Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Chiral Brønsted acid-catalyzed asymmetric dearomative spirocyclization of alkynyl thioethers

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1. General Information

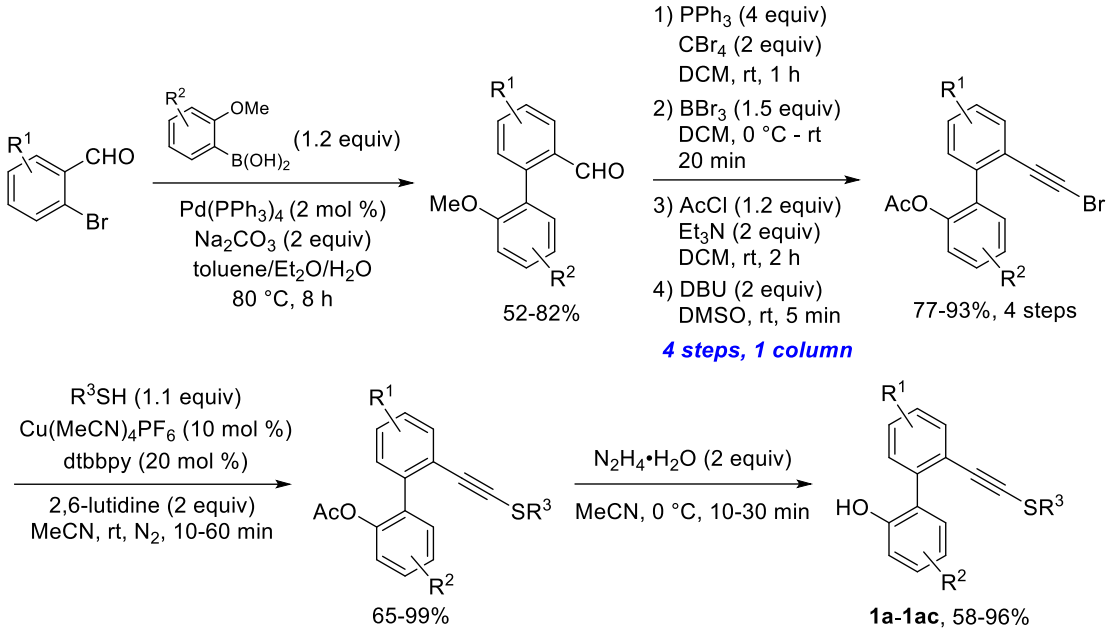
Ethyl acetate (ACS grade), hexanes (ACS grade), anhydrous 1,2-dichloroethane (ACS grade) and toluene (ACS grade) were obtained commercially and used without further purification. Methylene chloride and tetrahydrofuran were purified according to standard methods unless otherwise noted. Commercially available 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. HPLC analyses were carried out in a chromatograph equipped with a UV diode-array detector using chiral stationary columns from Daicel.

^{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**–**1ac** were prepared according to the following procedure.[1,2]



To a suspension of *o*-bromobenzaldehyde derivative (2 mmol), phenylboronic acid (2.4 mmol) and sodium carbonate (4 mmol, 424.0 mg) in the mixed solvent (toluene/EtOH/H_2O = 2/1/1, 20 mL) was added $Pd(PPh_3)_4$ (0.04 mmol, 46.0 mg) at room temperature under N_2 atmosphere. The resulting mixture was stirred at 80 °C for 8 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 residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate) to give the biaryl benzaldehyde in 52–82% yield.

To the solution of PPh_3 (8 mmol, 2.1 g) in DCM (6 mL) was added CBr_4 (4 mmol, 1.4 g) slowly at 0 °C, and the reaction was stirred at this temperature for additional 30 min. The solution of the above biaryl benzaldehyde (2 mmol) in DCM (2 mL) was then added to the reaction mixture at 0 °C. The reaction was warmed to room temperature and stirred for 1 h. Upon completion, the reaction was diluted with a mixed solvent (hexanes/ethyl acetate = 30/1, 100 mL), filtered through a pad of silica gel and concentrated under reduced pressure. The obtained dibromide was directly used in the next step without further purification.

To a solution of the above dibromide (1.5 mmol) in DCM (6 mL) was added BBr_3 (2.2

mmol, 2 M in DCM, 2.2 mL) carefully at 0 °C. The reaction mixture was then warmed to room temperature and stirred for 20 min. Upon completion (monitored by TLC), the reaction was quenched with $NaHCO_3$ (aq), extracted with DCM for three times, dried over $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure to give crude free phenol without further purification.

To the solution of above free phenol (1.5 mmol) and Et_3N (4 mmol, 0.5 mL) in DCM (8 mL) was slowly added acetylchloride (1.8 mmol, 0.13 mL) at 0 °C. Then the resulting mixture was stirred at room temperature for 2 h and the progress of the reaction was monitored by TLC. Upon completion, the reaction was quenched with $NaHCO_3$ (aq), extracted with DCM for 3 times, dried over $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure to afford the corresponding Ac-protected phenol without further purification.

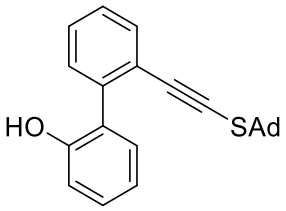
To a solution of the above Ac-protected phenol bearing alkenyl dibromide moiety (1.4 mmol) in DMSO (5 mL) was added DBU (2.8 mmol, 0.4 mL) slowly at room temperature and stirred for 5 min. Upon completion, the reaction was diluted with water, extracted with EtOAc, washed with brine, dried over $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure. Then the residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 30/1) to obtain alkynyl bromide in 77–93% yield (4 steps).

To a dry sealed tube equipped with a stir bar were added alkynyl bromide (1.2 mmol), thiol (1.3 mmol), dtbbpy (0.24 mmol, 64.3 mg) and 2,6-lutidine (2.4 mmol, 0.3 mL) under N_2 atmosphere. Aftrerwards, dry MeCN (5 mL) was added to the mixture under N_2 atmosphere. While stirring, the solution of $Cu(MeCN)_4PF_6$ (0.12 mmol, 44.6 mg in 1 mL dry MeCN) was added in one portion and the progress of the reaction was monitored by TLC. Upon completion, the reaction was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (eluent: hexanes/ethyl acetate = 15/1) to afford the desired Ac-protected alkynyl thioether.[1]

To a solution of above Ac-protected alkynyl thioether (1 mmol) in MeCN (10 mL) was added $N_2H_4 \cdot H_2O$ (2 mmol) dropwise at 0 °C and stirred for additional 10–30 min. 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 desired phenol-tethered alkynyl thioether **1a–1ac** in 58–96% yield.

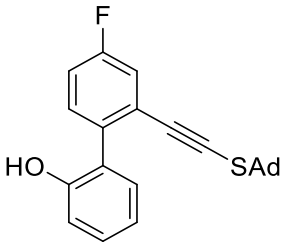
2'-((((3s,5s,7s)-adamantan-1-yl)thio)ethynyl)-[1,1'-biphenyl]-2-ol (1a)



1a

Compound **1a** was prepared in 67% overall yield (483.0 mg) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.52 (m, 1H), 7.36 – 7.25 (m, 3H), 7.24 – 7.21 (m, 2H), 6.98 – 6.94 (m, 2H), 5.07 (s, 1H), 1.98 – 1.93 (m, 3H), 1.72 – 1.68 (m, 6H), 1.63 – 1.54 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 138.2, 132.1, 130.7, 130.5, 129.2, 128.0, 128.0, 127.7, 123.9, 120.5, 116.0, 94.6, 82.0, 50.5, 42.7, 35.7, 30.0; IR (neat): 3502(bs), 2906, 2851, 2158(s), 2029, 1959, 1472, 1037, 752, 520; HRESIMS Calcd for $[C_{24}H_{24}NaOS]^+$ ($M + Na^+$) 383.1440, found 383.1437.

2'-((((3s,5s,7s)-adamantan-1-yl)thio)ethynyl)-4'-fluoro-[1,1'-biphenyl]-2-ol (1b)

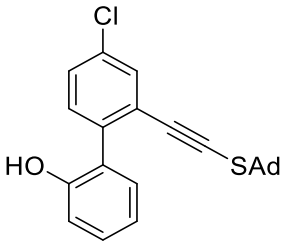


1b

Compound **1b** was prepared in 71% overall yield (537.9 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.18 (m, 4H), 7.07 – 7.02 (m, 1H), 6.97 – 6.94 (m, 2H), 5.05 (s, 1H), 2.00 – 1.90 (m, 3H), 1.72 – 1.65 (m, 6H), 1.63 – 1.53 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9 (d, J = 247.0 Hz), 152.7, 134.2 (d, J = 3.0 Hz), 132.2 (d, J

= 9.0 Hz), 130.9, 129.3, 126.7, 125.7 (d, J = 9.0 Hz), 120.5, 118.3 (d, J = 23.0 Hz), 115.0, 115.3 (d, J = 22.0 Hz), 93.8 (d, J = 3.0 Hz), 83.5, 50.7, 42.7, 35.6, 30.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.7; IR (neat): 3045(bs), 2906, 2152(s), 1959, 1601, 1307, 881, 726; HRESIMS Calcd for $[C_{24}H_{23}FNaOS]^+$ (M + Na^+) 401.1346, found 401.1338.

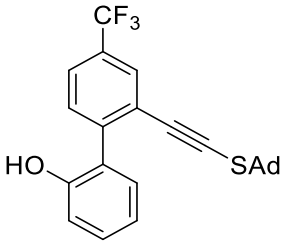
2'-((((3s,5s,7s)-adamantan-1-yl)thio)ethynyl)-4'-chloro-[1,1'-biphenyl]-2-ol (1c)



1c

Compound **1c** was prepared in 76% overall yield (600.7 mg) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 2.0 Hz, 1H), 7.31 (dd, J = 8.4, 2.4 Hz, 1H), 7.26 – 7.19 (m, 3H), 6.98 – 6.94 (m, 2H), 5.02 (s, 1H), 1.98 – 1.92 (m, 3H), 1.71 – 1.67 (m, 6H), 1.64 – 1.54 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 136.6, 133.8, 131.9, 131.6, 130.9, 129.5, 128.1, 126.6, 125.5, 120.6, 116.1, 93.7, 83.8, 50.8, 42.7, 35.7, 30.0; IR (neat): 3613(bs), 3102, 2985, 2157(s), 1957, 1412, 1056, 745; HRESIMS Calcd for $[C_{24}H_{23}ClNaOS]^+$ (M + Na^+) 417.1050, found 417.1048.

2'-((((3s,5s,7s)-adamantan-1-yl)thio)ethynyl)-4'-(trifluoromethyl)-[1,1'-biphenyl]-2-ol (1d)

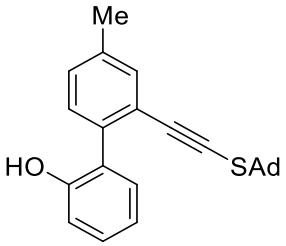


1d

Compound **1d** was prepared in 43% overall yield (368.6 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.28 – 7.21 (m, 2H), 7.00 – 6.95 (m, 2H), 5.11 (s, 1H), 1.98 – 1.93 (m, 3H), 1.71 – 1.67 (m, 6H), 1.64 – 1.53 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 141.9, 131.1, 130.7,

130.2 (q, J = 32.0 Hz), 129.7, 128.7 (q, J = 4.0 Hz), 126.6, 124.7, 124.2 (q, J = 3.0 Hz), 123.6 (q, J = 271.0 Hz), 120.8, 116.3, 93.8, 84.2, 50.9, 42.7, 35.7, 30.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4; IR (neat): 3498(bs), 3048, 2928, 2160(s), 1958, 1558, 729, 588,523; HRESIMS Calcd for $[C_{25}H_{23}F_3NaOS]^+$ (M + Na^+) 451.1314, found 451.1303.

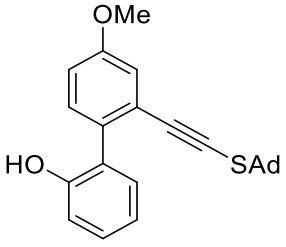
2'-((((3s,5s,7s)-adamantan-1-yl)thio)ethynyl)-4'-methyl-[1,1'-biphenyl]-2-ol (1e)



1e

Compound **1e** was prepared in 65% overall yield (486.1 mg) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.25 – 7.18 (m, 4H), 6.97 – 6.93 (m, 2H), 5.05 (s, 1H), 2.36 (s, 3H), 1.98 – 1.93 (m, 3H), 1.72 – 1.67 (m, 6H), 1.63 – 1.54 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 137.9, 135.2, 132.6, 130.8, 130.4, 129.1, 129.0, 127.5, 123.7, 120.4, 115.8, 94.7, 81.5, 50.5, 42.7, 35.7, 30.0, 20.9; IR (neat): 3494(bs), 3029, 2905, 2849, 2152(s), 1763, 1451, 1367, 1178, 1037, 758; HRESIMS Calcd for $[C_{25}H_{26}NaOS]^+$ (M + Na^+) 397.1597, found 397.1604.

2'-((((3s,5s,7s)-adamantan-1-yl)thio)ethynyl)-4'-methoxy-[1,1'-biphenyl]-2-ol (1f)

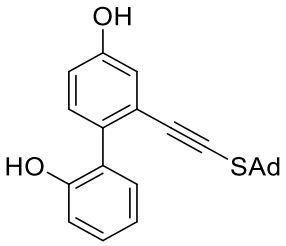


1f

Compound **1f** was prepared in 53% overall yield (413.5 mg) as a orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.19 (m, 3H), 7.05 (d, J = 2.8 Hz, 1H), 6.97 – 6.90 (m, 3H), 5.24 (s, 1H), 3.82 (s, 3H), 1.99 – 1.92 (m, 3H), 1.72 – 1.67 (m, 6H), 1.63 – 1.54 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 153.0, 131.7, 131.0, 130.5, 129.0, 127.3,

124.9, 120.3, 116.3, 115.7, 115.0, 94.7, 81.8, 55.4, 50.6, 42.7, 35.7, 30.0; IR (neat): 3444(bs), 2904, 2850, 2155(s), 1958, 1607, 1473, 1282, 1037, 774, 552; HRESIMS Calcd for $[C_{25}H_{26}NaO_2S]^+$ (M + Na^+) 413.1546, found 413.1555.

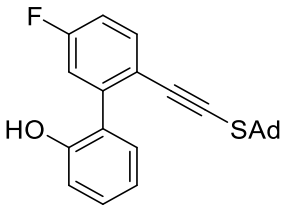
2'-((((3s,5s,7s)-adamantan-1-yl)thio)ethynyl)-[1,1'-biphenyl]-2,4'-diol (1g)



1g

Compound **1g** was prepared in 37% overall yield (274.1 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.11 (m, 2H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.89 – 6.85 (m, 3H), 6.75 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.17 (s, 1H), 5.20 (s, 1H), 1.88 – 1.84 (m, 3H), 1.61 – 1.58 (m, 6H), 1.55 – 1.45 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 152.8, 131.8, 131.0, 130.2, 128.9, 127.4, 124.9, 120.4, 118.4, 115.8, 115.7, 94.6, 81.7, 50.6, 42.7, 35.7, 30.0; IR (neat): 3620(bs), 3104, 2948, 2160(s), 1958, 1417, 1039, 843, 745, 530; HRESIMS Calcd for $[C_{24}H_{24}NaO_2S]^+$ (M + Na^+) 399.1389, found 399.1401.

2'-((((3s,5s,7s)-adamantan-1-yl)thio)ethynyl)-5'-fluoro-[1,1'-biphenyl]-2-ol (1h)

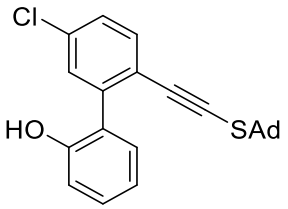


1h

Compound **1h** was prepared in 80% overall yield (566.8 mg) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.41 (m, 1H), 7.20– 7.13 (m, 2H), 6.99 – 6.95 (m, 2H), 6.92 – 6.88 (m, 2H), 5.01 (s, 1H), 1.90 – 1.84 (m, 3H), 1.63 – 1.60 (m, 6H), 1.56 – 1.46 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9 (d, *J* = 249.0 Hz), 152.5, 140.9 (d, *J* = 8.0 Hz), 134.0 (d, *J* = 9.0 Hz), 130.6, 129.6, 126.8 (d, *J* = 1.0 Hz), 120.7, 119.9 (d, *J* = 4.0 Hz), 117.7 (d, *J* = 22.0 Hz), 116.3, 115.3 (d, *J* = 22.0 Hz), 93.5, 81.5, 50.6,

42.7, 35.7, 30.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.1; IR (neat): 3459(bs), 2906, 2850, 2159(s), 1448, 1298, 1263, 1040, 752, 588; HRESIMS Calcd for $[C_{24}H_{23}FNaOS]^+$ (M + Na^+) 401.1346, found 401.1351.

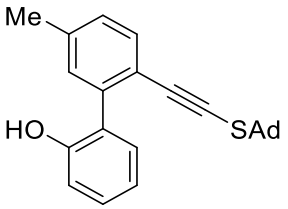
2'-((((3s,5s,7s)-adamantan-1-yl)thio)ethynyl)-5'-chloro-[1,1'-biphenyl]-2-ol (1i)



1i

Compound **1i** was prepared in 72% overall yield (413.5 mg) as a yellow solid (mp 201-203 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.24 – 7.19 (m, 4H), 6.99 – 6.95 (m, 2H), 5.06 (s, 1H), 1.98 – 1.92 (m, 3H), 1.71 –1.67 (m, 6H), 1.63 – 1.53 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 140.0, 133.6, 133.1, 130.6, 130.5, 129.6, 128.1, 126.6, 122.3, 120.7, 116.3, 93.8, 83.1, 50.7, 42.7, 35.7, 30.0; IR (neat): 3440(bs), 3079, 2904, 2158(s), 2028, 1737, 1298, 1041, 726, 684, 540; HRESIMS Calcd for $[C_{24}H_{23}ClNaOS]^+$ (M + Na^+) 417.1050, found 417.1074.

2'-((((3s,5s,7s)-adamantan-1-yl)thio)ethynyl)-5'-methyl-[1,1'-biphenyl]-2-ol (1j)

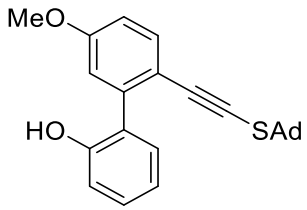


1j

Compound **1j** was prepared in 55% overall yield (409.8 mg) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.0 Hz, 1H), 7.18 – 7.14 (m, 2H), 7.10 – 7.05 (m, 2H), 6.91 – 6.87 (m, 2H), 5.00 (s, 1H), 2.30 (s, 3H), 1.91 – 1.86 (m, 3H), 1.64 – 1.51 (m, 6H), 1.56 – 1.47 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 138.4, 138.2, 132.2, 131.2, 130.7, 129.1, 128.9, 127.8, 120.9, 120.4, 115.9, 94.5, 80.9, 50.4, 42.7, 35.8, 30.0, 21.4; IR (neat): 3460(bs), 3057, 2907, 2849, 2153(s), 1709, 1447, 1231, 754,

589, 536; HRESIMS Calcd for $[C_{25}H_{26}NaOS]^+$ (M + Na^+) 397.1597, found 397.1600.

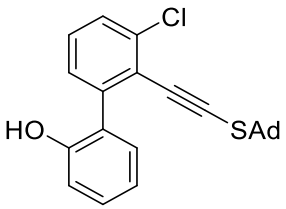
2'-((((3s,5s,7s)-adamantan-1-yl)thio)ethynyl)-5'-methoxy-[1,1'-biphenyl]-2-ol (1k)



1k

Compound **1k** was prepared in 58% overall yield (457.0 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.8 Hz, 1H), 7.27 – 7.22 (m, 2H), 6.99 – 6.95 (m, 2H), 6.89 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.84 (d, *J* = 2.4 Hz, 1H), 5.12 (s, 1H), 3.82 (s, 3H), 1.99 – 1.93 (m, 3H), 1.72 – 1.68 (m, 6H), 1.64 – 1.55 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 152.7, 140.3, 133.9, 130.6, 129.3, 127.7, 120.5, 116.1, 116.0, 115.6, 114.3, 94.1, 79.7, 55.4, 50.3, 42.7, 35.8, 30.1; IR (neat): 3440(bs), 3000, 2906, 2850, 2162(s), 1958, 1604, 1242, 1211, 1018, 751, 589; HRESIMS Calcd for $[C_{25}H_{26}NaO_2S]^+$ (M + Na^+) 413.1546, found 413.1558.

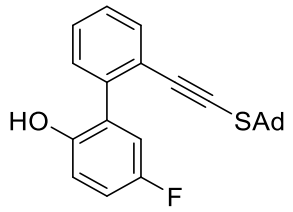
2'-((((3s,5s,7s)-adamantan-1-yl)thio)ethynyl)-3'-chloro-[1,1'-biphenyl]-2-ol (1l)



1l

Compound **1l** was prepared in 33% overall yield (262.6 mg) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.28 – 7.24 (m, 2H), 7.21 – 7.20 (m, 2H), 6.99 – 6.96 (m, 2H), 5.00 (s, 1H), 2.00 – 1.96 (m, 3H), 1.78 – 1.76 (m, 6H), 1.65 – 1.56 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 140.2, 136.1, 130.7, 129.6, 128.8, 128.7, 128.1, 127.1, 123.8, 120.6, 116.2, 91.8, 88.5, 51.0, 42.8, 35.8, 30.1; IR (neat): 3429(bs), 3063, 2906, 2850, 2158(s), 1958, 1297, 1102, 1040, 754, 635; HRESIMS Calcd for $[C_{24}H_{23}ClNaOS]^+$ (M + Na^+) 417.1050, found 417.1059.

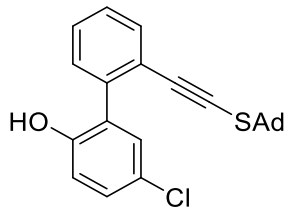
2'-((((3s,5s,7s)-adamantan-1-yl)thio)ethynyl)-5-fluoro-[1,1'-biphenyl]-2-ol (1m)



1m

Compound **1m** was prepared in 45% overall yield (338.7 mg) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.51 (m, 1H), 7.36 – 7.31 (m, 2H), 7.28 – 7.24 (m, 1H), 6.97 – 6.88 (m, 3H), 5.00 (s, 1H), 2.01 – 1.93 (s, 3H), 1.76 – 1.69 (m, 6H), 1.65 – 1.55 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7 (d, J = 237 Hz), 148.8 (d, J = 2.0 Hz), 137.2, 132.2, 130.2, 128.6 (d, J = 8.0 Hz), 128.3, 128.1, 123.7, 117.0, 116.9 (d, J = 14.0 Hz), 115.5 (d, J = 23.0 Hz), 94.3, 82.6, 50.6, 42.8, 35.7, 30.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.3; IR (neat): 3428(bs), 3012, 2907, 2850, 2160(s), 1958, 1737, 1578, 1109, 1072, 834, 730, 590; HRESIMS Calcd for $[C_{24}H_{23}FNaOS]^+$ (M + Na^+) 401.1346, found 401.1342.

2'-((((3s,5s,7s)-adamantan-1-yl)thio)ethynyl)-5-chloro-[1,1'-biphenyl]-2-ol (1n)

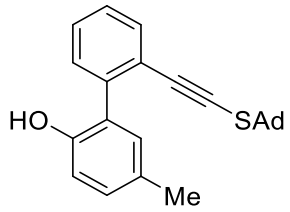


1n

Compound **1n** was prepared in 57% overall yield (451.5 mg) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.53 (m, 1H), 7.38 – 7.35 (m, 2H), 7.29 – 7.27 (m, 1H), 7.23 – 7.19 (m, 2H), 6.92 (d, J = 8.8 Hz, 1H), 5.05 (s, 1H), 2.02 – 1.96 (m, 3H), 1.75 – 1.70 (m, 6H), 1.66 – 1.55 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 136.8, 132.3, 130.3, 130.3, 129.1, 129.0, 128.5, 128.2, 125.2, 123.9, 117.4, 94.2, 82.8, 50.6, 42.8, 35.8, 30.1; IR (neat): 3441(bs), 3063, 2906, 2850, 2158(s), 1958, 1462, 1388, 1298, 1240, 1039, 834, 751, 601; HRESIMS Calcd for $[C_{24}H_{23}ClNaOS]^+$ (M + Na^+)

417.1050, found 417.1066.

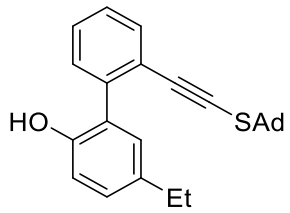
2'-((((3s,5s,7s)-adamantan-1-yl)thio)ethynyl)-5-methyl-[1,1'-biphenyl]-2-ol (1o)



1o

Compound **1o** was prepared in 68% overall yield (509.4 mg) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.51 (m, 1H), 7.34 – 7.27 (m, 3H), 7.04 – 7.02 (m, 2H), 6.88 – 6.86 (m, 1H), 4.92 (s, 1H), 2.28 (s, 3H), 1.98 – 1.91 (m, 3H), 1.72 – 1.68 (m, 6H), 1.63 – 1.53 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 138.5, 132.0, 131.0, 130.5, 129.7, 129.5, 128.0, 127.9, 127.4, 123.8, 115.9, 94.7, 81.8, 50.5, 42.7, 35.7, 30.0, 20.4; IR (neat): 3363 (bs), 3061, 2905, 2849, 2160(s), 1958, 1672, 1450, 1239, 1040, 824, 751, 583; HRESIMS Calcd for $[C_{25}H_{26}NaOS]^+$ (M + Na^+) 397.1597, found 397.1606.

2'-((((3s,5s,7s)-adamantan-1-yl)thio)ethynyl)-5-ethyl-[1,1'-biphenyl]-2-ol (1p)

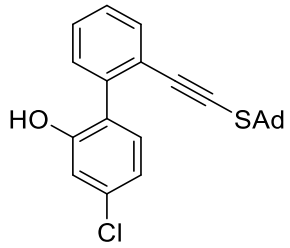


1p

Compound **1p** was prepared in 75% overall yield (583.7 mg) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, J = 6.0, 1.2 Hz, 1H), 7.35 – 7.29 (m, 3H), 7.08 – 7.05 (m, 2H), 6.89 (d, J =7.6 Hz, 1H), 4.97 (s, 1H), 2.59 (q, J = 7.6 Hz, 2H), 1.98 – 1.90 (m, 3H), 1.72 – 1.68 (m, 6H), 1.63 – 1.53 (m, 6H), 1.22 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 138.7, 136.0, 132.0, 130.6, 129.9, 128.5, 128.0, 127.8, 127.5, 123.8, 115.9, 94.8, 81.9, 50.4, 42.7, 35.7, 30.0, 27.9, 15.7; IR (neat): 3433(bs), 3068, 2905, 2850, 2157(s), 1958, 1450, 1407, 1297, 1039, 736, 626, 604; HRESIMS Calcd

for $[C_{26}H_{28}NaOS]^+$ (M + Na^+) 411.1753, found 411.1752.

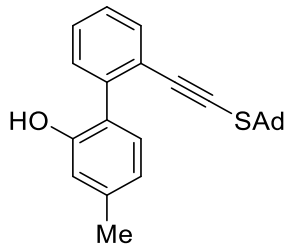
2'-((((3s,5s,7s)-adamantan-1-yl)thio)ethynyl)-4-chloro-[1,1'-biphenyl]-2-ol (1q)



1q

Compound **1q** was prepared in 59% overall yield (466.2 mg) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.52 (m, 1H), 7.37 – 7.35 (m, 2H), 7.27 (d, *J* = 4.0 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.01 (d, *J* = 1.6 Hz, 1H), 6.96 (dd, *J* = 8.0, 1.6 Hz, 1H), 5.19 (s, 1H), 2.05 – 1.96 (m, 3H), 1.76 – 1.69 (m, 6H), 1.67 – 1.55 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 136.9, 134.5, 132.1, 131.6, 130.4, 128.4, 128.1, 126.3, 124.0, 120.8, 116.4, 94.3, 82.6, 50.6, 42.8, 35.8, 30.0; IR (neat): 3597(bs), 3023, 2908, 2850, 2156(s), 2028, 1958, 1556, 1245, 1028, 747, 688, 583; HRESIMS Calcd for $[C_{24}H_{23}ClNaOS]^+$ (M + Na^+) 417.1050, found 417.1055.

2'-((((3s,5s,7s)-adamantan-1-yl)thio)ethynyl)-4-methyl-[1,1'-biphenyl]-2-ol (1r)

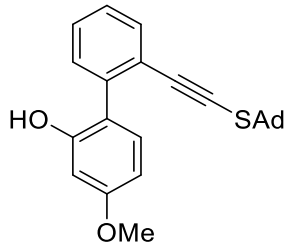


1r

Compound **1r** was prepared in 61% overall yield (457.8 mg) as a orange solid (mp 133–135 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.50 (m, 1H), 7.34 – 7.26 (m, 3H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.80 – 6.76 (m, 2H), 5.02 (s, 1H), 2.32 (s, 3H), 2.00 – 1.92 (m, 3H), 1.75 – 1.68 (m, 6H), 1.64 – 1.54 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 139.3, 138.1, 132.0, 130.6, 130.5, 127.9, 127.8, 124.8, 124.0, 121.3, 116.6, 94.8, 81.8, 50.4, 42.7, 35.7, 30.0, 21.2; IR (neat): 3489(bs), 3062, 2908, 2850, 2158(s), 1713, 1473, 1450, 1039, 1016, 824, 749, 622; HRESIMS Calcd for $[C_{25}H_{26}NaOS]^+$ (M + Na^+) 397.1597,

found 397.1596.

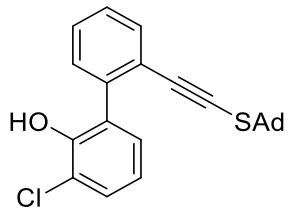
2'-((((3s,5s,7s)-adamantan-1-yl)thio)ethynyl)-4-methoxy-[1,1'-biphenyl]-2-ol (1s)



1s

Compound **1s** was prepared in 74% overall yield (576.3 mg) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.51 (m, 1H), 7.35 – 7.31 (m, 2H), 7.20 – 7.27 (m, 1H), 7.15 – 7.13 (m, 1H), 6.57 – 6.49 (m, 2H), 5.11 (s, 1H), 3.79 (s, 3H), 2.00 – 1.94 (m, 3H), 1.76 – 1.72 (m, 6H), 1.65 – 1.55 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 153.7, 137.9, 132.1, 131.3, 130.8, 128.1, 127.8, 124.2, 120.3, 106.7, 101.3, 94.8, 81.9, 55.2, 50.5, 42.8, 35.8, 30.1; IR (neat): 3454(bs), 2976, 2903, 2849, 2158(s), 2028, 1568, 1236, 1171, 1039, 617, 566, 539; HRESIMS Calcd for $[C_{25}H_{26}NaO_2S]^+$ (M + Na^+) 413.1546, found 413.1560.

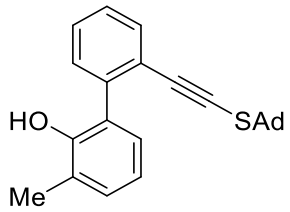
2'-((((3s,5s,7s)-adamantan-1-yl)thio)ethynyl)-3-chloro-[1,1'-biphenyl]-2-ol (1t)



1t

Compound **1t** was prepared in 36% overall yield (287.0 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.52 (m, 1H), 7.35 – 7.28 (m, 4H), 7.19 (dd, J = 7.6, 1.6 Hz, 1H), 6.93 – 6.90 (m, 1H), 5.55 (s, 1H), 2.01 – 1.95 (m, 3H), 1.73 – 1.69 (m, 6H), 1.65 – 1.53 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 138.3, 132.0, 130.1, 130.0, 129.3, 128.6, 127.9, 127.6, 123.8, 120.7, 120.5, 95.0, 81.2, 50.3, 42.8, 35.8, 30.1; IR (neat): 3501(bs), 3011, 2907, 2851, 2157(s), 2028, 1958, 1370, 1209, 968, 912, 750, 611; HRESIMS Calcd for $[C_{24}H_{23}ClNaOS]^+$ (M + Na^+) 417.1050, found 417.1068.

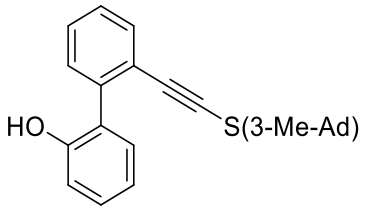
2'-((((3s,5s,7s)-adamantan-1-yl)thio)ethynyl)-3-chloro-[1,1'-biphenyl]-2-ol (1u)



1u

Compound **1u** was prepared in 46% overall yield (358.1 mg) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.51 (m, 1H), 7.37 – 7.27 (m, 3H), 7.09 (d, J = 7.2 Hz, 1H), 7.05 (dd, J = 7.6, 1.6 Hz, 1H), 6.87 – 6.84 (m, 1H), 5.03 (s, 1H), 2.28 (s, 3H), 1.97 – 1.90 (m, 3H), 1.65 – 1.68 (m, 6H), 1.62 – 1.50 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 138.5, 132.0, 130.6, 130.5, 128.2, 128.0, 127.9, 127.1, 124.7, 124.0, 119.9, 94.7, 81.9, 50.4, 42.6, 35.7, 30.0, 16.2; IR (neat): 3453(bs), 3061, 2906, 2850, 2160(s), 1736, 1659, 1450, 1251, 1166, 1039, 750; HRESIMS Calcd for $[C_{25}H_{26}NaOS]^+$ (M + Na^+) 397.1597, found 397.1590.

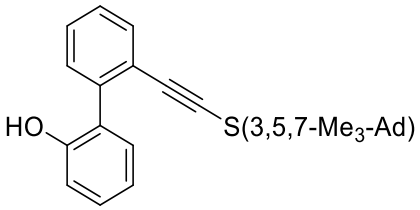
2'-((((1S,3S,5R)-3-methyladamantan-1-yl)thio)ethynyl)-[1,1'-biphenyl]-2-ol (1v)



1v

Compound **1v** was prepared in 66% overall yield (515.2 mg) as a red oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 6.0 Hz, 1H), 7.33 – 7.26 (m, 3H), 7.24 – 7.21 (m, 2H), 6.98 – 6.94 (m, 2H), 5.08 (s, 1H), 2.06 – 1.94 (m, 2H), 1.65 – 1.55 (m, 4H), 1.48 – 1.45 (m, 4H), 1.36 – 1.28 (m, 4H), 0.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 138.2, 132.2, 130.7, 130.5, 129.3, 128.0, 127.9, 127.6, 123.9, 120.5, 116.0, 94.6, 82.0, 50.8, 49.4, 42.8, 41.9, 34.9, 32.4, 30.4, 30.3; IR (neat): 3421(bs), 3062, 2904, 2844, 2162(s), 1738, 1455, 1308, 1239, 988, 776, 749, 687; HRESIMS Calcd for $[C_{25}H_{26}NaOS]^+$ (M + Na^+) 397.1597, found 397.1602.

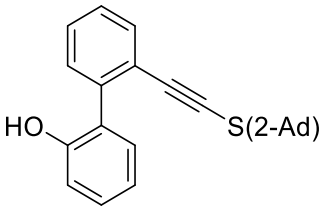
2'-((((1r,3R,5S)-3,5,7-trimethyladamantan-1-yl)thio)ethynyl)-[1,1'-biphenyl]-2-ol (1w)



1w

Compound **1w** was prepared in 60% overall yield (483.7 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.52 (m 1H), 7.35 – 7.28 (m, 3H), 7.25 – 7.22 (m, 2H), 7.01 – 6.94 (m, 2H), 5.51 (s, 1H), 1.33 – 1.27 (m, 6H), 1.03 – 0.95 (m, 6H), 0.80 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 138.3, 132.3, 130.8, 130.6, 129.5, 128.0, 127.9, 127.6, 123.8, 120.5, 116.2, 94.7, 81.8, 51.4, 49.4, 48.1, 33.6, 29.6; IR (neat): 3505(bs), 3010, 2907, 2837, 2160(s), 1557, 1472, 1456, 1181, 756, 583; HRESIMS Calcd for $[C_{27}H_{30}NaOS]^+$ (M + Na^+) 425.1910, found 425.1896.

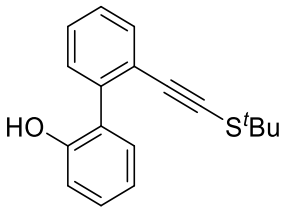
2'-((((1R,2r,3S,5r)-adamantan-2-yl)thio)ethynyl)-[1,1'-biphenyl]-2-ol (1x)



1x

Compound **1x** was prepared in 59% overall yield (451.5 mg) as a orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.49 (m, 1H), 7.35 – 7.27 (m, 4H), 7.20 (dd, *J* = 7.2, 1.6 Hz, 1H), 6.98 – 6.94 (m, 2H), 5.04 (s, 1H), 3.36 – 3.31 (m, 1H), 2,01 – 1.98 (m, 2H), 1.85 – 1.79 (m, 6H), 1.70 – 1.64 (m, 4H), 1.49 – 1.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 138.3, 131.7, 130.7, 130.4, 129.3, 128.0, 127.4, 123.8, 120.4, 115.9, 91.7, 84.6, 57.7, 38.5, 37.6, 31.9, 31.4, 27.5, 27.2; IR (neat): 3471(bs), 3061, 2906, 2850, 2156(s), 1958, 1737, 1461, 1449, 1238, 748, 588; HRESIMS Calcd for $[C_{24}H_{24}NaOS]^+$ (M + Na^+) 383.1440, found 383.1461.

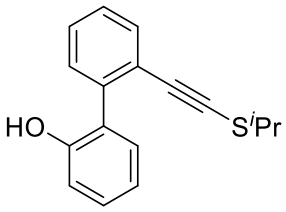
2'-((*tert*-butylthio)ethynyl)-[1,1'-biphenyl]-2-ol (1y)



1y

Compound **1y** was prepared in 63% overall yield (423.6 mg) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.52 (m, 1H), 7.35 – 7.29 (m, 3H), 7.25 – 7.21 (m, 2H), 6.97 – 6.94 (m, 2H), 5.06 (s, 1H), 1.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 138.1, 131.9, 130.7, 130.5, 129.3, 128.0, 128.0, 127.5, 123.9, 120.5, 116.0, 94.6, 83.5, 48.6, 30.1; IR (neat): 3520(bs), 3056, 2962, 2922, 2863, 2161(s), 1958, 1609, 1581, 1290, 1041, 934, 580; HRESIMS Calcd for $[C_{18}H_{18}NaOS]^+$ (M + Na^+) 305.0971, found 305.0959.

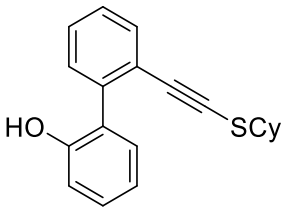
2'-((isopropylthio)ethynyl)-[1,1'-biphenyl]-2-ol (1z)



1z

Compound **1z** was prepared in 73% overall yield (353.8 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.55 (m, 1H), 7.41 – 7.35 (m, 3H), 7.31 – 7.25 (m, 2H), 7.02 – 6.98 (m, 2H), 5.07 (s, 1H), 3.06 – 2.96 (m, 1H), 1.20 (s, 3H), 1.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 138.3, 131.9, 130.8, 130.4, 129.4, 128.1, 128.0, 127.4, 123.8, 120.5, 116.0, 93.4, 83.2, 40.0, 22.7; IR (neat): 3449(bs), 3025, 2959, 2922, 2368, 2157(s), 2028, 1958, 1617, 1583, 1034, 729; HRESIMS Calcd for $[C_{17}H_{16}NaOS]^+$ (M + Na^+) 291.0814, found 291.0829.

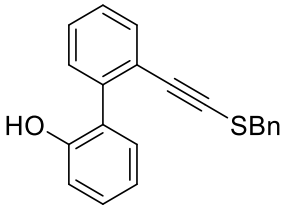
2'-((cyclohexylthio)ethynyl)-[1,1'-biphenyl]-2-ol (1aa)



1aa

Compound **1aa** was prepared in 78% overall yield (479.9 mg) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.50 (m, 1H), 7.37 – 7.29 (m, 3H), 7.28 – 7.20 (m, 2H), 6.99 – 6.94 (m, 2H), 5.06 (s, 1H), 2.73 – 2.65 (m, 1H), 1.80 – 1.75 (m, 2H), 1.68 – 1.65 (m, 2H), 1.56 – 1.52 (m, 1H), 1.26 – 1.11 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 138.3, 131.8, 130.8, 130.4, 129.3, 128.0, 127.9, 127.5, 123.8, 120.4, 115.9, 92.9, 83.3, 47.7, 32.8, 26.1, 25.1; IR (neat): 3440(bs), 3000, 2906, 2850, 2162(s), 1958, 1604, 1242, 1211, 1018, 751, 589; HRESIMS Calcd for $[C_{20}H_{20}NaOS]^+$ ($M + Na^+$) 331.1127, found 331.1126.

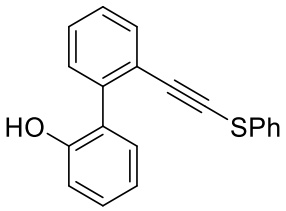
2'-((benzylthio)ethynyl)-[1,1'-biphenyl]-2-ol (1ab)



1ab

Compound **1ab** was prepared in 57% overall yield (631.2 mg) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.2 Hz, 1H), 7.30 – 7.20 (m, 8H), 7.07 – 7.05 (m, 2H), 6.98 – 6.94 (m, 2H), 5.13 (s, 1H), 3.72 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 138.4, 136.5, 131.9, 130.9, 130.3, 129.5, 128.8, 128.4, 128.2, 127.8, 127.5, 127.3, 123.3, 120.4, 116.0, 93.1, 83.9, 40.3; IR (neat): 3410(bs), 3060, 3029, 2927, 2163(s), 2028, 1958, 1610, 1580, 1423, 911, 894, 552; HRESIMS Calcd for $[C_{21}H_{16}NaOS]^+$ ($M + Na^+$) 339.0814, found 339.0795.

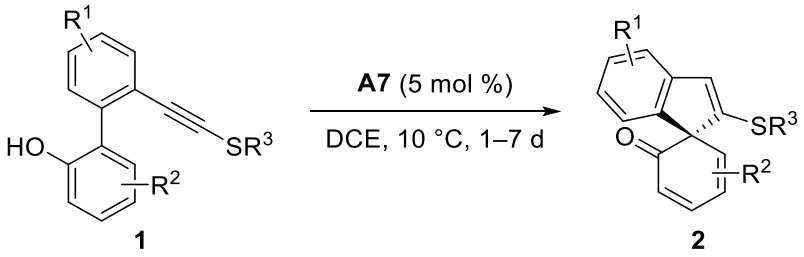
2'-((phenylthio)ethynyl)-[1,1'-biphenyl]-2-ol (1ac)



1ac

Compound **1ac** was prepared in 43% overall yield (260.6 mg) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.5 Hz, 1H), 7.43 – 7.35 (m, 3H), 7.33 – 7.27 (m, 2H), 7.20 – 7.14 (m, 3H), 7.05 – 6.99 (m, 4H), 5.02 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 138.4, 132.4, 132.1, 130.8, 130.5, 129.6, 129.2, 128.7, 128.1, 127.2, 126.2, 125.9, 123.3, 120.6, 116.0, 96.8, 79.5; IR (neat): 3523(bs), 3012, 2330, 2161(s), 1958, 1653, 1149, 986, 893, 834, 639; HRESIMS Calcd for $[C_{20}H_{14}NaOS]^+$ (M + Na^+) 325.0658, found 325.0659.

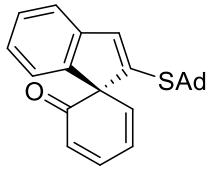
3. General Procedure for the Synthesis of Spirocyclic Enones 2



1 **2**

To a mixture of alkynyl thioether **1** (0.1 mmol) in DCE (2 mL) was added **A7** (0.005 mmol, 4.6 mg) at 10 ℃. Then, the reaction mixture was stirred at 10 ℃ 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) and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (eluent: hexanes/acetone) to afford the desired chiral spirocyclic enone **2**.

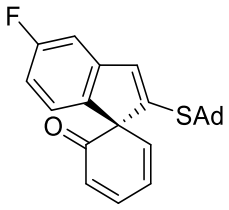
(*S*)-2'-(((3R,5R,7R)-adamantan-1-yl)thio)spiro[cyclohexane-1,1'-indene]-2,4-dien-6-one (2a)



2a

Compound **2a** was prepared in 93% yield (33.5 mg) according to the general procedure (Table 2, entry 1). The product was purified by chromatography on silica gel (eluent: hexanes/acetone = 15/1) as a yellow solid (mp 156–158 °C). $[\alpha]_D^{20}$ = +241.7º (c = 1.0, $CHCl_3$). 96:4 e.r. (determined by HPLC: Chiralpak IA Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR = 6.20 min (major), 7.58 min (minor)).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.18 (m, 3H), 7.08 – 7.04 (m, 1H), 7.02 – 6.99 (m, 2H), 6.48 (ddd, *J* = 9.2, 5.6, 0.4 Hz, 1H), 6.21 (d, *J* = 10.0 Hz, 1H), 5.95 – 5.92 (m, 1H), 2.06 – 1.98 (m, 9H), 1.69 – 1.68 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 145.2, 143.6, 142.7, 142.1, 140.5, 135.4, 128.1, 127.3, 125.3, 122.9, 122.0, 120.6, 72.7, 50.0, 43.5, 36.0, 29.9; IR (neat): 3441, 2905, 2848, 1958, 1666(s), 1630, 1461, 1039, 748, 688; HRESIMS Calcd for $[C_{24}H_{24}NaOS]^+$ (M + Na^+) 383.1440, found 383.1443.

(*S*)-2'-(((3R,5R,7R)-adamantan-1-yl)thio)-5'-fluorospiro[cyclohexane-1,1'-indene]-2,4-dien-6-one (2b)

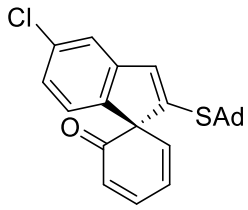


2b

Compound **2b** was prepared in 72% yield (27.2 mg) according to the general procedure (Table 2, entry 2). The product was purified by chromatography on silica gel (eluent: hexanes/acetone = 20/1) as an orange oil. $[\alpha]_D^{20}$ = +228.2º (c = 1.0, $CHCl_3$). 97:3 e.r. (determined by HPLC: Chiralpak IA Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR = 6.22 min (major), 7.17 min (minor)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.20 (m, 1H), 6.97 – 6.91 (m, 3H), 6.77 – 6.72 (m, 1H), 6.50 (dd, *J* = 9.2, 6.0 Hz, 1H),

6.22 (d, J = 9.6 Hz, 1H), 5.93 (d, J = 8.8 Hz, 1H), 2.11 – 2.06 (m, 3H), 2.03 – 2.01 (m, 6H), 1.73 – 1.67 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 163.1 (d, J = 244.0 Hz), 147.4 (d, J = 10.0 Hz), 145.1, 142.7, 140.3, 138.9 (d, J = 3.0 Hz), 133.4 (d, J = 2.0 Hz), 127.4, 123.1, 123.0, 111.8 (d, J = 23.0 Hz), 107.8 (d, J = 24.0 Hz), 71.9, 50.5, 43.5, 36.1, 30.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.0; IR (neat): 3058, 2907, 2850, 1958, 1712, 1591(s), 1559, 1540, 1488, 1193, 965, 754, 689; HRESIMS Calcd for $[C_{24}H_{23}FNaOS]^+$ (M + Na^+) 401.1346, found 401.1350.

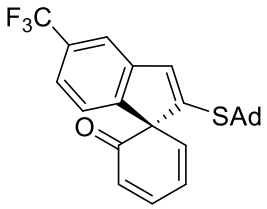
(*S*)-2'-(((3R,5R,7R)-adamantan-1-yl)thio)-5'-chlorospiro[cyclohexane-1,1'-indene]-2,4-dien-6-one (2c)



2c

Compound **2c** was prepared in 86% yield (33.9 mg) according to the general procedure (Table 2, entry 3). The product was purified by chromatography on silica gel (eluent: hexanes/acetone = 15/1) as a yellow oil. $[\alpha]_D^{20}$ = +283.4º (c = 1.0, $CHCl_3$). 96:4 e.r. (determined by HPLC: Chiralpak IC Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR = 7.99 min (major), 8.86 min (minor)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.20 (m, 2H), 7.03 (dd, J = 8.0, 1.6 Hz, 1H), 6.93 – 6.90 (m, 2H), 6.51 (dd, J = 9.2, 6.0 Hz, 1H), 6.22 (d, J = 10.0 Hz, 1H), 5.92 (d, J = 9.2 Hz, 1H), 2.08 – 1.98 (m, 9H), 1.74 – 1.66 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 147.0, 144.9, 142.8, 141.7, 139.9, 134.2, 133.0, 127.4, 125.1, 123.3, 123.0, 120.6, 72.1, 50.5, 43.4, 36.0, 30.0; IR (neat): 2906, 2850, 2028, 1958, 1668(s), 1635, 1445, 1297, 1037, 751, 551; HRESIMS Calcd for $[C_{24}H_{23}ClNaOS]^+$ (M + Na^+) 417.1050, found 417.1057.

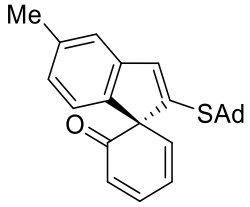
(*S*)-2'-(((3R,5R,7R)-adamantan-1-yl)thio)-5'-(trifluoromethyl)spiro[cyclohexane-1,1'-indene]-2,4-dien-6-one (2d)



2d

Compound **2d** was prepared in 71% yield (30.4 mg) according to the general procedure (Table 2, entry 4). The product was purified by chromatography on silica gel (eluent: hexanes/acetone = 15/1) as a brown oil. $[\alpha]_D^{20}$ = +3.8º (c = 1.0, $CHCl_3$). 90:10 e.r. (determined by HPLC: Chiralpak IA Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR =5.07 min (minor), 5.98 min (major)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.01 (s, 1H), 6.57 – 6.53 (m, 1H), 6.24 (d, *J* = 9.6 Hz, 1H), 5.92 (d, *J* = 9.2 Hz, 1H), 2.09 – 2.00 (m, 9H), 1.73 – 1.69 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 147.0, 146.1, 145.4, 142.9 139.4, 132.7, 130.7 (q, *J* = 32.0 Hz), 127.6, 124.2 (q, *J* = 270.0 Hz), 123.7, 122.3, 122.2 (q, *J* = 4.0 Hz), 117.2 (q, J = 4.0 Hz), 72.5, 50.6, 43.4, 36.1, 30.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.3; IR (neat): 2923, 2908, 2849, 2029, 1959, 1668(s), 1333, 1233, 619, 525; HRESIMS Calcd for $[C_{25}H_{23}F_3NaOS]^+$ (M + Na^+) 451.1314, found 451.1328.

(*S*)-2'-(((3R,5R,7R)-adamantan-1-yl)thio)-5'-methylspiro[cyclohexane-1,1'-indene]-2,4-dien-6-one (2e)

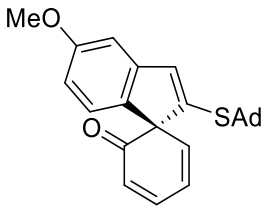


2e

Compound **2e** was prepared in 88% yield (32.9 mg) according to the general procedure (Table 2, entry 5). The product was purified by chromatography on silica gel (eluent: hexanes/acetone = 15/1) as a yellow oil. $[\alpha]_D^{20}$ = +128.7º (c = 1.0, $CHCl_3$). 97:3 e.r. (determined by HPLC: Chiralpak IA Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR = 8.27 min (major), 10.02 min (minor)). ^{1}H NMR (400 MHz, $CDCl_3$) δ

7.22 – 7.18 (m, 1H), 7.10 (s, 1H), 6.99 (s, 1H), 6.93 – 6.86 (m, 2H), 6.48 (dd, *J* = 8.8, 6.4 Hz, 1H), 6.20 (d, *J* = 10.0 Hz, 1H), 5.94 (d, *J* = 9.2 Hz, 1H), 2.33 (s, 3H), 2.06 – 1.96 (m, 9H), 1.70 –1.66 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 145.4, 142.7, 142.0, 141.0, 140.9, 138.0, 135.9, 127.4, 126.3, 122.8, 121.9, 121.5, 72.5, 50.2, 43.6, 36.1, 30.0, 21.5; IR (neat): 2912, 2851, 2029, 1959, 1669(s), 1540, 1539, 1039, 739, 729, 560; HRESIMS Calcd for $[C_{25}H_{26}NaOS]^+$ (M + Na^+) 397.1597, found 397.1597.

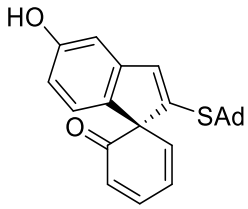
(*S*)-2'-(((3R,5R,7R)-adamantan-1-yl)thio)-5'-methoxyspiro[cyclohexane-1,1'-indene]-2,4-dien-6-one (2f)



2f

Compound **2f** was prepared in 69% yield (26.9 mg) according to the general procedure (Table 2, entry 6). The product was purified by chromatography on silica gel (eluent: hexanes/acetone = 12/1) as a yellow oil. $[\alpha]_D^{20}$ = +56.7º (c = 1.0, $CHCl_3$). 92:8 e.r. (determined by HPLC: Chiralpak IA Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR = 9.81 min (major), 11.63 min (minor)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.19 (m, 1H), 6.98 (s, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.85 (s, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 6.48 (dd, *J* = 9.2, 6.8 Hz, 1H), 6.21 (d, *J* = 10.0 Hz, 1H), 5.95 (d, *J* = 9.2 Hz, 1H), 3.80 (s, 3H), 2.07 – 1.98 (m, 9H), 1.71 –1.68 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 160.1, 146.8, 143.4, 142.7, 141.0, 135.7, 135.2, 127.4, 122.7(4), 122.7(1), 111.2, 106.5, 72.1, 55.5, 50.3, 43.4, 36.1, 30.1; IR (neat): 2905, 2849, 2029, 1959, 1666(s), 1464, 1226, 1039, 800, 586; HRESIMS Calcd for $[C_{25}H_{26}NaO_2S]^+$ (M + Na^+) 413.1546, found 413.1563.

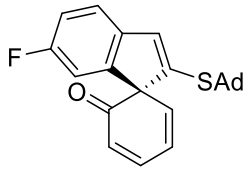
(*S*)-2'-(((3R,5R,7R)-adamantan-1-yl)thio)-5'-hydroxyspiro[cyclohexane-1,1'-indene]-2,4-dien-6-one (2g)



2g

Compound **2g** was prepared in 72% yield (27.1 mg) according to the general procedure (Table 2, entry 7). The product was purified by chromatography on silica gel (eluent: hexanes/acetone = 20/1) as a yellow oil. $[\alpha]_D^{20}$ = +85.4º (c = 1.0, $CHCl_3$). 64:36 e.r. (determined by HPLC: Chiralpak IC Column, 10/90 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR = 27.65 min (minor), 30.66 min (major)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.17 (m, 1H), 6.82 (s, 1H), 6.68 (d, *J* = 8.4 Hz, 1H), 6.47 (d, *J* = 2.0 Hz, 1H), 6.41 (dd, *J* = 9.2, 6.0 Hz, 1H), 6.36 – 6.34 (m, 2H), 6.16 (d, *J* = 9.6 Hz, 1H), 5.89 (d, *J* = 8.8 Hz, 1H), 2.00 – 1.90 (m, 9H), 1.64 –1.58 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 156.6, 146.8, 143.9, 142.4, 141.8, 135.6, 134.5, 127.1, 122.6, 122.5, 112.6, 108.4, 72.1, 50.3, 43.5, 36.1, 30.0; IR (neat): 3240(bs), 2906, 2850, 2028, 1958, 1665(s), 1502, 1403, 1270, 883, 799, 693; HRESIMS Calcd for $[C_{24}H_{24}NaO_2S]^+$ (M + Na^+) 399.1389, found 399.1388.

(*S*)-2'-(((3R,5R,7R)-adamantan-1-yl)thio)-6'-fluorospiro[cyclohexane-1,1'-indene]-2,4-dien-6-one (2h)

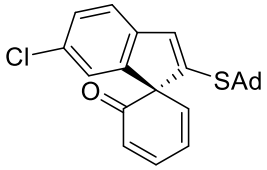


2h

Compound **2h** was prepared in 92% yield (34.8 mg) according to the general procedure (Table 2, entry 8). The product was purified by chromatography on silica gel (eluent: hexanes/acetone = 20/1) as a yellow solid (mp 185–186 °C). $[\alpha]_D^{20}$ = -70.6º (c = 1.0, $CHCl_3$). 90:10 e.r. (determined by HPLC: Chiralpak IA Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR = 5.00 min (major), 7.94 min (minor)). ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.17 – 7.13 (m, 2H), 6.91 – 6.87 (m, 2H), 6.68 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.45 (dd, *J* = 9.2, 6.0 Hz, 1H), 6.16 (d, *J* = 10.0 Hz, 1H), 5.86 (d, *J* = 9.2 Hz, 1H), 2.03 – 1.99 (m, 3H), 1.95 – 1.88 (m, 6H), 1.64 –1.60 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 161.3 (d, *J* = 245.0 Hz), 145.7 (d, *J* = 8.0 Hz), 142.8, 141.6 (d, *J* = 4.0 Hz), 141.2 (d, *J* = 3.0 Hz), 139.9, 135.2, 127.5, 123.4, 121.4 (d, *J* = 8.0 Hz), 115.0 (d, *J* = 22.0 Hz), 110.4 (d, *J* = 25.0 Hz), 72.7, 50.3, 43.6, 36.1, 30.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.0; IR (neat): 2956, 2907, 2850, 2029, 1959, 1667(s), 1476, 1264, 1039, 784, 575; HRESIMS Calcd for $[C_{24}H_{23}FNaOS]^+$ (M + Na^+) 401.1346, found 401.1356.

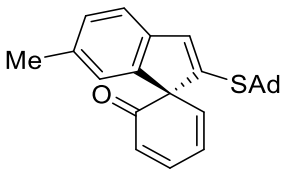
(*S*)-2'-(((3R,5R,7R)-adamantan-1-yl)thio)-6'-chlorospiro[cyclohexane-1,1'-indene]-2,4-dien-6-one (2i)



2i

Compound **2i** was prepared in 87% yield (34.6 mg) according to the general procedure (Table 2, entry 9). The product was purified by chromatography on silica gel (eluent: hexanes/acetone = 15/1) as a yellow oil. $[\alpha]_D^{20}$ = +283.8º (c = 1.0, $CHCl_3$). 95.5:4.5 e.r. (determined by HPLC: Chiralpak IA Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR = 5.08 min (major), 8.28 min (minor)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.17 (m, 3H), 6.98 (s, 1H), 6.96 (s, 1H), 6.52 (dd, *J* = 9.2, 6.4 Hz, 1H), 6.23 (d, *J* = 9.6 Hz, 1H), 5.93 (d, *J* = 9.2 Hz, 1H), 2.08 – 1.97 (m, 9H), 1.72 –1.67 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 145.1, 143.8, 143.1, 142.8, 139.7, 134.0, 131.1, 128.3, 127.5, 123.4, 122.8, 121.3, 72.5, 50.4, 43.5, 36.0, 30.0; IR (neat): 2918, 2852, 2028, 1959, 1668(s), 1452, 1262, 1037, 720, 627; HRESIMS Calcd for $[C_{24}H_{23}ClNaOS]^+$ (M + Na^+) 417.1050, found 417.1071.

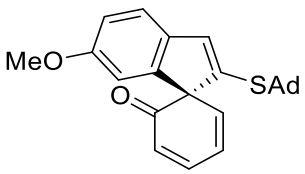
(*S*)-2'-(((3R,5R,7R)-adamantan-1-yl)thio)-6'-methylspiro[cyclohexane-1,1'-indene]-2,4-dien-6-one (2j)



2j

Compound **2j** was prepared in 91% yield (34.0 mg) according to the general procedure (Table 2, entry 10). The product was purified by chromatography on silica gel (eluent: hexanes/acetone = 15/1) as a brown oil. $[\alpha]_D^{20}$ = +268.9º (c = 1.0, $CHCl_3$). 95.5:4.5 e.r. (determined by HPLC: Chiralpak IA Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR = 4.93 min (major), 6.94 min (minor)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 7.6 Hz, 1H), 7.01 (s, 1H), 6.83 (s, 1H), 6.49 (dd, *J* = 9.2, 6.0 Hz, 1H), 6.22 (d, *J* = 10.0 Hz, 1H), 5.95 (d, *J* = 9.2 Hz, 1H), 2.28 (s, 3H), 2.09 – 2.04 (m, 3H), 2.02 – 1.96 (m, 6H), 1.70 –1.67 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 144.2, 142.8, 142.6, 141.0, 140.5, 136.5, 135.6, 128.9, 127.5, 123.1, 122.9, 120.5, 72.8, 50.1, 43.7, 36.1, 30.1, 21.4; IR (neat): 2904, 2847, 2361, 2029, 1959, 1667(s), 1456, 1297, 1039, 772, 595; HRESIMS Calcd for $[C_{25}H_{26}NaOS]^+$ (M + Na^+) 397.1597, found 397.1604.

(*S*)-2'-(((3R,5R,7R)-adamantan-1-yl)thio)-6'-methoxyspiro[cyclohexane-1,1'-indene]-2,4-dien-6-one (2k)

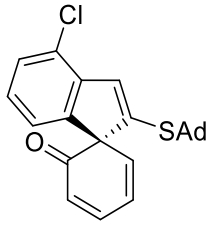


2k

Compound **2k** was prepared in 93% yield (36.3 mg) according to the general procedure (Table 2, entry 11). The product was purified by chromatography on silica gel (eluent: hexanes/acetone = 12/1) as a yellow oil. $[\alpha]_D^{20}$ = +149.7º (c = 1.0, $CHCl_3$). 90:10 e.r. (determined by HPLC: Chiralpak IA Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR = 6.17 min (major), 10.66 min (minor)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.19 (m, 2H), 7.00 (s, 1H), 6.81 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.59 (d, *J* = 2.0 Hz,

1H), 6.50 (dd, J = 9.2, 6.0 Hz, 1H), 6.22 (d, J = 9.6 Hz, 1H), 5.95 (d, J = 9.2 Hz, 1H), 3.74 (s, 3H), 2.08 – 2.03 (m, 3H), 1.99 – 1.93 (m, 6H), 1.69 –1.66 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 158.4, 146.0, 142.8, 140.8, 138.5, 138.1, 137.4, 127.5, 123.0, 121.4, 113.6, 109.1, 72.9, 55.6, 50.1, 43.8, 36.1, 30.1; IR (neat): 2904, 2849, 1958, 1667(s), 1475, 1282, 1229, 1038, 772, 731, 543; HRESIMS Calcd for $[C_{25}H_{26}NaO_2S]^+$ (M + Na^+) 413.1546, found 413.1539.

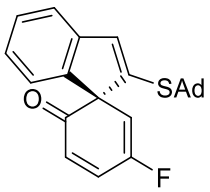
(*S*)-2'-(((3R,5R,7R)-adamantan-1-yl)thio)-4'-chlorospiro[cyclohexane-1,1'-indene]-2,4-dien-6-one (2l)



2l

Compound **2l** was prepared in 89% yield (35.2 mg) according to the general procedure (Table 2, entry 12). The product was purified by chromatography on silica gel (eluent: hexanes/acetone = 15/1) as a brown oil. $[\alpha]_D^{20}$ = +181.8º (c = 1.0, $CHCl_3$). 80:20 e.r. (determined by HPLC: Chiralpak IC Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR = 5.79 min (major), 6.70 min (minor)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 2H), 7.07 (s, 1H), 7.01 – 6.98 (m, 1H), 6.89 (d, J = 7.2 Hz, 1H), 6.51 (dd, J = 9.2, 5.6 Hz, 1H), 6.23 (d, J = 9.6 Hz, 1H), 5.92 (d, J = 9.2 Hz, 1H), 2.09 – 2.01 (m, 9H), 1.73 –1.69 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 144.9, 144.1, 143.7, 142.8, 139.7, 131.5, 128.5, 127.5, 126.5, 125.2, 123.3, 120.5, 73.3, 50.5, 43.4, 36.0, 30.0; IR (neat): 2907, 2850, 1959, 1668(s), 1450, 1298, 1039, 763, 730, 607; HRESIMS Calcd for $[C_{24}H_{23}ClNaOS]^+$ (M + Na^+) 417.1050, found 417.1060.

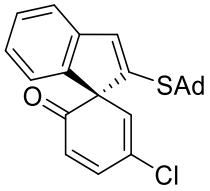
(*S*)-2'-(((3R,5R,7R)-adamantan-1-yl)thio)-3-fluorospiro[cyclohexane-1,1'-indene]-2,4-dien-6-one (2m)



2m

Compound **2m** was prepared in 79% yield (29.9 mg) according to the general procedure (Table 2, entry 13). The product was purified by chromatography on silica gel (eluent: hexanes/acetone = 15/1) as a brown solid (mp 141–143 °C). $[\alpha]_D^{20}$ = +87.3º (c = 1.0, $CHCl_3$). 95:5 e.r. (determined by HPLC: Chiralpak IA Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR = 5.29 min (major), 6.74 min (minor)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 2H), 7.14 – 7.08 (m, 2H), 7.05 (d, *J* = 7.6 Hz, 1H), 7.00 (s, 1H), 6.23 (dd, *J* = 10.4, 4.4 Hz, 1H), 5.46 (dd, *J* = 9.6, 3.2 Hz, 1H), 2.10 – 2.06 (m, 3H), 2.01 – 1.96 (m, 6H), 1.71 –1.68 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6 (d, *J* = 1.0 Hz), 155.9 (d, *J* = 250.0 Hz), 144.9, 144.2 (d, *J* = 3.0 Hz), 142.5 (d, *J* = 3.0 Hz), 138.4 (d, *J* = 37.0 Hz), 135.6, 129.5 (d, *J* = 8.0 Hz), 128.5, 125.7, 122.3, 120.9, 114.2 (d, *J* = 19.0 Hz), 70.4 (d, *J* = 8.0 Hz), 50.4, 43.6, 36.1, 30.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.3; IR (neat): 2909, 2850, 1958, 1649(s), 1462, 1403, 1298, 1219, 1039, 881, 740; HRESIMS Calcd for $[C_{24}H_{23}FNaOS]^+$ (M + Na^+) 401.1346, found 401.1359.

(*S*)-2'-(((3R,5R,7R)-adamantan-1-yl)thio)-3-chlorospiro[cyclohexane-1,1'-indene]-2,4-dien-6-one (2n)

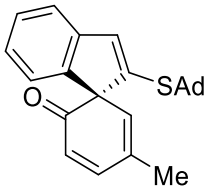


2n

Compound **2n** was prepared in 88% yield (31.5 mg) according to the general procedure (Table 2, entry 14). The product was purified by chromatography on silica gel (eluent: hexanes/acetone = 15/1) as a brown oil. $[\alpha]_D^{20}$ = -7.8º (c = 1.0, $CHCl_3$). 91.5:8.5 e.r. (determined by HPLC: Chiralpak IA Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR = 5.25 min (major), 6.49 min (minor)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28

– 7.26 (m, 2H), 7.11 – 7.08 (m, 2H), 7.05 (d, J = 7.2 Hz, 1H), 7.01 (s, 1H), 6.22 (d, J = 10.0 Hz, 1H), 5.94 (d, J = 2.4 Hz, 1H), 2.09 – 2.04 (m, 3H), 2.03 – 1.96 (m, 6H), 1.70 –1.67 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 144.9, 144.5, 143.4, 141.7, 136.2, 134.7, 128.7, 128.5, 127.7, 125.8, 122.4, 120.9, 72.8, 50.4, 43.6, 36.0, 30.0; IR (neat): 3062, 2930, 2852, 2029, 1958, 1668(s), 1452, 1298, 1219, 1039, 833, 749, 638; HRESIMS Calcd for $[C_{24}H_{23}ClNaOS]^+$ (M + Na^+) 417.1050, found 417.1052.

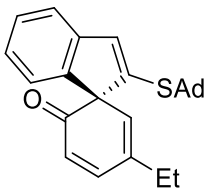
(*S*)-2'-(((3R,5R,7R)-adamantan-1-yl)thio)-3-methylspiro[cyclohexane-1,1'-indene]-2,4-dien-6-one (2o)



2o

Compound **2o** was prepared in 89% yield (33.3 mg) according to the general procedure (Table 2, entry 15). The product was purified by chromatography on silica gel (eluent: hexanes/acetone = 15/1) as a yellow oil. $[\alpha]_D^{20}$ = +140.7º (c = 1.0, $CHCl_3$). 92.5:7.5 e.r. (determined by HPLC: Chiralpak IA Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR = 5.67 min (major), 6.69 min (minor)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.21 (m, 2H), 7.09 – 7.04 (m, 2H), 7.00 – 6.99 (m, 2H), 6.19 (d, J = 10.0 Hz, 1H), 5.61 (s, 1H), 2.07 – 1.97 (m, 12H), 1.70 –1.67 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 147.1, 145.1, 144.4, 142.8, 134.9, 134.1, 130.7, 128.0, 127.1, 125.3, 122.1, 120.6, 72.1, 50.0, 43.5, 36.1, 30.0, 21.2; IR (neat): 3061, 2904, 2850, 2029, 1959, 1671(s), 1645, 1450, 1298, 1123, 1039, 824, 751, 738; HRESIMS Calcd for $[C_{25}H_{26}NaOS]^+$ (M + Na^+) 397.1597, found 397.1585.

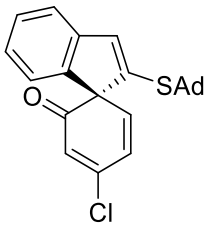
(1S)-2'-(((3S)-adamantan-1-yl)thio)-3-methoxyspiro[cyclohexane-1,1'-indene]-2,4-dien-6-one (2p)



2p

Compound **2p** was prepared in 88% yield (34.2 mg) according to the general procedure (Table 2, entry 16). The product was purified by chromatography on silica gel (eluent: hexanes/acetone = 15/1) as a yellow oil. $[\alpha]_D^{20}$ = +174.9º (c = 1.0, $CHCl_3$). 97.5:2.5 e.r. (determined by HPLC: Chiralpak IA Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR = 5.16 min (major), 6.27 min (minor)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 6.8 Hz, 1H), 7.12 (dd, *J* = 10.0, 2.4 Hz, 1H), 7.08 – 7.04 (m, 1H), 7.00 – 6.97 (m, 2H), 6.21 (d, *J* = 10.0 Hz, 1H), 5.58 (s, 1H), 2.35 – 2.40 (m, 2H), 2.09 – 2.05 (m, 3H), 2.01 – 1.97 (m, 6H), 1.70 –1.68 (m, 6H), 1.14 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 146.5, 145.2, 144.6, 142.9, 136.6, 135.3, 132.8, 128.0, 127.3, 125.4, 122.2, 120.6, 72.1, 50.0, 43.7, 36.1, 30.1, 28.2, 12.9; IR (neat): 2964, 2903, 2849, 2029, 1959, 1761, 1668(s), 1452, 1298, 1204, 1193, 1038, 750, 737; HRESIMS Calcd for $[C_{26}H_{28}NaOS]^+$ (M + Na^+) 411.1753, found 411.1761.

(1S)-2'-(((3S)-adamantan-1-yl)thio)-4-chlorospiro[cyclohexane-1,1'-indene]-2,4-dien-6-one (2q)

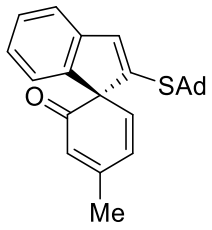


2q

Compound **2q** was prepared in 94% yield (37.1 mg) according to the general procedure (Table 2, entry 17). The product was purified by chromatography on silica gel (eluent: hexanes/acetone = 15/1) as a yellow solid (mp 189–191 °C). $[\alpha]_D^{20}$ = +33.2º (c = 1.0, $CHCl_3$). 90:10 e.r. (determined by HPLC: Chiralpak IA Column, 10/90 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR = 6.57 min (major), 7.78 min (minor)). ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.29 – 7.16 (m, 2H), 7.11 – 7.08 (m, 1H), 7.05 – 7.00 (m, 2H), 6.53 (d, *J* = 9.6 Hz, 1H), 6.42 (s, 1H), 5.98 (d, *J* = 9.6 Hz, 1H), 2.10 – 2.05 (m, 3H), 2.04 – 2.00 (m, 6H), 1.71 –1.67 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 152.4, 145.3, 143.4, 141.8, 141.3, 136.2, 128.5, 126.5, 125.7, 125.6, 122.4, 120.9, 71.6, 50.5, 43.6, 36.1, 30.1. IR (neat): 2905, 2850, 2029, 1959, 1662(s), 1558, 1456, 1284, 1039, 821, 673, 594; HRESIMS Calcd for $[C_{24}H_{23}ClNaOS]^+$ (M + Na^+) 417.1050, found 417.1063.

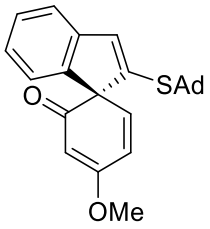
(1S)-2'-(((3S)-adamantan-1-yl)thio)-4-methylspiro[cyclohexane-1,1'-indene]-2,4-dien-6-one (2r)



2r

Compound **2r** was prepared in 93% yield (34.8 mg) according to the general procedure (Table 2, entry 18). The product was purified by chromatography on silica gel (eluent: hexanes/acetone = 15/1) as a brown oil. $[\alpha]_D^{20}$ = +111.2º (c = 1.0, $CHCl_3$). 91:9 e.r. (determined by HPLC: Chiralpak IA Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR = 6.25 min (major), 7.45 min (minor)). ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.25 (m, 1H), 7.25 – 7.21 (m, 1H), 7.06 – 6.97 (m, 3H), 6.38 (d, *J* = 9.6 Hz, 1H), 6.09 (s, 1H), 5.91 (d, *J* = 9.2 Hz, 1H), 2.20 (s, 3H), 2.07 – 1.99 (m, 9H), 1.71 –1.68 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 155.1, 145.3, 144.1, 142.5, 139.7, 135.3, 128.1, 126.9, 125.3, 125.1, 122.1, 120.6, 71.5, 50.1, 43.6, 36.1, 30.1, 23.2; IR (neat): 2908, 2850, 2029, 1959, 1661(s), 1461, 1185, 1039, 773, 746, 613; HRESIMS Calcd for $[C_{25}H_{26}NaOS]^+$ (M + Na^+) 397.1597, found 397.1607.

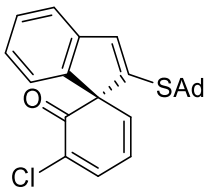
(1S)-2'-(((3S)-adamantan-1-yl)thio)-4-methoxyspiro[cyclohexane-1,1'-indene]-2,4-dien-6-one (2s)



2s

Compound **2s** was prepared in 90% yield (35.1 mg) according to the general procedure (Table 2, entry 19). The product was purified by chromatography on silica gel (eluent: hexanes/acetone = 12/1) as a red oil. $[\alpha]_D^{20}$ = +157.6º (c = 1.0, $CHCl_3$). 90:10 e.r. (determined by HPLC: Chiralpak IA Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR = 7.31 min (major), 10.76 min (minor)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.2 Hz, 1H), 7.24 – 7.22 (m, 1H), 7.09 – 7.05 (m, 1H), 7.04 (s, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.38 (dd, *J* = 10.0, 2.0 Hz, 1H), 5.95 (d, *J* = 10.0 Hz, 1H), 5.66 (d, *J* = 1.6 Hz, 1H), 3.84 (s, 3H), 2.07 – 2.00 (m, 9H), 1.72 – 1.68 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.2, 172.5, 145.3, 144.3, 142.4, 141.4, 135.5, 128.1, 125.4, 123.2, 122.2, 120.6, 101.6, 71.1, 55.9, 50.1, 43.6, 36.1, 30.0; IR (neat): 3060, 2920, 2852, 1959, 1648(s), 1568, 1506, 1265, 1196, 1034, 929, 921, 895, 564; HRESIMS Calcd for $[C_{25}H_{26}NaO_2S]^+$ (M + Na^+) 413.1546, found 413.1550.

(1S)-2'-(((3S)-adamantan-1-yl)thio)-5-chlorospiro[cyclohexane-1,1'-indene]-2,4-dien-6-one (2t)

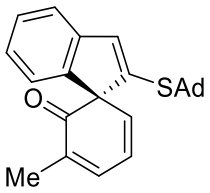


2t

Compound **2t** was prepared in 71% yield (28.0 mg) according to the general procedure (Table 2, entry 20). The product was purified by chromatography on silica gel (eluent: hexanes/acetone = 15/1) as a yellow soild (mp 166–170 °C). $[\alpha]_D^{20}$ = +217.7º (c = 1.0, $CHCl_3$). 97:3 e.r. (determined by HPLC: Chiralpak IA Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR = 10.29 min (major), 11.53 min (minor)). ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.37 (d, *J* = 6.8 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.10 – 7.06 (m, 1H), 7.02 (s, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.41 (dd, *J* = 9.2, 6.8 Hz, 1H), 5.88 (d, *J* = 9.2 Hz, 1H), 2.10 – 2.04 (m, 3H), 2.02 – 1.95 (m, 6H), 1.72 – 1.66 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.7, 145.1, 143.0, 141.3, 140.1, 139.5, 136.3, 132.0, 128.4, 125.7, 122.7, 122.2, 120.8, 73.9, 50.5, 43.6, 35.9, 30.0; IR (neat): 2905, 2848, 2029, 1959, 1679(s), 1632, 1461, 1450, 1328, 1038, 781, 635; HRESIMS Calcd for $[C_{24}H_{23}ClNaOS]^+$ (M + Na^+) 417.1050, found 417.1055.

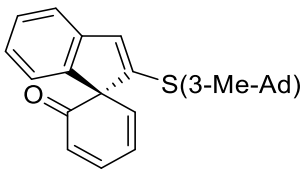
(1S)-2'-(((3S)-adamantan-1-yl)thio)-5-methylspiro[cyclohexane-1,1'-indene]-2,4-dien-6-one (2u)



2u

Compound **2u** was prepared in 93% yield (34.7 mg) according to the general procedure (Table 2, entry 21). The product was purified by chromatography on silica gel (eluent: hexanes/acetone = 15/1) as a yellow oil. $[\alpha]_D^{20}$ = +220.1º (c = 1.0, $CHCl_3$). 96:4 e.r. (determined by HPLC: Chiralpak IA Column, 10/90 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR = 6.66 min (major), 7.58 min (minor)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.21 (m, 2H), 7.07 – 7.04 (m, 1H), 7.01 – 6.98 (m, 3H), 6.42 (dd, *J* = 9.2, 6.0 Hz, 1H), 5.84 (d, *J* = 9.2, 1H), 2.10 – 2.05 (m, 3H), 2.04 – 1.97 (m, 6H), 1.92 (s, 3H), 1.71 – 1.68 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 145.3, 144.2, 142.4, 139.0, 138.0, 135.3, 135.1, 128.0, 125.4, 123.3, 122.0, 120.6, 72.6, 50.1, 43.6, 36.1, 30.1, 16.0; IR (neat): 2916, 2851, 2029, 1959, 1661(s), 1644, 1455, 1298, 776, 738, 577; HRESIMS Calcd for $[C_{25}H_{26}NaOS]^+$ (M + Na^+) 397.1597, found 397.1598.

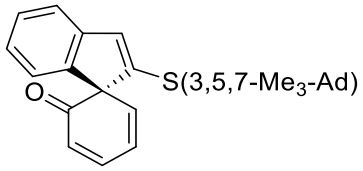
(*S*)-2'-(((1s,3R,5R,7S)-3-methyladamantan-1-yl)thio)spiro[cyclohexane-1,1'-indene]-2,4-dien-6-one (2v)



2v

Compound **2v** was prepared in 83% yield (31.0 mg) according to the general procedure (Table 3, entry 1). The product was purified by chromatography on silica gel (eluent: hexanes/acetone = 15/1) as a yellow oil. $[\alpha]_D^{20}$ = +91.2º (c = 1.0, $CHCl_3$). 95.5:3.5 e.r. (determined by HPLC: Chiralpak IA Column, 5/95 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR = 10.12 min (major), 12.49 min (minor)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 1H), 7.25 – 7.20 (m, 2H), 7.09 – 7.05 (m, 1H), 7.02 – 7.01 (m, 2H), 6.49 (dd, *J* = 9.2, 6.0 Hz, 1H), 6.22 (d, *J* = 9.6 Hz, 1H), 5.95 (d, *J* = 9.2 Hz, 1H), 2.13 – 2.08 (m, 2H), 1.98 – 1.85 (m, 4H), 1.75 – 1.69 (m, 2H), 1.65 – 1.54 (m, 2H), 1.45 – 1.40 (m, 4H), 0.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 145.3, 143.7, 142.7, 142.2, 140.7, 135.3, 128.2, 127.5, 125.4, 123.0, 122.1, 120.7, 72.8, 50.6, 50.2, 43.1, 42.8, 42.7, 35.3, 32.4, 30.6, 30.3(9), 30.3(8); IR (neat): 2904, 2845, 2333, 2029, 1959, 1668(s), 1631, 1455, 1308, 989, 744, 689; HRESIMS Calcd for $[C_{25}H_{26}NaOS]^+$ (M + Na^+) 397.1597, found 397.1610.

(*S*)-2'-(((3R,5R,7R)-3,5,7-trimethyladamantan-1-yl)thio)spiro[cyclohexane-1,1'-indene]-2,4-dien-6-one (2w)

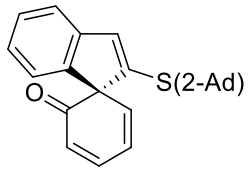


2w

Compound **2w** was prepared in 88% yield (35.3 mg) according to the general procedure (Table 3, entry 2). The product was purified by chromatography on silica gel (eluent: hexanes/acetone = 15/1) as a brown oil. $[\alpha]_D^{20}$ = +81.4º (c = 1.0, $CHCl_3$). 95.5:4.5 e.r. (determined by HPLC: Chiralpak IC Column, 5/95 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR = 16.89 min (major), 18.08 min (minor)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.19

(m, 3H), 7.08 – 7.04 (m, 1H), 7.00 (d, J = 7.6 Hz, 1H), 6.97 (s, 1H), 6.48 (dd, J = 9.2, 6.4 Hz, 1H), 6.21 (d, J = 9.6 Hz, 1H), 5.94 (d, J = 8.8 Hz, 1H), 1.61 – 1.54 (m, 6H), 1.14 – 1.04 (m, 6H), 0.86 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 145.3, 143.6, 142.7, 142.4, 140.8, 134.7, 128.2, 127.4, 125.4, 122.9, 122.1, 120.6, 72.7, 51.2, 49.7, 48.8, 33.5, 29.8; IR (neat): 2945, 2920, 2836, 2029, 1959, 1668(s), 1456, 1334, 1249, 748, 599; HRESIMS Calcd for $[C_{27}H_{30}NaOS]^+$ (M + Na^+) 425.1910, found 425.1883.

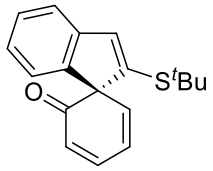
(S)-2'-(((1R,3S,5S,7S)-adamantan-2-yl)thio)spiro[cyclohexane-1,1'-indene]-2,4-dien-6-one (2x)



2x

Compound **2x** was prepared in 89% yield (32.0 mg) according to the general procedure (Table 3, entry 3). The product was purified by chromatography on silica gel (eluent: hexanes/acetone = 15/1) as a yellow oil. $[\alpha]_D^{20}$ = +127.5º (c = 1.0, $CHCl_3$). 90:10 e.r. (determined by HPLC: Chiralpak IA Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR = 7.71 min (major), 8.65 min (minor)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.23 (m, 1H), 7.22 – 7.20 (m, 2H), 7.01 – 7.00 (m, 2H), 6.64 (s, 1H), 6.50 (dd, J = 9.2, 6.0 Hz, 1H), 6.23 (d, J = 9.6 Hz, 1H), 6.01 (dd, J = 9.6, 1.2 Hz, 1H), 3.68 – 3.63 (m, 1H), 2.15 – 2.02 (m, 4H), 1.96 – 1.82 (m, 6H), 1.76 – 1.72 (m, 2H), 1.60 – 1.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 147.2, 145.2, 143.1, 142.6, 141.3, 128.2, 127.3, 127.2, 124.5, 122.6, 121.8, 119.9, 71.5, 54.1, 38.6, 38.5, 37.5, 32.8, 32.6, 32.3, 32.2, 27.5, 27.3; IR (neat):3065, 2908, 2851, 2029, 1959, 1667(s), 1593, 1203, 933, 774, 753, 690, 531; HRESIMS Calcd for $[C_{24}H_{24}NaOS]^+$ (M + Na^+) 383.1440, found 383.1443.

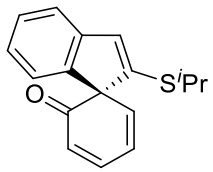
(*S*)-2'-(*tert*-butylthio)spiro[cyclohexane-1,1'-indene]-2,4-dien-6-one (2y)



2y

Compound **2y** was prepared in 77% yield (21.7 mg) according to the general procedure (Table 3, entry 4). The product was purified by chromatography on silica gel (eluent: hexanes/acetone = 12/1) as a yellow oil. $[\alpha]_D^{20}$ = +153.7º (c = 1.0, $CHCl_3$). 86:14 e.r. (determined by HPLC: Chiralpak IC Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR = 7.66 min (major), 10.76 min (minor)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.13 (m, 3H), 7.00 – 6.93 (m, 2H), 6.89 (s, 1H), 6.42 (dd, *J* = 9.2, 6.0 Hz, 1H), 6.15 (d, *J* = 10.0 Hz, 1H), 5.90 (d, *J* = 9.2 Hz, 1H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 145.4, 144.3, 143.4, 142.7, 140.9, 133.2, 128.2, 127.4, 125.3, 122.8, 122.1, 120.5, 72.6, 47.4, 31.1; IR (neat): 2961, 2924, 2029, 1959, 1667(s), 1489, 1456, 1196, 952, 751, 526; HRESIMS Calcd for $[C_{18}H_{18}NaOS]^+$ ($M + Na^+$) 305.0971, found 305.0981.

(*S*)-2'-(isopropylthio)spiro[cyclohexane-1,1'-indene]-2,4-dien-6-one (2z)

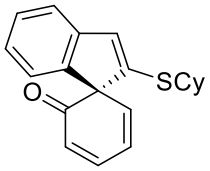


2z

Compound **2z** was prepared in 92% yield (24.7 mg) according to the general procedure (Table 3, entry 5). The product was purified by chromatography on silica gel (eluent: hexanes/acetone = 15/1) as a yellow oil. $[\alpha]_D^{20}$ = +114.4º (c = 1.0, $CHCl_3$). 85:15 e.r. (determined by HPLC: Chiralpak IA Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR = 5.40 min (minor), 10.45 min (major)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.19 (m, 3H), 7.04 – 7.00 (m, 2H), 6.69 (s, 1H), 6.48 (dd, *J* = 9.2, 6.0 Hz, 1H), 6.21 (d, *J* = 10.0 Hz, 1H), 5.99 (dd, *J* = 9.2, 0.8 Hz, 1H), 3.49 – 3.39 (m, 1H), 1.38 (d, *J* = 2.8 Hz, 3H), 1.36 (d, *J* = 2.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 146.3,

145.1, 143.2, 142.7, 141.0, 128.3, 128.2, 127.2, 124.7, 122.6, 121.8, 120.0, 71.3, 36.9, 22.8, 22.6; IR (neat): 2962, 2823, 2029, 1959, 1667(s), 1629, 1462, 1243, 748, 735, 689; HRESIMS Calcd for $[C_{17}H_{16}NaOS]^+$ (M + Na^+) 291.0814, found 291.0802.

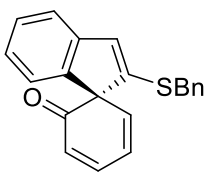
(*S*)-2'-(cyclohexylthio)spiro[cyclohexane-1,1'-indene]-2,4-dien-6-one (2aa)



2aa

Compound **2aa** was prepared in 90% yield (27.7 mg) according to the general procedure (Table 3, entry 6). The product was purified by chromatography on silica gel (eluent: hexanes/acetone = 20/1) as a brown oil. $[\alpha]_D^{20}$ = +179.8º (c = 1.0, $CHCl_3$). 90:10 e.r. (determined by HPLC: Chiralpak IA Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR = 9.00 min (major), 10.50 min (minor)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.20 (m, 3H), 7.02 – 6.99 (m, 2H), 6.69 (s, 1H), 6.49 (dd, *J* = 9.2, 6.0 Hz, 1H), 6.22 (d, *J* = 9.6 Hz, 1H), 5.99 (d, *J* = 9.2 Hz, 1H), 3.25 – 3.20 (m, 1H), 2.11 – 2.08 (m, 2H), 1.78 – 1.76 (m, 2H), 1.66 – 1.58 (m, 2H), 1.51 – 1.30 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 146.1, 145.2, 143.3, 142.7, 141.1, 128.2, 128.1, 127.2, 124.7, 122.7, 121.9, 120.0, 71.5, 45.3, 33.0, 32.7, 25.8, 25.7; IR (neat): 2930, 2851, 2029, 1959, 1668(s), 1632, 1461, 1450, 1243, 748, 687; HRESIMS Calcd for $[C_{20}H_{20}NaOS]^+$ (M + Na^+) 331.1127, found 331.1134.

(*S*)-2'-(benzylthio)spiro[cyclohexane-1,1'-indene]-2,4-dien-6-one (2ab)

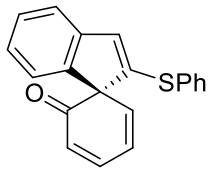


2ab

Compound **2ab** was prepared in 87% yield (27.5 mg) according to the general procedure (Table 3, entry 7). The product was purified by chromatography on silica gel

(eluent: hexanes/acetone = 10/1) as a yellow oil. $[\alpha]_D^{20}$ = +151.5º (c = 1.0, $CHCl_3$). 91.5:8.5 e.r. (determined by HPLC: Chiralpak IA Column, 30/70 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR = 7.14 min (minor), 19.58 min (major)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.29 (m, 2H), 7.25 – 7.22 (m, 2H), 7.20 – 7.12 (m, 4H), 6.98 – 6.93 (m, 2H), 6.60 (s, 1H), 6.41 (dd, *J* = 9.2, 6.0 Hz, 1H), 6.16 (d, *J* = 9.6 Hz, 1H), 5.92 (d, *J* = 9.2 Hz, 1H), 4.06 (dd, *J* = 16.8, 12.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 146.6, 144.9, 143.2, 142.8, 141.0, 135.9, 128.9, 128.6, 128.3, 128.0, 127.5, 127.2, 124.9, 122.8, 121.9, 120.2, 71.3, 37.5; IR (neat): 2932, 2029, 1959, 1667(s), 1489, 1196, 1023, 950, 751, 688; HRESIMS Calcd for $[C_{21}H_{16}NaOS]^+$ (M + Na^+) 339.0814, found 339.0821.

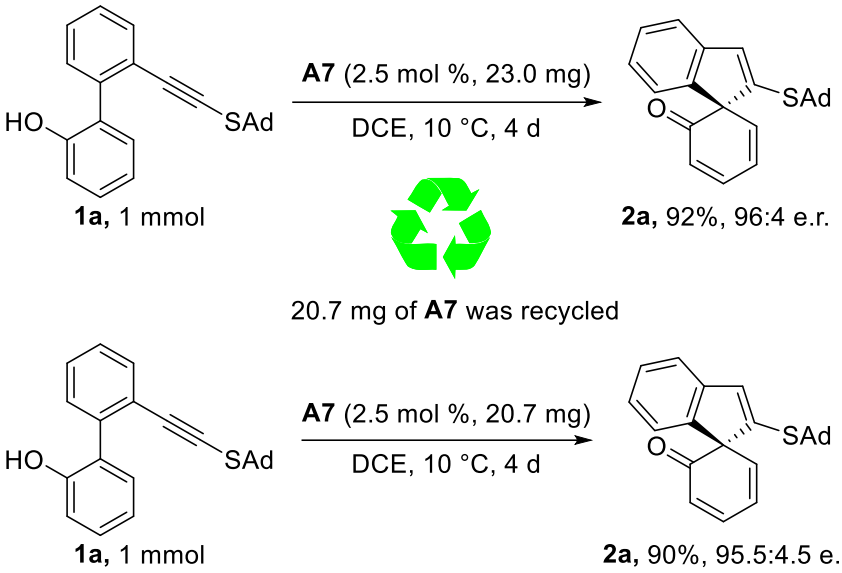
(*S*)-2'-(phenylthio)spiro[cyclohexane-1,1'-indene]-2,4-dien-6-one (2ac)



2ac

Compound **2ac** was prepared in 85% yield (25.7 mg) according to the general procedure (Table 3, entry 8). The product was purified by chromatography on silica gel (eluent: hexanes/acetone = 15/1) as a yellow oil. $[\alpha]_D^{20}$ = +136.2º (c = 1.0, $CHCl_3$). 82:18 e.r. (determined by HPLC: Chiralpak IC Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR = 9.76 min (major), 12.18 min (minor)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.54 (m, 2H), 7.34 – 7.33 (m, 3H), 7.23 – 7.15 (m, 3H), 7.06 – 7.00 (m, 2H), 6.57 (s, 1H), 6.42 (dd, *J* = 9.2, 6.0 Hz, 1H), 6.20 (d, *J* = 10.0 Hz, 1H), 6.00 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 146.9, 144.5, 143.9, 142.6, 140.5, 134.1, 131.7, 131.5, 129.2, 128.7, 128.3, 127.4, 125.2, 122.7, 122.0, 120.7, 71.2; IR (neat): 2029, 1959, 1662(s), 1629, 1433, 746, 688, 626, 587; HRESIMS Calcd for $[C_{20}H_{14}NaOS]^+$ (M + Na^+) 325.0658, found 325.0658.

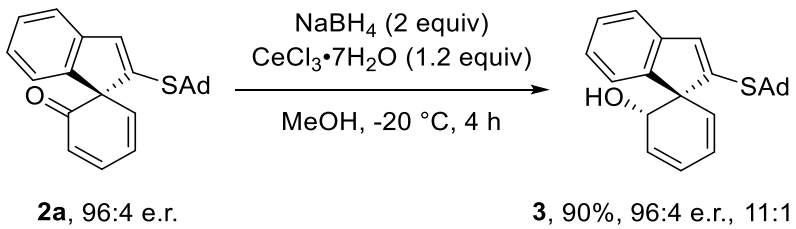
4. Synthetic Utility Study



Catalyst recycling experiment:

To a mixture of alkynyl thioether **1a** (1 mmol, 360.5 mg) in DCE (10 mL) was added **A7** (0.025 mmol, 23.0 mg) at 10 ℃. Then, the reaction mixture was stirred at 10 ℃ and the progress of the reaction was monitored by TLC. Upon completion, the mixture was quenched by Et_3N (0.06 mmol, 8.4 μL), concentrated under reduced pressure. The residue was purified by chromatography on silica gel (eluent: hexanes/ ethyl acetate) to give **2a** in 92% yield (331.6 mg) with 96:4 e.r. value, as well as recycled **A7**. The above-obtained **A7** was washed with 6 M HCl and brine, dried over $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure to deliver **A7** (20.7 mg) which could be used in next 1 mmol reaction and delivered **2a** in similar yield and enantioselectivity. This experiment shows that the CPA catalyst could be recycled well.

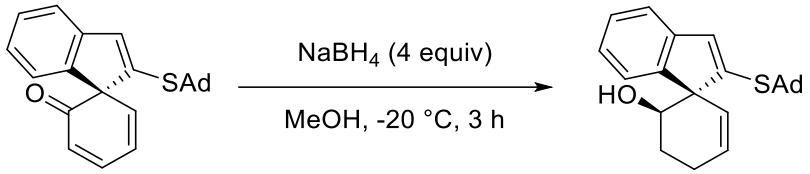
(1*S*,6*S*)-2'-(((3S)-adamantan-1-yl)thio)spiro[cyclohexane-1,1'-indene]-2,4-dien-6-ol (3)



To a solution of **2a** (0.1 mmol, 36.0 mg) in MeOH (1.5 mL) was added $CeCl_3•7H_2O$

(0.12 mmol, 44.6 mg). The resulting mixture was stirred at -20 ℃ for 5 min before $NaBH_4$ (0.2 mmol, 7.6 mg) was added. Then the reaction was stirred at -20 ℃ for additional 4 h and the progress of the reaction was monitored by TLC. Upon completion, the mixture was diluted with water, extracted EtOAc, washed with aqueous $NaHCO_3$ and brine, dried over anhydrous $MgSO_4$, filtered and concentrated. The residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate) to give the desired product **3** in 90% yield (32.6 mg) with the d.r. of 11:1. Pale yellow oil. $[\alpha]_D^{20}$ = -5.0º (c = 1.0, $CHCl_3$). 96:4 e.r. (determined by HPLC: Chiralpak IA Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR = 8.67 min (minor), 13.24 min (major)). ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.6 Hz, 1H), 7.22 – 7.19 (m, 2H), 7.12 – 7.08 (m, 1H), 6.77 (s, 1H), 6.20 (dd, *J* = 9.2, 5.2 Hz, 1H), 6.07 – 6.03 (m, 1H), 5.99 – 5.95 (m, 1H), 5.34 (d, *J* = 9.6 Hz, 1H), 4.71 (s, 1H), 2.12 (s, 1H), 2.10 – 2.05 (m, 9H), 1.73 – 1.70 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 143.8, 143.7, 131.0, 129.8, 129.3, 127.6, 125.0, 124.8, 124.1, 122.5, 119.6, 72.3, 63.0, 49.6, 43.3, 36.2, 30.0; IR (neat): 3431(bs), 2904, 2850, 2029, 1959, 1463, 1298, 1040, 745; HRESIMS Calcd for $[C_{24}H_{26}NaOS]^+$ (M + Na^+) 385.1597, found 385.1598.

(1*S*,6*R*)-2'-(((3S)-adamantan-1-yl)thio)spiro[cyclohexane-1,1'-inden]-2-en-6-ol (4)

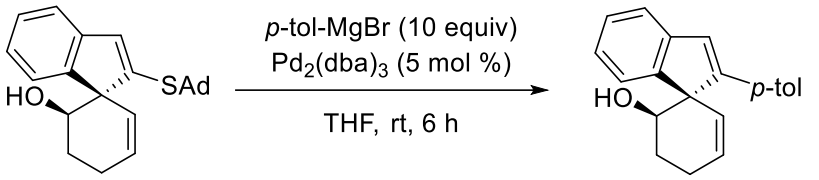


2a, 96:4 e.r. **4**, 88%, 96.5:3.5 e.r., 13:1 d.r.

To a solution of **2a** (0.1 mmol, 36.0 mg) in MeOH (1.0 mL) was added $NaBH_4$ (0.4 mmol, 15.2 mg) at -20 ℃ and stirred at this temperature for 3 h. The progress of the reaction was monitored by TLC. Upon completion, the reaction was quenched with water (0.5 mL), extracted with EtOAc, washed with aqueous $NaHCO_3$ and brine, dried over anhydrous $MgSO_4$, filtered and concentrated. The residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate) to give the desired product **4** in 88% yield (32.1 mg) with the d.r. of 13:1. Colourless oil. $[\alpha]_D^{20}$ = -127.4º (c = 1.0, $CHCl_3$). 96.5:3.5 e.r. (determined by HPLC: Chiralpak IA Column, 20/80 *i*-

PrOH/hexane, 1.0 mL/min, 254nm; TR = 6.01 min (major), 11.48 min (minor)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.19 (m, 3H), 7.13 – 7.08 (m, 1H), 6.86 (s, 1H), 6.04 – 6.00 (m, 1H), 5.04 (d, *J* = 10.0 Hz, 1H), 4.10 (d, *J* = 10.4 Hz, 1H), 2.55 – 2.25 (m, 3H), 2.10 – 2.07 (m, 9H), 1.99 – 1.93 (m, 1H), 1.75 – 1.72 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 144.4, 143.5, 131.7, 129.5, 127.3, 127.2, 124.7, 122.2, 119.6, 73.5, 63.7, 50.2, 43.5, 36.2, 30.0, 27.2, 24.2; IR (neat):3465(bs), 2906, 2850, 2029, 1959, 1452, 1341, 1297, 1056, 1039, 749, 733, 711; HRESIMS Calcd for $[C_{24}H_{28}NaOS]^+$ (M + Na^+) 387.1753, found 387.1751.

(1*R*,6*R*)-2'-(*p*-tolyl)spiro[cyclohexane-1,1'-inden]-2-en-6-ol (5)

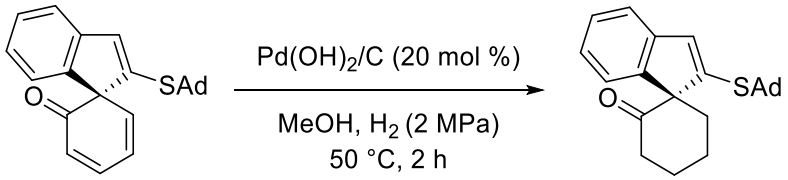


4, 96.5:3.5 e.r. **5**, 72%, 96.5:3.5 e.r.

To a dry sealed tube equipped with a stir bar were added **4** (0.1 mmol, 36.4 mg), $Pd_2(dba)_3$ (0.005 mmol, 4.6 mg) and THF (1.5 mL). Then *p*-tol-MgBr (1 mmol, 1.0 mol/L in THF, 1.0 mL) was added dropwise at room temperature and the resulting mixture was stirred under N_2 atmosphere for 6 h. The progress of the reaction was monitored by TLC. Upon completion, the reaction was quenched with water (0.5 mL) and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate) to give the desired product **5** in 72% yield (20.7 mg). Colourless oil. $[\alpha]_D^{20}$ = -100.5º (c = 1.0, $CHCl_3$). 96.5:3.5 e.r. (determined by HPLC: Chiralpak IA Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR = 5.66 min (minor), 6.93 min (major)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.26 (m, 3H), 7.20 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.15 – 7.13 (m, 2H), 6.85 (s, 1H), 6.12 – 6.08 (m, 1H), 5.44 – 5.41 (m, 1H), 4.19 (dd, *J* = 11.2, 4.0 Hz, 1H), 2.36 (s, 3H), 1.80 – 1.72 (m, 2H), 1.64 – 1.54 (m, 2H), 1.41 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 150.7, 143.6, 137.3, 136.1, 131.2, 129.5, 128.9, 128.1, 127.5, 127.5, 125.5, 122.6, 120.9, 73.9, 62.5, 26.5, 24.4, 21.2; IR (neat): 3440(bs), 3012, 1633, 1514, 1464, 1265, 819, 750, 510; HRESIMS Calcd for $[C_{21}H_{20}NaO]^+$ (M + Na^+) 311.1406, found

311.1413.

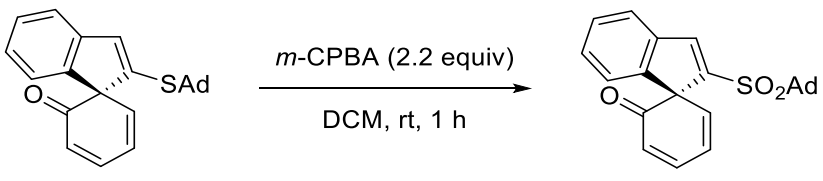
(*S*)-2'-(((3R,5R,7R)-adamantan-1-yl)thio)spiro[cyclohexane-1,1'-inden]-2-one (6)



2a, 96:4 e.r. **6**, 97%, 96:4 e.r.

To a solution of **2a** (0.1 mmol, 36.0 mg) in MeOH (1 mL) was added $Pd(OH)_2/C$ (10% on carbon, 0.02 mmol, 3 mg) and stirred at 50 °C under H_2 atmosphere (2 MPa) for 2 h. The progress of the reaction was monitored by TLC. Upon completion, the mixture was concentrated under vacuum and the residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 10/1) to afford the desired product **6** (35.3 mg, 97% yield). Colourless oil. $[\alpha]_D^{20}$ = -96.7º (c = 1.0, $CHCl_3$). 96:4 e.r. (determined by HPLC: Chiralpak IA Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR = 6.33 min (major), 9.26 min (minor)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.6 Hz, 1H), 7.27 – 7.20 (m, 2H), 7.15 – 7.10 (m, 1H), 6.90 (s, 1H), 2.85 – 2.76 (m, 1H), 2.70 – 2.65 (m, 1H), 2.58 – 2.51 (m, 1H), 2.25 – 2.15 (m, 2H), 2.07 – 1.95 (m, 12H), 1.72 – 1.69 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.4, 146.4, 146.1, 143.3, 133.5, 127.6, 124.3, 123.0, 120.9, 71.8, 50.0, 43.9, 40.7, 36.2, 35.9, 30.1, 25.9, 21.6; IR (neat): 2916, 2850, 2029, 1959, 1667(s), 1539, 1260, 1034, 807, 588, 542; HRESIMS Calcd for $[C_{24}H_{28}NaOS]^+$ (M + Na^+) 387.1753, found 387.1759.

(*S*)-2'-(((3R,5R,7R)-adamantan-1-yl)sulfonyl)spiro[cyclohexane-1,1'-indene]-2,4-dien-6-one (7)

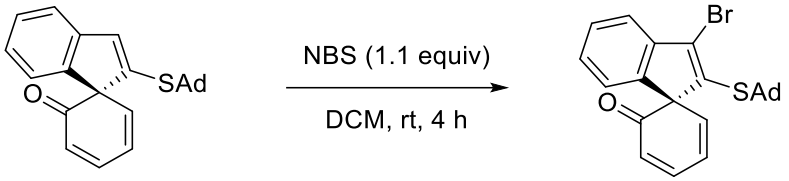


2a, 96:4 e.r. **7**, 99%, 96:4 e.r.

To a solution of **2a** (0.1 mmol, 36.1 mg) in DCM (2 mL) was added *m*-CPBA (0.22 mmol, 38.0 mg) and the resulting mixture was stirred at room temperature for 1 h. The

progress of the reaction was monitored by TLC. Upon completion, the reaction was quenched with saturated aqueous $NaHCO_3$ (0.1 mL), and directly concentrated under vacuum. The residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 5/1) to afford the desired product **7** (39.0 mg, 99% yield). Colourless oil. $[\alpha]_D^{20}$ = +41.3º (c = 1.0, $CHCl_3$). 96:4 e.r. (determined by HPLC: Chiralpak IA Column, 30/70 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR = 13.14 min (major), 24.42 min (minor)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.54 (d, *J* = 7.2, 1H), 7.39 – 7.35 (m, 1H), 7.32 – 7.26 (m, 2H), 7.13 (d, *J* = 7.6 Hz, 1H), 6.56 – 6.52 (m, 1H), 6.30 (d, *J* = 10.0 Hz, 1H), 6.13 (d, *J* = 9.2 Hz, 1H), 2.20 – 2.14 (m, 3H), 2.08 – 2.00 (m, 6H), 1.73 – 1.66 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 148.0, 145.4, 145.3, 142.9, 141.1, 138.9, 129.4, 128.7, 127.4, 124.8, 122.4, 122.2, 69.7, 62.7, 35.7, 34.7, 28.3; IR (neat): 2917, 2855, 2029, 1959, 1669(s), 1453, 1299, 1135, 756, 627, 546; HRESIMS Calcd for $[C_{24}H_{24}NaO_3S]^+$ (M + Na^+) 415.1338, found 415.1326.

(*S*)-2'-(((3R,5R,7R)-adamantan-1-yl)sulfonyl)spiro[cyclohexane-1,1'-indene]-2,4-dien-6-one (8)



2a, 96:4 e.r. **8**, 98%, 95.5:4.5 e.r.

To a solution of **2a** (0.1 mmol, 36.1 mg) in DCM (2 mL) was added NBS (0.11 mmol, 19.0 mg) and the resulting mixture was stirred at room temperature for 4 h. The progress of the reaction was monitored by TLC. Upon completion, the reaction concentrated under vacuum, and the residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate = 10/1) to afford the desired product **8** (43.0 mg, 98% yield). Yellow solid (mp 128–130 °C). $[\alpha]_D^{20}$ = +142.8º (c = 1.0, $CHCl_3$). 95.5:4.5 e.r. (determined by HPLC: Chiralpak IA Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254nm; TR = 4.58 min (major), 4.96 min (minor)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.6 Hz, 1H), 7.40 – 7.37 (m, 1H), 7.30 – 7.20 (m, 2H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.55 (dd, *J* = 9.2, 6.0 Hz, 1H), 6.25 (d, *J* = 9.6 Hz, 1H), 5.92 (d, *J* = 9.2 Hz, 1H), 2.02

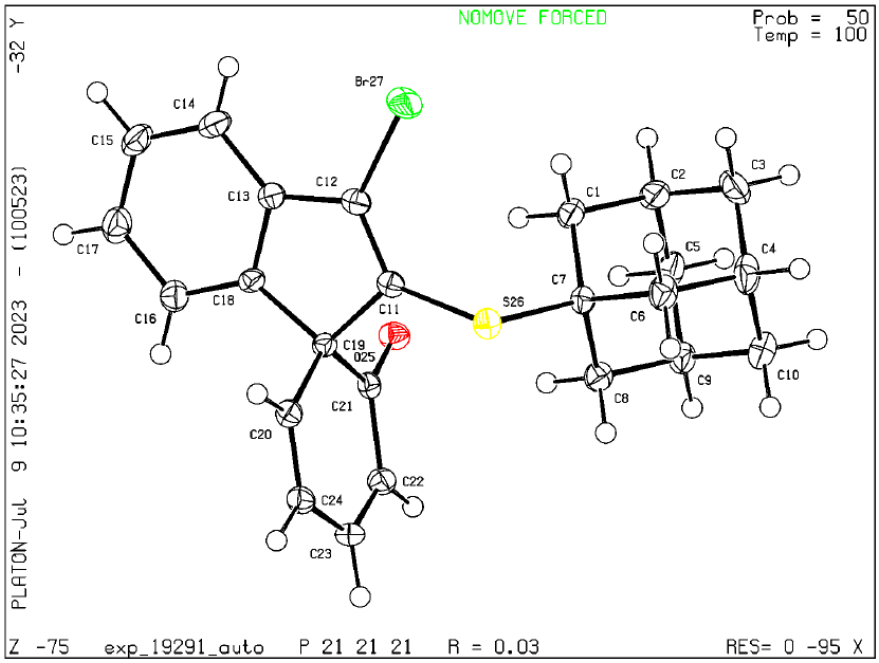
– 1.95 (m, 9H), 1.66 – 1.61 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 144.1, 143.3, 142.8, 139.9, 139.1, 137.5, 128.6, 128.3, 127.7, 123.5, 122.3, 122.2, 72.7, 54.3, 45.0, 35.9, 30.5; IR (neat): 2906, 2849, 2029, 1959, 1704(s), 1648, 1463, 1221, 1038, 722, 570; HRESIMS Calcd for $[C_{24}H_{23}BrNaOS]^+$ ($M + Na^+$) 461.0545, found 461.0545.

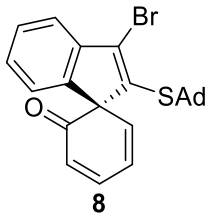
5. References

1. É. Godin, J. Santandrea, A. Caron and S. K. Collins, *Org. Lett.,* 2020, **22**, 5905.

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.

6. Crystal data of compound 8 (CCDC Number = 2289404)





8

Bond precision: C-C = 0.0044 A Wavelength=1.54184

Cell:	a=6.8294(1)	b=14.2435(2)	c=20.7154(2)
	alpha=90	beta=90	gamma=90
Temperature:	100 K		

	Calculated	Reported
Volume	2015.08(5)	2015.08(5)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C24 H23 Br O S	C24 H23 Br O S
Sum formula	C24 H23 Br O S	C24 H23 Br O S
Mr	439.38	439.39
Dx,g cm-3	1.448	1.448
Z	4	4
Mu (mm-1)	3.821	3.821
F000	904.0	904.0
F000'	904.49	
h,k,lmax	8,17,25	8,17,25
Nref	4125[2376]	4078
Tmin,Tmax	0.963,0.963	0.456,1.000
Tmin'	0.963	

Correction method= # Reported T Limits: Tmin=0.456 Tmax=1.000
AbsCorr = MULTI-SCAN

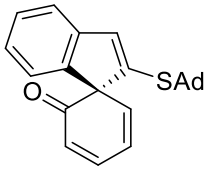
Data completeness= 1.72/0.99 Theta(max)= 74.402

R(reflections)= 0.0258(3892) wR2(reflections)= 0.0655(4078)

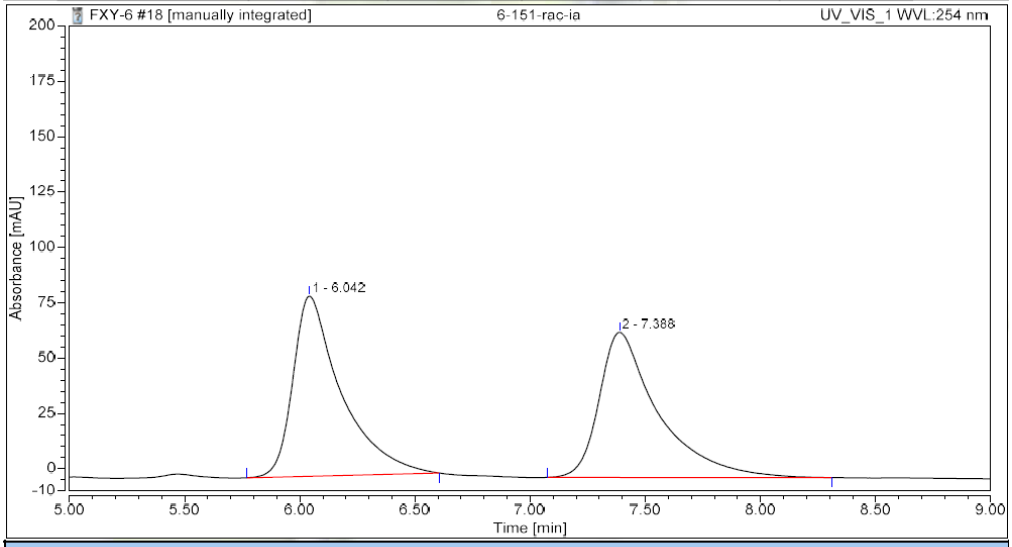
S = 1.038 Npar= 244

7. HPLC Chromatograms

Compound **2a:** HPLC (IA, *n*-hexane/2-propanol = 80/20, v = 1.0 mL/min, λ = 254 nm)



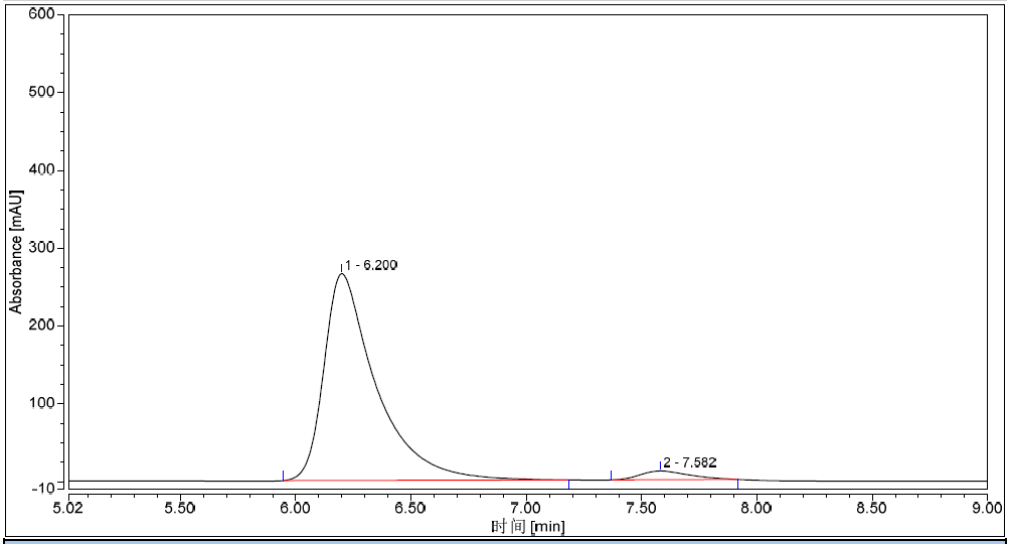
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.042	19.761	81.361	50.41	55.39	n.a.
2		7.388	19.439	65.537	49.59	44.61	n.a.
Total:			**39.200**	**146.898**	**100.00**	**100.00**	

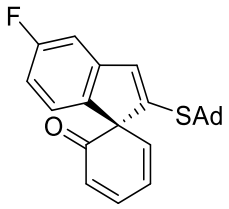
Chromatogram

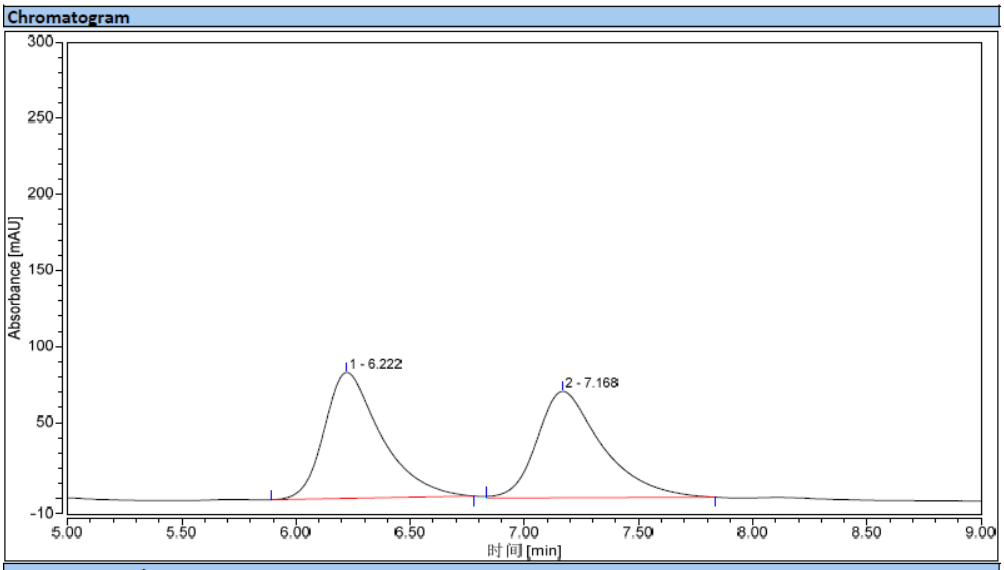


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.200	69.830	265.738	96.16	95.91	n.a.
2		7.582	2.785	11.325	3.84	4.09	n.a.
Total:			**72.615**	**277.064**	**100.00**	**100.00**	

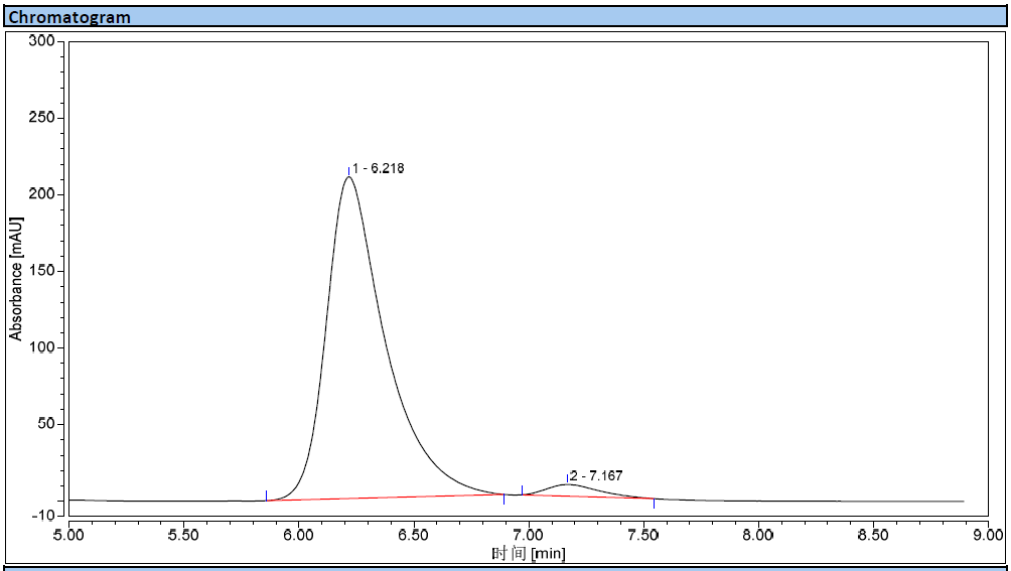
Compound **2b:** HPLC (IA, *n*-hexane/2-propanol = 80/20, v = 1.0 mL/min, λ = 254 nm)





Integration Results

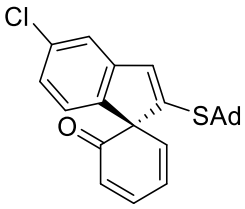
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.222	23.868	82.760	50.81	54.21	n.a.
2		7.168	23.104	69.918	49.19	45.79	n.a.
Total:			**46.972**	**152.678**	**100.00**	**100.00**	



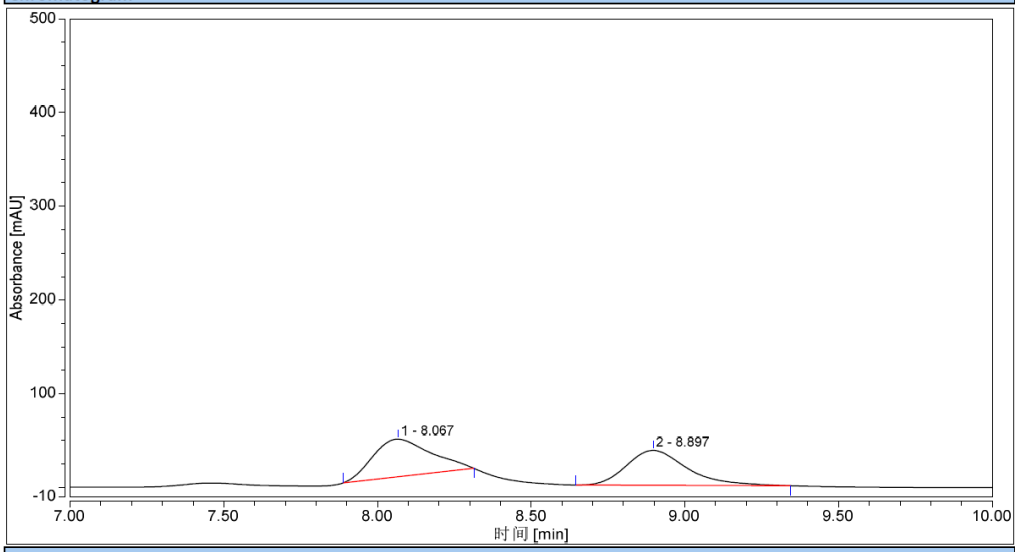
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.218	62.689	210.065	96.92	96.52	n.a.
2		7.167	1.990	7.572	3.08	3.48	n.a.
Total:			**64.678**	**217.637**	**100.00**	**100.00**	

Compound **2c:** HPLC (IC, *n*-hexane/2-propanol = 80/20, v = 1.0 mL/min, λ = 254 nm)



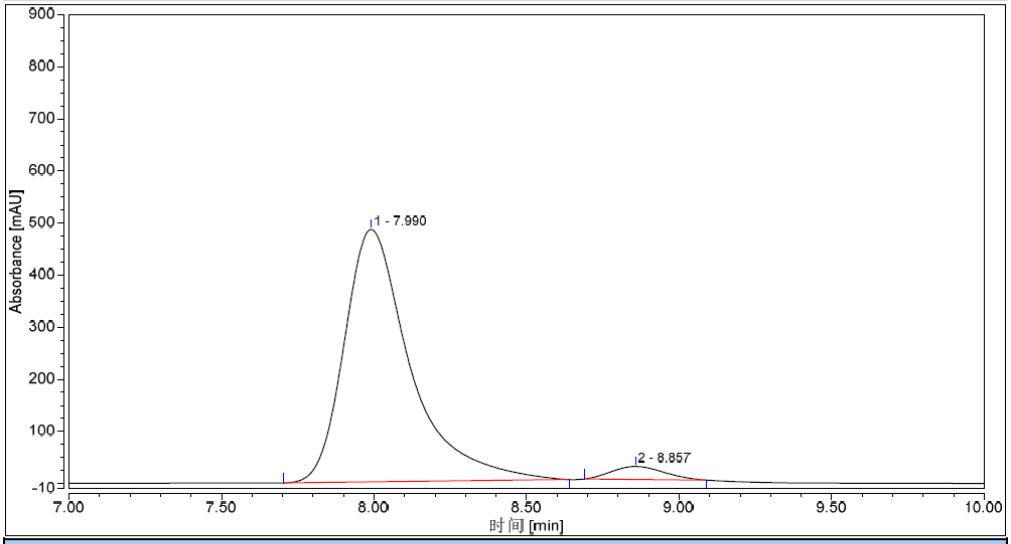
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.067	8.759	40.084	50.73	51.89	n.a.
2		8.897	8.506	37.171	49.27	48.11	n.a.
Total:			**17.264**	**77.255**	**100.00**	**100.00**	

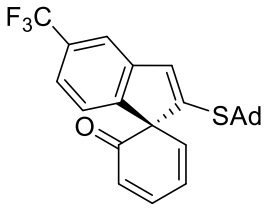
Chromatogram



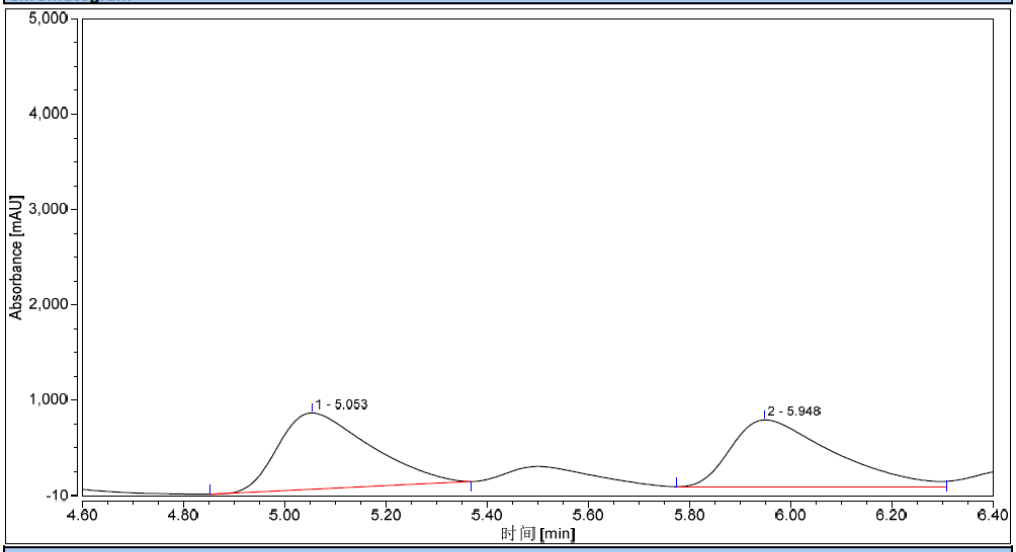
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.990	121.552	484.711	96.10	95.12	n.a.
2		8.857	4.936	24.854	3.90	4.88	n.a.
Total:			**126.488**	**509.565**	**100.00**	**100.00**	

Compound **2d:** HPLC (IA, *n*-hexane/2-propanol = 80/20, v = 1.0 mL/min, λ = 254 nm)



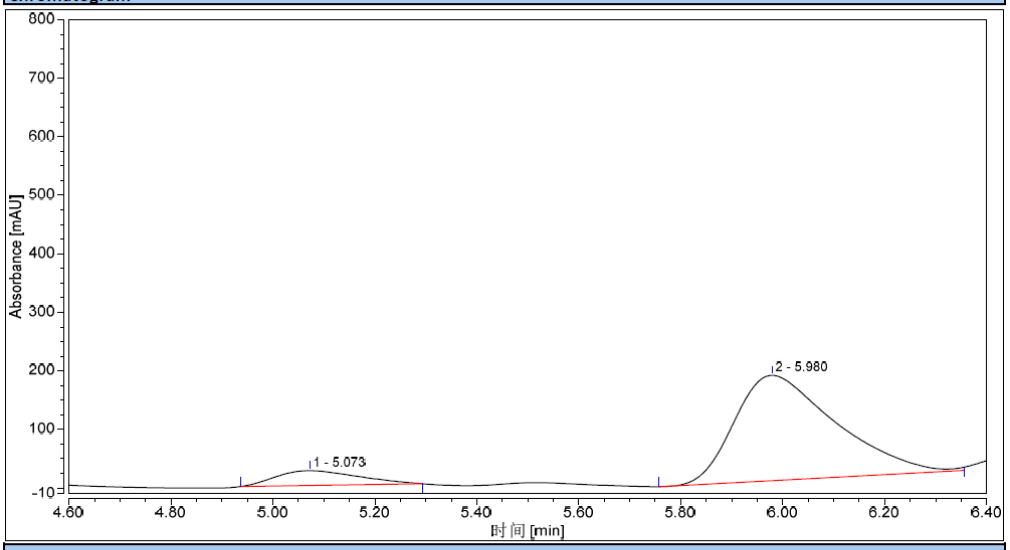
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.053	166.860	800.166	50.30	53.29	n.a.
2		5.948	164.898	701.315	49.70	46.71	n.a.
Total:			**331.757**	**1501.481**	**100.00**	**100.00**	

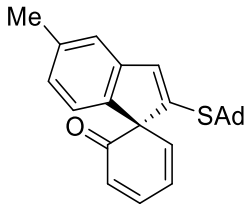
Chromatogram



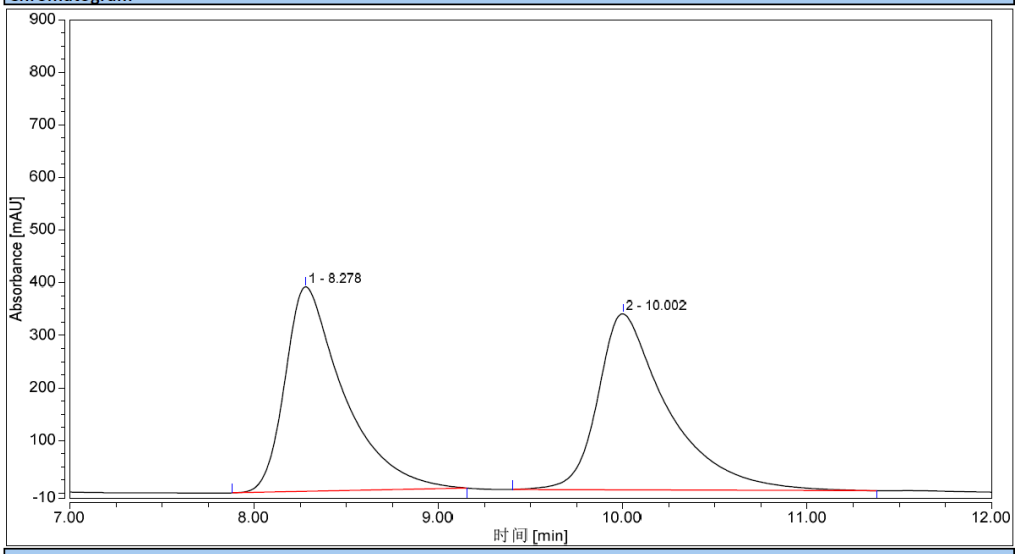
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.073	4.701	25.247	10.24	12.31	n.a.
2		5.980	41.194	179.761	89.76	87.69	n.a.
Total:			**45.895**	**205.007**	**100.00**	**100.00**	

Compound **2e:** HPLC (IA, *n*-hexane/2-propanol = 80/20, v = 1.0 mL/min, λ = 254 nm)



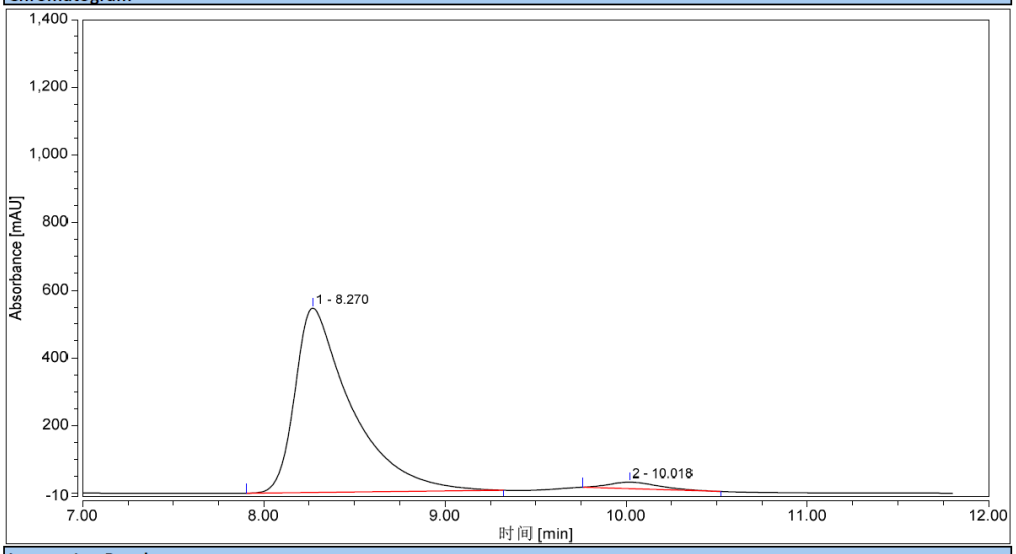
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.278	143.419	388.531	49.32	53.74	n.a.
2		10.002	147.371	334.394	50.68	46.26	n.a.
Total:			**290.790**	**722.925**	**100.00**	**100.00**	

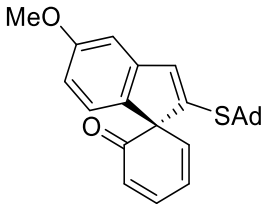
Chromatogram



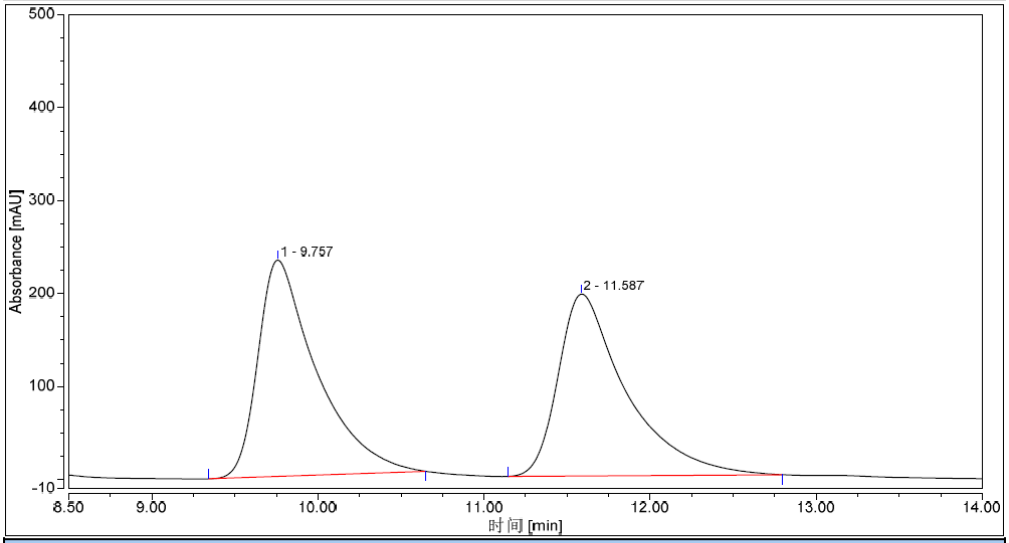
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.270	196.794	545.114	96.94	96.57	n.a.
2		10.018	6.214	19.378	3.06	3.43	n.a.
Total:			**203.008**	**564.493**	**100.00**	**100.00**	

Compound **2f:** HPLC (IA, *n*-hexane/2-propanol = 80/20, v = 1.0 mL/min, λ = 254 nm)



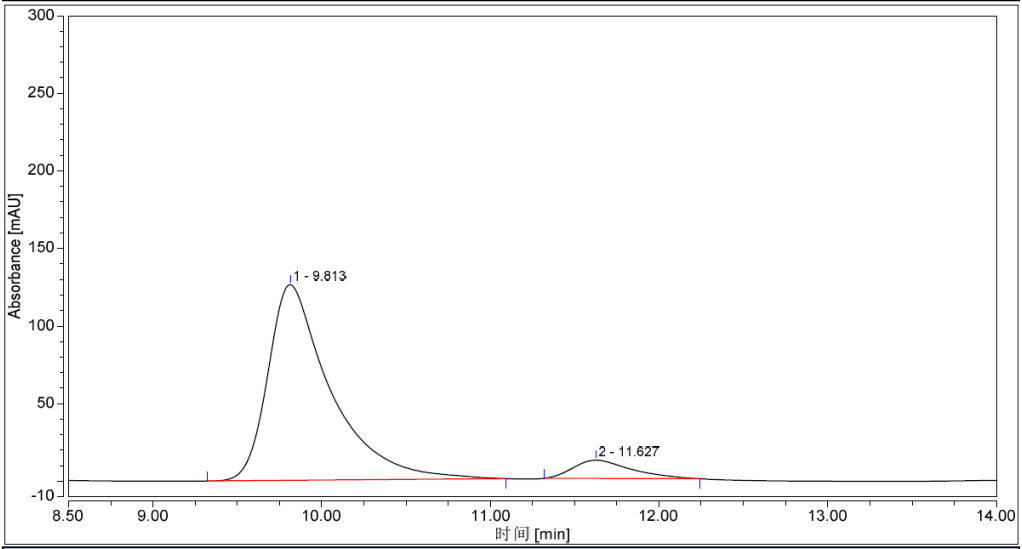
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.757	95.311	232.798	50.65	54.33	n.a.
2		11.587	92.850	195.702	49.35	45.67	n.a.
Total:			**188.161**	**428.500**	**100.00**	**100.00**	

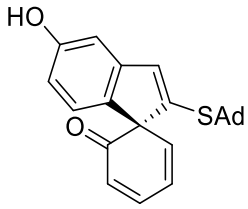
Chromatogram

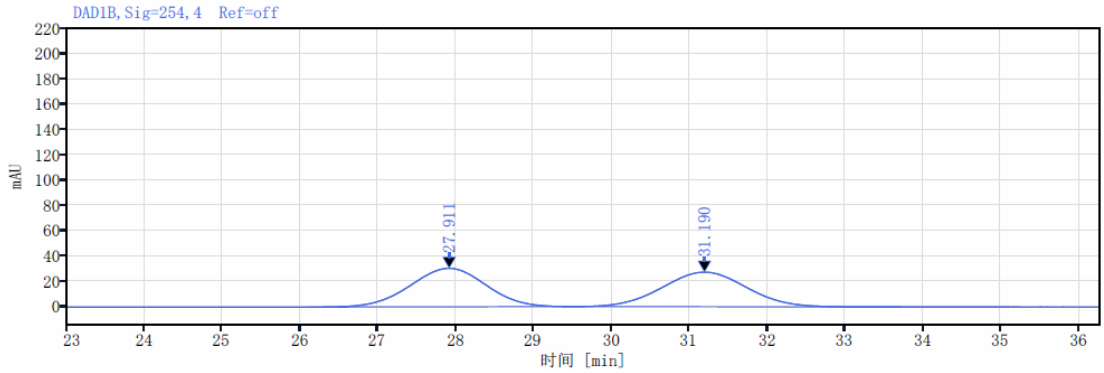


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.813	54.387	126.146	92.08	91.47	n.a.
2		11.627	4.678	11.758	7.92	8.53	n.a.
Total:			**59.065**	**137.904**	**100.00**	**100.00**	

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





信号: DAD1B, Sig=254, 4 Ref=off

保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%	名称
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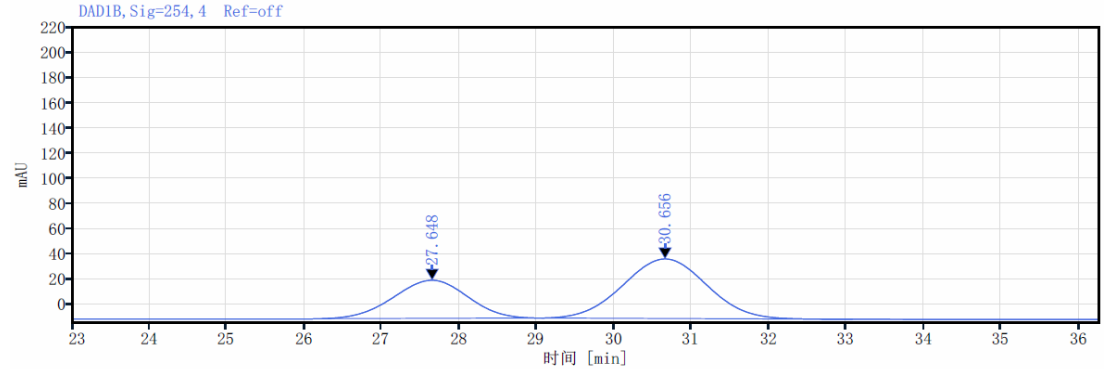
31.190	BB	4.23	2075.16	27.42	49.99	
		总和	4150.90			



信号: DAD1B, Sig=254, 4 Ref=off

保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%	名称
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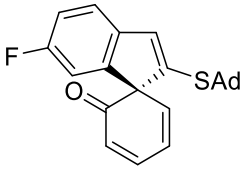
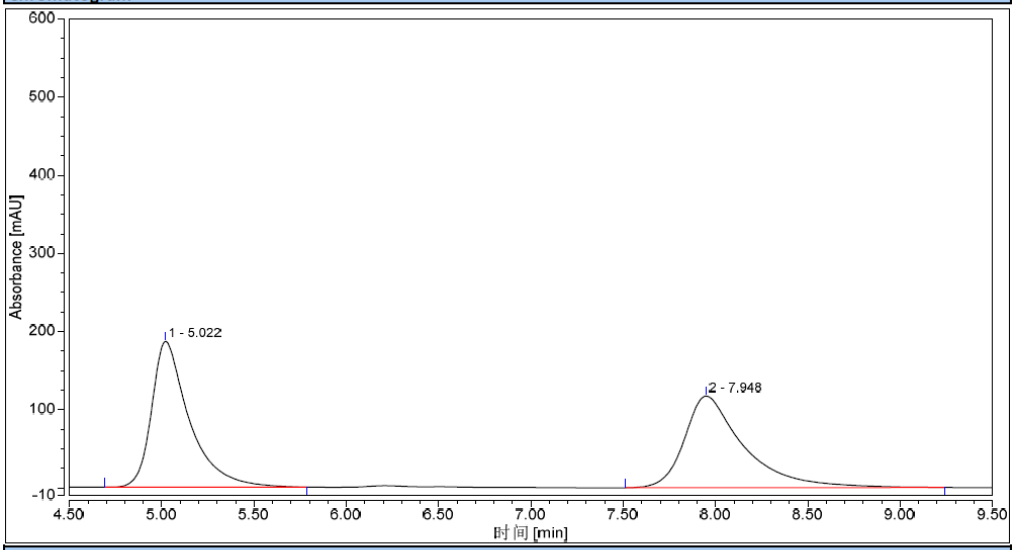
30.656	MM m	4.02	3571.44	47.36	63.98	
		总和	5581.99			

Compound **2h:** HPLC (IA, *n*-hexane/2-propanol = 80/20, v = 1.0 mL/min, λ = 254 nm)



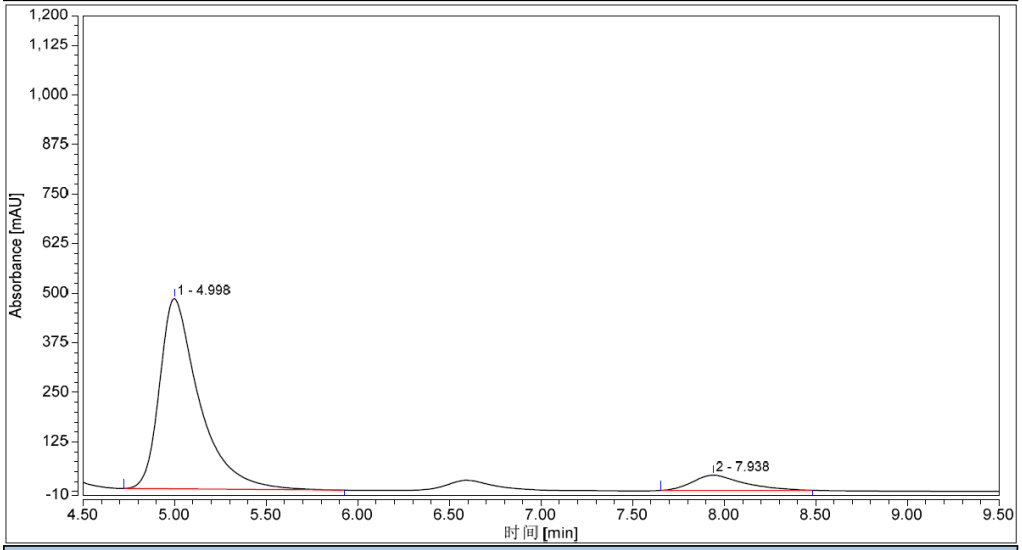
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.022	44.342	186.670	50.30	61.41	n.a.
2		7.948	43.811	117.324	49.70	38.59	n.a.
Total:			**88.154**	**303.994**	**100.00**	**100.00**	

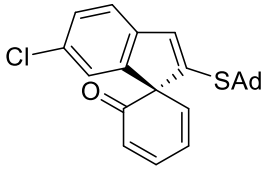
Chromatogram

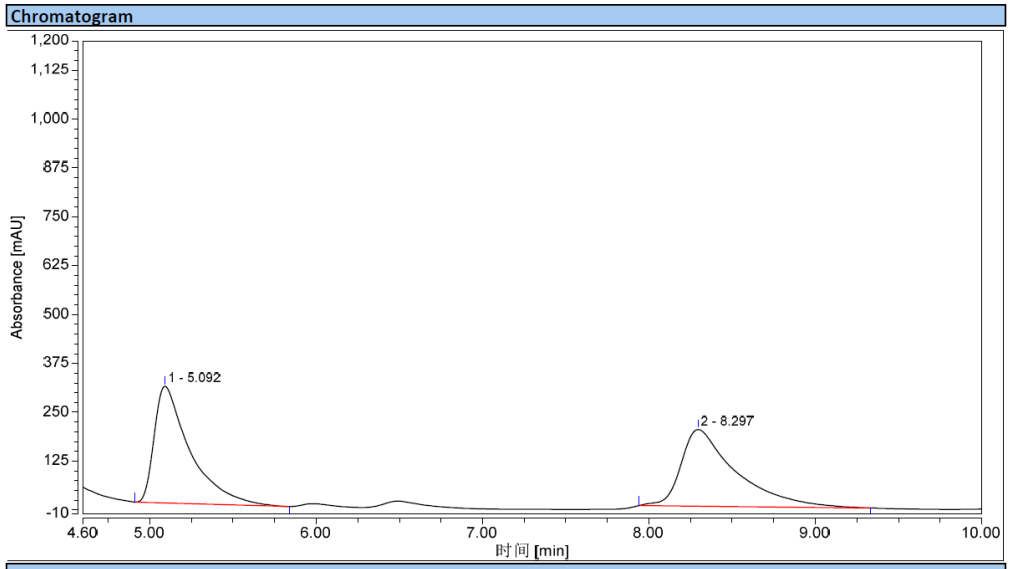


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.998	120.402	479.697	90.76	92.64	n.a.
2		7.938	12.260	38.109	9.24	7.36	n.a.
Total:			**132.662**	**517.806**	**100.00**	**100.00**	

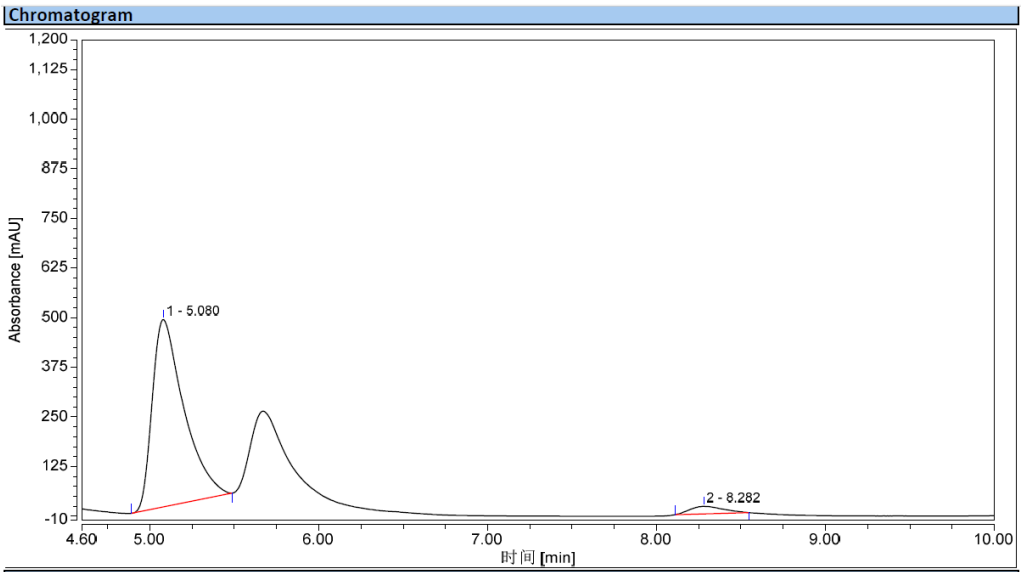
Compound **2i:** HPLC (IA, *n*-hexane/2-propanol = 80/20, v = 1.0 mL/min, λ = 254 nm)





Integration Results

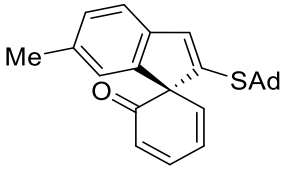
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.092	74.188	298.603	49.84	60.36	n.a.
2		8.297	74.658	196.135	50.16	39.64	n.a.
Total:			**148.846**	**494.738**	**100.00**	**100.00**	



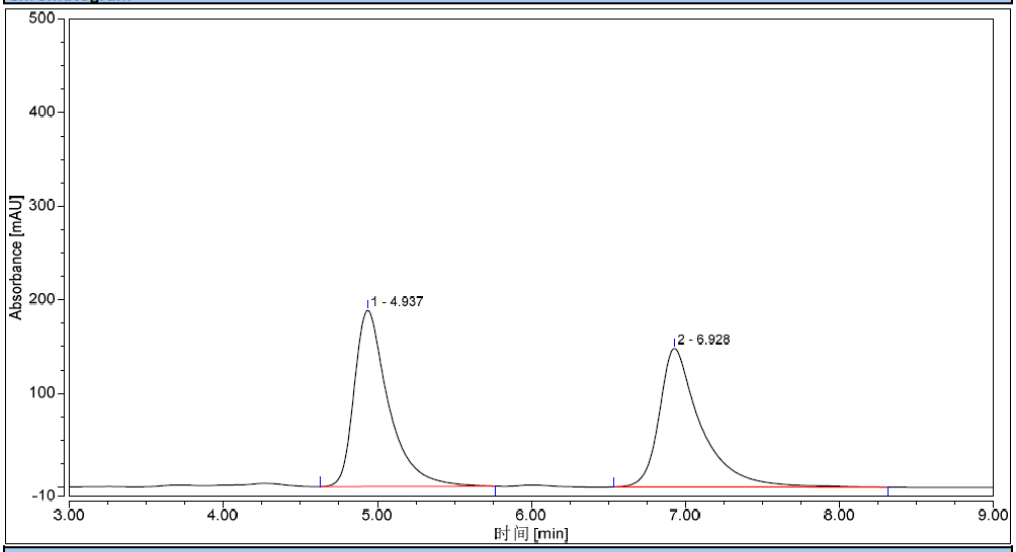
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.080	102.625	471.988	96.01	96.19	n.a.
2		8.282	4.261	18.720	3.99	3.81	n.a.
Total:			**106.885**	**490.708**	**100.00**	**100.00**	

Compound **2j:** HPLC (IA, *n*-hexane/2-propanol = 80/20, v = 1.0 mL/min, λ = 254 nm)



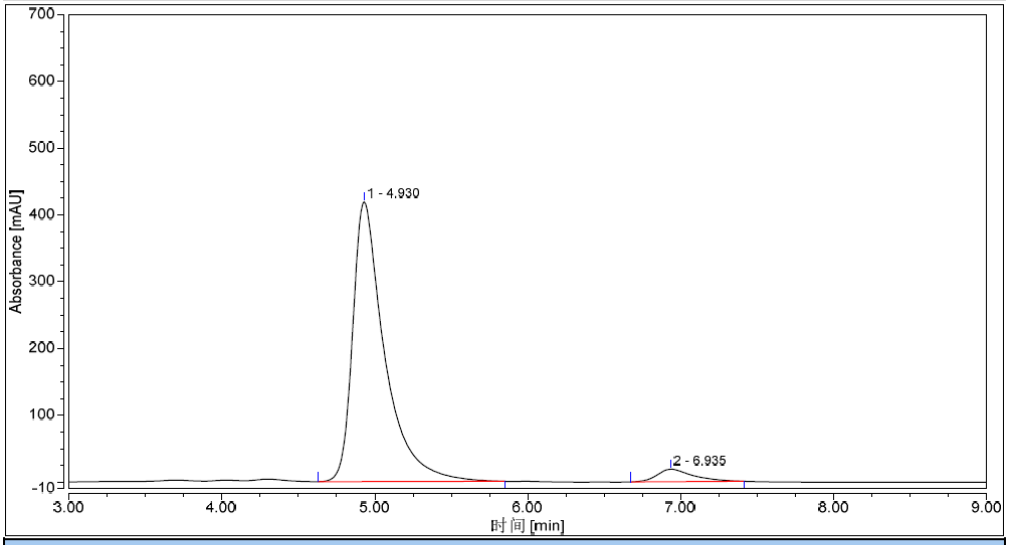
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.937	48.488	188.239	51.23	56.00	n.a.
2		6.928	46.167	147.919	48.77	44.00	n.a.
Total:			**94.655**	**336.157**	**100.00**	**100.00**	

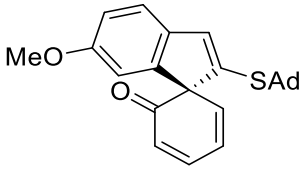
Chromatogram



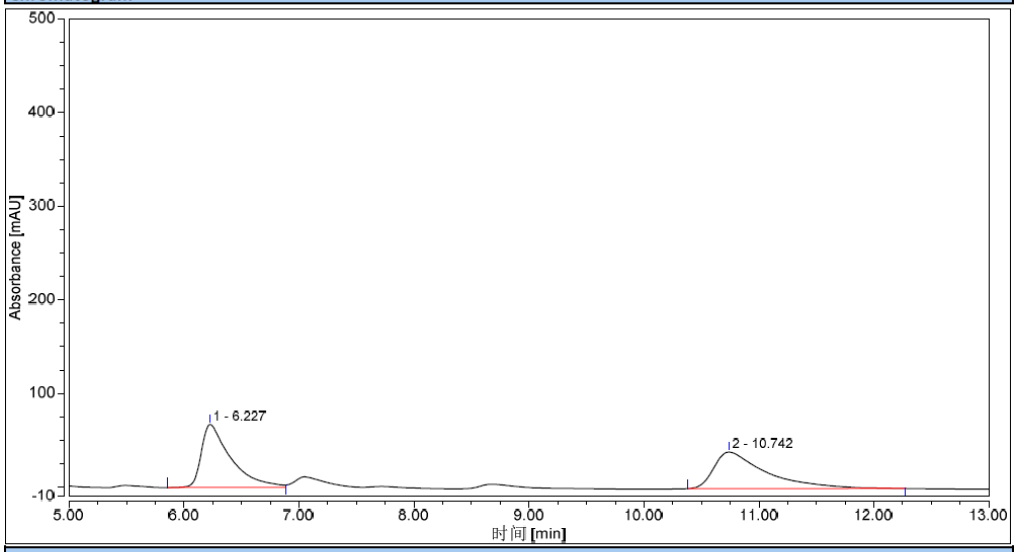
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.930	101.194	419.213	95.23	95.73	n.a.
2		6.935	5.069	18.700	4.77	4.27	n.a.
Total:			**106.263**	**437.912**	**100.00**	**100.00**	

Compound **2k:** HPLC (IA, *n*-hexane/2-propanol = 80/20, v = 1.0 mL/min, λ = 254 nm)



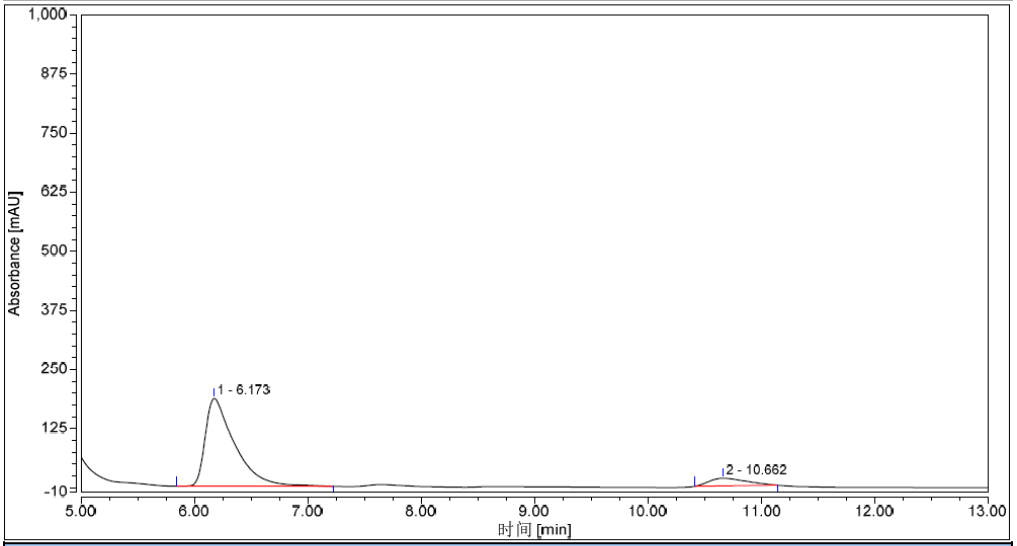
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.227	19.936	67.240	49.24	63.20	n.a.
2		10.742	20.550	39.152	50.76	36.80	n.a.
Total:			**40.486**	**106.391**	**100.00**	**100.00**	

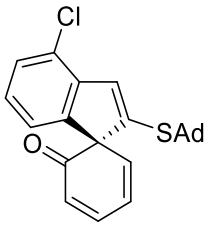
Chromatogram



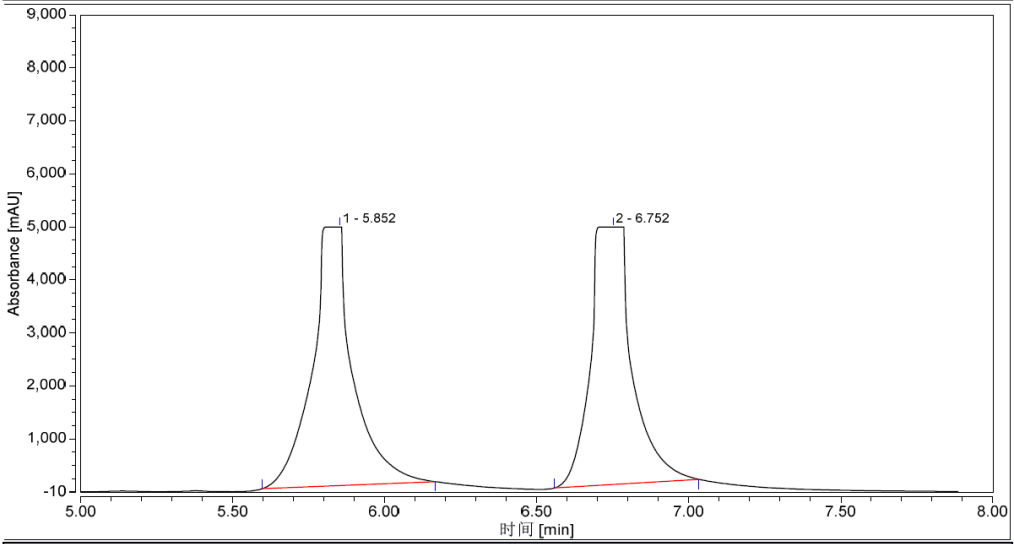
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.173	55.332	185.468	90.11	92.07	n.a.
2		10.662	6.070	15.978	9.89	7.93	n.a.
Total:			**61.402**	**201.446**	**100.00**	**100.00**	

Compound **2l:** HPLC (IC, *n*-hexane/2-propanol = 80/20, v = 1.0 mL/min, λ = 254 nm)



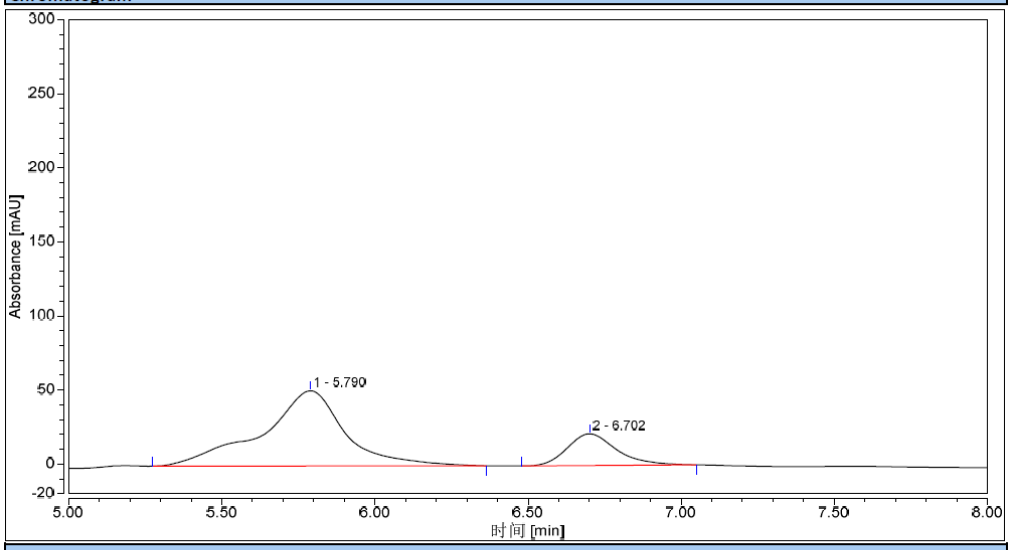
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.852	763.856	4879.609	49.53	50.10	n.a.
2		6.752	778.307	4859.288	50.47	49.90	n.a.
Total:			**1542.163**	**9738.897**	**100.00**	**100.00**	

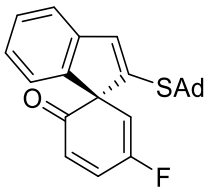
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.790	15.927	50.807	79.96	70.37	n.a.
2		6.702	3.991	21.397	20.04	29.63	n.a.
Total:			**19.918**	**72.203**	**100.00**	**100.00**	

Compound **2m:** HPLC (IA, *n*-hexane/2-propanol = 80/20, v = 1.0 mL/min, λ = 254 nm)



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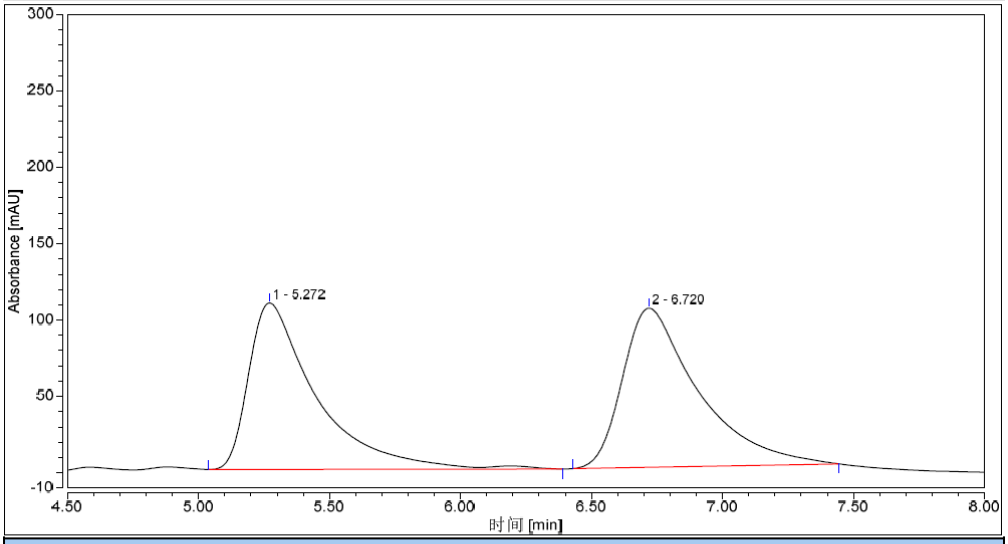
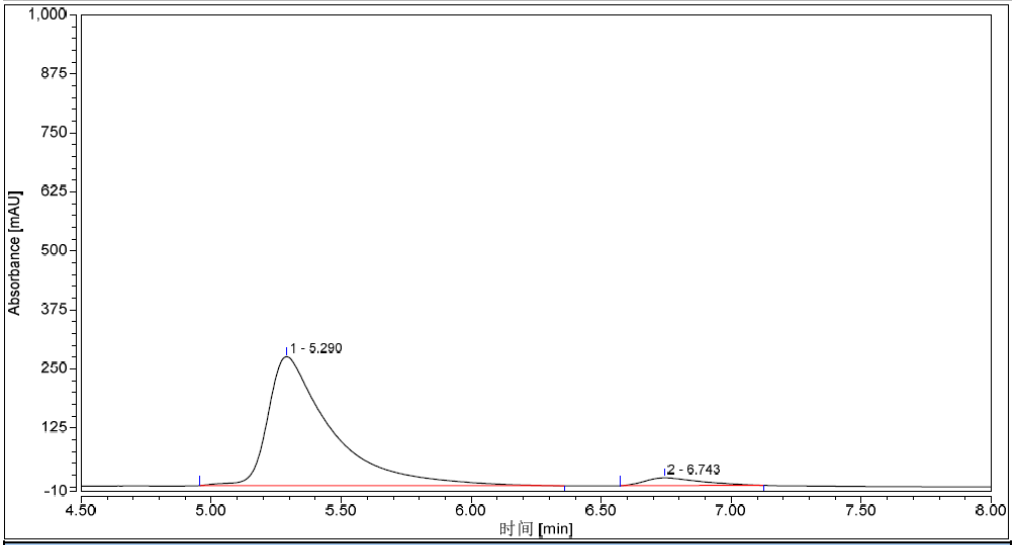


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.272	32.554	109.021	48.31	51.13	n.a.
2		6.720	34.825	104.219	51.69	48.87	n.a.
Total:			**67.379**	**213.240**	**100.00**	**100.00**	

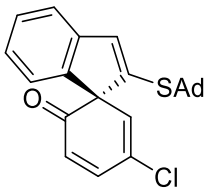
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.290	77.046	273.374	95.03	94.38	n.a.
2		6.743	4.030	16.293	4.97	5.62	n.a.
Total:			**81.076**	**289.667**	**100.00**	**100.00**	

Compound **2n:** HPLC (IA, *n*-hexane/2-propanol = 80/20, v = 1.0 mL/min, λ = 254 nm)



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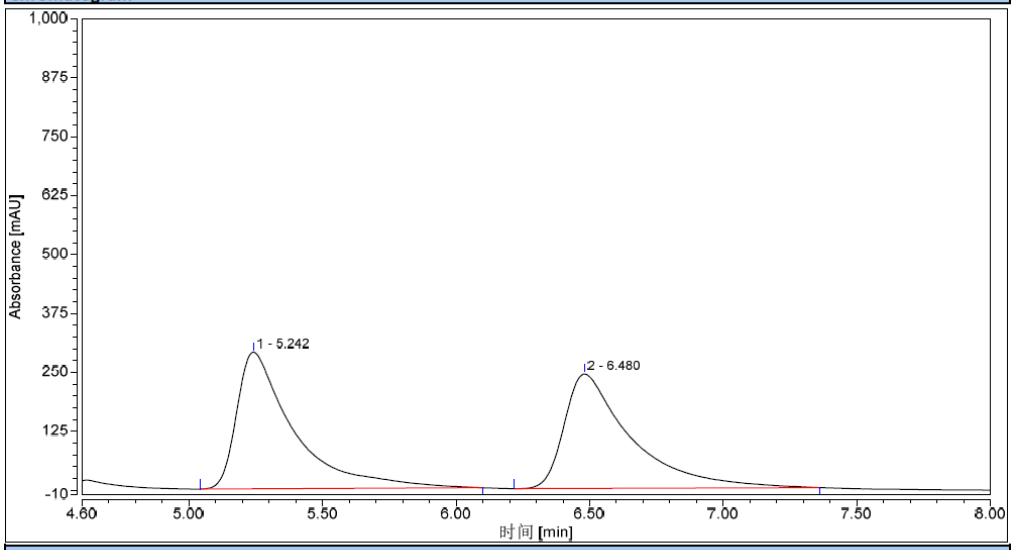
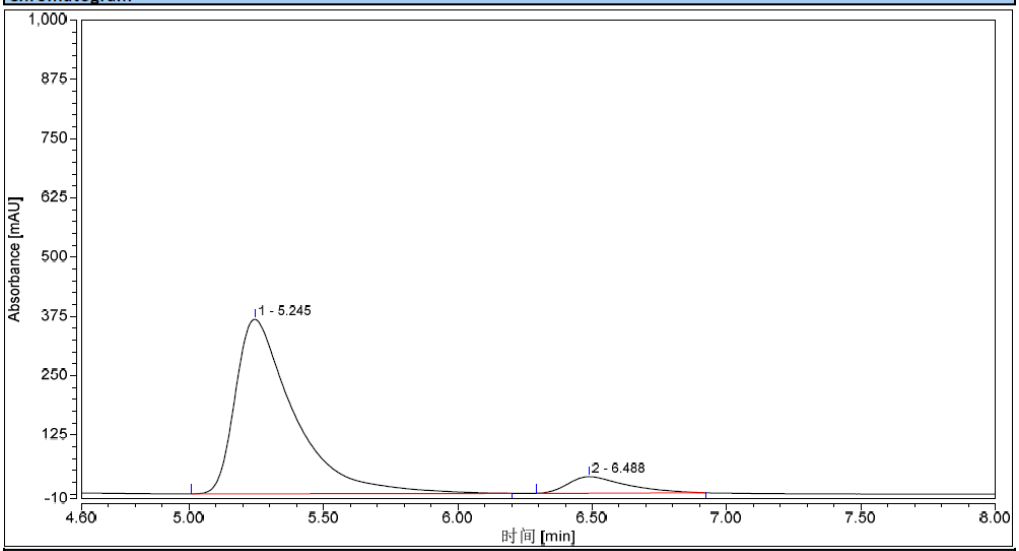


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.242	71.369	289.844	50.54	54.46	n.a.
2		6.480	69.834	242.411	49.46	45.54	n.a.
Total:			**141.203**	**532.255**	**100.00**	**100.00**	

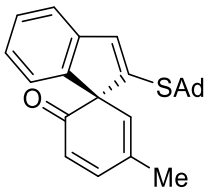
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.245	93.367	367.973	91.51	91.41	n.a.
2		6.488	8.666	34.558	8.49	8.59	n.a.
Total:			**102.033**	**402.530**	**100.00**	**100.00**	

Compound **2o:** HPLC (IA, *n*-hexane/2-propanol = 80/20, v = 1.0 mL/min, λ = 254 nm)



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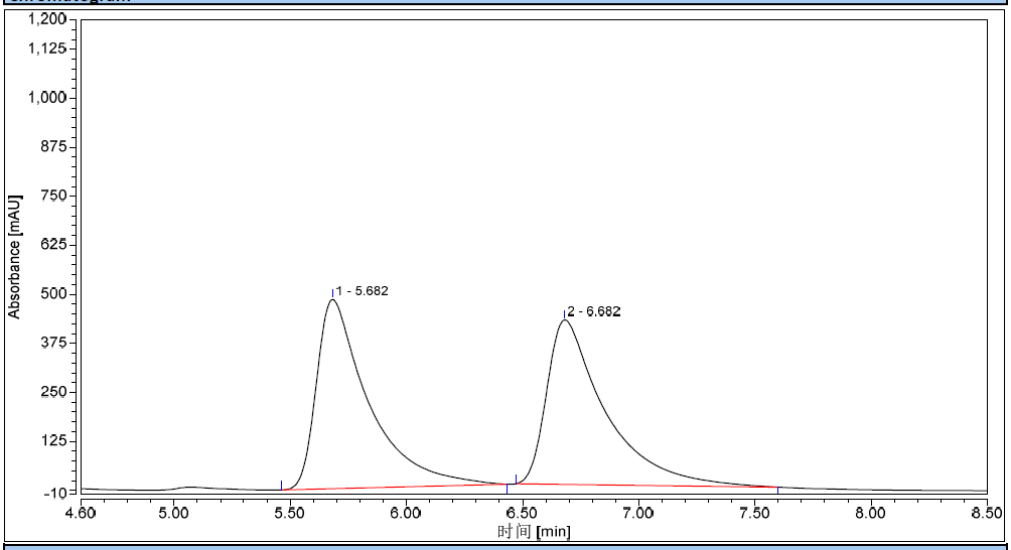
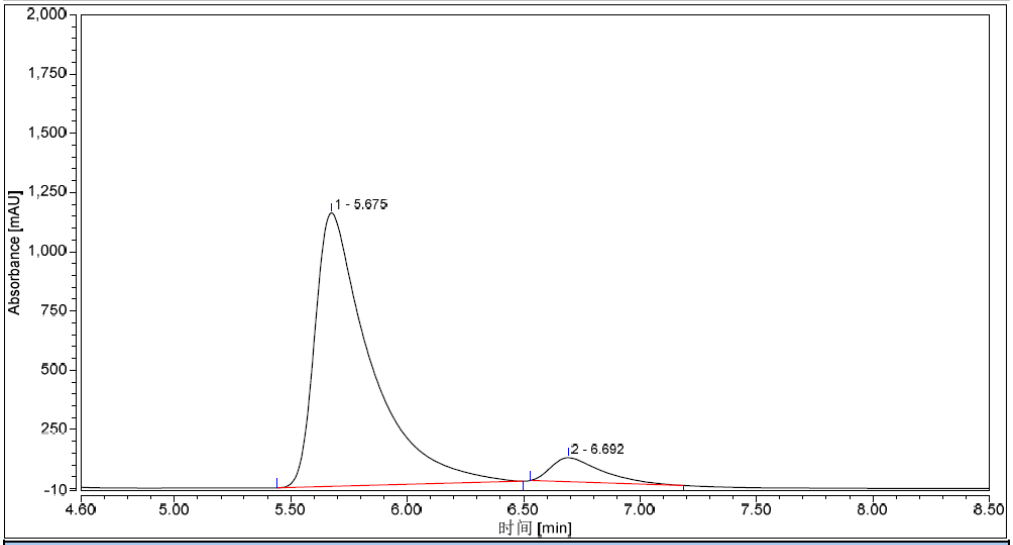


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.682	125.433	482.448	50.69	53.51	n.a.
2		6.682	122.014	419.155	49.31	46.49	n.a.
Total:			**247.448**	**901.603**	**100.00**	**100.00**	

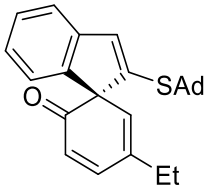
Chromatogram



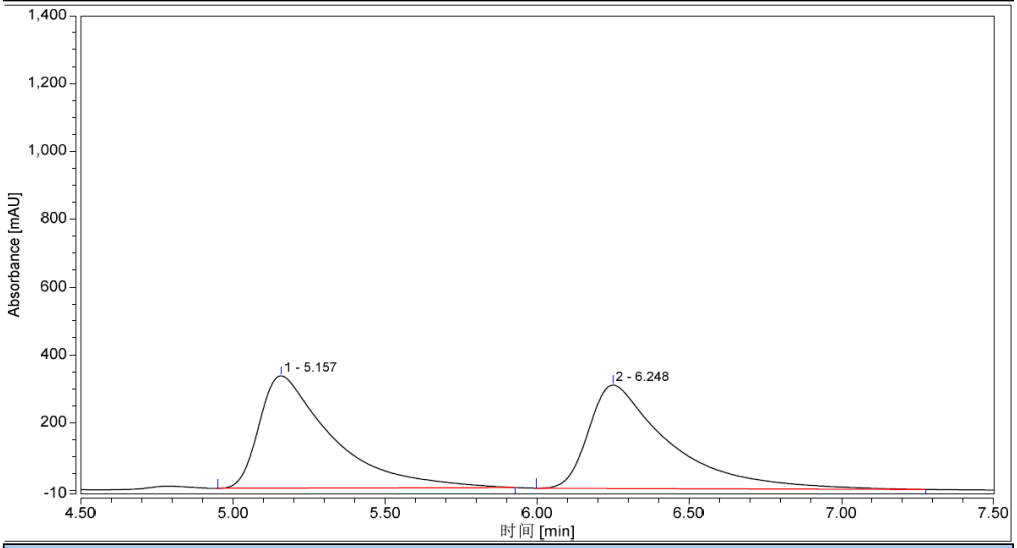
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.675	318.353	1154.973	92.57	91.95	n.a.
2		6.692	25.538	101.070	7.43	8.05	n.a.
Total:			**343.892**	**1256.043**	**100.00**	**100.00**	

Compound **2p:** HPLC (IA, *n*-hexane/2-propanol = 80/20, v = 1.0 mL/min, λ = 254 nm)



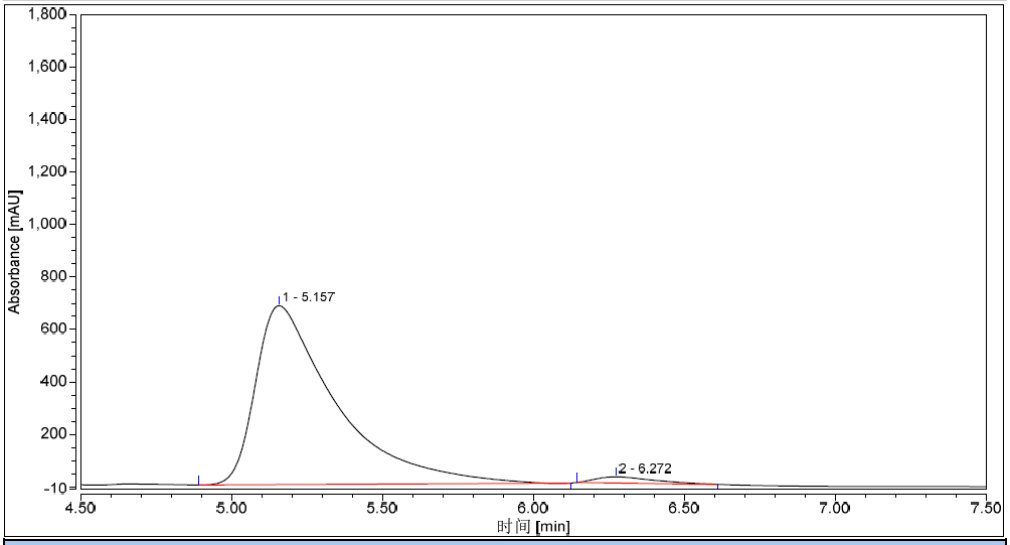
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.157	91.644	331.114	49.61	52.08	n.a.
2		6.248	93.077	304.614	50.39	47.92	n.a.
Total:			**184.722**	**635.728**	**100.00**	**100.00**	

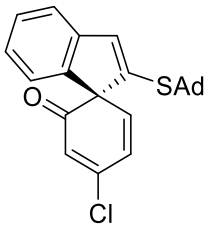
Chromatogram



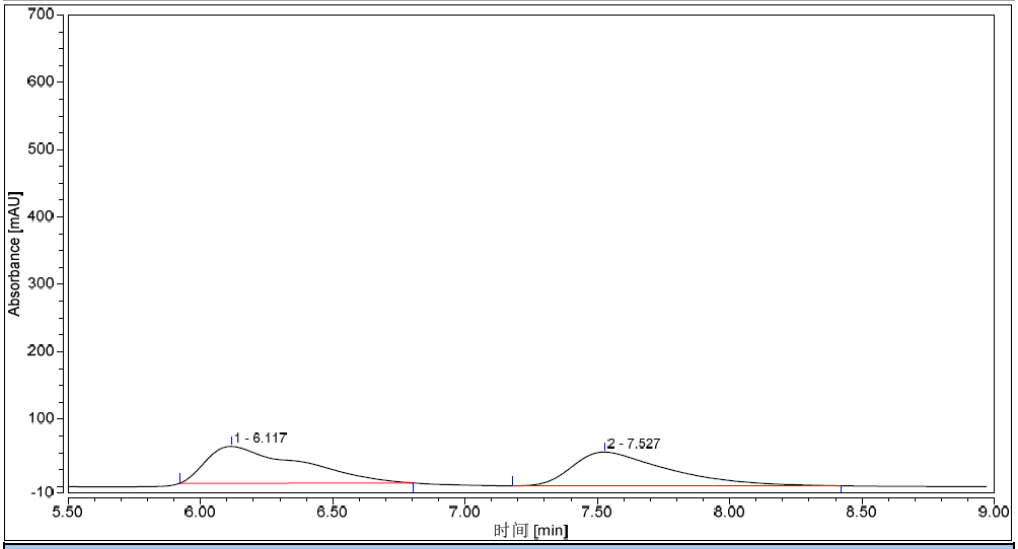
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.157	209.694	682.194	97.52	96.62	n.a.
2		6.272	5.334	23.845	2.48	3.38	n.a.
Total:			**215.028**	**706.039**	**100.00**	**100.00**	

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



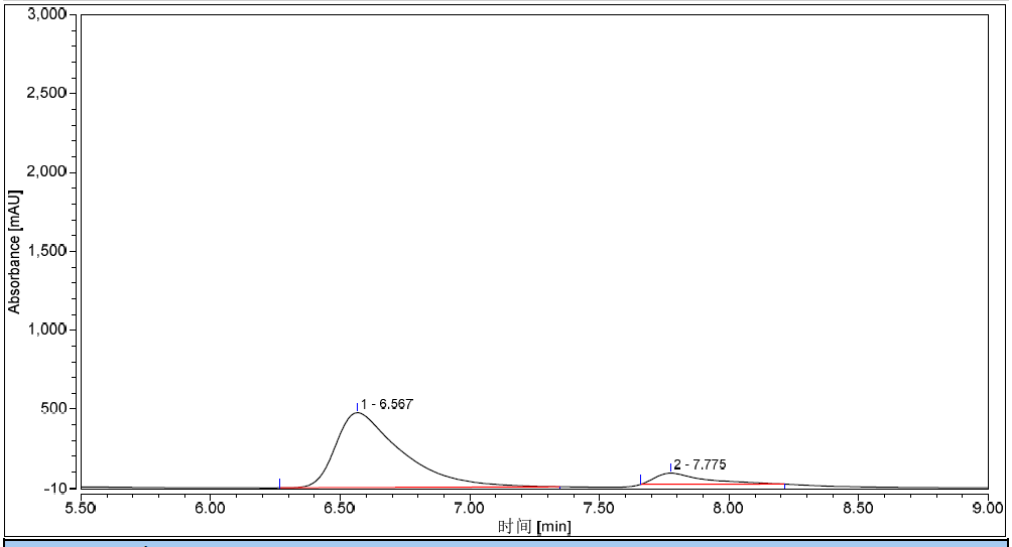
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.117	22.278	54.528	51.61	52.10	n.a.
2		7.527	20.887	50.137	48.39	47.90	n.a.
Total:			**43.165**	**104.665**	**100.00**	**100.00**	

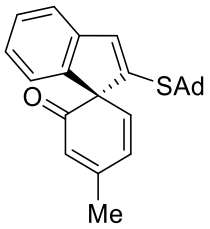
Chromatogram



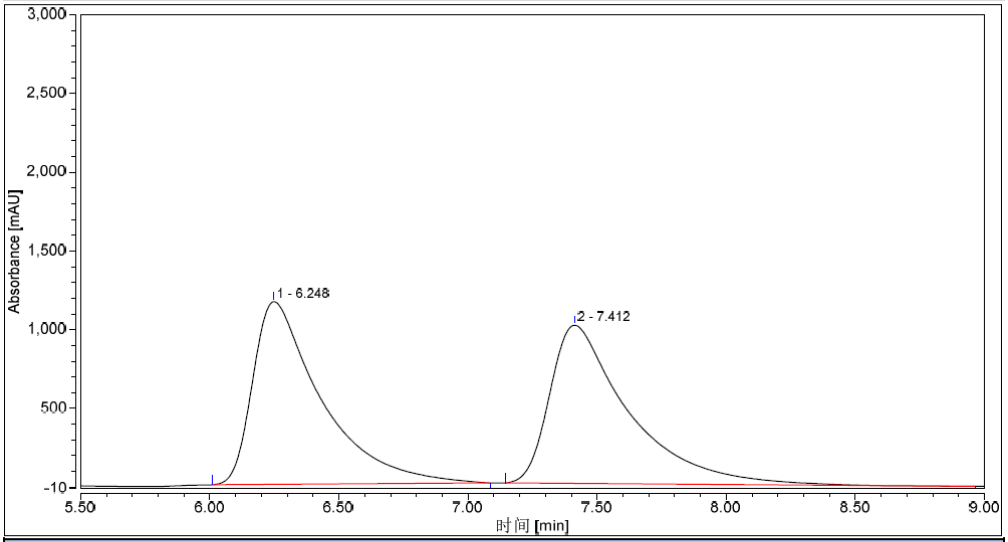
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.567	139.423	474.498	90.05	87.15	n.a.
2		7.775	15.402	69.982	9.95	12.85	n.a.
Total:			**154.826**	**544.480**	**100.00**	**100.00**	

Compound **2r:** HPLC (IA, *n*-hexane/2-propanol = 80/20, v = 1.0 mL/min, λ = 254 nm)



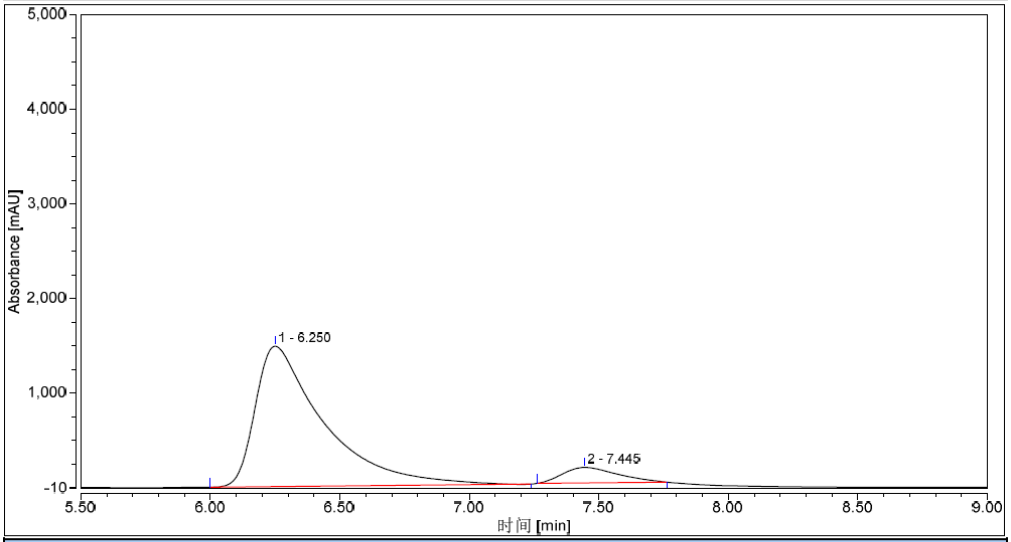
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.248	355.908	1159.694	50.16	53.61	n.a.
2		7.412	353.626	1003.611	49.84	46.39	n.a.
Total:			**709.534**	**2163.305**	**100.00**	**100.00**	

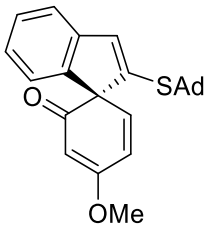
Chromatogram



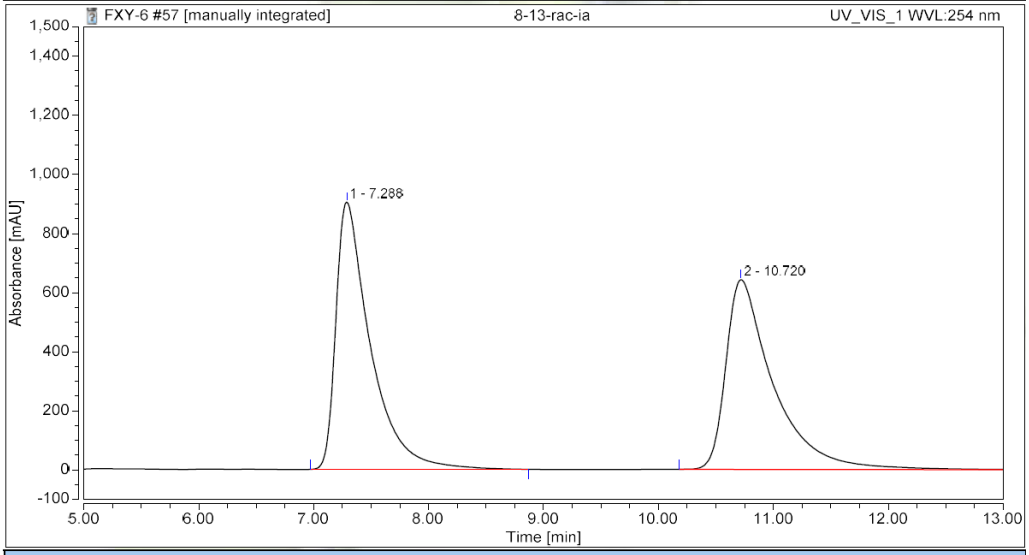
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.250	452.407	1483.592	91.90	90.10	n.a.
2		7.445	39.864	163.074	8.10	9.90	n.a.
Total:			**492.270**	**1646.667**	**100.00**	**100.00**	

Compound **2s:** HPLC (IA, *n*-hexane/2-propanol = 80/20, v = 1.0 mL/min, λ = 254 nm)



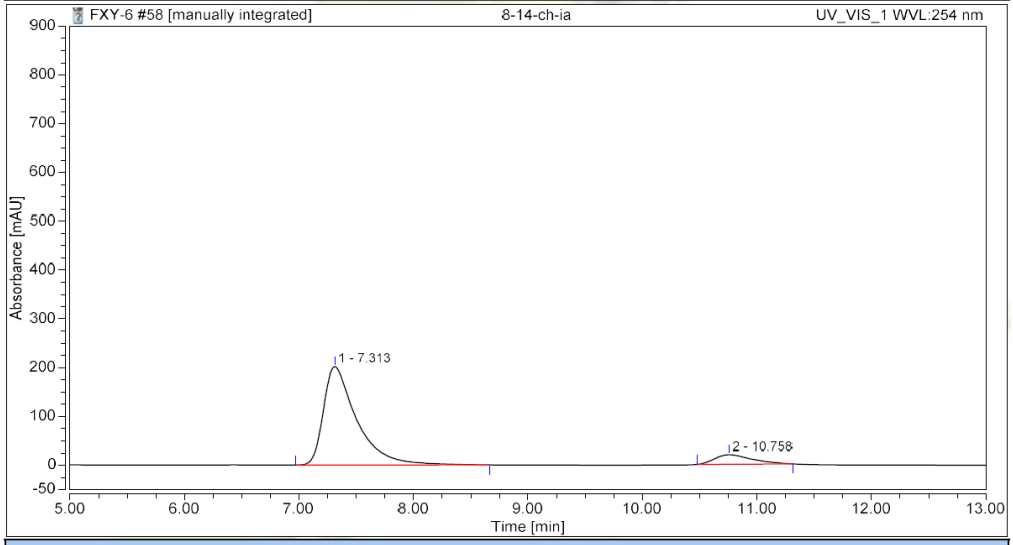
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.288	314.743	905.023	50.64	58.49	n.a.
2		10.720	306.766	642.171	49.36	41.51	n.a.
Total:			**621.509**	**1547.193**	**100.00**	**100.00**	

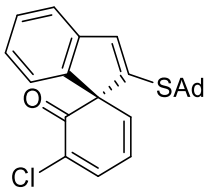
Chromatogram



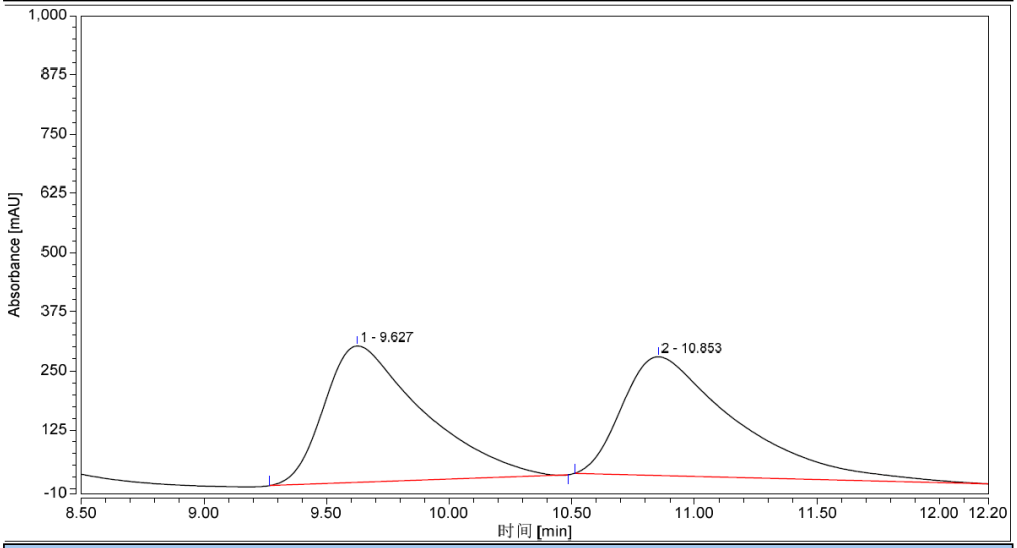
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.313	68.007	201.758	90.30	91.21	n.a.
2		10.758	7.306	19.435	9.70	8.79	n.a.
Total:			**75.312**	**221.193**	**100.00**	**100.00**	

Compound **2t:** HPLC (IA, *n*-hexane/2-propanol = 95/5, v = 1.0 mL/min, λ = 254 nm)



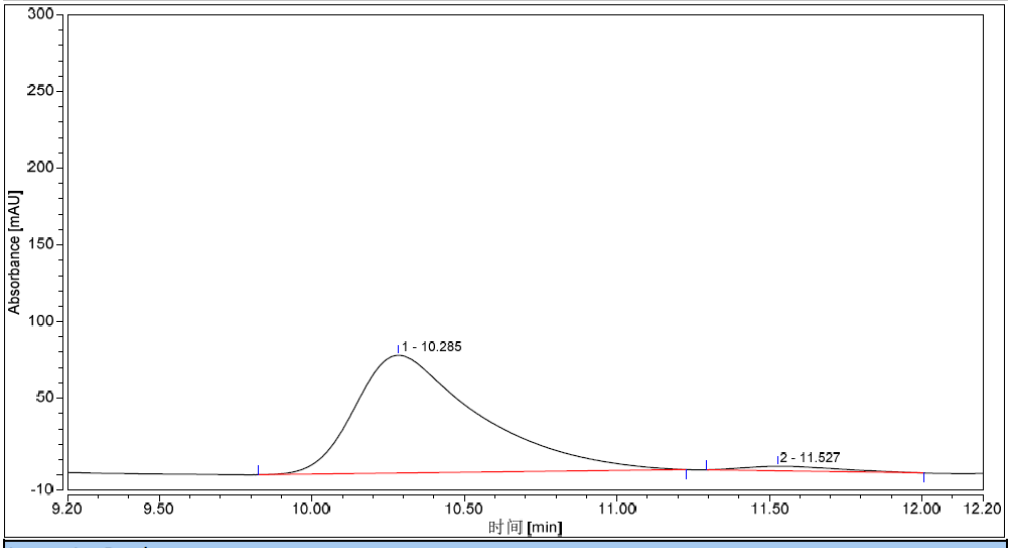
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.627	133.639	288.080	49.82	53.49	n.a.
2		10.853	134.594	250.466	50.18	46.51	n.a.
Total:			**268.233**	**538.546**	**100.00**	**100.00**	

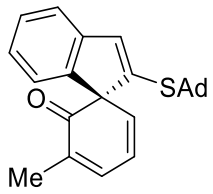
Chromatogram

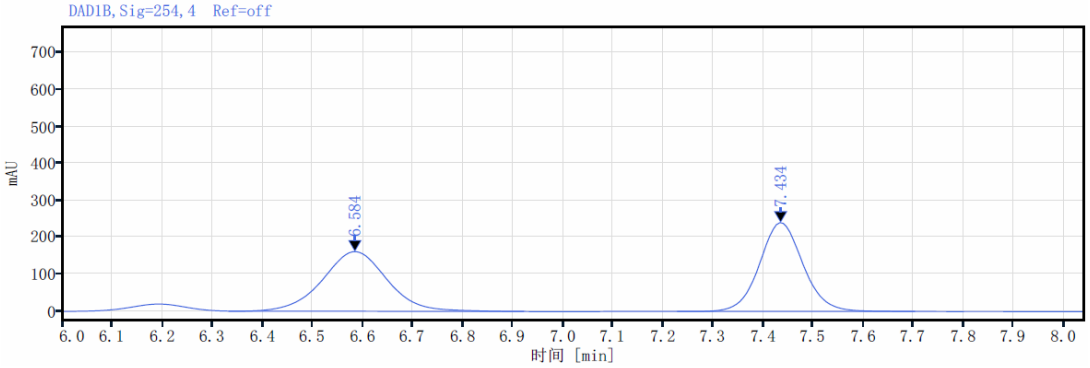


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.285	36.113	76.785	97.15	96.30	n.a.
2		11.527	1.060	2.951	2.85	3.70	n.a.
Total:			**37.173**	**79.736**	**100.00**	**100.00**	

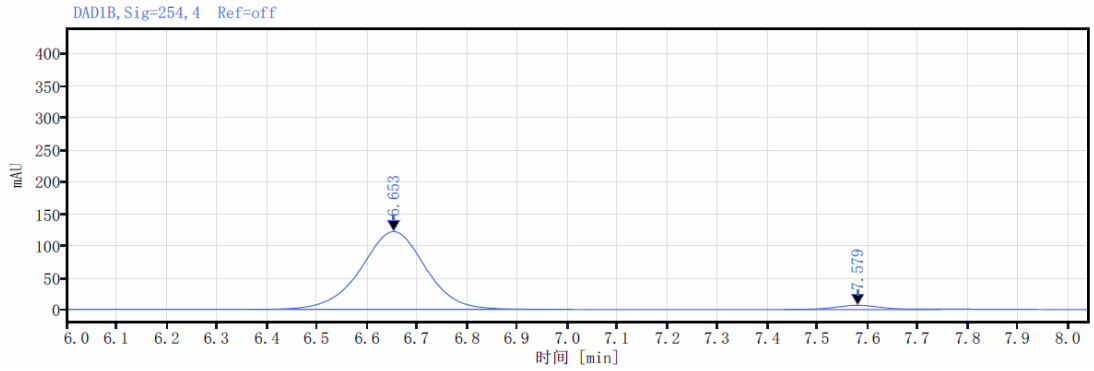
Compound **2u:** HPLC (IA, *n*-hexane/2-propanol = 90/10, v = 1.0 mL/min, λ = 254 nm)





信号: DAD1B, Sig=254, 4 Ref=off

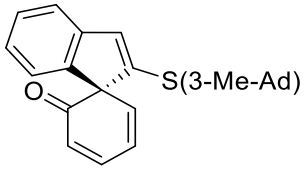
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%	名称
6.584	MM m	0.59	1454.36	161.72	50.02	
7.434	MM m	0.47	1453.43	240.70	49.98	
		总和	2907.79			



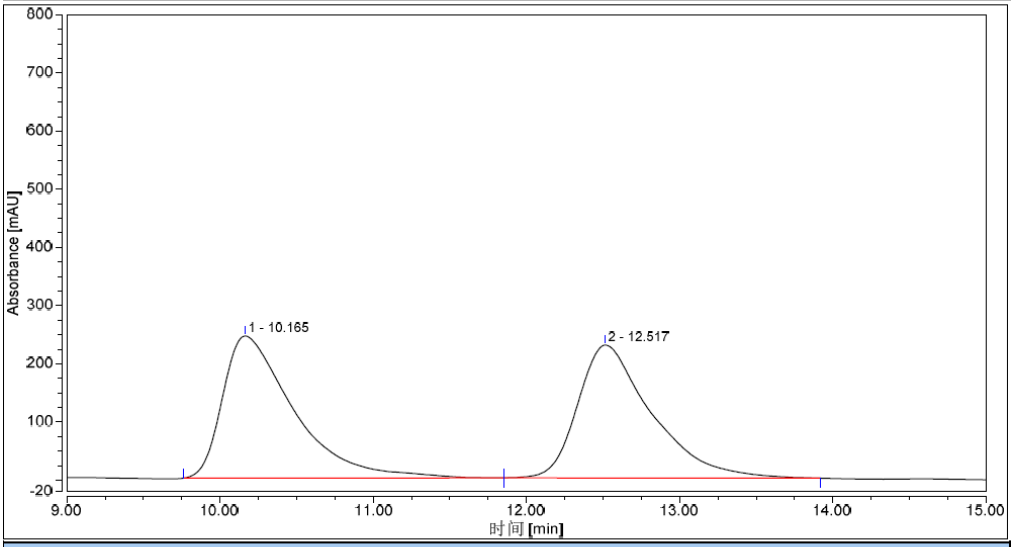
信号: DAD1B, Sig=254, 4 Ref=off

保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%	名称
6.653	MM m	0.65	1096.52	121.76	96.21	
7.579	MM m	0.31	43.20	6.49	3.79	
		总和	1139.72			

Compound **2v:** HPLC (IA, *n*-hexane/2-propanol = 95/5, v = 1.0 mL/min, λ = 254 nm)



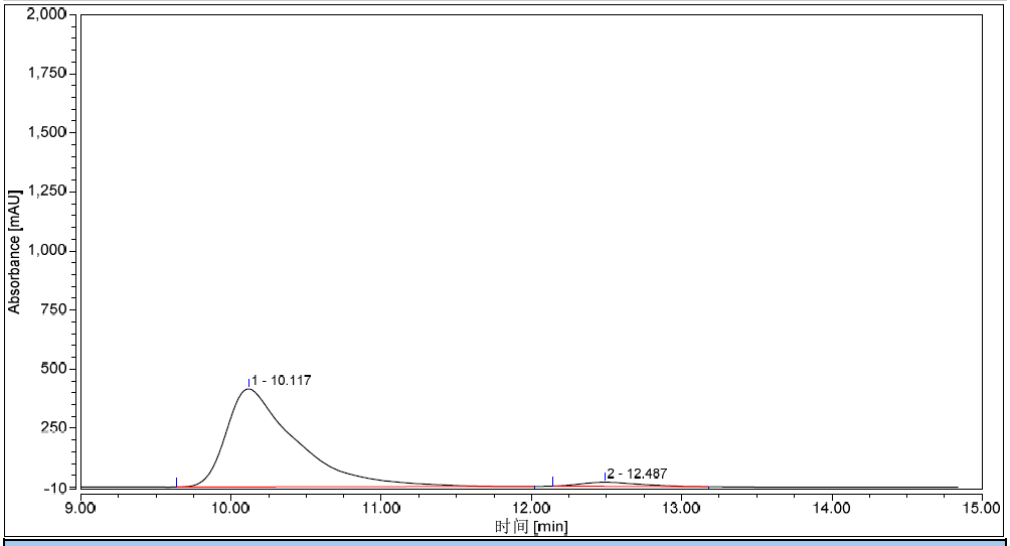
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.165	130.918	244.482	50.69	51.69	n.a.
2		12.517	127.363	228.506	49.31	48.31	n.a.
Total:			**258.281**	**472.987**	**100.00**	**100.00**	

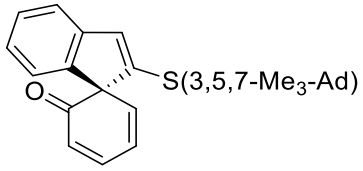
Chromatogram



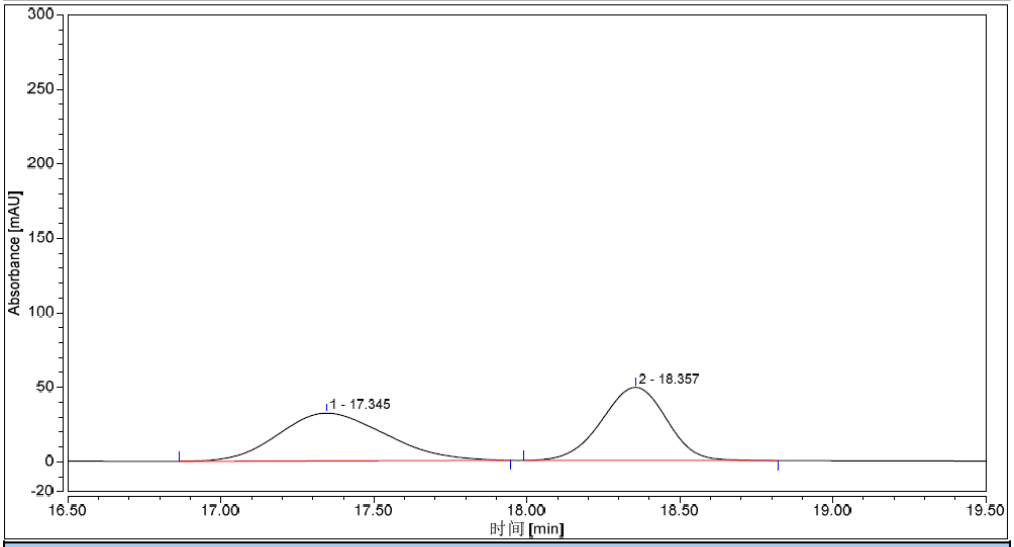
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.117	223.112	415.381	96.58	96.01	n.a.
2		12.487	7.891	17.269	3.42	3.99	n.a.
Total:			**231.003**	**432.650**	**100.00**	**100.00**	

Compound **2w:** HPLC (IC, *n*-hexane/2-propanol = 95/5, v = 1.0 mL/min, λ = 254 nm)



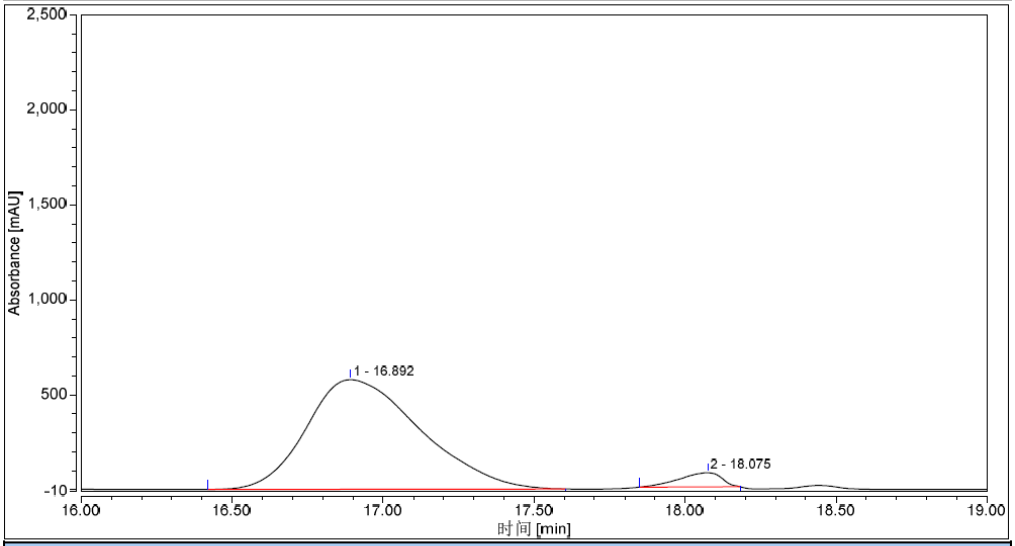
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17.345	12.969	32.069	51.83	39.53	n.a.
2		18.357	12.054	49.053	48.17	60.47	n.a.
Total:			**25.023**	**81.122**	**100.00**	**100.00**	

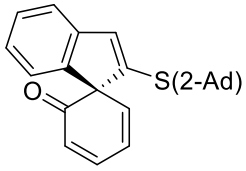
Chromatogram



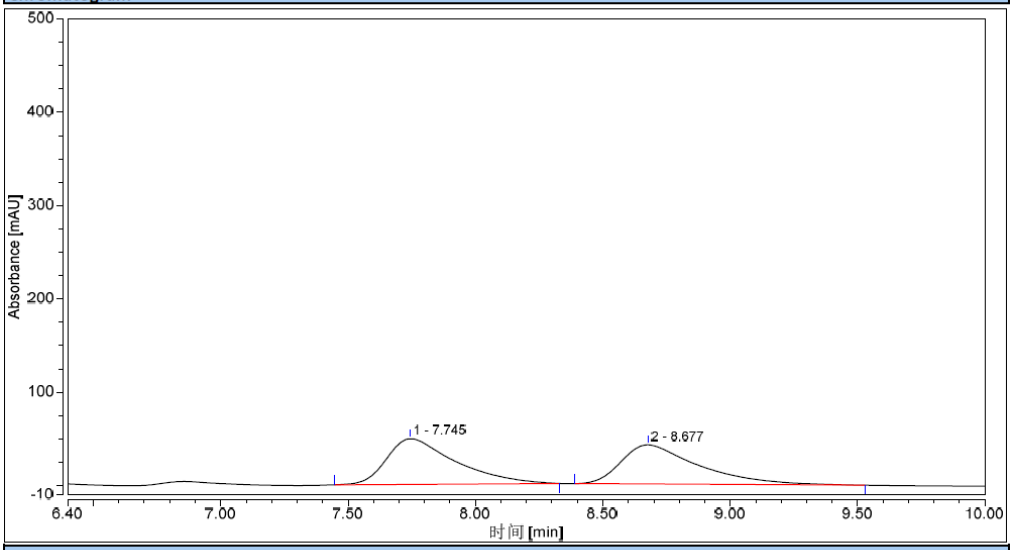
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.892	252.921	577.213	95.42	88.58	n.a.
2		18.075	12.141	74.387	4.58	11.42	n.a.
Total:			**265.062**	**651.600**	**100.00**	**100.00**	

Compound **2x:** HPLC (IA, *n*-hexane/2-propanol = 80/20, v = 1.0 mL/min, λ = 254 nm)



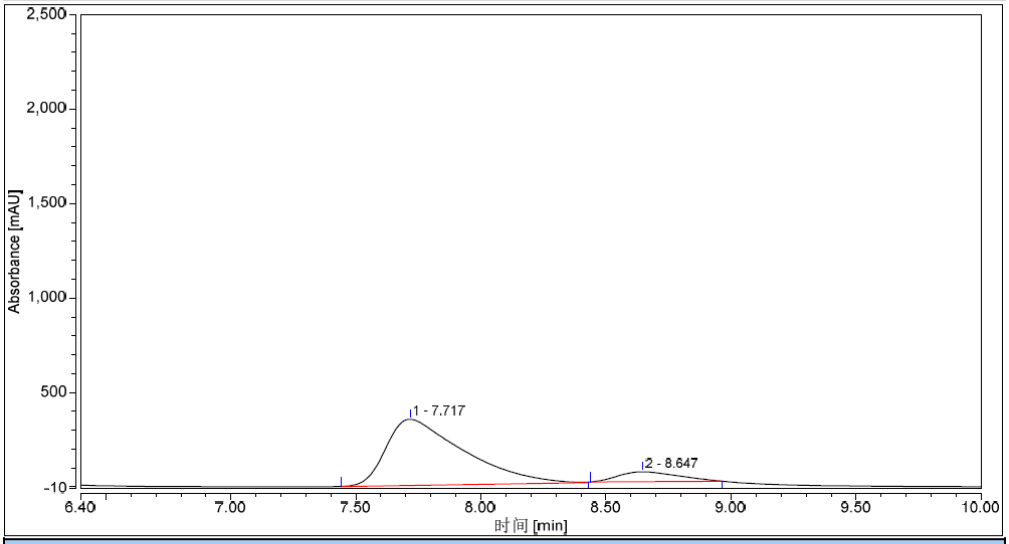
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.745	15.240	48.806	50.87	53.82	n.a.
2		8.677	14.719	41.873	49.13	46.18	n.a.
Total:			**29.959**	**90.680**	**100.00**	**100.00**	

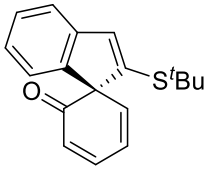
Chromatogram



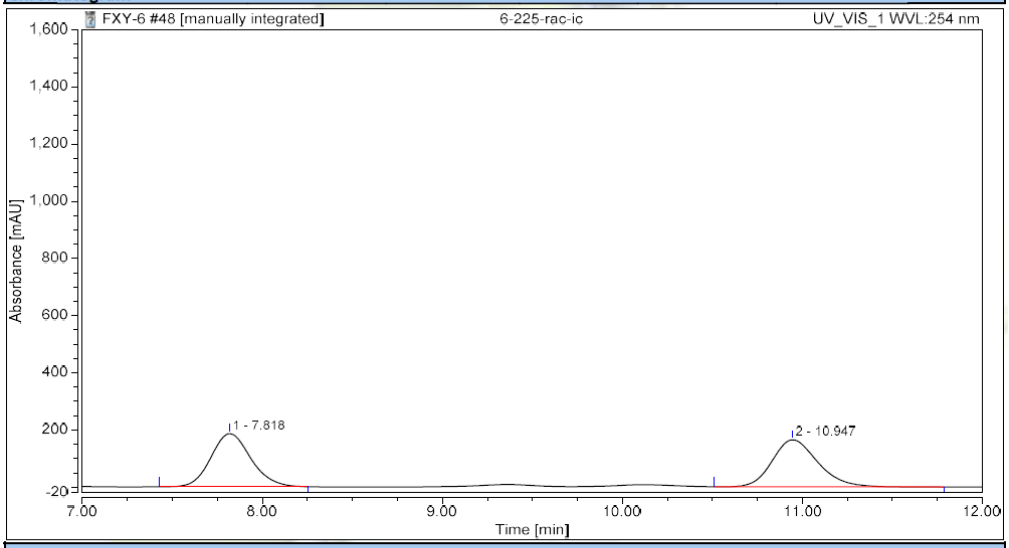
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.717	125.891	350.574	89.86	87.14	n.a.
2		8.647	14.211	51.717	10.14	12.86	n.a.
Total:			**140.102**	**402.291**	**100.00**	**100.00**	

Compound **2y:** HPLC (IC, *n*-hexane/2-propanol = 80/20, v = 1.0 mL/min, λ = 254 nm)



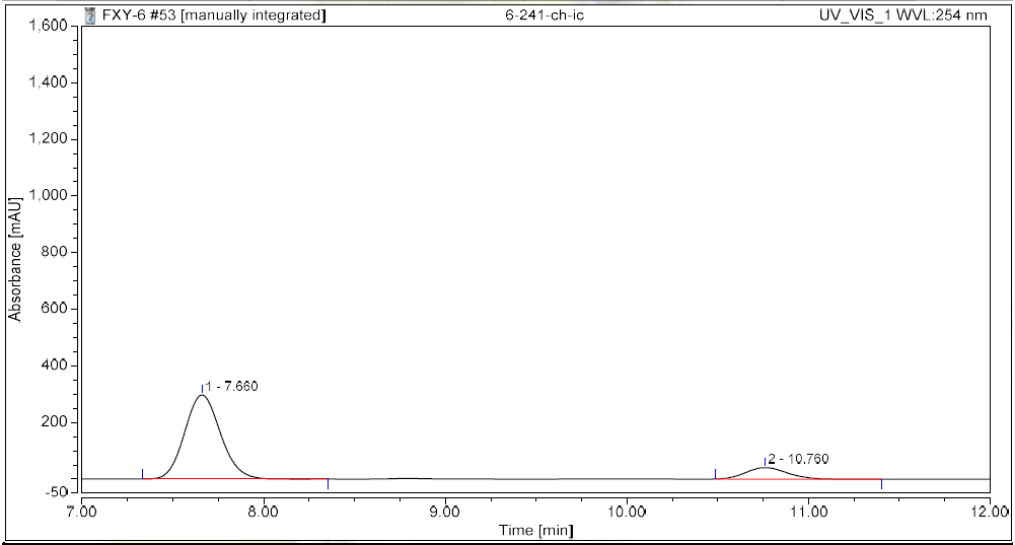
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.818	47.640	185.405	49.73	53.00	n.a.
2		10.947	48.160	164.383	50.27	47.00	n.a.
Total:			**95.800**	**349.787**	**100.00**	**100.00**	

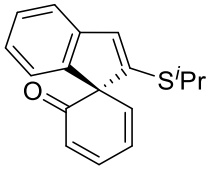
Chromatogram

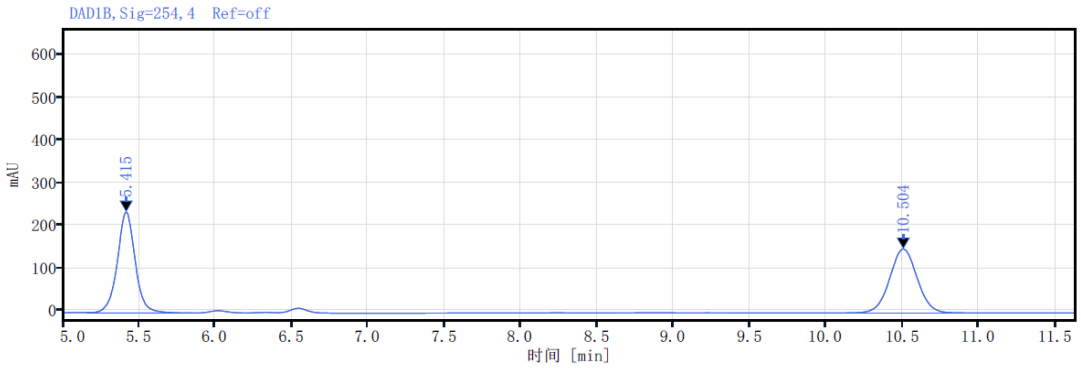


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.660	67.955	297.563	86.17	87.93	n.a.
2		10.760	10.906	40.840	13.83	12.07	n.a.
Total:			**78.861**	**338.403**	**100.00**	**100.00**	

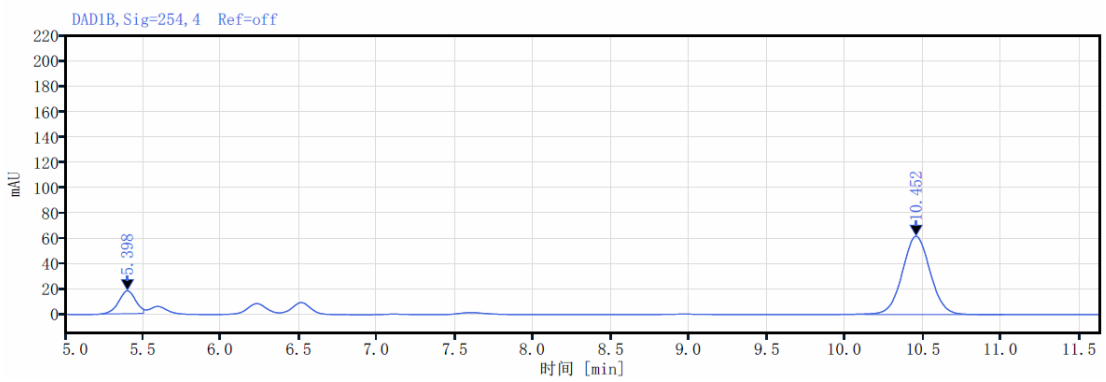
Compound **2z:** HPLC (IA, *n*-hexane/2-propanol = 80/20, v = 1.0 mL/min, λ = 254 nm)





信号: DAD1B, Sig=254, 4 Ref=off

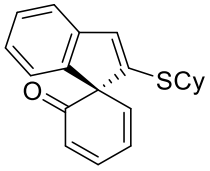
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%	名称
5.415	VB	0.69	1932.12	236.74	50.73	
10.504	BB	1.49	1876.75	149.94	49.27	
		总和	3808.86			



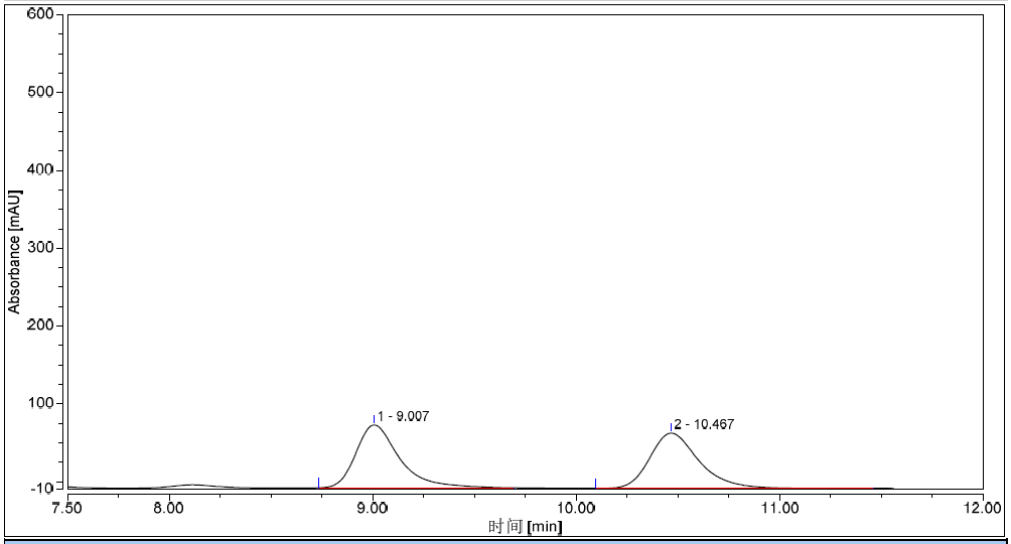
信号: DAD1B, Sig=254, 4 Ref=off

保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%	名称
5.398	MM m	0.27	135.93	18.06	15.04	
10.452	MM m	1.03	767.95	61.82	84.96	
		总和	903.88			

Compound **2aa:** HPLC (IC, *n*-hexane/2-propanol = 80/20, v = 1.0 mL/min, λ = 254 nm)



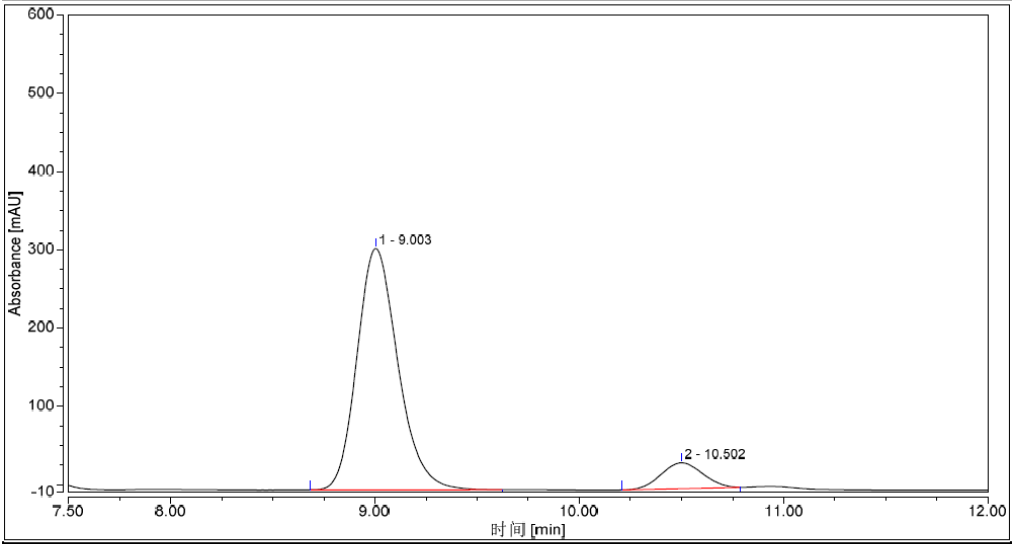
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.007	20.035	80.814	50.31	53.24	n.a.
2		10.467	19.790	70.992	49.69	46.76	n.a.
Total:			**39.825**	**151.807**	**100.00**	**100.00**	

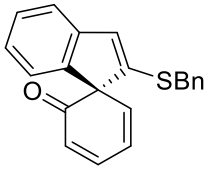
Chromatogram



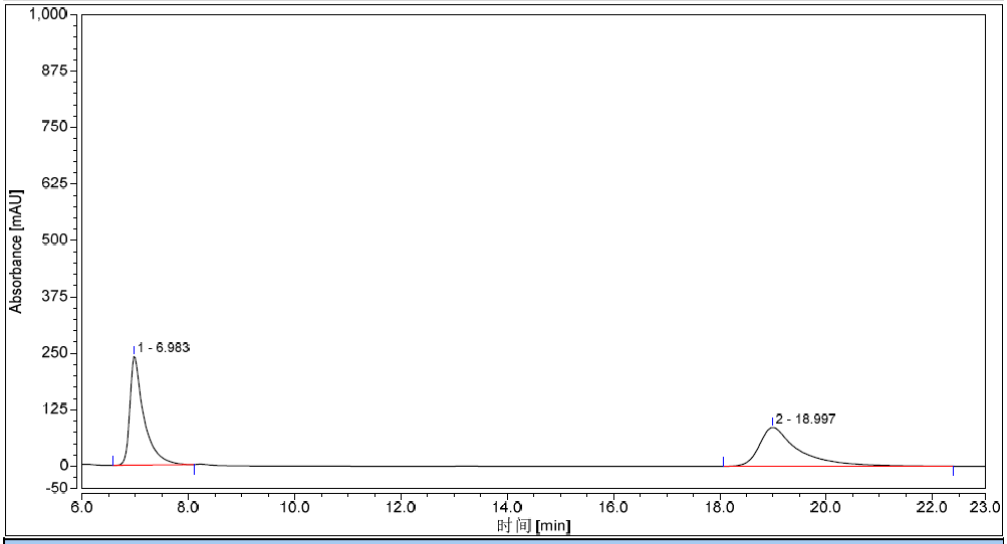
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.003	71.669	308.563	90.21	90.34	n.a.
2		10.502	7.780	33.001	9.79	9.66	n.a.
Total:			**79.449**	**341.563**	**100.00**	**100.00**	

Compound **2ab:** HPLC (IA, *n*-hexane/2-propanol = 70/30, v = 1.0 mL/min, λ = 254 nm)



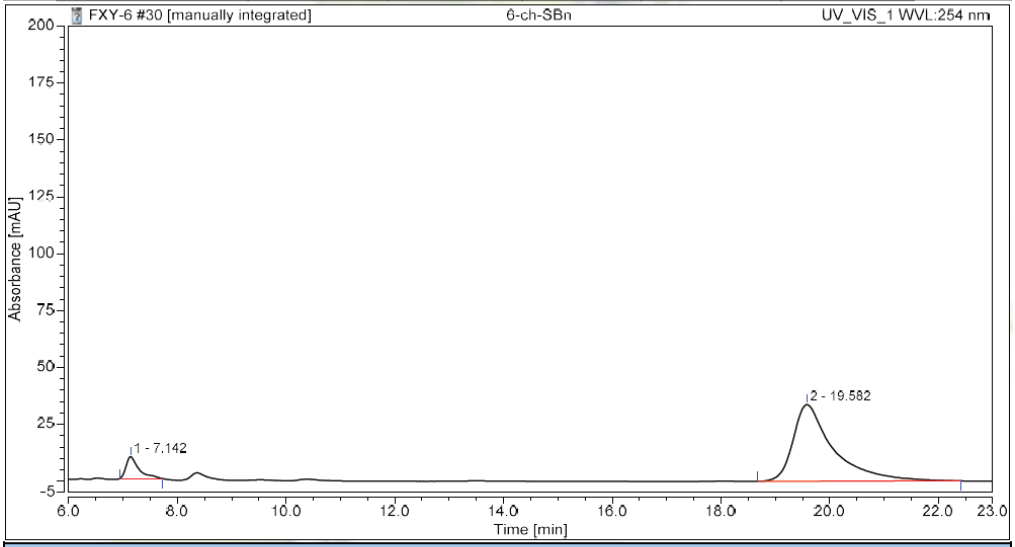
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.983	73.692	241.849	50.00	73.77	n.a.
2		18.997	73.693	85.999	50.00	26.23	n.a.
Total:			**147.385**	**327.848**	**100.00**	**100.00**	

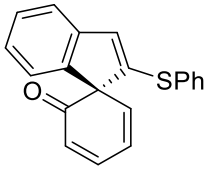
Chromatogram



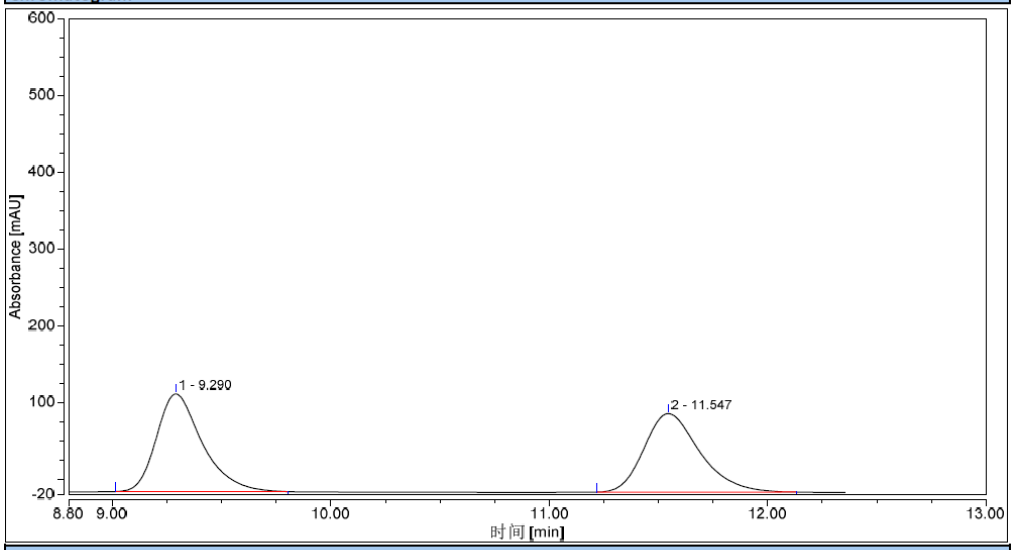
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.142	2.660	9.680	8.48	22.32	n.a.
2		19.582	28.700	33.689	91.52	77.68	n.a.
Total:			**31.360**	**43.368**	**100.00**	**100.00**	

Compound **2ac:** HPLC (IC, *n*-hexane/2-propanol = 80/20, v = 1.0 mL/min, λ = 254 nm)



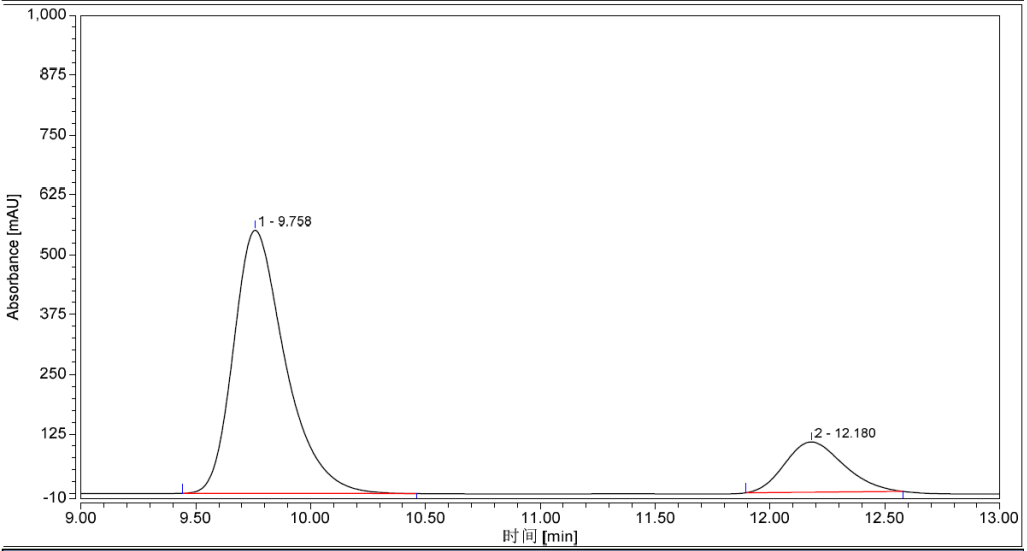
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.290	30.795	127.116	50.47	55.38	n.a.
2		11.547	30.224	102.411	49.53	44.62	n.a.
Total:			**61.020**	**229.527**	**100.00**	**100.00**	

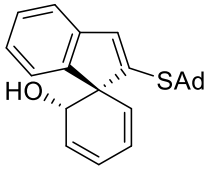
Chromatogram

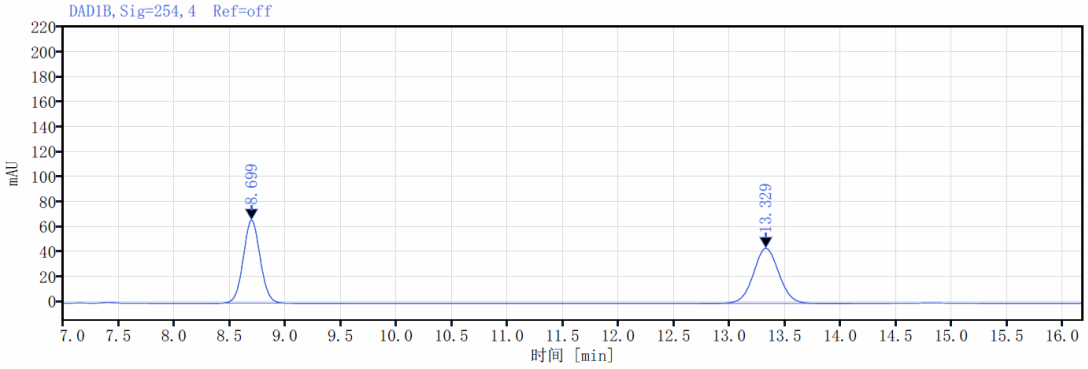


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.758	143.668	549.646	82.22	83.97	n.a.
2		12.180	31.060	104.911	17.78	16.03	n.a.
Total:			**174.728**	**654.557**	**100.00**	**100.00**	

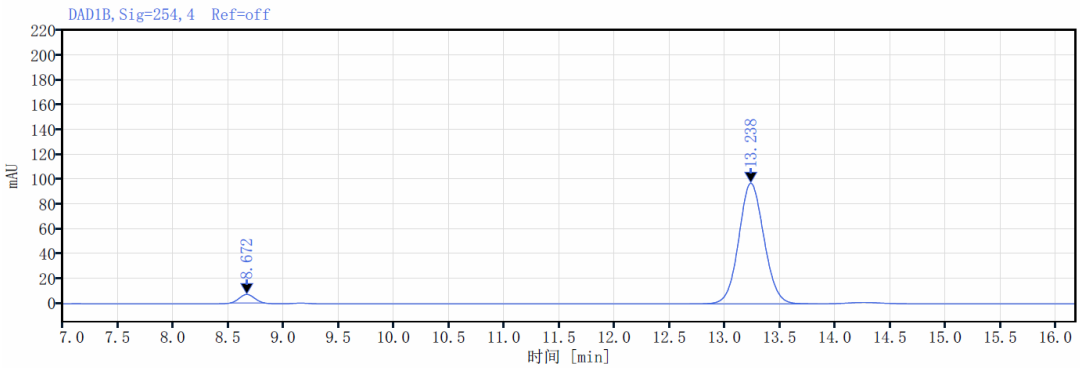
Compound **3:** HPLC (IA, *n*-hexane/2-propanol = 80/20, v = 1.0 mL/min, λ = 254 nm)





信号: DAD1B, Sig=254, 4 Ref=off

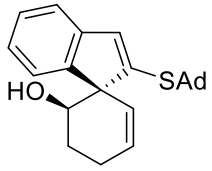
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%	名称
8.699	BB	1.23	711.66	66.76	50.21	
13.329	BB	1.35	705.77	44.20	49.79	
		总和	1417.42			

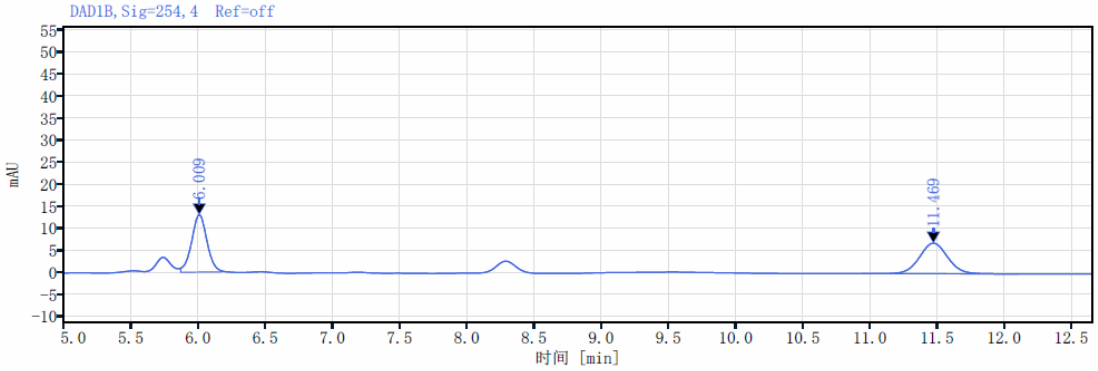


信号: DAD1B, Sig=254, 4 Ref=off

保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%	名称
8.672	MM m	0.32	64.45	6.92	4.00	
13.238	BB	1.16	1546.24	97.39	96.00	
		总和	1610.69			

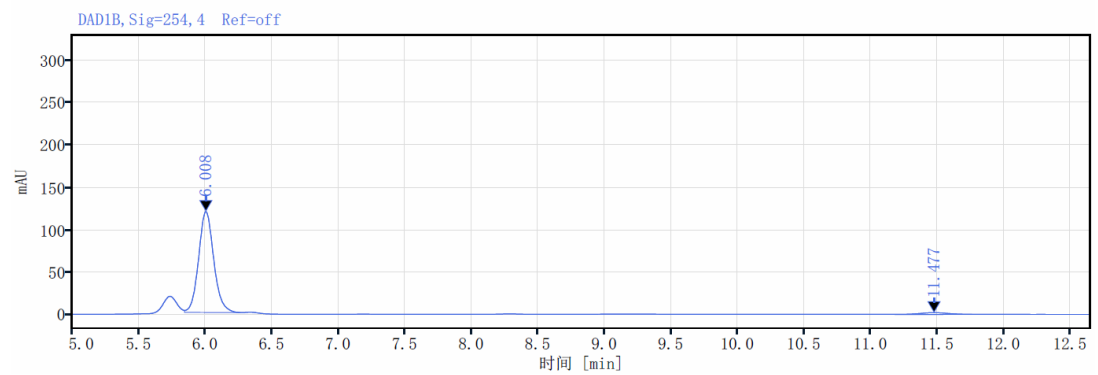
Compound **4:** HPLC (IA, *n*-hexane/2-propanol = 80/20, v = 1.0 mL/min, λ = 254 nm)





信号: DAD1B, Sig=254, 4 Ref=off

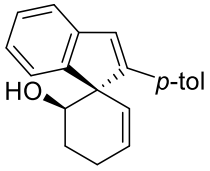
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%	名称
6.009	MM m	0.30	103.04	13.02	50.39	
11.469	MM m	1.17	101.44	6.96	49.61	
		总和	204.48			

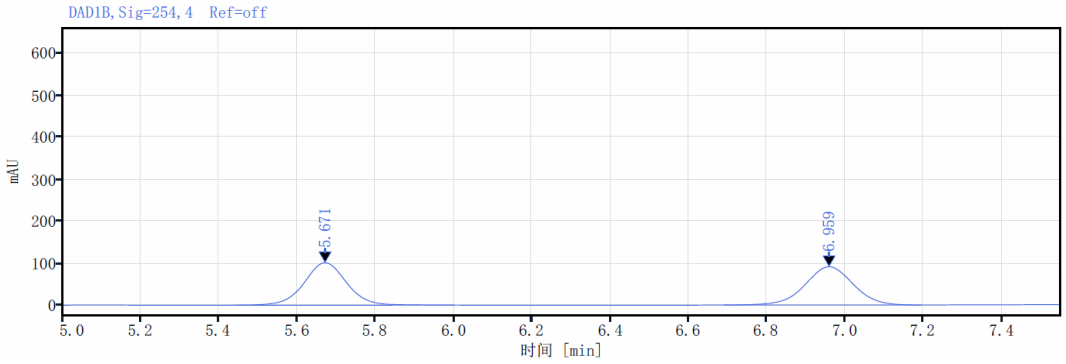


信号: DAD1B, Sig=254, 4 Ref=off

保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%	名称
6.008	MM m	0.42	946.21	119.66	96.79	
11.477	MM m	0.58	31.40	2.09	3.21	
		总和	977.61			

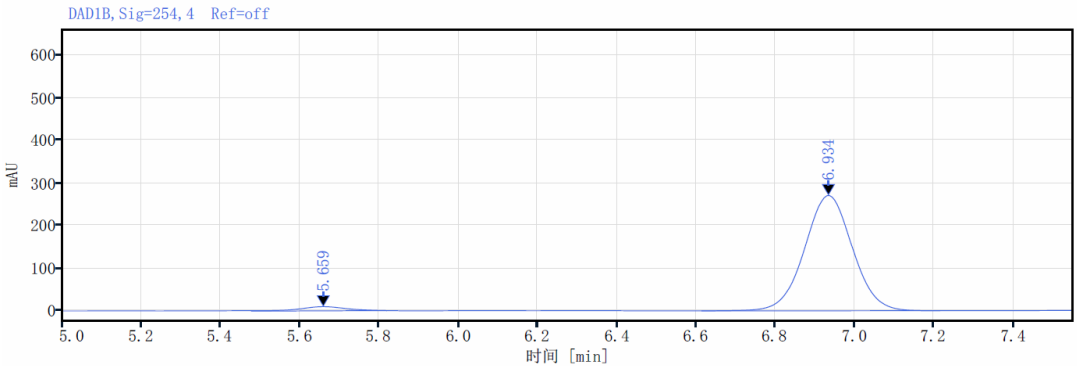
Compound **5:** HPLC (IA, *n*-hexane/2-propanol = 80/20, v = 1.0 mL/min, λ = 254 nm)





信号: DAD1B, Sig=254, 4 Ref=off

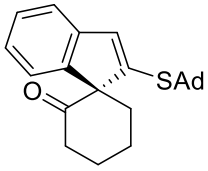
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%	名称
5.671	MM m	0.57	761.16	100.89	49.41	
6.959	MM m	0.51	779.49	91.12	50.59	
		总和	1540.64			

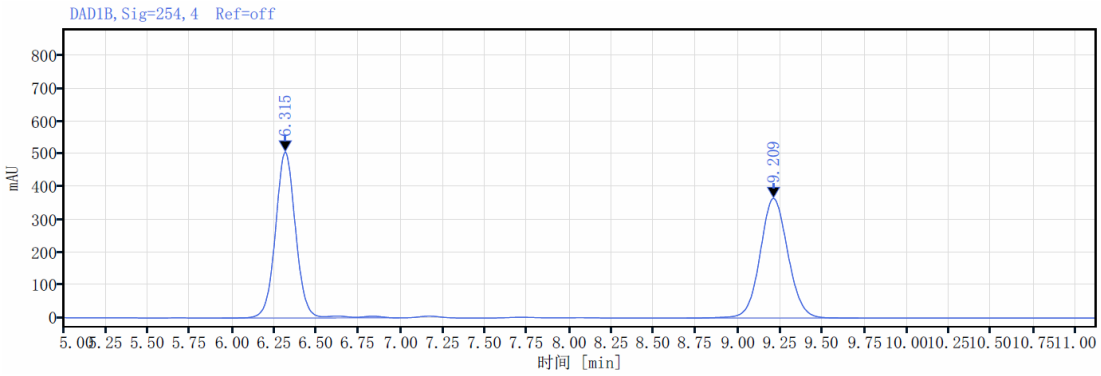


信号: DAD1B, Sig=254, 4 Ref=off

保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%	名称
5.659	MM m	0.34	81.70	9.88	3.46	
6.934	MM m	0.60	2276.64	270.77	96.54	
		总和	2358.34			

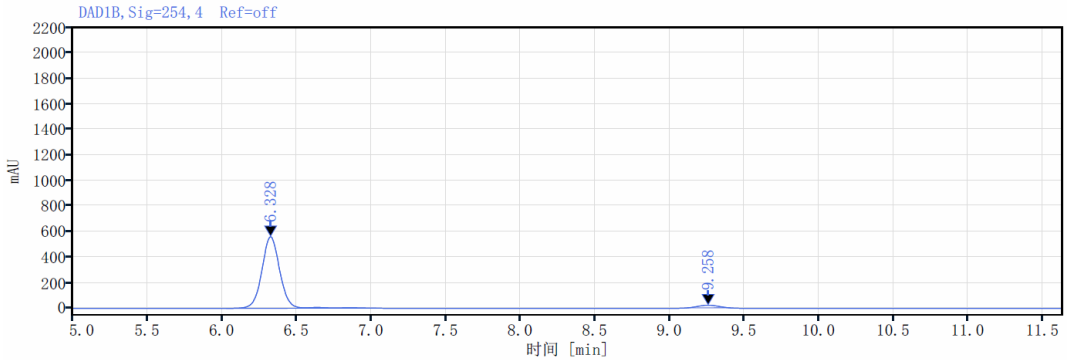
Compound **6:** HPLC (IA, *n*-hexane/2-propanol = 80/20, v = 1.0 mL/min, λ = 254 nm)





信号: DAD1B, Sig=254, 4 Ref=off

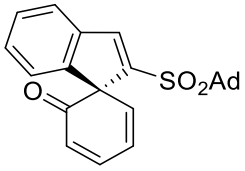
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%	名称
6.315	MM m	1.05	4246.79	506.97	50.35	
9.209	MM m	1.02	4187.18	365.37	49.65	
		总和	8433.97			



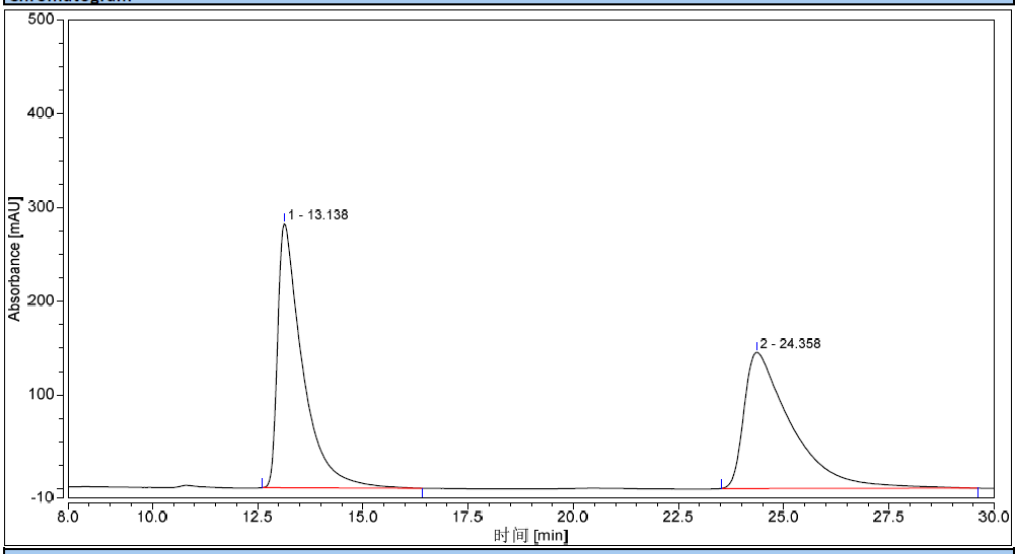
信号: DAD1B, Sig=254, 4 Ref=off

保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%	名称
6.328	MM m	1.00	4691.63	560.95	96.02	
9.258	MM m	0.29	194.64	20.90	3.98	
		总和	4886.27			

Compound **7:** HPLC (IA, *n*-hexane/2-propanol = 70/30, v = 1.0 mL/min, λ = 254 nm)



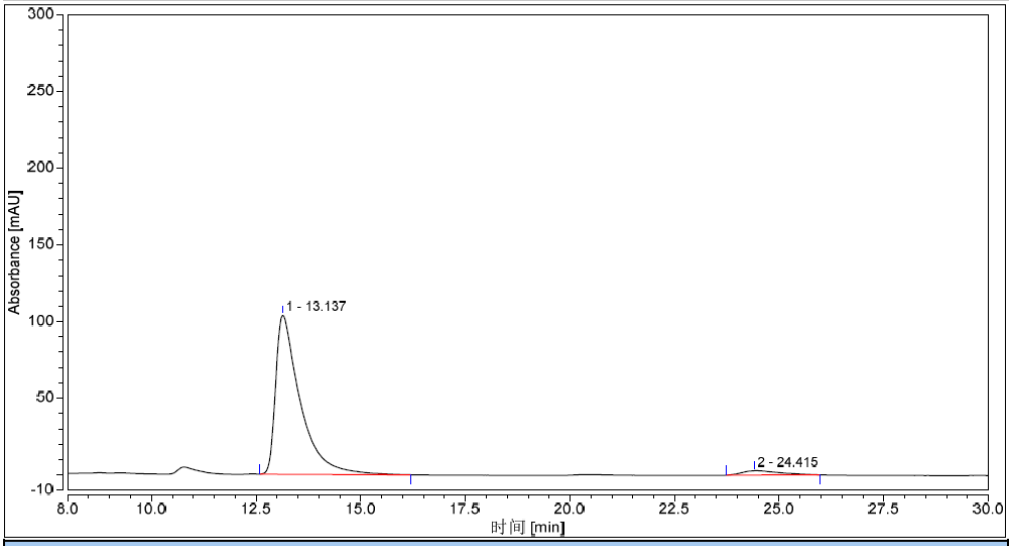
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.138	192.760	281.895	50.49	66.01	n.a.
2		24.358	189.026	145.173	49.51	33.99	n.a.
Total:			**381.786**	**427.068**	**100.00**	**100.00**	

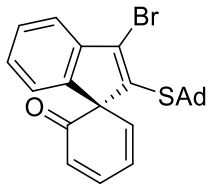
Chromatogram

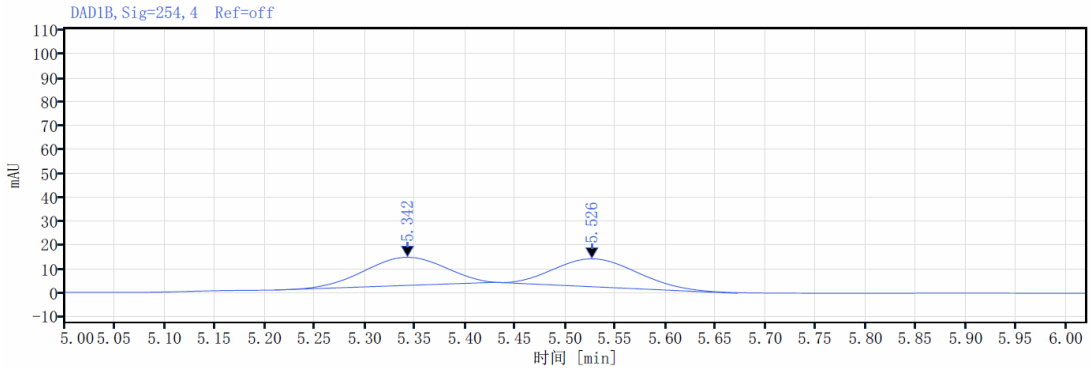


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.137	70.278	103.688	96.00	97.34	n.a.
2		24.415	2.930	2.835	4.00	2.66	n.a.
Total:			**73.208**	**106.523**	**100.00**	**100.00**	

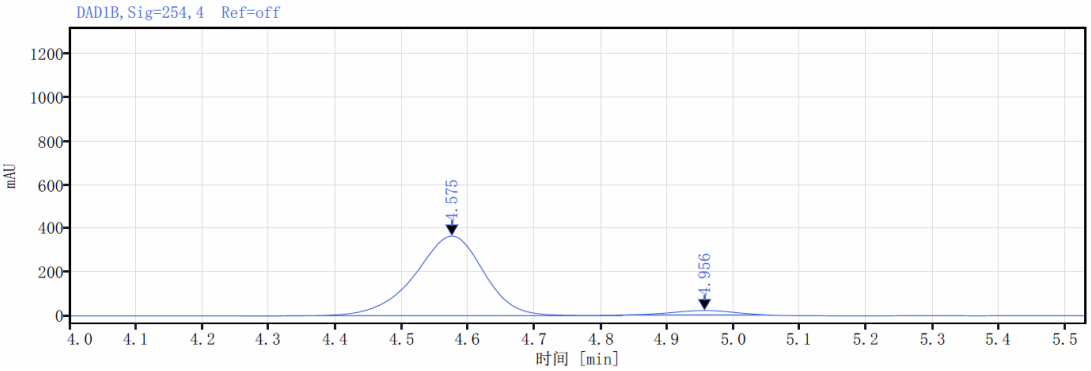
Compound **8:** HPLC (IA, *n*-hexane/2-propanol = 80/20, v = 1.0 mL/min, λ = 254 nm)





信号: DAD1B, Sig=254, 4 Ref=off

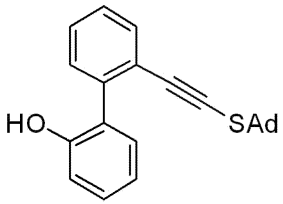
保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%	名称
5.342	MM m	0.22	66.01	11.80	49.02	
5.526	MM m	0.24	68.64	11.71	50.98	
		总和	134.65			



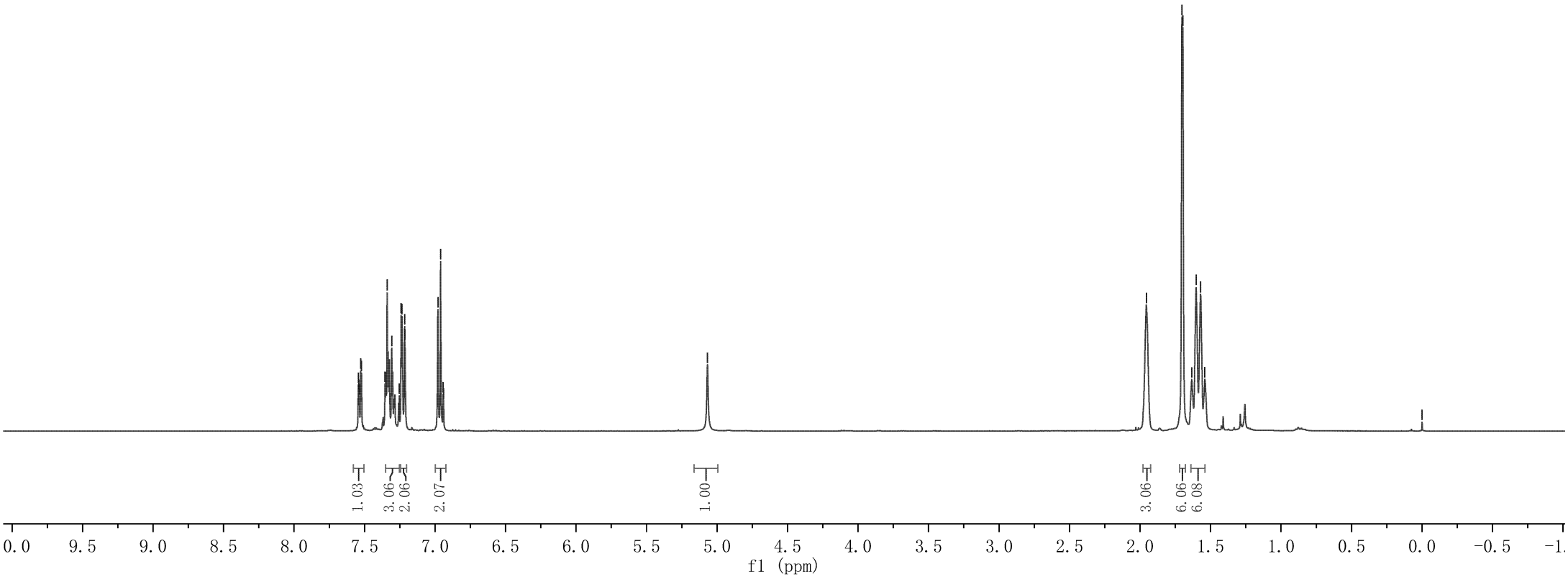
信号: DAD1B, Sig=254, 4 Ref=off

保留时间 [min]	类型	峰宽 [min]	峰面积	峰高	峰面积%	名称
4.575	MM m	0.58	2651.60	366.15	95.50	
4.956	MM m	0.21	124.86	20.03	4.50	
		总和	2776.46			

Parameter	Value
1 Title	FXY-13-194-1
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	2023-08-20T15:45:06
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8

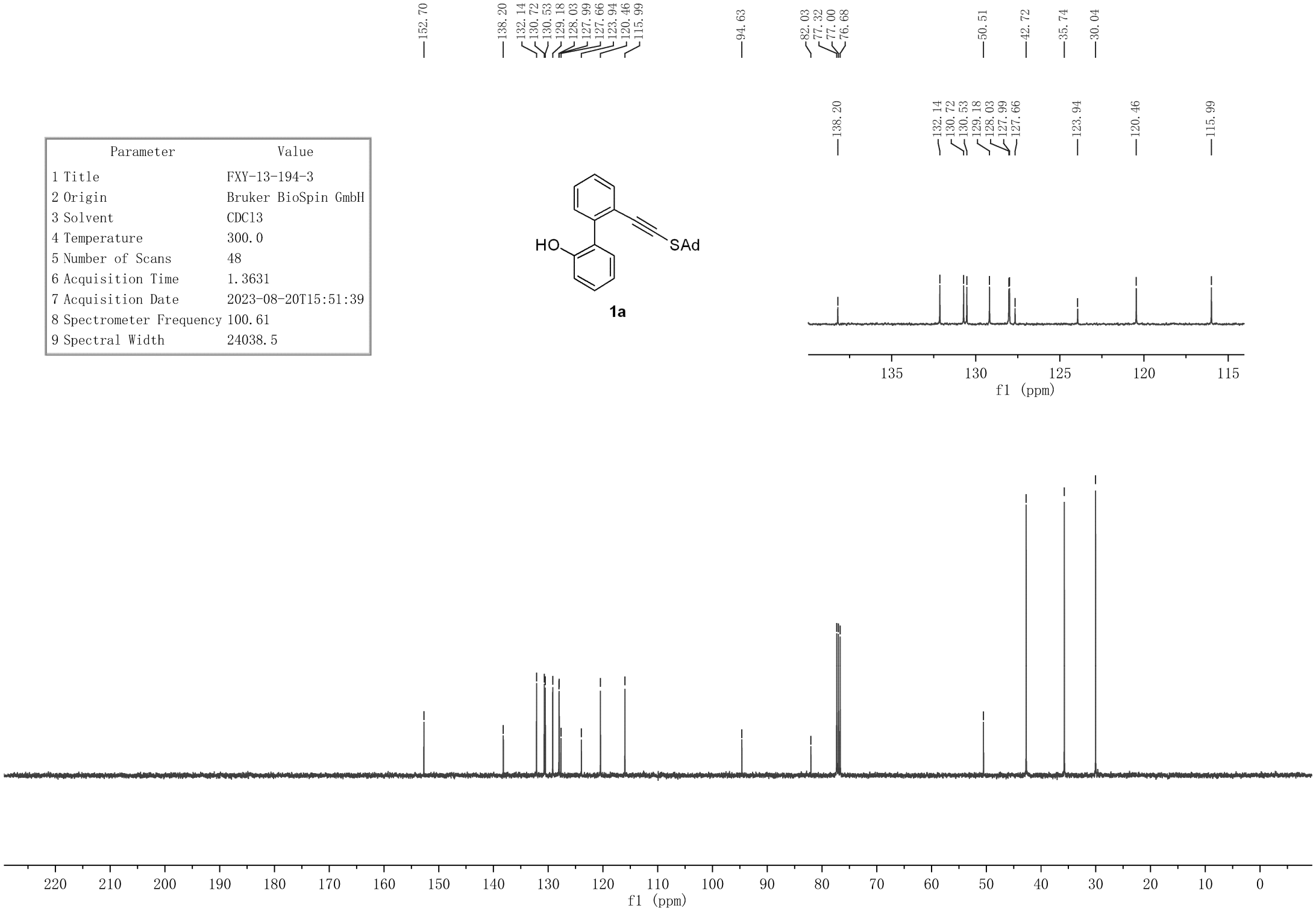


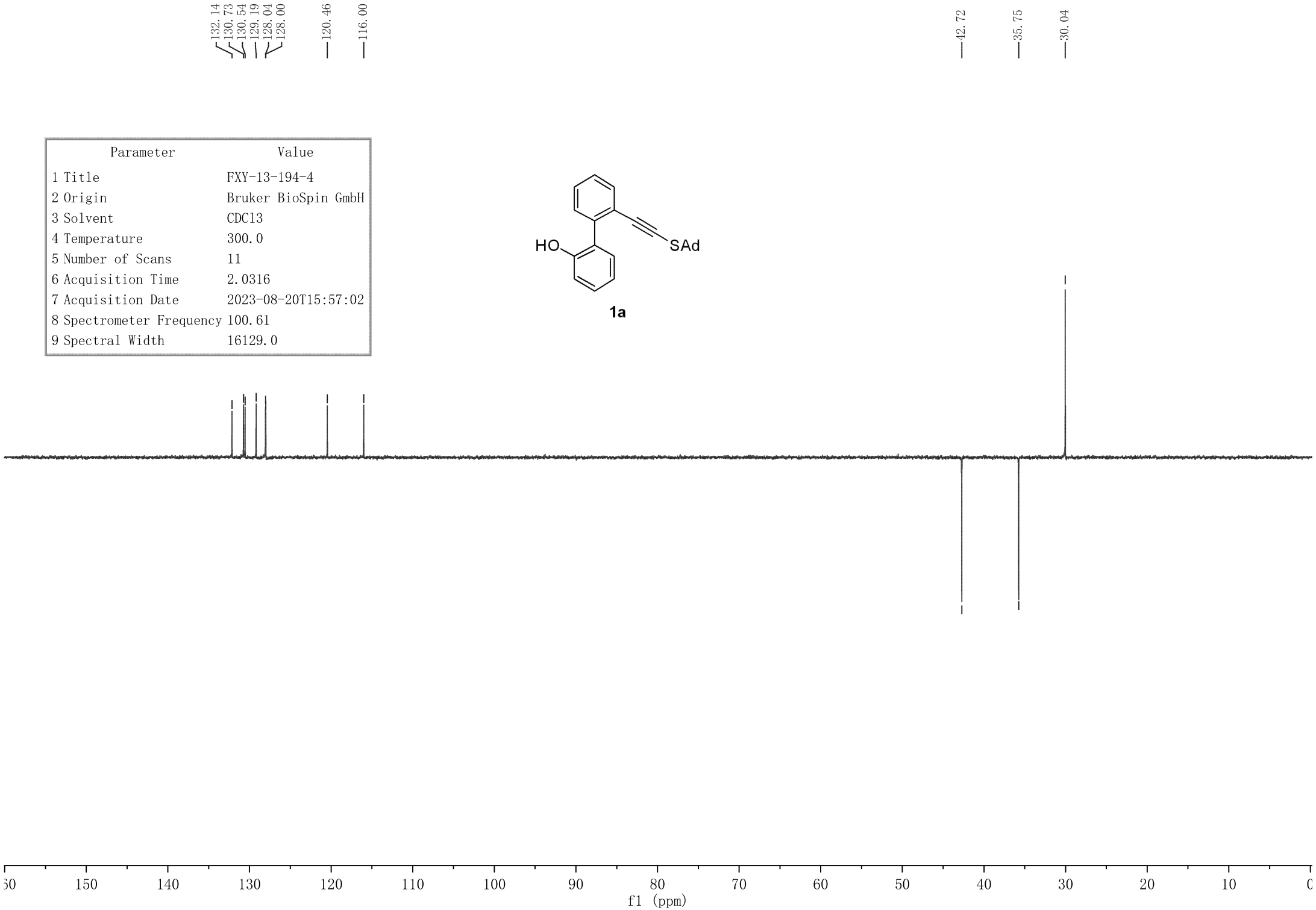
1a



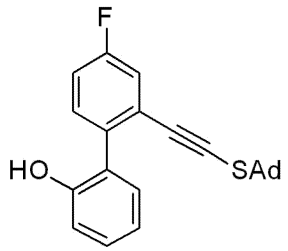
Parameter	Value
1 Title	FXY-13-194-3
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	48
6 Acquisition Time	1.3631
7 Acquisition Date	2023-08-20T15:51:39
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5

1a

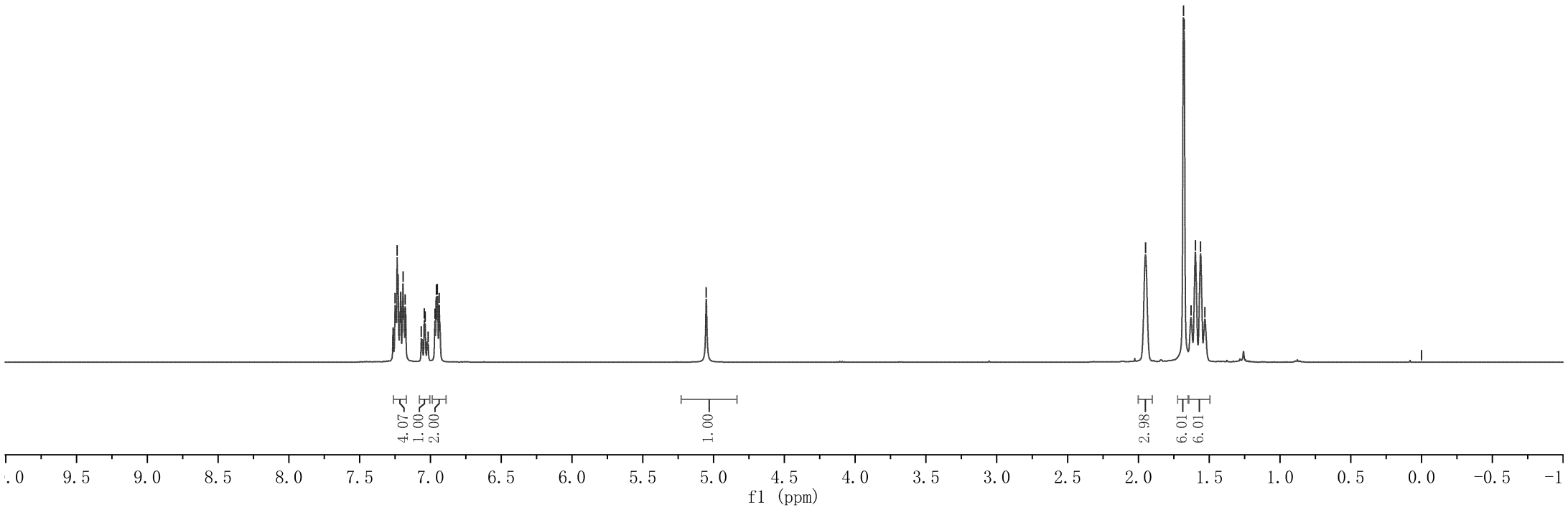



132.14
130.73
130.54
129.19
128.04
128.00
120.46
116.00
42.72
35.75
30.04
Parameter Value
1 Title FXY-13-194-4
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.0
5 Number of Scans 11
6 Acquisition Time 2.0316
7 Acquisition Date 2023-08-20T15:57:02
8 Spectrometer Frequency 100.61
9 Spectral Width 16129.0
HO
SAd
1a
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

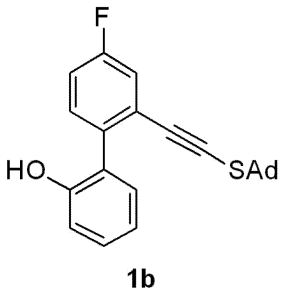
Parameter	Value
1 Title	1d
2 Origin	
3 Solvent	CDCl3
4 Temperature	295.8
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2022-01-13T15:45:57
8 Spectrometer Frequency	399.93
9 Spectral Width	8012.0



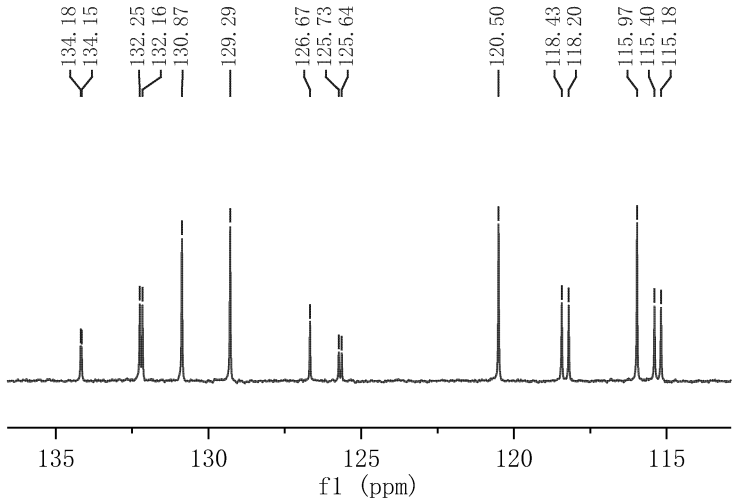
1b

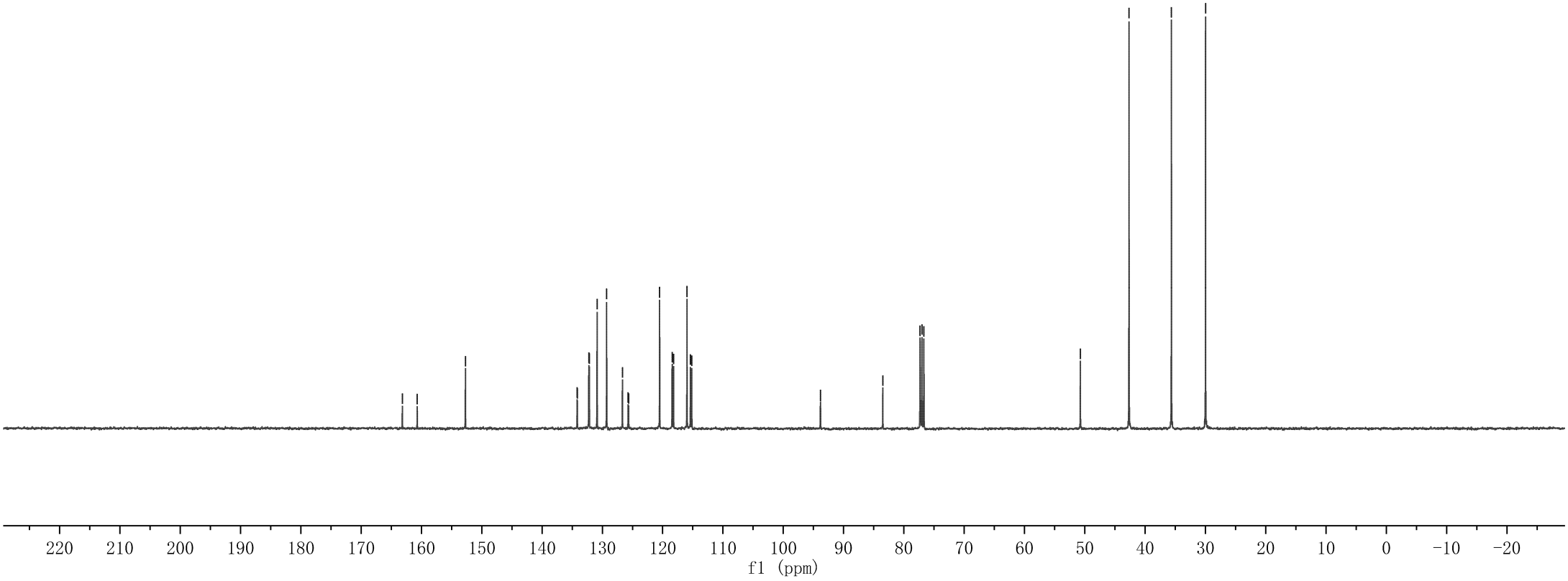


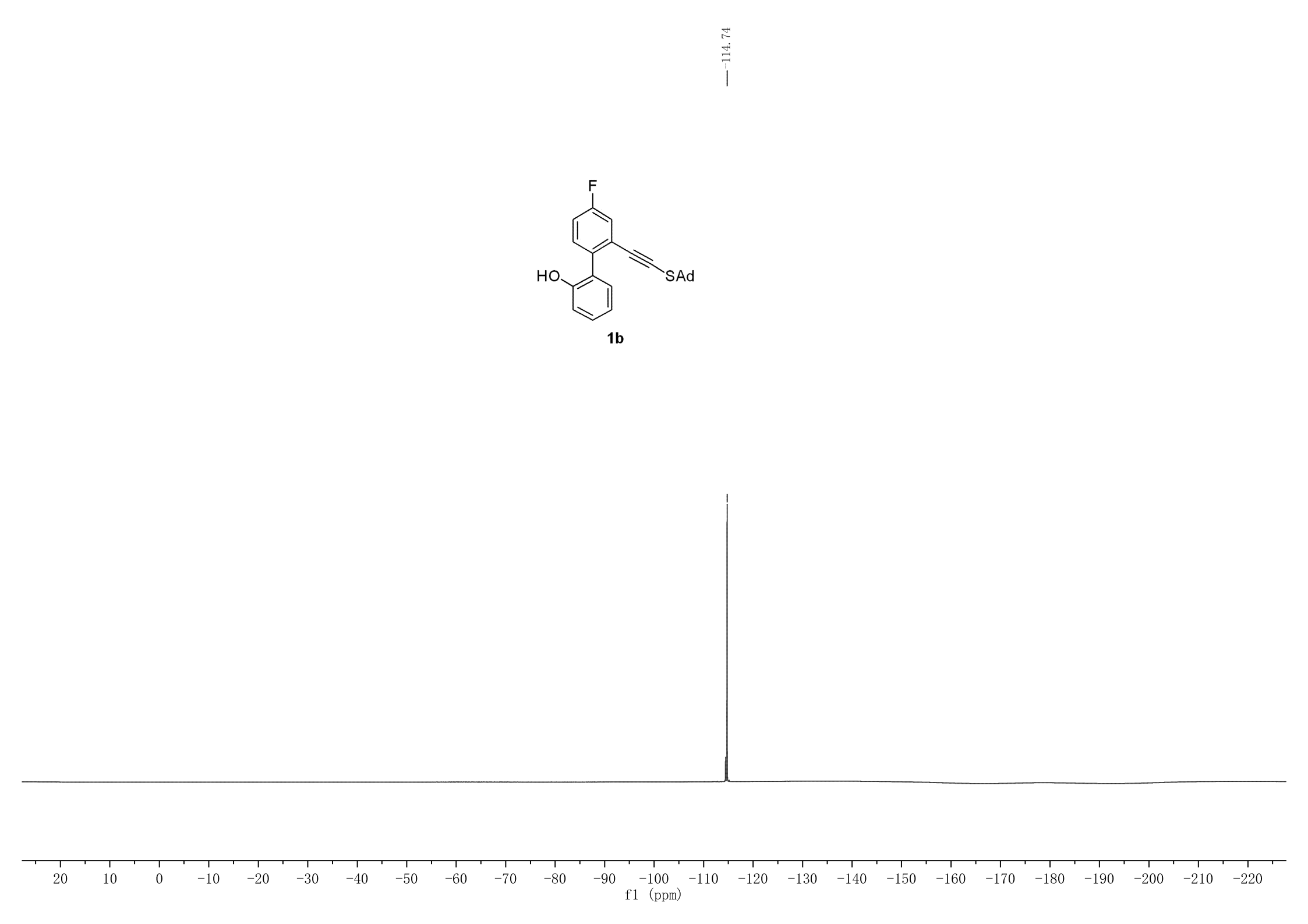
Parameter	Value
1 Title	1d
2 Origin	
3 Solvent	CDCl3
4 Temperature	296.2
5 Number of Scans	200
6 Acquisition Time	1.0000
7 Acquisition Date	2022-01-13T15:54:53
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

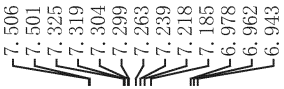


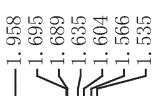
1b



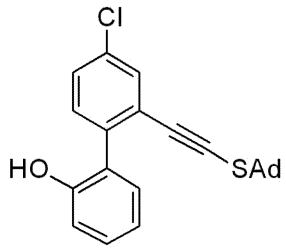



-114.74
F
HO
SAd
1b
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)

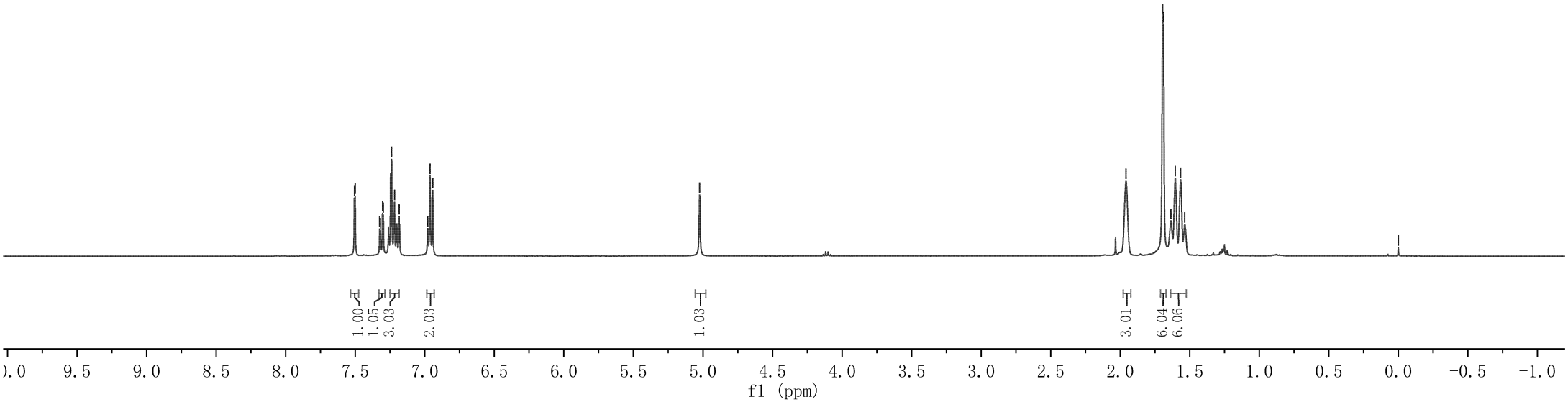




Parameter	Value
1 Title	fxy-7-120
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	11
6 Acquisition Time	4.0894
7 Acquisition Date	2022-02-17T10:28:57
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8

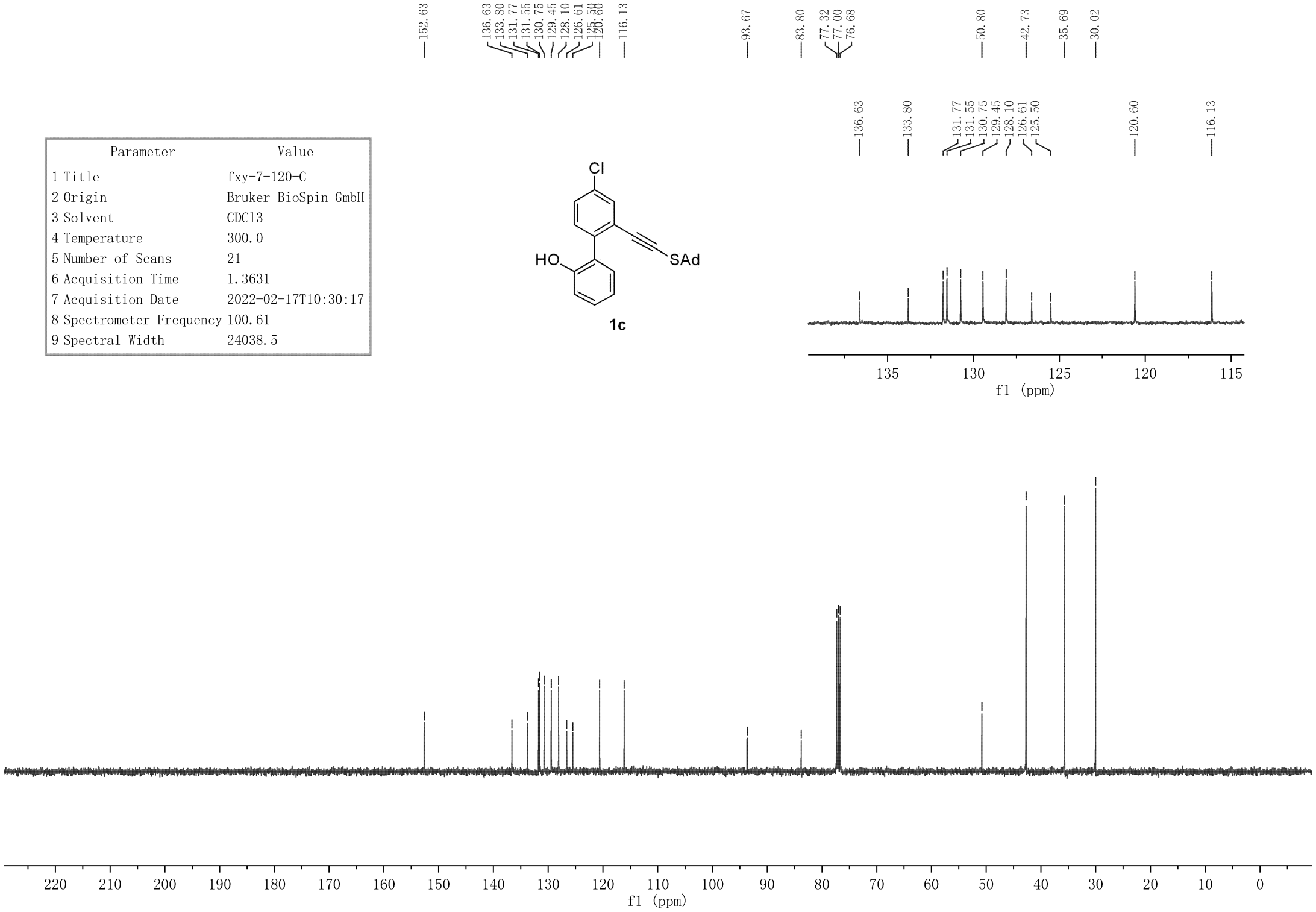


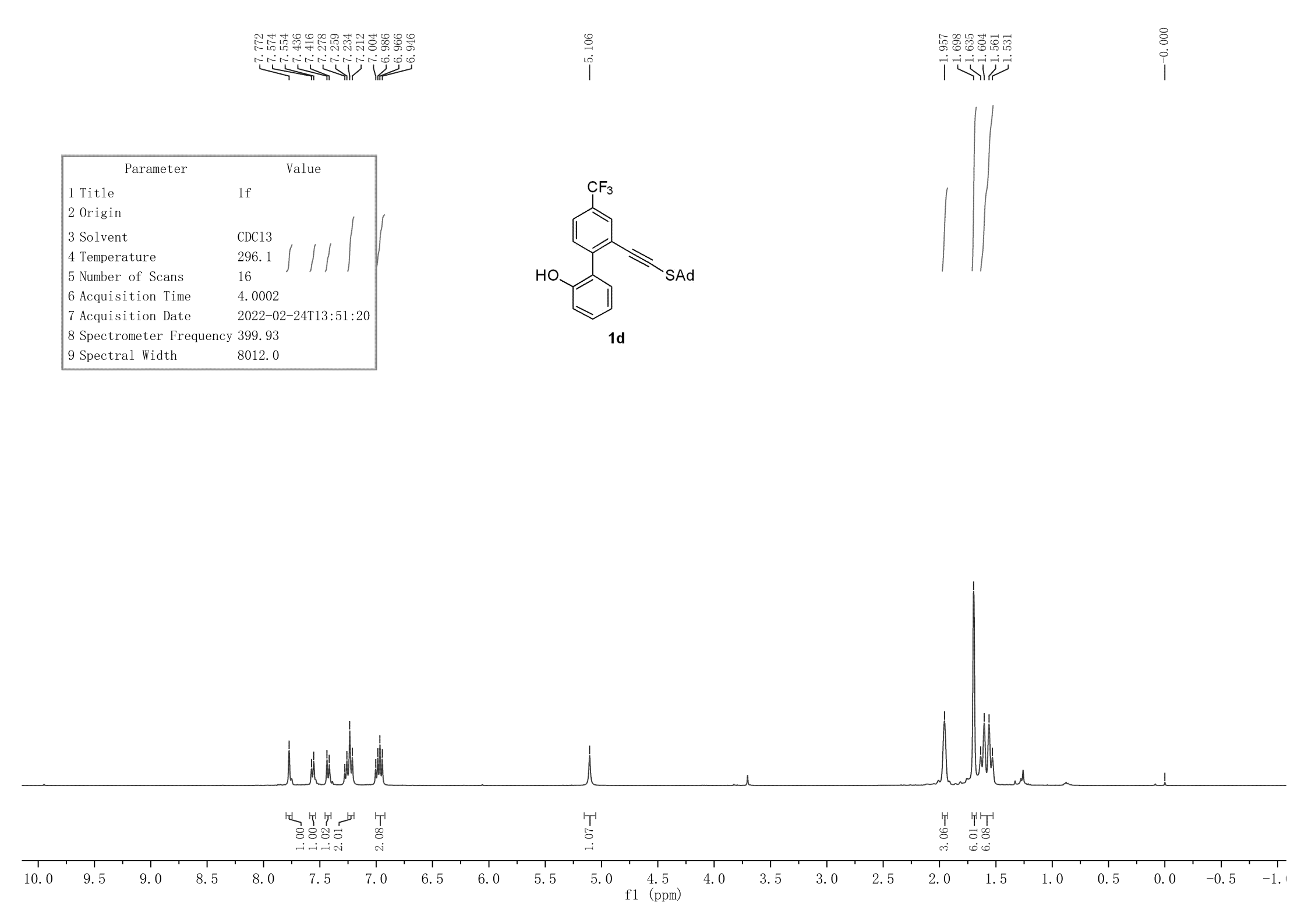
1c



Parameter	Value
1 Title	fxy-7-120-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	21
6 Acquisition Time	1.3631
7 Acquisition Date	2022-02-17T10:30:17
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5

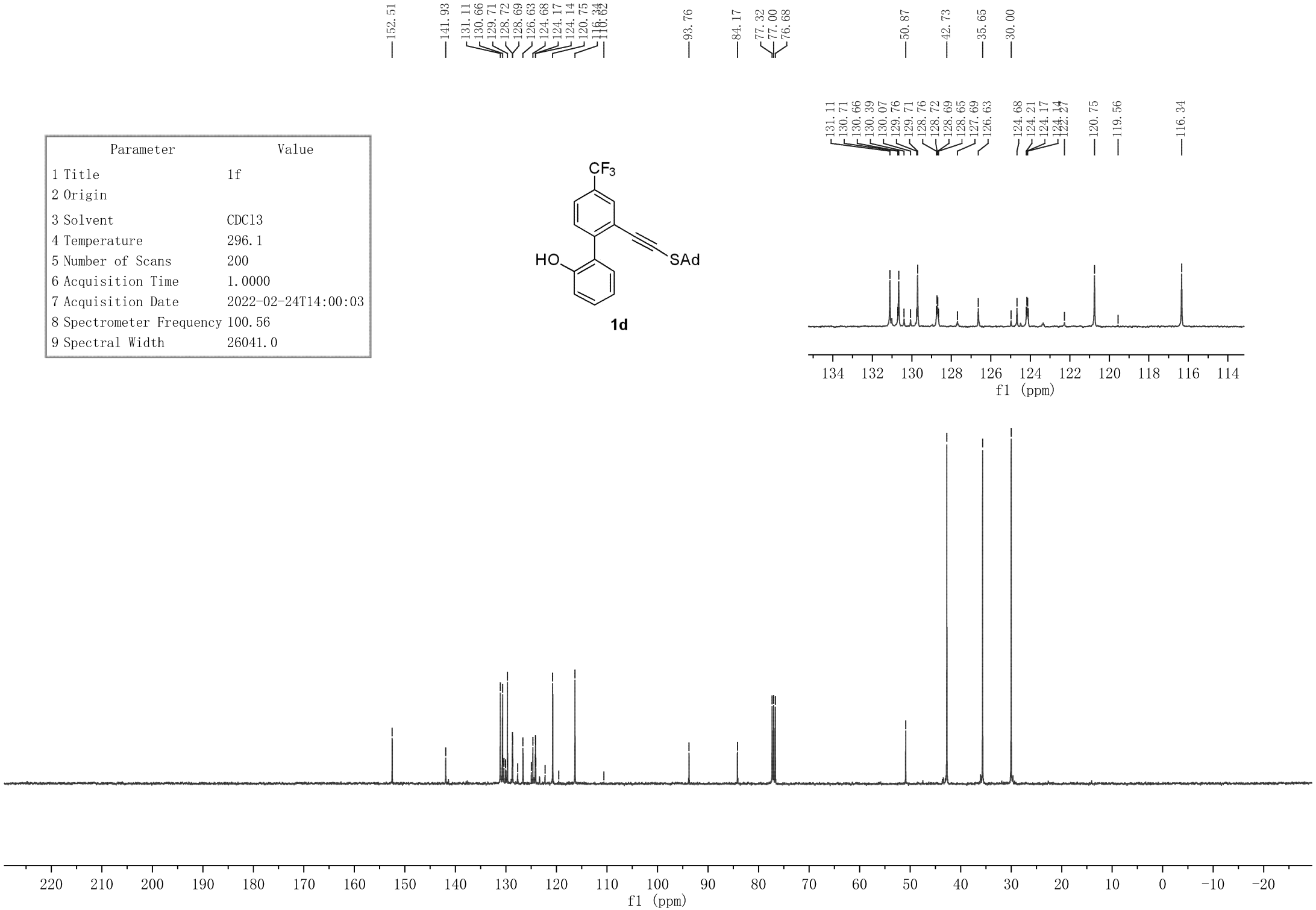
1c

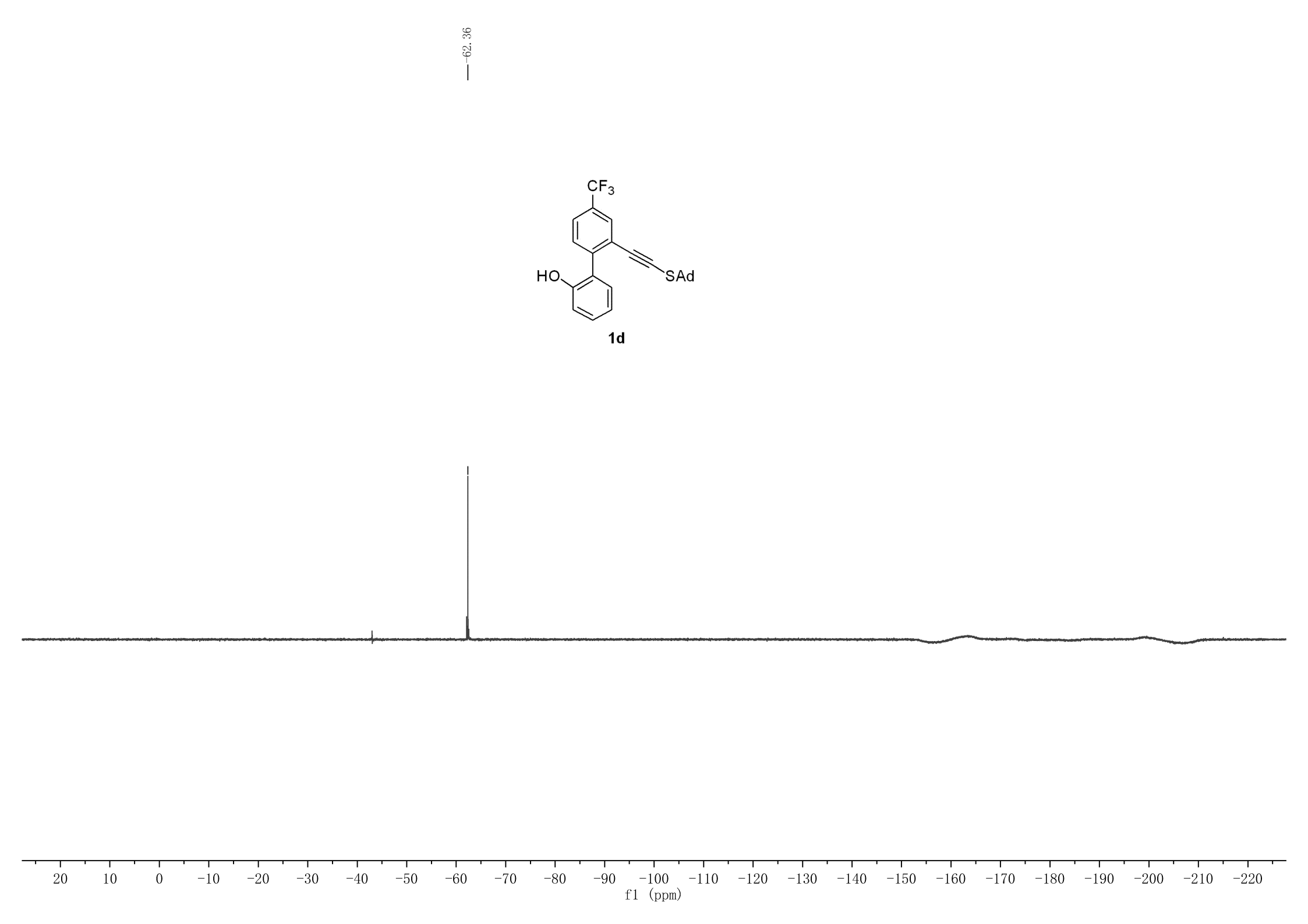



7.772
7.574
7.554
7.436
7.416
7.278
7.259
7.234
7.212
7.004
6.986
6.966
6.946
5.106
1.957
1.698
1.635
1.604
1.561
1.531
0.000
Parameter Value
1 Title 1f
2 Origin
3 Solvent CDCl3
4 Temperature 296.1
5 Number of Scans 16
6 Acquisition Time 4.0002
7 Acquisition Date 2022-02-24T13:51:20
8 Spectrometer Frequency 399.93
9 Spectral Width 8012.0
CF3
HO
SAd
1d
1.00
1.00
1.02
2.01
2.08
1.07
3.06
6.01
6.08
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
f1 (ppm)

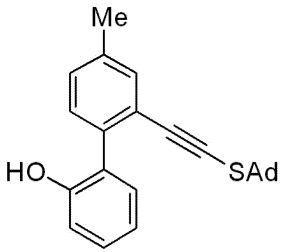
Parameter	Value
1 Title	1f
2 Origin	
3 Solvent	CDCl3
4 Temperature	296.1
5 Number of Scans	200
6 Acquisition Time	1.0000
7 Acquisition Date	2022-02-24T14:00:03
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

1d

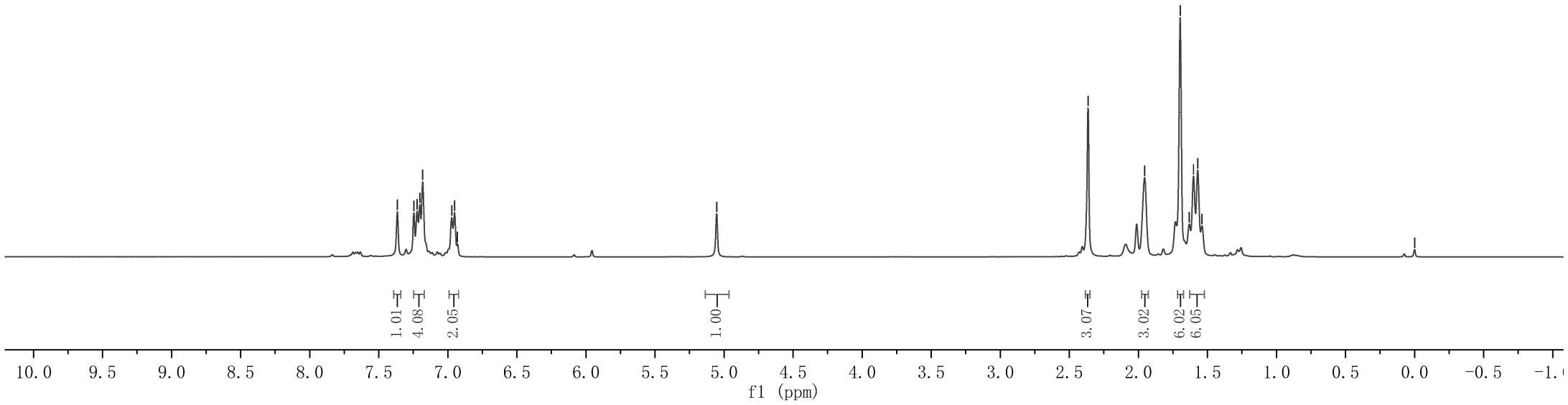



-62.36
CF3
HO
SAd
1d
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)

Parameter	Value
1 Title	1b
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.5
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2022-02-16T15:45:09
8 Spectrometer Frequency	399.93
9 Spectral Width	8012.0

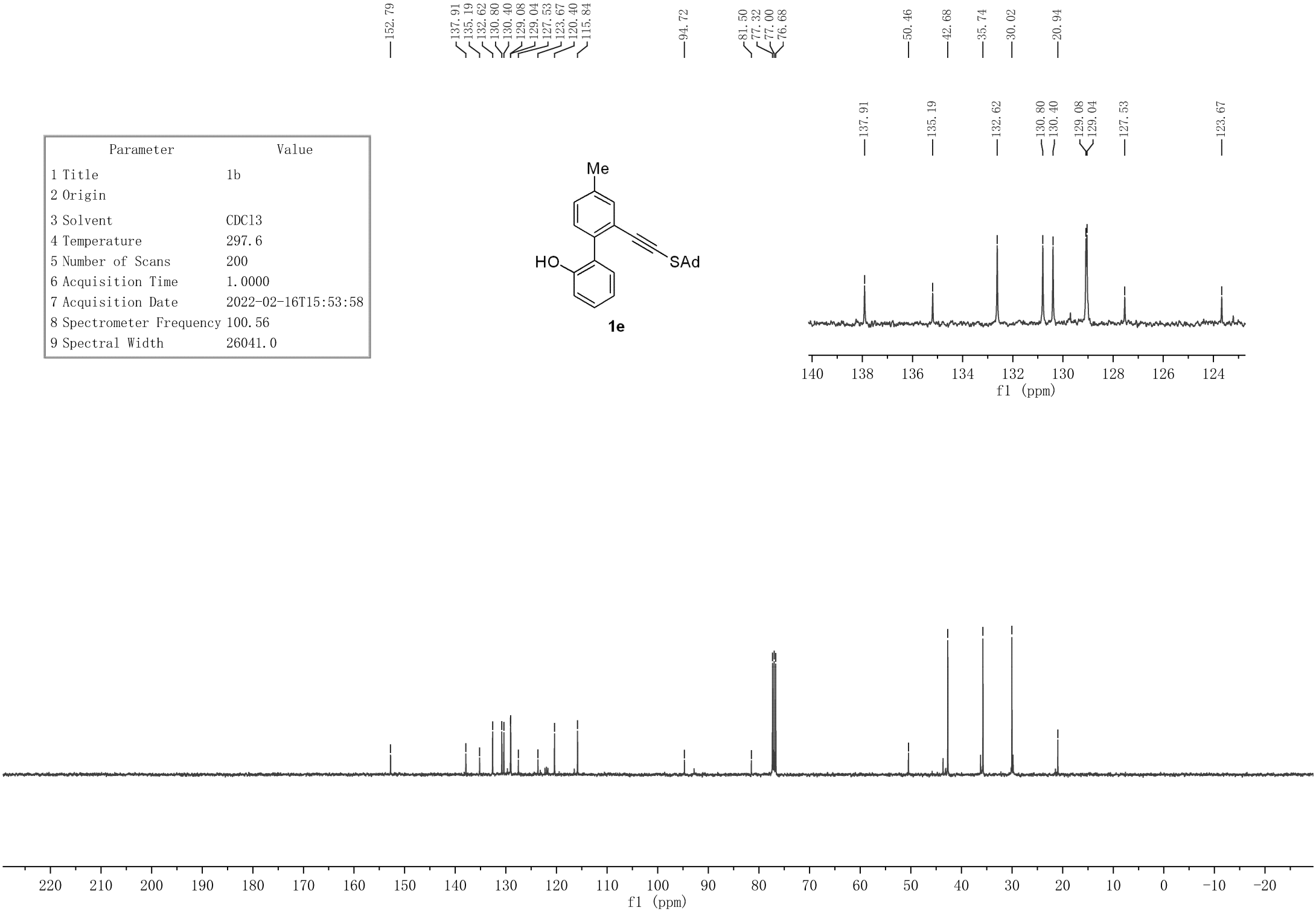


1e

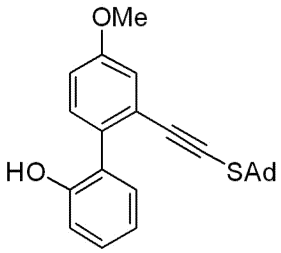


Parameter	Value
1 Title	1b
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.6
5 Number of Scans	200
6 Acquisition Time	1.0000
7 Acquisition Date	2022-02-16T15:53:58
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

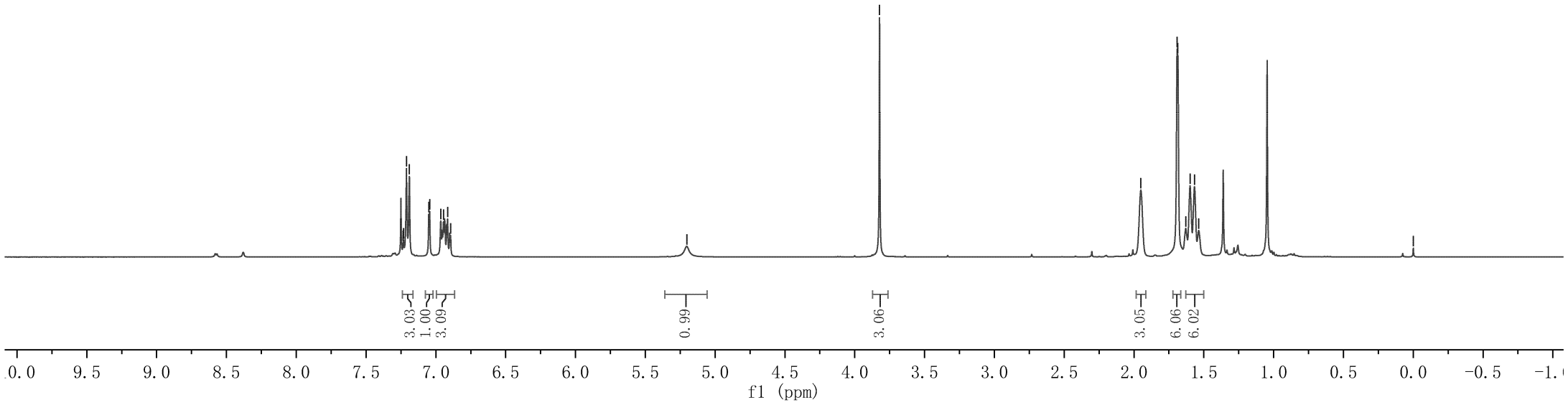
1e



Parameter	Value
1 Title	fxy-7-93
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	11
6 Acquisition Time	4.0894
7 Acquisition Date	2022-02-11T16:25:28
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8

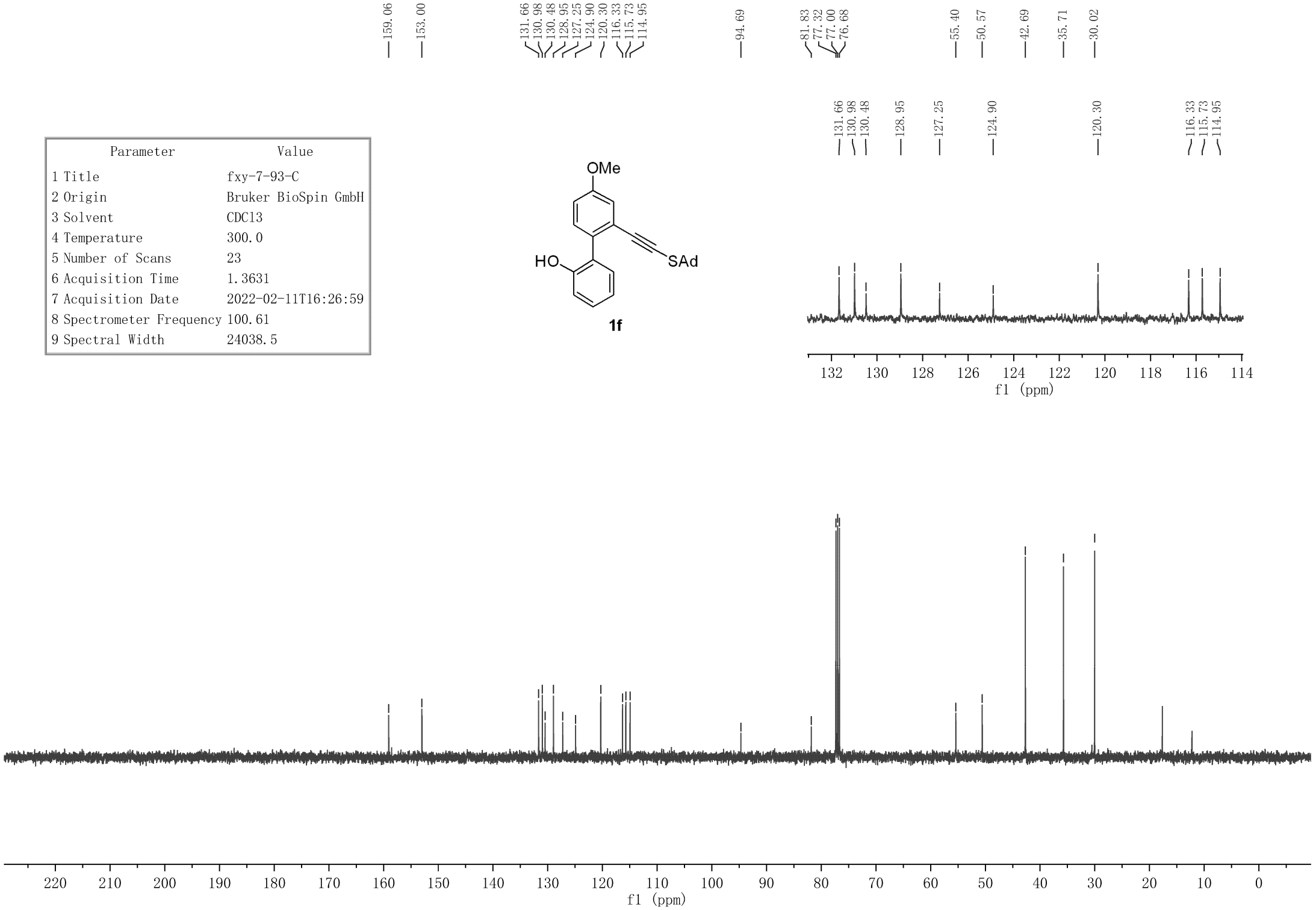


1f

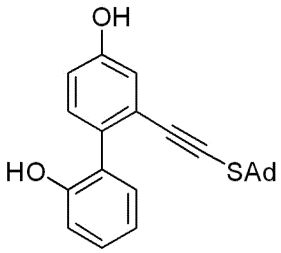


Parameter	Value
1 Title	fxy-7-93-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	23
6 Acquisition Time	1.3631
7 Acquisition Date	2022-02-11T16:26:59
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5

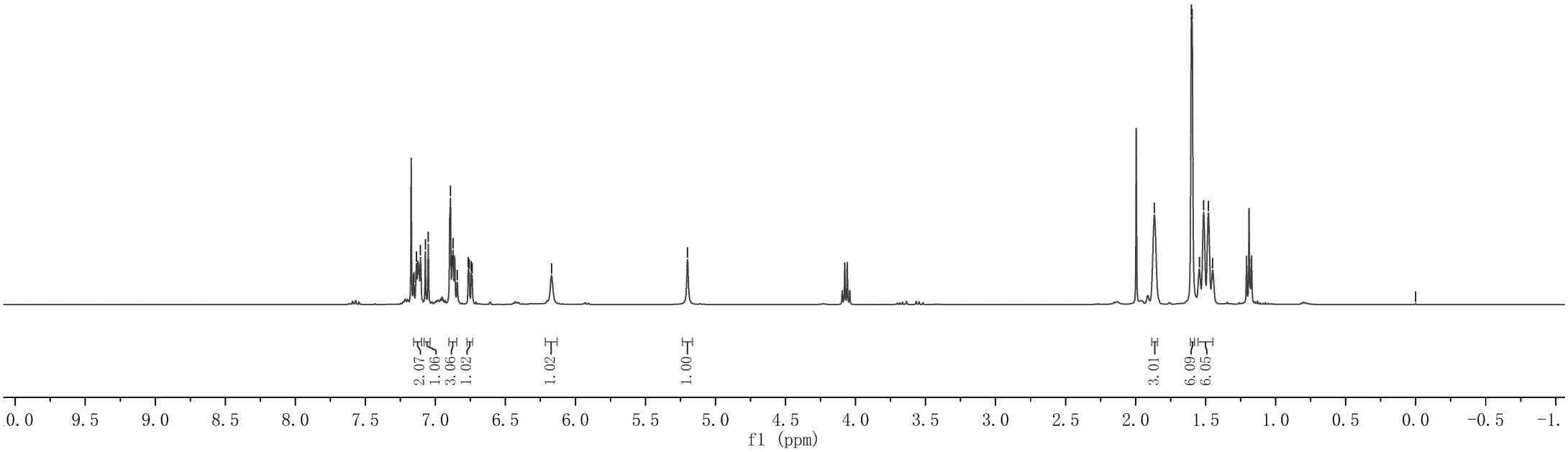
1f



Parameter	Value
1 Title	1g
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.4
5 Number of Scans	20
6 Acquisition Time	4.0002
7 Acquisition Date	2022-01-18T16:32:08
8 Spectrometer Frequency	399.93
9 Spectral Width	8012.0

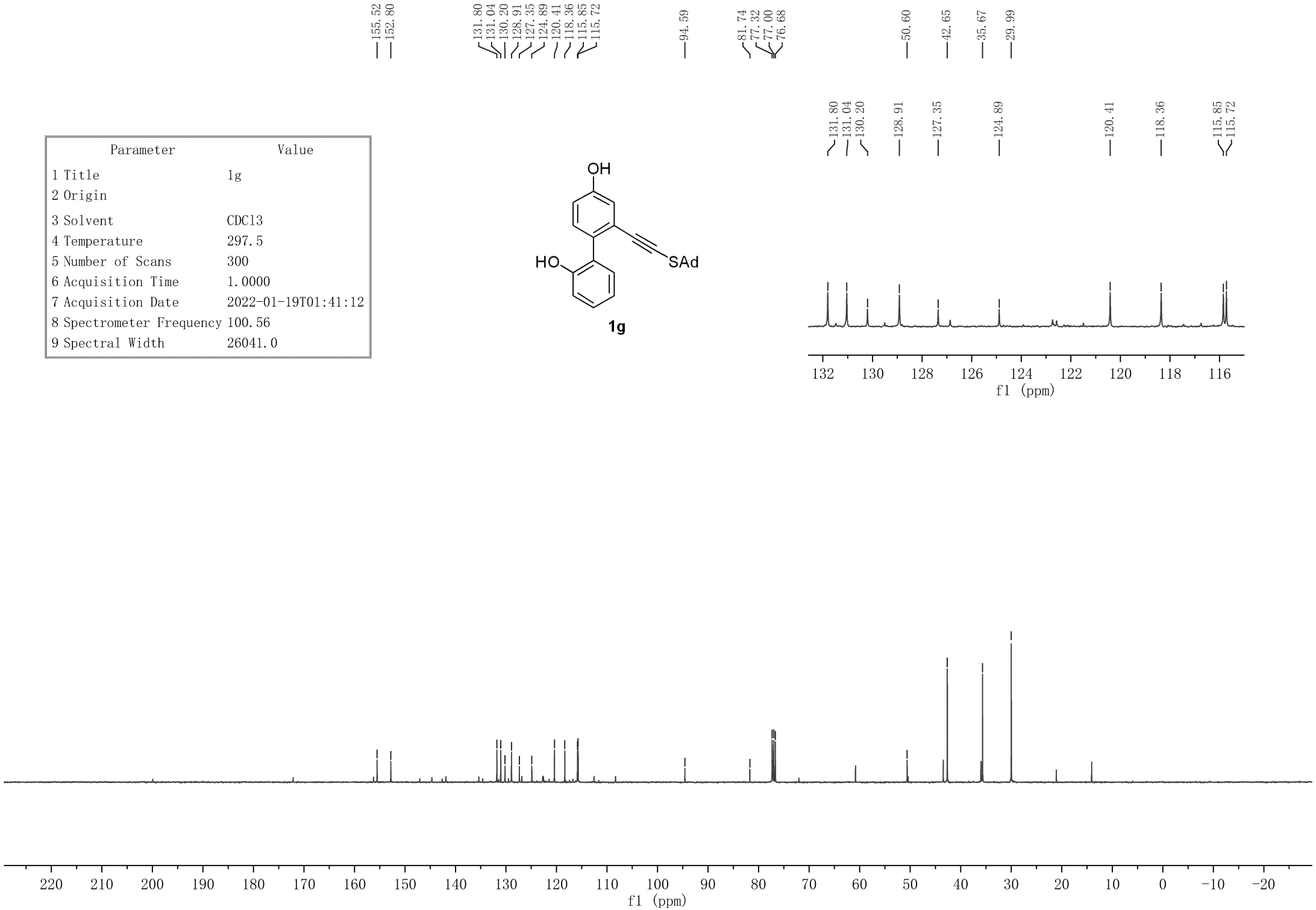


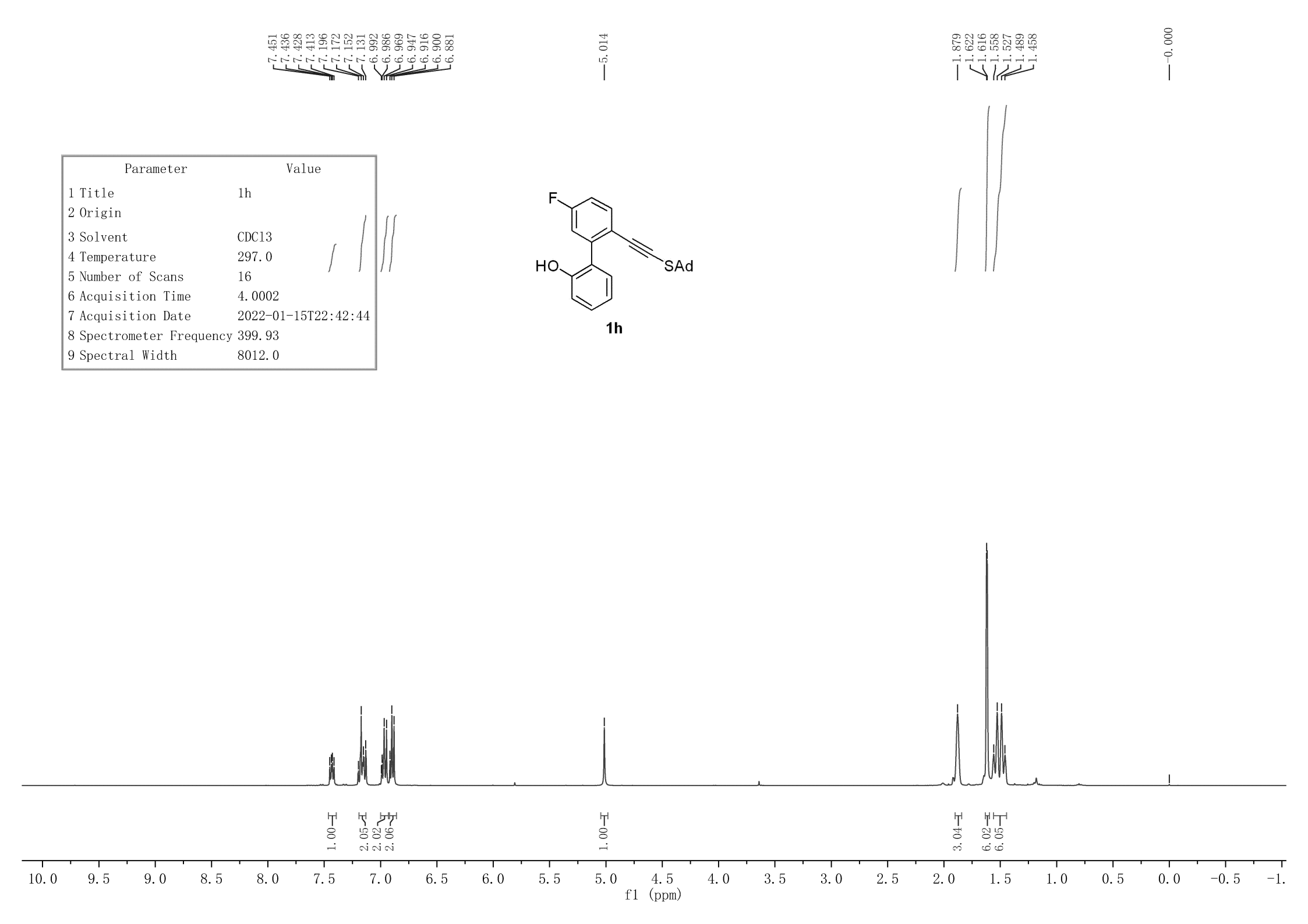
1g



Parameter	Value
1 Title	1g
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.5
5 Number of Scans	300
6 Acquisition Time	1.0000
7 Acquisition Date	2022-01-19T01:41:12
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

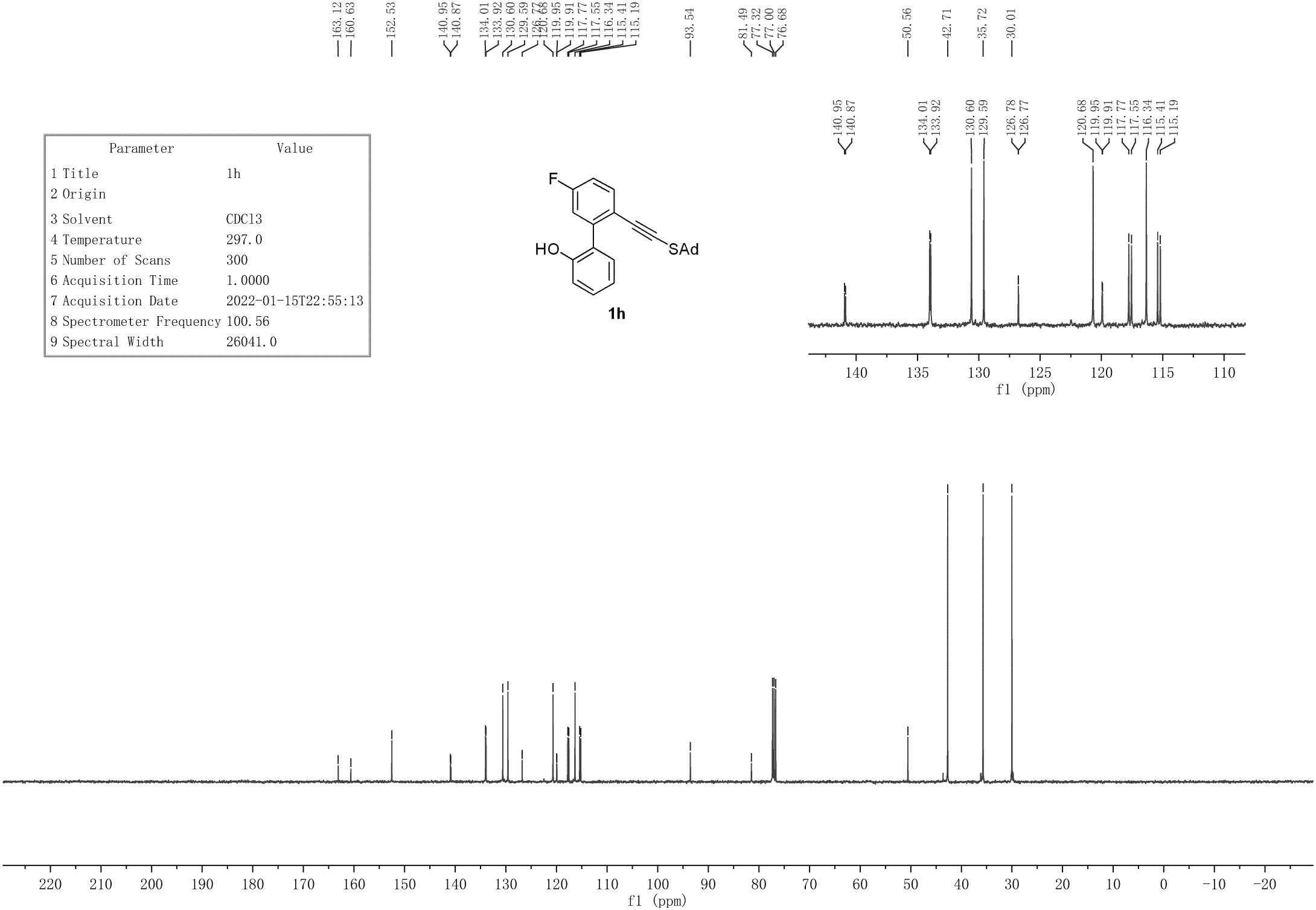
1g

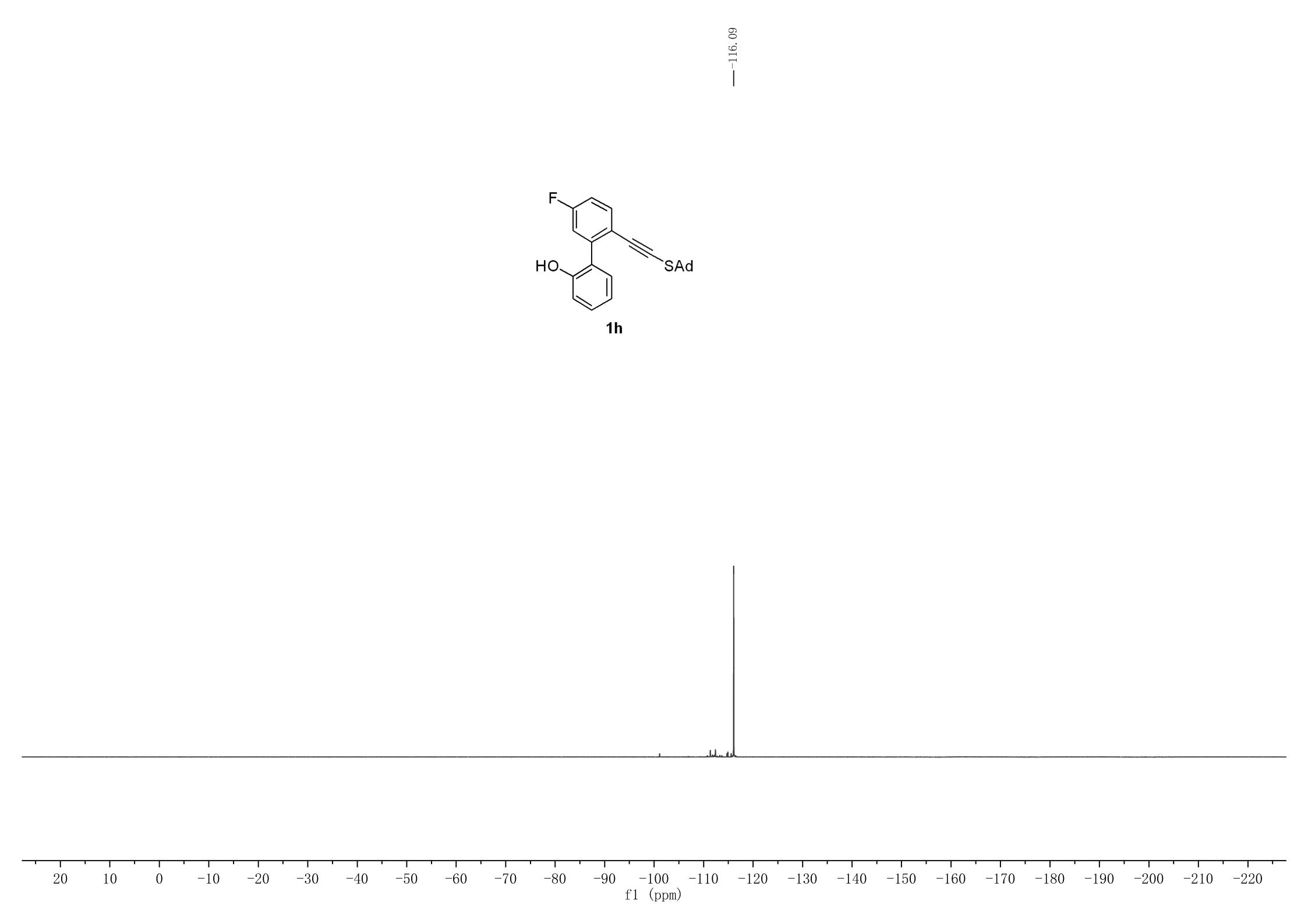



7.451
7.436
7.428
7.413
7.196
7.172
7.152
7.131
6.992
6.986
6.969
6.947
6.916
6.900
6.881
5.014
1.879
1.622
1.616
1.558
1.527
1.489
1.458
0.000
Parameter Value
1 Title 1h
2 Origin
3 Solvent CDCl3
4 Temperature 297.0
5 Number of Scans 16
6 Acquisition Time 4.0002
7 Acquisition Date 2022-01-15T22:42:44
8 Spectrometer Frequency 399.93
9 Spectral Width 8012.0
F
HO
SAd
1h
1.00
2.05
2.02
2.06
1.00
3.04
6.02
6.05
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	1h
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.0
5 Number of Scans	300
6 Acquisition Time	1.0000
7 Acquisition Date	2022-01-15T22:55:13
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

1h




-116.09
F
HO
SAd
1h
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
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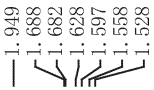
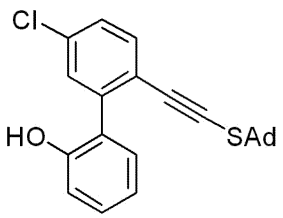
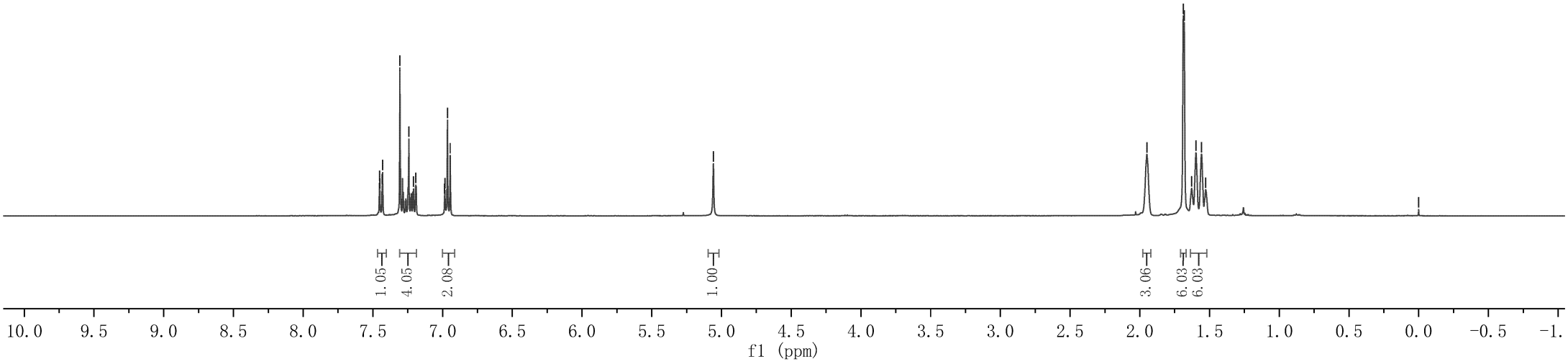
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)



Parameter	Value
1 Title	FXY-7-149
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	2022-02-25T16:55:05
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8

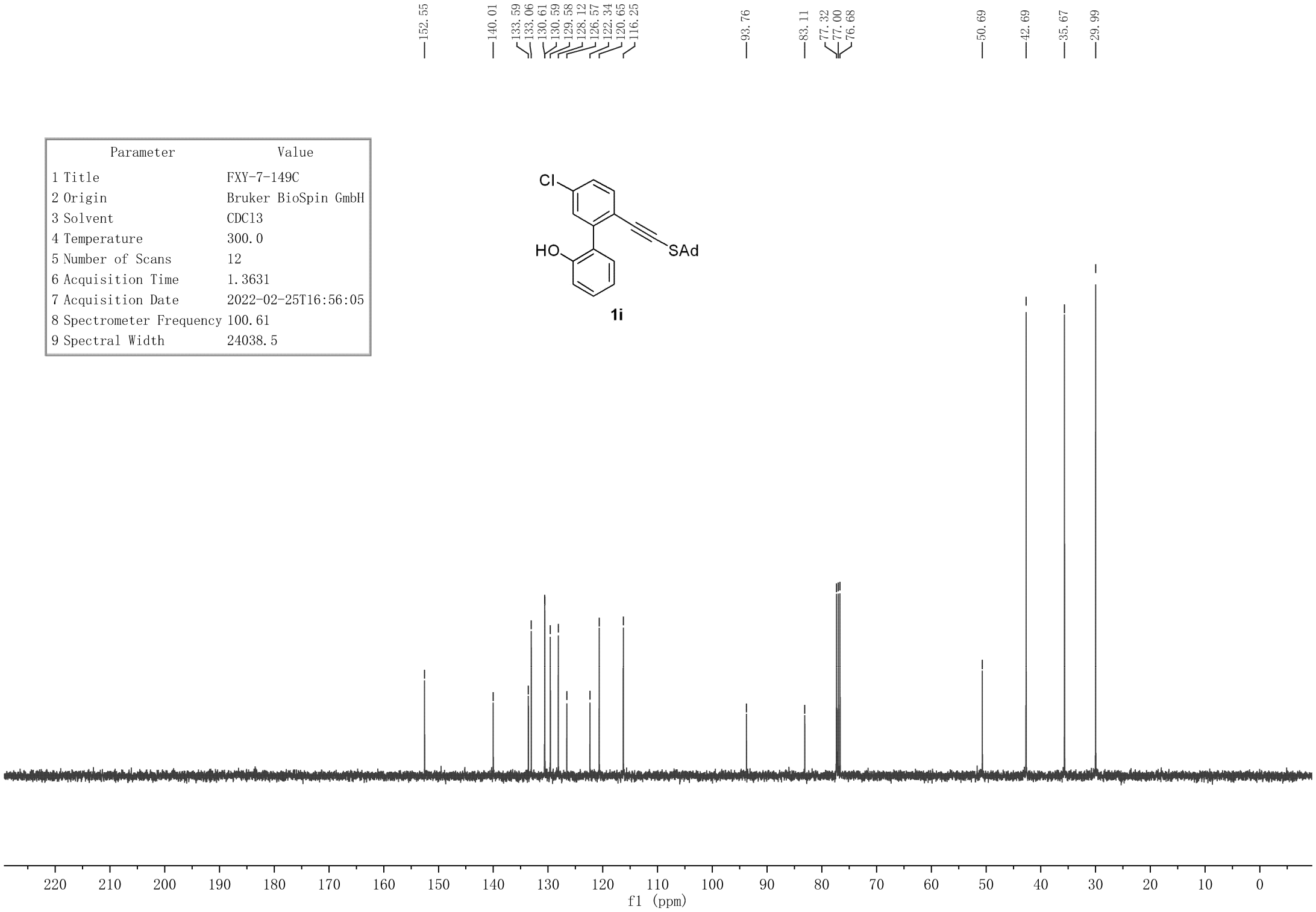


1i

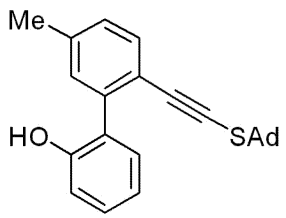


Parameter	Value
1 Title	FXY-7-149C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	12
6 Acquisition Time	1.3631
7 Acquisition Date	2022-02-25T16:56:05
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5

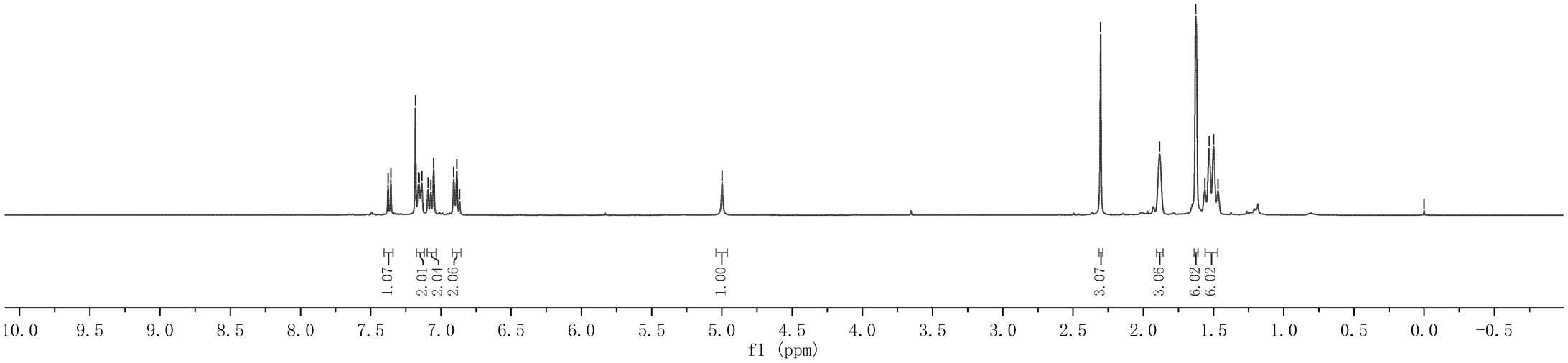
1i



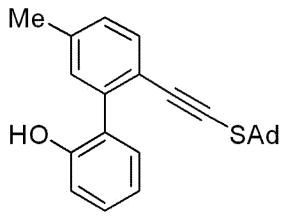
Parameter	Value
1 Title	1j
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.6
5 Number of Scans	32
6 Acquisition Time	4.0002
7 Acquisition Date	2022-01-19T01:11:53
8 Spectrometer Frequency	399.93
9 Spectral Width	8012.0



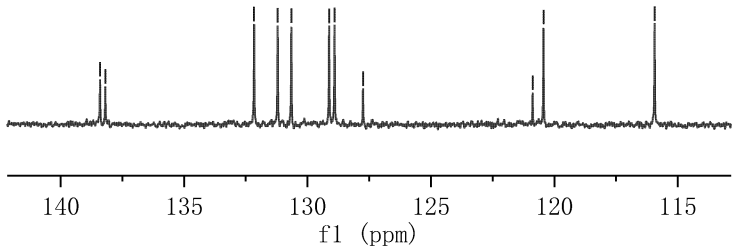
1j

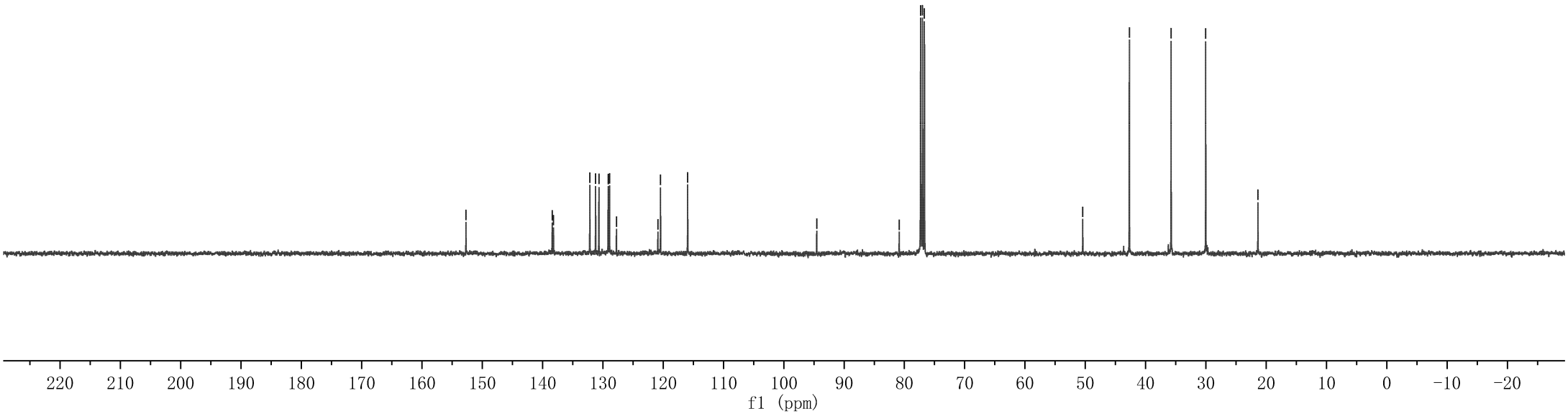


Parameter	Value
1 Title	1j
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.8
5 Number of Scans	400
6 Acquisition Time	1.0000
7 Acquisition Date	2022-01-19T01:27:42
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

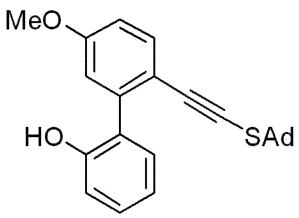


1j

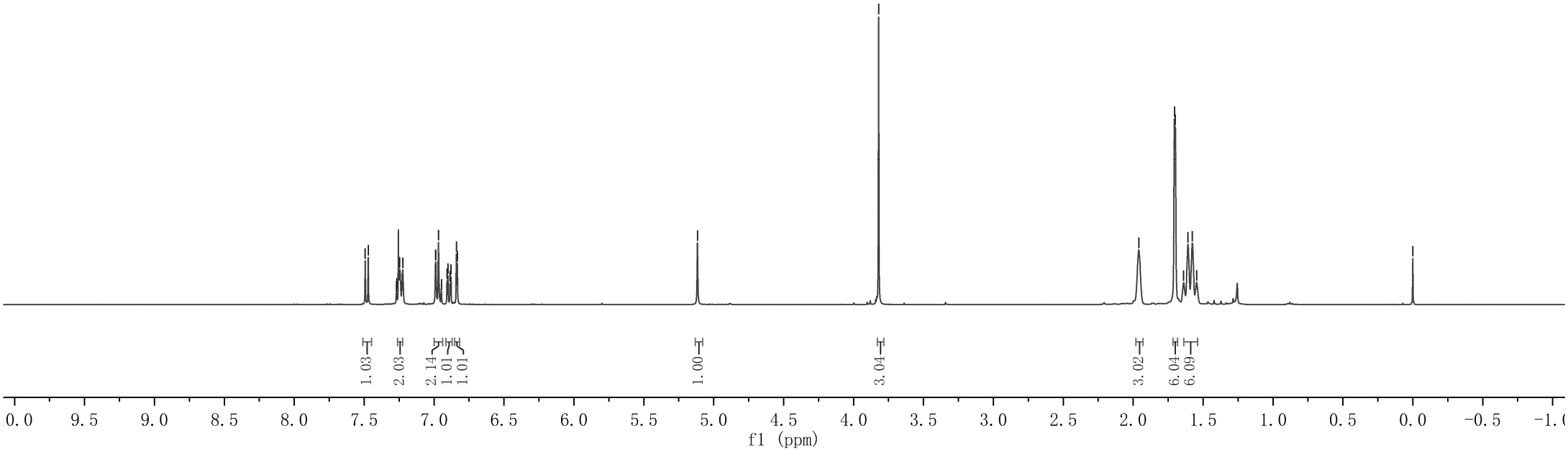


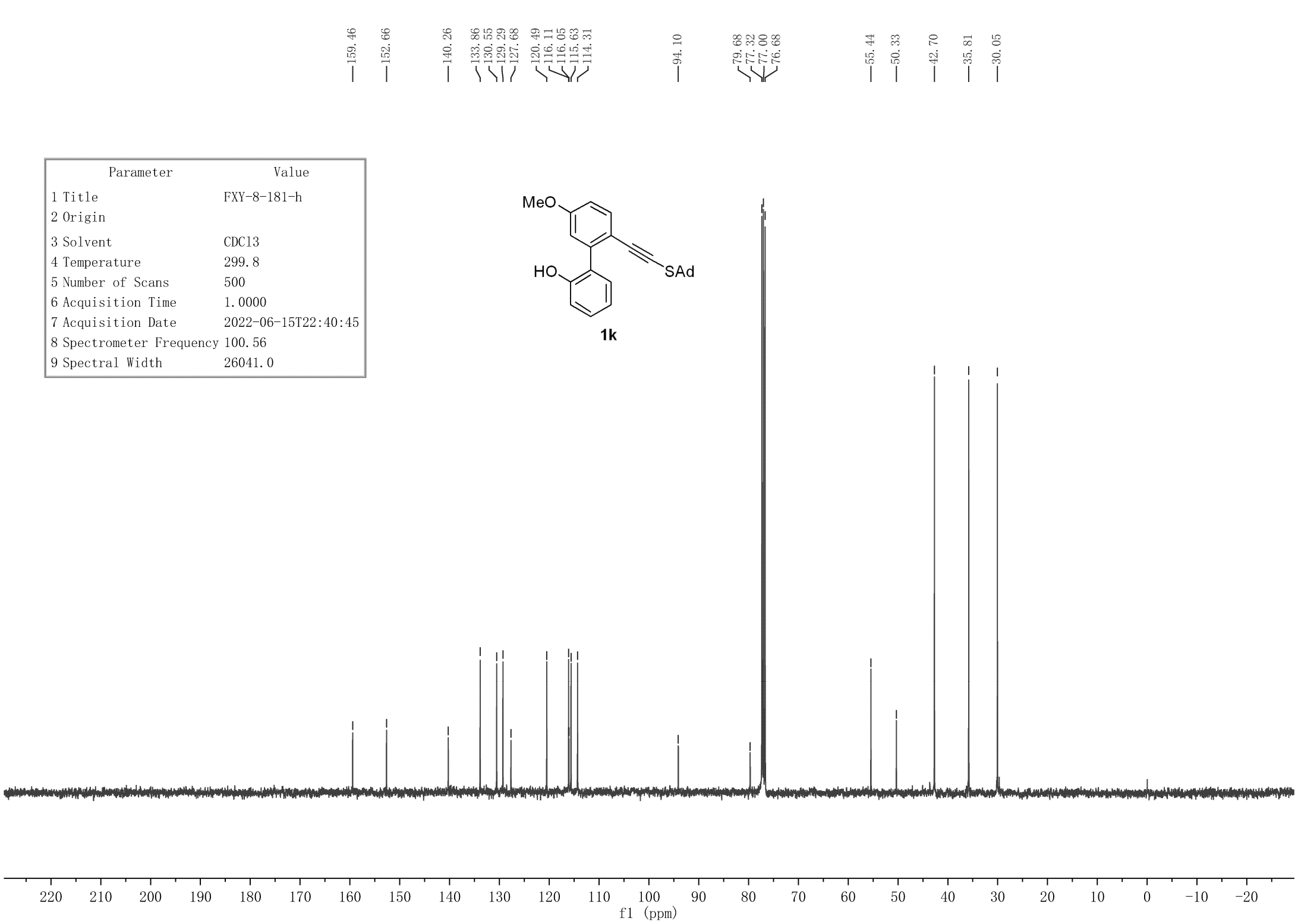


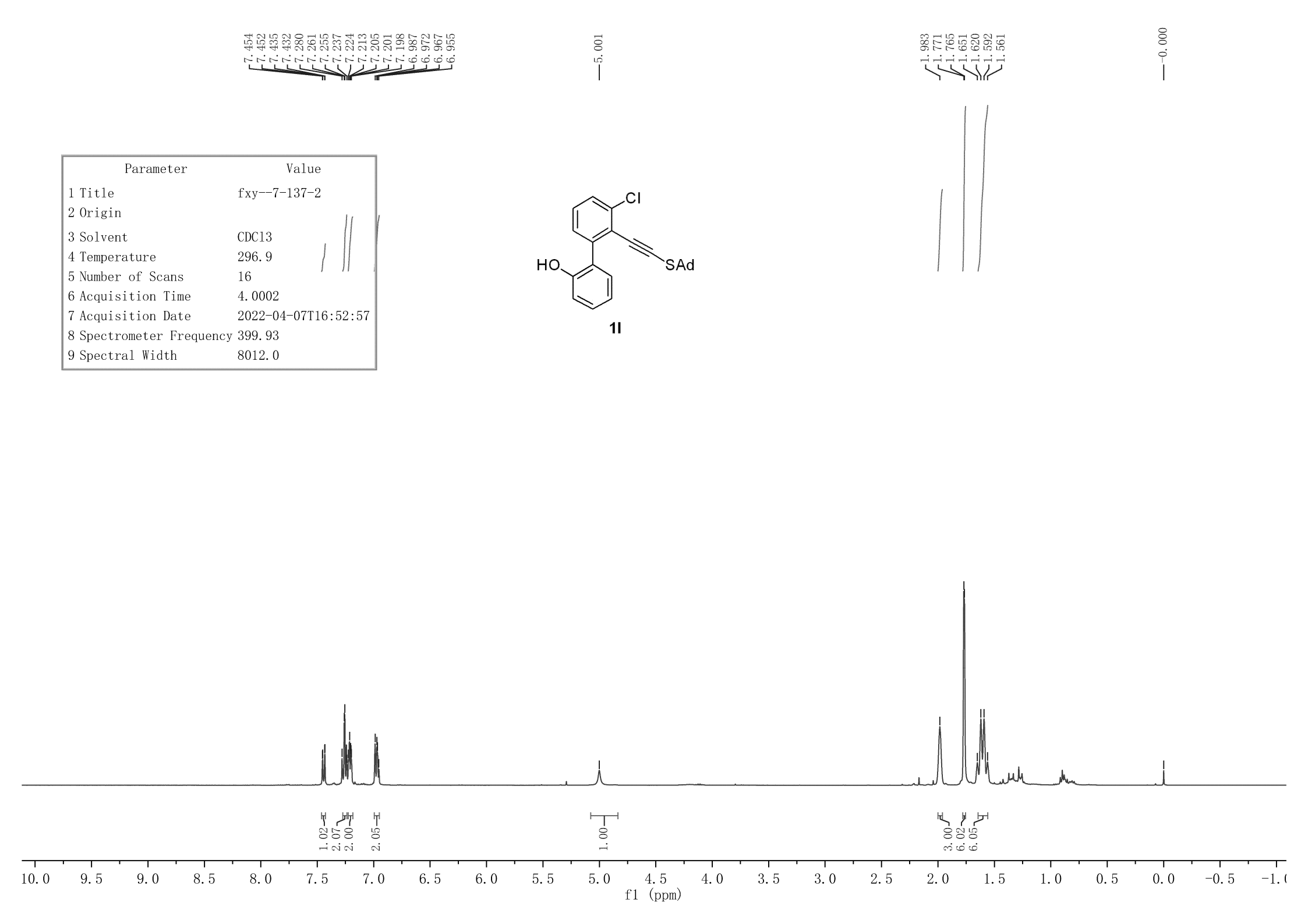
Parameter	Value
1 Title	FXY-8-181-h
2 Origin	
3 Solvent	CDCl3
4 Temperature	299.6
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2022-06-15T22:21:52
8 Spectrometer Frequency	399.92
9 Spectral Width	8012.0



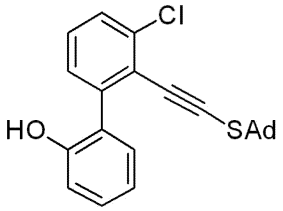
1k



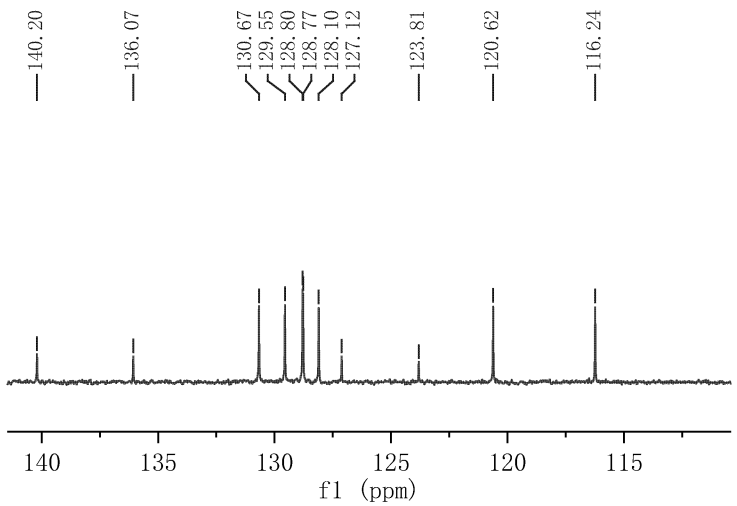

159.46
152.66
140.26
133.86
130.55
129.29
127.68
120.49
116.11
116.05
115.63
114.31
94.10
79.68
77.32
77.00
76.68
55.44
50.33
42.70
35.81
30.05
Parameter Value
1 Title FXY-8-181-h
2 Origin
3 Solvent CDCl3
4 Temperature 299.8
5 Number of Scans 500
6 Acquisition Time 1.0000
7 Acquisition Date 2022-06-15T22:40:45
8 Spectrometer Frequency 100.56
9 Spectral Width 26041.0
MeO
HO
SAd
1k
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

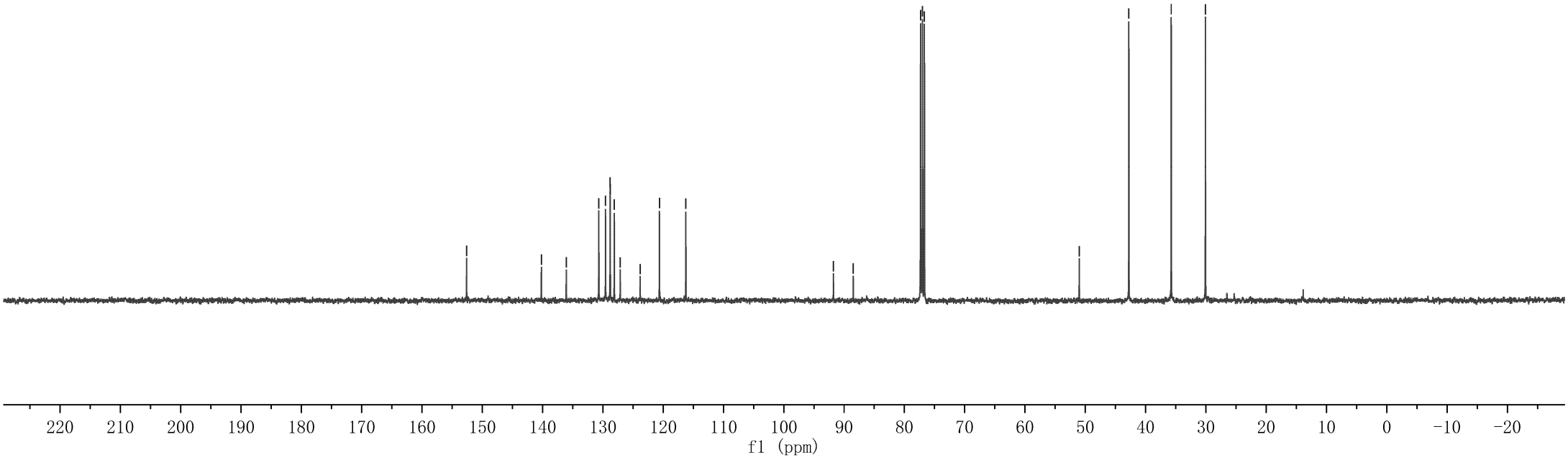

7.454
7.452
7.435
7.432
7.280
7.261
7.255
7.237
7.224
7.213
7.205
7.201
7.198
6.987
6.972
6.967
6.955
5.001
1.983
1.771
1.765
1.651
1.620
1.592
1.561
0.000
Parameter Value
1 Title fxy--7-137-2
2 Origin
3 Solvent CDCl3
4 Temperature 296.9
5 Number of Scans 16
6 Acquisition Time 4.0002
7 Acquisition Date 2022-04-07T16:52:57
8 Spectrometer Frequency 399.93
9 Spectral Width 8012.0
Cl
HO
SAd
1l
1.02
2.07
2.00
2.05
1.00
3.00
6.02
6.05
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
f1 (ppm)

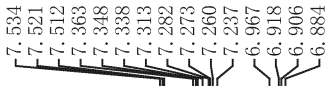
Parameter	Value
1 Title	fxy--7-137-2
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.3
5 Number of Scans	500
6 Acquisition Time	1.0000
7 Acquisition Date	2022-04-07T17:11:46
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

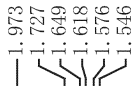


1l

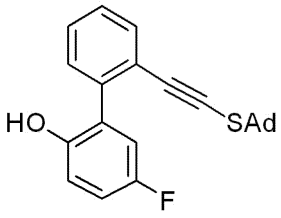




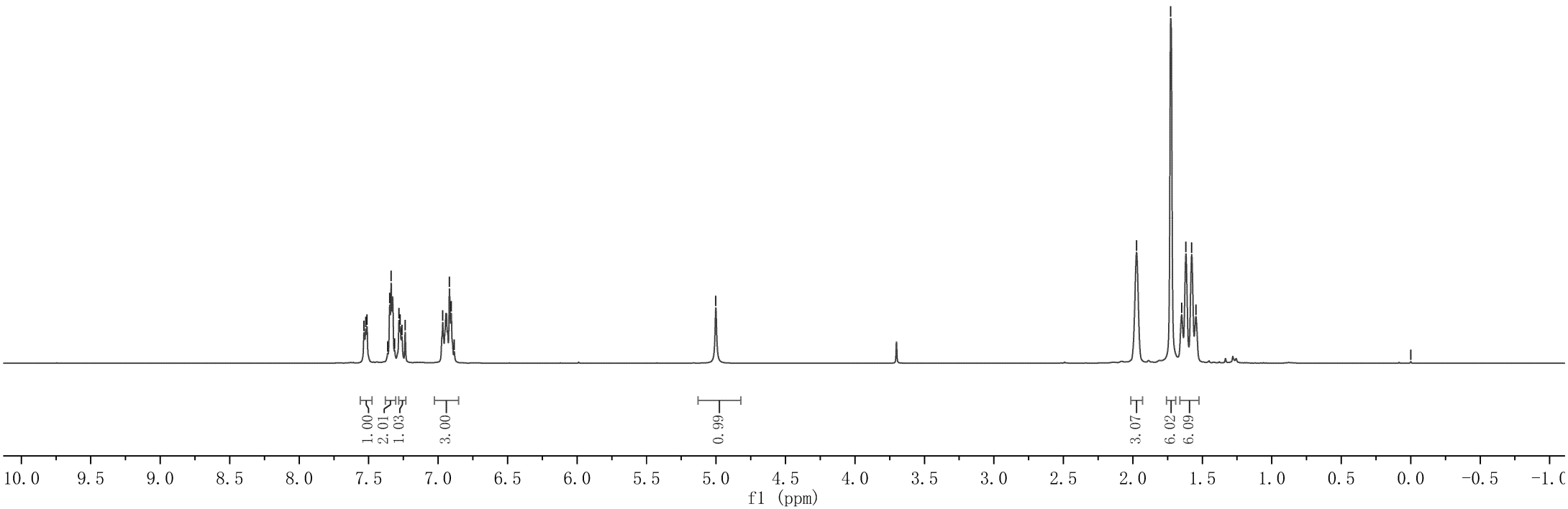




Parameter	Value
1 Title	1m
2 Origin	
3 Solvent	CDCl3
4 Temperature	298.8
5 Number of Scans	800
6 Acquisition Time	1.0000
7 Acquisition Date	2022-05-17T18:38:41
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

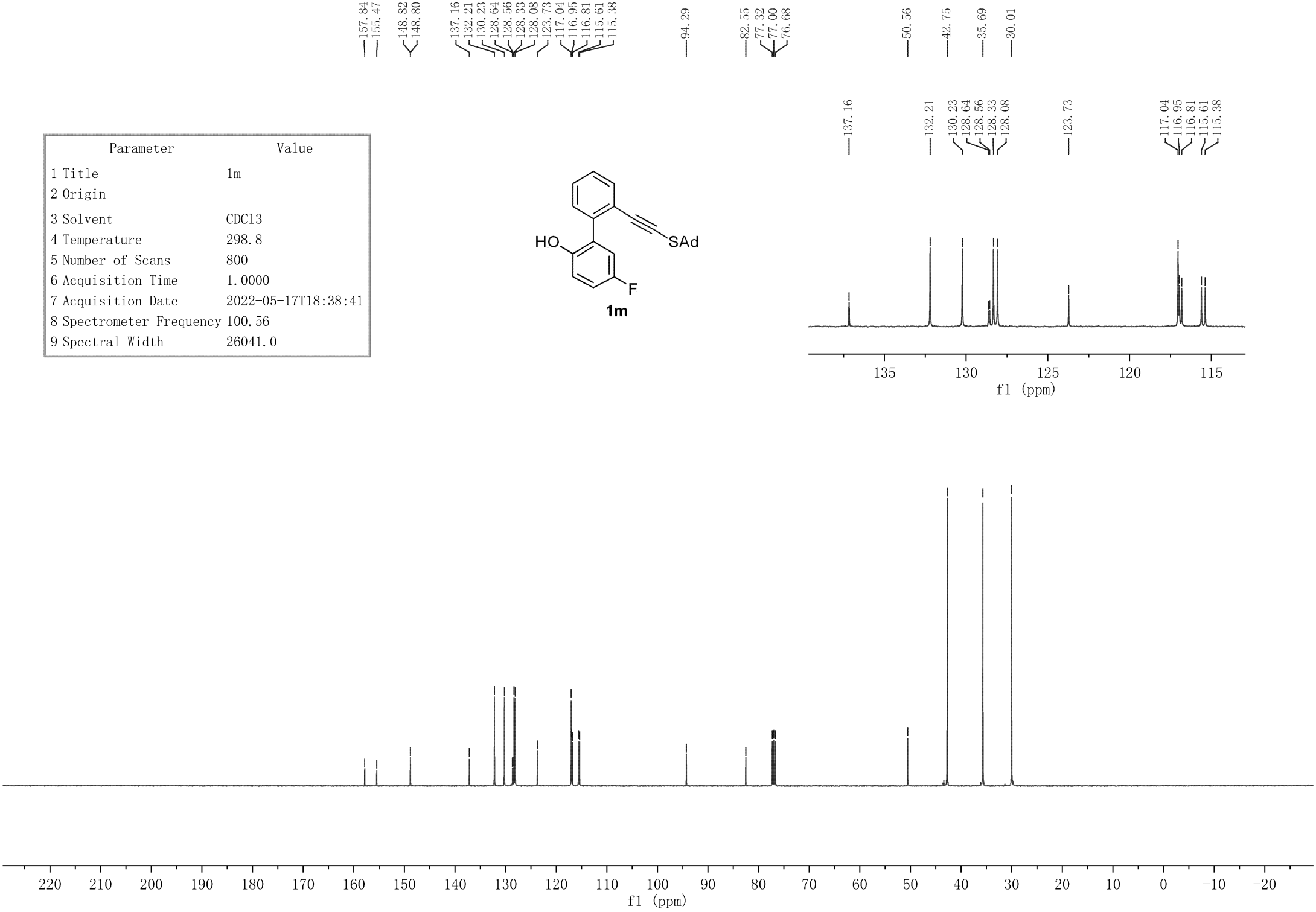


1m



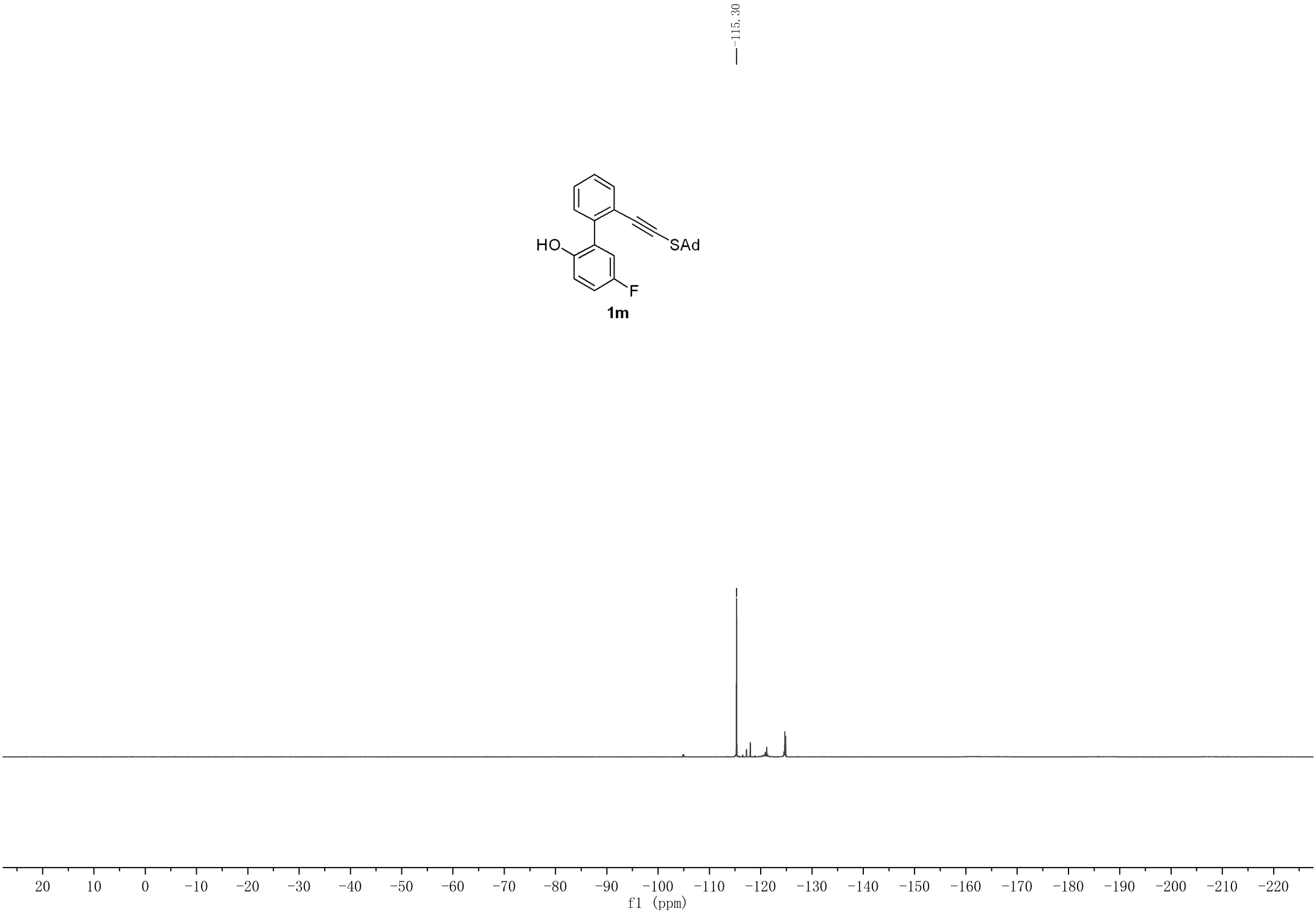
Parameter	Value
1 Title	1m
2 Origin	
3 Solvent	CDCl3
4 Temperature	298.8
5 Number of Scans	800
6 Acquisition Time	1.0000
7 Acquisition Date	2022-05-17T18:38:41
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

1m



HO
SAd
F

1m


-115.30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
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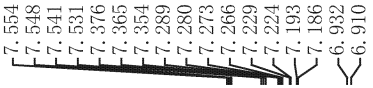
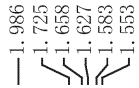
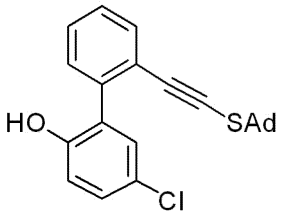
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)

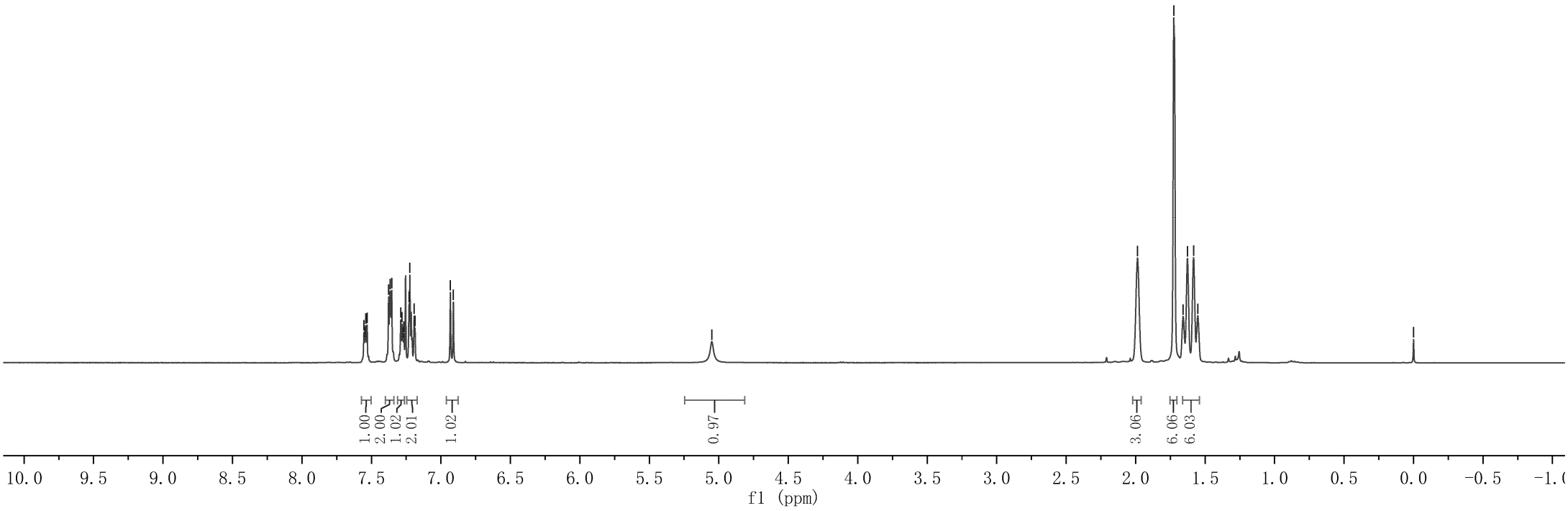




Parameter	Value
1 Title	fxy-7-165
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.5
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2022-03-02T10:49:29
8 Spectrometer Frequency	399.93
9 Spectral Width	8012.0

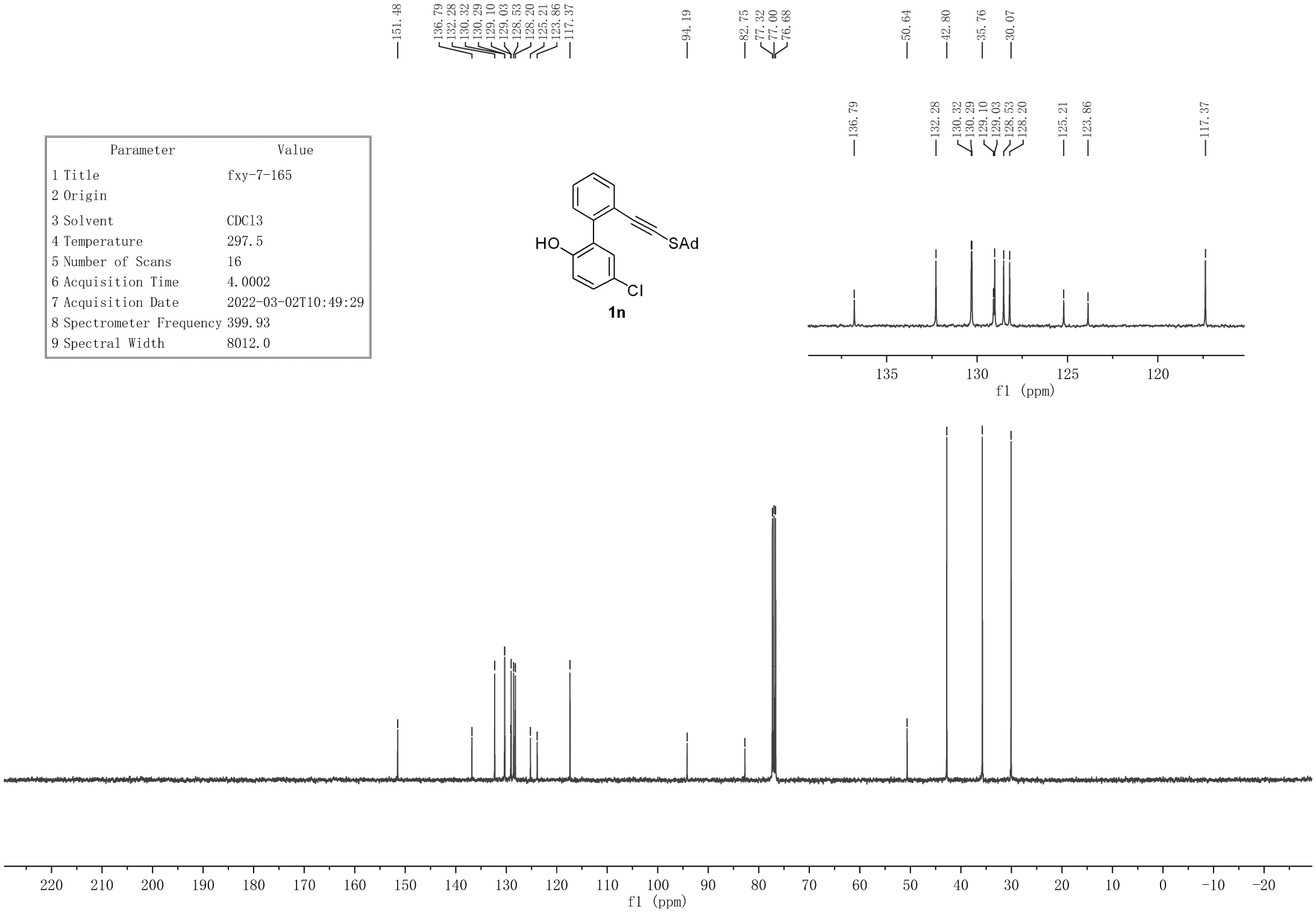


1n

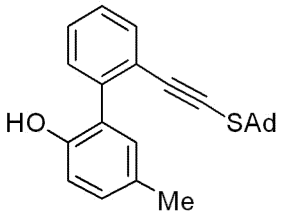


Parameter	Value
1 Title	fxy-7-165
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.5
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2022-03-02T10:49:29
8 Spectrometer Frequency	399.93
9 Spectral Width	8012.0

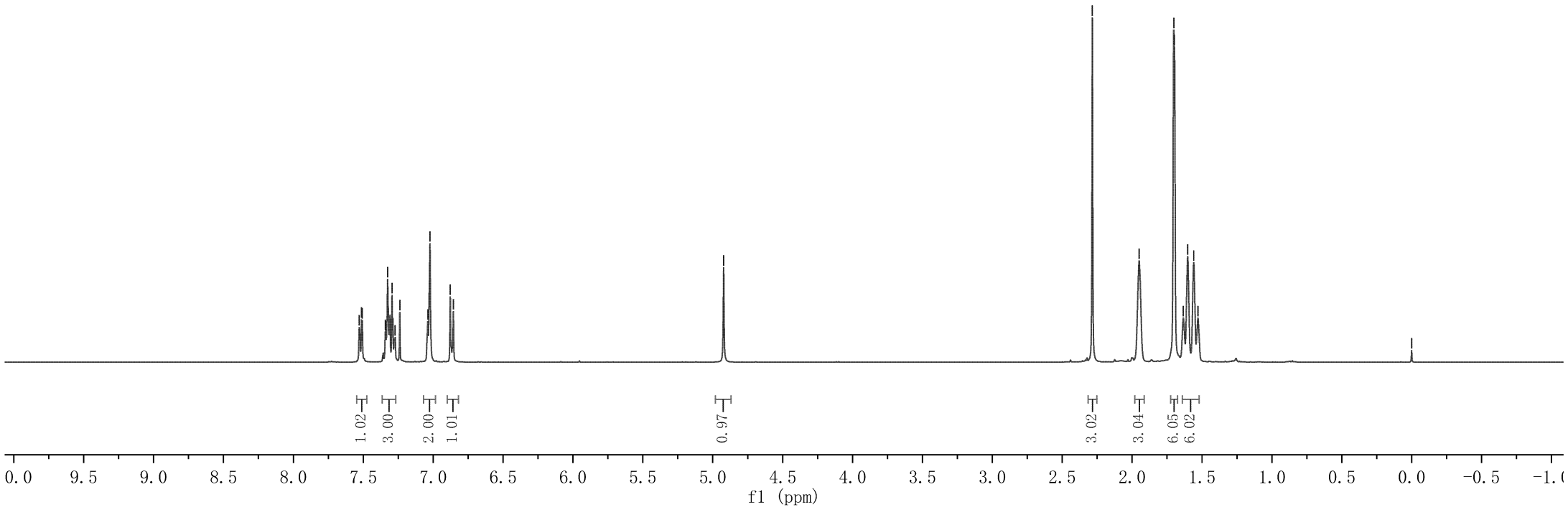
1n



Parameter	Value
1 Title	1o
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.5
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2022-03-02T11:09:48
8 Spectrometer Frequency	399.93
9 Spectral Width	8012.0

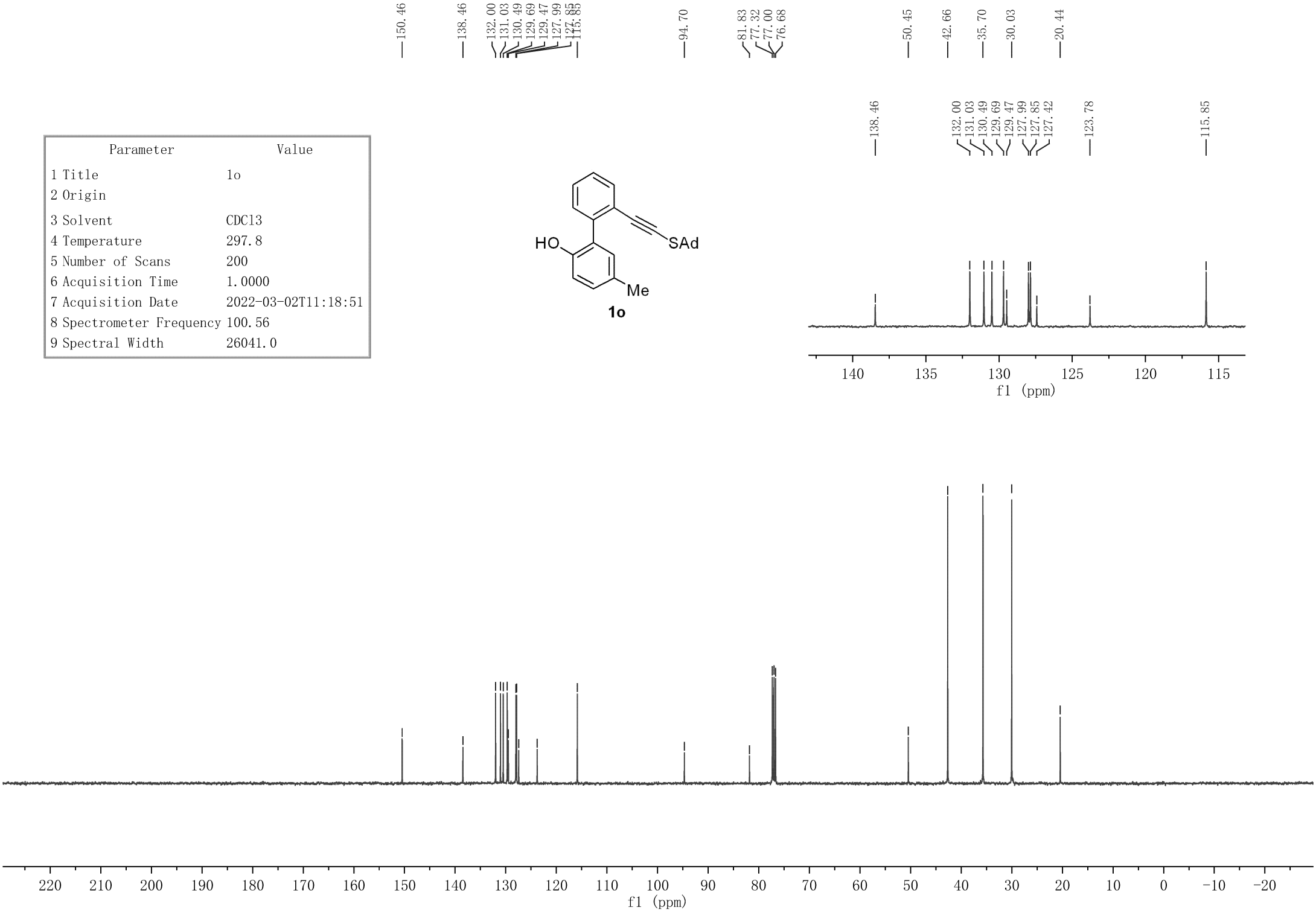


1o

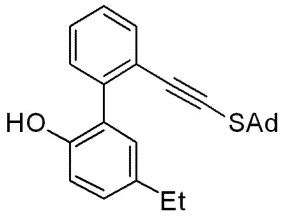


Parameter	Value
1 Title	1o
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.8
5 Number of Scans	200
6 Acquisition Time	1.0000
7 Acquisition Date	2022-03-02T11:18:51
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

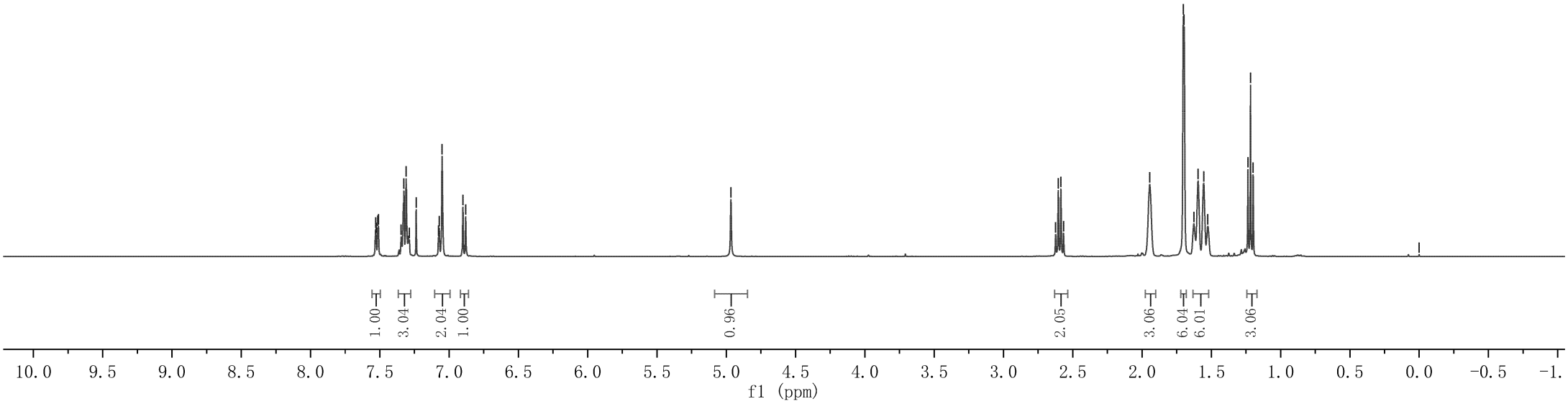
1o



Parameter	Value
1 Title	fxy-8-137-H
2 Origin	
3 Solvent	CDCl3
4 Temperature	299.5
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2022-05-26T20:06:19
8 Spectrometer Frequency	399.92
9 Spectral Width	8012.0

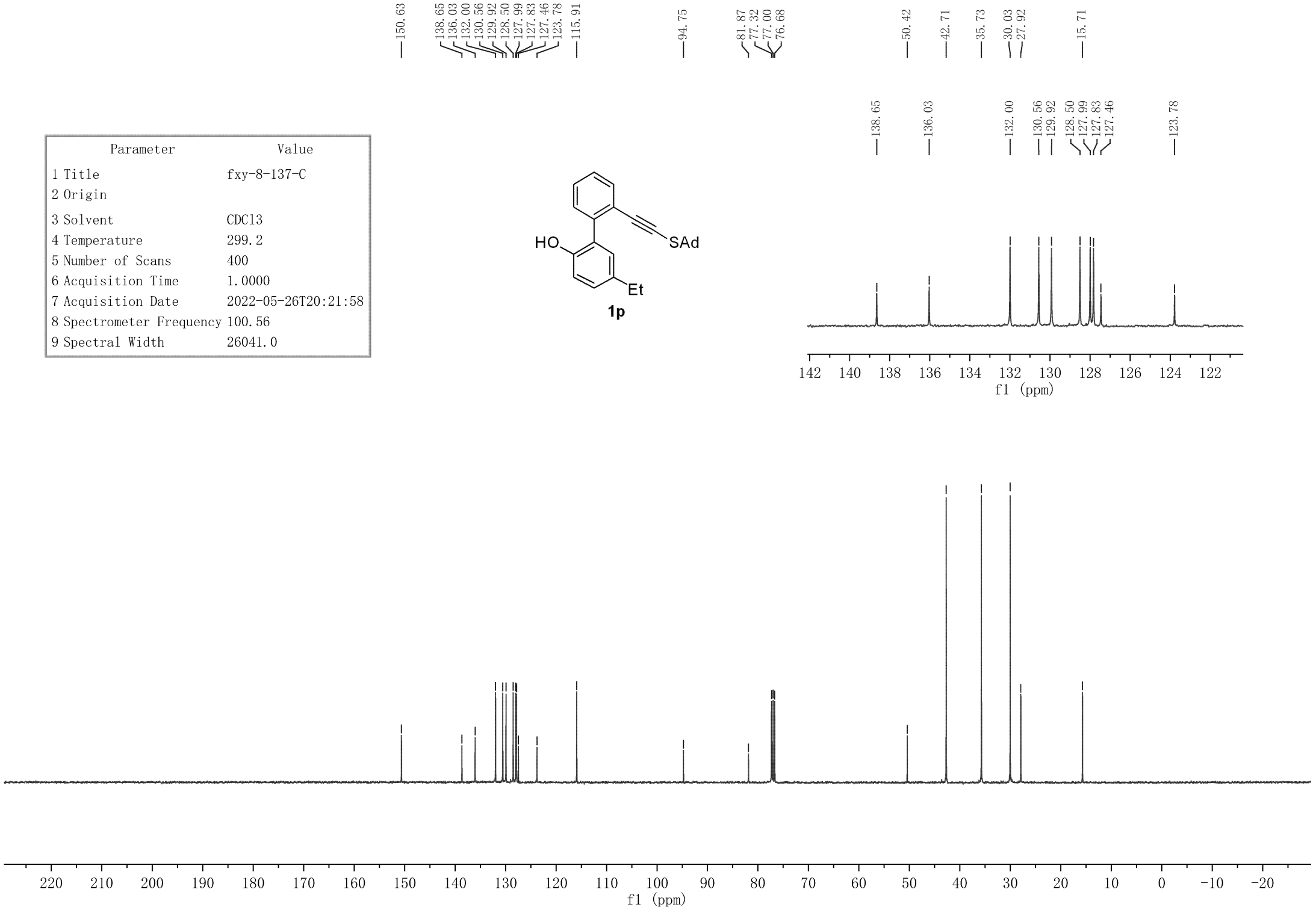


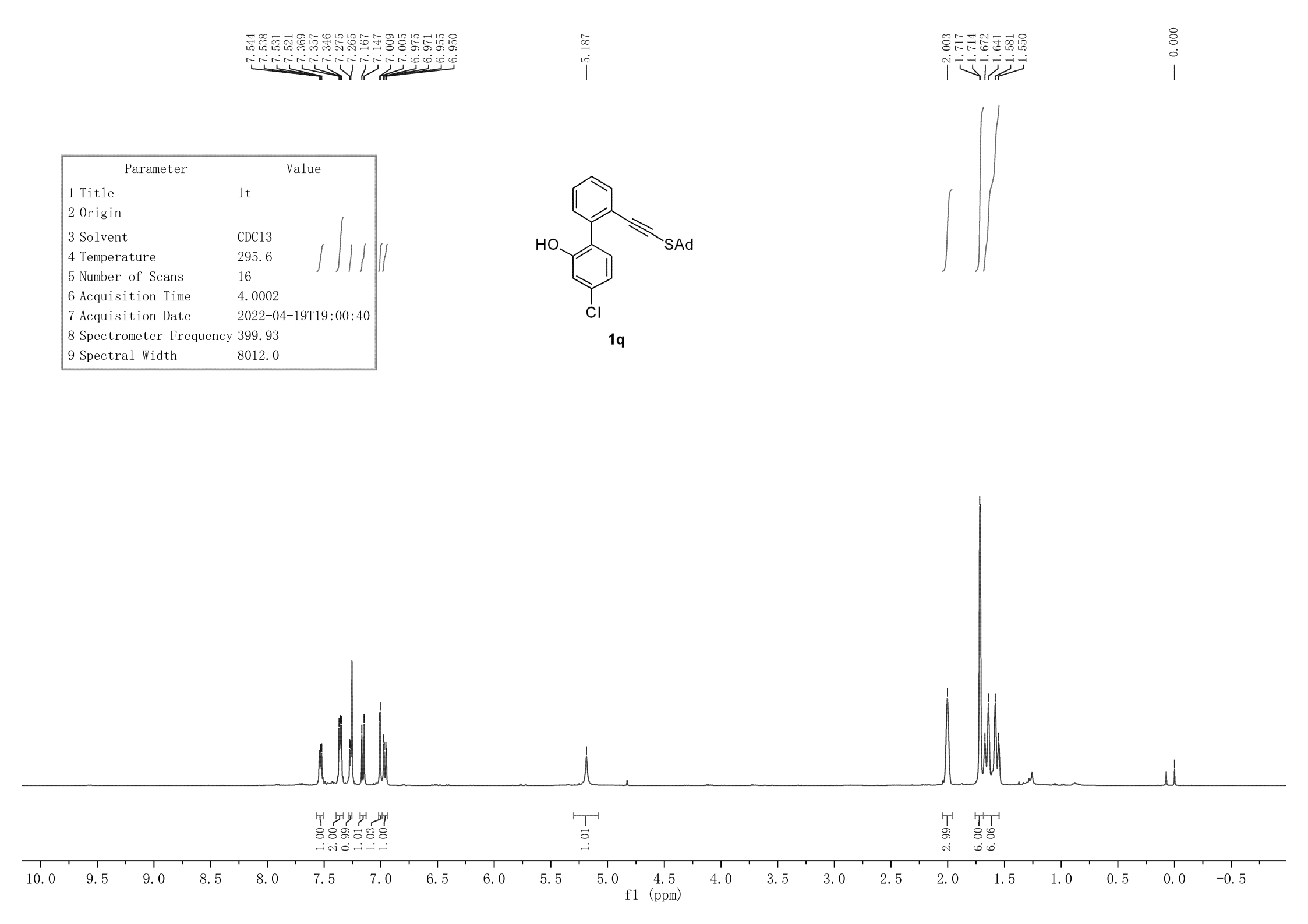
1p



Parameter	Value
1 Title	fxy-8-137-C
2 Origin	
3 Solvent	CDCl3
4 Temperature	299.2
5 Number of Scans	400
6 Acquisition Time	1.0000
7 Acquisition Date	2022-05-26T20:21:58
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

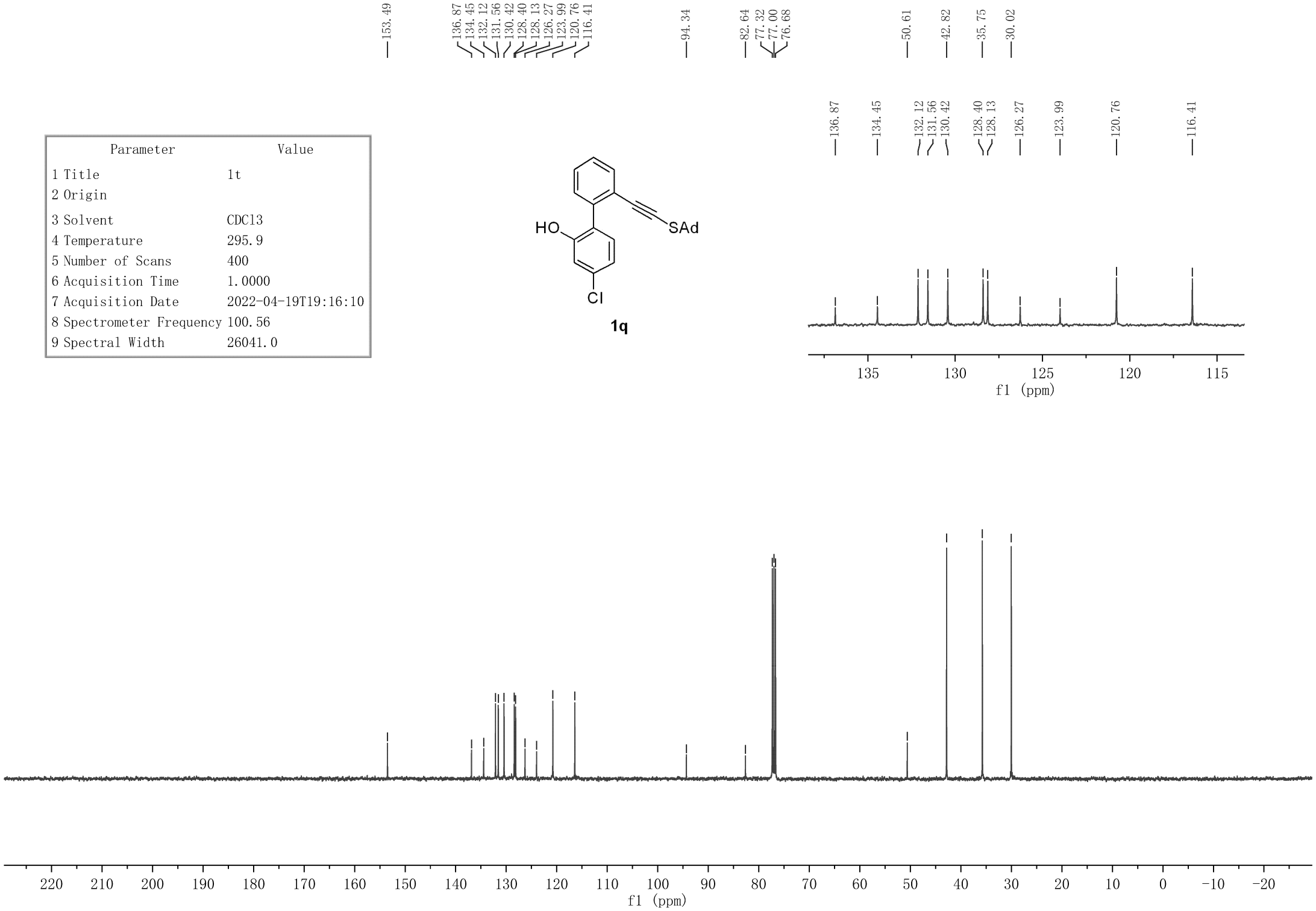
1p



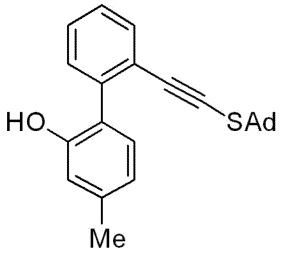

7.544
7.538
7.531
7.521
7.369
7.357
7.346
7.275
7.265
7.167
7.147
7.009
7.005
6.975
6.971
6.955
6.950
5.187
2.003
1.717
1.714
1.672
1.641
1.581
1.550
0.000
Parameter Value
1 Title 1t
2 Origin
3 Solvent CDCl3
4 Temperature 295.6
5 Number of Scans 16
6 Acquisition Time 4.0002
7 Acquisition Date 2022-04-19T19:00:40
8 Spectrometer Frequency 399.93
9 Spectral Width 8012.0
HO
SAd
Cl
1q
1.00
2.00
0.99
1.01
1.03
1.00
1.01
2.99
6.00
6.06
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
f1 (ppm)

Parameter	Value
1 Title	1t
2 Origin	
3 Solvent	CDCl3
4 Temperature	295.9
5 Number of Scans	400
6 Acquisition Time	1.0000
7 Acquisition Date	2022-04-19T19:16:10
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

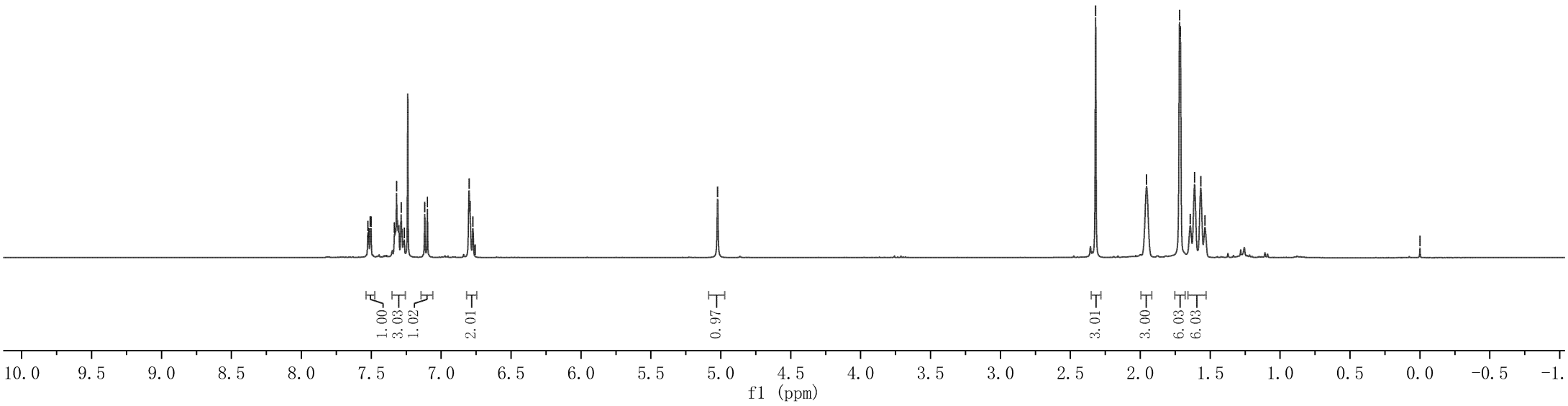
1q

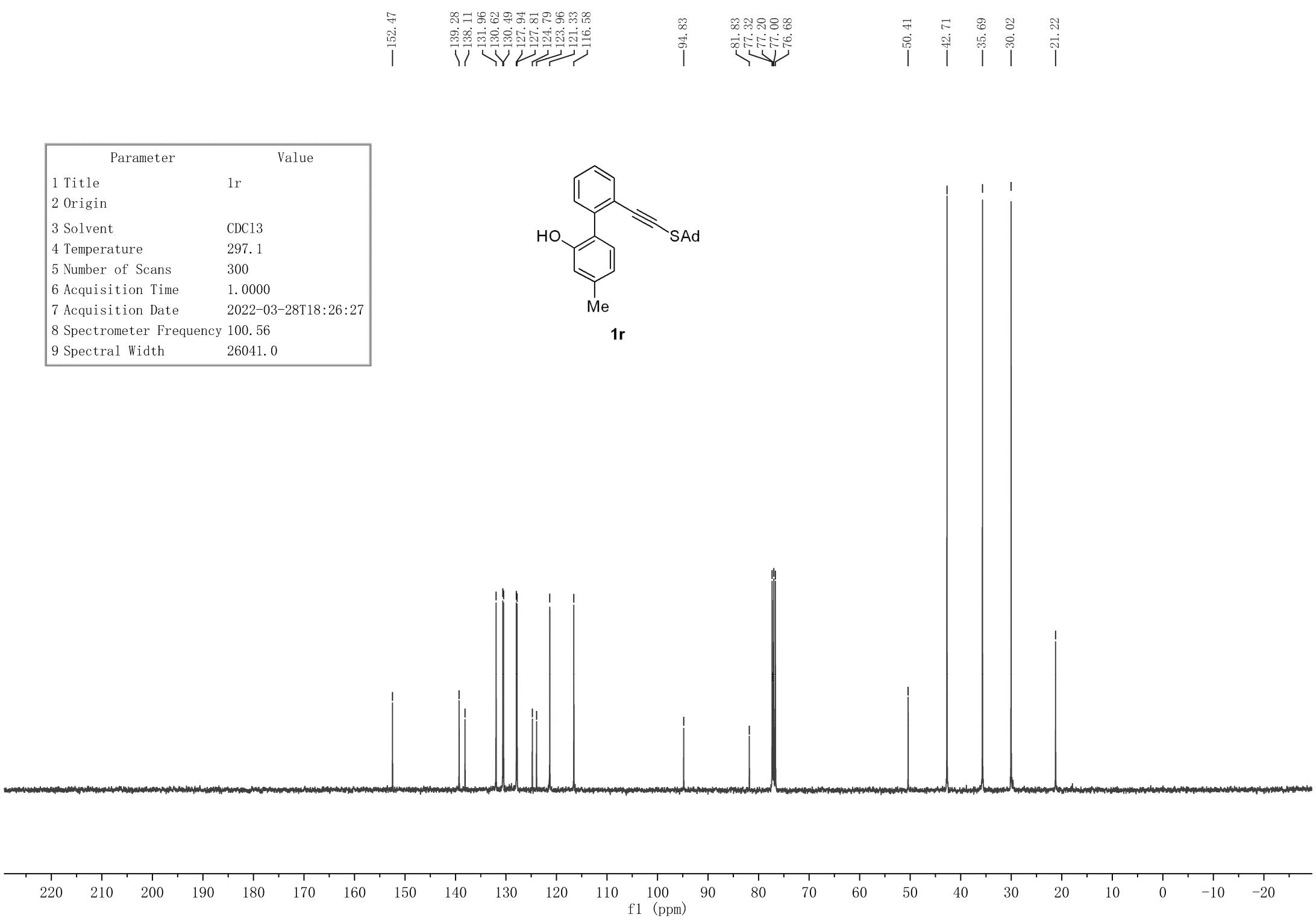


Parameter	Value
1 Title	1r
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.2
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2022-03-28T18:14:18
8 Spectrometer Frequency	399.93
9 Spectral Width	8012.0



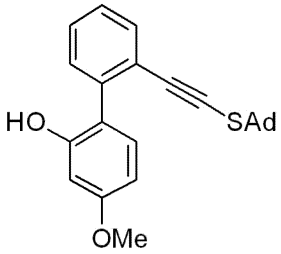
1r



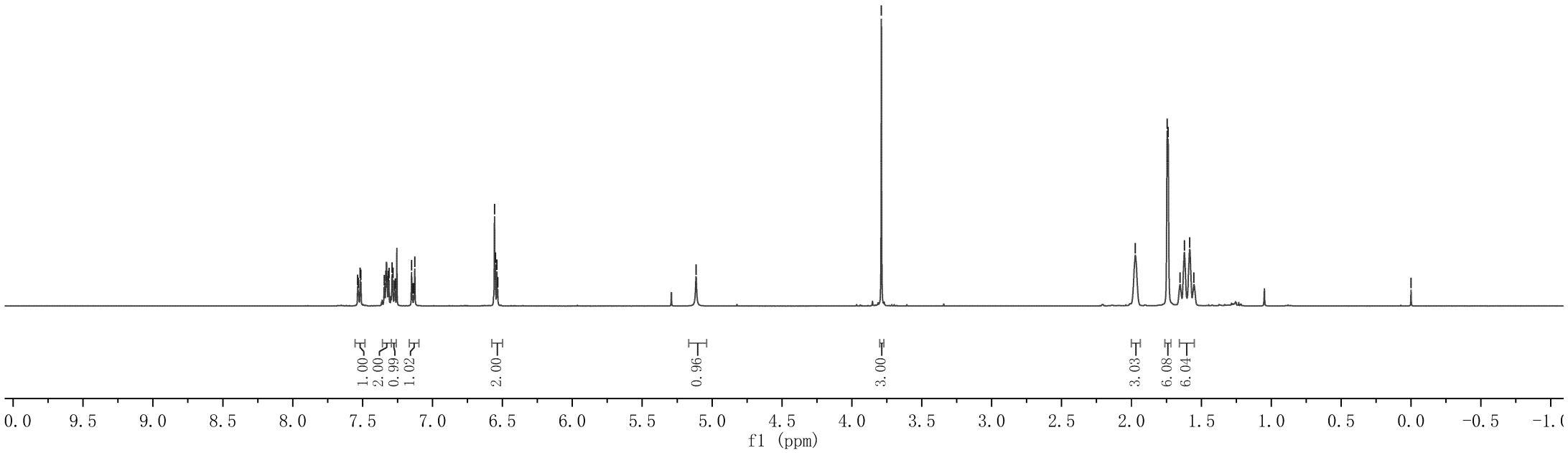


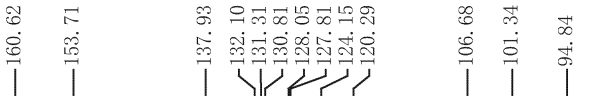
Parameter	Value
1 Title	1r
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.1
5 Number of Scans	300
6 Acquisition Time	1.0000
7 Acquisition Date	2022-03-28T18:26:27
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

Parameter	Value
1 Title	1s
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.8
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2022-04-01T18:13:14
8 Spectrometer Frequency	399.93
9 Spectral Width	8012.0

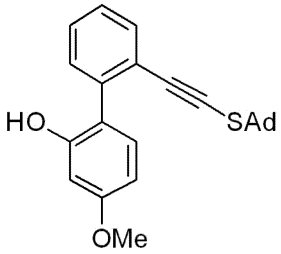


1s

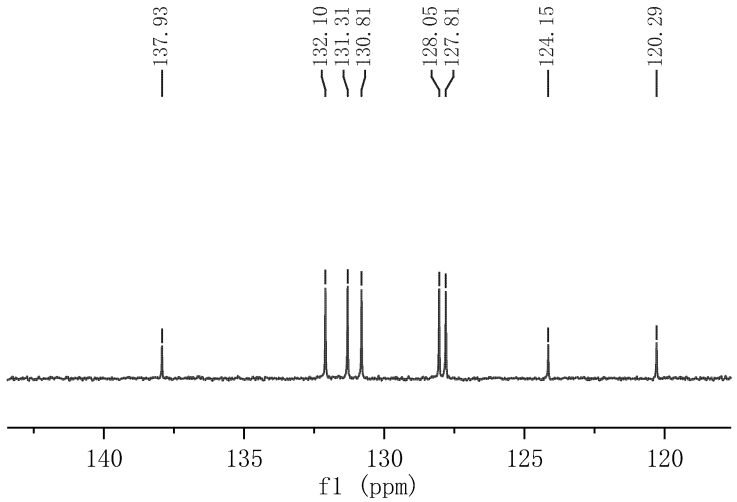


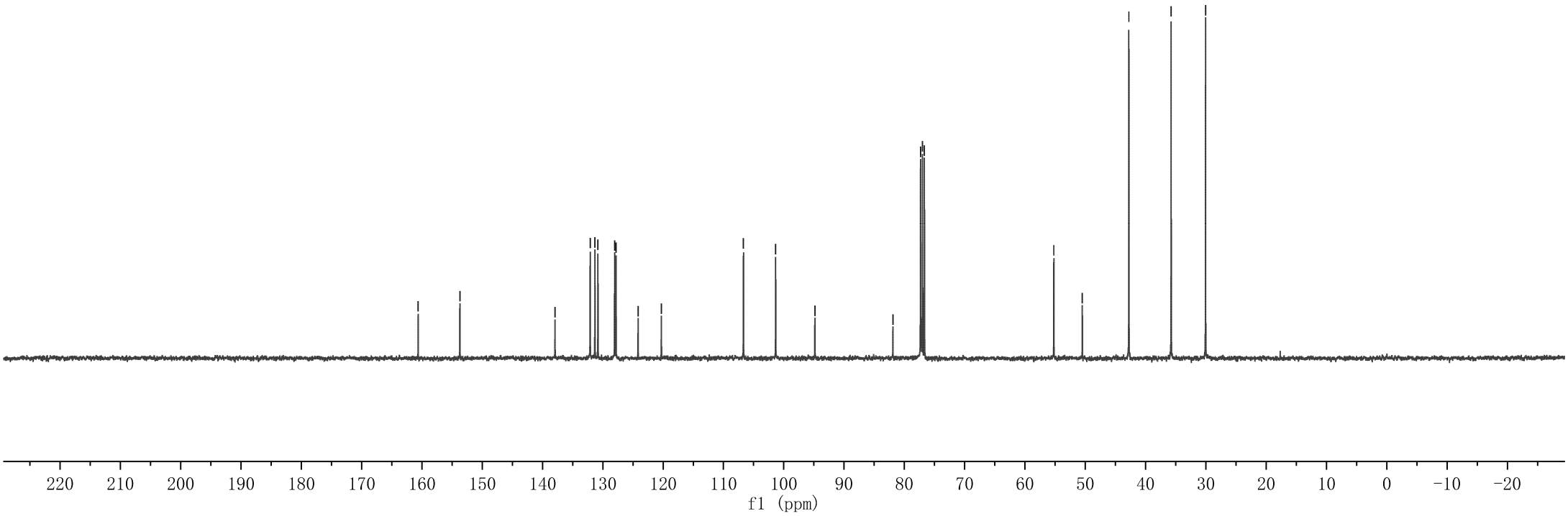


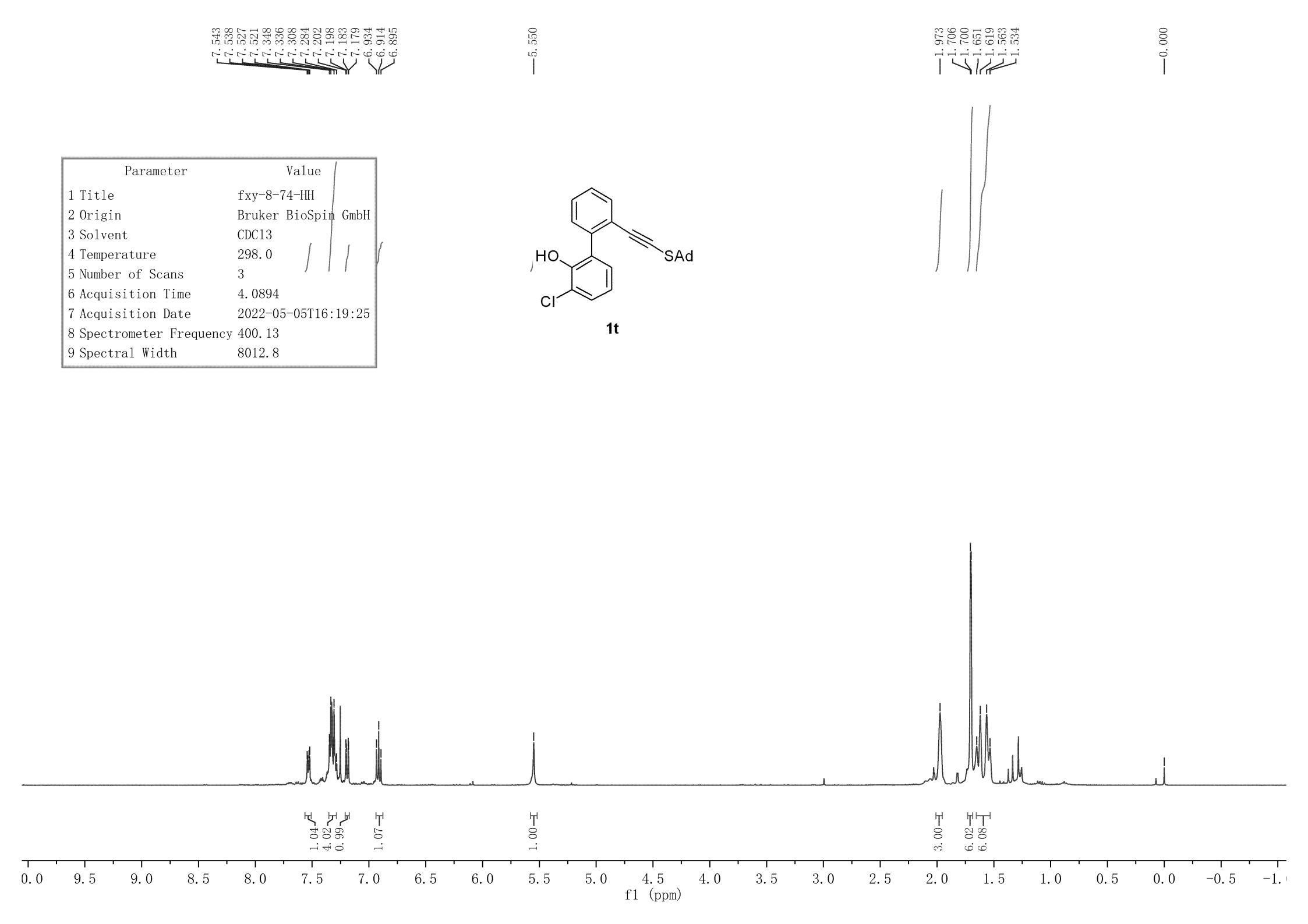
Parameter	Value
1 Title	1s
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.8
5 Number of Scans	600
6 Acquisition Time	1.0000
7 Acquisition Date	2022-04-01T18:35:36
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0



1s

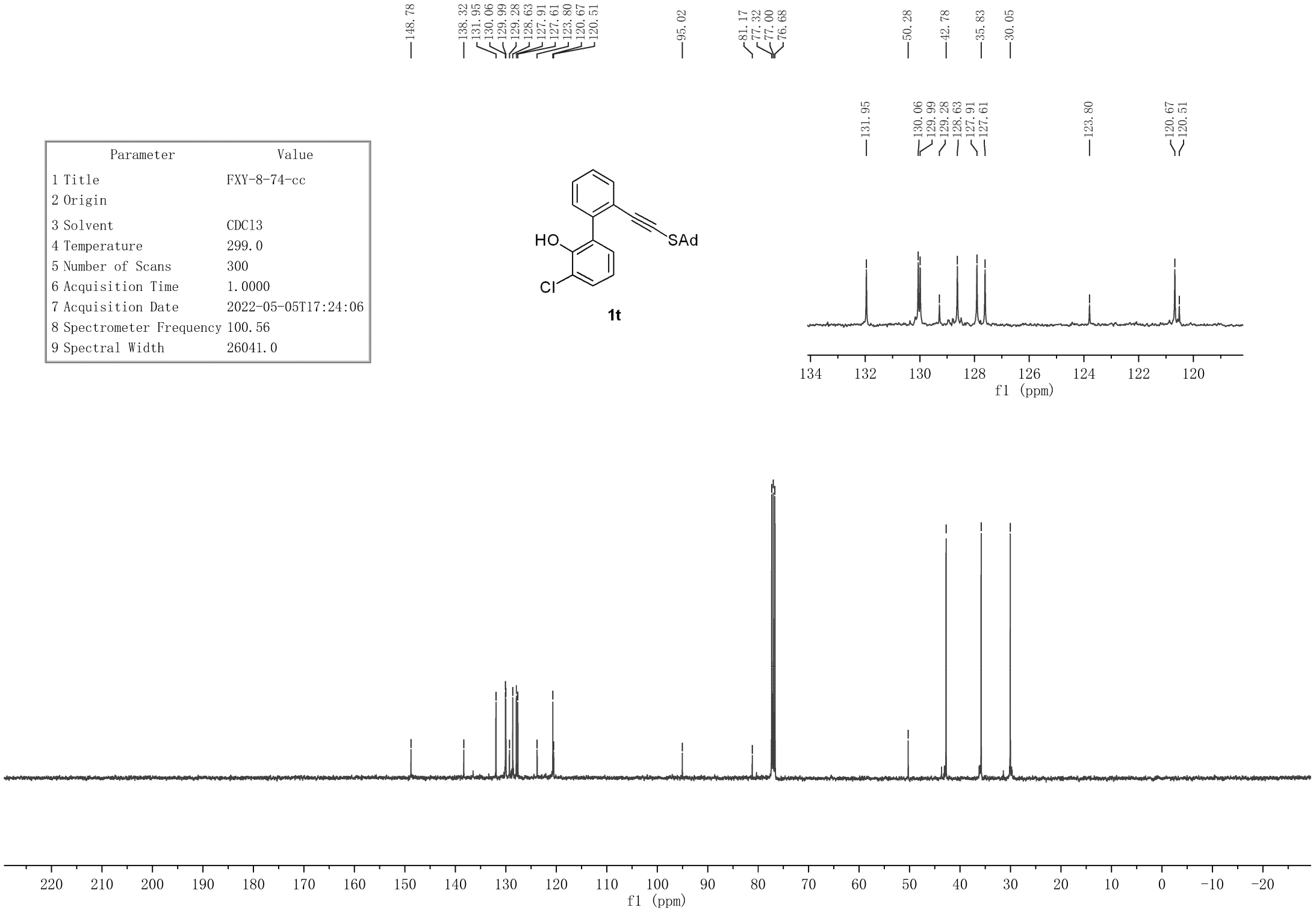




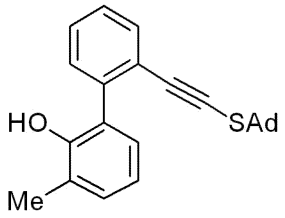

7.543
7.538
7.527
7.521
7.348
7.336
7.308
7.284
7.202
7.198
7.183
7.179
6.934
6.914
6.895
5.550
1.973
1.706
1.700
1.651
1.619
1.563
1.534
0.000
Parameter Value
1 Title fxy-8-74-HH
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 298.0
5 Number of Scans 3
6 Acquisition Time 4.0894
7 Acquisition Date 2022-05-05T16:19:25
8 Spectrometer Frequency 400.13
9 Spectral Width 8012.8
HO
SAd
Cl
1t
1.04
4.02
0.99
1.07
1.00
3.00
6.02
6.08
0.0
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
f1 (ppm)

Parameter	Value
1 Title	FXY-8-74-cc
2 Origin	
3 Solvent	CDCl3
4 Temperature	299.0
5 Number of Scans	300
6 Acquisition Time	1.0000
7 Acquisition Date	2022-05-05T17:24:06
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

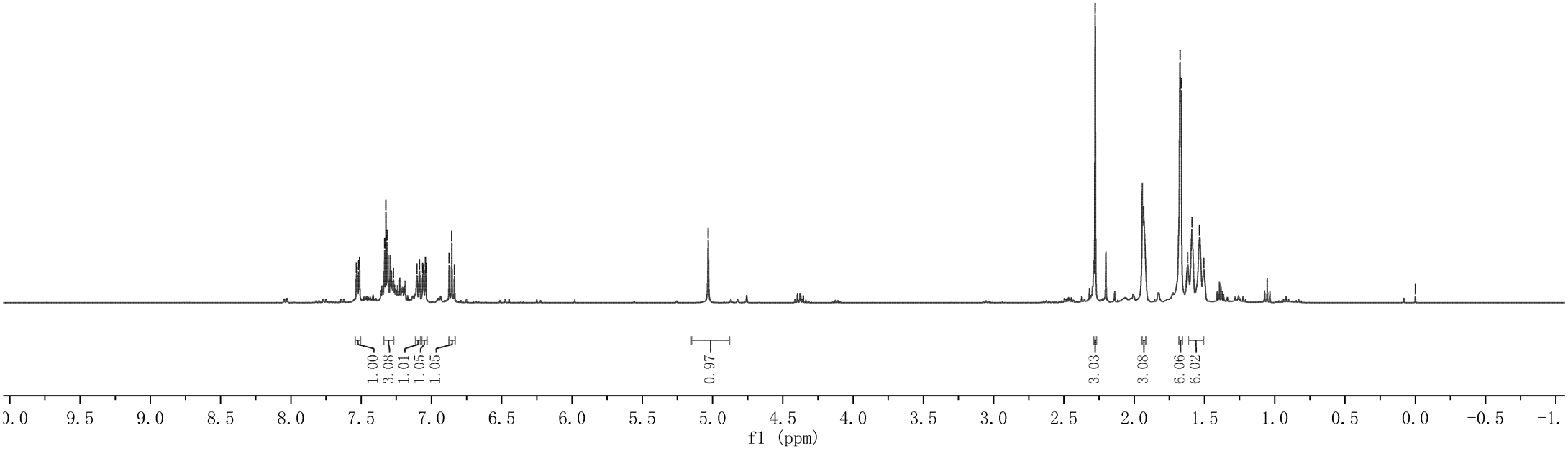
1t



Parameter	Value
1 Title	fxy-8-43
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	2022-04-14T08:40:26
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8

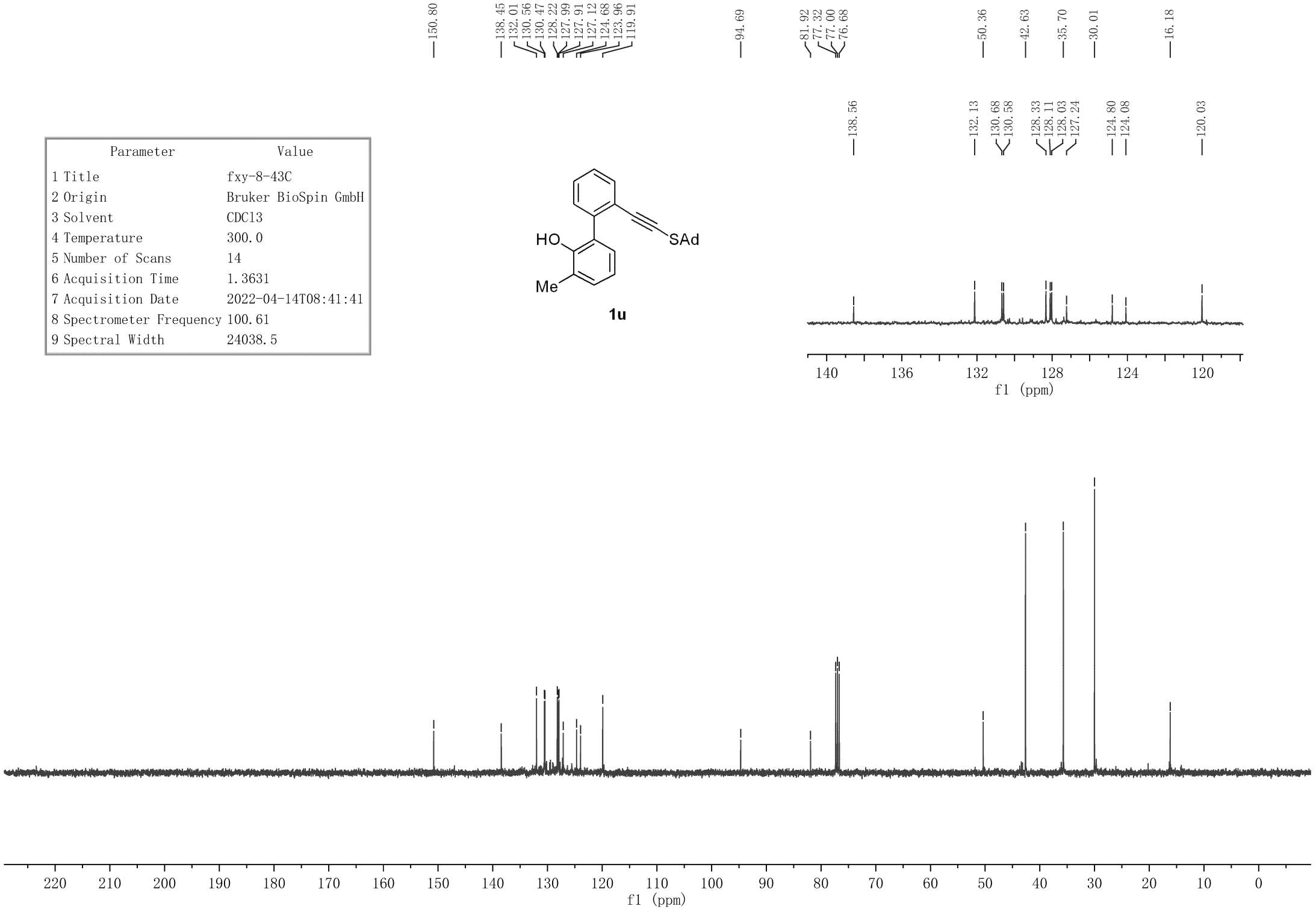


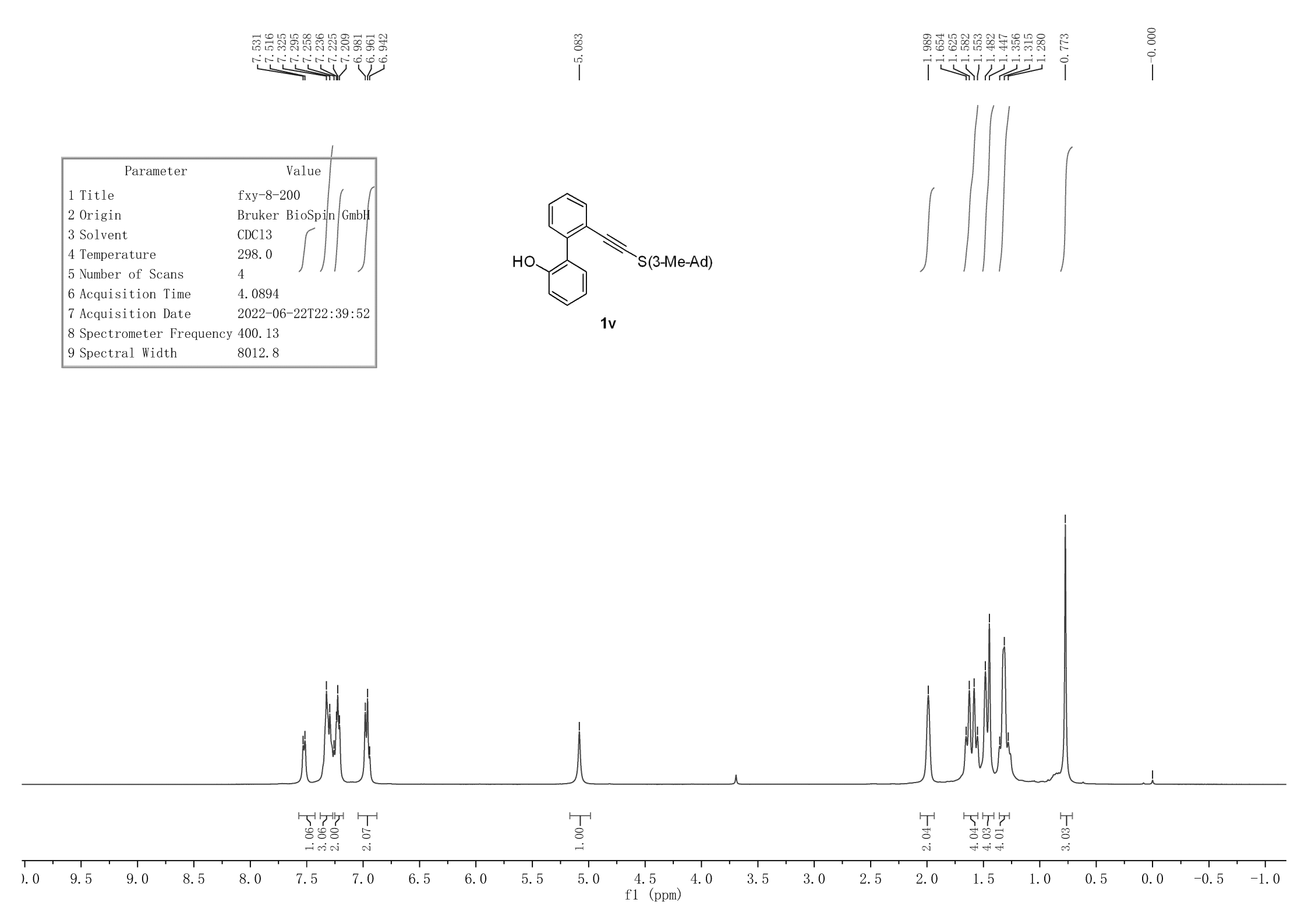
1u



Parameter	Value
1 Title	fxy-8-43C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	14
6 Acquisition Time	1.3631
7 Acquisition Date	2022-04-14T08:41:41
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5

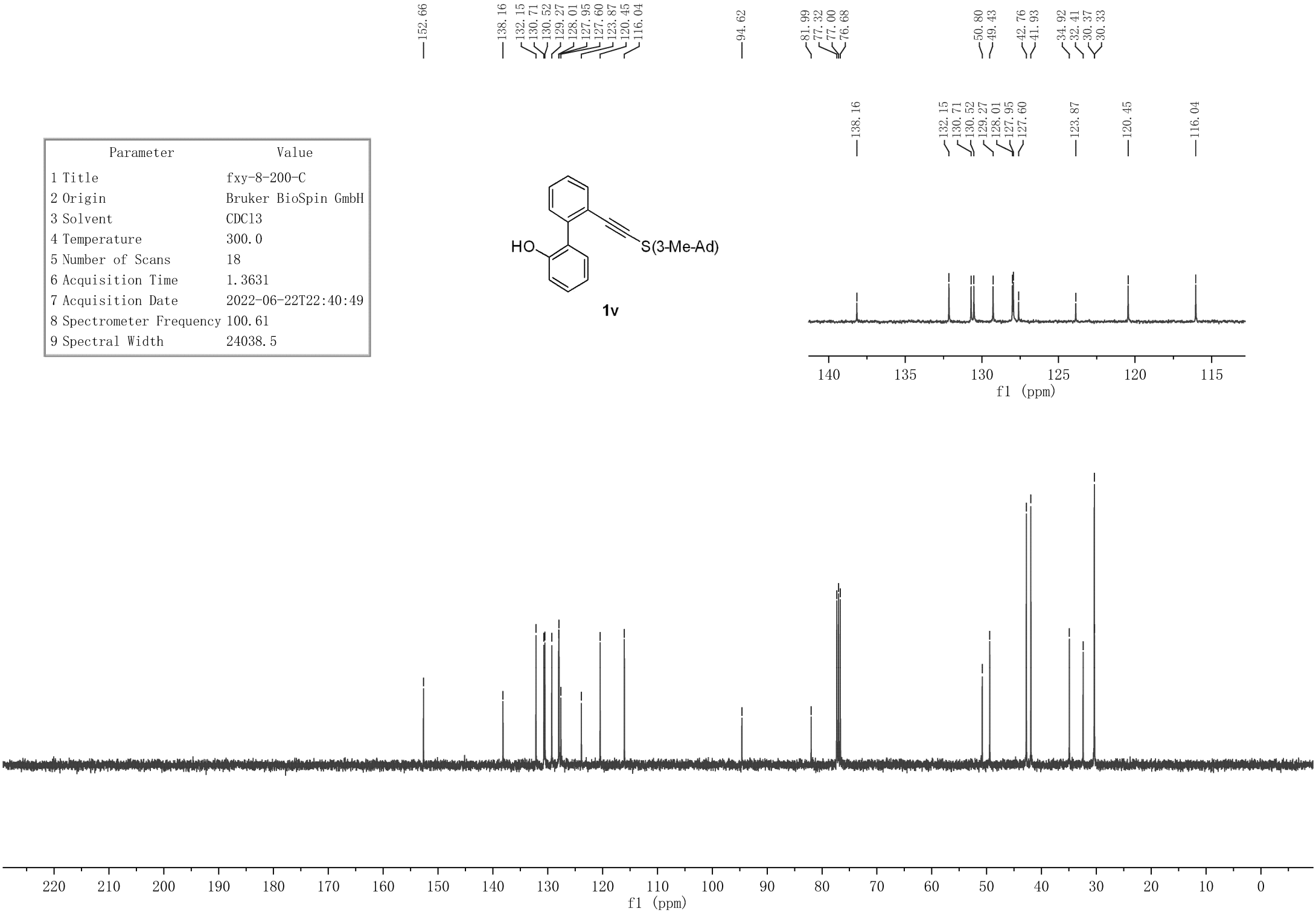
1u

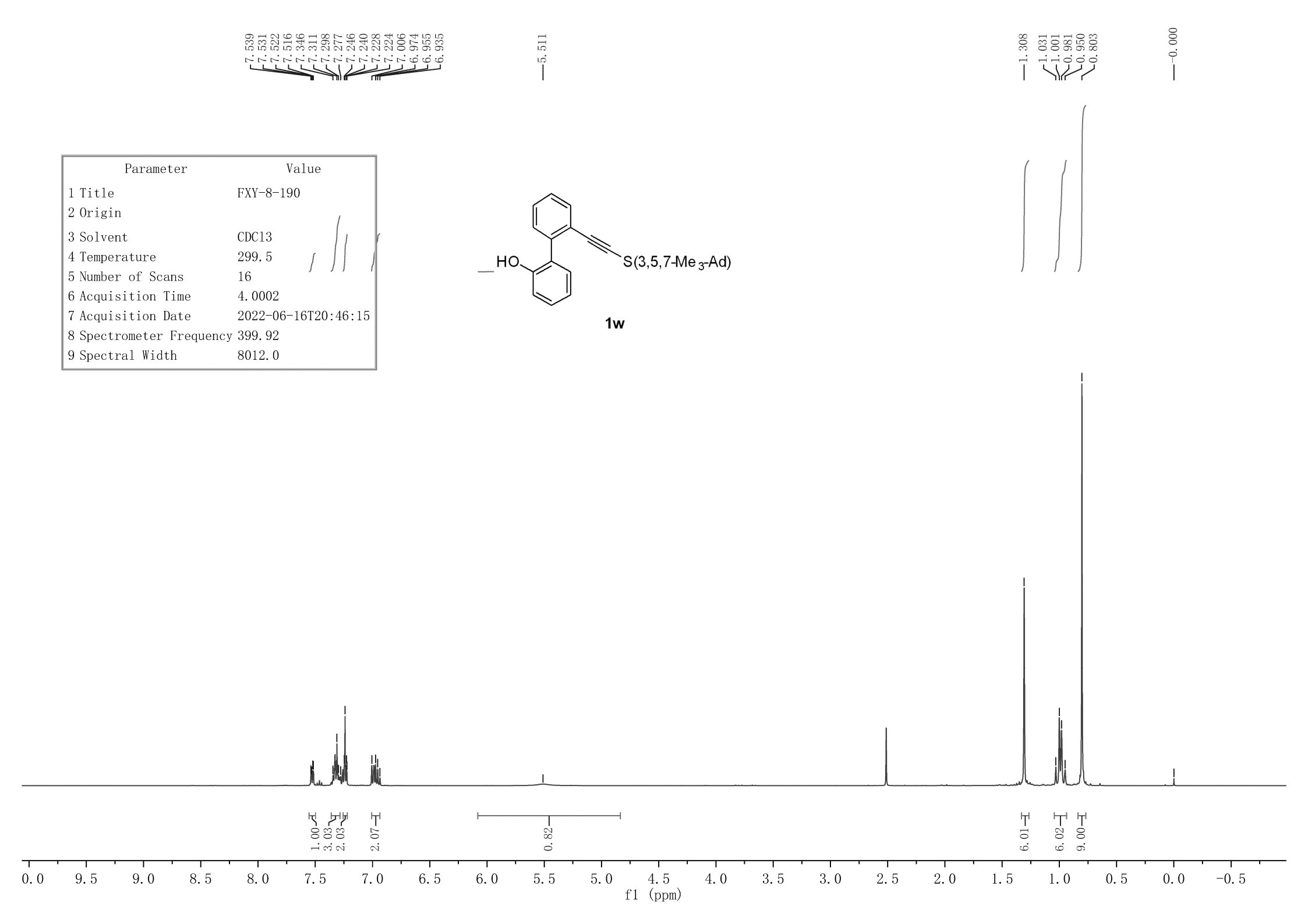



7.531
7.516
7.325
7.295
7.258
7.236
7.225
7.209
6.981
6.961
6.942
5.083
1.989
1.654
1.625
1.582
1.553
1.482
1.447
1.356
1.315
1.280
0.773
-0.000
Parameter Value
1 Title fxy-8-200
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 298.0
5 Number of Scans 4
6 Acquisition Time 4.0894
7 Acquisition Date 2022-06-22T22:39:52
8 Spectrometer Frequency 400.13
9 Spectral Width 8012.8
HO
S(3-Me-Ad)
1v
1.06
3.06
2.00
2.07
1.00
2.04
4.04
4.03
4.01
3.03
f1 (ppm)

Parameter	Value
1 Title	fxy-8-200-C
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	2022-06-22T22:40:49
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5

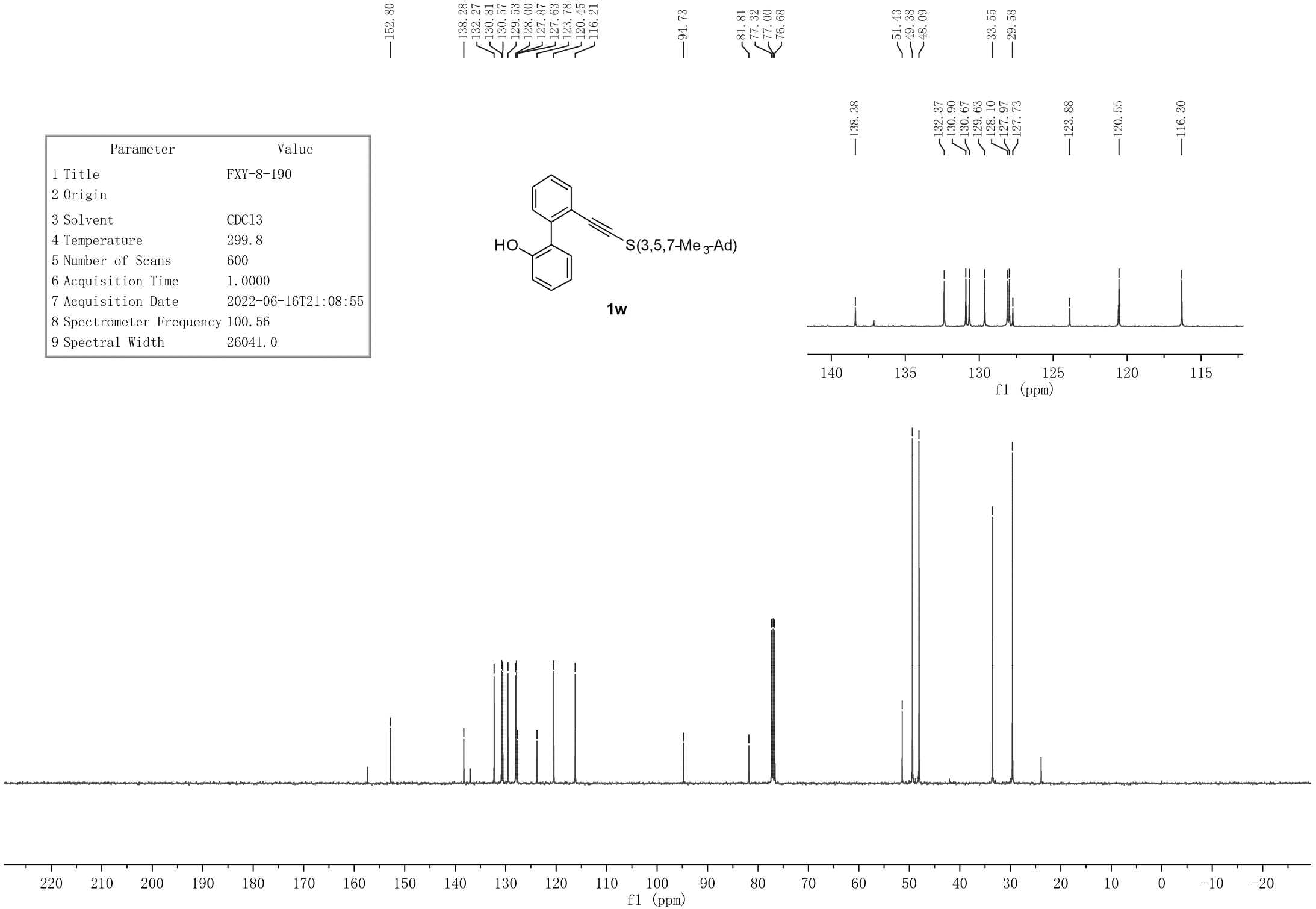
1v



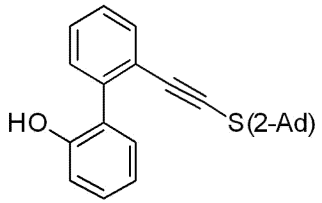

7.539
7.531
7.522
7.516
7.346
7.311
7.298
7.277
7.246
7.240
7.228
7.224
7.006
6.974
6.955
6.935
5.511
1.308
1.031
1.001
0.981
0.950
0.803
-0.000
Parameter Value
1 Title FXY-8-190
2 Origin
3 Solvent CDCl3
4 Temperature 299.5
5 Number of Scans 16
6 Acquisition Time 4.0002
7 Acquisition Date 2022-06-16T20:46:15
8 Spectrometer Frequency 399.92
9 Spectral Width 8012.0
HO
S(3,5,7-Me3-Ad)
1w
1.00
3.03
2.03
2.07
0.82
6.01
6.02
9.00
0.0
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
f1 (ppm)

Parameter	Value
1 Title	FXY-8-190
2 Origin	
3 Solvent	CDCl3
4 Temperature	299.8
5 Number of Scans	600
6 Acquisition Time	1.0000
7 Acquisition Date	2022-06-16T21:08:55
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

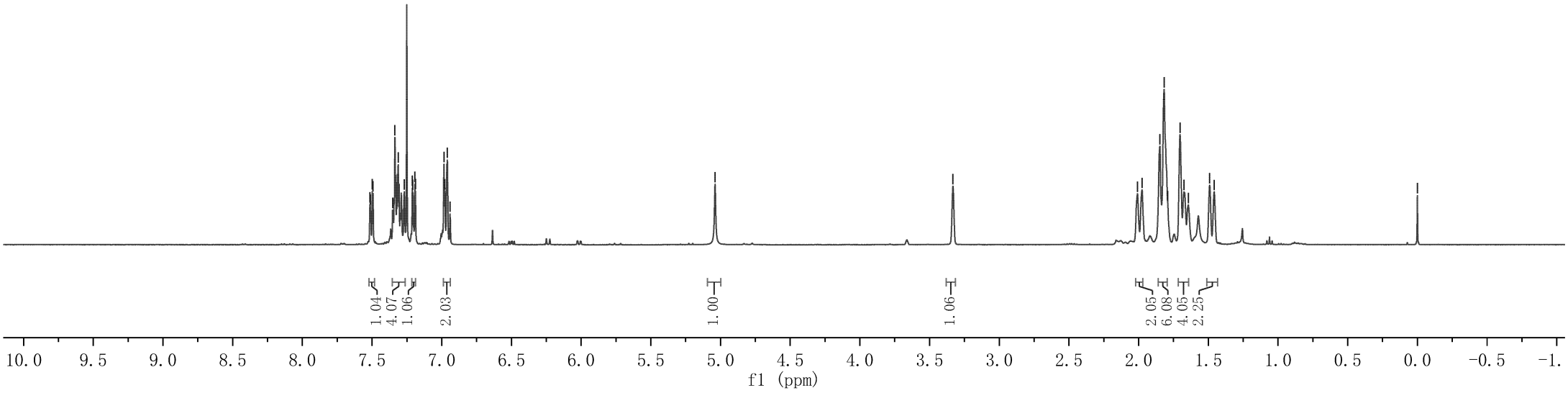
1w



Parameter	Value
1 Title	FXY-8-186
2 Origin	
3 Solvent	CDCl3
4 Temperature	299.8
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2022-06-15T22:45:26
8 Spectrometer Frequency	399.92
9 Spectral Width	8012.0

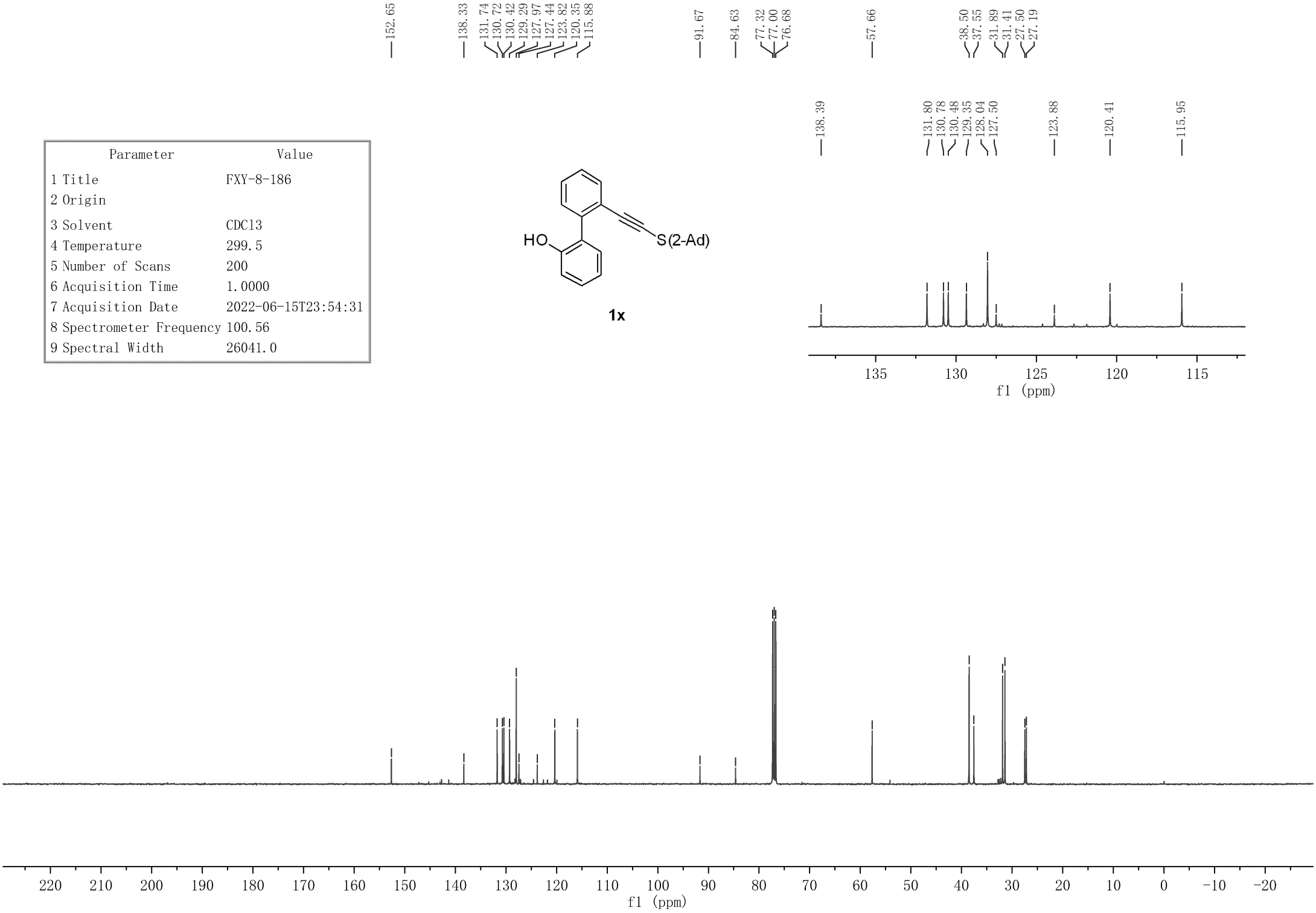


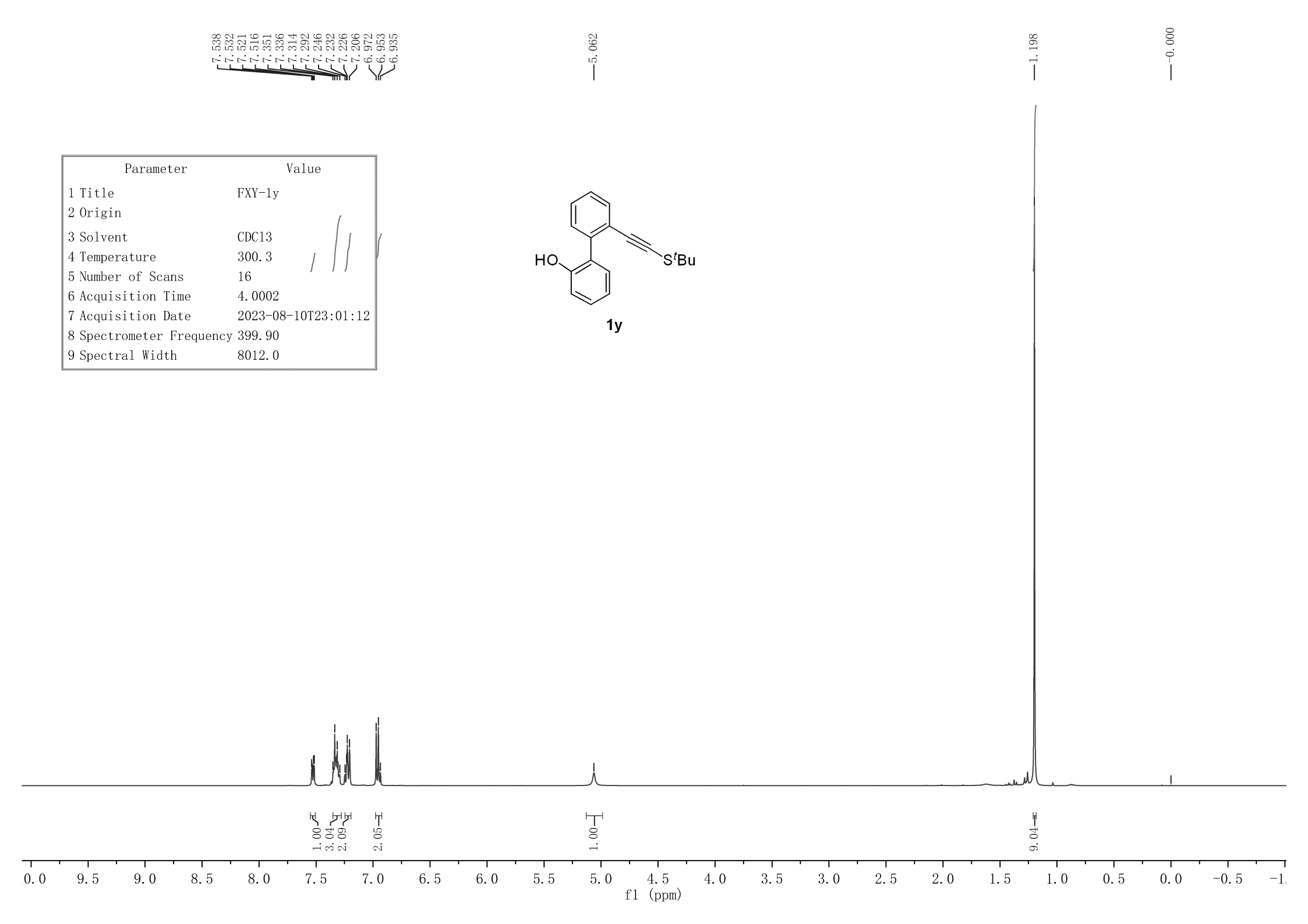
1x



Parameter	Value
1 Title	FXY-8-186
2 Origin	
3 Solvent	CDCl3
4 Temperature	299.5
5 Number of Scans	200
6 Acquisition Time	1.0000
7 Acquisition Date	2022-06-15T23:54:31
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

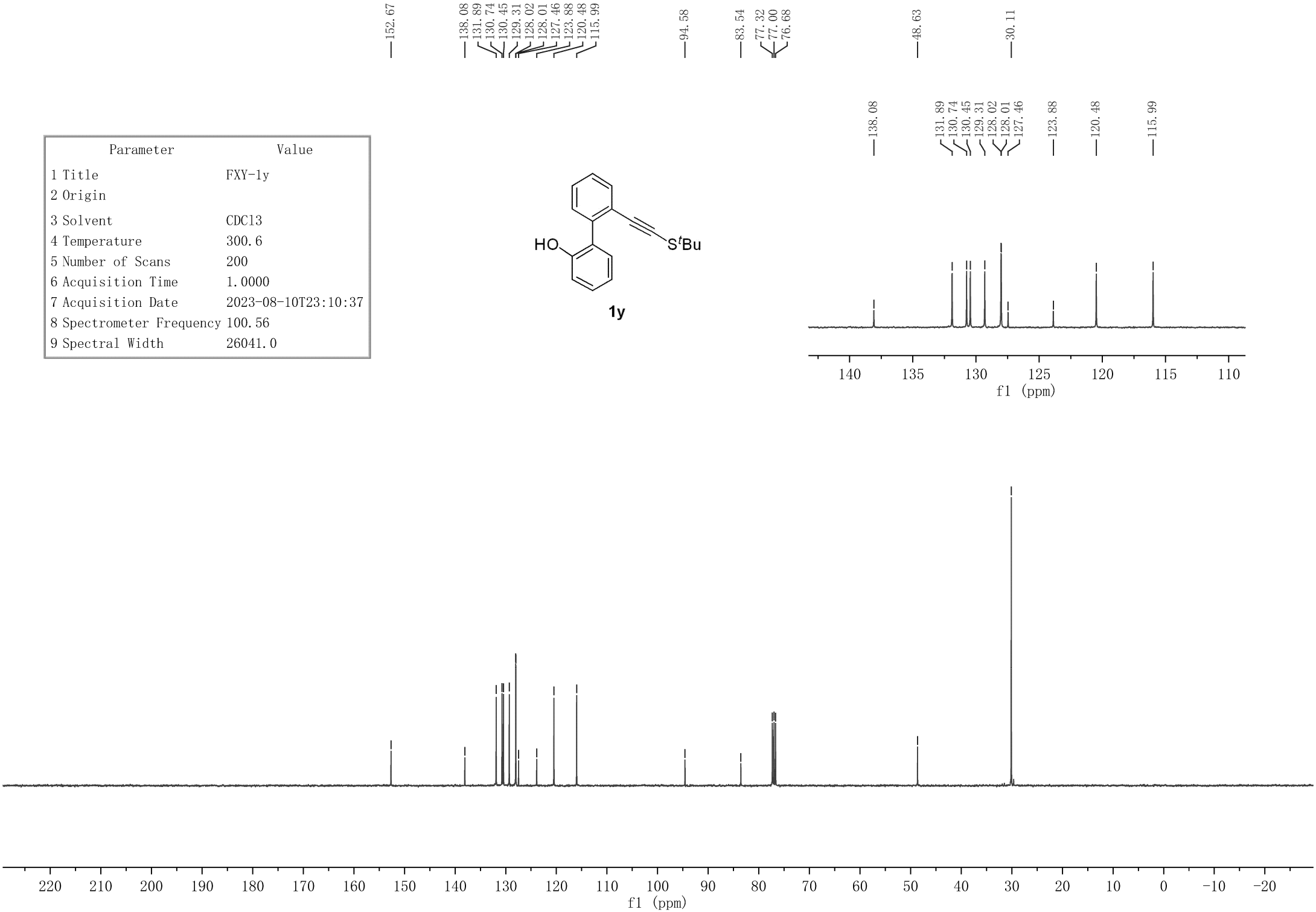
1x

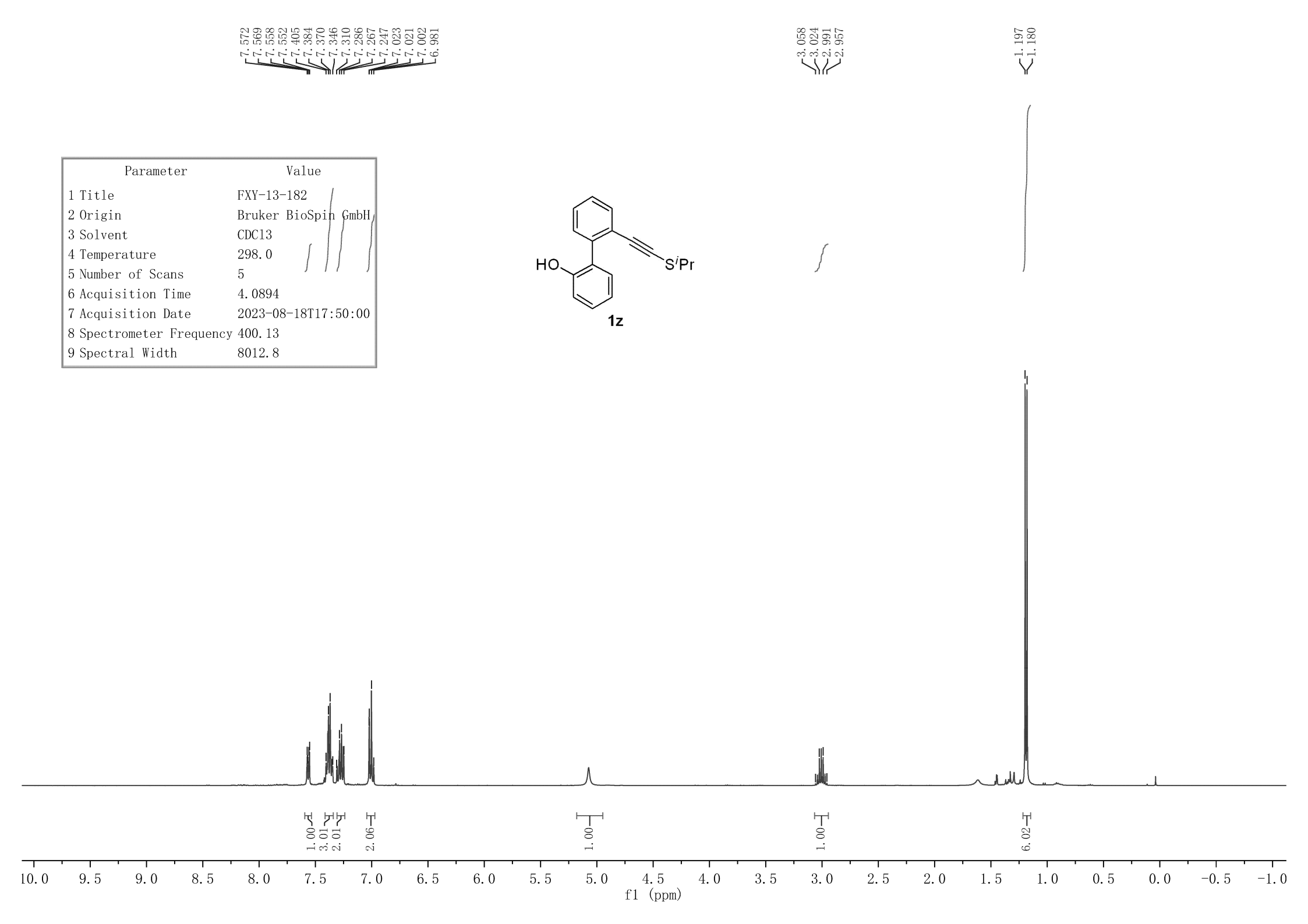



7.538
7.532
7.521
7.516
7.351
7.336
7.314
7.292
7.246
7.232
7.226
7.206
6.972
6.953
6.935
5.062
1.198
0.000
Parameter Value
1 Title FXY-1y
2 Origin
3 Solvent CDCl3
4 Temperature 300.3
5 Number of Scans 16
6 Acquisition Time 4.0002
7 Acquisition Date 2023-08-10T23:01:12
8 Spectrometer Frequency 399.90
9 Spectral Width 8012.0
HO
S^{t}Bu
1y
1.00
3.04
2.09
2.05
1.00
9.04
f1 (ppm)

Parameter	Value
1 Title	FXY-1y
2 Origin	
3 Solvent	CDCl3
4 Temperature	300.6
5 Number of Scans	200
6 Acquisition Time	1.0000
7 Acquisition Date	2023-08-10T23:10:37
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

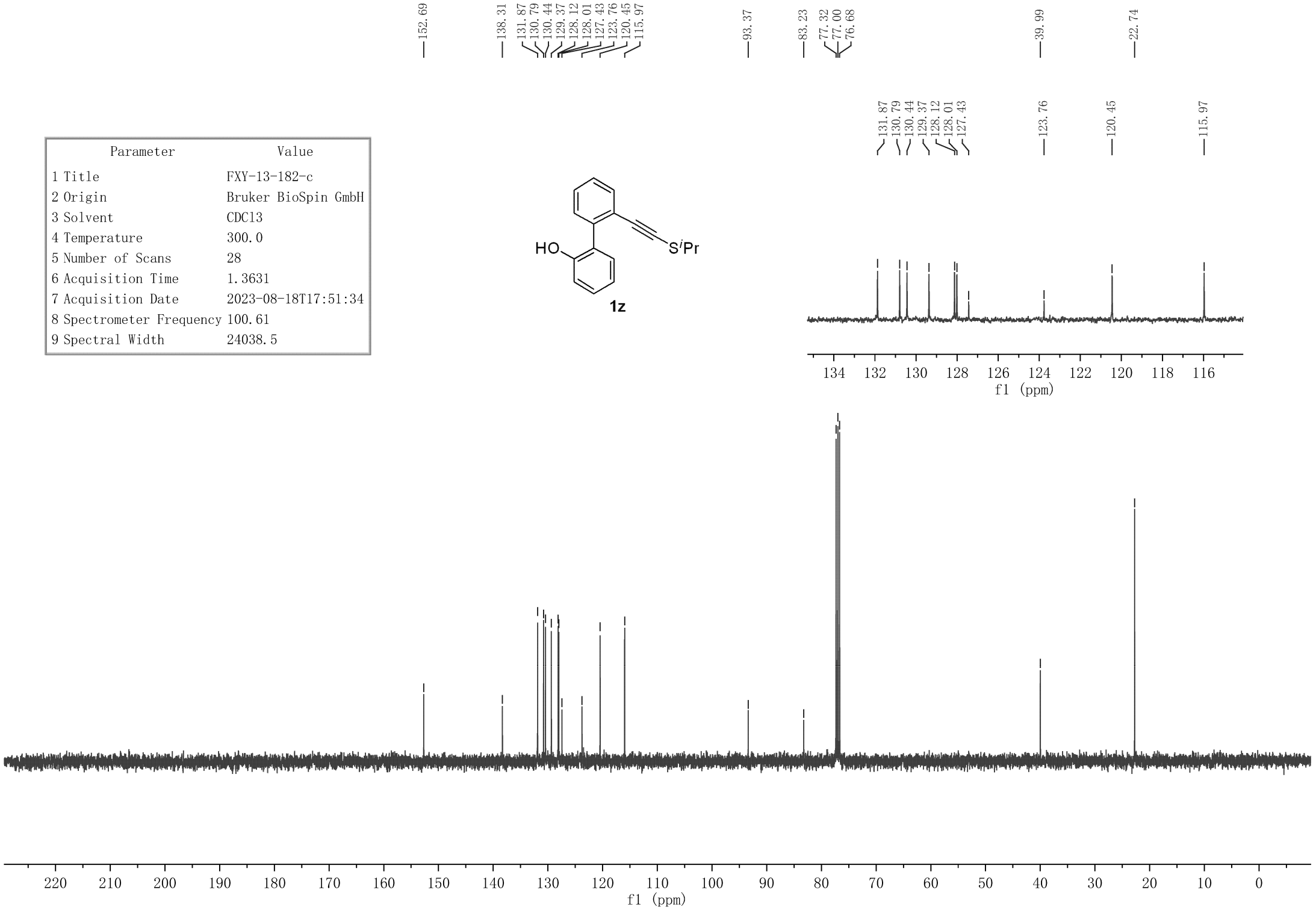
1y



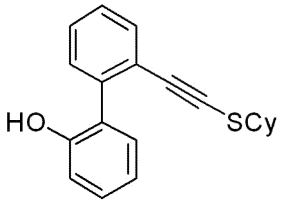

7.572
7.569
7.558
7.552
7.405
7.384
7.370
7.346
7.310
7.286
7.267
7.247
7.023
7.021
7.002
6.981
3.058
3.024
2.991
2.957
1.197
1.180
Parameter Value
1 Title FXY-13-182
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 298.0
5 Number of Scans 5
6 Acquisition Time 4.0894
7 Acquisition Date 2023-08-18T17:50:00
8 Spectrometer Frequency 400.13
9 Spectral Width 8012.8
HO
S^{i}Pr
1z
1.00
3.01
2.01
2.06
1.00
1.00
6.02
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	FXY-13-182-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	2023-08-18T17:51:34
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5

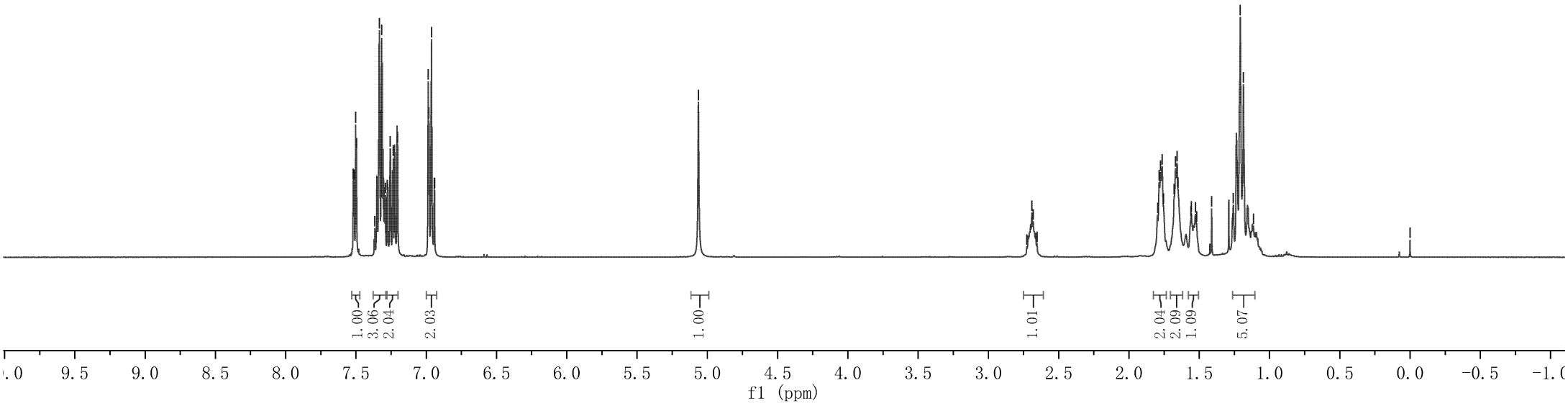
1z



Parameter	Value
1 Title	fxy-SCy-Sub
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	2023-08-20T12:09:08
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8

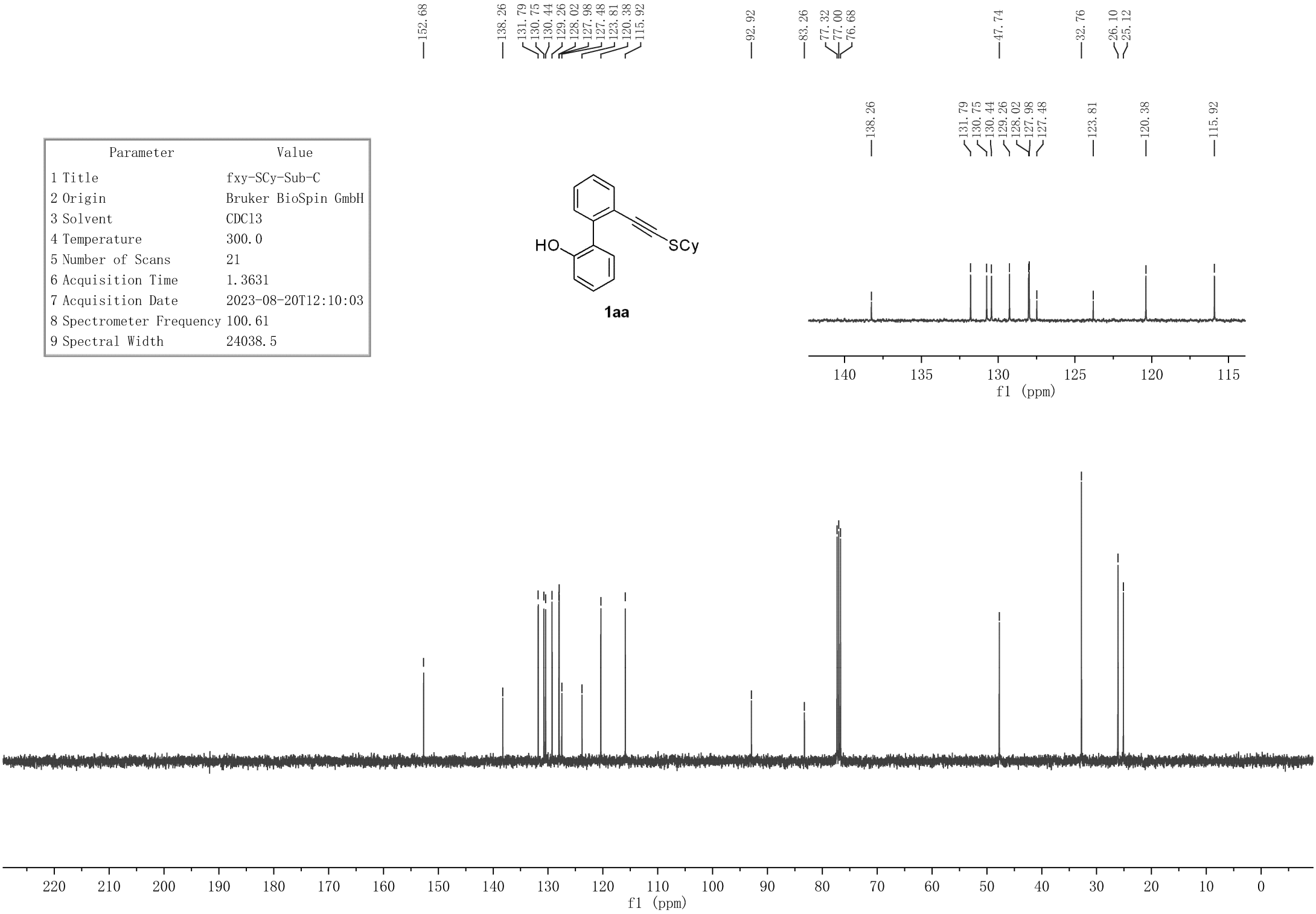


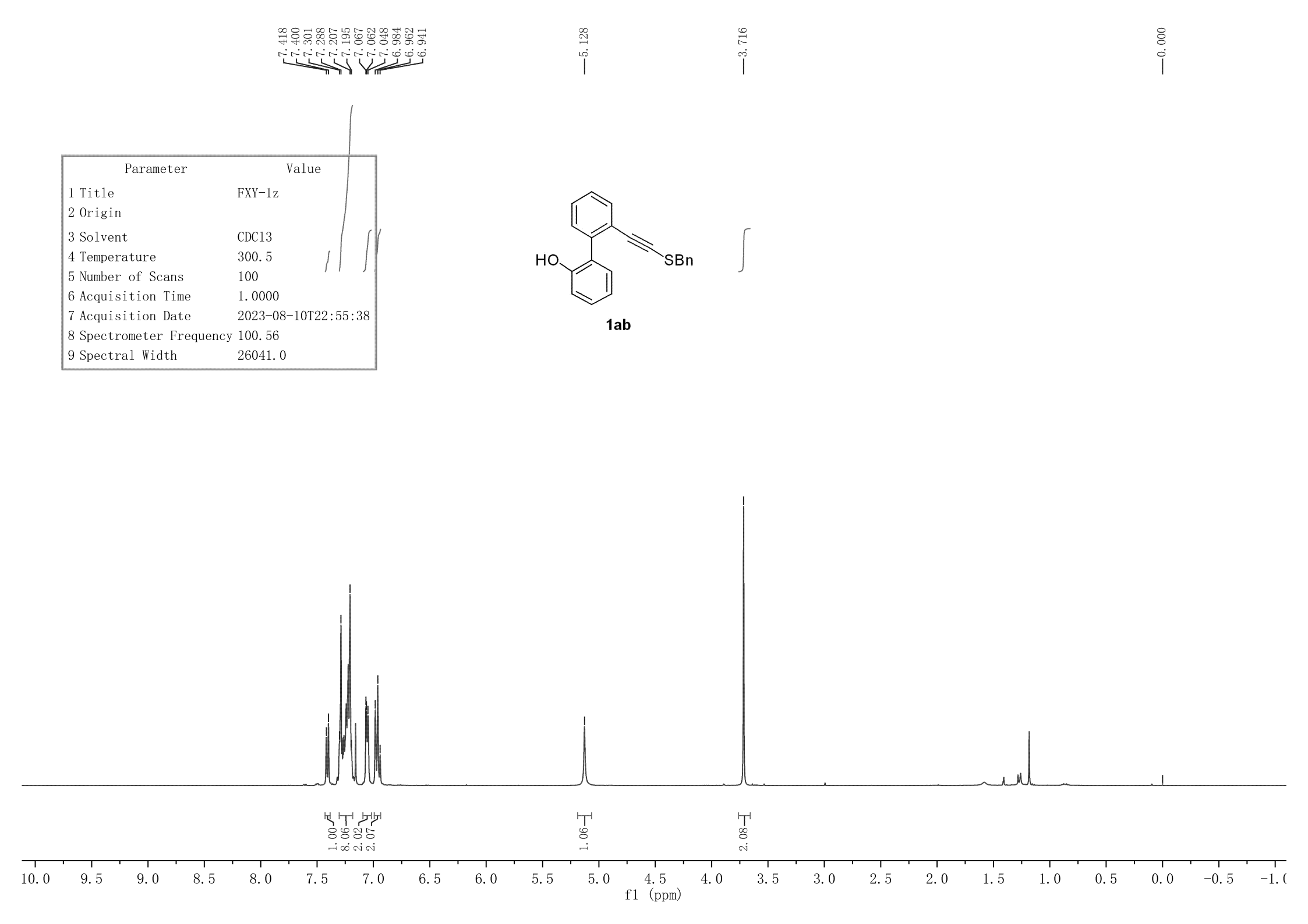
1aa



Parameter	Value
1 Title	fxy-SCy-Sub-C
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	2023-08-20T12:10:03
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5

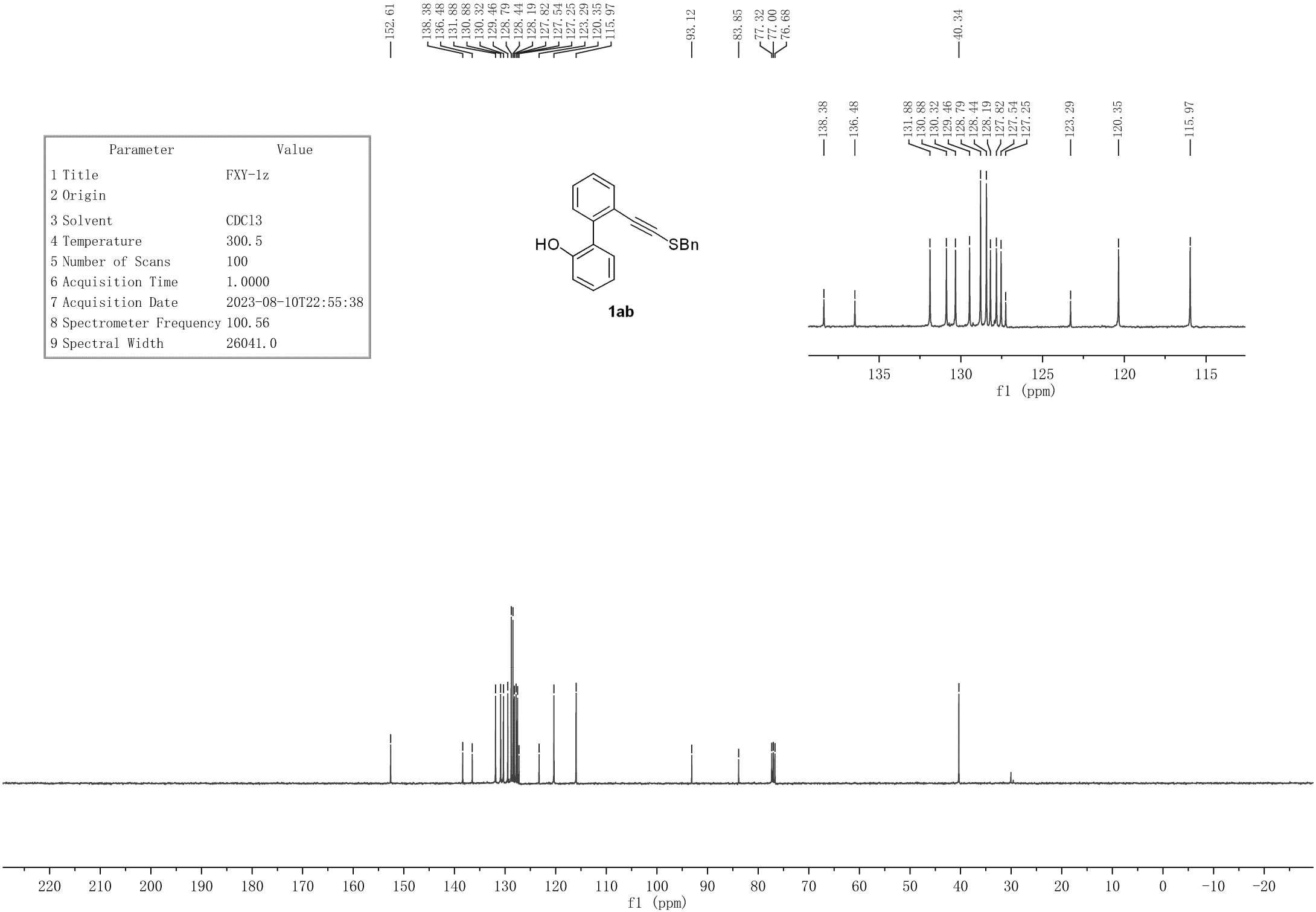
1aa



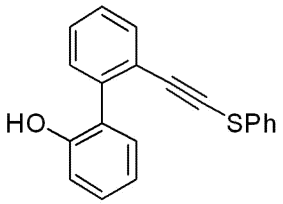

7.418
7.400
7.301
7.288
7.207
7.195
7.067
7.062
7.048
6.984
6.962
6.941
5.128
3.716
0.000
Parameter Value
1 Title FXY-1z
2 Origin
3 Solvent CDCl3
4 Temperature 300.5
5 Number of Scans 100
6 Acquisition Time 1.0000
7 Acquisition Date 2023-08-10T22:55:38
8 Spectrometer Frequency 100.56
9 Spectral Width 26041.0
HO
SBn
1ab
1.00
8.06
2.02
2.07
1.06
2.08
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
f1 (ppm)

Parameter	Value
1 Title	FXY-1z
2 Origin	
3 Solvent	CDCl3
4 Temperature	300.5
5 Number of Scans	100
6 Acquisition Time	1.0000
7 Acquisition Date	2023-08-10T22:55:38
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

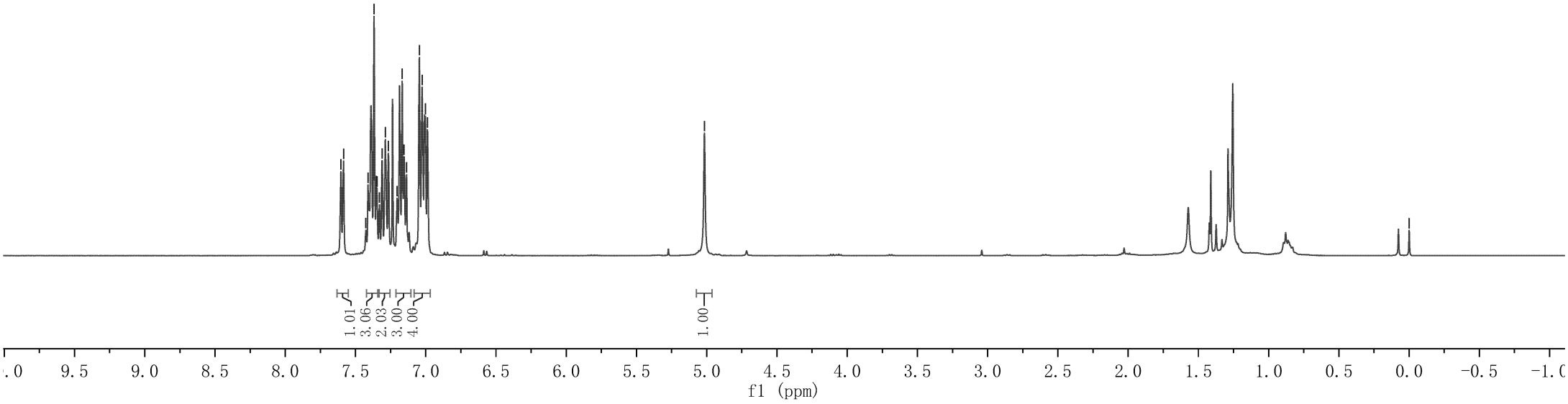
1ab



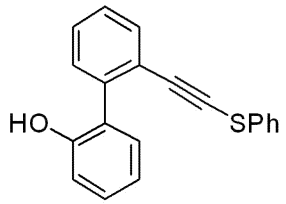
Parameter	Value
1 Title	FXY-13-206-H
2 Origin	
3 Solvent	CDCl3
4 Temperature	299.1
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2023-08-22T18:01:51
8 Spectrometer Frequency	399.90
9 Spectral Width	8012.0



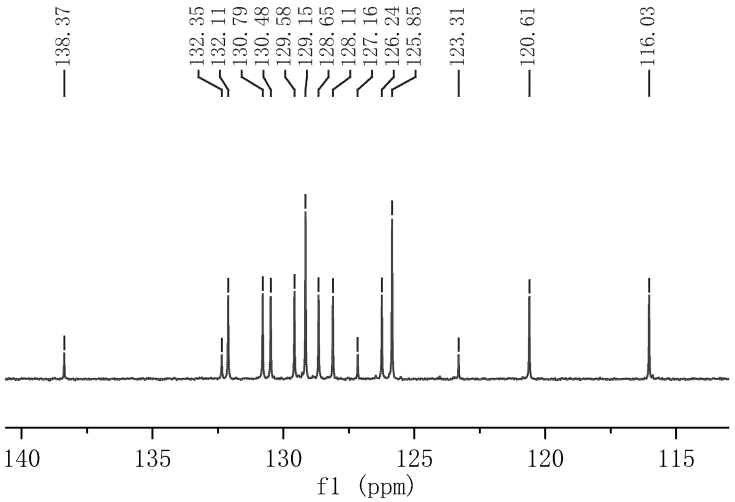
1ac

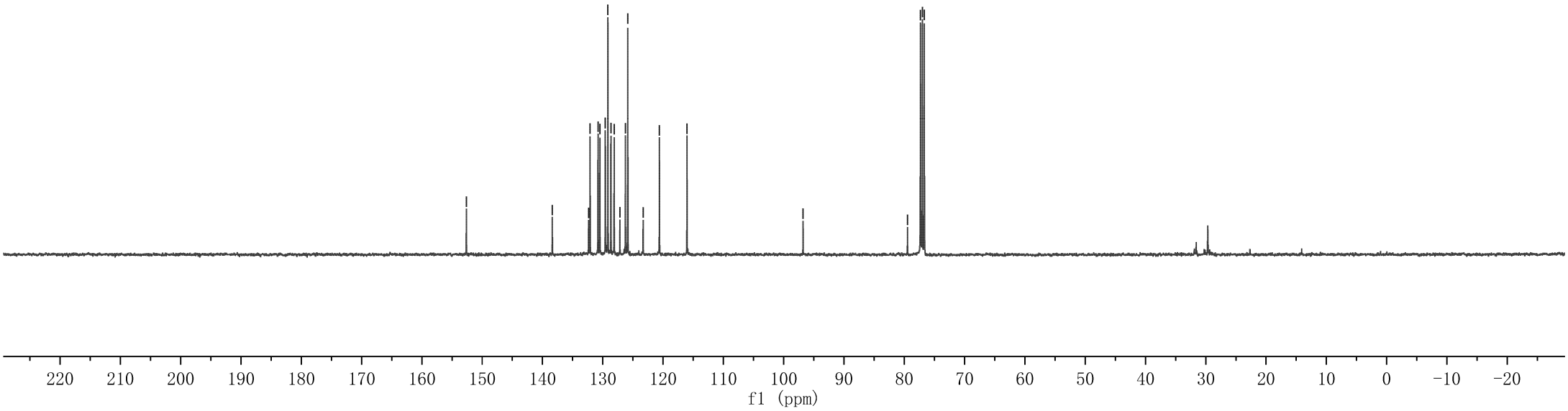


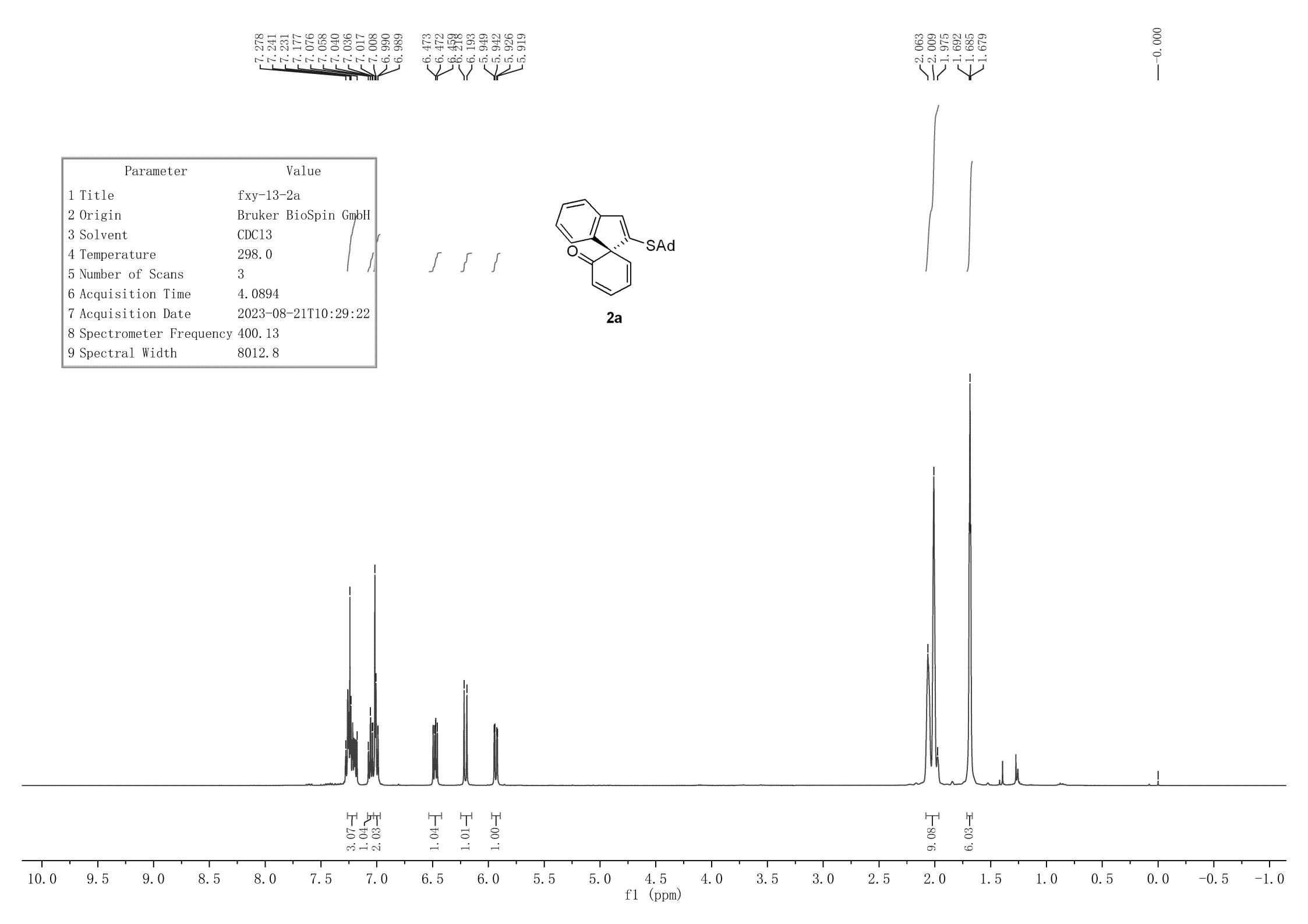
Parameter	Value
1 Title	FXY-13-206-C
2 Origin	
3 Solvent	CDCl3
4 Temperature	299.2
5 Number of Scans	1024
6 Acquisition Time	1.0000
7 Acquisition Date	2023-08-22T18:38:36
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

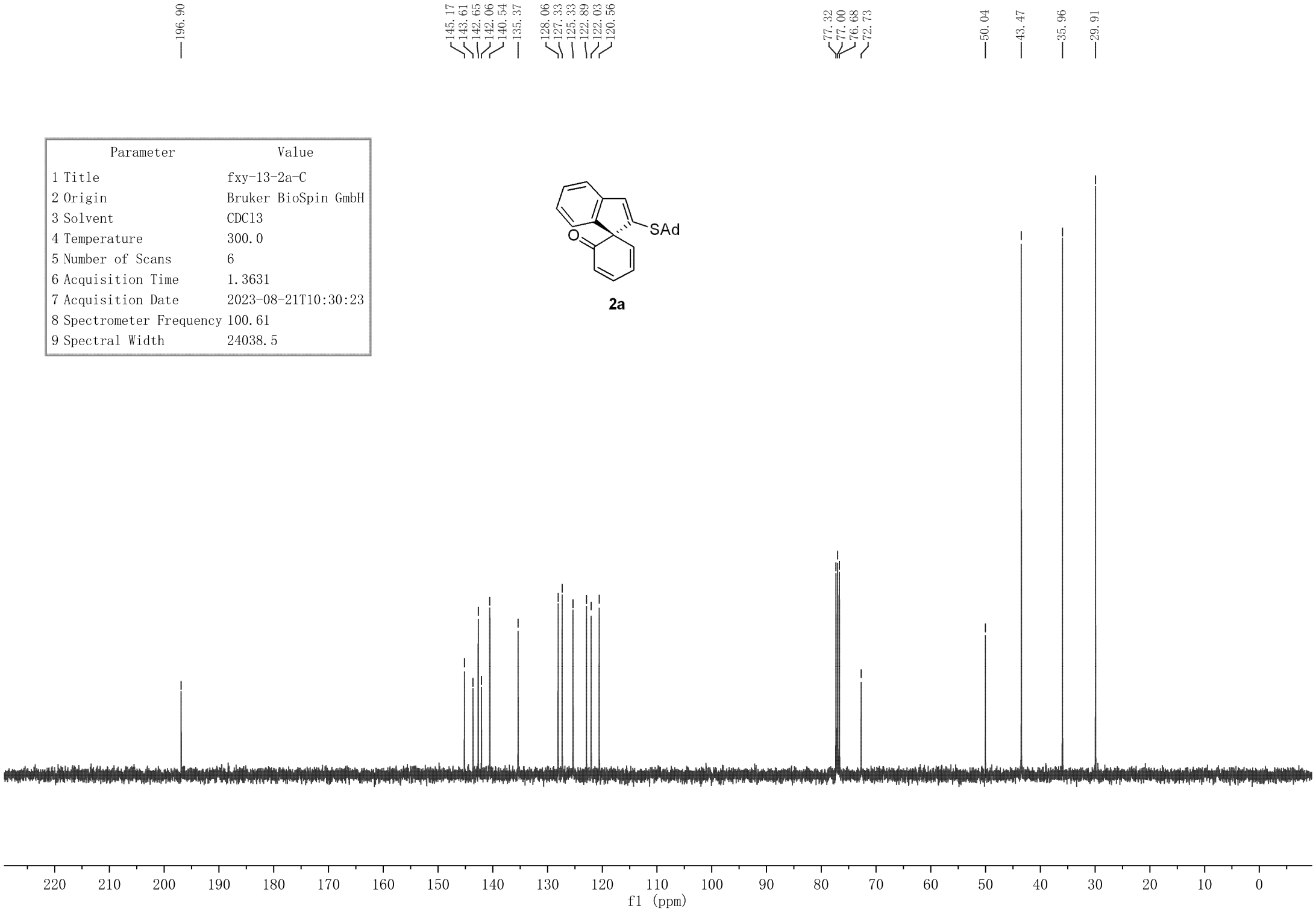


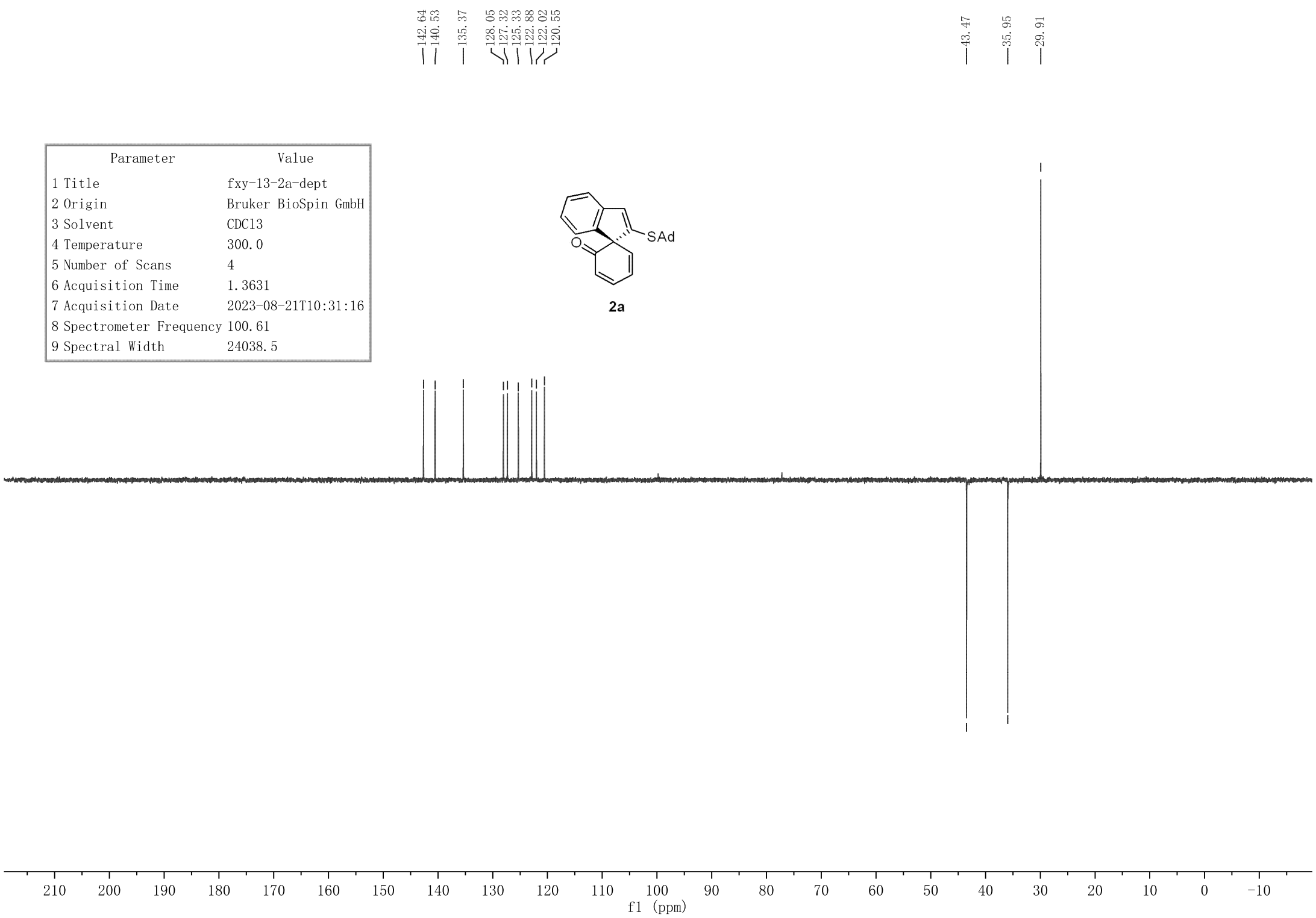
1ac

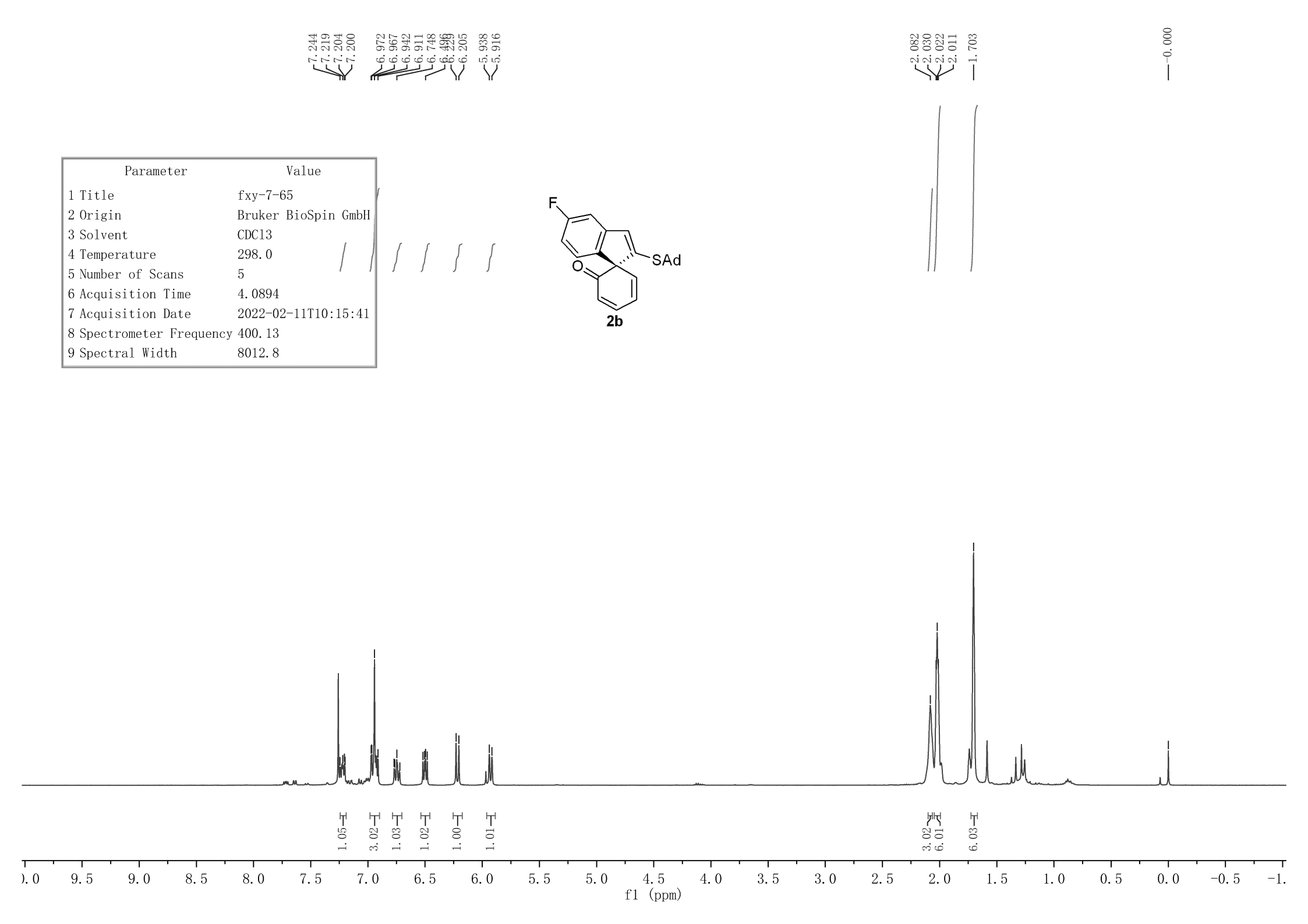





7.278
7.241
7.231
7.177
7.076
7.058
7.040
7.036
7.017
7.008
6.990
6.989
6.473
6.472
6.459
6.218
6.193
5.949
5.942
5.926
5.919
2.063
2.009
1.975
1.692
1.685
1.679
-0.000
Parameter Value
1 Title fxy-13-2a
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 298.0
5 Number of Scans 3
6 Acquisition Time 4.0894
7 Acquisition Date 2023-08-21T10:29:22
8 Spectrometer Frequency 400.13
9 Spectral Width 8012.8
O
SAd
2a
3.07
1.04
2.03
1.04
1.01
1.00
9.08
6.03
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)


196.90
145.17
143.61
142.65
142.06
140.54
135.37
128.06
127.33
125.33
122.89
122.03
120.56
77.32
77.00
76.68
72.73
50.04
43.47
35.96
29.91
Parameter Value
1 Title fxy-13-2a-C
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.0
5 Number of Scans 6
6 Acquisition Time 1.3631
7 Acquisition Date 2023-08-21T10:30:23
8 Spectrometer Frequency 100.61
9 Spectral Width 24038.5
O
SAd
2a
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)

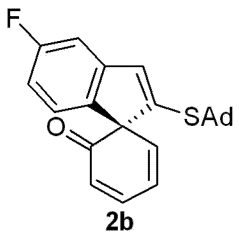

142.64
140.53
135.37
128.05
127.32
125.33
122.88
122.02
120.55
43.47
35.95
29.91
Parameter Value
1 Title fxy-13-2a-dept
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.0
5 Number of Scans 4
6 Acquisition Time 1.3631
7 Acquisition Date 2023-08-21T10:31:16
8 Spectrometer Frequency 100.61
9 Spectral Width 24038.5
SAd
O
2a
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)



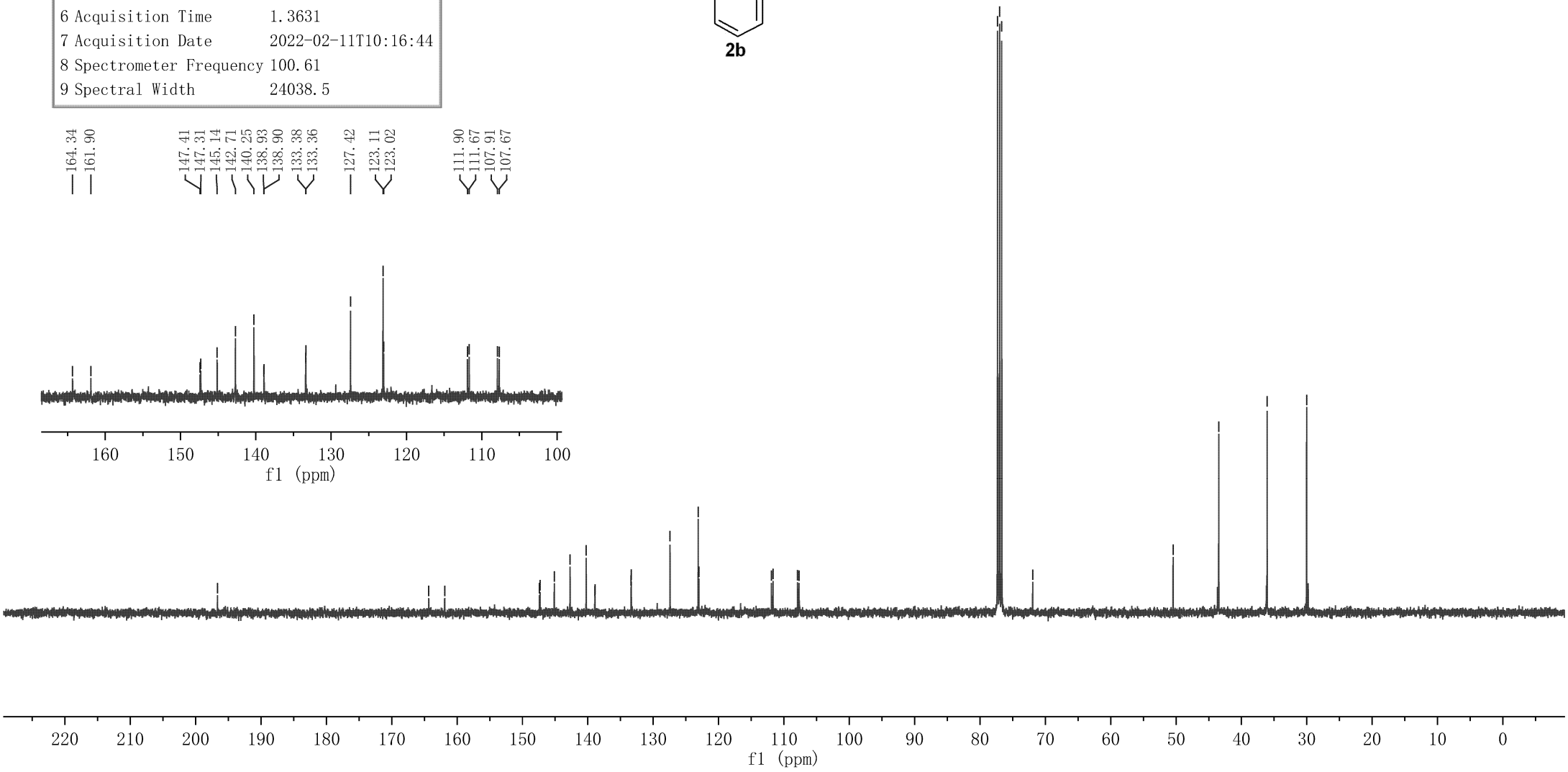
Parameter	Value
1 Title	fxy-7-65
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	5
6 Acquisition Time	4.0894
7 Acquisition Date	2022-02-11T10:15:41
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8

196.66
164.34
161.90
147.41
147.31
145.14
142.71
140.25
138.93
138.90
133.38
133.36
127.42
123.11
123.02
111.90
111.67
107.91
107.67
77.32
77.00
76.68
71.94
50.46
43.47
36.07
30.03

Parameter	Value
1 Title	fxy-7-65-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	197
6 Acquisition Time	1.3631
7 Acquisition Date	2022-02-11T10:16:44
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5

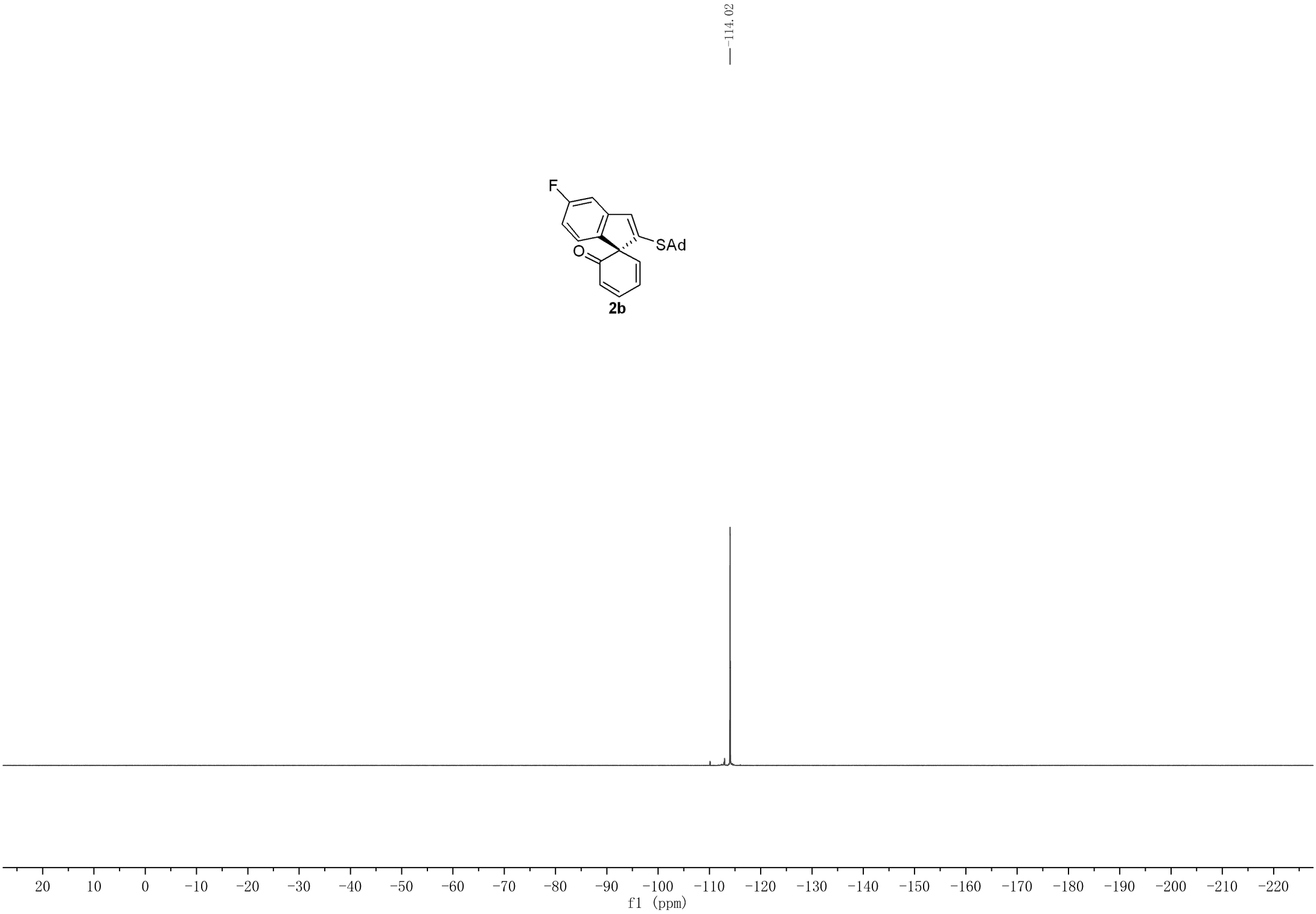


2b

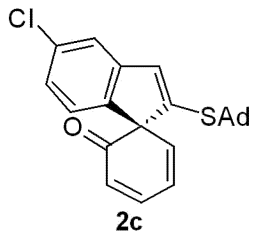


F
O
SAd

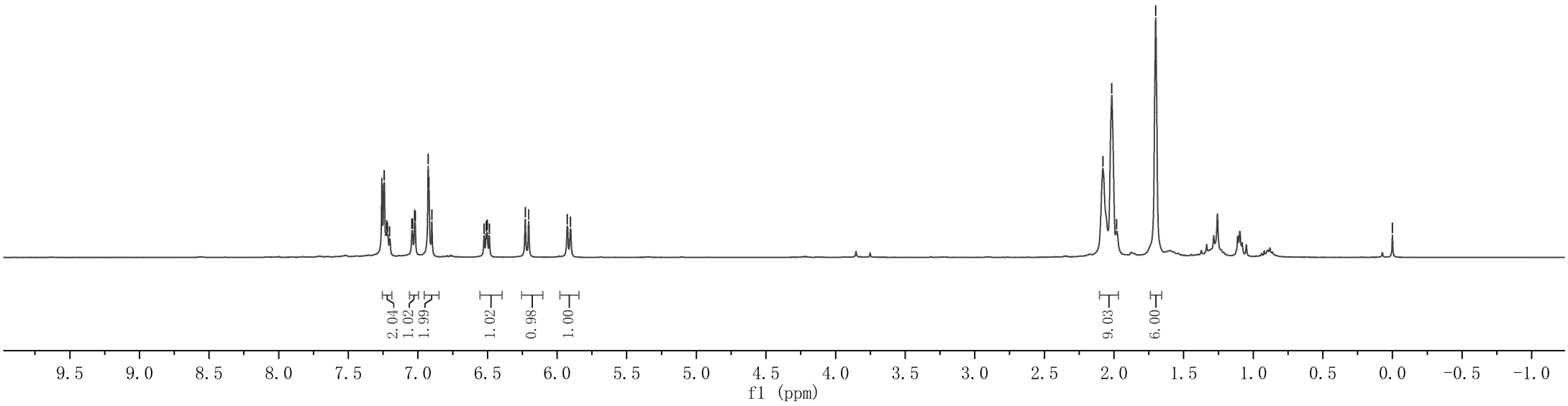
2b


−114.02
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
−220
f1 (ppm)

Parameter	Value
1 Title	2e
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	2022-02-26T09:12:42
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8

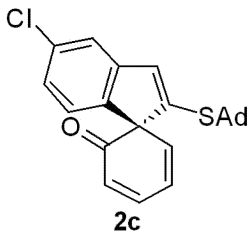


2c

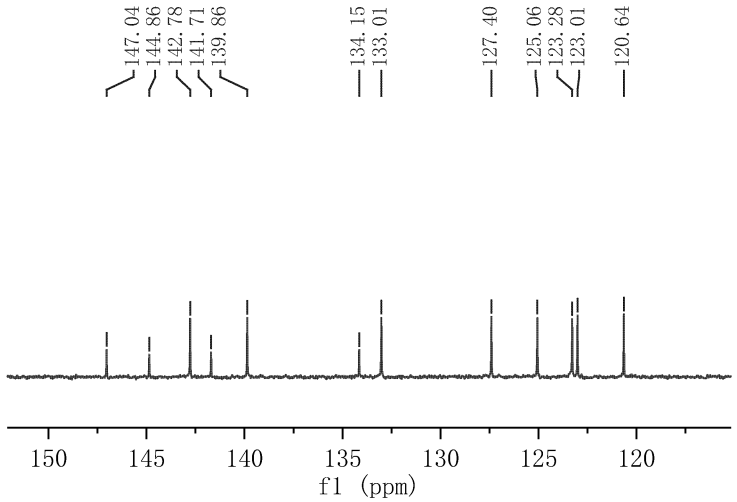


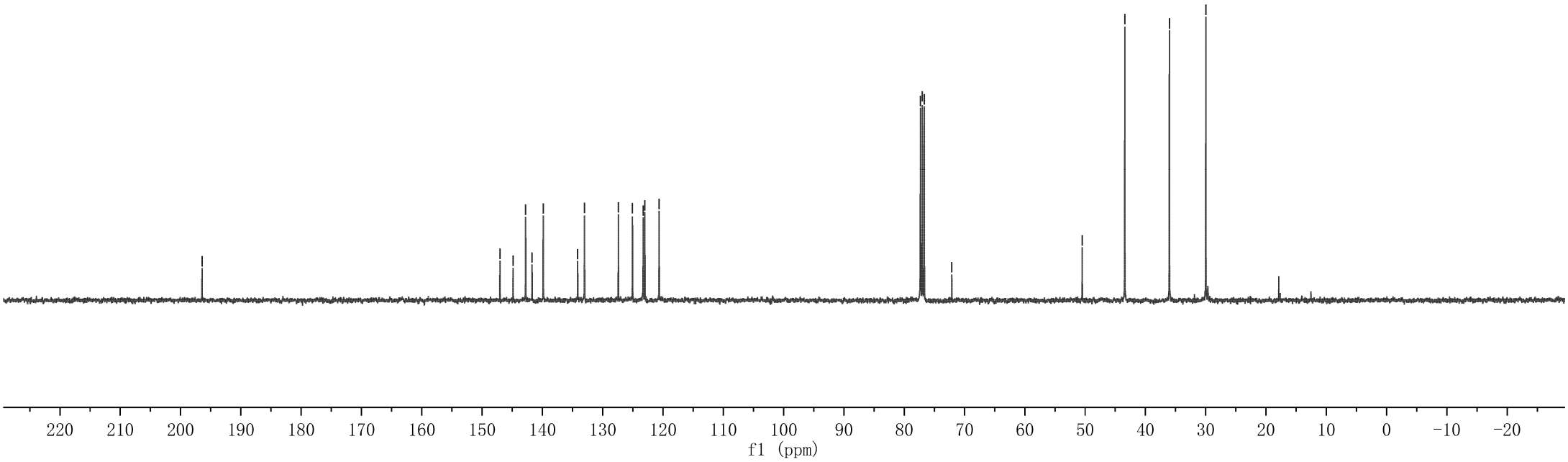
196.44
147.04
144.86
142.78
141.71
139.86
134.15
133.01
127.40
125.06
123.28
123.01
120.64
77.32
77.00
76.68
72.11
50.48
43.42
36.02
29.98

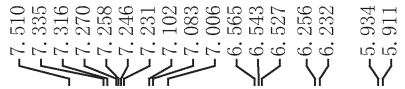
Parameter	Value
1 Title	2e
2 Origin	
3 Solvent	CDCl3
4 Temperature	296.6
5 Number of Scans	200
6 Acquisition Time	1.0000
7 Acquisition Date	2022-02-26T04:28:57
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0



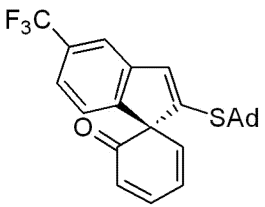
2c



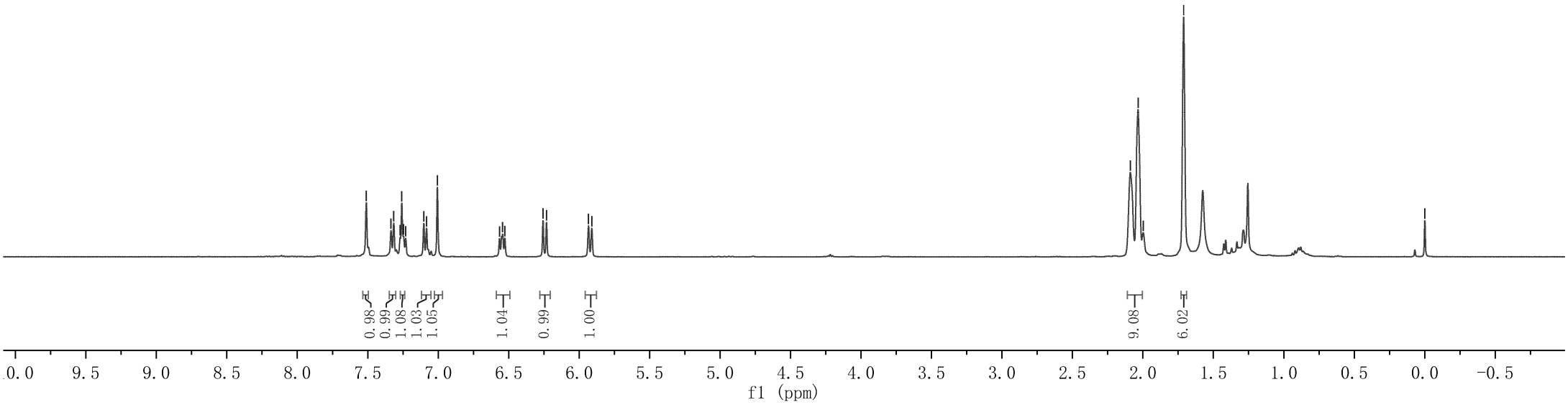




Parameter	Value
1 Title	FXY-7-143
2 Origin	
3 Solvent	CDCl3
4 Temperature	299.9
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2023-08-17T21:46:08
8 Spectrometer Frequency	399.90
9 Spectral Width	8012.0

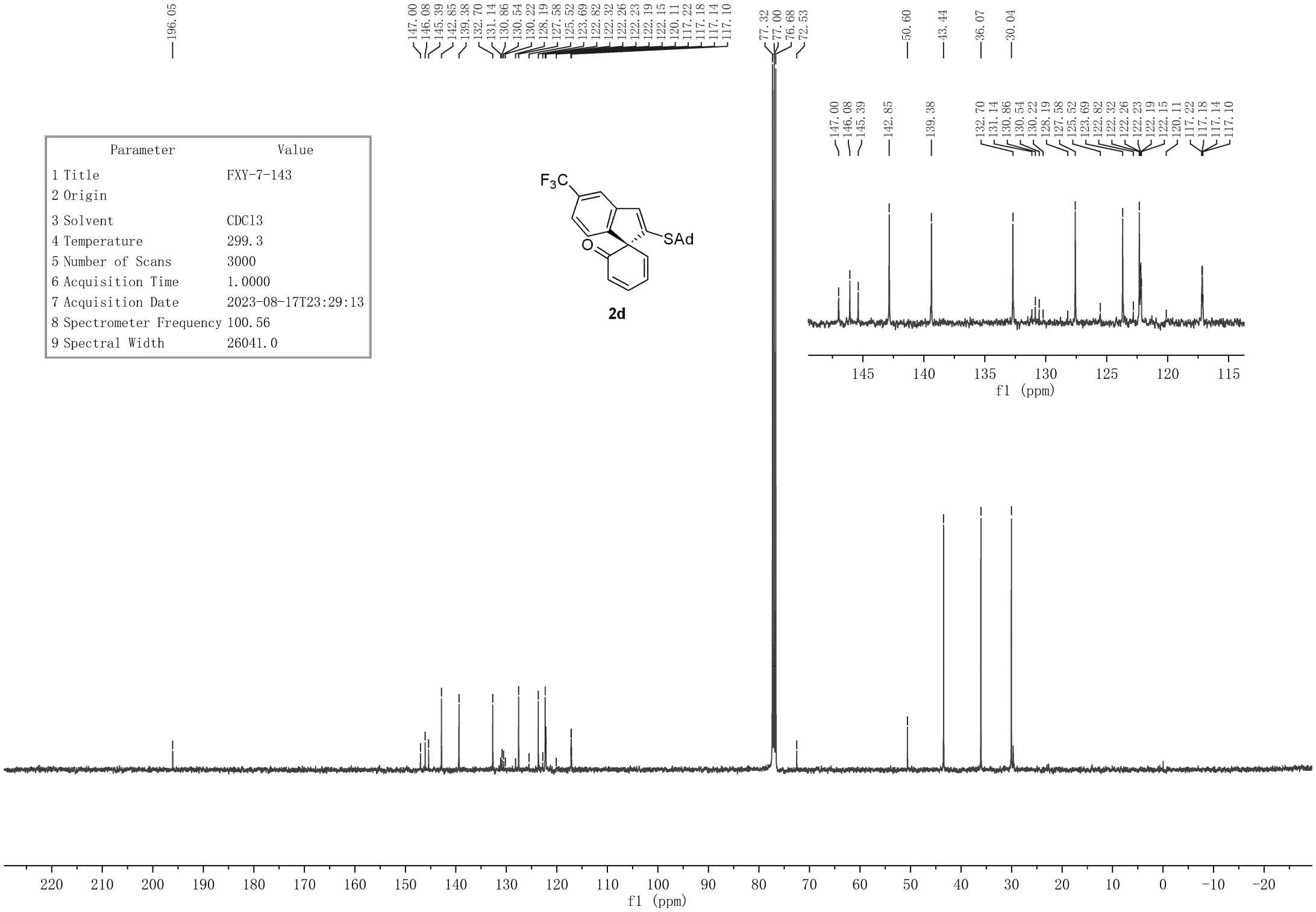


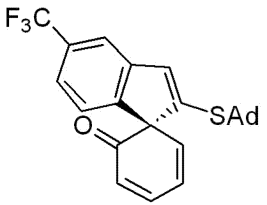
2d



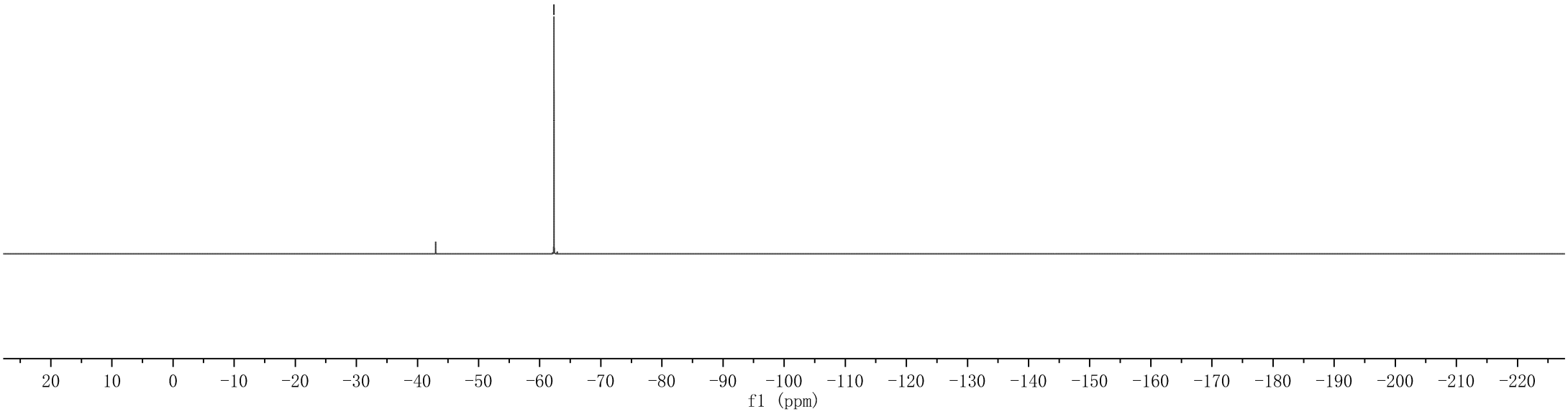
Parameter	Value
1 Title	FXY-7-143
2 Origin	
3 Solvent	CDCl3
4 Temperature	299.3
5 Number of Scans	3000
6 Acquisition Time	1.0000
7 Acquisition Date	2023-08-17T23:29:13
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

2d

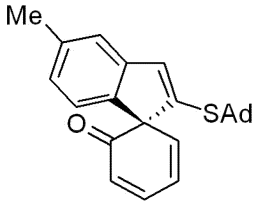



F3C
O
SAd

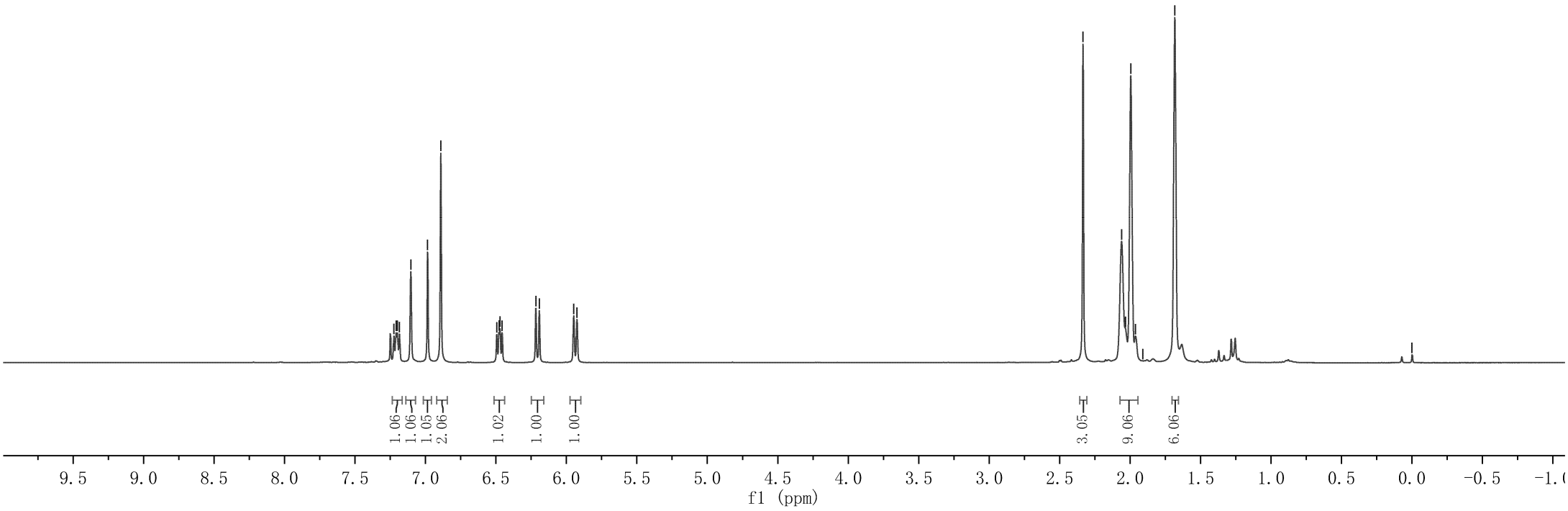
2d

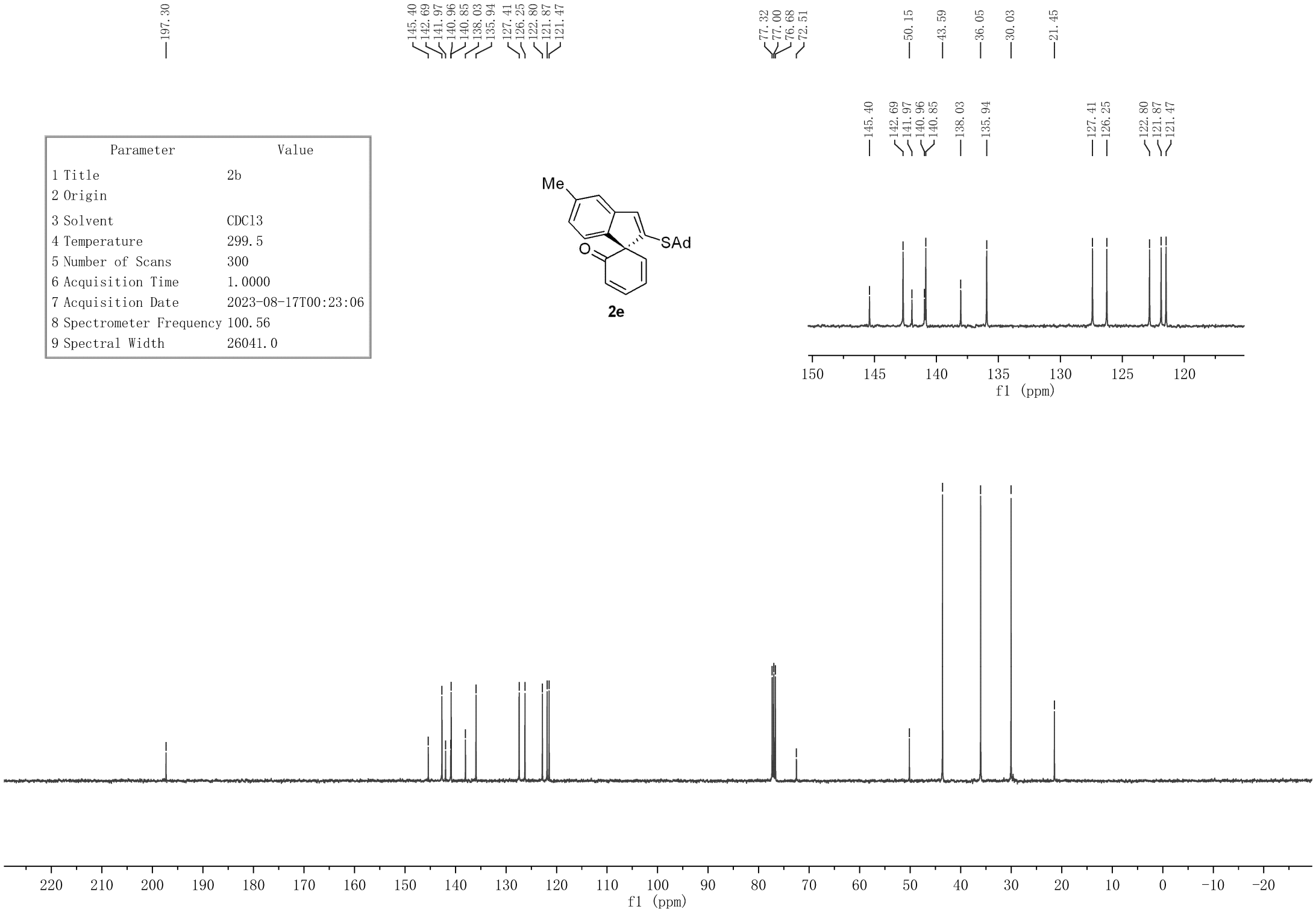

-62.34
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)

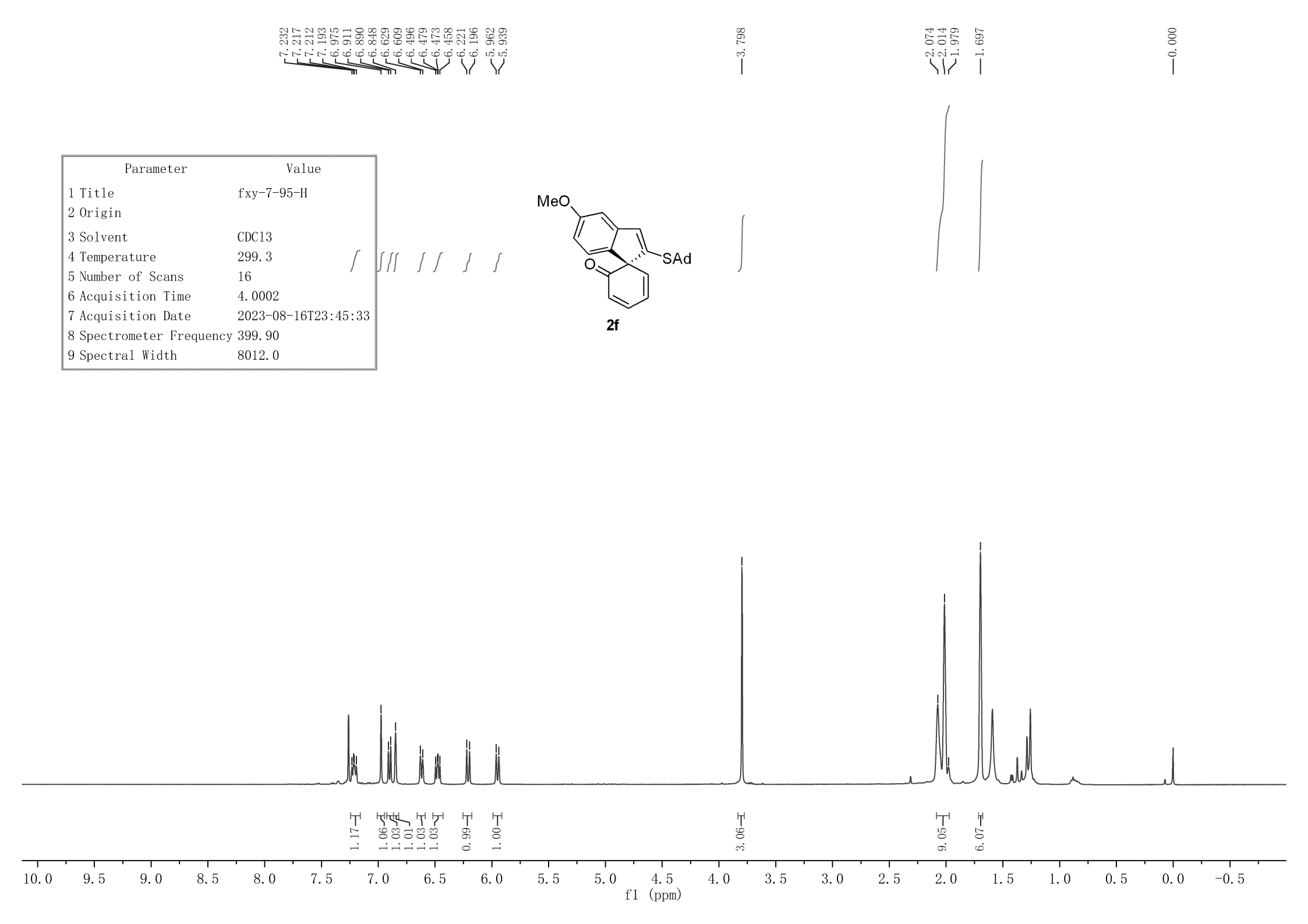
Parameter	Value
1 Title	2b
2 Origin	
3 Solvent	CDCl3
4 Temperature	299.3
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2023-08-17T00:10:19
8 Spectrometer Frequency	399.90
9 Spectral Width	8012.0

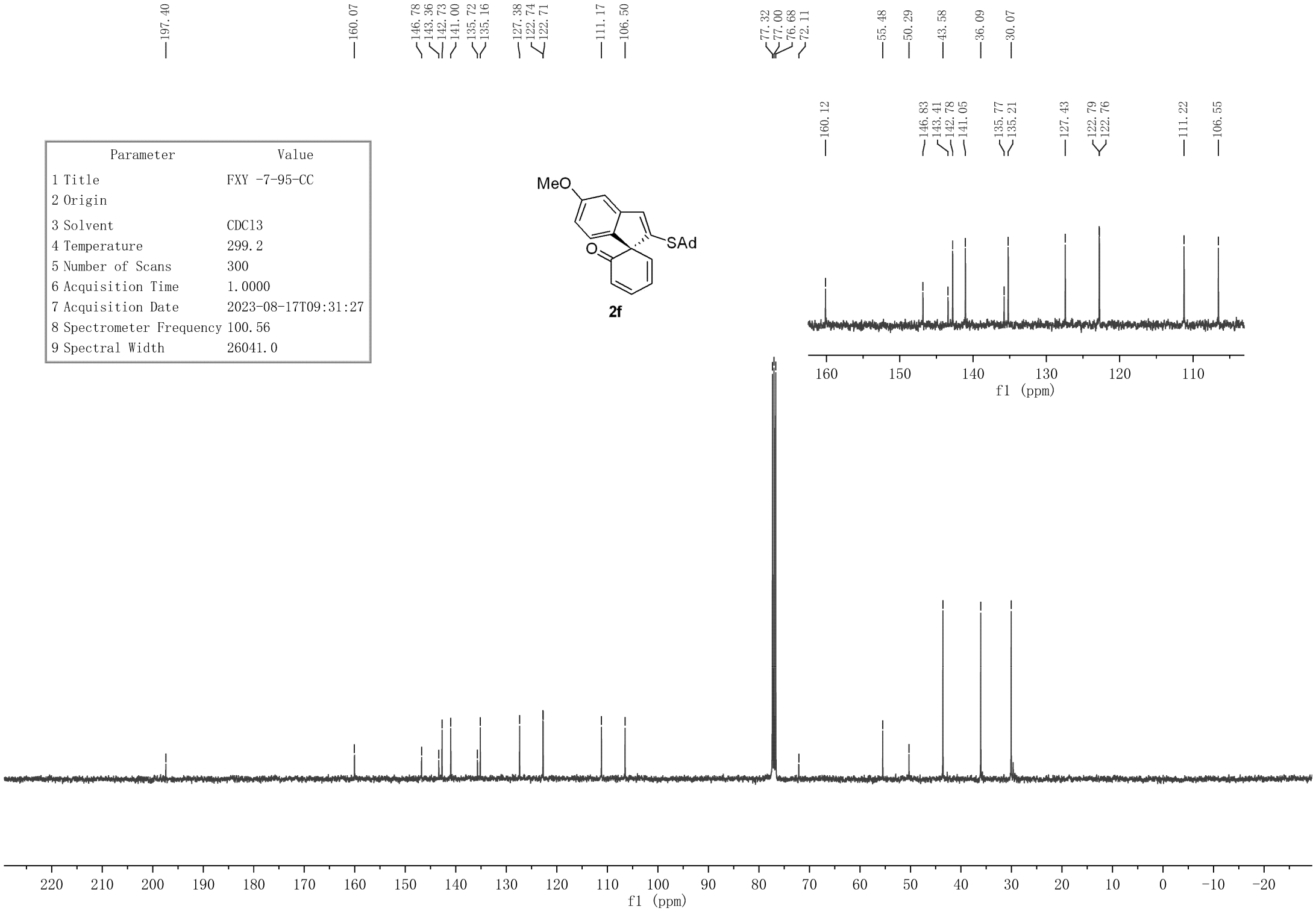


2e

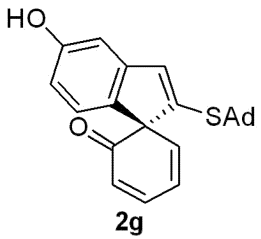



197.30
145.40
142.69
141.97
140.96
140.85
138.03
135.94
127.41
126.25
122.80
121.87
121.47
77.32
77.00
76.68
72.51
50.15
43.59
36.05
30.03
21.45
Parameter Value
1 Title 2b
2 Origin
3 Solvent CDCl3
4 Temperature 299.5
5 Number of Scans 300
6 Acquisition Time 1.0000
7 Acquisition Date 2023-08-17T00:23:06
8 Spectrometer Frequency 100.56
9 Spectral Width 26041.0
Me
SAd
O
2e
f1 (ppm)
f1 (ppm)

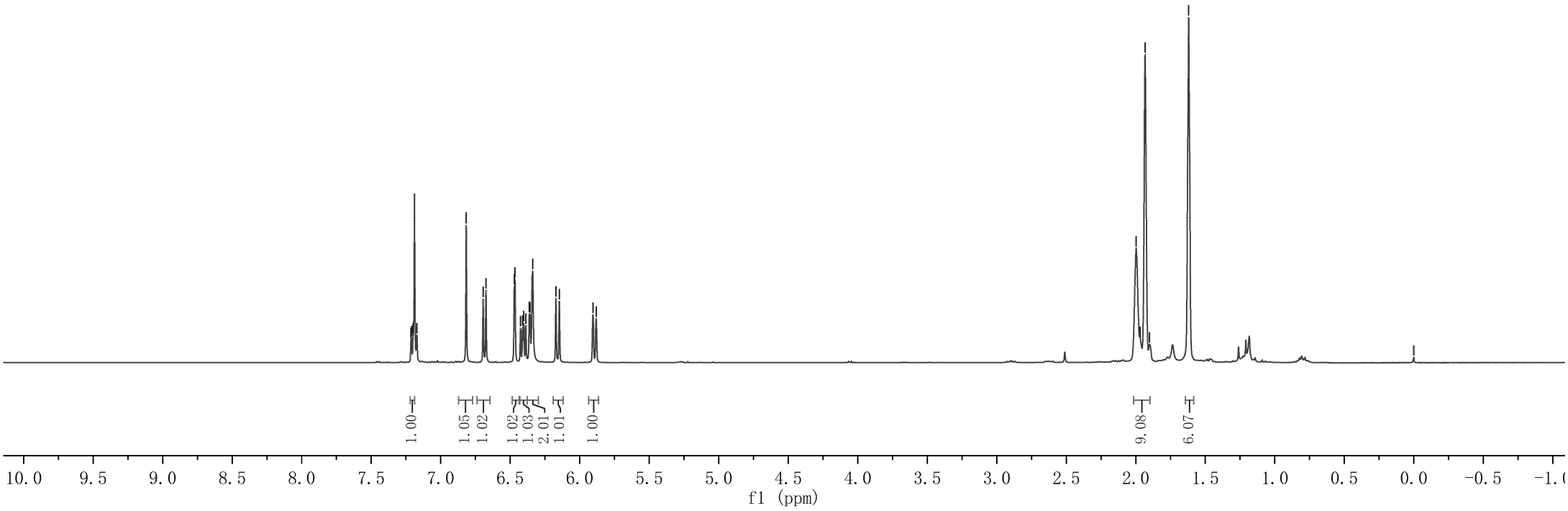

7.232
7.217
7.212
7.193
6.975
6.911
6.890
6.848
6.629
6.609
6.496
6.479
6.473
6.458
6.221
6.196
5.962
5.939
3.798
2.074
2.014
1.979
1.697
0.000
Parameter Value
1 Title fxy-7-95-H
2 Origin
3 Solvent CDCl3
4 Temperature 299.3
5 Number of Scans 16
6 Acquisition Time 4.0002
7 Acquisition Date 2023-08-16T23:45:33
8 Spectrometer Frequency 399.90
9 Spectral Width 8012.0
MeO
O
SAd
2f
1.17
1.06
1.03
1.01
1.03
1.03
0.99
1.00
3.06
9.05
6.07
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
f1 (ppm)


197.40
160.07
146.78
143.36
142.73
141.00
135.72
135.16
127.38
122.74
122.71
111.17
106.50
77.32
77.00
76.68
72.11
55.48
50.29
43.58
36.09
30.07
Parameter Value
1 Title FXY -7-95-CC
2 Origin
3 Solvent CDCl3
4 Temperature 299.2
5 Number of Scans 300
6 Acquisition Time 1.0000
7 Acquisition Date 2023-08-17T09:31:27
8 Spectrometer Frequency 100.56
9 Spectral Width 26041.0
MeO
O
SAd
2f
160.12
146.83
143.41
142.78
141.05
135.77
135.21
127.43
122.79
122.76
111.22
106.55
160
150
140
130
120
110
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
-10
-20
f1 (ppm)

Parameter	Value
1 Title	2g
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.1
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2022-01-20T17:30:15
8 Spectrometer Frequency	399.93
9 Spectral Width	8012.0

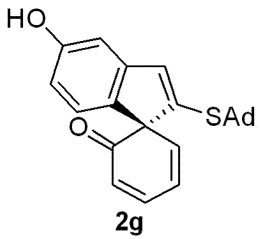


2g

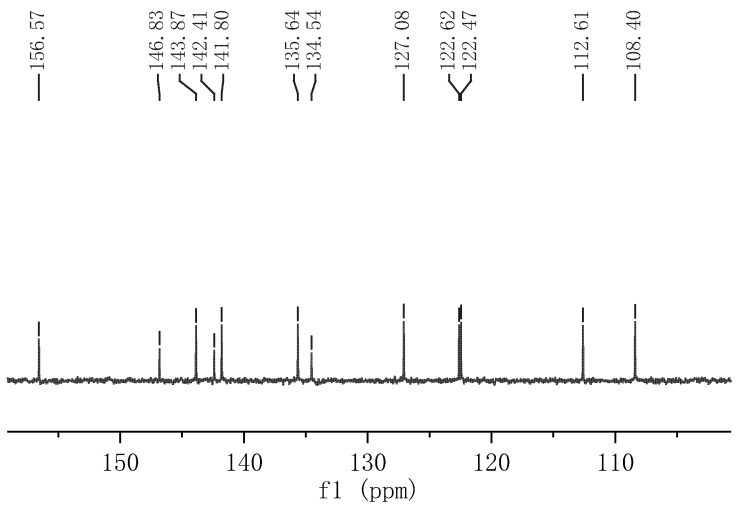


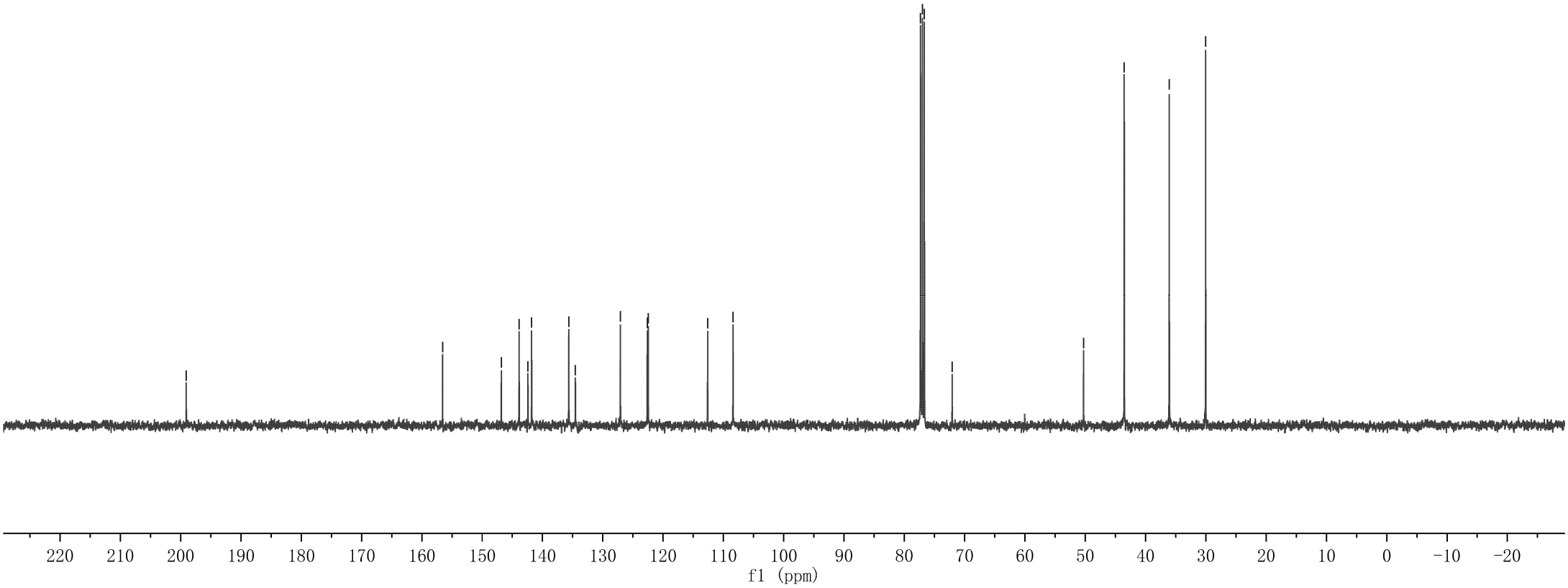
199.07
156.57
146.83
143.87
142.41
141.80
135.64
134.54
127.08
122.62
122.47
112.61
108.40
77.32
77.00
76.68
72.06
50.27
43.53
36.06
30.03

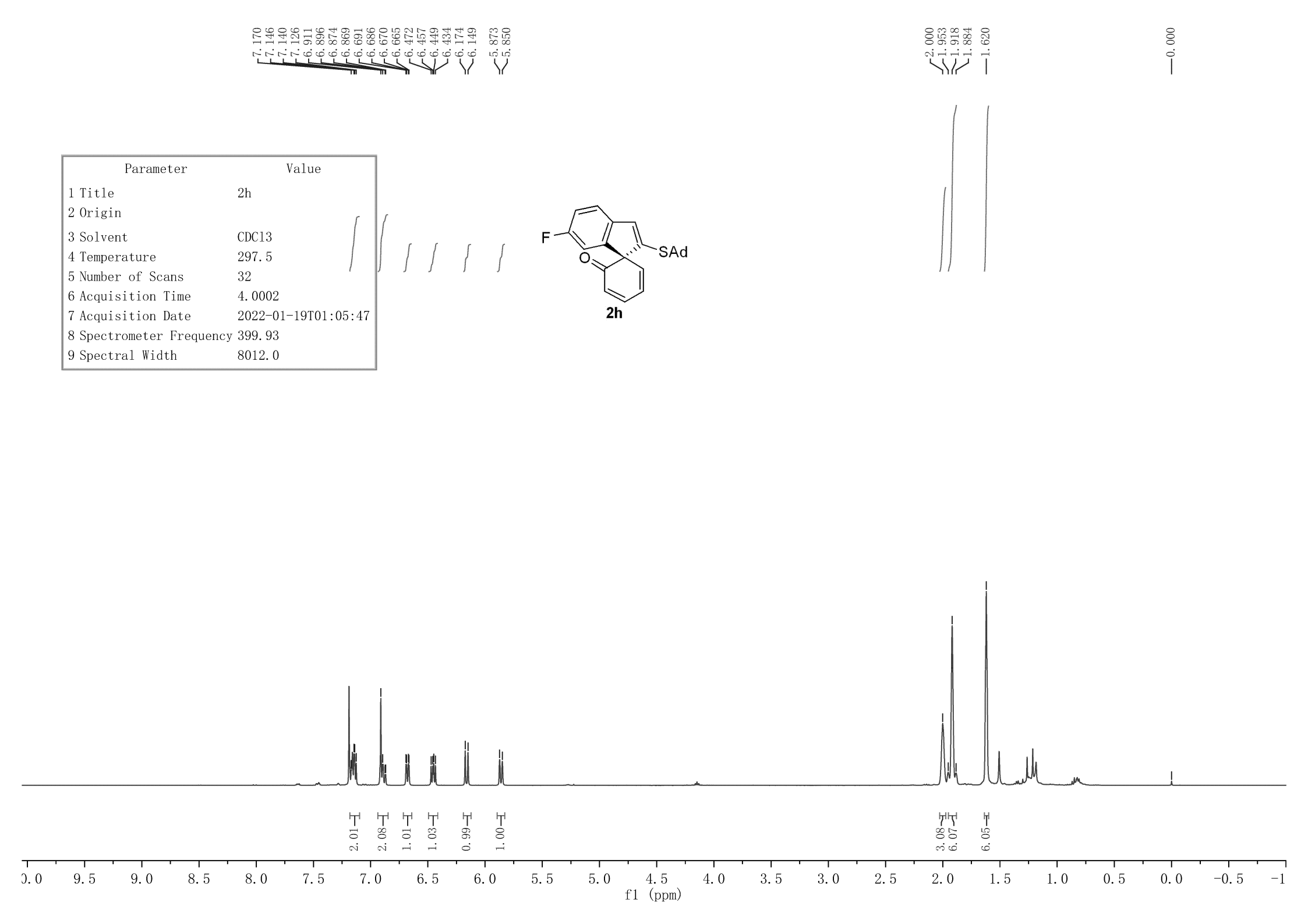
Parameter	Value
1 Title	2g
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.2
5 Number of Scans	200
6 Acquisition Time	1.0000
7 Acquisition Date	2022-01-20T17:39:39
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0



2g

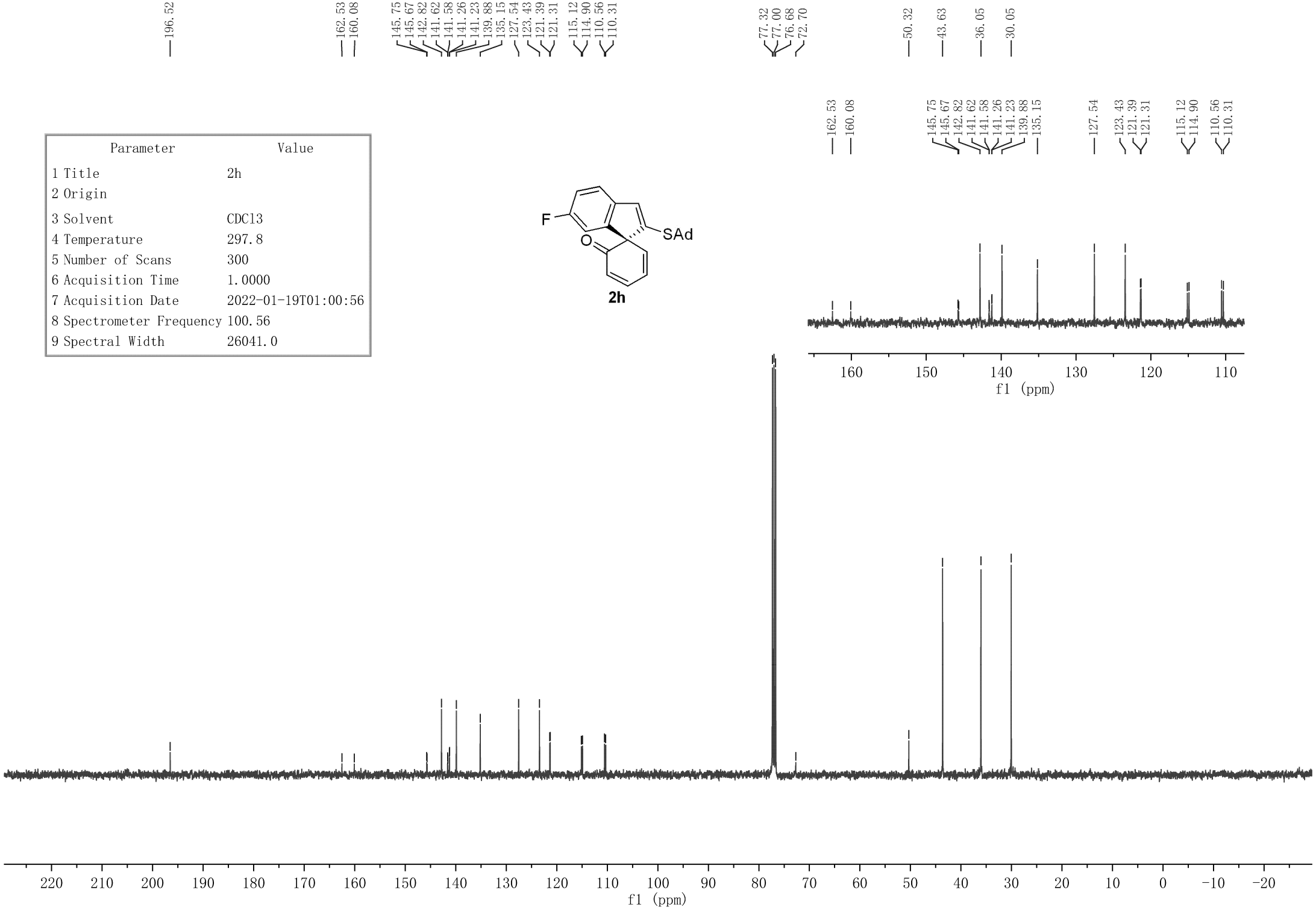


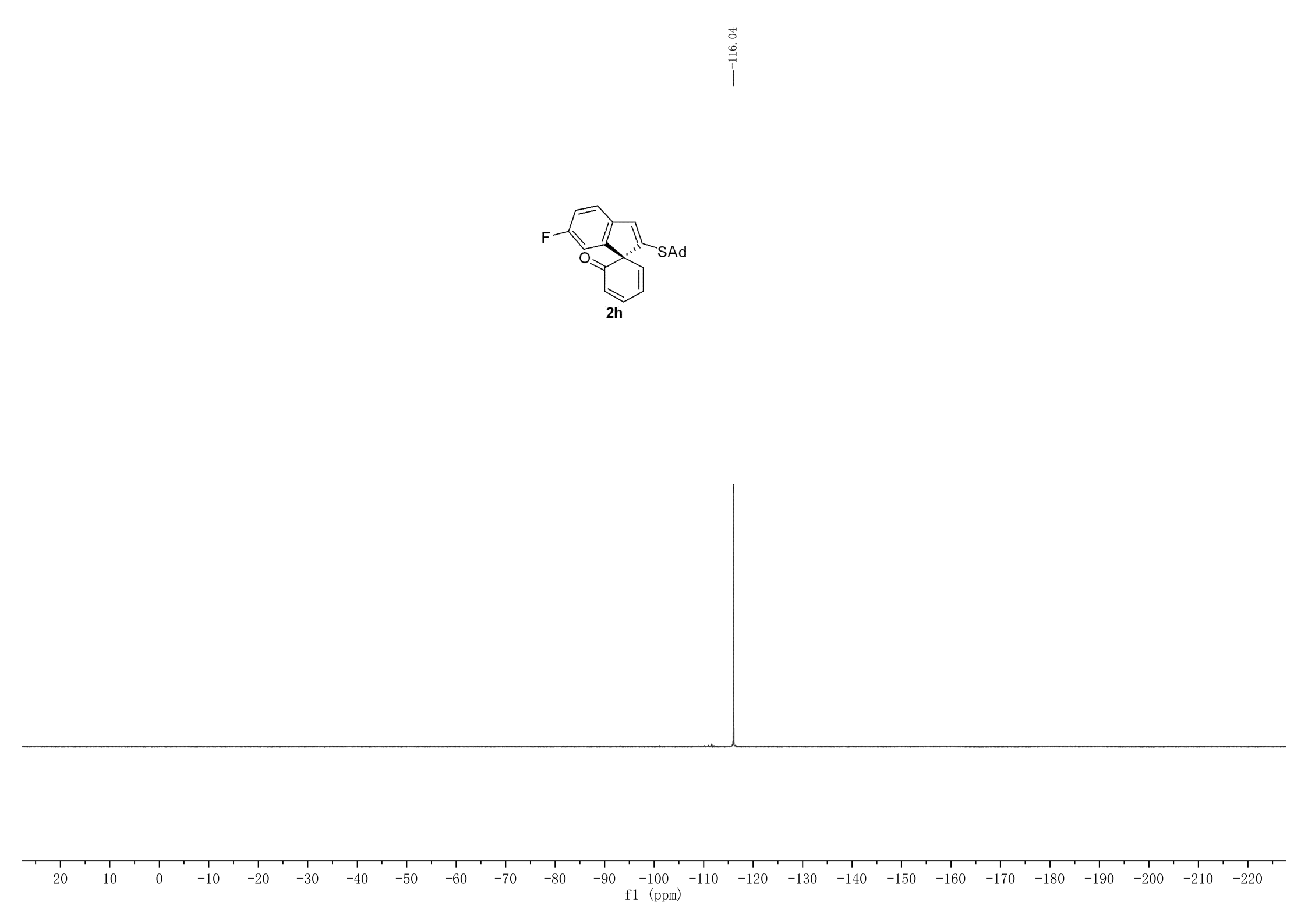



7.170
7.146
7.140
7.126
6.911
6.896
6.874
6.869
6.691
6.686
6.670
6.665
6.472
6.457
6.449
6.434
6.174
6.149
5.873
5.850
2.000
1.953
1.918
1.884
1.620
0.000
Parameter Value
1 Title 2h
2 Origin
3 Solvent CDCl3
4 Temperature 297.5
5 Number of Scans 32
6 Acquisition Time 4.0002
7 Acquisition Date 2022-01-19T01:05:47
8 Spectrometer Frequency 399.93
9 Spectral Width 8012.0
F
O
SAd
2h
2.01
2.08
1.01
1.03
0.99
1.00
3.08
6.07
6.05
f1 (ppm)

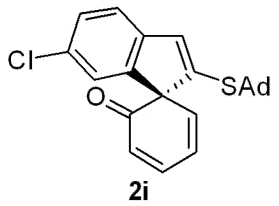
Parameter	Value
1 Title	2h
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.8
5 Number of Scans	300
6 Acquisition Time	1.0000
7 Acquisition Date	2022-01-19T01:00:56
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

2h

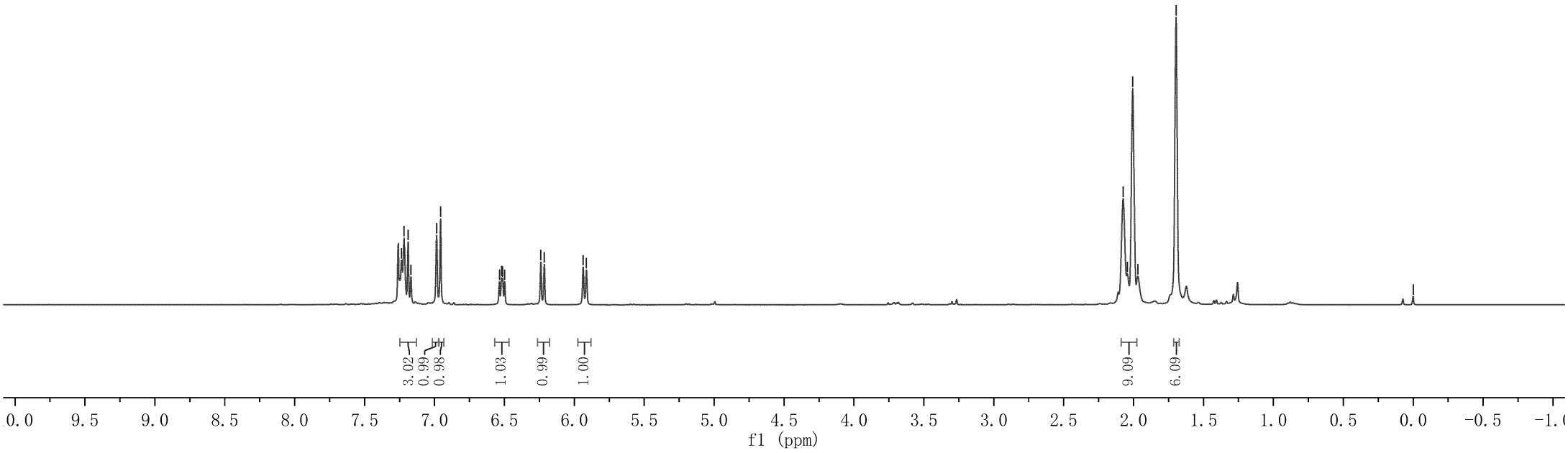



-116.04
F
O
SAd
2h
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)

Parameter	Value
1 Title	2i
2 Origin	
3 Solvent	CDCl3
4 Temperature	299.6
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2023-08-17T21:12:11
8 Spectrometer Frequency	399.90
9 Spectral Width	8012.0

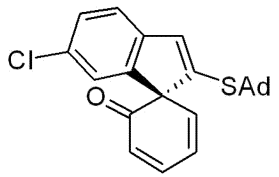


2i

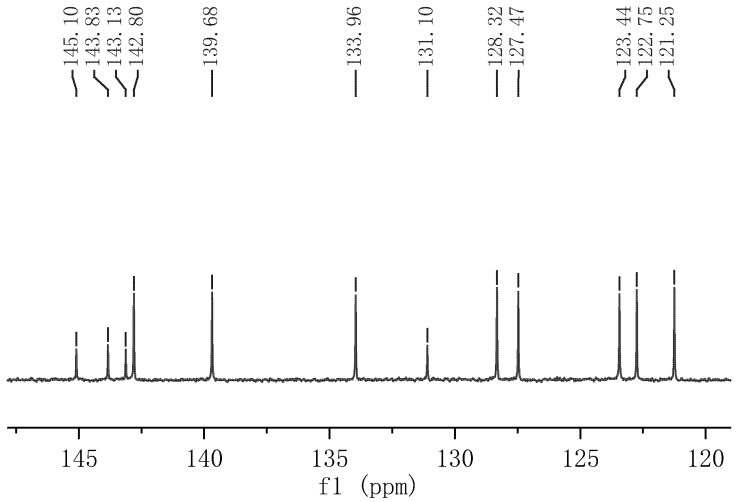


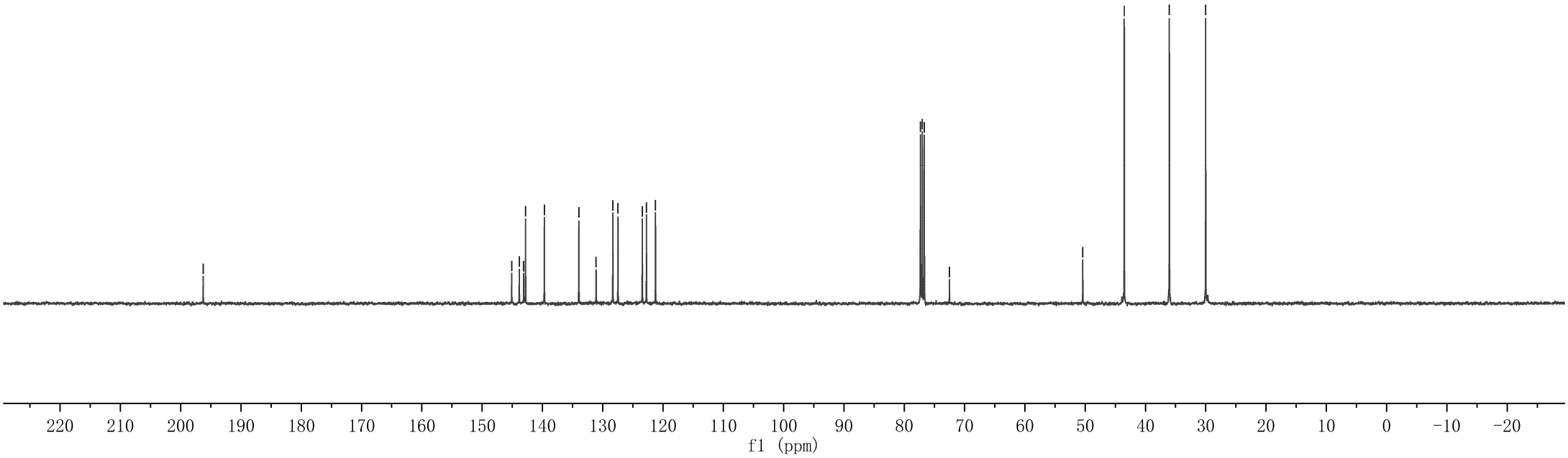
196.26
145.10
143.83
143.13
142.80
139.68
133.96
131.10
128.32
127.47
123.44
122.75
121.25
77.32
77.00
76.68
72.51
50.40
43.51
36.03
30.01

Parameter	Value
1 Title	2i
2 Origin	
3 Solvent	CDCl3
4 Temperature	299.6
5 Number of Scans	100
6 Acquisition Time	1.0000
7 Acquisition Date	2023-08-17T21:32:12
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0



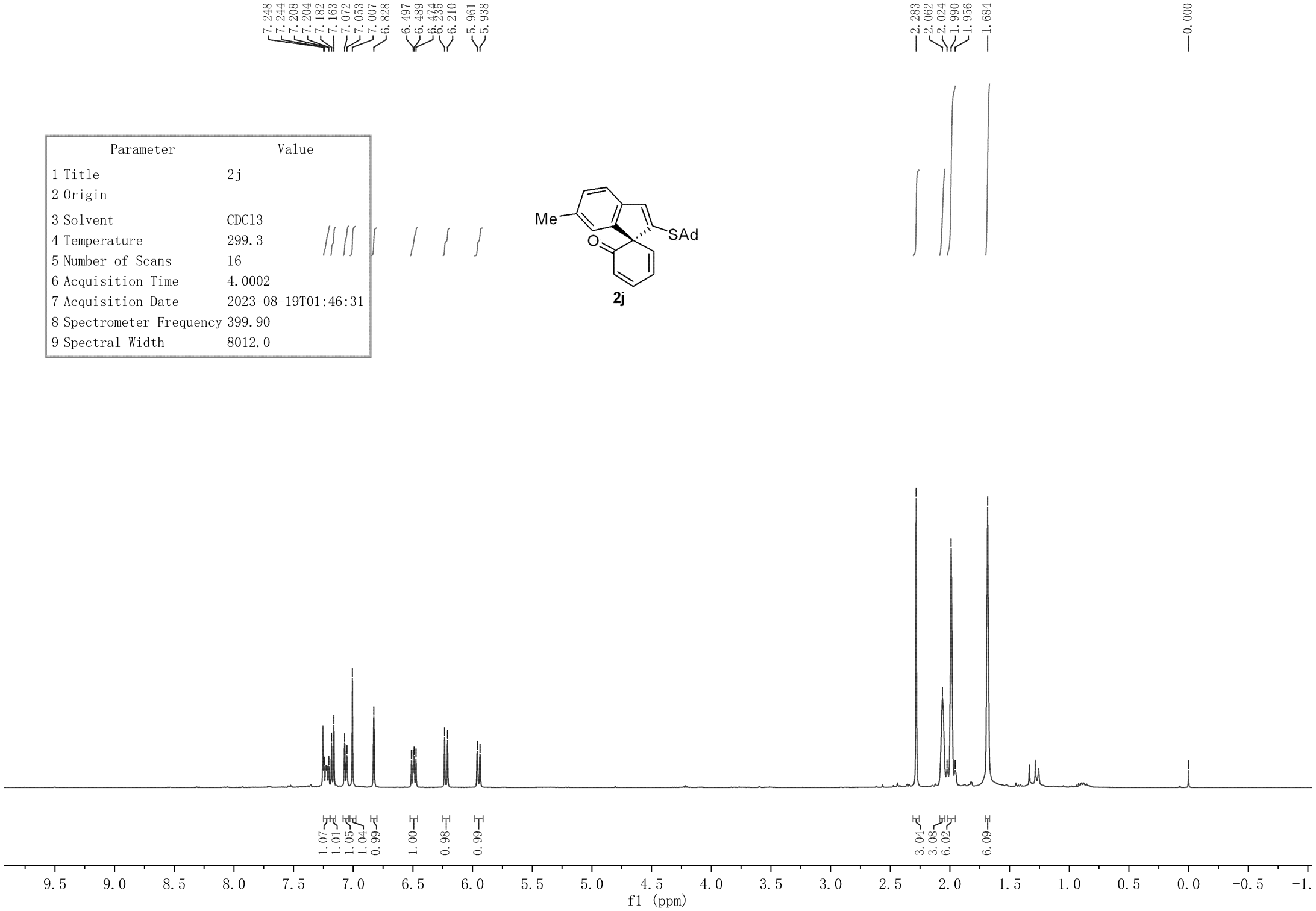
2i



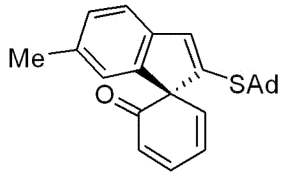


Parameter	Value
1 Title	2j
2 Origin	
3 Solvent	CDCl3
4 Temperature	299.3
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2023-08-19T01:46:31
8 Spectrometer Frequency	399.90
9 Spectral Width	8012.0

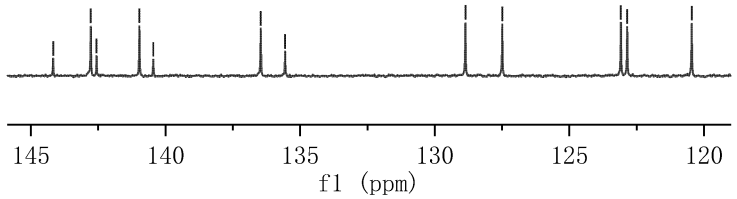
2j

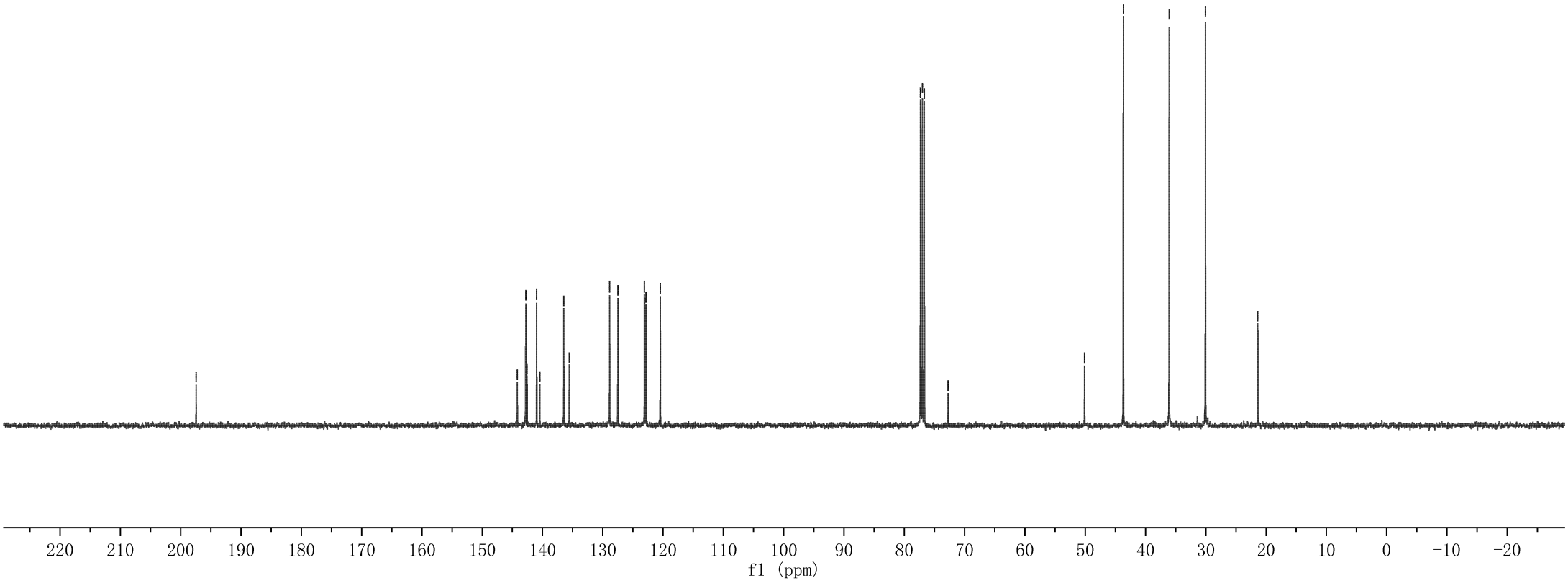


Parameter	Value
1 Title	2j
2 Origin	
3 Solvent	CDCl3
4 Temperature	299.6
5 Number of Scans	200
6 Acquisition Time	1.0000
7 Acquisition Date	2023-08-19T02:05:49
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

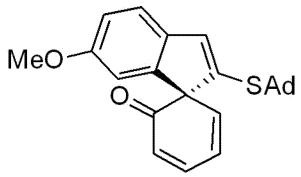


2j

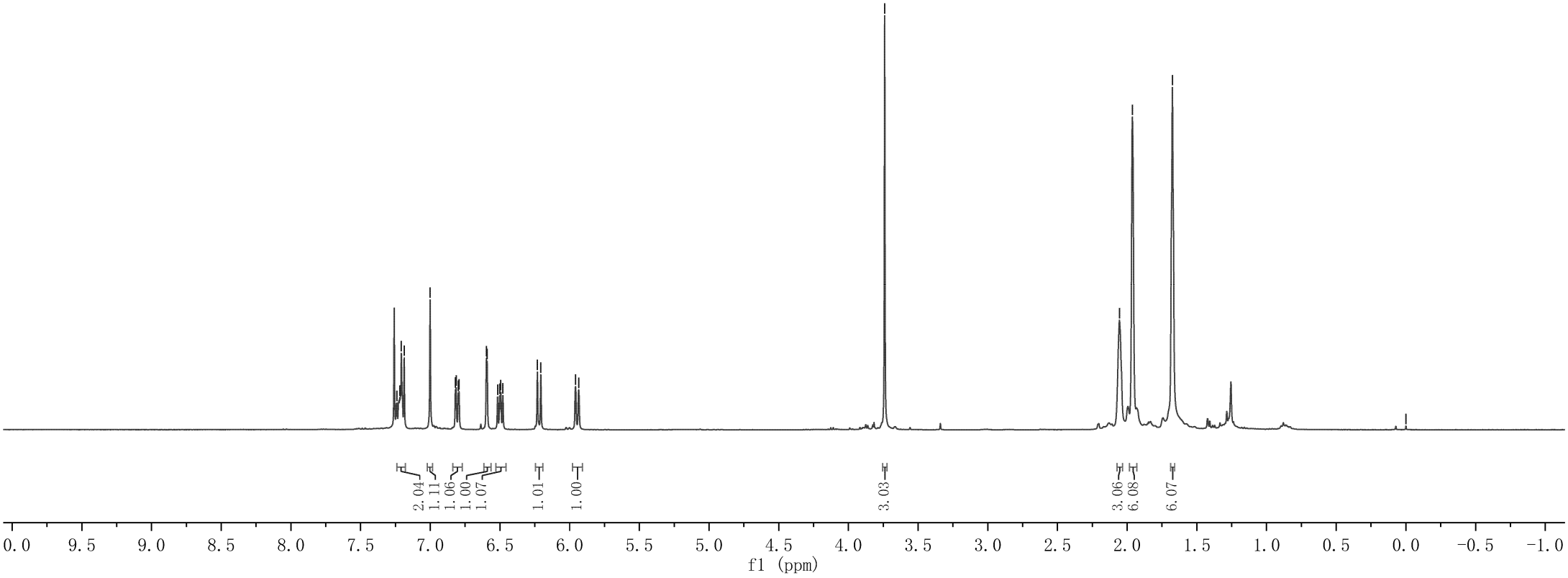




Parameter	Value
1 Title	FXY-2k
2 Origin	
3 Solvent	CDCl3
4 Temperature	299.9
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2023-08-09T21:52:09
8 Spectrometer Frequency	399.90
9 Spectral Width	8012.0

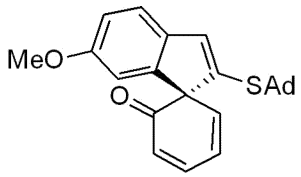


2k

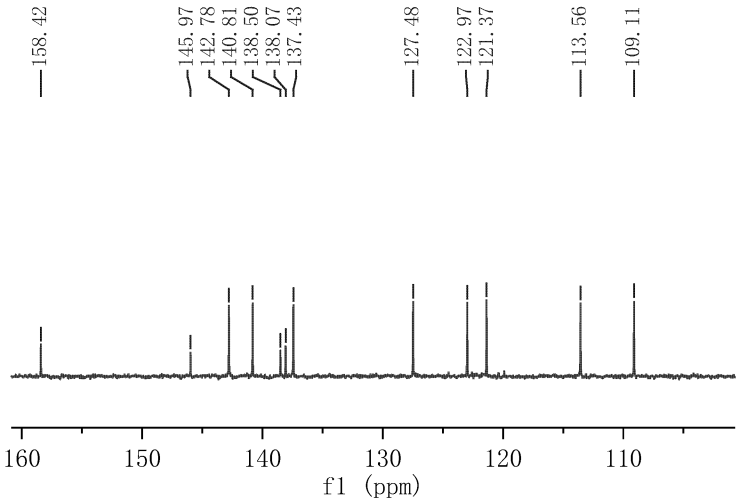


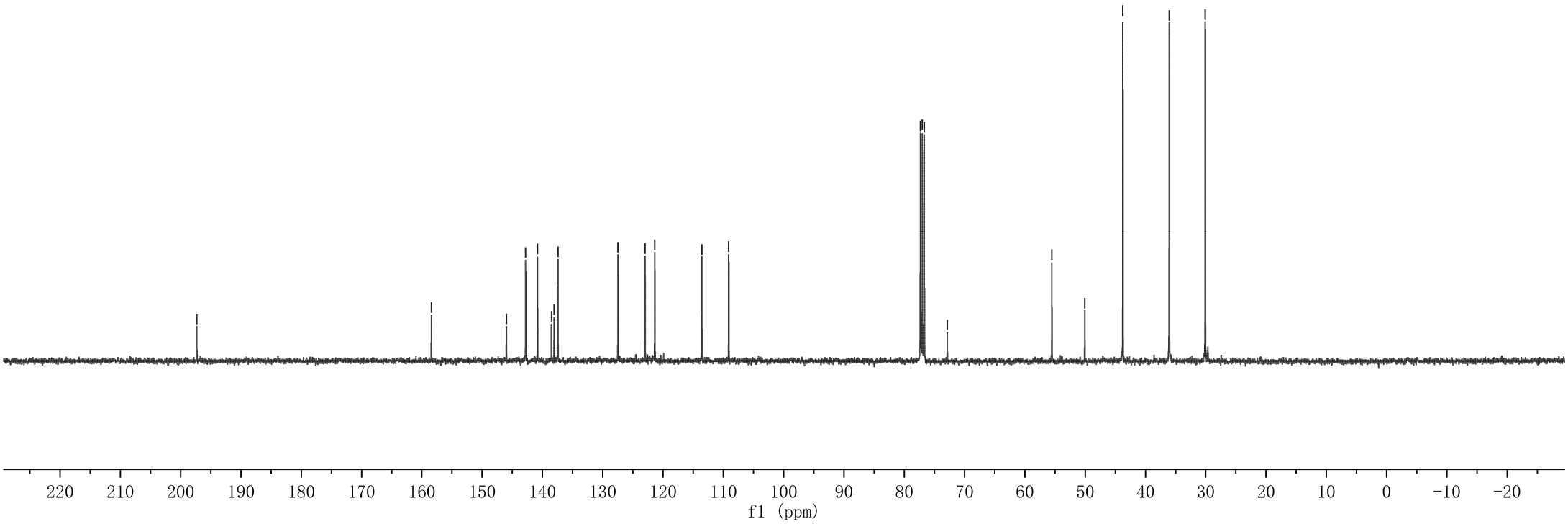
197.32
158.42
145.97
142.78
140.81
138.50
138.07
137.43
127.48
122.97
121.37
113.56
109.11
77.32
77.00
76.68
72.86
55.52
50.06
43.75
36.05
30.08

Parameter	Value
1 Title	FXY-2k
2 Origin	
3 Solvent	CDCl3
4 Temperature	300.3
5 Number of Scans	300
6 Acquisition Time	1.0000
7 Acquisition Date	2023-08-09T22:05:01
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

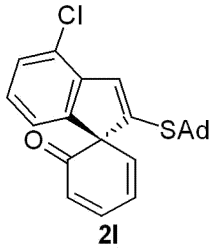


2k

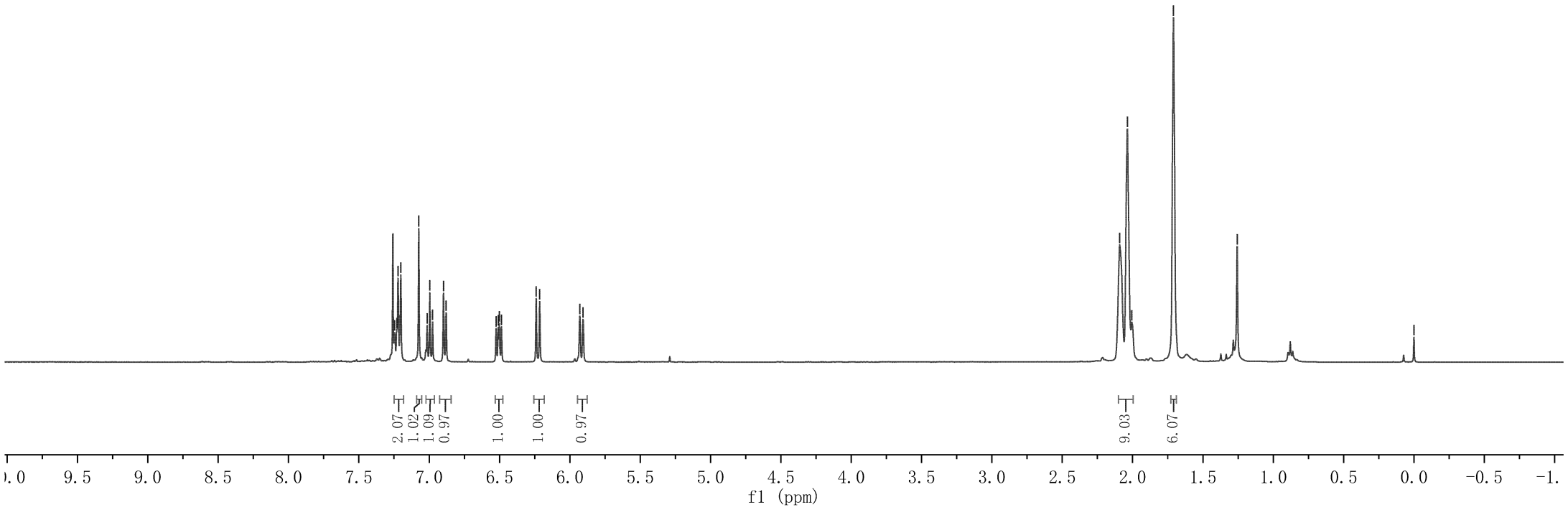




Parameter	Value
1 Title	FXY-7-136-h
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.1
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2022-02-26T15:50:52
8 Spectrometer Frequency	399.93
9 Spectral Width	8012.0

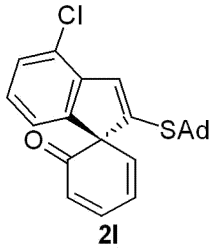


2l

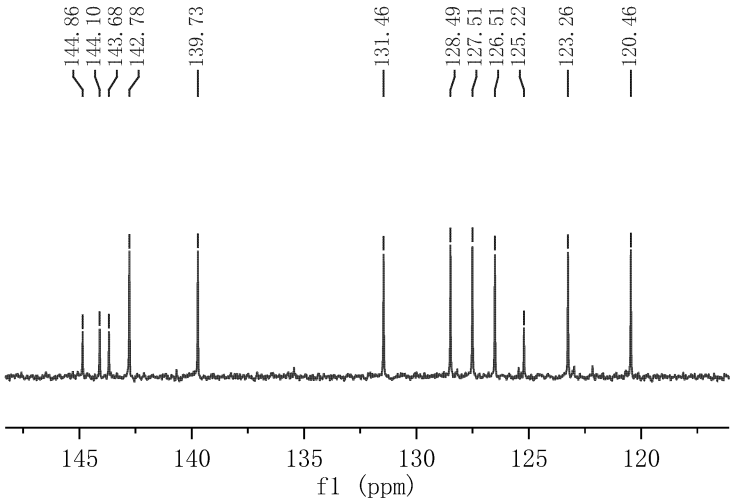


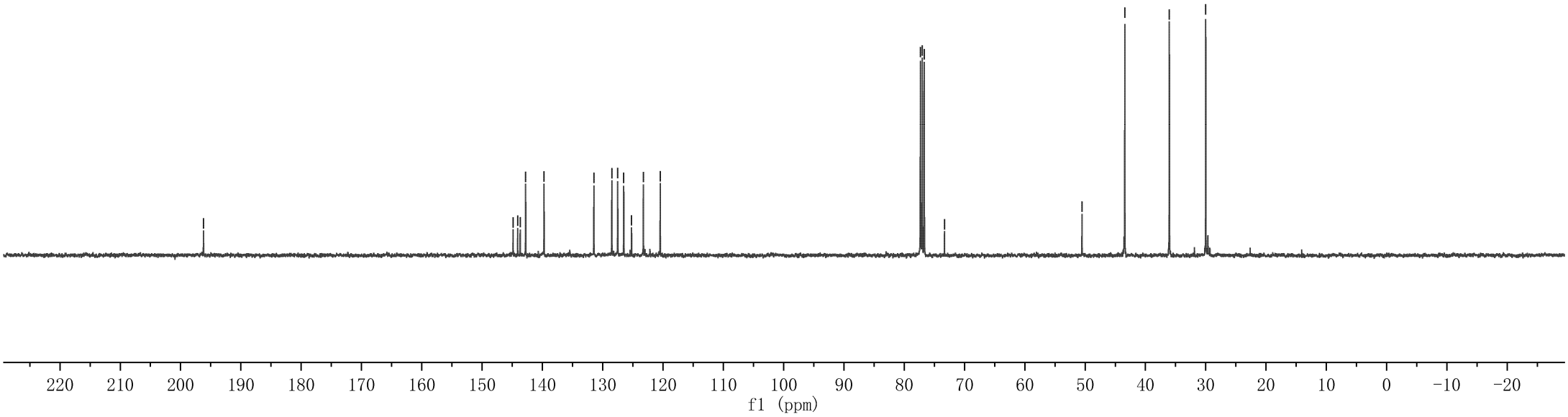
196.20
144.86
144.10
143.68
142.78
139.73
131.46
128.49
127.51
126.51
125.22
123.26
120.46
77.32
77.00
76.68
73.33
50.52
43.42
36.03
30.00

Parameter	Value
1 Title	FXY-7-136-c
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.1
5 Number of Scans	300
6 Acquisition Time	1.0000
7 Acquisition Date	2022-02-26T16:03:10
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

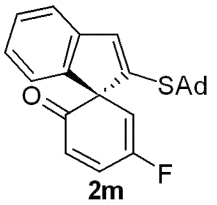


2l

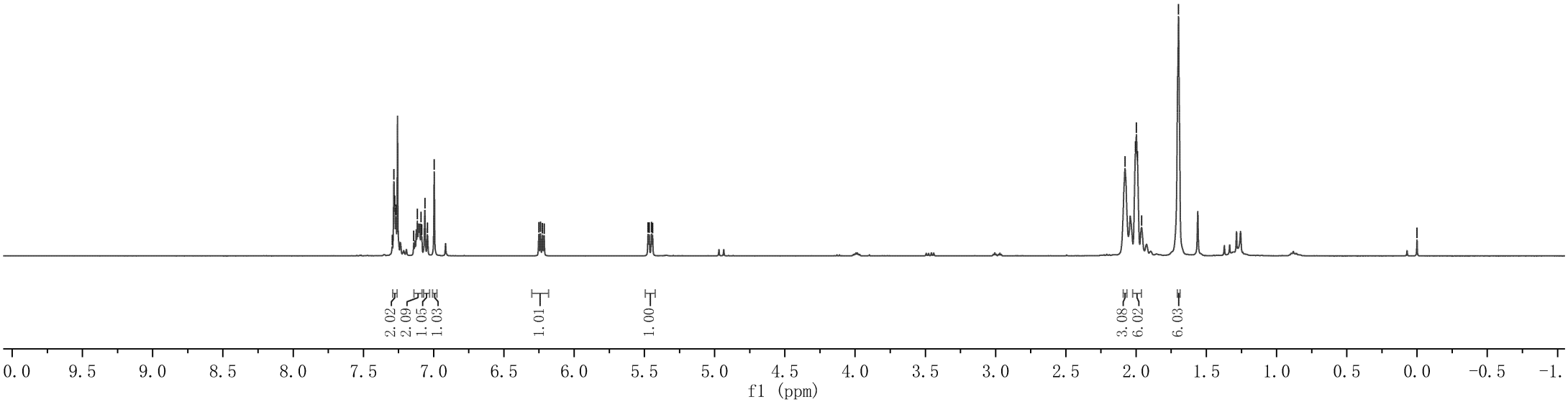




Parameter	Value
1 Title	FXY-8-119-H
2 Origin	
3 Solvent	CDCl3
4 Temperature	298.4
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2022-05-18T19:00:38
8 Spectrometer Frequency	399.92
9 Spectral Width	8012.0

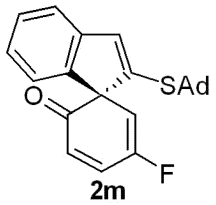


2m

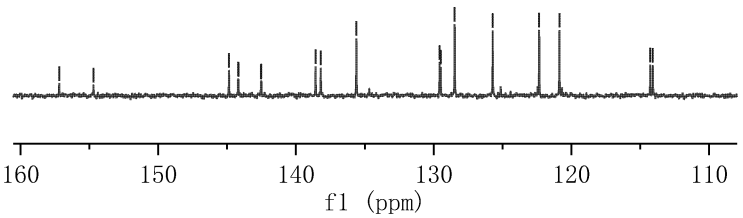


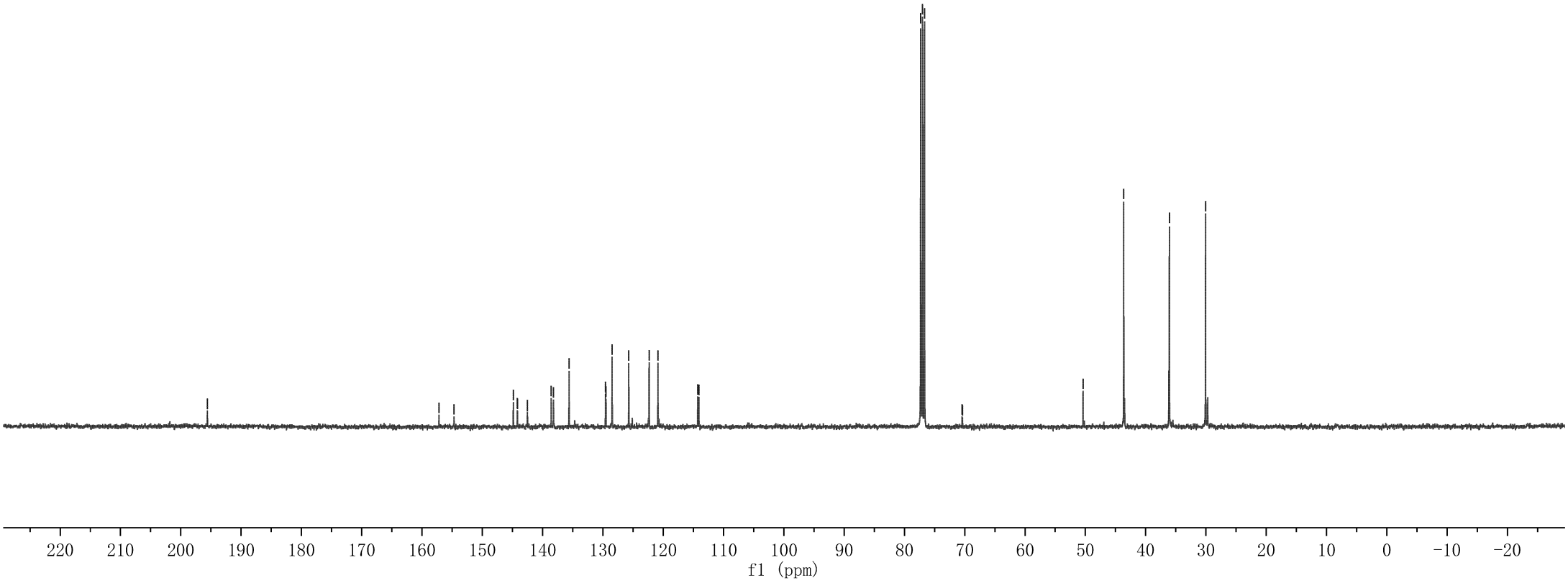
195.60
195.59
157.19
154.69
144.86
144.20
144.17
142.54
142.51
138.57
138.20
135.61
129.57
129.49
128.47
125.71
122.34
120.87
114.28
114.09
77.32
77.00
76.68
70.44
70.36
50.38
43.64
36.06
30.06

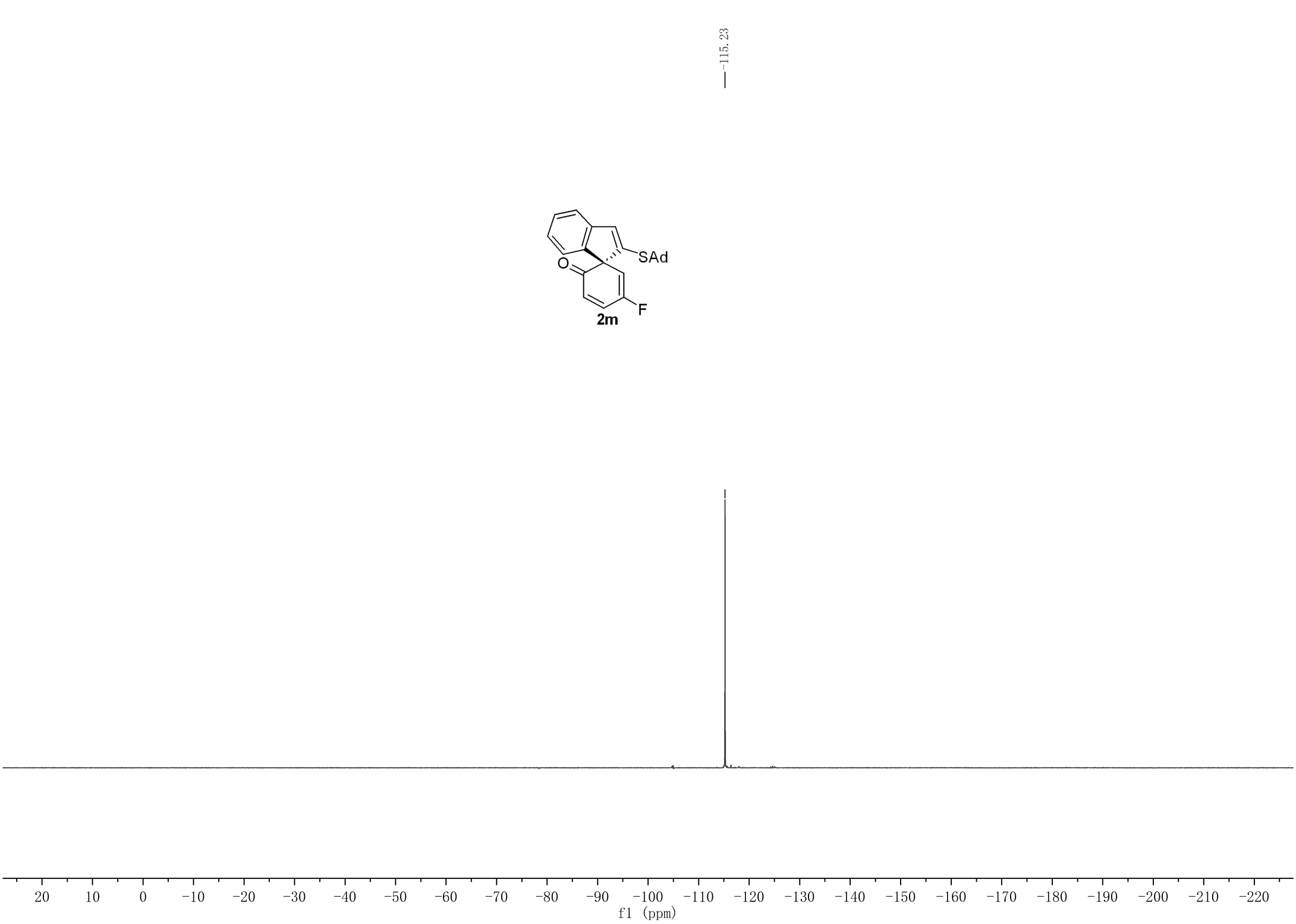
Parameter	Value
1 Title	FXY-8-119-C
2 Origin	
3 Solvent	CDCl3
4 Temperature	298.5
5 Number of Scans	500
6 Acquisition Time	1.0000
7 Acquisition Date	2022-05-18T19:36:52
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0



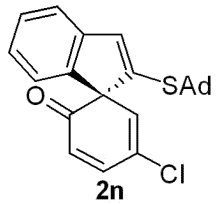
2m



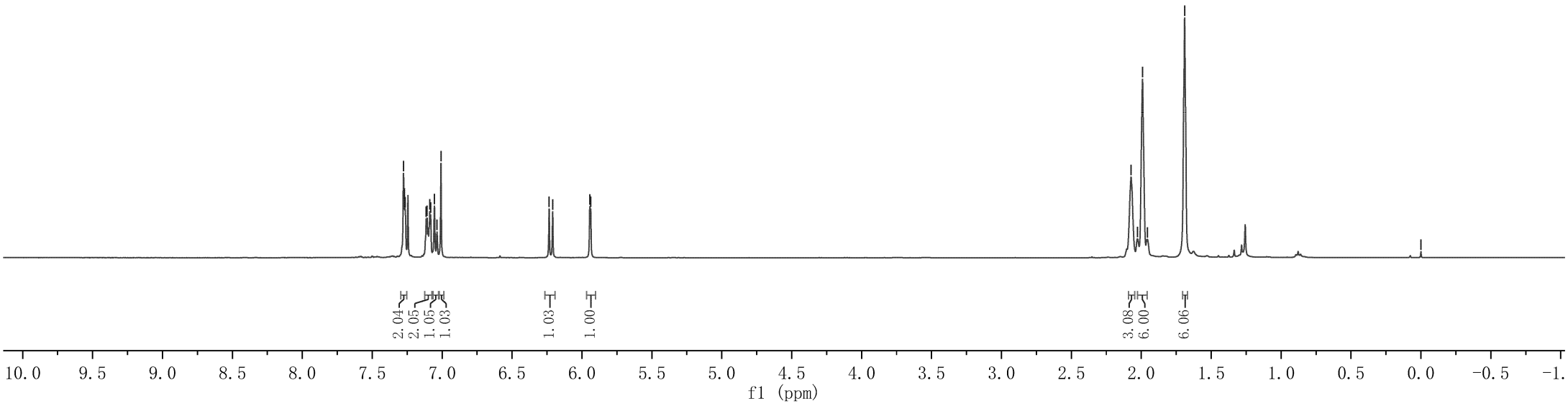



-115.23
SAd
O
F
2m
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)

Parameter	Value
1 Title	2n
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.6
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2022-03-03T21:13:54
8 Spectrometer Frequency	399.93
9 Spectral Width	8012.0

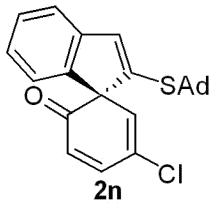


2n

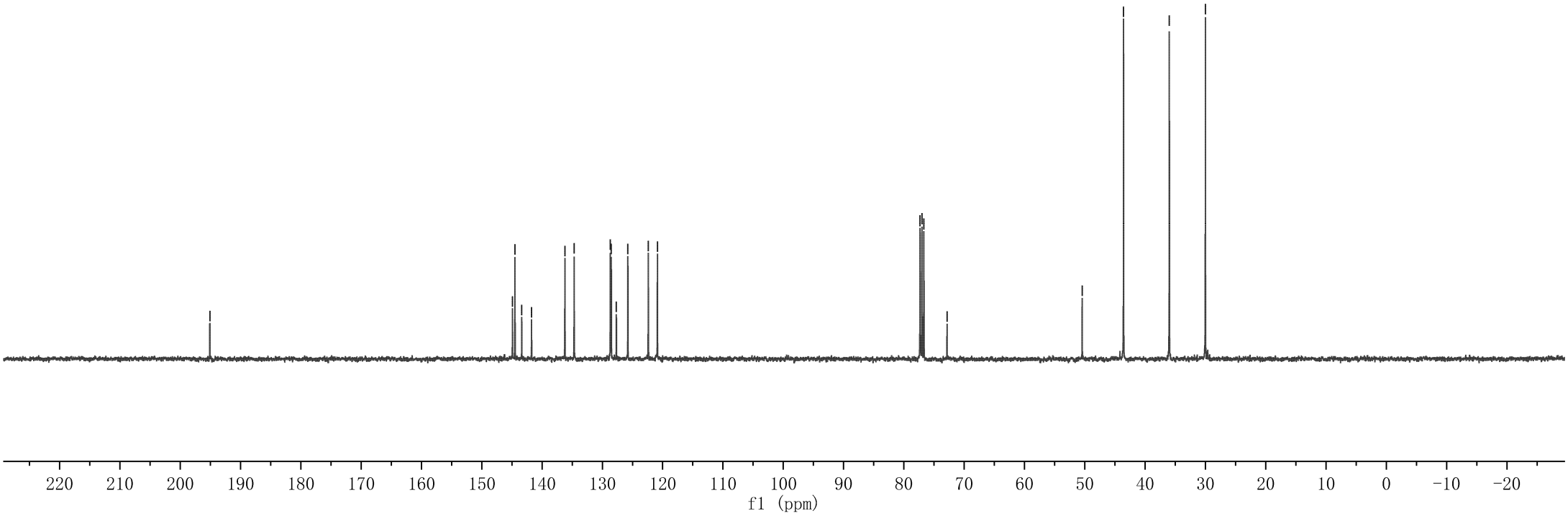


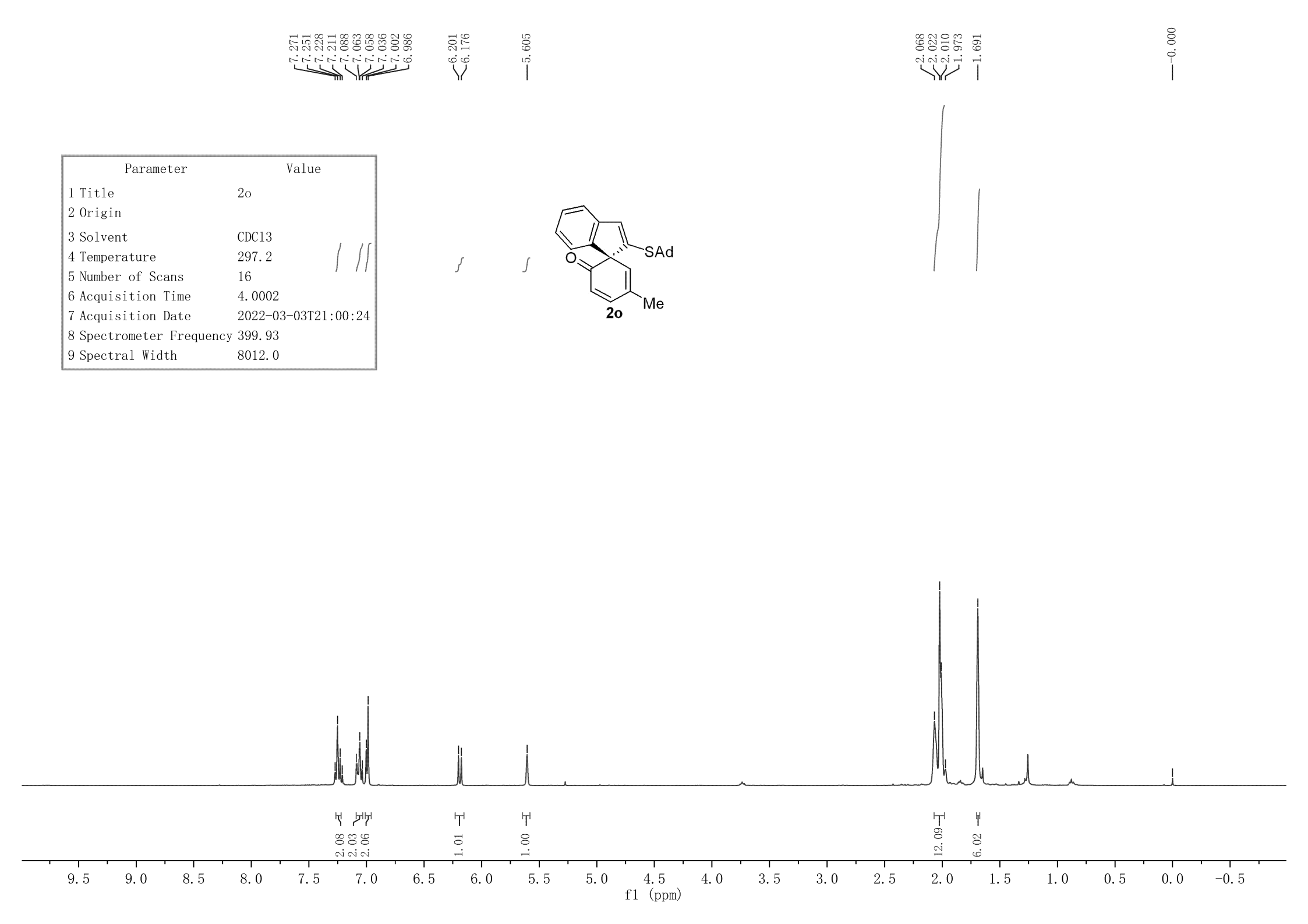
195.09
144.90
144.49
143.37
141.74
136.21
134.67
128.68
128.51
127.67
125.77
122.38
120.87
77.32
77.00
76.68
72.84
50.44
43.57
35.98
30.00

Parameter	Value
1 Title	2n
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.6
5 Number of Scans	100
6 Acquisition Time	1.0000
7 Acquisition Date	2022-03-03T21:19:39
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0



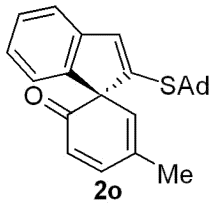
2n

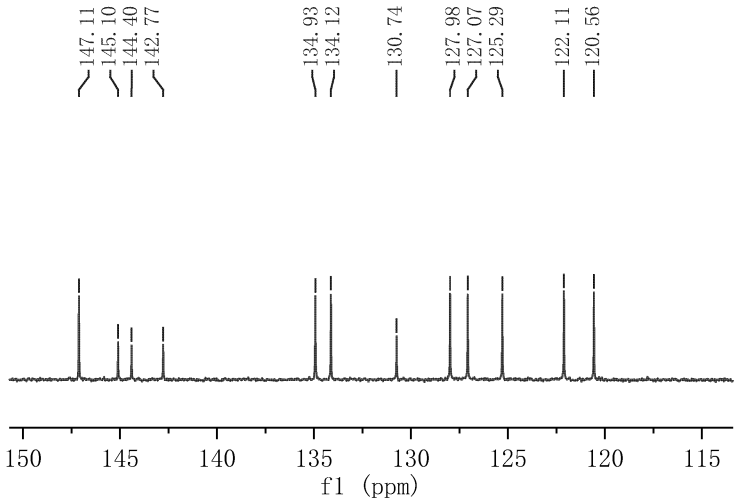


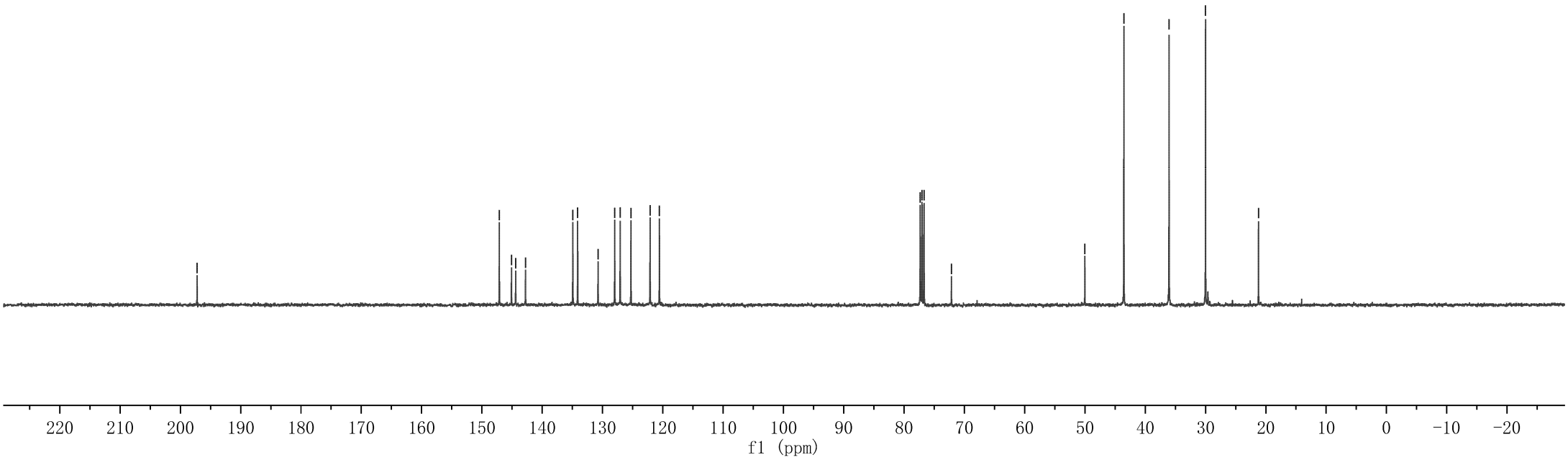

7.271
7.251
7.228
7.211
7.088
7.063
7.058
7.036
7.002
6.986
6.201
6.176
5.605
2.068
2.022
2.010
1.973
1.691
0.000
Parameter Value
1 Title 2o
2 Origin
3 Solvent CDCl3
4 Temperature 297.2
5 Number of Scans 16
6 Acquisition Time 4.0002
7 Acquisition Date 2022-03-03T21:00:24
8 Spectrometer Frequency 399.93
9 Spectral Width 8012.0
O
SAd
Me
2o
2.08
2.03
2.06
1.01
1.00
12.09
6.02
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
f1 (ppm)

197.23
147.11
145.10
144.40
142.77
134.93
134.12
130.74
127.98
127.07
125.29
122.11
120.56
77.32
77.00
76.68
72.14
50.02
43.54
36.05
30.00
21.22

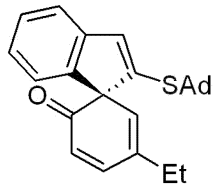
Parameter	Value
1 Title	2o
2 Origin	
3 Solvent	CDCl3
4 Temperature	297.4
5 Number of Scans	200
6 Acquisition Time	1.0000
7 Acquisition Date	2022-03-03T21:09:19
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0



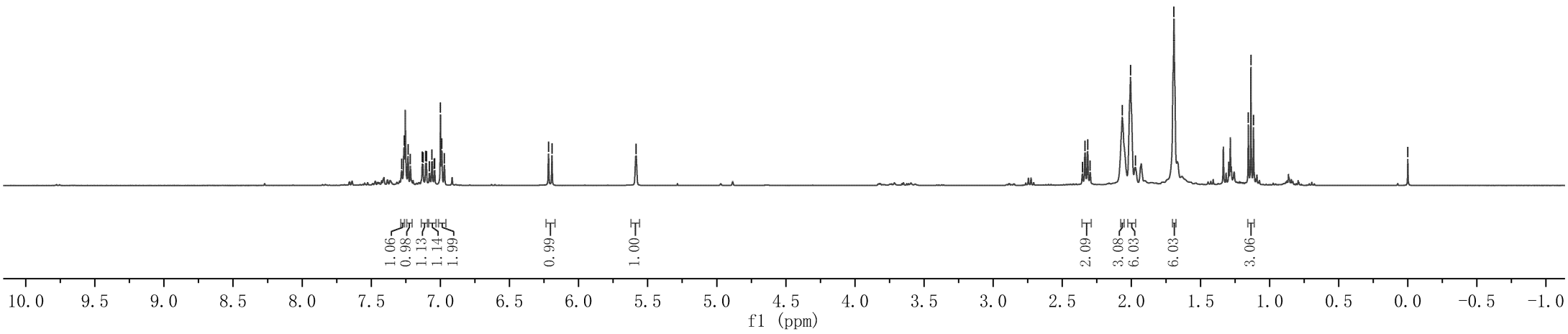




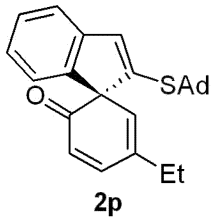
Parameter	Value
1 Title	FXY-8-138-1
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	5
6 Acquisition Time	4.0894
7 Acquisition Date	2022-06-03T15:42:14
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8



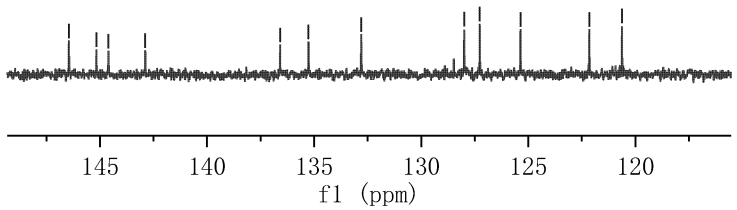
2p

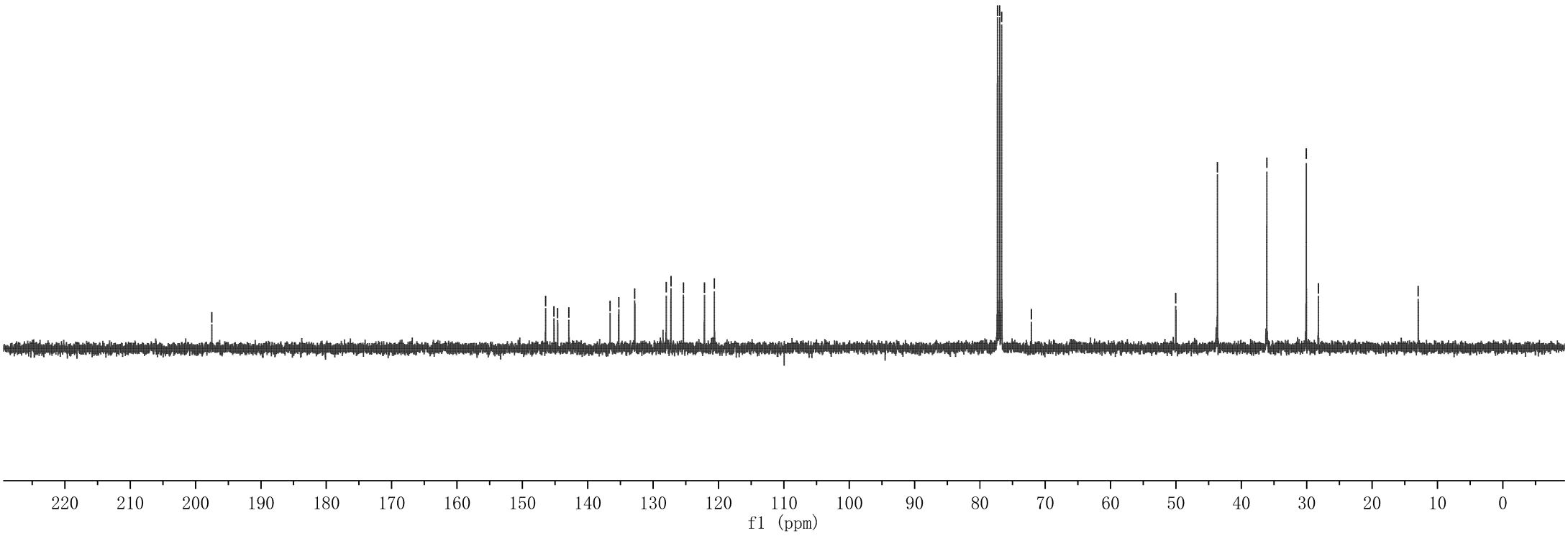


Parameter	Value
1 Title	FXY-8-138-1-c
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	27
6 Acquisition Time	1.3631
7 Acquisition Date	2022-06-03T15:43:15
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5

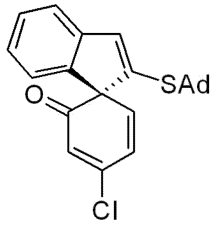


2p

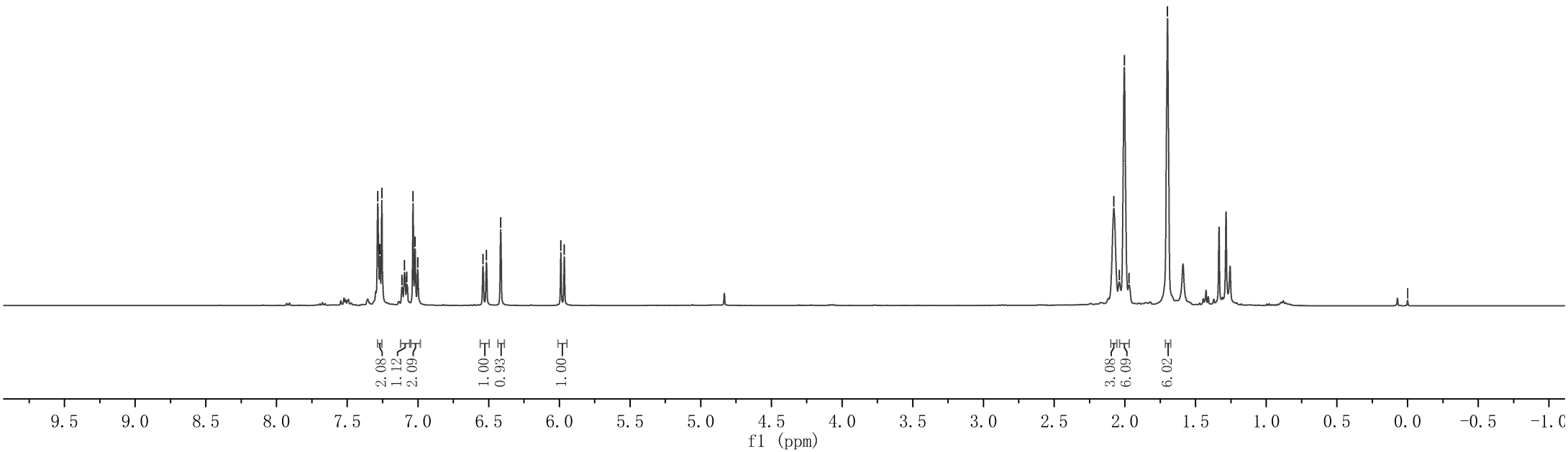




Parameter	Value
1 Title	FXY-2t-rac
2 Origin	
3 Solvent	CDCl3
4 Temperature	300.5
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2023-08-08T23:08:19
8 Spectrometer Frequency	399.90
9 Spectral Width	8012.0

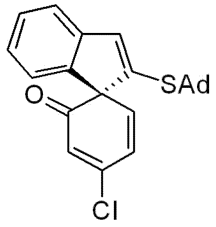


2q

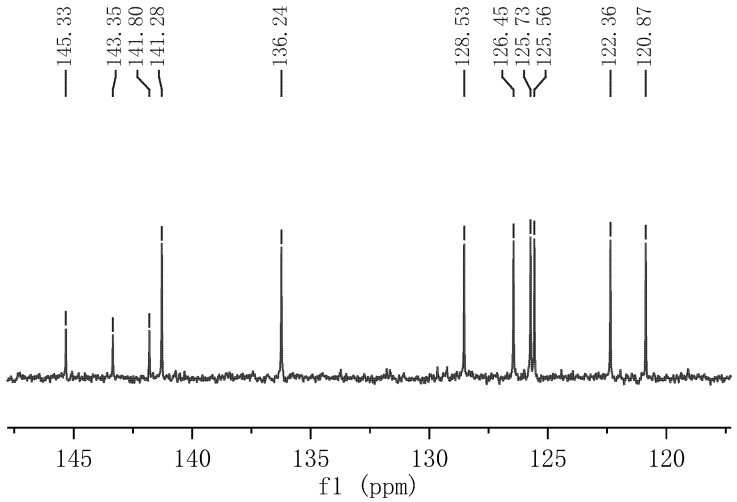


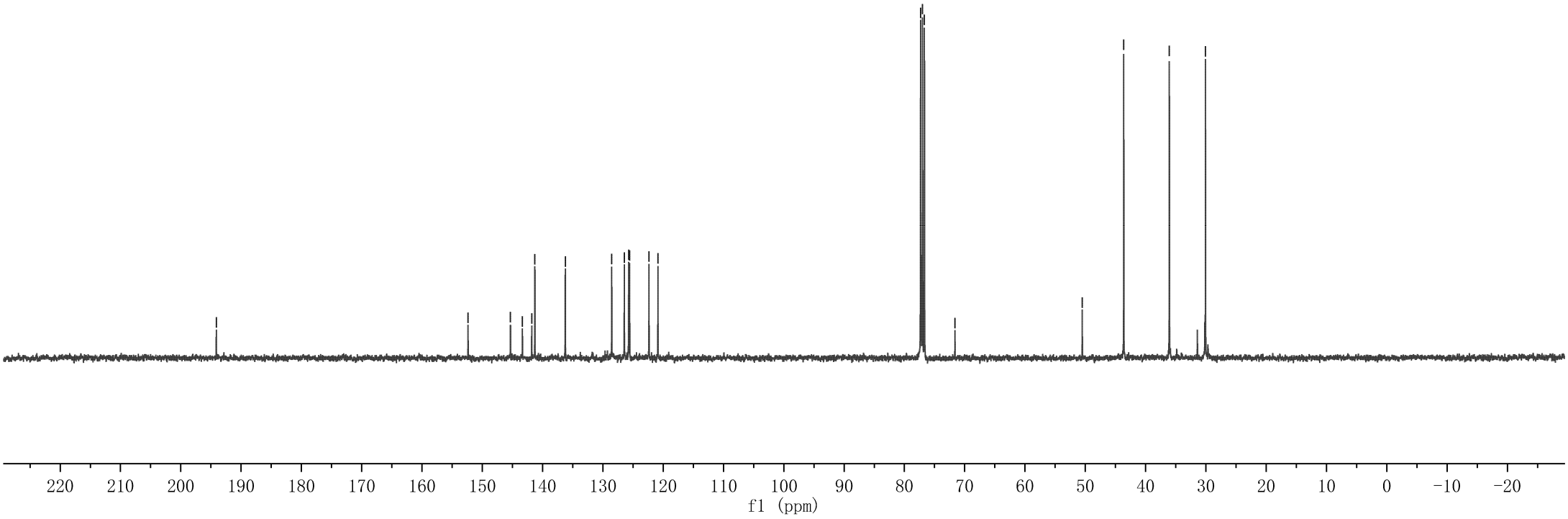
194.11
152.36
145.33
143.35
141.80
141.28
136.24
128.53
126.45
125.73
125.56
122.36
120.87
77.32
77.00
76.68
71.61
50.50
43.62
36.06
30.07

Parameter	Value
1 Title	FXY-2t-rac
2 Origin	
3 Solvent	CDCl3
4 Temperature	300.5
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2023-08-08T23:08:19
8 Spectrometer Frequency	399.90
9 Spectral Width	8012.0



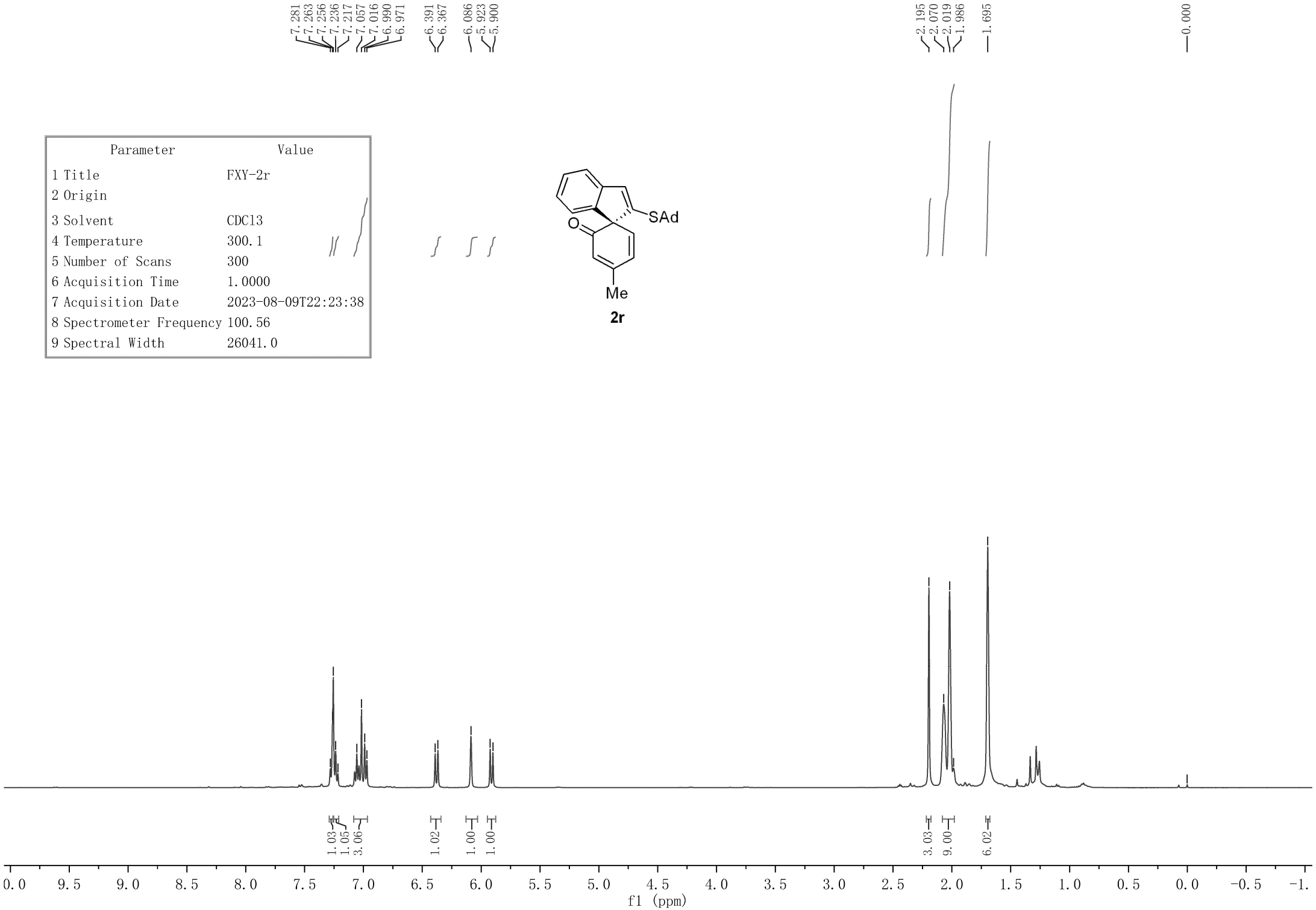
2q





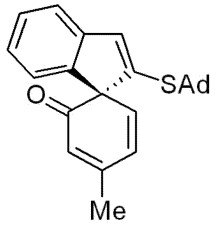
Parameter	Value
1 Title	FXY-2r
2 Origin	
3 Solvent	CDCl3
4 Temperature	300.1
5 Number of Scans	300
6 Acquisition Time	1.0000
7 Acquisition Date	2023-08-09T22:23:38
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

2r

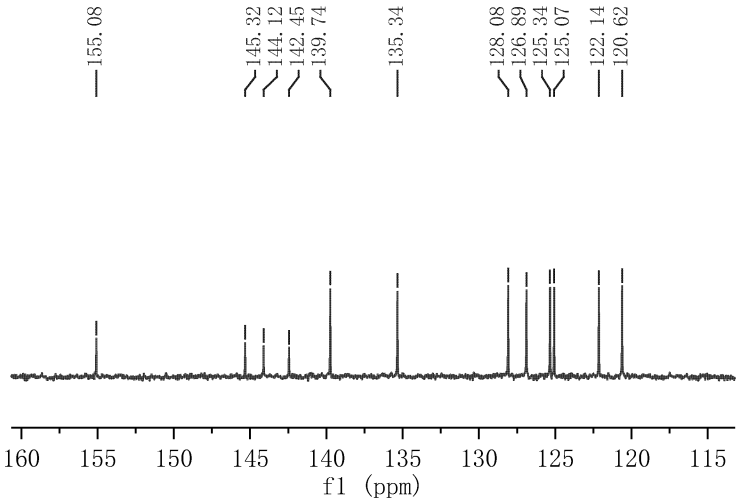


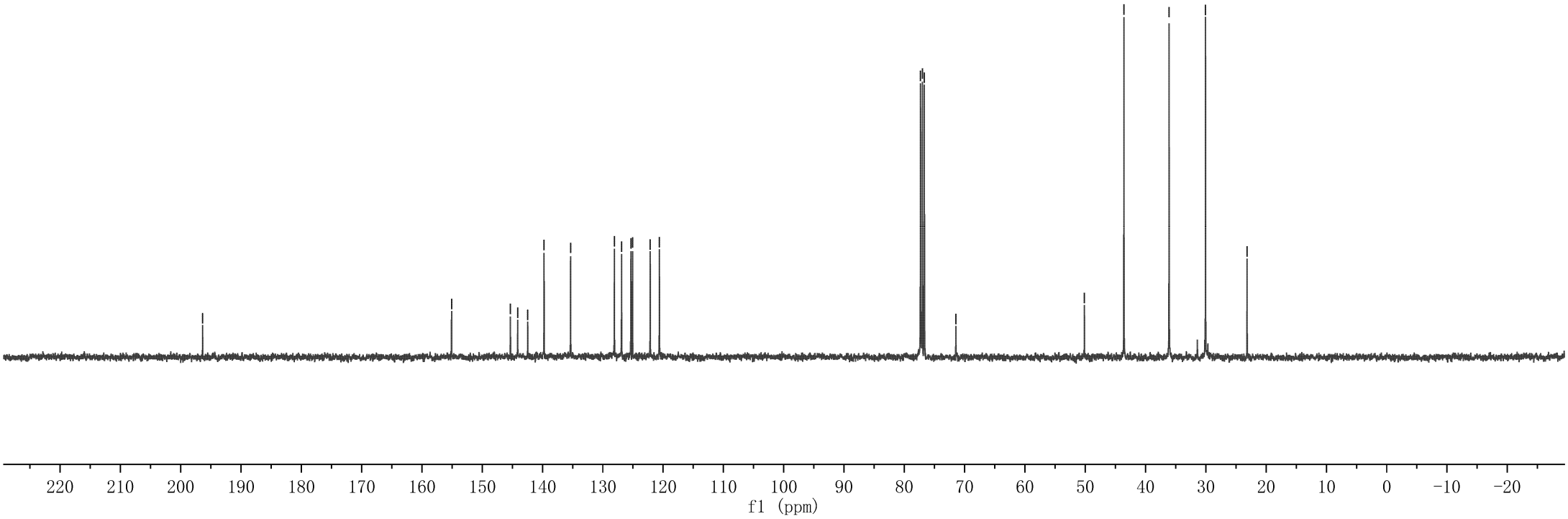
196.36
155.08
145.32
144.12
142.45
139.74
135.34
128.08
126.89
125.34
125.07
122.14
120.62
77.32
77.00
76.68
71.45
50.14
43.58
36.09
30.05
23.16

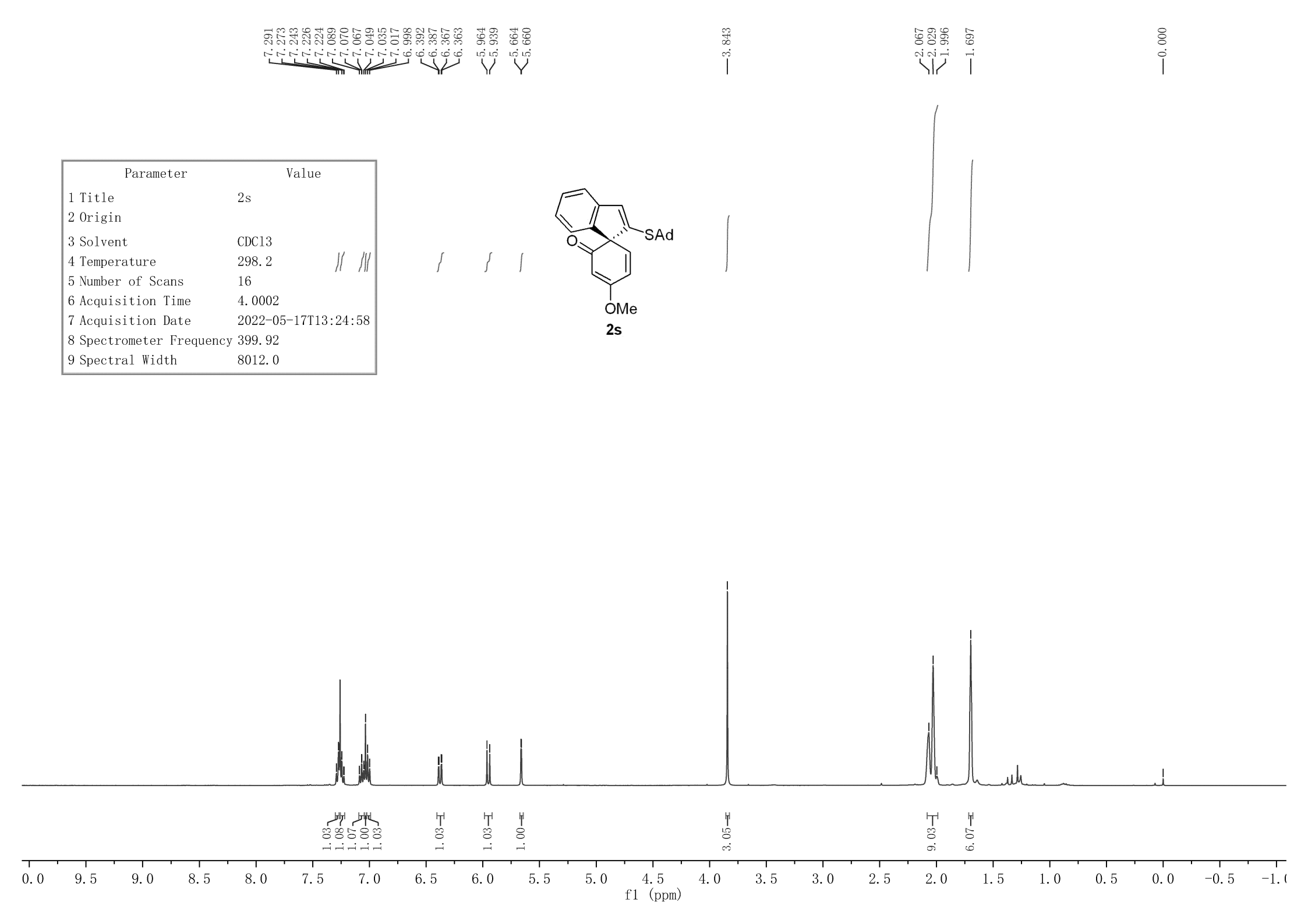
Parameter	Value
1 Title	FXY-2r
2 Origin	
3 Solvent	CDCl3
4 Temperature	300.1
5 Number of Scans	300
6 Acquisition Time	1.0000
7 Acquisition Date	2023-08-09T22:23:38
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0



2r

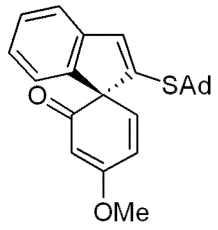





7.291
7.273
7.243
7.226
7.224
7.089
7.070
7.067
7.049
7.035
7.017
6.998
6.392
6.387
6.367
6.363
5.964
5.939
5.664
5.660
3.843
2.067
2.029
1.996
1.697
0.000
Parameter Value
1 Title 2s
2 Origin
3 Solvent CDCl3
4 Temperature 298.2
5 Number of Scans 16
6 Acquisition Time 4.0002
7 Acquisition Date 2022-05-17T13:24:58
8 Spectrometer Frequency 399.92
9 Spectral Width 8012.0
SAd
O
OMe
2s
1.03
1.08
1.07
1.00
1.03
1.03
1.03
1.00
3.05
9.03
6.07
0.0
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
f1 (ppm)

195.18
172.51
145.28
144.27
142.41
141.39
135.48
128.14
125.38
123.15
122.17
120.63
101.62
77.32
77.00
76.68
71.08
55.90
50.12
43.57
36.08
30.04

Parameter	Value
1 Title	2s
2 Origin	
3 Solvent	CDCl3
4 Temperature	298.5
5 Number of Scans	200
6 Acquisition Time	1.0000
7 Acquisition Date	2022-05-17T13:53:46
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

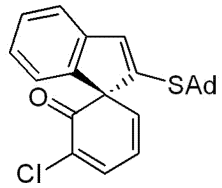


2s

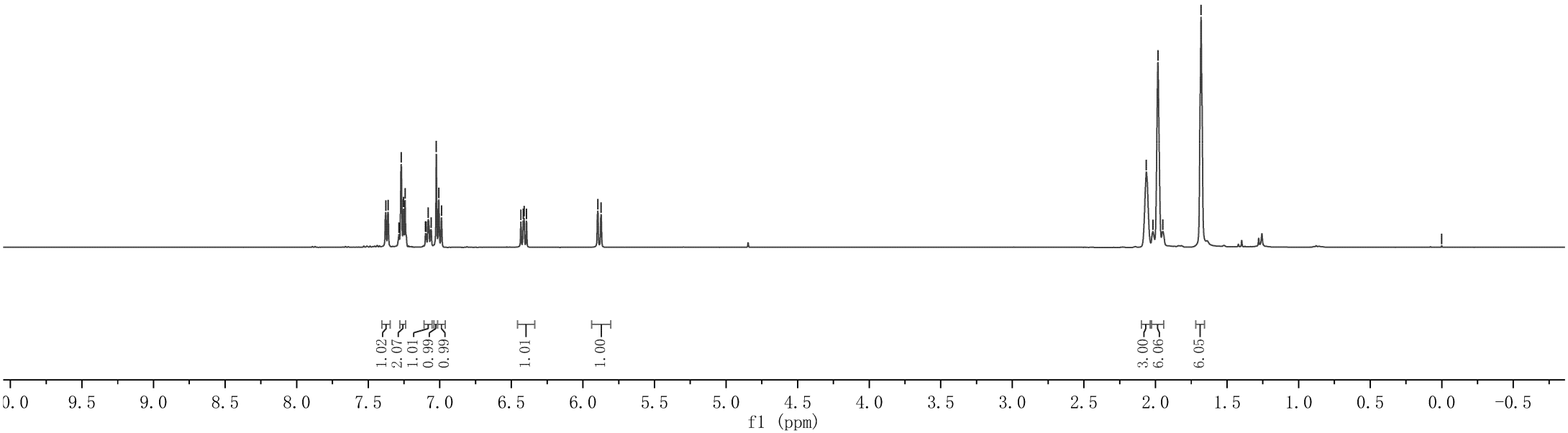
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20

f1 (ppm)

Parameter	Value
1 Title	fxy-13-203
2 Origin	
3 Solvent	CDCl3
4 Temperature	299.8
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2023-08-22T07:50:02
8 Spectrometer Frequency	399.90
9 Spectral Width	8012.0



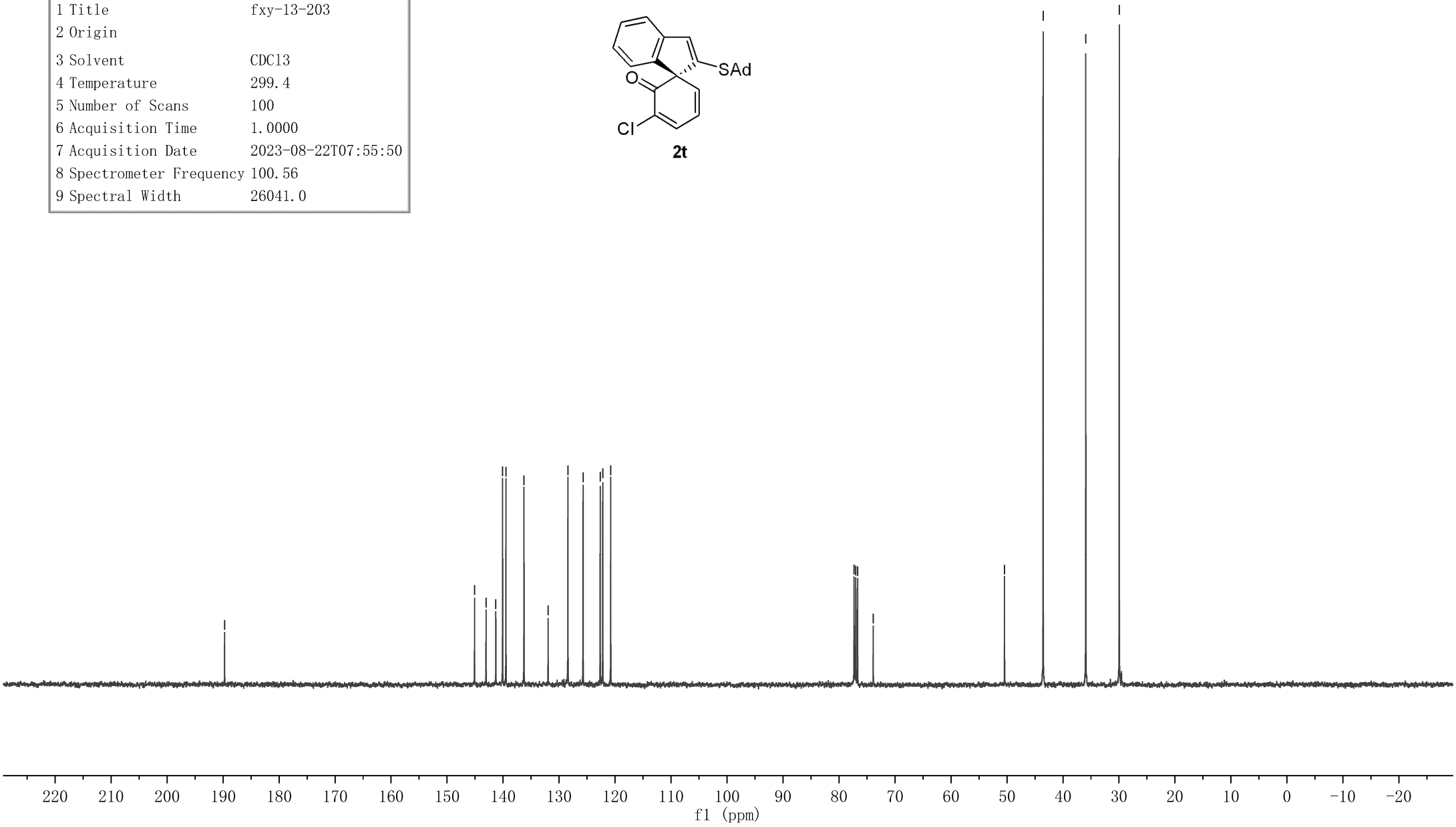
2t



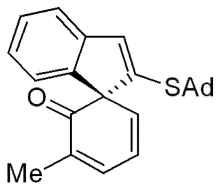
189.73
145.09
143.03
141.29
140.08
139.49
136.26
131.95
128.42
125.71
122.65
122.20
120.78
77.32
77.00
76.68
73.89
50.45
43.55
35.93
29.95

Parameter	Value
1 Title	fxy-13-203
2 Origin	
3 Solvent	CDCl3
4 Temperature	299.4
5 Number of Scans	100
6 Acquisition Time	1.0000
7 Acquisition Date	2023-08-22T07:55:50
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

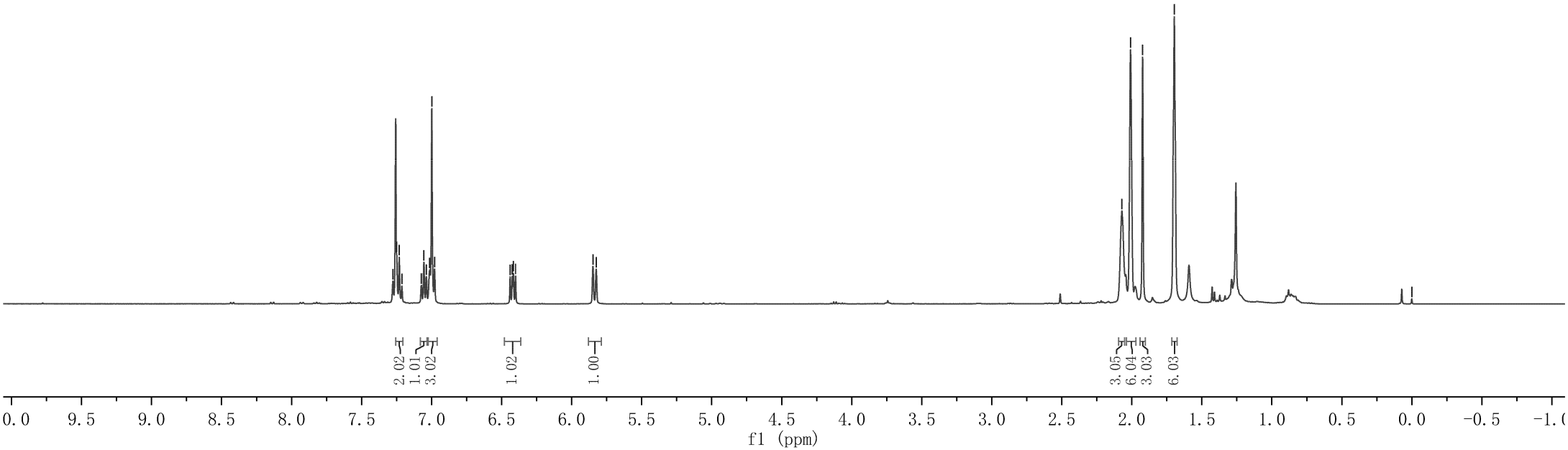
2t



Parameter	Value
1 Title	fxy-2v
2 Origin	
3 Solvent	CDCl3
4 Temperature	300.5
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2023-08-09T22:53:26
8 Spectrometer Frequency	399.90
9 Spectral Width	8012.0

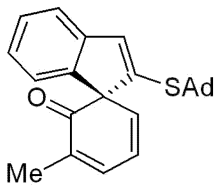


2u

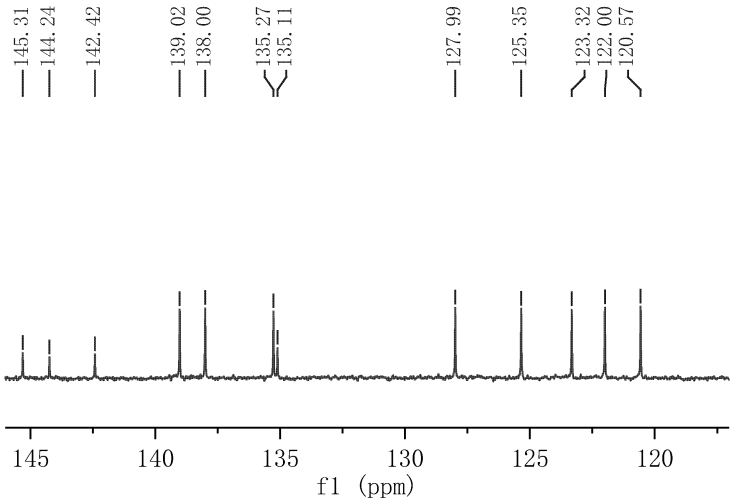


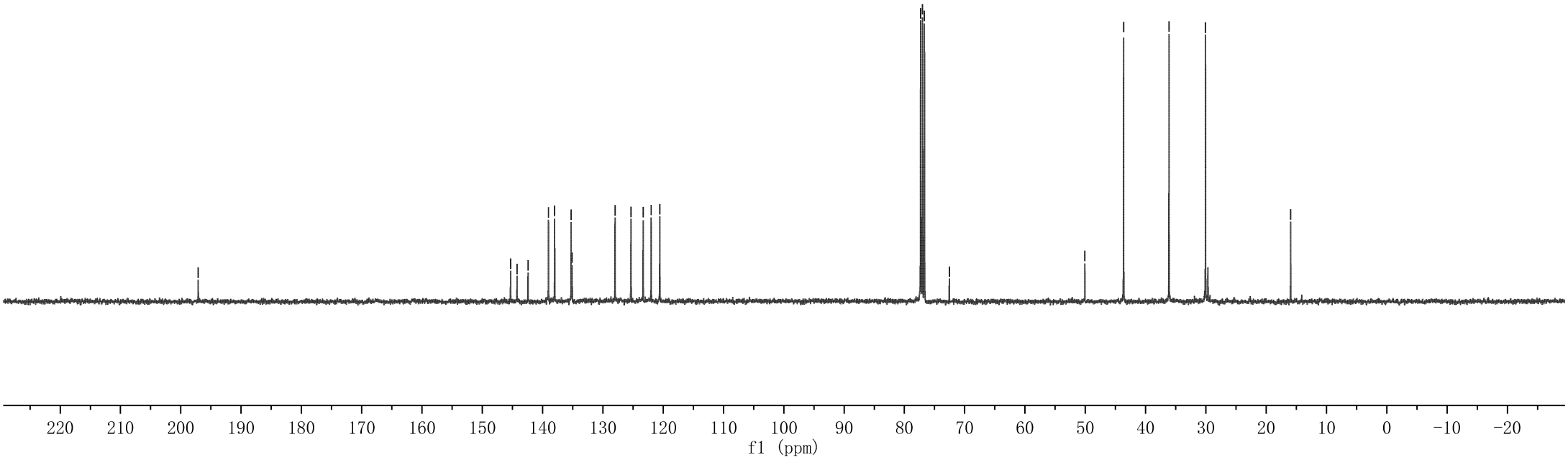
197.11
145.31
144.24
142.42
139.02
138.00
135.27
135.11
127.99
125.35
123.32
122.00
120.57
77.32
77.00
76.68
72.55
50.07
43.65
36.11
30.06
15.95

Parameter	Value
1 Title	fxy-2v
2 Origin	
3 Solvent	CDCl3
4 Temperature	300.3
5 Number of Scans	500
6 Acquisition Time	1.0000
7 Acquisition Date	2023-08-09T23:13:16
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

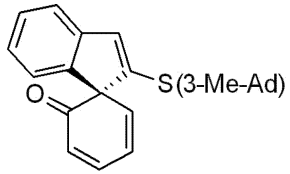


2u

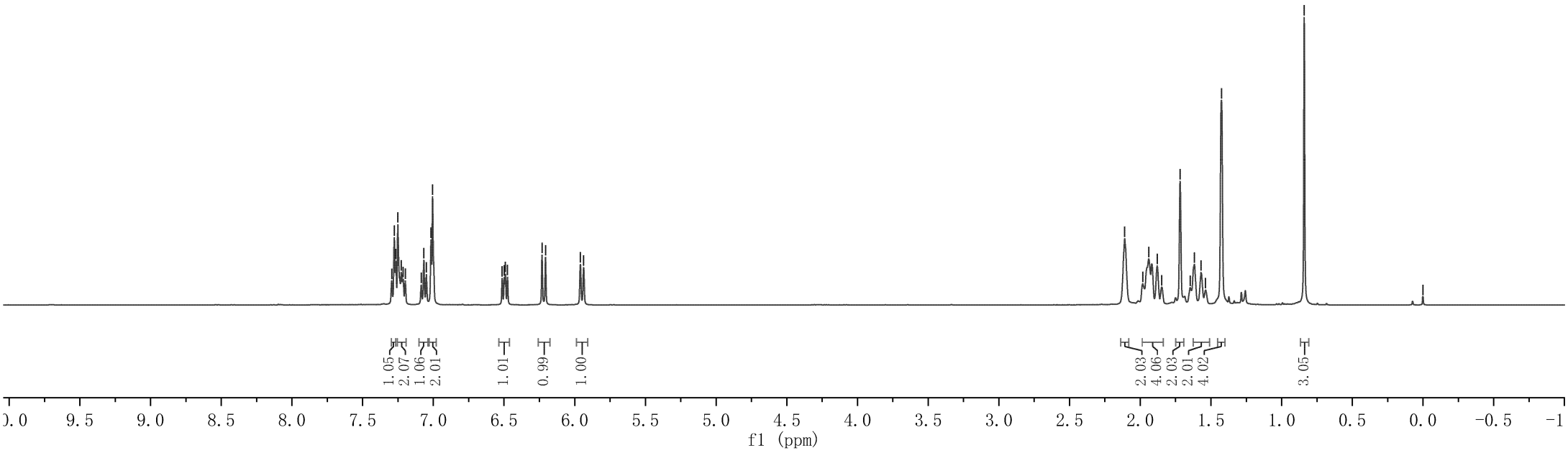




Parameter	Value
1 Title	2ac
2 Origin	
3 Solvent	CDCl3
4 Temperature	299.5
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2023-08-17T00:28:46
8 Spectrometer Frequency	399.90
9 Spectral Width	8012.0

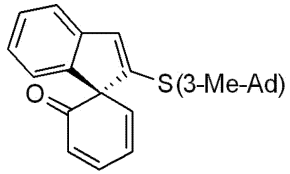


2v

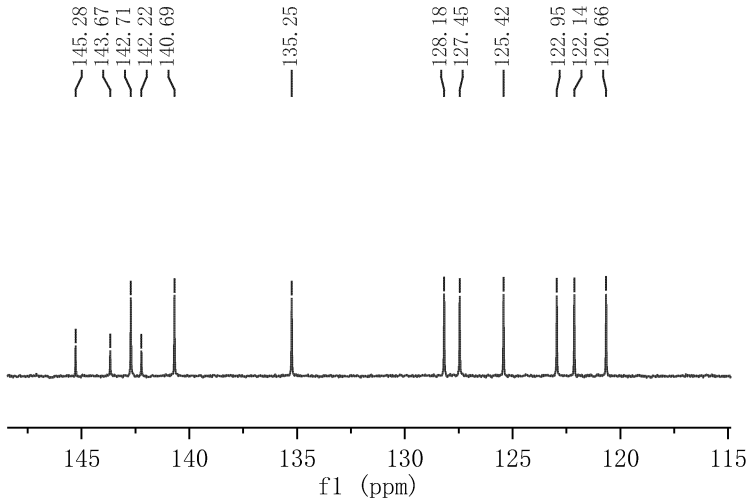


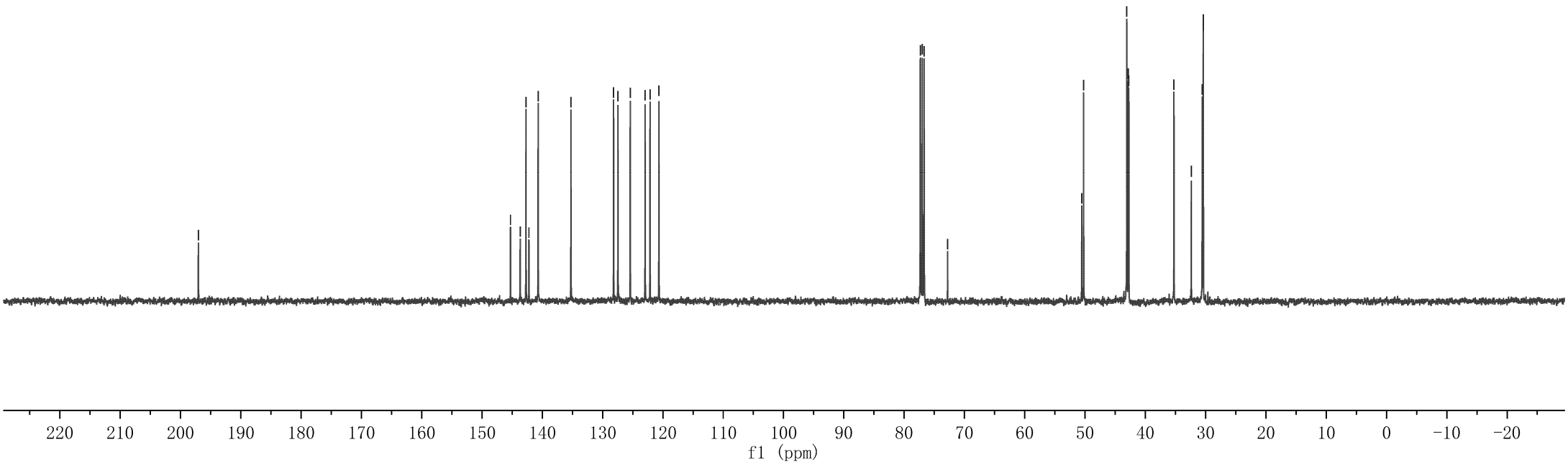
197.04
145.28
143.67
142.71
142.22
140.69
135.25
128.18
127.45
125.42
122.95
122.14
120.66
77.32
77.00
76.68
72.79
50.55
50.23
43.07
42.82
42.73
35.25
32.38
30.56
30.39
30.38

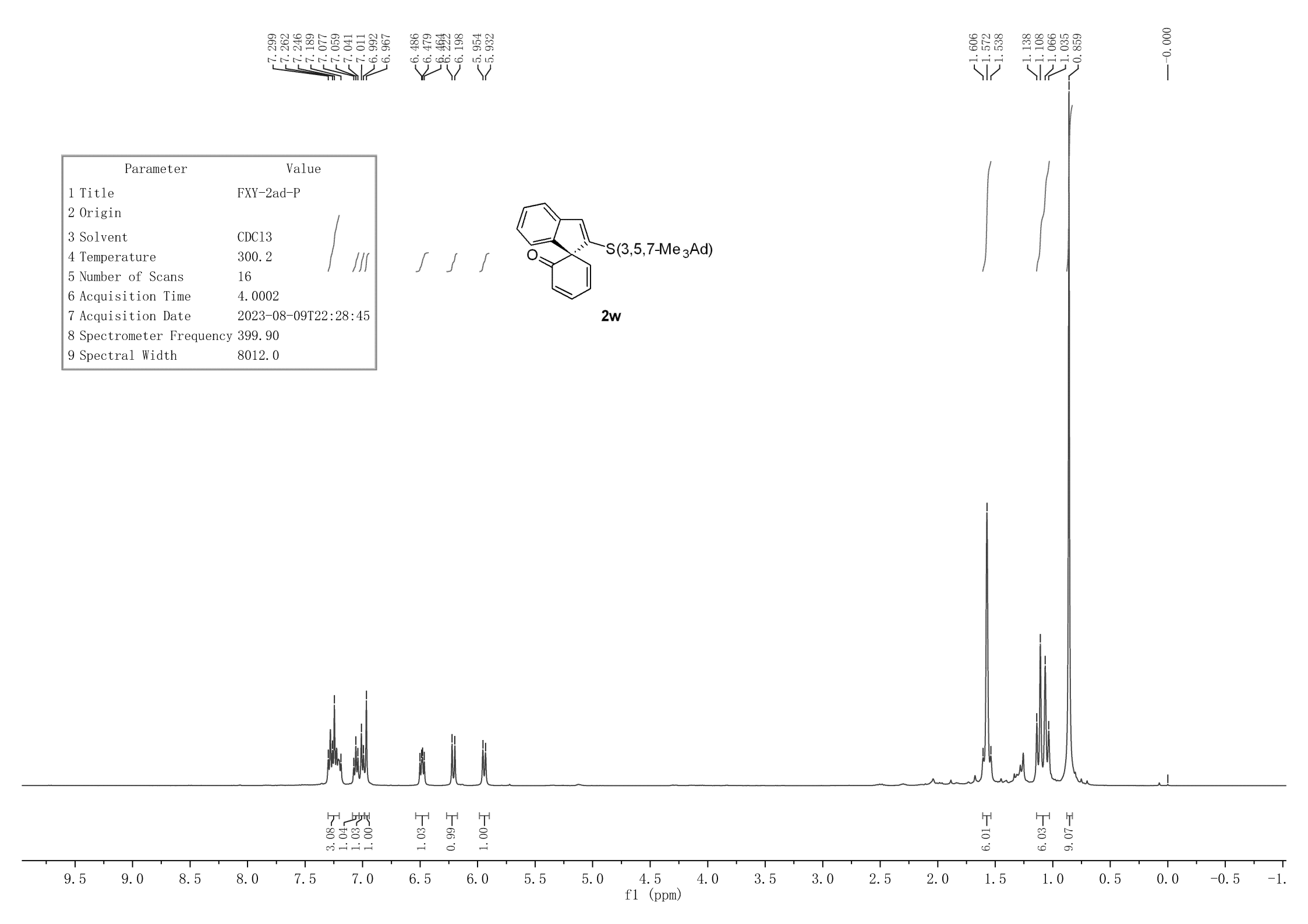
Parameter	Value
1 Title	2ac
2 Origin	
3 Solvent	CDCl3
4 Temperature	299.1
5 Number of Scans	300
6 Acquisition Time	1.0000
7 Acquisition Date	2023-08-17T00:41:16
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0



2v






7.299
7.262
7.246
7.189
7.077
7.059
7.041
7.011
6.992
6.967
6.486
6.479
6.464
6.222
6.198
5.954
5.932
1.606
1.572
1.538
1.138
1.108
1.066
1.035
0.859
0.000
Parameter Value
1 Title FXY-2ad-P
2 Origin
3 Solvent CDCl3
4 Temperature 300.2
5 Number of Scans 16
6 Acquisition Time 4.0002
7 Acquisition Date 2023-08-09T22:28:45
8 Spectrometer Frequency 399.90
9 Spectral Width 8012.0
O
S(3,5,7-Me3Ad)
2w
3.08
1.04
1.03
1.00
1.03
0.99
1.00
6.01
6.03
9.07
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)

196.95

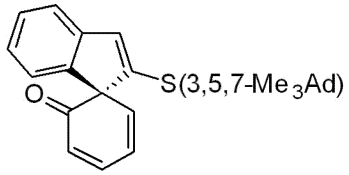
145.26
143.58
142.66
142.41
140.75
134.73
128.17
127.42
125.36
122.89
122.09
120.64

77.32
77.00
76.68
72.72

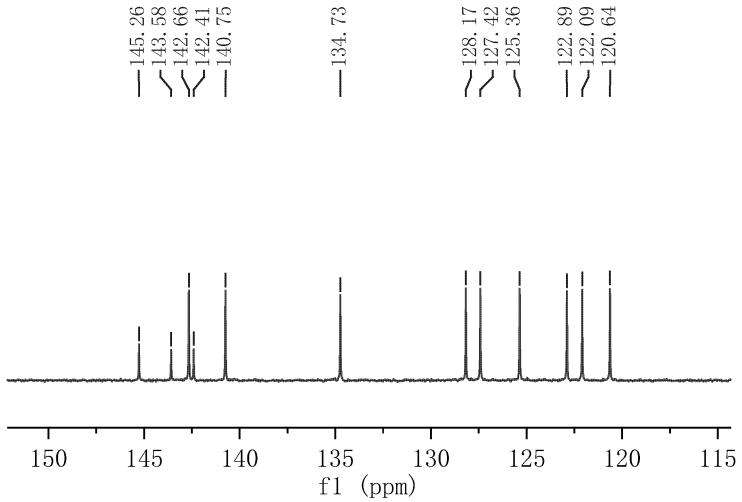
51.23
49.65
48.79

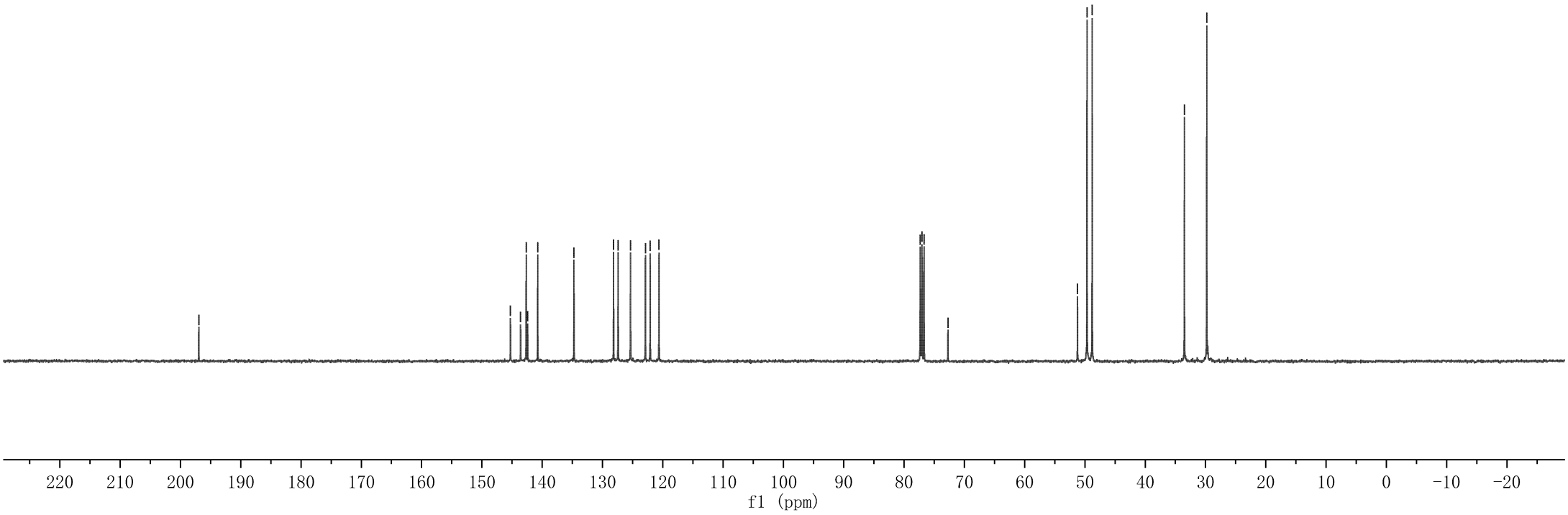
33.50
29.80

Parameter	Value
1 Title	FXY-2ad-P
2 Origin	
3 Solvent	CDCl3
4 Temperature	300.5
5 Number of Scans	500
6 Acquisition Time	1.0000
7 Acquisition Date	2023-08-09T22:47:53
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

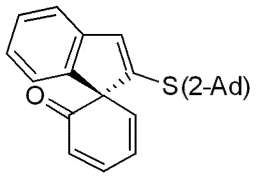


2w

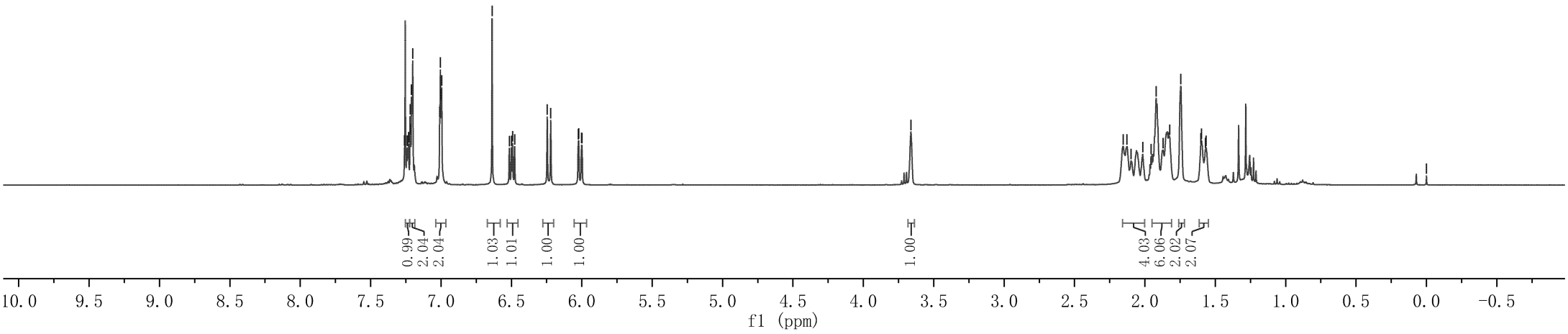




Parameter	Value
1 Title	fxy-8-188
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	6
6 Acquisition Time	4.0894
7 Acquisition Date	2022-06-22T22:44:53
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8



2x



196.71

147.23
145.23
143.08
142.63
141.28

128.20
127.25
127.16
124.54
122.59
121.79
119.91

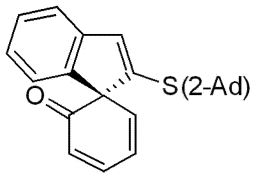
77.32
77.00
76.68

71.52

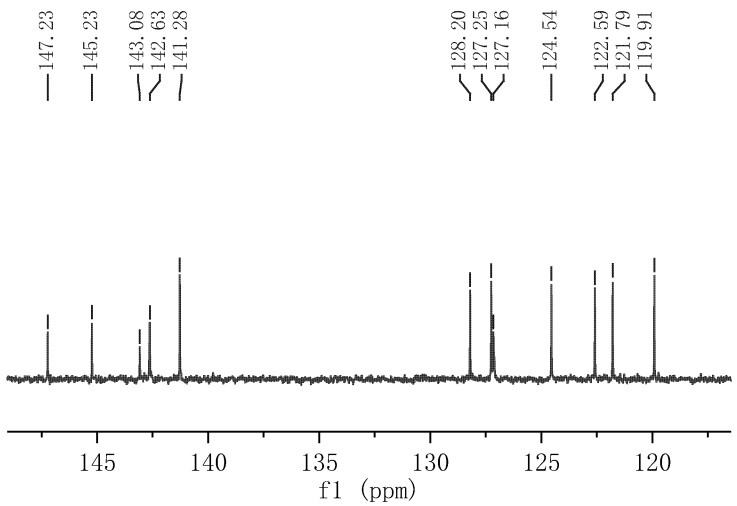
54.13

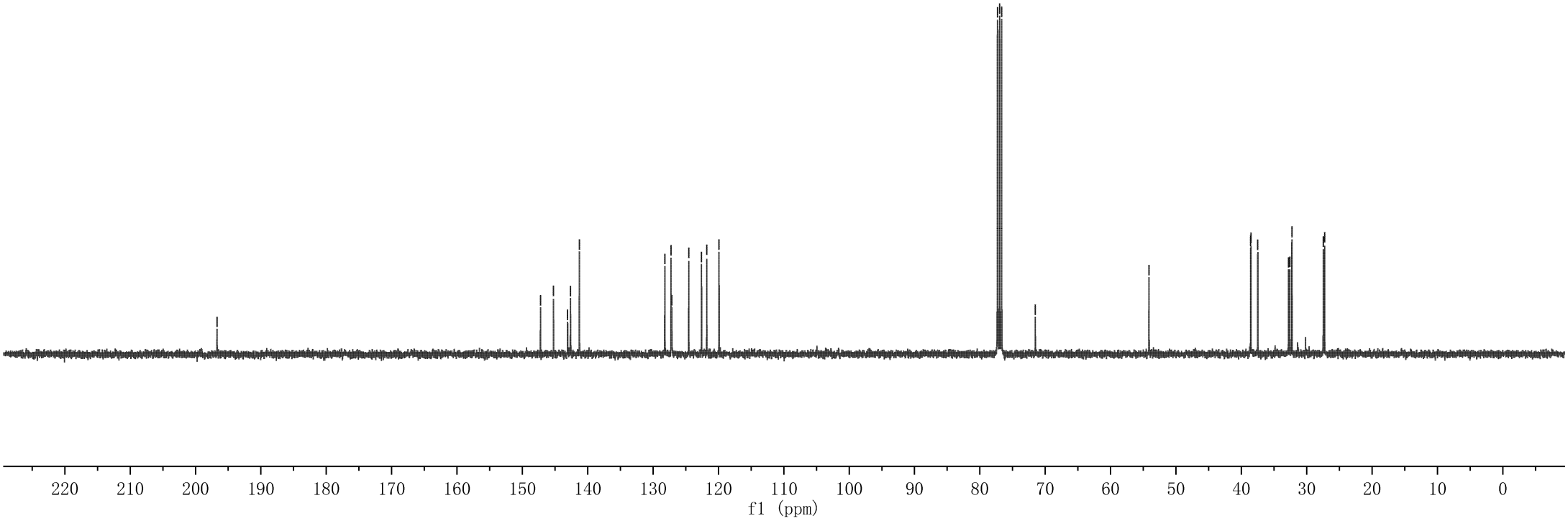
38.58
38.53
37.48
32.77
32.57
32.27
32.24
27.46
27.25

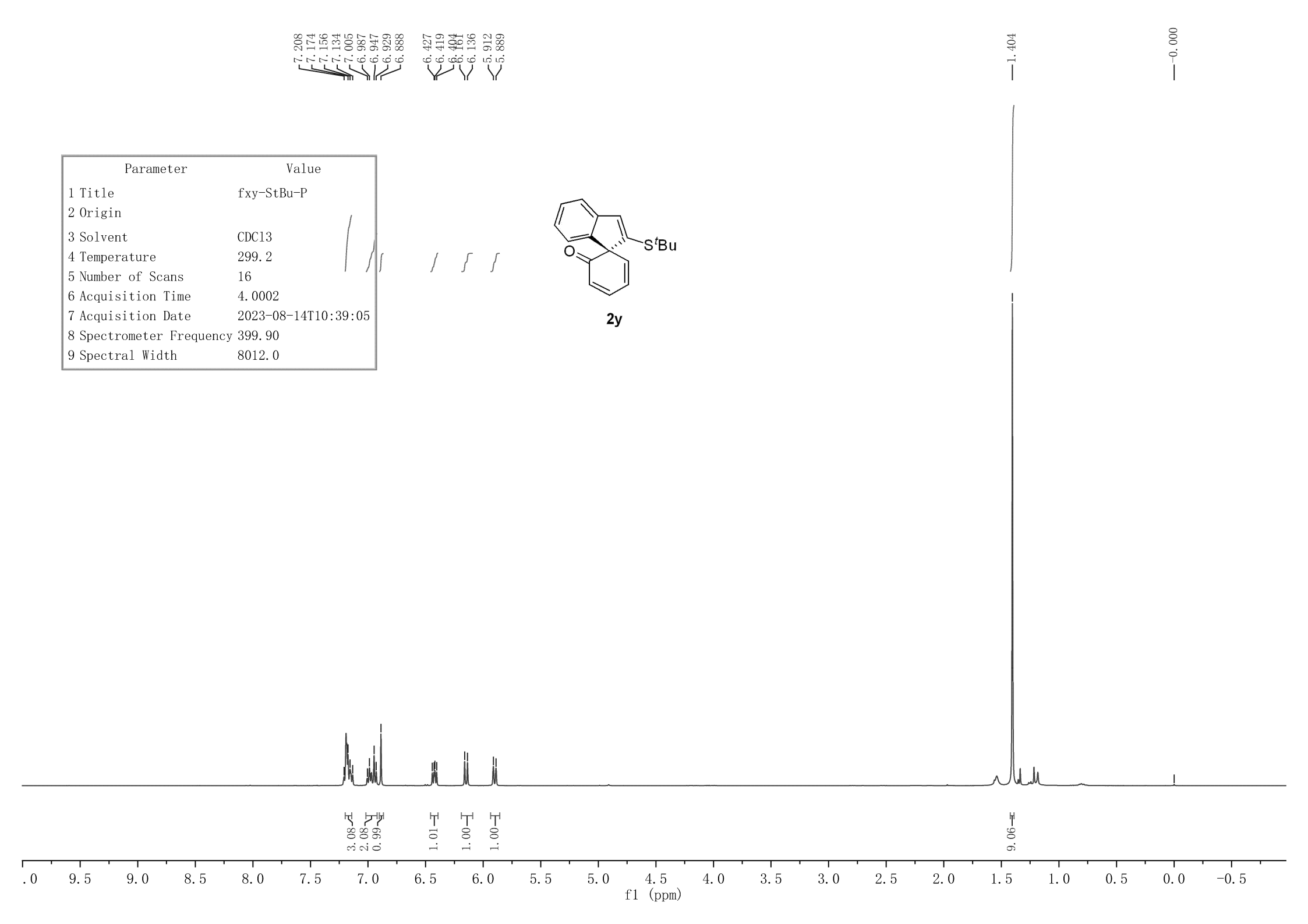
Parameter	Value
1 Title	fxy-8-188-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	113
6 Acquisition Time	1.3631
7 Acquisition Date	2022-06-22T22:45:52
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5



2x

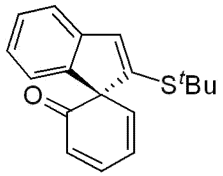




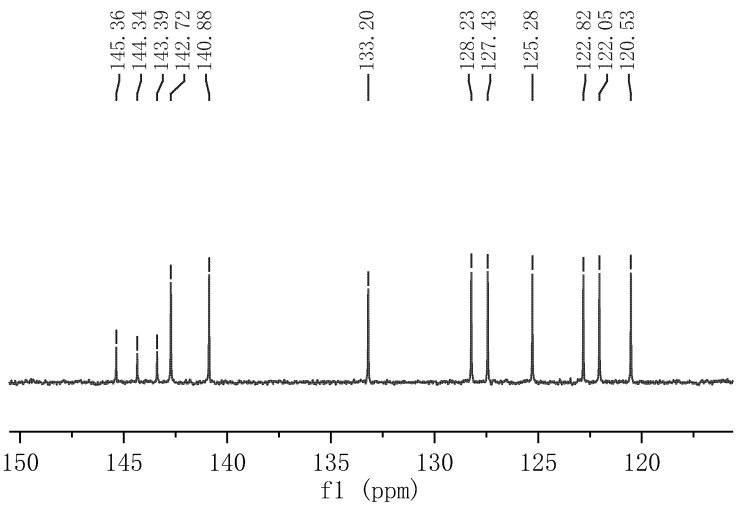

7.208
7.174
7.156
7.134
7.005
6.987
6.947
6.929
6.888
6.427
6.419
6.404
6.161
6.136
5.912
5.889
1.404
-0.000
Parameter Value
1 Title fxy-StBu-P
2 Origin
3 Solvent CDCl3
4 Temperature 299.2
5 Number of Scans 16
6 Acquisition Time 4.0002
7 Acquisition Date 2023-08-14T10:39:05
8 Spectrometer Frequency 399.90
9 Spectral Width 8012.0
O
S^{t}Bu
2y
3.08
2.08
0.99
1.01
1.00
1.00
9.06
f1 (ppm)

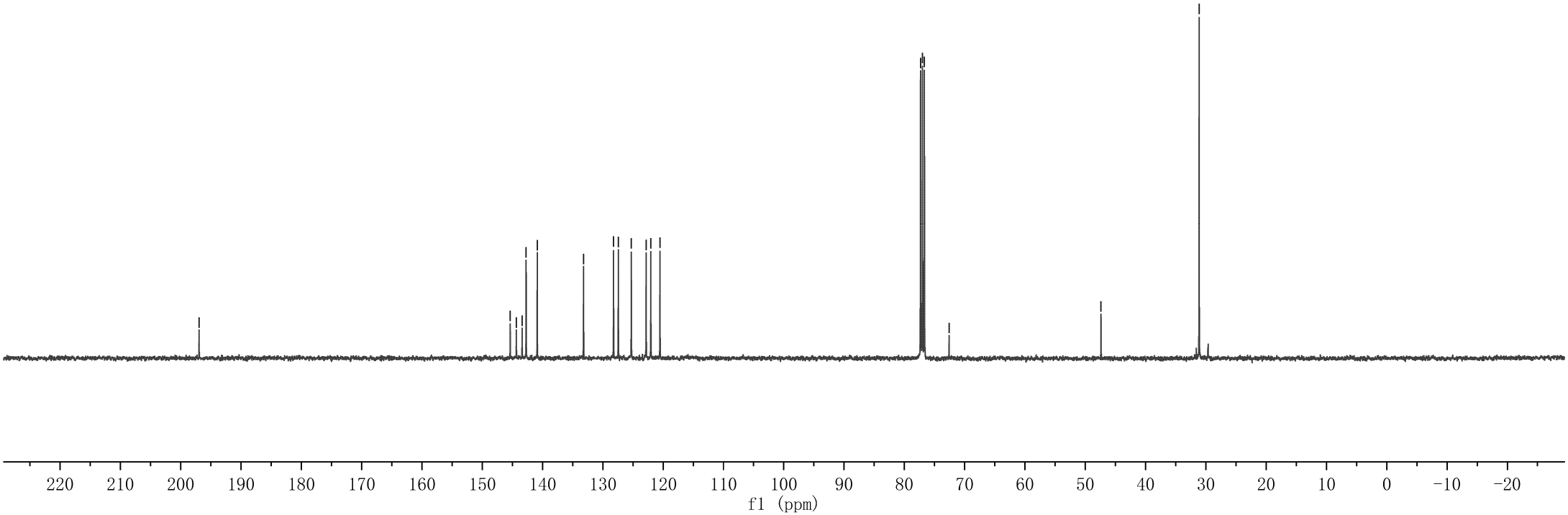
196.96
145.36
144.34
143.39
142.72
140.88
133.20
128.23
127.43
125.28
122.82
122.05
120.53
77.32
77.00
76.68
72.58
47.39
31.11

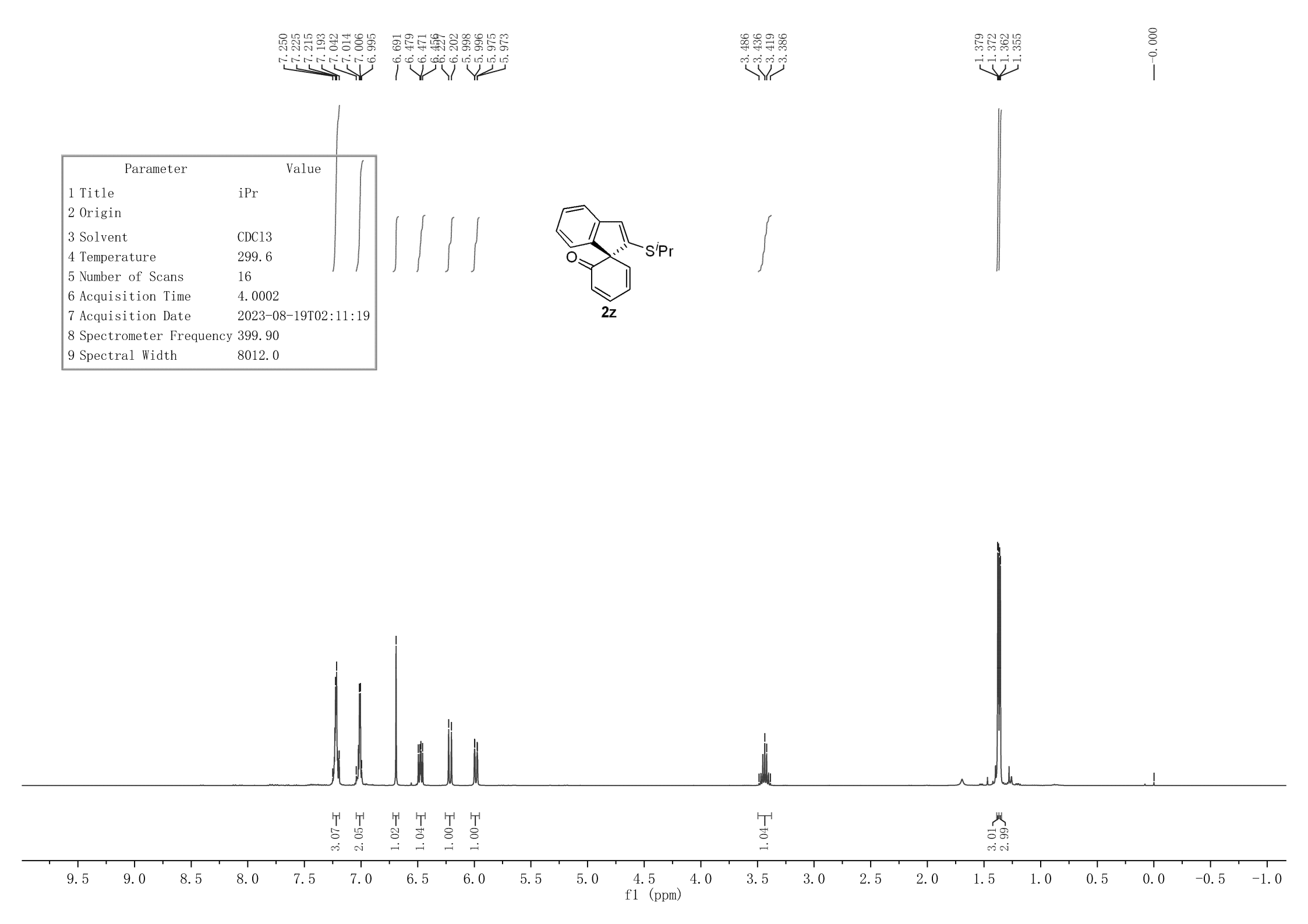
Parameter	Value
1 Title	fxy-StBu-P
2 Origin	
3 Solvent	CDCl3
4 Temperature	298.8
5 Number of Scans	200
6 Acquisition Time	1.0000
7 Acquisition Date	2023-08-14T11:05:16
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0



2y

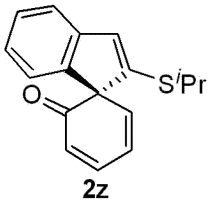




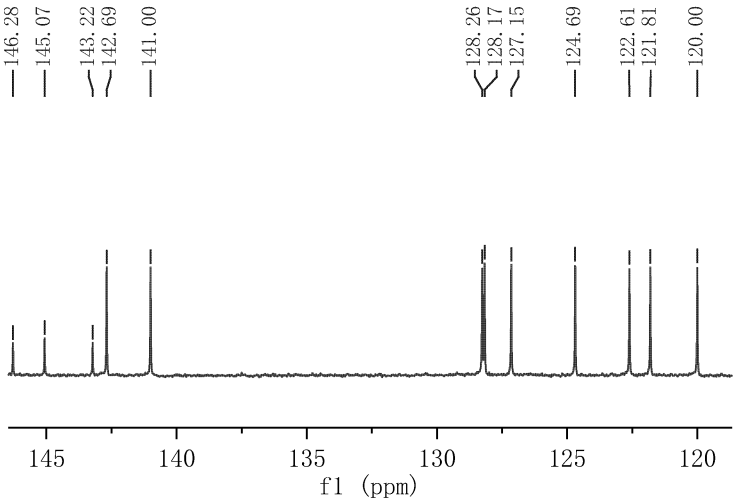

7.250
7.225
7.215
7.193
7.042
7.014
7.006
6.995
6.691
6.479
6.471
6.456
6.227
6.202
5.998
5.996
5.975
5.973
3.486
3.436
3.419
3.386
1.379
1.372
1.362
1.355
-0.000
Parameter Value
1 Title iPr
2 Origin
3 Solvent CDCl3
4 Temperature 299.6
5 Number of Scans 16
6 Acquisition Time 4.0002
7 Acquisition Date 2023-08-19T02:11:19
8 Spectrometer Frequency 399.90
9 Spectral Width 8012.0
O
S^{i}Pr
2z
3.07
2.05
1.02
1.04
1.00
1.00
1.04
3.01
2.99
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)

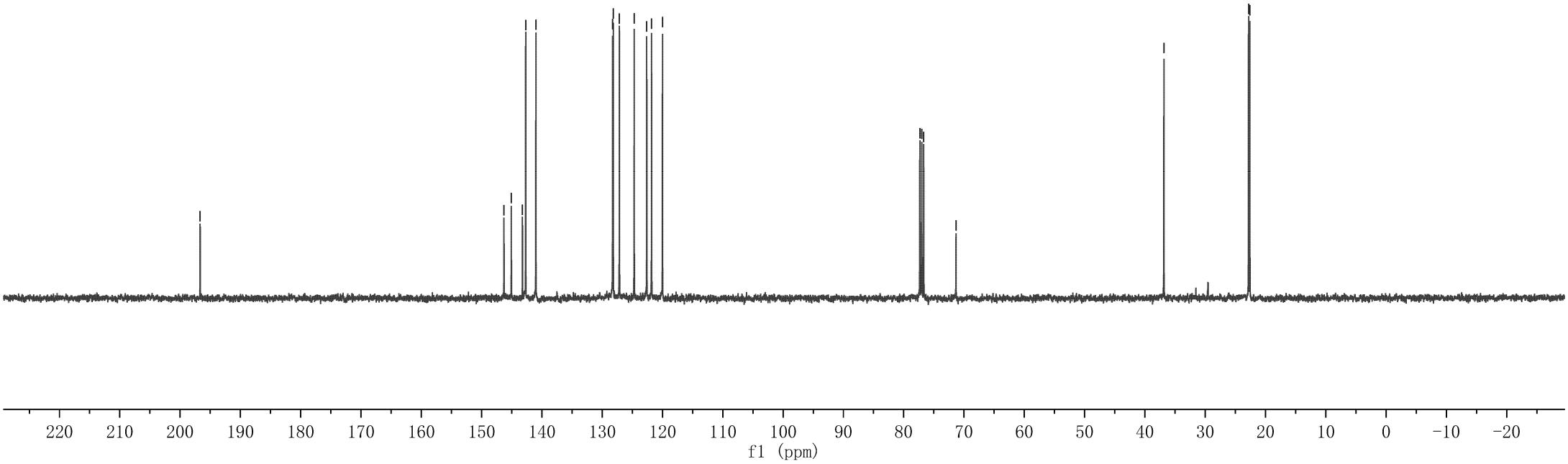
196.67
146.28
145.07
143.22
142.69
141.00
128.26
128.17
127.15
124.69
122.61
121.81
120.00
77.32
77.00
76.68
71.33
36.85
22.80
22.60

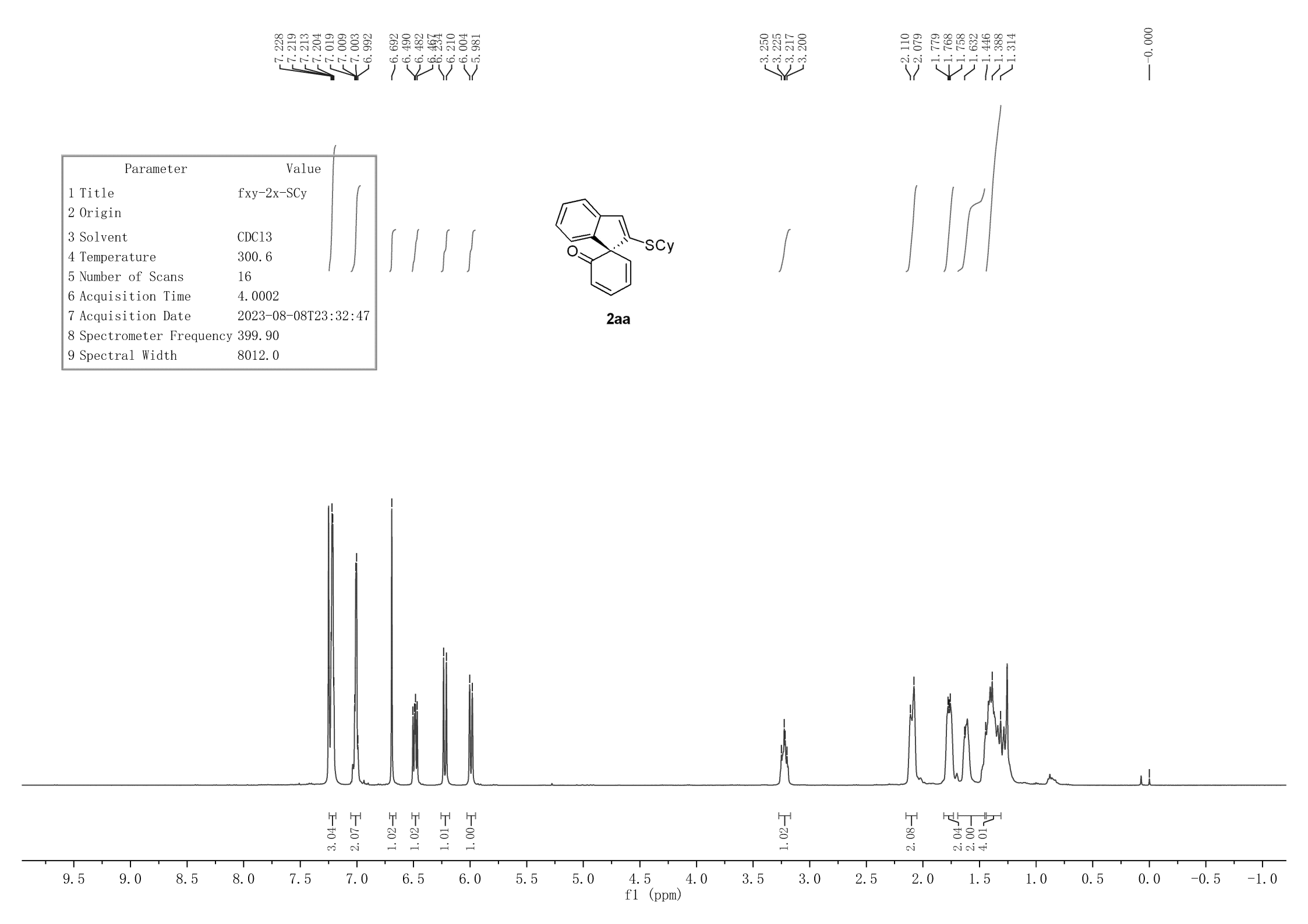
Parameter	Value
1 Title	iPr
2 Origin	
3 Solvent	CDCl3
4 Temperature	299.5
5 Number of Scans	100
6 Acquisition Time	1.0000
7 Acquisition Date	2023-08-19T02:17:11
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0



2z

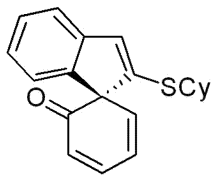




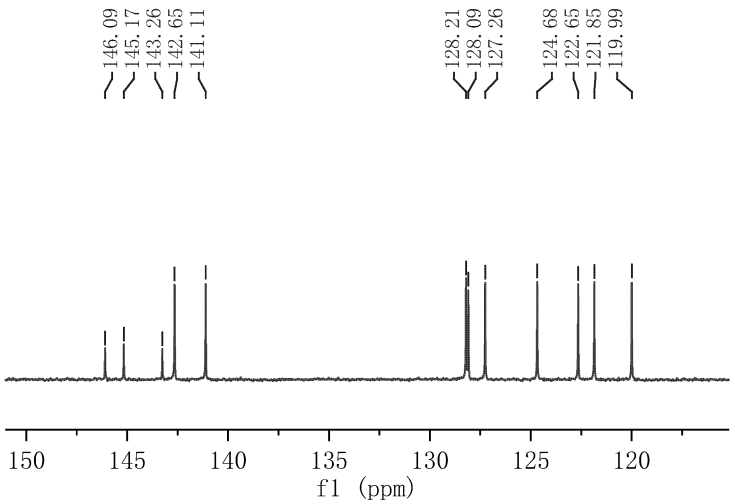

7.228
7.219
7.213
7.204
7.019
7.009
7.003
6.992
6.692
6.490
6.482
6.467
6.234
6.210
6.004
5.981
3.250
3.225
3.217
3.200
2.110
2.079
1.779
1.768
1.758
1.632
1.446
1.388
1.314
-0.000
Parameter Value
1 Title fxy-2x-SCy
2 Origin
3 Solvent CDCl3
4 Temperature 300.6
5 Number of Scans 16
6 Acquisition Time 4.0002
7 Acquisition Date 2023-08-08T23:32:47
8 Spectrometer Frequency 399.90
9 Spectral Width 8012.0
SCy
O
2aa
3.04
2.07
1.02
1.02
1.01
1.00
1.02
2.08
2.04
2.00
4.01
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)

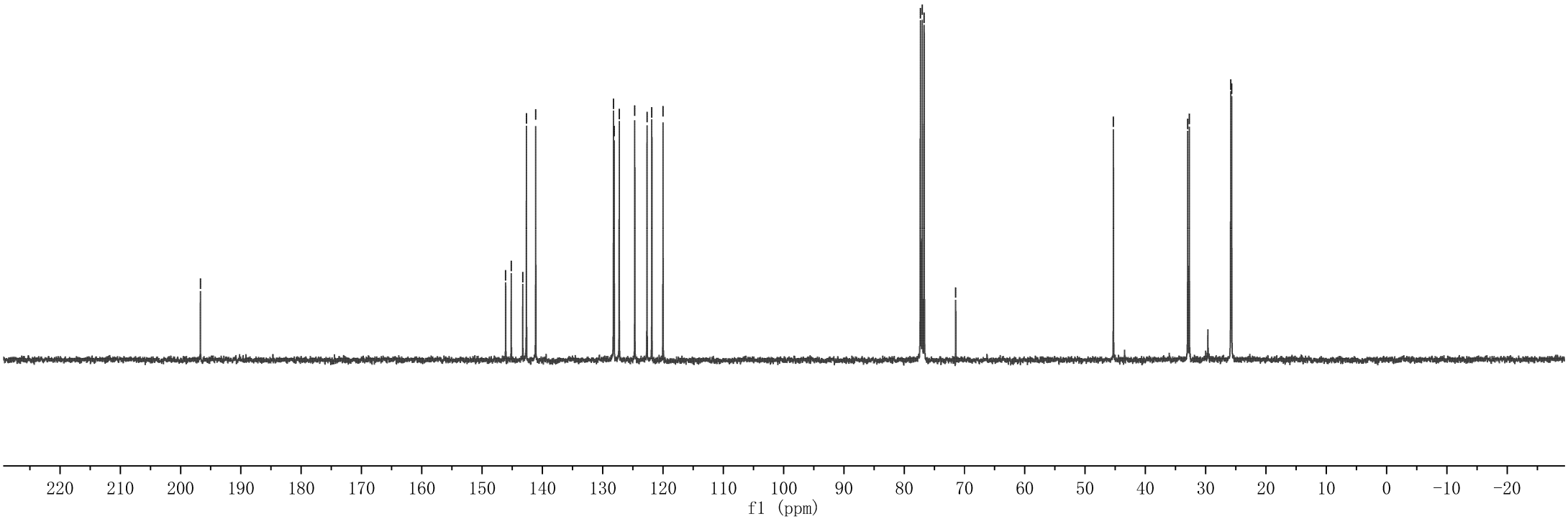
196.71
146.09
145.17
143.26
142.65
141.11
128.21
128.09
127.26
124.68
122.65
121.85
119.99
77.32
77.00
76.68
71.46
45.30
32.99
32.72
25.84
25.69

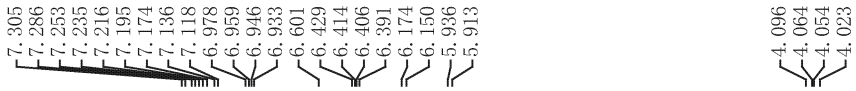
Parameter	Value
1 Title	fxy-2x-SCy
2 Origin	
3 Solvent	CDCl3
4 Temperature	300.8
5 Number of Scans	200
6 Acquisition Time	1.0000
7 Acquisition Date	2023-08-08T23:51:58
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0



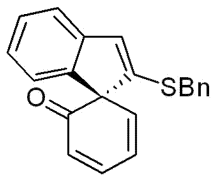
2aa



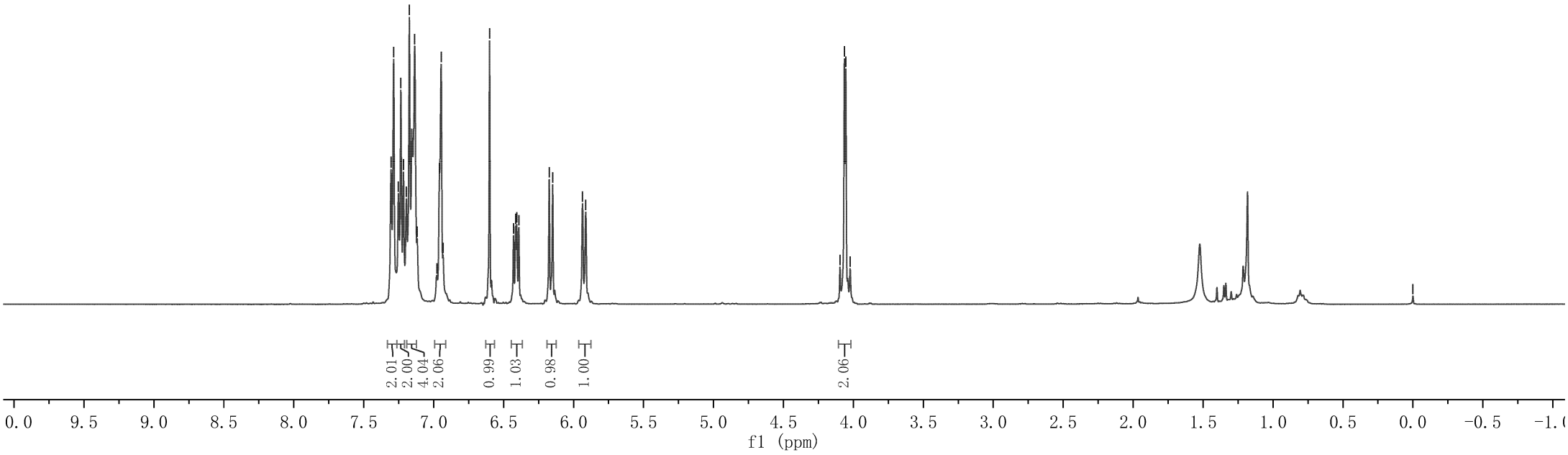




Parameter	Value
1 Title	fxy-SBn-P
2 Origin	
3 Solvent	CDCl3
4 Temperature	299.0
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2023-08-14T11:10:41
8 Spectrometer Frequency	399.90
9 Spectral Width	8012.0

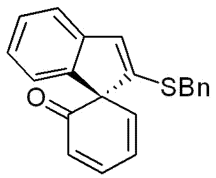


2ab

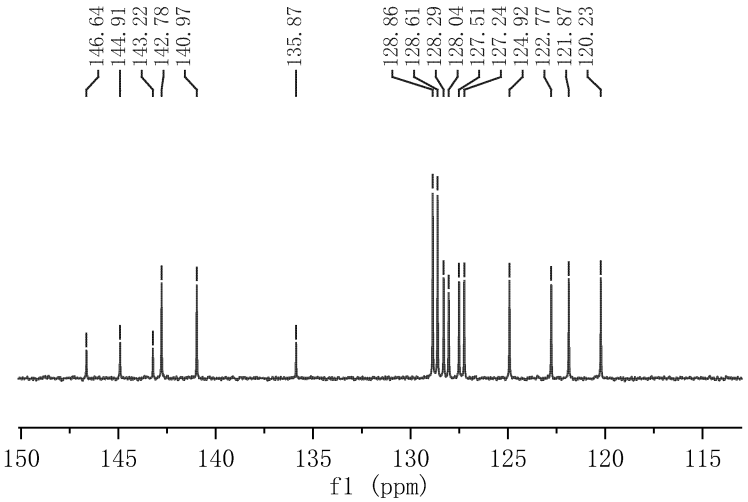


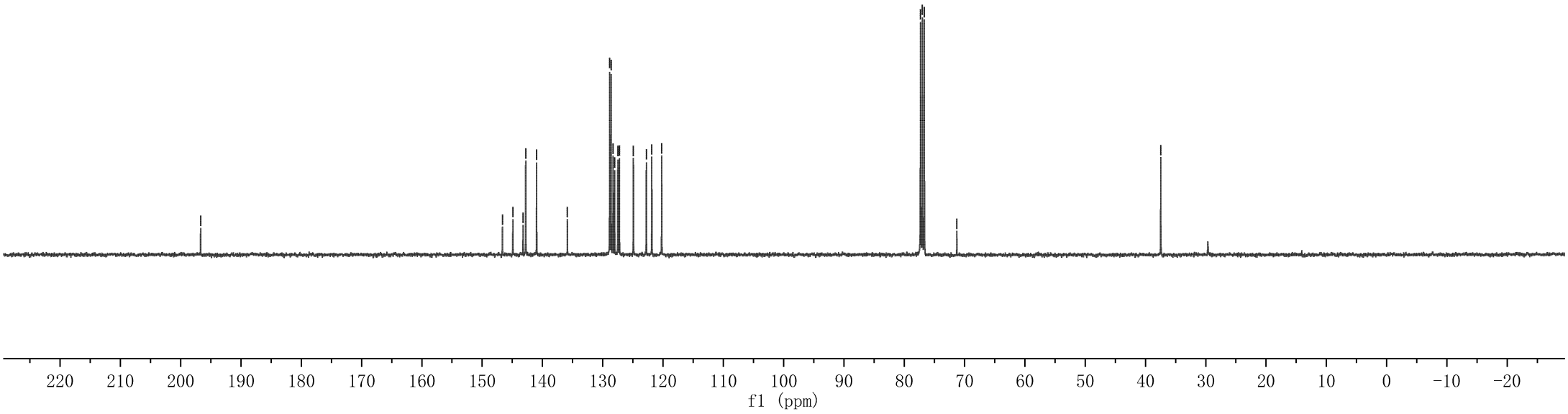
196.69
146.64
144.91
143.22
142.78
140.97
135.87
128.86
128.61
128.29
128.04
127.51
127.24
124.92
122.77
121.87
120.23
77.32
77.00
76.68
71.28
37.47

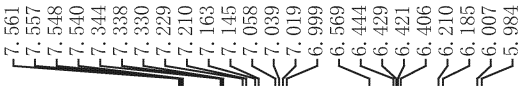
Parameter	Value
1 Title	fxy-SBn-P
2 Origin	
3 Solvent	CDCl3
4 Temperature	299.0
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2023-08-14T11:10:41
8 Spectrometer Frequency	399.90
9 Spectral Width	8012.0



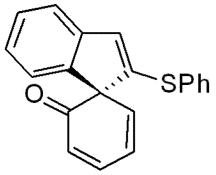
2ab



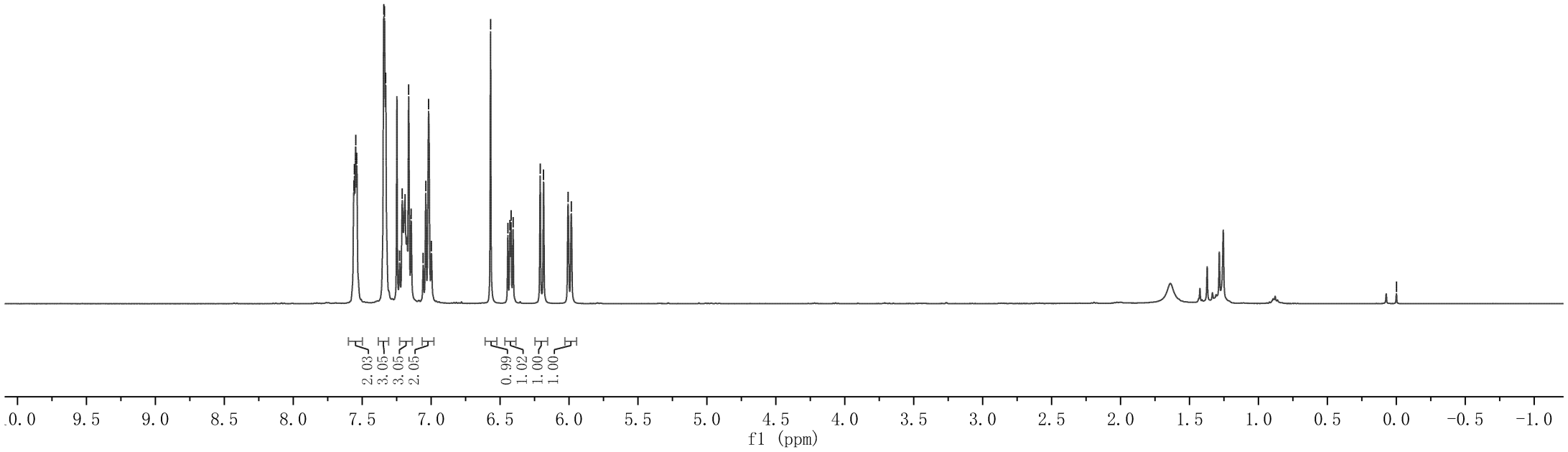




Parameter	Value
1 Title	fxy-2aa-SPh
2 Origin	
3 Solvent	CDCl3
4 Temperature	300.8
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2023-08-08T23:57:18
8 Spectrometer Frequency	399.90
9 Spectral Width	8012.0

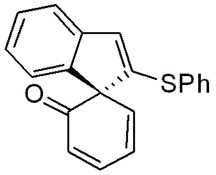


2ac

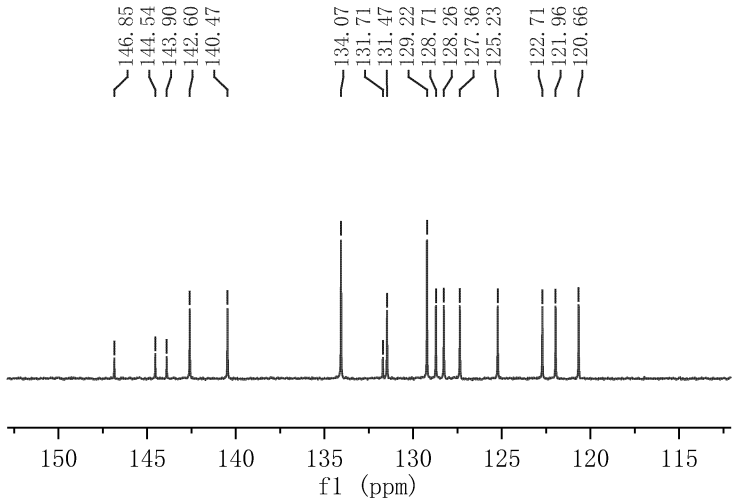


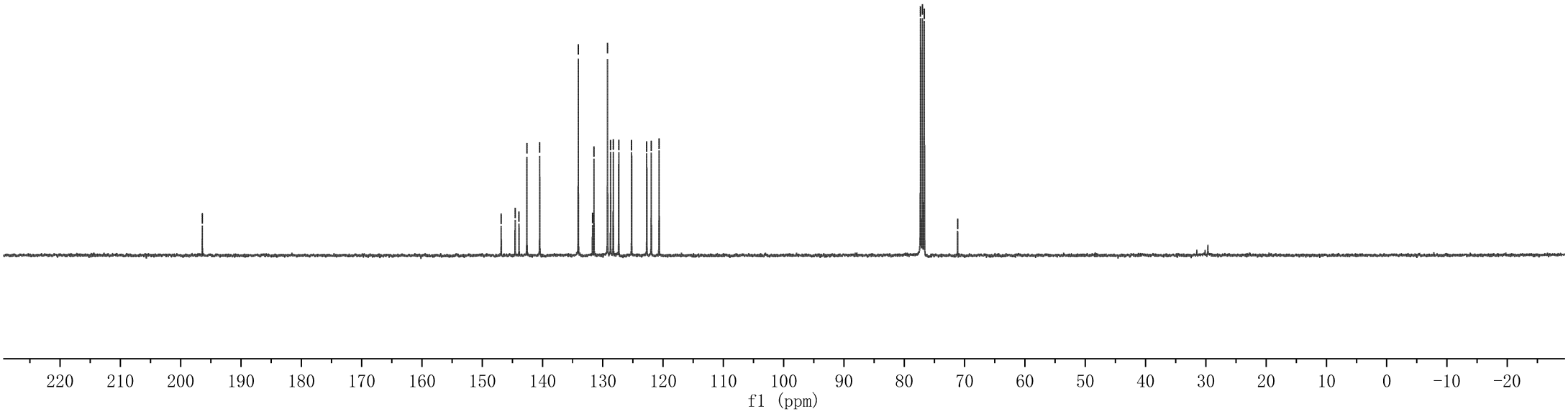
196.42
146.85
144.54
143.90
142.60
140.47
134.07
131.71
131.47
129.22
128.71
128.26
127.36
125.23
122.71
121.96
120.66
77.32
77.00
76.68
71.16

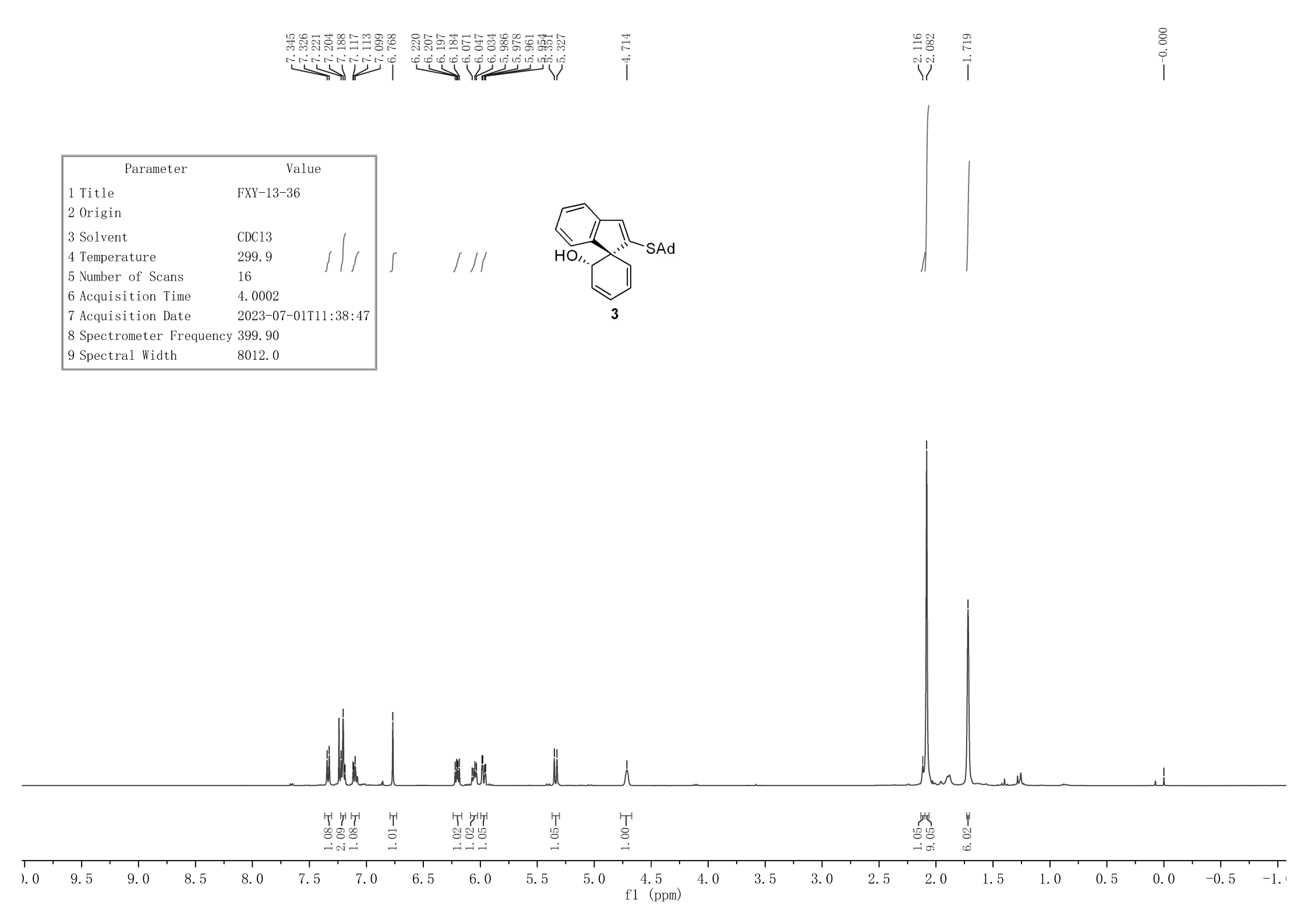
Parameter	Value
1 Title	fxy-2aa-SPh
2 Origin	
3 Solvent	CDCl3
4 Temperature	300.8
5 Number of Scans	1024
6 Acquisition Time	1.0000
7 Acquisition Date	2023-08-09T00:34:04
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0



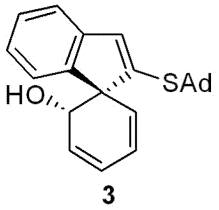
2ac





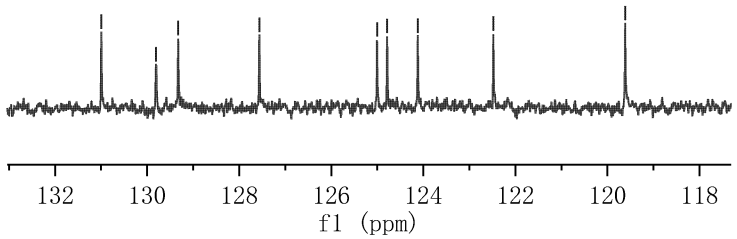

7.345
7.326
7.221
7.204
7.188
7.117
7.113
7.099
6.768
6.220
6.207
6.197
6.184
6.071
6.047
6.034
5.986
5.978
5.961
5.954
5.351
5.327
4.714
2.116
2.082
1.719
-0.000
Parameter Value
1 Title FXY-13-36
2 Origin
3 Solvent CDCl3
4 Temperature 299.9
5 Number of Scans 16
6 Acquisition Time 4.0002
7 Acquisition Date 2023-07-01T11:38:47
8 Spectrometer Frequency 399.90
9 Spectral Width 8012.0
HO
SAd
3
1.08
2.09
1.08
1.01
1.02
1.02
1.05
1.05
1.00
1.05
9.05
6.02
f1 (ppm)

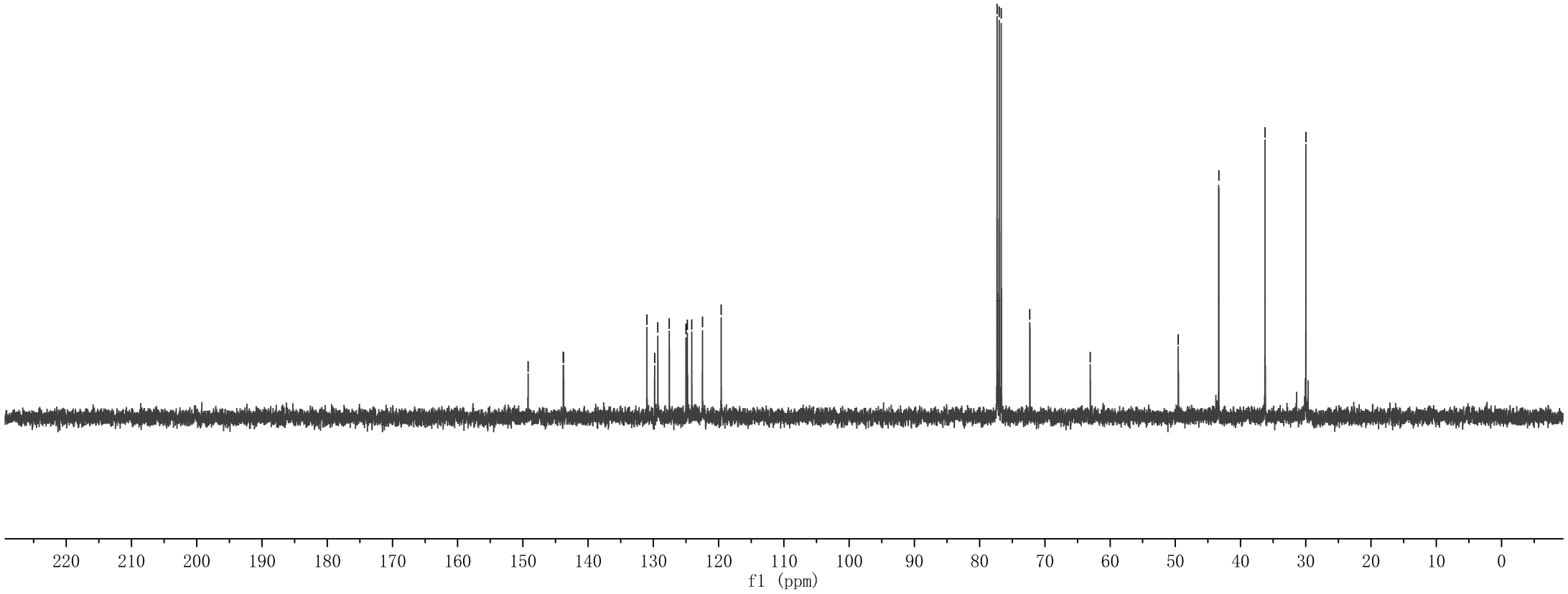
Parameter	Value
1 Title	fxy-13-28-c
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	28
6 Acquisition Time	1.3631
7 Acquisition Date	2023-06-29T17:08:48
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5

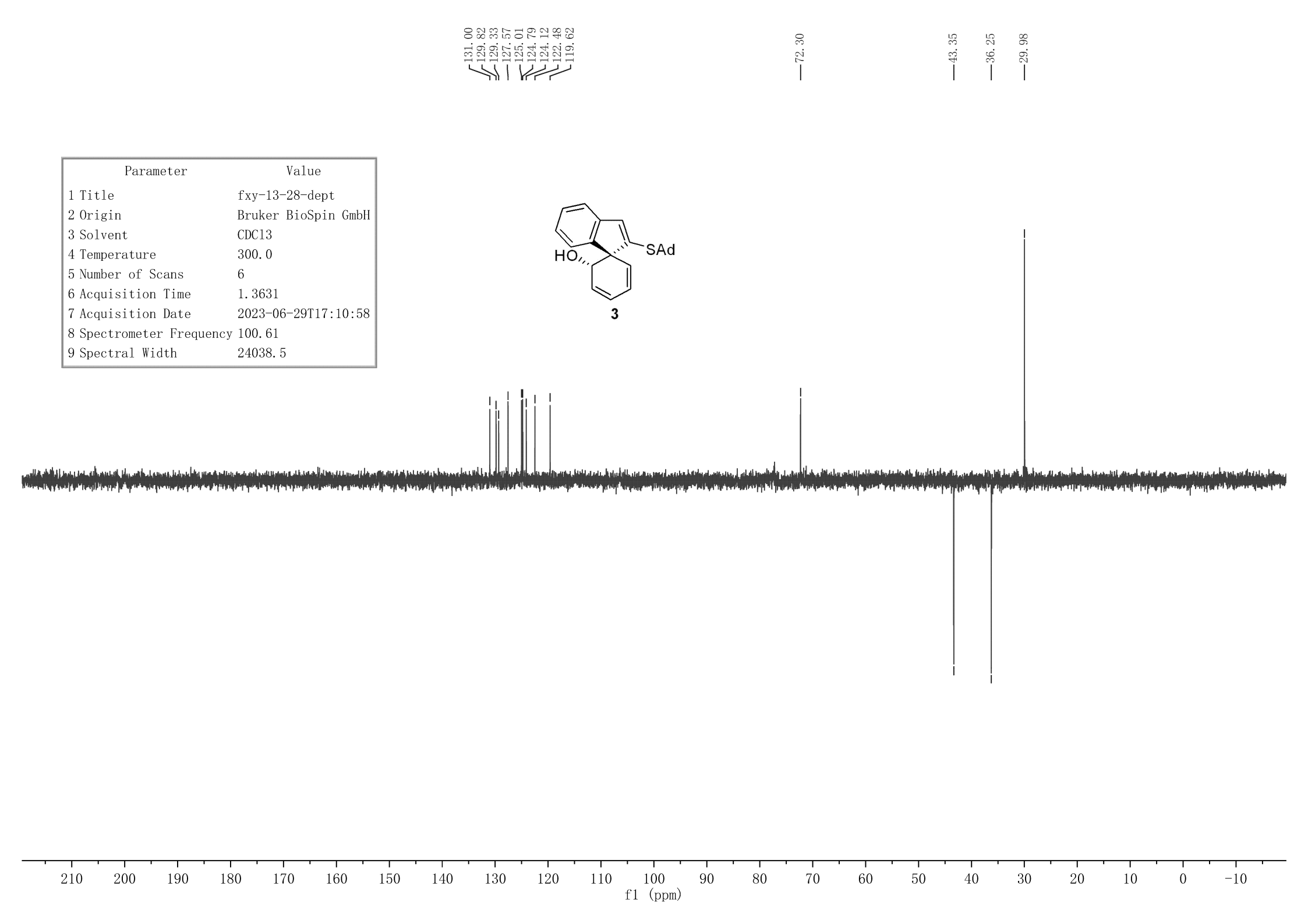


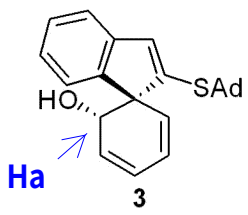
3

149.21
143.80
143.77
131.00
129.81
129.33
127.56
125.01
124.79
124.12
122.48
119.62
77.32
77.00
76.68
72.30
63.04
49.55
43.34
36.24
29.98

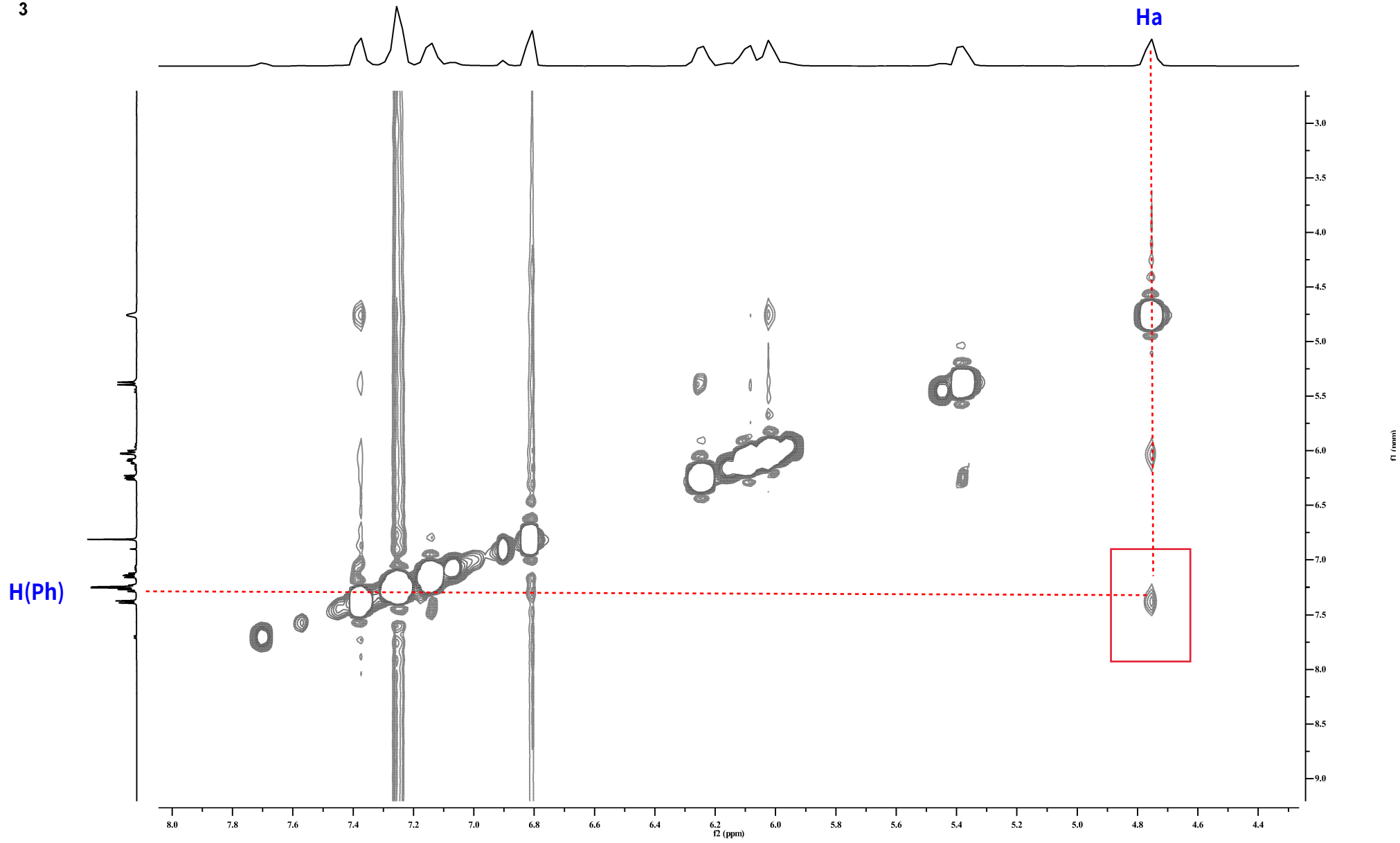




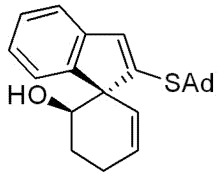

131.00
129.82
129.33
127.57
125.01
124.79
124.12
122.48
119.62
72.30
43.35
36.25
29.98
Parameter Value
1 Title fxy-13-28-dept
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.0
5 Number of Scans 6
6 Acquisition Time 1.3631
7 Acquisition Date 2023-06-29T17:10:58
8 Spectrometer Frequency 100.61
9 Spectral Width 24038.5
HO
SAd
3
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)


HO
SAd
Ha

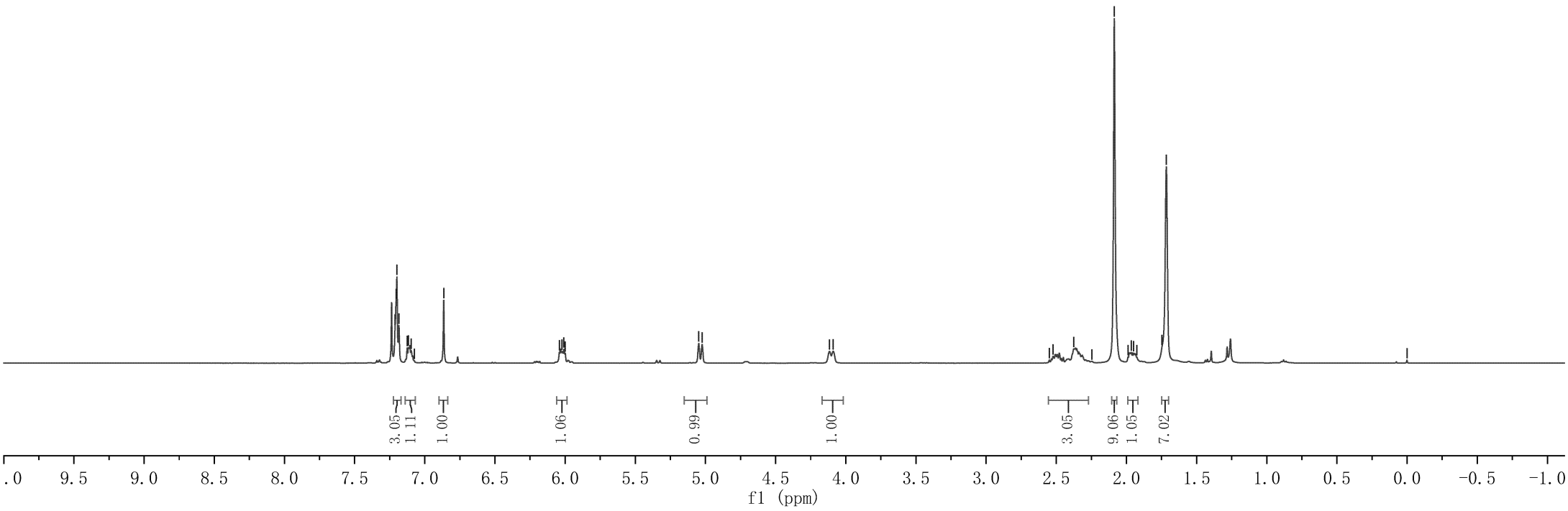
3


Ha
H(Ph)
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
f2 (ppm)
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
f1 (ppm)

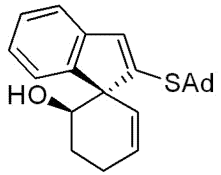
Parameter	Value
1 Title	FXY-13-73
2 Origin	
3 Solvent	CDCl3
4 Temperature	302.1
5 Number of Scans	16
6 Acquisition Time	4.0002
7 Acquisition Date	2023-07-11T23:50:58
8 Spectrometer Frequency	399.90
9 Spectral Width	8012.0



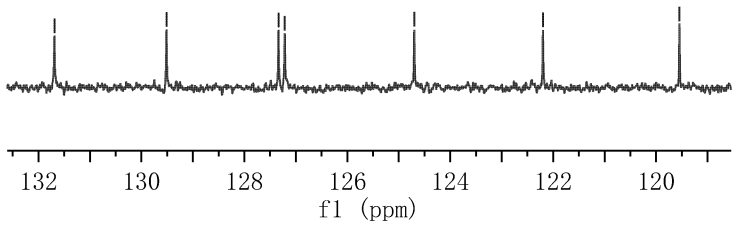
4

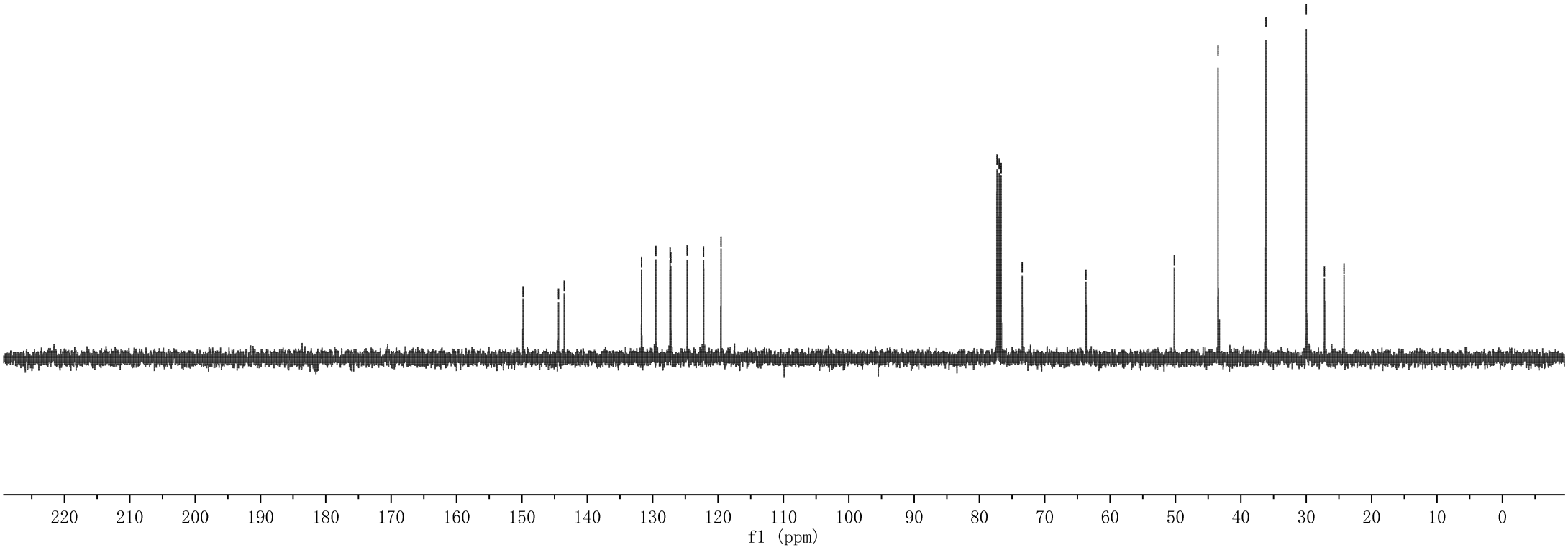


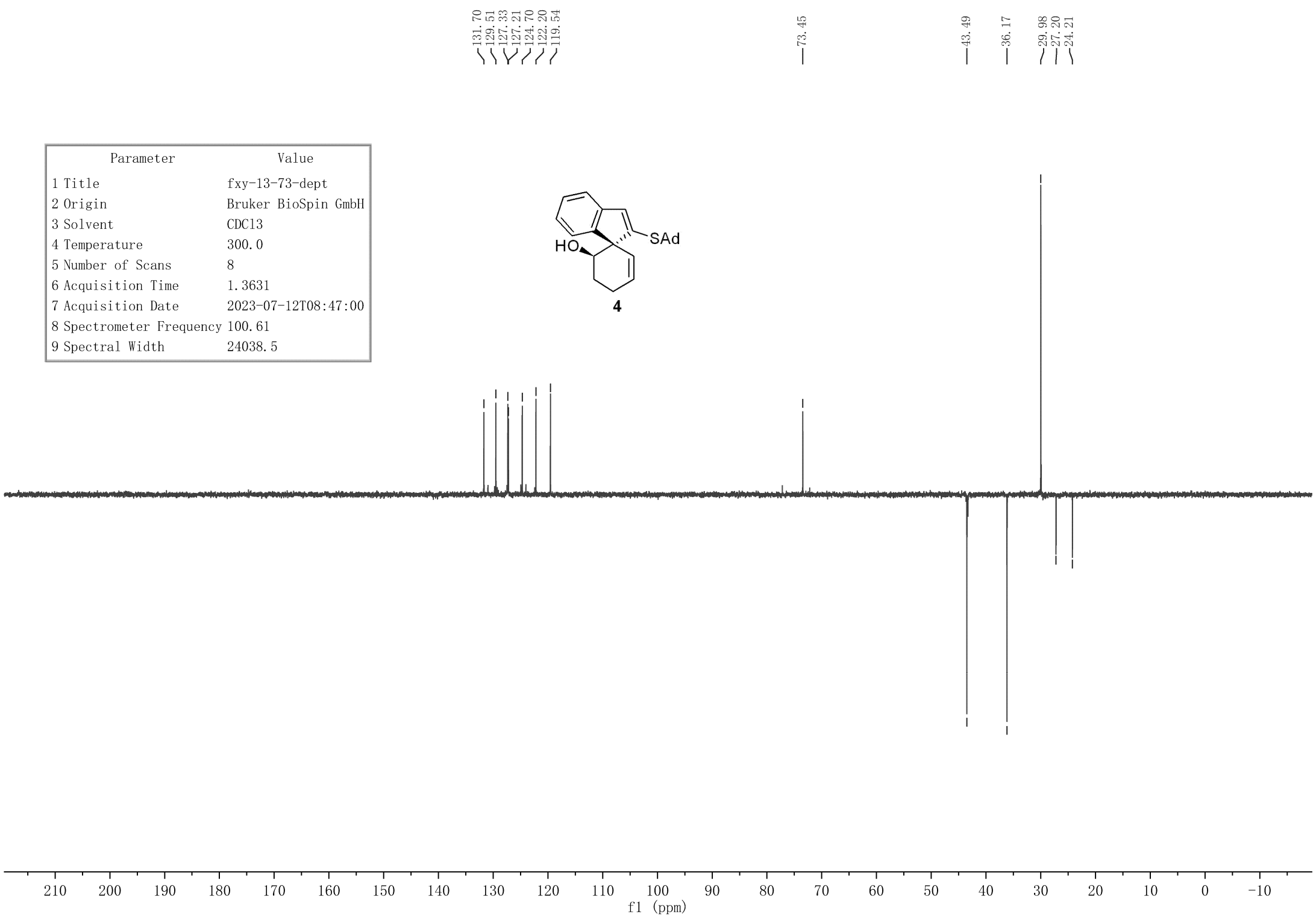
Parameter	Value
1 Title	fxy-13-73-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	4
6 Acquisition Time	1.3631
7 Acquisition Date	2023-07-12T08:45:52
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5

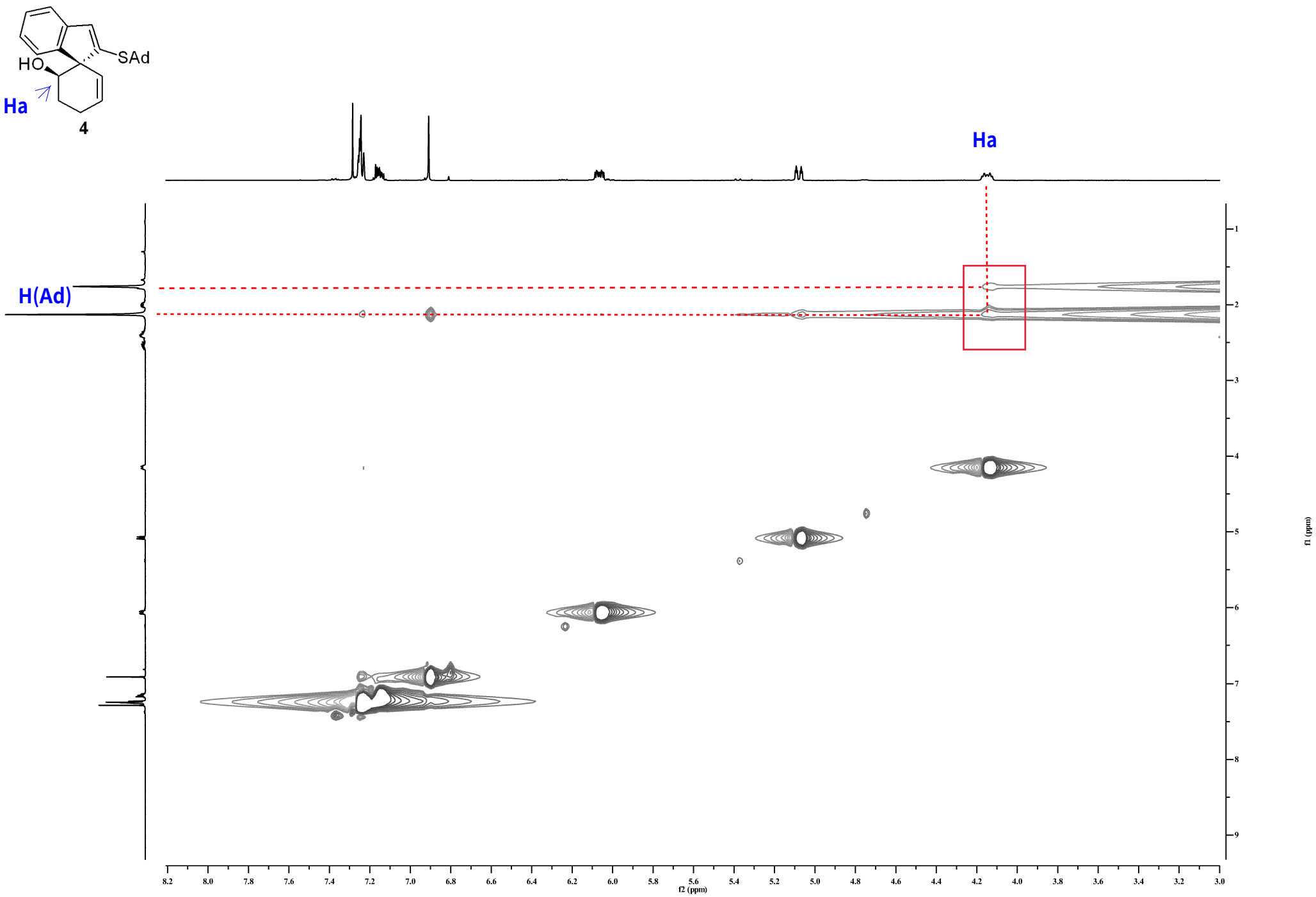


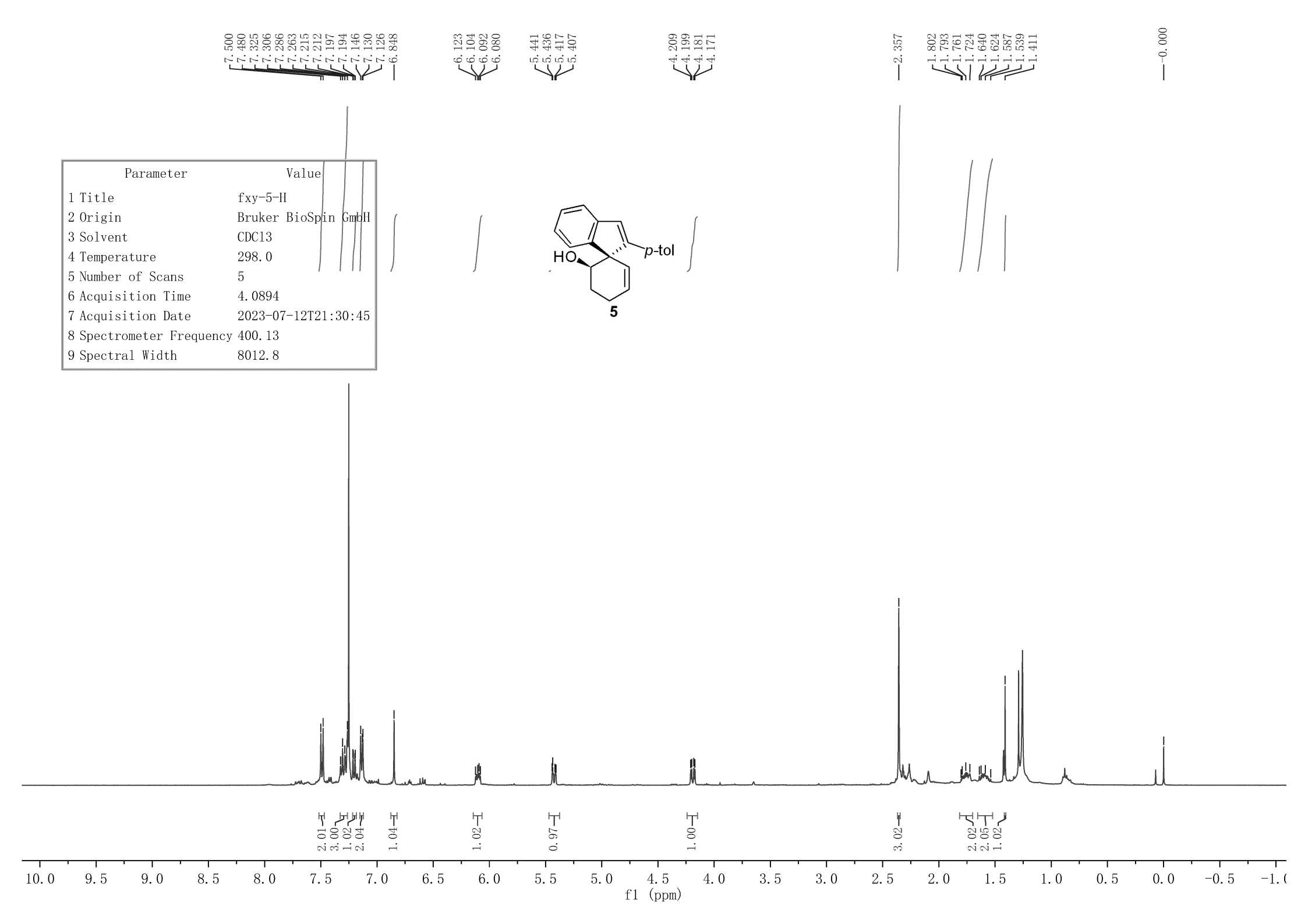
4

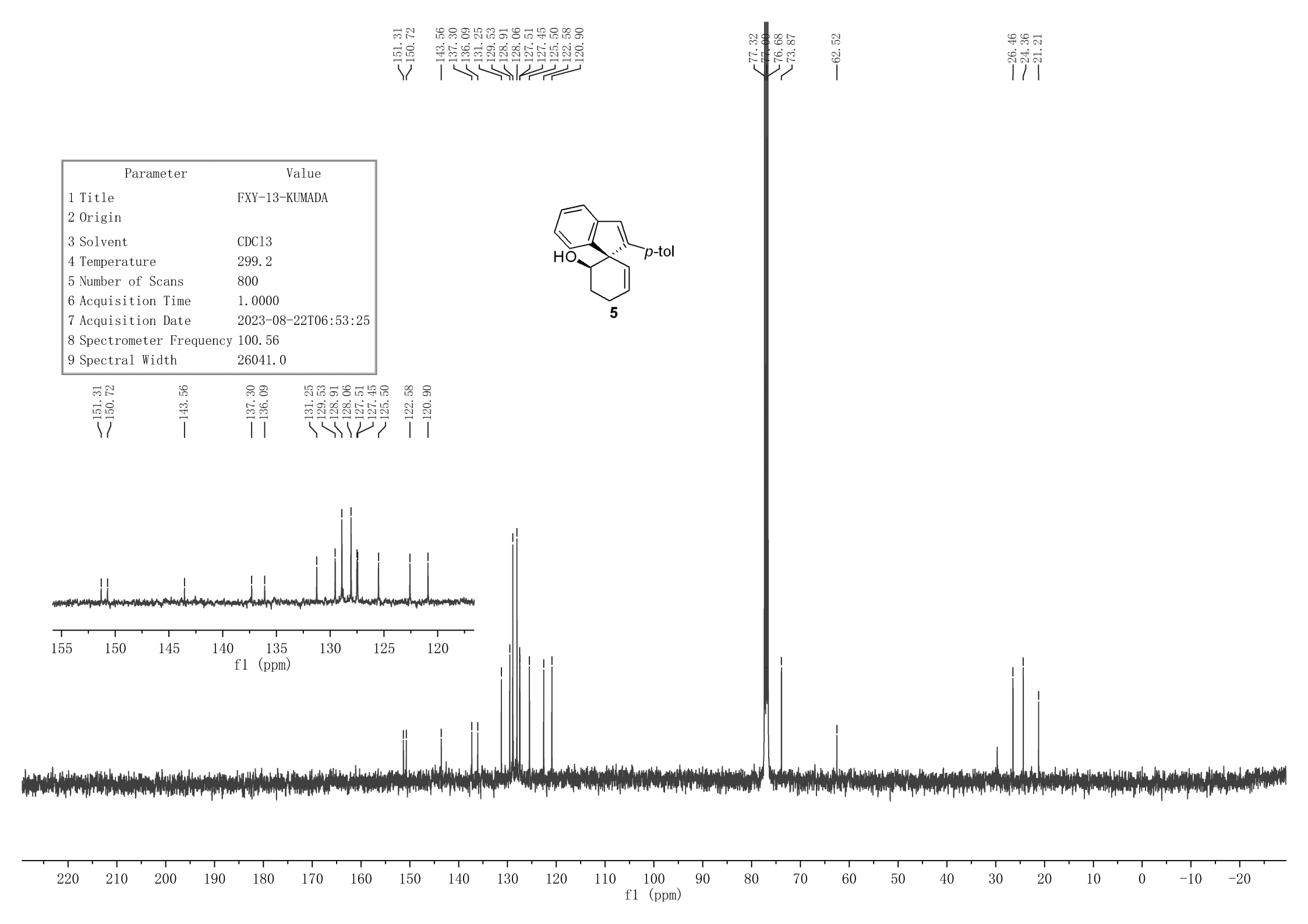





131.70
129.51
127.33
127.21
124.70
122.20
119.54
73.45
43.49
36.17
29.98
27.20
24.21
Parameter Value
1 Title fxy-13-73-dept
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.0
5 Number of Scans 8
6 Acquisition Time 1.3631
7 Acquisition Date 2023-07-12T08:47:00
8 Spectrometer Frequency 100.61
9 Spectral Width 24038.5
HO
SAd
4
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)


HO
SAd
Ha
4
Ha
H(Ad)
f2 (ppm)
f1 (ppm)


7.500
7.480
7.325
7.306
7.286
7.263
7.215
7.212
7.197
7.194
7.146
7.130
7.126
6.848
6.123
6.104
6.092
6.080
5.441
5.436
5.417
5.407
4.209
4.199
4.181
4.171
2.357
1.802
1.793
1.761
1.724
1.640
1.624
1.587
1.539
1.411
-0.000
Parameter Value
1 Title fxy-5-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 2023-07-12T21:30:45
8 Spectrometer Frequency 400.13
9 Spectral Width 8012.8
HO
p-tol
5
2.01
3.00
1.02
2.04
1.04
1.02
0.97
1.00
3.02
2.02
2.05
1.02
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
f1 (ppm)

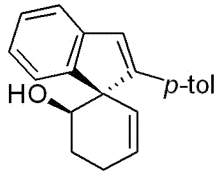

151.31
150.72
143.56
137.30
136.09
131.25
129.53
128.91
128.06
127.51
127.45
125.50
122.58
120.90
77.32
77.00
76.68
73.87
62.52
26.46
24.36
21.21
Parameter Value
1 Title FXY-13-KUMADA
2 Origin
3 Solvent CDCl3
4 Temperature 299.2
5 Number of Scans 800
6 Acquisition Time 1.0000
7 Acquisition Date 2023-08-22T06:53:25
8 Spectrometer Frequency 100.56
9 Spectral Width 26041.0
HO
p-tol
5
f1 (ppm)
f1 (ppm)

131.26
129.53
128.92
128.08
127.52
127.49
125.51
122.59
120.91

73.89

26.49
24.37
21.21

Parameter	Value
1 Title	fxy-5-dept
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	300.0
5 Number of Scans	48
6 Acquisition Time	1.3631
7 Acquisition Date	2023-07-12T21:33:39
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5



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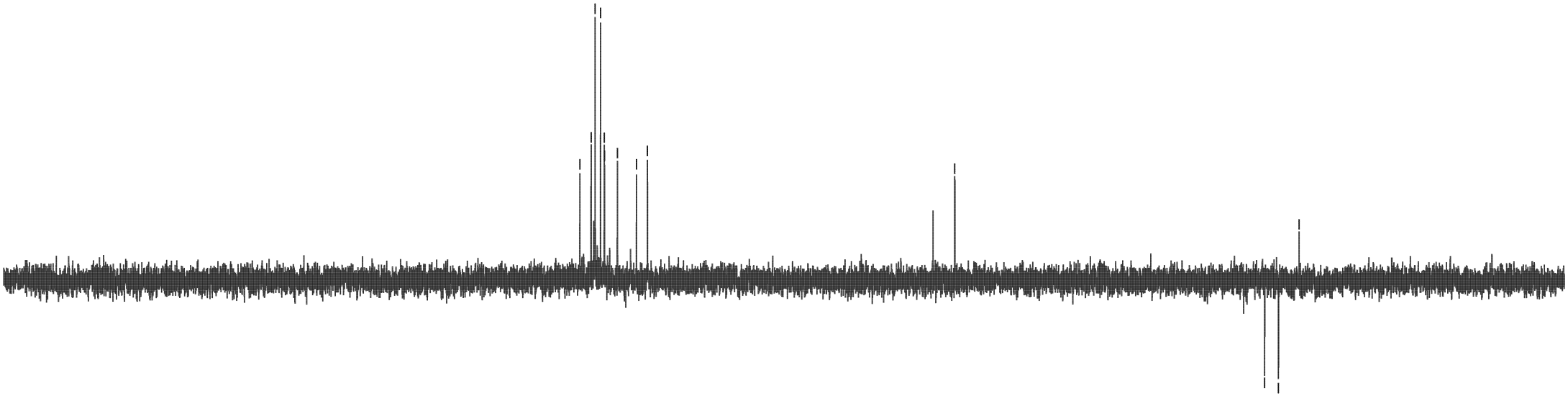
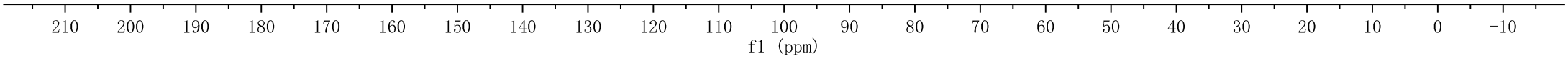
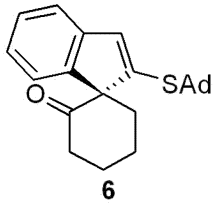
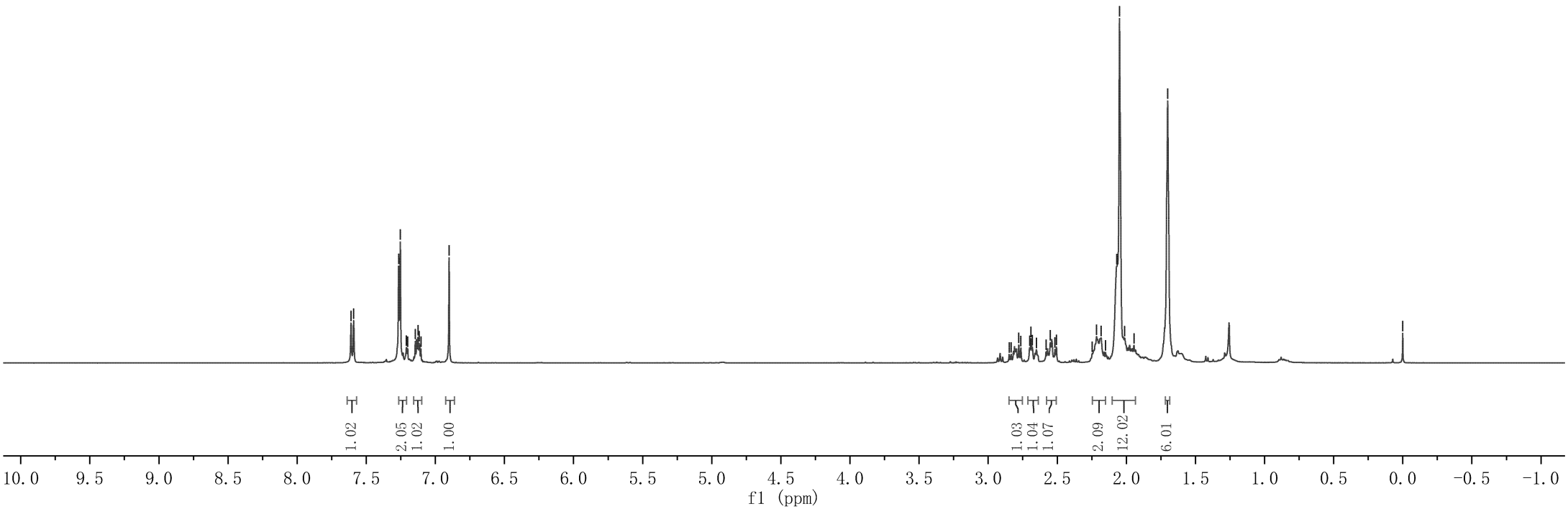




Parameter	Value
1 Title	fxy-13-78_H
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	4
6 Acquisition Time	4.0894
7 Acquisition Date	2023-07-13T20:50:04
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8

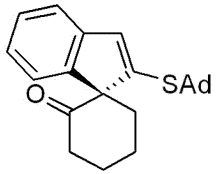


6



207.40
146.38
146.10
143.32
133.52
127.62
124.34
123.01
120.85
77.32
77.00
76.68
71.84
50.01
43.92
40.67
36.15
35.89
30.09
25.89
21.61

Parameter	Value
1 Title	fxy-13-78_C
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	2023-07-13T20:52:17
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5



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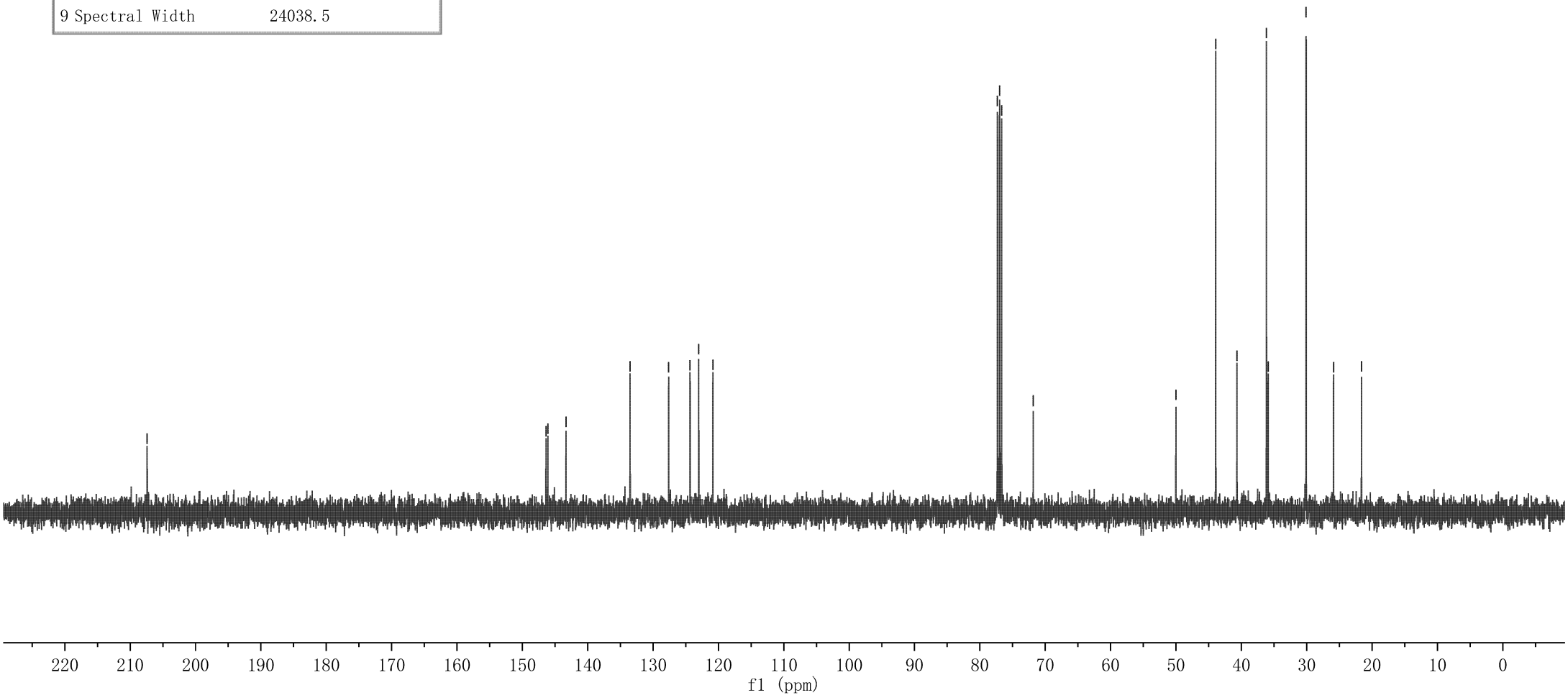
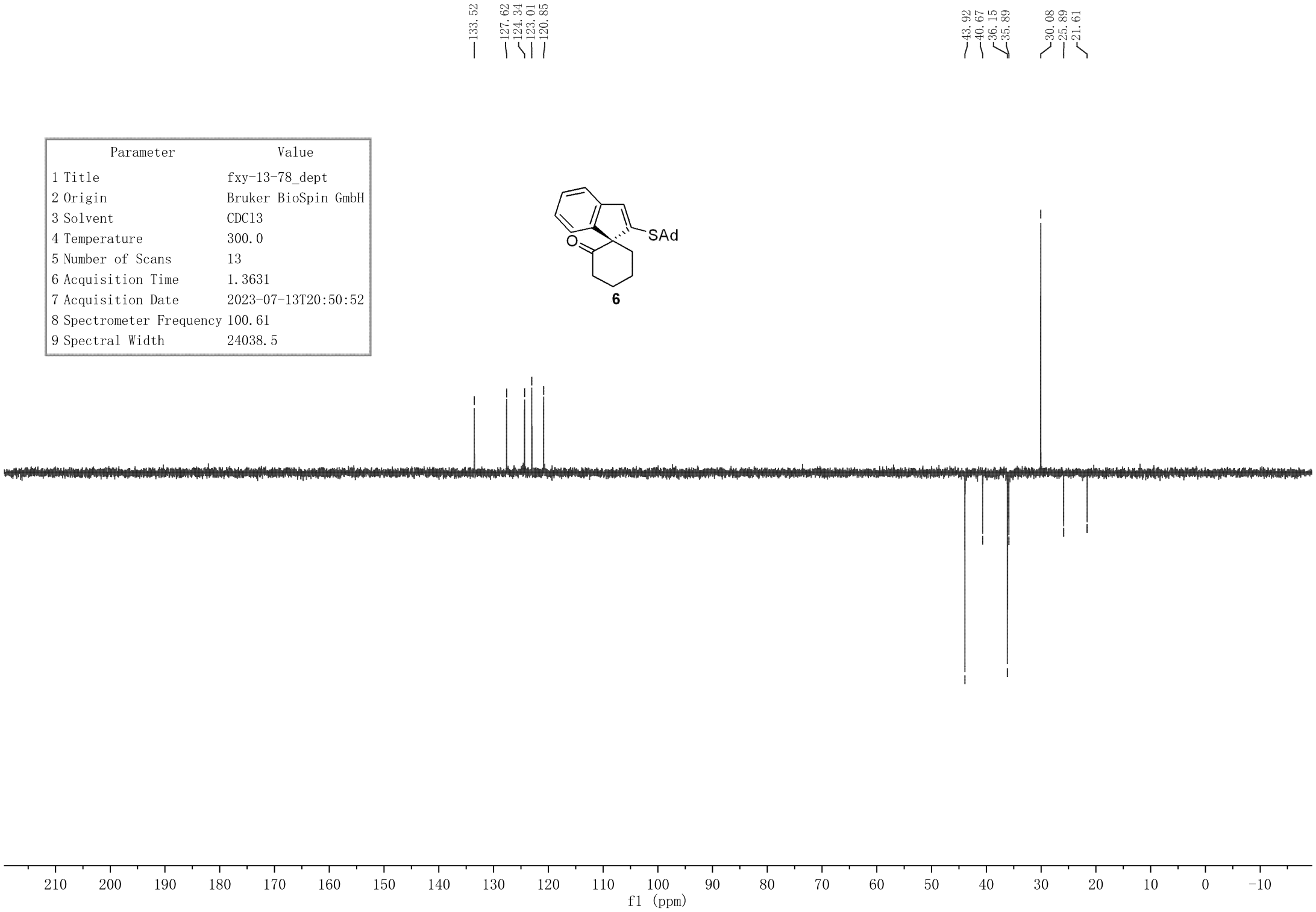
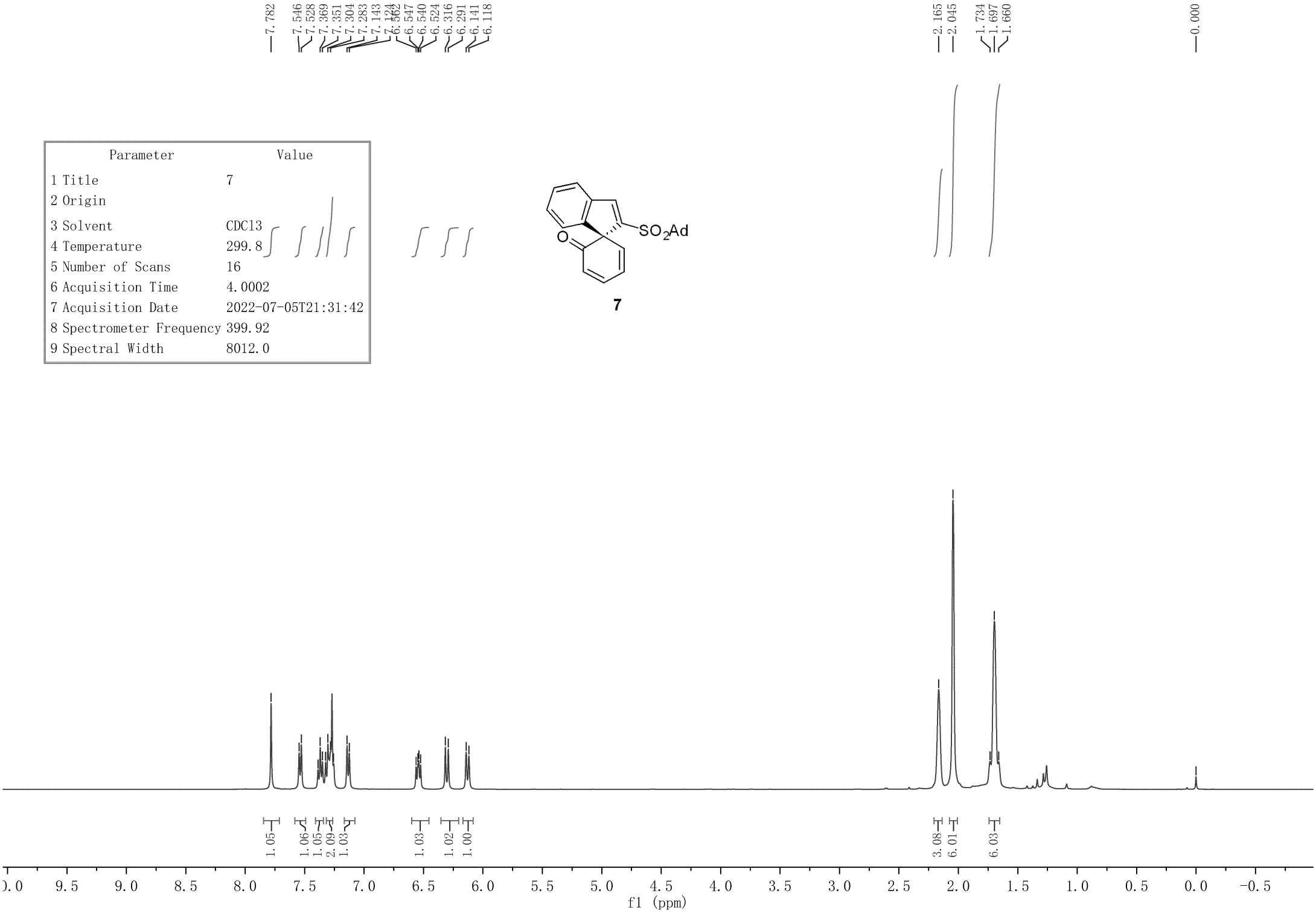
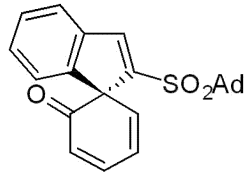



133.52
127.62
124.34
123.01
120.85
43.92
40.67
36.15
35.89
30.08
25.89
21.61
Parameter Value
1 Title fxy-13-78_dept
2 Origin Bruker BioSpin GmbH
3 Solvent CDCl3
4 Temperature 300.0
5 Number of Scans 13
6 Acquisition Time 1.3631
7 Acquisition Date 2023-07-13T20:50:52
8 Spectrometer Frequency 100.61
9 Spectral Width 24038.5
O
SAd
6
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)

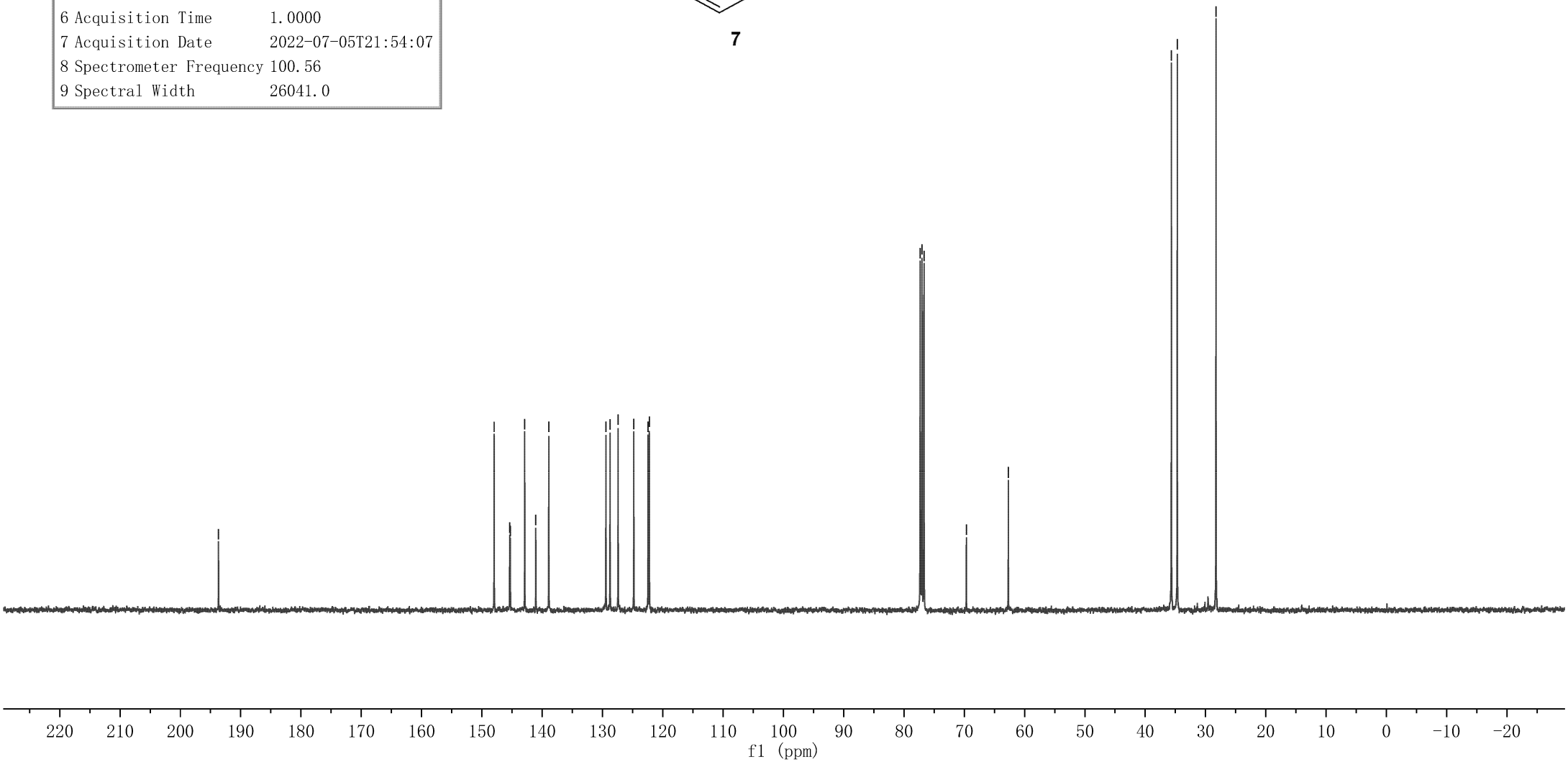

7.782
7.546
7.528
7.369
7.351
7.304
7.283
7.143
7.124
6.562
6.547
6.540
6.524
6.316
6.291
6.141
6.118
2.165
2.045
1.734
1.697
1.660
0.000
SO2Ad
O
7
Parameter Value
1 Title 7
2 Origin
3 Solvent CDCl3
4 Temperature 299.8
5 Number of Scans 16
6 Acquisition Time 4.0002
7 Acquisition Date 2022-07-05T21:31:42
8 Spectrometer Frequency 399.92
9 Spectral Width 8012.0
1.05
1.06
1.05
2.09
1.03
1.03
1.02
1.00
3.08
6.01
6.03
f1 (ppm)

193.67
147.96
145.39
145.28
142.89
141.06
138.90
129.43
128.74
127.41
124.81
122.44
122.23
77.32
77.00
76.68
69.66
62.70
35.66
34.68
28.26

Parameter	Value
1 Title	7
2 Origin	
3 Solvent	CDCl3
4 Temperature	299.8
5 Number of Scans	600
6 Acquisition Time	1.0000
7 Acquisition Date	2022-07-05T21:54:07
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

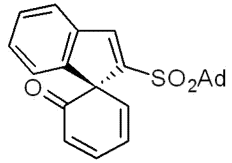


7



147.95
142.87
138.90
129.42
128.73
127.40
124.79
122.42
122.22
35.66
34.68
28.26

Parameter	Value
1 Title	7
2 Origin	
3 Solvent	CDCl3
4 Temperature	299.6
5 Number of Scans	256
6 Acquisition Time	1.0001
7 Acquisition Date	2022-07-05T22:09:43
8 Spectrometer Frequency	100.56
9 Spectral Width	18028.0



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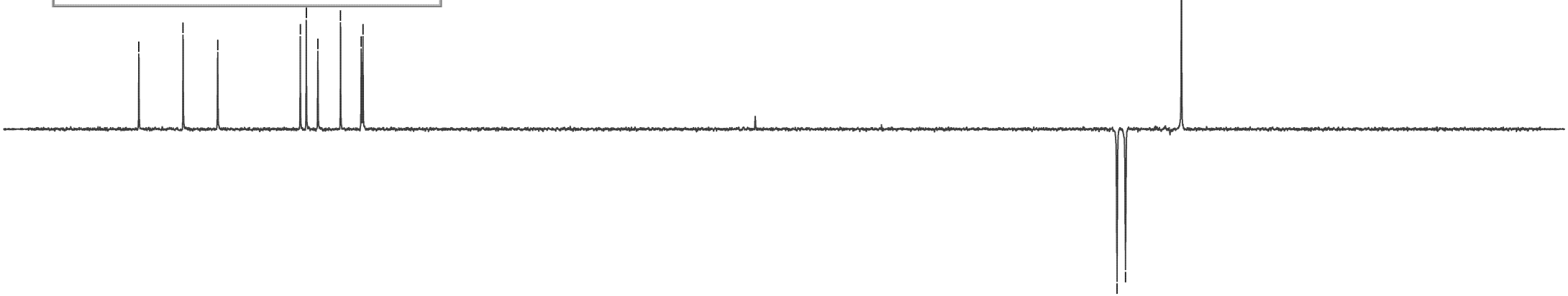
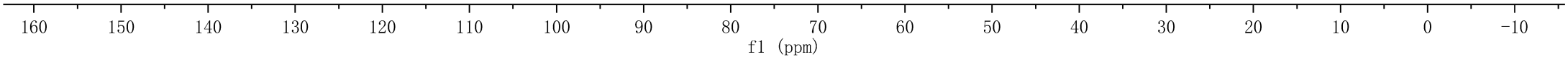
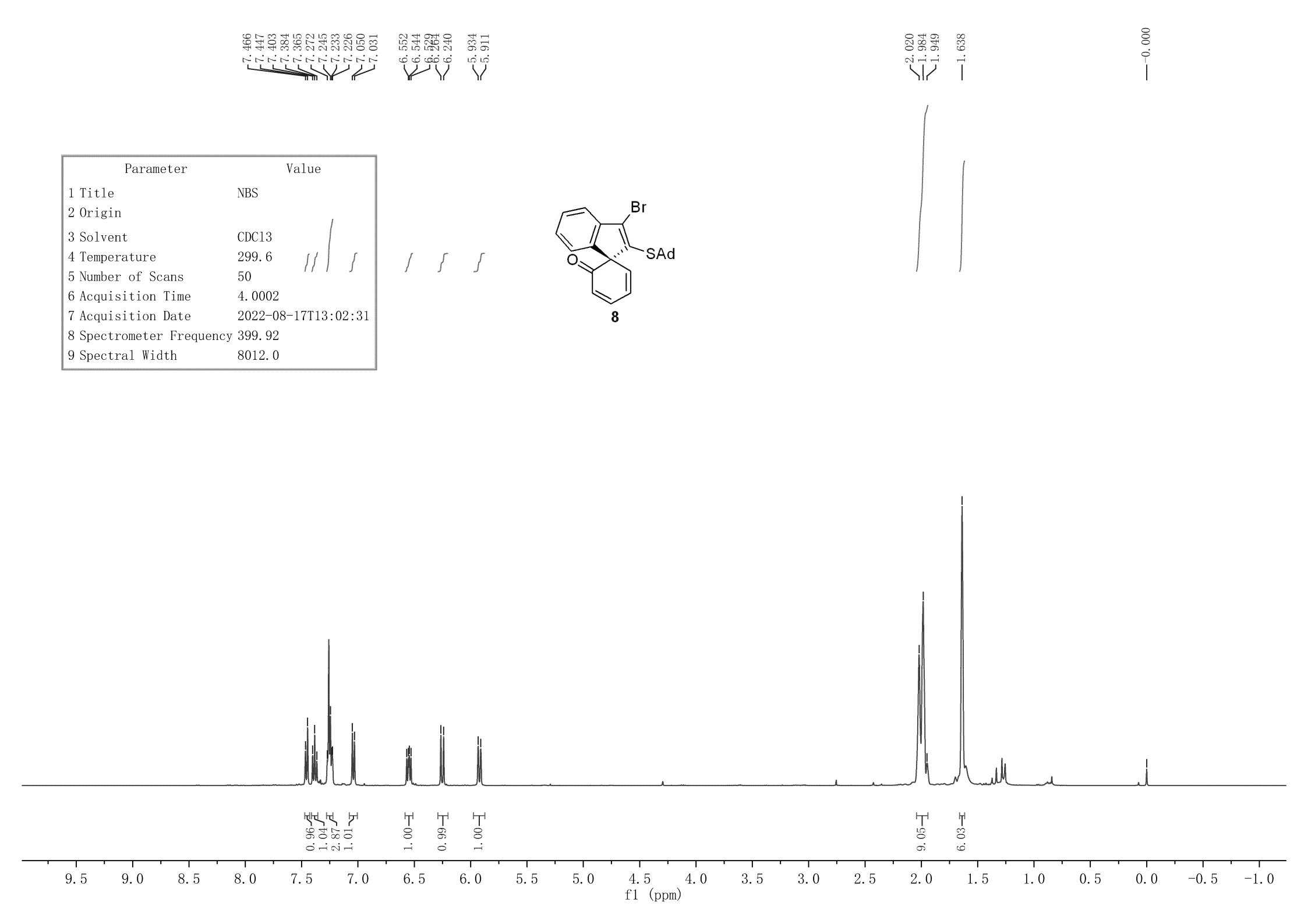





7.466
7.447
7.403
7.384
7.365
7.272
7.245
7.233
7.226
7.050
7.031
6.552
6.544
6.529
6.264
6.240
5.934
5.911
2.020
1.984
1.949
1.638
0.000
Parameter Value
1 Title NBS
2 Origin
3 Solvent CDCl3
4 Temperature 299.6
5 Number of Scans 50
6 Acquisition Time 4.0002
7 Acquisition Date 2022-08-17T13:02:31
8 Spectrometer Frequency 399.92
9 Spectral Width 8012.0
Br
SAd
O
8
0.96
1.04
2.87
1.01
1.00
0.99
1.00
9.05
6.03
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)

196.62

144.09
143.34
142.83
139.90
139.12
137.47
128.57
128.25
127.73
123.49
122.32
122.22

77.32
77.00
76.68
72.73

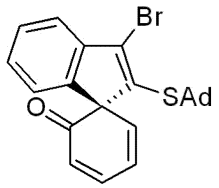
54.29

45.02

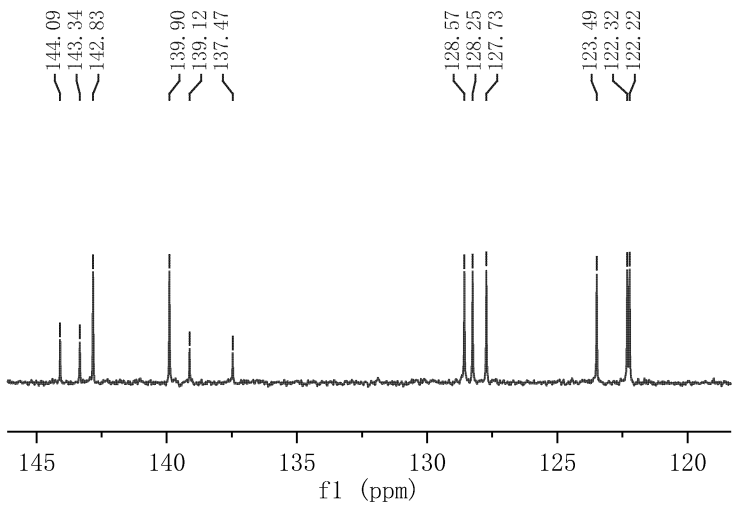
35.92

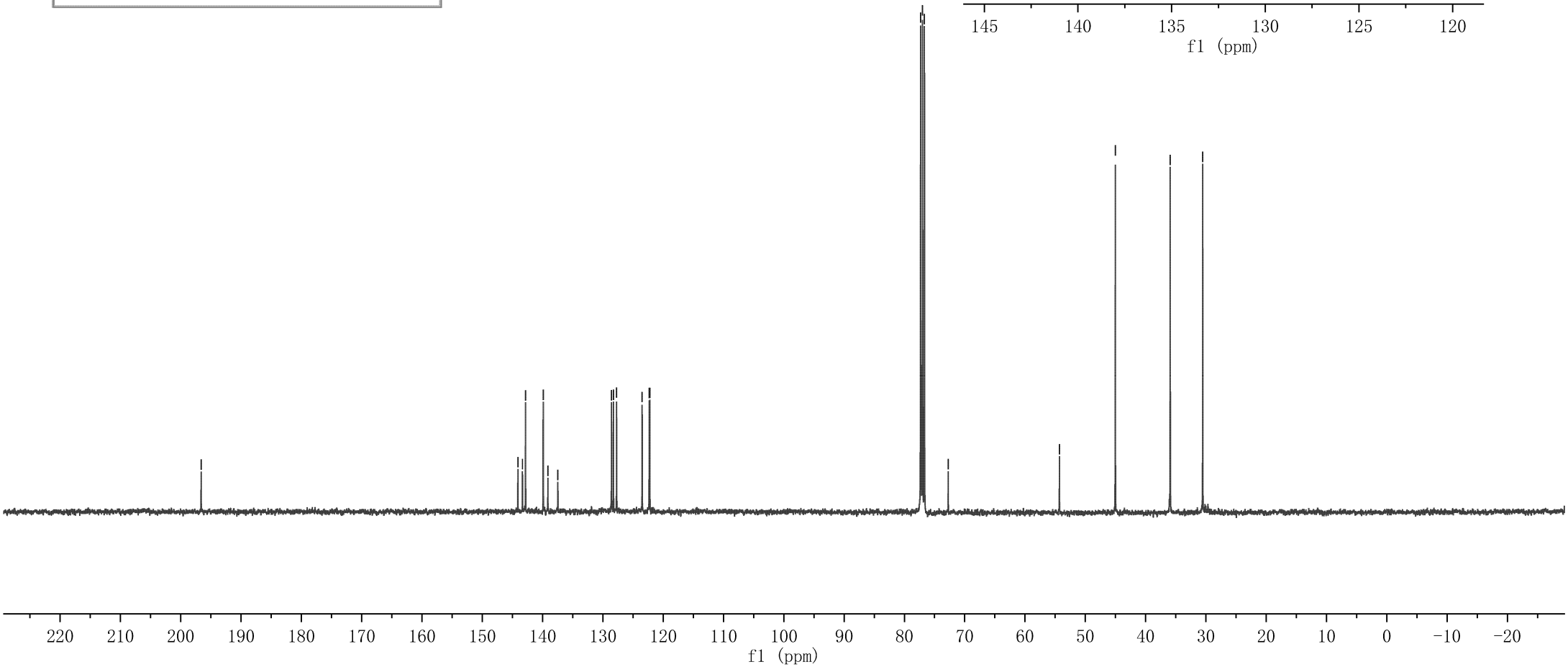
30.53

Parameter	Value
1 Title	NBS
2 Origin	
3 Solvent	CDCl3
4 Temperature	299.9
5 Number of Scans	1024
6 Acquisition Time	1.0000
7 Acquisition Date	2022-08-17T13:39:18
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0



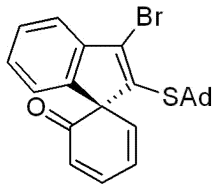
8



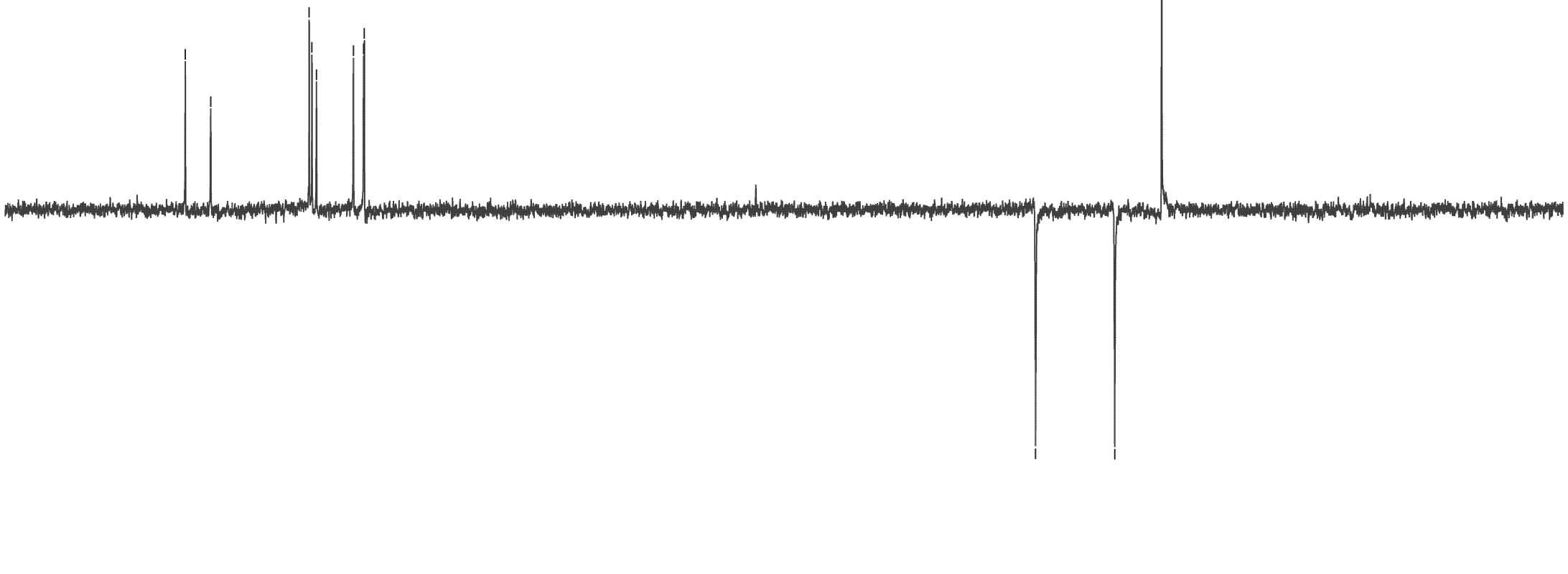


142.81
139.90
128.56
128.25
127.73
123.48
122.31
122.22
45.02
35.92
30.53

Parameter	Value
1 Title	NBS
2 Origin	
3 Solvent	CDCl3
4 Temperature	299.8
5 Number of Scans	25
6 Acquisition Time	1.0001
7 Acquisition Date	2022-08-17T13:55:12
8 Spectrometer Frequency	100.56
9 Spectral Width	18028.0



8



160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)