Supporting Information

Controllable cyclization of alkynyl thioethers via Brønsted acid-catalyzed dearomatization

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1. General Information

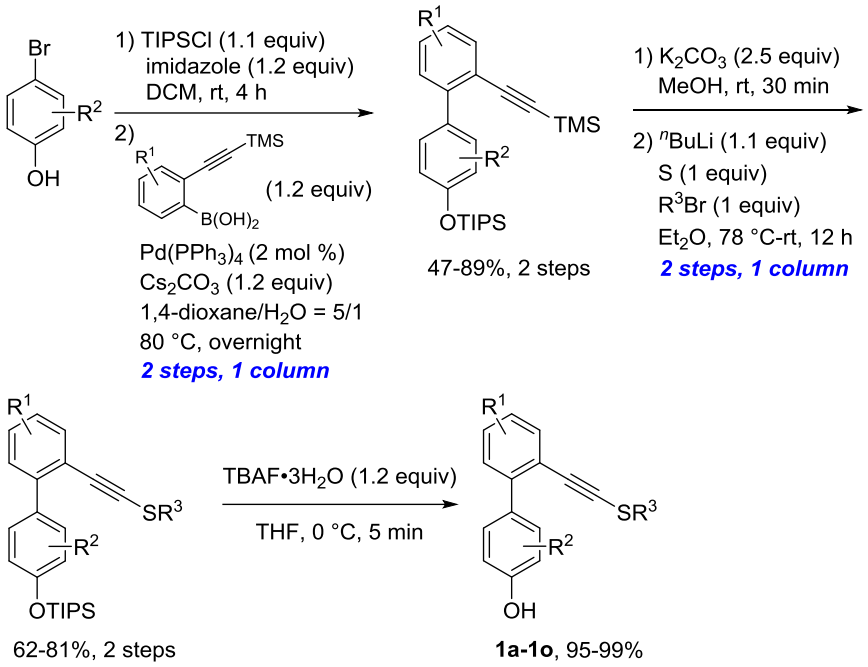
Ethyl acetate (ACS grade), hexanes (ACS grade), anhydrous 1,2-dichloroethane (ACS grade) and toluene (ACS grade) were obtained commercially and used without further purification. Methylene chloride and tetrahydrofuran were purified according to standard methods unless otherwise noted. Commercially available reagents were used without further purification. Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed over silica gel (300-400 mesh). Infrared spectra were recorded on a Nicolet AVATER FTIR330 spectrometer as thin film and are reported in reciprocal centimeter (cm^{-1}). Mass spectra were recorded with Micromass QTOF2 Quadrupole/Time-of-Flight Tandem mass spectrometer using electron spray ionization.

^{1}H NMR spectra were recorded on a Bruker AV-400 spectrometer and a Bruker AV-500 spectrometer in chloroform-d_3. 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_3. Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard.

2. Preparation of Starting Materials

Alkynyl thioethers **1a**–**1o** were prepared according to the following procedure.[1,2]



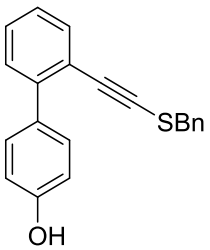
To a solution of 4-bromo-1-phenol derivative (2.0 mmol) and imidazole (2.4 mmol, 0.18 g) in DCM (10 mL) was added TIPSCl (2.2 mmol, 0.43 g) at room temperature. The resulting mixture was stirred at room temperature for 4 h, and the progress of the reaction was monitored by TLC. Upon completion, the solution was filtered through a pad of silica gel and concentrated under reduced pressure. The crude product was directly used in the next step without further purification. After dissolving above crude product in 1,4-dioxane (15 mL) and H_2O (3 mL), (2-((trimethylsilyl)ethynyl)aryl)boronic acid (2.4 mmol), Cs_2CO_3 (2.4 mmol, 0.78 g) and $Pd(PPh_3)_4$ (0.04 mmol, 46 mg) were sequentially added at room temperature under N_2 atmosphere. The reaction mixture was stirred at 80 °C overnight, and the progress of the reaction was monitored by TLC. Upon completion, the reaction was filtered, extracted with ethyl acetate for 3 times, dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate) to give the trimethyl(biarylethynyl)silane (47–89%, 2 steps).

The above trimethyl(biarylethynyl)silane (1.0 mmol) was dissolved in MeOH (5 mL), and K_2CO_3 (2.5 mmol, 0.35 g) was added in one portion. The mixture was stirred at

room temperature for 30 min. Upon completion, the mixture was filtered through a pad of silica gel and the filtrate was concentrated under vacuum. The crude product was directly used in the next step without further purification. The obtained crude product was dissolved in dry THF (5.0 mL), and ^{n}BuLi (2.5 M in hexane, 1.2 mmol) was added dropwise at -78 °C under N_2 atmosphere. After stirring at this temperature for 0.5 h, sulfur powder (1.0 mmol, 32 mg) was added and the mixture was stirred at -78 °C for another 1 h. Then corresponding organobromide (1.0 mmol) was added dropwise at 0 °C, and the reaction mixture was stirred room temperature for additional 12 h. The progress of the reaction was monitored by TLC. Upon completion, the reaction was quenched with saturated aqueous NH_4Cl and extracted with ethyl acetate for 3 times. The organic layer was dried over $MgSO_4$, concentrated and purified by chromatography on silica gel (eluent: hexanes/ethyl acetate) to afford the alkynyl thioether product (62–81%, 2 steps).

To a solution of above alkynyl thioether (0.2 mmol) in THF (2 mL) was added TBAF·$3H_2O$ (0.24 mmol, 76 mg in 2 mL THF) dropwise at 0 °C. After stirring for 5 min, the reaction was quenched by saturated aqueous NH_4Cl and extracted with ethyl acetate for 3 times. The organic layer was dried over $MgSO_4$, concentrated and purified by chromatography on silica gel (eluent: hexanes/ethyl acetate) to afford the desired alkynyl thioether **1a–1o** (95–99%).

2'-((benzylthio)ethynyl)-[1,1'-biphenyl]-4-ol (1a)

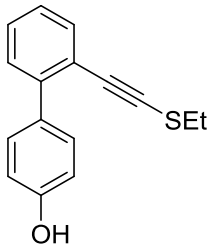


1a

Compound **1a** was prepared in 65% yield (246.5 mg) over 5 steps as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.40 (m, 3H), 7.32 – 7.30 (m, 2H), 7.29 – 7.26 (m, 3H), 7.24 – 7.20 (m, 3H), 6.86 – 6.82 (m, 2H), 5.09 (s, 1H), 3.89 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 142.9, 136.8, 133.1, 132.7, 130.5, 129.3, 128.9, 128.5,

128.1, 127.6, 126.6, 121.6, 114.8, 94.4, 81.8, 40.3; IR (neat): 3113(bs), 2164(s), 1653, 1616, 1405, 1117, 963, 739; HRESIMS Calcd for $[C_{21}H_{16}NaOS]^+$ (M + Na^+) 339.0814, found 339.0816.

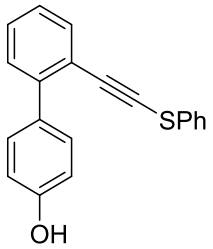
2'-((ethylthio)ethynyl)-[1,1'-biphenyl]-4-ol (1b)



1b

Compound **1b** was prepared in 57% yield (180.1 mg) over 5 steps as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.48 (m, 1H), 7.47 – 7.44 (m, 2H), 7.33 – 7.27 (m, 2H), 7.25 – 7.20 (m, 1H), 6.92 – 6.86 (m, 2H), 5.12 (s, 1H), 2.65 (q, *J* = 7.2 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 142.9, 132.9, 132.4, 130.5, 129.2, 127.9, 126.5, 121.8, 115.0, 93.5, 81.9, 29.8, 14.7; IR (neat): 3410(bs), 2162(s), 1612, 1474, 1258, 1172, 834, 760; HRESIMS Calcd for $[C_{16}H_{14}NaOS]^+$ (M + Na^+) 277.0658, found 277.0663.

2'-((phenylthio)ethynyl)-[1,1'-biphenyl]-4-ol (1c)

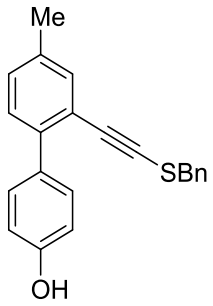


1c

Compound **1c** was prepared in 63% yield (199.2 mg) over 5 steps as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.35 – 7.33 (m, 2H), 7.29 – 7.16 (m, 6H), 6.87 (d, *J* = 8.4 Hz, 2H), 3.90 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 143.2, 133.1, 132.8, 132.5, 130.5, 129.4, 129.1, 128.4, 126.7, 126.3, 126.1, 121.4, 115.1, 98.0, 77.9; IR (neat): 3403(bs), 2228(s), 1635, 1405, 1107, 1080, 883, 739; HRESIMS Calcd for $[C_{20}H_{14}NaOS]^+$ (M + Na^+) 325.0658, found

325.0652.

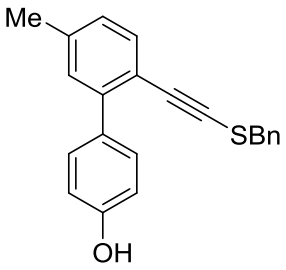
2'-((benzylthio)ethynyl)-4'-methyl-[1,1'-biphenyl]-4-ol (1d)



1d

Compound **1d** was prepared in 42% yield (132.7 mg) over 5 steps as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H), 7.27 – 7.23 (m, 5H), 7.21 – 7.19 (m, 2H), 7.11 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.83 – 6.80 (m, 2H), 5.23 (s, 1H), 3.86 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 140.1, 136.7, 136.2, 133.2, 133.0, 130.4, 129.1, 128.9, 128.5, 127.6, 121.3, 114.8, 94.6, 81.3, 40.3, 20.7; IR (neat): 3309(bs), 2193(s), 1511, 1262, 910, 883, 717, 686; HRESIMS Calcd for $[C_{22}H_{18}NaOS]^+$ (M + Na^+) 353.0971, found 353.0973.

2'-((benzylthio)ethynyl)-5'-methyl-[1,1'-biphenyl]-4-ol (1e)

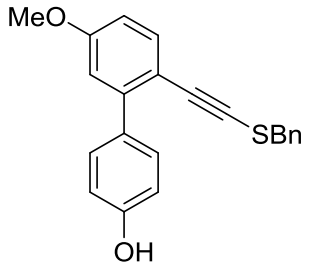


1e

Compound **1e** was prepared in 71% yield (224.3 mg) over 5 steps as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.39 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.28 – 7.25 (m, 3H), 7.22 – 7.20 (m, 2H), 7.13 (s, 1H), 7.04 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.84 – 6.81 (m, 2H), 5.05 (s, 1H), 3.87 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 142.9, 138.3, 136.8, 133.2, 132.8, 130.5, 130.0, 128.9, 128.5, 127.6, 127.4, 118.6, 114.8, 94.5, 80.7, 40.3, 21.4; IR (neat): 3447(bs), 2165(s), 1653, 1455, 1264, 1080, 819,

698; HRESIMS Calcd for $[C_{22}H_{18}NaOS]^+$ (M + Na^+) 353.0971, found 353.0956.

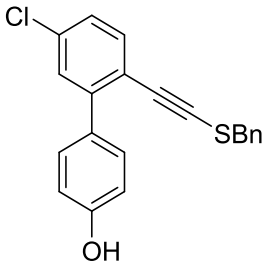
2'-((benzylthio)ethynyl)-5'-methoxy-[1,1'-biphenyl]-4-ol (1f)



1f

Compound **1f** was prepared in 51% yield (161.6 mg) over 5 steps as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 3H), 7.25 – 7.18 (m, 5H), 6.84 – 6.80 (m, 3H), 6.75 (dd, *J* = 8.6, 2.6 Hz, 1H), 5.27 (brs, 1H), 3.83 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 155.3, 145.0, 136.9, 134.6, 132.9, 130.4, 128.9, 128.5, 127.5, 114.8, 114.6, 113.9, 112.5, 94.2, 79.6, 55.3, 40.3; IR (neat): 3431(bs), 2160(s), 1600, 1517, 1481, 1221, 1173, 831, 698; HRESIMS Calcd for $[C_{22}H_{18}NaO_2S]^+$ (M + Na^+) 369.0920, found 369.0916.

2'-((benzylthio)ethynyl)-5'-chloro-[1,1'-biphenyl]-4-ol (1g)

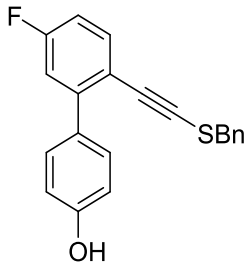


1g

Compound **1g** was prepared in 66% yield (208.6 mg) over 5 steps as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.38 (m, 2H), 7.33 – 7.27 (m, 5H), 7.20 – 7.17 (m, 3H), 6.85 – 6.82 (m, 2H), 5.12 (s, 1H), 3.87 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 144.4, 136.6, 135.3, 133.8, 131.8, 130.4, 129.2, 128.9, 128.5, 127.7, 126.7, 120.1, 115.0, 93.5, 82.9, 40.2; IR (neat): 3439(bs), 2160(s), 1610, 1515, 1237, 1174, 1095, 837; HRESIMS Calcd for $[C_{21}H_{15}ClNaOS]^+$ (M + Na^+) 373.0424, found

373.0438.

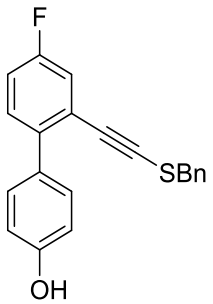
2'-((benzylthio)ethynyl)-5'-fluoro-[1,1'-biphenyl]-4-ol (1h)



1h

Compound **1h** was prepared in 37% yield (116.9 mg) over 5 steps as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 3H), 7.25 – 7.20 (m, 3H), 7.19 – 7.16 (m, 2H), 6.98 (dd, *J* = 9.6, 2.8 Hz, 1H), 6.90 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.32 (brs, 1H), 3.83 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1 (d, *J* = 249.0 Hz), 155.7, 145.4 (d, *J* = 8.0 Hz), 136.6, 134.7 (d, *J* = 8.0 Hz), 131.6, 130.4, 128.9, 128.5, 127.6, 117.5 (d, *J* = 3.0 Hz), 116.0 (d, *J* = 22.0 Hz), 115.0, 113.7 (d, *J* = 22.0 Hz), 93.5, 81.2, 40.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.0; IR (neat): 3362(bs), 2167(s), 1701, 1598, 1517, 1259, 1182, 831, 699; HRESIMS Calcd for $[C_{21}H_{15}FNaOS]^+$ (M + Na^+) 357.0720, found 357.0716.

2'-((benzylthio)ethynyl)-5'-methoxy-[1,1'-biphenyl]-4-ol (1i)

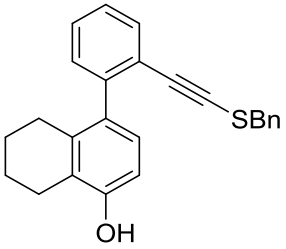


1i

Compound **1i** was prepared in 49% yield (155.8 mg) over 5 steps as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.32 – 7.27 (m, 4H), 7.23 – 7.21 (m, 2H), 7.10 (dd, *J* = 9.6, 2.8 Hz, 1H), 7.05 – 7.01 (m, 1H), 6.87 (d, *J* = 8.4 Hz, 2H), 4.54 (brs, 1H), 3.91 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1 (d, *J* = 246.0

Hz), 155.5, 139.1 (d, J = 3.0 Hz), 136.5, 132.0, 130.8 (d, J = 9.0 Hz), 130.5, 128.9, 128.6, 127.7, 123.1 (d, J = 10.0 Hz), 118.7 (d, J = 23.0 Hz), 115.3 (d, J = 21.0 Hz), 115.0, 93.6, 83.2, 40.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.5; IR (neat): 3383(bs), 2162(s), 1701, 1406, 1111, 1032, 880, 697; HRESIMS Calcd for $[C_{21}H_{15}FNaOS]^+$ (M + Na^+) 357.0720, found 357.0719.

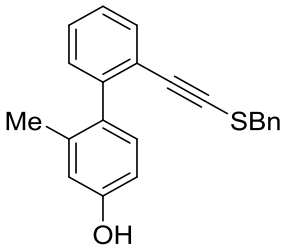
4-(2-((benzylthio)ethynyl)phenyl)-5,6,7,8-tetrahydronaphthalen-1-ol (1j)



1j

Compound **1j** was prepared in 56% yield (177.6 mg) over 5 steps as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, J = 7.2, 1.2 Hz, 1H), 7.30 – 7.22 (m, 5H), 7.18 (dd, J = 7.2, 1.2 Hz, 1H), 7.13 – 7.09 (m, 2H), 6.92 (d, J = 8.0 Hz, 1H), 6.68 (d, J = 8.0 Hz, 1H), 4.92 (brs, 1H), 3.71 (s, 2H), 2.71 (t, J = 6.4 Hz, 2H), 2.63 – 2.55 (m, 1H), 2.42 – 2.34 (m, 1H), 1.83 – 1.77 (m, 2H), 1.70 – 1.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 143.8, 137.0, 136.8, 133.4, 131.2, 130.0, 128.7, 128.6, 127.6, 127.5, 126.6, 123.5, 123.0, 111.3, 94.2, 82.1, 40.7, 27.9, 23.2, 22.8, 22.5; IR (neat): 3446(bs), 2162(s), 1652, 1558, 1257, 1057, 771, 699; HRESIMS Calcd for $[C_{25}H_{22}NaOS]^+$ (M + Na^+) 393.1284, found 393.1286.

2'-((benzylthio)ethynyl)-2-methyl-[1,1'-biphenyl]-4-ol (1k)

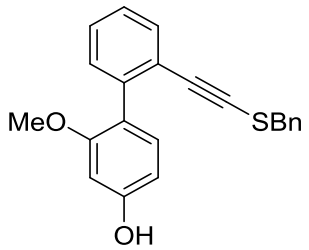


1k

Compound **1k** was prepared in 33% yield (124.3 mg) over 5 steps as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, J = 7.6, 1.2 Hz, 1H), 7.28 – 7.23 (m, 5H), 7.17

(dd, J = 7.2, 1.2 Hz, 1H), 7.13 – 7.11 (m, 2H), 7.06 (d, J = 8.4 Hz, 1H), 6.73 (d, J = 2.4 Hz, 1H), 6.69 (dd, J = 8.0, 2.4 Hz, 1H), 3.72 (s, 2H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 143.3, 137.9, 136.8, 133.5, 131.4, 131.0, 130.0, 128.8, 128.5, 127.6, 126.7, 123.4, 116.5, 112.2, 94.1, 82.1, 40.6, 20.1; IR (neat): 3369(bs), 2164(s), 1607, 1473, 1236, 1160, 760, 698; HRESIMS Calcd for $[C_{22}H_{18}NaOS]^+$ ($M + Na^+$) 353.0971, found 353.0977.

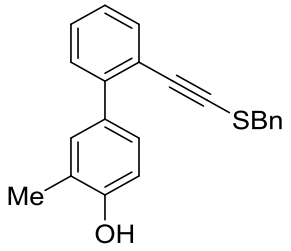
2'-((benzylthio)ethynyl)-2-methoxy-[1,1'-biphenyl]-4-ol (1l)



1l

Compound **1l** was prepared in 27% yield (105.3 mg) over 5 steps as an orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.2 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.42 (dd, J = 7.2, 1.2 Hz, 1H), 7.38 – 7.30 (m, 6H), 7.28 (d, J = 1.6 Hz, 1H), 7.15 (dd, J = 8.4, 1.6 Hz, 1H), 7.07 (d, J = 8.0 Hz, 1H), 5.55 (brs, 1H), 3.97 (s, 2H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 145.2, 143.1, 136.6, 132.8, 132.5, 129.2, 128.8, 128.4, 128.2, 127.6, 126.5, 122.1, 121.4, 114.0, 112.0, 94.5, 81.9, 55.9, 40.2; IR (neat): 3506(bs), 2162(s), 1519, 1477, 1263, 1205, 760, 698; HRESIMS Calcd for $[C_{22}H_{18}NaO_2S]^+$ ($M + Na^+$) 369.0920, found 369.0922.

2'-((benzylthio)ethynyl)-3-methyl-[1,1'-biphenyl]-4-ol (1m)

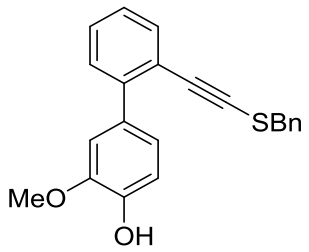


1m

Compound **1m** was prepared in 54% yield (170.6 mg) over 5 steps as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 7.6 Hz, 1H), 7.33 – 7.21 (m, 8H), 7.20 –

7.17 (m, 2H), 6.78 (d, J = 8.4 Hz, 1H), 4.04 (brs, 1H), 3.87 (s, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 143.1, 136.7, 133.0, 132.6, 131.8, 129.2, 128.9, 128.5, 128.1, 128.0, 127.6, 126.4, 123.2, 121.6, 114.4, 94.6, 81.8, 40.3, 15.8; IR (neat): 3415(bs), 2161(s), 1609, 1510, 1474, 1262, 757, 698; HRESIMS Calcd for $[C_{22}H_{18}NaOS]^+$ (M + Na^+) 353.0971, found 353.0963.

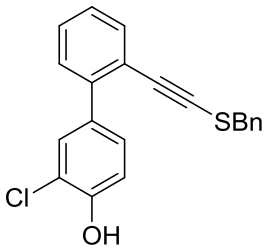
2'-((benzylthio)ethynyl)-3-methoxy-[1,1'-biphenyl]-4-ol (1n)



1n

Compound **1n** was prepared in 40% yield (124.0 mg) over 5 steps as an orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.6 Hz, 1H), 7.45 (dd, J = 7.6, 1.2 Hz, 1H), 7.42 – 7.38 (m, 1H), 7.36 – 7.33 (m, 3H), 7.31 – 7.27 (m, 3H), 7.26 (d, J = 1.6 Hz, 1H), 7.13 (dd, J = 8.0, 2.0 Hz, 1H), 7.06 (d, J = 8.4 Hz, 1H), 5.42 (brs, 1H), 3.95 (s, 2H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 145.2, 143.1, 136.6, 132.8, 132.4, 129.2, 128.8, 128.4, 128.2, 127.5, 126.5, 122.1, 121.3, 114.0, 112.0, 94.5, 81.9, 55.8, 40.2; IR (neat): 3510(bs), 2163(s), 1519, 1477, 1262, 1206, 923, 759, 698; HRESIMS Calcd for $[C_{22}H_{18}NaO_2S]^+$ (M + Na^+) 369.0920, found 369.0927.

2'-((benzylthio)ethynyl)-3-methoxy-[1,1'-biphenyl]-4-ol (1o)



1o

Compound **1o** was prepared in 69% yield (218.0 mg) over 5 steps as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 2.0 Hz, 1H), 7.40 (d, J = 7.6 Hz, 1H), 7.32 (dd, J = 8.4, 2.0 Hz, 1H), 7.27 – 7.18 (m, 8H), 7.00 (d, J = 8.4 Hz, 1H), 5.11 (s, 1H),

3.89 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 141.6, 136.5, 133.6, 132.6, 129.6, 129.3, 129.1, 128.9, 128.5, 128.2, 127.6, 126.9, 121.6, 119.6, 116.0, 94.0, 82.5, 40.3; IR (neat): 3509(bs), 2163(s), 1507, 1472, 1288, 1184, 872, 761, 698; HRESIMS Calcd for $[C_{21}H_{15}ClNaOS]^+$ (M + Na^+) 373.0424, found 373.0412.

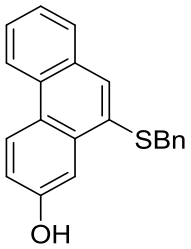
3. General Procedures and Transformations

3.1 General procedure for the synthesis of the phenanthrols 2

1 **2**

To a dry 4-mL vial were added alkynyl thioether **1** (0.1 mmol) and the solution of $HNTf_2$ in DCE (0.01 M, 0.01 mmol, 1 mL). The resulting mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. Upon completion, the mixture was quenched by Et_3N (0.012 mmol, 1.7 μL), concentrated under reduced pressure and the residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate) to afford the desired phenanthrol **2**.

10-(benzylthio)phenanthren-2-ol (2a)

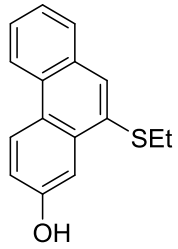


2a

Compound **2a** was prepared in 99% yield (31.5 mg) according to the general procedure (Table 2, entry 1). The product was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 5/1) as a white solid (mp 147–148 °C). ^{1}H NMR (400 MHz, CD_3OD) δ 8.58 (d, J = 8.8 Hz, 1H), 8.51 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 2.4 Hz, 1H),

7.66 – 7.64 (m, 2H), 7.54 – 7.50 (m, 1H), 7.44 – 7.40 (m, 1H), 7.25 – 7.15 (m, 6H), 4.17 (s, 2H); ^{13}C NMR (100 MHz, CD_3OD) δ 157.8, 138.9, 134.4, 131.9, 131.8, 131.4, 131.2, 130.1, 129.3, 129.0, 128.1, 127.8, 126.6, 126.0, 125.3, 122.9, 118.3, 110.1, 39.5; IR (neat): 3446(bs), 1635, 1540, 1452, 1219, 980, 745, 699; HRESIMS Calcd for $[C_{21}H_{16}NaOS]^+$ (M + Na^+) 339.0814, found 339.0819.

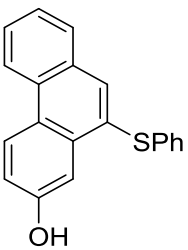
10-(ethylthio)phenanthren-2-ol (2b)



2b

Compound **2b** was prepared in 99% yield (25.2 mg) according to the general procedure (Table 2, entry 2). The product was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 5/1) as a white solid (mp 223–226 °C). ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.03 (s, 1H), 8.67 (d, *J* = 8.0 Hz, 1H), 8.59 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.79 (s, 1H), 7.65 (d, *J* = 1.6 Hz, 1H), 7.58 – 7.48 (m, 2H), 7.23 (d, *J* = 8.8 Hz, 1H), 3.12 (q, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H).; ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 156.6, 132.1, 130.8, 130.1, 128.9, 127.7, 126.5, 125.8, 125.7, 125.2, 123.0, 122.0, 117.6, 108.2, 26.1, 13.9; IR (neat): 3423(bs), 1652, 1559, 1540, 1456, 1220, 901, 743; HRESIMS Calcd for $[C_{16}H_{14}NaOS]^+$ (M + Na^+) 277.0658, found 277.0651.

10-(phenylthio)phenanthren-2-ol (2c)

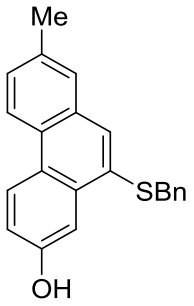


2c

Compound **2c** was prepared in 99% yield (29.9 mg) according to the general procedure (Table 2, entry 3). The product was purified by chromatography on silica gel (eluent:

hexanes/ethyl acetate = 6/1) as a white solid (mp 173–175 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.93 (brs, 1H), 8.71 (d, J = 8.8Hz, 1H), 8.67 (d, J = 8.4 Hz, 1H), 8.13 (s, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 2.0 Hz, 1H), 7.69 – 7.65 (m, 1H), 7.60 – 7.52 (m, 1H), 7.29 – 7.23 (m, 3H), 7.20 – 7.16 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.0, 136.1, 135.2, 133.0, 130.7, 129.8, 129.4, 128.6, 128.0, 127.9, 127.1, 126.2, 125.9, 125.4, 123.7, 122.2, 118.0, 109.3; IR (neat): 3433(bs), 1652, 1635, 1540, 1456, 1217, 741, 687; HRESIMS Calcd for $[C_{20}H_{14}NaOS]^{+}$ (M + Na^{+}) 325.0658, found 325.0663.

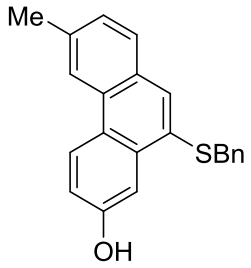
10-(benzylthio)-7-methylphenanthren-2-ol (2d)



2d

Compound **2d** was prepared in 99% yield (32.7 mg) according to the general procedure (Table 2, entry 4). The product was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 5/1) as a white solid (mp 153–156 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.96 (s, 1H), 8.61 (d, J = 9.2 Hz, 1H), 8.48 (d, J = 8.4 Hz, 1H), 7.74 (s, 1H), 7.65 (d, J = 2.0 Hz, 1H), 7.59 (s, 1H), 7.43 – 7.40 (m, 3H), 7.32 – 7.28 (m, 2H), 7.25 – 7.19 (m, 2H), 4.36 (s, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 156.3, 137.1, 134.9, 131.5, 130.5, 130.1, 129.0, 128.4, 128.3, 127.2, 127.1, 127.0, 126.4, 125.0, 123.1, 122.0, 117.5, 108.1, 36.6, 20.9; IR (neat): 3407(bs), 1652, 1506, 1362, 1028, 953, 698; HRESIMS Calcd for $[C_{22}H_{18}NaOS]^{+}$ (M + Na^{+}) 353.0971, found 353.0958.

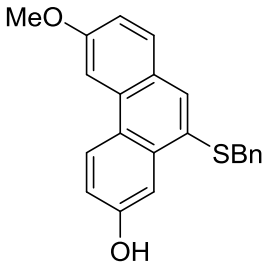
10-(benzylthio)-6-methylphenanthren-2-ol (2e)



2e

Compound **2e** was prepared in 95% yield (31.4 mg) according to the general procedure (Table 2, entry 5). The product was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 5/1) as a white solid (mp 138–139 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, J = 8.8 Hz, 1H), 8.30 (s, 1H), 7.86 (d, J = 2.8 Hz, 1H), 7.71 (s, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 7.2 Hz, 1H), 7.24 – 7.21 (m, 6H), 5.25 (s, 1H), 4.14 (s, 2H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 137.6, 136.9, 133.4, 131.8, 130.1, 129.1, 129.0, 128.6, 128.4, 128.0, 127.7, 127.2, 125.0, 124.8, 121.8, 116.5, 109.1, 39.6, 22.2; IR (neat): 3446(bs), 1636, 1452, 1219, 1059, 996, 736, 698; HRESIMS Calcd for $[C_{22}H_{18}NaOS]^+$ (M + Na^+) 353.0971, found 353.0963.

10-(benzylthio)-6-methoxyphenanthren-2-ol (2f)

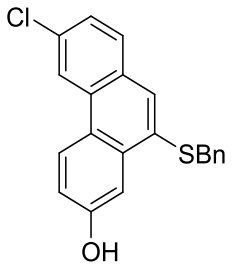


2f

Compound **2f** was prepared in 92% yield (31.9 mg) according to the general procedure (Table 2, entry 6). The product was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 4/1) as a white solid (mp 176–180 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, J = 8.8 Hz, 1H), 7.89 (s, 1H), 7.85 (s, 1H), 7.68 (s, 1H), 7.59 (d, J = 8.8 Hz, 1H), 7.21 – 7.11 (m, 7H), 5.55 (s, 1H), 4.07 (s, 2H), 3.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 154.8, 137.7, 133.8, 132.6, 131.6, 129.7, 129.0, 128.4, 127.1, 127.0, 125.4, 125.1, 124.5, 116.4, 116.0, 109.8, 103.4, 55.4, 39.8; IR (neat):

3403(bs), 1615, 1500, 1452, 1222, 1165, 818, 696; HRESIMS Calcd for $[C_{22}H_{18}NaO_2S]^+$ (M + Na^+) 369.0920, found 369.0918.

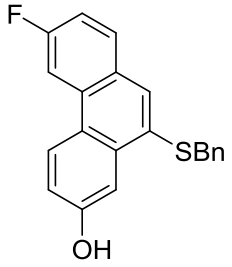
10-(benzylthio)-6-chlorophenanthren-2-ol (2g)



2g

Compound **2g** was prepared in 96% yield (33.3 mg) according to the general procedure (Table 2, entry 7). The product was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 6/1) as a yellow solid (mp 171–173 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.16 (s, 1H), 8.70 (d, J = 8.8 Hz, 1H), 8.66 (s, 1H), 7.85 – 7.83 (m, 2H), 7.64 (d, J = 2.0 Hz, 1H), 7.51 (d, J = 8.4 Hz, 1H), 7.43 (d, J = 7.2 Hz, 2H), 7.32 – 7.28 (m, 2H), 7.25 – 7.22 (m, 2H), 4.39 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.2, 136.9, 132.1, 131.6, 131.4, 130.2, 129.6, 129.1, 128.5, 128.4, 127.3, 125.9, 125.8, 125.3, 121.9, 121.5, 117.9, 108.0, 36.4; IR (neat): 3443(bs), 1653, 1616, 1488, 1214, 1085, 860, 746; HRESIMS Calcd for $[C_{21}H_{15}ClNaOS]^+$ (M + Na^+) 373.0424, found 373.0425.

10-(benzylthio)-6-fluorophenanthren-2-ol (2h)

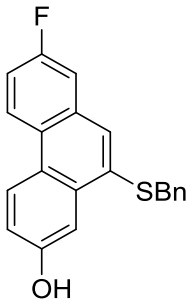


2h

Compound **2h** was prepared in 99% yield (33.1 mg) according to the general procedure (Table 2, entry 8). The product was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 5/1) as a white solid (mp 123–126 °C). ^{1}H NMR (400 MHz,

$CDCl_3$) δ 8.40 (d, *J* = 8.8 Hz, 1H), 8.08 (dd, *J* = 11.2, 2.0 Hz, 1H), 7.86 (d, *J* = 2.8 Hz, 1H), 7.67 – 7.62 (m, 2H), 7.24 – 7.20 (m, 7H), 5.50 (s, 1H), 4.13 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8 (d, *J* = 245.8 Hz), 155.1, 137.4, 133.5, 131.6 (d, *J* = 9.0 Hz), 130.9, 130.2, 130.1, 129.6 (d, *J* = 2.0 Hz), 129.0, 128.4, 127.2, 125.3, 124.3 (d, *J* = 4.0 Hz), 116.9, 114.9 (d, *J* = 24.0 Hz), 109.8, 107.1 (d, *J* = 20.0 Hz), 39.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.6; IR (neat): 3416(bs), 1616, 1496, 1212, 1171, 1078, 821, 698, 654; HRESIMS Calcd for $[C_{21}H_{15}FNaOS]^+$ (M + Na^+) 357.0720, found 357.0724.

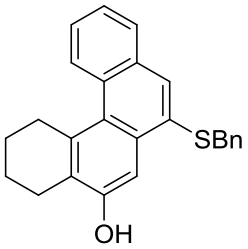
10-(benzylthio)-7-fluorophenanthren-2-ol (2i)



2i

Compound **2i** was prepared in 91% yield (30.3 mg) according to the general procedure (Table 2, entry 9). The product was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 5/1) as a white solid (mp 147–149 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.98 (brs, 1H), 8.67 – 8.61 (m, 2H), 7.83 (s, 1H), 7.65 – 7.60 (m, 2H), 7.46 – 7.42 (m, 2H), 7.40 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.26 – 7.22 (m, 2H), 4.39 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.1 (d, *J* = 241.0 Hz), 156.5, 136.8, 132.7, 131.3 (d, *J* = 9.0 Hz), 131.2, 129.1, 128.5, 127.3, 125.7 (d, *J* = 1.0 Hz), 125.2, 124.8 (d, *J* = 5.0 Hz), 124.7, 122.7, 118.0, 115.0 (d, *J* = 23.0 Hz), 111.4 (d, *J* = 20.0 Hz), 108.0, 36.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.1; IR (neat): 3377(bs), 1617, 1487, 1455, 1231, 1164, 804, 697; HRESIMS Calcd for $[C_{21}H_{15}FNaOS]^+$ (M + Na^+) 357.0720, found 357.0709.

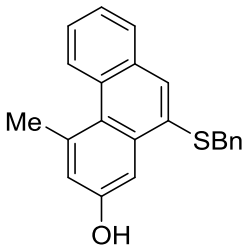
7-(benzylthio)-1,2,3,4-tetrahydrobenzo[*c*]phenanthren-5-ol (2j)



2j

Compound **2j** was prepared in 81% yield (30.1 mg) according to the general procedure (Table 2, entry 10). The product was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 5/1) as a white solid (mp 132–134 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, J = 8.4 Hz, 1H), 7.81 (s, 1H), 7.70 (dd, J = 7.2, 1.2 Hz, 1H), 7.66 (s, 1H), 7.51 – 7.44 (m, 2H), 7.26 – 7.23 (m, 5H), 5.28 (brs, 1H), 4.16 (s, 2H), 3.51 (t, J = 5.6 Hz, 2H), 2.93 (t, J = 6.8 Hz, 2H), 2.02 – 1.96 (m, 2H), 1.80 – 1.74 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 138.1, 137.5, 132.1, 131.8, 130.8, 130.4, 130.2, 129.0, 128.4, 128.0, 127.6, 127.2, 125.7, 125.6, 125.0, 106.9, 39.4, 34.4, 24.1, 24.0, 22.1; IR (neat): 3384(bs), 1652, 1596, 1456, 1257, 1056, 747, 698; HRESIMS Calcd for $[C_{25}H_{22}NaOS]^+$ (M + Na^+) 393.1284, found 393.1278.

10-(benzylthio)-4-methylphenanthren-2-ol (2k)

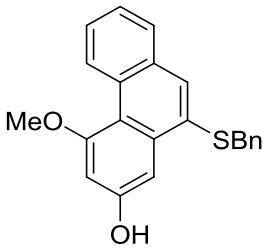


2k

Compound **2k** was prepared in 94% yield (31.1 mg) according to the general procedure (Table 2, entry 11). The product was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 5/1) as a white solid (mp 133–134 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.63 (d, J = 8.4 Hz, 1H), 7.81 (dd, J = 7.6, 1.2 Hz, 1H), 7.77 (s, 1H), 7.63 (d, J = 2.4 Hz, 1H), 7.55 – 7.46 (m, 2H), 7.40 – 7.38 (m, 2H), 7.29 – 7.25 (m, 2H), 7.23 – 7.19 (m, 1H), 7.10 (d, J = 2.4 Hz, 1H), 4.32 (s, 2H), 2.97 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 155.3, 137.8, 137.1, 133.5, 131.2(3), 131.2(0), 129.9, 129.1, 128.4, 127.9, 127.2, 126.9, 126.2, 125.7, 125.0, 122.9, 121.5, 107.0, 36.7, 27.0; IR (neat): 3398(bs),

1653, 1558, 1418, 1283, 1106, 881, 779, 669; HRESIMS Calcd for $[C_{22}H_{18}NaOS]^+$ (M + Na^+) 353.0971, found 353.0979.

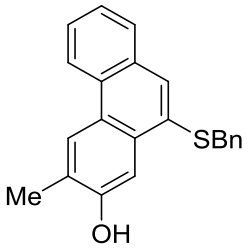
10-(benzylthio)-4-methoxyphenanthren-2-ol (2l)



2l

Compound **2l** was prepared in 99% yield (34.3 mg) according to the general procedure (Table 2, entry 12). The product was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 4/1) as a white solid (mp 176–180 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.86 (s, 1H), 8.66 (d, J = 8.4 Hz, 1H), 8.15 (s, 1H), 7.80 (d, J = 7.6 Hz, 1H), 7.71 (s, 1H), 7.69 (s, 1H), 7.58 – 7.53 (m, 1H), 7.52 – 7.47 (m, 1H), 7.41 – 7.39 (m, 2H), 7.32 – 7.27 (m, 2H), 7.24 – 7.20 (m, 1H), 4.34 (s, 2H), 4.03 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 149.1, 147.5, 137.3, 130.6, 130.4, 129.2, 128.6, 128.5, 127.8, 127.3, 126.2, 125.8, 125.6, 124.4, 124.0, 122.7, 108.9, 104.7, 56.0, 36.8; IR (neat): 3426(bs), 1597, 1271, 1221, 1145, 1026, 804, 698; HRESIMS Calcd for $[C_{22}H_{18}NaO_2S]^+$ (M + Na^+) 369.0920, found 369.0934.

10-(benzylthio)-3-methylphenanthren-2-ol (2m)

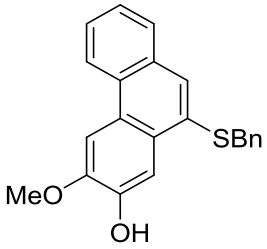


2m

Compound **2m** was prepared in 99% yield (32.7 mg) according to the general procedure (Table 2, entry 13). The product was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 5/1) as a white solid (mp 161–165 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.05 (s, 1H), 8.61 (d, J = 8.0 Hz, 1H), 8.56 (s, 1H), 7.79 (d, J = 7.6 Hz,

1H), 7.75 (d, J = 10.0 Hz, 2H), 7.56 – 7.53 (m, 1H), 7.49 – 7.42 (m, 3H), 7.32 – 7.23 (m, 3H), 4.37 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 155.4, 137.1, 130.5, 130.2, 130.1, 129.0, 128.8, 128.4, 127.7, 127.2, 126.7, 126.3, 125.6, 125.5, 125.2, 123.0, 122.0, 107.5, 36.6, 16.6; IR (neat): 3410(bs), 1623, 1451, 1270, 1134, 1021, 745, 696; HRESIMS Calcd for $[C_{22}H_{18}NaOS]^+$ (M + Na^+) 353.0971, found 353.0968.

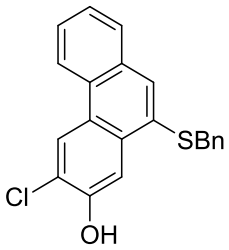
10-(benzylthio)-3-methoxyphenanthren-2-ol (2n)



2n

Compound **2n** was prepared in 99% yield (34.3 mg) according to the general procedure (Table 2, entry 14). The product was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 5/1) as a white solid (mp 182–188 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.82 (s, 1H), 8.68 (d, J = 7.6 Hz, 1H), 8.17 (s, 1H), 7.80 (d, J = 7.2 Hz, 1H), 7.77 – 7.69 (m, 2H), 7.58 – 7.48 (m, 2H), 7.45 –7.38 (m, 2H), 7.32 – 7.22 (m, 3H), 4.36 (s, 2H), 4.04 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 149.0, 147.4, 137.2, 130.4, 130.3, 129.0, 128.4, 127.7, 127.2, 126.0, 125.7, 125.5, 124.3, 123.9, 122.5, 108.9, 105.9, 104.7, 55.8, 36.7; IR (neat): 3422(bs), 1497, 1457, 1270, 1194, 1143, 1016, 752; HRESIMS Calcd for $[C_{22}H_{18}NaO_2S]^+$ (M + Na^+) 369.0920, found 369.0918.

10-(benzylthio)-3-chlorophenanthren-2-ol (2o)

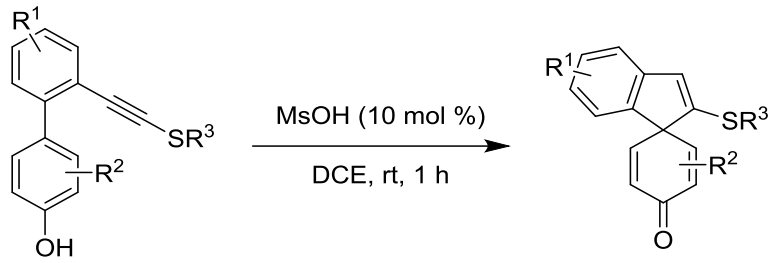


2o

Compound **2o** was prepared in 87% yield (30.5 mg) according to the general procedure (Table 2, entry 15). The product was purified by chromatography on silica gel (eluent:

hexanes/ethyl acetate = 5/1) as a white solid (mp 177–178 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.39 (d, *J* = 8.0 Hz, 1H), 8.08 (s, 1H), 7.69 – 7.64 (m, 2H), 7.60 – 7.56 (m, 1H), 7.52 – 7.48 (m, 1H), 7.25 – 7.20 (m, 5H), 5.82 (s, 1H), 4.16 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 137.1, 132.2, 131.2, 130.9, 130.5, 129.0, 128.5, 128.2, 127.3, 127.1, 126.5, 125.5, 123.8, 122.0, 121.5, 111.0, 39.2; IR (neat): 3437(bs), 1523, 1456, 1016, 1056, 939, 676; HRESIMS Calcd for $[C_{21}H_{15}ClNaOS]^+$ (M + Na^+) 373.0424, found 373.0429.

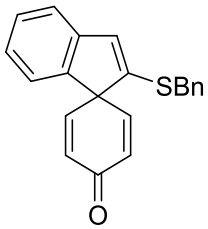
3.2. General procedure for the synthesis of the spirohexenones 3



1 **3**

To a dry 4-mL vial were added alkynyl thioether **1** (0.1 mmol) and the solution of MsOH in DCE (0.01 M, 0.01 mmol, 1 mL). The resulting mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. Upon completion, the mixture was quenched by Et_3N (0.012 mmol, 1.7 μL), concentrated under reduced pressure and the residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate) to afford the desired spirohexenone **3**.

2'-(benzylthio)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3a)

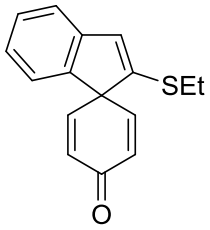


3a

Compound **3a** was prepared in 99% yield (31.3 mg) according to the general procedure (Table 3, entry 1). The product was purified by chromatography on silica gel (eluent:

hexanes/ethyl acetate = 5/1) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.23 (m, 7H), 7.13 – 7.10 (m, 1H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.71 (s, 1H), 6.49 (d, *J* = 10.0 Hz, 2H), 6.33 (d, *J* = 10.0 Hz, 2H), 4.13 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.0, 147.8, 145.9, 144.3, 141.1, 135.7, 130.8, 128.7, 128.6, 127.6, 127.3, 125.3, 123.3, 120.0, 61.0, 37.4; IR (neat): 2925, 1660(s), 1594, 1489, 1195, 1025, 753, 691; HRESIMS Calcd for $[C_{21}H_{16}NaOS]^+$ (M + Na^+) 339.0814, found 339.0819.

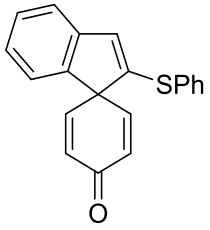
2'-(ethylthio)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3b)



3b

Compound **3b** was prepared in 99% yield (25.2 mg) according to the general procedure (Table 3, entry 2). The product was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 7/1) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 2H), 7.14 – 7.10 (m, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.66 (s, 1H), 6.52 (d, *J* = 10.0 Hz, 2H), 6.39 (d, *J* = 10.0 Hz, 2H), 2.96 (q, *J* = 7.2 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.1, 148.2, 146.6, 144.6, 141.0, 130.7, 128.7, 125.6, 125.0, 123.3, 119.7, 60.9, 26.6, 13.4; IR (neat): 2977, 1659(s), 1540, 1464, 1165, 1063, 840, 813, 697; HRESIMS Calcd for $[C_{16}H_{14}NaOS]^+$ (M + Na^+) 277.0658, found 277.0670.

2'-(phenylthio)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3c)

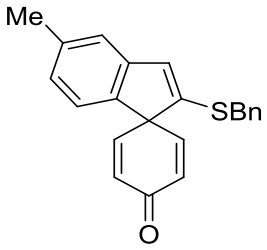


3c

Compound **3c** was prepared in 91% yield (27.5 mg) according to the general procedure

(Table 3, entry 3). The product was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 6/1) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.50 (m, 2H), 7.39 – 7.35 (m, 3H), 7.29 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.22 – 7.19 (m, 1H), 7.16 – 7.11 (m, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.61 (s, 1H), 6.48 – 6.43 (m, 2H), 6.39 – 6.33 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.0, 147.6, 146.0, 143.8, 141.9, 134.0, 131.4, 130.9, 130.7, 129.4, 128.9, 128.7, 125.7, 123.4, 120.5, 61.0; IR (neat): 2873, 1656(s), 1612, 1478, 1326, 1034, 920, 714, 689; HRESIMS Calcd for $[C_{20}H_{14}NaOS]^+$ (M + Na^+) 325.0658, found 325.0655.

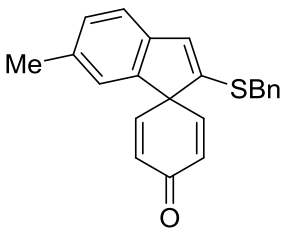
2'-(benzylthio)-5'-methylspiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3d)



3d

Compound **3d** was prepared in 99% yield (32.7 mg) according to the general procedure (Table 3, entry 4). The product was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 5/1) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 5H), 7.07 (s, 1H), 6.95 – 6.91 (m, 2H), 6.66 (s, 1H), 6.47 (d, *J* = 10.0 Hz, 2H), 6.32 (d, *J* = 10.0 Hz, 2H), 4.12 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.1, 148.1, 145.9, 144.5, 138.7, 138.1, 135.8, 130.7, 128.7, 128.6, 127.6, 127.5, 126.1, 123.0, 120.8, 60.8, 37.5, 21.5; IR (neat): 2923, 1662(s), 1623, 1540, 1456, 1062, 883, 712, 679; HRESIMS Calcd for $[C_{22}H_{18}NaOS]^+$ (M + Na^+) 353.0971, found 353.0965.

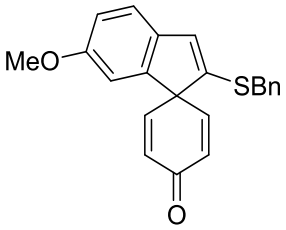
2'-(benzylthio)-6'-methylspiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3e)



3e

Compound **3e** was prepared in 97% yield (32.0mg) according to the general procedure (Table 3, entry 5). The product was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 6/1) as a white solid (mp 117–120 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 5H), 7.13 (d, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.86 (s, 1H), 6.69 (s, 1H), 6.49 (d, *J* = 10.0 Hz, 2H), 6.33 (d, *J* = 10.0 Hz, 2H), 4.11 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.1, 148.1, 144.3, 141.8, 141.4, 135.9, 135.5, 130.8, 129.3, 128.8, 128.7, 128.0, 127.6, 124.2, 119.8, 61.0, 37.6, 21.3; IR (neat): 2921, 1662(s), 1623, 1558, 1540, 1063, 863, 699; HRESIMS Calcd for $[C_{22}H_{18}NaOS]^+$ ($M + Na^+$) 353.0971, found 353.0979.

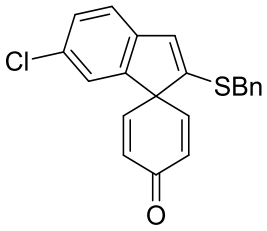
2'-(benzylthio)-6'-methoxyspiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3f)



3f

Compound **3f** was prepared in 95% yield (32.9 mg) according to the general procedure (Table 3, entry 6). The product was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 5/1) as a white solid (mp 109–113 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 5H), 7.15 (d, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.68 (s, 1H), 6.61 (s, 1H), 6.48 (d, *J* = 9.6 Hz, 2H), 6.31 (d, *J* = 9.6 Hz, 2H), 4.06 (s, 2H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.9, 158.3, 147.9, 143.1, 142.0, 137.2, 136.0, 130.7, 128.7, 128.5, 127.4, 120.6, 114.2, 109.6, 61.1, 55.5, 37.8; IR (neat): 2934, 1663(s), 1622, 1474, 1282, 1232, 864, 712, 696; HRESIMS Calcd for $[C_{22}H_{18}NaO_2S]^+$ ($M + Na^+$) 369.0920, found 369.0903.

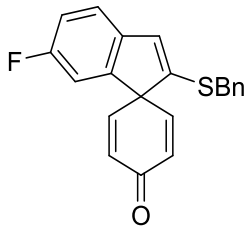
2'-(benzylthio)-6'-chlorospiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3g)



3g

Compound **3g** was prepared in 93% yield (32.6 mg) according to the general procedure (Table 3, entry 7). The product was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 5/1) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 6H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.01 (d, *J* = 1.6 Hz, 1H), 6.65 (s, 1H), 6.51 (d, *J* = 10.0 Hz, 2H), 6.31 (d, *J* = 10.0 Hz, 2H), 4.13 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.6, 146.9, 146.8, 142.9, 142.7, 135.5, 131.2, 131.1, 128.9, 128.7, 128.7, 127.7, 126.1, 123.8, 120.6, 60.8, 37.4; IR (neat): 2924, 1663(s), 1623, 1454, 1063, 860, 731, 697; HRESIMS Calcd for $[C_{21}H_{15}ClNaOS]^+$ (M + Na^+) 373.0424, found 373.0426.

2'-(benzylthio)-6'-fluorospiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3h)

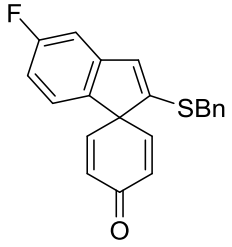


3h

Compound **3h** was prepared in 95% yield (31.7 mg) according to the general procedure (Table 3, entry 8). The product was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 5/1) as a yellow solid (mp 122–124 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 5H), 7.17 (dd, J = 8.4, 4.8 Hz, 1H), 7.00 – 6.95 (m, 1H), 6.76 (dd, J = 8.0, 2.4 Hz, 1H), 6.67 (s, 1H), 6.51 – 6.45 (m, 2H), 6.32 – 6.28 (m, 2H), 4.11 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.7, 161.3 (d, *J* = 246.0 Hz), 147.1, 145.4 (d, *J* = 4.0 Hz), 143.3 (d, *J* = 8.0 Hz), 140.3 (d, *J* = 2.0 Hz), 135.7, 131.1, 128.7, 128.6, 127.7, 126.7, 120.6 (d, *J* = 9.0 Hz), 115.5 (d, *J* = 22.0 Hz), 111.4 (d, *J* = 24.0 Hz), 60.9, 37.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.2; IR (neat): 2923, 1664(s), 1624, 1469, 1266, 1103, 865, 797, 713; HRESIMS Calcd for $[C_{21}H_{15}FNaOS]^+$ (M + Na^+) 357.0720, found

357.0723.

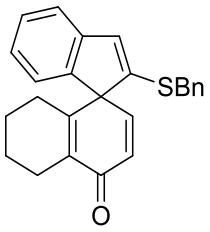
2'-(benzylthio)-5'-fluorospiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3i)



3i

Compound **3i** was prepared in 99% yield (33.3 mg) according to the general procedure (Table 3, entry 9). The product was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 5/1) as a yellow solid (mp 126–128 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 5H), 6.96 – 6.90 (m, 2H), 6.80 – 6.76 (m, 1H), 6.64 (s, 1H), 6.48 (d, *J* = 10.0 Hz, 2H), 6.30 (d, *J* = 10.0 Hz, 2H), 4.14 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.6, 163.4 (d, *J* = 244.0 Hz), 148.7, 147.4, 146.1 (d, *J* = 9.0 Hz), 136.3 (d, *J* = 2.0 Hz), 135.3, 130.7, 128.6, 127.6, 125.7, 124.2 (d, *J* = 9.0 Hz), 111.7 (d, *J* = 23.0 Hz), 107.2 (d, *J* = 24.0 Hz), 60.1, 37.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.2; IR (neat): 2956, 1662(s), 1622, 1462, 1226, 1134, 885, 771, 697; HRESIMS Calcd for $[C_{21}H_{15}FNaOS]^+$ ($M + Na^+$) 357.0720, found 357.0710.

2-(benzylthio)-5',6',7',8'-tetrahydro-4'H-spiro[indene-1,1'-naphthalen]-4'-one (3j)

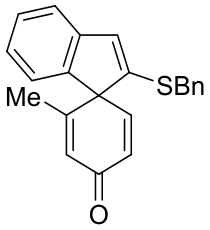


3j

Compound **3j** was prepared in 99% yield (36.7 mg) according to the general procedure (Table 3, entry 10). The product was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 6/1) as a white solid (mp 155–158 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.34 – 7.29 (m, 2H), 7.28 – 7.21 (m, 3H), 7.10 –7.05 (m, 1H), 6.93 (d, *J* = 7.2 Hz, 1H), 6.68 (s, 1H), 6.45 (d, *J* = 10.0 Hz, 1H), 6.19 (d, *J* = 10.0

Hz, 1H), 4.13 (s, 2H), 2.46 – 2.41 (m, 2H), 1.81 – 1.75 (m, 1H), 1.69 – 1.61 (m, 3H), 1.54 – 1.48 (m, 1H), 1.44 – 1.41 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.6, 151.6, 148.0, 147.8, 144.8, 143.6, 135.9, 135.6, 129.5, 128.7, 128.6, 128.2, 127.6, 126.3, 125.1, 122.5, 119.8, 63.6, 36.9, 25.1, 22.6, 21.9, 21.7; IR (neat): 2923, 1653(s), 1635, 1540, 1456, 1300, 1043, 772, 754; HRESIMS Calcd for $[C_{25}H_{22}NaOS]^+$ (M + Na^+) 393.1284, found 393.1284.

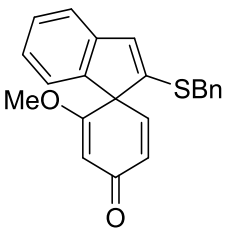
2'-(benzylthio)-2-methylspiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3k)



3k

Compound **3k** was prepared in 95% yield (31.4 mg) according to the general procedure (Table 3, entry 11). The product was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 5/1) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.37 (m, 2H), 7.34 – 7.31 (m, 2H), 7.28 – 7.25 (m, 3H), 7.12 – 7.08 (zm, 1H), 6.95 (d, J = 7.6 Hz, 1H), 6.71 (s, 1H), 6.44 (dd, J =10.0, 1.6 Hz, 1H), 6.41 – 6.37 (m, 1H), 6.24 (d, J = 10.0 Hz, 1H), 4.15 (s, 2H), 1.43 (d, J = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.0, 157.1, 148.5, 147.1, 144.8, 142.7, 135.8, 129.9, 129.7, 128.7(4), 128.7(3), 128.6, 127.7, 126.8, 125.3, 122.7, 119.9, 63.8, 37.0, 18.4; IR (neat): 2917, 1670(s), 1522, 1457, 1289, 1126, 1056, 792, 698; HRESIMS Calcd for $[C_{22}H_{18}NaOS]^+$ (M + Na^+) 353.0971, found 353.0965.

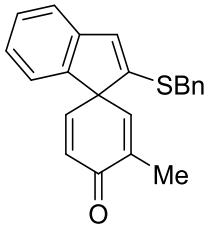
2'-(benzylthio)-2-methoxyspiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3l)



3l

Compound **3l** was prepared in 99% yield (34.3 mg) according to the general procedure (Table 3, entry 12). The product was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 5/1) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.34 (m, 2H), 7.33 – 7.29 (m, 2H), 7.28 – 7.23 (m, 3H), 7.13 – 7.08 (m, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.68 (s, 1H), 6.49 (d, *J* = 10.0 Hz, 1H), 6.24 (dd, *J* = 10.0, 2.4 Hz, 1H), 5.31 (d, *J* = 2.4 Hz, 1H), 4.12 (s, 2H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.1, 153.0, 148.4, 147.0, 143.9, 142.1, 135.8, 130.2, 128.6, 128.5, 128.4, 127.5, 126.3, 125.2, 123.0, 119.9, 114.3, 61.3, 55.0, 37.2; IR (neat): 2932, 1655(s), 1518, 1440, 1270, 1207, 1037, 867, 758, 696; HRESIMS Calcd for $[C_{22}H_{18}NaO_2S]^+$ (M + Na^+) 369.0920, found 369.0917.

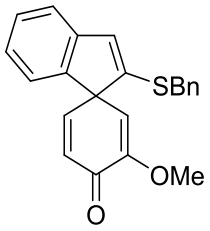
2'-(benzylthio)-3-methylspiro[cyclohexane-1,1'-indene]-2,5-dien-4-ol (3m)



3m

Compound **3m** was prepared in 99% yield (32.8 mg) according to the general procedure (Table 3, entry 13). The product was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 5/1) as a white solid (mp 183–185 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 4H), 7.29 – 7.25 (m, 2H), 7.25 – 7.21 (m, 1H), 7.13 – 7.09 (m, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.69 (s, 1H), 6.49 (d, *J* = 10.0 Hz, 1H), 6.31 (dd, *J* = 10.0, 2.8 Hz, 1H), 6.13 – 6.09 (m, 1H), 4.12 (s, 2H), 1.95 (d, *J* = 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.7, 147.5, 146.5, 144.3, 142.7, 141.7, 137.5, 135.8, 130.6, 128.8, 128.7, 128.5, 127.6, 126.8, 125.2, 123.2, 119.9, 61.3, 37.4, 16.1; IR (neat): 2921, 1662(s), 1636, 1462, 1393, 1140, 910, 752, 715; HRESIMS Calcd for $[C_{22}H_{18}NaOS]^+$ (M + Na^+) 353.0971, found 353.0978.

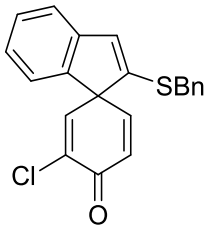
2'-(benzylthio)-3-methoxyspiro[cyclohexane-1,1'-indene]-2,5-dien-4-ol (3n)



3n

Compound **3n** was prepared in 99% yield (34.3 mg) according to the general procedure (Table 3, entry 14). The product was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 4/1) as a yellow solid (mp 164–169 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.24 (m, 7H), 7.14 – 7.09 (m, 1H), 7.04 (d, *J* = 7.2 Hz, 1H), 6.68 (s, 1H), 6.51 (d, *J* = 10.0 Hz, 1H), 6.27 (dd, *J* = 10.0, 2.4 Hz, 1H), 5.31 (d, *J* = 2.4 Hz, 1H), 4.13 (s, 2H), 3.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.2, 153.1, 148.5, 147.2, 144.0, 142.2, 135.9, 130.3, 128.7, 128.6, 128.5, 127.6, 126.4, 125.3, 123.1, 119.9, 114.3, 61.4, 55.1, 37.3; IR (neat): 2928, 1669(s), 1635, 1452, 1206, 1098, 895, 750, 714; HRESIMS Calcd for $[C_{22}H_{18}NaO_2S]^+$ (M + Na^+) 369.0920, found 369.0934.

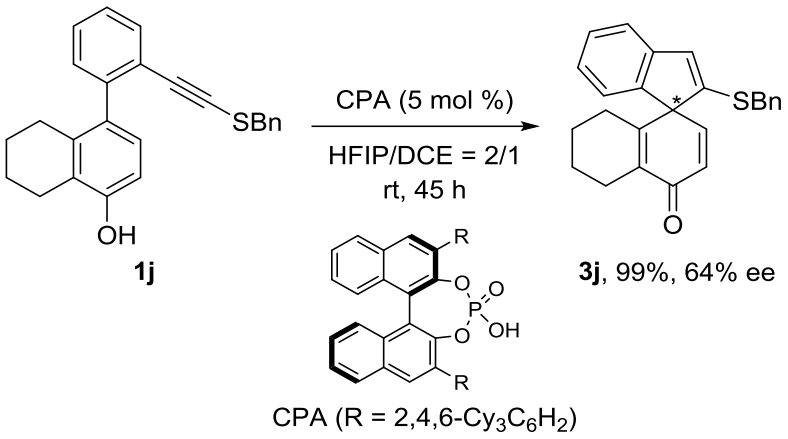
2'-(benzylthio)-3-chlorospiro[cyclohexane-1,1'-indene]-2,5-dien-4-one (3o)



3o

Compound **3o** was prepared in 85% yield (29.8 mg) according to the general procedure (Table 3, entry 15). The product was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 7/1) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 7H), 7.16 – 7.11 (m, 1H), 7.05 (d, *J* = 7.2 Hz, 1H), 6.74 (s, 1H), 6.58 (d, *J* = 10.0 Hz, 1H), 6.47 (d, *J* = 2.0 Hz, 1H), 6.33 (dd, *J* = 10.0, 2.4 Hz, 1H), 4.13 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.0, 147.9, 144.9, 144.2, 143.5, 140.0, 135.6, 134.5, 130.1, 129.1, 128.8, 128.7, 128.4, 127.7, 125.7, 123.4, 120.3, 62.8, 37.7; IR (neat): 2926, 1669(s), 1653, 1558, 1457, 1062, 831, 749, 711; HRESIMS Calcd for $[C_{21}H_{15}ClNaOS]^+$ (M + Na^+) 373.0424, found 373.0438.

3.3 Asymmetric dearomatization reaction



To a mixture of substrate **1j** (0.1 mmol, 37.1 mg) in HFIP (1.4 mL) and DCE (0.7 mL) was added CPA (0.005 mmol, 5.0 mg) at room temperature. The resulting mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. Upon completion, the mixture was quenched by Et_3N (0.012 mmol, 1.7 μL), concentrated under reduced pressure and the residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 5/1) to afford the desired spirohexenone **3j** in 99% yield (36.7 mg). $[\alpha]_D^{20}$ = -33.7º (c = 1.0, $CHCl_3$). 82:18 e.r. (determined by HPLC: Chiralpak IC Column, 10/90 i-PrOH/hexane, 1.0 mL/min, 254 nm; TR = 20.162 min (major), 23.022 min (minor).

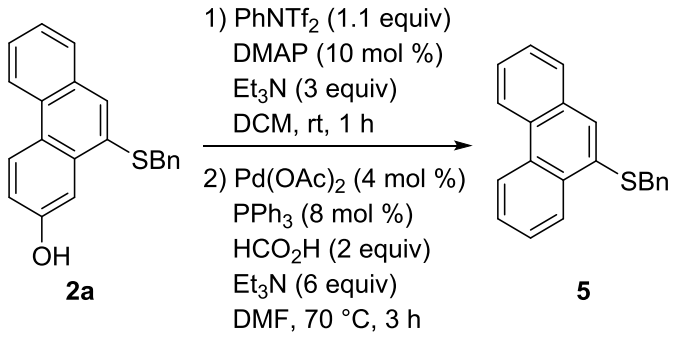
3.4 Synthetic transformations

((10-(benzylthio)phenanthren-2-yl)oxy)triisopropylsilane (4)

To a solution of **2a** (0.1 mmol, 31.6 mg) in DCM (1 mL) were added TIPSCl (0.12 mmol, 23.2 mg) and imidazole (0.12 mmol, 8.2 mg) sequentially. The mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. Upon completion, the mixture was filtered through a pad of silica gel and concentrated

under reduced pressure. The residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate) to give the desired product **4** in 95% yield (44.9 mg). White solid (mp 106–108 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, J = 9.2 Hz, 1H), 8.52 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 2.4 Hz, 1H), 7.72 (s, 1H), 7.69 (d, J = 7.2 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.50 – 7.46 (m, 1H), 7.31 – 7.22 (m, 6H), 4.18 (s, 2H), 1.40 – 1.34 (m, 3H), 1.16 (d, J = 7.2 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 137.4, 133.0, 130.8, 130.7, 130.0, 128.9, 128.5, 128.0, 127.2, 126.8, 125.9, 125.1, 124.6, 122.0, 121.2, 114.3, 39.2, 18.1, 12.8; IR (neat): 2943, 1635, 1450, 1275, 1196, 993, 913, 749; HRESIMS Calcd for $[C_{30}H_{36}NaOSSi]^+$ (M + Na^+) 495.2148, found 495.2152.

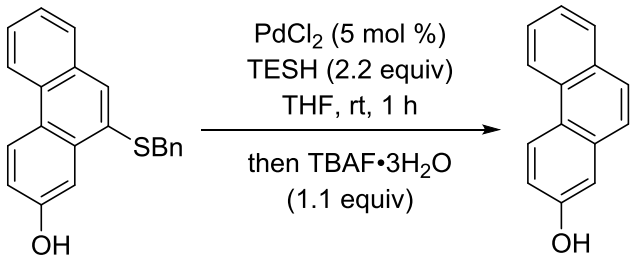
benzyl(phenanthren-9-yl)sulfane (5)



To a solution of **2a** (0.1 mmol, 31.7 mg) and Et_3N (0.3 mmol, 30.3 mg)in DCM (1 mL) was added DMAP (0.01 mmol, 1.2 mg) and $PhNTf_2$ (0.11 mmol, 39.5 mg) sequentially. The mixture was reacted at room temperature for 1 h. The progress of the reaction was monitored by TLC. Upon completion, the reaction was quenched with 1M HCl, extracted with DCM for 3 times, dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 15/1) to afford the desired triflate as a colorless oil. To the solution of triflate and Et_3N (0.6 mmol, 61.0 mg)in DMF (1 mL) was added formic acid (0.2 mmol, 9.2 mg) and PPh_3 (0.008 mmol, 2.1 mg) and $Pd(OAc)_2$ (0.004 mmol, 0.9 mg) sequentially. The mixture was reacted at 70 °C for 3 h. The progress of the reaction was monitored by TLC. Upon completion, the reaction was quenched with H_2O, extracted with EA for 3 times, dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 50/1) to afford the desired

product **5** (26.1 mg, 87% yield). Pale yellow solid (mp 98–99 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 – 8.64 (m, 1H), 8.58 (d, *J* = 8.0 Hz, 1H), 8.50 – 8.48 (m, 1H), 7.71 – 7.66 (m, 2H), 7.65 – 7.60 (m, 2H), 7.59 – 7.50 (m, 2H), 7.28 – 7.19 (m, 5H), 4.18 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 132.0, 131.7, 131.2, 130.6, 129.7, 129.2, 129.0, 128.5, 127.9, 127.2, 126.9, 126.8, 126.6, 125.6, 123.0, 122.5, 39.0; IR (neat): 3059, 3027, 2923, 1959, 1585, 1491, 1450, 1429, 745, 721; HRESIMS Calcd for $[C_{21}H_{16}NaS]^+$ (M + Na^+) 323.0865, found 323.0871.

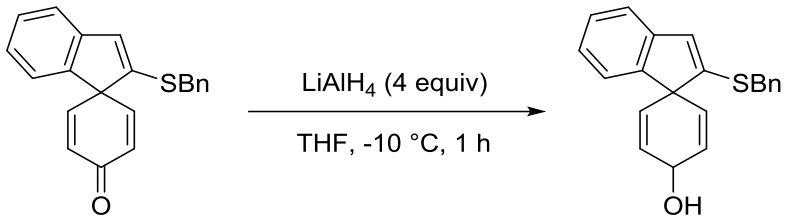
phenanthren-2-ol (6)



2a **6**

To a solution of **2a** (0.1 mmol, 31.6 mg) in THF (1 mL) was added $PdCl_2$ (0.005 mmol, 0.9 mg) and triethylsilane (0.22 mmol, 25.3 mg) sequentially. The mixture was reacted at room temperature for 1 h. The progress of the reaction was monitored by TLC. Upon completion, the mixture was added Tetrabutylammonium fluoride trihydrate (0.11 mmol, 34.7 mg), then quenched with NH_4Cl aqueous solution, extracted with EA for 3 times, dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 5/1) to afford the desired product **6** (17.7 mg, 91% yield). White solid (mp 158–164 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.55 (s, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 8.9 Hz, 1H), 7.64 – 7.58 (m, 2H), 7.55 – 7.51 (m, 1H), 7.24 – 7.19 (m, 2H), 5.15 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 133.6, 131.0, 130.4, 128.6, 127.7, 126.7, 126.0, 125.7, 124.8, 124.6, 122.1, 116.6, 111.8; IR (neat): 3440(bs), 2029, 1959, 1620, 1464, 1423, 1261, 810, 741; HRESIMS Calcd for $[C_{14}H_{10}NaO]^+$ (M + Na^+) 217.0624, found 217.0614.

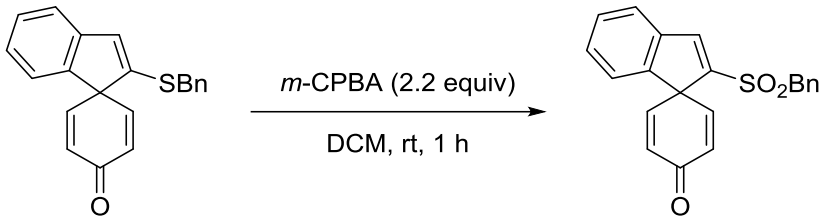
2'-(benzylthio)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-ol (7)



3a **7**, 99% (dr =6:1)

To a solution of **3a** (0.1 mmol, 31.6 mg) in THF (1 mL) was added $LiAlH_4$ (0.4 mmol, 15.6 mg) in THF (1 mL) slowly at -10 °C and stirred at this temperature for 1 h. The progress of the reaction was monitored by TLC. Upon completion, the mixture was quenched with 10% NaOH (aq), extracted with ethyl acetate for 3 times, dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 7/1) to give **7** in 99% yield (31.5 mg) with 6:1 dr. White solid (mp 139–143 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.34 – 7.29 (m, 2H), 7.28 – 7.18 (m, 3H), 7.11 – 7.03 (m, 2H), 6.53 (s, 1H), 6.23 (dd, J = 10.0, 3.6 Hz, 2H), 5.34 (d, J = 9.6 Hz, 2H), 4.76 – 4.64 (m, 1H), 4.11 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 148.1, 143.2, 136.2, 129.9, 129.8, 128.9, 128.6, 127.7, 127.5, 125.2, 124.7, 123.4, 119.5, 61.6, 58.3, 37.4; IR (neat): 3449(bs), 2923, 1636, 1457, 1093, 1052, 747, 697; HRESIMS Calcd for $[C_{21}H_{18}NaOS]^+$ (M + Na^+) 341.0971, found 341.0966.

2'-(benzylsulfonyl)spiro[cyclohexane-1,1'-indene]-2,5-dien-4-ol (8)

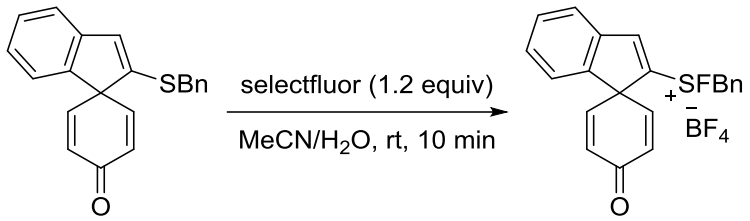


3a **8**, 99%

To a solution of **3a** (0.1 mmol, 31.6 mg) in DCM (2 mL) was added *m*-CPBA (0.22 mmol, 38.0 mg) and the mixture was reacted at room temperature for 1 h. The progress of the reaction was monitored by TLC. Upon completion, the reaction was quenched with $NaHCO_3$, extracted with DCM for 3 times, dried over $MgSO_4$ and concentrated

under vacuum. The residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 1/1) to afford the desired product **8** (34.5 mg, 99% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.56 – 7.52 (m, 1H), 7.45 – 7.42 (m, 2H), 7.38 – 7.32 (m, 5H), 7.17 – 7.13 (m, 1H), 6.58 (d, *J* = 10.0 Hz, 2H), 6.33 (d, *J* =10.0 Hz, 2H), 4.31 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.2, 147.2, 144.6, 144.4, 144.2, 139.6, 131.4, 131.0, 130.5, 129.5, 129.1, 128.9, 127.2, 125.1, 124.2, 62.1, 58.5; IR (neat): 2949, 1698(s), 1574, 1416, 1306, 1263, 748, 720; HRESIMS Calcd for $[C_{21}H_{16}NaO_3S]^+$ ($M + Na^+$) 371.0712, found 371.0714.

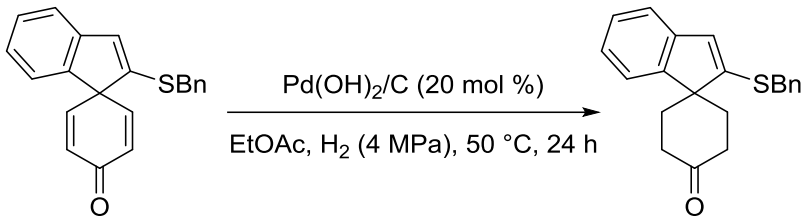
benzylfluoro(4-oxospiro[cyclohexane-1,1'-indene]-2,5-dien-2'-yl)sulfonium tetrafluoroborate (9)



3a **9**, 78%

To a solution of **3a** (0.1 mmol, 31.6 mg) in MeCN (0.9 mL) and H_2O (90 uL) was added selectfluor (0.12 mmol, 42.5 mg), and the mixture was stirred at room temperature for 10 min. The progress of the reaction was monitored by TLC. Upon completion, the reaction was extracted with ethyl acetate for 3 times, dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 1/1) to afford the desired product **9** (32.9 mg, 78% yield). White solid (mp 196–197 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.44 – 7.39 (m, 1H), 7.37 – 7.32 (m, 4H), 7.24 – 7.20 (m, 2H), 7.15 (d, J = 7.6 Hz, 1H), 6.61 (d, J = 9.6 Hz, 1H), 6.53 – 6.47 (m, 2H), 6.25 (dd, J = 10.0, 2.8 Hz, 1H), 4.20 (d, J = 12.8 Hz, 1H), 4.04 (d, J = 12.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.2, 150.2, 146.2, 145.1, 143.7, 141.2, 139.5, 131.6, 131.3, 130.4, 129.3, 129.1, 128.8, 128.6 (d, J = 5.0 Hz), 123.6 (d, J = 15.0 Hz), 61.7, 58.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -151.1, -151.0; IR (neat): 2923, 1623(s), 1621, 1455, 1397, 1048, 858, 767, 701, 616; HRESIMS Calcd for $[C_{21}H_{16}FOS]^+$ (M^+) 335.0900, found 335.0904.

2'-(benzylthio)spiro[cyclohexane-1,1'-inden]-4-one (10)



3a **10**, 71%

To a solution of **3a** (0.1 mmol, 32.6 mg) in ethyl acetate (1 mL) was added $Pd(OH)_2$ (10% on carbon, 0.02 mmol, 3 mg) and stirred at 50 °C under H_2 atmosphere (4 MPa) for 24 h. The progress of the reaction was monitored by TLC. Upon completion, the mixture was concentrated and the residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 5/1) to afford the desired product **10** (23.4 mg, 71% yield). White solid (mp 109–111 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 7.6 Hz, 1H), 7.45 – 7.38 (m, 2H), 7.37 – 7.31 (m, 2H), 7.30 – 7.20 (m, 3H), 7.13 – 7.10 (m, 1H), 6.43 (s, 1H), 4.18 (s, 2H), 2.89 – 2.70 (m, 4H), 2.31 – 2.23 (m, 2H), 1.89 – 1.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.3, 153.4, 150.4, 142.7, 136.0, 128.8, 128.7, 127.6, 127.4, 123.7, 122.5, 121.9, 120.0, 53.9, 38.3, 37.5, 33.5; IR (neat): 2923, 1654(s), 1459, 1384, 1032, 897, 749, 787; HRESIMS Calcd for $[C_{21}H_{20}NaOS]^+$ (M + Na^+) 343.1127, found 343.1138.

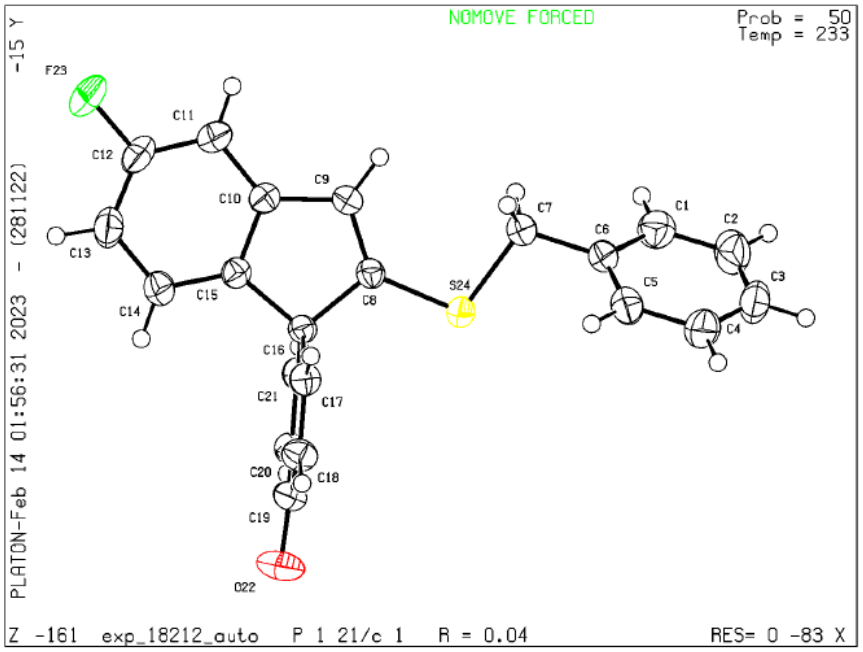
References:

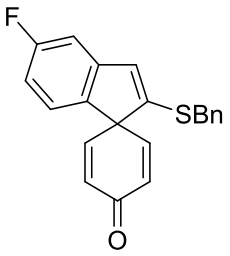
1. Y.-Q. Zhang, X.-Q. Zhu, Y.-B. Chen, T.-D. Tan, M.-Y. Yang and L.-W. Ye, *Org. Lett.*, 2018, **20**, 23, 7721.

2. Y.-Q. Zhang, Y.-B. Chen, J.-R. Liu, S.-Q. Wu, X.-Y. Fan, Z.-X. Zhang, X. Hong and L.-W. Ye, *Nat. Chem.*, 2021, **13**, 1093.

4. Crystal Data

Crystal data and structure refinement for 3i. CCDC Number = 2243822





3i

Bond precision: C-C = 0.0022 A Wavelength=1.54184

Cell: a=18.5422(2) b=9.4148(1) c=9.6744(1)
alpha=90 beta=90.082(1) gamma=90
Temperature: 233 K

	Calculated	Reported
Volume	1688.87(3)	1688.87(3)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C21 H15 F O S	C21 H15 F O S
Sum formula	C21 H15 F O S	C21 H15 F O S
Mr	334.39	334.39
Dx,g cm-3	1.315	1.315
Z	4	4
Mu (mm-1)	1.817	1.817
F000	696.0	696.0
F000'	699.27	
h,k,lmax	23,11,12	22,11,11
Nref	3427	3374
Tmin,Tmax	0.982,0.982	0.896,1.000
Tmin'	0.982	

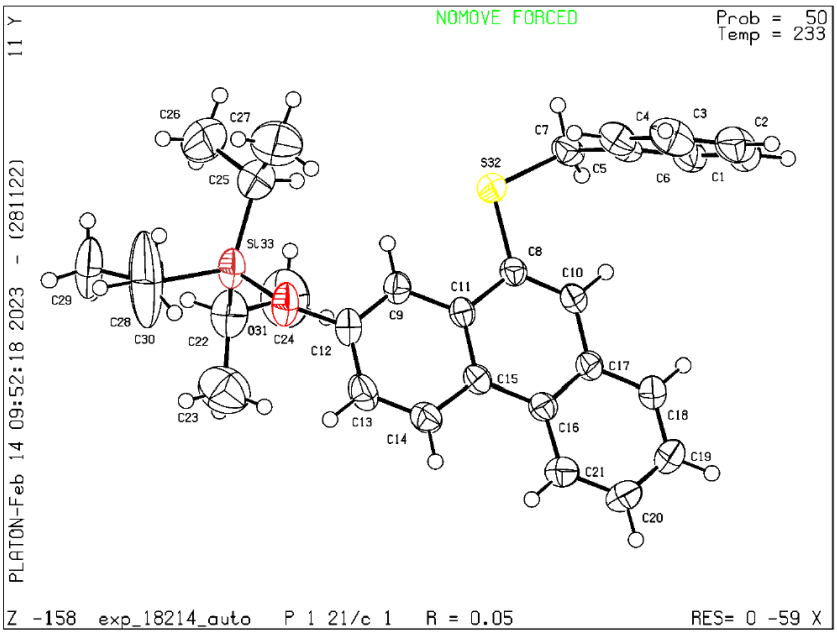
Correction method= # Reported T Limits: Tmin=0.896 Tmax=1.000
AbsCorr = MULTI-SCAN

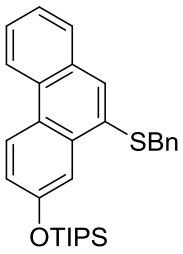
Data completeness= 0.985 Theta(max)= 74.231

R(reflections)= 0.0436(3020) wR2(reflections)= 0.1145(3374)

S = 1.137 Npar= 217

Crystal data and structure refinement for 4. CCDC Number = 2243824





4

Bond precision: C-C = 0.0032 A Wavelength=1.54184

Cell: a=27.2173(3) b=10.9230(2) c=9.0261(1)
alpha=90 beta=93.968(1) gamma=90
Temperature: 233 K

	Calculated	Reported
Volume	2676.98(6)	2676.98(6)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C30 H35 O S Si	C30 H35 O S Si
Sum formula	C30 H35 O S Si	C30 H35 O S Si
Mr	471.73	471.73
Dx,g cm-3	1.171	1.170
Z	4	4
Mu (mm-1)	1.638	1.638
F000	1012.0	1012.0
F000'	1016.61	
h,k,lmax	33,13,11	33,13,10
Nref	5466	5296
Tmin,Tmax	0.984,0.984	0.784,1.000
Tmin'	0.984	

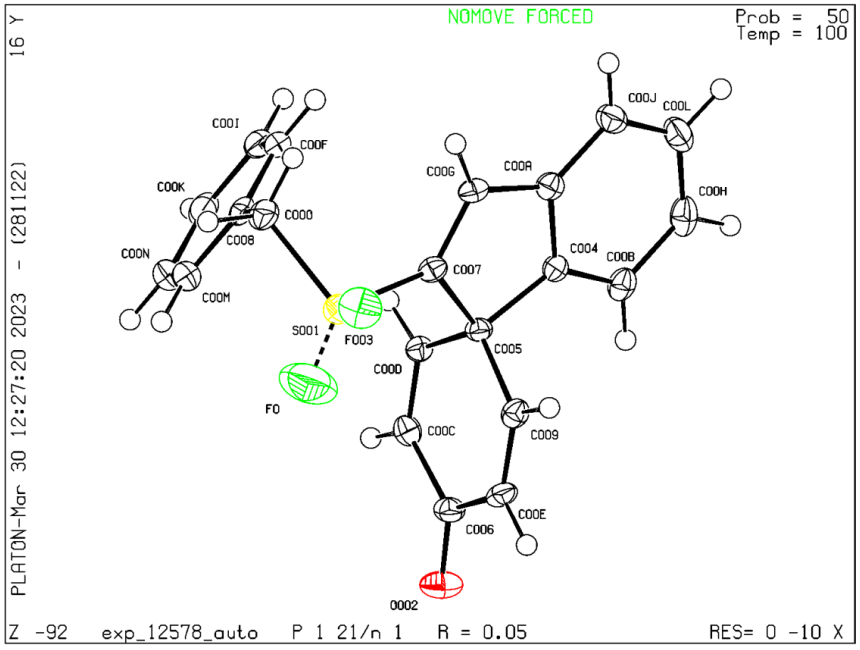
Correction method= # Reported T Limits: Tmin=0.784 Tmax=1.000
AbsCorr = MULTI-SCAN

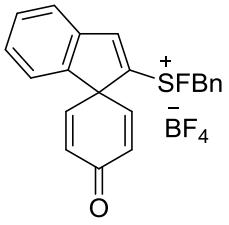
Data completeness= 0.969 Theta(max)= 74.321

R(reflections)= 0.0464(4430) wR2(reflections)= 0.1312(5296)

S = 1.046 Npar= 304

Crystal data and structure refinement for 9. CCDC Number = 2253023





9

Bond precision: C-C = 0.0040 A Wavelength=1.54184

Cell: a=9.2311(1) b=18.8323(3) c=9.3096(1)
alpha=90 beta=94.465(1) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	1613.50(4)	1613.50(4)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C21 H16 F O S	C21 H16 F O S
Sum formula	C21 H16 F O S	C21 H16 F O S
Mr	335.40	335.40
Dx,g cm-3	1.381	1.381
Z	4	4
Mu (mm-1)	1.902	1.902
F000	700.0	700.0
F000'	703.27	
h,k,lmax	10,22,11	10,22,11
Nref	2836	2819
Tmin,Tmax	0.892,0.909	0.775,1.000
Tmin'	0.827	

Correction method= # Reported T Limits: Tmin=0.775 Tmax=1.000
AbsCorr = MULTI-SCAN

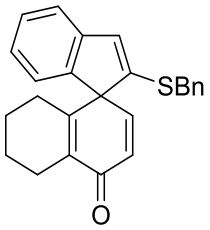
Data completeness= 0.994 Theta(max)= 66.596

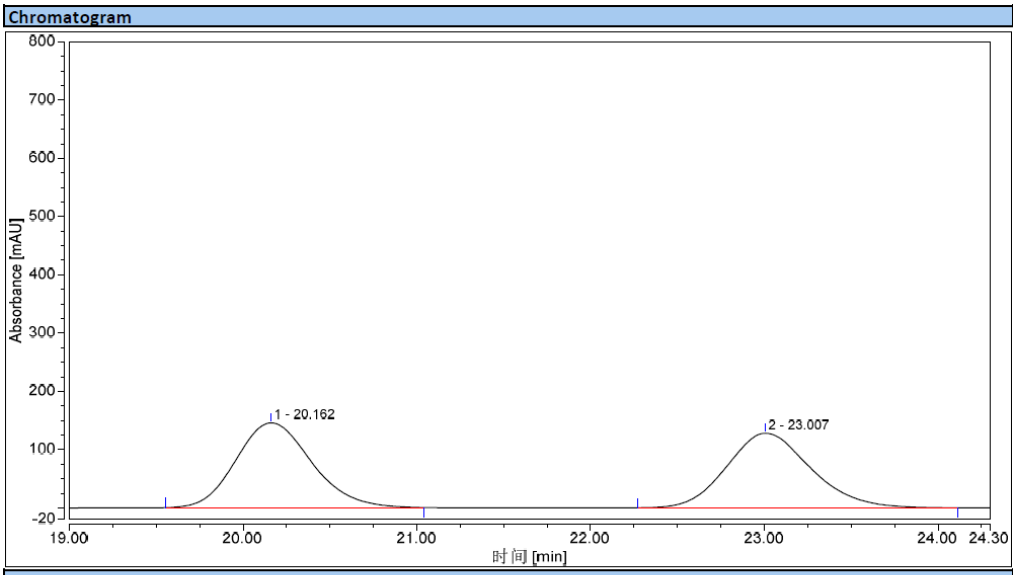
R(reflections)= 0.0522(2712) wR2(reflections)= 0.1269(2819)

S = 1.202 Npar= 227

5. HPLC Chromatograms

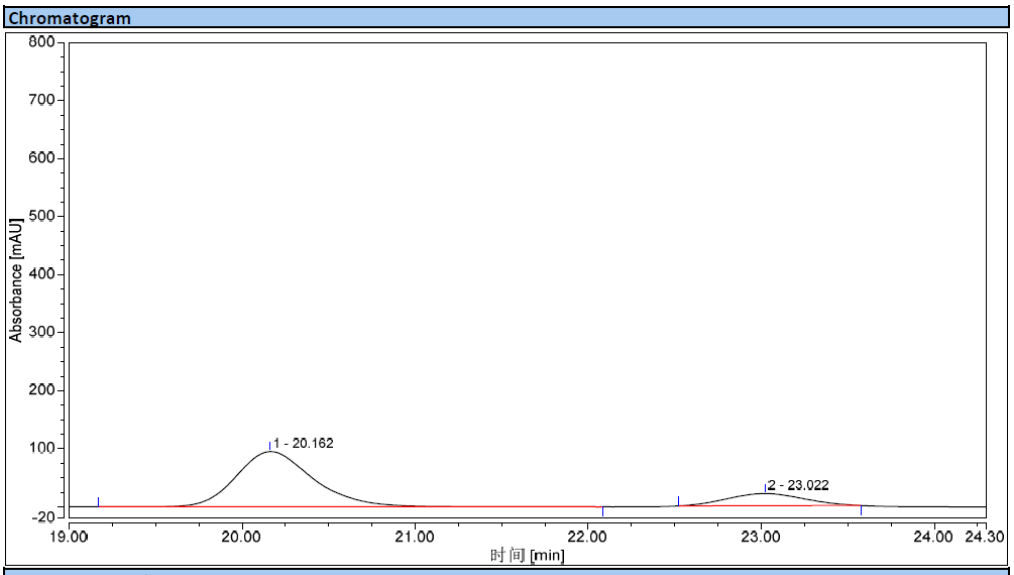
Compound **3j:** HPLC (IC, *n*-hexane/2-propanol = 90/10, v = 1.0 mL/min, λ = 254 nm)





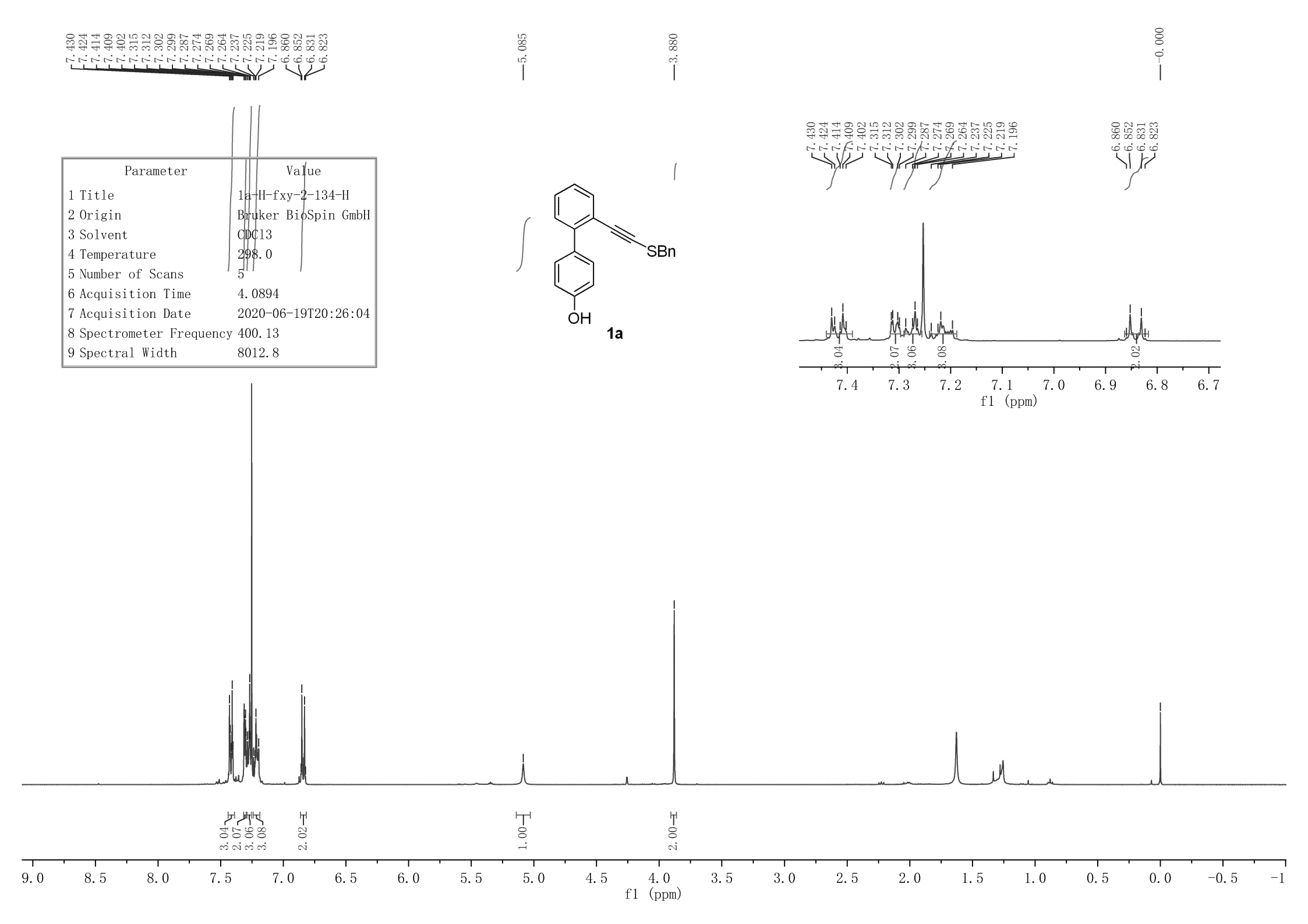
Integration Results

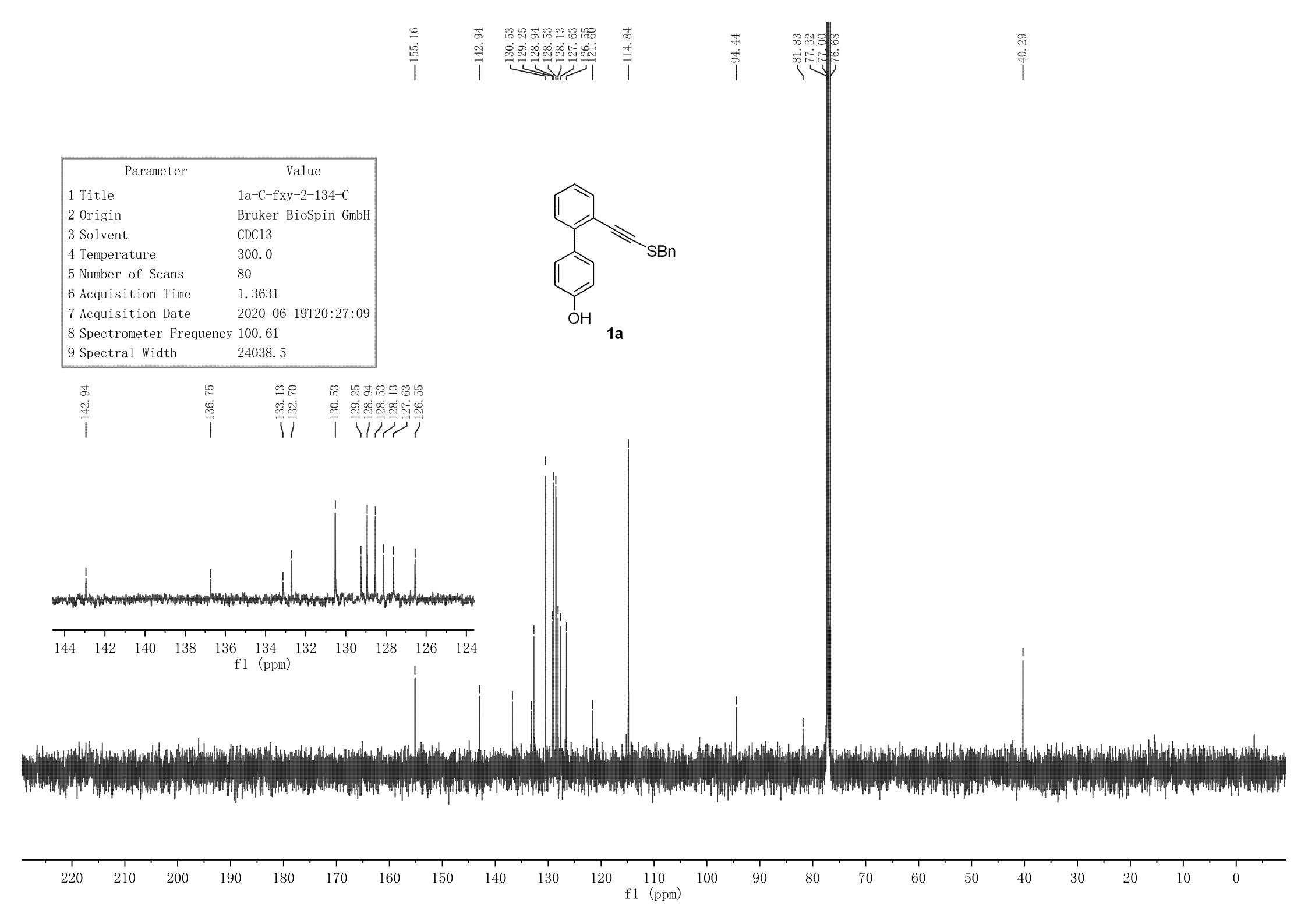
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.162	73.395	145.357	50.60	53.23	n.a.
2		23.007	71.668	127.736	49.40	46.77	n.a.
Total:			**145.064**	**273.093**	**100.00**	**100.00**	

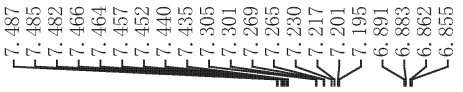


Integration Results

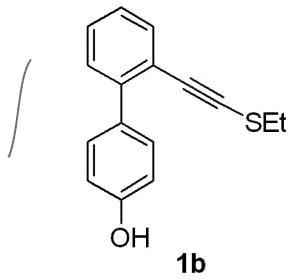
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.162	48.796	94.920	82.00	81.93	n.a.
2		23.022	10.709	20.941	18.00	18.07	n.a.
Total:			**59.506**	**115.861**	**100.00**	**100.00**	


7.430
7.424
7.414
7.409
7.402
7.315
7.312
7.302
7.299
7.287
7.274
7.269
7.264
7.237
7.225
7.219
7.196
6.860
6.852
6.831
6.823
5.085
3.880
0.000
Parameter Value
1 Title 1a-H-fxy-2-134-H
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 298.0
5 Number of Scans 5
6 Acquisition Time 4.0894
7 Acquisition Date 2020-06-19T20:26:04
8 Spectrometer Frequency 400.13
9 Spectral Width 8012.8
SBn
OH
1a
3.04
2.07
3.06
3.08
2.02
1.00
2.00
f1 (ppm)

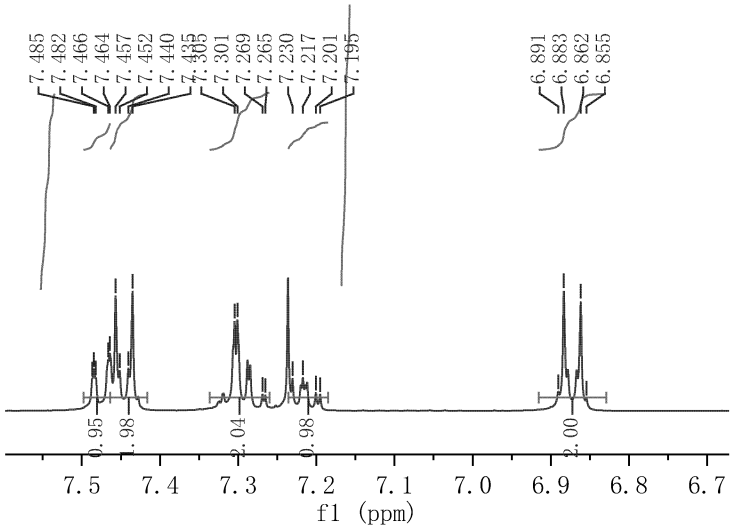

155.16
142.94
130.53
129.25
128.94
128.53
128.13
127.63
126.55
121.60
114.84
94.44
81.83
77.32
77.00
76.68
40.29
Parameter Value
1 Title 1a-C-fxy-2-134-C
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.0
5 Number of Scans 80
6 Acquisition Time 1.3631
7 Acquisition Date 2020-06-19T20:27:09
8 Spectrometer Frequency 100.61
9 Spectral Width 24038.5
SBn
OH
1a
142.94
136.75
133.13
132.70
130.53
129.25
128.94
128.53
128.13
127.63
126.55
144 142 140 138 136 134 132 130 128 126 124
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

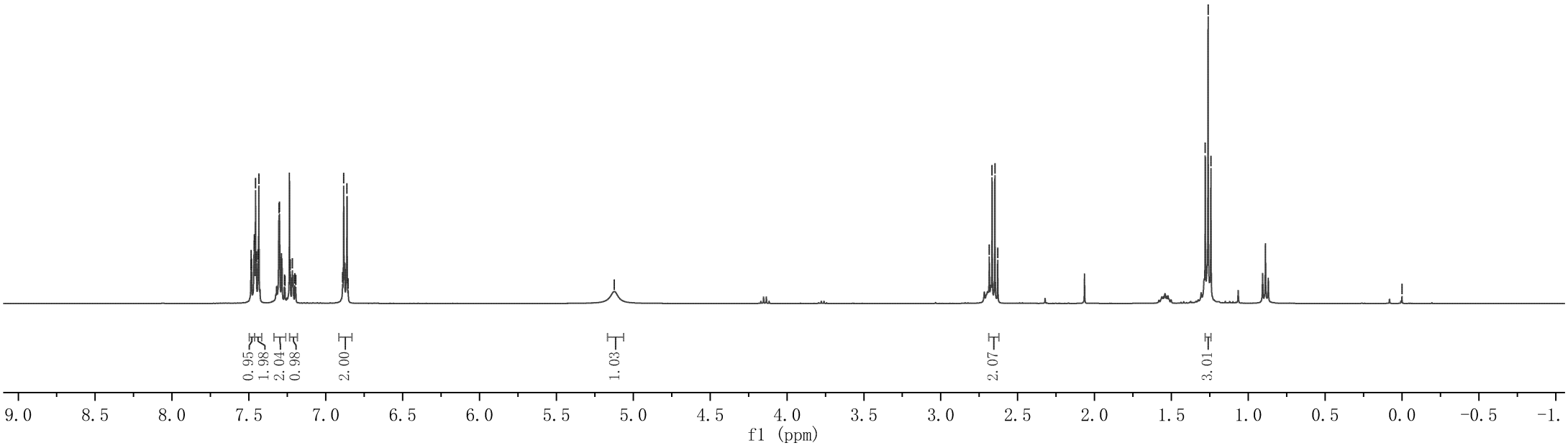


Parameter	Value
1 Title	1b-Hfxy-4-242-hex-H
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	7
6 Acquisition Time	4.0894
7 Acquisition Date	2021-05-20T16:04:12
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8

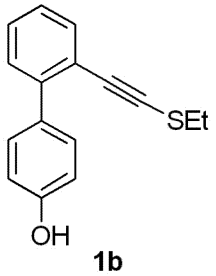


1b





Parameter	Value
1 Title	1b-cfxy-4-242-hex-CC
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	18
6 Acquisition Time	1.3631
7 Acquisition Date	2021-05-20T16:05:29
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5



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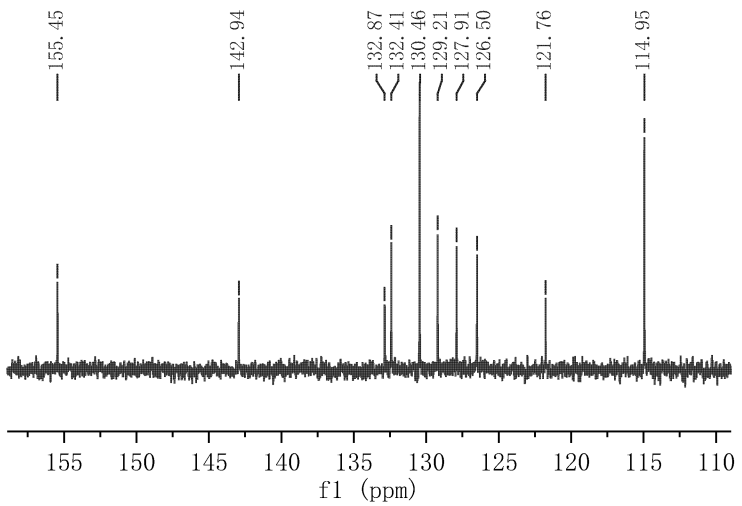
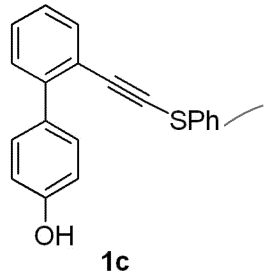


Parameter	Value
1 Title	1c-H-fxy-4-244-new
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	43
6 Acquisition Time	4.0894
7 Acquisition Date	2021-05-21T10:03:23
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8



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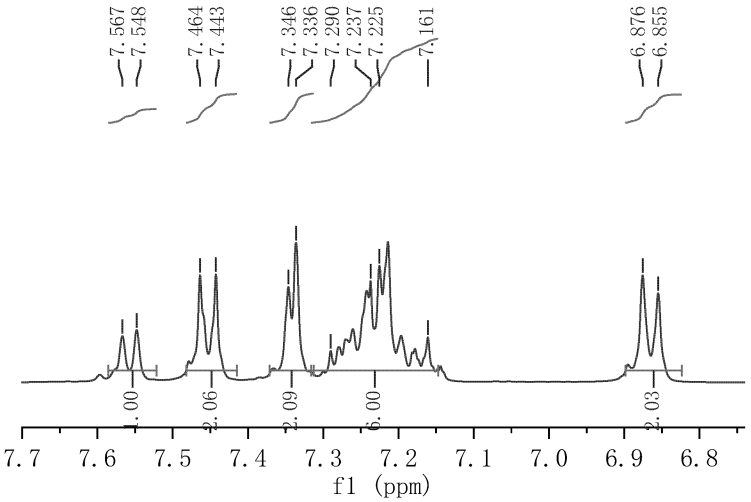
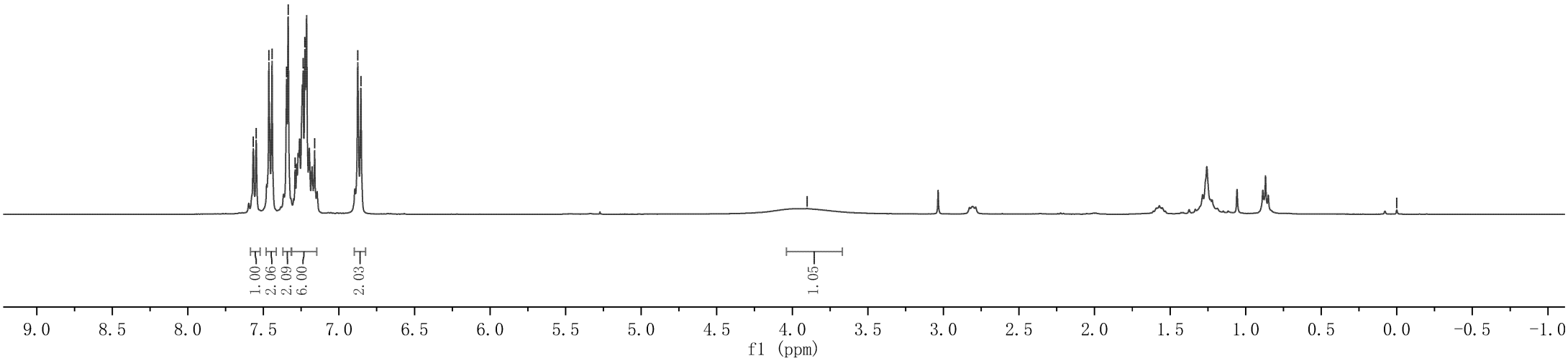
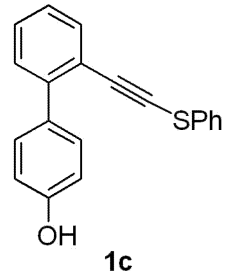
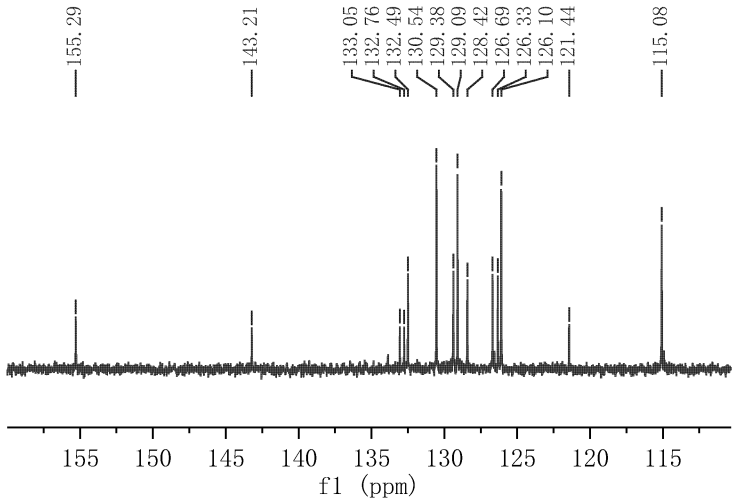


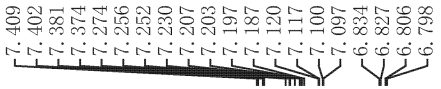


Parameter	Value
1 Title	1c-C-fxy-4-244-new-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	37
6 Acquisition Time	1.3631
7 Acquisition Date	2021-05-21T10:07:21
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5

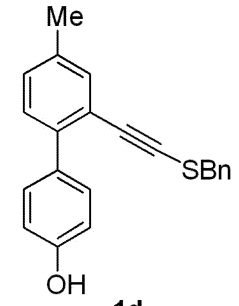


1c





Parameter	Value
1 Title	1d-H-FXY-2-205
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	2020-07-14T09:38:07
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8



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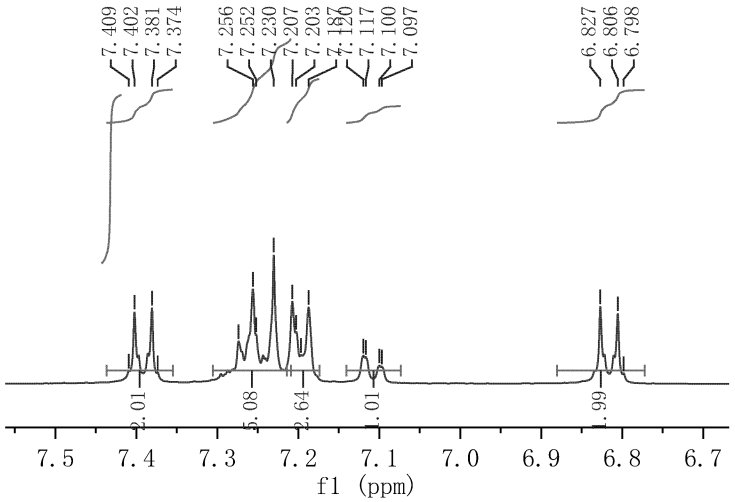
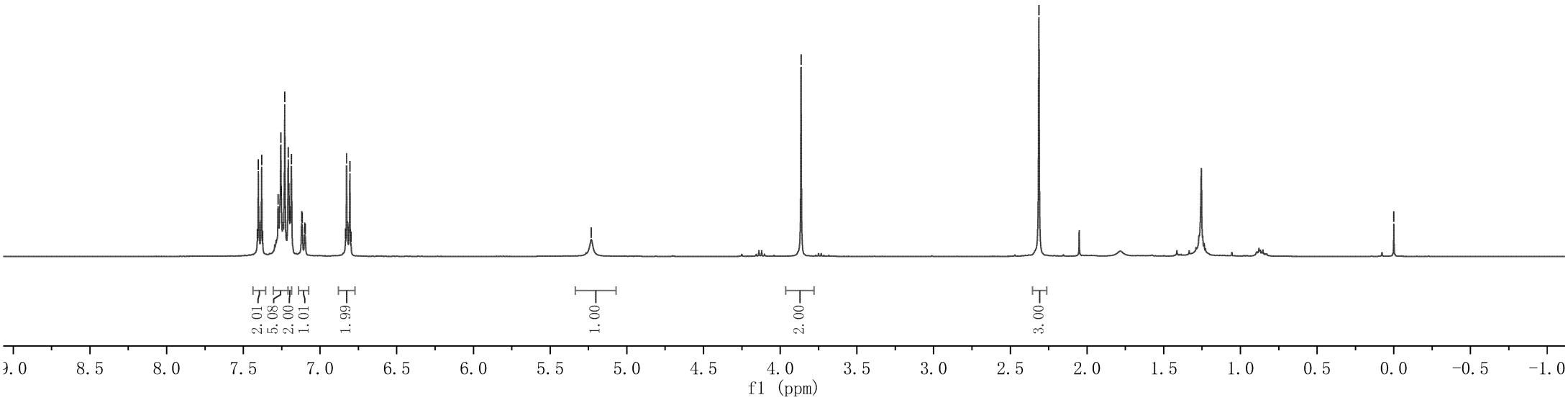
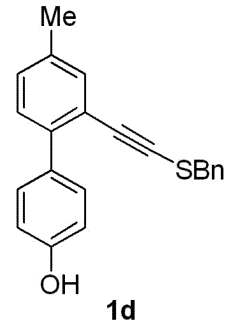
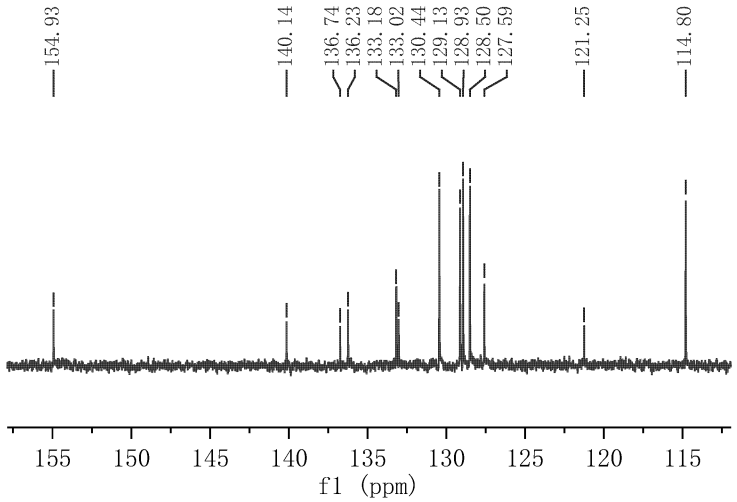


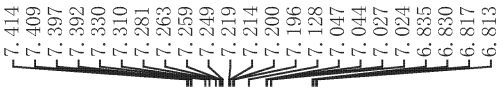


Parameter	Value
1 Title	1d-C-FXY-2-205-C-2
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	18
6 Acquisition Time	1.3631
7 Acquisition Date	2020-07-14T09:41:25
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5

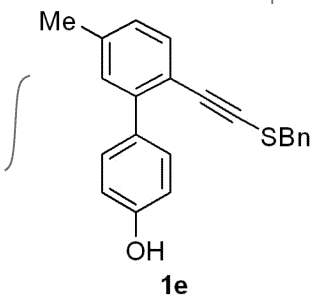


1d

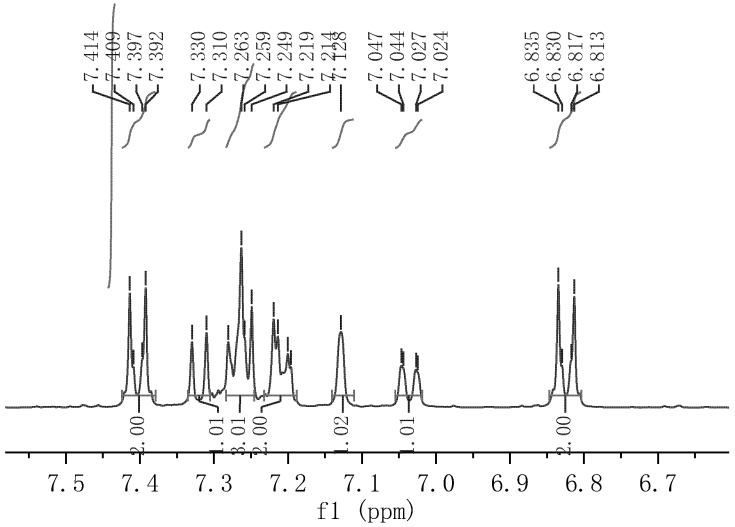


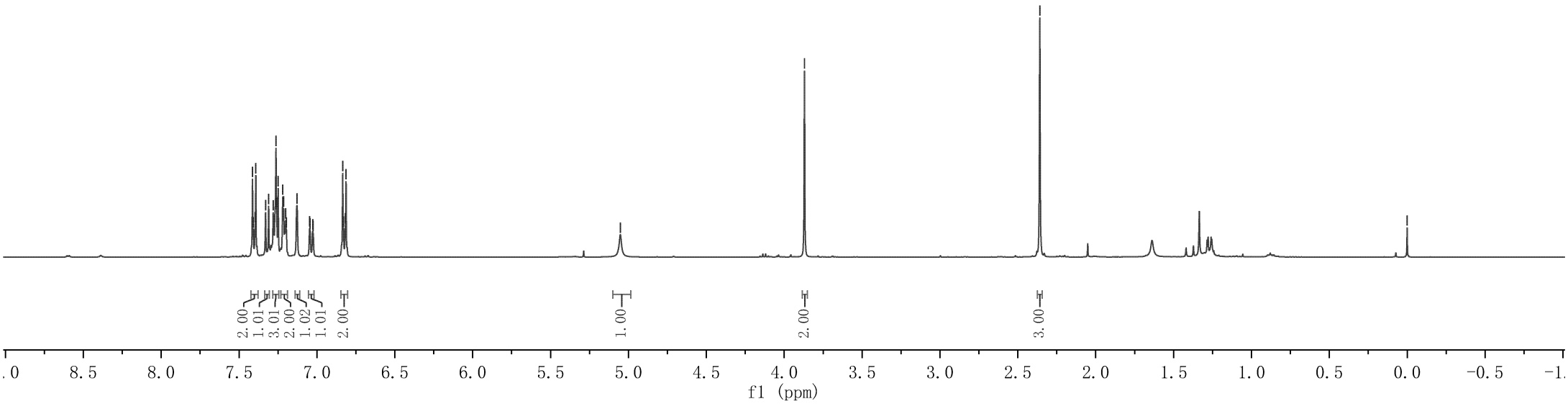


Parameter	Value
1 Title	1e-H
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.8
5 Number of Scans	50
6 Acquisition Time	4.0002
7 Acquisition Date	2023-02-08T14:50:35
8 Spectrometer Frequency	399.90
9 Spectral Width	8012.0

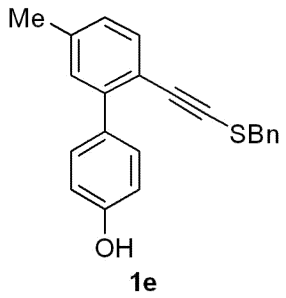


1e



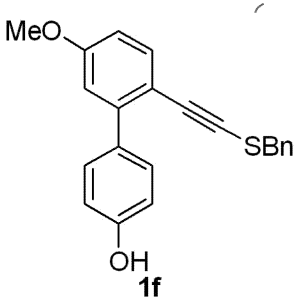


Parameter	Value
1 Title	1e-C
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.8
5 Number of Scans	800
6 Acquisition Time	1.0000
7 Acquisition Date	2023-02-08T15:19:53
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0



1e

Parameter	Value
1 Title	1f-H-fxy-4-243
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	2021-05-20T16:12:24
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8



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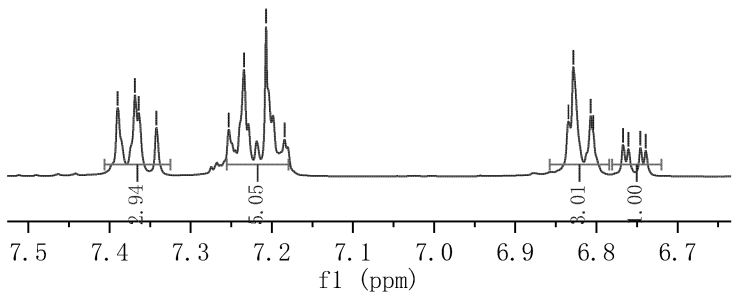
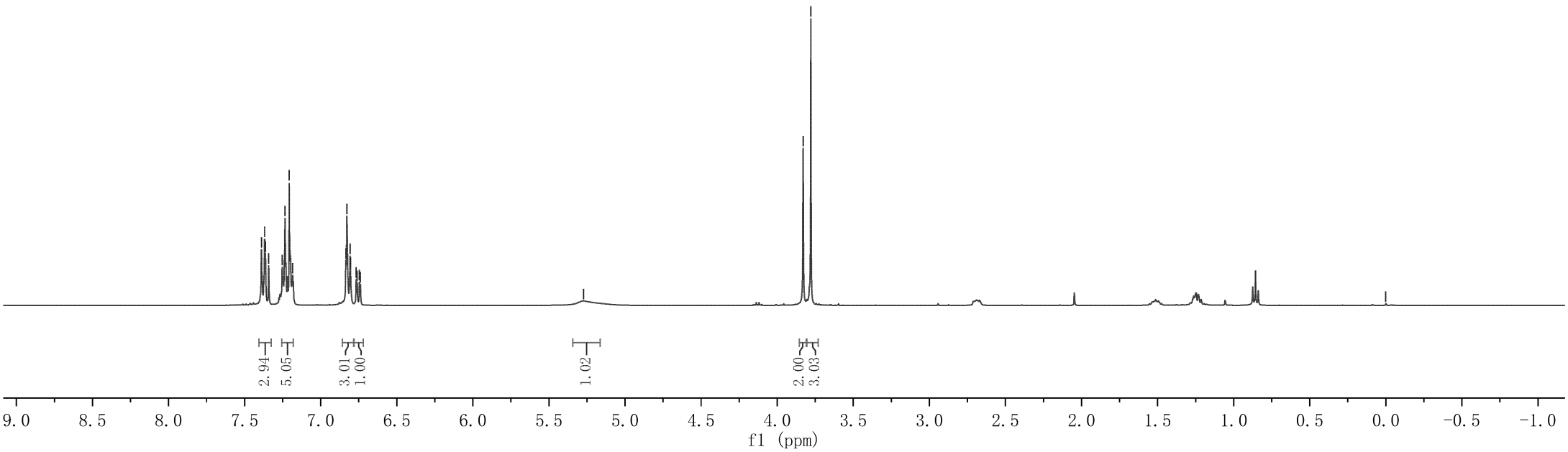
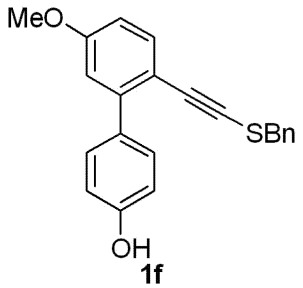
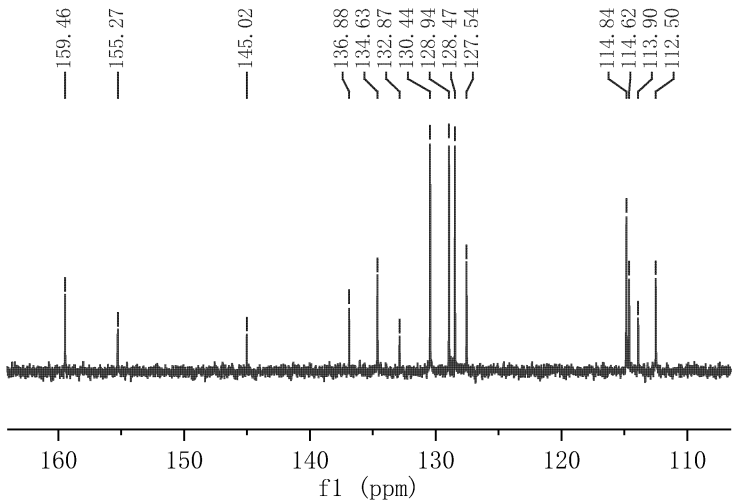


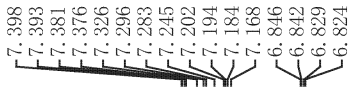


Parameter	Value
1 Title	1f-C-FXY-2-223-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	33
6 Acquisition Time	1.3631
7 Acquisition Date	2020-07-21T14:37:12
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5

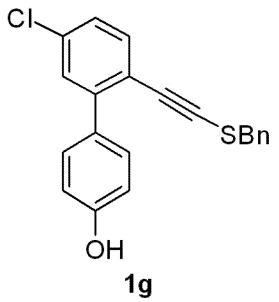


1f

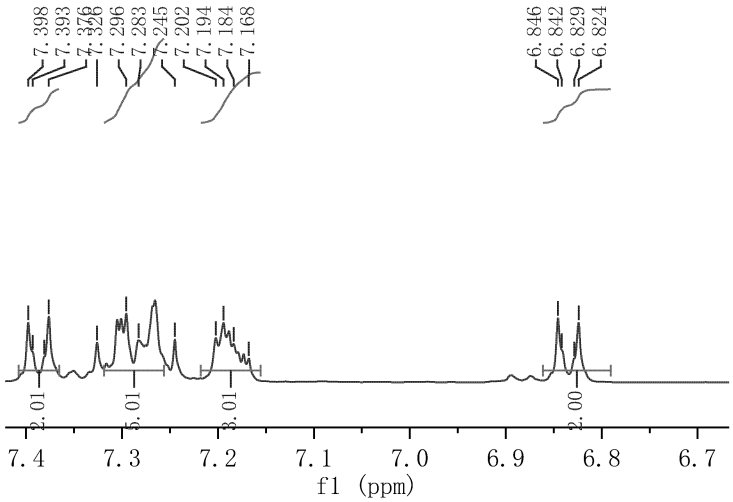


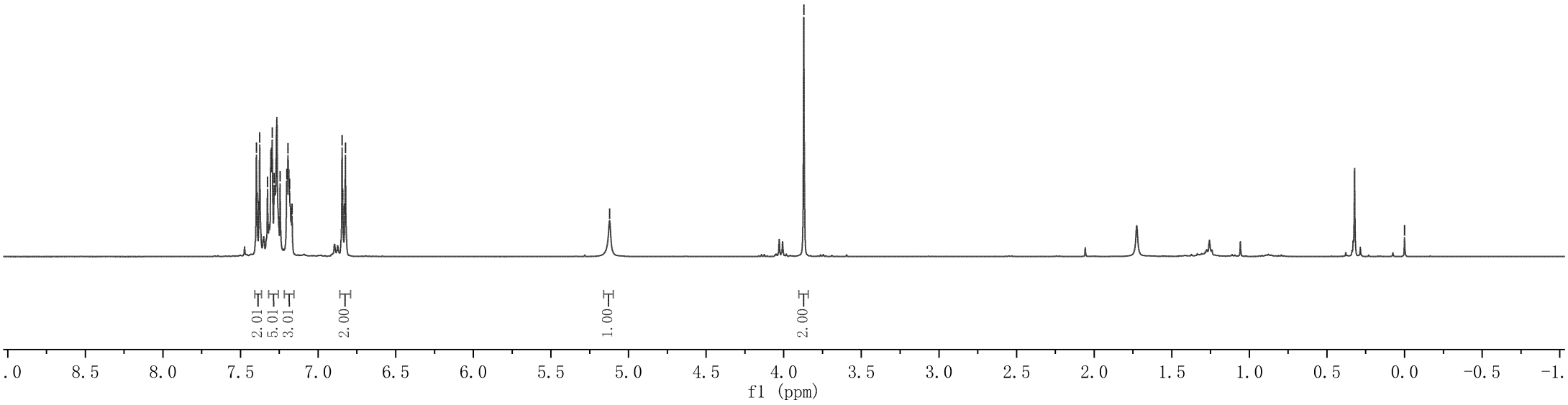


Parameter	Value
1 Title	1g-H
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.8
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2023-02-10T14:39:59
8 Spectrometer Frequency	399.90
9 Spectral Width	8012.0

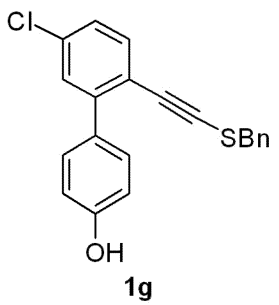


1g

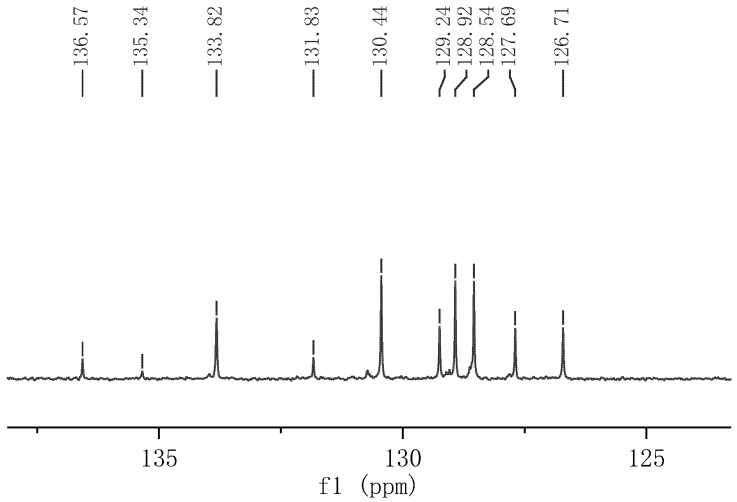


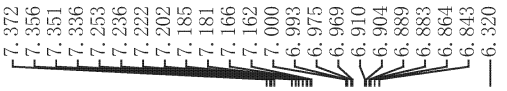


Parameter	Value
1 Title	1g-C
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.6
5 Number of Scans	800
6 Acquisition Time	1.0000
7 Acquisition Date	2023-02-10T15:09:22
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

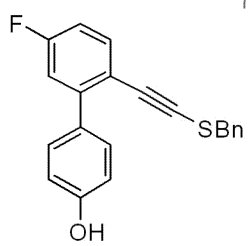


1g

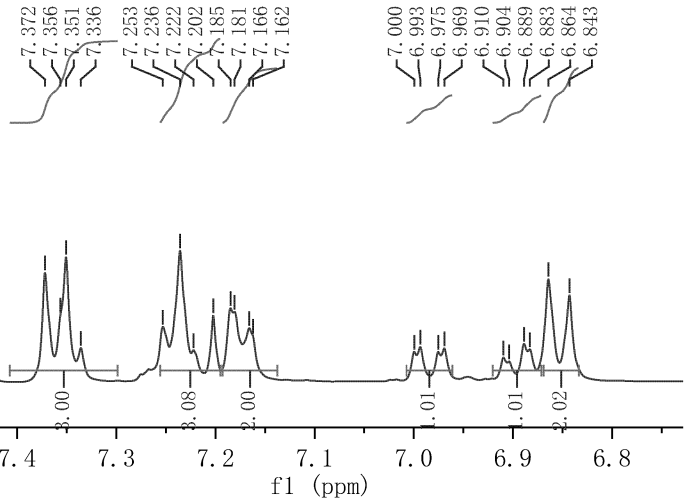


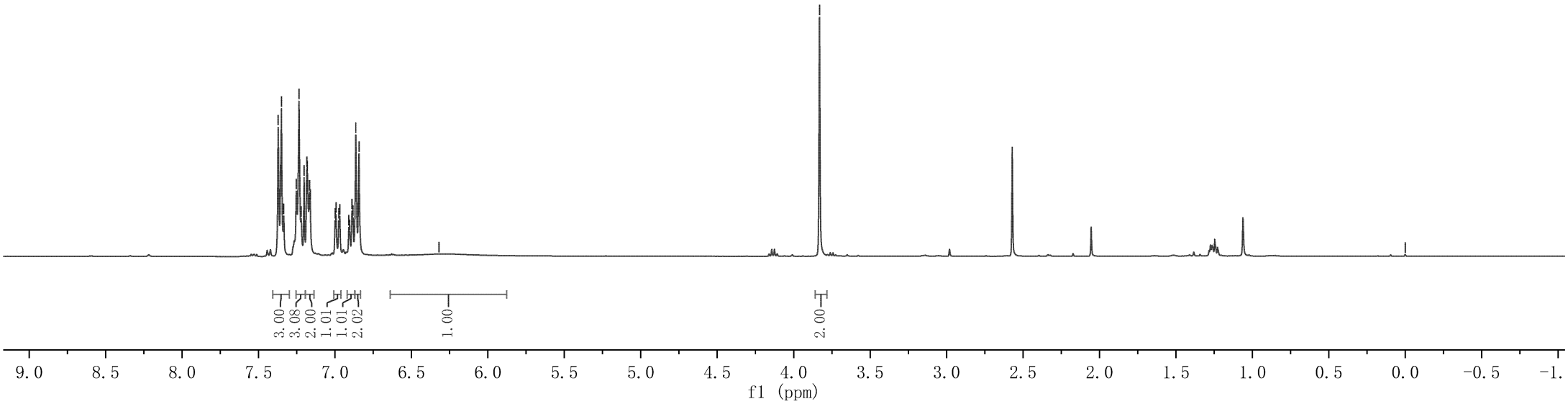


Parameter	Value
1 Title	1h-H
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.8
5 Number of Scans	30
6 Acquisition Time	4.0002
7 Acquisition Date	2023-02-08T11:07:18
8 Spectrometer Frequency	399.90
9 Spectral Width	8012.0

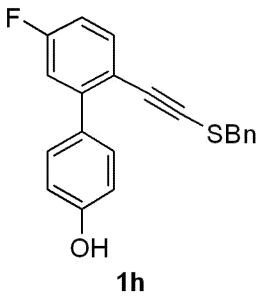


1h

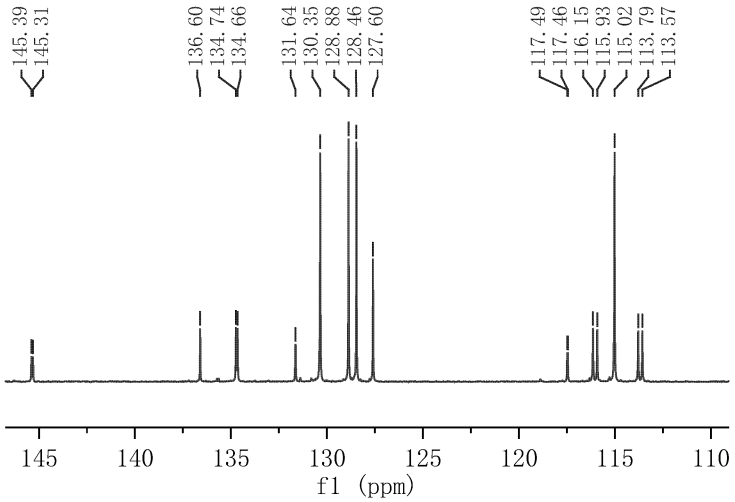




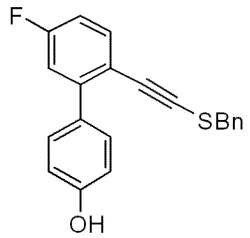
Parameter	Value
1 Title	1h-C
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.8
5 Number of Scans	30
6 Acquisition Time	4.0002
7 Acquisition Date	2023-02-08T11:07:18
8 Spectrometer Frequency	399.90
9 Spectral Width	8012.0



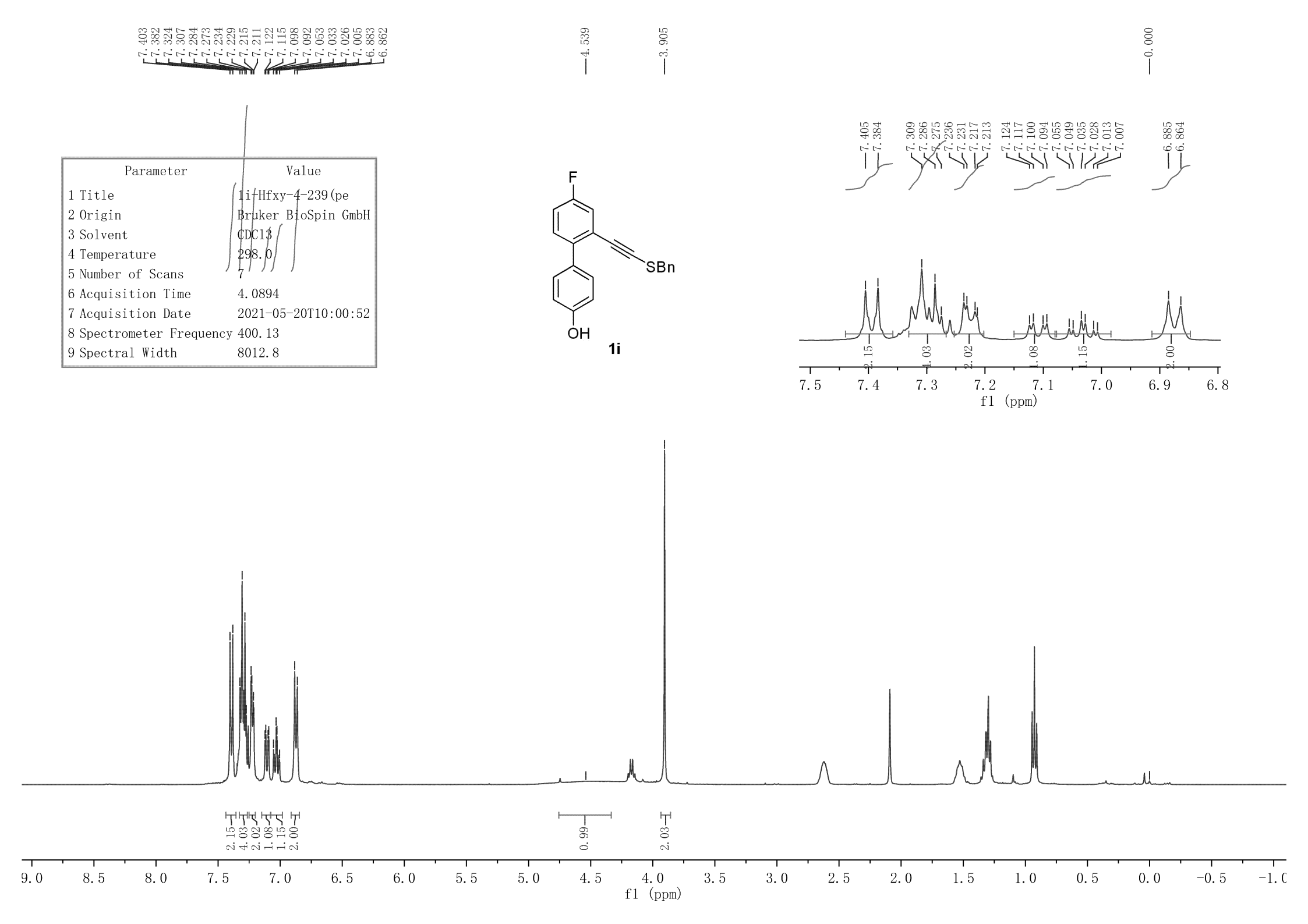
1h



Parameter	Value
1 Title	1h-F
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.8
5 Number of Scans	30
6 Acquisition Time	1.0000
7 Acquisition Date	2023-02-08T12:12:17
8 Spectrometer Frequency	376.28
9 Spectral Width	96153.0



1h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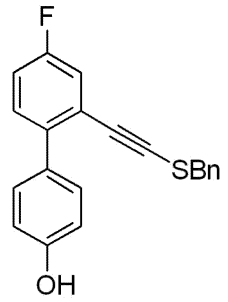
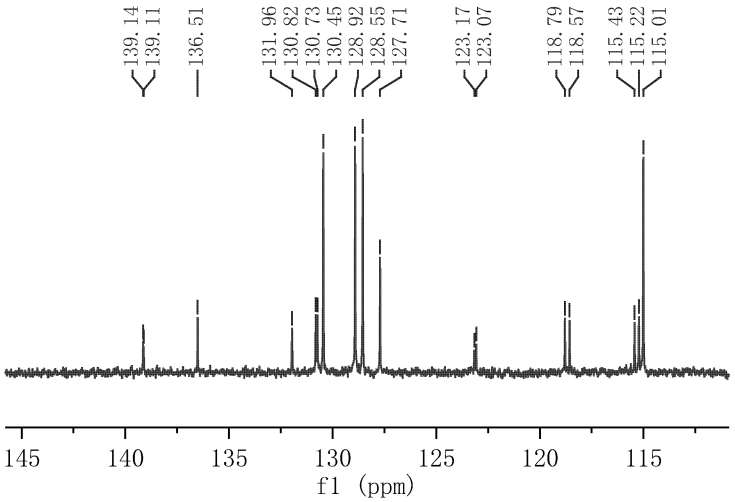
7.324
7.307
7.284
7.273
7.234
7.229
7.215
7.211
7.122
7.115
7.098
7.092
7.053
7.033
7.026
7.005
6.883
6.862
4.539
3.905
0.000
7.405
7.384
7.309
7.286
7.275
7.236
7.231
7.217
7.213
7.124
7.117
7.100
7.094
7.055
7.049
7.035
7.028
7.013
7.007
6.885
6.864
Parameter
Value
1 Title
1i-Hfxy-4-239(pe
2 Origin
Bruker BioSpin GmbH
3 Solvent
CDCl3
4 Temperature
298.0
5 Number of Scans
7
6 Acquisition Time
4.0894
7 Acquisition Date
2021-05-20T10:00:52
8 Spectrometer Frequency
400.13
9 Spectral Width
8012.8
F
SBn
OH
1i
2.15
4.03
2.02
1.08
1.15
2.00
f1 (ppm)
2.15
4.03
2.02
1.08
1.15
2.00
0.99
2.03
f1 (ppm)

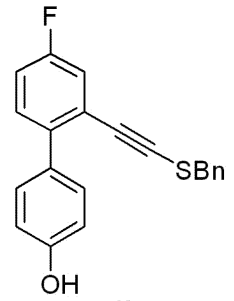
Parameter	Value
1 Title	FXY-4-239-NEW-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	84
6 Acquisition Time	1.3631
7 Acquisition Date	2021-05-21T16:04:45
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5



1i

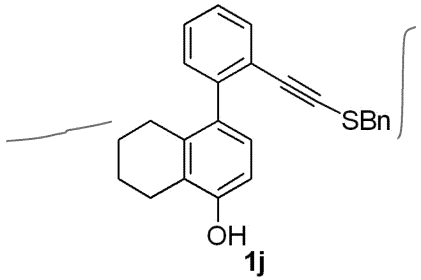


Parameter	Value
1 Title	fxy-1i-f-nmr
2 Origin	
3 Solvent	CDCl3
4 Temperature	296.8
5 Number of Scans	32
6 Acquisition Time	1.0000
7 Acquisition Date	2023-03-03T09:14:24
8 Spectrometer Frequency	376.28
9 Spectral Width	96153.0

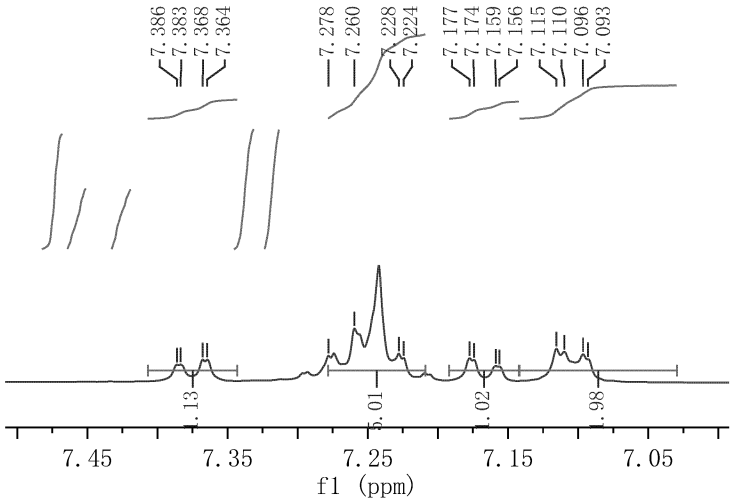


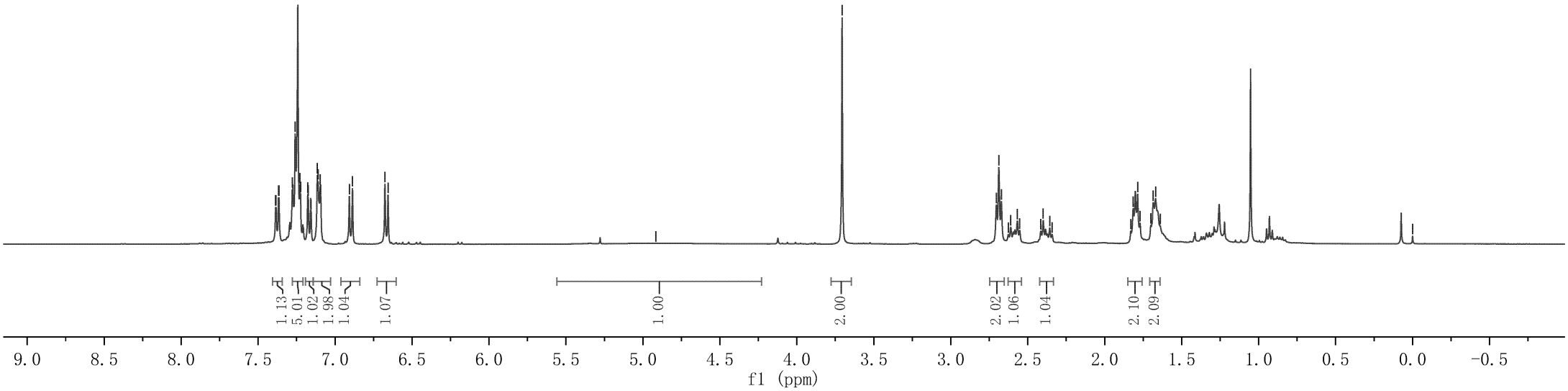
1i

Parameter	Value
1 Title	1j-H-fxy-5-2-new
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	2021-05-21T10:18:13
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8

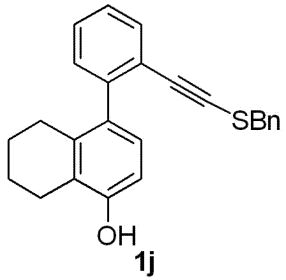


1j

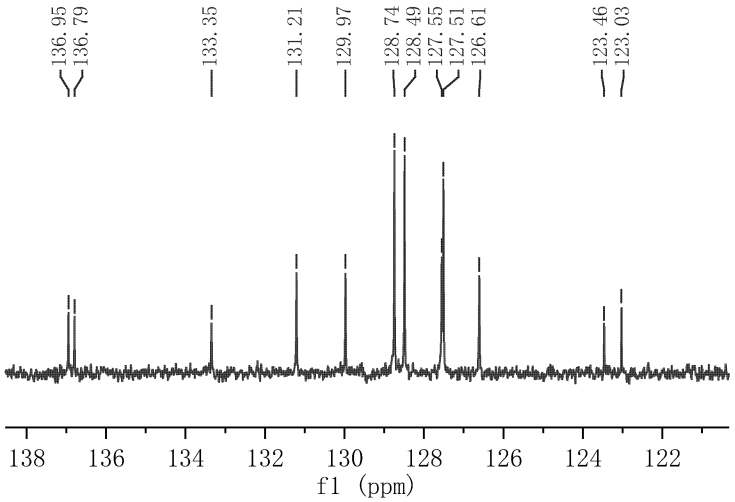


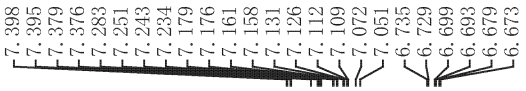


Parameter	Value
1 Title	1j-c-fxy-5-2-new-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	49
6 Acquisition Time	1.3631
7 Acquisition Date	2021-05-21T10:19:40
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5

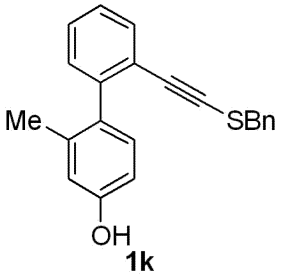


1j

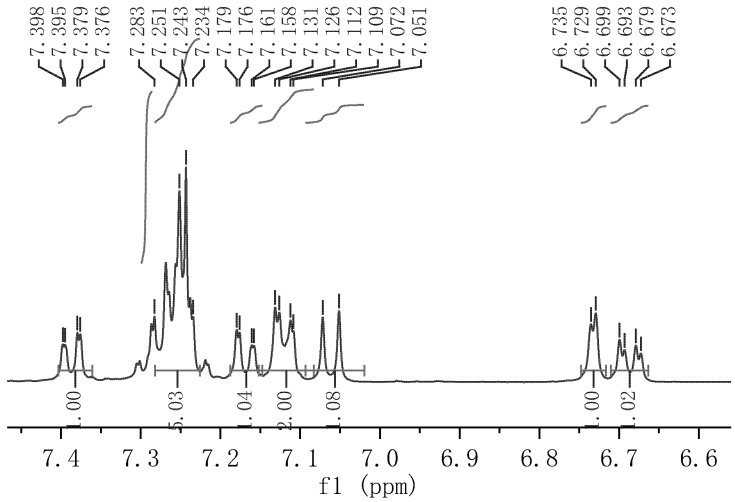


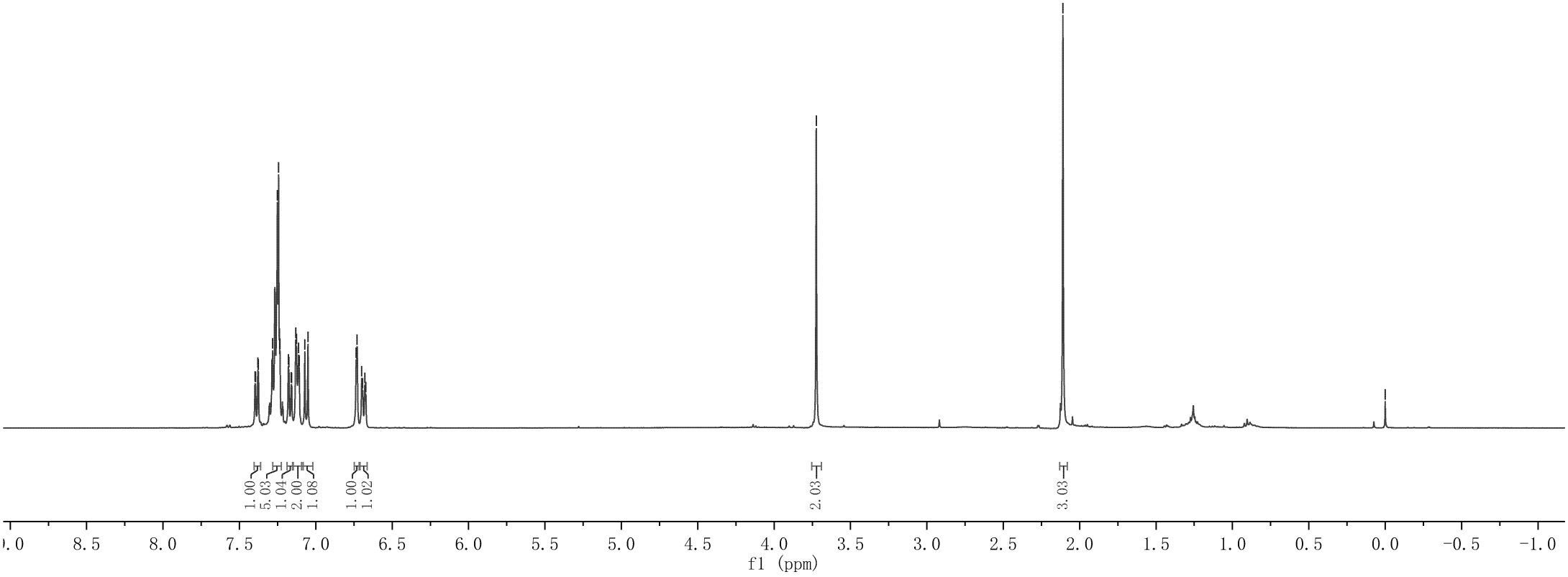


Parameter	Value
1 Title	1k-H-fxy-4-235-hhh
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	10
6 Acquisition Time	4.0894
7 Acquisition Date	2021-05-19T10:14:57
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8

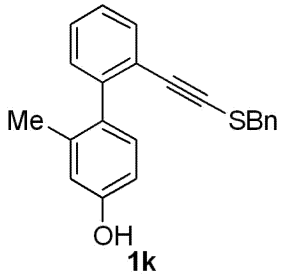


1k

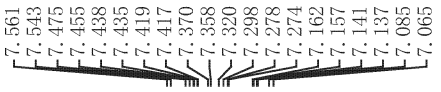




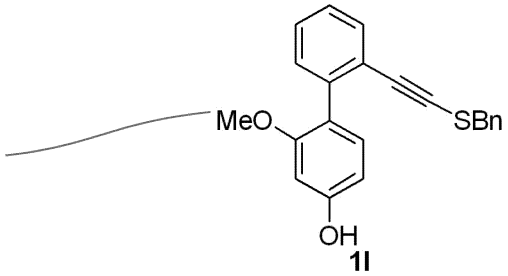
Parameter	Value
1 Title	1k-C-FXY-4-235-c'
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	75
6 Acquisition Time	1.3631
7 Acquisition Date	2021-05-19T15:24:57
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5



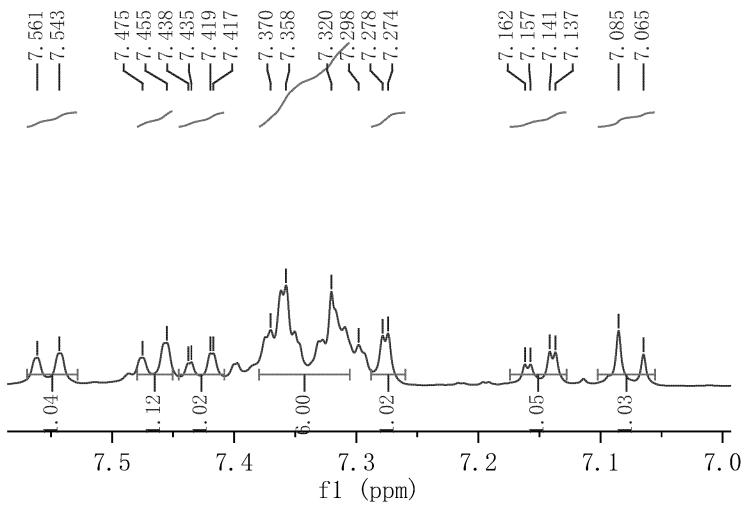
1k

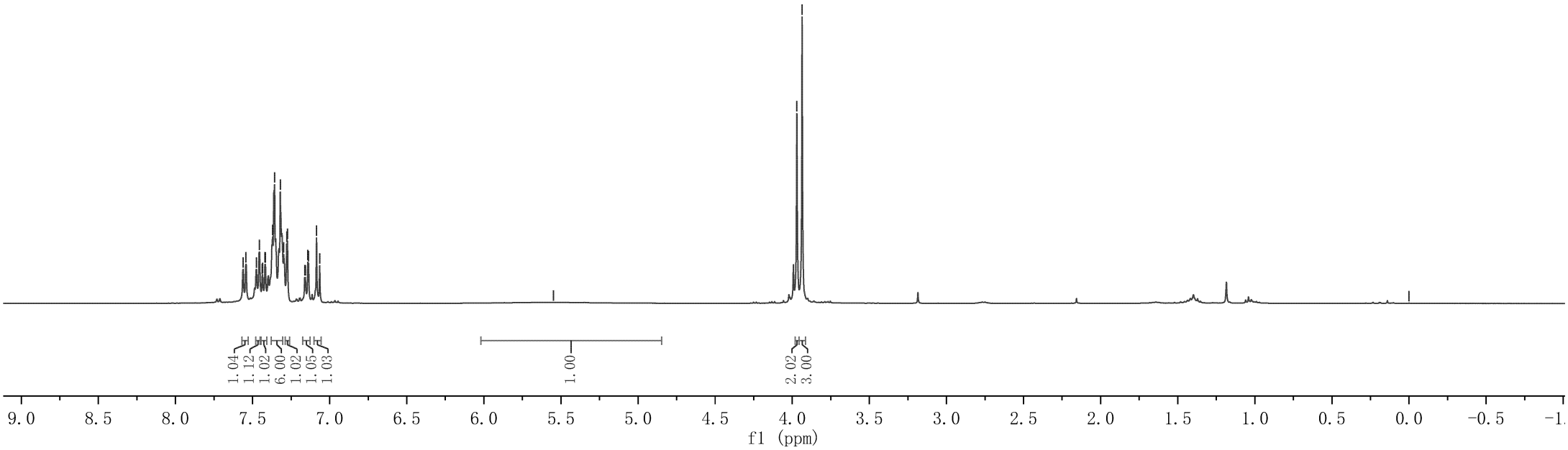


Parameter	Value
1 Title	11-Hfxy-4-240-hex
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	8
6 Acquisition Time	4.0894
7 Acquisition Date	2021-05-20T15:59:04
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8

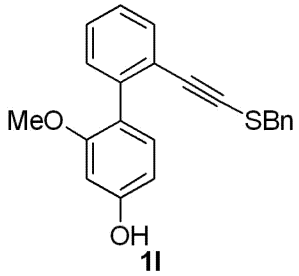


1l

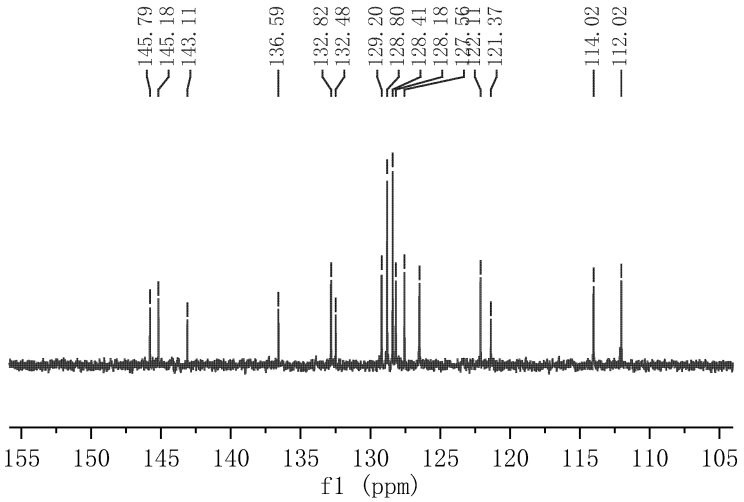


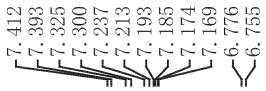


Parameter	Value
1 Title	1l-C-fxy-4-240-hex-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	13
6 Acquisition Time	1.3631
7 Acquisition Date	2021-05-20T16:00:26
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5

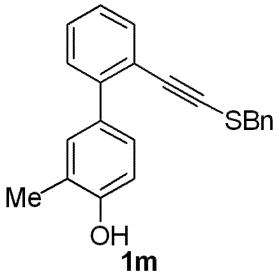


1l

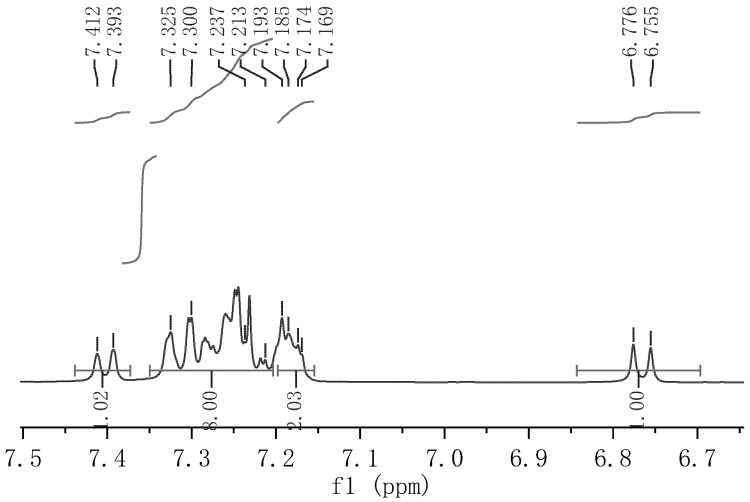


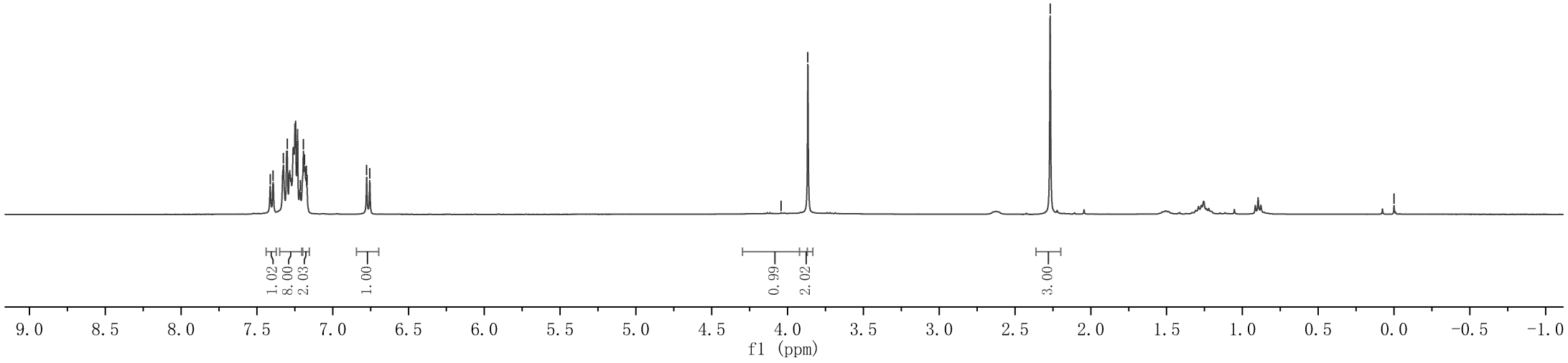


Parameter	Value
1 Title	1m-H-fxy-4-234-real
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	6
6 Acquisition Time	4.0894
7 Acquisition Date	2021-05-19T10:20:31
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8

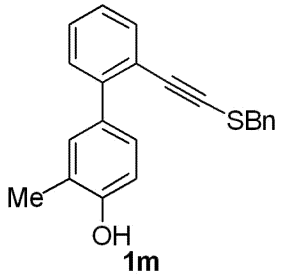


1m



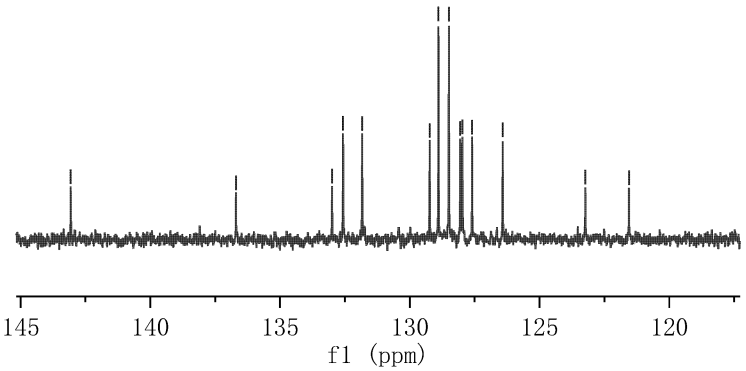


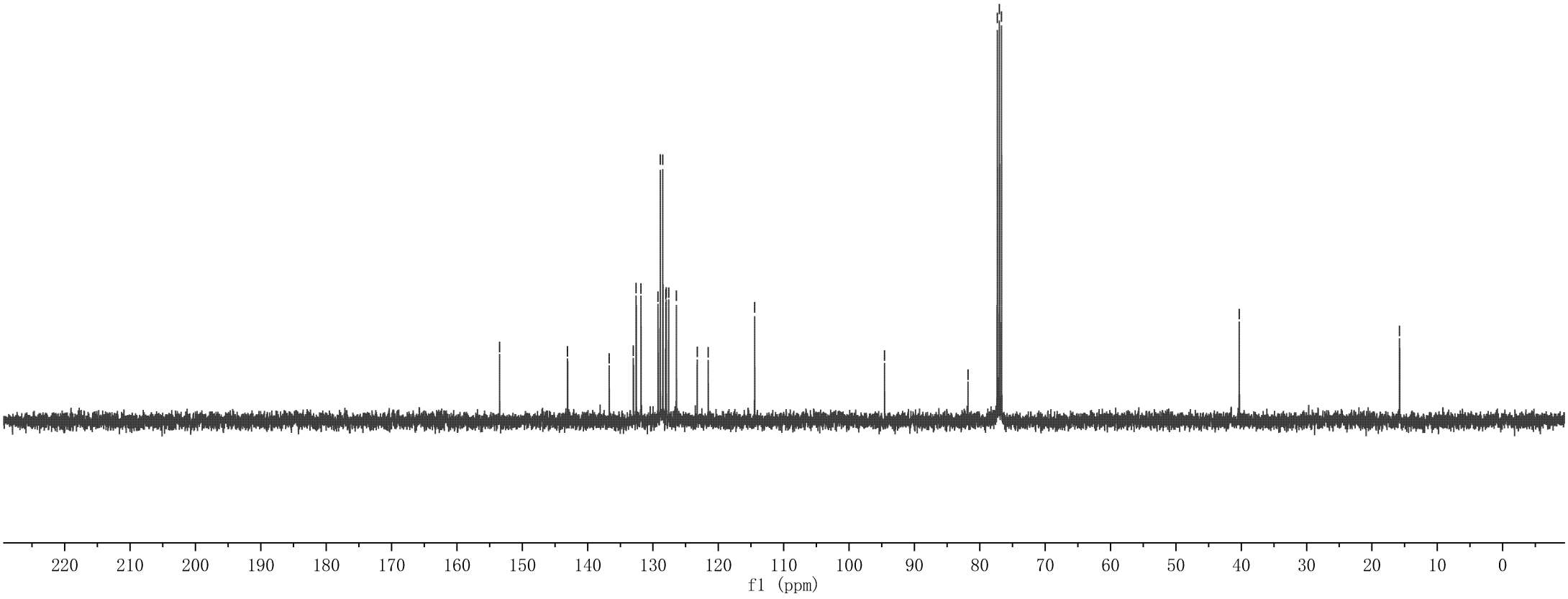
Parameter	Value
1 Title	1m-C-FXY-4-234-c'
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	23
6 Acquisition Time	1.3631
7 Acquisition Date	2021-05-19T15:22:40
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5

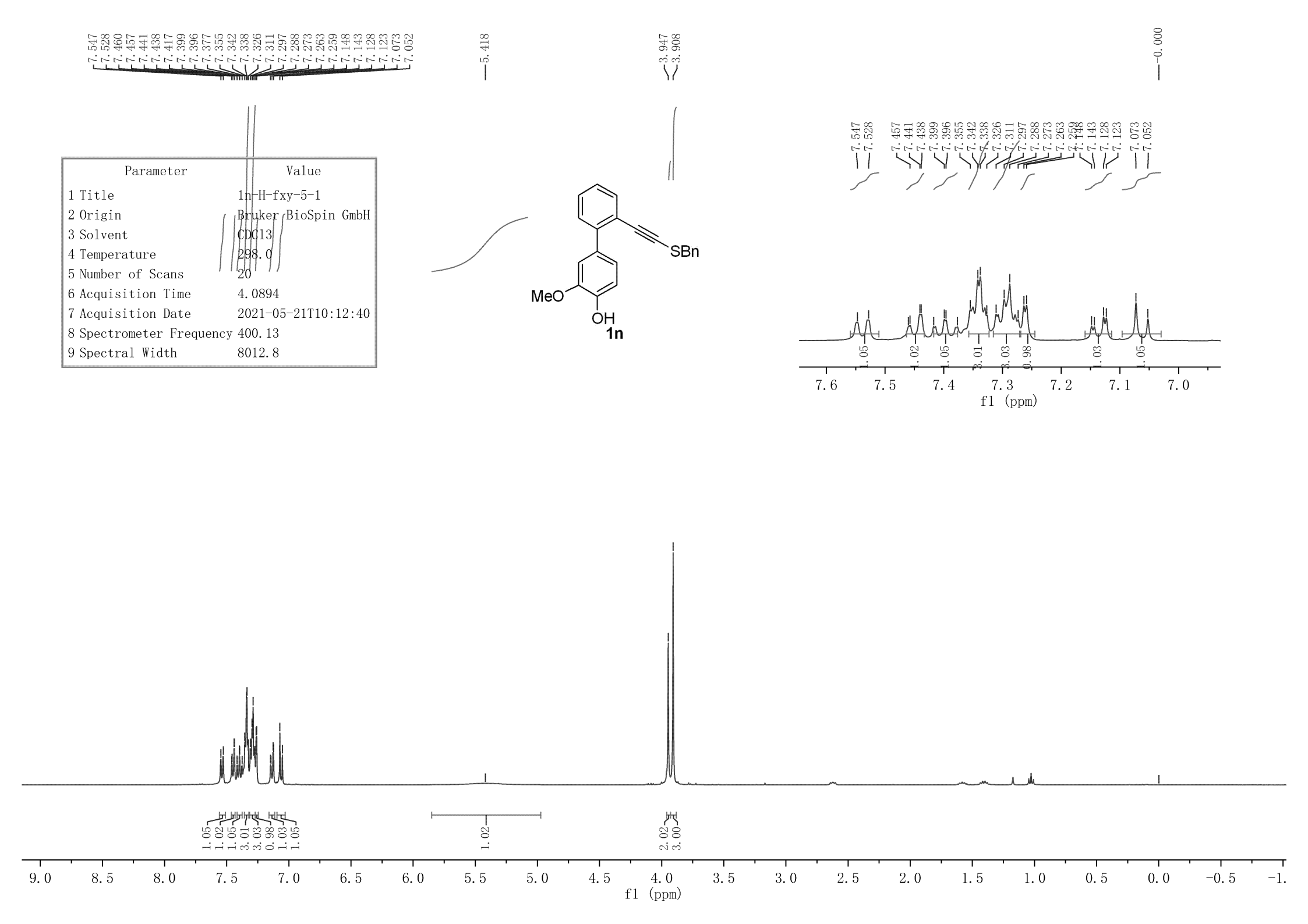


1m

153.47 143.07 133.00 132.57 131.84 129.23 128.89 128.49 128.06 127.98 127.60 126.42 114.44 94.57 81.80 77.32 77.00 76.68 40.30 15.77



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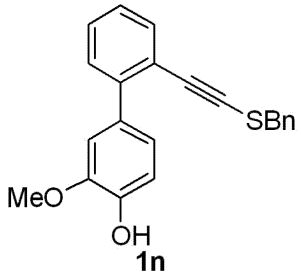
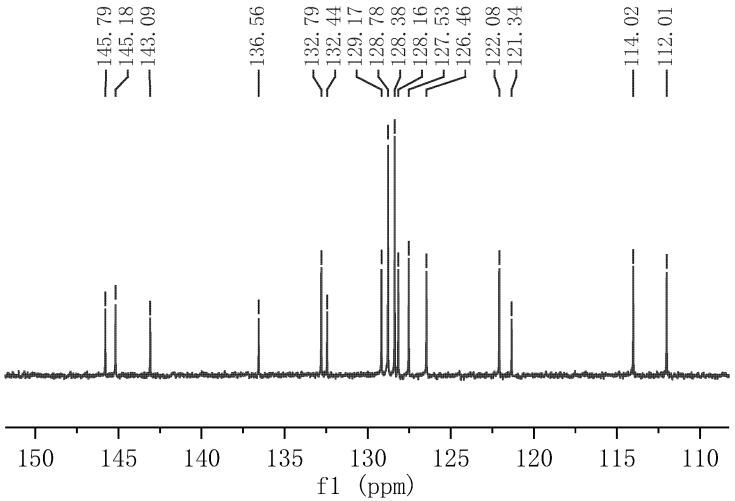
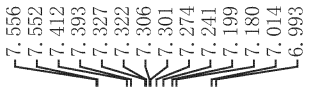
7.273
7.263
7.259
7.148
7.143
7.128
7.123
7.073
7.052
5.418
3.947
3.908
0.000
Parameter Value
1 Title 1n-H-fxy-5-1
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 298.0
5 Number of Scans 20
6 Acquisition Time 4.0894
7 Acquisition Date 2021-05-21T10:12:40
8 Spectrometer Frequency 400.13
9 Spectral Width 8012.8
SBn
MeO
OH
1n
1.05
1.02
1.05
3.01
3.03
0.98
1.03
1.05
1.02
2.02
3.00
f1 (ppm)

Parameter	Value
1 Title	1n-C-fxy-5-1-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	10
6 Acquisition Time	1.3631
7 Acquisition Date	2021-05-21T10:15:11
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5

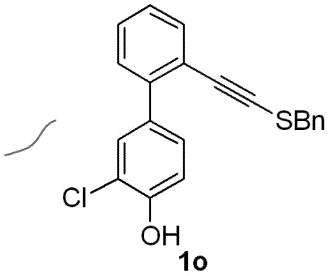


1n





Parameter	Value
1 Title	1o-H-fxy-4-238-new
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	2021-05-21T09:57:23
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8



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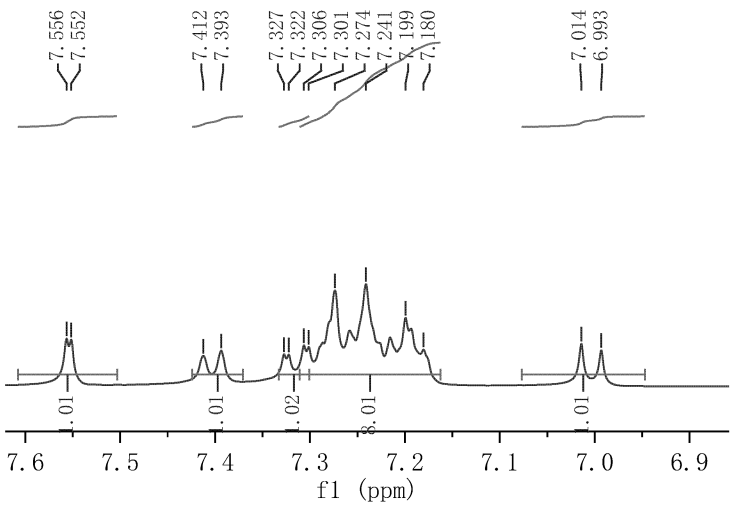
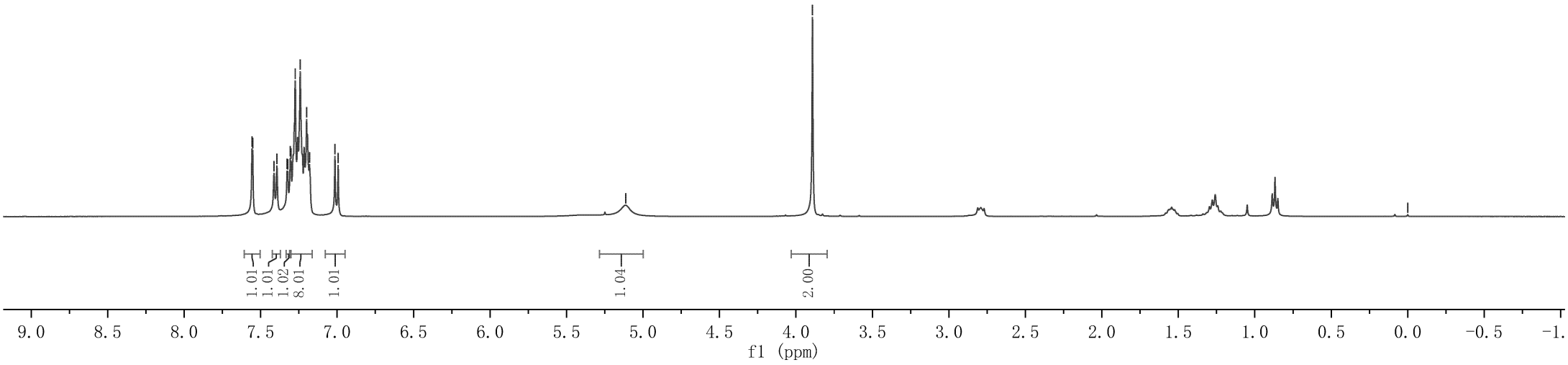
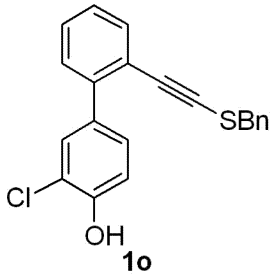
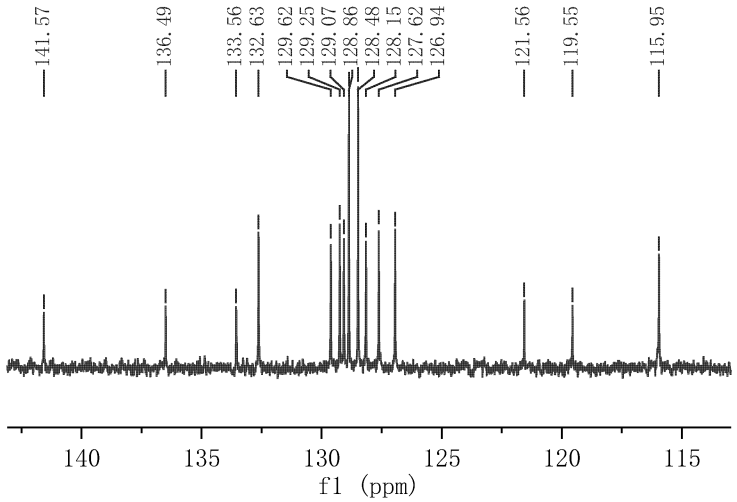




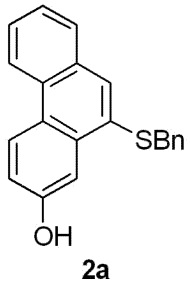
Parameter	Value
1 Title	1o-C-fxy-4-238-new-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	13
6 Acquisition Time	1.3631
7 Acquisition Date	2021-05-21T09:59:35
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5



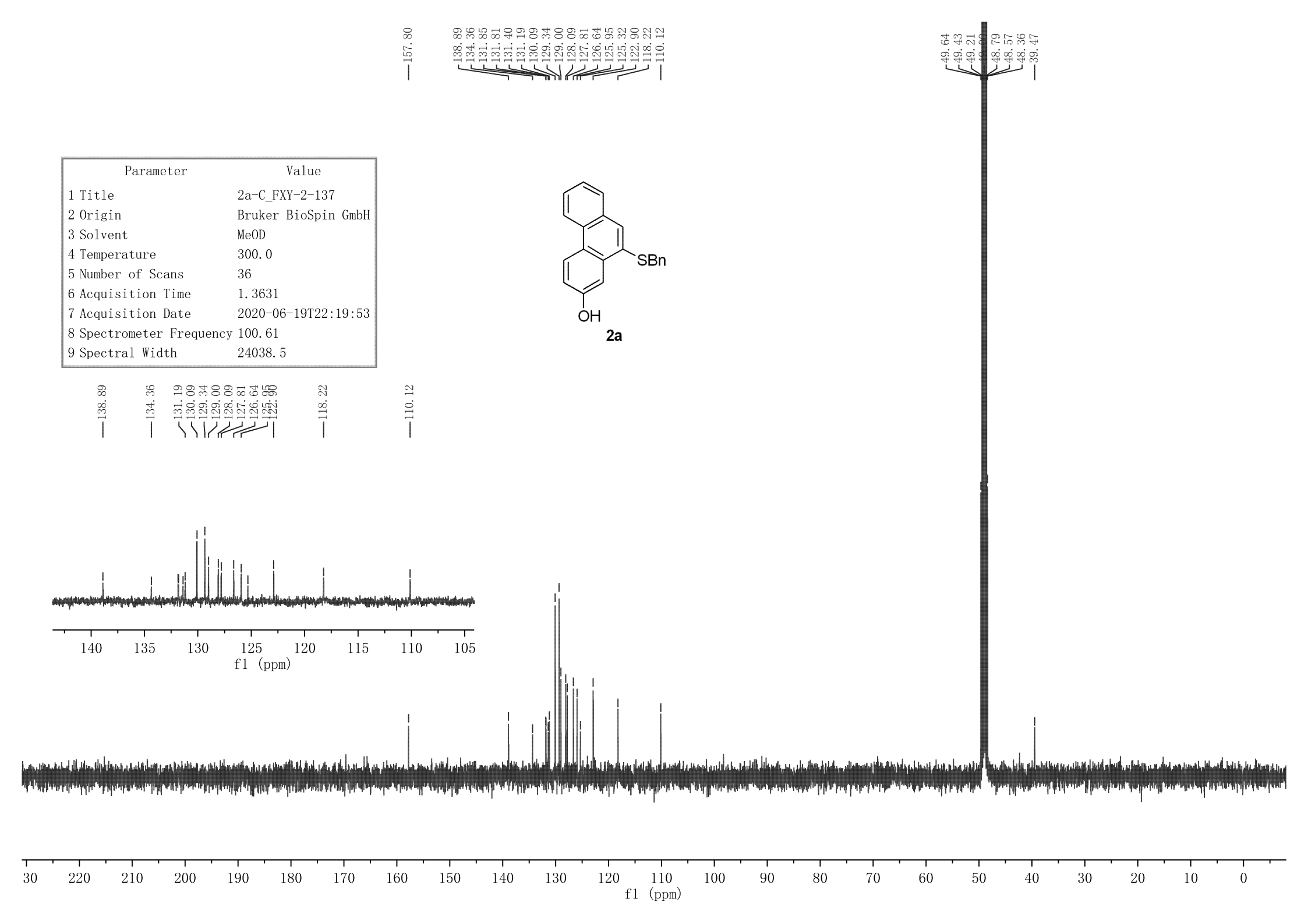
1o



Parameter	Value
1 Title	2a-H-FXY-2-137-H
2 Origin	Bruker BioSpin GmbH
3 Solvent	MeOD
4 Temperature	298.0
5 Number of Scans	5
6 Acquisition Time	4.0894
7 Acquisition Date	2020-06-19T22:17:48
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8

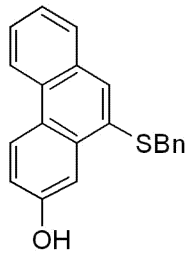


2a

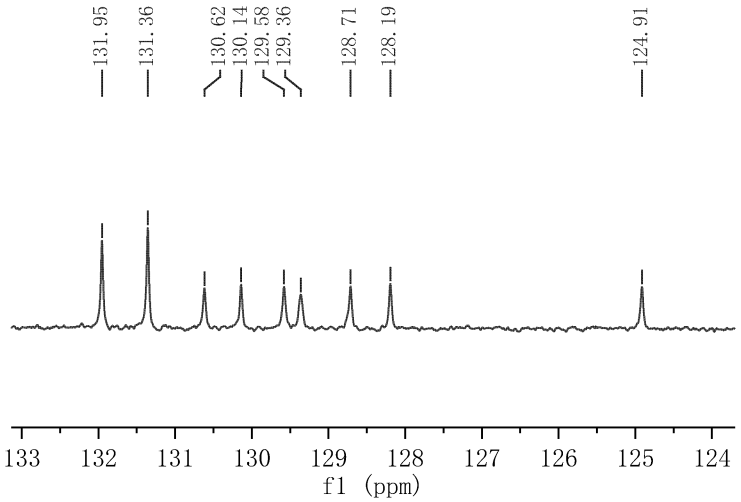

157.80
138.89
134.36
131.85
131.81
131.40
131.19
130.09
129.34
129.00
128.09
127.81
126.64
125.95
125.32
122.90
118.22
110.12
49.64
49.43
49.21
48.79
48.57
48.36
39.47
Parameter Value
1 Title 2a-C_FXY-2-137
2 Origin Bruker BioSpin GmbH
3 Solvent MeOD
4 Temperature 300.0
5 Number of Scans 36
6 Acquisition Time 1.3631
7 Acquisition Date 2020-06-19T22:19:53
8 Spectrometer Frequency 100.61
9 Spectral Width 24038.5
SBn
OH
2a
f1 (ppm)
f1 (ppm)

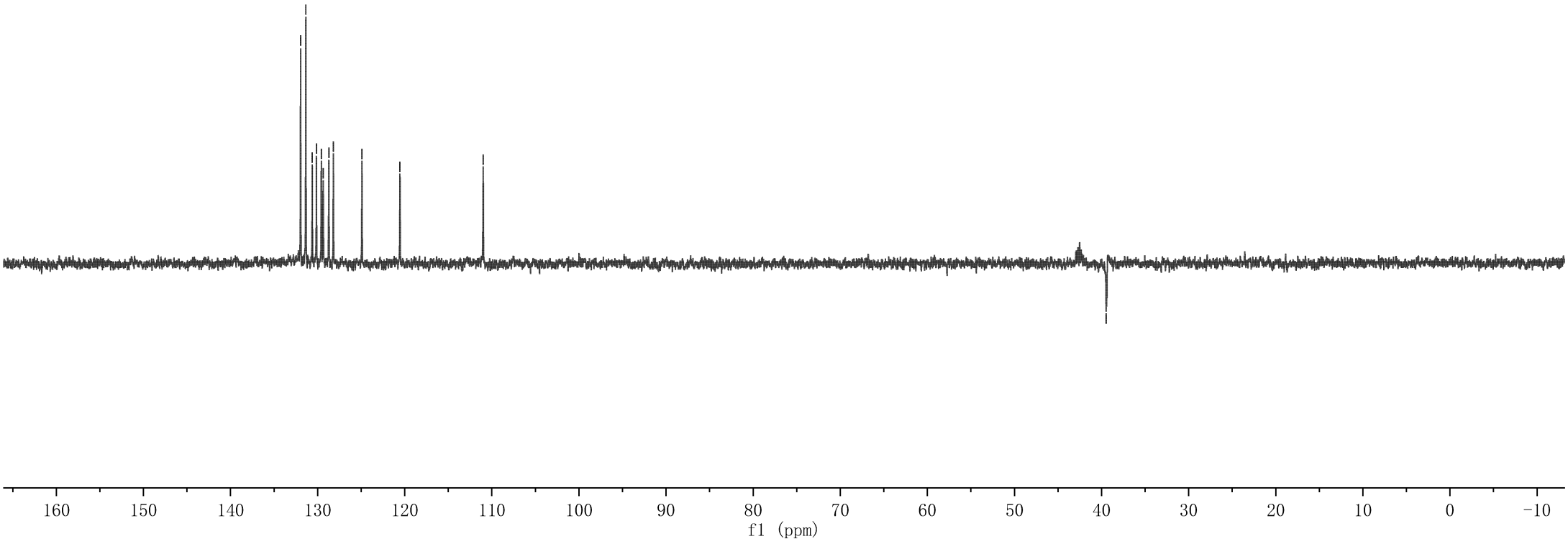
131.95
131.36
130.62
130.14
129.58
129.36
128.71
128.19
124.91
120.55
110.99
39.47

Parameter	Value
1 Title	FXY-2adept
2 Origin	
3 Solvent	DMSO
4 Temperature	297.2
5 Number of Scans	200
6 Acquisition Time	1.0001
7 Acquisition Date	2023-02-11T03:57:33
8 Spectrometer Frequency	100.56
9 Spectral Width	18028.0

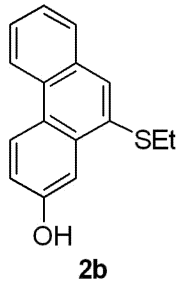


2a

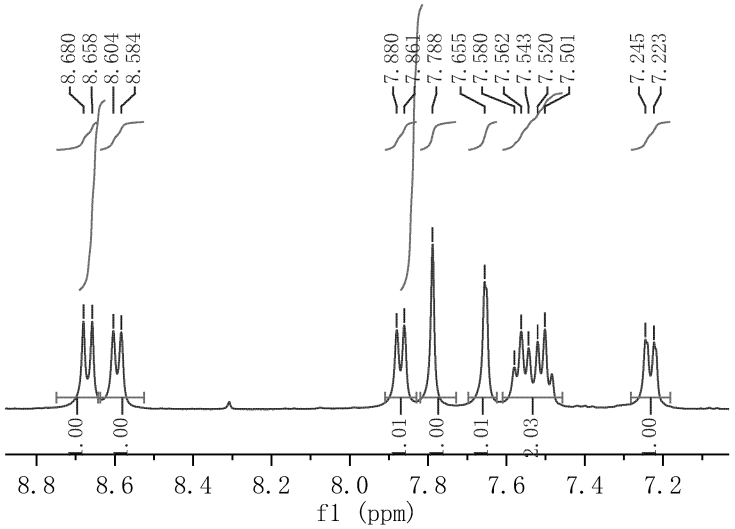




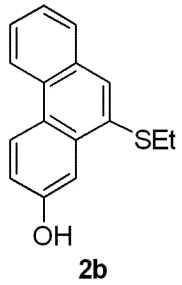
Parameter	Value
1 Title	2b-H-FXY-2-200-1
2 Origin	Bruker BioSpin GmbH
3 Solvent	DMSO
4 Temperature	298.0
5 Number of Scans	4
6 Acquisition Time	4.0894
7 Acquisition Date	2020-07-13T16:28:39
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8



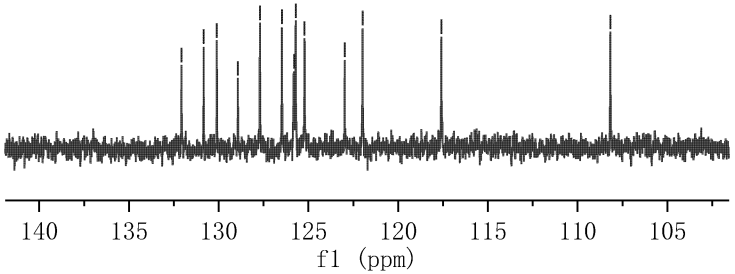
2b

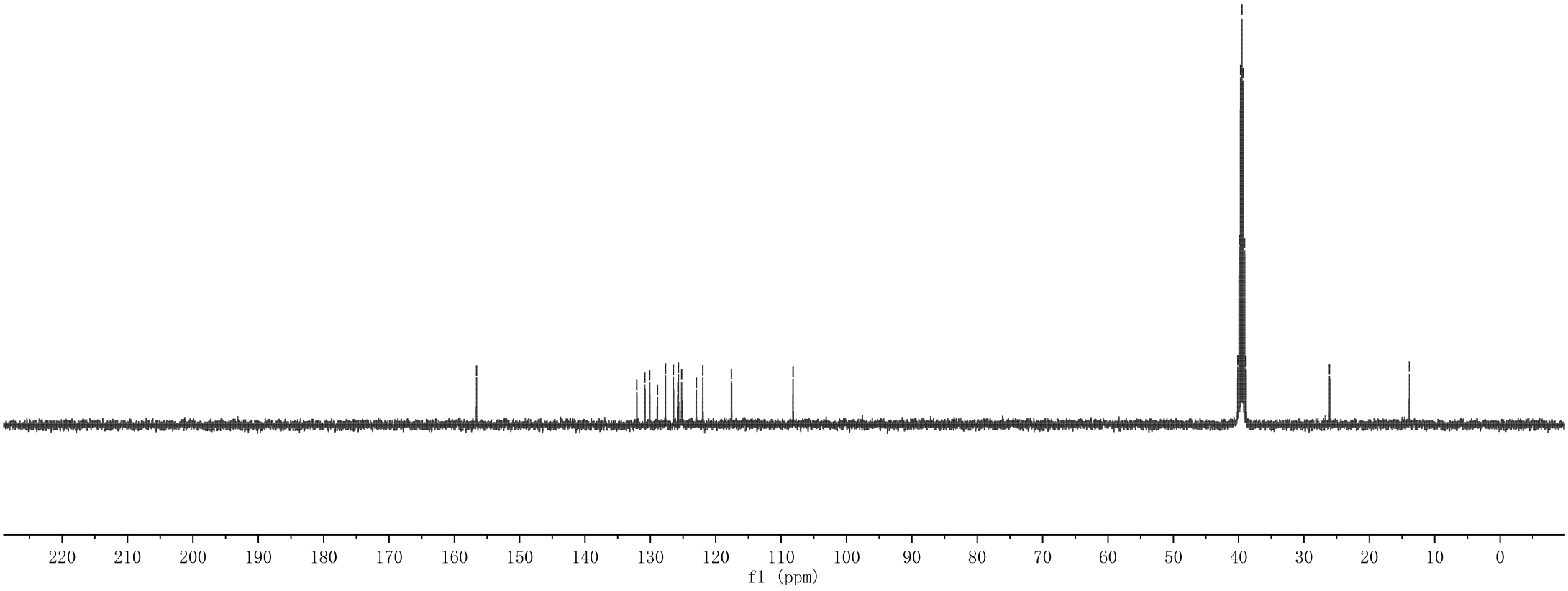


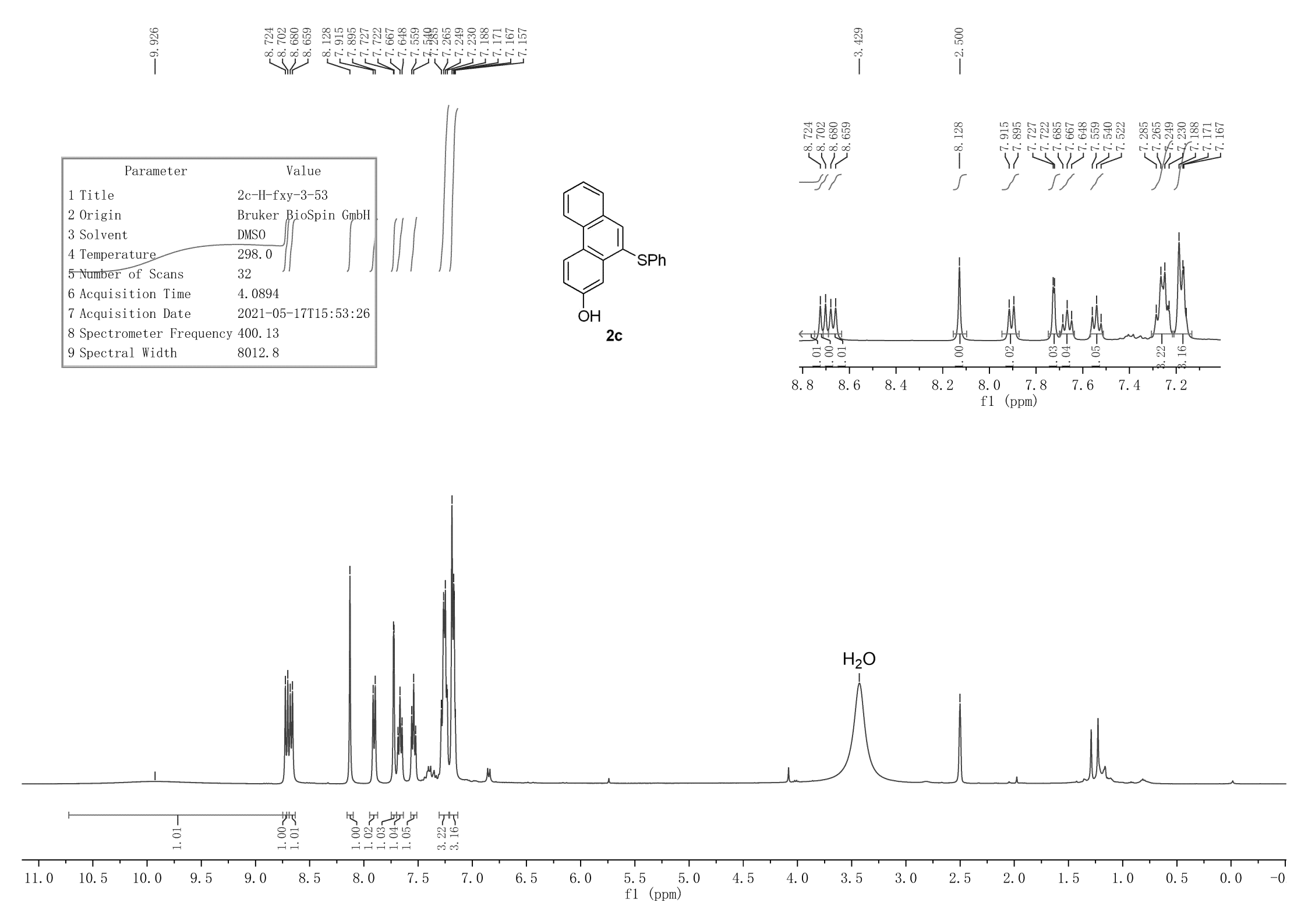
Parameter	Value
1 Title	2b-C-FXY-2-200-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	DMSO
4 Temperature	300.0
5 Number of Scans	55
6 Acquisition Time	1.3631
7 Acquisition Date	2020-07-14T14:43:07
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5

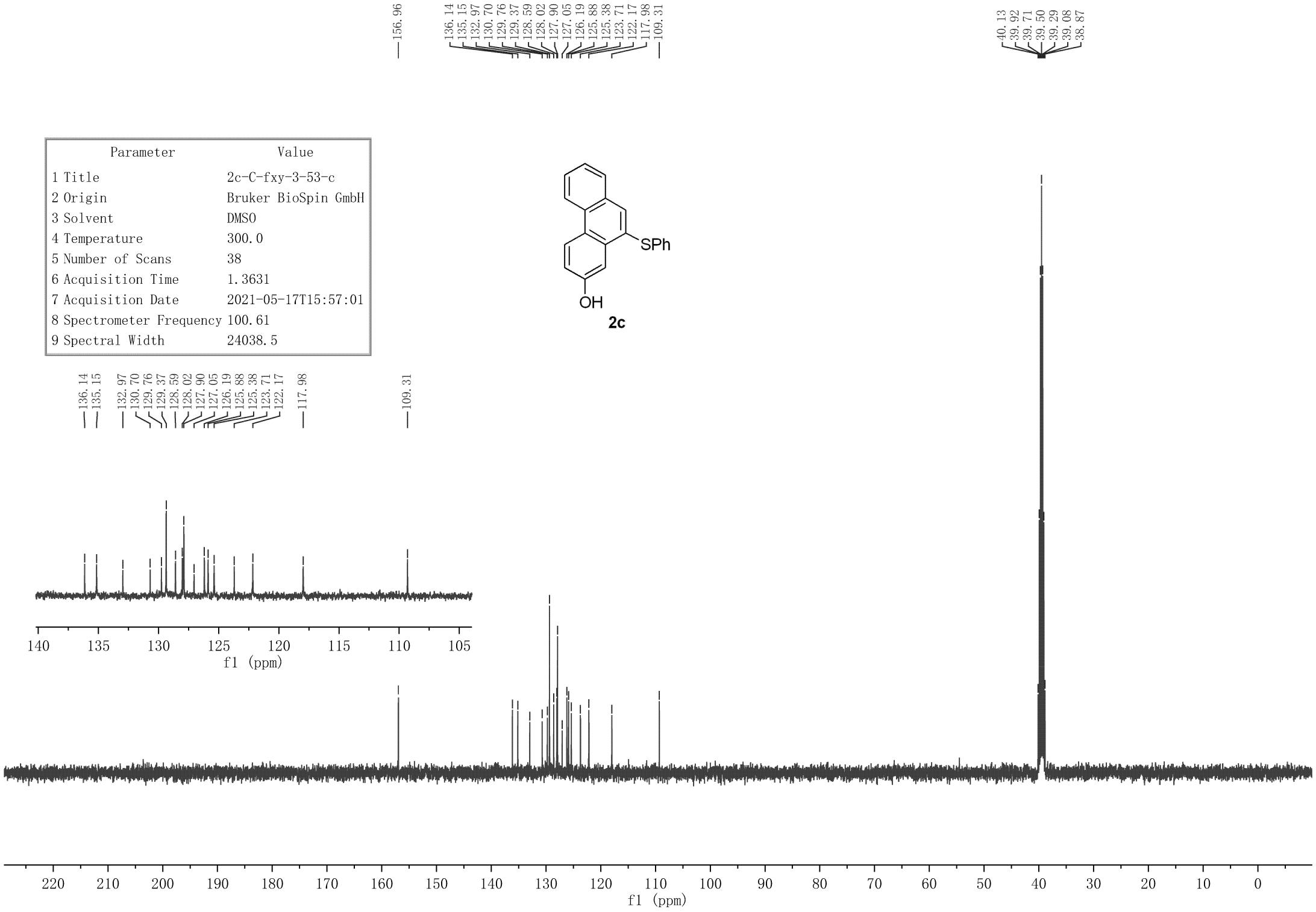


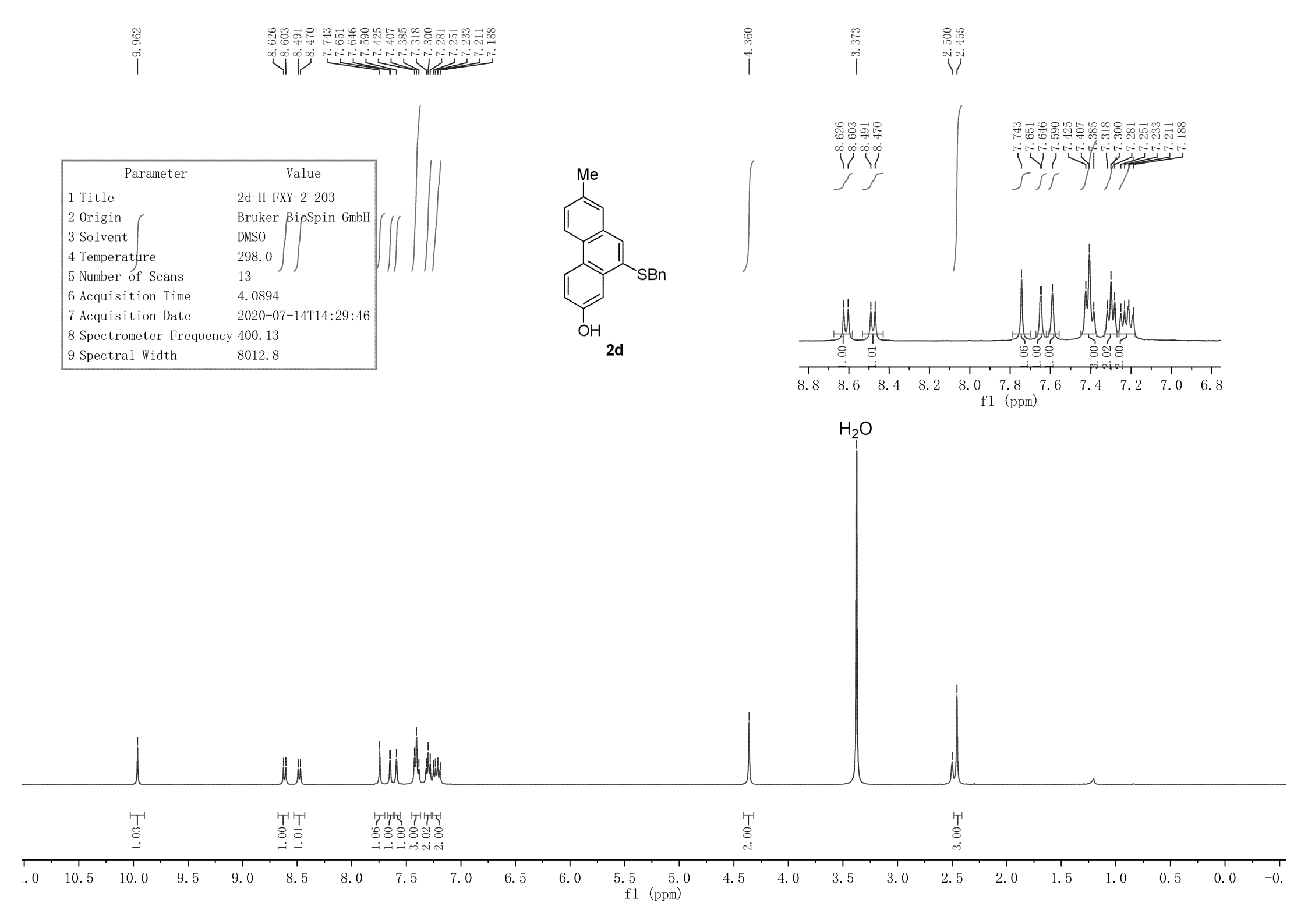
2b

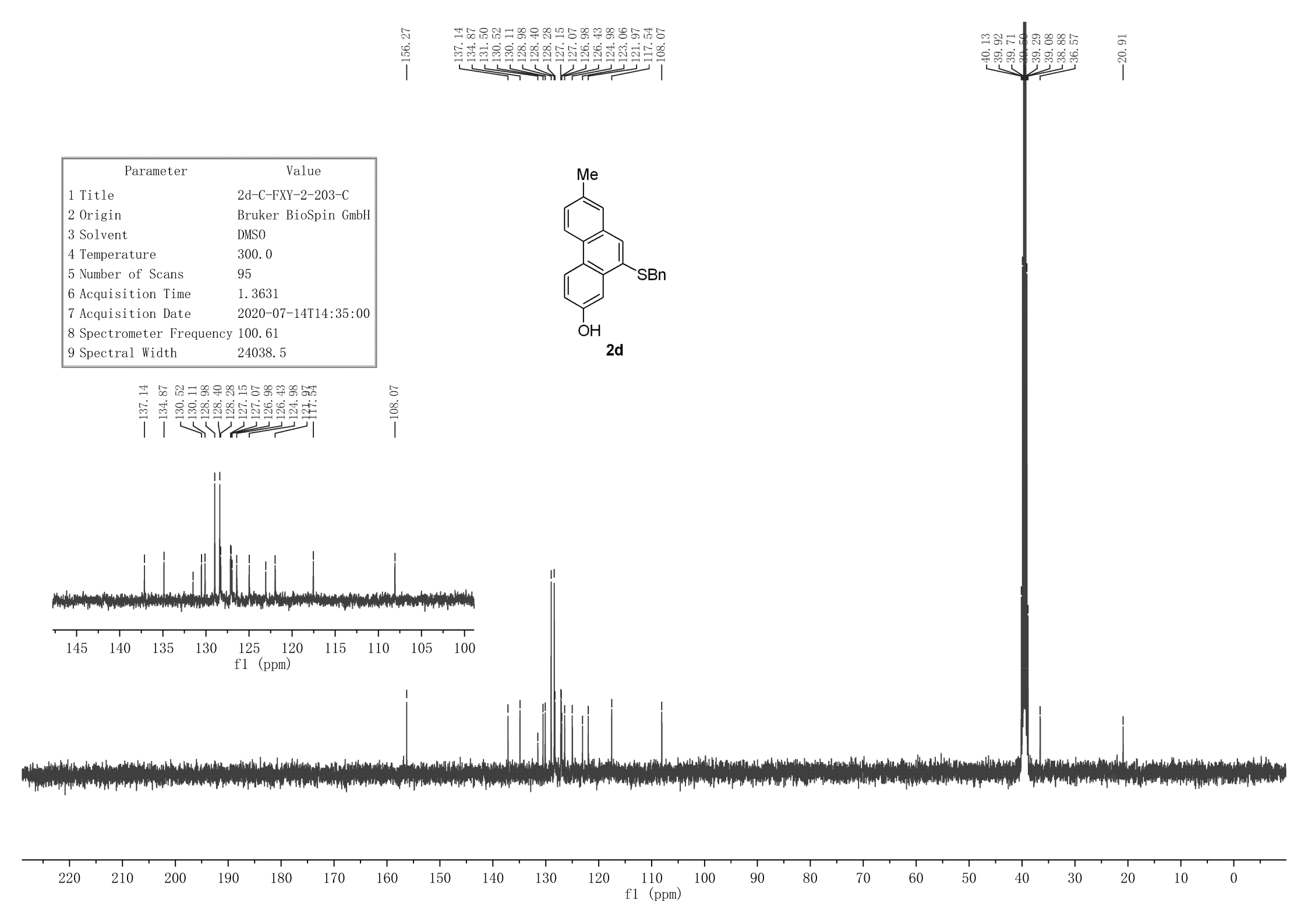


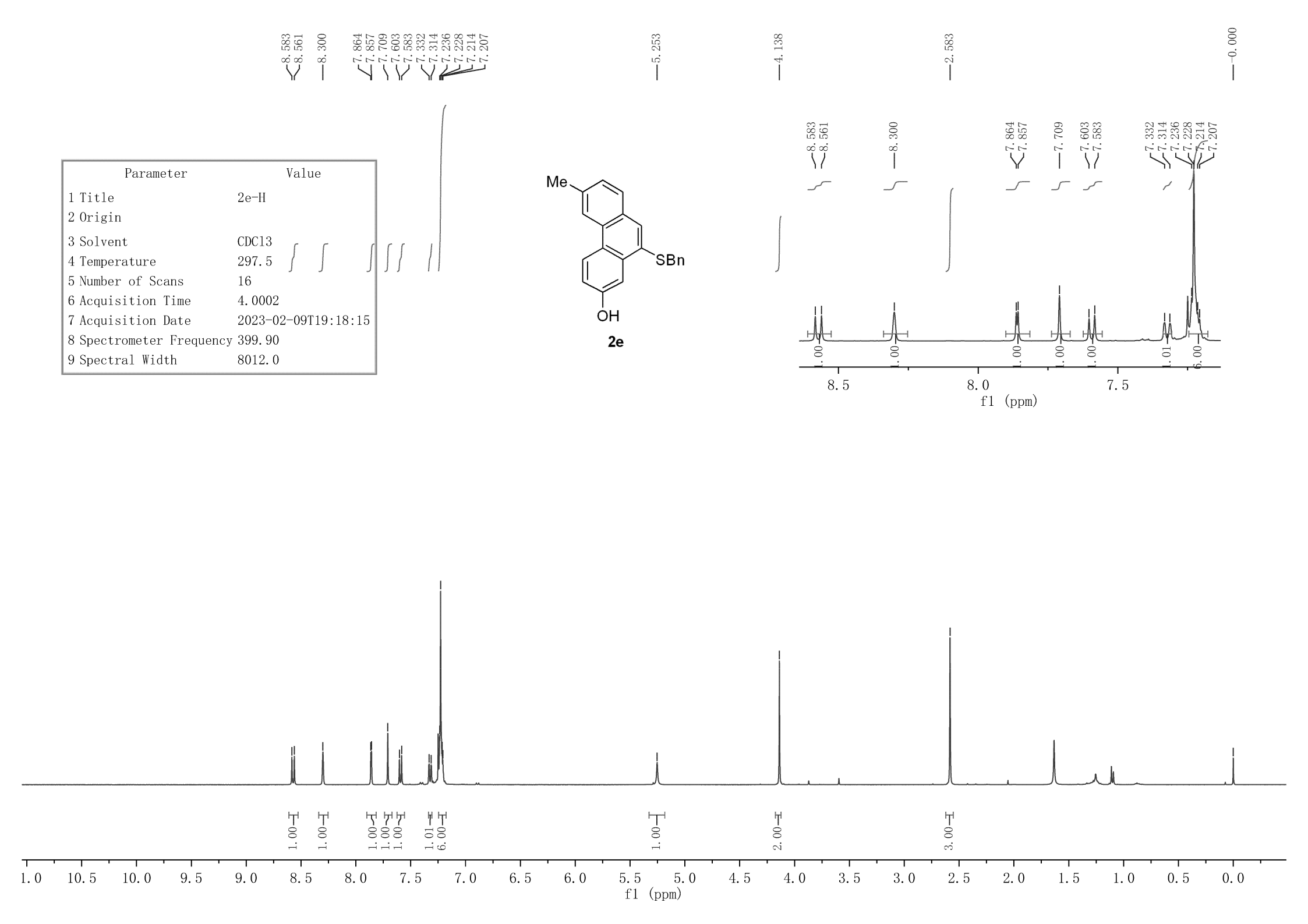



9.926
8.724
8.702
8.680
8.659
8.128
7.915
7.895
7.727
7.722
7.667
7.648
7.559
7.540
7.285
7.265
7.249
7.230
7.188
7.171
7.167
7.157
3.429
2.500
Parameter Value
1 Title 2c-H-fxy-3-53
2 Origin Bruker BioSpin GmbH
3 Solvent DMSO
4 Temperature 298.0
5 Number of Scans 32
6 Acquisition Time 4.0894
7 Acquisition Date 2021-05-17T15:53:26
8 Spectrometer Frequency 400.13
9 Spectral Width 8012.8
SPh
OH
2c
8.724
8.702
8.680
8.659
8.128
7.915
7.895
7.727
7.722
7.685
7.667
7.648
7.559
7.540
7.522
7.285
7.265
7.249
7.230
7.188
7.171
7.167
1.01
1.00
1.02
1.03
1.04
1.05
3.22
3.16
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
f1 (ppm)
H2O
1.01
1.00
1.01
1.00
1.02
1.03
1.04
1.05
3.22
3.16
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

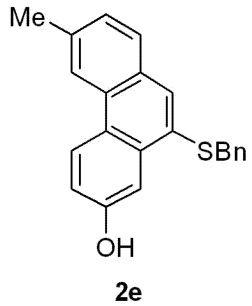

156.96
136.14
135.15
132.97
130.70
129.76
129.37
128.59
128.02
127.90
127.05
126.19
125.88
125.38
123.71
122.17
117.98
109.31
40.13
39.92
39.71
39.50
39.29
39.08
38.87
Parameter Value
1 Title 2c-C-fxy-3-53-c
2 Origin Bruker BioSpin GmbH
3 Solvent DMSO
4 Temperature 300.0
5 Number of Scans 38
6 Acquisition Time 1.3631
7 Acquisition Date 2021-05-17T15:57:01
8 Spectrometer Frequency 100.61
9 Spectral Width 24038.5
SPh
OH
2c
f1 (ppm)
f1 (ppm)


9.962
8.626
8.603
8.491
8.470
7.743
7.651
7.646
7.590
7.425
7.407
7.385
7.318
7.300
7.281
7.251
7.233
7.211
7.188
4.360
3.373
2.500
2.455
Parameter Value
1 Title 2d-H-FXY-2-203
2 Origin Bruker BioSpin GmbH
3 Solvent DMSO
4 Temperature 298.0
5 Number of Scans 13
6 Acquisition Time 4.0894
7 Acquisition Date 2020-07-14T14:29:46
8 Spectrometer Frequency 400.13
9 Spectral Width 8012.8
Me
SBn
OH
2d
1.03
1.00
1.01
1.06
1.00
1.00
3.00
2.02
2.00
2.00
3.00
f1 (ppm)
H2O

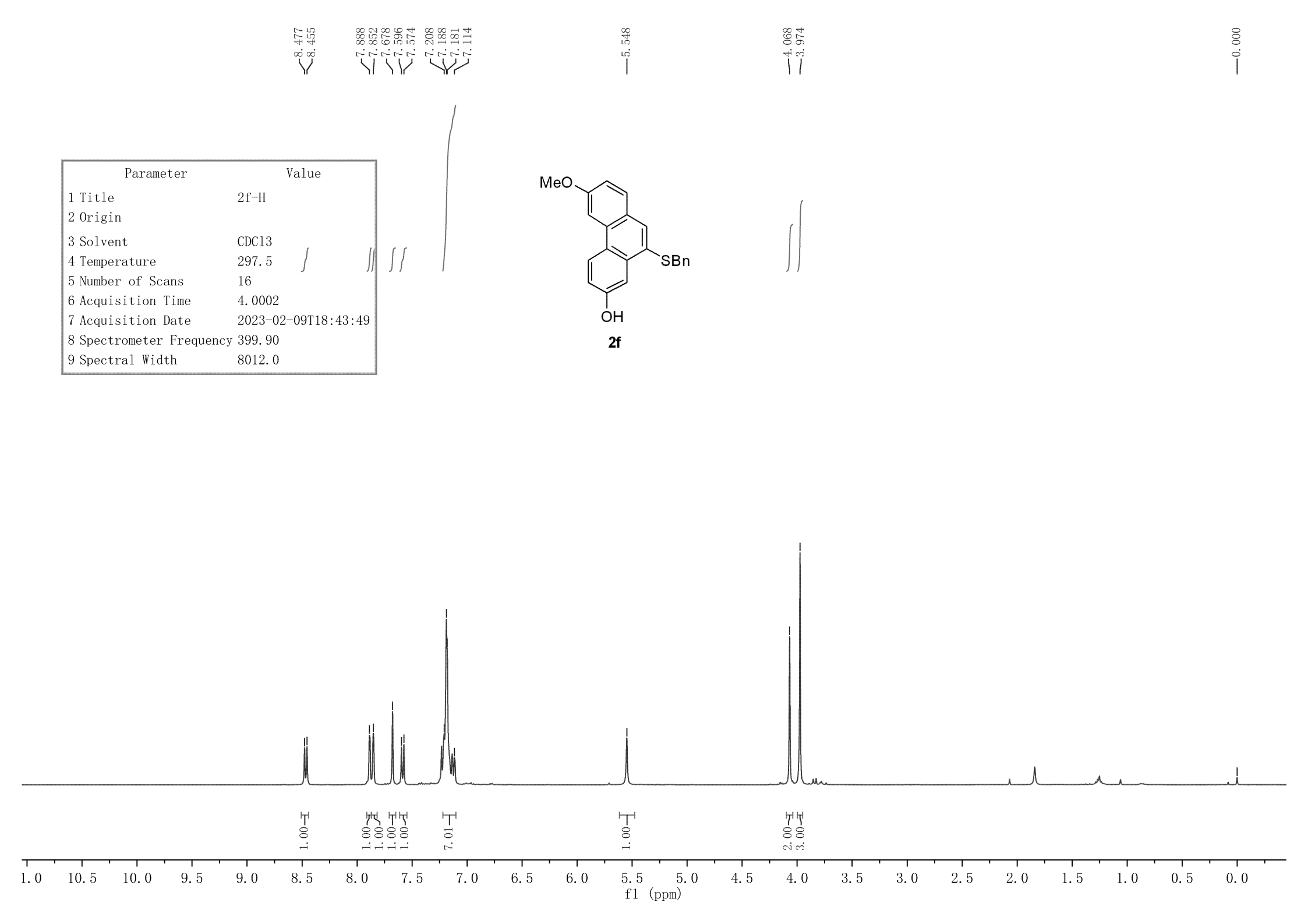

156.27
137.14
134.87
131.50
130.52
130.11
128.98
128.40
128.28
127.15
127.07
126.98
126.43
124.98
123.06
121.97
117.54
108.07
40.13
39.92
39.71
39.50
39.29
39.08
38.88
36.57
20.91
Parameter Value
1 Title 2d-C-FXY-2-203-C
2 Origin Bruker BioSpin GmbH
3 Solvent DMSO
4 Temperature 300.0
5 Number of Scans 95
6 Acquisition Time 1.3631
7 Acquisition Date 2020-07-14T14:35:00
8 Spectrometer Frequency 100.61
9 Spectral Width 24038.5
Me
SBn
OH
2d
f1 (ppm)
f1 (ppm)


8.583
8.561
8.300
7.864
7.857
7.709
7.603
7.583
7.332
7.314
7.236
7.228
7.214
7.207
5.253
4.138
2.583
0.000
Parameter Value
1 Title 2e-H
2 Origin
3 Solvent CDCl3
4 Temperature 297.5
5 Number of Scans 16
6 Acquisition Time 4.0002
7 Acquisition Date 2023-02-09T19:18:15
8 Spectrometer Frequency 399.90
9 Spectral Width 8012.0
Me
SBn
OH
2e
1.00
1.00
1.00
1.00
1.00
1.01
6.00
1.00
2.00
3.00
f1 (ppm)

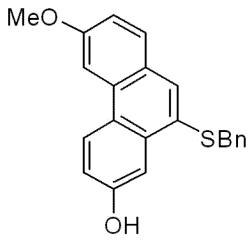
Parameter	Value
1 Title	2e-C
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.6
5 Number of Scans	800
6 Acquisition Time	1.0000
7 Acquisition Date	2023-02-09T19:47:44
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0



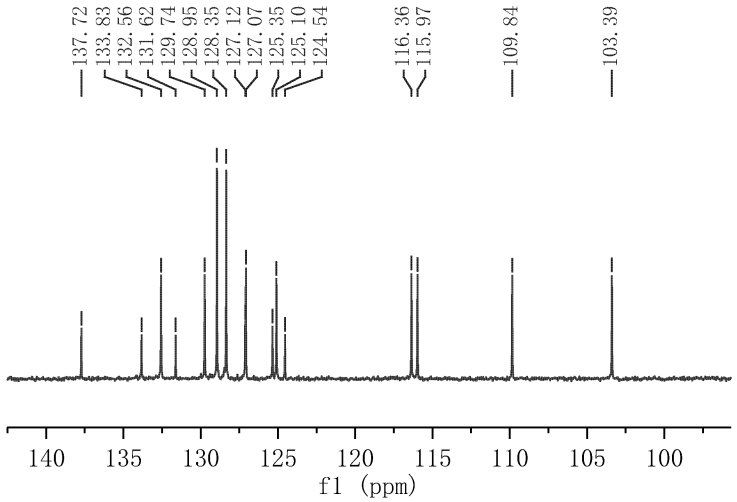
2e

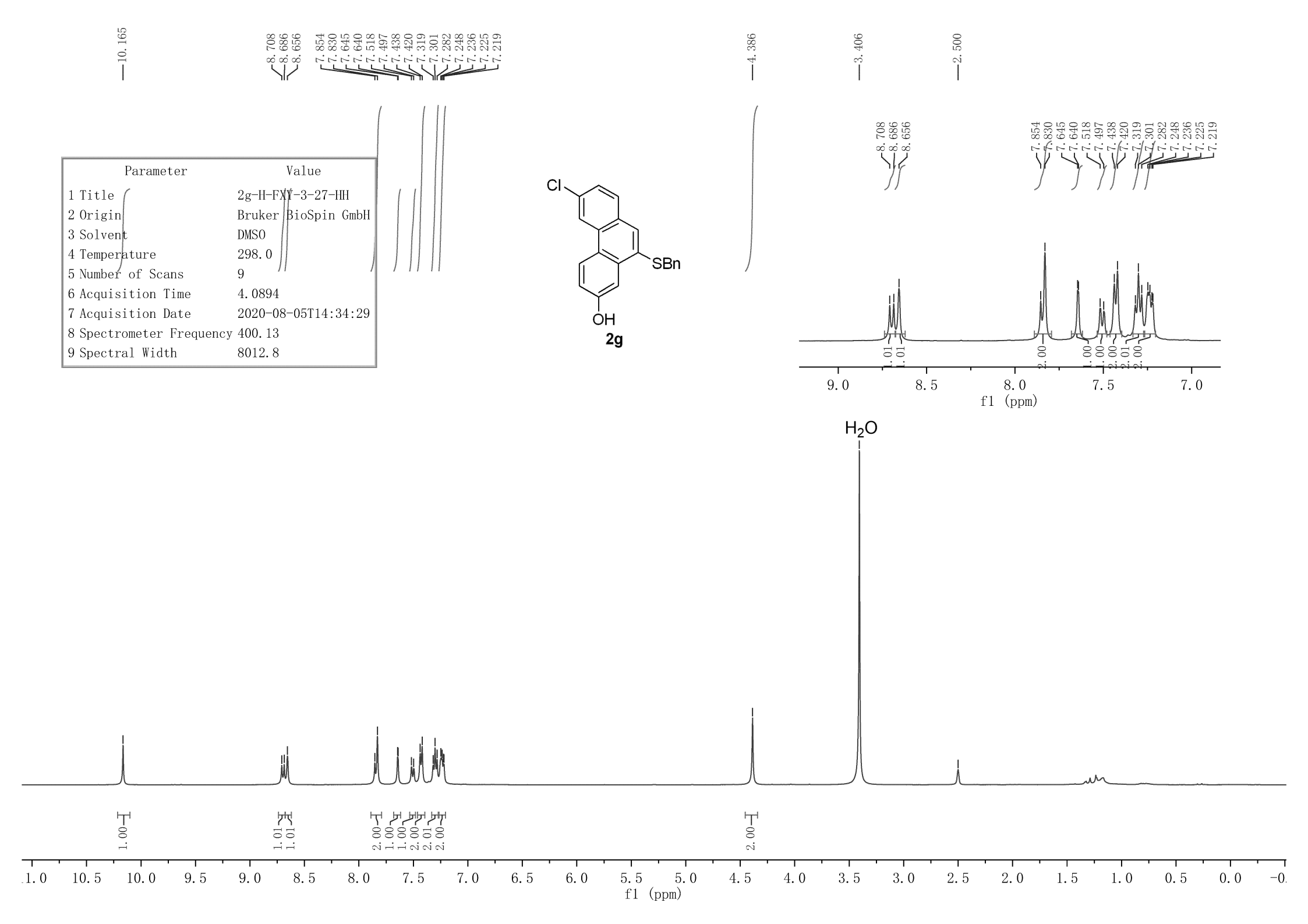

8.477
8.455
7.888
7.852
7.678
7.596
7.574
7.208
7.188
7.181
7.114
5.548
4.068
3.974
0.000
Parameter Value
1 Title 2f-H
2 Origin
3 Solvent CDCl3
4 Temperature 297.5
5 Number of Scans 16
6 Acquisition Time 4.0002
7 Acquisition Date 2023-02-09T18:43:49
8 Spectrometer Frequency 399.90
9 Spectral Width 8012.0
MeO
SBn
OH
2f
1.00
1.00
1.00
1.00
7.01
1.00
2.00
3.00
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

Parameter	Value
1 Title	2f-C
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.5
5 Number of Scans	800
6 Acquisition Time	1.0000
7 Acquisition Date	2023-02-09T19:13:05
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

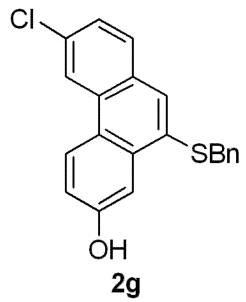


2f

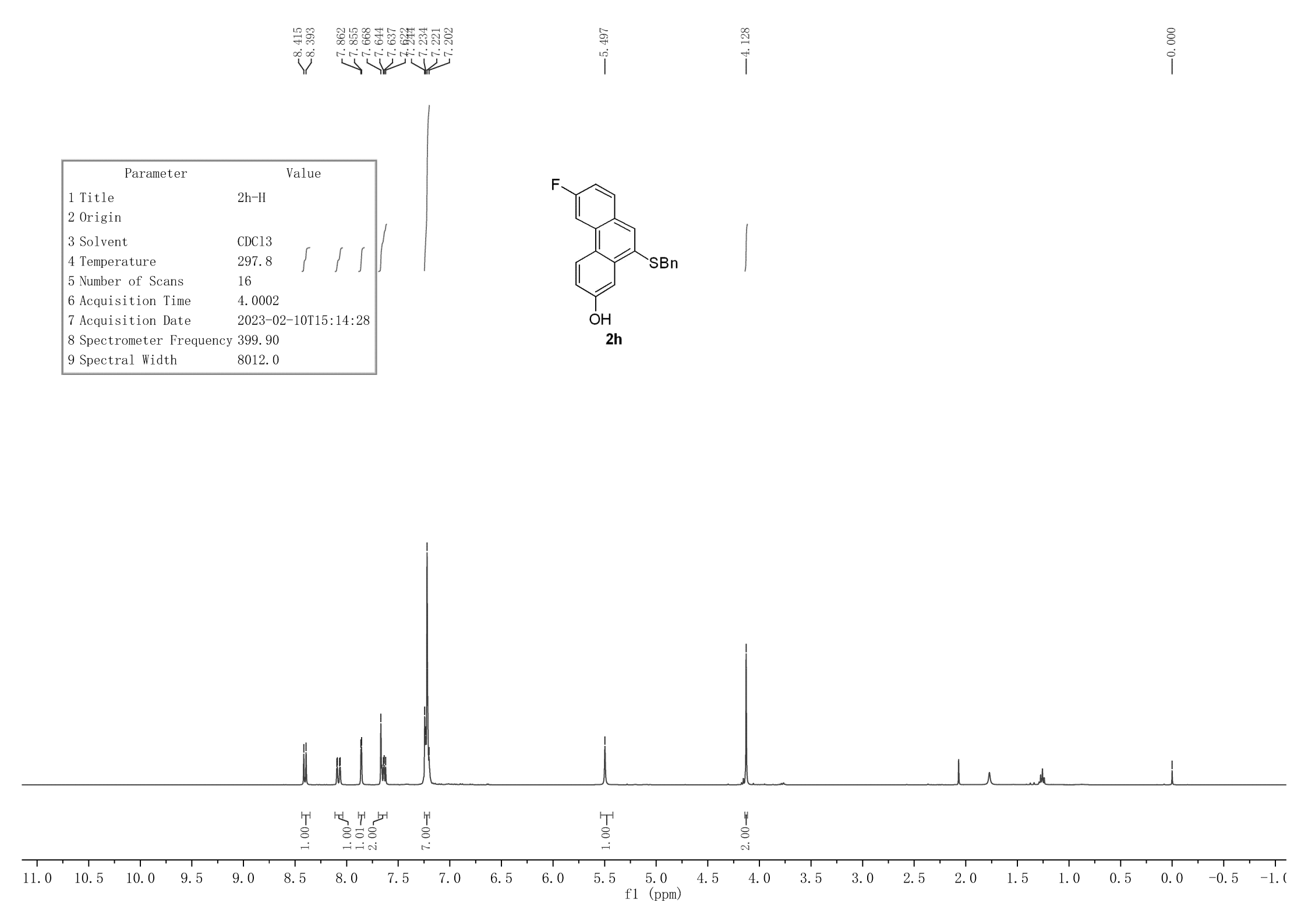



10.165
8.708
8.686
8.656
7.854
7.830
7.645
7.640
7.518
7.497
7.438
7.420
7.319
7.301
7.282
7.248
7.236
7.225
7.219
4.386
3.406
2.500
Parameter Value
1 Title 2g-H-FXY-3-27-HH
2 Origin Bruker BioSpin GmbH
3 Solvent DMSO
4 Temperature 298.0
5 Number of Scans 9
6 Acquisition Time 4.0894
7 Acquisition Date 2020-08-05T14:34:29
8 Spectrometer Frequency 400.13
9 Spectral Width 8012.8
Cl
SBn
OH
2g
f1 (ppm)
H2O
1.00
1.01
1.01
2.00
1.00
1.00
2.00
2.01
2.00
2.00

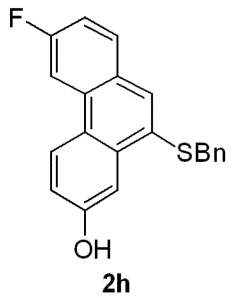
Parameter	Value
1 Title	2g-C-FXY-3-27-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	DMSO
4 Temperature	300.0
5 Number of Scans	47
6 Acquisition Time	1.3631
7 Acquisition Date	2020-08-05T14:36:08
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5



2g

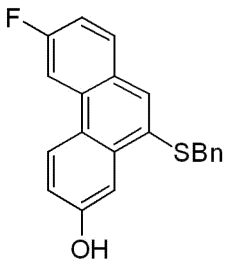

8.415
8.393
7.862
7.855
7.668
7.644
7.637
7.622
7.244
7.234
7.221
7.202
5.497
4.128
0.000
Parameter Value
1 Title 2h-H
2 Origin
3 Solvent CDC13
4 Temperature 297.8
5 Number of Scans 16
6 Acquisition Time 4.0002
7 Acquisition Date 2023-02-10T15:14:28
8 Spectrometer Frequency 399.90
9 Spectral Width 8012.0
F
SBn
OH
2h
1.00
1.00
1.01
2.00
7.00
1.00
2.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

Parameter	Value
1 Title	2h-C
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.8
5 Number of Scans	500
6 Acquisition Time	1.0000
7 Acquisition Date	2023-02-10T15:33:43
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

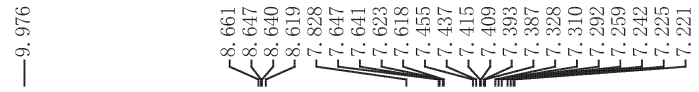


2h

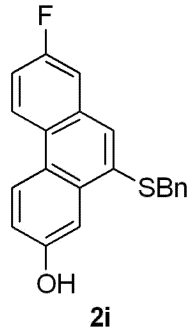
Parameter	Value
1 Title	2h-F
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.8
5 Number of Scans	16
6 Acquisition Time	1.0000
7 Acquisition Date	2023-02-10T15:36:58
8 Spectrometer Frequency	376.28
9 Spectral Width	96153.0



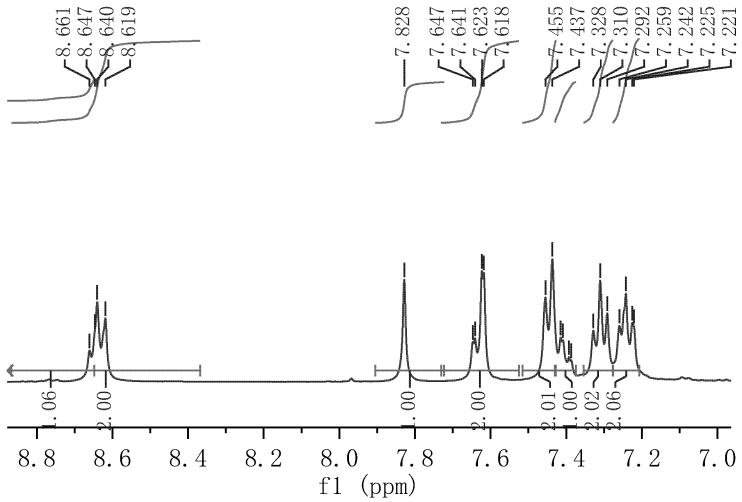
2h

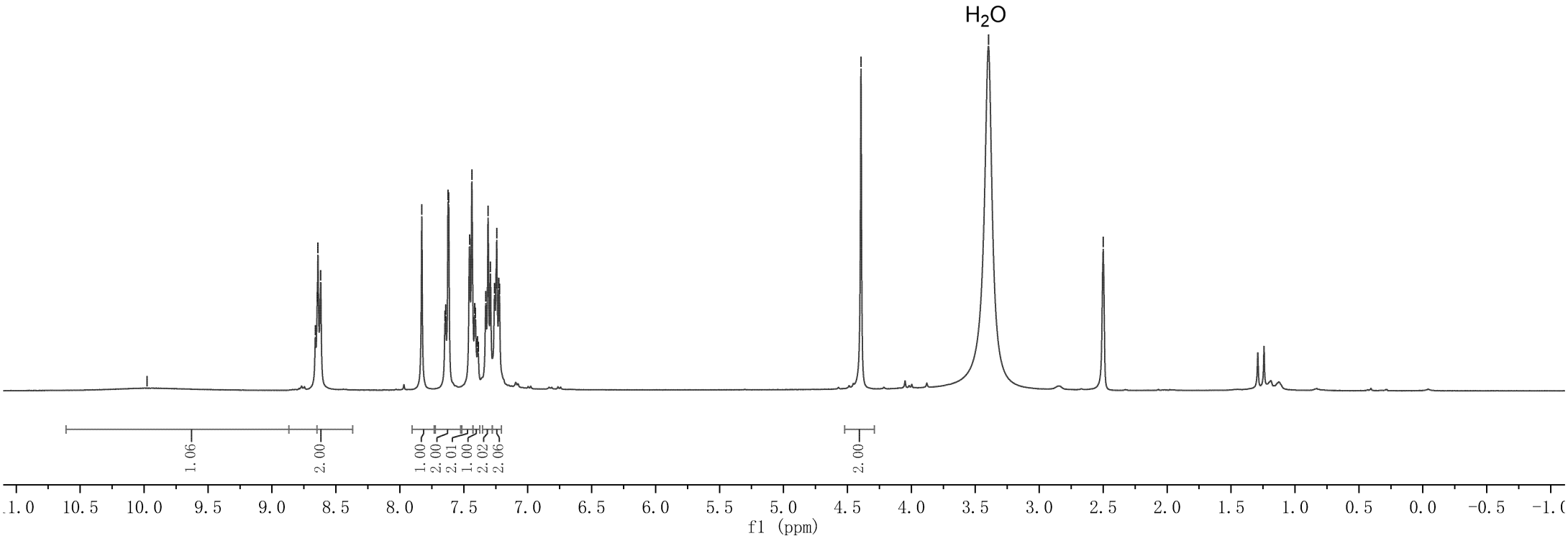


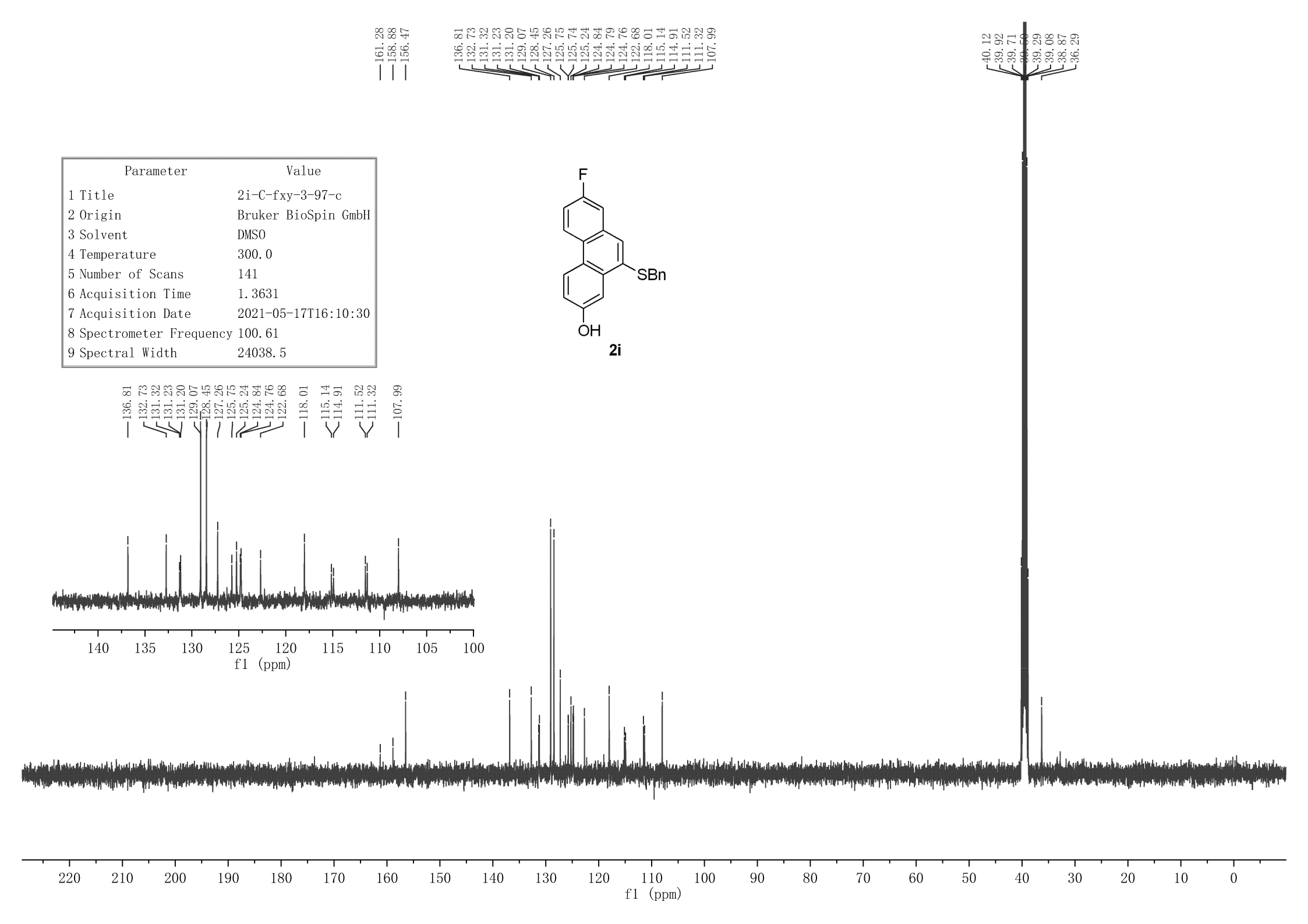
Parameter	Value
1 Title	2i-H-fxy-3-97
2 Origin	Bruker BioSpin GmbH
3 Solvent	DMSO
4 Temperature	298.0
5 Number of Scans	12
6 Acquisition Time	4.0894
7 Acquisition Date	2021-05-17T16:08:36
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8



2i



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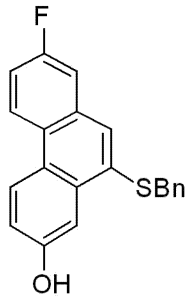
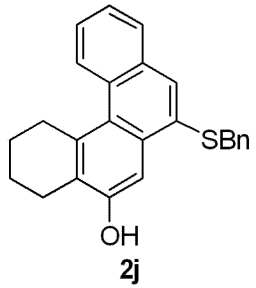
158.88
156.47
136.81
132.73
131.32
131.23
131.20
129.07
128.45
127.26
125.75
125.74
125.24
124.84
124.79
124.76
122.68
118.01
115.14
114.91
111.52
111.32
107.99
40.12
39.92
39.71
39.50
39.29
39.08
38.87
36.29
Parameter Value
1 Title 2i-C-fxy-3-97-c
2 Origin Bruker BioSpin GmbH
3 Solvent DMSO
4 Temperature 300.0
5 Number of Scans 141
6 Acquisition Time 1.3631
7 Acquisition Date 2021-05-17T16:10:30
8 Spectrometer Frequency 100.61
9 Spectral Width 24038.5
F
SBn
OH
2i
f1 (ppm)
f1 (ppm)

Parameter	Value
1 Title	fxy-2i-f-nmr
2 Origin	
3 Solvent	CDCl3
4 Temperature	296.3
5 Number of Scans	16
6 Acquisition Time	1.0000
7 Acquisition Date	2023-03-03T09:05:15
8 Spectrometer Frequency	376.28
9 Spectral Width	96153.0

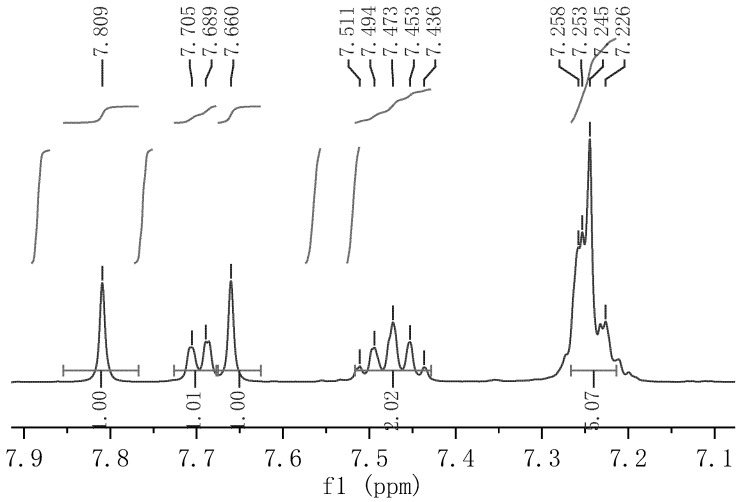


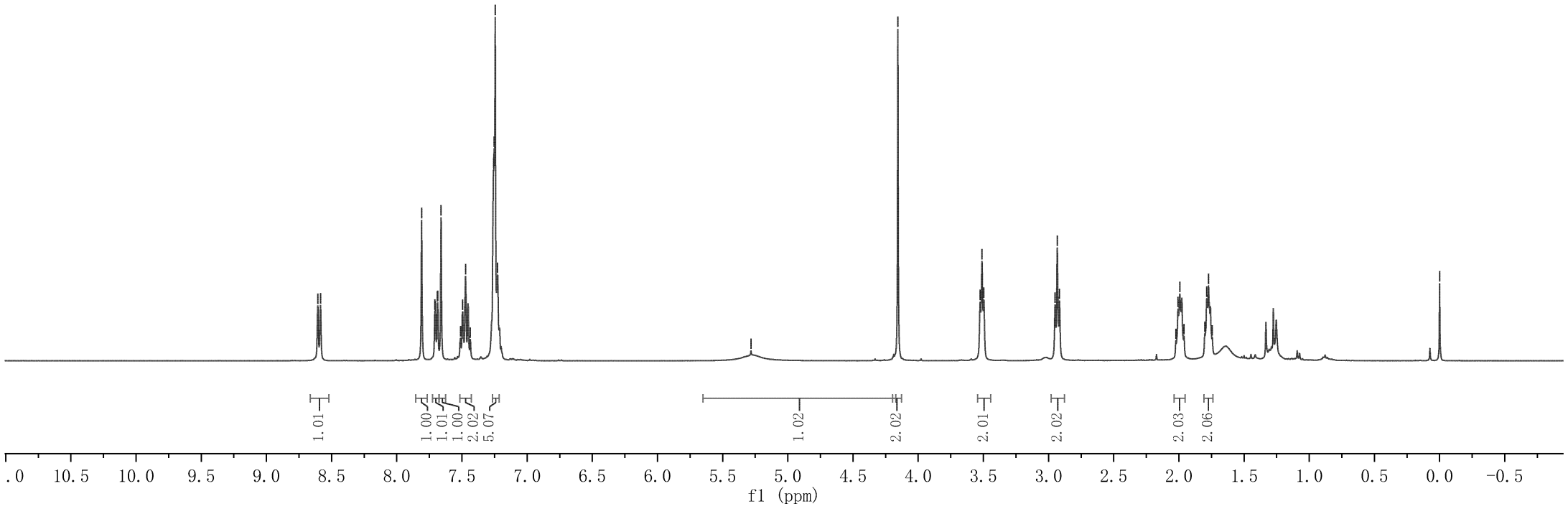
2i

Parameter	Value
1 Title	2j-H-fxy-5-124-h
2 Origin	
3 Solvent	CDCl3
4 Temperature	298.8
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2021-07-21T10:59:09
8 Spectrometer Frequency	399.93
9 Spectral Width	8012.0

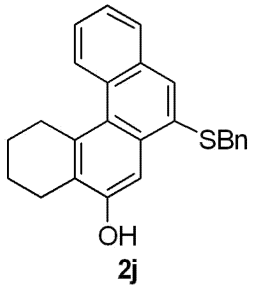


2j

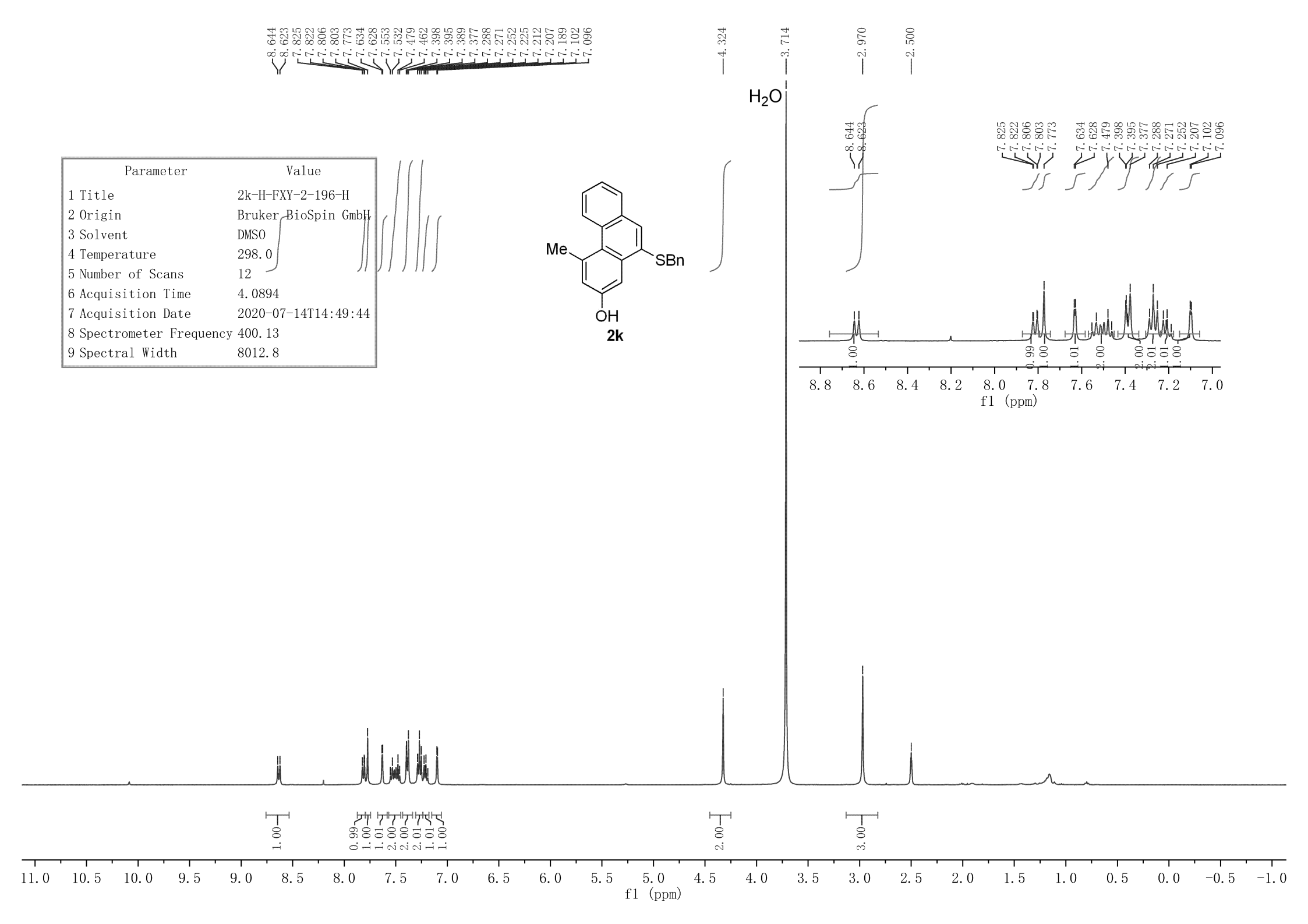


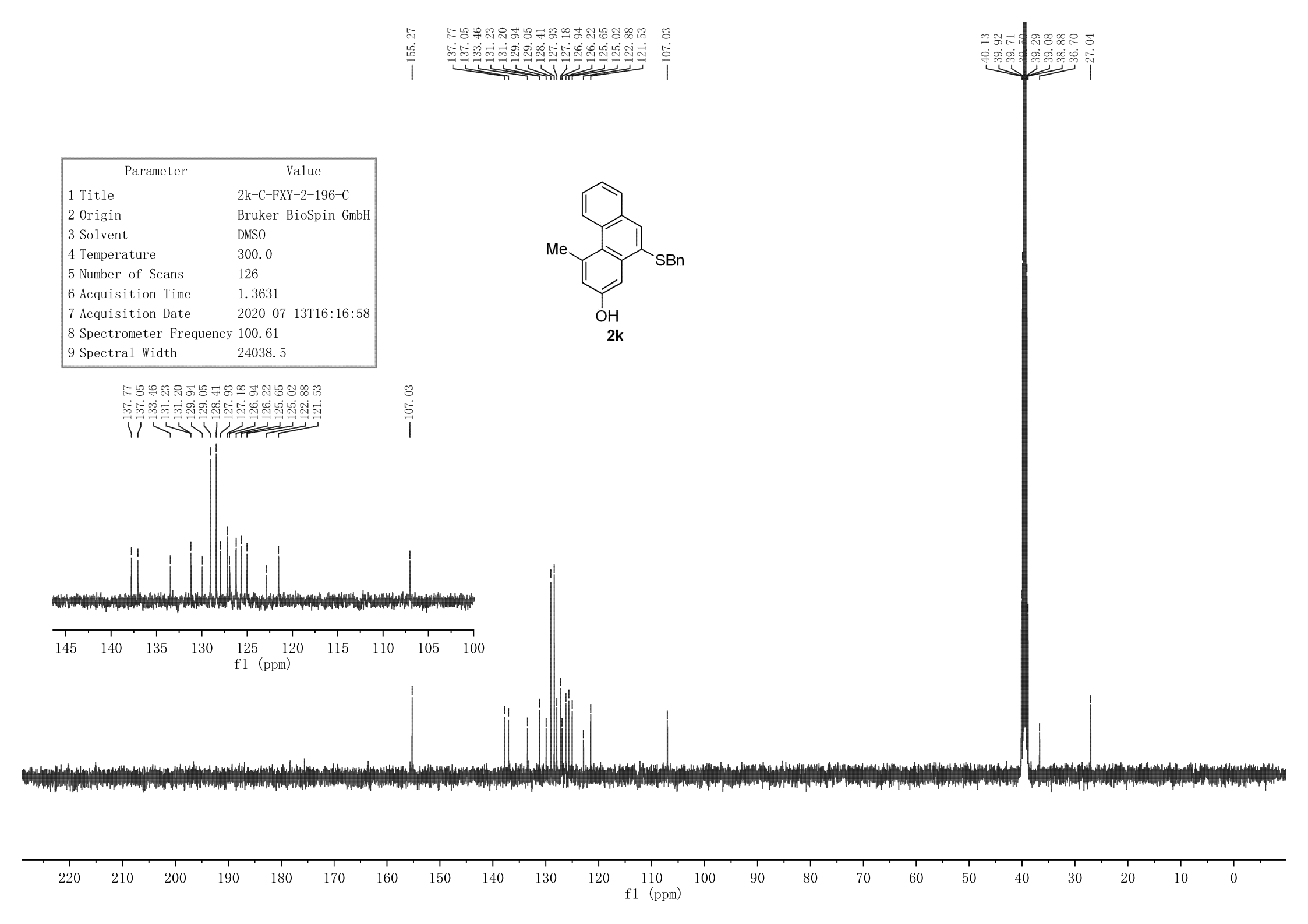


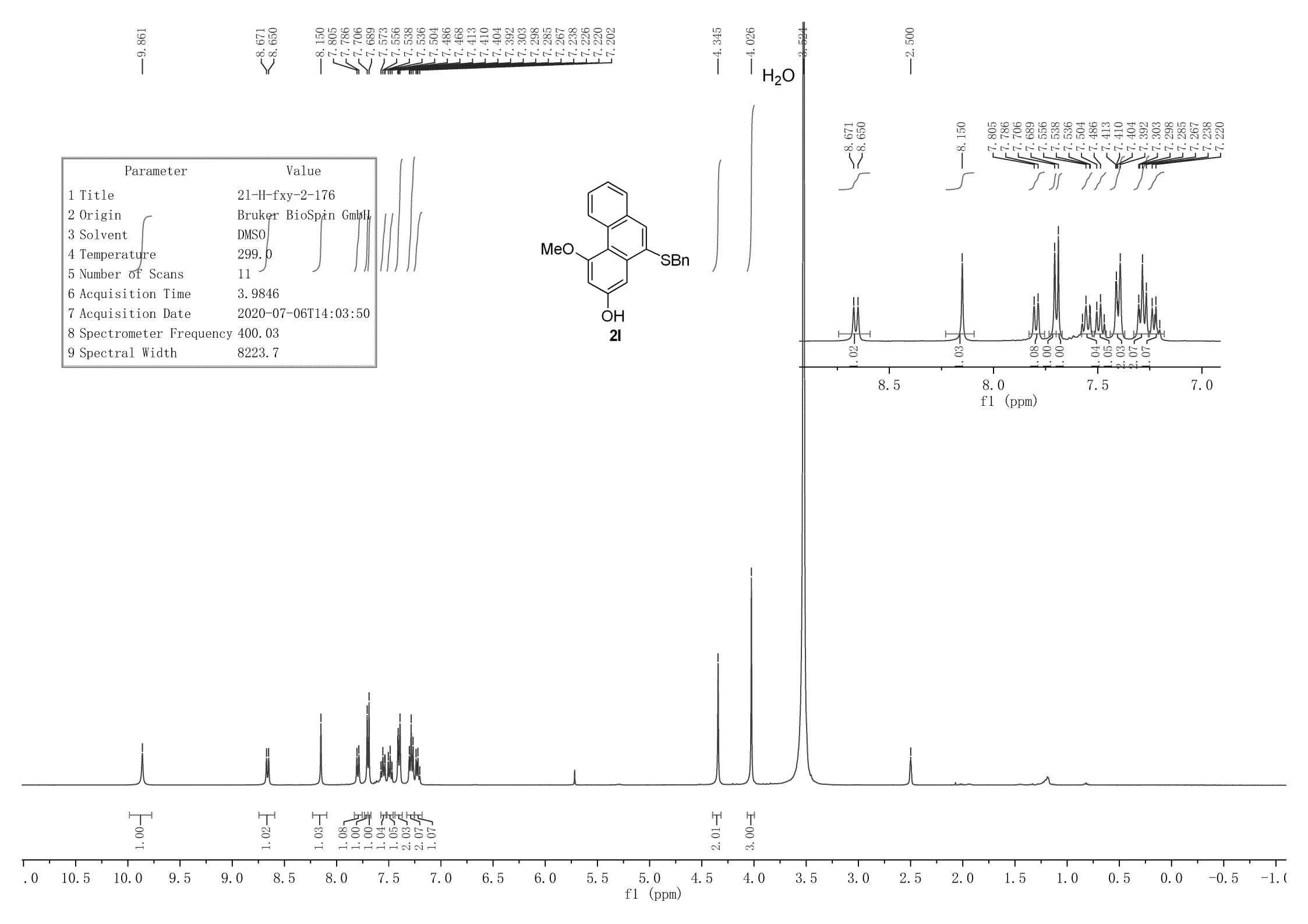
Parameter	Value
1 Title	2j-C-fxy-5-124-c
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.8
5 Number of Scans	200
6 Acquisition Time	1.0000
7 Acquisition Date	2021-07-21T11:07:54
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0



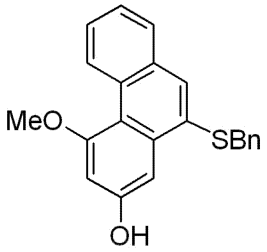
2j


8.644
8.623
7.825
7.822
7.806
7.803
7.773
7.634
7.628
7.553
7.532
7.479
7.462
7.398
7.395
7.389
7.377
7.288
7.271
7.252
7.225
7.212
7.207
7.189
7.102
7.096
4.324
3.714
2.970
2.500
H2O
Parameter Value
1 Title 2k-H-FXY-2-196-H
2 Origin Bruker BioSpin GmbH
3 Solvent DMSO
4 Temperature 298.0
5 Number of Scans 12
6 Acquisition Time 4.0894
7 Acquisition Date 2020-07-14T14:49:44
8 Spectrometer Frequency 400.13
9 Spectral Width 8012.8
Me
SBn
OH
2k
f1 (ppm)

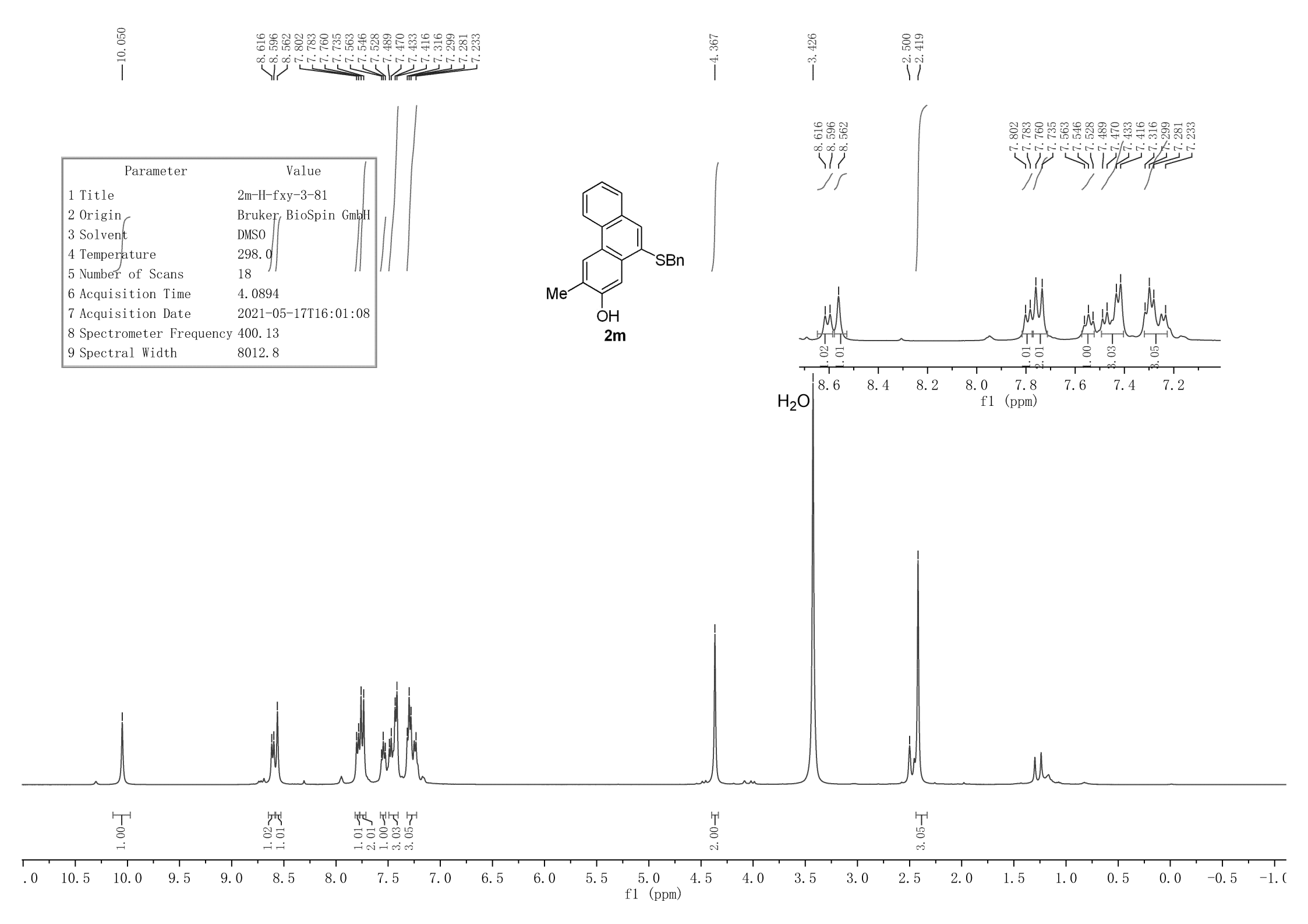

155.27
137.77
137.05
133.46
131.23
131.20
129.94
129.05
128.41
127.93
127.18
126.94
126.22
125.65
125.02
122.88
121.53
107.03
40.13
39.92
39.71
39.50
39.29
39.08
38.88
36.70
27.04
Parameter Value
1 Title 2k-C-FXY-2-196-C
2 Origin Bruker BioSpin GmbH
3 Solvent DMSO
4 Temperature 300.0
5 Number of Scans 126
6 Acquisition Time 1.3631
7 Acquisition Date 2020-07-13T16:16:58
8 Spectrometer Frequency 100.61
9 Spectral Width 24038.5
Me
SBn
OH
2k
f1 (ppm)
f1 (ppm)


9.861
8.671
8.650
8.150
7.805
7.786
7.706
7.689
7.573
7.556
7.538
7.536
7.504
7.486
7.468
7.413
7.410
7.404
7.392
7.303
7.298
7.285
7.267
7.238
7.226
7.220
7.202
4.345
4.026
2.524
2.500
H2O
Parameter Value
1 Title 2l-H-fxy-2-176
2 Origin Bruker BioSpin GmbH
3 Solvent DMSO
4 Temperature 299.0
5 Number of Scans 11
6 Acquisition Time 3.9846
7 Acquisition Date 2020-07-06T14:03:50
8 Spectrometer Frequency 400.03
9 Spectral Width 8223.7
MeO
SBn
OH
2l
f1 (ppm)
1.00
1.02
1.03
1.08
1.00
1.00
1.04
1.05
2.03
2.07
1.07
2.01
3.00

Parameter	Value
1 Title	2l-C-fxy-2-176-c
2 Origin	Bruker BioSpin GmbH
3 Solvent	DMSO
4 Temperature	299.0
5 Number of Scans	103
6 Acquisition Time	1.3631
7 Acquisition Date	2020-07-06T14:07:20
8 Spectrometer Frequency	100.59
9 Spectral Width	24038.5



2l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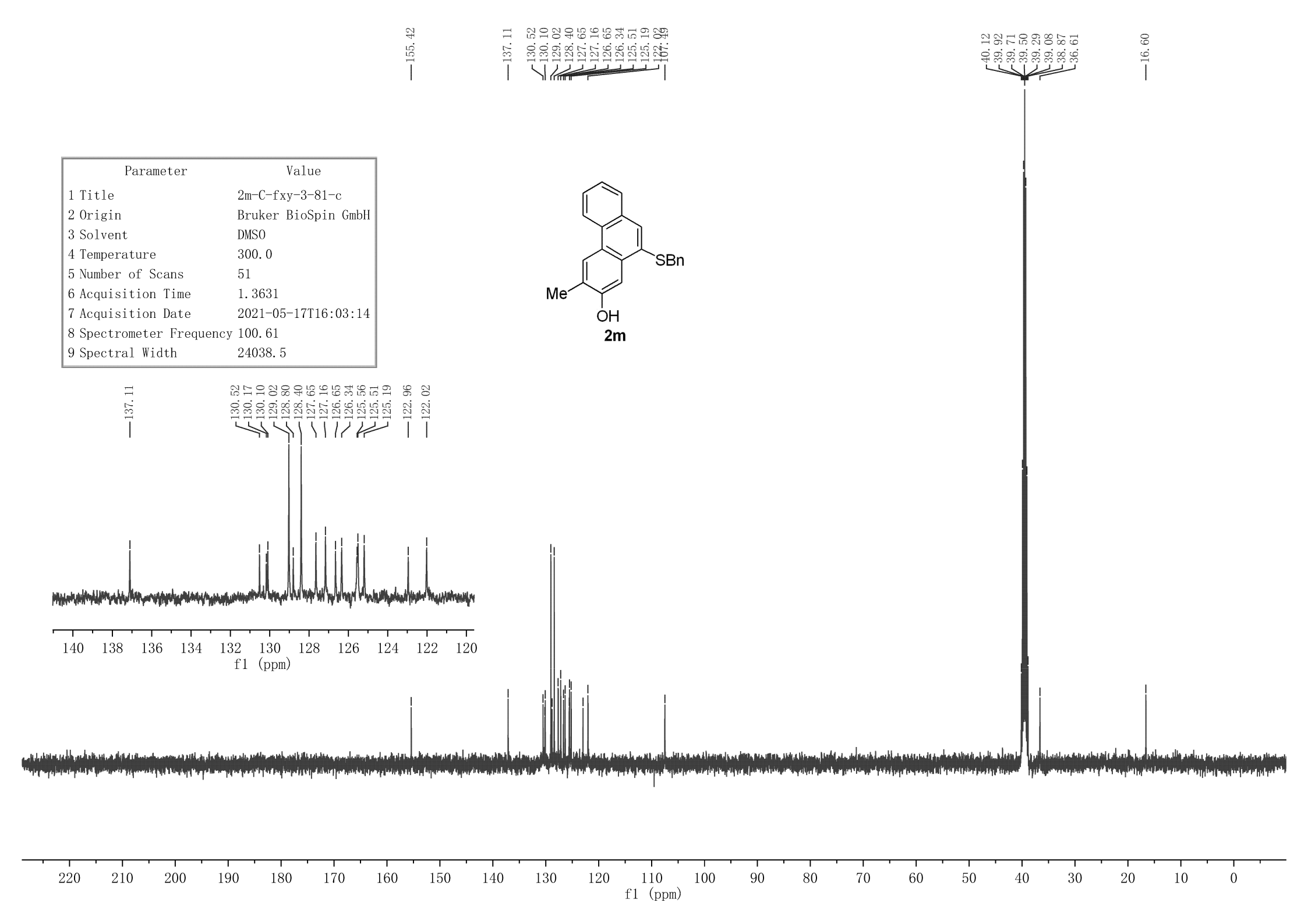
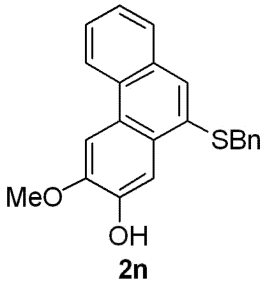
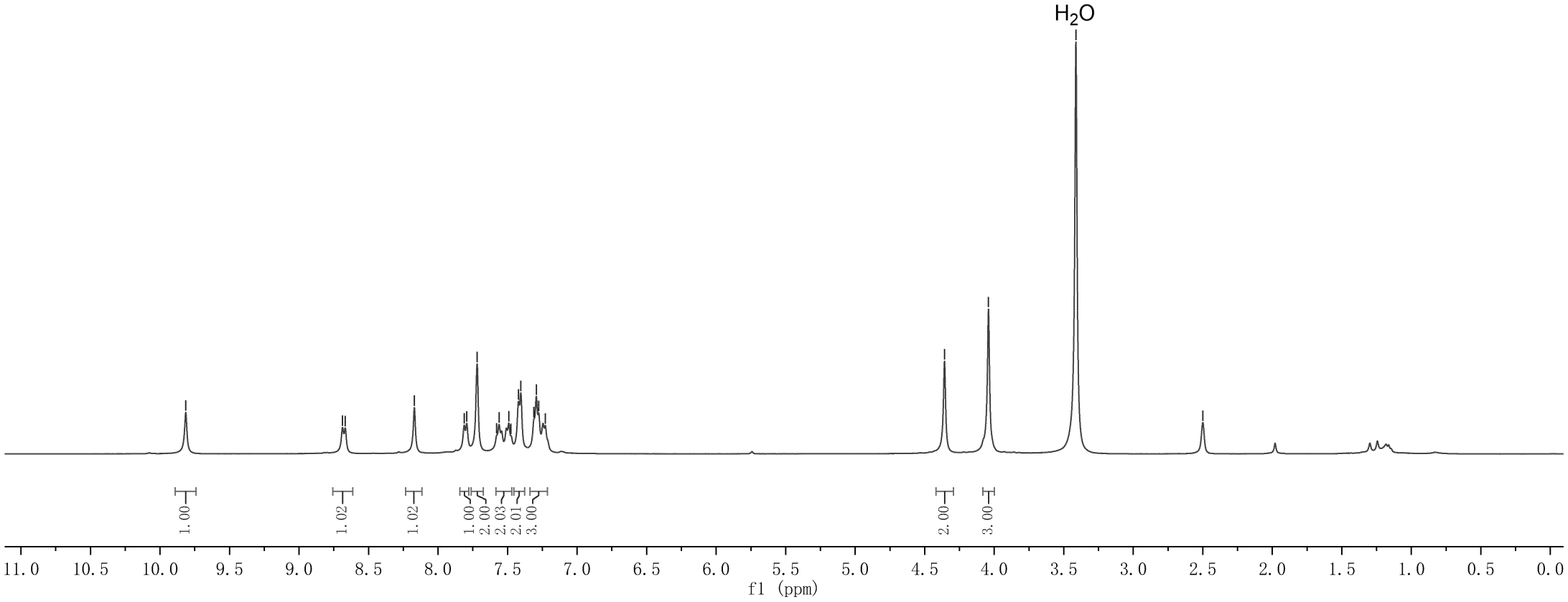
8.616
8.596
8.562
7.802
7.783
7.760
7.735
7.563
7.546
7.528
7.489
7.470
7.433
7.416
7.316
7.299
7.281
7.233
4.367
3.426
2.500
2.419
Parameter Value
1 Title 2m-H-fxy-3-81
2 Origin Bruker BioSpin GmbH
3 Solvent DMSO
4 Temperature 298.0
5 Number of Scans 18
6 Acquisition Time 4.0894
7 Acquisition Date 2021-05-17T16:01:08
8 Spectrometer Frequency 400.13
9 Spectral Width 8012.8
SBn
Me
OH
2m
H2O
1.00
1.02
1.01
1.01
2.01
1.00
3.03
3.05
2.00
3.05
f1 (ppm)


155.42
137.11
130.52
130.10
129.02
128.40
127.65
127.16
126.65
126.34
125.51
125.19
122.96
122.02
40.12
39.92
39.71
39.50
39.29
39.08
38.87
36.61
16.60
Parameter Value
1 Title 2m-C-fxy-3-81-c
2 Origin Bruker BioSpin GmbH
3 Solvent DMSO
4 Temperature 300.0
5 Number of Scans 51
6 Acquisition Time 1.3631
7 Acquisition Date 2021-05-17T16:03:14
8 Spectrometer Frequency 100.61
9 Spectral Width 24038.5
SBn
Me
OH
2m
f1 (ppm)
f1 (ppm)

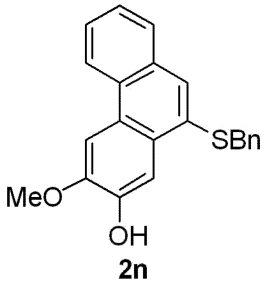
Parameter	Value
1 Title	2n-H-fxy-3-107
2 Origin	Bruker BioSpin GmbH
3 Solvent	DMSO
4 Temperature	298.0
5 Number of Scans	8
6 Acquisition Time	4.0894
7 Acquisition Date	2021-05-17T16:20:17
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8



2n



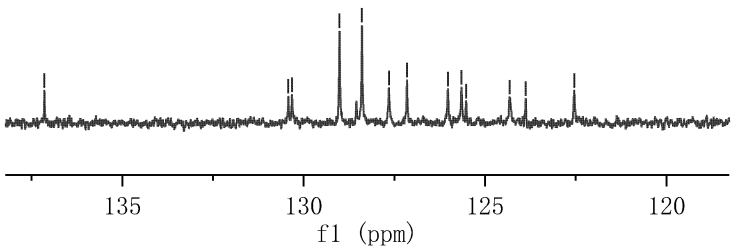
Parameter	Value
1 Title	2n-C-fxy-3-107-c
2 Origin	Bruker BioSpin GmbH
3 Solvent	DMSO
4 Temperature	300.0
5 Number of Scans	63
6 Acquisition Time	1.3631
7 Acquisition Date	2021-05-17T16:21:38
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5

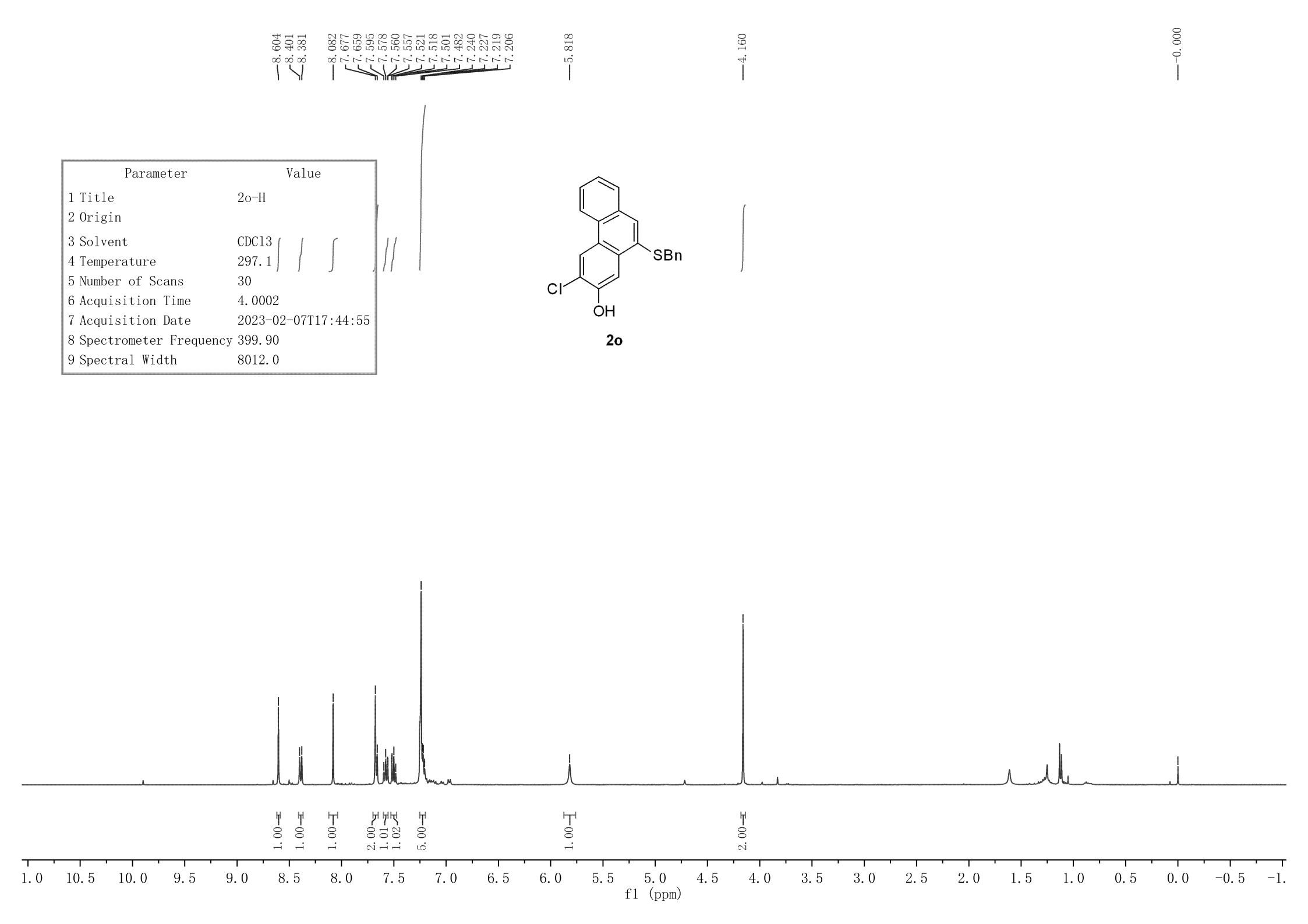


2n

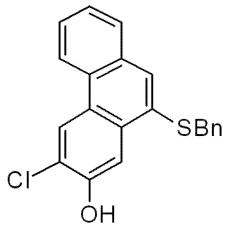
148.99, 147.42, 137.15, 130.42, 130.32, 129.01, 128.39, 127.65, 127.15, 126.02, 125.65, 124.32, 122.54, 108.85, 105.91, 104.65, 55.84, 40.13, 39.92, 39.71, 39.50, 39.29, 39.08, 38.87, 36.73

137.15, 130.42, 130.32, 129.01, 128.39, 127.65, 127.15, 126.02, 125.65, 125.52, 124.32, 123.88, 122.54

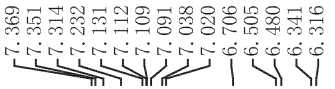



8.604
8.401
8.381
8.082
7.677
7.659
7.595
7.578
7.560
7.557
7.521
7.518
7.501
7.482
7.240
7.227
7.219
7.206
5.818
4.160
0.000
Parameter Value
1 Title 2o-H
2 Origin
3 Solvent CDCl3
4 Temperature 297.1
5 Number of Scans 30
6 Acquisition Time 4.0002
7 Acquisition Date 2023-02-07T17:44:55
8 Spectrometer Frequency 399.90
9 Spectral Width 8012.0
SBn
Cl
OH
2o
1.00
1.00
1.00
2.00
1.01
1.02
5.00
1.00
2.00
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)

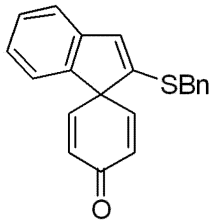
Parameter	Value
1 Title	2o-C
2 Origin	
3 Solvent	CDCl3
4 Temperature	295.6
5 Number of Scans	300
6 Acquisition Time	1.0000
7 Acquisition Date	2023-02-05T21:54:41
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0



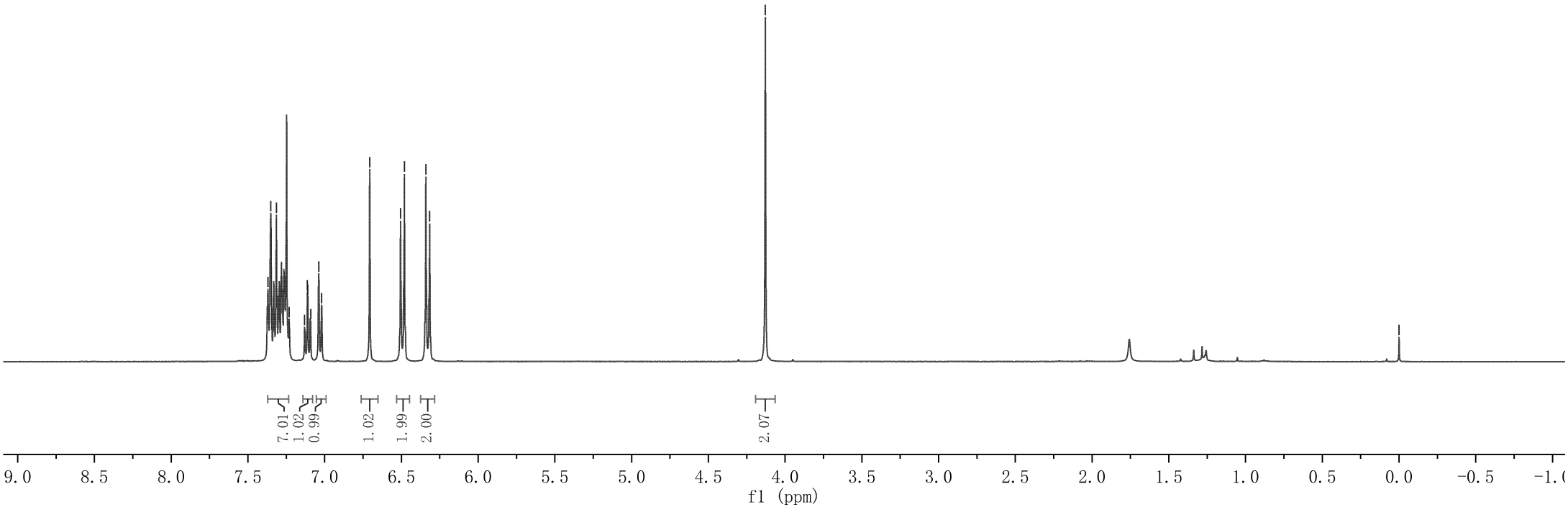
2o

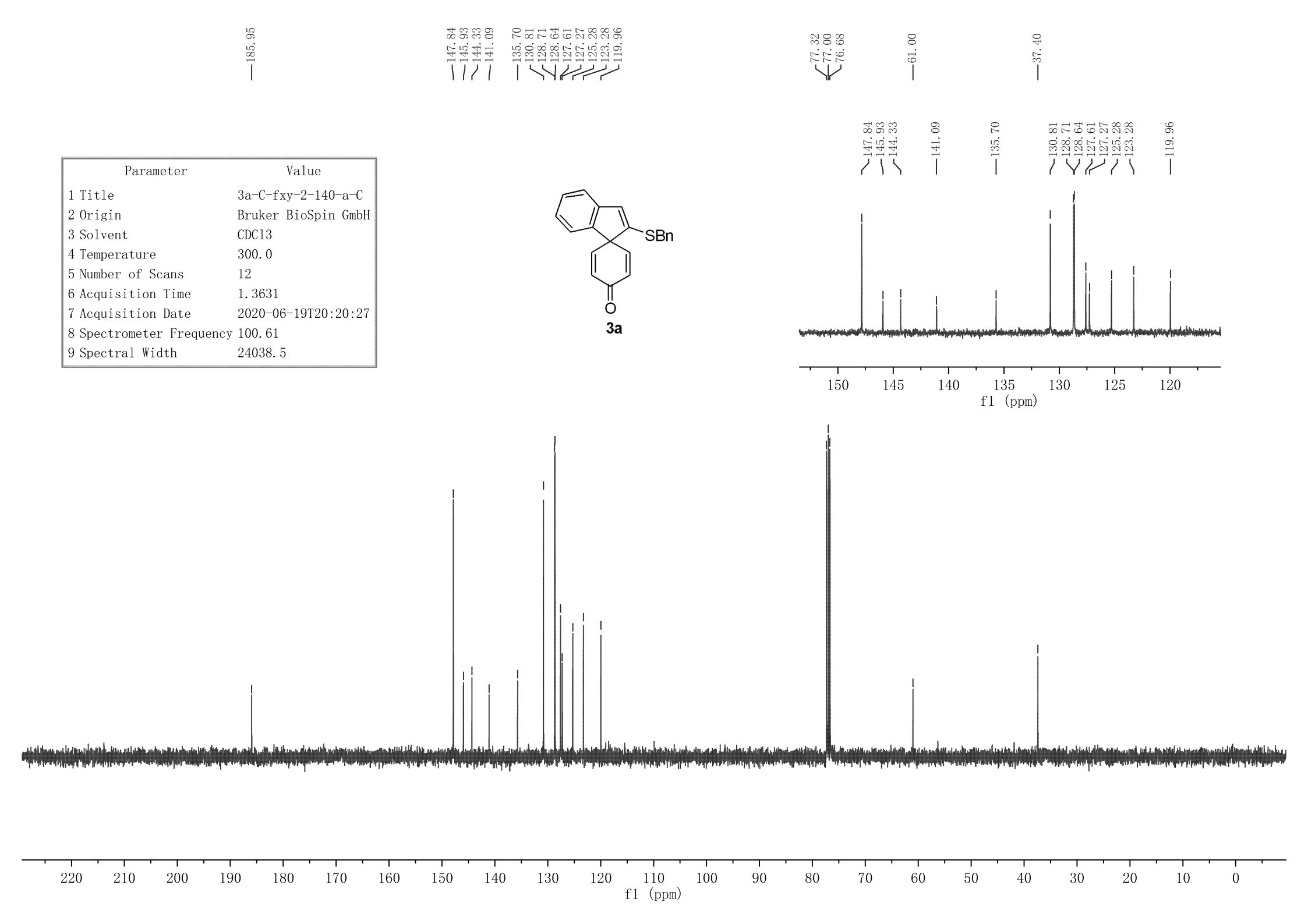


Parameter	Value
1 Title	3a-H-fxy-2-140-a
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	5
6 Acquisition Time	4.0894
7 Acquisition Date	2020-06-19T20:19:20
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8



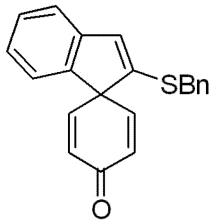
3a



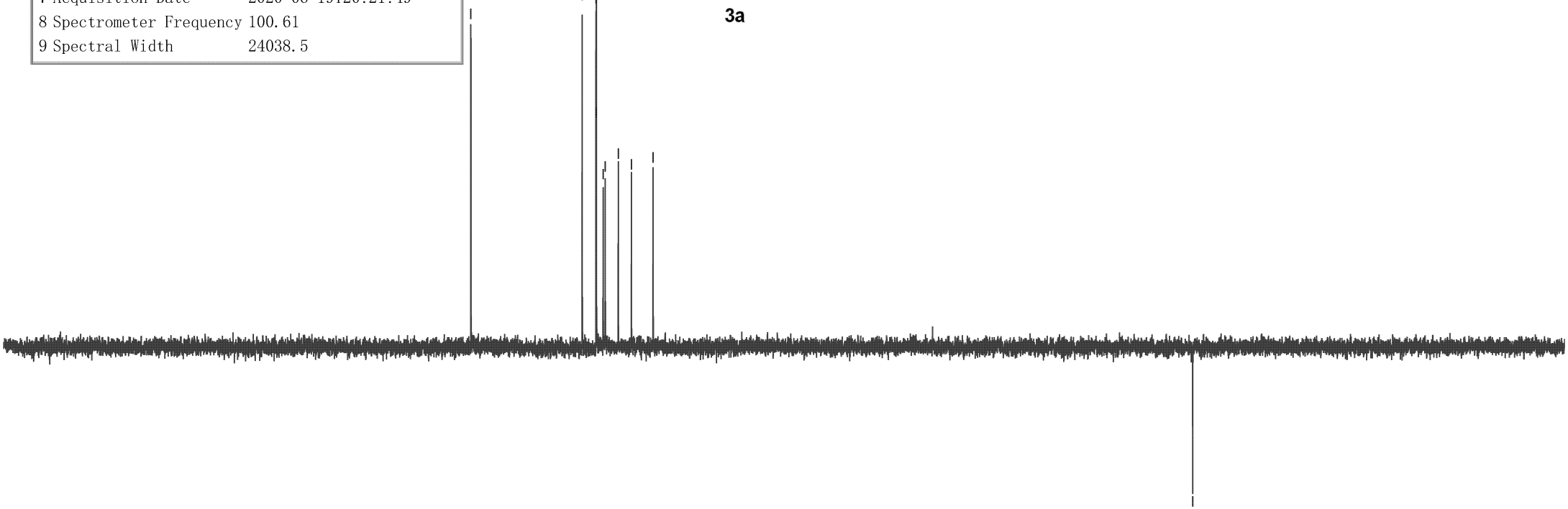

185.95
147.84
145.93
144.33
141.09
135.70
130.81
128.71
128.64
127.61
127.27
125.28
123.28
119.96
77.32
77.00
76.68
61.00
37.40
Parameter Value
1 Title 3a-C-fxy-2-140-a-C
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.0
5 Number of Scans 12
6 Acquisition Time 1.3631
7 Acquisition Date 2020-06-19T20:20:27
8 Spectrometer Frequency 100.61
9 Spectral Width 24038.5
SBn
O
3a
f1 (ppm)
f1 (ppm)

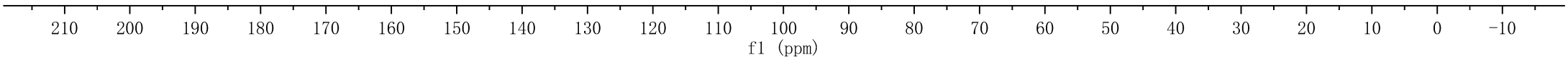
147.83
130.81
128.70
128.65
128.64
127.60
127.28
125.28
123.27
119.96
37.40

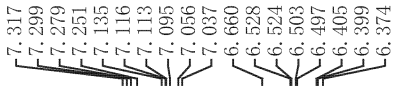
Parameter	Value
1 Title	3a-dept-fxy-2-140-a-DEPT
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	5
6 Acquisition Time	1.3631
7 Acquisition Date	2020-06-19T20:21:49
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5



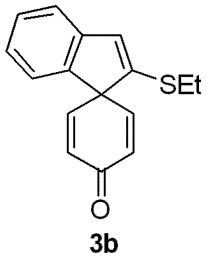
3a



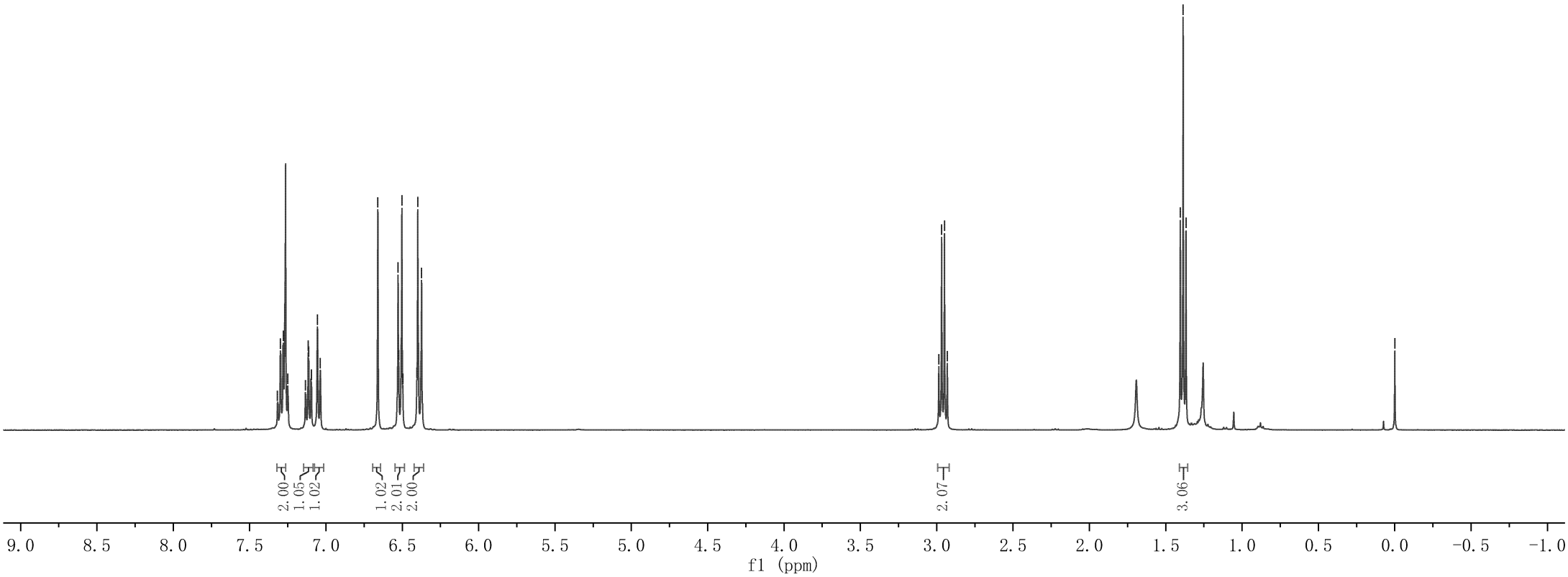




Parameter	Value
1 Title	3b-H-fxy-2-213
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	7
6 Acquisition Time	4.0894
7 Acquisition Date	2020-07-15T14:26:36
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8

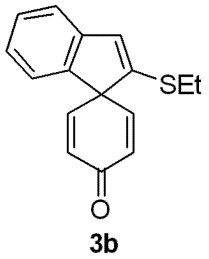


3b

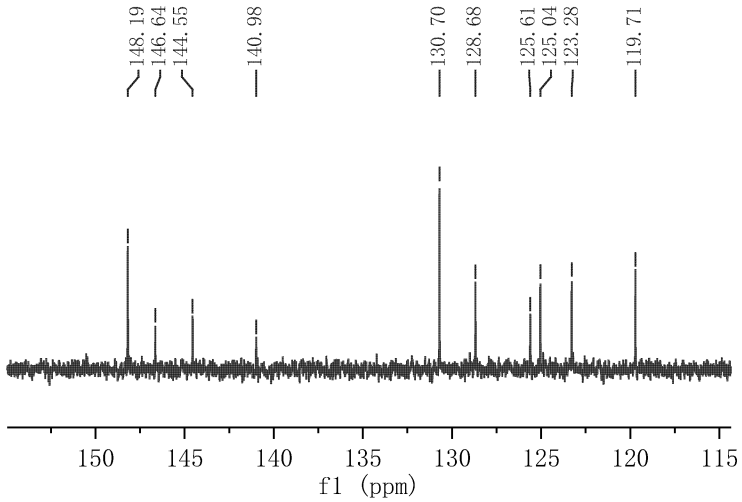


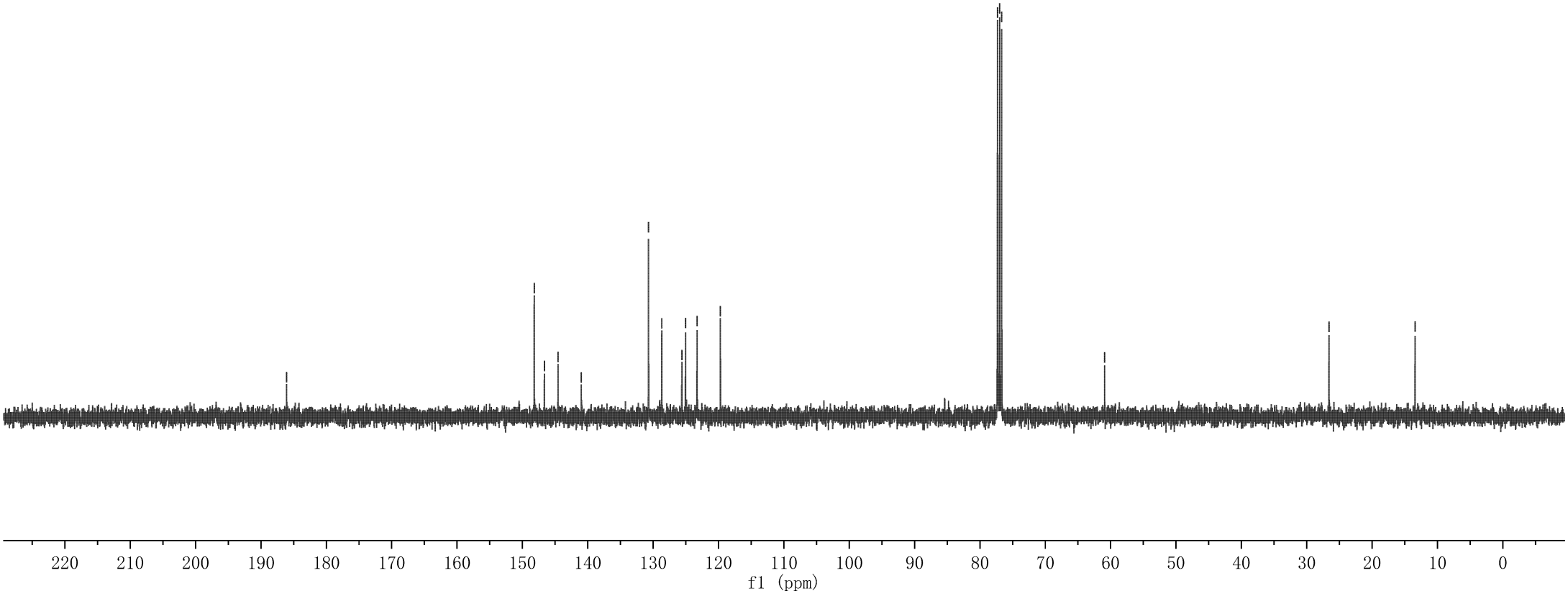
186.08
148.19
146.64
144.55
140.98
130.70
128.68
125.61
125.04
123.28
119.71
77.32
77.00
76.68
60.93
26.60
13.43

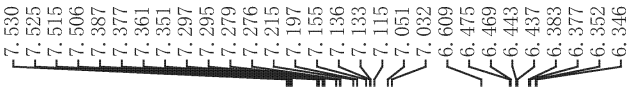
Parameter	Value
1 Title	3b-C-fxy-2-213-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	35
6 Acquisition Time	1.3631
7 Acquisition Date	2020-07-15T14:28:34
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5



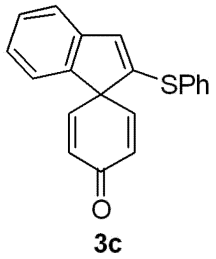
3b



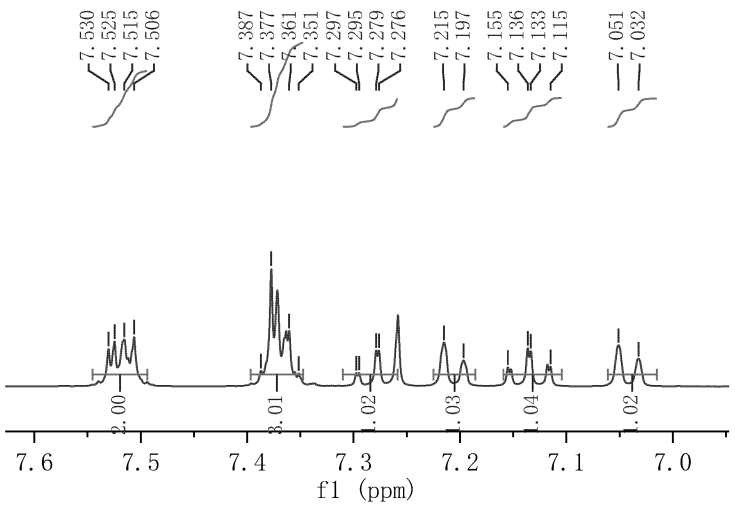


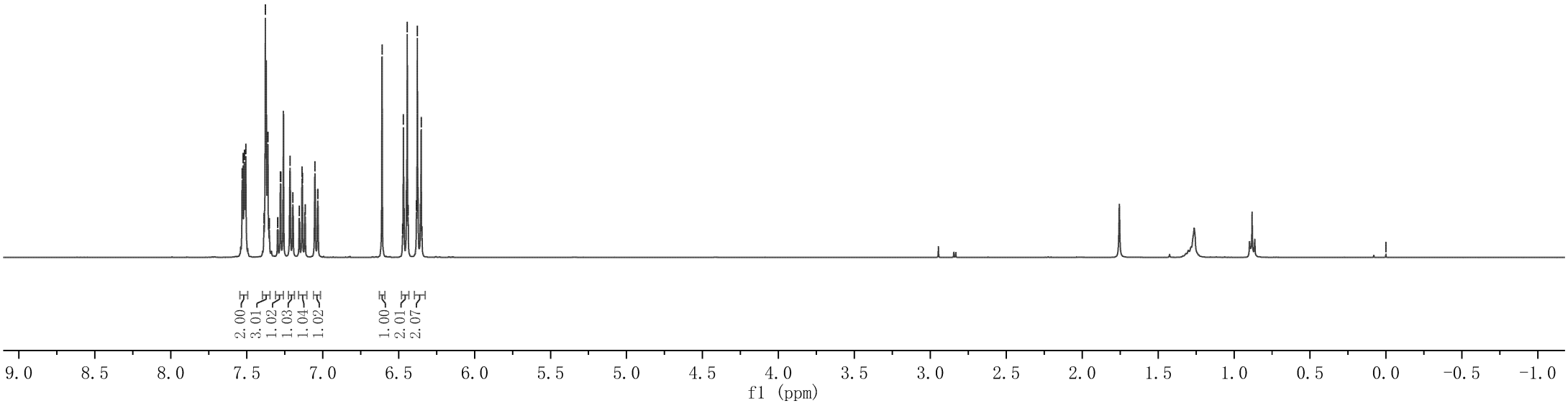


Parameter	Value
1 Title	3c-H-fxy-3-52
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	4
6 Acquisition Time	4.0894
7 Acquisition Date	2021-05-25T16:50:53
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8

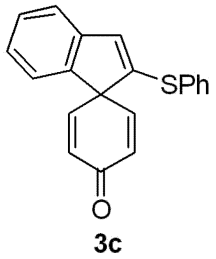


3c

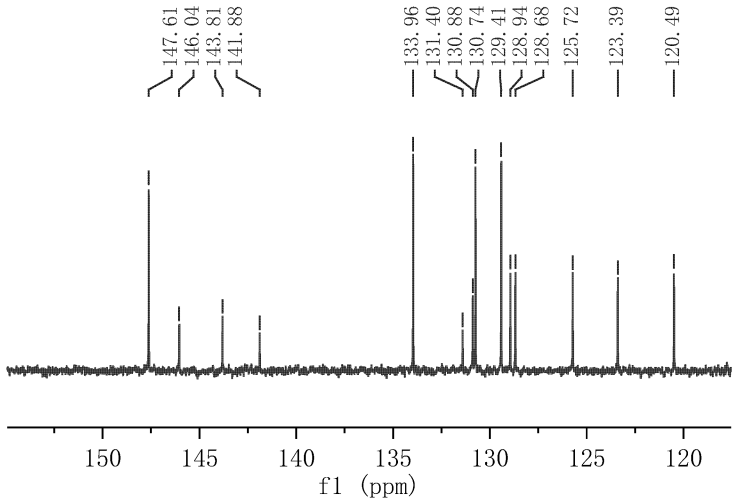


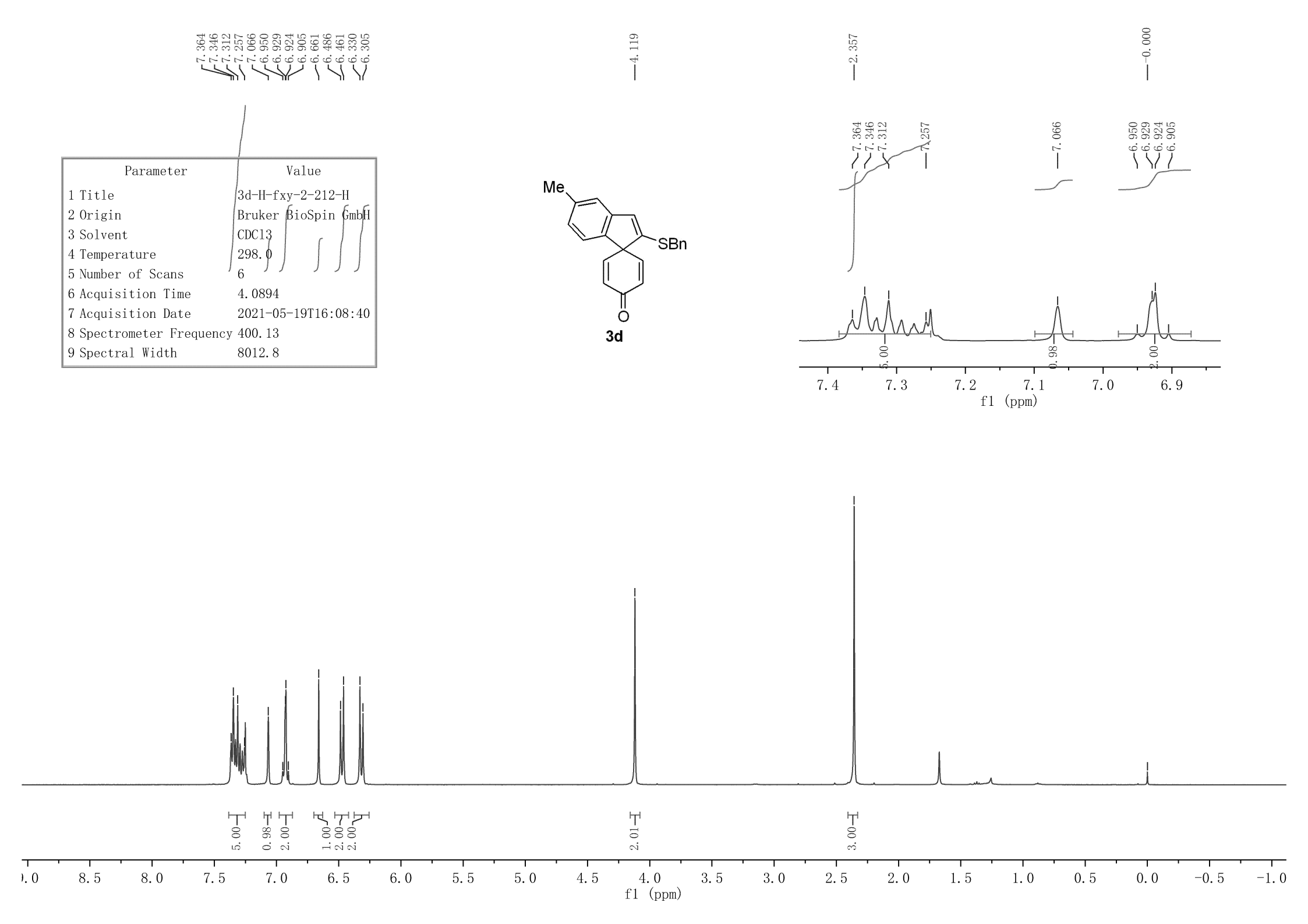


Parameter	Value
1 Title	3c-C-fxy-3-52-Cc
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	18
6 Acquisition Time	1.3631
7 Acquisition Date	2021-05-25T16:51:52
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5

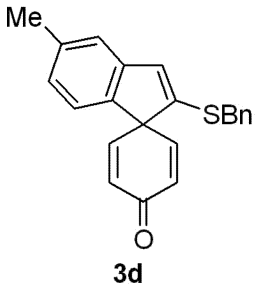


3c

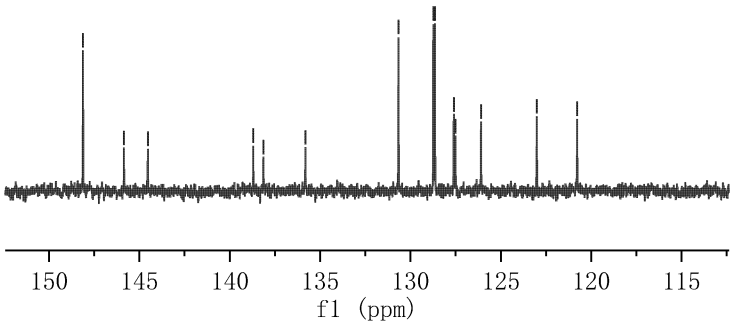


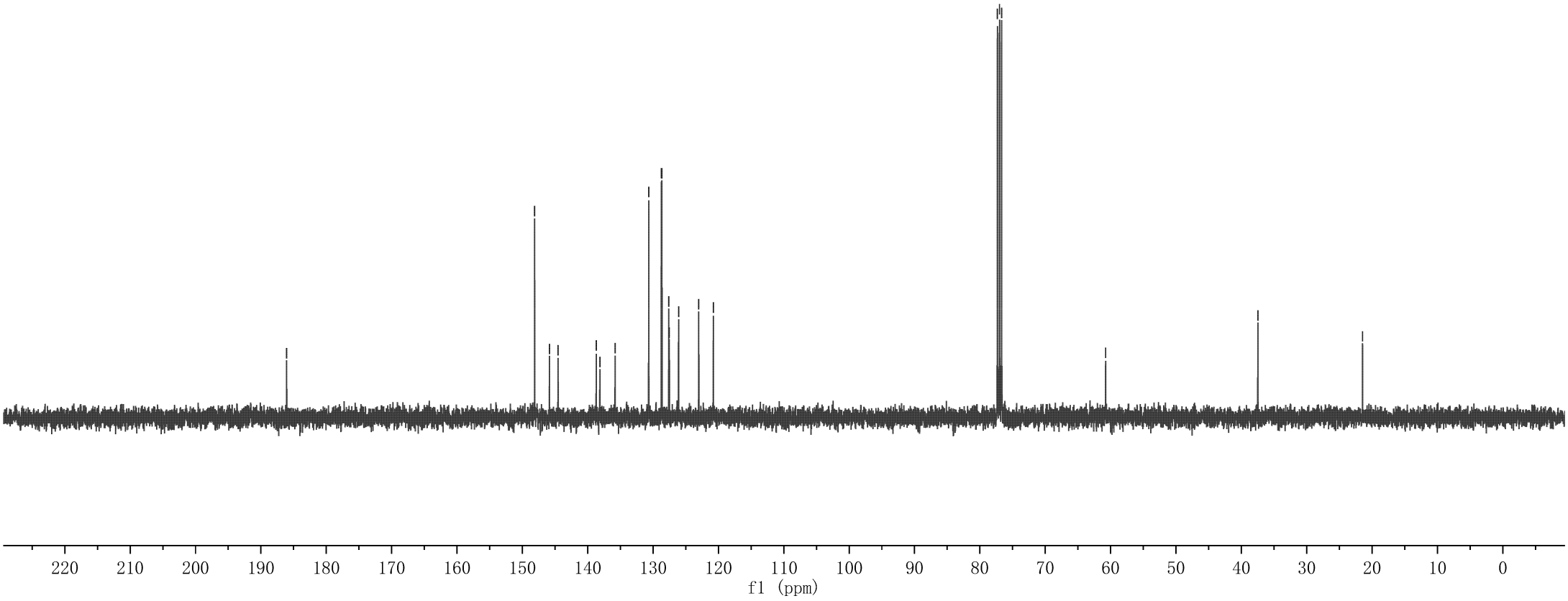

7.364
7.346
7.312
7.257
7.066
6.950
6.929
6.924
6.905
6.661
6.486
6.461
6.330
6.305
4.119
2.357
0.000
Parameter Value
1 Title 3d-H-fxy-2-212-H
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 298.0
5 Number of Scans 6
6 Acquisition Time 4.0894
7 Acquisition Date 2021-05-19T16:08:40
8 Spectrometer Frequency 400.13
9 Spectral Width 8012.8
Me
SBn
O
3d
5.00
0.98
2.00
f1 (ppm)
2.01
3.00
f1 (ppm)

Parameter	Value
1 Title	3d-C-fxy-2-212-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	15
6 Acquisition Time	1.3631
7 Acquisition Date	2021-05-19T16:09:49
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5

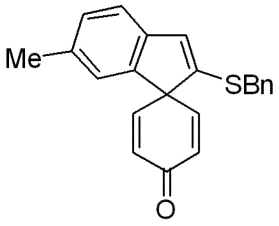


3d

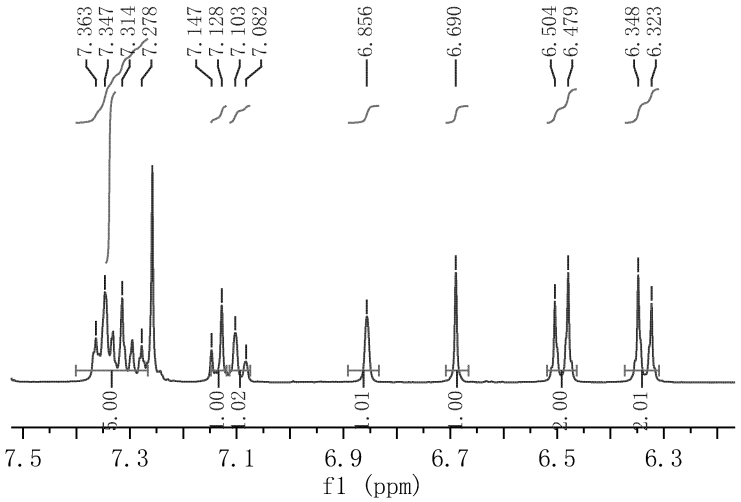


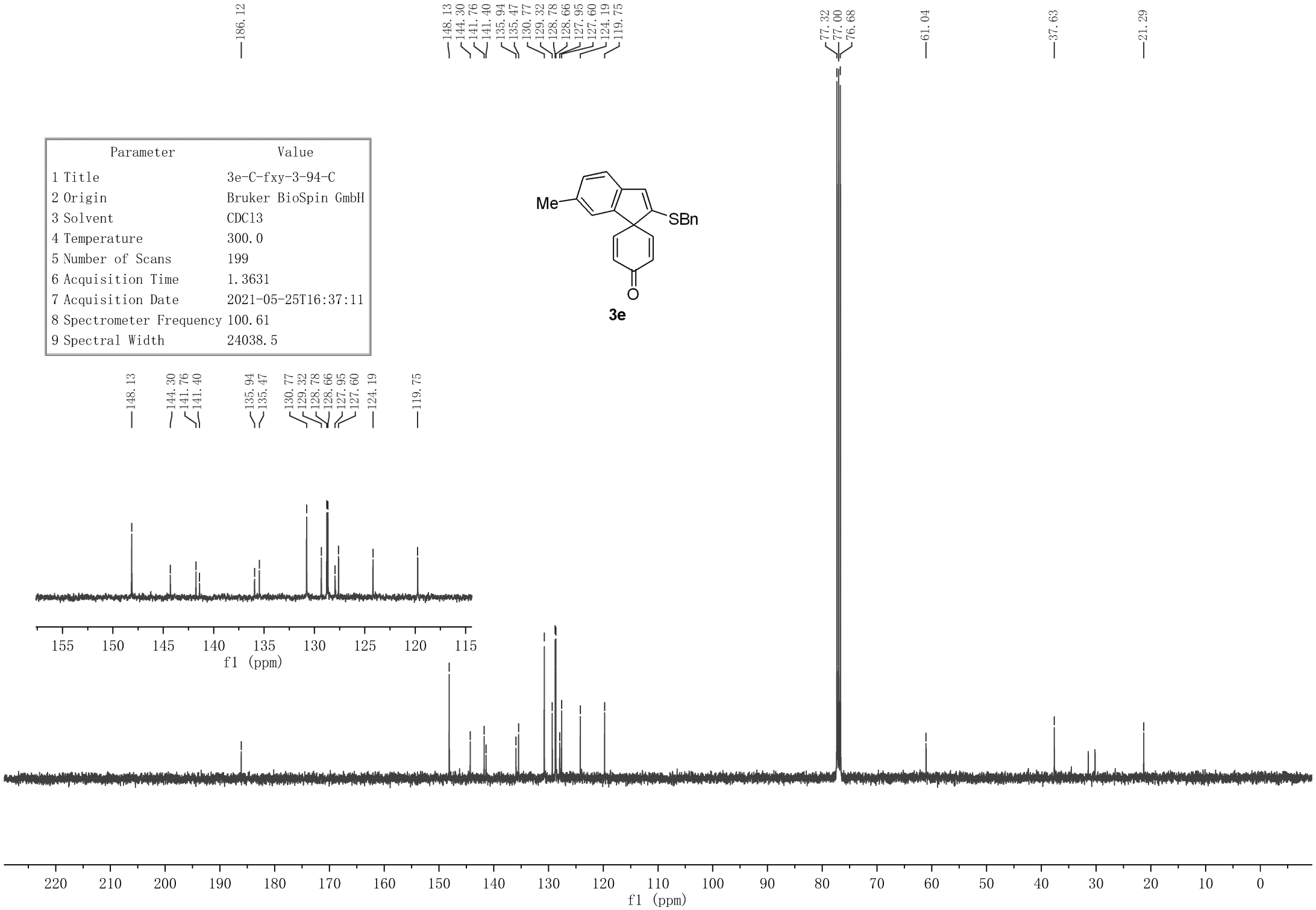


Parameter	Value
1 Title	3e-H-fxy-3-94-H
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	12
6 Acquisition Time	4.0894
7 Acquisition Date	2021-05-25T16:35:28
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8

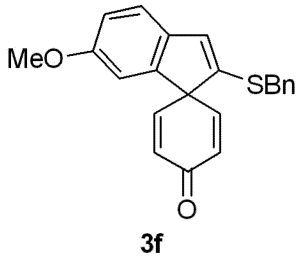


3e

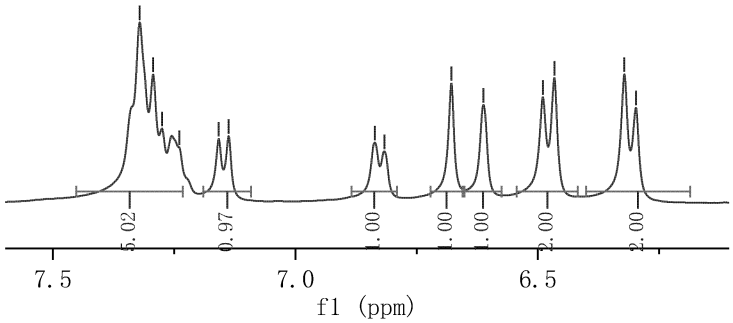


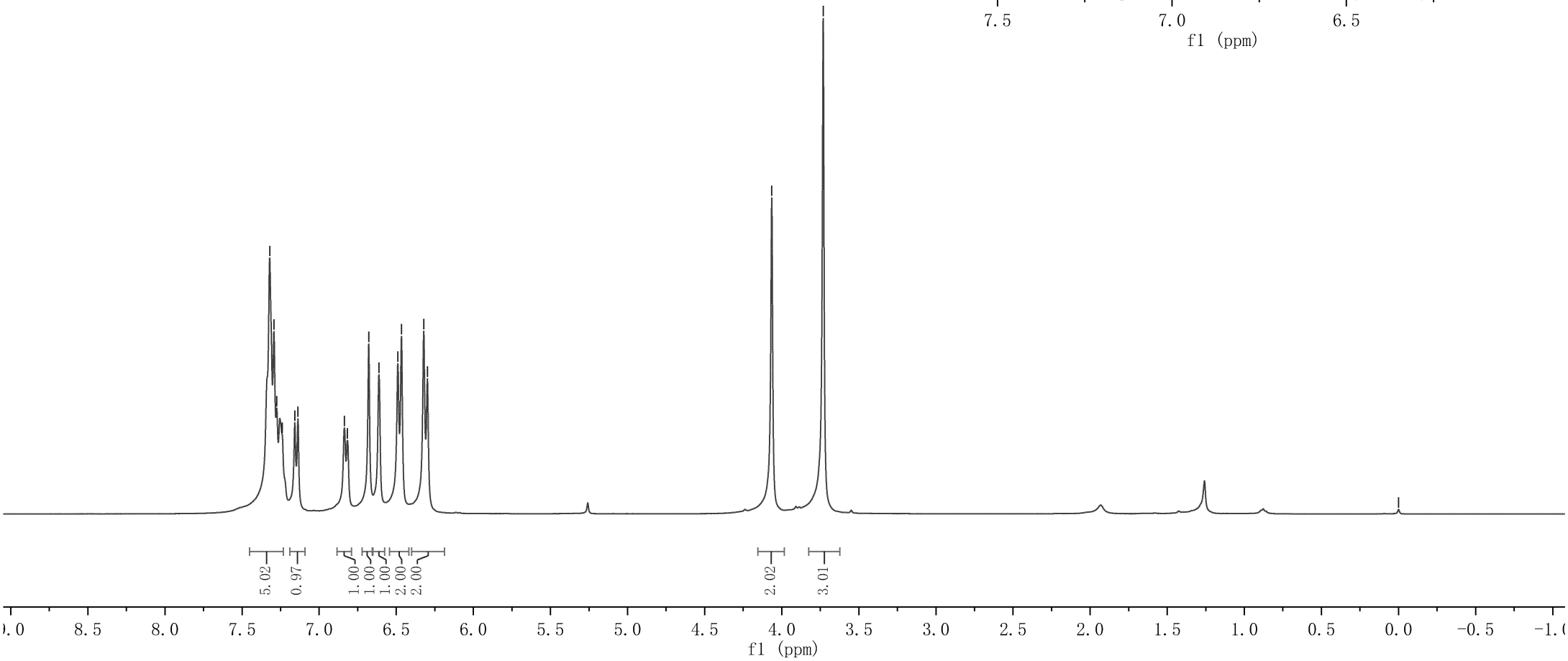

186.12
148.13
144.30
141.76
141.40
135.94
135.47
130.77
129.32
128.78
128.66
127.95
127.60
124.19
119.75
77.32
77.00
76.68
61.04
37.63
21.29
Parameter Value
1 Title 3e-C-fxy-3-94-C
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.0
5 Number of Scans 199
6 Acquisition Time 1.3631
7 Acquisition Date 2021-05-25T16:37:11
8 Spectrometer Frequency 100.61
9 Spectral Width 24038.5
Me
SBn
O
3e
f1 (ppm)
f1 (ppm)

Parameter	Value
1 Title	3f-H-fxy-2-230-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	2021-05-19T16:14:15
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8



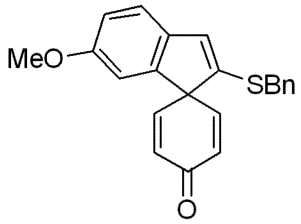
3f



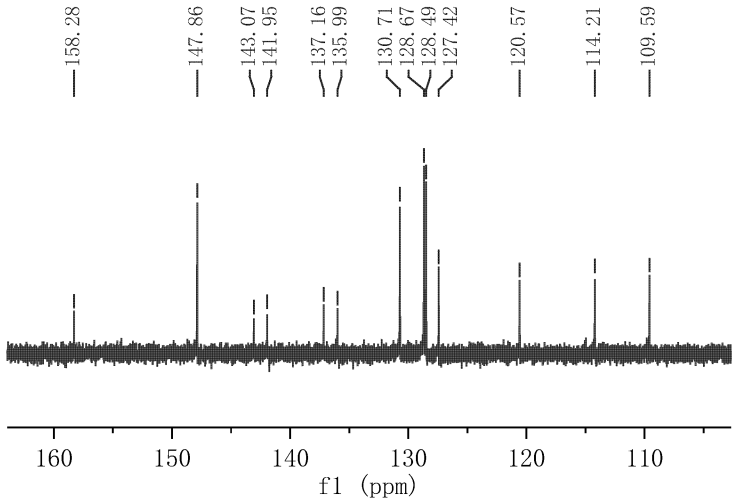


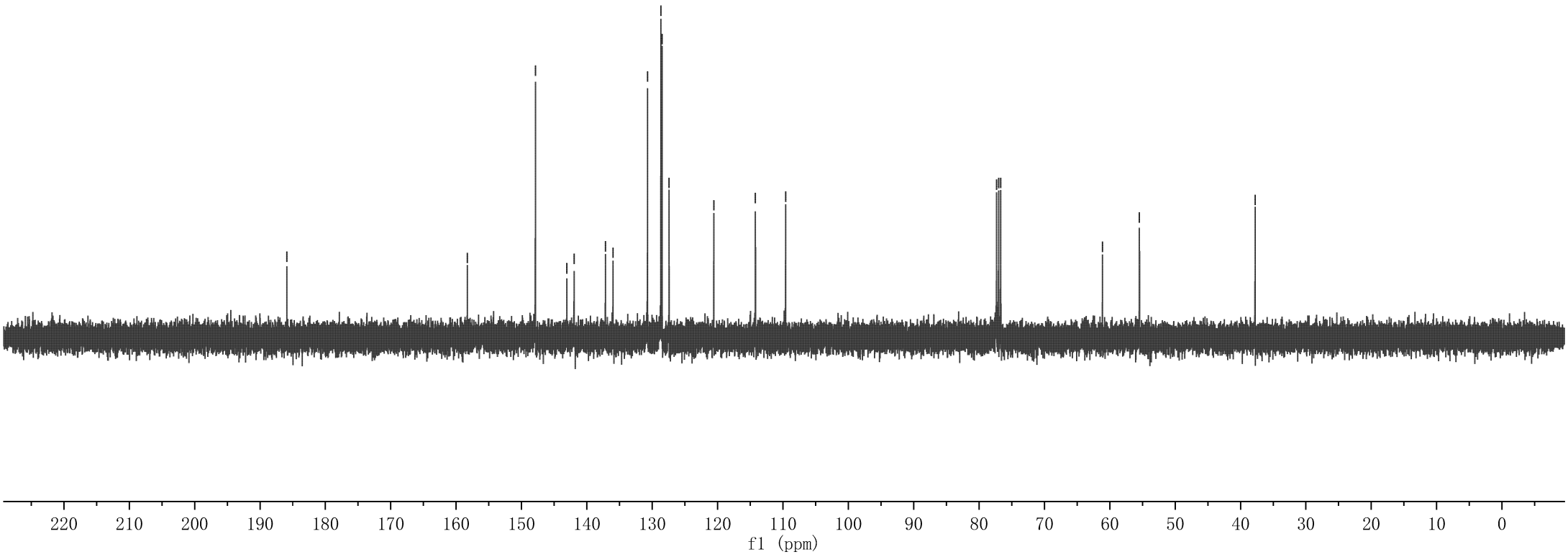
185.90
158.28
147.86
143.07
141.95
137.16
135.99
130.71
128.67
128.49
127.42
120.57
114.21
109.59
77.32
77.00
76.68
61.12
55.47
37.77

Parameter	Value
1 Title	3f-C-fxy-2-230-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	9
6 Acquisition Time	1.3631
7 Acquisition Date	2021-05-19T16:15:21
8 Spectrometer Frequency	100.62
9 Spectral Width	24038.5

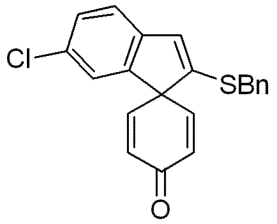


3f

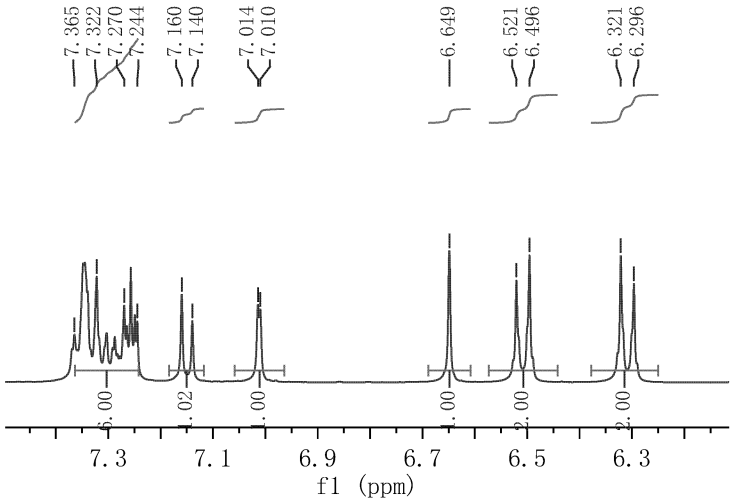


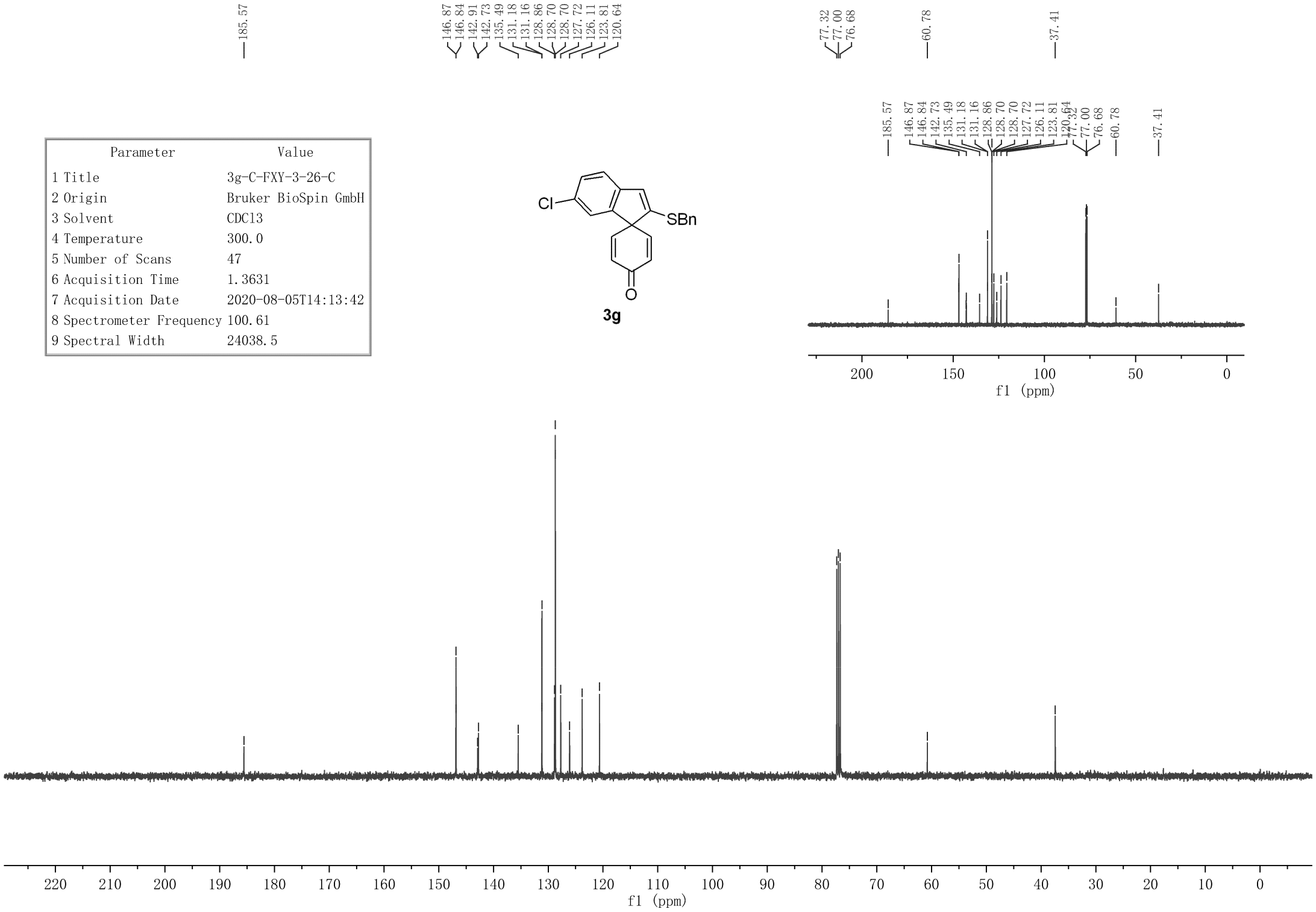


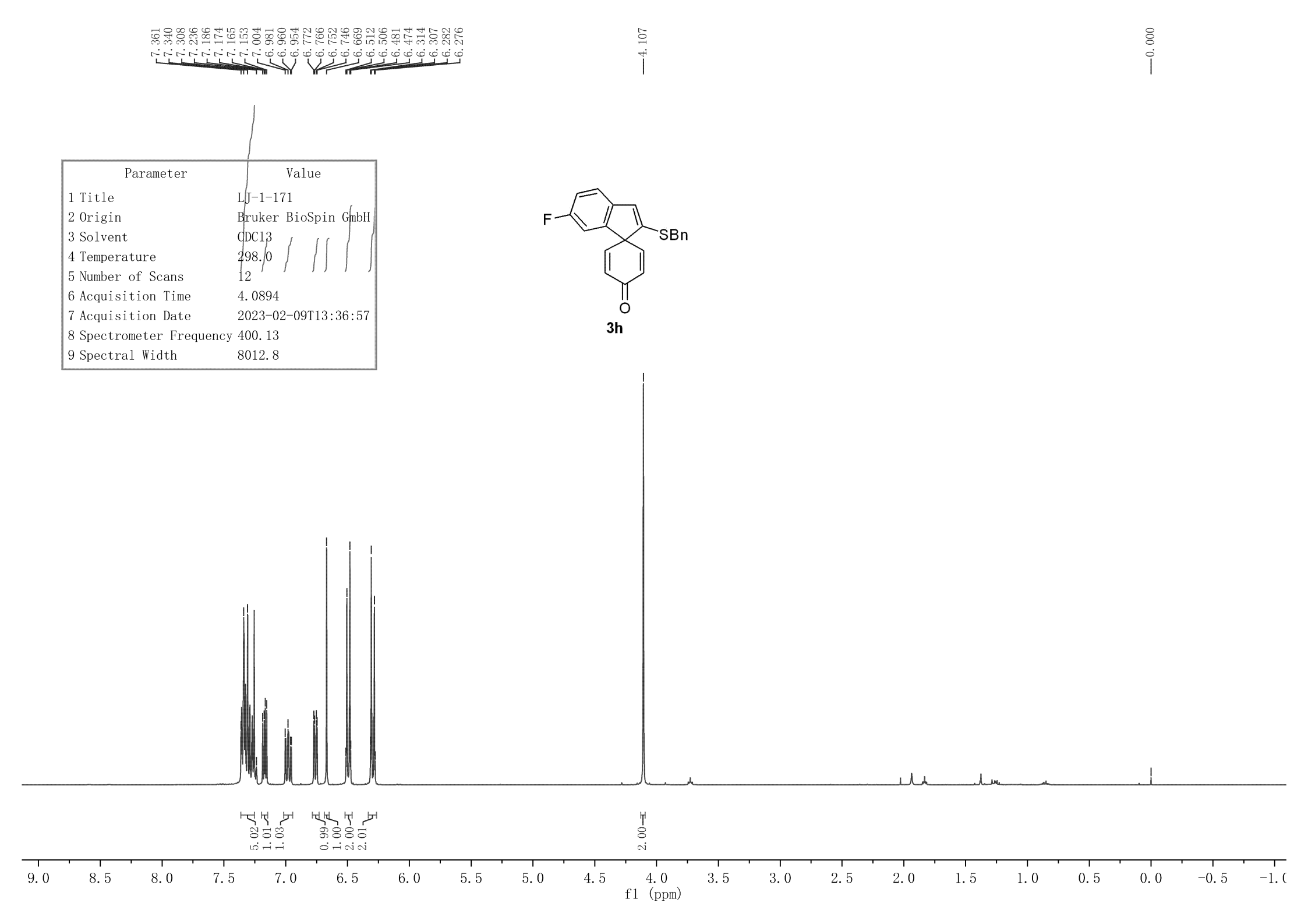
Parameter	Value
1 Title	3g-H-FXY-3-26-H
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	7
6 Acquisition Time	4.0894
7 Acquisition Date	2020-08-05T14:12:20
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8



3g

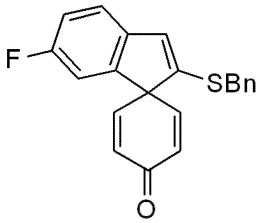



185.57
146.87
146.84
142.91
142.73
135.49
131.18
131.16
128.86
128.70
128.70
127.72
126.11
123.81
120.64
77.32
77.00
76.68
60.78
37.41
Parameter Value
1 Title 3g-C-FXY-3-26-C
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.0
5 Number of Scans 47
6 Acquisition Time 1.3631
7 Acquisition Date 2020-08-05T14:13:42
8 Spectrometer Frequency 100.61
9 Spectral Width 24038.5
Cl
SBn
O
3g
f1 (ppm)
f1 (ppm)

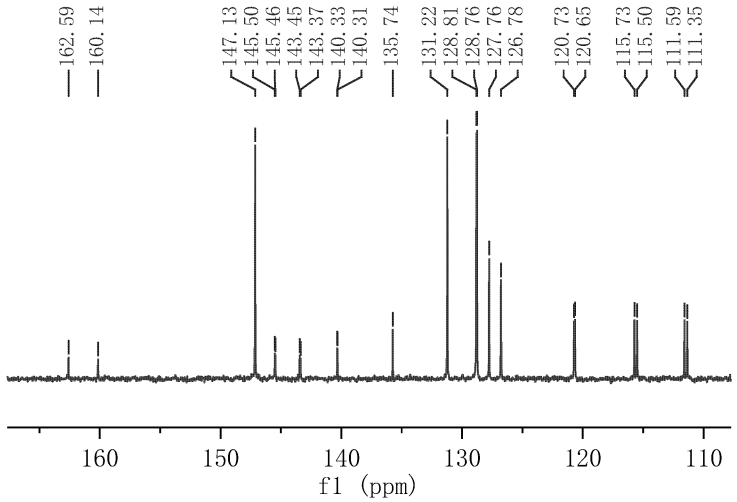

7.361
7.340
7.308
7.236
7.186
7.174
7.165
7.153
7.004
6.981
6.960
6.954
6.772
6.766
6.752
6.746
6.669
6.512
6.506
6.481
6.474
6.314
6.307
6.282
6.276
4.107
0.000
Parameter Value
1 Title LJ-1-171
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 298.0
5 Number of Scans 12
6 Acquisition Time 4.0894
7 Acquisition Date 2023-02-09T13:36:57
8 Spectrometer Frequency 400.13
9 Spectral Width 8012.8
F
SBn
O
3h
5.02
1.01
1.03
0.99
1.00
2.00
2.01
2.00
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
-0.5
f1 (ppm)

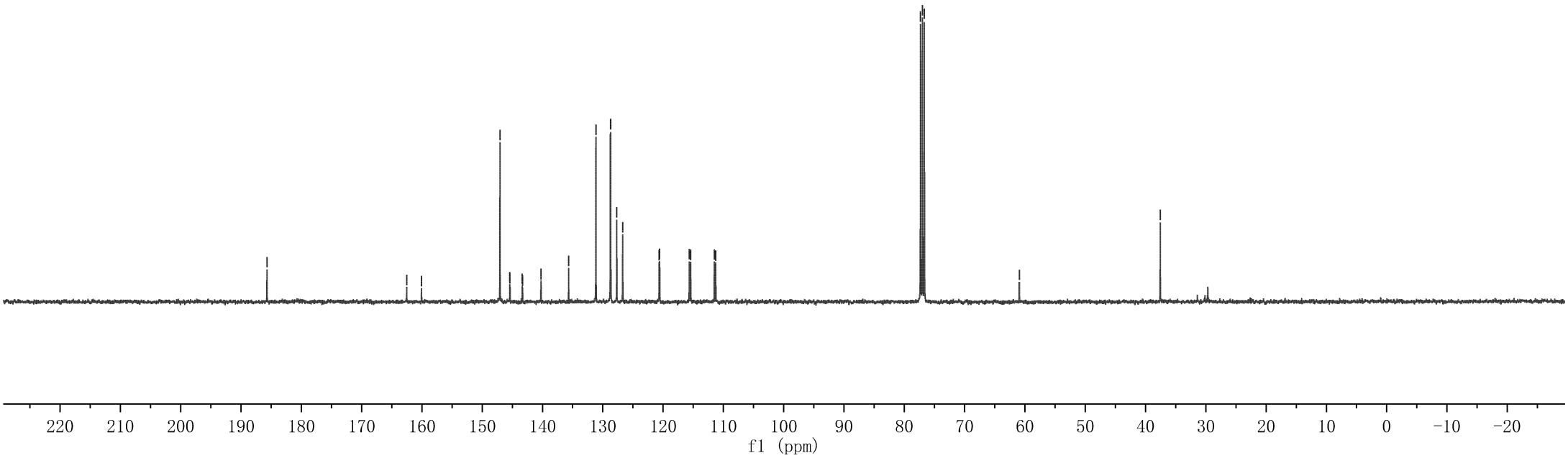
185.69
162.51
160.07
147.06
145.43
145.39
143.37
143.29
140.26
140.24
135.67
131.14
128.74
128.69
127.68
126.70
120.66
120.57
115.65
115.43
111.51
111.27
77.32
77.00
76.68
60.92
37.55

Parameter	Value
1 Title	FXY-3-28
2 Origin	
3 Solvent	CDCl3
4 Temperature	295.8
5 Number of Scans	500
6 Acquisition Time	1.0000
7 Acquisition Date	2023-02-04T12:07:39
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

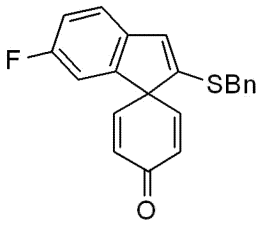


3h

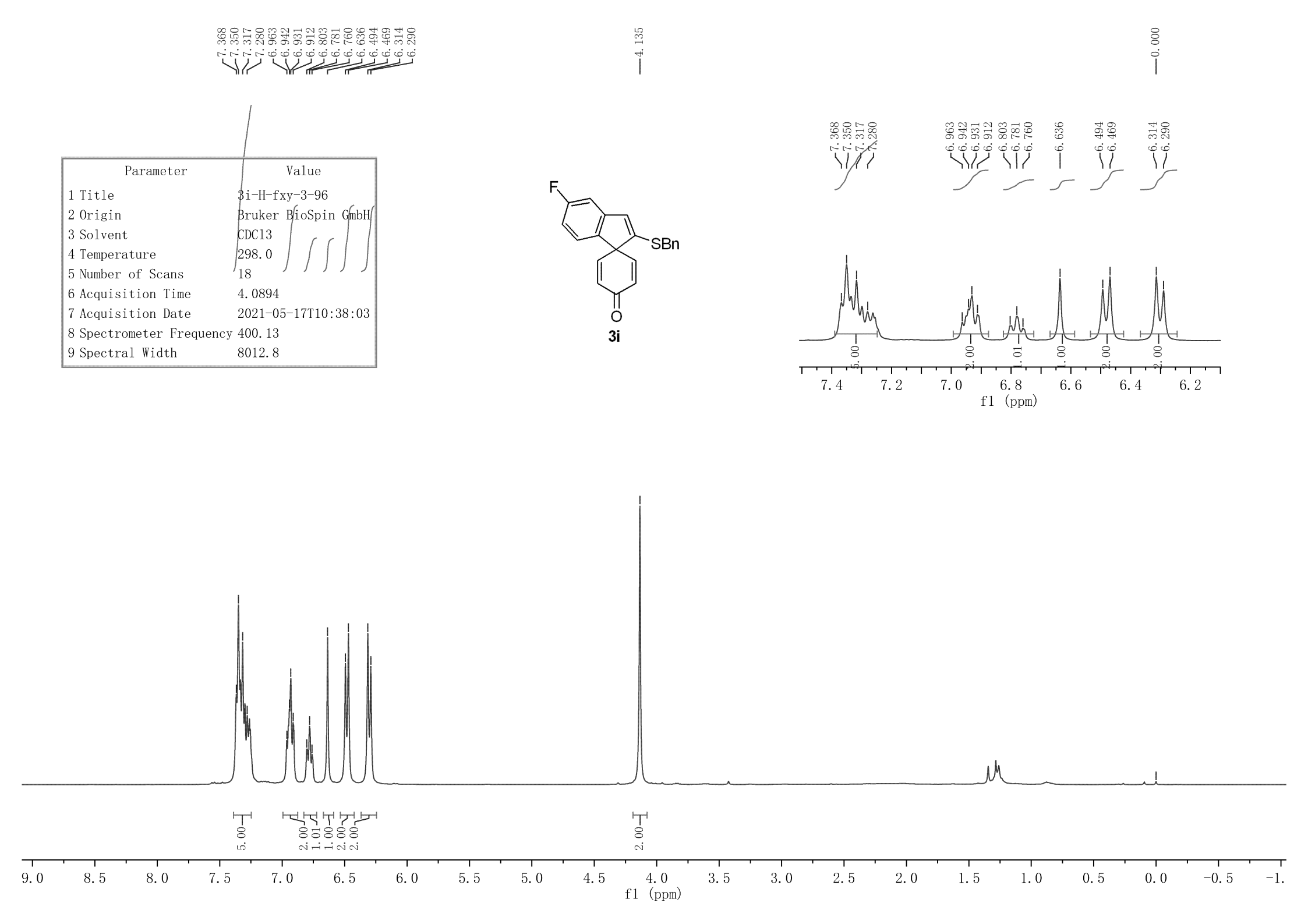


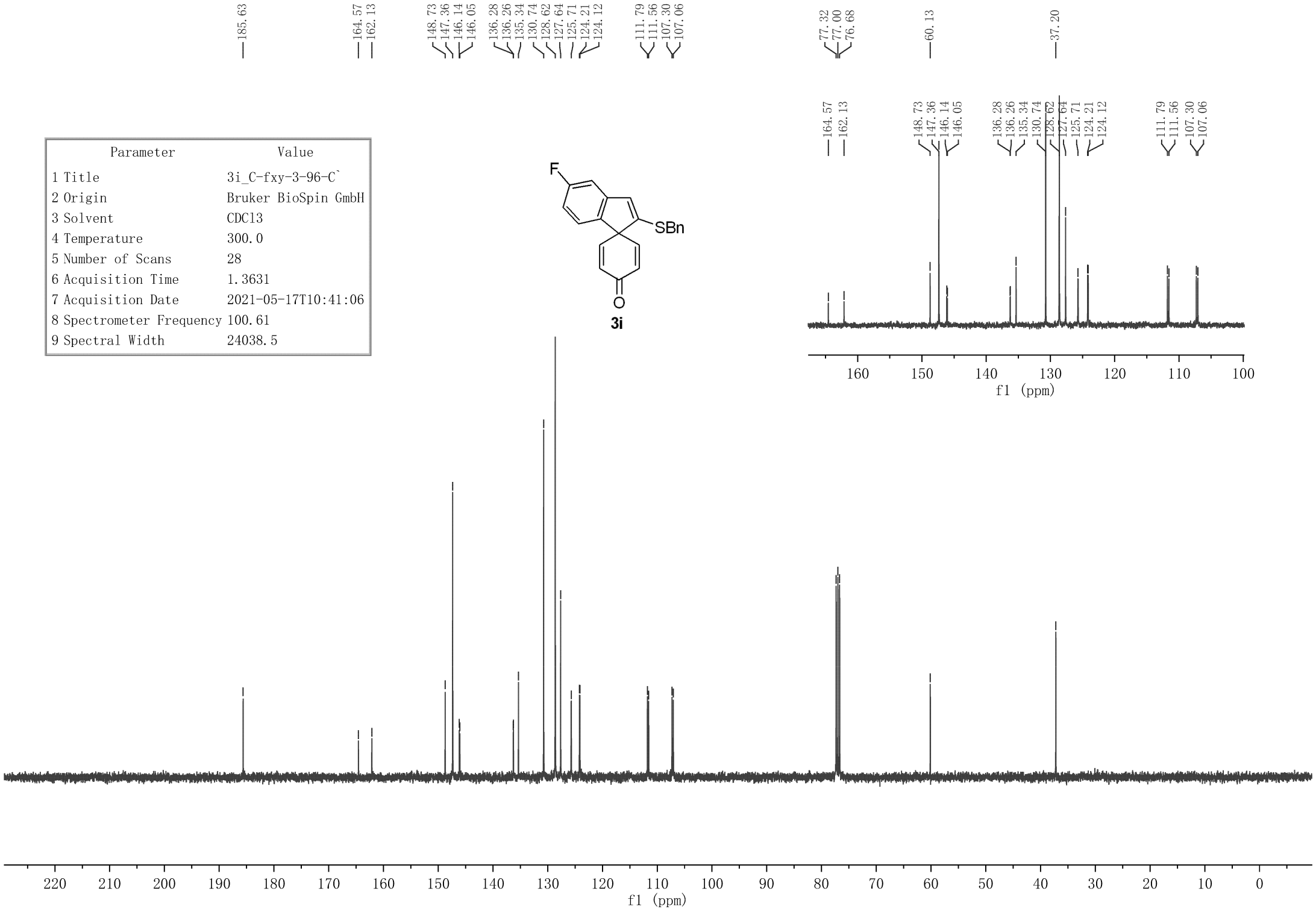


Parameter	Value
1 Title	FXY-3-28
2 Origin	
3 Solvent	CDCl3
4 Temperature	295.9
5 Number of Scans	16
6 Acquisition Time	1.0000
7 Acquisition Date	2023-02-04T12:10:50
8 Spectrometer Frequency	376.28
9 Spectral Width	96153.0

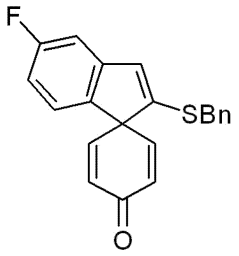


3h


7.368
7.350
7.317
7.280
6.963
6.942
6.931
6.912
6.803
6.781
6.760
6.636
6.494
6.469
6.314
6.290
4.135
0.000
Parameter Value
1 Title 3i-H-fxy-3-96
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 2021-05-17T10:38:03
8 Spectrometer Frequency 400.13
9 Spectral Width 8012.8
F
SBn
O
3i
f1 (ppm)
5.00
2.00
1.01
1.00
2.00
2.00
2.00

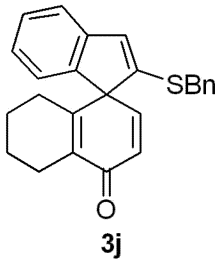

185.63
164.57
162.13
148.73
147.36
146.14
146.05
136.28
136.26
135.34
130.74
128.62
127.64
125.71
124.21
124.12
111.79
111.56
107.30
107.06
77.32
77.00
76.68
60.13
37.20
Parameter Value
1 Title 3i_C-fxy-3-96-C`
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.0
5 Number of Scans 28
6 Acquisition Time 1.3631
7 Acquisition Date 2021-05-17T10:41:06
8 Spectrometer Frequency 100.61
9 Spectral Width 24038.5
F
SBn
O
3i
f1 (ppm)
f1 (ppm)

Parameter	Value
1 Title	fxy-3i-f-nmr
2 Origin	
3 Solvent	CDCl3
4 Temperature	296.6
5 Number of Scans	32
6 Acquisition Time	1.0000
7 Acquisition Date	2023-03-03T09:09:49
8 Spectrometer Frequency	376.28
9 Spectral Width	96153.0

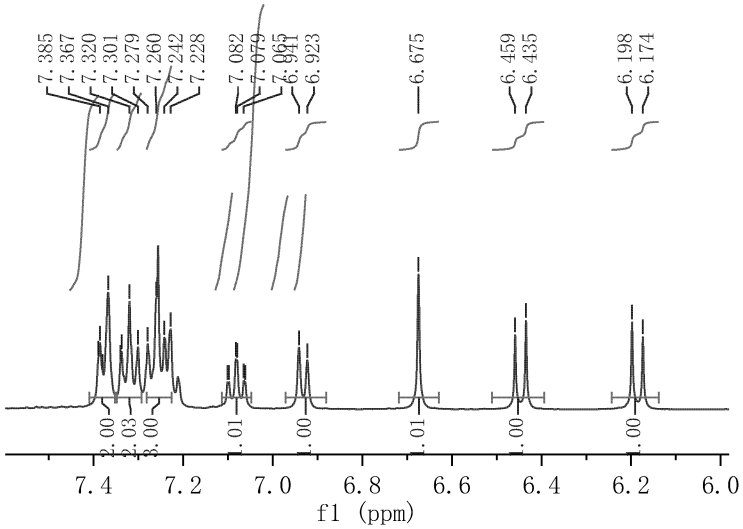


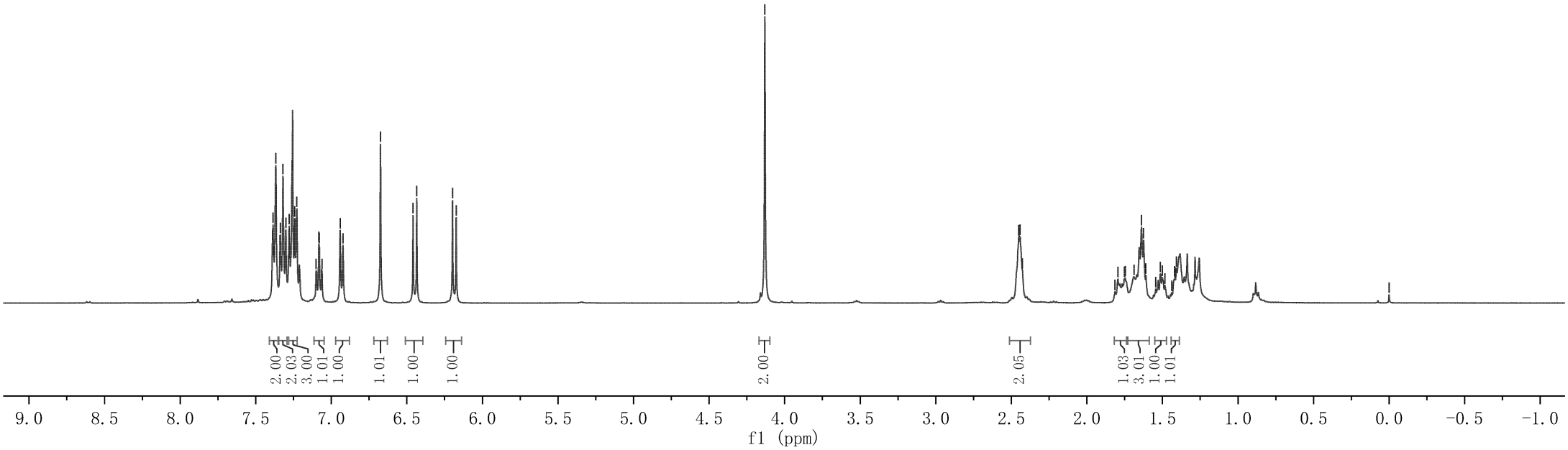
3i

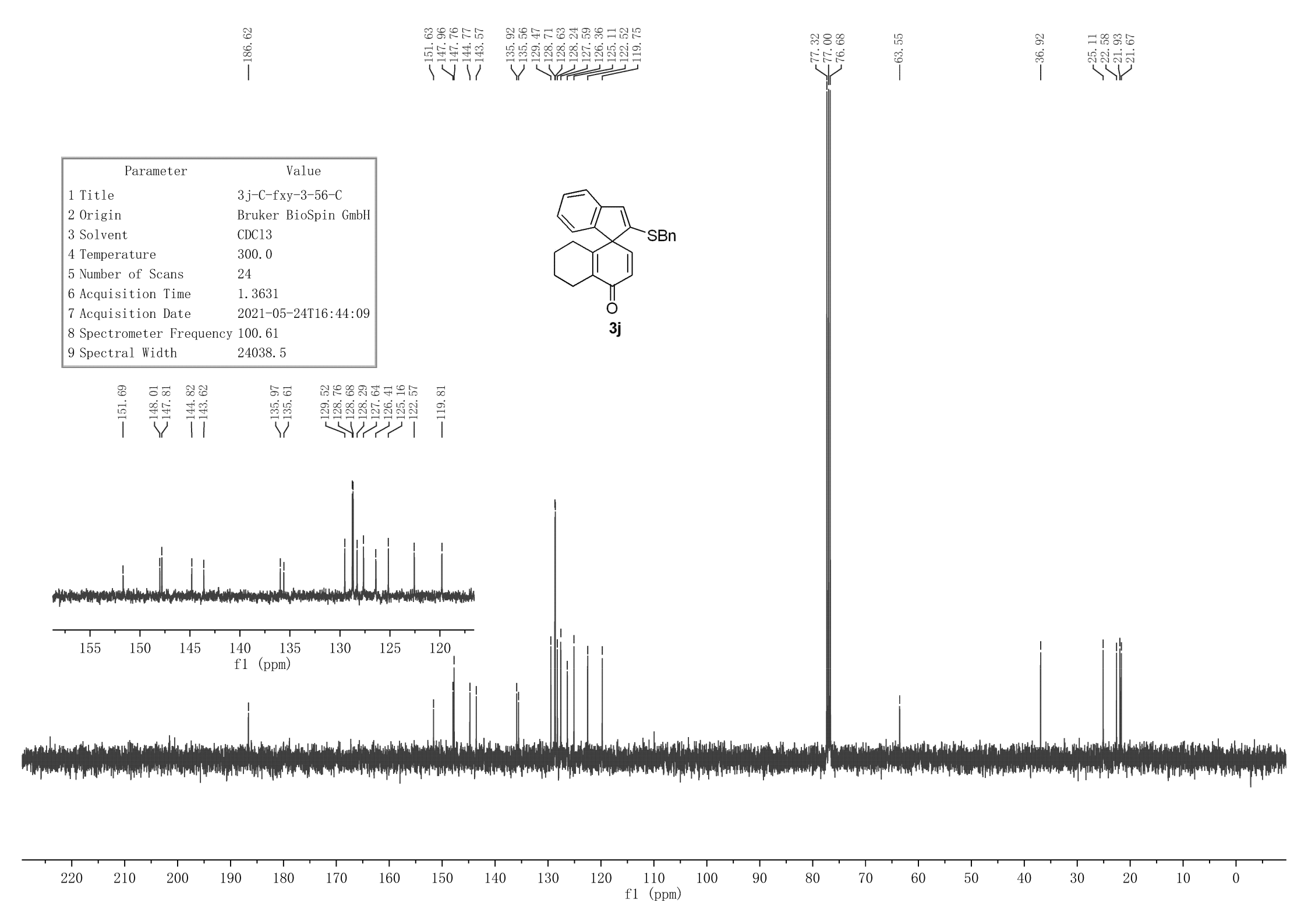
Parameter	Value
1 Title	3j-H-fxy-3-56
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	8
6 Acquisition Time	4.0894
7 Acquisition Date	2021-05-24T16:42:38
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8

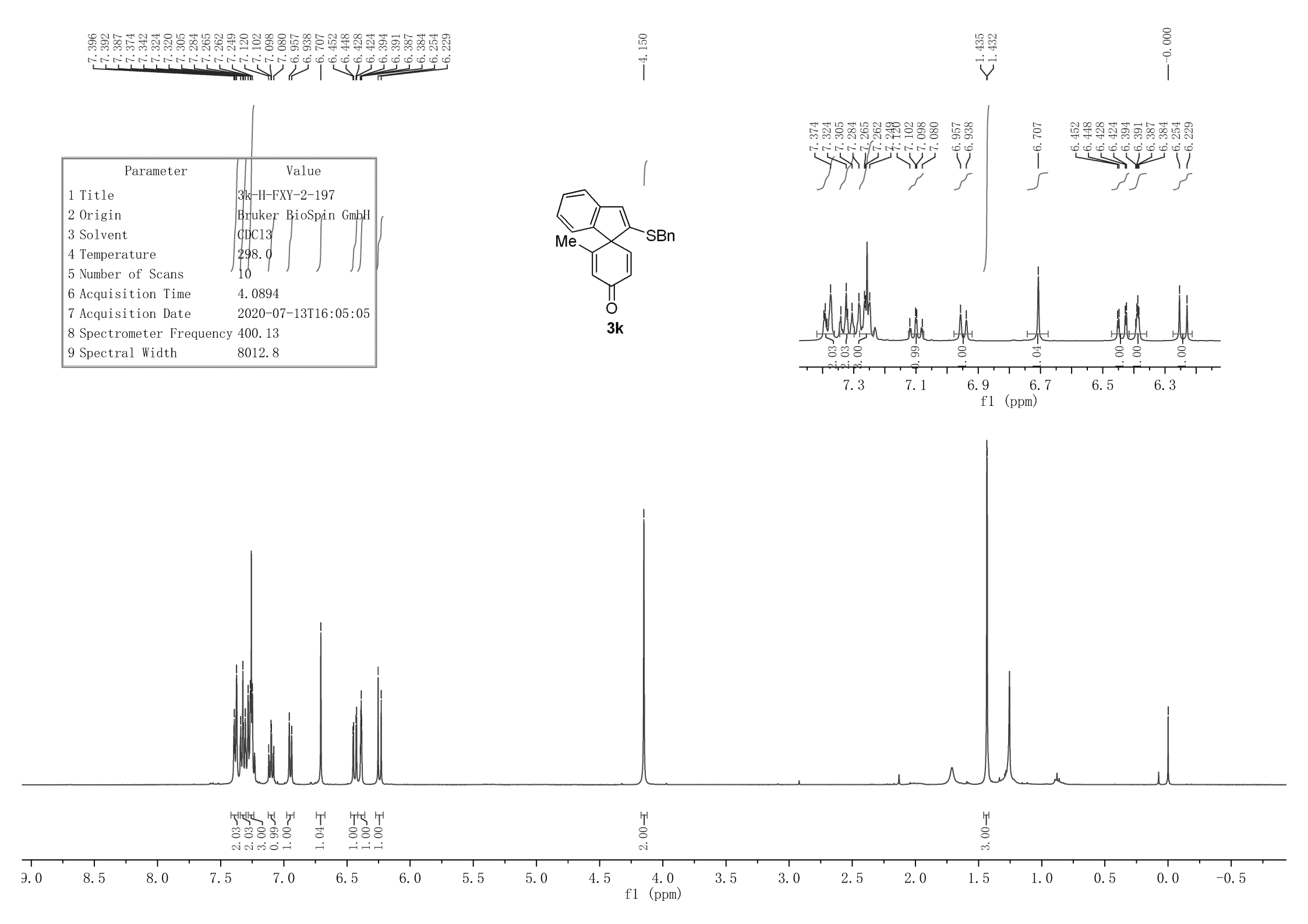


3j

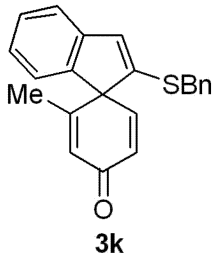




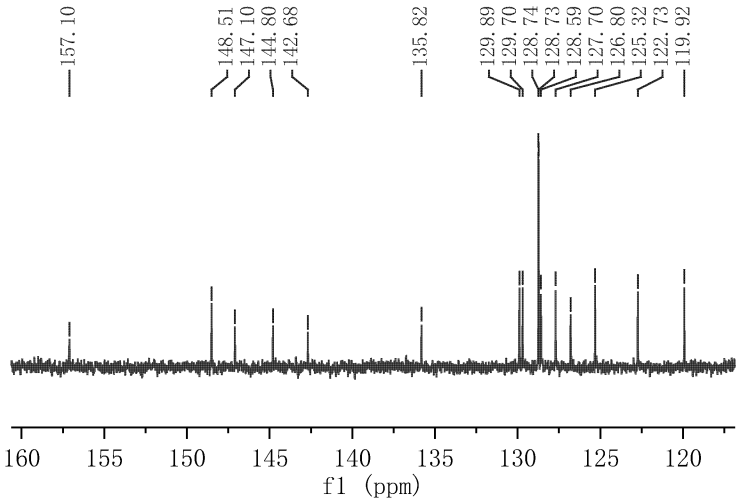

186.62
151.63
147.96
147.76
144.77
143.57
135.92
135.56
129.47
128.71
128.63
128.24
127.59
126.36
125.11
122.52
119.75
77.32
77.00
76.68
63.55
36.92
25.11
22.58
21.93
21.67
Parameter Value
1 Title 3j-C-fxy-3-56-C
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.0
5 Number of Scans 24
6 Acquisition Time 1.3631
7 Acquisition Date 2021-05-24T16:44:09
8 Spectrometer Frequency 100.61
9 Spectral Width 24038.5
SBn
O
3j
151.69
148.01
147.81
144.82
143.62
135.97
135.61
129.52
128.76
128.68
128.29
127.64
126.41
125.16
122.57
119.81
155 150 145 140 135 130 125 120
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

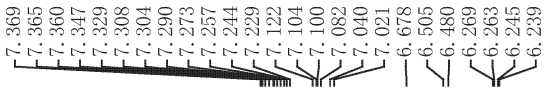

7.396
7.392
7.387
7.374
7.342
7.324
7.320
7.305
7.284
7.265
7.262
7.249
7.120
7.102
7.098
7.080
6.957
6.938
6.707
6.452
6.448
6.428
6.424
6.394
6.391
6.387
6.384
6.254
6.229
4.150
1.435
1.432
0.000
Parameter Value
1 Title 3k-H-FXY-2-197
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 298.0
5 Number of Scans 10
6 Acquisition Time 4.0894
7 Acquisition Date 2020-07-13T16:05:05
8 Spectrometer Frequency 400.13
9 Spectral Width 8012.8
Me
SBn
O
3k
2.03
2.03
3.00
0.99
1.00
1.04
1.00
1.00
1.00
2.00
3.00
f1 (ppm)

Parameter	Value
1 Title	3k-C-FXY-2-197-C
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	2020-07-13T16:07:38
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5

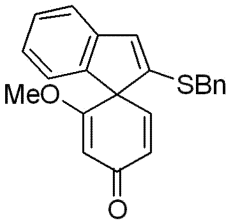


3k

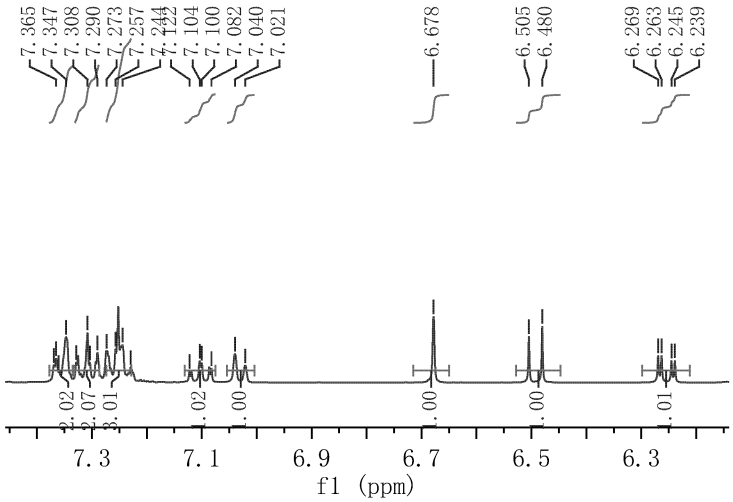


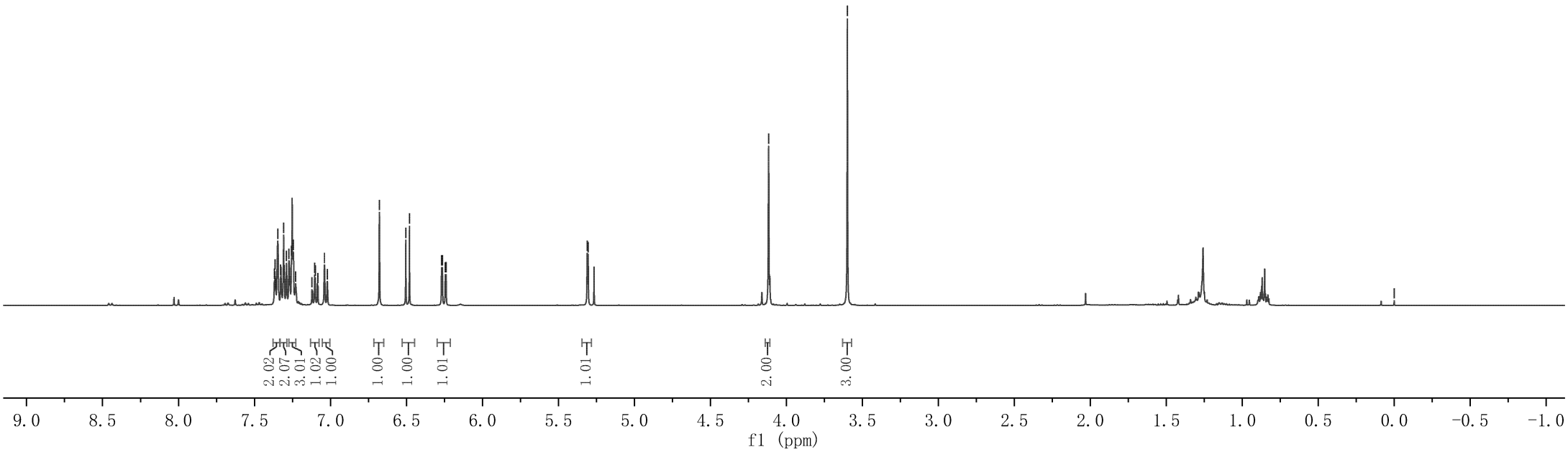


Parameter	Value
1 Title	3l-H-fxy-2-175-H
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.7
5 Number of Scans	23
6 Acquisition Time	3.9846
7 Acquisition Date	2020-07-06T14:39:09
8 Spectrometer Frequency	400.03
9 Spectral Width	8223.7

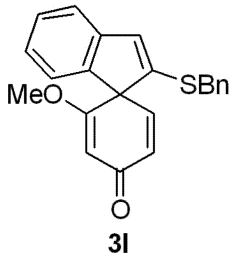


3l

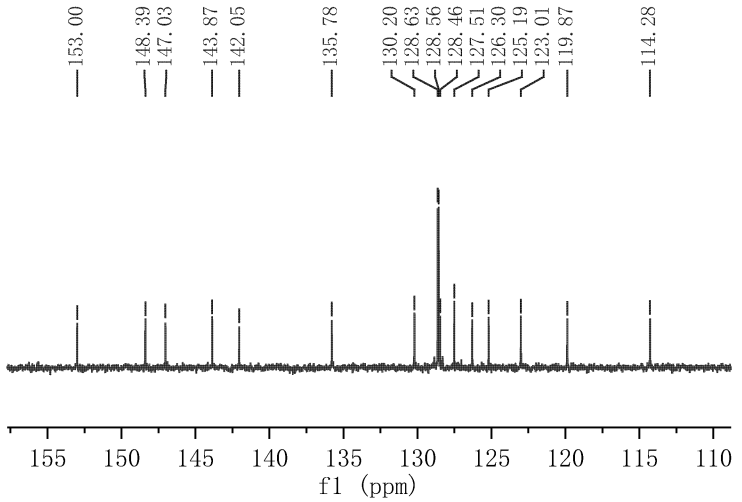


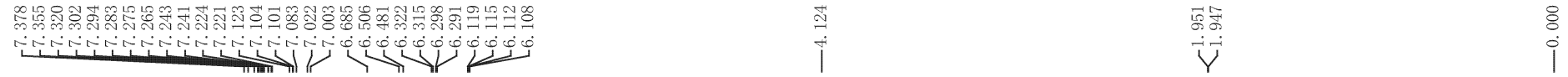


Parameter	Value
1 Title	3l-C-fxy-2-175-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.8
5 Number of Scans	22
6 Acquisition Time	1.3631
7 Acquisition Date	2020-07-06T14:41:33
8 Spectrometer Frequency	100.59
9 Spectral Width	24038.5

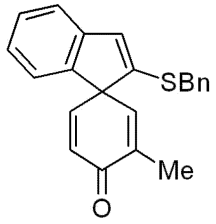


3l

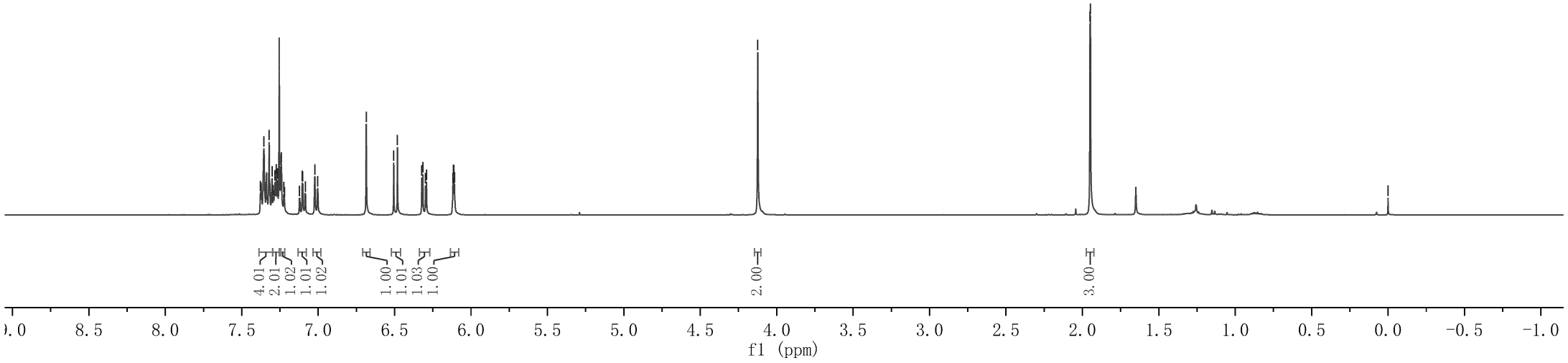


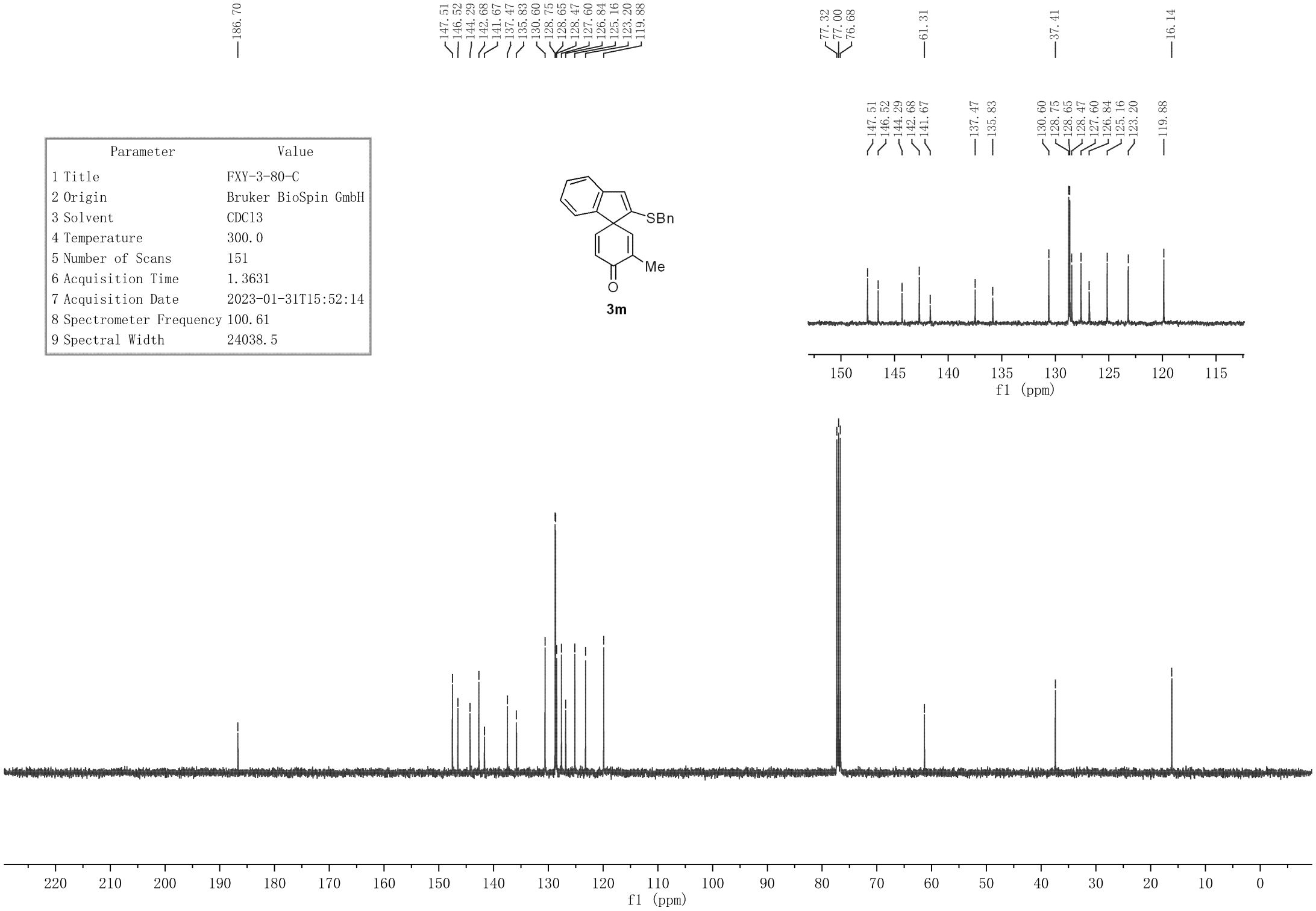


Parameter	Value
1 Title	FXY-3-80-h
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	22
6 Acquisition Time	4.0894
7 Acquisition Date	2023-01-31T15:51:03
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8

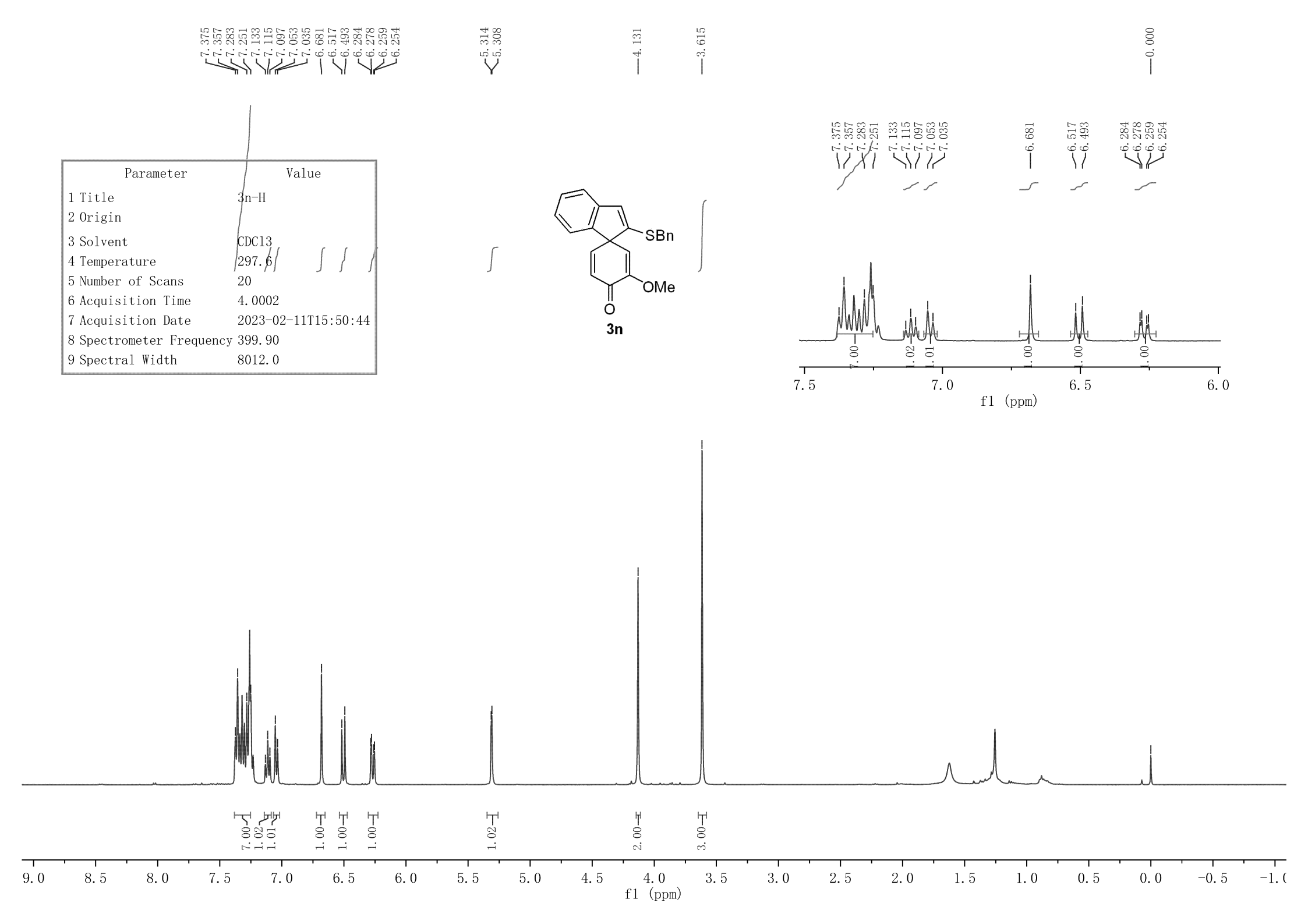


3m



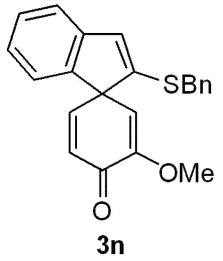


Parameter	Value
1 Title	FXY-3-80-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	151
6 Acquisition Time	1.3631
7 Acquisition Date	2023-01-31T15:52:14
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5

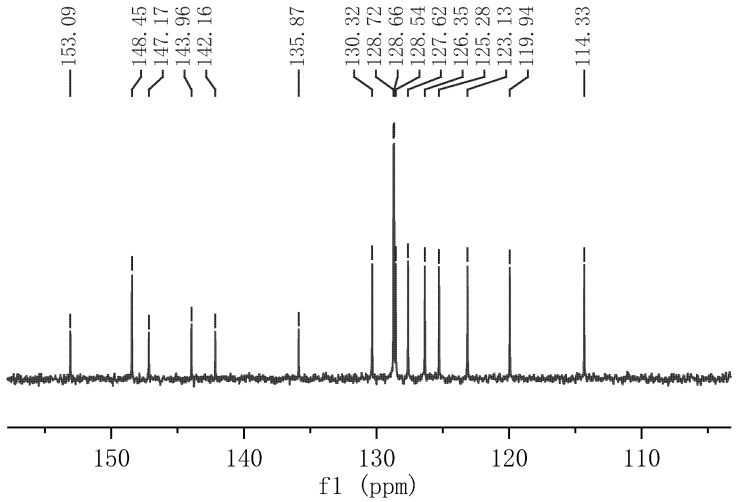

7.375
7.357
7.283
7.251
7.133
7.115
7.097
7.053
7.035
6.681
6.517
6.493
6.284
6.278
6.259
6.254
5.314
5.308
4.131
3.615
0.000
Parameter Value
1 Title 3n-H
2 Origin
3 Solvent CDC13
4 Temperature 297.6
5 Number of Scans 20
6 Acquisition Time 4.0002
7 Acquisition Date 2023-02-11T15:50:44
8 Spectrometer Frequency 399.90
9 Spectral Width 8012.0
SBn
OMe
O
3n
7.00
1.02
1.01
1.00
1.00
1.00
1.02
2.00
3.00
f1 (ppm)

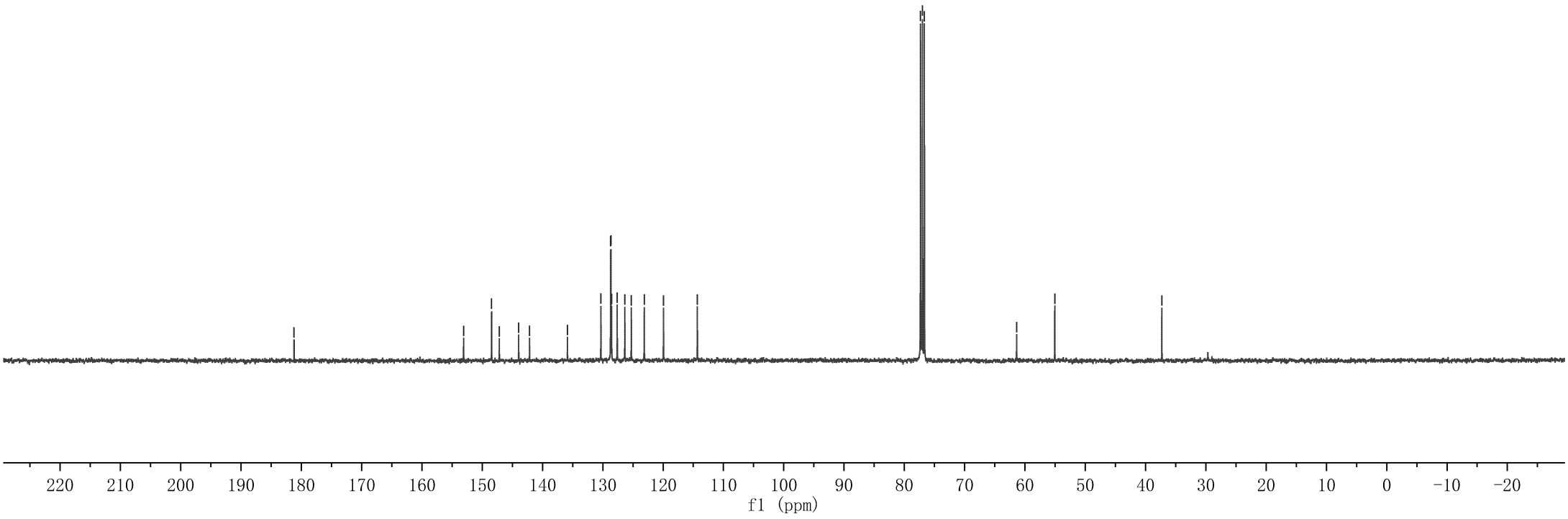
181.20
153.09
148.45
147.17
143.96
142.16
135.87
130.32
128.72
128.66
128.54
127.62
126.35
123.13
114.33
77.32
77.00
76.68
61.38
55.06
37.30

Parameter	Value
1 Title	3n-C
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.5
5 Number of Scans	800
6 Acquisition Time	1.0000
7 Acquisition Date	2023-02-11T16:20:03
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

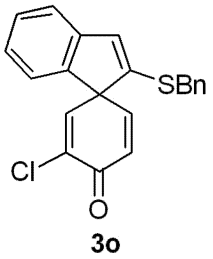


3n

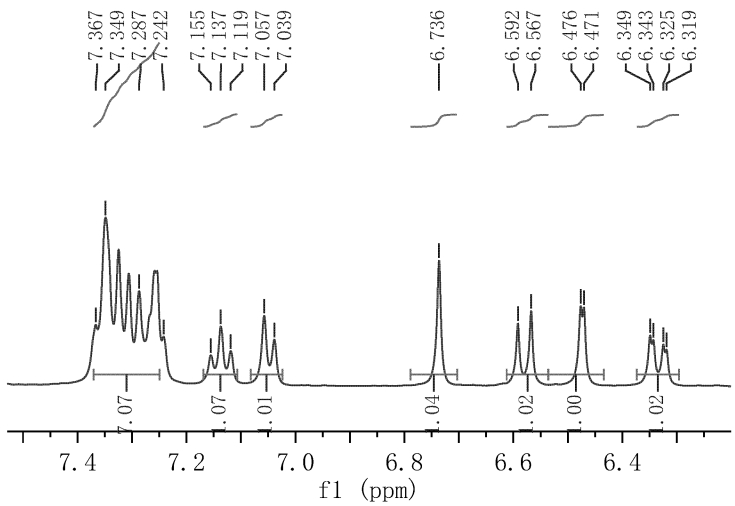


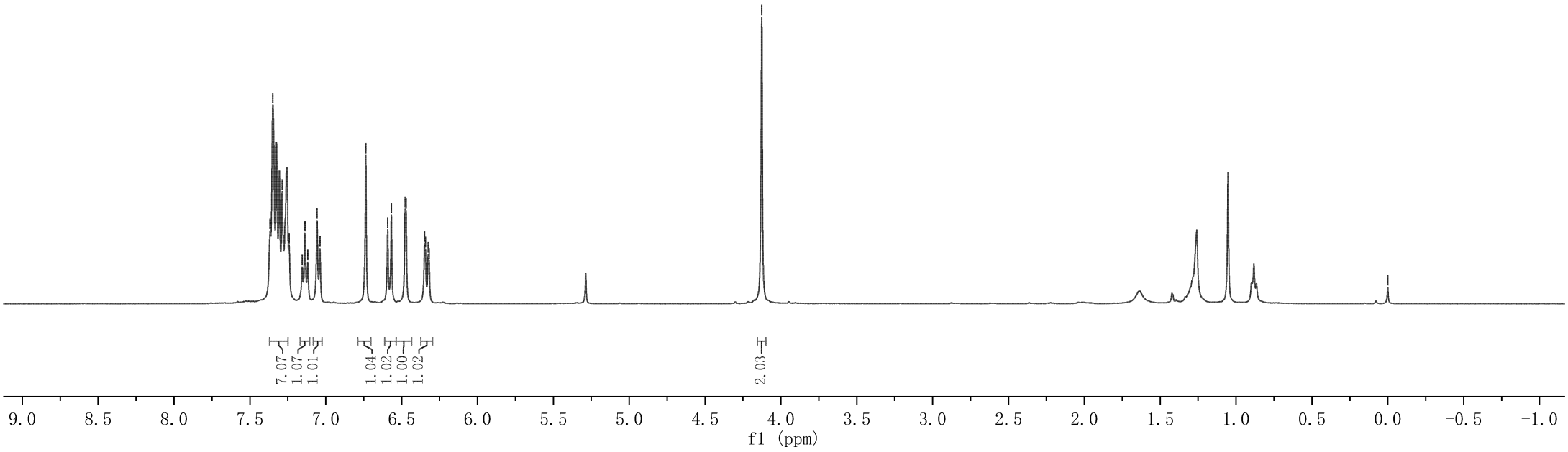


Parameter	Value
1 Title	30-H-FXY-2-228-H
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	5
6 Acquisition Time	4.0894
7 Acquisition Date	2021-05-19T15:37:26
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8



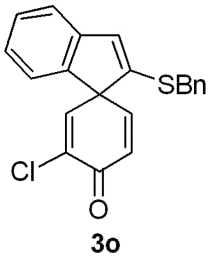
3o



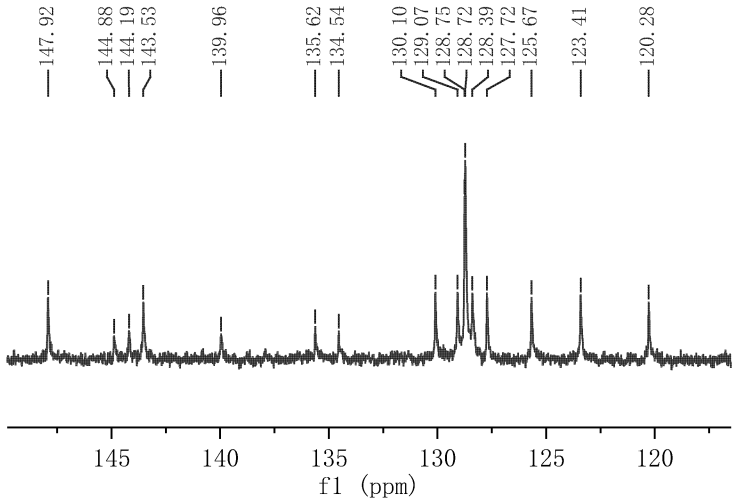


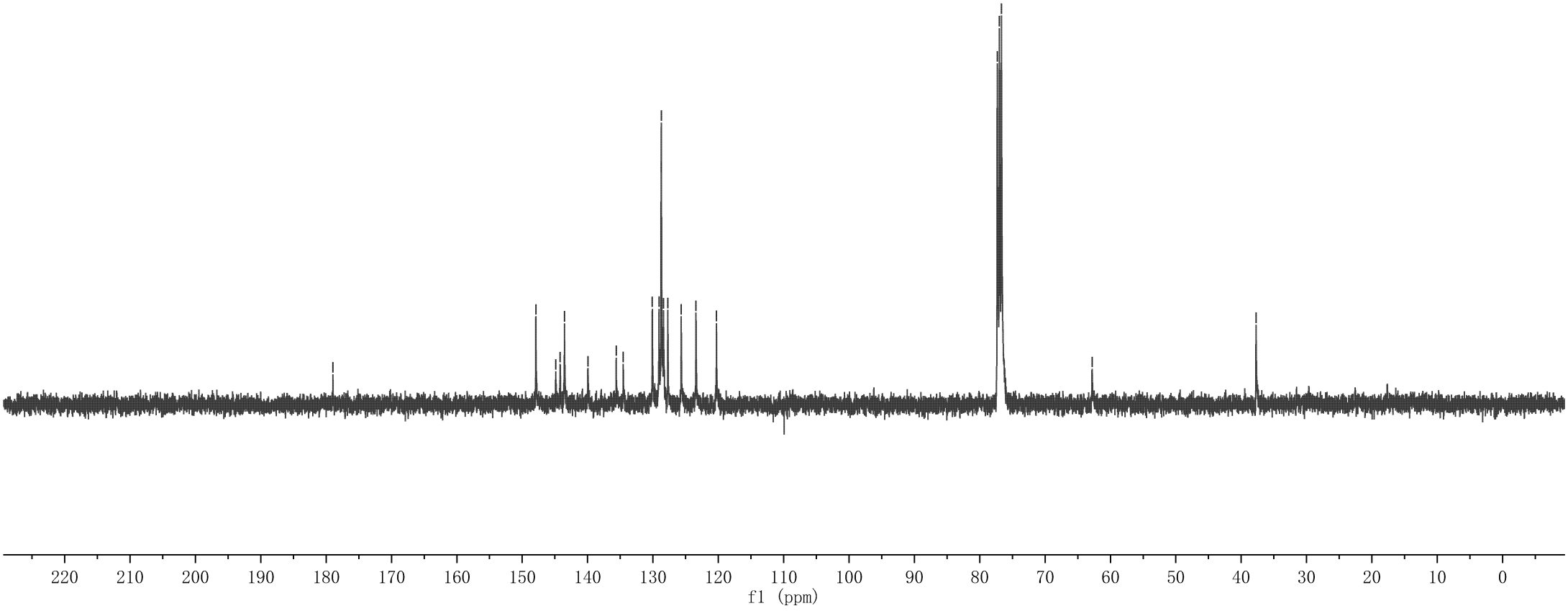
178.96
147.92
144.88
144.19
143.53
139.96
135.62
134.54
130.10
129.07
128.75
128.72
128.39
127.72
125.67
123.41
120.28
77.32
77.00
76.69
62.81
37.72

Parameter	Value
1 Title	30-C-fxy-2-228-C'
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	257
6 Acquisition Time	1.3631
7 Acquisition Date	2021-05-19T15:43:38
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5

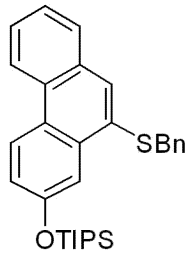


3o

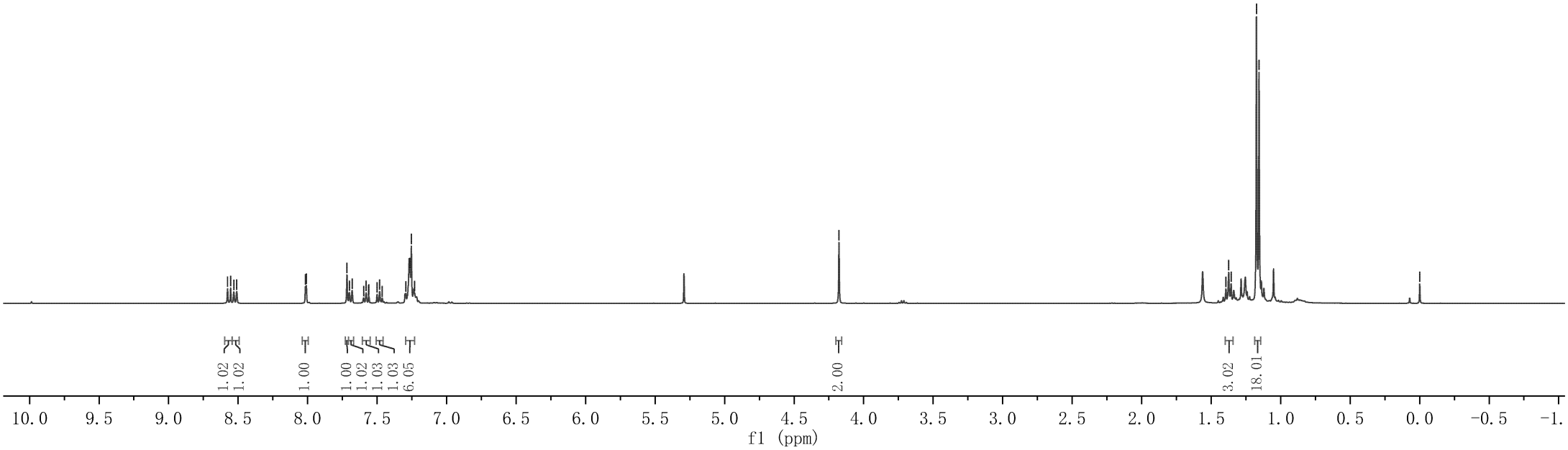




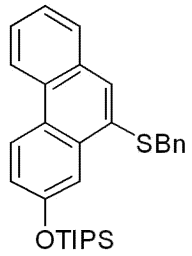
Parameter	Value
1 Title	FXY-11-19
2 Origin	
3 Solvent	CDC13
4 Temperature	295.5
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2023-02-15T22:47:39
8 Spectrometer Frequency	399.90
9 Spectral Width	8012.0



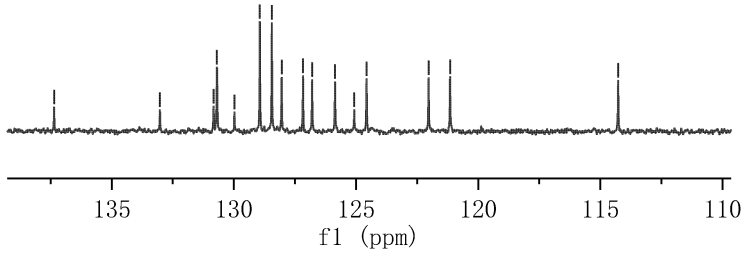
4

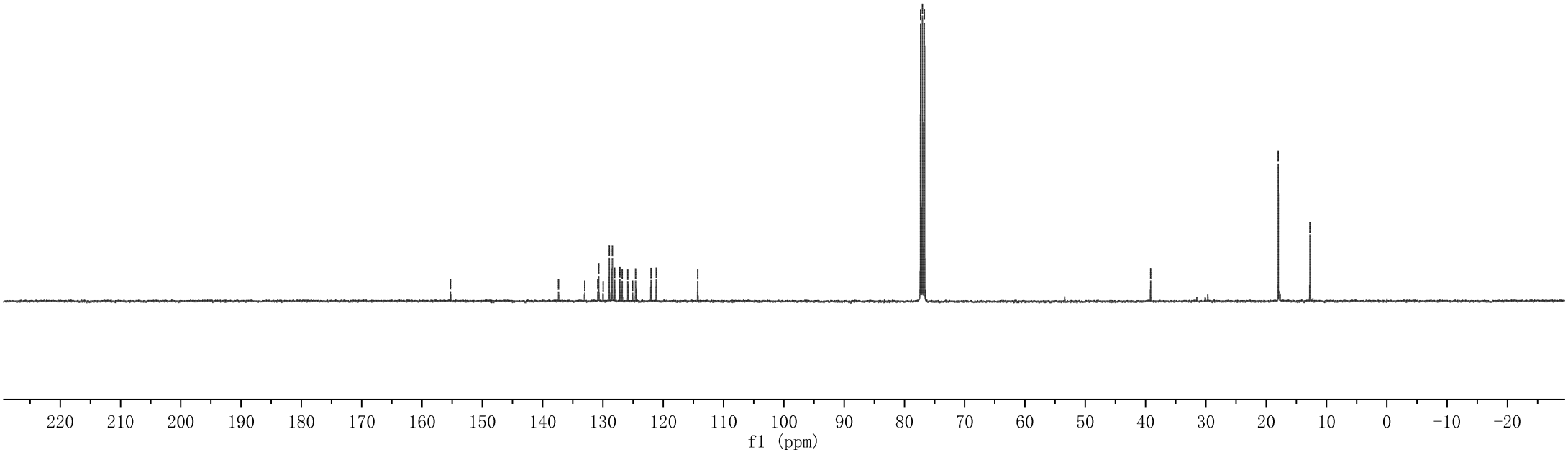


Parameter	Value
1 Title	FXY-11-19
2 Origin	
3 Solvent	CDCl3
4 Temperature	295.5
5 Number of Scans	800
6 Acquisition Time	1.0000
7 Acquisition Date	2023-02-15T23:56:54
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0



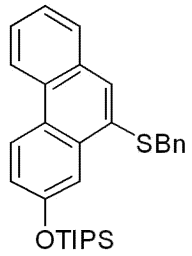
4



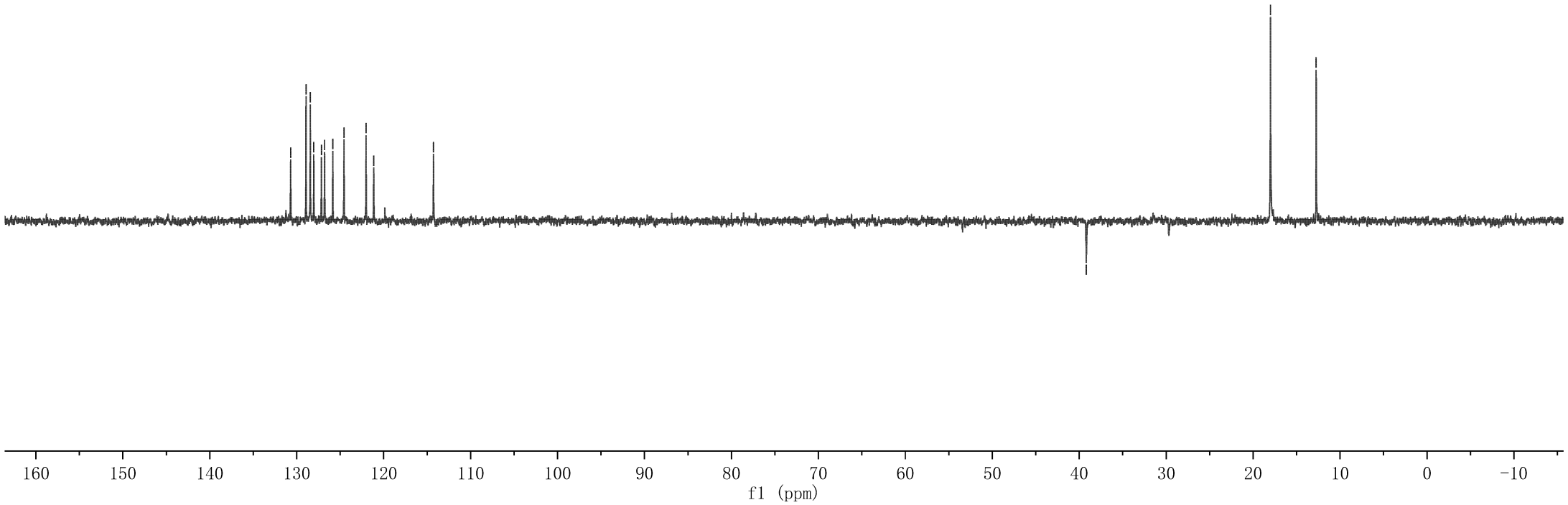


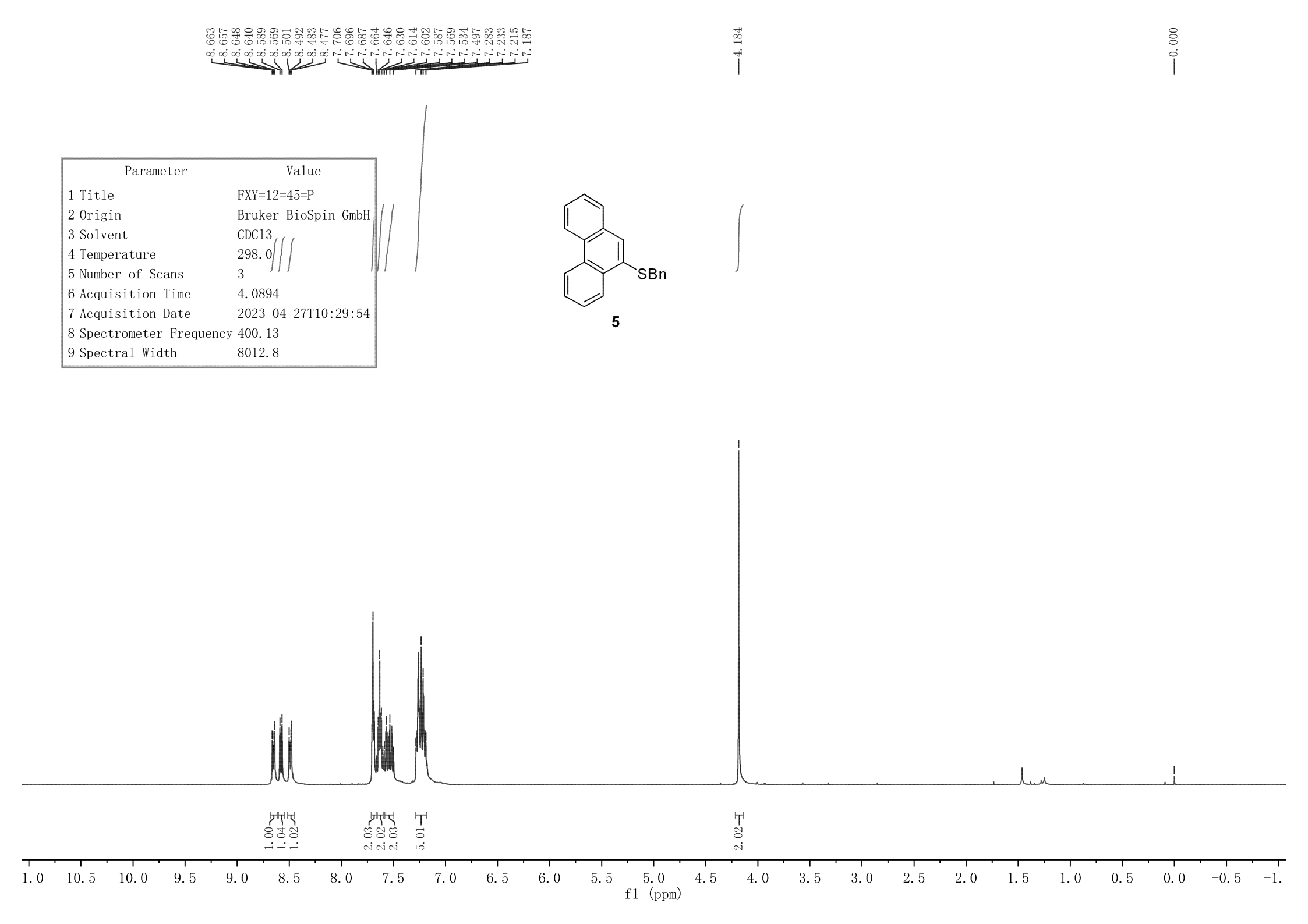
130.70
128.93
128.44
128.04
127.16
126.79
125.85
124.56
122.02
121.14
114.27
39.18
18.00
12.74

Parameter	Value
1 Title	FXY-11-19
2 Origin	
3 Solvent	CDC13
4 Temperature	295.2
5 Number of Scans	200
6 Acquisition Time	1.0001
7 Acquisition Date	2023-02-16T00:40:07
8 Spectrometer Frequency	100.56
9 Spectral Width	18028.0

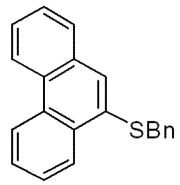


4




8.663
8.657
8.648
8.640
8.589
8.569
8.501
8.492
8.483
8.477
7.706
7.696
7.687
7.664
7.646
7.630
7.614
7.602
7.587
7.569
7.534
7.497
7.283
7.233
7.215
7.187
4.184
0.000
Parameter Value
1 Title FXY=12=45=P
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 298.0
5 Number of Scans 3
6 Acquisition Time 4.0894
7 Acquisition Date 2023-04-27T10:29:54
8 Spectrometer Frequency 400.13
9 Spectral Width 8012.8
SBn
5
1.00
1.04
1.02
2.03
2.02
2.03
5.01
2.02
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)

Parameter	Value
1 Title	FXY=12=45=c
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	26
6 Acquisition Time	1.3631
7 Acquisition Date	2023-04-27T10:30:43
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5



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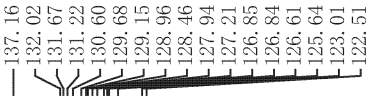
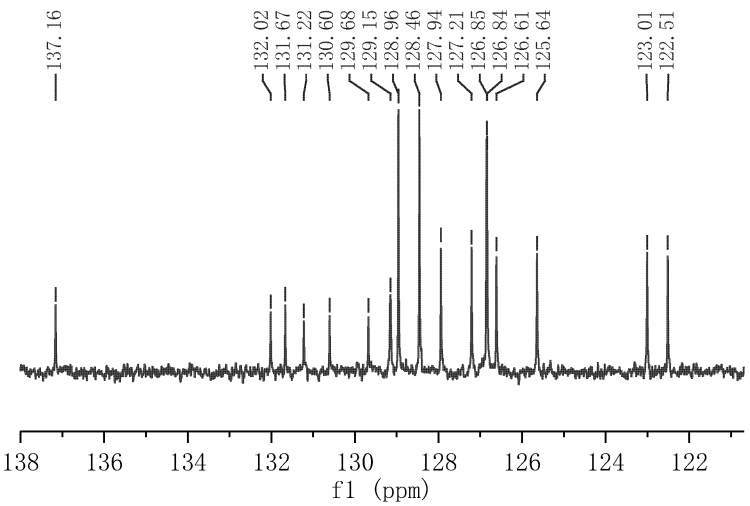
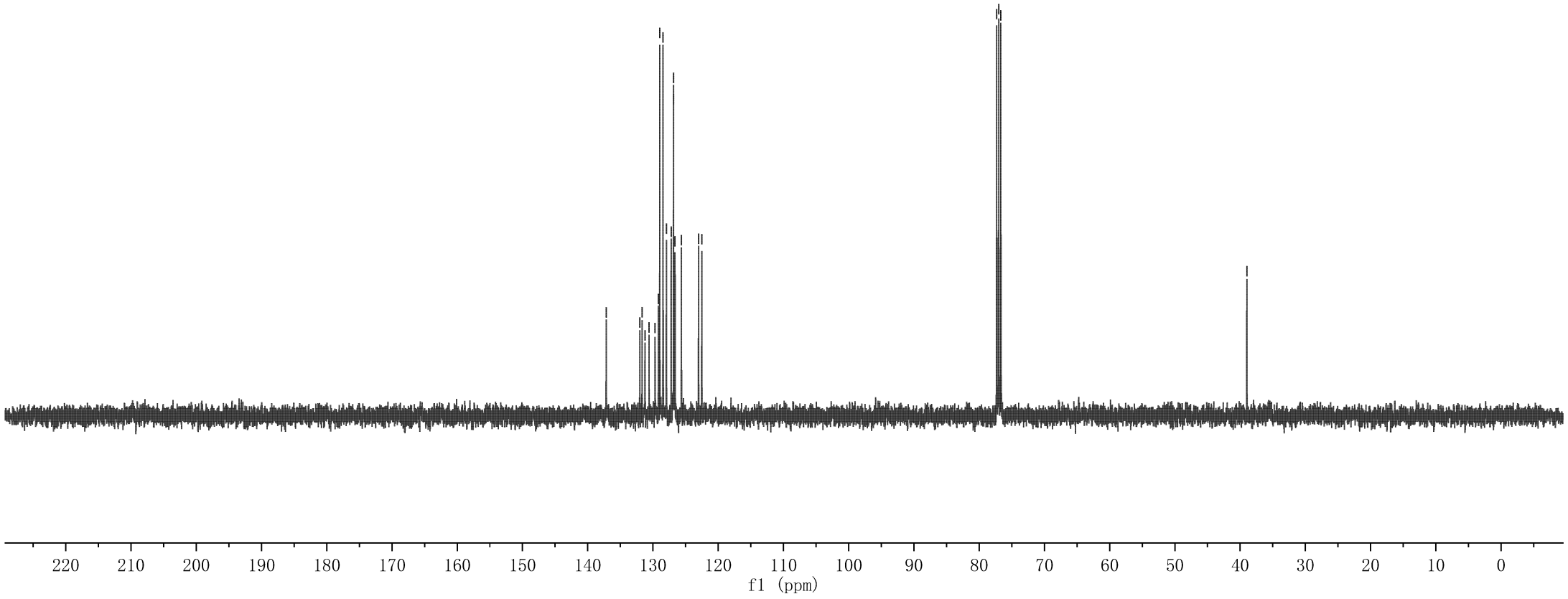


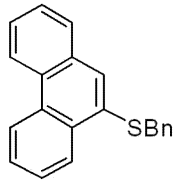




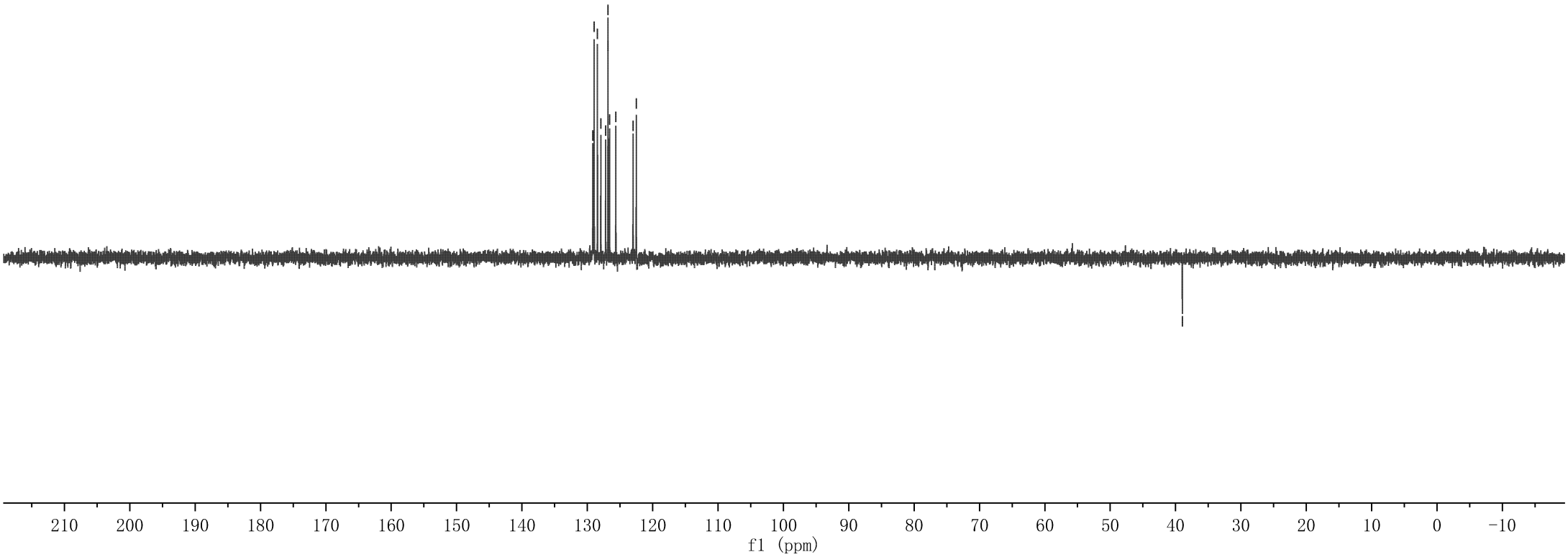
129.16
128.95
128.45
127.94
127.20
126.84
126.83
126.61
125.64
123.00
122.51

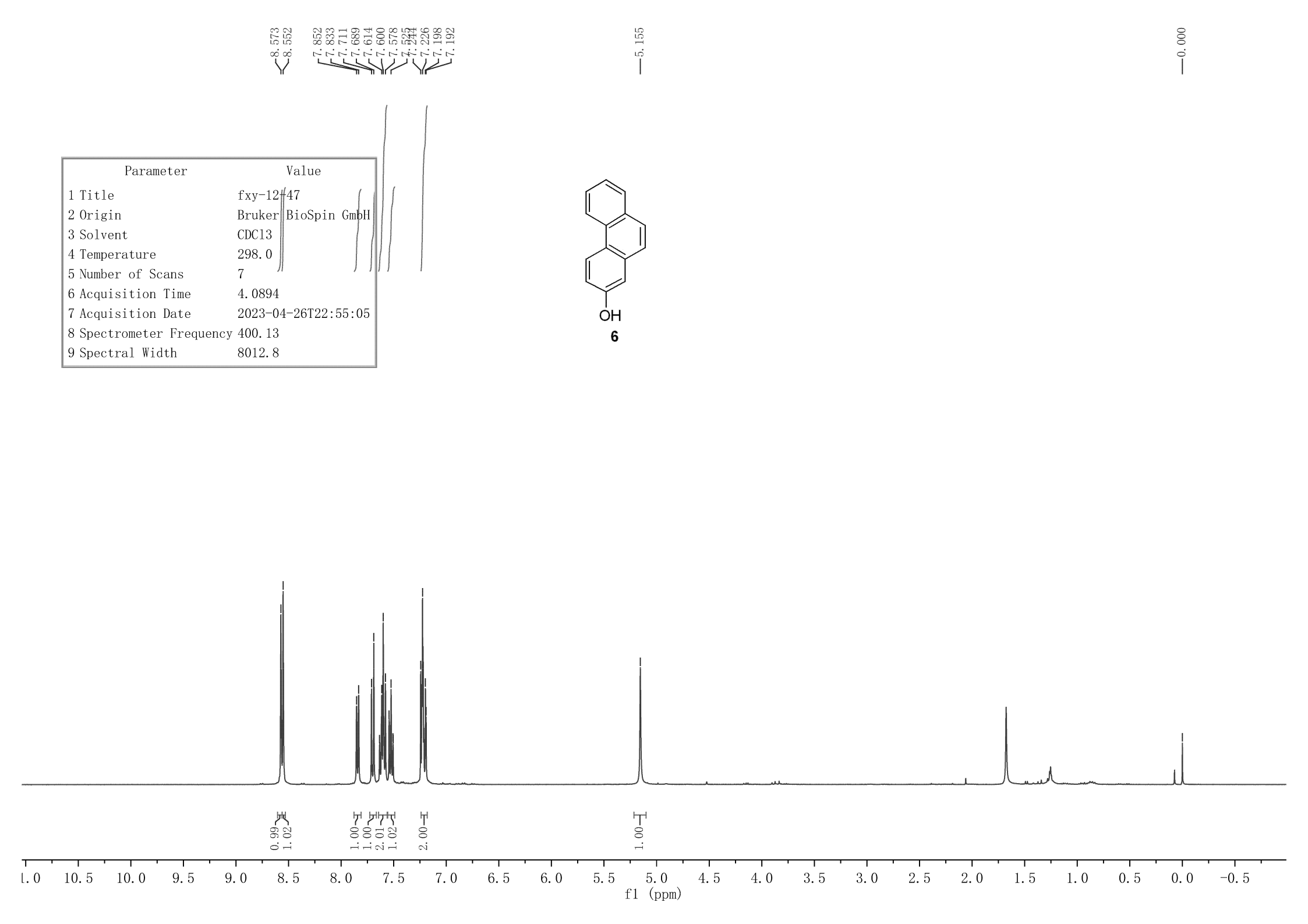
38.97

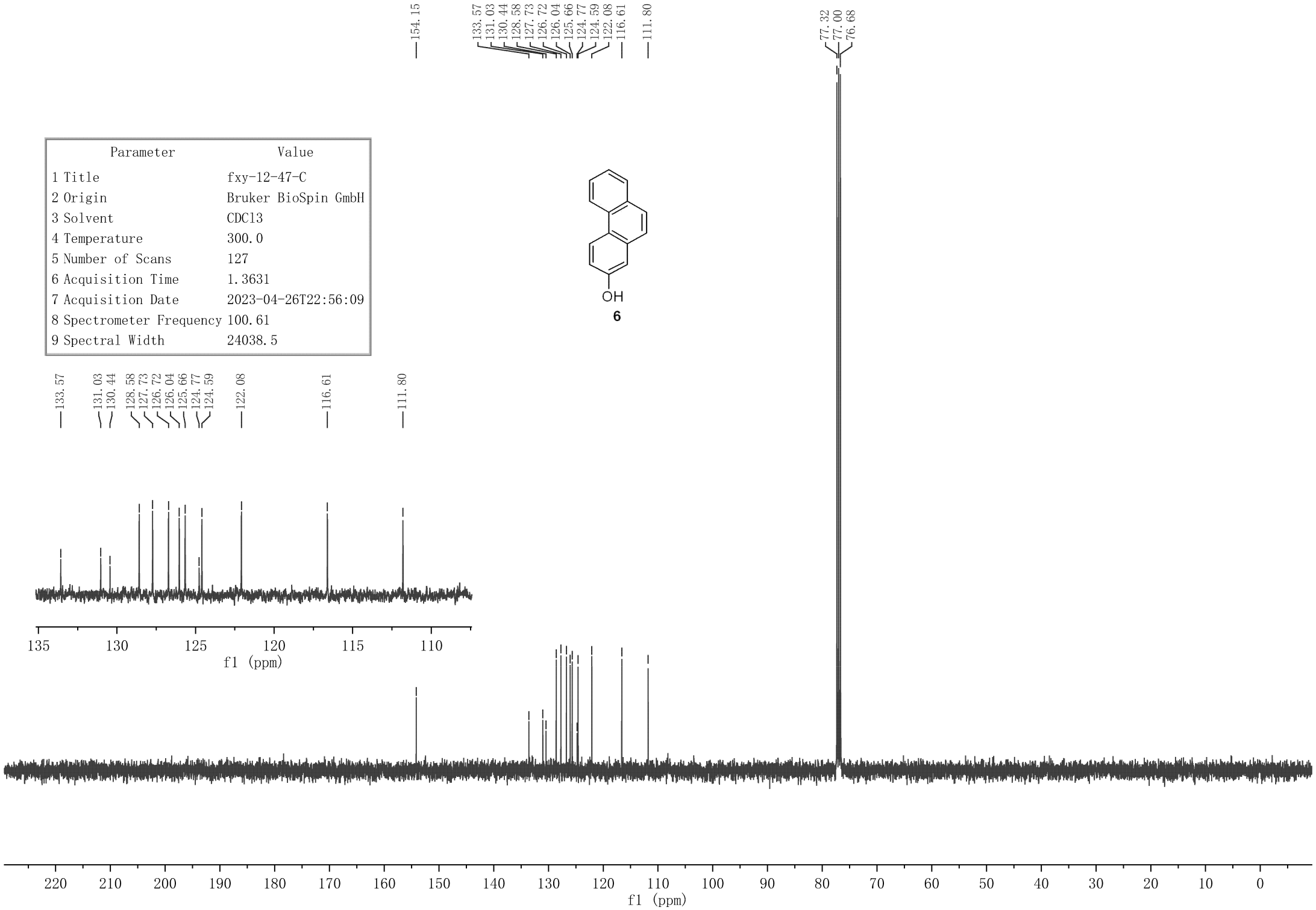
Parameter	Value
1 Title	FXY=12=45=DEPT
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	8
6 Acquisition Time	1.3631
7 Acquisition Date	2023-04-27T10:32:45
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5



5

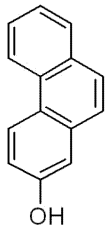



8.573
8.552
7.852
7.833
7.711
7.689
7.614
7.600
7.578
7.525
7.226
7.198
7.192
5.155
0.000
Parameter Value
1 Title fxy-12#47
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 298.0
5 Number of Scans 7
6 Acquisition Time 4.0894
7 Acquisition Date 2023-04-26T22:55:05
8 Spectrometer Frequency 400.13
9 Spectral Width 8012.8
OH
6
0.99
1.02
1.00
1.00
2.01
1.02
2.00
1.00
f1 (ppm)


154.15
133.57
131.03
130.44
128.58
127.73
126.72
126.04
125.66
124.77
124.59
122.08
116.61
111.80
77.32
77.00
76.68
OH
6
Parameter Value
1 Title fxy-12-47-C
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.0
5 Number of Scans 127
6 Acquisition Time 1.3631
7 Acquisition Date 2023-04-26T22:56:09
8 Spectrometer Frequency 100.61
9 Spectral Width 24038.5
f1 (ppm)
f1 (ppm)

128.58
127.73
126.72
126.03
125.66
124.59
122.08
116.61
111.80

Parameter	Value
1 Title	fxy-12-47-DEPT
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	2023-04-26T23:04:28
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5



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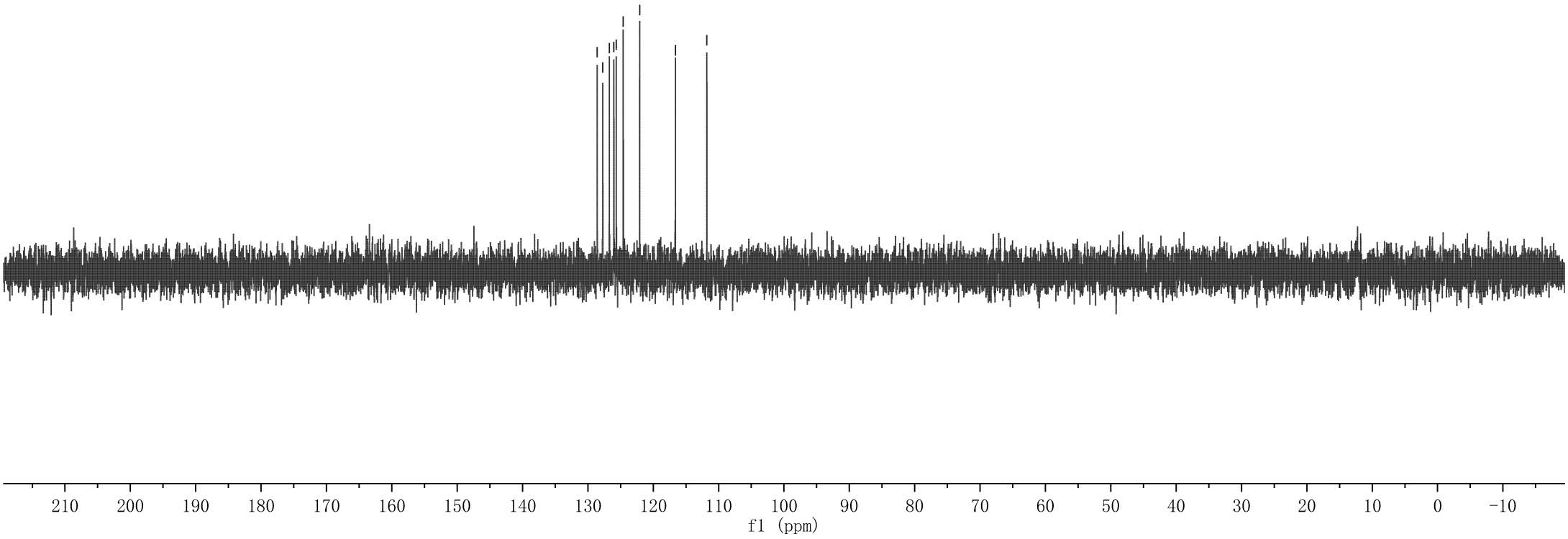
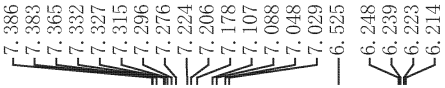
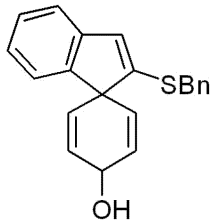




Parameter	Value
1 Title	LJ-1-194-1
2 Origin	
3 Solvent	CDCl3
4 Temperature	295.6
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2023-02-16T21:36:17
8 Spectrometer Frequency	399.90
9 Spectral Width	8012.0



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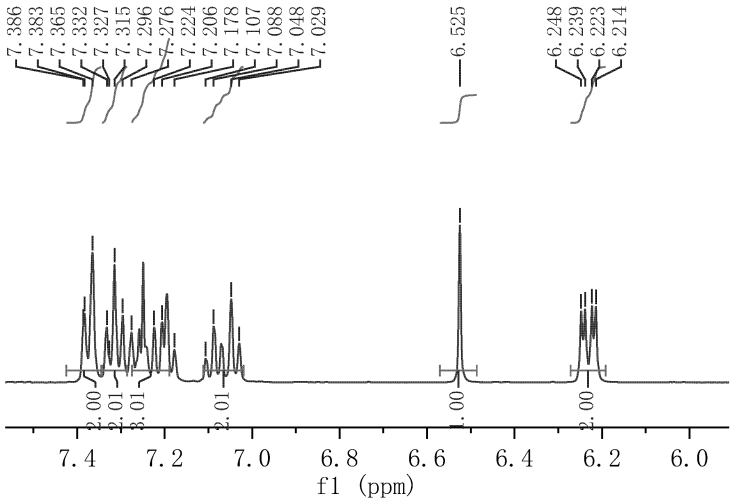
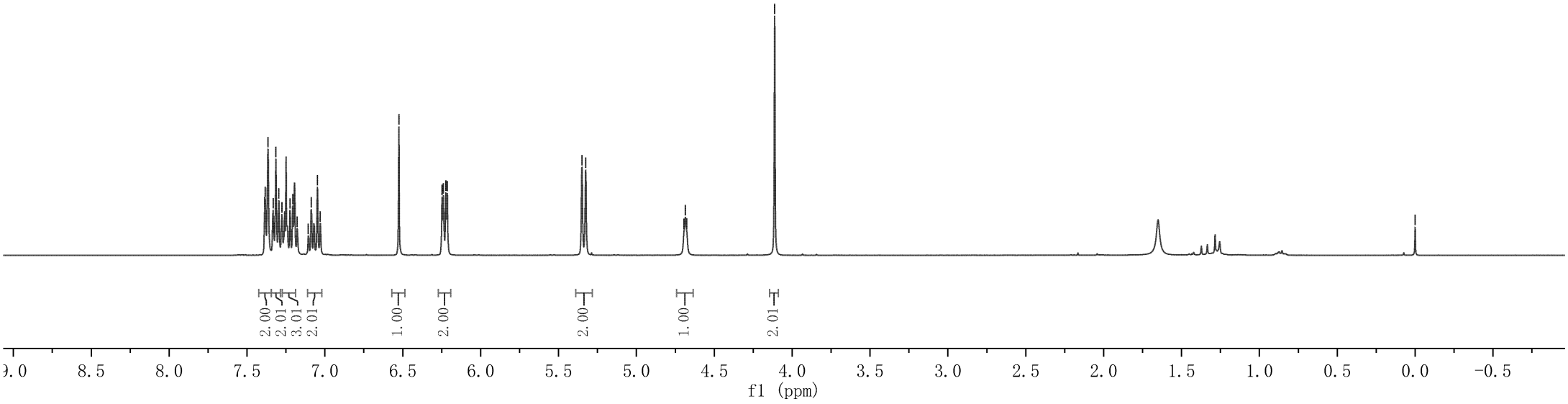
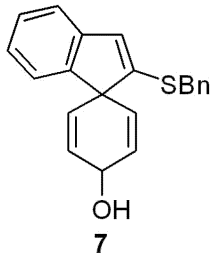




Parameter	Value
1 Title	LJ-1-194-1
2 Origin	
3 Solvent	CDCl3
4 Temperature	295.6
5 Number of Scans	160
6 Acquisition Time	1.0000
7 Acquisition Date	2023-02-16T22:32:18
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0



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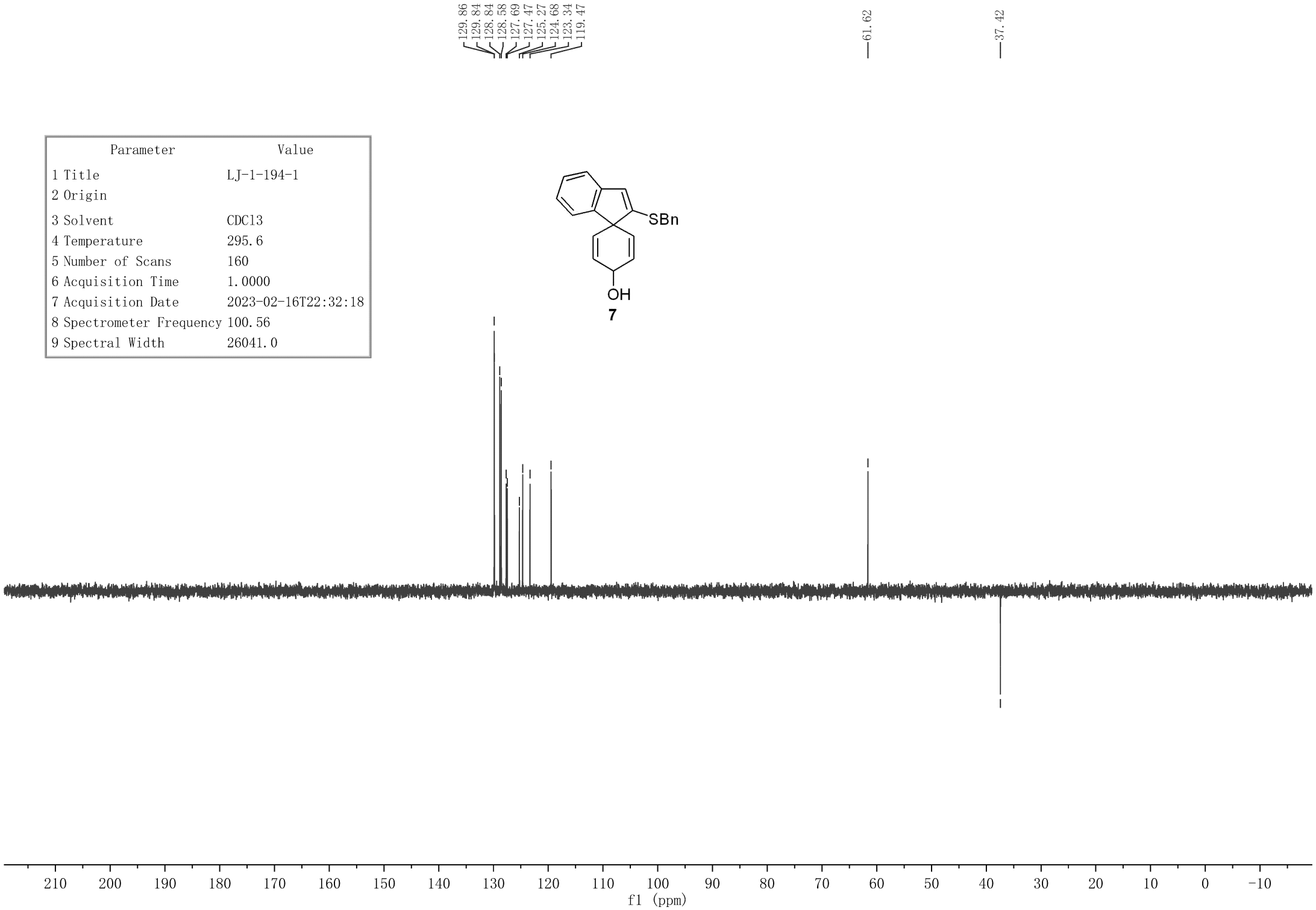
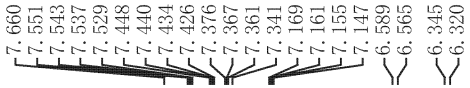
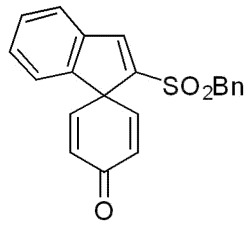
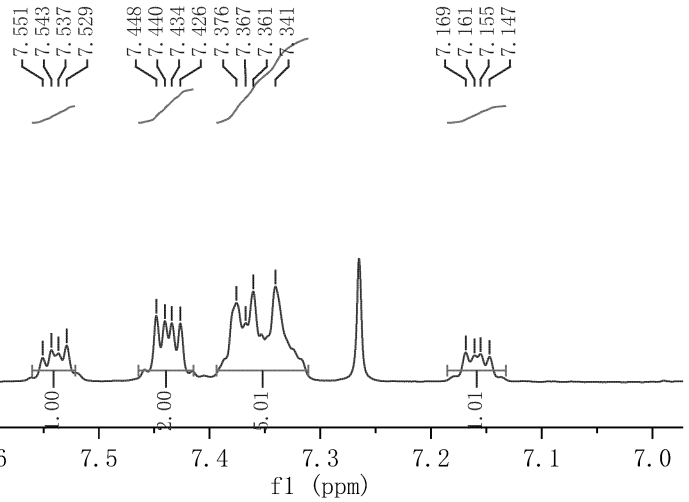

129.86
129.84
128.84
128.58
127.69
127.47
125.27
124.68
123.34
119.47
61.62
37.42
SBn
OH
7
Parameter Value
1 Title LJ-1-194-1
2 Origin
3 Solvent CDCl3
4 Temperature 295.6
5 Number of Scans 160
6 Acquisition Time 1.0000
7 Acquisition Date 2023-02-16T22:32:18
8 Spectrometer Frequency 100.56
9 Spectral Width 26041.0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

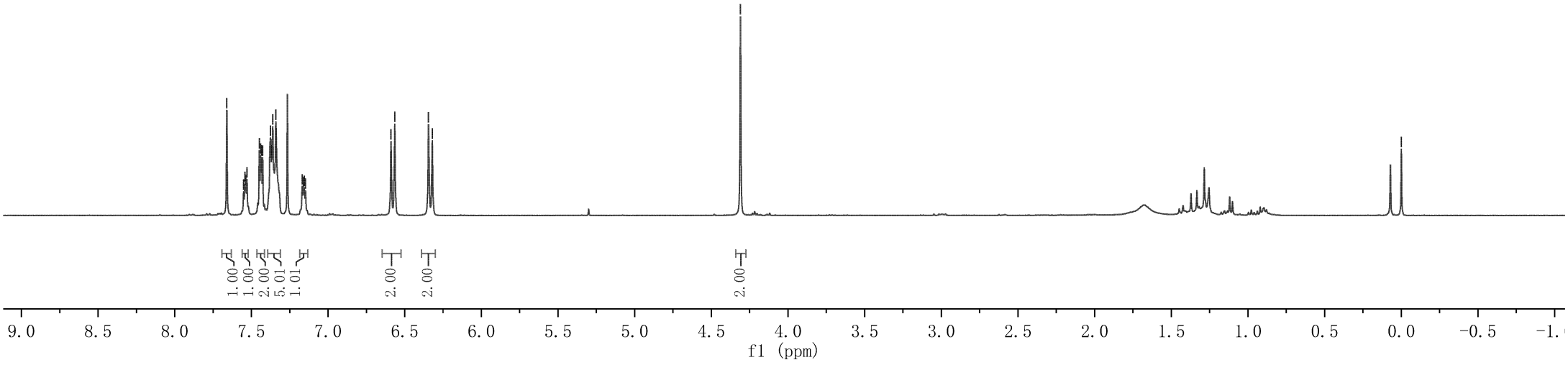


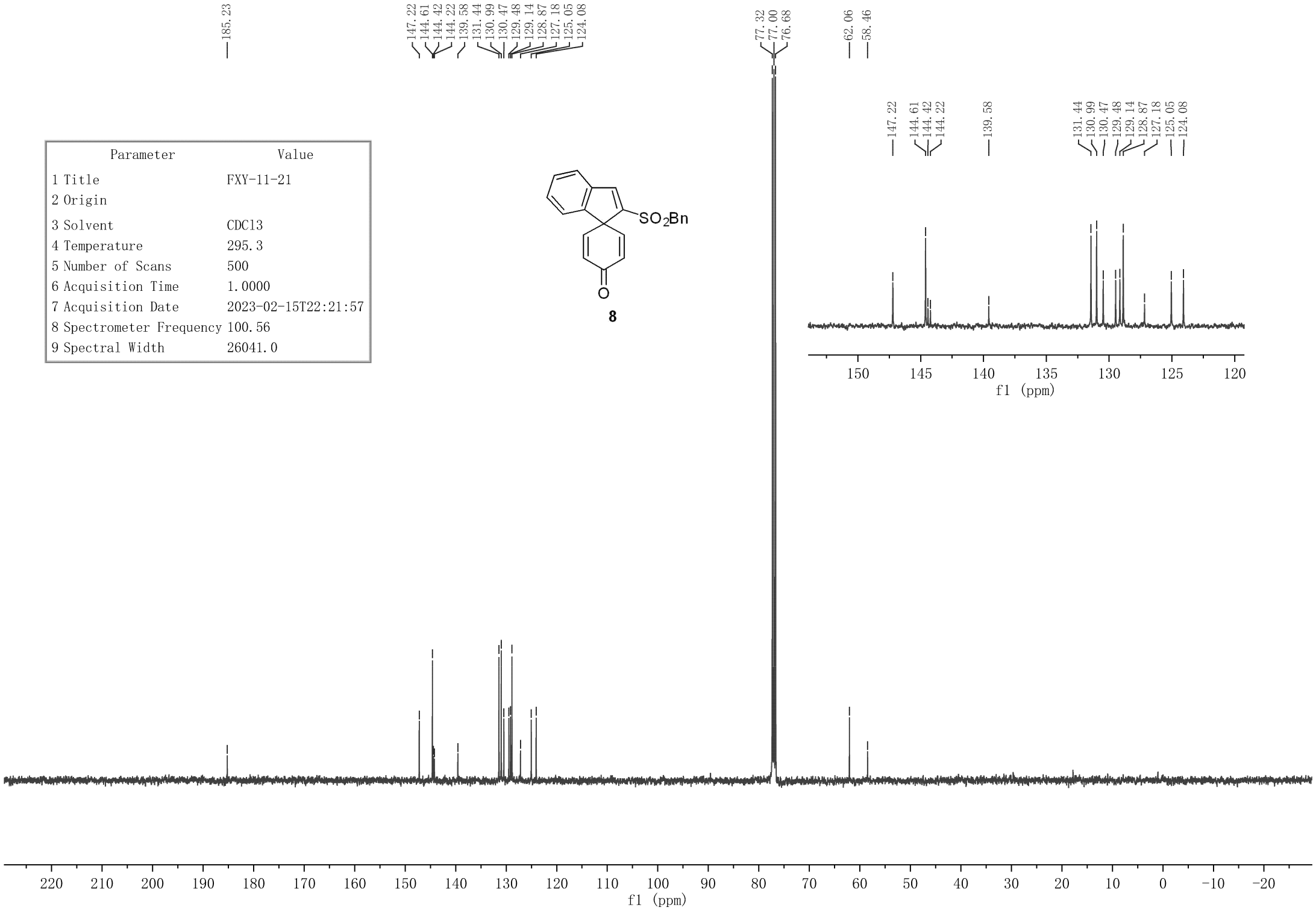
Parameter	Value
1 Title	FXY-11-21
2 Origin	
3 Solvent	CDCl3
4 Temperature	295.4
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2023-02-15T21:45:17
8 Spectrometer Frequency	399.90
9 Spectral Width	8012.0



8

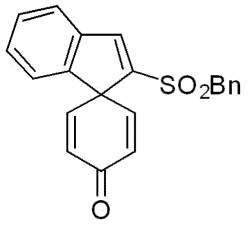




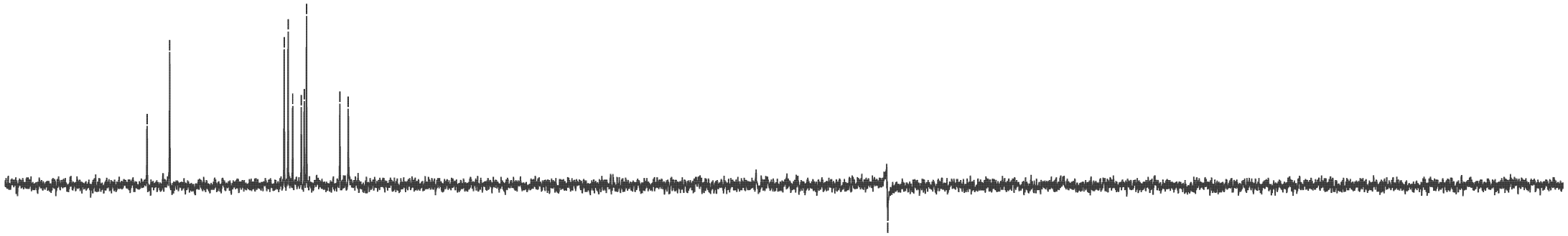

185.23
147.22
144.61
144.42
144.22
139.58
131.44
130.99
130.47
129.48
129.14
128.87
127.18
125.05
124.08
77.32
77.00
76.68
62.06
58.46
Parameter Value
1 Title FXY-11-21
2 Origin
3 Solvent CDCl3
4 Temperature 295.3
5 Number of Scans 500
6 Acquisition Time 1.0000
7 Acquisition Date 2023-02-15T22:21:57
8 Spectrometer Frequency 100.56
9 Spectral Width 26041.0
SO2Bn
O
8
f1 (ppm)
f1 (ppm)

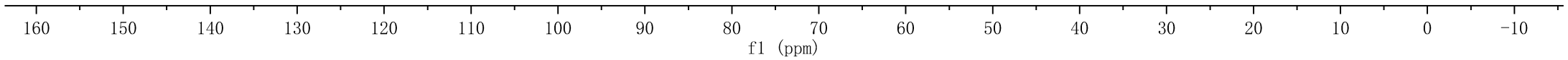
147.27
144.66
131.49
131.04
130.52
129.52
129.19
128.92
125.09
124.12
62.06

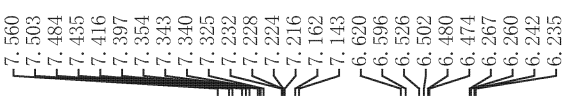
Parameter	Value
1 Title	FXY-11-21
2 Origin	
3 Solvent	CDC13
4 Temperature	295.4
5 Number of Scans	150
6 Acquisition Time	1.0001
7 Acquisition Date	2023-02-15T22:42:35
8 Spectrometer Frequency	100.56
9 Spectral Width	18028.0



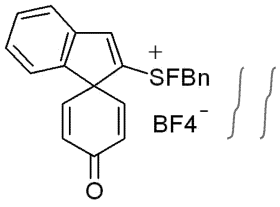
8



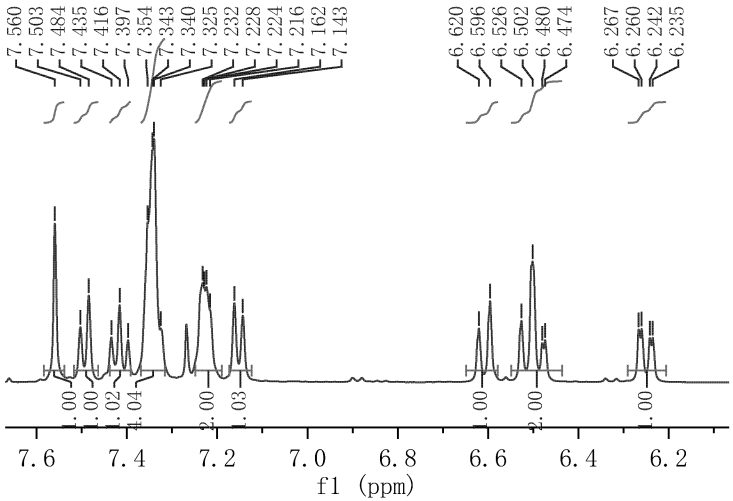


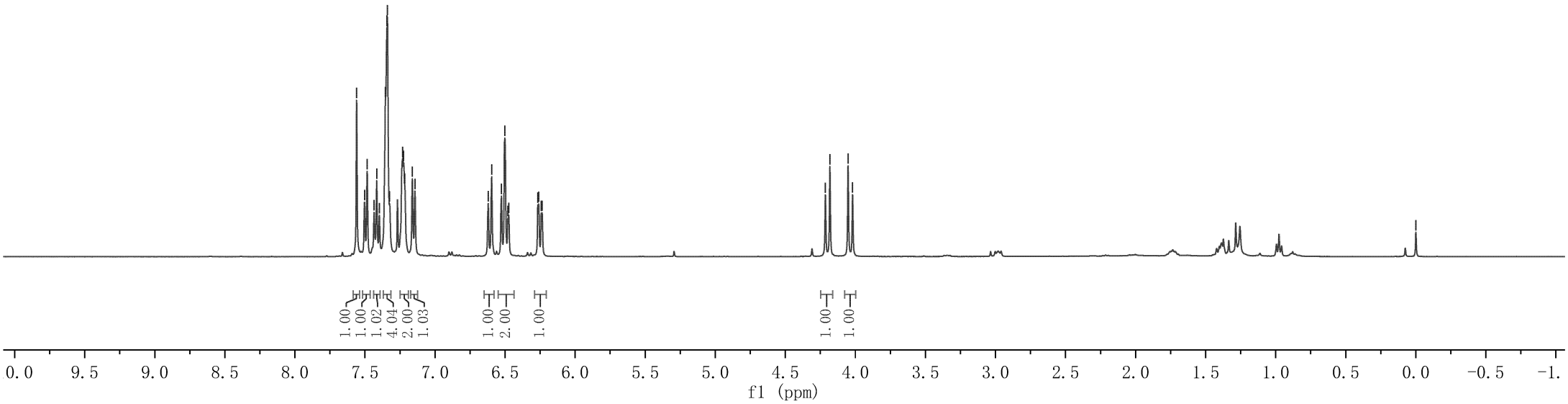


Parameter	Value
1 Title	9-H
2 Origin	
3 Solvent	CDCl3
4 Temperature	295.1
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2023-02-16T00:44:59
8 Spectrometer Frequency	399.90
9 Spectral Width	8012.0



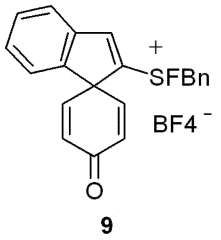
9



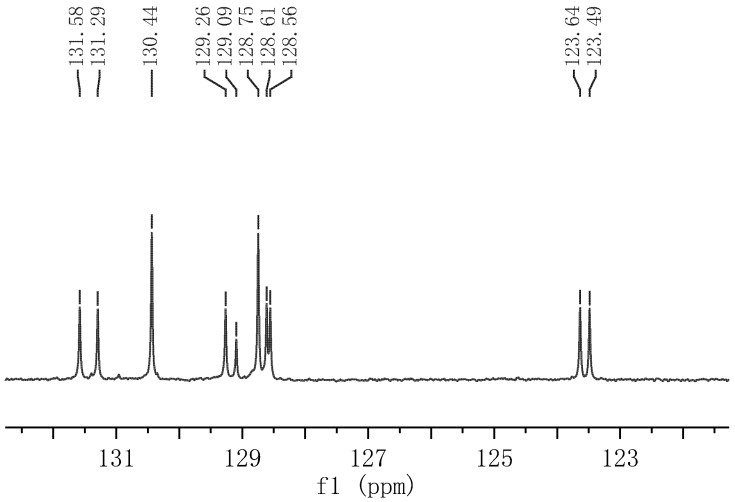


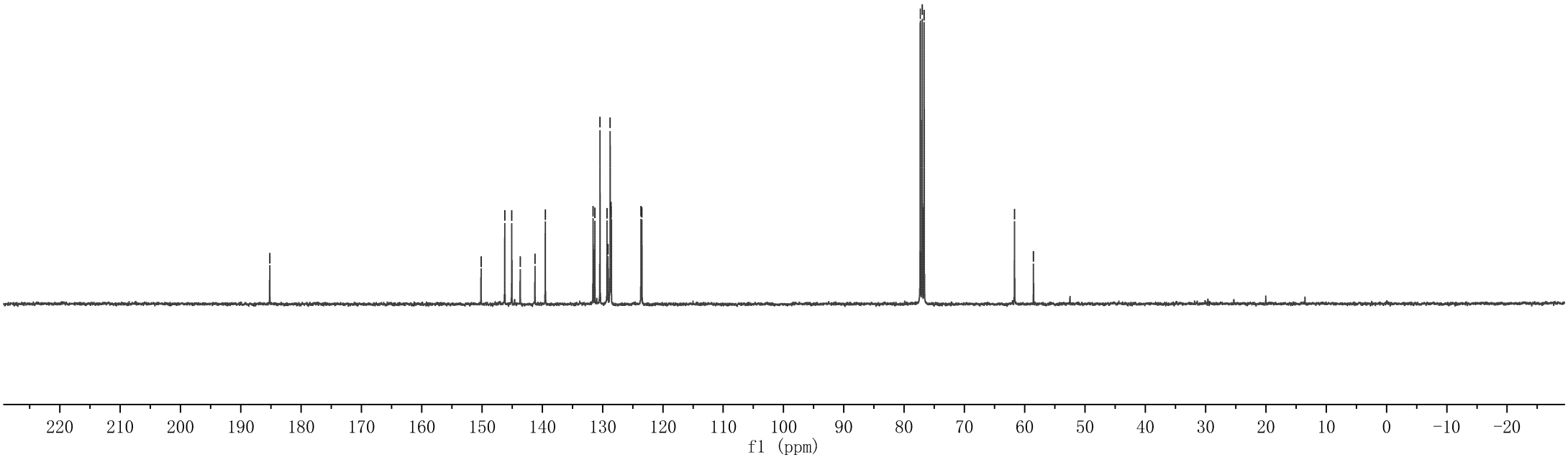
185.20
150.16
146.23
145.06
143.66
141.22
139.51
131.58
131.29
130.44
129.26
129.09
128.75
128.61
128.56
123.64
123.49
77.32
77.00
76.68
61.69
58.55

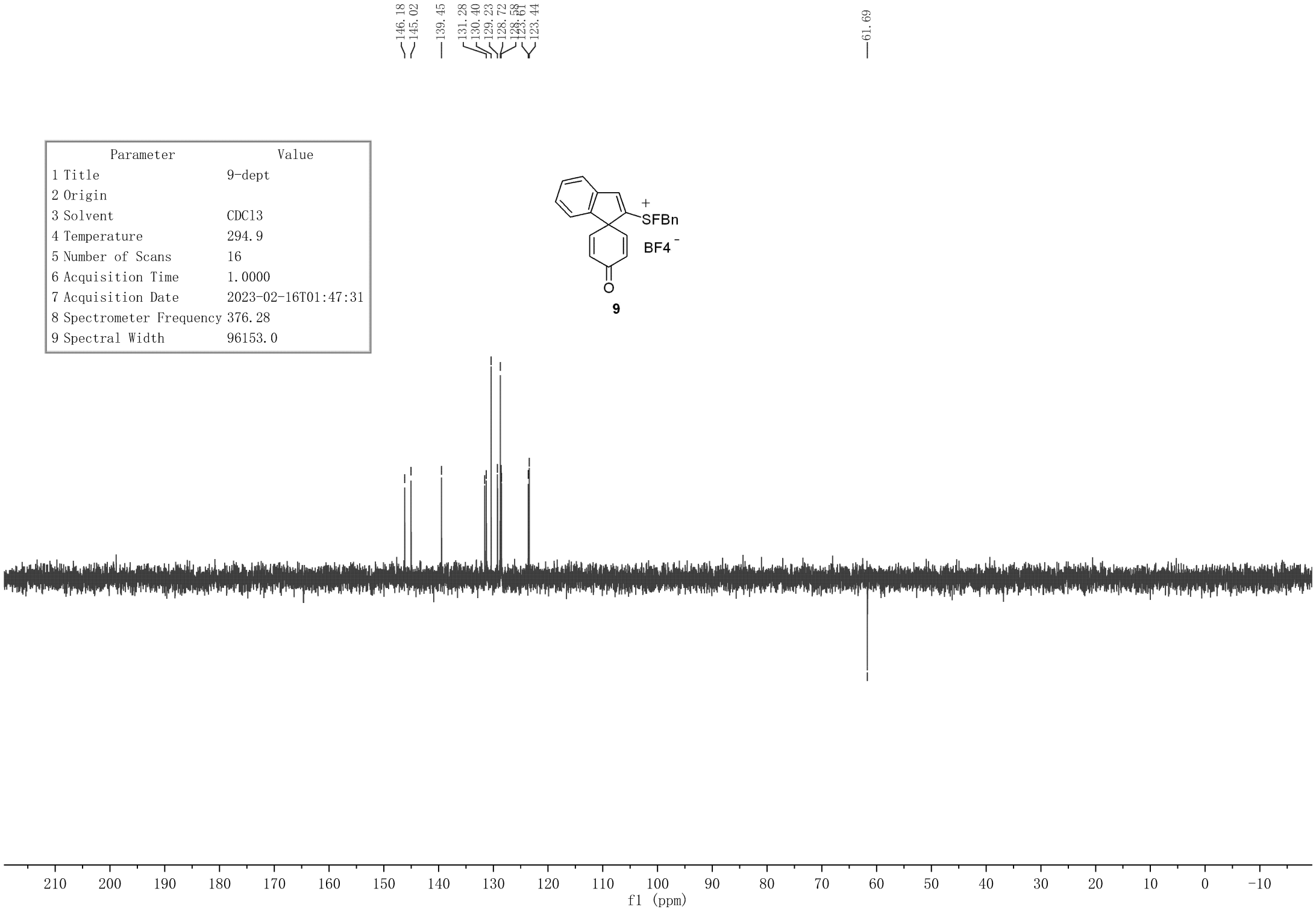
Parameter	Value
1 Title	9-c
2 Origin	
3 Solvent	CDCl3
4 Temperature	295.2
5 Number of Scans	102
6 Acquisition Time	1.0000
7 Acquisition Date	2023-02-16T01:21:38
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

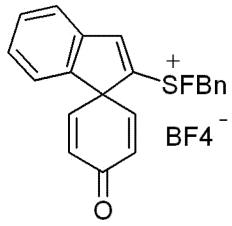


9






146.18
145.02
139.45
131.28
130.40
129.23
128.72
123.44
61.69
Parameter Value
1 Title 9-dept
2 Origin
3 Solvent CDCl3
4 Temperature 294.9
5 Number of Scans 16
6 Acquisition Time 1.0000
7 Acquisition Date 2023-02-16T01:47:31
8 Spectrometer Frequency 376.28
9 Spectral Width 96153.0
+
SFBn
BF4 -
O
9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

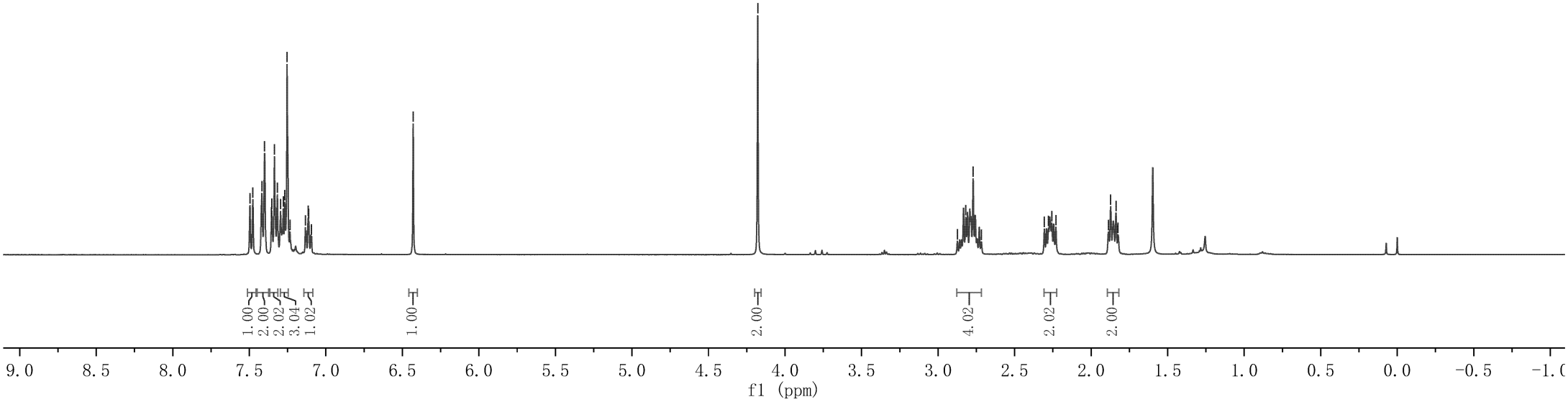


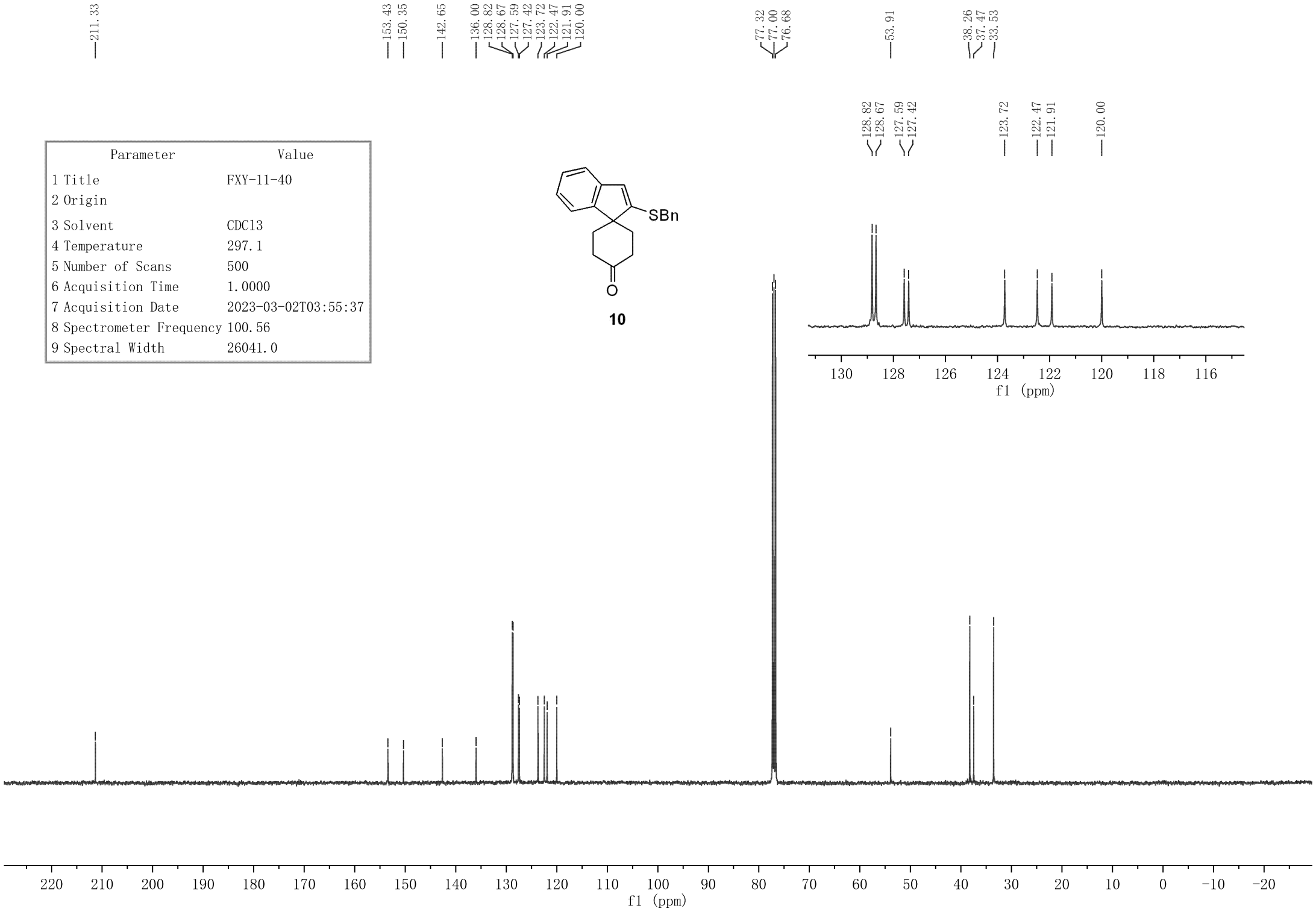
9

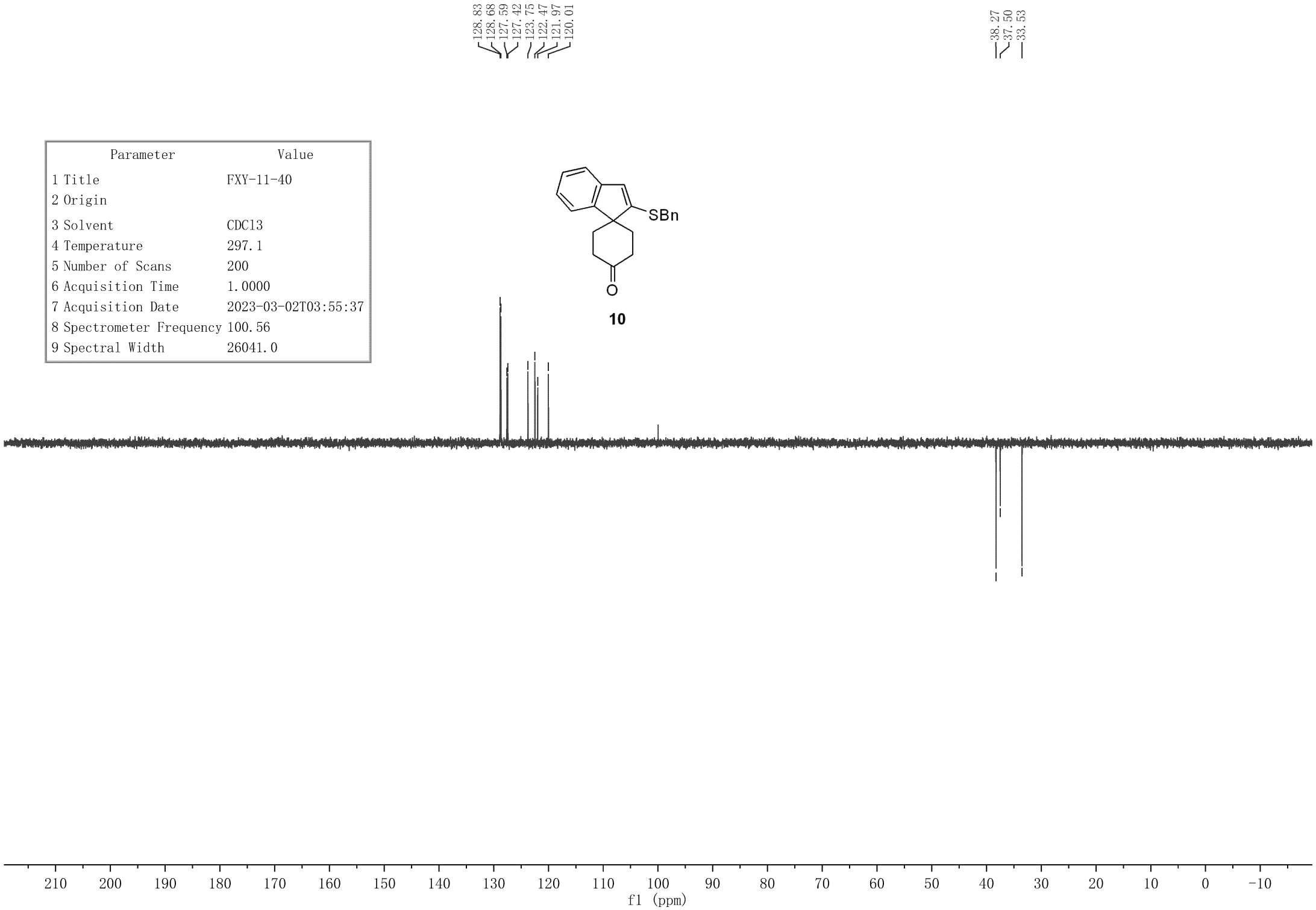
Parameter	Value
1 Title	9-F
2 Origin	
3 Solvent	CDCl3
4 Temperature	294.9
5 Number of Scans	16
6 Acquisition Time	1.0000
7 Acquisition Date	2023-02-16T01:47:31
8 Spectrometer Frequency	376.28
9 Spectral Width	96153.0

Parameter	Value
1 Title	FXY-11-40
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.1
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2023-03-02T02:46:29
8 Spectrometer Frequency	399.90
9 Spectral Width	8012.0

10




211.33
153.43
150.35
142.65
136.00
128.82
128.67
127.59
127.42
123.72
122.47
121.91
120.00
77.32
77.00
76.68
53.91
38.26
37.47
33.53
Parameter Value
1 Title FXY-11-40
2 Origin
3 Solvent CDCl3
4 Temperature 297.1
5 Number of Scans 500
6 Acquisition Time 1.0000
7 Acquisition Date 2023-03-02T03:55:37
8 Spectrometer Frequency 100.56
9 Spectral Width 26041.0
SBn
O
10
f1 (ppm)


128.83
128.68
127.59
127.42
123.75
122.47
121.97
120.01
38.27
37.50
33.53
Parameter Value
1 Title FXY-11-40
2 Origin
3 Solvent CDCl3
4 Temperature 297.1
5 Number of Scans 200
6 Acquisition Time 1.0000
7 Acquisition Date 2023-03-02T03:55:37
8 Spectrometer Frequency 100.56
9 Spectral Width 26041.0
SBn
O
10
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)