Supporting Information

Formal one-carbon insertion into esters via copper-catalyzed diyne cyclization/[1,2]-acyl shift

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1. General Information

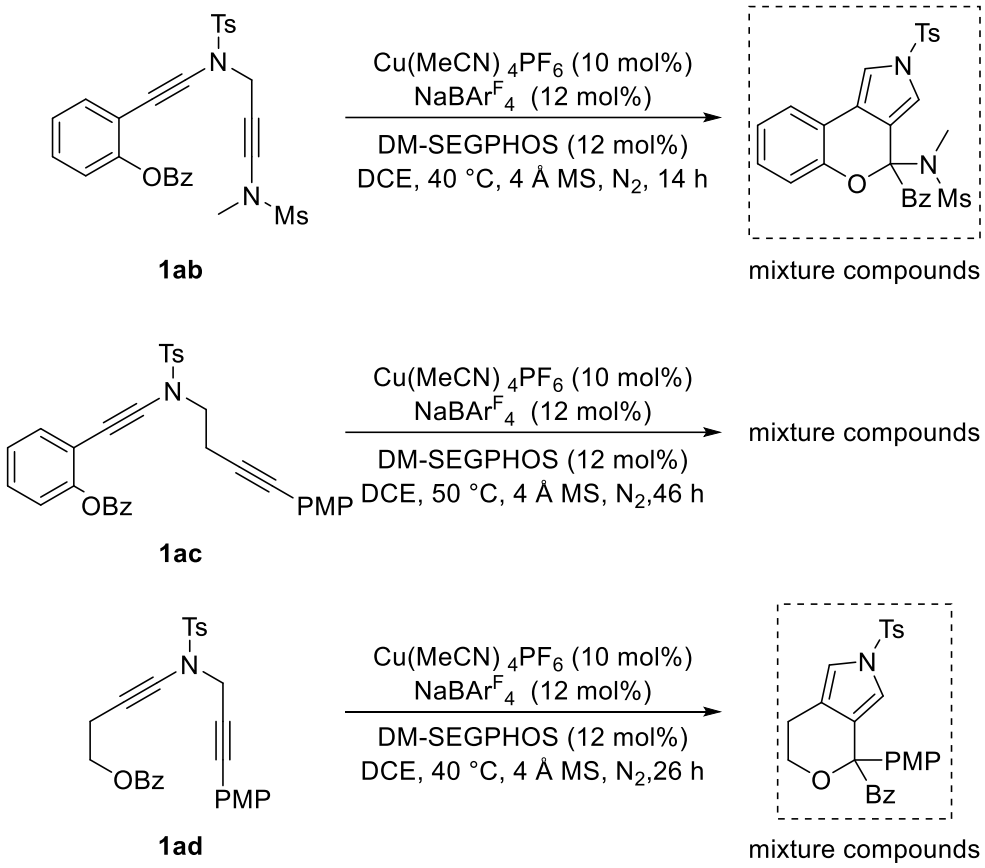
Ethyl acetate (ACS grade), hexanes (ACS grade), DCE (ACS grade) and $CHCl_3$ (ACS grade) were obtained commercially and used without further purification. Methylene chloride, tetrahydrofuran and diethyl ether were purified according to standard methods unless otherwise noted. Commercially available reagents were used without further purification. All reactions were carried out with a Titan HMS-14 digital magnetic stirrer with hot plate. Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed over silica gel (200-300 mesh). Infrared spectra were recorded on a Nicolet IS50 spectrometer as thin film and are reported in reciprocal centimeter (cm^{-1}). Mass spectra were recorded with Micromass $QTOF_2$ Quadrupole/Time-of-Flight Tandem mass spectrometer using electron spray ionization. X-ray diffraction analysis was recorded on a Rigaku AFC7R X-ray single crystal diffractometer. HPLC analyses were carried out in a chromatograph equipped with a UV diode-array detector using chiral stationarycolumns from Daicel.

^1H NMR spectra were recorded on a Bruker AV-400 spectrometer and a Bruker AV-500 spectrometer in chloroform-d. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data is being reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, brs = broad singlet, coupling constant(s) in Hz, integration).

^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer and a Bruker AV-500 spectrometer in chloroform-d. Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard.

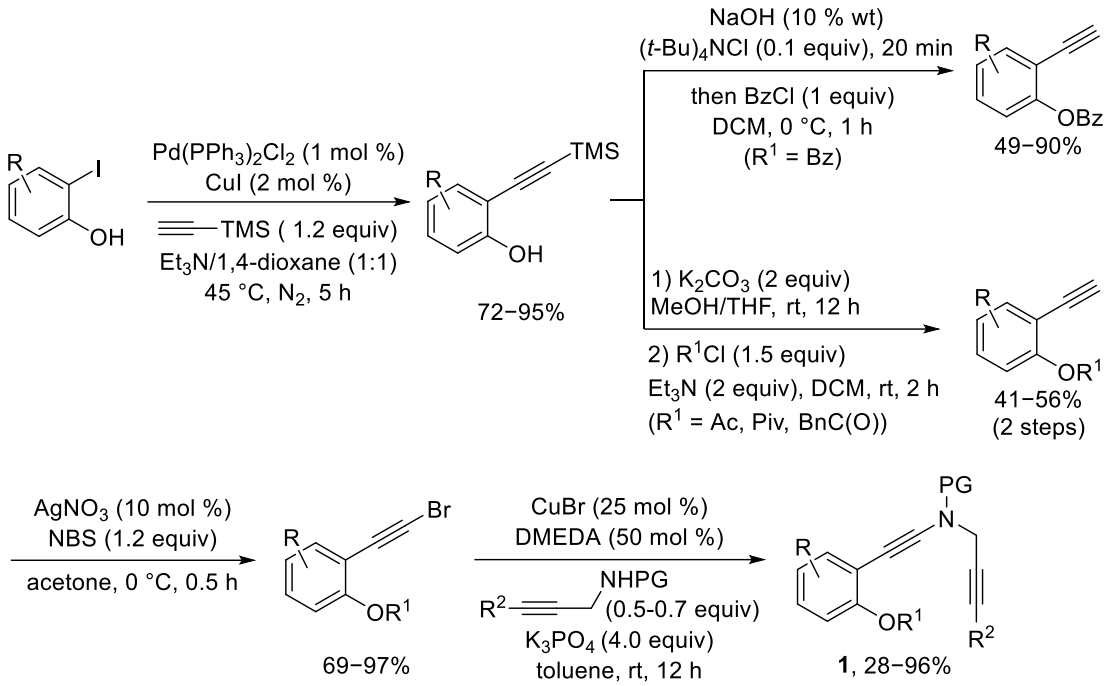
2. More Substrate Scope Study

(1) The reaction of di-ynamide **1ab**, homo-propargyl amine derived ynamide **1ac** and alkyl-linked ynamide **1ad** only led to a complicated mixture of products (the desired products could not be detected) under the standard reaction conditions.



3. Preparation of Starting Materials

3.1 Typical diynes 1 were synthesized according to the following procedures.[1–4]



The powered $Pd(PPh_3)_2Cl_2$ (0.2 mmol, 140.0 mg), CuI (0.4 mmol, 76.0 mg) and *o*-iodophenol derivative (20.0 mmol) were introduced into an oven-dried Schlenk tube under nitrogen atmosphere. Then, 1,4-dioxane (20 mL), triethylamine (20 mL) and ethynyltrimethylsilane (24.0 mmol, 3.4 mL) were added. This reaction was stirred at 45 °C for 5 h and the progress of the reaction was monitored by TLC. Upon completion, the solution was filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexanes/EtOAc) to afford the desired alkyne (72–95% yield).[1]

When R^1 is the benzoyl group, the substituted terminal alkyne was synthesized according to the following procedures: To a mixture of the above alkyne (16.0 mmol) and NaOH (aq, 10 wt%, 15 mL) was slowly added the solution of $(t\text{-Bu})_4NCl$ (1.6 mmol, 0.45 g) in DCM (2 mL) at 0 °C, and the mixture was stirred for 20 min. Next, the solution of BzCl (16.0 mmol) in DCM (16 mL) was added at 0 °C and the reaction was stirred for additional 1 h. The progress of the reaction was monitored by TLC. Upon completion, the reaction was quenched with water, extracted with ethyl acetate,

dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography on silica gel (eluent: hexanes/EtOAc) to afford the terminal alkyne (49–90% yield).[2]

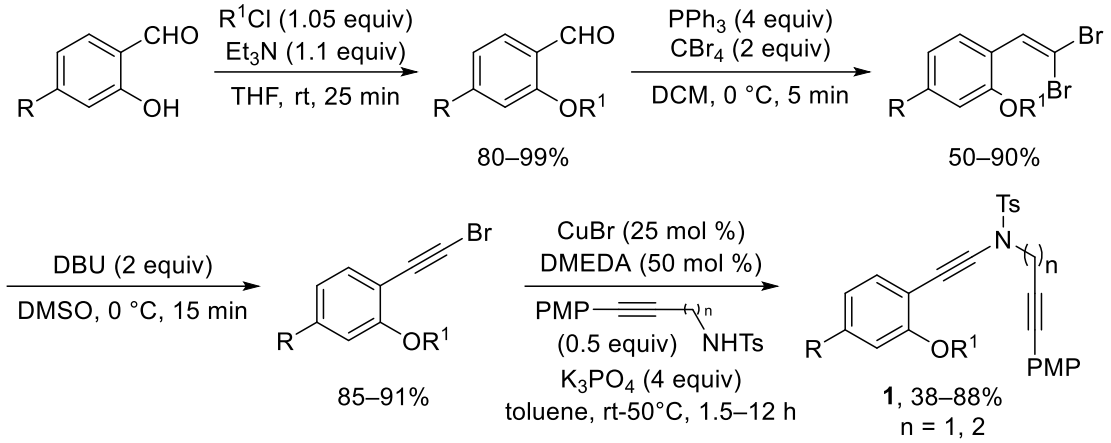
When R^1 is the Ac, Piv or BnC(O) group, the substituted terminal alkyne was synthesized according to the following procedures: To a solution of the above alkyne (16.0 mmol) in MeOH (10 mL) and THF (10 mL) was added K_2CO_3 (32.0 mmol, 4.42 g), and the mixture was stirred for 12 h at room temperature. The progress of the reaction was monitored by TLC. Upon completion, the mixture was filtered and concentrated. The residue was purified by column chromatography on silica gel (eluent: hexanes/EtOAc) to afford the desired product in 90% yield.[3] To a solution of the above product (14.4 mmol) in DCM (20 mL) were added triethylamine (28.8 mmol, 4.0 mL) and the corresponding acyl chloride (21.6 mmol). The reaction was stirred for 2 h at room temperature, and the progress of the reaction was monitored by TLC. Upon completion, the reaction mixture was quenched with water, extracted with ethyl acetate, dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography on silica gel (eluent: hexanes/EtOAc) to give the terminal alkyne (45–62% yield).[2]

To a solution of the above terminal alkyne (12.8 mmol) in acetone (20 mL) were slowly added NBS (15.36 mmol, 2.73 g) and $AgNO_3$ (1.28 mmol, 0.22 g) at 0 °C, and stirred for 0.5 h. The progress of the reaction was monitored by TLC. Upon completion, the solution was concentrated under reduced pressure, dissolved in hexanes, filtered, and concentrated under reduced pressure to give the alkynyl bromide without further purification (69–97% yield).

To a dry flask were added CuBr (0.25 mmol, 0.036 g), DMEDA (0.5 mmol, 0.044 g), K_3PO_4 (4.0 mmol, 0.85 g), protected propargylamide derivative (1.0 mmol), toluene (8 mL). Then alkynyl bromide (2.0 mmol) in toluene (2 mL) was added into the mixture, and the reaction was stirred at room temperature for 12 h. The progress of the reaction was monitored by TLC. Upon completion, the mixture solution was filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexanes/EtOAc) to afford the desired product **1**

(28–96% yield).[4]

3.2 Diynes 1m, 1n, 1u-1x, 1aa and 1ac were synthesized according to the following procedures.[5]



To a solution of salicylaldehyde derivative (10.0 mmol) in THF (20 mL) were added triethylamine (11.0 mmol, 1.5 mL) and the corresponding acyl chloride (10.5 mmol) at room temperature. The reaction was stirred at room temperature for 25 min, and the progress of the reaction was monitored by TLC. Upon completion, the reaction was quenched with water, extracted with ethyl acetate, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography on silica gel (eluent: hexanes/EtOAc) to afford the desired product (80–99% yield).

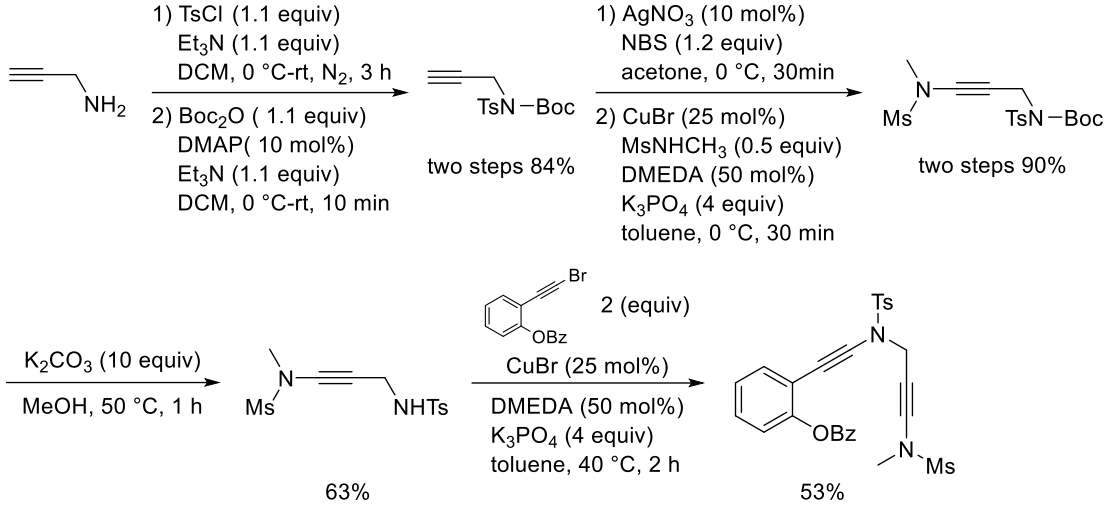
To a solution of PPh_3 (36.0 mmol, 9.44 g) in DCM (10 mL) was slowly added the solution of CBr_4 (16 mmol, 5.97 g) in DCM (5 mL) at 0 °C, and the mixture was stirred at 0 °C for 15 min. Next, the solution of the above product (9.0 mmol) in DCM (8 mL) was slowly added to the mixture. The reaction was stirred at 0 °C for 5 min, and the progress of the reaction was monitored by TLC. Upon completion, the mixture was diluted with petroleum ether, filtered through a pad of silica gel and concentrated to give the desired product without further purification (50–90% yield).

To a solution of the above product (6.0 mmol) in DMSO (10 mL) was added DBU (12 mmol, 1.79 mL) at 0 °C, and the mixture was stirred at 0 °C for 15 min. The progress of the reaction was monitored by TLC. Upon completion, the mixture was diluted with water, extracted with diethyl ether, dried over $MgSO_4$ and concentrated to afford

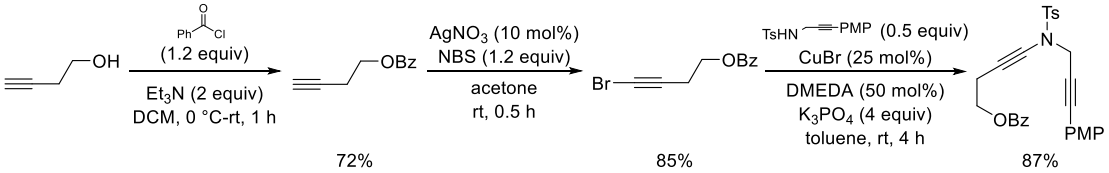
the desired alkynyl bromide without further purification (85–91% yield).

To a dry flask were added CuBr (0.25 mmol, 0.036 g), DMEDA (0.5 mmol, 0.044 g), K_3PO_4 (4.0 mmol, 0.85 g), protected propargylamide or homopropargylamide derivatives (1.0 mmol), toluene (8 mL). Then alkynyl bromide (2.0 mmol) in toluene (2 mL) was added into the mixture, and the reaction was stirred at room temperature for 12 h. The progress of the reaction was monitored by TLC. Upon completion, the mixture solution was filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexanes/EtOAc) to afford the desired product **1** (38–88% yield).[4]

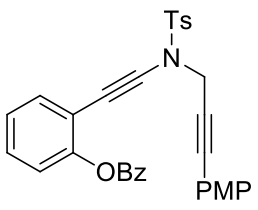
3.3 Diyne 1ab was synthesized according to the following procedures.



2.4 Diyne 1ad was synthesized according to the following procedures.



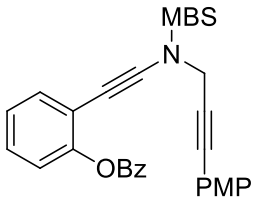
2-((*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methylphenylsulfonamido)ethynyl) phenyl benzoate (1a)



1a

The product **1a** was afforded as a pale yellow oil (80%, 428.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.60 – 7.52 (m, 1H), 7.48 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.36 – 7.30 (m, 1H), 7.27 – 7.17 (m, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 9.2 Hz, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 4.32 (s, 2H), 3.78 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 159.7, 151.0, 144.6, 134.3, 133.5, 133.1, 132.8, 130.3, 129.5, 129.3, 128.7, 128.4, 128.0, 125.8, 122.4, 117.0, 114.0, 113.7, 86.8, 86.4, 79.5, 66.4, 55.2, 42.9, 21.5; IR (neat): 2932, 2236, 1740, 1606, 1509, 1369, 1252, 1170, 1071, 749, 587; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{25}NNaO_5S$ 558.1346; Found 558.1350.

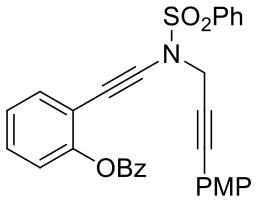
2-((4-methoxy-*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)phenylsulfonamido)ethynyl)phenyl benzoate (1b)



1b

The product **1b** was afforded as a pale yellow oil (73%, 402.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.80 (d, *J* = 9.2 Hz, 2H), 7.61 – 7.52 (m, 1H), 7.48 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.37 – 7.31 (m, 1H), 7.28 – 7.17 (m, 2H), 7.07 (d, *J* = 9.2 Hz, 2H), 6.84 – 6.69 (m, 4H), 4.31 (s, 2H), 3.78 (s, 3H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 163.7, 159.8, 151.0, 133.5, 133.2, 132.8, 130.3, 130.2, 129.3, 128.8, 128.7, 128.4, 125.8, 122.4, 117.0, 114.1, 114.0, 113.7, 87.0, 86.3, 79.6, 66.4, 55.5, 55.2, 42.8; IR (neat): 3063, 2935, 2236, 1740, 1596, 1497, 1367, 1251, 1090, 833, 587; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{25}NNaO_6S$ 574.1295; Found 574.1307.

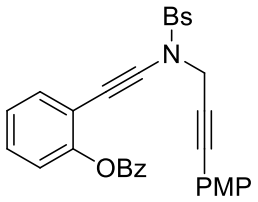
2-((*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)phenylsulfonamido)ethynyl)phenyl benzoate (1c)



1c

The product **1c** was afforded as a pale yellow oil (92%, 479.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.2 Hz, 2H), 7.86 (d, *J* = 7.6 Hz, 2H), 7.60 – 7.10 (m, 10H), 7.06 (d, *J* = 8.8 Hz, 2H), 6.71 (d, *J* = 8.4 Hz, 2H), 4.33 (s, 2H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 159.6, 150.8, 136.8, 133.4, 133.3, 132.9, 132.5, 129.9, 128.9, 128.7, 128.6, 128.2, 127.5, 125.5, 122.1, 116.5, 113.5, 113.4, 86.3(3), 86.2(9), 79.2, 66.3, 54.8, 42.6; IR (neat): 3062, 2237, 1741, 1605, 1509, 1370, 1250, 1172, 1089, 750, 591; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{23}NNaO_5S$ 544.1189; Found 544.1207.

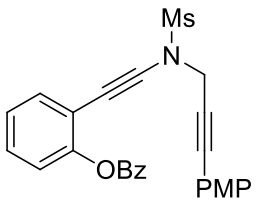
2-((4-bromo-*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)phenylsulfonamido)ethynyl) phenyl benzoate (1d)



1d

The product **1d** was afforded as a pale yellow oil (79%, 474.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.12 (m, 2H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.62 – 7.53 (m, 1H), 7.49 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.46 – 7.31 (m, 5H), 7.26 – 7.16 (m, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 4.35 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 159.8, 151.2, 136.3, 133.6, 133.1, 133.0, 132.1, 130.2, 129.4, 129.1(0), 129.0(9), 128.9, 128.5, 125.8, 122.4, 116.6, 113.8, 113.6, 86.8, 86.1, 79.1, 66.5, 55.2, 43.1; IR (neat): 2933, 2237, 1740, 1606, 1509, 1369, 1252, 1170, 1071, 749, 587; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{22}BrNNaO_5S$ 622.0294; Found 622.0286.

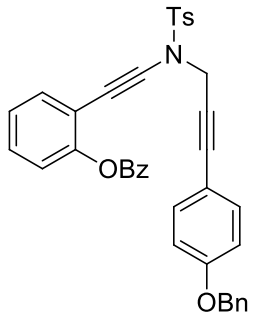
2-((*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)methylsulfonamido)ethynyl)phenyl benzoate (1e)



1e

The product **1e** was afforded as a pale yellow oil (86%, 395.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 – 8.14 (m, 2H), 7.60 – 7.48 (m, 2H), 7.45 – 7.28 (m, 5H), 7.28 – 7.17 (m, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 4.36 (s, 2H), 3.77 (s, 3H), 2.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 160.0, 151.2, 133.6, 133.3, 132.6, 130.2, 129.0, 128.4, 125.8, 122.3, 116.5, 113.9, 113.5, 86.8, 86.0, 79.7, 66.5, 55.2, 42.9, 38.3; IR (neat): 2932, 2239, 1740, 1606, 1510, 1366, 1250, 1167, 1060, 708; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{21}NNaO_5S$ 482.1033; Found 482.1050.

2-((*N*-(3-(4-(benzyloxy)phenyl)prop-2-yn-1-yl)-4-methylphenylsulfonamido)ethynyl)phenyl benzoate (1f)

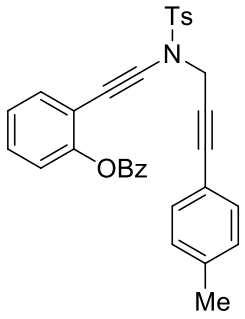


1f

The product **1f** was afforded as a pale yellow oil (52%, 318.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.10 (m, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.54 – 7.42 (m, 2H), 7.41 – 7.23 (m, 8H), 7.22 – 7.09 (m, 2H), 7.09 – 6.96 (m, 4H), 6.79 (d, *J* = 8.8 Hz, 2H), 4.97 (s, 2H), 4.28 (s, 2H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 158.7, 150.9, 144.5, 136.3, 134.1, 133.3, 133.0, 132.6, 130.0, 129.3, 129.0, 128.6, 128.4, 128.2, 127.8, 127.7, 127.2, 125.6, 122.2, 116.7, 114.4, 114.0, 86.7, 86.2, 79.4, 69.7, 66.2, 42.7, 21.2; IR (neat): 3064, 2236, 1741, 1604, 1508, 1370, 1248, 1170,

1060, 706, 545; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{38}H_{29}NNaO_5S$ 634.1659; Found 634.1687.

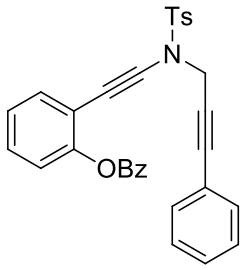
2-((4-methyl-*N*-(3-(p-tolyl)prop-2-yn-1-yl)phenylsulfonamido)ethynyl)phenyl benzoate (1g)



1g

The product **1g** was afforded as a pale yellow oil (85%, 441.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.2 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.56 – 7.49 (m, 1H), 7.46 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.41 – 7.33 (m, 2H), 7.33 – 7.25 (m, 1H), 7.24 – 7.12 (m, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.04 – 6.95 (m, 4H), 4.31 (s, 2H), 2.28 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 150.9, 144.6, 138.5, 134.1, 133.4, 132.6, 131.4, 130.1, 129.4, 129.1, 128.7, 128.3, 127.8, 125.6, 122.2, 118.7, 116.8, 86.6, 86.4, 80.1, 66.3, 42.7, 21.3, 21.2; IR (neat): 2923, 2236, 1742, 1449, 1370, 1250, 1171, 1089, 816, 707, 585; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{25}NNaO_4S$ 542.1397; Found 542.1404.

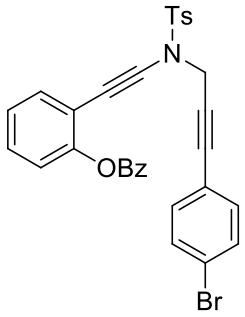
2-((4-methyl-*N*-(3-phenylprop-2-yn-1-yl)phenylsulfonamido)ethynyl)phenyl benzoate (1h)



1h

The product **1h** was afforded as a pale yellow oil (74%, 374.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.57 – 7.49 (m, 1H), 7.47 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.41 – 7.13 (m, 8H), 7.13 – 7.02 (m, 4H), 4.32 (s, 2H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 151.0, 144.7, 134.1, 133.4, 132.7, 131.5, 130.1, 129.4, 129.1, 128.7, 128.4, 128.3, 127.9, 127.8, 125.7, 122.3, 121.8, 116.8, 86.6, 86.3, 80.8, 66.3, 42.6, 21.3; IR (neat): 2922, 2236, 1741, 1491, 1370, 1250, 1170, 1059, 756, 590; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{23}NNaO_4S$ 528.1240; Found 528.1248.

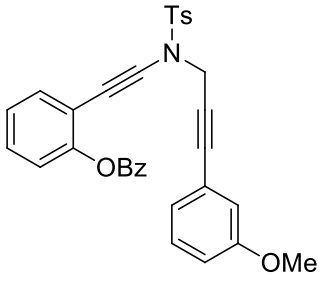
2-((*N*-(3-(4-bromophenyl)prop-2-yn-1-yl)-4-methylphenylsulfonamido)ethynyl)phenyl benzoate (1i)



1i

The product **1i** was afforded as a pale yellow oil (92%, 536.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.61 – 7.52 (m, 1H), 7.48 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.44 – 7.30 (m, 5H), 7.27 – 7.17 (m, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 4.31 (s, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 151.1, 144.7, 134.3, 133.5, 133.0, 132.8, 131.3, 130.2, 129.5, 129.2, 128.9, 128.4, 128.0, 125.8, 122.8, 122.4, 120.8, 116.9, 86.5, 85.2, 82.1, 66.5, 42.7, 21.5; IR (neat): 2923, 2236, 1741, 1597, 1487, 1370, 1250, 1170, 1089, 707, 593; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{22}BrNNaO_4S$ 606.0345; Found 606.0347.

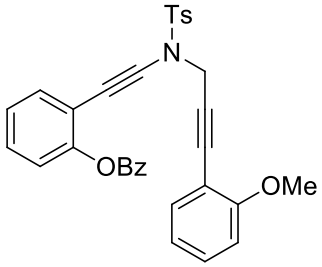
2-((*N*-(3-(3-methoxyphenyl)prop-2-yn-1-yl)-4-methylphenylsulfonamido)ethynyl)phenyl benzoate (1j)



1j

The product **1j** was afforded as a pale yellow oil (76%, 407.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.57 – 7.43 (m, 2H), 7.43 – 7.33 (m, 2H), 7.33 – 7.25 (m, 1H), 7.25 – 7.03 (m, 5H), 6.81 (ddd, *J* = 8.4, 2.4, 0.8 Hz, 1H), 6.69 (d, *J* = 7.6 Hz, 1H), 6.65 – 6.63 (m, 1H), 4.32 (s, 2H), 3.67 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 159.0, 151.0, 144.7, 134.1, 133.4, 132.7, 130.1, 129.4, 129.1, 129.0, 128.7, 128.3, 127.8, 125.7, 124.0, 122.7, 122.3, 116.8, 116.7, 114.7, 86.6, 86.2, 80.6, 66.4, 55.0, 42.6, 21.3; IR (neat): 3067, 2938, 2236, 1741, 1597, 1370, 1202, 1090, 754, 590; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{25}NNaO_5S$ 558.1346; Found 558.1356.

2-((*N*-(3-(2-methoxyphenyl)prop-2-yn-1-yl)-4-methylphenylsulfonamido)ethynyl) phenyl benzoate (1k)

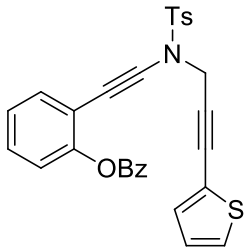


1k

The product **1k** was afforded as a pale yellow oil (56%, 300.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.16 (m, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.59 – 7.51 (m, 1H), 7.48 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.37 – 7.30 (m, 1H), 7.29 – 7.16 (m, 3H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.99 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.86 – 6.74 (m, 2H), 4.40 (s, 2H), 3.76 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 160.0, 151.0, 144.6, 134.2, 133.8, 133.5, 132.8, 130.3, 130.0, 129.4, 129.3, 128.7, 128.4,

128.0, 125.7, 122.4, 120.1, 117.0, 111.2, 110.5, 86.7, 84.8, 83.0, 66.5, 55.5, 43.1, 21.5; IR (neat): 3067, 2935, 2236, 1741, 1591, 1493, 1369, 1265, 1171, 1089, 754, 592; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{25}NNaO_5S$ 558.1346; Found 558.1362.

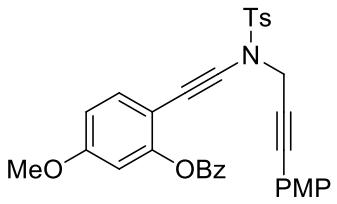
2-((4-methyl-*N*-(3-(thiophen-2-yl)prop-2-yn-1-yl)phenylsulfonamido)ethynyl)phenyl benzoate (1l)



1l

The product **1l** was afforded as a pale yellow oil (96%, 490.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.2 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.60 – 7.49 (m, 1H), 7.46 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.43 – 7.34 (m, 2H), 7.34 – 7.26 (m, 1H), 7.25 – 7.05 (m, 5H), 6.99 – 6.90 (m, 1H), 6.90 – 6.80 (m, 1H), 4.32 (s, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 150.9, 144.7, 133.9, 133.4, 132.6, 132.6, 130.1, 129.4, 129.1, 128.7, 128.3, 127.7, 127.5, 126.7, 125.6, 122.2, 121.5, 116.7, 86.5, 84.7, 79.6, 66.4, 42.7, 21.4; IR (neat): 2924, 2236, 1740, 1598, 1369, 1251, 1170, 1089, 706, 590; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{21}NNaO_4S_2$ 534.0804; Found 534.0804.

5-methoxy-2-((*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methylphenylsulfonamido)ethynyl)phenyl benzoate (1m)

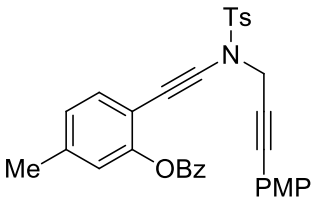


1m

The product **1m** was afforded as a pale yellow oil (83%, 469.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.2 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.59 – 7.47 (m, 1H),

7.45 – 7.30 (m, 3H), 7.15 – 6.96 (m, 4H), 6.84 – 6.66 (m, 4H), 4.31 (s, 2H), 3.76 (s, 3H), 3.74 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 160.2, 159.6, 152.6, 144.4, 134.2, 134.0, 133.4, 133.0, 130.1, 129.3, 129.1, 128.3, 127.8, 113.9, 113.6, 111.9, 108.7, 108.2, 86.2, 85.0, 79.5, 65.8, 55.4, 55.1, 42.8, 21.4; IR (neat): 3066, 2938, 2236, 1741, 1597, 1370, 1202, 1170, 1059, 707, 590; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{27}NNaO_6S$ 588.1451; Found 588.1454.

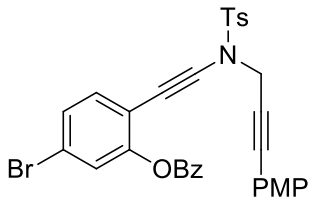
2-((*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methylphenylsulfonamido)ethynyl)-5-methylphenyl benzoate (1n)



1n

The product **1n** was afforded as a pale yellow oil (88%, 483.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.6 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.60 – 7.48 (m, 1H), 7.45 – 7.30 (m, 3H), 7.16 – 6.94 (m, 6H), 6.74 (d, *J* = 8.8 Hz, 2H), 4.30 (s, 2H), 3.76 (s, 3H), 2.35 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 159.6, 151.0, 144.5, 139.5, 134.2, 133.4, 133.1, 132.6, 130.2, 129.4, 129.3, 128.3, 127.9, 126.6, 122.9, 114.0, 113.7, 113.6, 86.3, 85.9, 79.5, 66.2, 55.2, 42.8, 21.4, 21.3; IR (neat): 2923, 2237, 1736, 1605, 1509, 1367, 1250, 1171, 1089, 707, 584; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{27}NNaO_5S$ 572.1502; Found 572.1513.

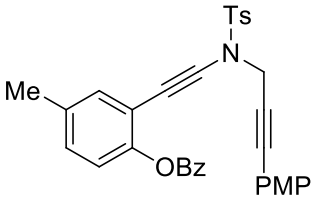
5-bromo-2-((*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methylphenylsulfonamido)ethynyl)phenyl benzoate (1o)



1o

The product **1o** was afforded as a pale yellow oil (43%, 264.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.2 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.61 – 7.50 (m, 1H), 7.48 – 7.35 (m, 3H), 7.35 – 7.27 (m, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 6.74 (d, *J* = 8.4 Hz, 2H), 4.31 (s, 2H), 3.77 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 159.7, 151.3, 144.7, 134.2, 133.7, 133.4, 133.1, 130.3, 129.5, 129.0, 128.7, 128.5, 127.9, 125.8, 121.4, 116.2, 113.9, 113.7, 87.8, 86.4, 79.3, 65.8, 55.2, 42.8, 21.5; IR (neat): 2927, 2237, 1744, 1605, 1509, 1370, 1248, 1171, 1055, 706, 577; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{24}BrNNaO_5S$ 636.0451; Found 636.0449.

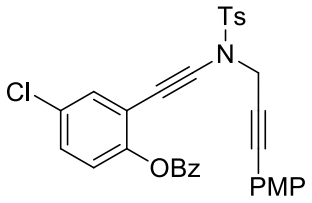
2-((*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methylphenylsulfonamido)ethynyl)-4-methylphenyl benzoate (1p)



1p

The product **1p** was afforded as a pale yellow oil (91%, 500.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.57 – 7.49 (m, 1H), 7.43 – 7.32 (m, 2H), 7.27 (s, 1H), 7.15 – 6.99 (m, 6H), 6.73 (d, *J* = 8.8 Hz, 2H), 4.30 (s, 2H), 3.74 (s, 3H), 2.28 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 159.6, 148.7, 144.5, 135.4, 134.2, 133.3, 133.0(3), 132.9(7), 130.1, 129.4(1), 129.3(7), 129.2, 128.3, 127.8, 121.9, 116.4, 113.9, 113.6, 86.3, 79.4, 66.5, 55.1, 42.8, 21.4, 20.5; IR (neat): 3062, 2925, 2240, 1735, 1605, 1509, 1370, 1251, 1089, 834, 708, 590; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{27}NNaO_5S$ 572.1502; Found 572.1502.

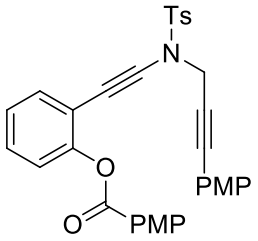
4-chloro-2-((*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methylphenylsulfonamido)ethynyl)phenyl benzoate (1q)



1q

The product **1q** was afforded as a pale yellow oil (85%, 484.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.60 – 7.50 (m, 1H), 7.46 – 7.32 (m, 3H), 7.30 – 7.20 (m, 1H), 7.20 – 7.09 (m, 3H), 7.05 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 4.31 (s, 2H), 3.75 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 159.7, 149.3, 144.8, 134.1, 133.6, 133.1, 131.9, 130.9, 130.2, 129.5, 128.8, 128.5, 128.4, 127.8, 123.5, 118.6, 113.7, 113.6, 88.0, 86.5, 79.2, 65.6, 55.1, 42.7, 21.4; IR (neat): 2933, 2237, 1744, 1605, 1509, 1371, 1248, 1171, 1055, 707, 590; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{24}ClNNaO_5S$ 592.0956; Found 592.0974.

2-((*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methylphenylsulfonamido)ethynyl) phenyl 4-methoxybenzoate (1r)

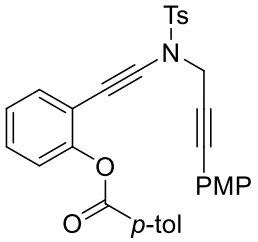


1r

The product **1r** was afforded as a pale yellow oil (83%, 469.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 9.2 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.47 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.37 – 7.28 (m, 1H), 7.27 – 7.15 (m, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.74 (d, *J* = 8.8 Hz, 2H), 4.34 (s, 2H), 3.81 (s, 3H), 3.78 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 163.8, 159.7, 151.2, 144.6, 134.3, 133.1, 132.7, 132.4, 129.5, 128.7, 128.0, 125.6, 122.4, 121.6, 116.9, 114.0, 113.7, 113.6, 86.6, 86.3, 79.5, 66.5, 55.4, 55.2, 42.9, 21.5; IR

(neat): 2934, 2237, 1734, 1606, 1510, 1368, 1251, 1168, 1030, 834, 752, 588; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{27}NNaO_6S$ 588.1451; Found 588.1467.

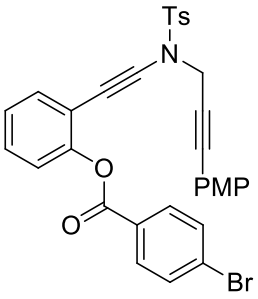
2-((*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methylphenylsulfonamido)ethynyl) phenyl 4-methylbenzoate (1s)



1s

The product **1s** was afforded as a pale yellow oil (61%, 335.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.46 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.34 – 7.26 (m, 1H), 7.25 – 7.13 (m, 4H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 9.2 Hz, 2H), 4.33 (s, 2H), 3.74 (s, 3H), 2.35 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 159.6, 151.0, 144.5, 144.2, 134.2, 133.0, 132.7, 130.2, 129.4, 129.0, 128.7, 127.8, 126.4, 125.5, 122.3, 116.8, 113.9, 113.6, 86.6, 86.3, 79.4, 66.3, 55.1, 42.8, 21.5, 21.3; IR (neat): 3038, 2965, 2236, 1736, 1607, 1509, 1369, 1170, 1065, 833, 747, 545; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{27}NNaO_5S$ 572.1502; Found 572.1502.

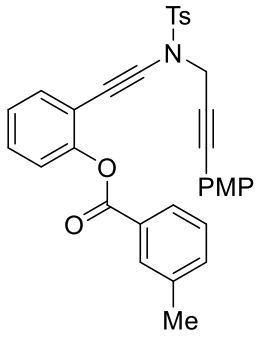
2-((*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methylphenylsulfonamido)ethynyl) phenyl 4-bromobenzoate (1t)



1t

The product **1t** was afforded as a pale yellow oil (90%, 553.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.54 – 7.41 (m, 3H), 7.37 – 7.27 (m, 1H), 7.27 – 7.08 (m, 4H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 8.4 Hz, 2H), 4.37 (s, 2H), 3.76 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 159.7, 150.8, 144.6, 134.3, 133.0, 132.9, 131.6(4), 131.6(2), 129.4, 128.8, 128.6, 128.1, 127.8, 125.8, 122.1, 116.7, 113.8, 113.7, 86.7, 86.3, 79.4, 66.1, 55.1, 42.8, 21.4; IR (neat): 2933, 2236, 1740, 1606, 1509, 1369, 1252, 1170, 1071, 833, 750, 587; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{24}BrNNaO_5S$ 636.0451; Found 636.0457.

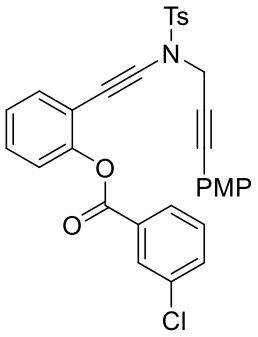
2-(((*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methylphenyl)sulfonamido)ethynyl)phenyl 3-methylbenzoate (1u)



1u

The product **1u** was afforded as a pale yellow oil (38%, 167.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 – 7.92 (m, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.47 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.40 – 7.26 (m, 3H), 7.26 – 7.16 (m, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.5 Hz, 2H), 6.74 (d, *J* = 9.0 Hz, 2H), 4.31 (s, 2H), 3.78 (s, 3H), 2.36 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 159.8, 151.1, 144.6, 138.3, 134.5, 134.3, 133.1, 132.7, 130.8, 129.5, 129.3, 128.7, 128.3, 128.0, 127.5, 125.7, 122.4, 117.1, 114.1, 113.7, 86.8, 86.4, 79.5, 66.6, 55.2, 42.9, 21.5, 21.2; IR (neat) : 3068, 2995, 2929, 2238, 1742, 1509, 1369, 1247, 632, 737, 587; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{27}NNaO_5S$ 572.1502; Found 572.1515.

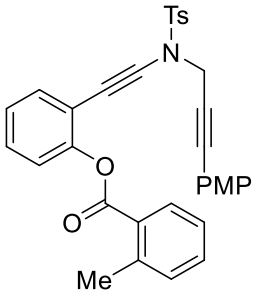
2-(((*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methylphenyl)sulfonamido)ethynyl)phenyl 3-chlorobenzoate (1v)



1v

The product **1v** was afforded as a pale yellow oil (47%, 192.6 mg).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 – 8.11 (m, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.54 – 7.46 (m, 2H), 7.37 – 7.27 (m, 2H), 7.24 – 7.19 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.5 Hz, 2H), 6.74 (d, *J* = 9.0 Hz, 2H), 4.36 (s, 2H), 3.78 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.4, 159.8, 150.8, 144.7, 134.6, 134.5, 133.5, 133.1, 132.9, 131.1, 130.2, 129.8, 129.5, 128.8, 128.5, 128.0, 126.0, 122.2, 117.0, 114.0, 113.7, 87.0, 86.5, 79.4, 66.4, 55.3, 42.9, 21.5; IR (neat) : 3068, 2927, 2836, 2238, 1743, 1507, 1371, 1163, 834, 749, 666; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{24}ClNNaO_5S$ 592.0956; Found 592.0966.

2-(((*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methylphenyl)sulfonamido)ethynyl)phenyl 2-methylbenzoate (1w)

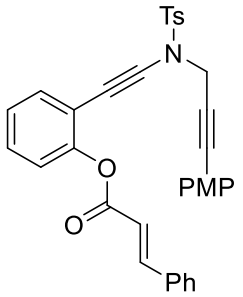


1w

The product **1w** was afforded as a pale yellow oil (50%, 167.0 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.48 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.43 – 7.37 (m, 1H), 7.36 – 7.31 (m, 1H), 7.26 – 7.17 (m, 4H), 7.11 (d, *J* = 8.5 Hz, 2H), 7.04 (d, *J* = 8.5 Hz, 2H), 6.73 (d, *J* = 9.0 Hz, 2H), 4.36 (s, 2H), 3.77 (s,

3H), 2.62 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.2, 159.8, 151.2, 144.6, 141.3, 134.5, 133.1(4), 133.0(7), 132.6, 131.7, 131.5, 129.5, 128.8, 128.4, 128.0, 125.8, 125.7, 122.6, 117.2, 114.1, 113.7, 86.7, 86.5, 79.6, 66.7, 55.2, 42.9, 21.7, 21.4; IR (neat) : 3066, 2967, 2931, 2240, 1742, 1509, 1368, 1247, 834, 738, 583; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{27}NNaO_5S$ 572.1502; Found 572.1520.

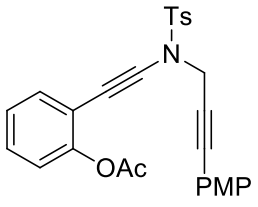
2-(((*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methylphenyl)sulfonamido)ethynyl)phenyl cinnamate (1x)



1x

The product **1x** was afforded as a pale yellow solid (44%, 596.0 mg, mp 122–123 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.79 (m, 3H), 7.53 – 7.42 (m, 3H), 7.41 – 7.28 (m, 4H), 7.23 – 7.15 (m, 4H), 7.09 (d, *J* = 11.0 Hz, 2H), 6.73 (d, *J* = 11.0 Hz, 2H), 6.60 (d, *J* = 20.0 Hz, 1H), 4.47 (s, 2H), 3.78 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 159.7, 151.0, 146.6, 144.7, 134.5, 134.2, 133.2, 132.7, 130.5, 129.5, 128.8, 128.7, 128.3, 128.1, 125.7, 122.3, 117.0(4), 116.9(6), 114.1, 113.7, 86.8, 86.4, 79.5, 66.5, 55.2, 43.0, 21.5; IR (neat): 2954, 2919, 2949, 2237, 1731, 1625, 1513, 1368, 1169, 733, 686; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{27}NNaO_5S$ 584.1502; Found 584.1510.

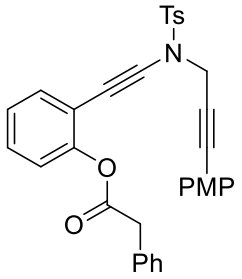
2-((*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methylphenylsulfonamido)ethynyl)phenyl acetate (1y)



1y

The product **1y** was afforded as a pale yellow oil (28%, 265.2 mg, 2 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.41 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.34 – 7.22 (m, 3H), 7.20 – 7.03 (m, 4H), 6.77 (d, *J* = 8.8 Hz, 2H), 4.53 (s, 2H), 3.79 (s, 3H), 2.34 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 159.8, 151.1, 144.8, 134.4, 133.2, 132.6, 129.6, 128.9, 128.1, 125.8, 122.3, 117.0, 114.0, 113.7, 86.6, 86.5, 79.5, 66.4, 55.2, 42.9, 21.5, 20.7; IR (neat): 2920, 2237, 1762, 1605, 1509, 1367, 1249, 1169, 1088, 751, 588; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{23}NNaO_5S$ 496.1189; Found 496.1190.

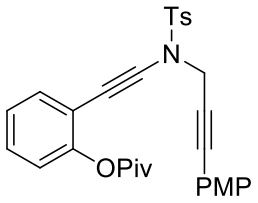
2-(((*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methylphenyl)sulfonamido)ethynyl)phenyl 2-phenylacetate (1z)



1z

The product **1z** was afforded as a pale yellow oil (35%, 659.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.34 – 7.17 (m, 8H), 7.15 – 7.03 (m, 3H), 7.00 (d, *J* = 8.5 Hz, 1H), 6.72 (d, *J* = 8.5 Hz, 2H), 4.46 (s, 2H), 3.88 (s, 2H), 3.74 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 159.8, 151.1, 144.8, 134.5, 133.5, 133.2, 132.6, 129.6, 129.5, 128.8, 128.5, 128.2, 127.1, 125.8, 122.2, 117.0, 114.0, 113.8, 86.7, 86.5, 79.6, 66.5, 55.2, 42.9, 40.7, 21.5; IR (neat): 2920, 2849, 2236, 1780, 1500, 1367, 1364, 1248, 1168, 748, 683; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{27}NNaO_5S$ 572.1502; Found 572.1511.

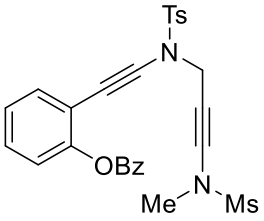
2-((*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methylphenylsulfonamido)ethynyl)phenyl pivalate (1aa)



1aa

The product **1aa** was afforded as a pale yellow oil (58%, 299.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.42 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.34 – 7.24 (m, 3H), 7.18 – 7.09 (m, 3H), 7.04 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.77 (d, *J* = 8.8 Hz, 2H), 4.51 (s, 2H), 3.79 (s, 3H), 2.36 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 159.8, 151.5, 144.8, 134.5, 133.8, 133.2, 129.6, 129.1, 128.2, 125.5, 122.3, 116.8, 114.1, 113.8, 86.6, 86.2, 79.7, 66.4, 55.3, 43.1, 39.1, 27.1, 21.6; IR (neat): 2973, 2235, 1751, 1606, 1510, 1370, 1250, 1170, 1034, 834, 752, 588; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{29}NNaO_5S$ 538.1659; Found 538.1670.

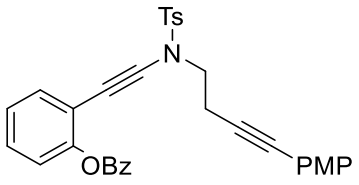
2-(((4-methyl-*N*-(3-(*N*-methylmethylsulfonamido)prop-2-yn-1-yl)phenyl)sulfona mido)ethynyl)phenyl benzoate (1ab)



1ab

The product **1ab** was afforded as a light yellow solid (53%, 254.1 mg, mp 98.0-99.4℃)). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.0 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.66 – 7.60 (m, 1H), 7.54 – 7.43 (m, 3H), 7.39 – 7.32 (m, 1H), 7.25 – 7.16 (m, 4H), 4.21 (s, 2H), 2.95 (s, 3H), 2.82 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.6, 151.2, 144.8, 134.2, 133.6, 132.7, 130.2, 129.6, 129.2, 129.0, 128.5, 127.8, 125.8, 122.4, 116.8, 86.5, 80.8, 66.8, 62.6, 42.3, 38.6, 36.4, 21.5; IR (neat) : 3066, 2927, 2252, 1741, 1597, 1448, 1365, 1252, 757, 709, 587; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{24}N_2NaO_6S_2$ 559.0968; Found 559.0978.

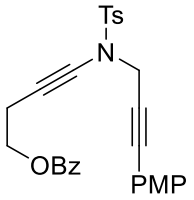
2-(((*N*-(4-(4-methoxyphenyl)but-3-yn-1-yl)-4-methylphenyl)sulfonamido)ethynyl) phenyl benzoate (1ac)



1ac

The product **1ac** was afforded as a pale yellow oil (39%, 212.0 mg).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.0 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.59 – 7.52 (m, 1H), 7.50 – 7.39 (m, 3H), 7.37 – 7.29 (m, 1H), 7.28 – 7.11 (m, 6H), 6.79 (d, *J* = 9.0 Hz, 2H), 3.77 (s, 3H), 3.41 (t, *J* = 7.5 Hz, 2H), 2.54 (t, *J* = 7.5 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.5, 159.3, 151.2, 144.6, 134.6, 133.5, 132.9, 132.7, 130.2, 129.7, 129.2, 128.8, 128.5, 127.4, 125.8, 122.3, 117.0, 115.3, 113.8, 86.5, 83.4, 82.3, 66.5, 55.2, 50.3, 21.5, 19.1; IR (neat) : 3058, 2935, 2832, 2237, 1738, 1603, 1507, 1247, 833, 667, 544; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{27}NNaO_5S$ 572.1502; Found 572.1520.

4-((*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methylphenyl)sulfonamido)but-3-yn-1-yl benzoate (1ad)

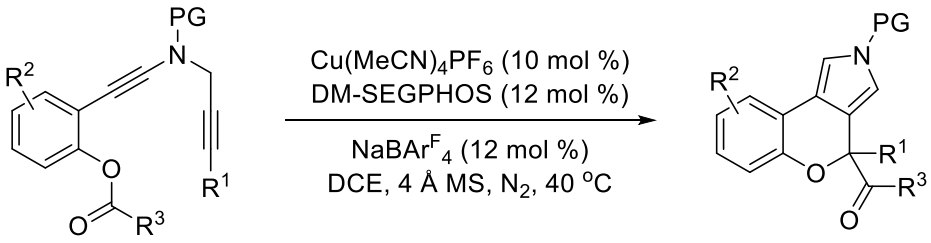


1ad

The product **1ad** was afforded as a pale yellow oil (87%, 188.0 mg).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.58 – 7.48 (m, 1H), 7.43 – 7.33 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 9.0 Hz, 2H), 6.75 (d, *J* = 8.5 Hz, 2H), 4.43 (s, 2H), 4.38 (t, *J* = 7.0 Hz, 2H), 3.79 (s, 3H), 2.79 (t, *J* = 7.0 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.3, 159.8, 144.5, 134.5, 133.1, 133.0, 130.1, 129.6, 129.4, 128.3, 128.1, 114.2, 113.8, 86.3, 79.9 , 74.5, 66.8, 63.1, 55.3, 42.8, 21.5, 19.2; IR (neat) : 3068, 2955, 2838, 2252, 1722, 1516, 1366,

1274, 833, 713, 672; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{25}NNaO_5S$ 510.1346; Found 510.1350.

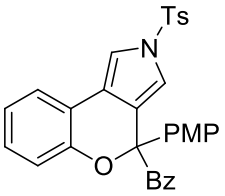
4. General Procedure for the Copper-Catalyzed Diyne Cyclization/[1,2]-Acyl Shift



1 **2**

The powered $Cu(MeCN)_4PF_6$ (0.015 mmol, 5.6 mg), $NaBAr^F_4$ (0.018 mmol, 16.0 mg), DM-SEGPHOS (0.018 mmol, 13.0 mg) and 4 Å MS (45.0 mg) were introduced into an oven-dried Schlenk tube under N_2 atmosphere. After injecting DCE (1.5 mL) into the Schlenk tube, the mixture was stirred at 25 °C for 1 h. Then the solution of diyne **1** (0.15 mmol) in DCE (1.5 mL) was introduced into the reaction system, and the mixture was stirred at 40 °C. The progress of the reaction was monitored by TLC. Upon completion, the mixture was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (eluent: hexanes/ EtOAc) to give the desired dihydrochromeno[3,4-*c*]pyrrole **2**.

(4-(4-methoxyphenyl)-2-tosyl-2,4-dihydrochromeno[3,4-*c*]pyrrol-4-yl)(phenyl)methanone (2a)

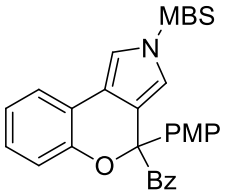


2a

The product **2a** was afforded in 83% yield (66.7 mg) according to the general procedure. Pale yellow solid (mp 193-195 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.6 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.47 – 7.31 (m, 5H), 7.31 – 7.13 (m, 4H), 7.10 – 6.94 (m, 2H), 6.93 – 6.74 (m, 4H), 3.72 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 197.5, 159.4, 151.0, 145.2, 135.6, 135.0, 132.5, 130.9, 130.3, 130.0, 128.6, 127.8, 127.4, 126.7, 124.5, 123.5, 122.5, 120.0, 118.7, 118.4, 118.2, 113.9, 113.5, 86.3, 55.1, 21.5; IR (neat): 2961, 2926, 1686, 1511, 1374, 1173, 1075, 812, 670, 537; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{25}NNaO_5S$ 558.1346; Found 558.1369.

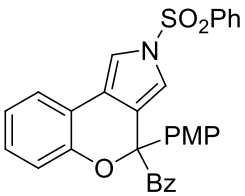
(4-(4-methoxyphenyl)-2-((4-methoxyphenyl)sulfonyl)-2,4-dihydrochromeno[3,4-*c*]pyrrol-4-yl)(phenyl)methanone (2b)



2b

The product **2b** was afforded in 69% yield (57.1 mg) according to the general procedure. Pale yellow solid (mp 185-186 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.81 (m, 2H), 7.78 (d, *J* = 8.8 Hz, 2H), 7.48 – 7.41 (m, 1H), 7.41 – 7.34 (m, 4H), 7.32 – 7.26 (m, 2H), 7.07 – 6.98 (m, 2H), 6.96 – 6.78 (m, 6H), 3.84 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 164.0, 159.5, 151.1, 135.2, 132.6, 131.1, 130.4, 130.1, 129.2, 128.6, 127.9, 127.5, 124.4, 123.6, 122.6, 120.0, 118.7, 118.6, 118.3, 114.7, 114.0, 113.5, 86.4, 55.7, 55.2; IR (neat): 2925, 2853, 1686, 1595, 1470, 1372, 1167, 1074, 835, 603, 549; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{25}NNaO_6S$ 574.1295; Found 574.1294.

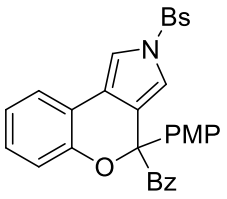
(4-(4-methoxyphenyl)-2-(phenylsulfonyl)-2,4-dihydrochromeno[3,4-*c*]pyrrol-4-yl)(phenyl)methanone (2c)



2c

The product **2c** was afforded in 80% yield (62.6 mg) according to the general procedure. Pale yellow solid (mp 168-169 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.77 (m, 4H), 7.64 – 7.54 (m, 1H), 7.53 – 7.33 (m, 7H), 7.33 – 7.23 (m, 2H), 7.08 – 6.97 (m, 2H), 6.96 – 6.76 (m, 4H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 159.5, 151.2, 138.8, 135.1, 134.0, 132.6, 131.0, 130.4, 129.5, 128.7, 127.9, 127.4, 126.8, 124.8, 123.6, 122.6, 120.3, 118.9, 118.4, 118.3, 114.0, 113.6, 86.4, 55.2; IR (neat): 2926, 2853, 1686, 1511, 1375, 1252, 1174, 1074, 728, 618, 590; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{23}NNaO_5S$ 544.1189; Found 544.1197.

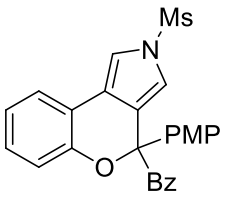
(2-((4-bromophenyl)sulfonyl)-4-(4-methoxyphenyl)-2,4-dihydrochromeno[3,4-*c*]pyrrol-4-yl)(phenyl)methanone (2d)



2d

The product **2d** was afforded in 84% yield (75.7 mg) according to the general procedure. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.72 – 7.65 (m, 2H), 7.65 – 7.56 (m, 2H), 7.50 – 7.41 (m, 1H), 7.41 – 7.33 (m, 4H), 7.33 – 7.25 (m, 2H), 7.07 – 6.97 (m, 2H), 6.96 – 6.85 (m, 3H), 6.81 (d, *J* = 8.0 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 159.6, 151.2, 137.6, 134.9, 132.8, 132.7, 130.8, 130.4, 129.4, 128.9, 128.2, 127.9, 127.3, 125.4, 123.7, 122.7, 120.7, 118.9, 118.3, 118.2, 114.1, 113.5, 86.3, 55.2; IR (neat): 2957, 2925, 2854, 1686, 1574, 1391, 1252, 1175, 1075, 745, 630; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{22}BrNNaO_5S$ 622.0294; Found 622.0284.

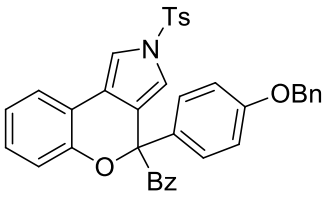
(4-(4-methoxyphenyl)-2-(methylsulfonyl)-2,4-dihydrochromeno[3,4-*c*]pyrrol-4-yl)(phenyl)methanone (2e)



2e

The product **2e** was afforded in 91% yield (62.7 mg) according to the general procedure. Pale yellow solid (mp 84-85 ^{o}C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.84 (m, 2H), 7.50 – 7.43 (m, 3H), 7.41 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.37 (d, *J* = 2.4 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.08 – 7.00 (m, 1H), 6.99 – 6.89 (m, 4H), 6.81 (dd, *J* = 8.0, 0.8 Hz, 1H), 3.80 (s, 3H), 3.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 159.6, 151.3, 135.0, 132.7, 130.9, 130.4, 128.7, 127.9, 127.0, 125.3, 123.6, 122.7, 120.1, 118.6, 118.5, 118.3, 114.2, 113.2, 86.4, 55.3, 43.0; IR (neat): 2928, 1735, 1608, 1152, 1367, 1253, 1174, 1077, 982, 764; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{21}NNaO_5S$ 482.1033; Found 482.1037.

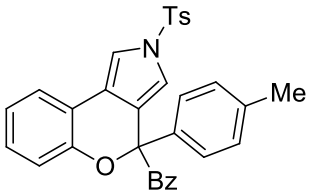
(4-(4-(benzyloxy)phenyl)-2-tosyl-2,4-dihydrochromeno[3,4-*c*]pyrrol-4-yl)(phenyl) methanone (2f)



2f

The product **2f** was afforded in 70% yield (64.2 mg) according to the general procedure. Pale yellow solid (mp 80-81 ^{o}C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.48 – 7.22 (m, 14H), 7.07 – 6.98 (m, 2H), 6.97 – 6.87 (m, 3H), 6.81 (d, *J* = 8.0 Hz, 1H), 5.02 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 158.8, 151.1, 145.2, 136.7, 135.8, 135.1, 132.6, 131.3, 130.4, 130.1, 128.6(3), 128.5(8), 128.0, 127.9, 127.5, 126.8, 124.5, 123.6, 122.6, 120.1, 118.8, 118.5, 118.3, 114.9, 113.6, 86.4, 70.1, 21.6; IR (neat): 2924, 2854, 1686, 1596, 1470, 1375, 1247, 1173, 1075, 696, 603; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{38}H_{29}NNaO_5S$ 634.1659; Found 634.1664.

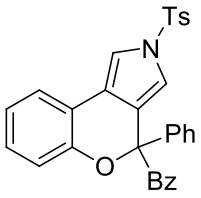
phenyl(4-(*p*-tolyl)-2-tosyl-2,4-dihydrochromeno[3,4-*c*]pyrrol-4-yl)methanone (2g)



2g

The product **2g** was afforded in 85% yield (66.2 mg) according to the general procedure. Pale yellow solid (mp 88-89 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.49 – 7.40 (m, 1H), 7.40 – 7.32 (m, 4H), 7.32 – 7.21 (m, 4H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.07 – 6.96 (m, 2H), 6.96 – 6.87 (m, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 2.40 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 151.2, 145.2, 138.2, 136.0, 135.8, 135.1, 132.6, 130.4, 130.1, 129.4, 128.6, 127.8, 126.8, 125.9, 124.5, 123.6, 122.6, 120.1, 118.9, 118.5, 118.3, 113.5, 86.6, 21.6, 21.1; IR (neat): 3061, 2925, 2854, 1690, 1597, 1470, 1374, 1248, 1074, 869, 757, 603; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{25}NNaO_4S$ 542.1397; Found 542.1411.

phenyl(4-phenyl-2-tosyl-2,4-dihydrochromeno[3,4-*c*]pyrrol-4-yl)methanone (2h)

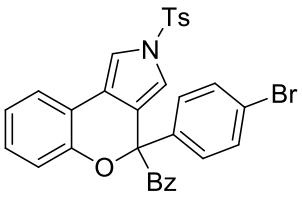


2h

The product **2h** was afforded in 70% yield (53.1 mg) according to the general procedure. Pale yellow solid (mp 80-82 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.53 – 7.46 (m, 2H), 7.46 – 7.40 (m, 1H), 7.40 – 7.22 (m, 9H), 7.05 – 6.97 (m, 2H), 6.94 – 6.87 (m, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 151.1, 145.2, 138.9, 135.8, 135.0, 132.6, 130.4, 130.1, 128.7, 128.6, 128.3, 127.9, 126.8, 125.9, 124.4, 123.6, 122.6, 120.0, 118.9, 118.5, 118.2, 113.6, 86.6, 21.6; IR (neat): 2923, 1685, 1596,

1371, 1173, 1074, 750, 703, 670, 588; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{23}NNaO_4S$ 528.1240; Found 528.1251.

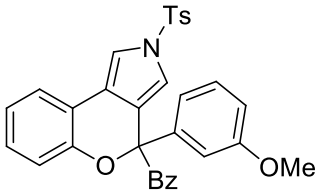
(4-(4-bromophenyl)-2-tosyl-2,4-dihydrochromeno[3,4-*c*]pyrrol-4-yl)(phenyl)methanone (2i)



2i

The product **2i** was afforded in 65% yield (57.0 mg) according to the general procedure. Pale yellow solid (mp 204-205 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.52 – 7.43 (m, 3H), 7.43 – 7.23 (m, 8H), 7.10 – 6.99 (m, 2H), 6.98 – 6.89 (m, 1H), 6.83 (dd, *J* = 8.0, 0.4 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 150.7, 145.4, 138.1, 135.7, 134.7, 132.8, 131.8, 130.4, 130.1, 128.8, 128.0, 126.9, 123.7, 122.9, 122.7, 119.8, 118.7, 118.4, 118.3, 113.8, 86.2, 21.6; IR (neat): 2923, 1685, 1596, 1469, 1371, 1173, 1075, 810, 671, 586; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{22}BrNNaO_4S$ 606.0345; Found 606.0331.

(4-(3-methoxyphenyl)-2-tosyl-2,4-dihydrochromeno[3,4-*c*]pyrrol-4-yl)(phenyl)methanone (2j)

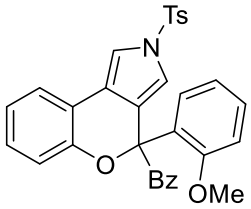


2j

The product **2j** was afforded in 63% yield (50.6 mg) according to the general procedure. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.6 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.48 – 7.40 (m, 1H), 7.40 – 7.34 (m, 2H), 7.33 – 7.21 (m, 5H), 7.11 – 6.97 (m, 4H), 6.96 – 6.88 (m, 1H), 6.85 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 3.75 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2,

159.9, 151.1, 145.2, 140.4, 135.8, 135.0, 132.6, 130.3, 130.1, 129.7, 128.6, 127.9, 126.8, 124.3, 123.6, 122.7, 120.0, 119.0, 118.6, 118.2, 113.7, 113.5, 111.8, 86.4, 55.2, 21.6; IR (neat): 3064, 2925, 2854, 2236, 1741, 1686, 1597, 1470, 1372, 1256, 760, 589; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{25}NNaO_5S$ 558.1346; Found 558.1365.

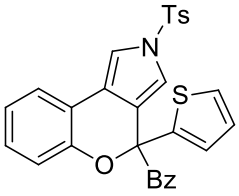
(4-(2-methoxyphenyl)-2-tosyl-2,4-dihydrochromeno[3,4-*c*]pyrrol-4-yl)(phenyl)methanone (2k)



2k

The product **2k** was afforded in 77% yield (61.9 mg) according to the general procedure. Pale yellow solid (mp 96-97 ^oC). ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.6 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.49 – 7.37 (m, 3H), 7.33 – 7.19 (m, 5H), 7.10 (d, *J* = 7.2 Hz, 1H), 7.06 – 6.99 (m, 1H), 6.98 – 6.88 (m, 2H), 6.88 – 6.76 (m, 3H), 3.61 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 155.8, 150.9, 145.2, 135.8, 135.7, 131.9, 130.2, 130.0, 129.9, 129.5, 128.7, 128.1, 127.7, 126.8, 123.4, 122.3(1), 122.2(6), 121.1, 120.7, 118.8, 118.0, 113.5, 111.9, 84.3, 55.5, 21.6; IR (neat): 2960, 2925, 1686, 1596, 1470, 1375, 1188, 1073, 757, 670, 588; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{25}NNaO_5S$ 558.1346; Found 558.1365.

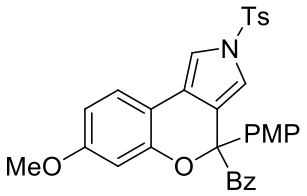
phenyl(4-(thiophen-2-yl)-2-tosyl-2,4-dihydrochromeno[3,4-*c*]pyrrol-4-yl)methanone (2l)



2l

The product **2l** was afforded in 65% yield (49.9 mg) according to the general procedure. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.6 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.52 – 7.43 (m, 1H), 7.43 – 7.35 (m, 2H), 7.35 – 7.21 (m, 5H), 7.21 – 7.12 (m, 1H), 7.11 – 7.01 (m, 1H), 7.00 – 6.80 (m, 4H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 150.6, 145.3, 143.3, 135.7, 134.7, 132.8, 130.4, 130.1, 128.8, 127.9, 126.9, 126.8, 126.7, 126.6, 123.7, 123.6, 122.8, 119.7, 118.5, 118.4, 118.1, 113.7, 84.5, 21.6; IR (neat): 2927, 1686, 1597, 1511, 1372, 1253, 1173, 1074, 822, 678, 584; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{21}NNaO_4S_2$ 534.0804; Found 534.0816.

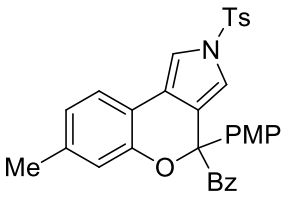
(7-methoxy-4-(4-methoxyphenyl)-2-tosyl-2,4-dihydrochromeno[3,4-*c*]pyrrol-4-yl) (phenyl)methanone (2m)



2m

The product **2m** was afforded in 66% yield (56.0 mg) according to the general procedure. Pale yellow solid (mp 201-202 ^{o}C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.49 – 7.40 (m, 1H), 7.39 – 7.19 (m, 8H), 6.99 (d, *J* = 2.0 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.50 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.36 (d, *J* = 2.4 Hz, 1H), 3.78 (s, 3H), 3.65 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 160.1, 159.6, 152.3, 145.1, 135.8, 135.2, 132.5, 131.0, 130.3, 130.0, 127.9, 127.6, 126.8, 124.4, 124.0, 120.2, 118.8, 114.0, 112.4, 111.3, 109.2, 103.5, 86.6, 55.3, 55.2, 21.6; IR (neat): 2927, 1686, 1597, 1511, 1372, 1188, 1157, 703,538; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{27}NNaO_6S$ 588.1451; Found 588.1469.

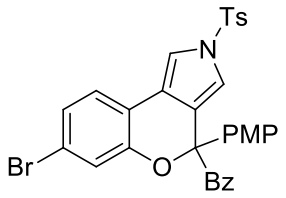
(4-(4-methoxyphenyl)-7-methyl-2-tosyl-2,4-dihydrochromeno[3,4-*c*]pyrrol-4-yl)(phenyl)methanone (2n)



2n

The product **2n** was afforded in 73% yield (60.2 mg) according to the general procedure. Pale yellow solid (mp 195-197 ^{o}C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.50 – 7.39 (m, 1H), 7.39 – 7.17 (m, 8H), 7.02 (d, *J* = 1.6 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.72 (d, *J* = 7.6 Hz, 1H), 6.66 (s, 1H), 3.76 (s, 3H), 2.38 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 159.5, 151.0, 145.1, 139.0, 135.8, 135.1, 132.5, 131.2, 130.4, 130.0, 127.8, 127.6, 126.8, 124.2, 123.5, 123.3, 120.2, 118.7, 118.6, 115.5, 113.9, 113.1, 86.3, 55.2, 21.6, 21.3; IR (neat): 2925, 1685, 1511, 1372, 1253, 1173, 1072, 814, 678, 586; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{27}NNaO_5S$ 572.1502; Found 572.1518.

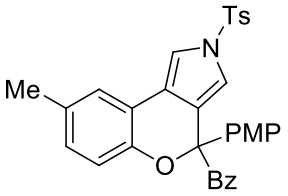
(7-bromo-4-(4-methoxyphenyl)-2-tosyl-2,4-dihydrochromeno[3,4-*c*]pyrrol-4-yl)(phenyl)methanone (2o)



2o

The product **2o** was afforded in 71% yield (65.4 mg) according to the general procedure. Pale yellow solid (mp 185-186 ^{o}C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.51 – 7.42 (m, 1H), 7.37 (d, *J* = 2.0 Hz, 1H), 7.35 – 7.19 (m, 7H), 7.09 – 6.98 (m, 3H), 6.86 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 159.7, 151.7, 145.4, 135.6, 134.9, 132.7, 130.7, 130.3, 130.1, 128.0, 127.5, 126.9, 125.7, 124.6, 123.7, 121.4, 121.2, 119.2, 118.9, 117.5, 114.1, 113.7, 86.7, 55.2, 21.6; IR (neat): 2926, 1735, 1596, 1510, 1371, 1254, 1173, 1075, 812, 672; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{24}BrNNaO_5S$ 636.0451; Found 636.0456.

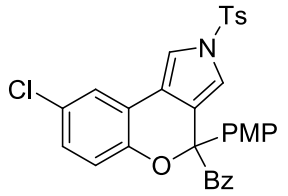
(4-(4-methoxyphenyl)-8-methyl-2-tosyl-2,4-dihydrochromeno[3,4-*c*]pyrrol-4-yl)(phenyl)methanone (2p)



2p

The product **2p** was afforded in 53% yield (43.7 mg) according to the general procedure. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.2 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.47 – 7.40 (m, 1H), 7.40 – 7.32 (m, 3H), 7.31 – 7.21 (m, 4H), 7.17 (d, *J* = 1.2 Hz, 1H), 7.00 (d, *J* = 2.0 Hz, 1H), 6.91 – 6.77 (m, 3H), 6.70 (d, *J* = 8.4 Hz, 1H), 3.78 (s, 3H), 2.39 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 159.5, 149.0, 145.1, 135.8, 135.1, 132.5, 131.9, 131.0, 130.4, 130.1, 129.3, 127.8, 127.5, 126.8, 124.8, 123.9, 120.3, 118.8, 118.2, 118.0, 114.0, 113.4, 86.3, 55.2, 21.6, 20.7; IR (neat): 2957, 2924, 2854, 1686, 1511, 1373, 1252, 1174, 1075, 814, 672, 606; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{27}NNaO_5S$ 572.1502; Found 572.1524.

(8-chloro-4-(4-methoxyphenyl)-2-tosyl-2,4-dihydrochromeno[3,4-*c*]pyrrol-4-yl)(phenyl)methanone (2q)

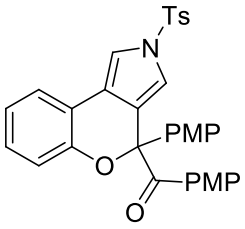


2q

The product **2q** was afforded in 61% yield (52.2 mg) according to the general procedure. Pale yellow solid (mp 215-216 ^{o}C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.51 – 7.41 (m, 1H), 7.41 – 7.21 (m, 8H), 7.01 (d, *J* = 1.6 Hz, 1H), 6.95 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 8.4 Hz, 1H), 3.79 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2,

159.7, 149.7, 145.4, 135.6, 135.0, 132.7, 130.6, 130.3, 130.2, 128.3, 127.9, 127.6, 127.4, 126.9, 124.2, 123.4, 120.1, 119.6, 119.2, 119.0, 114.1, 114.0, 86.6, 55.3, 21.6; IR (neat): 2926, 2854, 1686, 1596, 1466, 1375, 1173, 1072, 814, 673, 604; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{24}ClNNaO_5S$ 592.0956; Found 592.0964.

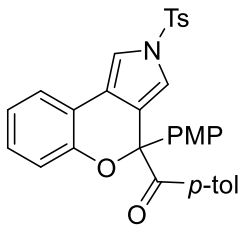
(4-methoxyphenyl)(4-(4-methoxyphenyl)-2-tosyl-2,4-dihydrochromeno[3,4-*c*]pyrrol-4-yl)methanone (2r)



2r

The product **2r** was afforded in 64% yield (54.3 mg) according to the general procedure. Pale yellow solid (mp 99-100 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.8 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.42 – 7.31 (m, 4H), 7.31 – 7.22 (m, 2H), 7.07 – 7.00 (m, 1H), 6.98 (d, *J* = 2.0 Hz, 1H), 6.94 – 6.88 (m, 1H), 6.88 – 6.81 (m, 3H), 6.77 (d, *J* = 9.2 Hz, 2H), 3.80 (s, 3H), 3.78 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 163.1, 159.4, 151.2, 145.2, 135.8, 133.0, 131.4, 130.1, 128.6, 127.5, 127.4, 126.8, 125.0, 123.6, 122.5, 120.2, 118.9, 118.6, 118.3, 114.0, 113.5, 113.2, 86.4, 55.3, 55.2, 21.6; IR (neat): 2925, 2853, 1676, 1593, 1510, 1371, 1253, 1172, 1034, 751, 603; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{27}NNaO_6S$ 588.1451; Found 588.1461.

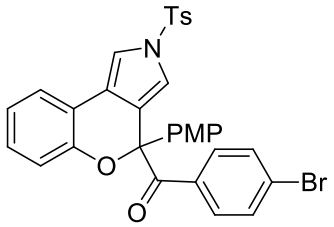
(4-(4-methoxyphenyl)-2-tosyl-2,4-dihydrochromeno[3,4-*c*]pyrrol-4-yl)(p-tolyl)methanone (2s)



2s

The product **2s** was afforded in 83% yield (68.4 mg) according to the general procedure. Pale yellow solid (mp 93-94 ^{o}C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.44 – 7.31 (m, 4H), 7.31 – 7.20 (m, 2H), 7.14 – 6.96 (m, 4H), 6.95 – 6.77 (m, 4H), 3.77 (s, 3H), 2.39 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 159.4, 151.2, 145.2, 143.4, 135.8, 132.3, 131.2, 130.7, 130.1, 128.6, 127.4, 126.8, 124.7, 123.6, 122.5, 120.2, 118.8, 118.5, 118.3, 114.0, 113.5, 86.4, 55.2, 21.6; IR (neat): 2925, 1685, 1605, 1470, 1372, 1253, 1173, 1075, 759, 670, 603; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{27}NNaO_5S$ 572.1502; Found 572.1527.

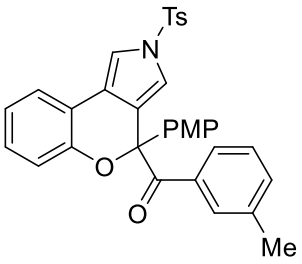
(4-bromophenyl)(4-(4-methoxyphenyl)-2-tosyl-2,4-dihydrochromeno[3,4-*c*]pyrrol-4-yl)methanone (2t)



2t

The product **2t** was afforded in 65% yield (60.0 mg) according to the general procedure. Pale yellow solid (mp 74-75 ^{o}C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.64 (m, 4H), 7.47 – 7.22 (m, 8H), 7.09 – 7.01 (m, 1H), 7.01 – 6.96 (m, 1H), 6.96 – 6.90 (m, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 1H), 3.79 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 159.7, 151.0, 145.3, 135.8, 133.7, 132.0, 131.2, 130.6, 130.1, 128.7, 127.9, 127.4, 126.9, 124.4, 123.7, 122.8, 120.0, 118.8, 118.5, 118.2, 114.1, 113.7, 86.3, 55.3, 21.6; IR (neat): 2926, 1686, 1583, 1511, 1371, 1252, 1173, 1071, 763, 670, 539; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{24}BrNNaO_5S$ 636.0451; Found 636.0473.

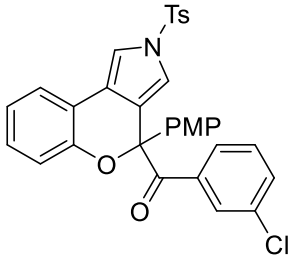
(4-(4-methoxyphenyl)-2-tosyl-2,4-dihydrochromeno[3,4-*c*]pyrrol-4-yl)(*m*-tolyl)methanone (2u)



2u

The product **2u** was afforded in 69% yield (57.0 mg) according to the general procedure. Light yellow solid (mp 159.1-161.1 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0, 2H), 7.67 – 7.63 (m, 2H), 7.43 – 7.29 (m, 4H), 7.29 – 7.19 (m, 3H), 7.18 – 7.09 (m, 1H), 7.07 – 6.95 (m, 2H), 6.94 – 6.76 (m, 4H), 3.76 (s, 3H), 2.38 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.8, 159.5, 151.2, 145.1, 137.6, 135.9, 135.2, 133.3, 131.2, 130.7, 130.1, 128.6, 127.7, 127.6, 127.5, 126.8, 124.6, 123.6, 122.5, 120.2, 118.9, 118.5, 118.3, 114.0, 113.5, 86.5, 55.2, 21.6, 21.3; IR (neat) : 3135, 3064, 2923, 1604, 1597, 1470, 1169, 1080, 672, 602, 533; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{27}NNaO_5S$ 572.1502; Found 572.1519.

(3-chlorophenyl)(4-(4-methoxyphenyl)-2-tosyl-2,4-dihydrochromeno[3,4-*c*]pyrrol-4-yl)methanone (2v)

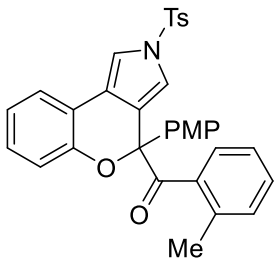


2v

The product **2v** was afforded in 78% yield (66.0 mg) according to the general procedure. Light yellow solid (mp 168.0-169.3 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.74 – 7.70 (m, 3H), 7.46 – 7.29 (m, 5H), 7.29 – 7.14 (m, 3H), 7.08 – 6.97 (m, 2H), 6.94 – 6.76 (m, 4H), 3.77 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.4, 159.7, 151.0, 145.2, 136.8, 135.8, 134.0, 132.4, 130.6, 130.2, 130.1, 129.1, 128.7, 128.5, 127.4, 126.8, 124.2, 123.6, 122.7, 120.0, 118.9, 118.5, 118.2,

114.2, 113.6, 86.4, 55.2, 21.5; IR (neat) : 3138, 3068, 2929, 1690, 1515, 1376, 1251, 1178, 733, 663, 604; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{24}ClNNaO_5S$ 592.0956; Found 592.0969.

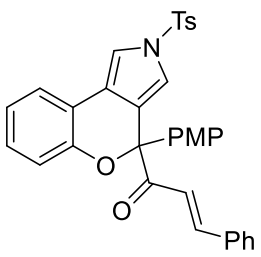
(4-(4-methoxyphenyl)-2-tosyl-2,4-dihydrochromeno[3,4-*c*]pyrrol-4-yl)(o-tolyl)methanone (2w)



2w

The product **2w** was afforded in 50% yield (41.0 mg) according to the general procedure. Light yellow solid (mp 53.2-54.6 ℃). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.44 – 7.14 (m, 9H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.06 – 6.94 (m, 2H), 6.91 – 6.78 (m, 3H), 6.67 (d, *J* = 8.0 Hz, 1H), 3.76 (s, 3H), 2.39 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.2, 159.6, 151.2, 145.2, 137.5, 137.1, 135.9, 130.6(7), 130.6(5), 130.1, 130.0, 128.6, 128.0, 127.8, 126.9, 124.4, 124.1, 123.4, 122.4, 120.3, 118.8, 118.5, 118.4, 113.9, 113.6, 86.3, 55.2, 21.5, 19.7; IR (neat) : 3137, 3062, 2929, 1698, 1507, 1375, 1248, 1074, 735, 670, 602; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{27}NNaO_5S$ 572.1502; Found 572.1521.

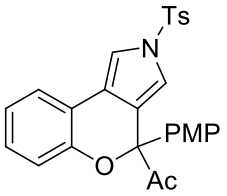
(*E*)-1-(4-(4-methoxyphenyl)-2-tosyl-2,4-dihydrochromeno[3,4-*c*]pyrrol-4-yl)-3-phenylprop-2-en-1-one (2x)



2x

The product **2x** was afforded in 33% yield (57.8 mg, 0.3 mmol scale) according to the general procedure. Pale yellow solid (mp 76-77 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 16.0 Hz, 1H), 7.63 – 7.46 (m, 3H), 7.44 – 7.30 (m, 8H), 7.27 – 7.21 (m, 2H), 7.14 (d, *J* = 3.5 Hz, 2H), 7.01 – 6.87 (m, 1H), 6.78 (d, *J* = 8.5 Hz, 2H), 3.72 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 182.2, 159.6, 151.2, 145.2, 135.7, 134.6, 130.7, 130.4, 130.1, 128.8, 128.7, 128.6, 128.0, 126.9, 123.6, 122.8, 122.5, 120.5, 119.9, 118.5, 118.4, 113.9, 113.5, 85.4, 55.2, 21.6; IR (neat): 3052, 2925, 2848, 1686, 1608, 1508, 1330, 1265, 740, 737, 670; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{27}NNaO_5S$ 584.1502; Found 584.1509.

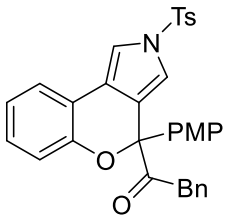
1-(4-(4-methoxyphenyl)-2-tosyl-2,4-dihydrochromeno[3,4-*c*]pyrrol-4-yl)ethanone (2y)



2y

The product **2y** was afforded in 55% yield (39.1 mg) according to the general procedure. Pale yellow solid (mp 77-79 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.46 – 7.21 (m, 7H), 7.22 – 7.06 (m, 2H), 7.00 – 6.87 (m, 1H), 6.77 (d, *J* = 8.4 Hz, 2H), 3.73 (s, 3H), 2.40 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.0, 159.5, 151.1, 145.3, 135.7, 130.1, 128.7, 127.7, 127.0, 123.6, 122.6, 122.5, 120.2, 118.4, 118.2, 113.8, 113.5, 85.8, 55.2, 25.5, 21.6; IR (neat): 2924, 2853, 1721, 1606, 1508, 1373, 1256, 1173, 1074, 811, 671, 603; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{23}NNaO_5S$ 496.1189; Found 496.1217.

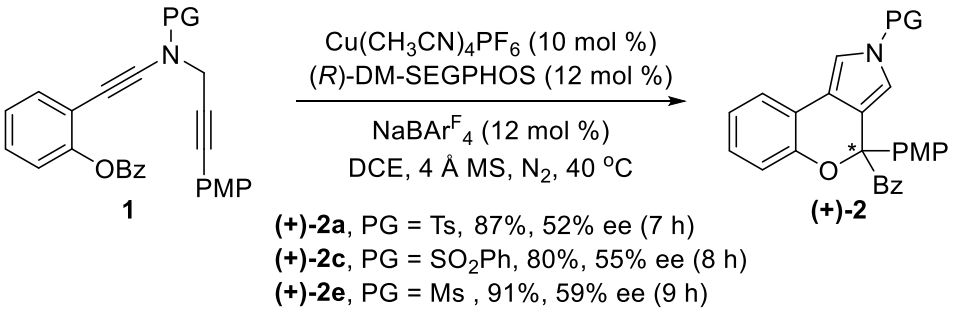
1-(4-(4-methoxyphenyl)-2-tosyl-2,4-dihydrochromeno[3,4-*c*]pyrrol-4-yl)-2-phenyl ethan-1-one (2z)



2z

The product **2z** was afforded in 31% yield (51.0 mg, 0.3 mmol scale) according to the general procedure. Pale yellow solid (55-57 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.32 (m, 3H), 7.31 – 7.14 (m, 9H), 7.00 (d, *J* = 7.0 Hz, 2H), 6.98 – 6.92 (m, 1H), 6.76 (d, *J* = 8.5 Hz, 2H), 4.20 – 4.03 (m, 2H), 3.73 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.9, 159.5, 151.0, 145.3, 135.7, 133.7, 130.1, 130.0, 129.8, 128.8, 128.3, 127.7, 127.0, 126.8, 123.6, 122.6, 122.4, 120.1, 118.3, 118.2, 113.8, 113.5, 86.1, 55.2, 43.9, 21.6; IR (neat): 2955, 2920, 2850, 1725, 1606, 1507, 1374, 1254, 736, 703, 669; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{27}NNaO_5S$ 572.1502; Found 572.1505.

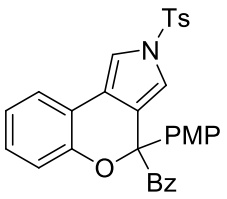
Synthesis of chiral dihydrochromeno[3,4-*c*]pyrrols (+)-2



To an oven-dried Schlenk tube were added $Cu(MeCN)_4PF_6$ (0.02 mmol, 7.4 mg), $NaBAr^F_4$ (0.024 mmol, 21.2 mg), (*R*)-DM-SEGPHOS (0.024 mmol, 17.3 mg) and 4 Å MS (45.0 mg) under N_2 atmosphere. After injecting DCE (1.5 mL) into the Schlenk tube, the mixture was stirred at 25 °C for 1 h. Then the solution of diyne **1** (0.2 mmol) in DCE (1.5 mL) was introduced into the reaction system, and the mixture was stirred at 40 °C. The progress of the reaction was monitored by TLC. Upon completion, the mixture was concentrated under reduced pressure, and the residue was purified by

column chromatography on silica gel (eluent: hexanes/ EtOAc) to give the desired chiral dihydrochromeno[3,4-*c*]pyrrole (+)-**2**.

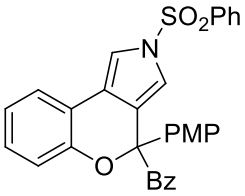
chiral dihydrochromeno[3,4-*c*]pyrrole (+)-2a



(+)-2a

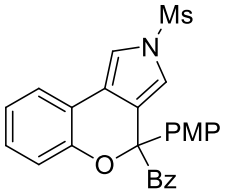
Compound (+)-**2a** was prepared in 87% yield (93.1 mg) according to the above procedure. Pale yellow solid. $[\alpha]_D^{20}$ = +101.5 º (c = 1.0, $CHCl_3$). 52% ee (determined by HPLC: Chiralcel IC Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; TR = 11.75 min (minor), 14.29 min (major)).

chiral dihydrochromeno[3,4-*c*]pyrrole (+)-2c



(+)-2c

Compound (+)-**2c** was prepared in 80% yield (62.6 mg) according to the above procedure. Pale yellow solid. $[\alpha]_D^{20}$ = +53.3 º (c = 1.0, $CHCl_3$). 55% ee (determined by HPLC: Chiralcel IC Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; TR = 9.77 min (minor), 11.65 min (major)).



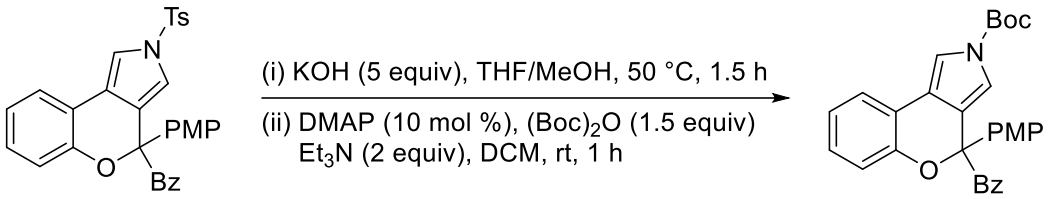
(+)2e

Compound (+)-**2e** was prepared in 91% yield (62.7 mg) according to the above procedure. Pale yellow solid. $[\alpha]_D^{20}$ = +150.2 º (c = 1.0, $CHCl_3$). 59% ee (determined

by HPLC: Chiralcel IC Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; TR = 11.25 min (major), 12.22 min (minor)).

5. Product Transformations

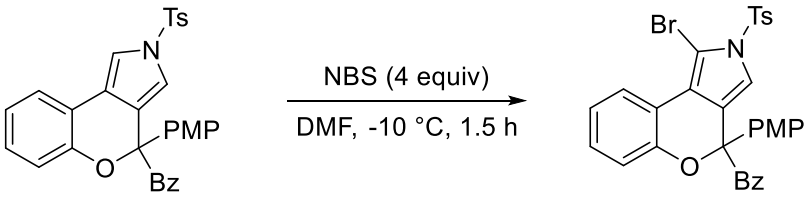
tert-butyl 4-benzoyl-4-(4-methoxyphenyl)chromeno[3,4-*c*]pyrrole-2(4*H*)-carboxylate (3)



2a **3**, 80% (2 steps)

The product **3** was prepared in 80% yield (77.0 mg) according to the known procedure (0.2 mmol scale).[4] Pale yellow solid (mp 78-79 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.6 Hz, 2H), 7.58 – 7.41 (m, 5H), 7.38 – 7.28 (m, 2H), 7.11 – 6.99 (m, 2H), 6.99 – 6.88 (m, 3H), 6.84 (d, *J* = 8.0 Hz, 1H), 3.80 (s, 3H), 1.61 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 159.4, 151.1, 148.6, 135.3, 132.5, 131.6, 130.5, 128.0, 127.8, 127.4, 123.5, 123.0, 122.5, 119.3, 118.2, 118.1, 117.7, 113.9, 113.0, 86.5, 84.3, 55.2, 27.9; IR (neat): 2929, 1744, 1686, 1511, 1396, 1270, 1173, 1033, 980, 770, 695; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{27}NNaO_5$ 504.1781; Found 504.1803.

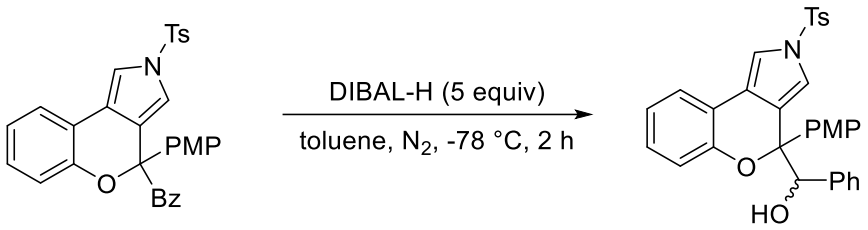
(1-bromo-4-(4-methoxyphenyl)-2-tosyl-2,4-dihydrochromeno[3,4-*c*]pyrrol-4-yl)(phenyl)methanone (4)



2a **4**, 93%

The product **4** was prepared in 93% yield (99.4 mg) according to the known procedure (0.2 mmol scale).[6] Brown solid (mp 167-169 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.88 (d, *J* = 7.5 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.50 – 7.43 (m, 3H), 7.34 – 7.28 (m, 5H), 7.06 – 6.99 (m, 1H), 6.97 – 6.91 (m,

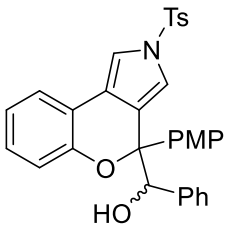
3H), 6.77 (d, *J* = 8.0 Hz, 1H), 3.82 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.4, 159.7, 151.6, 145.7, 134.9(2), 134.8(9), 132.7, 130.4, 130.2, 130.0, 128.9, 127.9, 127.3, 124.4, 123.6, 122.4, 121.9, 119.1, 118.5, 118.4, 114.2, 95.5, 86.1, 55.3, 21.7; IR (neat):2956, 2925, 2853, 1684, 1464, 1379, 1249, 1104, 701, 692, 668; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{24}BrNNaO_5S$ 638.0430; Found 638.0431.



2a **5**, 71%, d.r. = 3:2

To a dry 10 mL Schlenk tube with a magnetic stir bar were added compound **2a** (0.3 mmol, 160.8 mg) and toluene (3 mL) under N_2 atmosphere. After cooling to -78 ℃, DIBAL-H (1.5 mmol, 1.5 mL, 1 M in toluene) was slowly added, and the reaction was stirred at -78 ℃ for 2 h. The progress of the reaction was monitored by TLC. Upon completion, the reaction was quenched with saturated ammonium chloride solution (aq), extracted with ethyl acetate, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane/EtOAc) to give product **5** in 71% yield with the d.r. of 3:2.

(4-(4-methoxyphenyl)-2-tosyl-2,4-dihydrochromeno[3,4-*c*]pyrrol-4-yl)(phenyl)methanol (5)

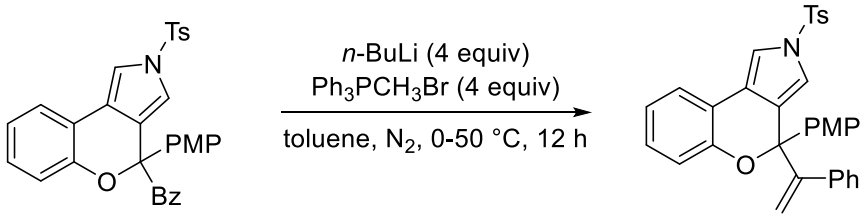


5

The product **5** was prepared in 71% yield (0.3 mmol scale, 114 mg, 3:2 d.r.). Pale yellow solid (mp 67-69 ℃). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.70 (m, 3H, major + minor), 7.46 (d, *J* = 2.0 Hz, 0.6H, minor), 7.36 – 7.28 (m, 5H, major + minor), 7.28

– 7.21 (m, 4H, major + minor), 7.20 – 7.14 (m, 4H, major + minor), 7.13 – 7.03 (m, 6H, major + minor), 7.01 – 6.93 (m, 3.6H, major + minor), 6.89 – 6.79 (m, 2H, major + minor), 6.74 – 6.67 (m, 3H, major + minor), 5.30 (d, *J* = 4.0 Hz, 1H, major), 5.16 (d, *J* = 4.5 Hz, 0.6H, minor), 3.73 (s, 3H, major), 3.72 (s, 1.8H, minor), 2.78 (d, *J* = 4.0 Hz, 1H, major), 2.46 – 2.40 (m, 5.4H, major + minor). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2(1), 159.2(0), 151.3, 145.2, 145.1, 138.6, 137.9, 135.9, 135.8, 132.2, 130.6, 130.0, 129.2, 128.7, 128.5, 128.4, 128.2, 127.9, 127.4, 127.2(1), 127.1(6), 126.8(4), 126.7(5), 123.9, 123.2(8), 123.2(6), 122.7, 122.0, 121.9, 121.5, 121.3, 118.3, 118.2(3), 118.1(9), 118.1, 117.7(4), 117.7(1), 113.3(2), 113.2(9), 113.1, 113.0, 84.1, 83.8, 79.5, 79.4, 55.1(4), 55.1(2), 21.6; IR (neat): 3569, 2956, 2930, 1733, 1609, 1374, 1265, 1188, 1037, 737, 703; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{32}H_{28}NO_5S$ 538.1683; Found 538.1690.

4-(4-methoxyphenyl)-4-(1-phenylvinyl)-2-tosyl-2,4-dihydrochromeno[3,4-*c*]pyrrole (6)



2a **6**, 41%

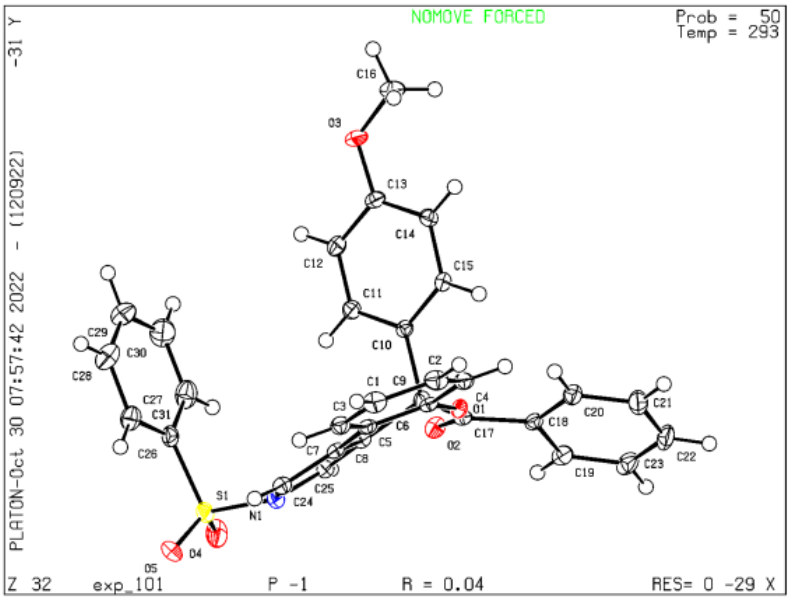
The product **6** was prepared in 41% yield (0.1 mmol scale, 21.9 mg) according to the known procedure.[7] Pale yellow solid (50-51 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 9.0 Hz, 2H), 7.38 – 7.30 (m, 2H), 7.28 – 7.21 (m, 2H), 7.20 – 7.15 (m, 1H), 7.13 – 7.05 (m, 4H), 7.04 – 6.98 (m, 1H), 6.92 – 6.80 (m, 3H), 6.73 (d, *J* = 2.0 Hz, 1H), 6.68 (dd, *J* = 8.0, 0.5 Hz, 1H), 5.46 (d, *J* = 0.5 Hz, 1H), 4.95 (d, *J* = 0.5 Hz, 1H), 3.79 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.2, 152.0, 150.7, 145.0, 139.8, 136.0, 133.8, 130.0, 128.6, 128.4(9), 128.4(8), 127.8, 127.4, 127.1, 126.7, 123.3, 121.9, 121.4, 119.9, 118.9, 118.7, 118.4, 113.5(2), 113.5(0), 83.7, 55.2, 21.6; IR (neat): 3052, 2928, 2054, 1609, 1509, 1375, 1285, 1175,

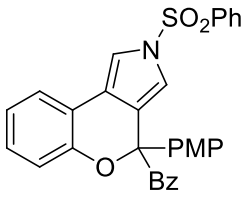
742, 737, 703; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{33}H_{27}NNaO_4S$ 556.1553; Found 556.1558.

6. Crystal Data

Crystal data and structure refinement for 2c. CCDC Number = 2216587

ORTEP drawing of **2c** (thermal ellipsoids set at 50% probability). Recrystallization from *n*-hexane/DCM afforded single crystals suitable for X-ray diffraction analysis.





Bond precision: C-C = 0.0020 A Wavelength=1.54184

Cell: a=9.3096(2) b=10.6135(2) c=12.8982(2)
alpha=82.485(2) beta=82.467(1) gamma=87.667(2)
Temperature: 293 K

	Calculated	Reported
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Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C31 H23 N O5 S	C31 H23 N O5 S
Sum formula	C31 H23 N O5 S	C31 H23 N O5 S
Mr	521.56	521.56
Dx,g cm-3	1.383	1.383
Z	2	2
Mu (mm-1)	1.512	1.512
F000	544.0	544.0
F000'	546.28	
h,k,lmax	11,13,15	11,13,15
Nref	4878	4622
Tmin,Tmax	0.913,0.927	0.849,1.000
Tmin'	0.860	

Correction method= # Reported T Limits: Tmin=0.849 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.948 Theta(max)= 71.455

R(reflections)= 0.0361(4429) wR2(reflections)= 0.0948(4622)

S = 1.080 Npar= 344

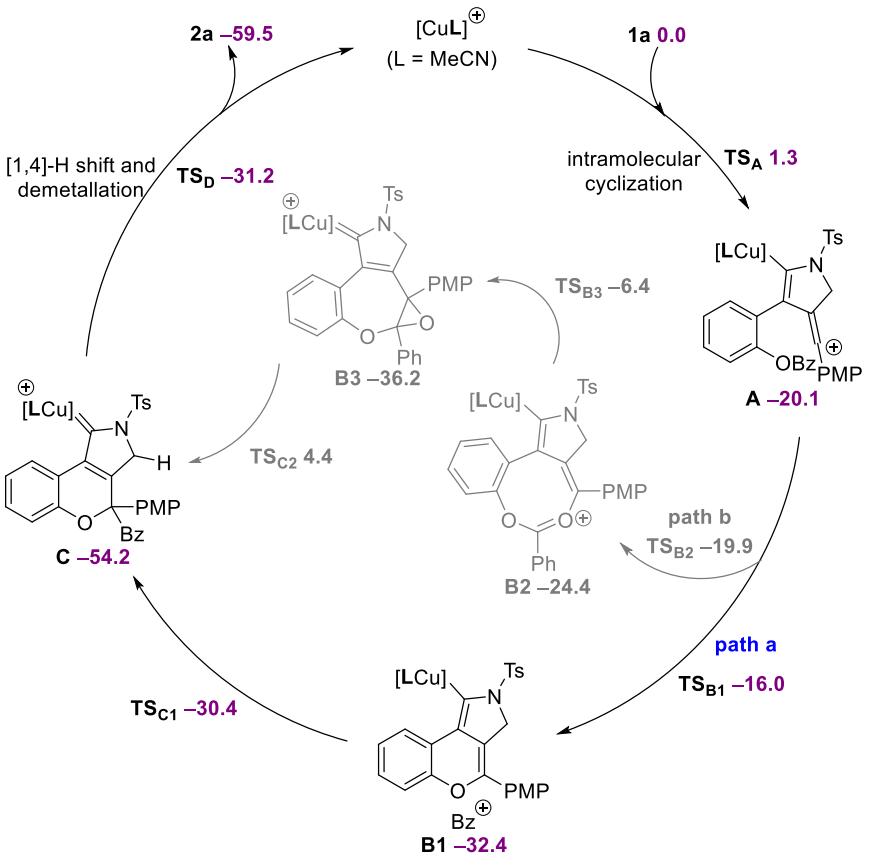
7. Computational Studies

All calculations were performed using Gaussian16 package.[8] Geometry optimizations and vibrational analysis were conducted under the B3LYP-D3(BJ) level of theory[9,10] with the LANL2DZ basis set[11,12] for Cu atom, and the 6-31G(d) basis set[13] for C, H, O, N, P and S atom. Electronic energy of all the intermediates and transition states were recomputed at the B3LYP-D3(BJ)/def2TZVPP[14,15] level of theory. All local minimums were confirmed with no imaginary frequency and all transition states had only one imaginary frequency. And every transition state was checked by intrinsic reaction coordinate (IRC) analysis. The SMD solvation model[16] with dichloromethane was used for single point calculations. The ball stick models of molecules were drawn by CYLview 1.0.[17]

To correct the Gibbs free energies under 1 atm to the standard state in solution (1 mol/L), a correction of RTln(cs/cg) is added to energies of all species. cs stands for the standard molar concentration in solution (1 mol/L), cg stands for the standard molar concentration in gas phase (0.040876 mol/L), and R is the gas constant. For calculated intermediates at the standard state of 1 mol/L at 298.15 K, the correction value equaling to 1.89 kcal/mol was used.

Density functional theory (DFT) calculations were carried out to demonstrate the reaction mechanism (Scheme S1). Firstly, the copper (I) complex activates the triple bond of ynamide moiety to facilitate an intramolecular cyclization, delivering vinyl cation intermediate **A** with a free energy barrier of 1.3 kcal/mol. Then, intermediate **A** can be trapped by the ester moiety through two different pathways. In path a, the nucleophilic attack of oxygen onto vinyl cation **A** affords the 6-membered intermediate **B1** and releases the benzoyl cation species with a free energy barrier of 4.1 kcal/mol. Further capture of benzoyl cation forms the copper carbene intermediate **C** with a free energy barrier of 2.0 kcal/mol. Path b involves the formation of 8-membered intermediate **B2** through the addition of carbonyl group onto vinyl cation **A**, subsequent generation of epoxide intermediate **B3** through ring contraction, as well as ring-opening of epoxide to give intermediate **C** with a free energy barrier of 40.6 kcal/mol. Therefore, path a is kinetically and thermodynamically more favourable

than path b. The attempt to locate a transition state for the formation of intermediate **C** via a concerted [1,2]-acyl shift was unsuccessful. Finally, the substrate-assisted [1,4]-H shift and demetallation take place to produce the desired product **2a** and regenerate the copper catalyst.



Scheme S1. Plausible reaction mechanism for the formation of **2a**. Relative free energies (ΔG, in kcal/mol) of the key intermediates and transition states are computed at the SMD(DCM)-B3LYP-D3(BJ)/def2TZVPP//B3LYP-D3(BJ)/6-31G(d)-LANL2DZ level of theory at 298.15 K.

Cartesian Coordinates and Thermochemical Data (Energies in Hartree)

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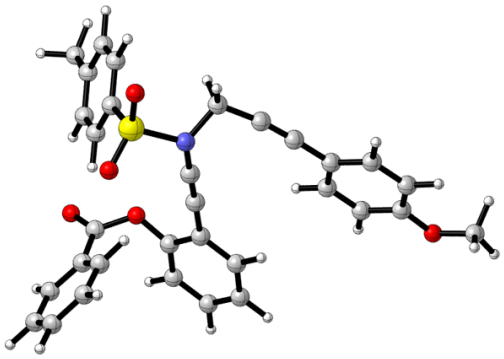
Electronic Energy(Hartree) = -2064.240089
Imaginary Frequency(cm^{-1}) = NO



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TS_A
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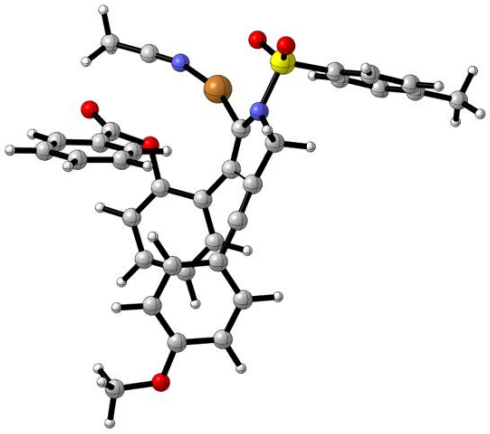
Electronic Energy(Hartree) = -3837.550074
Imaginary Frequency(cm^{-1}) = 320.40*i*



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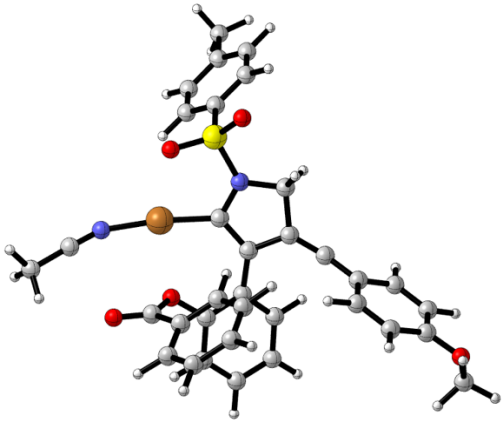
Imaginary Frequency(cm^{-1}) = NO



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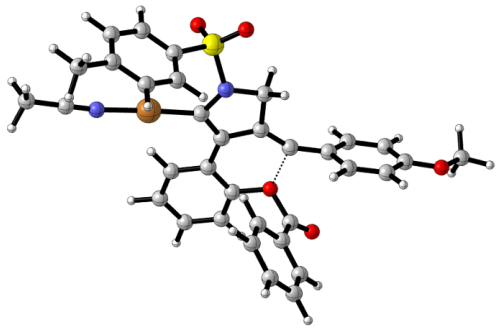

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C	5.94081600	-1.05875600	1.77071800
H	4.53502800	-0.63838500	3.35386200
H	7.06799800	-1.61763400	0.02193700
C	7.13479600	-0.56242700	2.54732700
H	6.97386100	0.45561000	2.92222700
H	7.32423200	-1.19541300	3.42227500
H	8.04334500	-0.56916900	1.93705600
C	-0.26392200	-1.98661700	-0.42065800
H	-0.36166800	-2.67716800	-1.26567600
H	-0.60159800	-2.49258600	0.48449800
C	-0.98253900	-0.67634400	-0.69678700
C	-2.29670800	-0.59095800	-0.64731800
C	-3.54654000	-1.16950100	-0.37164800
C	-4.40583100	-1.58000500	-1.41815900
C	-3.98865600	-1.31678600	0.97218100
C	-5.64350800	-2.13459200	-1.14870200
H	-4.08113000	-1.44820800	-2.44486200
C	-5.21386000	-1.88004600	1.24817000
H	-3.34290600	-0.98450300	1.77824900
C	-6.05614800	-2.29049600	0.19083600
H	-6.28364000	-2.44264100	-1.96553800

H	-5.56412700	-2.01548300	2.26535800
O	-7.22875900	-2.81609400	0.56328400
C	-8.15272700	-3.25372500	-0.43817600
H	-7.71848400	-4.05507100	-1.04551500
H	-9.01549300	-3.63249800	0.10842600
H	-8.45703500	-2.41912200	-1.07875100
C	1.28714700	-0.19247300	-0.71342900
C	0.03592200	0.33570300	-0.95691000
C	-0.30441300	1.67576600	-1.42823300
C	-1.63437500	2.11836200	-1.45042200
C	0.64863500	2.58305600	-1.92558600
C	-2.02348300	3.36491700	-1.92555000
C	0.29267400	3.84874500	-2.37821400
H	1.68736600	2.27071200	-1.96857000
C	-1.04589100	4.24777800	-2.38023700
H	-3.07459000	3.63173000	-1.94429800
H	1.06051300	4.52033100	-2.74944700
H	-1.33264000	5.22756300	-2.74709100
O	-2.65085100	1.23982400	-0.99524400
C	-3.66307400	1.78912500	-0.10303800
O	-4.77569100	1.85404700	-0.53620800
C	-3.19804700	2.14097300	1.24352700
C	-4.14377100	2.73454600	2.09867400
C	-1.89908500	1.87549600	1.70785000
C	-3.79175700	3.06415200	3.40200100
H	-5.14296100	2.92527400	1.72299700
C	-1.55801500	2.20416700	3.01637600
H	-1.16116100	1.41553900	1.06465900
C	-2.49840700	2.79872400	3.86195700
H	-4.52128900	3.52558400	4.05968400
H	-0.55509700	1.99796700	3.37685400
H	-2.22380100	3.05535200	4.88069500
Cu	3.03778400	0.58988000	-0.71557500
N	4.74651300	1.40904900	-0.64618500
C	5.84087800	1.76192900	-0.52113000
C	7.22068000	2.19365000	-0.36056000
H	7.70134000	1.59561200	0.41980600
H	7.76369300	2.06025100	-1.30146200
H	7.25303900	3.24982600	-0.07584100

TS_{B2}
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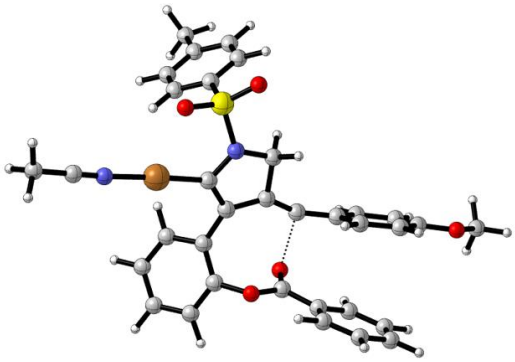
Electronic Energy(Hartree) = -3837.584518
Imaginary Frequency(cm^{-1}) = 100.25*i*



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O	3.78484400	0.72870100	-2.12771800
O	2.10533700	2.57918500	-2.72541600
C	3.26561000	2.62448900	-0.35467200
C	4.07548300	2.02019700	0.61180600
C	2.81545000	3.93678900	-0.20521500
C	4.43225800	2.74898100	1.74022500
H	4.42764500	1.00418600	0.47142500
C	3.18714300	4.65030900	0.93318800
H	2.20530300	4.38945400	-0.97897800
C	3.99650900	4.07225100	1.91938900
H	5.06547900	2.28982800	2.49448100
H	2.84820500	5.67528800	1.05362500
C	4.42017500	4.85848300	3.13357200
H	4.42069800	4.23452600	4.03327500
H	5.43858600	5.24717000	3.00692700
H	3.76087400	5.71349200	3.30819800
C	0.18526300	1.36195400	-0.79646100
H	0.35160700	2.30495000	-0.26433000
H	-0.41699900	1.55942200	-1.68566800
C	-0.45147200	0.29096600	0.11266900
C	-1.67423200	0.58985000	0.52781000
C	-2.91450700	1.12546000	0.20832500
C	-3.65749100	1.88437300	1.15102200
C	-3.48557800	0.90150900	-1.08268800
C	-4.89627100	2.40291500	0.83272600
H	-3.23657200	2.03513700	2.13927500
C	-4.70554100	1.43691000	-1.41585800
H	-2.93631200	0.30109800	-1.79961600

C	-5.42914600	2.18386400	-0.45831700
H	-5.44806400	2.97389200	1.56871100
H	-5.15124900	1.28331400	-2.39197400
O	-6.61640900	2.63799800	-0.86682000
C	-7.42424100	3.41572600	0.02475100
H	-6.90473700	4.33344100	0.31892500
H	-8.32161700	3.66445900	-0.54015000
H	-7.69372100	2.83428100	0.91275900
C	1.67649300	-0.44670900	-0.44893200
C	0.54887400	-0.74337400	0.30220400
C	0.52817400	-1.92515100	1.18873100
C	-0.46614700	-2.90552600	1.20877800
C	1.63921300	-2.15292100	2.02402000
C	-0.37911600	-4.05678300	1.98178800
C	1.75390600	-3.30184000	2.80230900
H	2.41369100	-1.39382900	2.05804400
C	0.74410300	-4.26485200	2.77976000
H	-1.18820200	-4.77839700	1.94181500
H	2.62569500	-3.43855700	3.43485600
H	0.82005500	-5.16257800	3.38470600
O	-1.61909400	-2.79430400	0.40260300
C	-2.56368500	-1.94171600	0.83967300
O	-2.34160800	-1.12302500	1.73614800
C	-3.84749800	-2.04971600	0.13316300
C	-3.96775600	-2.73968300	-1.08395200
C	-4.95789800	-1.39386400	0.68704000
C	-5.18814300	-2.74380000	-1.75272800
H	-3.10574100	-3.25004200	-1.49840800
C	-6.17852900	-1.41876000	0.02263800
H	-4.84138200	-0.87159100	1.62920100
C	-6.29174400	-2.08470800	-1.20107000
H	-5.28360500	-3.26362100	-2.70076500
H	-7.04096300	-0.91862000	0.45208100
H	-7.24336300	-2.09695000	-1.72414900
Cu	3.30415800	-1.42264800	-0.74364300
N	4.87342600	-2.44584900	-1.03909100
C	5.83742500	-3.02475600	-1.31169200
C	7.04986000	-3.75072500	-1.66000400
H	7.68644000	-3.85960200	-0.77648500
H	6.79145200	-4.74405000	-2.03991100
H	7.59866300	-3.20312600	-2.43256400

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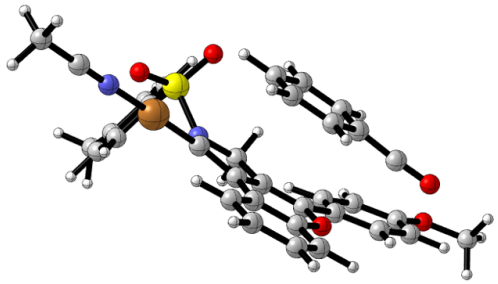
Electronic Energy(Hartree) = -3837.606107
Imaginary Frequency(cm^{-1}) = NO



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O	-3.63276300	0.71226600	0.86575800
O	-1.69334500	1.59481500	2.25176500
C	-2.55118300	3.07384600	0.23832700
C	-3.10311900	3.18963200	-1.04164300
C	-2.15367700	4.19268600	0.96760100
C	-3.24813300	4.45611700	-1.59285100
H	-3.40501200	2.30377100	-1.59061200
C	-2.31141600	5.45435800	0.39541700
H	-1.73177400	4.07046900	1.95874300
C	-2.85892900	5.60648300	-0.88437000
H	-3.67119200	4.56024900	-2.58805900
H	-2.00503900	6.33411000	0.95366900
C	-3.04843400	6.97321100	-1.49037700
H	-2.72879600	6.99201900	-2.53771600
H	-4.10672800	7.26204000	-1.46969100
H	-2.48551400	7.73599000	-0.94554200
C	0.06501500	1.21638500	-0.27650000
H	0.09753400	2.02947500	-1.01138400
H	0.42367700	1.60282100	0.68270300
C	0.78664000	-0.02876700	-0.72263900
C	2.12464600	-0.26216500	-0.86712400
C	3.25579600	0.62169700	-0.62264200
C	4.56565900	0.10504100	-0.60576300
C	3.09783400	2.00210600	-0.36062900
C	5.66539500	0.90633500	-0.31398400
H	4.72958400	-0.93864400	-0.83975700
C	4.18512700	2.80584800	-0.07154900
H	2.12307100	2.46756000	-0.40918500
C	5.48364200	2.26796200	-0.03615100
H	6.65436200	0.46460900	-0.31394200

H	4.06120500	3.86590700	0.12201200
O	6.47387500	3.13706500	0.26257900
C	7.81518700	2.65837400	0.28213300
H	8.43341500	3.51996800	0.53442200
H	7.94668400	1.87805700	1.04162600
H	8.11089600	2.26921100	-0.69948700
C	-1.45090800	-0.65071900	-0.44369100
C	-0.19530900	-1.06797400	-0.86805900
C	0.24749400	-2.36555100	-1.32053100
C	1.63430600	-2.54221200	-1.48001100
C	-0.58342000	-3.46858900	-1.58093700
C	2.18373300	-3.76402400	-1.86681100
C	-0.04931200	-4.69174300	-1.96753600
H	-1.65680200	-3.34381200	-1.47808300
C	1.33681100	-4.84181400	-2.11094800
H	3.26003700	-3.84687800	-1.97820900
H	-0.70840200	-5.53058500	-2.16794400
H	1.75487400	-5.79404000	-2.42130100
O	2.53484400	-1.53840900	-1.20842000
C	3.54896100	-2.59143500	1.28629300
O	4.63901000	-2.88621000	1.03657900
C	2.26559700	-2.32316700	1.65210600
C	1.88605900	-1.00592400	2.07952900
C	1.27486100	-3.35347400	1.49289200
C	0.56081100	-0.75985300	2.36406700
H	2.64364100	-0.24038700	2.19688500
C	-0.03841500	-3.05344300	1.76783700
H	1.57067000	-4.34073200	1.15991800
C	-0.41275900	-1.75438500	2.16119900
H	0.24731200	0.22031900	2.70486500
H	-0.79415700	-3.82055700	1.63985400
H	-1.44879500	-1.53192400	2.38694600
Cu	-3.16736400	-1.46060400	-0.17821000
N	-4.81783300	-2.37164900	0.04270700
C	-5.87012100	-2.82438600	0.20773000
C	-7.19572800	-3.38832600	0.41639500
H	-7.67129500	-3.58758500	-0.54900000
H	-7.11908300	-4.32463600	0.97781700
H	-7.81253800	-2.68175700	0.98053400

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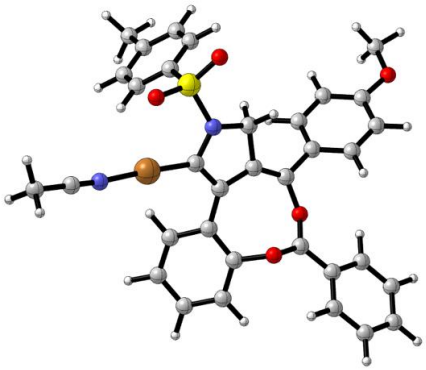
Electronic Energy(Hartree) = -3837.593933
Imaginary Frequency(cm^{-1}) = NO



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O	3.96413600	0.23229400	-1.74883200
O	2.51037500	2.13434200	-2.67982300
C	3.28682500	2.23764100	-0.15804700
C	3.92989500	1.64678100	0.93351000
C	2.86295700	3.56661500	-0.11934300
C	4.14816600	2.40793800	2.07599200
H	4.26238100	0.61597500	0.87815000
C	3.09287600	4.31156700	1.03611900
H	2.38263800	4.00594300	-0.98668900
C	3.73591300	3.74887800	2.14628100
H	4.65300900	1.96039100	2.92771900
H	2.77508900	5.34970300	1.07255100
C	4.01097700	4.56936100	3.38040200
H	3.87729700	3.97778200	4.29190100
H	5.04571900	4.93482900	3.37894300
H	3.35424900	5.44220400	3.43690000
C	0.24451400	1.10283600	-0.97031100
H	0.39185800	2.01342900	-0.38177200
H	-0.17442300	1.38909500	-1.93818300
C	-0.59990200	0.05642100	-0.25084400
C	-1.91510900	0.34853600	-0.02429900
C	-2.53894700	1.67194600	-0.16825500
C	-2.03128500	2.79362200	0.50129000
C	-3.68553700	1.84112400	-0.97189100
C	-2.61787300	4.04959500	0.36547500
H	-1.17520200	2.67980600	1.16011100
C	-4.28579100	3.08093500	-1.10784300
H	-4.09725700	0.98832100	-1.50375000
C	-3.75374900	4.20027700	-0.44382800

H	-2.20150500	4.89273500	0.90286200
H	-5.16217100	3.22006400	-1.73172600
O	-4.40691900	5.36658700	-0.64548300
C	-3.91872700	6.53985400	-0.00440000
H	-2.89464400	6.76915100	-0.32354700
H	-4.58508300	7.34538400	-0.31333000
H	-3.94921000	6.43785300	1.08728100
C	1.55307500	-0.80654900	-0.47685800
C	0.27788100	-1.04663400	0.04181400
C	-0.00434700	-2.24877200	0.82956900
C	-1.16443700	-3.01199600	0.70838000
C	0.94876300	-2.72874800	1.75402600
C	-1.39075100	-4.18830600	1.41545900
C	0.74806700	-3.89604900	2.48024800
H	1.85157900	-2.14549600	1.89939300
C	-0.42769200	-4.63471900	2.31550000
H	-2.31451900	-4.73482800	1.26071300
H	1.50230400	-4.22488600	3.18844200
H	-0.59935100	-5.54033900	2.88790800
O	-2.17071200	-2.66900500	-0.23314000
C	-3.13806000	-1.81887500	0.04939300
O	-2.91329000	-0.58045500	0.32739300
C	-4.50680000	-2.25675400	-0.00489600
C	-4.79880700	-3.60880400	-0.28877300
C	-5.56046900	-1.33926200	0.21176800
C	-6.11985300	-4.03092600	-0.34957200
H	-3.98798200	-4.30178600	-0.47906600
C	-6.87498600	-1.77763300	0.15437100
H	-5.33148500	-0.30238500	0.42904500
C	-7.15799500	-3.12042100	-0.12529600
H	-6.34493500	-5.06848300	-0.57356800
H	-7.68479700	-1.07610500	0.32617900
H	-8.18936900	-3.45615200	-0.17051400
Cu	3.16268400	-1.85382200	-0.57731800
N	4.69626300	-2.96611400	-0.69639700
C	5.65692700	-3.58497900	-0.87803900
C	6.86606300	-4.36037600	-1.11275300
H	7.33040100	-4.62672200	-0.15822800
H	6.61923100	-5.27603500	-1.65909300
H	7.57336700	-3.77036600	-1.70397800

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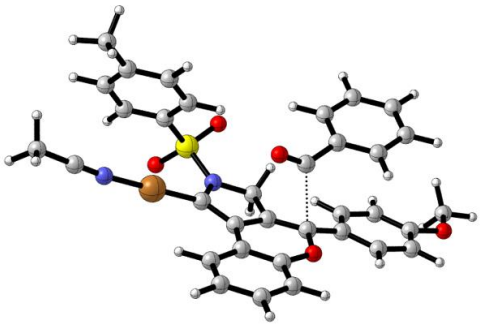

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O	2.18967200	-2.12443600	-2.93265100
C	2.88193400	-2.03595100	-0.39225100
C	2.59548800	-1.74975100	0.94896300
C	4.17556400	-2.35112900	-0.80708700
C	3.63630400	-1.74657400	1.86903900
H	1.58756400	-1.49889200	1.26095700
C	5.20158200	-2.36141200	0.13843200
H	4.36760600	-2.57328900	-1.85065400
C	4.95270200	-2.05410400	1.48045500
H	3.42634600	-1.50603800	2.90742400
H	6.21007200	-2.61474900	-0.17641800
C	6.06341800	-2.05683500	2.49978500
H	6.09286900	-1.11393600	3.05864600
H	5.91832600	-2.85703000	3.23513100
H	7.03953400	-2.21484600	2.03116400
C	-0.70771100	-0.57329900	-1.41090600
H	-1.04638800	-0.67034000	-2.45101300
H	-1.13648500	-1.39622000	-0.83950400
C	-0.96305300	0.79934100	-0.86463100
C	-2.14337400	1.32743500	-0.30197000
C	-3.52196000	0.86956200	-0.50233500
C	-3.83691300	-0.36165800	-1.09888400
C	-4.59162400	1.65771100	-0.02285600
C	-5.14860800	-0.81451100	-1.18815600
H	-3.06626100	-1.00150900	-1.50408200
C	-5.89989700	1.22089200	-0.11288000
H	-4.38068100	2.61884800	0.42851600
C	-6.19426300	-0.02948900	-0.68305600

H	-5.34343500	-1.77366300	-1.65094100
H	-6.72050300	1.82790400	0.25416800
O	-7.49809100	-0.37961300	-0.70036500
C	-7.85744100	-1.63538700	-1.26840800
H	-7.38206000	-2.46347700	-0.72823300
H	-8.94040200	-1.70711700	-1.16790200
H	-7.58363300	-1.68359900	-2.32898300
C	1.33331200	0.57380400	-1.01554400
C	0.26933500	1.46386300	-0.75029200
C	0.29949900	2.82814800	-0.24230900
C	-0.92001400	3.35042900	0.21550600
C	1.43165600	3.64734500	-0.16619400
C	-1.02000000	4.63147000	0.74354500
C	1.35016200	4.93395700	0.36295200
H	2.38024700	3.27355900	-0.54167500
C	0.12507600	5.42499100	0.82020400
H	-1.98560600	4.99074200	1.08270900
H	2.23834800	5.55581500	0.41100100
H	0.05562400	6.42677100	1.23149200
O	-2.10051000	2.62510400	0.15039800
C	-1.36148000	0.06469600	1.46410800
O	-0.24697000	0.25318400	1.81280000
C	-2.39806900	-0.90207600	1.78038800
C	-2.13129500	-2.25381400	1.48600200
C	-3.67251700	-0.49886100	2.20988900
C	-3.15148700	-3.19171000	1.62396500
H	-1.14515900	-2.55909100	1.14822700
C	-4.67103100	-1.45250300	2.36408400
H	-3.86850300	0.54443900	2.42266800
C	-4.41750200	-2.79368500	2.05940700
H	-2.95278400	-4.23418300	1.39617100
H	-5.65419500	-1.14656400	2.70632000
H	-5.20790600	-3.53025800	2.16541900
Cu	3.21278300	0.79456500	-0.72941000
N	5.05083500	1.06273800	-0.35563400
C	6.17393800	1.11343000	-0.08404600
C	7.58621400	1.16582500	0.26060700
H	7.80657800	2.09589600	0.79368800
H	7.83867900	0.31554400	0.90199200
H	8.19267900	1.12275400	-0.64951500

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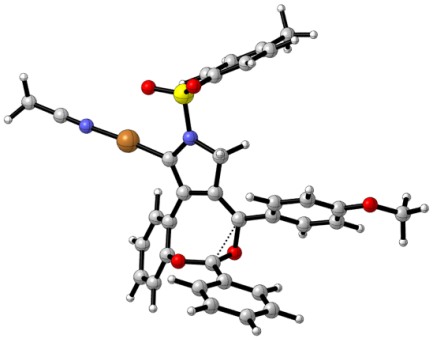
Electronic Energy(Hartree) = -3837.565588
Imaginary Frequency(cm^{-1}) = 225.80*i*



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O	1.74817100	2.08472500	-2.79517100
C	2.77044300	2.85859700	-0.48330900
C	3.64879500	2.63869200	0.58186100
C	2.07804000	4.06173600	-0.62308600
C	3.82846000	3.64914100	1.51876100
H	4.18559000	1.69965300	0.66308900
C	2.27518300	5.06105600	0.32790200
H	1.41526400	4.21143600	-1.46811400
C	3.14849900	4.87353300	1.40736800
H	4.51116400	3.49217600	2.34915100
H	1.74637600	6.00424400	0.22600300
C	3.38091000	5.97063900	2.41401800
H	3.49738000	5.56723900	3.42499600
H	4.29847200	6.52387900	2.17661900
H	2.55635900	6.68908400	2.42220400
C	-0.02190600	0.88787100	-0.67460100
H	-0.14160300	1.84017200	-0.14474100
H	-0.48639200	0.98700800	-1.65807800
C	-0.54245600	-0.28241100	0.13221400
C	-1.86652200	-0.32555700	0.53522400
C	-2.87243300	0.72097900	0.32973900
C	-3.53314900	1.28748800	1.42913400
C	-3.22886200	1.15502300	-0.96087800
C	-4.50757100	2.26785000	1.26059300
H	-3.28473000	0.95008200	2.43114400
C	-4.19070500	2.13476500	-1.14260700
H	-2.77040800	0.69187800	-1.82931100
C	-4.83913000	2.70188600	-0.03240400

H	-4.99676000	2.68715100	2.13122400
H	-4.47667700	2.46844400	-2.13422900
O	-5.76807400	3.64391600	-0.31308300
C	-6.46658200	4.25406500	0.76694700
H	-5.77808400	4.78297200	1.43715100
H	-7.15148700	4.96891700	0.31059400
H	-7.03834500	3.51342600	1.33942300
C	1.72479900	-0.63801500	-0.22044000
C	0.55281700	-1.16180600	0.36101100
C	0.54284000	-2.41312900	1.13550000
C	-0.49672900	-3.33307100	1.01490300
C	1.57899400	-2.75074700	2.02069400
C	-0.55740800	-4.52381300	1.71924700
C	1.55955700	-3.95192500	2.72906100
H	2.39388500	-2.04730800	2.15883600
C	0.49302500	-4.84052000	2.58368100
H	-1.39630300	-5.19506400	1.56995400
H	2.37365900	-4.18817100	3.40722100
H	0.47390500	-5.77454700	3.13541400
O	-1.52591200	-3.08309500	0.06729300
C	-2.46194700	-2.19134900	0.37433500
O	-2.26606400	-1.39879200	1.44087800
C	-3.71933800	-2.27785100	-0.33389100
C	-3.79864200	-3.01731900	-1.53213200
C	-4.86142600	-1.62255200	0.16603000
C	-4.99965000	-3.07712900	-2.22527300
H	-2.91786800	-3.52660900	-1.90601800
C	-6.05863600	-1.69430200	-0.53599000
H	-4.80269900	-1.07840600	1.09893300
C	-6.12932400	-2.41348900	-1.73172100
H	-5.06063200	-3.64039900	-3.15086400
H	-6.93908800	-1.19229300	-0.14836800
H	-7.06635700	-2.46421200	-2.27776600
Cu	3.51038500	-1.32449700	-0.40526100
N	5.23039400	-2.10836100	-0.57833300
C	6.28161900	-2.54779500	-0.77974100
C	7.60351500	-3.09914100	-1.03793000
H	8.10248300	-2.51266400	-1.81574800
H	8.20496400	-3.06899200	-0.12409000
H	7.51342400	-4.13693400	-1.37366500

C

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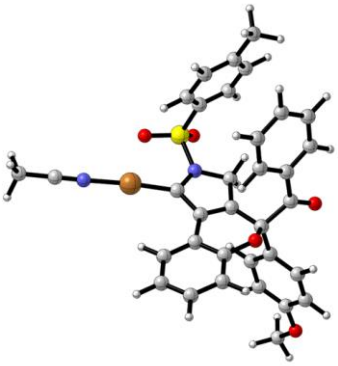
Electronic Energy(Hartree) = -3837.643602

Imaginary Frequency(cm^{-1}) = NO



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O	1.89930900	0.03161400	-3.55504500
O	3.12710400	1.57522200	-1.91116000
C	3.16667600	-1.05705700	-1.49088500
C	2.99679200	-2.30807600	-2.09149000
C	3.85009900	-0.90535000	-0.28210900
C	3.52750400	-3.42559400	-1.45659400
H	2.46901100	-2.39386300	-3.03495100
C	4.37230400	-2.03885800	0.33136500
H	3.97306100	0.07680400	0.16149700
C	4.21894500	-3.31064500	-0.24085700
H	3.40476500	-4.40383000	-1.91190500
H	4.90838800	-1.93759000	1.27011500
C	4.79935100	-4.53296500	0.41909100
H	4.07618600	-5.35485500	0.42912700
H	5.68295100	-4.88421900	-0.12774300
H	5.10520000	-4.32850600	1.44862600
C	-0.06202000	-0.62128600	-1.23055100
H	-0.57535400	-0.64833200	-2.19850900
H	0.41930000	-1.59116700	-1.06563300
C	-0.92689300	-0.19271000	-0.09887500
C	-2.11308100	-0.90403600	0.48085900
C	-3.40968100	-0.56523900	-0.22344500
C	-3.48011500	0.36704500	-1.25662300
C	-4.60060500	-1.16236100	0.22661800
C	-4.69765600	0.69694400	-1.85697200
H	-2.58284300	0.86766000	-1.60842400
C	-5.81428800	-0.84042800	-0.35136400
H	-4.56872200	-1.88116700	1.03759500
C	-5.87402900	0.08975900	-1.40506100
H	-4.71547800	1.42493600	-2.65850100

H	-6.73835500	-1.29668400	-0.01309300
O	-7.10922500	0.33025900	-1.90534200
C	-7.23509900	1.25298400	-2.97945600
H	-6.66645300	0.92160800	-3.85728800
H	-8.29726100	1.28201100	-3.22402900
H	-6.90045600	2.25553500	-2.68461300
C	0.74880100	1.37767300	-0.27740300
C	-0.46716200	0.98000700	0.42058400
C	-1.13024400	1.58972200	1.56237600
C	-2.03738800	0.75821900	2.25288600
C	-0.92664400	2.89893300	2.01493000
C	-2.70773800	1.22112500	3.38081200
C	-1.60040900	3.36857200	3.13879300
H	-0.24830800	3.55020700	1.47045600
C	-2.48495400	2.52616600	3.82022500
H	-3.39377300	0.55635300	3.89390300
H	-1.44378800	4.38627500	3.48097500
H	-3.01423100	2.89012900	4.69529900
O	-2.21576600	-0.55633200	1.89298500
C	-1.79955600	-2.44425700	0.46581300
O	-2.50362500	-3.18283300	-0.19306300
C	-0.56428000	-2.95018200	1.14395200
C	-0.17957900	-4.26682900	0.83300400
C	0.24073600	-2.19103600	2.01186100
C	0.98202000	-4.81113800	1.37044200
H	-0.81108200	-4.84332600	0.16607200
C	1.40428400	-2.74069800	2.54636600
H	-0.05073800	-1.19025300	2.29607900
C	1.77673000	-4.04809900	2.22993000
H	1.26322700	-5.83160800	1.12766500
H	2.01153200	-2.15099200	3.22650500
H	2.67769000	-4.47532000	2.65970200
Cu	1.97040000	2.84826000	-0.08506100
N	3.08004700	4.36438100	0.18650500
C	3.77268900	5.28695000	0.27469700
C	4.64362600	6.44728700	0.38261100
H	4.04275800	7.36215100	0.38684700
H	5.22118100	6.39279200	1.31074500
H	5.33138500	6.47287500	-0.46849900

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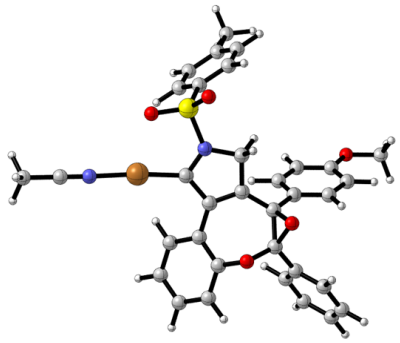
Imaginary Frequency(cm^{-1}) = NO



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O	-3.02291100	1.55504800	2.94943100
C	-3.04930300	2.63373200	0.52465800
C	-3.43527500	2.55782000	-0.81674800
C	-2.49078100	3.79353200	1.06778500
C	-3.24993300	3.67392400	-1.62427700
H	-3.88019700	1.65018000	-1.20994500
C	-2.31625300	4.89712000	0.23800400
H	-2.21611000	3.82889300	2.11625400
C	-2.68992700	4.85664900	-1.11365900
H	-3.54807700	3.63239600	-2.66776100
H	-1.88699200	5.80688500	0.64696100
C	-2.52338900	6.06840000	-1.99236100
H	-2.38146500	5.78790300	-3.04012300
H	-3.41662500	6.70401600	-1.94050300
H	-1.67064900	6.67691500	-1.67745000
C	-0.42579000	0.74216700	1.53790000
H	-0.19991000	1.74256700	1.15330400
H	-0.37206000	0.76852100	2.63252900
C	0.42621500	-0.32415200	0.93393600
C	1.90811700	-0.28127900	0.97136800
C	2.53990900	0.92882800	0.36361800
C	3.67109100	1.51216600	0.93484200
C	2.01221200	1.47931000	-0.81542200
C	4.27335300	2.62624000	0.35127600
H	4.08491900	1.08656100	1.84167500
C	2.60171400	2.58747900	-1.40439500
H	1.14092400	1.02718900	-1.28331000
C	3.74011700	3.17143100	-0.82431200
H	5.15107800	3.05721600	0.81694300

H	2.20867300	3.01819700	-2.31917500
O	4.24229000	4.25082700	-1.47304100
C	5.41403300	4.86607900	-0.95062800
H	6.25578700	4.16321900	-0.92814700
H	5.64502700	5.68878700	-1.62791500
H	5.24119500	5.26068300	0.05837300
C	-1.76403800	-0.81763300	0.40378300
C	-0.36391900	-1.22718600	0.27898800
C	0.07730600	-2.43822400	-0.41682100
C	1.18820000	-3.15962700	0.06503200
C	-0.59876200	-2.93353500	-1.54374200
C	1.59748600	-4.34074300	-0.54877300
C	-0.18753400	-4.10877800	-2.16591800
H	-1.44256500	-2.37660400	-1.94112300
C	0.90849200	-4.81604900	-1.66353800
H	2.45303000	-4.86634500	-0.13991900
H	-0.71610200	-4.47098100	-3.04196600
H	1.23262000	-5.73351200	-2.14466400
O	1.83889900	-2.74945000	1.20917400
C	2.61888500	-1.57841300	1.09263100
O	2.48275300	-0.75663200	2.22227800
C	3.98374000	-1.80779100	0.53894900
C	5.06584500	-2.00481200	1.40034200
C	4.16701200	-1.86320600	-0.84615900
C	6.33150400	-2.26143300	0.87484100
H	4.91206400	-1.94873600	2.47358200
C	5.43374700	-2.12091900	-1.36834000
H	3.32491600	-1.69116500	-1.50973900
C	6.51565300	-2.32128000	-0.50845700
H	7.17357800	-2.41296700	1.54339300
H	5.57788600	-2.15756600	-2.44393200
H	7.50269900	-2.51855000	-0.91600300
Cu	-3.40898900	-1.66606400	-0.11597500
N	-4.96053200	-2.63853100	-0.61677200
C	-5.93402200	-3.22586500	-0.83110000
C	-7.15874000	-3.96494200	-1.09657200
H	-7.90414500	-3.29914600	-1.54289000
H	-6.95379200	-4.79042900	-1.78545300
H	-7.55481600	-4.36881200	-0.15932100

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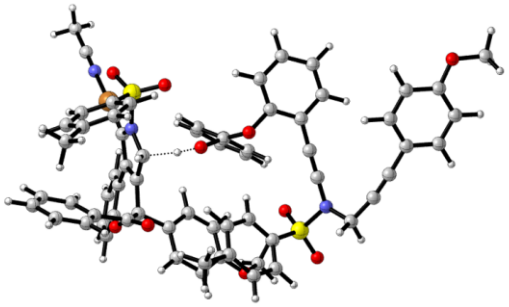
Imaginary Frequency(cm^{-1}) = 1137.47*i*



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O	-3.91965900	4.06673600	0.19677700
C	-3.54458400	2.80076800	2.53860800
C	-2.61808500	2.73811800	3.57722800
C	-4.87711800	2.40939000	2.71116700
C	-3.04521600	2.27260900	4.82074500
H	-1.58743000	3.02697500	3.40514600
C	-5.27542200	1.94032600	3.95433600
H	-5.57405200	2.44941500	1.88083500
C	-4.36663900	1.85667100	5.02403500
H	-2.33461100	2.21575600	5.63978000
H	-6.29933700	1.60996900	4.09628100
C	-4.81569800	1.30465700	6.35117800
H	-5.13096700	0.26058900	6.24003600
H	-4.01657000	1.34300200	7.09603500
H	-5.67376800	1.86350900	6.74163300
C	-2.65165900	0.44642100	0.77497900
H	-1.14588600	0.54533900	0.70318100
H	-2.65882100	0.37737400	1.85937600
C	-3.10749800	-0.57857200	-0.08192100
C	-3.06355900	-2.06968400	0.12900700
C	-1.82529500	-2.74907900	-0.42356900
C	-1.13039800	-2.19677900	-1.50203400
C	-1.47884800	-4.04193500	0.00304100
C	-0.11797200	-2.90526100	-2.15181000
H	-1.38350400	-1.20657700	-1.86391200
C	-0.46429200	-4.74759600	-0.62087100
H	-2.00974900	-4.50093300	0.82876600
C	0.21998000	-4.18843700	-1.71099300
H	0.40953300	-2.44718700	-2.97726800

H	-0.18311300	-5.74106300	-0.28929700
O	1.19614000	-4.95889600	-2.25681600
C	1.62192700	-4.66720500	-3.58831400
H	2.15785300	-3.71670100	-3.63658800
H	2.30034300	-5.47628000	-3.86060000
H	0.76264700	-4.65365100	-4.27027400
C	-3.83962200	1.39292300	-1.00844300
C	-3.77028000	-0.01295000	-1.17728900
C	-4.33367300	-0.89496400	-2.19222400
C	-4.51388400	-2.23950700	-1.80307900
C	-4.70336700	-0.51300200	-3.48601400
C	-5.06264400	-3.16920800	-2.68082100
C	-5.25610300	-1.43906800	-4.36856500
H	-4.54624500	0.51720400	-3.79485800
C	-5.43760900	-2.76427100	-3.96240800
H	-5.18759800	-4.19374800	-2.34763300
H	-5.53848400	-1.13273100	-5.37103800
H	-5.86266500	-3.49028100	-4.64866900
O	-4.22927500	-2.65512400	-0.51963100
C	-3.25071900	-2.24154700	1.66252000
O	-2.25854800	-2.45040500	2.34446200
C	-4.56995500	-1.97446300	2.31171800
C	-4.64117500	-2.21098800	3.69599100
C	-5.68856200	-1.43372600	1.65457900
C	-5.80345400	-1.92999000	4.40573500
H	-3.76867200	-2.61697600	4.19532700
C	-6.84495600	-1.13550500	2.37309700
H	-5.66175600	-1.24583100	0.59141600
C	-6.90942700	-1.38685700	3.74492300
H	-5.85253300	-2.14070100	5.47012200
H	-7.70341700	-0.71839000	1.85499100
H	-7.82000000	-1.16928900	4.29613300
Cu	-4.59348500	2.83816200	-2.00506400
N	-5.37902800	4.20989800	-3.05312600
C	-5.86111700	5.08722600	-3.63348200
C	-6.46808200	6.19223400	-4.36065600
H	-7.51335300	5.95880000	-4.58594500
H	-6.42643700	7.10164100	-3.75311100
H	-5.92892900	6.36193900	-5.29783300
N	5.07728600	-2.03954800	-0.53422300
S	3.82726600	-3.07797500	-1.12896400
O	3.10275600	-2.25144200	-2.09750400
O	4.51190800	-4.31048300	-1.50602000
C	2.79054100	-3.37030700	0.27550300

C	1.83451200	-2.41422600	0.62863600
C	2.96431100	-4.53712500	1.01845500
C	1.04810500	-2.63099900	1.75172800
H	1.68294000	-1.54855700	-0.00037100
C	2.16397500	-4.73624600	2.14142100
H	3.69015700	-5.27821700	0.70356200
C	1.20538700	-3.79060500	2.52798600
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H	2.27969900	-5.64706900	2.72207100
C	0.35459600	-4.00778600	3.75233800
H	-0.67116800	-3.67400200	3.57697200
H	0.34162600	-5.06135800	4.04751600
H	0.74712700	-3.43300600	4.60157600
C	6.19846300	-2.65875400	0.24528400
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H	6.56478300	-3.49846000	-0.34986400
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C	10.79846600	1.72866300	0.47894700
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C	10.17217800	2.89641700	0.93585200
H	11.84562900	1.72988800	0.20227000
H	8.34946500	3.77935000	1.64491300
O	10.78646300	4.09908500	1.07038900
C	12.16720300	4.18970500	0.74530700
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C	2.87503900	2.24576400	0.11912500
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H	5.41271800	4.86544200	-1.08167100

H	3.10491000	5.56339000	-0.46142200
O	1.99440200	1.30713300	0.70612000
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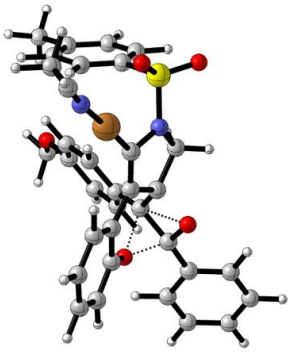
Electronic Energy(Hartree) = -3837.552728
Imaginary Frequency(cm^{-1}) = 301.48*i*



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H	-1.23674100	3.11847100	2.84969000
C	-1.67062700	4.52768600	-0.23807900
H	-2.75900700	3.59821200	-1.85008400
H	-0.68245100	5.17505500	1.56457100
C	-1.32397900	5.77506100	-1.01198400

H	-1.87664100	5.83024800	-1.95409000
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C	-0.03600300	-0.14520600	1.88448700
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H	0.20245200	-0.51047600	2.88564300
C	0.68466200	-0.95745000	0.81039200
C	1.89408000	-0.33202900	0.13637500
C	2.09520300	0.95221800	-0.41457900
C	3.37815500	1.53788200	-0.49306500
C	0.97005800	1.67823400	-0.88626300
C	3.54092400	2.81401800	-1.00348900
H	4.24000700	0.98861500	-0.12934500
C	1.13127900	2.93655200	-1.41516700
H	-0.01694000	1.22921400	-0.84652700
C	2.41373400	3.52422200	-1.46737600
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H	0.28800800	3.49746300	-1.79448500
O	2.45310500	4.76475400	-1.97116700
C	3.71048900	5.44212200	-2.07669100
H	4.39387800	4.89241600	-2.73229600
H	3.48187800	6.41310100	-2.51411800
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C	-1.62298100	-1.14881100	0.38536700
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C	0.01784100	-2.49018700	-1.06724800
C	1.37483500	-2.62315300	-1.41800400
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C	-0.44418600	-4.31191500	-2.62572900
H	-1.92924600	-3.31265900	-1.43463800
C	0.91461500	-4.42693700	-2.93535900
H	2.89193600	-3.62646300	-2.54613700
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O	2.35746000	-1.72751100	-0.95859300
C	2.65931200	-1.49722500	0.61028200
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C	5.08305100	-1.61562300	0.00726500
C	5.67716900	-2.47549400	2.60392500
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C	6.40160800	-1.87035800	0.37328400

H	4.83934200	-1.31213000	-1.00499600
C	6.69983900	-2.29728600	1.67086000
H	5.90806500	-2.81502200	3.60854700
H	7.19659300	-1.74630200	-0.35531500
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Cu	-3.43954100	-1.49977400	-0.13698700
N	-5.20184100	-1.93837900	-0.69135300
C	-6.31030900	-2.18445800	-0.91414900
C	-7.70601000	-2.49332200	-1.18815000
H	-7.94323300	-2.25756500	-2.23017200
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H	-8.35060300	-1.90224600	-0.53009600

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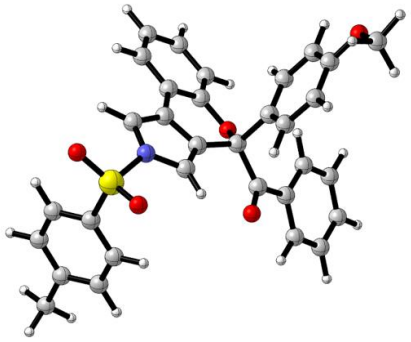
Imaginary Frequency(cm^{-1}) = NO



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C	-4.36219300	-0.60573100	-0.76305300
C	-4.22556800	0.51312000	-1.58691400
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C	-4.93568600	1.66671300	-1.27185600
H	-3.57990500	0.47406600	-2.45692400
C	-5.89487400	0.57604800	0.65374100
H	-5.28347700	-1.47505800	0.97541300
C	-5.77846600	1.71673000	-0.15123700
H	-4.83497900	2.54417400	-1.90478500
H	-6.54497800	0.60018600	1.52395300
C	-6.56124500	2.96716500	0.16179300
H	-5.97256400	3.86744500	-0.04308700
H	-7.46828500	3.02424100	-0.45385400
H	-6.87261100	2.99262700	1.21036600

C	-0.97026100	-0.82653300	-0.93991600
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H	-2.31636900	-2.44010000	1.59942400
C	-0.12490100	-0.44110800	0.06423300
C	1.14722200	0.36525400	0.06889000
C	2.35541700	-0.51668400	-0.29263100
C	2.40450600	-1.12822900	-1.54694700
C	3.41734000	-0.72668000	0.59603000
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H	1.59211200	-0.97640500	-2.24997700
C	4.49126100	-1.53315900	0.23984800
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C	4.53314300	-2.14117400	-1.02125000
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C	5.70986800	-3.55265800	-2.53764800
H	5.72510500	-2.82529600	-3.35998900
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C	-1.66887900	-1.82873200	0.99178700
C	-0.55689900	-1.07615200	1.28302800
C	0.14614300	-0.81369200	2.52639100
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C	0.61453100	-1.11616900	4.89217000
H	-0.76285900	-2.32171600	3.75754800
C	1.51348300	-0.04577600	4.85522200
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H	0.44226700	-1.65379300	5.81951300
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O	1.32295800	0.97425900	1.36484000
C	1.10826100	1.53003800	-0.95602000
O	0.39169100	1.41879900	-1.93946600
C	1.96738700	2.73764900	-0.78099100
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C	3.08614700	2.79983700	0.06406400
C	2.39747800	5.01984300	-1.49149700
H	0.78153600	3.78851900	-2.22480200
C	3.85473800	3.96057600	0.12100400
H	3.36316100	1.94402000	0.66143400
C	3.51020100	5.07354800	-0.64787600
H	2.12699800	5.88226300	-2.09391100

H	4.72575300	3.99537600	0.76898200
H	4.10853700	5.97881100	-0.59295900

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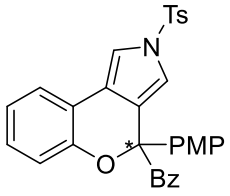
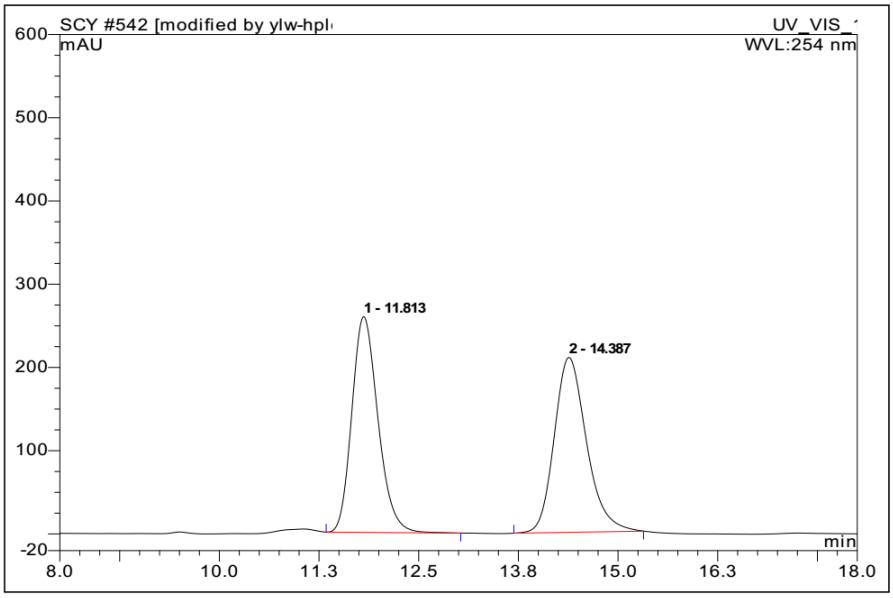
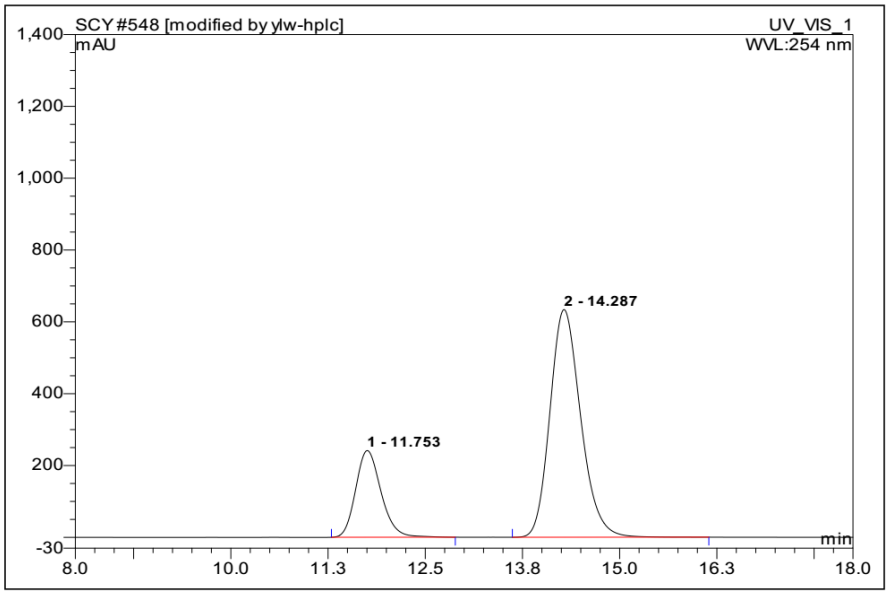
8. HPLC Chromatograms

(+)-**2a**: HPLC (IC, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, I = 254 nm)



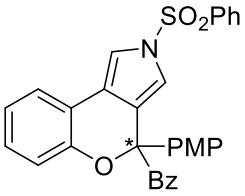


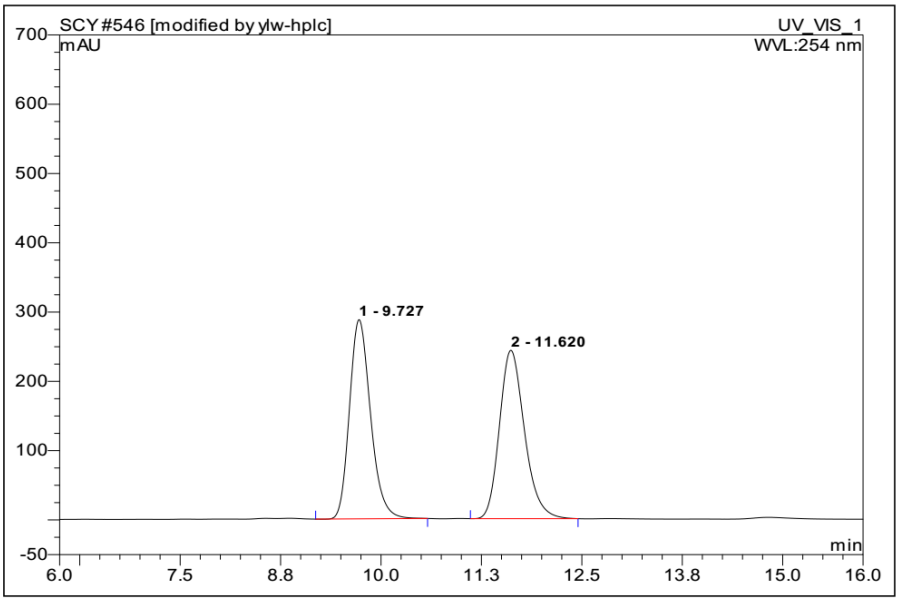
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount n.a.	Type
1	11.81	n.a.	259.105	98.441	49.99	n.a.	BMB*
2	14.39	n.a.	210.054	98.499	50.01	n.a.	BMB*
Total:			469.159	196.941	100.00	0.000	



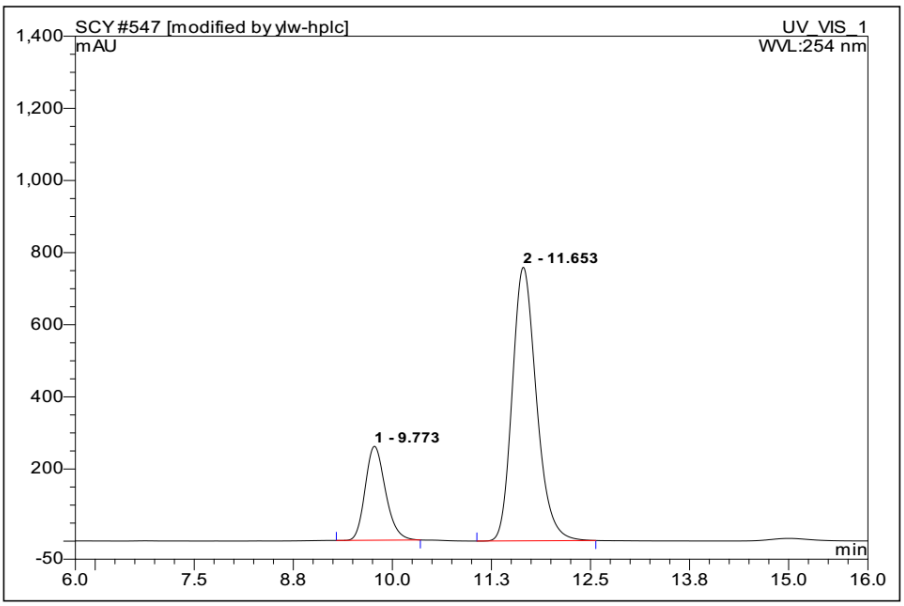
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount n.a.	Type
1	11.75	n.a.	241.332	91.412	23.95	n.a.	BMB*
2	14.29	n.a.	633.837	290.225	76.05	n.a.	BMB*
Total:			875.169	381.637	100.00	0.000	

(+)-**2c**: HPLC (IC, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, I = 254 nm)



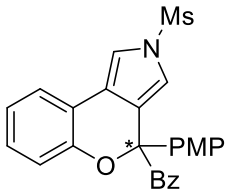


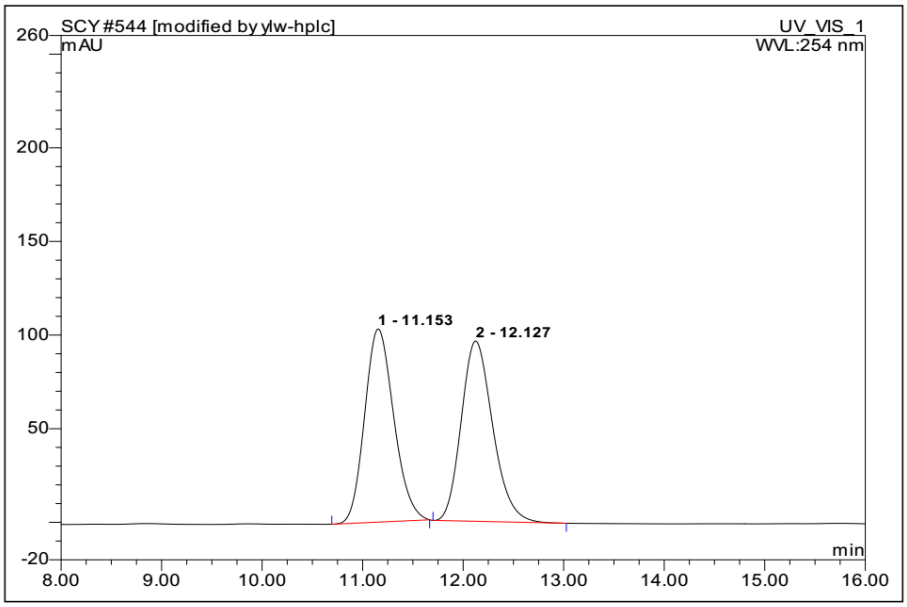
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount n.a.	Type
1	9.73	n.a.	287.514	87.494	49.95	n.a.	BMB*
2	11.62	n.a.	242.975	87.679	50.05	n.a.	BMB*
Total:			530.490	175.173	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount n.a.	Type
1	9.77	n.a.	260.464	77.125	22.35	n.a.	BMB*
2	11.65	n.a.	758.444	268.012	77.65	n.a.	BMB*
Total:			1018.908	345.137	100.00	0.000	

(+)-**2e**: HPLC (IC, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, I = 254 nm)





No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount n.a.	Type
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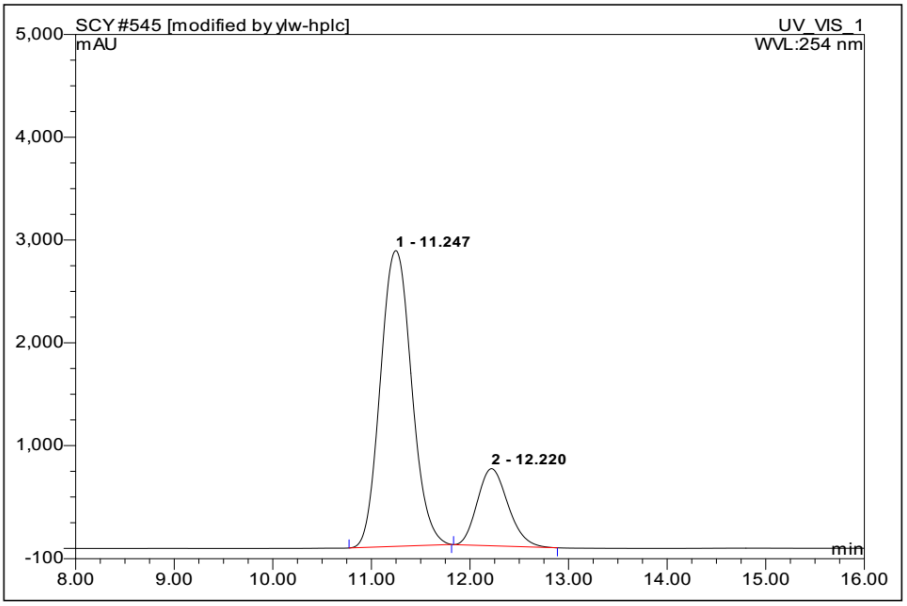
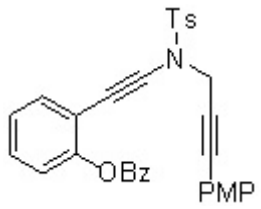
2	12.13	n.a.	96.216	34.936	50.22	n.a.	BMB*
Total:			199.353	69.561	100.00	0.000	

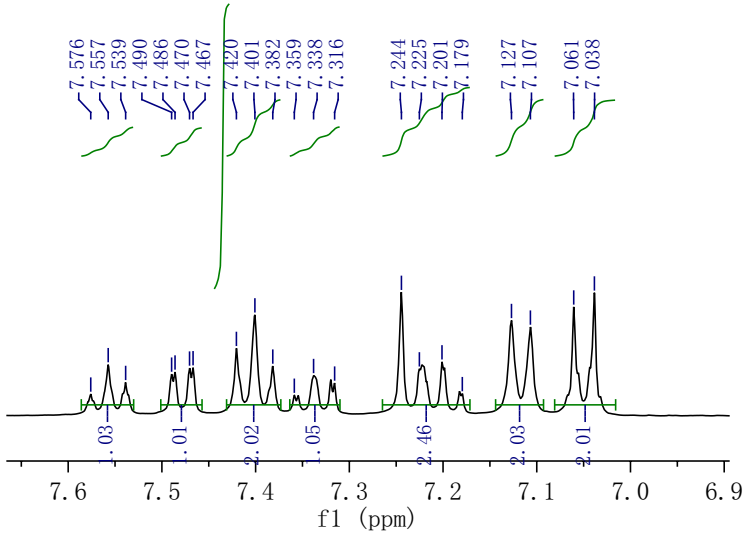


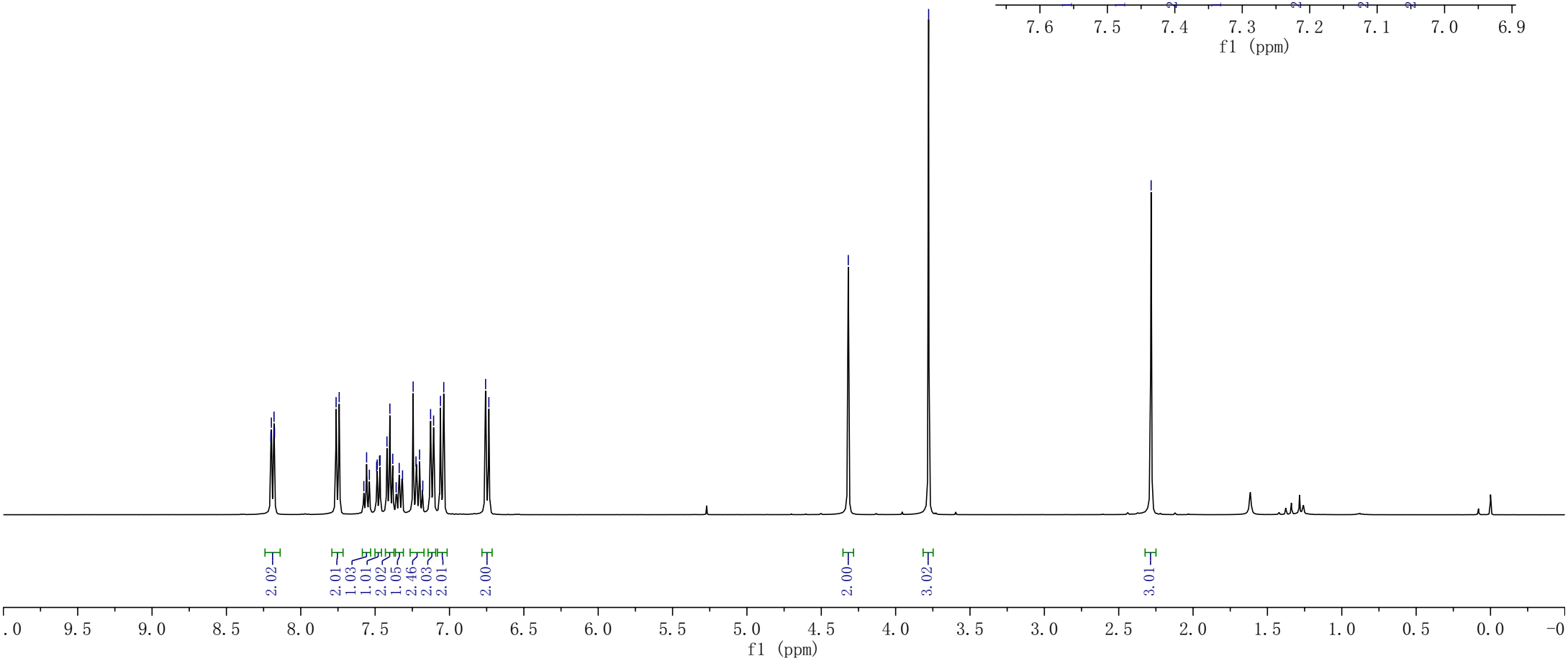
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount n.a.	Type
1	11.25	n.a.	2877.404	1056.045	79.59	n.a.	BMB*
2	12.22	n.a.	750.480	270.767	20.41	n.a.	BMB*
Total:			3627.884	1326.812	100.00	0.000	

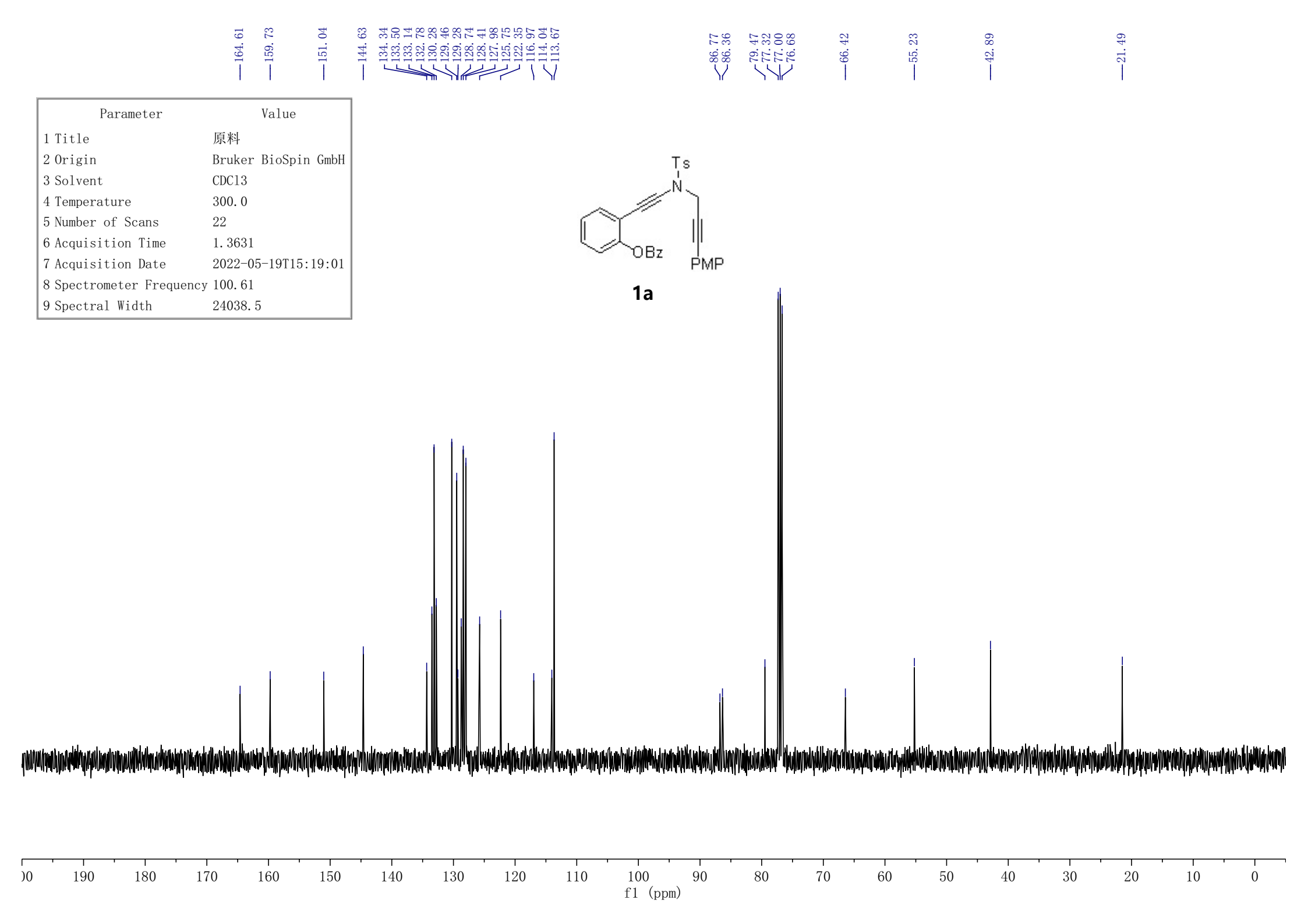
Parameter	Value
1 Title	原料
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	6
6 Acquisition Time	4.0894
7 Acquisition Date	2022-05-19T15:17:40
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8



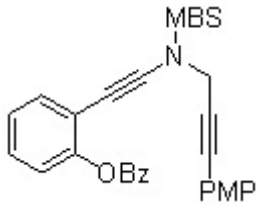
1a



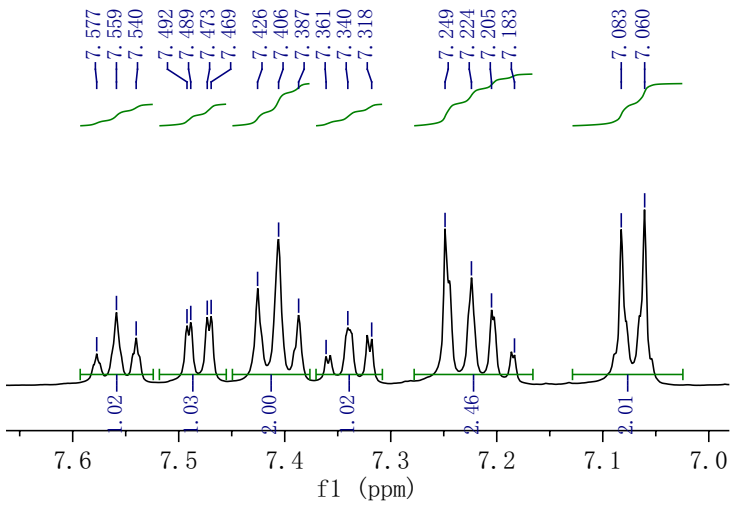


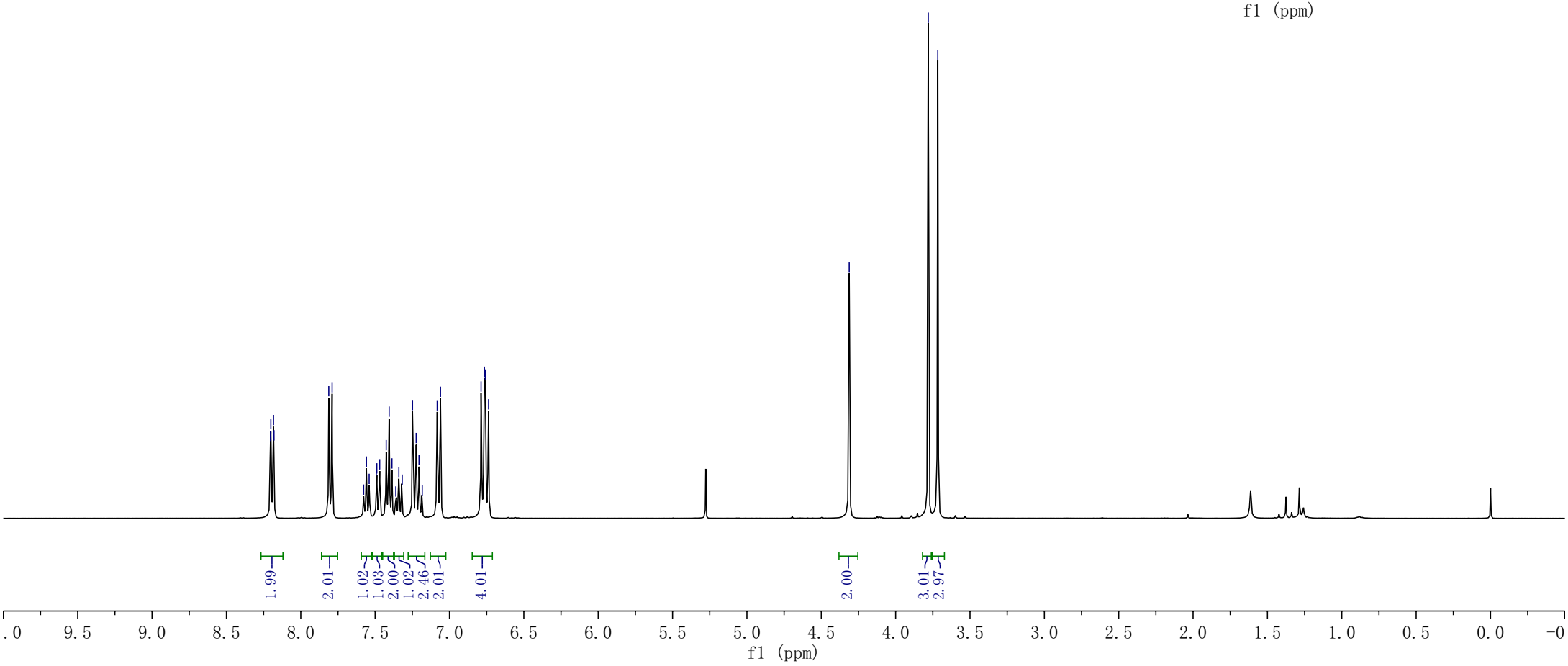

164.61
159.73
151.04
144.63
134.34
133.50
133.14
132.78
130.28
129.46
129.28
128.74
128.41
127.98
125.75
122.35
116.97
114.04
113.67
86.77
86.36
79.47
77.32
77.00
76.68
66.42
55.23
42.89
21.49
Parameter Value
1 Title 原料
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.0
5 Number of Scans 22
6 Acquisition Time 1.3631
7 Acquisition Date 2022-05-19T15:19:01
8 Spectrometer Frequency 100.61
9 Spectral Width 24038.5
Ts
N
OBz
PMP
1a
f1 (ppm)

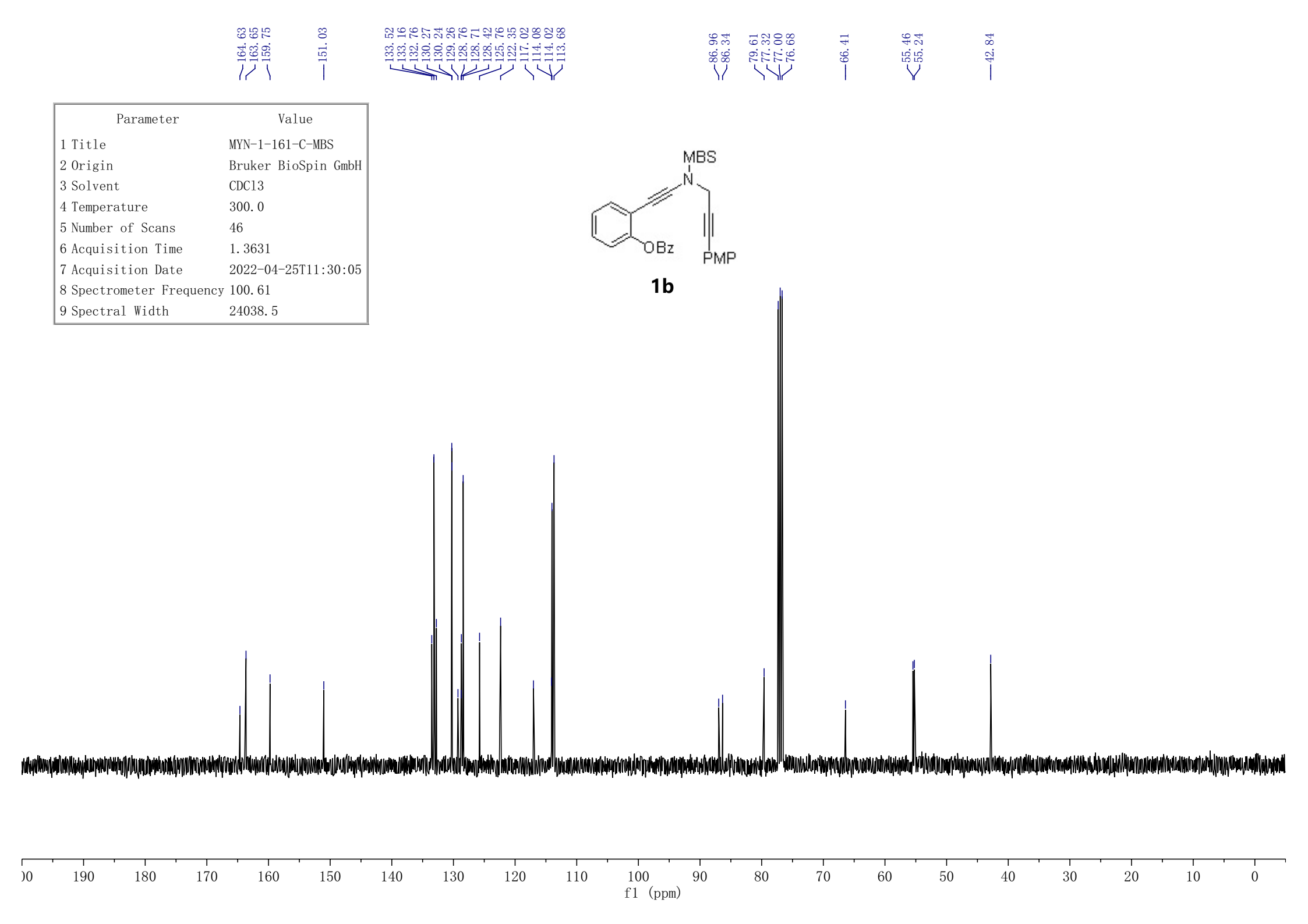
Parameter	Value
1 Title	MYN-1-161-H-MBS
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	20
6 Acquisition Time	4.0894
7 Acquisition Date	2022-04-25T11:34:51
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8

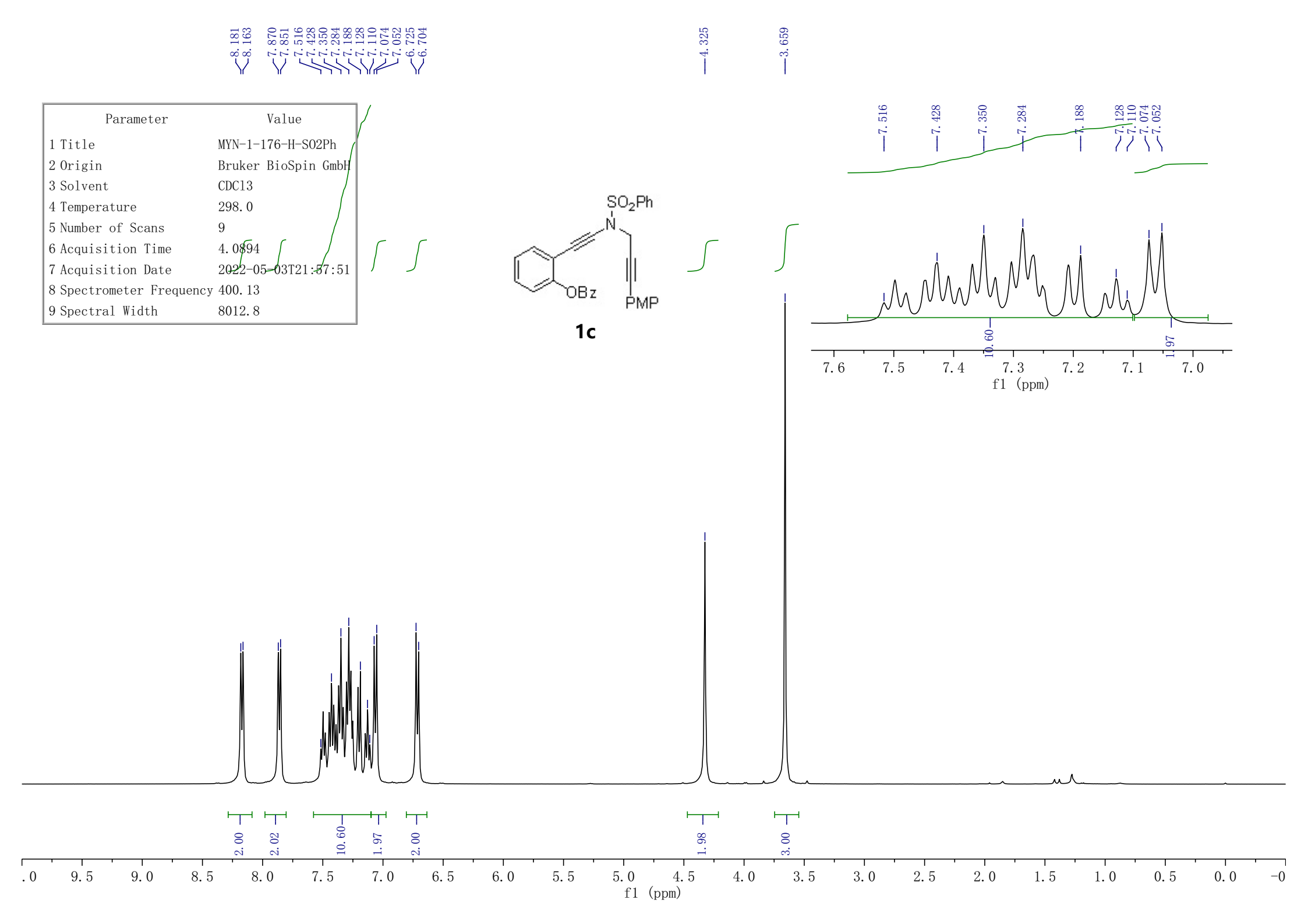


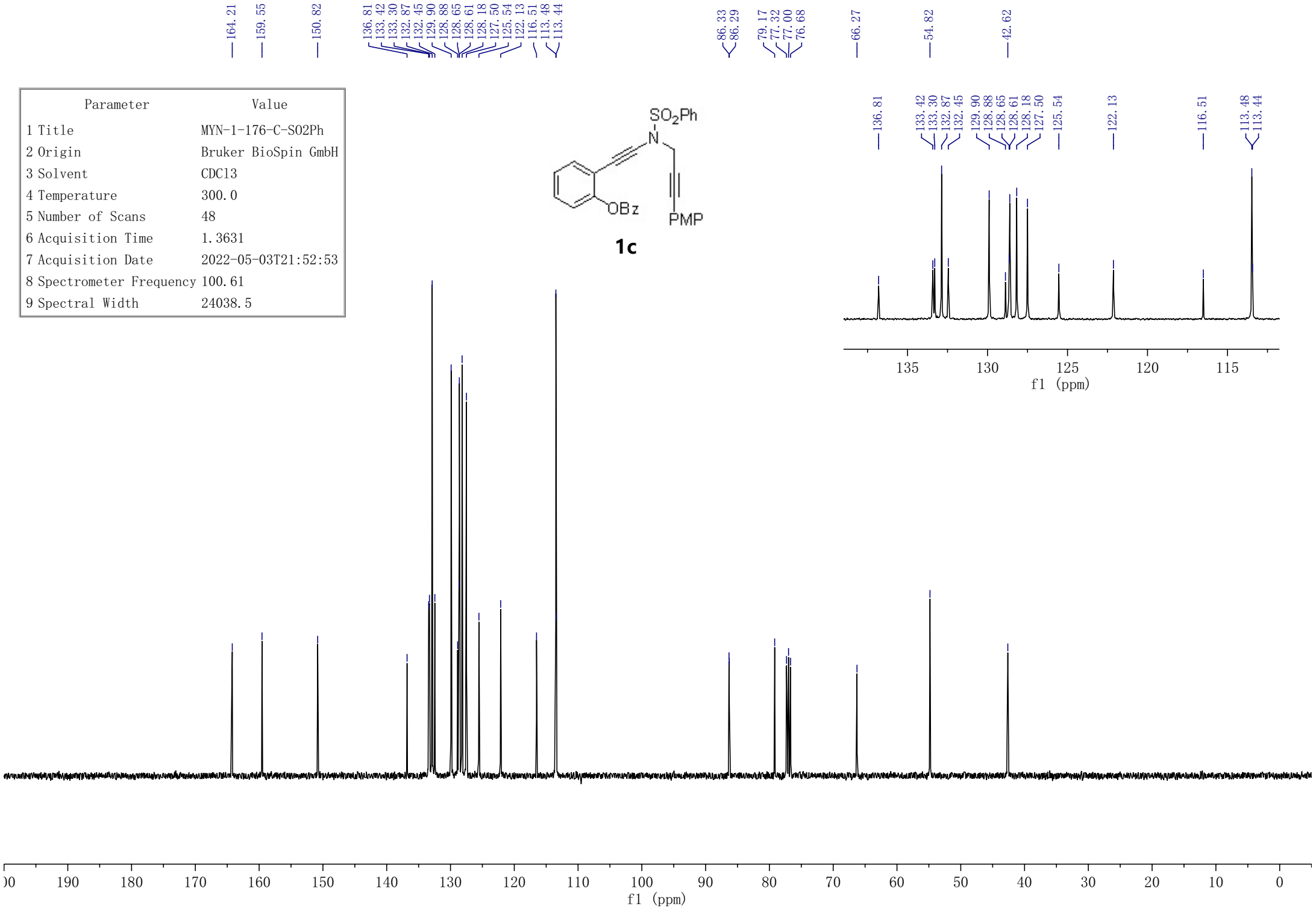
1b





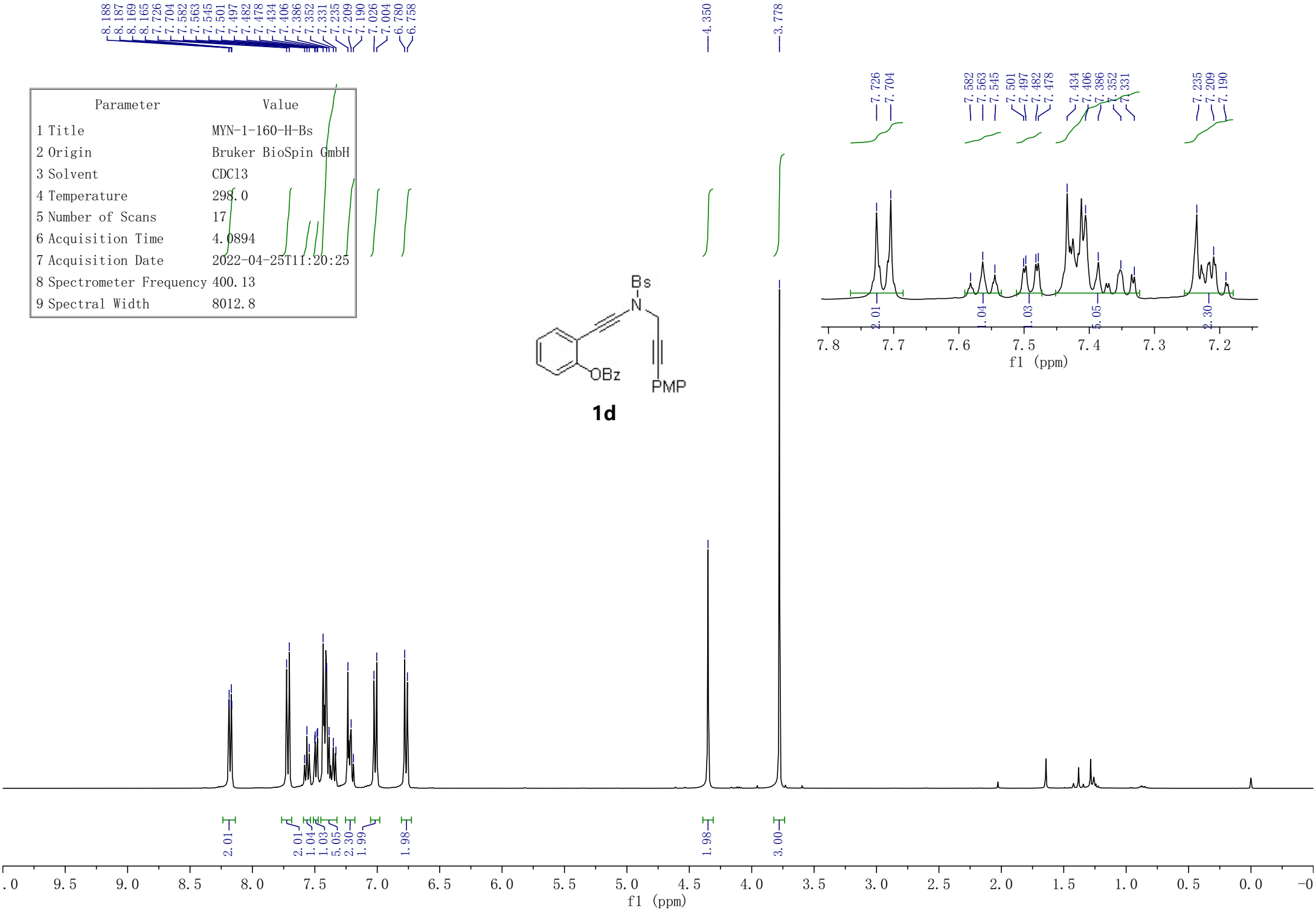

164.63
163.65
159.75
151.03
133.52
133.16
132.76
130.27
130.24
129.26
128.76
128.71
128.42
125.76
122.35
117.02
114.08
114.02
113.68
86.96
86.34
79.61
77.32
77.00
76.68
66.41
55.46
55.24
42.84
Parameter Value
1 Title MYN-1-161-C-MBS
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.0
5 Number of Scans 46
6 Acquisition Time 1.3631
7 Acquisition Date 2022-04-25T11:30:05
8 Spectrometer Frequency 100.61
9 Spectral Width 24038.5
MBS
N
OBz
PMP
1b
f1 (ppm)

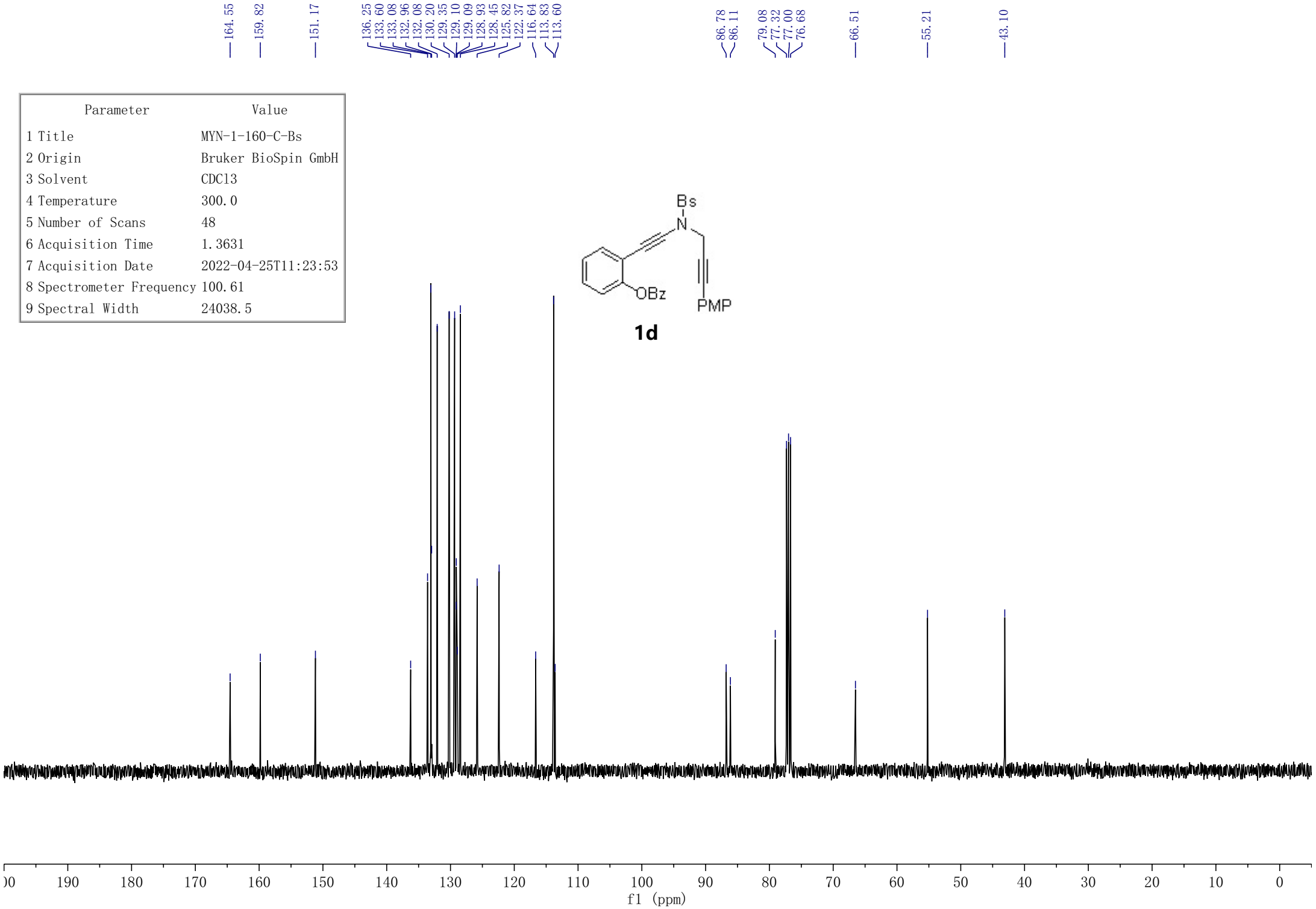

8.181
8.163
7.870
7.851
7.516
7.428
7.350
7.284
7.188
7.128
7.110
7.074
7.052
6.725
6.704
4.325
3.659
Parameter Value
1 Title MYN-1-176-H-SO2Ph
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 298.0
5 Number of Scans 9
6 Acquisition Time 4.0894
7 Acquisition Date 2022-05-03T21:57:51
8 Spectrometer Frequency 400.13
9 Spectral Width 8012.8
SO2Ph
N
OBz
PMP
1c
10.60
1.97
f1 (ppm)
2.00
2.02
10.60
1.97
2.00
1.98
3.00
f1 (ppm)


164.21
159.55
150.82
136.81
133.42
133.30
132.87
132.45
129.90
128.88
128.65
128.61
128.18
127.50
125.54
122.13
116.51
113.48
113.44
86.33
86.29
79.17
77.32
77.00
76.68
66.27
54.82
42.62
SO2Ph
N
OBz
PMP
1c
Parameter Value
1 Title MYN-1-176-C-SO2Ph
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.0
5 Number of Scans 48
6 Acquisition Time 1.3631
7 Acquisition Date 2022-05-03T21:52:53
8 Spectrometer Frequency 100.61
9 Spectral Width 24038.5
f1 (ppm)

Parameter	Value
1 Title	MYN-1-160-H-Bs
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	17
6 Acquisition Time	4.0894
7 Acquisition Date	2022-04-25T11:20:25
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8

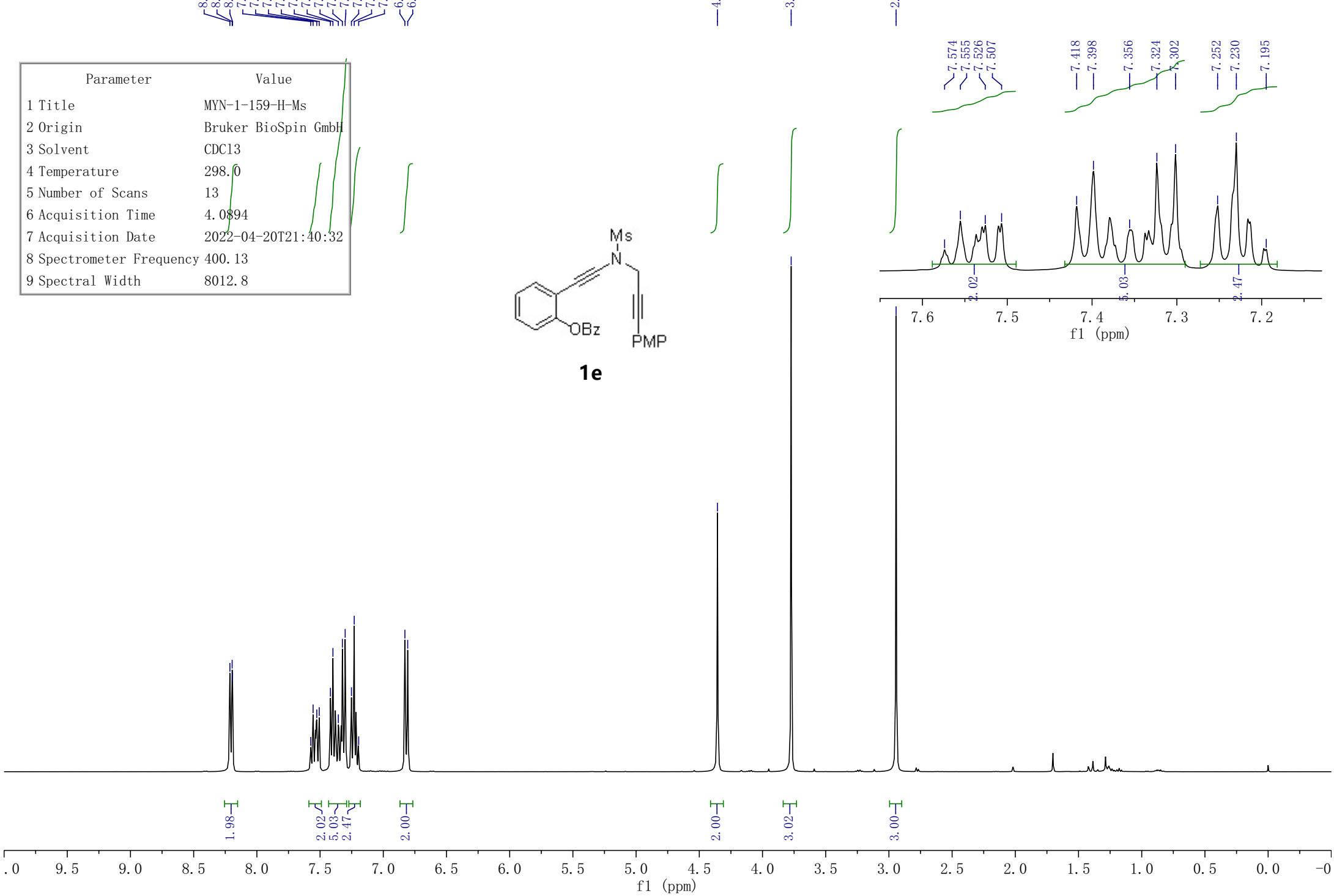
1d

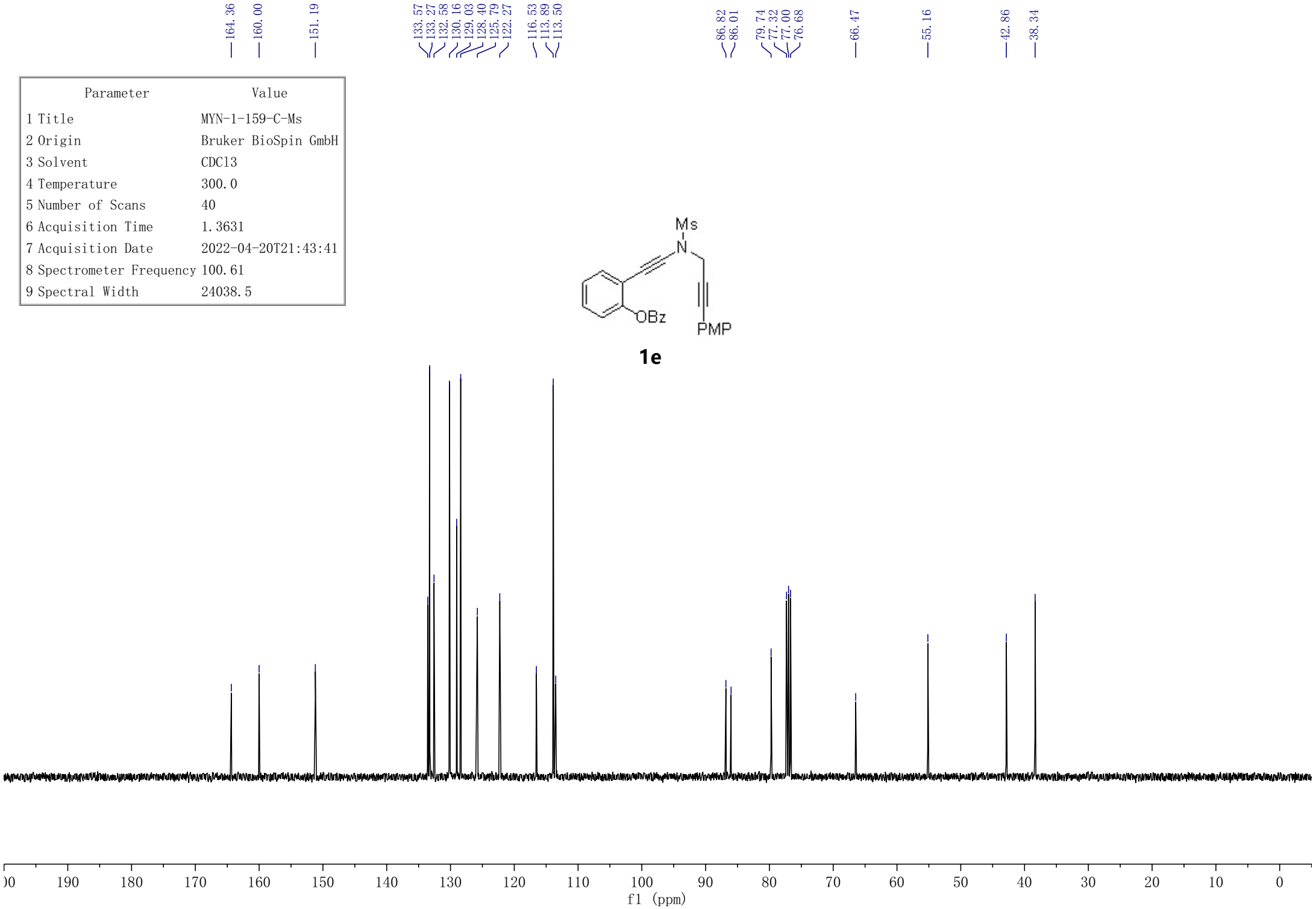



164.55
159.82
151.17
136.25
133.60
133.08
132.96
132.08
130.20
129.35
129.10
129.09
128.93
128.45
125.82
122.37
116.64
113.83
113.60
86.78
86.11
79.08
77.32
77.00
76.68
66.51
55.21
43.10
Parameter Value
1 Title MYN-1-160-C-Bs
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.0
5 Number of Scans 48
6 Acquisition Time 1.3631
7 Acquisition Date 2022-04-25T11:23:53
8 Spectrometer Frequency 100.61
9 Spectral Width 24038.5
Bs
N
OBz
PMP
1d
f1 (ppm)

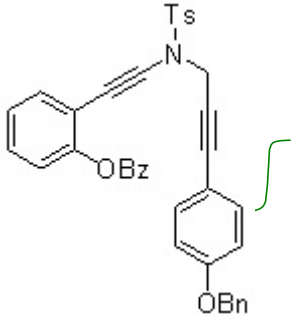
Parameter	Value
1 Title	MYN-1-159-H-Ms
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	13
6 Acquisition Time	4.0894
7 Acquisition Date	2022-04-20T21:40:32
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8

1e

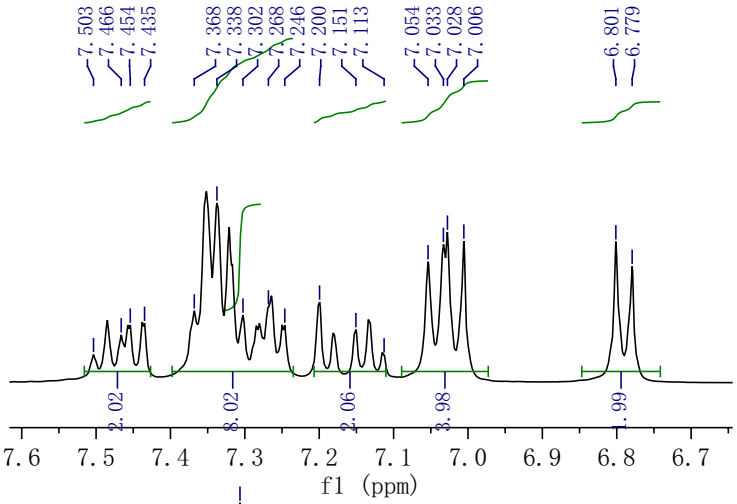


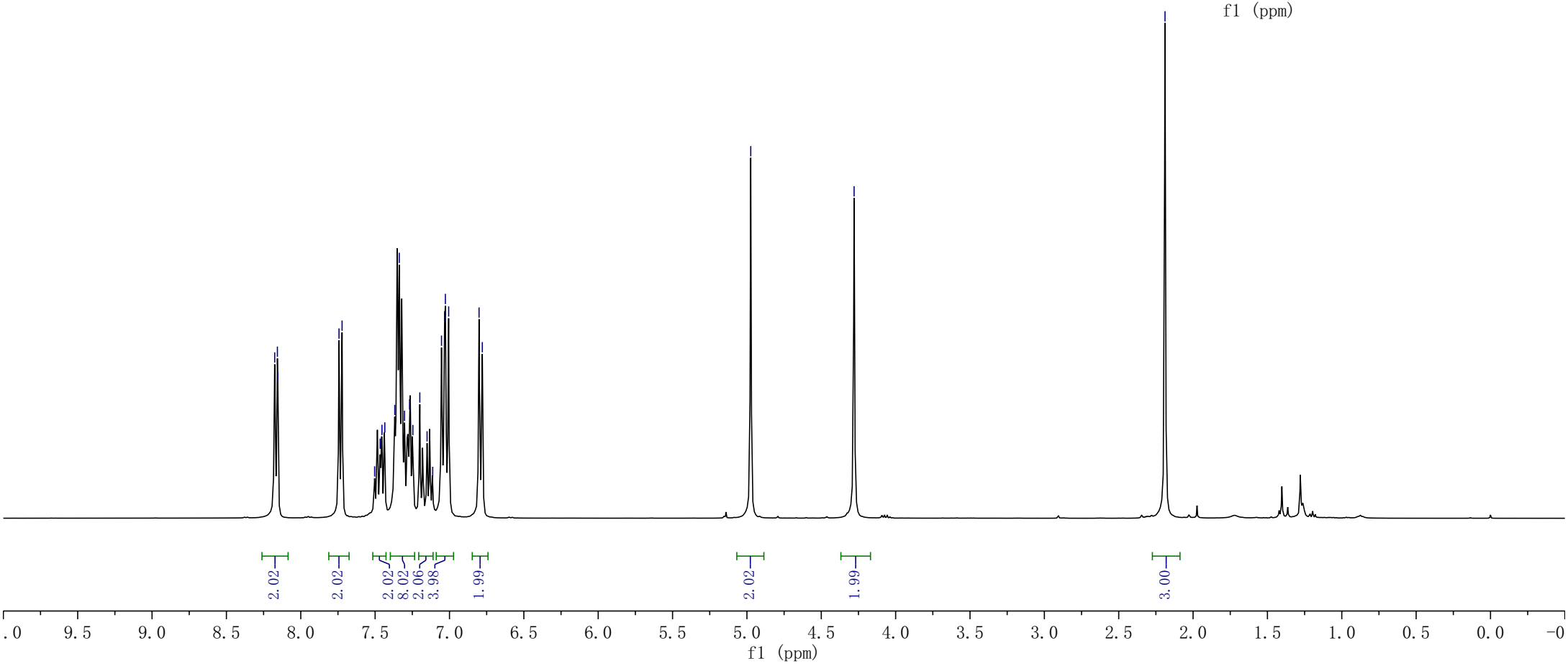

164.36
160.00
151.19
133.57
133.27
132.58
130.16
129.03
128.40
125.79
122.27
116.53
113.89
113.50
86.82
86.01
79.74
77.32
77.00
76.68
66.47
55.16
42.86
38.34
Parameter Value
1 Title MYN-1-159-C-Ms
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.0
5 Number of Scans 40
6 Acquisition Time 1.3631
7 Acquisition Date 2022-04-20T21:43:41
8 Spectrometer Frequency 100.61
9 Spectral Width 24038.5
Ms
N
OBz
PMP
1e
f1 (ppm)

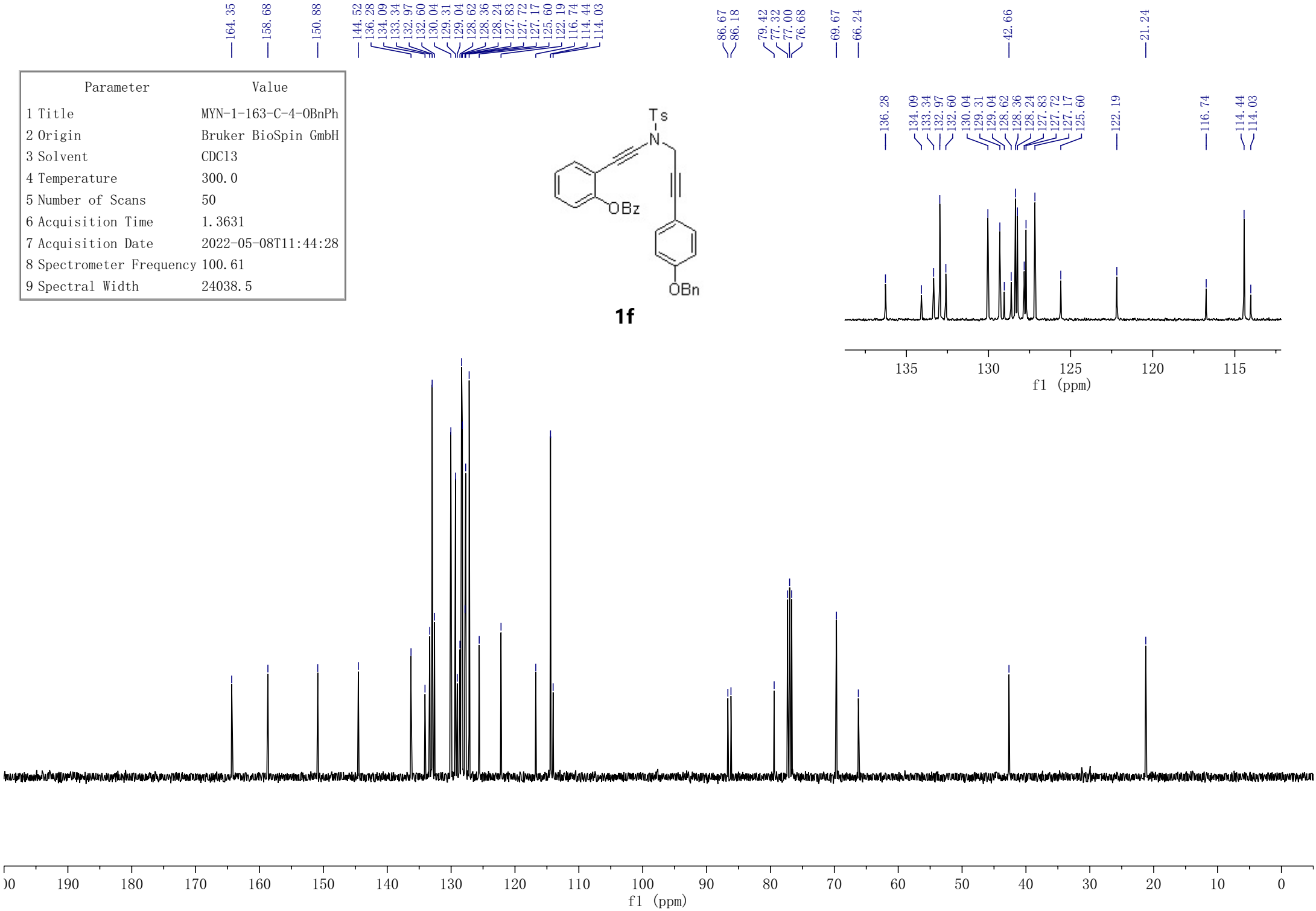
Parameter	Value
1 Title	MYN-1-163-H-4-OBnPh
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	18
6 Acquisition Time	4.0894
7 Acquisition Date	2022-05-08T11:40:57
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8



1f

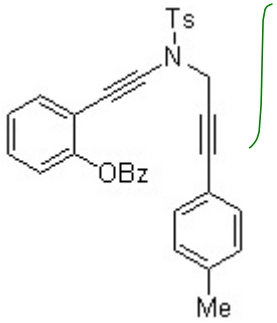




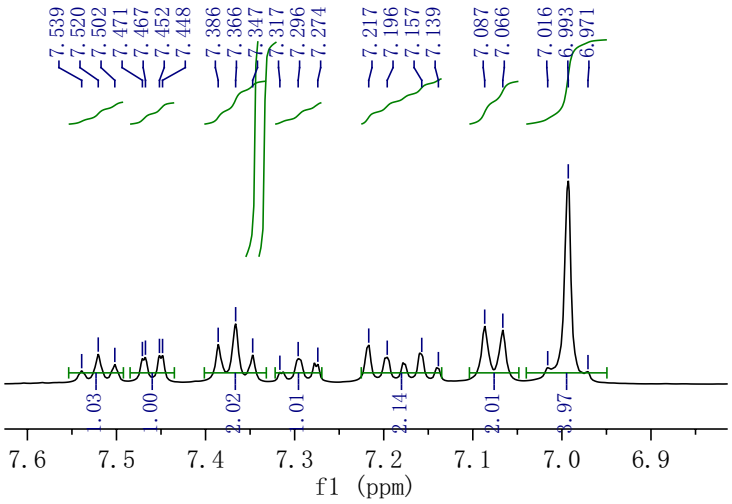


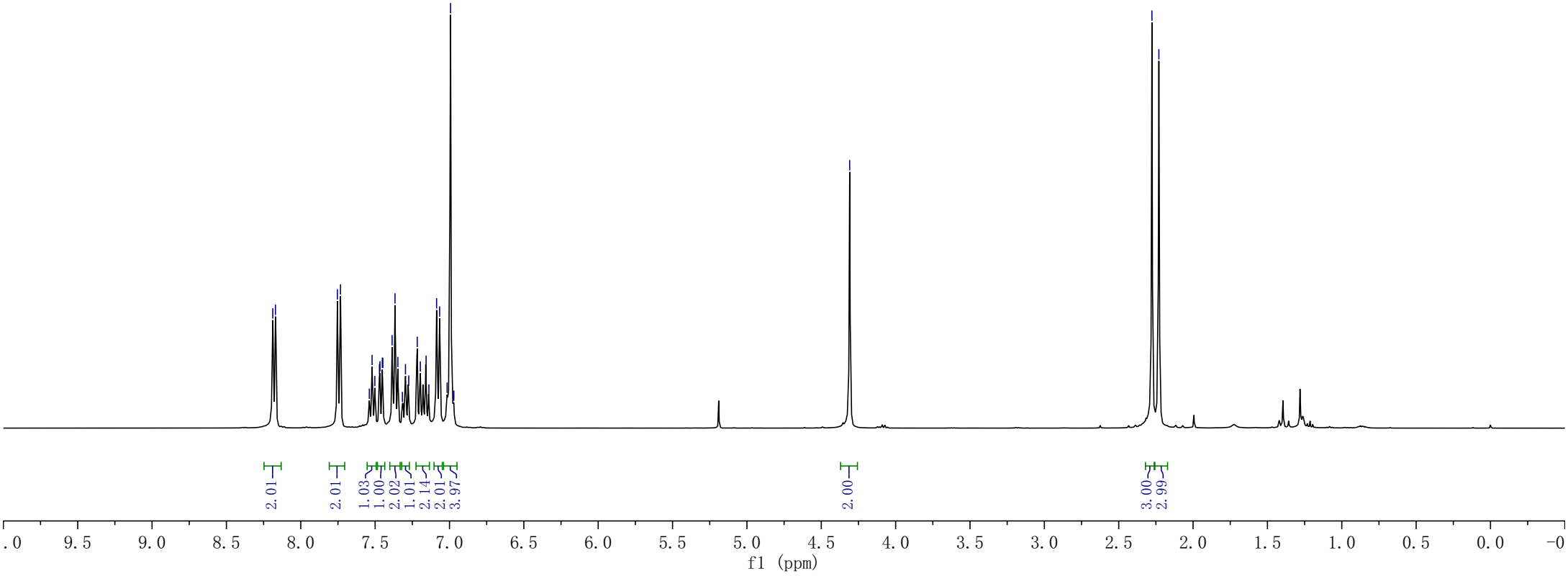
Parameter	Value
1 Title	MYN-1-163-C-4-OBnPh
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	50
6 Acquisition Time	1.3631
7 Acquisition Date	2022-05-08T11:44:28
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5

Parameter	Value
1 Title	MYN-1-162-H-4-MePh
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	14
6 Acquisition Time	4.0894
7 Acquisition Date	2022-05-09T19:10:25
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8

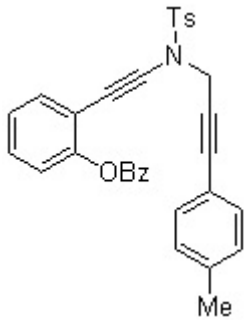


1g

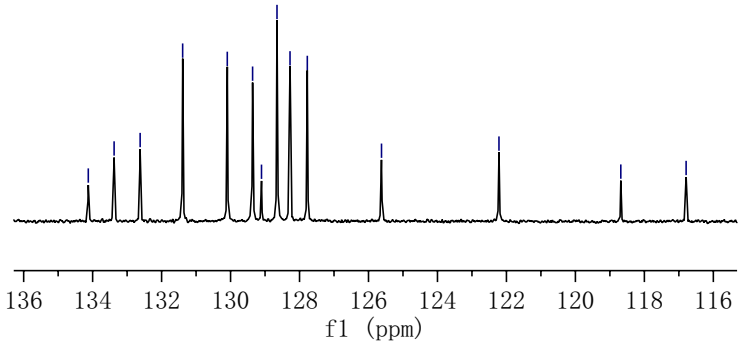


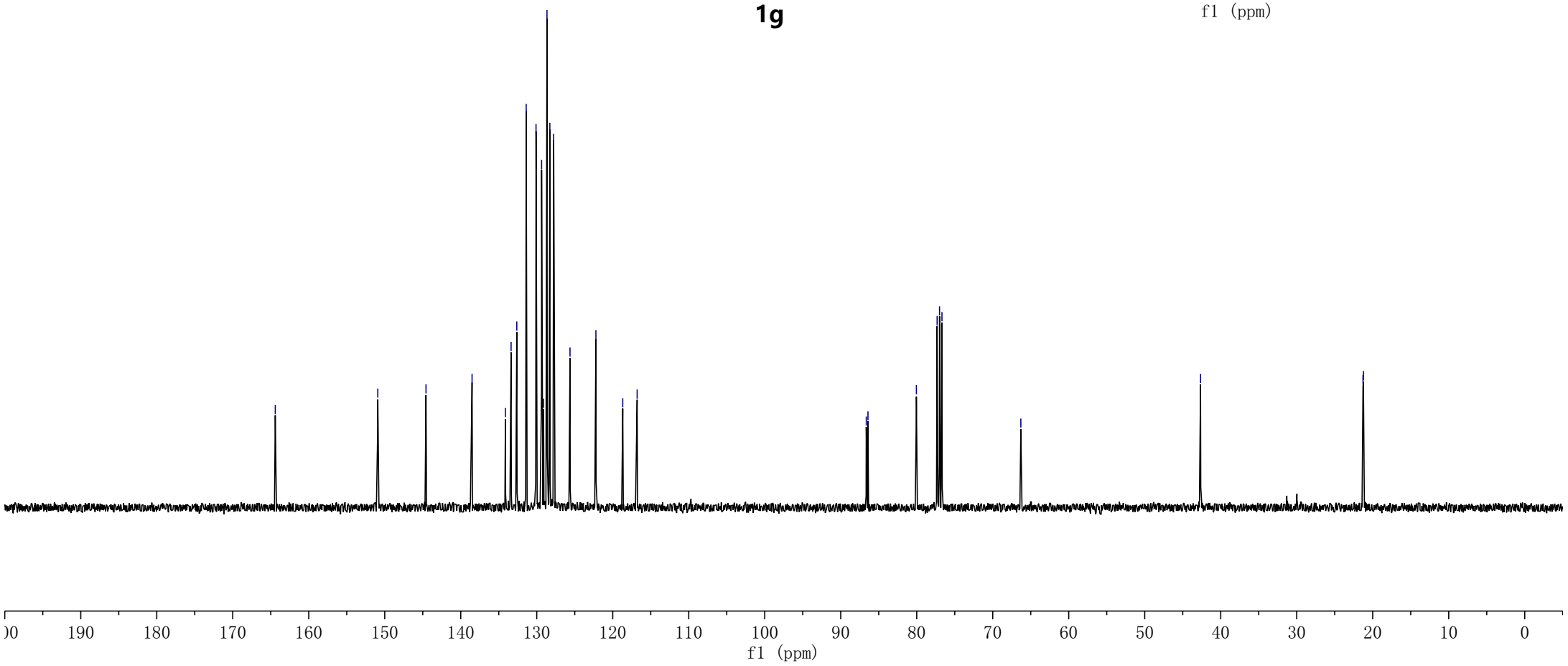


Parameter	Value
1 Title	MYN-1-162-C-4-MePh
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	54
6 Acquisition Time	1.3631
7 Acquisition Date	2022-05-09T19:13:24
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5



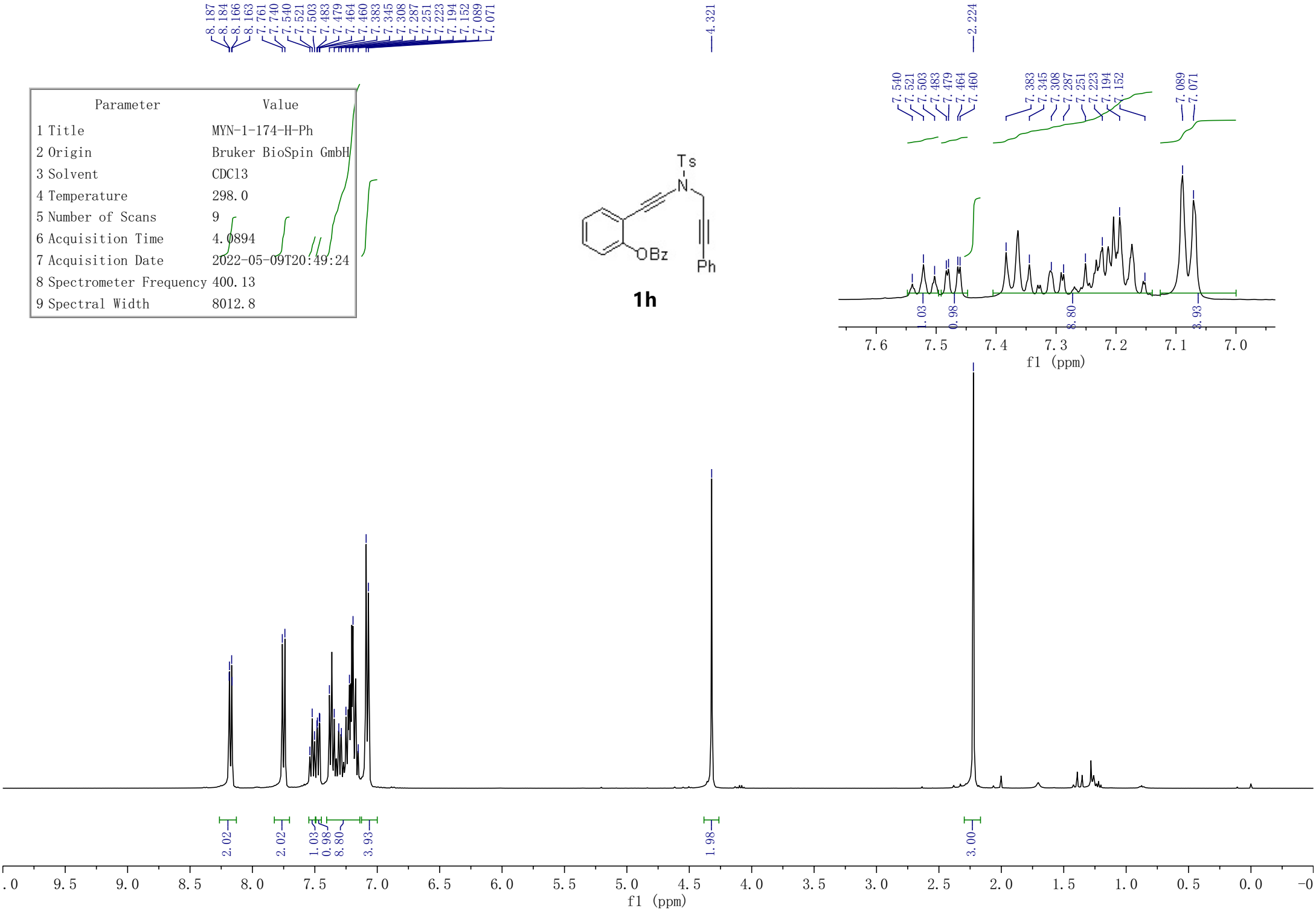
1g

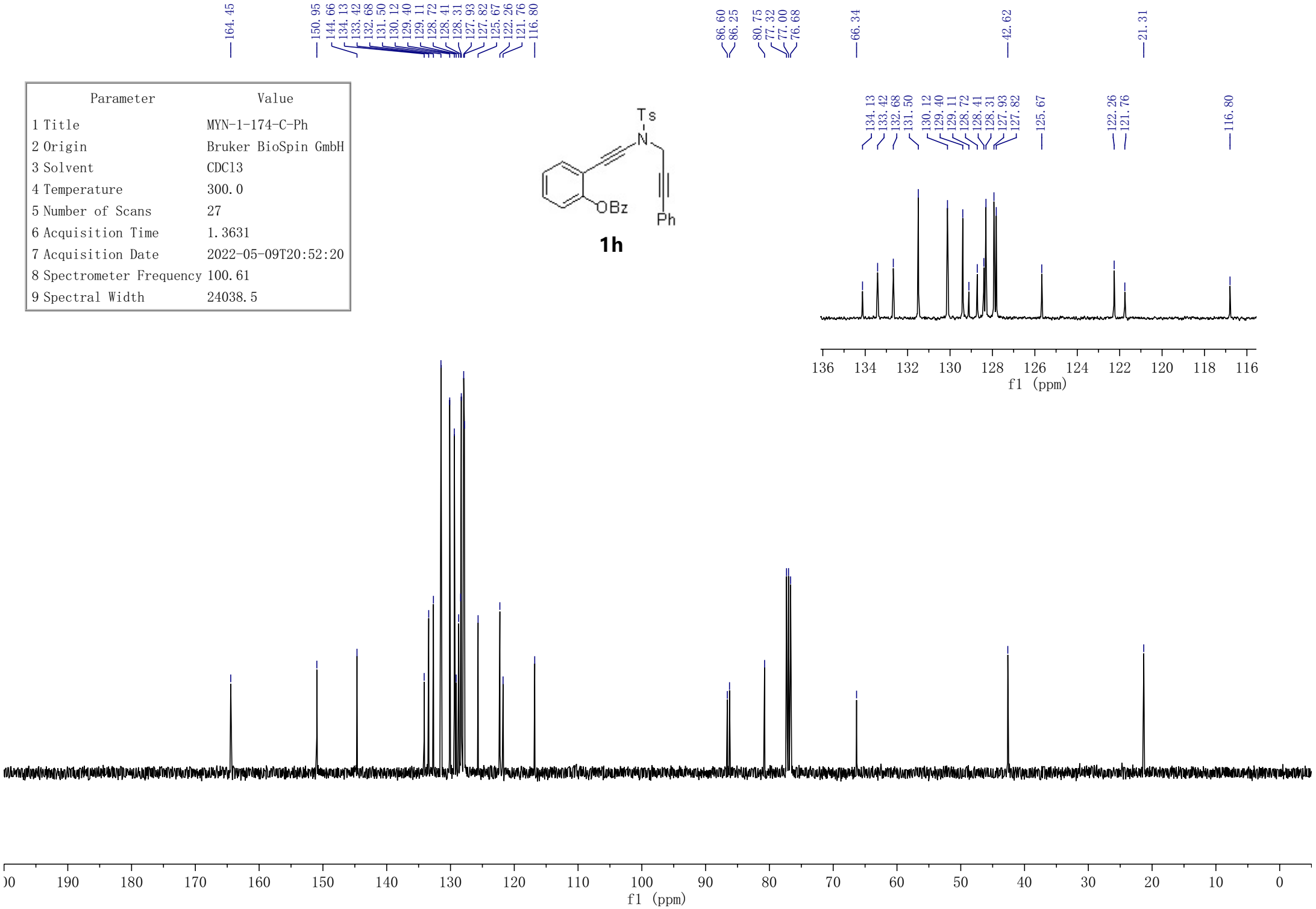




Parameter	Value
1 Title	MYN-1-174-H-Ph
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	9
6 Acquisition Time	4.0894
7 Acquisition Date	2022-05-09T20:49:24
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8

1h

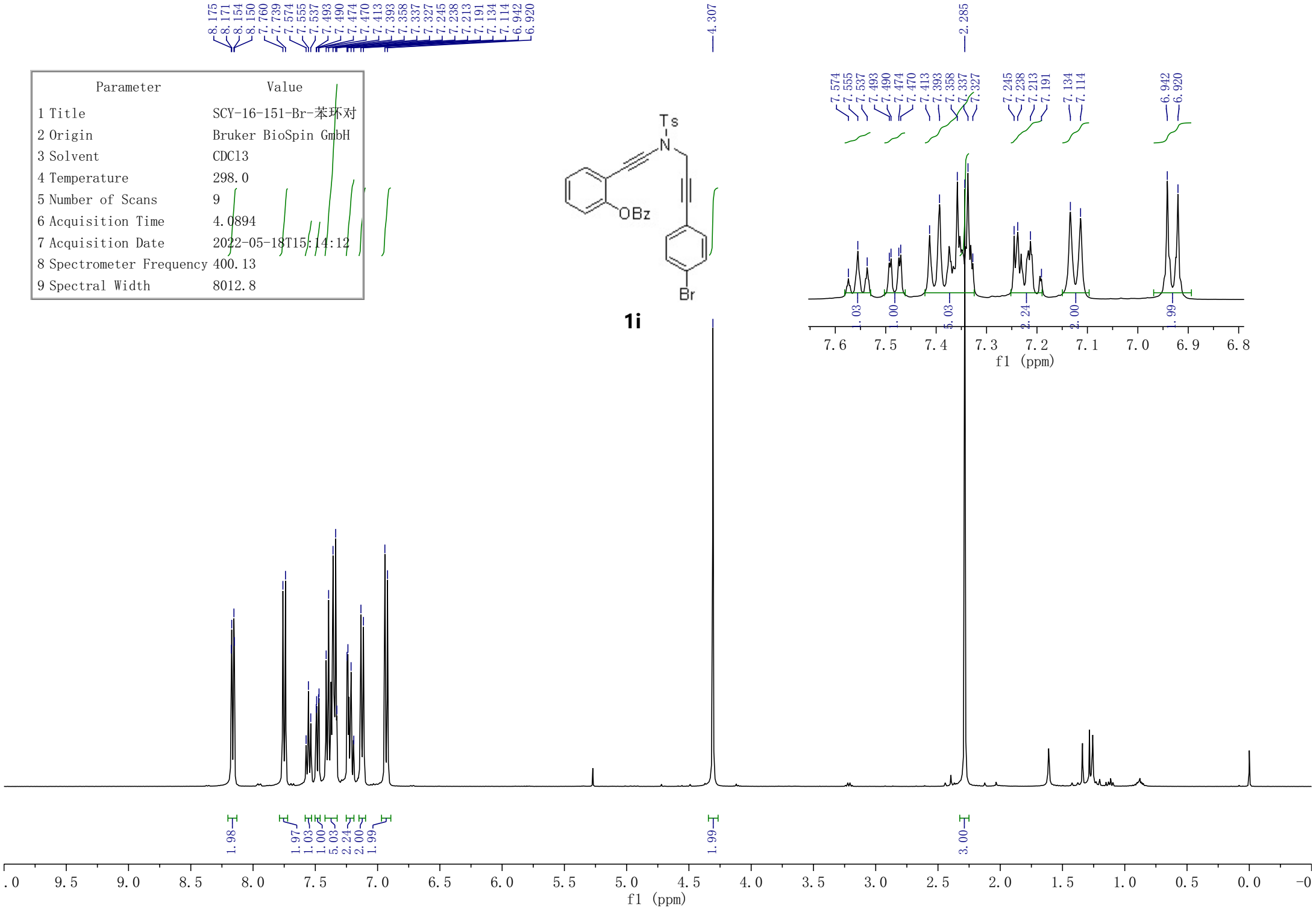


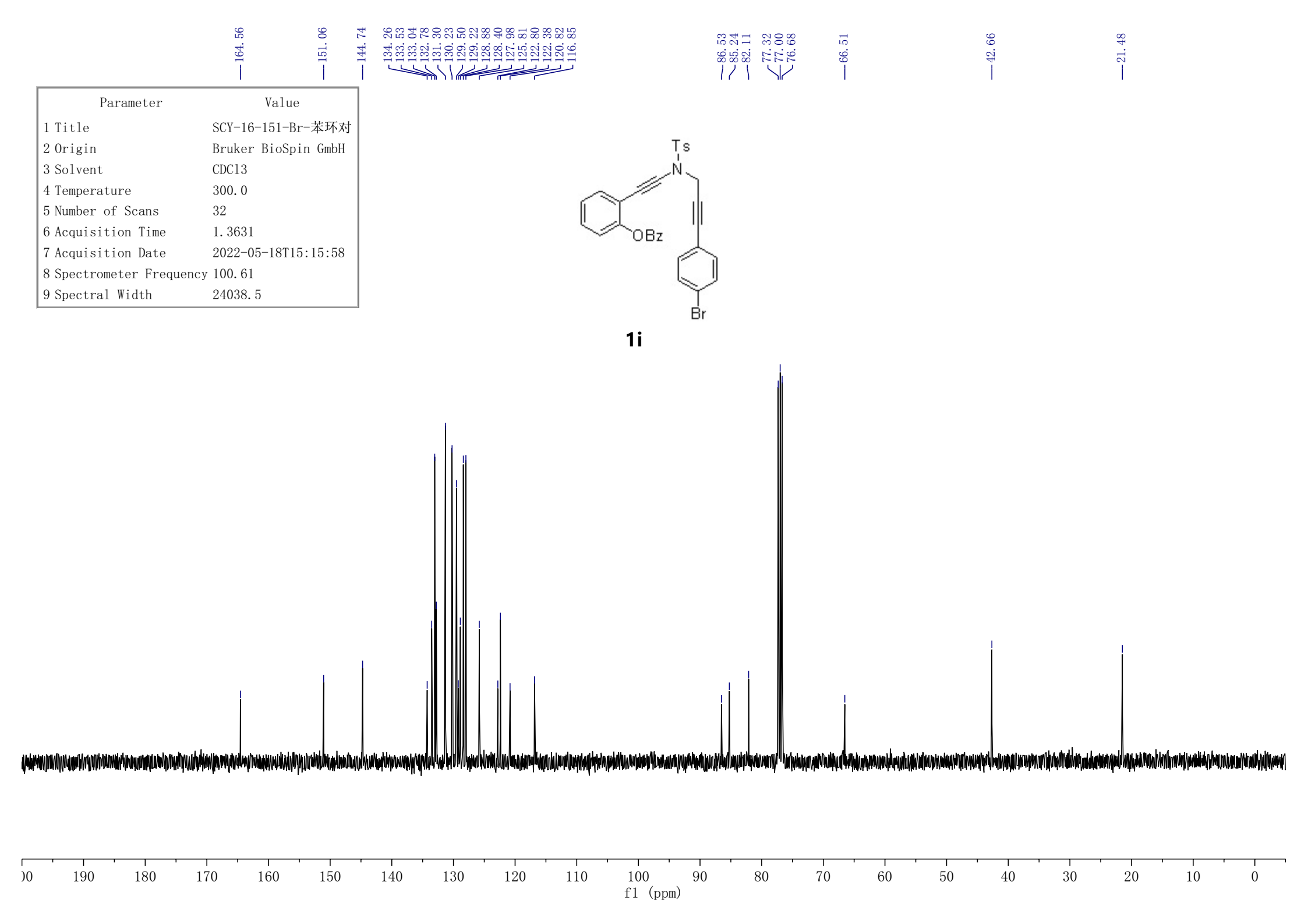


Parameter	Value
1 Title	MYN-1-174-C-Ph
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	27
6 Acquisition Time	1.3631
7 Acquisition Date	2022-05-09T20:52:20
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5

Parameter	Value
1 Title	SCY-16-151-Br-苯环对
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	9
6 Acquisition Time	4.0894
7 Acquisition Date	2022-05-18T15:14:12
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8

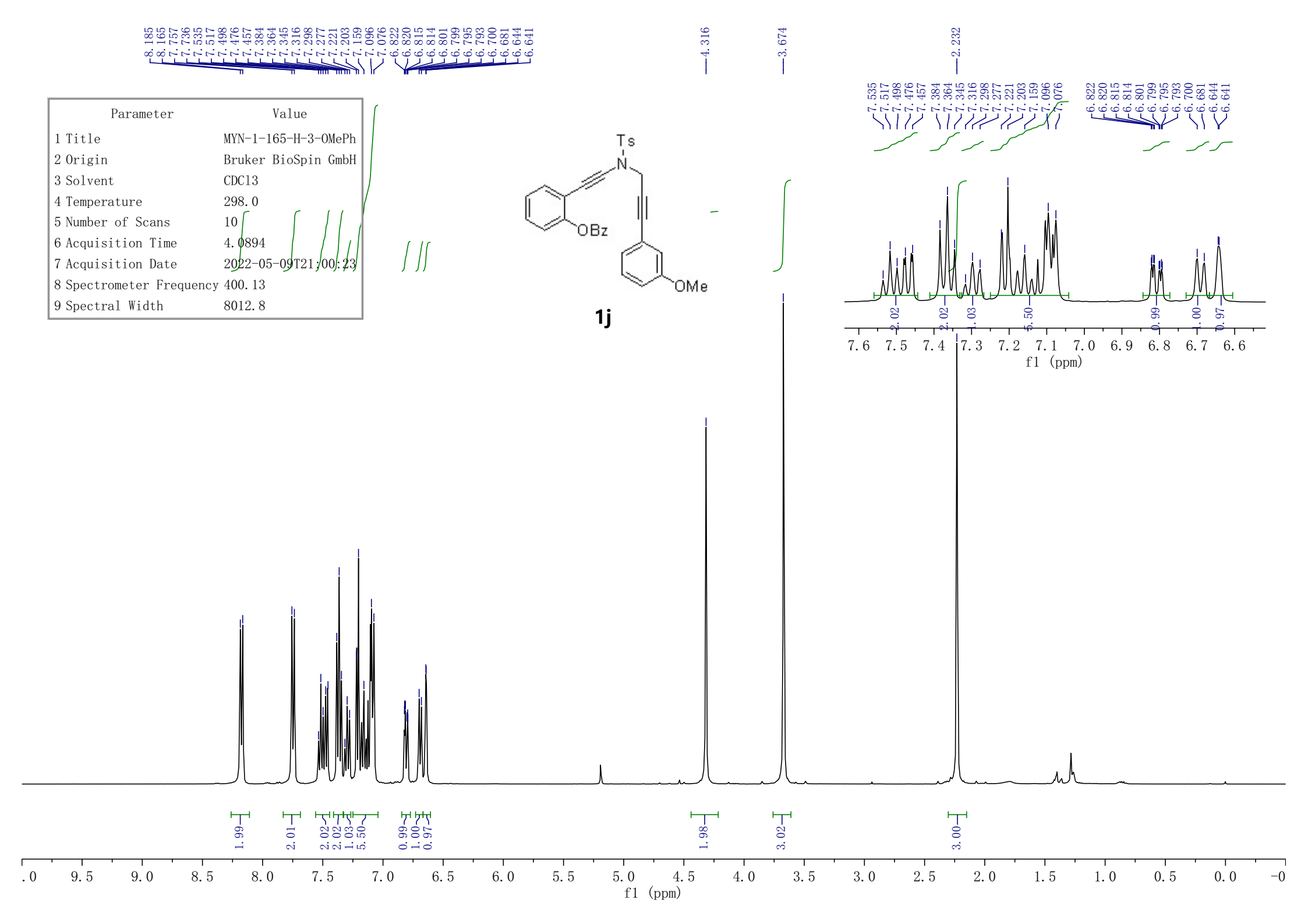
1i

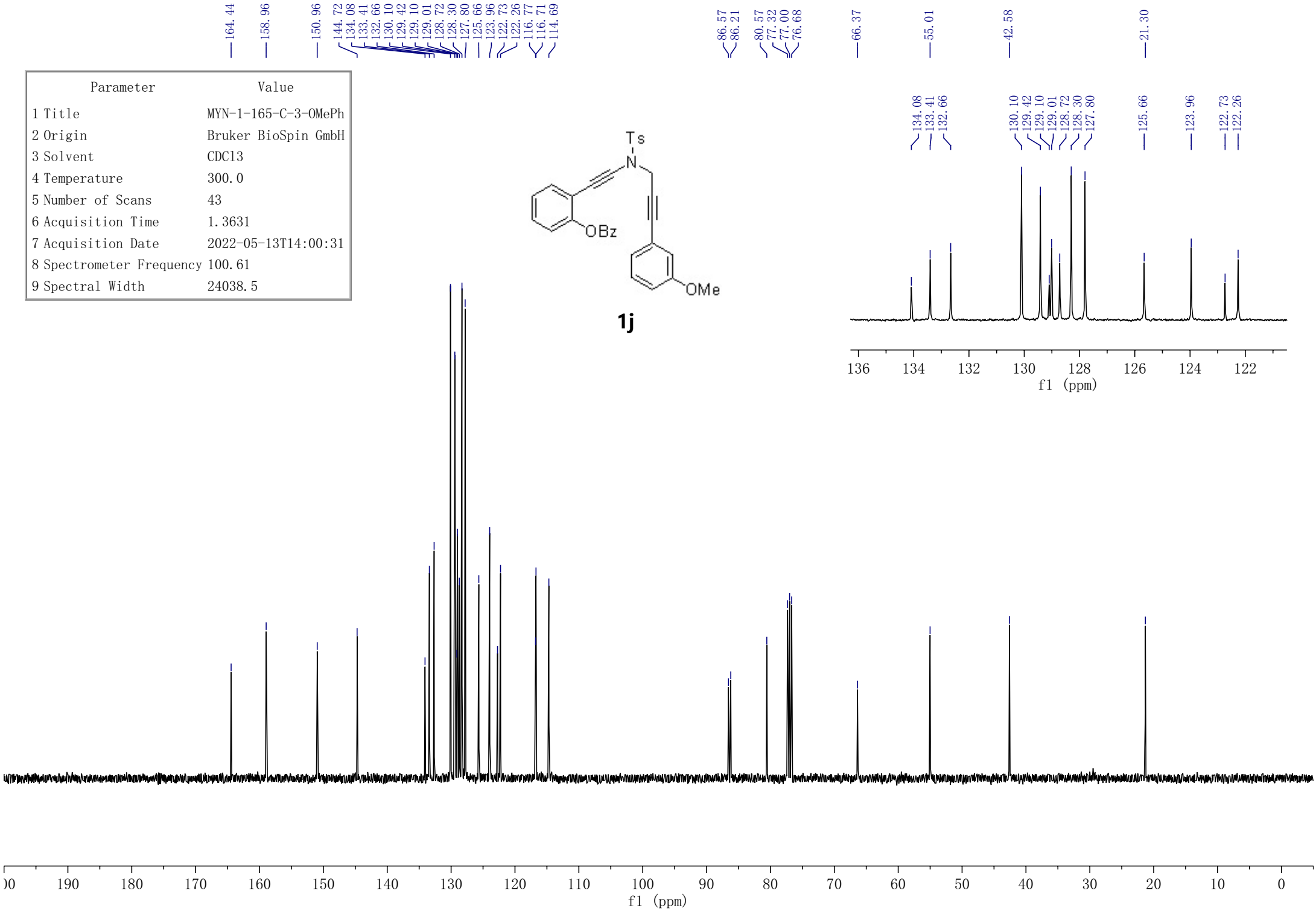



164.56
151.06
144.74
134.26
133.53
133.04
132.78
131.30
130.23
129.50
129.22
128.88
128.40
127.98
125.81
122.80
122.38
120.82
116.85
86.53
85.24
82.11
77.32
77.00
76.68
66.51
42.66
21.48
Parameter Value
1 Title SCY-16-151-Br-苯环对
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.0
5 Number of Scans 32
6 Acquisition Time 1.3631
7 Acquisition Date 2022-05-18T15:15:58
8 Spectrometer Frequency 100.61
9 Spectral Width 24038.5
Ts
N
OBz
Br
1i
f1 (ppm)

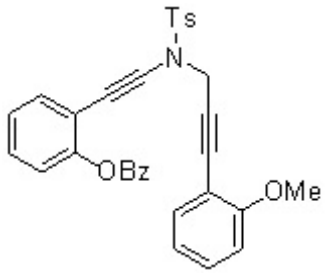
Parameter	Value
1 Title	MYN-1-165-H-3-OMePh
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	10
6 Acquisition Time	4.0894
7 Acquisition Date	2022-05-09T21:00:23
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8

1j

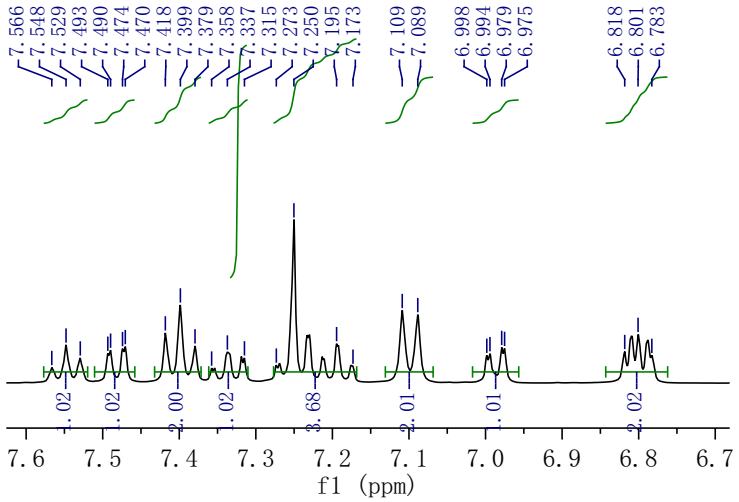


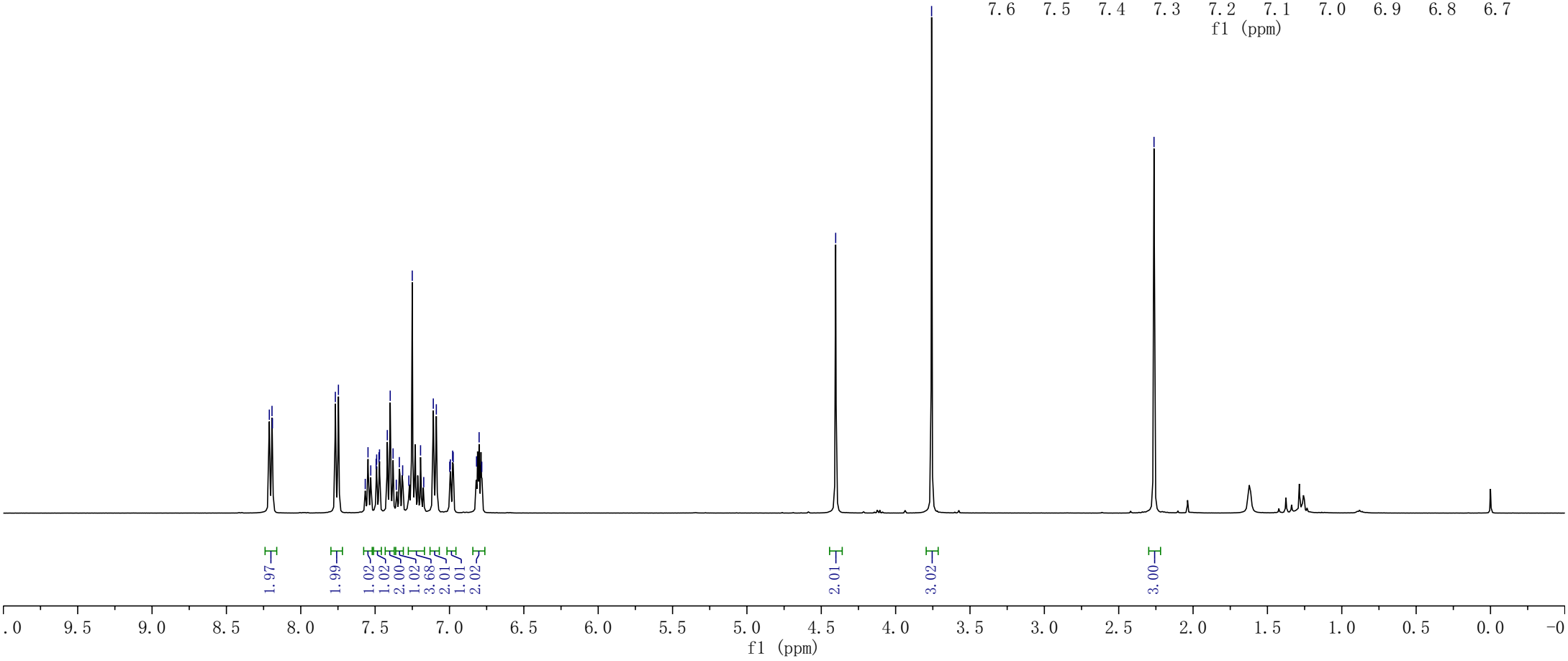

164.44
158.96
150.96
144.72
134.08
133.41
132.66
130.10
129.42
129.10
129.01
128.72
128.30
127.80
125.66
123.96
122.73
122.26
116.77
116.71
114.69
86.57
86.21
80.57
77.32
77.00
76.68
66.37
55.01
42.58
21.30
Parameter Value
1 Title MYN-1-165-C-3-OMePh
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.0
5 Number of Scans 43
6 Acquisition Time 1.3631
7 Acquisition Date 2022-05-13T14:00:31
8 Spectrometer Frequency 100.61
9 Spectral Width 24038.5
Ts
N
OBz
OMe
1j
f1 (ppm)
f1 (ppm)

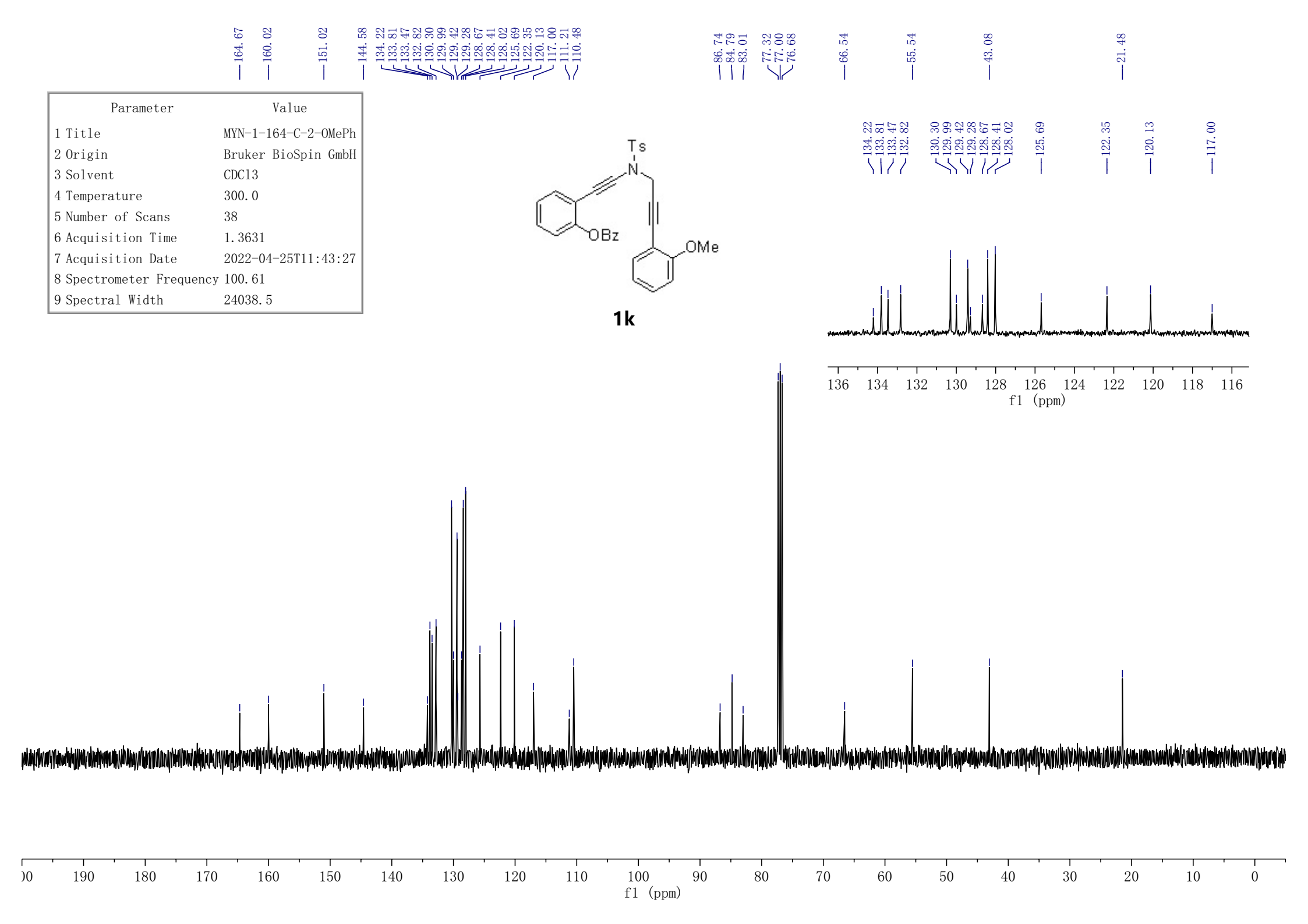
Parameter	Value
1 Title	MYN-1-164-H-2-OMePh
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	14
6 Acquisition Time	4.0894
7 Acquisition Date	2022-04-25T11:40:08
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8



1k

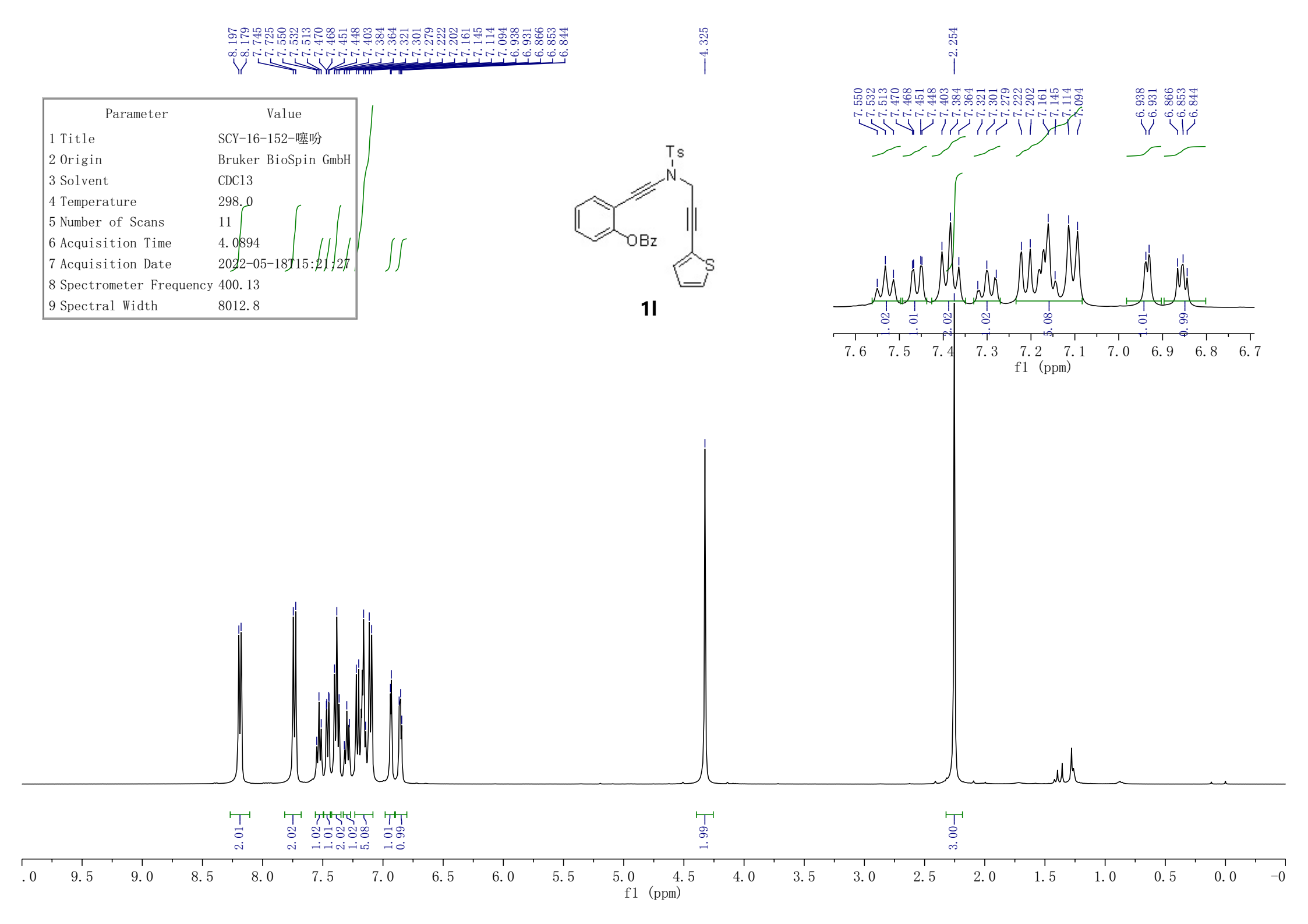





164.67
160.02
151.02
144.58
134.22
133.81
133.47
132.82
130.30
129.99
129.42
129.28
128.67
128.41
128.02
125.69
122.35
120.13
117.00
111.21
110.48
86.74
84.79
83.01
77.32
77.00
76.68
66.54
55.54
43.08
21.48
Parameter Value
1 Title MYN-1-164-C-2-OMePh
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.0
5 Number of Scans 38
6 Acquisition Time 1.3631
7 Acquisition Date 2022-04-25T11:43:27
8 Spectrometer Frequency 100.61
9 Spectral Width 24038.5
Ts
N
OBz
OMe
1k
f1 (ppm)
f1 (ppm)

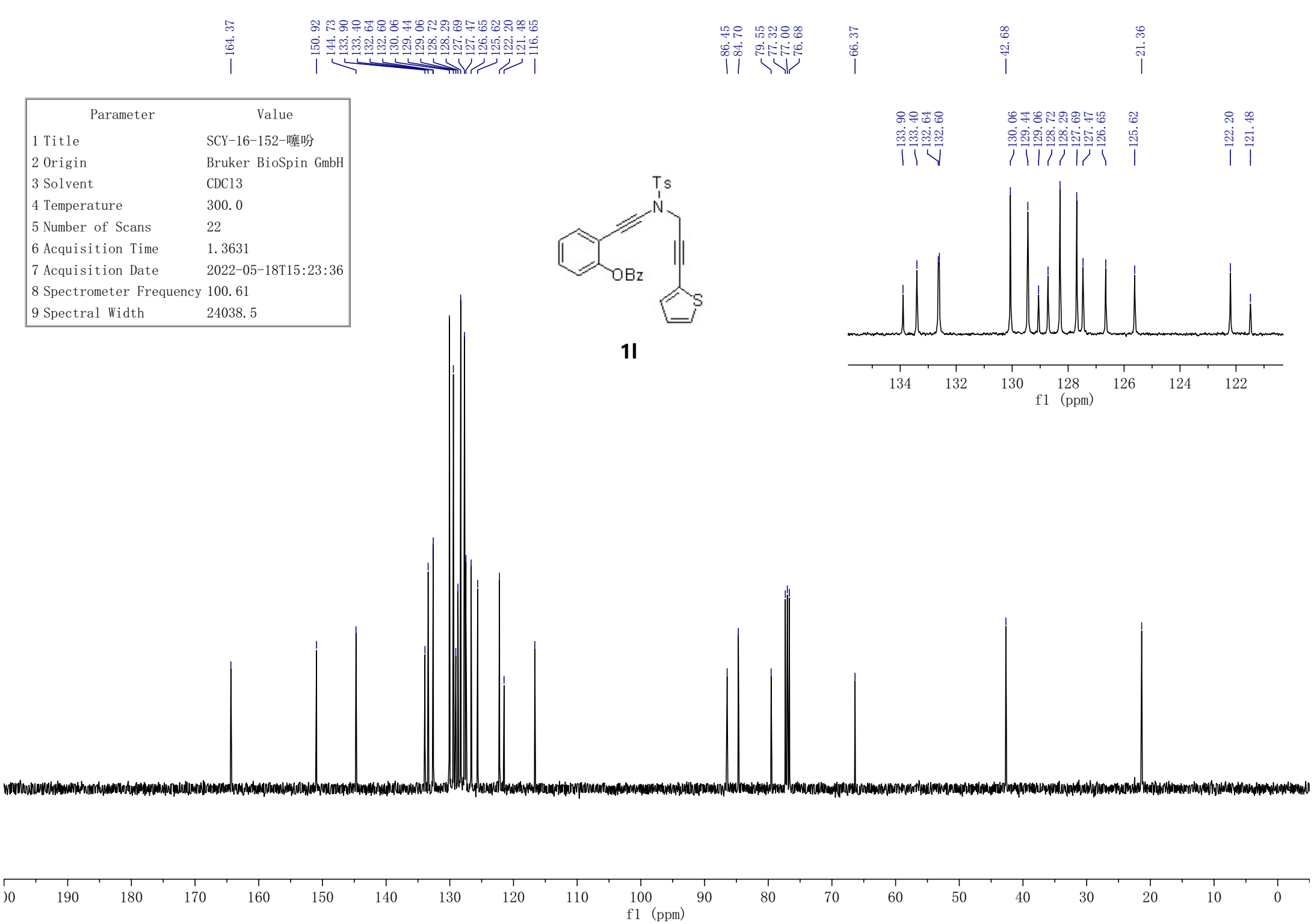
Parameter	Value
1 Title	SCY-16-152-噻吩
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	11
6 Acquisition Time	4.0894
7 Acquisition Date	2022-05-18T15:21:27
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8

1l

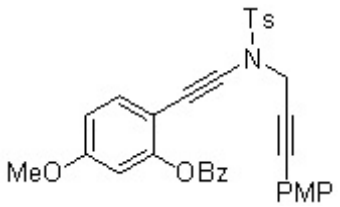


Parameter	Value
1 Title	SCY-16-152-噻吩
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	22
6 Acquisition Time	1.3631
7 Acquisition Date	2022-05-18T15:23:36
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5

1l



Parameter	Value
1 Title	scy-16-164-OMe-炔对
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	10
6 Acquisition Time	4.0894
7 Acquisition Date	2022-05-21T20:48:55
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8



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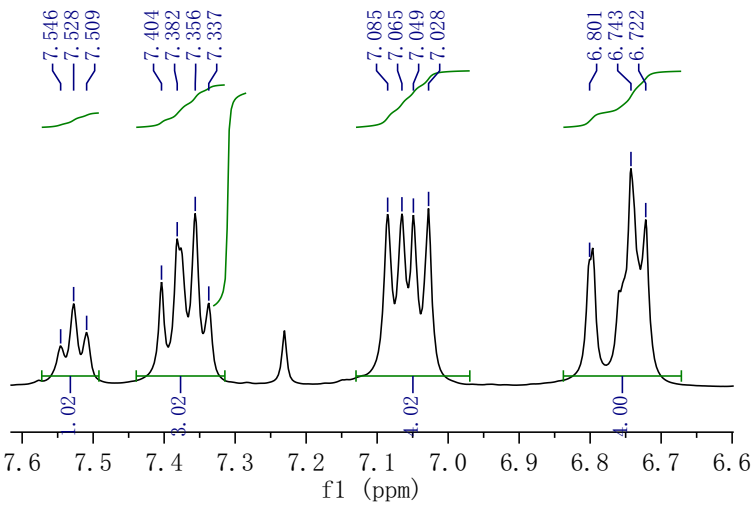
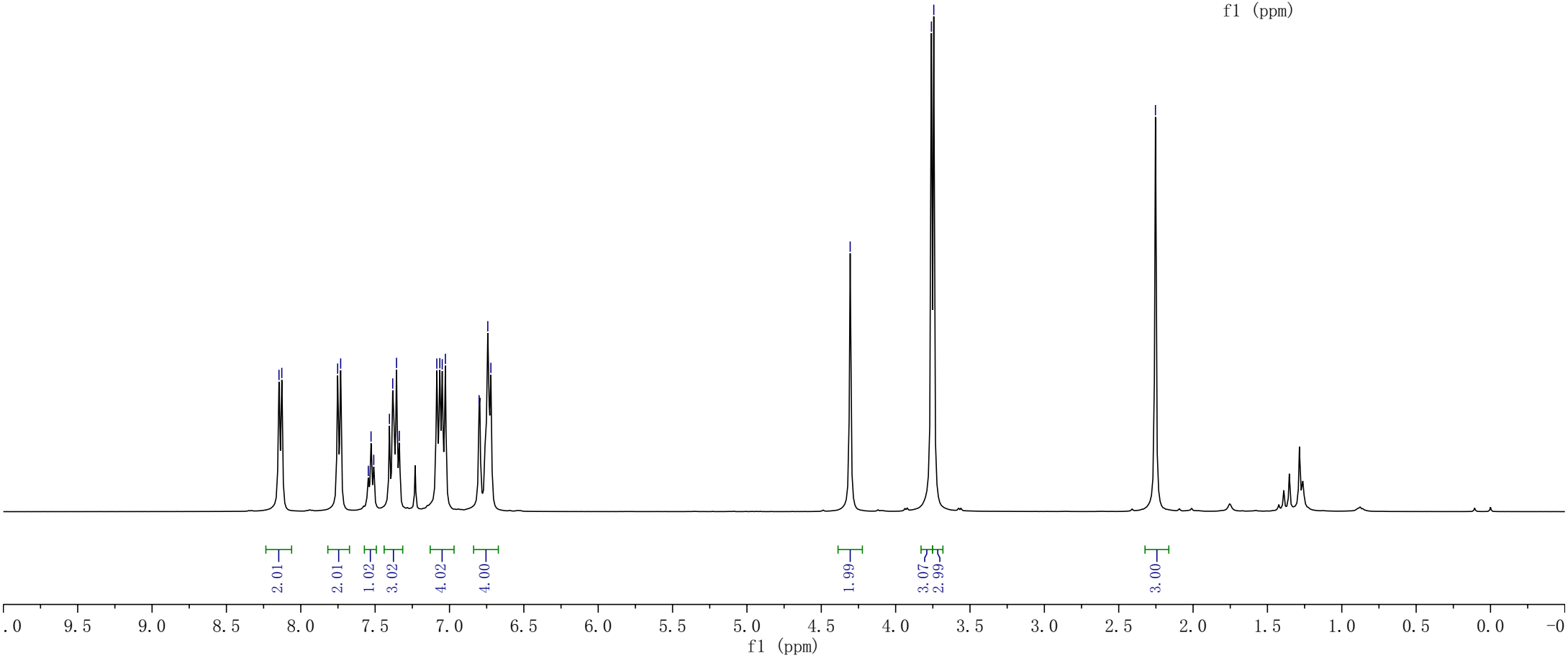
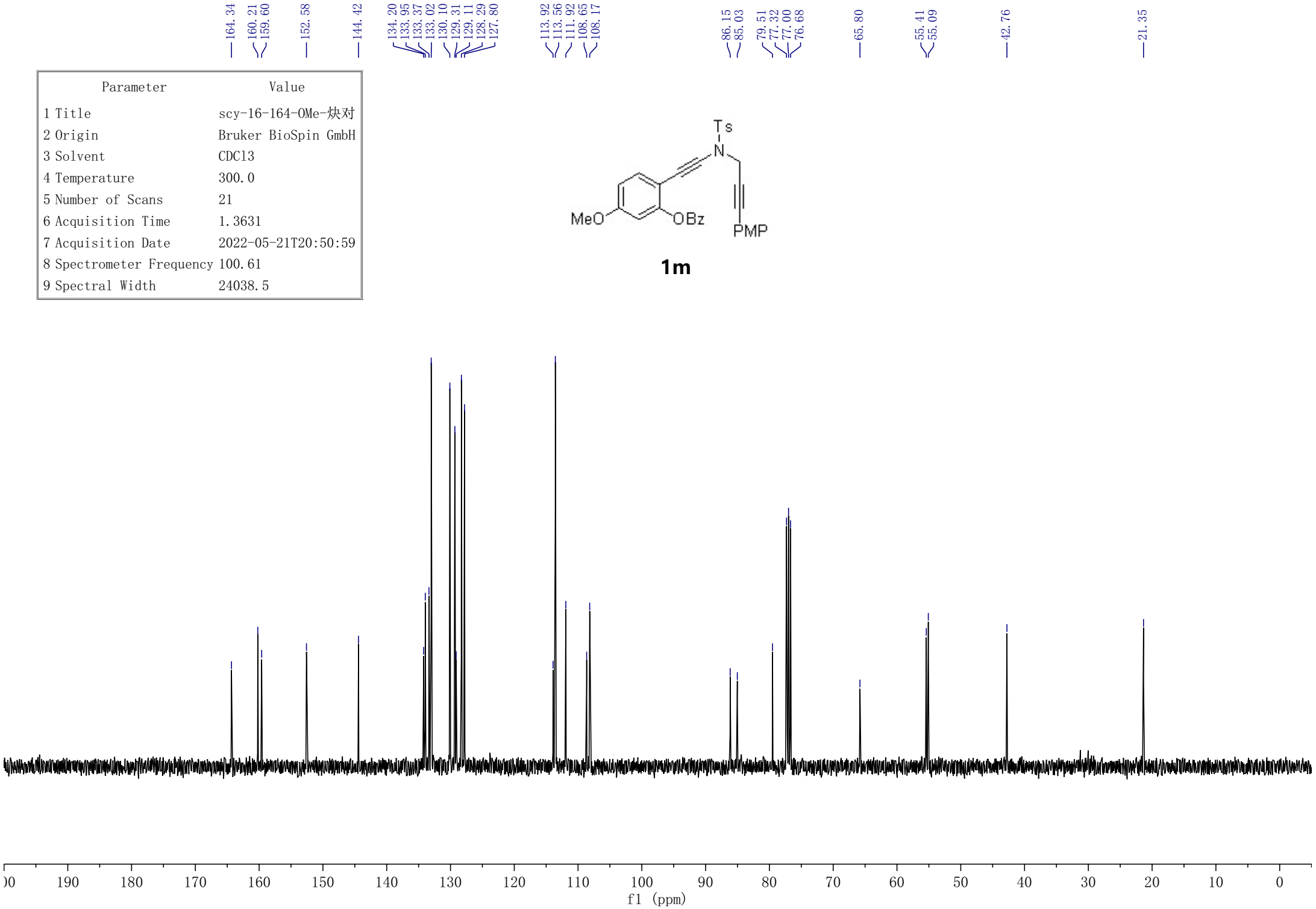
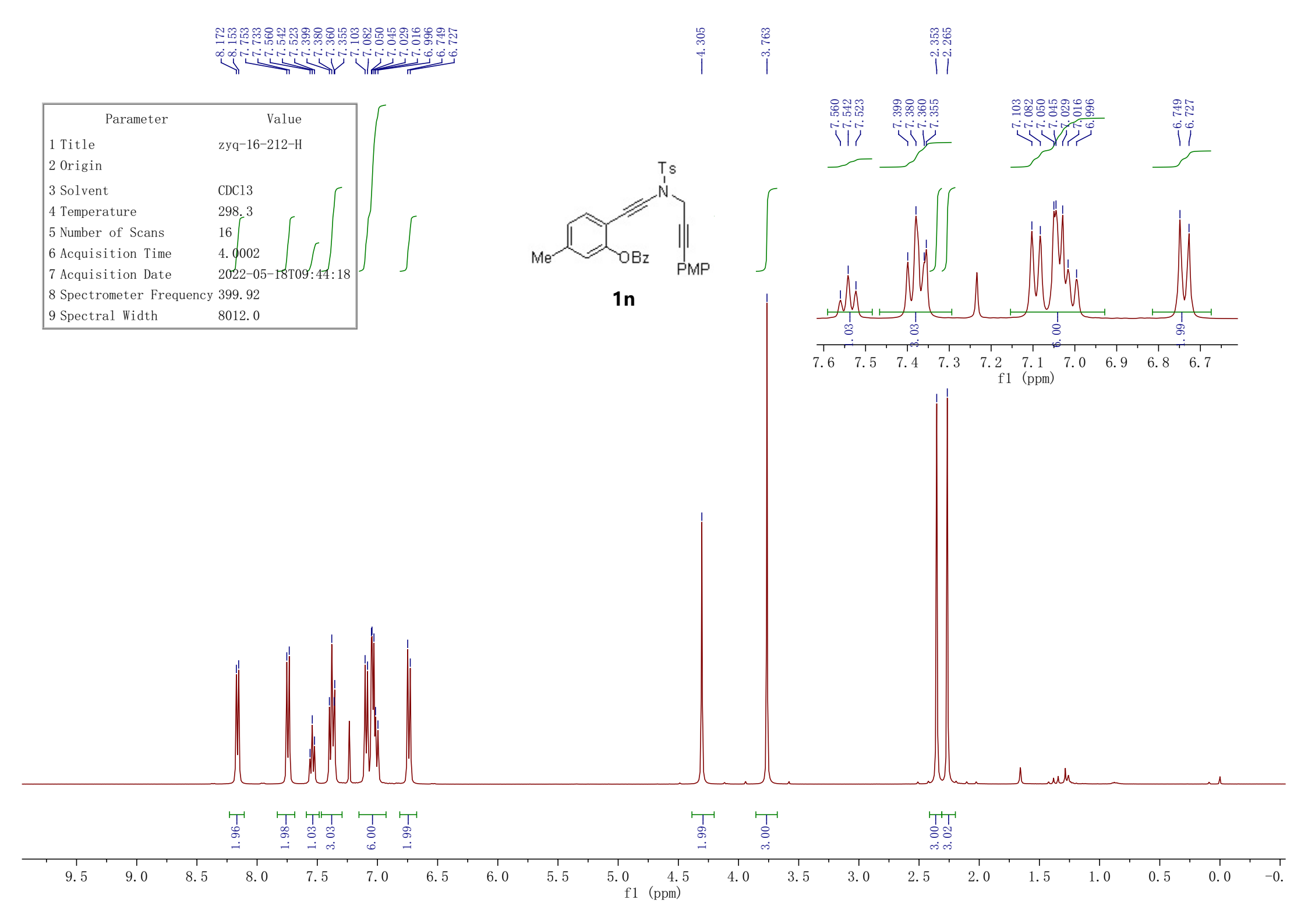






Parameter	Value
1 Title	scy-16-164-OMe-炔对
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	21
6 Acquisition Time	1.3631
7 Acquisition Date	2022-05-21T20:50:59
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5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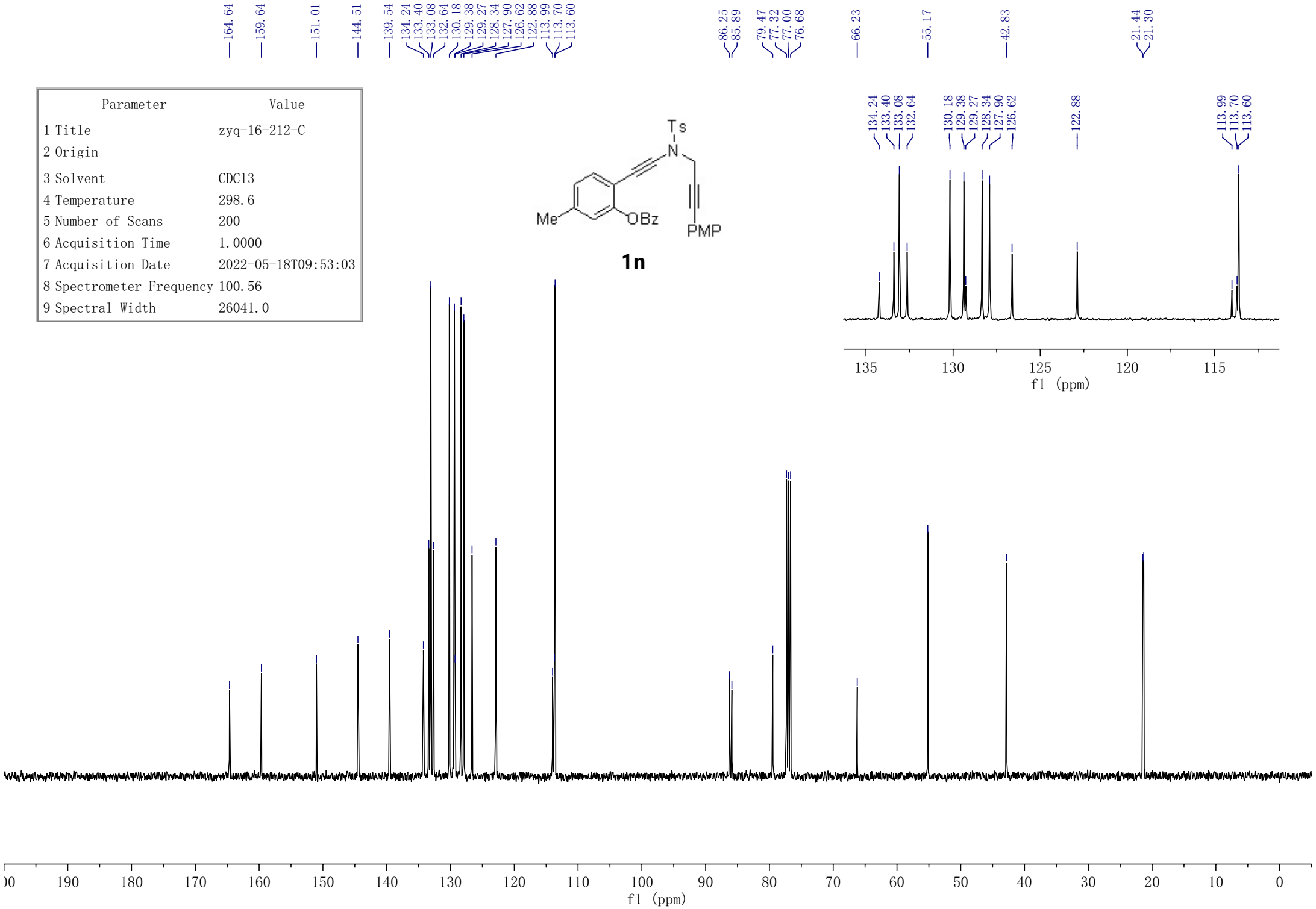
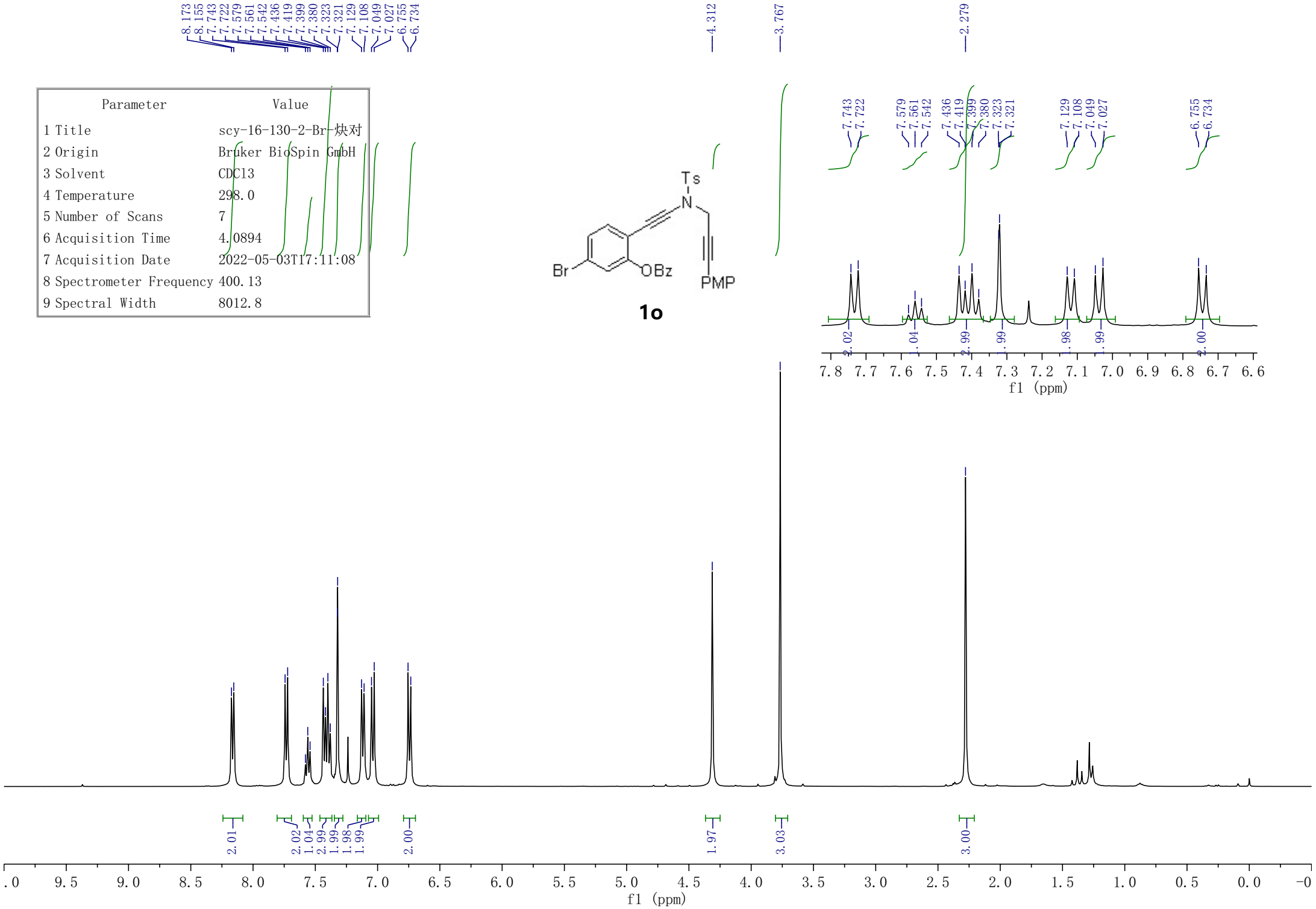
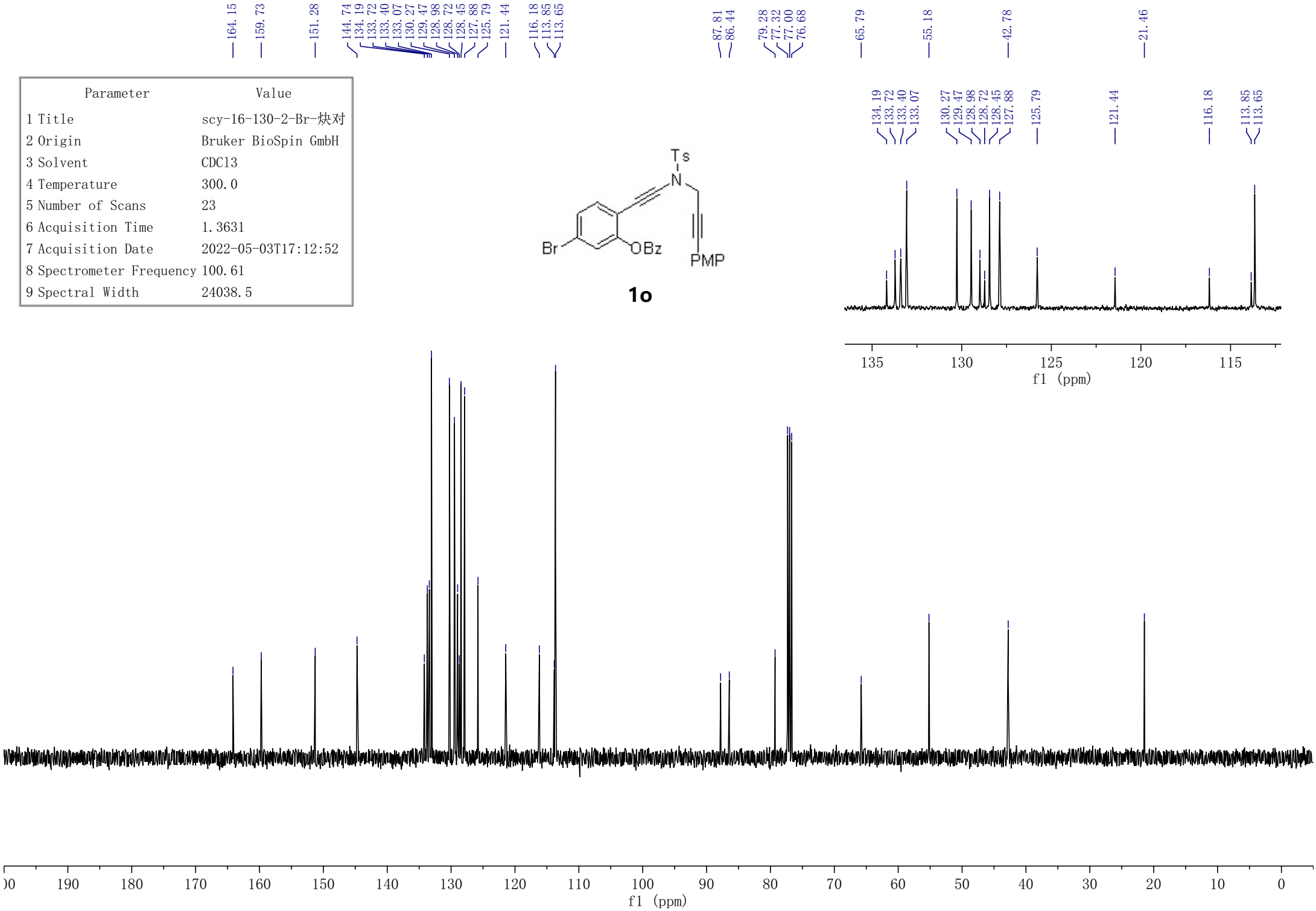
7.753
7.733
7.560
7.542
7.523
7.399
7.380
7.360
7.355
7.103
7.082
7.050
7.045
7.029
7.016
6.996
6.749
6.727
4.305
3.763
2.353
2.265
Parameter Value
1 Title zyq-16-212-H
2 Origin
3 Solvent CDCl3
4 Temperature 298.3
5 Number of Scans 16
6 Acquisition Time 4.0002
7 Acquisition Date 2022-05-18T09:44:18
8 Spectrometer Frequency 399.92
9 Spectral Width 8012.0
Ts
N
Me
OBz
PMP
1n
1.96
1.98
1.03
3.03
6.00
1.99
1.99
3.00
3.00
3.02
f1 (ppm)


164.64
159.64
151.01
144.51
139.54
134.24
133.40
133.08
132.64
130.18
129.38
129.27
128.34
127.90
126.62
122.88
113.99
113.70
113.60
86.25
85.89
79.47
77.32
77.00
76.68
66.23
55.17
42.83
21.44
21.30
Parameter Value
1 Title zyq-16-212-C
2 Origin
3 Solvent CDCl3
4 Temperature 298.6
5 Number of Scans 200
6 Acquisition Time 1.0000
7 Acquisition Date 2022-05-18T09:53:03
8 Spectrometer Frequency 100.56
9 Spectral Width 26041.0
Ts
N
Me
OBz
PMP
1n
f1 (ppm)

Parameter	Value
1 Title	scy-16-130-2-Br-炔对
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	7
6 Acquisition Time	4.0894
7 Acquisition Date	2022-05-03T17:11:08
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8

1o

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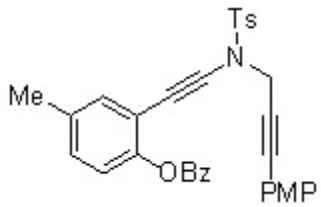
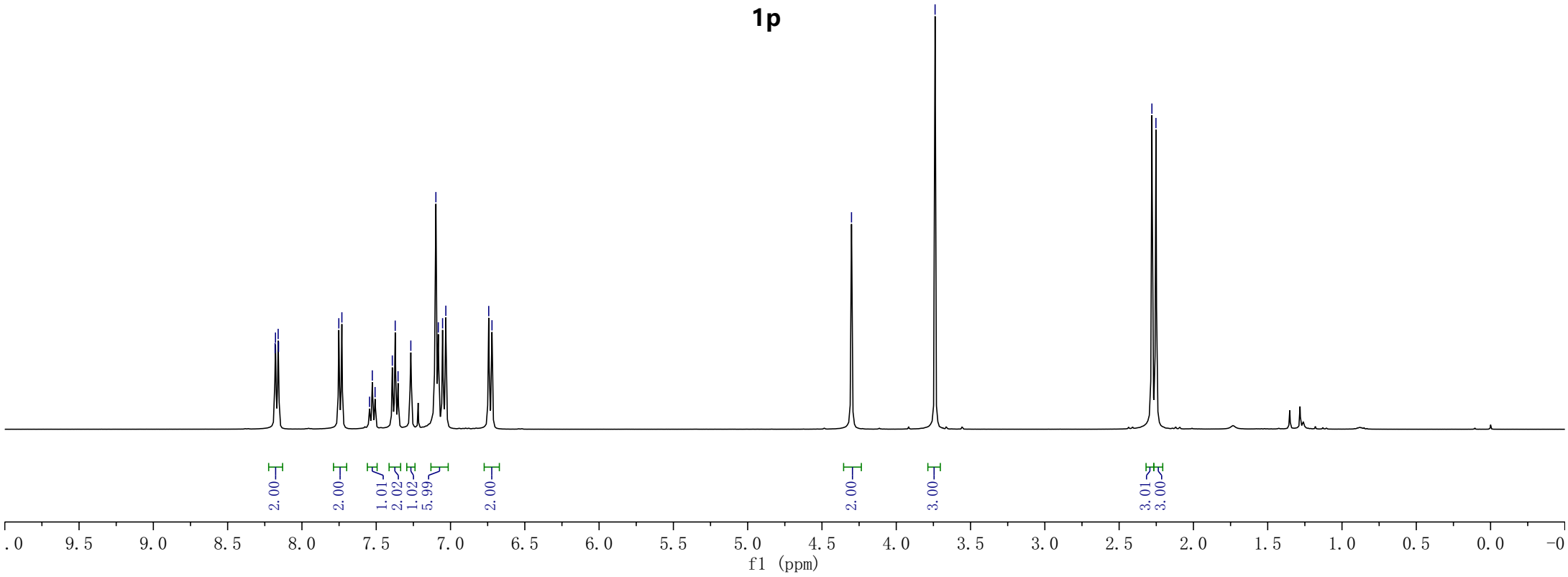
151.28
144.74
134.19
133.72
133.40
133.07
130.27
129.47
128.98
128.72
128.45
127.88
125.79
121.44
116.18
113.85
113.65
87.81
86.44
79.28
77.32
77.00
76.68
65.79
55.18
42.78
21.46
Parameter Value
1 Title scy-16-130-2-Br-炔对
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.0
5 Number of Scans 23
6 Acquisition Time 1.3631
7 Acquisition Date 2022-05-03T17:12:52
8 Spectrometer Frequency 100.61
9 Spectral Width 24038.5
Ts
N
Br
OBz
PMP
1o
f1 (ppm)
f1 (ppm)

Parameter	Value
1 Title	SCY-16-143-Me-氧对
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	8
6 Acquisition Time	4.0894
7 Acquisition Date	2022-05-16T15:00:56
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8

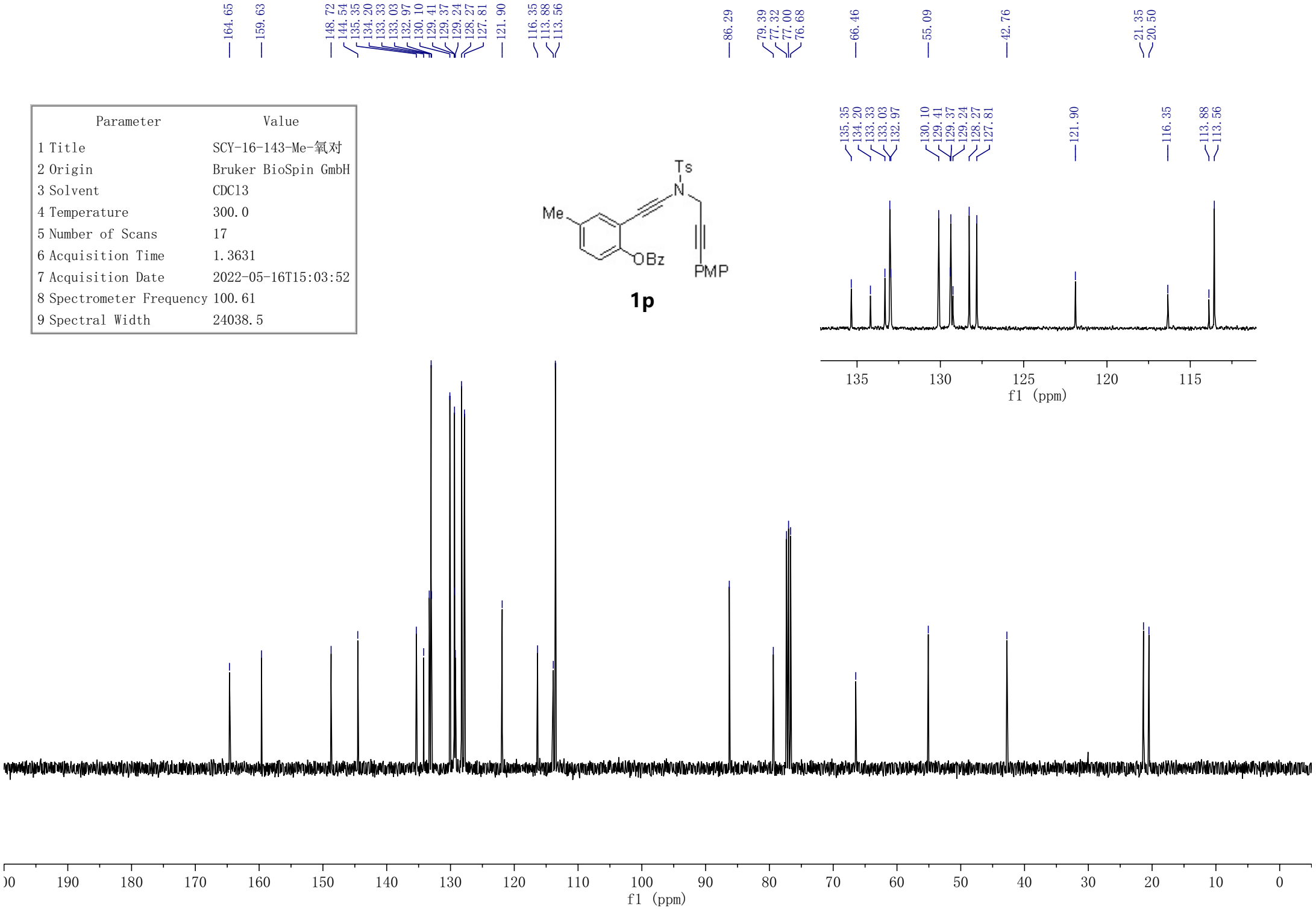


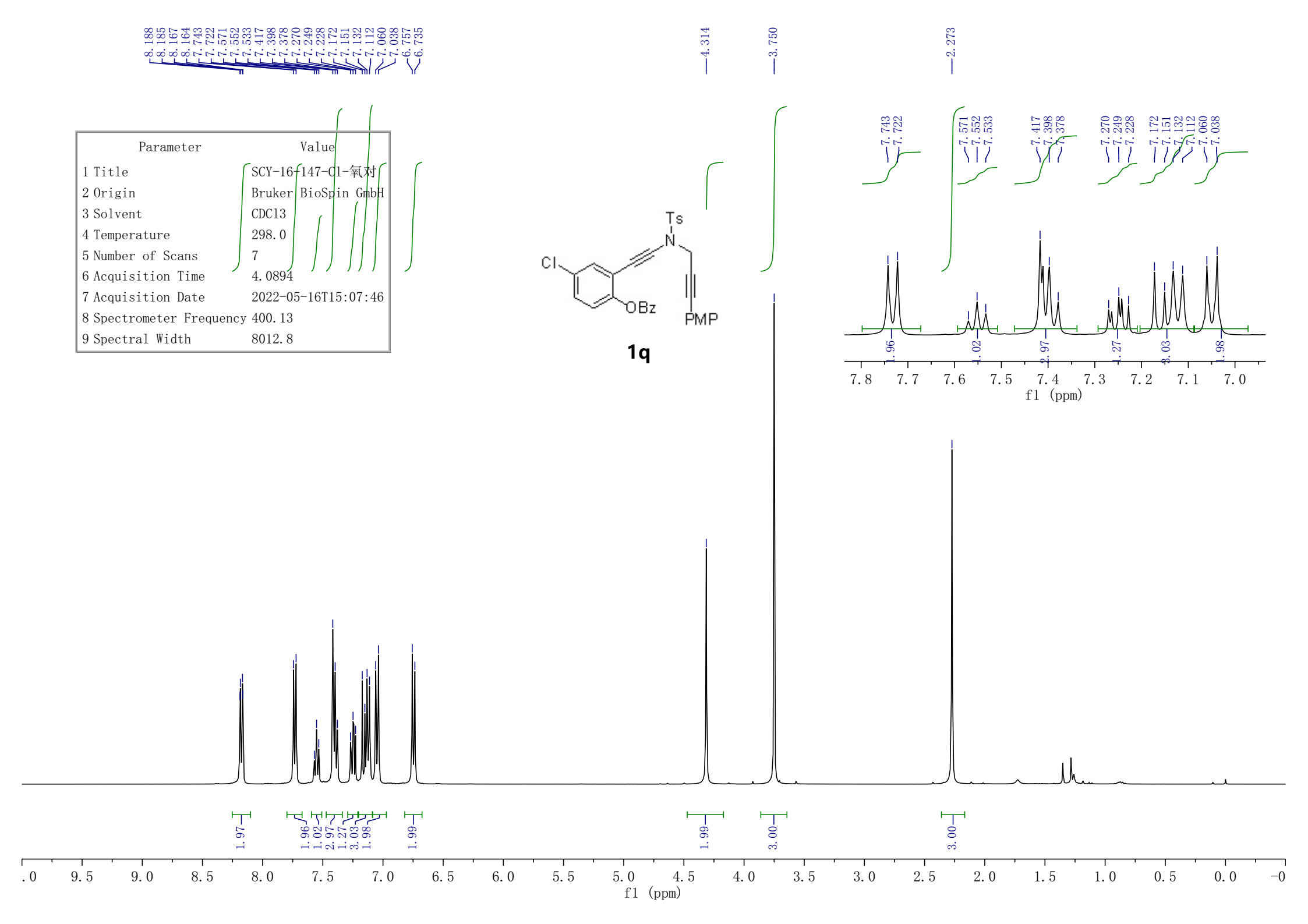
1p



Parameter	Value
1 Title	SCY-16-143-Me-氧对
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	17
6 Acquisition Time	1.3631
7 Acquisition Date	2022-05-16T15:03:52
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5

1p

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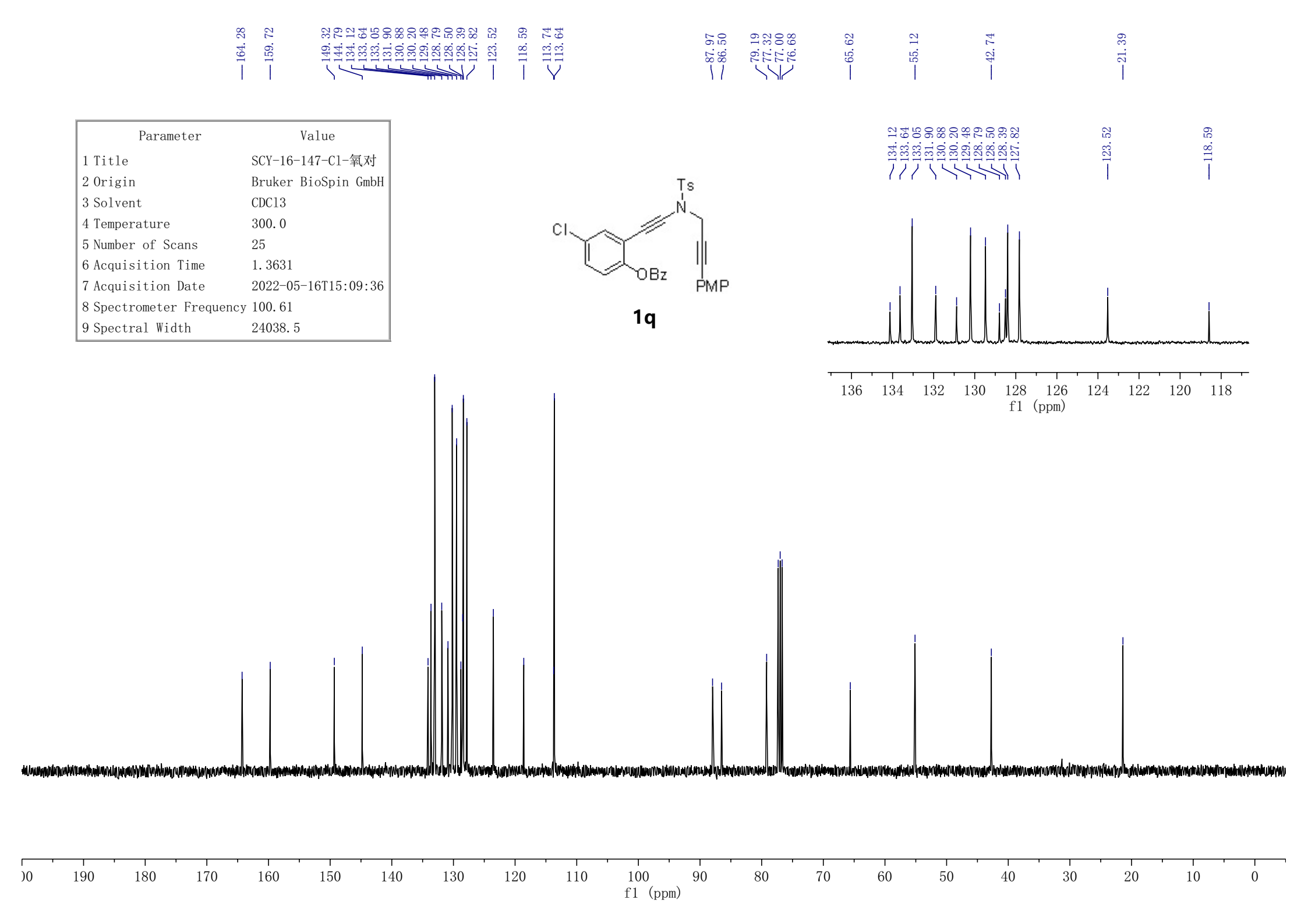
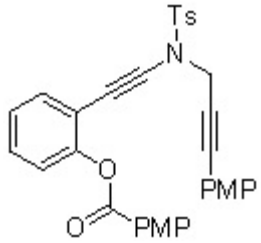
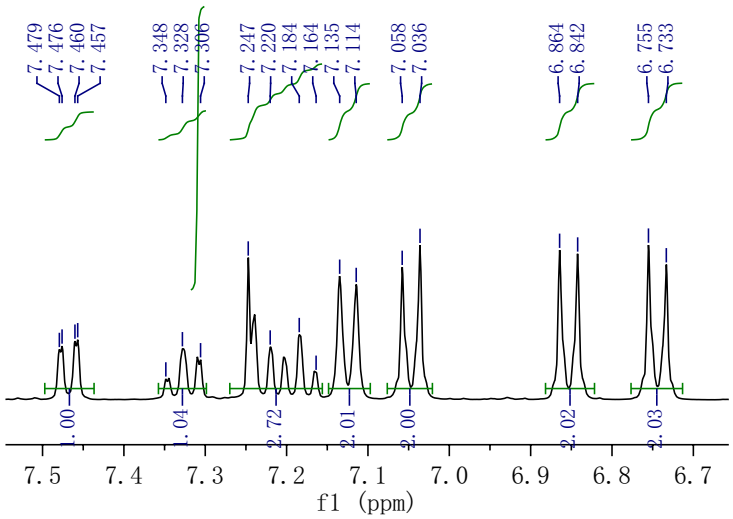
7.722
7.571
7.552
7.533
7.417
7.398
7.378
7.270
7.249
7.228
7.172
7.151
7.132
7.112
7.060
7.038
6.757
6.735
4.314
3.750
2.273
Parameter Value
1 Title SCY-16-147-Cl-氧对
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 298.0
5 Number of Scans 7
6 Acquisition Time 4.0894
7 Acquisition Date 2022-05-16T15:07:46
8 Spectrometer Frequency 400.13
9 Spectral Width 8012.8
Ts
N
Cl
OBz
PMP
1q
1.97
1.96
1.02
2.97
1.27
3.03
1.98
1.99
1.99
3.00
3.00
f1 (ppm)

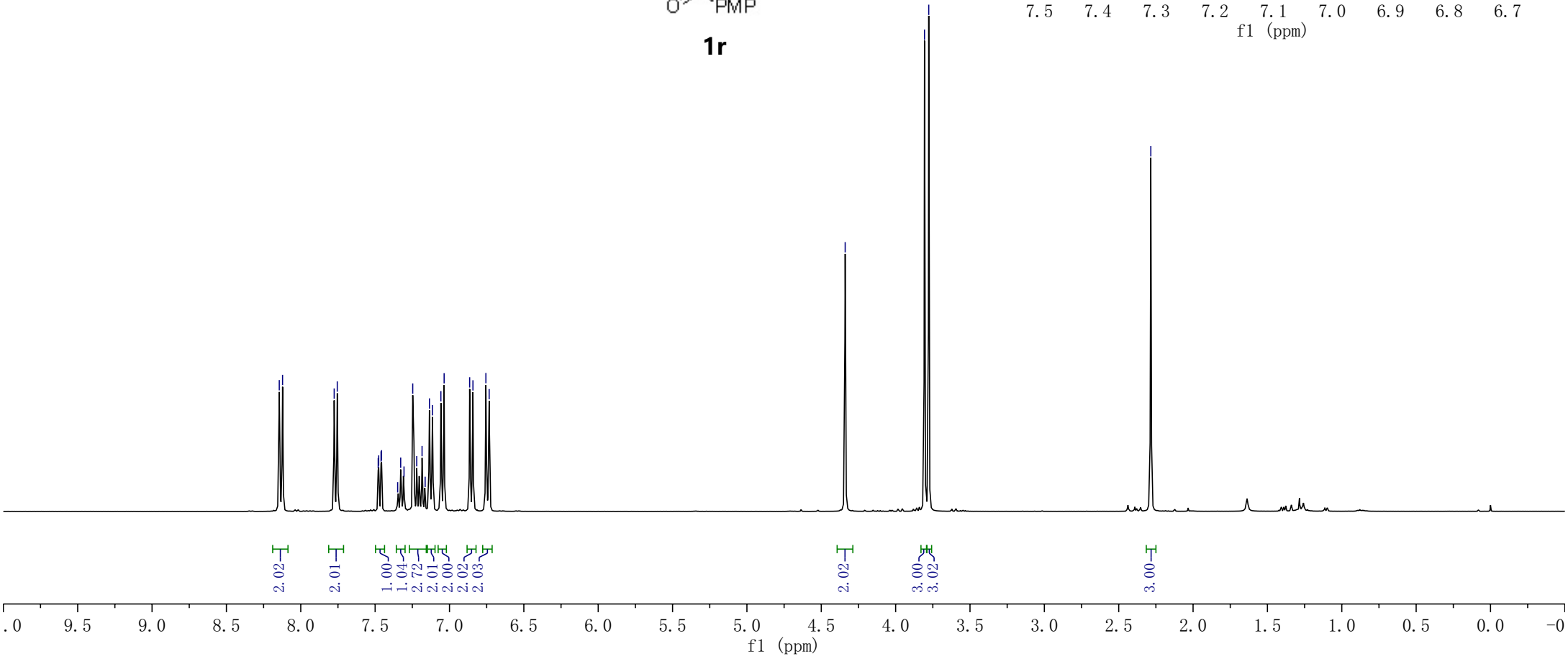

164.28
159.72
149.32
144.79
134.12
133.64
133.05
131.90
130.88
130.20
129.48
128.79
128.50
128.39
127.82
123.52
118.59
113.74
113.64
87.97
86.50
79.19
77.32
77.00
76.68
65.62
55.12
42.74
21.39
Parameter Value
1 Title SCY-16-147-Cl-氧对
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.0
5 Number of Scans 25
6 Acquisition Time 1.3631
7 Acquisition Date 2022-05-16T15:09:36
8 Spectrometer Frequency 100.61
9 Spectral Width 24038.5
Ts
N
Cl
OBz
PMP
1q
f1 (ppm)

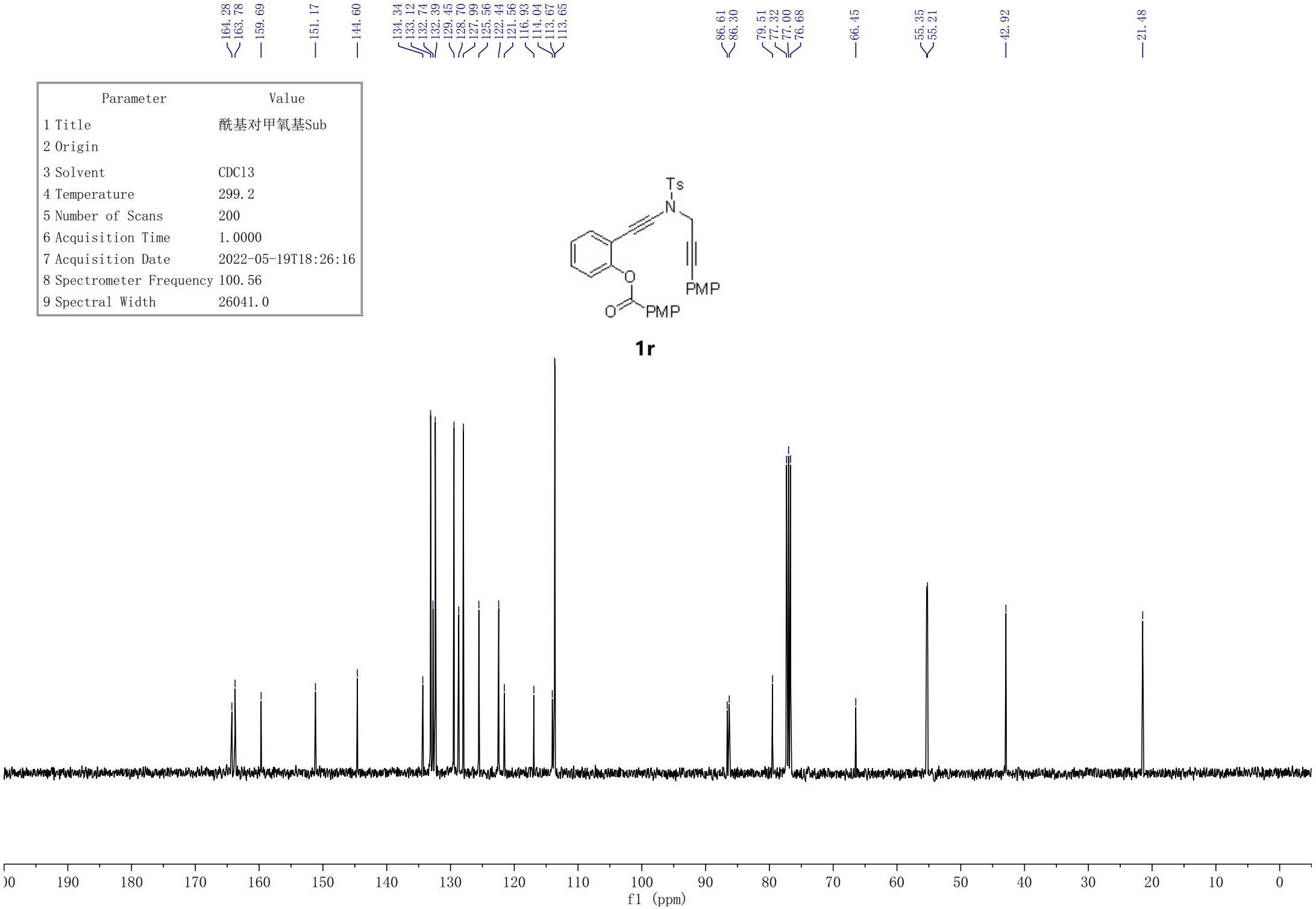
Parameter	Value
1 Title	酰基对甲氧基Sub
2 Origin	
3 Solvent	CDCl3
4 Temperature	299.4
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2022-05-19T18:17:14
8 Spectrometer Frequency	399.92
9 Spectral Width	8012.0



1r



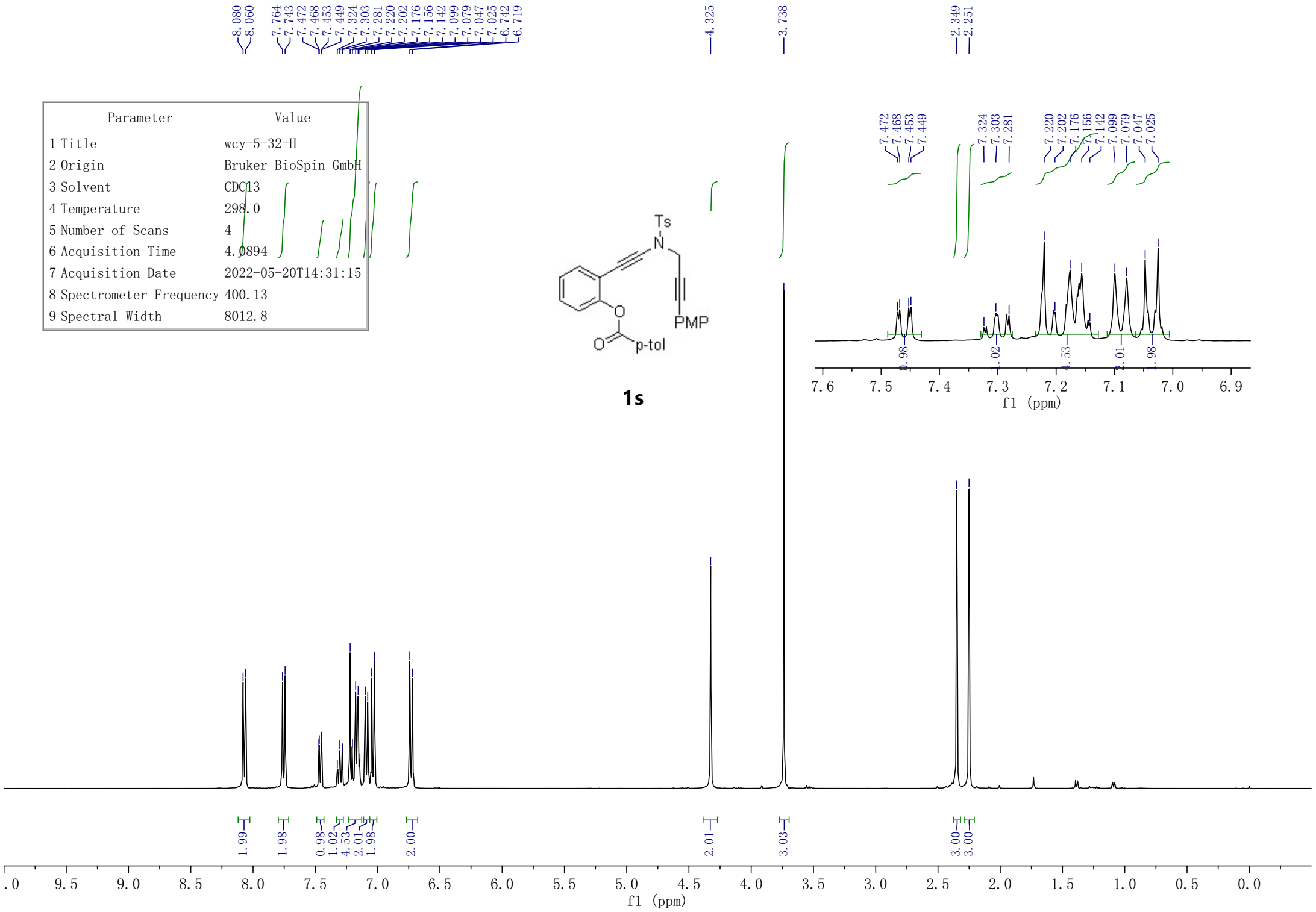


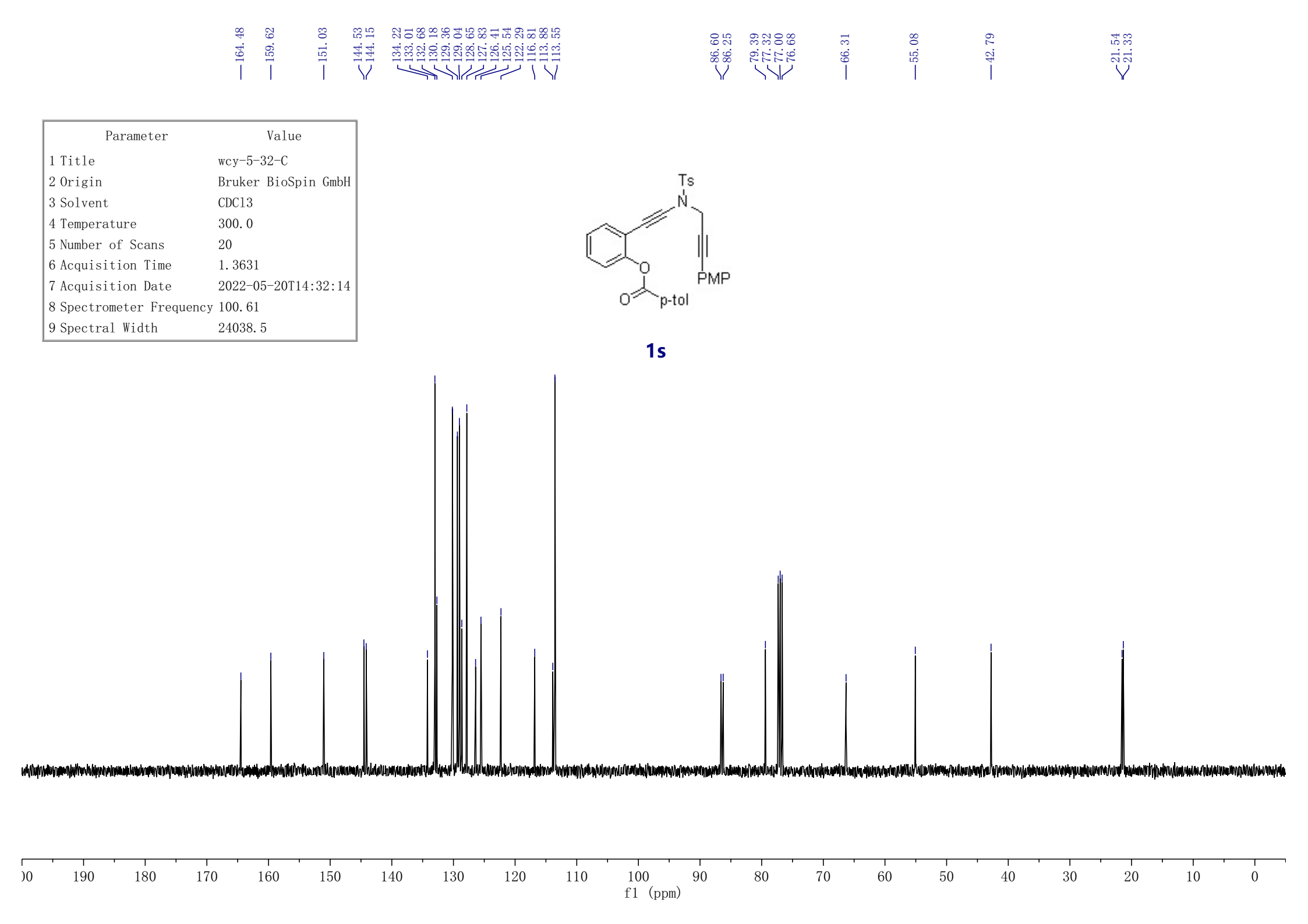


Parameter	Value
1 Title	酰基对甲氧基Sub
2 Origin	
3 Solvent	CDCl3
4 Temperature	299.2
5 Number of Scans	200
6 Acquisition Time	1.0000
7 Acquisition Date	2022-05-19T18:26:16
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

Parameter	Value
1 Title	wcy-5-32-H
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	4
6 Acquisition Time	4.0894
7 Acquisition Date	2022-05-20T14:31:15
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8

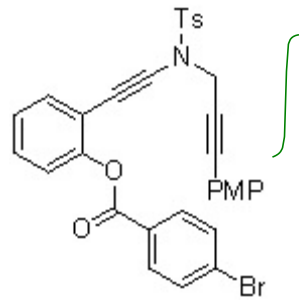
1s



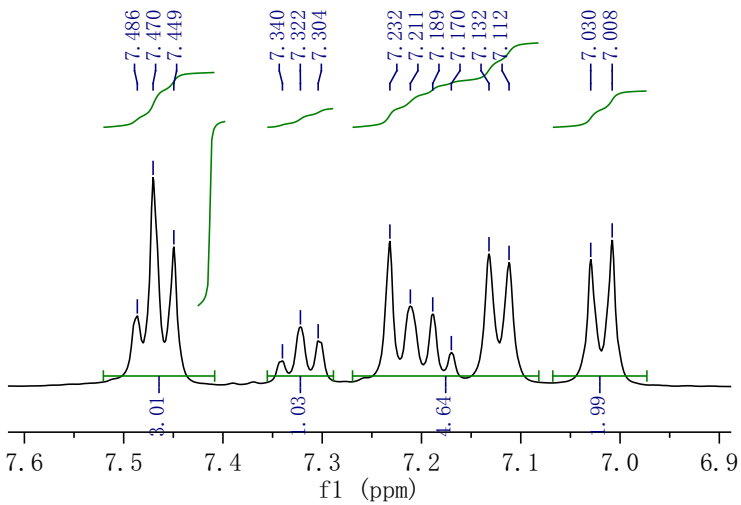


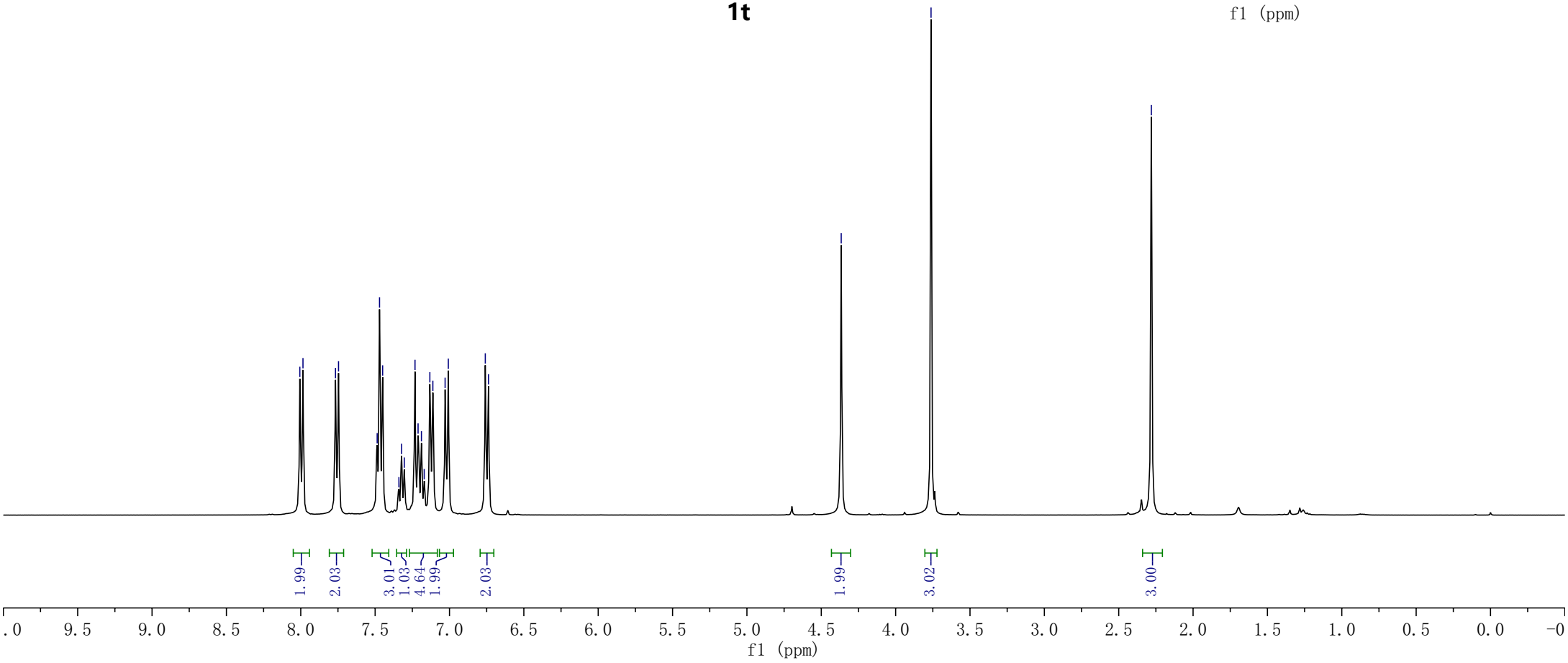
Parameter	Value
1 Title	wcy-5-32-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	20
6 Acquisition Time	1.3631
7 Acquisition Date	2022-05-20T14:32:14
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5

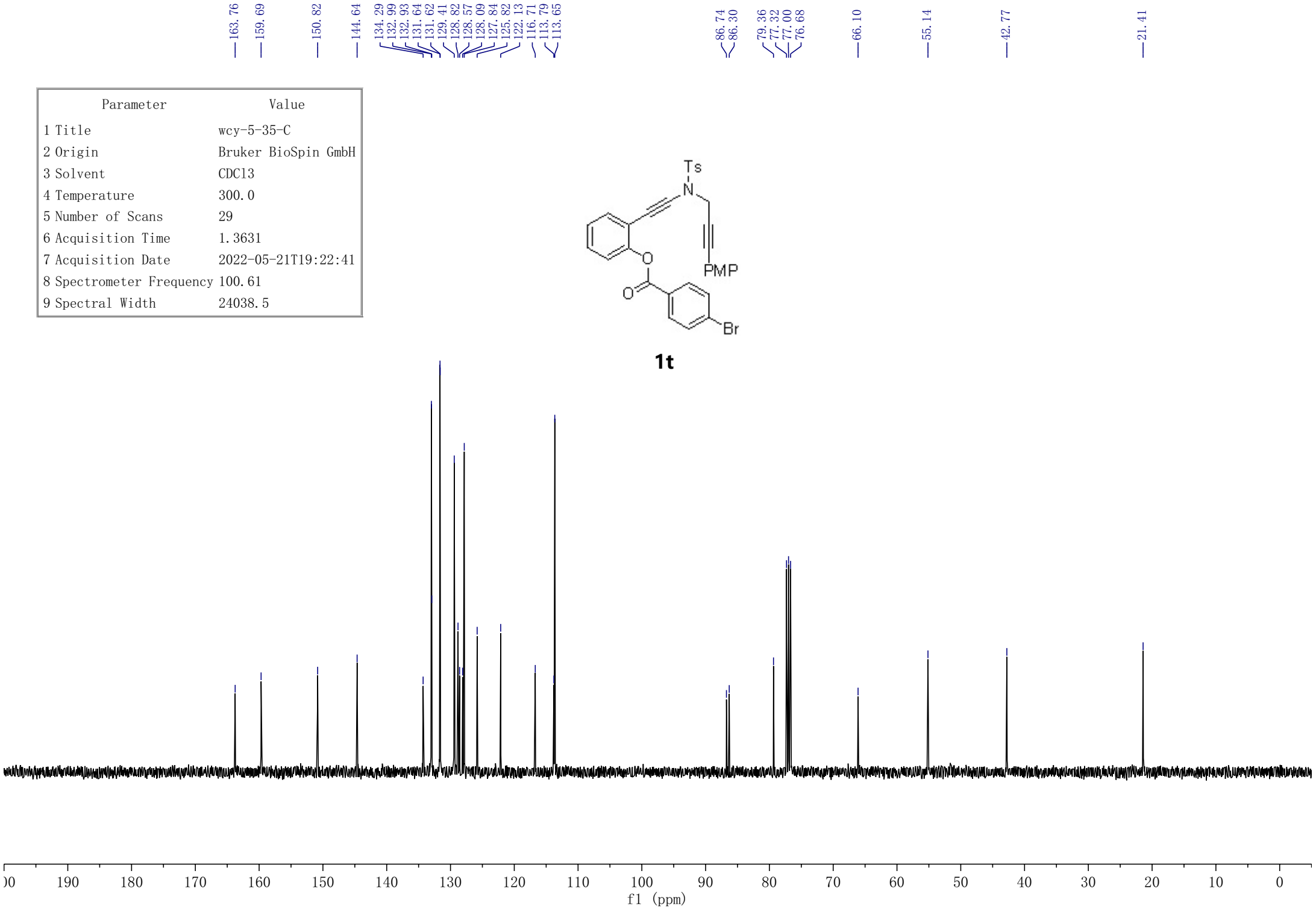
Parameter	Value
1 Title	wcy-5-35-H
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	6
6 Acquisition Time	4.0894
7 Acquisition Date	2022-05-21T19:21:18
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8



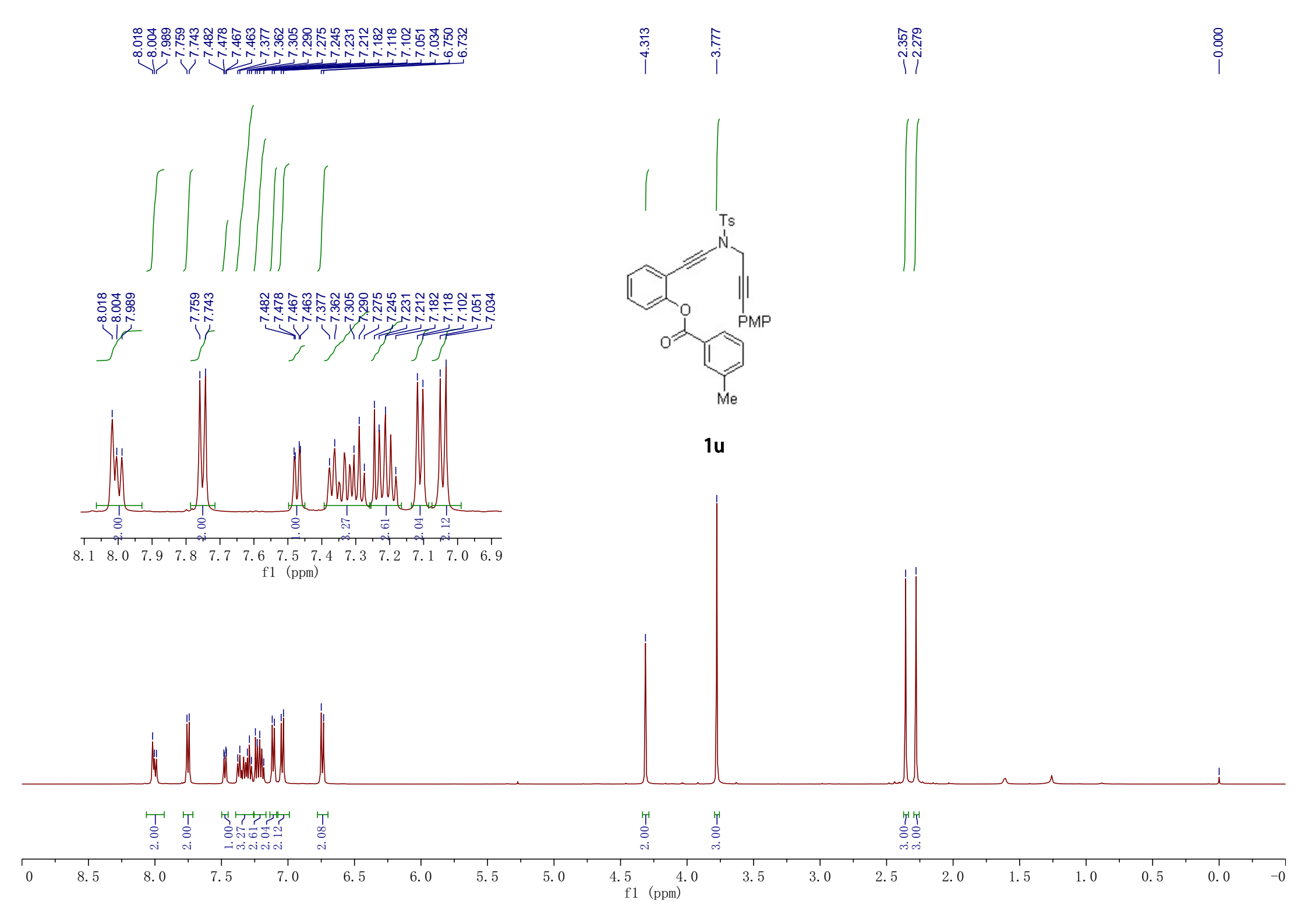
1t







Parameter	Value
1 Title	wcy-5-35-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	29
6 Acquisition Time	1.3631
7 Acquisition Date	2022-05-21T19:22:41
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5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7.305
7.290
7.275
7.245
7.231
7.212
7.182
7.118
7.102
7.051
7.034
6.750
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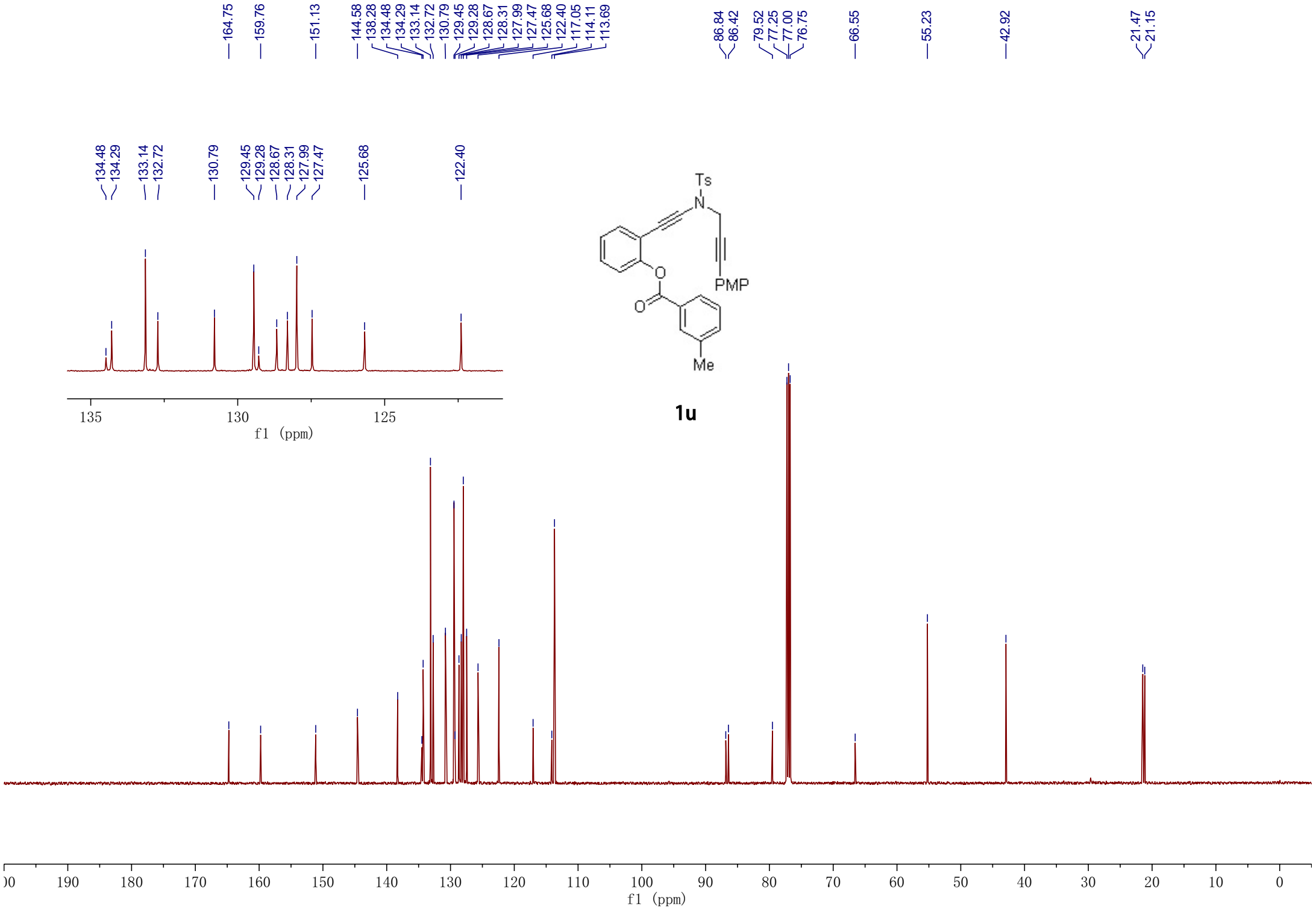
3.777
2.357
2.279
0.000
Ts
N
O
O
PMP
Me
1u
f1 (ppm)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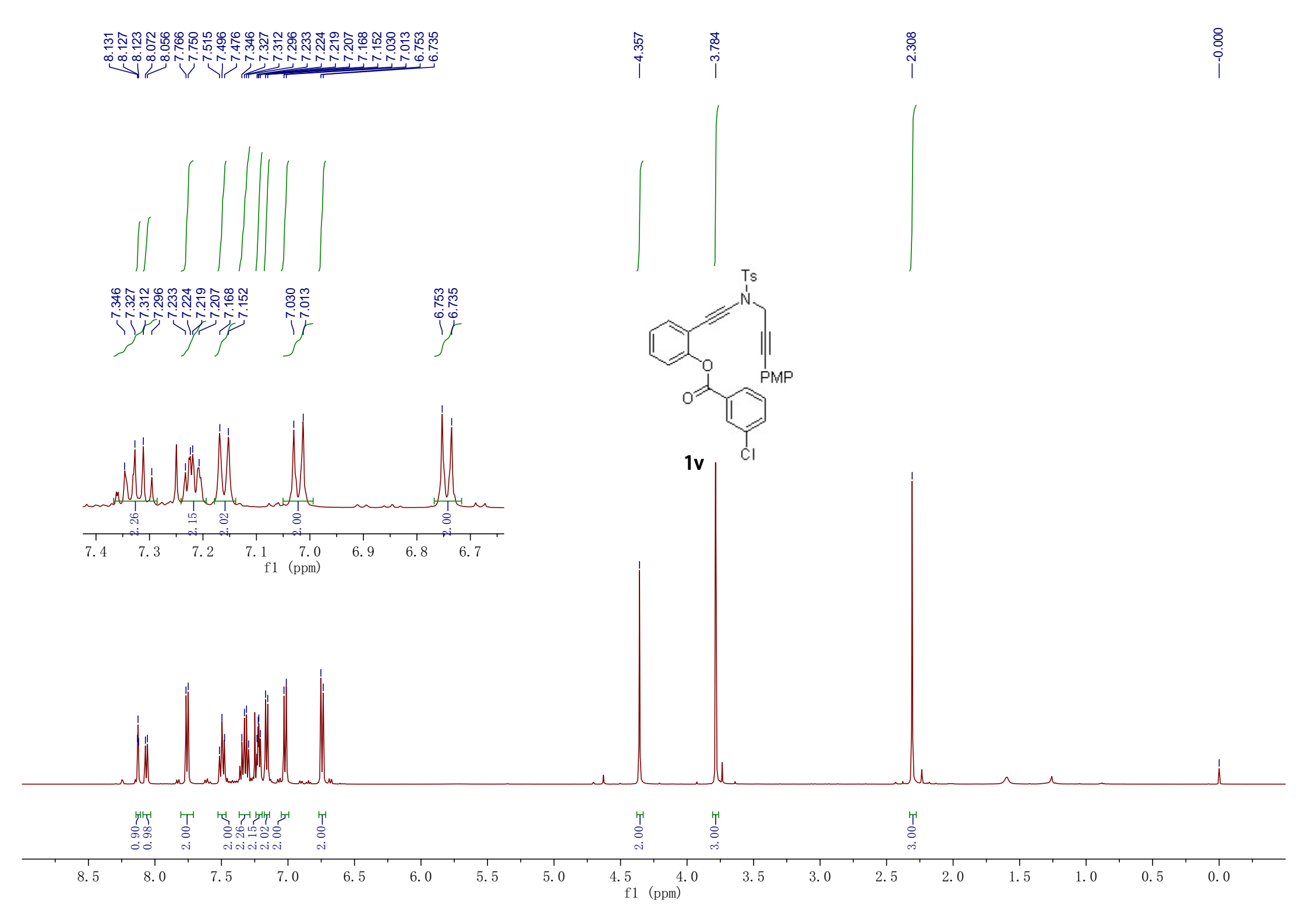
144.58
138.28
134.48
134.29
133.14
132.72
130.79
129.45
129.28
128.67
128.31
127.99
127.47
125.68
122.40
117.05
114.11
113.69
86.84
86.42
79.52
77.25
77.00
76.75
66.55
55.23
42.92
21.47
21.15
Ts
N
O
O
PMP
Me
1u
135
130
125
f1 (ppm)
f1 (ppm)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7.766
7.750
7.515
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7.476
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7.327
7.312
7.296
7.233
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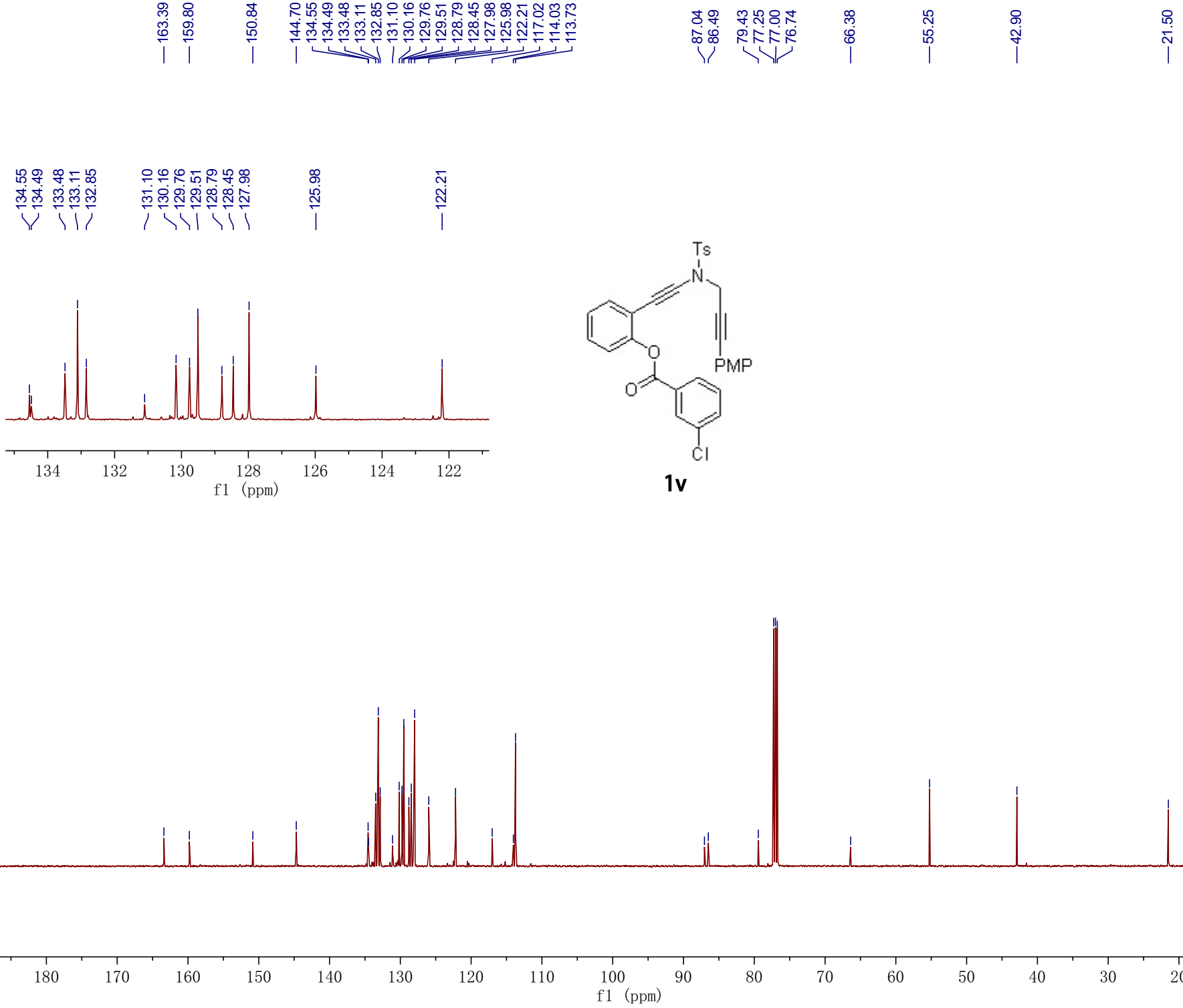
7.219
7.207
7.168
7.152
7.030
7.013
6.753
6.735
4.357
3.784
2.308
-0.000
Ts
N
O
O
PMP
Cl
1v
f1 (ppm)
f1 (ppm)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131.10
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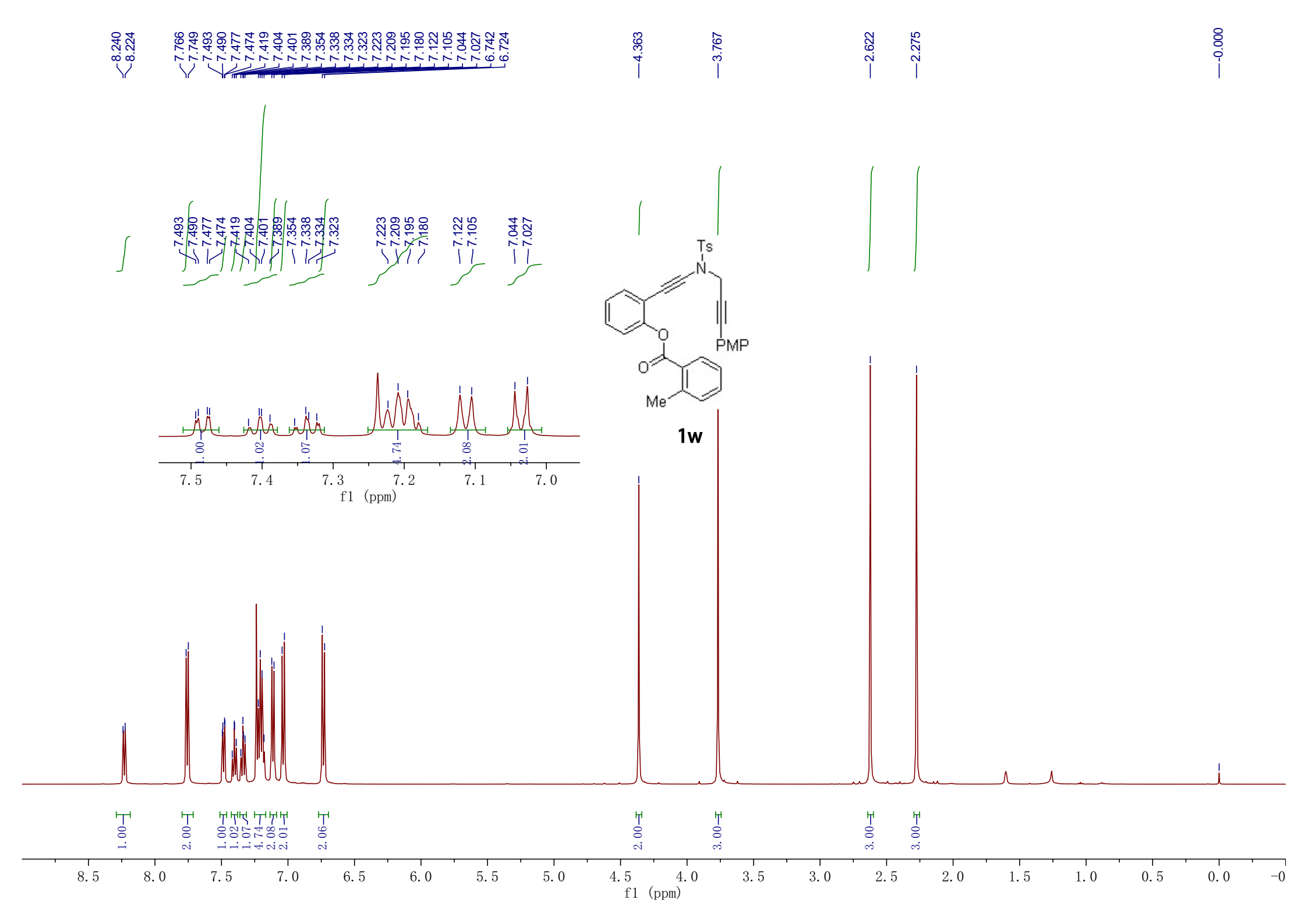
129.76
129.51
128.79
128.45
127.98
125.98
122.21
117.02
114.03
113.73
87.04
86.49
79.43
77.25
77.00
76.74
66.38
55.25
42.90
21.50
f1 (ppm)
Ts
N
PMP
O
O
Cl
1v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8.224
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7.493
7.490
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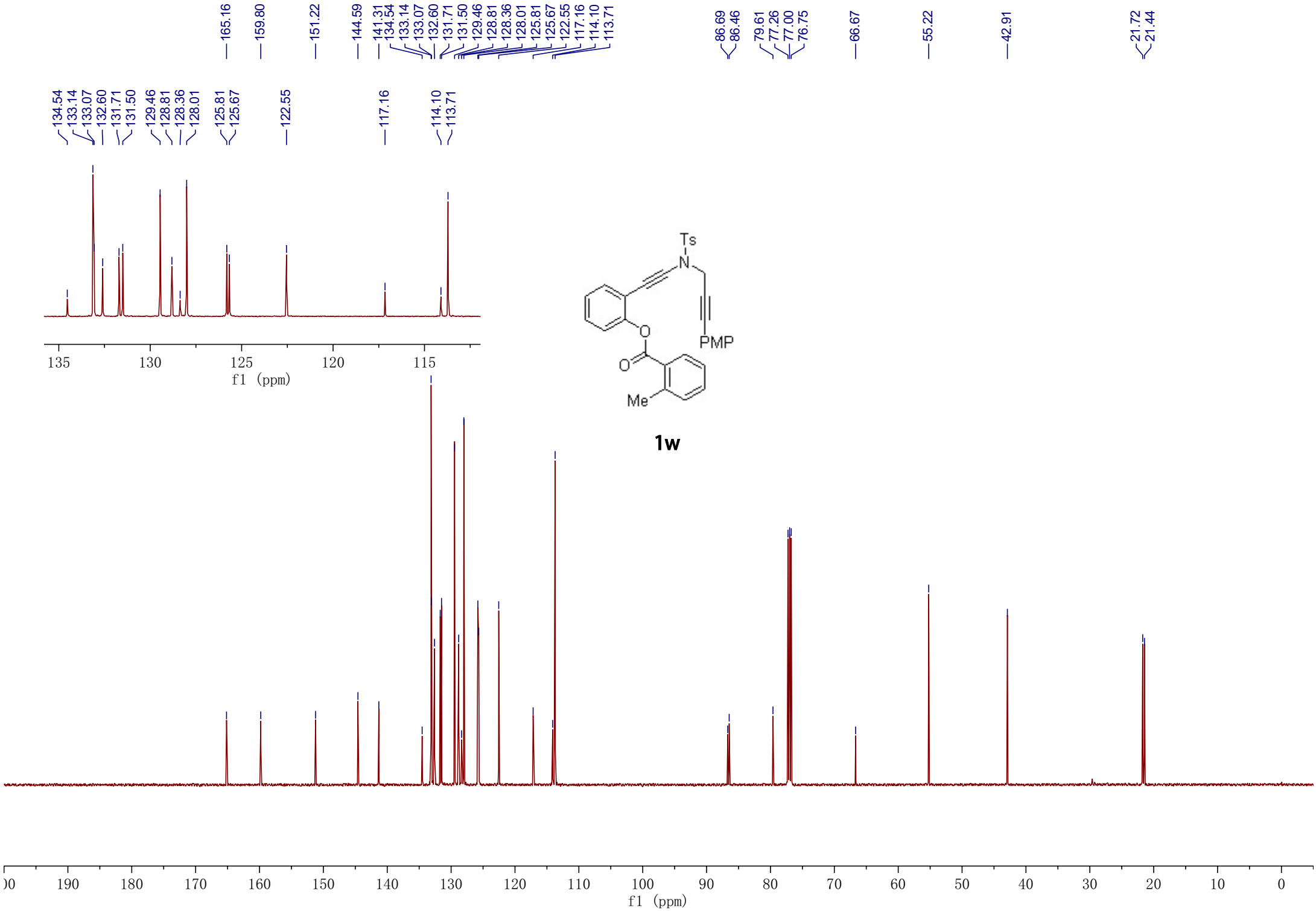
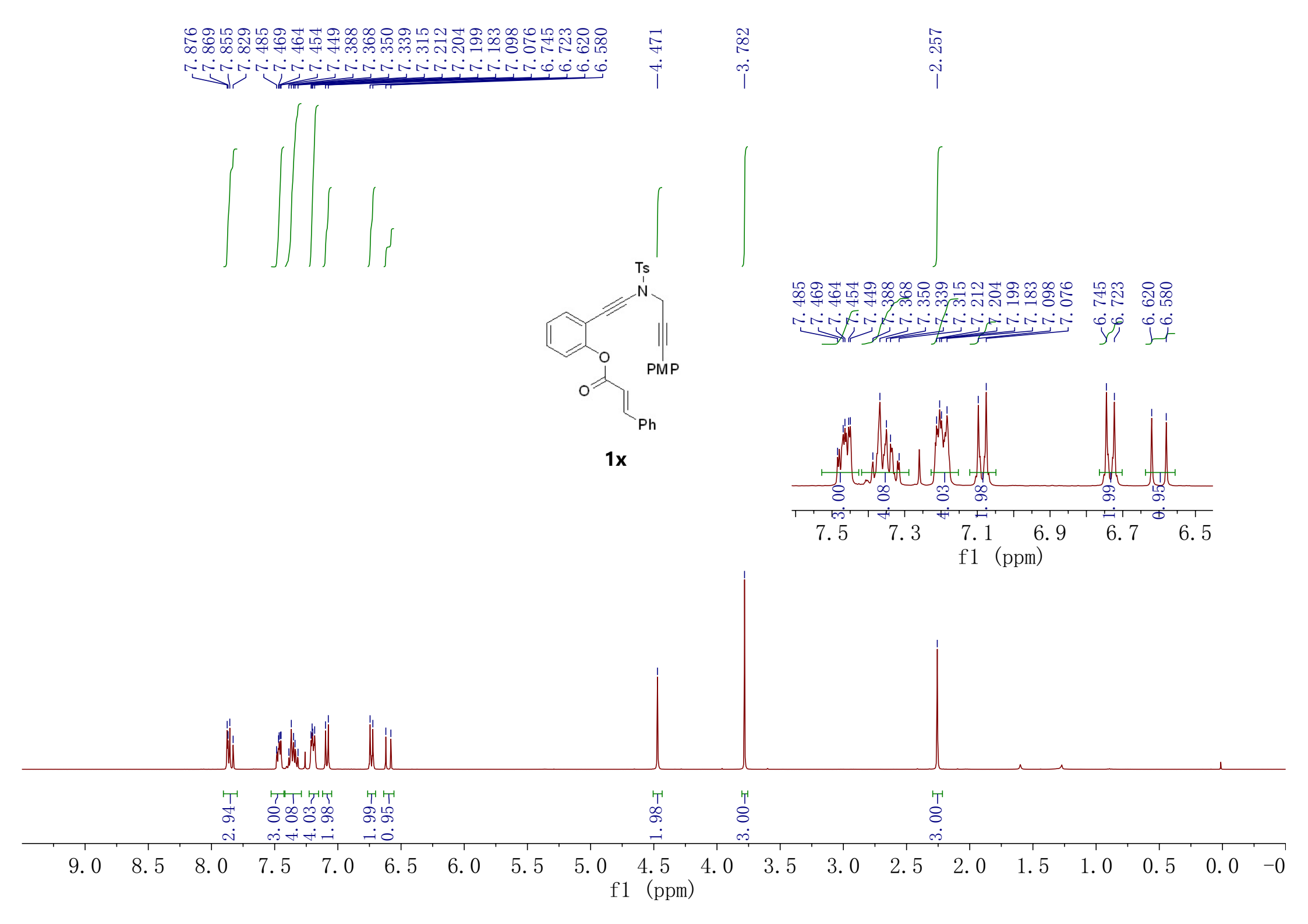
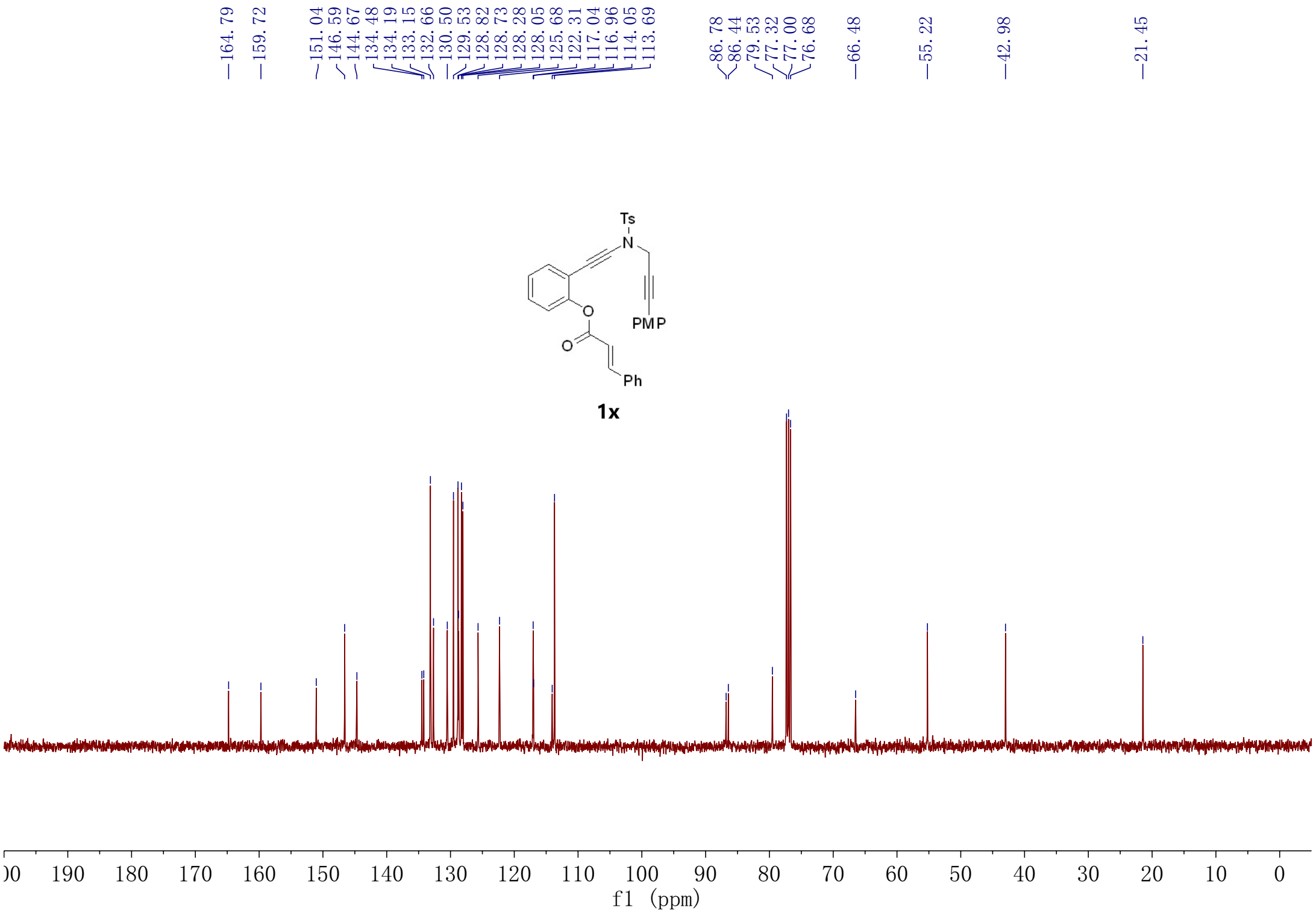
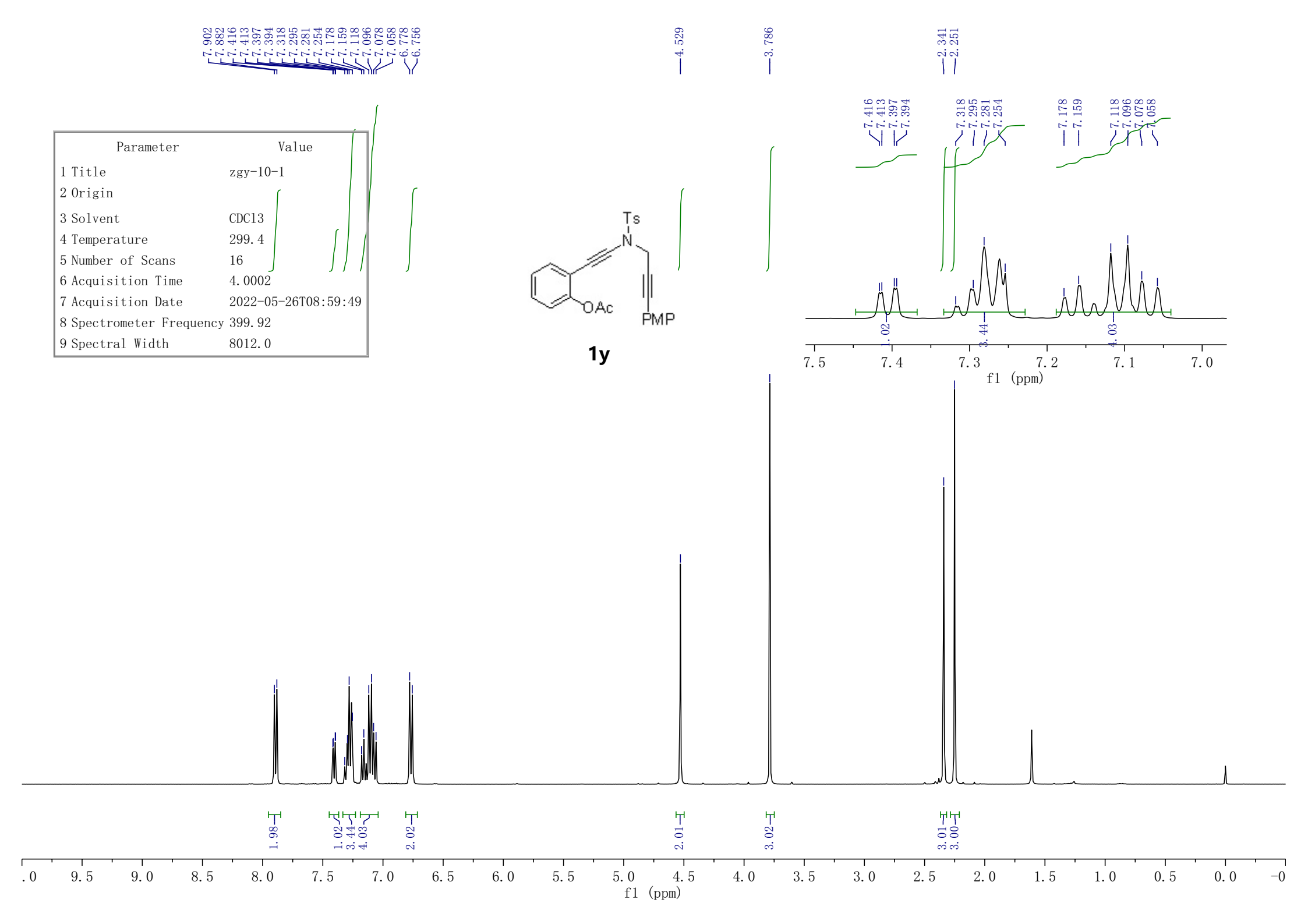
7.474
7.419
7.404
7.401
7.389
7.354
7.338
7.334
7.323
7.223
7.209
7.195
7.180
7.122
7.105
7.044
7.027
6.742
6.724
4.363
3.767
2.622
2.275
-0.000
Ts
N
O
PMP
O
Me
1w
1.00
1.02
1.07
4.74
2.08
2.01
7.5
7.4
7.3
7.2
7.1
7.0
f1 (ppm)
1.00
2.00
1.00
1.02
1.07
4.74
2.08
2.01
2.06
2.00
3.00
3.00
3.00
8.5
8.0
7.5
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
f1 (ppm)

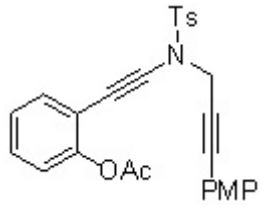

165.16
159.80
151.22
144.59
141.31
134.54
133.14
133.07
132.60
131.71
131.50
129.46
128.81
128.36
128.01
125.81
125.67
122.55
117.16
114.10
113.71
86.69
86.46
79.61
77.26
77.00
76.75
66.67
55.22
42.91
21.72
21.44
135
130
125
120
115
f1 (ppm)
Ts
N
PMP
O
O
Me
1w
f1 (ppm)


7.876
7.869
7.855
7.829
7.485
7.469
7.464
7.454
7.449
7.388
7.368
7.350
7.339
7.315
7.212
7.204
7.199
7.183
7.098
7.076
6.745
6.723
6.620
6.580
4.471
3.782
2.257
Ts
N
O
O
PMP
Ph
1x
3.00
4.08
4.03
1.98
1.99
0.95
7.5
7.3
7.1
6.9
6.7
6.5
f1 (ppm)
2.94
3.00
4.08
4.03
1.98
1.99
0.95
1.98
3.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

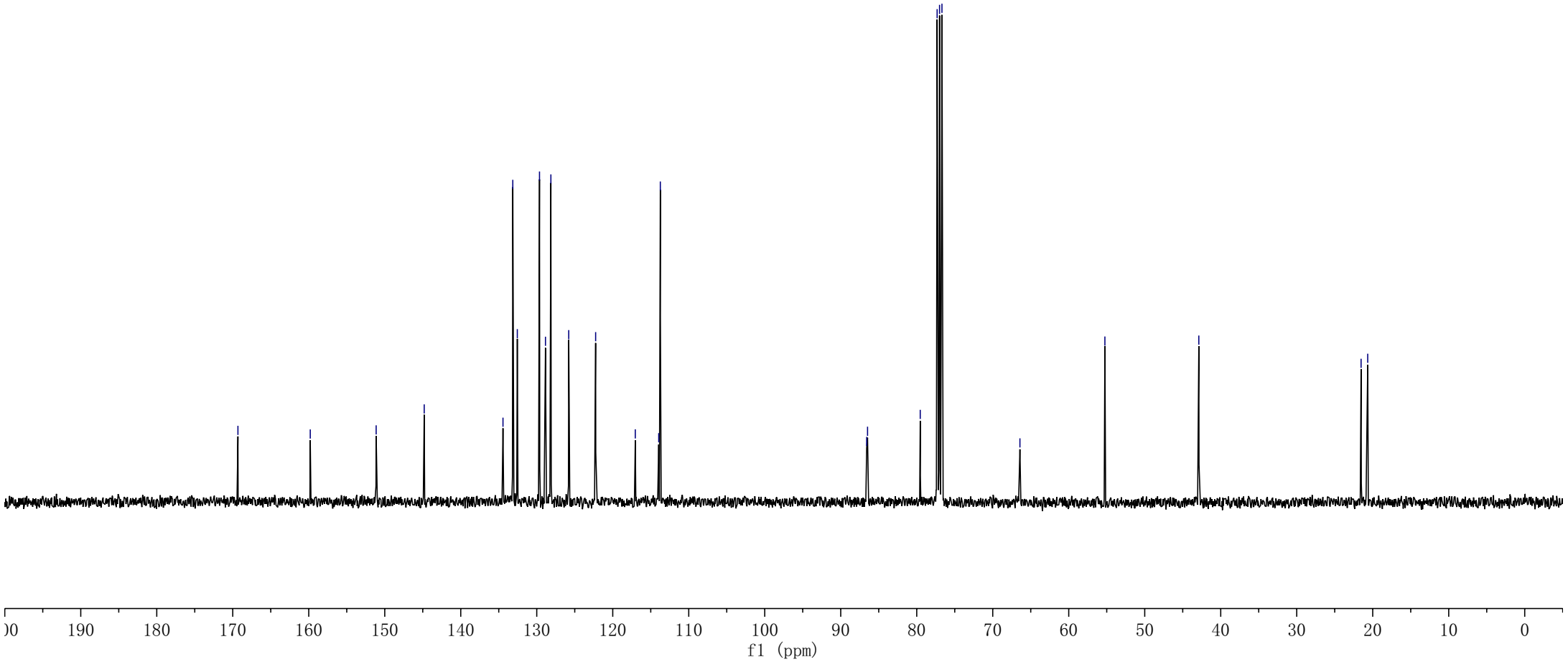

164.79
159.72
151.04
146.59
144.67
134.48
134.19
133.15
132.66
130.50
129.53
128.82
128.73
128.28
128.05
125.68
122.31
117.04
116.96
114.05
113.69
86.78
86.44
79.53
77.32
77.00
76.68
66.48
55.22
42.98
21.45
Ts
N
O
PMP
O
Ph
1x
f1 (ppm)


7.902
7.882
7.416
7.413
7.397
7.394
7.318
7.295
7.281
7.254
7.178
7.159
7.118
7.096
7.078
7.058
6.778
6.756
4.529
3.786
2.341
2.251
Parameter Value
1 Title zgy-10-1
2 Origin
3 Solvent CDCl3
4 Temperature 299.4
5 Number of Scans 16
6 Acquisition Time 4.0002
7 Acquisition Date 2022-05-26T08:59:49
8 Spectrometer Frequency 399.92
9 Spectral Width 8012.0
Ts
N
OAc
PMP
1y
1.02
3.44
4.03
f1 (ppm)
1.98
1.02
3.44
4.03
2.02
2.01
3.02
3.01
3.00
f1 (ppm)

Parameter	Value
1 Title	zgy-10-1-C
2 Origin	
3 Solvent	CDCl3
4 Temperature	299.6
5 Number of Scans	300
6 Acquisition Time	1.0000
7 Acquisition Date	2022-05-26T09:11:23
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

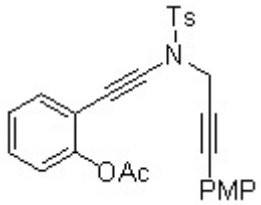


1y

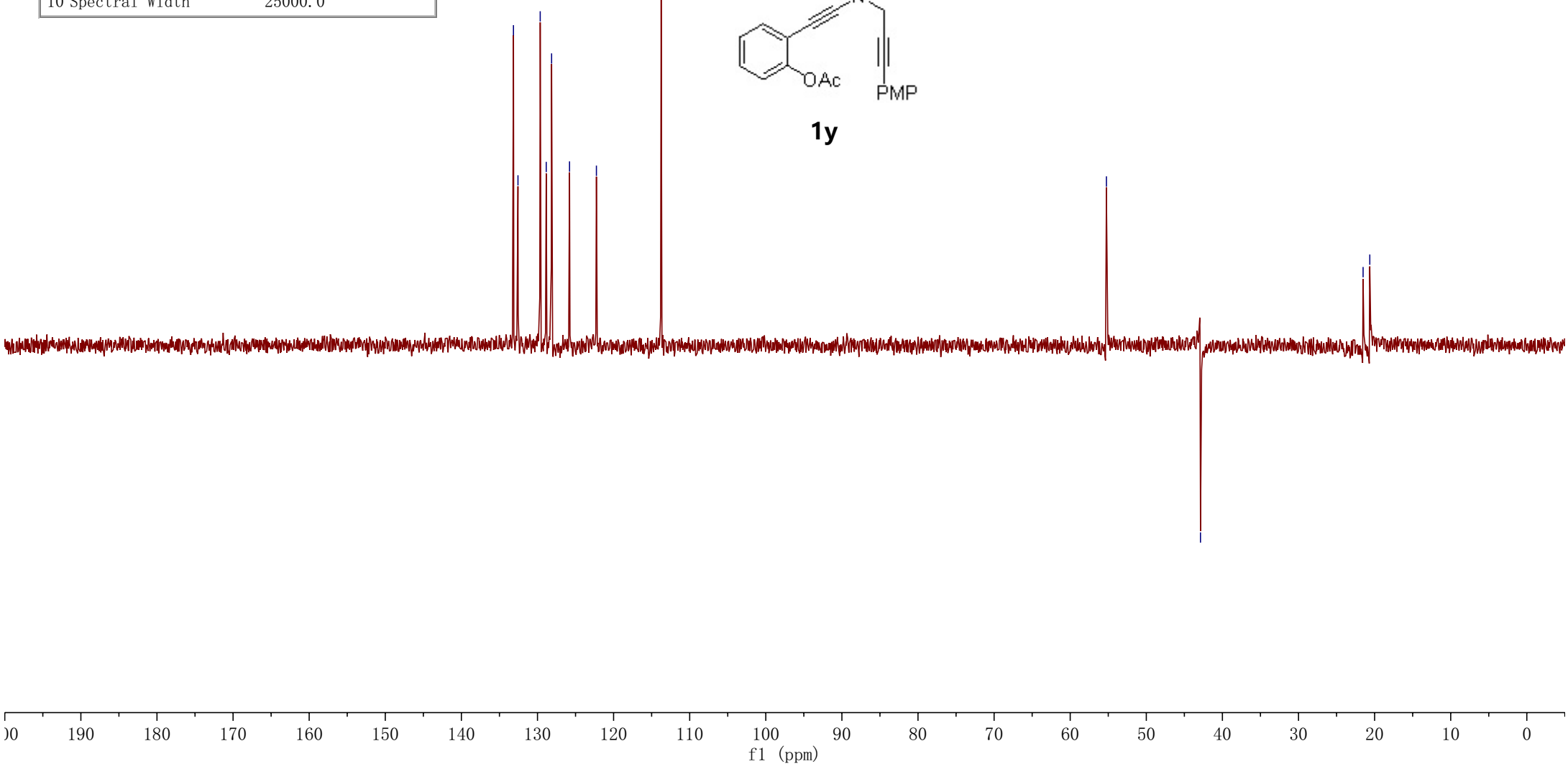


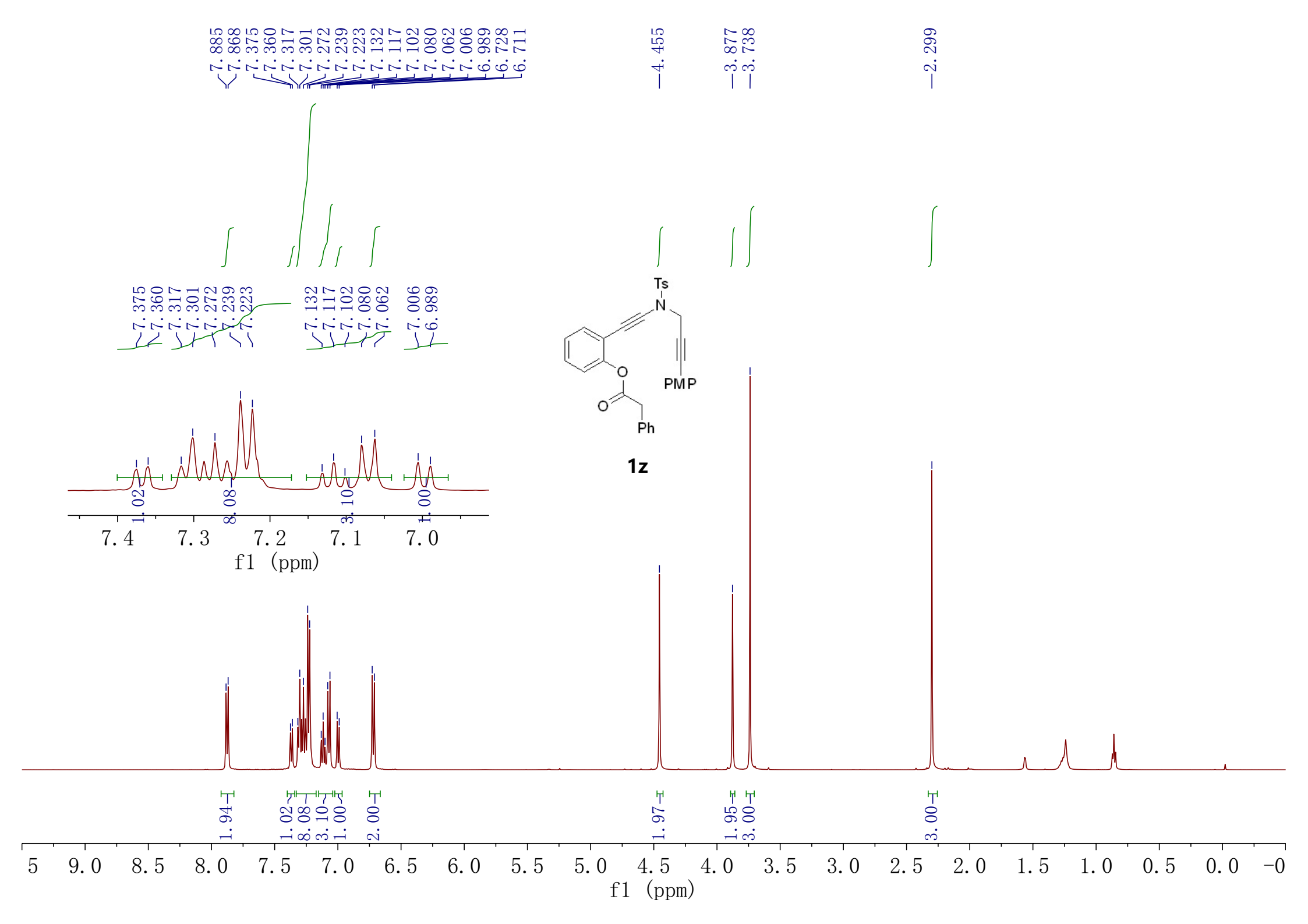
	Parameter	Value
1	Title	zgy-10-1-C-dept
2	Origin	
3	Solvent	CDCl3
4	Temperature	299.6
5	Experiment	1D
6	Number of Scans	150
7	Acquisition Time	1.0000
8	Acquisition Date	2022-05-26T09:20:31
9	Spectrometer Frequency	100.56
10	Spectral Width	25000.0

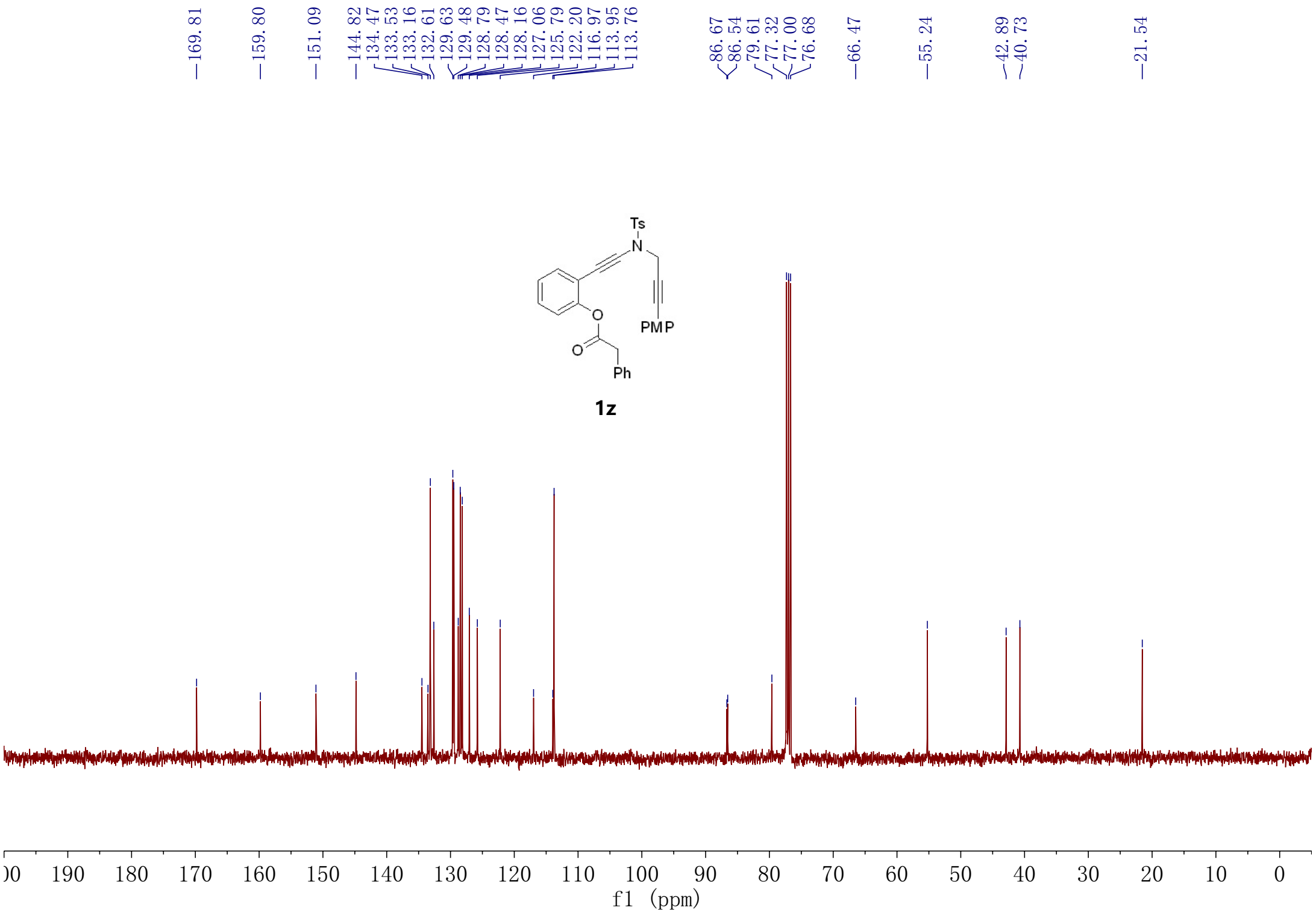
133.16
132.56
129.64
128.85
128.15
125.79
122.26
113.75
55.24
42.88
21.51
20.63

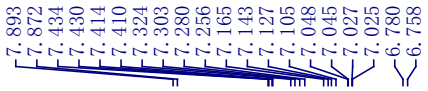


1y

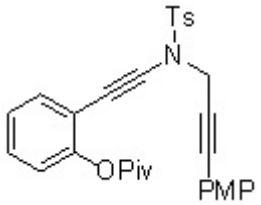



7.885
7.868
7.375
7.360
7.317
7.301
7.272
7.239
7.223
7.132
7.117
7.102
7.080
7.062
7.006
6.989
6.728
6.711
4.455
3.877
3.738
2.299
Ts
N
O
O
PMP
Ph
1z
1.02
8.08
3.10
1.00
7.4
7.3
7.2
7.1
7.0
f1 (ppm)
1.94
1.02
8.08
3.10
1.00
2.00
1.97
1.95
3.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

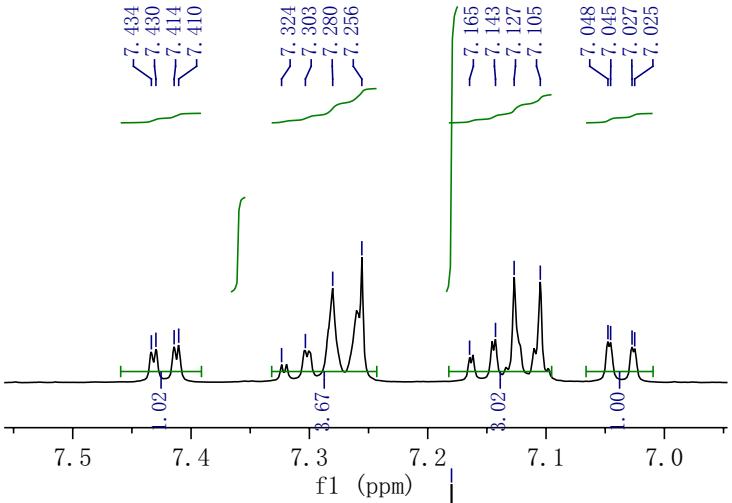

169.81
159.80
151.09
144.82
134.47
133.53
133.16
132.61
129.63
129.48
128.79
128.47
128.16
127.06
125.79
122.20
116.97
113.95
113.76
86.67
86.54
79.61
77.32
77.00
76.68
66.47
55.24
42.89
40.73
21.54
Ts
N
O
O
PMP
Ph
1z
f1 (ppm)

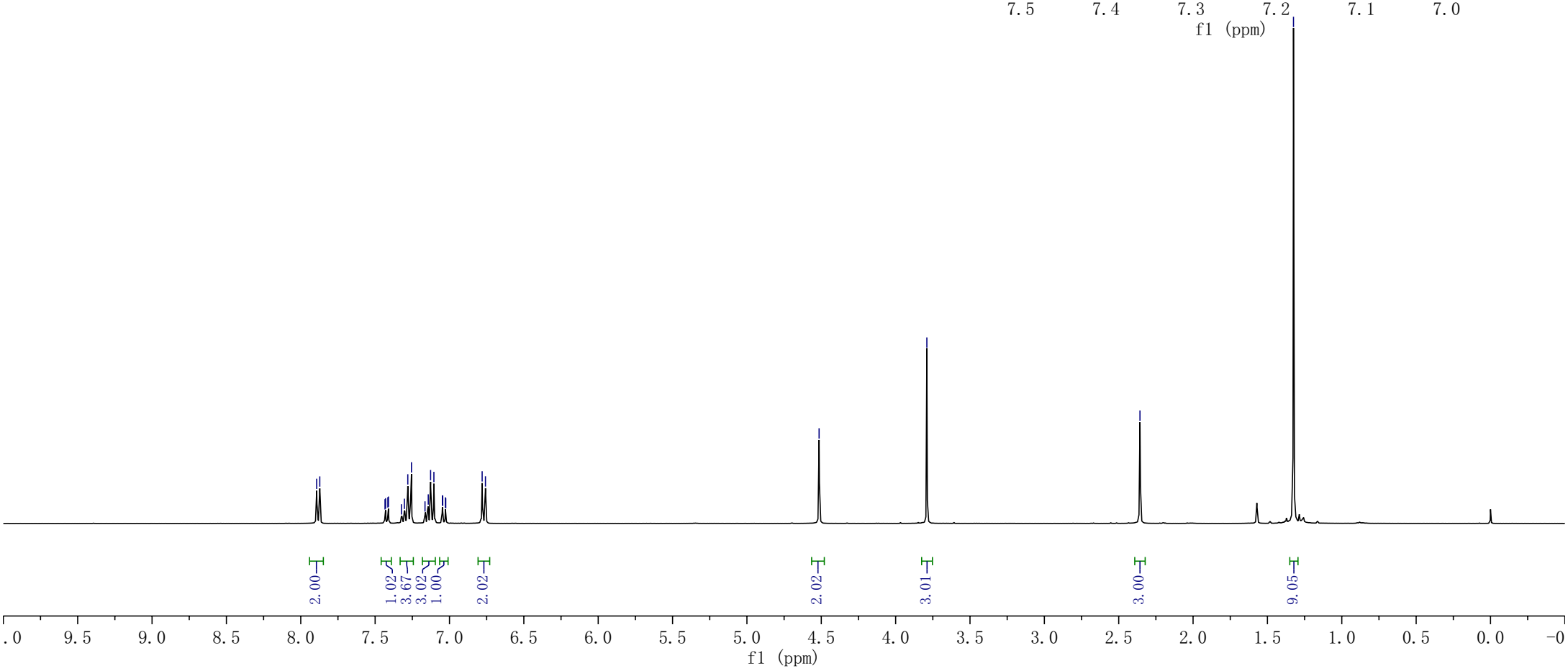


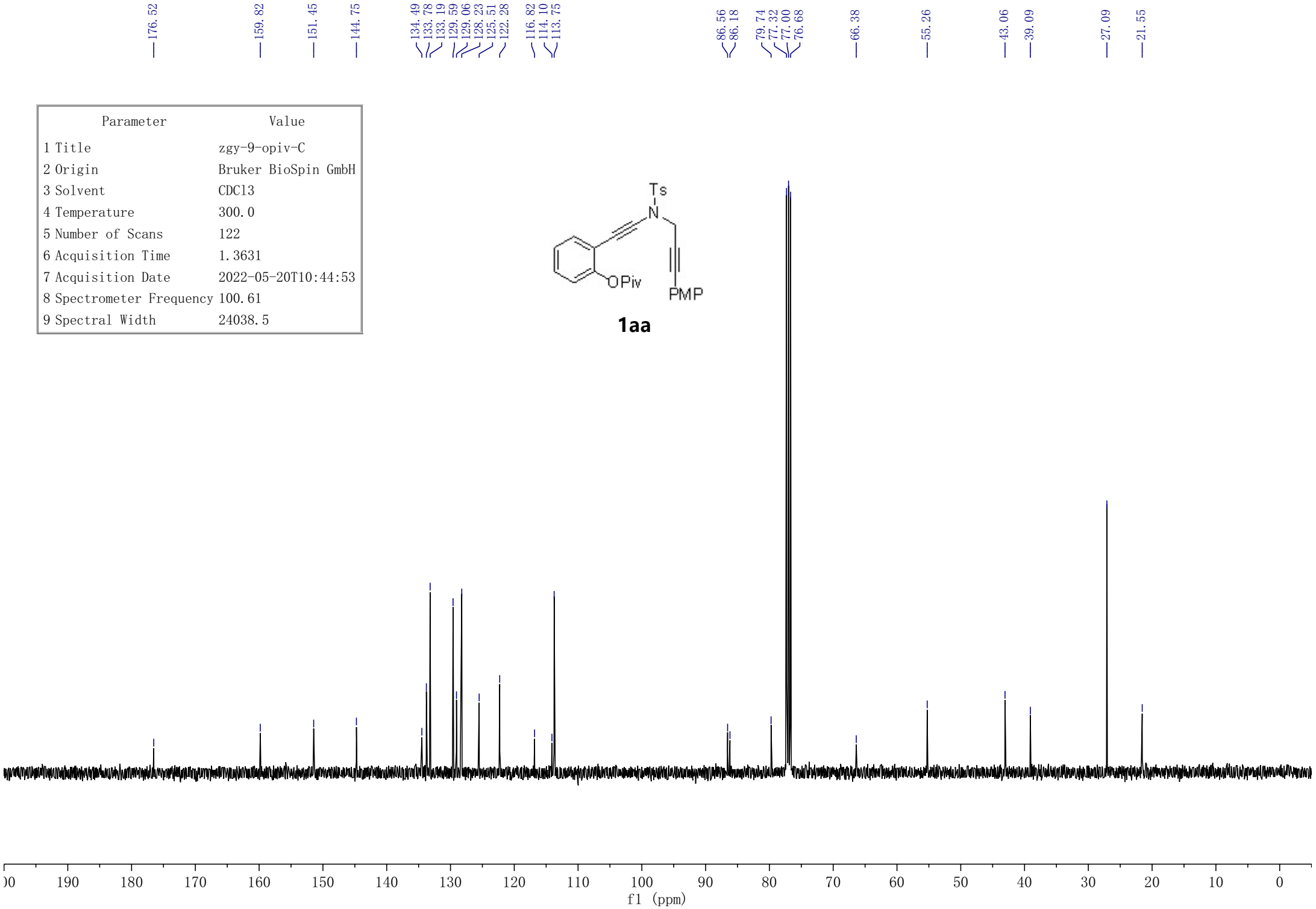
Parameter	Value
1 Title	zgy-9-opiv-H
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	7
6 Acquisition Time	4.0894
7 Acquisition Date	2022-05-20T15:03:22
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8



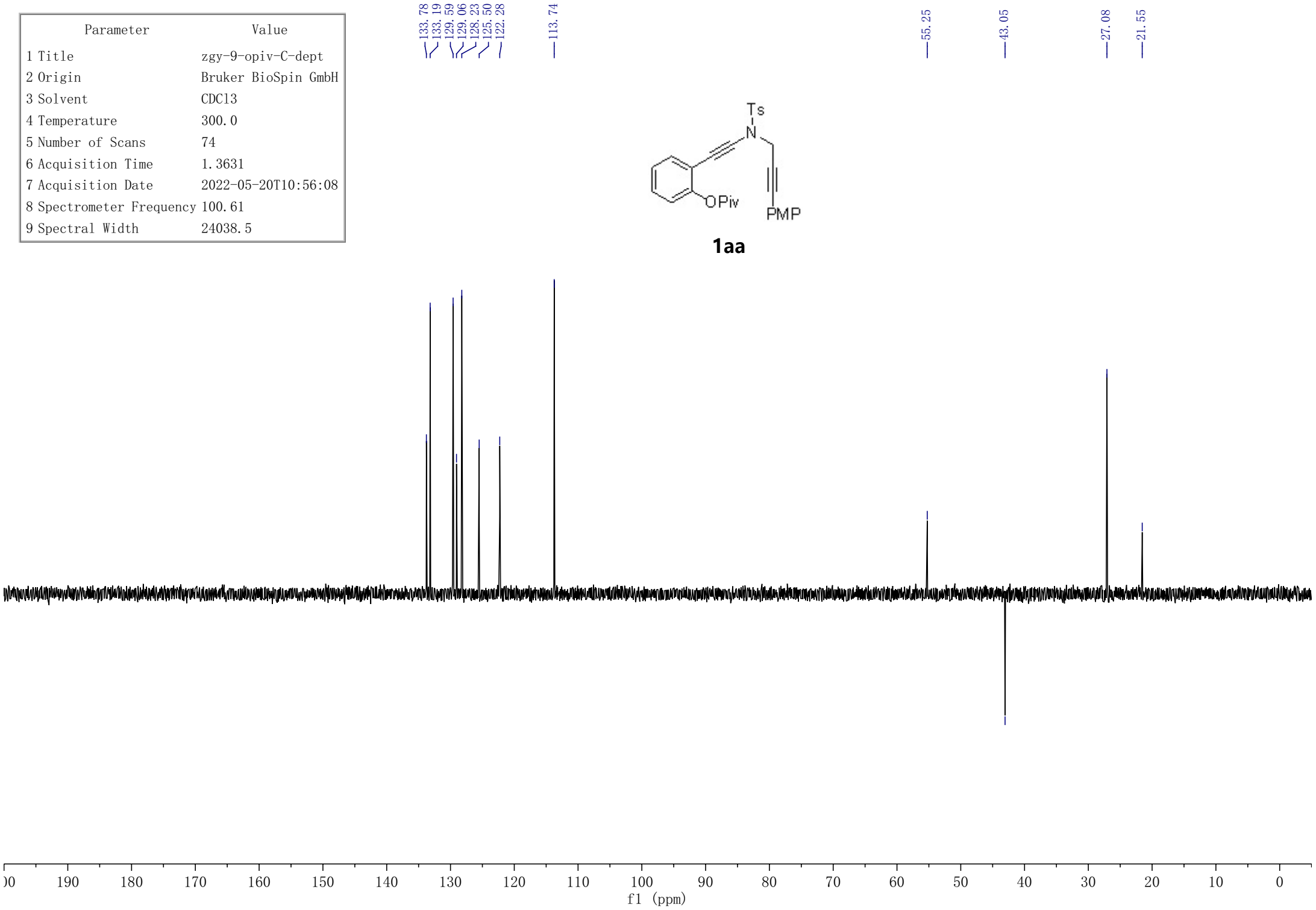
1aa

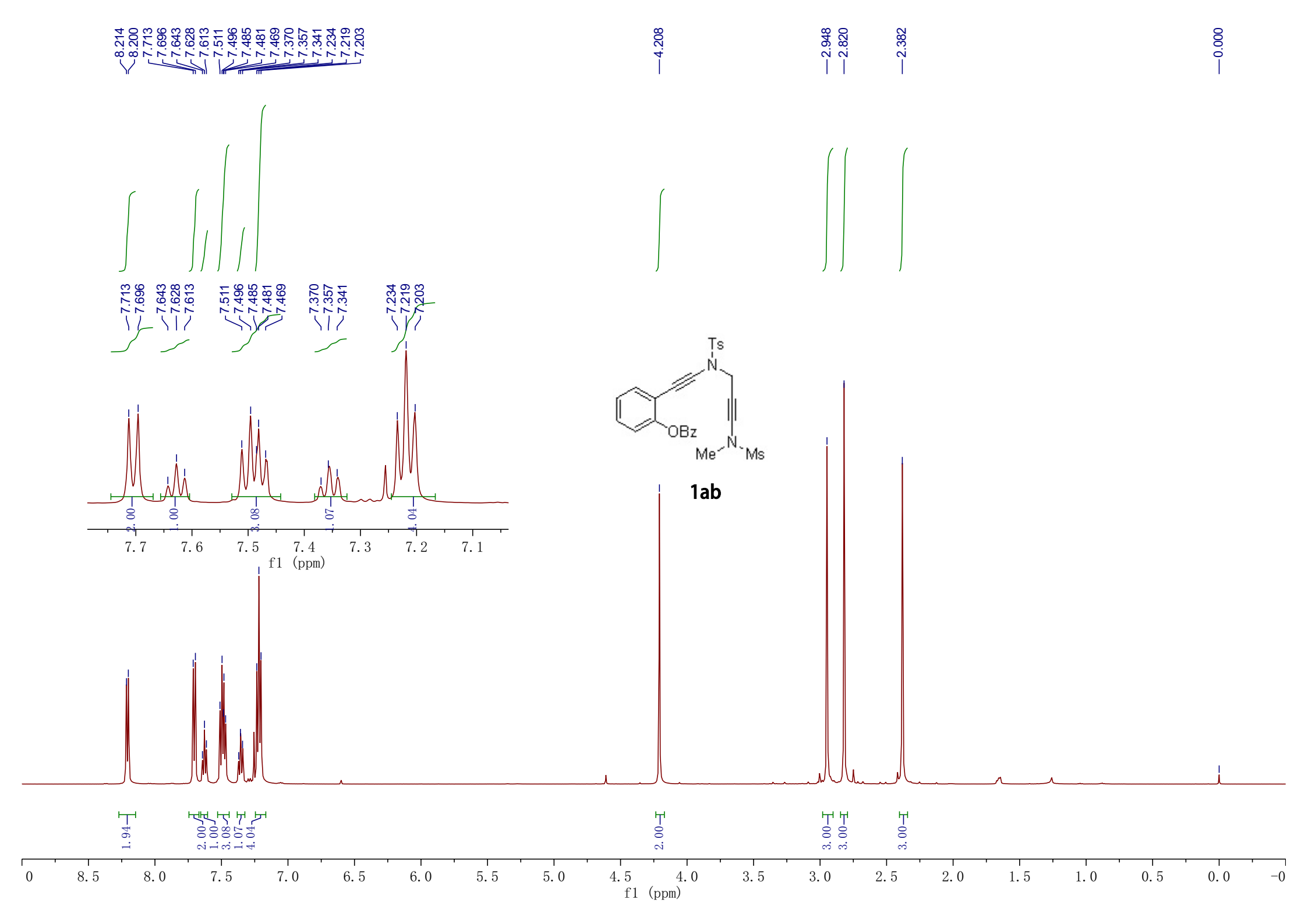


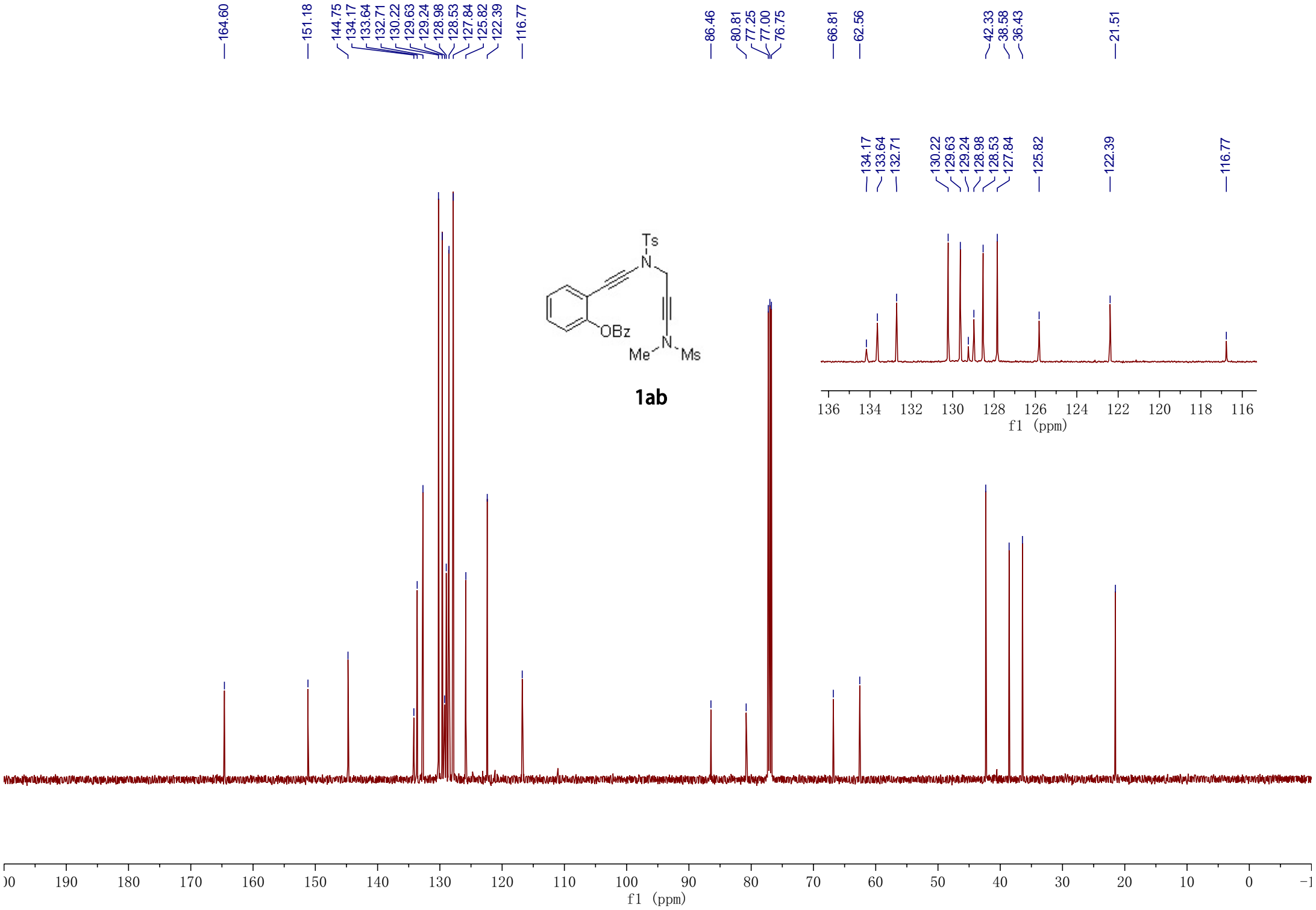


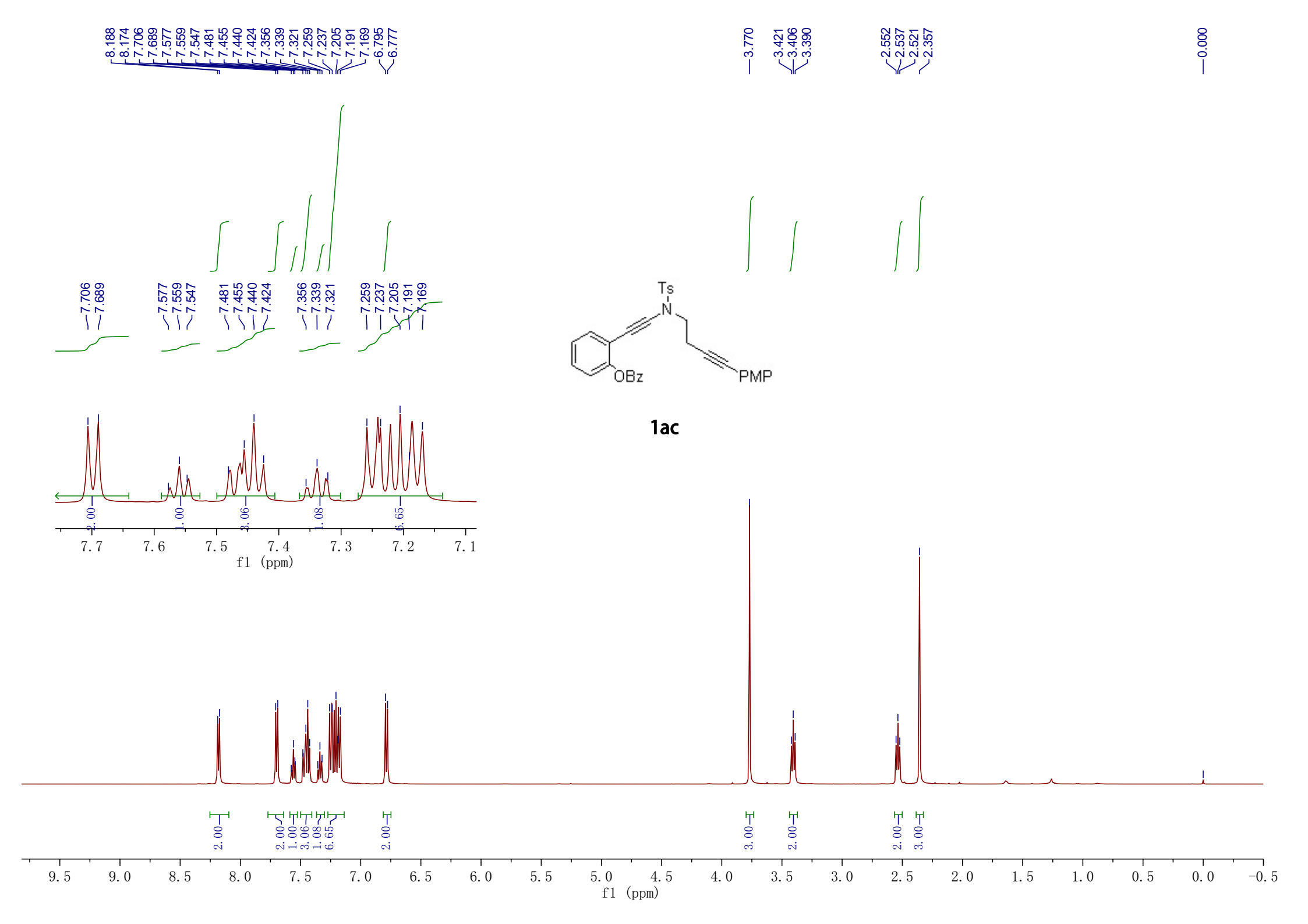

176.52
159.82
151.45
144.75
134.49
133.78
133.19
129.59
129.06
128.23
125.51
122.28
116.82
114.10
113.75
86.56
86.18
79.74
77.32
77.00
76.68
66.38
55.26
43.06
39.09
27.09
21.55
Parameter Value
1 Title zgy-9-opiv-C
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.0
5 Number of Scans 122
6 Acquisition Time 1.3631
7 Acquisition Date 2022-05-20T10:44:53
8 Spectrometer Frequency 100.61
9 Spectral Width 24038.5
Ts
N
OPiv
PMP
1aa
f1 (ppm)

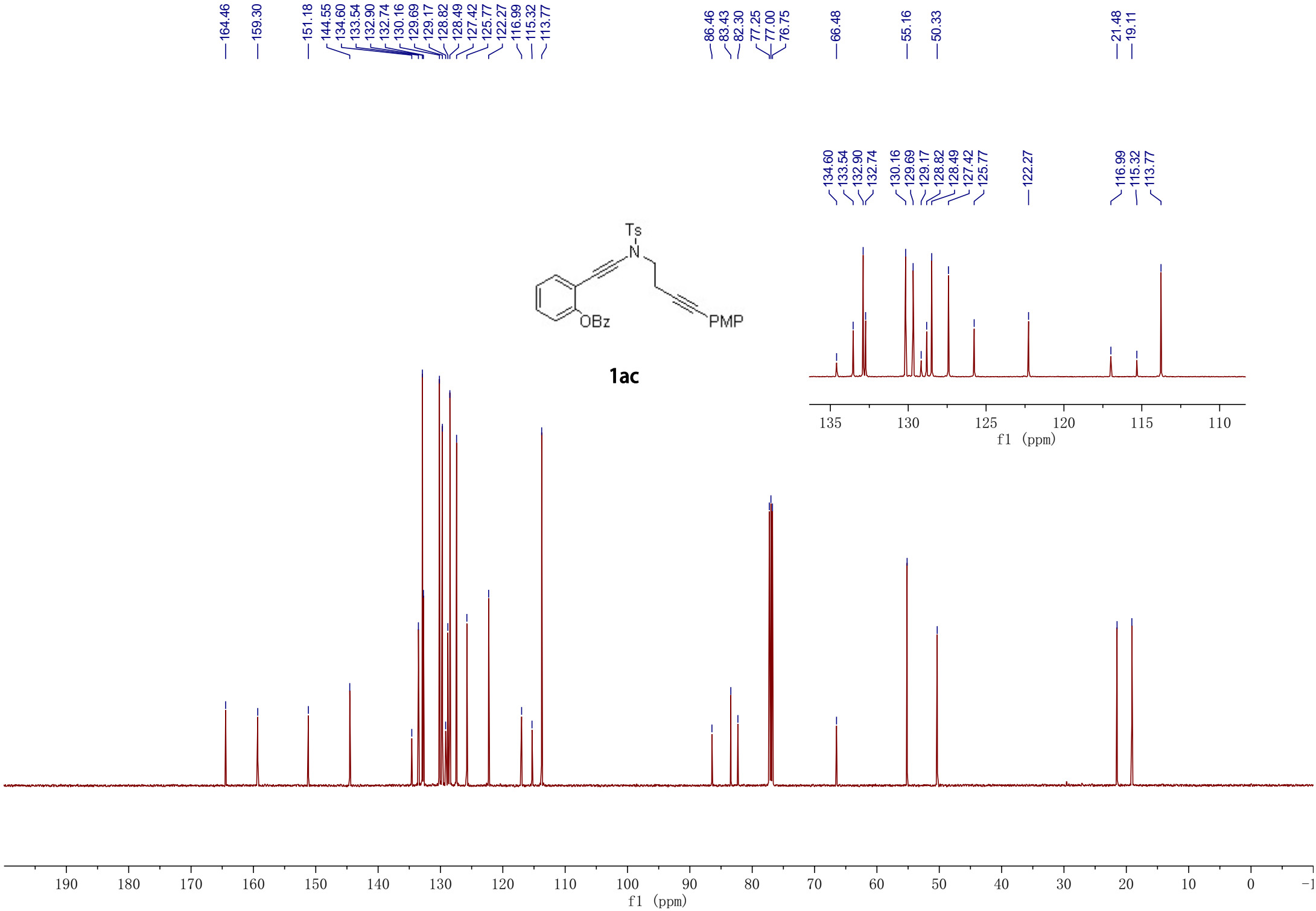
Parameter	Value
1 Title	zgy-9-opiv-C-dept
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	74
6 Acquisition Time	1.3631
7 Acquisition Date	2022-05-20T10:56:08
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5

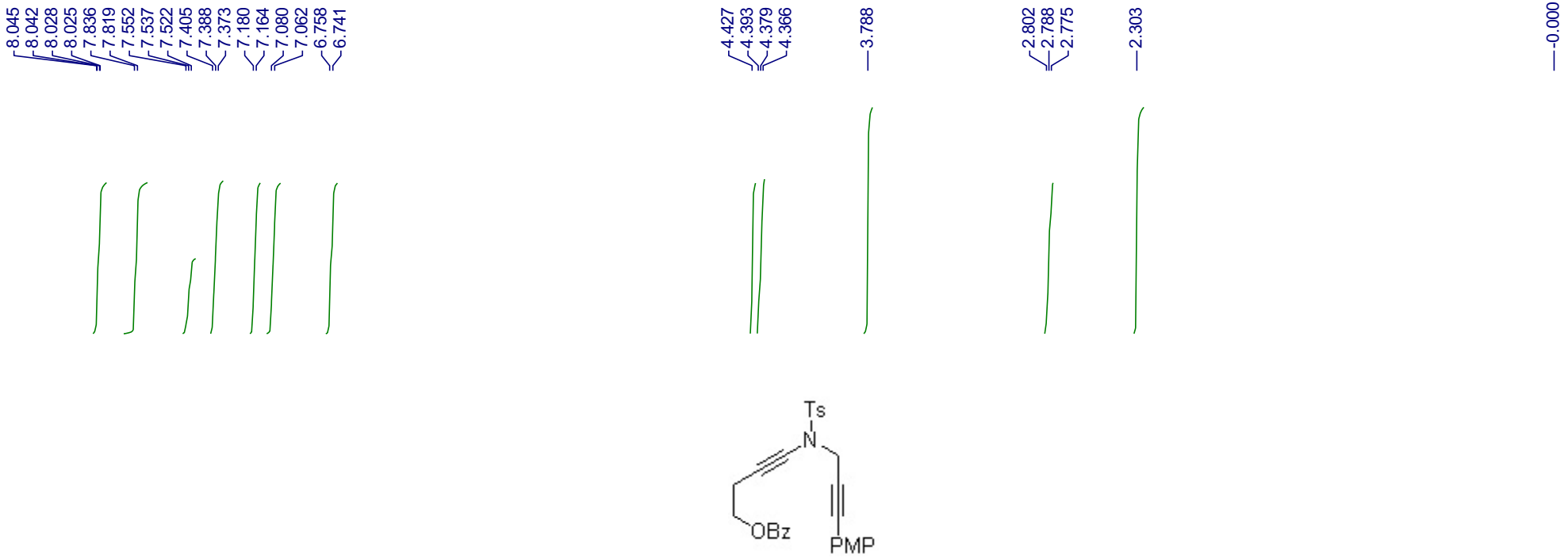



8.214
8.200
7.713
7.696
7.643
7.628
7.613
7.511
7.496
7.485
7.481
7.469
7.370
7.357
7.341
7.234
7.219
7.203
4.208
2.948
2.820
2.382
0.000
Ts
N
OBz
N
Me
Ms
1ab
f1 (ppm)
f1 (ppm)

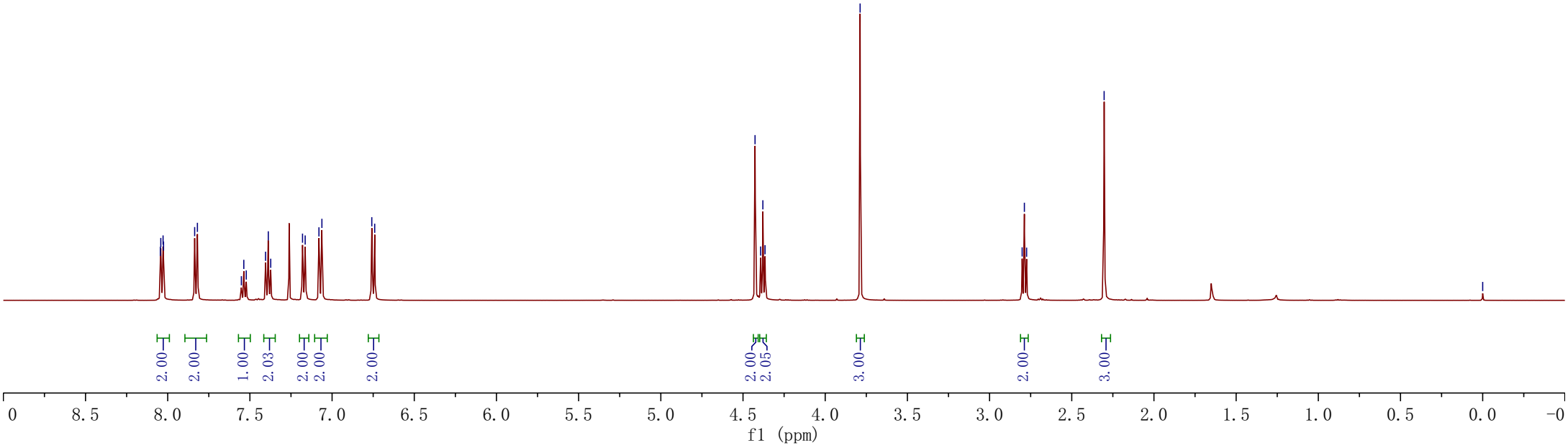

164.60
151.18
144.75
134.17
133.64
132.71
130.22
129.63
129.24
128.98
128.53
127.84
125.82
122.39
116.77
86.46
80.81
77.25
77.00
76.75
66.81
62.56
42.33
38.58
36.43
21.51
Ts
N
OBz
N
Me
Ms
1ab
f1 (ppm)
f1 (ppm)

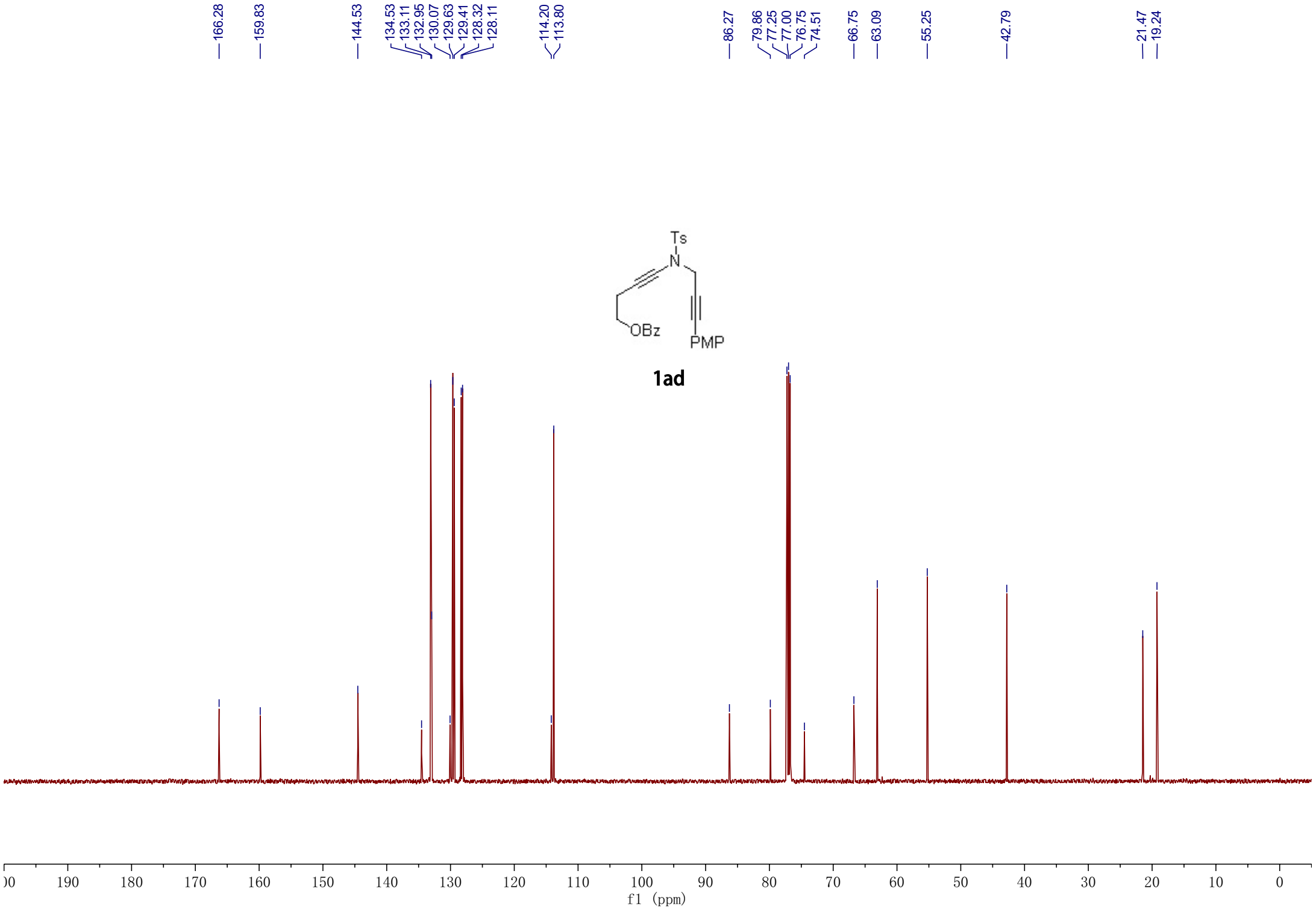

8.188
8.174
7.706
7.689
7.577
7.559
7.547
7.481
7.455
7.440
7.424
7.356
7.339
7.321
7.259
7.237
7.205
7.191
7.169
6.795
6.777
3.770
3.421
3.406
3.390
2.552
2.537
2.521
2.357
0.000
Ts
N
OBz
PMP
1ac
f1 (ppm)
f1 (ppm)


164.46
159.30
151.18
144.55
134.60
133.54
132.90
132.74
130.16
129.69
129.17
128.82
128.49
127.42
125.77
122.27
116.99
115.32
113.77
86.46
83.43
82.30
77.25
77.00
76.75
66.48
55.16
50.33
21.48
19.11
Ts
N
OBz
PMP
1ac
f1 (ppm)


8.045
8.042
8.028
8.025
7.836
7.819
7.552
7.537
7.522
7.405
7.388
7.373
7.180
7.164
7.080
7.062
6.758
6.741
4.427
4.393
4.379
4.366
3.788
2.802
2.788
2.775
2.303
-0.000
Ts
N
OBz
PMP

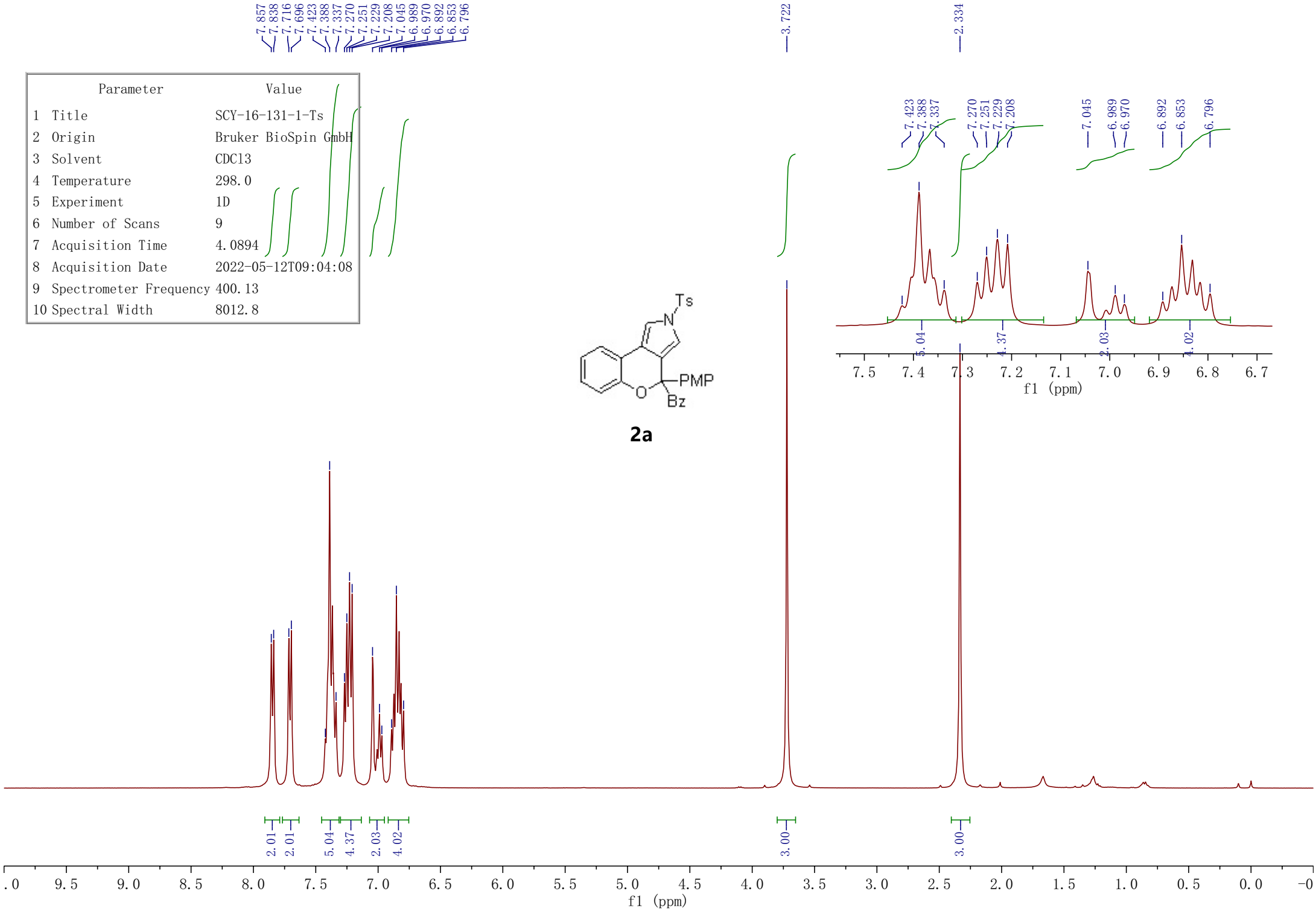
1ad


2.00
2.00
1.00
2.03
2.00
2.00
2.00
2.00
2.05
3.00
2.00
3.00
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
f1 (ppm)


166.28
159.83
144.53
134.53
133.11
132.95
130.07
129.63
129.41
128.32
128.11
114.20
113.80
86.27
79.86
77.25
77.00
76.75
74.51
66.75
63.09
55.25
42.79
21.47
19.24
Ts
N
OBz
PMP
1ad
f1 (ppm)

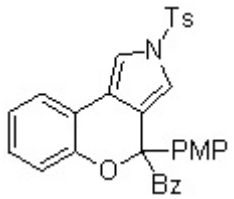
Parameter	Value
1 Title	SCY-16-131-1-Ts
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Experiment	1D
6 Number of Scans	9
7 Acquisition Time	4.0894
8 Acquisition Date	2022-05-12T09:04:08
9 Spectrometer Frequency	400.13
10 Spectral Width	8012.8

2a

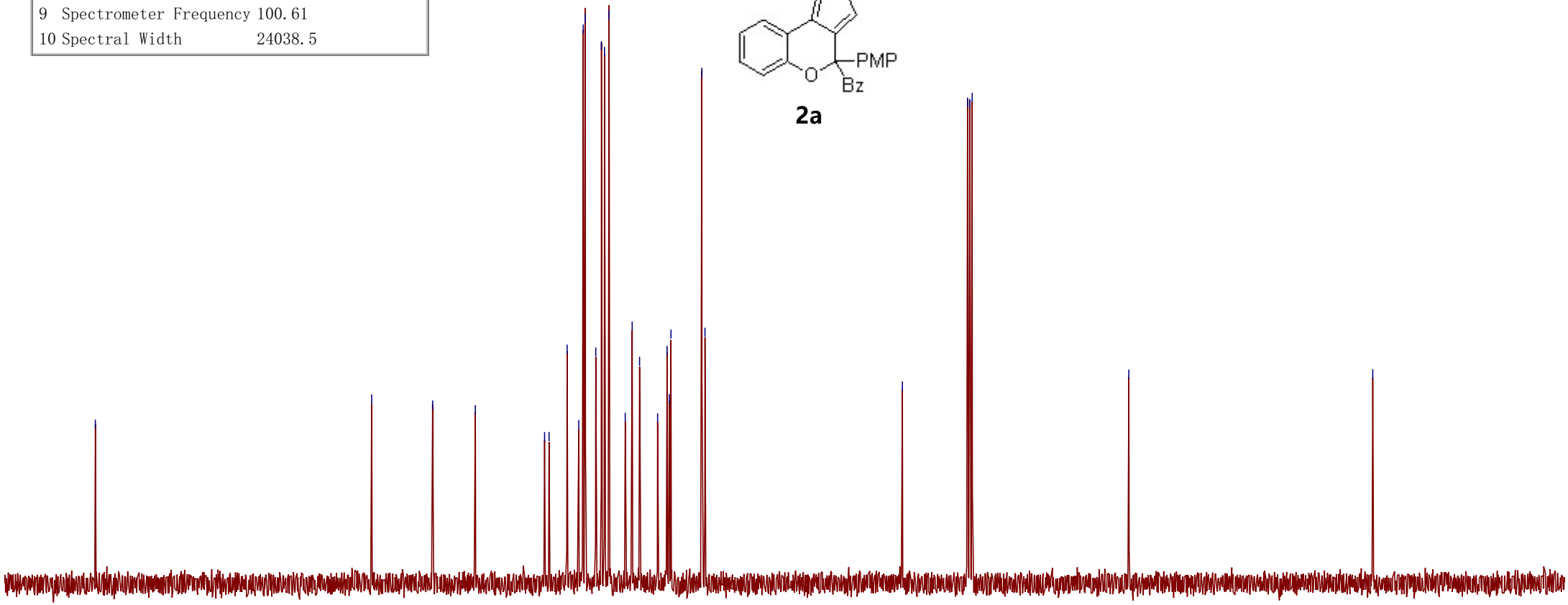


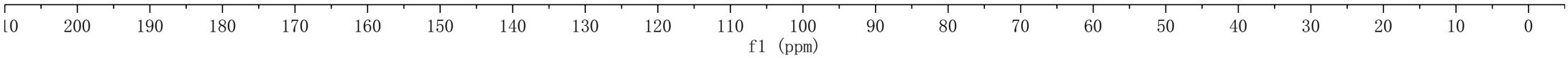
197.51
159.43
151.04
145.15
135.61
134.99
132.50
130.90
130.27
129.99
128.55
127.77
127.35
126.72
124.49
123.54
122.52
120.03
118.72
118.42
118.19
113.93
113.50
86.30
77.32
77.00
76.68
55.09
21.47

	Parameter	Value
1	Title	SCY-16-131-1-Ts
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	300.0
5	Experiment	1D
6	Number of Scans	42
7	Acquisition Time	1.3631
8	Acquisition Date	2022-05-12T09:07:22
9	Spectrometer Frequency	100.61
10	Spectral Width	24038.5



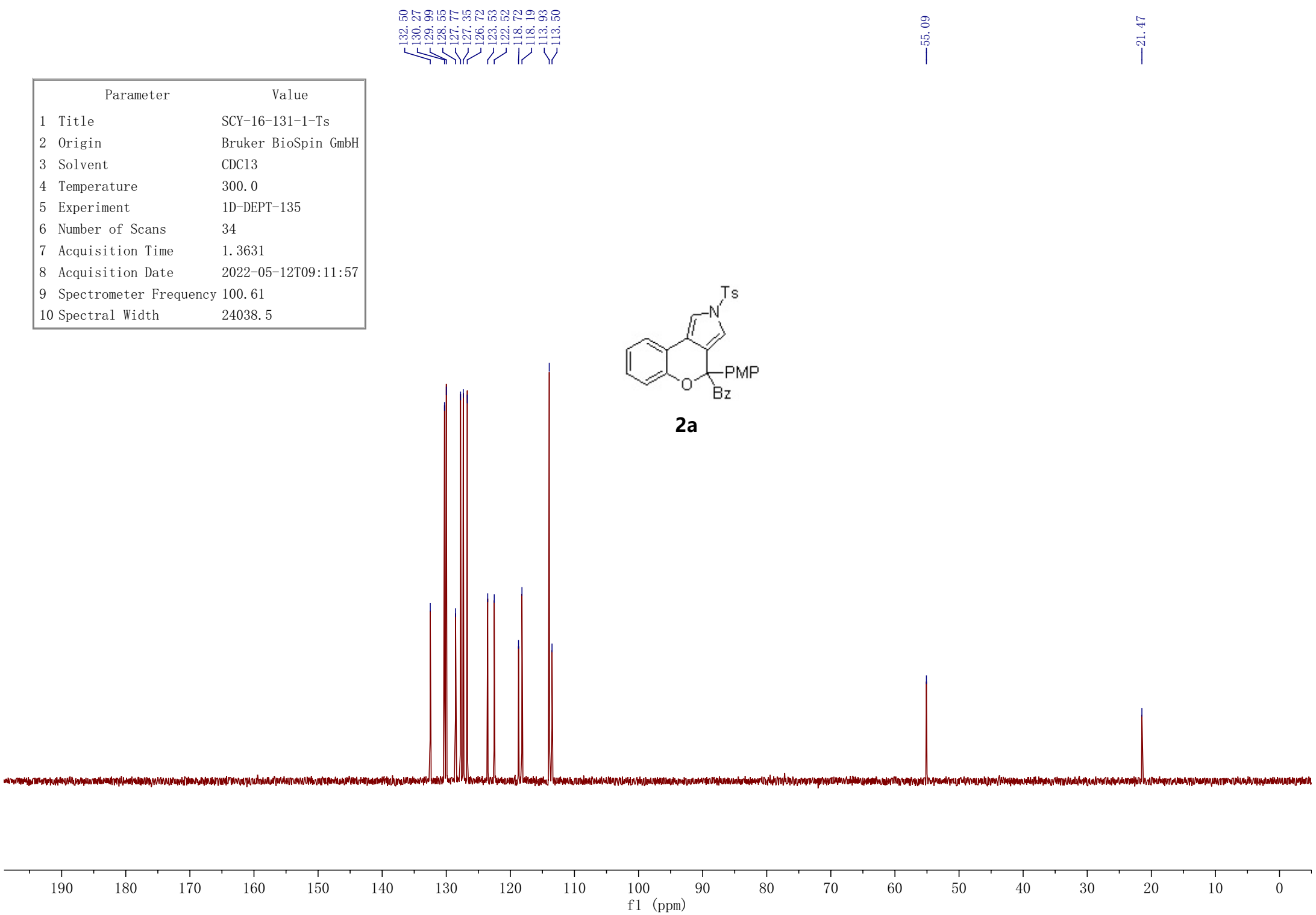
2a



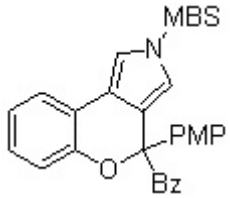


	Parameter	Value
1	Title	SCY-16-131-1-Ts
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	300.0
5	Experiment	1D-DEPT-135
6	Number of Scans	34
7	Acquisition Time	1.3631
8	Acquisition Date	2022-05-12T09:11:57
9	Spectrometer Frequency	100.61
10	Spectral Width	24038.5

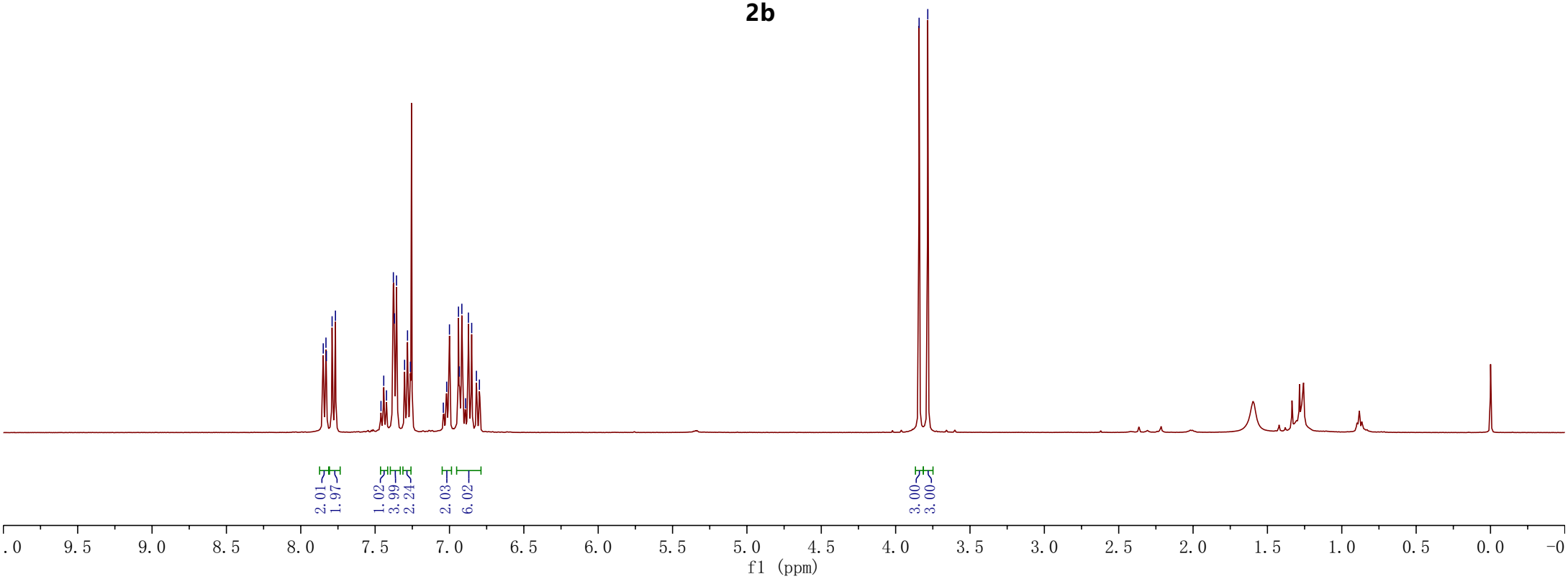
2a

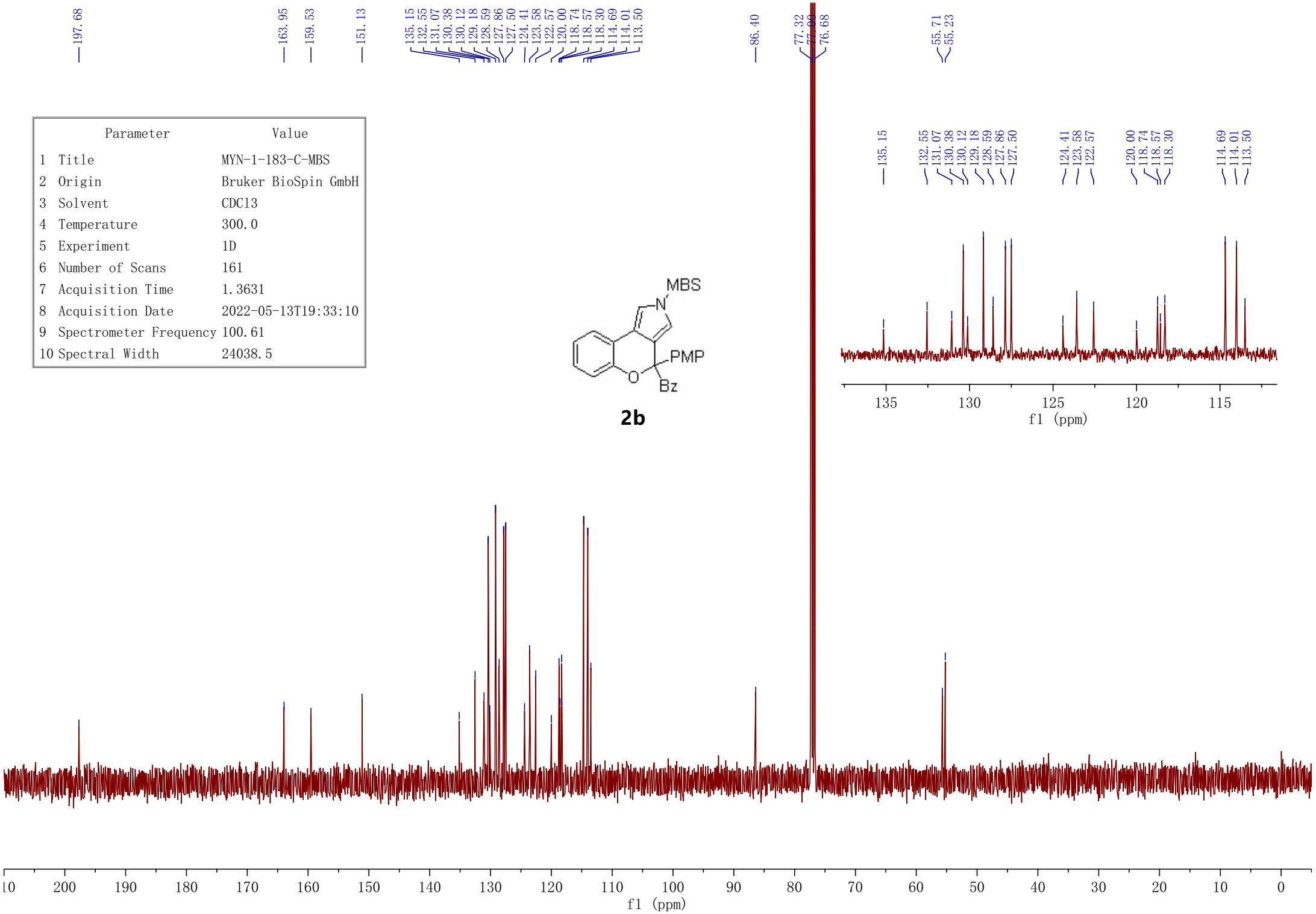


	Parameter	Value
1	Title	MYN-1-183-H-MBS
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	298.0
5	Experiment	1D
6	Number of Scans	17
7	Acquisition Time	4.0894
8	Acquisition Date	2022-05-13T19:30:27
9	Spectrometer Frequency	400.13
10	Spectral Width	8012.8



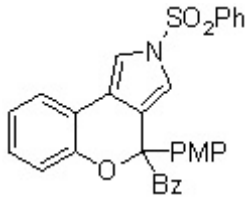
2b





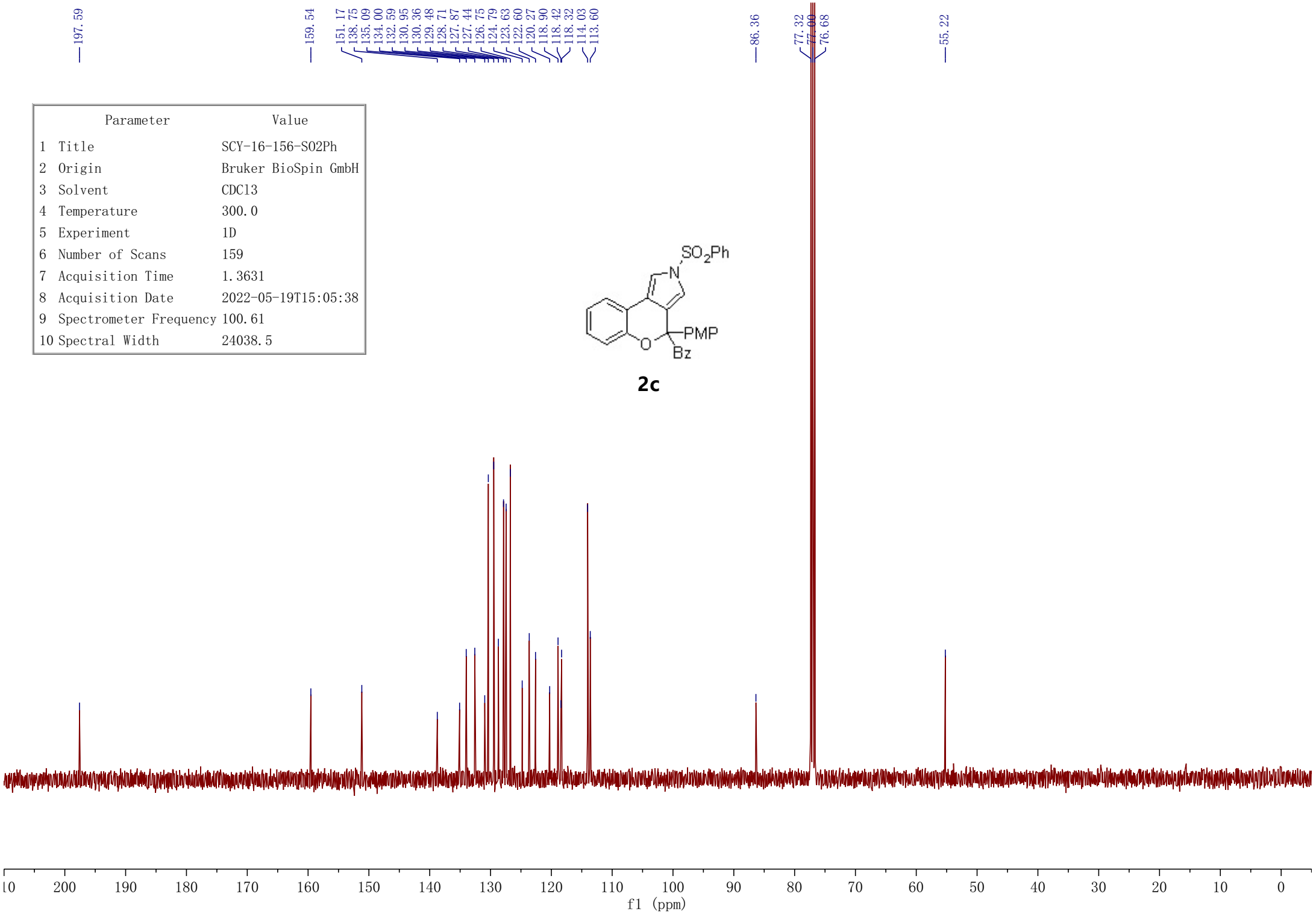
	Parameter	Value
1	Title	MYN-1-183-C-MBS
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	300.0
5	Experiment	1D
6	Number of Scans	161
7	Acquisition Time	1.3631
8	Acquisition Date	2022-05-13T19:33:10
9	Spectrometer Frequency	100.61
10	Spectral Width	24038.5

	Parameter	Value
1	Title	SCY-16-156-SO2Ph
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	298.0
5	Experiment	1D
6	Number of Scans	13
7	Acquisition Time	4.0894
8	Acquisition Date	2022-05-19T15:02:07
9	Spectrometer Frequency	400.13
10	Spectral Width	8012.8

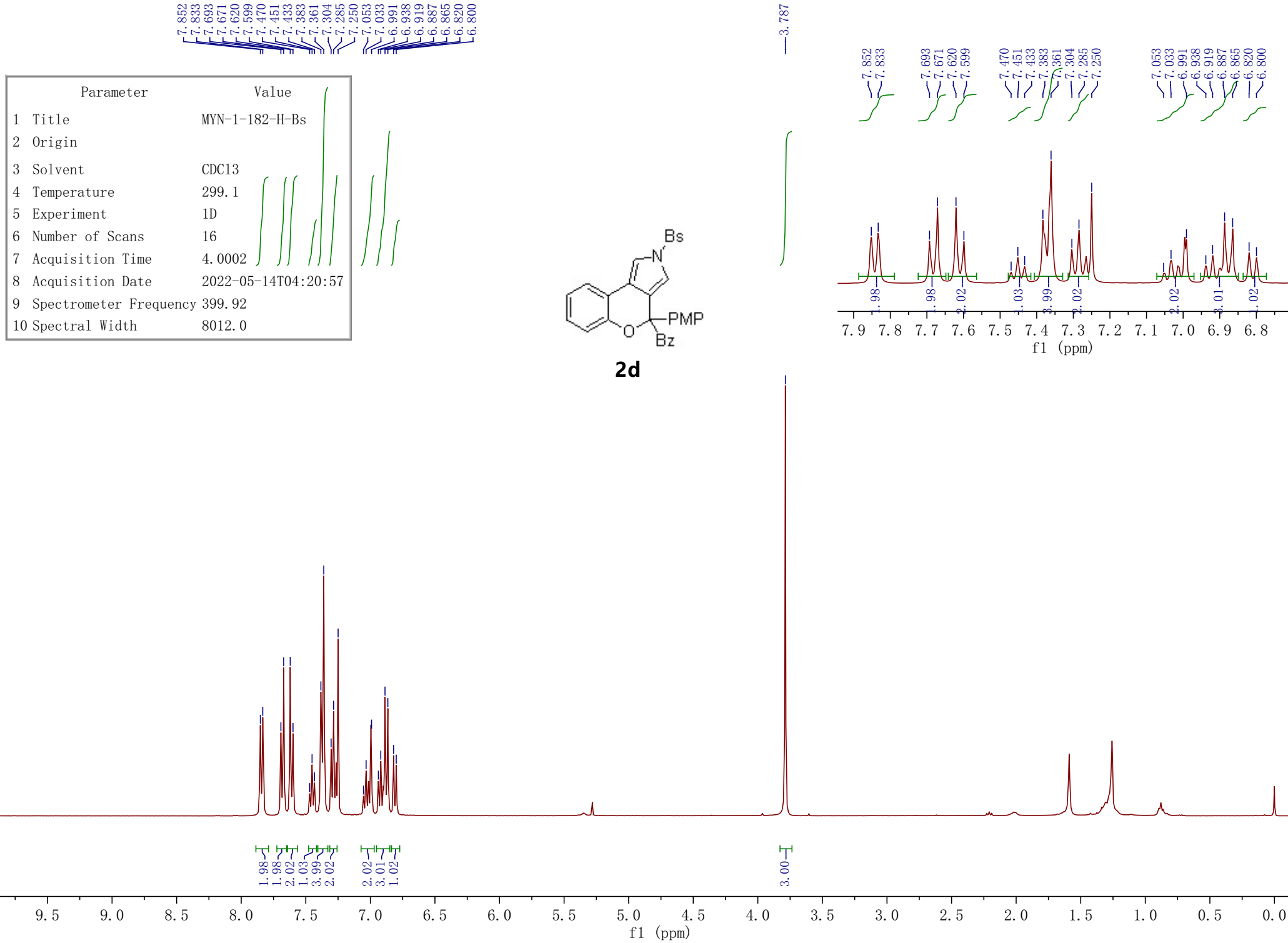


2c

f1 (ppm)



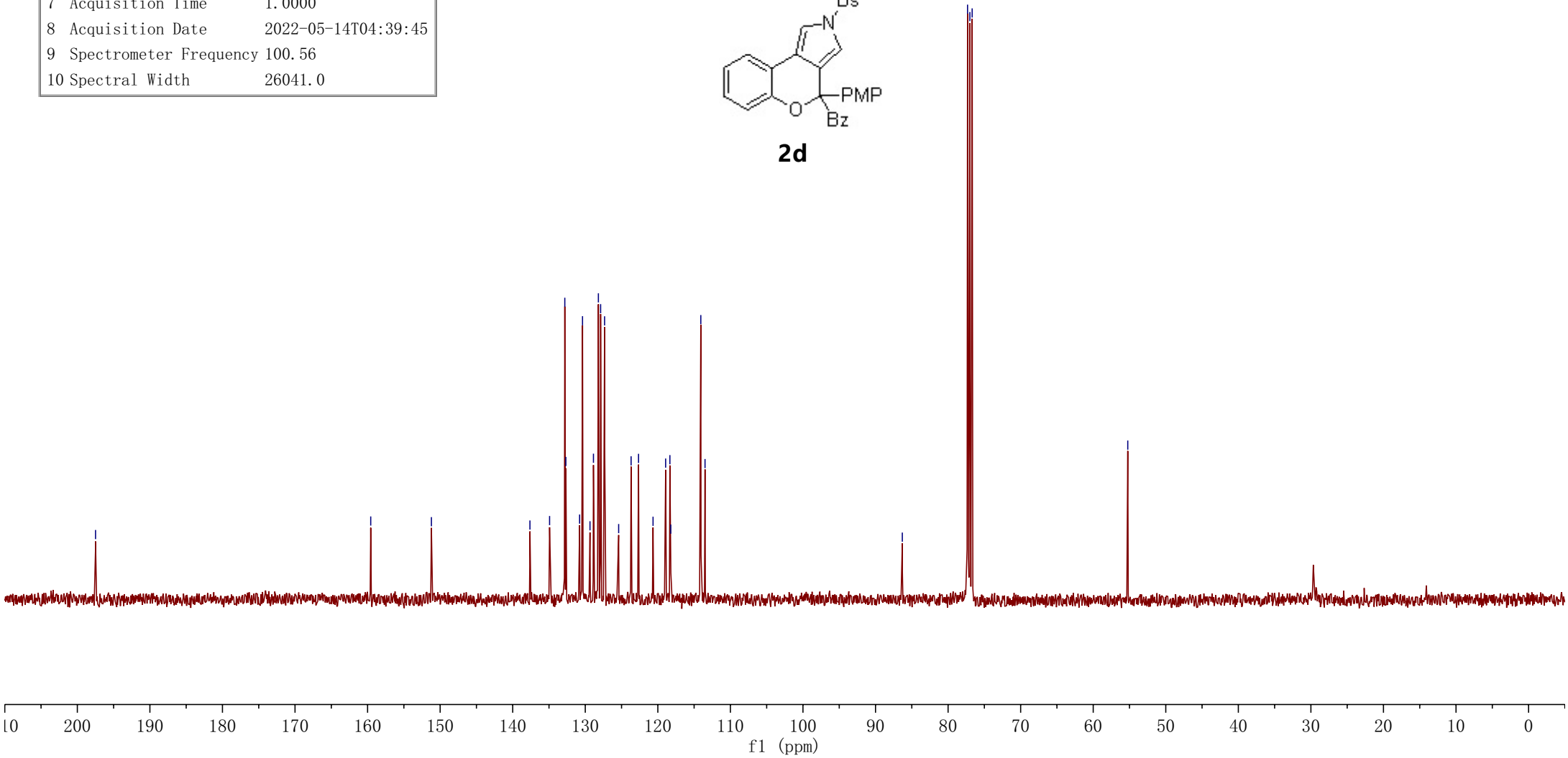
	Parameter	Value
1	Title	SCY-16-156-SO2Ph
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	300.0
5	Experiment	1D
6	Number of Scans	159
7	Acquisition Time	1.3631
8	Acquisition Date	2022-05-19T15:05:38
9	Spectrometer Frequency	100.61
10	Spectral Width	24038.5


7.852
7.833
7.693
7.671
7.620
7.599
7.470
7.451
7.433
7.383
7.361
7.304
7.285
7.250
7.053
7.033
6.991
6.938
6.919
6.887
6.865
6.820
6.800
3.787
Parameter Value
1 Title MYN-1-182-H-Bs
2 Origin
3 Solvent CDCl3
4 Temperature 299.1
5 Experiment 1D
6 Number of Scans 16
7 Acquisition Time 4.0002
8 Acquisition Date 2022-05-14T04:20:57
9 Spectrometer Frequency 399.92
10 Spectral Width 8012.0
Bs
N
PMP
O
Bz
2d
1.98
1.98
2.02
1.03
3.99
2.02
2.02
3.01
1.02
3.00
f1 (ppm)

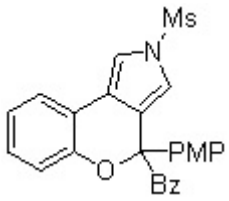
197.49
159.57
151.20
137.63
134.92
132.82
132.68
130.78
130.38
129.35
128.87
128.19
127.88
127.34
125.40
123.68
122.66
120.66
118.92
118.34
118.22
114.08
113.50
86.31
77.32
77.00
76.68
55.24

	Parameter	Value
1	Title	MYN-1-182-C-Bs
2	Origin	
3	Solvent	CDCl3
4	Temperature	299.3
5	Experiment	1D
6	Number of Scans	500
7	Acquisition Time	1.0000
8	Acquisition Date	2022-05-14T04:39:45
9	Spectrometer Frequency	100.56
10	Spectral Width	26041.0

2d

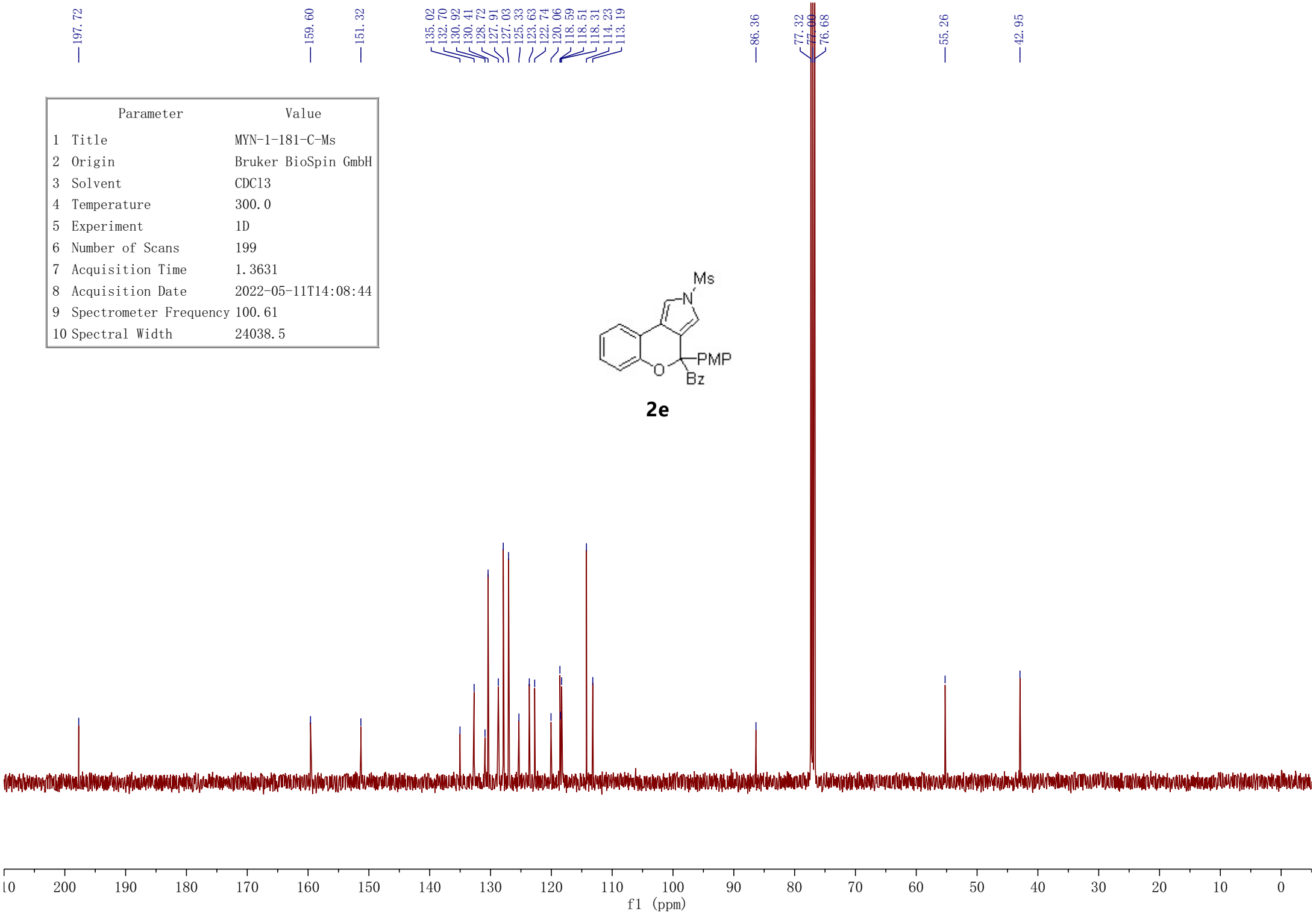


	Parameter	Value
1	Title	MYN-1-181-H-Ms
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	298.0
5	Experiment	1D
6	Number of Scans	14
7	Acquisition Time	4.0894
8	Acquisition Date	2022-05-11T13:24:30
9	Spectrometer Frequency	400.13
10	Spectral Width	8012.8



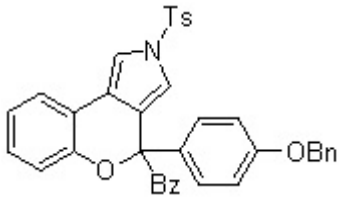
2e

f1 (ppm)

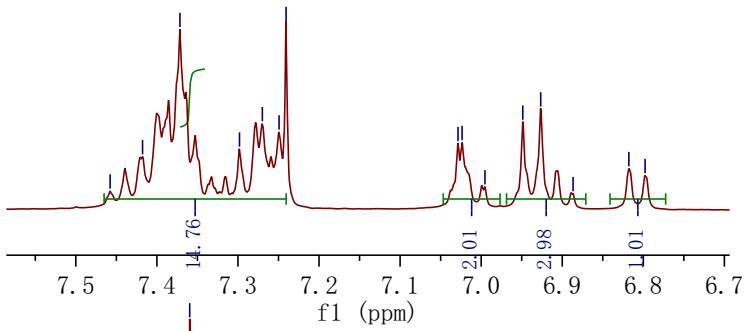


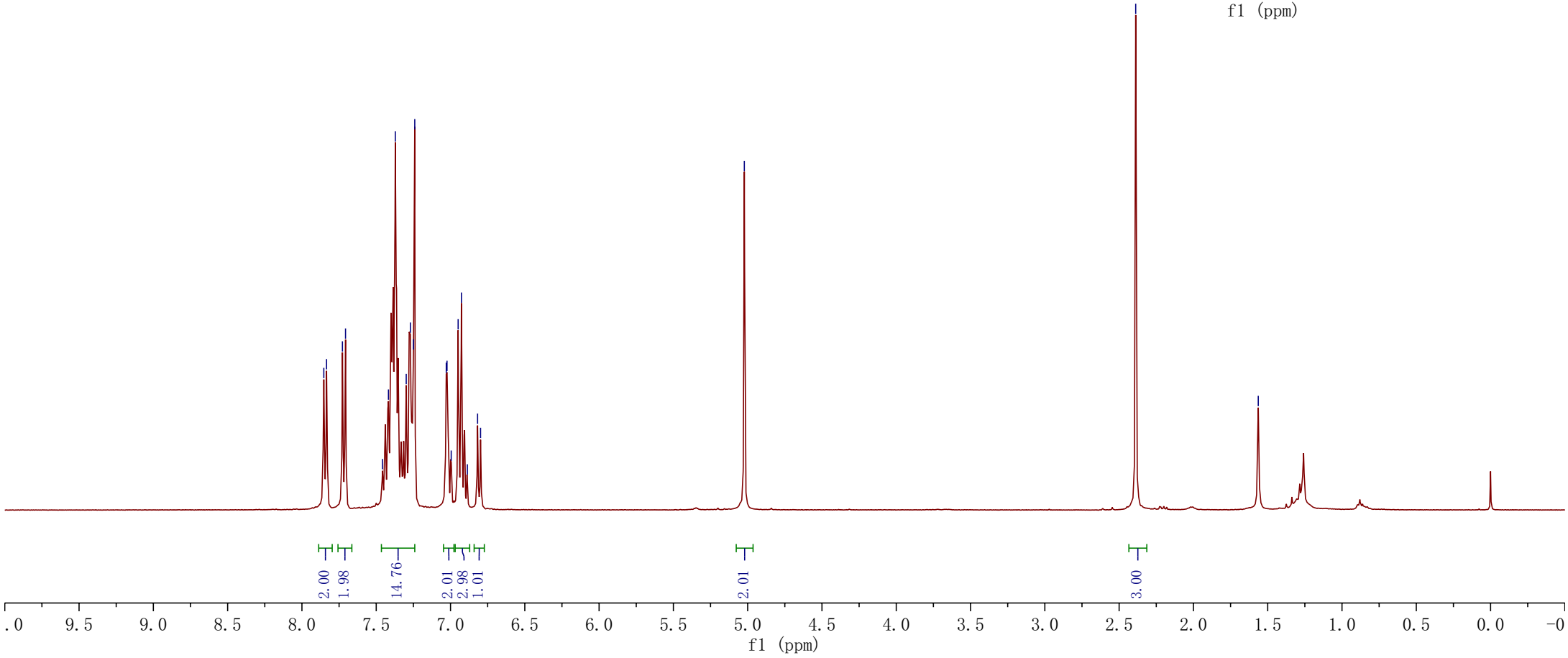
	Parameter	Value
1	Title	MYN-1-181-C-Ms
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	300.0
5	Experiment	1D
6	Number of Scans	199
7	Acquisition Time	1.3631
8	Acquisition Date	2022-05-11T14:08:44
9	Spectrometer Frequency	100.61
10	Spectral Width	24038.5

	Parameter	Value
1	Title	scy-16-155-40Bn苯基
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	298.0
5	Experiment	1D
6	Number of Scans	8
7	Acquisition Time	4.0894
8	Acquisition Date	2022-05-19T15:22:50
9	Spectrometer Frequency	400.13
10	Spectral Width	8012.8



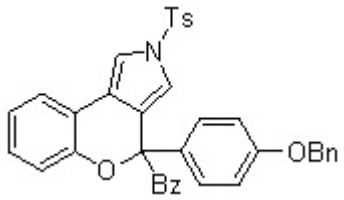
2f



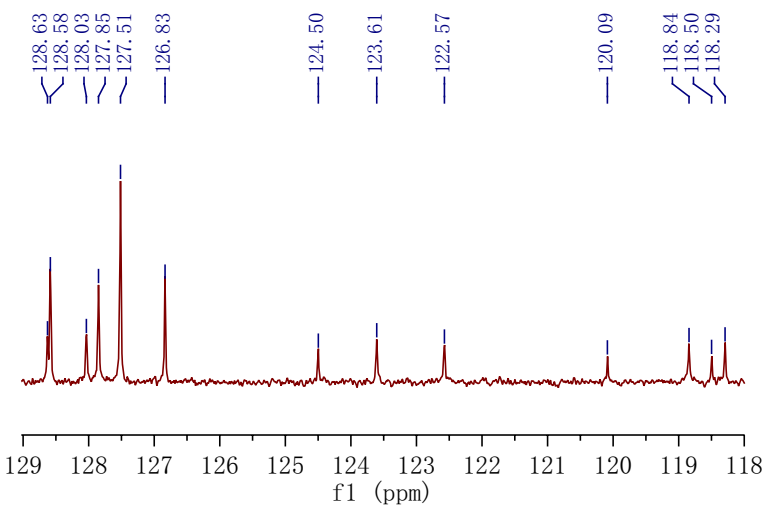


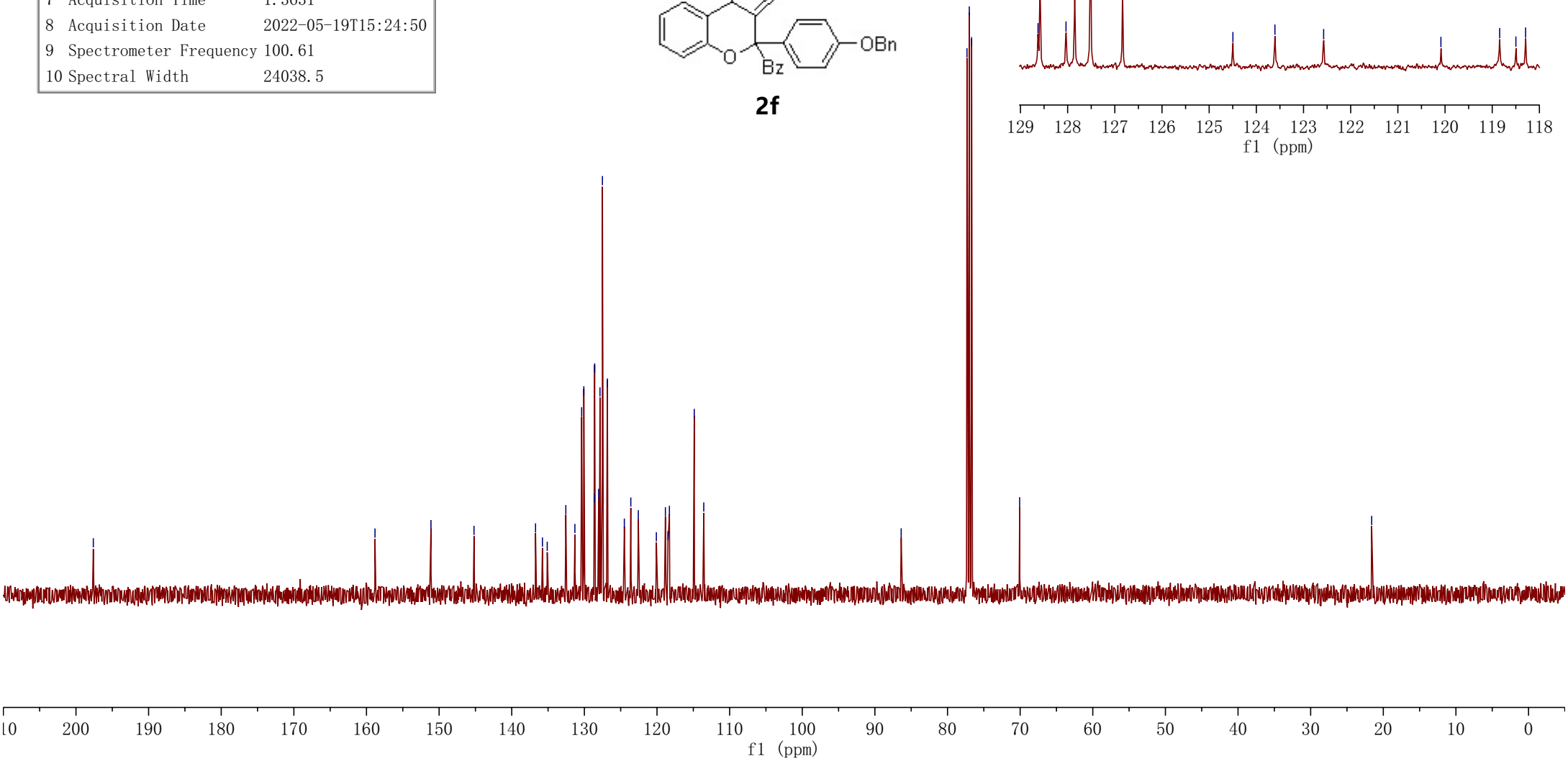
197.61 158.83 151.12 145.20 136.72 135.77 135.11 132.55 131.31 130.38 130.08 128.63 128.58 128.03 127.85 127.51 126.83 124.50 123.61 122.57 120.09 118.84 118.50 118.29 114.87 113.56 86.38 77.32 77.00 76.68 70.07 21.60

	Parameter	Value
1	Title	scy-16-155-4OBn苯基
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	300.0
5	Experiment	1D
6	Number of Scans	102
7	Acquisition Time	1.3631
8	Acquisition Date	2022-05-19T15:24:50
9	Spectrometer Frequency	100.61
10	Spectral Width	24038.5

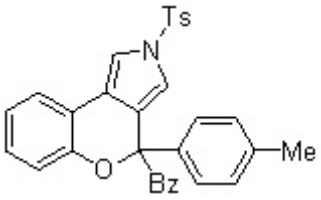


2f

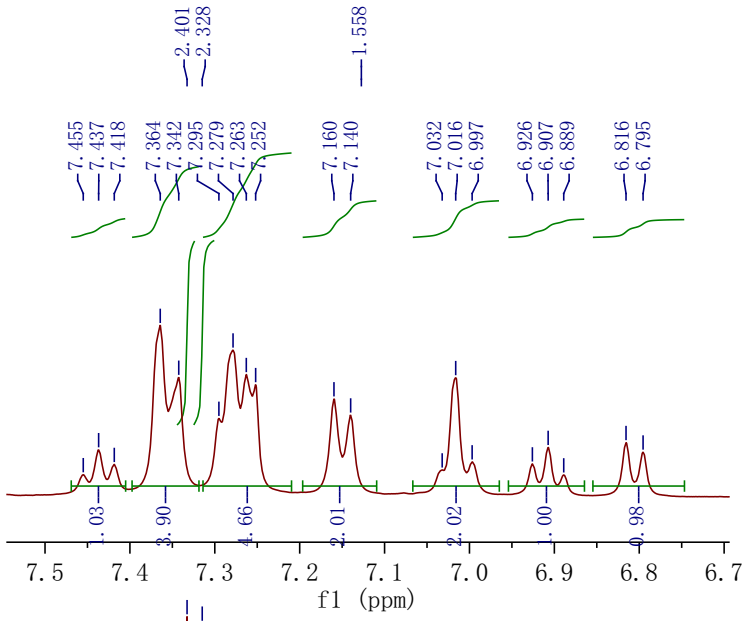


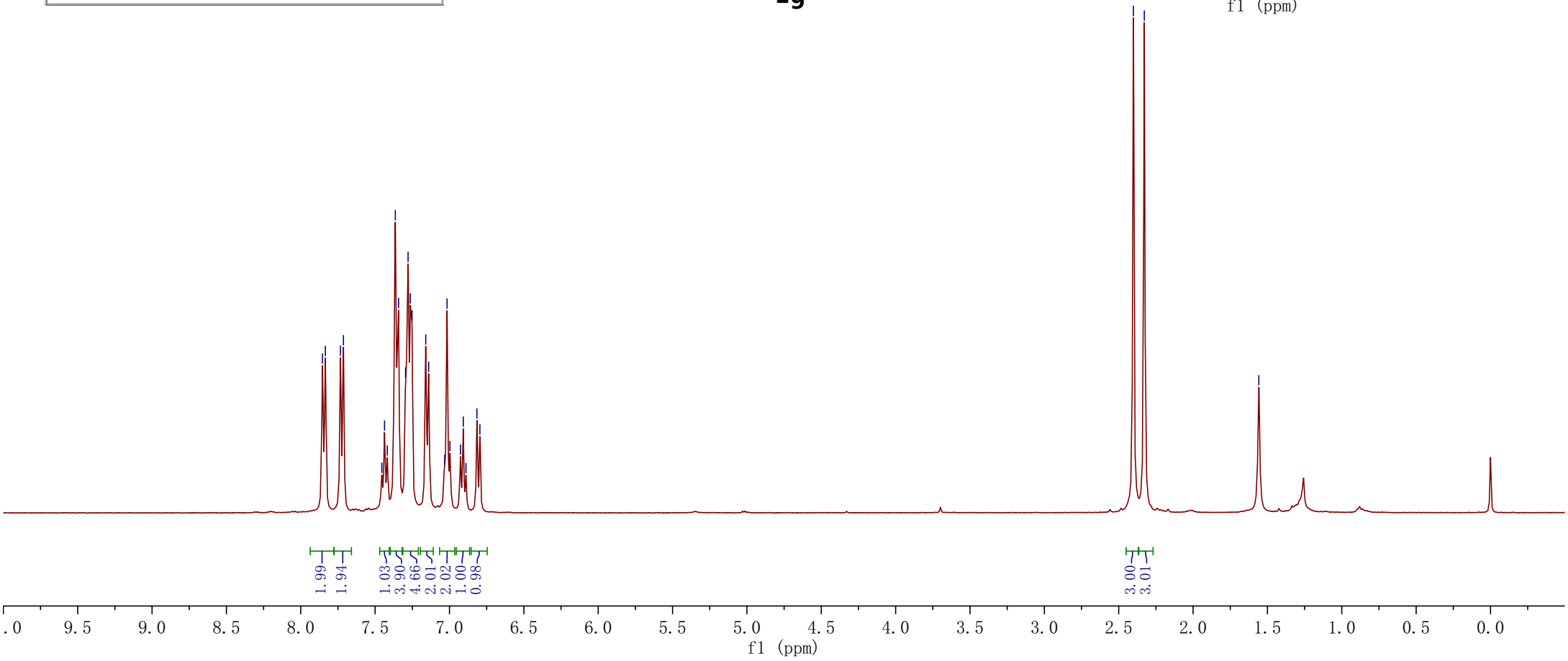


Parameter		Value
1	Title	MYN-1-186-H-4-Me
2	Origin	
3	Solvent	CDCl3
4	Temperature	299.6
5	Experiment	1D
6	Number of Scans	16
7	Acquisition Time	4.0002
8	Acquisition Date	2022-05-25T23:35:31
9	Spectrometer Frequency	399.92
10	Spectral Width	8012.0

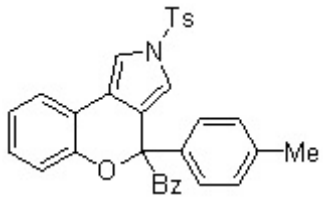


2g

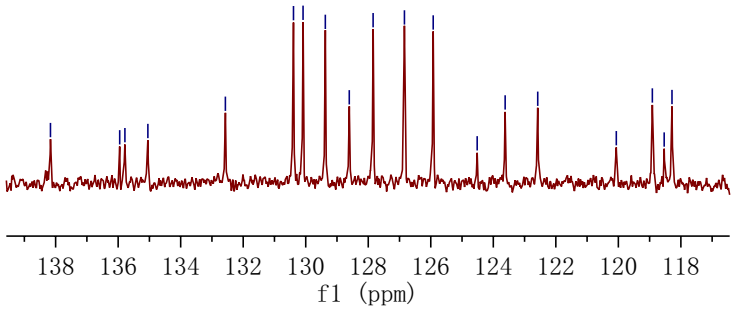


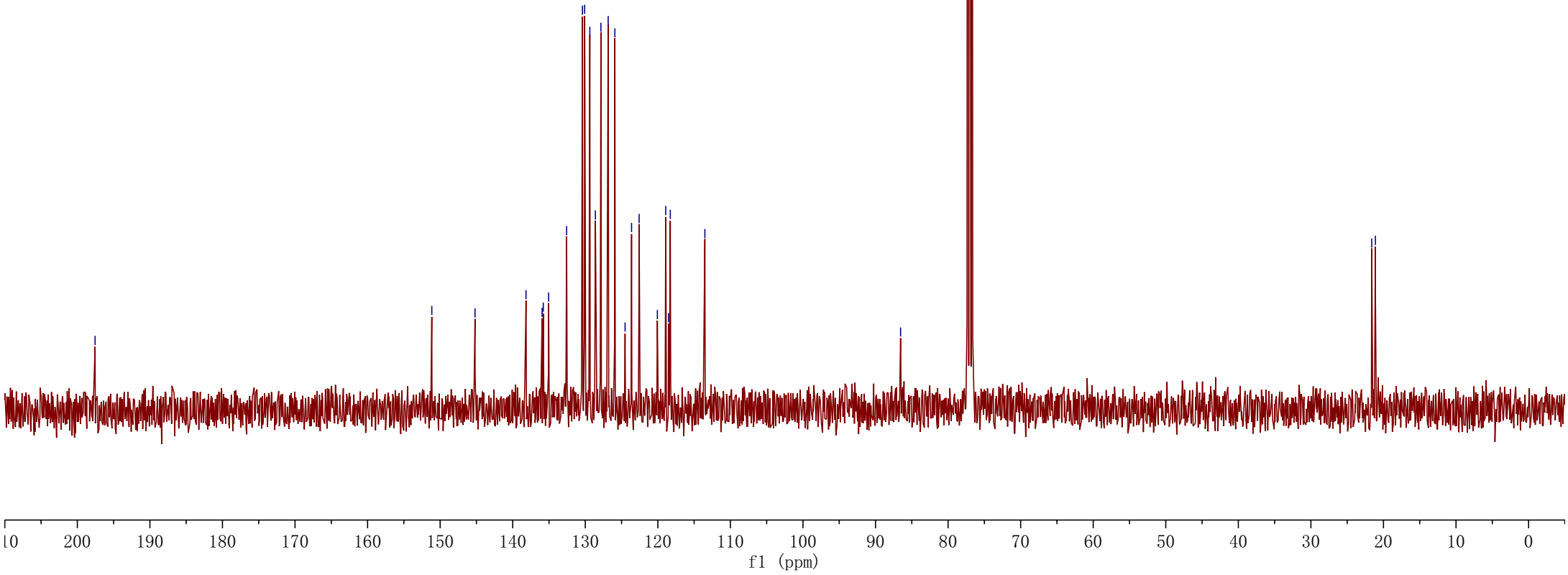


Parameter	Value
1 Title	MYN-1-186-C-4-Me
2 Origin	
3 Solvent	CDCl3
4 Temperature	299.3
5 Experiment	1D
6 Number of Scans	300
7 Acquisition Time	1.0000
8 Acquisition Date	2022-05-25T23:47:47
9 Spectrometer Frequency	100.56
10 Spectral Width	26041.0



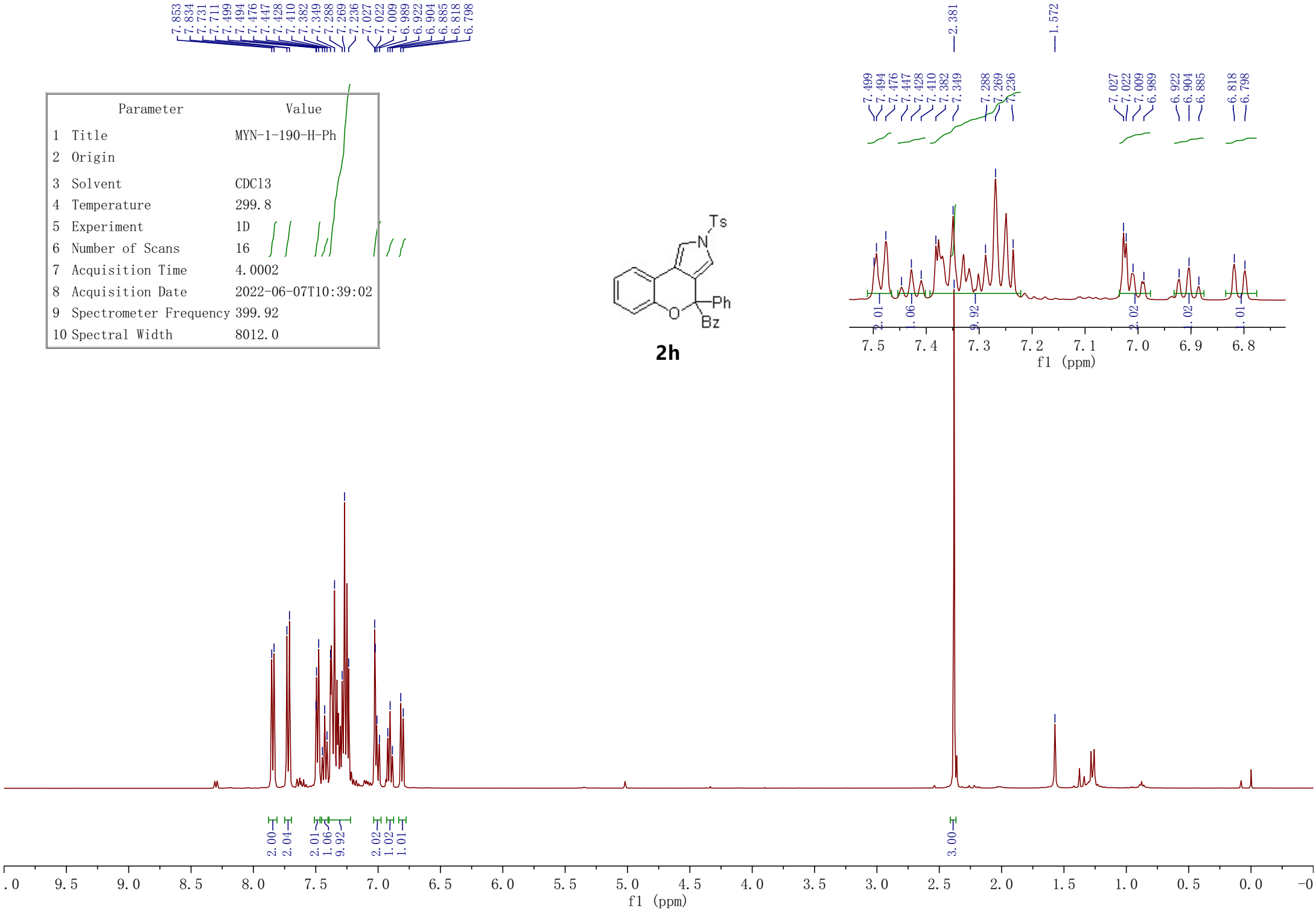
2g

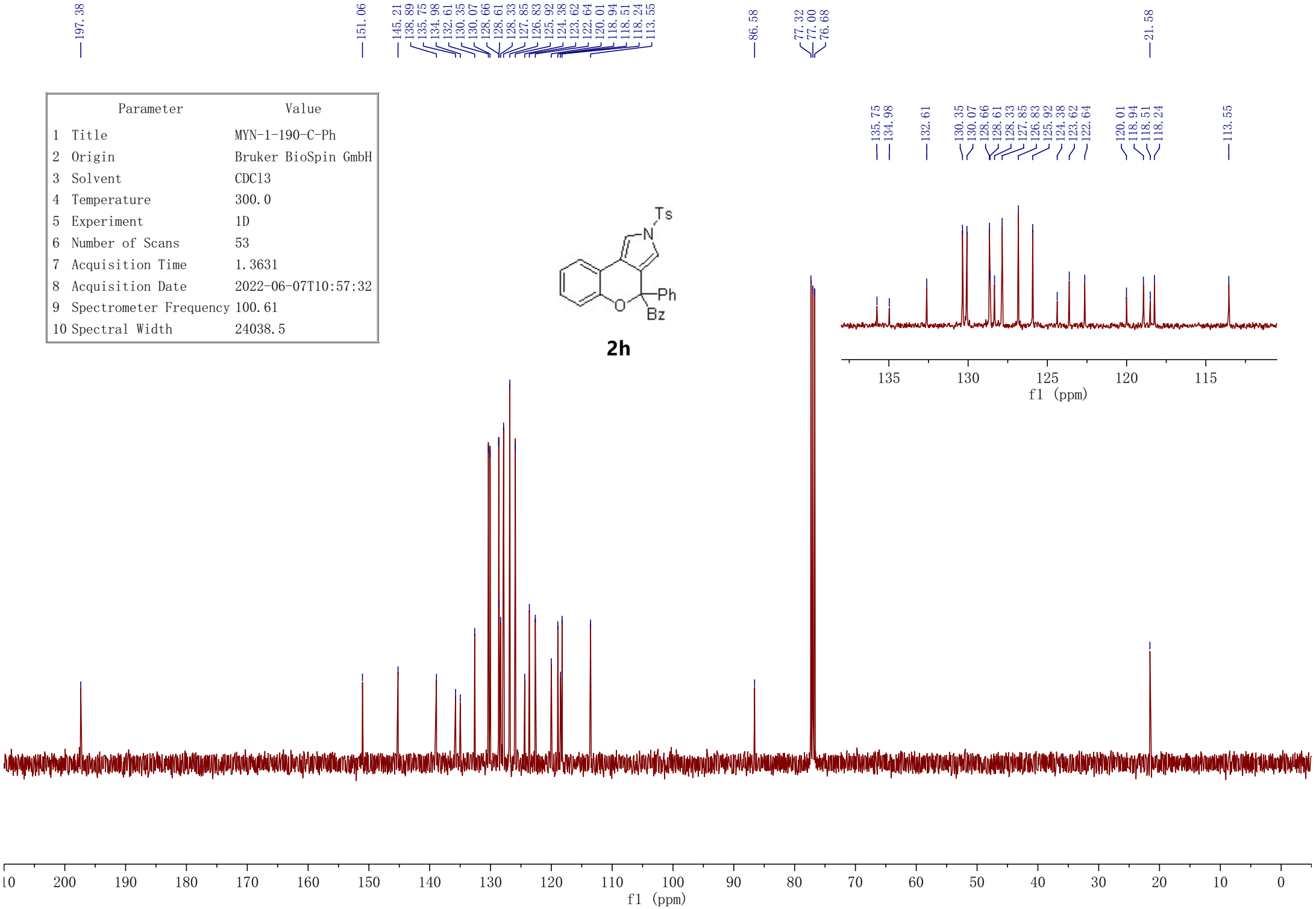




	Parameter	Value
1	Title	MYN-1-190-H-Ph
2	Origin	
3	Solvent	CDCl3
4	Temperature	299.8
5	Experiment	1D
6	Number of Scans	16
7	Acquisition Time	4.0002
8	Acquisition Date	2022-06-07T10:39:02
9	Spectrometer Frequency	399.92
10	Spectral Width	8012.0

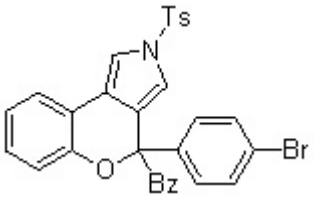
2h



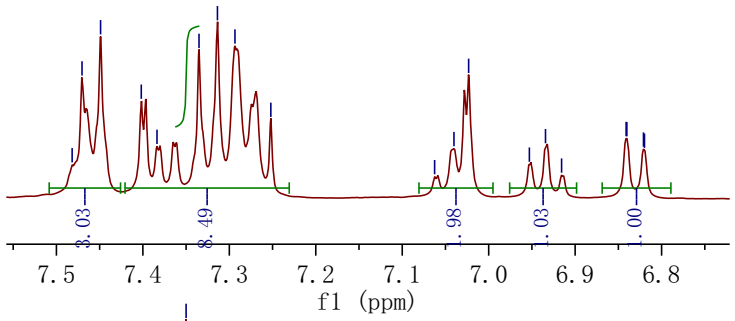


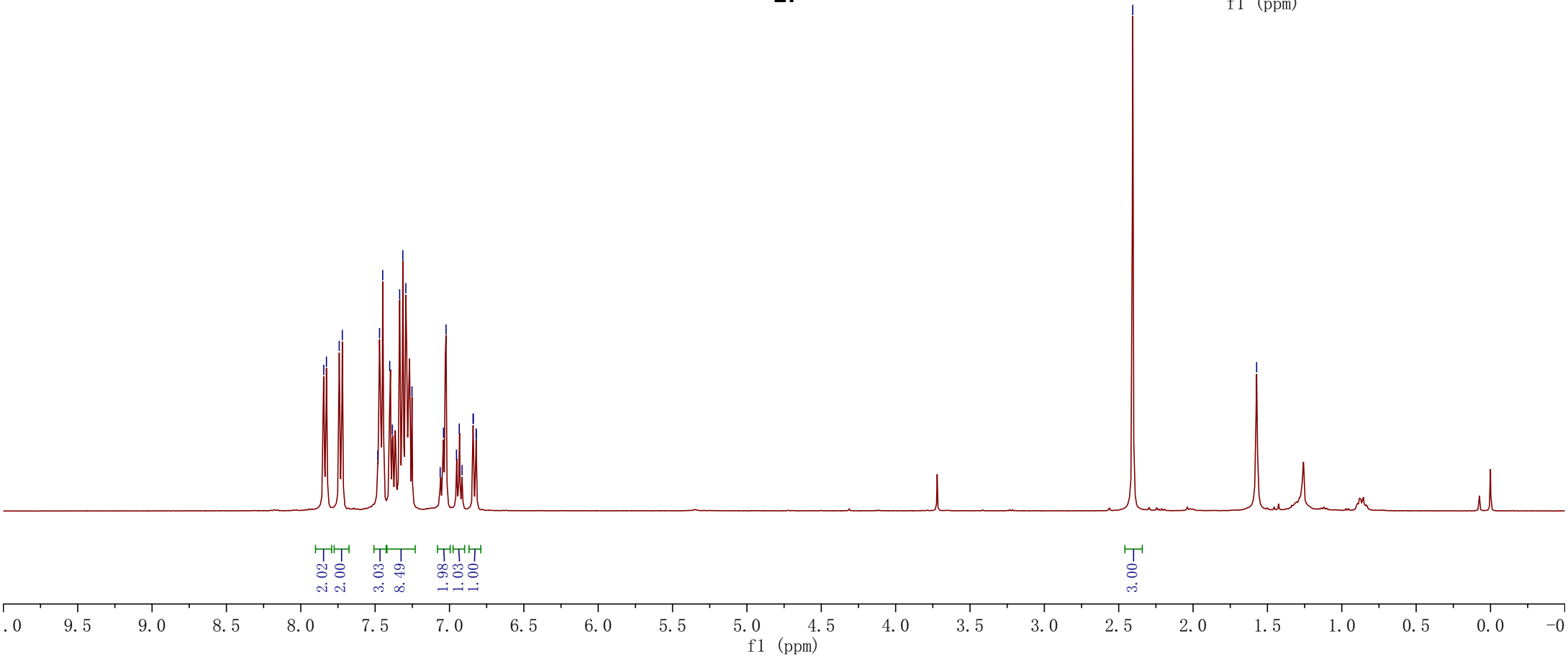
	Parameter	Value
1	Title	MYN-1-190-C-Ph
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	300.0
5	Experiment	1D
6	Number of Scans	53
7	Acquisition Time	1.3631
8	Acquisition Date	2022-06-07T10:57:32
9	Spectrometer Frequency	100.61
10	Spectral Width	24038.5

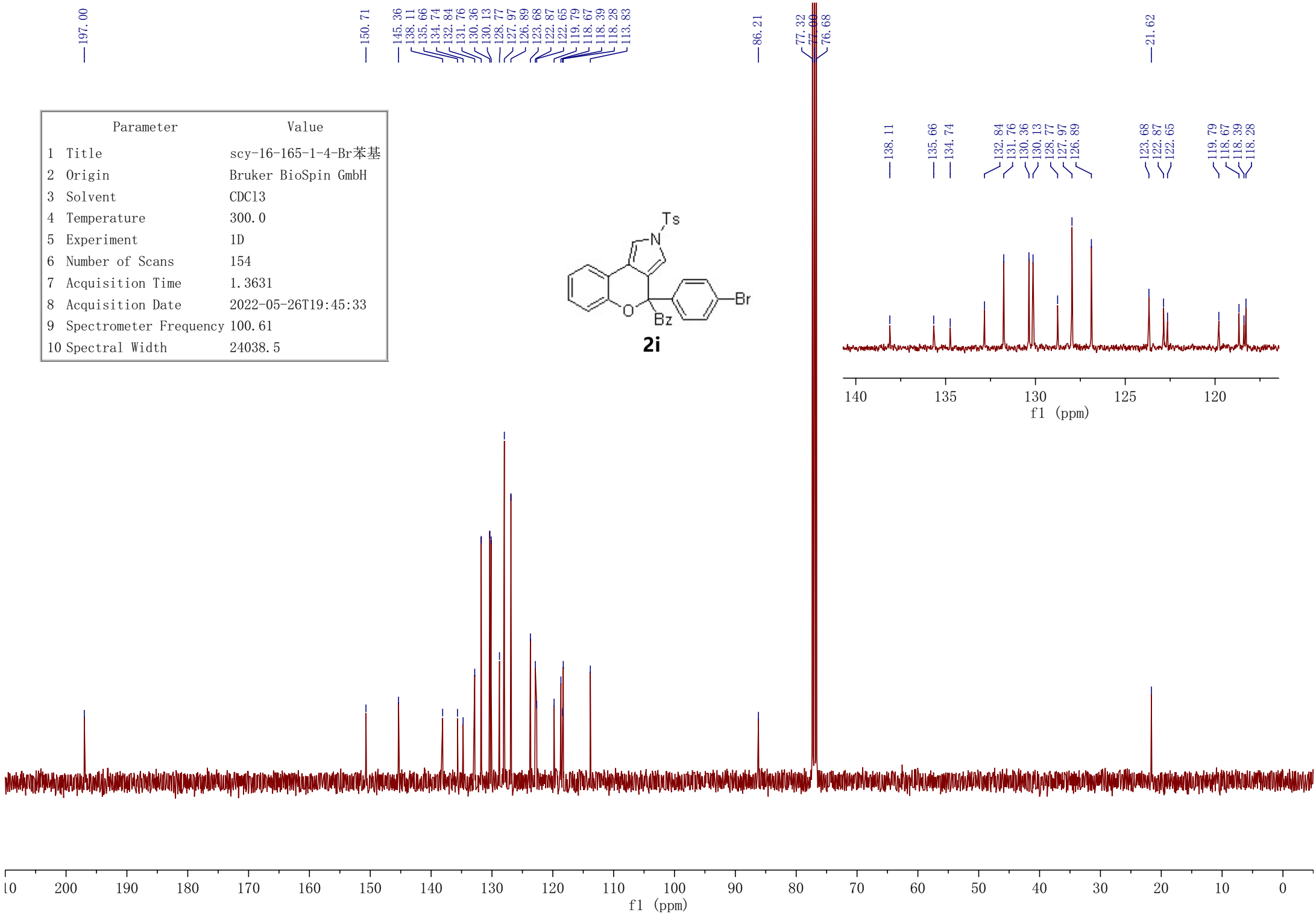
Parameter		Value
1	Title	scy-16-165-1-4-Br苯基
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	298.0
5	Experiment	1D
6	Number of Scans	14
7	Acquisition Time	4.0894
8	Acquisition Date	2022-05-26T19:42:59
9	Spectrometer Frequency	400.13
10	Spectral Width	8012.8

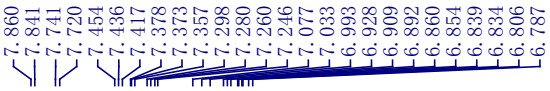


2i

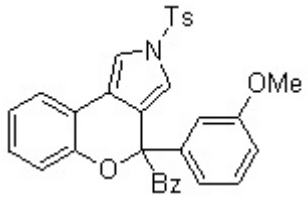




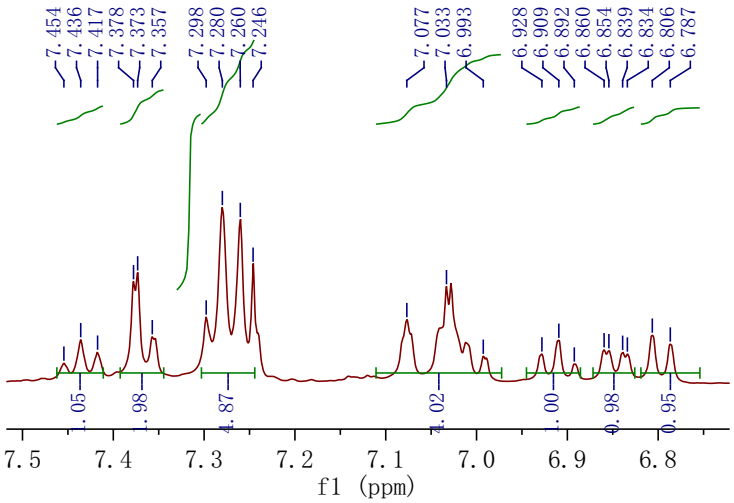

197.00
150.71
145.36
138.11
135.66
134.74
132.84
131.76
130.36
130.13
128.77
127.97
126.89
123.68
122.87
122.65
119.79
118.67
118.39
118.28
113.83
86.21
77.32
77.00
76.68
21.62
Parameter Value
1 Title scy-16-165-1-4-Br苯基
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.0
5 Experiment 1D
6 Number of Scans 154
7 Acquisition Time 1.3631
8 Acquisition Date 2022-05-26T19:45:33
9 Spectrometer Frequency 100.61
10 Spectral Width 24038.5
Ts
N
Br
O
Bz
2i
f1 (ppm)
f1 (ppm)

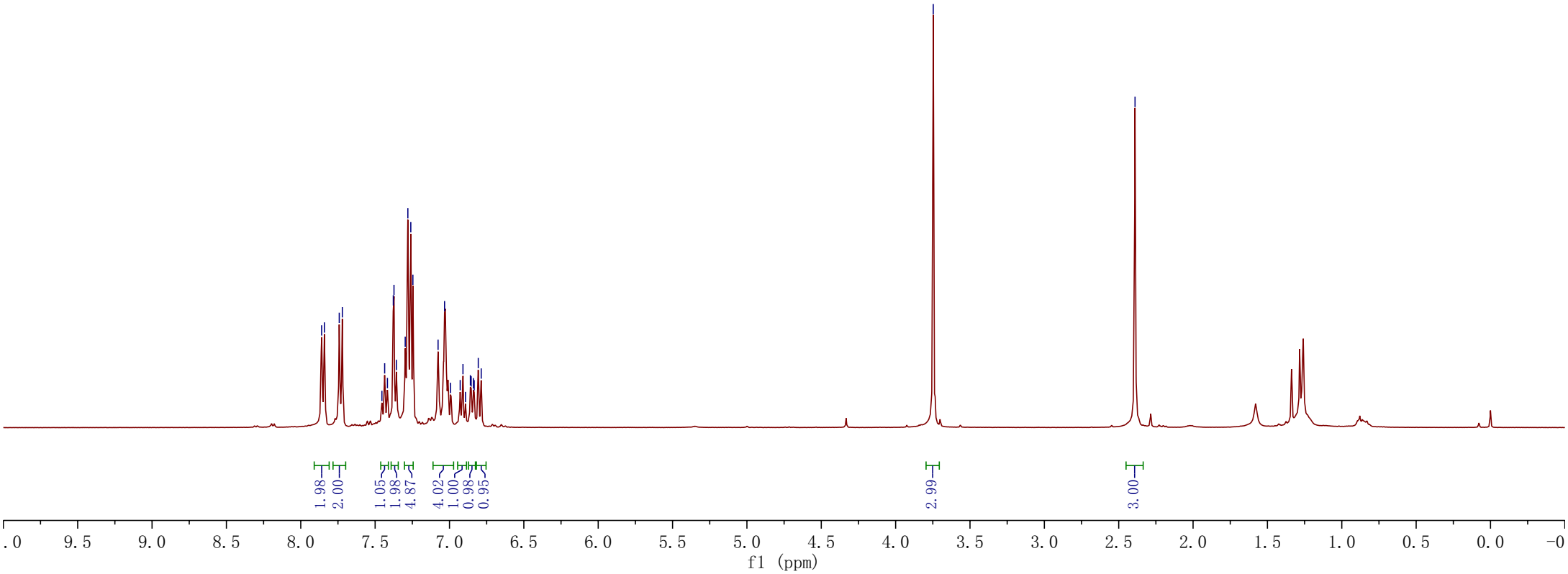


Parameter		Value
1	Title	MYN-1-192-H-3-MeO
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	298.0
5	Experiment	1D
6	Number of Scans	13
7	Acquisition Time	4.0894
8	Acquisition Date	2022-05-29T19:25:42
9	Spectrometer Frequency	400.13
10	Spectral Width	8012.8



2j

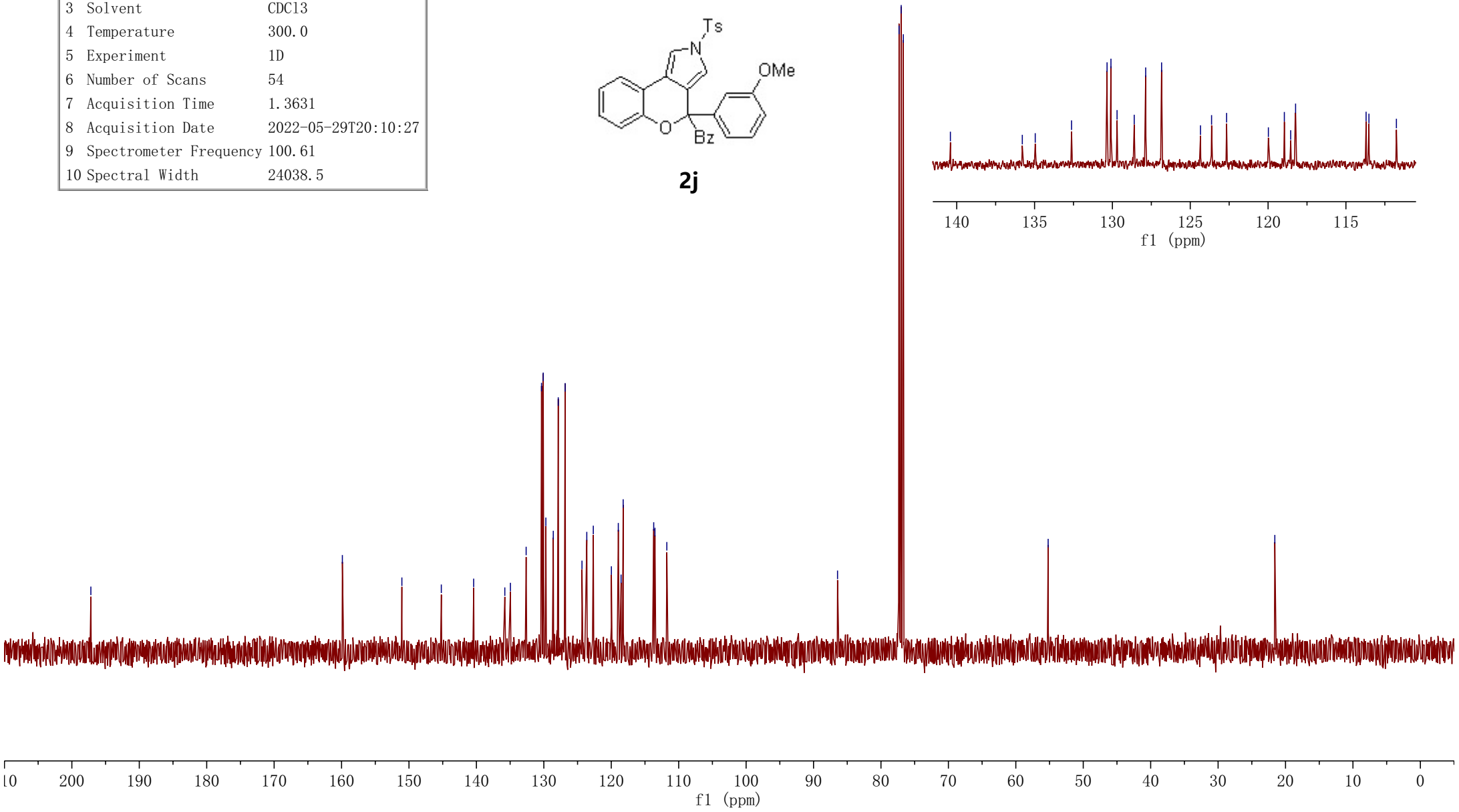




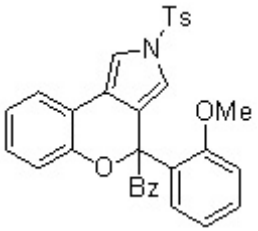
197.18
159.88
151.05
145.21
140.41
135.79
134.96
132.62
130.34
130.09
129.70
128.60
127.86
126.84
124.34
123.63
122.66
119.98
118.96
118.55
118.23
113.70
113.52
111.76
86.44
77.32
77.00
76.68
55.20
21.59

	Parameter	Value
1	Title	MYN-1-192-C-3-MeO
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	300.0
5	Experiment	1D
6	Number of Scans	54
7	Acquisition Time	1.3631
8	Acquisition Date	2022-05-29T20:10:27
9	Spectrometer Frequency	100.61
10	Spectral Width	24038.5

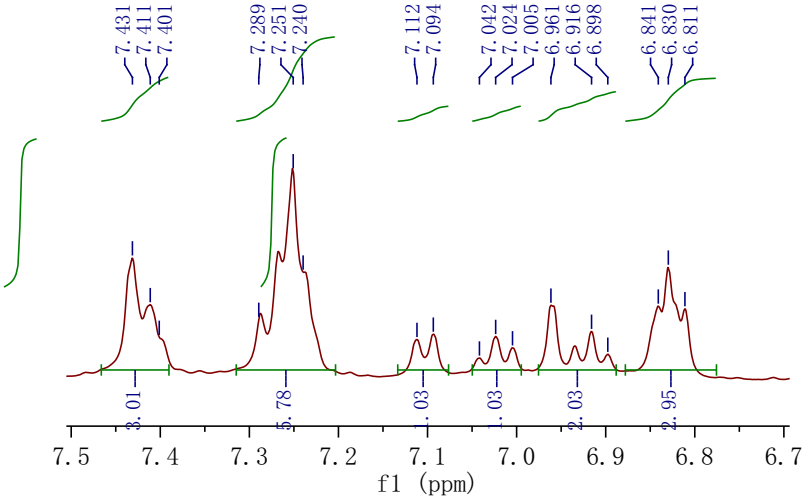
2j

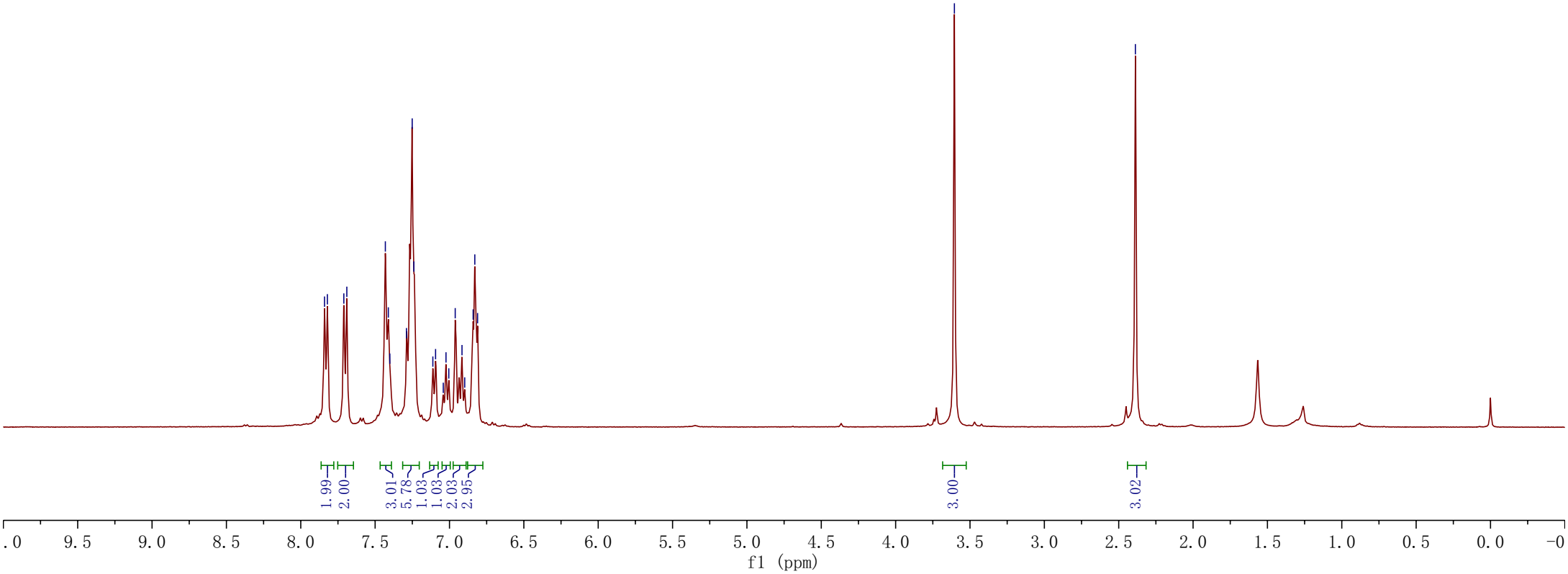


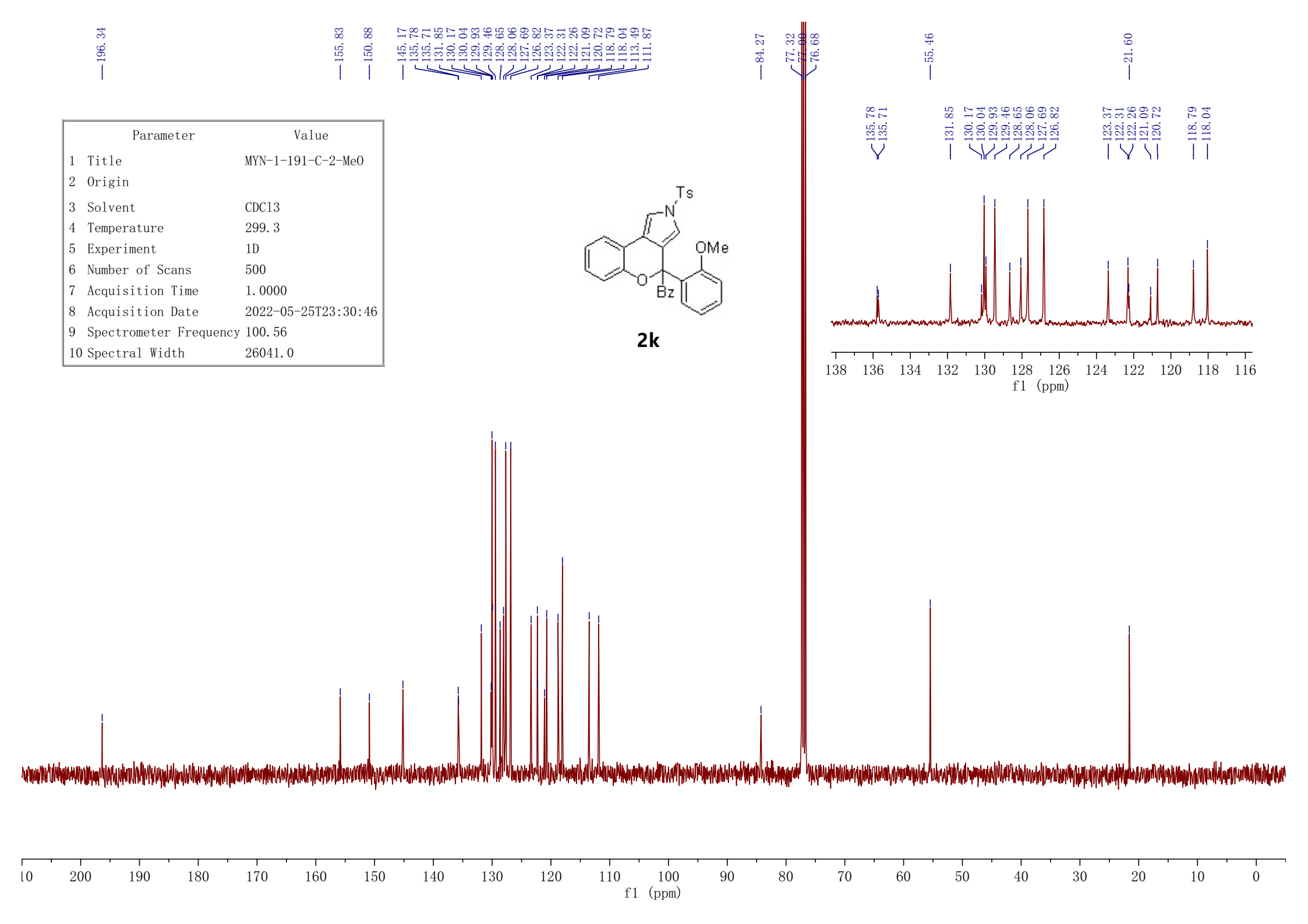
Parameter	Value
1 Title	MYN-1-191-H-2-MeO
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Experiment	1D
6 Number of Scans	15
7 Acquisition Time	4.0894
8 Acquisition Date	2022-05-25T21:58:56
9 Spectrometer Frequency	400.13
10 Spectral Width	8012.8

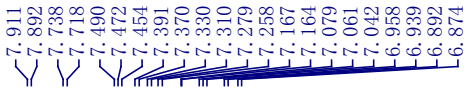


2k

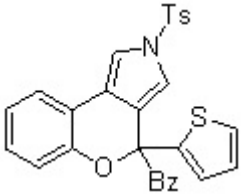




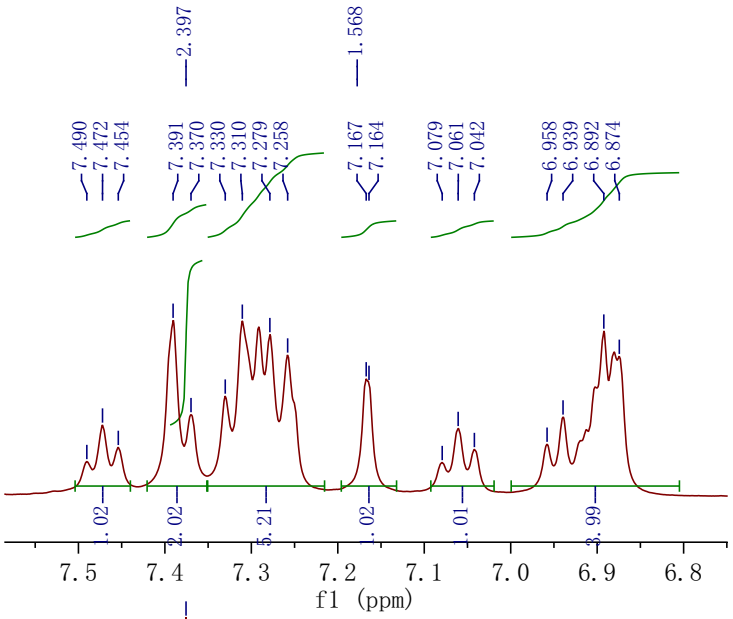

196.34
155.83
150.88
145.17
135.78
135.71
131.85
130.17
130.04
129.93
129.46
128.65
128.06
127.69
126.82
123.37
122.31
122.26
121.09
120.72
118.79
118.04
113.49
111.87
84.27
77.32
77.00
76.68
55.46
21.60
Parameter Value
1 Title MYN-1-191-C-2-MeO
2 Origin
3 Solvent CDCl3
4 Temperature 299.3
5 Experiment 1D
6 Number of Scans 500
7 Acquisition Time 1.0000
8 Acquisition Date 2022-05-25T23:30:46
9 Spectrometer Frequency 100.56
10 Spectral Width 26041.0
Ts
N
OMe
O
Bz
2k
f1 (ppm)
f1 (ppm)

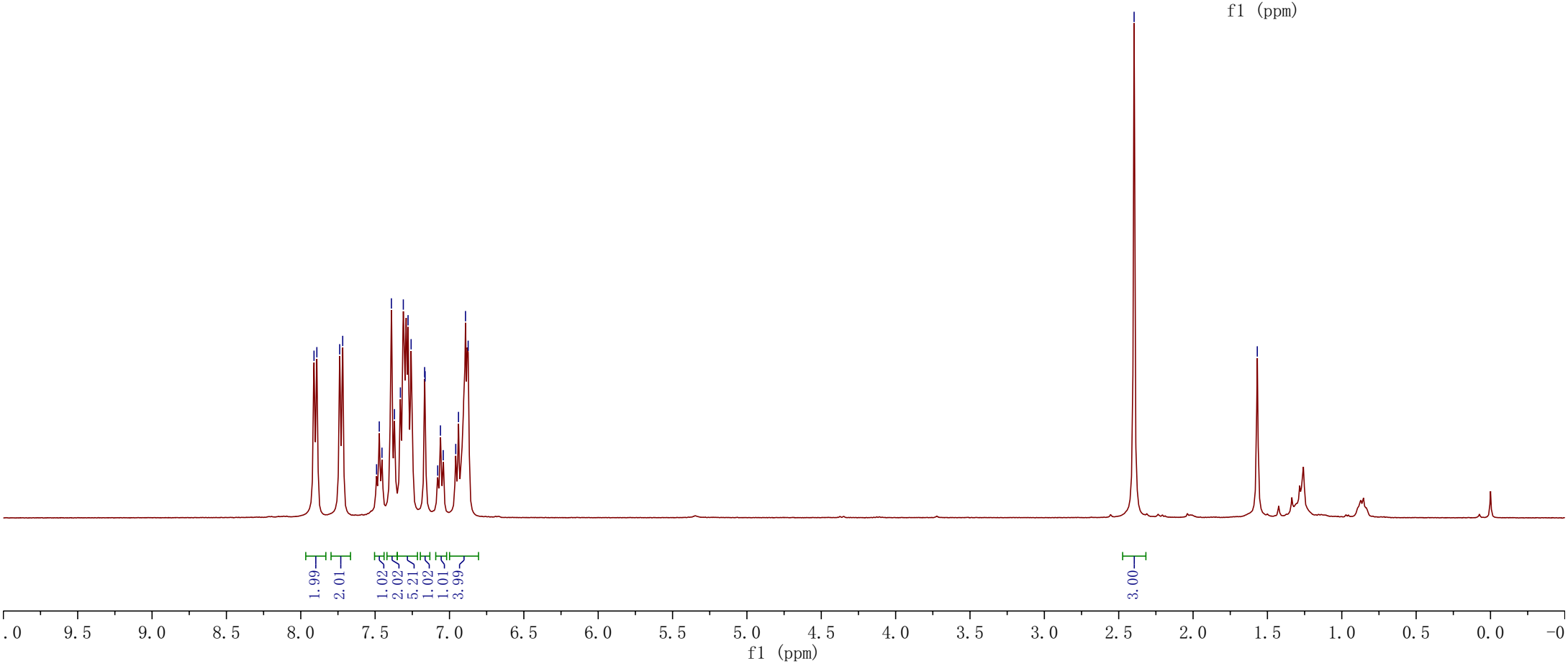


Parameter		Value
1	Title	scy-16-177-噻吩
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	298.0
5	Experiment	1D
6	Number of Scans	16
7	Acquisition Time	4.0894
8	Acquisition Date	2022-06-08T10:52:07
9	Spectrometer Frequency	400.13
10	Spectral Width	8012.8



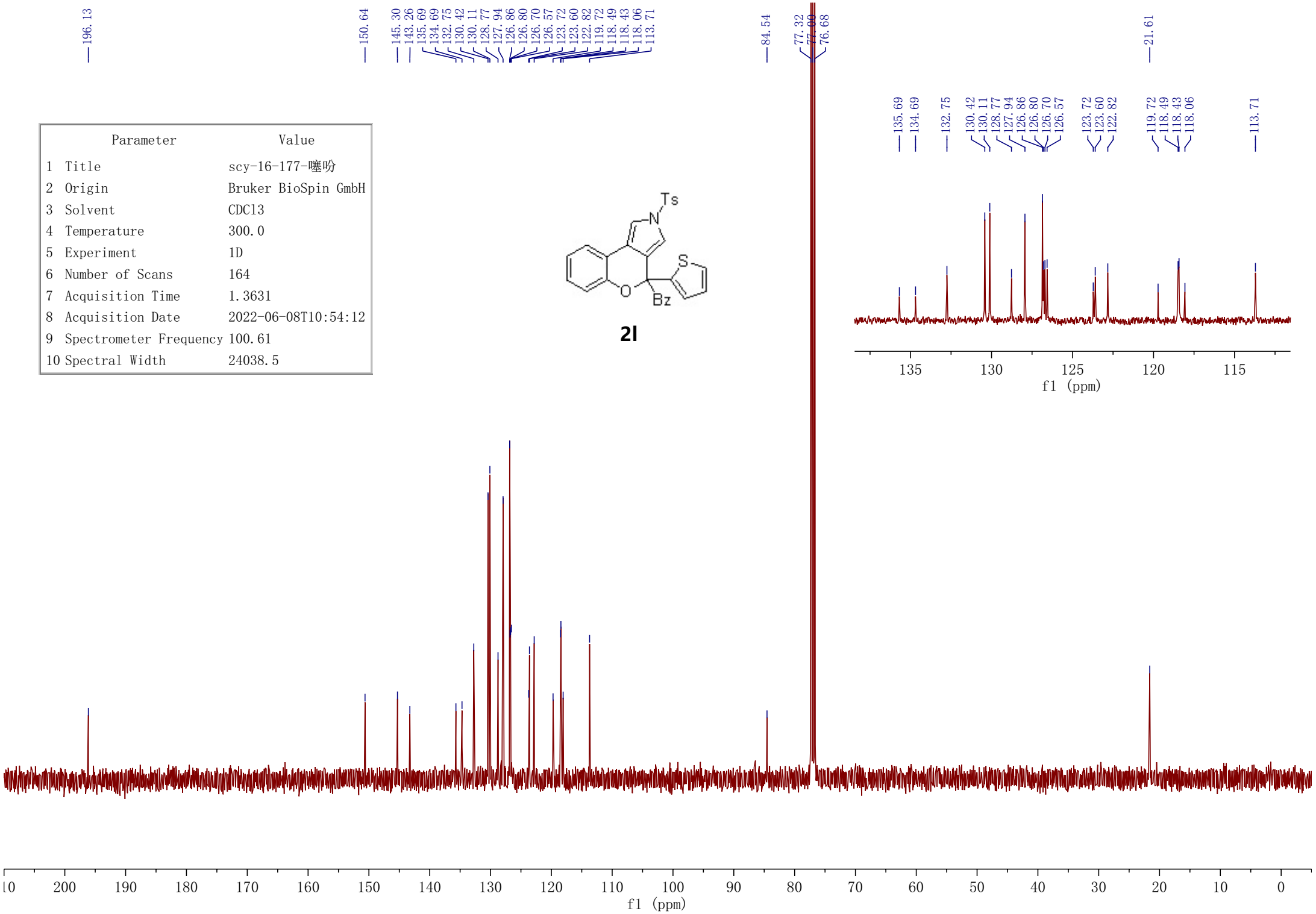
2l

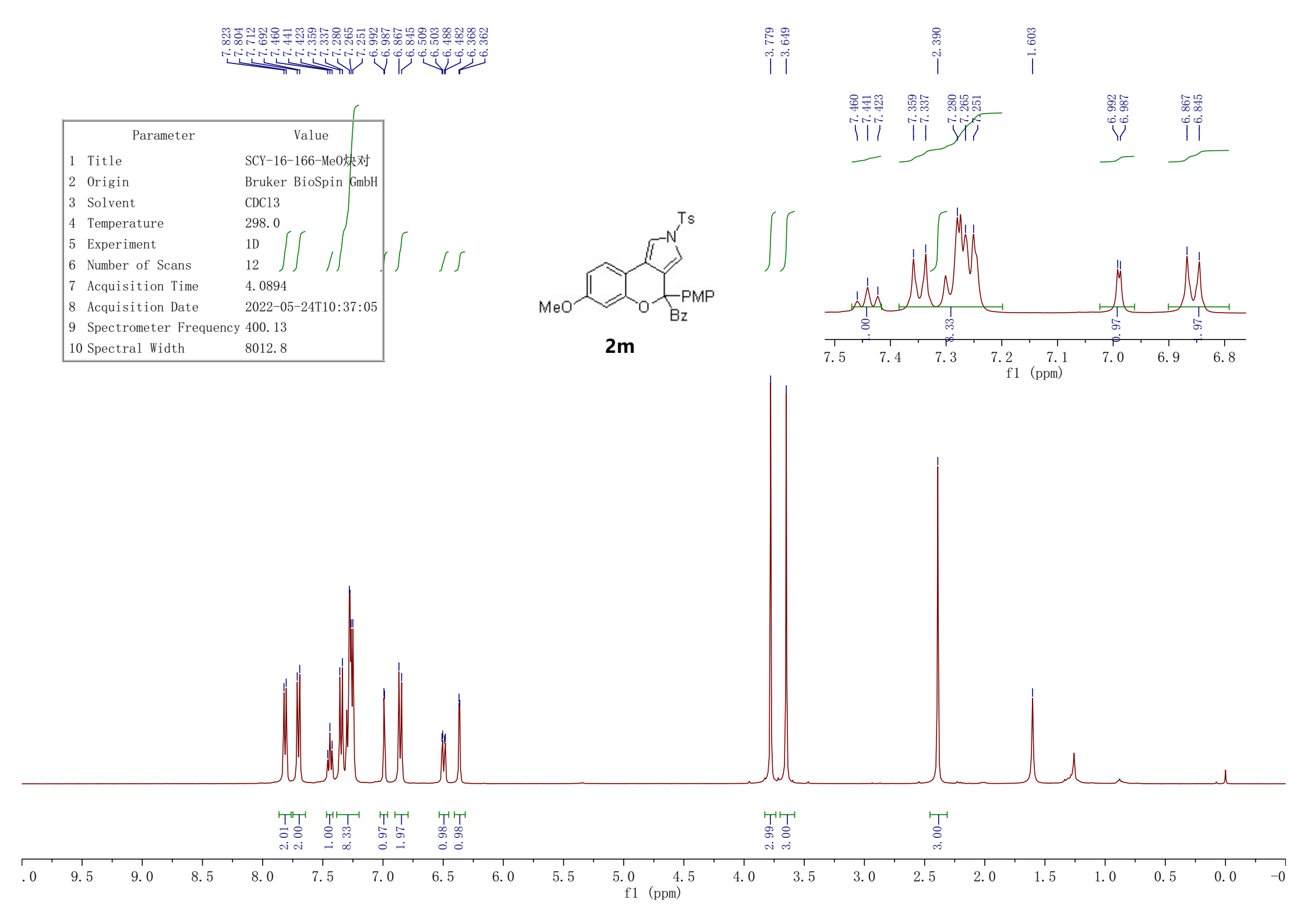




Parameter	Value
1 Title	scy-16-177-噻吩
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Experiment	1D
6 Number of Scans	164
7 Acquisition Time	1.3631
8 Acquisition Date	2022-06-08T10:54:12
9 Spectrometer Frequency	100.61
10 Spectral Width	24038.5

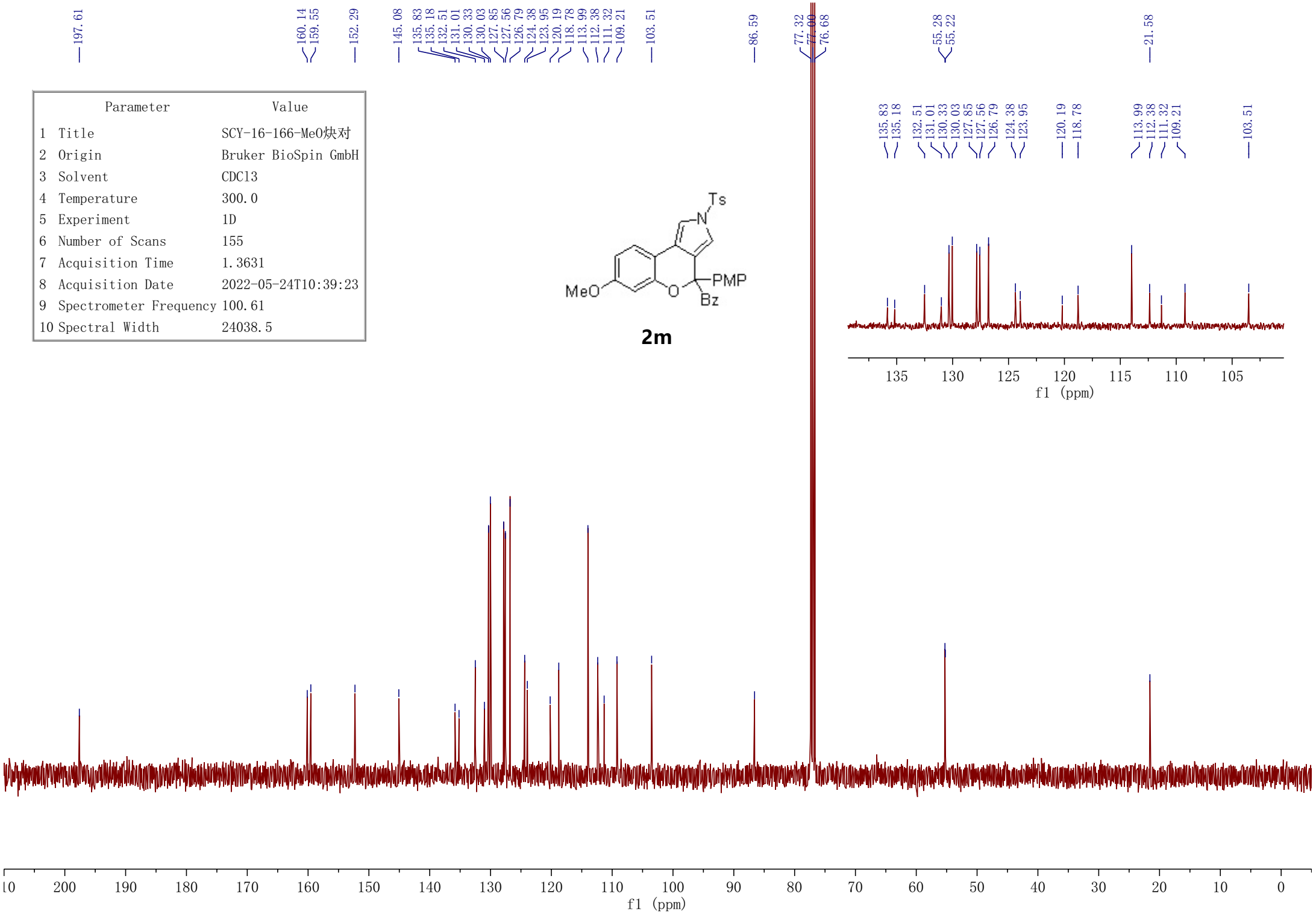
2l



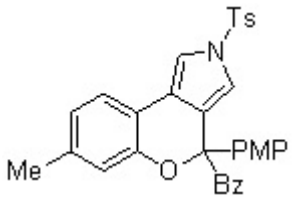

7.823
7.804
7.712
7.692
7.460
7.441
7.423
7.359
7.337
7.280
7.265
7.251
6.992
6.987
6.867
6.845
6.509
6.503
6.488
6.482
6.368
6.362
3.779
3.649
2.390
1.603
Parameter Value
1 Title SCY-16-166-MeO炔对
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 298.0
5 Experiment 1D
6 Number of Scans 12
7 Acquisition Time 4.0894
8 Acquisition Date 2022-05-24T10:37:05
9 Spectrometer Frequency 400.13
10 Spectral Width 8012.8
Ts
N
MeO
O
PMP
Bz
2m
2.01
2.00
1.00
8.33
0.97
1.97
0.98
0.98
2.99
3.00
3.00
f1 (ppm)

	Parameter	Value
1	Title	SCY-16-166-MeO炔对
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	300.0
5	Experiment	1D
6	Number of Scans	155
7	Acquisition Time	1.3631
8	Acquisition Date	2022-05-24T10:39:23
9	Spectrometer Frequency	100.61
10	Spectral Width	24038.5

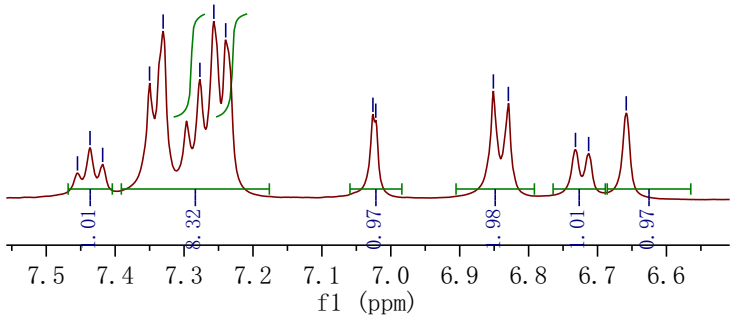
2m

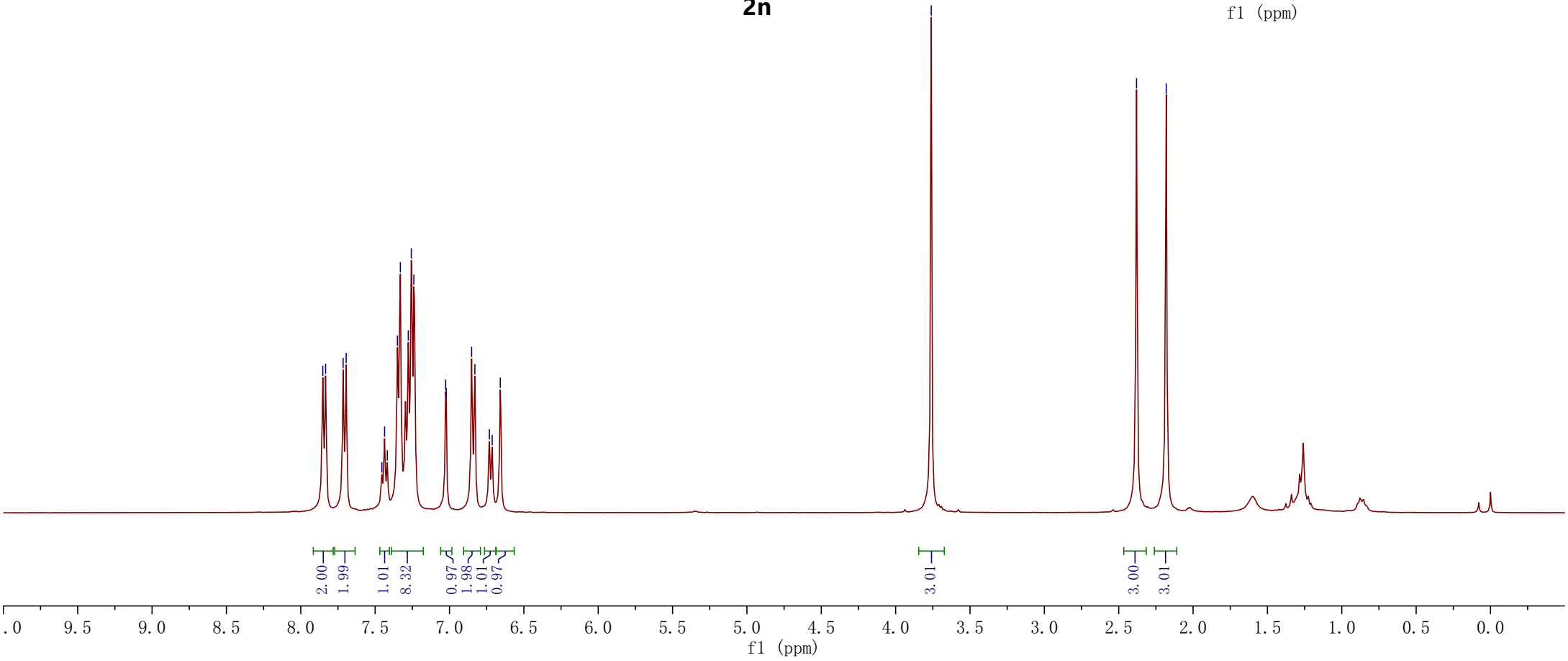


	Parameter	Value
1	Title	scy-16-160-Me-炔对
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	298.0
5	Experiment	1D
6	Number of Scans	9
7	Acquisition Time	4.0894
8	Acquisition Date	2022-05-20T15:07:13
9	Spectrometer Frequency	400.13
10	Spectral Width	8012.8



2n

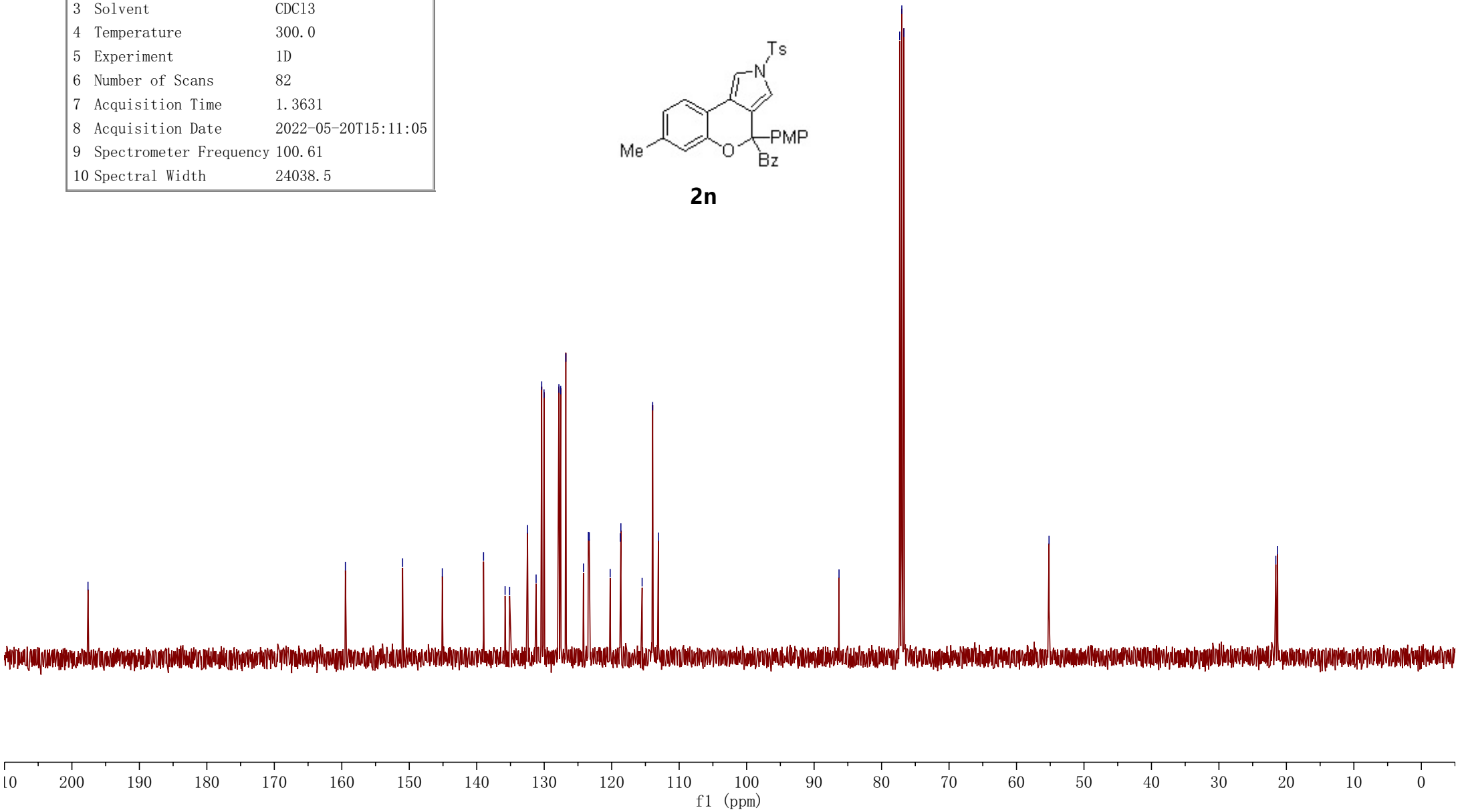




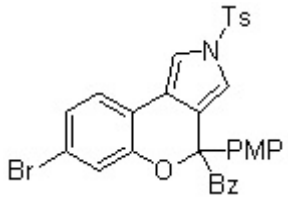
197.62
159.46
150.99
145.10
138.99
135.80
135.13
132.47
131.20
130.37
130.03
127.82
127.56
126.79
124.18
123.46
123.33
120.22
118.72
118.64
115.49
113.93
113.08
86.31
77.32
77.00
76.68
55.18
21.57
21.30

	Parameter	Value
1	Title	scy-16-160-Me-炔对
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	300.0
5	Experiment	1D
6	Number of Scans	82
7	Acquisition Time	1.3631
8	Acquisition Date	2022-05-20T15:11:05
9	Spectrometer Frequency	100.61
10	Spectral Width	24038.5

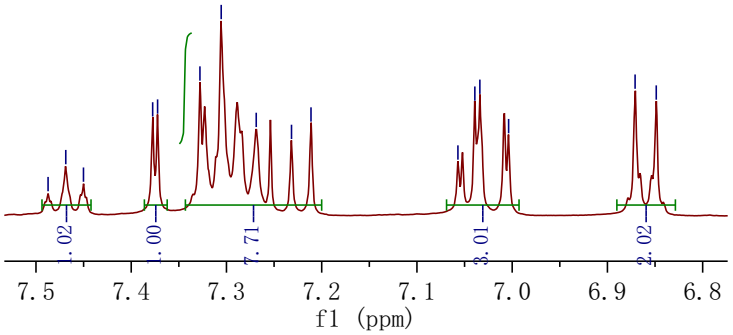
2n

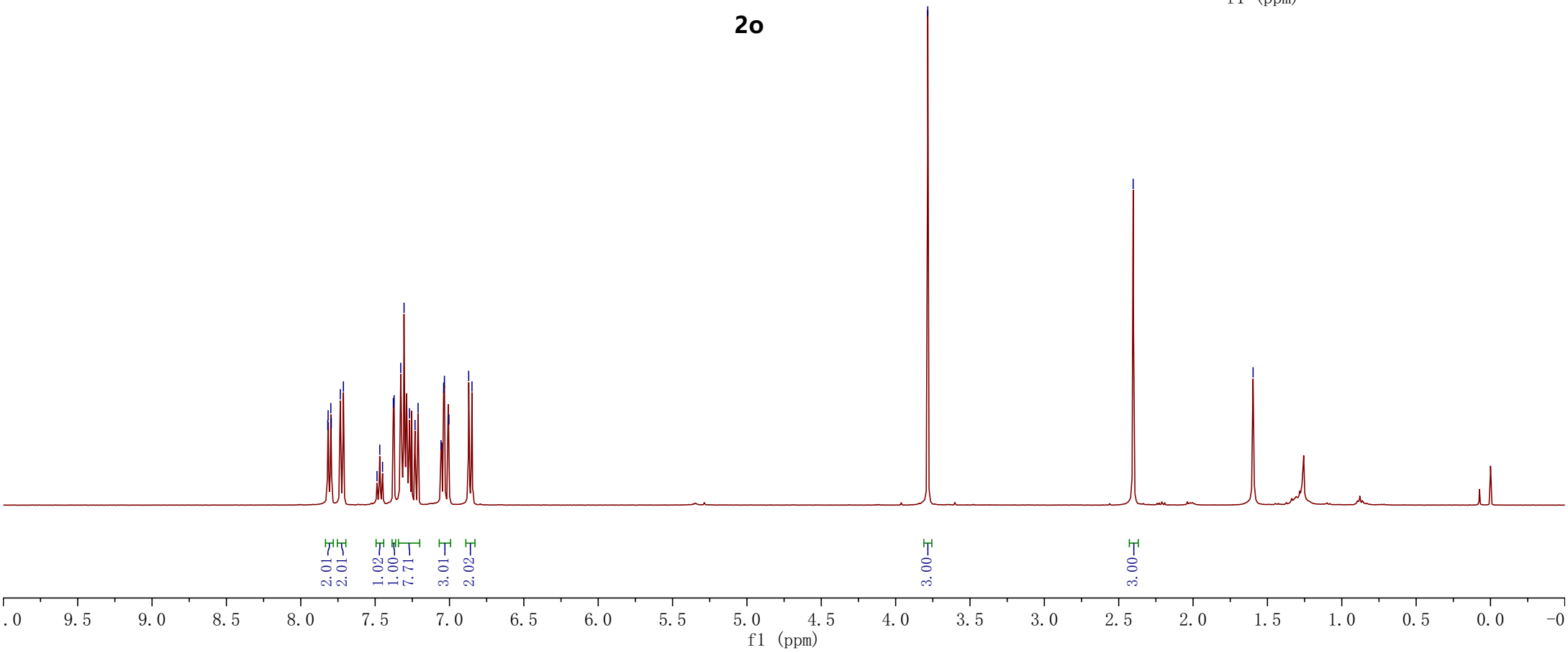


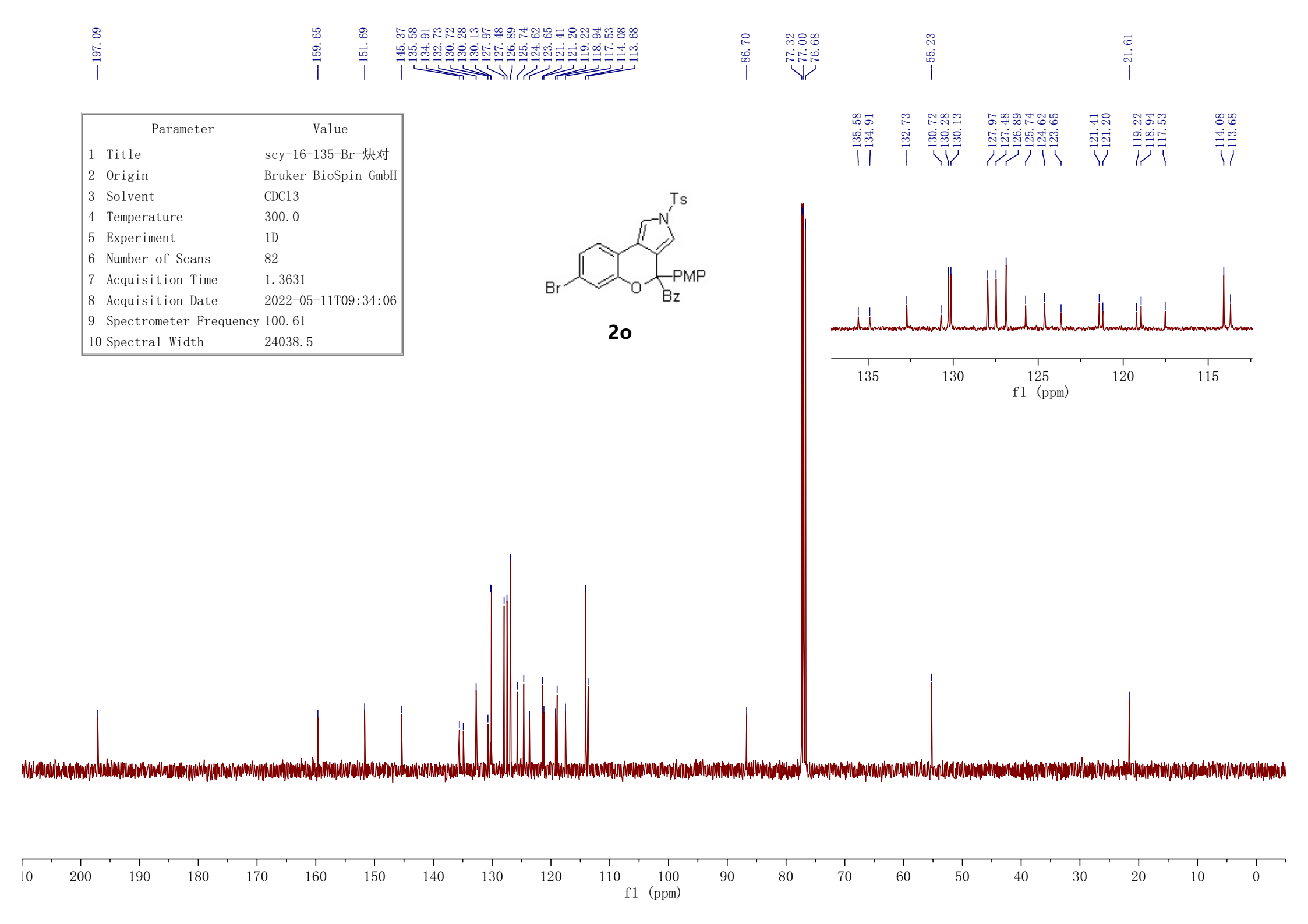
	Parameter	Value
1	Title	scy-16-135-Br-炔对
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	298.0
5	Experiment	1D
6	Number of Scans	6
7	Acquisition Time	4.0894
8	Acquisition Date	2022-05-11T20:50:17
9	Spectrometer Frequency	400.13
10	Spectral Width	8012.8



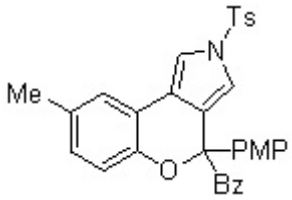
2o



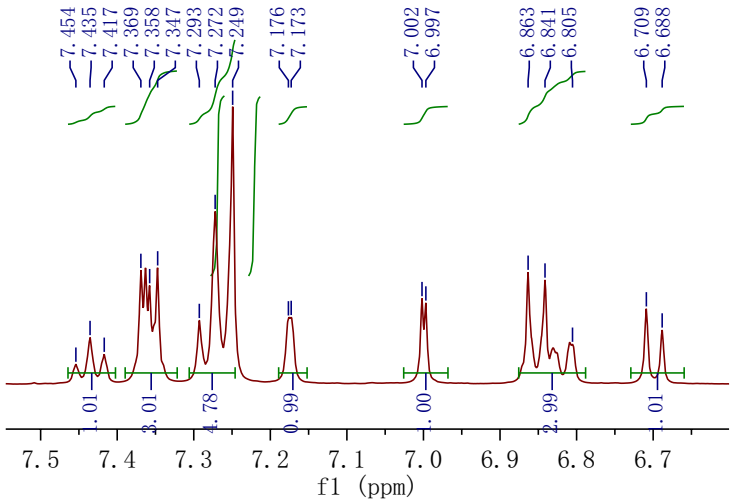


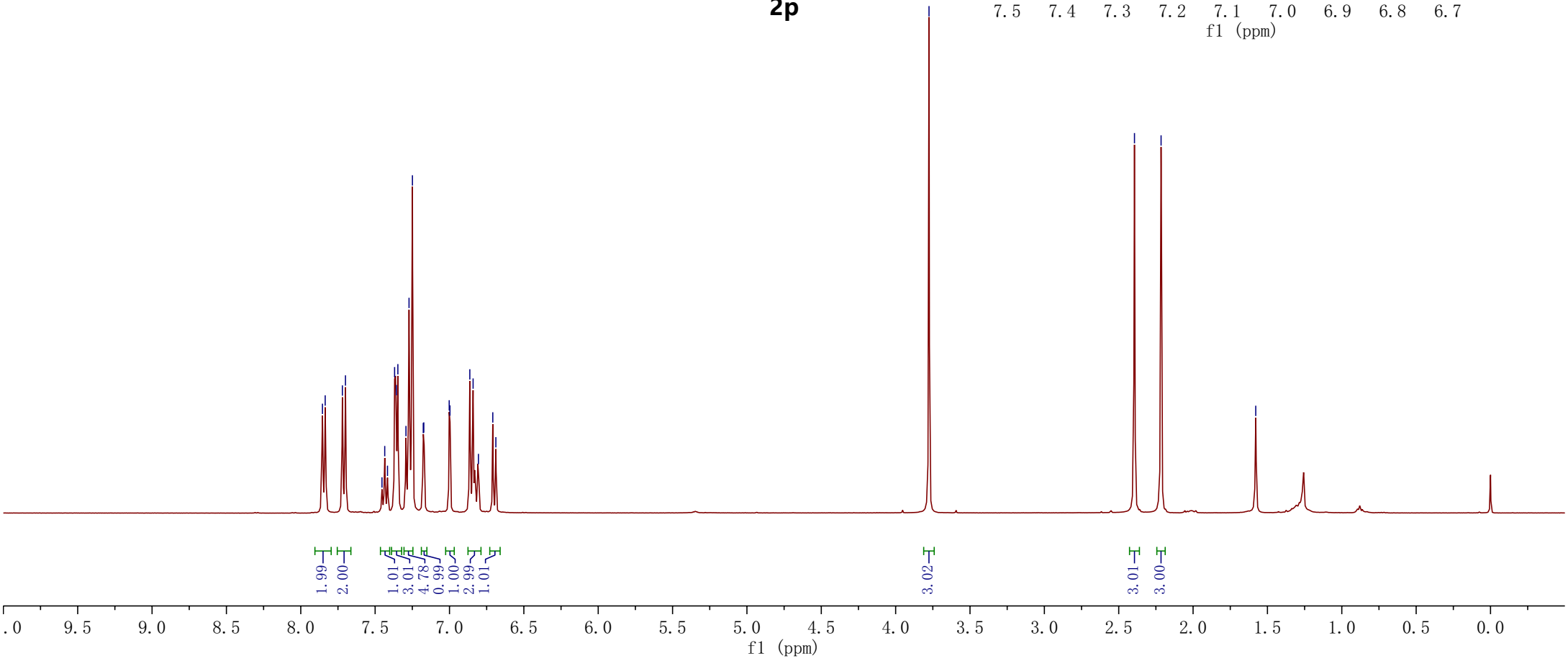

197.09
159.65
151.69
145.37
135.58
134.91
132.73
130.72
130.28
130.13
127.97
127.48
126.89
125.74
124.62
123.65
121.41
121.20
119.22
118.94
117.53
114.08
113.68
86.70
77.32
77.00
76.68
55.23
21.61
Parameter Value
1 Title scy-16-135-Br-炔对
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.0
5 Experiment 1D
6 Number of Scans 82
7 Acquisition Time 1.3631
8 Acquisition Date 2022-05-11T09:34:06
9 Spectrometer Frequency 100.61
10 Spectral Width 24038.5
Ts
N
PMP
Br
O
Bz
2o
f1 (ppm)
f1 (ppm)

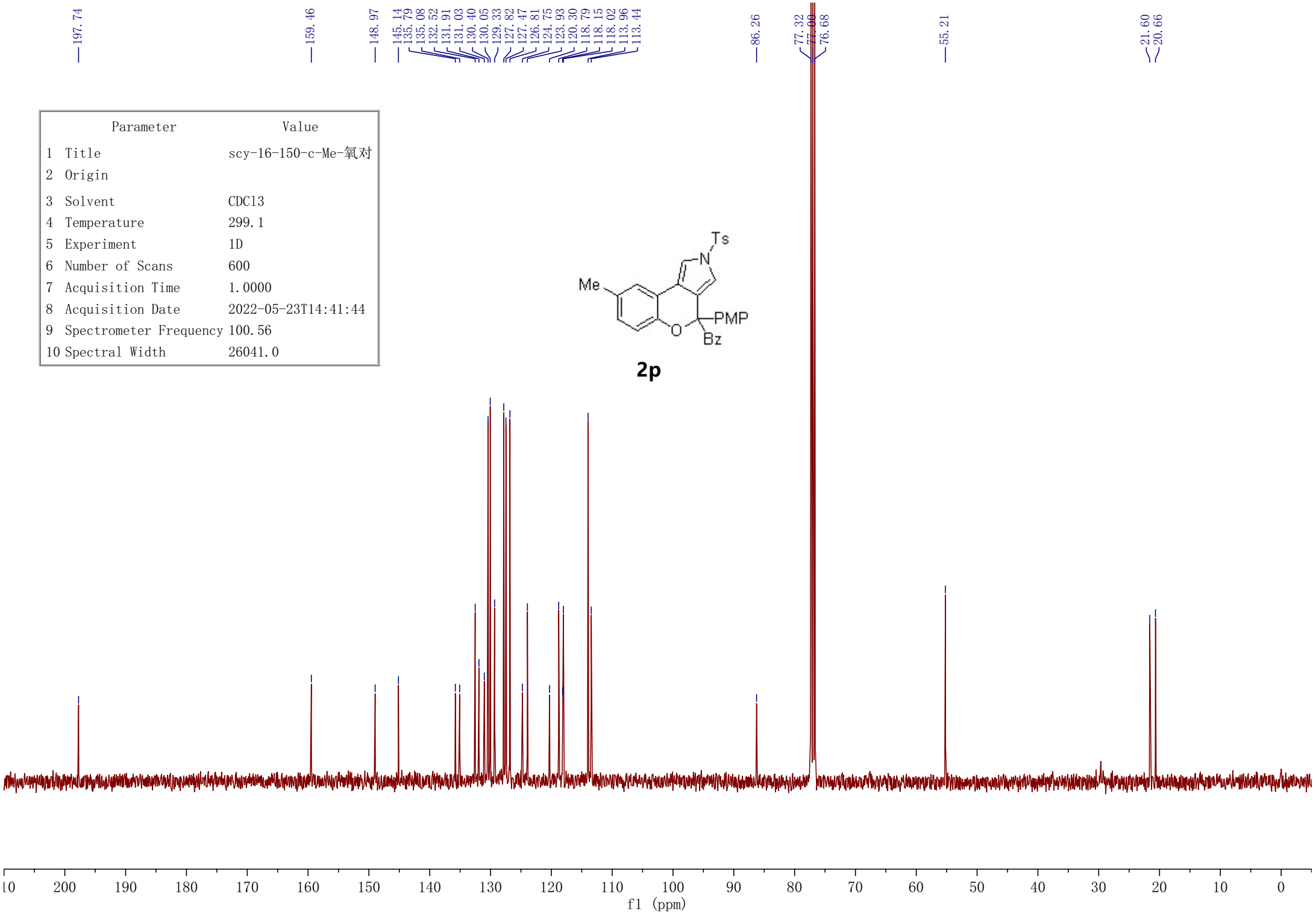
Parameter		Value
1	Title	scy-16-150-h-Me-氧对
2	Origin	
3	Solvent	CDCl3
4	Temperature	299.0
5	Experiment	1D
6	Number of Scans	16
7	Acquisition Time	4.0002
8	Acquisition Date	2022-05-23T13:49:56
9	Spectrometer Frequency	399.92
10	Spectral Width	8012.0



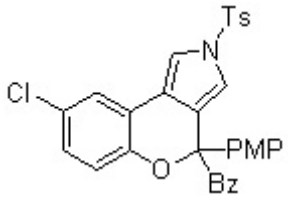
2p



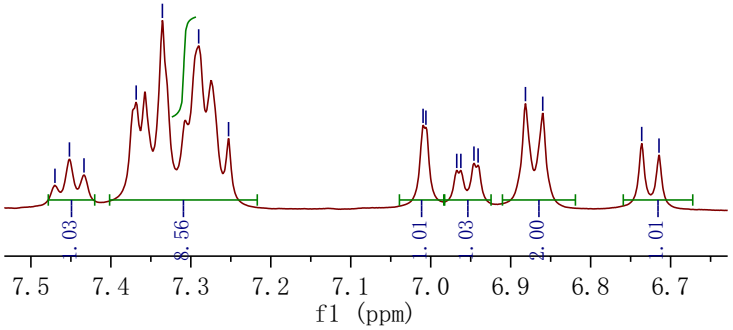


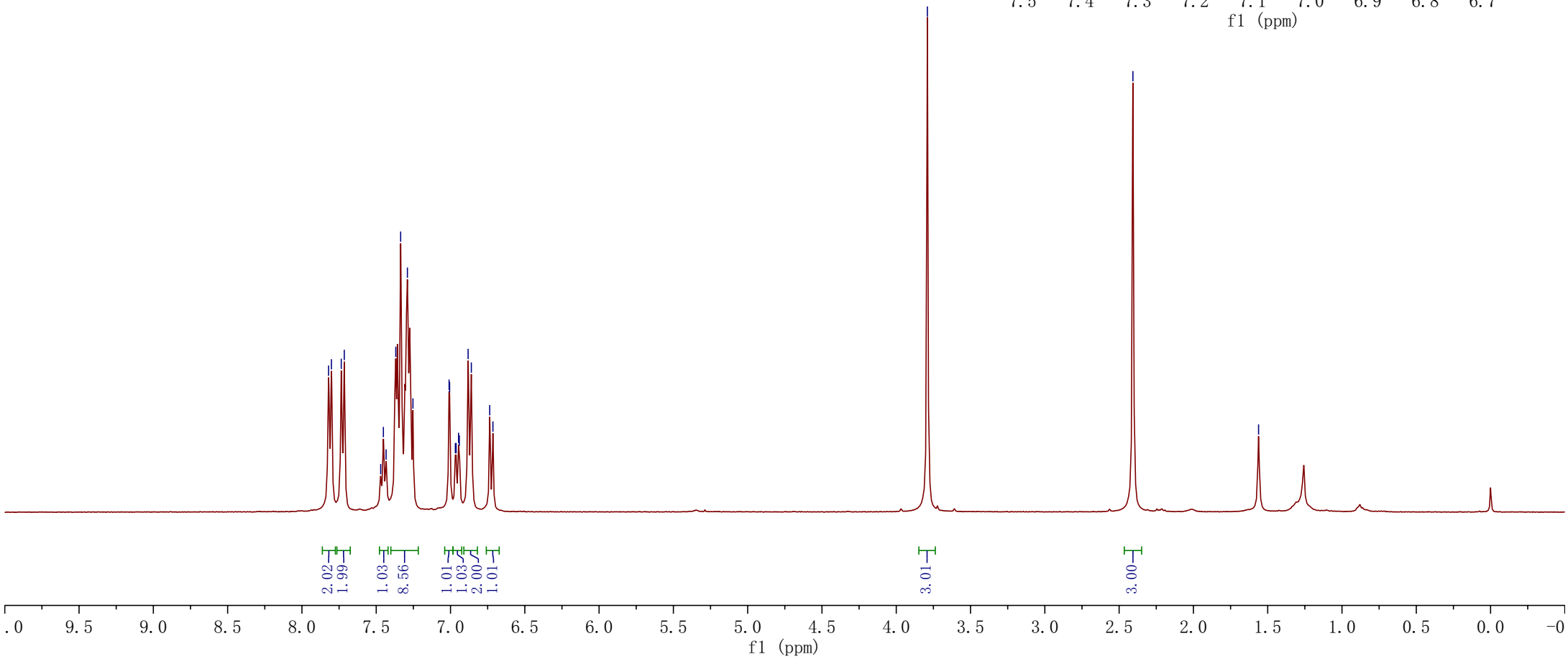

197.74
159.46
148.97
145.14
135.79
135.08
132.52
131.91
131.03
130.40
130.05
129.33
127.82
127.47
126.81
124.75
123.93
120.30
118.79
118.15
118.02
113.96
113.44
86.26
77.32
77.00
76.68
55.21
21.60
20.66
Parameter Value
1 Title scy-16-150-c-Me-氧对
2 Origin
3 Solvent CDCl3
4 Temperature 299.1
5 Experiment 1D
6 Number of Scans 600
7 Acquisition Time 1.0000
8 Acquisition Date 2022-05-23T14:41:44
9 Spectrometer Frequency 100.56
10 Spectral Width 26041.0
Ts
N
Me
PMP
O
Bz
2p
f1 (ppm)

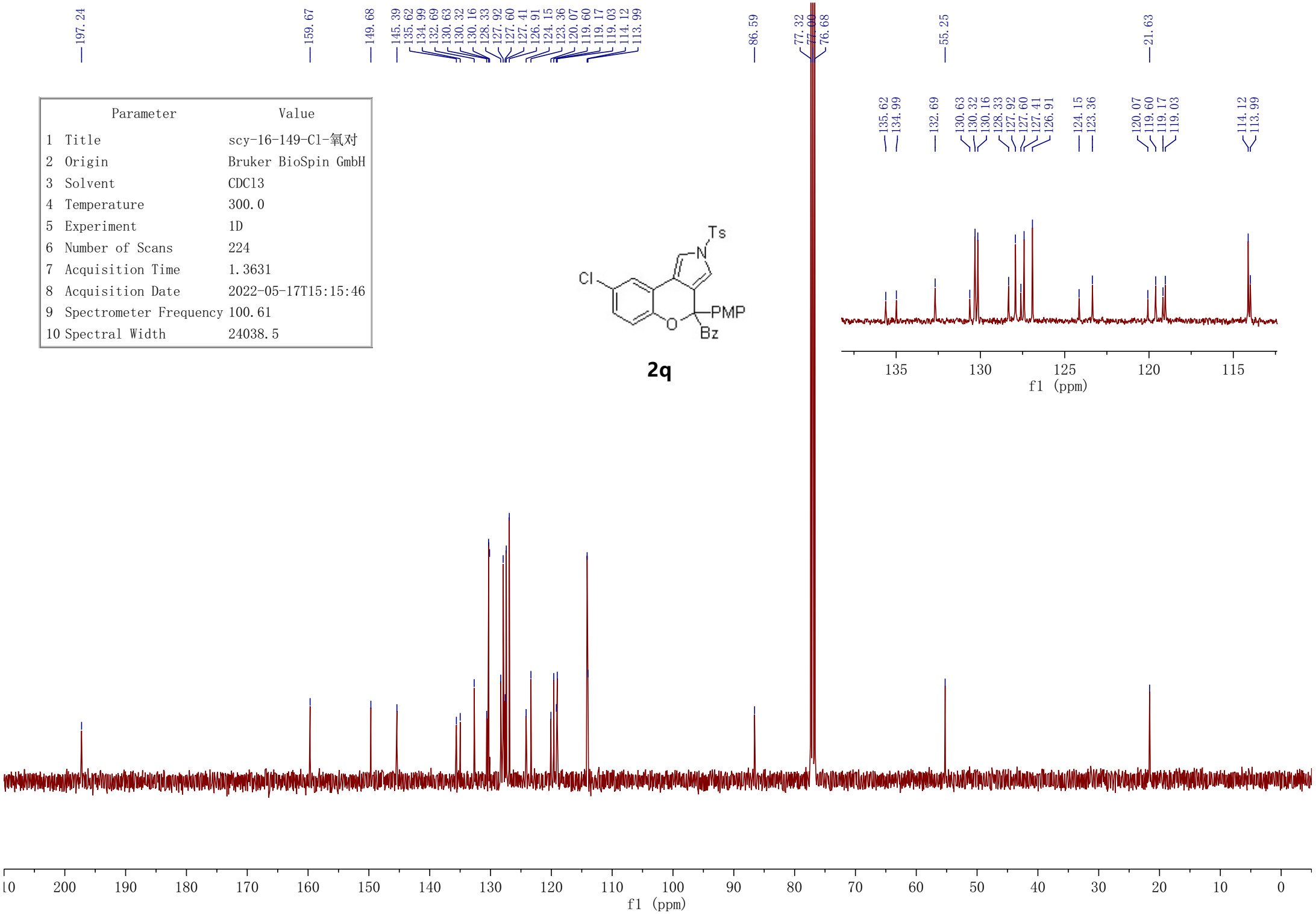
	Parameter	Value
1	Title	scy-16-149-Cl-氧对
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	298.0
5	Experiment	1D
6	Number of Scans	10
7	Acquisition Time	4.0894
8	Acquisition Date	2022-05-17T15:11:54
9	Spectrometer Frequency	400.13
10	Spectral Width	8012.8



2q

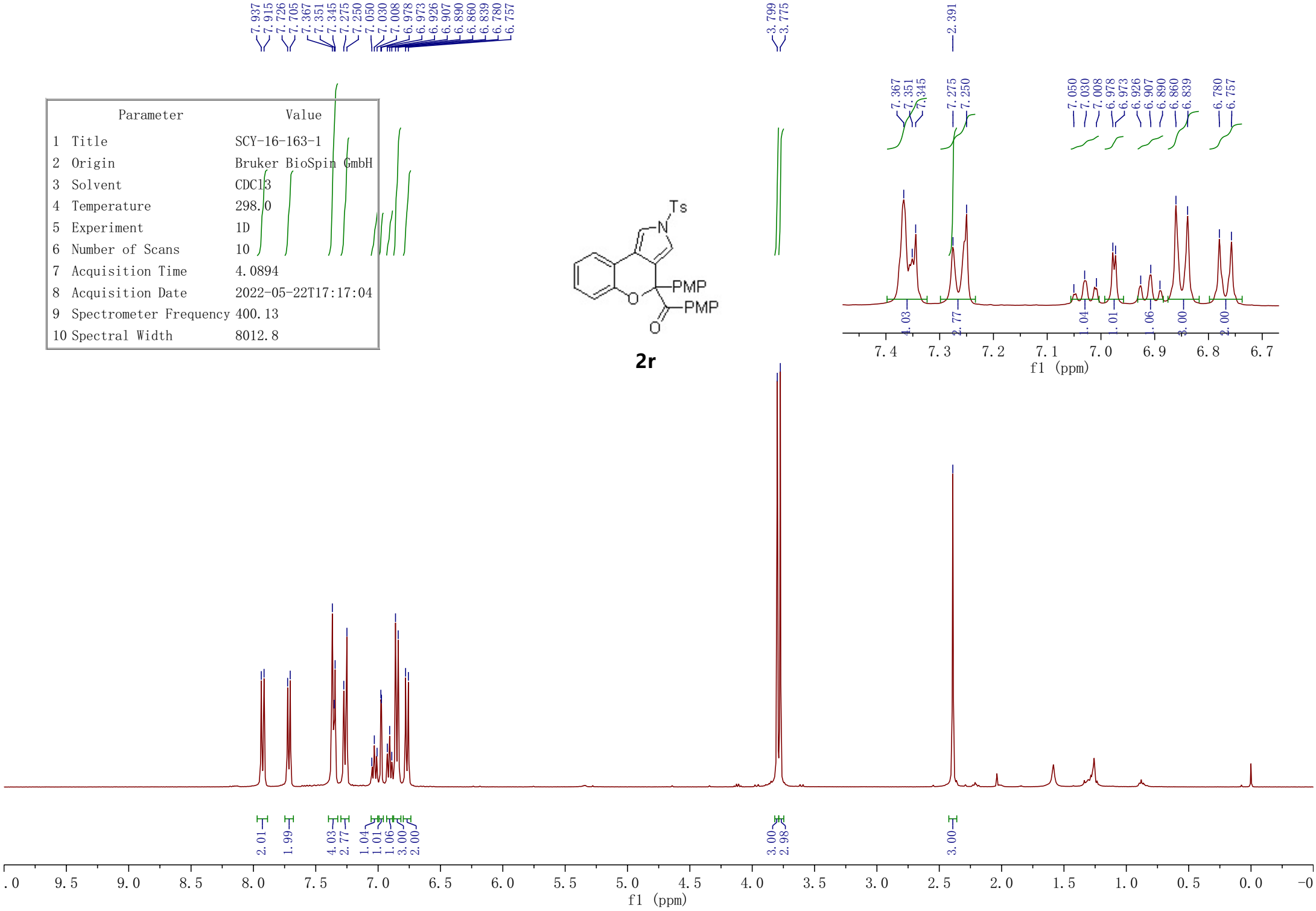


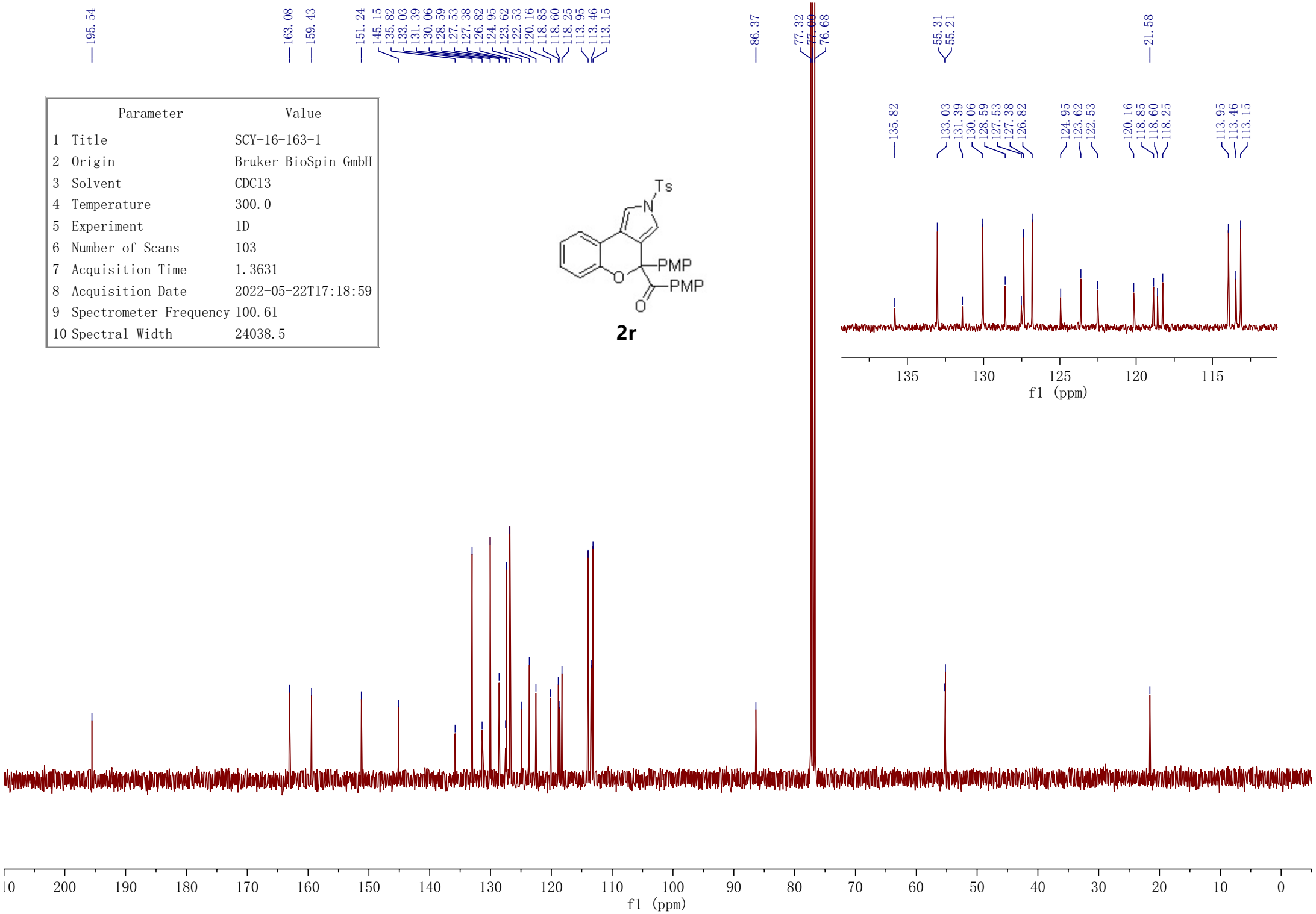



197.24
159.67
149.68
145.39
135.62
134.99
132.69
130.63
130.32
130.16
128.33
127.92
127.60
127.41
126.91
124.15
123.36
120.07
119.60
119.17
119.03
114.12
113.99
86.59
77.32
77.00
76.68
55.25
21.63
Parameter Value
1 Title scy-16-149-Cl-氧对
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.0
5 Experiment 1D
6 Number of Scans 224
7 Acquisition Time 1.3631
8 Acquisition Date 2022-05-17T15:15:46
9 Spectrometer Frequency 100.61
10 Spectral Width 24038.5
Ts
N
Cl
PMP
O
Bz
2q
f1 (ppm)
f1 (ppm)

Parameter		Value
1	Title	SCY-16-163-1
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	298.0
5	Experiment	1D
6	Number of Scans	10
7	Acquisition Time	4.0894
8	Acquisition Date	2022-05-22T17:17:04
9	Spectrometer Frequency	400.13
10	Spectral Width	8012.8

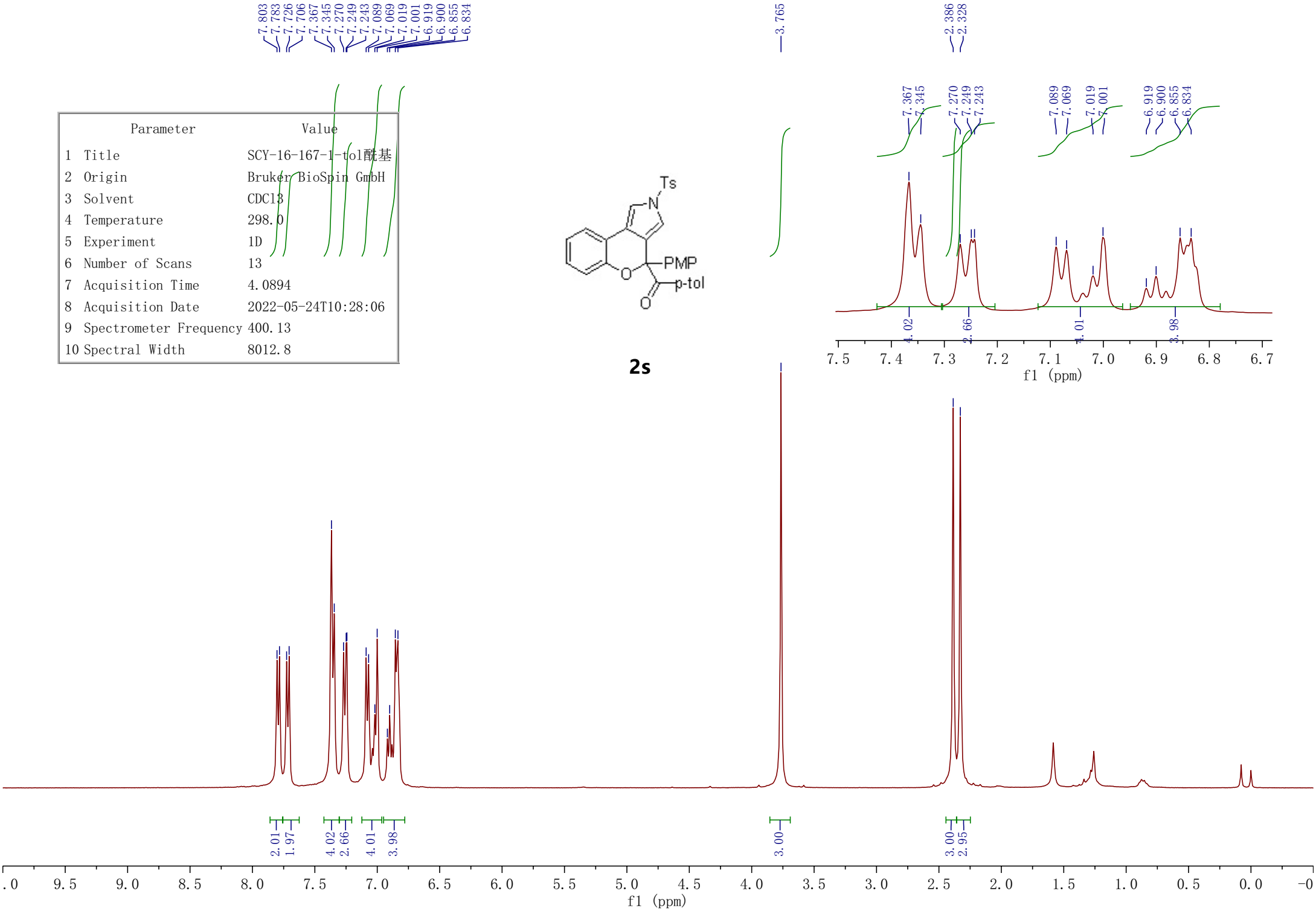
2r




195.54
163.08
159.43
151.24
145.15
135.82
133.03
131.39
130.06
128.59
127.53
127.38
126.82
124.95
123.62
122.53
120.16
118.85
118.60
118.25
113.95
113.46
113.15
86.37
77.32
77.00
76.68
55.31
55.21
21.58
Parameter Value
1 Title SCY-16-163-1
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.0
5 Experiment 1D
6 Number of Scans 103
7 Acquisition Time 1.3631
8 Acquisition Date 2022-05-22T17:18:59
9 Spectrometer Frequency 100.61
10 Spectral Width 24038.5
Ts
N
PMP
PMP
O
O
2r
f1 (ppm)
f1 (ppm)

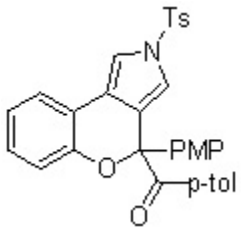
	Parameter	Value
1	Title	SCY-16-167-1-tol酰基
2	Origin	Bruker BioSpin GmbH
3	Solvent	CDCl3
4	Temperature	298.0
5	Experiment	1D
6	Number of Scans	13
7	Acquisition Time	4.0894
8	Acquisition Date	2022-05-24T10:28:06
9	Spectrometer Frequency	400.13
10	Spectral Width	8012.8

2s



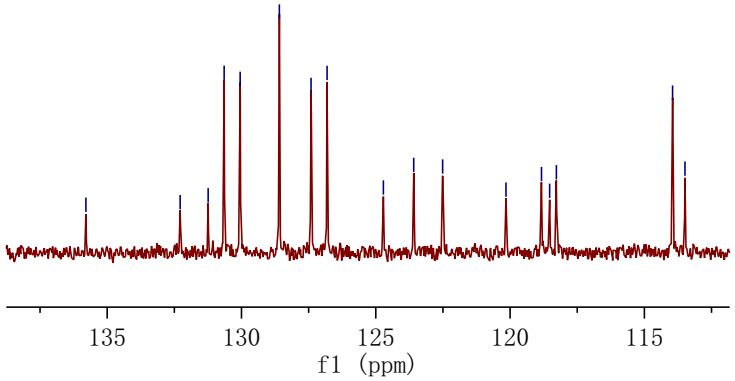
196.88 159.44 151.20 145.15 143.42 135.79 132.28 131.24 130.65 130.05 128.59 127.41 126.81 124.72 123.59 122.51 120.15 118.83 118.53 118.28 113.95 113.49 86.36 77.32 77.00 76.68 55.19 21.59

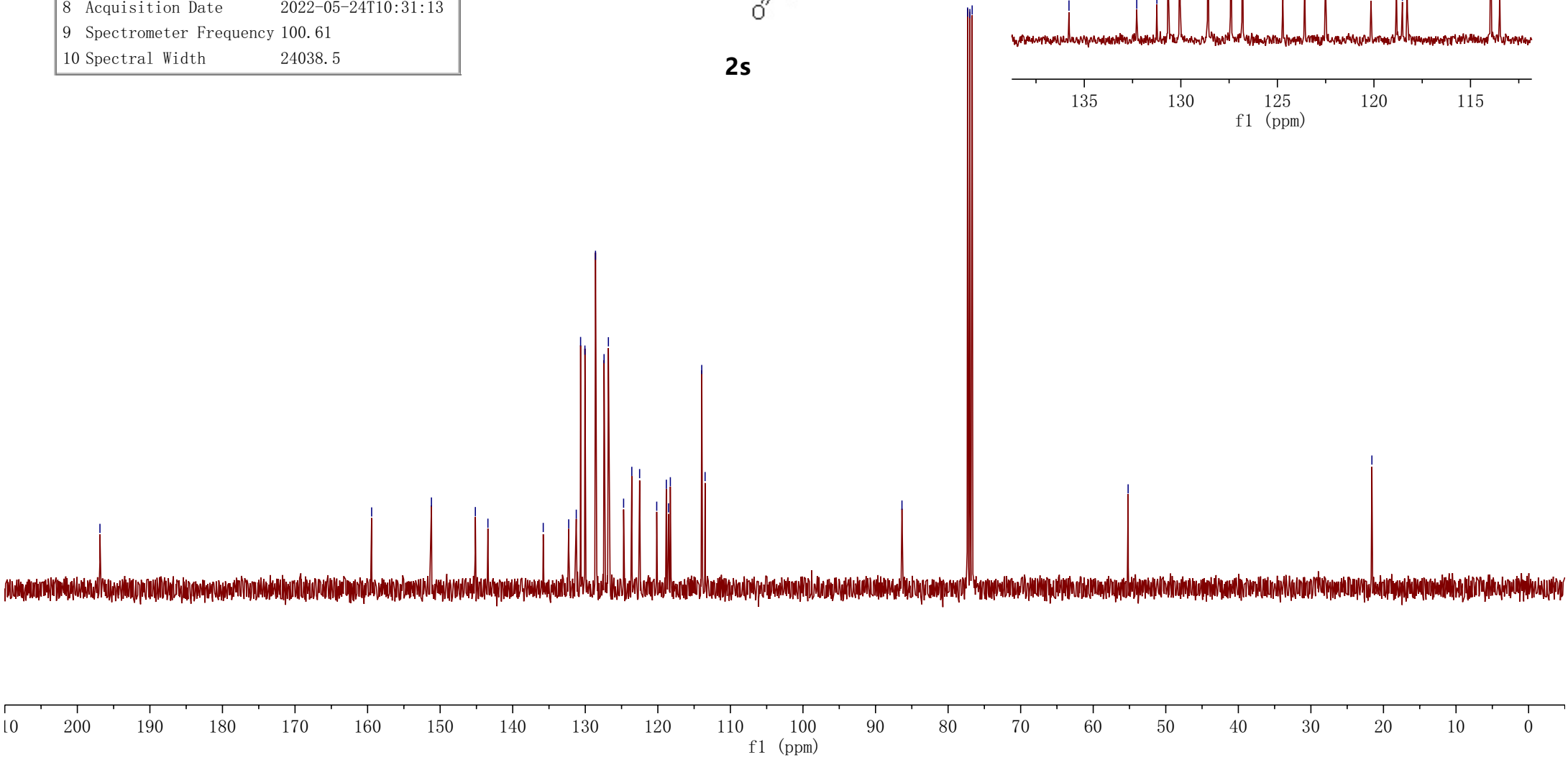
Parameter	Value
1 Title	SCY-16-167-1-tol酰基
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Experiment	1D
6 Number of Scans	63
7 Acquisition Time	1.3631
8 Acquisition Date	2022-05-24T10:31:13
9 Spectrometer Frequency	100.61
10 Spectral Width	24038.5



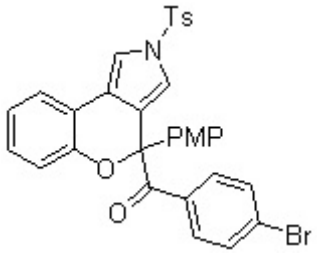
2s

135.79 132.28 131.24 130.65 130.05 128.59 127.41 126.81 124.72 123.59 122.51 120.15 118.83 118.53 118.28 113.95 113.49

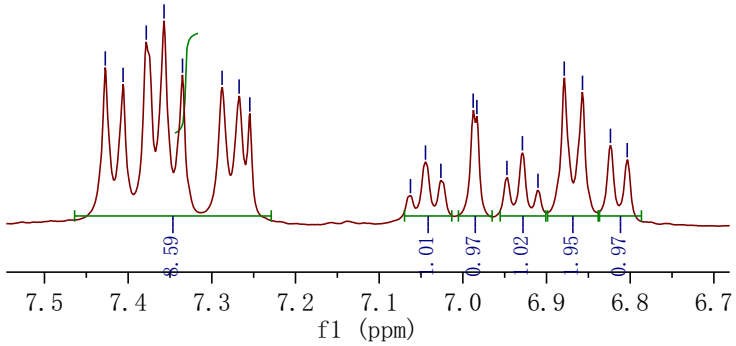


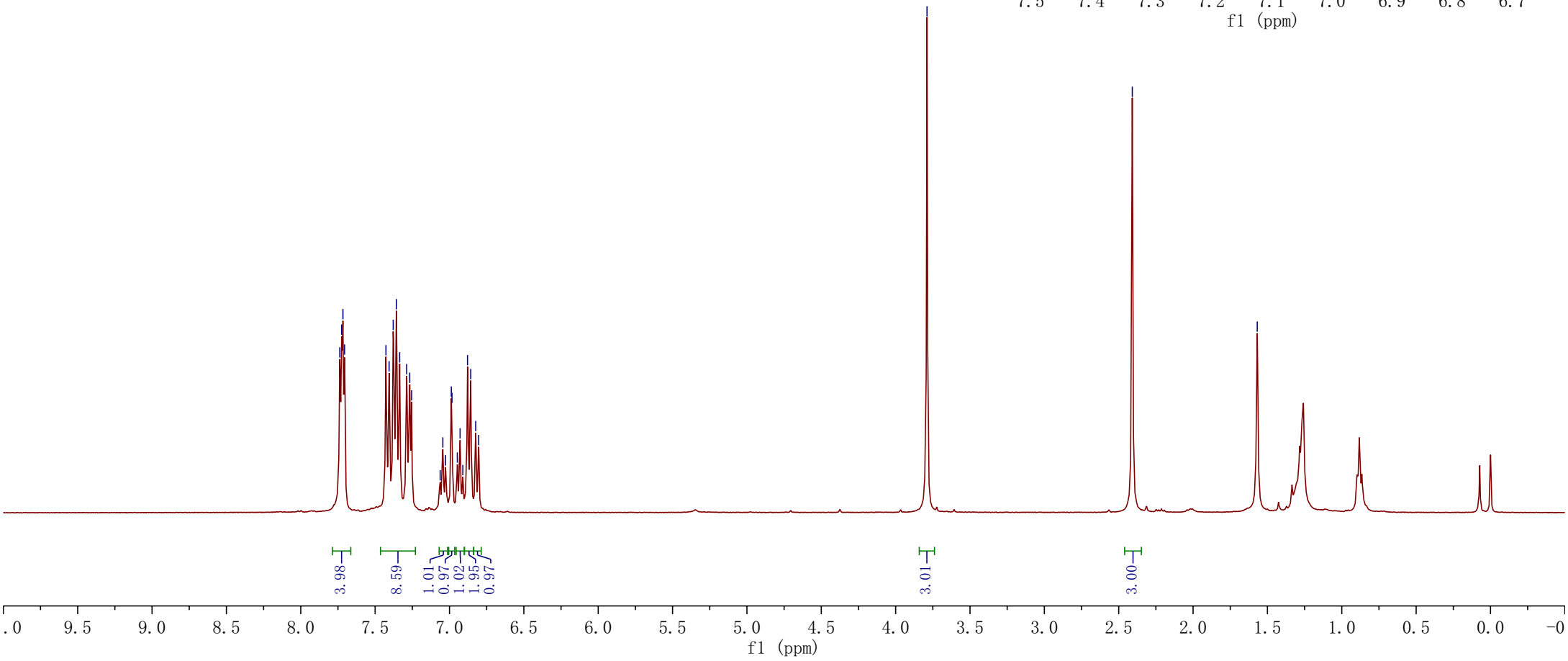


Parameter	Value
1 Title	scy-16-171-4-溴酰基
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Experiment	1D
6 Number of Scans	14
7 Acquisition Time	4.0894
8 Acquisition Date	2022-05-26T19:28:48
9 Spectrometer Frequency	400.13
10 Spectral Width	8012.8



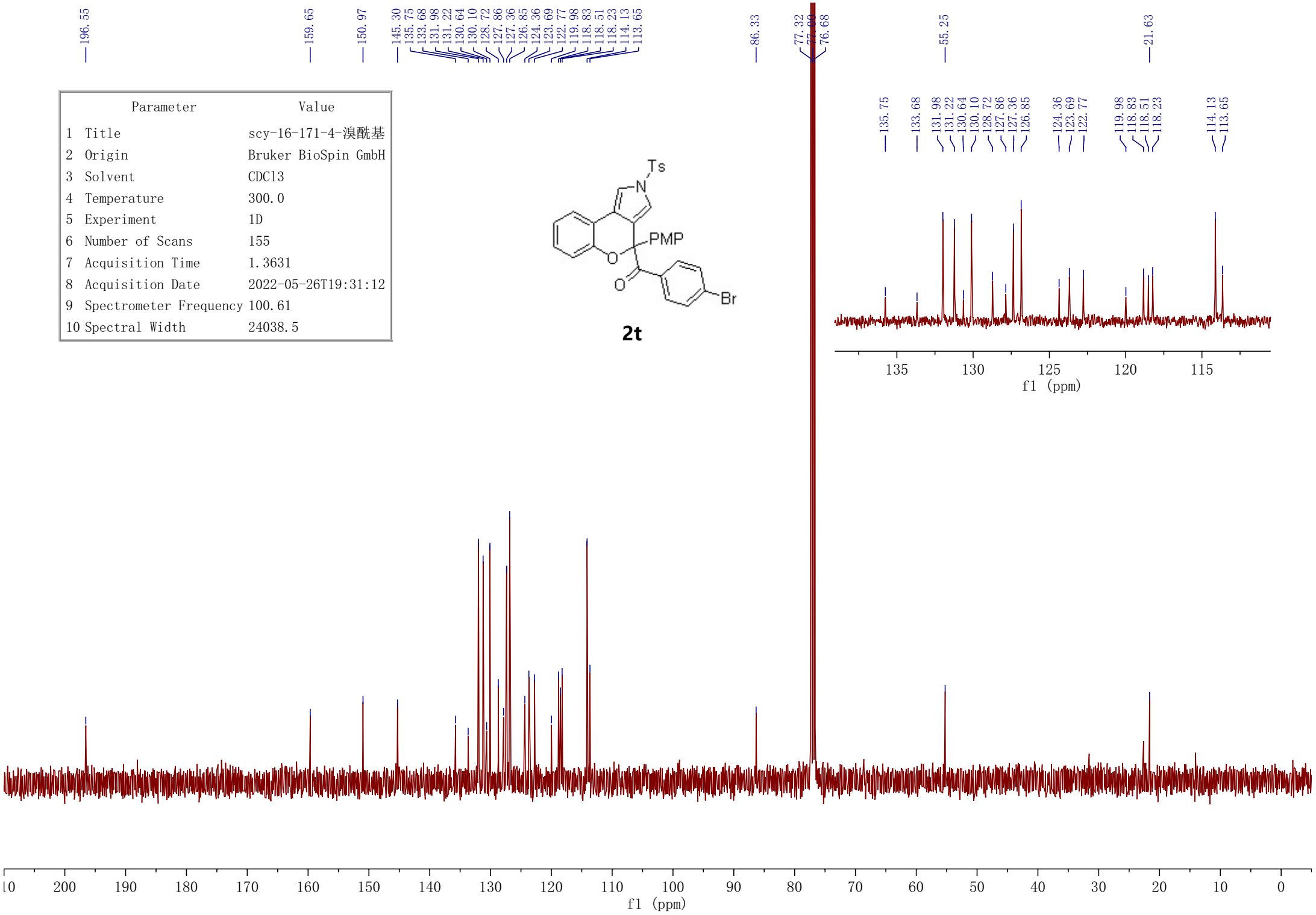
2t

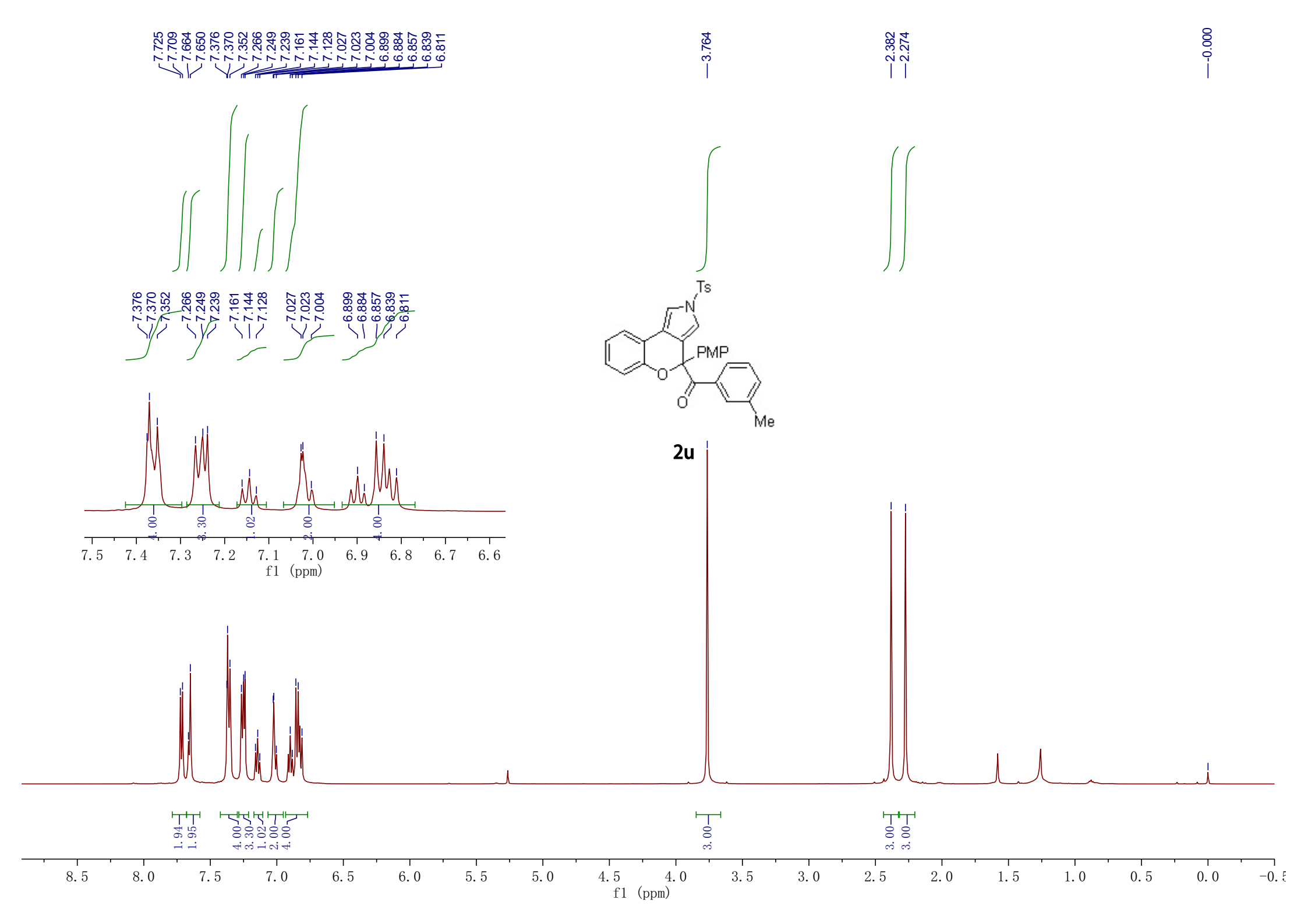


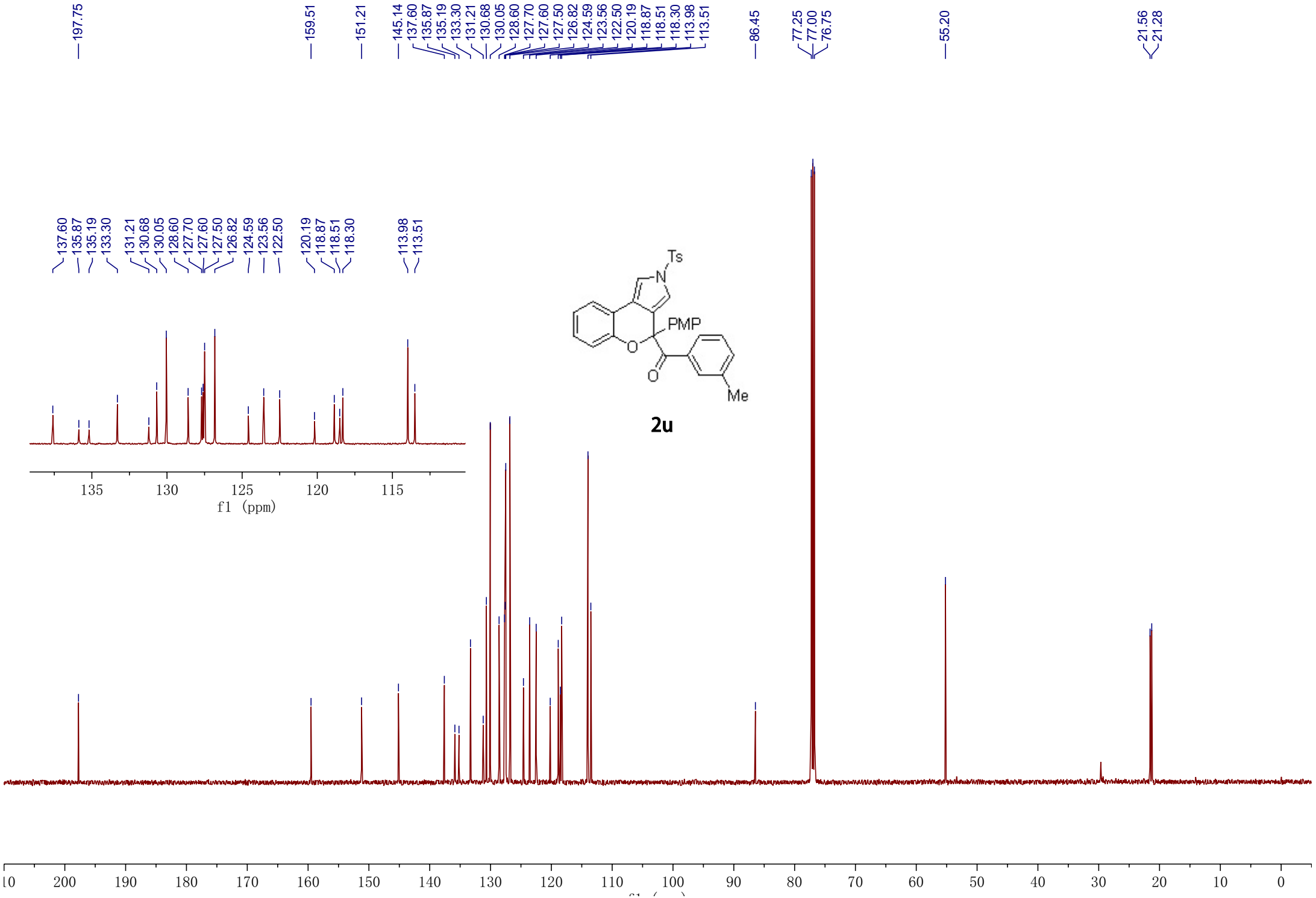


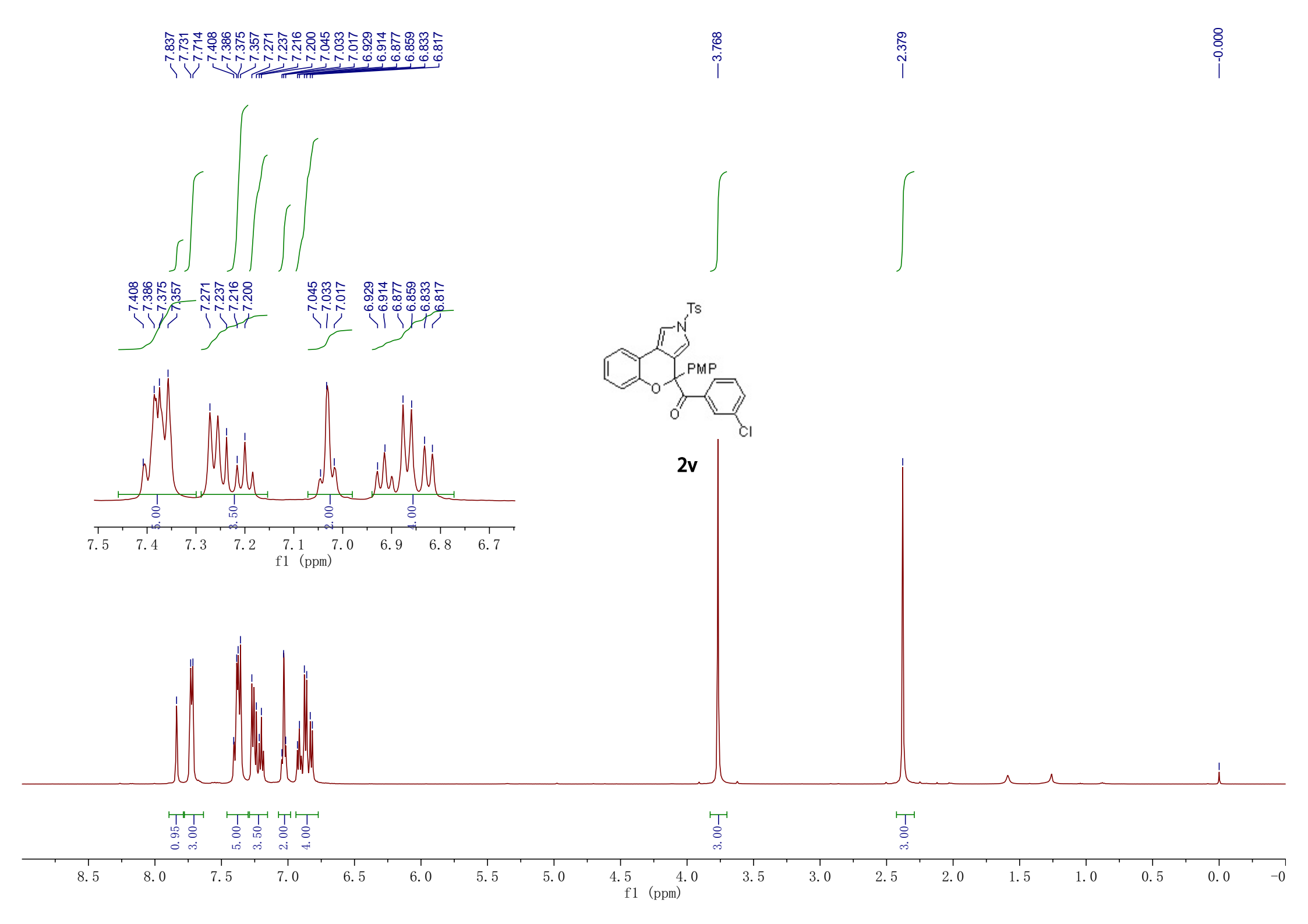
Parameter	Value
1 Title	scy-16-171-4-溴酰基
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Experiment	1D
6 Number of Scans	155
7 Acquisition Time	1.3631
8 Acquisition Date	2022-05-26T19:31:12
9 Spectrometer Frequency	100.61
10 Spectral Width	24038.5

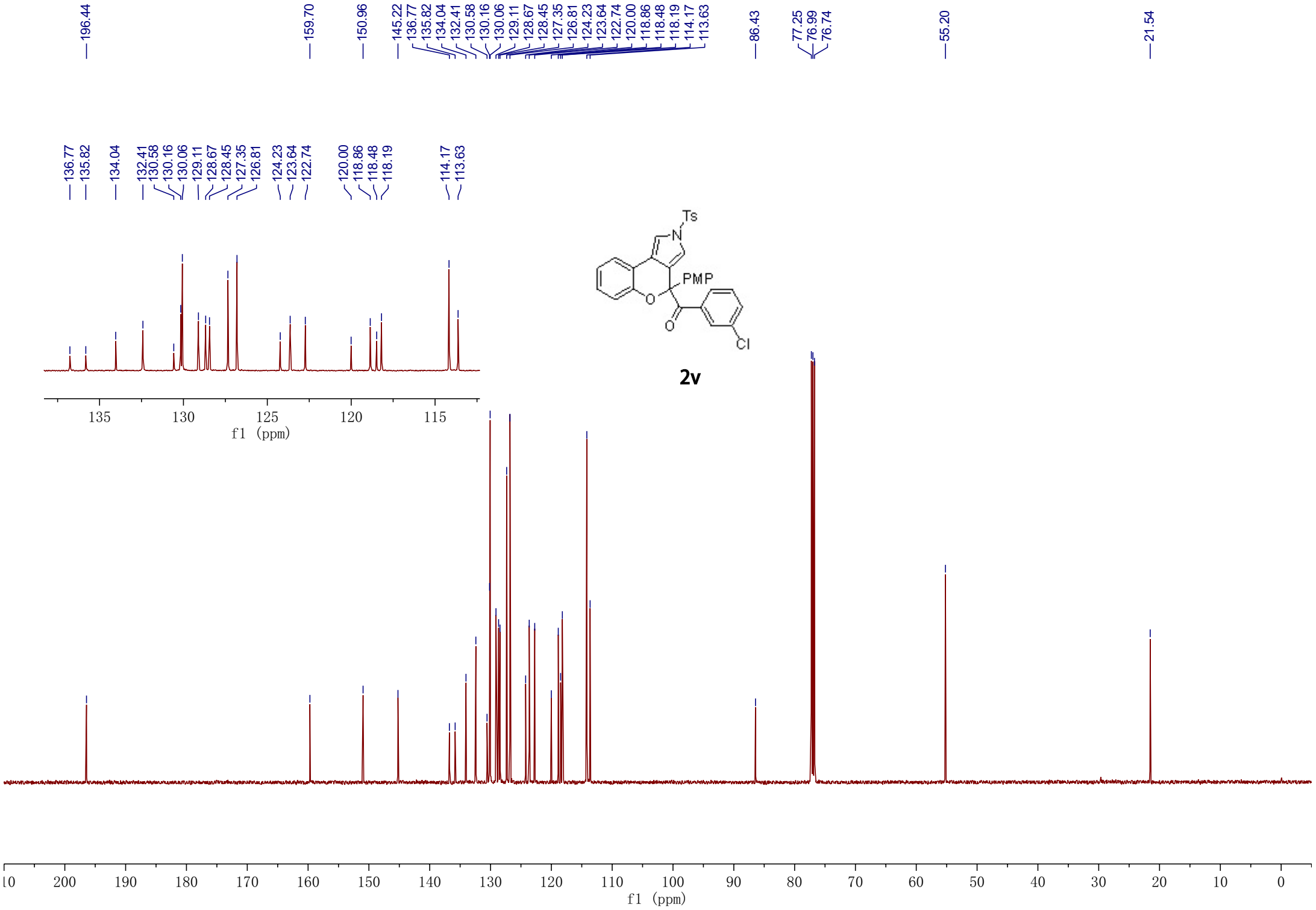
2t

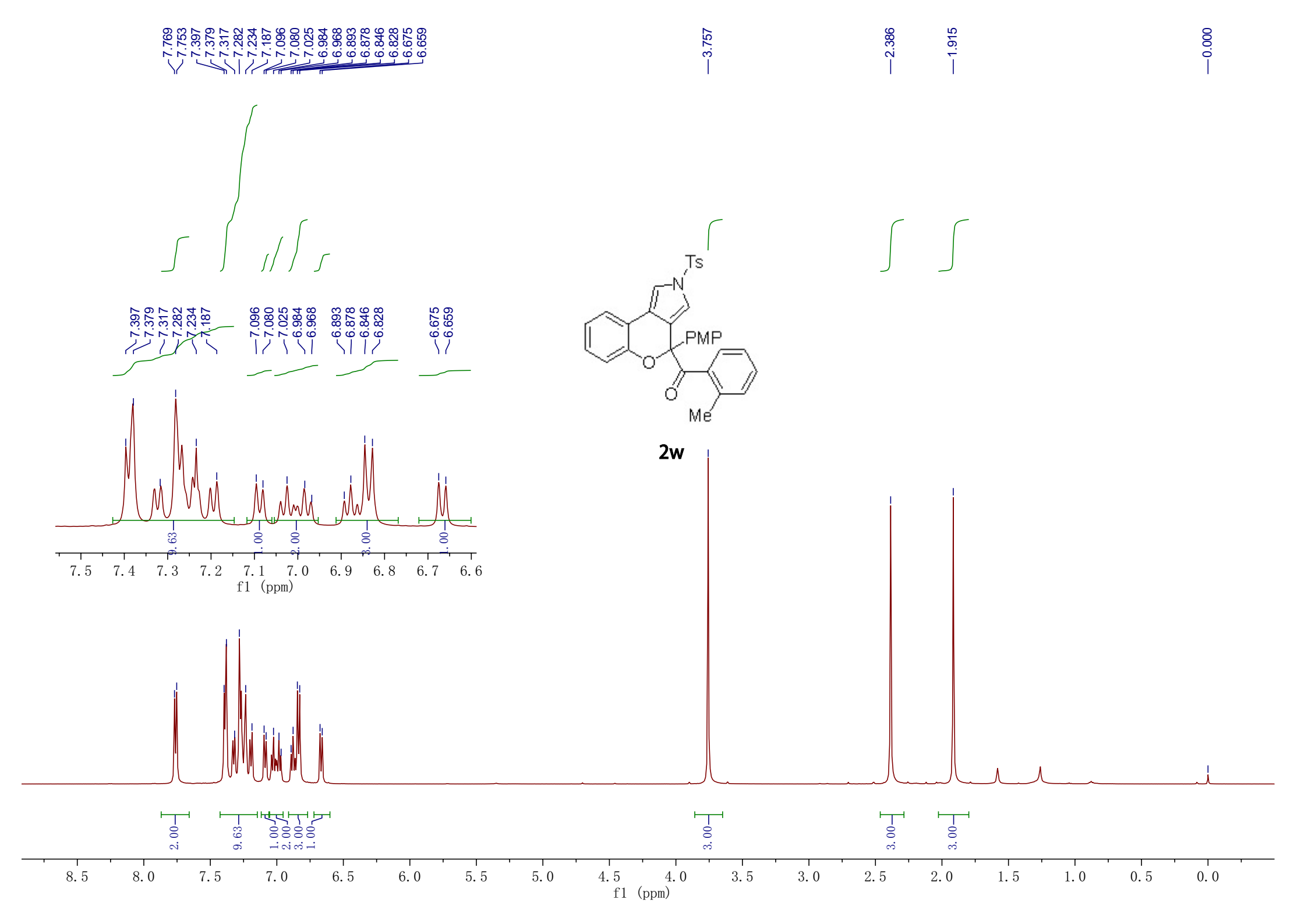


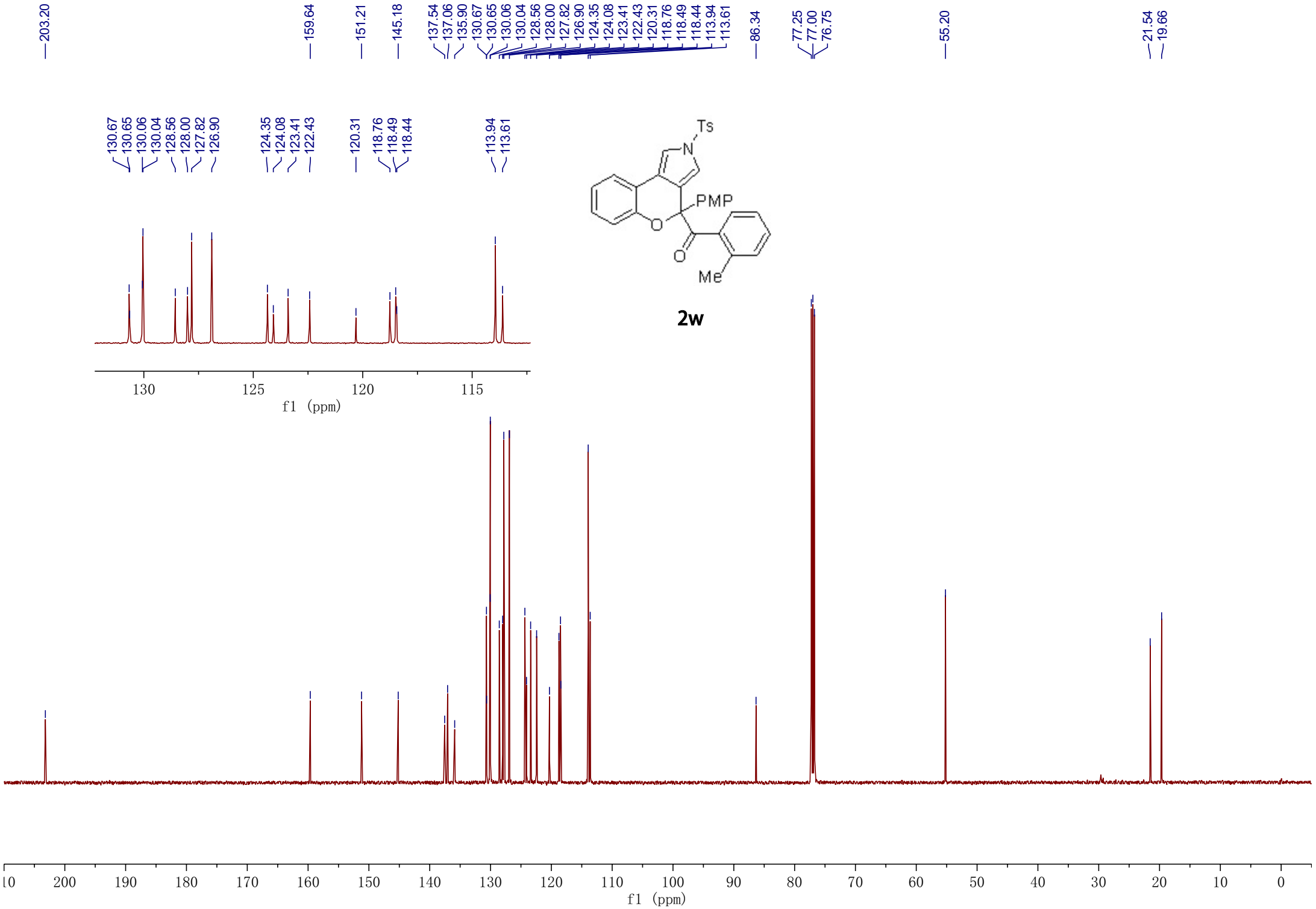

7.725
7.709
7.664
7.650
7.376
7.370
7.352
7.266
7.249
7.239
7.161
7.144
7.128
7.027
7.023
7.004
6.899
6.884
6.857
6.839
6.811
3.764
2.382
2.274
-0.000
Ts
N
PMP
O
O
Me
2u
4.00
3.30
1.02
2.00
4.00
7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6
f1 (ppm)
1.94
1.95
4.00
3.30
1.02
2.00
4.00
3.00
3.00
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

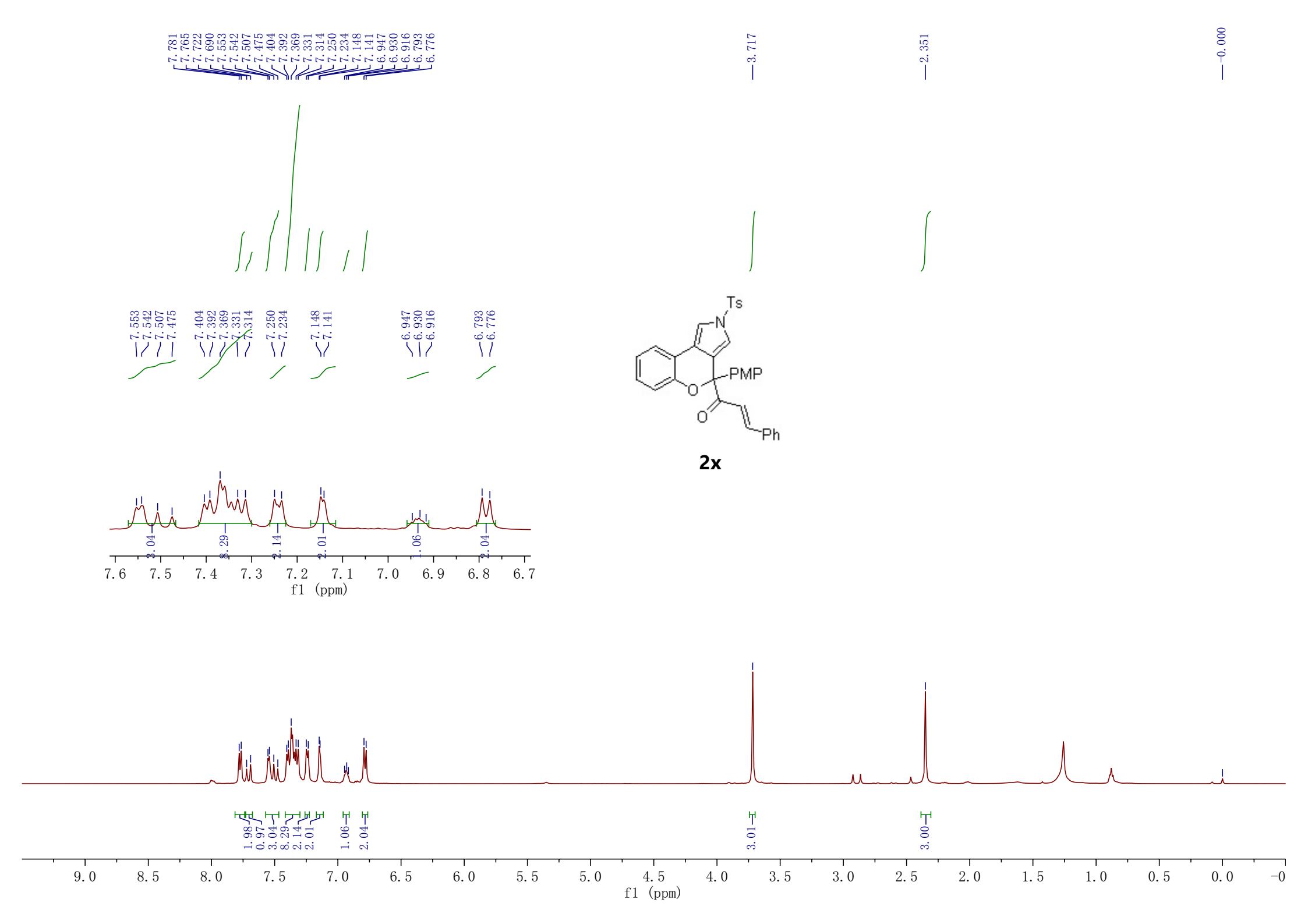

197.75
159.51
151.21
145.14
137.60
135.87
135.19
133.30
131.21
130.68
130.05
128.60
127.70
127.60
127.50
126.82
124.59
123.56
122.50
120.19
118.87
118.51
118.30
113.98
113.51
86.45
77.25
77.00
76.75
55.20
21.56
21.28
Ts
N
PMP
O
O
Me
2u
f1 (ppm)

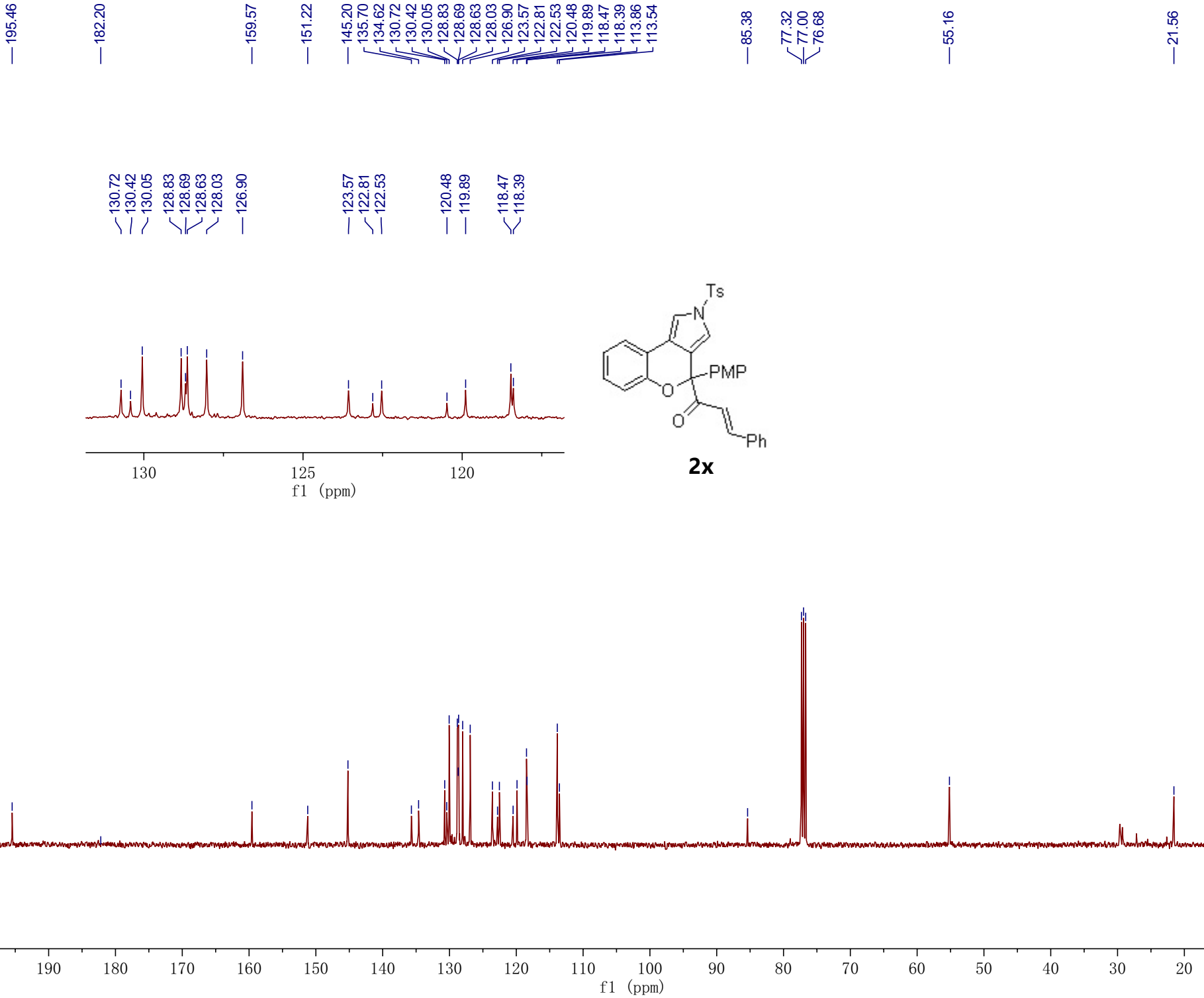

7.837
7.731
7.714
7.408
7.386
7.375
7.357
7.271
7.237
7.216
7.200
7.045
7.033
7.017
6.929
6.914
6.877
6.859
6.833
6.817
3.768
2.379
-0.000
Ts
N
PMP
O
O
Cl
2v
5.00
3.50
2.00
4.00
f1 (ppm)
0.95
3.00
5.00
3.50
2.00
4.00
3.00
3.00
f1 (ppm)

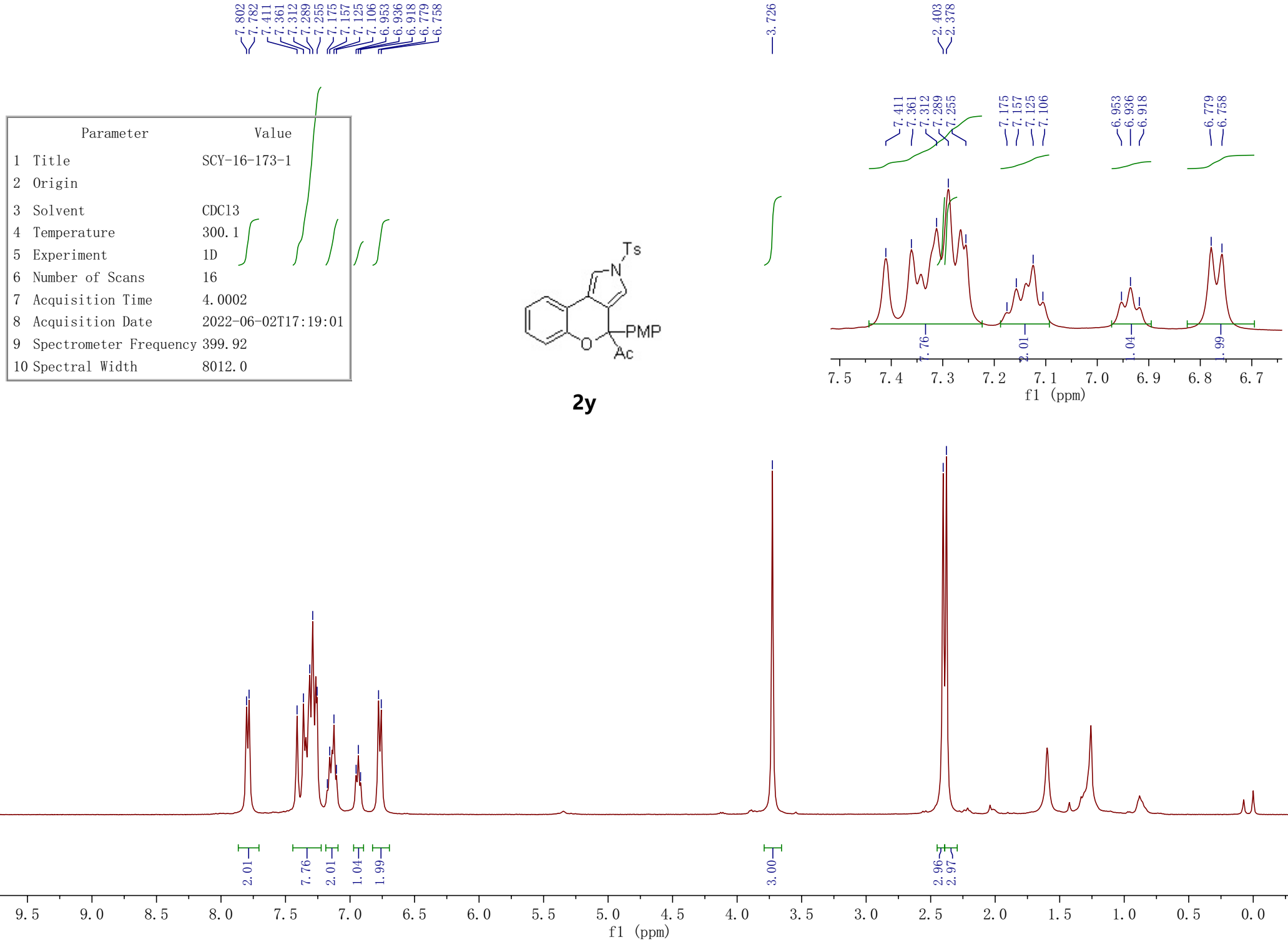

196.44
159.70
150.96
145.22
136.77
135.82
134.04
132.41
130.58
130.16
130.06
129.11
128.67
128.45
127.35
126.81
124.23
123.64
122.74
120.00
118.86
118.48
118.19
114.17
113.63
86.43
77.25
76.99
76.74
55.20
21.54
Ts
N
PMP
O
O
Cl
2v
f1 (ppm)
f1 (ppm)


7.769
7.753
7.397
7.379
7.317
7.282
7.234
7.187
7.096
7.080
7.025
6.984
6.968
6.893
6.878
6.846
6.828
6.675
6.659
3.757
2.386
1.915
0.000
Ts
N
PMP
O
O
Me
2w
9.63
1.00
2.00
3.00
1.00
f1 (ppm)
2.00
9.63
1.00
2.00
3.00
1.00
3.00
3.00
3.00
f1 (ppm)


203.20
159.64
151.21
145.18
137.54
137.06
135.90
130.67
130.65
130.06
130.04
128.56
128.00
127.82
126.90
124.35
124.08
123.41
122.43
120.31
118.76
118.49
118.44
113.94
113.61
86.34
77.25
77.00
76.75
55.20
21.54
19.66
Ts
N
PMP
O
O
Me
2w
f1 (ppm)
f1 (ppm)

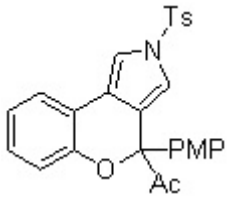

7.781
7.765
7.722
7.690
7.553
7.542
7.507
7.475
7.404
7.392
7.369
7.331
7.314
7.250
7.234
7.148
7.141
6.947
6.930
6.916
6.793
6.776
3.717
2.351
-0.000
Ts
N
PMP
O
O
Ph
2x
3.04
8.29
2.14
2.01
1.06
2.04
f1 (ppm)
1.98
0.97
3.04
8.29
2.14
2.01
1.06
2.04
3.01
3.00
f1 (ppm)


195.46
182.20
159.57
151.22
145.20
135.70
134.62
130.72
130.42
130.05
128.83
128.69
128.63
128.03
126.90
123.57
122.81
122.53
120.48
119.89
118.47
118.39
113.86
113.54
85.38
77.32
77.00
76.68
55.16
21.56
130.72
130.42
130.05
128.83
128.69
128.63
128.03
126.90
123.57
122.81
122.53
120.48
119.89
118.47
118.39
130
125
120
f1 (ppm)
Ts
N
PMP
O
O
Ph
2x
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

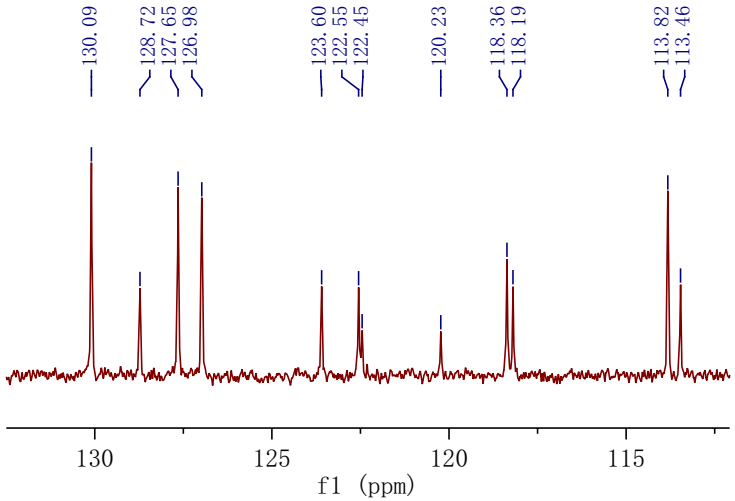

7.802
7.782
7.411
7.361
7.312
7.289
7.255
7.175
7.157
7.125
7.106
6.953
6.936
6.918
6.779
6.758
3.726
2.403
2.378
Parameter Value
1 Title SCY-16-173-1
2 Origin
3 Solvent CDCl3
4 Temperature 300.1
5 Experiment 1D
6 Number of Scans 16
7 Acquisition Time 4.0002
8 Acquisition Date 2022-06-02T17:19:01
9 Spectrometer Frequency 399.92
10 Spectral Width 8012.0
Ts
N
PMP
O
Ac
2y
7.76
2.01
1.04
1.99
7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
f1 (ppm)
2.01
7.76
2.01
1.04
1.99
3.00
2.96
2.97
.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

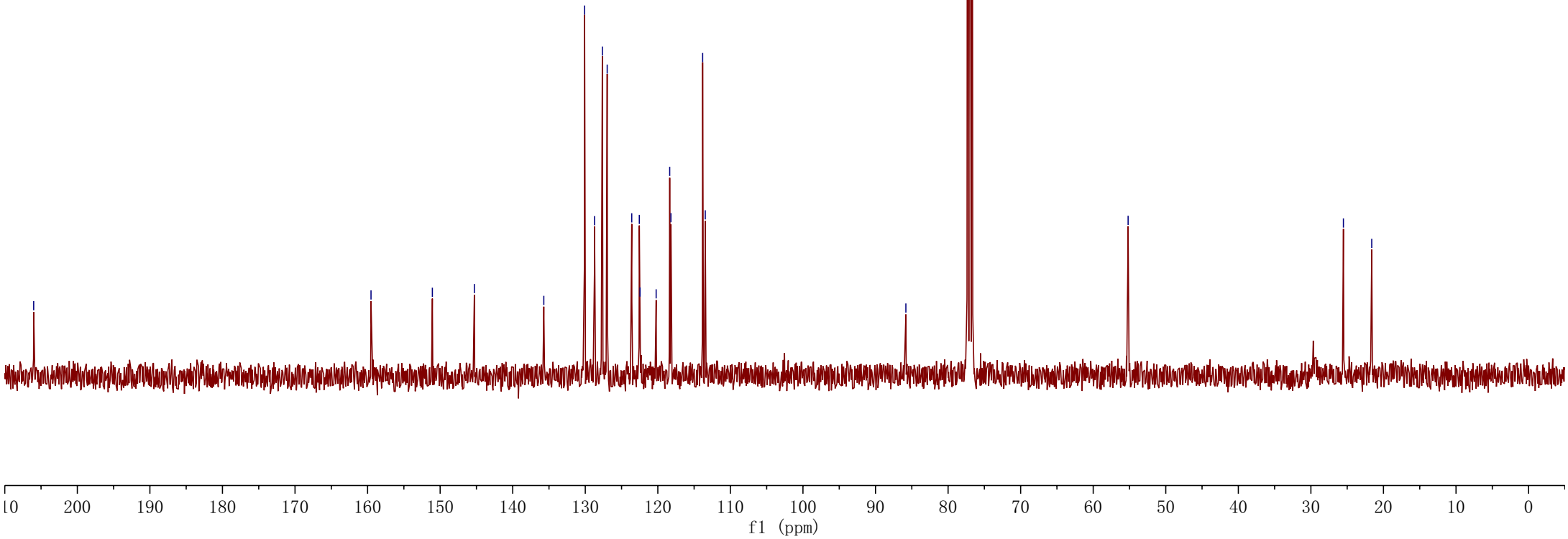
206.01
159.53
151.07
145.29
135.71
130.09
128.72
127.65
126.98
123.60
122.55
122.45
120.23
118.36
118.19
113.82
113.46
85.82
77.32
77.00
76.68
55.19
25.52
21.61

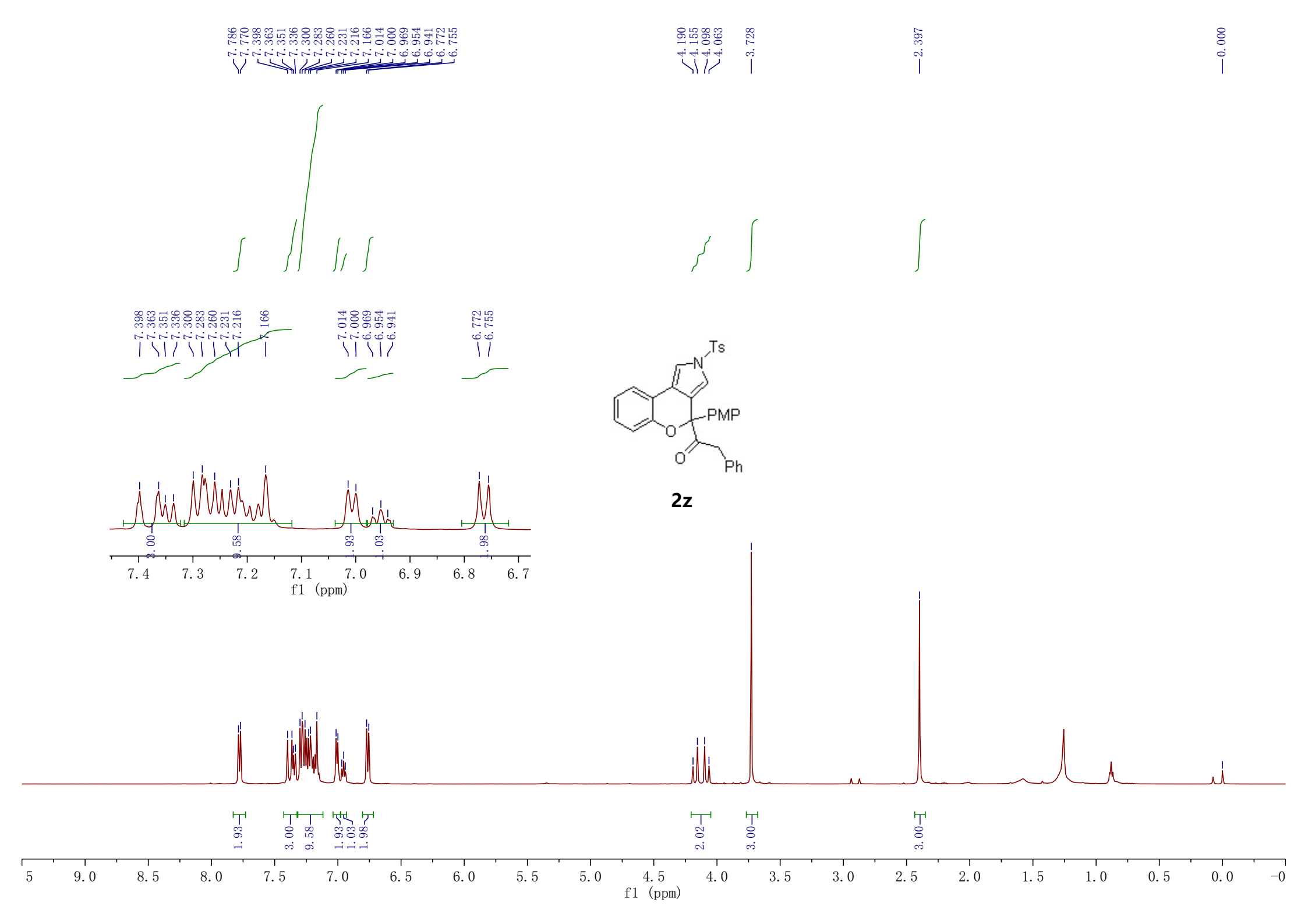
Parameter	Value
1 Title	SCY-16-173-1
2 Origin	
3 Solvent	CDCl3
4 Temperature	300.1
5 Experiment	1D
6 Number of Scans	400
7 Acquisition Time	1.0000
8 Acquisition Date	2022-06-02T17:32:56
9 Spectrometer Frequency	100.56
10 Spectral Width	26041.0



2y

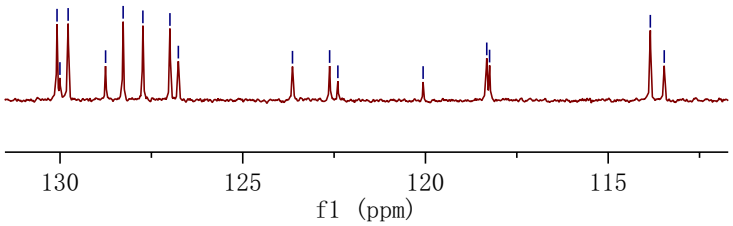


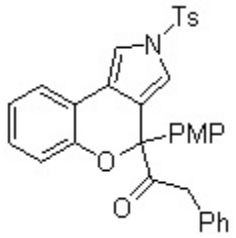



7.786
7.770
7.398
7.363
7.351
7.336
7.300
7.283
7.260
7.231
7.216
7.166
7.014
7.000
6.969
6.954
6.941
6.772
6.755
4.190
4.155
4.098
4.063
3.728
2.397
0.000
Ts
N
PMP
O
O
Ph
2z
3.00
9.58
1.93
1.03
1.98
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
f1 (ppm)
1.93
3.00
9.58
1.93
1.03
1.98
2.02
3.00
3.00
5
9.0
8.5
8.0
7.5
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
f1 (ppm)

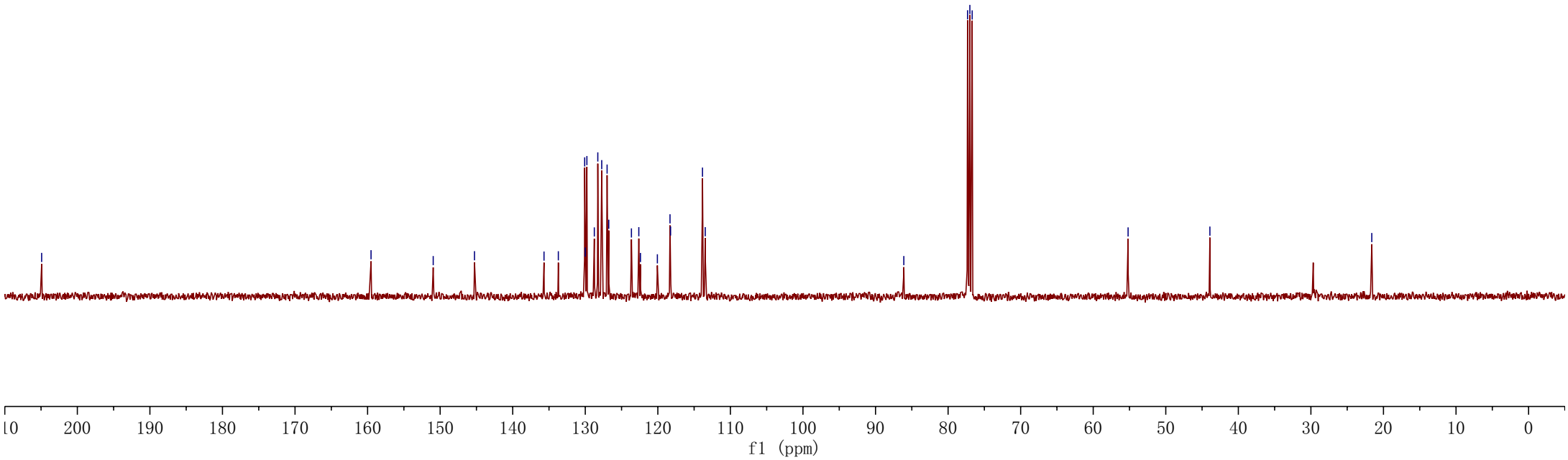
204.92
159.53
150.96
145.27
135.69
133.71
130.08
130.00
129.78
128.75
128.27
127.73
126.99
126.76
123.64
122.62
122.40
120.06
118.32
118.25
113.85
113.47
86.10
77.32
77.00
76.68
55.19
43.92
21.61

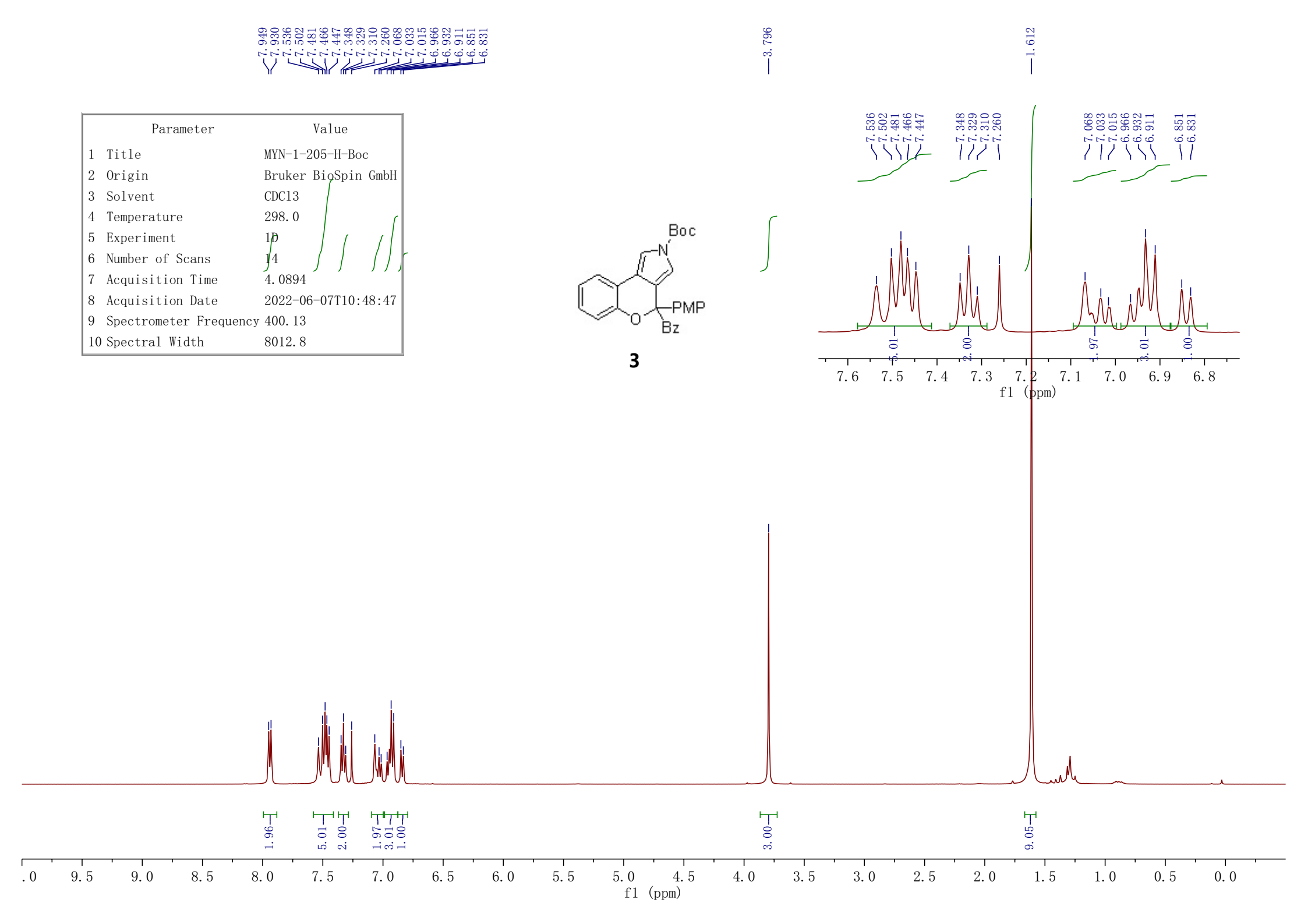
130.082
130.003
129.778
128.753
128.273
127.733
126.992
126.762
123.639
122.622
122.397
120.064
118.323
118.245
113.847
113.466





2z

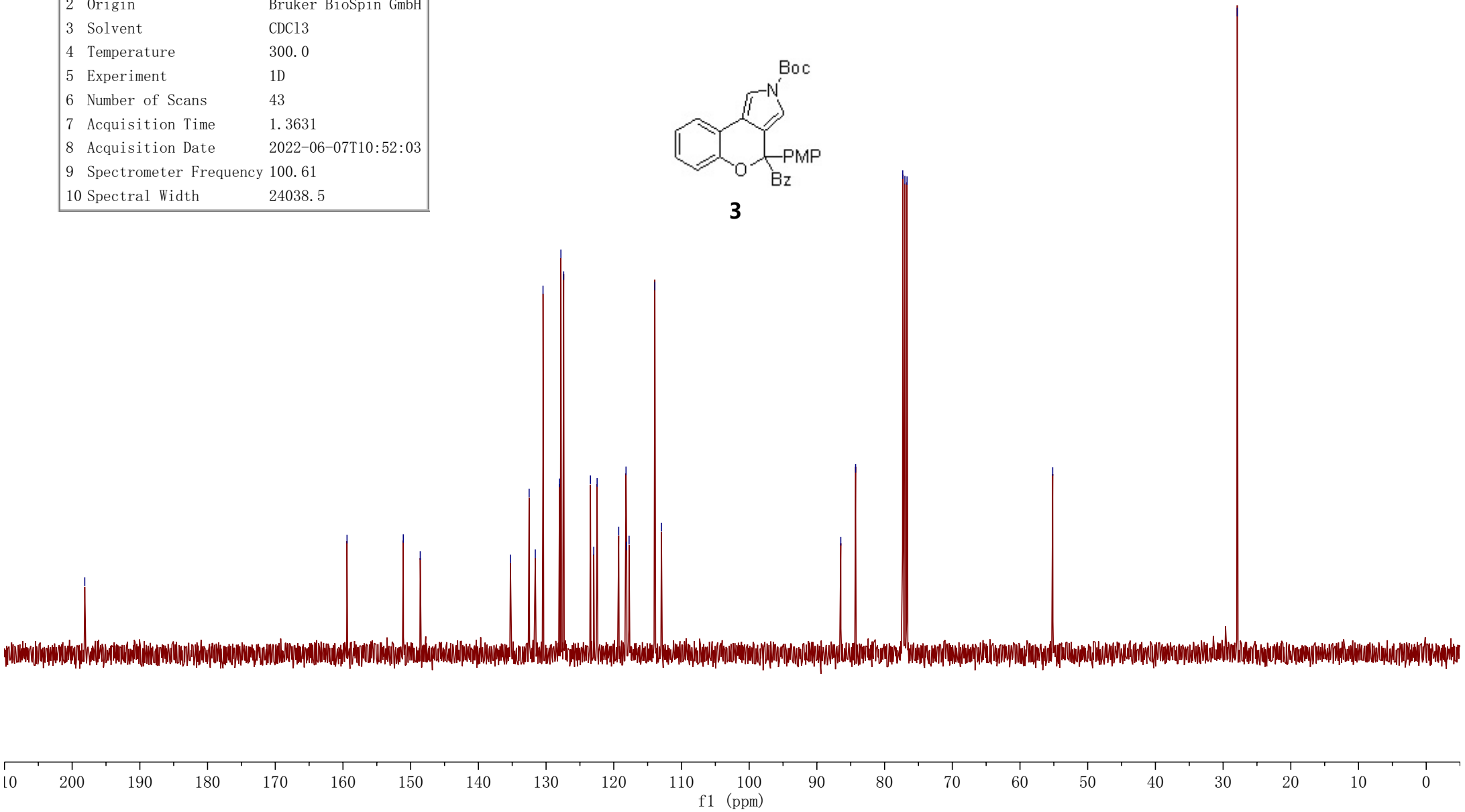


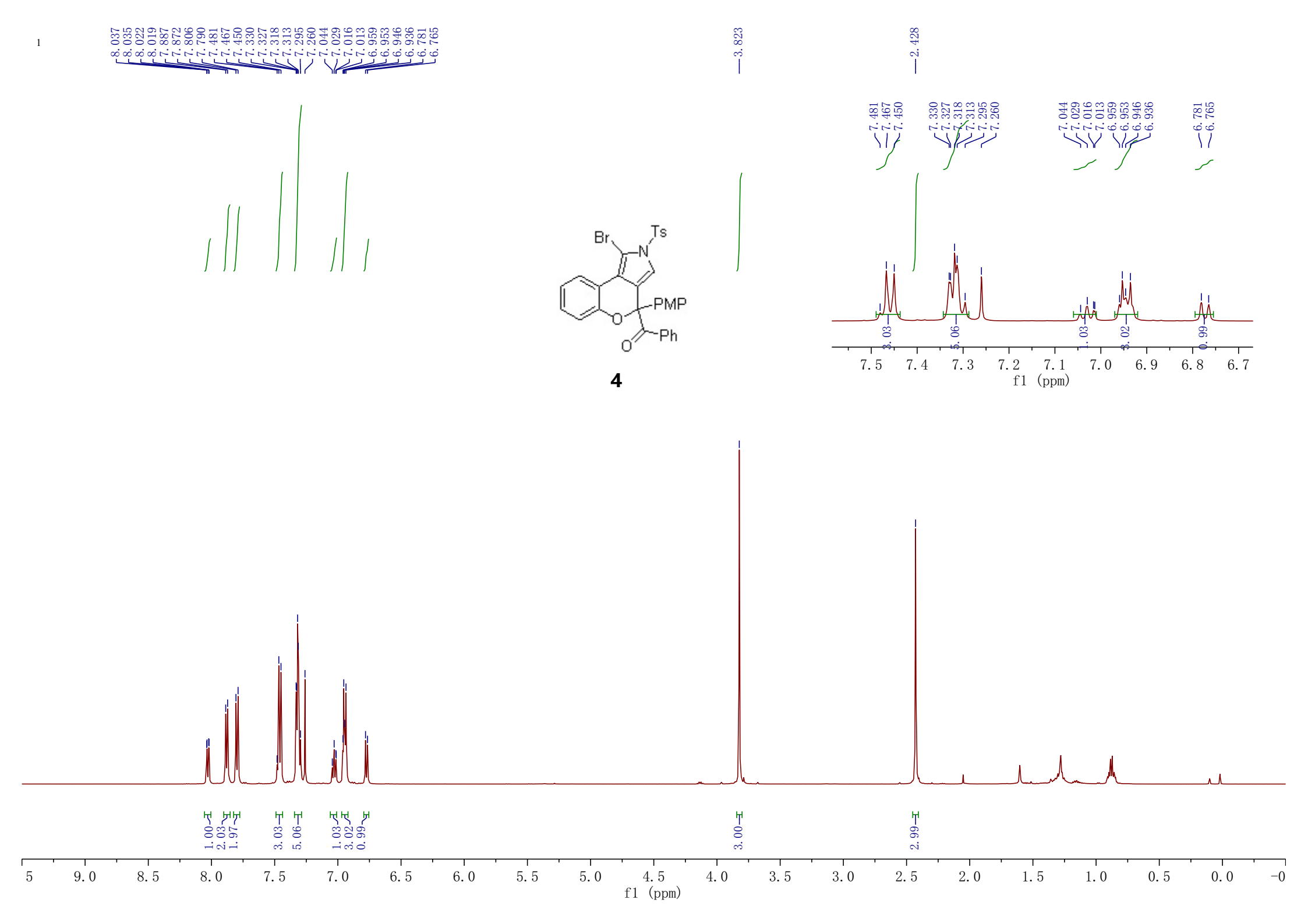

7.949
7.930
7.536
7.502
7.481
7.466
7.447
7.348
7.329
7.310
7.260
7.068
7.033
7.015
6.966
6.932
6.911
6.851
6.831
3.796
1.612
Parameter Value
1 Title MYN-1-205-H-Boc
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 298.0
5 Experiment 1D
6 Number of Scans 14
7 Acquisition Time 4.0894
8 Acquisition Date 2022-06-07T10:48:47
9 Spectrometer Frequency 400.13
10 Spectral Width 8012.8
Boc
N
PMP
O
Bz
3
1.96
5.01
2.00
1.97
3.01
1.00
3.00
9.05
f1 (ppm)

198.14
159.40
151.09
148.59
135.27
132.50
131.60
130.45
128.02
127.81
127.40
123.45
122.96
122.46
119.27
118.19
118.10
117.74
113.93
112.96
86.47
84.28
77.32
77.00
76.68
55.17
27.91

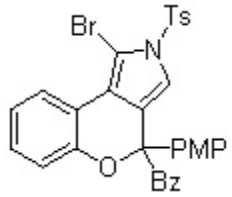
Parameter	Value
1 Title	MYN-1-205-C-Boc
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Experiment	1D
6 Number of Scans	43
7 Acquisition Time	1.3631
8 Acquisition Date	2022-06-07T10:52:03
9 Spectrometer Frequency	100.61
10 Spectral Width	24038.5

3

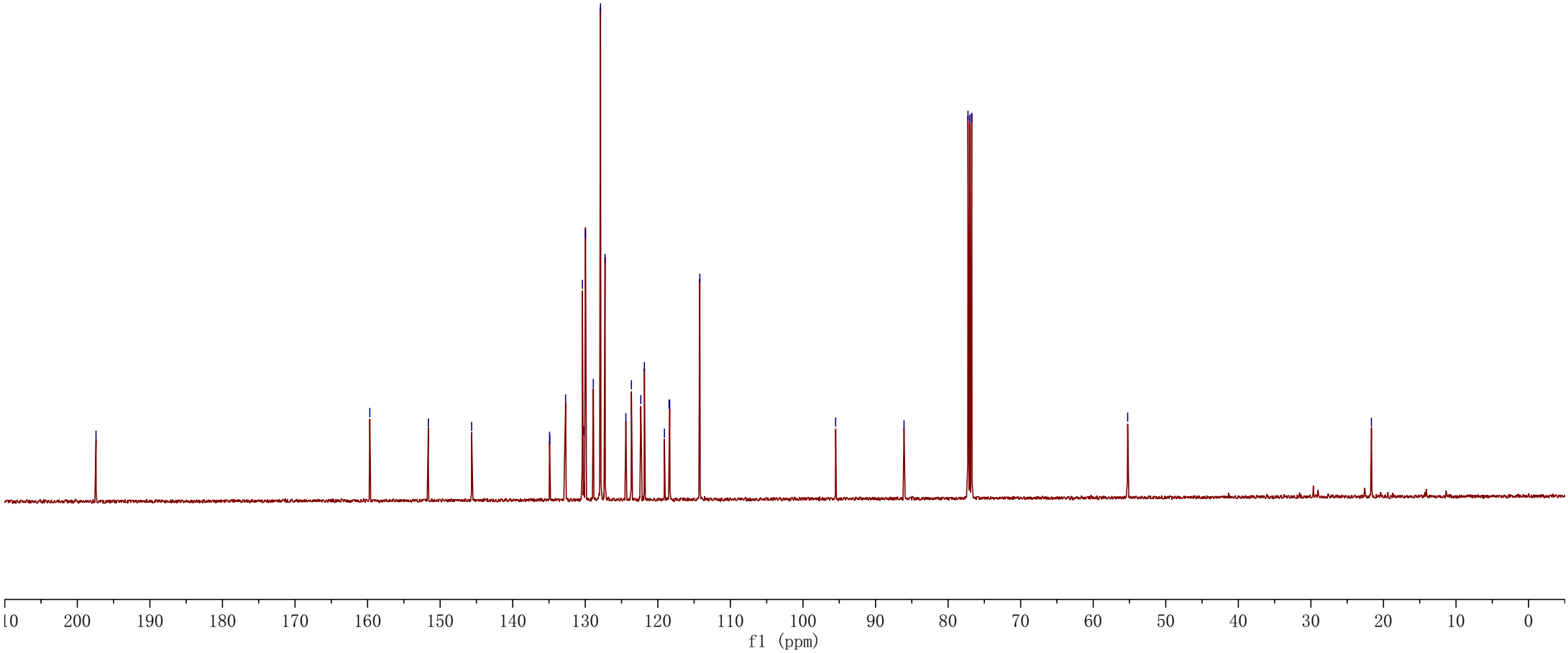


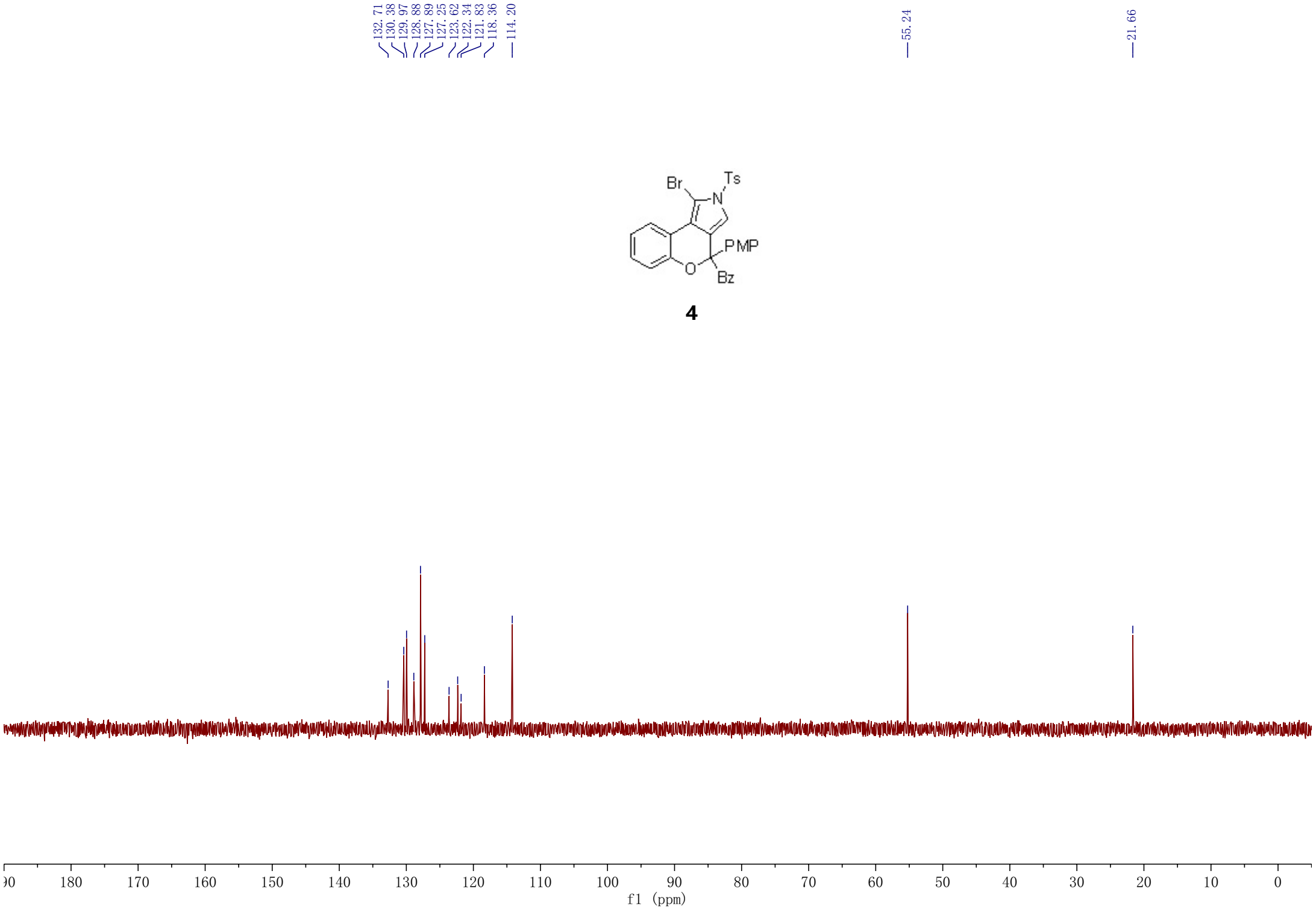

8.037
8.035
8.022
8.019
7.887
7.872
7.806
7.790
7.481
7.467
7.450
7.330
7.327
7.318
7.313
7.295
7.260
7.044
7.029
7.016
7.013
6.959
6.953
6.946
6.936
6.781
6.765
3.823
2.428
Br
Ts
N
PMP
O
Ph
O
4
1.00
2.03
1.97
3.03
5.06
1.03
3.02
0.99
3.00
2.99
f1 (ppm)

197.43
159.69
151.62
145.66
134.92
134.89
132.71
130.39
130.23
129.98
128.89
127.90
127.27
124.41
123.64
122.35
121.85
119.09
118.46
118.37
114.22
95.49
86.07
77.26
77.00
76.75
55.25
21.66

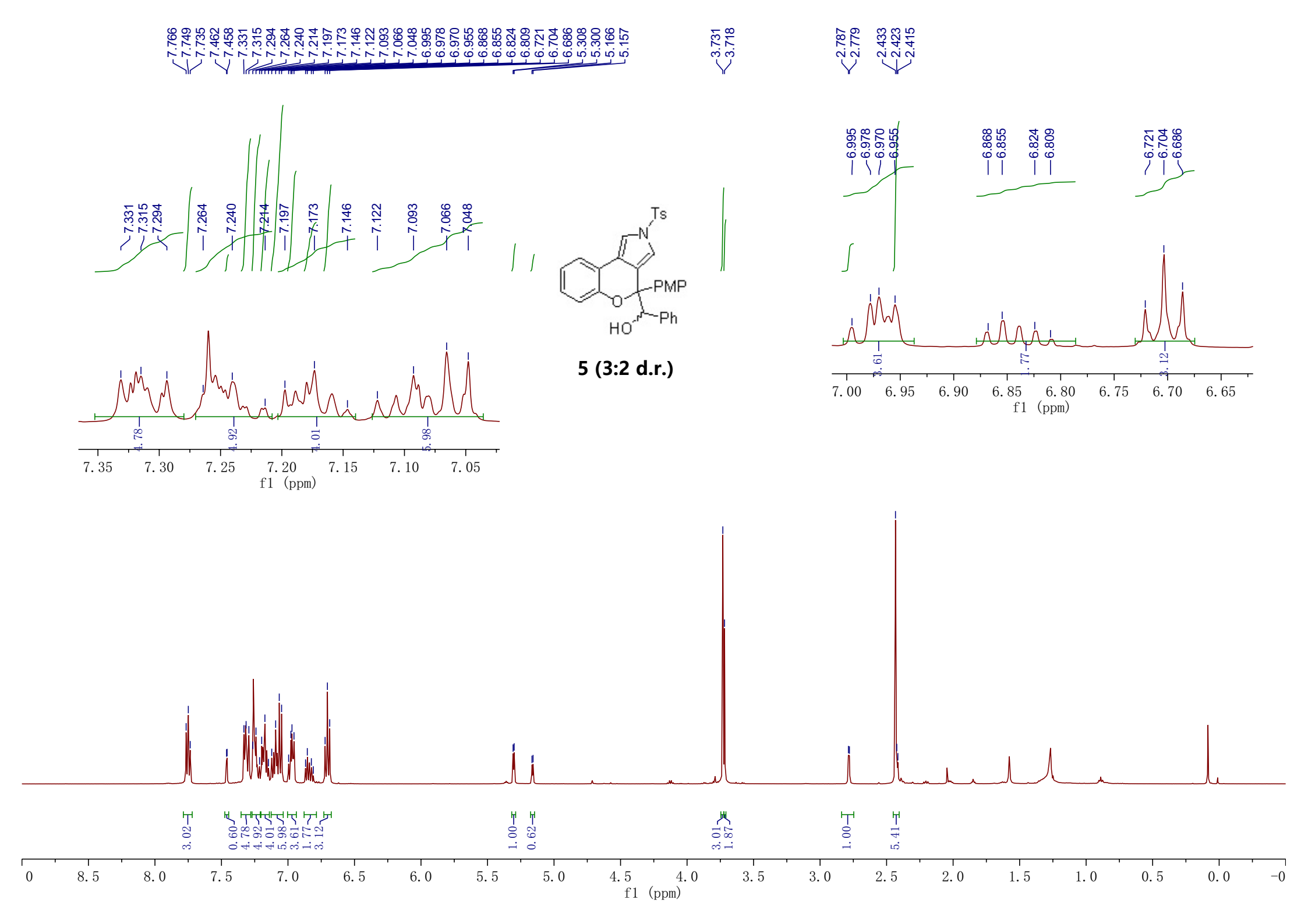


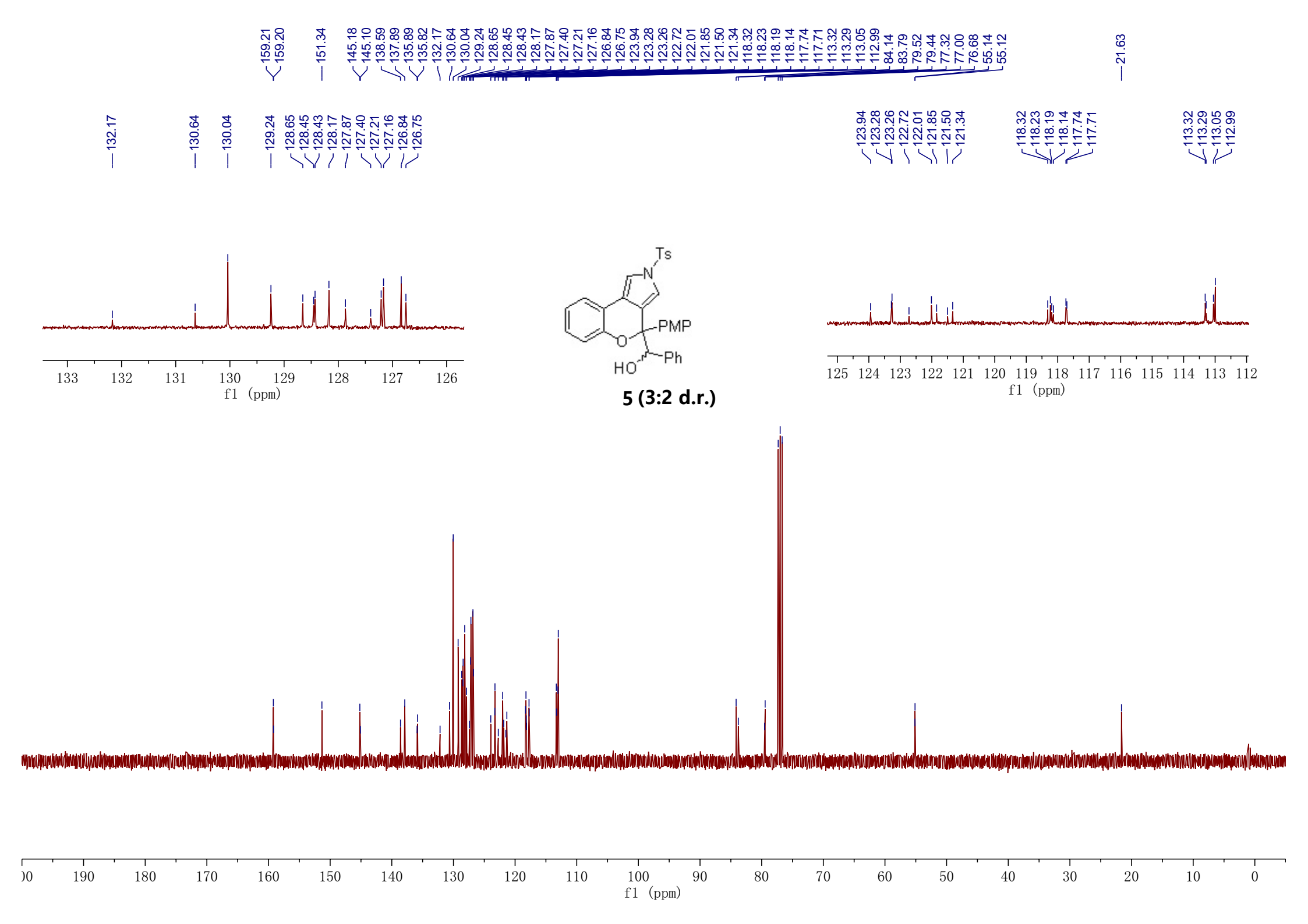
4



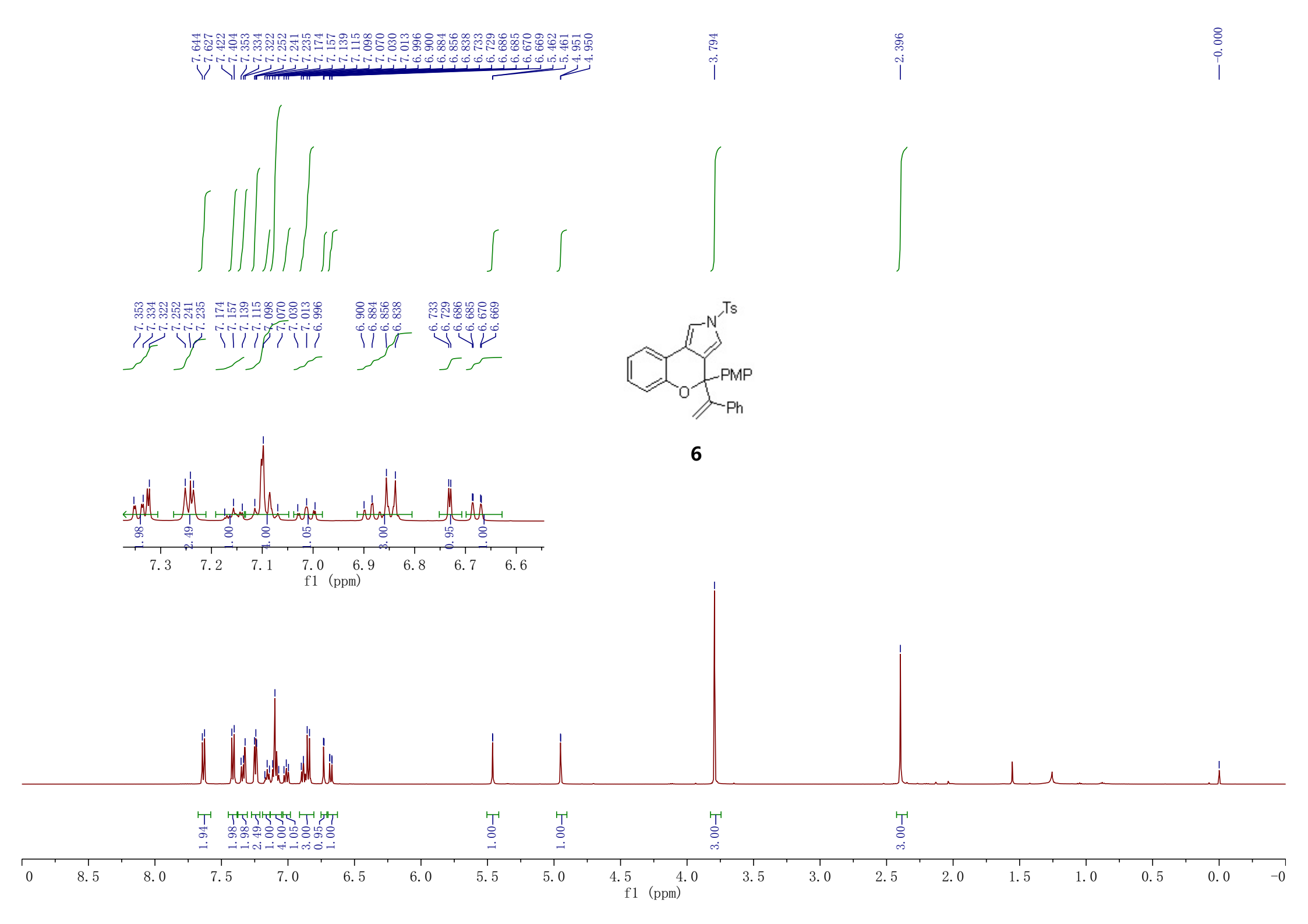

132.71
130.38
129.97
128.88
127.89
127.25
123.62
122.34
121.83
118.36
114.20
55.24
21.66
Br
Ts
N
PMP
O
Bz
f1 (ppm)

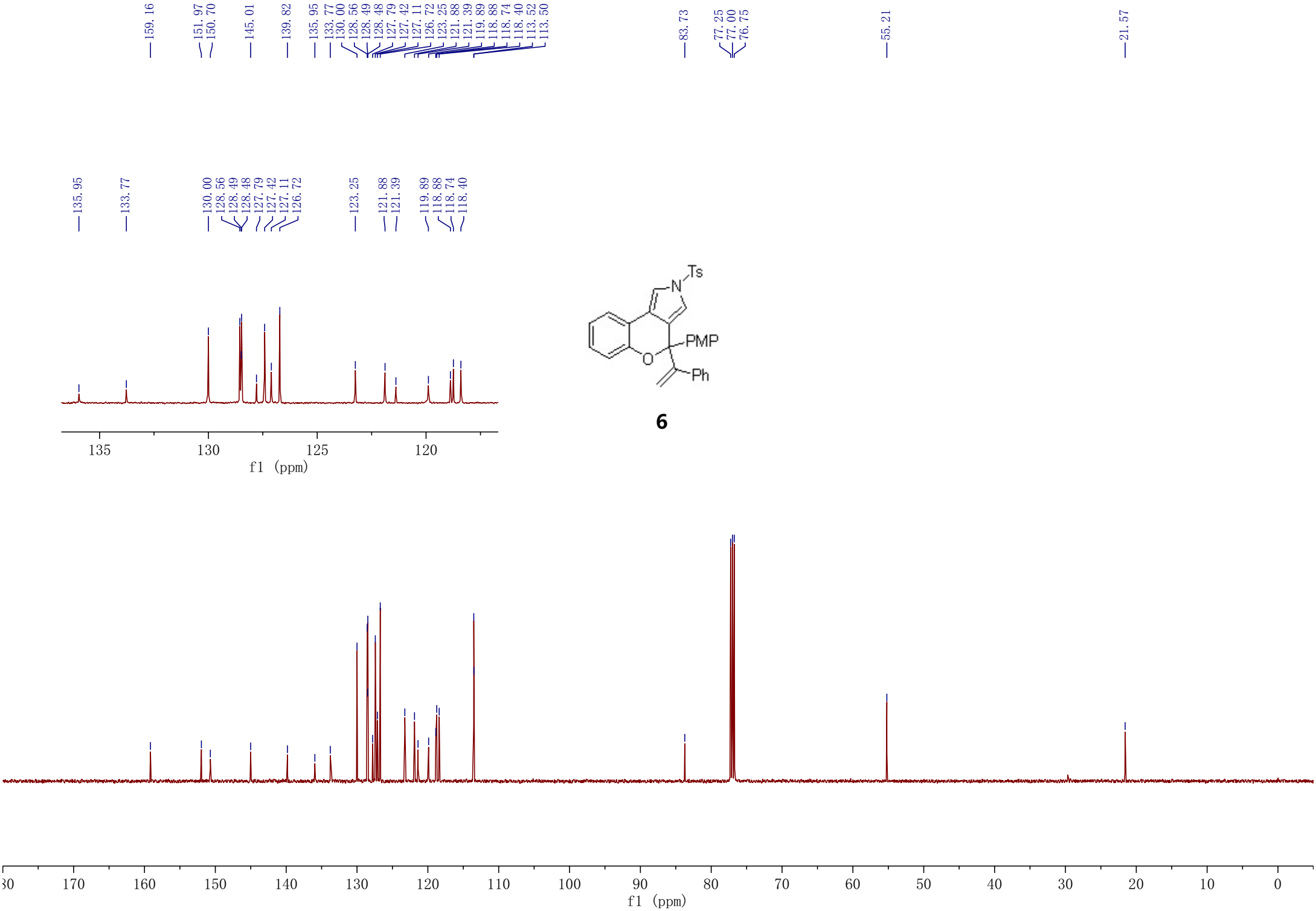
4


7.766
7.749
7.735
7.462
7.458
7.331
7.315
7.294
7.264
7.240
7.214
7.197
7.173
7.146
7.122
7.093
7.066
7.048
6.995
6.978
6.970
6.955
6.868
6.855
6.824
6.809
6.721
6.704
6.686
5.308
5.300
5.166
5.157
3.731
3.718
2.787
2.779
2.433
2.423
2.415
Ts
N
PMP
O
Ph
HO
5 (3:2 d.r.)
f1 (ppm)
f1 (ppm)
f1 (ppm)


159.21
159.20
151.34
145.18
145.10
138.59
137.89
135.89
135.82
132.17
130.64
130.04
129.24
128.65
128.45
128.43
128.17
127.87
127.40
127.21
127.16
126.84
126.75
123.94
123.28
123.26
122.72
122.01
121.85
121.50
121.34
118.32
118.23
118.19
118.14
117.74
117.71
113.32
113.29
113.05
112.99
84.14
83.79
79.52
79.44
77.32
77.00
76.68
55.14
55.12
21.63
Ts
N
PMP
O
Ph
HO
f1 (ppm)
f1 (ppm)
f1 (ppm)

5 (3:2 d.r.)


7.644
7.627
7.422
7.404
7.353
7.334
7.322
7.252
7.241
7.235
7.174
7.157
7.139
7.115
7.098
7.070
7.030
7.013
6.996
6.900
6.884
6.856
6.838
6.733
6.729
6.686
6.685
6.670
6.669
5.462
5.461
4.951
4.950
3.794
2.396
0.000
Ts
N
PMP
O
Ph
6
1.98
2.49
1.00
4.00
1.05
3.00
0.95
1.00
f1 (ppm)
1.94
1.98
1.98
2.49
1.00
4.00
1.05
3.00
0.95
1.00
1.00
1.00
3.00
3.00
f1 (ppm)


159.16
151.97
150.70
145.01
139.82
135.95
133.77
130.00
128.56
128.49
128.48
127.79
127.42
127.11
126.72
123.25
121.88
121.39
119.89
118.88
118.74
118.40
113.52
113.50
83.73
77.25
77.00
76.75
55.21
21.57
135.95
133.77
130.00
128.56
128.49
128.48
127.79
127.42
127.11
126.72
123.25
121.88
121.39
119.89
118.88
118.74
118.40
135
130
125
120
f1 (ppm)
Ts
N
PMP
O
Ph
6
30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)