanol, and dried *in vacuo*. To the resulting salt was added a 10% aqueous solution of NaOH at 0 °C. The liberated amine was extracted with Et_2O (3 × 30 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was subjected to the above crystallization/ neutralization method for additional two times, affording (+)-(benzyl(methyl)(phenyl)silyl)methanamine as a colorless oil (400 mg, 20%). $[\alpha]^{25}_D$ = +12.3 (*c* = 0.35, $CHCl_3$)

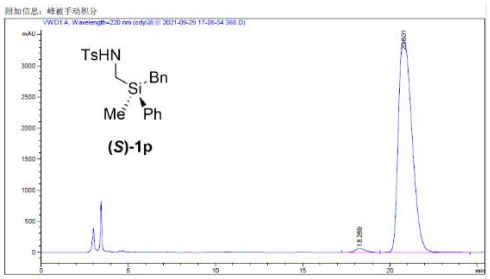
Step 3: To a solution of (+)-(benzyl(methyl)(phenyl)silyl)methanamine (400 mg, 1.66 mmol) in anhydrous CH_2Cl_2 (5 mL) was added tosyl chloride (474 mg, 2.49 mmol, 1.5 equiv.) and 4-dimethylaminopyridine (20 mg, 0.17 mmol, 0.1 equiv.) and *N*, *N*-diisopropylethylamine (428 mg, 3.31 mmol, 2.0 equiv.) at 0 °C under argon atmosphere. The reaction was warmed up to room temperature and stirred for 5 h before quenching with sat. aq. $NaHCO_3$ and extracting with CH_2Cl_2 (3 × 15 mL). The combined organic layers were washed with sat. aq. NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (eluent: EtOAc/petroleum ether = 1/6) to give **(*S*)-1p** as a white solid (517 mg, 79%, *er* = 99:1); $[\alpha]^{25}_D$ = -3.7 (*c* = 0.35, $CHCl_3$). The *er* of **(*S*)-1p** was determined on a Chiralpak® AS-H column with hexane/ 2-propanol = 89:11, wavelength = 220 nm, flow = 1 mL/min. Reaction times: 18.27 min [minor enantiomer], 22.80 min [major enantiomer].

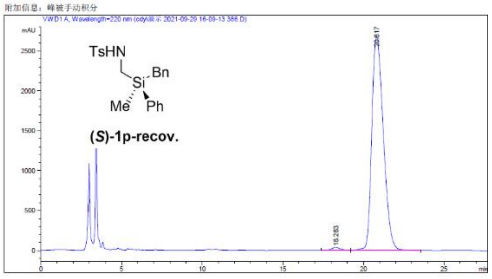
6. Mechanistic Studies.

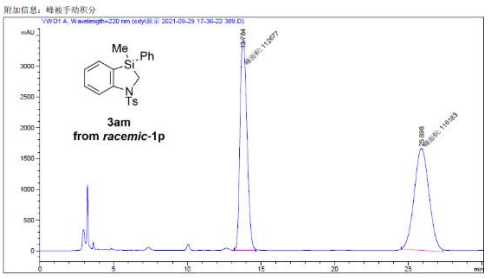


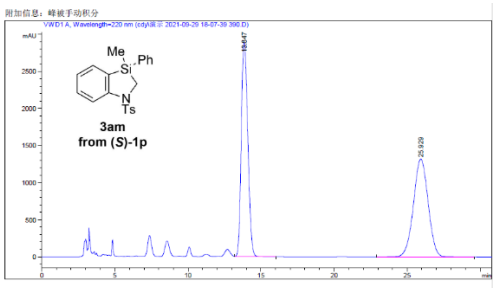








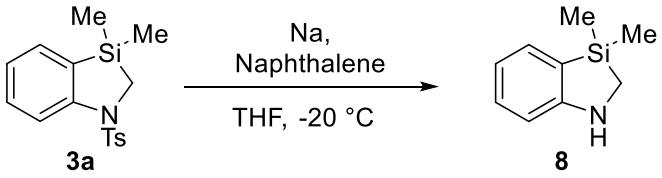




Note: The *er* of **3am** was determined on a Chiralpak® AS-H column with hexane/ 2-propanol = 80:20, wavelength = 220 nm, flow = 1 mL/min.

7. Functionalization of 3-Silaindoline 3

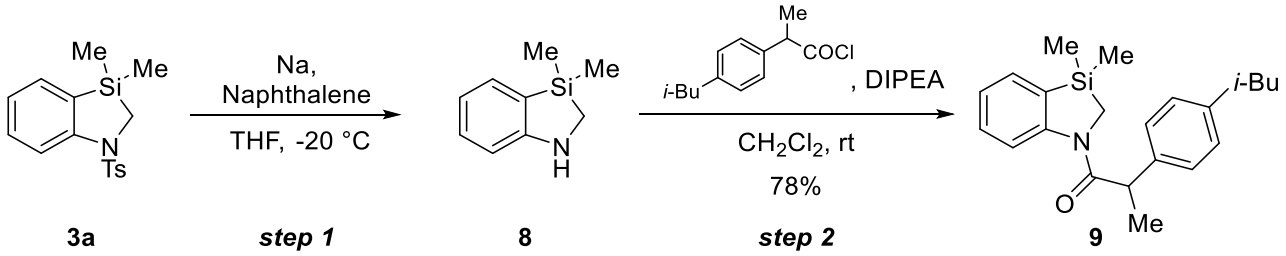
3,3-dimethyl-2,3-dihydro-1H-benzo[d][1,3]azasilole **(8)**



General Method D:

Naphthalene (472 mg, 3.69 mmol, 6.0 equiv.) was dissolved in anhydrous THF (3 mL) in an oven-dried, 10-mL Schlenk flask under a stream of argon, followed by the addition of lacerated and hexane-rinsed pieces of sodium metal (86 mg, 3.75 mmol, 6.1 equiv.). The mixture was stirred at 23 °C until a green color persisted. The reaction was cooled to -20 ºC before addition of a solution of tosyl-protected silaindoline **3a** (195 mg, 0.62 mmol) in anhydrous THF (1 mL). The turbid orange reaction mixture was stirred at same temperature for 2 h until the reaction was completed. The reaction was slowly quenched with MeOH (3 mL) at 0 °C, followed by addition of sat. aq. $NaHCO_3$ solution only after complete consumption. The mixture was then diluted with hexanes (3 × 10 mL), washed with sat. aq. NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue **8** was conducted next step without purification.

1-(3,3-dimethyl-2,3-dihydro-1H-benzo[d][1,3]azasilol-1-yl)-2-(4-isobutylphenyl)propan-1-one **(9)**



Step 1: **8** was prepared according to General Method D. Naphthalene (472 mg, 3.69 mmol, 6.0 equiv), sodium metal (86 mg, 3.75 mmol, 6.1 equiv), tosyl-protected silaindoline **3a** (195 mg, 0.61 mmol) in anhydrous THF (4mL) at -20 ºC for 2 h afforded **8** which was used in the next step without purification.

Step 2: To a solution of 2-(4-isobutylphenyl)propanoyl chloride which was prepared from ibuprofen (98 mg, 0.47 mmol, 0.77 equiv.), oxalyl chloride (90 mg, 0.71 mmol, 1.15 equiv.) and 2 drops of dry DMF in CH_2Cl_2 (3 mL)[20] were added DIPEA (119 mg, 0.92 mmol, 1.5 equiv.) and a solution of **8** in CH_2Cl_2 (0.5 mL). The reaction stirred at room temperature for 2 h before quenching with sat. aq. $NaHCO_3$ and extracting with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with sat. aq. NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (eluent: EtOAc/petroleum ether = 1/30) to give **9** as a white solid (133 mg, 78%).

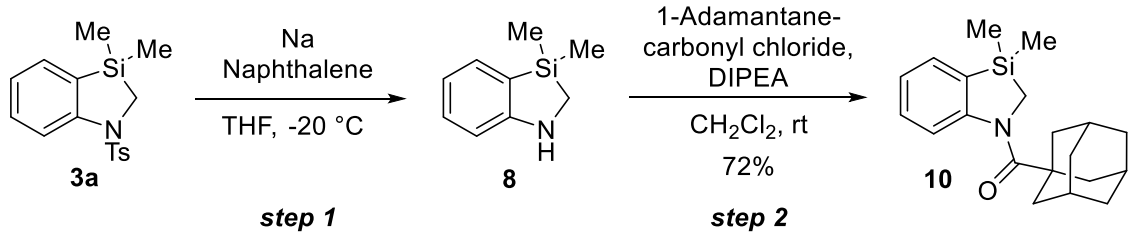
- R_f = 0.3 (EtOAc/Petroleum Ether = 1/30).
- mp: 99.2 – 102.7 ºC.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.44 (d, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 1H),

[20] N. Radhoff, A. Studer, *Angew. Chem. Int. Ed*, **2021**, *60*, 3561.

7.23 (d, J = 8.0 Hz, 2H), 7.14 – 7.04 (m, 3H), 4.18 (q, J = 6.8 Hz, 1H), 3.32 – 2.93 (m, 2H), 2.44 (d, J = 7.2 Hz, 2H), 1.83 (dp, J = 13.6, 6.8 Hz, 1H), 1.52 (d, J = 6.8 Hz, 3H), 0.87 (d, J = 6.4 Hz, 6H), 0.36 (s, 3H), 0.13 (s, 3H).

- ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 152.0, 140.2, 139.1, 132.1, 130.9, 129.6, 127.1, 123.4, 120.2, 46.1, 45.0, 37.5, 30.2, 22.3, 21.1, -2.3, -2.3.
- IR (neat) cm^{-1} 3050, 2954, 2867, 1653, 1584, 1461, 1438, 1270, 1132, 1060, 827.
- HRMS calcd for $C_{22}H_{30}NO_3Si$ $(M+H)^+$: 352.2091, found 352.2091.

<u>((3r,5r,7r)-adamantan-1-yl)(3,3-dimethyl-2,3-dihydro-1H-benzo[d][1,3]azasilol-1-yl)methanone</u> **(10)**

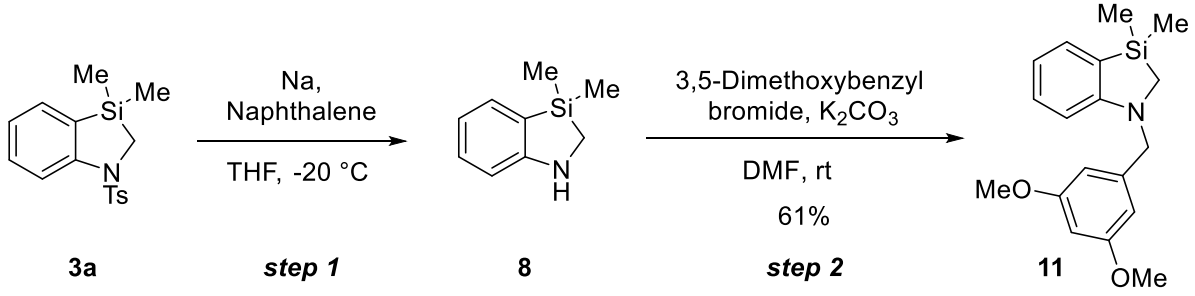


Step 1: **8** was prepared according to General Method D. Naphthalene (472 mg, 3.69 mmol, 6.0 equiv), sodium metal (86 mg, 3.75 mmol, 6.1 equiv), tosyl-protected silaindoline **3a** (195 mg, 0.61 mmol) in anhydrous THF (4mL) at -20 ºC for 2 h afforded **8** which was used in the next step without purification.

Step 2: To a solution of **8** in CH_2Cl_2 (3 mL) was added 1-adamantanecarbony chloride (182 mg, 0.92 mmol, 1.5 equiv.) and DIPEA (238 mg, 1.84 mmol, 3.0 equiv.) under argon atmosphere. The reaction was stirred at room temperature for 2 h before quenching with sat. aq. $NaHCO_3$ and extracting with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with sat. aq. NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (eluent: EtOAc/petroleum ether = 1/30) to give **10** as a white solid (124 mg, 72%).

- R_f = 0.4 (EtOAc/ petroleum ether = 1/10).
- mp : 148.2 – 151.7 ºC.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.4 Hz, 1H), 7.46 (d, J = 7.2 Hz, 1H), 7.31 (t, J = 8.4 Hz, 1H), 7.03 (t, J = 7.2 Hz, 1H), 3.41 (s, 2H), 2.19 (s, 6H), 2.09 (s, 3H), 1.77 (s, 6H), 0.38 (s, 6H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6, 153.4, 131.8, 130.1, 127.7, 123.2, 121.7, 43.8, 39.7, 39.0, 36.7, 28.6, -2.7.
- IR (neat) cm^{-1} 3006, 2903, 2989, 2847, 1632, 1584, 1324, 1275, 1261, 764, 725.
- HRMS calcd for $C_{20}H_{28}NOSi$ $(M+H)^+$: 326.1935, found 326.1933.

<u>1-(3,5-dimethoxybenzyl)-3,3-dimethyl-2,3-dihydro-1H-benzo[d][1,3]azasilole</u> **(11)**

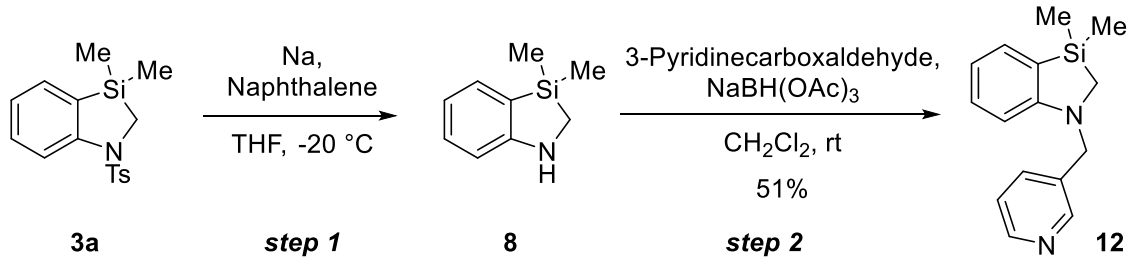


Step 1: **8** was prepared according to General Method D. Naphthalene (472 mg, 3.69 mmol, 6.0 equiv), sodium metal (86 mg, 3.75 mmol, 6.1 equiv), tosyl-protected silaindoline **3a** (195 mg, 0.61 mmol) in anhydrous THF (4mL) at -20 °C for 2 h afforded **8** which was used in the next step without purification.

Step 2: To a solution of **8** in DMF (3 mL) was added 3,5-dimethoxybenzyl bromide (156 mg, 0.67 mmol, 1.1 equiv.) and K_2CO_3 (186 mg, 1.35 mmol, 2.2 equiv.) under argon atmosphere. The reaction was stirred for 3 h at room temperature before quenching with sat. aq. $NaHCO_3$ and extracting with EtOAc (3 × 10 mL). The combined organic layers were washed with sat. aq. NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (eluent: EtOAc/petroleum ether = 1/30) to give **11** as a pale yellow oil (117 mg, 61%).

- R_f = 0.7 (EtOAc/Petroleum Ether = 1/10).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.17 (ddd, *J* = 8.8, 7.2, 1.6 Hz, 1H), 6.61 (t, *J* = 7.2 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 1H), 6.40 (d, *J* = 2.0 Hz, 2H), 6.34 (t, *J* = 2.4 Hz, 1H), 4.41 (s, 2H), 3.75 (s, 6H), 2.69 (s, 2H), 0.35 (s, 6H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 158.9, 141.6, 133.2, 131.3, 121.4, 115.7, 107.7, 104.9, 98.6, 55.2, 54.6, 41.3, -1.5.
- IR (neat) cm^{-1} 3378, 2924, 2852, 1669, 1594, 1461, 1430, 1202, 1158, 1061, 829, 792.
- HRMS calcd for $C_{18}H_{24}NO_2Si$ $(M+H)^+$: 314.1571, found 314.1567 .

3,3-dimethyl-1-(pyridin-3-ylmethyl)-2,3-dihydro-1H-benzo[d][1,3]azasilole **(12)**



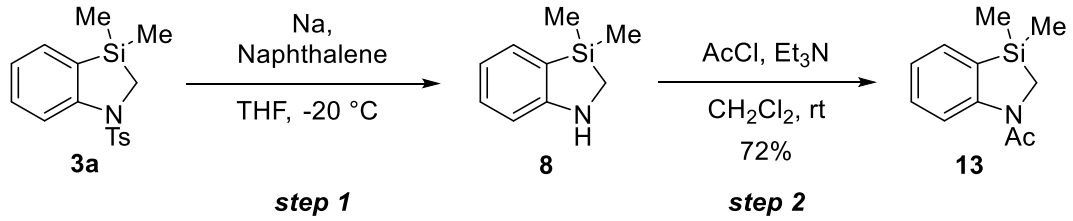
Step 1: **8** was prepared according to General Method D. Naphthalene (472 mg, 3.69 mmol, 6.0 equiv), sodium metal (86 mg, 3.75 mmol, 6.1 equiv), tosyl-protected silaindoline **3a** (195 mg, 0.61 mmol) in anhydrous THF (4mL) at -20 °C for 2 h afforded **8** which was used in the next step without purification.

Step 2: To a solution of **8** in CH_2Cl_2 (3 mL) was added nicotinaldehyde (72 mg, 0.67 mmol, 1.1 equiv.) and $NaBH(OAc)_3$ (389 mg, 1.84 mmol, 3.0 equiv.) under argon atmosphere. The reaction was stirred at room temperature for 3 h before quenching with sat. aq. $NaHCO_3$ and extracting with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with sat. aq. NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (eluent: EtOAc/petroleum ether = 1/5) to give **12** as a pale yellow oil (79 mg, 51%).

- R_f = 0.4 (EtOAc/Petroleum Ether = 1/2).
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.51 (d, *J* = 4.4 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.39 (dd, *J* = 6.8, 1.2 Hz, 1H), 7.27 (t, *J* = 6.4 Hz, 1H), 7.19 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 6.65 (t, *J* = 7.2 Hz, 1H), 6.50 (d, *J* = 8.4 Hz, 1H), 4.50 (s, 2H), 2.66 (s, 2H), 0.35 (s, 6H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 147.5, 146.8, 136.5, 135.3, 133.4, 131.4, 124.0, 121.8, 116.5, 107.5, 52.2, 41.4, -1.6.

- IR (neat) cm^{-1} 2954, 1735, 1674, 1587, 1472, 1425, 1351, 1247, 1187, 1026.
- HRMS calcd for $C_{15}H_{19}N_2Si$ $(M+H)^+$: 255.1312, found 255.1312 .

1-(3,3-dimethyl-2,3-dihydro-1H-benzo[d][1,3]azasilol-1-yl)ethan-1-one **(13)**

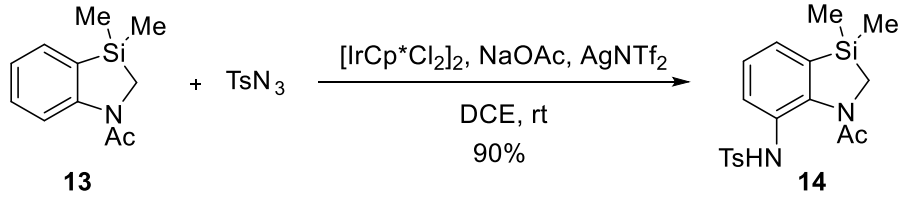


Step 1: **8** was prepared according to General Method D. Naphthalene (472 mg, 3.69 mmol, 6.0 equiv), sodium metal (86 mg, 3.75 mmol, 6.1 equiv), tosyl-protected silaindoline **3a** (195 mg, 0.61 mmol) in anhydrous THF (4mL) at -20 °C for 2 h afforded **8** which was used in the next step without purification.

Step 2: To a solution of **8** in CH_2Cl_2 (3 mL) was added acetyl chloride (72 mg, 0.92 mmol, 1.5 equiv.) and Et_3N (186 mg, 1.84 mmol, 3.0 equiv.) under argon atmosphere. The reaction was stirred at room temperature for 2 h before quenching with sat. aq. $NaHCO_3$ and extracting with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with sat. aq. NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (eluent: EtOAc/petroleum ether = 1/6) to give **13** as a white solid (90 mg, 72%).

- R_f = 0.3 (EtOAc/Petroleum Ether = 1/4).
- mp: 103.8 – 106.1 °C.
- ^1H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.48 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.37 (ddd, *J* = 8.8, 7.2, 1.6 Hz, 1H), 7.07 (td, *J* = 7.2, 1.2 Hz, 1H), 3.16 (s, 2H), 2.36 (s, 3H), 0.40 (s, 6H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 151.5, 132.2, 131.0, 123.3, 119.6, 38.8, 25.8, -2.0.
- IR (neat) cm^{-1} 2916, 1658, 1582, 1461, 1432, 1375, 1225, 1132, 825, 751.
- HRMS calcd for $C_{11}H_{16}NOSi$ $(M+H)^+$: 206.0996, found 206.0996.

N-(1-acetyl-3,3-dimethyl-2,3-dihydro-1H-benzo[d][1,3]azasilol-7-yl)-4-methylbenzenesulfonamide **(14)**

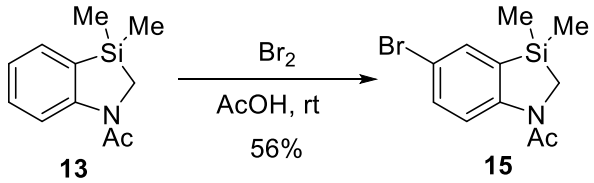


A sealed tube was charged with **13** (70 mg, 0.34 mmol), sulfonyl azide (101 mg, 0.51 mmol, 1.5 equiv.), $[IrCp^*Cl_2]_2$ (5 mg, 0.01 mmol, 2 mol %), $AgNTf_2$ (10 mg, 0.03 mmol, 8 mol %), NaOAc (8 mg, 0.10 mmol, 30 mol %) and DCE (1.5 mL). The mixture was stirred at room temperature for 6 h. After the completion of the reaction, the solvent was evaporated under reduced pressure. The residue was purified by silica gel flash column chromatography (eluent: EtOAc/petroleum ether = 1/4) to give the product **14** as a white solid (115 mg, 90%).

- R_f = 0.2 (EtOAc/Petroleum Ether = 1/2).
- mp: 164.0 – 165.8 °C.

- ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.51 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.36 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 2.63 (s, 2H), 2.38 (s, 3H), 2.15 (s, 3H), 0.30 (s, 6H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 144.7, 142.8, 137.9, 132.1, 131.6, 130.8, 129.0, 127.9, 126.9, 126.8, 41.7, 24.8, 21.4, -3.2.
- IR (neat) cm^{-1} 3007, 1624, 1598, 1493, 1416, 1345, 1302, 1276, 1162, 1091, 835.
- HRMS calcd for $C_{18}H_{23}N_2O_3SSi$ $(M+H)^+$: 375.1193, found 375.1193.

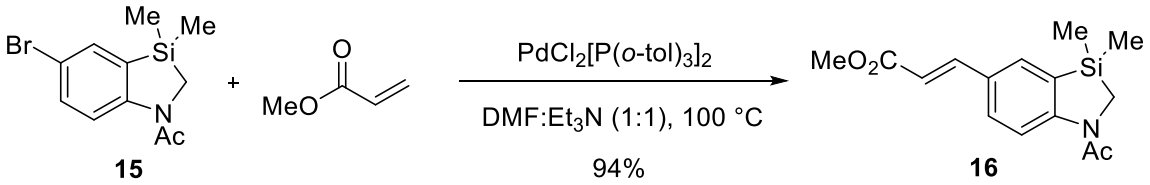
1-(5-bromo-3,3-dimethyl-2,3-dihydro-1H-benzo[d][1,3]azasilol-1-yl)ethan-1-one **(15)**



To a solution of **13** (1.00 g, 4.87 mmol) in AcOH (8 mL) was added a solution of bromine (778 mg, 4.87 mmol, 1.0 equiv.) in AcOH (2 mL) dropwise at room temperature. The reaction was stirred for 3 h before quenching with H_2O and extracting with EtOAc (3 × 20 mL). The combined organic layers were washed with sat. aq. NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (eluent: EtOAc/petroleum ether = 1/8) to give **15** as a white solid (773 mg, 56%).

- R_f = 0.5 (EtOAc/Petroleum Ether = 1/4).
- mp: 92.5 – 94.0 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.54 (d, *J* = 2.4 Hz, 1H), 7.44 (dd, *J* = 9.2, 2.4 Hz, 1H), 3.16 (s, 2H), 2.35 (s, 3H), 0.41 (s, 6H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 150.4, 134.6, 133.7, 121.5, 116.4, 38.9, 25.8, -2.0.
- IR (neat) cm^{-1} 2956, 1656, 1574, 1448, 1369, 1287, 1183, 1083, 1061, 655.
- HRMS calcd for $C_{11}H_{15}BrNOSi$ $(M+H)^+$: 284.0101, found 284.0100.

methyl (E)-3-(1-acetyl-3,3-dimethyl-2,3-dihydro-1H-benzo[d][1,3]azasilol-5-yl)acrylate **(16)**

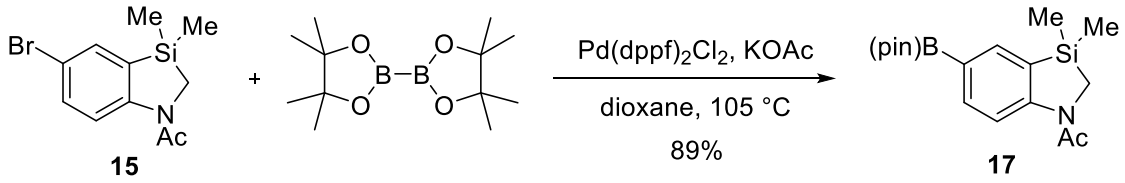


A sealed tube was charged with **15** (50 mg, 0.18 mmol), methyl acrylate (76 mg, 0.88 mmol, 5.0 equiv.), $PdCl_2[P(o\text{-tol})_3]_2$ (35 mg, 0.04 mmol, 25 mol %), DMF and H_2O (1:1, 1 mL) under argon atmosphere. The mixture was stirred at 100 °C for 16 h before quenching with H_2O and extracting with EtOAc (3 × 10 mL). The combined organic layers were washed with sat. aq. NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (eluent: EtOAc/petroleum ether = 1/5) to give **16** as a white solid (48 mg, 94%).

- R_f = 0.3 (EtOAc/Petroleum Ether = 1/4).

- mp: 154.4 – 156.2 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.66 (d, *J* = 15.6 Hz, 1H), 7.62 (d, *J* = 2.0 Hz, 1H), 7.54 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 3.79 (s, 3H), 3.18 (s, 2H), 2.37 (s, 3H), 0.42 (s, 6H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 167.7, 153.2, 144.3, 132.3, 131.1, 129.3, 128.0, 119.8, 116.1, 51.6, 39.1, 25.9, -2.0.
- IR (neat) cm^{-1} 2950, 1711, 1663, 1631, 1591, 1462, 1371, 1319, 1260, 1167, 831.
- HRMS calcd for $C_{15}H_{20}NO_3Si$ $(M+H)^+$: 290.1207, found 290.1209.

<u>1-(3,3-dimethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-1H-benzo[d][1,3]-azasilol-1-yl)ethan-1-one</u> **(17)**



A sealed tube was charged with **15** (60 mg, 0.21 mmol), bis(pinacolato)diboron (107 mg, 0.42 mmol, 2.0 equiv.), $Pd(dppf)_2Cl_2$ (17 mg, 0.02 mmol, 10 mol %), KOAc (103 mg, 1.06 mmol, 5.0 equiv.) and dioxane (1.5 mL) under argon atmosphere. The mixture was stirred at 105 °C for 2 h before quenching with H_2O and extracting with EtOAc (3 × 10 mL). The combined organic layers were washed with sat. aq. NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (eluent: EtOAc/petroleum ether = 1/5) to give **17** as a white solid (62 mg, 89%).

- R_f = 0.3 (EtOAc/Petroleum Ether = 1/4).
- mp: 231.0 – 233.8 °C.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.94 (d, *J* = 1.6 Hz, 1H), 7.82 (dd, *J* = 8.4, 1.6 Hz, 1H), 3.15 (s, 1H), 2.36 (s, 2H), 1.34 (s, 12H), 0.39 (s, 6H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 154.1, 139.4, 138.0, 118.7, 83.7, 38.9, 25.9, 24.8, -1.9.
- IR (neat) cm^{-1} 2977, 1658, 1595, 1398, 1352, 1331, 1261, 1186, 1110, 963, 826.
- HRMS calcd for $C_{17}H_{27}BNO_3Si$ $(M+H)^+$: 322.1848, found 322.1848.

8. X-Ray Crystallographic Data of 3a and (*S*)-1p

- **Compound 3a**

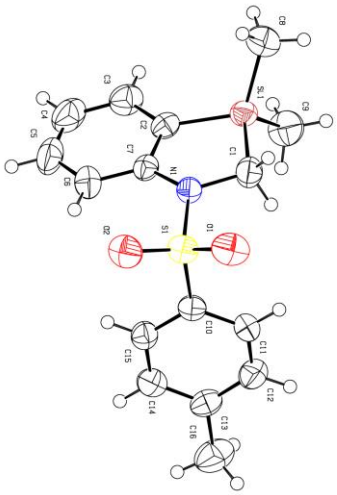


Table 1 Crystal data and structure refinement for 3a.

Identification code	**3a**
Empirical formula	$C_{16}H_{19}NO_2SSi$
Formula weight	317.47
Temperature/K	293.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.4608(5)
b/Å	11.5644(5)
c/Å	14.9921(10)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1640.27(15)
Z	4
ρ_{calc}g/cm^3	1.286
μ/mm^{-1}	0.274
F(000)	672.0
Crystal size/mm^3	0.35 × 0.3 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.192 to 52.738
Index ranges	$-11 \le h \le 9$, $-14 \le k \le 9$, $-18 \le l \le 13$
Reflections collected	4691
Independent reflections	3071 [R_{int} = 0.0243, R_{sigma} = 0.0513]
Data/restraints/parameters	3071/0/193
Goodness-of-fit on F^2	1.033

Final R indexes [I>=2σ (I)]	R_1 = 0.0438, wR_2 = 0.0901
Final R indexes [all data]	R_1 = 0.0562, wR_2 = 0.0982
Largest diff. peak/hole / e Å^{-3}	0.21/-0.25
Flack parameter	-0.06(7)

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

Atom	*x*	*y*	*z*	U(eq)
S1	4588.1(10)	5676.8(8)	7199.0(7)	43.4(3)
Si1	8635.4(11)	4117.4(9)	7552.1(8)	42.3(3)
O1	4097(3)	5490(3)	8085.7(19)	59.6(8)
O2	4394(3)	6779(2)	6787(2)	57.2(8)
N1	6295(3)	5401(2)	7220(2)	36.3(7)
C1	6735(4)	4454(4)	7830(3)	52.0(11)
C2	8571(4)	5100(3)	6578(2)	39.8(9)
C3	9598(5)	5320(4)	5939(3)	57.2(11)
C4	9343(6)	6078(5)	5245(3)	69.6(14)
C5	8066(6)	6626(4)	5192(3)	67.5(15)
C6	7016(5)	6436(4)	5823(3)	52.7(11)
C7	7261(4)	5659(3)	6516(2)	36.4(8)
C8	9903(5)	4572(4)	8429(3)	69.5(14)
C9	8952(5)	2571(3)	7275(4)	68.6(14)
C10	3787(4)	4627(3)	6513(3)	38.2(9)
C11	3404(4)	3563(3)	6865(3)	49.1(10)
C12	2756(4)	2766(4)	6323(3)	55.2(12)
C13	2438(4)	3000(4)	5439(3)	47.0(10)
C14	2832(4)	4064(4)	5102(3)	47.3(10)
C15	3506(4)	4873(3)	5623(3)	42.3(9)
C16	1666(6)	2126(5)	4870(3)	75.6(16)

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

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	39.9(5)	44.5(5)	45.7(6)	-9.3(5)	2.9(4)	8.7(5)
Si1	37.3(5)	38.2(5)	51.5(7)	1.5(5)	-4.2(5)	0.0(5)
O1	48.5(17)	84(2)	46.5(16)	-17.1(16)	12.4(14)	8.9(15)
O2	60.7(18)	36.0(14)	75(2)	-8.8(14)	-7.1(16)	14.8(13)
N1	35.2(15)	36.3(15)	37.4(16)	1.5(14)	2.4(14)	2.1(13)
C1	46(2)	53(2)	57(3)	15(2)	5(2)	2.6(19)
C2	41(2)	38(2)	40(2)	-8.4(17)	4.1(18)	-5.2(18)

C3	47(2)	69(3)	56(3)	-4(2)	10(2)	-2(2)
C4	67(3)	86(4)	56(3)	2(3)	16(3)	-23(3)
C5	96(4)	61(3)	45(3)	11(2)	3(3)	-26(3)
C6	61(3)	47(2)	51(3)	9(2)	0(2)	1(2)
C7	44(2)	31.6(19)	33.8(19)	-4.0(17)	0.1(16)	-5.4(17)
C8	70(3)	74(3)	64(3)	3(3)	-18(3)	-9(2)
C9	67(3)	42(2)	96(4)	-3(3)	-3(3)	10(2)
C10	32.0(19)	41(2)	42(2)	-3.2(17)	2.3(17)	4.7(16)
C11	47(2)	51(2)	48(2)	12(2)	-8(2)	-1.6(19)
C12	53(3)	46(2)	66(3)	7(2)	-2(2)	-7(2)
C13	38(2)	50(2)	53(3)	-8(2)	7.2(19)	-4(2)
C14	41(2)	61(3)	39(2)	-2(2)	4.3(18)	3(2)
C15	39(2)	45(2)	44(2)	4.0(18)	5.5(19)	3.1(19)
C16	75(4)	77(4)	75(4)	-17(3)	4(3)	-23(3)

Table 4 Bond Lengths for 3a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O1	1.425(3)	C3	C4	1.382(7)
S1	O2	1.429(3)	C4	C5	1.367(7)
S1	N1	1.647(3)	C5	C6	1.389(6)
S1	C10	1.763(4)	C6	C7	1.393(5)
Si1	C1	1.887(4)	C10	C11	1.387(5)
Si1	C2	1.851(4)	C10	C15	1.389(5)
Si1	C8	1.856(4)	C11	C12	1.373(6)
Si1	C9	1.861(4)	C12	C13	1.386(5)
N1	C1	1.485(5)	C13	C14	1.381(5)
N1	C7	1.427(4)	C13	C16	1.511(6)
C2	C3	1.387(5)	C14	C15	1.376(5)
C2	C7	1.401(5)			

Table 5 Bond Angles for 3a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	S1	O2	119.80(18)	C7	C2	Si1	111.4(3)
O1	S1	N1	105.82(17)	C4	C3	C2	120.9(4)
O1	S1	C10	107.45(18)	C5	C4	C3	119.5(5)
O2	S1	N1	107.91(16)	C4	C5	C6	121.3(5)
O2	S1	C10	107.86(17)	C5	C6	C7	119.4(4)
N1	S1	C10	107.44(16)	C2	C7	N1	114.9(3)
C2	Si1	C1	90.91(17)	C6	C7	N1	125.4(3)
C2	Si1	C8	114.0(2)	C6	C7	C2	119.6(4)

C2	Si1	C9	114.8(2)	C11	C10	S1	120.1(3)
C8	Si1	C1	113.7(2)	C11	C10	C15	119.8(4)
C8	Si1	C9	109.1(2)	C15	C10	S1	120.1(3)
C9	Si1	C1	113.7(2)	C12	C11	C10	119.1(4)
C1	N1	S1	115.4(2)	C11	C12	C13	122.1(4)
C7	N1	S1	125.0(2)	C12	C13	C16	121.0(4)
C7	N1	C1	115.5(3)	C14	C13	C12	117.8(4)
N1	C1	Si1	106.4(2)	C14	C13	C16	121.3(4)
C3	C2	Si1	129.3(3)	C15	C14	C13	121.5(4)
C3	C2	C7	119.3(4)	C14	C15	C10	119.7(4)

Table 6 Torsion Angles for 3a.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	N1	C1	Si1	168.62(18)	C3	C2	C7	N1	-178.2(3)
S1	N1	C7	C2	-164.7(3)	C3	C2	C7	C6	-0.8(5)
S1	N1	C7	C6	18.1(5)	C3	C4	C5	C6	0.0(8)
S1	C10	C11	C12	178.8(3)	C4	C5	C6	C7	-1.0(7)
S1	C10	C15	C14	-177.5(3)	C5	C6	C7	N1	178.4(4)
Si1	C2	C3	C4	179.0(3)	C5	C6	C7	C2	1.4(6)
Si1	C2	C7	N1	2.5(4)	C7	N1	C1	Si1	10.4(4)
Si1	C2	C7	C6	179.9(3)	C7	C2	C3	C4	-0.1(6)
O1	S1	N1	C1	35.0(3)	C8	Si1	C1	N1	109.6(3)
O1	S1	N1	C7	-169.0(3)	C8	Si1	C2	C3	67.3(4)
O1	S1	C10	C11	-28.5(4)	C8	Si1	C2	C7	-113.5(3)
O1	S1	C10	C15	149.9(3)	C9	Si1	C1	N1	-124.9(3)
O2	S1	N1	C1	164.4(3)	C9	Si1	C2	C3	-59.5(4)
O2	S1	N1	C7	-39.7(3)	C9	Si1	C2	C7	119.7(3)
O2	S1	C10	C11	-159.0(3)	C10	S1	N1	C1	-79.5(3)
O2	S1	C10	C15	19.5(4)	C10	S1	N1	C7	76.4(3)
N1	S1	C10	C11	84.9(3)	C10	C11	C12	C13	-1.7(6)
N1	S1	C10	C15	-96.6(3)	C11	C10	C15	C14	0.9(6)
C1	Si1	C2	C3	-176.2(4)	C11	C12	C13	C14	1.8(6)
C1	Si1	C2	C7	3.0(3)	C11	C12	C13	C16	-177.2(4)
C1	N1	C7	C2	-8.8(4)	C12	C13	C14	C15	-0.5(6)
C1	N1	C7	C6	174.0(4)	C13	C14	C15	C10	-0.8(6)
C2	Si1	C1	N1	-7.2(3)	C15	C10	C11	C12	0.3(6)
C2	C3	C4	C5	0.5(7)	C16	C13	C14	C15	178.5(4)

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

Atom	*x*	*y*	*z*	U(eq)
H1A	6147	3777	7740	62
H1B	6650	4698	8446	62
H3	10469	4951	5979	69
H4	10036	6215	4818	84
H5	7896	7136	4725	81
H6	6157	6824	5784	63
H8A	9725	5362	8589	104
H8B	10851	4500	8207	104
H8C	9790	4089	8945	104
H9A	8978	2124	7814	103
H9B	9838	2497	6968	103
H9C	8203	2293	6899	103
H11	3583	3392	7460	59
H12	2523	2046	6557	66
H14	2637	4237	4509	57
H15	3773	5580	5381	51
H16A	1461	2460	4298	113
H16B	799	1910	5158	113
H16C	2248	1454	4792	113

➢ **Compound (*S*)-1p**

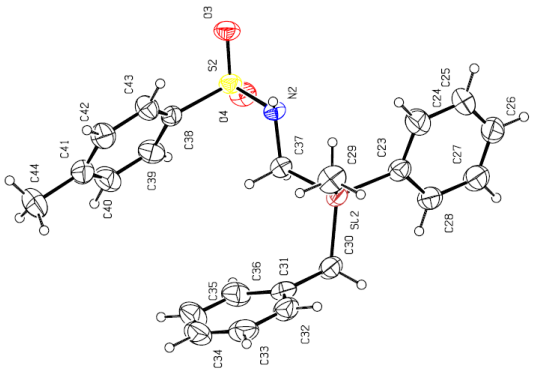


Table 1 Crystal data and structure refinement for (*S*)-1p.

Identification code	**(*S*)-1p**
Empirical formula	$C_{22}H_{25}NO_2SSi$
Formula weight	395.58
Temperature/K	293.15
Crystal system	triclinic
Space group	P1
a/Å	9.2196(8)

b/Å	10.7779(7)
c/Å	11.4849(8)
α/°	74.785(6)
β/°	87.069(6)
γ/°	82.553(6)
Volume/Å^3	1091.76(14)
Z	2
ρ_{calc}g/cm^3	1.203
μ/mm^{-1}	0.219
F(000)	420.0
Crystal size/mm^3	0.35 × 0.3 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.048 to 52.744
Index ranges	-11 ≤ h ≤ 11, -8 ≤ k ≤ 13, -14 ≤ l ≤ 14
Reflections collected	9039
Independent reflections	5843 [R_{int} = 0.0228, R_{sigma} = 0.0451]
Data/restraints/parameters	5843/3/499
Goodness-of-fit on F^2	0.884
Final R indexes [I>=2σ (I)]	R_1 = 0.0463, wR_2 = 0.1216
Final R indexes [all data]	R_1 = 0.0679, wR_2 = 0.1454
Largest diff. peak/hole / e Å^{-3}	0.18/-0.25
Flack parameter	0.00(4)

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

Atom	*x*	*y*	*z*	U(eq)
S2	5041.9(13)	4917.6(11)	3094.1(11)	53.5(4)
S1	6237.7(14)	4852.6(13)	6935.4(11)	56.8(4)
Si1	8180.3(15)	1086.3(15)	6576.3(13)	53.7(4)
Si2	3076.1(15)	8754.0(15)	3266.1(14)	53.4(4)
O3	5370(4)	3876(4)	4151(3)	66.0(11)
O1	7195(5)	5052(4)	7791(4)	74.3(13)
N1	6965(6)	3618(5)	6467(4)	55.9(13)
O4	4077(4)	4755(4)	2227(4)	67.5(12)
O2	5884(5)	5876(4)	5877(4)	71.9(12)
C38	6681(6)	5343(5)	2332(5)	48.8(13)
N2	4330(5)	6147(4)	3581(4)	52.1(12)
C16	4584(6)	4461(5)	7695(5)	52.1(14)
C37	4060(7)	7392(6)	2681(5)	58.5(14)

C9	5494(6)	-19(6)	6899(5)	61.1(14)
C19	1977(7)	3791(7)	8865(6)	70.2(17)
C23	1177(6)	8378(5)	3754(5)	58.5(13)
C43	7871(7)	5415(7)	2973(5)	64.9(16)
C42	9117(7)	5836(7)	2373(6)	73.4(18)
C39	6745(8)	5676(7)	1085(6)	68.7(17)
C4	11308(7)	2907(7)	3478(7)	80.1(18)
C8	6580(7)	574(6)	5955(5)	65.2(15)
C17	4518(7)	4028(6)	8935(5)	63.2(17)
C21	3336(7)	4559(7)	7045(5)	69.9(18)
C10	5629(8)	-1331(6)	7397(6)	73.0(17)
C15	7479(6)	2404(6)	7331(5)	57.3(14)
C31	4555(6)	10625(5)	1600(5)	60.1(14)
C1	9435(6)	1774(6)	5337(5)	60.5(14)
C41	9207(8)	6184(7)	1127(7)	73.3(18)
C14	4340(6)	745(7)	7268(6)	77.1(17)
C32	5092(7)	11506(5)	2110(6)	72.4(16)
C33	6440(8)	11899(7)	1790(8)	86(2)
C40	8010(8)	6101(8)	515(6)	82(2)
C6	9205(7)	1878(7)	4151(6)	78.7(18)
C29	4059(7)	8989(7)	4542(6)	79.4(19)
C18	3236(7)	3706(7)	9516(6)	72.6(19)
C12	3469(10)	-1084(12)	8616(8)	106(3)
C20	2062(7)	4237(7)	7620(6)	77(2)
C44	10574(9)	6666(9)	475(8)	110(3)
C11	4601(11)	-1870(8)	8251(7)	98(3)
C7	9138(7)	-283(6)	7711(6)	78.9(18)
C30	3066(6)	10207(5)	1943(6)	66.9(15)
C26	-1626(8)	7798(7)	4540(8)	85(2)
C5	10101(9)	2446(8)	3221(6)	99(2)
C27	-1415(7)	8614(7)	3442(7)	87(2)
C24	918(8)	7573(8)	4866(6)	95(2)
C28	-27(6)	8904(6)	3043(6)	70.8(16)
C34	7304(9)	11421(9)	1012(9)	96(3)
C22	561(8)	3398(9)	9494(8)	109(3)
C36	5466(8)	10148(7)	786(5)	79.3(18)
C25	-468(9)	7265(8)	5250(8)	94(2)
C13	3348(8)	207(10)	8137(8)	102(2)
C35	6846(9)	10536(9)	493(6)	98(2)
C2	10691(9)	2243(9)	5550(7)	107(3)

C3	11605(10)	2831(11)	4631(10)	122(3)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for (*S*)-1p. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S2	59.1(8)	39.7(8)	60.7(8)	-9.3(6)	-1.1(7)	-9.7(6)
S1	64.2(9)	46.3(9)	60.7(8)	-12.1(7)	-3.1(7)	-13.0(7)
Si1	51.2(8)	51.0(10)	57.6(9)	-11.5(8)	-3.9(7)	-5.7(7)
Si2	46.1(8)	45.5(9)	66.8(10)	-12.3(8)	-7.4(7)	-1.4(7)
O3	80(3)	44(2)	68(2)	-2(2)	1(2)	-13(2)
O1	75(3)	67(3)	89(3)	-28(3)	-10(2)	-22(2)
N1	67(3)	54(3)	46(3)	-9(2)	-4(2)	-12(2)
O4	69(2)	60(3)	79(3)	-19(2)	-11(2)	-20(2)
O2	93(3)	46(2)	69(3)	1(2)	0(2)	-12(2)
C38	50(3)	38(3)	59(3)	-15(3)	1(3)	-4(2)
N2	56(3)	38(3)	58(3)	-6(2)	-1(2)	-3(2)
C16	64(4)	45(3)	47(3)	-12(3)	-4(3)	-2(3)
C37	60(3)	47(3)	64(3)	-9(3)	5(3)	-1(3)
C9	65(3)	59(4)	64(3)	-13(3)	-11(3)	-23(3)
C19	69(4)	69(4)	66(4)	-9(3)	4(3)	-1(3)
C23	62(3)	48(3)	67(3)	-17(3)	-3(3)	-3(3)
C43	65(4)	77(4)	55(3)	-17(3)	2(3)	-15(3)
C42	62(4)	77(5)	83(5)	-19(4)	-3(3)	-17(3)
C39	80(4)	70(4)	56(3)	-13(3)	-5(3)	-15(4)
C4	69(4)	74(5)	98(5)	-30(4)	31(4)	-10(3)
C8	76(4)	57(4)	65(3)	-16(3)	-8(3)	-14(3)
C17	59(4)	74(4)	50(3)	-9(3)	-13(3)	6(3)
C21	70(4)	86(5)	49(3)	-4(3)	-12(3)	-17(4)
C10	91(4)	60(4)	72(4)	-16(3)	-8(3)	-24(3)
C15	57(3)	59(4)	54(3)	-11(3)	-5(2)	-8(3)
C31	68(3)	41(3)	64(3)	0(3)	-16(3)	-3(3)
C1	63(3)	55(3)	64(4)	-15(3)	1(3)	-11(3)
C41	64(4)	59(4)	93(5)	-14(4)	9(4)	-7(3)
C14	59(3)	71(4)	100(5)	-19(4)	-11(3)	-8(3)
C32	74(4)	47(4)	96(4)	-19(3)	-3(3)	-5(3)
C33	77(5)	60(4)	108(5)	5(4)	-20(4)	-18(4)
C40	91(5)	94(6)	55(4)	-8(4)	11(4)	-15(4)
C6	75(4)	102(5)	71(4)	-33(4)	16(3)	-33(4)

C29	80(4)	79(5)	86(4)	-30(4)	-22(4)	-9(4)
C18	77(4)	81(5)	50(3)	-8(3)	1(3)	5(4)
C12	88(6)	141(9)	99(6)	-22(6)	8(5)	-68(6)
C20	68(4)	100(6)	60(4)	-11(4)	-14(3)	-11(4)
C44	87(5)	111(7)	122(6)	-15(5)	42(5)	-29(5)
C11	128(7)	76(5)	85(5)	7(4)	-23(5)	-49(5)
C7	73(4)	71(4)	82(4)	-9(3)	-12(3)	12(3)
C30	58(3)	50(3)	88(4)	-12(3)	-6(3)	0(3)
C26	67(4)	59(4)	129(6)	-23(4)	22(4)	-13(3)
C5	102(5)	129(7)	72(4)	-34(4)	19(4)	-30(5)
C27	63(4)	66(4)	126(6)	-13(4)	-7(4)	-10(3)
C24	80(5)	109(6)	76(5)	2(4)	10(4)	1(4)
C28	55(3)	60(4)	91(4)	-4(3)	-10(3)	-10(3)
C34	68(4)	94(6)	104(6)	19(5)	5(4)	-25(4)
C22	75(4)	130(8)	107(6)	-2(6)	10(5)	-26(5)
C36	100(5)	77(5)	57(3)	-10(3)	-5(3)	-13(4)
C25	82(5)	95(6)	91(5)	-8(4)	33(4)	-9(4)
C13	68(4)	129(8)	115(6)	-36(6)	19(4)	-29(5)
C35	98(5)	117(7)	65(4)	0(4)	18(4)	-15(5)
C2	90(5)	156(8)	80(5)	-13(5)	-1(4)	-69(5)
C3	85(5)	157(9)	130(8)	-28(7)	11(6)	-63(6)

Table 4 Bond Lengths for (*S*)-1p.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S2	O3	1.436(4)	C23	C28	1.381(7)
S2	O4	1.427(4)	C43	C42	1.375(8)
S2	C38	1.759(6)	C42	C41	1.382(10)
S2	N2	1.620(5)	C39	C40	1.378(9)
S1	O1	1.428(4)	C4	C5	1.351(10)
S1	N1	1.618(5)	C4	C3	1.344(12)
S1	O2	1.429(4)	C17	C18	1.367(9)
S1	C16	1.761(6)	C21	C20	1.357(9)
Si1	C8	1.875(6)	C10	C11	1.395(10)
Si1	C15	1.881(6)	C31	C32	1.391(8)
Si1	C1	1.848(6)	C31	C30	1.501(8)
Si1	C7	1.851(6)	C31	C36	1.380(8)
Si2	C37	1.882(6)	C1	C6	1.363(8)
Si2	C23	1.873(6)	C1	C2	1.379(8)

Si2	C29	1.850(6)	C41	C40	1.362(9)
Si2	C30	1.873(6)	C41	C44	1.512(9)
N1	C15	1.458(7)	C14	C13	1.382(10)
C38	C43	1.374(8)	C32	C33	1.367(9)
C38	C39	1.382(8)	C33	C34	1.327(11)
N2	C37	1.464(6)	C6	C5	1.377(9)
C16	C17	1.378(8)	C12	C11	1.376(12)
C16	C21	1.381(8)	C12	C13	1.348(12)
C9	C8	1.510(8)	C26	C27	1.356(10)
C9	C10	1.371(8)	C26	C25	1.349(10)
C9	C14	1.378(8)	C27	C28	1.384(8)
C19	C18	1.392(9)	C24	C25	1.383(10)
C19	C20	1.386(9)	C34	C35	1.368(12)
C19	C22	1.514(10)	C36	C35	1.388(10)
C23	C24	1.372(9)	C2	C3	1.387(12)

Table 5 Bond Angles for (*S*)-1p.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O3	S2	C38	109.4(3)	C28	C23	Si2	122.7(4)
O3	S2	N2	105.8(2)	C38	C43	C42	120.0(6)
O4	S2	O3	119.0(3)	C43	C42	C41	121.3(6)
O4	S2	C38	107.5(3)	C40	C39	C38	118.4(6)
O4	S2	N2	107.8(3)	C3	C4	C5	119.9(7)
N2	S2	C38	106.7(3)	C9	C8	Si1	114.4(4)
O1	S1	N1	108.2(3)	C18	C17	C16	120.6(6)
O1	S1	O2	118.8(3)	C20	C21	C16	120.4(6)
O1	S1	C16	107.8(3)	C9	C10	C11	120.0(7)
N1	S1	C16	107.9(3)	N1	C15	Si1	112.5(4)
O2	S1	N1	106.2(3)	C32	C31	C30	121.0(6)
O2	S1	C16	107.6(3)	C36	C31	C32	116.6(6)
C8	Si1	C15	108.3(3)	C36	C31	C30	122.3(6)
C1	Si1	C8	110.1(3)	C6	C1	Si1	123.8(5)
C1	Si1	C15	107.4(3)	C6	C1	C2	114.4(6)
C1	Si1	C7	111.4(3)	C2	C1	Si1	121.8(5)
C7	Si1	C8	111.0(3)	C42	C41	C44	120.9(7)
C7	Si1	C15	108.5(3)	C40	C41	C42	117.5(7)
C23	Si2	C37	108.9(3)	C40	C41	C44	121.7(7)
C23	Si2	C30	111.7(2)	C9	C14	C13	120.9(7)

C29	Si2	C37	111.0(3)	C33	C32	C31	121.2(7)
C29	Si2	C23	110.2(3)	C34	C33	C32	121.2(8)
C29	Si2	C30	110.7(3)	C41	C40	C39	122.9(6)
C30	Si2	C37	104.1(3)	C1	C6	C5	123.9(6)
C15	N1	S1	120.3(4)	C17	C18	C19	120.6(6)
C43	C38	S2	120.0(4)	C13	C12	C11	119.8(8)
C43	C38	C39	119.9(6)	C21	C20	C19	121.3(6)
C39	C38	S2	120.0(5)	C12	C11	C10	120.1(8)
C37	N2	S2	116.8(3)	C31	C30	Si2	113.5(3)
C17	C16	S1	120.9(5)	C25	C26	C27	119.5(7)
C17	C16	C21	119.1(6)	C4	C5	C6	119.3(7)
C21	C16	S1	120.0(5)	C26	C27	C28	120.7(6)
N2	C37	Si2	115.2(4)	C23	C24	C25	122.2(7)
C10	C9	C8	120.5(6)	C23	C28	C27	121.0(6)
C10	C9	C14	118.7(6)	C33	C34	C35	120.3(8)
C14	C9	C8	120.7(5)	C31	C36	C35	121.4(7)
C18	C19	C22	121.2(6)	C26	C25	C24	120.0(7)
C20	C19	C18	117.9(7)	C12	C13	C14	120.4(8)
C20	C19	C22	120.9(6)	C34	C35	C36	119.3(7)
C24	C23	Si2	120.7(5)	C1	C2	C3	122.8(8)
C24	C23	C28	116.6(6)	C4	C3	C2	119.6(8)

Table 6 Torsion Angles for (*S*)-1p.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S2	C38	C43	C42	-175.4(5)	C17	C16	C21	C20	0.2(11)
S2	C38	C39	C40	175.0(5)	C21	C16	C17	C18	-0.3(10)
S2	N2	C37	Si2	174.6(3)	C10	C9	C8	Si1	-91.3(6)
S1	N1	C15	Si1	176.7(3)	C10	C9	C14	C13	1.0(9)
S1	C16	C17	C18	-178.9(5)	C15	Si1	C8	C9	-63.5(5)
S1	C16	C21	C20	178.8(5)	C15	Si1	C1	C6	-118.0(6)
Si1	C1	C6	C5	176.8(6)	C15	Si1	C1	C2	61.3(6)
Si1	C1	C2	C3	-176.2(8)	C31	C32	C33	C34	-2.4(10)
Si2	C23	C24	C25	-179.4(6)	C31	C36	C35	C34	-0.7(10)
Si2	C23	C28	C27	-179.2(5)	C1	Si1	C8	C9	179.3(4)
O3	S2	C38	C43	-42.1(5)	C1	Si1	C15	N1	48.1(5)
O3	S2	C38	C39	141.7(5)	C1	C6	C5	C4	1.7(12)
O3	S2	N2	C37	172.6(4)	C1	C2	C3	C4	-3.0(16)
O1	S1	N1	C15	50.4(5)	C14	C9	C8	Si1	89.3(6)

O1	S1	C16	C17	-18.9(6)	C14	C9	C10	C11	0.6(8)
O1	S1	C16	C21	162.6(5)	C32	C31	C30	Si2	-89.4(5)
N1	S1	C16	C17	97.7(5)	C32	C31	C36	C35	-0.2(8)
N1	S1	C16	C21	-80.8(6)	C32	C33	C34	C35	1.3(11)
O4	S2	C38	C43	-172.6(5)	C33	C34	C35	C36	0.2(11)
O4	S2	C38	C39	11.2(6)	C6	C1	C2	C3	3.1(13)
O4	S2	N2	C37	-59.1(4)	C29	Si2	C37	N2	55.8(5)
O2	S1	N1	C15	178.9(4)	C29	Si2	C23	C24	-40.2(6)
O2	S1	C16	C17	-148.1(5)	C29	Si2	C23	C28	138.4(5)
O2	S1	C16	C21	33.3(6)	C29	Si2	C30	C31	50.9(5)
C38	S2	N2	C37	56.2(5)	C18	C19	C20	C21	1.1(12)
C38	C43	C42	C41	-0.4(11)	C20	C19	C18	C17	-1.3(11)
C38	C39	C40	C41	1.2(12)	C44	C41	C40	C39	-179.4(8)
N2	S2	C38	C43	72.0(5)	C11	C12	C13	C14	1.1(12)
N2	S2	C38	C39	-104.3(5)	C7	Si1	C8	C9	55.5(5)
C16	S1	N1	C15	-66.0(5)	C7	Si1	C15	N1	168.6(4)
C16	C17	C18	C19	0.9(11)	C7	Si1	C1	C6	123.3(6)
C16	C21	C20	C19	-0.6(11)	C7	Si1	C1	C2	-57.4(7)
C37	Si2	C23	C24	81.8(6)	C30	Si2	C37	N2	175.0(4)
C37	Si2	C23	C28	-99.5(5)	C30	Si2	C23	C24	-163.7(5)
C37	Si2	C30	C31	-68.5(5)	C30	Si2	C23	C28	15.0(6)
C9	C10	C11	C12	-1.5(10)	C30	C31	C32	C33	-179.3(5)
C9	C14	C13	C12	-1.9(11)	C30	C31	C36	C35	-179.2(5)
C23	Si2	C37	N2	-65.7(5)	C26	C27	C28	C23	-0.5(10)
C23	Si2	C30	C31	174.1(4)	C5	C4	C3	C2	2.0(15)
C23	C24	C25	C26	-2.3(13)	C27	C26	C25	C24	1.3(12)
C43	C38	C39	C40	-1.2(10)	C24	C23	C28	C27	-0.5(9)
C43	C42	C41	C40	0.4(11)	C28	C23	C24	C25	1.9(11)
C43	C42	C41	C44	179.0(7)	C22	C19	C18	C17	178.1(7)
C42	C41	C40	C39	-0.8(12)	C22	C19	C20	C21	-178.3(7)
C39	C38	C43	C42	0.8(10)	C36	C31	C32	C33	1.8(8)
C8	Si1	C15	N1	-70.8(4)	C36	C31	C30	Si2	89.5(6)
C8	Si1	C1	C6	-0.2(7)	C25	C26	C27	C28	0.1(11)
C8	Si1	C1	C2	179.1(6)	C13	C12	C11	C10	0.6(12)
C8	C9	C10	C11	-178.7(5)	C2	C1	C6	C5	-2.5(11)
C8	C9	C14	C13	-179.6(6)	C3	C4	C5	C6	-1.4(12)

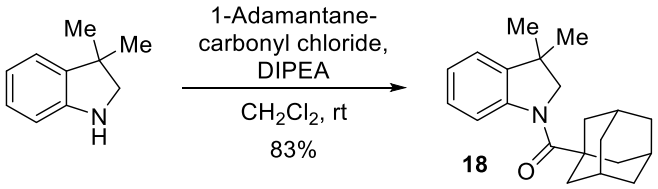
Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for (*S*)-1p.

Atom	*x*	*y*	*z*	U(eq)
H37A	3490.91	7275.69	2038.64	70
H37B	4992.68	7642.98	2332.35	70
H43	7833.83	5180.37	3812.23	78
H42	9915.37	5888.18	2814.4	88
H39	5953.8	5616.21	640.42	82
H4	11932.78	3276.66	2858.98	96
H8A	6076.96	1323.14	5395.98	78
H8B	6942.81	-49.82	5502.07	78
H17	5354.2	3955	9379.99	76
H21	3368.65	4847.97	6207.42	84
H10	6405.31	-1861.85	7165.94	88
H15A	6682.16	2123.85	7881.58	69
H15B	8254.9	2549.95	7800.76	69
H14	4227.36	1634.43	6927.38	92
H32	4523.32	11832.62	2680.11	87
H33	6757.95	12513.29	2122.83	103
H40	8048.31	6341.14	-323.72	99
H6	8394.54	1545.25	3957.29	94
H29A	4120.45	8210.03	5186.78	119
H29B	3538.69	9689.88	4822.15	119
H29C	5026.46	9188.81	4280.22	119
H18	3203.83	3426.51	10353.69	87
H12	2790.07	-1443.26	9190.92	128
H20	1229.98	4315.93	7168.67	93
H44A	10597.54	7549.78	488.13	164
H44B	10570.48	6611.32	-345.51	164
H44C	11420.42	6141.6	870.12	164
H11	4680.74	-2762.18	8574.73	117
H7A	8441.13	-678.88	8294.55	118
H7B	9848.46	30.9	8109.16	118
H7C	9621.35	-909.69	7317.09	118
H30A	2664.12	10011.97	1255.96	80
H30B	2428.12	10919.8	2131.35	80
H26	-2562.74	7607.1	4801.69	102
H5	9878.59	2512.36	2424.93	119
H27	-2212.84	8983.82	2952.07	104
H24	1699.65	7221.94	5378.01	114
H28	97.11	9460.42	2285.03	85
H34	8225.27	11688.33	818.63	116

H22A	659.96	3238.43	10350.68	163
H22B	343.69	2625.36	9307.69	163
H22C	-218.28	4082.21	9223.23	163
H36	5149.35	9554.13	426.38	95
H25	-600.88	6690.6	5997.32	112
H13	2592.45	739.44	8393.46	123
H35	7452.18	10198.58	-50.25	118
H2A	10935.21	2160.79	6344.48	128
H3	12417.5	3170.73	4810.32	146
H1	6510(50)	3560(50)	5920(40)	43(15)
H2	4770(60)	6230(60)	4210(50)	62(18)

9. Bioactivity Evaluation

((3r,5r,7r)-adamantan-1-yl)(3,3-dimethylindolin-1-yl)methanone **(18)**



Compound **18** was prepared according to the literature[21]. To a solution of 3,3-dimethylindoline (100 mg, 0.60 mmol) in CH_2Cl_2 (3 mL) was added 1-adamantanecarbony chloride (202 mg, 0.90 mmol, 1.5 equiv.) and DIPEA (263 mg, 1.79 mmol, 3.0 equiv.) under argon atmosphere. The reaction was stirred at room temperature for 2 h before quenching with sat. aq. $NaHCO_3$ and extracting with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with sat. aq. NaCl, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (eluent: EtOAc/petroleum ether = 1/20) to give **18** as a white solid (175 mg, 83%).

- R_f = 0.7 (EtOAc/ petroleum ether = 1/10).
- mp : 134.8 – 136.5 ºC.
- ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.25 – 6.92 (m, 3H), 4.03 (s, 2H), 2.10 (s, 9H), 1.77 (s, 6H), 1.33 (s, 6H).
- ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 143.6, 139.9, 127.4, 123.8, 121.3, 118.6, 63.8, 42.9, 41.0, 38.2, 36.6, 28.4, 27.1.
- IR (neat) cm^{-1} 3006, 2903, 2989, 2849, 1639, 1597, 1452, 1275, 1260, 764, 751.
- HRMS calcd for $C_{21}H_{28}NO$ $(M+H)^+$: 310.2165, found 310.2163.

HPLC analysis

Analytical HPLC was performed with an Agilent 1100 Series pump system equipped with a reversed-phase ODS column (Welch ultimate XB-C_{18} column (4.6 mm × 150 mm，5 μm)) with a flow rate of 1.0 mL/min using a gradient of MeOH and water (0.1% TFA) and UV detection at 254 nm. Mobile phase system for purity determination by area normalization method was (0~3.0 min, 5% B; 3.0~4.0 min, 5%~90% B; 4.0~12.0 min, 90% B; 12.0~13.0 min, 90%~5% B; 13.0~15.0 min, 5% B). The column temperature was 30 ℃, and the sample size was 5 μL. All compounds were tested parallelly in three groups.

Cell-based cAMP assay

Determination of cAMP levels in CHO cells stably expressing human CB_1R and CB_2R was performed using the Lance-Ultra cAMP kit (Perkin Elmer, TRF0263). Cells were washed and re-suspended in 1× stimulation buffer and dispensed in white 384-well microplates at a density of 3000 cells per well and incubated for 15 min at rt with compounds, followed by 15 min incubation with forskolin, and 1h more with homogeneous time-resolved fluorescence (HTRF) assay reagents. Fluorescence at 665 nm and 615 nm was analyzed on a BioTek Synergy HT. Forskolin-stimulated cAMP levels were normalized to 100%.

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21. M. Nettekoven, J. Fingerle, U. Grether, S. Gruner, A. Kimbara, B. Pullmann, M. Rogers-Evans, S. Rover, F. Schuler, T. Schulz-Gasch, C. Ullmer, *Bioorg. Med. Chem. Lett*. **2013**, *23*, 1177.

n-Octanol-water partition coefficient determination by the shake flask method

Experimental log D values were determined using a shake-flask method combined RP-HPLC. Tri-distilled water (pH 7.4) served as aqueous phase of the system. The pH values of the aqueous phase for the shake-flask method were measured with a pH-Meter with an accuracy of ±0.002. As a non-polar phase, n-octanol was used. Equal volume of n-octanol and tri-distilled water are shaken at 37 ℃ for 24 hours to make them mutually saturated. After standing overnight, the two phases are separated after stratification. For each compound, a 20 mg/mL solution was prepared in a water-saturated n-octanol. The solution was mixed in 1.0 mL n-octanol-saturated pH 7.4 water aliquotly. The mixed solution was heavily shaken at 37 ℃ for 24 h. After 24 h, the two phases were separated with resting overnight to ensure complete separation of the two phases. Each phase was transferred to a 1.5 mL microcentrifuge tube and centrifugated at 20000 rpm for 10 min. 100 μL of both phases was transferred to disposable injection bottles and injected into an HPLC chromatograph. The relative peak areas of the samples in each phase were then determined by HPLC analysis. The Log D value was obtained from the ratio of peak areas in the octanol and buffer phases, respectively. Log D = log (C octanol/C water)

HPLC conditions. Analytical HPLC was performed with a Shimadzu pump system equipped with a reversed-phase ODS column (SWELL C18 column (4.6 mm×150 mm, 5 μm) with a flow rate of 1.0 mL/min using a gradient of ACN and water (0.1% TFA) and UV detection at 254 nm. The column temperature was 30℃, and the sample size was 10 μL. The mobile phase consisted of an ACN/0.1% aqueous trifluoroacetic acid (pH 2.0) mixture. The ratio of the two solvents in the mixture was (0~2.0 min, 20%~30% B; 2.0~18.0 min, 30%~80% B; 18.0~20.0 min, 80% B; 20.0~25.0 min, 80%~20% B; 25.0~30.0 min, 20% B).

Animals

ICR mice were used in all animal studies. Equally sized cohorts of male and female mice aged 8 to 26 weeks were used. Animals were housed in a conventional facility at 21 ℃ on a 12 h light-dark cycle with unrestricted access to food and water.

Ethical Statement: All animal experiments were performed in compliance with the Guide for the Care and Use of Laboratory Animals (Ministry of Science and Technology of China, 2013, IACUC-2013-012) and approved by Animal Ethics Committee of West China Hospital (Approval No. 2019222A).

Determination of plasma - brain distribution in mice

The mice were randomly divided into two groups. Animals were fasted for 12 h. Each animal was administered once (**18** at 300 mg/kg and **10** at isomole), and blood was collected 40 min after administration. The mice were deeply anesthetized with isoflurane (2%) . And the head was cut off and the chest cavity was opened for cardiac blood extraction. After the blood was taken, the brain tissue of the mouse was taken out immediately. After that, 500 μl normal saline was added, and the brain homogenate was made by grinding with a high-throughput tissue fragmentation machine. The plasma and brain homogenates were centrifuged at 3500 rpm for 10 min for separation, and 100 μL of supernatant was taken. Three times the volume of acetonitrile were added to completely precipitate protein, and the protein was shaken by vortex, then the homogenates were oscillated with ultrasonic

wave for 3-5 min, and centrifuged at 20,000 rpm for 10 min. Appropriate amount of supernatant was taken for HPLC analysis.

CFA model

A volume of 20 μl Complete Freund's Adjuvant (CFA) (Sigma-Aldrich, F5881) or normal saline was injected into the left hindpaw. One day after CFA model setting up, the CFA mice were individually placed in the chamber as described in the spontaneous pain test. Before inflammatory pain experiment, mice were randomly divided into the following groups: model group, **18**- 0.7 mmol/kg group, **18**- 1.0 mmol/kg group, **18**- 1.3 mmol/kg group and **10**- 0.7 mmol/kg group, **10**- 1.0 mmol/kg group, **10**- 1.3 mmol/kg group. Mechanical responses were tested by stimulating the region comprising the sural nerve territory with electronic von Frey (IITC, #2391).

Statistical analysis

Statistical analyses were carried out using Origin 9.0 software (Origin Lab Corporation). Differences in measured variables were assessed by using one-way or two-way analysis of variance (ANOVA) followed by Dunnett's T3 or Tukey–Kramer HSD post hoc corrections for multiple comparison testing. The normality of the data distribution was determined using the Shapiro-Wilk test before appropriate statistical methods were chosen. * $P < 0.05$, ** $P < 0.01$ and ***$P < 0.001$, vehicle versus **10** 1.3 mmol/kg. &$P < 0.05$ and &&&$P < 0.001$, vehicle versus **10** 1.0 mmol/kg. #$P < 0.05$, vehicle versus **18** 1.3 mmol/kg and **18** 1.0 mmol/kg. ##$P < 0.01$, vehicle versus **18** 1.3 mmol/kg. ###$P < 0.001$, **18** 1.3 mmol/kg and **10** 1.3 mmol/kg.

Table 1. n-Octanol-water partition coefficient determination

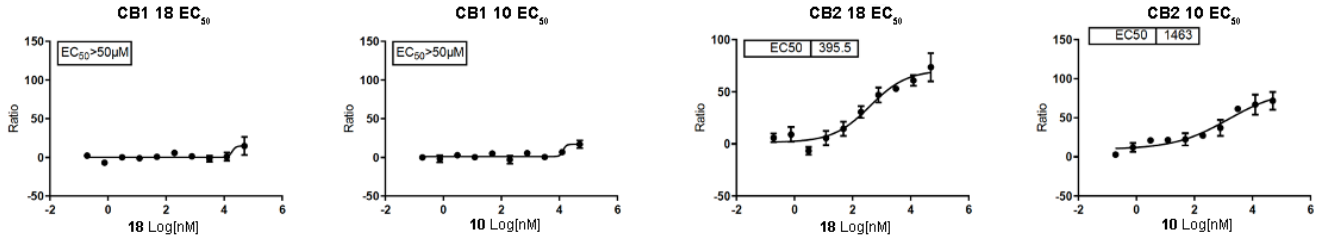
Compound	Peak area						Log D
	n-Octanol			Water			
18	21478303	23437093	29286989	4316	2712	6631	4.75
10	19337076	25293145	27327905	275	333	454	5.84

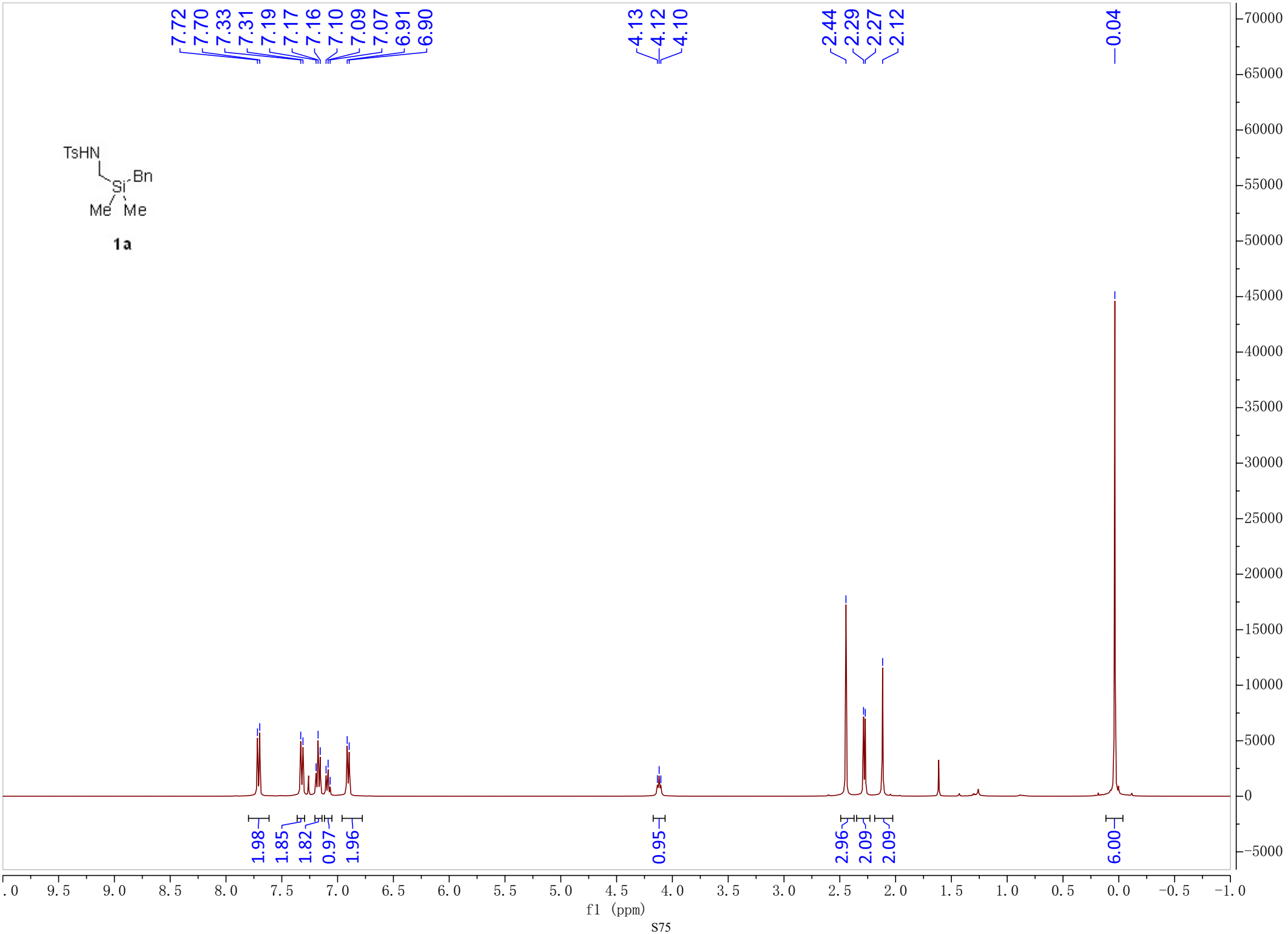
Table 2. Determination of plasma - brain distribution of 18 and 10 in mice

Compound	Peak area*					
	Group 1		Group 2		Group 3	
	Plasma	Brain	Plasma	Brain	Plasma	Brain
18	30.3	27	28.5	24.4	37.8	34.6
10	3.8	19.3	5.3	30.3	9	22.1

*: Samples were collected 40 min after administration with 300mg/kg

Figure 1. CB_1R and CB_2R Agonistic Activity of Compound 18 and 10

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7.33
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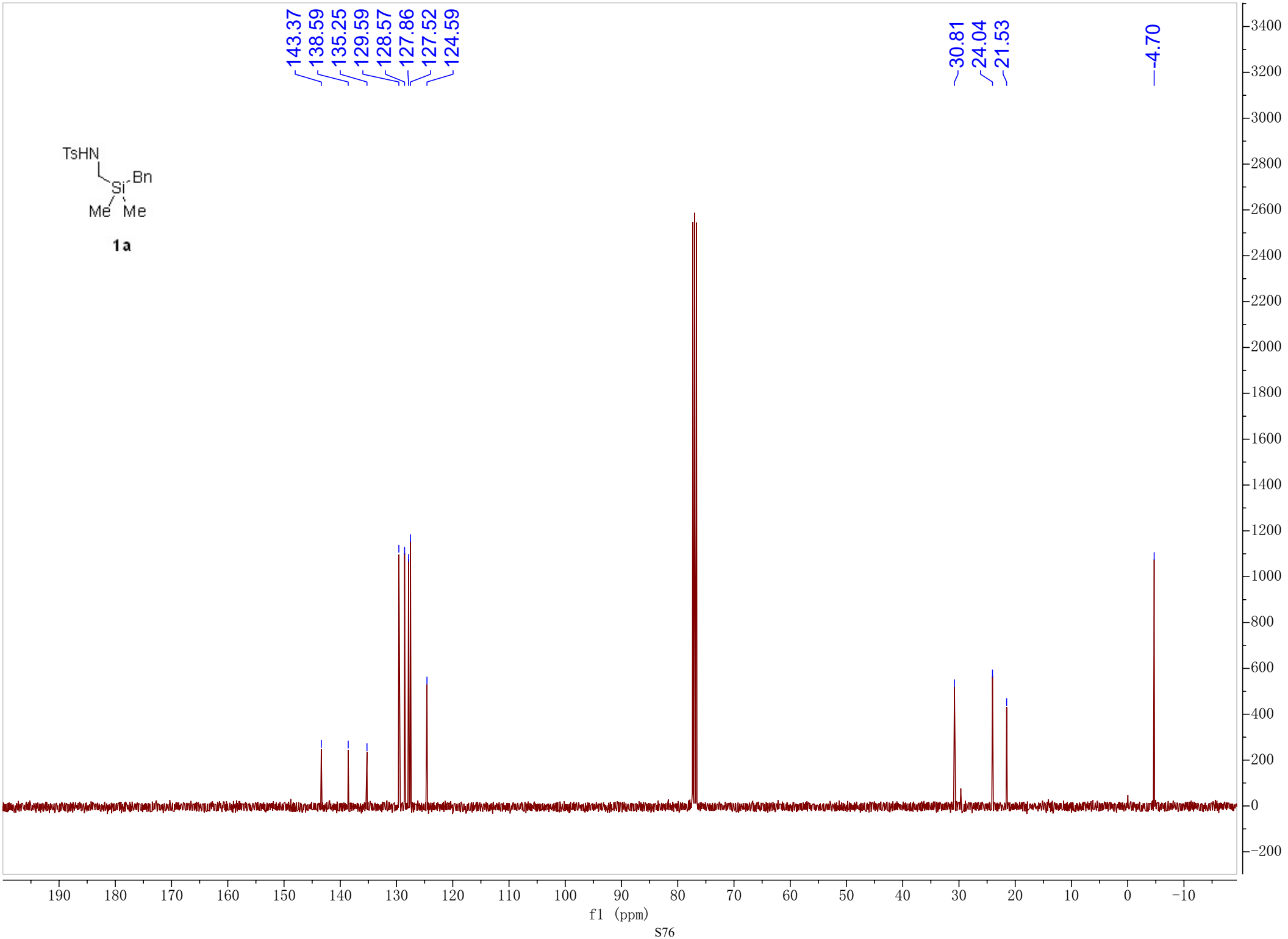
7.17
7.16
7.10
7.09
7.07
6.91
6.90
4.13
4.12
4.10
2.44
2.29
2.27
2.12
0.04
TsHN
Si
Bn
Me
Me
1a
1.98
1.85
1.82
0.97
1.96
0.95
2.96
2.09
2.09
6.00
f1 (ppm)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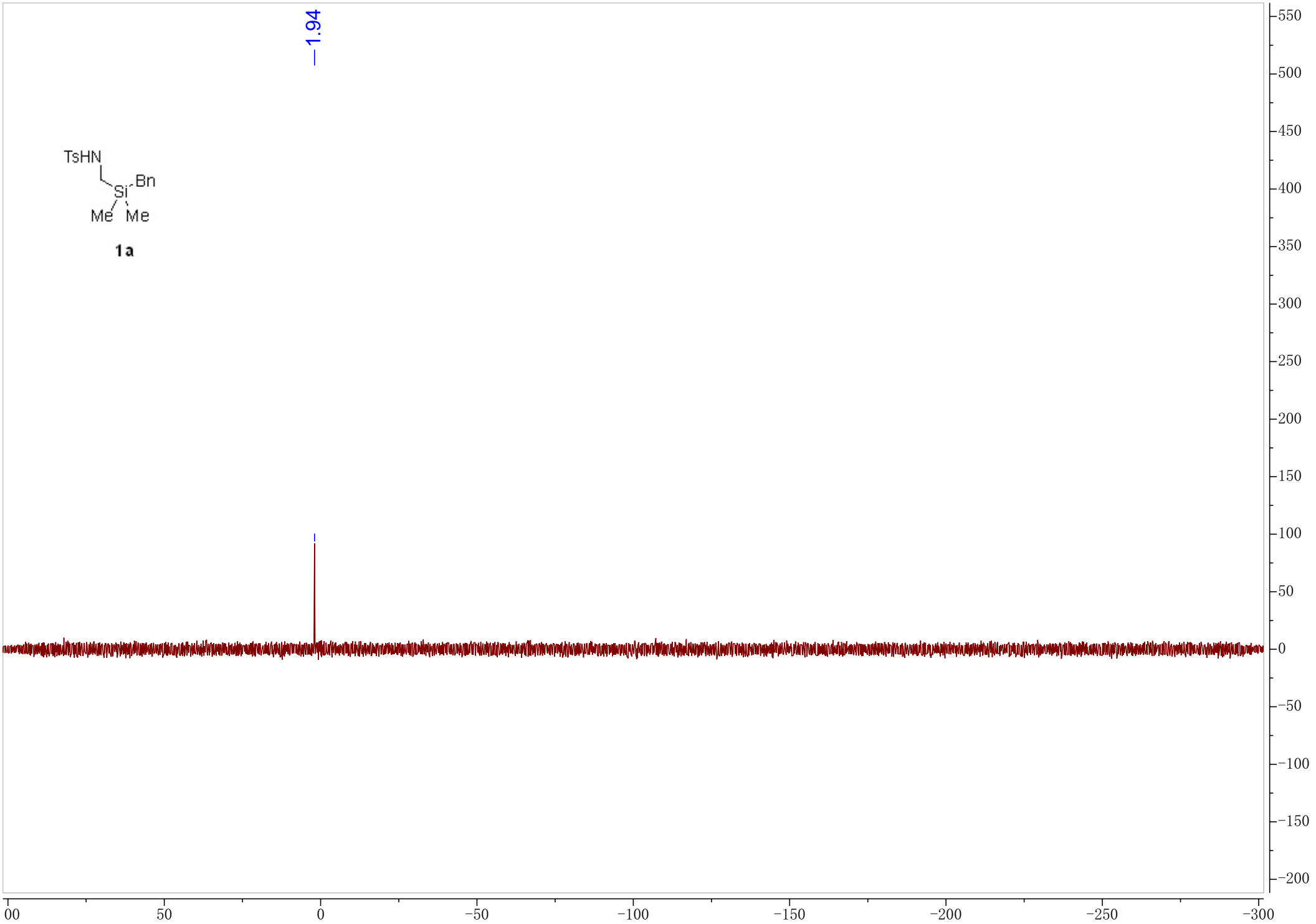
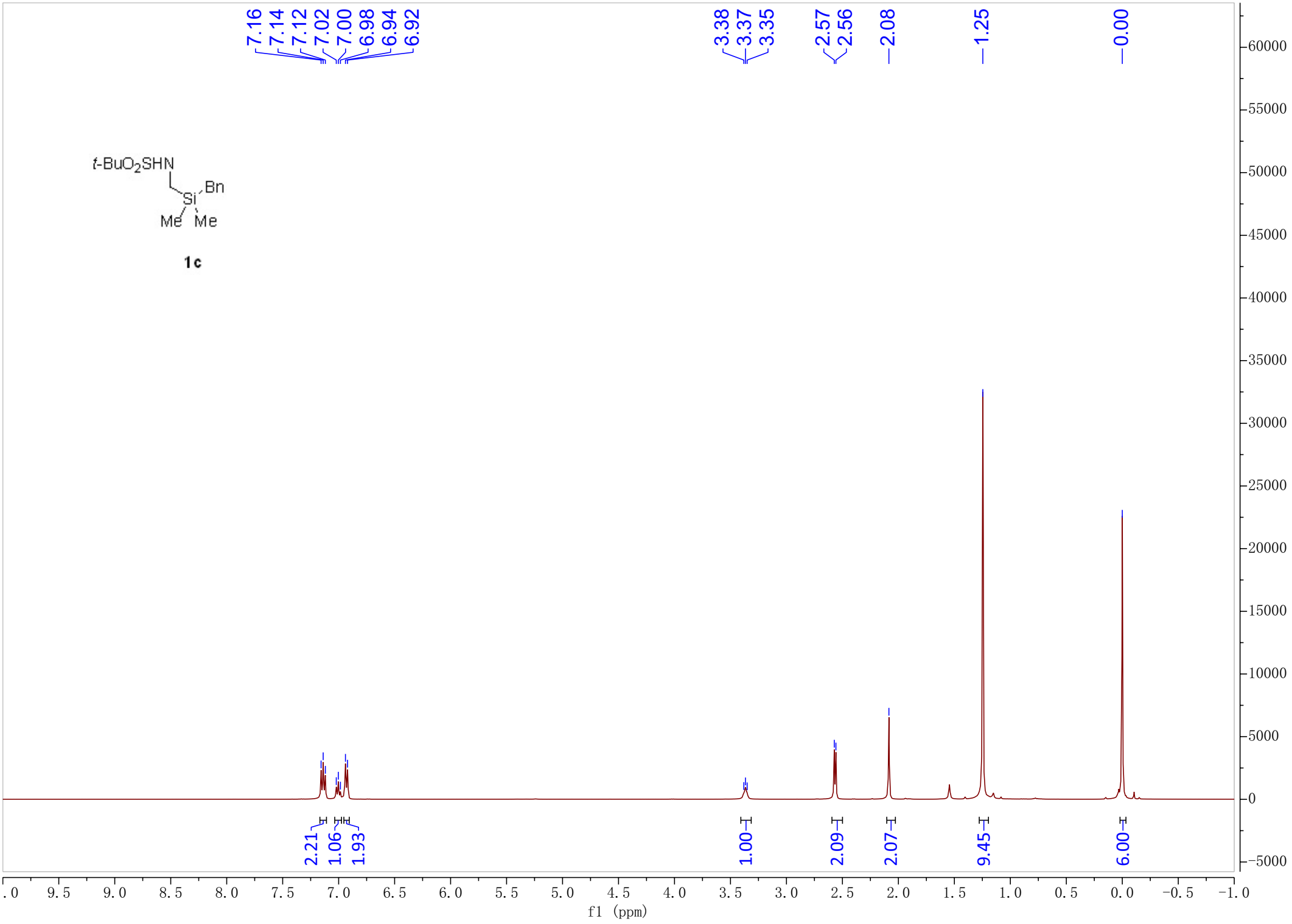
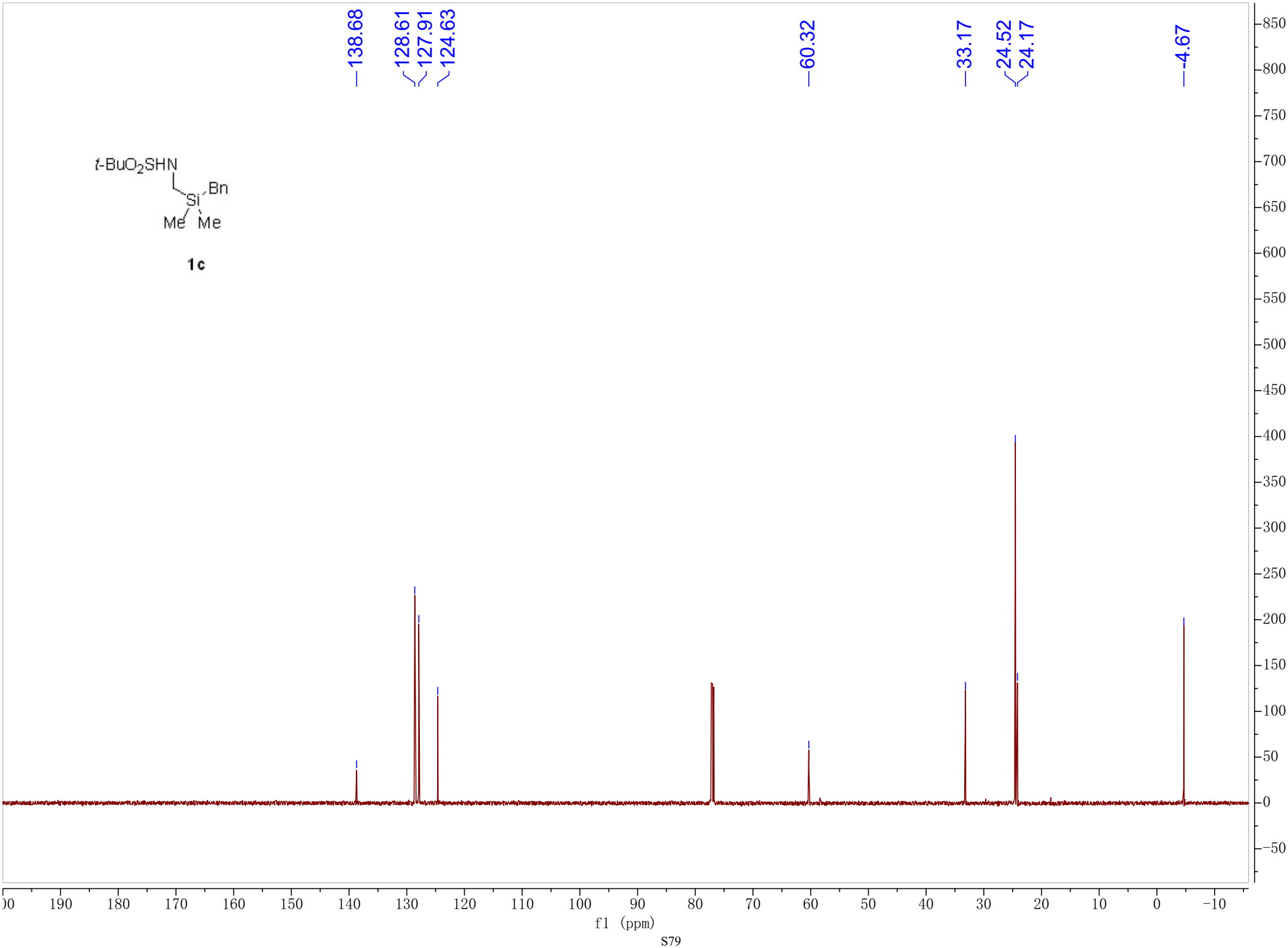
138.59
135.25
129.59
128.57
127.86
127.52
124.59
30.81
24.04
21.53
-4.70
TsHN
Si
Bn
Me
Me
1a
f1 (ppm)


1.94
TsHN
Si
Bn
Me
Me
1a
550
500
450
400
350
300
250
200
150
100
50
0
−50
−100
−150
−200
00
50
0
−50
−100
−150
−200
−250
−300
f1 (ppm)


7.16
7.14
7.12
7.02
7.00
6.98
6.94
6.92
3.38
3.37
3.35
2.57
2.56
2.08
1.25
0.00
t-BuO2SHN
Si
Bn
Me
Me
1c
2.21
1.06
1.93
1.00
2.09
2.07
9.45
6.00
f1 (ppm)


138.68
128.61
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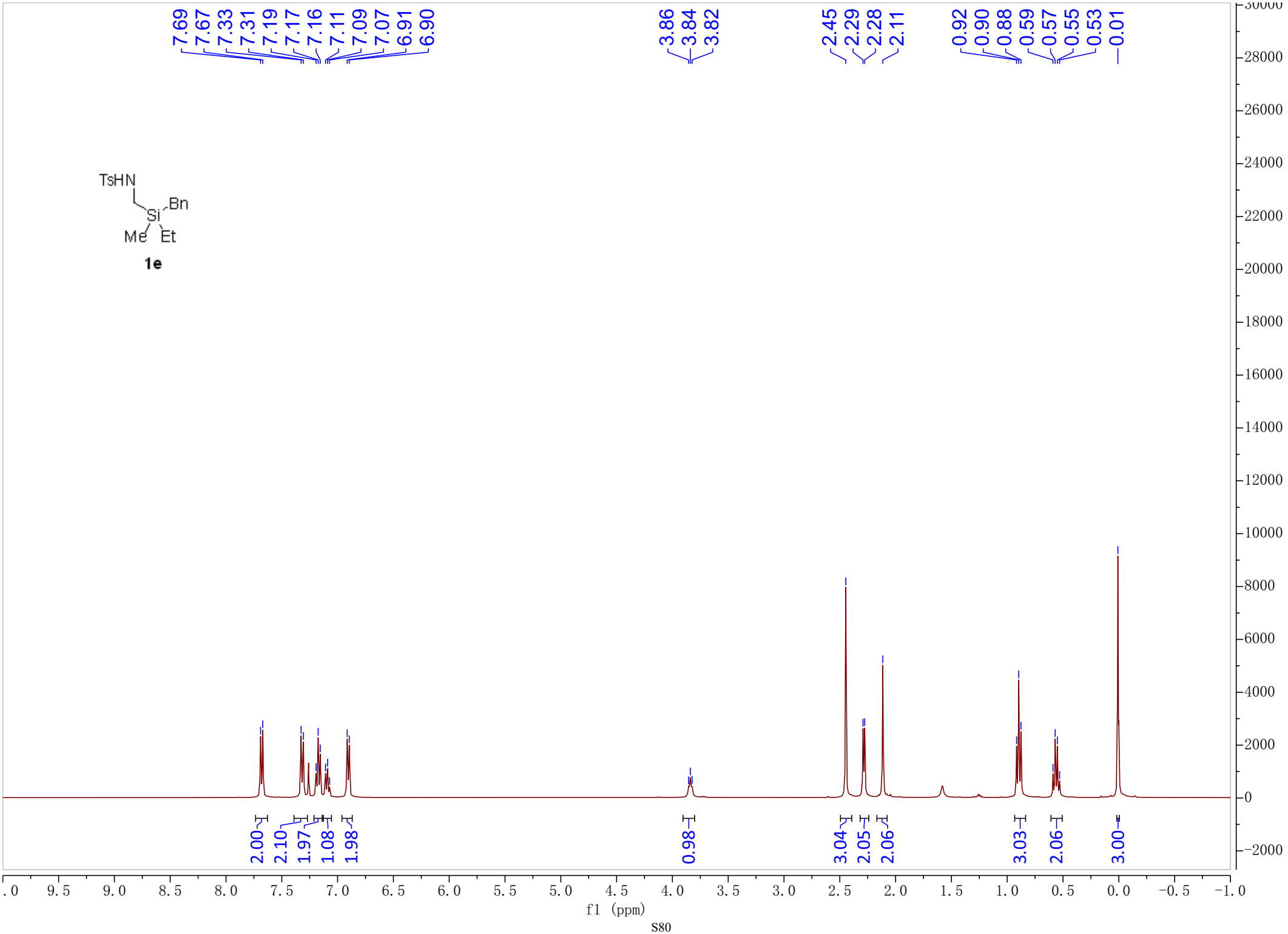
124.63
60.32
33.17
24.52
24.17
-4.67
t-BuO2SHN
Si
Bn
Me
Me
1c
f1 (ppm)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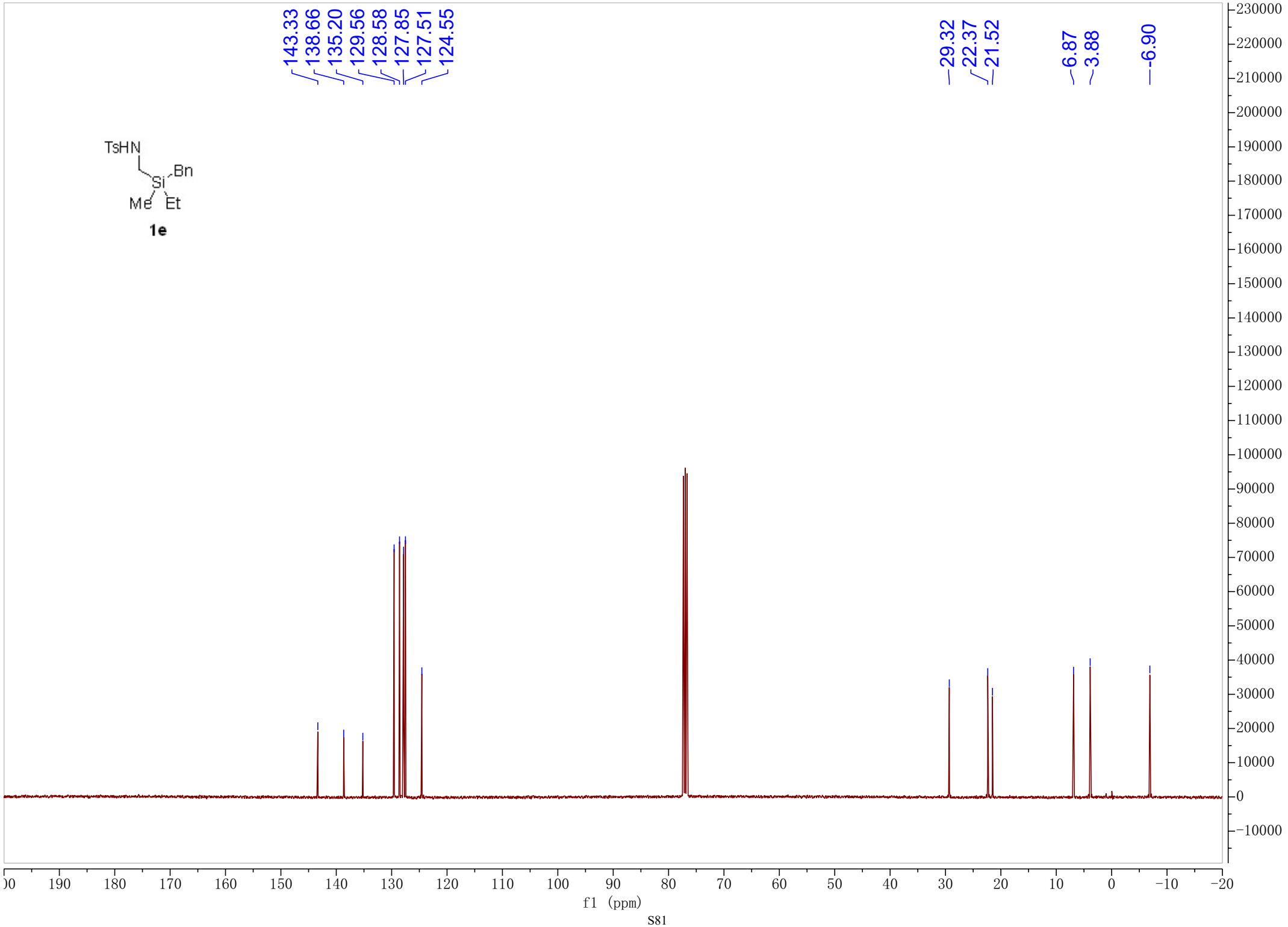
7.11
7.09
7.07
6.91
6.90
3.86
3.84
3.82
2.45
2.29
2.28
2.11
0.92
0.90
0.88
0.59
0.57
0.55
0.53
0.01
TsHN
Si
Bn
Me
Et
1e
2.00
2.10
1.97
1.08
1.98
0.98
3.04
2.05
2.06
3.03
2.06
3.00
f1 (ppm)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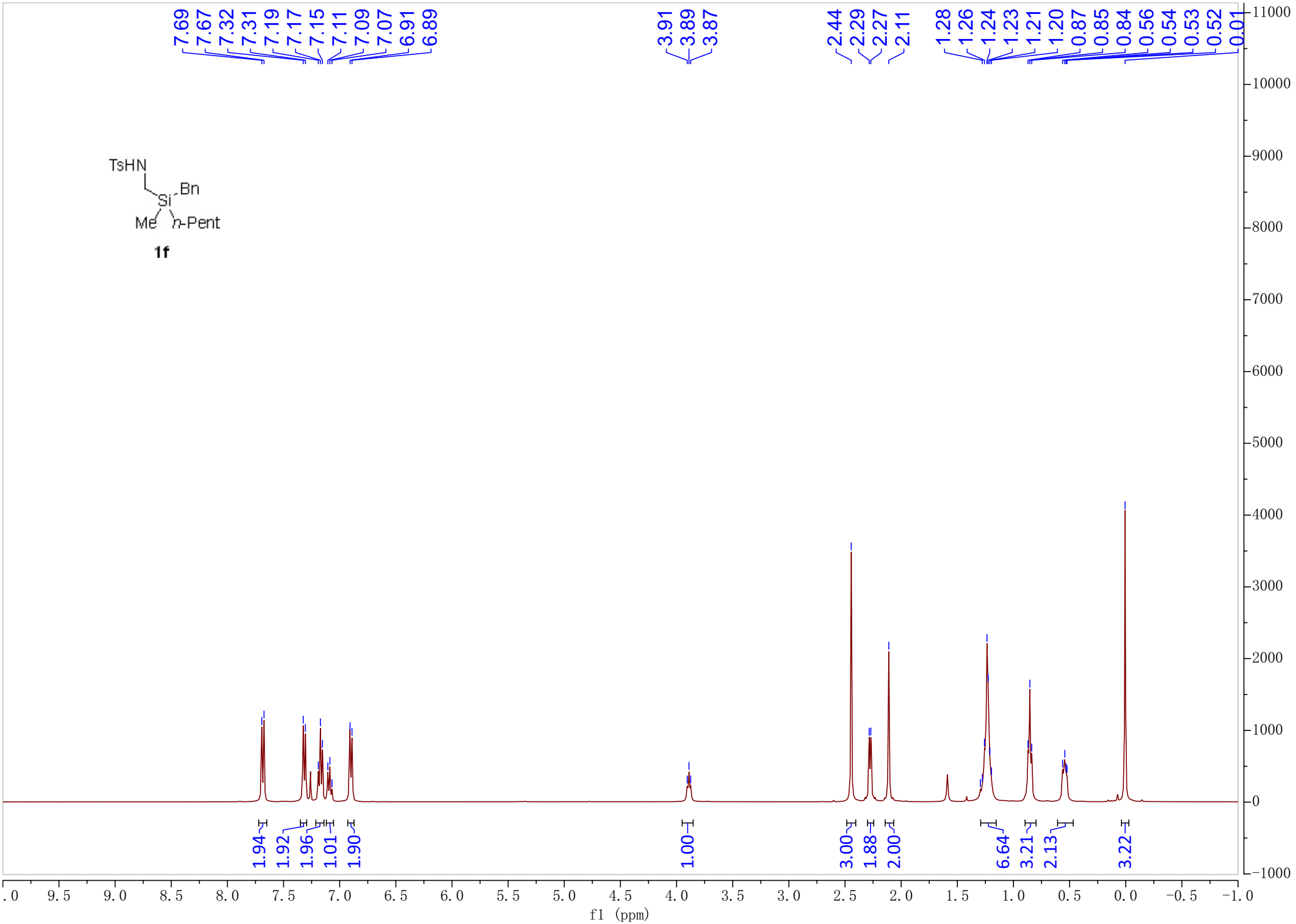
127.85
127.51
124.55
29.32
22.37
21.52
6.87
3.88
-6.90
TsHN
Si
Bn
Me
Et
1e
f1 (ppm)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7.67
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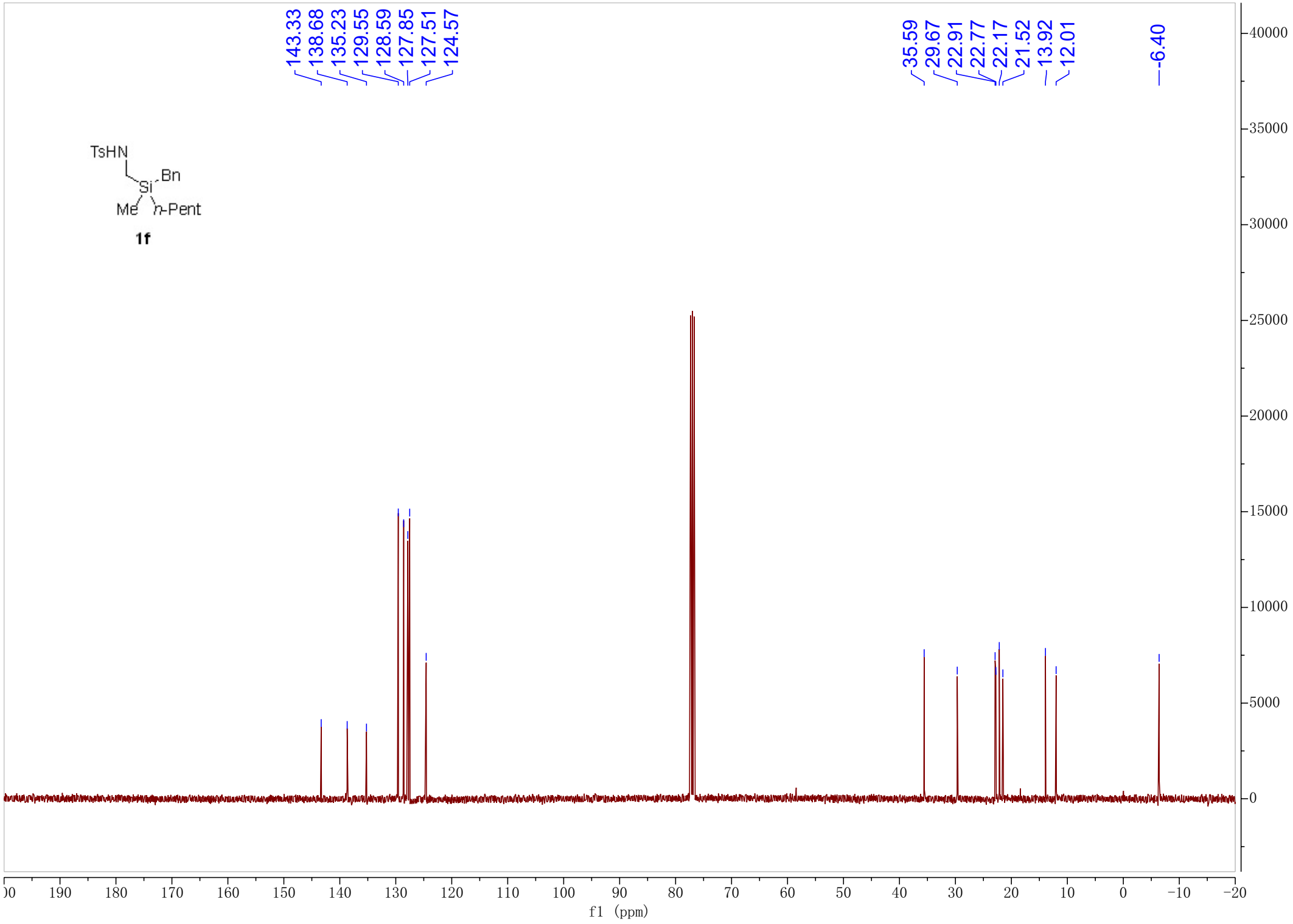
7.31
7.19
7.17
7.15
7.11
7.09
7.07
6.91
6.89
3.91
3.89
3.87
2.44
2.29
2.27
2.11
1.28
1.26
1.24
1.23
1.21
1.20
0.87
0.85
0.84
0.56
0.54
0.53
0.52
0.01
TsHN
Si
Bn
Me
n-Pent
1f
1.94
1.92
1.96
1.01
1.90
1.00
3.00
1.88
2.00
6.64
3.21
2.13
3.22
f1 (ppm)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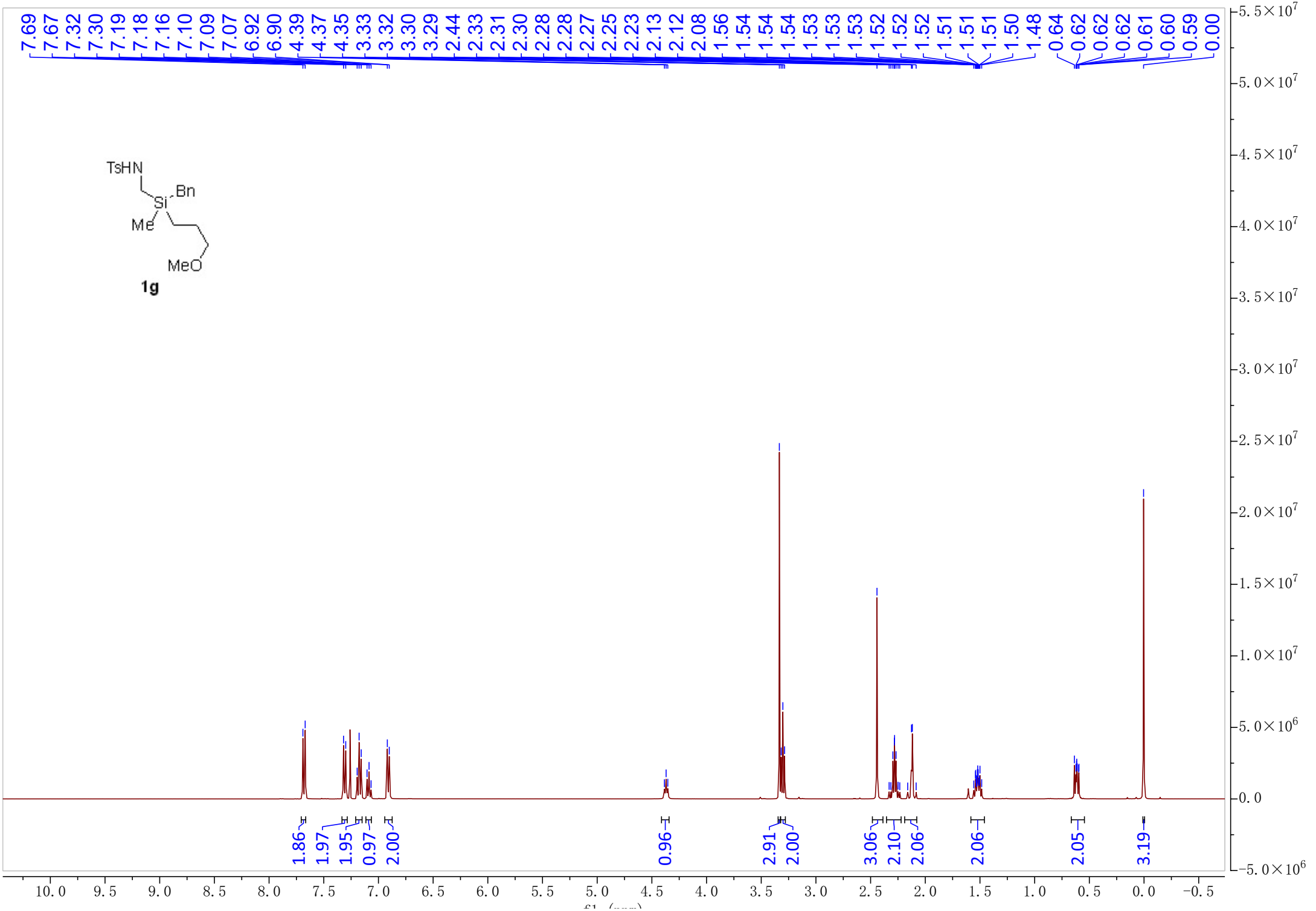
138.68
135.23
129.55
128.59
127.85
127.51
124.57
35.59
29.67
22.91
22.77
22.17
21.52
13.92
12.01
-6.40
TsHN
Si
Bn
Me
n-Pent
1f
40000
35000
30000
25000
20000
15000
10000
5000
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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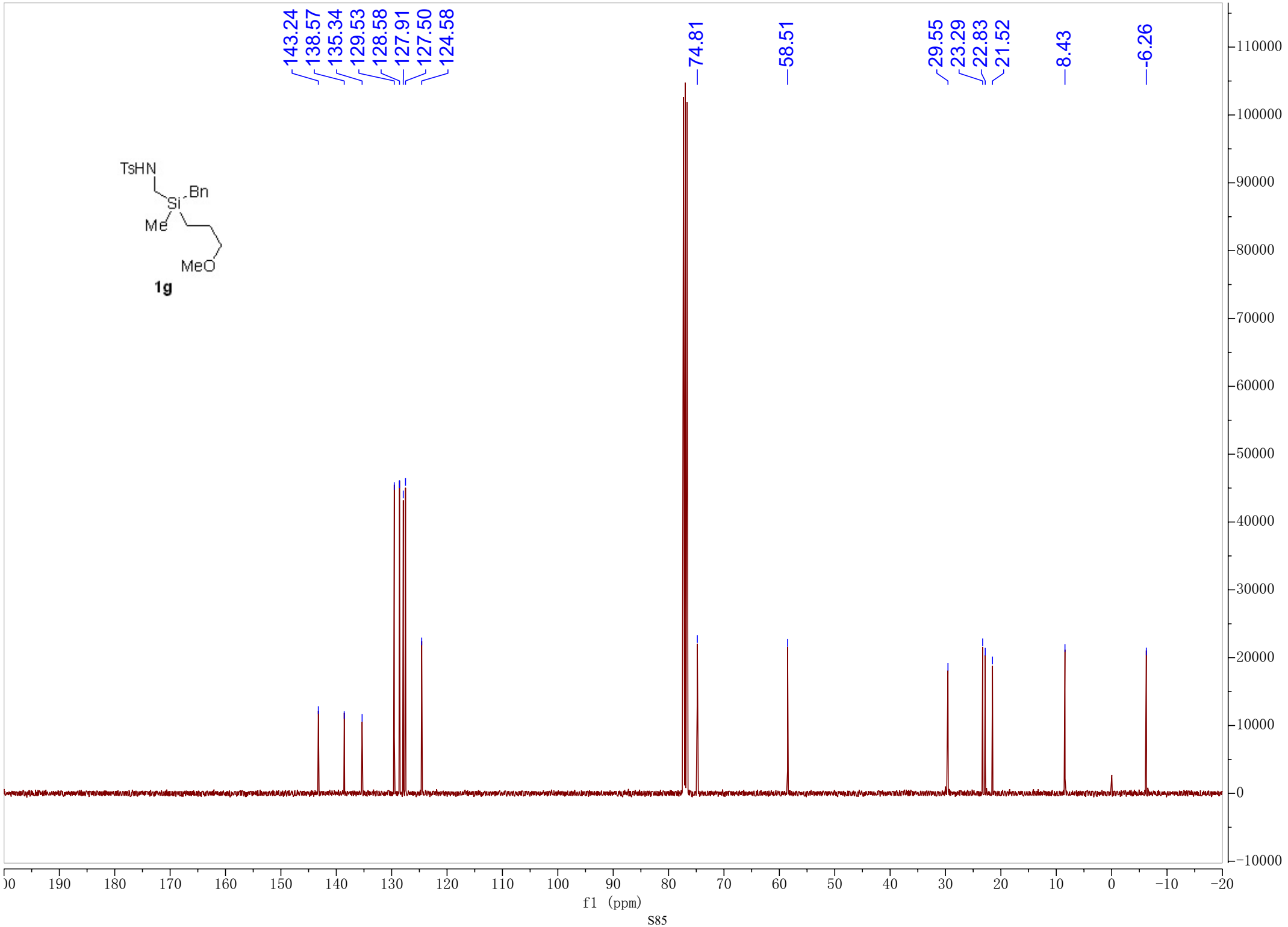
TsHN
Si
Bn
Me
MeO
1g
1.86 1.97 1.95 0.97 2.00 0.96 2.91 2.00 3.06 2.10 2.06 2.06 2.05 3.19
5.5×10^7
5.0×10^7
4.5×10^7
4.0×10^7
3.5×10^7
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
-5.0×10^6
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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127.50
124.58
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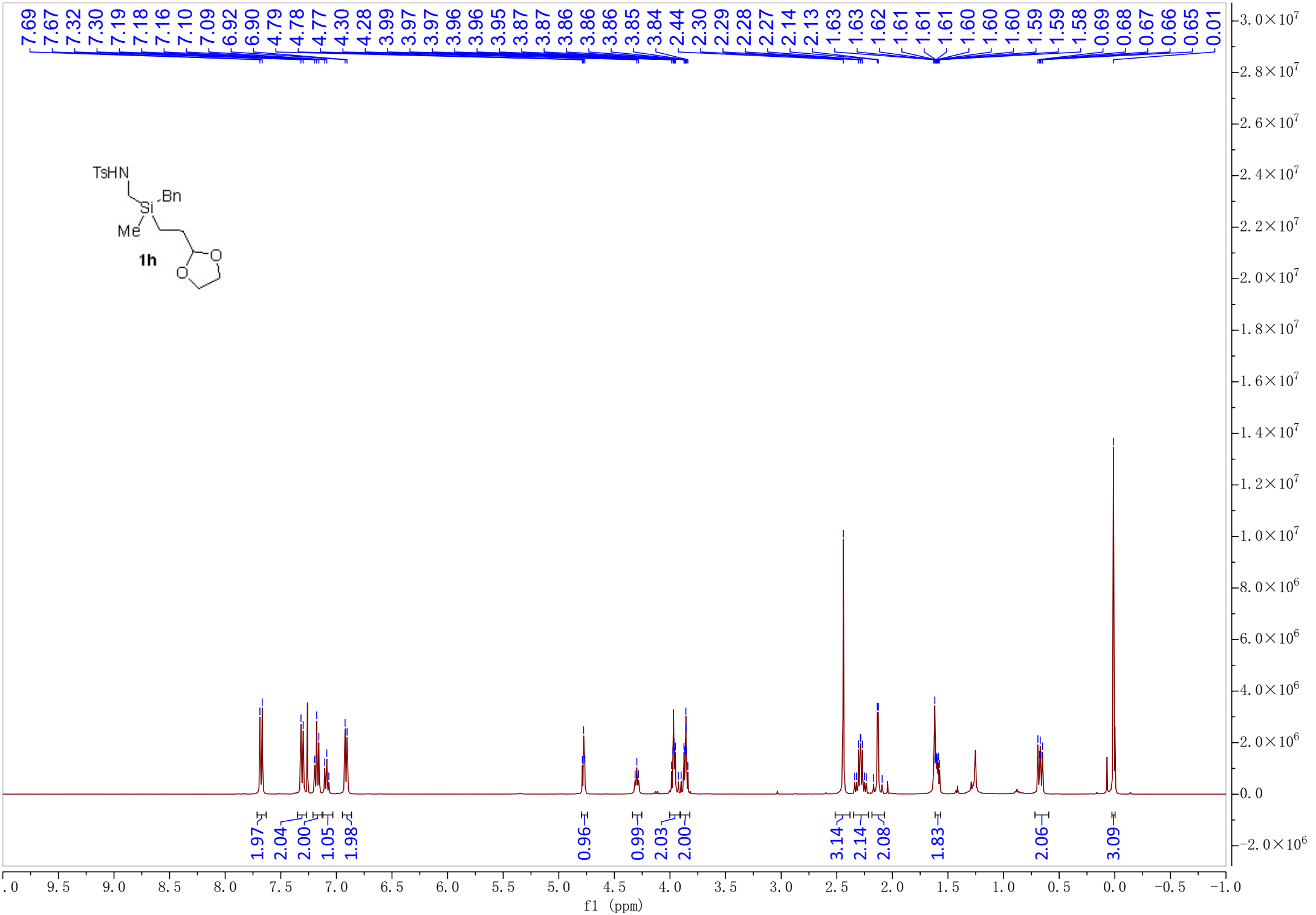
58.51
29.55
23.29
22.83
21.52
8.43
6.26
TsHN
Bn
Si
Me
MeO
1g
f1 (ppm)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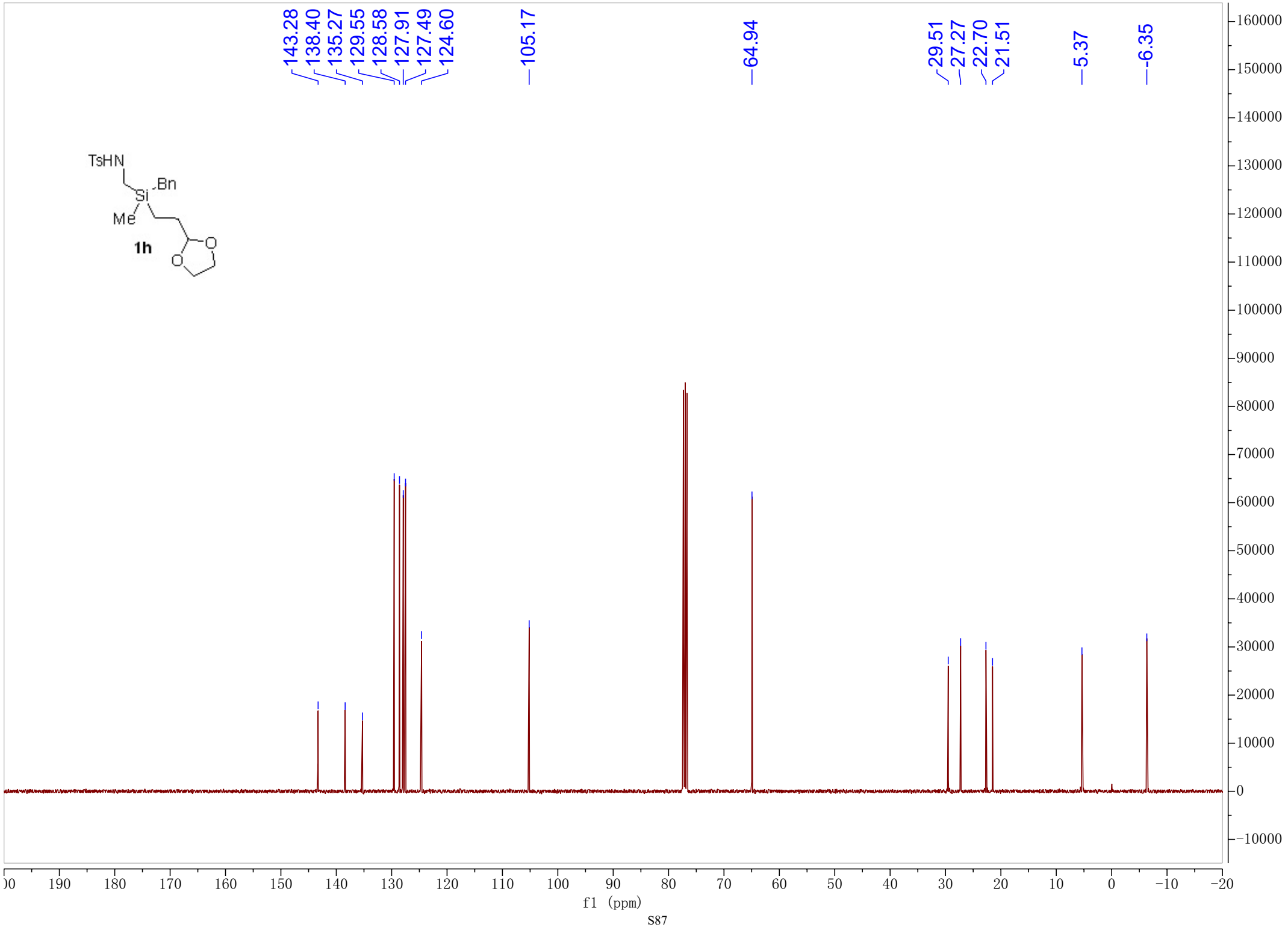
TsHN
Si
Bn
Me
1h
O
O
1.97 2.04 2.00 1.05 1.98 0.96 0.99 2.03 2.00 3.14 2.14 2.08 1.83 2.06 3.09
f1 (ppm)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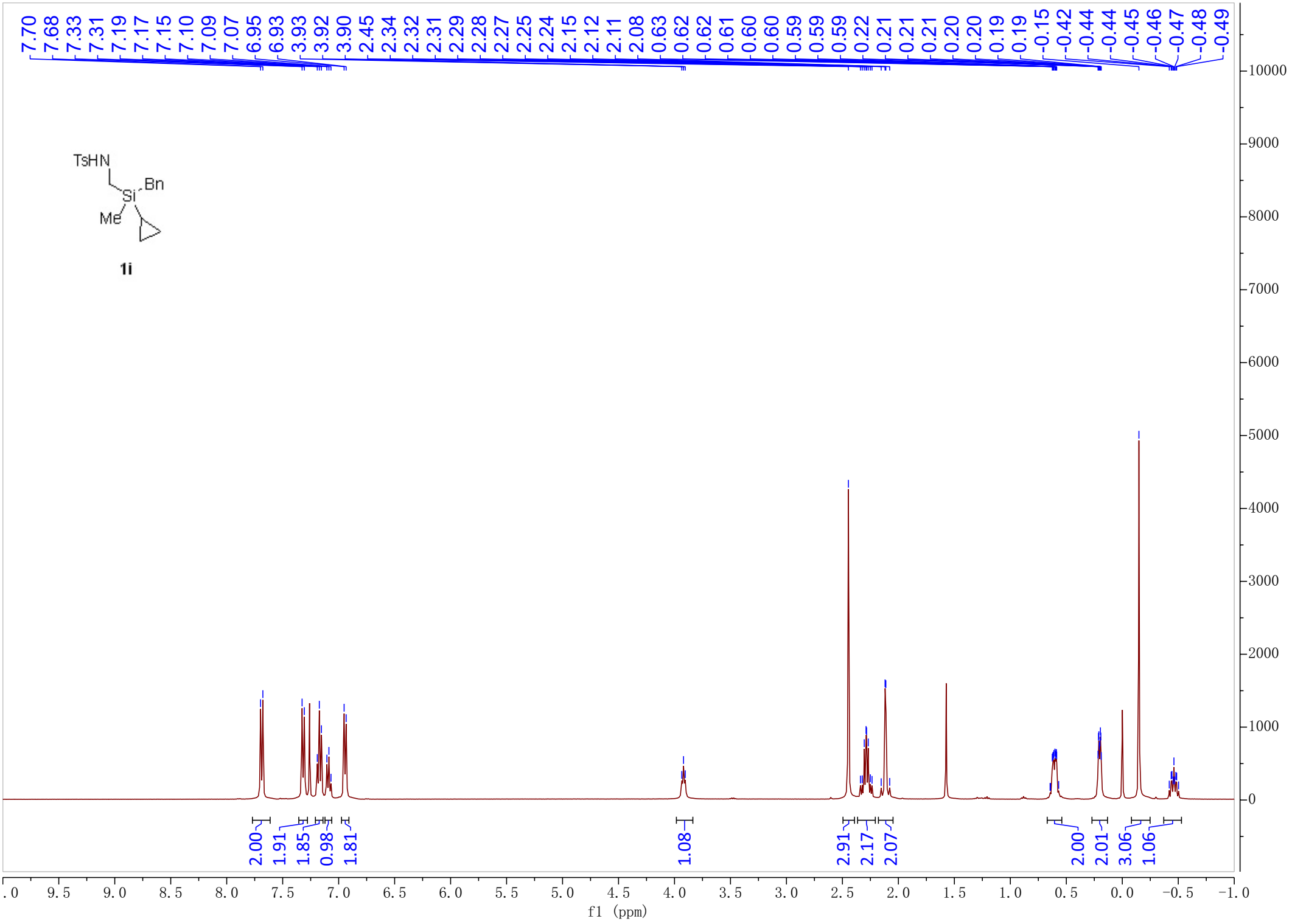
128.58
127.91
127.49
124.60
105.17
64.94
29.51
27.27
22.70
21.51
5.37
-6.35
TsHN
Bn
Si
Me
1h
f1 (ppm)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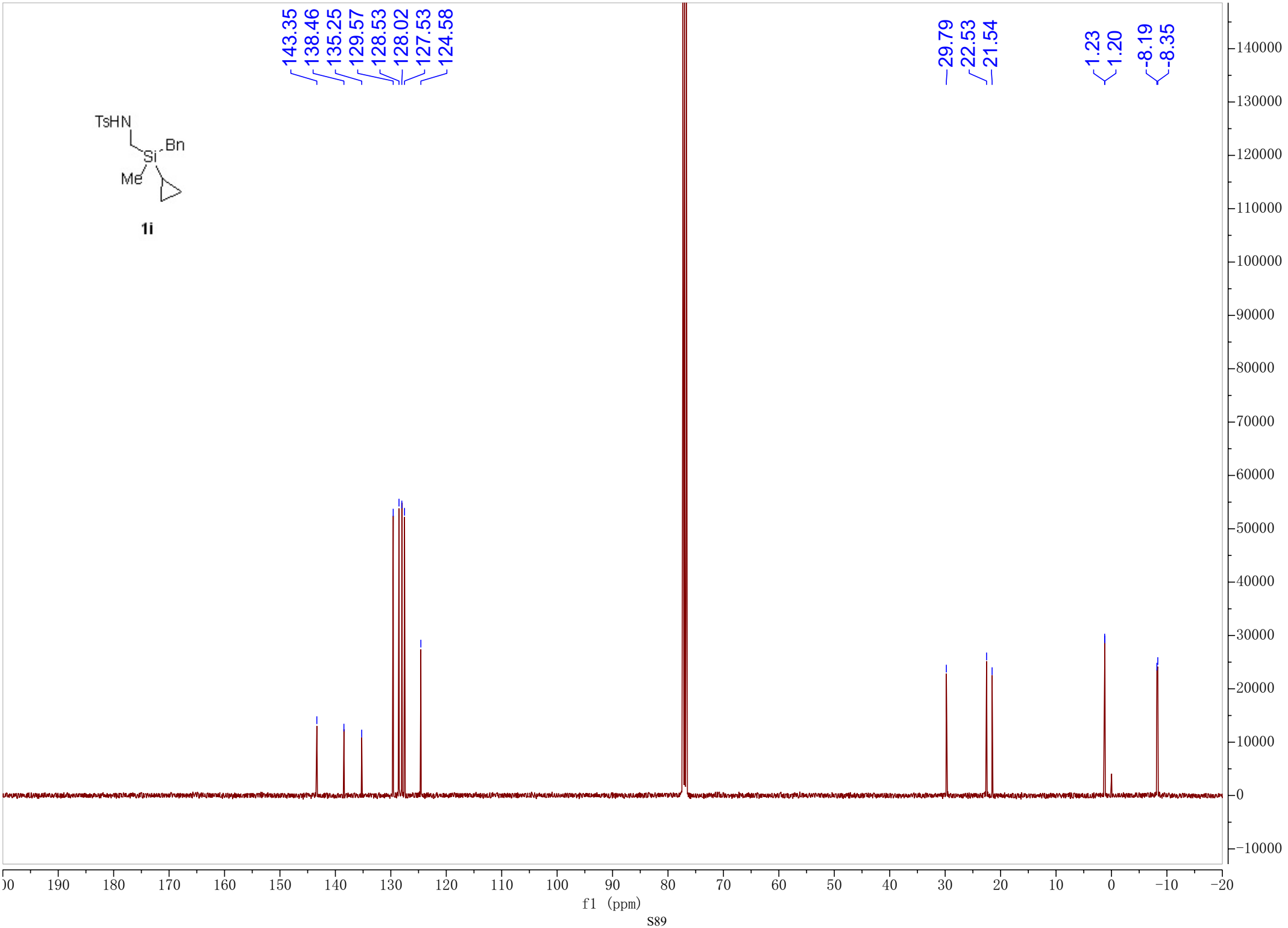
7.31
7.19
7.17
7.15
7.10
7.09
7.07
6.95
6.93
3.93
3.92
3.90
2.45
2.34
2.32
2.31
2.29
2.28
2.27
2.25
2.24
2.15
2.12
2.11
2.08
0.63
0.62
0.62
0.61
0.60
0.60
0.59
0.59
0.59
0.22
0.21
0.21
0.21
0.20
0.20
0.19
0.19
-0.15
-0.42
-0.44
-0.44
-0.45
-0.46
-0.47
-0.48
-0.49
TsHN
Si
Bn
Me
1i
2.00
1.91
1.85
0.98
1.81
1.08
2.91
2.17
2.07
2.00
2.01
3.06
1.06
f1 (ppm)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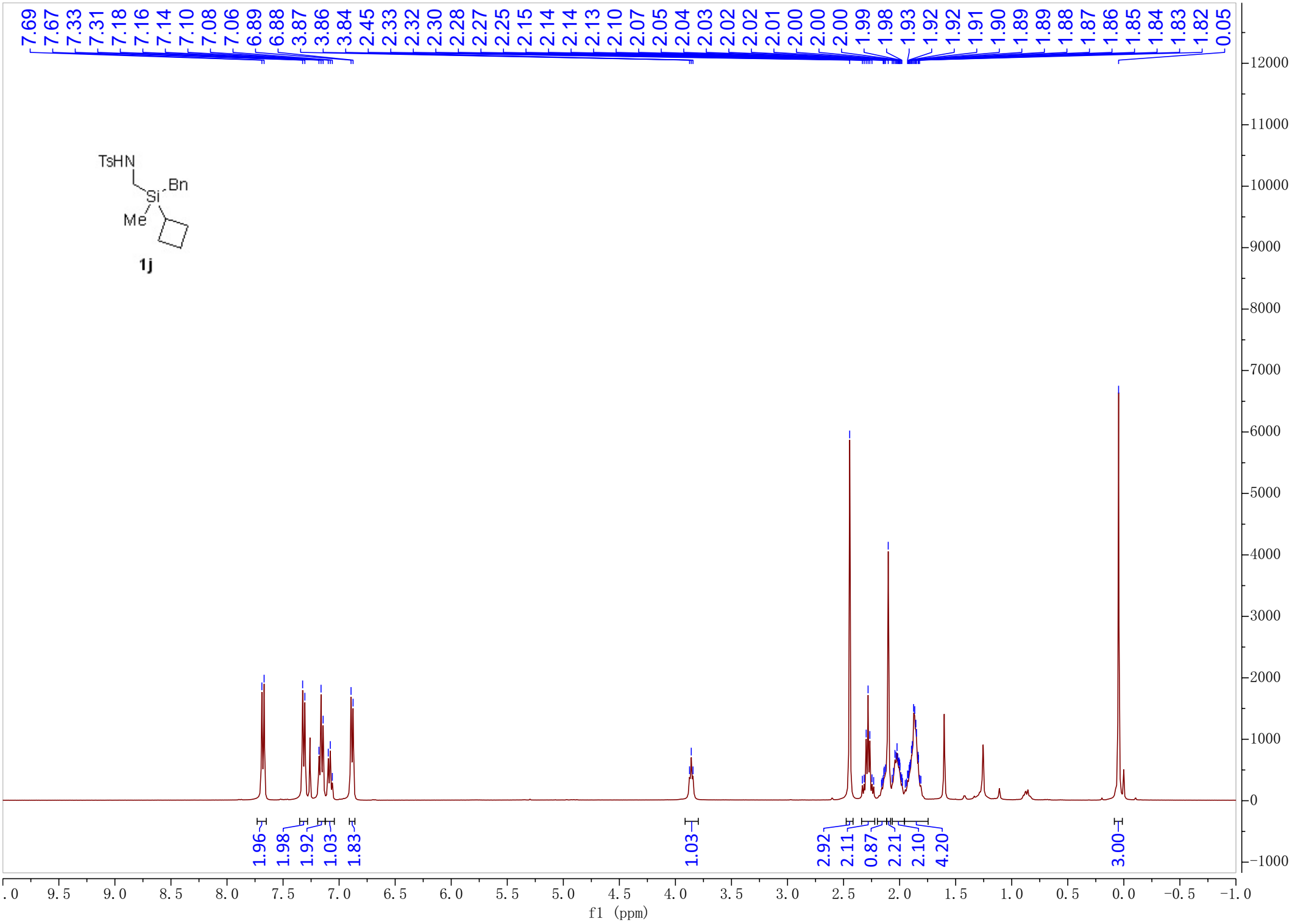
128.02
127.53
124.58
29.79
22.53
21.54
1.23
1.20
-8.19
-8.35
TsHN
Si
Bn
Me
1i
f1 (ppm)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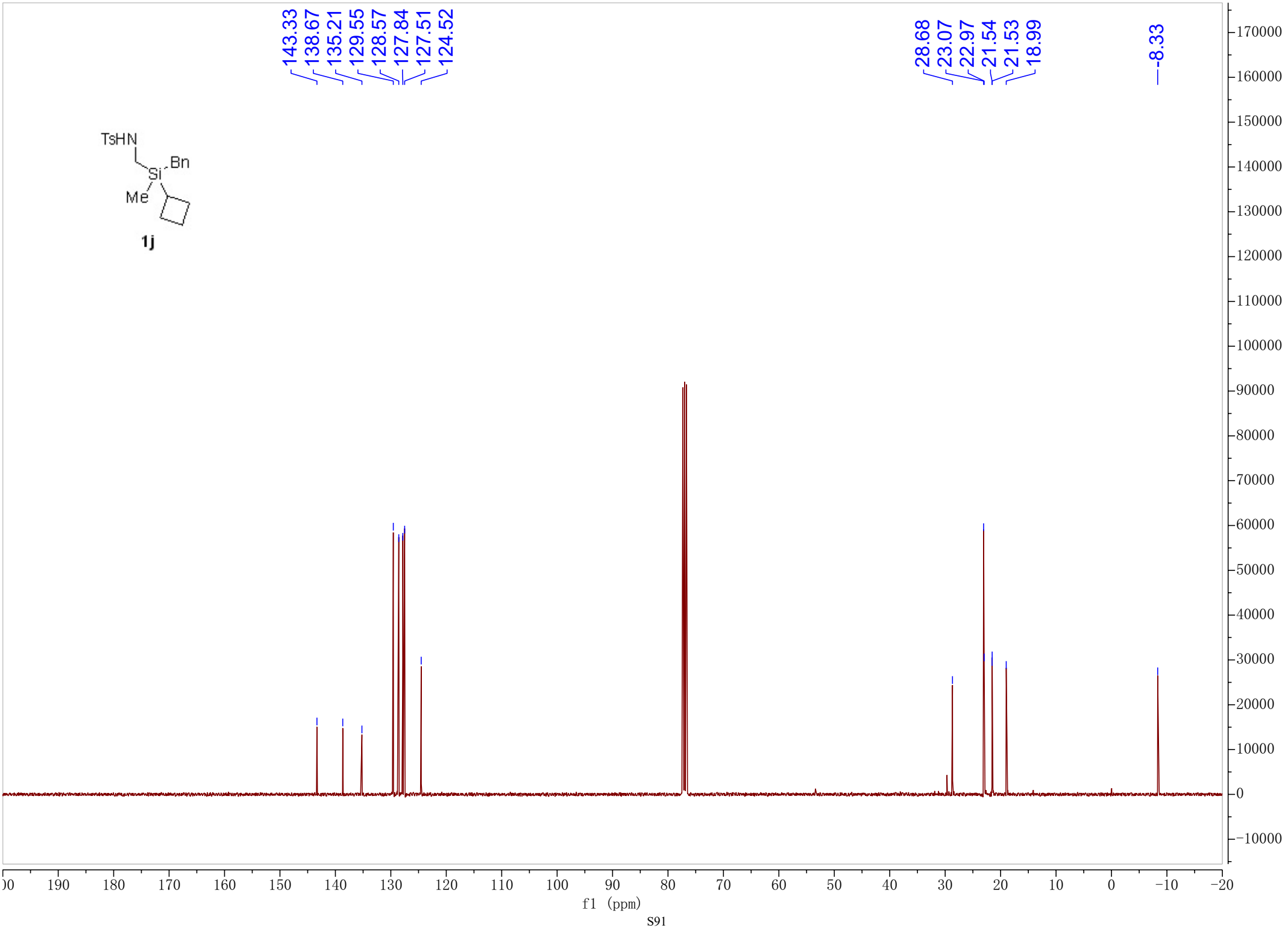
TsHN
Si
Bn
Me
1j
1.96 1.98 1.92 1.03 1.83 1.03 2.92 2.11 0.87 2.21 2.10 4.20 3.00
f1 (ppm)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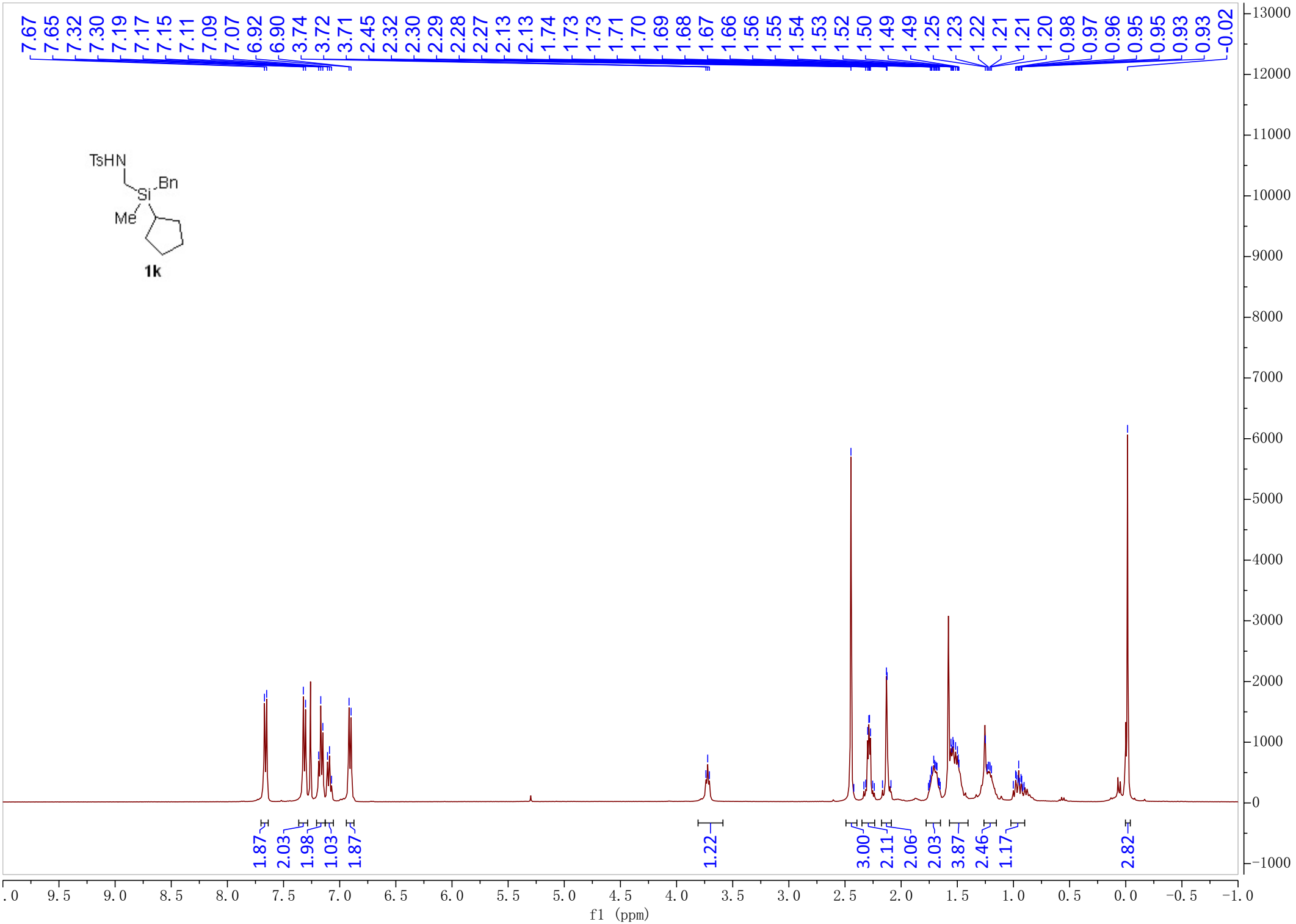
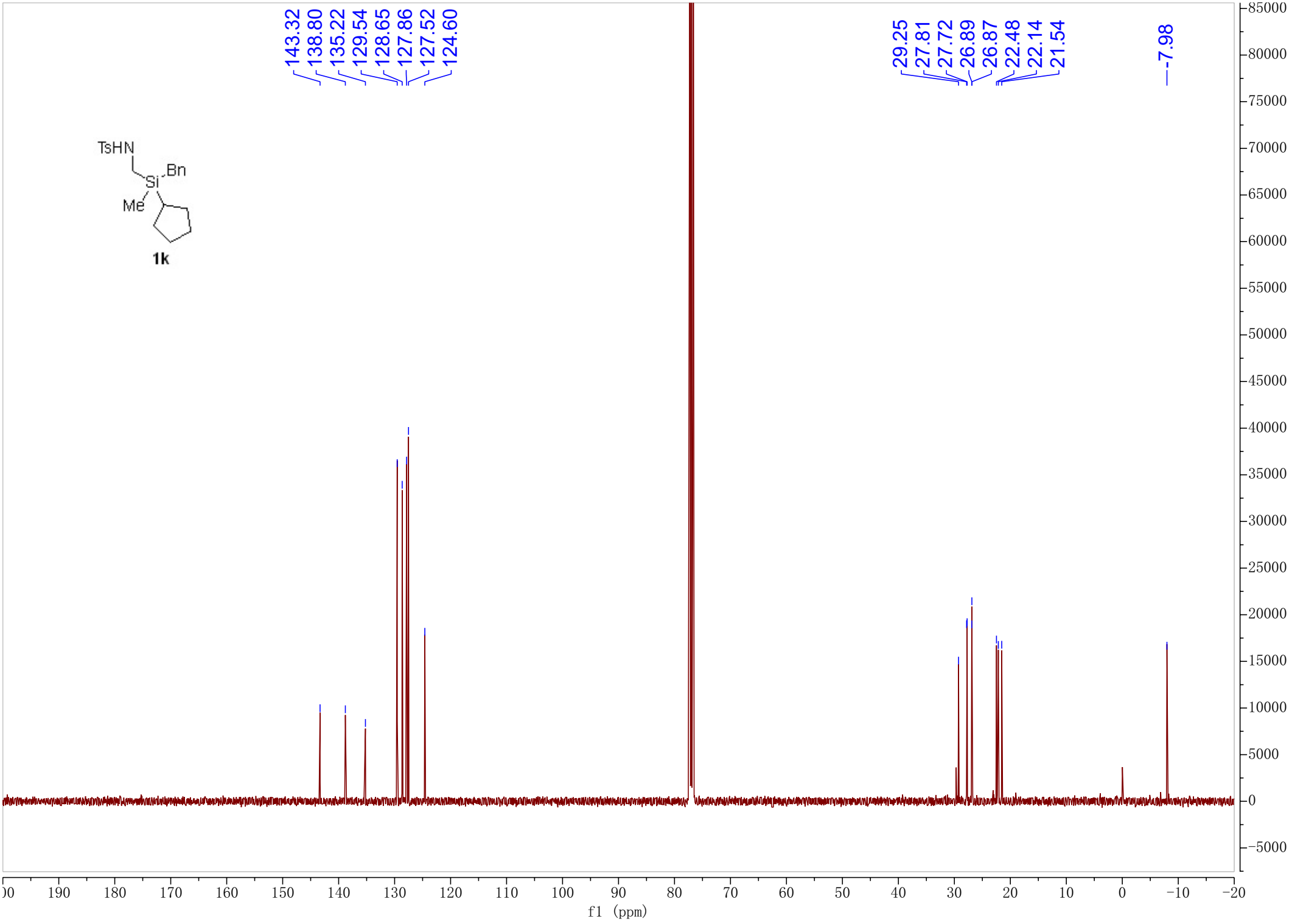
135.21
129.55
128.57
127.84
127.51
124.52
28.68
23.07
22.97
21.54
21.53
18.99
-8.33
TsHN
Si
Bn
Me
1j
f1 (ppm)


7.67 7.65 7.32 7.30 7.19 7.17 7.15 7.11 7.09 7.07 6.92 6.90 3.74 3.72 3.71 2.45 2.32 2.30 2.29 2.28 2.27 2.13 2.13 1.74 1.73 1.73 1.71 1.70 1.69 1.68 1.67 1.66 1.56 1.55 1.54 1.53 1.52 1.50 1.49 1.49 1.25 1.23 1.22 1.21 1.21 1.20 0.98 0.97 0.96 0.95 0.95 0.93 0.93 -0.02
TsHN
Si
Bn
Me
1k
1.87 2.03 1.98 1.03 1.87 1.22 3.00 2.11 2.06 2.03 3.87 2.46 1.17 2.82
f1 (ppm)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129.54
128.65
127.86
127.52
124.60
29.25
27.81
27.72
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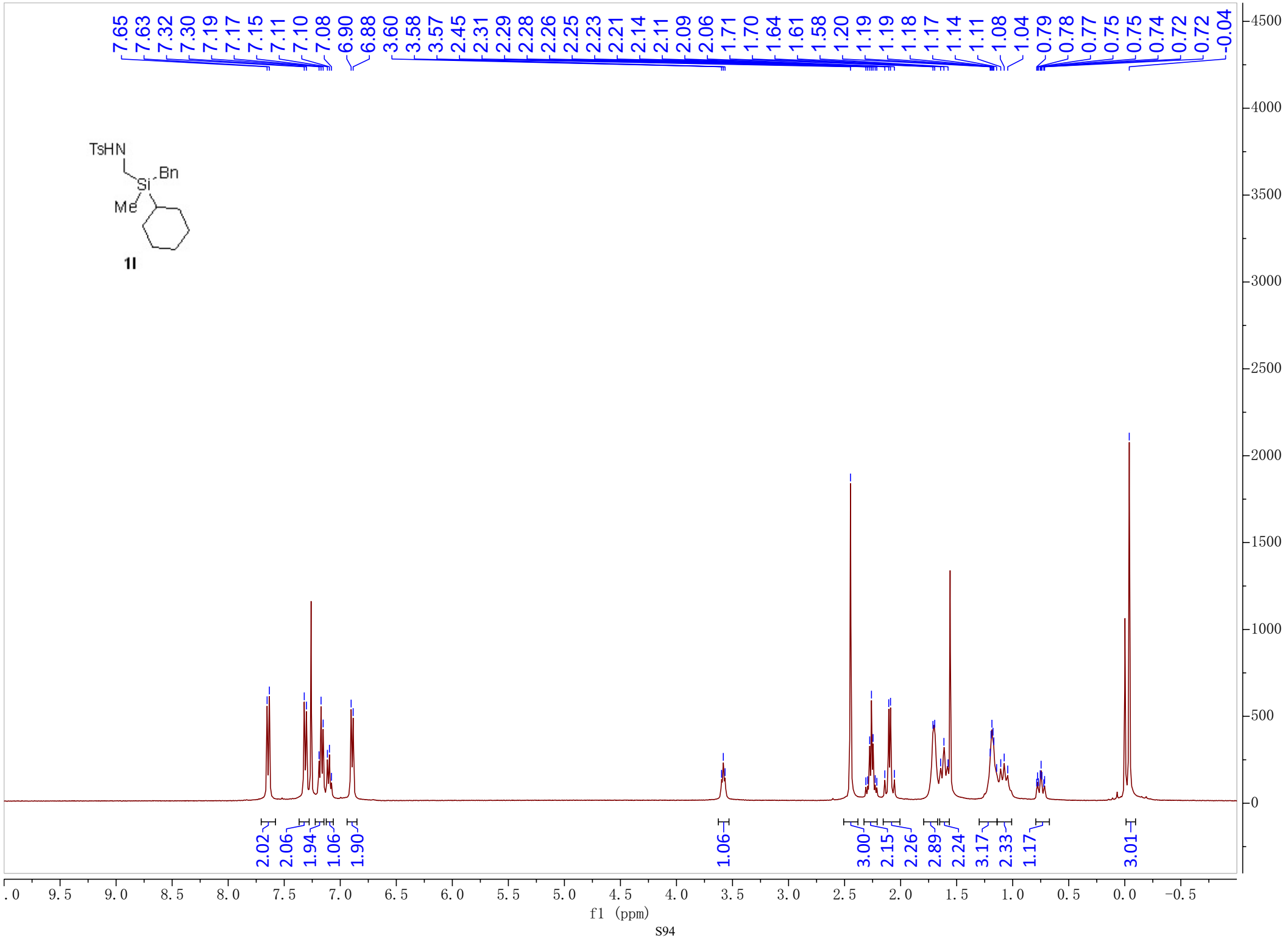
26.87
22.48
22.14
21.54
-7.98
TsHN
Bn
Si
Me
1k
f1 (ppm)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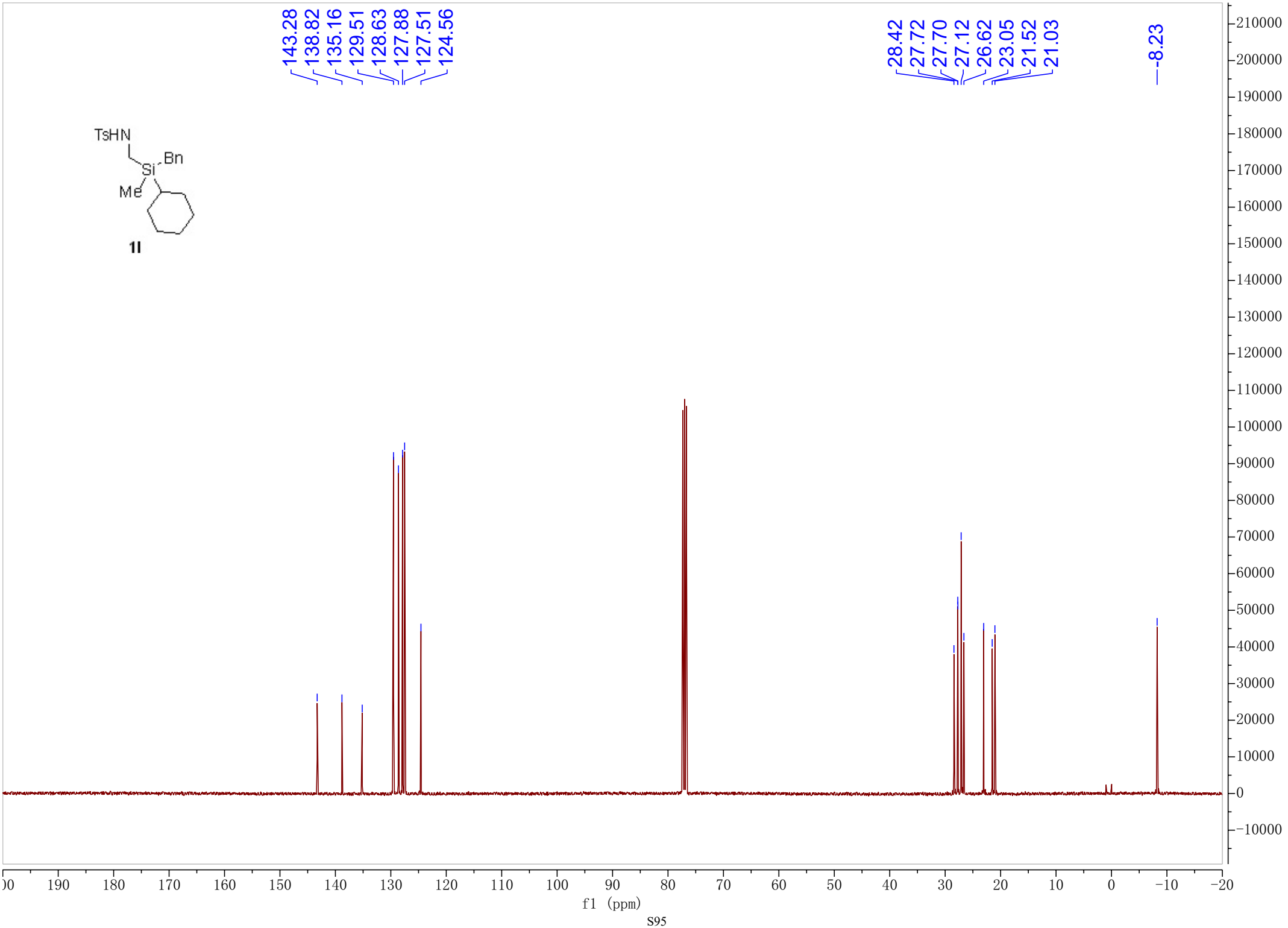
7.11
7.10
7.08
6.90
6.88
3.60
3.58
3.57
2.45
2.31
2.29
2.28
2.26
2.25
2.23
2.21
2.14
2.11
2.09
2.06
1.71
1.70
1.64
1.61
1.58
1.20
1.19
1.19
1.18
1.17
1.14
1.11
1.08
1.04
0.79
0.78
0.77
0.75
0.75
0.74
0.72
0.72
-0.04
TsHN
Si
Bn
Me
1l
2.02
2.06
1.94
1.06
1.90
1.06
3.00
2.15
2.26
2.89
2.24
3.17
2.33
1.17
3.01
f1 (ppm)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28.42
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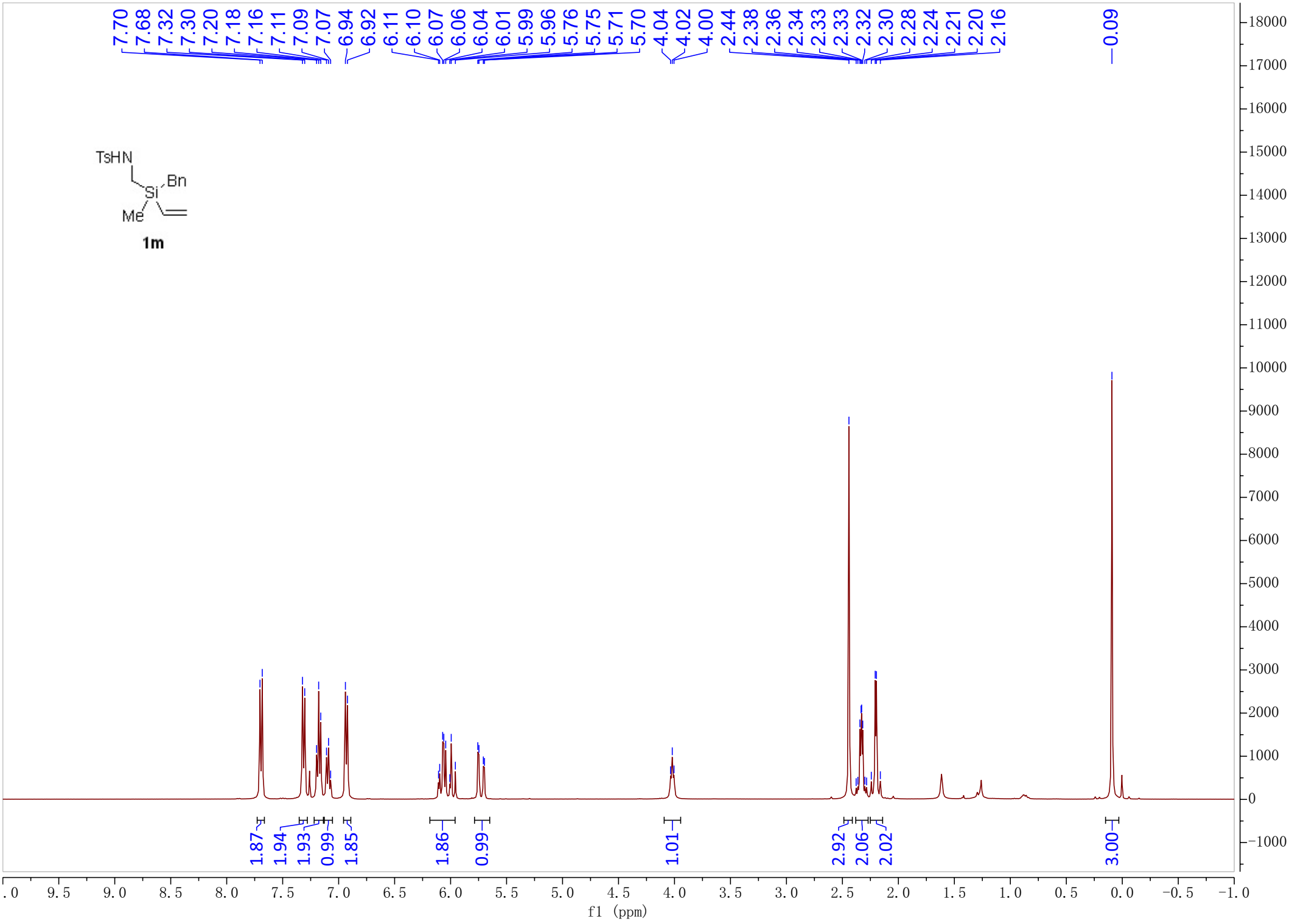
27.12
26.62
23.05
21.52
21.03
-8.23
TsHN
Bn
Si
Me
1l
f1 (ppm)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7.11
7.09
7.07
6.94
6.92
6.11
6.10
6.07
6.06
6.04
6.01
5.99
5.96
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5.75
5.71
5.70
4.04
4.02
4.00
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2.38
2.36
2.34
2.33
2.33
2.32
2.30
2.28
2.24
2.21
2.20
2.16
0.09
TsHN
Si
Bn
Me
1m
1.87
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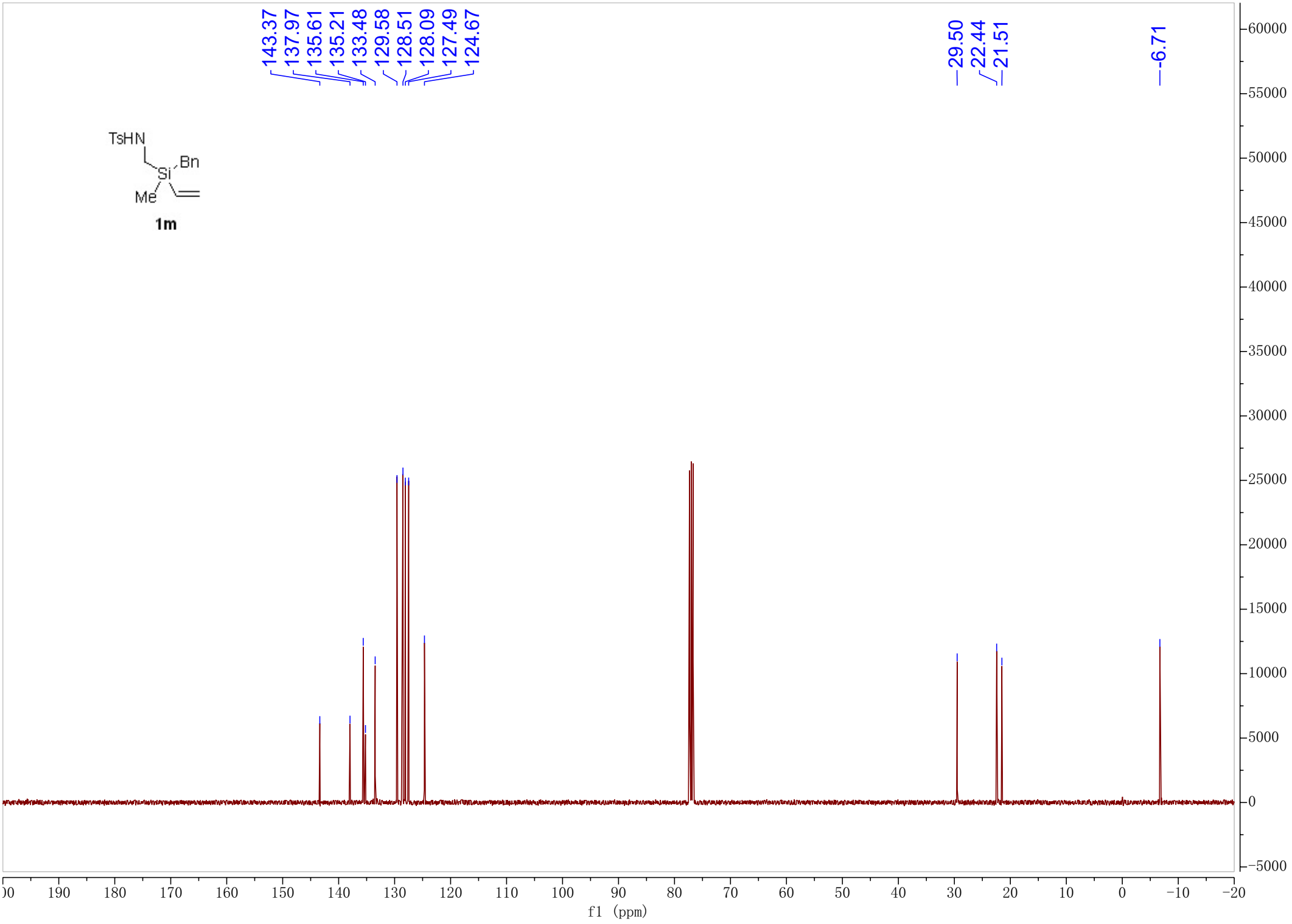
1.85
1.86
0.99
1.01
2.92
2.06
2.02
3.00
f1 (ppm)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128.51
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127.49
124.67
29.50
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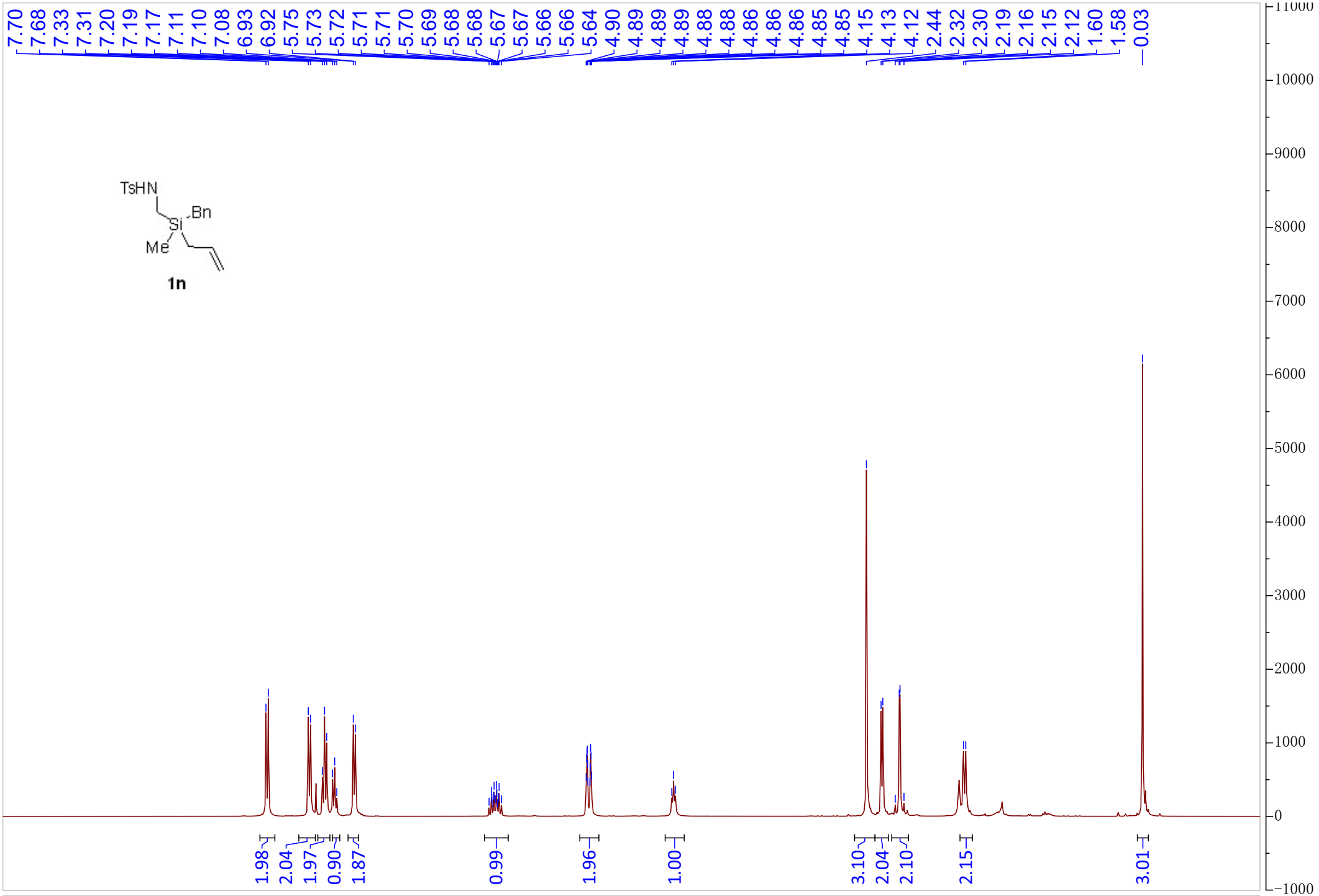
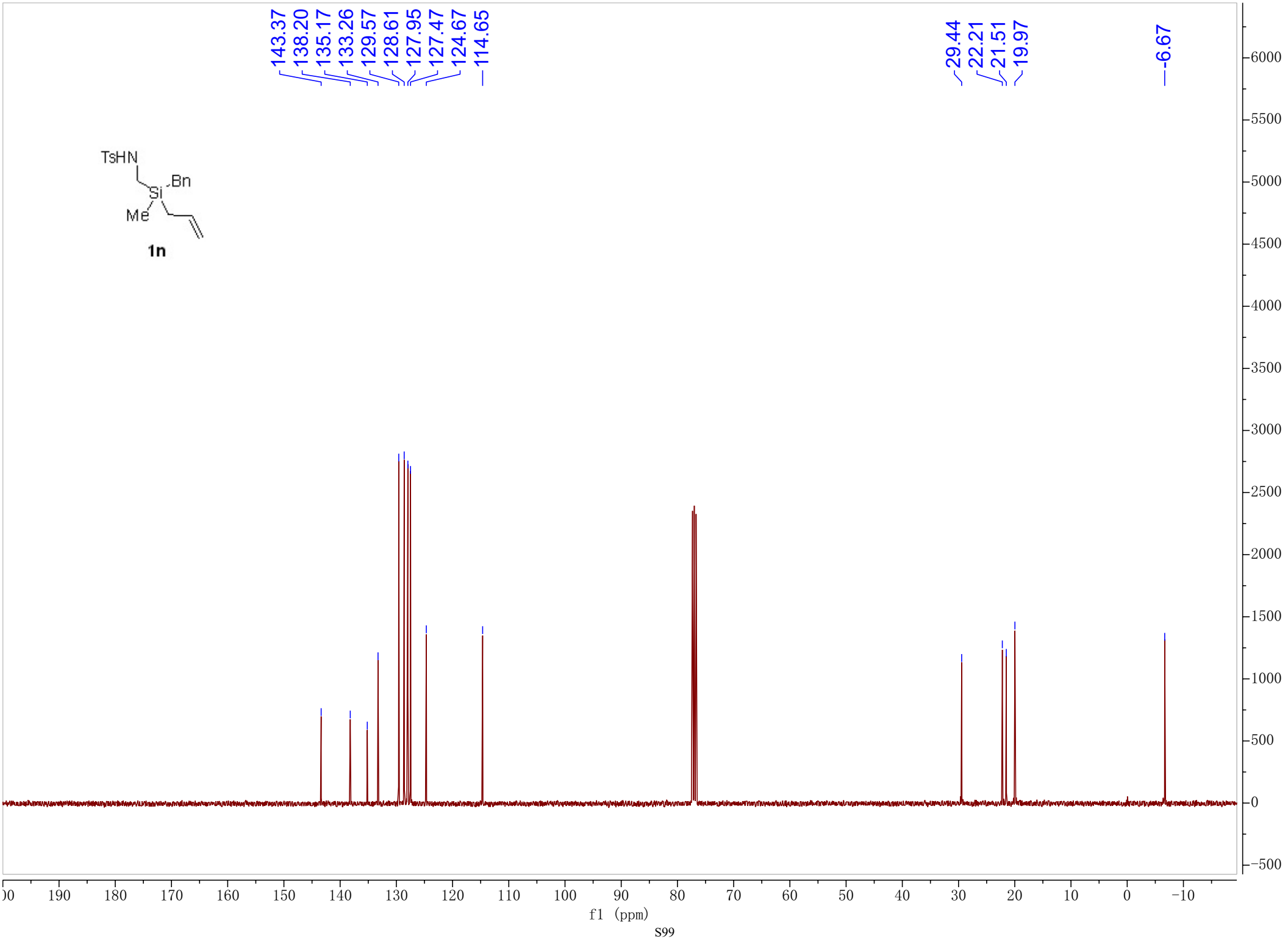
21.51
6.71
TsHN
Si
Bn
Me
1m
f1 (ppm)


7.70
7.68
7.33
7.31
7.20
7.19
7.17
7.11
7.10
7.08
6.93
6.92
5.75
5.73
5.72
5.71
5.71
5.70
5.69
5.68
5.68
5.67
5.67
5.66
5.66
5.64
4.90
4.89
4.89
4.89
4.88
4.88
4.86
4.86
4.86
4.85
4.85
4.15
4.13
4.12
2.44
2.32
2.30
2.19
2.16
2.15
2.12
1.60
1.58
0.03
TsHN
Si
Bn
Me
1n
1.98
2.04
1.97
0.90
1.87
0.99
1.96
1.00
3.10
2.04
2.10
2.15
3.01
f1 (ppm)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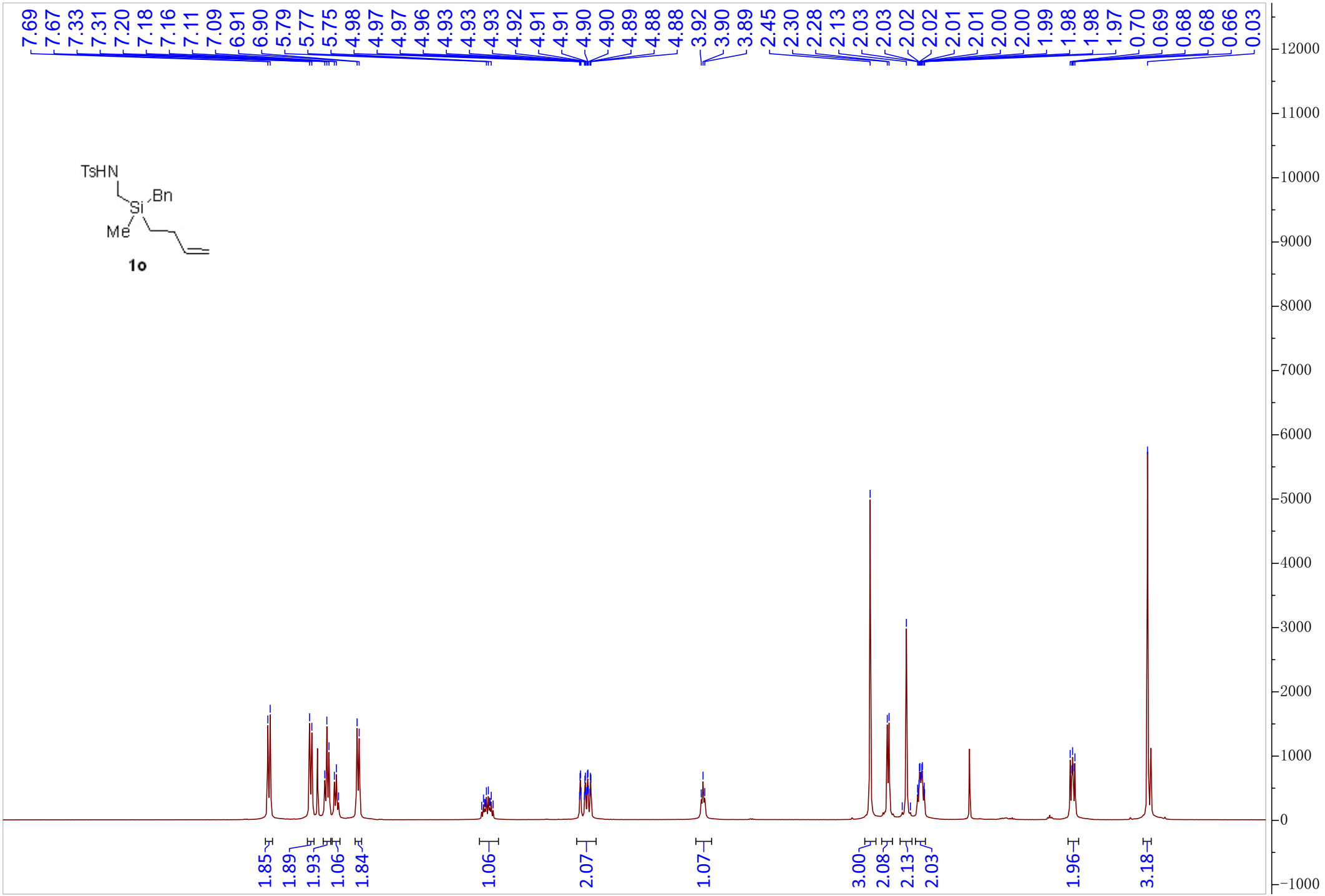
133.26
129.57
128.61
127.95
127.47
124.67
114.65
29.44
22.21
21.51
19.97
-6.67
TsHN
Bn
Si
Me
1n
f1 (ppm)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TsHN
Si
Bn
Me
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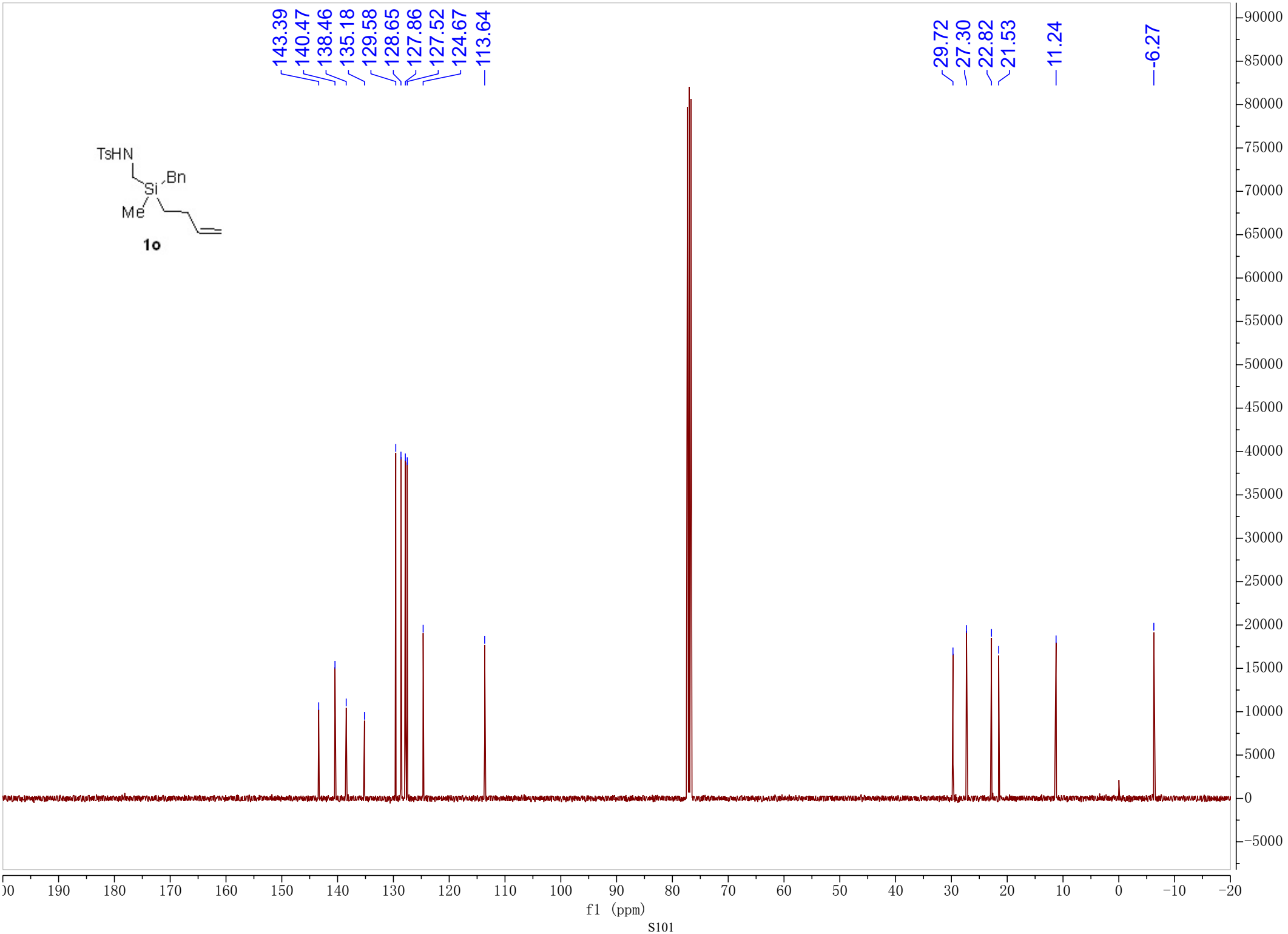
f1 (ppm)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11.24
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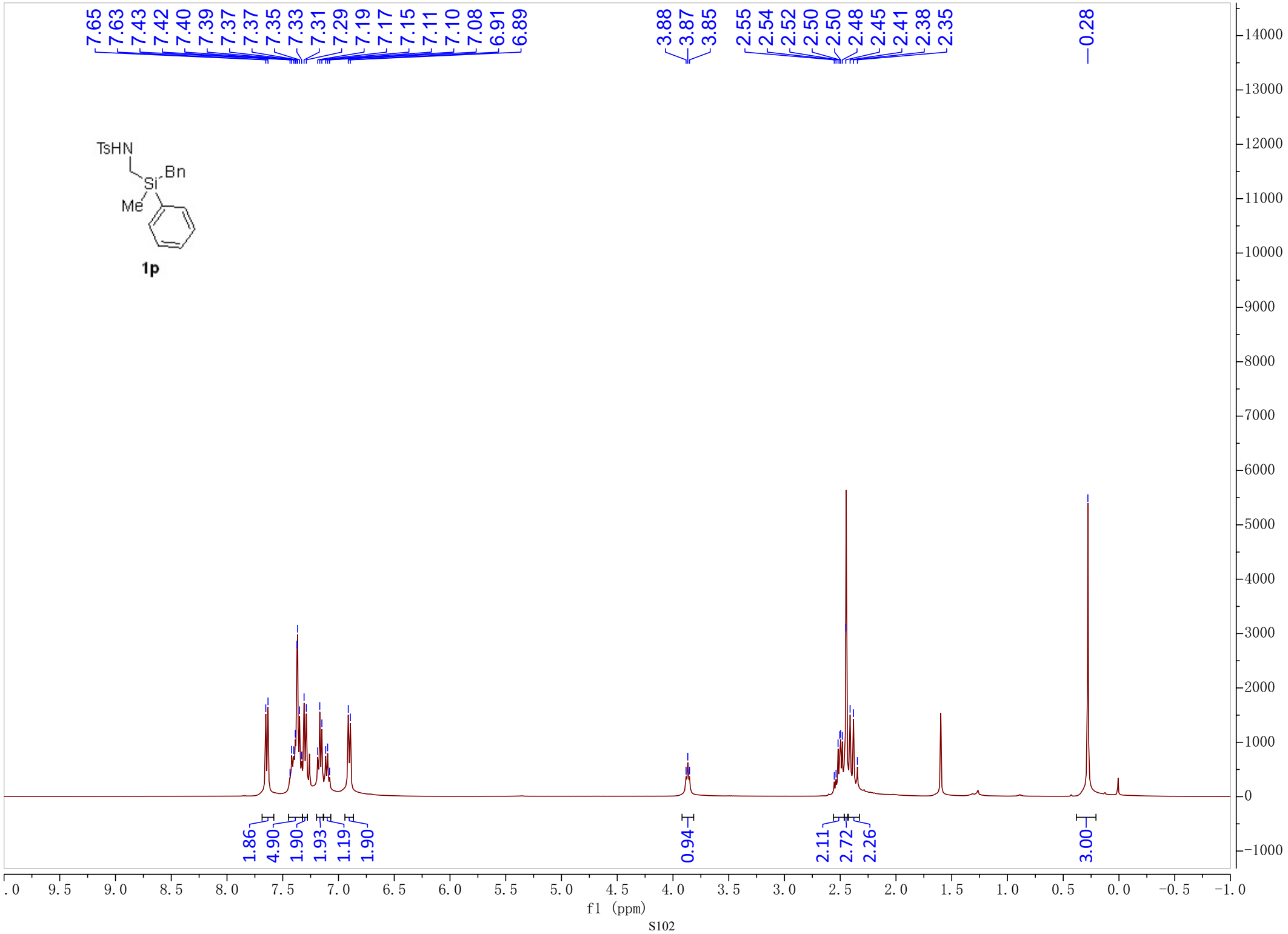
Si
Bn
Me
1o
f1 (ppm)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7.19
7.17
7.15
7.11
7.10
7.08
6.91
6.89
3.88
3.87
3.85
2.55
2.54
2.52
2.50
2.50
2.48
2.45
2.41
2.38
2.35
0.28
TsHN
Si
Bn
Me
1p
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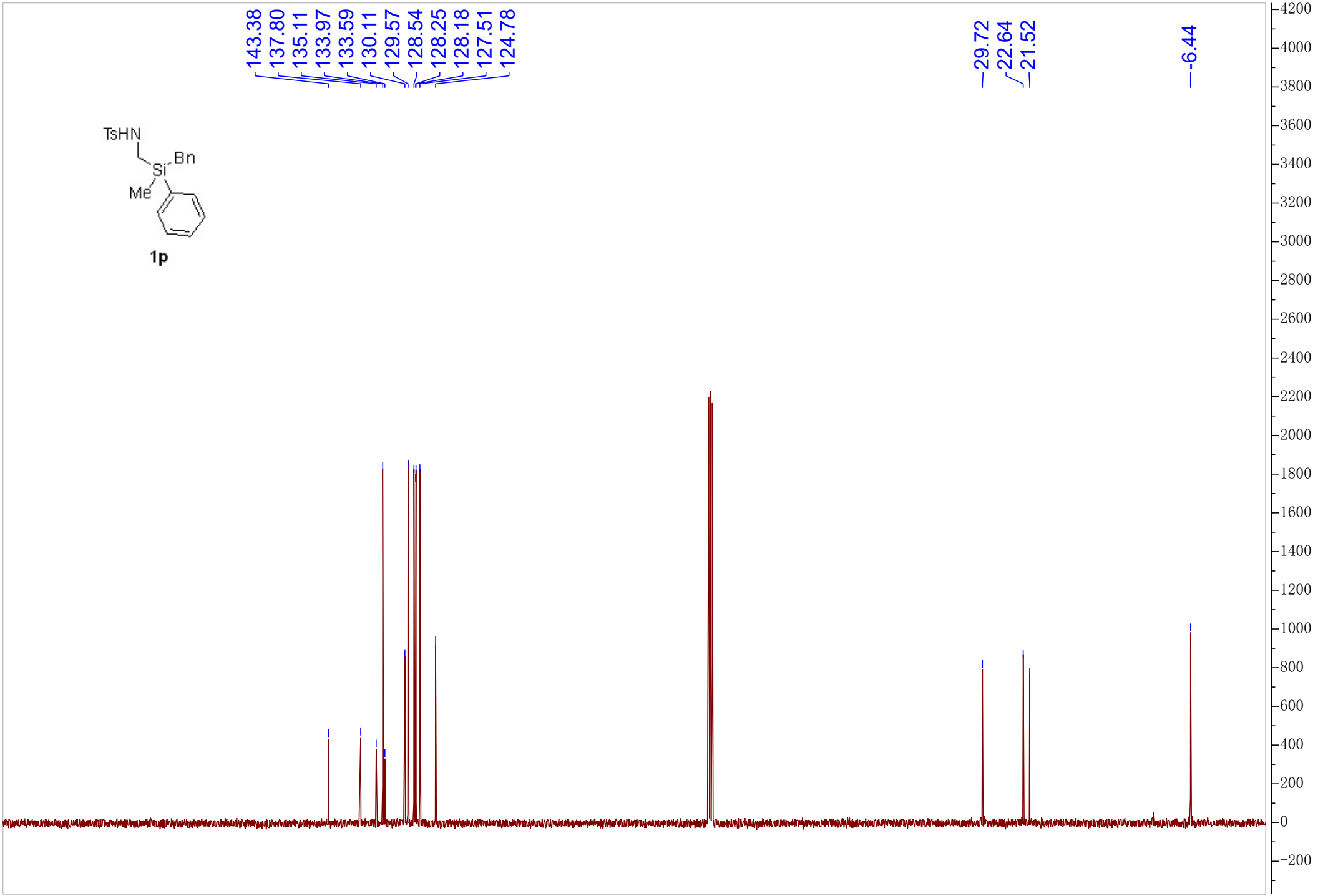
3.00
f1 (ppm)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21.52
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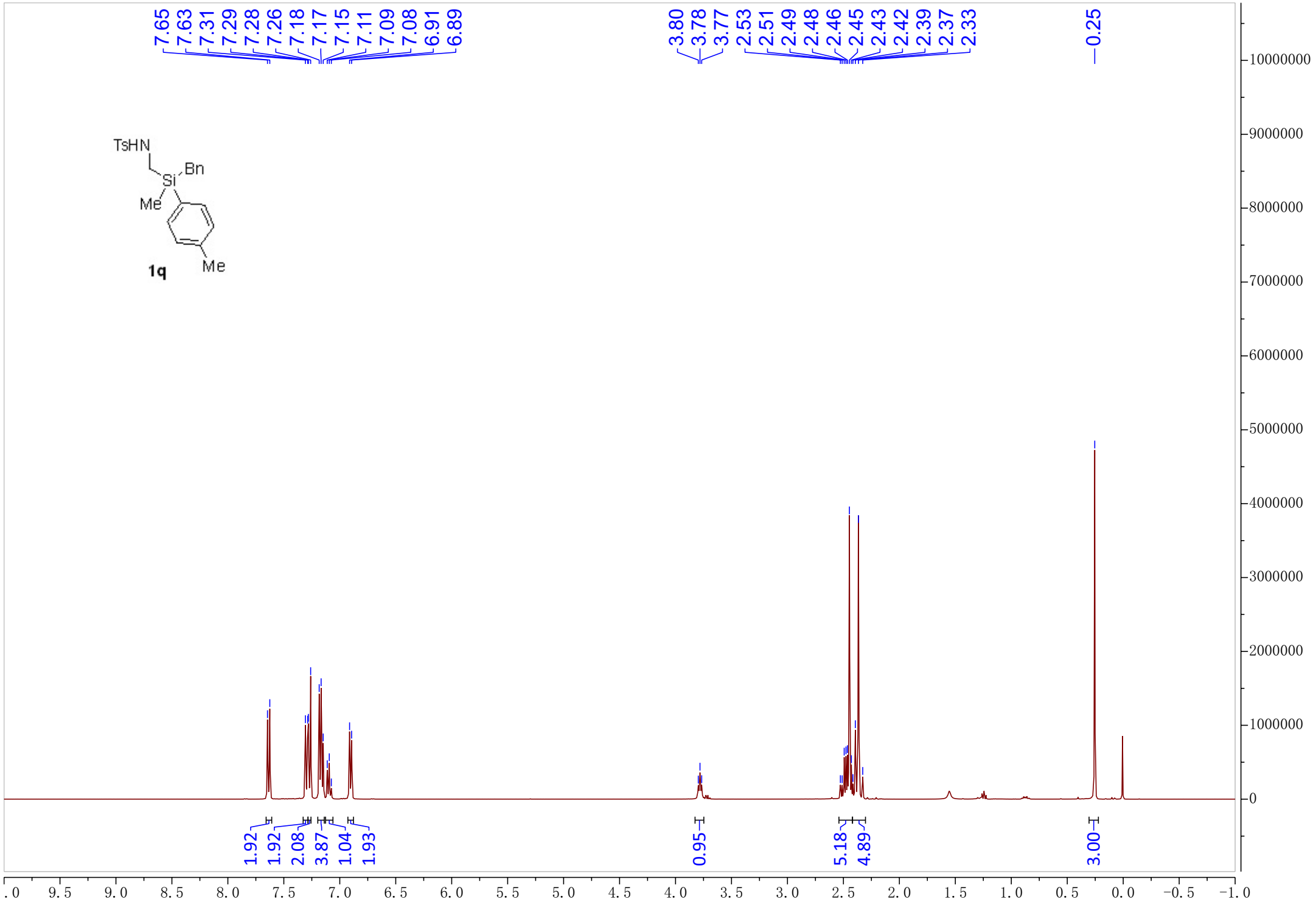
Si
Bn
Me
1p
f1 (ppm)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6.89
3.80
3.78
3.77
2.53
2.51
2.49
2.48
2.46
2.45
2.43
2.42
2.39
2.37
2.33
0.25
TsHN
Si
Bn
Me
Me
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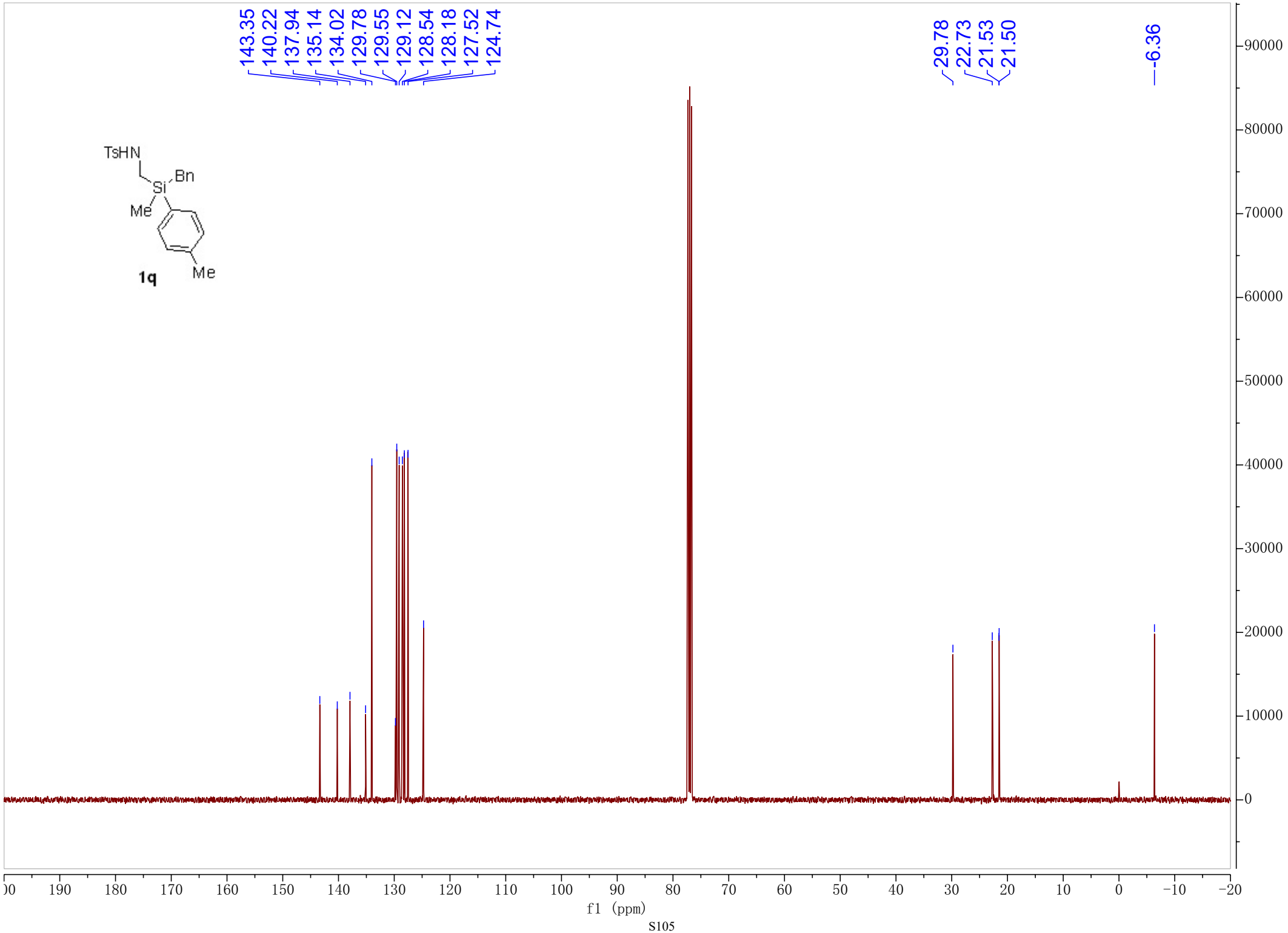
3.00
f1 (ppm)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128.18
127.52
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29.78
22.73
21.53
21.50
-6.36
TsHN
Si
Bn
Me
Me
1q
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
200
190
180
170
160
150
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100
90
80
70
60
50
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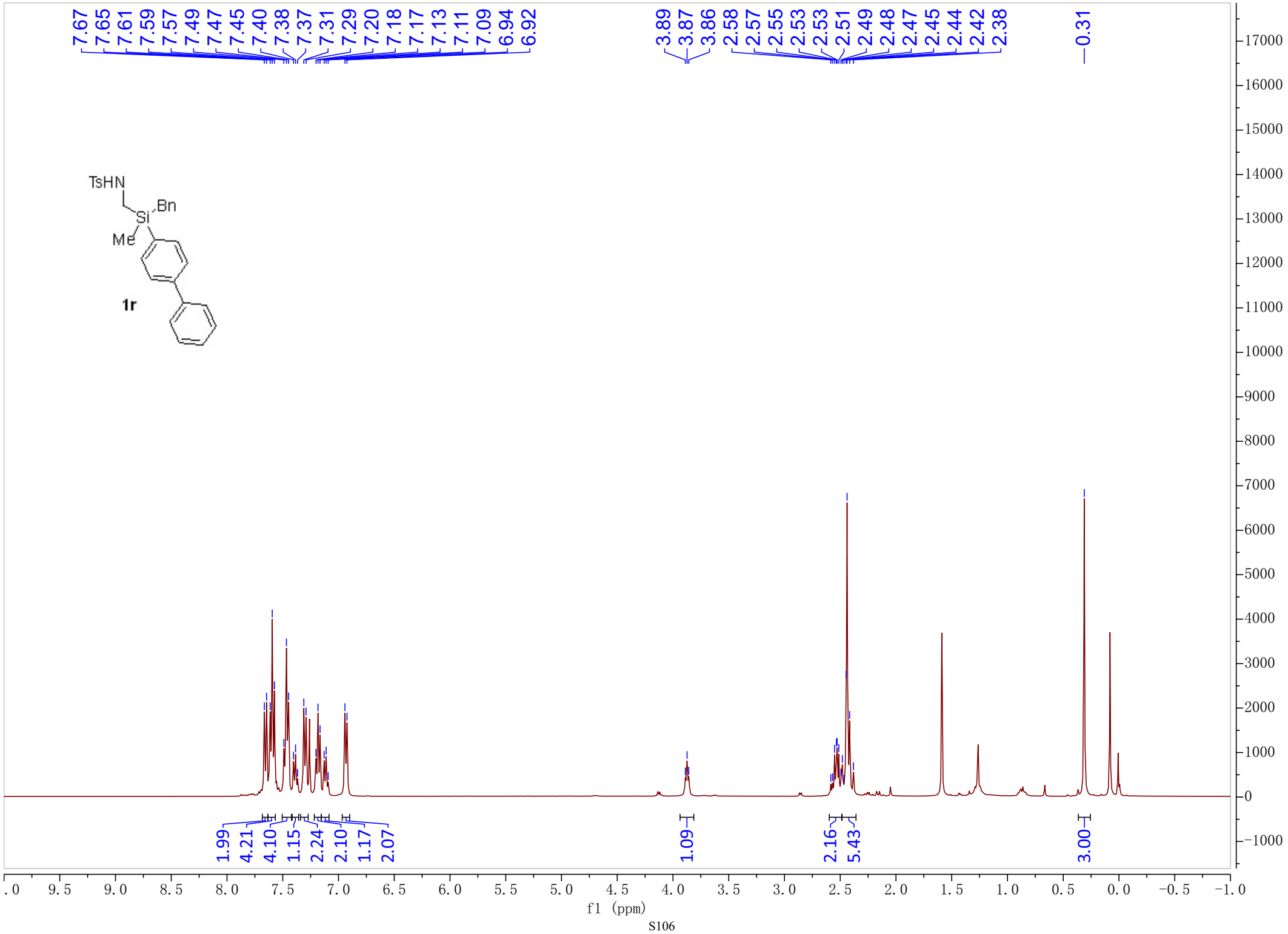
30
20
10
0
-10
-20
f1 (ppm)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7.38
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7.31
7.29
7.20
7.18
7.17
7.13
7.11
7.09
6.94
6.92
3.89
3.87
3.86
2.58
2.57
2.55
2.53
2.53
2.51
2.49
2.48
2.47
2.45
2.44
2.42
2.38
0.31
TsHN
Si
Bn
Me
1r
1.99
4.21
4.10
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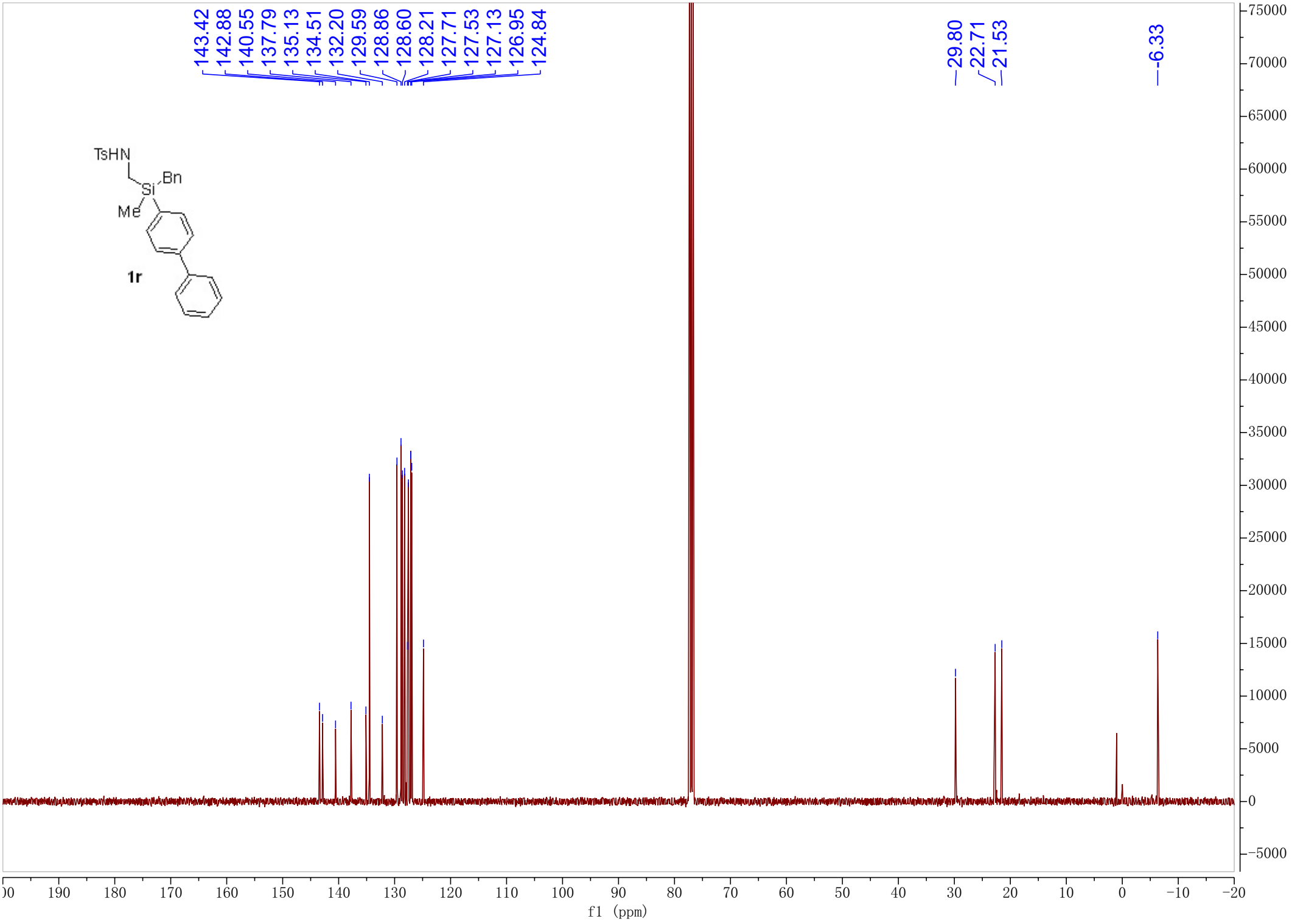
2.24
2.10
1.17
2.07
1.09
2.16
5.43
3.00
f1 (ppm)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134.51
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129.59
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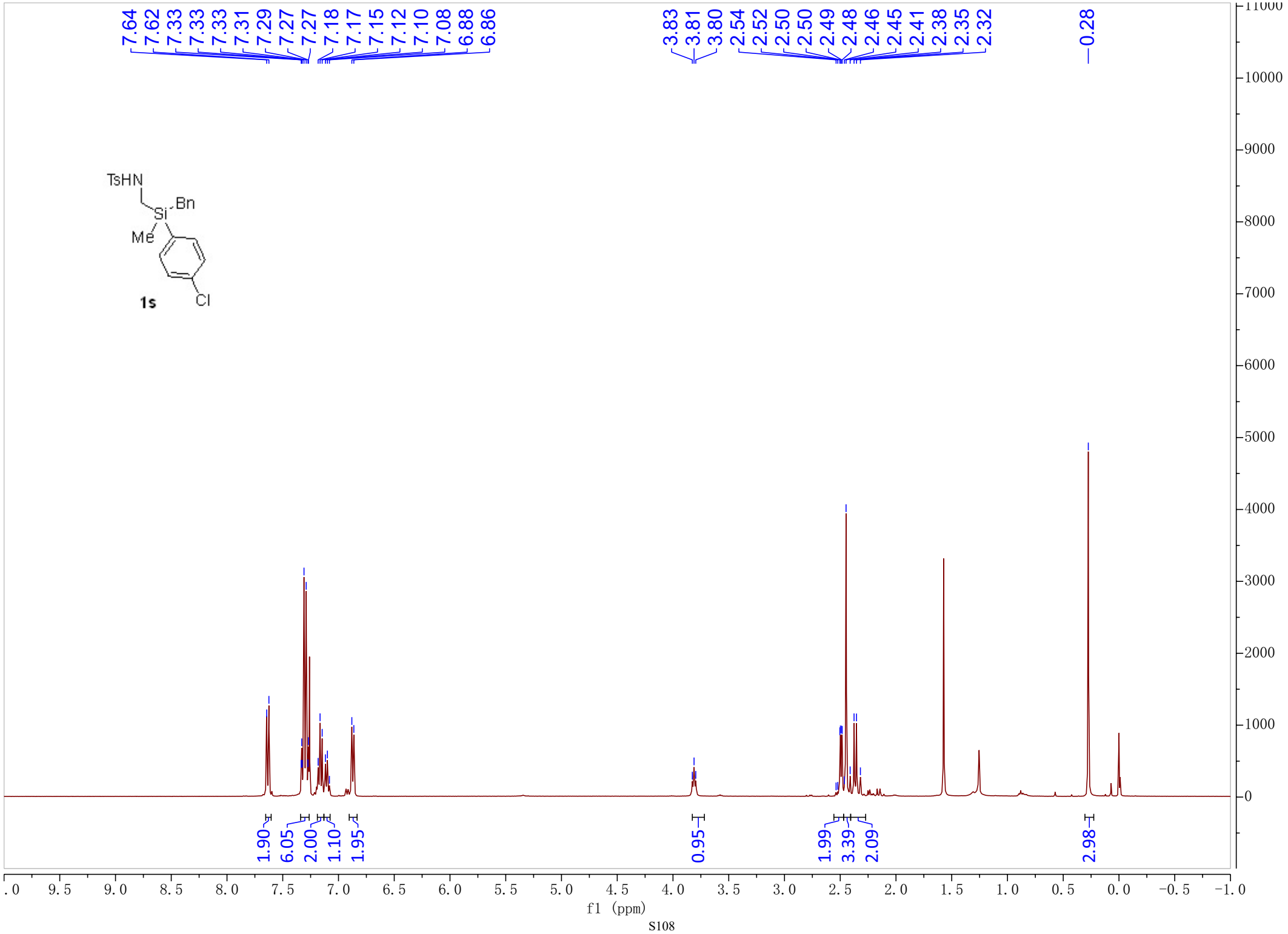
128.60
128.21
127.71
127.53
127.13
126.95
124.84
29.80
22.71
21.53
6.33
TsHN
Si
Bn
Me
1r
f1 (ppm)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7.27
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7.18
7.17
7.15
7.12
7.10
7.08
6.88
6.86
3.83
3.81
3.80
2.54
2.52
2.50
2.50
2.49
2.48
2.46
2.45
2.41
2.38
2.35
2.32
0.28
TsHN
Si
Bn
Me
Cl
1s
1.90
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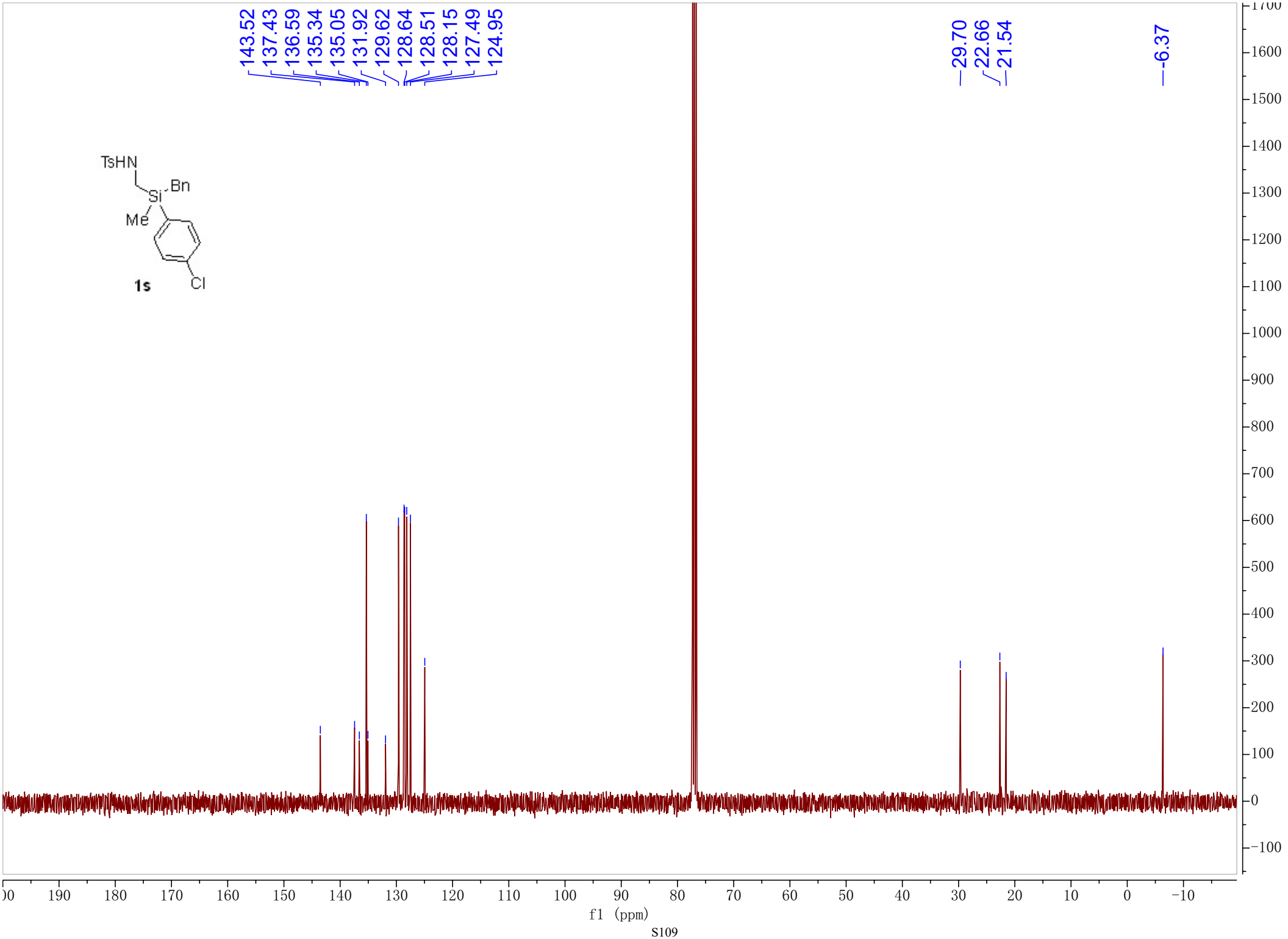
2.00
1.10
1.95
0.95
1.99
3.39
2.09
2.98
f1 (ppm)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131.92
129.62
128.64
128.51
128.15
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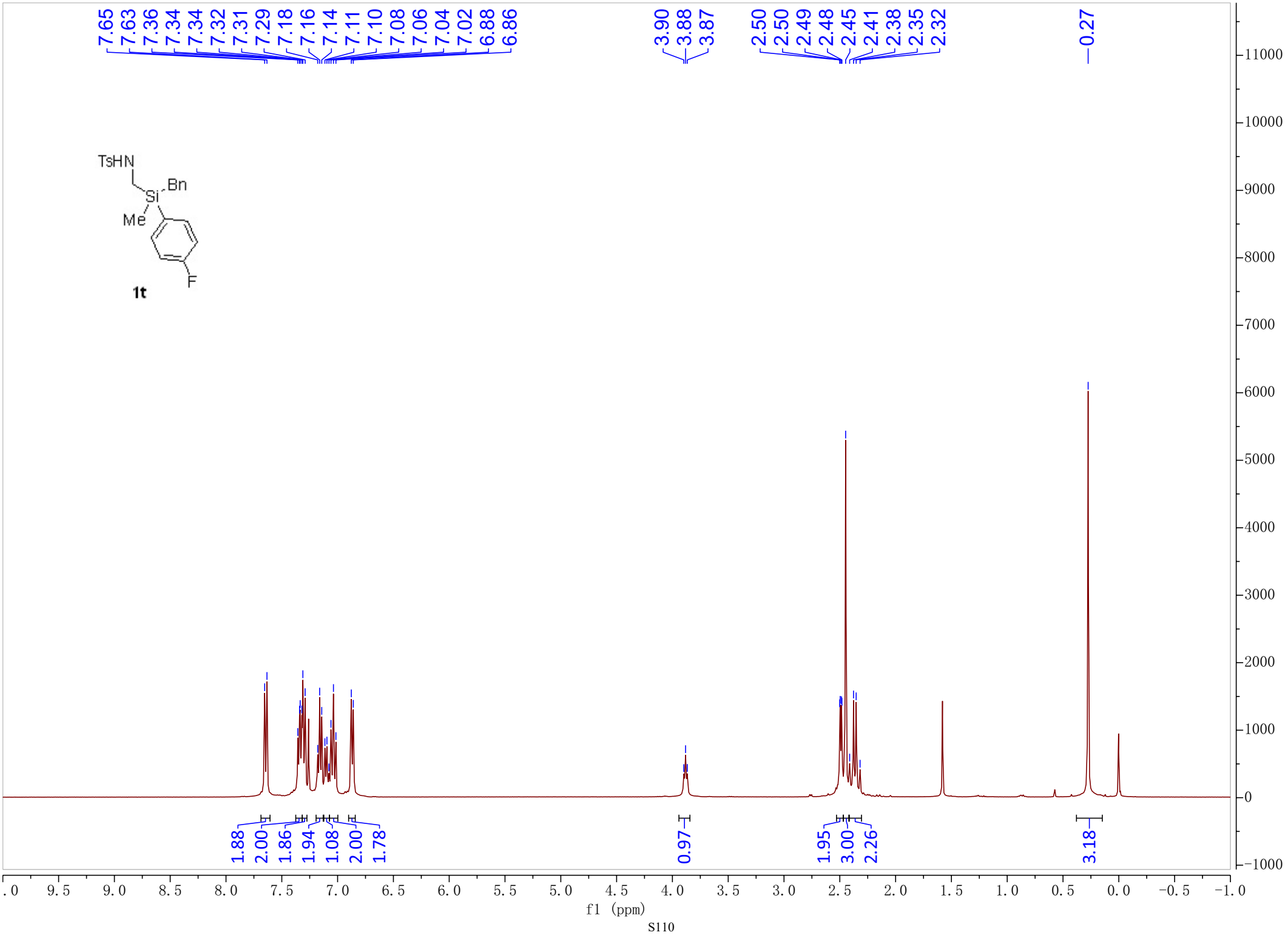
124.95
29.70
22.66
21.54
-6.37
TsHN
Si
Bn
Me
Cl
1s
f1 (ppm)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7.16
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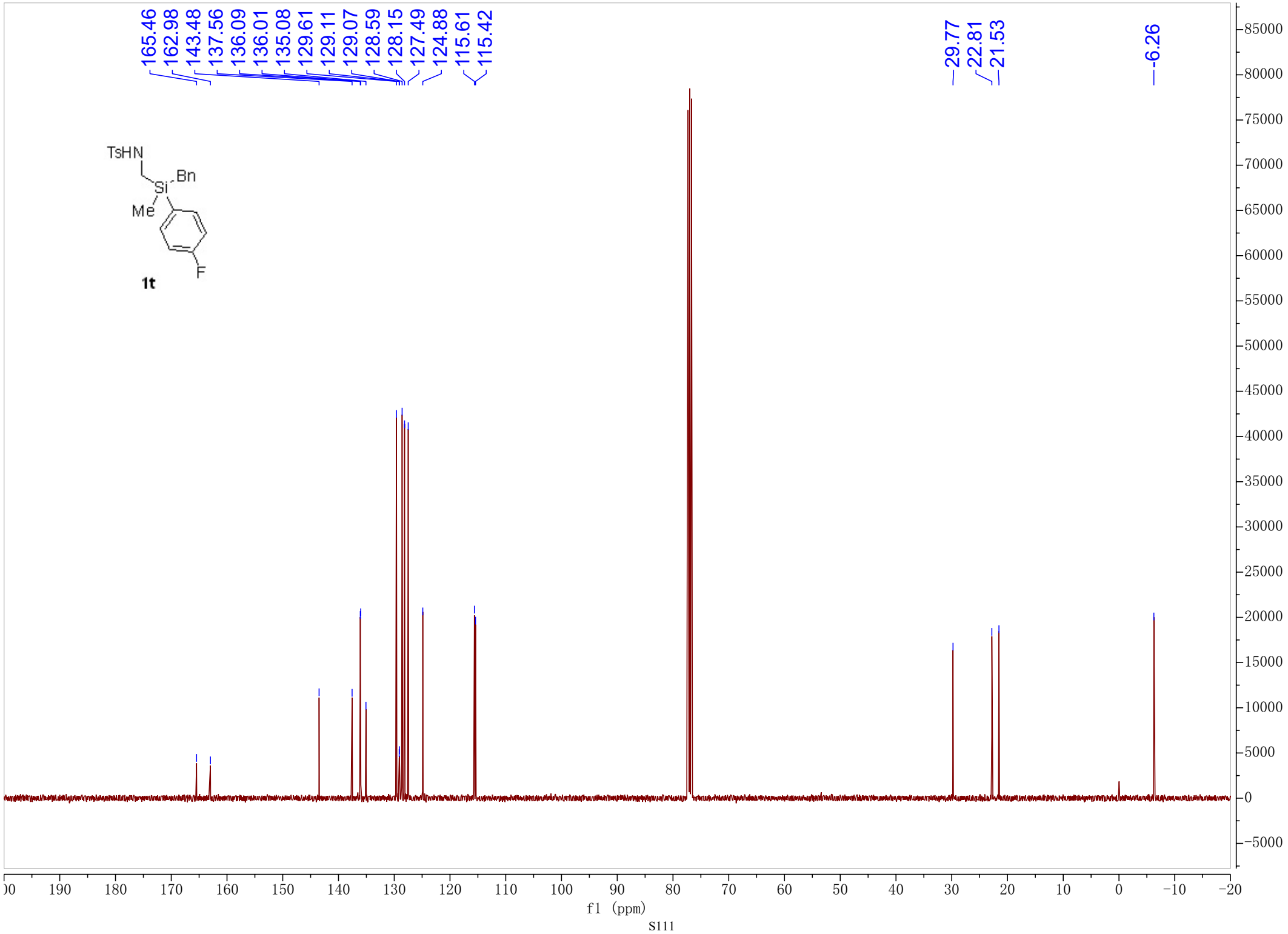
7.08
7.06
7.04
7.02
6.88
6.86
3.90
3.88
3.87
2.50
2.50
2.49
2.48
2.45
2.41
2.38
2.35
2.32
0.27
TsHN
Bn
Si
Me
F
1t
1.88
2.00
1.86
1.94
1.08
2.00
1.78
0.97
1.95
3.00
2.26
3.18
f1 (ppm)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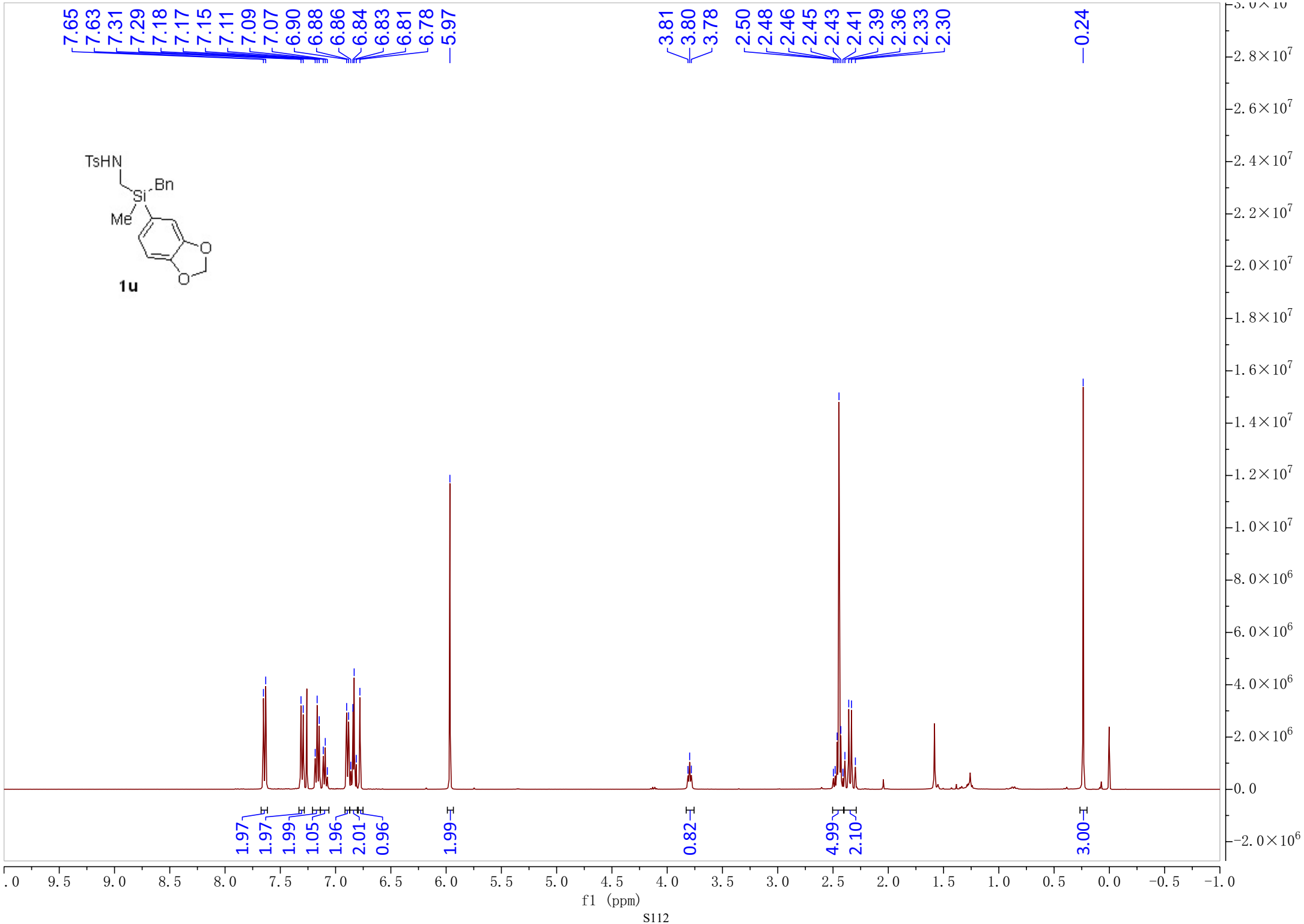
136.01
135.08
129.61
129.11
129.07
128.59
128.15
127.49
124.88
115.61
115.42
29.77
22.81
21.53
-6.26
TsHN
Bn
Si
Me
F
1t
f1 (ppm)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7.11
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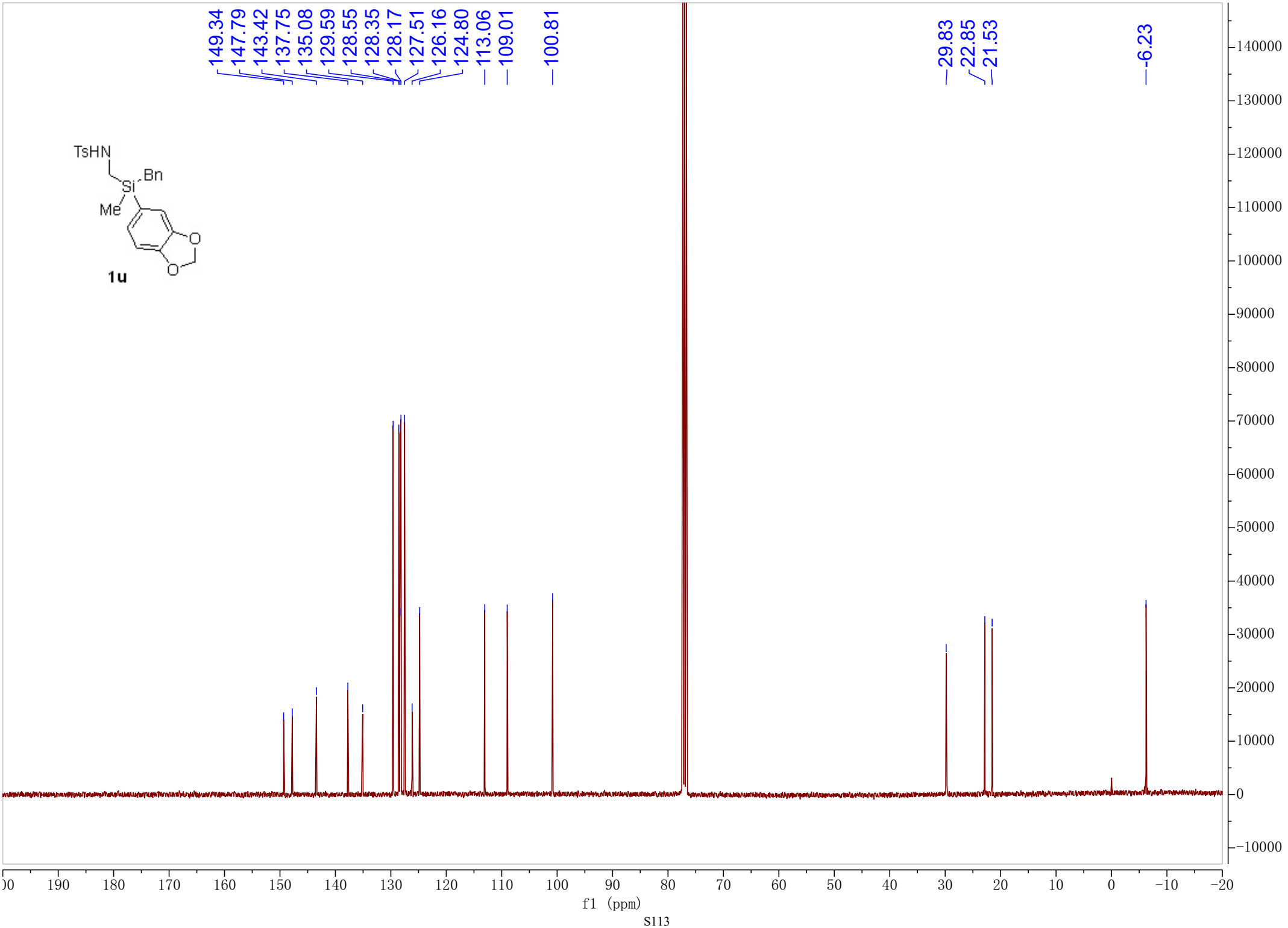
7.07
6.90
6.88
6.86
6.84
6.83
6.81
6.78
5.97
3.81
3.80
3.78
2.50
2.48
2.46
2.45
2.43
2.41
2.39
2.36
2.33
2.30
0.24
TsHN
Si
Bn
Me
O
O
1u
1.97
1.97
1.99
1.05
1.96
2.01
0.96
1.99
0.82
4.99
2.10
3.00
f1 (ppm)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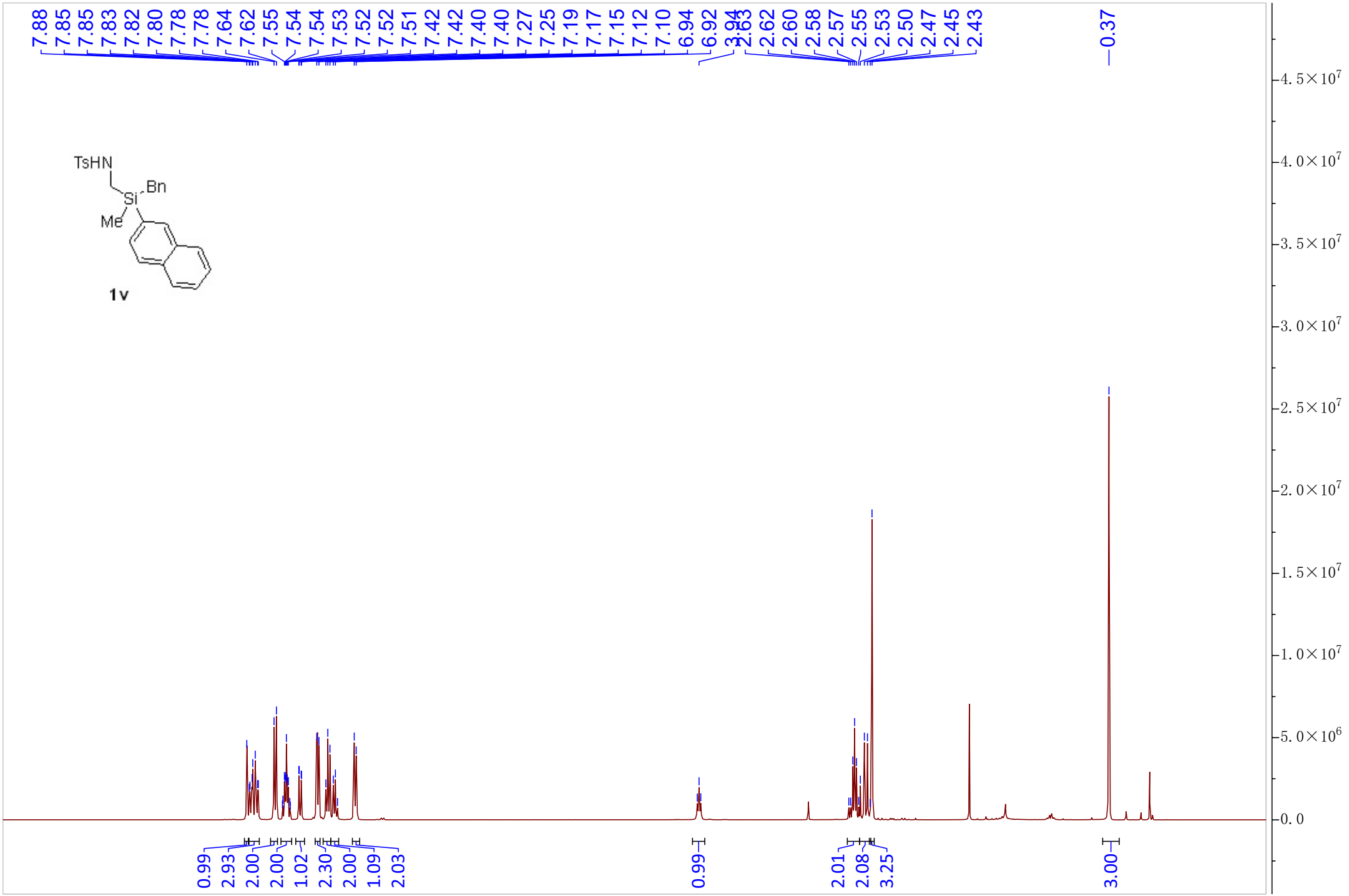
129.59
128.55
128.35
128.17
127.51
126.16
124.80
113.06
109.01
100.81
29.83
22.85
21.53
6.23
TsHN
Si
Bn
Me
O
O
1u
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
−10000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)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7.83
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7.80
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7.78
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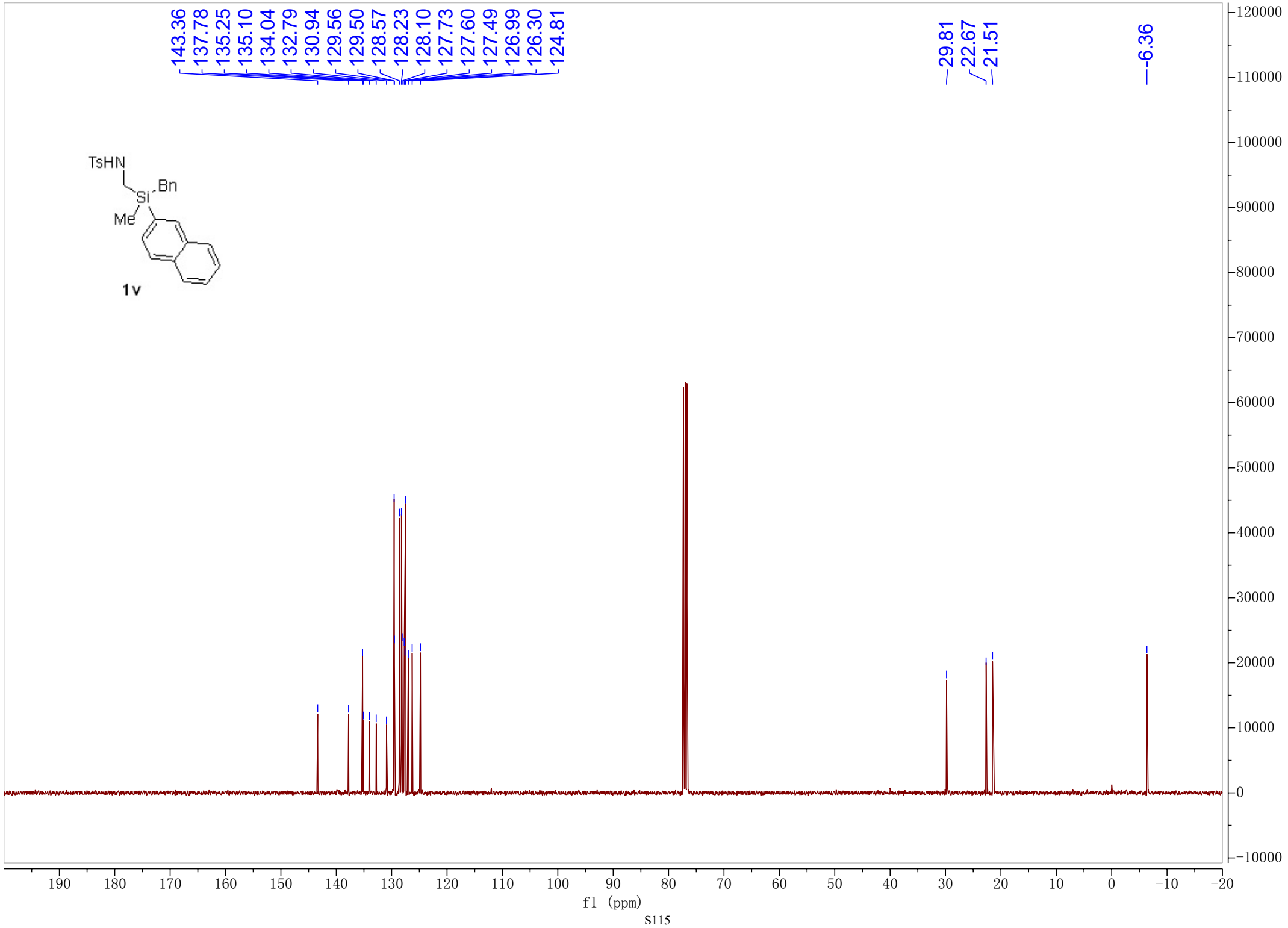
7.62
7.55
7.54
7.54
7.53
7.52
7.52
7.51
7.42
7.42
7.40
7.40
7.27
7.25
7.19
7.17
7.15
7.12
7.10
6.94
6.92
3.94
3.63
2.62
2.60
2.58
2.57
2.55
2.53
2.50
2.47
2.45
2.43
0.37
TsHN
Si
Bn
Me
1v
4.5×10^7
4.0×10^7
3.5×10^7
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
0.99
2.93
2.00
2.00
1.02
2.30
2.00
1.09
2.03
0.99
2.01
2.08
3.25
3.00
f1 (ppm)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128.57
128.23
128.10
127.73
127.60
127.49
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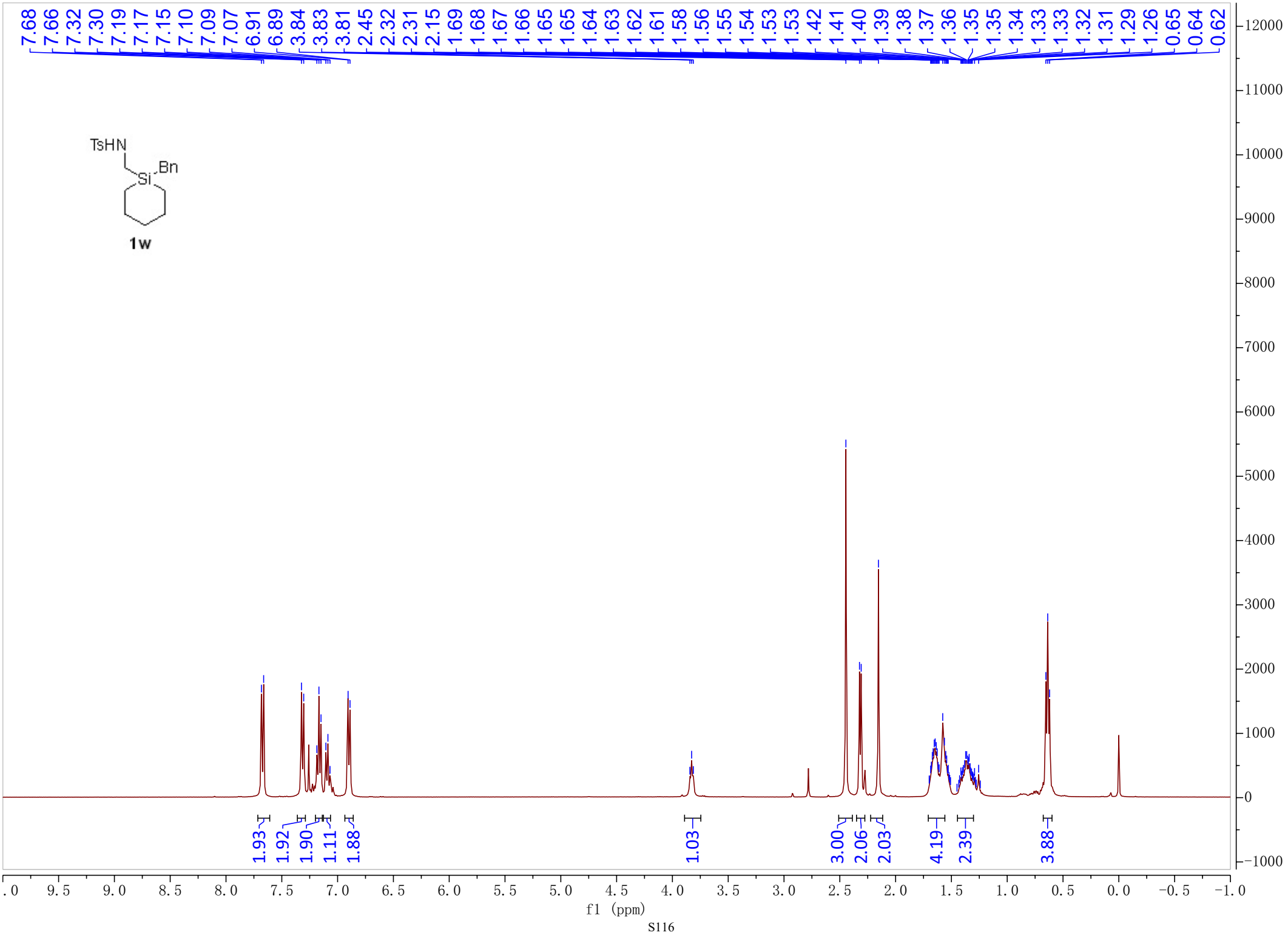
126.30
124.81
29.81
22.67
21.51
6.36
TsHN
Si
Bn
Me
1v
f1 (ppm)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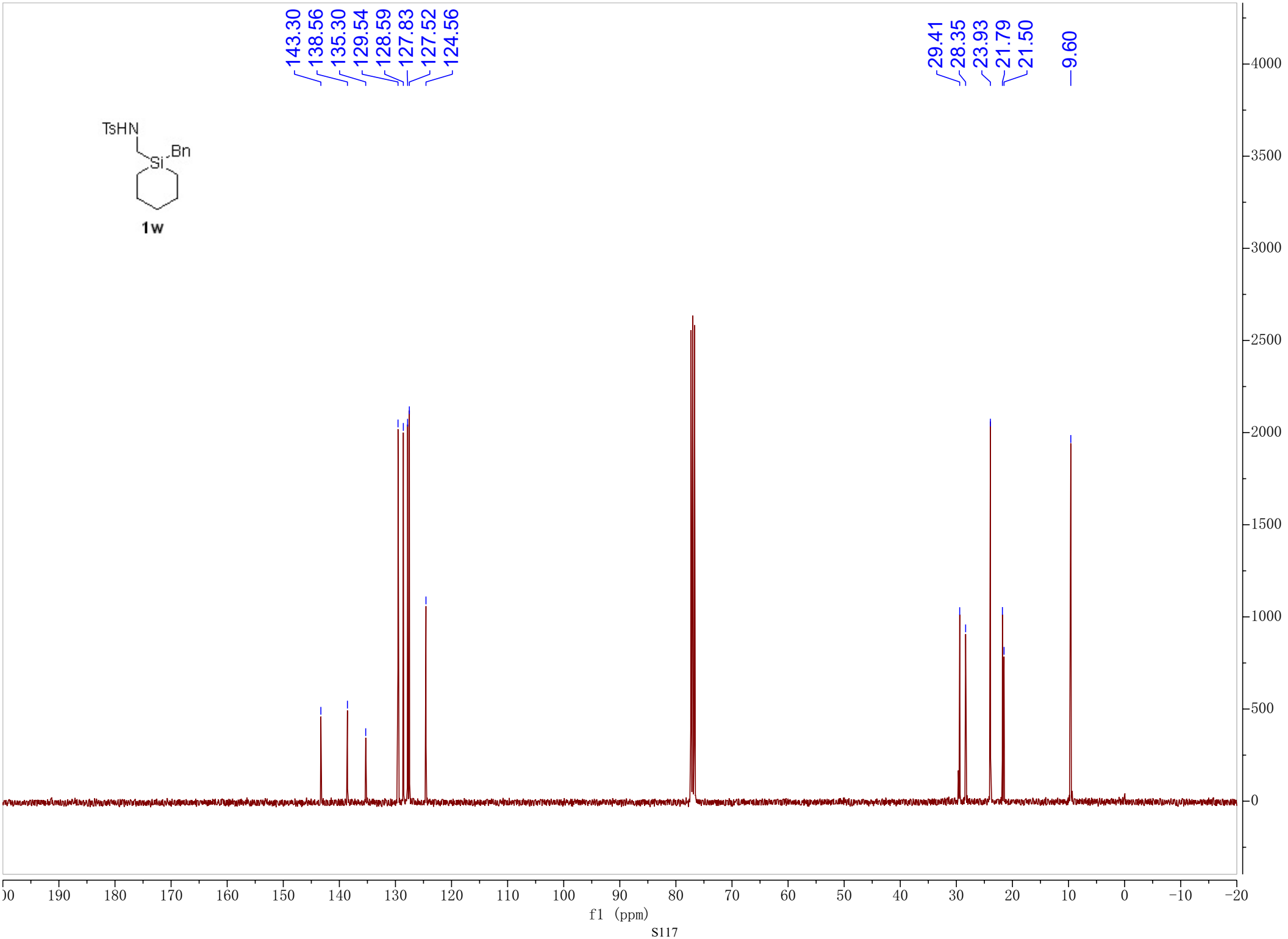
TsHN
Si
Bn
1w
1.93 1.92 1.90 1.11 1.88 1.03 3.00 2.06 2.03 4.19 2.39 3.88
f1 (ppm)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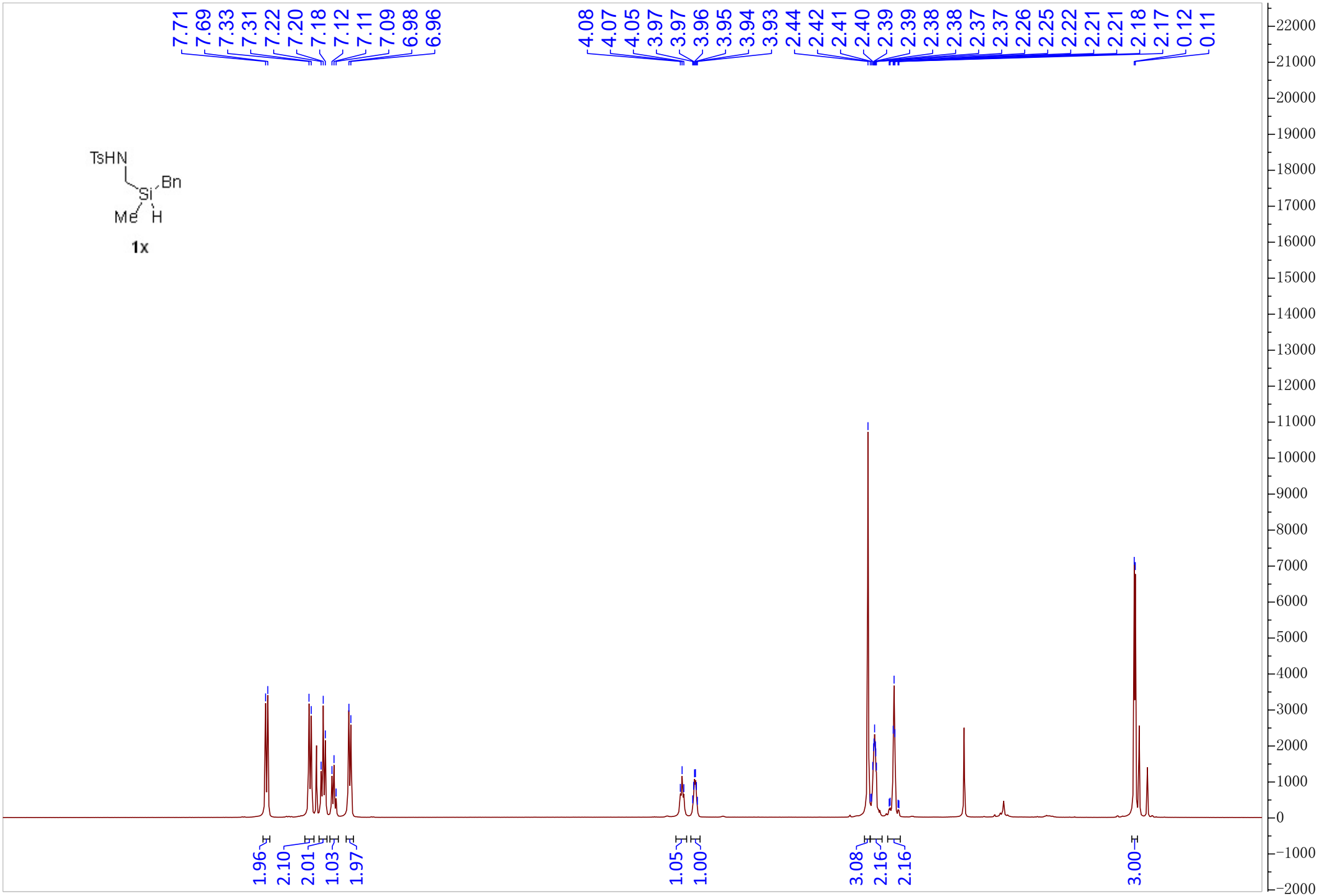
127.52
124.56
29.41
28.35
23.93
21.79
21.50
9.60
TsHN
Si
Bn
1w
4000
3500
3000
2500
2000
1500
1000
500
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)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7.12
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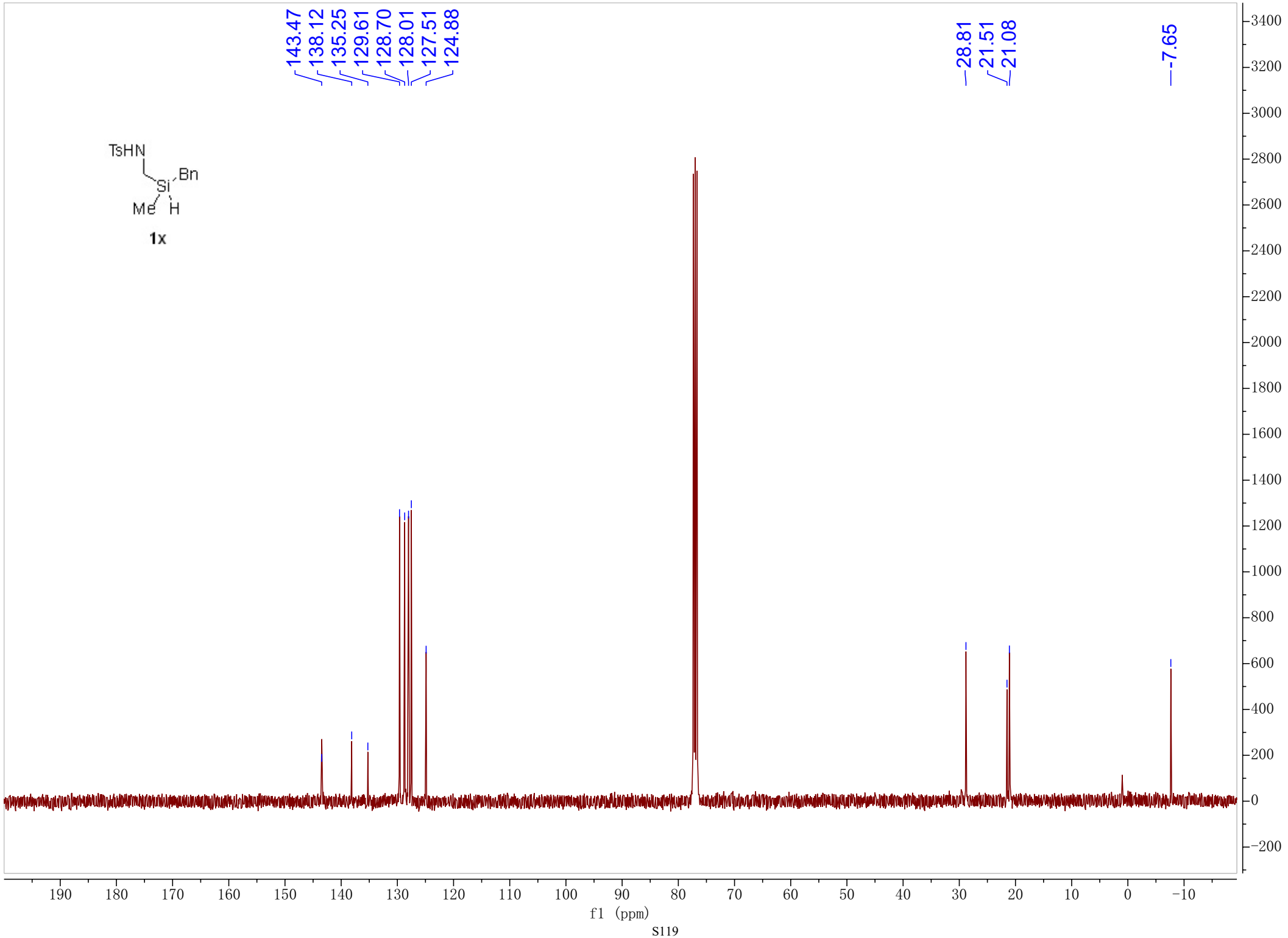
7.09
6.98
6.96
4.08
4.07
4.05
3.97
3.97
3.96
3.95
3.94
3.93
2.44
2.42
2.41
2.40
2.39
2.39
2.38
2.38
2.37
2.37
2.26
2.25
2.22
2.21
2.21
2.18
2.17
0.12
0.11
TsHN
Bn
Si
Me
H
1x
1.96
2.10
2.01
1.03
1.97
1.05
1.00
3.08
2.16
2.16
3.00
f1 (ppm)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21.51
21.08
7.65
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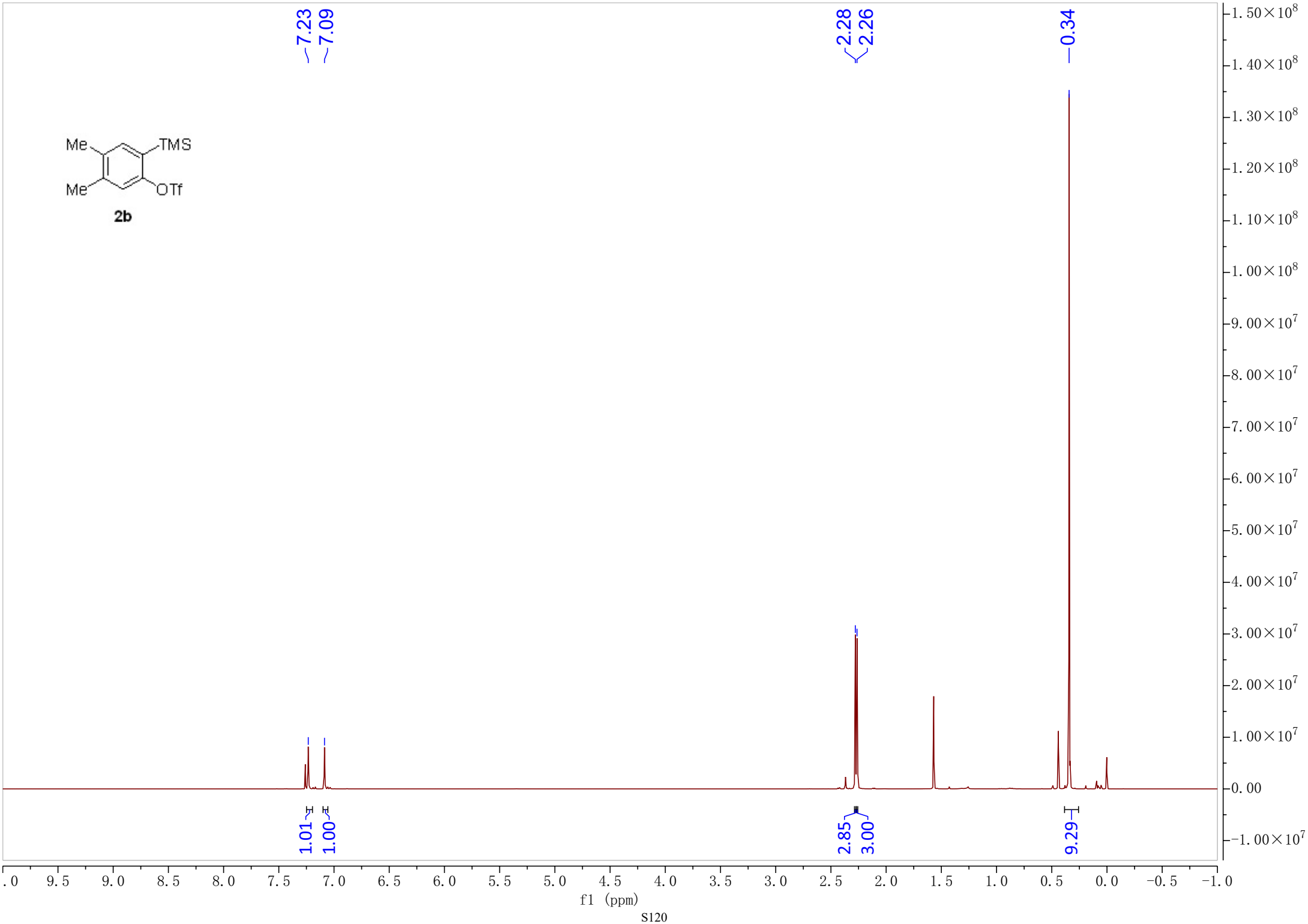
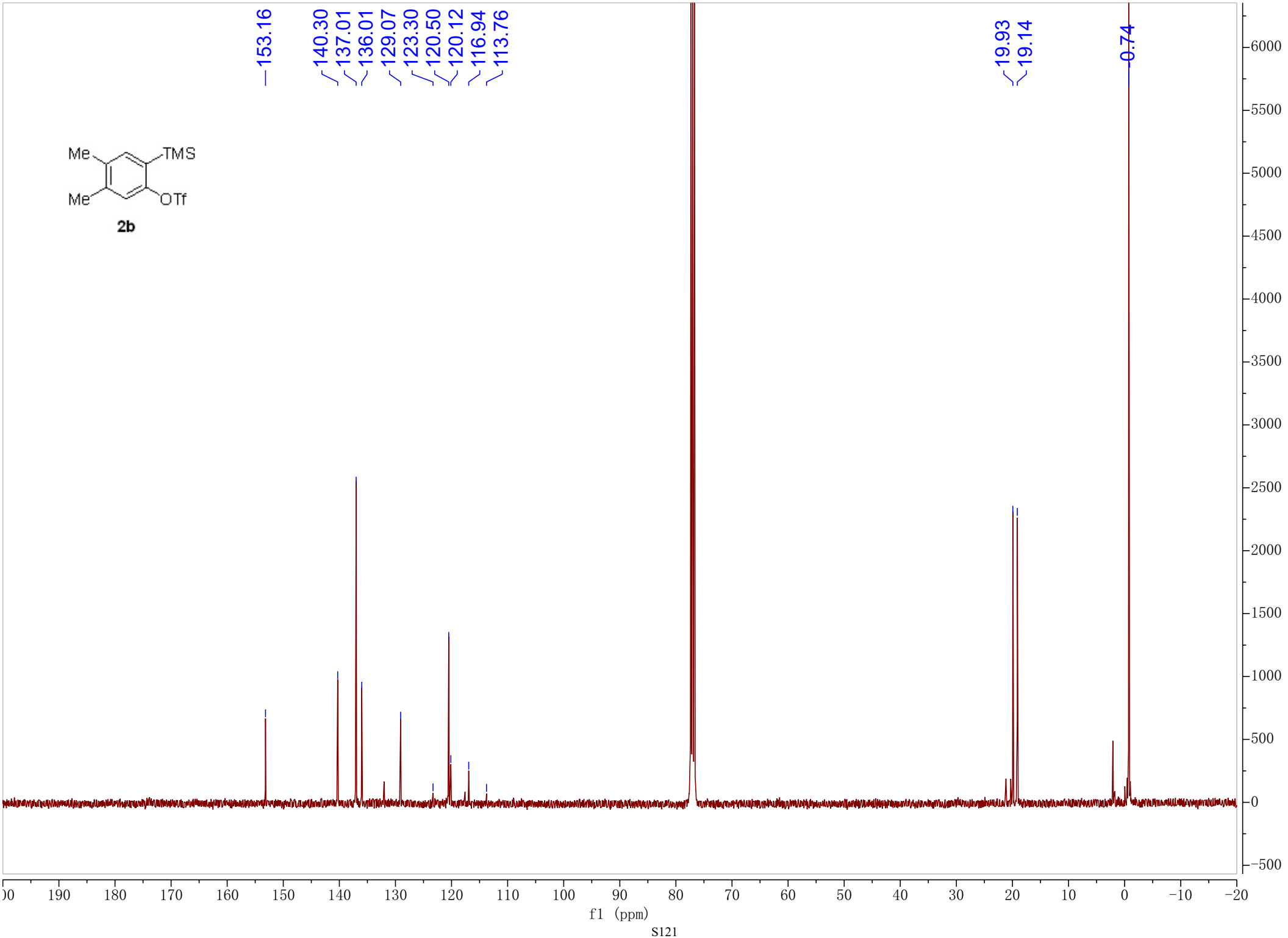
Si
Bn
Me
H
1x
f1 (ppm)


7.23
7.09
2.28
2.26
0.34
Me
TMS
Me
OTf
2b
1.01
1.00
2.85
3.00
9.29
f1 (ppm)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140.30
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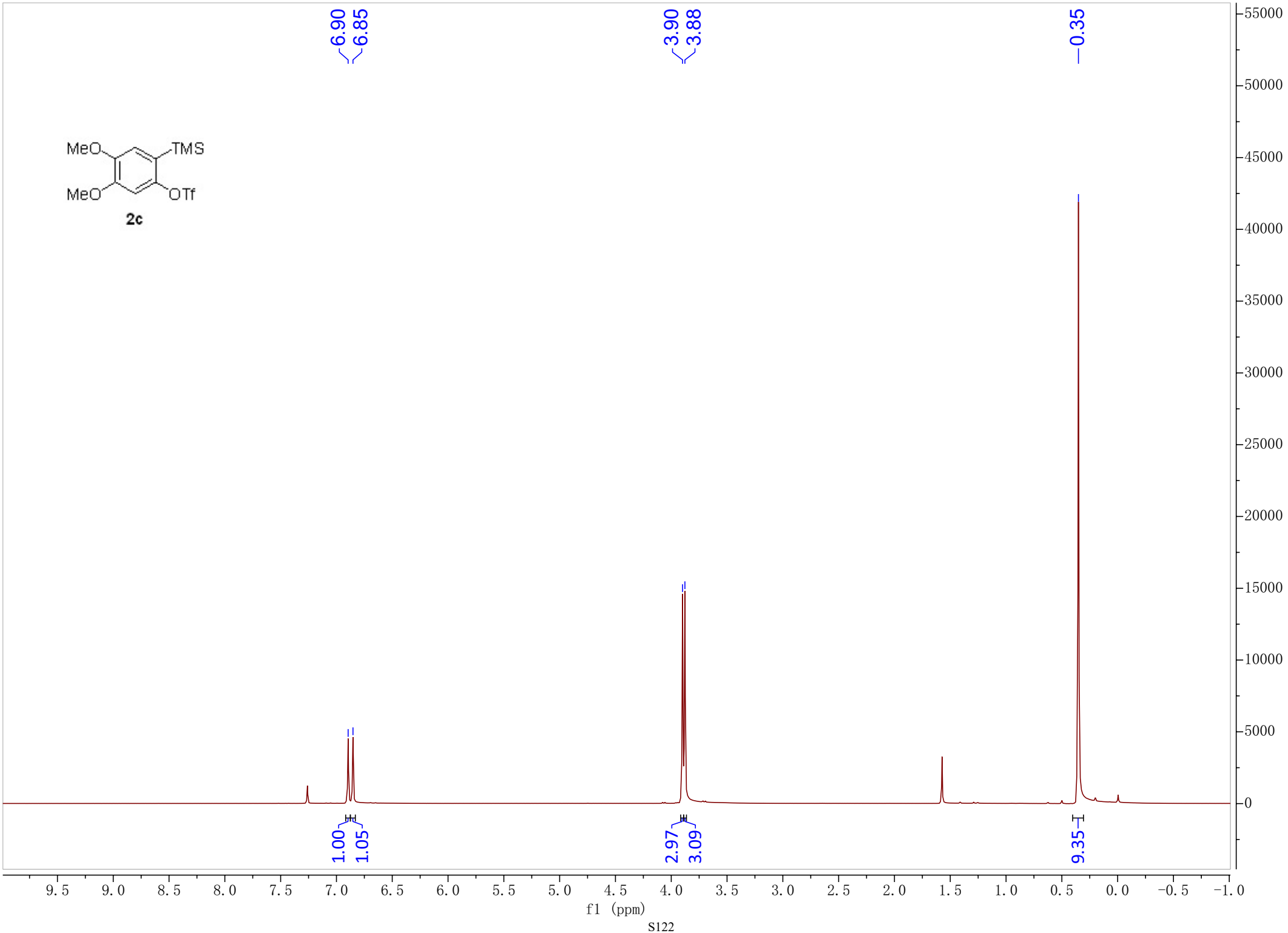
136.01
129.07
123.30
120.50
120.12
116.94
113.76
19.93
19.14
0.74
Me
TMS
Me
OTf
2b
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)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6.85
3.90
3.88
0.35
MeO
TMS
MeO
OTf
2c
1.00
1.05
2.97
3.09
9.35
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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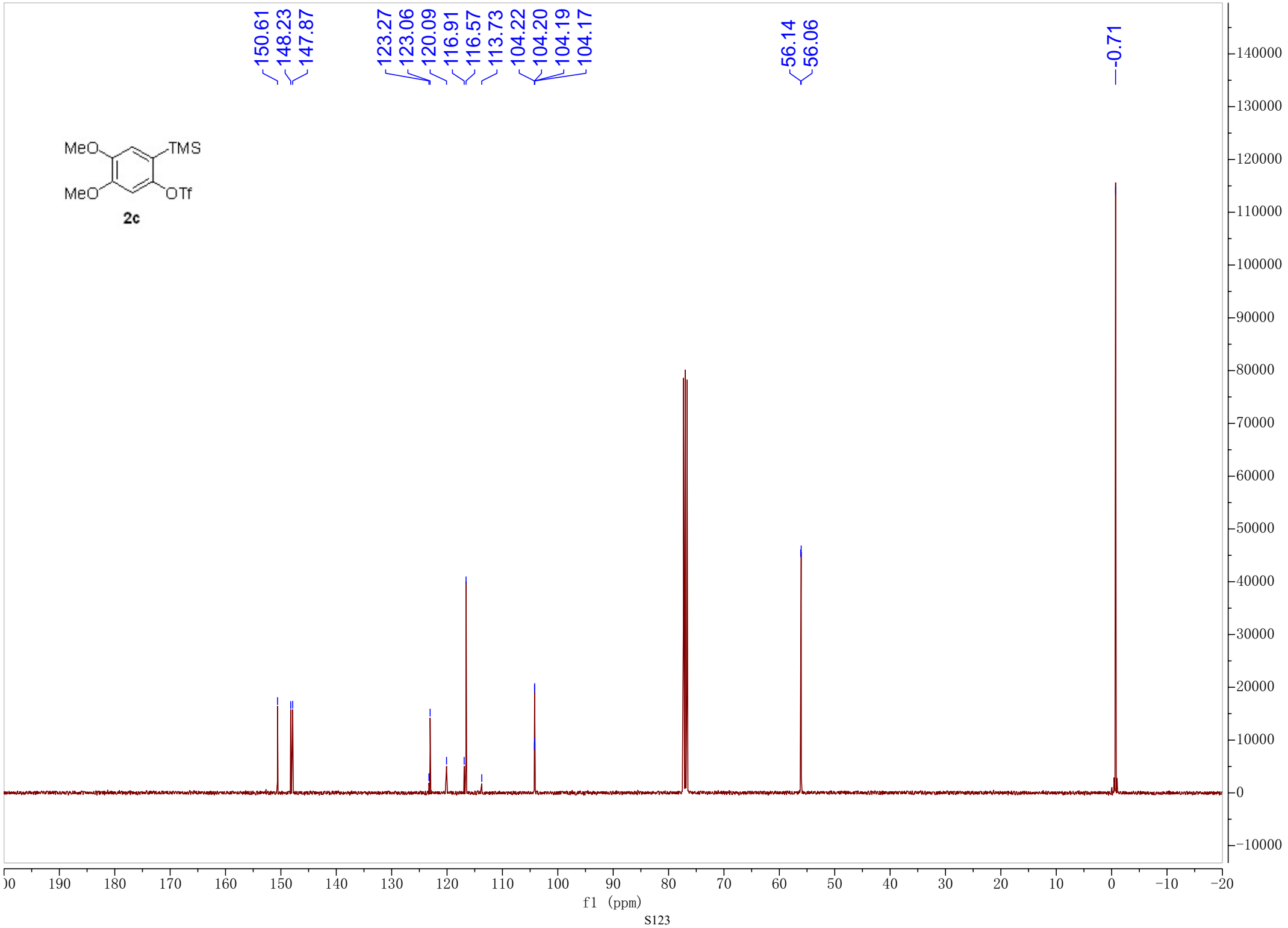
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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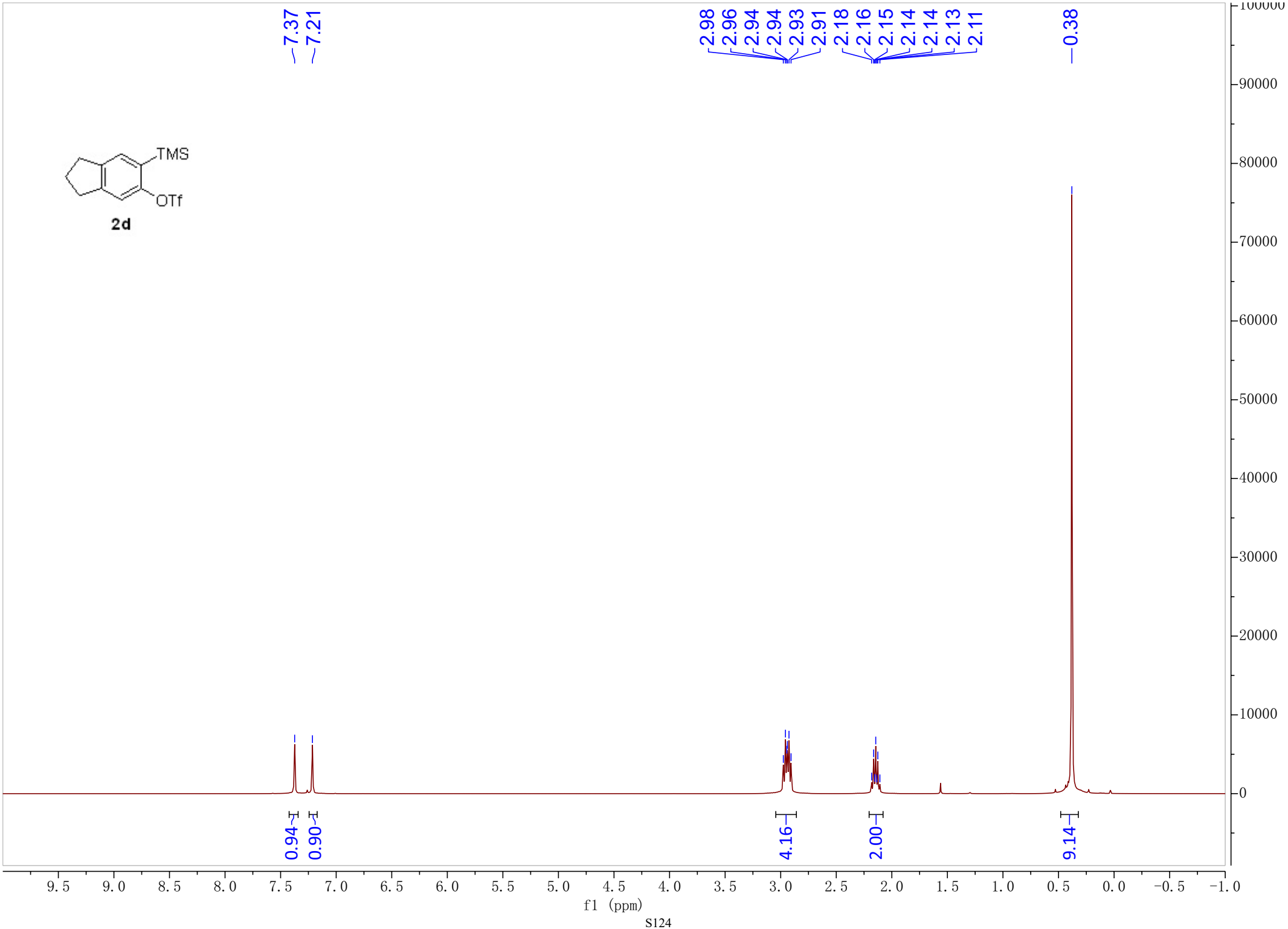
116.57
113.73
104.22
104.20
104.19
104.17
56.14
56.06
-0.71
MeO
TMS
MeO
OTf
2c
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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7.21
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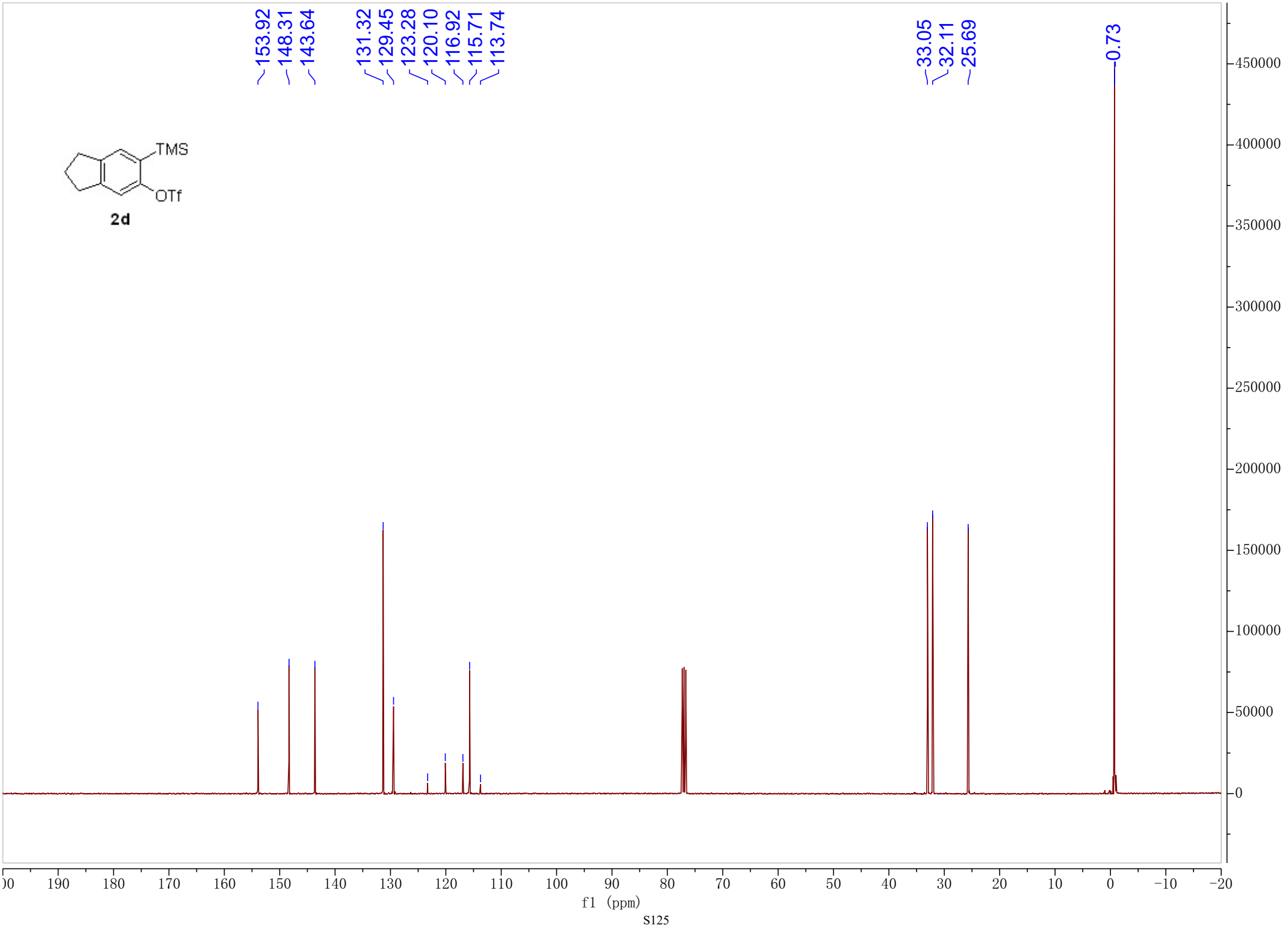
2.96
2.94
2.94
2.93
2.91
2.18
2.16
2.15
2.14
2.14
2.13
2.11
0.38
TMS
OTf
2d
0.94
0.90
4.16
2.00
9.14
f1 (ppm)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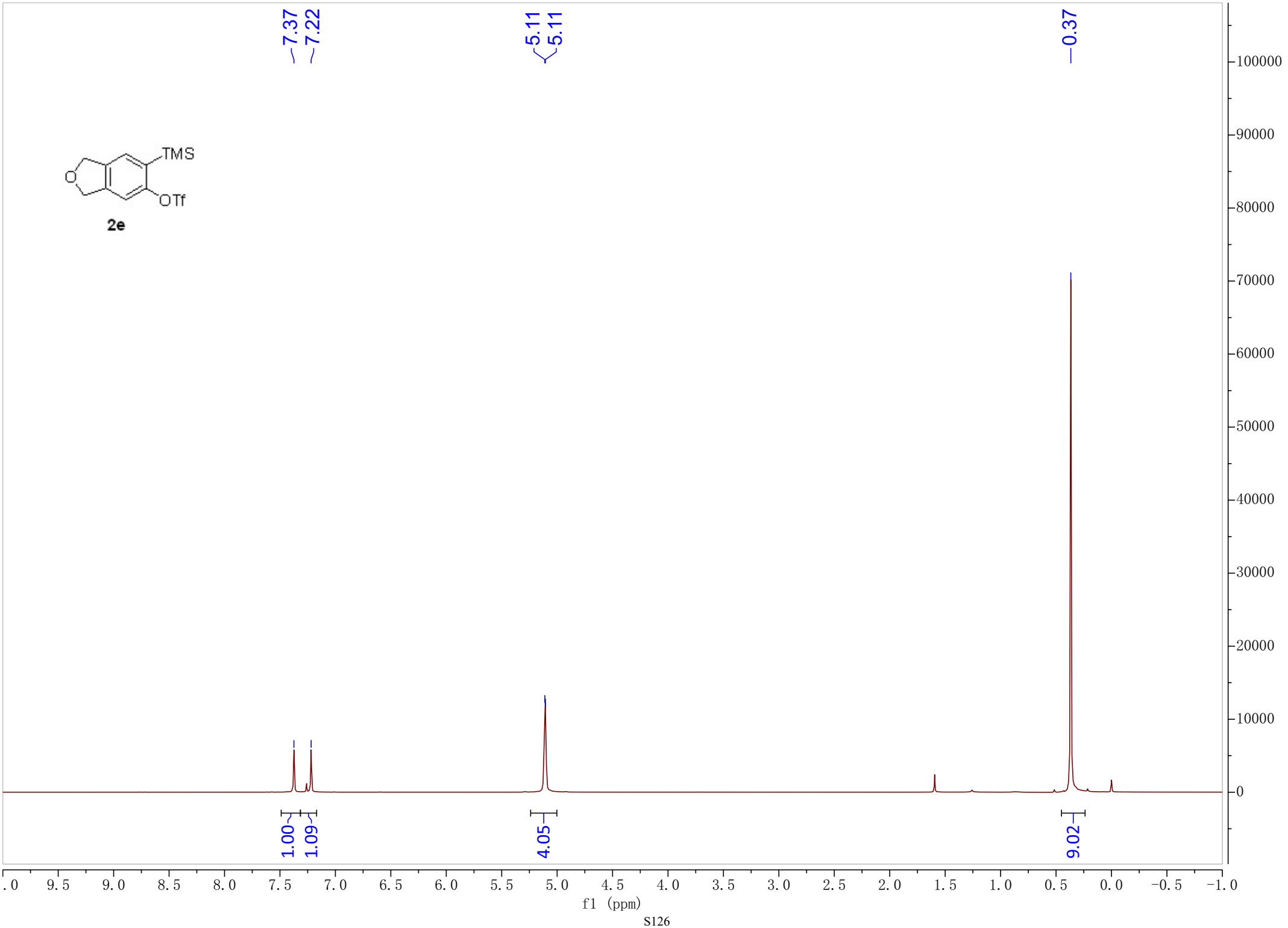
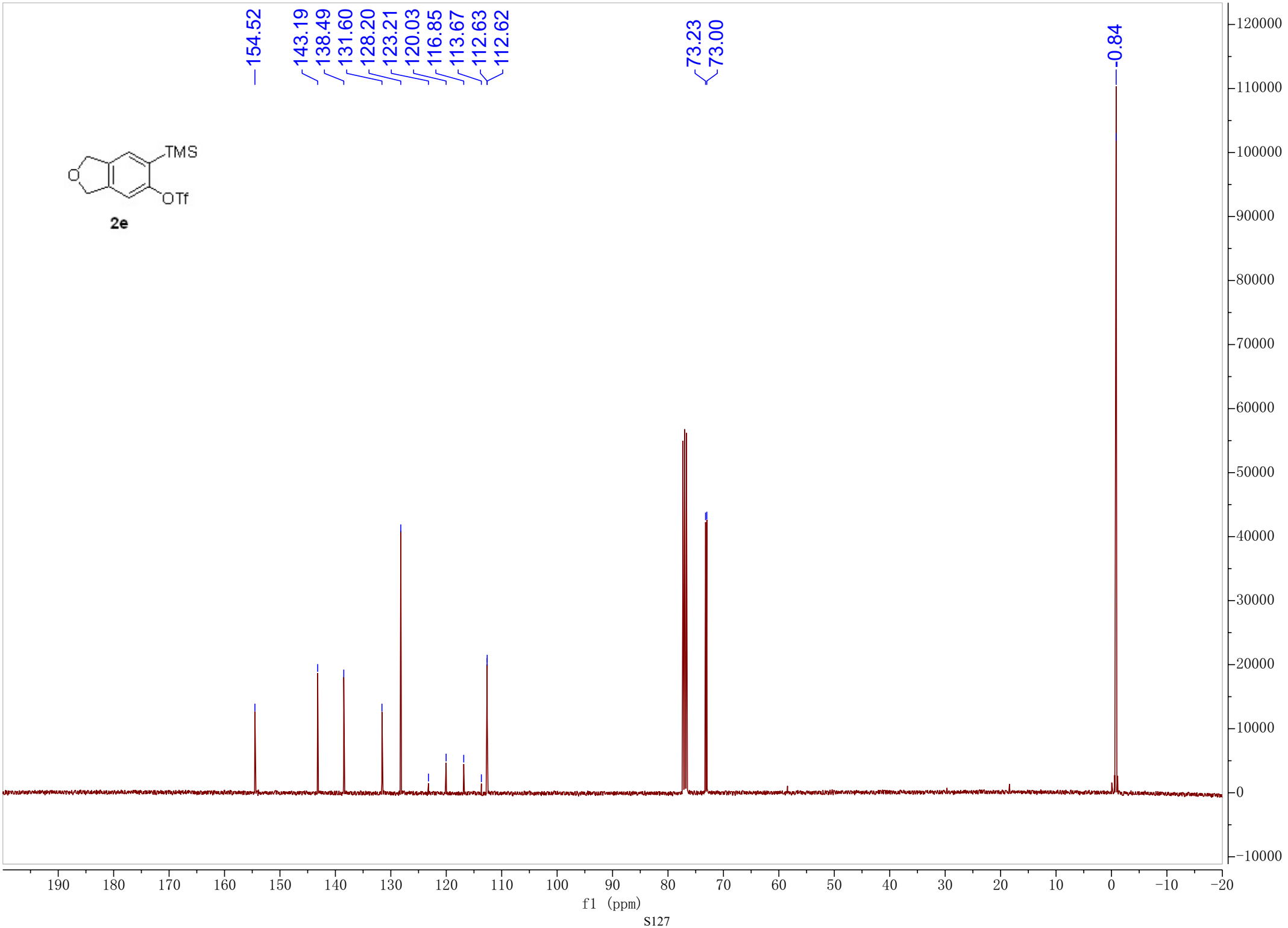
148.31
143.64
131.32
129.45
123.28
120.10
116.92
115.71
113.74
33.05
32.11
25.69
0.73
TMS
OTf
2d
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


7.37
7.22
5.11
5.11
0.37
TMS
OTf
2e
1.00
1.09
4.05
9.02
f1 (ppm)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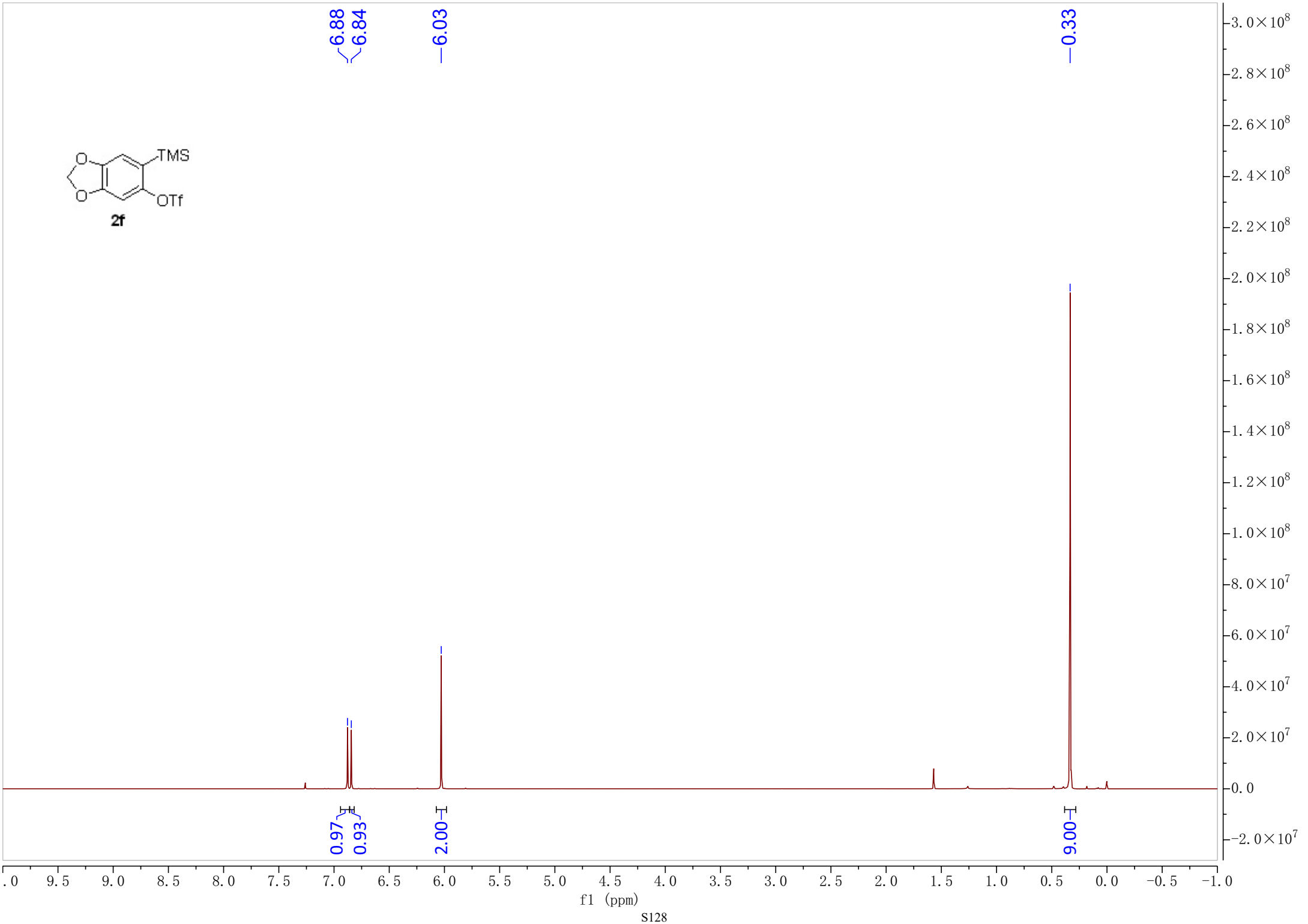
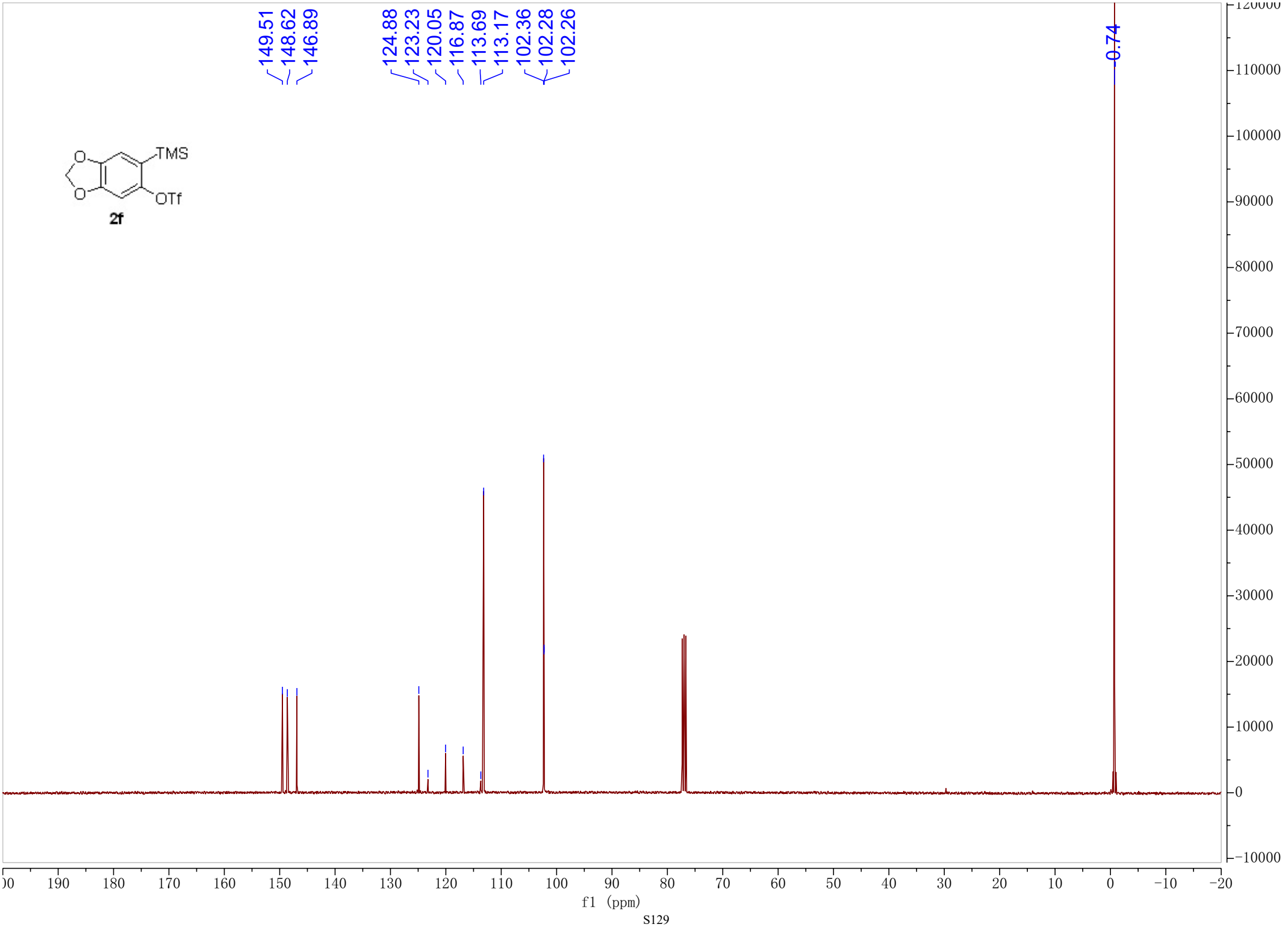
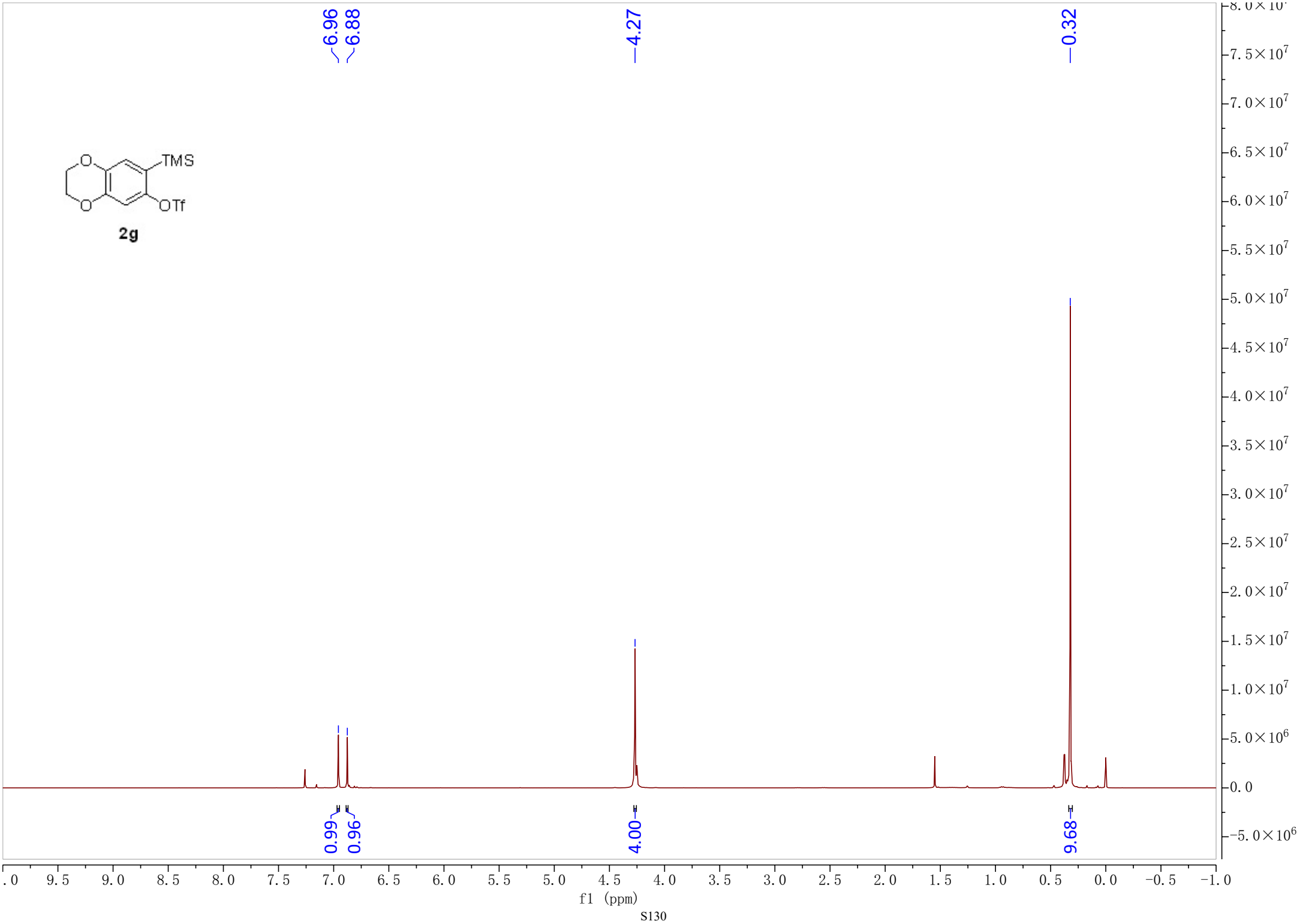
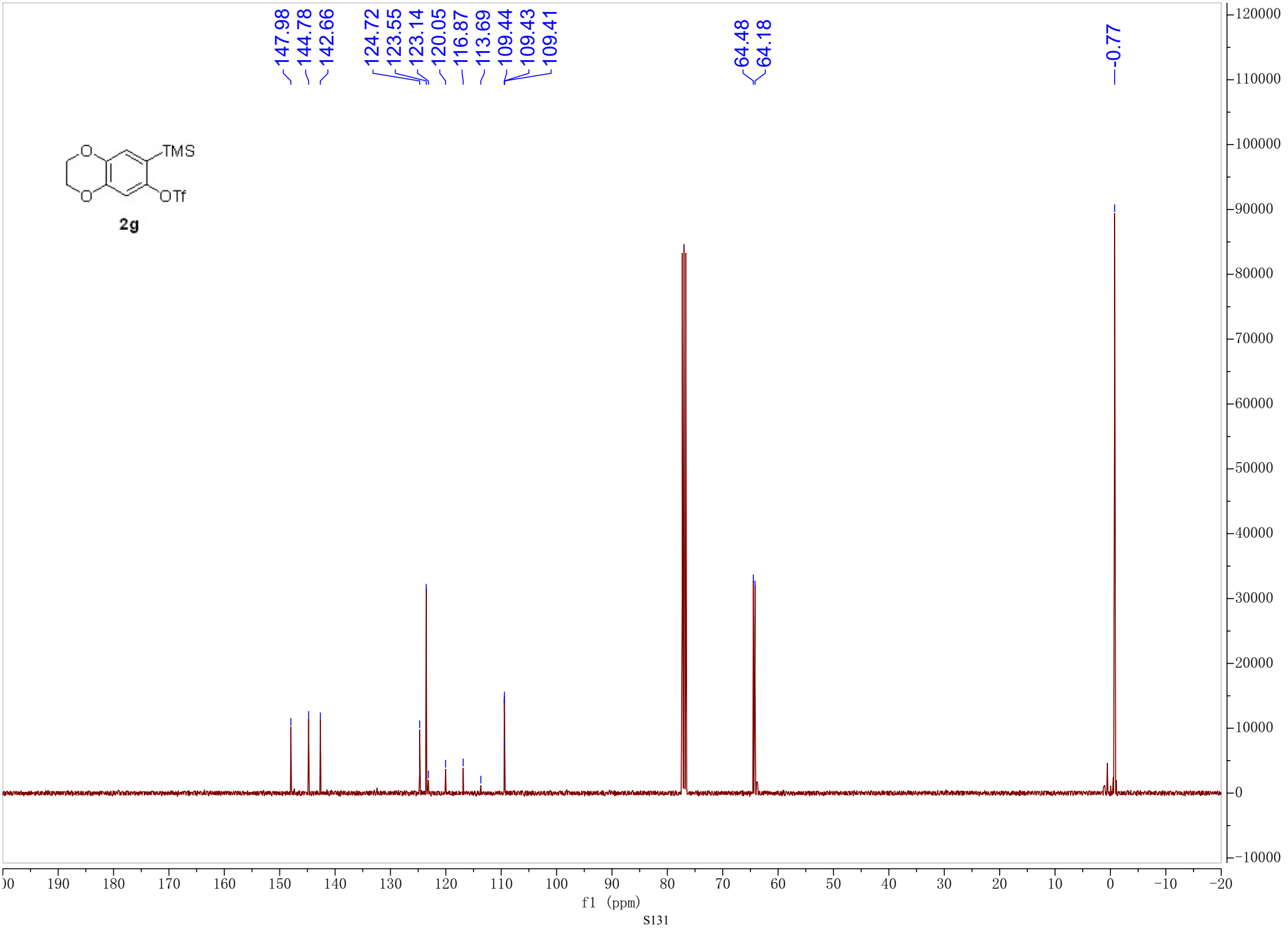
143.19
138.49
131.60
128.20
123.21
120.03
116.85
113.67
112.63
112.62
73.23
73.00
-0.84
TMS
OTf
2e
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

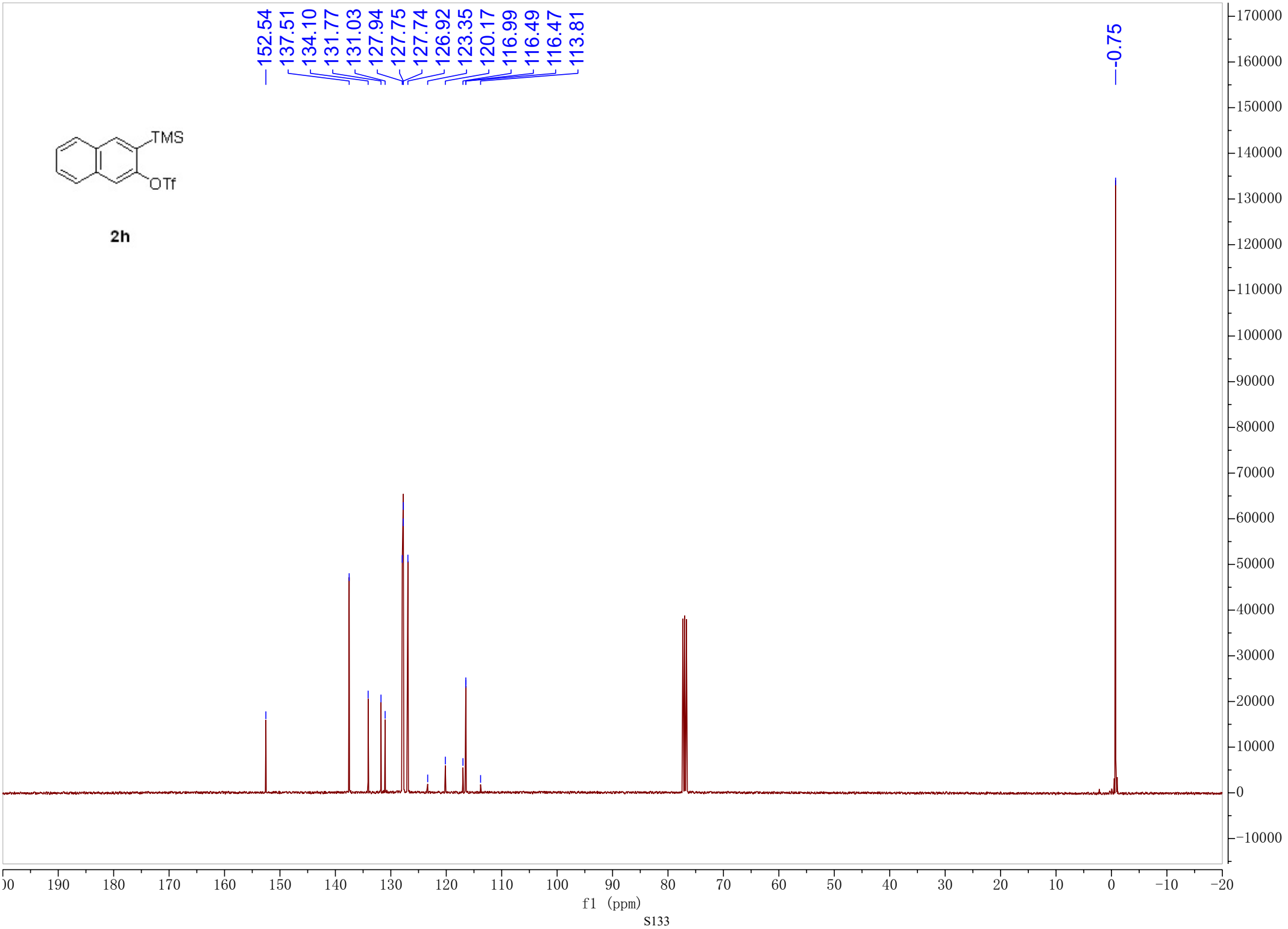

6.88
6.84
6.03
0.33
TMS
OTf
2f
0.97
0.93
2.00
9.00
f1 (ppm)

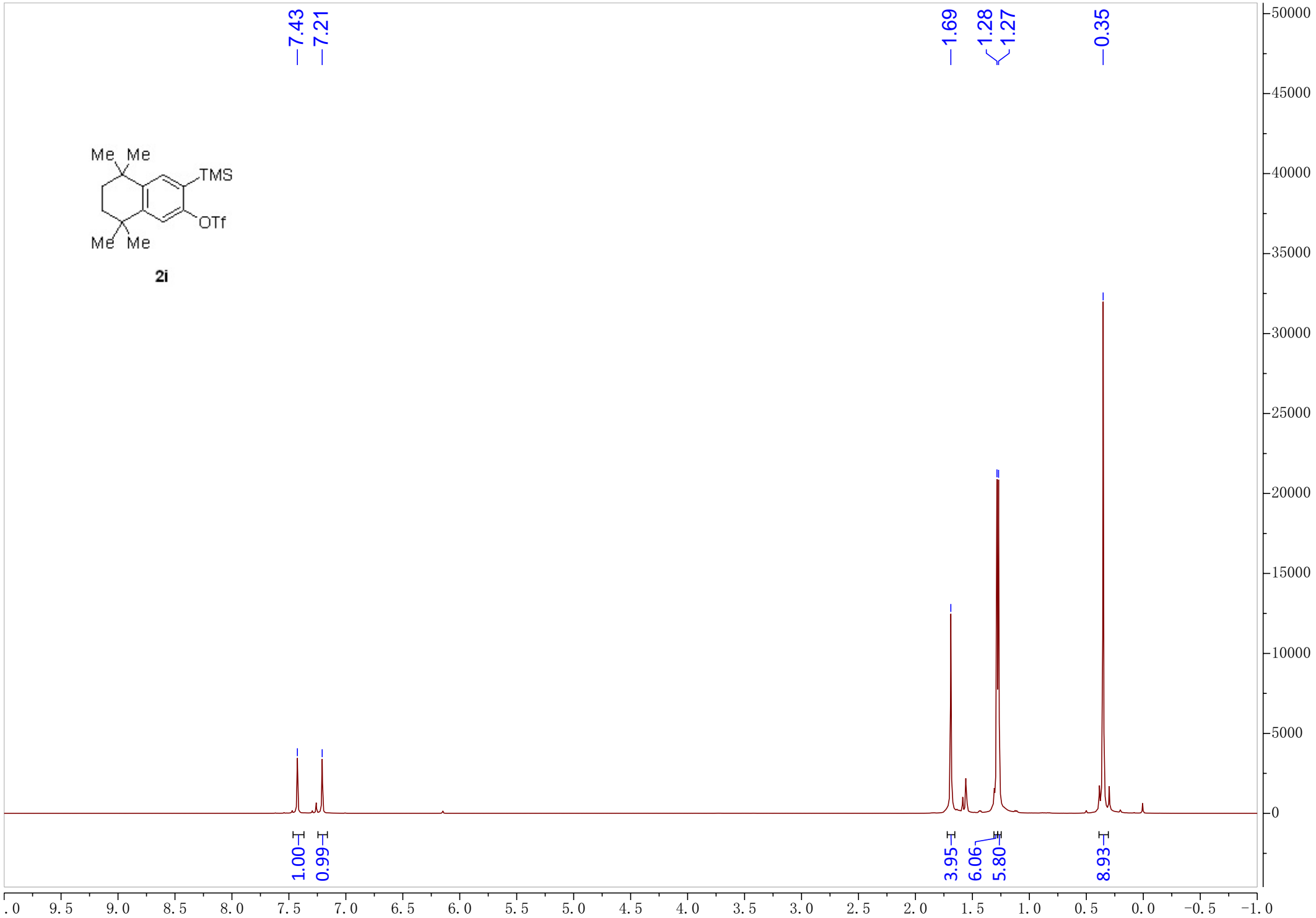

149.51
148.62
146.89
124.88
123.23
120.05
116.87
113.69
113.17
102.36
102.28
102.26
0.74
TMS
OTf
2f
f1 (ppm)

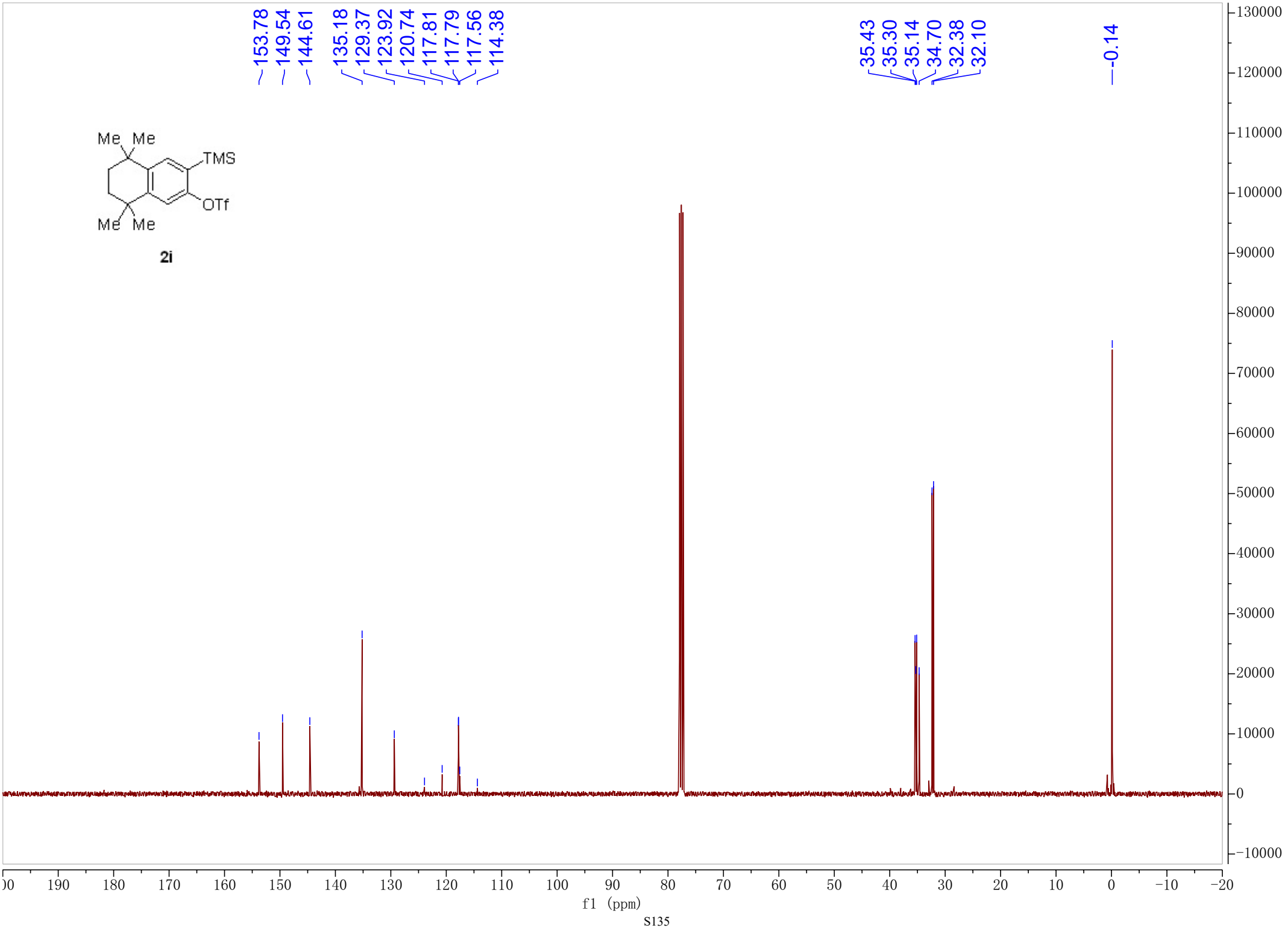

6.96
6.88
4.27
0.32
TMS
OTf
2g
0.99
0.96
4.00
9.68
f1 (ppm)


147.98
144.78
142.66
124.72
123.55
123.14
120.05
116.87
113.69
109.44
109.43
109.41
64.48
64.18
-0.77
TMS
OTf
2g
f1 (ppm)


8.02
7.89
7.88
7.88
7.87
7.85
7.85
7.84
7.83
7.82
7.59
7.59
7.58
7.57
7.57
7.56
7.55
7.55
7.54
7.53
7.53
0.46
TMS
OTf
2h
1.00
2.40
1.05
2.01
9.78
f1 (ppm)


152.54
137.51
134.10
131.77
131.03
127.94
127.75
127.74
126.92
123.35
120.17
116.99
116.49
116.47
113.81
-0.75
TMS
OTf
2h
f1 (ppm)


7.43
7.21
1.69
1.28
1.27
0.35
Me Me
TMS
OTf
Me Me
2i
1.00
0.99
3.95
6.06
5.80
8.93
f1 (ppm)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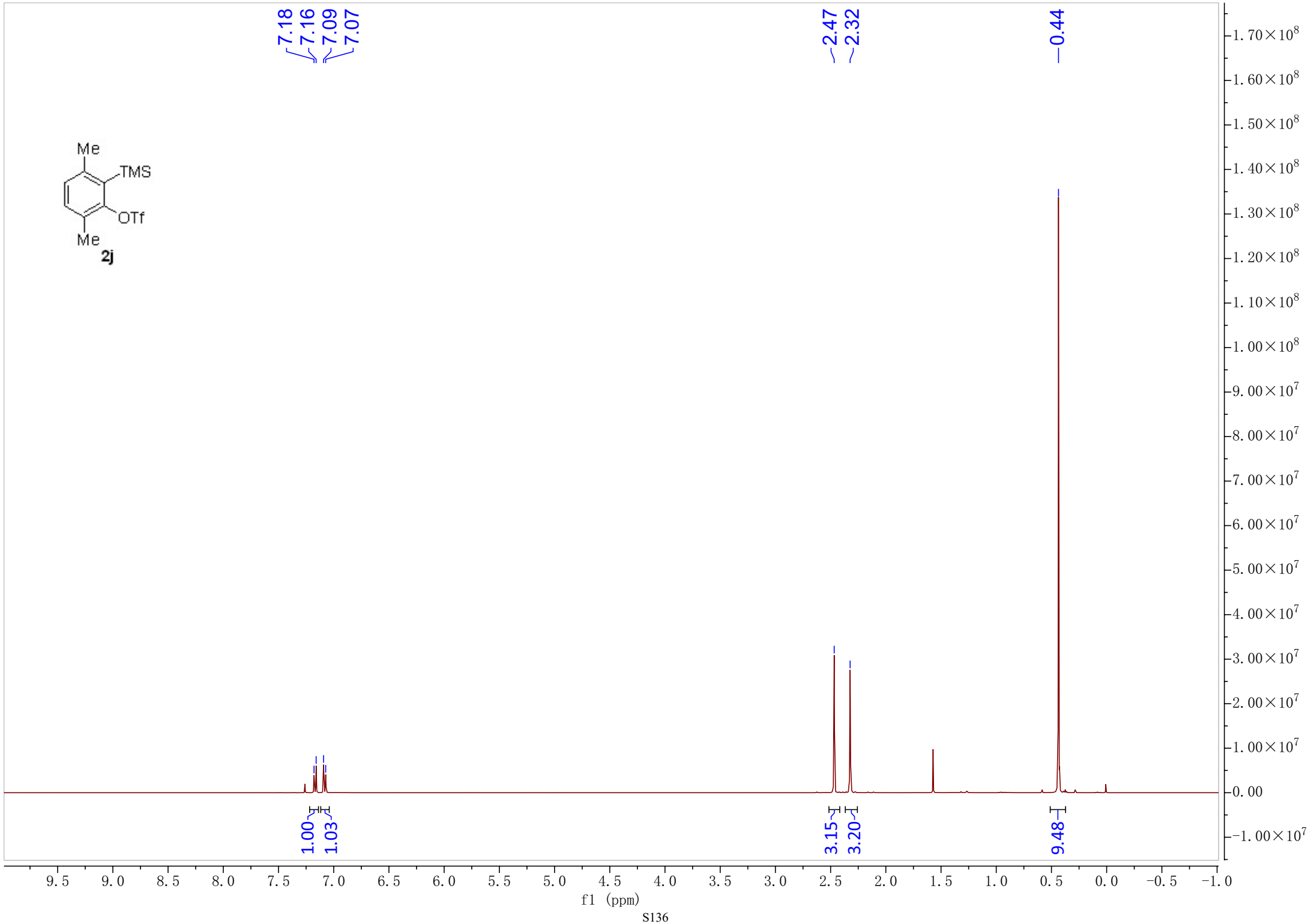
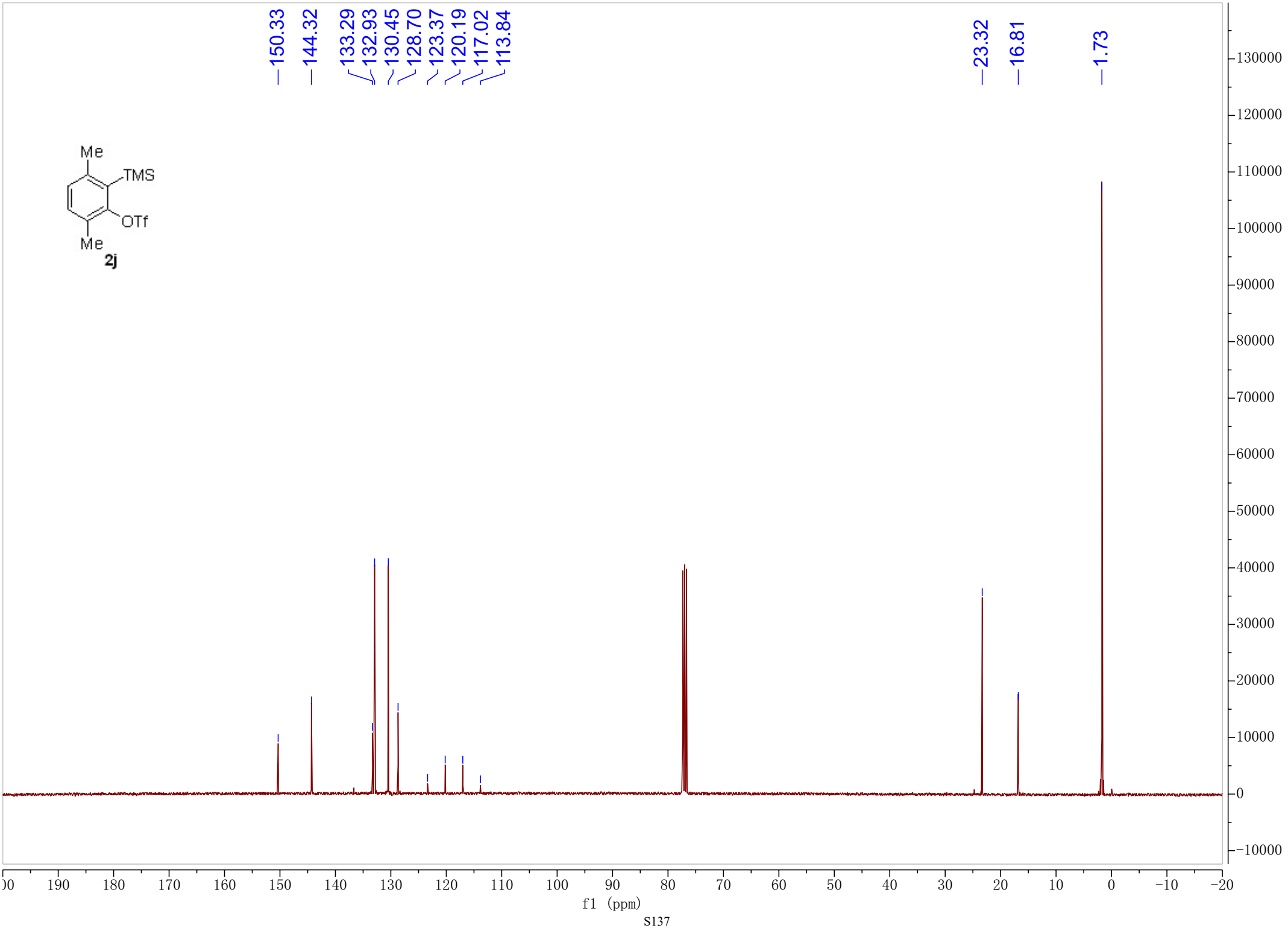
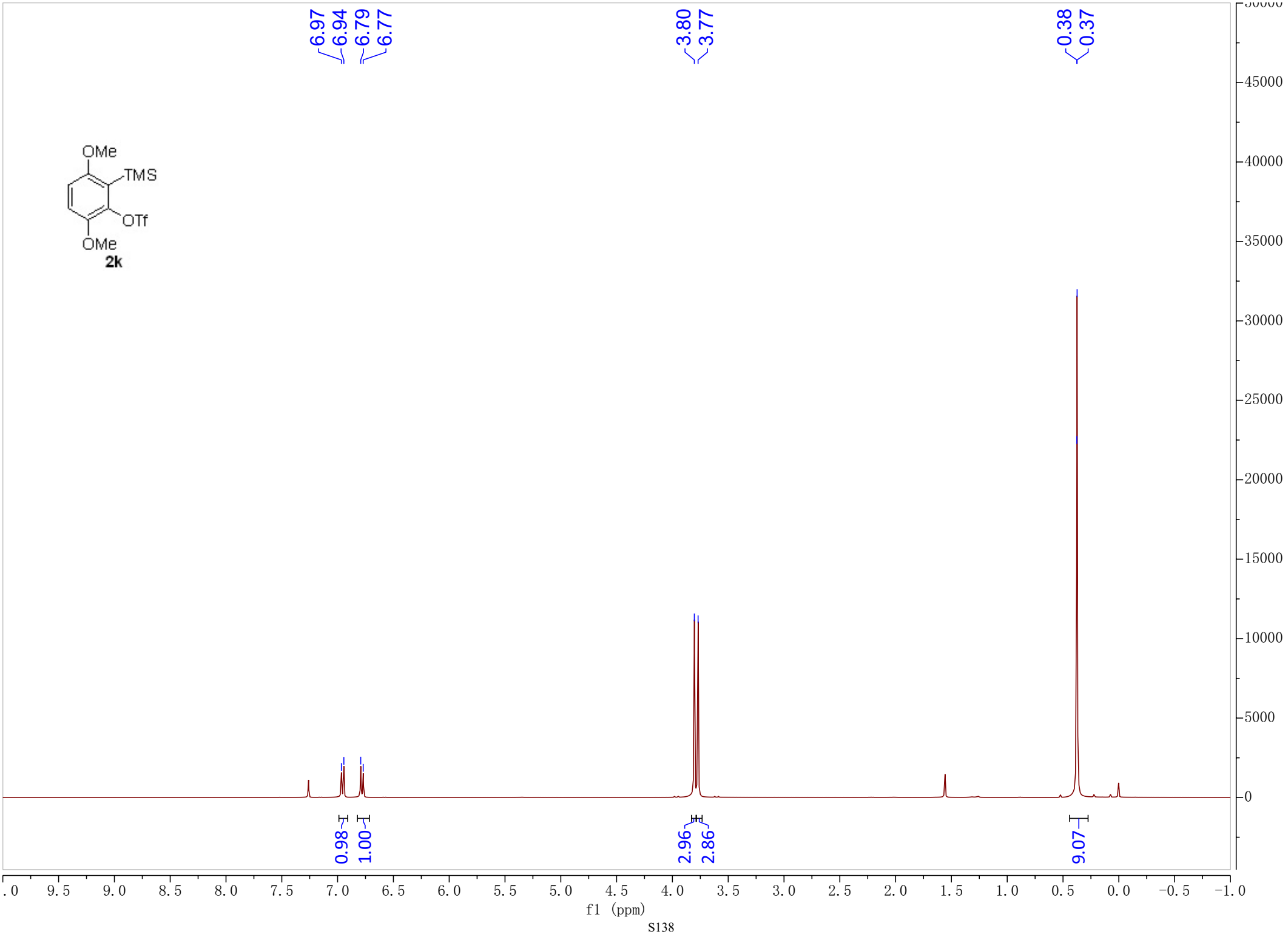
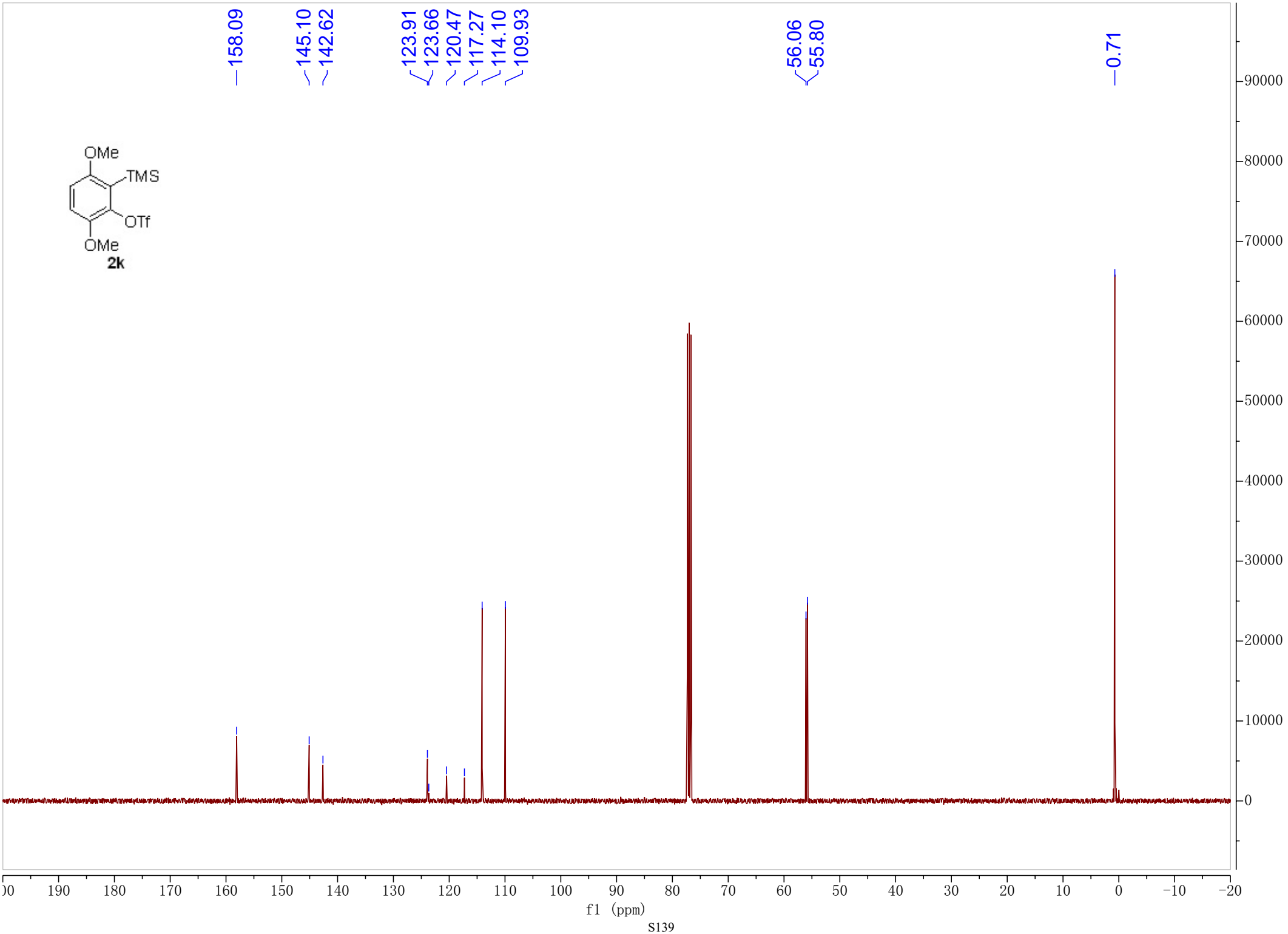
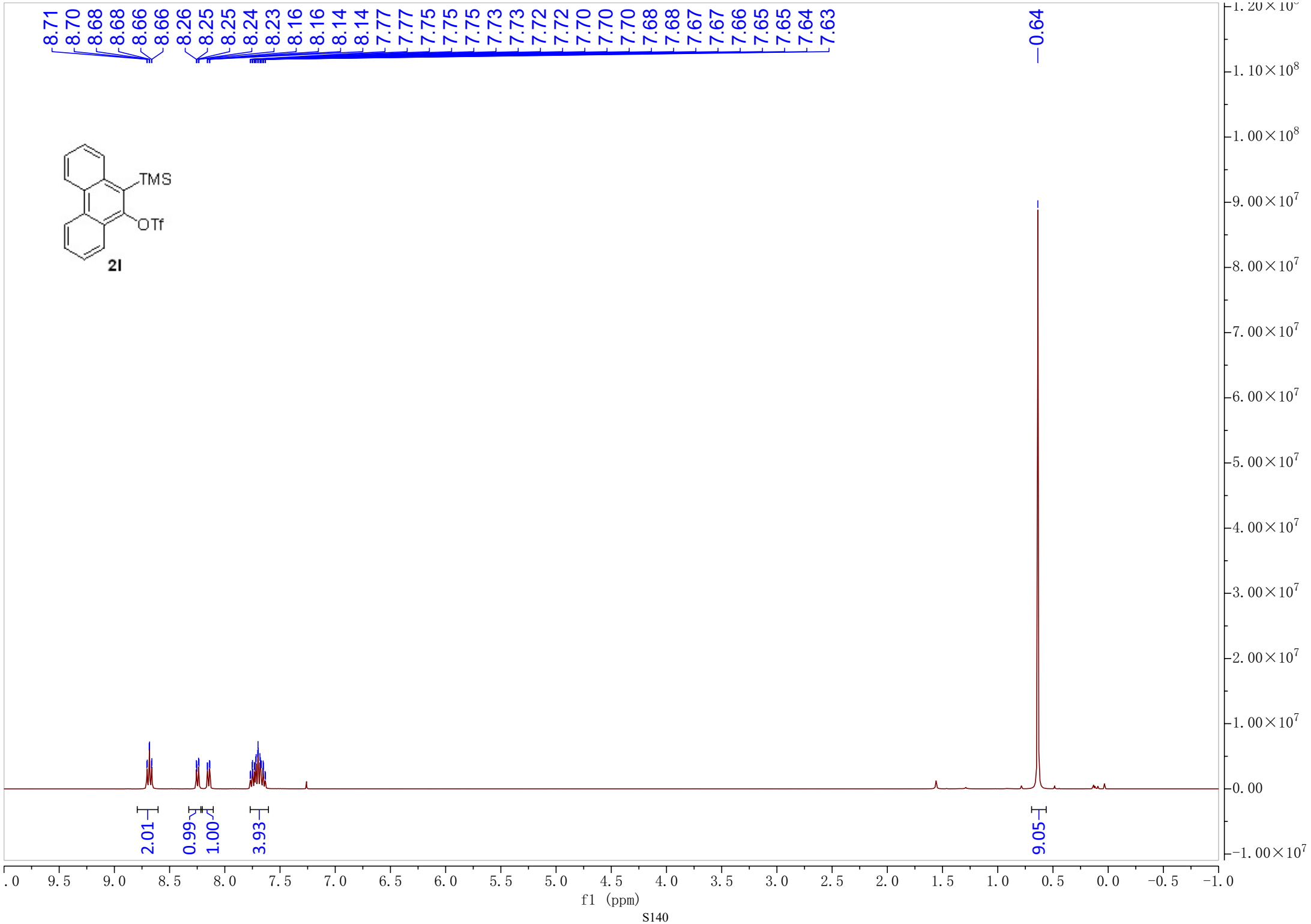
149.54
144.61
135.18
129.37
123.92
120.74
117.81
117.79
117.56
114.38
35.43
35.30
35.14
34.70
32.38
32.10
-0.14
Me Me
TMS
OTf
Me Me
2i
f1 (ppm)

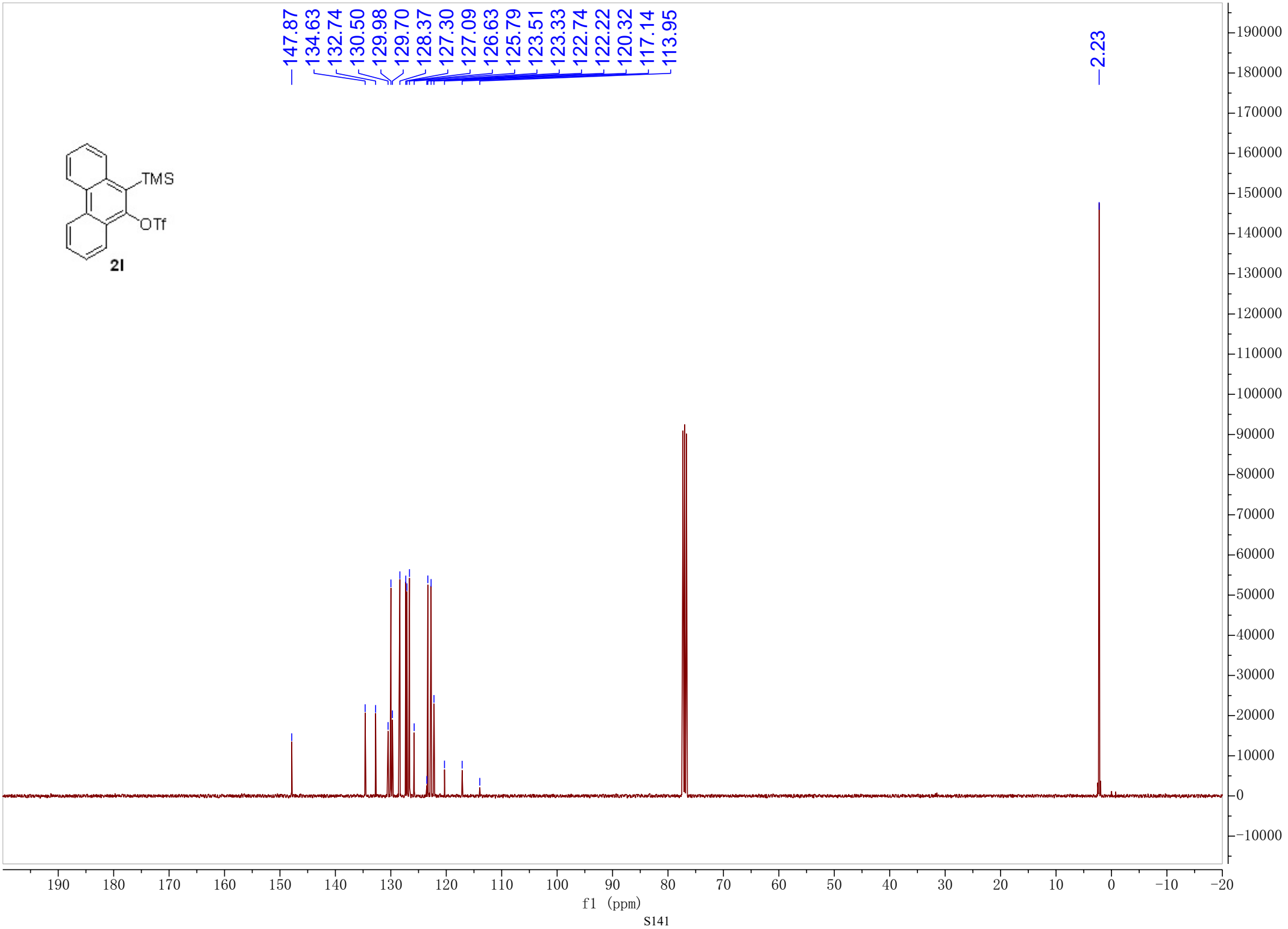

7.18
7.16
7.09
7.07
2.47
2.32
0.44
Me
TMS
OTf
Me
2j
1.00
1.03
3.15
3.20
9.48
f1 (ppm)

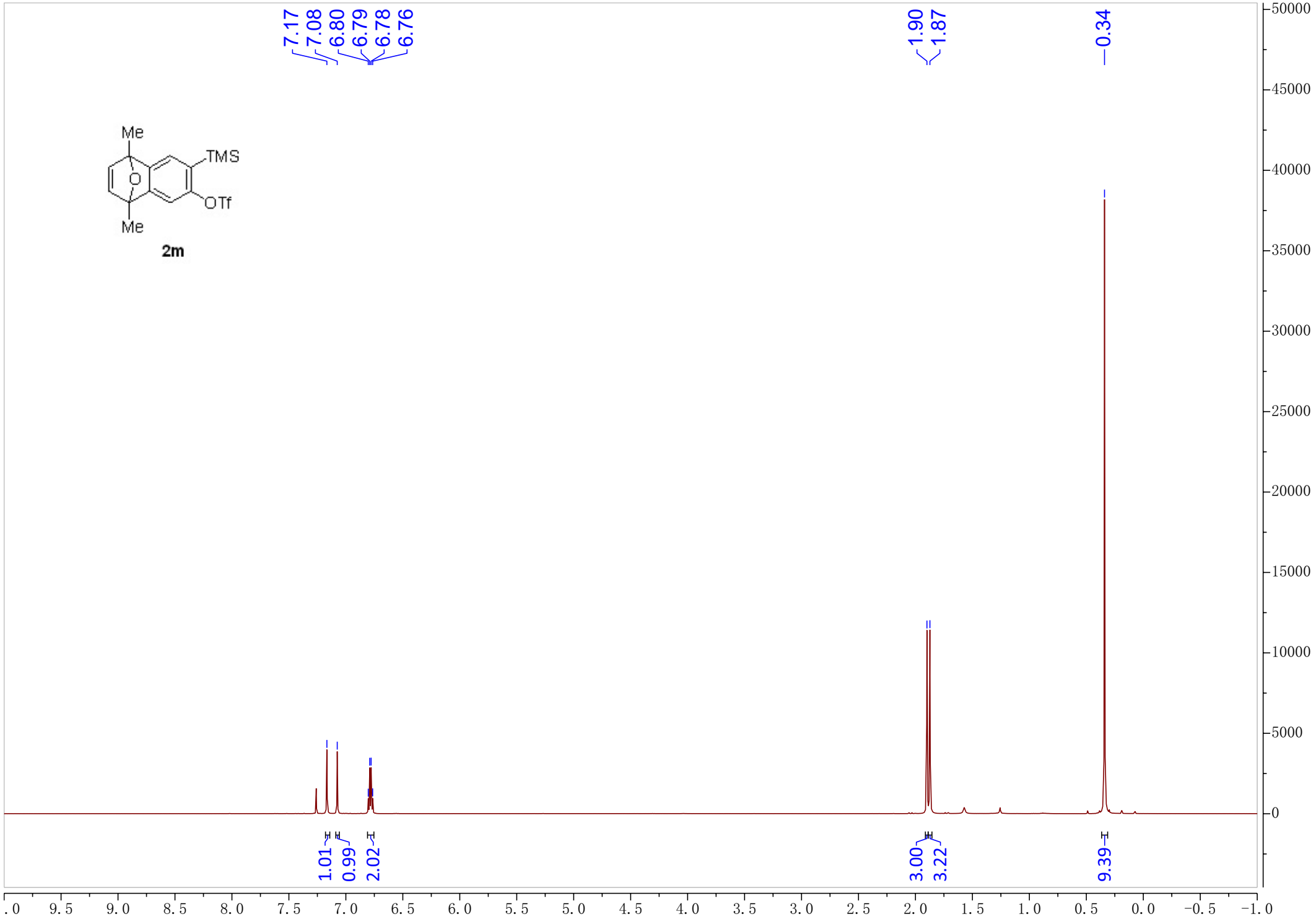

150.33
144.32
133.29
132.93
130.45
128.70
123.37
120.19
117.02
113.84
23.32
16.81
1.73
Me
TMS
OTf
Me
2j
f1 (ppm)

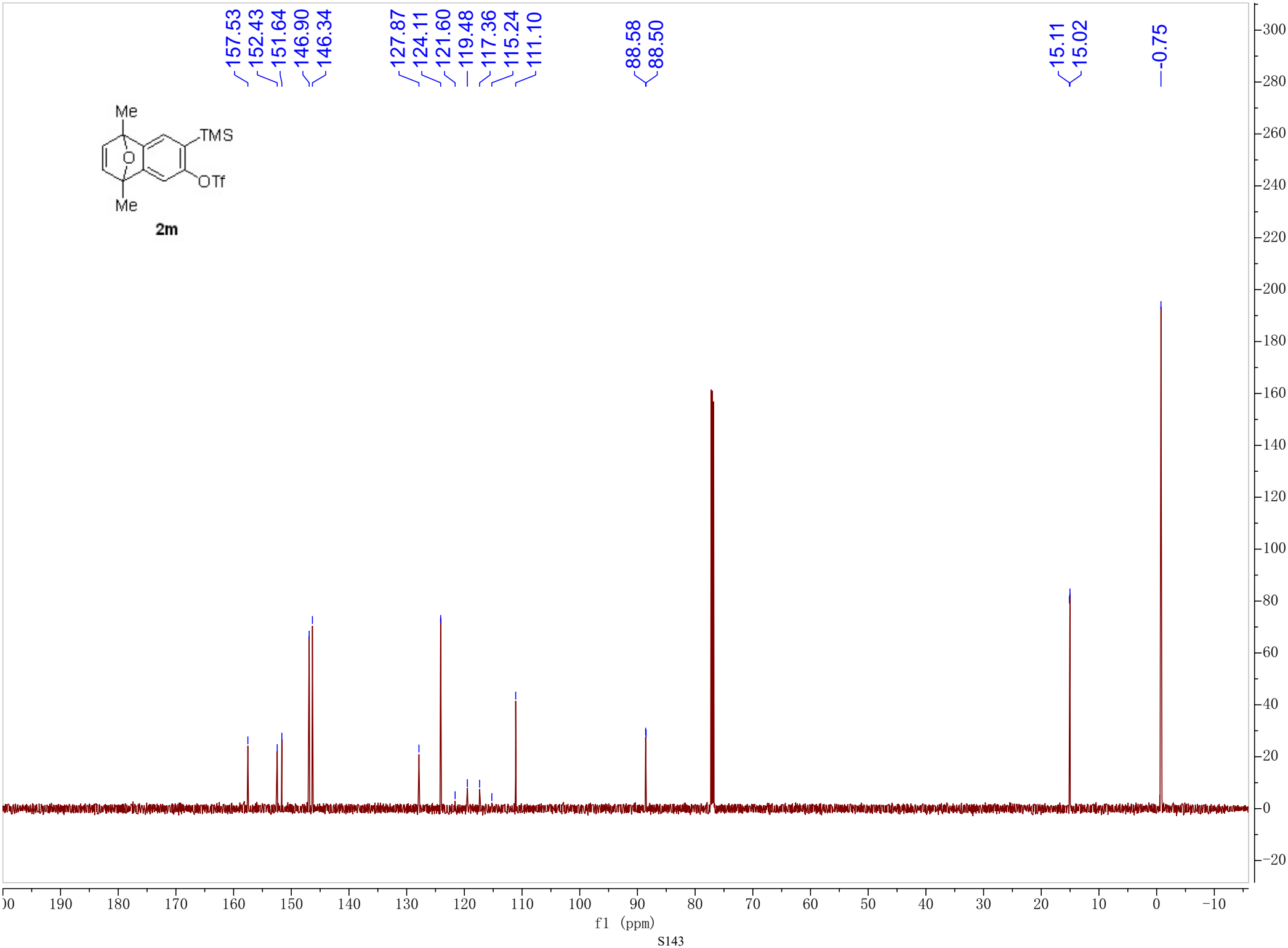

6.97
6.94
6.79
6.77
3.80
3.77
0.38
0.37
OMe
TMS
OTf
OMe
2k
0.98
1.00
2.96
2.86
9.07
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
f1 (ppm)


158.09
145.10
142.62
123.91
123.66
120.47
117.27
114.10
109.93
56.06
55.80
0.71
OMe
TMS
OTf
OMe
2k
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


8.71
8.70
8.68
8.68
8.66
8.66
8.26
8.25
8.25
8.24
8.23
8.16
8.16
8.14
8.14
7.77
7.77
7.75
7.75
7.75
7.73
7.73
7.72
7.72
7.70
7.70
7.70
7.68
7.68
7.67
7.67
7.66
7.65
7.65
7.64
7.63
0.64
TMS
OTf
2l
2.01
0.99
1.00
3.93
9.05
f1 (ppm)


147.87
134.63
132.74
130.50
129.98
129.70
128.37
127.30
127.09
126.63
125.79
123.51
123.33
122.74
122.22
120.32
117.14
113.95
2.23
TMS
OTf
2l
f1 (ppm)


7.17
7.08
6.80
6.79
6.78
6.76
1.90
1.87
0.34
Me
TMS
O
OTf
Me
2m
1.01
0.99
2.02
3.00
3.22
9.39
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
f1 (ppm)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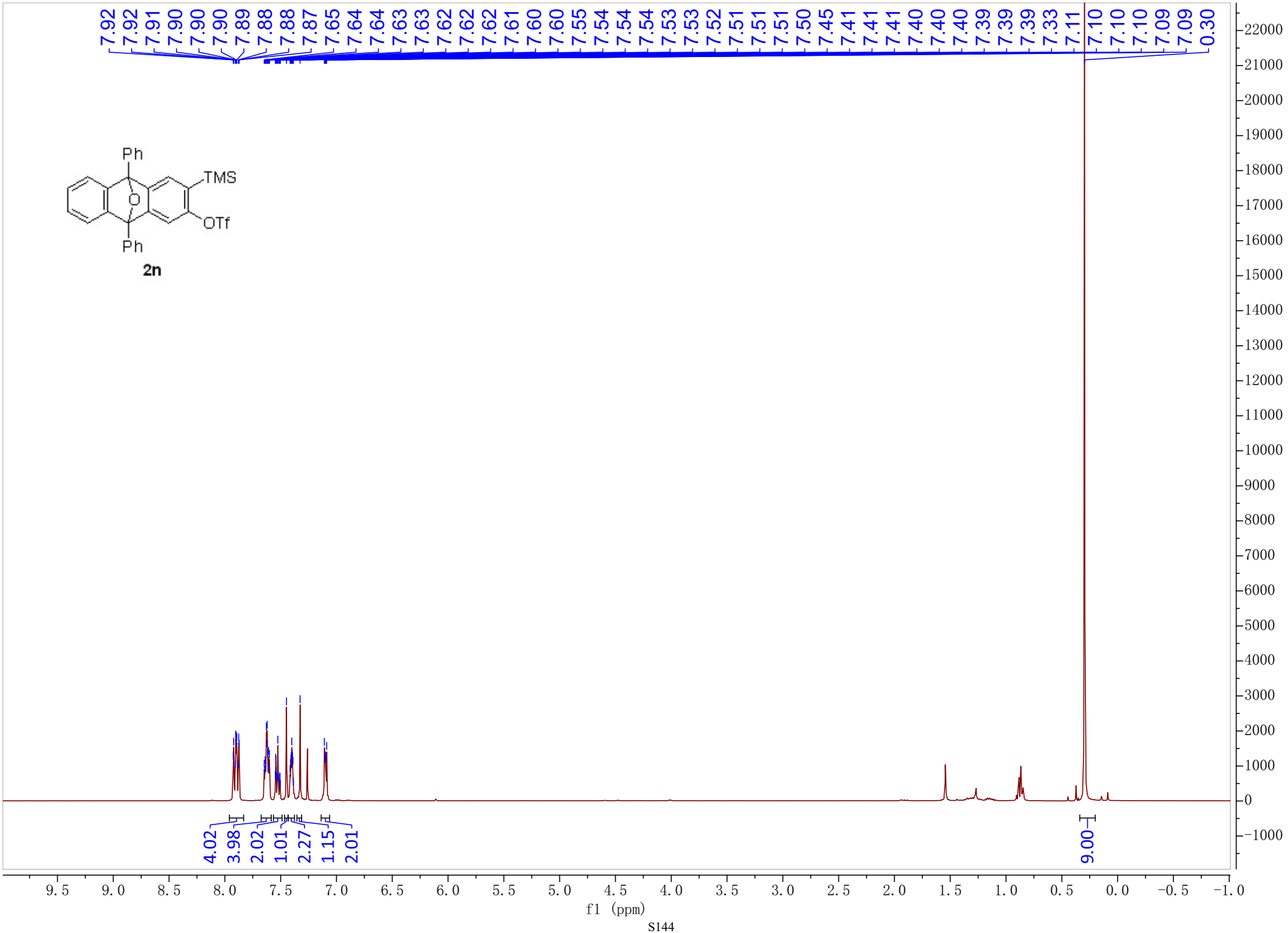
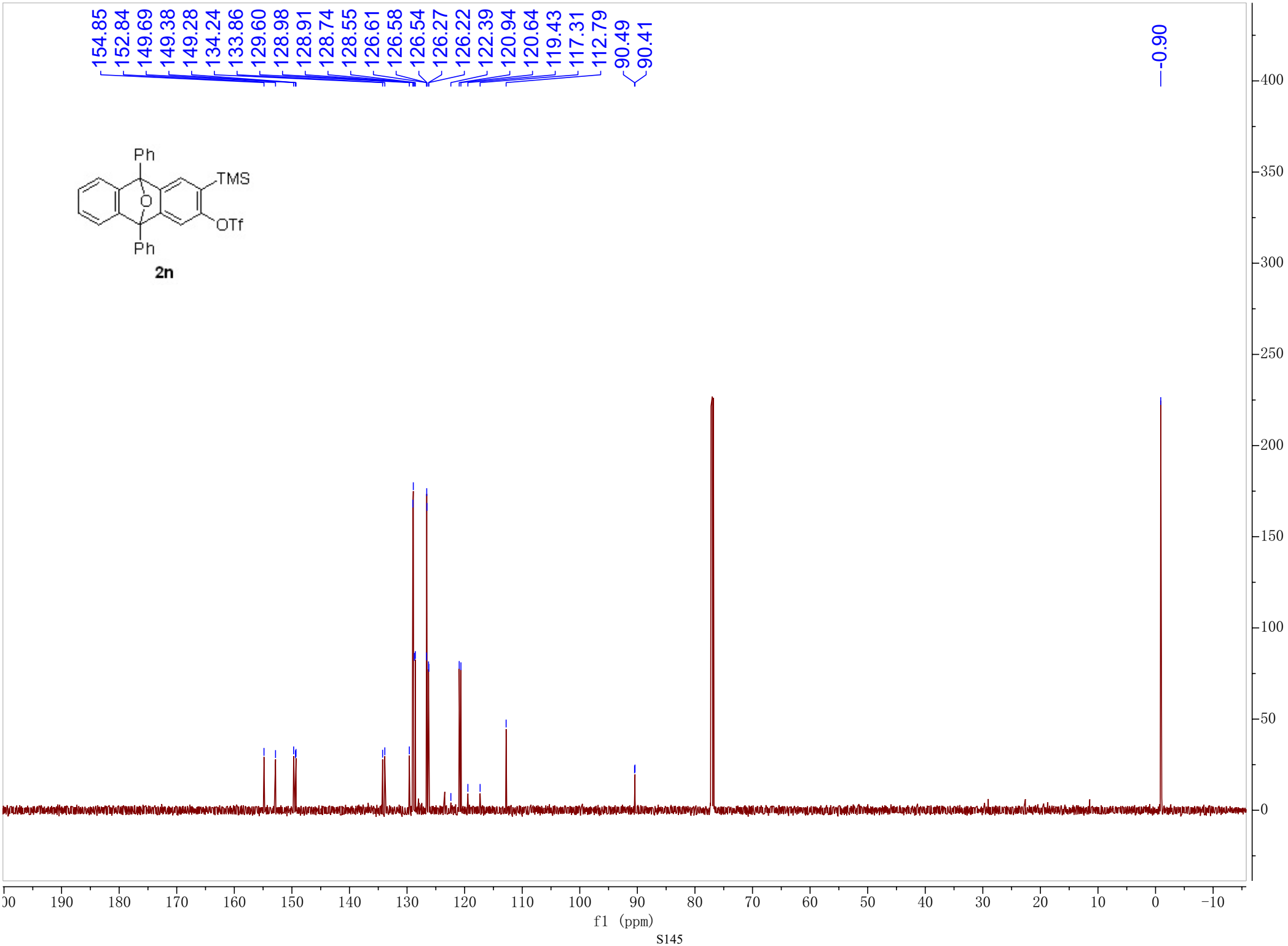
152.43
151.64
146.90
146.34
127.87
124.11
121.60
119.48
117.36
115.24
111.10
88.58
88.50
15.11
15.02
-0.75
Me
TMS
O
OTf
Me
2m
f1 (ppm)


7.92 7.92 7.91 7.90 7.90 7.90 7.89 7.88 7.88 7.87 7.65 7.64 7.64 7.63 7.63 7.62 7.62 7.62 7.61 7.60 7.60 7.55 7.54 7.54 7.54 7.53 7.53 7.52 7.51 7.51 7.51 7.50 7.45 7.41 7.41 7.41 7.40 7.40 7.40 7.39 7.39 7.39 7.33 7.11 7.10 7.10 7.10 7.09 7.09 0.30
Ph
TMS
O
OTf
Ph
2n
4.02 3.98 2.02 1.01 2.27 1.15 2.01
9.00
f1 (ppm)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149.28
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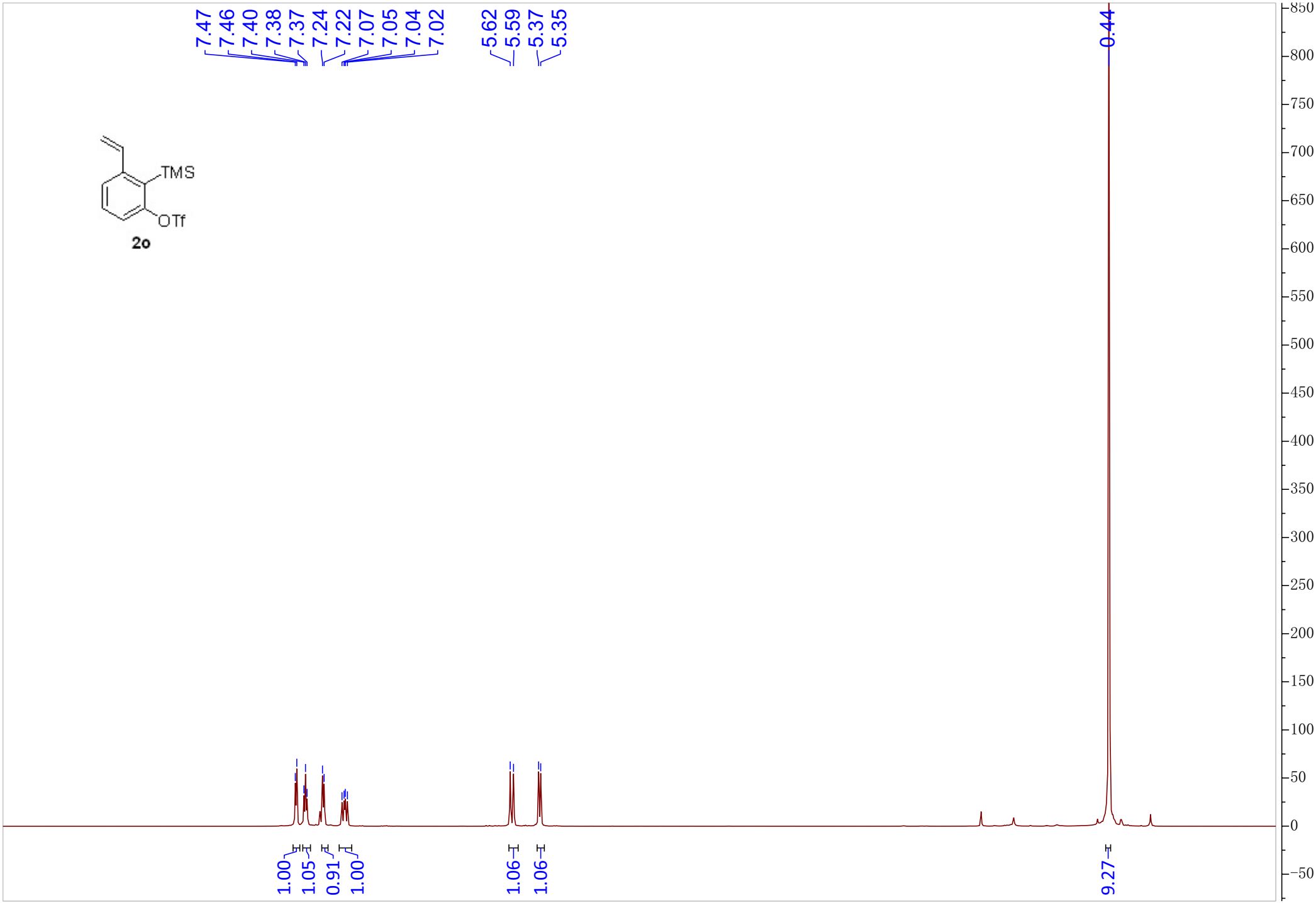
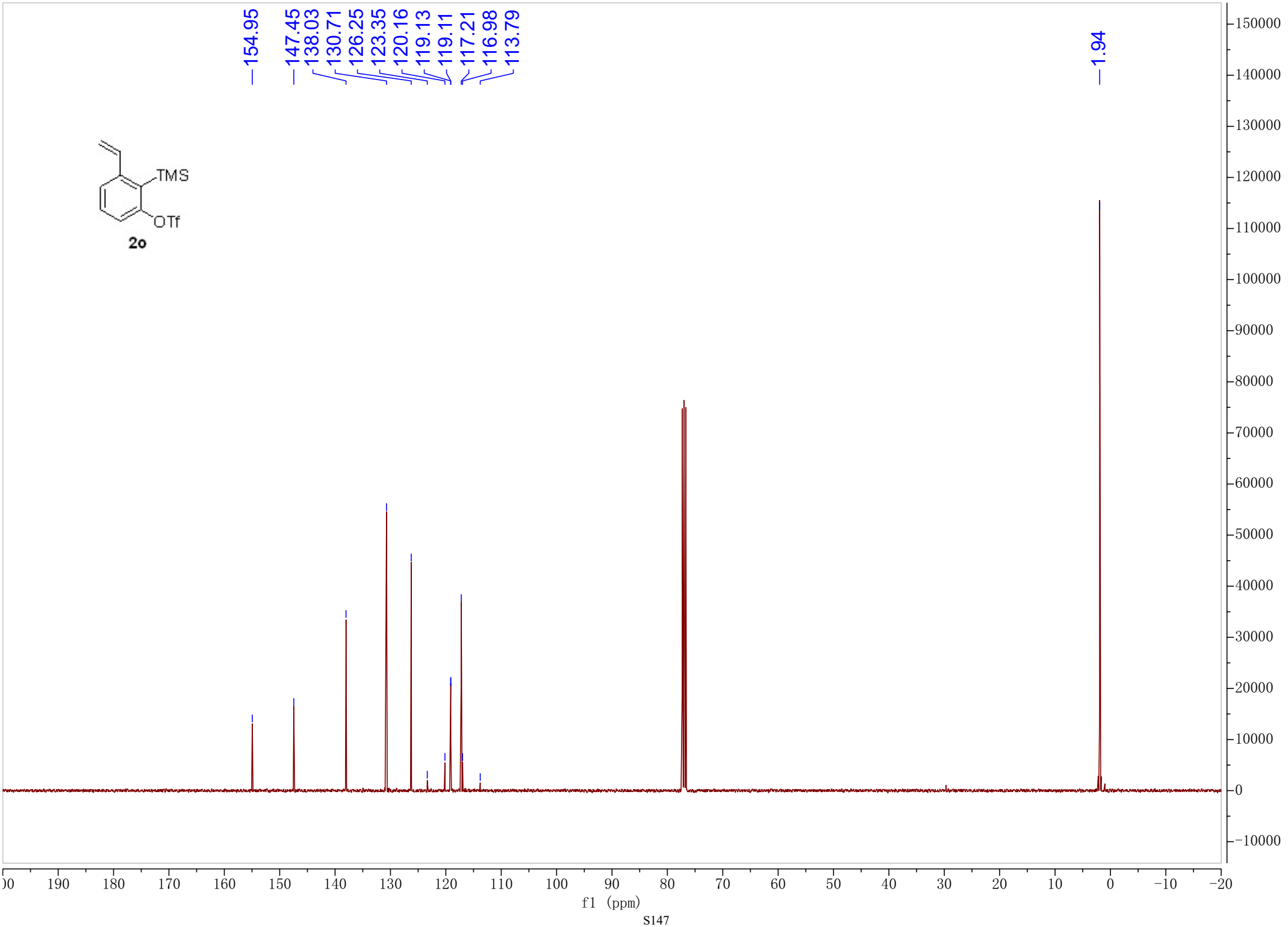
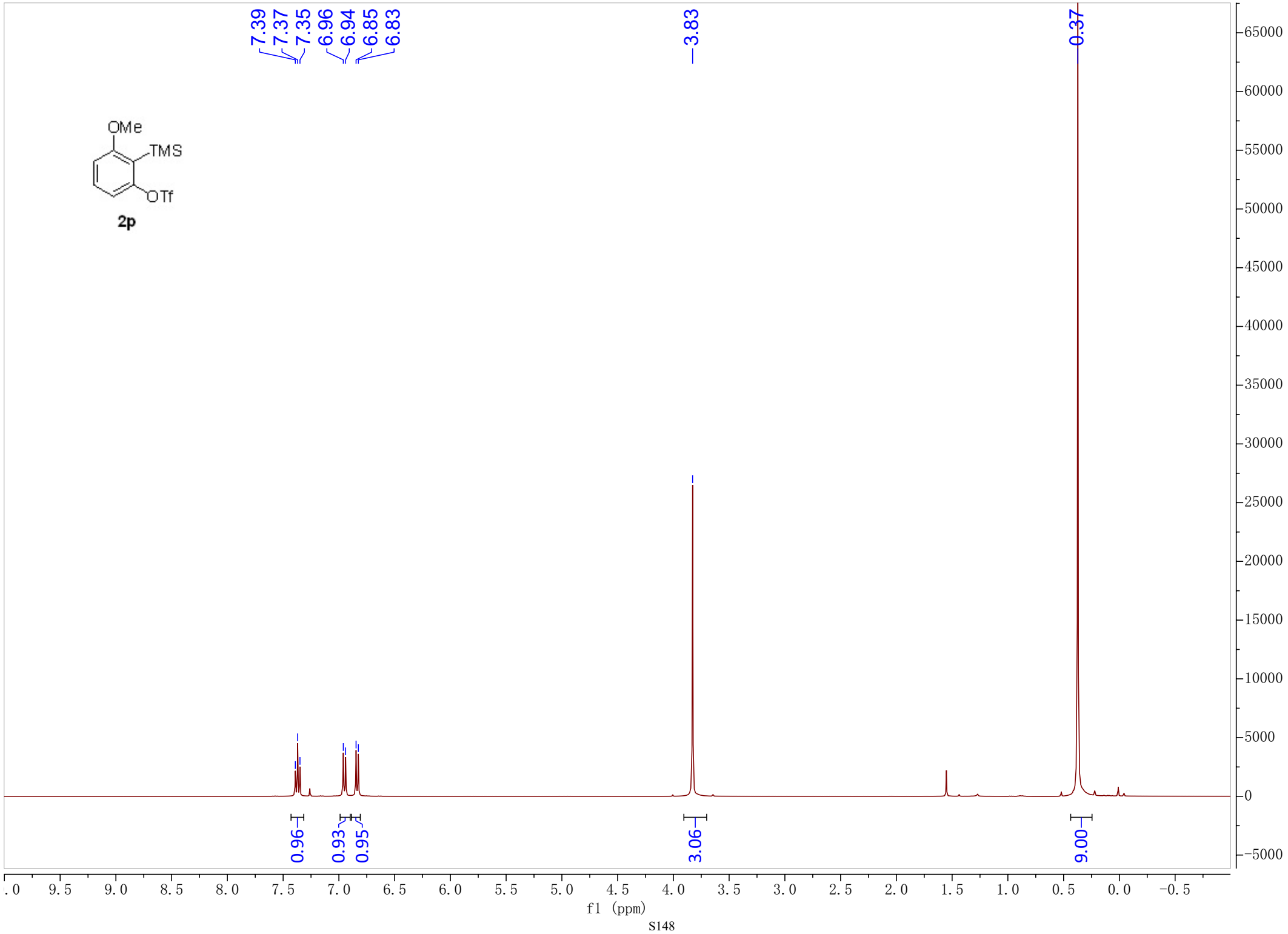
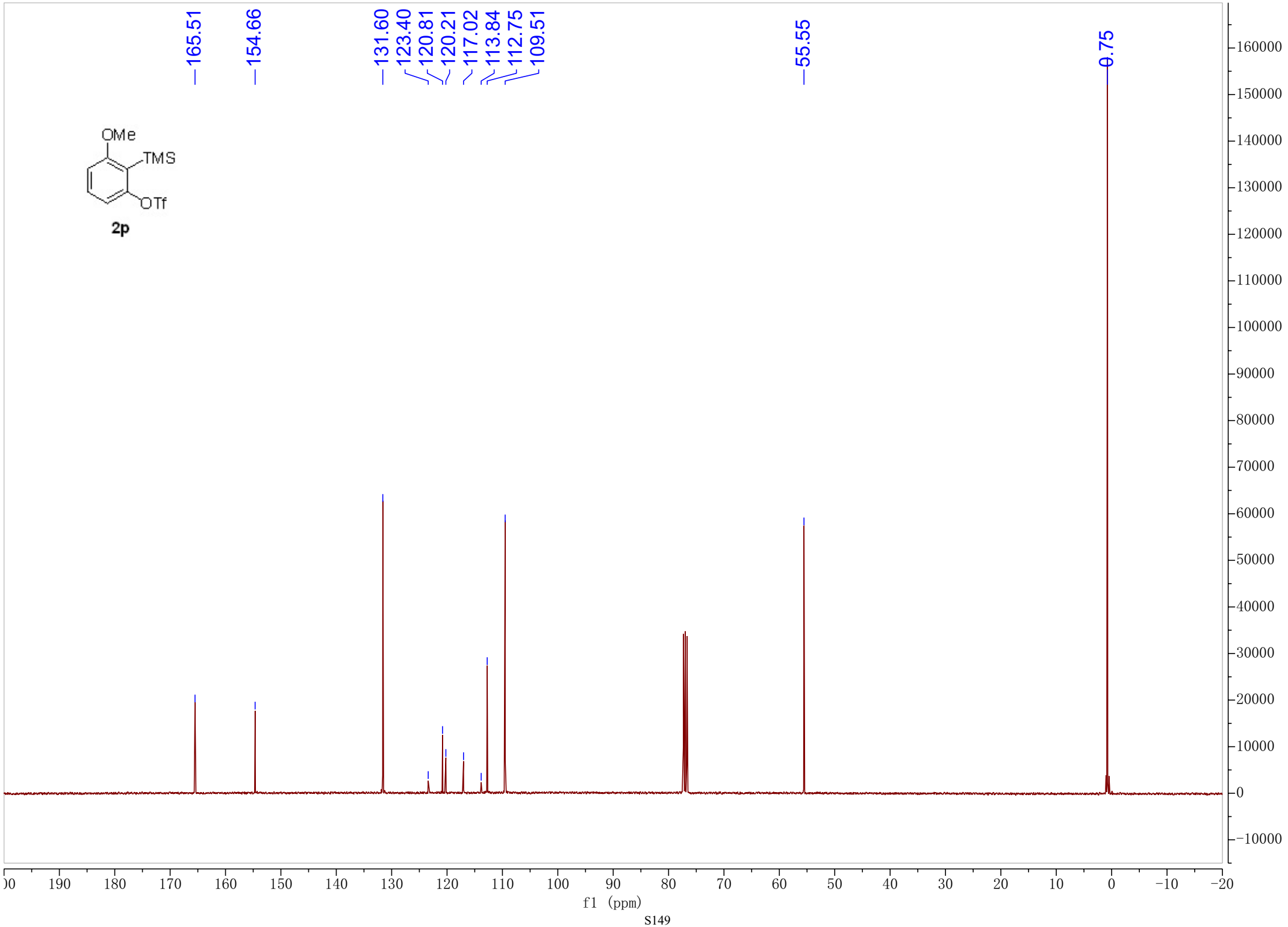
133.86
129.60
128.98
128.91
128.74
128.55
126.61
126.58
126.54
126.27
126.22
122.39
120.94
120.64
119.43
117.31
112.79
90.49
90.41
-0.90
Ph
TMS
O
OTf
Ph
2n
400
350
300
250
200
150
100
50
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.47
7.46
7.40
7.38
7.37
7.24
7.22
7.07
7.05
7.04
7.02
5.62
5.59
5.37
5.35
0.44
TMS
OTf
2o
1.00
1.05
0.91
1.00
1.06
1.06
9.27
f1 (ppm)


154.95
147.45
138.03
130.71
126.25
123.35
120.16
119.13
119.11
117.21
116.98
113.79
1.94
TMS
OTf
2o
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
−10000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)


7.39
7.37
7.35
6.96
6.94
6.85
6.83
3.83
0.37
OMe
TMS
OTf
2p
0.96
0.93
0.95
3.06
9.00
f1 (ppm)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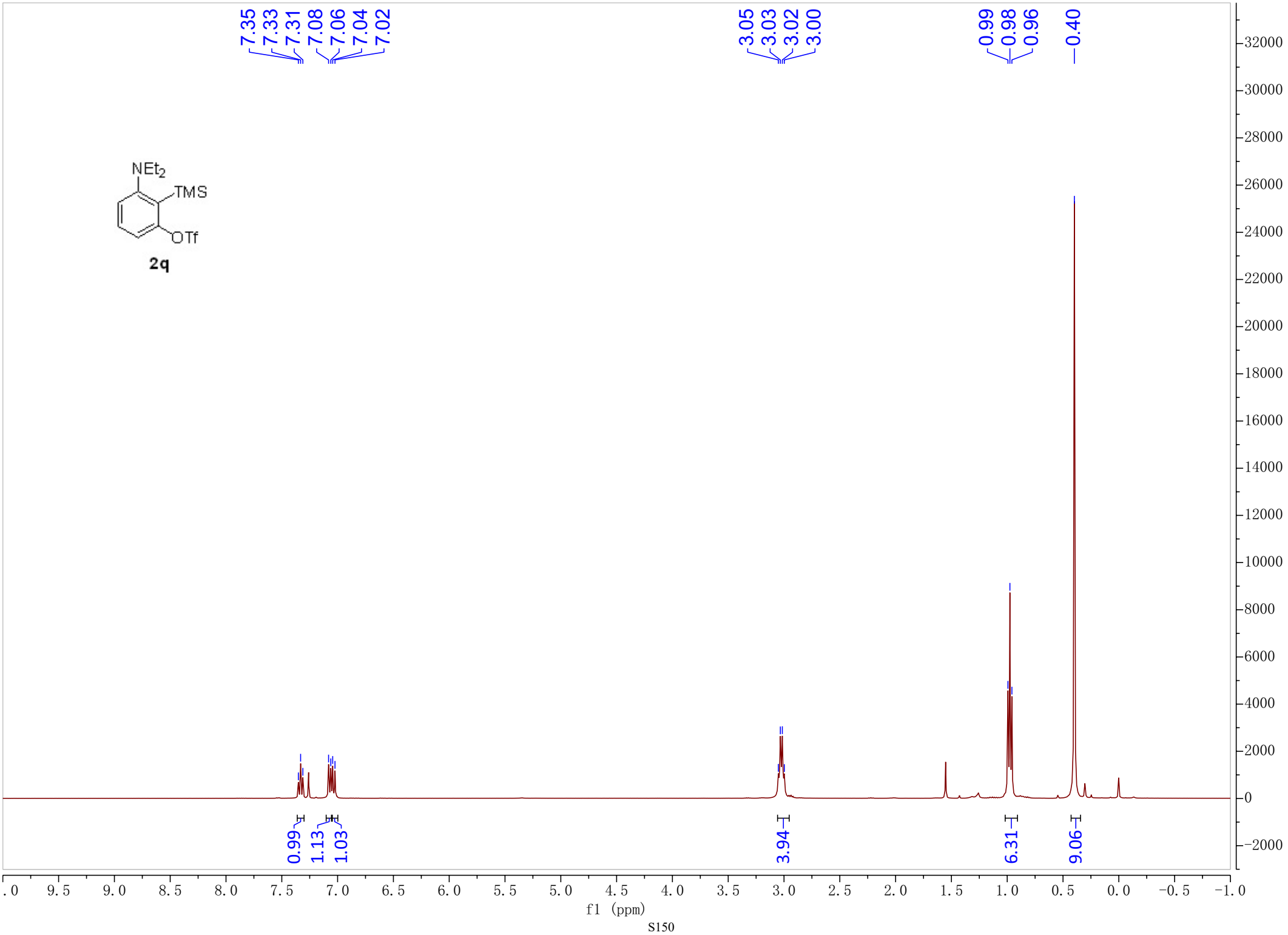
131.60
123.40
120.81
120.21
117.02
113.84
112.75
109.51
55.55
0.75
OMe
TMS
OTf
2p
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
−10000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)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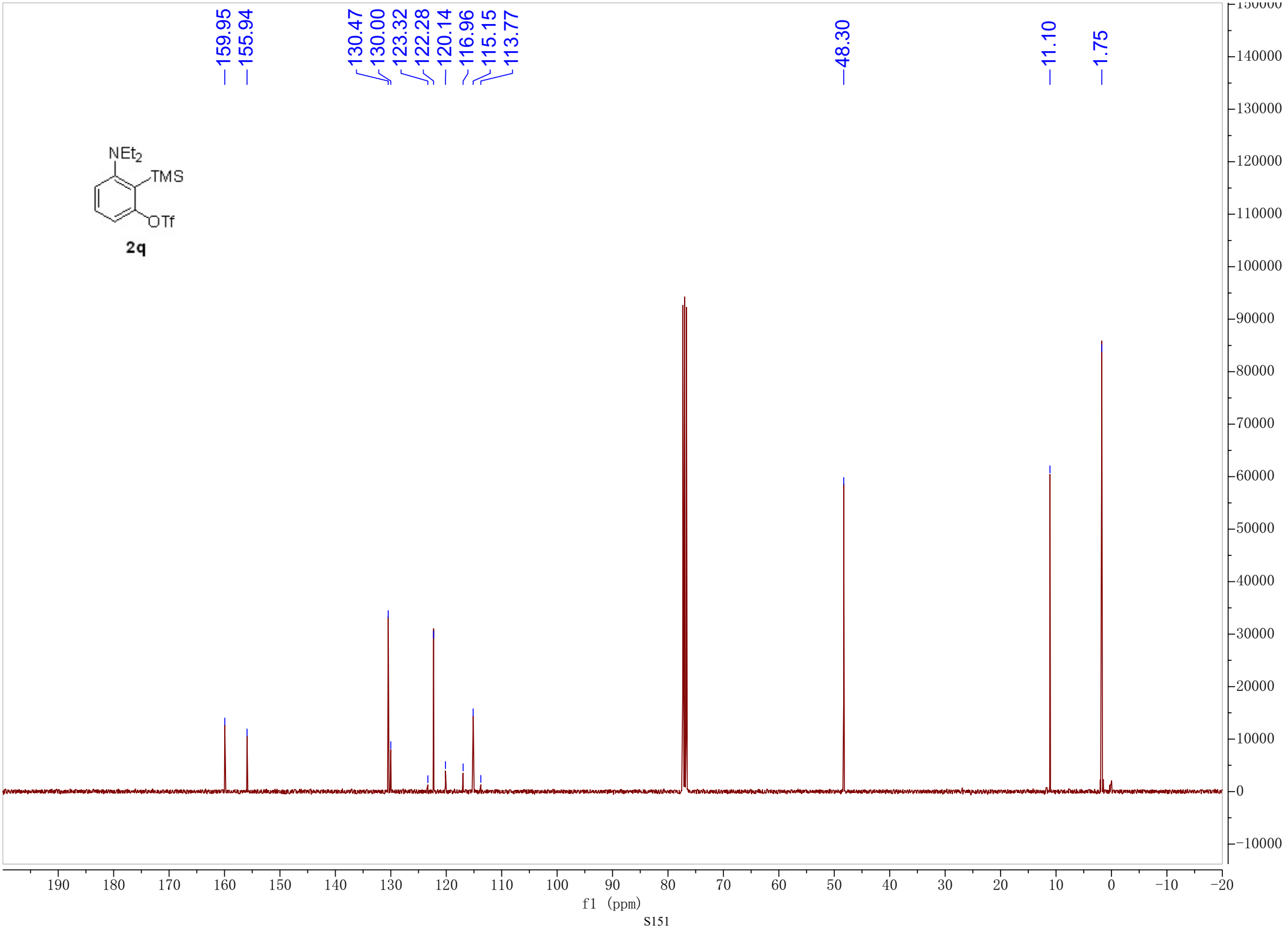
7.33
7.31
7.08
7.06
7.04
7.02
3.05
3.03
3.02
3.00
0.99
0.98
0.96
0.40
NEt2
TMS
OTf
2q
0.99
1.13
1.03
3.94
6.31
9.06
f1 (ppm)


159.95
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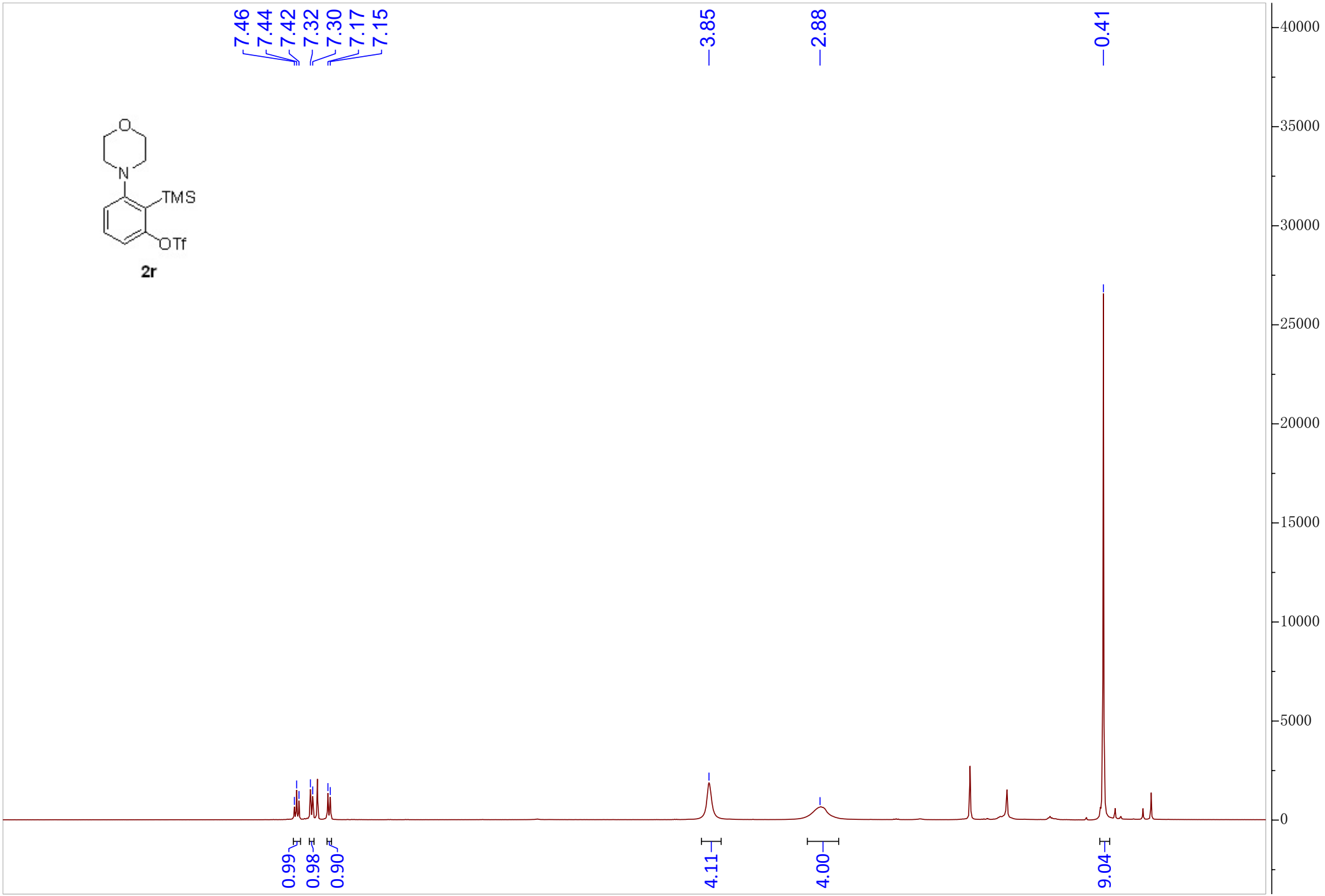
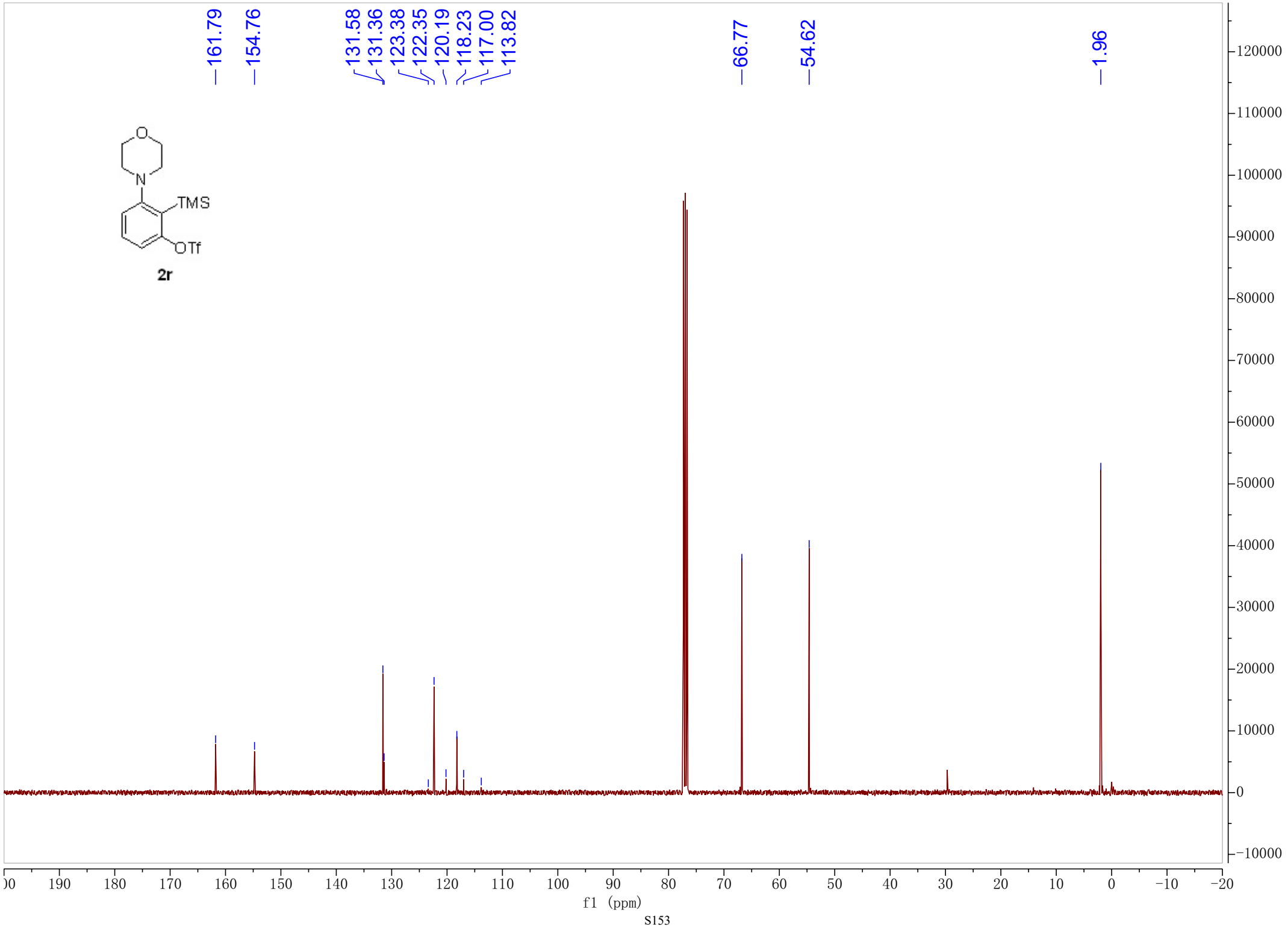
130.00
123.32
122.28
120.14
116.96
115.15
113.77
48.30
11.10
1.75
NEt2
TMS
OTf
2q
f1 (ppm)


7.46
7.44
7.42
7.32
7.30
7.17
7.15
3.85
2.88
0.41
TMS
OTf
2r
0.99
0.98
0.90
4.11
4.00
9.04
f1 (ppm)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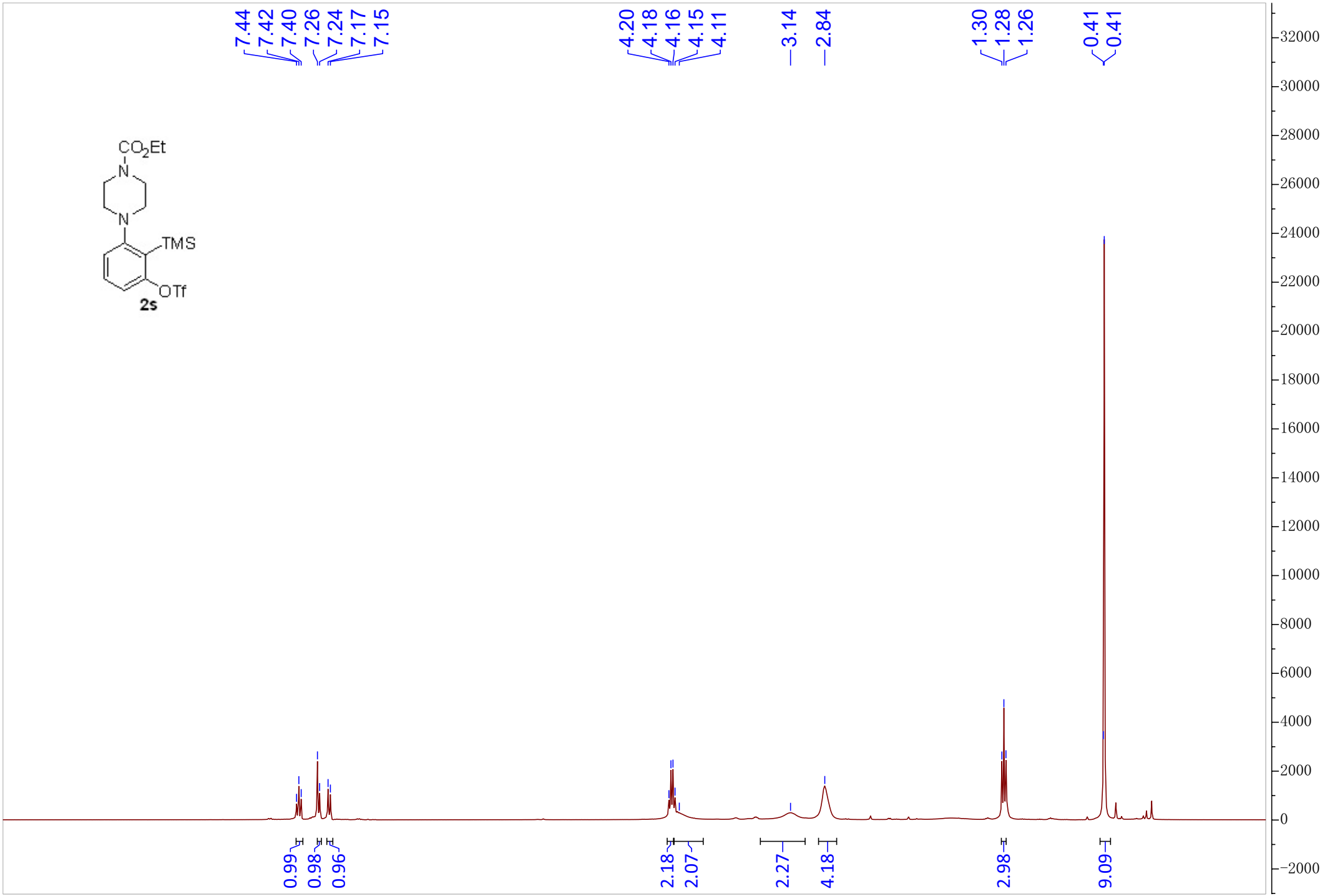
154.76
131.58
131.36
123.38
122.35
120.19
118.23
117.00
113.82
66.77
54.62
1.96
TMS
OTf
2r
f1 (ppm)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7.42
7.40
7.26
7.24
7.17
7.15
4.20
4.18
4.16
4.15
4.11
3.14
2.84
1.30
1.28
1.26
0.41
0.41
CO2Et
N
N
TMS
OTf
2s
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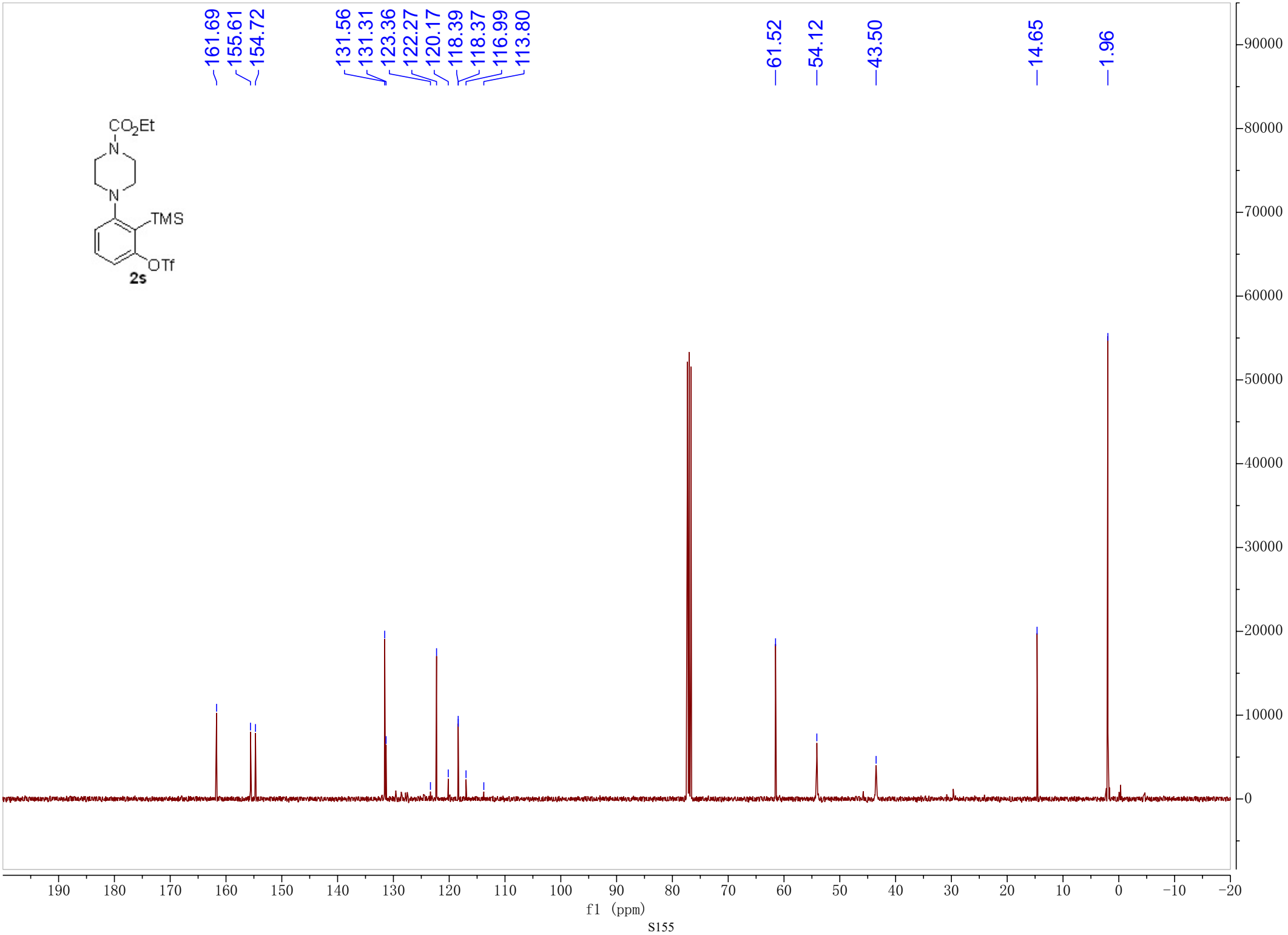
0.98
0.96
2.18
2.07
2.27
4.18
2.98
9.09
f1 (ppm)


161.69
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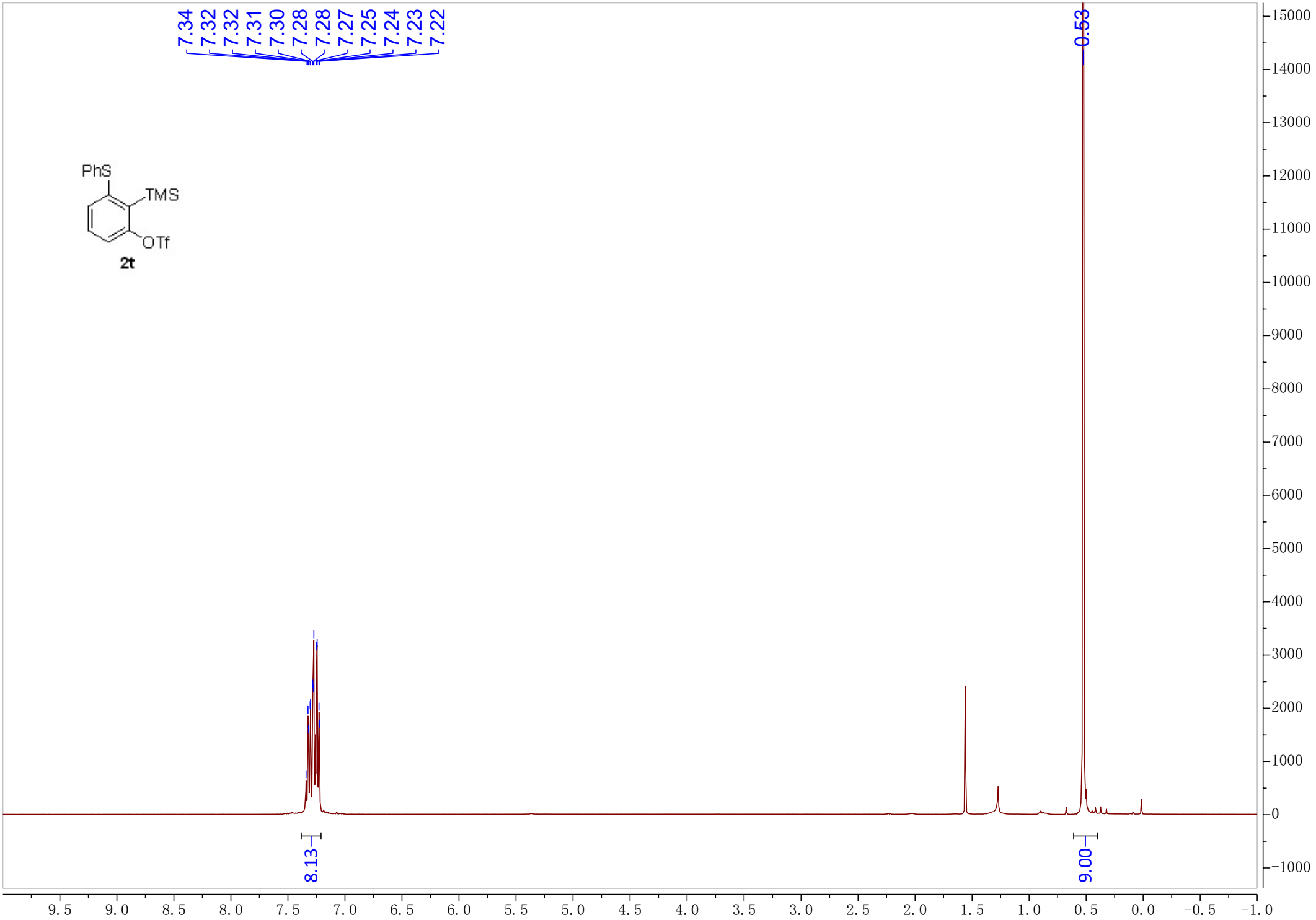
123.36
122.27
120.17
118.39
118.37
116.99
113.80
61.52
54.12
43.50
14.65
1.96
CO2Et
N
N
TMS
OTf
2s
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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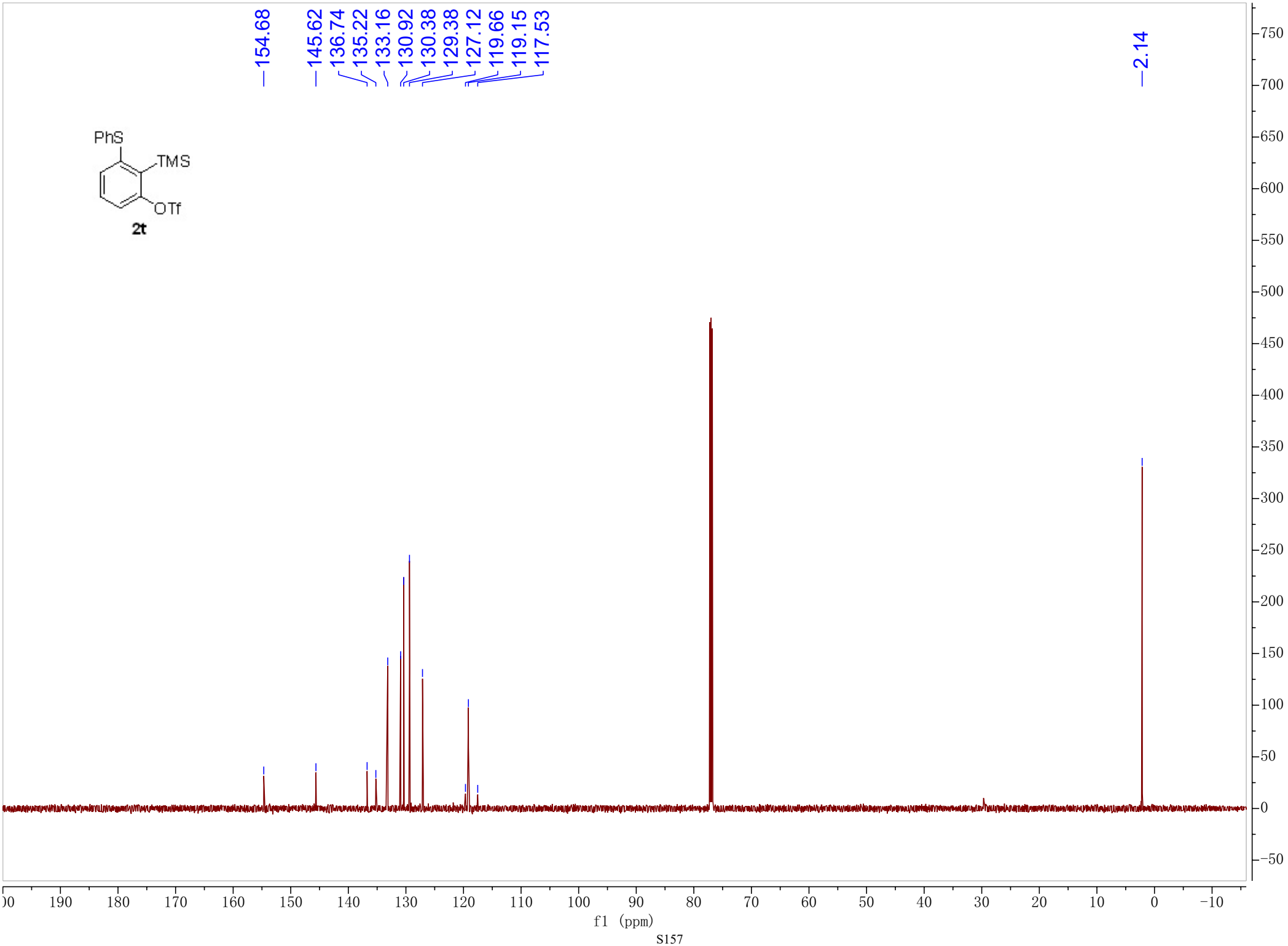
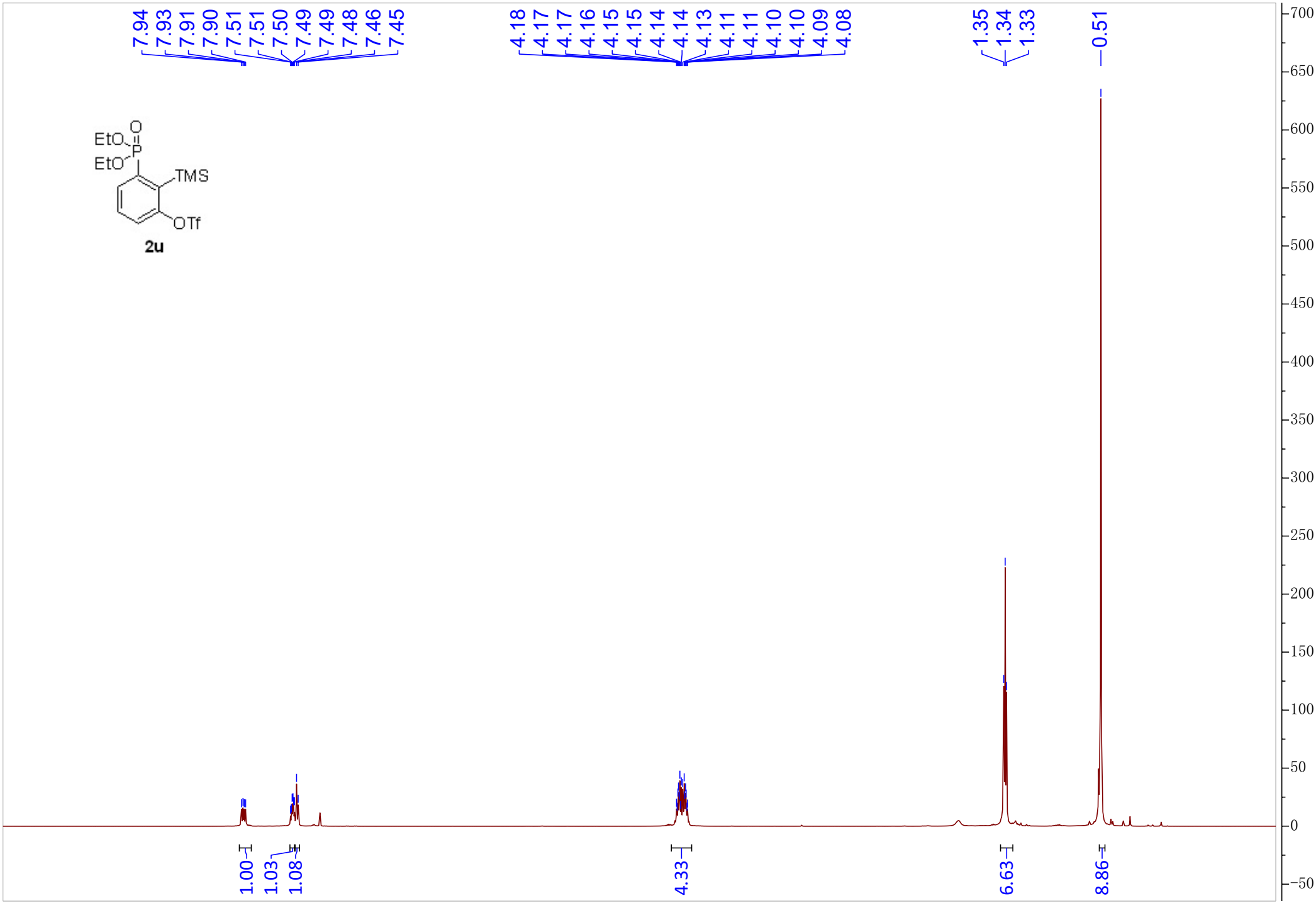
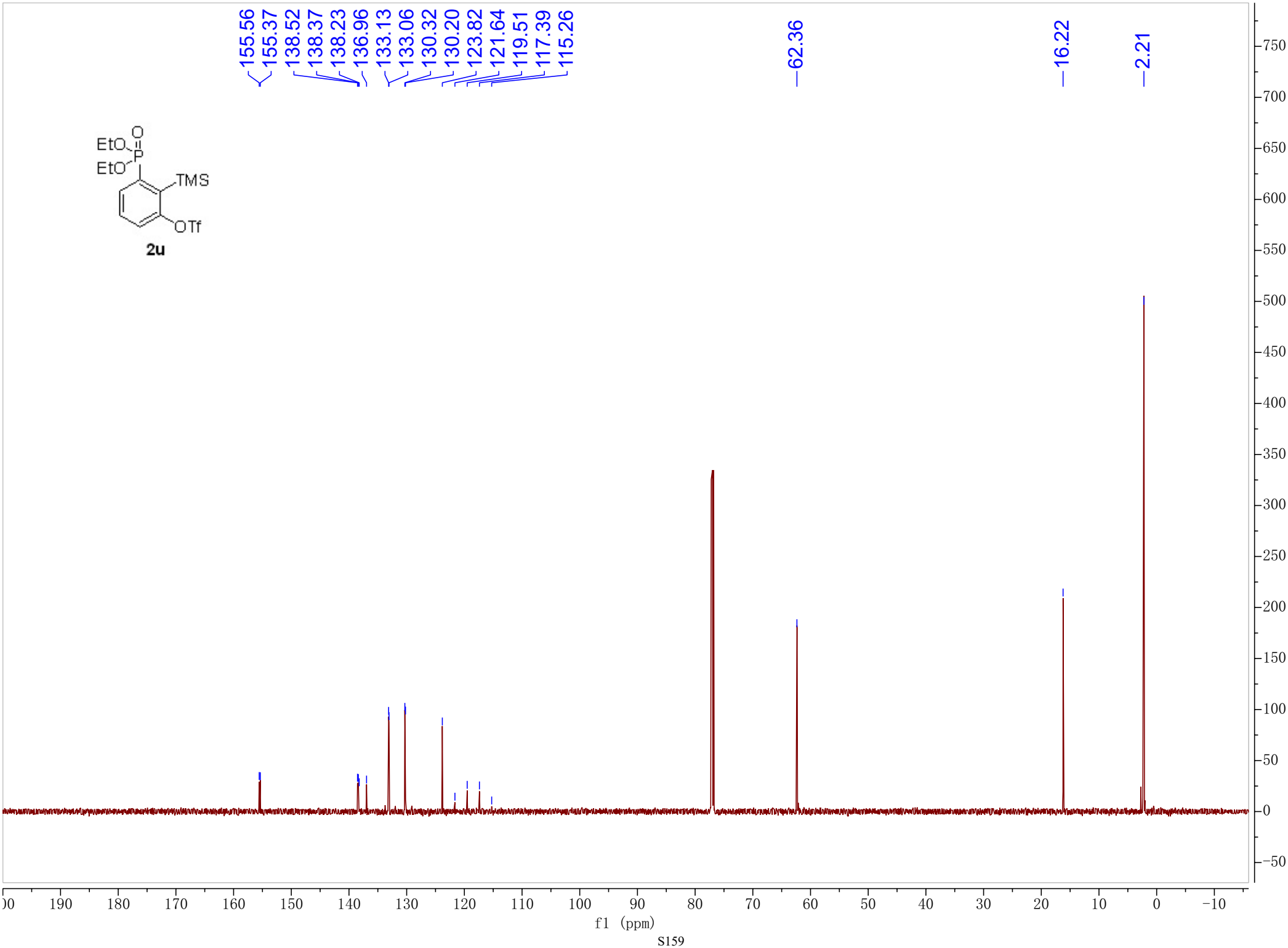
7.32
7.32
7.31
7.30
7.28
7.28
7.27
7.25
7.24
7.23
7.22
0.53
PhS
TMS
OTf
2t
8.13
9.00
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f1 (ppm)


154.68
145.62
136.74
135.22
133.16
130.92
130.38
129.38
127.12
119.66
119.15
117.53
2.14
PhS
TMS
OTf
2t
f1 (ppm)


7.94
7.93
7.91
7.90
7.51
7.51
7.50
7.49
7.49
7.48
7.46
7.45
4.18
4.17
4.17
4.16
4.15
4.15
4.14
4.14
4.13
4.11
4.11
4.10
4.10
4.09
4.08
1.35
1.34
1.33
0.51
EtO
EtO
O
P
TMS
OTf
2u
1.00
1.03
1.08
4.33
6.63
8.86
f1 (ppm)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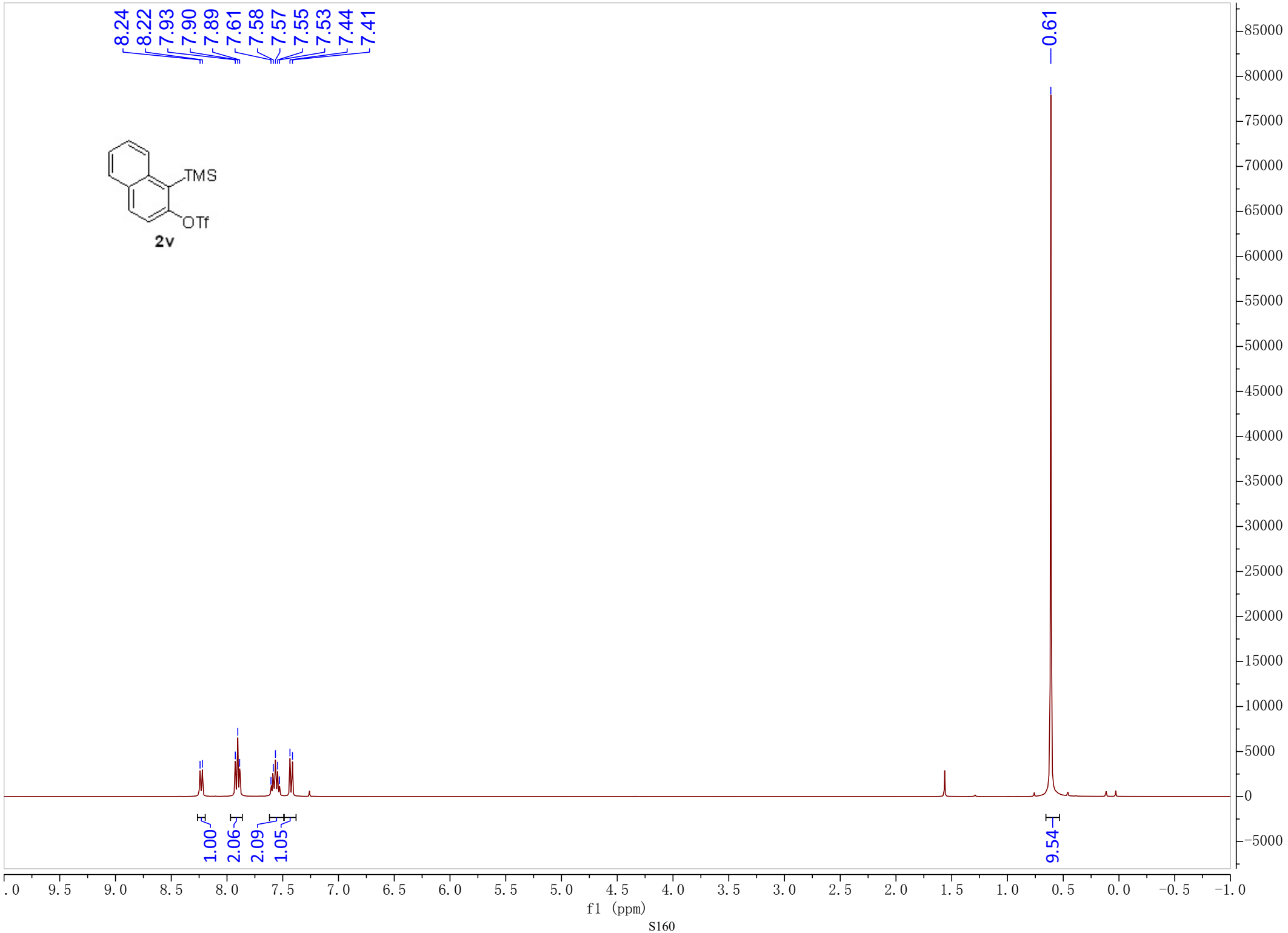
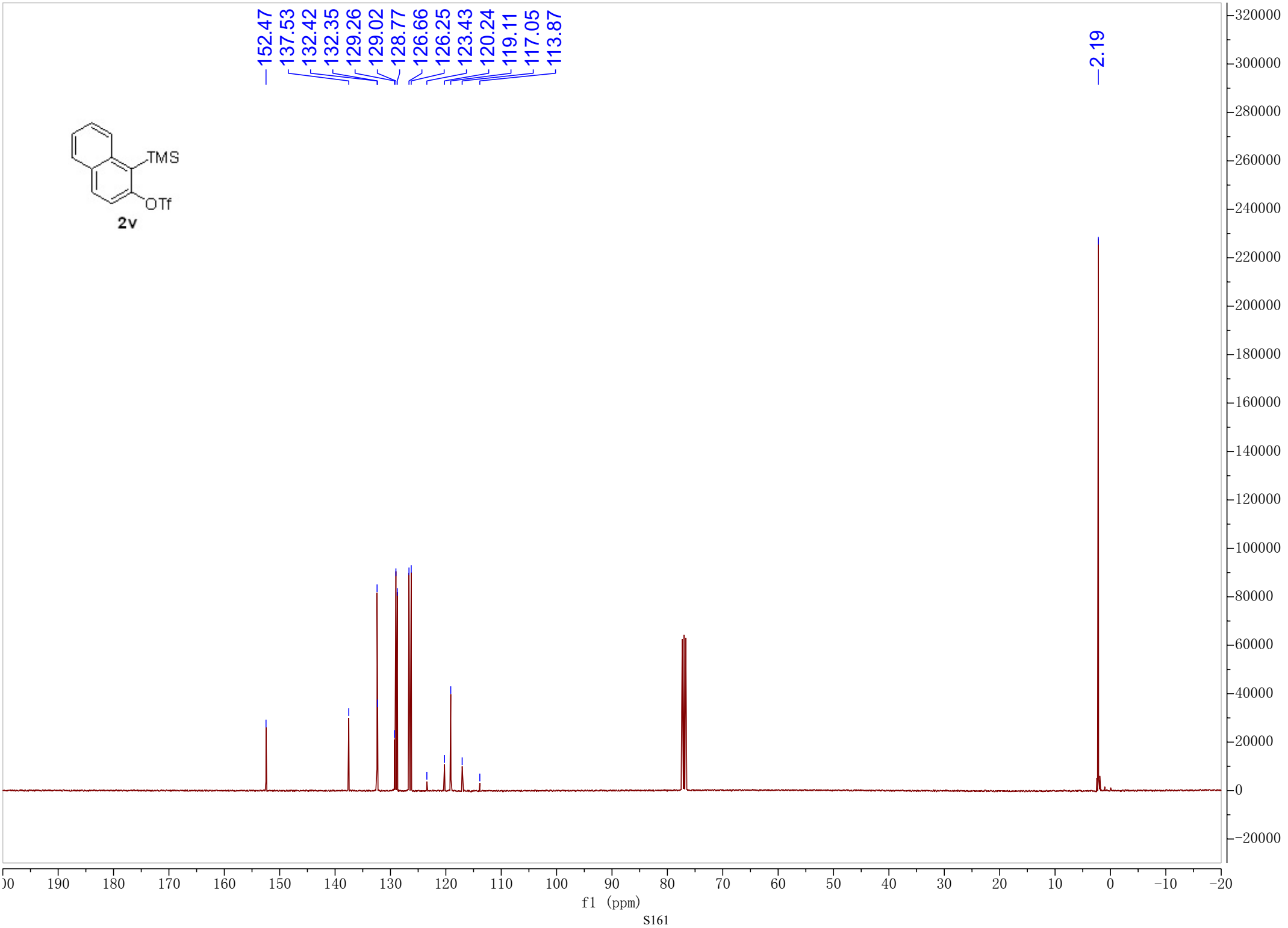
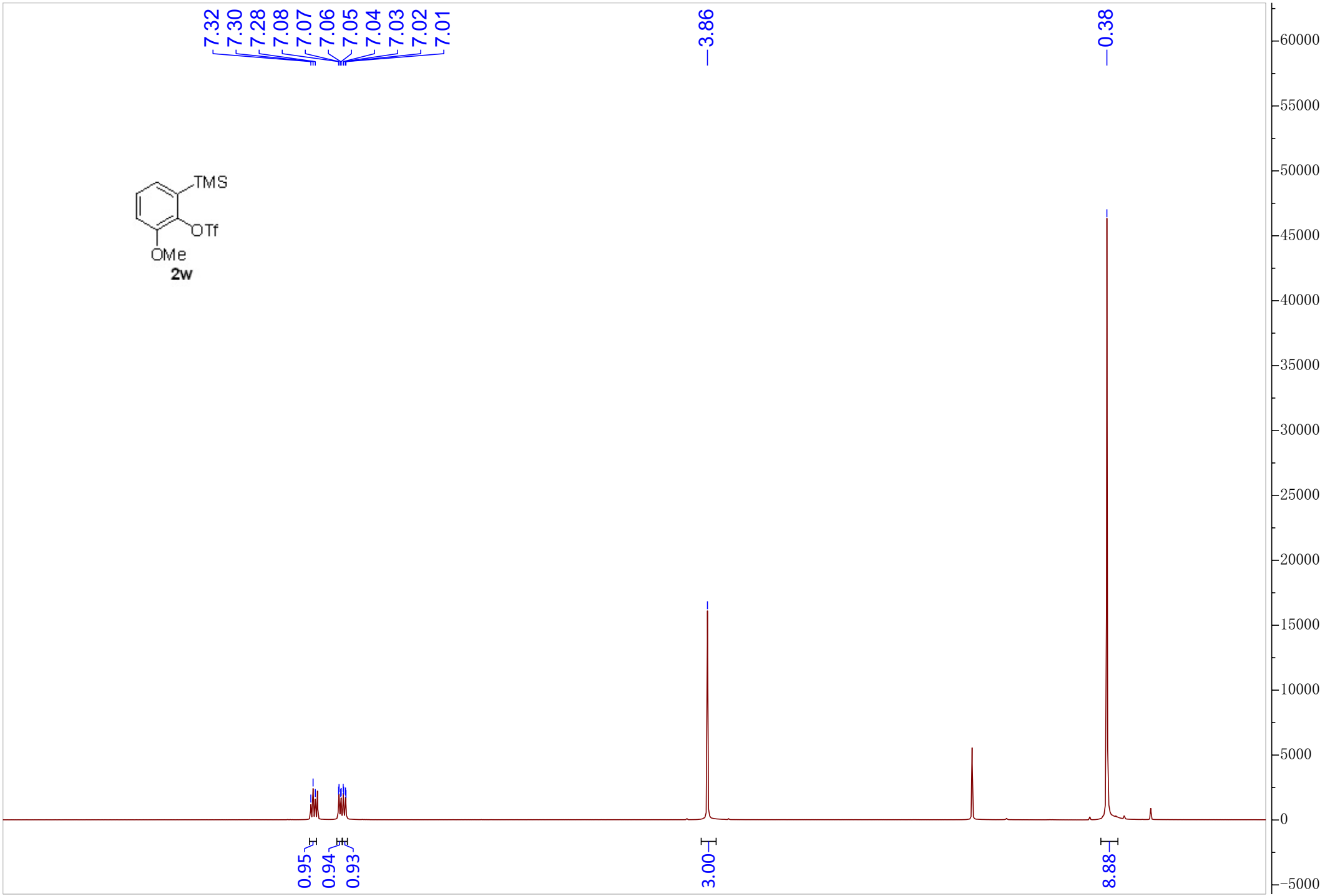
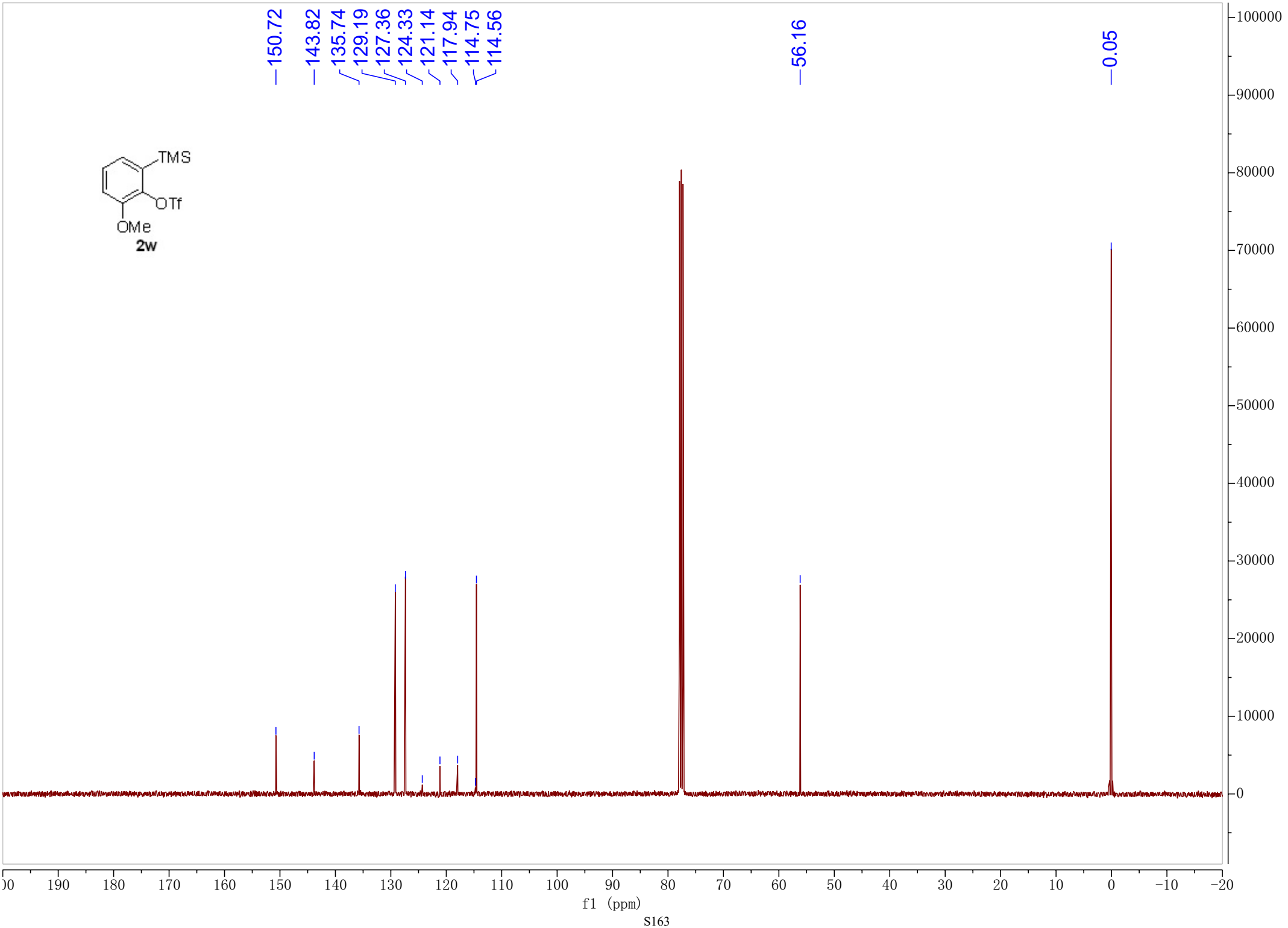
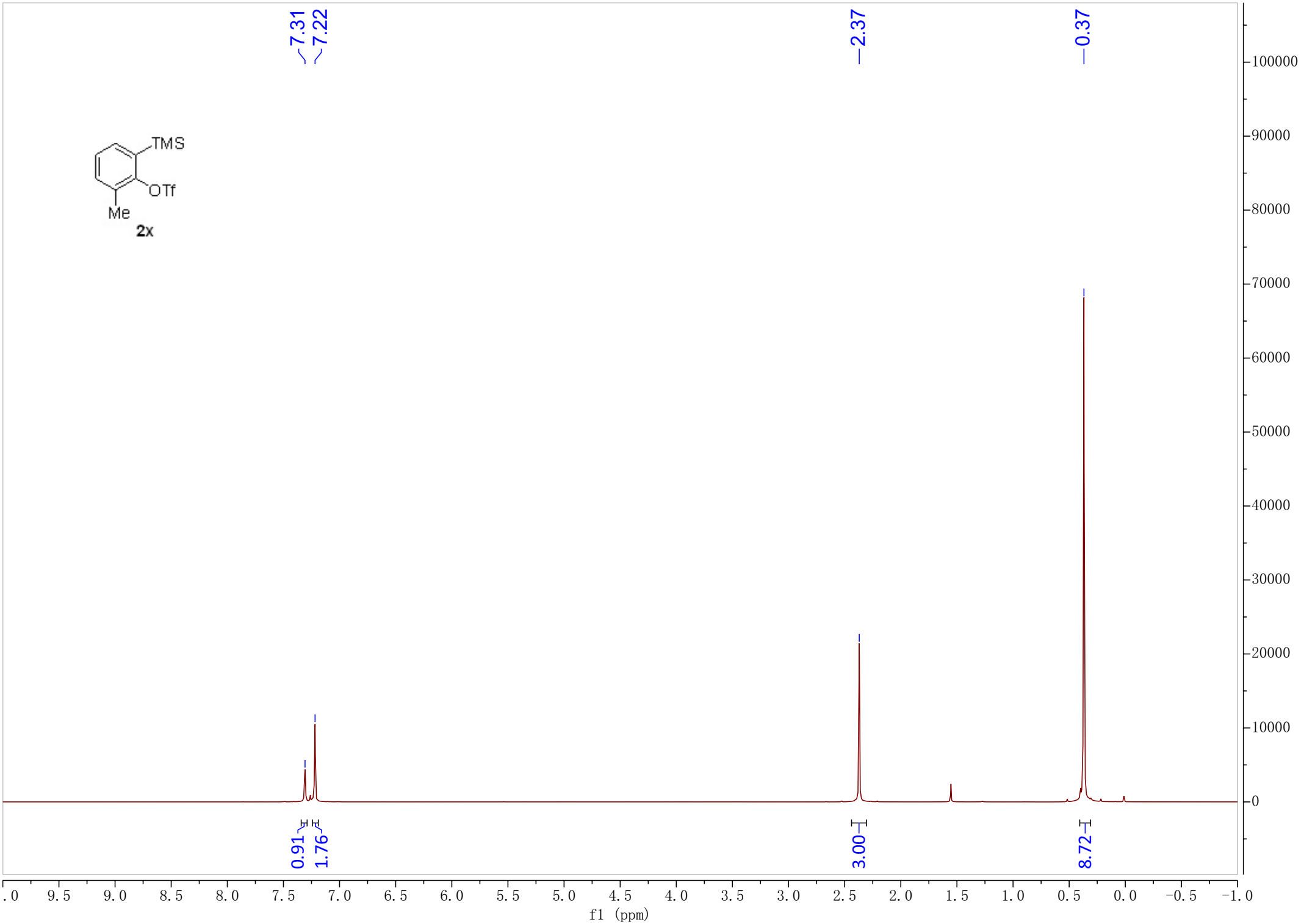
155.37
138.52
138.37
138.23
136.96
133.13
133.06
130.32
130.20
123.82
121.64
119.51
117.39
115.26
62.36
16.22
2.21
EtO
EtO
P
O
TMS
OTf
2u
f1 (ppm)

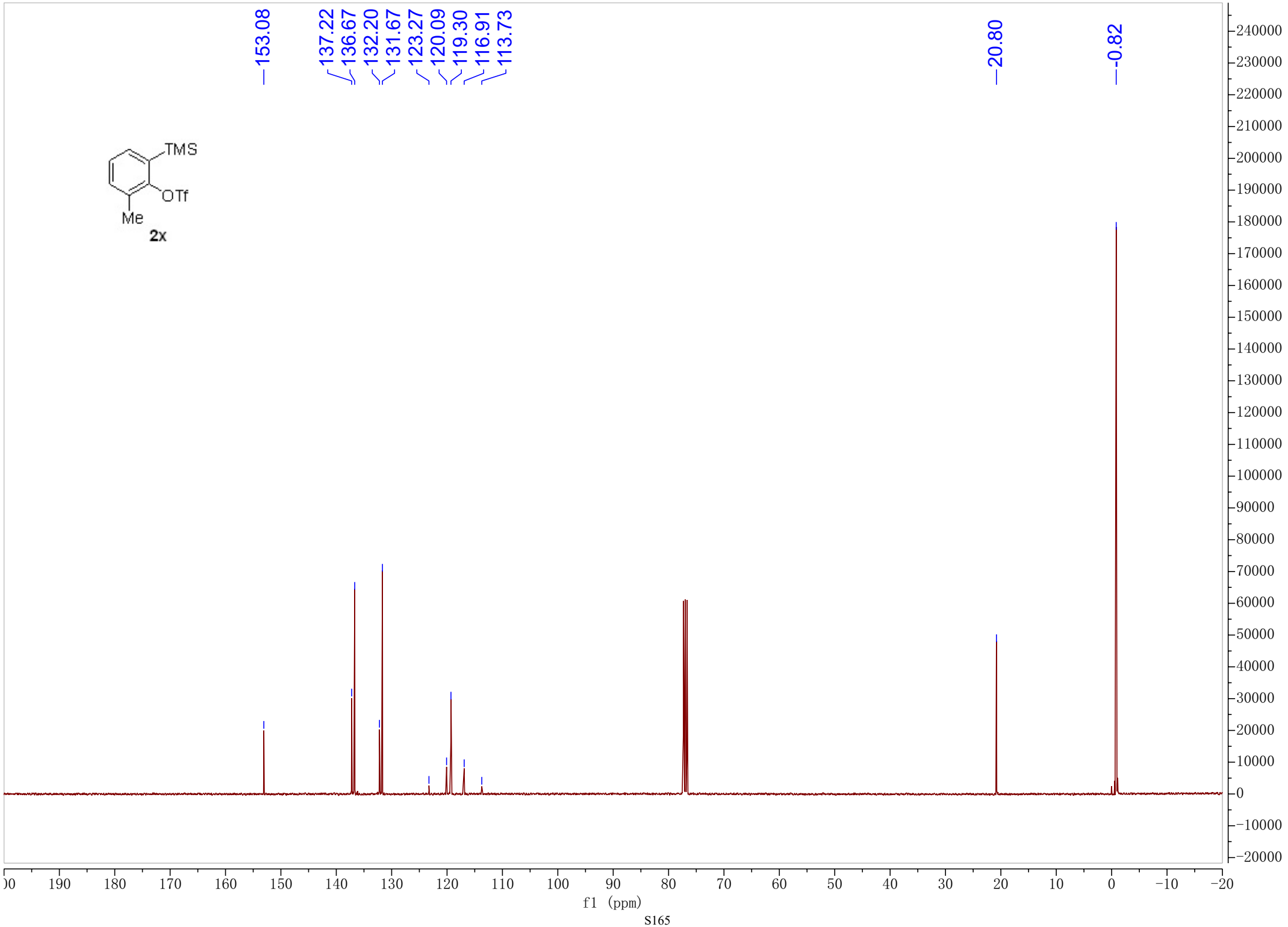

8.24
8.22
7.93
7.90
7.89
7.61
7.58
7.57
7.55
7.53
7.44
7.41
0.61
TMS
OTf
2v
1.00
2.06
2.09
1.05
9.54
f1 (ppm)

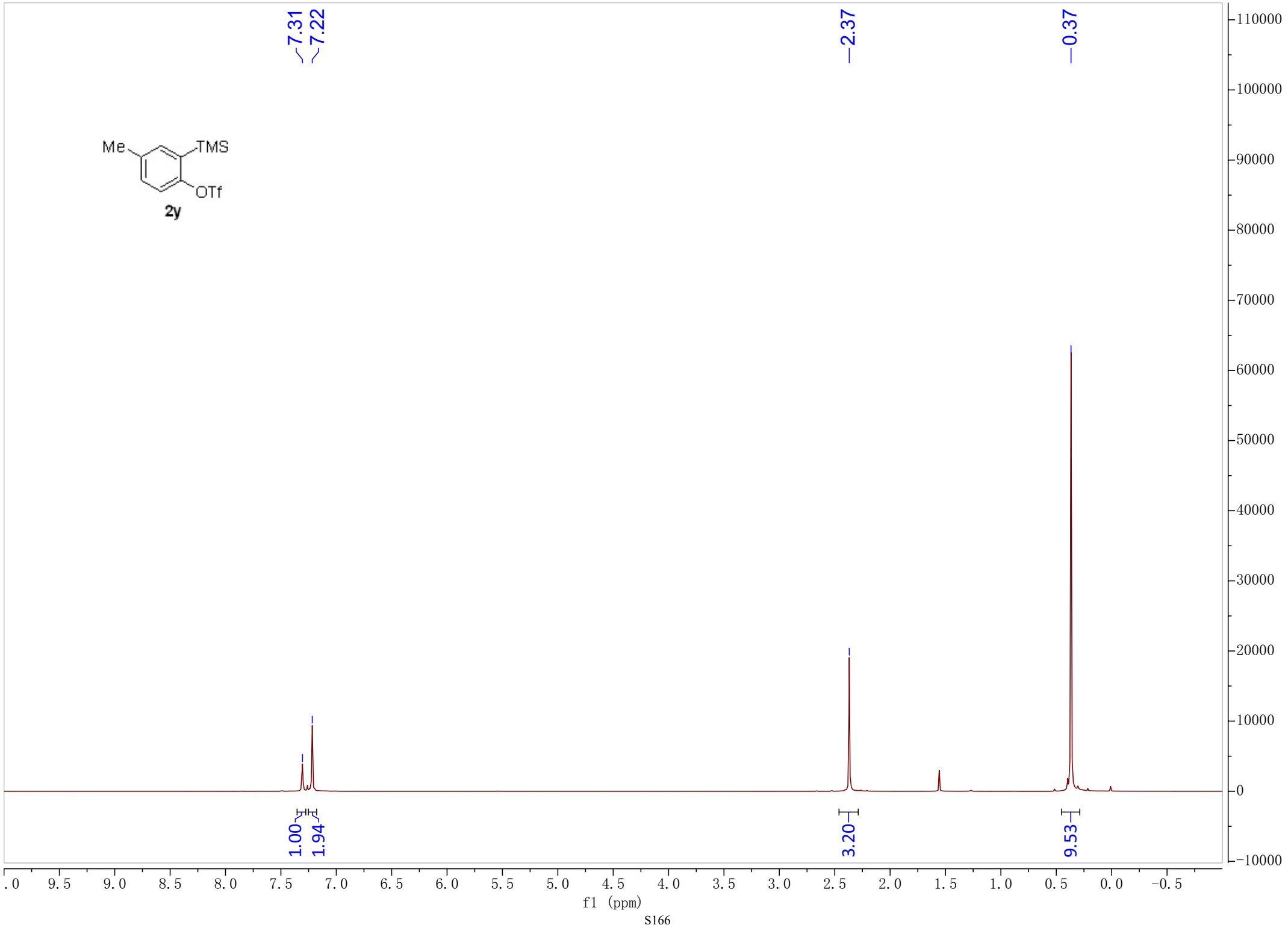

152.47
137.53
132.42
132.35
129.26
129.02
128.77
126.66
126.25
123.43
120.24
119.11
117.05
113.87
2.19
TMS
OTf
2v
f1 (ppm)

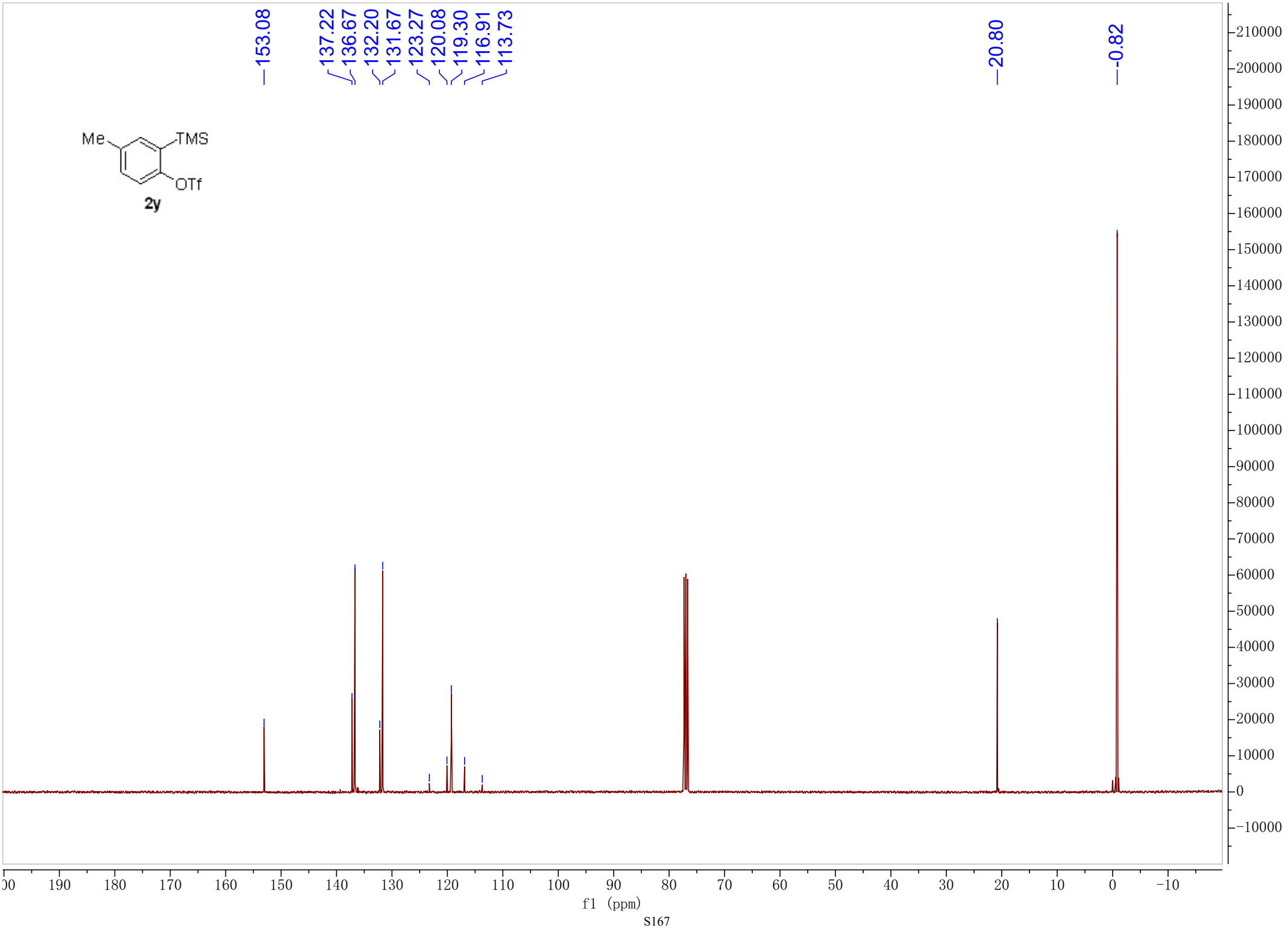

7.32
7.30
7.28
7.08
7.07
7.06
7.05
7.04
7.03
7.02
7.01
3.86
0.38
TMS
OTf
OMe
2w
0.95
0.94
0.93
3.00
8.88
f1 (ppm)

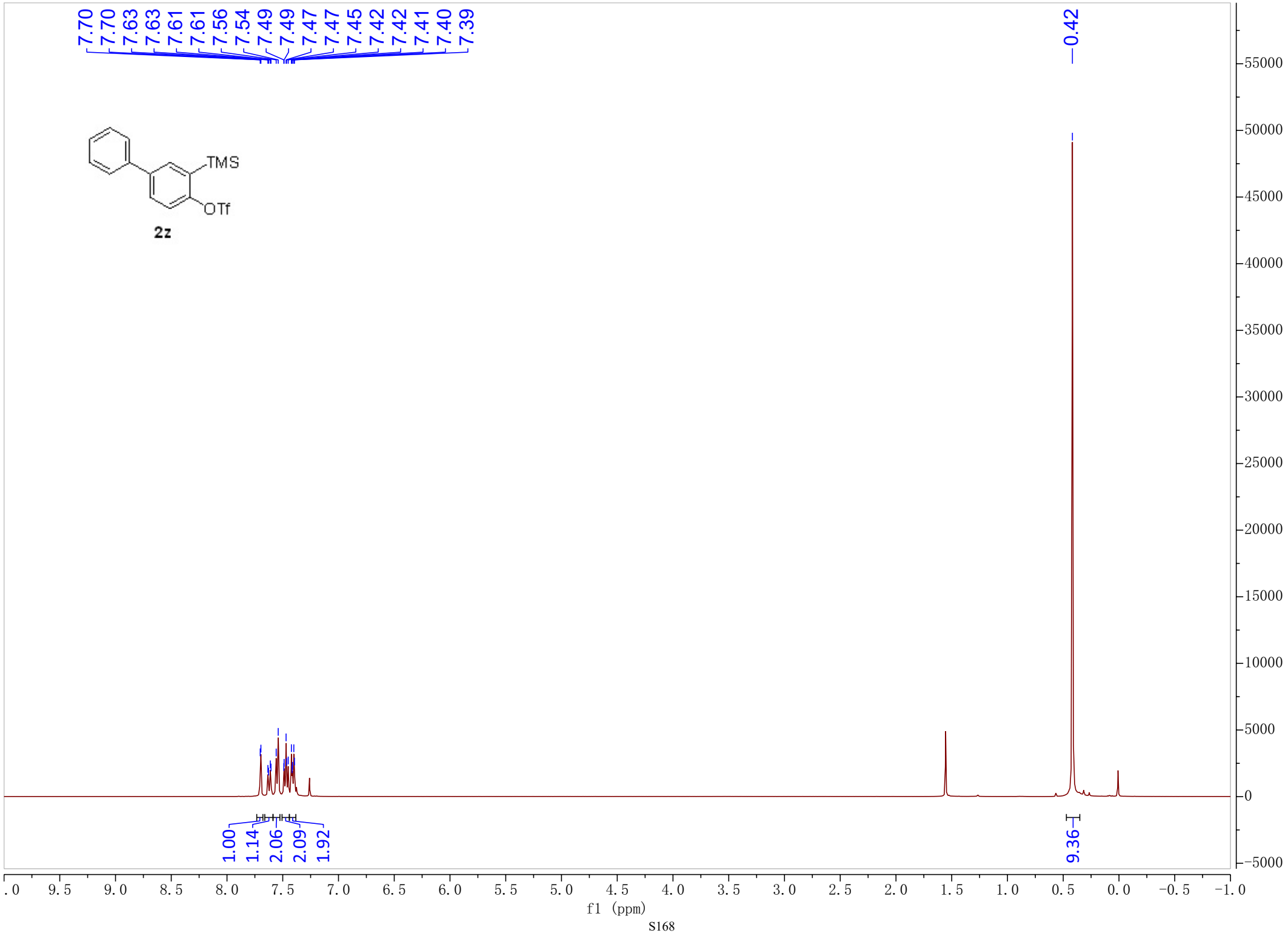

150.72
143.82
135.74
129.19
127.36
124.33
121.14
117.94
114.75
114.56
56.16
0.05
TMS
OTf
OMe
2w
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

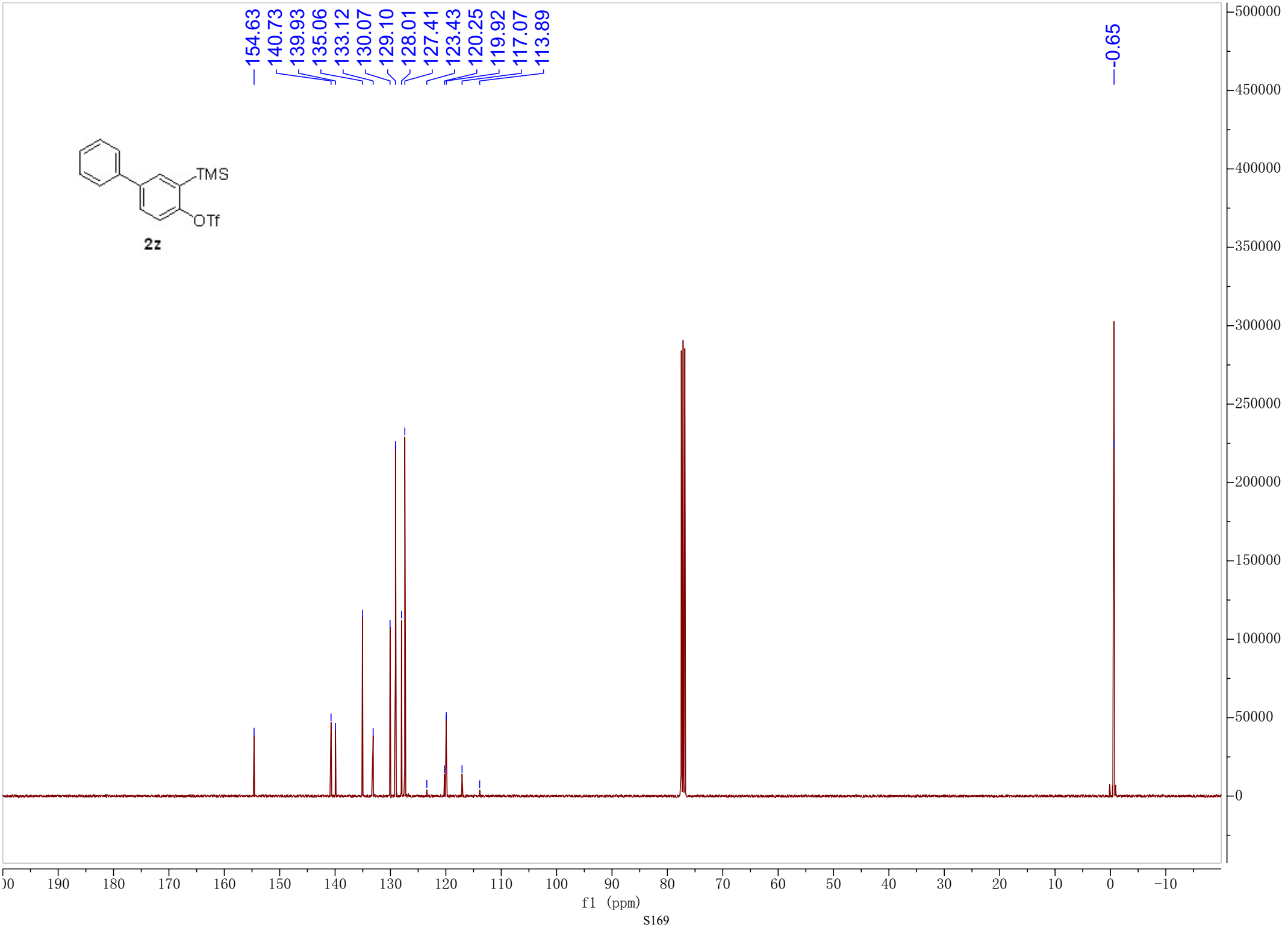

7.31
7.22
2.37
0.37
TMS
OTf
Me
2x
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
0.91
1.76
3.00
8.72
f1 (ppm)

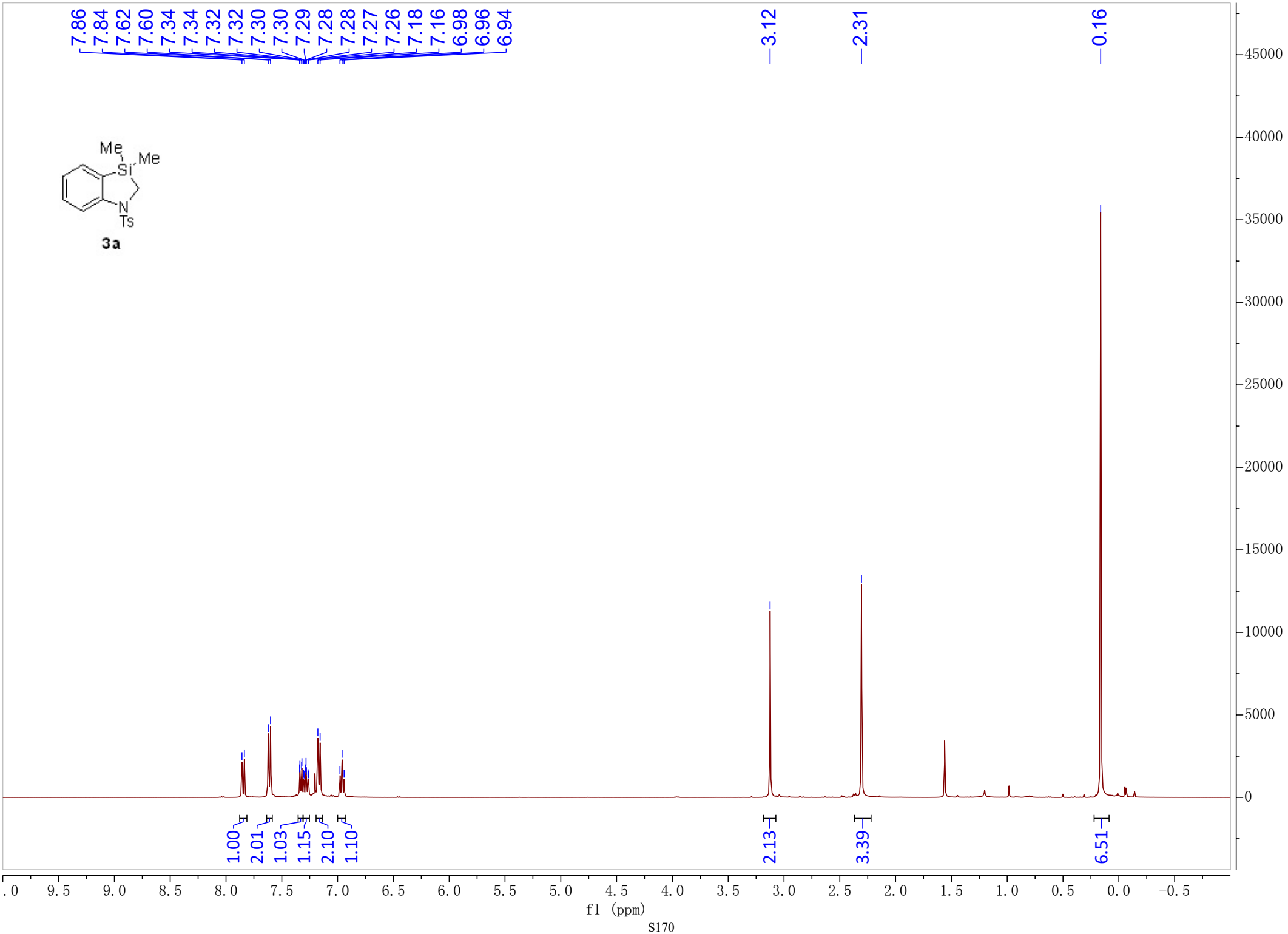

153.08
137.22
136.67
132.20
131.67
123.27
120.09
119.30
116.91
113.73
20.80
-0.82
TMS
OTf
Me
2x
f1 (ppm)

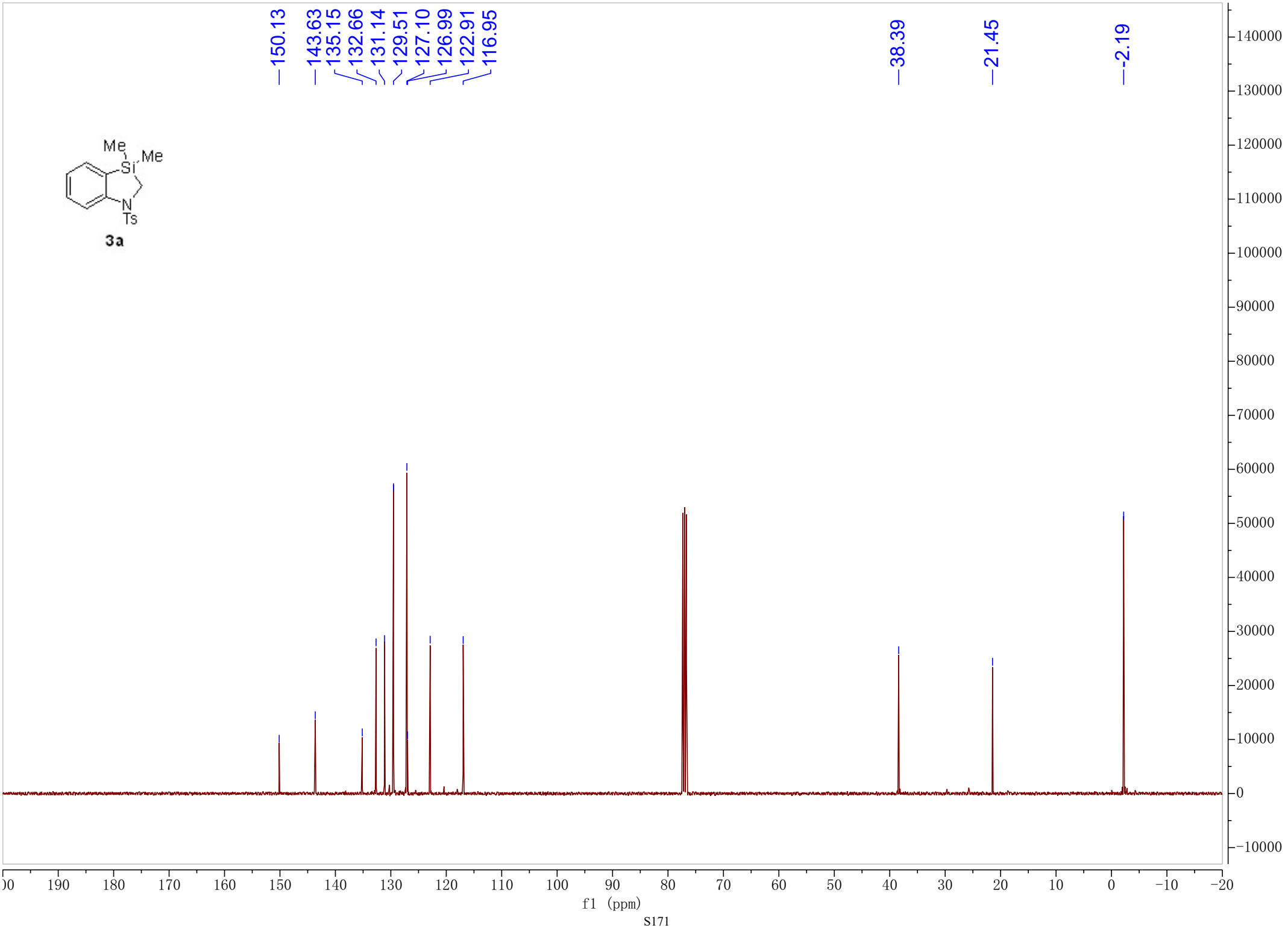

7.31
7.22
2.37
0.37
Me
TMS
OTf
2y
1.00
1.94
3.20
9.53
f1 (ppm)

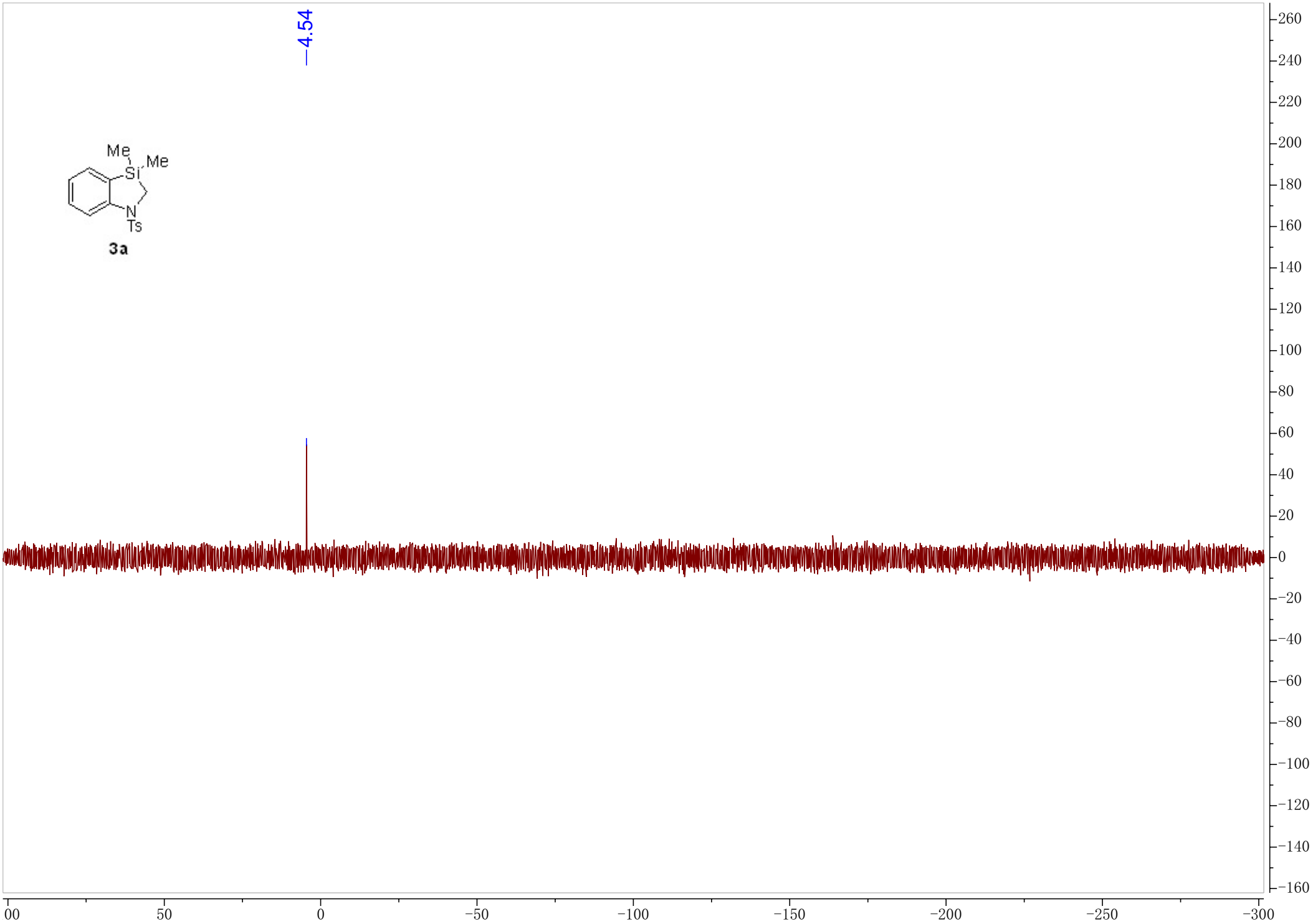

153.08
137.22
136.67
132.20
131.67
123.27
120.08
119.30
116.91
113.73
20.80
-0.82
Me
TMS
OTf
2y
f1 (ppm)

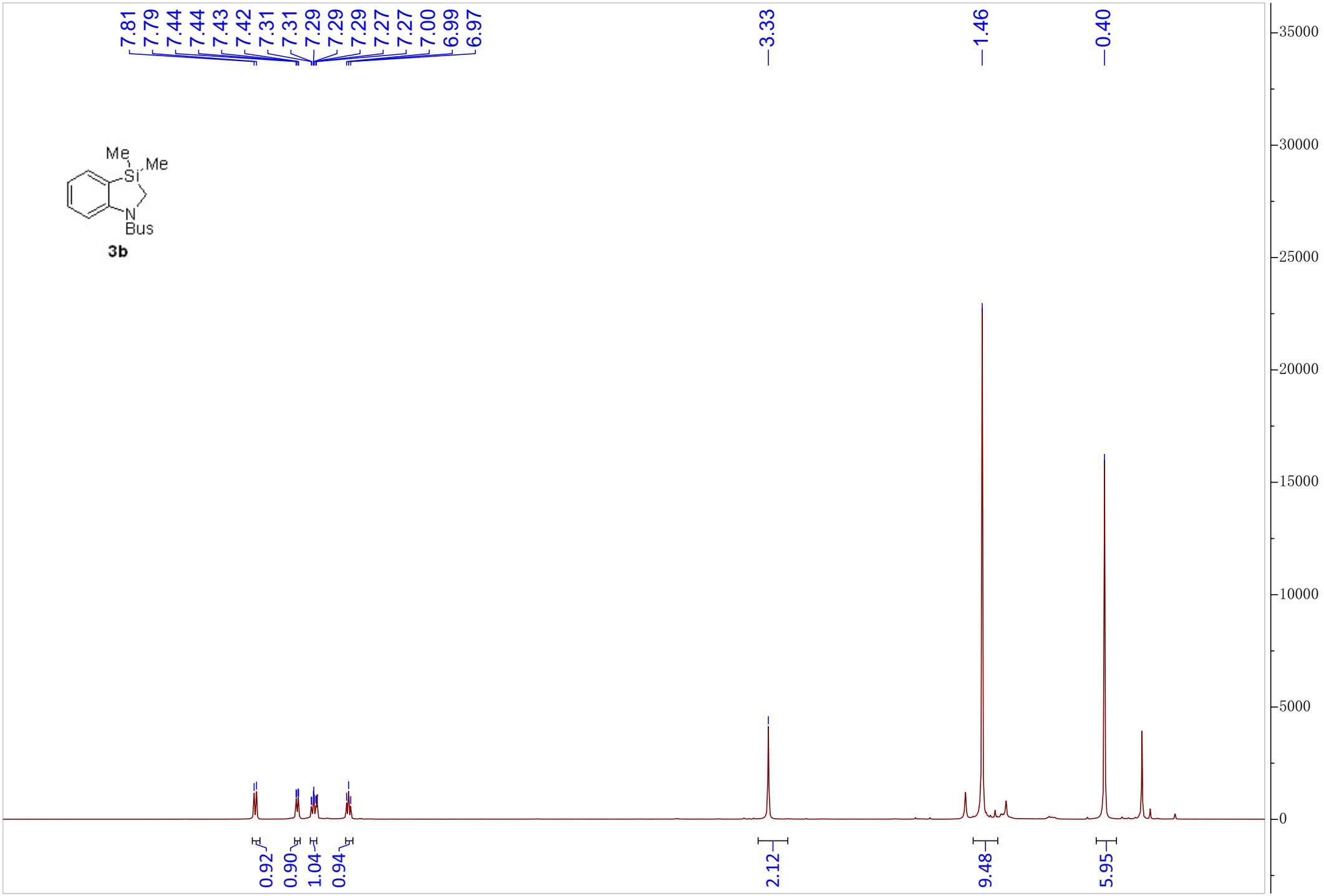

7.70
7.70
7.63
7.63
7.61
7.61
7.56
7.54
7.49
7.49
7.47
7.47
7.45
7.42
7.42
7.41
7.40
7.39
0.42
TMS
OTf
2z
1.00
1.14
2.06
2.09
1.92
9.36
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
f1 (ppm)

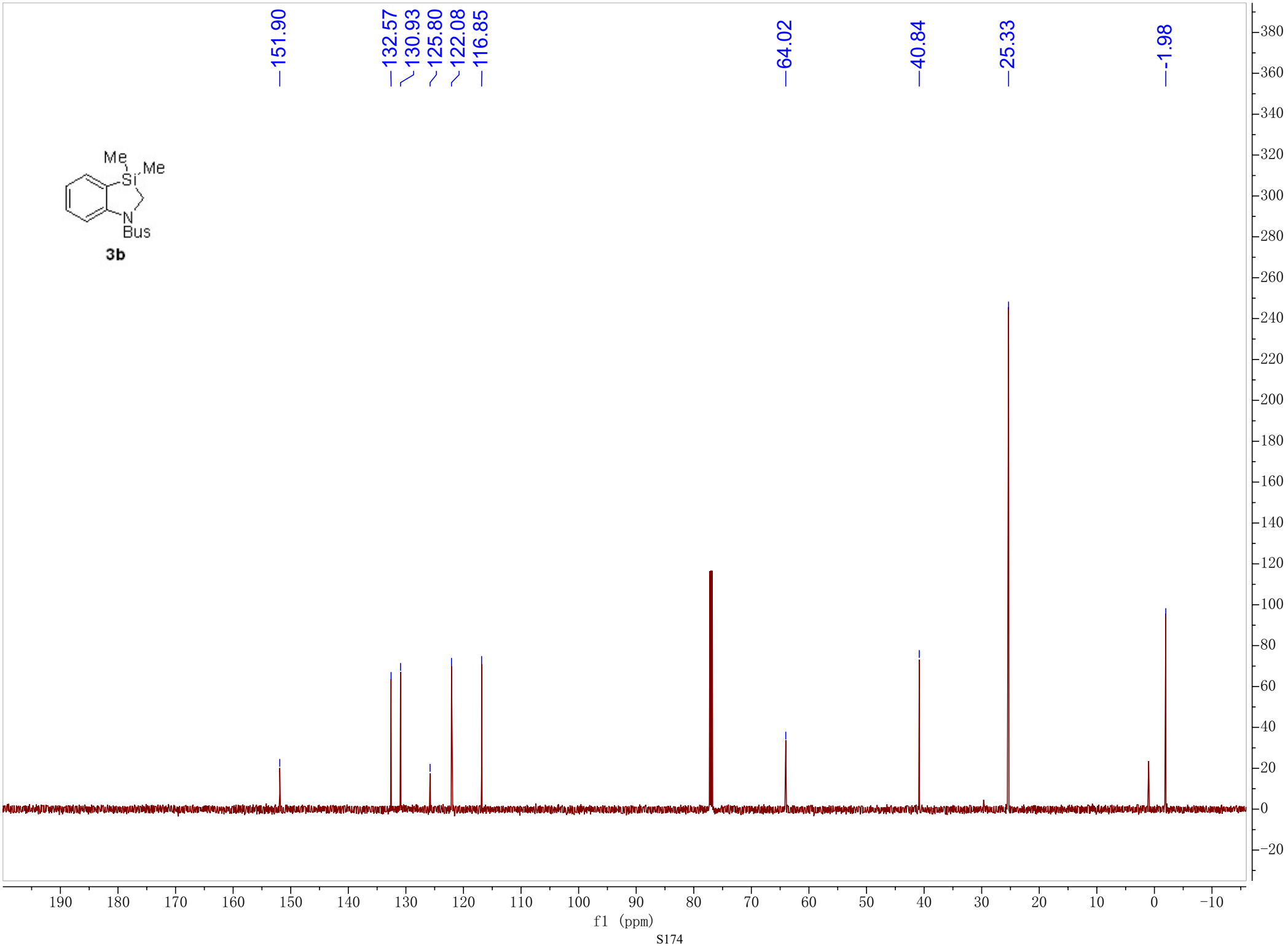

154.63
140.73
139.93
135.06
133.12
130.07
129.10
128.01
127.41
123.43
120.25
119.92
117.07
113.89
-0.65
TMS
OTf
2z
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

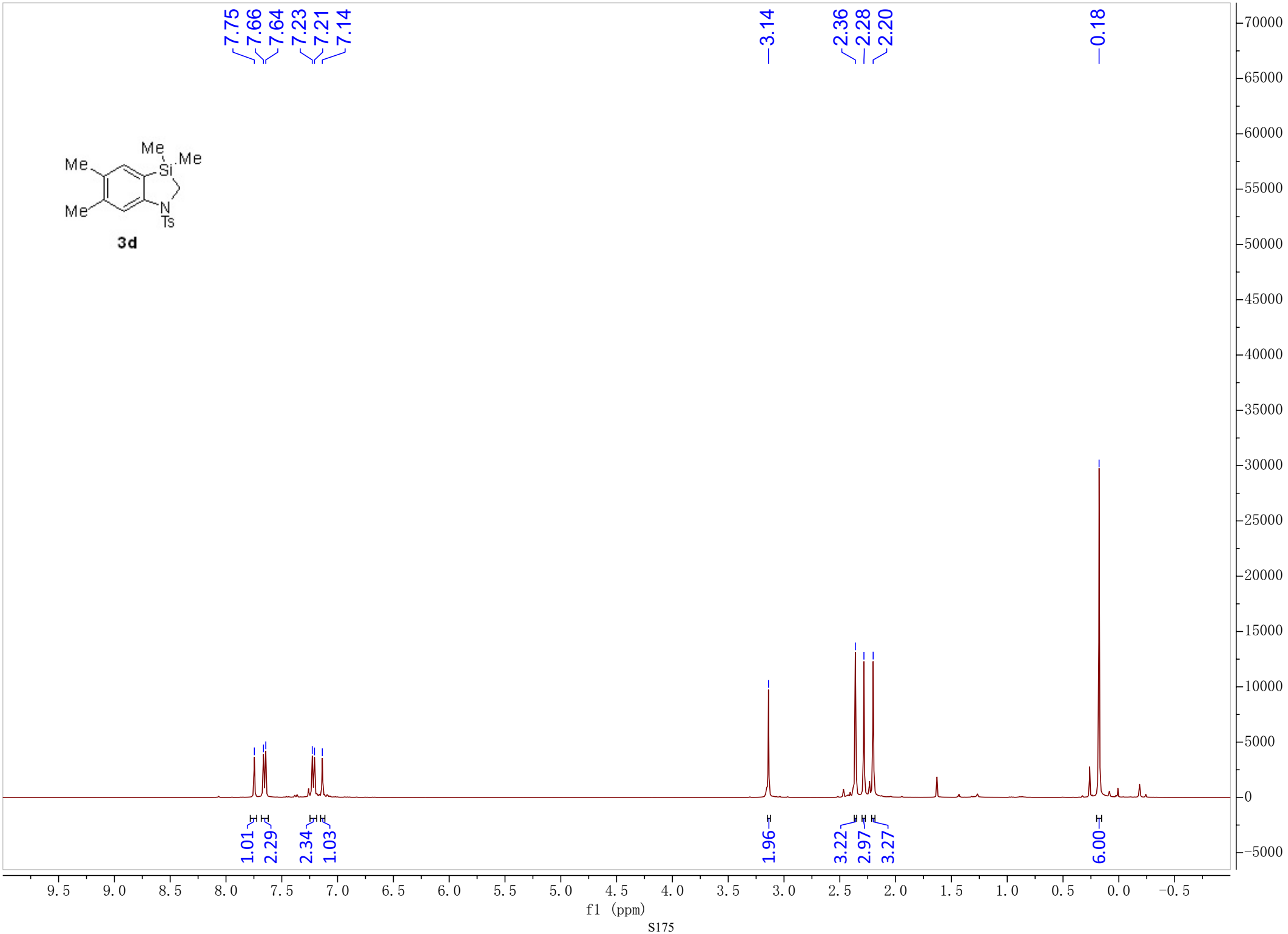

7.86
7.84
7.62
7.60
7.34
7.34
7.32
7.32
7.30
7.30
7.29
7.28
7.28
7.27
7.26
7.18
7.16
6.98
6.96
6.94
3.12
2.31
0.16
Me
Me
Si
N
Ts
3a
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
1.00
2.01
1.03
1.15
2.10
1.10
2.13
3.39
6.51
f1 (ppm)

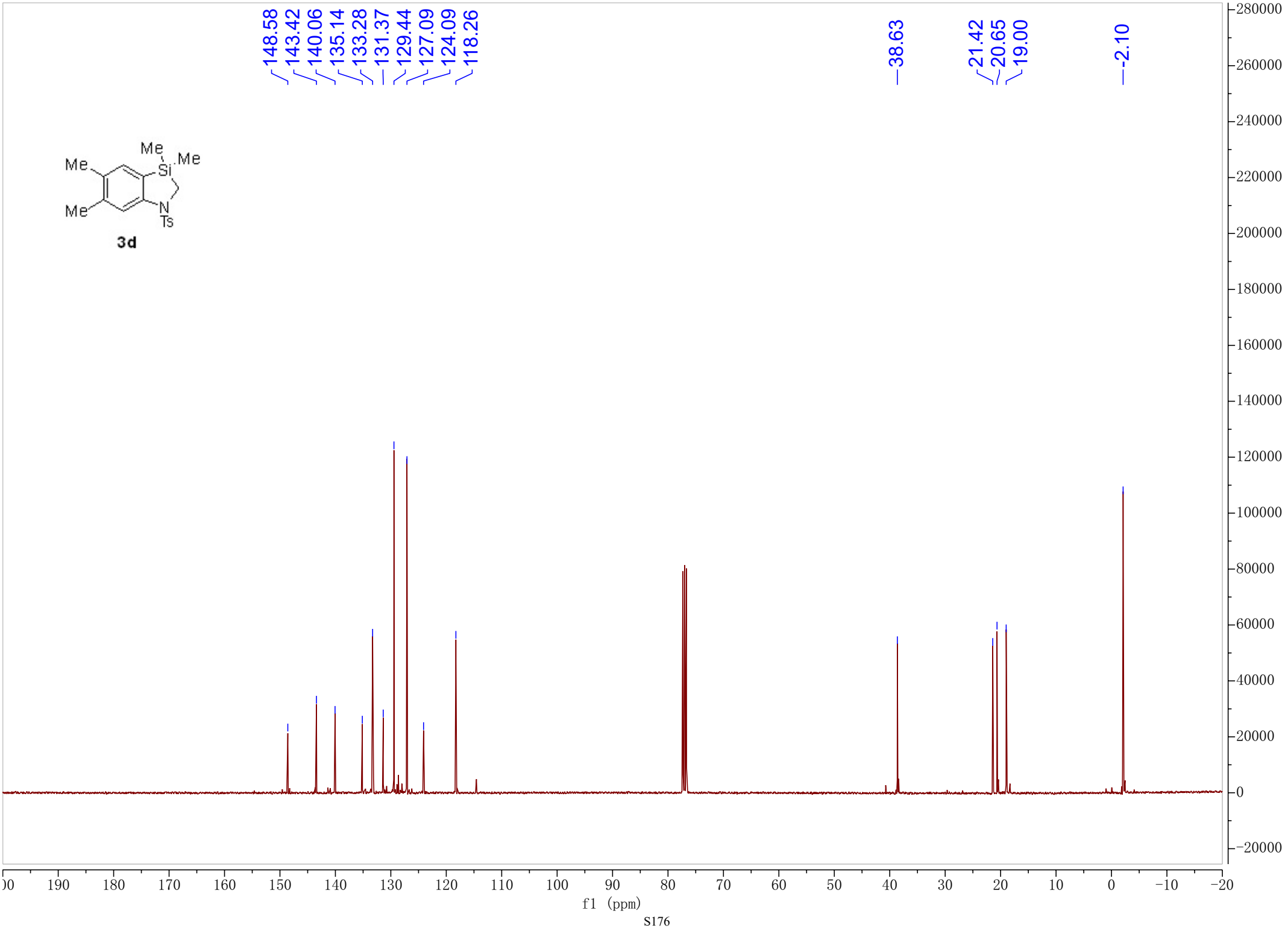

150.13
143.63
135.15
132.66
131.14
129.51
127.10
126.99
122.91
116.95
38.39
21.45
-2.19
Me
Si
Me
N
Ts
3a
f1 (ppm)


-4.54
Me
Si
Me
N
Ts
3a
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
00
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)


7.81
7.79
7.44
7.44
7.43
7.42
7.31
7.31
7.29
7.29
7.29
7.27
7.27
7.00
6.99
6.97
3.33
1.46
0.40
Me
Me
Si
N
Bus
3b
0.92
0.90
1.04
0.94
2.12
9.48
5.95
f1 (ppm)


151.90
132.57
130.93
125.80
122.08
116.85
64.02
40.84
25.33
-1.98
Me
Me
Si
N
Bus
3b
f1 (ppm)


7.75
7.66
7.64
7.23
7.21
7.14
3.14
2.36
2.28
2.20
0.18
Me
Me
Me
Si
N
Ts
3d
1.01
2.29
2.34
1.03
1.96
3.22
2.97
3.27
6.00
f1 (ppm)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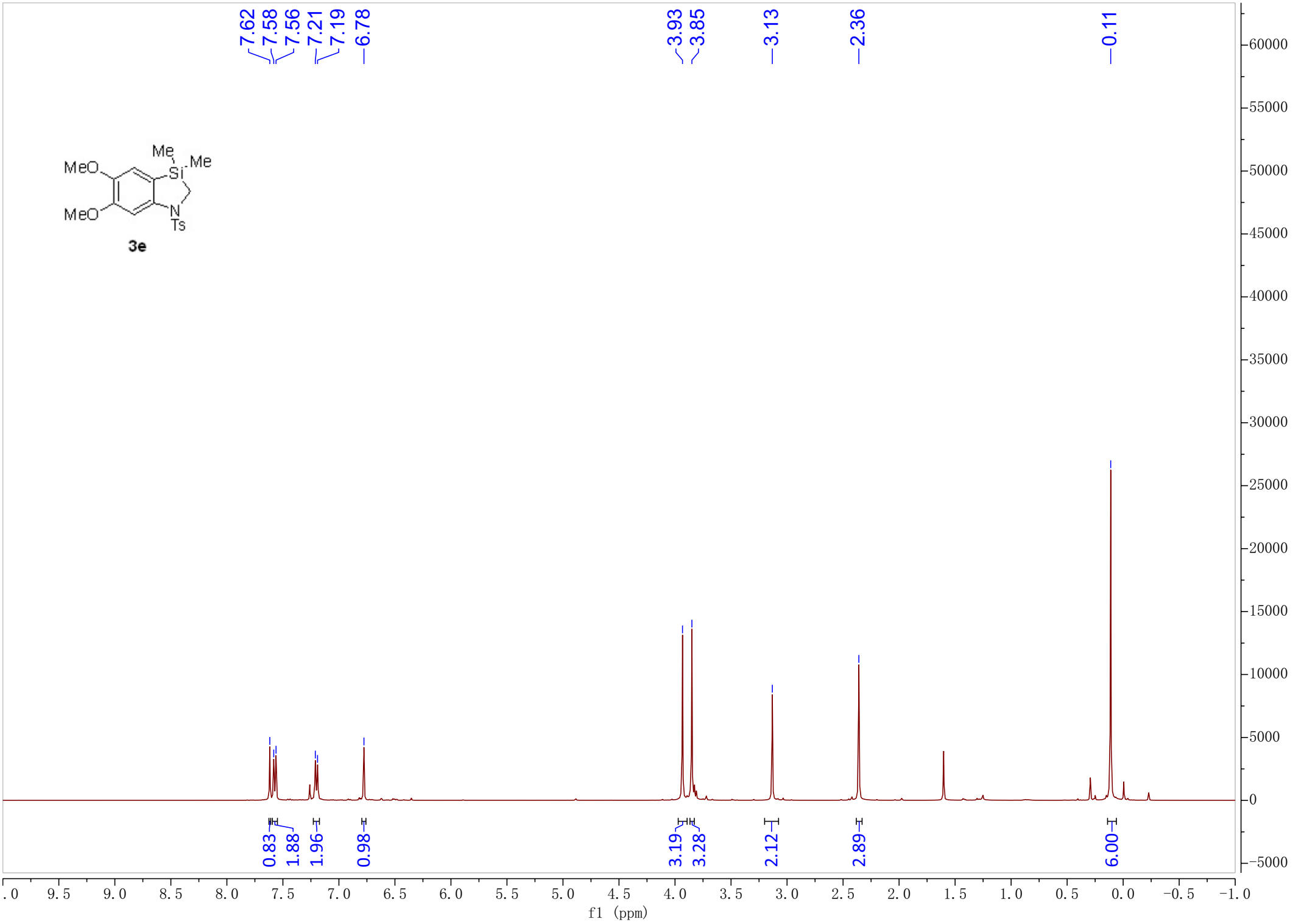
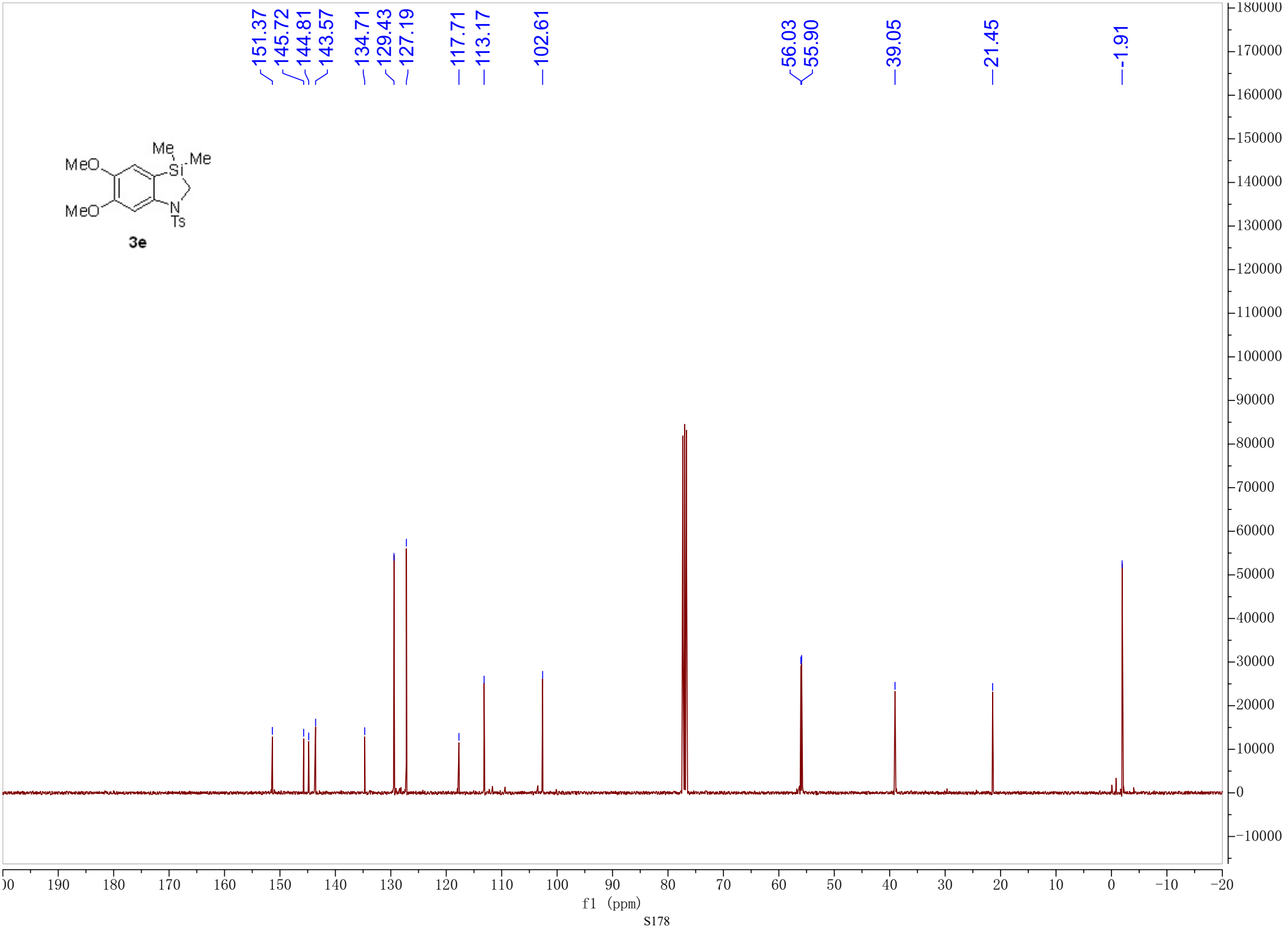
135.14
133.28
131.37
129.44
127.09
124.09
118.26
38.63
21.42
20.65
19.00
2.10
Me
Me
Me
Me
Si
N
Ts
3d
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
−20000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)


7.62
7.58
7.56
7.21
7.19
6.78
3.93
3.85
3.13
2.36
0.11
MeO
MeO
Me
Me
Si
N
Ts
3e
0.83
1.88
1.96
0.98
3.19
3.28
2.12
2.89
6.00
f1 (ppm)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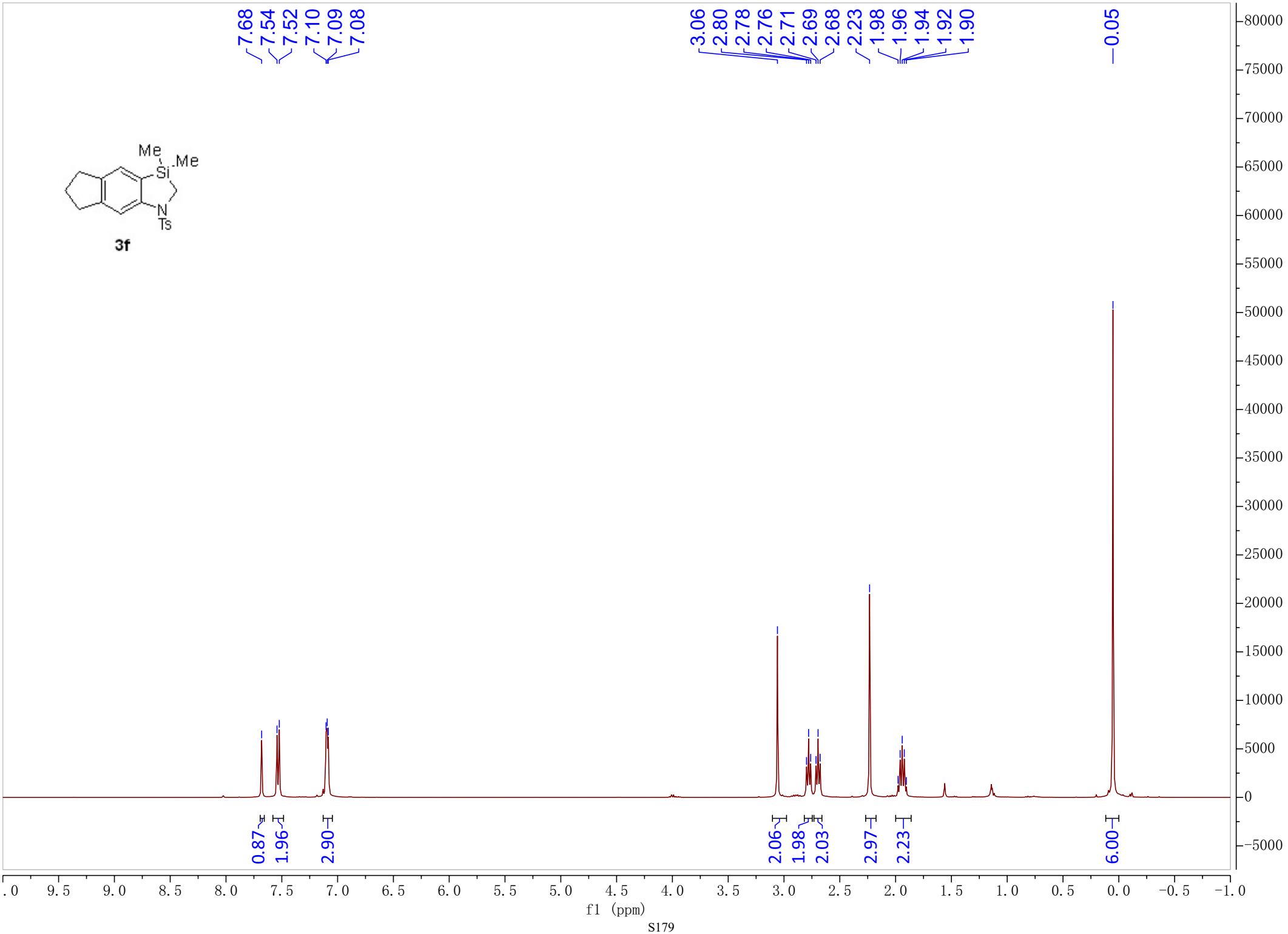
144.81
143.57
134.71
129.43
127.19
117.71
113.17
102.61
56.03
55.90
39.05
21.45
-1.91
Me
Me
Si
MeO
MeO
N
Ts
3e
f1 (ppm)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7.54
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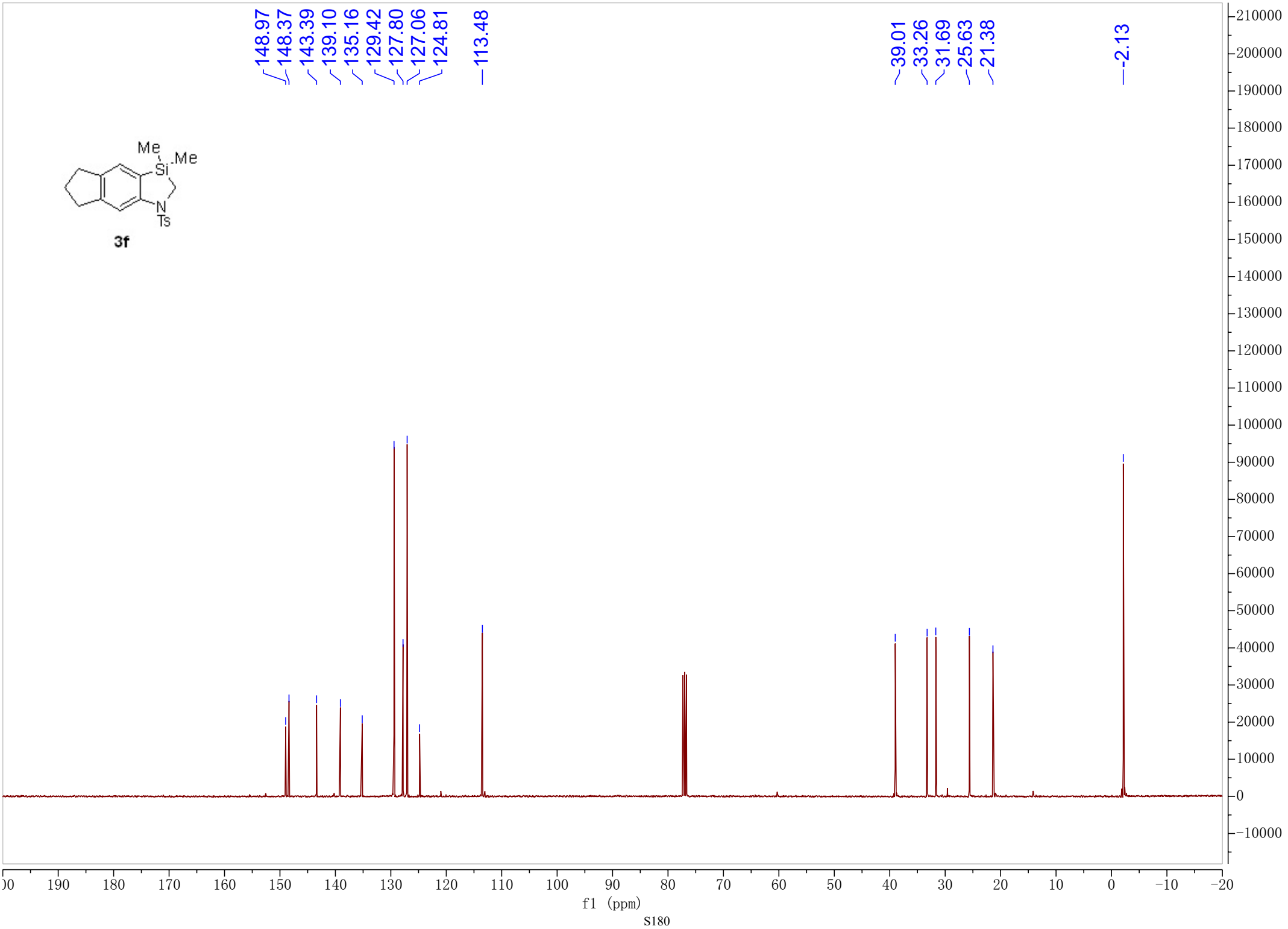
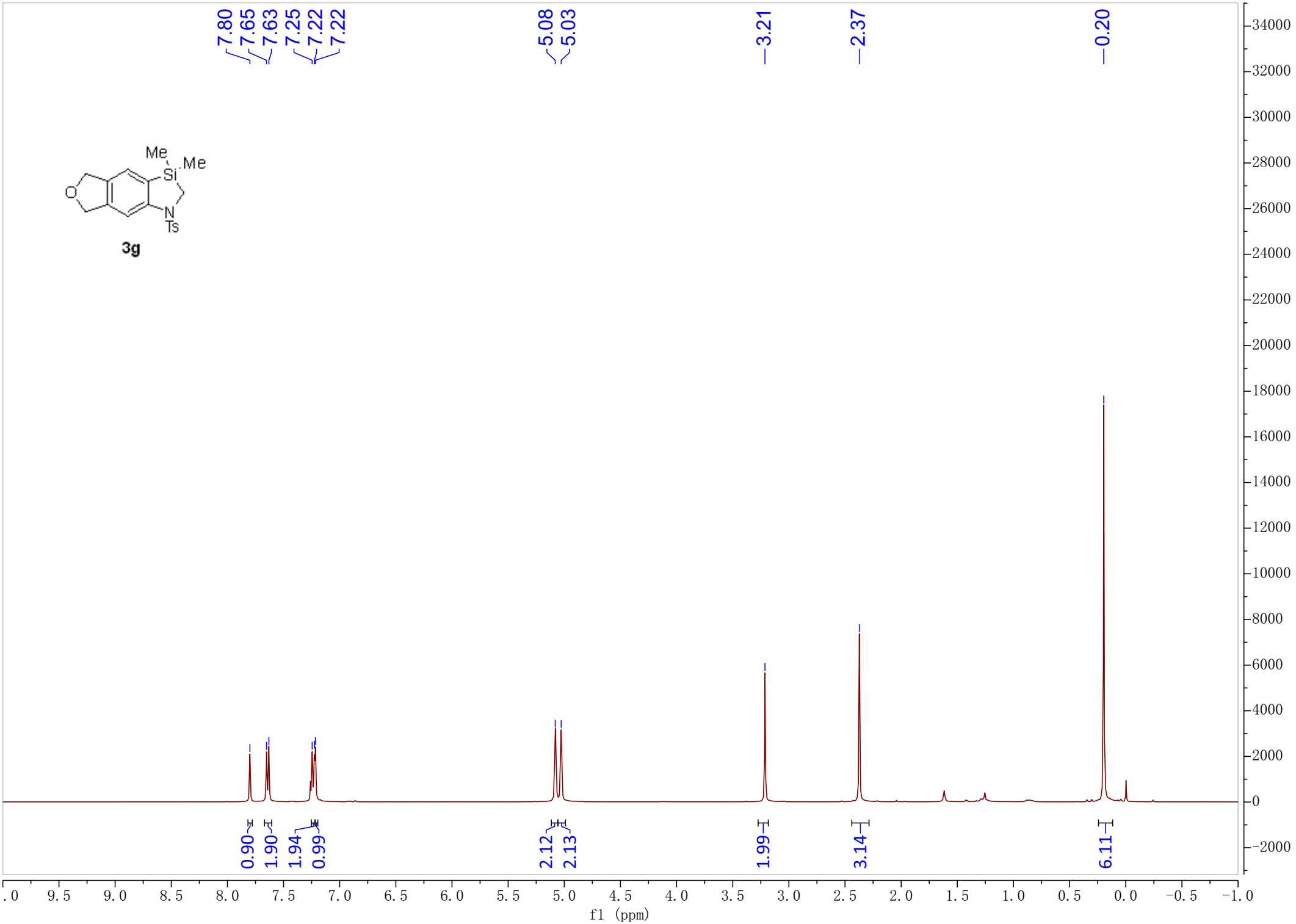
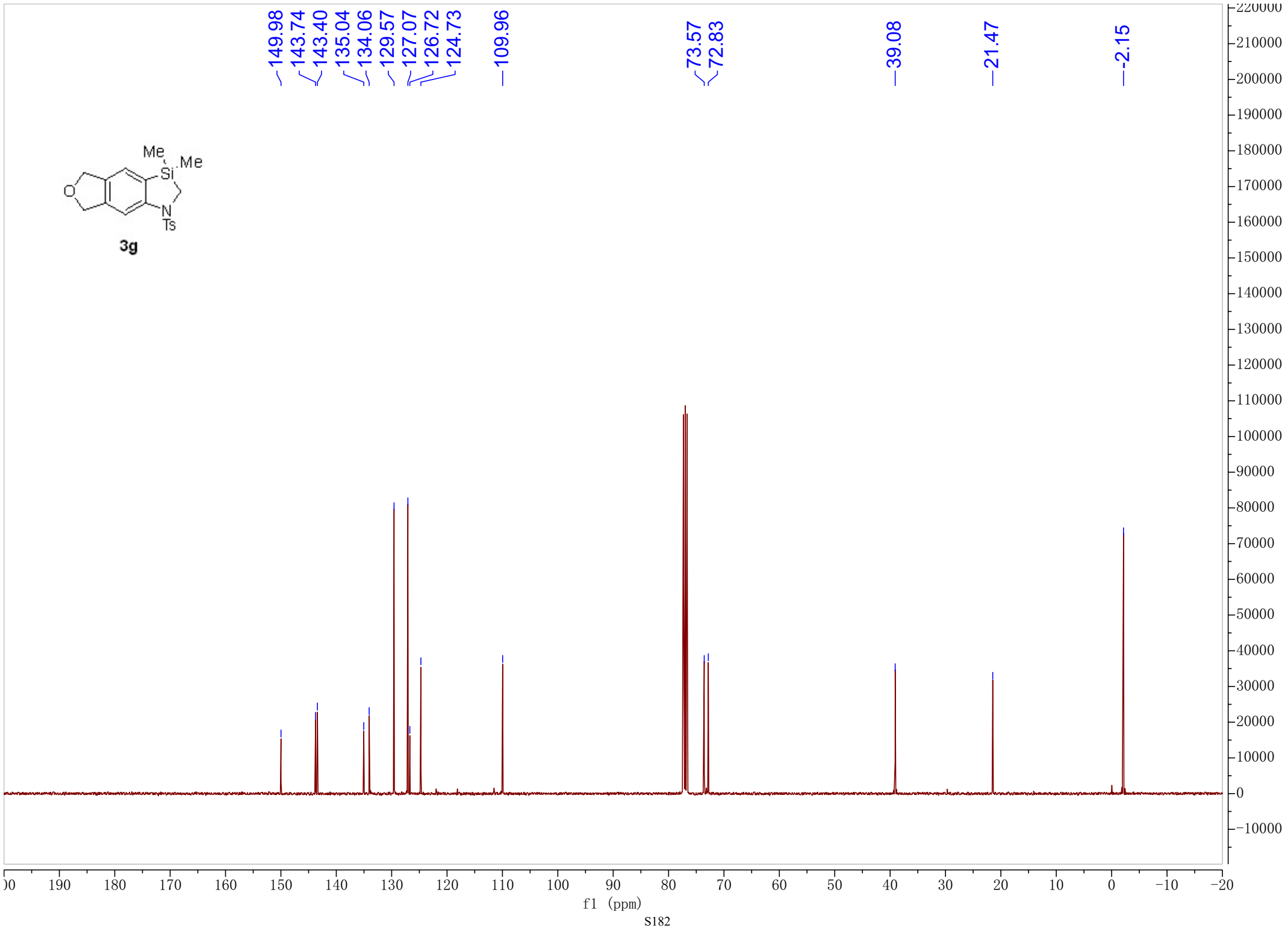
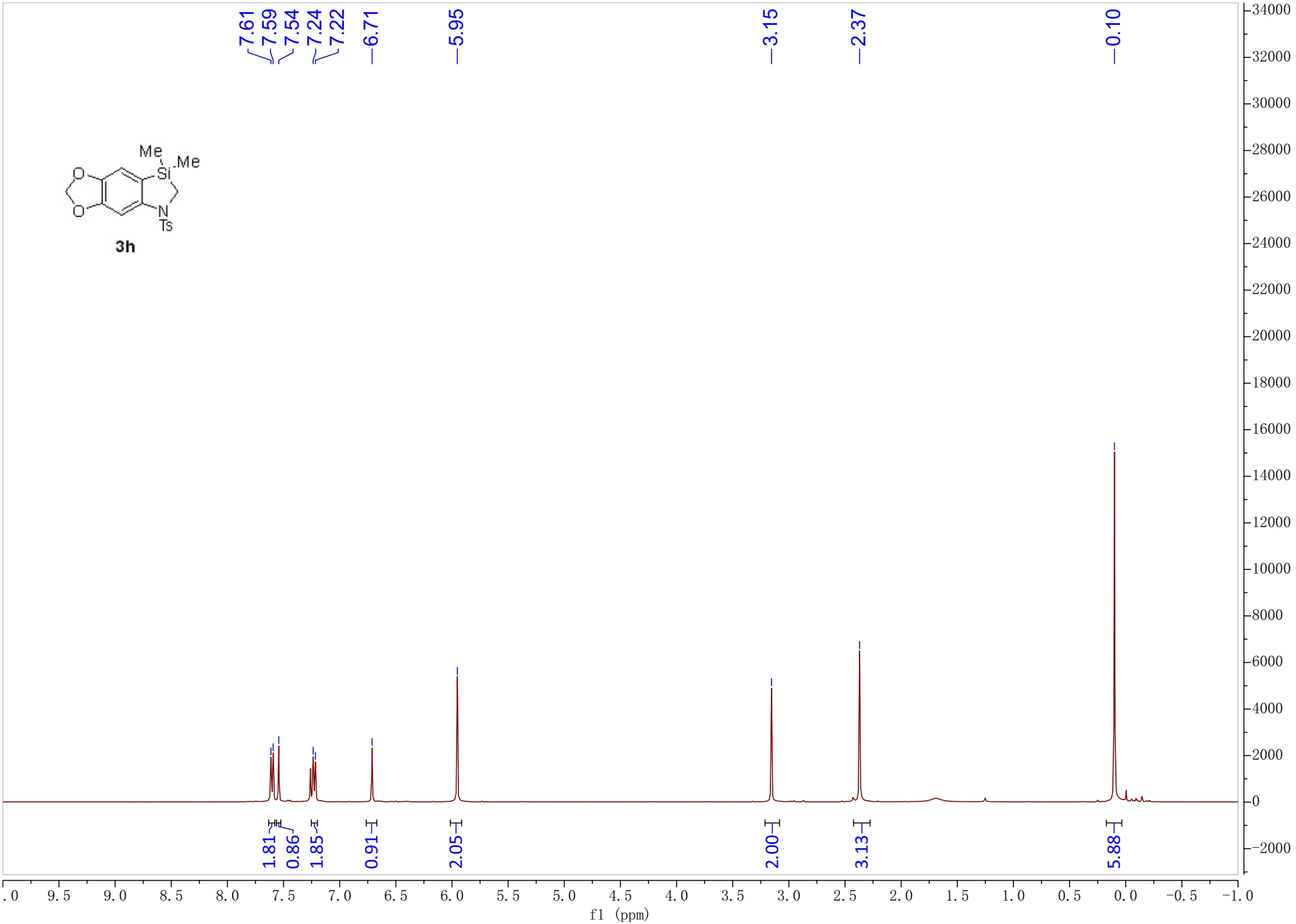
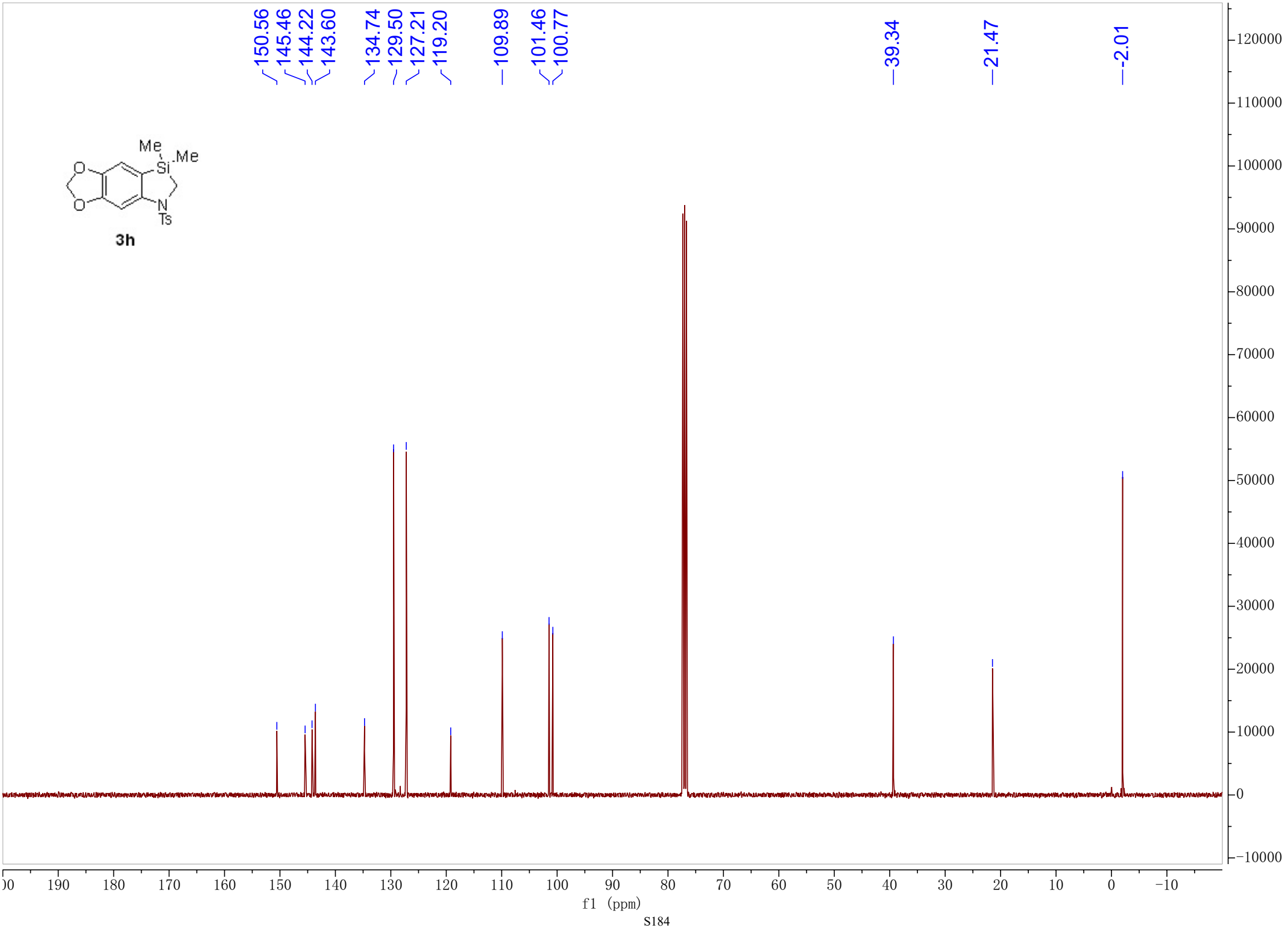
7.10
7.09
7.08
3.06
2.80
2.78
2.76
2.71
2.69
2.68
2.23
1.98
1.96
1.94
1.92
1.90
0.05
Me
Si
Me
N
Ts
3f
0.87
1.96
2.90
2.06
1.98
2.03
2.97
2.23
6.00
f1 (ppm)


148.97
148.37
143.39
139.10
135.16
129.42
127.80
127.06
124.81
113.48
39.01
33.26
31.69
25.63
21.38
-2.13
Me
Si
Me
N
Ts
3f
f1 (ppm)


7.80
7.65
7.63
7.25
7.22
7.22
5.08
5.03
3.21
2.37
0.20
Me
Me
Si
O
N
Ts
3g
0.90
1.90
1.94
0.99
2.12
2.13
1.99
3.14
6.11
f1 (ppm)


149.98
143.74
143.40
135.04
134.06
129.57
127.07
126.72
124.73
109.96
73.57
72.83
39.08
21.47
-2.15
Me
Me
Si
O
N
Ts
3g
f1 (ppm)


7.61
7.59
7.54
7.24
7.22
6.71
5.95
3.15
2.37
0.10
Me
Si
Me
O
O
N
Ts
3h
1.81
0.86
1.85
0.91
2.05
2.00
3.13
5.88
f1 (ppm)


150.56
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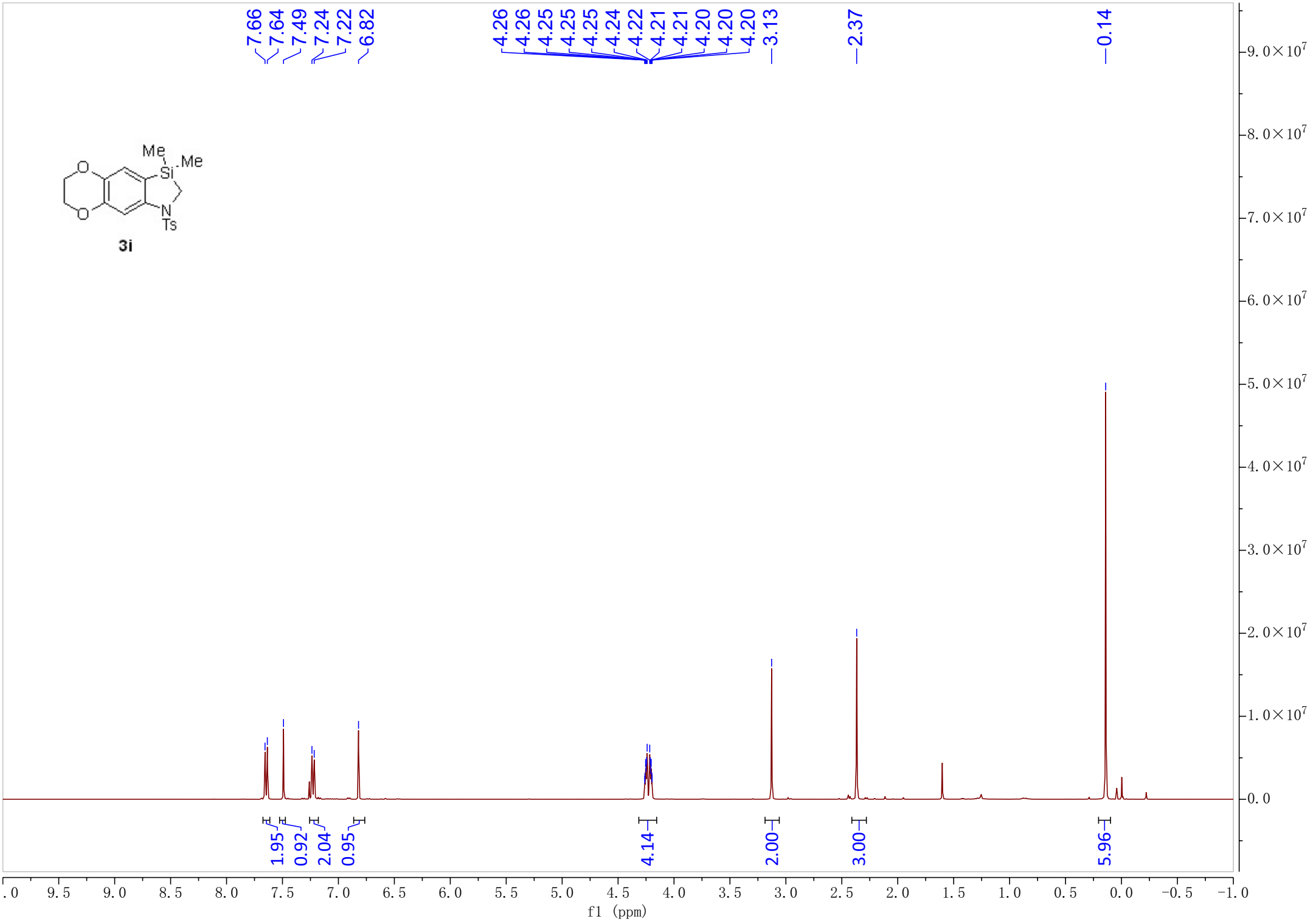
143.60
134.74
129.50
127.21
119.20
109.89
101.46
100.77
39.34
21.47
-2.01
Me
Si
Me
O
O
N
Ts
3h
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.66
7.64
7.49
7.24
7.22
6.82
4.26
4.26
4.25
4.25
4.25
4.24
4.22
4.21
4.21
4.20
4.20
4.20
3.13
2.37
0.14
Me
Me
Si
O
O
N
Ts
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0.92
2.04
0.95
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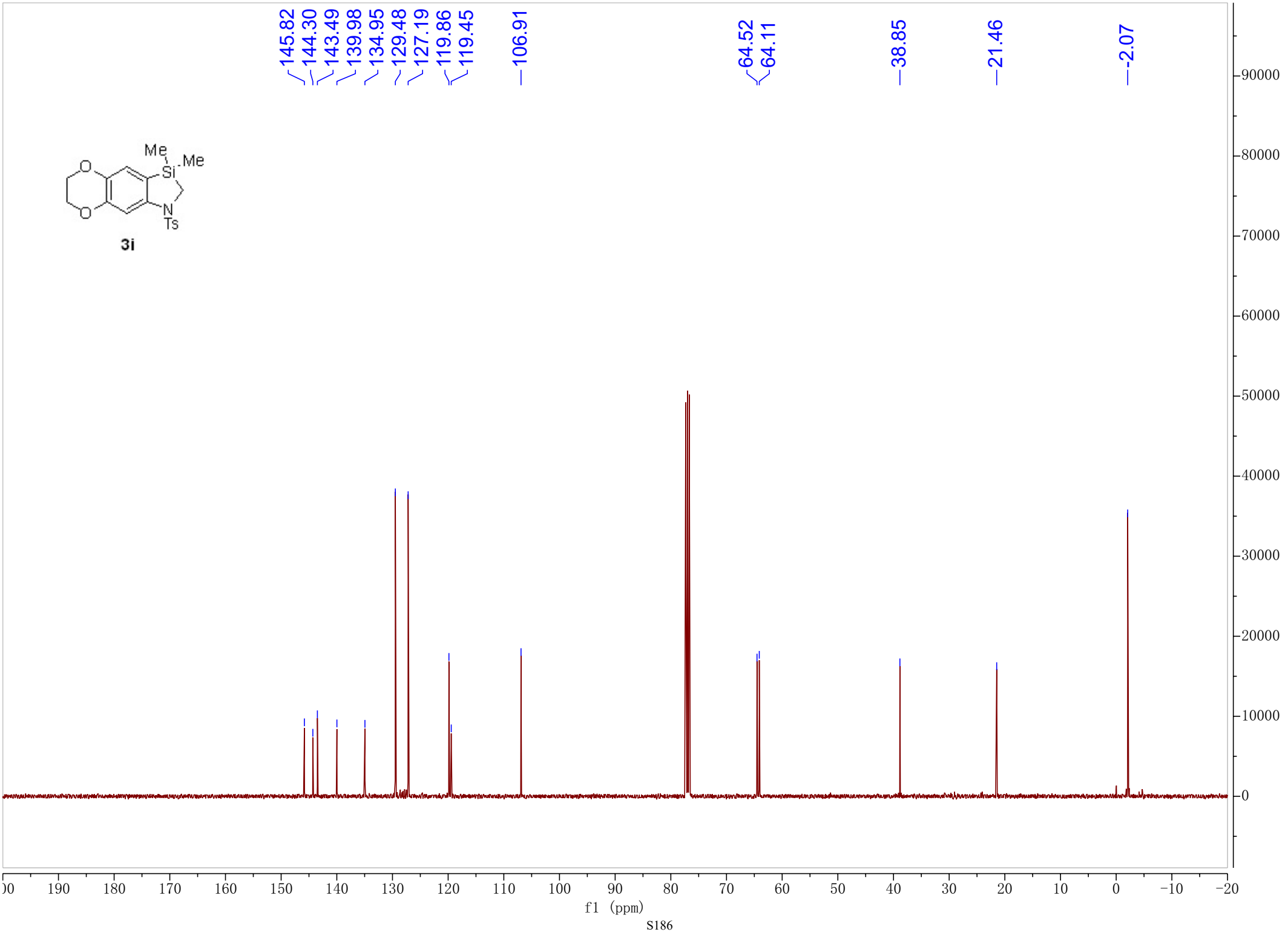
2.00
3.00
5.96
f1 (ppm)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129.48
127.19
119.86
119.45
106.91
64.52
64.11
38.85
21.46
-2.07
Me
Me
Si
O
O
N
Ts
3i
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
190
180
170
160
150
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60
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40
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20
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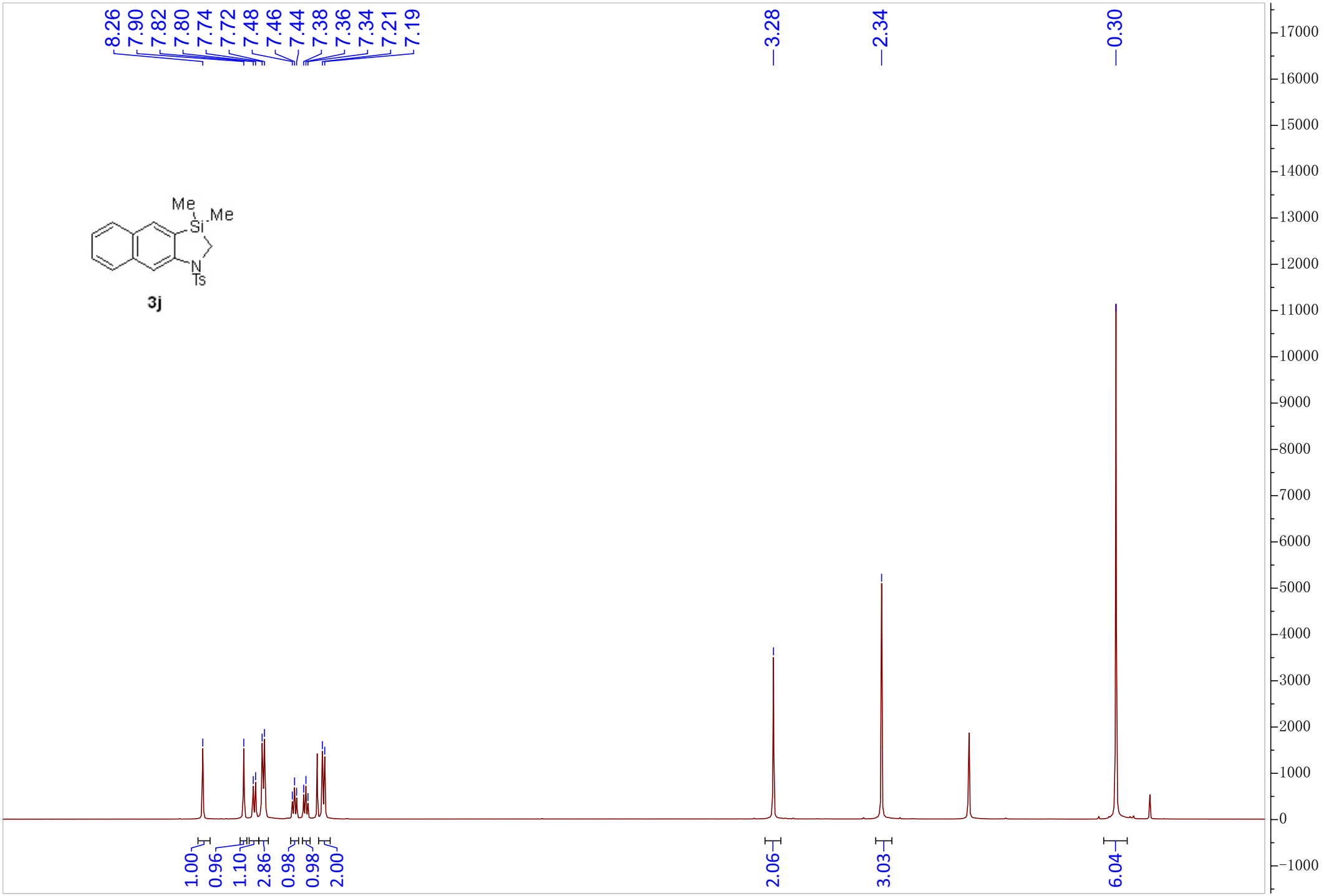
0
-10
-20
f1 (ppm)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7.48
7.46
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7.38
7.36
7.34
7.21
7.19
3.28
2.34
0.30
Me
Me
Si
N
Ts
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1.10
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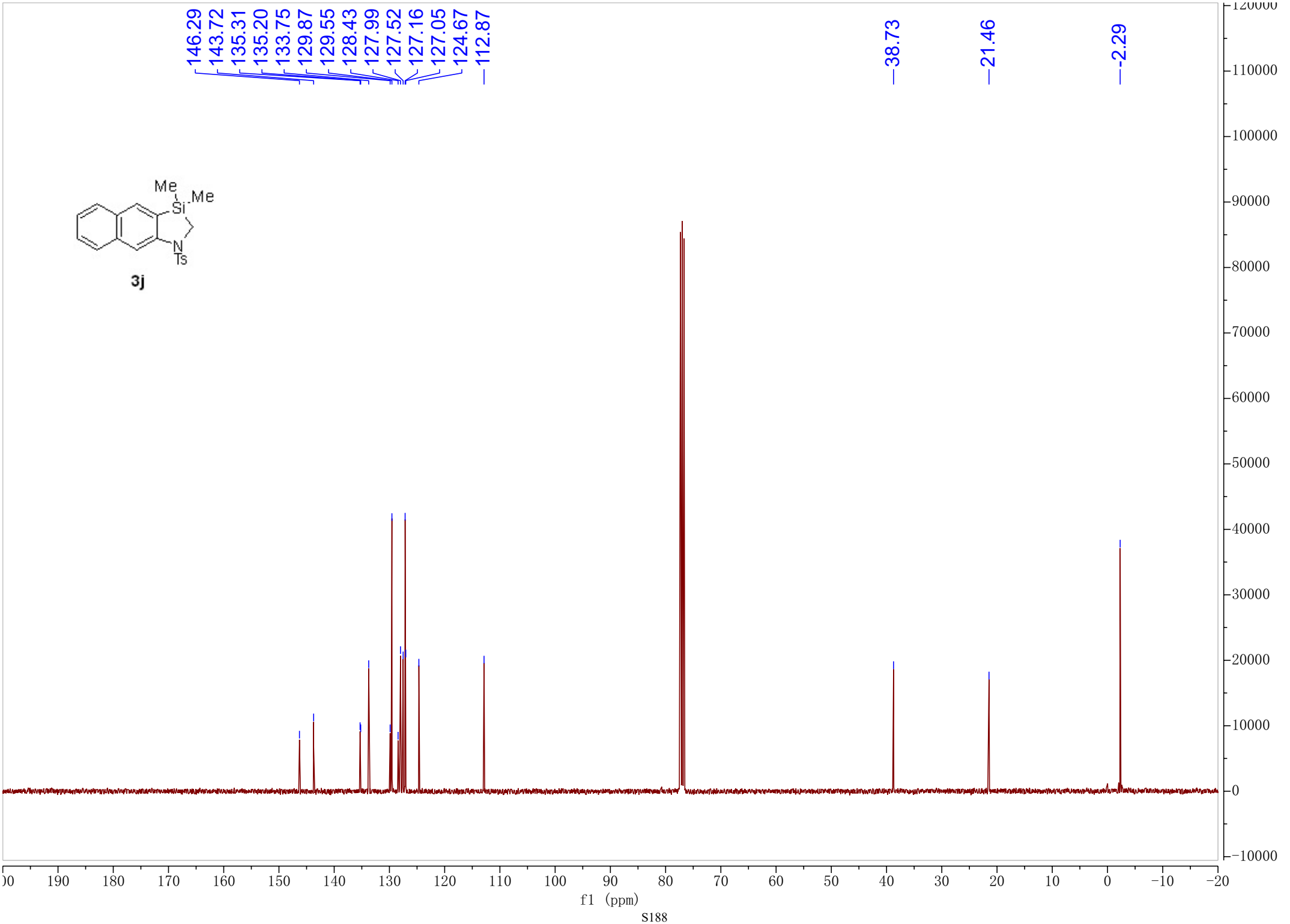
0.98
0.98
2.00
2.06
3.03
6.04
f1 (ppm)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128.43
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127.52
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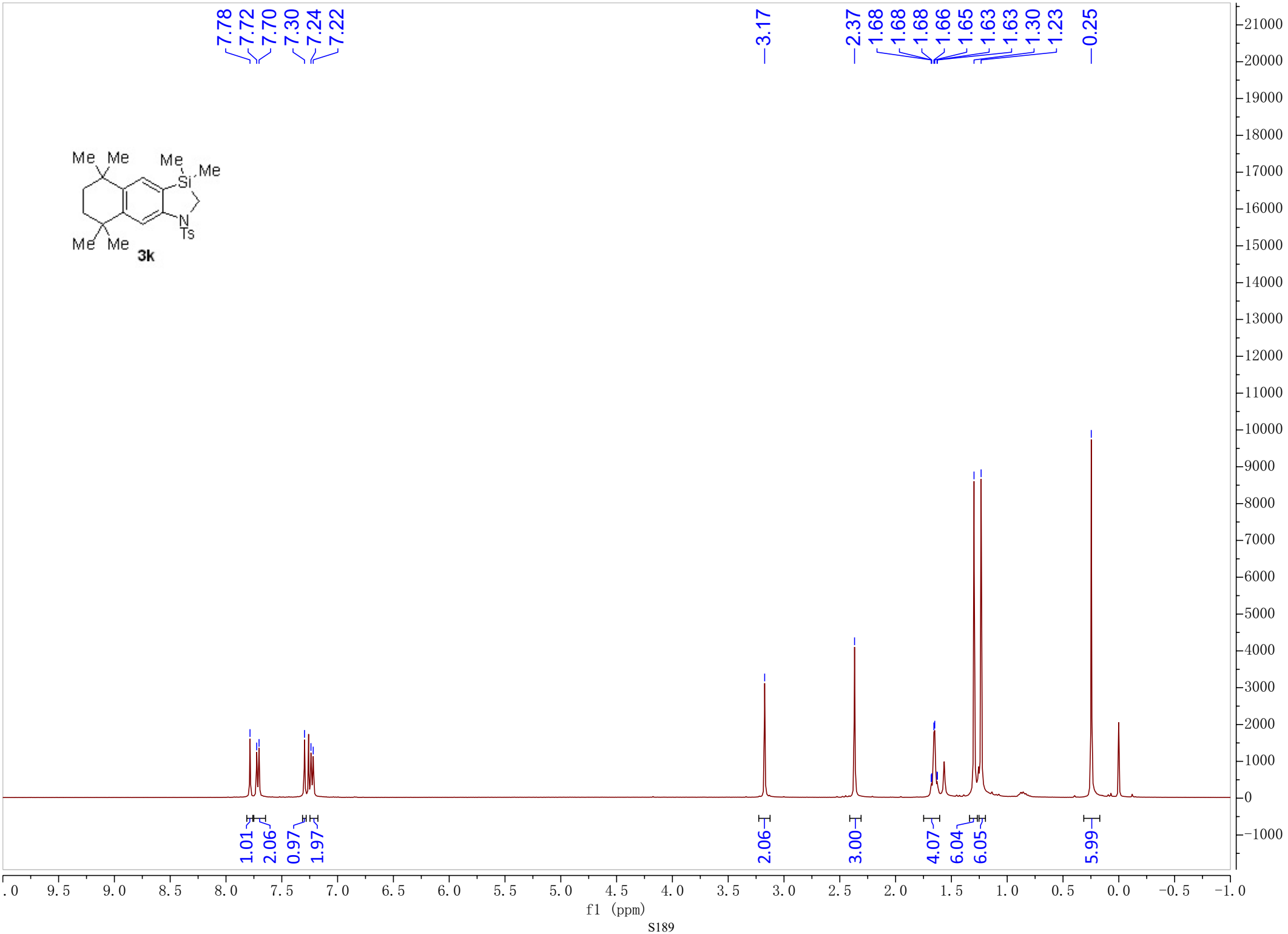
38.73
21.46
-2.29
Me
Me
Si
N
Ts
3j
f1 (ppm)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7.72
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7.22
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2.37
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1.68
1.66
1.65
1.63
1.63
1.30
1.23
0.25
Me
Me
Me
Si
Me
N
Ts
Me
Me
3k
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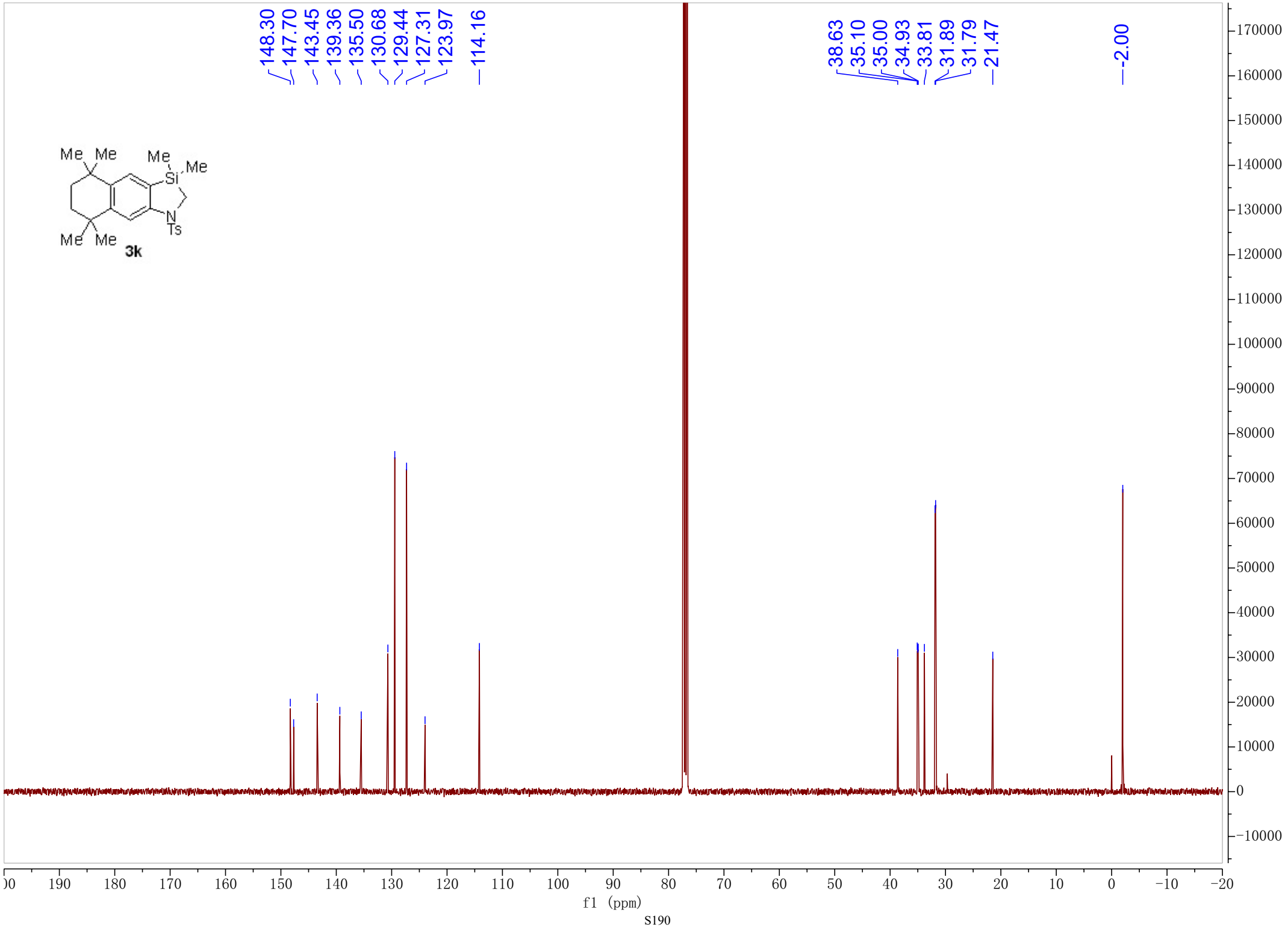
1.97
2.06
3.00
4.07
6.04
6.05
5.99
f1 (ppm)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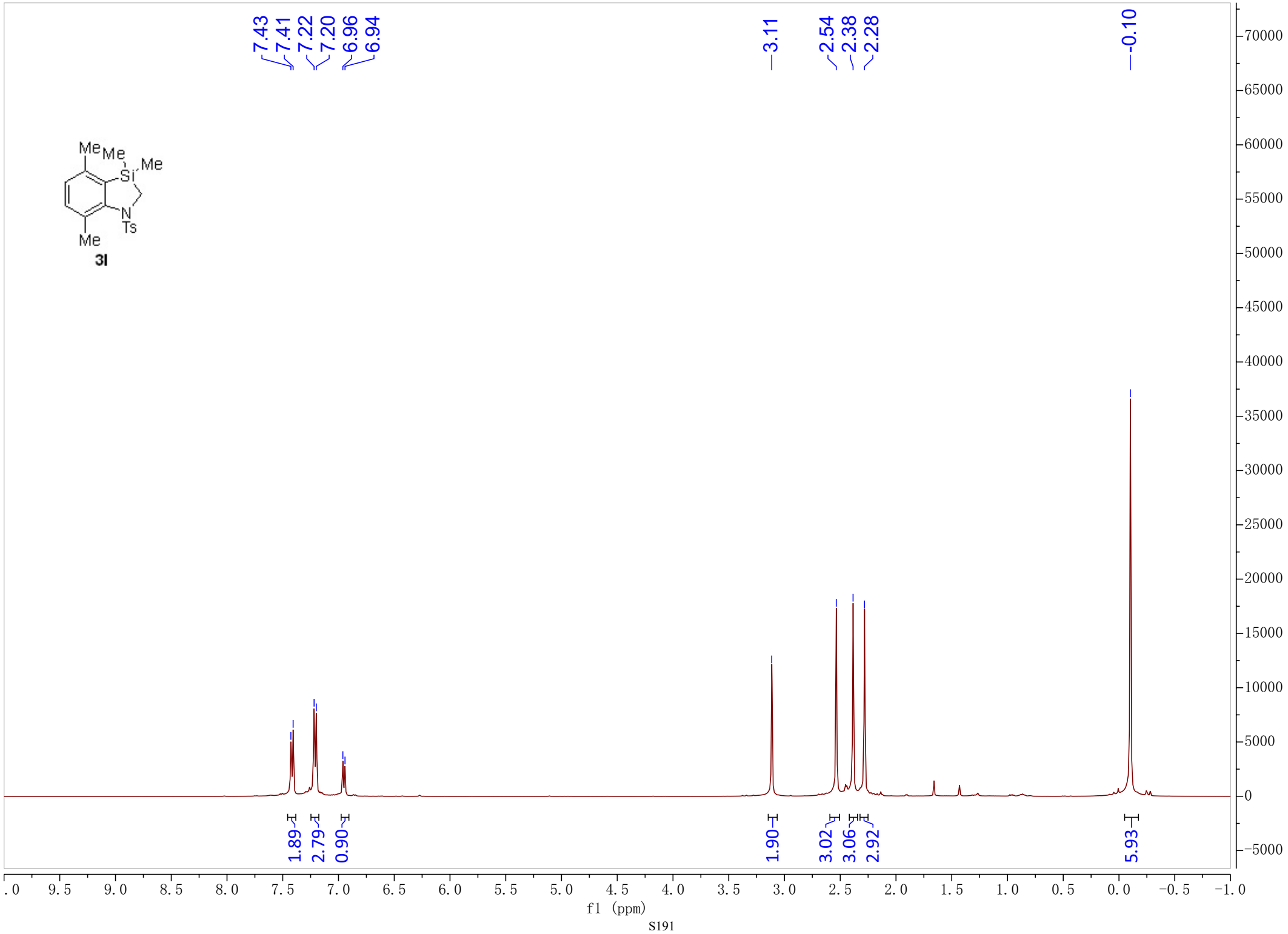
130.68
129.44
127.31
123.97
114.16
38.63
35.10
35.00
34.93
33.81
31.89
31.79
21.47
2.00
Me
Me
Me
Si
Me
N
Ts
Me
Me
3k
f1 (ppm)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7.41
7.22
7.20
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6.94
3.11
2.54
2.38
2.28
-0.10
Me
Me
Si
Me
N
Ts
Me
3l
1.89
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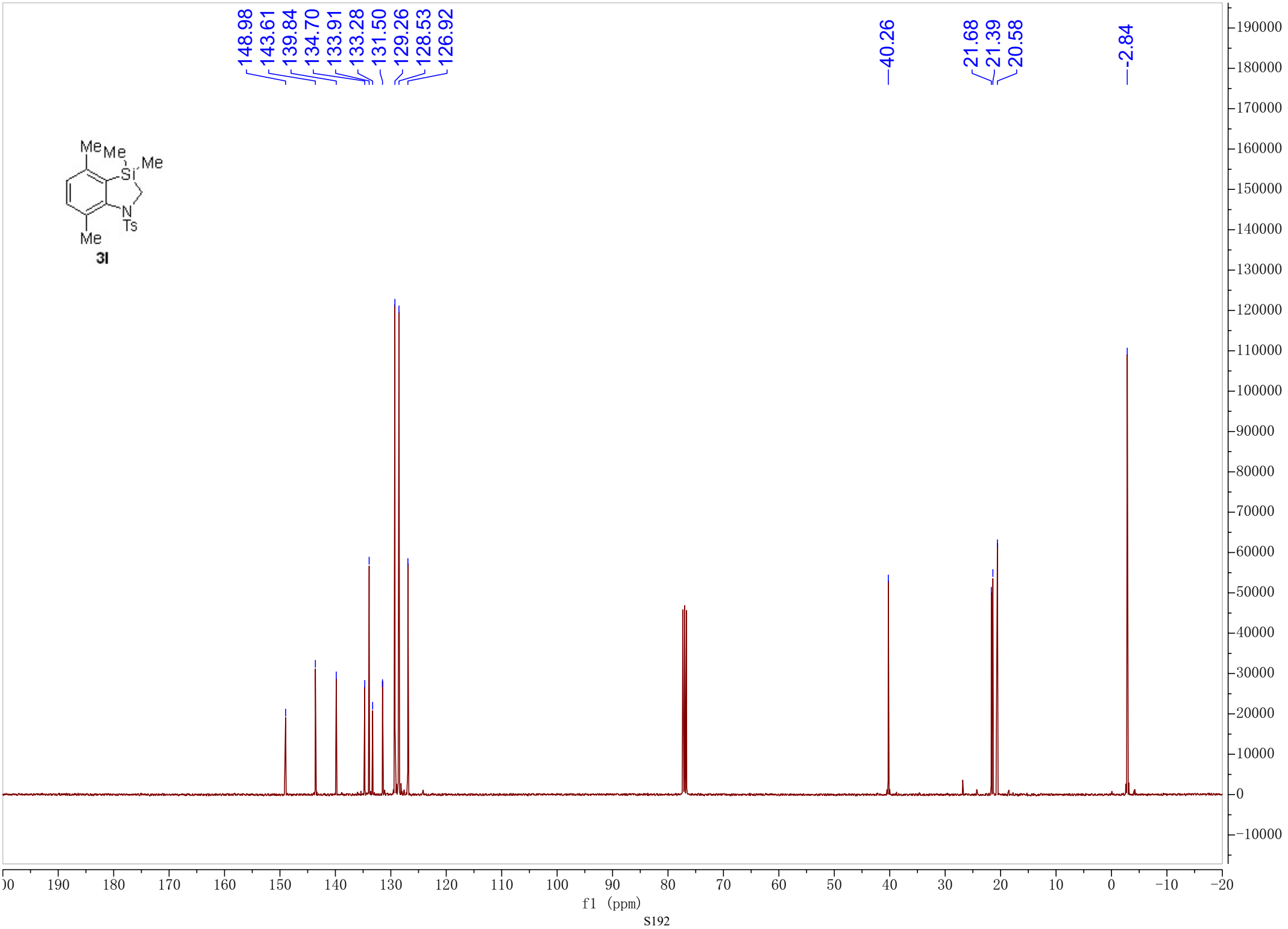
0.90
1.90
3.02
3.06
2.92
5.93
f1 (ppm)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133.28
131.50
129.26
128.53
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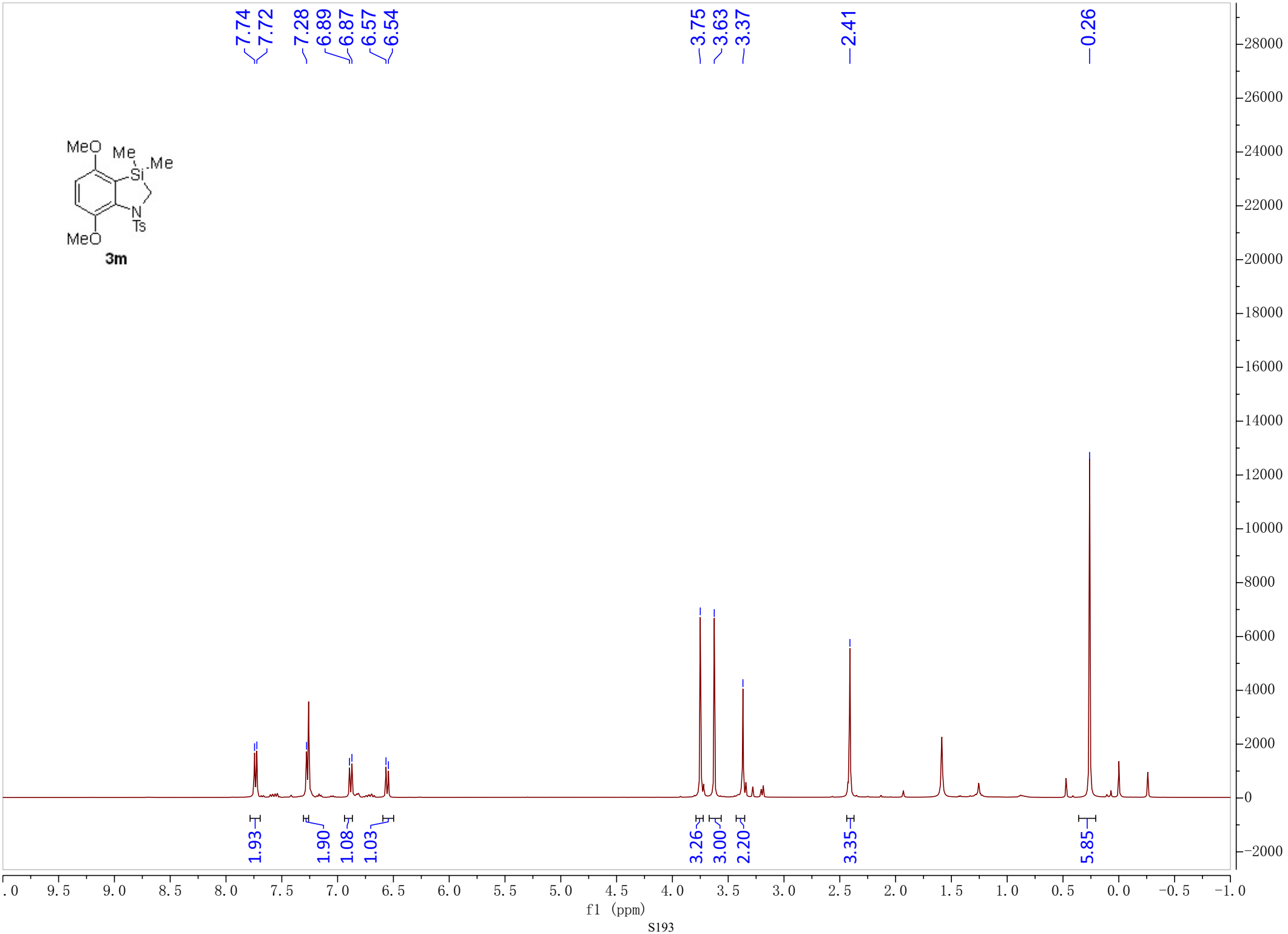
21.39
20.58
-2.84
Me
Me
Si
Me
N
Ts
Me
3l
f1 (ppm)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6.57
6.54
3.75
3.63
3.37
2.41
0.26
MeO
Me
Si
Me
N
Ts
MeO
3m
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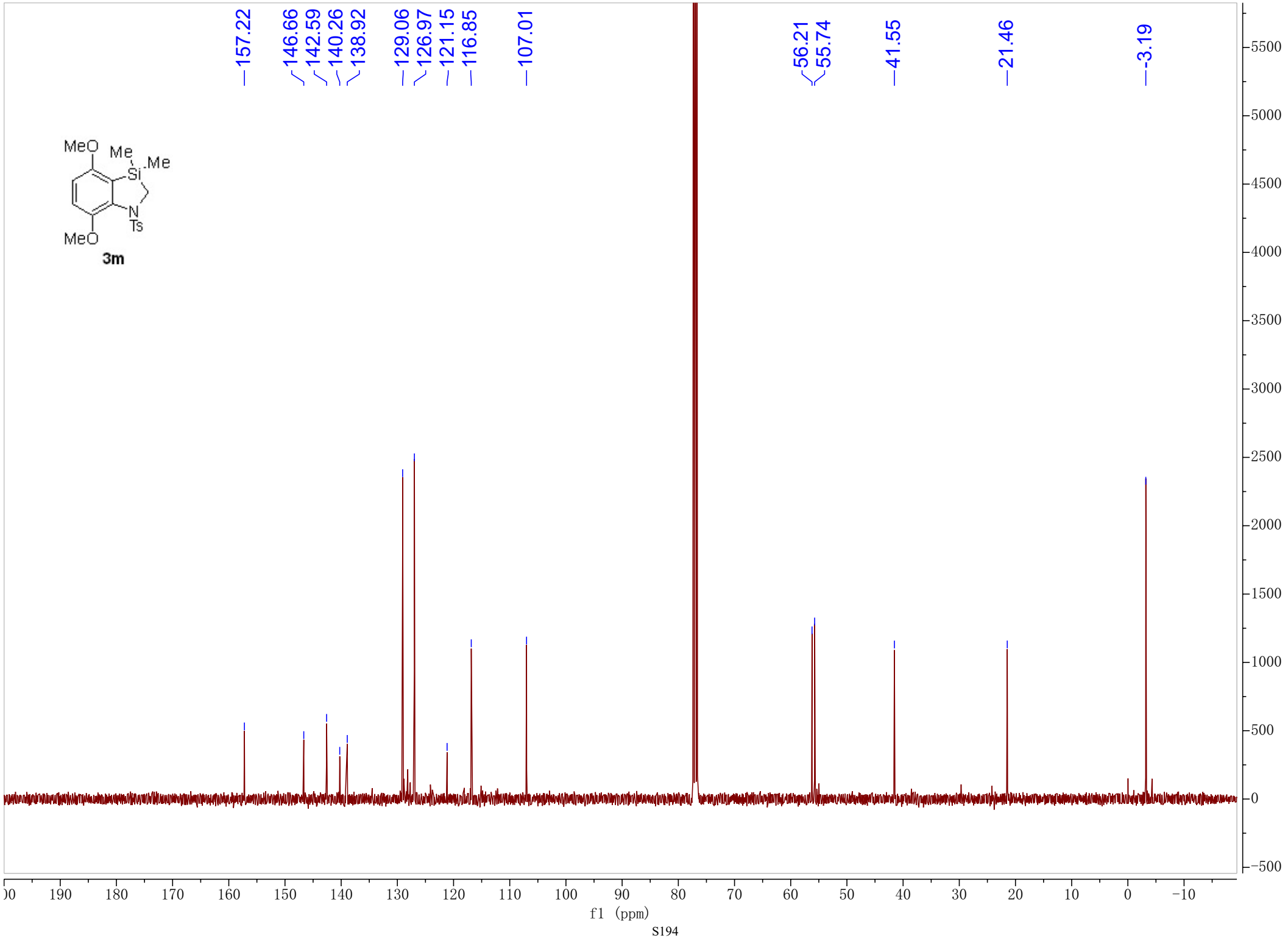
1.90
1.08
1.03
3.26
3.00
2.20
3.35
5.85
f1 (ppm)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142.59
140.26
138.92
129.06
126.97
121.15
116.85
107.01
56.21
55.74
41.55
21.46
-3.19
MeO
Me
Me
Si
N
Ts
MeO
3m
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
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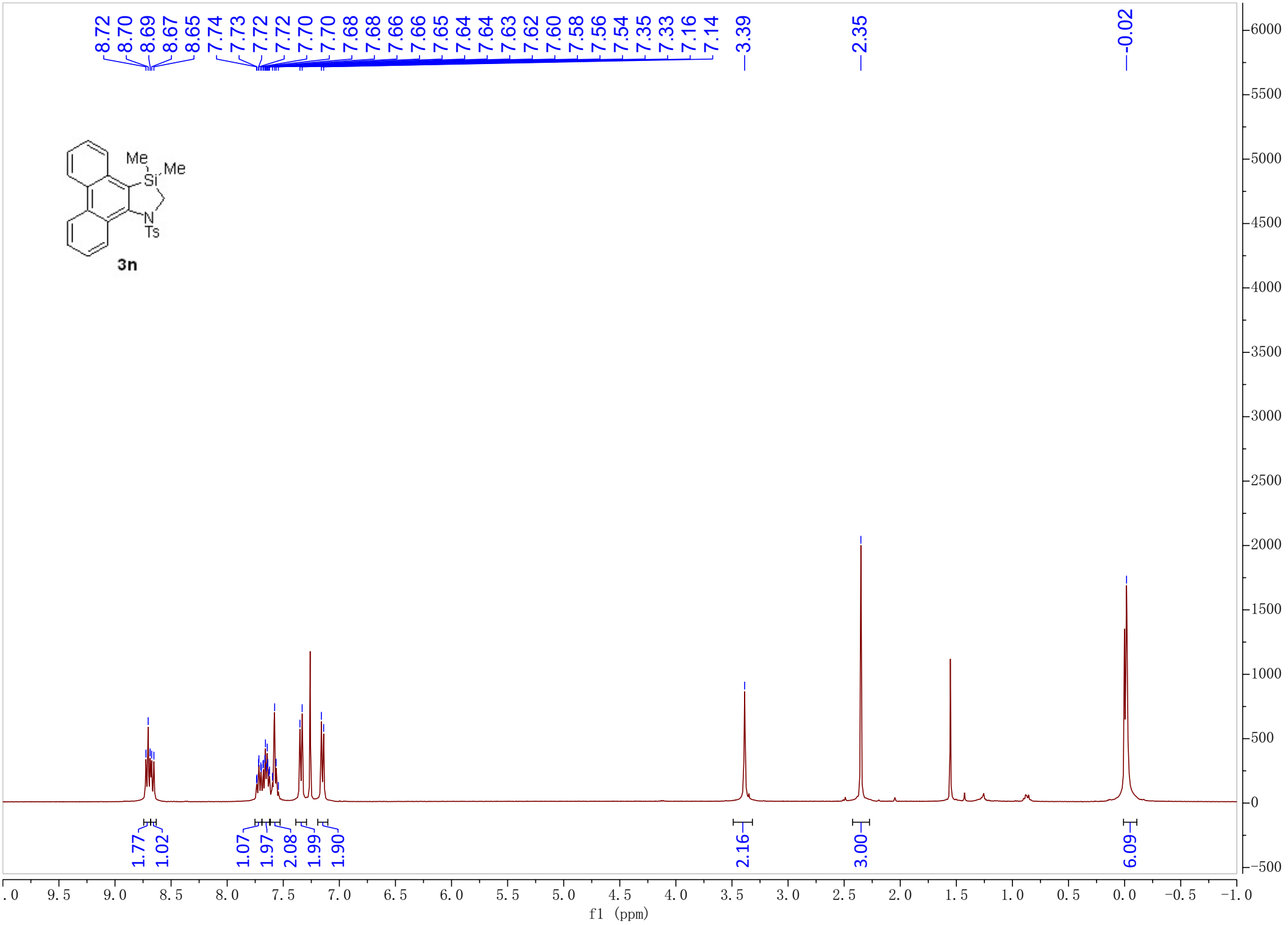
0
-10
f1 (ppm)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7.74
7.73
7.72
7.72
7.70
7.70
7.68
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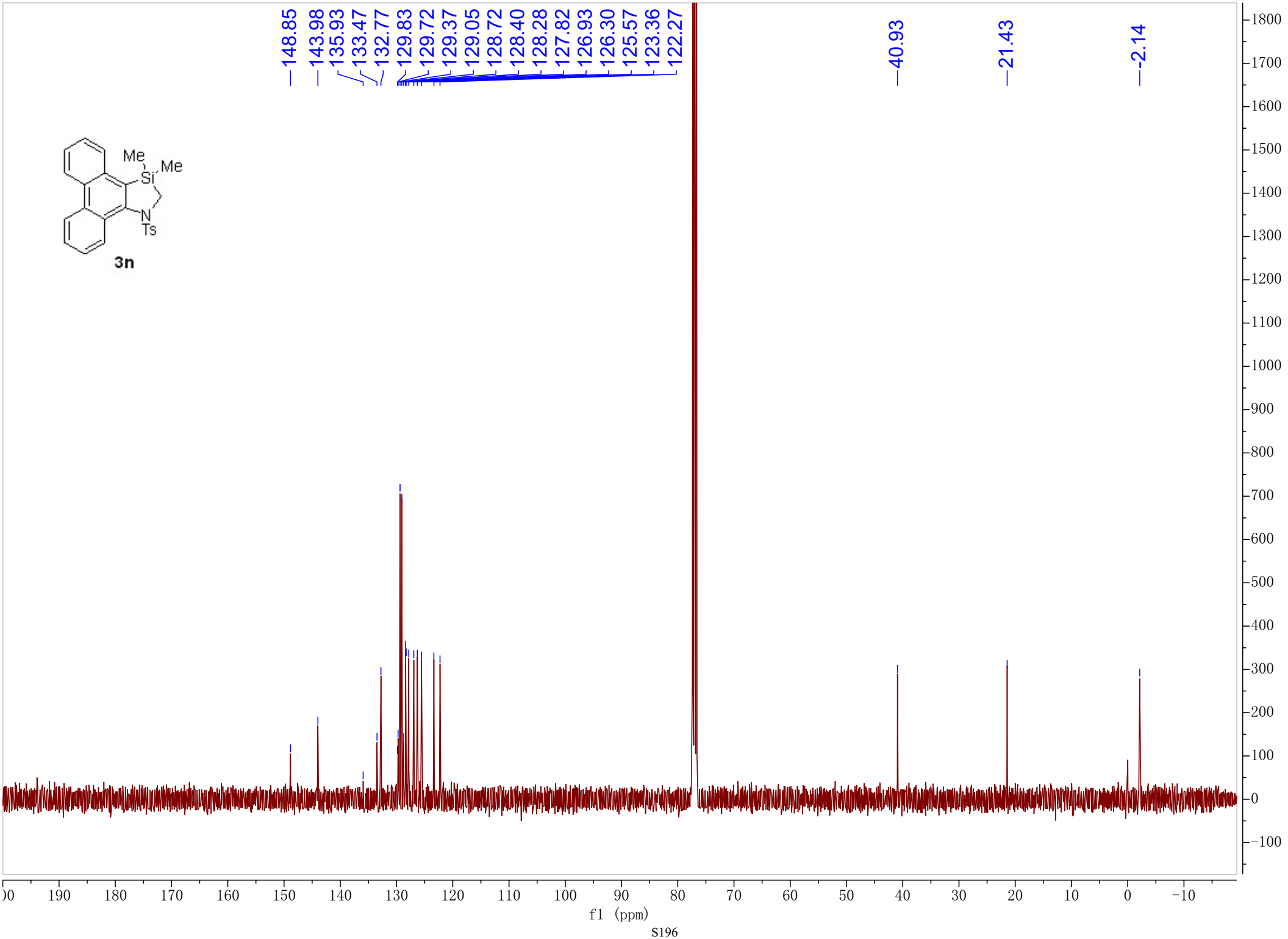
7.66
7.66
7.65
7.64
7.64
7.63
7.62
7.60
7.58
7.56
7.54
7.35
7.33
7.16
7.14
3.39
2.35
-0.02
Me
Si
Me
N
Ts
3n
1.77
1.02
1.07
1.97
2.08
1.99
1.90
2.16
3.00
6.09
f1 (ppm)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129.72
129.37
129.05
128.72
128.40
128.28
127.82
126.93
126.30
125.57
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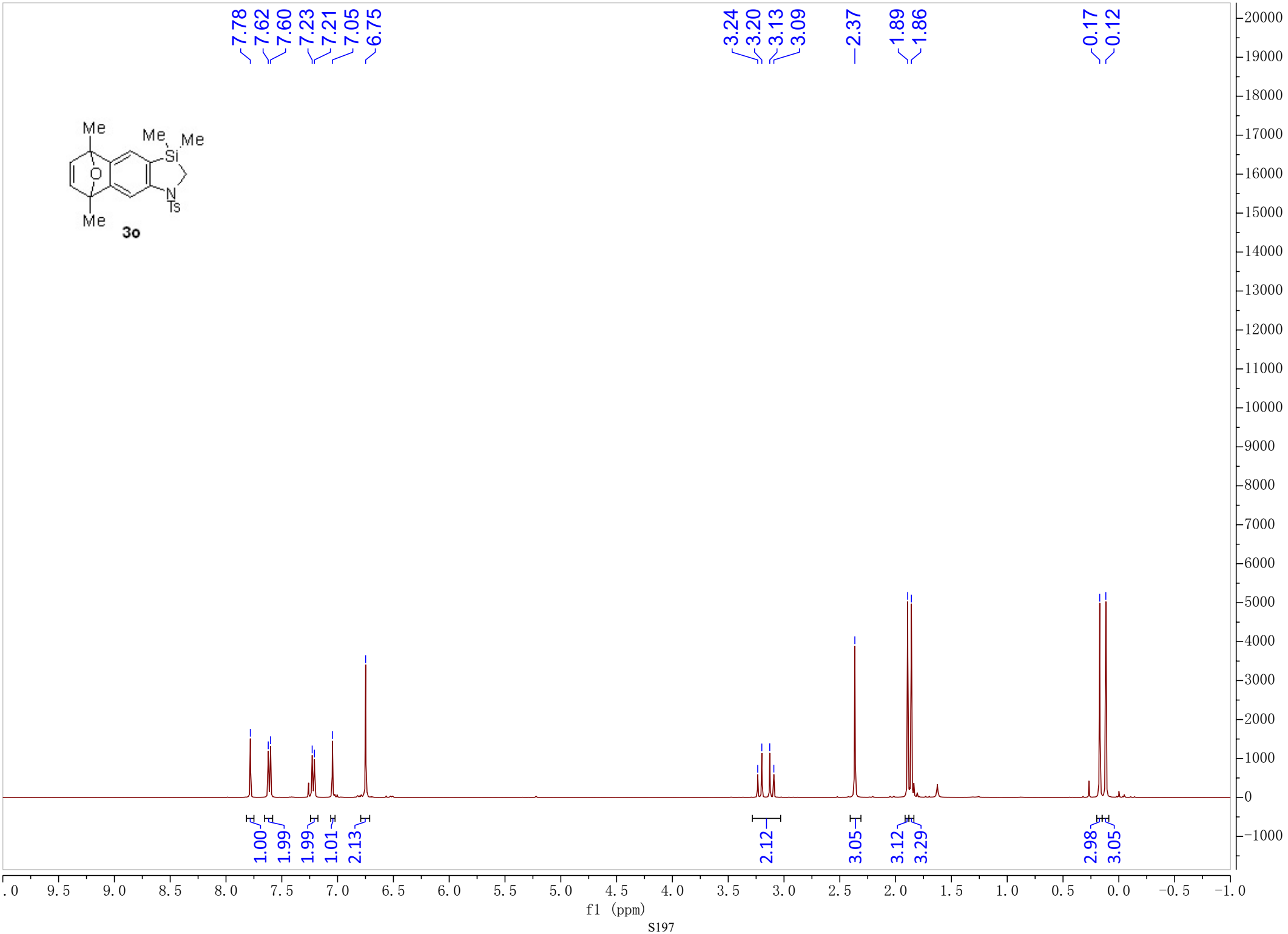
122.27
40.93
21.43
-2.14
Me
Si
Me
N
Ts
3n
f1 (ppm)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7.62
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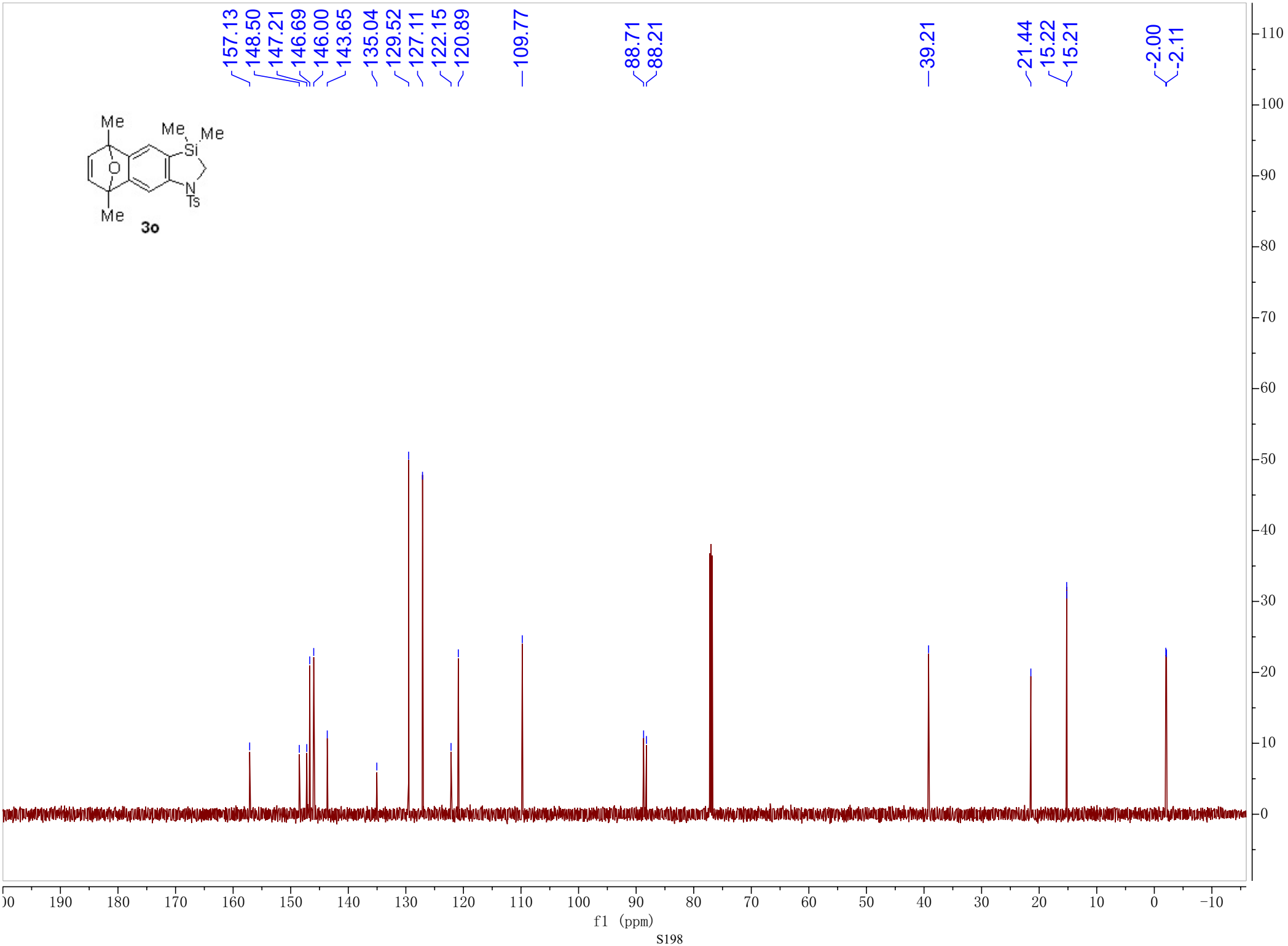
7.23
7.21
7.05
6.75
3.24
3.20
3.13
3.09
2.37
1.89
1.86
0.17
0.12
Me
Me
Me
Si
O
N
Ts
Me
3o
1.00
1.99
1.99
1.01
2.13
2.12
3.05
3.12
3.29
2.98
3.05
f1 (ppm)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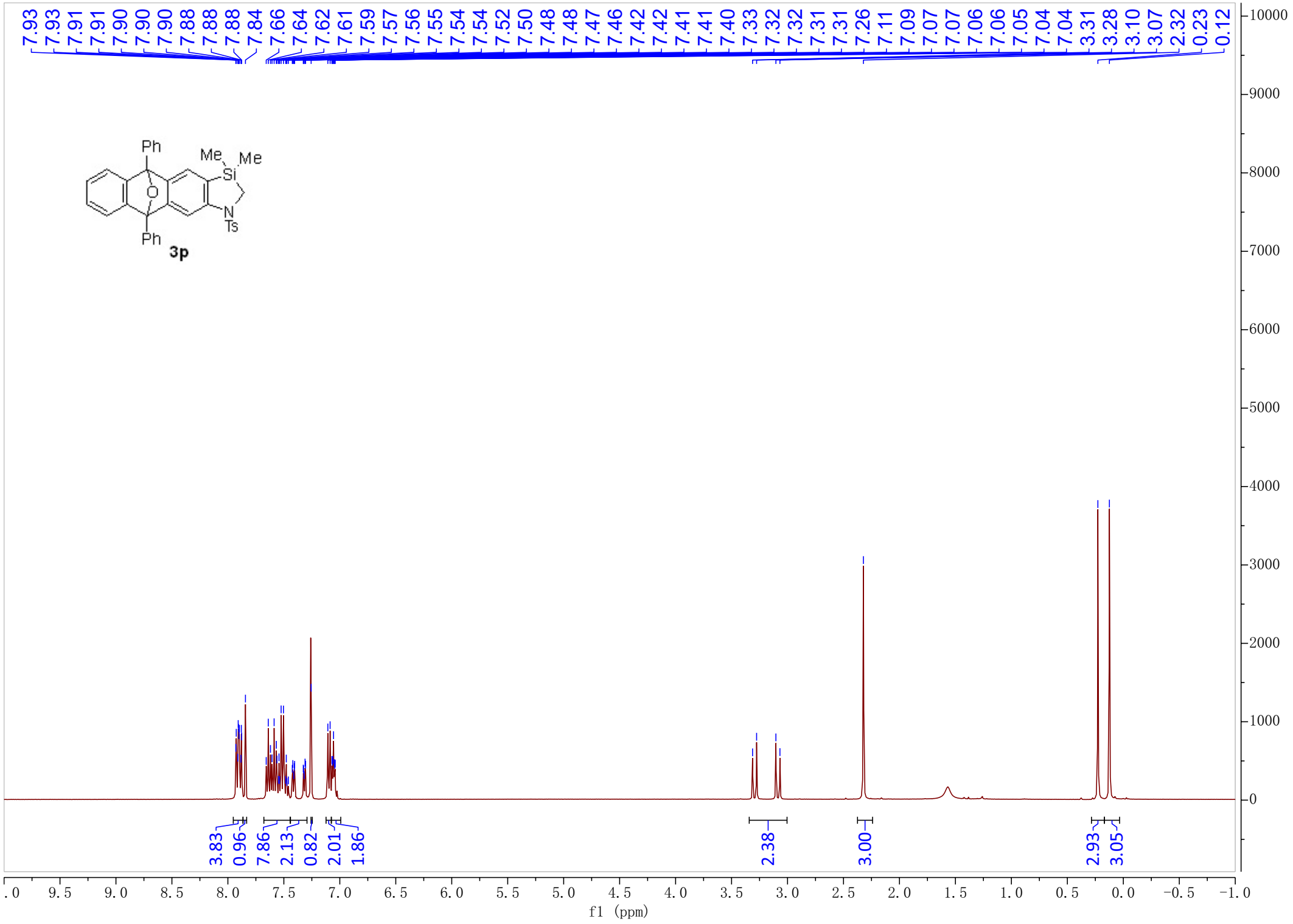
129.52
127.11
122.15
120.89
109.77
88.71
88.21
39.21
21.44
15.22
15.21
2.00
2.11
Me
Me
Me
Si
O
N
Ts
Me
3o
f1 (ppm)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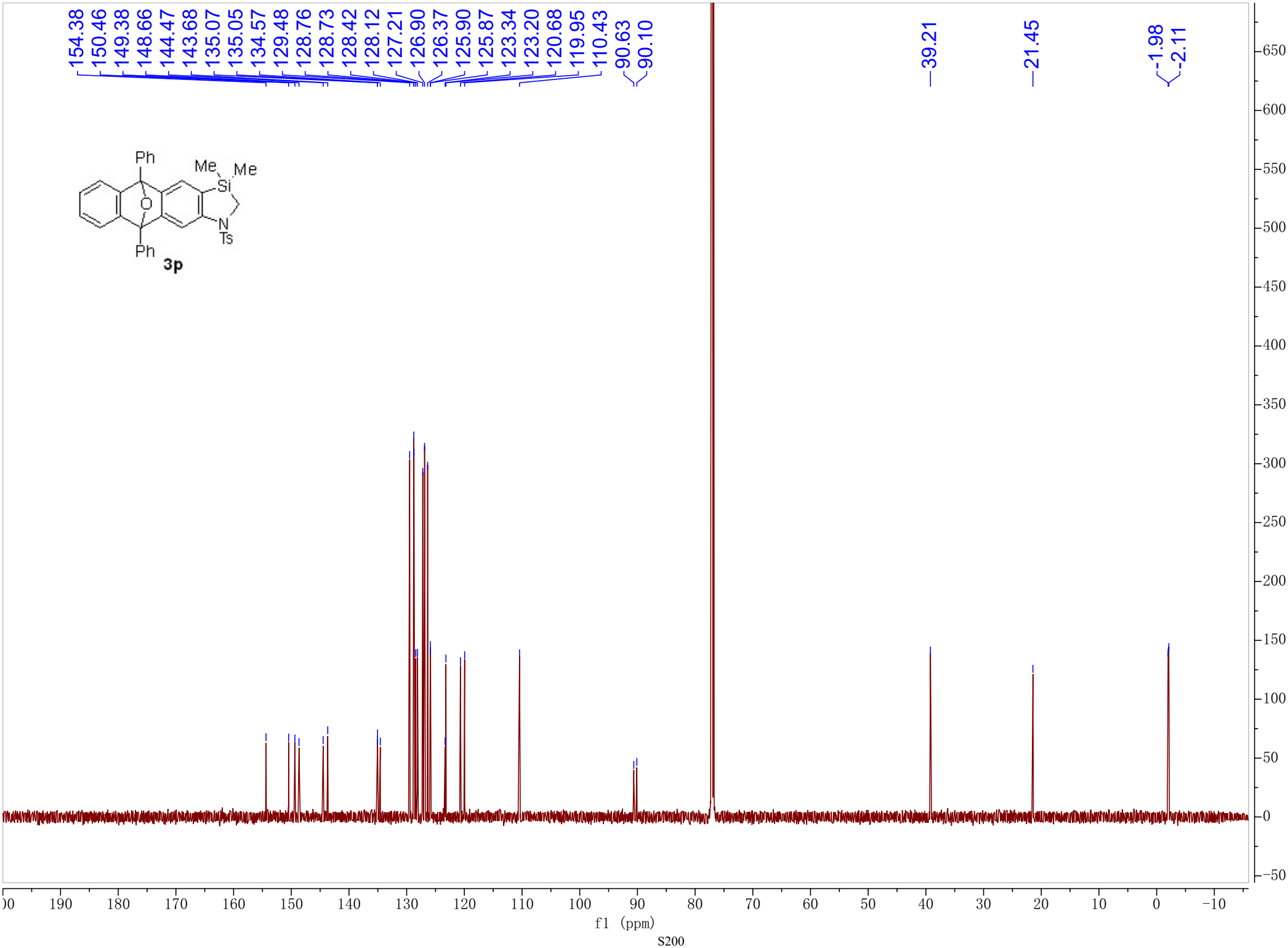
Ph
Me
Me
Si
O
N
Ts
Ph
3p
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
3.83 0.96 7.86 2.13 0.82 2.01 1.86 2.38 3.00 2.93 3.05
.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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135.07
135.05
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129.48
128.76
128.73
128.42
128.12
127.21
126.90
126.37
125.90
125.87
123.34
123.20
120.68
119.95
110.43
90.63
90.10
39.21
21.45
-1.98
-2.11
Ph
Me
Me
Si
O
N
Ts
Ph
3p
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
190
180
170
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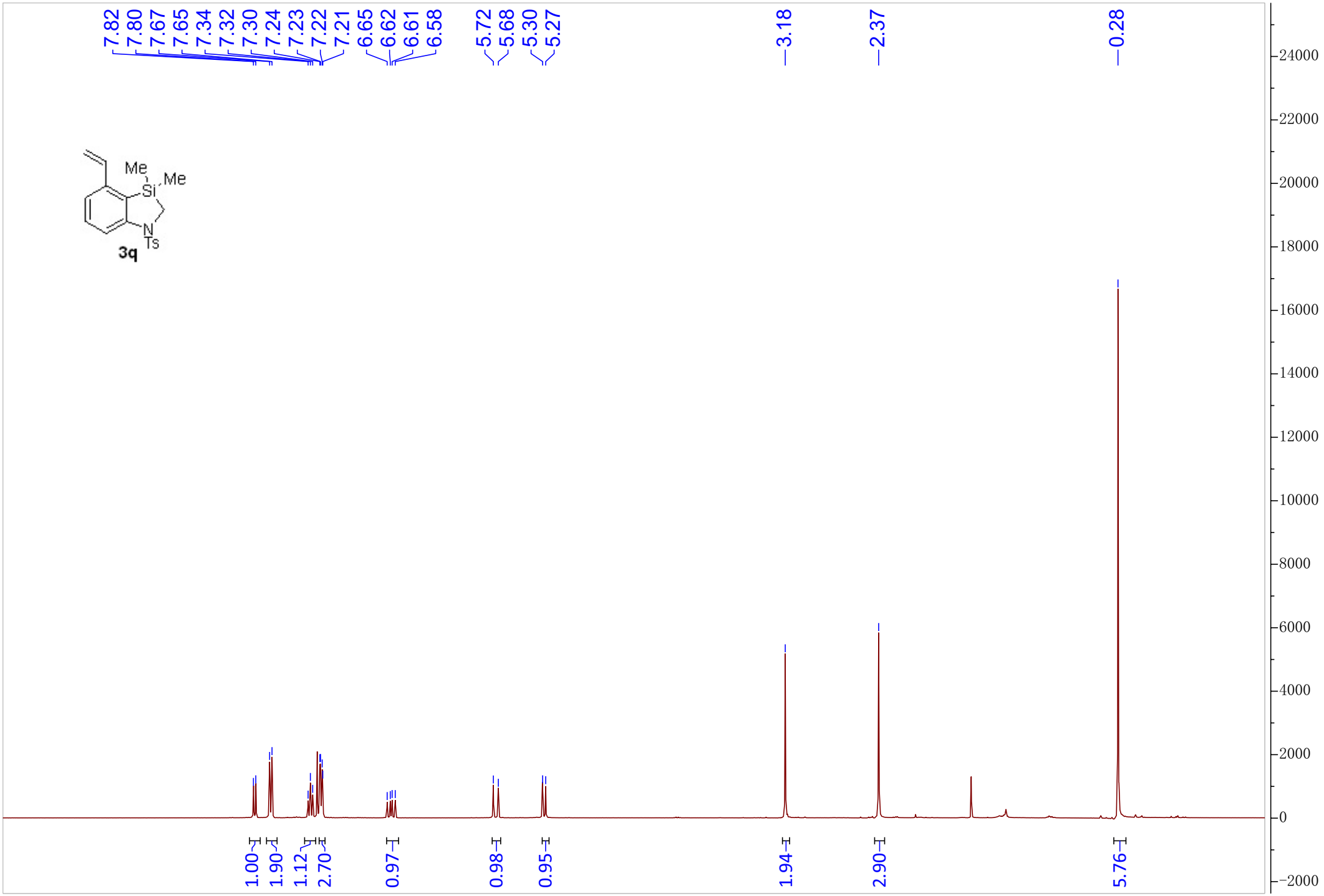
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.32
7.30
7.24
7.23
7.22
7.21
6.65
6.62
6.61
6.58
5.72
5.68
5.30
5.27
3.18
2.37
0.28
Me
Si
Me
N
Ts
3q
1.00
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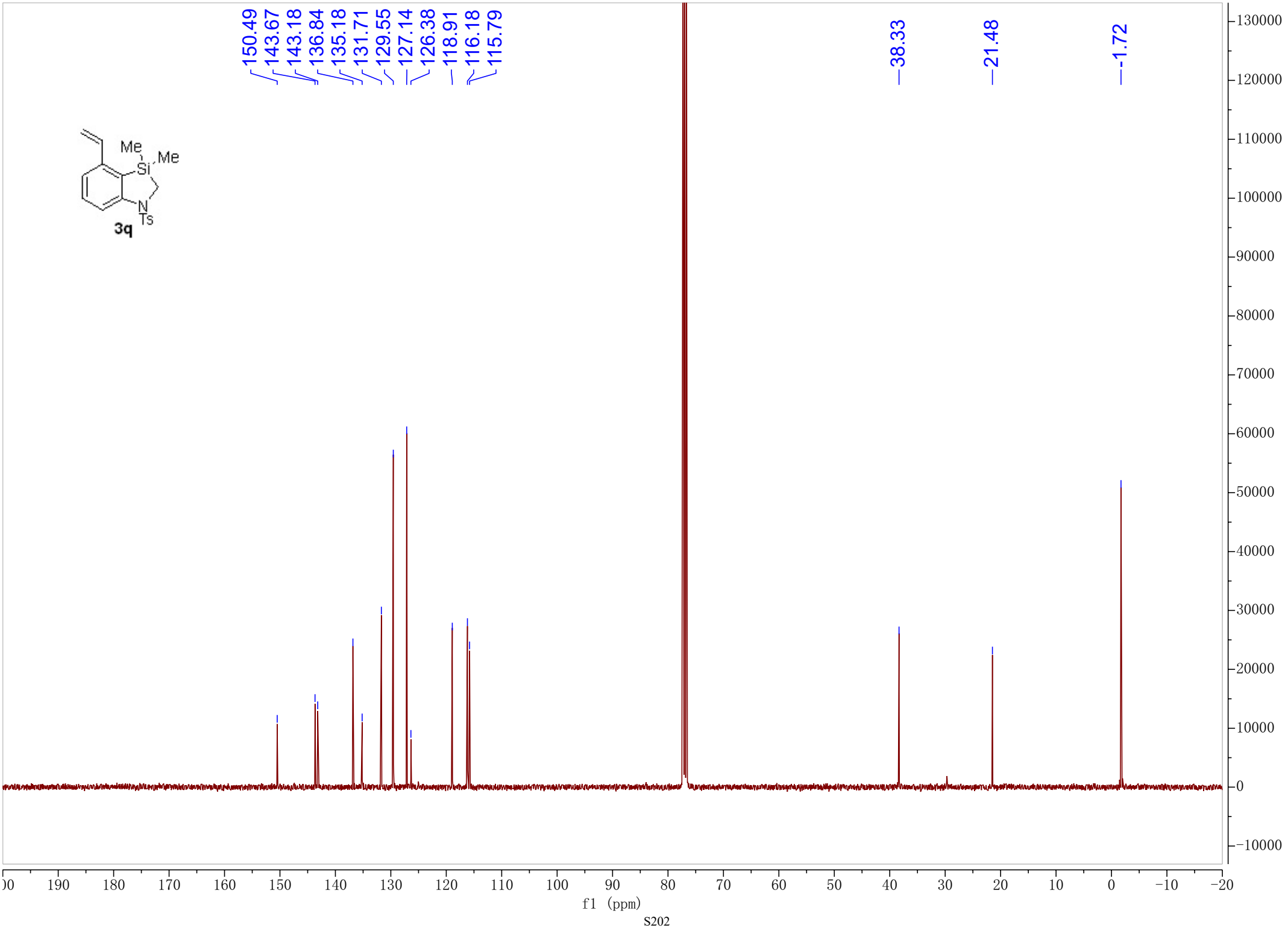
1.12
2.70
0.97
0.98
0.95
1.94
2.90
5.76
f1 (ppm)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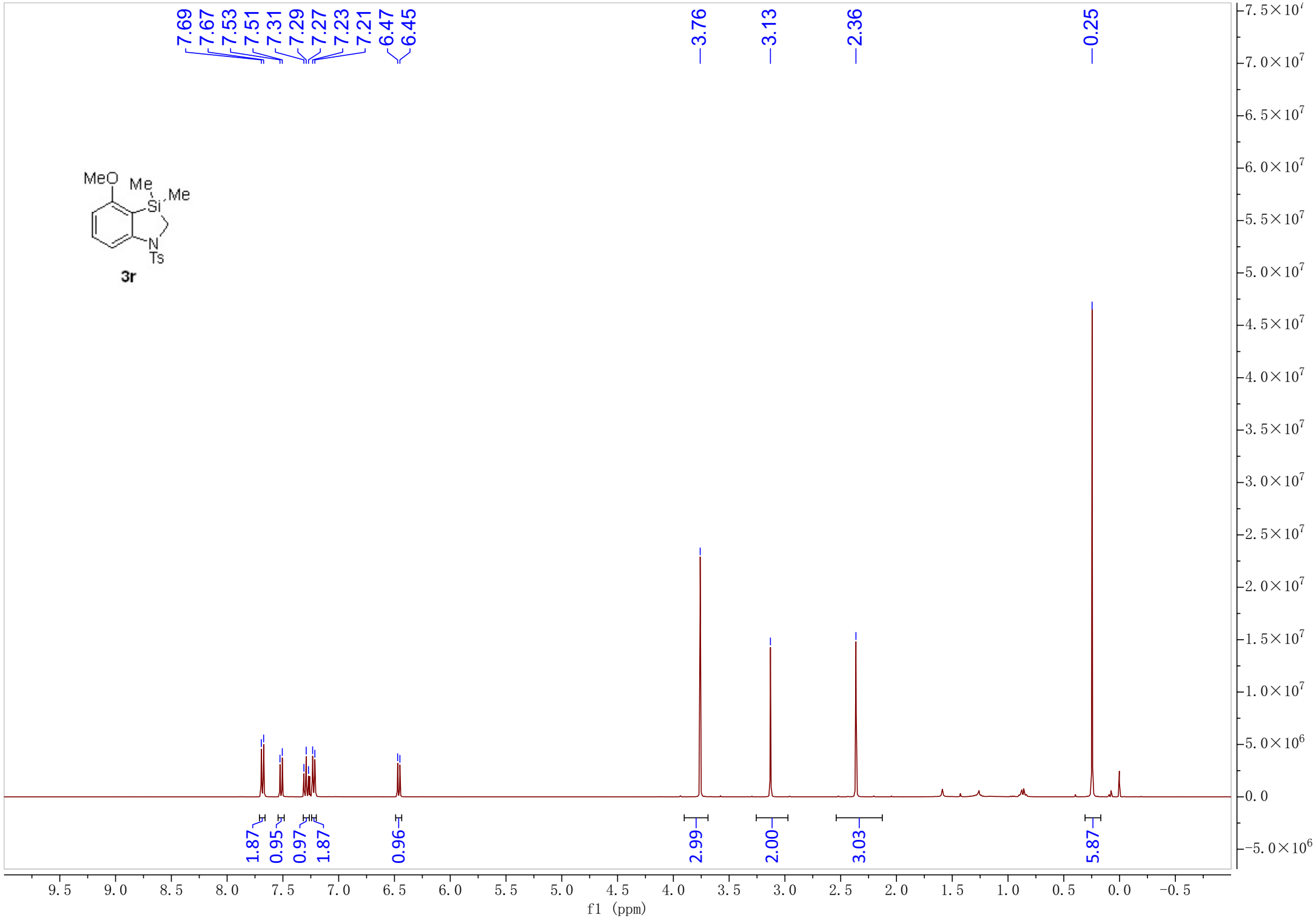
129.55
127.14
126.38
118.91
116.18
115.79
38.33
21.48
-1.72
Me
Si
Me
N
Ts
3q
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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7.31
7.29
7.27
7.23
7.21
6.47
6.45
3.76
3.13
2.36
0.25
MeO
Me
Si
Me
N
Ts
3r
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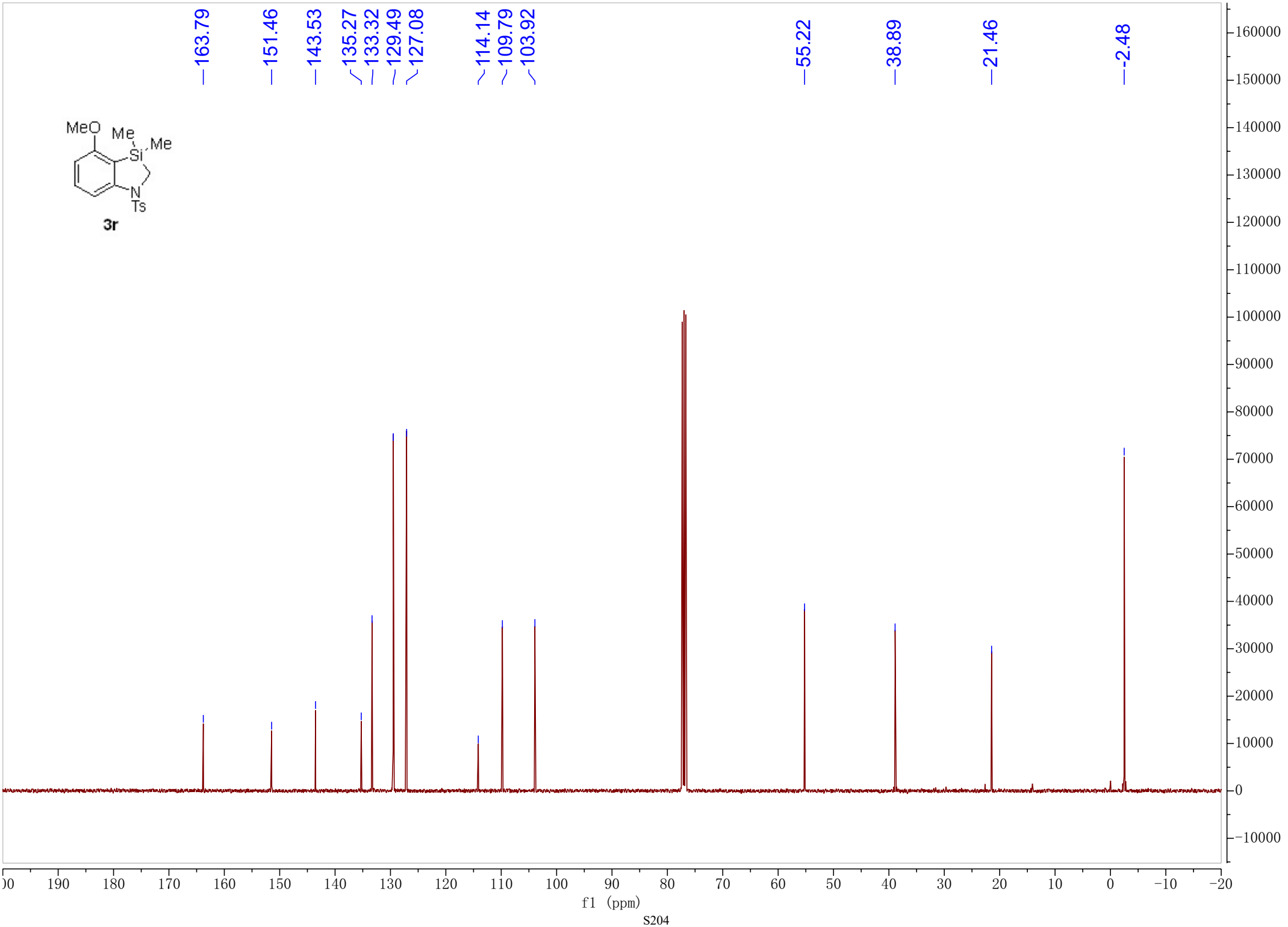
0.95
0.97
1.87
0.96
2.99
2.00
3.03
5.87
f1 (ppm)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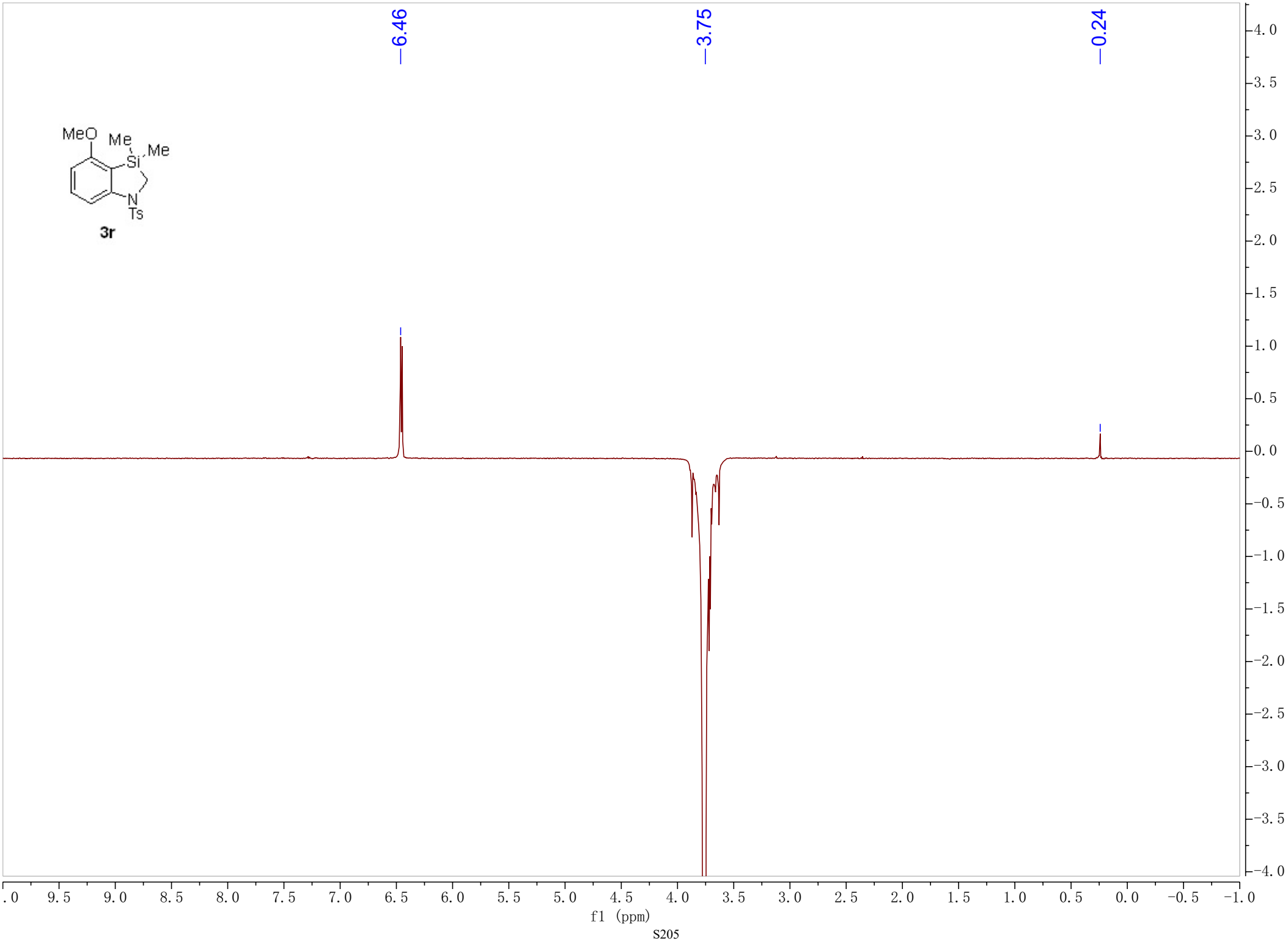
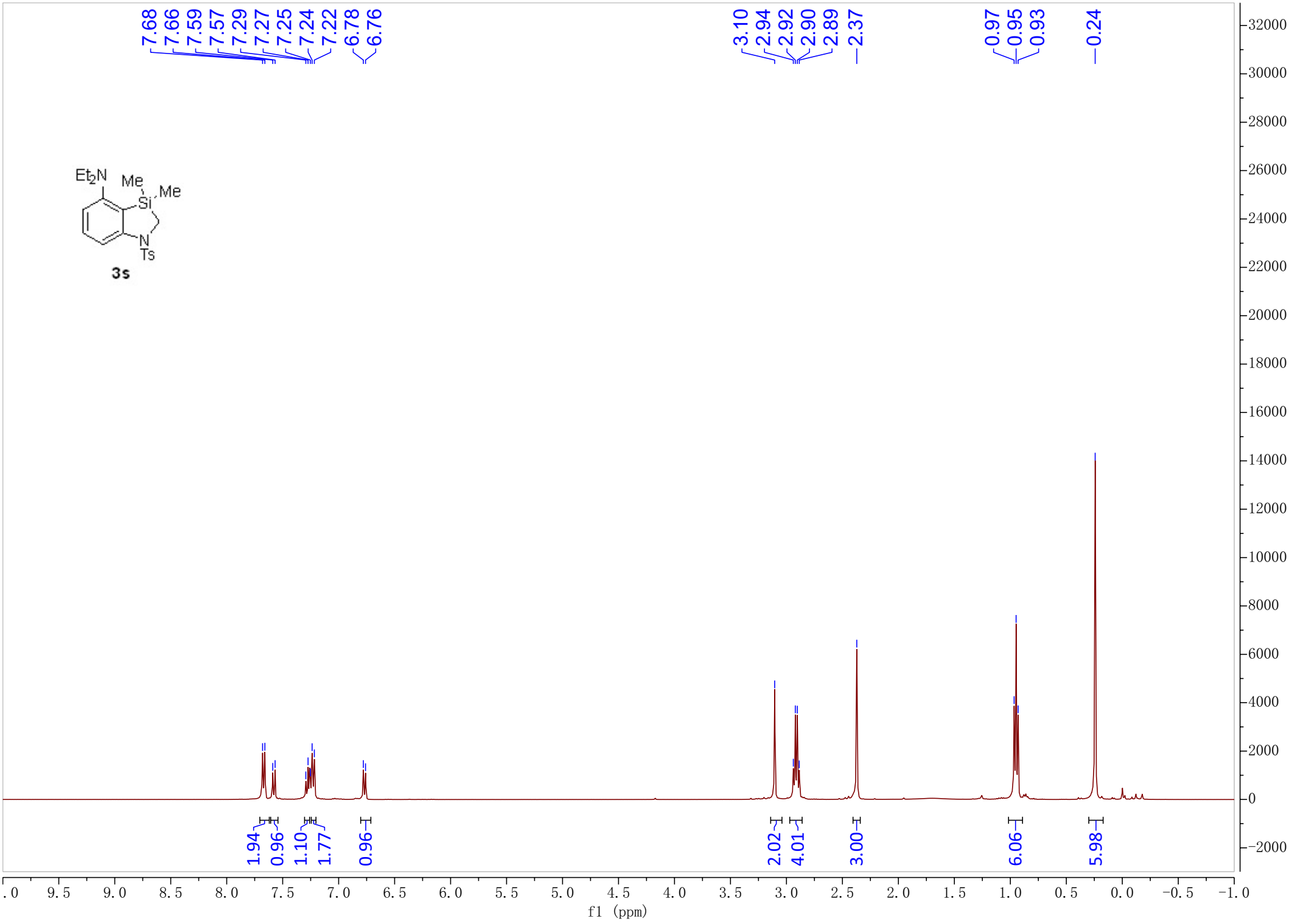
135.27
133.32
129.49
127.08
114.14
109.79
103.92
55.22
38.89
21.46
-2.48
MeO
Me
Si
Me
N
Ts
3r
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


6.46
3.75
0.24
MeO
Me
Si
Me
N
Ts
3r
f1 (ppm)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7.57
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7.27
7.25
7.24
7.22
6.78
6.76
3.10
2.94
2.92
2.90
2.89
2.37
0.97
0.95
0.93
0.24
Et2N
Me
Si
Me
N
Ts
3s
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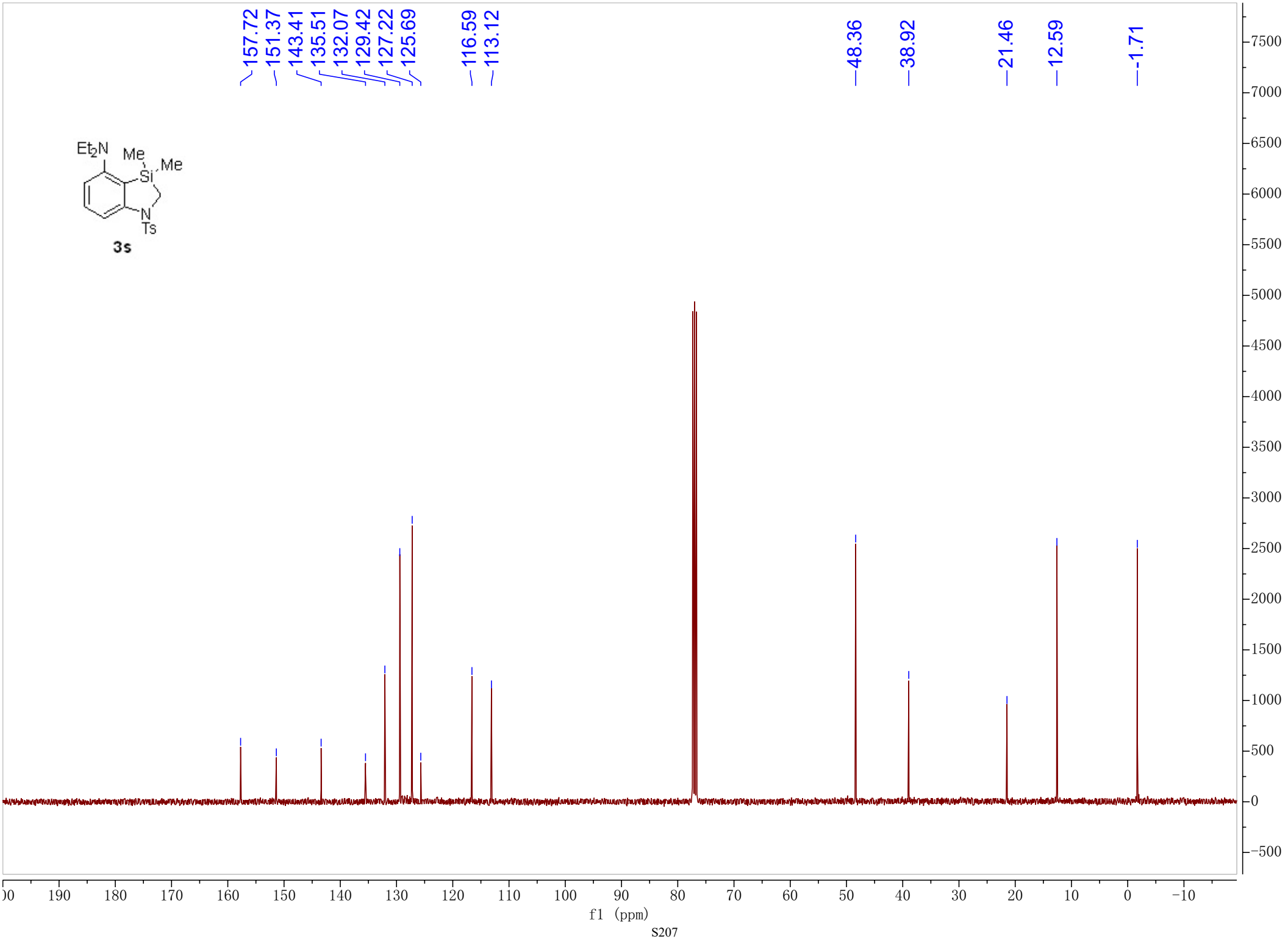
0.96
1.10
1.77
0.96
2.02
4.01
3.00
6.06
5.98
f1 (ppm)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132.07
129.42
127.22
125.69
116.59
113.12
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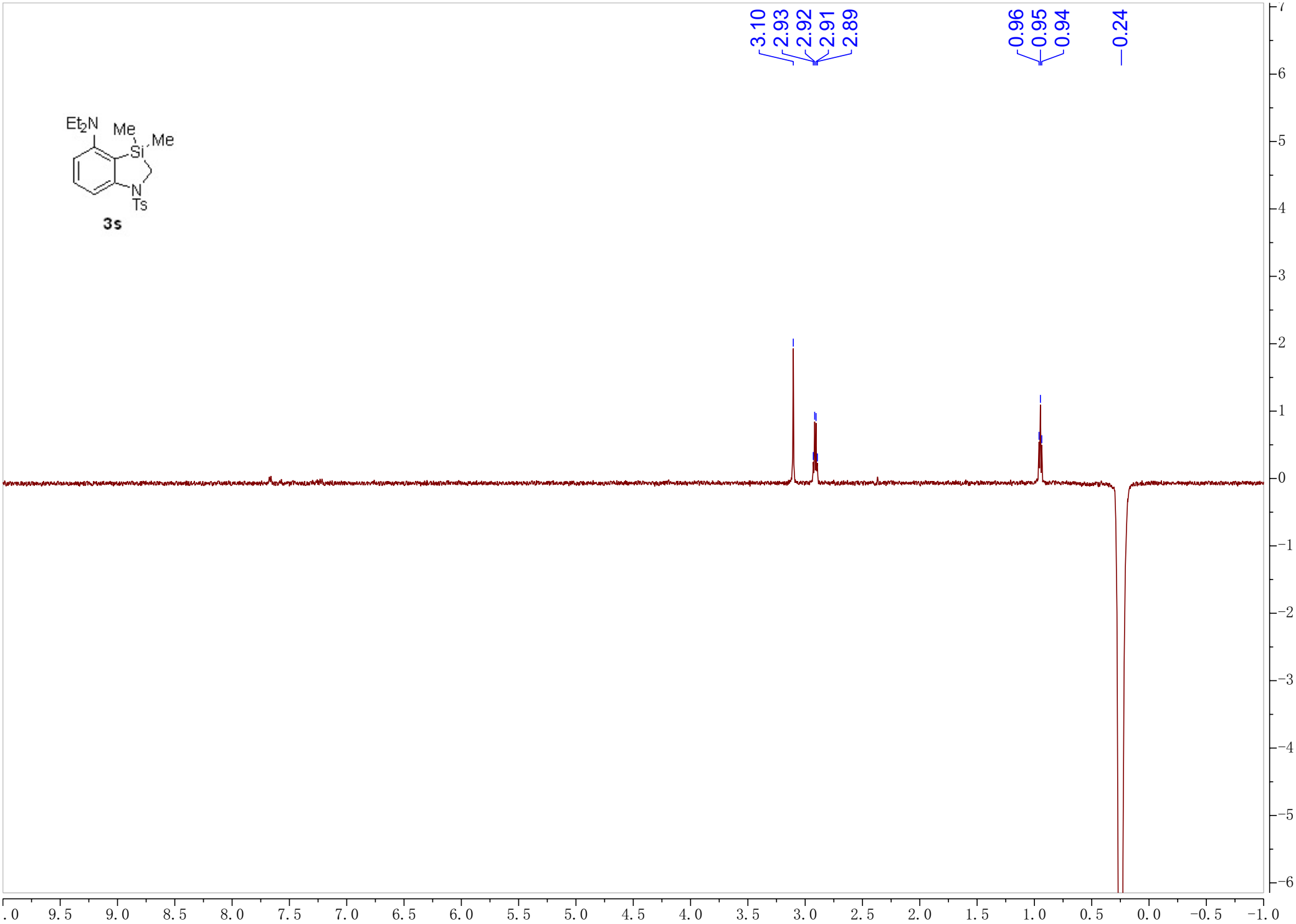
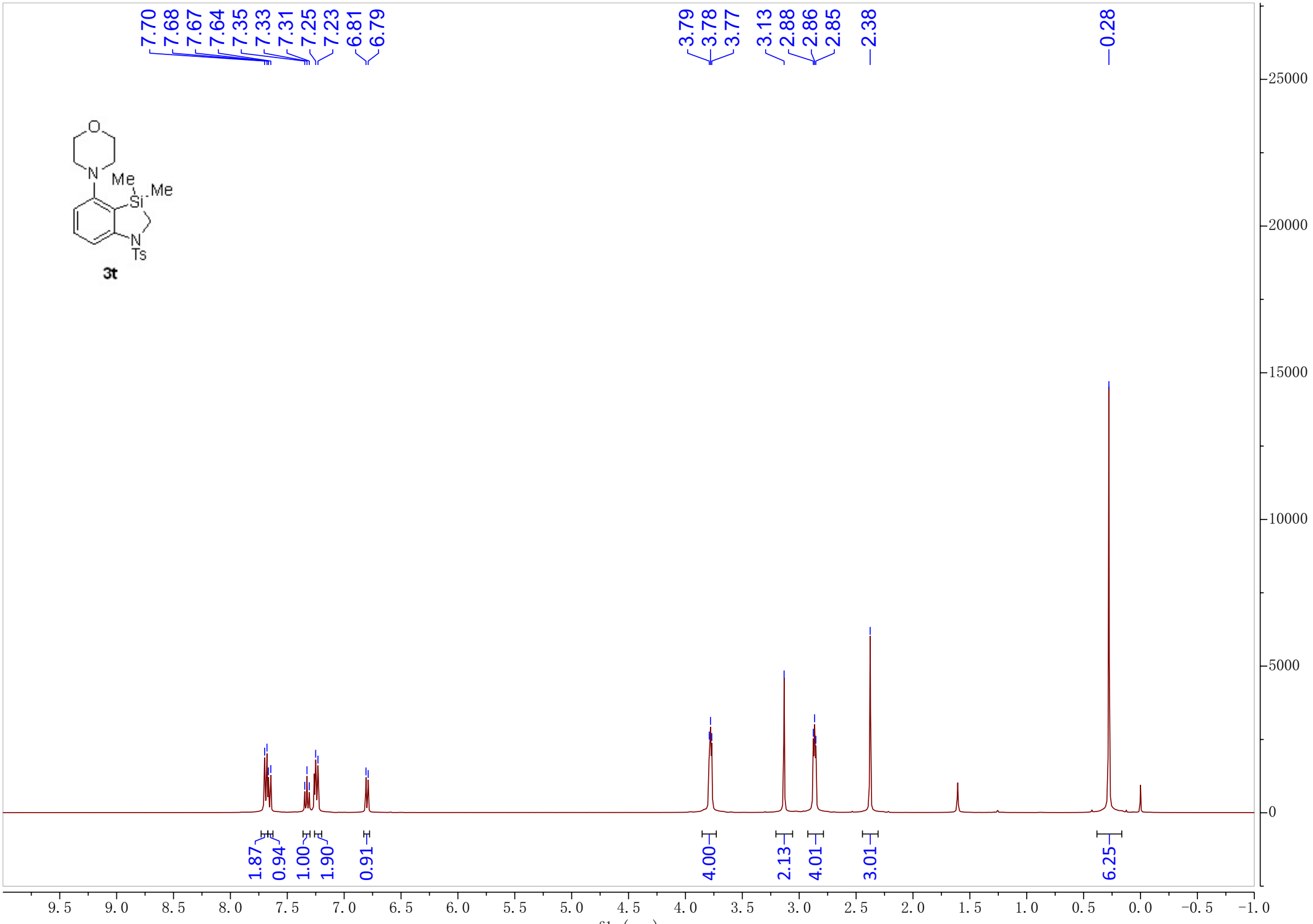
21.46
12.59
-1.71
Et2N
Me
Me
Si
N
Ts
3s
f1 (ppm)


3.10
2.93
2.92
2.91
2.89
0.96
0.95
0.94
0.24
Et2N
Me
Me
Si
N
Ts
3s
f1 (ppm)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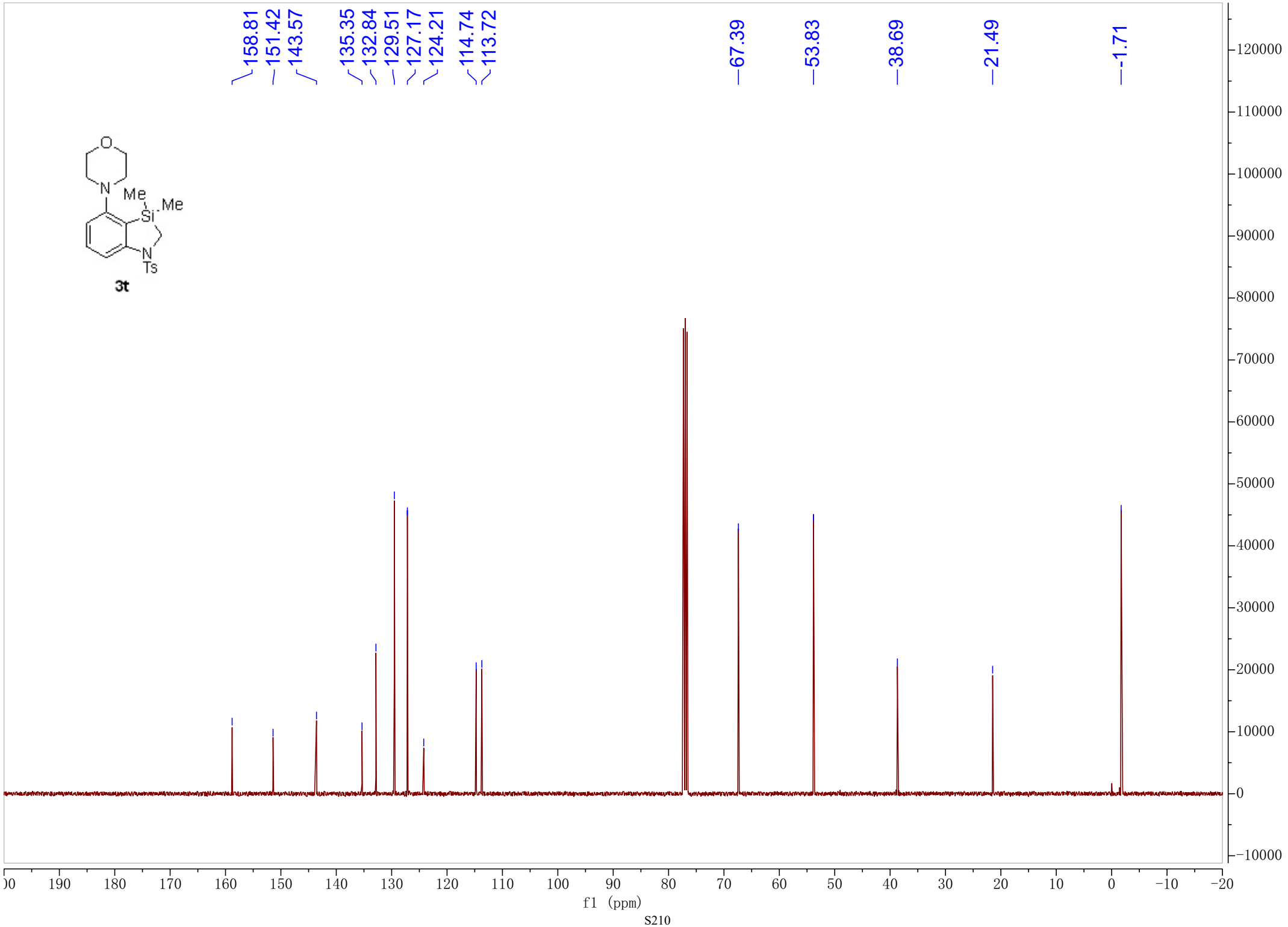
7.33
7.31
7.25
7.23
6.81
6.79
3.79
3.78
3.77
3.13
2.88
2.86
2.85
2.38
0.28
Me
Me
Si
N
Ts
O
N
3t
25000
20000
15000
10000
5000
0
1.87
0.94
1.00
1.90
0.91
4.00
2.13
4.01
3.01
6.25
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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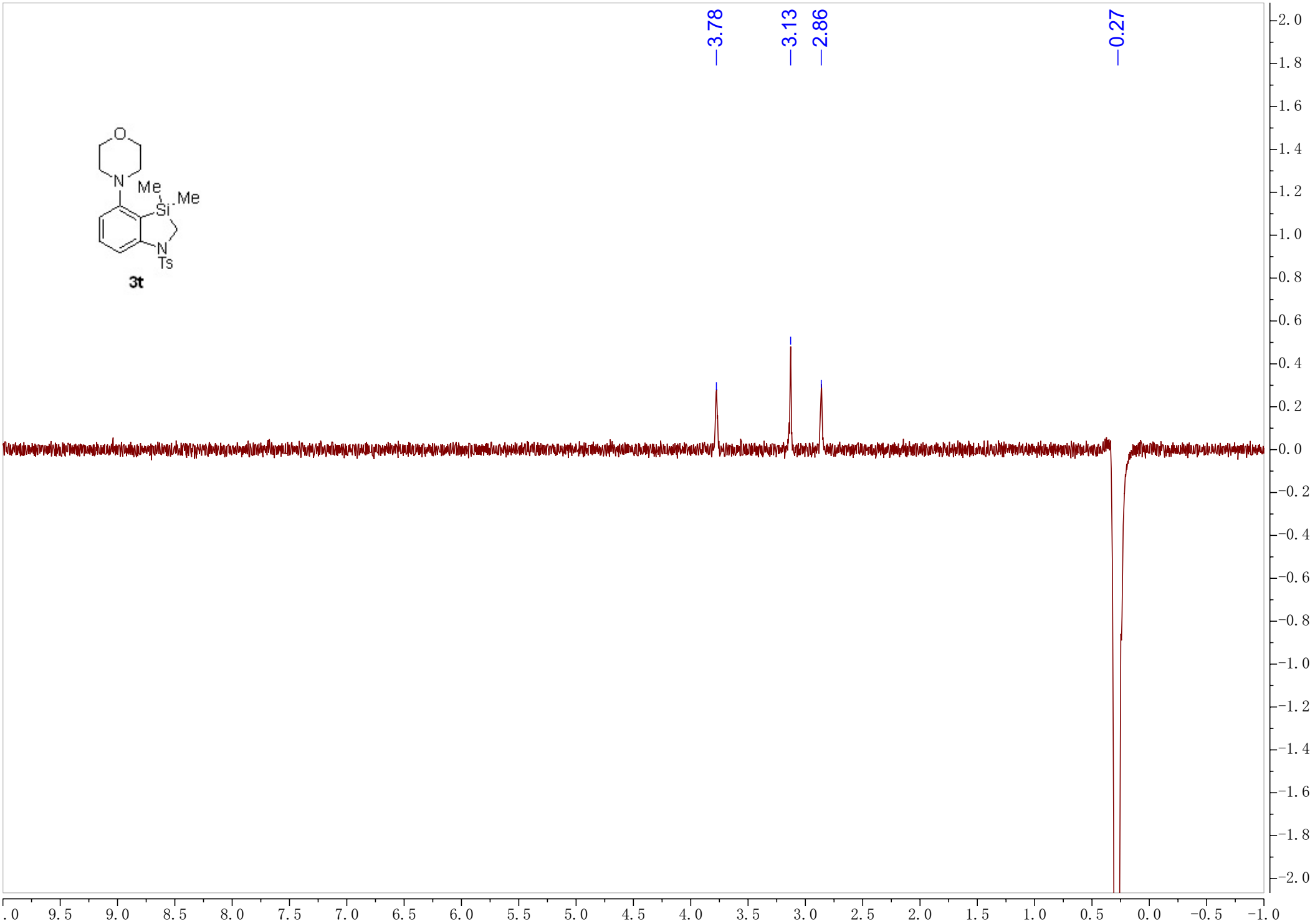
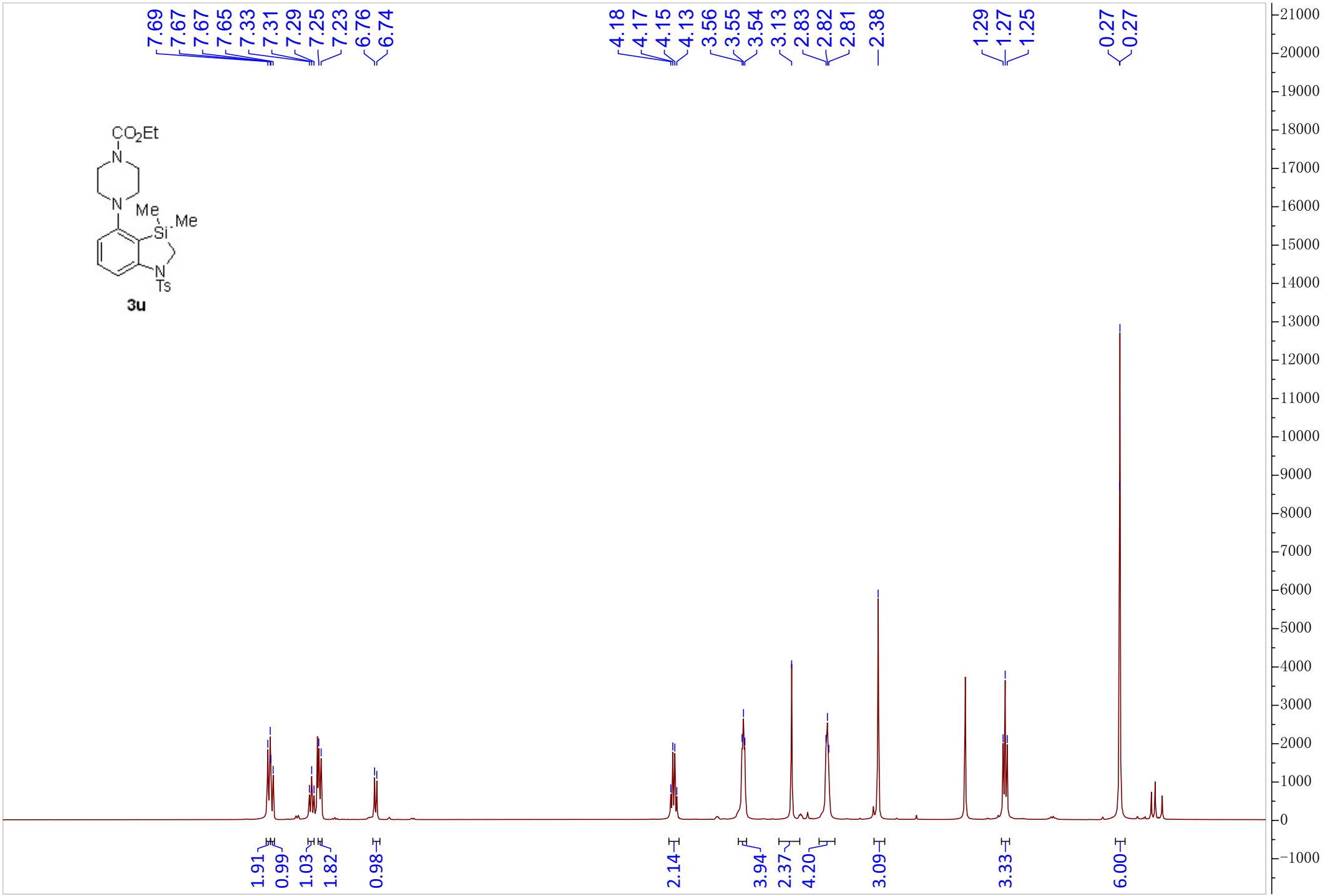
67.39
53.83
38.69
21.49
-1.71
O
N
Me
Si
Me
N
Ts
3t
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


3.78
3.13
2.86
0.27
O
N
Me
Si
Me
N
Ts
3t
f1 (ppm)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7.67
7.67
7.65
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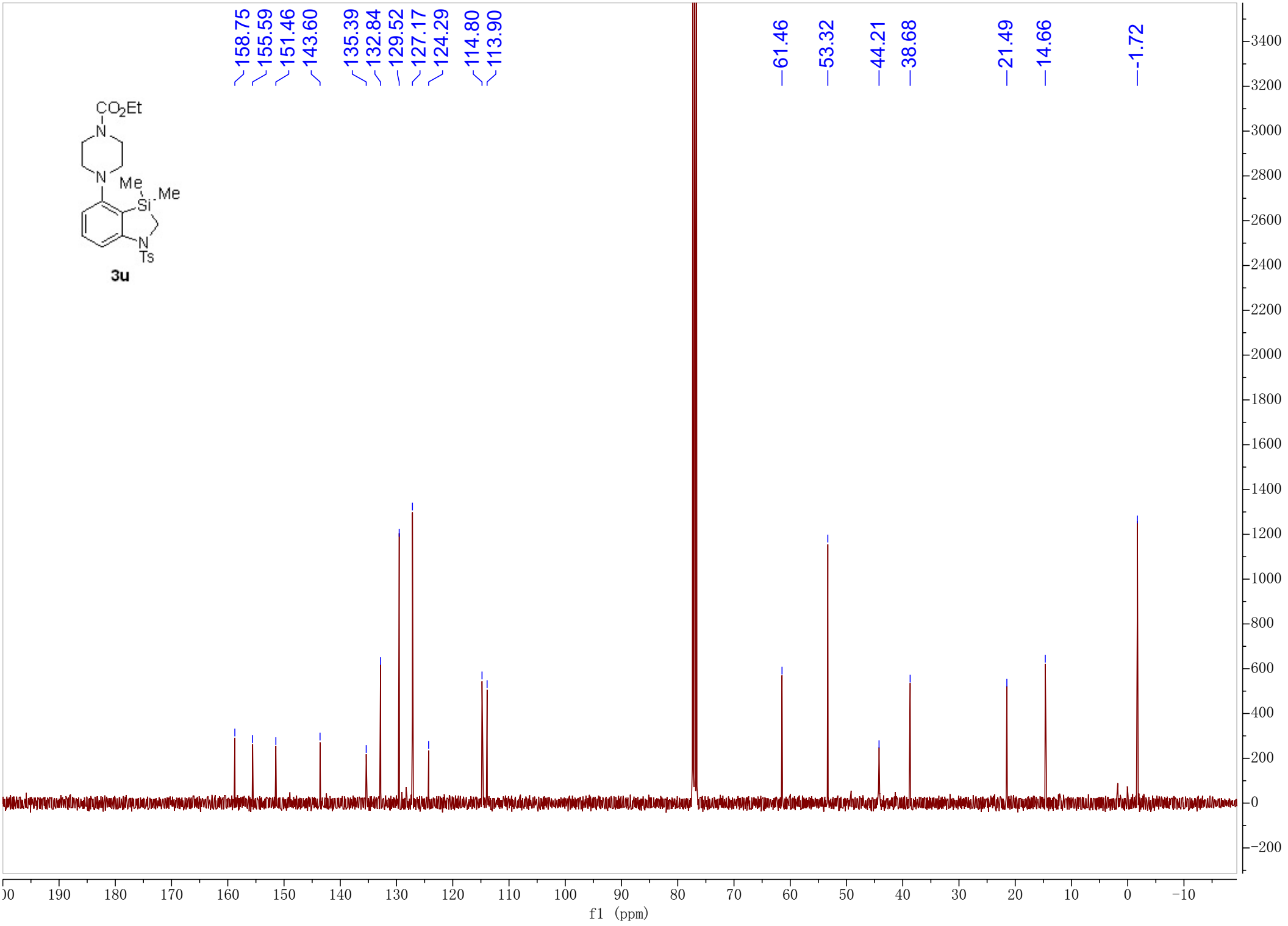
7.31
7.29
7.25
7.23
6.76
6.74
4.18
4.17
4.15
4.13
3.56
3.55
3.54
3.13
2.83
2.82
2.81
2.38
1.29
1.27
1.25
0.27
0.27
CO2Et
N
N
Me
Si
Me
N
Ts
3u
1.91
0.99
1.03
1.82
0.98
2.14
3.94
2.37
4.20
3.09
3.33
6.00
f1 (ppm)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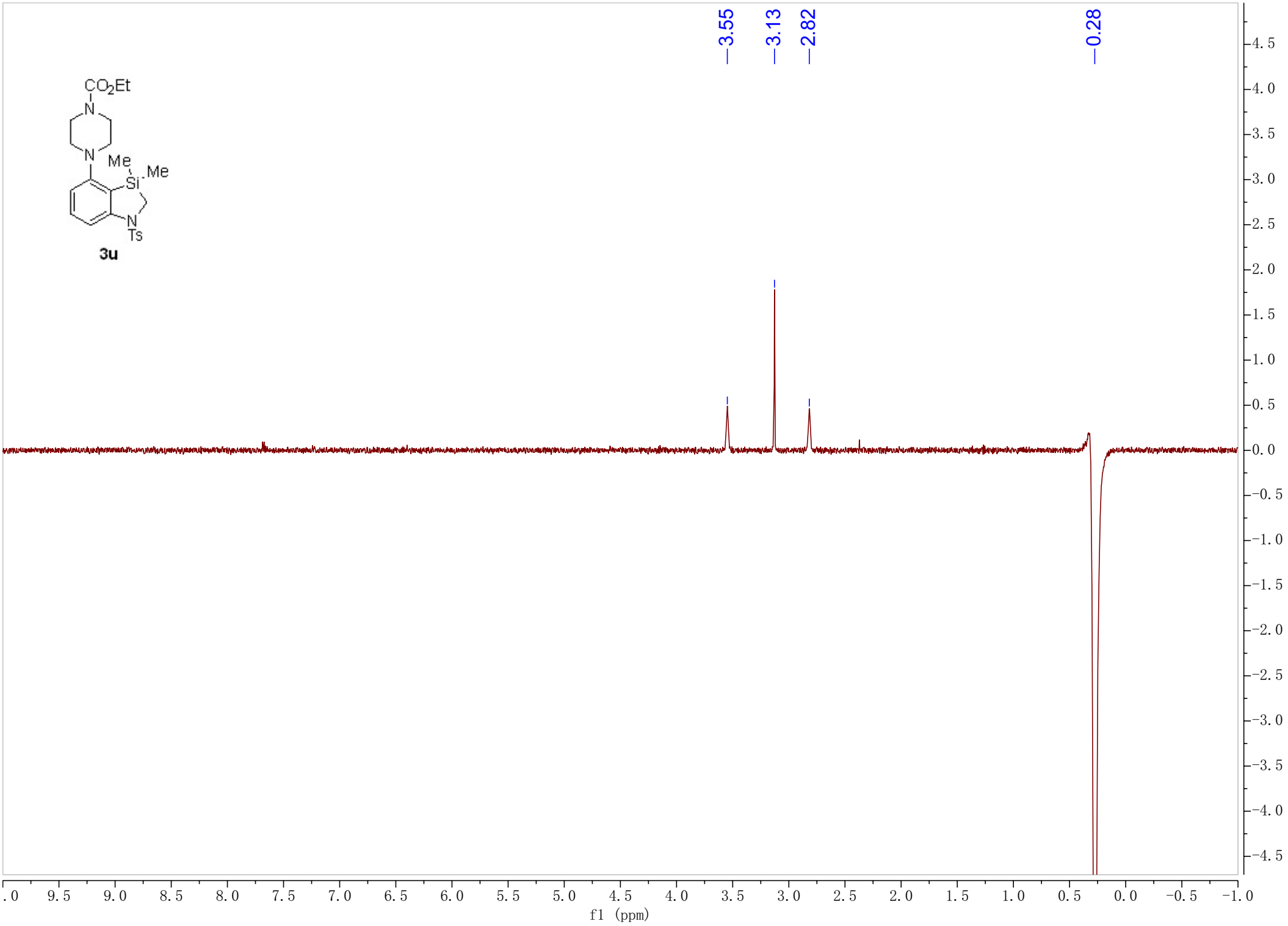
129.52
127.17
124.29
114.80
113.90
61.46
53.32
44.21
38.68
21.49
14.66
-1.72
CO2Et
N
N
Me
Si
Me
N
Ts
3u
f1 (ppm)


3.55
3.13
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0.28
CO2Et
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N
Me
Si
Me
N
Ts
3u
4.5
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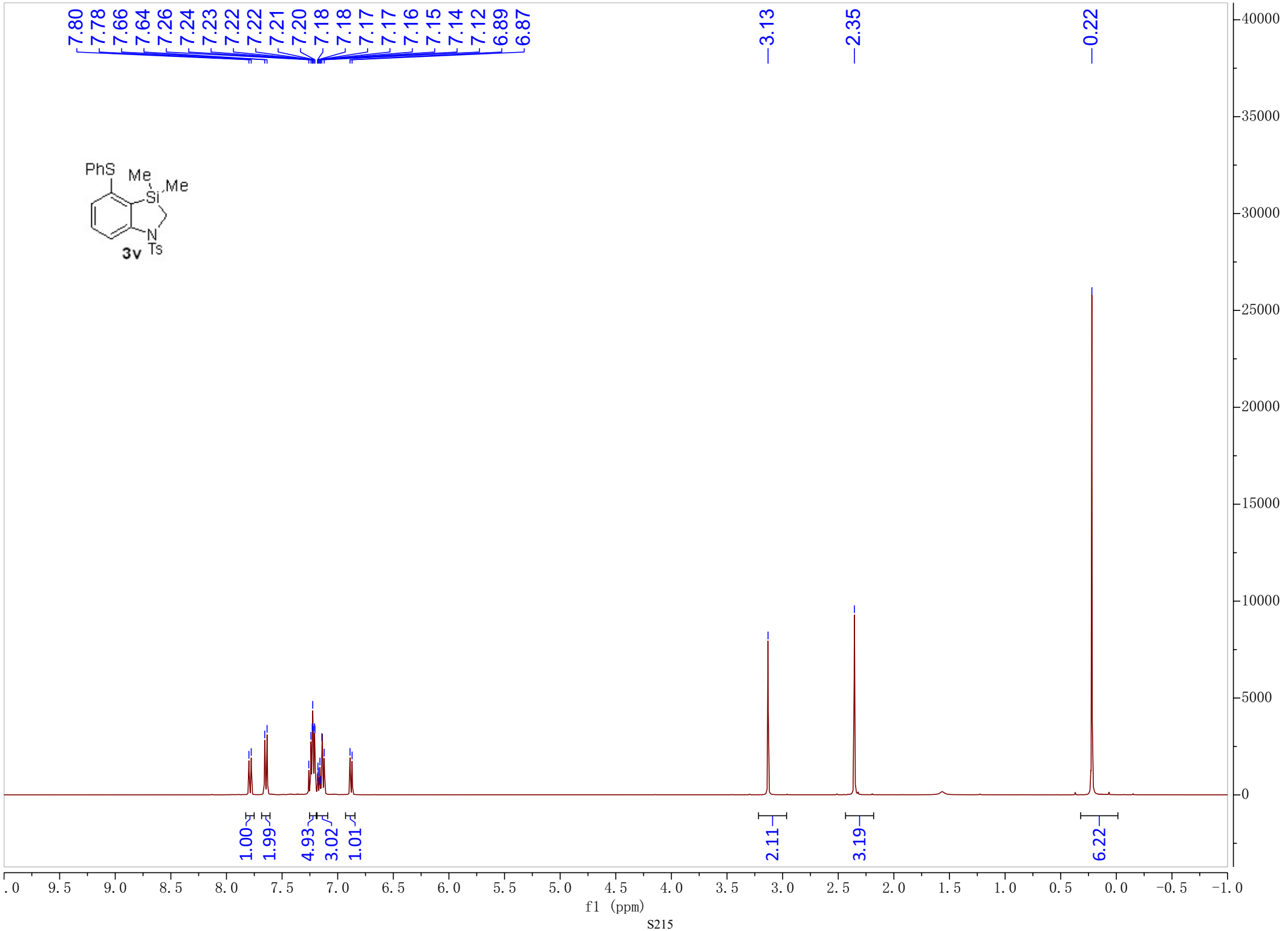
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
−1.5
−2.0
−2.5
−3.0
−3.5
−4.0
−4.5
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f1 (ppm)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7.66
7.64
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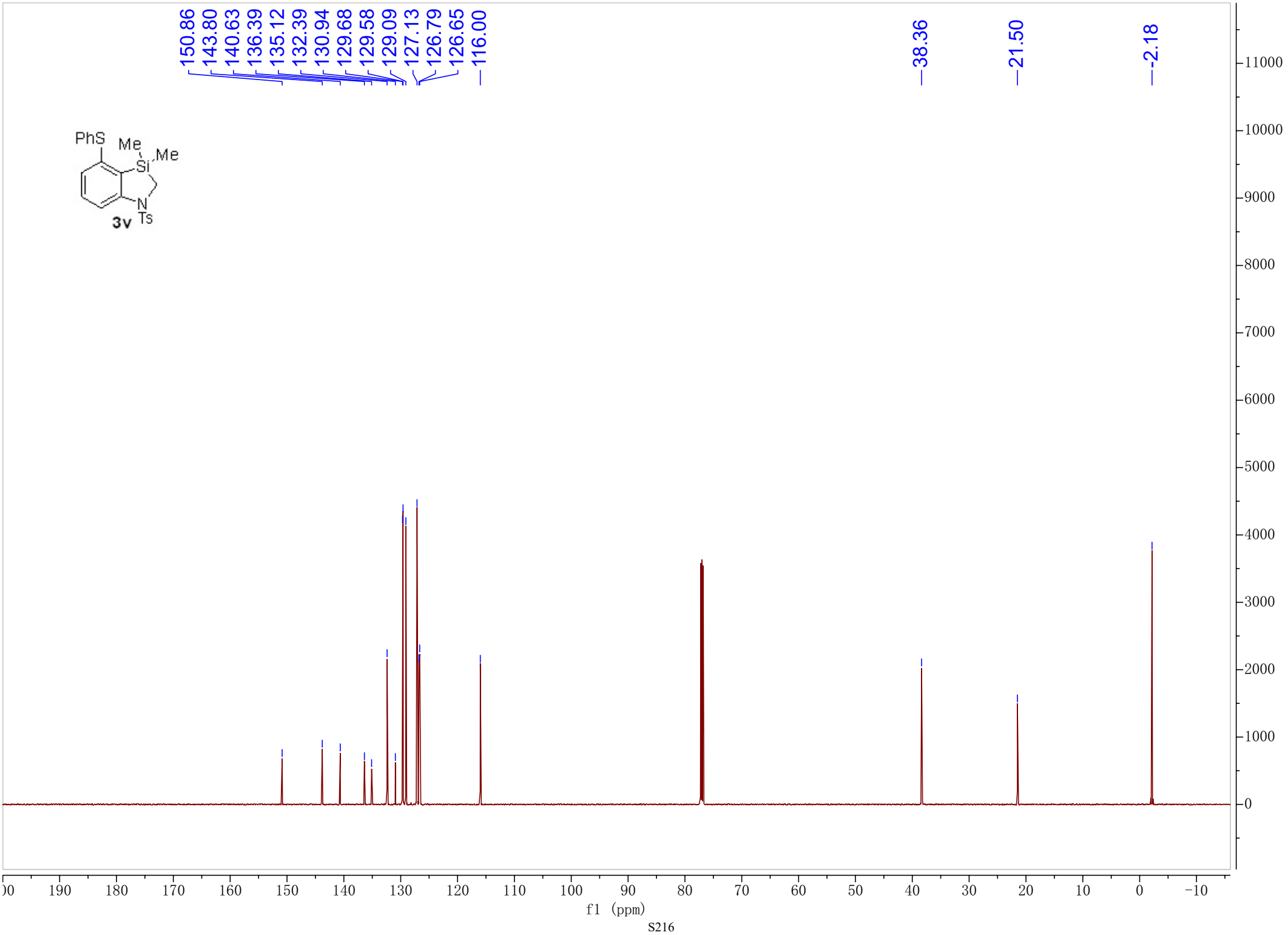
7.24
7.23
7.22
7.22
7.21
7.20
7.18
7.18
7.17
7.17
7.16
7.15
7.14
7.12
6.89
6.87
3.13
2.35
0.22
PhS
Me
Si
Me
N
Ts
3v
40000
35000
30000
25000
20000
15000
10000
5000
0
1.00
1.99
4.93
3.02
1.01
2.11
3.19
6.22
f1 (ppm)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129.68
129.58
129.09
127.13
126.79
126.65
116.00
38.36
21.50
-2.18
PhS
Me
Me
Si
N
Ts
3v
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
190
180
170
160
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140
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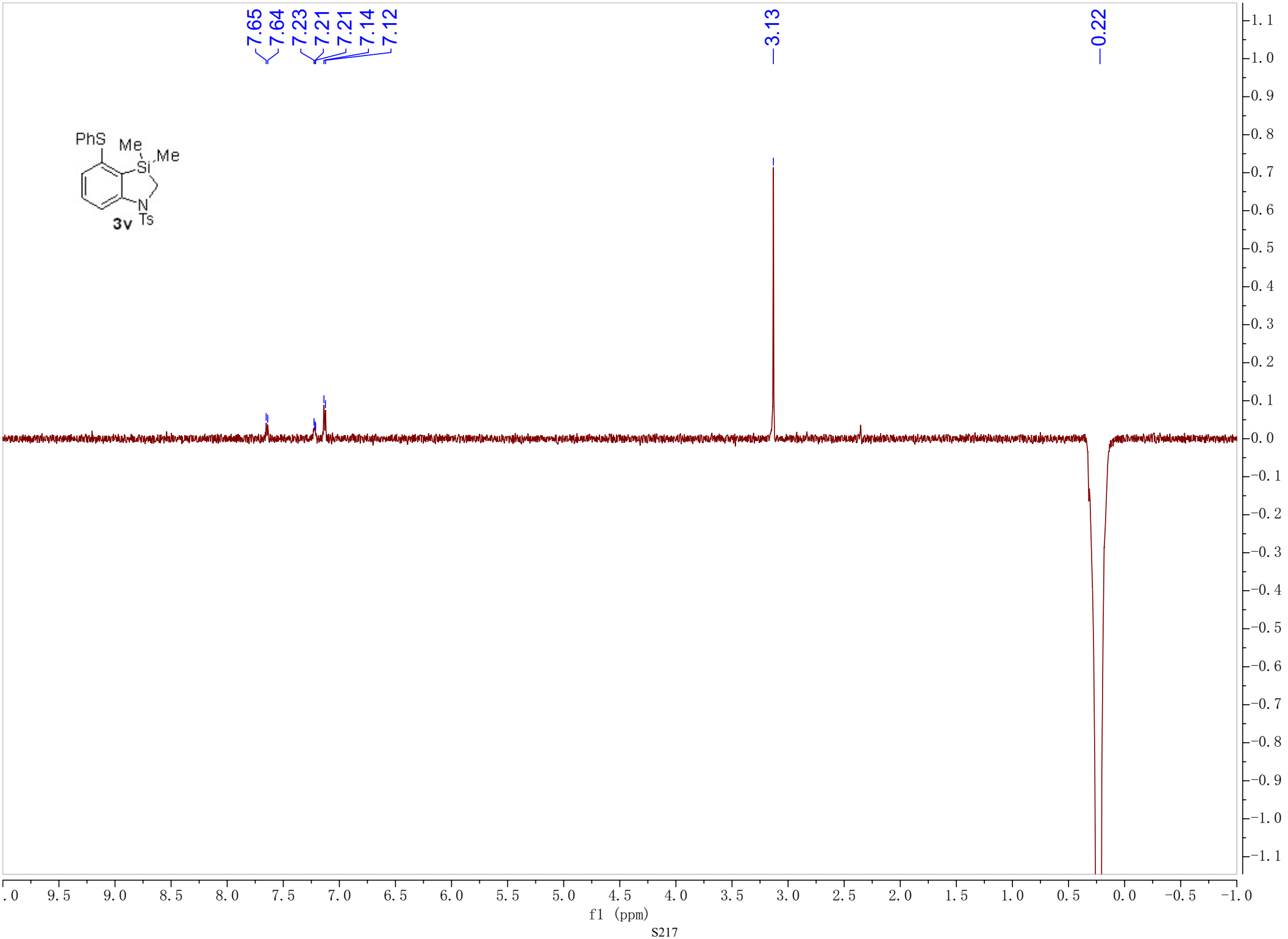
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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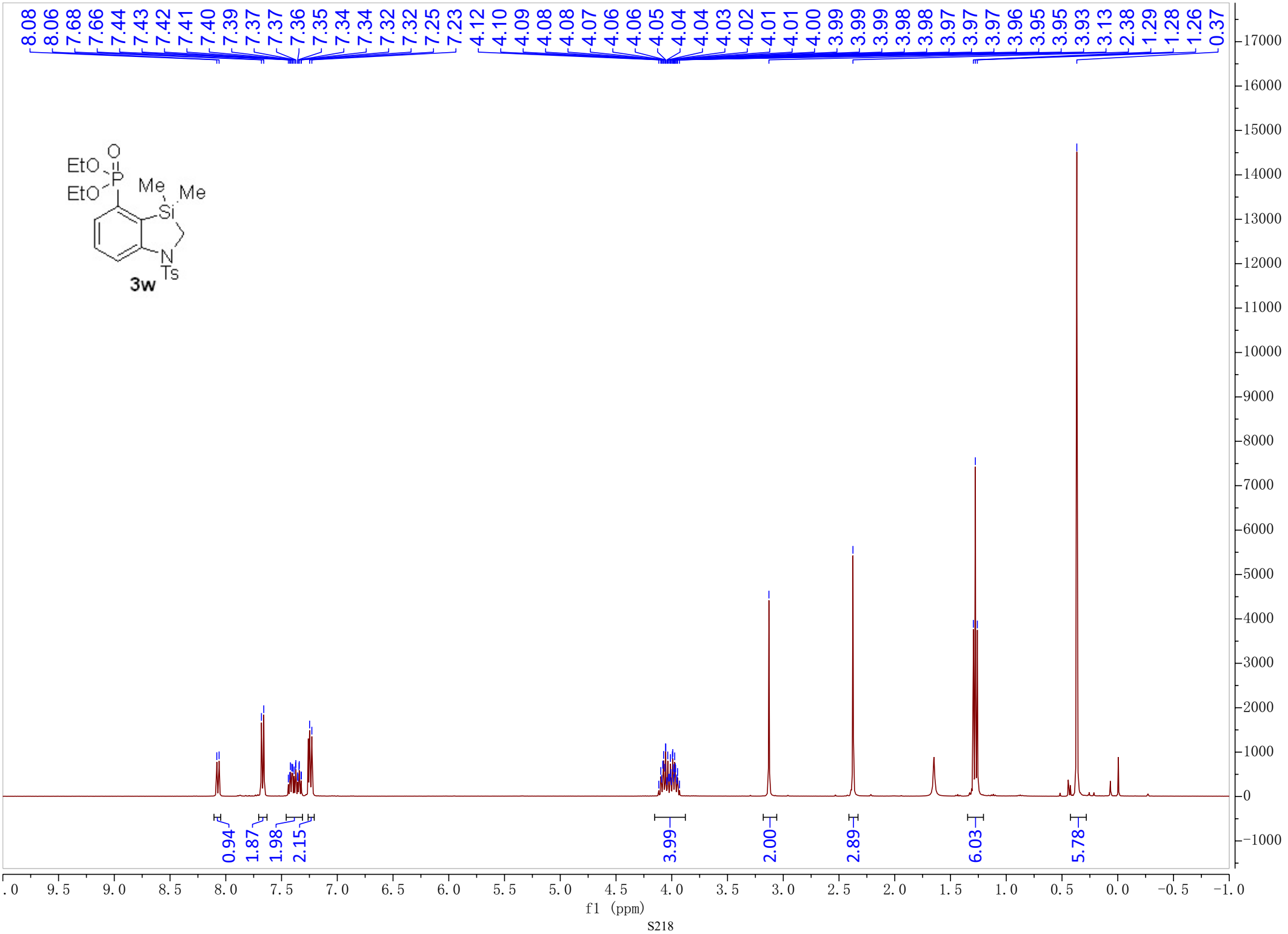
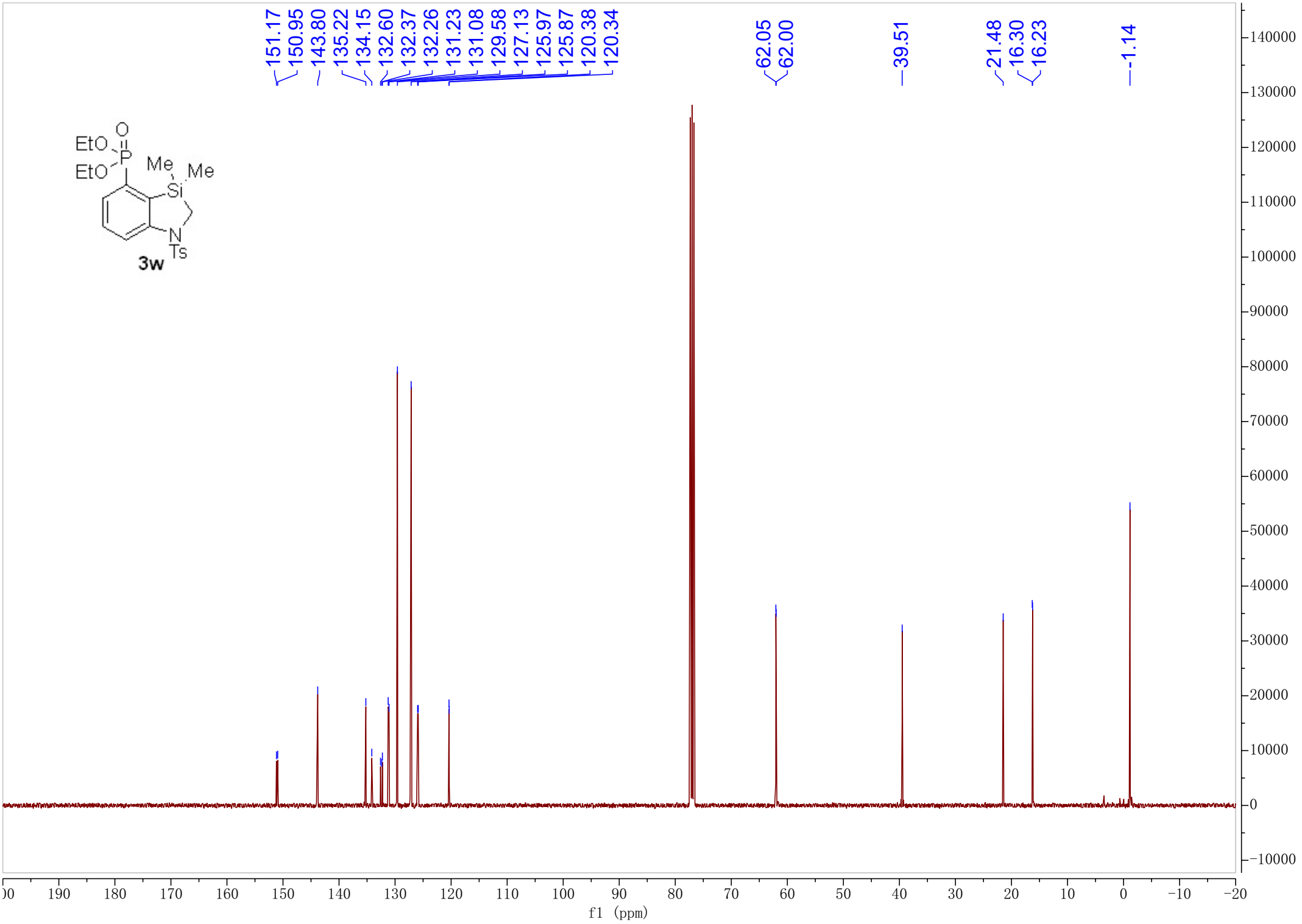
7.23
7.21
7.21
7.14
7.12
3.13
0.22
PhS
Me
Me
Si
N
Ts
3v
f1 (ppm)


8.08 8.06 7.68 7.66 7.44 7.43 7.42 7.41 7.40 7.39 7.37 7.37 7.36 7.35 7.34 7.34 7.32 7.32 7.25 7.23
4.12 4.10 4.09 4.08 4.08 4.07 4.06 4.06 4.05 4.04 4.04 4.03 4.02 4.01 4.01 4.00 3.99 3.99 3.99 3.98 3.98 3.97 3.97 3.97 3.96 3.95 3.95 3.93 3.13 2.38 1.29 1.28 1.26 0.37
EtO
EtO
O
P
Me
Me
Si
N
Ts
3w
0.94
1.87
1.98
2.15
3.99
2.00
2.89
6.03
5.78
f1 (ppm)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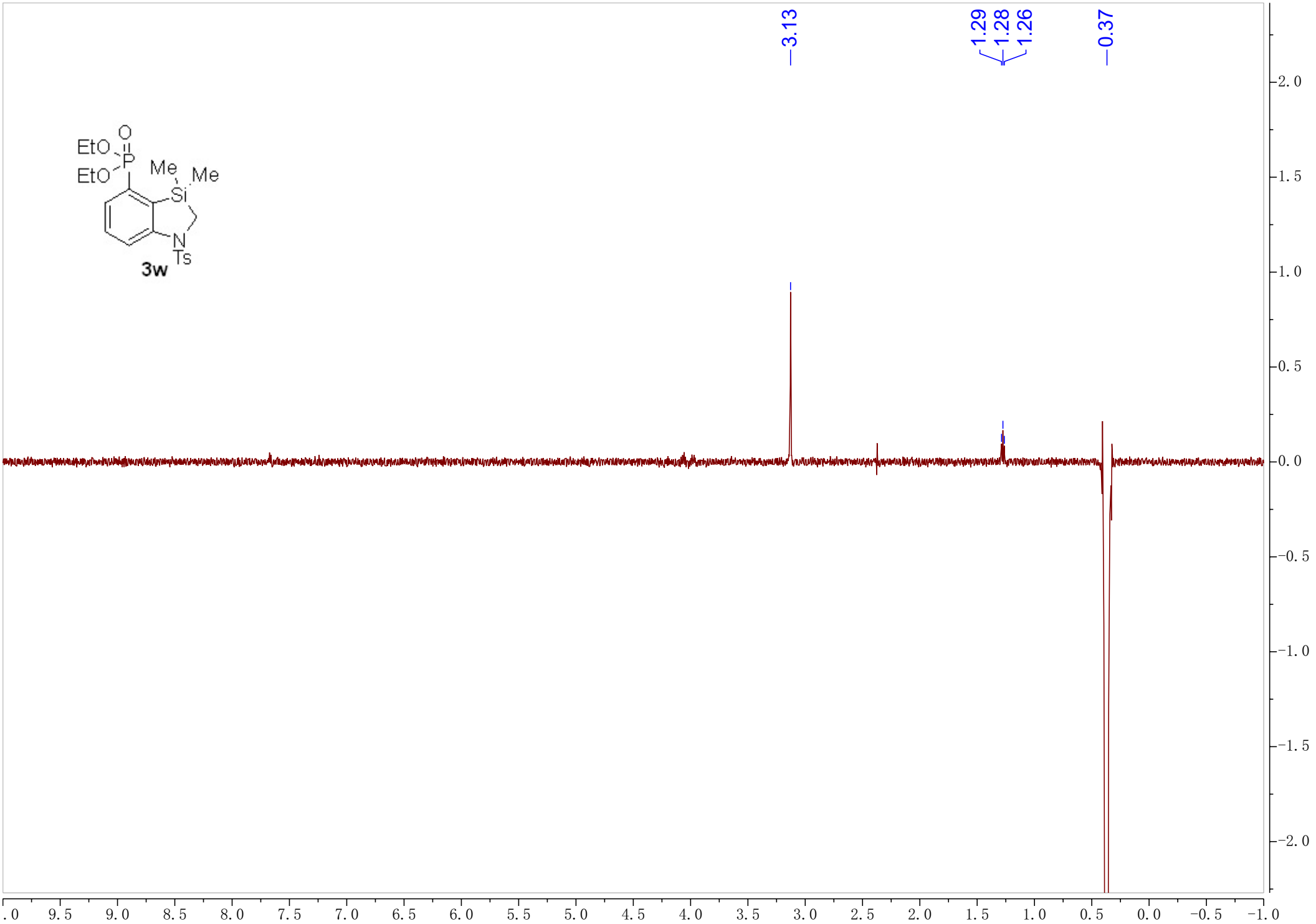
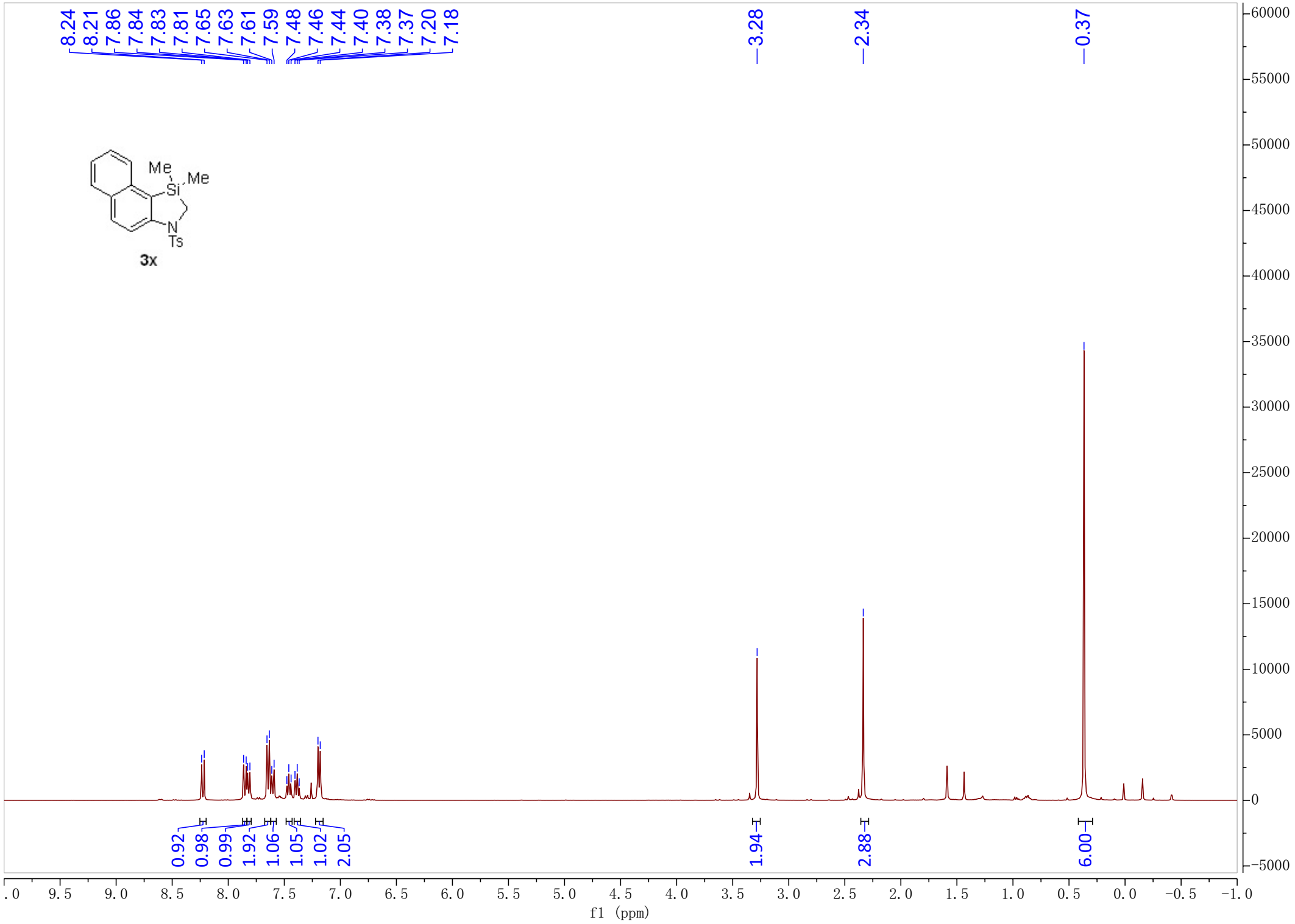
132.26
131.23
131.08
129.58
127.13
125.97
125.87
120.38
120.34
62.05
62.00
39.51
21.48
16.30
16.23
-1.14
EtO
EtO
O
P
Me
Me
Si
N
Ts
3w
f1 (ppm)


3.13
1.29
1.28
1.26
0.37
EtO
EtO
P
O
Me
Me
Si
N
Ts
3w
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
−1.5
−2.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f1 (ppm)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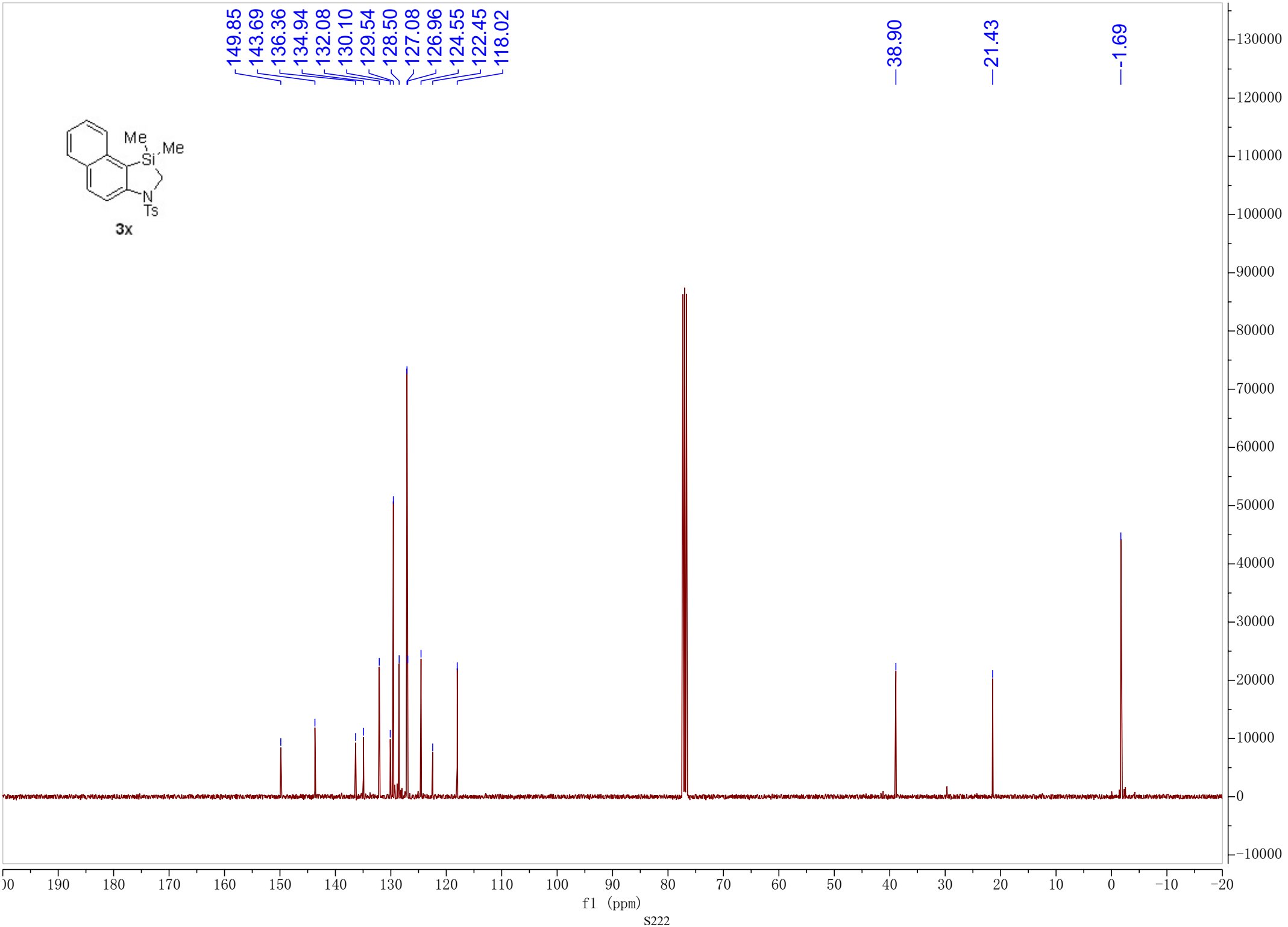
7.84
7.83
7.81
7.65
7.63
7.61
7.59
7.48
7.46
7.44
7.40
7.38
7.37
7.20
7.18
3.28
2.34
0.37
Me
Si
Me
N
Ts
3x
0.92
0.98
0.99
1.92
1.06
1.05
1.02
2.05
1.94
2.88
6.00
f1 (ppm)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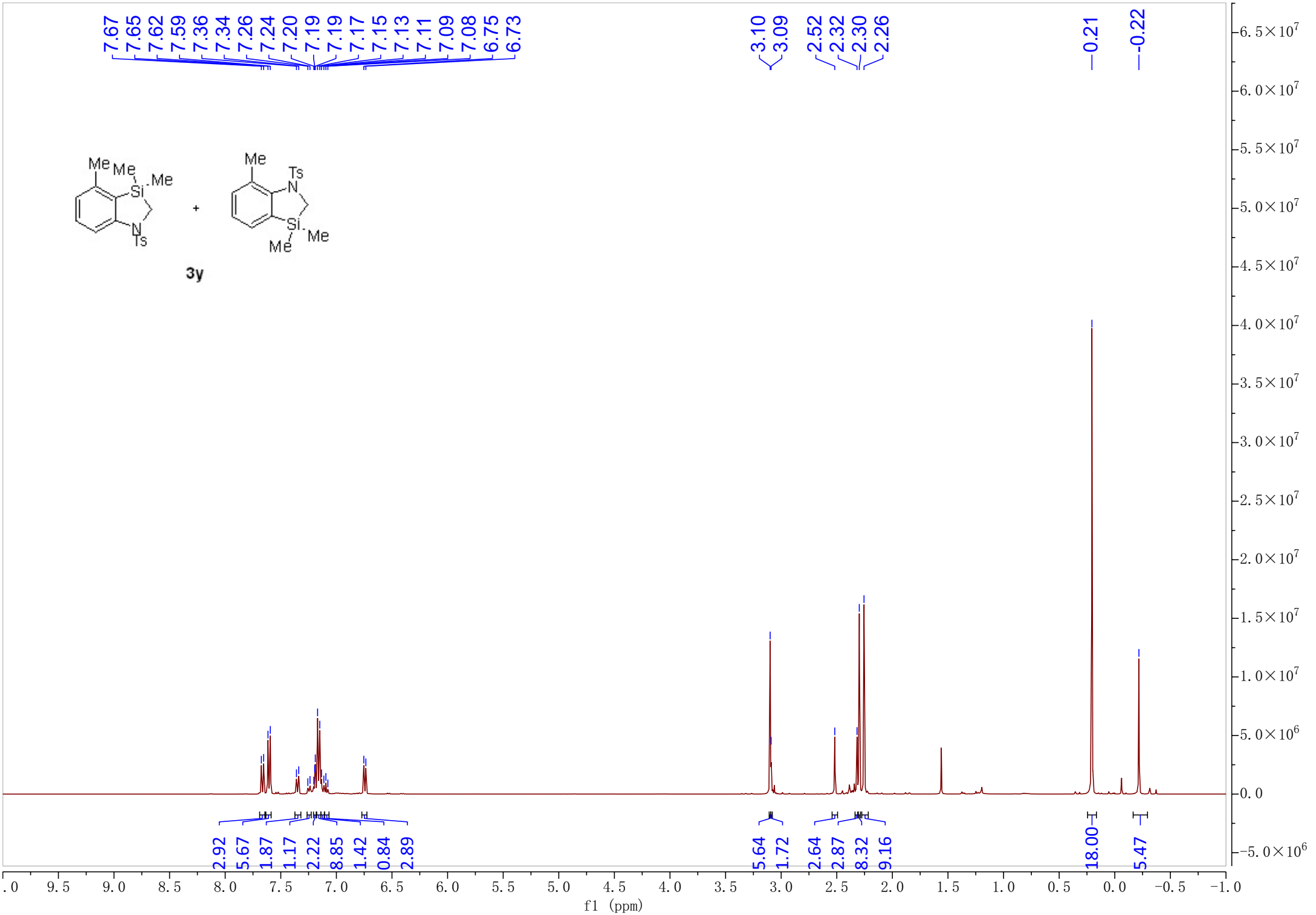
130.10
129.54
128.50
127.08
126.96
124.55
122.45
118.02
38.90
21.43
-1.69
Me
Si
Me
N
Ts
3x
f1 (ppm)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7.19
7.19
7.17
7.15
7.13
7.11
7.09
7.08
6.75
6.73
3.10
3.09
2.52
2.32
2.30
2.26
0.21
-0.22
Me
Me
Si
Me
N
Ts
+
Me
Ts
N
Si
Me
Me
3y
2.92
5.67
1.87
1.17
2.22
8.85
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5.64
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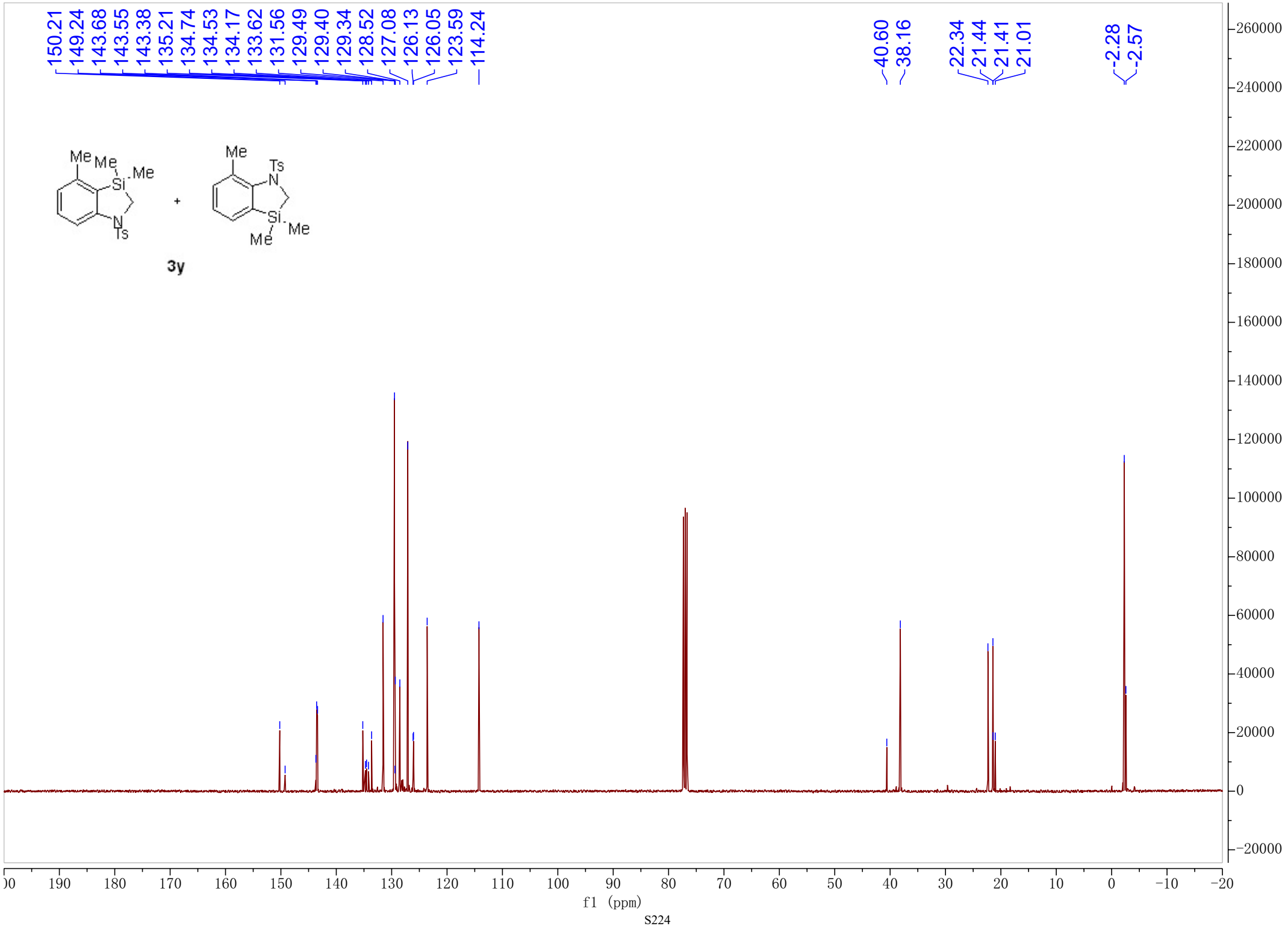
2.64
2.87
8.32
9.16
18.00
5.47
f1 (ppm)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129.49
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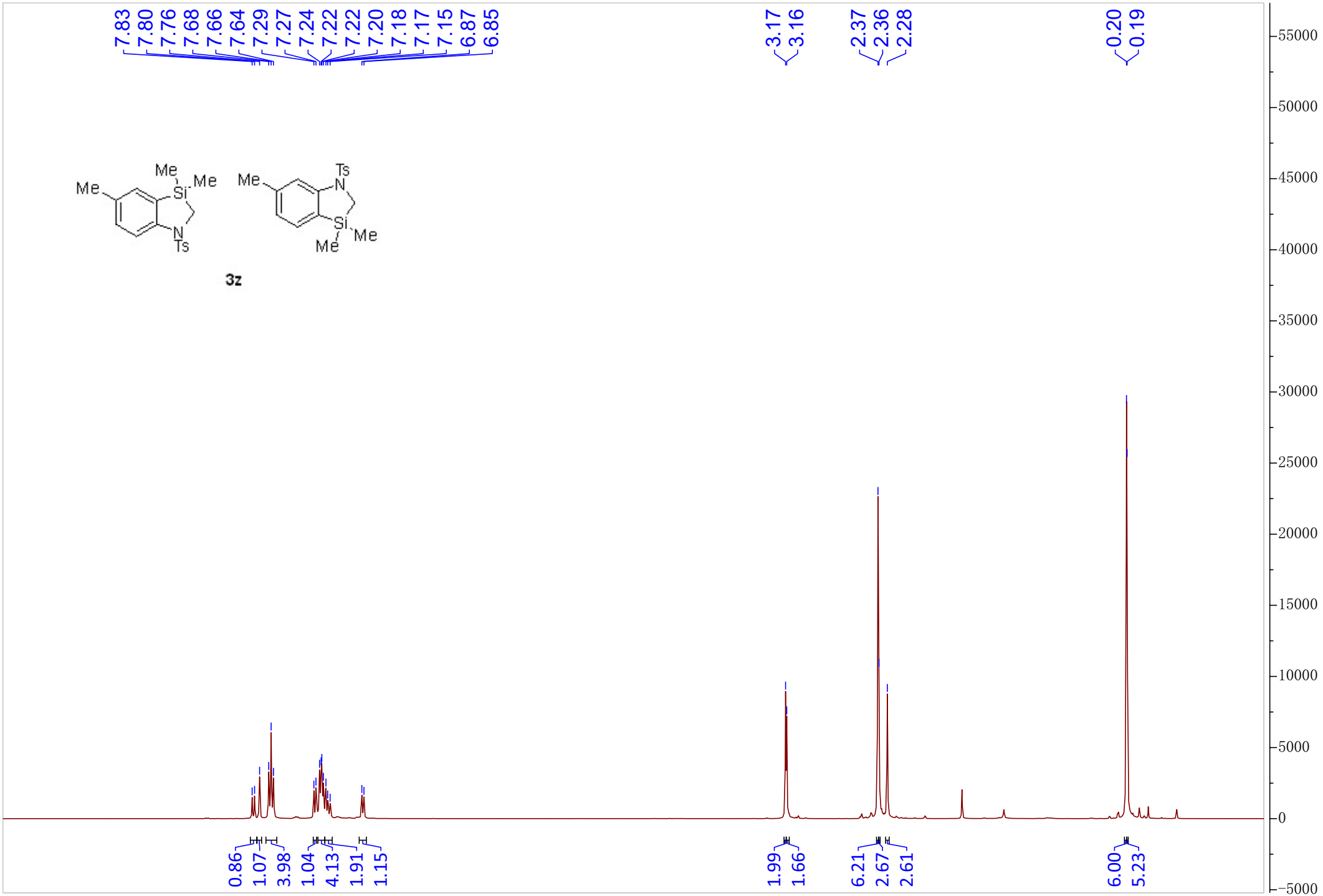
129.34
128.52
127.08
126.13
126.05
123.59
114.24
40.60
38.16
22.34
21.44
21.41
21.01
-2.28
-2.57
Me
Me
Me
Si
N
Ts
+
Me
Ts
N
Si
Me
Me
3y
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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7.64
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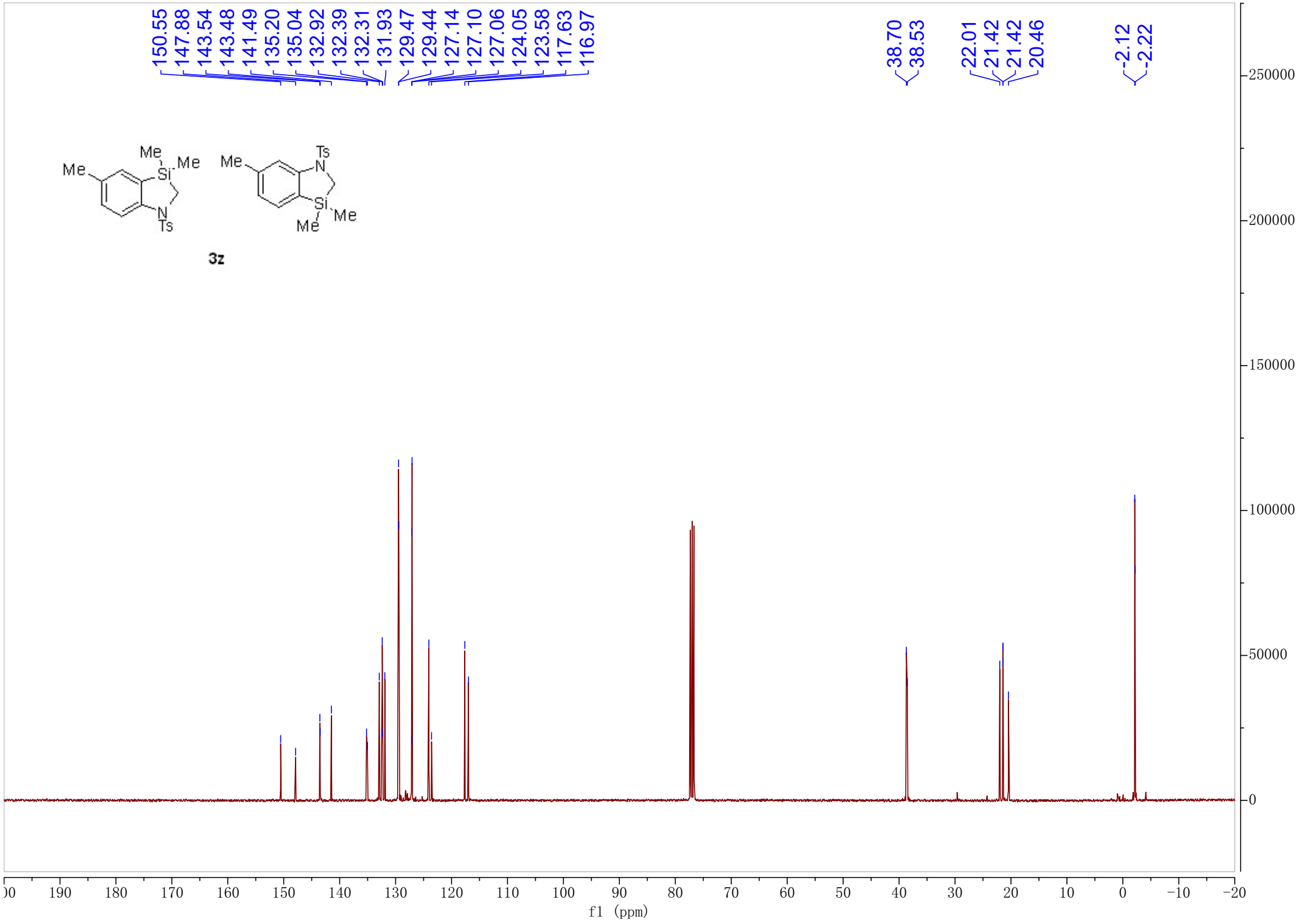
7.27
7.24
7.22
7.22
7.20
7.18
7.17
7.15
6.87
6.85
3.17
3.16
2.37
2.36
2.28
0.20
0.19
Me
Me
Si
Me
N
Ts
Me
Ts
N
Me
Si
Me
Me
3z
0.86
1.07
3.98
1.04
4.13
1.91
1.15
1.99
1.66
6.21
2.67
2.61
6.00
5.23
f1 (ppm)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135.04
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132.39
132.31
131.93
129.47
129.44
127.14
127.10
127.06
124.05
123.58
117.63
116.97
38.70
38.53
22.01
21.42
21.42
20.46
-2.12
-2.22
Me
Me
Me
Si
N
Ts
Me
Ts
N
Me
Si
Me
Me
3z
250000
200000
150000
100000
50000
0
190
180
170
160
150
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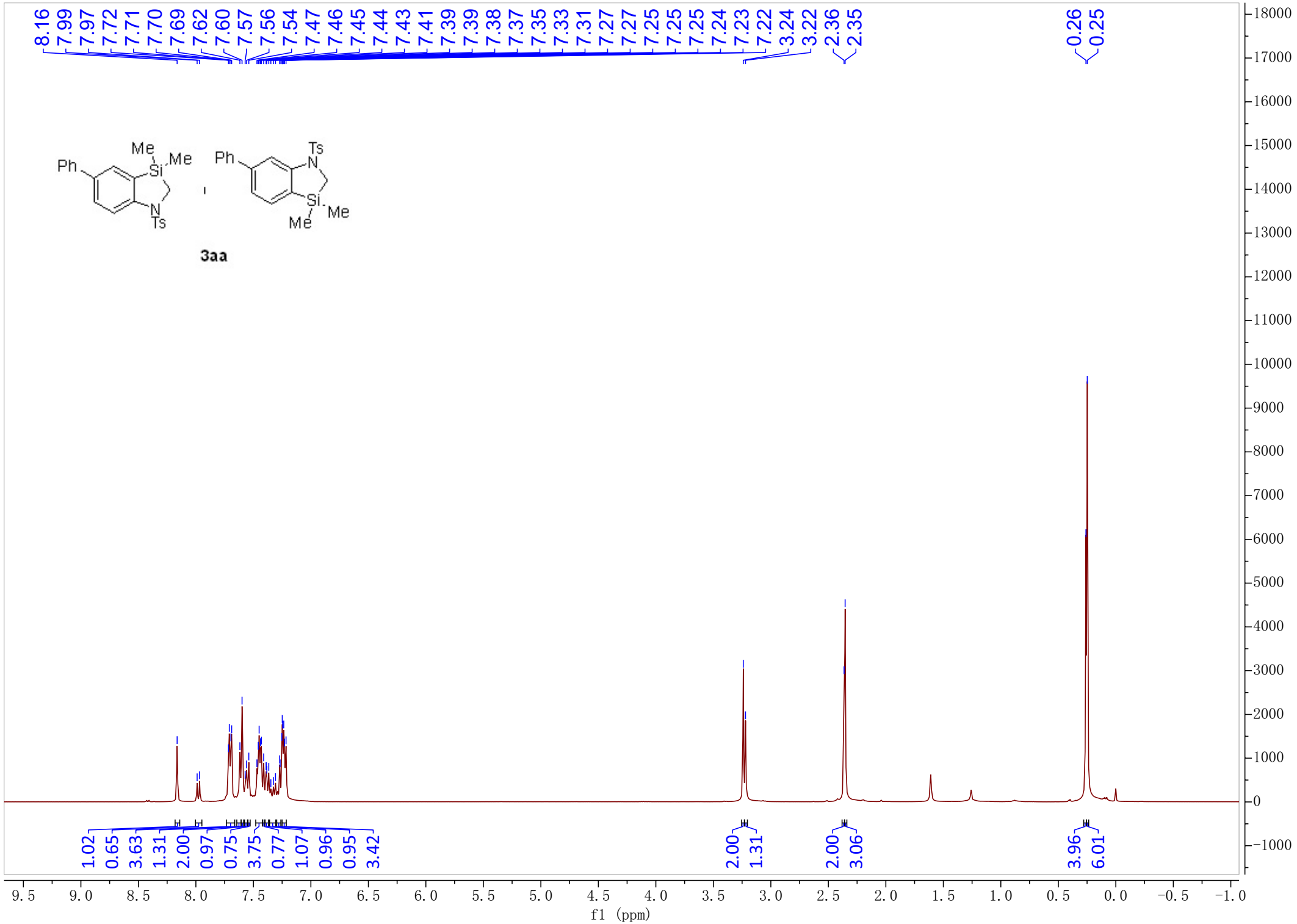
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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7.47
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7.45
7.44
7.43
7.41
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7.39
7.38
7.37
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7.33
7.31
7.27
7.27
7.25
7.25
7.25
7.24
7.23
7.22
3.24
3.22
2.36
2.35
0.26
0.25
Me
Me
Si
Ph
N
Ts
Ts
N
Ph
Si
Me
Me
3aa
1.02
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3.63
1.31
2.00
0.97
0.75
3.75
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0.95
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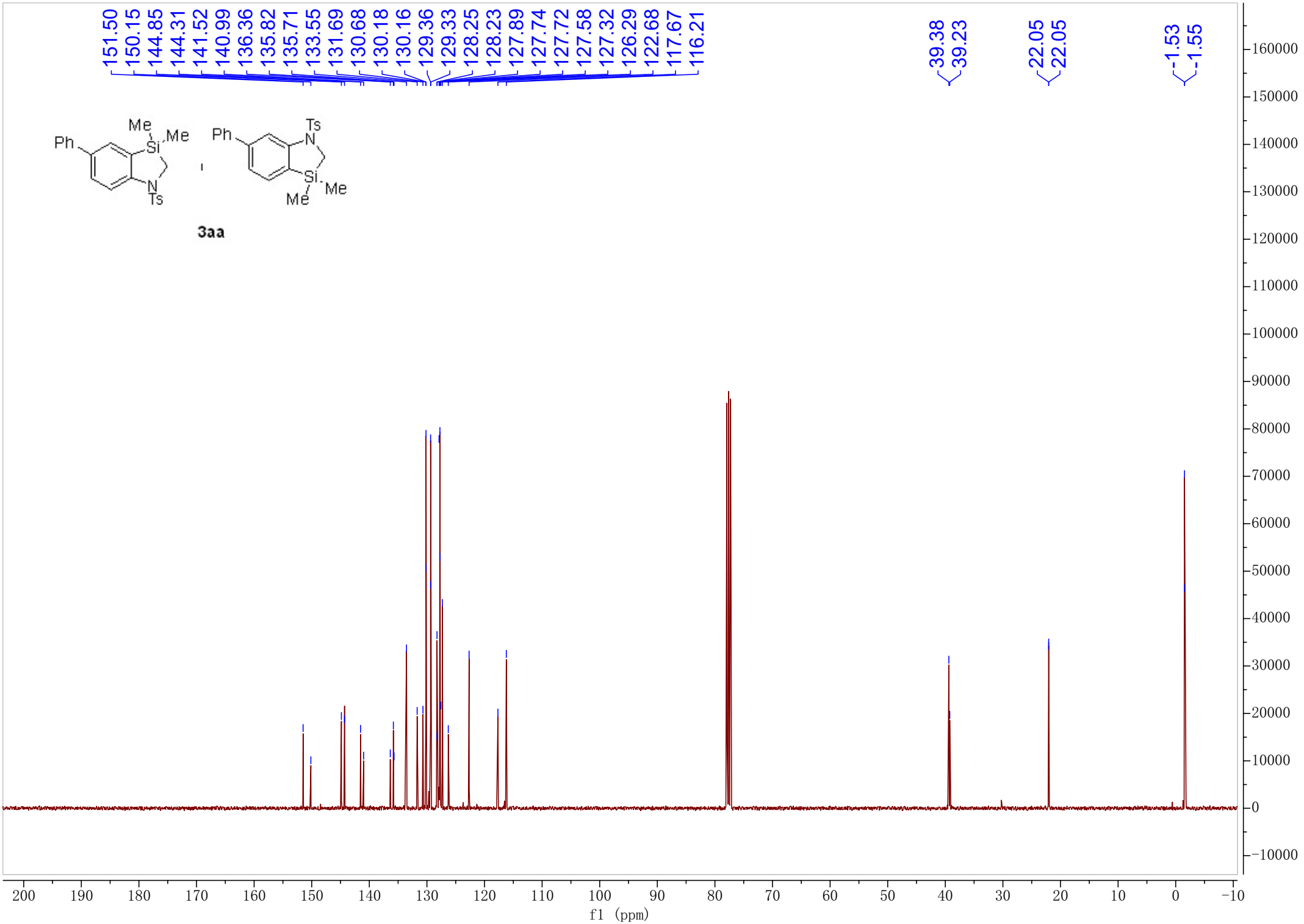
2.00
1.31
2.00
3.06
3.96
6.01
f1 (ppm)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130.16
129.36
129.33
128.25
128.23
127.89
127.74
127.72
127.58
127.32
126.29
122.68
117.67
116.21
39.38
39.23
22.05
22.05
-1.53
-1.55
Me
Me
Si
Ph
N
Ts
Ts
N
Ph
Si
Me
Me
3aa
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
−10000
200
190
180
170
160
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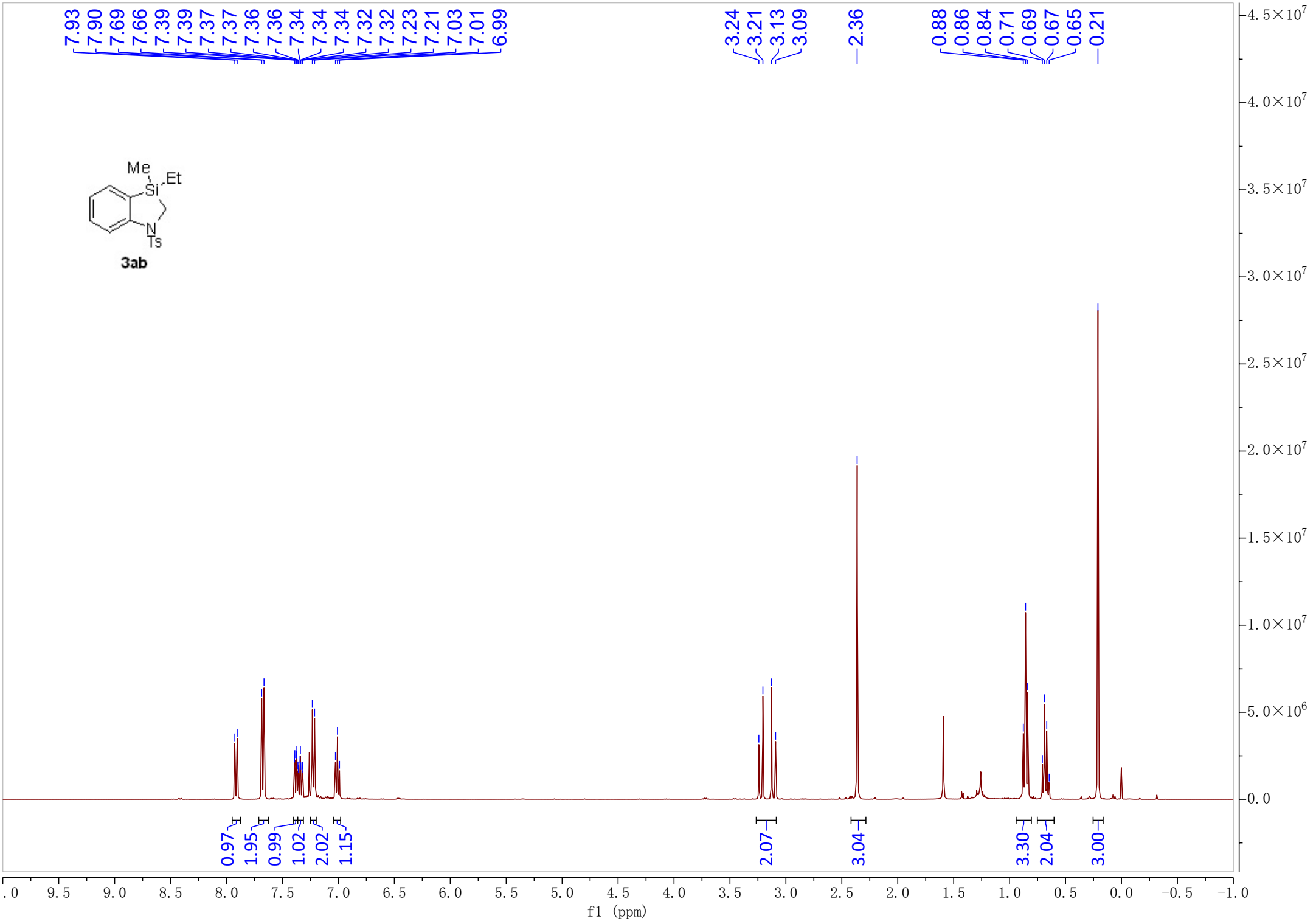
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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7.34
7.34
7.32
7.32
7.23
7.21
7.03
7.01
6.99
3.24
3.21
3.13
3.09
2.36
0.88
0.86
0.84
0.71
0.69
0.67
0.65
0.21
Me
Et
Si
N
Ts
3ab
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1.02
2.02
1.15
2.07
3.04
3.30
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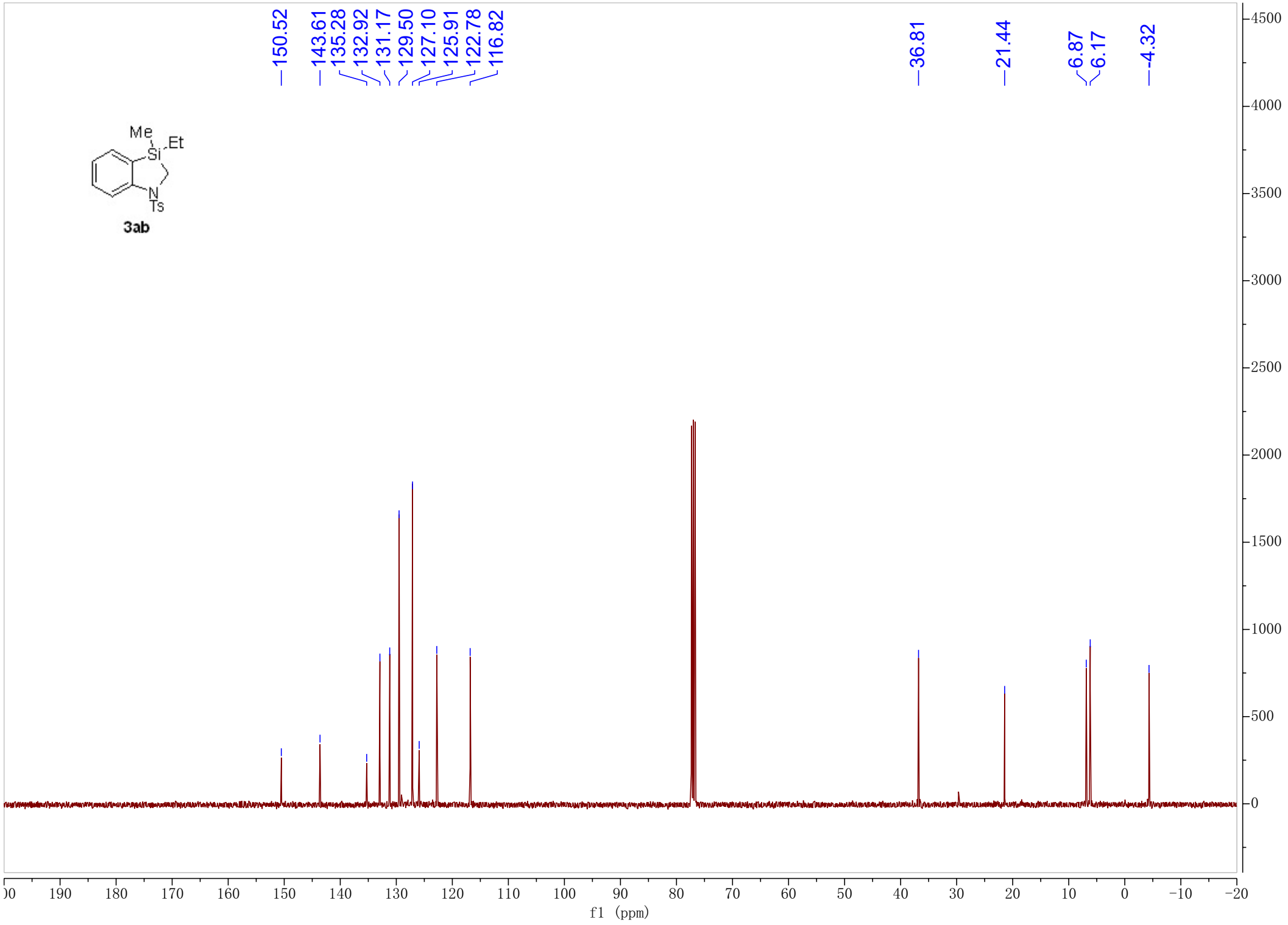
3.00
f1 (ppm)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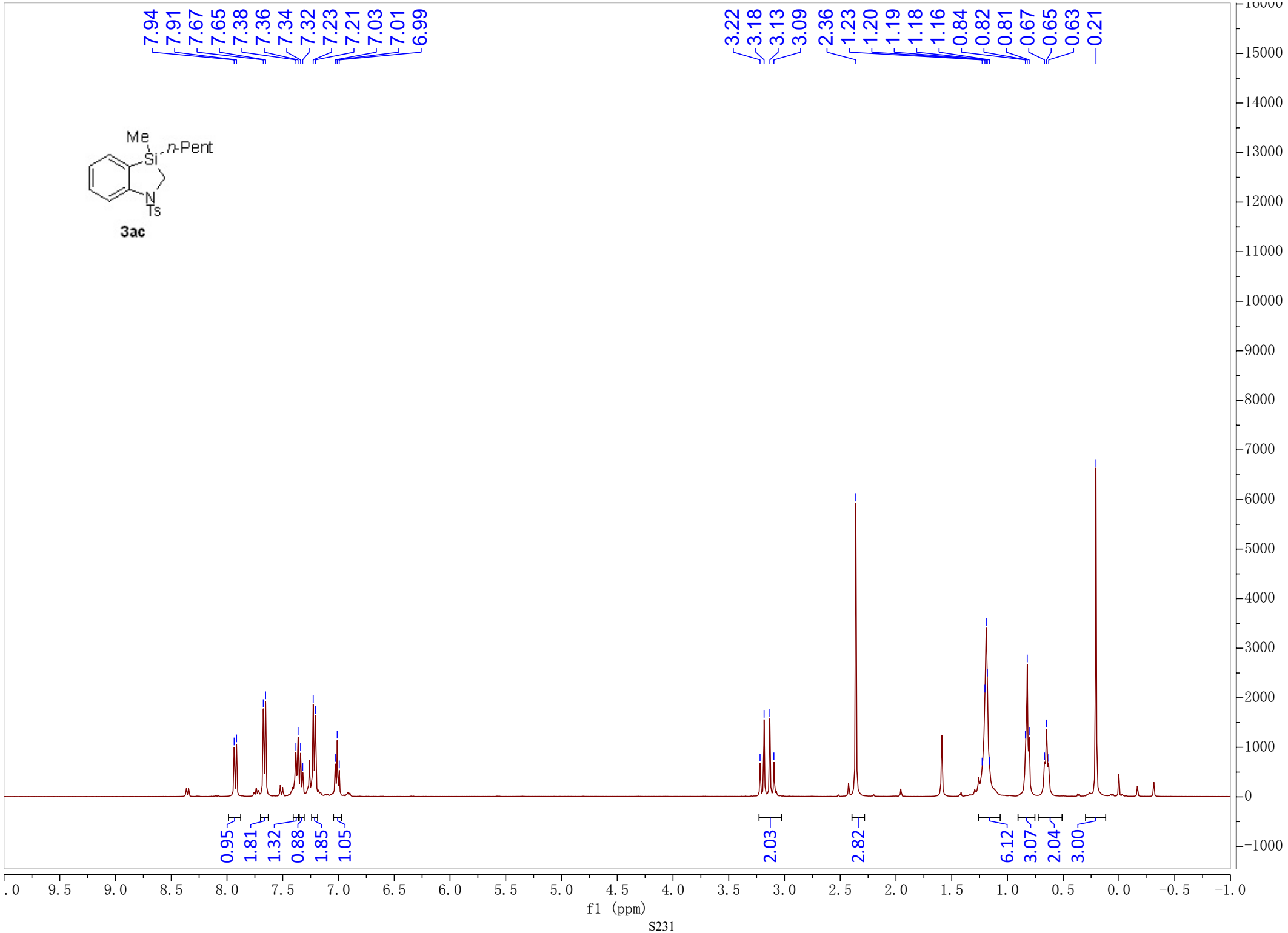
122.78
116.82
36.81
21.44
6.87
6.17
-4.32
Me
Et
Si
N
Ts
3ab
4500
4000
3500
3000
2500
2000
1500
1000
500
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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7.36
7.34
7.32
7.23
7.21
7.03
7.01
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3.22
3.18
3.13
3.09
2.36
1.23
1.20
1.19
1.18
1.16
0.84
0.82
0.81
0.67
0.65
0.63
0.21
Me
Si
n-Pent
N
Ts
3ac
0.95
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1.32
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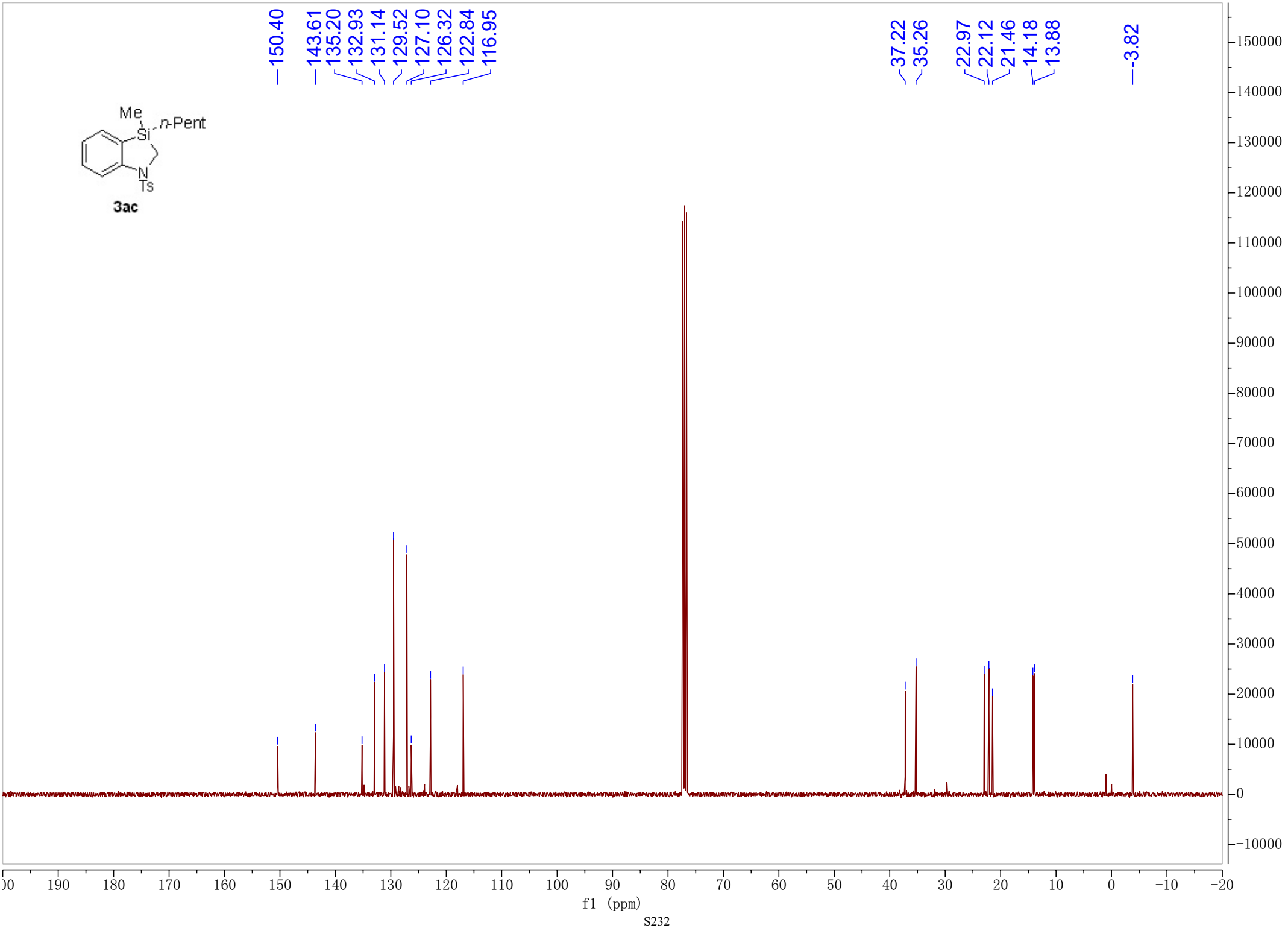
1.85
1.05
2.03
2.82
6.12
3.07
2.04
3.00
f1 (ppm)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116.95
37.22
35.26
22.97
22.12
21.46
14.18
13.88
-3.82
Me
Si
n-Pent
N
Ts
3ac
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
190
180
170
160
150
140
130
120
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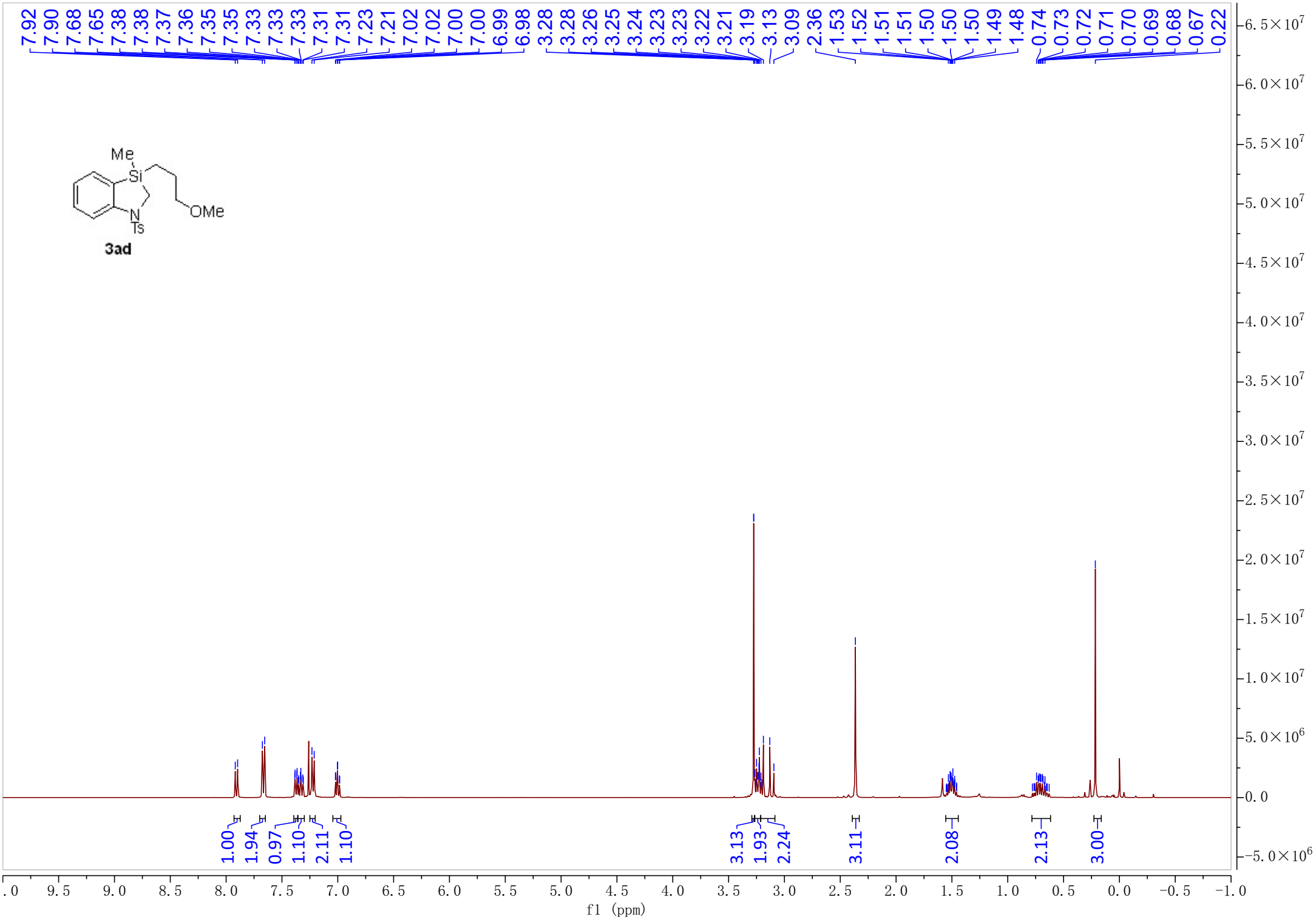
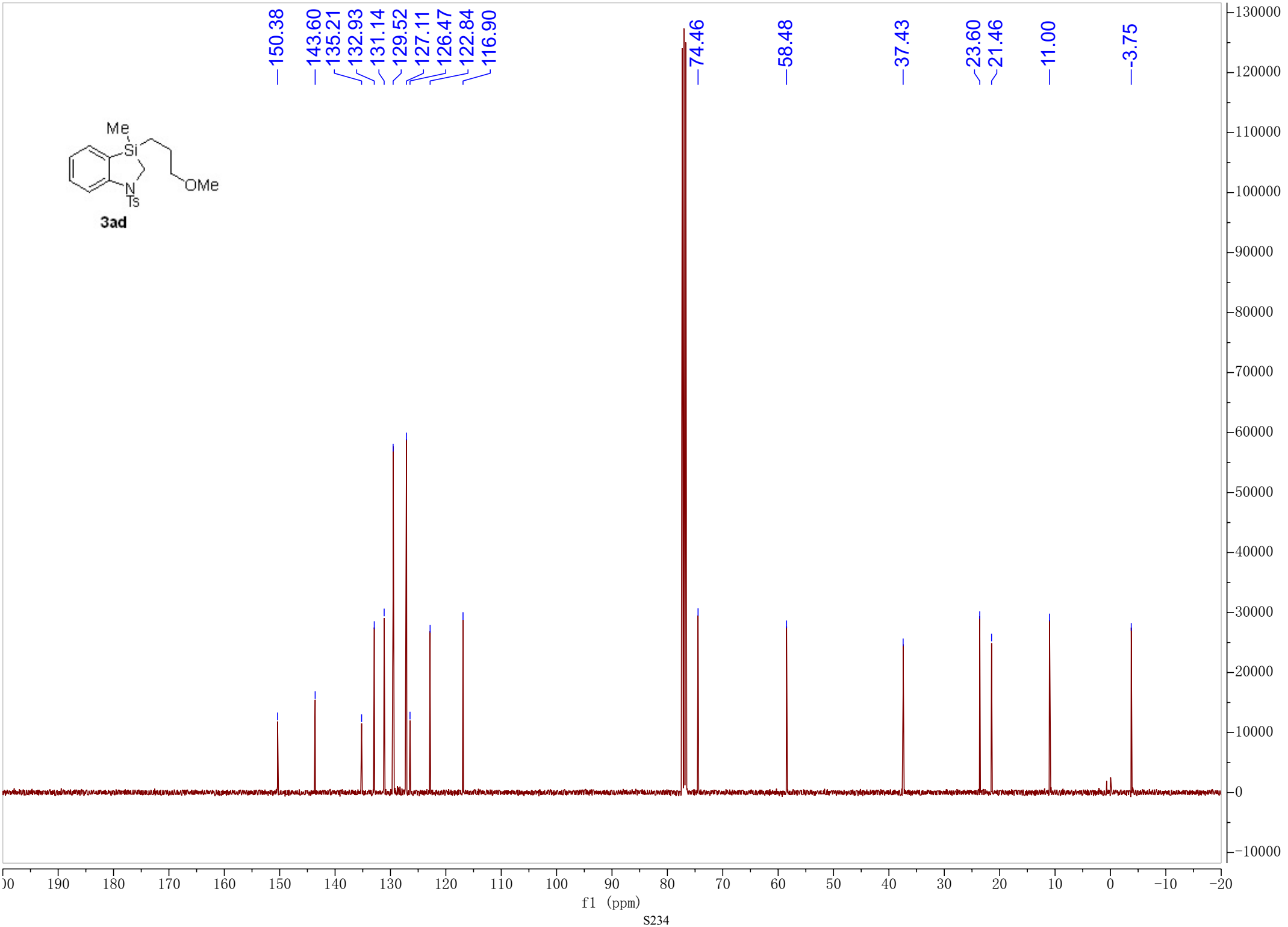
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


7.92 7.90 7.68 7.65 7.38 7.38 7.37 7.36 7.35 7.35 7.33 7.33 7.33 7.31 7.31 7.23 7.21 7.02 7.02 7.00 7.00 6.99 6.98
3.28 3.28 3.26 3.25 3.24 3.23 3.23 3.22 3.21 3.19 3.13 3.09
2.36 1.53 1.52 1.51 1.51 1.50 1.50 1.50 1.49 1.48
0.74 0.73 0.72 0.71 0.70 0.69 0.68 0.67 0.22
Me
Si
N
Ts
OMe
3ad
1.00 1.94 0.97 1.10 2.11 1.10
3.13 1.93 2.24 3.11 2.08 2.13 3.00
f1 (ppm)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127.11
126.47
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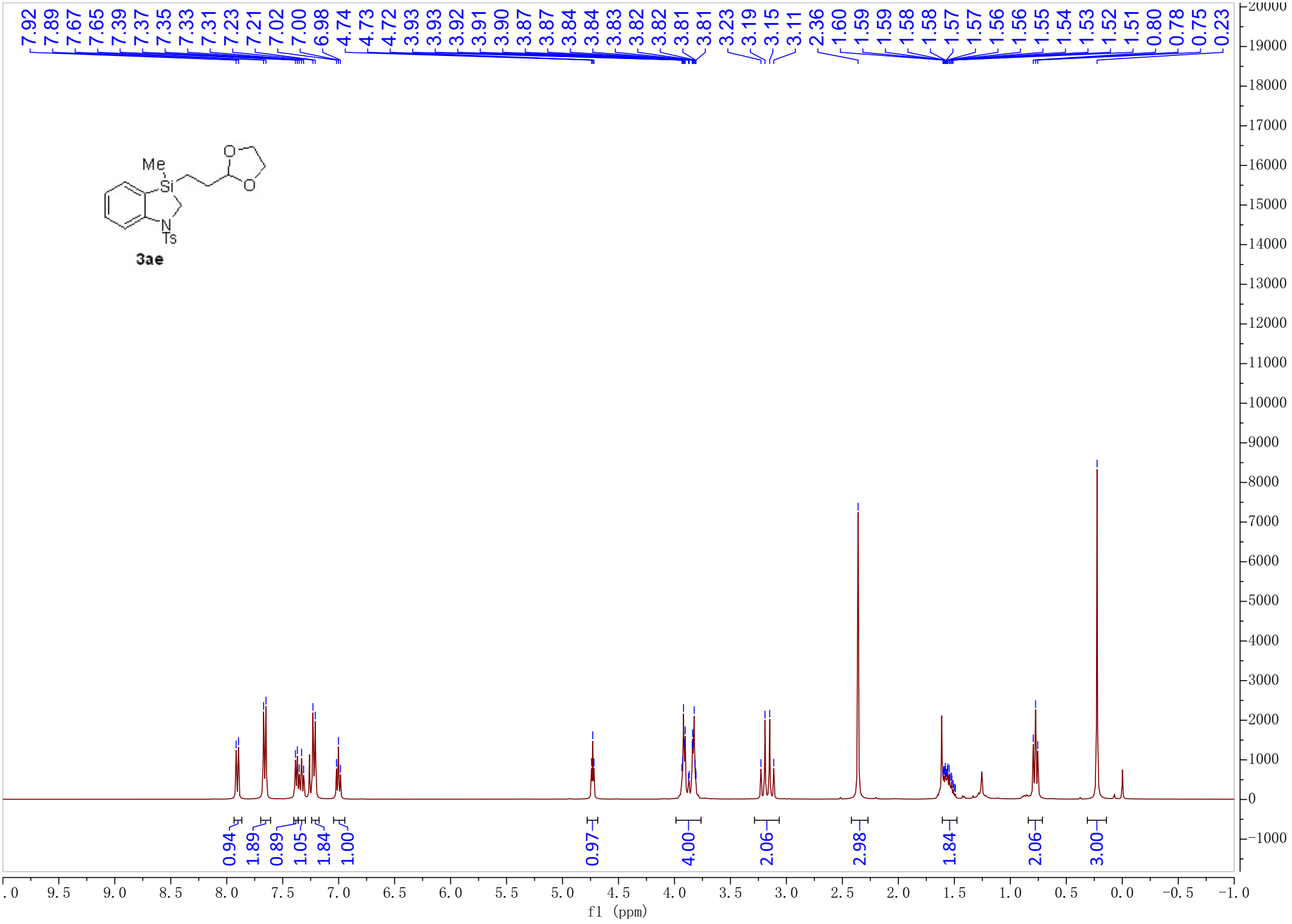
23.60
21.46
11.00
-3.75
Me
Si
N
Ts
OMe
3ad
f1 (ppm)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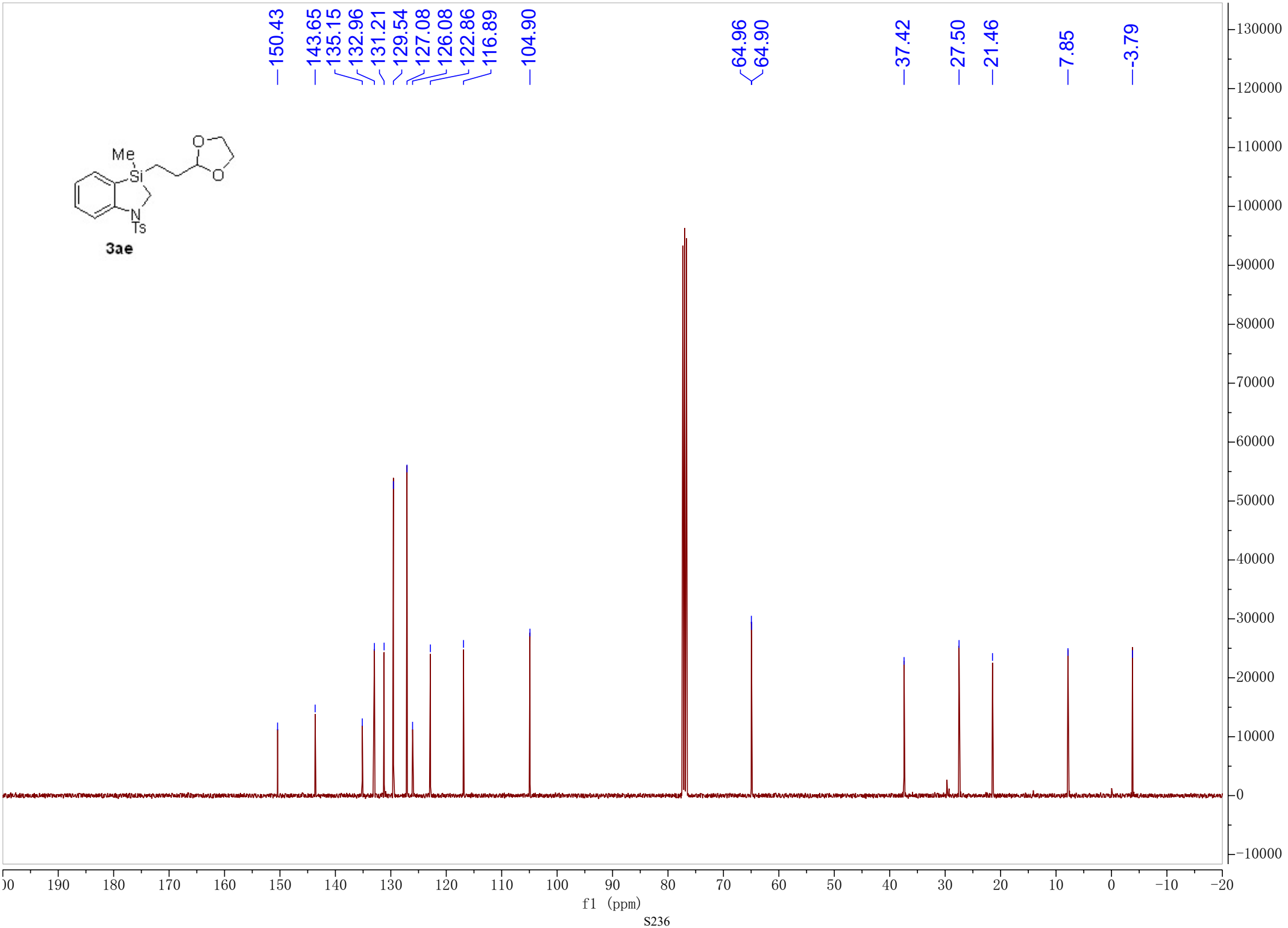
Me
Si
O
O
N
Ts
3ae
0.94 1.89 0.89 1.05 1.84 1.00 0.97 4.00 2.06 2.98 1.84 2.06 3.00
f1 (ppm)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126.08
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116.89
104.90
64.96
64.90
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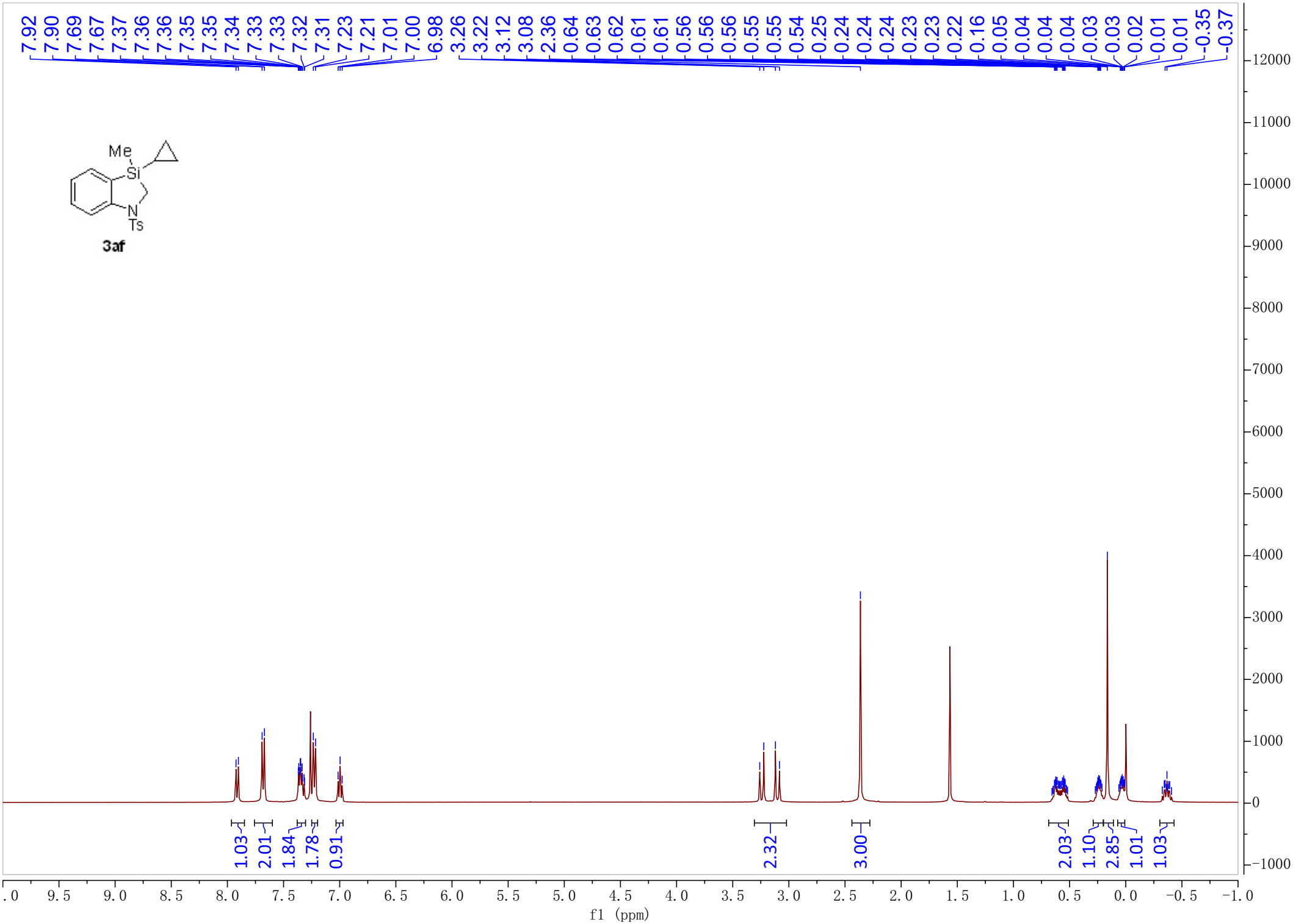
27.50
21.46
7.85
-3.79
Me
Si
O
O
N
Ts
3ae
f1 (ppm)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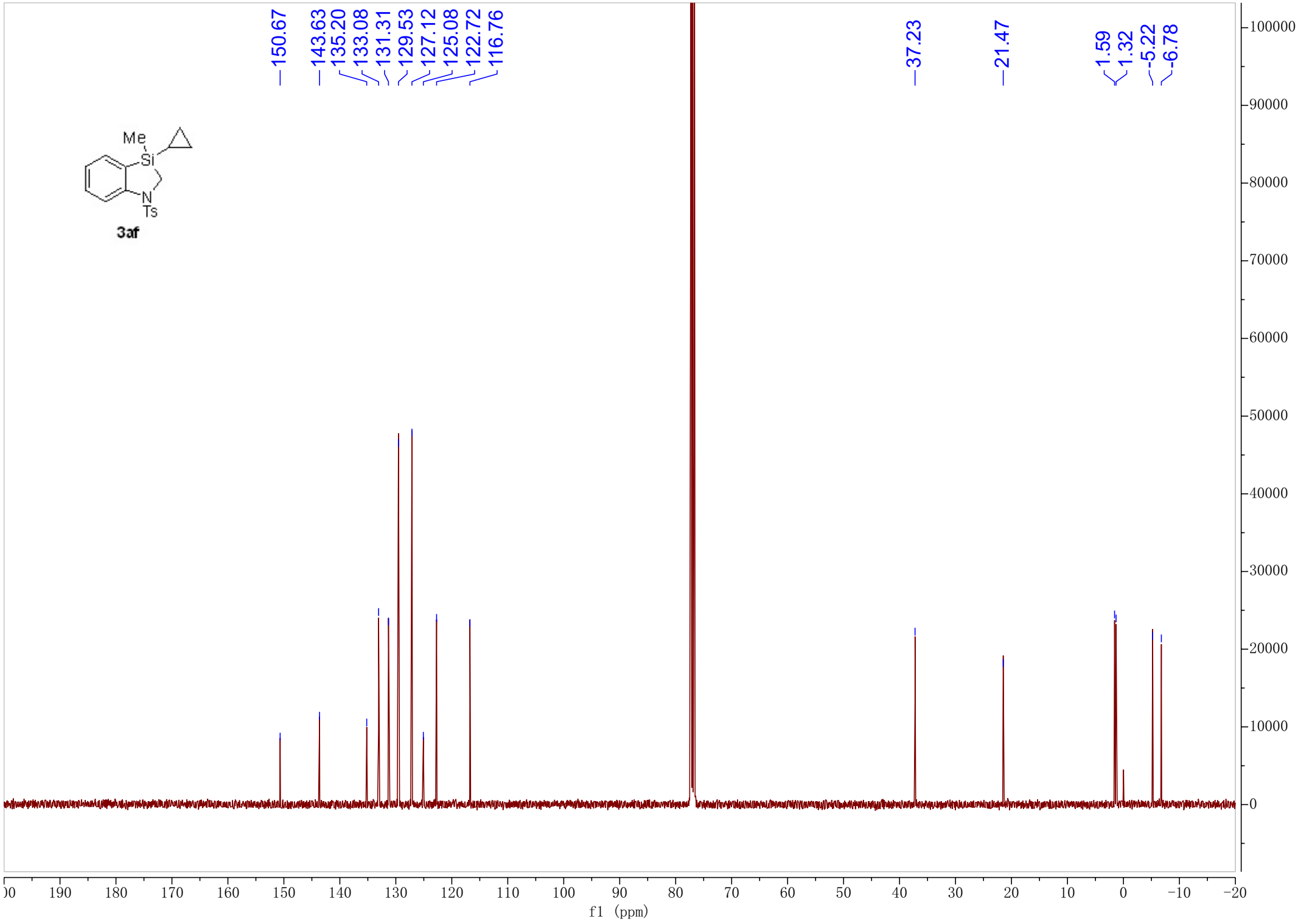
Me
Si
N
Ts
3af
1.03 2.01 1.84 1.78 0.91 2.32 3.00 2.03 1.10 2.85 1.01 1.03
f1 (ppm)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125.08
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116.76
37.23
21.47
1.59
1.32
-5.22
-6.78
Me
Si
N
Ts
3af
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
190
180
170
160
150
140
130
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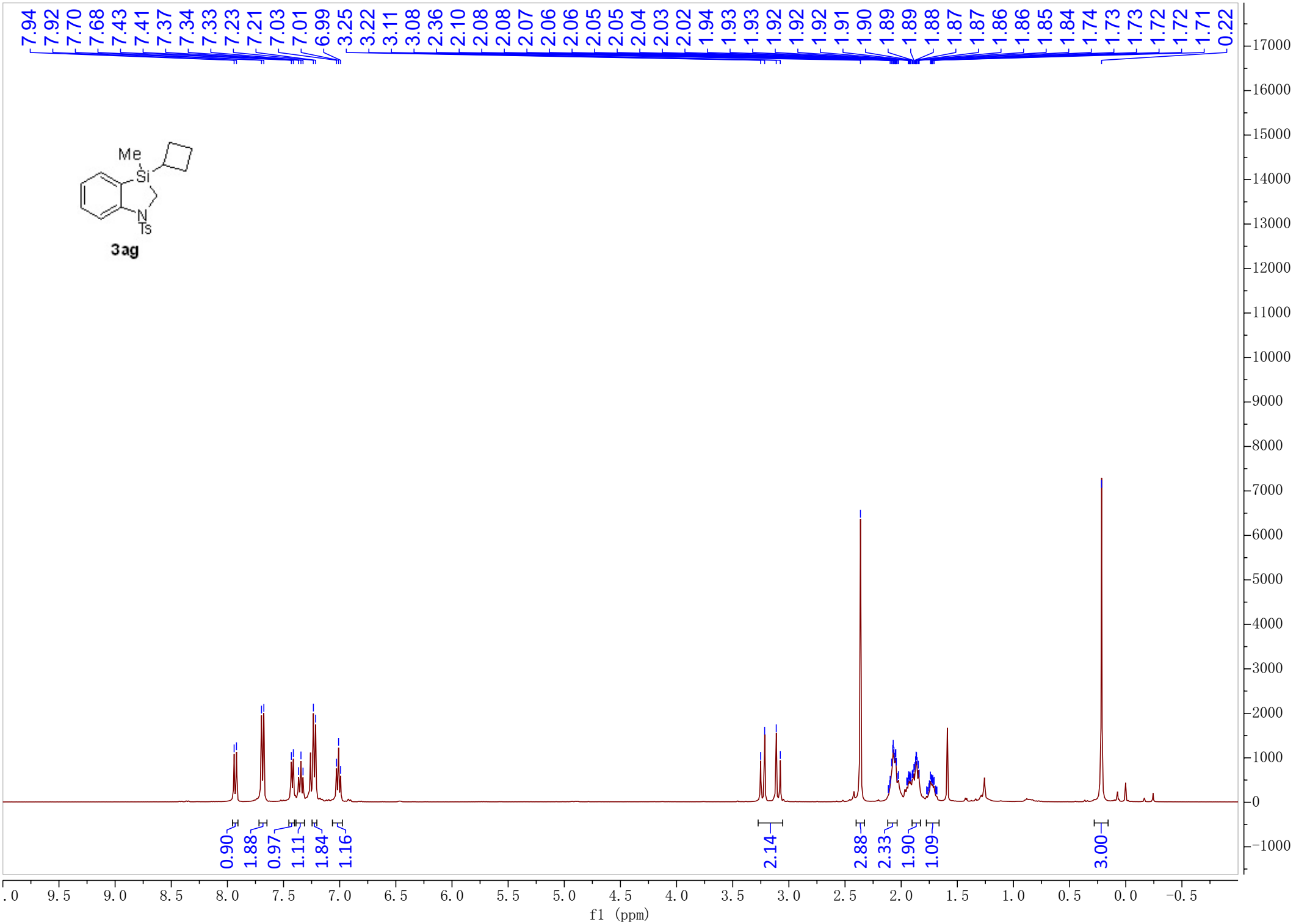
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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7.01
6.99
3.25
3.22
3.11
3.08
2.36
2.10
2.08
2.08
2.07
2.06
2.06
2.05
2.05
2.04
2.03
2.02
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1.93
1.93
1.92
1.92
1.92
1.91
1.90
1.89
1.89
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1.87
1.87
1.86
1.86
1.85
1.84
1.74
1.73
1.73
1.72
1.72
1.71
0.22
Me
Si
N
Ts
3ag
0.90
1.88
0.97
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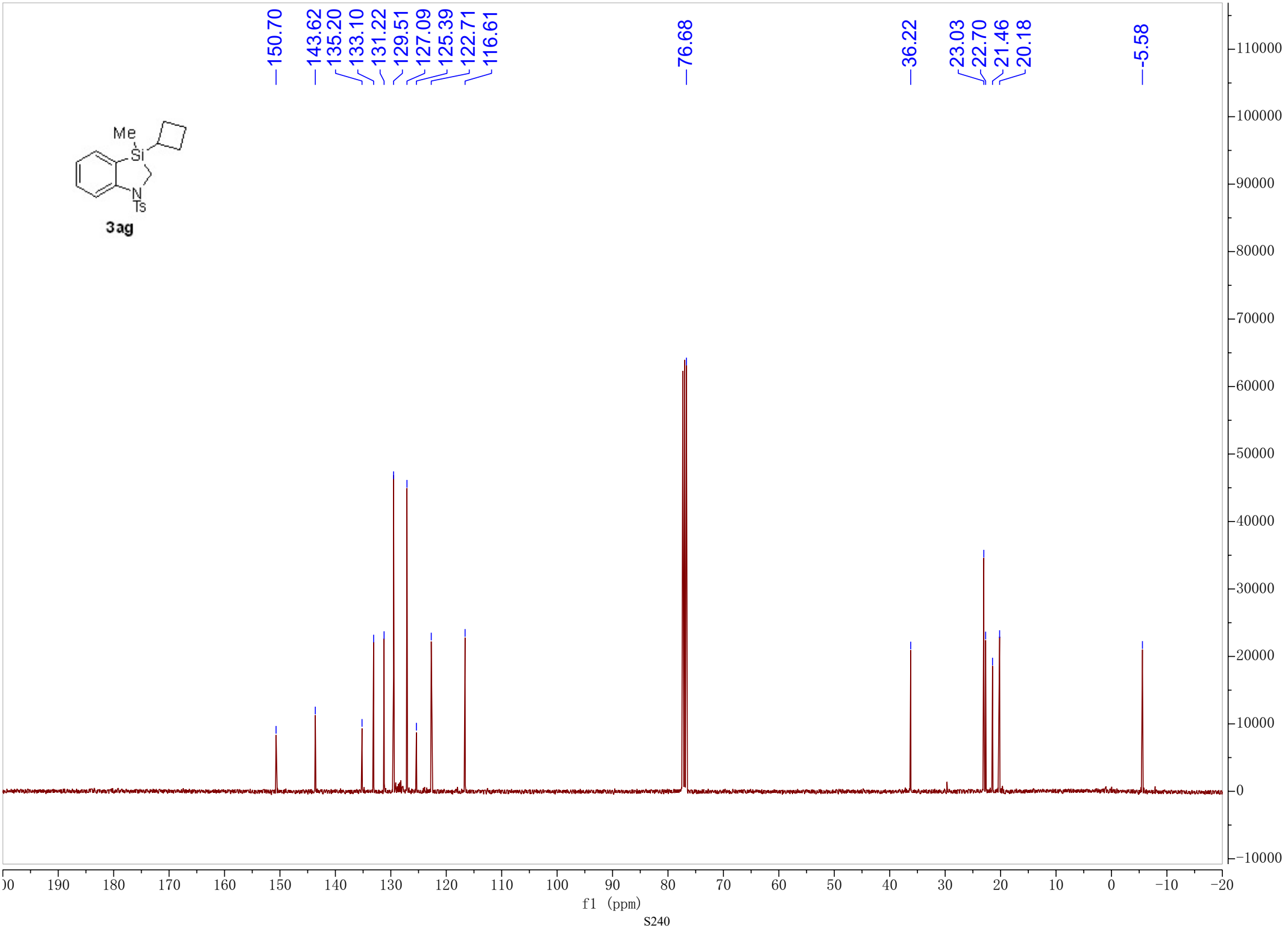
1.84
1.16
2.14
2.88
2.33
1.90
1.09
3.00
f1 (ppm)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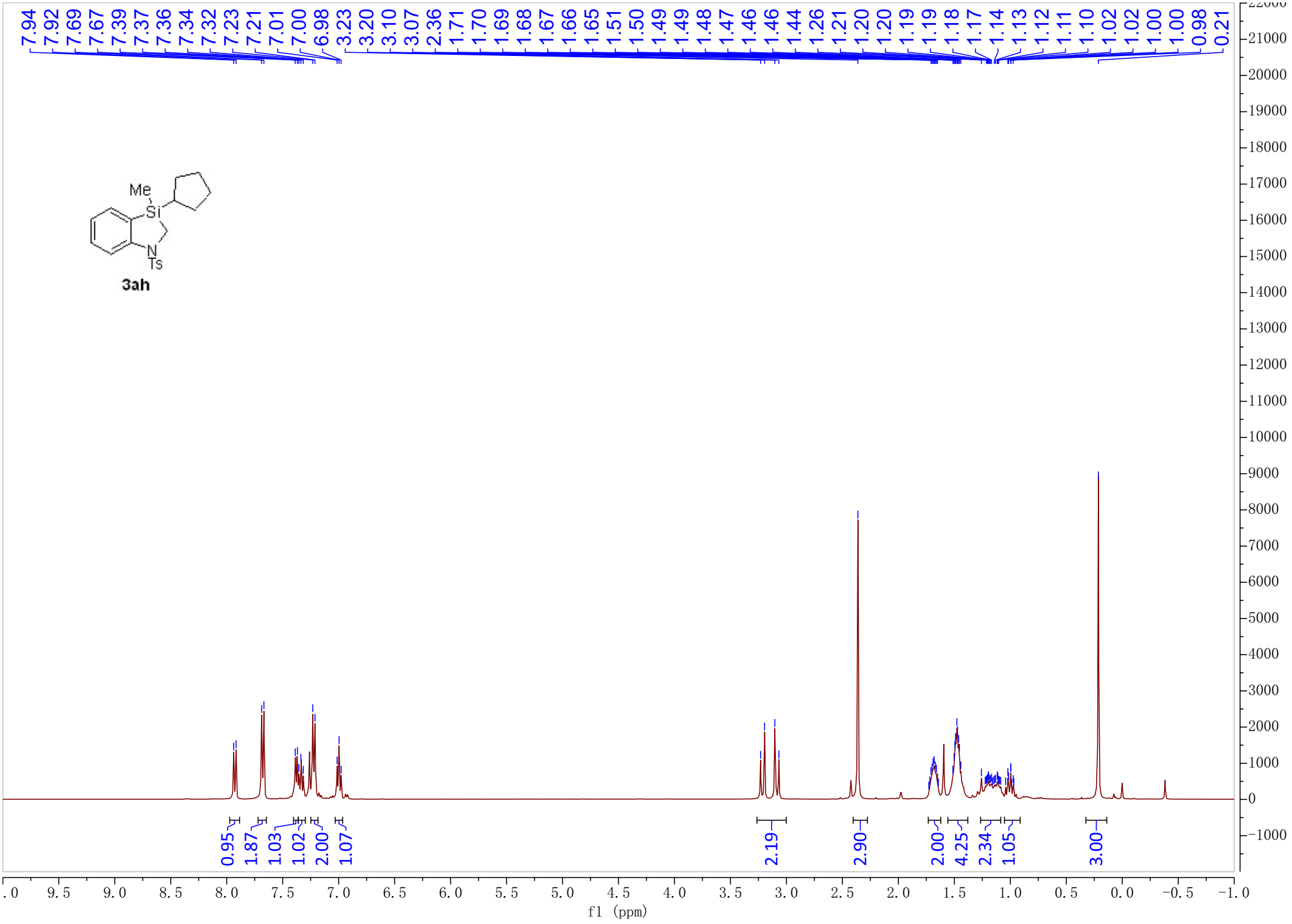
76.68
36.22
23.03
22.70
21.46
20.18
-5.58
Me
Si
N
Ts
3ag
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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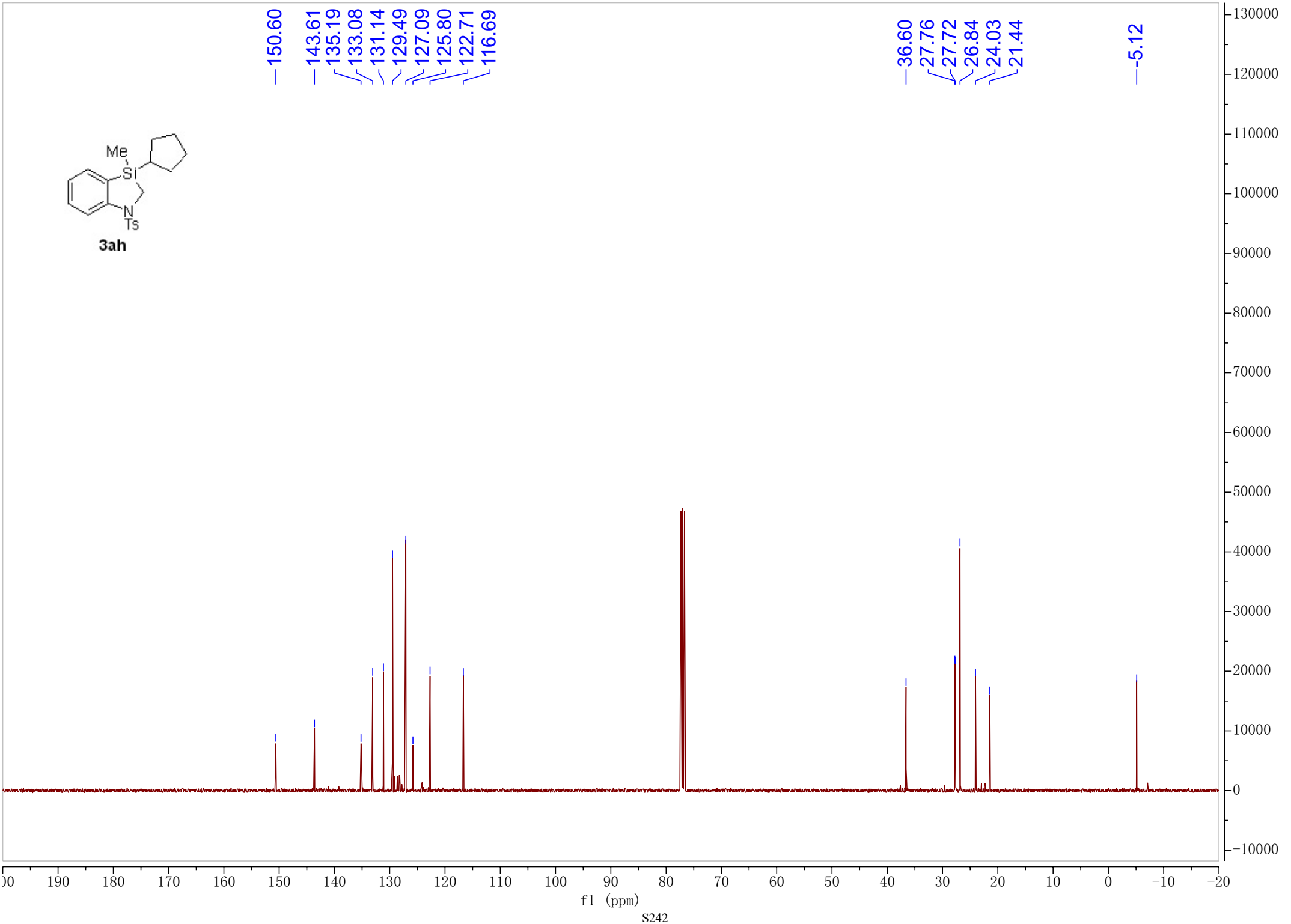
Me
Si
N
Ts
3ah
0.95 1.87 1.03 1.02 2.00 1.07 2.19 2.90 2.00 4.25 2.34 1.05 3.00
f1 (ppm)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127.09
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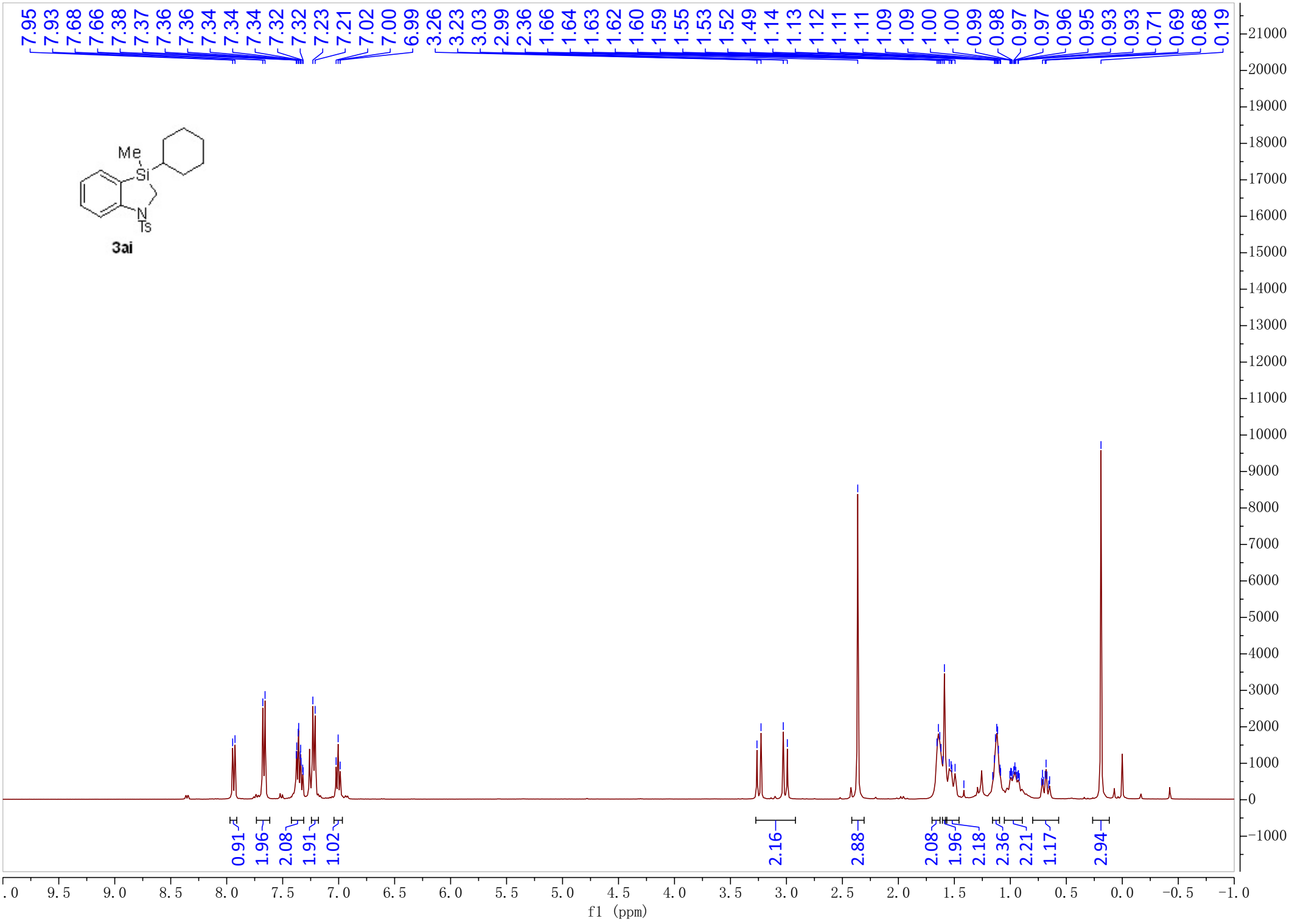
116.69
36.60
27.76
27.72
26.84
24.03
21.44
-5.12
Me
Si
N
Ts
3ah
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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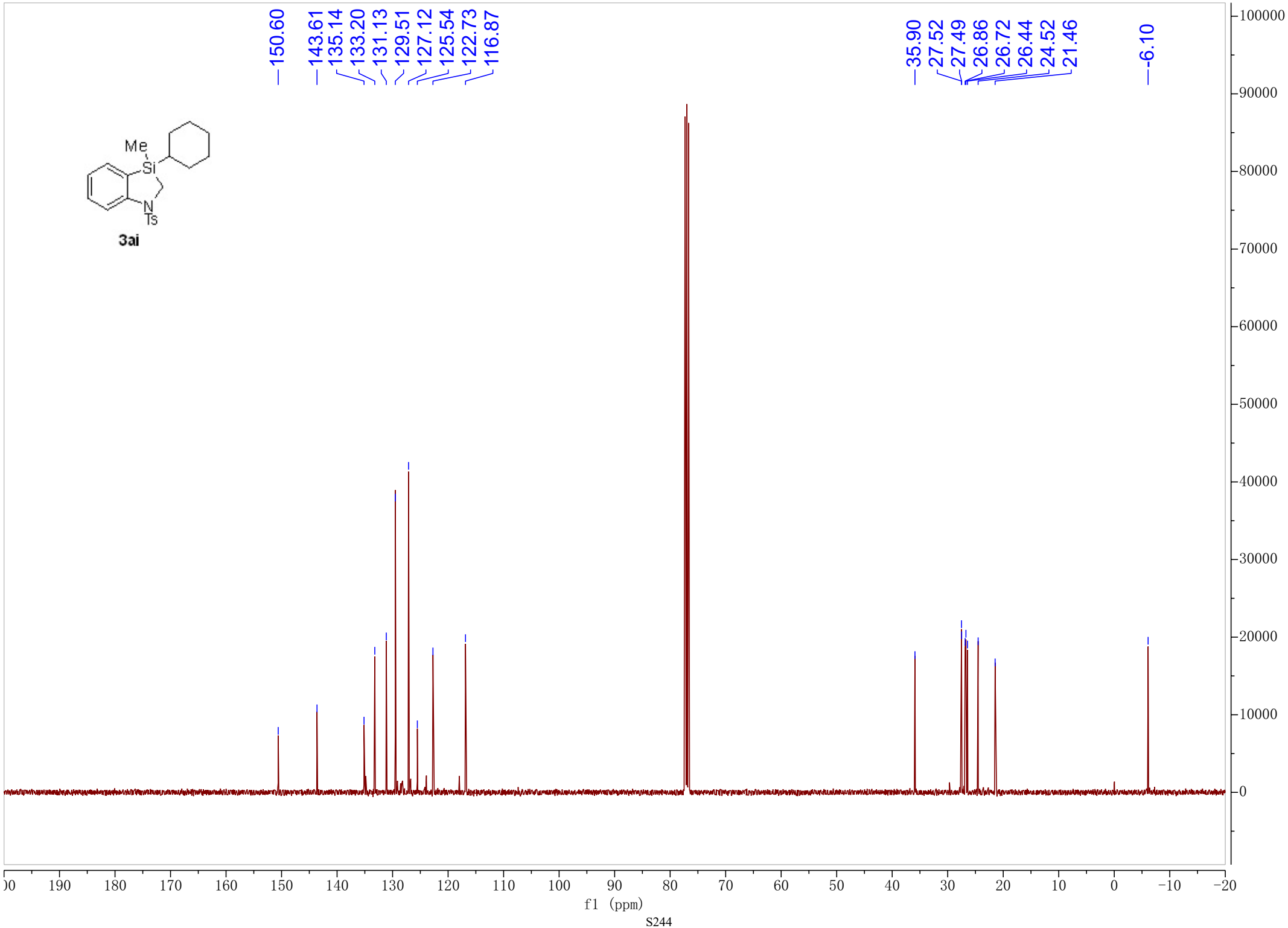
3.26 3.23 3.03 2.99 2.36 1.66 1.64 1.63 1.62 1.60 1.59 1.55 1.53 1.52 1.49 1.14 1.13 1.12 1.11 1.11 1.09 1.09 1.00 1.00 0.99 0.98 0.97 0.97 0.96 0.95 0.93 0.93 0.71 0.69 0.68 0.19
Me
Si
N
Ts
3ai
0.91 1.96 2.08 1.91 1.02 2.16 2.88 2.08 1.96 2.18 2.36 2.21 1.17 2.94
f1 (ppm)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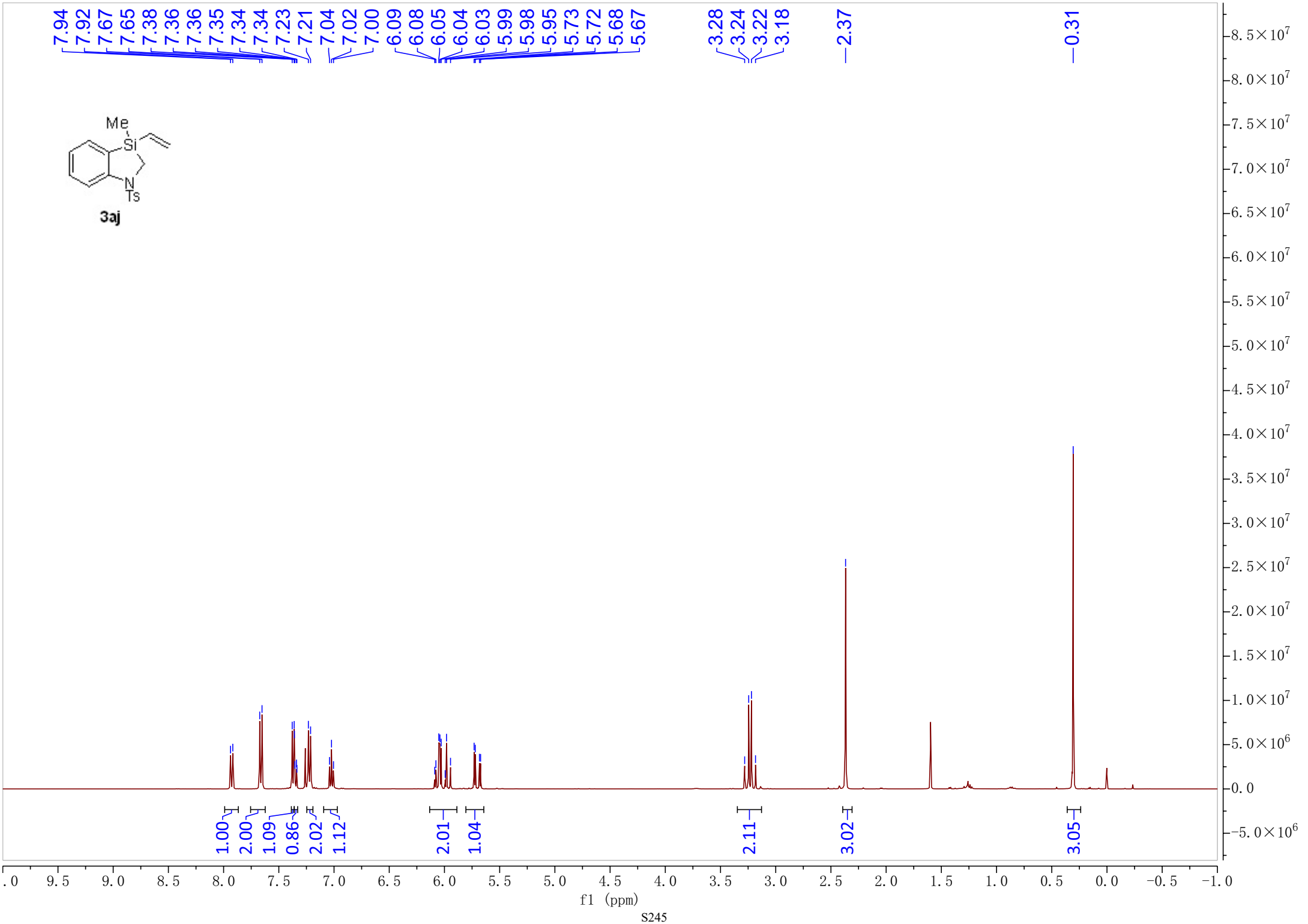
26.72
26.44
24.52
21.46
6.10
Me
Si
N
Ts
3ai
f1 (ppm)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7.92
7.67
7.65
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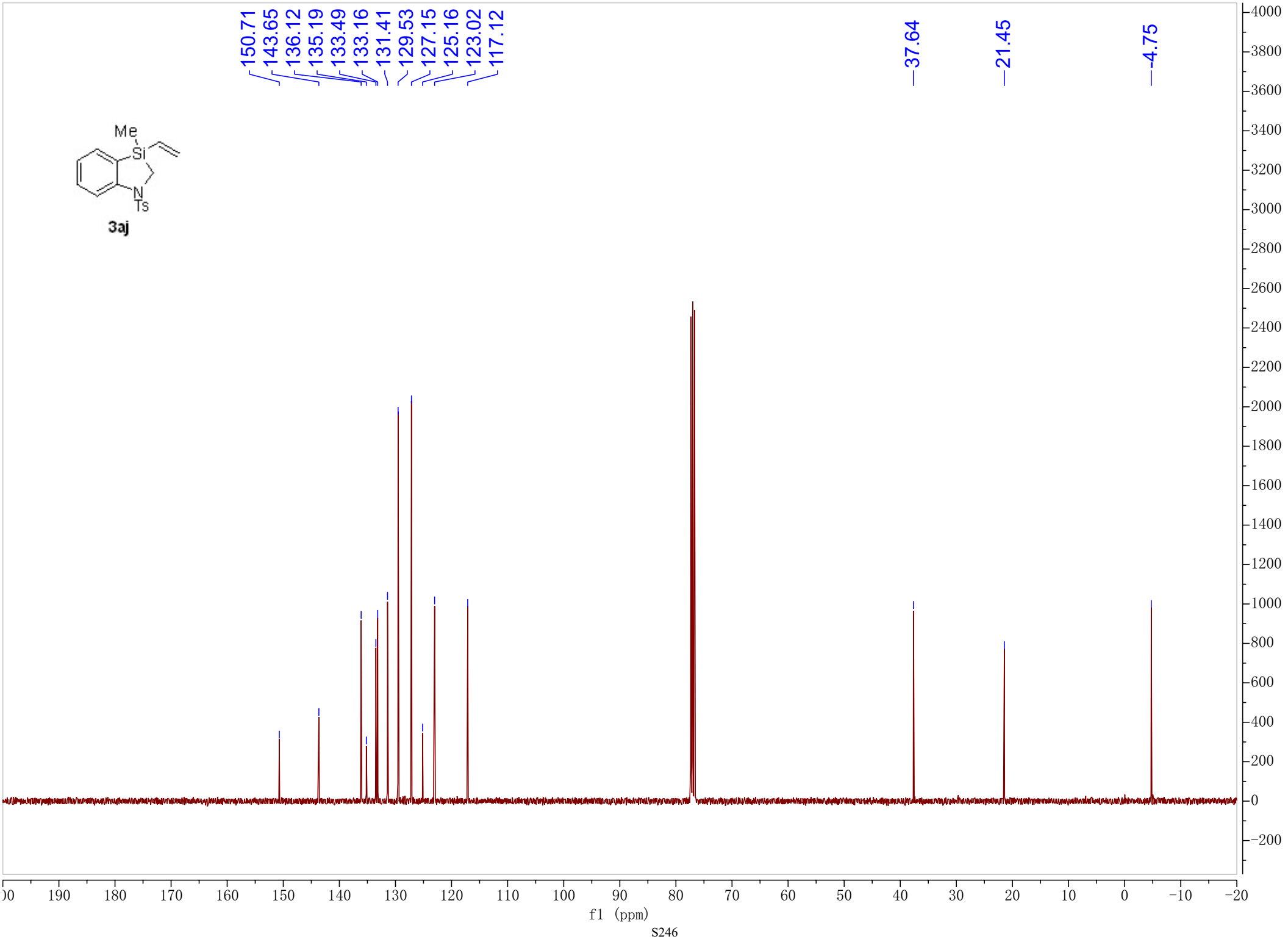
7.35
7.34
7.34
7.23
7.21
7.04
7.02
7.00
6.09
6.08
6.05
6.04
6.03
5.99
5.98
5.95
5.73
5.72
5.68
5.67
3.28
3.24
3.22
3.18
2.37
0.31
Me
Si
N
Ts
3aj
1.00
2.00
1.09
0.86
2.02
1.12
2.01
1.04
2.11
3.02
3.05
f1 (ppm)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123.02
117.12
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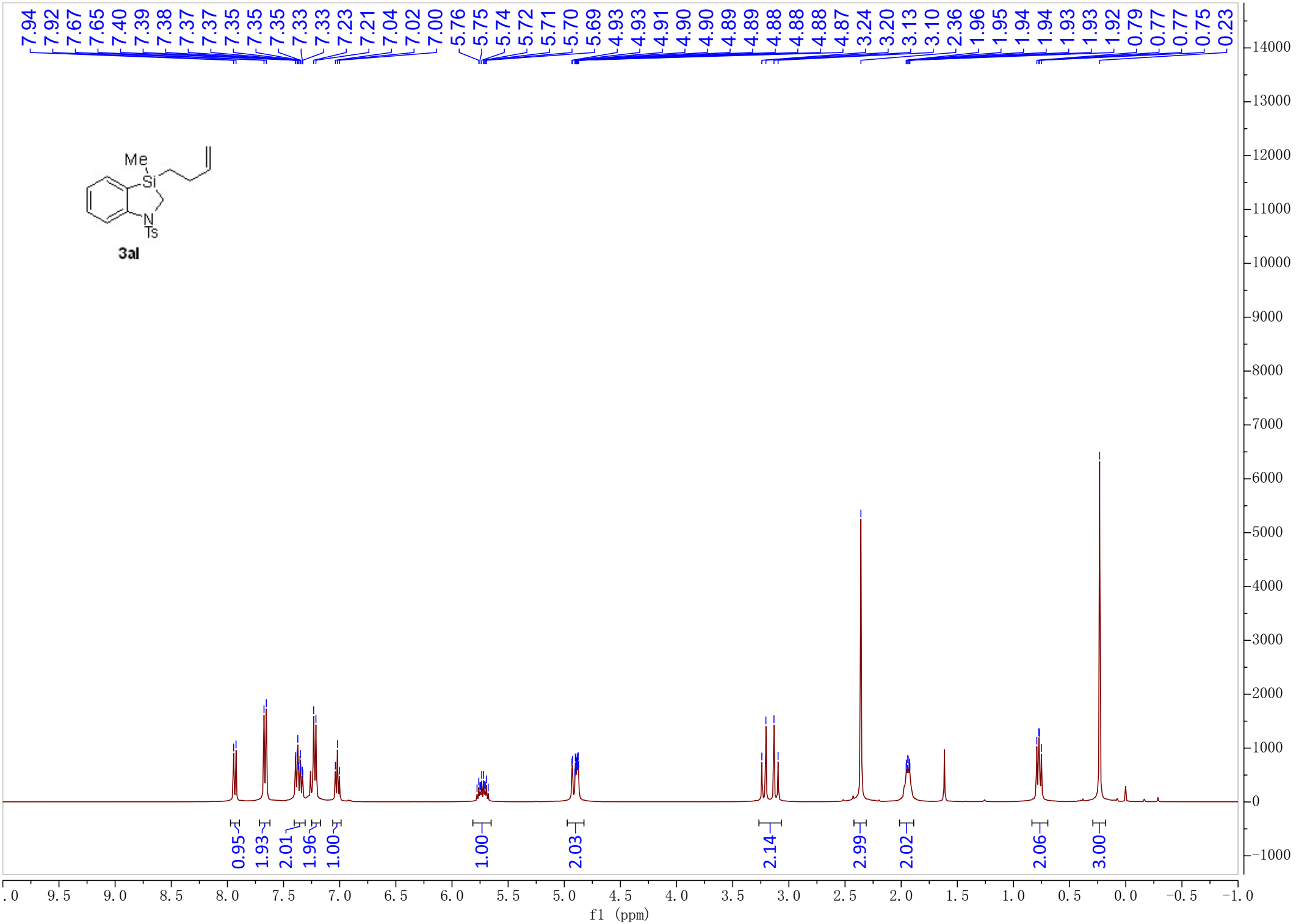
21.45
-4.75
Me
Si
N
Ts
3aj
f1 (ppm)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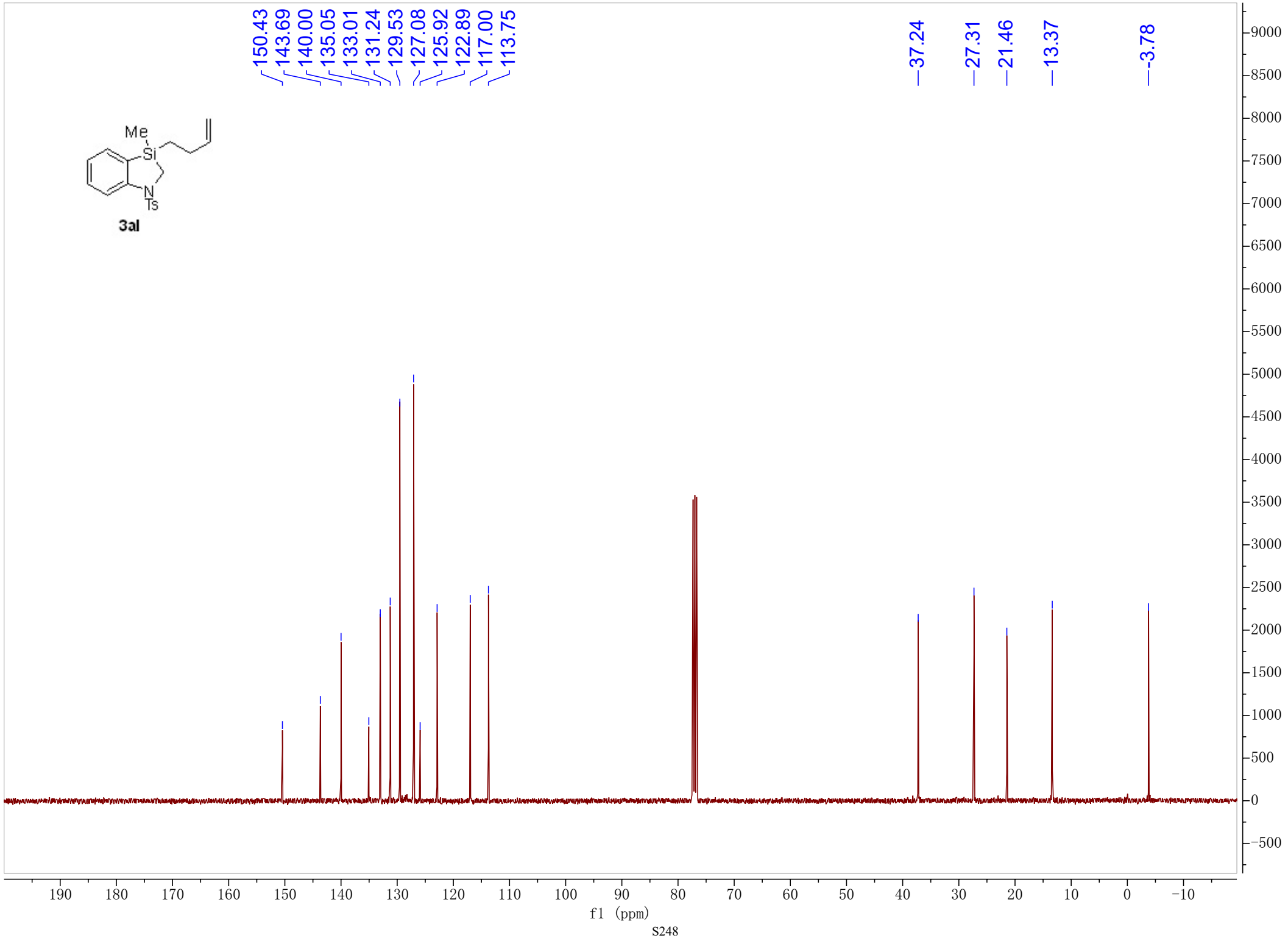
5.76 5.75 5.74 5.72 5.71 5.70 5.69 4.93 4.93 4.91 4.90 4.90 4.89 4.89 4.88 4.88 4.88 4.87 3.24 3.20 3.13 3.10 2.36 1.96 1.95 1.94 1.94 1.93 1.93 1.92 0.79 0.77 0.77 0.75 0.23
Me
Si
N
Ts
3al
0.95 1.93 2.01 1.96 1.00 1.00 2.03 2.14 2.99 2.02 2.06 3.00
f1 (ppm)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122.89
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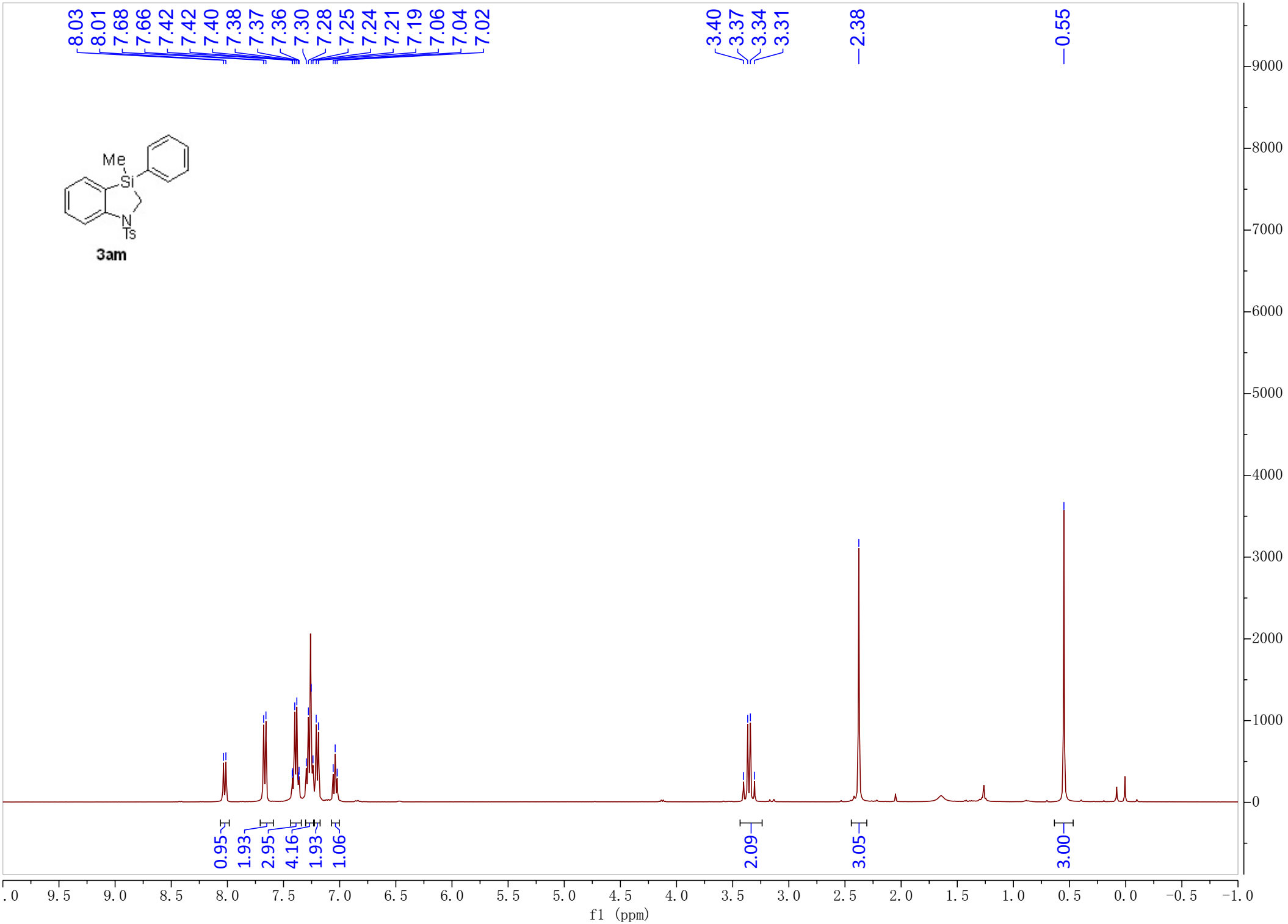
37.24
27.31
21.46
13.37
-3.78
Me
Si
N
Ts
3al
f1 (ppm)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7.25
7.24
7.21
7.19
7.06
7.04
7.02
3.40
3.37
3.34
3.31
2.38
0.55
Me
Si
N
Ts
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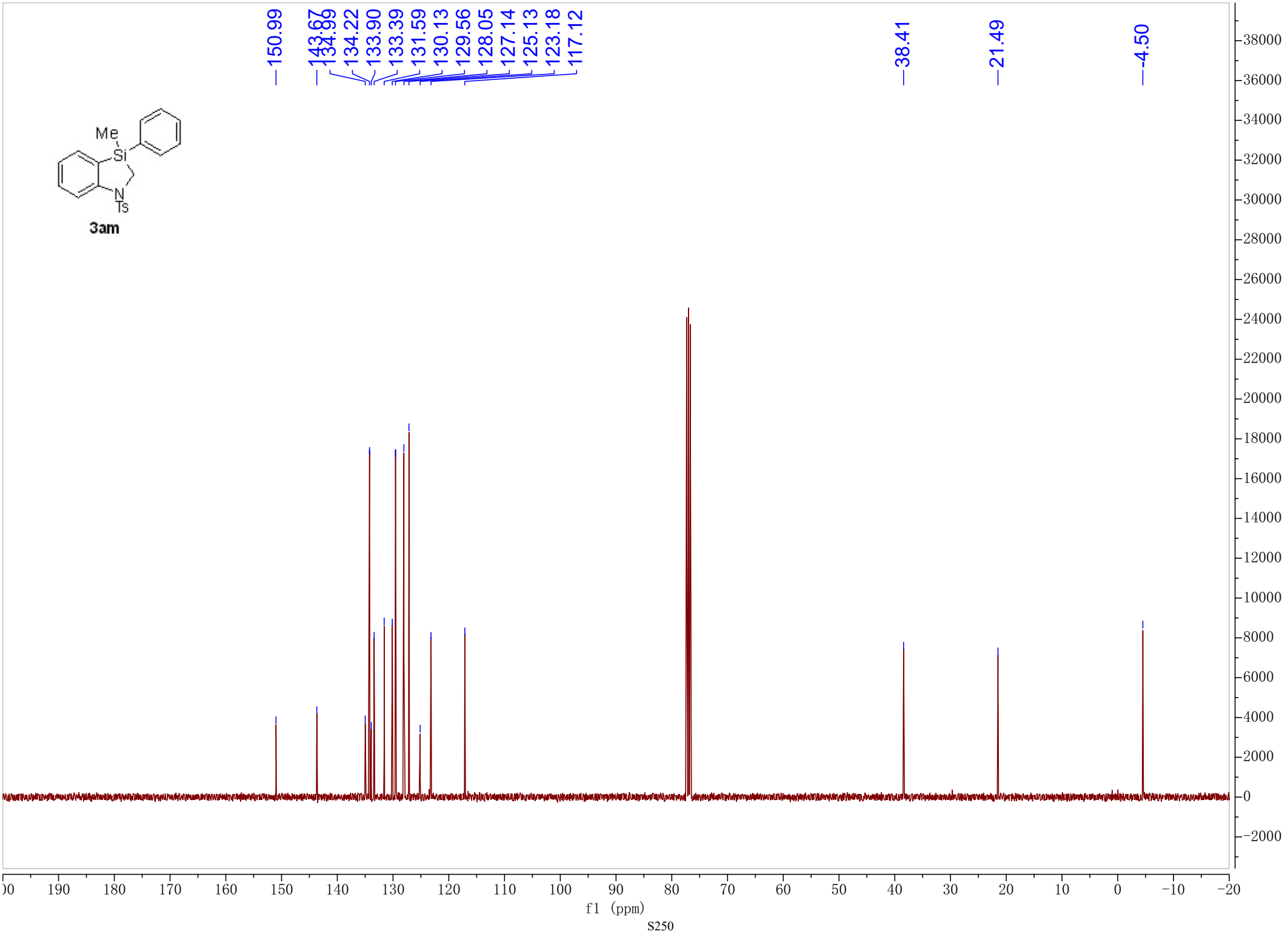
2.95
4.16
1.93
1.06
2.09
3.05
3.00
f1 (ppm)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127.14
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123.18
117.12
38.41
21.49
-4.50
Me
Si
N
Ts
3am
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
190
180
170
160
150
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130
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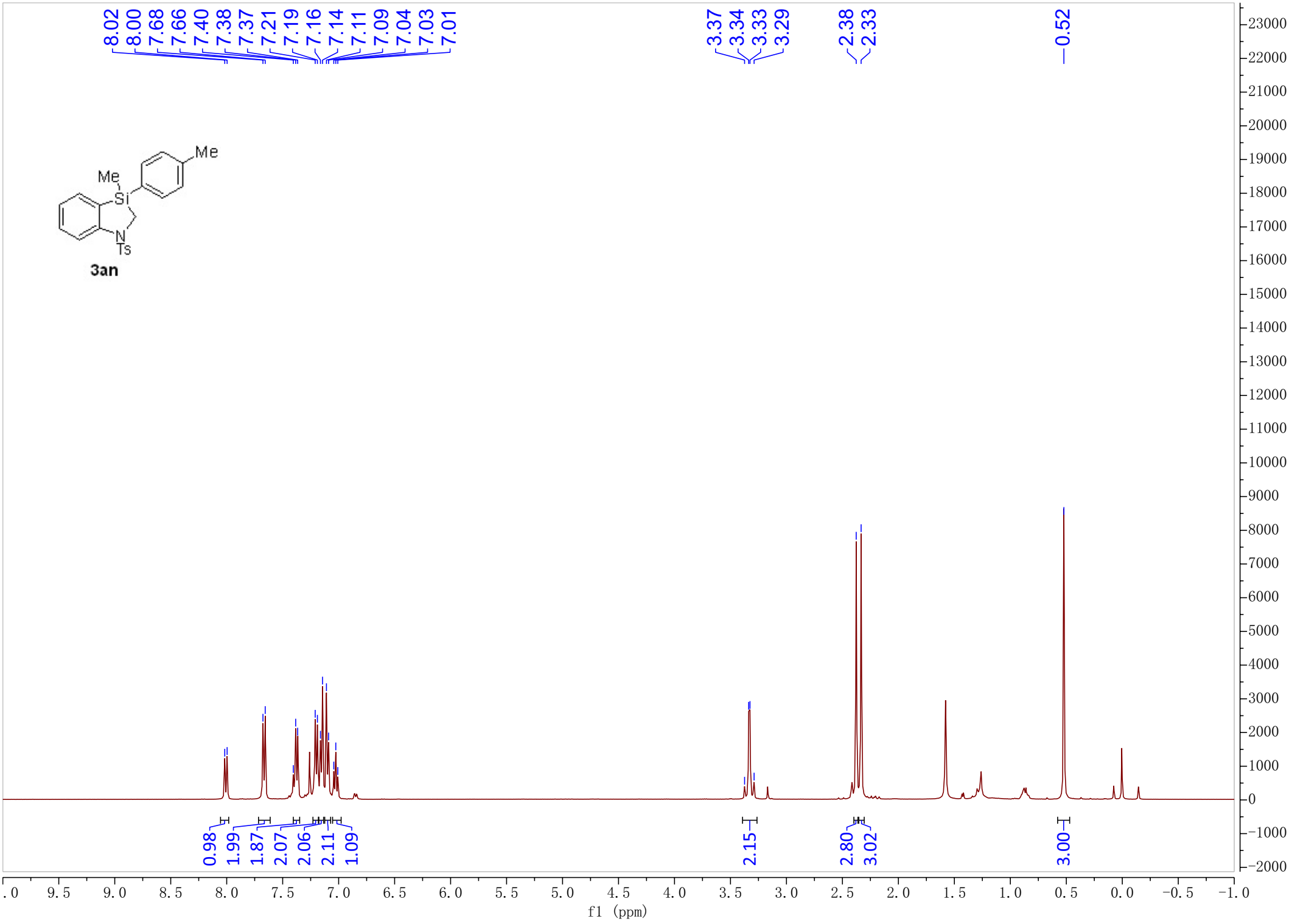
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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7.14
7.11
7.09
7.04
7.03
7.01
3.37
3.34
3.33
3.29
2.38
2.33
0.52
Me
Me
Si
N
Ts
Me
3an
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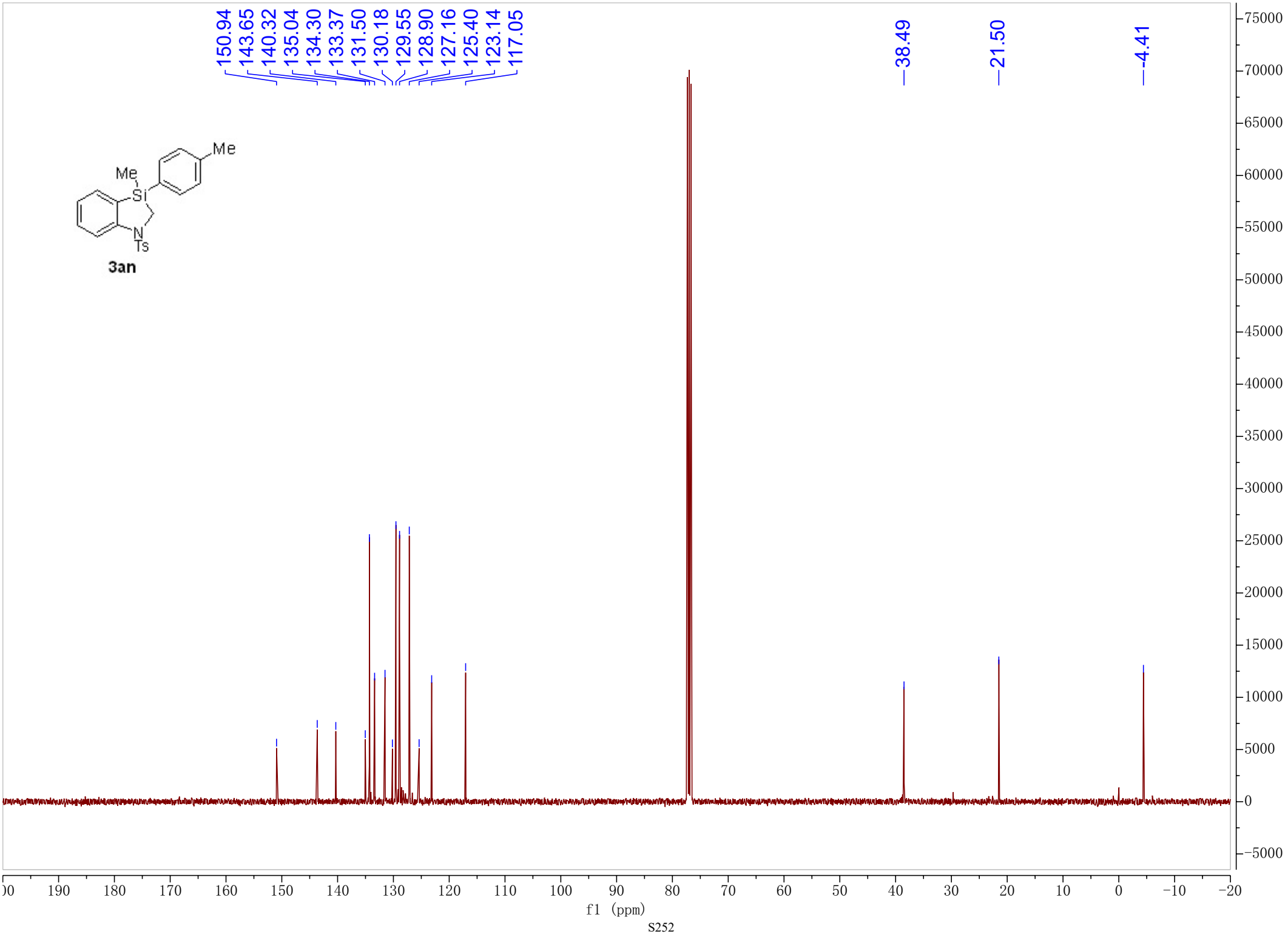
2.06
2.11
1.09
2.15
2.80
3.02
3.00
f1 (ppm)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128.90
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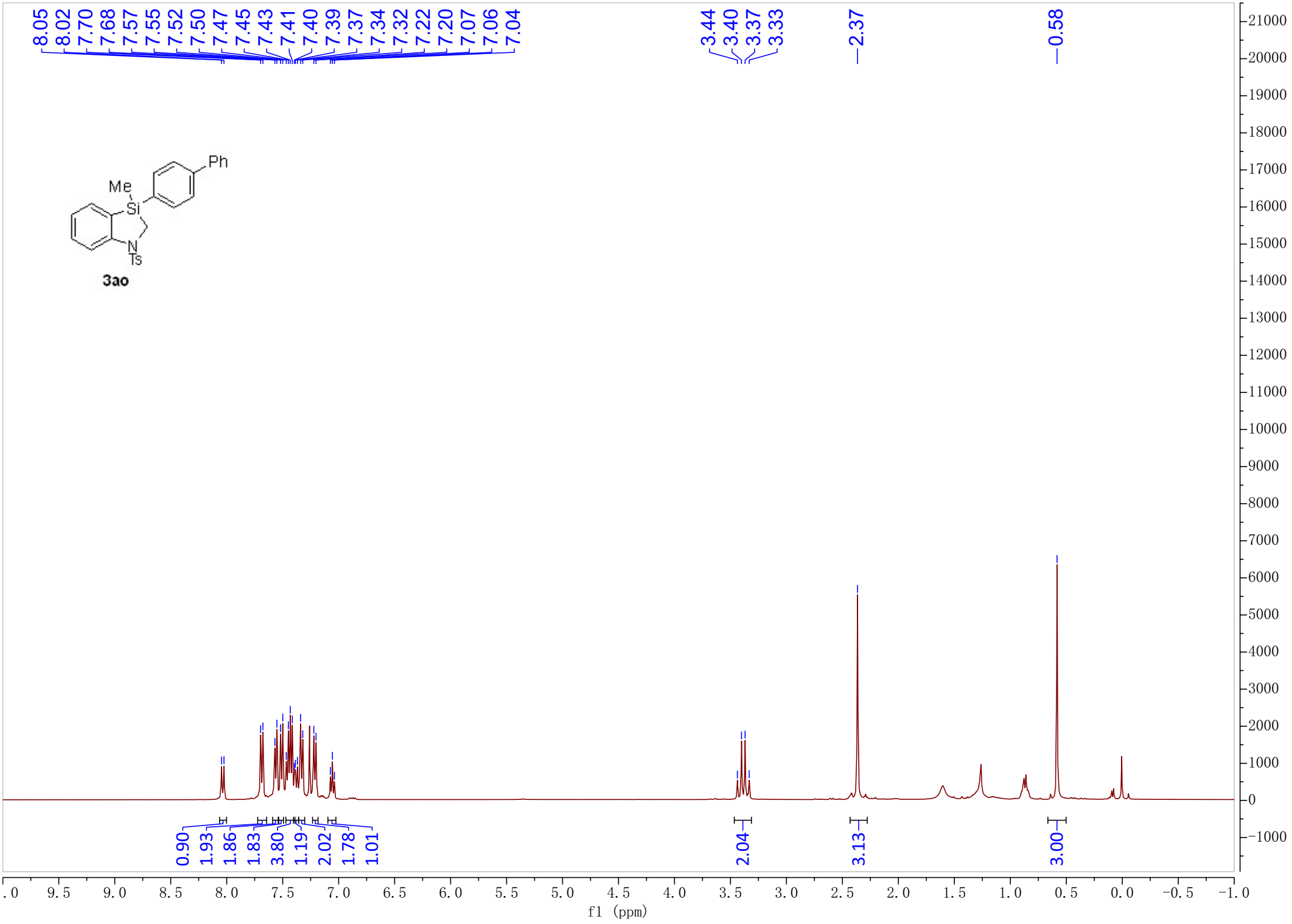
117.05
38.49
21.50
4.41
Me
Me
Si
N
Ts
3an
f1 (ppm)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7.50
7.47
7.45
7.43
7.41
7.40
7.39
7.37
7.34
7.32
7.22
7.20
7.07
7.06
7.04
3.44
3.40
3.37
3.33
2.37
0.58
Ph
Me
Si
N
Ts
3ao
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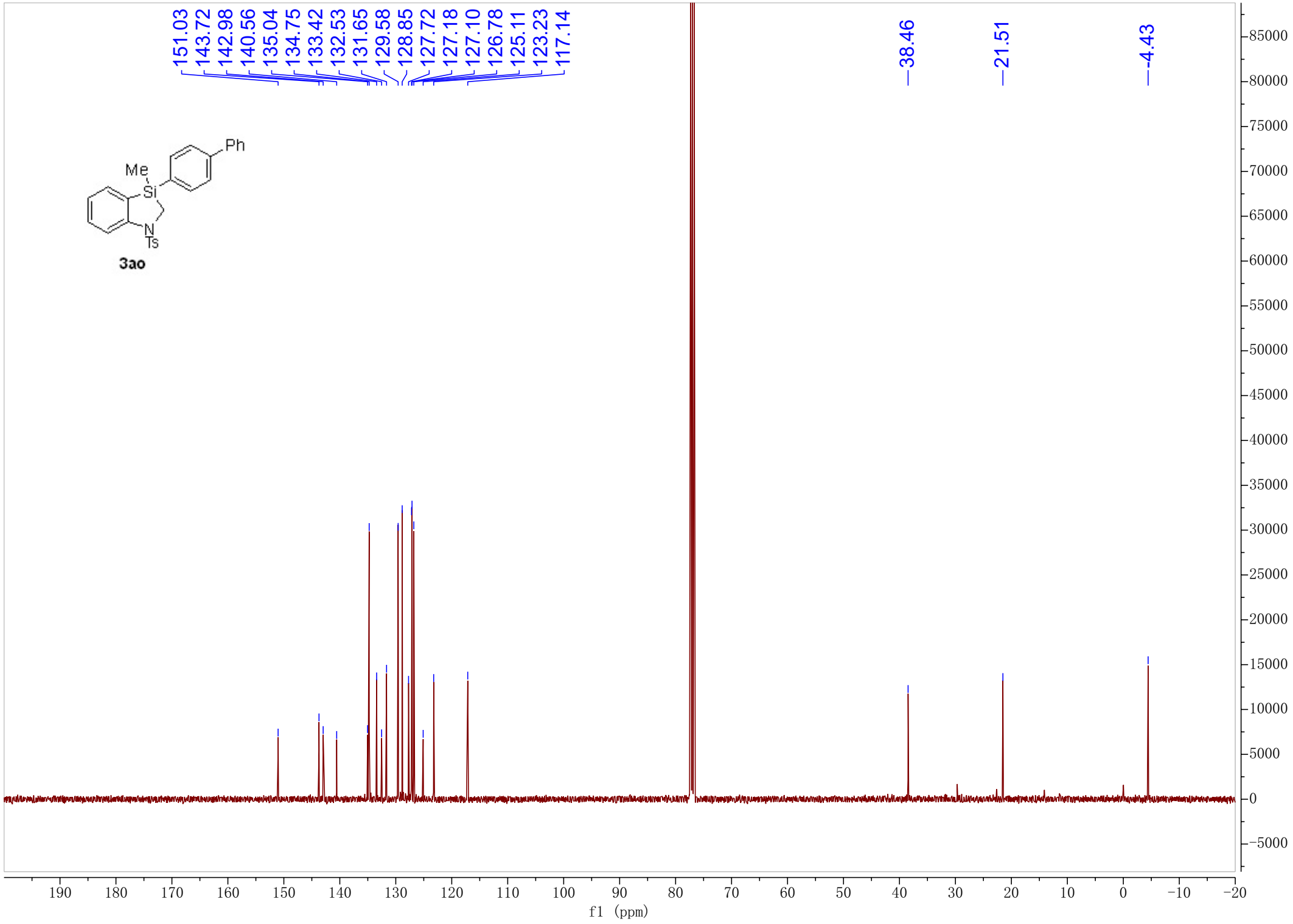
1.19
2.02
1.78
1.01
2.04
3.13
3.00
f1 (ppm)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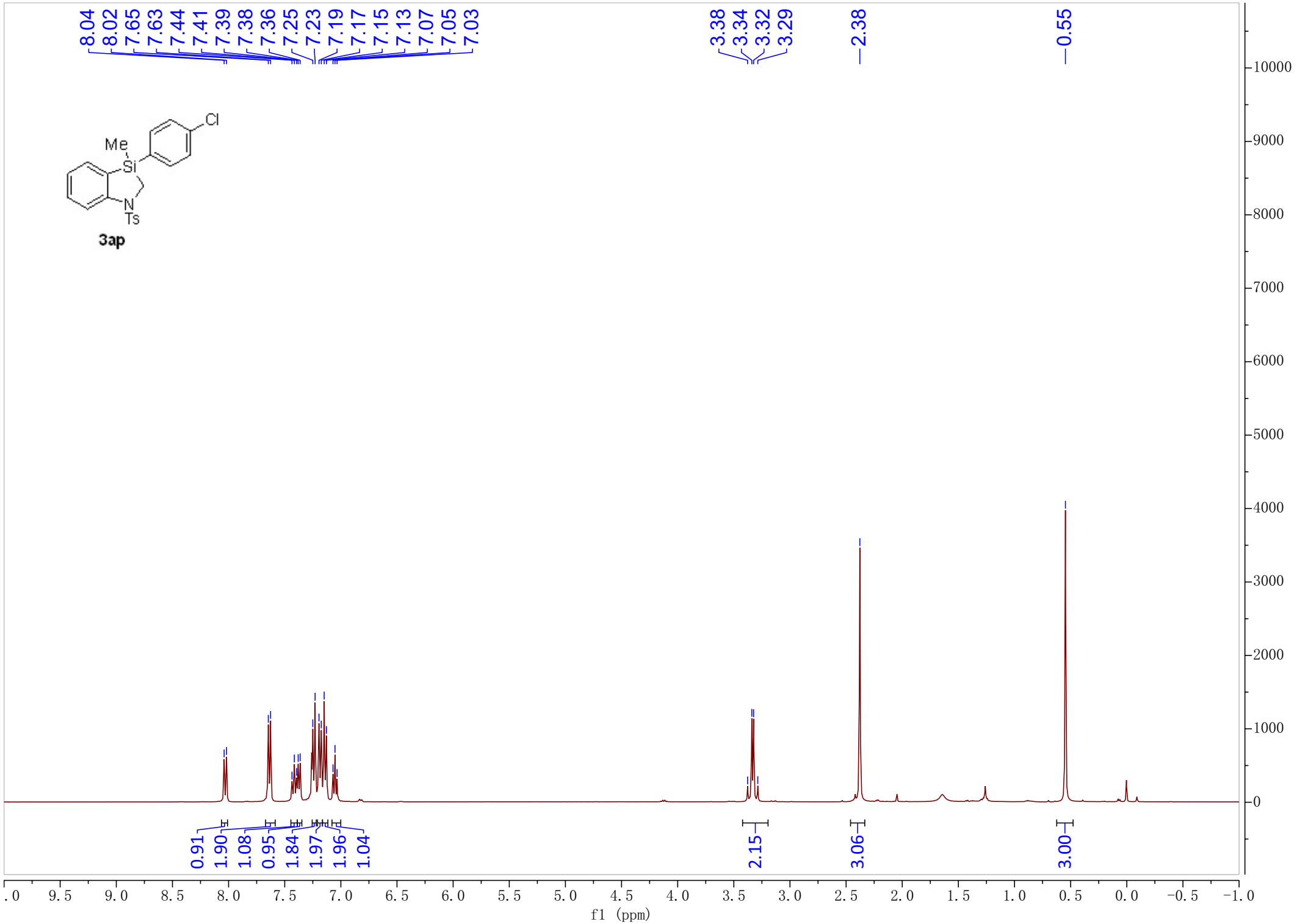
Me
Si
Ph
N
Ts
3ao
f1 (ppm)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7.23
7.19
7.17
7.15
7.13
7.07
7.05
7.03
3.38
3.34
3.32
3.29
2.38
0.55
Me
Si
Cl
N
Ts
3ap
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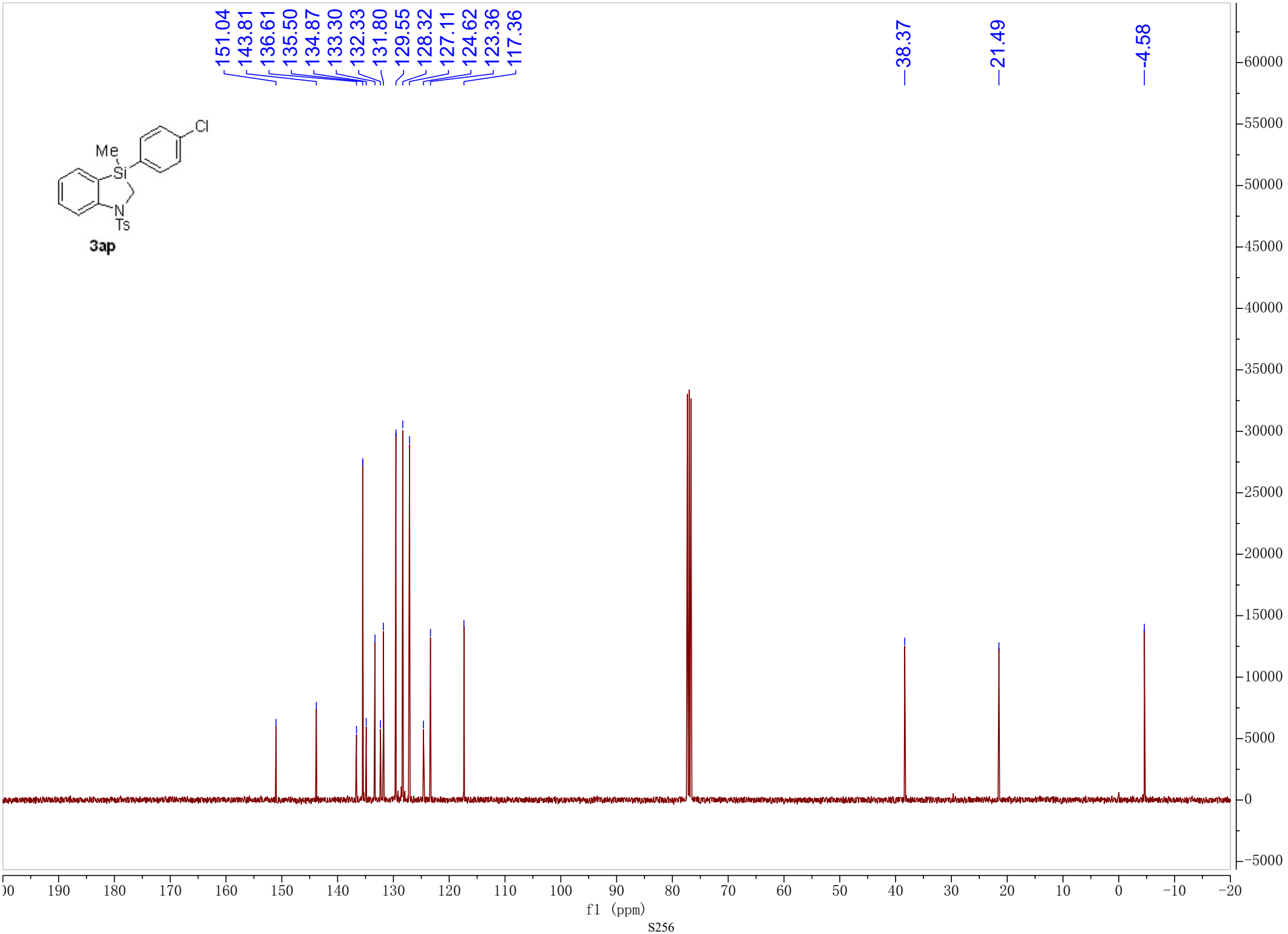
0.95
1.84
1.97
1.96
1.04
2.15
3.06
3.00
f1 (ppm)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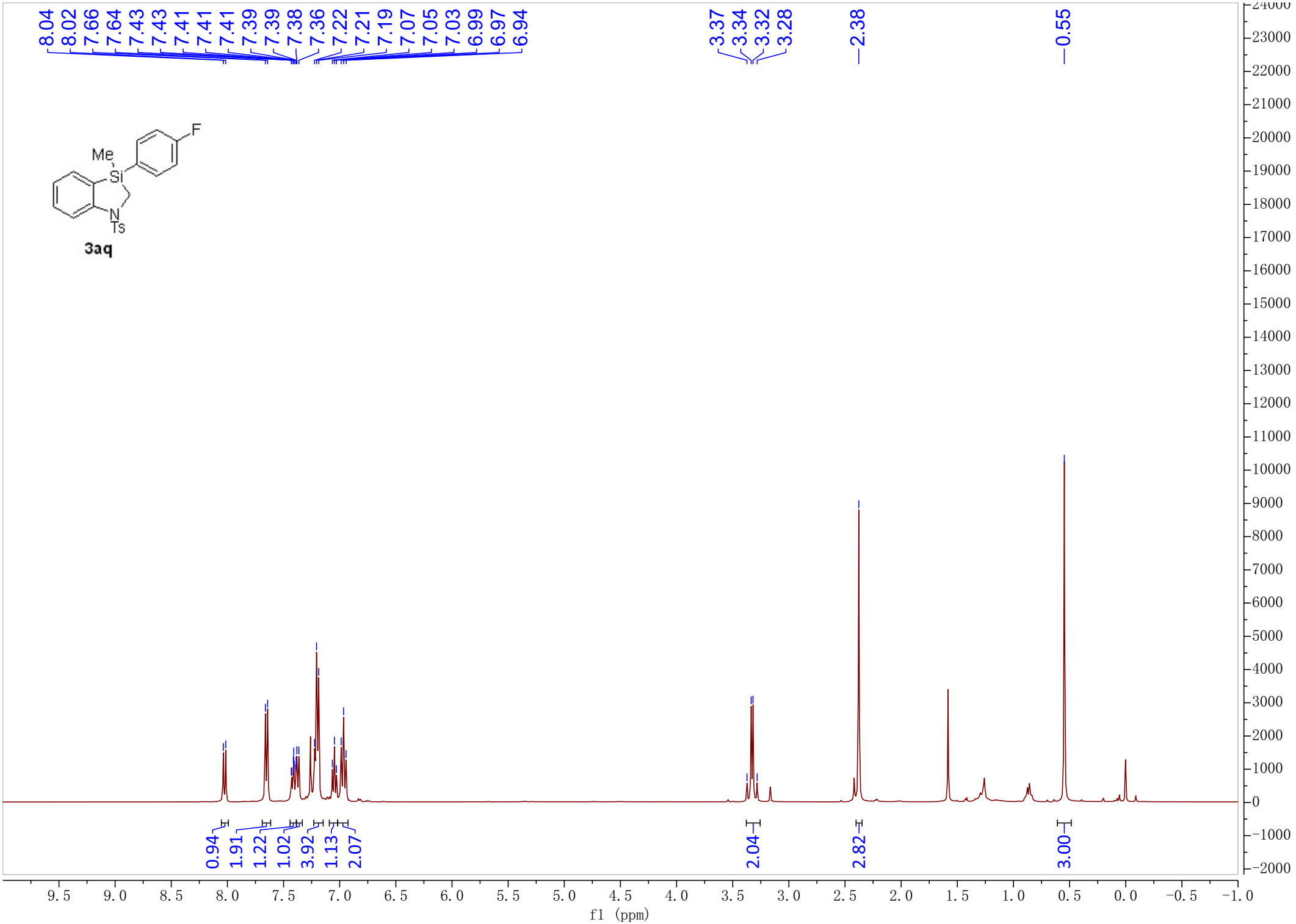
123.36
117.36
38.37
21.49
4.58
Me
Si
Cl
N
Ts
3ap
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
−5000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)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7.38
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7.22
7.21
7.19
7.07
7.05
7.03
6.99
6.97
6.94
3.37
3.34
3.32
3.28
2.38
0.55
F
Me
Si
N
Ts
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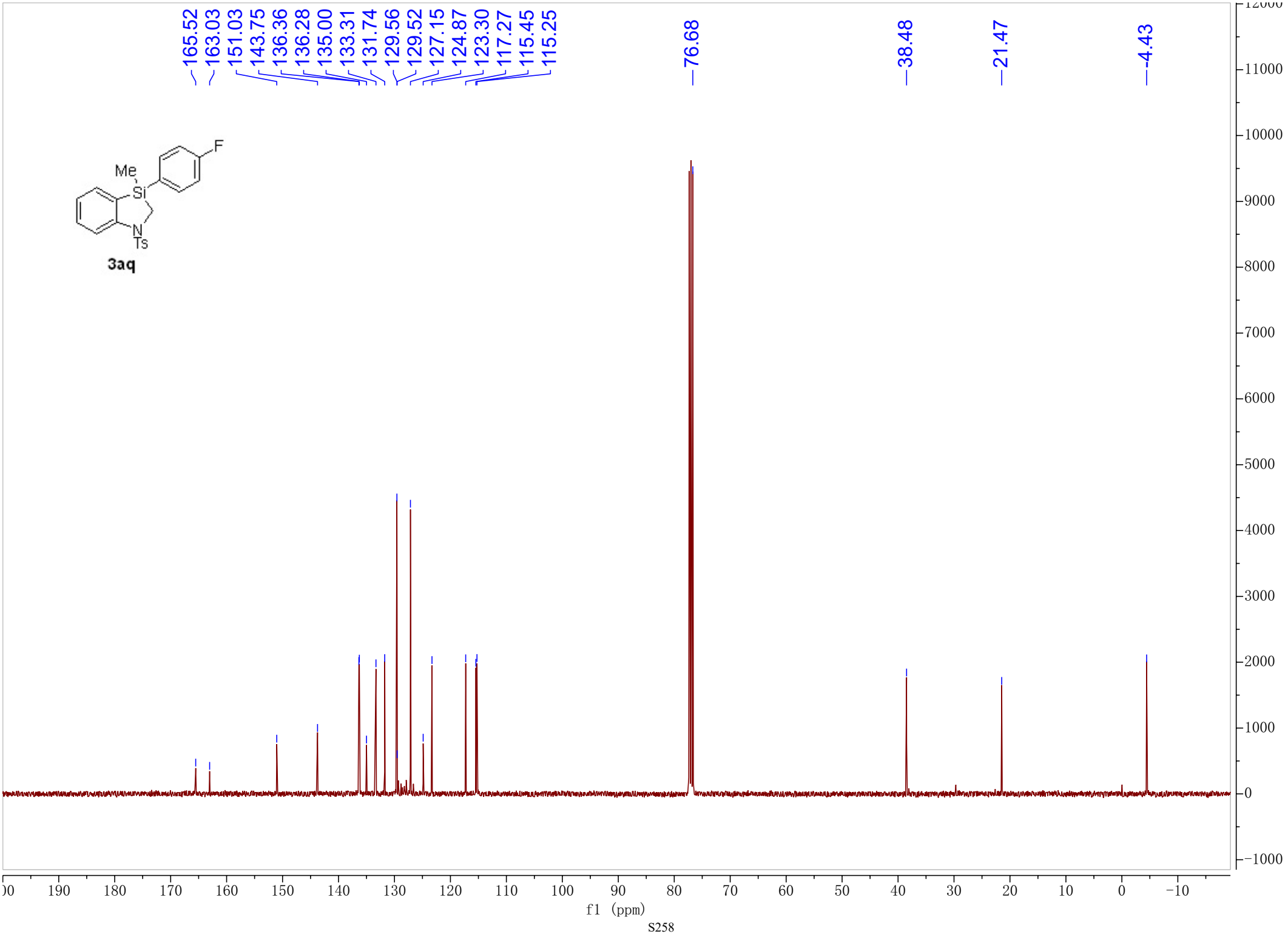
1.22
1.02
3.92
1.13
2.07
2.04
2.82
3.00
f1 (ppm)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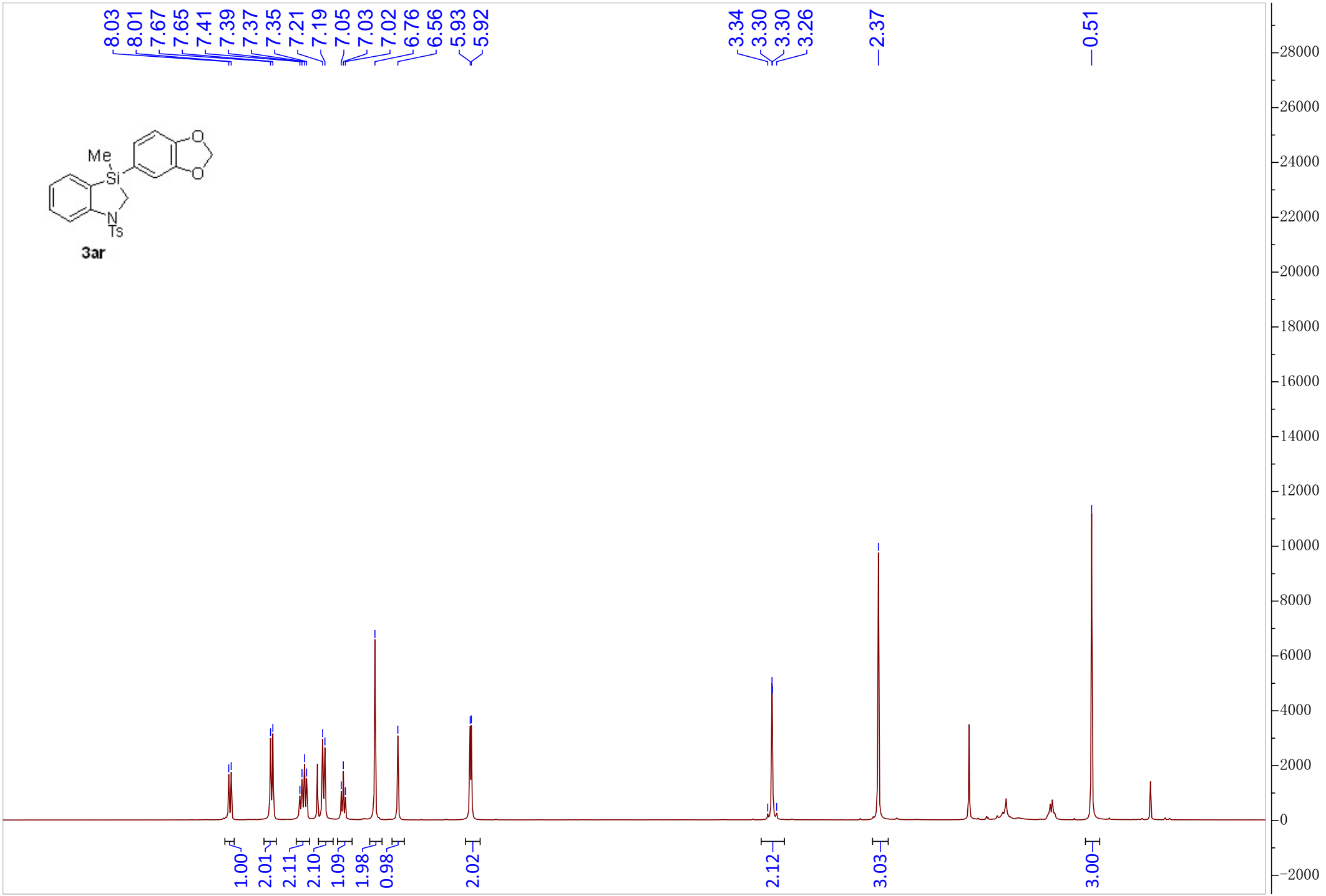
Si
F
N
Ts
3aq
f1 (ppm)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5.92
3.34
3.30
3.30
3.26
2.37
0.51
Me
Si
N
Ts
O
O
3ar
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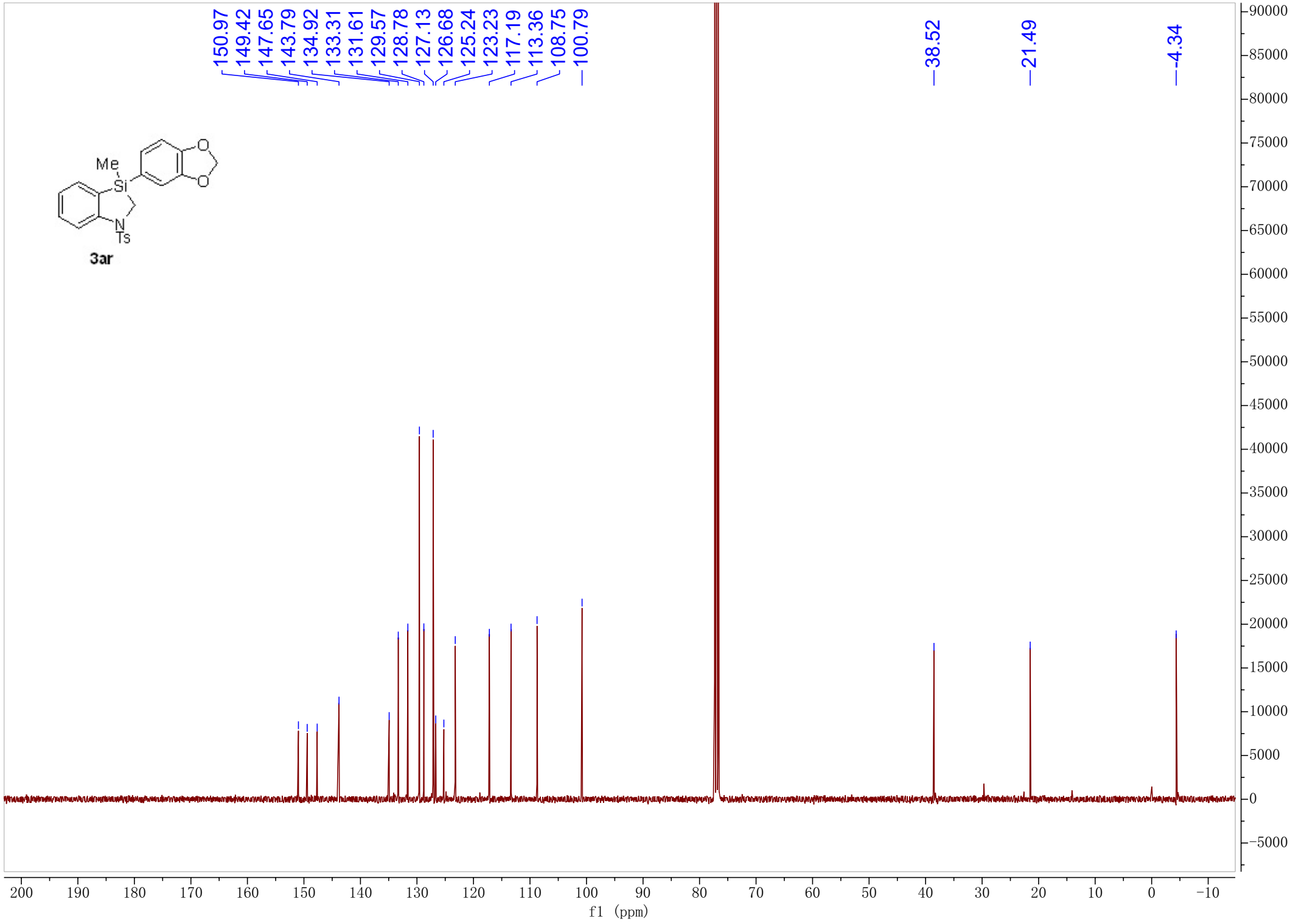
1.09
1.98
0.98
2.02
2.12
3.03
3.00
f1 (ppm)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126.68
125.24
123.23
117.19
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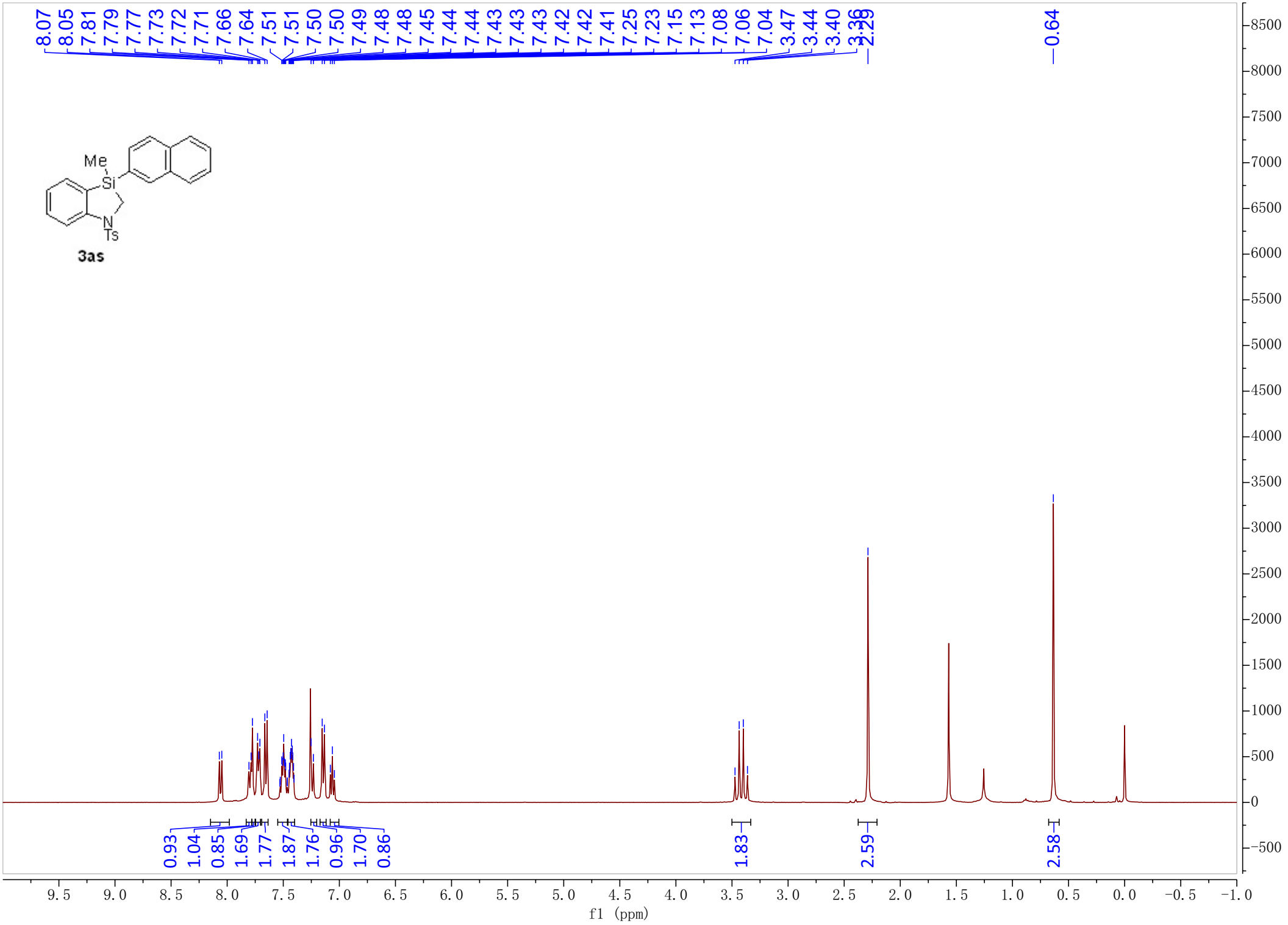
100.79
38.52
21.49
4.34
Me
Si
N
Ts
O
O
3ar
f1 (ppm)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7.71
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7.64
7.51
7.51
7.50
7.50
7.49
7.48
7.48
7.45
7.44
7.44
7.43
7.43
7.43
7.42
7.42
7.41
7.25
7.23
7.15
7.13
7.08
7.06
7.04
3.47
3.44
3.40
3.36
2.29
0.64
Me
Si
N
Ts
3as
0.93
1.04
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1.87
1.76
0.96
1.70
0.86
1.83
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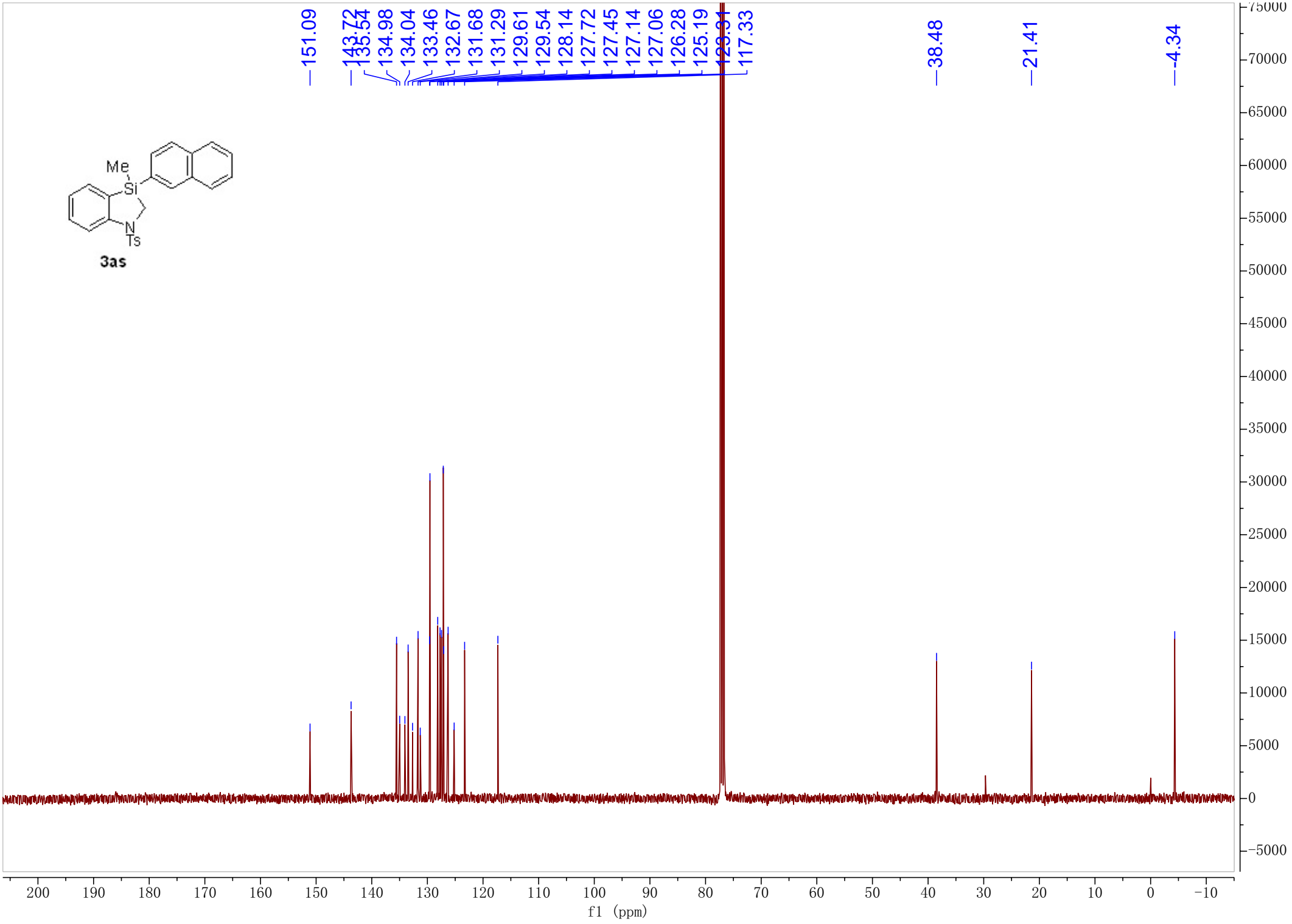
2.58
f1 (ppm)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128.14
127.72
127.45
127.14
127.06
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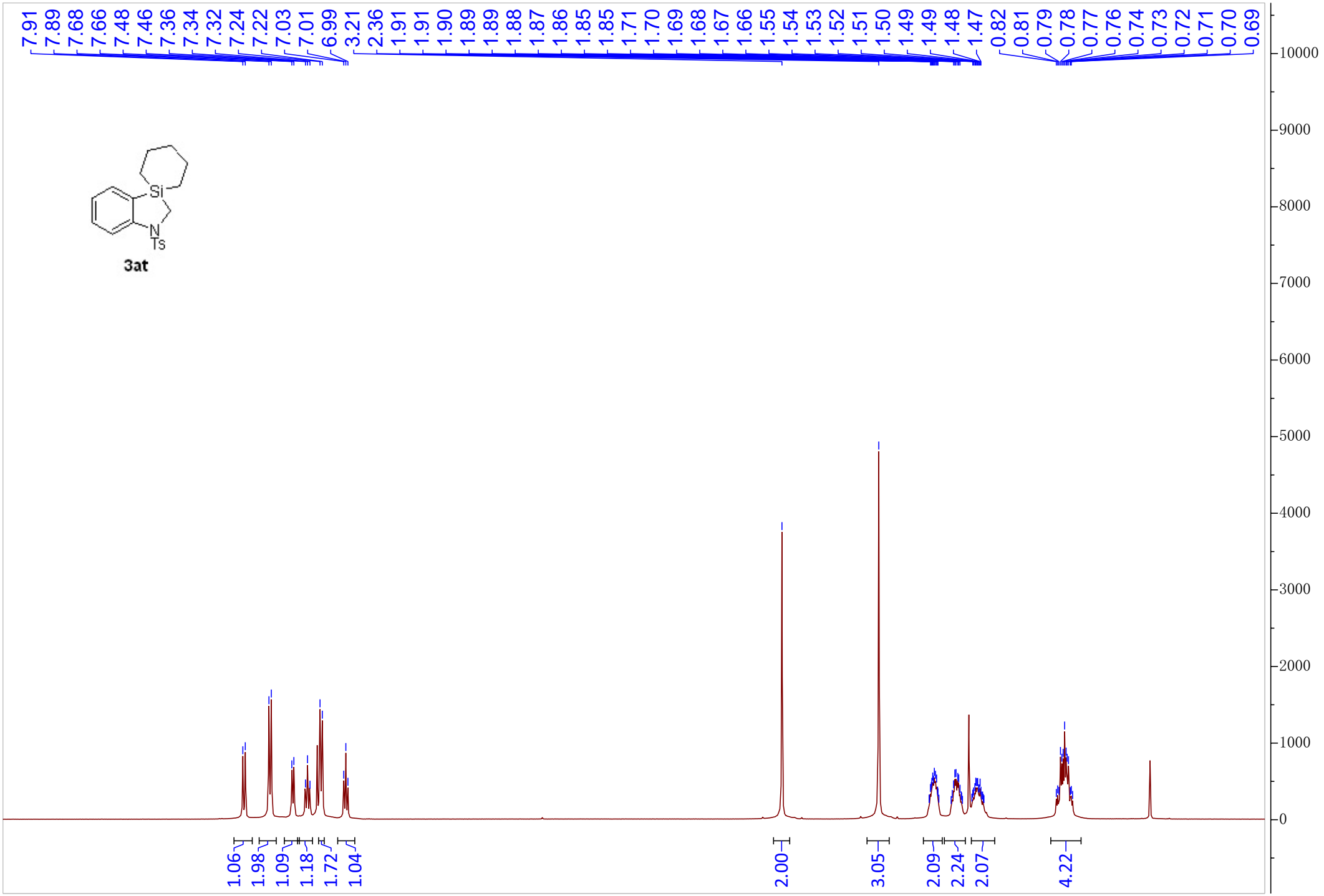
123.91
117.33
38.48
21.41
-4.34
Me
Si
N
Ts
3as
f1 (ppm)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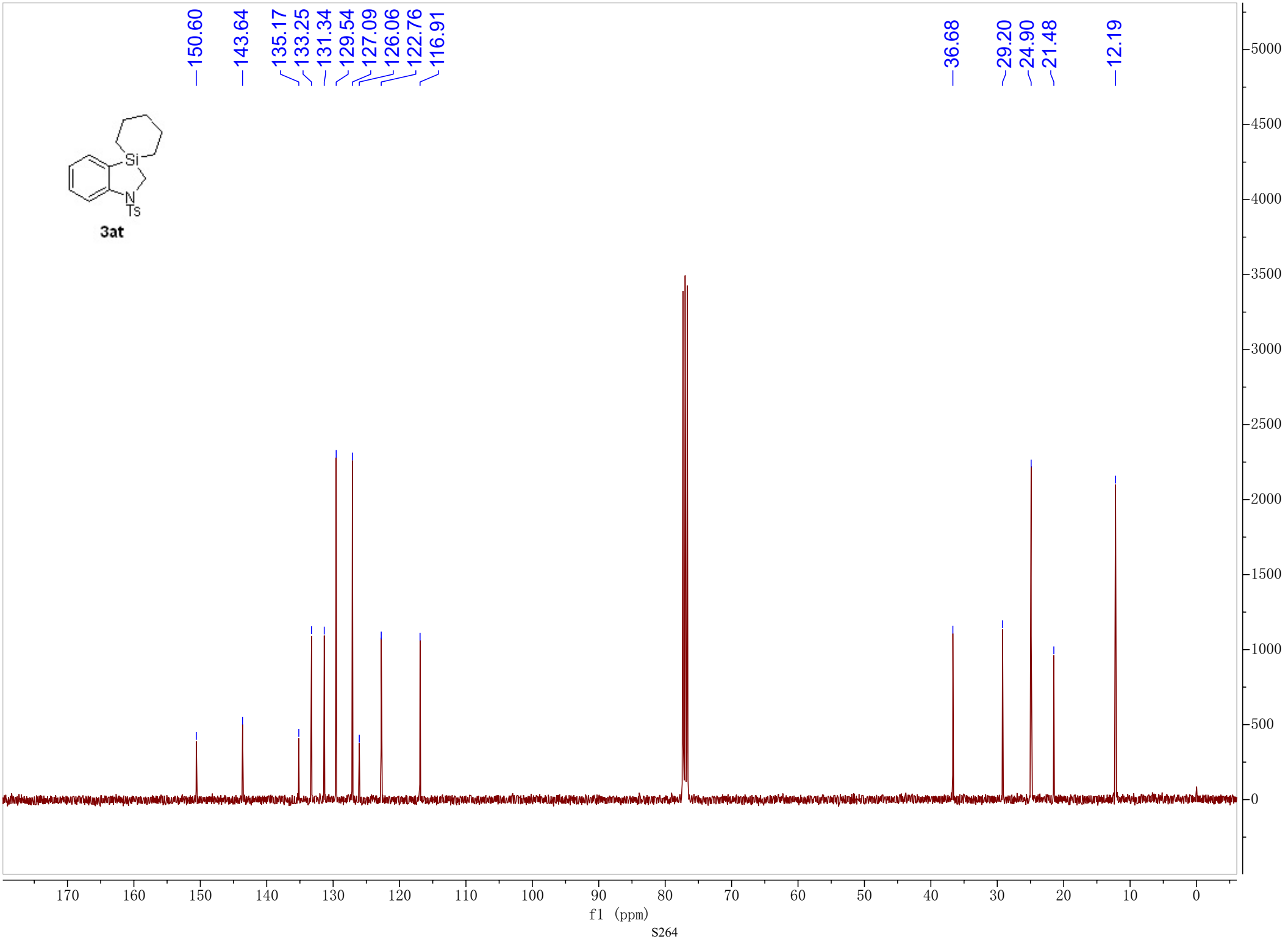
Si
N
Ts
3at
1.06 1.98 1.09 1.18 1.72 1.04 2.00 3.05 2.09 2.24 2.07 4.22
f1 (ppm)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129.54
127.09
126.06
122.76
116.91
36.68
29.20
24.90
21.48
12.19
Si
N
Ts
3at
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
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150
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130
120
110
100
90
80
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50
40
30
20
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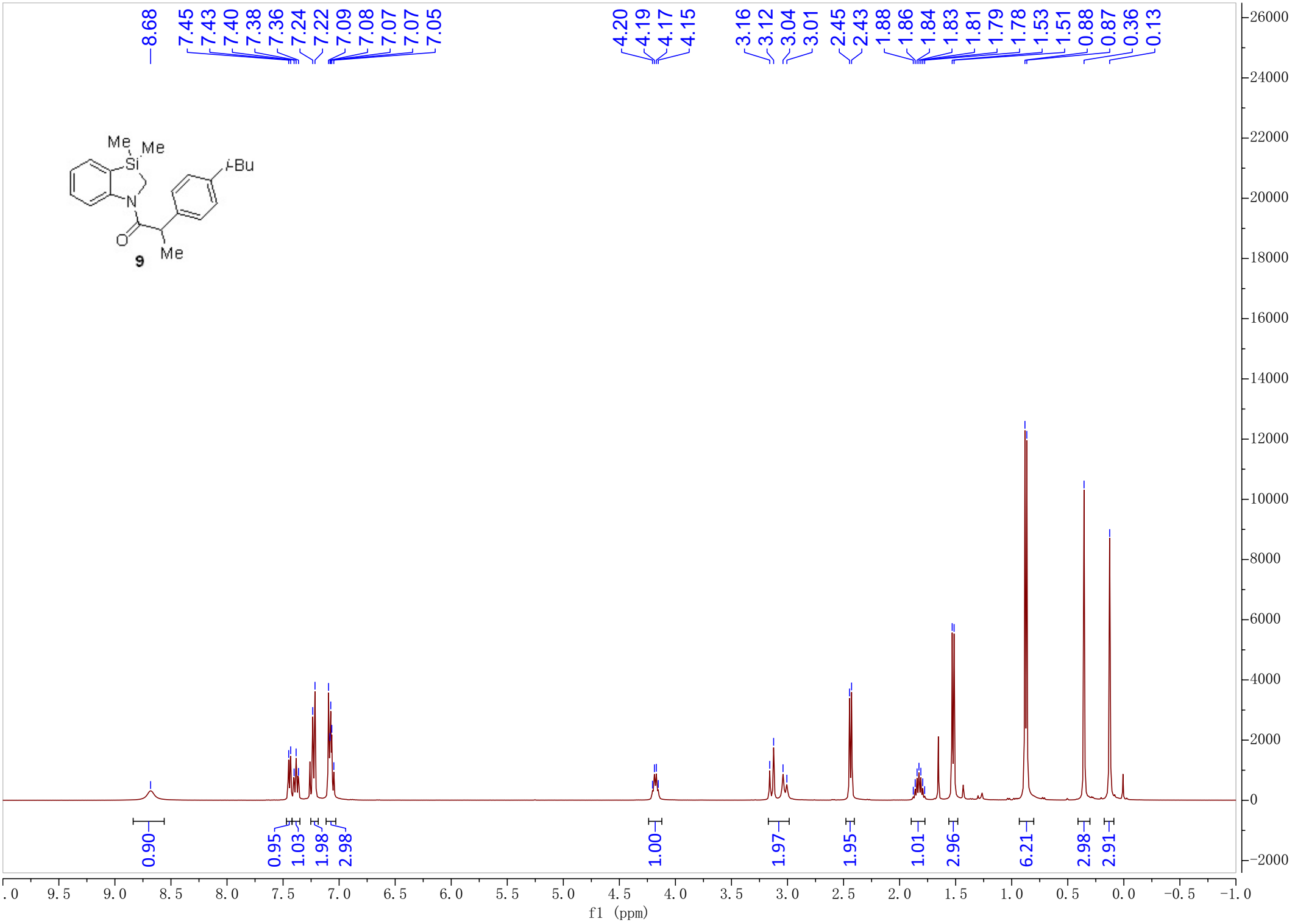
0
f1 (ppm)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7.22
7.09
7.08
7.07
7.07
7.05
4.20
4.19
4.17
4.15
3.16
3.12
3.04
3.01
2.45
2.43
1.88
1.86
1.84
1.83
1.81
1.79
1.78
1.53
1.51
0.88
0.87
0.36
0.13
Me
Me
Si
N
O
Me
t-Bu
9
0.90
0.95
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1.00
1.97
1.95
1.01
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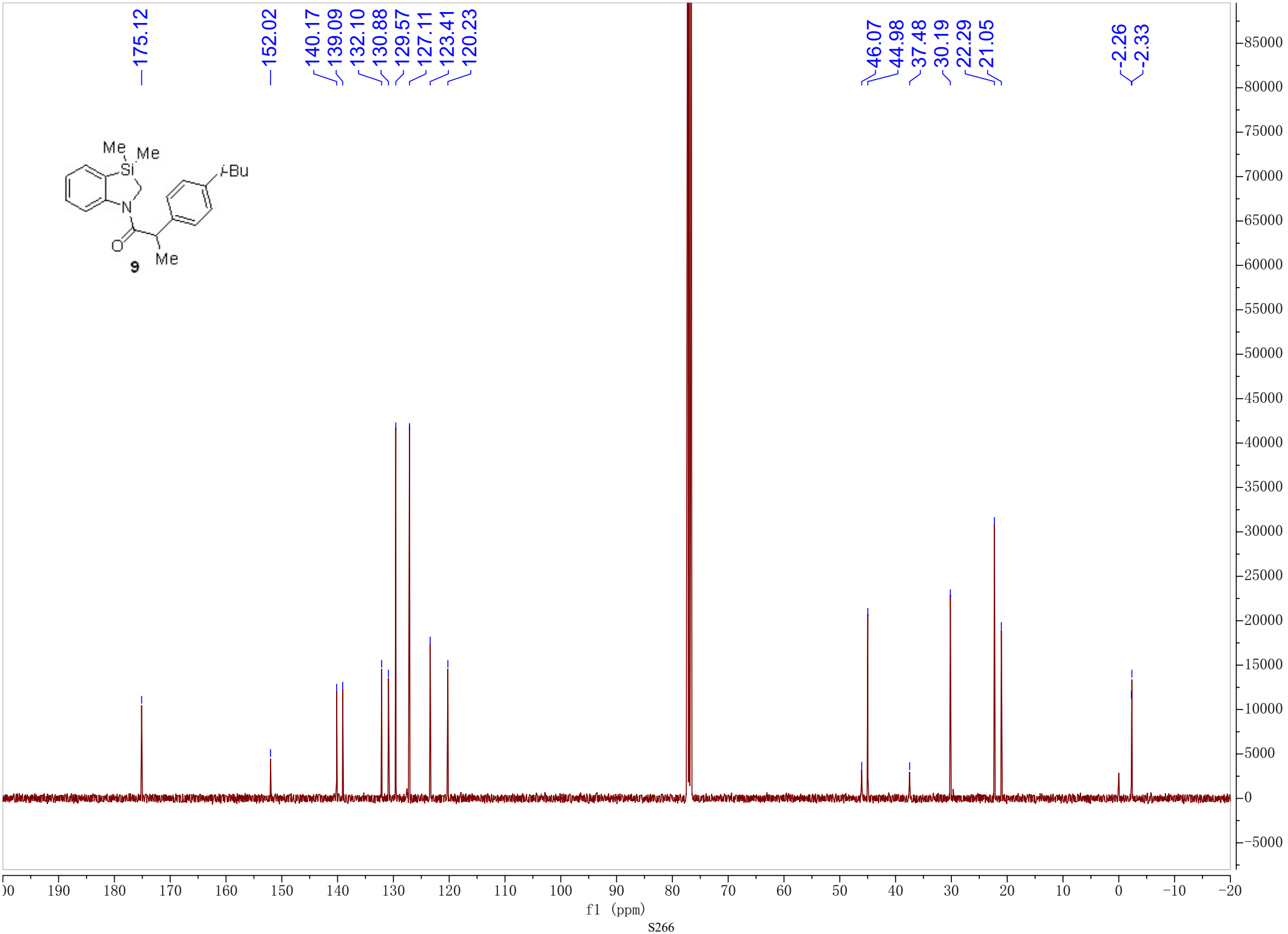
6.21
2.98
2.91
f1 (ppm)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152.02
140.17
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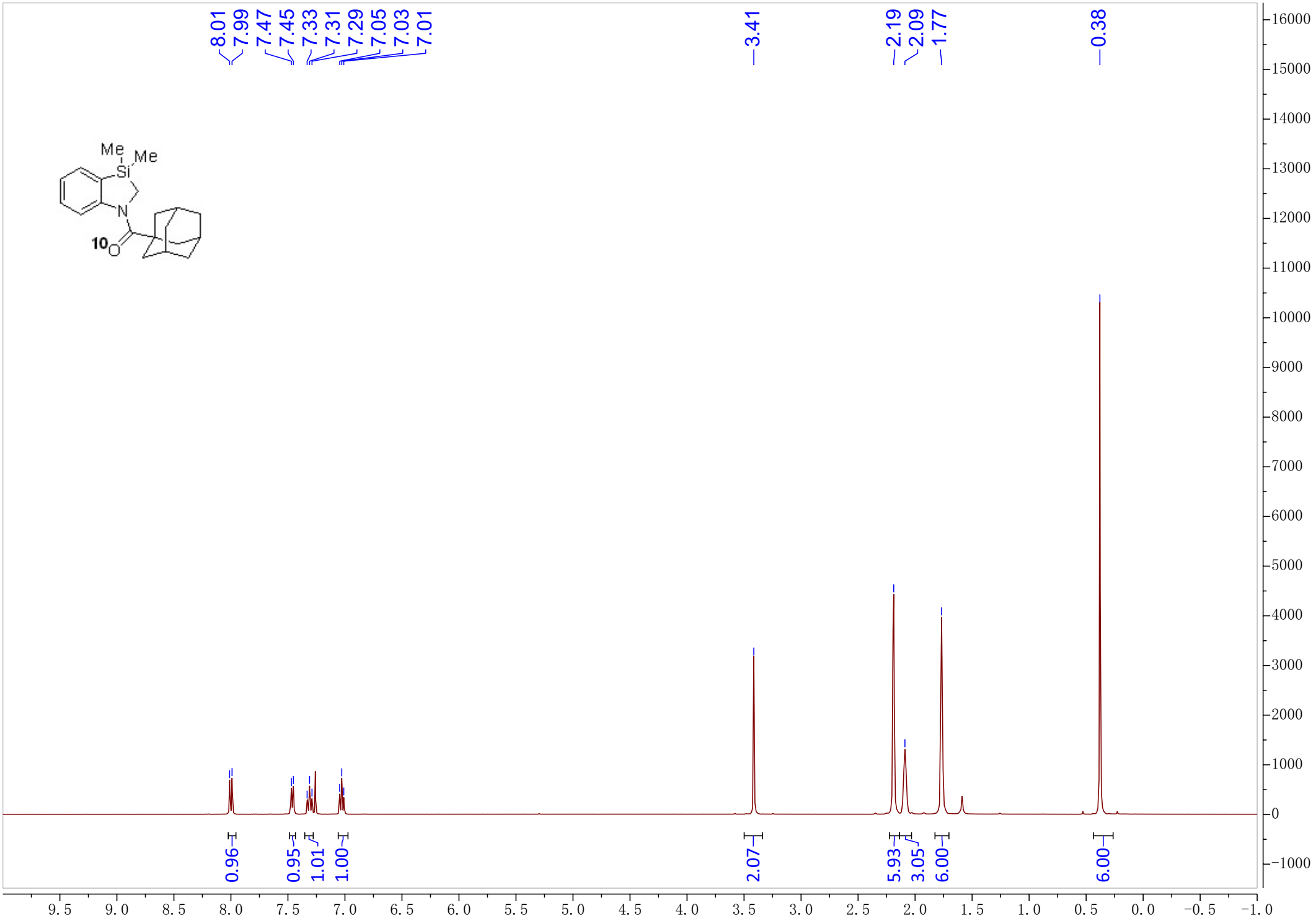
130.88
129.57
127.11
123.41
120.23
46.07
44.98
37.48
30.19
22.29
21.05
-2.26
-2.33
Me
Me
Si
N
O
Me
i-Bu
9
f1 (ppm)


8.01
7.99
7.47
7.45
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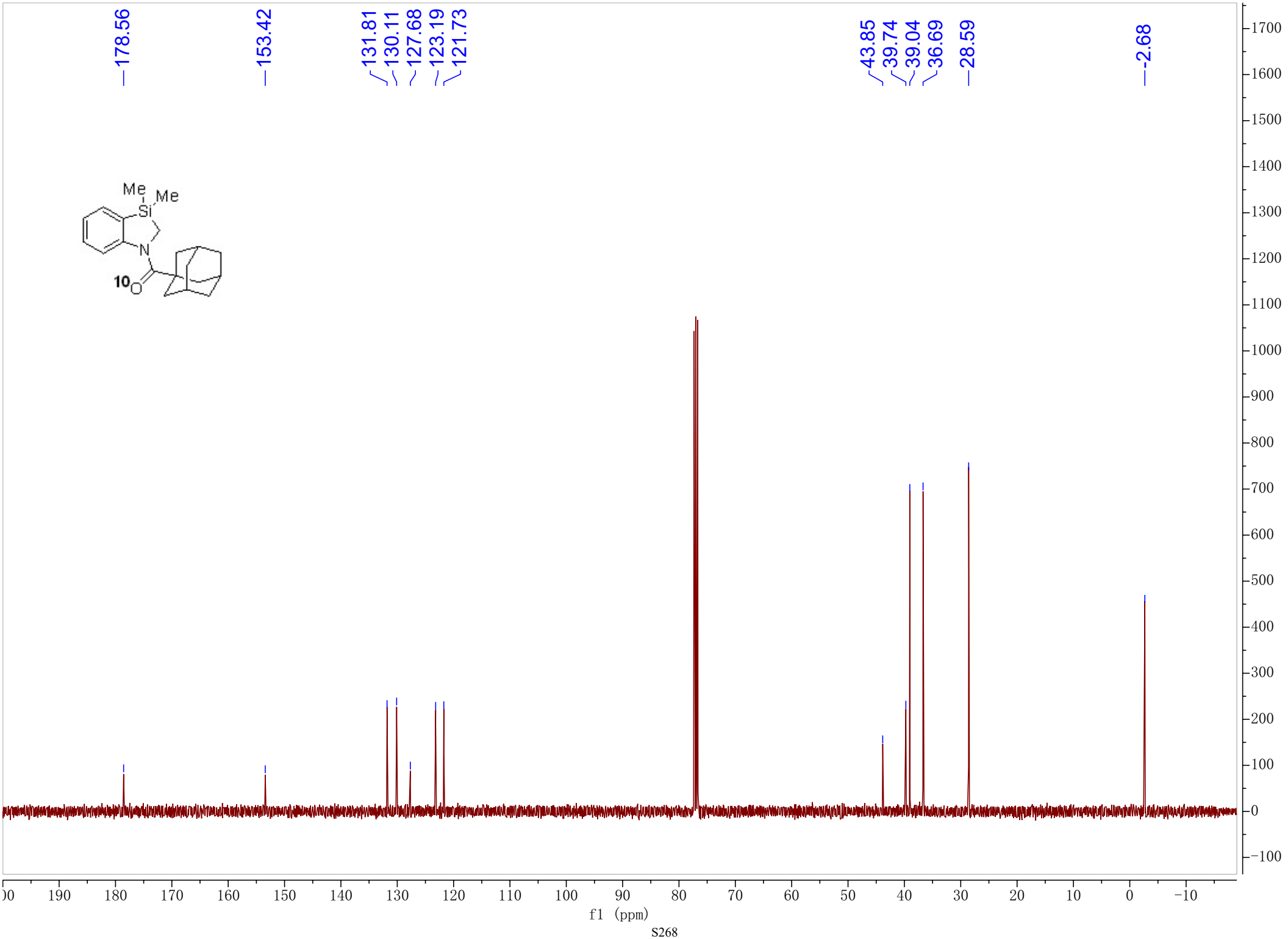
7.31
7.29
7.05
7.03
7.01
3.41
2.19
2.09
1.77
0.38
Me
Me
Si
N
10
O
0.96
0.95
1.01
1.00
2.07
5.93
3.05
6.00
6.00
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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153.42
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123.19
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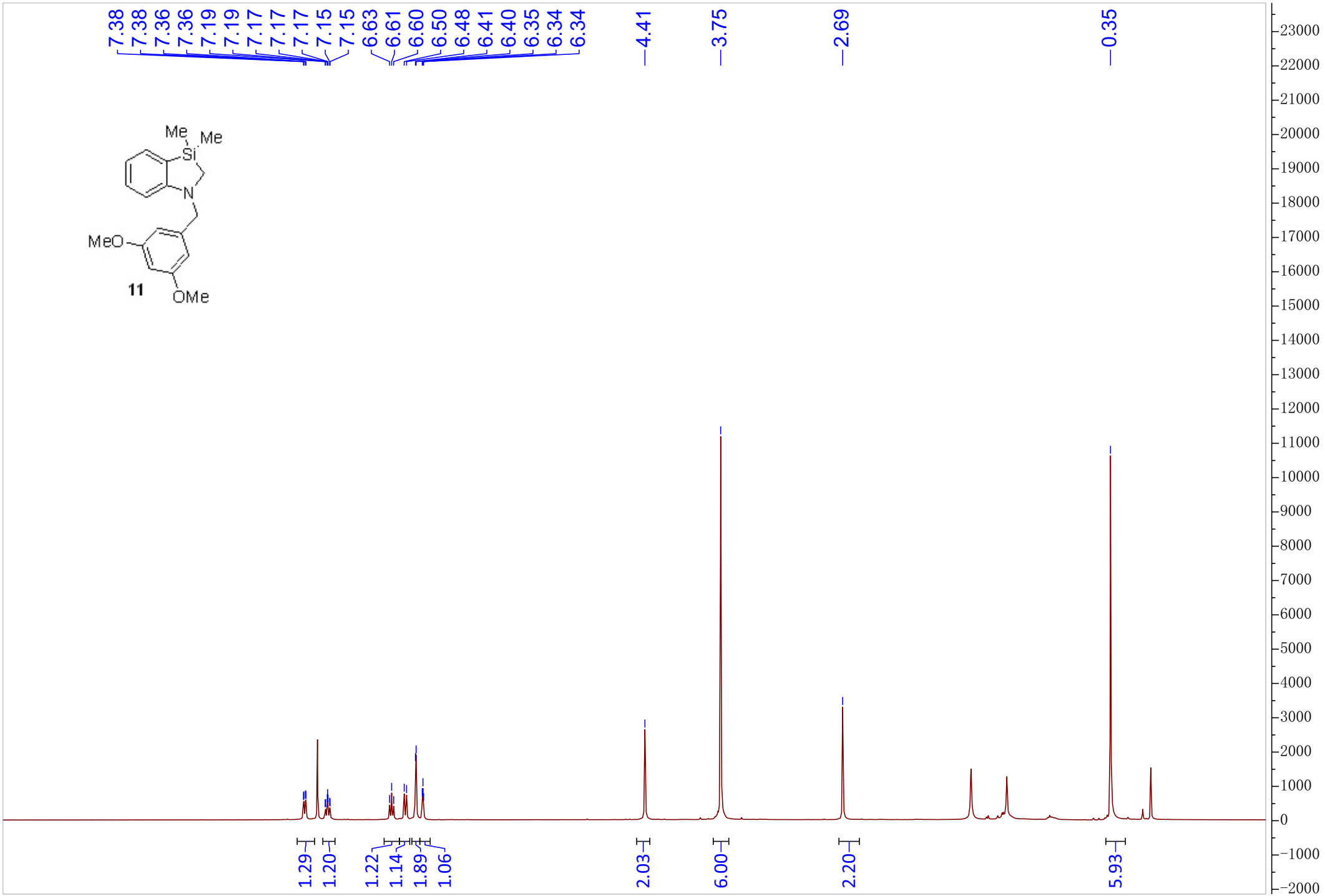
39.04
36.69
28.59
2.68
Me
Me
Si
N
10
O
f1 (ppm)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7.38
7.36
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7.19
7.19
7.17
7.17
7.17
7.15
7.15
6.63
6.61
6.60
6.50
6.48
6.41
6.40
6.35
6.34
6.34
4.41
3.75
2.69
0.35
Me
Me
Si
N
MeO
OMe
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1.29
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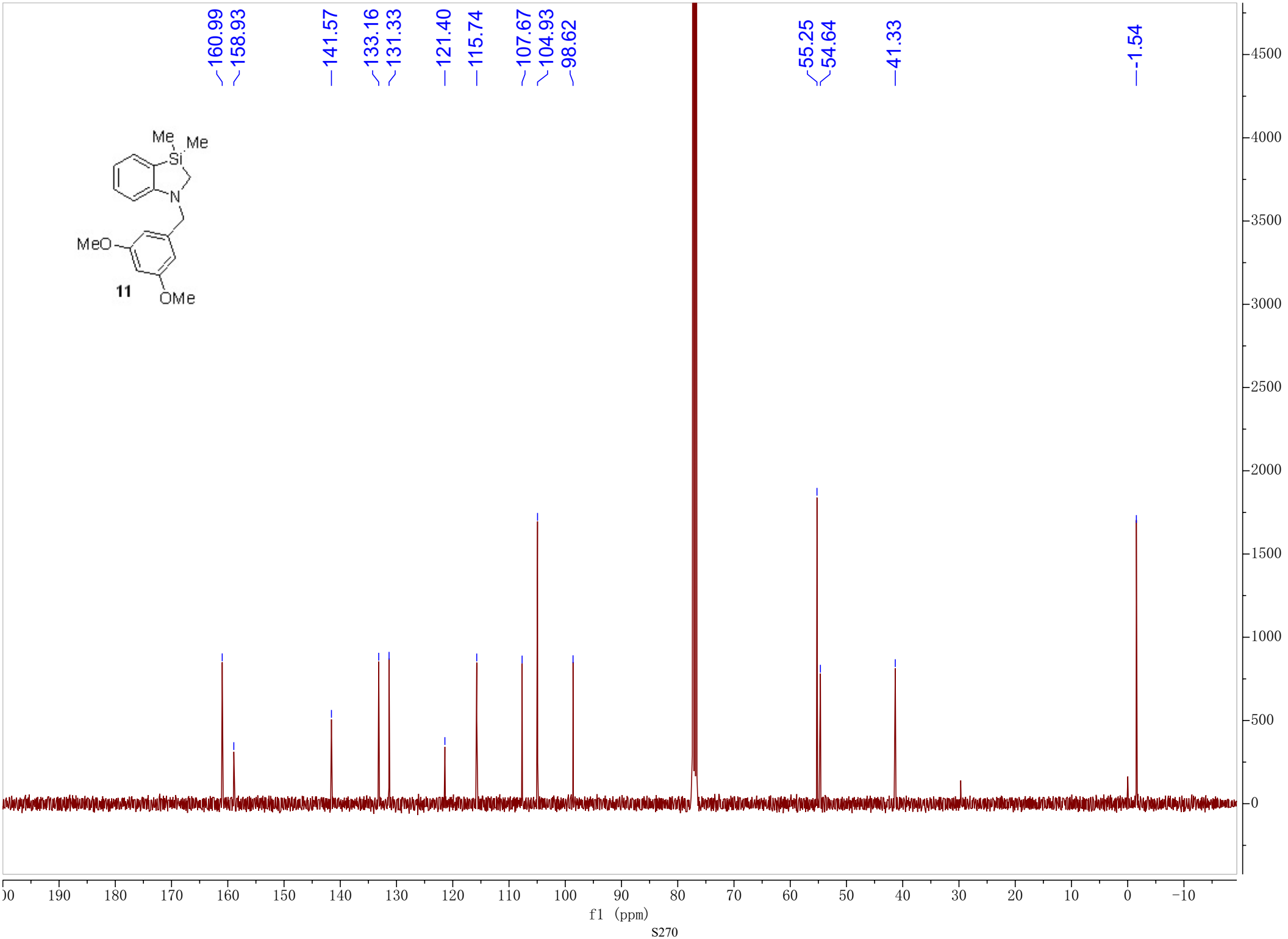
1.22
1.14
1.89
1.06
2.03
6.00
2.20
5.93
f1 (ppm)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115.74
107.67
104.93
98.62
55.25
54.64
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-1.54
Me
Me
Si
N
MeO
OMe
11
4500
4000
3500
3000
2500
2000
1500
1000
500
0
190
180
170
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120
110
100
90
80
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60
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40
30
20
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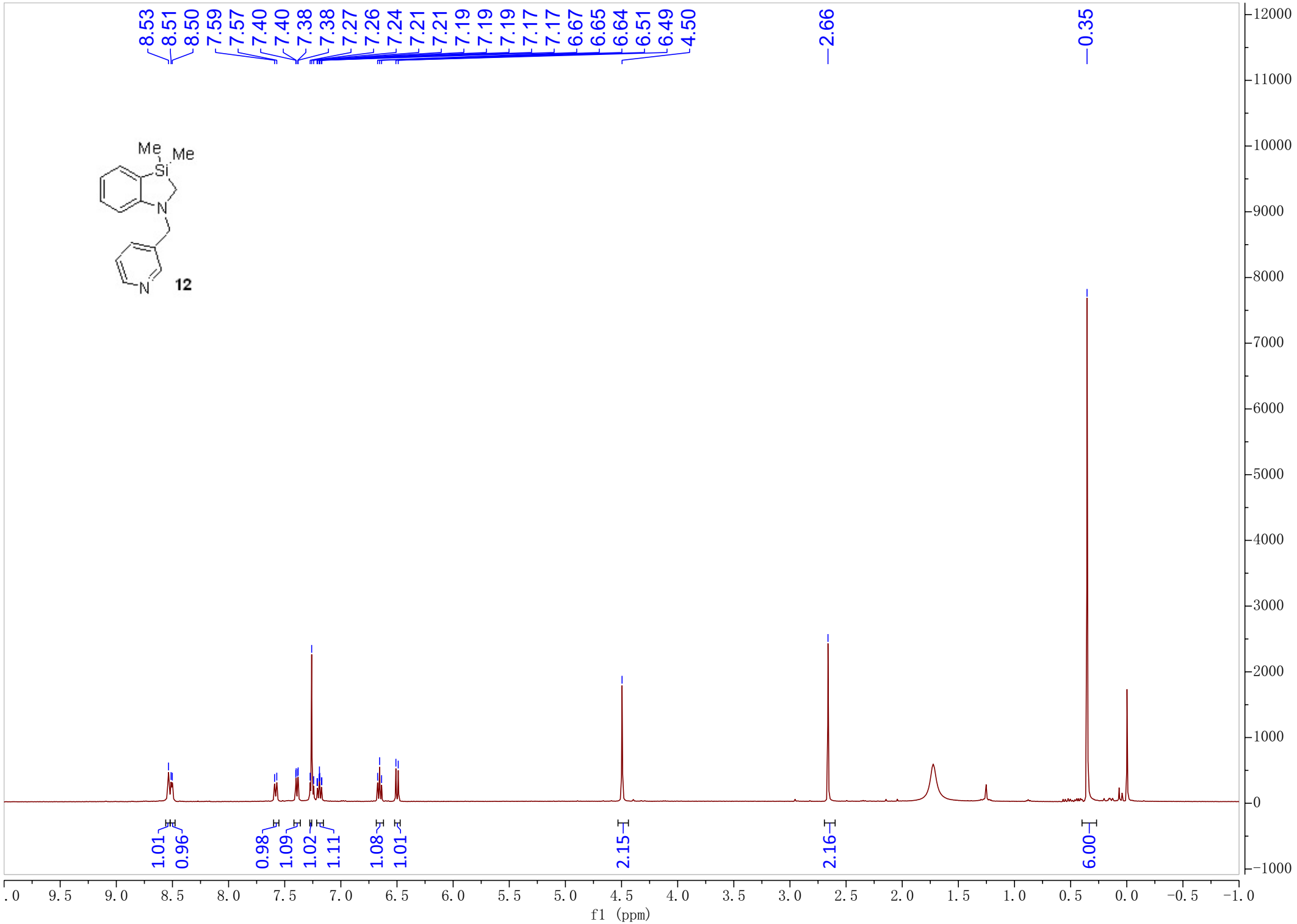
0
-10
f1 (ppm)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7.57
7.40
7.40
7.38
7.38
7.27
7.26
7.24
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7.21
7.19
7.19
7.19
7.17
7.17
6.67
6.65
6.64
6.51
6.49
4.50
2.66
0.35
Me
Me
Si
N
N
12
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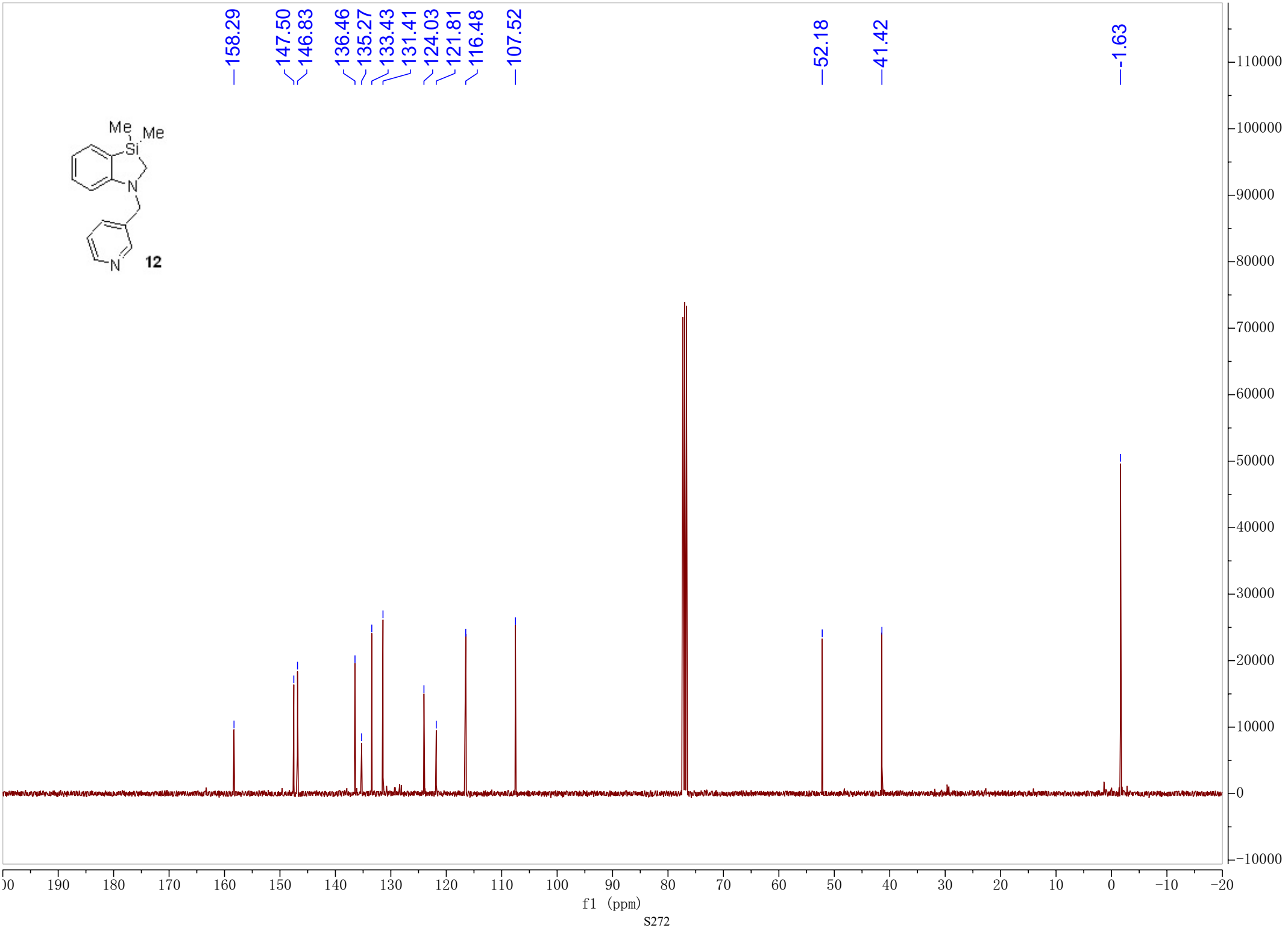
1.09
1.02
1.11
1.08
1.01
2.15
2.16
6.00
f1 (ppm)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146.83
136.46
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124.03
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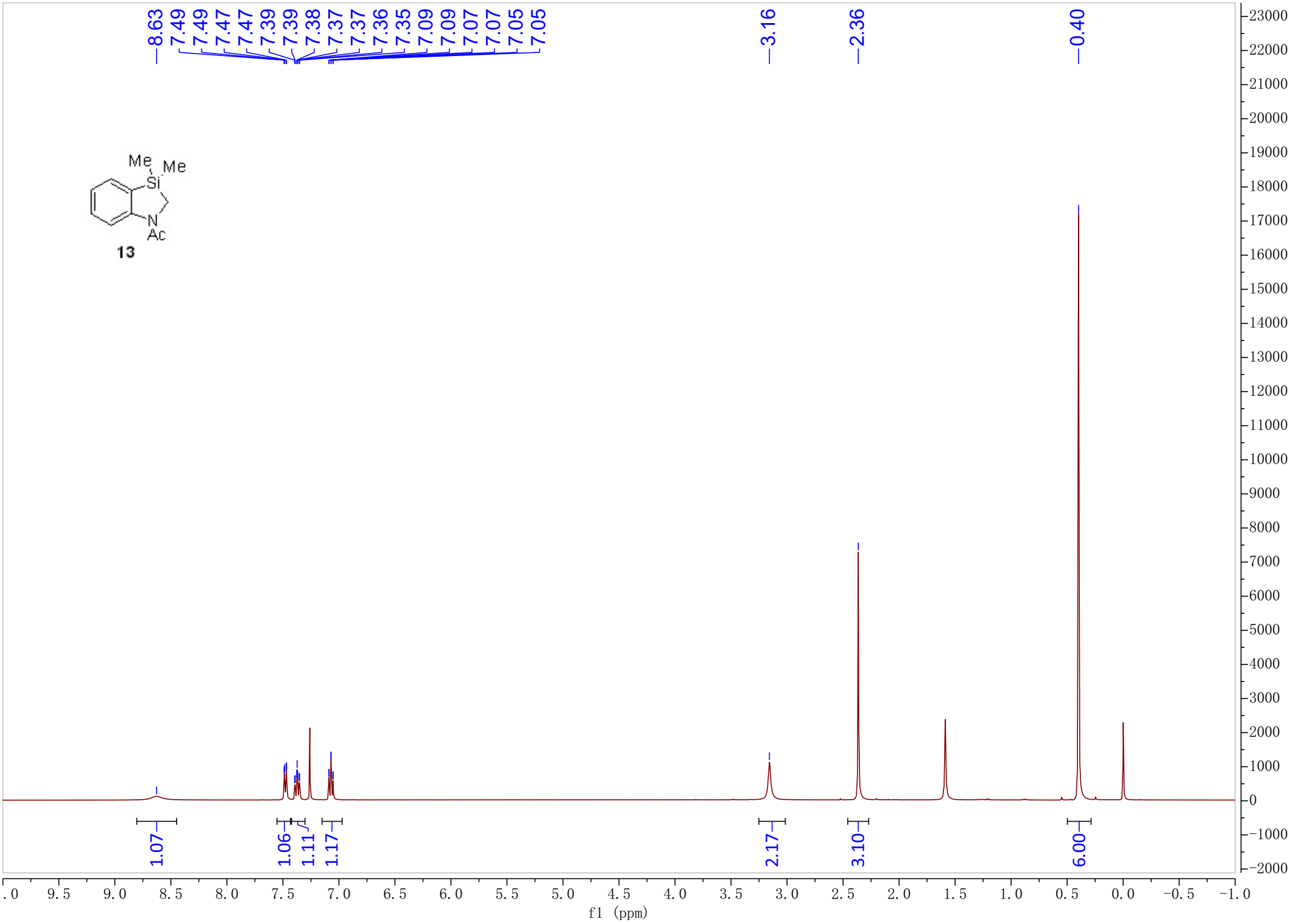
116.48
107.52
52.18
41.42
1.63
Me
Me
Si
N
N
12
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
−10000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)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7.47
7.39
7.39
7.38
7.37
7.37
7.36
7.35
7.09
7.09
7.07
7.07
7.05
7.05
3.16
2.36
0.40
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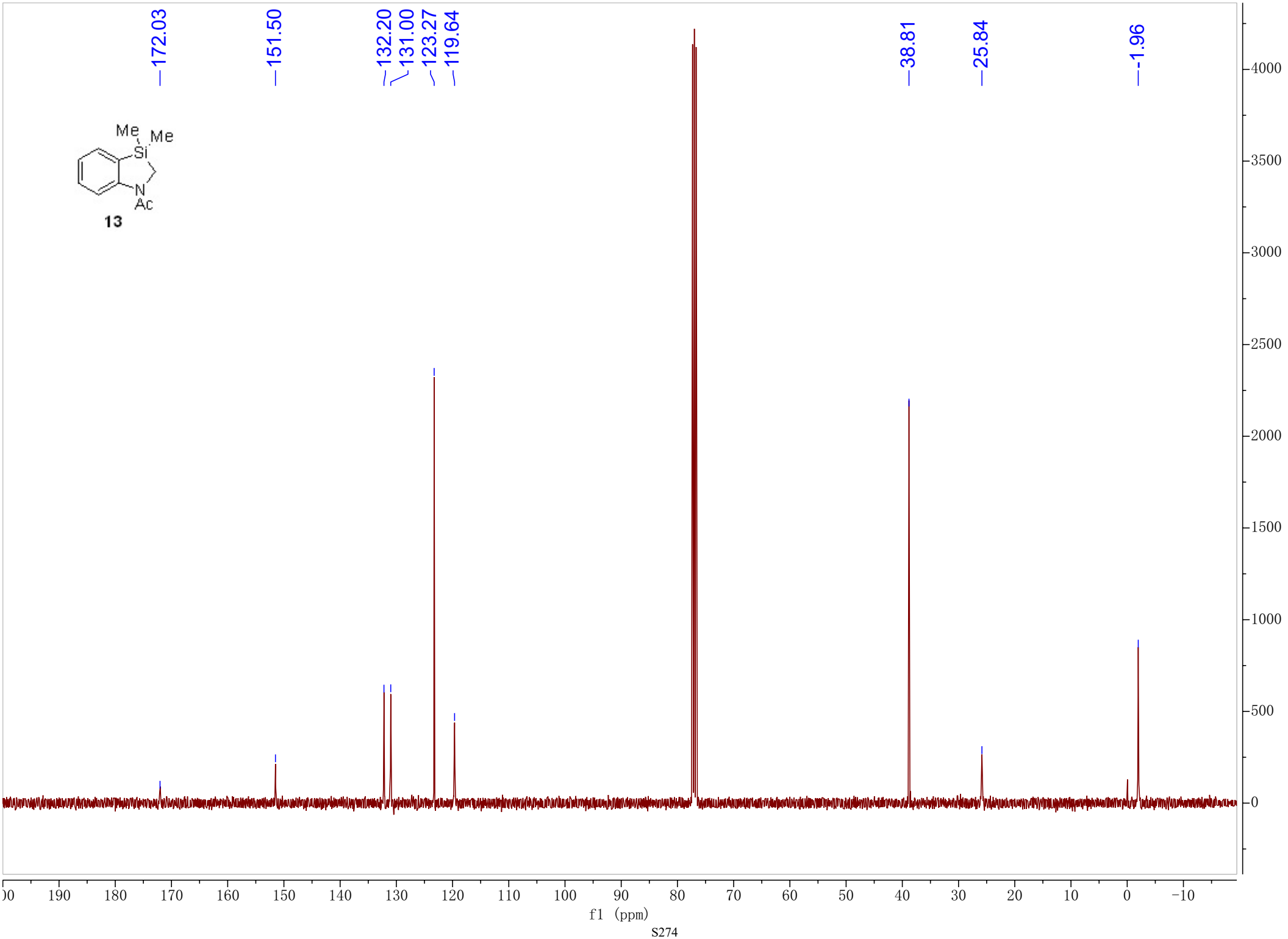
Me
Si
N
Ac
13
1.07
1.06
1.11
1.17
2.17
3.10
6.00
f1 (ppm)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132.20
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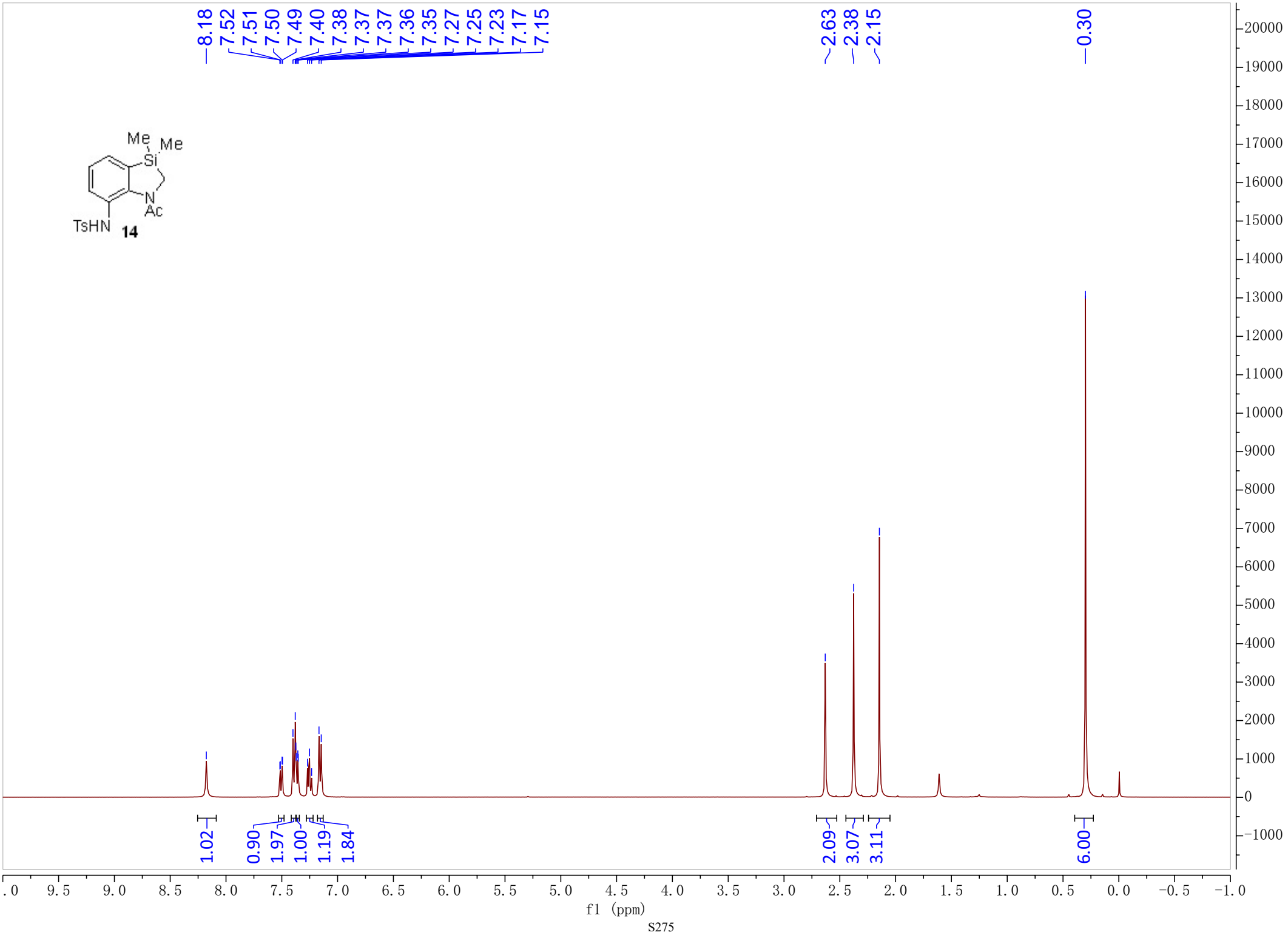
25.84
-1.96
Me
Me
Si
N
Ac
13
4000
3500
3000
2500
2000
1500
1000
500
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.37
7.37
7.36
7.35
7.27
7.25
7.23
7.17
7.15
2.63
2.38
2.15
0.30
Me
Me
Si
N
Ac
TsHN
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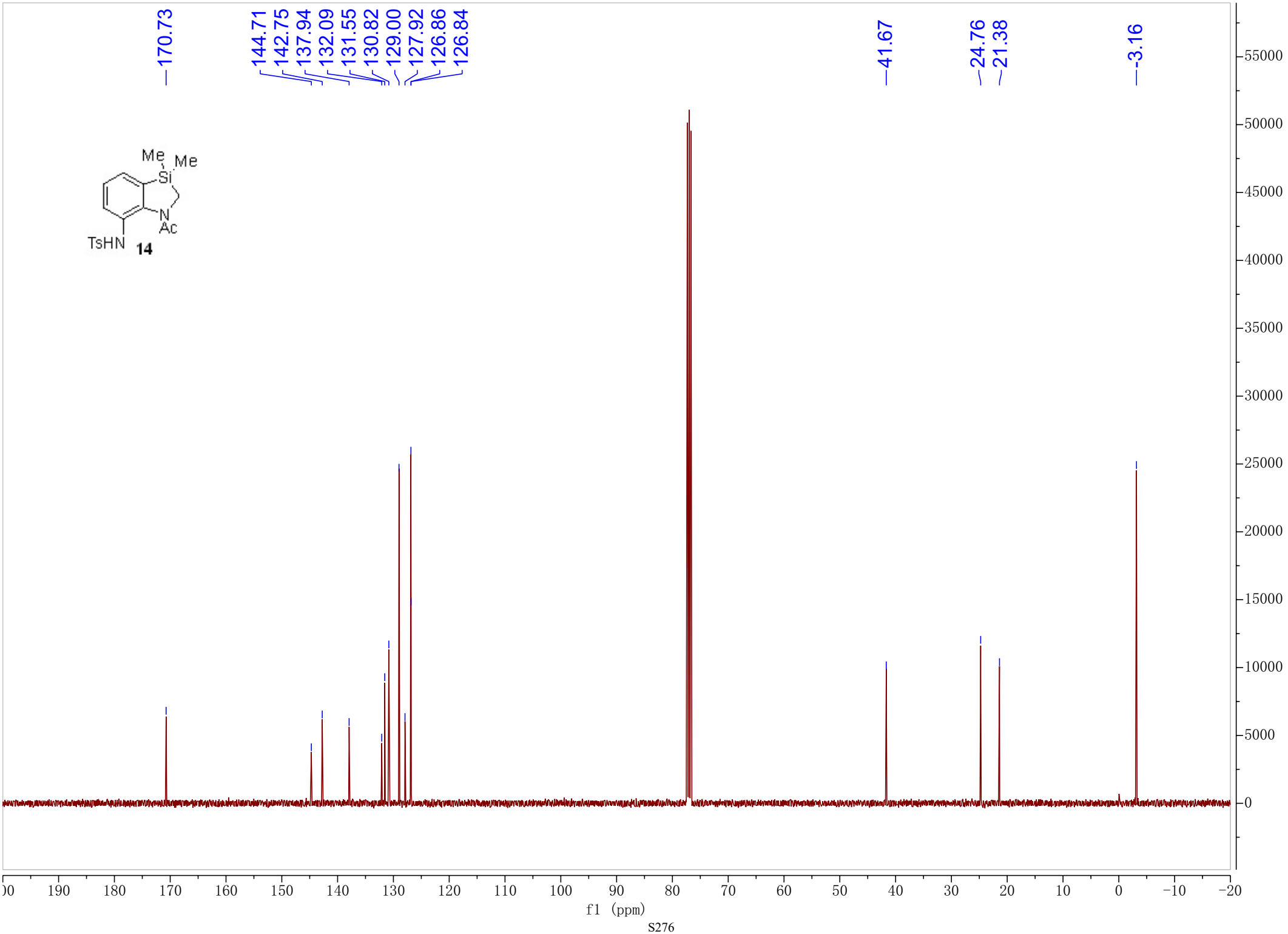
1.97
1.00
1.19
1.84
2.09
3.07
3.11
6.00
f1 (ppm)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126.86
126.84
41.67
24.76
21.38
3.16
Me
Me
Si
N
Ac
TsHN
14
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
190
180
170
160
150
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130
120
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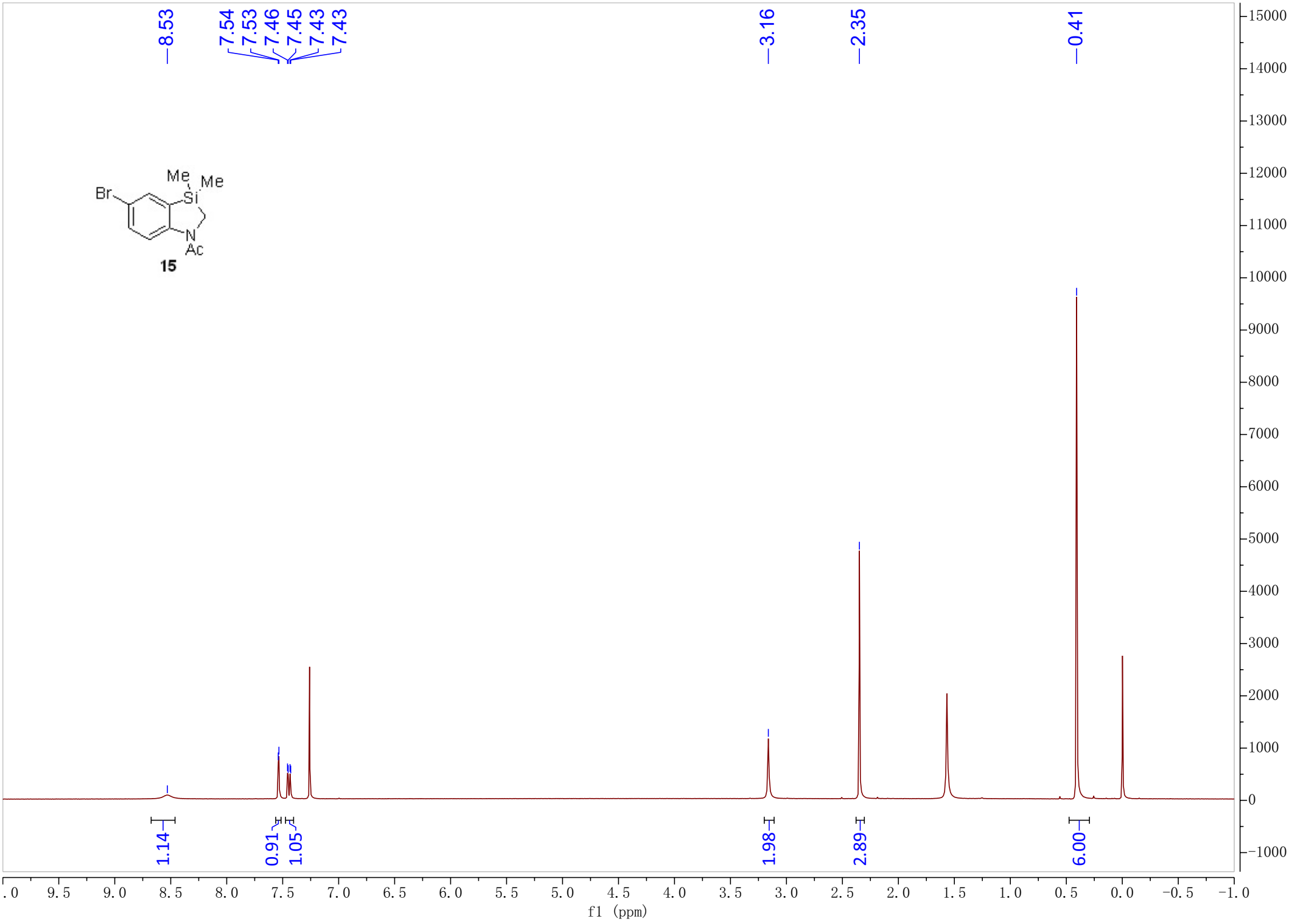
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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7.46
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7.43
7.43
3.16
2.35
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Me
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Br
N
Ac
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1.14
0.91
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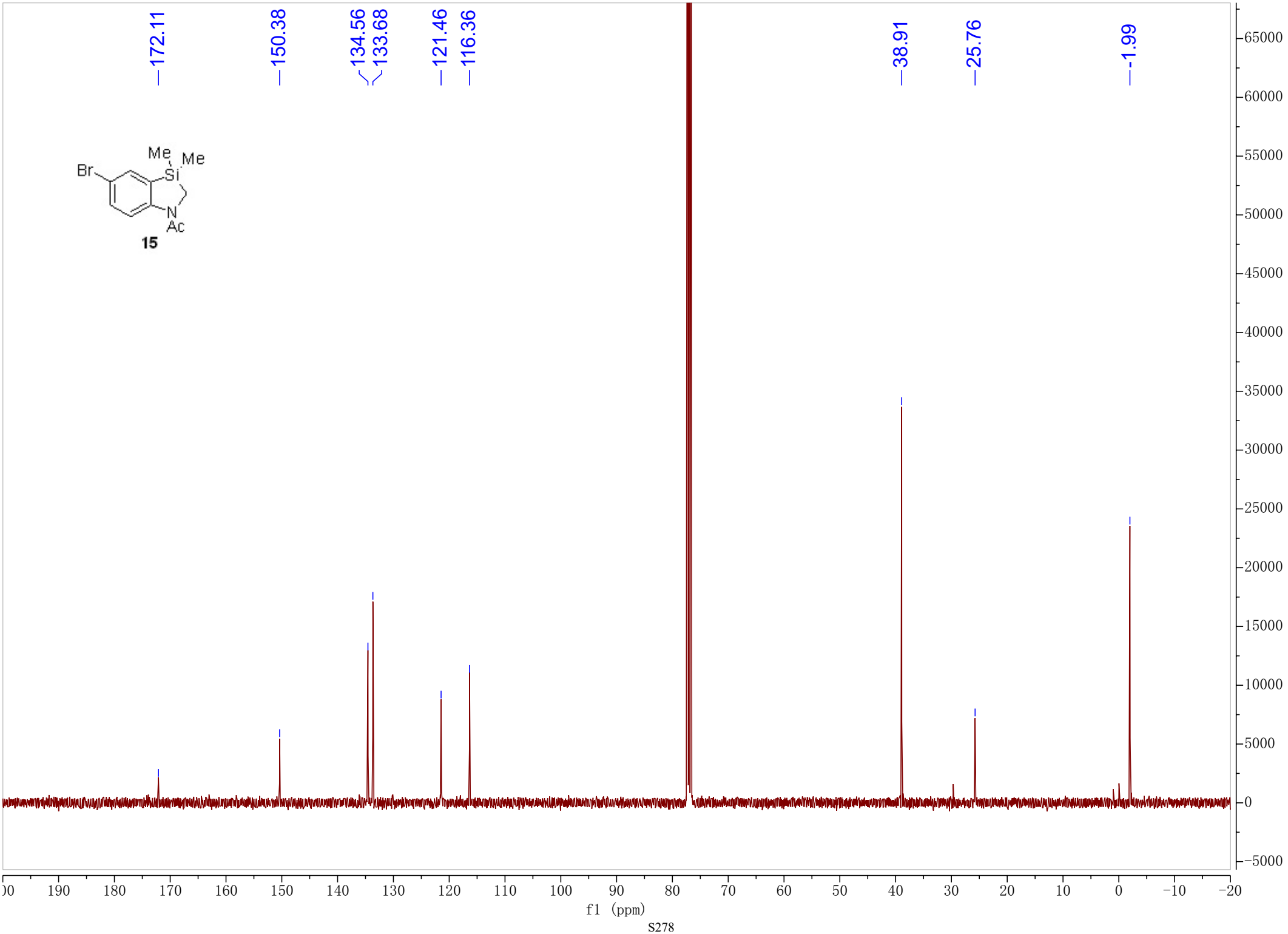
1.98
2.89
6.00
f1 (ppm)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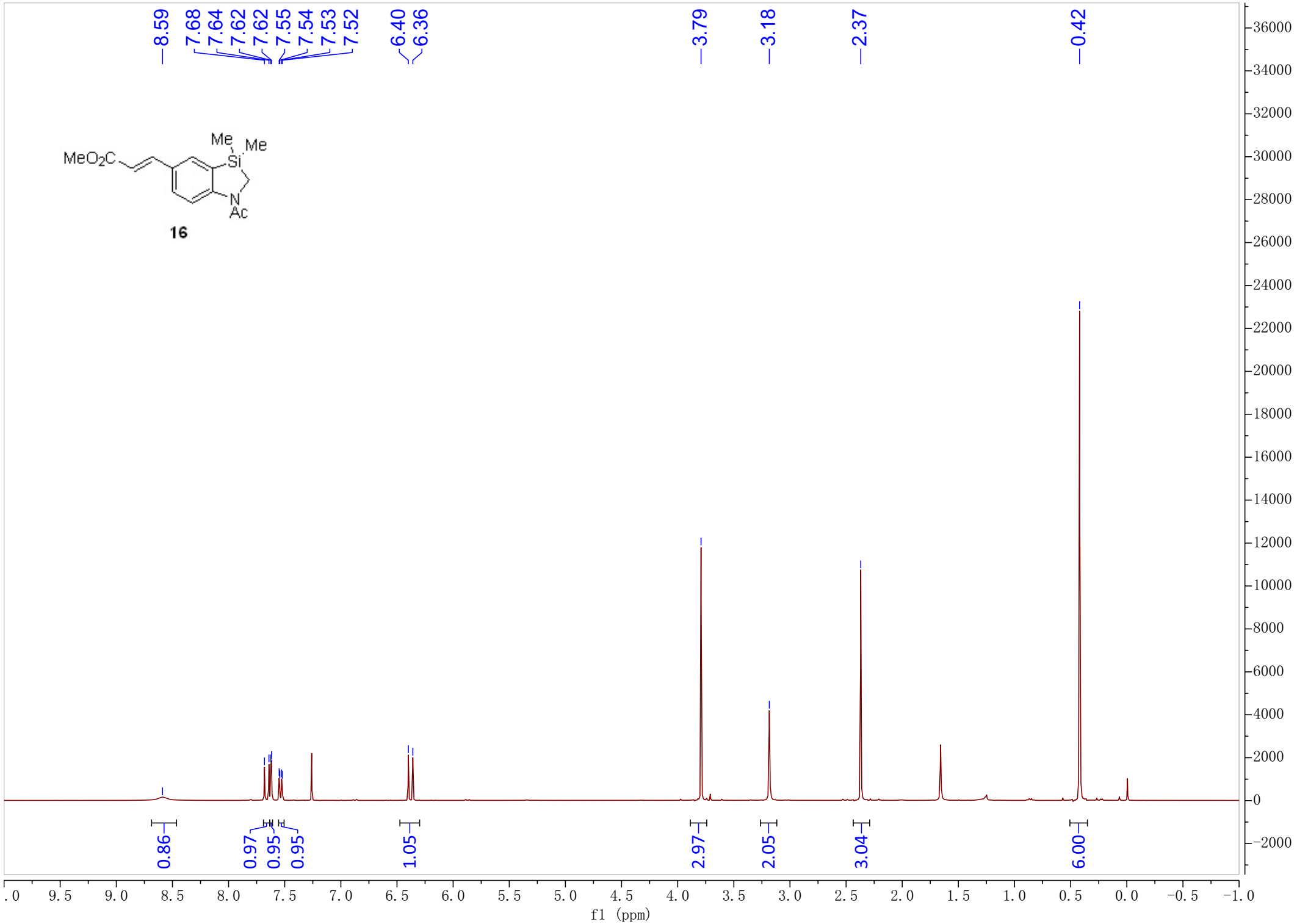
25.76
-1.99
Me
Me
Si
Br
N
Ac
15
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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7.54
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6.36
3.79
3.18
2.37
0.42
Me
Me
MeO2C
Si
N
Ac
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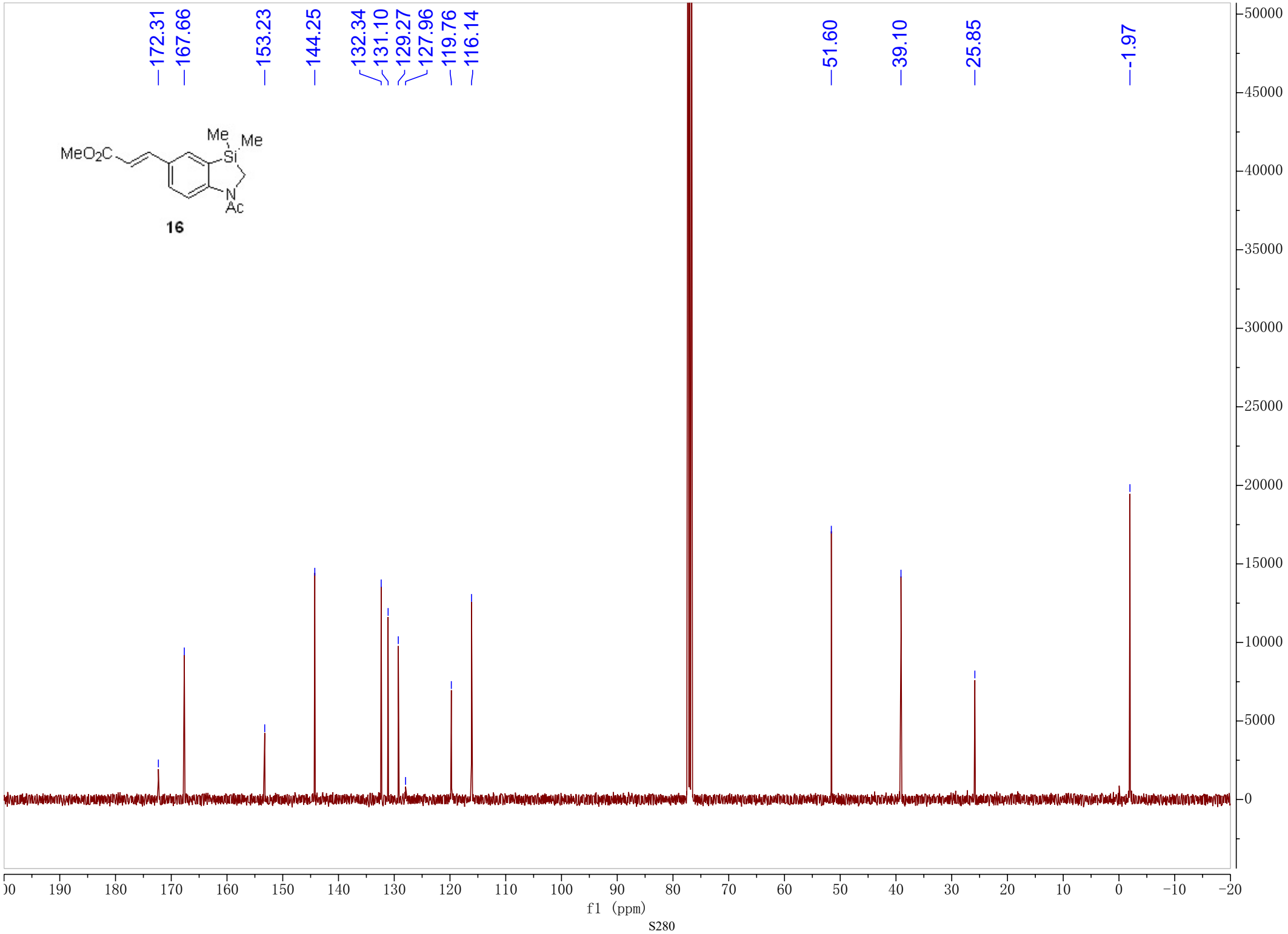
0.97
0.95
0.95
1.05
2.97
2.05
3.04
6.00
f1 (ppm)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131.10
129.27
127.96
119.76
116.14
51.60
39.10
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-1.97
MeO2C
Me
Me
Si
N
Ac
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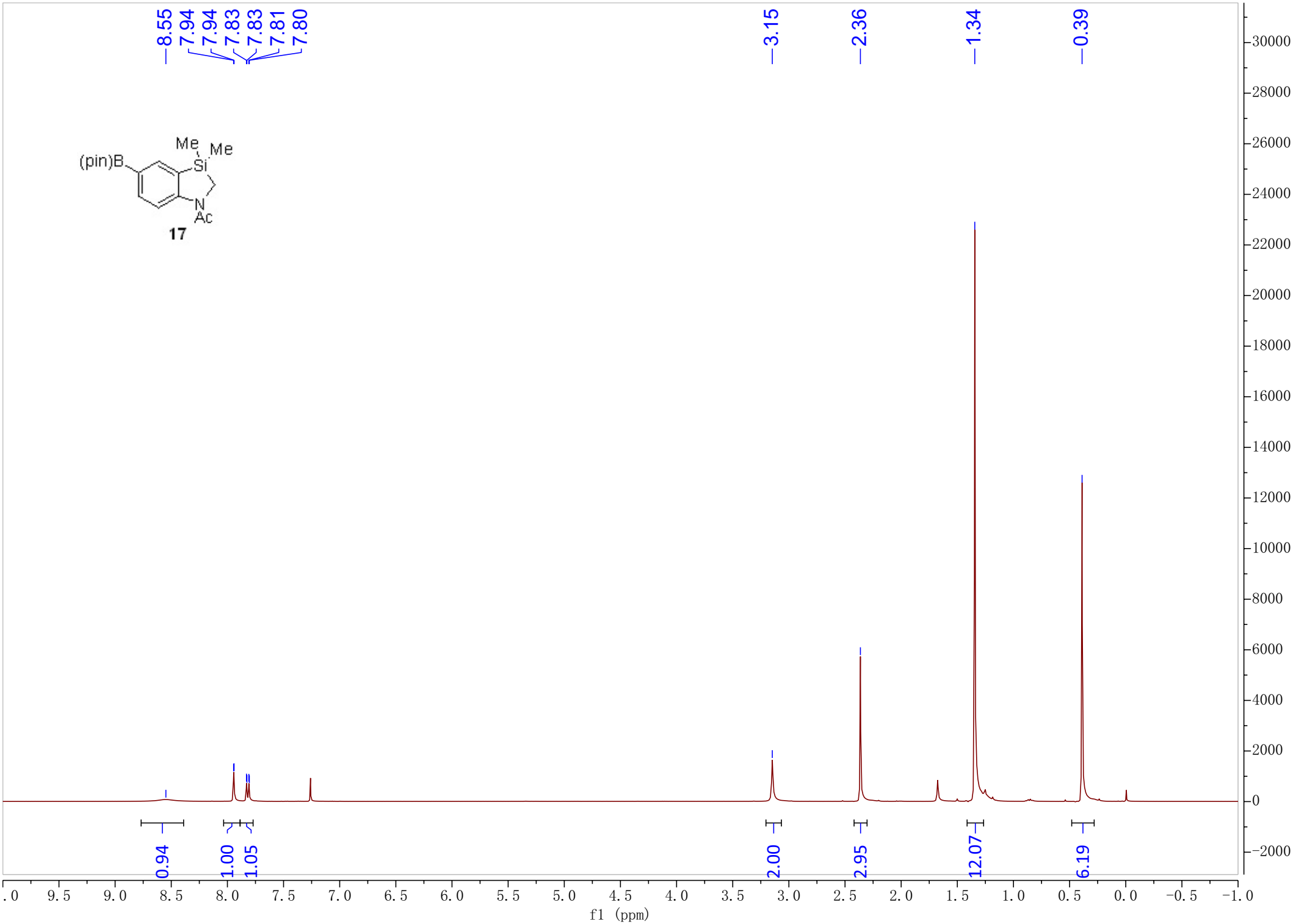
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
f1 (ppm)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7.94
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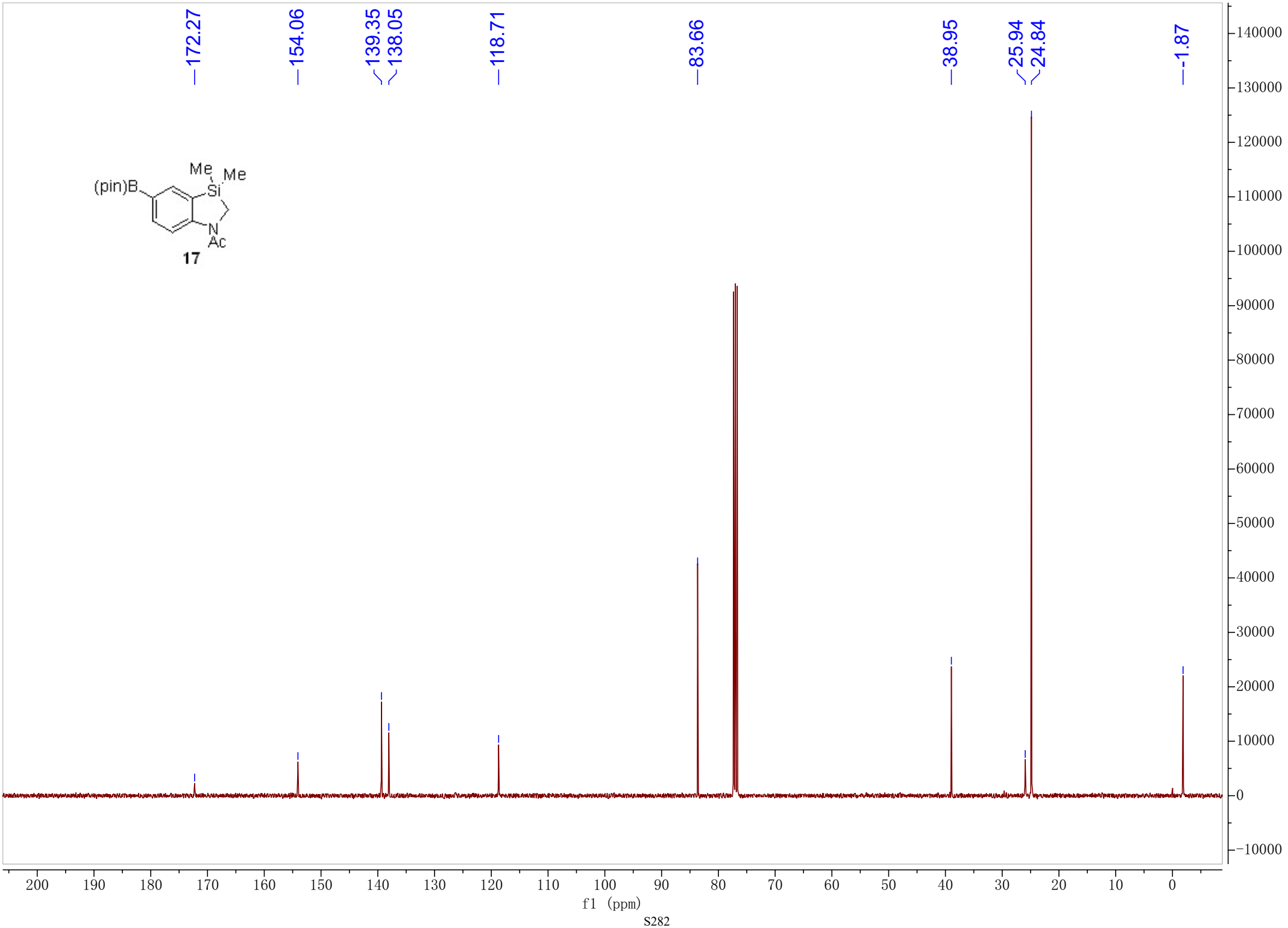
7.83
7.81
7.80
3.15
2.36
1.34
0.39
Me
Me
(pin)B
Si
N
Ac
17
0.94
1.00
1.05
2.00
2.95
12.07
6.19
f1 (ppm)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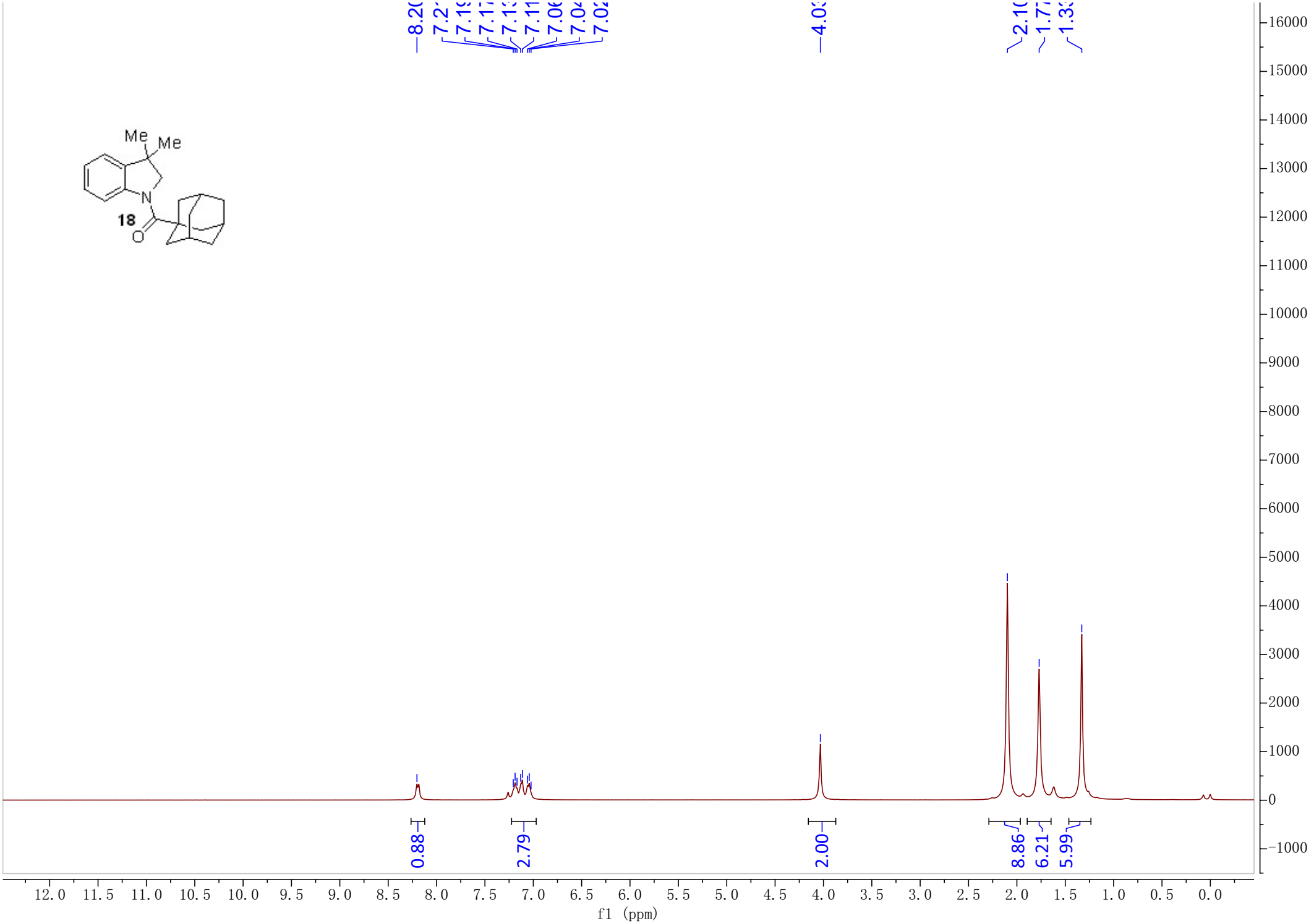
25.94
24.84
-1.87
(pin)B
Me
Me
Si
N
Ac
17
f1 (ppm)


Me
Me
N
18
O
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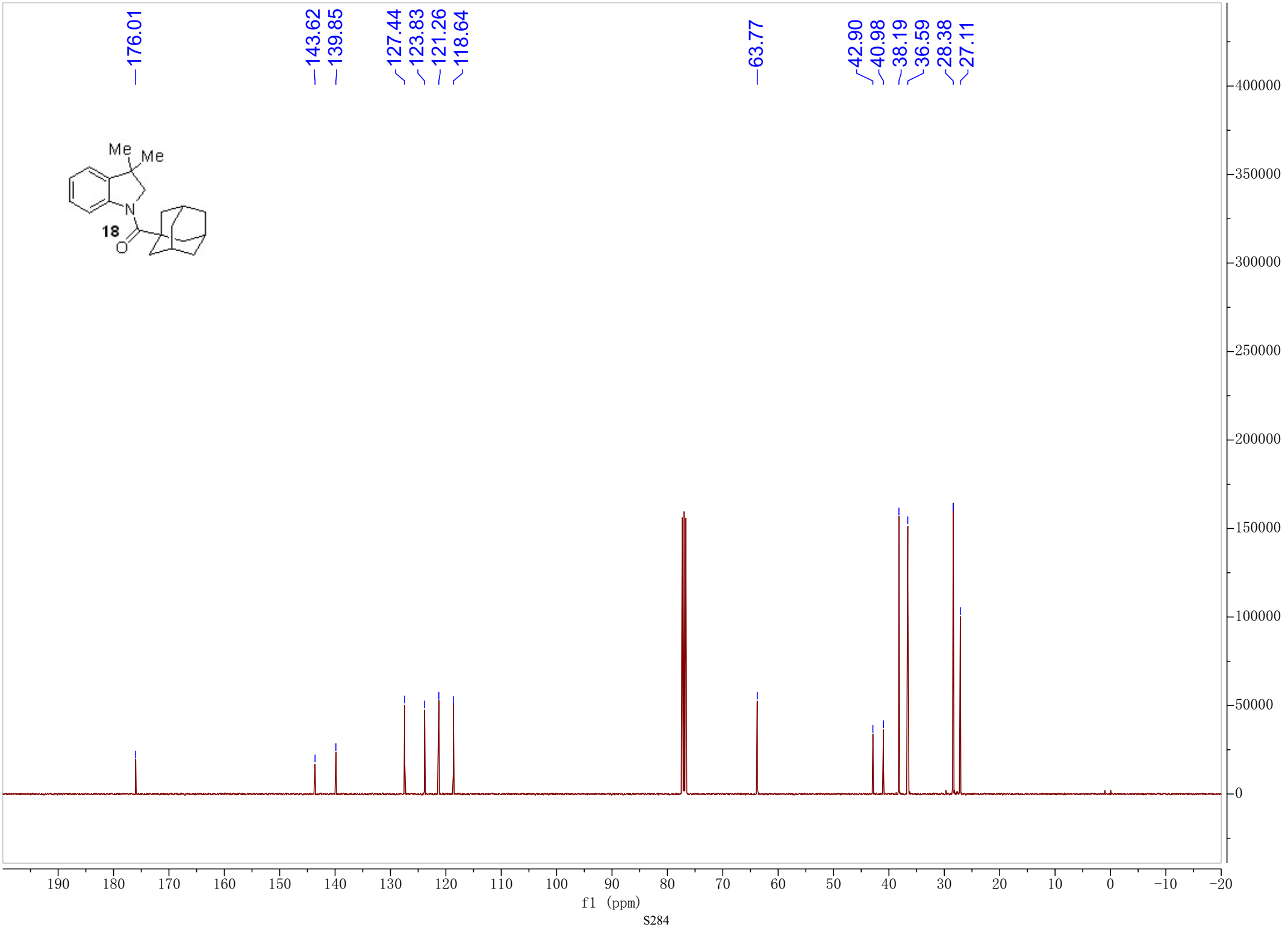
7.23
7.19
7.17
7.13
7.11
7.08
7.04
7.02
4.03
2.10
1.77
1.33
0.88
2.79
2.00
8.86
6.21
5.99
f1 (ppm)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63.77
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40.98
38.19
36.59
28.38
27.11
Me
Me
N
18
O
400000
350000
300000
250000
200000
150000
100000
50000
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)