

Supporting Information

Copper-catalyzed atroposelective formal [4+1] annulation of 1,2-diketones with vinyl cations

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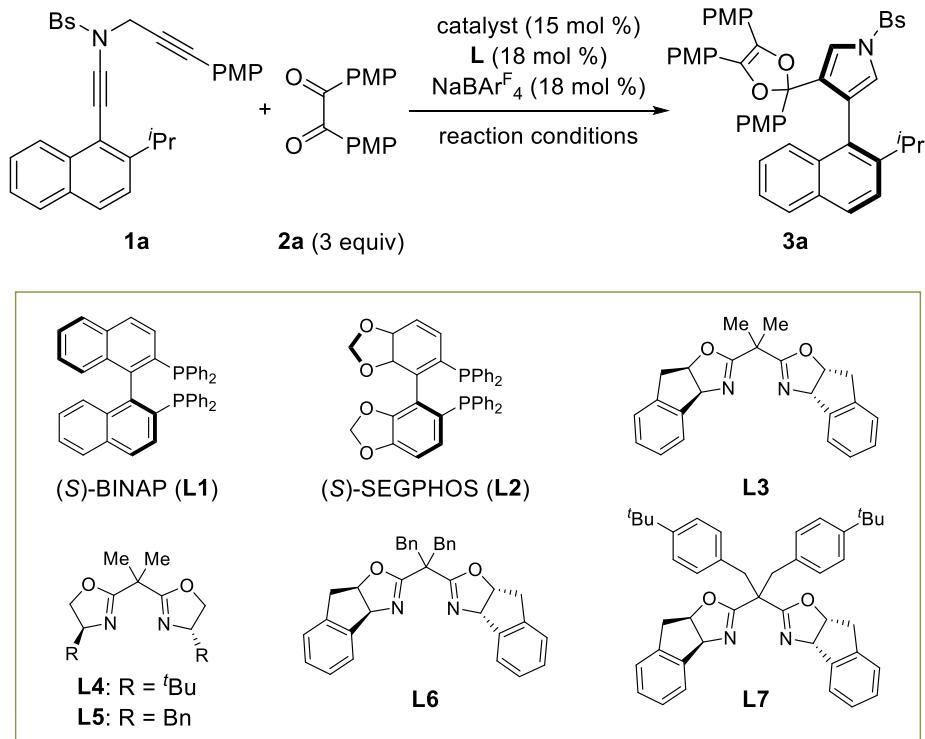
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General Information. Acetonitrile (ACS grade), toluene (ACS grade), ethyl acetate (ACS grade) and hexanes (ACS grade) were obtained commercially and used without further purification. Methylene chloride, tetrahydrofuran and diethyl ether were purified according to standard methods unless otherwise noted. Commercially available reagents were used without further purification. All reactions were carried out with a Titan HMS-14 digital magnetic stirrer with hot plate. Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed over silica gel (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 Agilent 6230 ESI-TOF MS using electron spray ionization. X-ray diffraction analysis was recorded on a Rigaku AFC7R X-ray single crystal diffractometer. HPLC analyses were carried out in a chromatograph equipped with a UV diode-array detector using chiral stationary columns from Daicel.

^1H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer and a Bruker AV-500 spectrometer in chloroform-d₃. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard for ^1H NMR spectra and with the internal chloroform signal at 77.0 ppm as a standard for ^{13}C NMR spectra. 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).

2. Optimization of Reaction Conditions

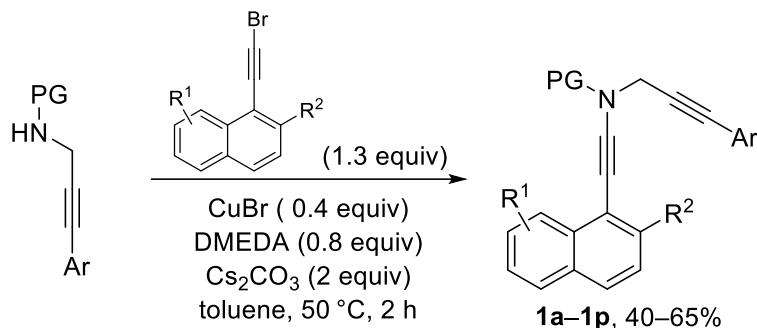


Entry	Catalyst	Ligand	Reaction conditions	Yield ^b (%)	Ee ^c (%)
1	CuTC	L1	DCM, 25 °C, 10 h	70	73
2	CuTC	L2	DCM, 25 °C, 10 h	69	48
3	CuTC	L3	DCM, 25 °C, 13 h	48	81
4	CuTC	L4	DCM, 25 °C, 10 h	67	90
5	CuTC	L5	DCM, 25 °C, 10 h	55	70
6	CuTC	L6	DCM, 25 °C, 10 h	71	90
7	CuTC	L7	DCM, 25 °C, 23 h	75	93
8	Cu(MeCN) ₄ PF ₆	L7	DCM, 25 °C, 23 h	57	91
9 ^d	(CuOTf) ₂ ·C ₆ H ₆	L7	DCM, 25 °C, 23 h	63	90
10	CuI	L7	DCM, 25 °C, 23 h	60	90
11	CuTC	L7	THF, 25 °C, 24 h	<1	-
12	CuTC	L7	toluene, 25 °C, 24 h	29	92

^a Reaction conditions: **1a** (0.05 mmol), **2a** (0.15 mmol), catalyst (0.0075 mmol), **L** (0.009 mmol), NaBAr^F₄ (0.009 mmol), solvent (2.5 mL), 25 °C, N₂, 10–24 h, in vials. ^b Measured by ¹H NMR using 1,3,5-trimethoxybenzene as the internal reference. ^c Determined by HPLC analysis. ^d (CuOTf)₂·C₆H₆ (0.00375 mmol) was used. Bs = 4-bromobenzenesulfonyl, PMP = 4-methoxyphenyl, NaBAr^F₄ = sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate.

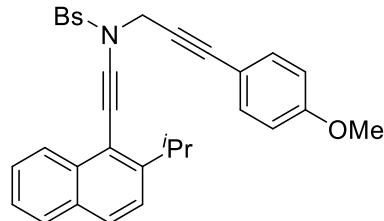
3. General Procedures and Transformation

3.1 Representative synthetic procedure for the preparation of ynamides **1** (**1a–1p**)^{1,2}



To a solution of the *N*-protected propargylamide derivative (1 mmol) in toluene (10 mL) were added copper bromide (0.4 mmol, 57.4 mg), DMEDA (0.8 mmol, 70.5 mg, 86 µL), Cs₂CO₃ (2 mmol, 651.6 mg) and 1-naphthylethyne bromide derivative (1.3 mmol). The reaction was stirred at 50 °C for 2 h. Upon completion (monitored by TLC), the reaction mixture was filtered through a Celite pad and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: PE/EtOAc) to afford the desired ynamide **1** (40–65% yield).

4-bromo-*N*-(2-isopropynaphthalen-1-yl)ethynyl-*N*-(3-(4-methoxyphenyl)prop-2-yn-1-yl)benzenesulfonamide (1a)

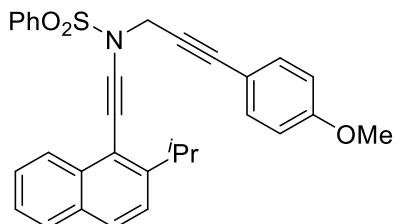


1a

Compound **1a** was prepared in 50% yield (286.3 mg) according to the general procedure. The substrate was isolated through silica gel column chromatography (PE:EA = 15:1) as a pale yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 8.27 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 9.0 Hz, 2H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.48 – 7.37 (m, 2H), 7.37 – 7.28 (m, 1H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 2H), 4.68 (s, 2H), 3.79 (s, 3H), 3.73 – 3.61 (m, 1H), 1.24 (d, *J* = 7.0 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 160.0, 149.4, 136.3, 133.7, 133.2, 132.3, 131.6, 129.8, 129.1, 128.7, 127.9, 126.8, 126.2, 125.6,

123.1, 117.0, 113.9, 113.7, 89.9, 87.0, 79.6, 68.1, 55.3, 43.4, 32.2, 23.2; IR (neat): 2961(bs), 2868, 2231(s), 1606, 1574, 1470, 1292, 1032, 968, 727 cm⁻¹; HRESIMS Calcd for [C₃₁H₂₆BrNNaO₃S]⁺ (M + Na⁺) 594.0709, found 594.0715.

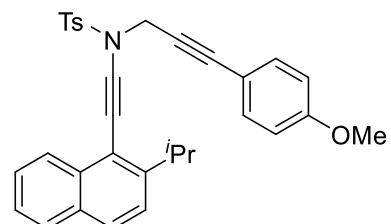
N-((2-isopropynaphthalen-1-yl)ethynyl)-N-(3-(4-methoxyphenyl)prop-2-yn-1-yl)benzenesulfonamide (1b)



1b

Compound **1b** was prepared in 40% yield (197.4 mg) according to the general procedure. The substrate was isolated through silica gel column chromatography (PE:EA = 15:1) as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.30 (d, J = 8.0 Hz, 1H), 8.07 (d, J = 7.2 Hz, 2H), 7.74 (d, J = 8.4 Hz, 2H), 7.60 – 7.54 (m, 1H), 7.50 – 7.43 (m, 2H), 7.43 – 7.34 (m, 2H), 7.33 – 7.28 (m, 1H), 7.13 (d, J = 8.8 Hz, 2H), 6.75 (d, J = 8.8 Hz, 2H), 4.69 (s, 2H), 3.76 (s, 3H), 3.73 – 3.62 (m, 1H), 1.23 (d, J = 6.8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 159.9, 149.0, 137.4, 133.7, 133.6, 133.2, 131.5, 129.0, 128.4, 128.2, 127.8, 126.7, 126.3, 125.4, 123.1, 117.3, 113.9, 113.8, 90.2, 86.7, 79.8, 68.0, 55.2, 43.1, 32.1, 23.1; IR (neat): 2962(bs), 2922, 2231(s), 1606, 1509, 1448, 1292, 1031, 911, 820 cm⁻¹; HRESIMS Calcd for [C₃₁H₂₇KNO₃S]⁺ (M + K⁺) 532.1343, found 532.1335.

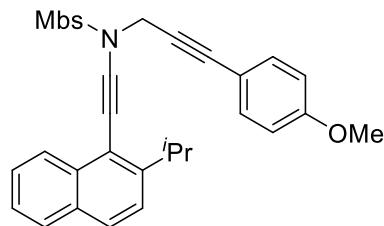
N-((2-isopropynaphthalen-1-yl)ethynyl)-N-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1c)



1c

Compound **1c** was prepared in 55% yield (279.2 mg) according to the general procedure. The substrate was isolated through silica gel column chromatography (PE:EA = 15:1) as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.31 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.79 – 7.71 (m, 2H), 7.44 – 7.36 (m, 2H), 7.33 – 7.28 (m, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 2H), 6.76 (d, *J* = 8.8 Hz, 2H), 4.67 (s, 2H), 3.79 (s, 3H), 3.75 – 3.63 (m, 1H), 2.35 (s, 3H), 1.24 (d, *J* = 6.8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 159.8, 149.0, 144.8, 134.4, 133.6, 133.2, 131.6, 129.6, 128.3, 127.8, 126.7, 126.4, 125.5, 123.1, 117.4, 114.0, 113.7, 90.5, 86.6, 79.9, 67.9, 55.3, 43.1, 32.1, 23.2, 21.6; IR (neat): 2961(bs), 2930, 2230(s), 1606, 1508, 1457, 1369, 1168, 1136, 911 cm⁻¹; HRESIMS Calcd for [C₃₂H₂₉NNaO₃S]⁺ (M + Na⁺) 530.1760, found 530.1771.

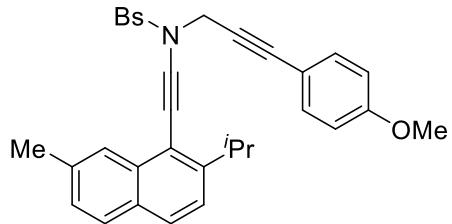
N-((2-isopropylnaphthalen-1-yl)ethynyl)-4-methoxy-N-(3-(4-methoxyphenyl)prop-2-yn-1-yl)benzenesulfonamide (1d)



1d

Compound **1d** was prepared in 54% yield (282.8 mg) according to the general procedure. The substrate was isolated through silica gel column chromatography (PE:EA = 15:1) as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.31 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.8 Hz, 2H), 7.81 – 7.66 (m, 2H), 7.47 – 7.34 (m, 2H), 7.34 – 7.27 (m, 1H), 7.14 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 9.2 Hz, 2H), 6.76 (d, *J* = 8.8 Hz, 2H), 4.66 (s, 2H), 3.78 (s, 3H), 3.74 (s, 3H), 3.72 – 3.64 (m, 1H), 1.24 (d, *J* = 7.2 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 163.8, 159.8, 148.9, 133.6, 133.2, 131.6, 130.5, 128.8, 128.3, 127.8, 126.7, 126.4, 125.5, 123.1, 117.5, 114.2, 114.1, 113.7, 90.7, 86.6, 80.1, 67.9, 55.5, 55.3, 43.1, 32.1, 23.2; IR (neat): 2926(bs), 2839, 2229(s), 1605, 1509, 1441, 1367, 1162, 1107, 911 cm⁻¹; HRESIMS Calcd for [C₃₂H₂₉NNaO₄S]⁺ (M + Na⁺) 546.1710, found 546.1703.

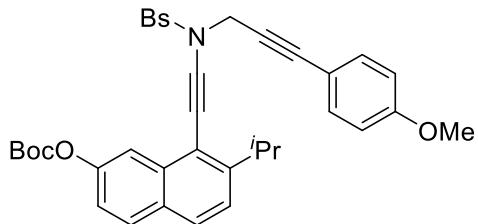
4-bromo-N-((2-isopropyl-7-methylnaphthalen-1-yl)ethynyl)-N-(3-(4-methoxyphenyl)prop-2-yn-1-yl)benzenesulfonamide (1e)



1e

Compound **1e** was prepared in 61% yield (357.8 mg) according to the general procedure. The substrate was isolated through silica gel column chromatography (PE:EA = 15:1) as a pale yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 8.15 – 8.00 (m, 1H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.75 (d, *J* = 8.0 Hz, 2H), 4.68 (s, 2H), 3.74 (s, 3H), 3.73 – 3.58 (m, 1H), 2.34 (s, 3H), 1.36 – 1.08 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 159.9, 149.4, 136.7, 136.3, 133.9, 133.1, 132.2, 129.8, 129.7, 129.0, 128.4, 127.7, 125.2, 122.1, 116.2, 113.9, 113.6, 89.7, 86.9, 79.5, 68.1, 55.2, 43.3, 32.1, 23.1, 21.8; IR (neat): 2960(bs), 2928, 2233(s), 1605, 1574, 1442, 1292, 1032, 835, 751 cm⁻¹; HRESIMS Calcd for [C₃₂H₂₈BrNNaO₃S]⁺ (M + Na⁺) 608.0865, found 608.0871.

8-(((4-bromo-N-(3-(4-methoxyphenyl)prop-2-yn-1-yl)phenyl)sulfonamido)ethynyl)-7-isopropynaphthalen-2-yl tert-butyl carbonate (1f**)**

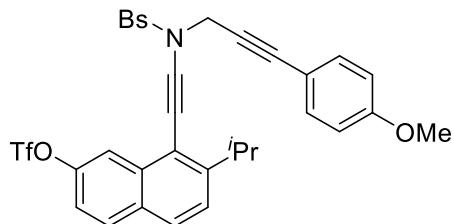


1f

Compound **1f** was prepared in 65% yield (447.6 mg) according to the general procedure. The substrate was isolated through silica gel column chromatography (PE:EA = 15:1) as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 2.4 Hz, 1H), 7.85 (d, *J* = 8.8 Hz, 2H), 7.69 (d, *J* = 8.8 Hz, 1H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 1H), 7.21 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 4.59 (s, 2H), 3.67 (s, 3H), 3.56 – 3.45 (m, 1H), 1.45 (s, 9H), 1.10 (d, *J* = 6.8

Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.9, 151.9, 149.7, 149.5, 136.3, 134.1, 133.1, 132.3, 129.7, 129.5, 129.4, 129.1, 128.1, 123.0, 120.6, 117.1, 117.0, 113.9, 113.6, 90.3, 87.0, 83.5, 79.4, 67.9, 55.2, 43.3, 32.2, 27.7, 23.0; IR (neat): 2963(bs), 2934, 2233(s), 1756, 1573, 1273, 1172, 1032, 835, 750 cm^{-1} ; HRESIMS Calcd for $[\text{C}_{36}\text{H}_{34}\text{BrNNaO}_6\text{S}]^+$ ($\text{M} + \text{Na}^+$) 710.1182, found 710.1180.

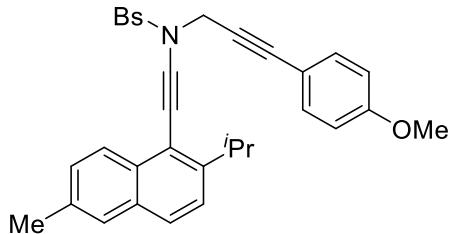
8-(((4-bromo-N-(3-(4-methoxyphenyl)prop-2-yn-1-yl)phenyl)sulfonamido)ethynyl)-7-isopropynaphthalen-2-yl trifluoromethanesulfonate (1g)



1g

Compound **1g** was prepared in 63% yield (454.0 mg) according to the general procedure. The substrate was isolated through silica gel column chromatography (PE:EA = 12:1) as a pale yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, $J = 2.0$ Hz, 1H), 7.83 (d, $J = 8.4$ Hz, 2H), 7.75 (d, $J = 8.8$ Hz, 1H), 7.69 (d, $J = 8.8$ Hz, 1H), 7.52 (d, $J = 8.4$ Hz, 2H), 7.38 (d, $J = 8.8$ Hz, 1H), 7.24 (dd, $J = 8.8, 2.0$ Hz, 1H), 6.99 (d, $J = 8.8$ Hz, 2H), 6.69 (d, $J = 8.8$ Hz, 2H), 4.60 (s, 2H), 3.68 (s, 3H), 3.59 – 3.48 (m, 1H), 1.13 (d, $J = 6.8$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.0, 150.4, 148.0, 136.4, 133.8, 133.1, 132.4, 130.6(2), 130.5(9), 129.6, 129.3, 128.0, 124.6, 119.3, 118.8 (q, $J = 319.0$ Hz), 118.0, 117.9, 113.9, 113.5, 91.2, 87.1, 79.2, 67.4, 55.2, 43.2, 32.3, 22.9; ^{19}F NMR (376 MHz, CDCl_3) δ -72.6; IR (neat): 2963(bs), 2838, 2232(s), 1574, 1468, 1391, 1140, 1010, 979, 799 cm^{-1} ; HRESIMS Calcd for $[\text{C}_{32}\text{H}_{25}\text{BrF}_3\text{NNaO}_6\text{S}_2]^+$ ($\text{M} + \text{Na}^+$) 742.0151, found 742.0160.

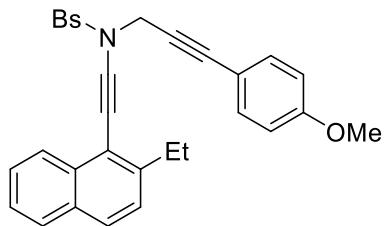
4-bromo-N-((2-isopropyl-6-methylnaphthalen-1-yl)ethynyl)-N-(3-(4-methoxyphenyl)prop-2-yn-1-yl)benzenesulfonamide (1h)



1h

Compound **1h** was prepared in 40% yield (234.6 mg) according to the general procedure. The substrate was isolated through silica gel column chromatography (PE:EA = 12:1) as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.8 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.51 (s, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.16 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.08 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 4.67 (s, 2H), 3.77 (s, 3H), 3.70 – 3.56 (m, 1H), 2.44 (s, 3H), 1.22 (d, *J* = 6.8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 159.9, 148.4, 136.2, 135.1, 133.1, 132.2, 131.9, 131.7, 129.7, 129.1, 129.0, 128.1, 126.9, 126.0, 123.1, 116.7, 113.9, 113.6, 89.6, 87.0, 79.6, 68.2, 55.2, 43.3, 32.0, 23.2, 21.4; IR (neat): 2960(bs), 2869, 2233(s), 1606, 1507, 1373, 1174, 1035, 891, 767 cm⁻¹; HRESIMS Calcd for [C₃₂H₂₈BrNNaO₃S]⁺ (M + Na⁺) 608.0865, found 608.0875.

4-bromo-N-((2-ethylnaphthalen-1-yl)ethynyl)-N-(3-(4-methoxyphenyl)prop-2-yn-1-yl)benzenesulfonamide (1i)

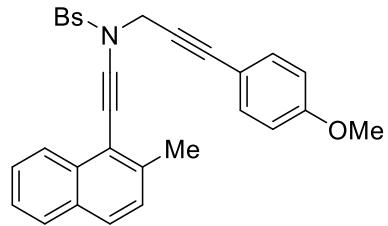


1i

Compound **1i** was prepared in 40% yield (223.4 mg) according to the general procedure. The substrate was isolated through silica gel column chromatography (PE:EA = 15:1) as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.8 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.43 – 7.36 (m, 1H), 7.36 – 7.29 (m, 2H), 7.09 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 4.68 (s, 2H), 3.78 (s, 3H), 2.95 (q, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H); ¹³C NMR

(100 MHz, CDCl₃) δ 159.9, 145.4, 136.2, 133.7, 133.1, 132.2, 131.5, 129.7, 129.1, 128.4, 127.9, 126.8, 126.5, 125.9, 125.5, 117.4, 113.9, 113.6, 89.6, 87.0, 79.5, 68.1, 55.3, 43.3, 28.4, 15.2; IR (neat): 2966(bs), 2932, 2231(s), 1606, 1574, 1441, 1390, 1172, 1069, 919 cm⁻¹; HRESIMS Calcd for [C₃₀H₂₄BrNNaO₃S]⁺ (M + Na⁺) 580.0552, found 580.0560.

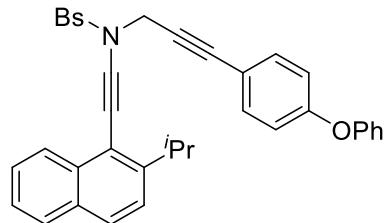
4-bromo-N-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-N-((2-methylnaphthalen-1-yl)ethynyl)benzenesulfonamide (1j)



1j

Compound **1j** was prepared in 65% yield (353.9 mg) according to the general procedure. The substrate was isolated through silica gel column chromatography (PE:EA = 15:1) as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.41 – 7.36 (m, 1H), 7.35 – 7.27 (m, 2H), 7.09 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 4.67 (s, 2H), 3.77 (s, 3H), 2.58 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 159.9, 139.2, 136.2, 133.5, 133.1, 132.2, 131.4, 129.7, 129.1, 128.0, 127.9(3), 127.8(6), 126.8, 125.8, 125.4, 118.3, 113.9, 113.6, 90.2, 87.0, 79.5, 68.6, 55.2, 43.4, 21.3; IR (neat): 2932(bs), 2838, 2233(s), 1606, 1574, 1508, 1372, 1249, 1172, 815 cm⁻¹; HRESIMS Calcd for [C₂₉H₂₂BrNNaO₃S]⁺ (M + Na⁺) 566.0396, found 566.0391.

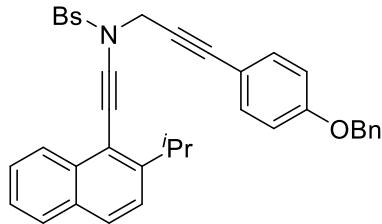
4-bromo-N-((2-isopropylnaphthalen-1-yl)ethynyl)-N-(3-(4-phenoxyphenyl)prop-2-yn-1-yl)benzenesulfonamide (1k)



1k

Compound **1k** was prepared in 57% yield (361.2 mg) according to the general procedure. The substrate was isolated through silica gel column chromatography (PE:EA = 15:1) as a pale yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 8.17 (d, *J* = 8.5 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.31 – 7.24 (m, 2H), 7.23 – 7.16 (m, 3H), 7.03 – 6.95 (m, 3H), 6.88 (d, *J* = 8.0 Hz, 2H), 6.77 (d, *J* = 9.0 Hz, 2H), 4.56 (s, 2H), 3.68 – 3.39 (m, 1H), 1.13 (d, *J* = 6.5 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 157.9, 156.1, 149.3, 136.2, 133.6, 133.3, 132.2, 131.5, 129.8, 129.7, 129.1, 128.7, 127.9, 126.7, 126.1, 125.5, 123.9, 123.1, 119.3, 118.2, 116.9, 116.0, 89.9, 86.6, 80.3, 68.1, 43.2, 32.1, 23.1; IR (neat): 3056(bs), 2961, 2231(s), 1588, 1503, 1370, 1243, 1087, 868, 757 cm⁻¹; HRESIMS Calcd for [C₃₆H₂₈BrNNaO₃S]⁺ (M + Na⁺) 656.0865, found 656.0878.

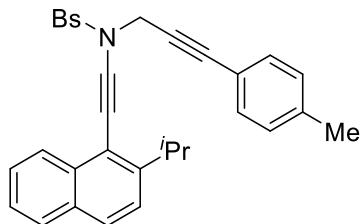
N-(3-(4-(benzyloxy)phenyl)prop-2-yn-1-yl)-4-bromo-N-((2-isopropynaphthalen-1-yl)ethynyl)benzenesulfonamide (1l)



1l

Compound **1l** was prepared in 50% yield (324.3 mg) according to the general procedure. The substrate was isolated through silica gel column chromatography (PE:EA = 15:1) as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.28 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.41 – 7.28 (m, 8H), 7.08 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.02 (s, 2H), 4.66 (s, 2H), 3.74 – 3.59 (m, 1H), 1.23 (d, *J* = 6.8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 159.1, 149.3, 136.4, 136.2, 133.7, 133.2, 132.2, 131.6, 129.7, 129.1, 128.7, 128.6, 128.1, 127.9, 127.4, 126.8, 126.2, 125.5, 123.1, 117.0, 114.9, 113.9, 89.9, 87.0, 79.7, 69.9, 68.1, 43.3, 32.1, 23.1; IR (neat): 2961(bs), 2927, 2232(s), 1605, 1508, 1390, 1173, 1010, 821, 750 cm⁻¹; HRESIMS Calcd for [C₃₇H₃₀BrNNaO₃S]⁺ (M + Na⁺) 670.1022, found 670.1030.

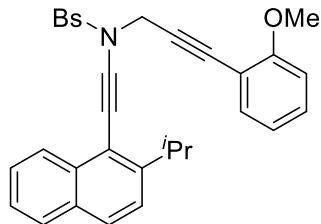
4-bromo-N-((2-isopropynaphthalen-1-yl)ethynyl)-N-(3-(p-tolyl)prop-2-yn-1-yl)benzenesulfonamide (1m)



1m

Compound **1m** was prepared in 52% yield (289.4 mg) according to the general procedure. The substrate was isolated through silica gel column chromatography (PE:EA = 15:1) as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.27 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.47 – 7.37 (m, 2H), 7.36 – 7.28 (m, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 4.70 (s, 2H), 3.81 – 3.56 (m, 1H), 2.33 (s, 3H), 1.23 (d, *J* = 7.2 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 149.4, 139.0, 136.2, 133.7, 132.3, 131.5, 129.8, 129.2, 129.1, 128.7, 127.9, 126.8, 126.2, 125.6, 123.1, 118.5, 116.9, 89.9, 87.2, 80.3, 68.0, 43.3, 32.1, 23.2, 21.5; IR (neat): 2961(bs), 2925, 2232(s), 1574, 1509, 1390, 1371, 1173, 1088, 817 cm⁻¹; HRESIMS Calcd for [C₃₁H₂₆BrNNaO₂S]⁺ (M + Na⁺) 578.0760, found 578.0768.

4-bromo-N-((2-isopropynaphthalen-1-yl)ethynyl)-N-(3-(2-methoxyphenyl)prop-2-yn-1-yl)benzenesulfonamide (1n)

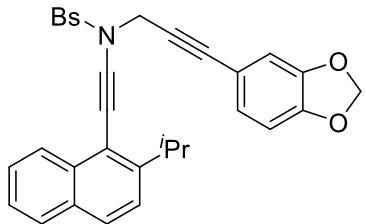


1n

Compound **1n** was prepared in 58% yield (332.1 mg) according to the general procedure. The substrate was isolated through silica gel column chromatography (PE:EA = 15:1) as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.27 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.43 – 7.33 (m, 2H), 7.32 – 7.22 (m, 2H), 7.00 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.86 – 6.80 (m, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 4.76 (s, 2H), 3.69 (s, 3H), 3.68 – 3.61 (m, 1H), 1.22 (d, *J* = 6.8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 160.0, 149.2, 136.1, 133.7, 133.6, 132.1, 131.5, 130.3, 129.7, 129.0,

128.5, 127.8, 126.6, 126.2, 125.5, 123.0, 120.3, 117.0, 110.7, 110.5, 89.8, 84.8, 83.6, 68.1, 55.5, 43.4, 32.0, 23.1; IR (neat): 2961(bs), 2930, 2231(s), 1574, 1493, 1463, 1176, 1049, 819, 751 cm⁻¹; HRESIMS Calcd for [C₃₁H₂₆BrNKO₃S]⁺ (M + K⁺) 610.0448, found 610.0445.

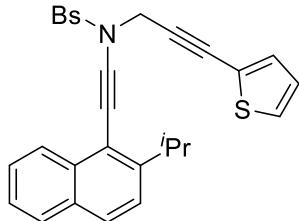
N-(3-(benzo[d][1,3]dioxol-5-yl)prop-2-yn-1-yl)-4-bromo-N-((2-isopropynaphthalen-1-yl)ethynyl)benzenesulfonamide (1o)



1o

Compound **1o** was prepared in 58% yield (340.2 mg) according to the general procedure. The substrate was isolated through silica gel column chromatography (PE:EA = 15:1) as a pale yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 8.27 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 9.0 Hz, 2H), 7.75 (d, J = 9.0 Hz, 2H), 7.57 (d, J = 9.0 Hz, 2H), 7.42 – 7.34 (m, 3H), 6.71 – 6.64 (m, 2H), 6.60 (d, J = 1.5 Hz, 1H), 5.93 (s, 2H), 4.66 (s, 2H), 3.72 – 3.62 (m, 1H), 1.25 (d, J = 7.0 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 149.3, 148.3, 147.3, 136.2, 133.6, 132.2, 131.5, 129.7, 129.1, 128.7, 127.9, 126.8, 126.5, 126.1, 125.5, 123.1, 116.9, 114.7, 111.4, 108.4, 101.4, 89.9, 86.9, 79.3, 68.1, 43.2, 32.1, 23.1; IR (neat): 2962(bs), 2231(s), 1574, 1490, 1365, 1213, 1069, 1034, 817 cm⁻¹; HRESIMS Calcd for [C₃₁H₂₄BrNNaO₄S]⁺ (M + Na⁺) 608.0502, found 608.0510.

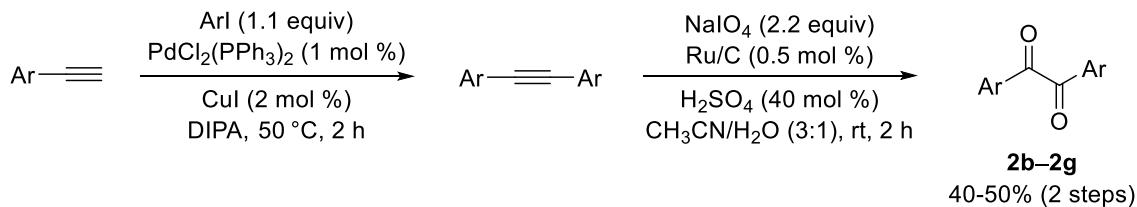
4-bromo-N-((2-isopropynaphthalen-1-yl)ethynyl)-N-(3-(thiophen-2-yl)prop-2-yn-1-yl)benzenesulfonamide (1p)



1p

Compound **1p** was prepared in 45% yield (228.6 mg) according to the general procedure. The substrate was isolated through silica gel column chromatography (PE:EA = 15:1) as a pale yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 8.25 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 8.5 Hz, 2H), 7.78 – 7.74 (m, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.42 – 7.35 (m, 3H), 7.25 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.02 (dd, *J* = 3.5, 1.0 Hz, 1H), 6.93 (dd, *J* = 5.0, 3.5 Hz, 1H), 4.71 (s, 2H), 3.70 – 3.59 (m, 1H), 1.25 (d, *J* = 7.0 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 149.5, 136.1, 133.7, 132.9, 132.4, 131.6, 129.7, 129.4, 128.8, 127.9, 126.9, 126.8, 126.1, 125.6, 123.1, 121.4, 116.8, 89.7, 84.9, 80.3, 68.2, 43.3, 32.2, 23.1; IR (neat): 2961(bs), 2868, 2232(s), 1591, 1574, 1470, 1174, 1069, 912 cm⁻¹; HRESIMS Calcd for [C₂₈H₂₂BrNNaO₂S₂]⁺ (M + Na⁺) 570.0168, found 570.0161.

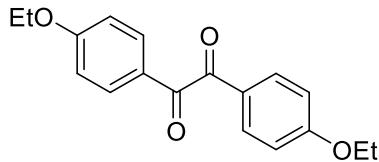
3.2 General procedure for the synthesis of 1,2-diketones **2** (**2b–2g**) ^{3,4}



To a solution of terminal aryl acetylene (2.0 mmol) in diisopropylamine (10 mL) were added copper iodide (0.04 mmol, 7.6 mg), Pd(PPh₃)₂Cl₂ (0.01 mmol, 7.0 mg) and aryl iodide (2.2 mmol) sequentially. The reaction was stirred at 50 °C for 2 h. Upon completion (monitored by TLC), the reaction mixture was filtered through a Celite pad and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: PE/EtOAc) to afford the target internal alkyne.

To a solution of the above internal alkyne (2 mmol) in CH₃CN/H₂O (3:1, 10 mL) were added Ru/C (5% on carbon, 0.5 mol %, 20.0 mg), concentrated H₂SO₄ (0.8 mmol) and NaIO₄ (4.4 mmol, 941.1 mg) sequentially. The reaction was stirred at room temperature for 2 h. Upon completion (monitored by TLC), the reaction mixture was filtered through a Celite pad and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: PE/EtOAc) to afford the target product **2** (40–50% yield). 1,2-diketones **2a** and **2f** are commercially available compounds.

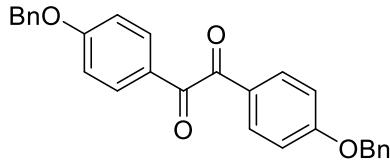
1,2-bis(4-ethoxyphenyl)ethane-1,2-dione (2b)



2b

Compound **2b** was prepared in 50% yield (149.2 mg) according to the general procedure. The substrate was isolated through silica gel column chromatography (PE:EA = 15:1) as a white solid (mp 148–149 °C). ¹H NMR (500 MHz, CDCl₃) δ 7.93 (d, *J* = 9.0 Hz, 4H), 6.94 (d, *J* = 9.0 Hz, 4H), 4.11 (q, *J* = 7.0 Hz, 4H), 1.44 (t, *J* = 7.0 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 193.5, 164.3, 132.3, 126.1, 114.7, 64.0, 14.6; IR (neat): 2978(bs), 2860, 1657(s), 1574, 1510, 1477, 1312, 1167, 921, 850 cm⁻¹; HRESIMS Calcd for [C₁₈H₁₈NaO₄]⁺ (M + Na⁺) 321.1089, found 321.1087.

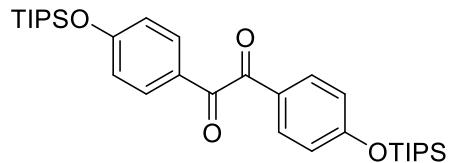
1,2-bis(4-(benzyloxy)phenyl)ethane-1,2-dione (2c)



2c

Compound **2c** was prepared in 45% yield (190.1 mg) according to the general procedure. The substrate was isolated through silica gel column chromatography (PE:EA = 18:1) as yellow solid (mp 180–181 °C). ¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, *J* = 9.2 Hz, 4H), 7.41 – 7.30 (m, 10H), 7.01 (d, *J* = 8.8 Hz, 4H), 5.11 (s, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 193.3, 163.9, 135.8, 132.3, 128.7, 128.3, 127.4, 126.4, 115.1, 70.2; IR (neat): 3067(bs), 3035, 2915, 1668(s), 1601, 1498, 1313, 1169, 898, 852 cm⁻¹; HRESIMS Calcd for [C₂₈H₂₂NaO₄]⁺ (M + Na⁺) 445.1410, found 445.1417.

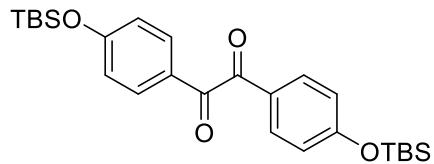
1,2-bis(4-((triisopropylsilyl)oxy)phenyl)ethane-1,2-dione (2d)



2d

Compound **2d** was prepared in 40% yield (222.0 mg) according to the general procedure. The substrate was isolated through silica gel column chromatography (PE:EA = 30:1) as yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, *J* = 8.8 Hz, 4H), 6.94 (d, *J* = 8.8 Hz, 4H), 1.33 – 1.25 (m, 6H), 1.10 (d, *J* = 7.2 Hz, 36H); ¹³C NMR (100 MHz, CDCl₃) δ 193.4, 162.2, 132.3, 126.5, 120.1, 17.8, 12.7; IR (neat): 3041(bs), 2943, 2869, 1668(s), 1596, 1464, 1368, 1156, 997, 848 cm⁻¹; HRESIMS Calcd for [C₃₂H₅₀NaO₄Si₂]⁺ (M + Na⁺) 577.3140, found 577.3134.

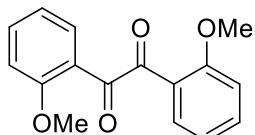
1,2-bis(4-(benzyloxy)phenyl)ethane-1,2-dione (2e)



2e

Compound **2e** was prepared in 43% yield (202.4 mg) according to the general procedure. The substrate was isolated through silica gel column chromatography (PE:EA = 30:1) as yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 8.8 Hz, 4H), 6.91 (d, *J* = 8.8 Hz, 4H), 0.98 (s, 18H), 0.24 (s, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 193.4, 161.7, 132.2, 126.7, 120.3, 25.5, 18.2, -4.4; IR (neat): 3044(bs), 2953, 2871, 1668(s), 1599, 1465, 1366, 1157, 998, 841 cm⁻¹; HRESIMS Calcd for [C₂₆H₃₈NaO₄Si₂]⁺ (M + Na⁺) 493.2201, found 493.2190.

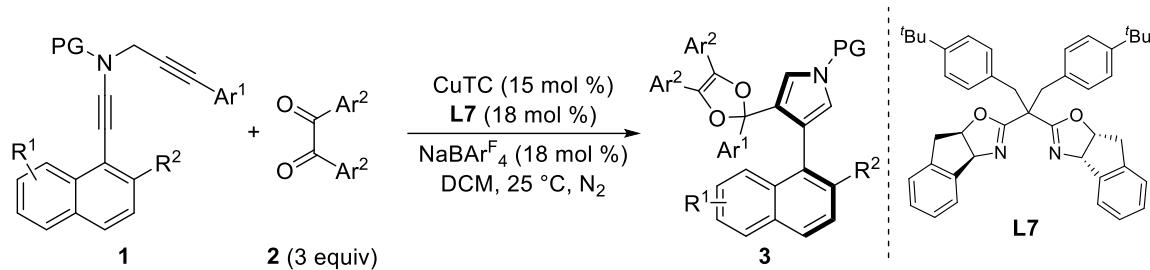
1,2-bis(2-methoxyphenyl)ethane-1,2-dione (2g)



2g

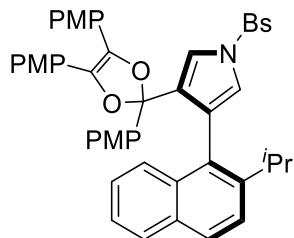
Compound **2g** was prepared in 45% yield (121.6 mg) according to the general procedure. The substrate was isolated through silica gel column chromatography (PE:EA = 15:1) as a pale brown solid (mp 154–155 °C). ¹H NMR (400 MHz, CDCl₃) δ 8.08 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.63 – 7.52 (m, 2H), 7.16 – 7.09 (m, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 3.58 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 192.4, 160.3, 135.5, 130.4, 123.4, 121.3, 112.5, 55.8; IR (neat): 2931(bs), 2887, 2856, 1667(s), 1593, 1472, 1277, 1158, 906, 842 cm⁻¹; HRESIMS Calcd for [C₁₆H₁₄NaO₄]⁺ (M + Na⁺) 293.0784, found 293.0778.

3.3 General procedure for the synthesis of axially chiral naphthylpyrroles **3**:



The powered CuTC (0.015 mmol, 2.9 mg), ligand **L7** (0.018 mmol, 11.2 mg) and NaBArF₄ (0.018 mmol, 16.0 mg) were introduced into an oven-dried vial tube under nitrogen atmosphere. After adding DCM (2.5 mL) into the vial tube, the solution was stirred at 30 °C under the nitrogen atmosphere for 2 h. Then the solution of *N*-propargyl ynamide **1** (0.1 mmol) and diketone **2** (0.3 mmol) in DCM (2.5 mL) was introduced into the system subsequently. The resulting mixture was stirred at 25 °C and the progress of the reaction was monitored by TLC. Upon completion, the mixture was concentrated under reduced pressure, and the residue was purified chromatography on silica gel (eluent: toluene/acetone) to give the desired axially chiral naphthylpyrrole **3**.

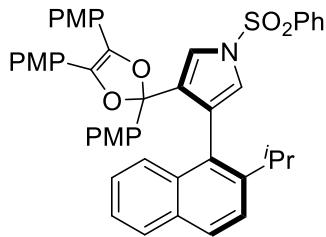
(*S*)-1-((4-bromophenyl)sulfonyl)-3-(2-isopropylnaphthalen-1-yl)-4-(2,4,5-tris(4-methoxyphenyl)-1,3-dioxol-2-yl)-1*H*-pyrrole (**3a**)



3a

Compound **3a** was prepared in 72% yield (60.7 mg) according to the general procedure. Pale yellow solid (mp 211–212 °C). $[\alpha]_D^{25} = +28.1^\circ$ ($c = 1.0$, CHCl_3). 93% ee (determined by HPLC: Chiraldak IC Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; TR = 5.81 min (minor), 6.51 min (major)). ^1H NMR (600 MHz, CDCl_3) δ 7.73 (d, $J = 8.4$ Hz, 2H), 7.71 – 7.63 (m, 4H), 7.30 – 7.26 (m, 2H), 7.22 (d, $J = 9.0$ Hz, 2H), 7.20 – 7.16 (m, 2H), 7.15 – 7.10 (m, 1H), 7.05 (d, $J = 2.4$ Hz, 1H), 6.91 (d, $J = 8.4$ Hz, 2H), 6.72 (d, $J = 9.0$ Hz, 2H), 6.65 (d, $J = 8.4$ Hz, 2H), 6.62 (d, $J = 8.4$ Hz, 2H), 6.59 (d, $J = 9.0$ Hz, 2H), 3.76 (s, 3H), 3.74 (s, 3H), 3.72 (s, 3H), 2.79 – 2.72 (m, 1H), 0.96 (d, $J = 6.6$ Hz, 3H), 0.89 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 159.5, 158.9, 158.8, 145.2, 137.8, 133.8, 133.2, 132.7, 131.9, 131.7, 131.4, 129.3, 128.3, 128.2, 127.7, 127.5(4), 127.4(9), 127.1(3), 127.0(7), 126.9, 126.1, 125.2, 124.4, 122.9, 121.6, 121.3(3), 121.3(0), 113.3(1), 113.2(5), 112.9, 108.0, 55.1(7), 55.1(5), 30.8, 25.7, 21.4; IR (neat): 2957(bs), 2924, 1608, 1515, 1392, 1174, 1124, 1066, 832, 745 cm^{-1} ; HRESIMS Calcd for $[\text{C}_{47}\text{H}_{40}\text{BrNNaO}_7\text{S}]^+$ ($M + \text{Na}^+$) 864.1601, found 864.1598.

(S)-3-(2-isopropylnaphthalen-1-yl)-1-(phenylsulfonyl)-4-(2,4,5-tris(4-methoxyphenyl)-1,3-dioxol-2-yl)-1*H*-pyrrole (3b)

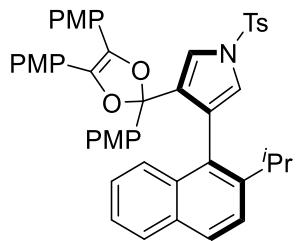


3b

Compound **3b** was prepared in 65% yield (49.7 mg) according to the general procedure. Pale yellow oil. $[\alpha]_D^{25} = +28.1^\circ$ ($c = 1.0$, CHCl_3). 89% ee (determined by HPLC: Chiraldak IA Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; TR = 5.91 min (major), 6.35 min (minor)). ^1H NMR (500 MHz, CDCl_3) δ 7.88 (d, $J = 7.5$ Hz, 2H), 7.70 – 7.63 (m, 3H), 7.56 – 7.52 (m, 2H), 7.27 (d, $J = 8.5$ Hz, 2H), 7.24 – 7.19 (m, 4H), 7.13 – 7.09 (m, 1H), 7.07 (d, $J = 2.5$ Hz, 1H), 6.90 (d, $J = 9.0$ Hz, 2H), 6.70 (d, $J = 8.5$ Hz, 2H), 6.66 – 6.61 (m, 4H), 6.58 (d, $J = 8.5$ Hz, 2H), 3.75 (s, 3H), 3.73 (s, 3H), 3.72 (s, 3H),

2.83 – 2.71 (m, 1H), 0.94 (d, J = 7.0 Hz, 3H), 0.87 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.5, 158.9, 158.8, 145.3, 138.9, 134.0, 133.9, 133.4, 131.8, 131.7, 131.5, 130.9, 129.4, 128.1, 127.8, 127.7, 127.6, 127.2, 127.1, 126.9, 126.8, 125.7, 125.2, 124.3, 122.9, 121.7, 121.4, 121.4, 113.3, 113.2, 112.9, 108.1, 55.2, 55.1, 30.8, 25.6, 21.5; IR (neat): 2958(bs), 2925, 1607, 1515, 1248, 1173, 1089, 1066, 831, 744 cm^{-1} ; HRESIMS Calcd for $[\text{C}_{47}\text{H}_{41}\text{NNaO}_7\text{S}]^+$ ($\text{M} + \text{Na}^+$) 786.2496, found 786.2500.

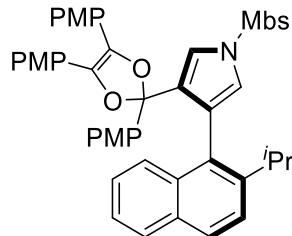
(*S*)-3-(2-isopropylnaphthalen-1-yl)-1-tosyl-4-(2,4,5-tris(4-methoxyphenyl)-1,3-dioxol-2-yl)-1*H*-pyrrole (3c)



3c

Compound **3c** was prepared in 73% yield (56.8 mg) according to the general procedure. Pale yellow solid (mp 185–186 °C). $[\alpha]_D^{25} = +131.2^\circ$ ($c = 1.0$, CHCl_3). 92% ee (determined by HPLC: Chiralpak IC Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; TR = 6.54 min (minor), 7.35 min (major)). ^1H NMR (600 MHz, CDCl_3) δ 7.76 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.4 Hz, 1H), 7.65 (d, J = 7.8 Hz, 1H), 7.33 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.25 – 7.22 (m, 3H), 7.18 (d, J = 2.4 Hz, 1H), 7.14 – 7.09 (m, 1H), 7.06 (d, J = 2.4 Hz, 1H), 6.90 (d, J = 9.0 Hz, 2H), 6.69 (d, J = 9.0 Hz, 2H), 6.67 – 6.59 (m, 4H), 6.58 (d, J = 9.0 Hz, 2H), 3.75 (s, 3H), 3.73 (s, 3H), 3.72 (s, 3H), 2.84 – 2.75 (m, 1H), 2.46 (s, 3H), 0.95 (d, J = 6.6 Hz, 3H), 0.88 (d, J = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 159.5, 158.8, 158.7, 145.3, 145.1, 135.9, 133.9, 133.4, 131.8, 131.7, 131.5, 130.6, 130.0, 128.0, 127.9, 127.7, 127.5, 127.3, 127.1, 126.9(3), 126.8(8), 125.4, 125.1, 124.3, 122.9, 121.7, 121.4, 121.3, 113.3, 113.2, 112.9, 108.1, 55.1(7), 55.1(5), 30.8, 25.7, 21.7, 21.5; IR (neat): 2958(bs), 2925, 1959, 1608, 1515, 1248, 1173, 1066 cm^{-1} ; HRESIMS Calcd for $[\text{C}_{48}\text{H}_{43}\text{NNaO}_7\text{S}]^+$ ($\text{M} + \text{Na}^+$) 800.2652, found 800.2640.

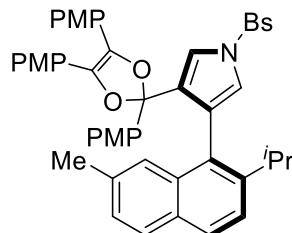
(S)-3-(2-isopropylnaphthalen-1-yl)-1-((4-methoxyphenyl)sulfonyl)-4-(2,4,5-tris(4-methoxyphenyl)-1,3-dioxol-2-yl)-1*H*-pyrrole (3d)



3d

Compound **3d** was prepared in 70% yield (55.6 mg) according to the general procedure. Pale yellow solid (mp 199–200 °C). $[\alpha]_D^{25} = +28.1^\circ$ ($c = 1.0$, CHCl_3). 94% ee (determined by HPLC: Chiralpak IC Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; TR = 8.12 min (minor), 9.16 min (major)). ^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, $J = 8.8$ Hz, 2H), 7.70 – 7.64 (m, 2H), 7.28 (d, $J = 8.4$ Hz, 2H), 7.25 – 7.20 (m, 3H), 7.17 (d, $J = 2.4$ Hz, 1H), 7.15 – 7.10 (m, 1H), 7.06 (d, $J = 2.4$ Hz, 1H), 6.98 (d, $J = 8.8$ Hz, 2H), 6.91 (d, $J = 8.8$ Hz, 2H), 6.69 (d, $J = 8.8$ Hz, 2H), 6.65 (d, $J = 6.6$ Hz, 2H), 6.63 (d, $J = 6.6$ Hz, 2H), 6.58 (d, $J = 8.8$ Hz, 2H), 3.89 (s, 3H), 3.75 (s, 3H), 3.73 (s, 3H), 3.72 (s, 3H), 2.85 – 2.75 (m, 1H), 0.96 (d, $J = 6.8$ Hz, 3H), 0.88 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.9, 159.5, 158.8, 158.7, 145.3, 133.9, 133.4, 131.8, 131.7, 131.5, 130.5, 130.3, 129.2, 128.0(2), 127.9(5), 127.7, 127.5, 127.3, 127.1, 126.9, 125.3, 125.1, 124.3, 122.9, 121.7, 121.2(4), 121.2(0), 114.6, 113.3, 113.2, 112.9, 108.2, 55.8, 55.2, 30.8, 25.7, 21.5; IR (neat): 2955(bs), 2920, 1959, 1595, 1516, 1374, 1248, 1167 cm^{-1} ; HRESIMS Calcd for $[\text{C}_{48}\text{H}_{43}\text{NNaO}_8\text{S}]^+$ ($\text{M} + \text{Na}^+$) 816.2602, found 816.2592.

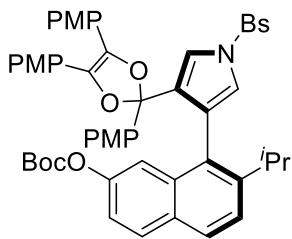
(S)-1-((4-bromophenyl)sulfonyl)-3-(2-isopropyl-7-methylnaphthalen-1-yl)-4-(2,4,5-tris(4-methoxyphenyl)-1,3-dioxol-2-yl)-1*H*-pyrrole (3e)



3e

Compound **3e** was prepared in 61% yield (52.3 mg) according to the general procedure. Pale yellow oil. $[\alpha]_D^{25} = +18.5^\circ$ ($c = 1.0$, CHCl_3). 96% ee (determined by HPLC: Chiralpak ODH Column, 10/90 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; TR = 8.45 min (major), 19.78 min (minor)). ^1H NMR (500 MHz, CDCl_3) δ 7.73 (d, $J = 8.5$ Hz, 2H), 7.68 – 7.64 (m, 3H), 7.53 (d, $J = 8.5$ Hz, 1H), 7.29 (d, $J = 2.5$ Hz, 1H), 7.23 (d, $J = 8.5$ Hz, 1H), 7.15 (d, $J = 9.0$ Hz, 2H), 7.07 – 7.04 (m, 1H), 7.02 (d, $J = 2.5$ Hz, 1H), 6.93 (d, $J = 8.5$ Hz, 2H), 6.86 (d, $J = 8.5$ Hz, 2H), 6.80 (s, 1H), 6.65 (d, $J = 7.0$ Hz, 2H), 6.64 (d, $J = 7.0$ Hz, 2H), 6.56 (d, $J = 8.5$ Hz, 2H), 3.75 (s, 3H), 3.74 (s, 3H), 3.68 (s, 3H), 2.78 – 2.69 (m, 1H), 2.14 (s, 3H), 0.95 (d, $J = 7.0$ Hz, 3H), 0.93 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.4, 158.9, 158.9, 145.2, 137.9, 134.6, 133.8, 133.1, 132.7, 131.8, 131.6, 129.6, 129.2, 128.2, 127.9, 127.6(1), 127.5(7), 126.9, 126.7(8), 126.7(6), 126.6, 126.2, 126.1, 122.0, 121.7, 121.6, 121.3, 120.9, 113.3(2), 113.2(9), 112.7, 108.0, 55.2, 55.1, 30.8, 25.6, 21.8, 21.6; IR (neat): 2958(bs), 2928, 1608, 1574, 1299, 1175, 1089, 1065, 832, 745 cm^{-1} ; HRESIMS Calcd for $[\text{C}_{48}\text{H}_{42}\text{BrNNaO}_7\text{S}]^+$ ($\text{M} + \text{Na}^+$) 878.1758, found 878.1769.

(*S*)-8-((4-bromophenyl)sulfonyl)-4-(2,4,5-tris(4-methoxyphenyl)-1,3-dioxol-2-yl)-1*H*-pyrrol-3-yl)-7-isopropynaphthalen-2-yl tert-butyl carbonate (3f)

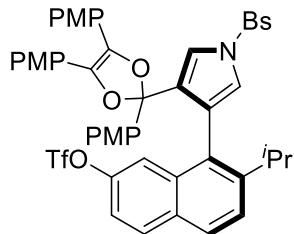


3f

Compound **3f** was prepared in 50% yield (47.9 mg) according to the general procedure. Pale yellow solid (mp 210–212 °C). $[\alpha]_D^{25} = +120.1^\circ$ ($c = 1.0$, CHCl_3). 88% ee (determined by HPLC: Chiralpak ODH Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; TR = 6.52 min (major), 10.48 min (minor)). ^1H NMR (500 MHz, CDCl_3) δ 7.74 (d, $J = 8.5$ Hz, 2H), 7.68 (d, $J = 8.5$ Hz, 2H), 7.65 (d, $J = 9.0$ Hz, 1H), 7.63 (d, $J = 9.0$ Hz, 1H), 7.26 – 7.22 (m, 3H), 7.19 (dd, $J = 8.5, 2.5$ Hz, 1H), 7.15 (d, $J = 2.5$ Hz, 1H), 7.10 (d, $J = 2.5$ Hz, 1H), 7.08 (d, $J = 2.5$ Hz, 1H), 6.99 (d, $J = 9.0$ Hz, 2H), 6.77 (d, $J = 9.0$ Hz, 2H),

6.68 (d, $J = 8.5$ Hz, 2H), 6.61 (d, $J = 7.0$ Hz, 2H), 6.60 (d, $J = 7.0$ Hz, 2H), 3.75 (s, 3H), 3.73 (s, 3H), 3.71 (s, 3H), 2.84 – 2.71 (m, 1H), 1.57 (s, 9H), 0.93 (d, $J = 7.0$ Hz, 3H), 0.91 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.5, 159.0, 158.7, 151.8, 148.4, 146.2, 137.9, 134.4, 133.0, 132.8, 131.8, 131.7, 131.0, 129.3, 128.4, 128.3, 127.9, 127.4, 127.2, 126.9, 125.3, 122.8, 121.7, 121.6, 121.2, 119.5, 117.3, 113.4, 113.3, 112.9, 107.9, 83.2, 55.2, 55.1(2), 55.1(0), 30.8, 27.8, 25.7, 21.3; IR (neat): 2958(bs), 2933, 1758, 1515, 1298, 1249, 1173, 1089, 834, 745 cm^{-1} ; HRESIMS Calcd for $[\text{C}_{52}\text{H}_{48}\text{BrNNaO}_{10}\text{S}]^+$ ($M + \text{Na}^+$) 980.2075, found 980.2076.

(*S*)-8-((4-bromophenyl)sulfonyl)-4-(2,4,5-tris(4-methoxyphenyl)-1,3-dioxol-2-yl)-1*H*-pyrrol-3-yl)-7-isopropynaphthalen-2-yl trifluoromethanesulfonate (3g)

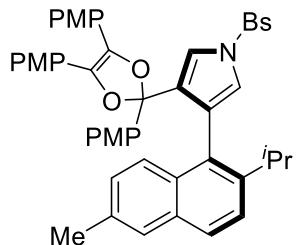


3g

Compound **3g** was prepared in 76% yield (75.3 mg) according to the general procedure. Pale yellow oil. $[\alpha]_D^{25} = +28.7^\circ$ ($c = 1.0$, CHCl_3). 83% ee (determined by HPLC: Chiralpak IA Column, 10/90 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; TR = 6.03 min (minor), 6.58 min (major)). ^1H NMR (500 MHz, CDCl_3) δ 7.67 (d, $J = 8.5$ Hz, 2H), 7.64 – 7.58 (m, 4H), 7.30 (d, $J = 8.5$ Hz, 1H), 7.19 (d, $J = 8.5$ Hz, 2H), 7.08 (d, $J = 2.5$ Hz, 1H), 7.05 (d, $J = 2.5$ Hz, 1H), 7.04 – 7.00 (m, 2H), 6.88 (d, $J = 8.5$ Hz, 2H), 6.67 (d, $J = 8.5$ Hz, 2H), 6.60 (d, $J = 8.5$ Hz, 2H), 6.58 (d, $J = 8.5$ Hz, 2H), 6.51 (d, $J = 8.5$ Hz, 2H), 3.68 (s, 3H), 3.65 (s, 3H), 3.65 (s, 3H), 2.88 – 2.78 (m, 1H), 0.93 (d, $J = 7.0$ Hz, 3H), 0.89 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.6, 159.0, 158.8, 147.5, 146.8, 137.6, 134.2, 132.9(9), 132.9(5), 131.8, 131.6, 130.9, 130.3, 129.7, 129.6, 128.2, 128.1, 128.0, 127.8, 127.1, 126.9, 124.5, 121.5, 121.4(3), 121.3(5), 121.1, 118.7(0), 118.6(7) (q, $J = 318.8$ Hz), 117.8, 113.4, 113.3, 113.0, 107.8, 55.1(7), 55.1(5), 55.1(1), 31.0, 25.6, 21.4; ^{19}F NMR (376 MHz, CDCl_3) δ -73.0; IR (neat): 2961(bs), 2932, 1608,

1516, 1248, 1213, 1176, 1066, 834, 745 cm⁻¹; HRESIMS Calcd for [C₄₈H₃₉BrF₃NNaO₁₀S₂]⁺ (M + Na⁺) 1012.1043, found 1012.1049.

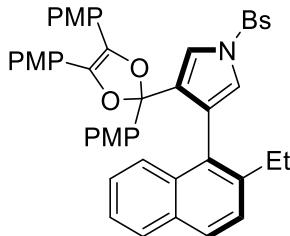
(S)-1-((4-bromophenyl)sulfonyl)-3-(2-isopropyl-6-methylnaphthalen-1-yl)-4-(2,4,5-tris(4-methoxyphenyl)-1,3-dioxol-2-yl)-1*H*-pyrrole (3h)



3h

Compound **3h** was prepared in 63% yield (54.0 mg) according to the general procedure. Pale yellow oil. $[\alpha]_D^{25} = +15.4^\circ$ (c = 1.0, CHCl₃). 89% ee (determined by HPLC: Chiralpak IC Column, 10/90 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; TR = 7.57 min (minor), 8.50 min (major)). ¹H NMR (500 MHz, CDCl₃) δ 7.73 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 9.0 Hz, 1H), 7.42 (s, 1H), 7.25 (s, 1H), 7.24 – 7.21 (m, 2H), 7.18 (d, *J* = 2.5 Hz, 1H), 7.06 (d, *J* = 8.5 Hz, 1H), 7.04 (d, *J* = 2.5 Hz, 1H), 6.92 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.90 (d, *J* = 9.0 Hz, 2H), 6.75 (d, *J* = 9.0 Hz, 2H), 6.65 (d, *J* = 5.0 Hz, 2H), 6.63 (d, *J* = 5.0 Hz, 2H), 6.61 (d, *J* = 9.0 Hz, 2H), 3.75 (s, 3H), 3.74 (s, 3H), 3.72 (s, 3H), 2.76 – 2.66 (m, 1H), 2.40 (s, 3H), 0.95 (d, *J* = 7.0 Hz, 3H), 0.87 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 159.6, 158.9, 158.8, 144.2, 137.8, 133.8, 133.2, 132.8, 132.7, 132.0, 131.9, 131.7, 131.6, 131.5, 129.2, 128.3, 128.2, 127.6(5), 127.5(7), 127.4, 127.3, 127.0, 126.9, 126.3, 126.0, 122.9, 121.7, 121.3, 121.3, 113.3, 113.2, 112.9, 108.0, 55.2, 55.1, 30.7, 25.7, 21.5, 21.3; IR (neat): 2958(bs), 2926, 1608, 1516, 1249, 1174, 1089, 1067, 831, 745 cm⁻¹; HRESIMS Calcd for [C₄₈H₄₂BrNNaO₇S]⁺ (M + Na⁺) 878.1758, found 878.1765.

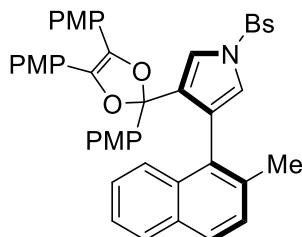
(S)-1-((4-bromophenyl)sulfonyl)-3-(2-ethylnaphthalen-1-yl)-4-(2,4,5-tris(4-methoxyphenyl)-1,3-dioxol-2-yl)-1*H*-pyrrole (3i)



3i

Compound **3i** was prepared in 74% yield (61.3 mg) according to the general procedure. Pale yellow solid (mp 188–190 °C). $[\alpha]_D^{25} = +28.1^\circ$ ($c = 1.0$, CHCl_3). 88% ee (determined by HPLC: Chiralpak IC Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; TR = 6.42 min (minor), 7.12 min (major)). ^1H NMR (400 MHz, CDCl_3) δ 7.76 – 7.66 (m, 4H), 7.66 – 7.60 (m, 2H), 7.32 – 7.26 (m, 1H), 7.24 – 7.11 (m, 6H), 7.09 – 7.03 (m, 1H), 6.96 (d, $J = 8.4$ Hz, 2H), 6.68 (d, $J = 8.4$ Hz, 4H), 6.64 (d, $J = 8.4$ Hz, 2H), 6.58 (d, $J = 8.4$ Hz, 2H), 3.77 (s, 3H), 3.73 (s, 6H), 2.37 – 2.24 (m, 1H), 2.17 – 2.06 (m, 1H), 0.91 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.6, 158.9, 158.8, 141.5, 137.8, 133.9, 133.0, 132.8, 131.7, 131.6(3), 131.5(7), 131.5(1), 129.3, 128.3, 128.0, 127.9, 127.5, 127.4, 127.3, 126.9, 126.7, 126.4, 126.3, 125.3, 124.3, 121.7, 121.6, 121.2, 120.9, 113.4, 113.3, 112.9, 107.8, 55.1(8), 55.1(6), 27.3, 15.7; IR (neat): 2951(bs), 2924, 1608, 1515, 1391, 1248, 1174, 1063 cm^{-1} ; HRESIMS Calcd for $[\text{C}_{46}\text{H}_{38}\text{BrNNaO}_7\text{S}]^+$ ($M + \text{Na}^+$) 850.1445, found 850.1440.

(*S*)-1-((4-bromophenyl)sulfonyl)-3-(2-methylnaphthalen-1-yl)-4-(2,4,5-tris(4-methoxyphenyl)-1,3-dioxol-2-yl)-1*H*-pyrrole (3j)

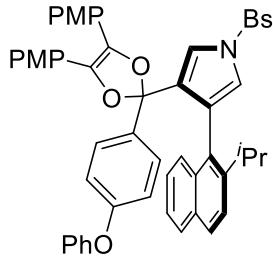


3j

Compound **3j** was prepared in 71% yield (57.8 mg) according to the general procedure. Pale yellow oil. $[\alpha]_D^{25} = +28.1^\circ$ ($c = 1.0$, CHCl_3). 86% ee (determined by HPLC: Chiralpak IC Column, 5/95 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; TR = 15.39 min (minor), 17.11 min (major)). ^1H NMR (400 MHz, CDCl_3) δ 7.74 (d, $J = 8.8$ Hz, 2H), 7.70

– 7.63 (m, 3H), 7.59 (d, J = 8.4 Hz, 1H), 7.32 – 7.26 (m, 1H), 7.23 – 7.13 (m, 5H), 7.10 (d, J = 8.4 Hz, 1H), 7.04 (d, J = 2.4 Hz, 1H), 6.98 (d, J = 8.8 Hz, 2H), 6.74 – 6.66 (m, 4H), 6.63 (d, J = 8.4 Hz, 2H), 6.59 (d, J = 8.4 Hz, 2H), 3.77 (s, 3H), 3.74 (s, 3H), 3.73 (s, 3H), 1.93 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.6, 158.9, 158.8, 137.8, 135.6, 133.9, 133.0, 132.8, 131.7, 131.6, 131.5, 129.3, 128.7, 128.3, 127.9, 127.6, 127.5, 127.4, 127.3, 126.9, 126.6, 126.5, 125.3, 124.2, 121.7, 121.6, 120.9, 113.4, 113.3, 112.9, 107.8, 55.1(8), 55.1(6), 20.8; IR (neat): 2920(bs), 2853, 1958, 1608, 1515, 1391, 1248, 1174 cm^{-1} ; HRESIMS Calcd for $[\text{C}_{45}\text{H}_{36}\text{BrNNaO}_7\text{S}]^+$ ($\text{M} + \text{Na}^+$) 836.1288, found 836.1273.

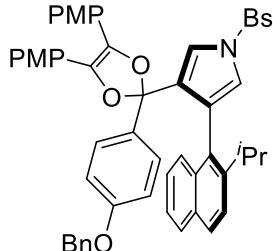
(*S*)-3-(4,5-bis(4-methoxyphenyl)-2-(4-phenoxyphenyl)-1,3-dioxol-2-yl)-1-((4-bromophenyl)sulfonyl)-4-(2-isopropynaphthalen-1-yl)-1*H*-pyrrole (3k)



3k

Compound **3k** was prepared in 57% yield (51.6 mg) according to the general procedure. Pale yellow oil. $[\alpha]_D^{25} = +24.9^\circ$ ($c = 1.0$, CHCl_3). 90% ee (determined by HPLC: Chiralpak IC Column, 5/95 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; TR = 10.13 min (minor), 12.66 min (major)). ^1H NMR (500 MHz, CDCl_3) δ 7.74 (d, J = 8.5 Hz, 2H), 7.71 – 7.66 (m, 4H), 7.35 – 7.28 (m, 4H), 7.25 – 7.23 (m, 3H), 7.21 – 7.18 (m, 1H), 7.17 – 7.14 (m, 1H), 7.12 – 7.09 (m, 1H), 7.06 (d, J = 2.5 Hz, 1H), 6.98 – 6.95 (m, 2H), 6.93 (d, J = 8.5 Hz, 2H), 6.77 (d, J = 8.5 Hz, 2H), 6.70 (d, J = 9.0 Hz, 2H), 6.66 (d, J = 9.0 Hz, 2H), 6.62 (d, J = 9.0 Hz, 2H), 3.76 (s, 3H), 3.74 (s, 3H), 2.82 – 2.72 (m, 1H), 0.96 (d, J = 7.0 Hz, 3H), 0.91 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.0, 158.9, 157.6, 156.4, 145.3, 137.8, 135.5, 133.8, 132.8(1), 132.7(6), 131.9, 131.8, 131.5, 131.1, 129.7, 129.3, 128.2(9), 128.2(5), 127.6, 127.4, 127.2, 127.1, 127.0, 126.0, 125.2, 124.5, 123.6, 122.9, 121.5, 121.4, 121.3, 119.5, 117.1, 113.4, 113.3, 107.9, 55.1(9), 55.1(8), 30.8, 25.7, 21.5; IR (neat): 2958(bs), 2928, 1516, 1247, 1177, 1090, 1066, 1033, 832, 744 cm^{-1} ; HRESIMS Calcd for $[\text{C}_{52}\text{H}_{42}\text{BrNNaO}_7\text{S}]^+$ ($\text{M} + \text{Na}^+$) 926.1758, found 926.1788.

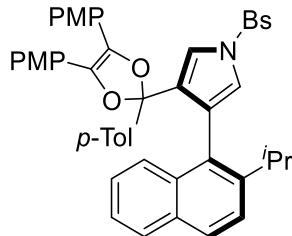
(S)-3-(2-(4-(benzyloxy)phenyl)-4,5-bis(4-methoxyphenyl)-1,3-dioxol-2-yl)-1-((4-bromophenyl)sulfonyl)-4-(2-isopropynaphthalen-1-yl)-1*H*-pyrrole (3l)



3l

Compound **3l** was prepared in 72% yield (66.2 mg) according to the general procedure. Pale yellow oil. $[\alpha]_D^{25} = +34.5^\circ$ ($c = 1.0$, CHCl_3). 89% ee (determined by HPLC: Chiralpak IA Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; TR = 7.48 min (major), 8.43 min (minor)). ^1H NMR (500 MHz, CDCl_3) δ 7.72 (d, $J = 8.5$ Hz, 2H), 7.70 – 7.61 (m, 4H), 7.42 – 7.36 (m, 4H), 7.33 – 7.29 (m, 1H), 7.29 – 7.25 (m, 2H), 7.23 – 7.20 (m, 3H), 7.19 – 7.16 (m, 1H), 7.14 – 7.10 (m, 1H), 7.05 (d, $J = 2.5$ Hz, 1H), 6.92 (d, $J = 8.5$ Hz, 2H), 6.74 (d, $J = 8.5$ Hz, 2H), 6.69 (d, $J = 9.0$ Hz, 2H), 6.65 (d, $J = 9.0$ Hz, 2H), 6.60 (d, $J = 8.5$ Hz, 2H), 4.94 (s, 2H), 3.74 (s, 3H), 3.73 (s, 3H), 2.89 – 2.67 (m, 1H), 0.95 (d, $J = 7.0$ Hz, 3H), 0.88 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 158.9, 158.8(4), 158.8(0), 145.2, 137.7, 136.9, 133.8, 133.4, 132.8, 132.7, 131.9, 131.7, 131.4(3), 131.4(1), 129.3, 128.6, 128.3, 128.2, 128.0, 127.6, 127.5(4), 127.4(6), 127.1(2), 127.0(6), 126.9, 126.1, 125.2, 124.3, 122.9, 121.6, 121.3(3), 121.2(7), 113.8, 113.3(1), 113.2(7), 108.0, 69.9, 55.1(5), 55.1(3), 30.8, 25.7, 21.4; IR (neat): 2958(bs), 2927, 1607, 1516, 1391, 1247, 1174, 1089, 833, 745 cm^{-1} ; HRESIMS Calcd for $[\text{C}_{52}\text{H}_{43}\text{BrNO}_7\text{S}]^+$ ($M + \text{H}^+$) 918.2095, found 918.2105.

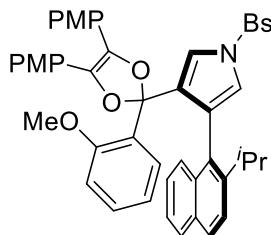
(S)-1-((4-bromophenyl)sulfonyl)-3-(2-isopropynaphthalen-1-yl)-4-(2-(4-methoxyphenyl)-4,5-di-*p*-tolyl-1,3-dioxol-2-yl)-1*H*-pyrrole (3m)



3m

Compound **3m** was prepared in 65% yield (53.7 mg) according to the general procedure. Pale yellow oil. $[\alpha]_D^{25} = +28.1^\circ$ ($c = 1.0$, CHCl_3). 92% ee (determined by HPLC: Chiralpak IC Column, 15/85 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; TR = 5.27 min (minor), 5.90 min (major)). ^1H NMR (400 MHz, CDCl_3) δ 7.78 – 7.62 (m, 6H), 7.31 – 7.25 (m, 2H), 7.23 – 7.09 (m, 5H), 7.05 (d, $J = 2.4$ Hz, 1H), 6.92 (d, $J = 8.0$ Hz, 2H), 6.88 (s, 2H), 6.75 – 6.66 (m, 2H), 6.64 (d, $J = 8.8$ Hz, 2H), 6.58 (d, $J = 8.8$ Hz, 2H), 3.75 (s, 3H), 3.73 (s, 3H), 2.82 – 2.68 (m, 1H), 2.24 (s, 3H), 0.95 (d, $J = 6.8$ Hz, 3H), 0.87 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.9, 158.8, 145.2, 138.1(4), 138.1(0), 137.8, 133.8, 132.7, 131.9, 131.8, 131.5, 131.4, 129.3, 128.3, 128.2, 127.7, 127.6, 127.2, 127.1, 126.3, 125.5, 125.2, 124.3, 122.9, 121.7, 121.5, 121.3, 113.3(1), 113.2(6), 108.1, 55.1(7), 55.1(5), 30.8, 25.7, 21.4, 21.1; IR (neat): 2958(bs), 2921, 1959, 1609, 1510, 1391, 1250, 1064 cm^{-1} ; HRESIMS Calcd for $[\text{C}_{47}\text{H}_{40}\text{BrNNaO}_6\text{S}]^+$ ($M + \text{Na}^+$) 848.1652, found 848.1638.

(*S*)-1-((4-bromophenyl)sulfonyl)-3-(2-isopropynaphthalen-1-yl)-4-(2-(2-methoxyphenyl)-4,5-bis(4-methoxyphenyl)-1,3-dioxol-2-yl)-1*H*-pyrrole (3n)

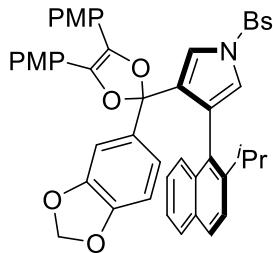


3n

Compound **3n** was prepared in 31% yield (26.1 mg) according to the general procedure. Pale yellow oil. $[\alpha]_D^{25} = +10.0^\circ$ ($c = 1.0$, CHCl_3). 89% ee (determined by HPLC: Chiralpak IC Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; TR = 5.95 min (minor), 7.00 min (major)). ^1H NMR (500 MHz, CDCl_3) δ 7.72 (d, $J = 8.5$ Hz, 2H), 7.65

(d, $J = 8.5$ Hz, 2H), 7.63 – 7.58 (m, 2H), 7.29 – 7.25 (m, 2H), 7.24 – 7.21 (m, 2H), 7.20 – 7.17 (m, 1H), 7.11 – 7.06 (m, 2H), 7.02 (d, $J = 2.5$ Hz, 1H), 6.89 (d, $J = 8.5$ Hz, 2H), 6.82 (d, $J = 8.5$ Hz, 2H), 6.73 (d, $J = 8.0$ Hz, 1H), 6.65 – 6.58 (m, 5H), 3.75 (s, 6H), 3.64 (s, 3H), 2.88 – 2.80 (m, 1H), 1.00 – 0.94 (m, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 158.8, 158.7(9), 157.4, 145.0, 138.2, 133.7, 132.5, 131.9, 131.4(8), 131.4(5), 131.3, 129.9, 128.9, 128.3, 128.2, 128.0, 127.9, 127.7, 127.5, 127.2, 127.0, 126.4, 126.2, 125.0, 124.3, 122.8, 121.8, 121.7, 121.1, 120.9, 119.5, 113.2(8), 113.2(5), 112.4, 107.6, 55.7, 55.2, 30.7, 25.7, 21.7; IR (neat): 2957(bs), 2926, 1606, 1516, 1248, 1178, 1090, 1065, 819, 745 cm^{-1} ; HRESIMS Calcd for $[\text{C}_{47}\text{H}_{40}\text{BrNNaO}_7\text{S}]^+$ ($\text{M} + \text{Na}^+$) 864.1601, found 864.1600.

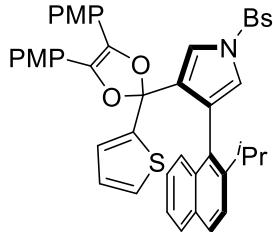
(*S*)-3-(2-(benzo[*d*][1,3]dioxol-5-yl)-4,5-bis(4-methoxyphenyl)-1,3-dioxol-2-yl)-1-((4-bromophenyl)sulfonyl)-4-(2-isopropynaphthalen-1-yl)-1*H*-pyrrole (3o)



3o

Compound **3o** was prepared in 53% yield (45.4 mg) according to the general procedure. Pale yellow solid (mp 226–228 °C). $[\alpha]_D^{25} = +28.1^\circ$ ($c = 1.0$, CHCl_3). 93% ee (determined by HPLC: Chiraldak IE Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; TR = 6.07 min (minor), 6.80 min (major)). ^1H NMR (500 MHz, CDCl_3) δ 7.75 (d, $J = 9.0$ Hz, 2H), 7.72 – 7.61 (m, 4H), 7.32 – 7.25 (m, 3H), 7.15 – 7.10 (m, 2H), 7.05 (d, $J = 2.5$ Hz, 1H), 6.96 (d, $J = 7.5$ Hz, 2H), 6.84 – 6.73 (m, 3H), 6.72 (d, $J = 1.5$ Hz, 1H), 6.67 (d, $J = 8.5$ Hz, 2H), 6.62 (d, $J = 9.0$ Hz, 2H), 6.45 (d, $J = 8.0$ Hz, 1H), 5.83 (d, $J = 1.5$ Hz, 2H), 3.76 (s, 3H), 3.74 (s, 3H), 2.83 – 2.72 (m, 1H), 1.00 – 0.91 (m, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 147.5, 146.9, 145.3, 137.8, 133.7, 132.8, 131.4, 129.3, 128.3, 127.7, 127.4, 127.2, 126.9, 126.0, 125.1, 124.3, 122.9, 121.4, 121.1, 119.2, 113.4, 113.3, 107.2, 106.6, 101.0, 55.1(9), 55.1(7), 30.8, 25.7, 21.5; IR (neat): 2958(bs), 2922, 1608, 1517, 1391, 1248, 1176, 1065 cm^{-1} ; HRESIMS Calcd for $[\text{C}_{47}\text{H}_{38}\text{BrNNaO}_8\text{S}]^+$ ($\text{M} + \text{Na}^+$) 878.1394, found 878.1395.

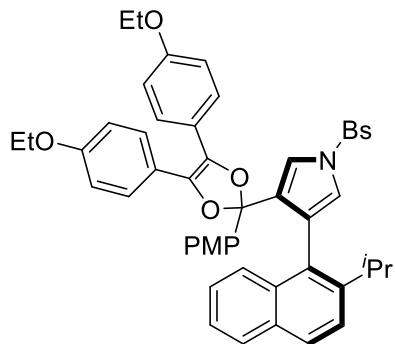
(S)-3-(4,5-bis(4-methoxyphenyl)-2-(thiophen-2-yl)-1,3-dioxol-2-yl)-1-((4-bromophenyl)sulfonyl)-4-(2-isopropynaphthalen-1-yl)-1*H*-pyrrole (3p)



3p

Compound **3p** was prepared in 51% yield (41.8 mg) according to the general procedure. Pale yellow solid (mp 179–180 °C). $[\alpha]_D^{25} = +28.1^\circ$ ($c = 1.0$, CHCl_3). 94% ee (determined by HPLC: Chiralpak IC Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; TR = 5.01 min (minor), 5.32 min (major)). ^1H NMR (600 MHz, CDCl_3) δ 7.75 (d, $J = 9.0$ Hz, 2H), 7.72 – 7.64 (m, 4H), 7.35 – 7.26 (m, 4H), 7.20 – 7.14 (m, 2H), 7.08 (d, $J = 2.4$ Hz, 1H), 6.98 (d, $J = 3.0$ Hz, 1H), 6.88 – 6.79 (m, 3H), 6.63 (d, $J = 7.8$ Hz, 4H), 6.57 (d, $J = 9.0$ Hz, 2H), 3.75 (s, 3H), 3.73 (s, 3H), 2.91 – 2.69 (m, 1H), 0.97 (d, $J = 6.6$ Hz, 3H), 0.87 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 159.0, 158.8, 145.3, 145.1, 137.7, 133.8, 132.8, 131.9, 131.8, 131.5, 130.5, 129.4, 128.3, 128.2, 127.8, 127.5, 127.4, 127.2, 127.1, 126.5, 126.1, 125.7, 125.6, 125.3, 124.4, 123.0, 121.8, 121.3, 121.2, 113.3, 113.2, 106.5, 55.1(7), 55.1(5), 30.9, 25.6, 21.5; IR (neat): 2959(bs), 2925, 2853, 1958, 1667, 1598, 1510, 1251, 1066 cm^{-1} ; HRESIMS Calcd for $[\text{C}_{44}\text{H}_{36}\text{BrNNaO}_6\text{S}_2]^+$ ($M + \text{Na}^+$) 840.1060, found 840.1028.

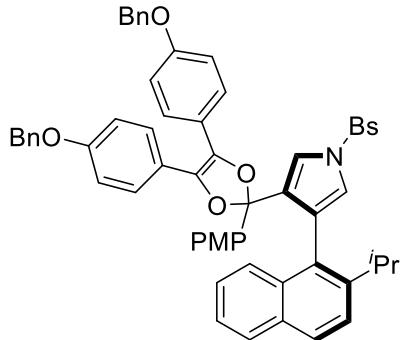
(S)-3-(4,5-bis(4-ethoxyphenyl)-2-(4-methoxyphenyl)-1,3-dioxol-2-yl)-1-((4-bromophenyl)sulfonyl)-4-(2-isopropynaphthalen-1-yl)-1*H*-pyrrole (3q)



3q

Compound **3q** was prepared in 53% yield (46.2 mg) according to the general procedure. Pale yellow oil. $[\alpha]_D^{25} = +61.8^\circ$ ($c = 1.0$, CHCl_3). 92% ee (determined by HPLC: Chiralpak IC Column, 15/85 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; TR = 5.68 min (minor), 6.33 min (major)). ^1H NMR (500 MHz, CDCl_3) δ 7.73 (d, $J = 8.5$ Hz, 2H), 7.69 – 7.64 (m, 4H), 7.28 (d, $J = 8.5$ Hz, 2H), 7.22 (d, $J = 9.0$ Hz, 2H), 7.19 (d, $J = 3.0$ Hz, 1H), 7.18 – 7.15 (m, 1H), 7.14 – 7.11 (m, 1H), 7.05 (d, $J = 2.5$ Hz, 1H), 6.90 (d, $J = 9.0$ Hz, 2H), 6.71 (d, $J = 9.0$ Hz, 2H), 6.64 (d, $J = 9.0$ Hz, 2H), 6.62 (d, $J = 9.0$ Hz, 2H), 6.58 (d, $J = 9.0$ Hz, 2H), 3.99 – 3.93 (m, 4H), 3.71 (s, 3H), 2.81 – 2.70 (m, 1H), 1.39 – 1.35 (m, 6H), 0.95 (d, $J = 7.0$ Hz, 3H), 0.88 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.5, 158.3, 158.2, 145.2, 137.8, 133.8, 133.2, 132.7, 131.9, 131.7, 131.5(2), 131.4(6), 129.3, 128.3, 128.2, 127.6, 127.5(5), 127.5(1), 127.1(2), 127.0(7), 126.9, 126.2, 125.2, 124.3, 122.9, 121.5, 121.4, 121.3, 113.9, 113.8, 112.9, 107.9, 63.4, 63.3, 55.2, 30.8, 25.7, 21.4, 14.8; IR (neat): 2946(bs), 2868, 1670, 1595, 1278, 1185, 1158, 1066, 908, 685 cm^{-1} ; HRESIMS Calcd for $[\text{C}_{49}\text{H}_{45}\text{BrNO}_7\text{S}]^+$ ($\text{M} + \text{H}^+$) 870.2095, found 870.2096.

(*S*)-3-(4,5-bis(4-(benzyloxy)phenyl)-2-(4-methoxyphenyl)-1,3-dioxol-2-yl)-1-((4-bromophenyl)sulfonyl)-4-(2-isopropynaphthalen-1-yl)-1*H*-pyrrole (3r)

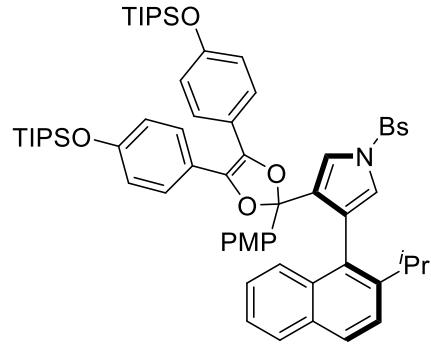


3r

Compound **3r** was prepared in 56% yield (55.7 mg) according to the general procedure. Pale yellow oil. $[\alpha]_D^{25} = +14.0^\circ$ ($c = 1.0$, CHCl_3). 90% ee (determined by HPLC: Chiralpak IC Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; TR = 6.37 min (minor), 7.05 min (major)). ^1H NMR (500 MHz, CDCl_3) δ 7.73 (d, $J = 8.5$ Hz, 2H), 7.69 – 7.65 (m, 3H), 7.64 – 7.61 (m, 1H), 7.42 – 7.35 (m, 8H), 7.34 – 7.30 (m, 2H), 7.27 (d, $J = 9.0$ Hz, 1H), 7.25 – 7.23 (m, 2H), 7.22 (d, $J = 8.5$ Hz, 2H), 7.18 (d, $J = 2.5$ Hz, 1H),

7.17 (s, 1H), 7.13 – 7.09 (m, 1H), 7.05 (d, J = 2.5 Hz, 1H), 6.90 (d, J = 9.0 Hz, 2H), 6.73 – 6.71 (m, 3H), 6.67 (d, J = 9.0 Hz, 2H), 6.63 (d, J = 9.0 Hz, 2H), 5.01 (s, 2H), 4.99 (s, 2H), 3.72 (s, 3H), 2.81 – 2.68 (m, 1H), 0.95 (d, J = 7.0 Hz, 3H), 0.87 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.6, 158.1, 158.0, 145.2, 137.8, 136.8, 133.8, 133.2, 132.7, 131.9, 131.8, 131.4(9), 131.4(6), 129.3, 128.6, 128.3, 128.2, 128.0, 127.7, 127.6, 127.5(0), 127.4(6), 127.1(4), 127.0(7), 126.9, 126.2, 125.2, 124.4, 122.9, 121.9, 121.4, 121.3, 114.3, 114.2, 113.0, 108.0, 69.9(4), 69.9(2), 55.2, 30.8, 25.7, 21.5; IR (neat): 2958(bs), 2925, 2907, 1607, 1514, 1245, 1175, 1089, 1066, 831, 745 cm^{-1} ; HRESIMS Calcd for $[\text{C}_{59}\text{H}_{48}\text{BrKNO}_7\text{S}]^+$ ($\text{M} + \text{K}^+$) 1032.1966, found 1032.1983.

(*S*)-1-((4-bromophenyl)sulfonyl)-3-(2-isopropylnaphthalen-1-yl)-4-(2-(4-methoxyphenyl)-4,5-bis(4-((triisopropylsilyl)oxy)phenyl)-1,3-dioxol-2-yl)-1*H*-pyrrole (3s)

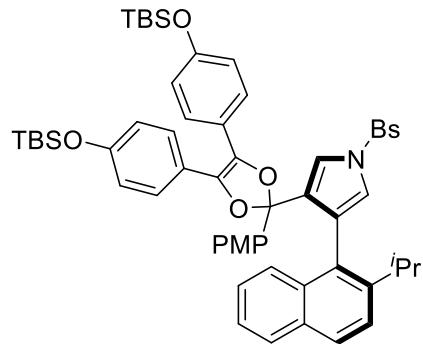


3s

Compound **3s** was prepared in 70% yield (78.9 mg) according to the general procedure. Pale yellow oil. $[\alpha]_D^{25} = +19.5^\circ$ ($c = 1.0$, CHCl_3). 92% ee (determined by HPLC: Chiralpak ODH Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; TR = 4.00 min (major), 5.22 min (minor)). ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, J = 8.8 Hz, 2H), 7.67 (d, J = 8.8 Hz, 2H), 7.65 – 7.59 (m, 2H), 7.28 – 7.26 (m, 2H), 7.25 – 7.22 (m, 2H), 7.19 – 7.16 (m, 1H), 7.14 (d, J = 2.4 Hz, 1H), 7.13 – 7.09 (m, 1H), 7.04 (d, J = 2.4 Hz, 1H), 6.82 (d, J = 8.8 Hz, 2H), 6.70 – 6.58 (m, 6H), 6.55 (d, J = 8.8 Hz, 2H), 3.73 (s, 3H), 2.80 – 2.70 (m, 1H), 1.24 – 1.17 (m, 6H), 1.11 – 1.05 (m, 36H), 0.94 (d, J = 6.8 Hz, 3H), 0.86 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.6, 155.5, 155.3, 145.2, 137.8, 133.8, 133.3, 132.7, 132.0, 131.8, 131.7(2), 131.7(0), 131.5, 129.3, 128.3, 128.2, 127.8, 127.5,

127.4, 127.1, 127.0, 126.9, 126.3, 125.2, 124.3, 122.9, 121.9(3), 121.8(5), 121.4, 119.4, 119.2, 113.0, 107.9, 55.2, 30.8, 25.7, 21.4, 17.9, 12.6; IR (neat): 2946(bs), 2868, 1595, 1508, 1277, 1214, 1159, 1066, 909, 884 cm⁻¹; HRESIMS Calcd for [C₆₃H₇₆BrNNaO₇SSi₂]⁺ (M + Na⁺) 1148.3957, found 1148.3963.

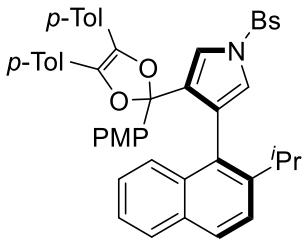
(S)-3-(4,5-bis(4-((tert-butyldimethylsilyl)oxy)phenyl)-2-(4-methoxyphenyl)-1,3-dioxol-2-yl)-1-((4-bromophenyl)sulfonyl)-4-(2-isopropylnaphthalen-1-yl)-1*H*-pyrrole (3t)



3t

Compound **3t** was prepared in 55% yield (57.4 mg) according to the general procedure. Pale yellow oil. $[\alpha]_D^{25} = +1.8^\circ$ (c = 1.0, CHCl₃). 92% ee (determined by HPLC: Chiralpak ODH Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; TR = 3.98 min (major), 5.13 min (minor)). ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 8.8 Hz, 2H), 7.69 – 7.59 (m, 5H), 7.27 (s, 1H), 7.23 (d, *J* = 8.8 Hz, 2H), 7.17 (d, *J* = 2.4 Hz, 1H), 7.16 (s, 1H), 7.12 – 7.09 (m, 1H), 7.04 (d, *J* = 2.4 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 6.64 (d, *J* = 8.8 Hz, 2H), 6.58 (d, *J* = 8.8 Hz, 2H), 6.52 (d, *J* = 8.8 Hz, 2H), 3.72 (s, 3H), 2.79 – 2.71 (m, 1H), 0.98 – 0.93 (m, 21H), 0.87 (d, *J* = 6.8 Hz, 3H), 0.18 – 0.13 (m, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 159.6, 155.1, 154.9, 145.2, 137.8, 133.8, 133.2, 132.7, 131.9, 131.8, 131.6, 131.5, 129.3, 128.3, 128.2, 127.7, 127.5, 127.1(2), 127.0(5), 126.9, 126.2, 125.2, 124.3, 122.9, 122.2(3), 122.1(6), 121.4, 121.3, 119.5, 119.4, 113.0, 107.9, 55.2, 30.8, 25.7, 21.4, 18.2(1), 18.1(8), -4.4; IR (neat): 2957(bs), 2930, 1596, 1508, 1278, 1215, 1185, 1067, 911, 842 cm⁻¹; HRESIMS Calcd for [C₅₇H₆₄BrNNaO₇SSi₂]⁺ (M + Na⁺) 1064.3018, found 1064.3031.

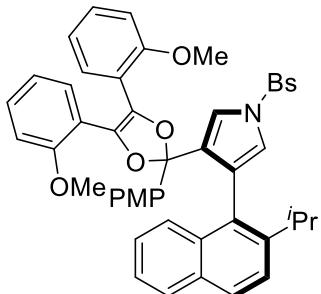
(S)-1-((4-bromophenyl)sulfonyl)-3-(2-isopropynaphthalen-1-yl)-4-(2-(4-methoxyphenyl)-4,5-di-p-tolyl-1,3-dioxol-2-yl)-1*H*-pyrrole (3u)



3u

Compound **3u** was prepared in 67% yield (54.3 mg) according to the general procedure. Pale yellow oil. $[\alpha]_D^{25} = +28.1^\circ$ ($c = 1.0$, CHCl₃). 94% ee (determined by HPLC: Chiralpak IC Column, 5/95 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; TR = 5.98 min (minor), 7.32 min (major)). ¹H NMR (600 MHz, CDCl₃) δ 7.73 (d, $J = 9.0$ Hz, 2H), 7.71 – 7.61 (m, 4H), 7.30 – 7.25 (m, 2H), 7.23 – 7.10 (m, 5H), 7.05 (d, $J = 2.4$ Hz, 1H), 6.96 – 6.89 (m, 4H), 6.87 (d, $J = 7.8$ Hz, 2H), 6.71 (d, $J = 7.8$ Hz, 2H), 6.60 (d, $J = 8.4$ Hz, 2H), 3.70 (s, 3H), 2.80 – 2.71 (m, 1H), 2.27 (s, 3H), 2.25 (s, 3H), 0.95 (d, $J = 6.6$ Hz, 3H), 0.88 (d, $J = 6.6$ Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 159.5, 145.2, 137.7, 137.3(4), 137.2(6), 133.8, 133.1, 132.7(3), 132.7(0), 132.6, 131.4, 131.3, 129.3, 128.5(2), 128.4(8), 128.3, 128.2, 127.4, 127.1, 127.0, 126.9, 126.2, 126.1(1), 126.0(8), 125.2, 124.4, 122.9, 121.3(3), 121.2(7), 112.9, 108.2, 55.1, 30.8, 25.7, 21.4, 21.3, 21.2; IR (neat): 2958(bs), 2927, 2870, 1610, 1508, 1392, 1250, 1185 cm⁻¹; HRESIMS Calcd for [C₄₇H₄₀BrNNaO₅S]⁺ (M + Na⁺) 832.1703, found 832.1694.

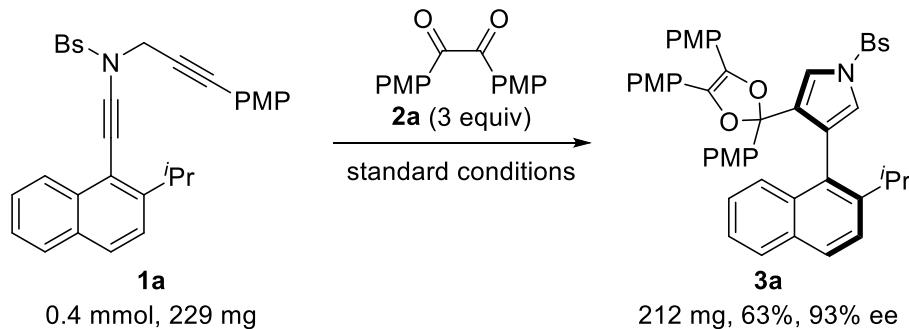
(S)-3-(4,5-bis(2-methoxyphenyl)-2-(4-methoxyphenyl)-1,3-dioxol-2-yl)-1-((4-bromophenyl)sulfonyl)-4-(2-isopropynaphthalen-1-yl)-1*H*-pyrrole (3v)



3v

Compound **3v** was prepared in 75% yield (63.2 mg) according to the general procedure. Pale yellow oil. $[\alpha]_D^{25} = +20.9^\circ$ ($c = 1.0$, CHCl_3). 92% ee (determined by HPLC: Chiralpak IA Column, 10/90 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; TR = 6.12 min (minor), 6.61 min (major)). ^1H NMR (400 MHz, CDCl_3) δ 7.75 (d, $J = 8.4$ Hz, 2H), 7.69 – 7.66 (m, 2H), 7.65 – 7.61 (m, 3H), 7.27 (d, $J = 8.8$ Hz, 1H), 7.23 – 7.19 (m, 1H), 7.17 – 7.12 (m, 2H), 7.10 (d, $J = 9.2$ Hz, 2H), 6.98 (d, $J = 2.4$ Hz, 1H), 6.96 – 6.93 (m, 2H), 6.86 – 6.82 (m, 1H), 6.74 – 6.70 (m, 3H), 6.70 – 6.64 (m, 2H), 6.46 (d, $J = 8.8$ Hz, 2H), 3.65 (s, 3H), 3.34 (s, 3H), 3.29 (s, 3H), 2.71 – 2.64 (m, 1H), 0.89 (d, $J = 6.8$ Hz, 3H), 0.84 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.2, 156.6, 156.4, 145.3, 137.9, 133.7, 132.8, 132.6, 131.9(0), 131.8(8), 131.5, 131.3, 129.1(2), 129.0(5), 128.9, 128.7, 128.6, 128.2, 128.1, 127.4, 127.0(0), 126.9(5), 126.8(8), 126.2, 125.1, 124.3, 122.8, 121.7, 121.5, 119.7(2), 119.6(9), 119.6(7), 119.6(0), 112.7, 110.4, 110.3, 108.5, 55.1, 54.8, 54.7, 30.8, 25.7, 21.3; IR (neat): 2958(bs), 2930, 1597, 1510, 1249, 1176, 1064, 1029, 820, 745 cm^{-1} ; HRESIMS Calcd for $[\text{C}_{47}\text{H}_{40}\text{BrNKO}_7\text{S}]^+$ ($\text{M} + \text{K}^+$) 880.1340 found 880.1337.

3.4 Preparative-scale synthesis of **3a**

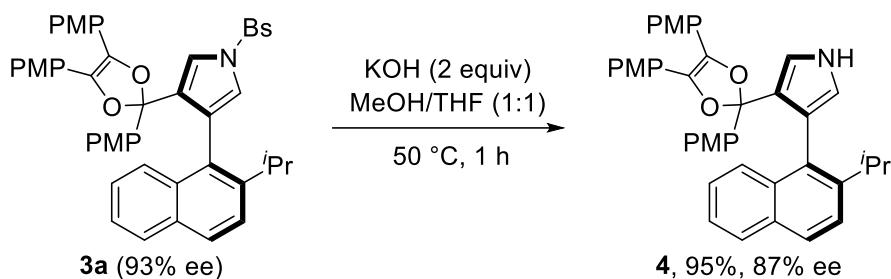


The powered CuTC (0.06 mmol, 11.4 mg), ligand **L7** (0.172 mmol, 44.9 mg) and NaBAr_4^F (0.072 mmol, 63.8 mg) were introduced into an oven-dried vial tube under nitrogen atmosphere. After adding DCM (10 mL) into the vial tube, the solution was stirred at 30 °C under the nitrogen atmosphere for 2 h. Then the solution of *N*-propargyl ynamide **1a** (0.4 mmol) and diketone **2** (1.2 mmol) in DCM (10 mL) was introduced into the system subsequently. The resulting mixture was stirred at 25 °C and the progress of the reaction was monitored by TLC. Upon completion, the mixture was concentrated under reduced pressure, and the residue was purified chromatography on silica gel (eluent:

toluene/acetone) to give the desired axially chiral naphthylpyrrole **3a** (211 mg, 63%, 93% ee).

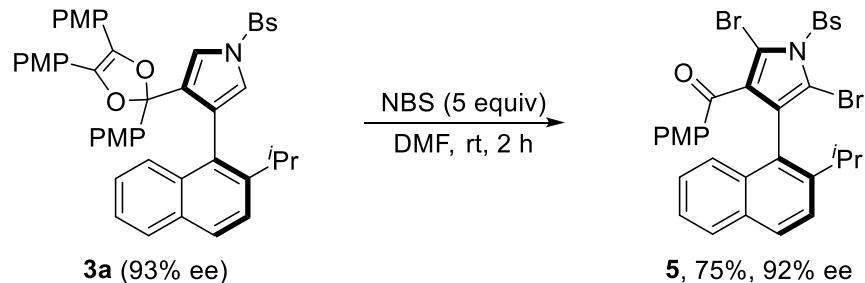
3.5 Transformation

3-(2-isopropynaphthalen-1-yl)-4-(2,4,5-tris(4-methoxyphenyl)-1,3-dioxol-2-yl)-1*H*-pyrrole (**4**)



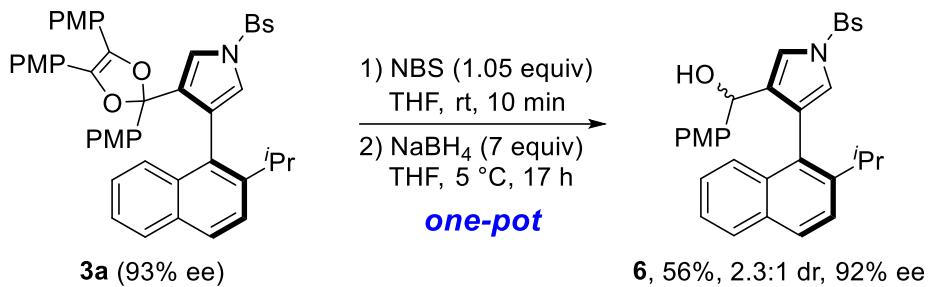
To a solution of **3a** (0.1 mmol) in MeOH/THF (1:1, 2 mL) was added KOH (0.2 mmol, 11.2 mg) and the reaction was stirred at 50 °C for 1 h. Upon completion (monitored by TLC), the reaction mixture was filtered through a Celite pad and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE:EA = 10:1) to afford the target product **4** in 95% yield (59.3 mg) as a colourless oil.⁵ $[\alpha]_D^{25} = +26.8^\circ$ (c = 1.0, CHCl₃). 87% ee (determined by HPLC: Chiralpak IA Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; TR = 5.61 min (minor), 6.14 min (major)). ¹H NMR (500 MHz, CDCl₃) δ 8.29 (s, 1H), 7.70 – 7.67 (m, 1H), 7.67 – 7.64 (m, 1H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.40 (d, *J* = 9.0 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.21 – 7.17 (m, 1H), 6.96 (d, *J* = 9.0 Hz, 2H), 6.70 – 6.68 (m, 2H), 6.68 – 6.66 (m, 2H), 6.65 (s, 2H), 6.64 – 6.61 (m, 2H), 6.56 (d, *J* = 8.5 Hz, 2H), 3.73 (s, 3H), 3.71 (s, 3H), 3.70 (s, 3H), 3.15 – 3.07 (m, 1H), 1.06 (d, *J* = 7.0 Hz, 3H), 0.99 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 159.1, 158.6, 158.5, 145.4, 135.3, 134.9, 131.8, 131.7, 131.5, 130.7, 128.1, 127.7, 127.4, 127.2, 127.0, 126.9, 124.9, 124.7, 124.0, 123.1, 122.3, 120.0, 119.0, 118.8, 113.2, 113.1, 112.6, 109.3, 55.1(2), 55.1(0), 30.7, 25.7, 21.9; IR (neat): 3003(bs), 2983, 1598, 1485, 1321, 1119, 1242, 1018, 884, 793 cm⁻¹; HRESIMS Calcd for [C₄₁H₃₇NNaO₅]⁺ [M + Na⁺] 646.2564; Found 646.2563.

(2,5-dibromo-1-((4-bromophenyl)sulfonyl)-4-(2-isopropynaphthalen-1-yl)-1*H*-pyrrol-3-yl)(4-methoxyphenyl)methanone (5)



To a solution of **3a** (0.1 mmol) in DMF (2 mL) was added NBS (0.5 mmol, 89.0 mg) and the reaction was stirred at room temperature for 2 h. Upon completion (monitored by TLC), the reaction was diluted with H₂O. The mixture was then extracted with EA/H₂O and washed with brine for 3 times. The organic phase was dried over Na₂SO₄ and concentrated. The residue was purified by column chromatography on silica gel (eluent: PE:EA = 10:1) to afford the target product **5** in 75% yield (56.3 mg) as a pale yellow solid (mp 95–96 °C). [α]_D²⁵ = -90.8° (c = 1.0, CHCl₃). 92% ee (determined by HPLC: Chiralpak ADH Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; TR = 9.28 min (minor), 16.52 min (major)). ¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 8.8 Hz, 2H), 7.80 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.73 – 7.69 (m, 1H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.37 – 7.30 (m, 3H), 7.22 – 7.16 (m, 1H), 6.72 (d, *J* = 8.8 Hz, 2H), 3.77 (s, 3H), 2.78 – 2.68 (m, 1H), 1.12 (d, *J* = 6.8 Hz, 3H), 1.01 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 188.2, 164.0, 145.9, 136.8, 132.9, 132.3, 132.1, 132.0, 131.8, 130.5, 129.8, 129.5, 129.2, 128.8, 128.0, 126.2, 125.3, 125.1, 125.0, 123.4, 113.6, 105.9, 103.0, 55.4, 31.5, 24.3, 22.9; IR (neat): 3058(bs), 2961, 2868, 1657(s), 1597, 1399, 1255, 1199, 824, 745 cm⁻¹; HRESIMS Calcd for [C₃₁H₂₄Br₃NNaO₄S]⁺ [M + Na⁺] 765.8868; Found 765.8860.

(1-((4-bromophenyl)sulfonyl)-4-(2-isopropynaphthalen-1-yl)-1*H*-pyrrol-3-yl)(4-methoxyphenyl)methanol (6)

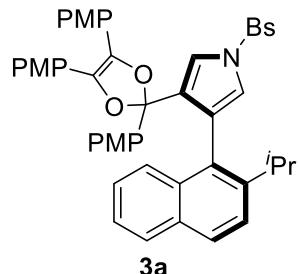
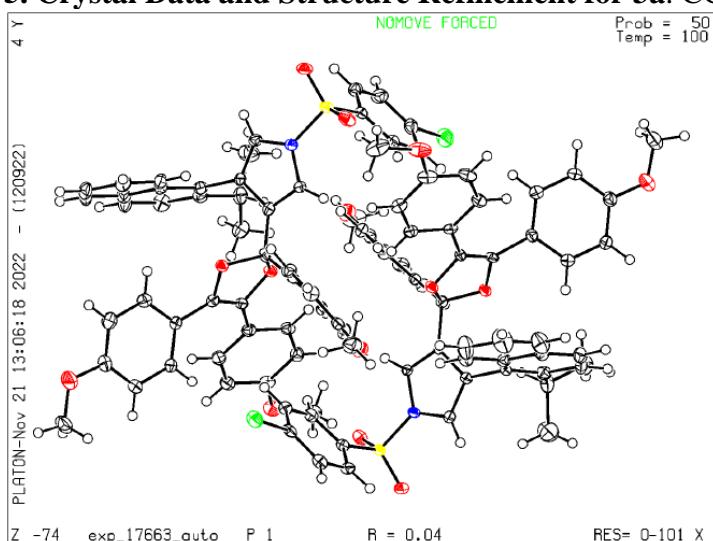


To a solution of **3a** (0.1 mmol) in THF (2 mL) was added NBS (0.105 mmol, 18.7 mg) and the reaction was stirred at room temperature for 10 min. Then NaBH₄ (0.7 mmol, 26.5 mg) was added to the solution at 5 °C and the reaction was stirred at 5 °C for 17 h. Upon completion (monitored by TLC), the reaction was diluted with H₂O. The mixture was then extracted by EA/H₂O for three times. The organic phase was dried over Na₂SO₄ and concentrated. The residue was purified by column chromatography on silica gel (eluent: PE:EA = 15:1) to afford the target product **6** in 56% yield with 2.3:1 dr (33.1 mg) as a colorless solid (mp 97–98 °C). [α]_D²⁵ = +207.1° (c = 1.0, CHCl₃). 92% ee (determined by HPLC: Chiraldak IA Column, 20/80 *i*-PrOH/hexane, 1.0 mL/min, 254 nm; TR = 9.67 min (major), 13.93 min (minor)). ¹H NMR (500 MHz, CDCl₃) δ 7.80 (d, *J* = 8.5 Hz, 1H), 7.74 (d, *J* = 9.0 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.68 (d, *J* = 9.0 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.20 (dd, *J* = 2.5, 1.0 Hz, 1H), 7.07 – 7.04 (m, 1H), 7.02 (d, *J* = 2.5 Hz, 1H), 6.80 (d, *J* = 8.5 Hz, 1H), 6.75 (d, *J* = 9.0 Hz, 2H), 6.48 (d, *J* = 9.0 Hz, 2H), 5.15 (s, 1H), 3.66 (s, 3H), 2.93 – 2.82 (m, 1H), 1.81 (s, 1H), 1.26 (d, *J* = 7.0 Hz, 3H), 1.06 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 158.9, 145.2, 137.9, 134.8, 134.0, 133.1, 132.6, 131.6, 129.1, 128.7, 128.2, 127.4(3), 127.3(8), 126.7, 126.0, 125.8, 125.7, 124.8, 123.2, 120.7, 118.5, 113.4, 69.8, 55.2, 30.8, 24.9, 22.8; IR (neat): 2955(bs), 2927, 1573, 1512, 1374, 1177, 1089, 1065, 808, 745 cm⁻¹; HRESIMS Calcd for [C₃₁H₂₈BrNNaO₄S]⁺ [M + Na⁺] 612.0815; Found 612.0811.

4. References

- 1) L.-J. Qi, C.-T. Li, Z.-Q. Huang, J.-T. Jiang, X.-Q. Zhu, X. Lu and L.-W. Ye, *Angew. Chem., Int. Ed.*, 2022, **61**, e202210637.
- 2) X.-Q. Zhu, P. Hong, Y.-X. Zheng, Y.-Y. Zhen, F.-L. Hong, X. Lu and L.-W. Ye, *Chem. Sci.*, 2021, **11**, 9466.
- 3) D. J. Cassar, E. Nagaradja, D. C. D. Butler, D. Villemin and C. J. Richards, *Org. Lett.*, 2012, **14**, 894.
- 4) P. Daw, R. Petakamsetty, A. Sarbajna, S. Laha, R. Ramapanicker and J. K. A. Bera, *J. Am. Chem. Soc.*, 2014, **136**, 13987.
- 5) F.-L. Hong, Y.-B. Chen, S.-H. Ye, G.-Y. Zhu, X.-Q. Zhu, X. Lu, R.-S. Liu and L.-W. Ye, *J. Am. Chem. Soc.*, 2020, **142**, 7618.

5. Crystal Data and Structure Refinement for 3a. CCDC Number = 2295809.



Bond precision: C-C = 0.0075 Å

Wavelength=1.54184

Cell:
 $a=13.2375(3)$ $b=13.7370(3)$ $c=14.5028(3)$
 $\alpha=97.822(2)$ $\beta=104.257(2)$ $\gamma=117.863(2)$

Temperature: 100 K

	Calculated	Reported
Volume	2160.41(11)	2160.40(9)
Space group	P 1	P 1
Hall group	P 1	P 1
Moiety formula	C47 H40 Br N O7 S [+ solvent]	2(C47 H40 Br N O7 S)
Sum formula	C47 H40 Br N O7 S [+ solvent]	C94 H80 Br2 N2 O14 S2
Mr	842.76	1685.54
Dx, g cm ⁻³	1.296	1.296
Z	2	1
μ (mm ⁻¹)	2.159	2.159
F000	872.0	872.0
F000'	873.67	
h, k, lmax	16, 17, 18	16, 17, 18
Nref	17640 [8820]	15457
Tmin, Tmax		0.803, 1.000
Tmin'		

Correction method= # Reported T Limits: Tmin=0.803 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.75/0.88

Theta (max) = 74.315

B (reflections) = 0.0375 (15043)

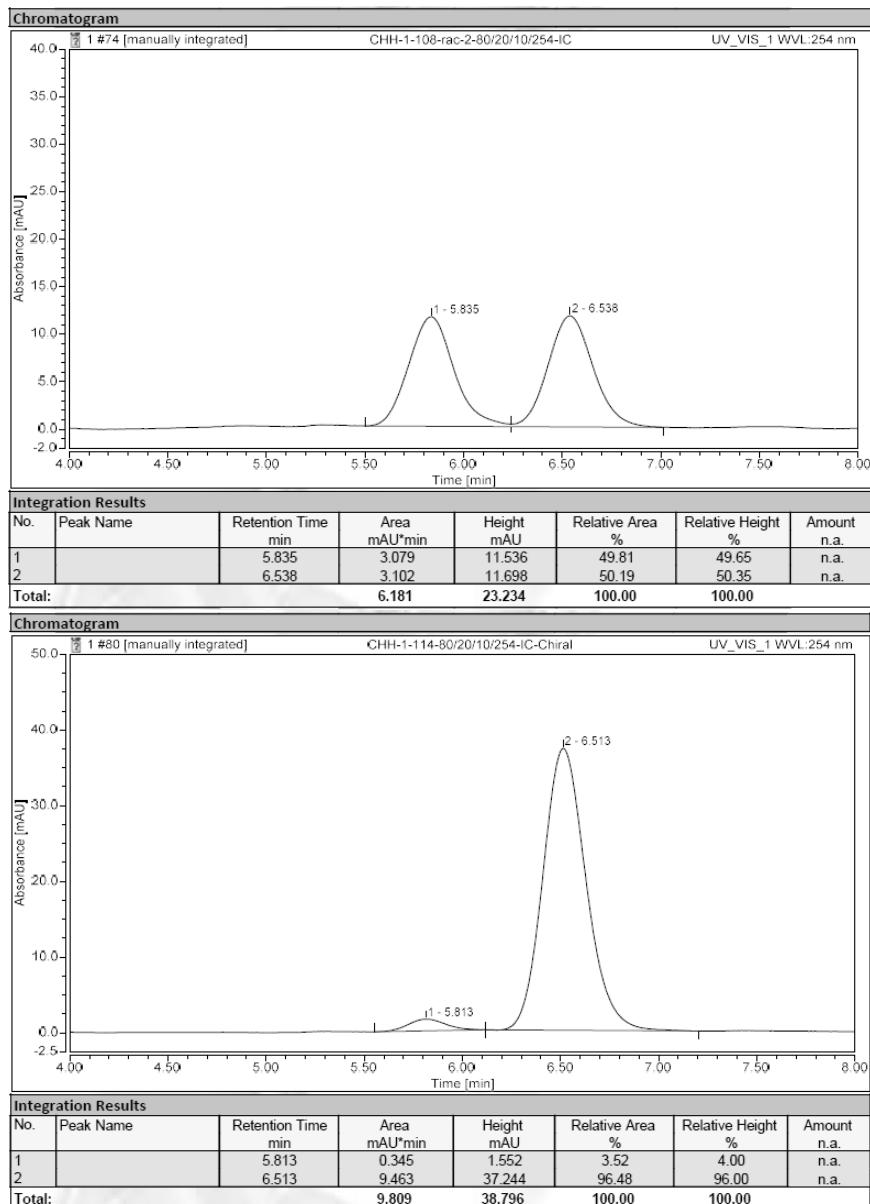
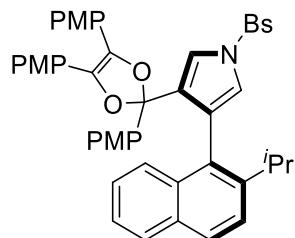
wR2 (reflections) =
0.0973 (15457)

$$S = 1,028$$

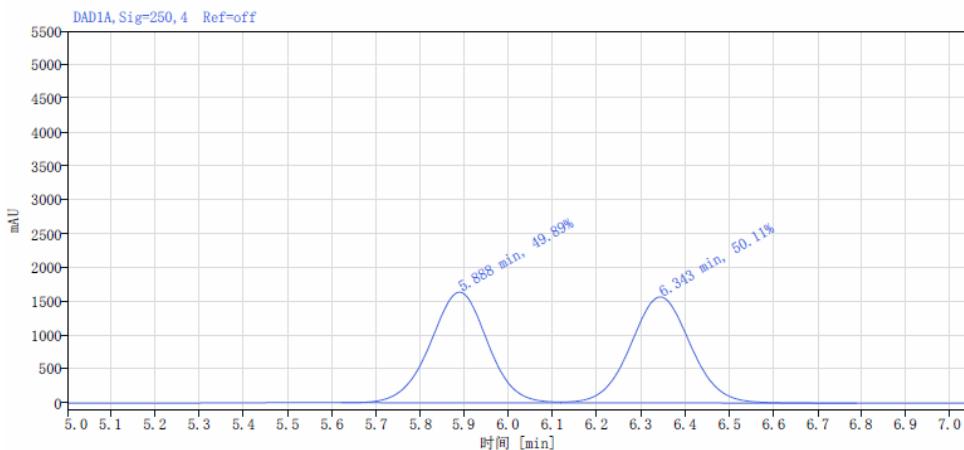
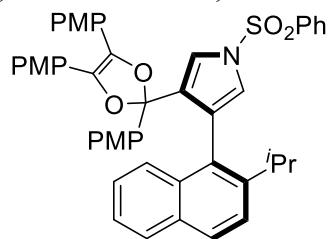
Npar= 1037

6. HPLC Chromatograms

3a: IC, *i*-PrOH/hexane = 20/80, v = 1.0 mL/min, λ = 254 nm

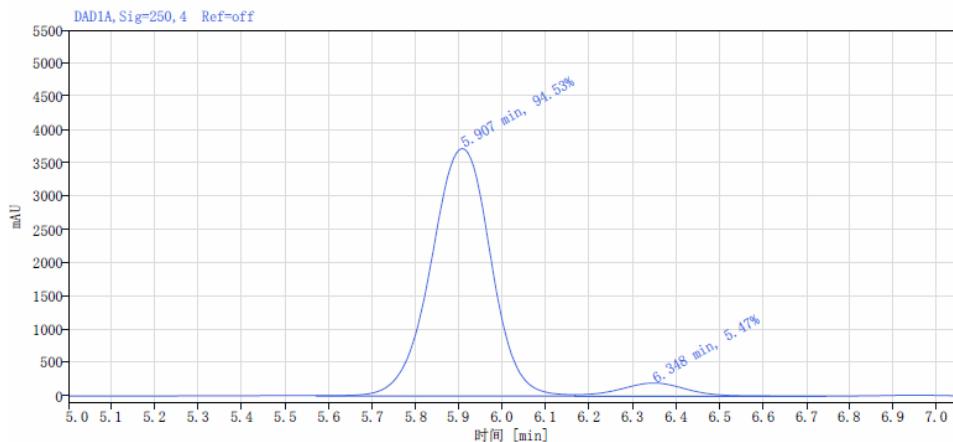


3b: IA, *i*-PrOH/hexane = 20/80, v = 1.0 mL/min, λ = 254 nm



峰结果 (最少峰面积百分比 1%)

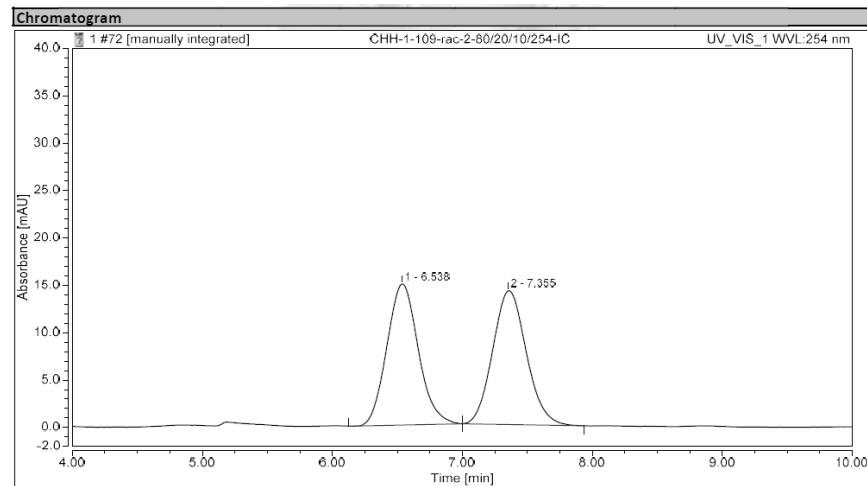
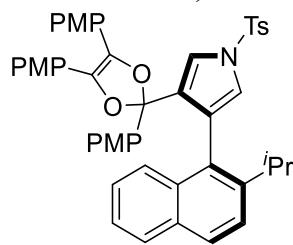
保留时间 (min)	信号说明	峰宽 (min)	峰面积	峰高	峰面积%
5.888	DAD1A, Sig=250, 4 Ref=off	0.498	14876.6	1638.6	49.89
6.343	DAD1A, Sig=250, 4 Ref=off	0.670	14941.2	1570.5	50.11



峰结果 (最少峰面积百分比 1%)

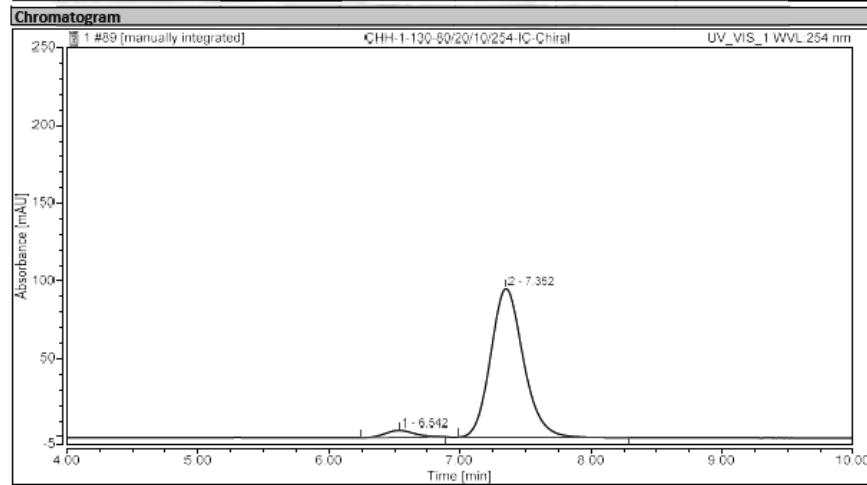
保留时间 (min)	信号说明	峰宽 (min)	峰面积	峰高	峰面积%
5.907	DAD1A, Sig=250, 4 Ref=off	0.596	35728.6	3722.2	94.53
6.348	DAD1A, Sig=250, 4 Ref=off	0.577	2065.6	196.8	5.47

3c: IC, *i*-PrOH/hexane = 20/80, v = 1.0 mL/min, λ = 254 nm



Integration Results

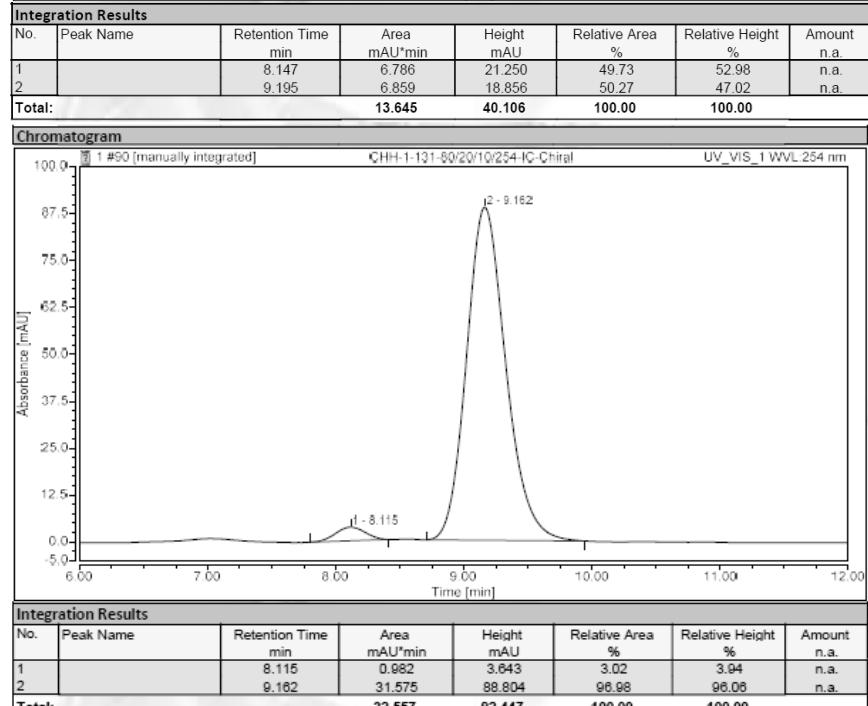
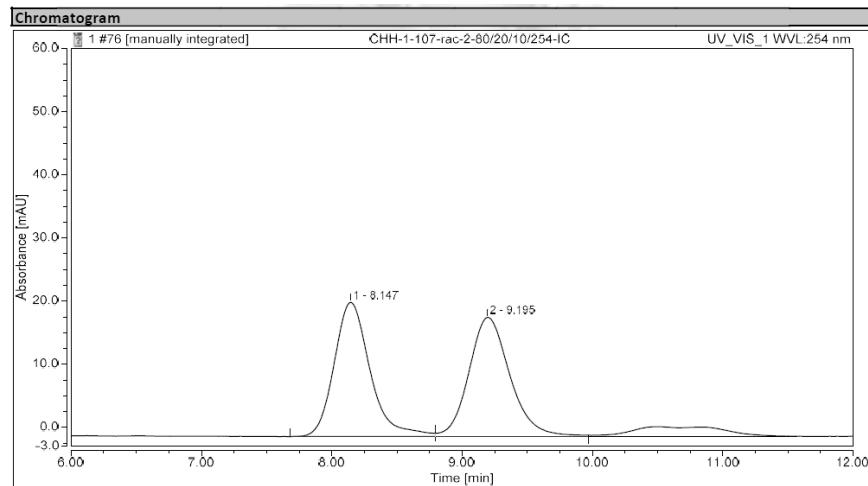
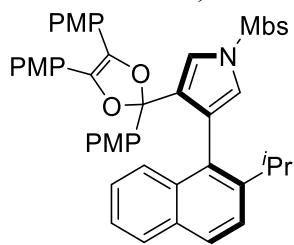
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.538	4.164	14.881	49.57	51.30	n.a.
2		7.355	4.237	14.128	50.43	48.70	n.a.
Total:			8.401	29.008	100.00	100.00	



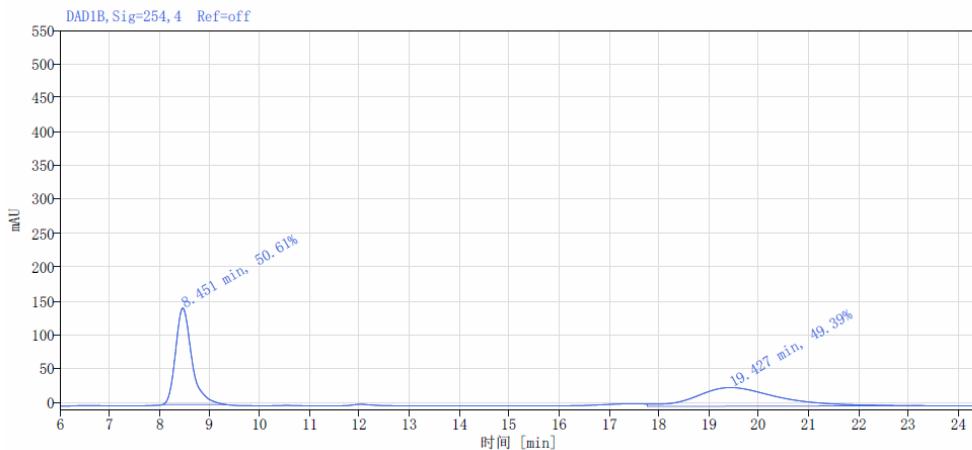
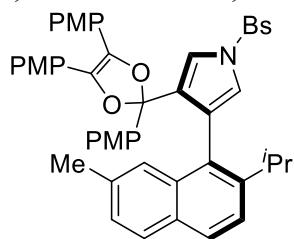
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.542	1.165	4.460	4.03	4.46	n.a.
2		7.352	27.761	95.605	95.97	95.54	n.a.
Total:			28.926	100.065	100.00	100.00	

3d: IC, *i*-PrOH/hexane = 20/80, v = 1.0 mL/min, λ = 254 nm

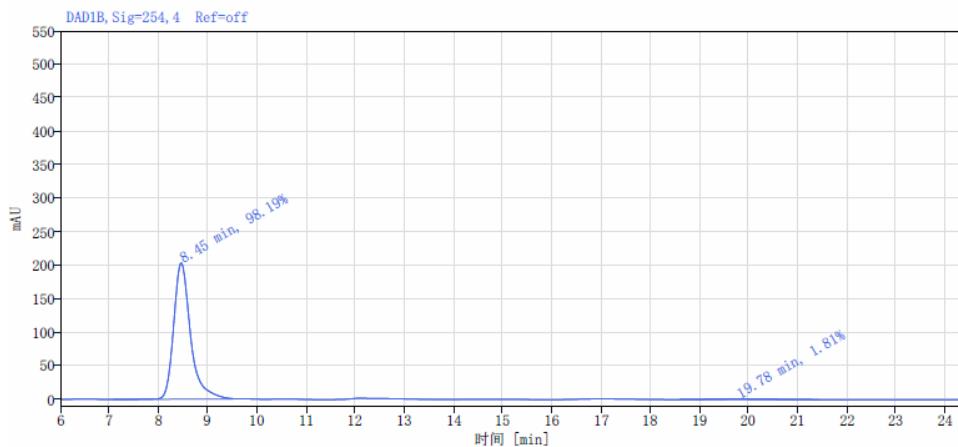


3e: ODH, *i*-PrOH/hexane = 10/90, v = 1.0 mL/min, $\lambda = 254$ nm



峰结果 (最少峰面积百分比 1%)

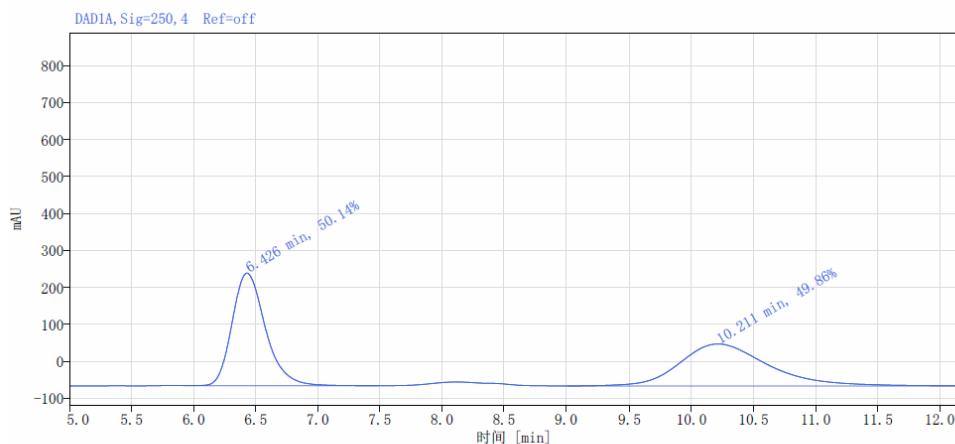
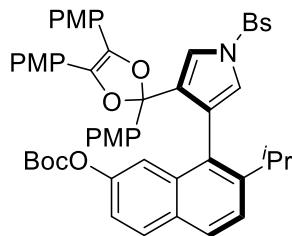
保留时间 (min)	信号说明	峰宽 (min)	峰面积	峰高	峰面积%
8.451	DAD1B, Sig=254, 4 Ref=off	1.262	3208.5	142.3	50.61
19.427	DAD1B, Sig=254, 4 Ref=off	5.487	3130.6	27.5	49.39



峰结果 (最少峰面积百分比 1%)

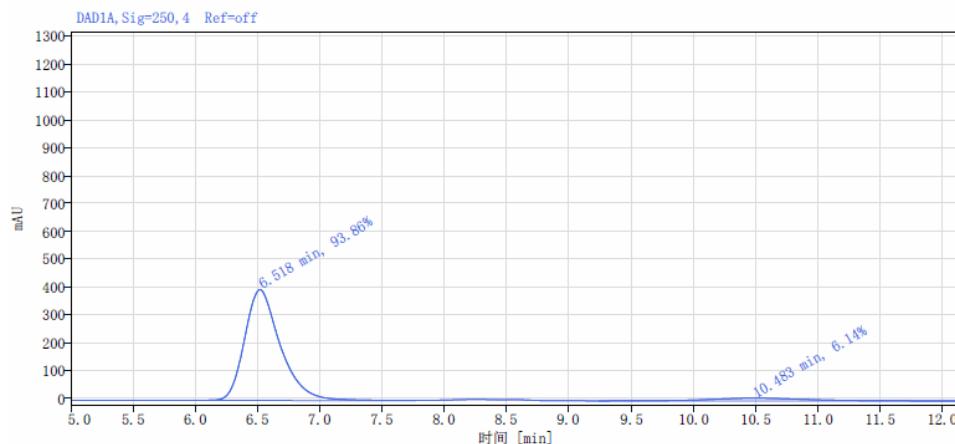
保留时间 (min)	信号说明	峰宽 (min)	峰面积	峰高	峰面积%
8.450	DAD1B, Sig=254, 4 Ref=off	2.590	4869.8	203.2	98.19
19.780	DAD1B, Sig=254, 4 Ref=off	2.830	89.7	1.0	1.81

3f: ODH, *i*-PrOH/hexane = 20/80, v = 1.0 mL/min, λ = 254 nm



峰结果 (最少峰面积百分比 1%)

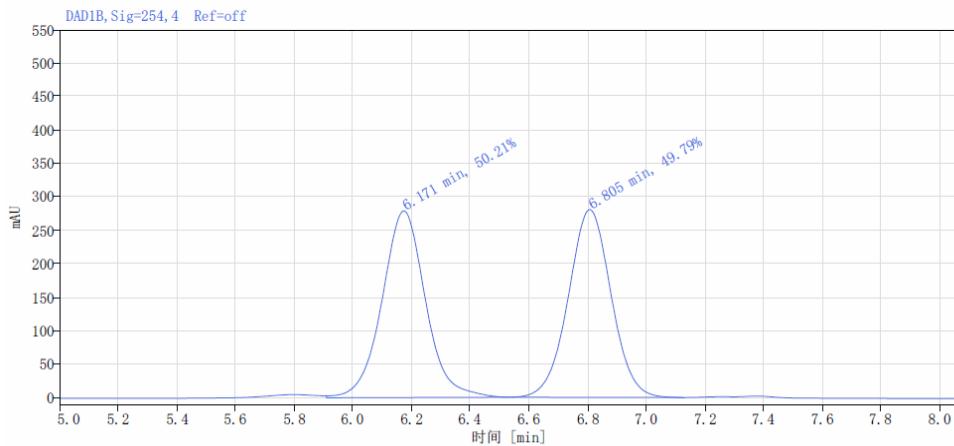
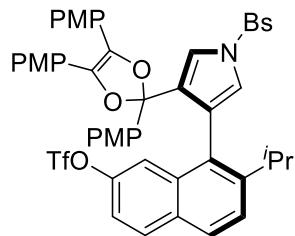
保留时间 (min)	信号说明	峰宽 (min)	峰面积	峰高	峰面积%
6.426	DAD1A, Sig=250, 4 Ref=off	1.568	5686.7	304.8	50.14
10.211	DAD1A, Sig=250, 4 Ref=off	5.410	5655.8	113.6	49.86



峰结果 (最少峰面积百分比 1%)

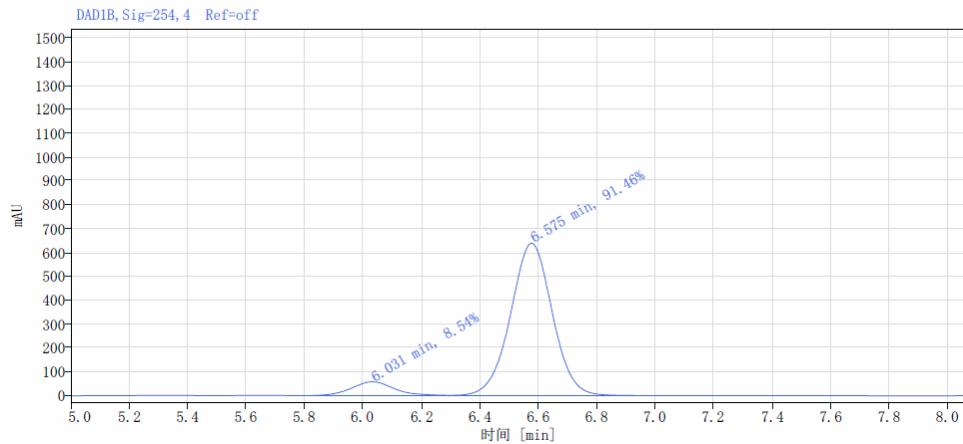
保留时间 (min)	信号说明	峰宽 (min)	峰面积	峰高	峰面积%
6.518	DAD1A, Sig=250, 4 Ref=off	1.785	7966.7	398.8	93.86
10.483	DAD1A, Sig=250, 4 Ref=off	2.873	521.1	9.5	6.14

3g: IA, *i*-PrOH/hexane = 10/90, v = 1.0 mL/min, λ = 254 nm



峰结果 (最少峰面积百分比 1%)

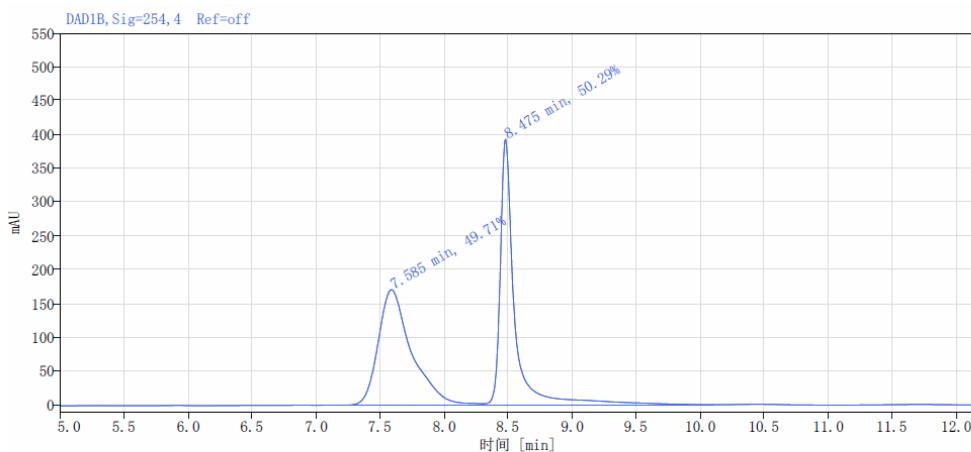
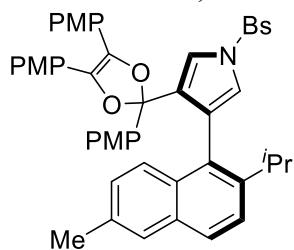
保留时间 (min)	信号说明	峰宽 (min)	峰面积	峰高	峰面积%
6.171	DAD1B, Sig=254, 4 Ref=off	0.623	2866.8	278.9	50.21
6.805	DAD1B, Sig=254, 4 Ref=off	0.593	2842.3	280.6	49.79



峰结果 (最少峰面积百分比 1%)

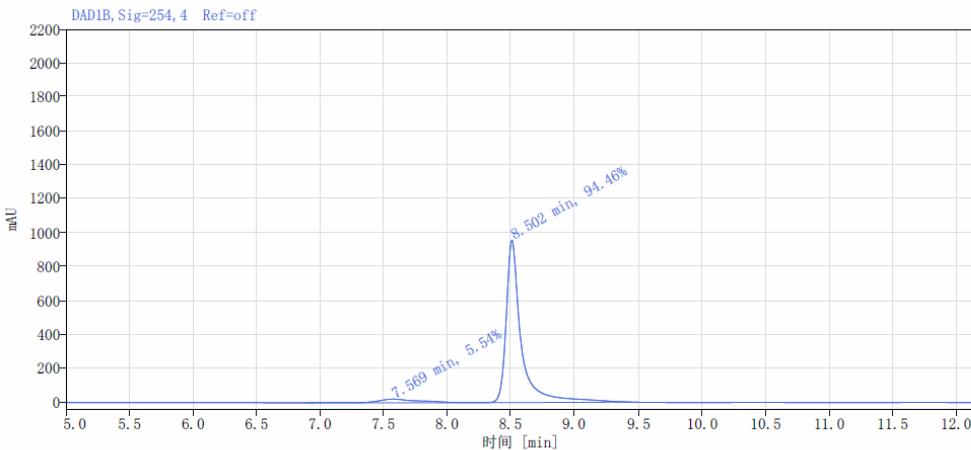
保留时间 (min)	信号说明	峰宽 (min)	峰面积	峰高	峰面积%
6.031	DAD1B, Sig=254, 4 Ref=off	0.507	594.0	58.1	8.54
6.575	DAD1B, Sig=254, 4 Ref=off	0.766	6361.0	639.9	91.46

3h: IC, *i*-PrOH/hexane = 10/90, v = 1.0 mL/min, $\lambda = 254$ nm



峰结果 (最少峰面积百分比 1%)

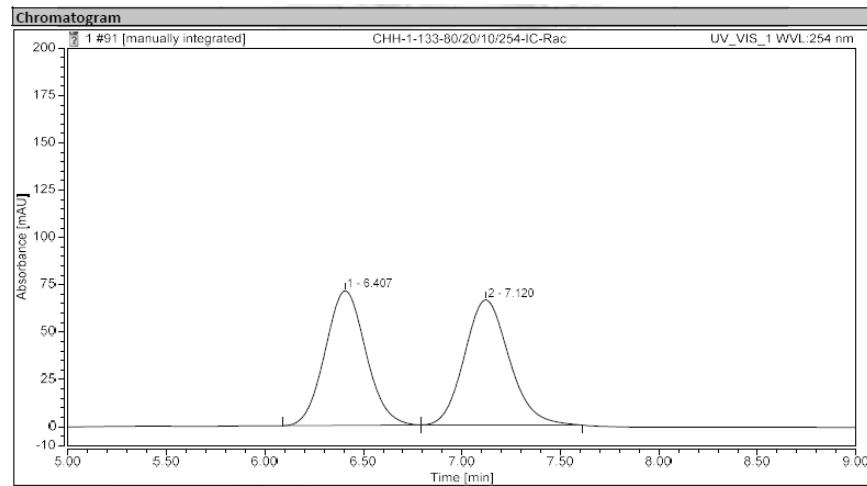
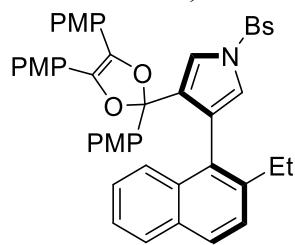
保留时间 (min)	信号说明	峰宽 (min)	峰面积	峰高	峰面积%
7.585	DAD1B, Sig=254, 4 Ref=off	1.342	3084.0	170.7	49.71
8.475	DAD1B, Sig=254, 4 Ref=off	1.806	3120.6	393.5	50.29



峰结果 (最少峰面积百分比 1%)

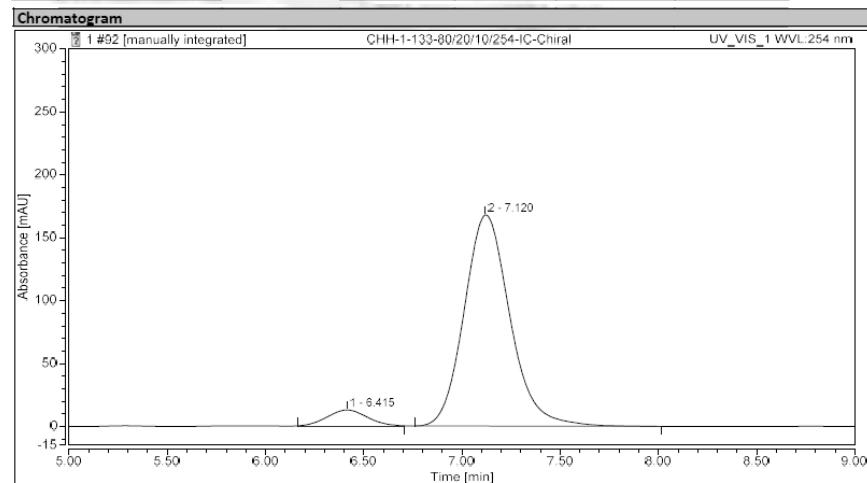
保留时间 (min)	信号说明	峰宽 (min)	峰面积	峰高	峰面积%
7.569	DAD1B, Sig=254, 4 Ref=off	1.378	462.1	21.0	5.54
8.502	DAD1B, Sig=254, 4 Ref=off	1.194	7883.7	957.5	94.46

3i: IC, *i*-PrOH/hexane = 20/80, v = 1.0 mL/min, λ = 254 nm



Integration Results

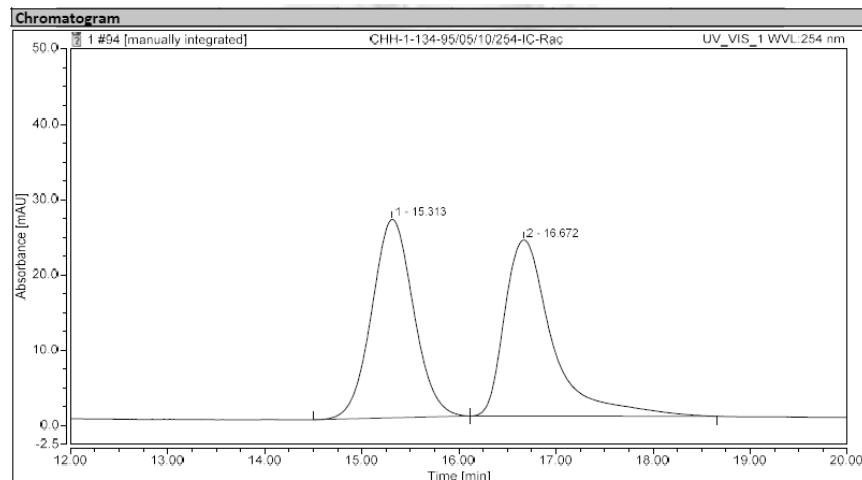
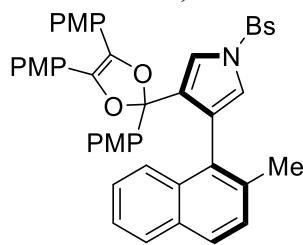
No.	Peak Name	Retention Time min	Area mAU·min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.407	17.042	71.106	49.44	51.83	n.a.
2		7.120	17.428	66.085	50.56	48.17	n.a.
Total:		34.469	137.192	100.00	100.00		



Integration Results

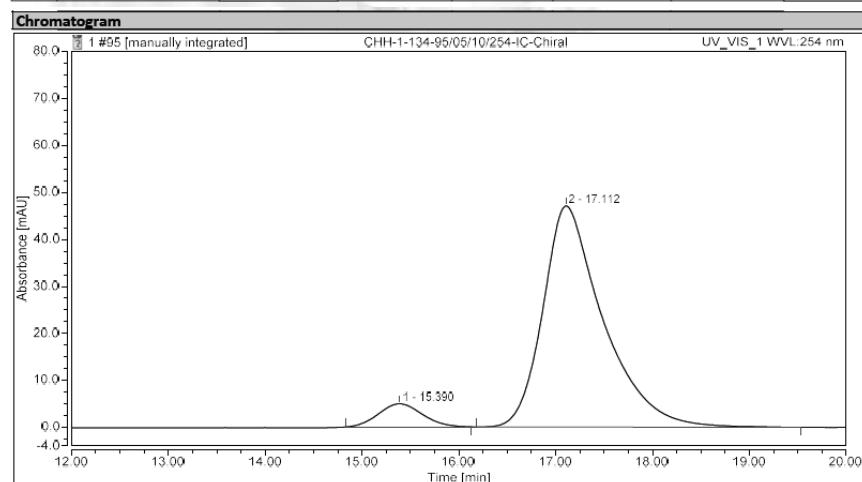
No.	Peak Name	Retention Time min	Area mAU·min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.415	2.952	12.583	6.10	6.97	n.a.
2		7.120	45.409	167.869	93.90	93.03	n.a.
Total:		48.361	180.452	100.00	100.00		

3j: IC, *i*-PrOH/hexane = 5/95, v = 1.0 mL/min, λ = 254 nm



Integration Results

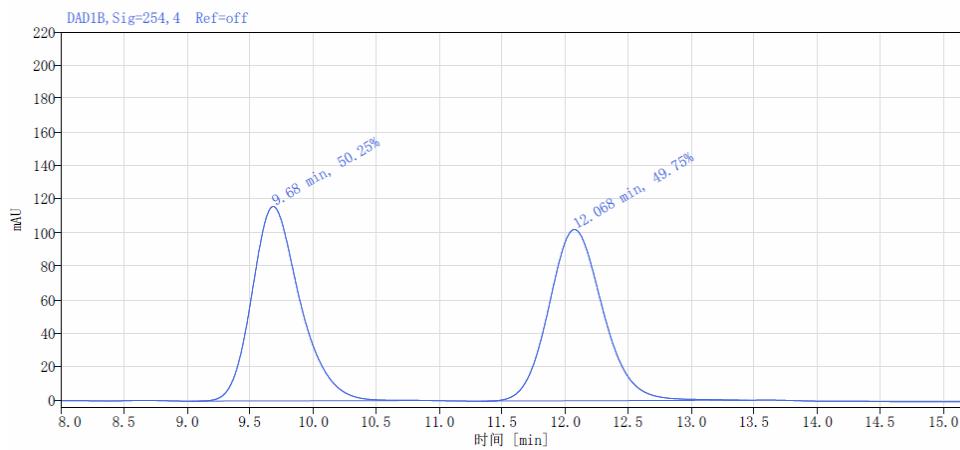
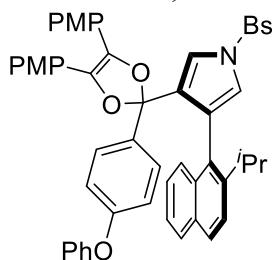
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.313	13.139	26.348	49.54	52.99	n.a.
2		16.672	13.385	23.377	50.46	47.01	n.a.
Total:			26.524	49.724	100.00	100.00	



Integration Results

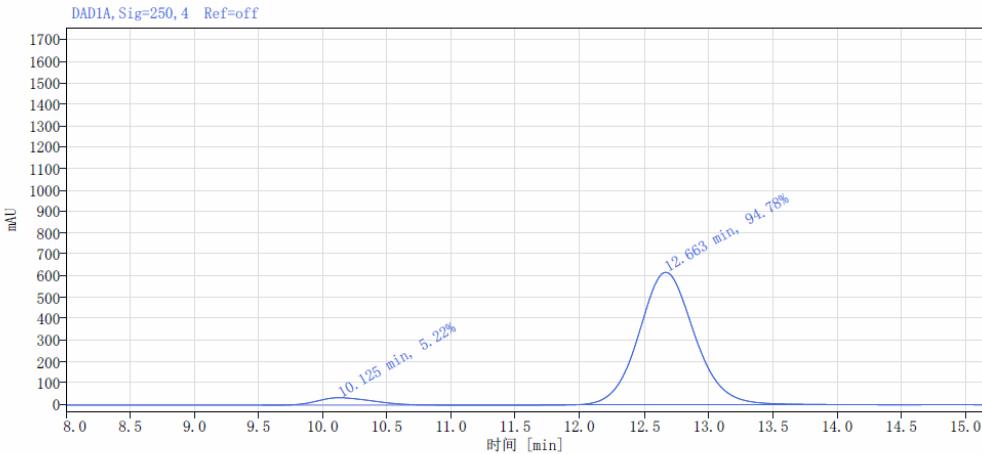
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.390	2.573	4.924	7.04	9.47	n.a.
2		17.112	33.982	47.099	92.96	90.53	n.a.
Total:			36.555	52.023	100.00	100.00	

3k: IC, *i*-PrOH/hexane = 5/95, v = 1.0 mL/min, λ = 254 nm



峰结果 (最少峰面积百分比 1%)

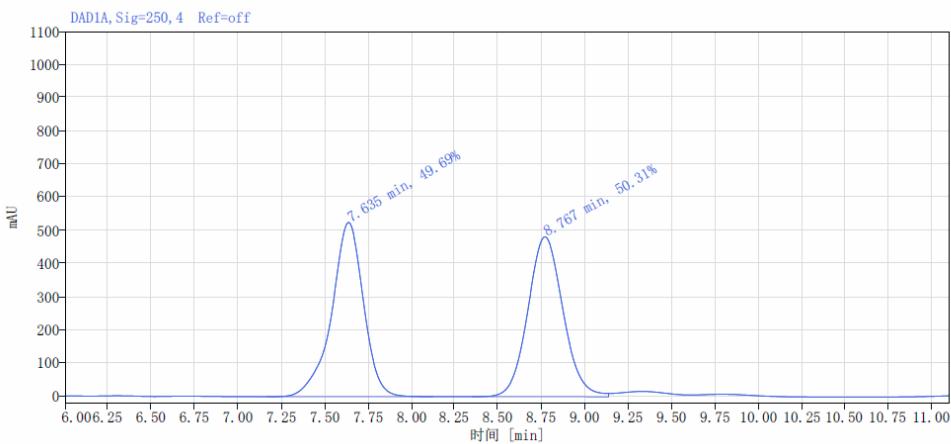
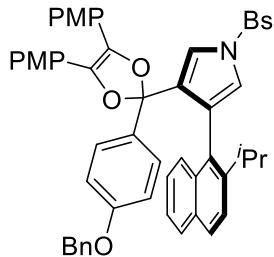
保留时间 (min)	信号说明	峰宽 (min)	峰面积	峰高	峰面积%
9.680	DAD1B, Sig=254, 4 Ref=off	1.869	3075.0	116.0	50.25
12.068	DAD1B, Sig=254, 4 Ref=off	2.117	3043.9	102.2	49.75



峰结果 (最少峰面积百分比 1%)

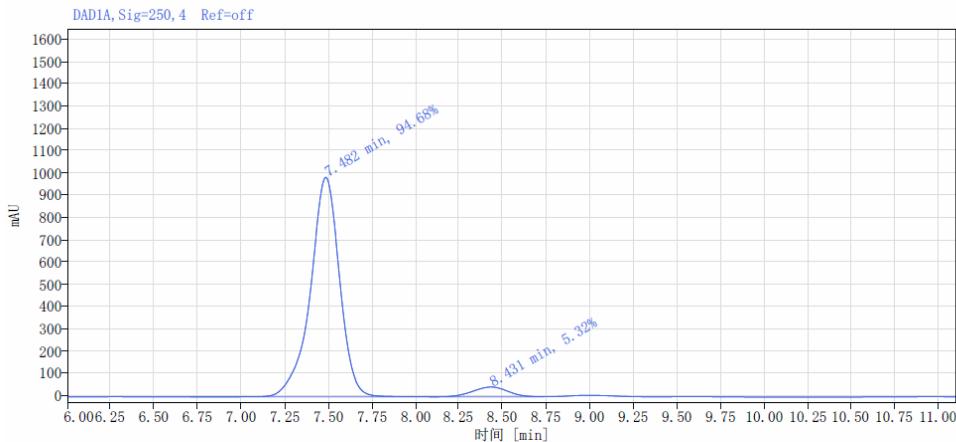
保留时间 (min)	信号说明	峰宽 (min)	峰面积	峰高	峰面积%
10.125	DAD1A, Sig=250, 4 Ref=off	2.170	1039.2	34.7	5.22
12.663	DAD1A, Sig=250, 4 Ref=off	2.823	18856.7	619.4	94.78

3l: IA, *i*-PrOH/hexane = 20/80, v = 1.0 mL/min, $\lambda = 254$ nm



峰结果 (最少峰面积百分比 1%)

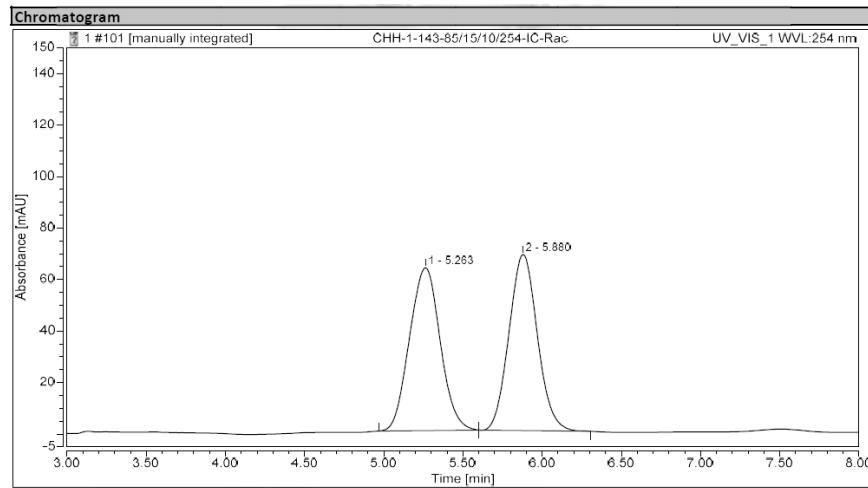
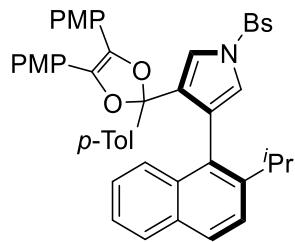
保留时间 (min)	信号说明	峰宽 (min)	峰面积	峰高	峰面积%
7.635	DAD1A, Sig=250, 4 Ref=off	0.959	6719.5	525.3	49.69
8.767	DAD1A, Sig=250, 4 Ref=off	0.787	6802.0	481.9	50.31



峰结果 (最少峰面积百分比 1%)

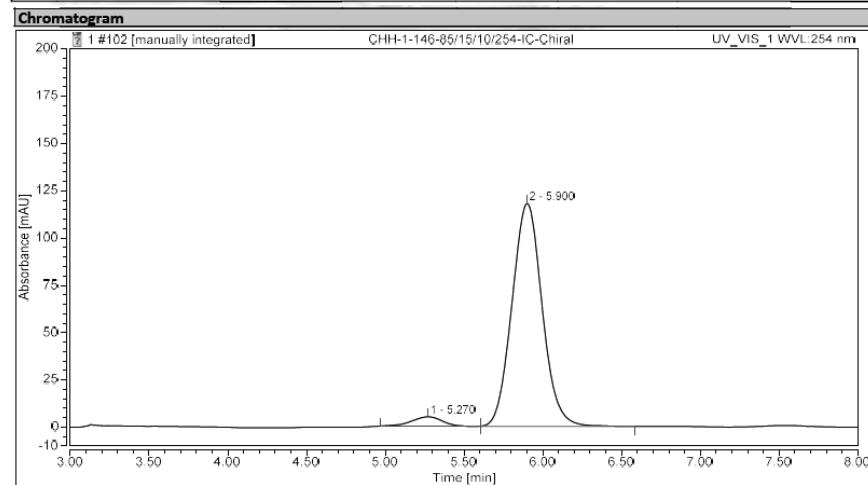
保留时间 (min)	信号说明	峰宽 (min)	峰面积	峰高	峰面积%
7.482	DAD1A, Sig=250, 4 Ref=off	1.404	11519.4	987.2	94.68
8.431	DAD1A, Sig=250, 4 Ref=off	0.625	647.2	44.8	5.32

3m: IC, *i*-PrOH/hexane = 15/85, v = 1.0 mL/min, λ = 254 nm



Integration Results

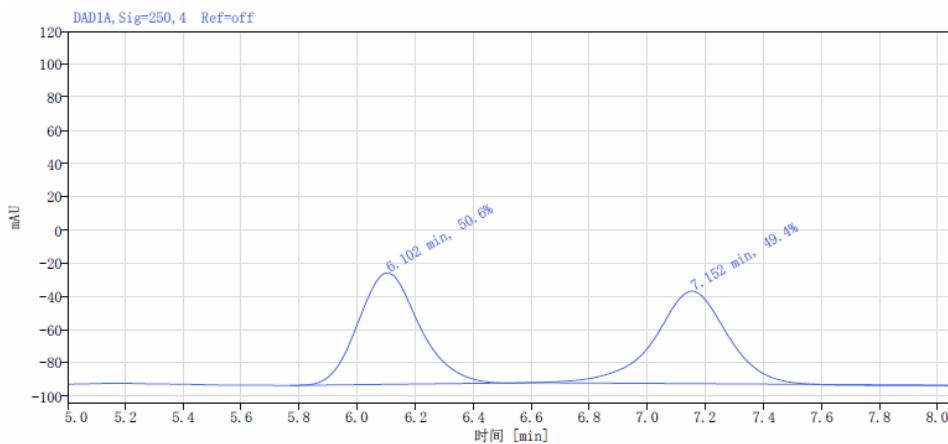
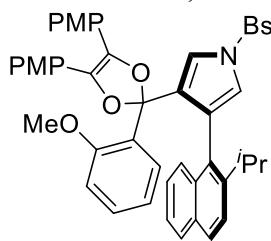
No.	Peak Name	Retention Time min	Area mAU·min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.263	14.225	63.290	49.98	48.04	n.a.
2		5.880	14.236	68.453	50.02	51.96	n.a.
Total:			28.461	131.742	100.00	100.00	



Integration Results

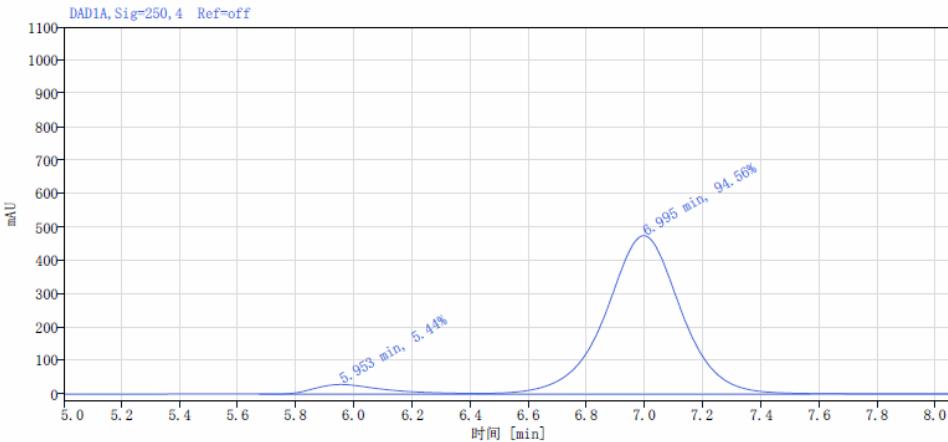
No.	Peak Name	Retention Time min	Area mAU·min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.270	1.114	4.952	4.08	4.03	n.a.
2		5.900	26.210	117.964	95.92	95.97	n.a.
Total:			27.324	122.917	100.00	100.00	

3n: IC, *i*-PrOH/hexane = 20/80, v = 1.0 mL/min, λ = 254 nm



峰结果 (最少峰面积百分比 1%)

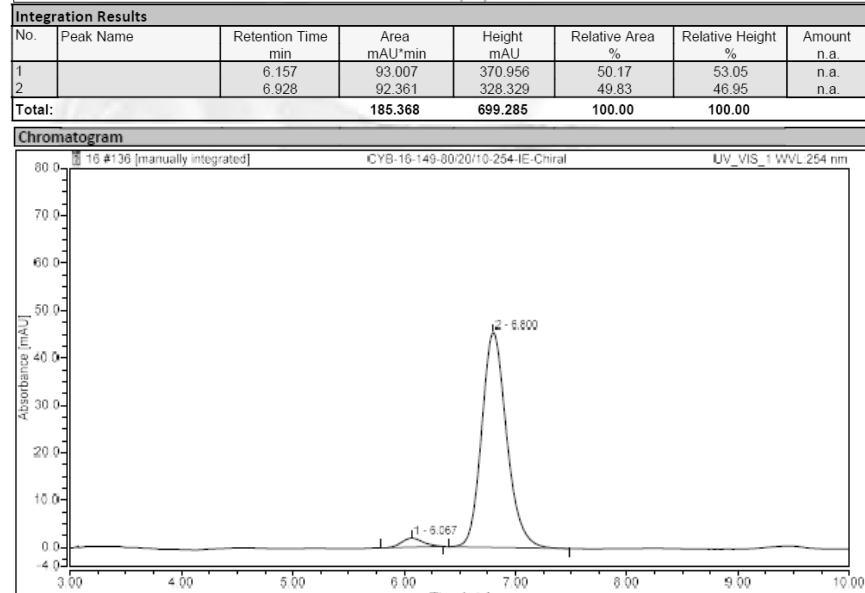
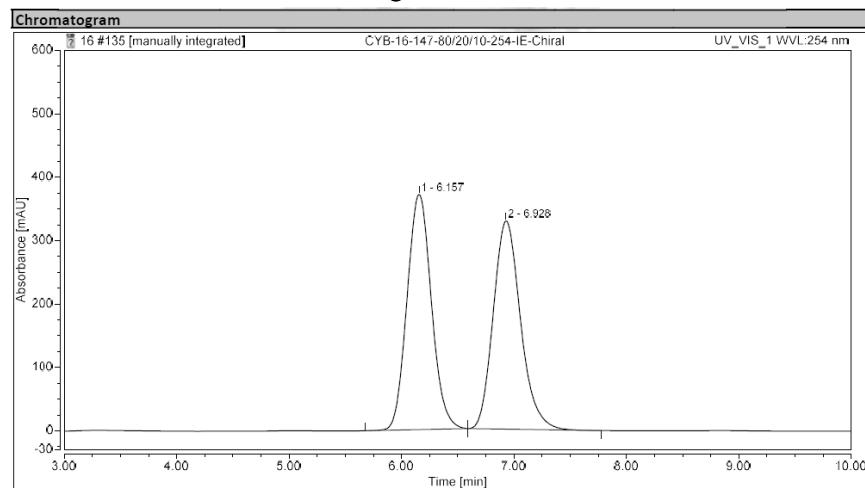
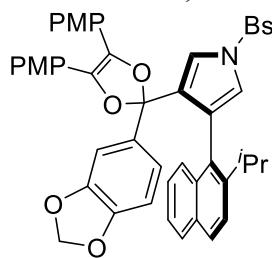
保留时间 (min)	信号说明	峰宽 (min)	峰面积	峰高	峰面积%
6.102	DAD1A, Sig=250, 4 Ref=off	0.833	983.6	67.2	50.60
7.152	DAD1A, Sig=250, 4 Ref=off	1.843	960.1	55.7	49.40



峰结果 (最少峰面积百分比 1%)

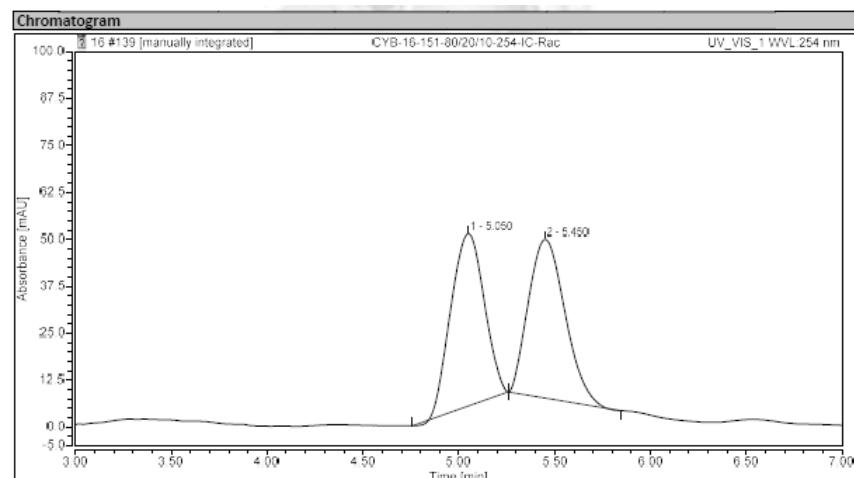
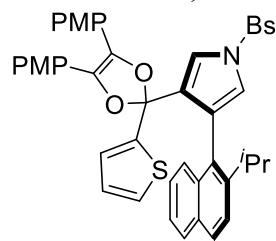
保留时间 (min)	信号说明	峰宽 (min)	峰面积	峰高	峰面积%
5.953	DAD1A, Sig=250, 4 Ref=off	0.751	498.7	29.1	5.44
6.995	DAD1A, Sig=250, 4 Ref=off	2.130	8677.4	475.1	94.56

3o: IE, *i*-PrOH/hexane = 20/80, v = 1.0 mL/min, λ = 254 nm



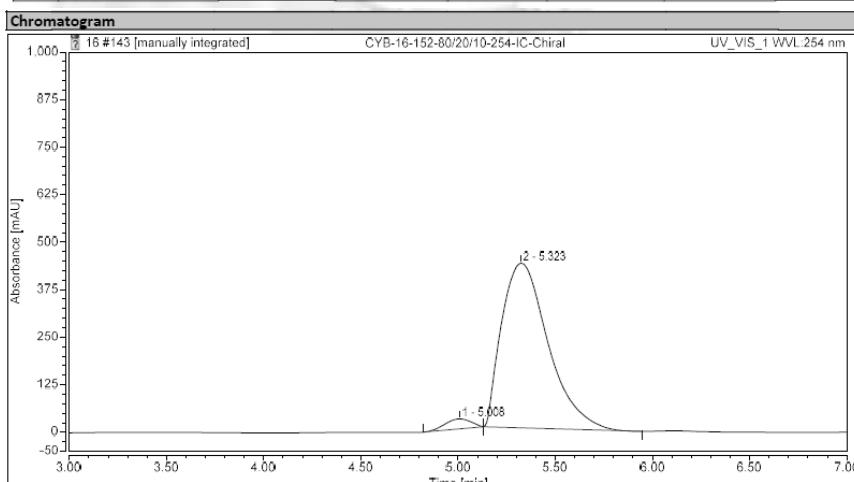
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.067	0.426	1.917	3.49	4.06	n.a.
2		6.800	11.804	45.357	96.51	95.94	n.a.
Total:			12.230	47.274	100.00	100.00	

3p: IC, *i*-PrOH/hexane = 20/80, v = 1.0 mL/min, λ = 254 nm



Integration Results

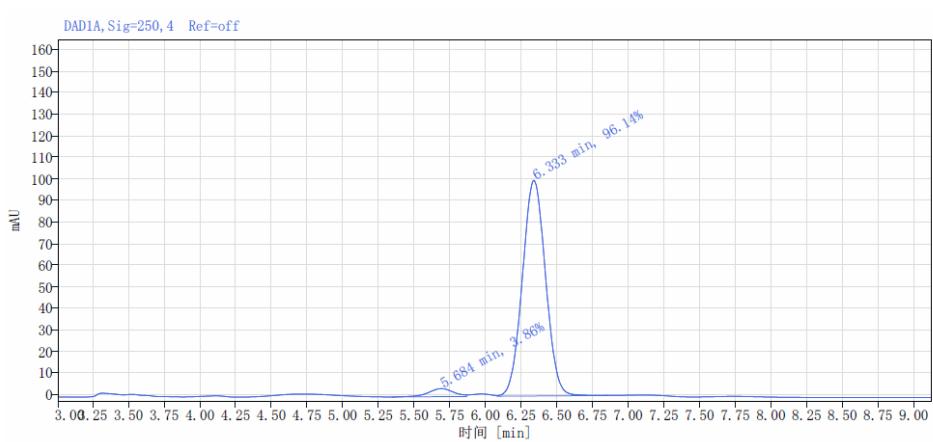
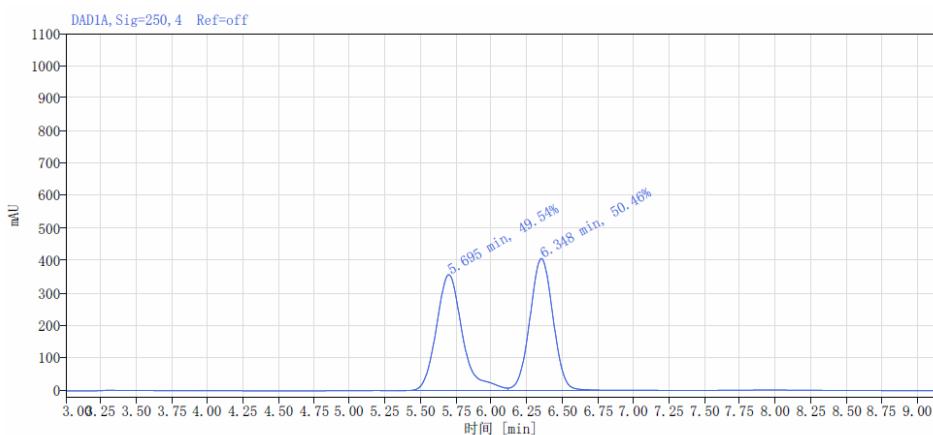
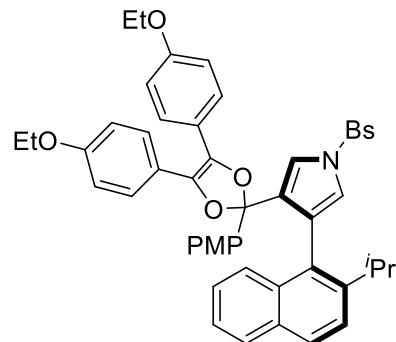
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.050	9.264	45.940	49.68	52.08	n.a.
2		5.450	9.385	42.277	50.32	47.92	n.a.
Total:			18.649	88.217	100.00	100.00	



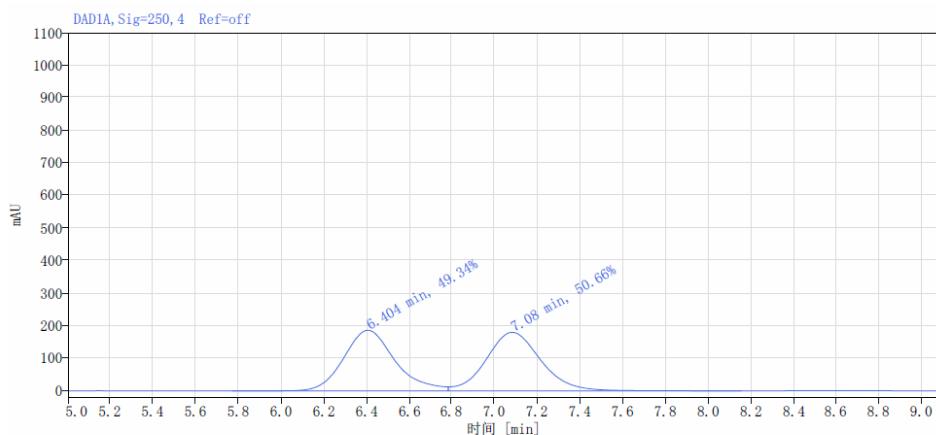
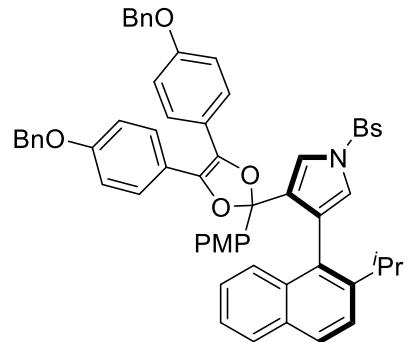
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.008	4.033	26.033	3.25	5.67	n.a.
2		5.323	120.022	433.083	96.75	94.33	n.a.
Total:			124.055	459.117	100.00	100.00	

3q: IC, *i*-PrOH/hexane = 15/85, v = 1.0 mL/min, $\lambda = 254$ nm

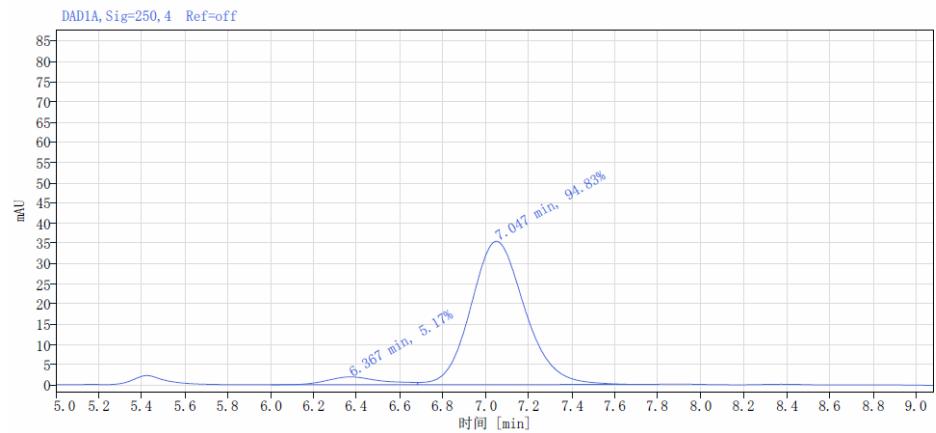


3r: IC, *i*-PrOH/hexane = 20/80, v = 1.0 mL/min, λ = 254 nm



峰结果 (最少峰面积百分比 1%)

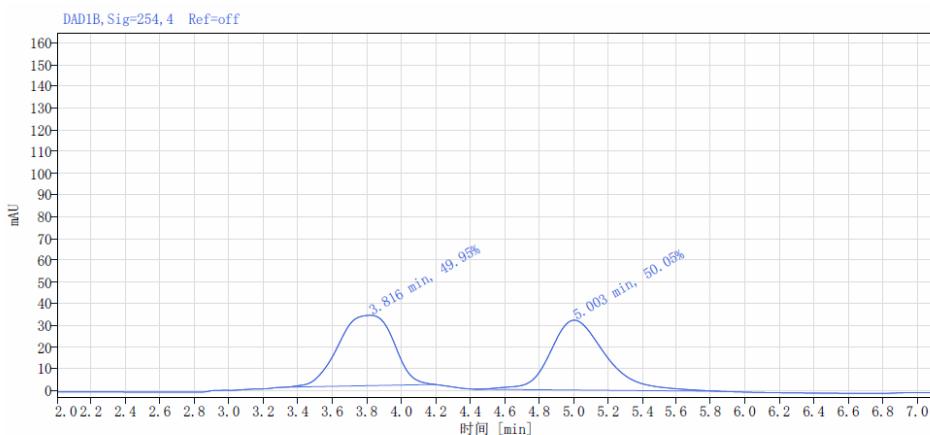
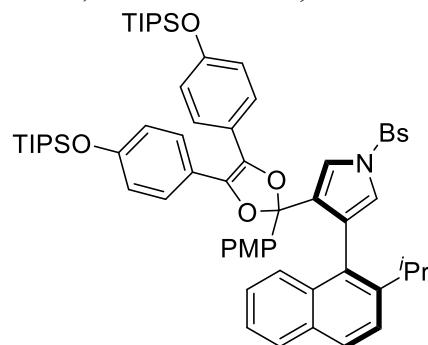
保留时间 (min)	信号说明	峰宽 (min)	峰面积	峰高	峰面积%
6.404	DAD1A, Sig=250, 4 Ref=off	1.014	3121.2	186.4	49.34
7.080	DAD1A, Sig=250, 4 Ref=off	1.374	3205.0	180.0	50.66



峰结果 (最少峰面积百分比 1%)

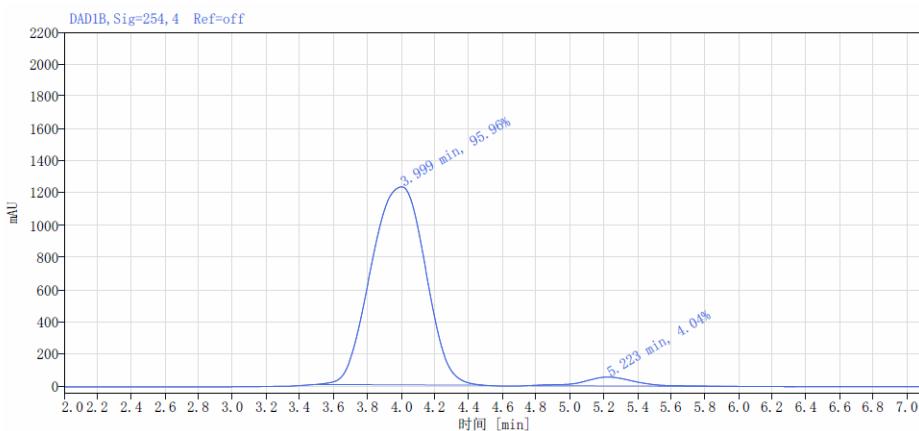
保留时间 (min)	信号说明	峰宽 (min)	峰面积	峰高	峰面积%
6.367	DAD1A, Sig=250, 4 Ref=off	0.682	33.8	1.9	5.17
7.047	DAD1A, Sig=250, 4 Ref=off	1.037	618.6	35.4	94.83

3s: ODH, *i*-PrOH/hexane = 20/80, v = 1.0 mL/min, $\lambda = 254$ nm



峰结果 (最少峰面积百分比 1%)

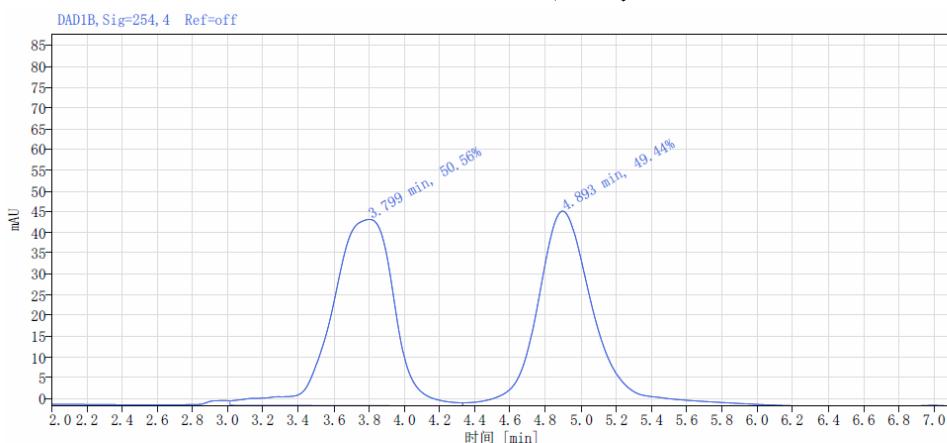
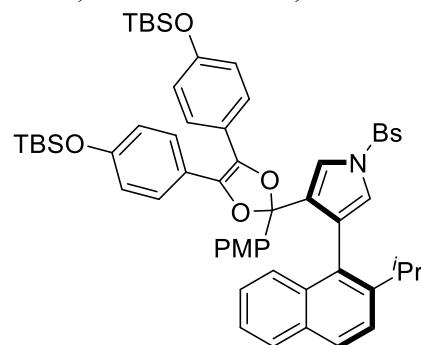
保留时间 (min)	信号说明	峰宽 (min)	峰面积	峰高	峰面积%
3.816	DAD1B, Sig=254, 4 Ref=off	0.865	722.5	32.4	49.95
5.003	DAD1B, Sig=254, 4 Ref=off	1.421	723.9	32.2	50.05



峰结果 (最少峰面积百分比 1%)

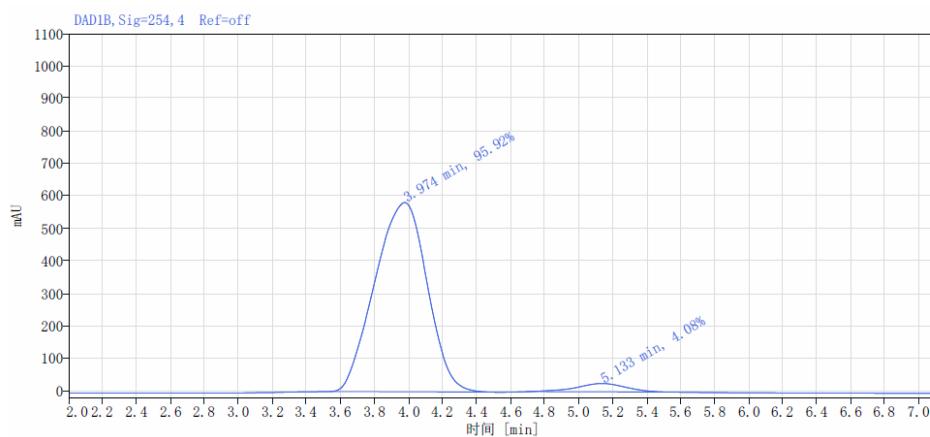
保留时间 (min)	信号说明	峰宽 (min)	峰面积	峰高	峰面积%
3.999	DAD1B, Sig=254, 4 Ref=off	0.989	27521.5	1228.5	95.96
5.223	DAD1B, Sig=254, 4 Ref=off	1.583	1159.7	54.9	4.04

3t: ODH, *i*-PrOH/hexane = 20/80, v = 1.0 mL/min, λ = 254 nm



峰结果 (最少峰面积百分比 1%)

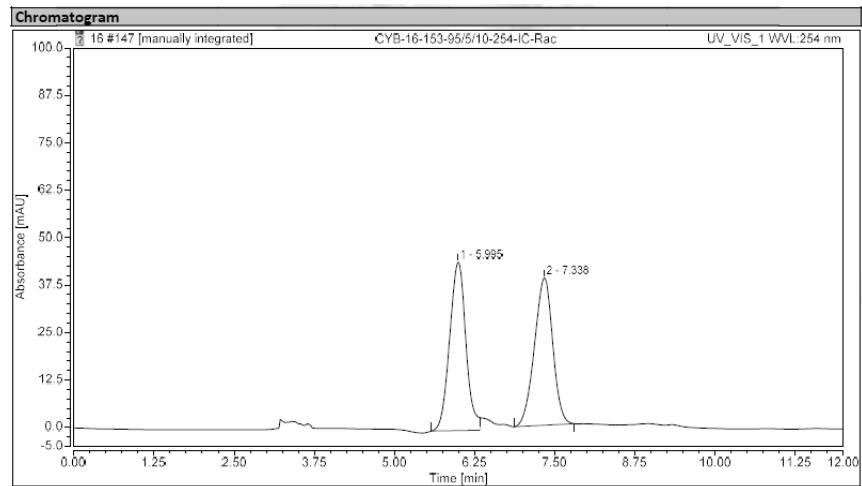
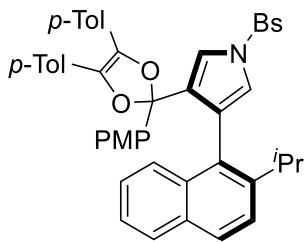
保留时间 (min)	信号说明	峰宽 (min)	峰面积	峰高	峰面积%
3.799	DAD1B, Sig=254, 4 Ref=off	1.318	1091.6	44.8	50.56
4.893	DAD1B, Sig=254, 4 Ref=off	2.413	1067.5	47.0	49.44



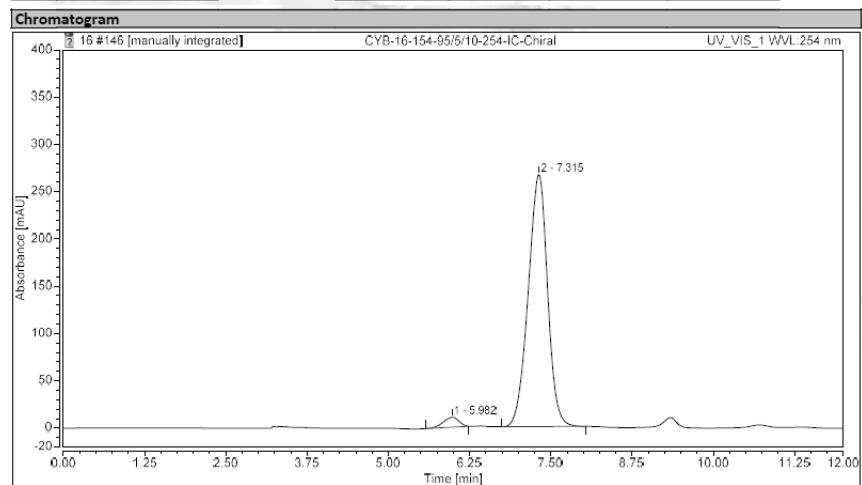
峰结果 (最少峰面积百分比 1%)

保留时间 (min)	信号说明	峰宽 (min)	峰面积	峰高	峰面积%
3.974	DAD1B, Sig=254, 4 Ref=off	0.978	12464.1	582.2	95.92
5.133	DAD1B, Sig=254, 4 Ref=off	0.889	529.9	25.9	4.08

3u: IC, *i*-PrOH/hexane = 5/95, v = 1.0 mL/min, λ = 254 nm

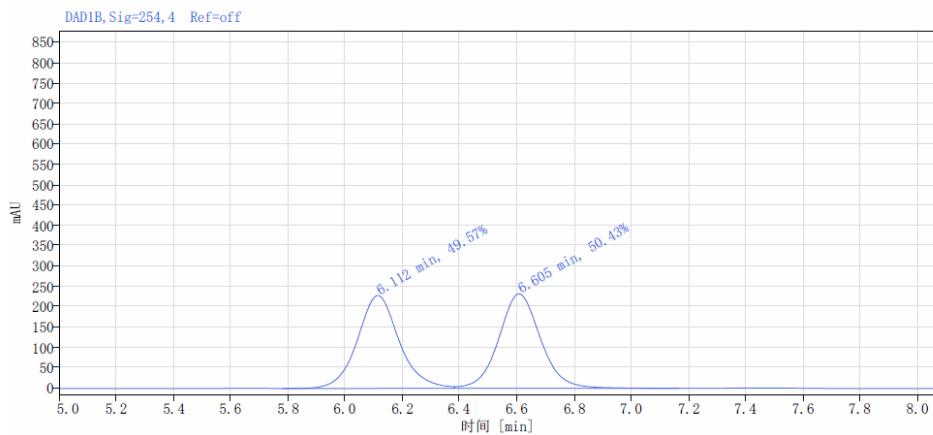
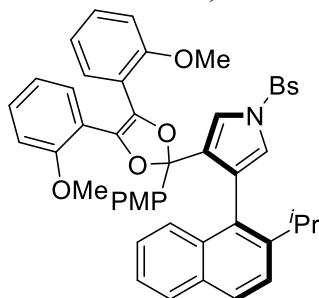


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.995	13.018	44.466	50.38	53.39	n.a.
2		7.338	12.823	38.824	49.62	46.61	n.a.
Total:			25.841	83.289	100.00	100.00	



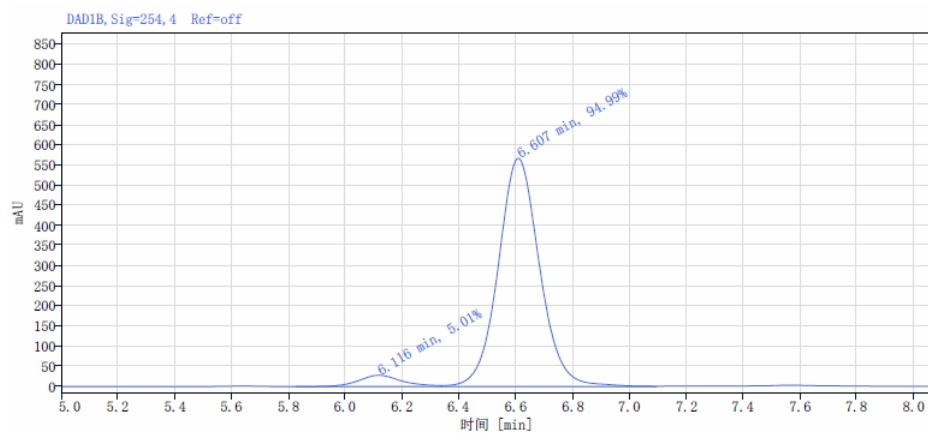
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.982	2.872	10.398	3.03	3.75	n.a.
2		7.315	91.989	266.750	96.97	96.25	n.a.
Total:			94.861	277.148	100.00	100.00	

3v: IA, *i*-PrOH/hexane = 10/90, v = 1.0 mL/min, $\lambda = 254$ nm



峰结果 (最少峰面积百分比 1%)

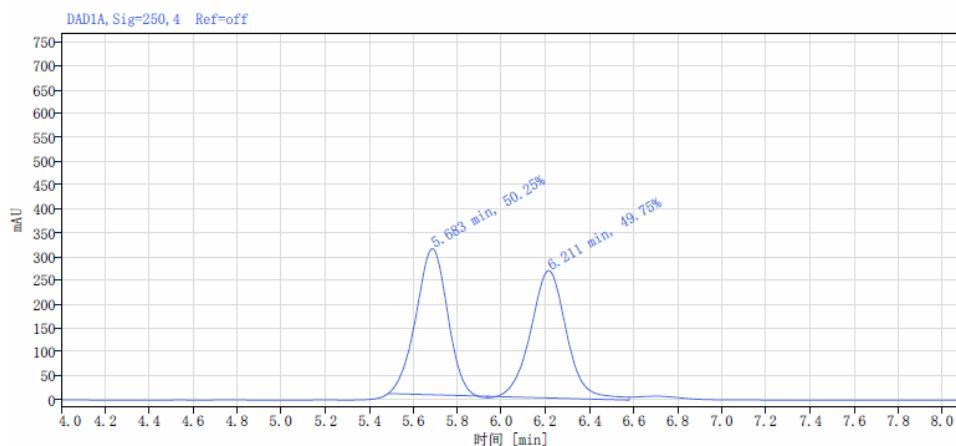
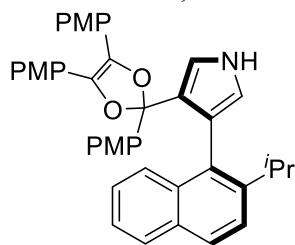
保留时间 (min)	信号说明	峰宽 (min)	峰面积	峰高	峰面积%
6.112	DAD1B, Sig=254, 4 Ref=off	0.602	2324.5	228.9	49.57
6.605	DAD1B, Sig=254, 4 Ref=off	0.784	2364.5	232.7	50.43



峰结果 (最少峰面积百分比 1%)

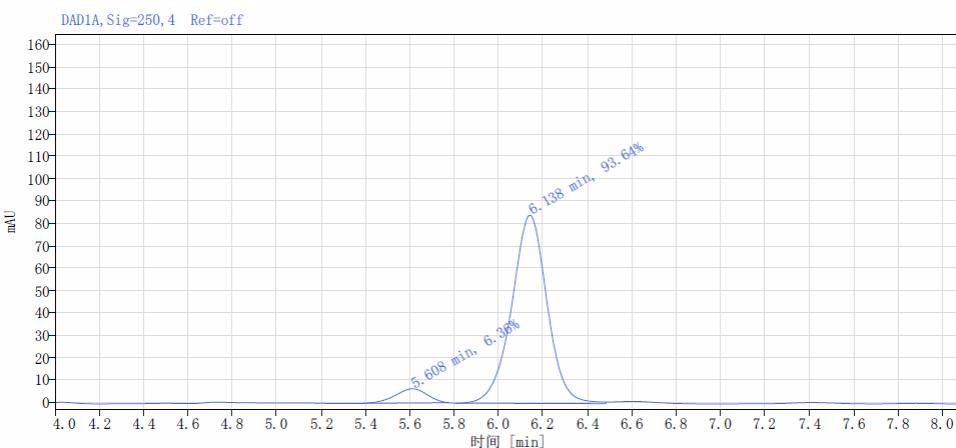
保留时间 (min)	信号说明	峰宽 (min)	峰面积	峰高	峰面积%
6.116	DAD1B, Sig=254, 4 Ref=off	0.513	303.2	28.4	5.01
6.607	DAD1B, Sig=254, 4 Ref=off	0.755	5746.9	568.1	94.99

4: IA, *i*-PrOH/hexane = 20/80, v = 1.0 mL/min, λ = 254 nm



峰结果 (最少峰面积百分比 1%)

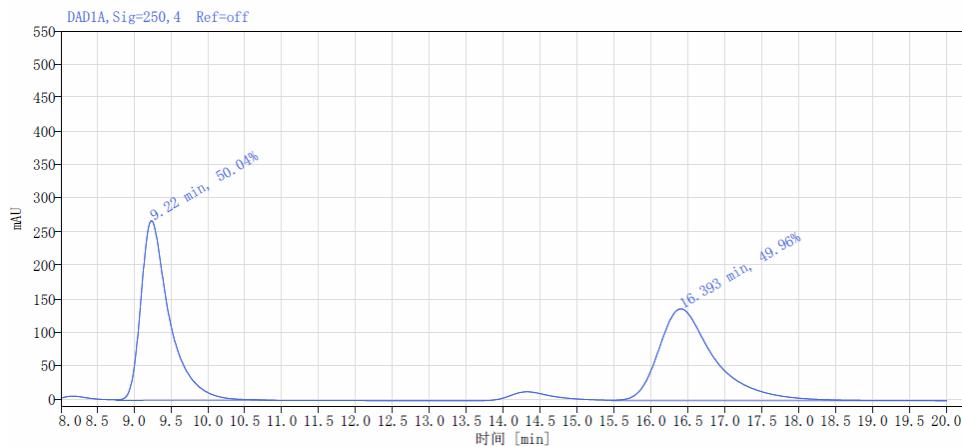
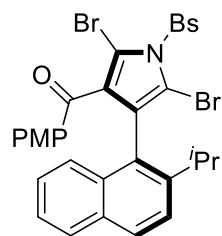
保留时间 (min)	信号说明	峰宽 (min)	峰面积	峰高	峰面积%
5.683	DAD1A, Sig=250, 4 Ref=off	0.451	3046.0	306.6	50.25
6.211	DAD1A, Sig=250, 4 Ref=off	0.642	3015.1	267.2	49.75



峰结果 (最少峰面积百分比 1%)

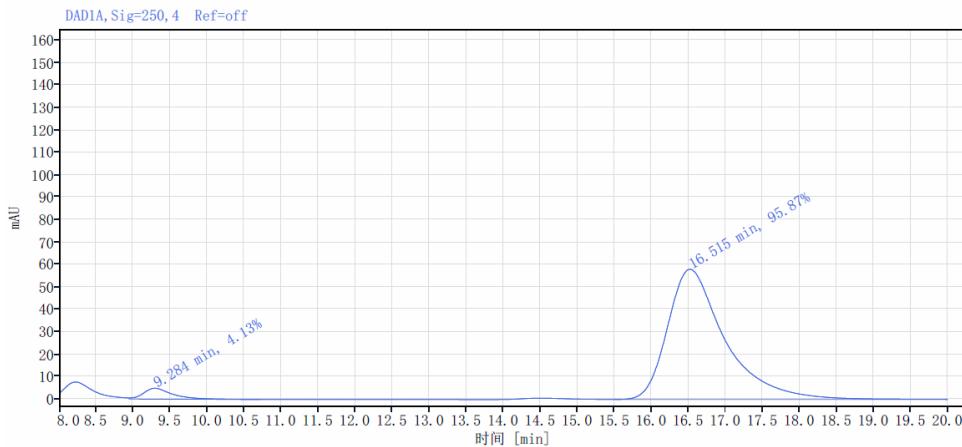
保留时间 (min)	信号说明	峰宽 (min)	峰面积	峰高	峰面积%
5.608	DAD1A, Sig=250, 4 Ref=off	0.384	63.7	6.4	6.36
6.138	DAD1A, Sig=250, 4 Ref=off	0.675	937.3	84.2	93.64

5: ADH, *i*-PrOH/hexane = 20/80, v = 1.0 mL/min, λ = 254 nm



峰结果 (最少峰面积百分比 1%)

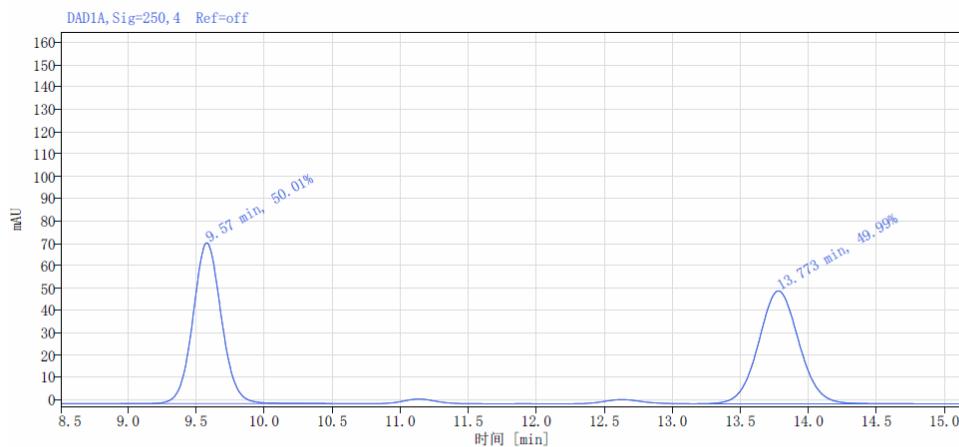
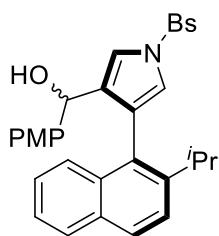
保留时间 (min)	信号说明	峰宽 (min)	峰面积	峰高	峰面积%
9.220	DAD1A, Sig=250, 4 Ref=off	2.139	7215.7	267.8	50.04
16.393	DAD1A, Sig=250, 4 Ref=off	4.540	7205.2	136.9	49.96



峰结果 (最少峰面积百分比 1%)

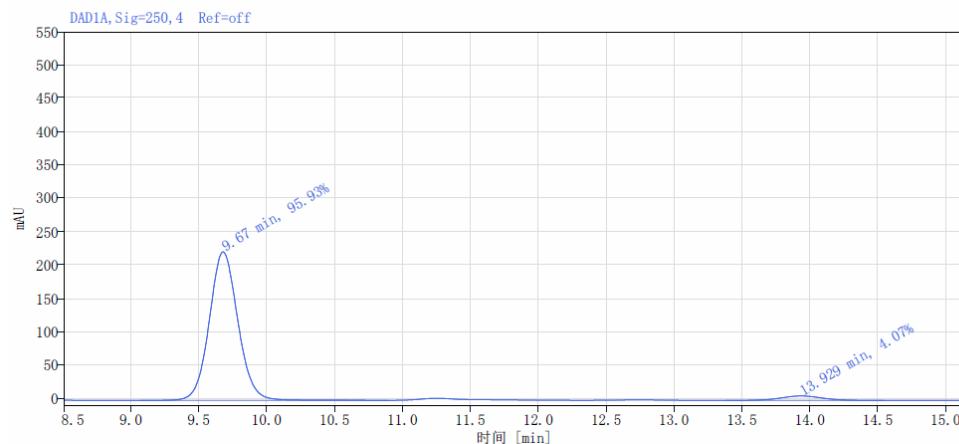
保留时间 (min)	信号说明	峰宽 (min)	峰面积	峰高	峰面积%
9.284	DAD1A, Sig=250, 4 Ref=off	1.786	134.5	4.9	4.13
16.515	DAD1A, Sig=250, 4 Ref=off	4.507	3122.9	58.1	95.87

6: IA, *i*-PrOH/hexane = 20/80, v = 1.0 mL/min, λ = 254 nm



峰结果 (最少峰面积百分比 1%)

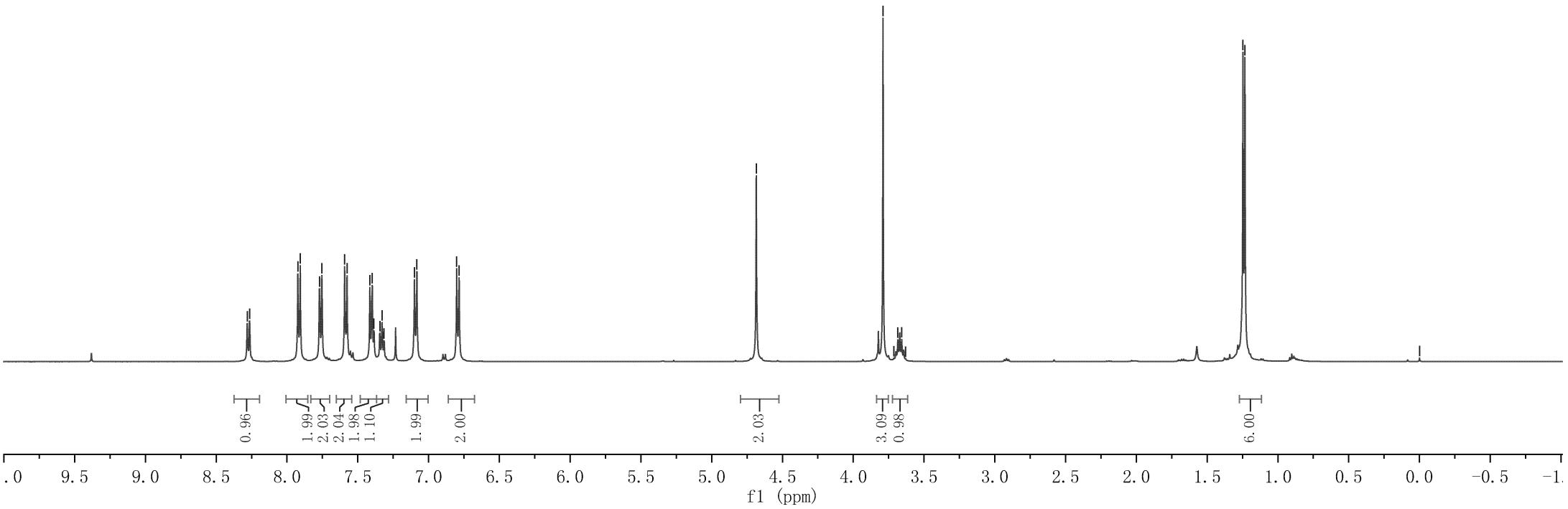
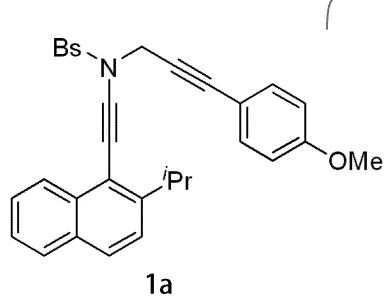
保留时间 (min)	信号说明	峰宽 (min)	峰面积	峰高	峰面积%
9.570	DAD1A, Sig=250, 4 Ref=off	1.554	1049.9	72.1	50.01
13.773	DAD1A, Sig=250, 4 Ref=off	2.173	1049.6	50.6	49.99

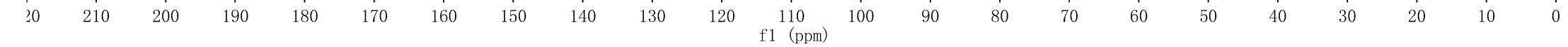


峰结果 (最少峰面积百分比 1%)

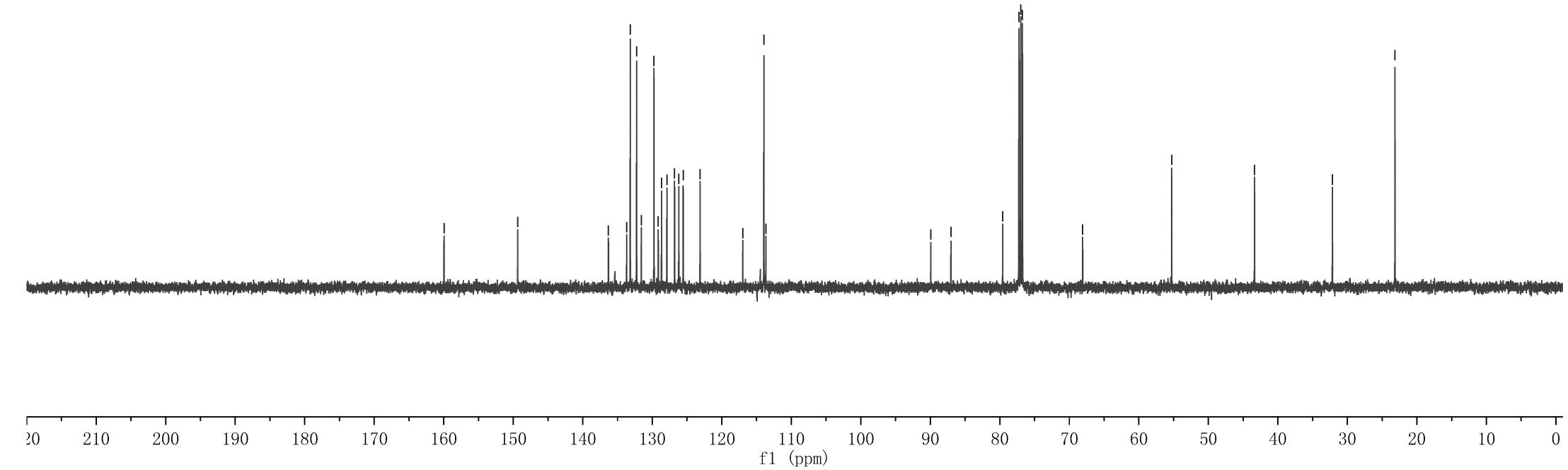
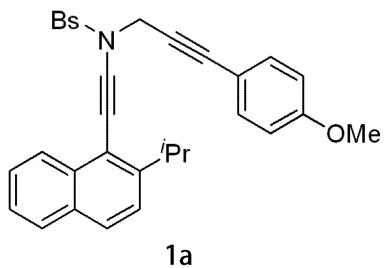
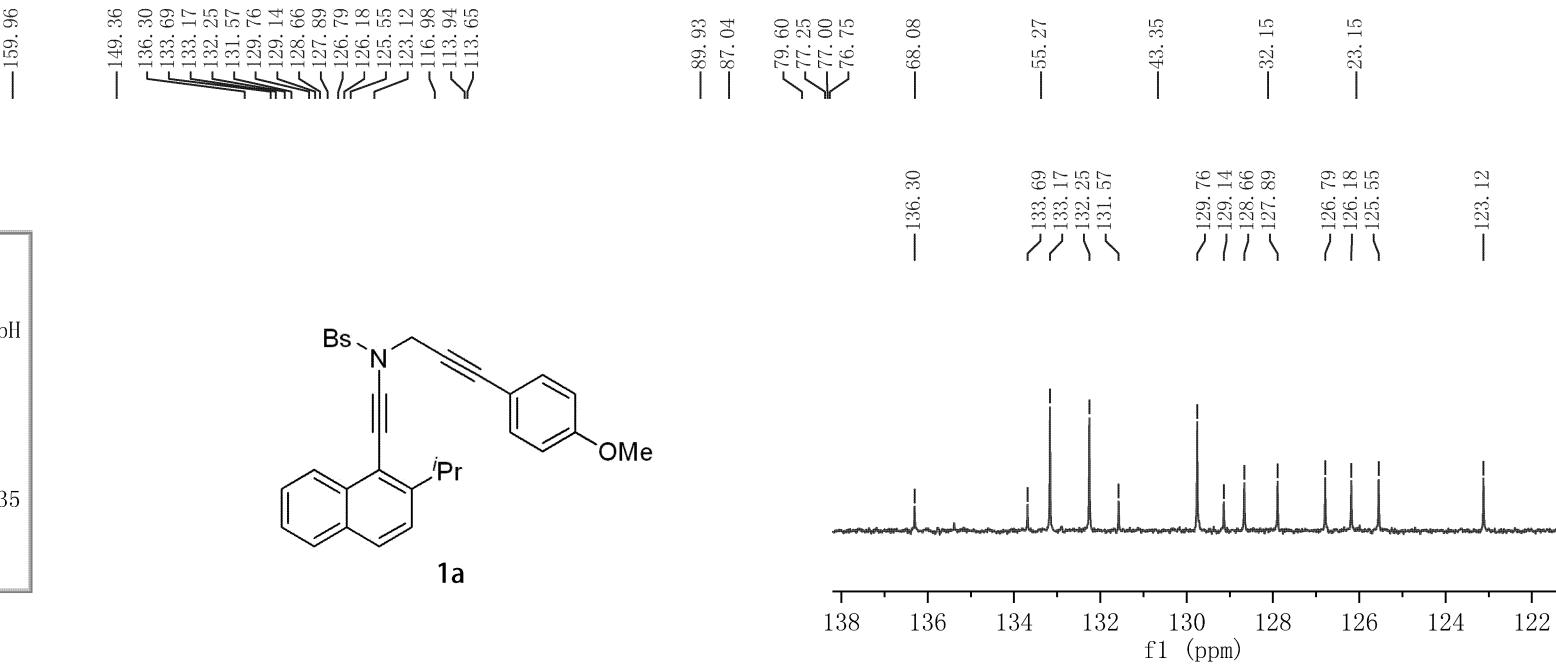
保留时间 (min)	信号说明	峰宽 (min)	峰面积	峰高	峰面积%
9.670	DAD1A, Sig=250, 4 Ref=off	1.829	3258.2	222.5	95.93
13.929	DAD1A, Sig=250, 4 Ref=off	1.170	138.2	6.6	4.07

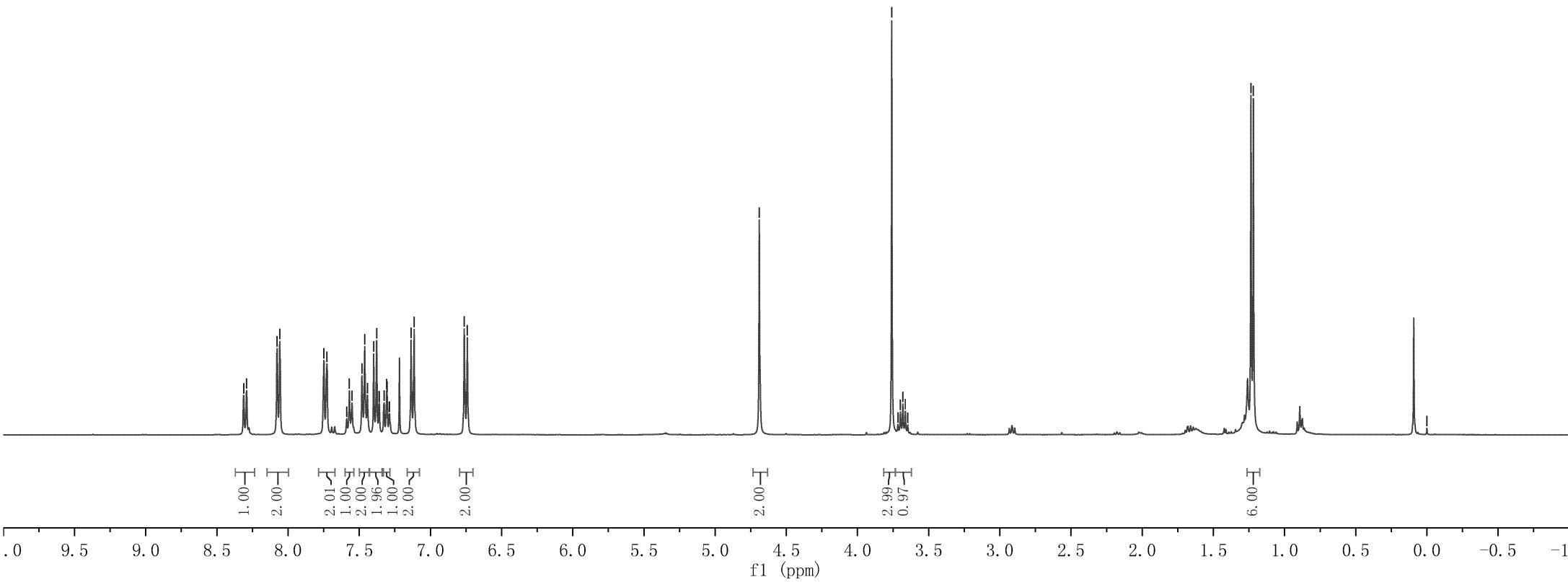
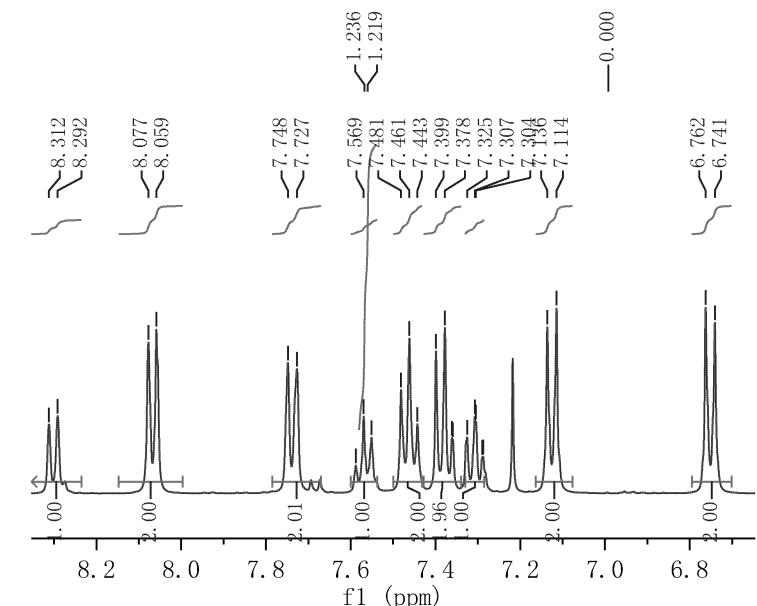
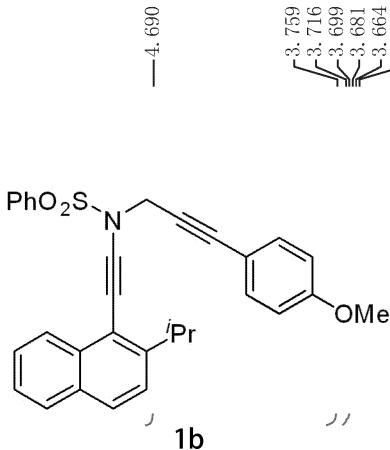
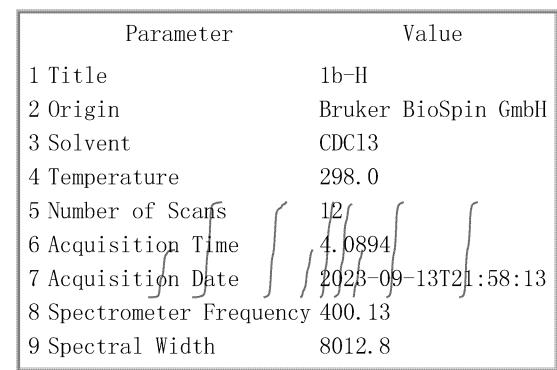
Parameter	Value
1 Title	CHH-1-120
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	299.7
5 Number of Scans	16
6 Acquisition Time	3.1719
7 Acquisition Date	2022-11-08T22:13:16
8 Spectrometer Frequency	500.17
9 Spectral Width	10330.6

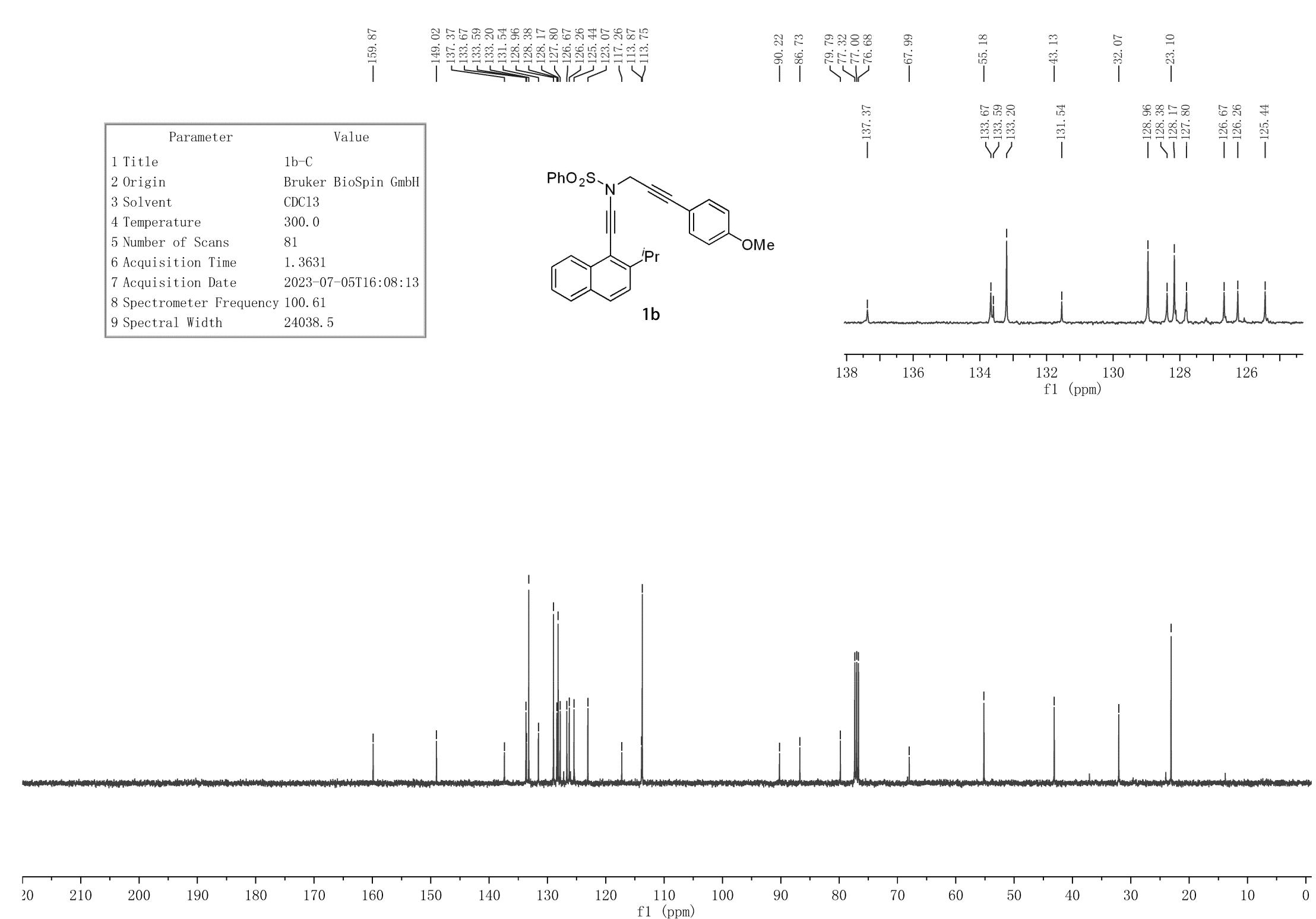




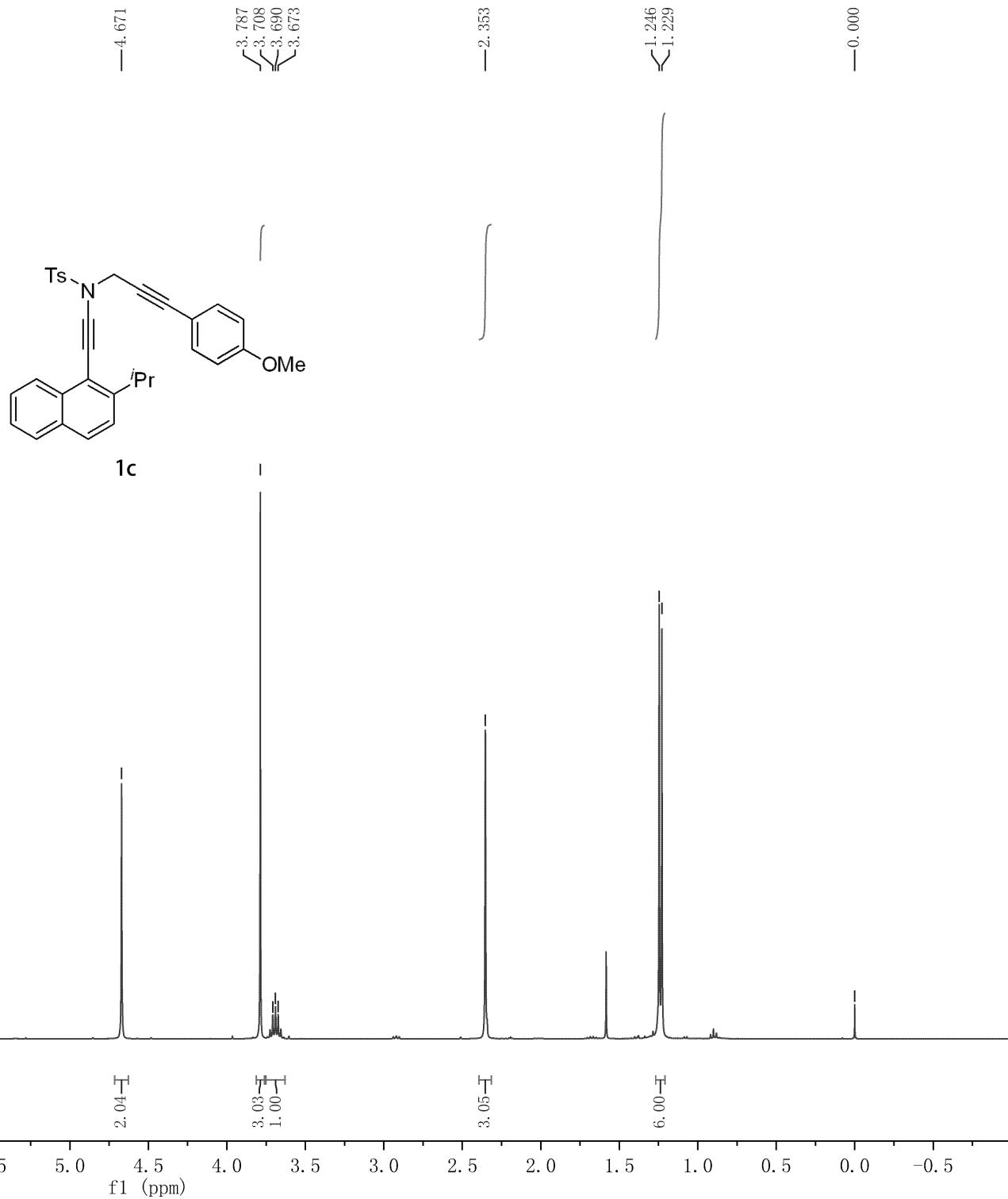
Parameter	Value
1 Title	CHH-1-120
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	299.9
5 Number of Scans	51
6 Acquisition Time	1.1010
7 Acquisition Date	2022-11-08T22:16:35
8 Spectrometer Frequency	125.77
9 Spectral Width	29761.9



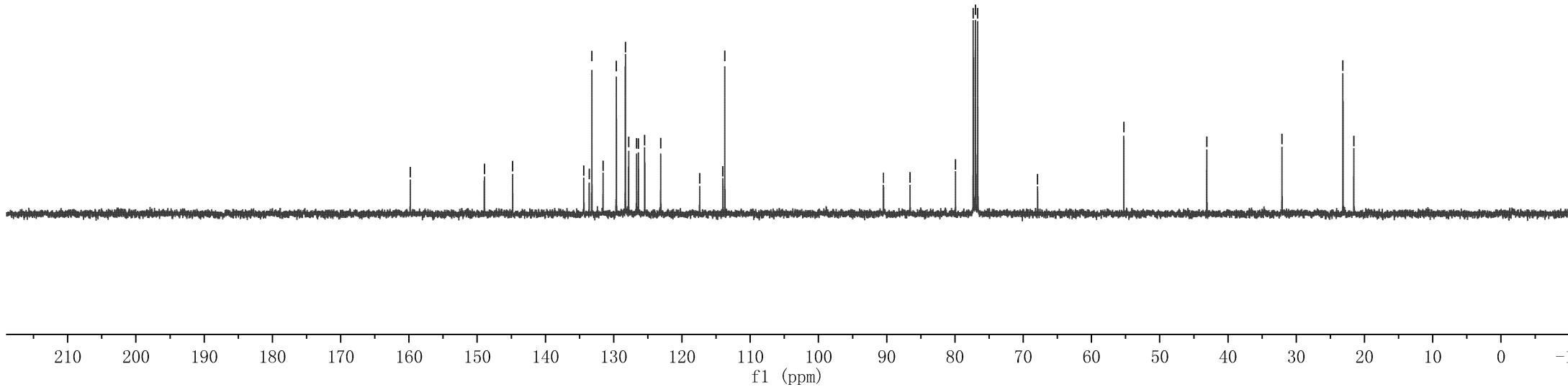
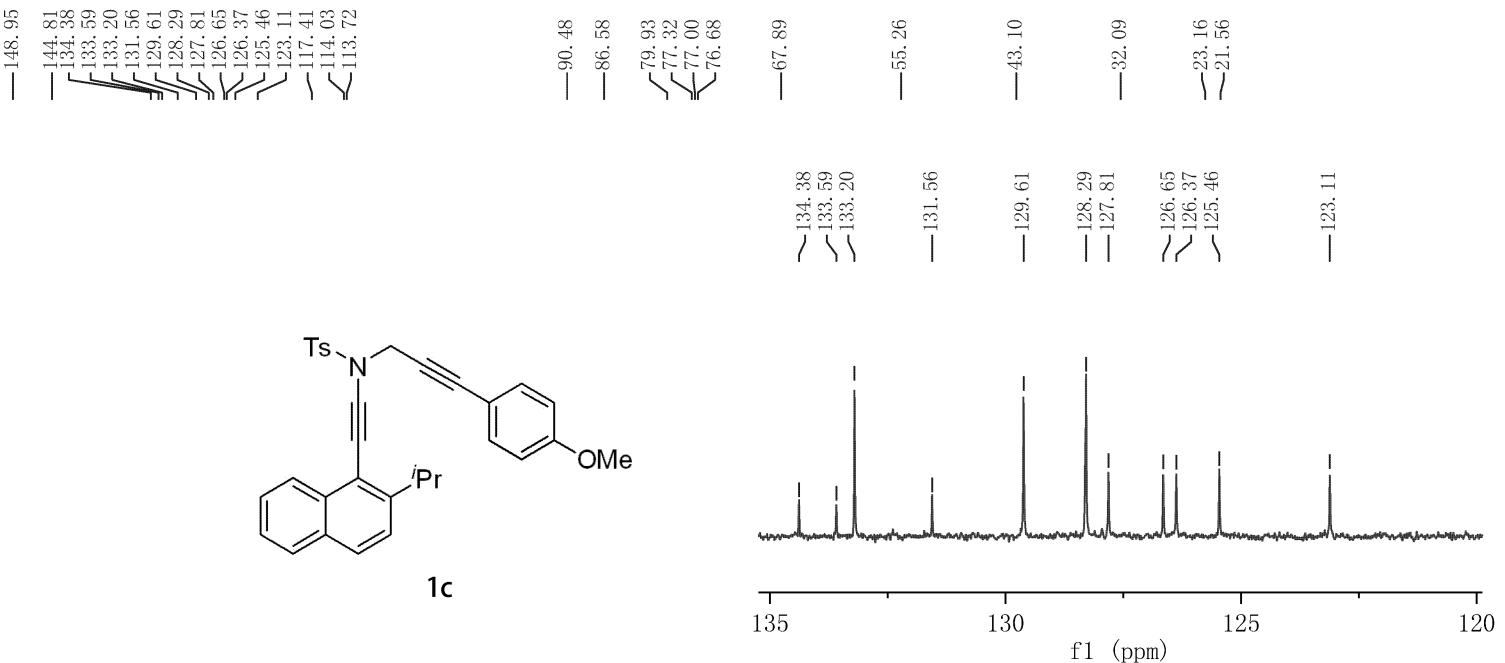


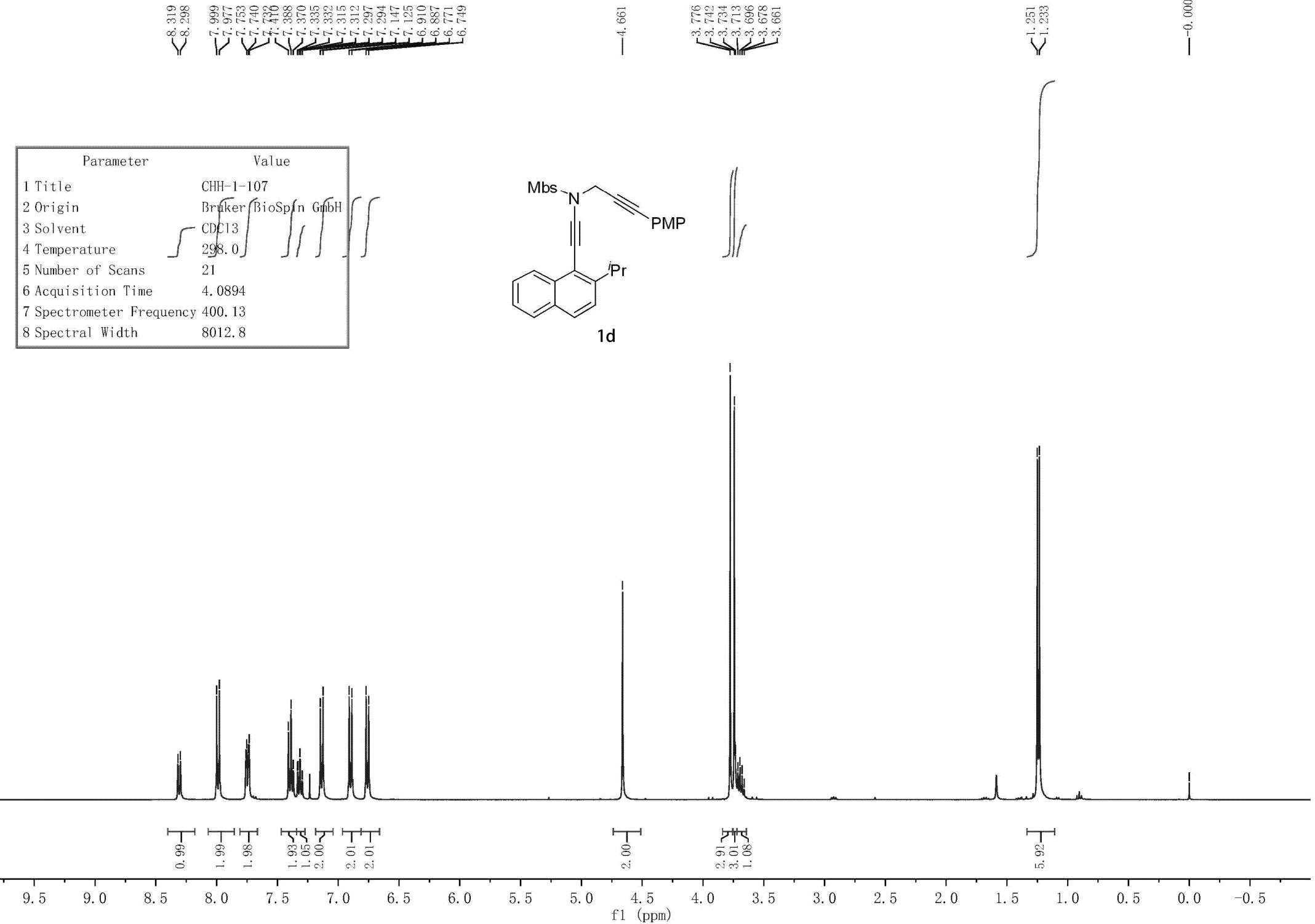


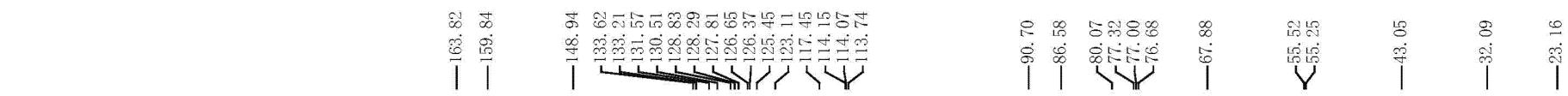
Parameter	Value
1 Title	CHH-1-122-Ts-iPr
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	294.1
5 Number of Scans	11
6 Acquisition Time	3.9846
7 Acquisition Date	2022-11-09T10:33:55
8 Spectrometer Frequency	399.93
9 Spectral Width	8223.7



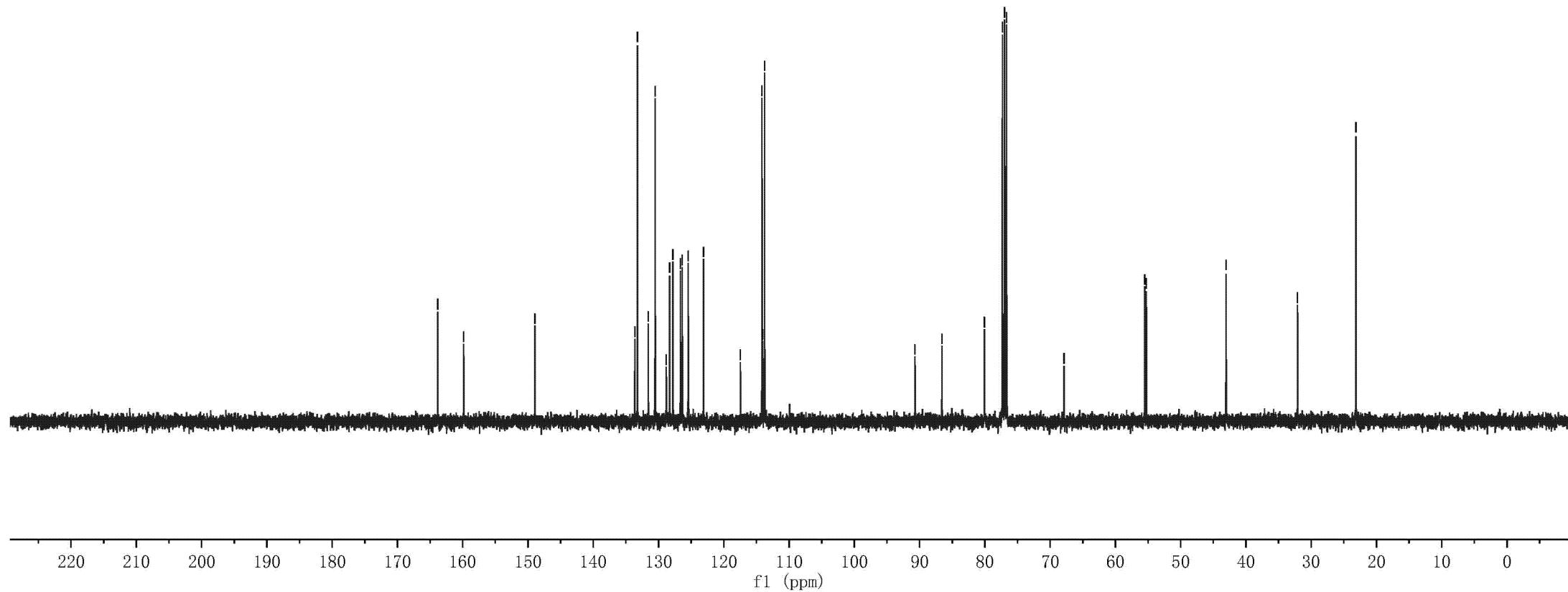
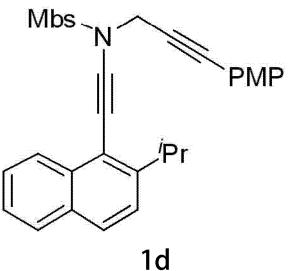
Parameter	Value
1 Title	CHH-1-122-Ts-iPr
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	294.1
5 Number of Scans	11
6 Acquisition Time	3.9846
7 Acquisition Date	2022-11-09T10:33:55
8 Spectrometer Frequency	399.93
9 Spectral Width	8223.7



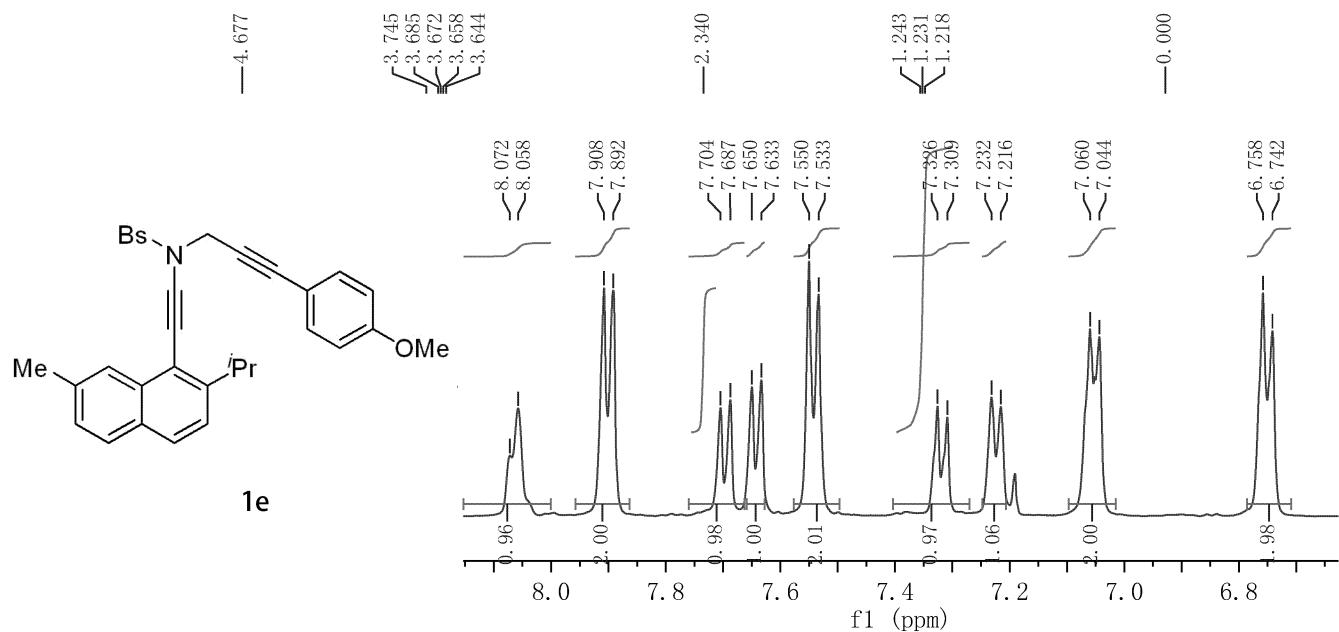




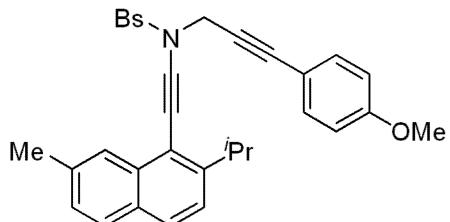
Parameter	Value
1 Title	CHH-1-107
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	300.0
5 Number of Scans	51
6 Acquisition Time	1.3631
7 Spectrometer Frequency	100.61
8 Spectral Width	24038.5



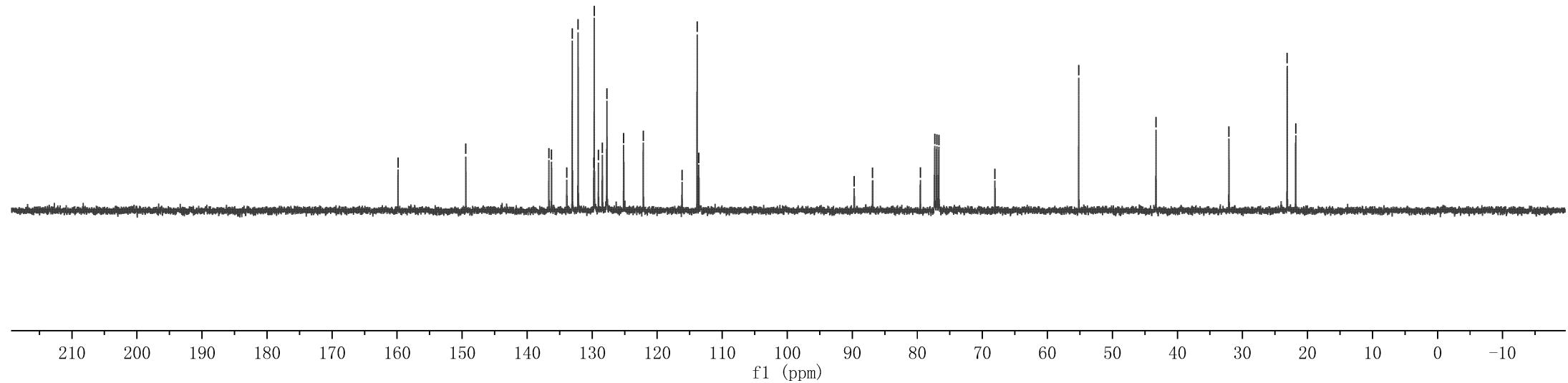
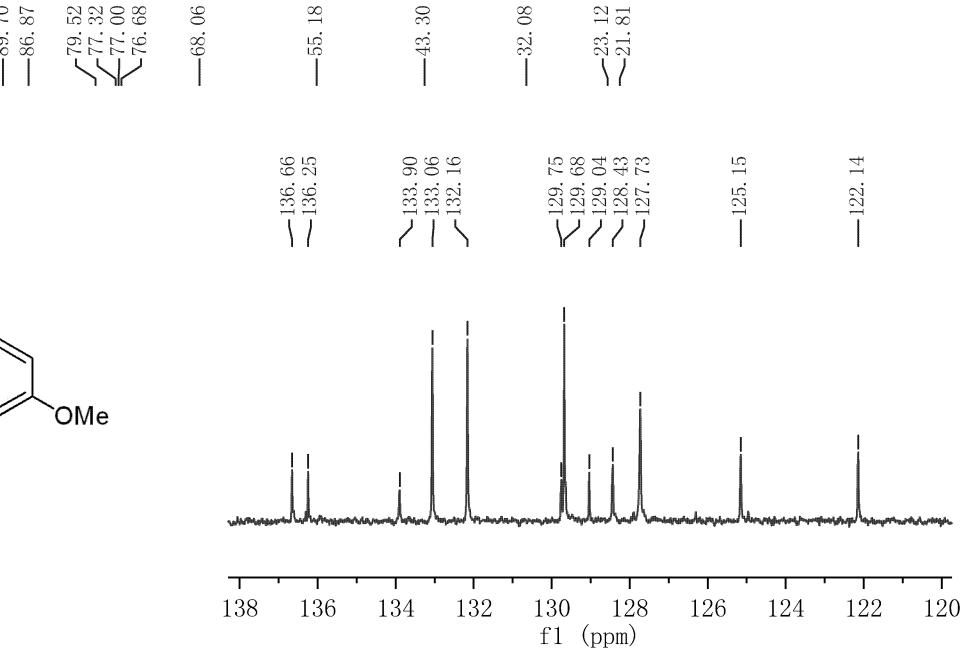
Parameter	Value
1 Title	1e-H
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	297.8
5 Number of Scans	5
6 Acquisition Time	3.1719
7 Acquisition Date	2023-07-31T17:09:09
8 Spectrometer Frequency	500.17
9 Spectral Width	10330.6

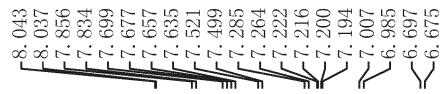


Parameter	Value
1 Title	1e-H
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDC13
4 Temperature	297.8
5 Number of Scans	5
6 Acquisition Time	3.1719
7 Acquisition Date	2023-07-31T17:09:09
8 Spectrometer Frequency	500.17
9 Spectral Width	10330.6

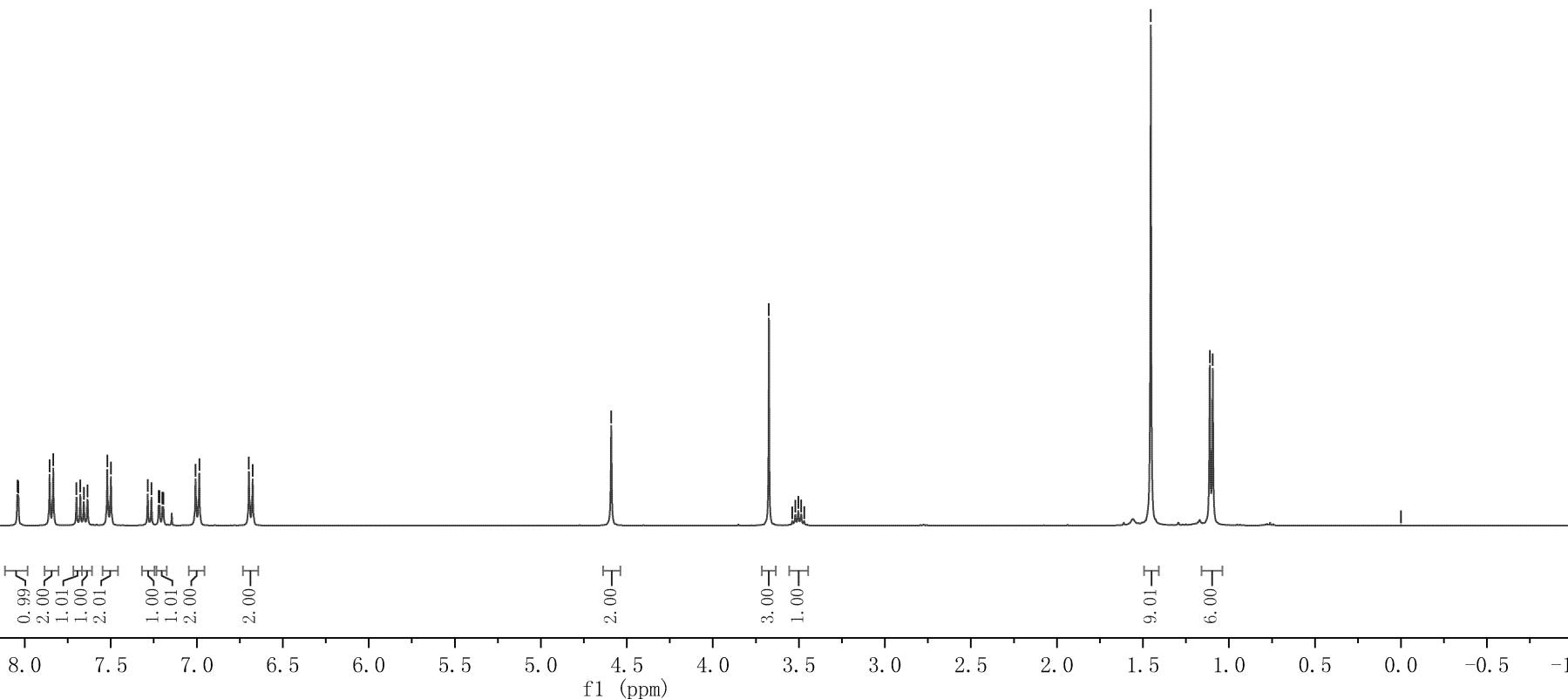
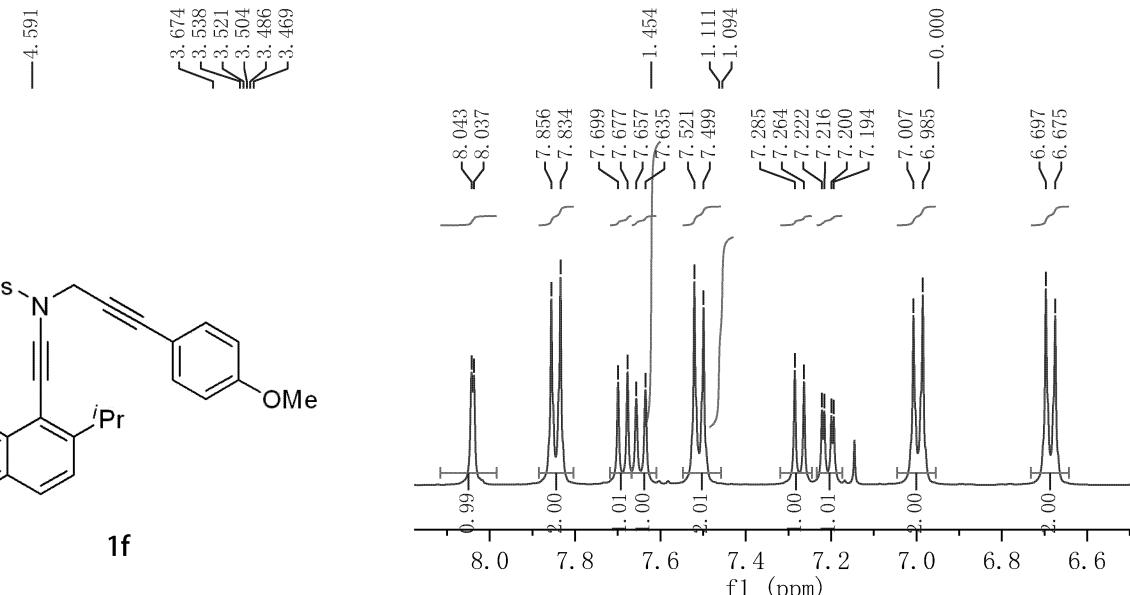
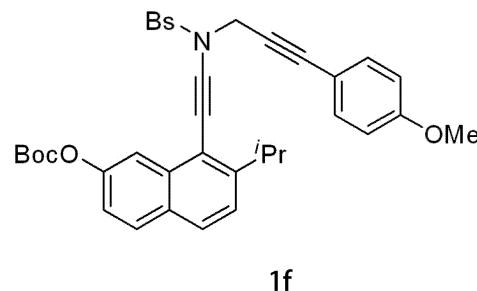


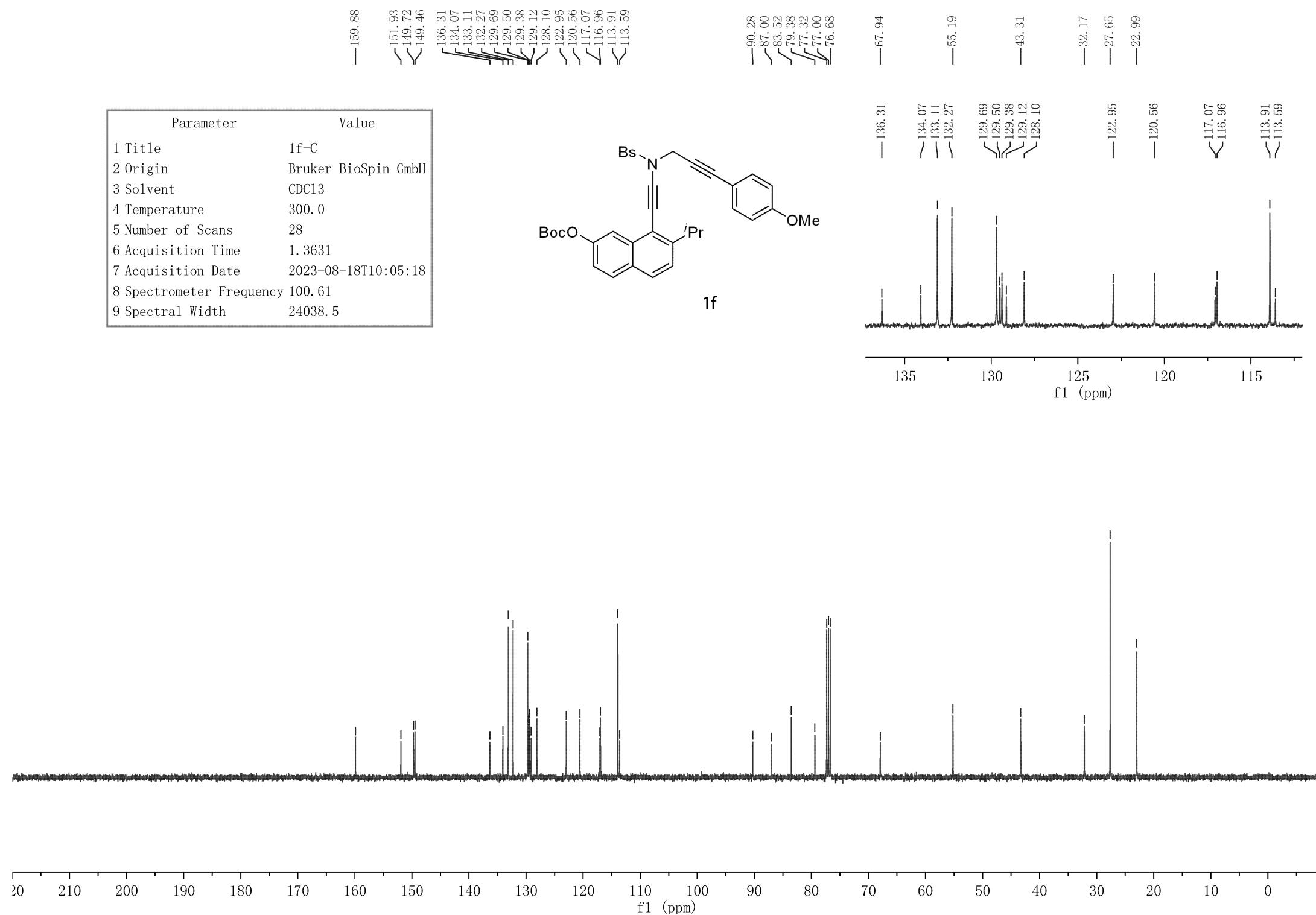
1e



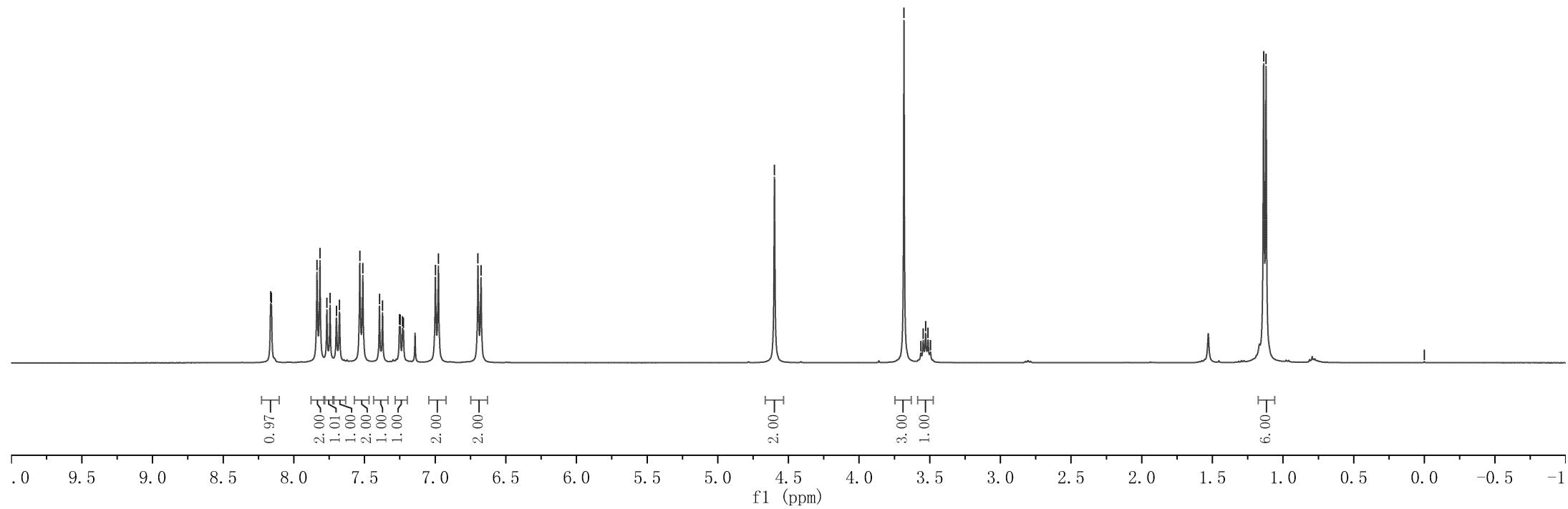
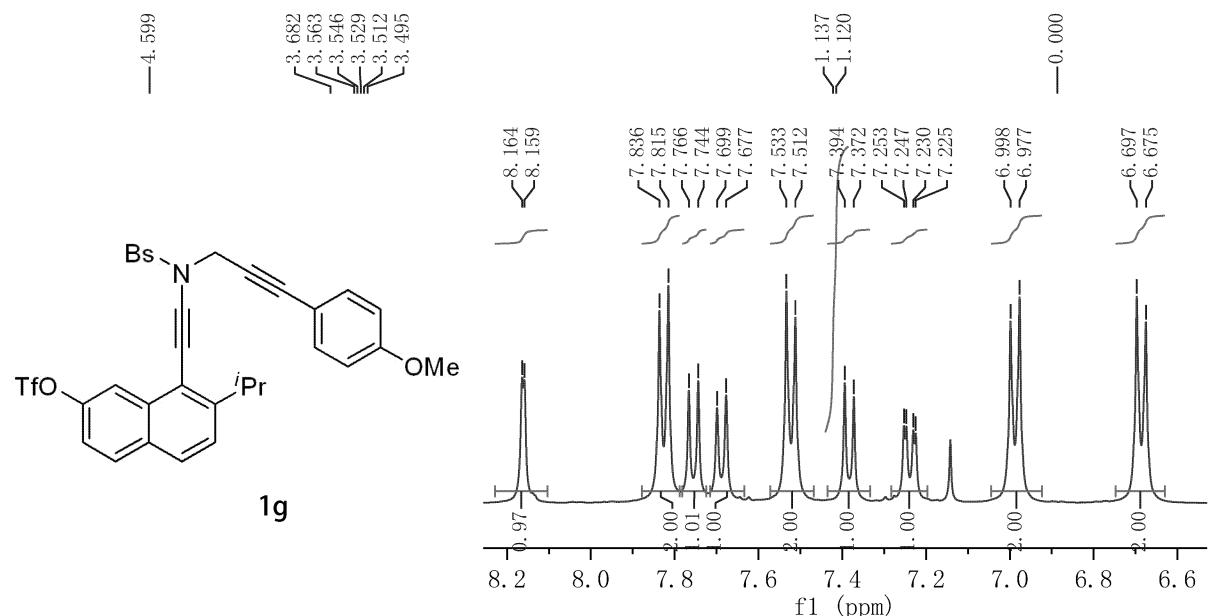


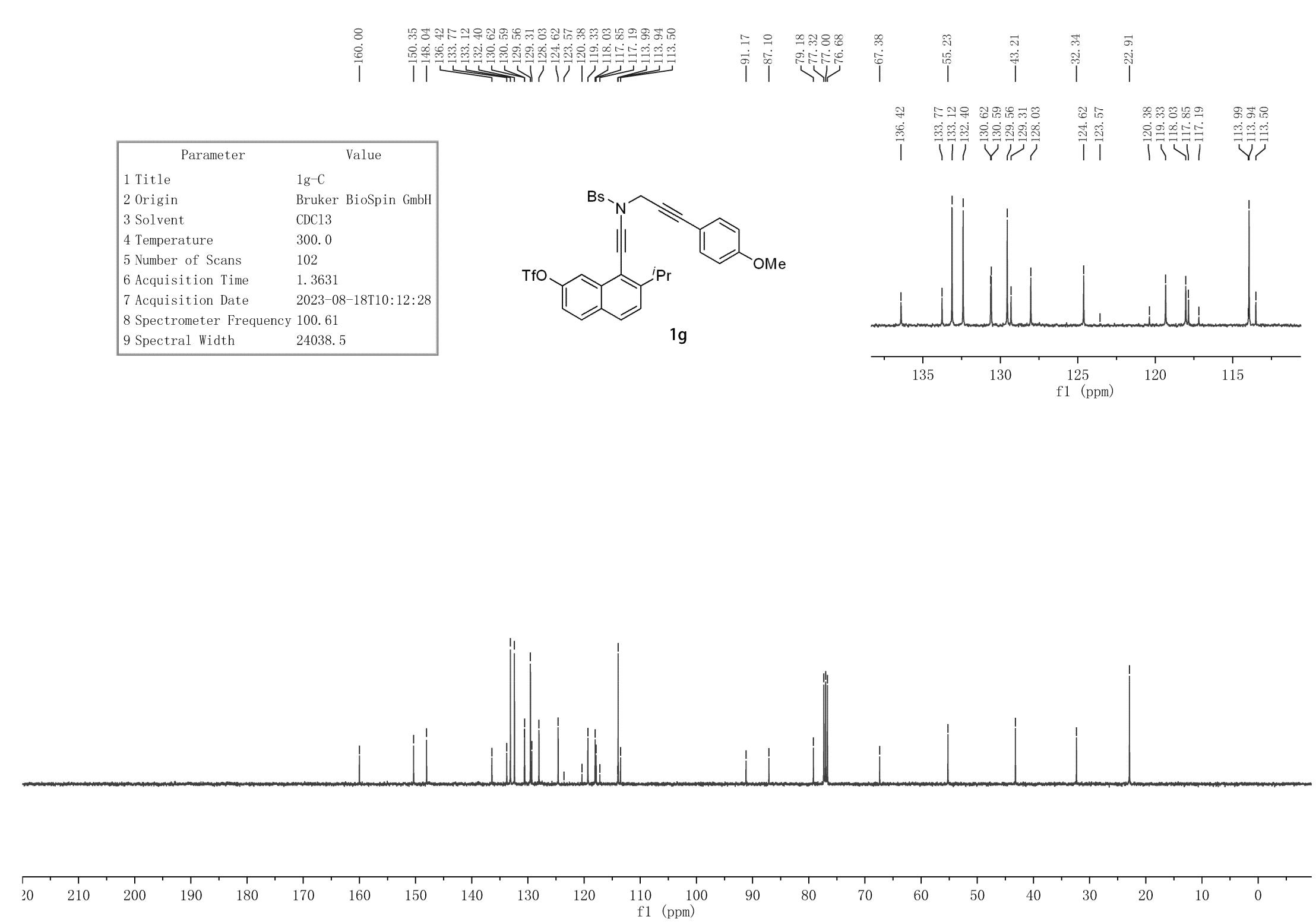
Parameter	Value
1 Title	1f-H
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	11
6 Acquisition Time	4.0894
7 Acquisition Date	2023-08-18T10:03:34
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8





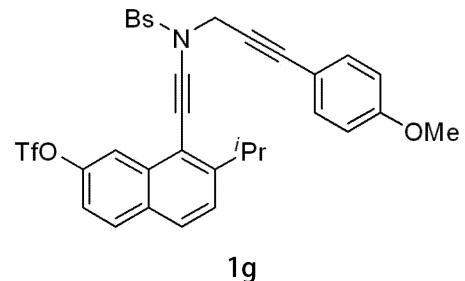
Parameter	Value
1 Title	1g-H
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	298.0
5 Number of Scans	15
6 Acquisition Time	4.0894
7 Acquisition Date	2023-08-18T10:10:04
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8





Parameter	Value
1 Title	1g-F
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	297.1
5 Number of Scans	16
6 Acquisition Time	0.7340
7 Acquisition Date	2023-09-12T11:26:36
8 Spectrometer Frequency	376.31
9 Spectral Width	89285.7

-72.62

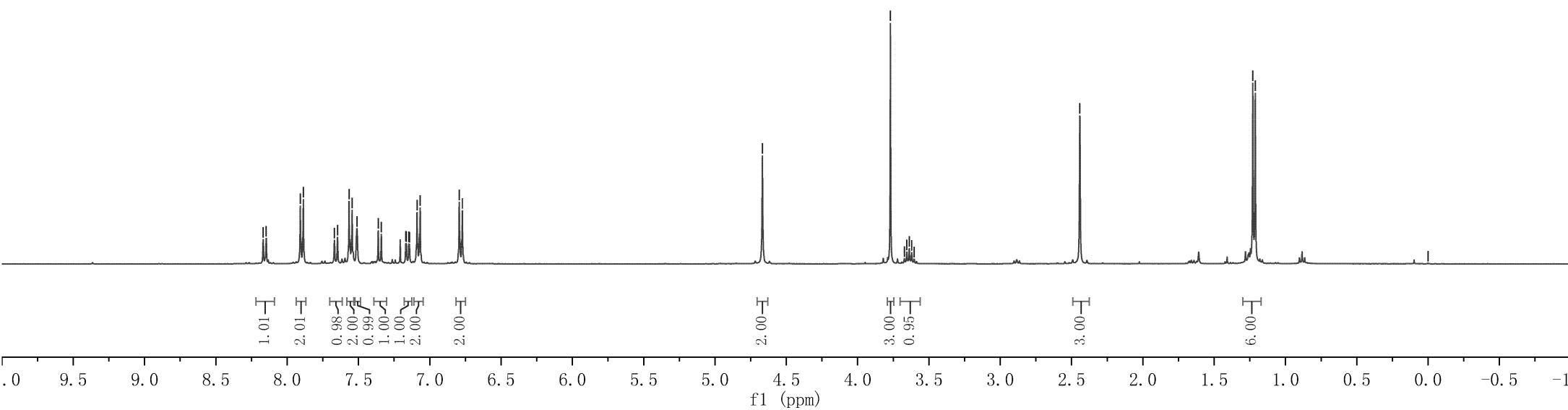
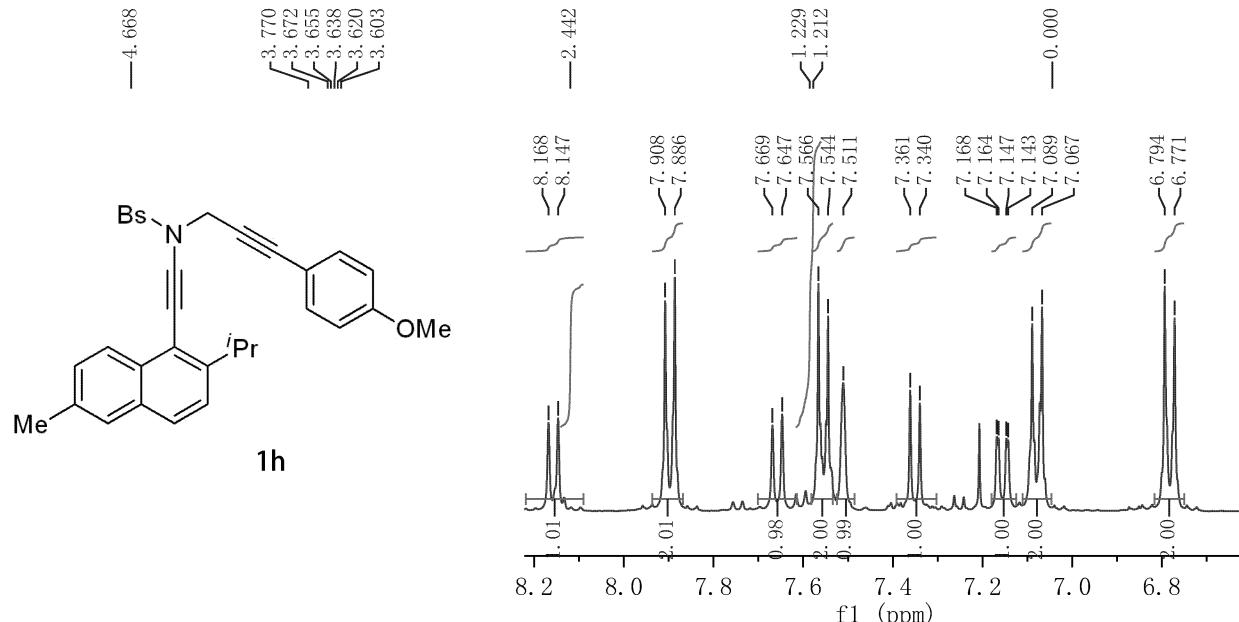


-72.62

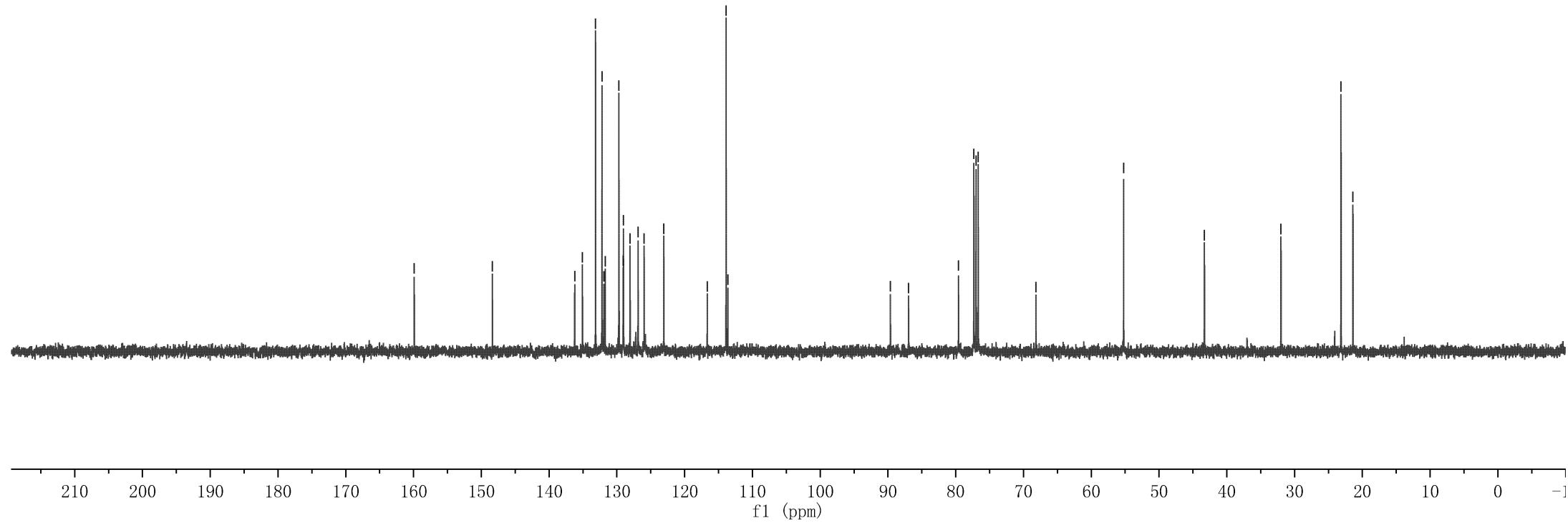
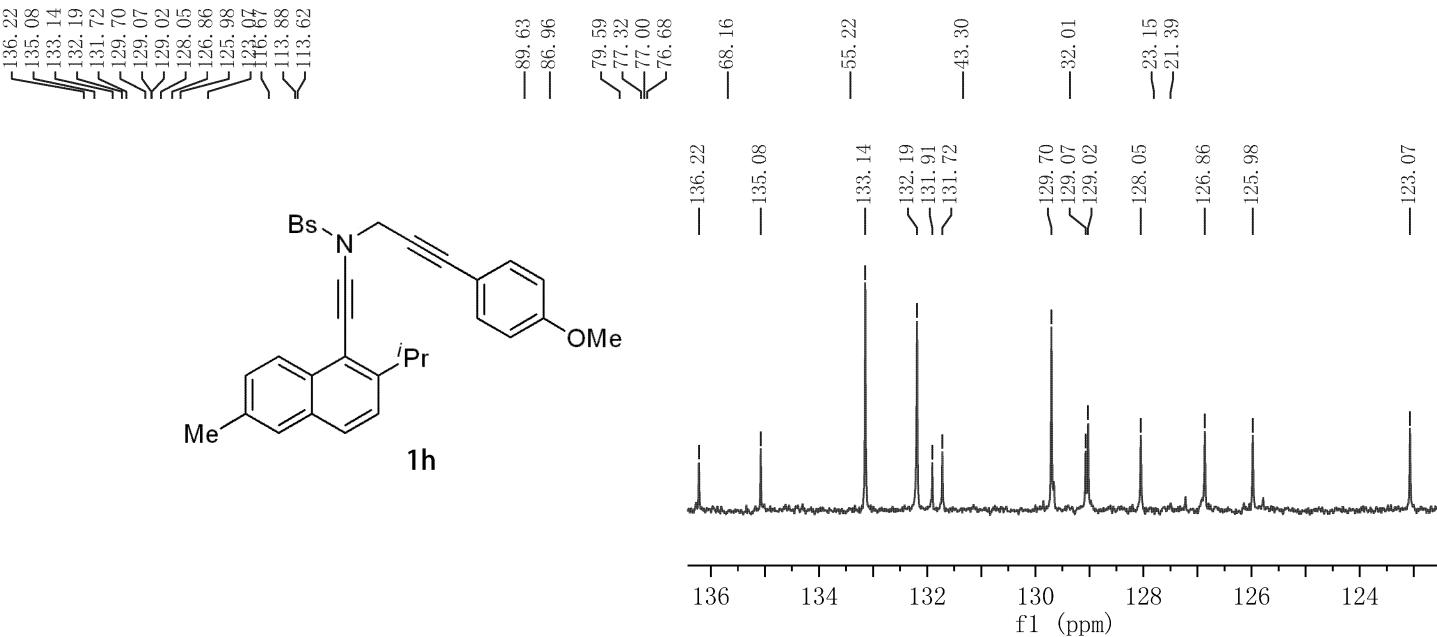
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

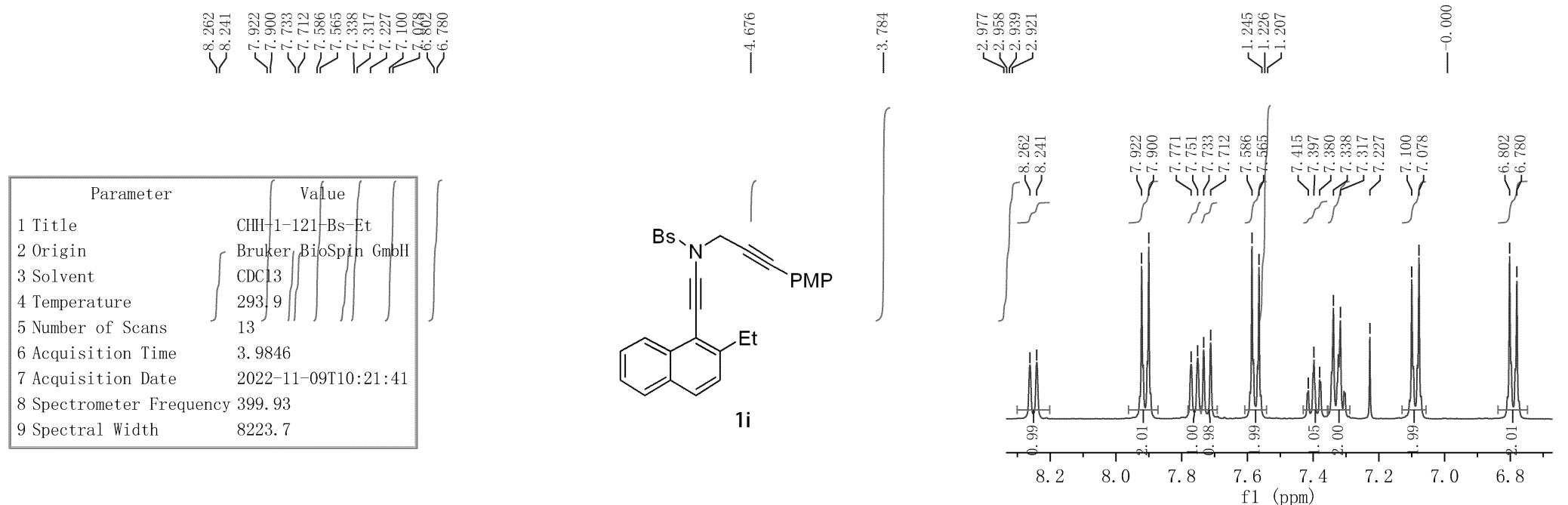
f1 (ppm)

Parameter	Value
1 Title	1h-H
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	300.0
5 Number of Scans	11
6 Acquisition Time	3.9846
7 Acquisition Date	2023-07-31T21:35:06
8 Spectrometer Frequency	399.93
9 Spectral Width	8223.7

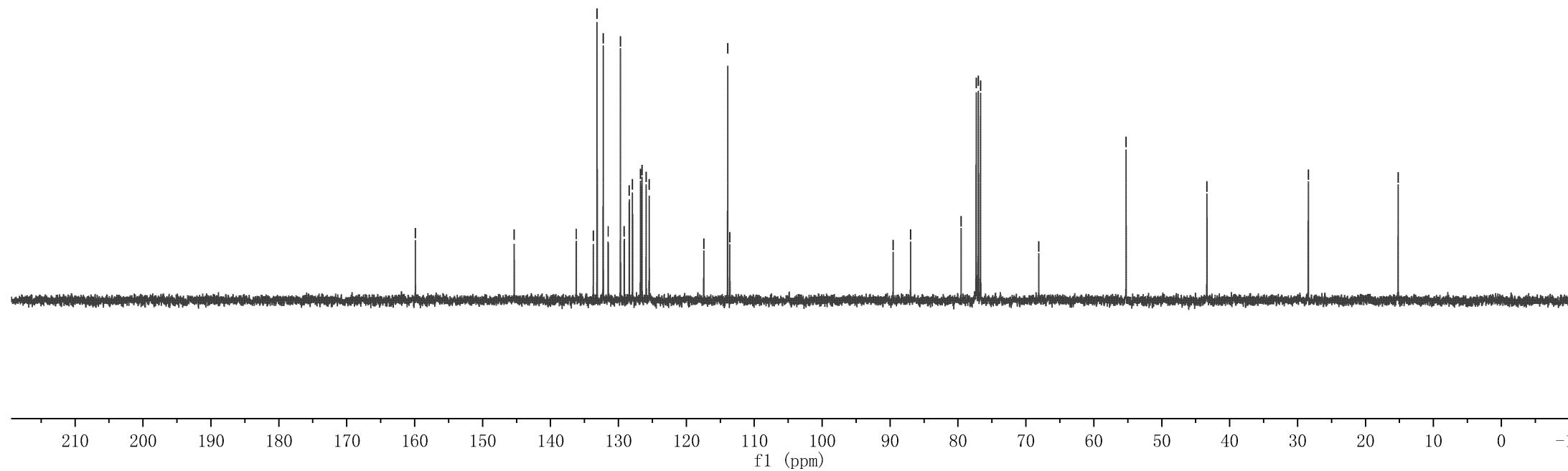
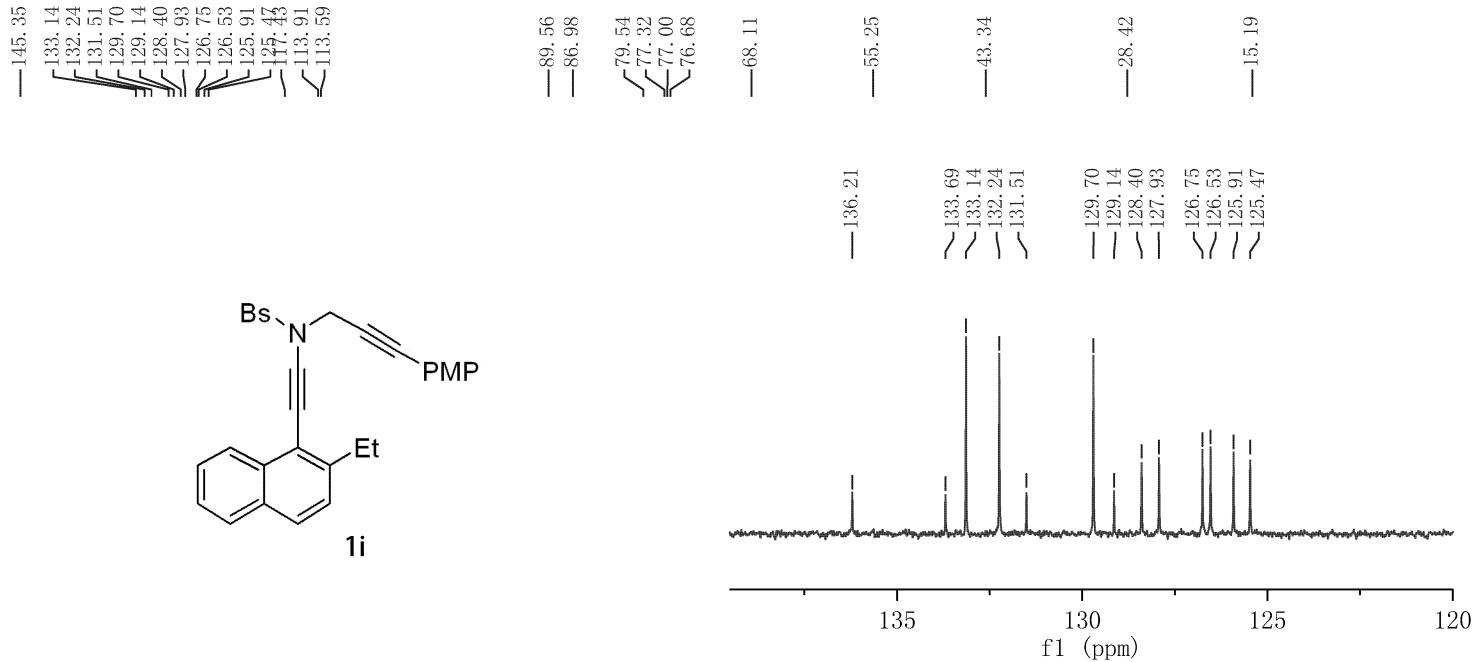


Parameter	Value
1 Title	1h-H
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	300.0
5 Number of Scans	11
6 Acquisition Time	3.9846
7 Acquisition Date	2023-07-31T21:35:06
8 Spectrometer Frequency	399.93
9 Spectral Width	8223.7

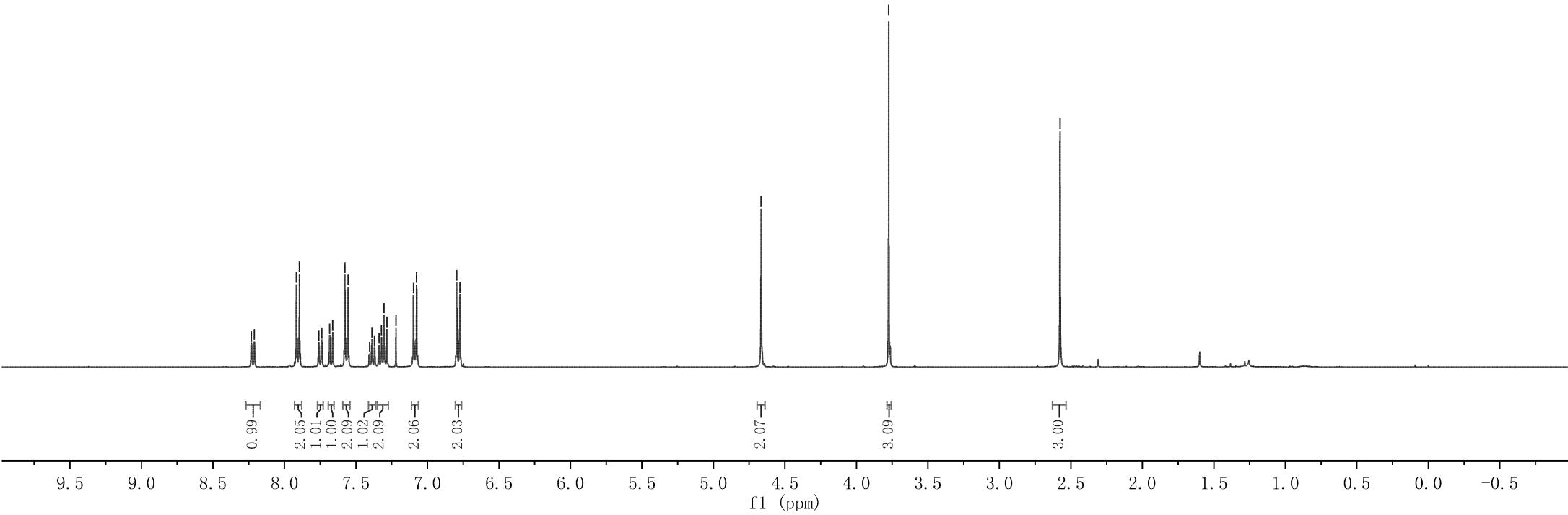
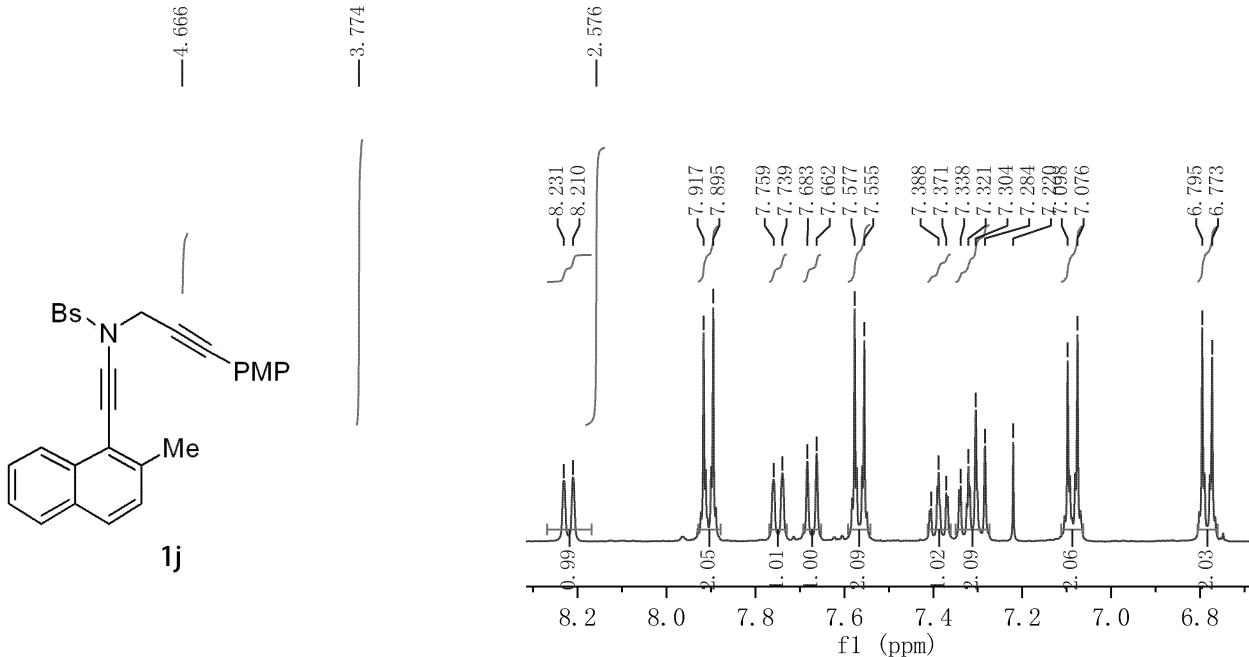




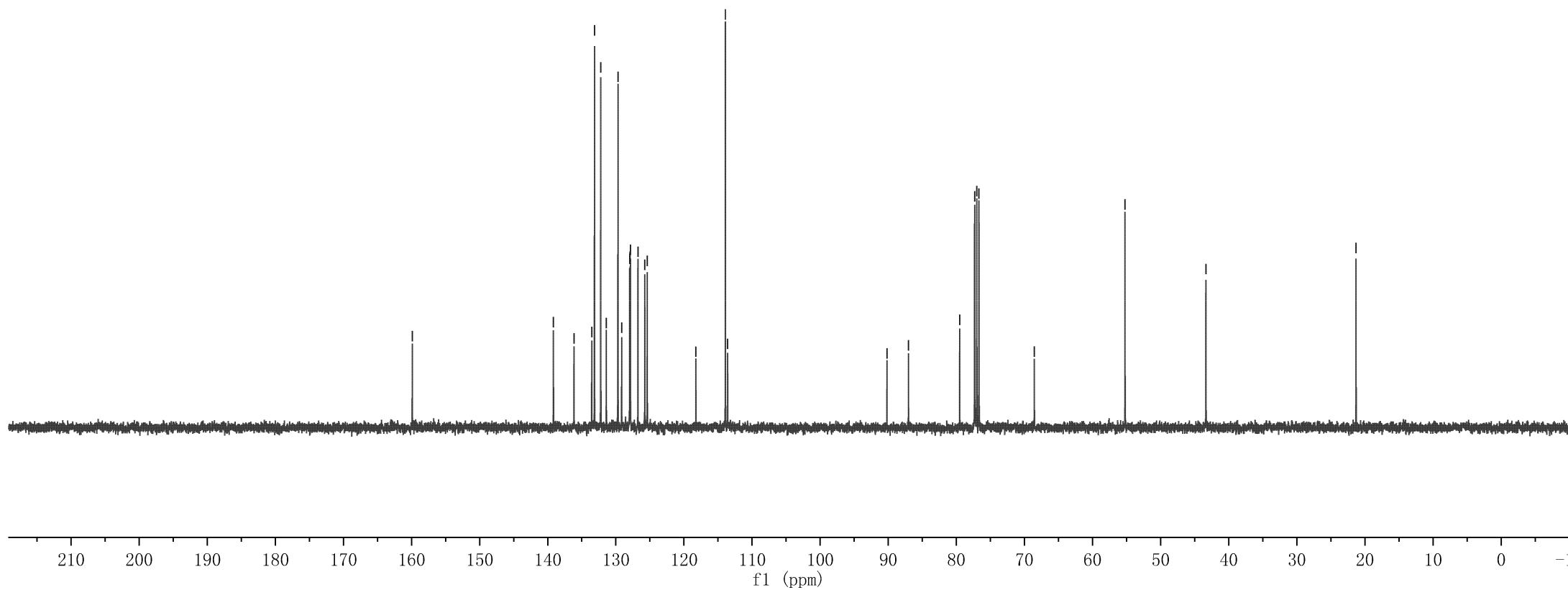
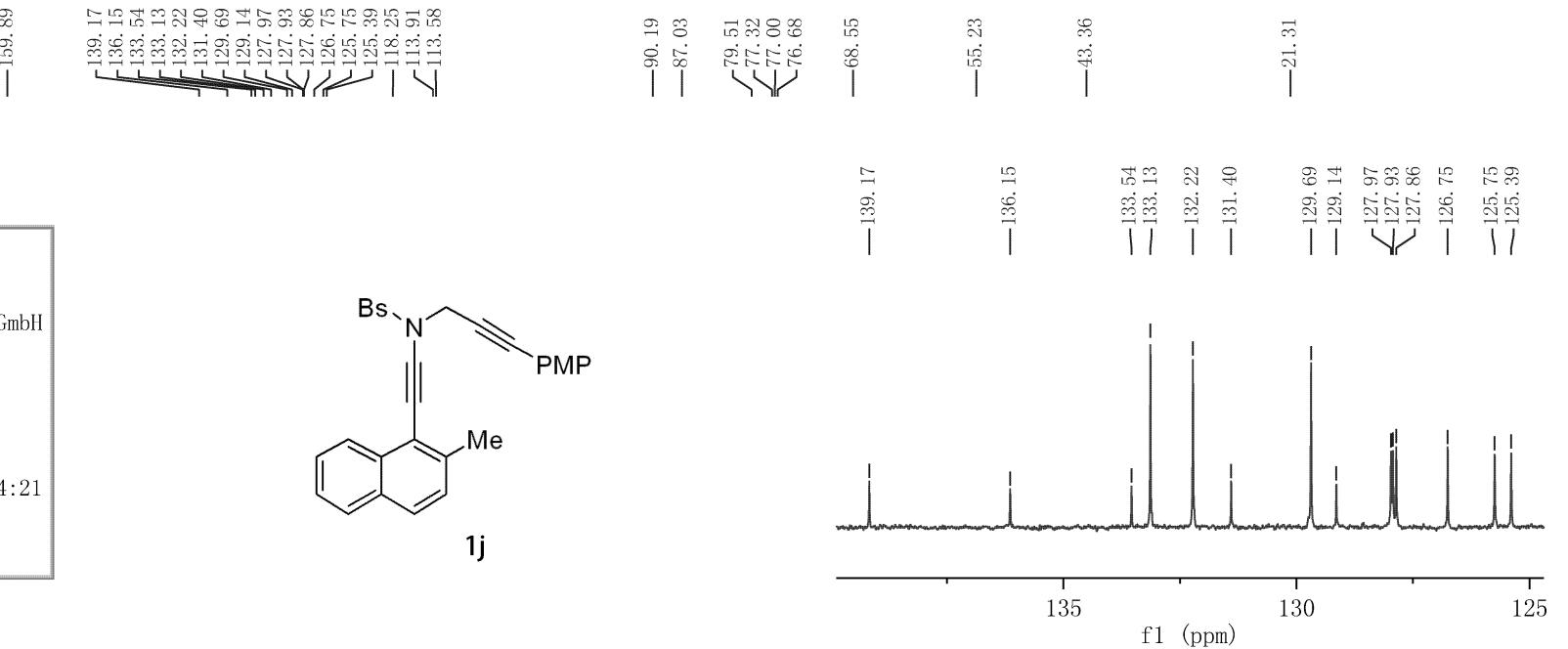
Parameter	Value
1 Title	CHH-1-121-Bs-Et
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	294.1
5 Number of Scans	47
6 Acquisition Time	1.3631
7 Acquisition Date	2022-11-09T10:26:49
8 Spectrometer Frequency	100.56
9 Spectral Width	24038.5

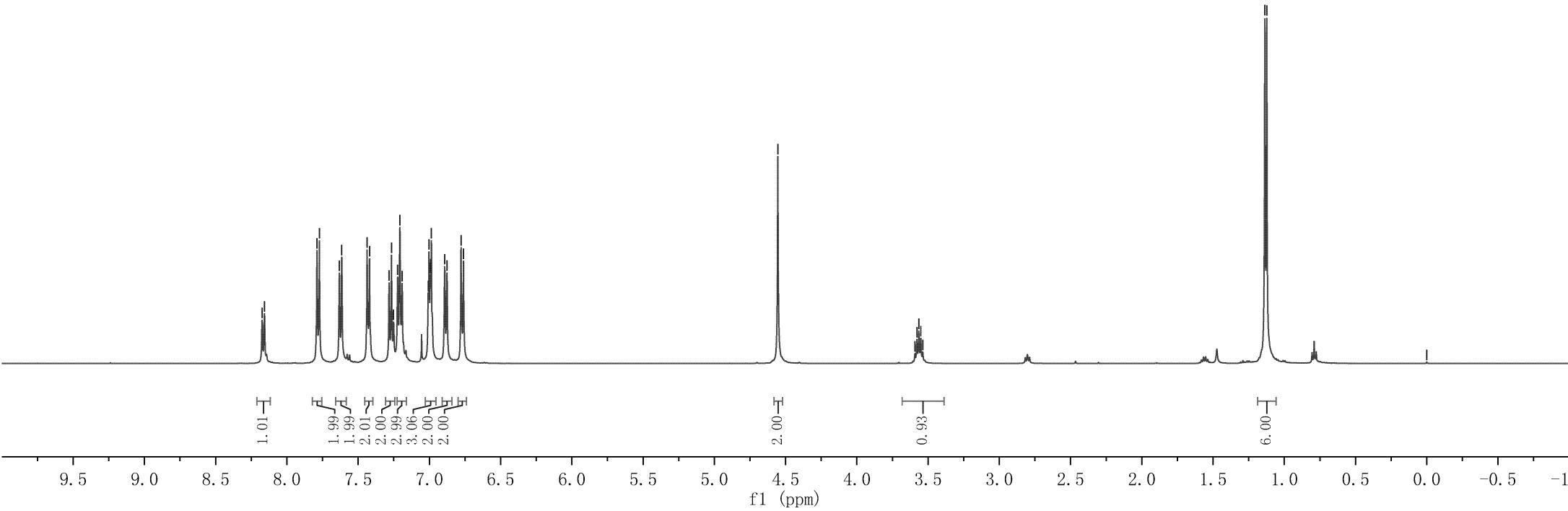
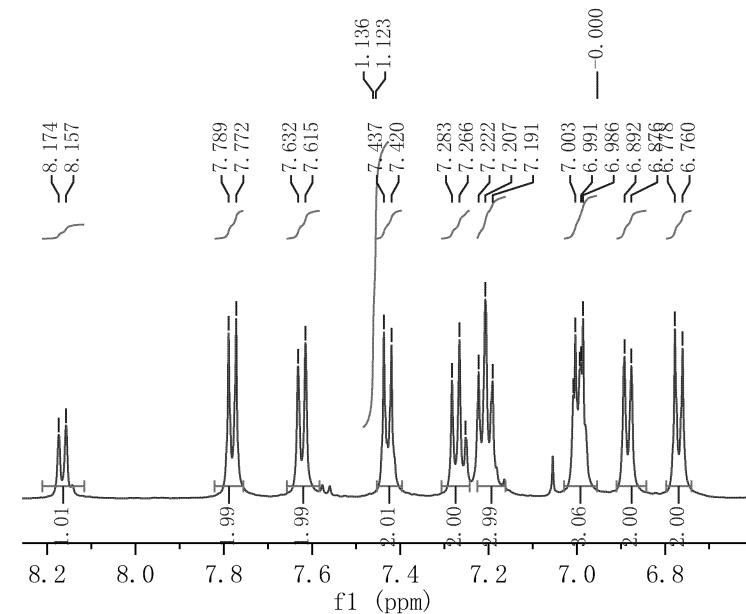
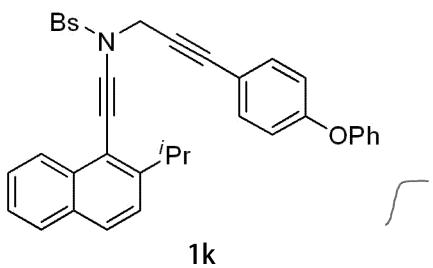
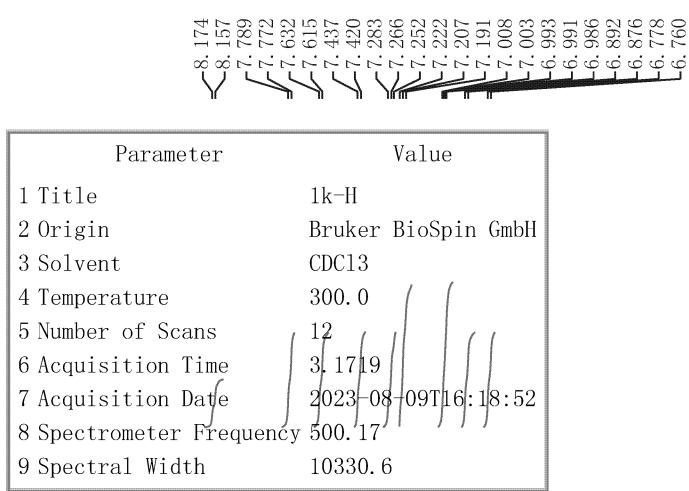


Parameter	Value
1 Title	CHH-1-126
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	295.4
5 Number of Scans	13
6 Acquisition Time	3.9846
7 Acquisition Date	2022-11-10T10:01:10
8 Spectrometer Frequency	399.93
9 Spectral Width	8223.7



Parameter	Value
1 Title	CHH-1-126
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	295.6
5 Number of Scans	59
6 Acquisition Time	1.3631
7 Acquisition Date	2022-11-10T10:04:21
8 Spectrometer Frequency	100.56
9 Spectral Width	24038.5

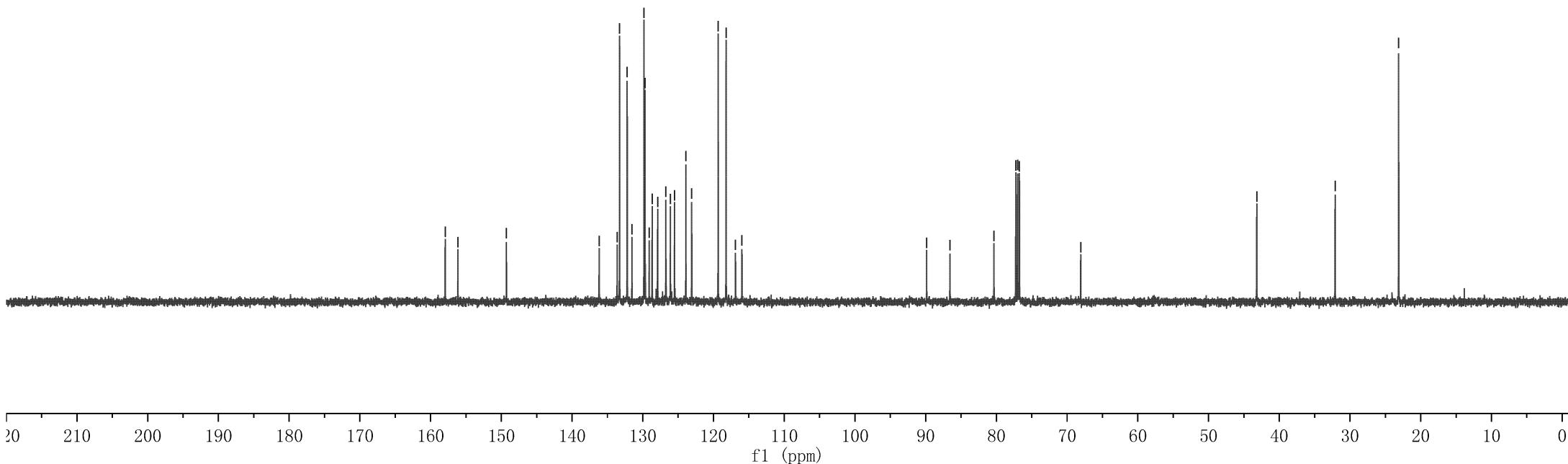
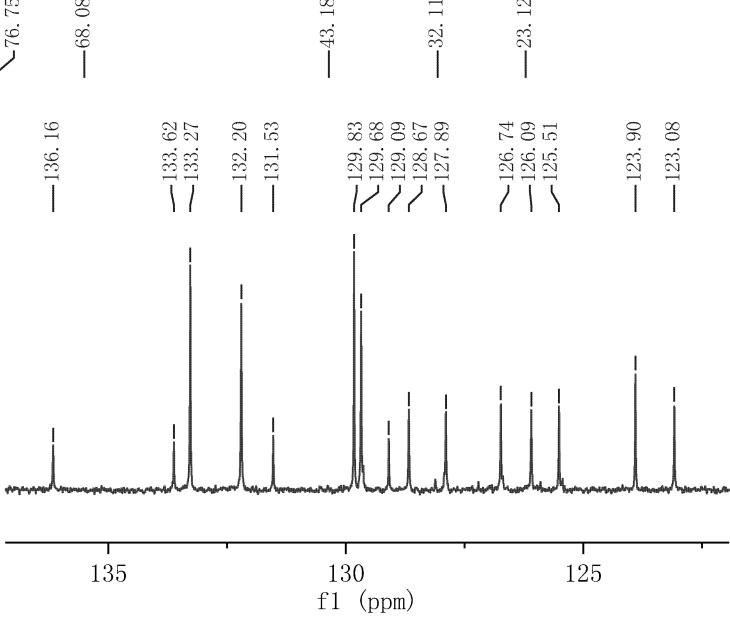
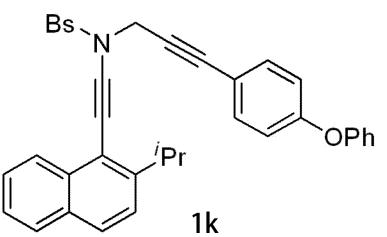


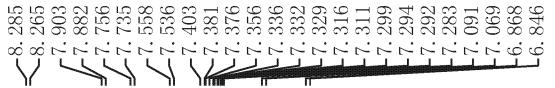


Parameter	Value
1 Title	1k-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDC13
4 Temperature	299.1
5 Number of Scans	13
6 Acquisition Time	1.1010
7 Acquisition Date	2023-08-09T16:23:04
8 Spectrometer Frequency	125.77
9 Spectral Width	29761.9

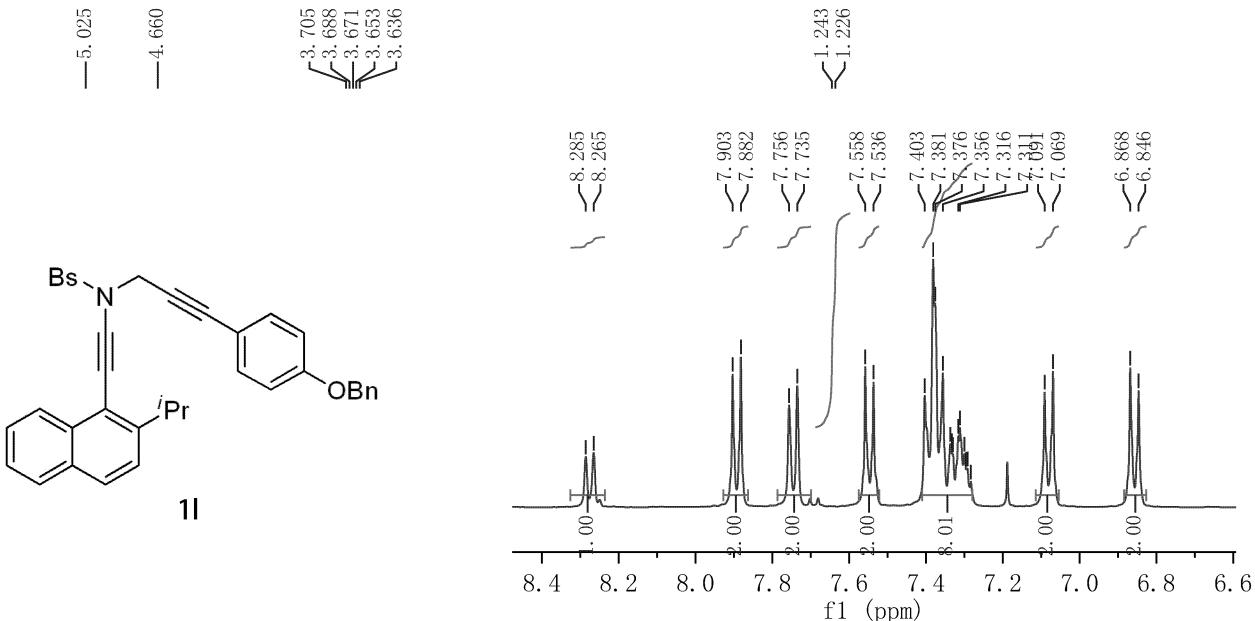
—157.94
—156.13
—149.28
—136.16
—133.62
—133.27
—132.20
—131.53
—129.83
—129.68
—129.09
—128.67
—127.89
—126.74
—126.09
—125.51
—123.90
—123.08
—119.34
—118.22
—116.89
—115.98

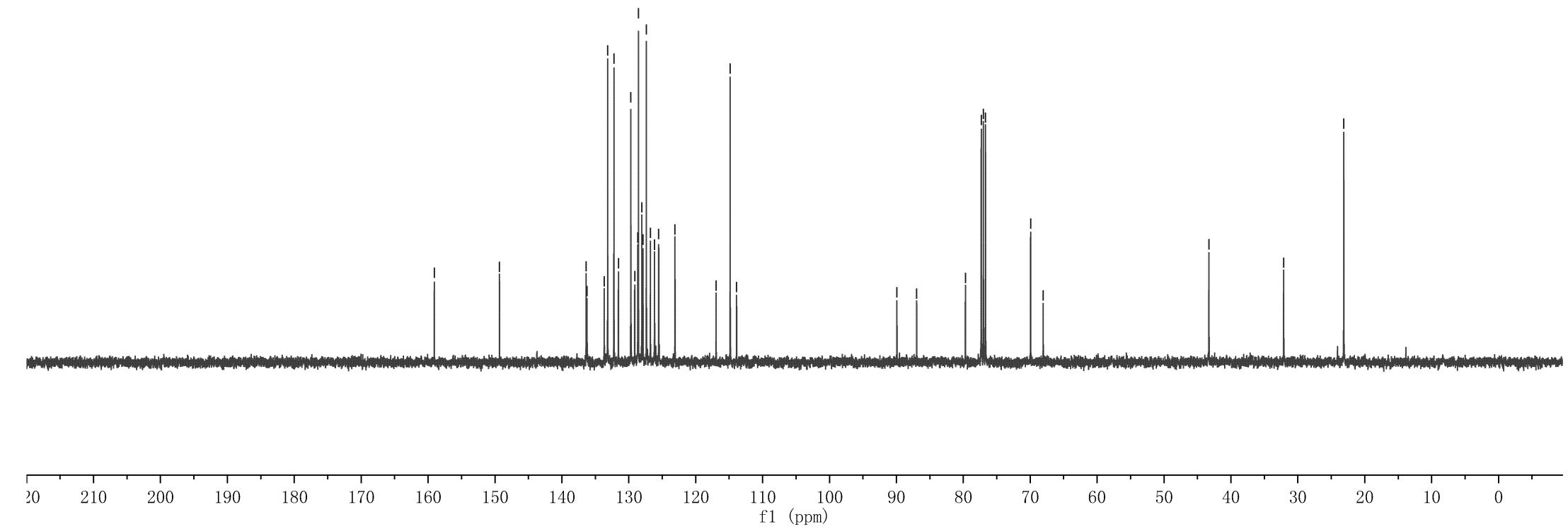
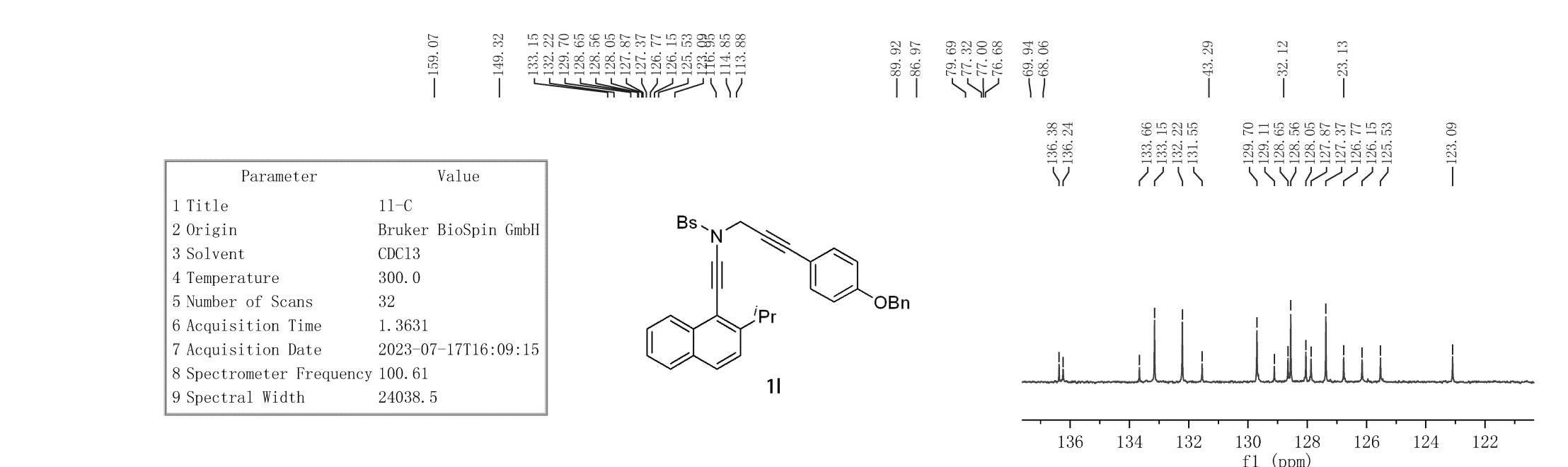
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—86.57
—80.34
—77.25
—77.00
—76.75
—136.16
—68.08





Parameter	Value
1 Title	11-H
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	298.0
5 Number of Scans	14
6 Acquisition Time	4.0894
7 Acquisition Date	2023-07-17T16:07:01
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8





8.282
8.261
7.927
7.906
7.777
7.756
7.595
7.574
7.419
7.403
7.397
7.386
7.348
7.346
7.328
7.311
7.091
7.071
7.047
7.027

—4.695

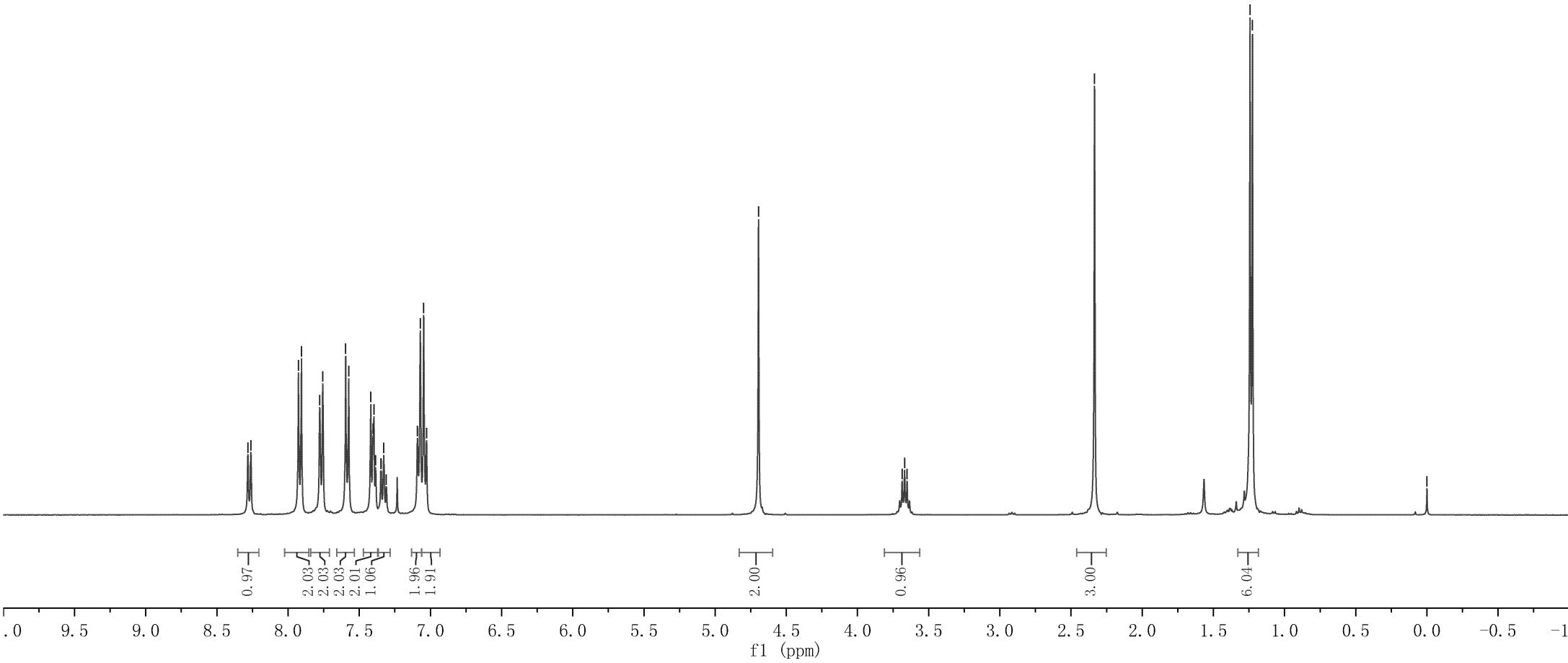
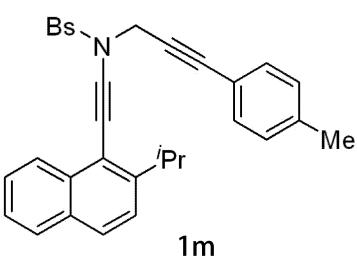
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3.652

—2.335

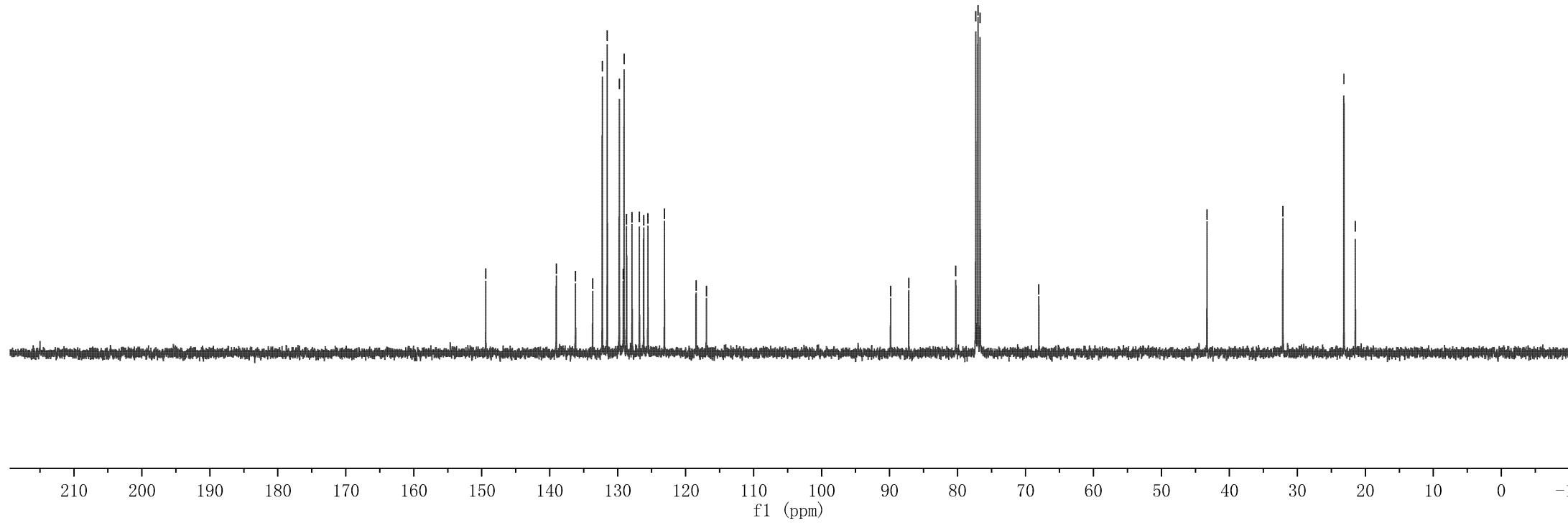
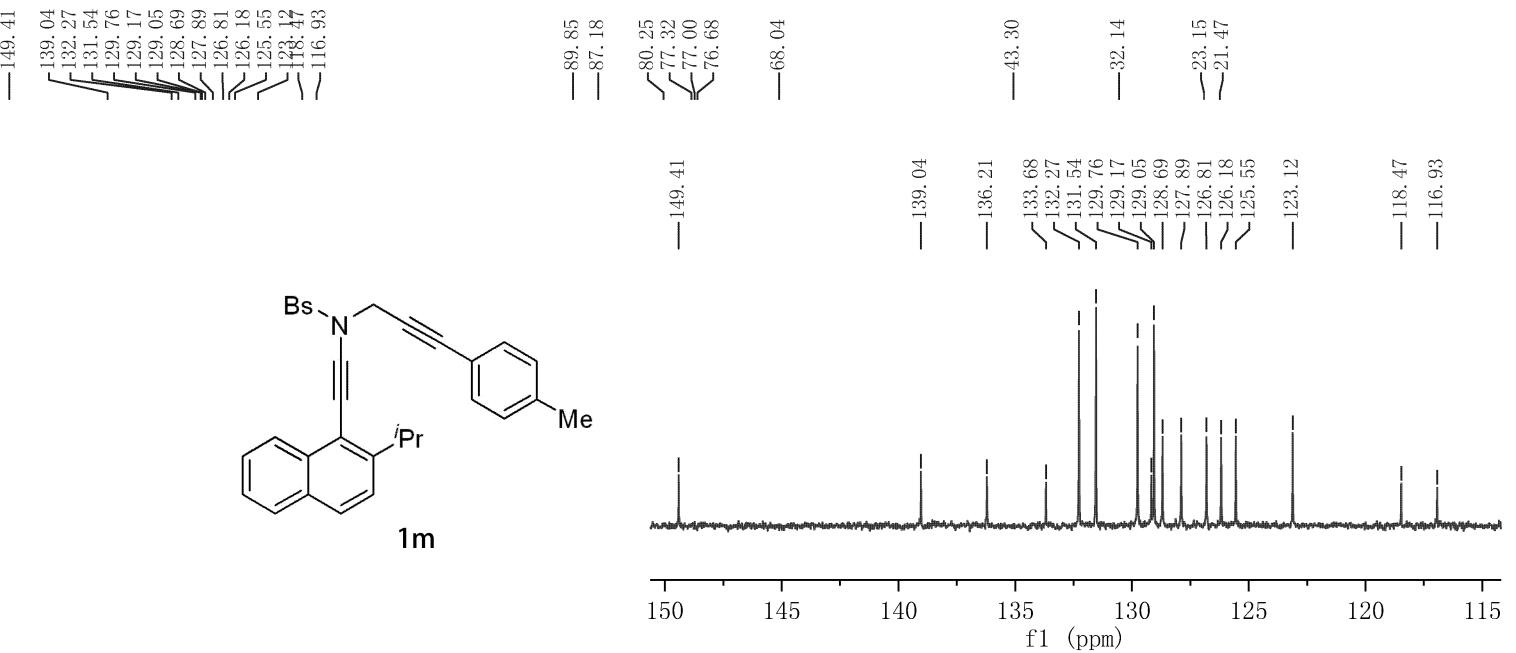
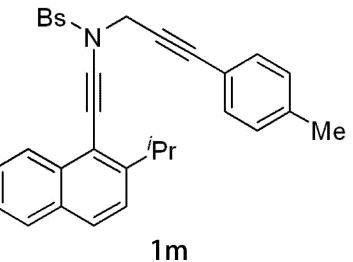
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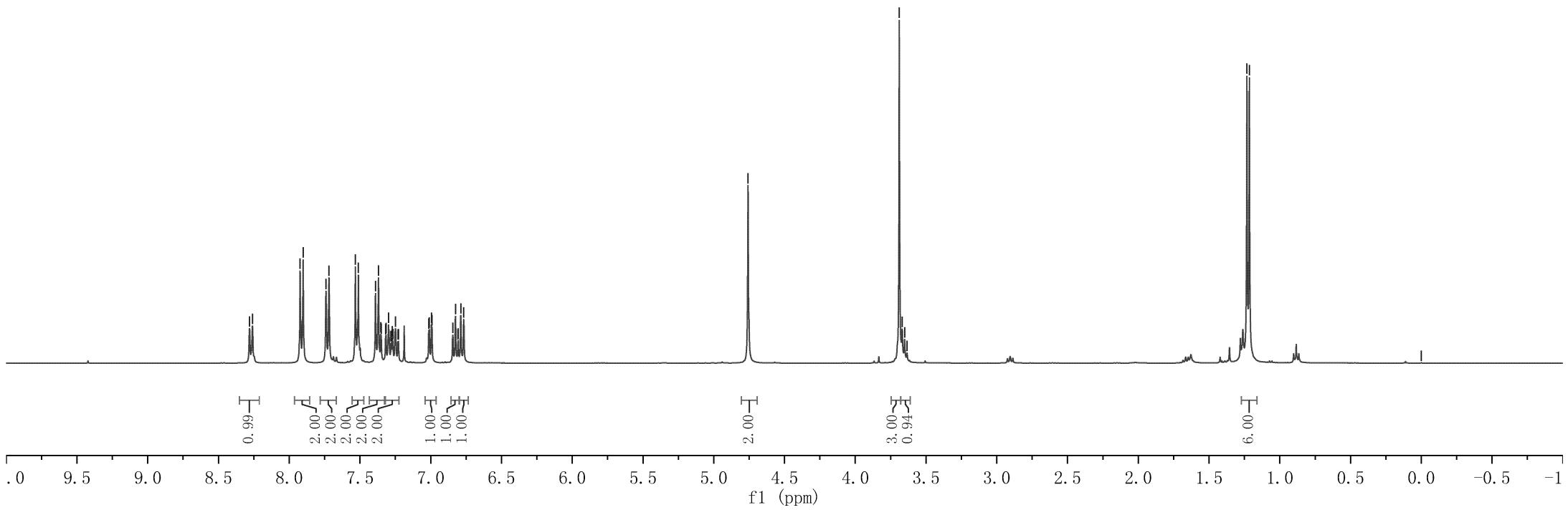
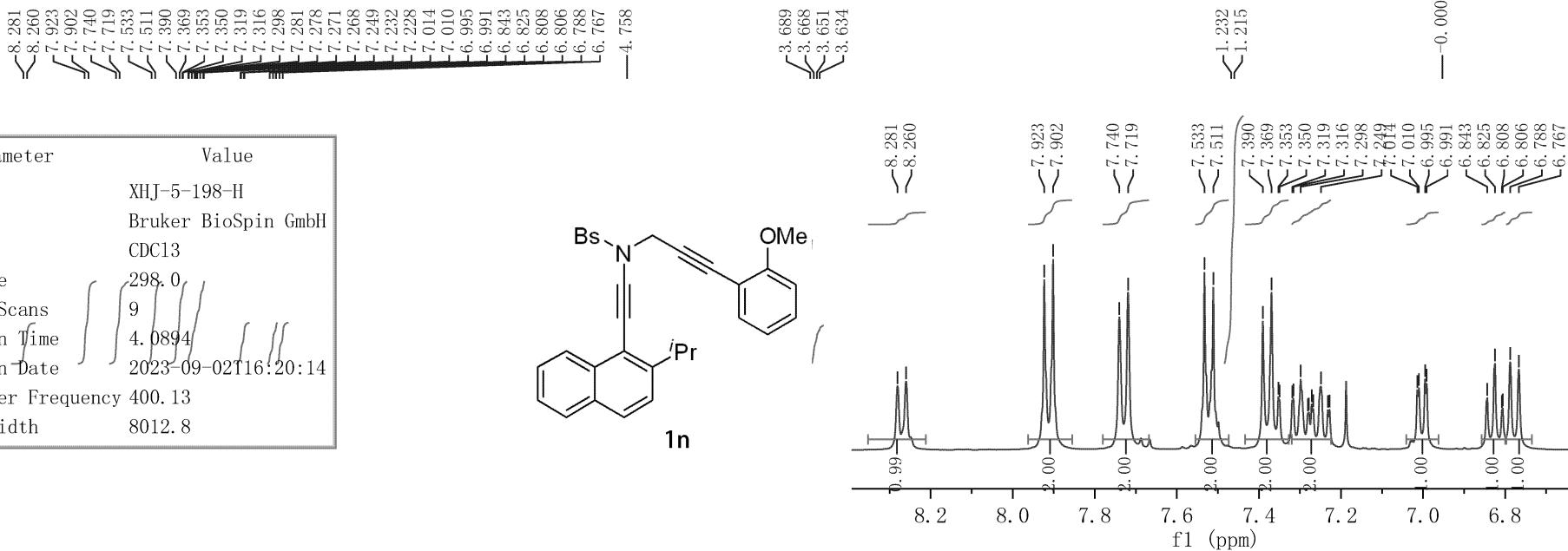
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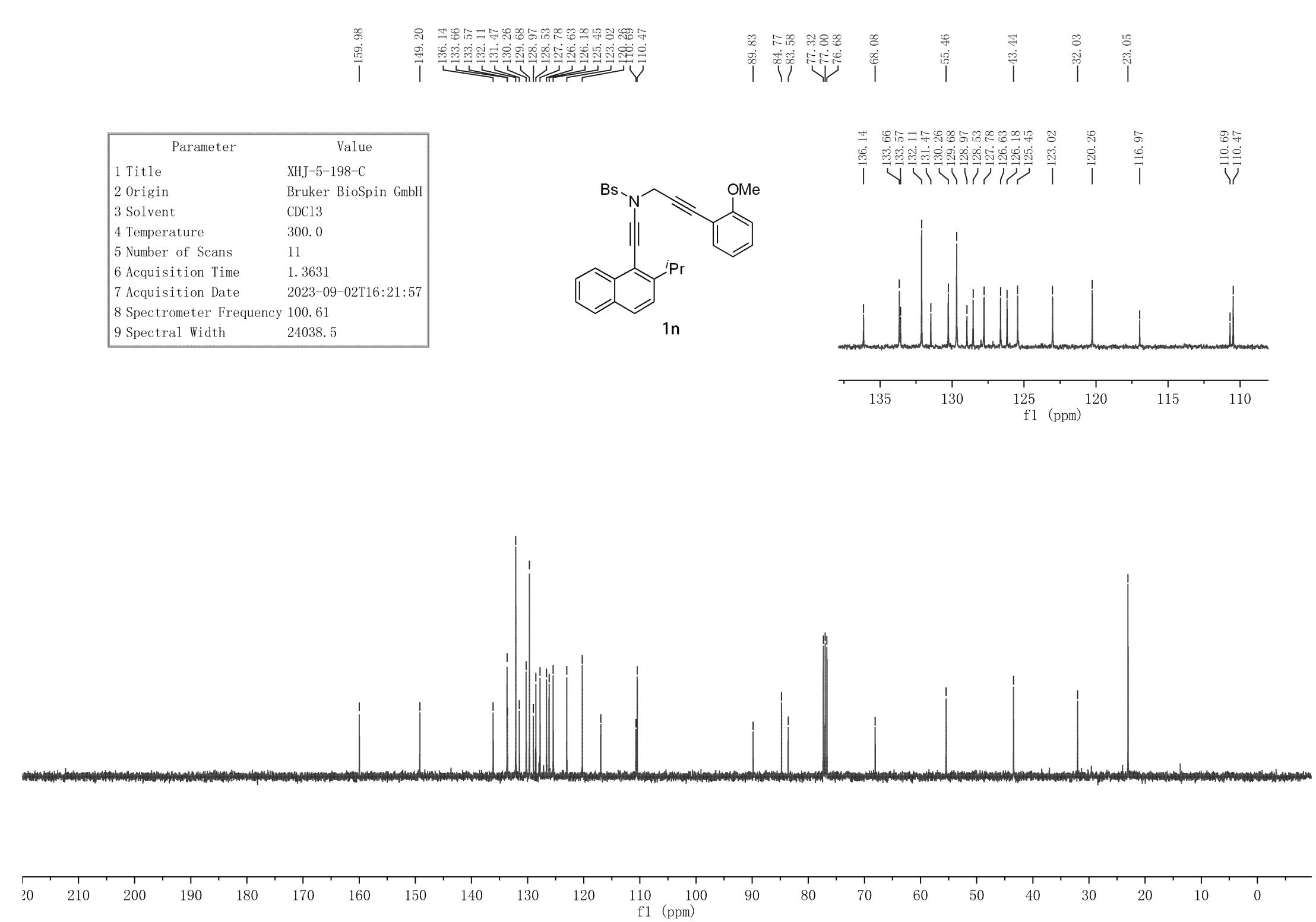
Parameter	Value
1 Title	CHH-1-141-Bs-iPr-Tol
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	294.5
5 Number of Scans	19
6 Acquisition Time	3.9846
7 Acquisition Date	2022-11-21T10:08:51
8 Spectrometer Frequency	399.93
9 Spectral Width	8223.7

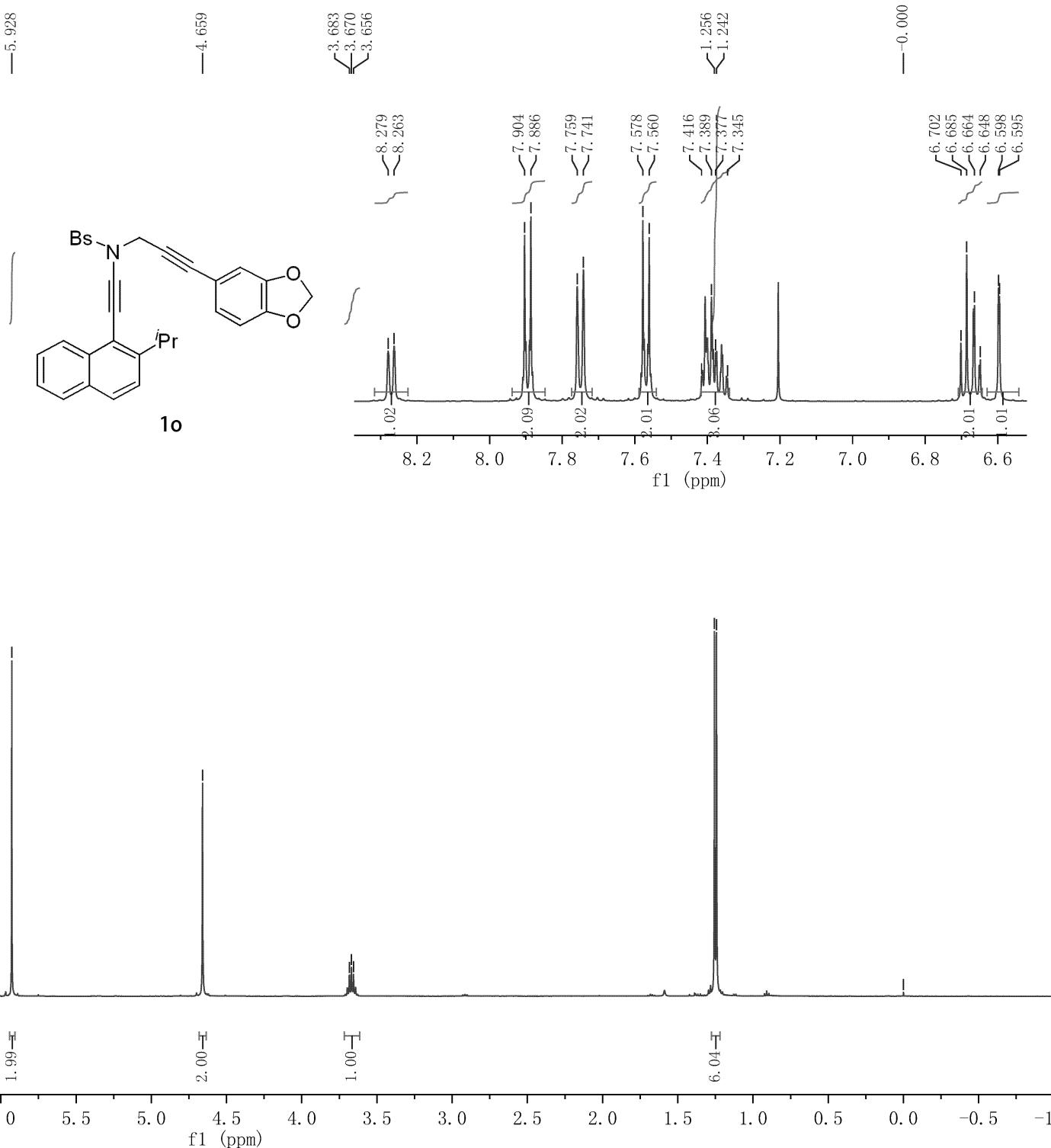
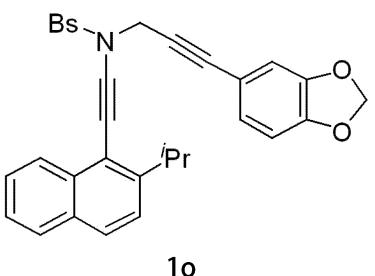
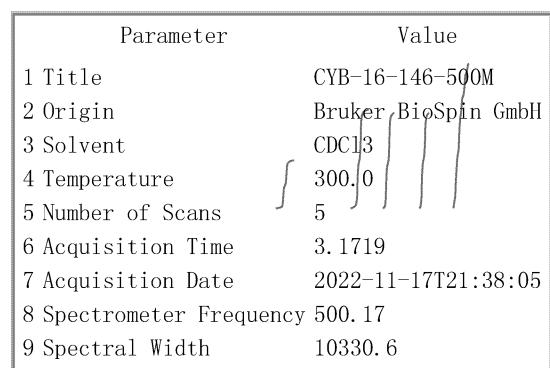


Parameter	Value
1 Title	CHH-1-141-Bs-iPr-Tol
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDC13
4 Temperature	294.7
5 Number of Scans	177
6 Acquisition Time	1.3631
7 Acquisition Date	2022-11-21T10:11:58
8 Spectrometer Frequency	100.56
9 Spectral Width	24038.5

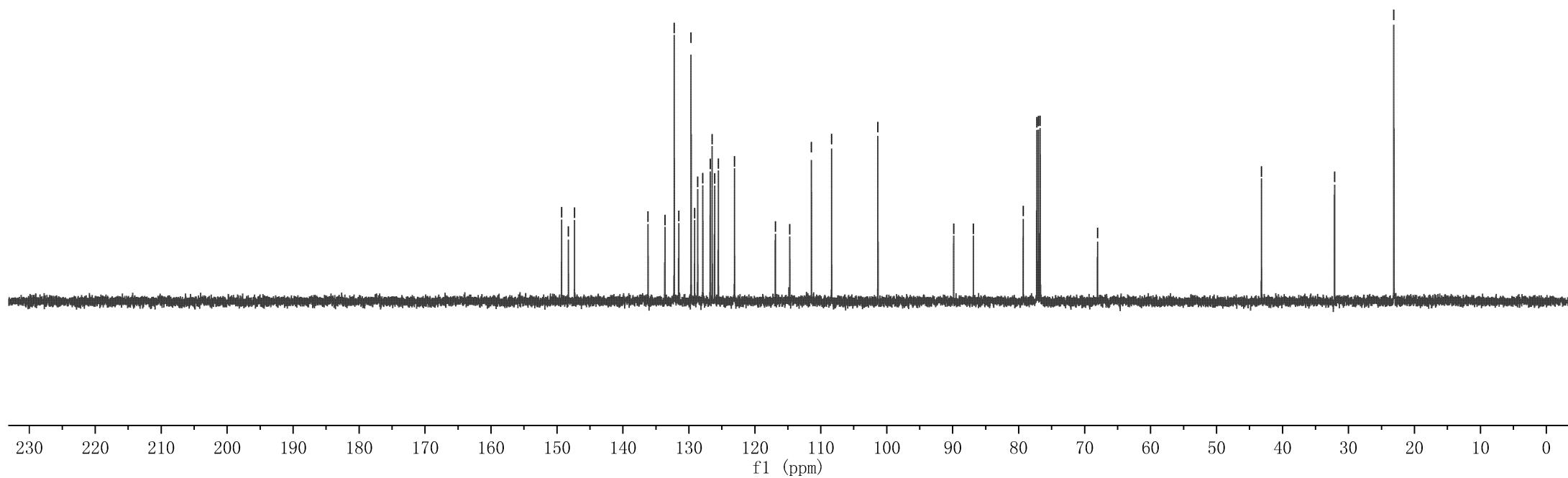
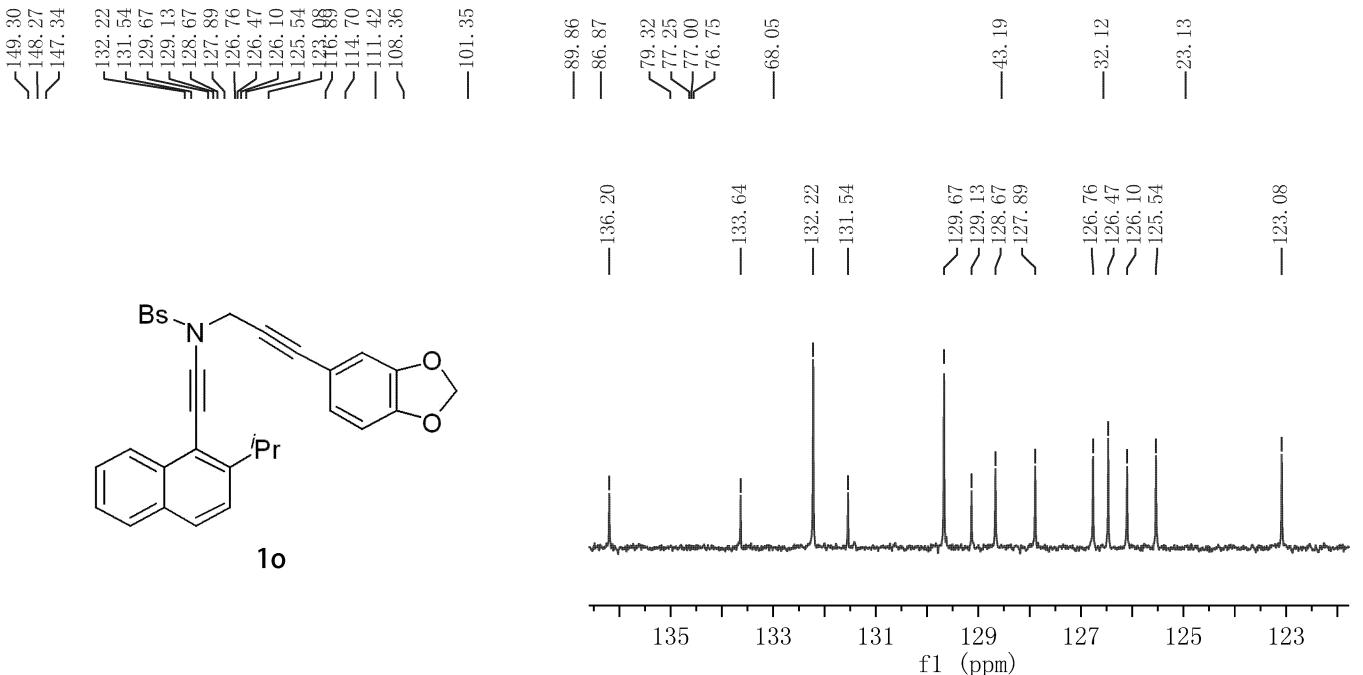




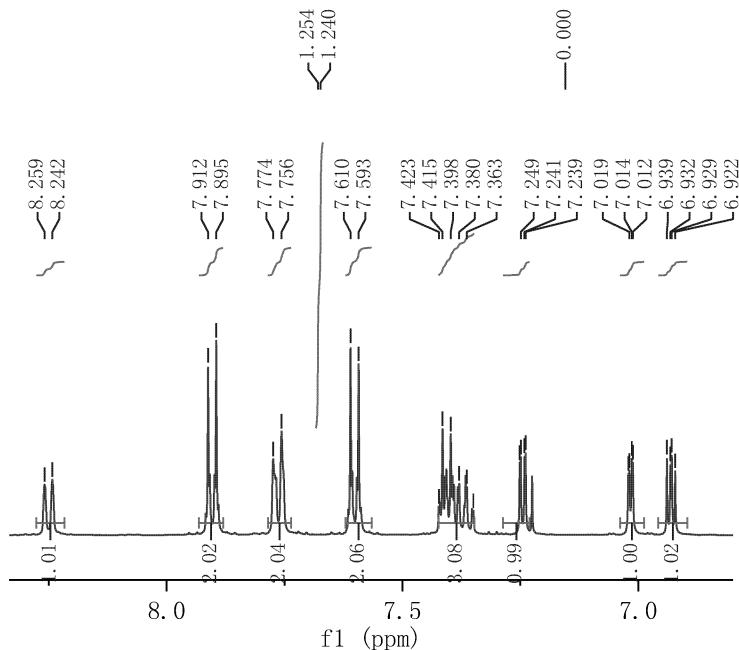
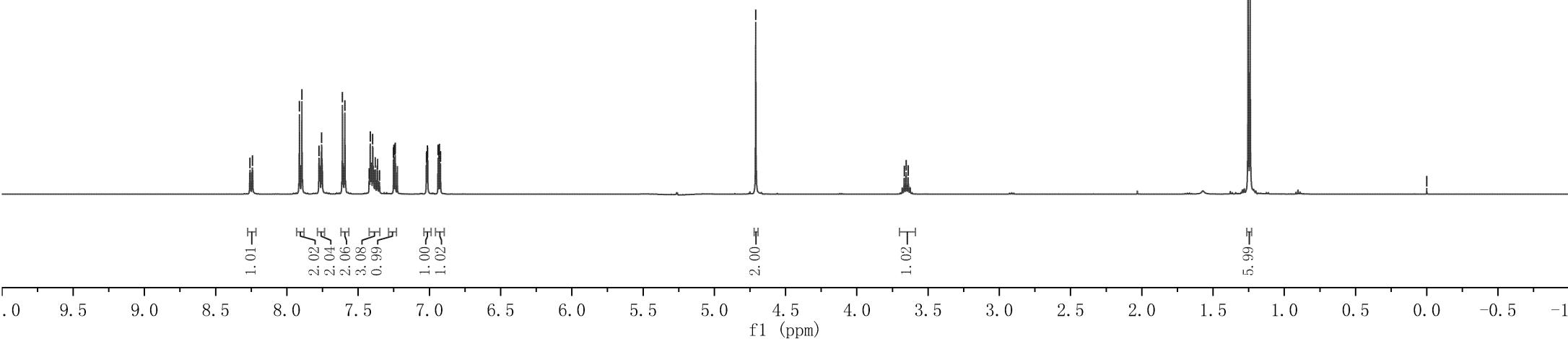
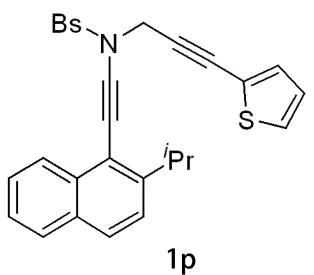




Parameter	Value
1 Title	CYB-16-146-500M
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	300.1
5 Number of Scans	11
6 Acquisition Time	1.1010
7 Acquisition Date	2022-11-17T21:39:05
8 Spectrometer Frequency	125.77
9 Spectral Width	29761.9



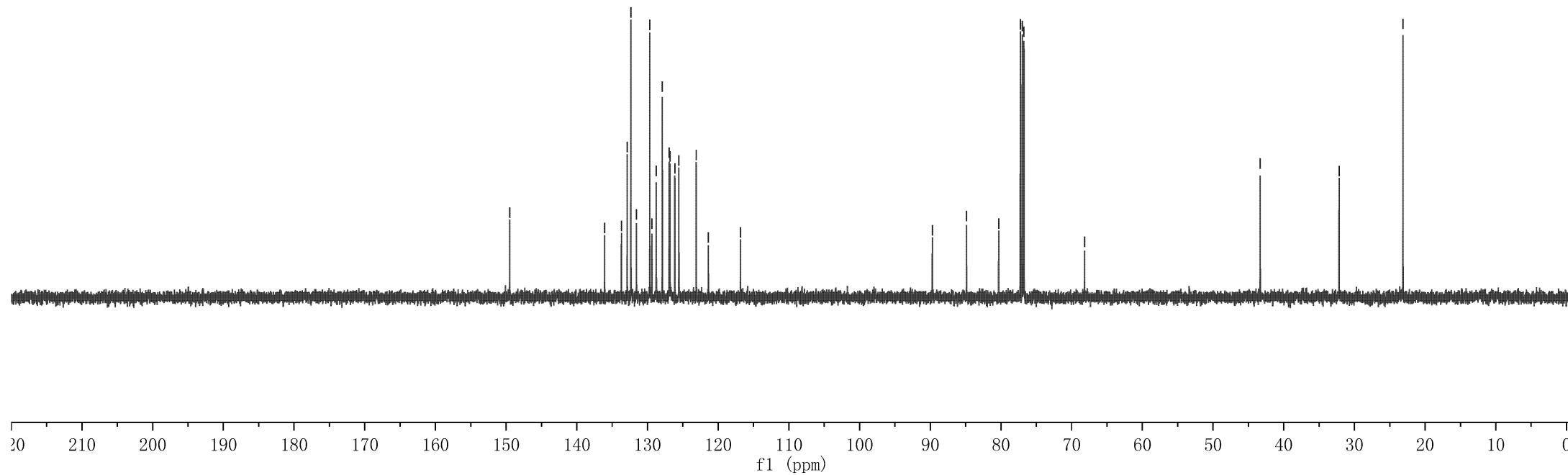
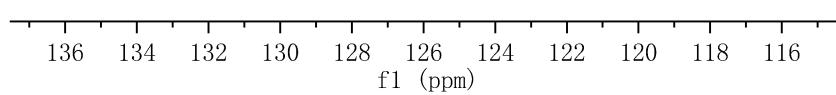
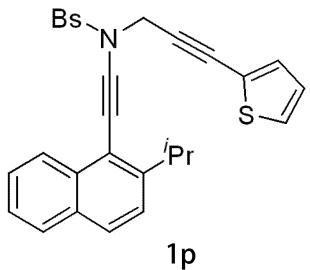
Parameter	Value
1 Title	CYB-16-150-500M
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	300.0
5 Number of Scans	4
6 Acquisition Time	3.1719
7 Acquisition Date	2022-11-17T21:33:54
8 Spectrometer Frequency	500.17
9 Spectral Width	10330.6

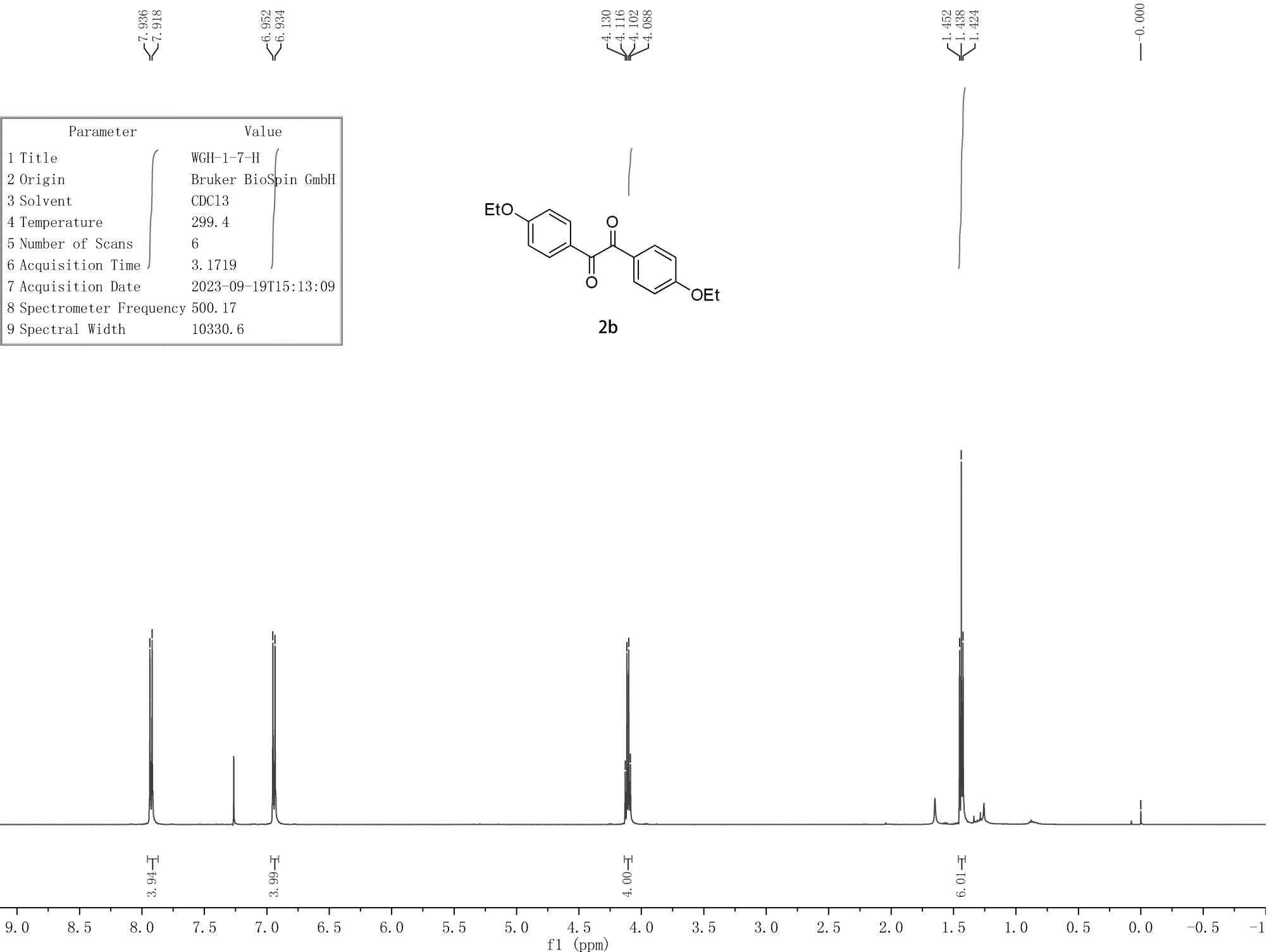


Parameter	Value
1 Title	CYB-16-150-500M
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	300.2
5 Number of Scans	17
6 Acquisition Time	1.1010
7 Acquisition Date	2022-11-17T21:35:18
8 Spectrometer Frequency	125.77
9 Spectral Width	29761.9

—149.49
 —133.70
 —132.87
 —132.35
 —131.56
 —129.67
 —129.37
 —128.76
 —127.91
 —126.94
 —126.82
 —126.14
 —125.56
 —123.84

—89.71
 —84.86
 —80.32
 —77.25
 —77.00
 —76.75
 —68.17
 —136.06
 —132.35
 —131.56
 —129.67
 —129.37
 —128.76
 —127.91
 —126.94
 —126.82
 —126.14
 —125.56
 —123.11
 —121.39
 —32.17
 —23.13
 —116.84





—193.53

—164.26

—132.33

—126.11

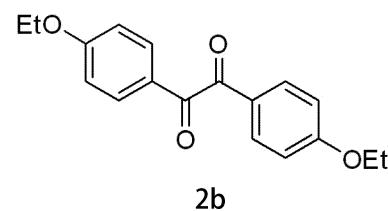
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77.25
77.00
76.75

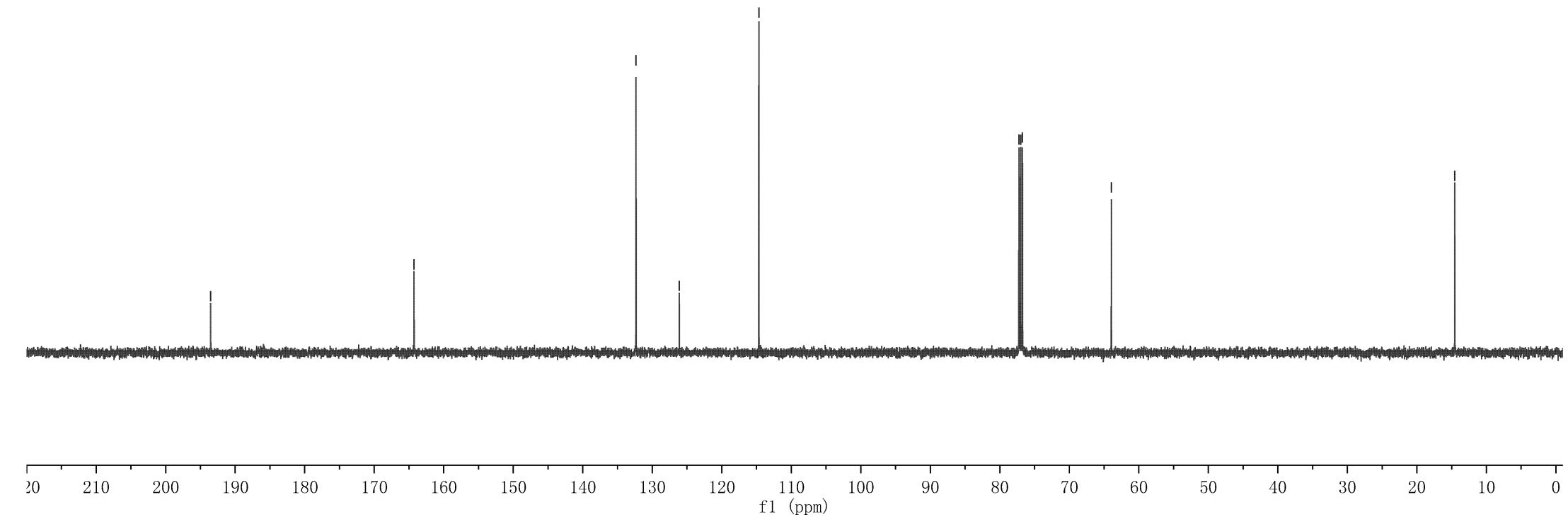
—63.96

—14.55

Parameter	Value
1 Title	WGH-1-7-C-2
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	299.9
5 Number of Scans	27
6 Acquisition Time	1.1010
7 Acquisition Date	2023-09-19T15:21:13
8 Spectrometer Frequency	125.77
9 Spectral Width	29761.9



2b

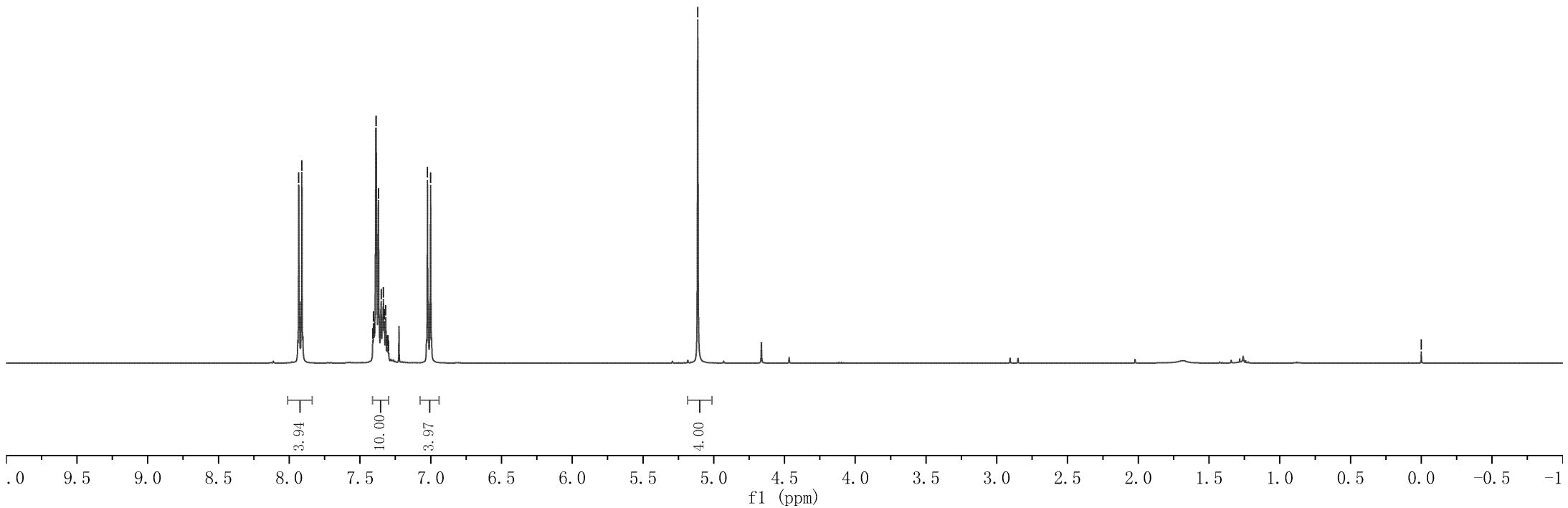
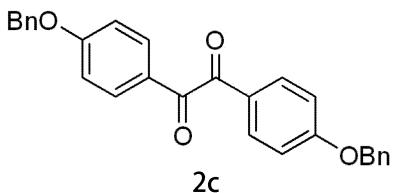


—0.000

—5.113

—7.933
—7.910
—7.388
—7.386
—7.369
—7.350
—7.335
—7.318
—7.023
—7.001

Parameter	Value
1 Title	2c-H
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	298.0
5 Number of Scans	18
6 Acquisition Time	4.0894
7 Acquisition Date	2023-09-09T22:41:03
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8



—193.34

—163.91

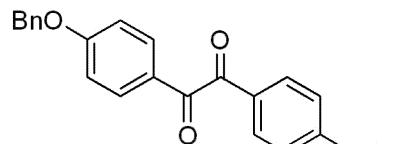
—
135.78
132.29
128.65
128.26
127.39
126.40

—115.07

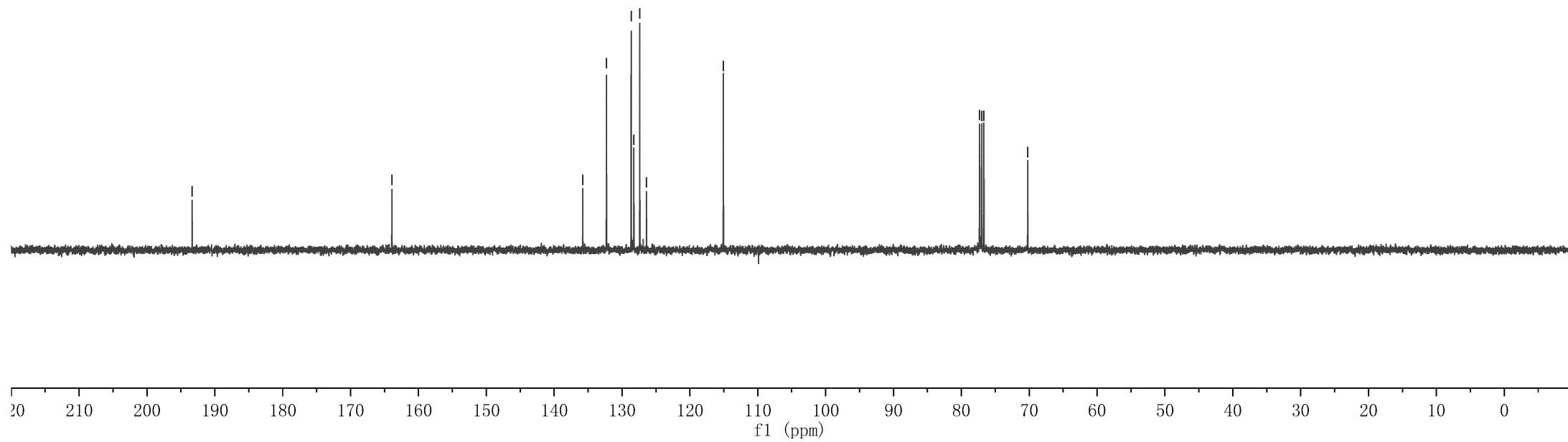
—
77.32
77.00
76.68

—70.22

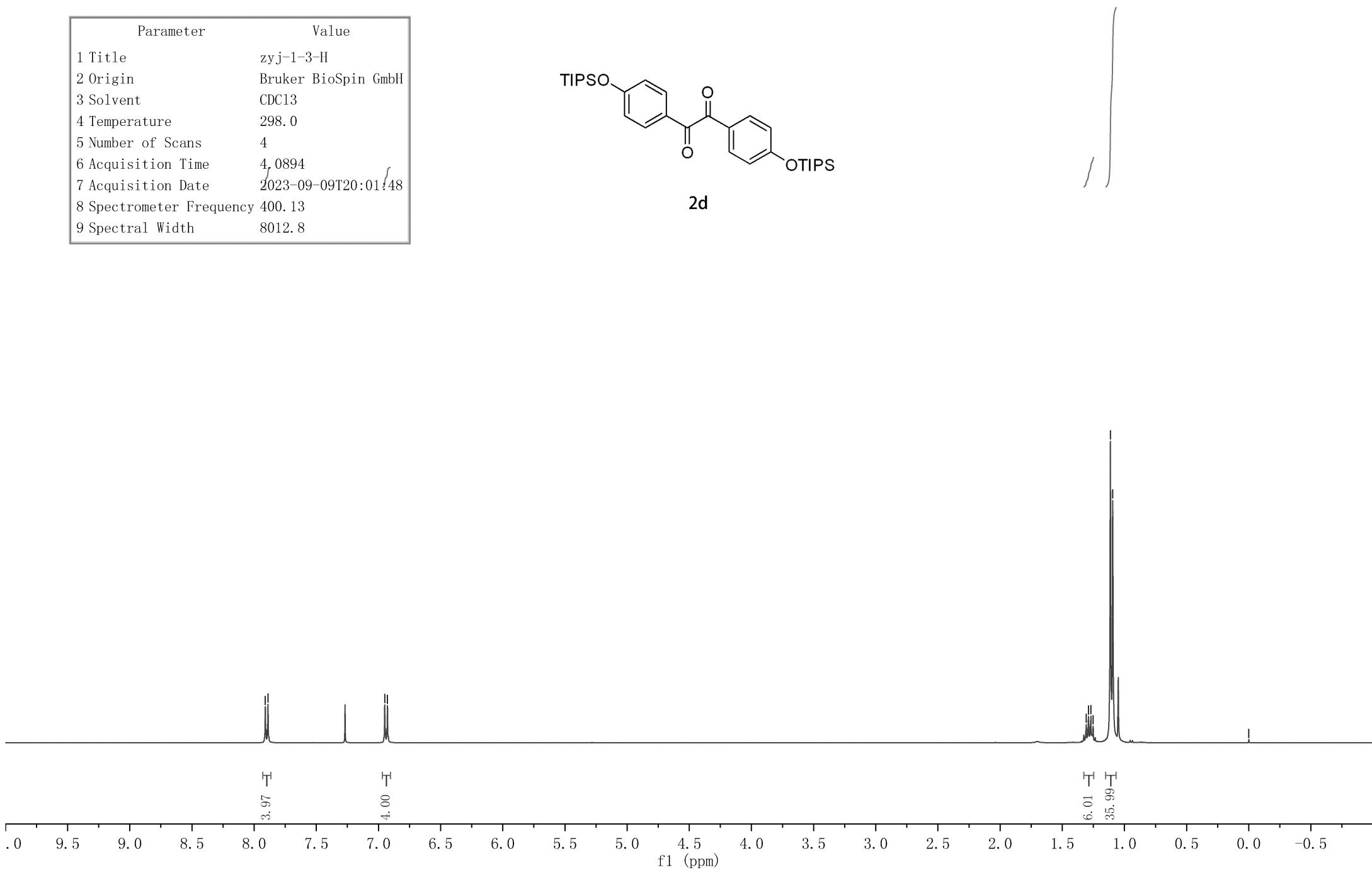
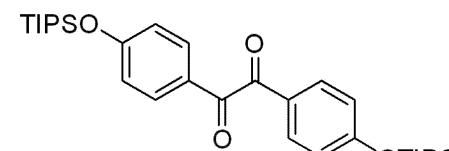
Parameter	Value
1 Title	2c-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	300.0
5 Number of Scans	7
6 Acquisition Time	1.3631
7 Acquisition Date	2023-09-09T22:42:47
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5



2c



Parameter	Value
1 Title	zyj-1-3-H
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDC13
4 Temperature	298.0
5 Number of Scans	4
6 Acquisition Time	4.0894
7 Acquisition Date	2023-09-09T20:01:48
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8



—193.43

—162.17

—132.29

—126.49

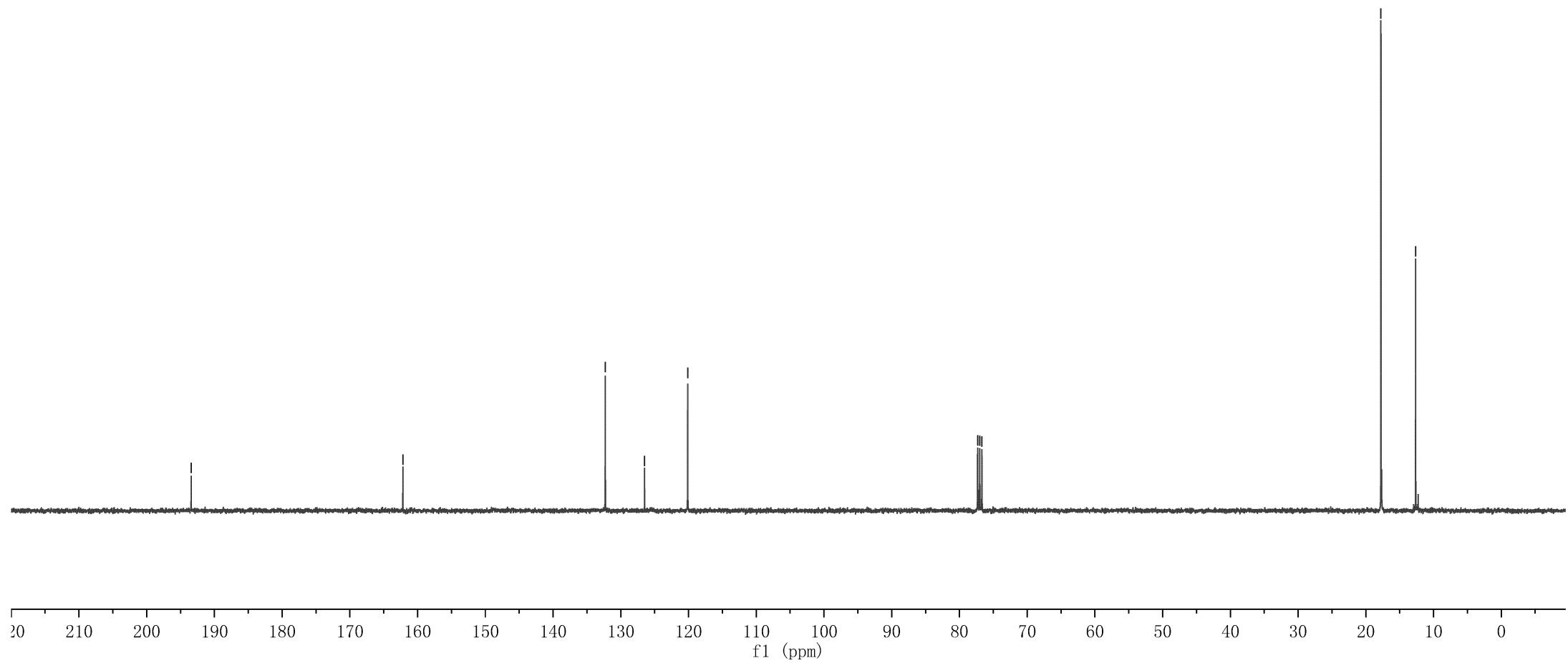
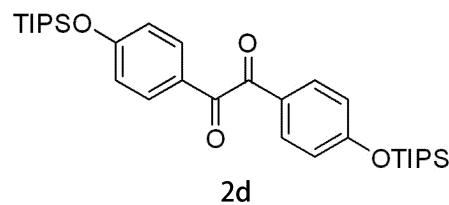
—120.12

77.32
77.00
76.68

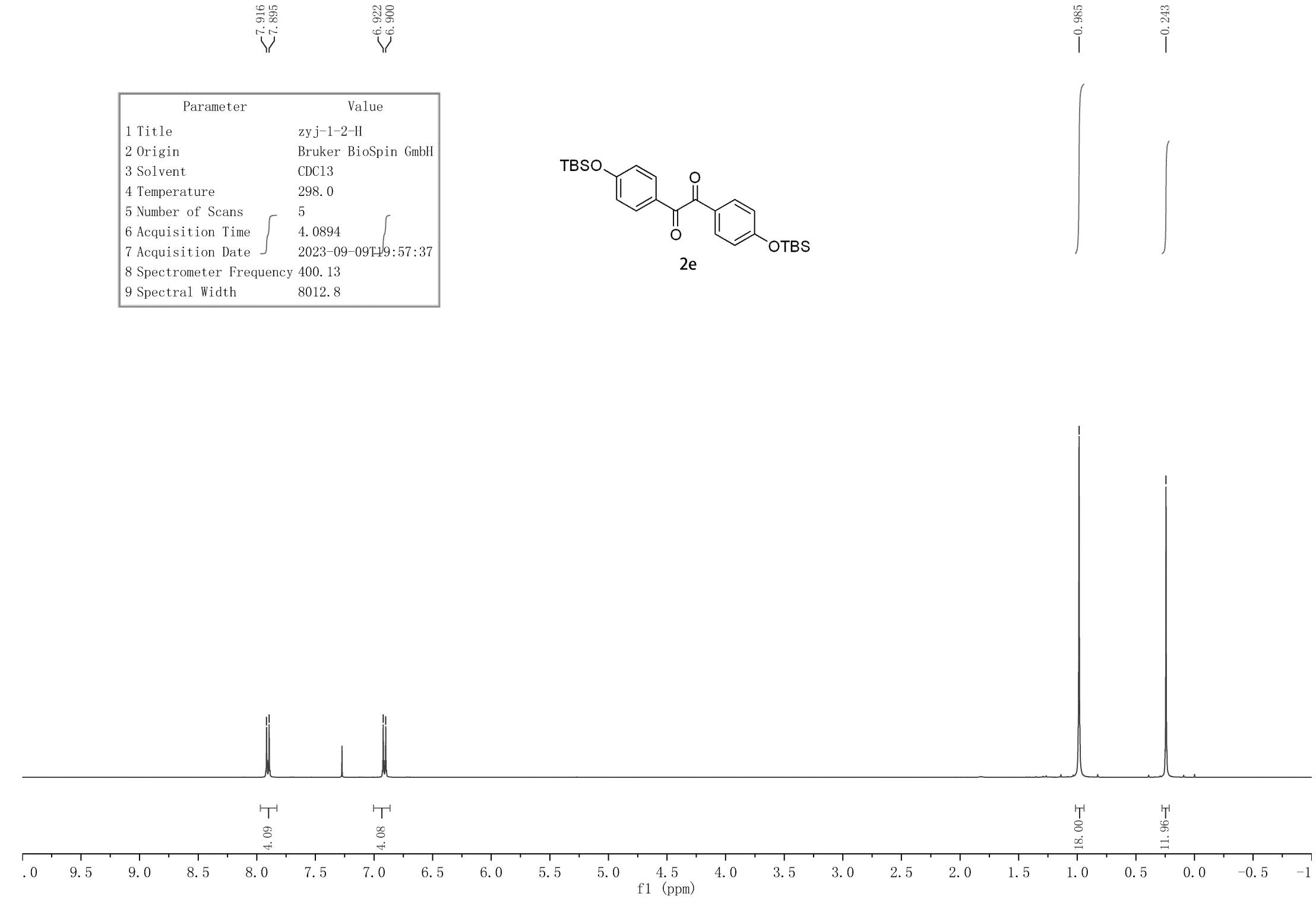
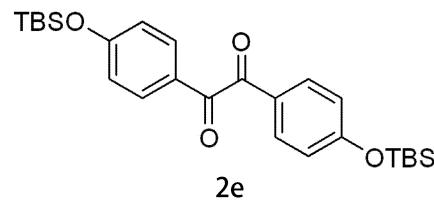
—17.77

—12.65

Parameter	Value
1 Title	zyj-1-3-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	300.0
5 Number of Scans	9
6 Acquisition Time	1.3631
7 Acquisition Date	2023-09-09T20:02:50
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5



Parameter	Value
1 Title	zyj-1-2-II
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	298.0
5 Number of Scans	5
6 Acquisition Time	4.0894
7 Acquisition Date	2023-09-09T19:57:37
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8



—193.39

—161.73

—132.20

—126.71

—120.30

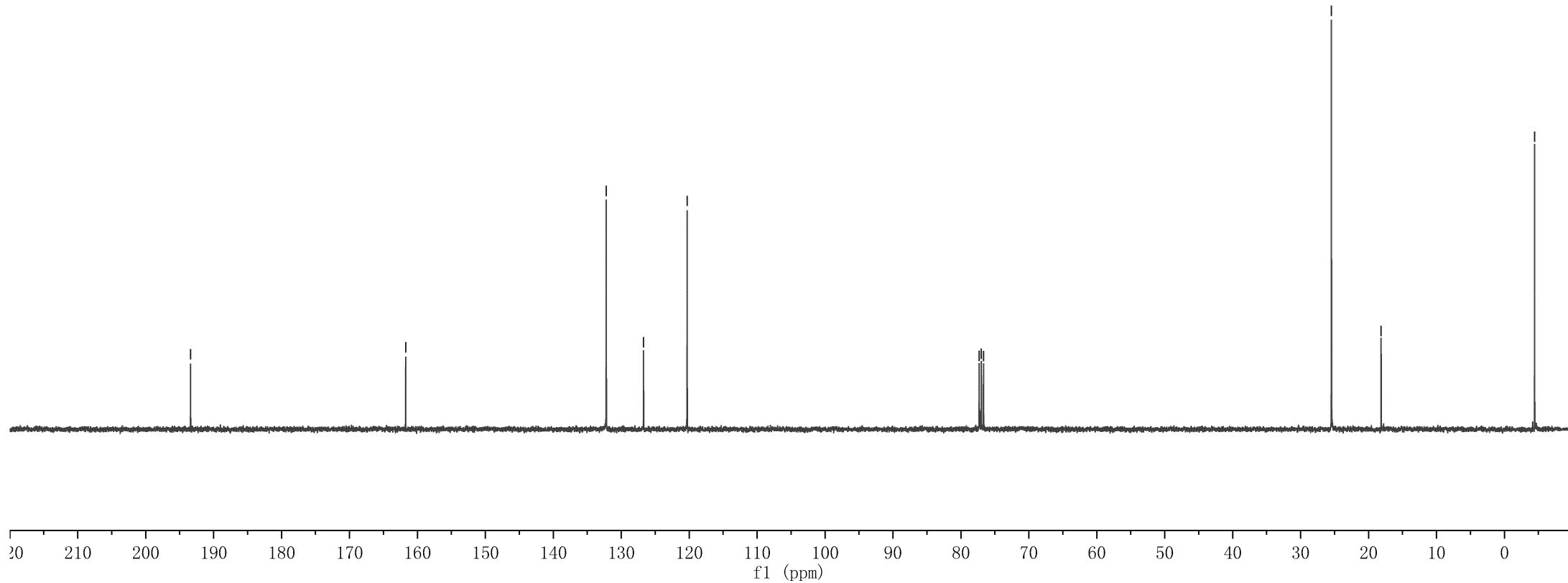
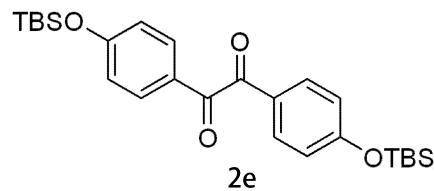
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77.00
76.68

—25.46

—18.15

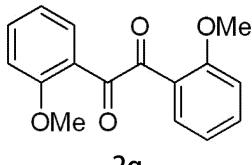
—4.44

Parameter	Value
1 Title	zyj-1-2-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	300.0
5 Number of Scans	6
6 Acquisition Time	1.3631
7 Acquisition Date	2023-09-09T19:58:42
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5



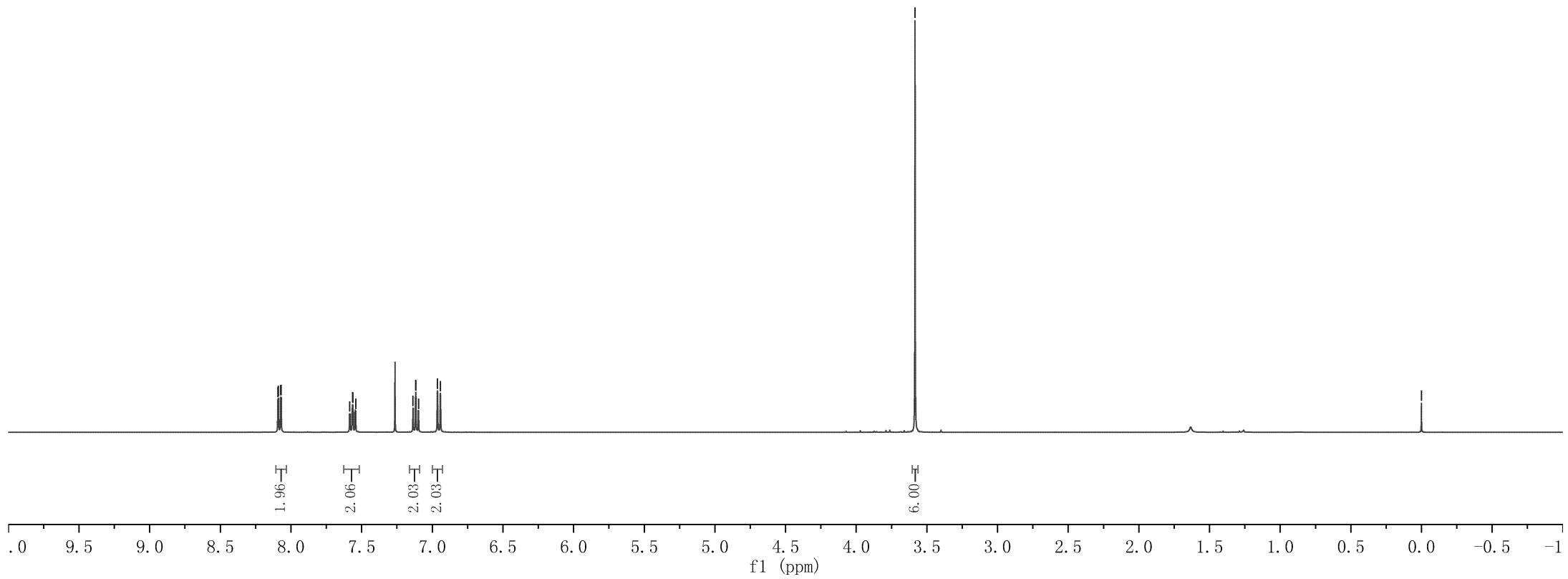
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—3.584



8.093
8.088
8.073
8.069
7.585
7.564
7.563
7.542
7.137
7.117
7.116
7.097
6.964
6.943

Parameter	Value
1 Title	ZZX-19-196
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	298.0
5 Number of Scans	8
6 Acquisition Time	4.0894
7 Acquisition Date	2023-09-11T20:44:56
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8



—192.41

—160.33

—135.49

—130.39

—123.41

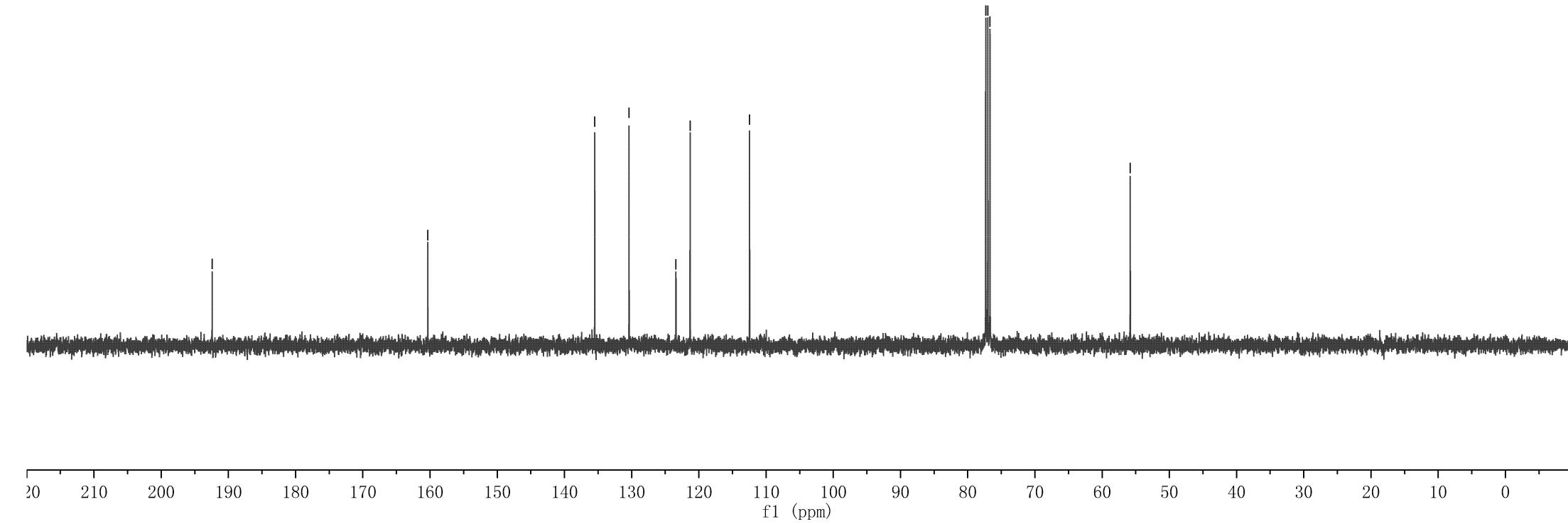
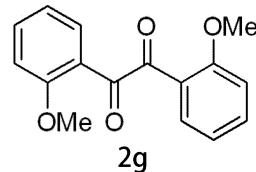
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—112.45

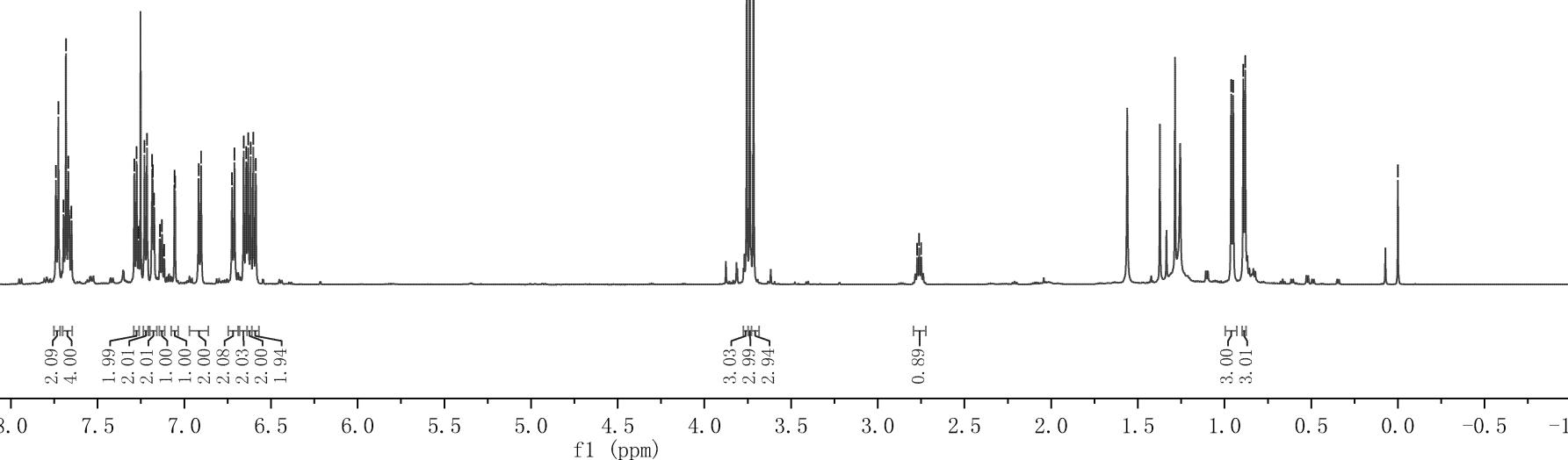
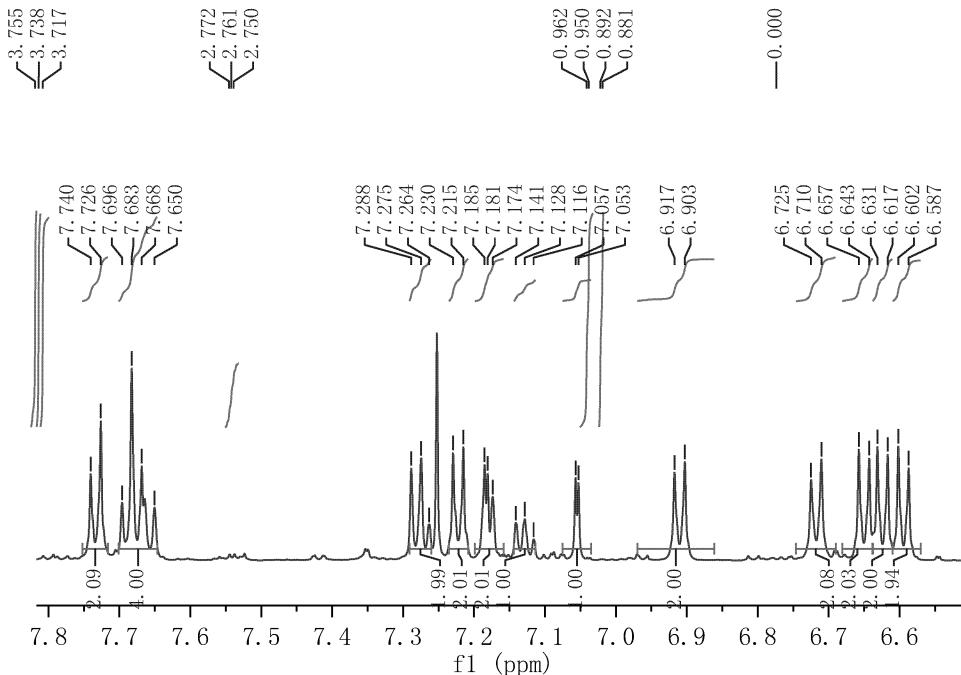
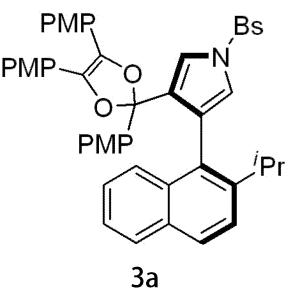
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77.00
76.68

—55.82

Parameter	Value
1 Title	ZZX-19-196-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	300.0
5 Number of Scans	17
6 Acquisition Time	1.3631
7 Acquisition Date	2023-09-11T20:46:49
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5



Parameter	Value
1 Title	CYB-3
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	298.0
5 Number of Scans	4
6 Acquisition Time	2.7263
7 Acquisition Date	2022-11-18T15:02:33
8 Spectrometer Frequency	600.13
9 Spectral Width	12019.2



Parameter	Value
1 Title	CYB-3
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	298.0
5 Number of Scans	26
6 Acquisition Time	0.9044
7 Acquisition Date	2022-11-18T15:04:31
8 Spectrometer Frequency	150.90
9 Spectral Width	36231.9

159.53
158.88
158.78

-145.23

132.74
131.44
128.29
127.65
127.54
127.13
126.89
125.20
124.35
121.33
121.30
113.25
112.92
-107.97

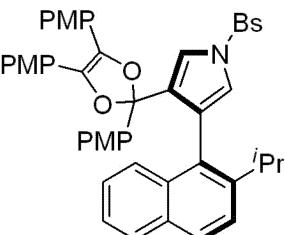
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76.79

-137.75

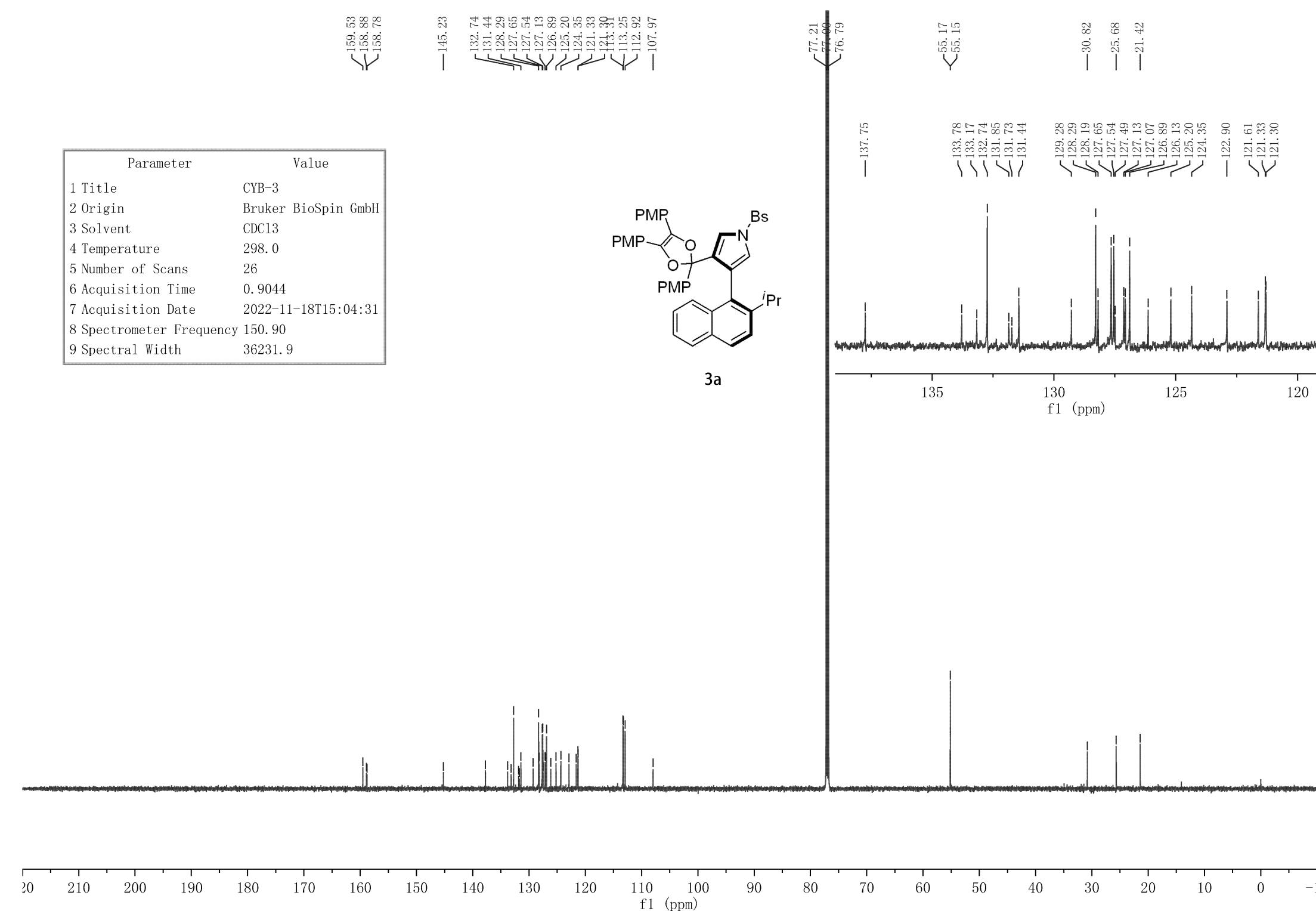
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132.74
131.85
131.73
131.44

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128.29
128.19
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127.07
126.89
126.13
125.20
124.35
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-25.68
-21.42

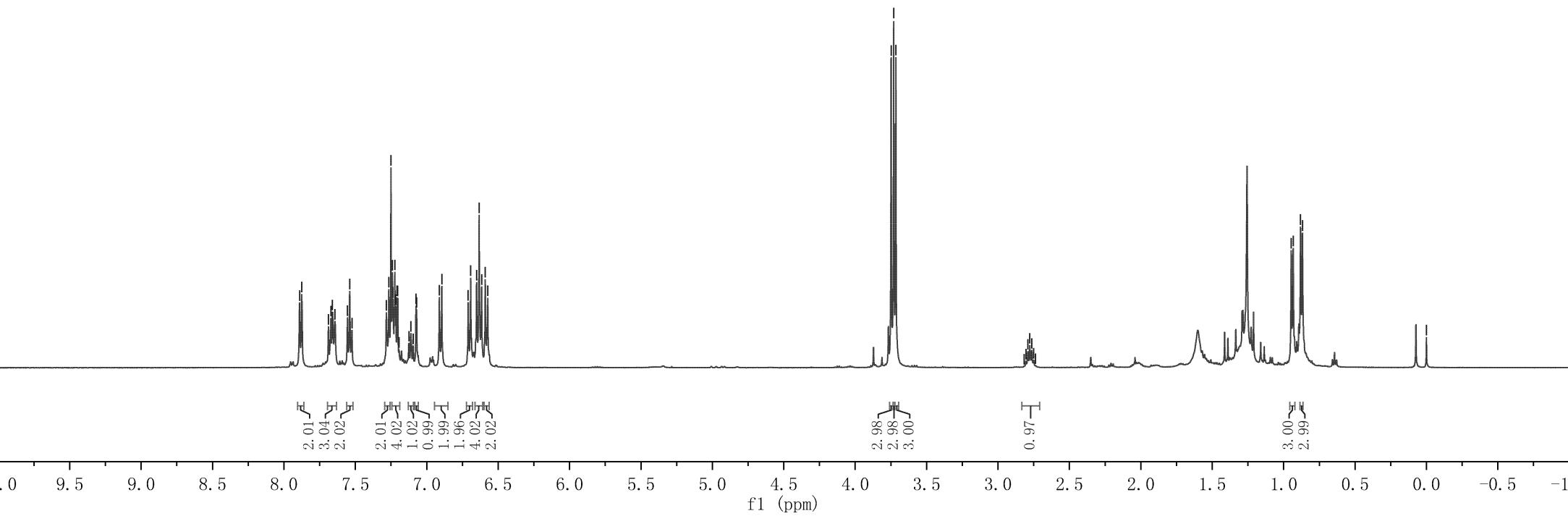
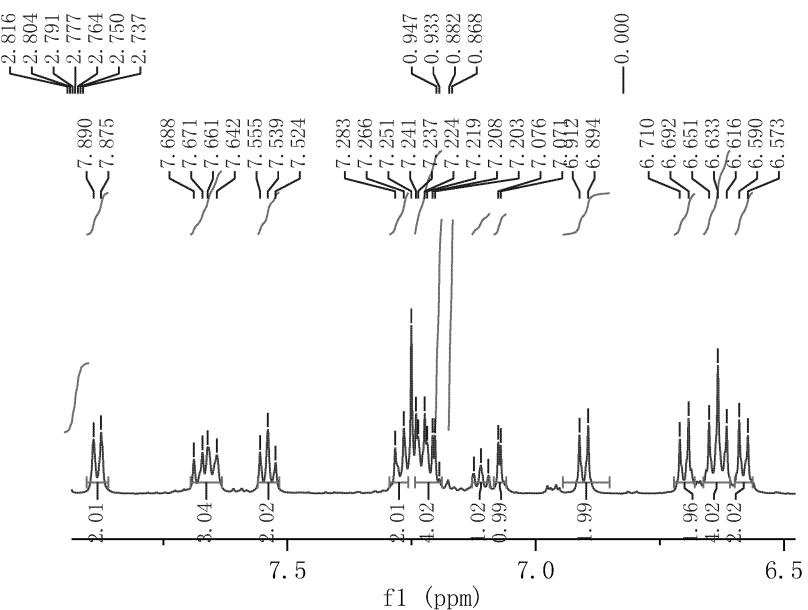
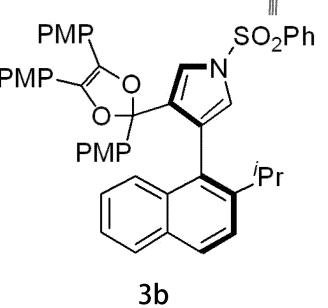
122.90
121.61
121.33
121.30



3a



Parameter	Value
1 Title	3b-H
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	299.0
5 Number of Scans	18
6 Acquisition Time	3.1719
7 Acquisition Date	2023-09-15T16:30:56
8 Spectrometer Frequency	500.17
9 Spectral Width	10330.6



Parameter	Value
1 Title	3b-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDC13
4 Temperature	299.4
5 Number of Scans	220
6 Acquisition Time	1.1010
7 Acquisition Date	2023-09-15T16:37:01
8 Spectrometer Frequency	125.77
9 Spectral Width	29761.9

159.52
158.87
158.77

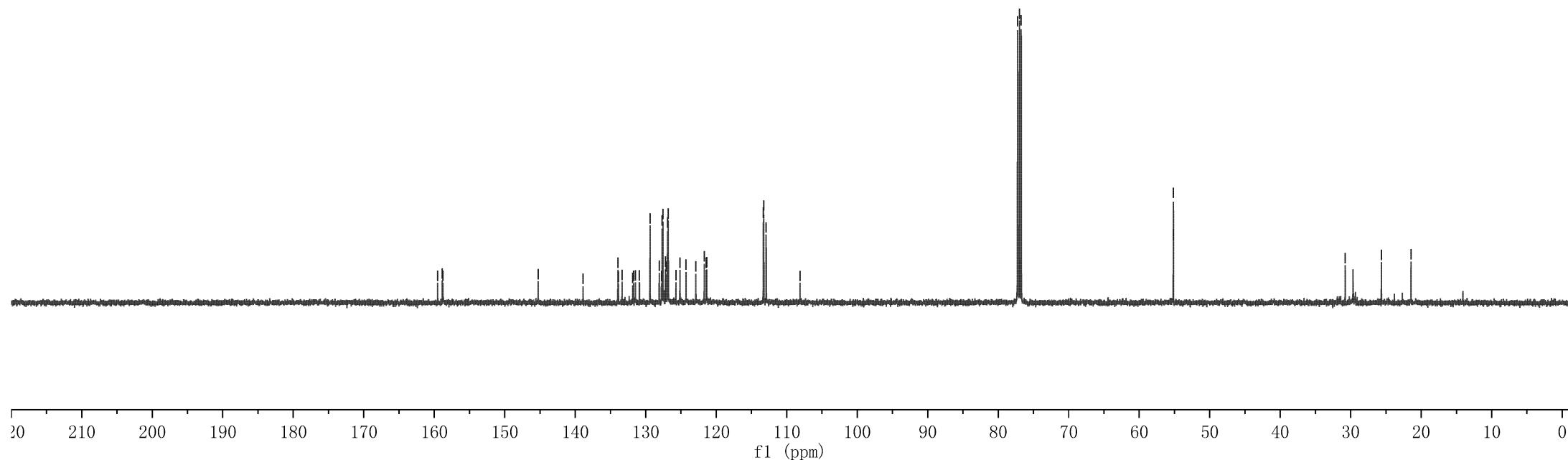
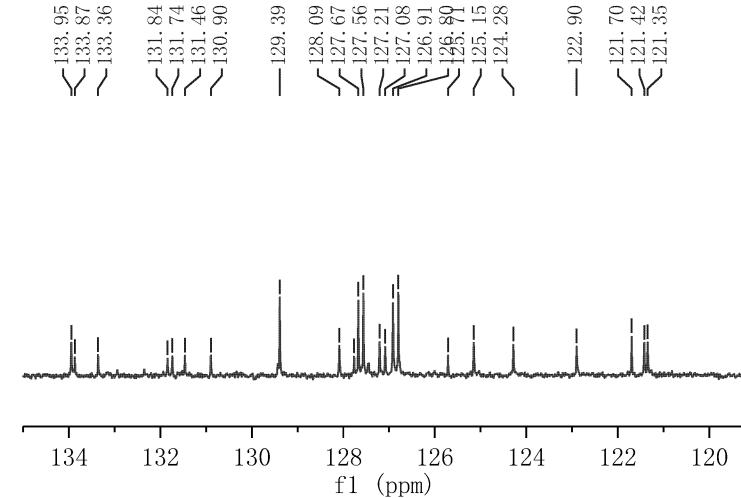
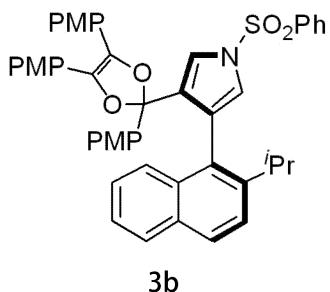
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—138.89

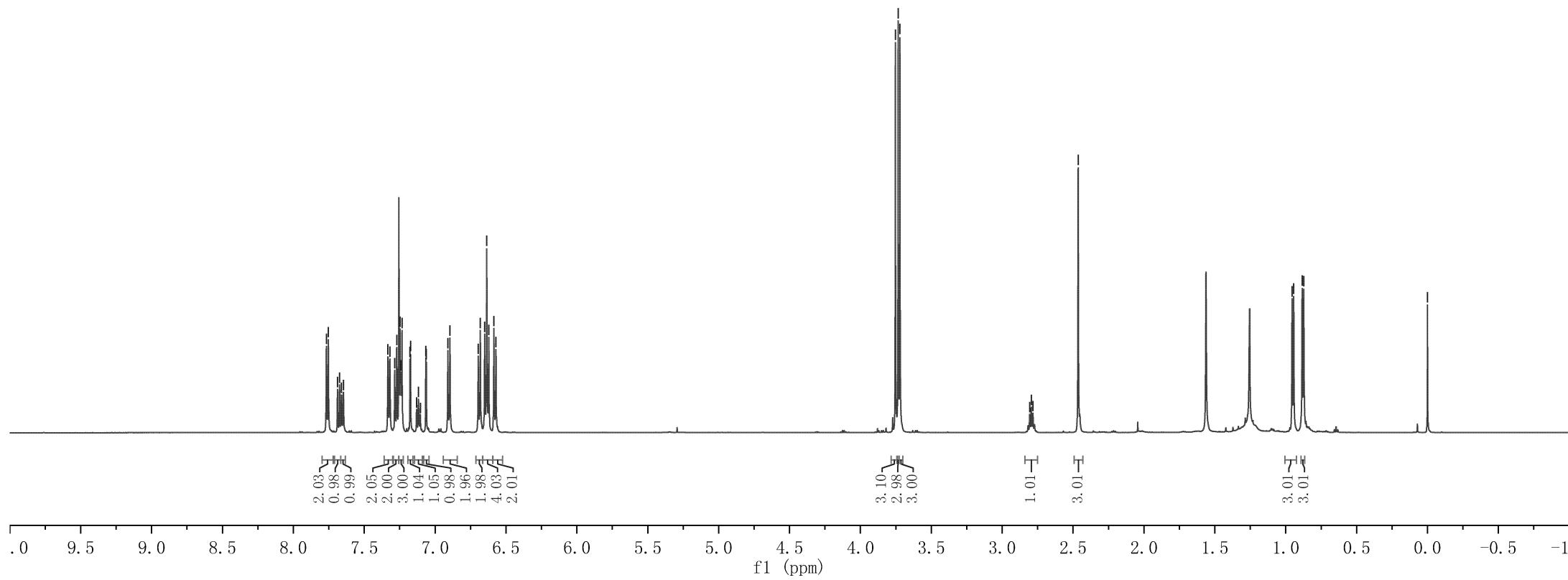
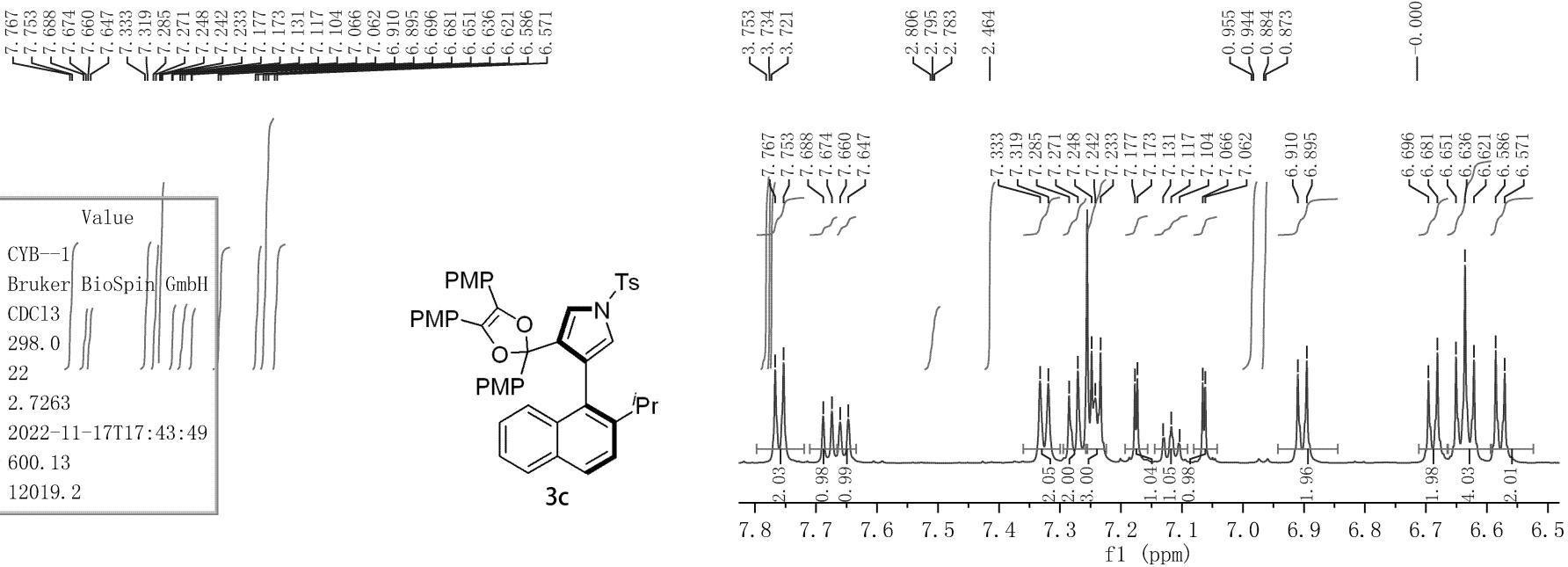
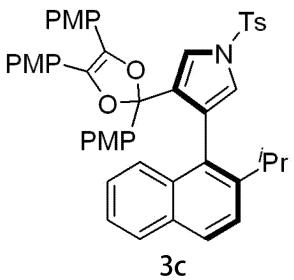
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127.21
126.91
126.80
121.70
121.42
121.35
113.24
112.91
—108.10

77.25
77.00
76.75
—
55.16
55.14

—30.77
—25.64
—21.45
—
122.90
121.70
121.42
121.35



Parameter	Value
1 Title	CYB-1
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	298.0
5 Number of Scans	22
6 Acquisition Time	2.7263
7 Acquisition Date	2022-11-17T17:43:49
8 Spectrometer Frequency	600.13
9 Spectral Width	12019.2



Parameter	Value
1 Title	CYB--1
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	298.0
5 Number of Scans	43
6 Acquisition Time	0.9044
7 Acquisition Date	2022-11-17T17:49:59
8 Spectrometer Frequency	150.90
9 Spectral Width	36231.9

159.48
158.83
158.72

145.27
145.12

129.99
128.04
127.68
127.53
127.09
126.93
126.88
125.09
121.71
121.35
113.21
112.88
108.12

77.21
77.00
76.79

135.91

133.90
133.41

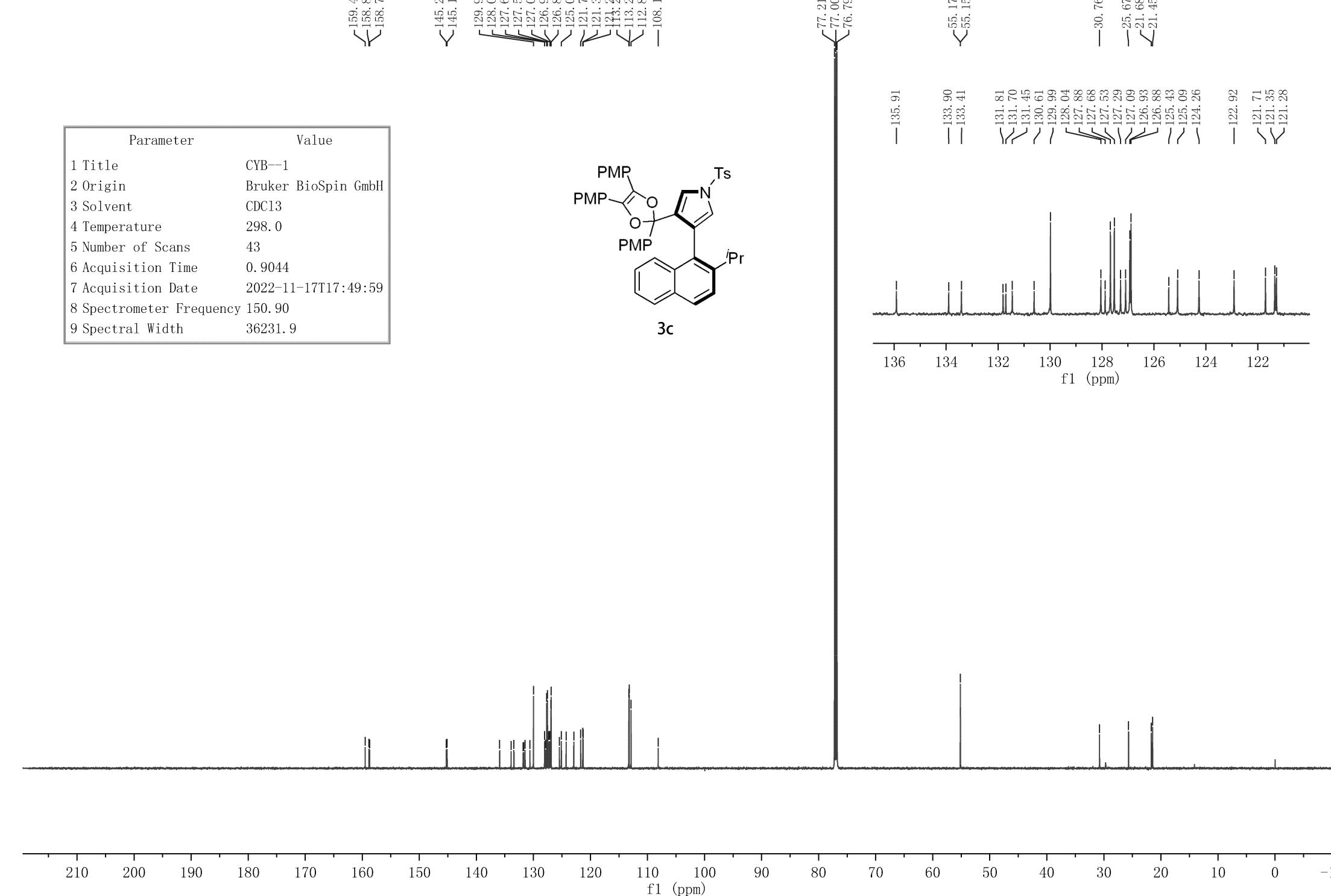
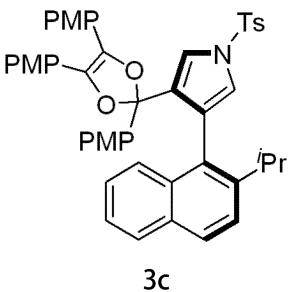
55.17
55.15

131.81
131.70
131.45
130.61
129.99
128.04
127.88
127.68
127.53
127.29
127.09
126.93
126.88
125.43
125.09
124.26

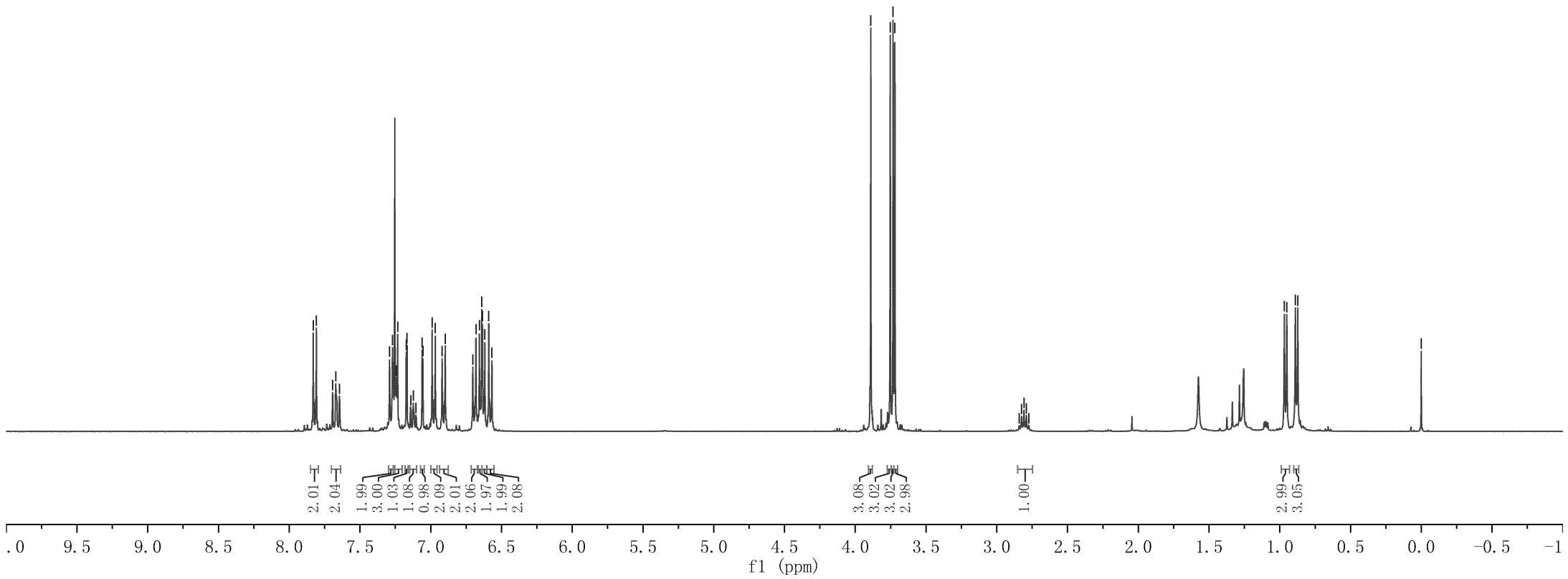
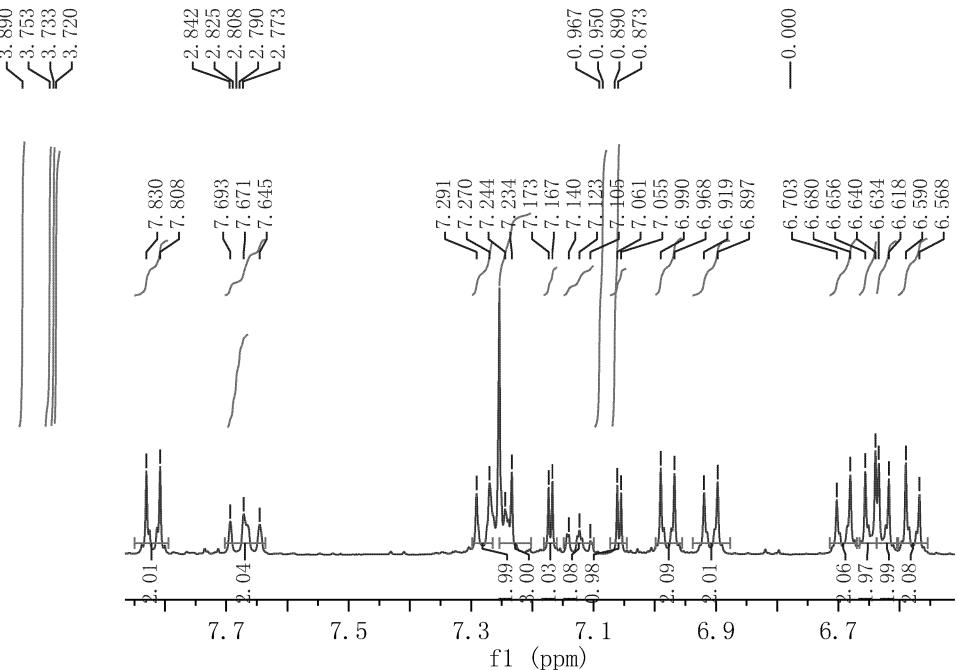
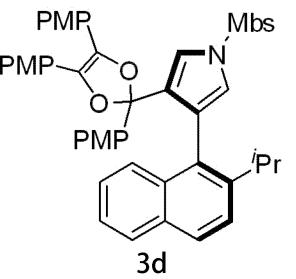
30.76

25.67
21.68
21.45

122.92
121.71
121.35
121.28



Parameter	Value
1 Title	CHH-1-131-II
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	294.6
5 Number of Scans	31
6 Acquisition Time	3.9846
7 Acquisition Date	2022-11-14T10:08:10
8 Spectrometer Frequency	399.93
9 Spectral Width	8223.7



Parameter	Value
1 Title	CHH-1-131-C-PURE
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	295.7
5 Number of Scans	655
6 Acquisition Time	1.3631
7 Acquisition Date	2022-11-14T15:00:08
8 Spectrometer Frequency	100.56
9 Spectral Width	24038.5

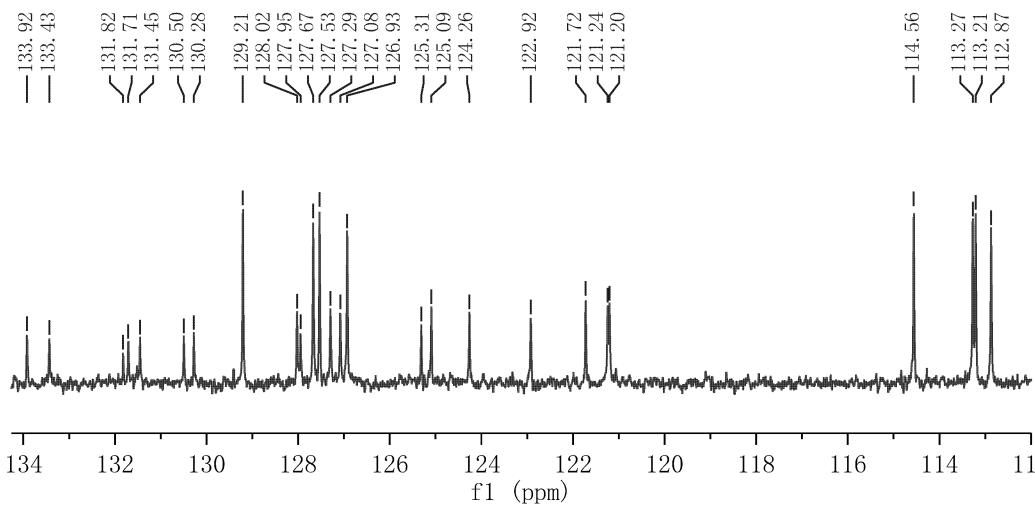
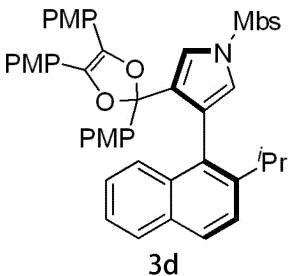
— 163.92
— 159.47
— 158.83
— 158.72

— 145.26
— 129.21
— 128.02
— 127.67
— 127.53
— 127.29
— 127.08
— 126.93
— 125.09
— 121.72
— 121.24
— 121.20
— 114.56
— 113.27
— 103.46

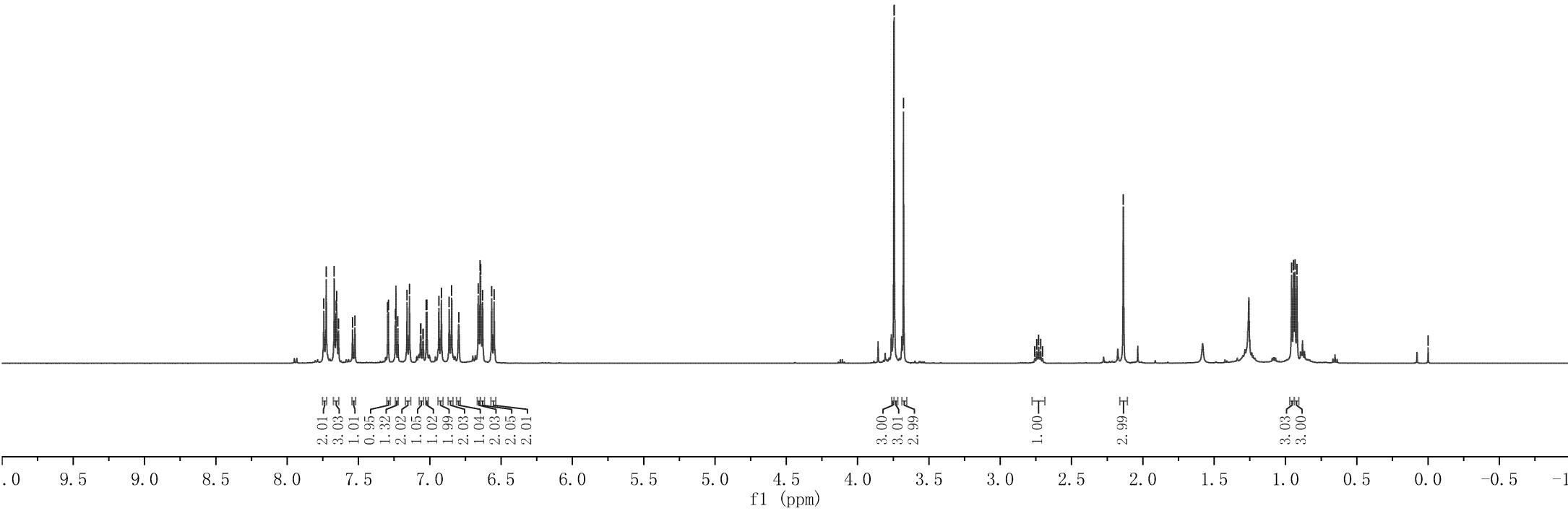
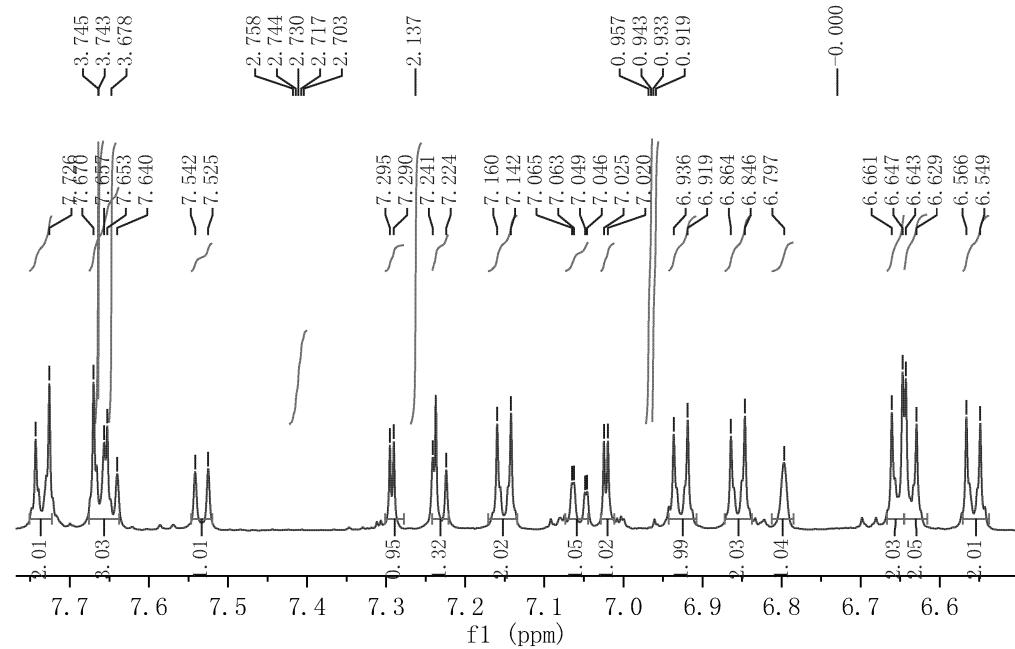
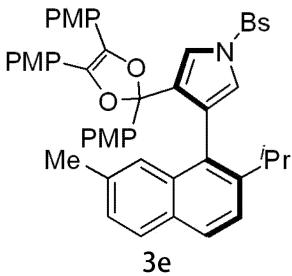
— 133.92
— 133.43
— 131.82
— 131.71
— 131.45
— 130.50
— 130.28
— 129.21
— 128.02
— 127.95
— 127.67
— 127.53
— 127.29
— 127.08
— 126.93
— 125.31
— 125.09
— 124.26
— 122.92
— 121.72
— 121.24
— 121.20
— 30.76

— 25.69
— 21.47

— 114.56
— 113.27
— 113.21
— 112.87



Parameter	Value
1 Title	3e-H
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	297.8
5 Number of Scans	18
6 Acquisition Time	3.1719
7 Acquisition Date	2023-08-03T17:19:27
8 Spectrometer Frequency	500.17
9 Spectral Width	10330.6



Parameter	Value
1 Title	3e-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	298.0
5 Number of Scans	44
6 Acquisition Time	1.1010
7 Acquisition Date	2023-08-03T17:24:16
8 Spectrometer Frequency	125.77
9 Spectral Width	29761.9

159.38
158.87
158.85

-145.22

132.67
131.82
128.20
127.94
127.61
127.57
126.93
126.78
126.05
121.96
121.30
120.99
113.29
112.72
-108.02

-137.86

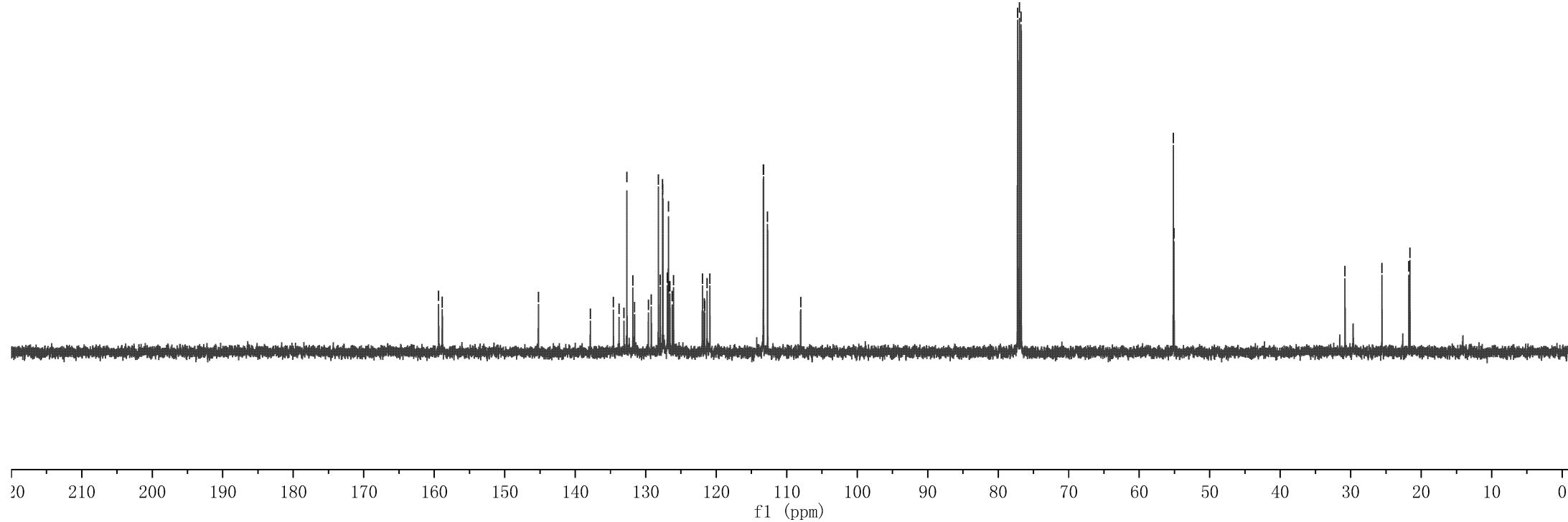
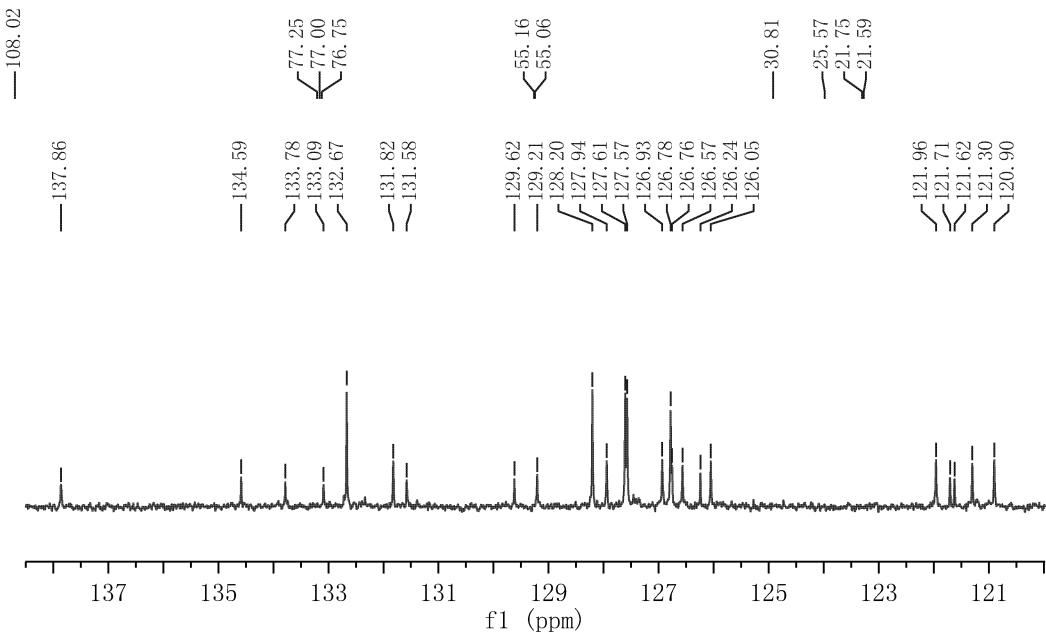
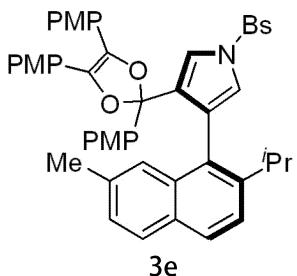
-134.59
~133.78
~133.09
~132.67
~131.82
~131.58

-129.62
-129.21
128.20
127.94
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127.57
126.93
126.78
126.76
126.57
126.24
126.05

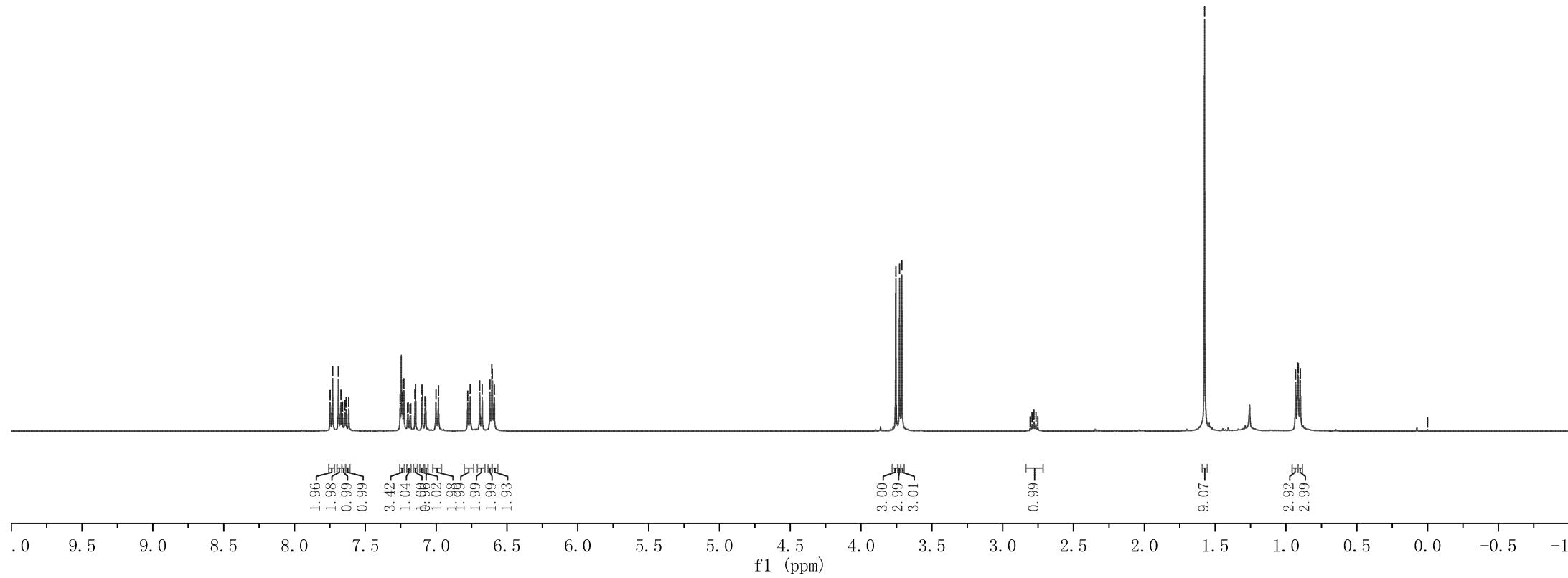
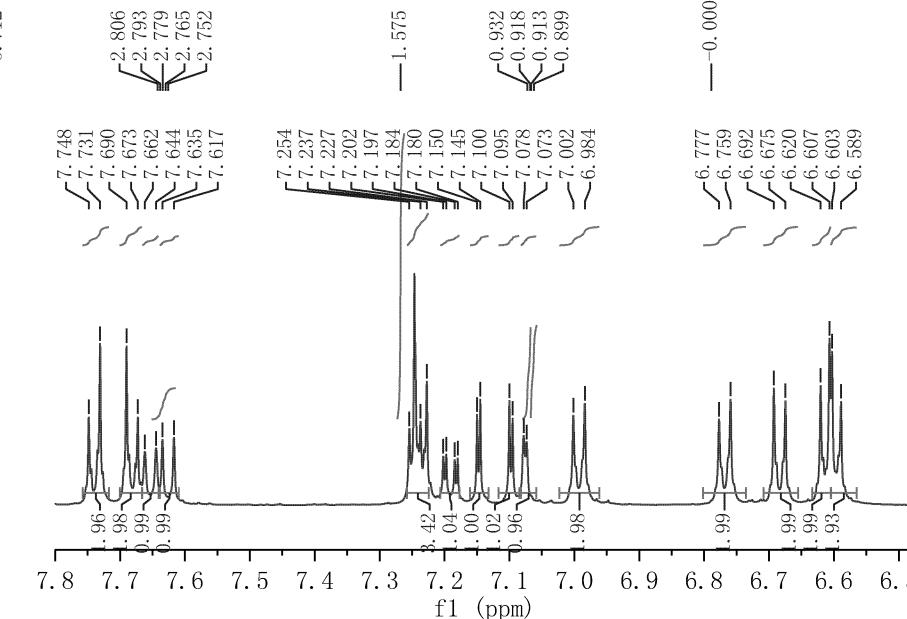
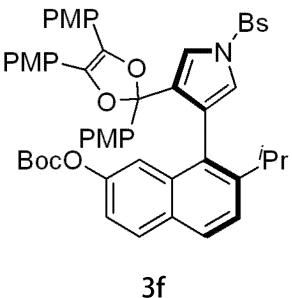
-30.81

-25.57
21.75
21.59

121.96
121.71
121.62
121.30
120.90



Parameter	Value
1 Title	3f-H
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDC13
4 Temperature	298.18
5 Number of Scans	15
6 Acquisition Time	3.1719
7 Acquisition Date	2023-08-23T16:29:47
8 Spectrometer Frequency	500.17
9 Spectral Width	10330.6



Parameter	Value
1 Title	3f-II
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	298.8
5 Number of Scans	15
6 Acquisition Time	3.1719
7 Acquisition Date	2023-08-23T16:29:47
8 Spectrometer Frequency	500.17
9 Spectral Width	10330.6

159.47
 158.97
 158.69

151.84
 148.41
 146.19

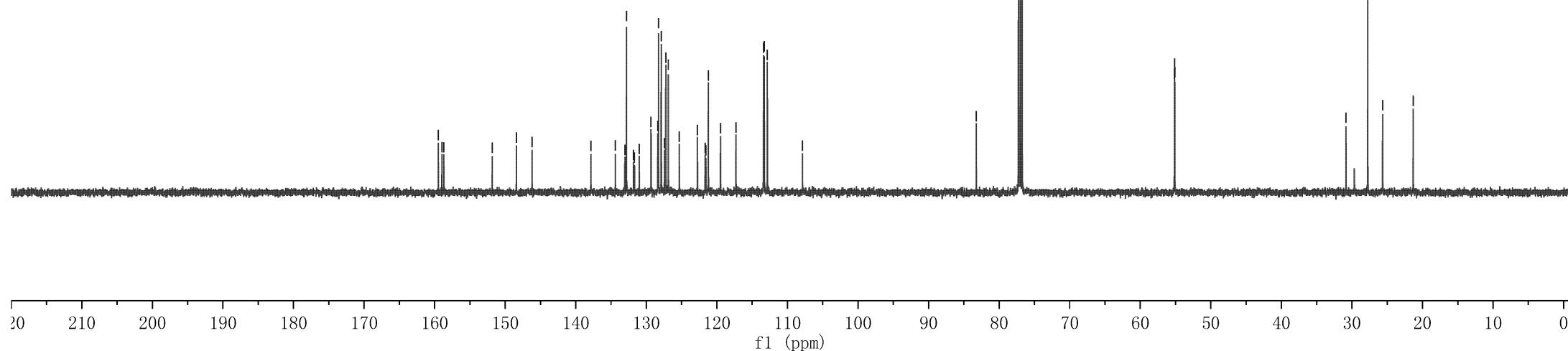
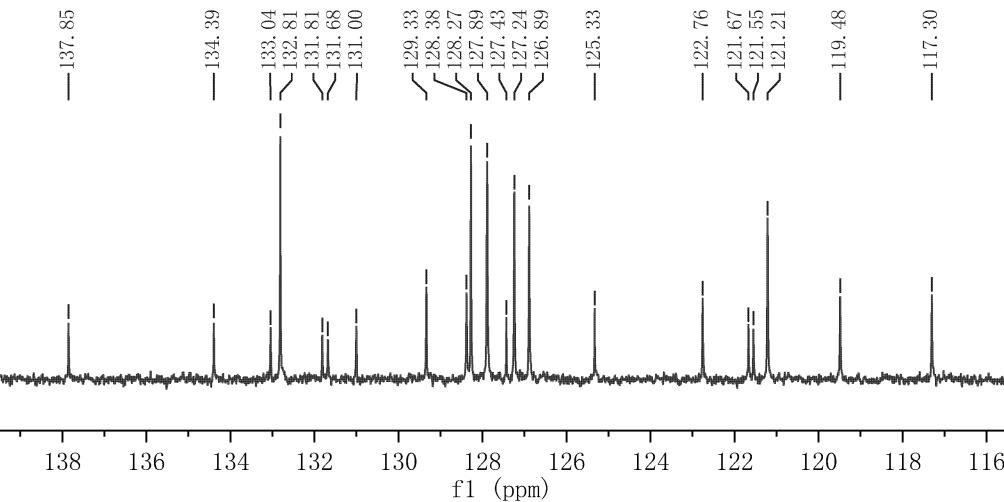
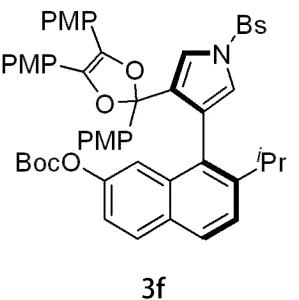
132.81
 129.33
 128.38
 128.27
 127.89
 127.43
 127.24
 126.89
 125.33
 122.76
 121.21
 119.48
 117.30
 113.39
 113.28
 107.87

83.24
 77.25
 77.00
 76.75

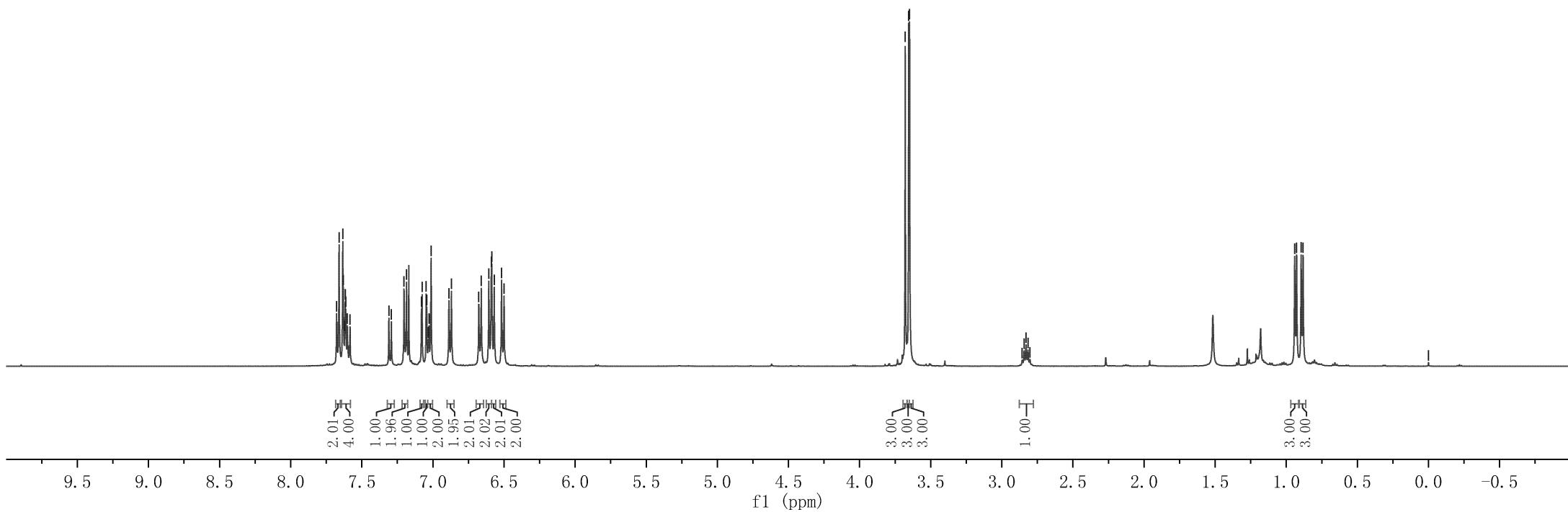
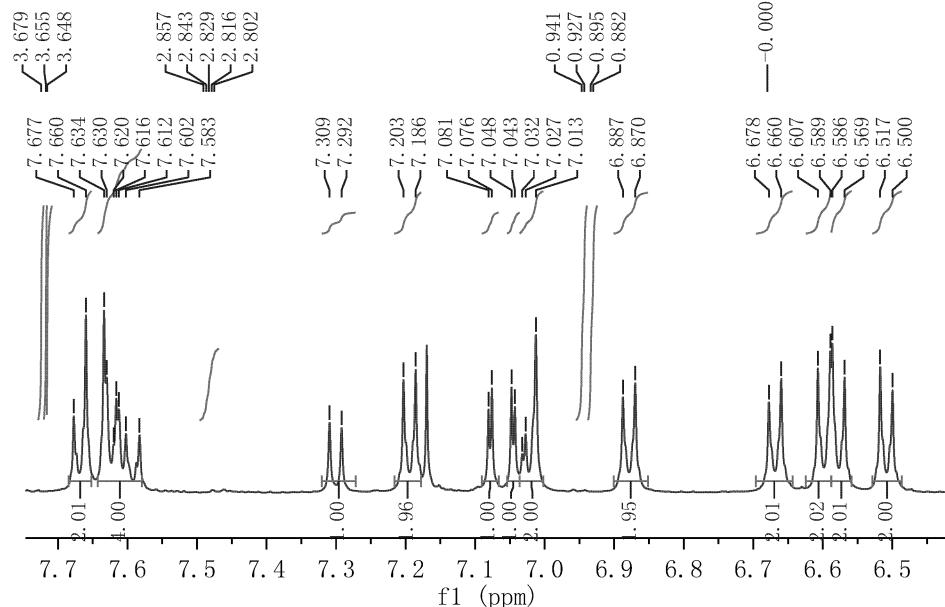
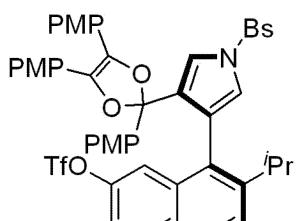
137.85
 134.39
 133.04
 132.81
 131.81
 131.68
 131.00

122.76
 121.67
 121.55
 121.21
 30.84
 27.76
 25.65
 21.31

119.48
 117.30



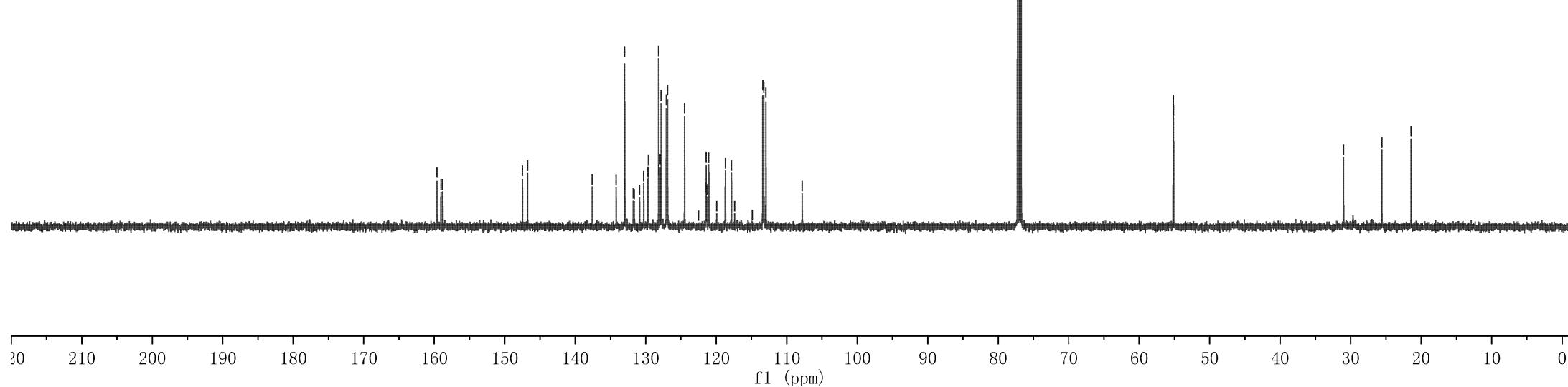
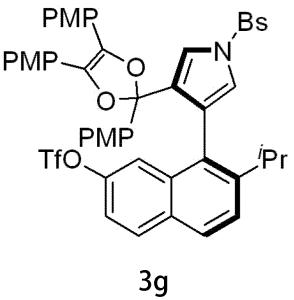
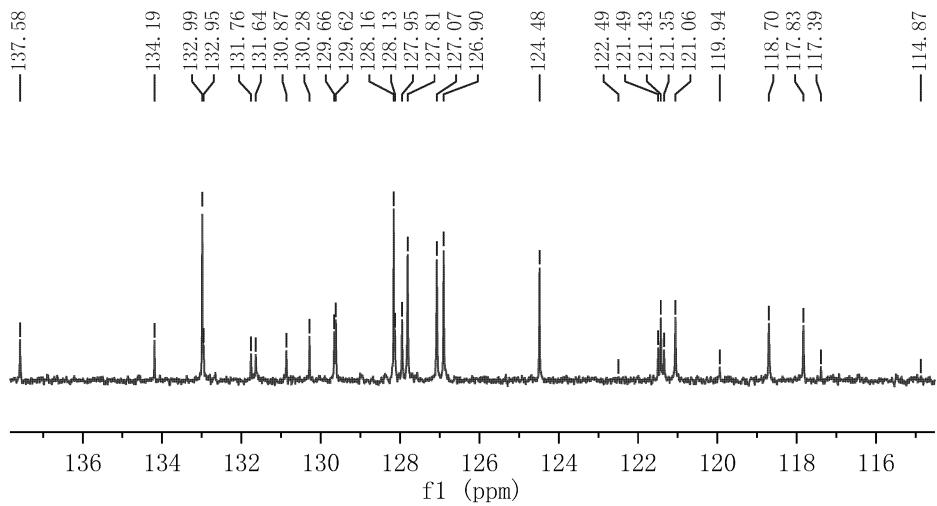
Parameter	Value
1 Title	3g-H
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	298.8
5 Number of Scans	14
6 Acquisition Time	3.1719
7 Acquisition Date	2023-08-21T16:37:40
8 Spectrometer Frequency	500.17
9 Spectral Width	10330.6



Parameter	Value
1 Title	3g-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	299.1
5 Number of Scans	123
6 Acquisition Time	1.1010
7 Acquisition Date	2023-08-21T16:41:40
8 Spectrometer Frequency	125.77
9 Spectral Width	29761.9

¹³
 159.61
 159.04
 158.80

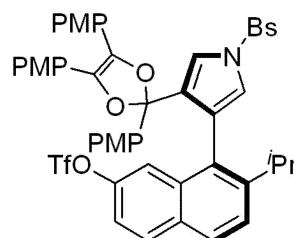
¹⁴
 147.48
 146.75
 132.99
 129.62
 128.16
 128.13
 127.95
 127.81
 127.07
 124.48
 121.43
 121.06
 118.70
 117.83
 113.40
 113.26
 107.85



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

Parameter	Value
1 Title	3g-F
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	296.9
5 Number of Scans	16
6 Acquisition Time	0.7340
7 Acquisition Date	2023-09-12T11:34:13
8 Spectrometer Frequency	376.31
9 Spectral Width	89285.7

-72.96



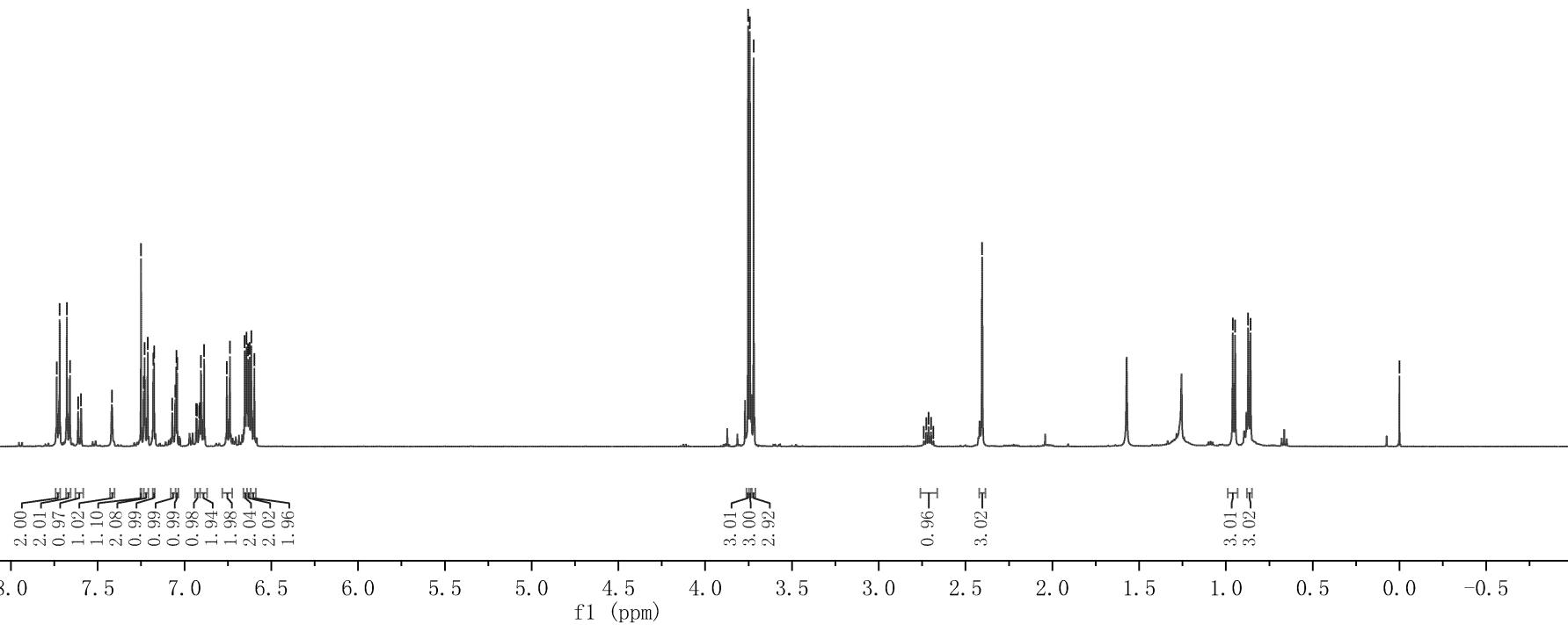
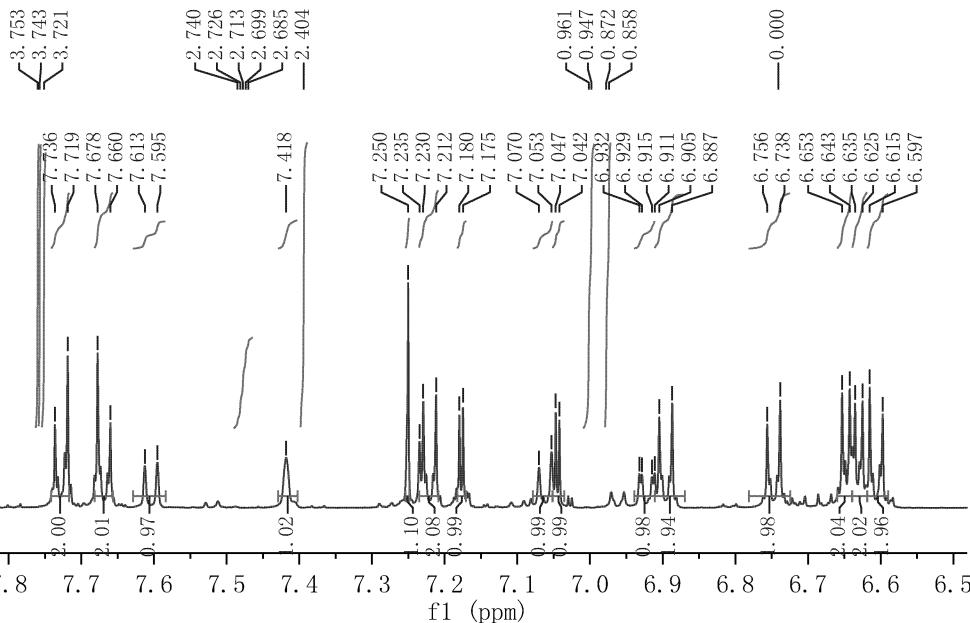
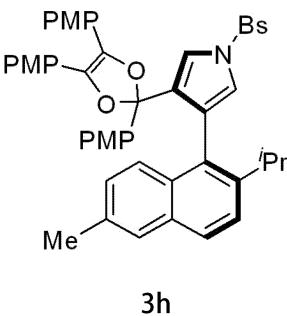
3g

-

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

f1 (ppm)

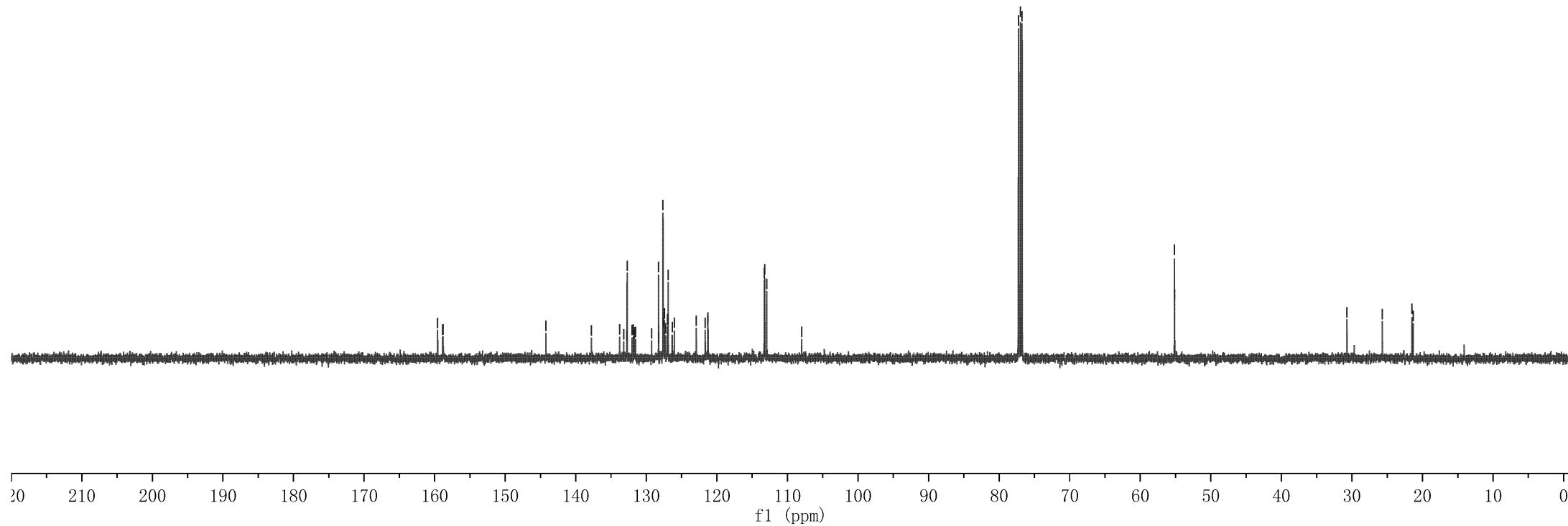
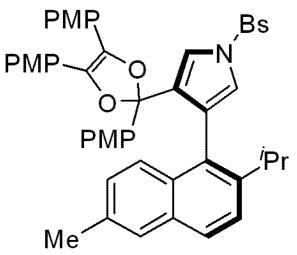
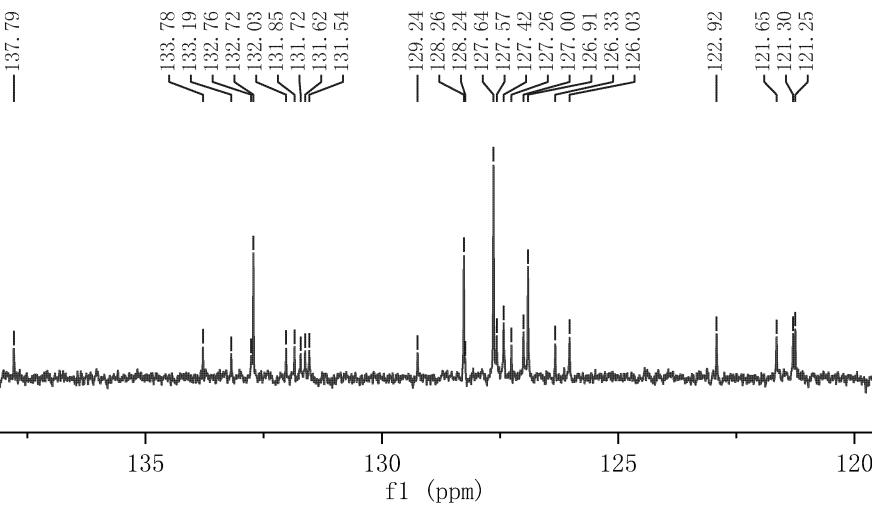
Parameter	Value
1 Title	XHJ-5-135-H
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	297.9
5 Number of Scans	8
6 Acquisition Time	3.1719
7 Acquisition Date	2023-08-03T17:42:48
8 Spectrometer Frequency	500.17
9 Spectral Width	10330.6



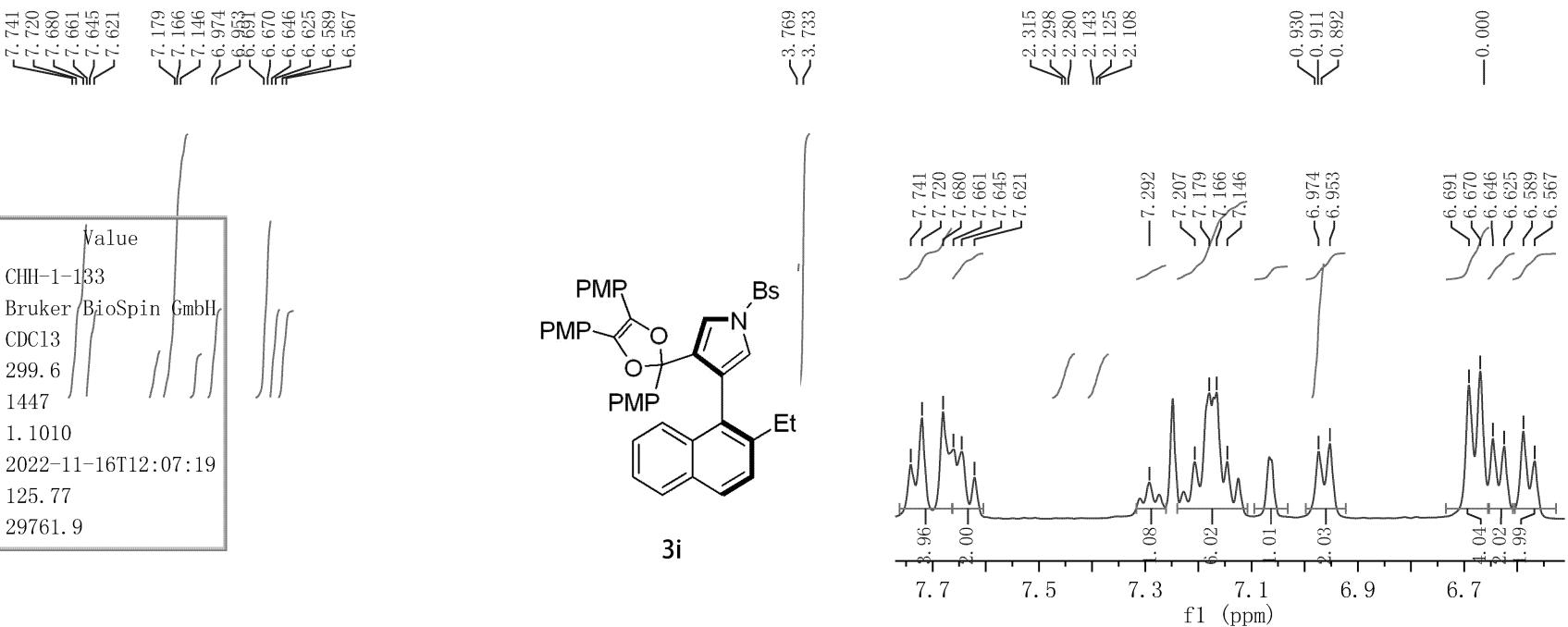
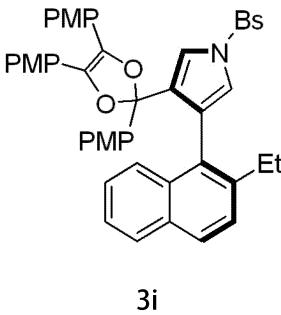
Parameter	Value
1 Title	3h-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	298.0
5 Number of Scans	76
6 Acquisition Time	1.1010
7 Acquisition Date	2023-08-03T17:48:36
8 Spectrometer Frequency	125.77
9 Spectral Width	29761.9

159.57
158.85
158.80

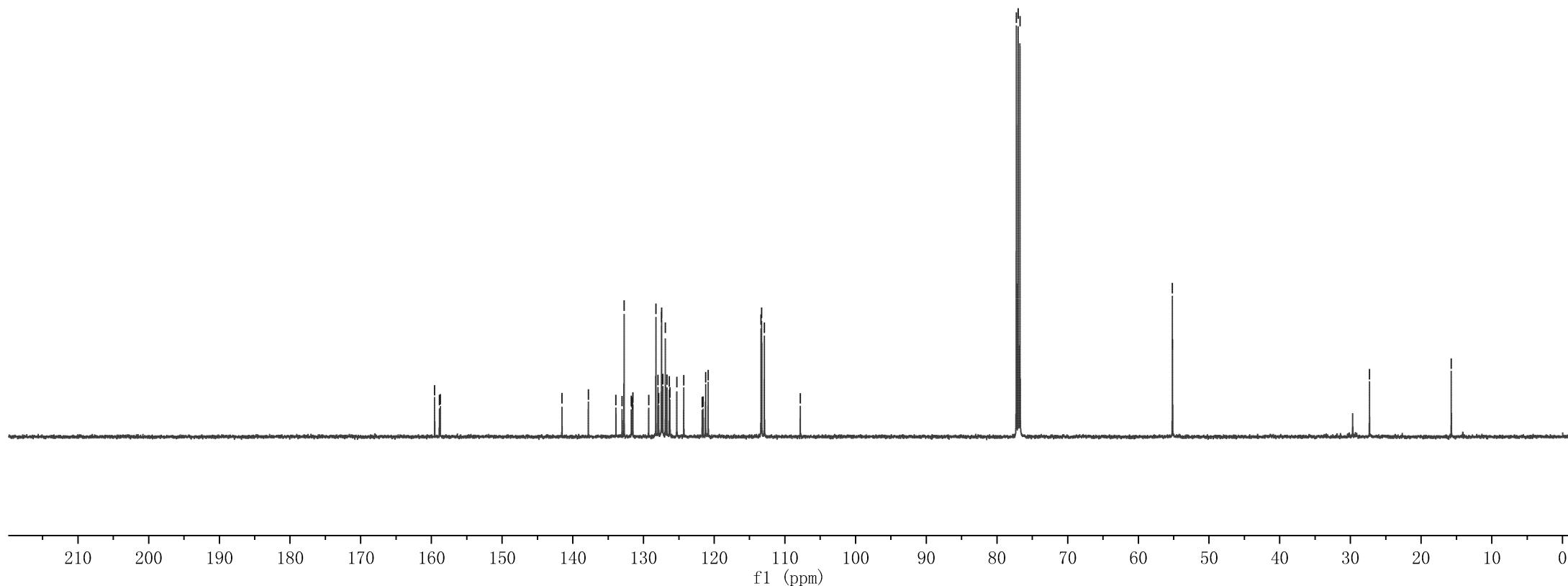
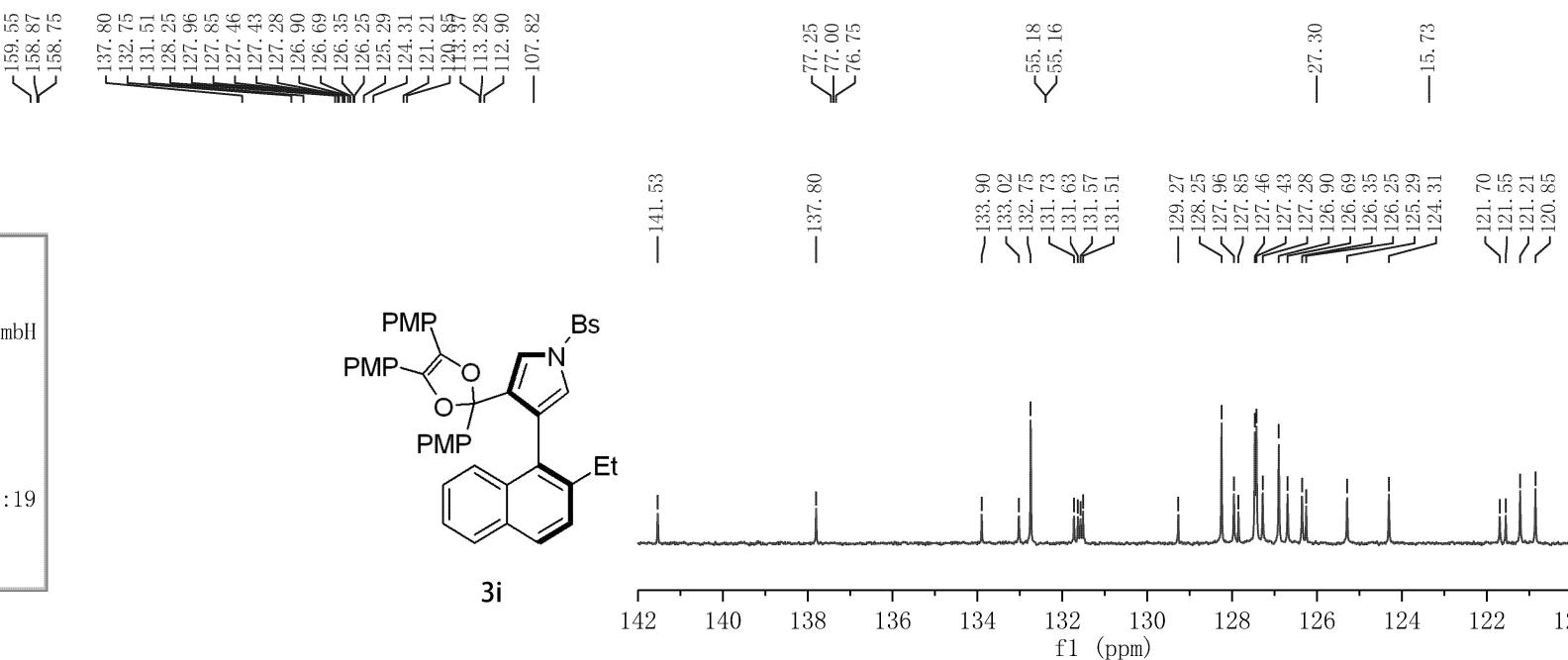
—144.23
—132.72
—128.26
—127.64
—127.57
—127.42
—127.00
—126.91
—126.03
—122.92
—121.65
—121.30
—121.25
—113.21
—112.94
—107.98

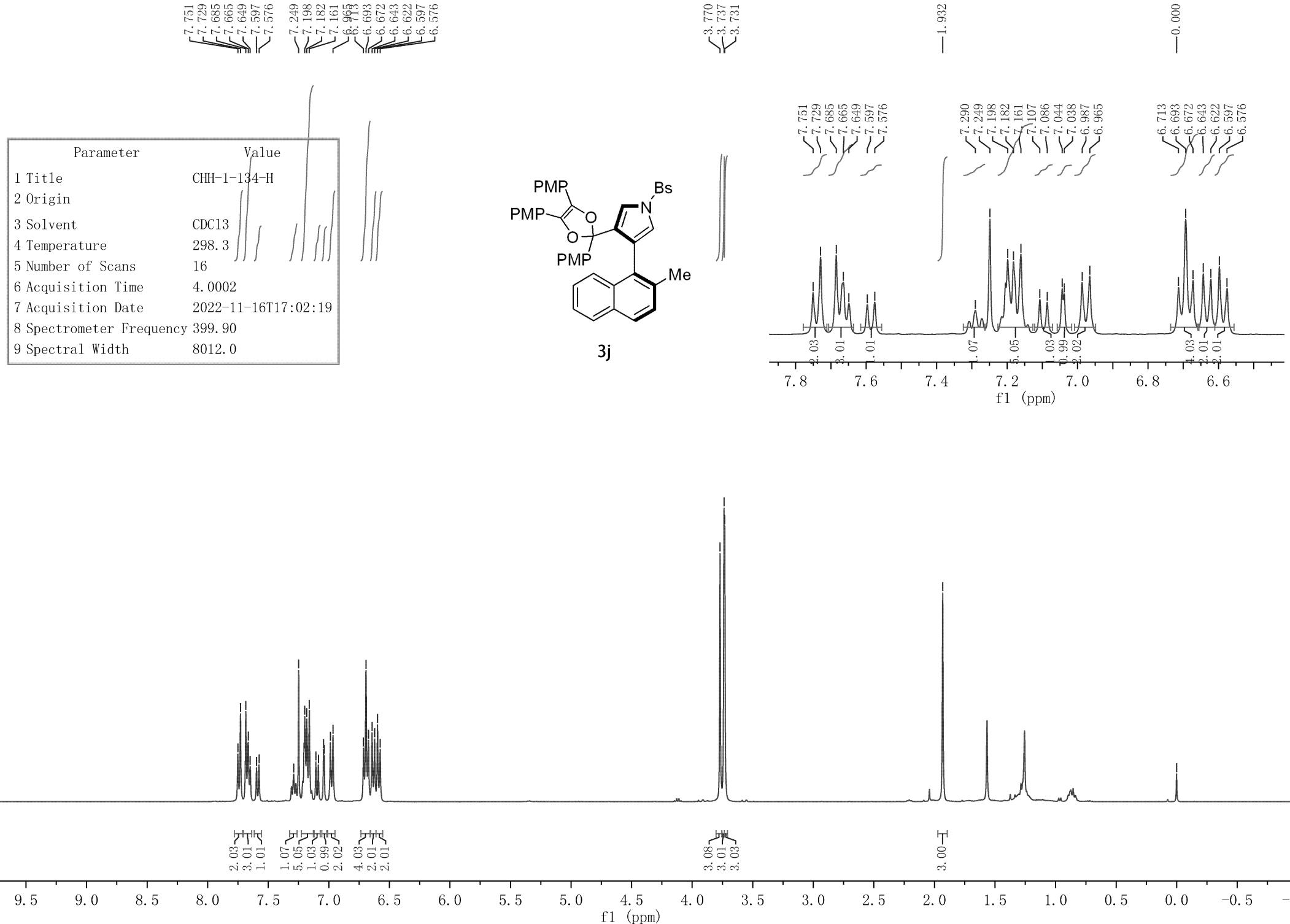


Parameter	Value
1 Title	CHH-1-133
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	299.6
5 Number of Scans	1447
6 Acquisition Time	1.1010
7 Acquisition Date	2022-11-16T12:07:19
8 Spectrometer Frequency	125.77
9 Spectral Width	29761.9

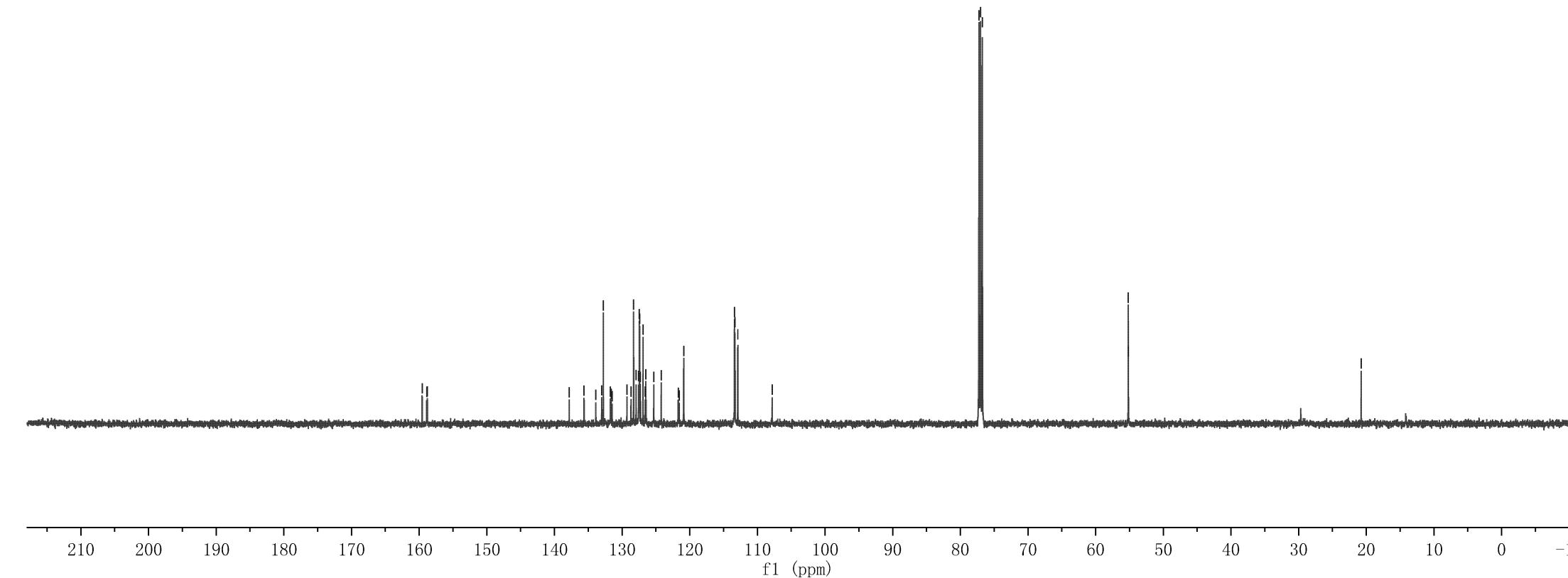
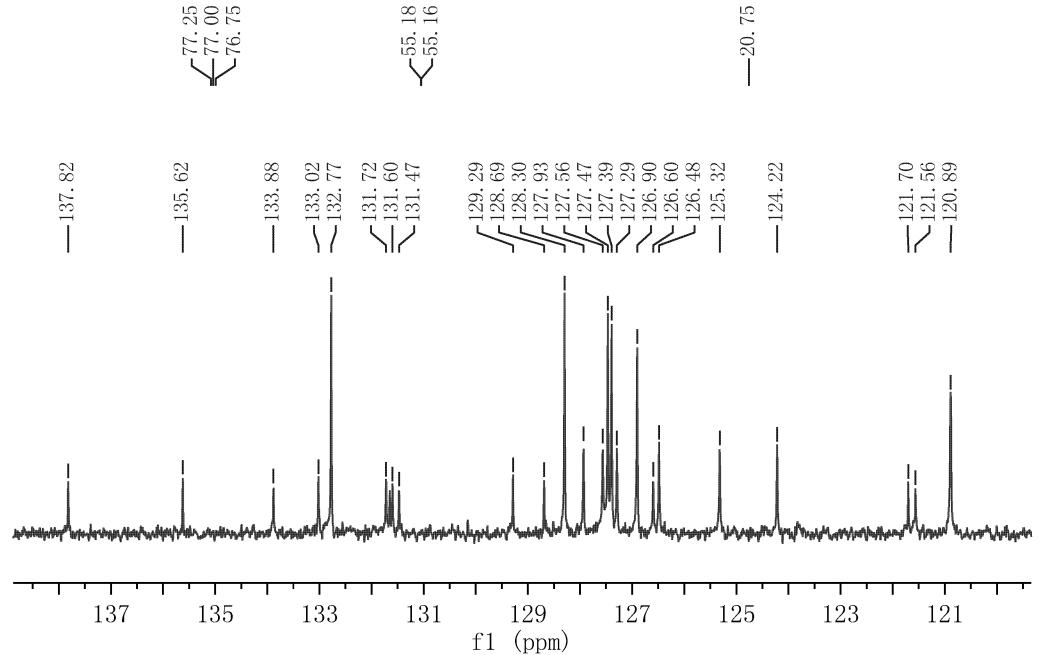
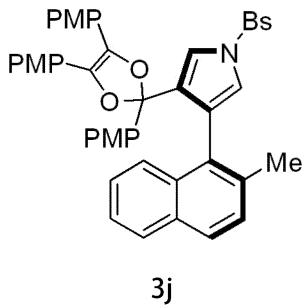


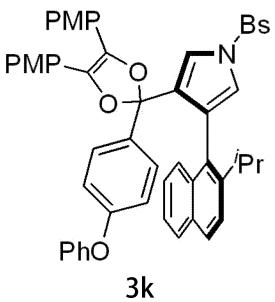
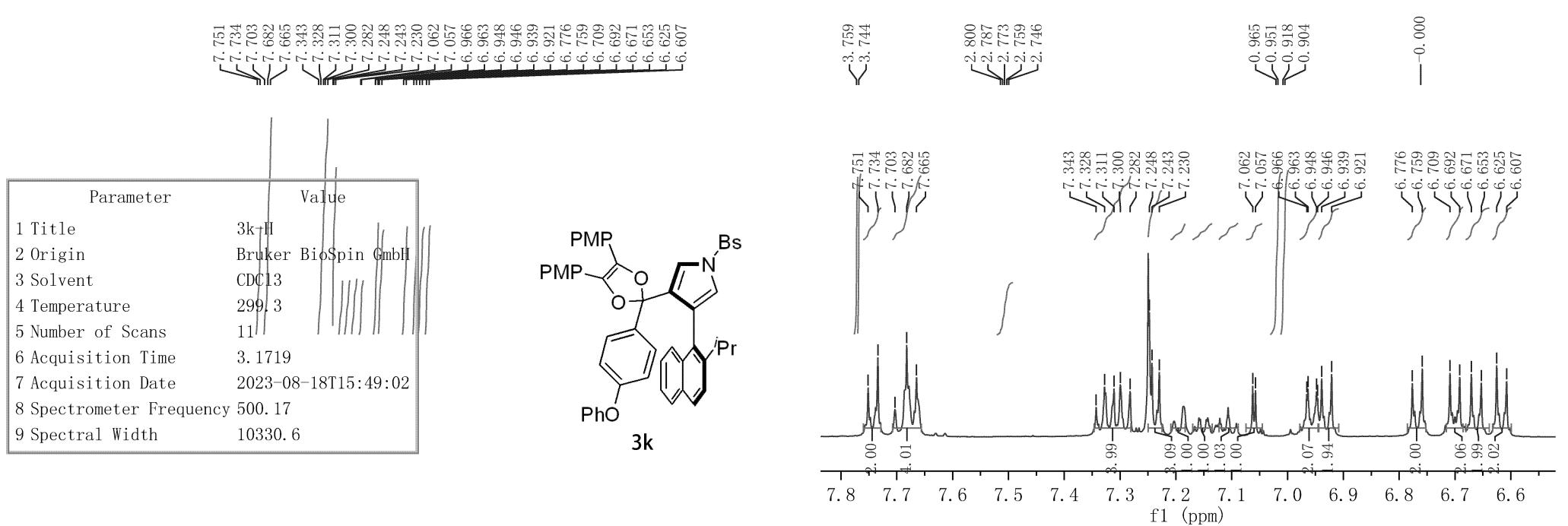
Parameter	Value
1 Title	CHH-1-133
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	299.6
5 Number of Scans	1447
6 Acquisition Time	1.1010
7 Acquisition Date	2022-11-16T12:07:19
8 Spectrometer Frequency	125.77
9 Spectral Width	29761.9





Parameter	Value
1 Title	1-134-Bs-Me-13C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	301.3
5 Number of Scans	400
6 Acquisition Time	1.1010
7 Acquisition Date	2022-11-17T18:53:00
8 Spectrometer Frequency	125.77
9 Spectral Width	29761.9



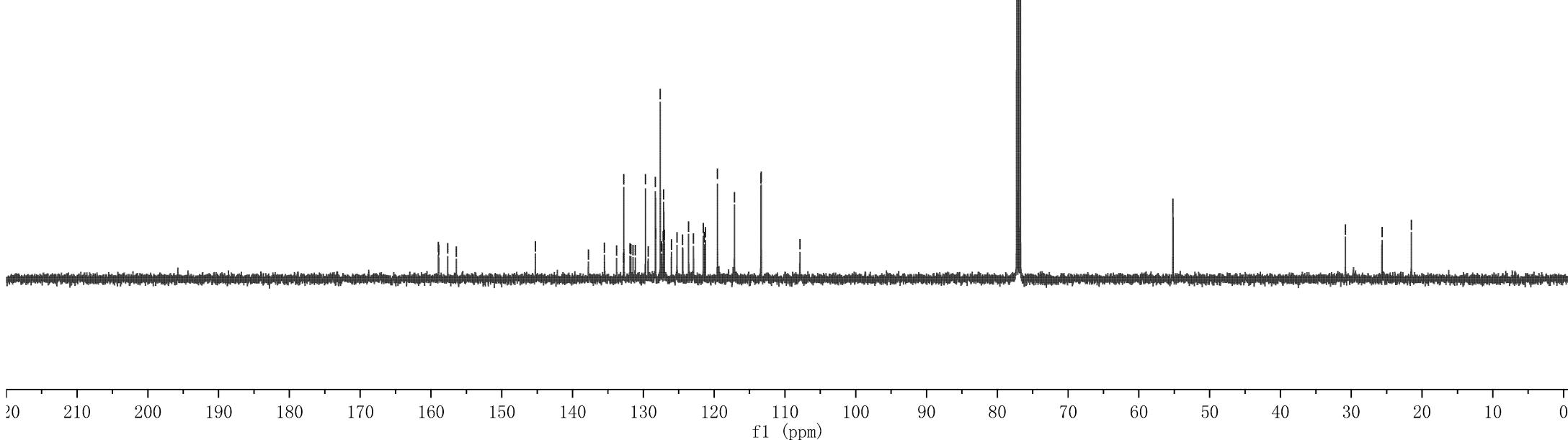
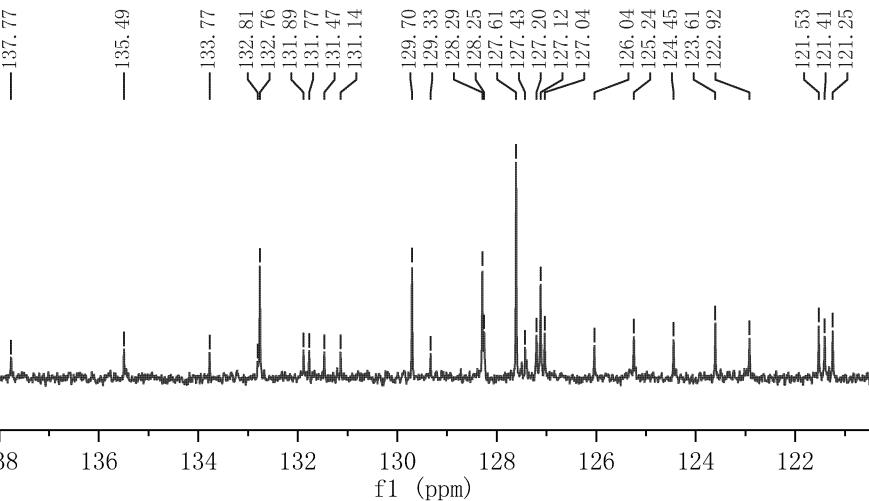


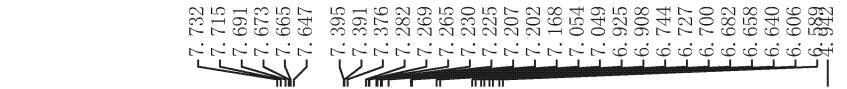
Parameter	Value
1 Title	3k-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDC13
4 Temperature	299.3
5 Number of Scans	97
6 Acquisition Time	1.1010
7 Acquisition Date	2023-08-18T15:52:39
8 Spectrometer Frequency	125.77
9 Spectral Width	29761.9

158.97
158.91
157.63
156.43

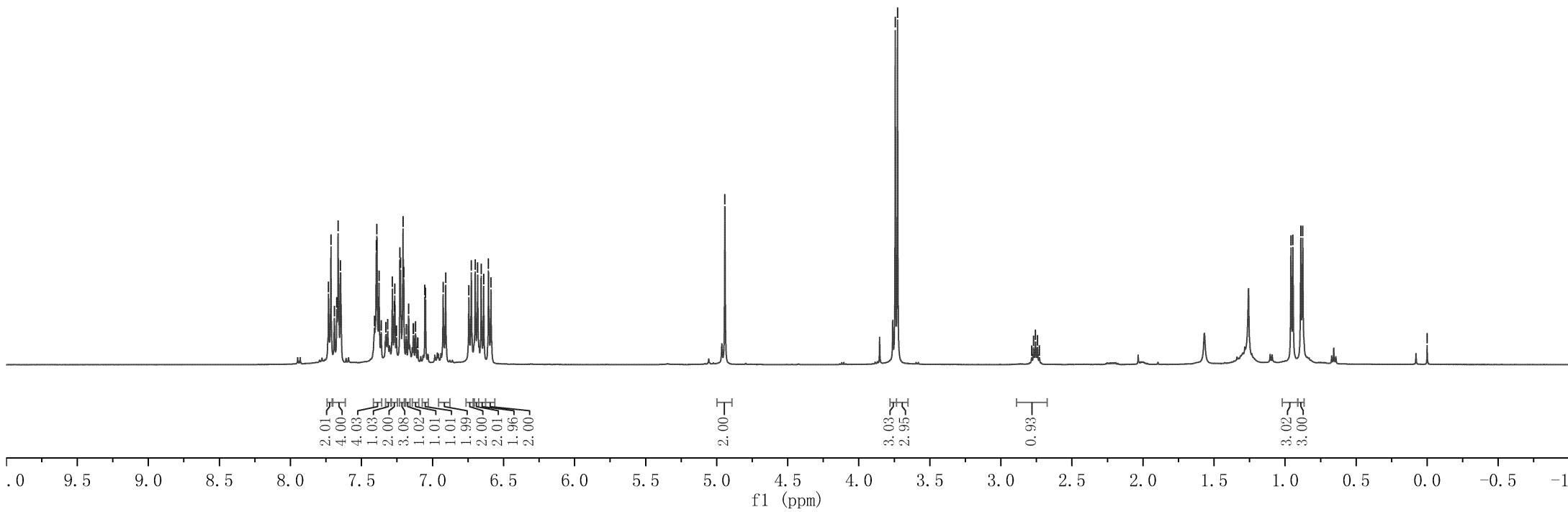
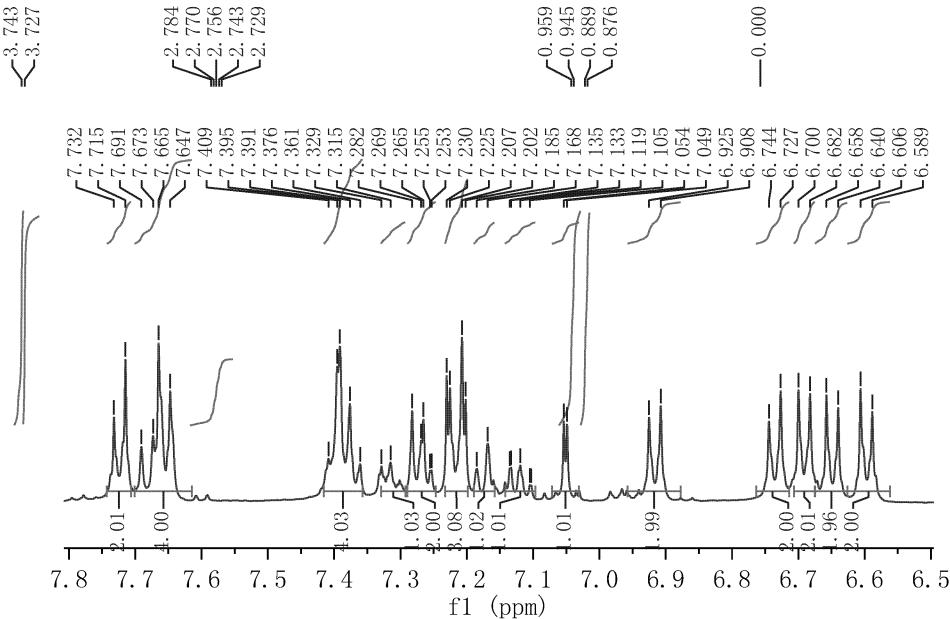
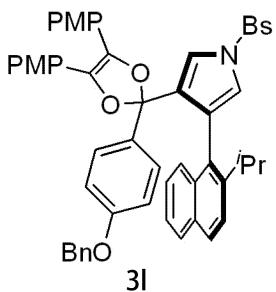
-145.26

132.76
129.70
128.29
128.25
127.61
127.20
127.12
127.04
123.61
121.53
121.25
119.54
117.13
113.38
107.89

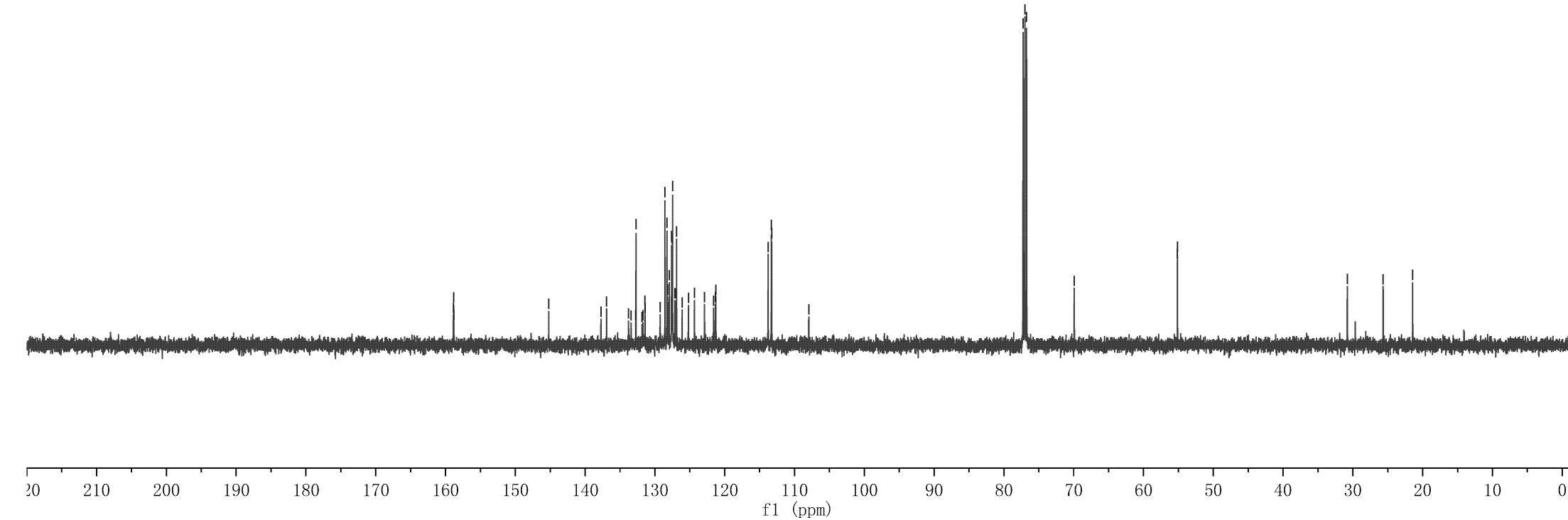
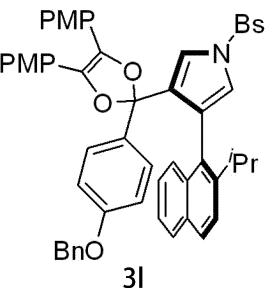


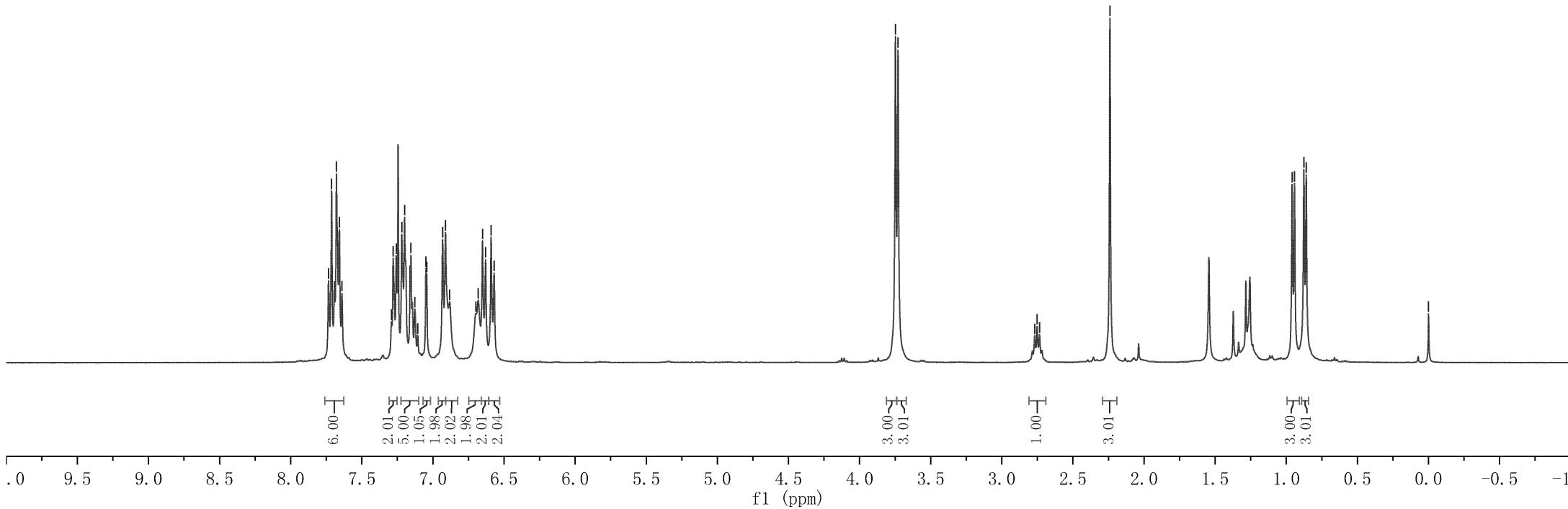
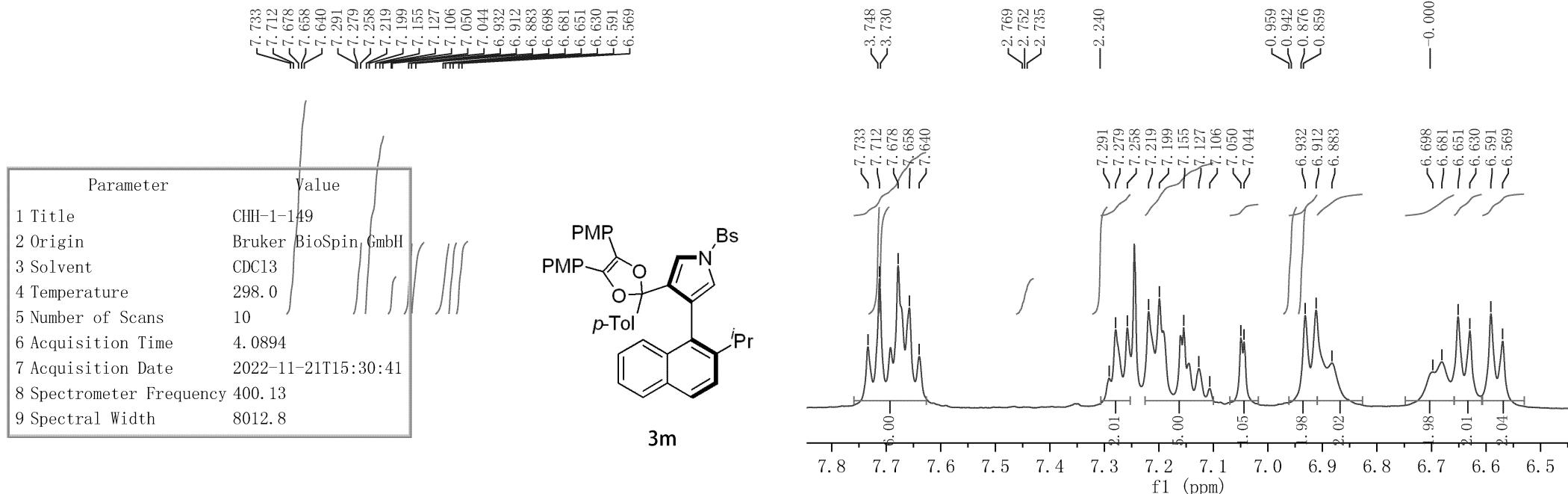


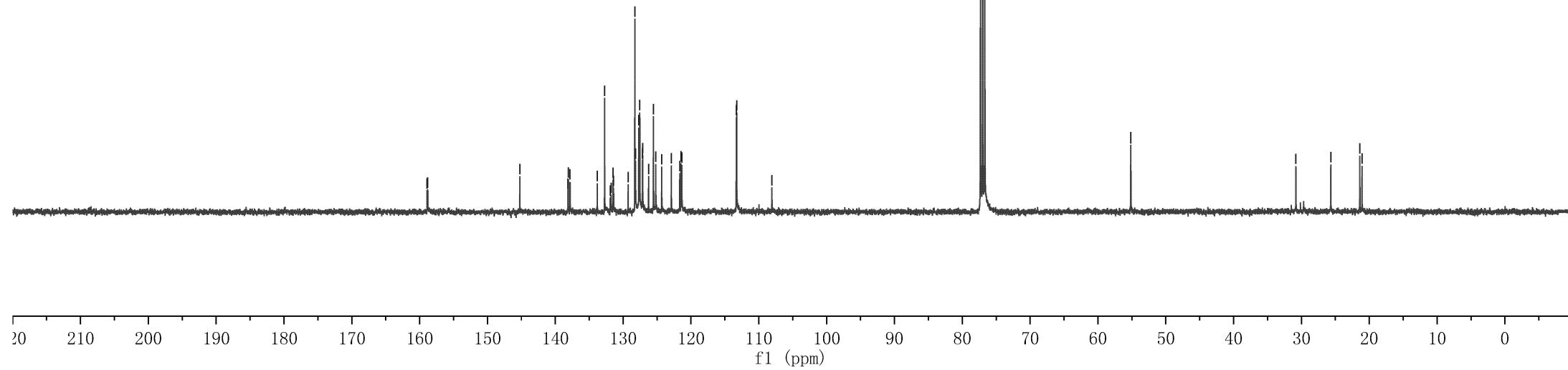
Parameter	Value
1 Title	31-H
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	298.0
5 Number of Scans	11
6 Acquisition Time	3.1719
7 Acquisition Date	2023-08-03T17:57:41
8 Spectrometer Frequency	500.17
9 Spectral Width	10330.6



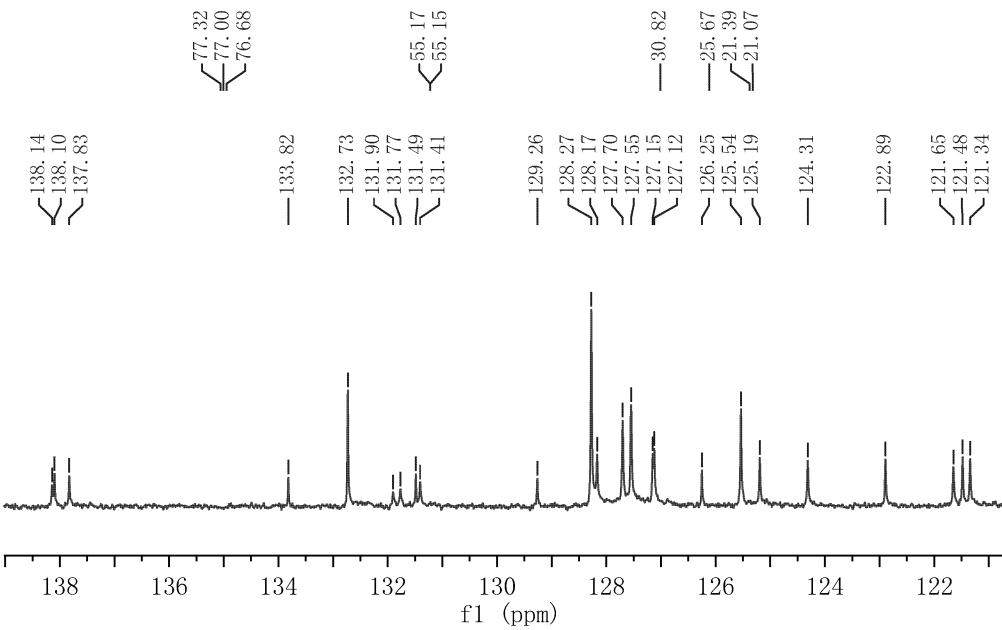
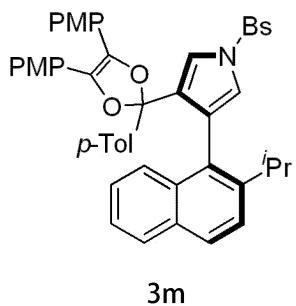
Parameter	Value
1 Title	31-H
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDC13
4 Temperature	298.0
5 Number of Scans	11
6 Acquisition Time	3.1719
7 Acquisition Date	2023-08-03T17:57:41
8 Spectrometer Frequency	500.17
9 Spectral Width	10330.6



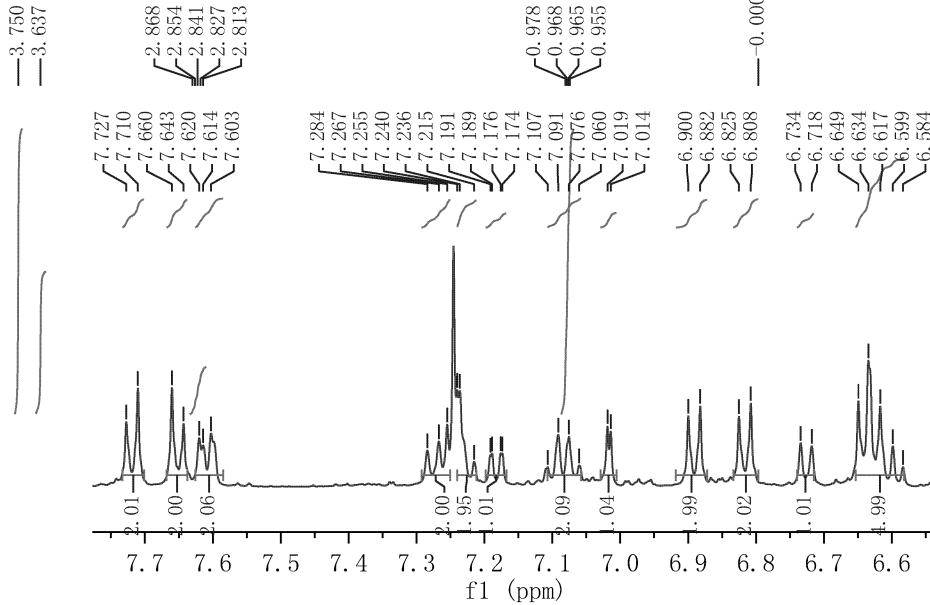
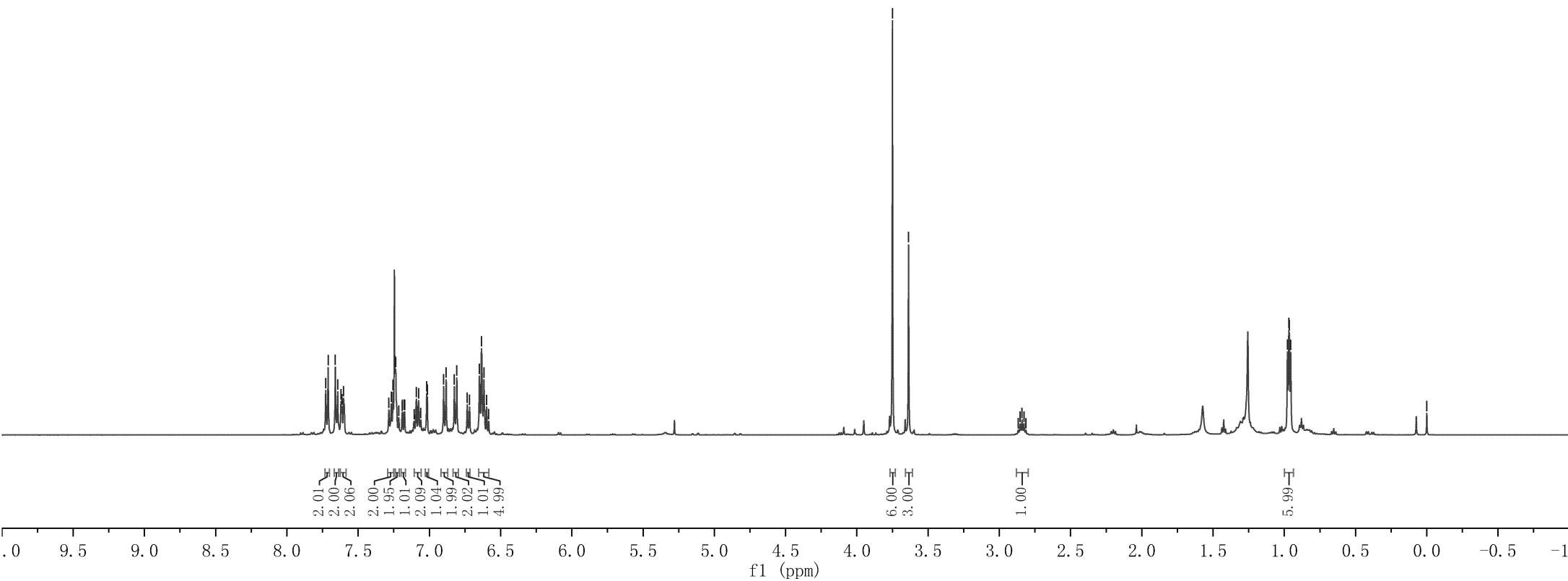
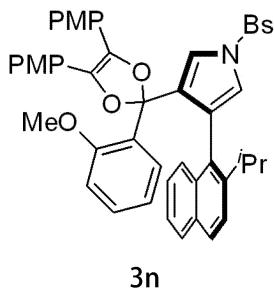




Parameter	Value
1 Title	CHH-1-149-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	300.0
5 Number of Scans	852
6 Acquisition Time	1.3631
7 Spectrometer Frequency	100.61
8 Spectral Width	24038.5



Parameter	Value
1 Title	3n-H
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	299.6
5 Number of Scans	17
6 Acquisition Time	3.1719
7 Acquisition Date	2023-09-09T15:07:38
8 Spectrometer Frequency	500.17
9 Spectral Width	10330.6



Parameter	Value
1 Title	3n-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDC13
4 Temperature	299.8
5 Number of Scans	213
6 Acquisition Time	1.1010
7 Acquisition Date	2023-09-09T15:11:20
8 Spectrometer Frequency	125.77
9 Spectral Width	29761.9

158.79
158.79
157.41

—145.01

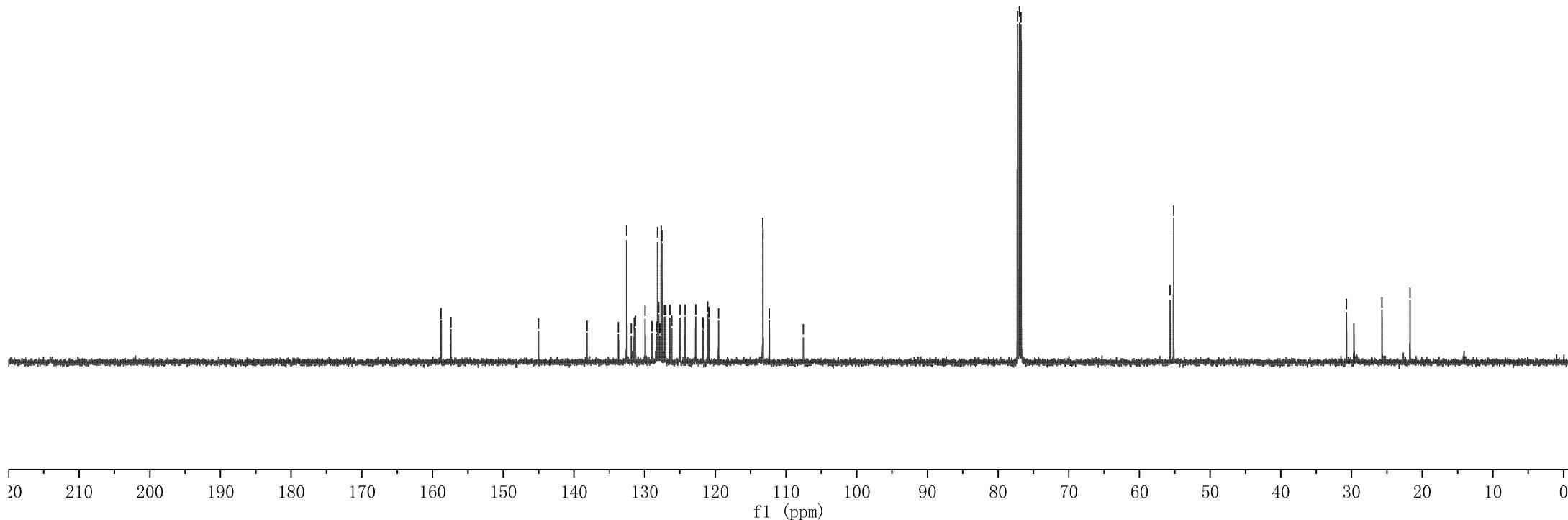
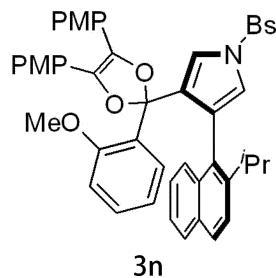
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—122.78
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—112.36
—107.55

—133.70
—132.53
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—131.48
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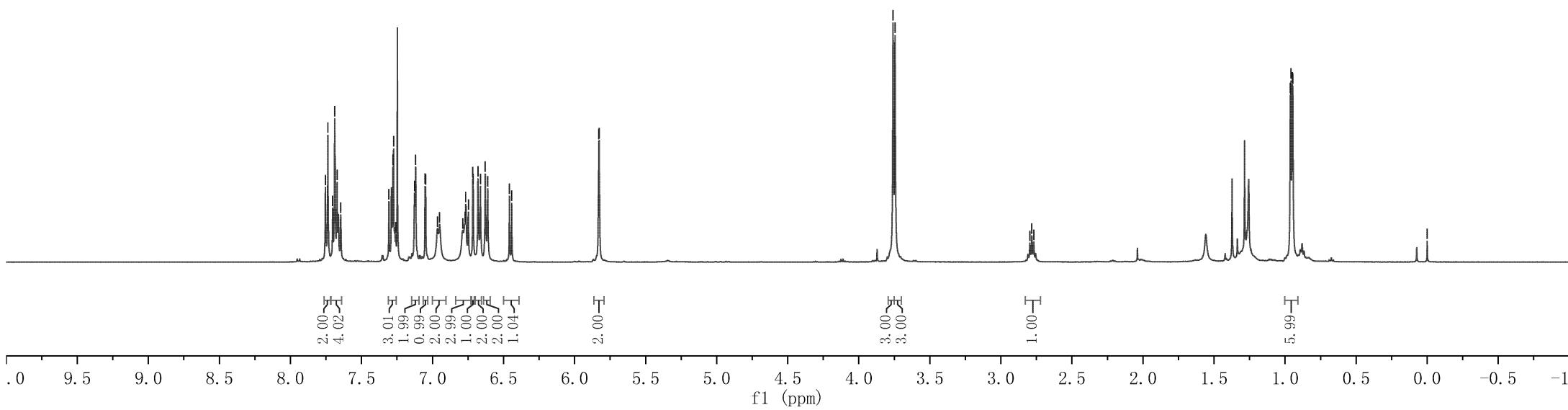
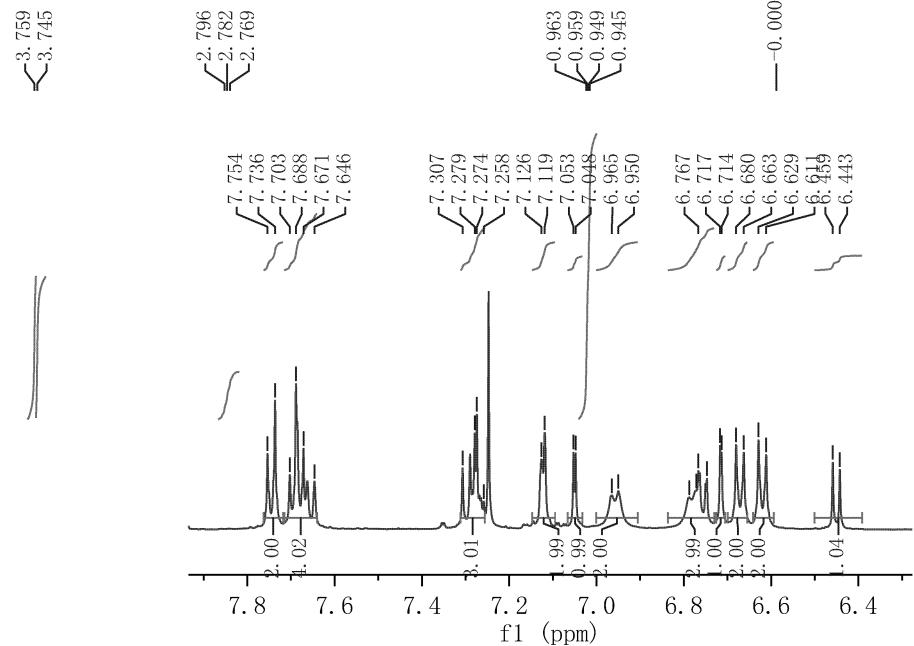
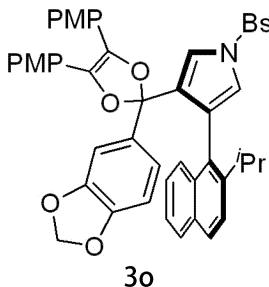
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—127.19
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—126.42
—126.16
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—122.78
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—121.70
—121.06
—120.91

—119.54

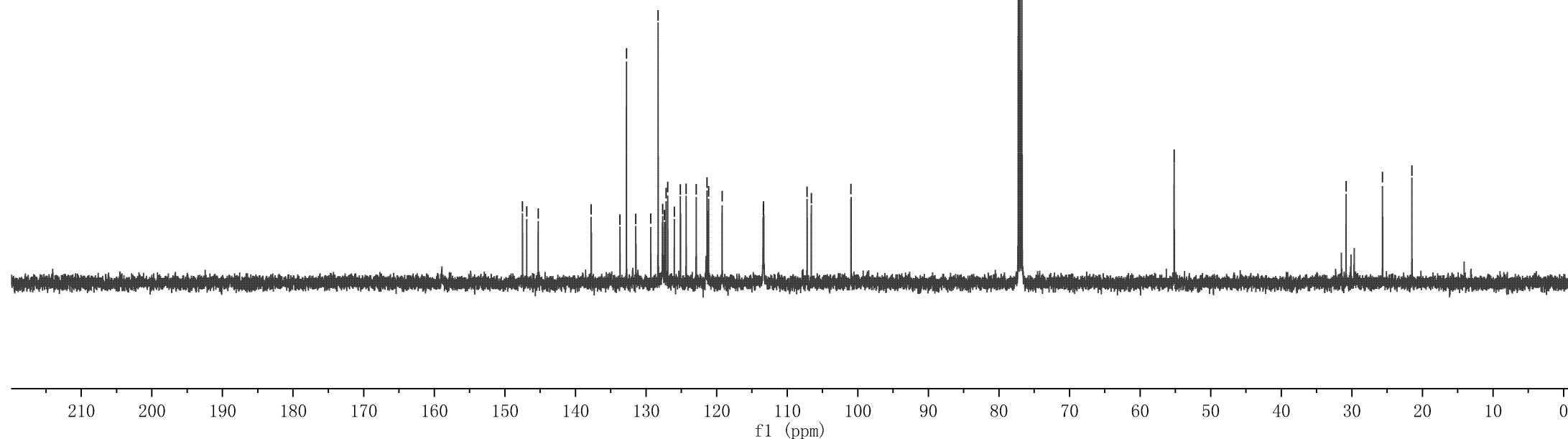
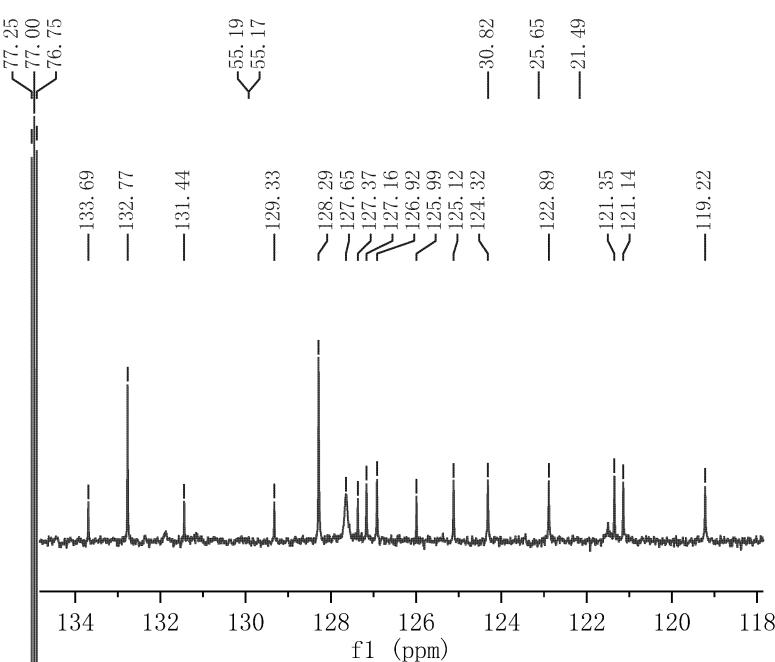
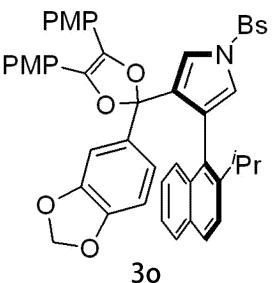


Parameter	Value
1 Title	CYB-16-155-500M
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	299.7
5 Number of Scans	7
6 Acquisition Time	3.1719
7 Acquisition Date	2022-11-17T21:13:13
8 Spectrometer Frequency	500.17
9 Spectral Width	10330.6

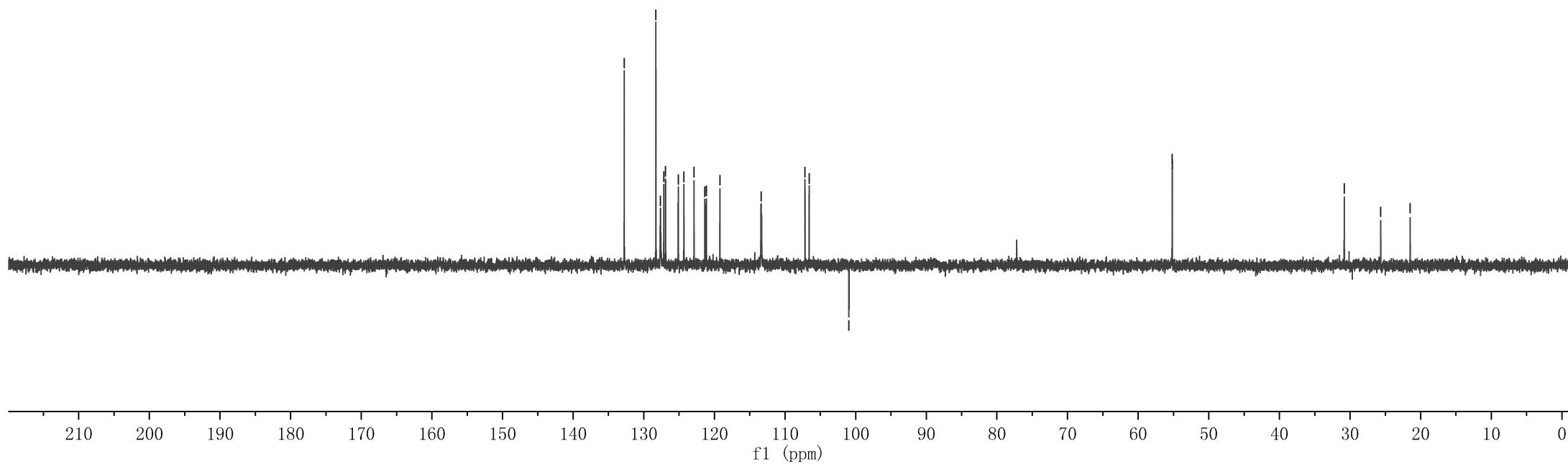
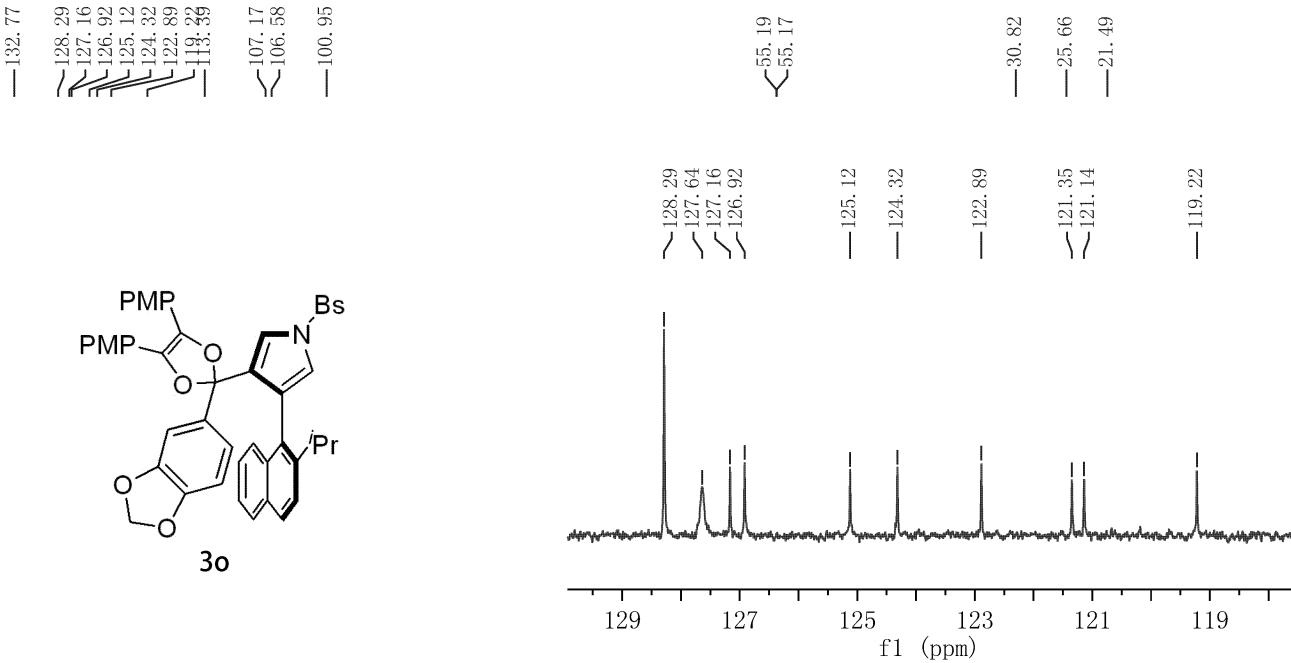


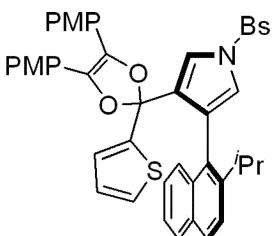
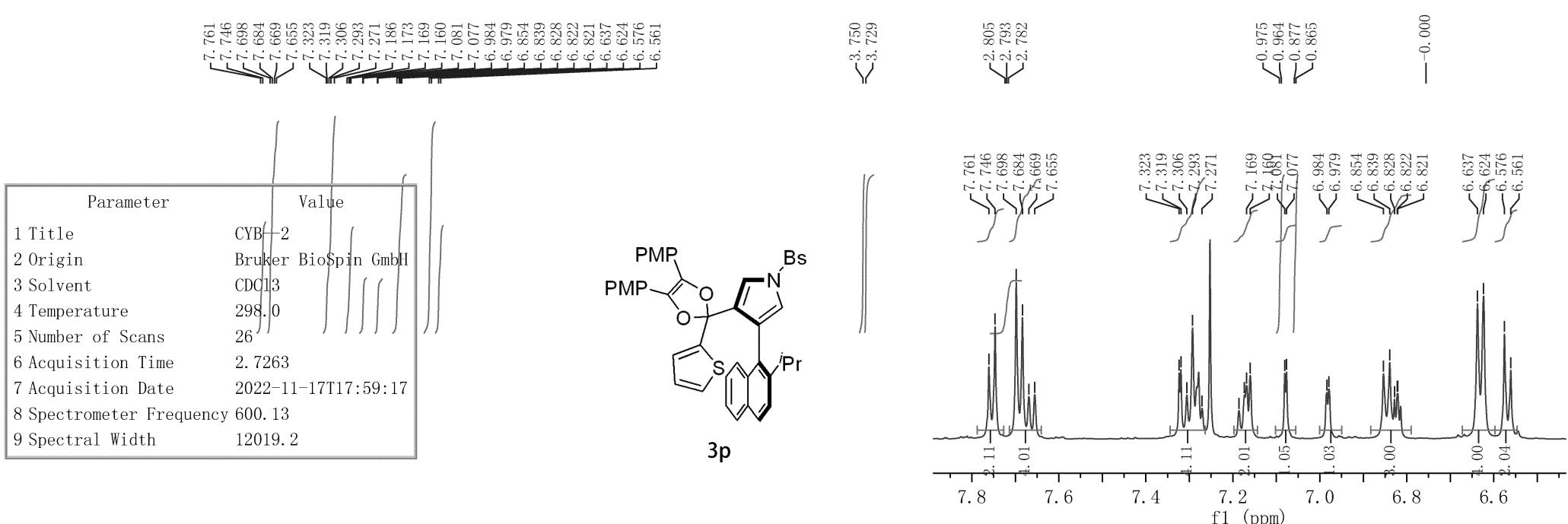
Parameter	Value
1 Title	CYB-16-155-500M
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	300.0
5 Number of Scans	222
6 Acquisition Time	1.1010
7 Acquisition Date	2022-11-17T21:15:42
8 Spectrometer Frequency	125.77
9 Spectral Width	29761.9

>147.50
 >146.90
 >145.28
 >137.76
 >132.77
 >128.29
 >127.65
 >127.16
 >126.92
 >125.12
 >124.32
 >122.89
 >121.35
 >121.14
 >119.39
 >113.33
 >107.17
 >106.58
 -100.95

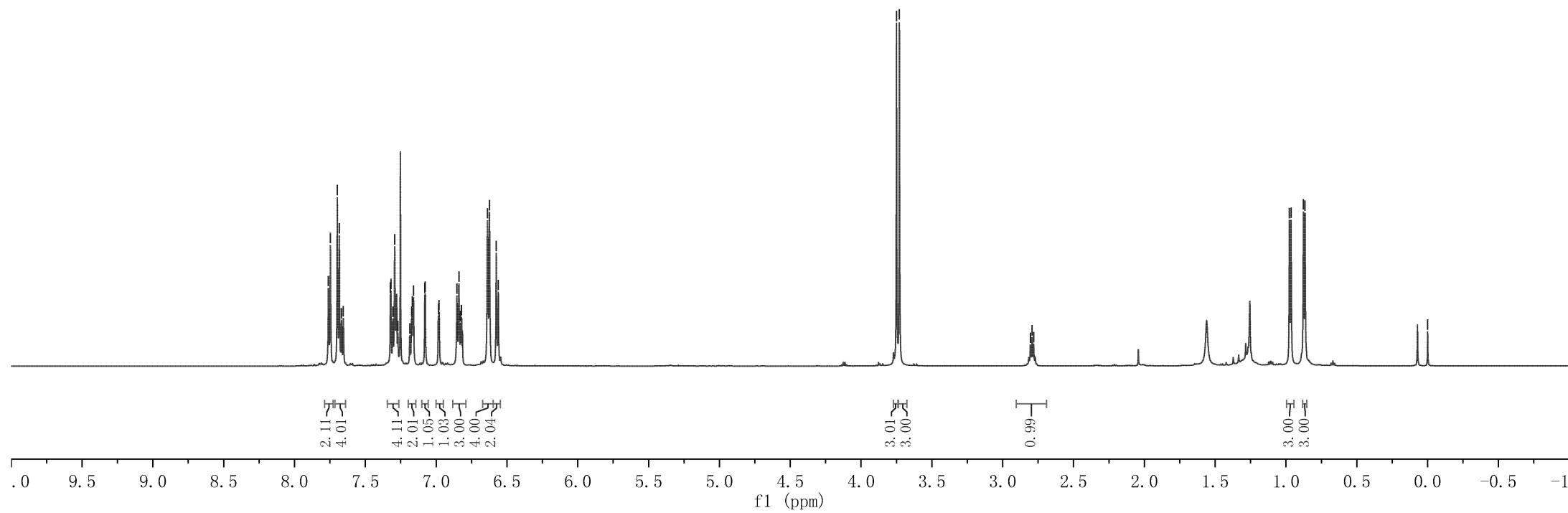


Parameter	Value
1 Title	CYB-16-155-500M
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	300.5
5 Number of Scans	61
6 Acquisition Time	1.1010
7 Acquisition Date	2022-11-17T21:28:30
8 Spectrometer Frequency	125.77
9 Spectral Width	29761.9





3p



Parameter	Value
1 Title	CYB--2
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	298.0
5 Number of Scans	59
6 Acquisition Time	0.9044
7 Acquisition Date	2022-11-17T17:55:53
8 Spectrometer Frequency	150.90
9 Spectral Width	36231.9

<158.96
<158.84

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<145.11

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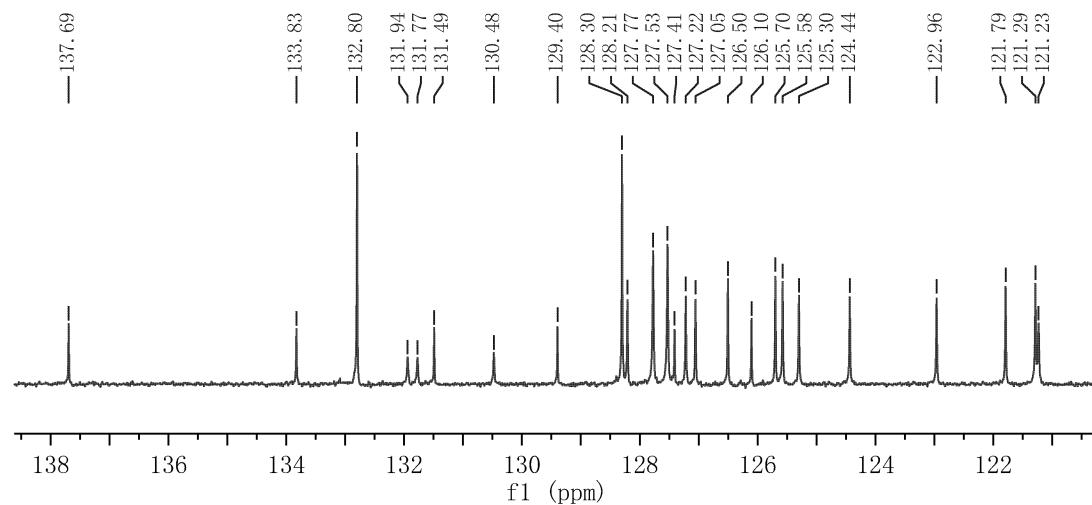
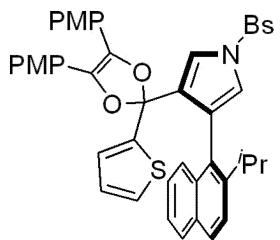
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<77.21
<77.00
<76.79

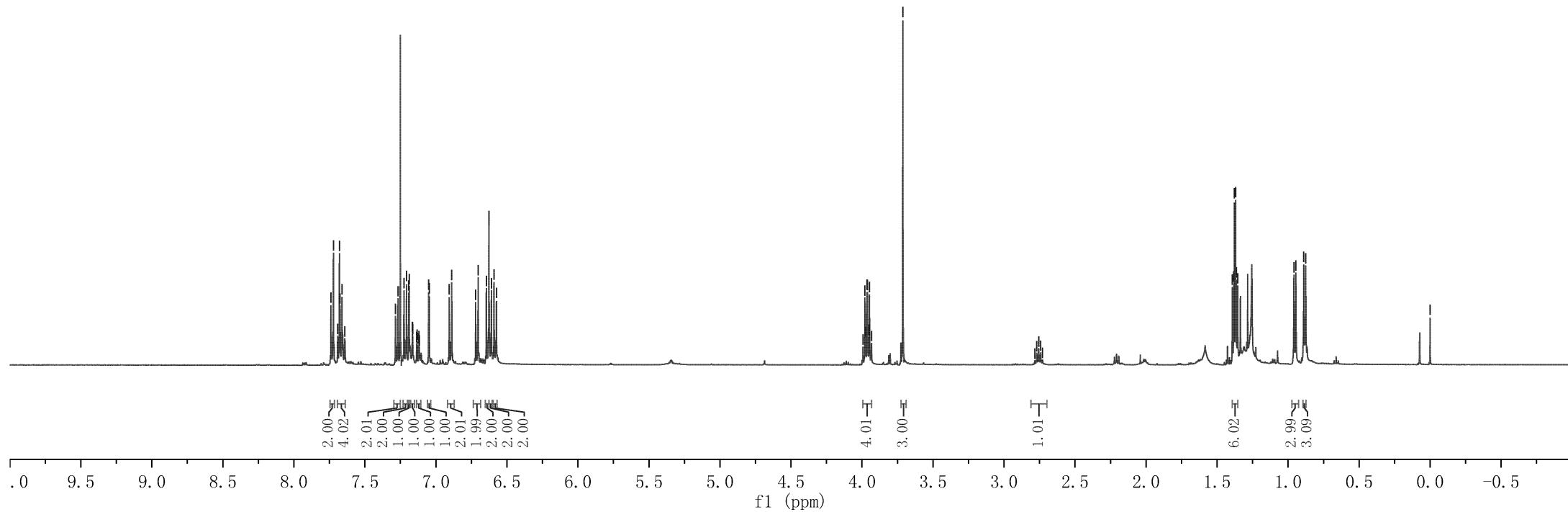
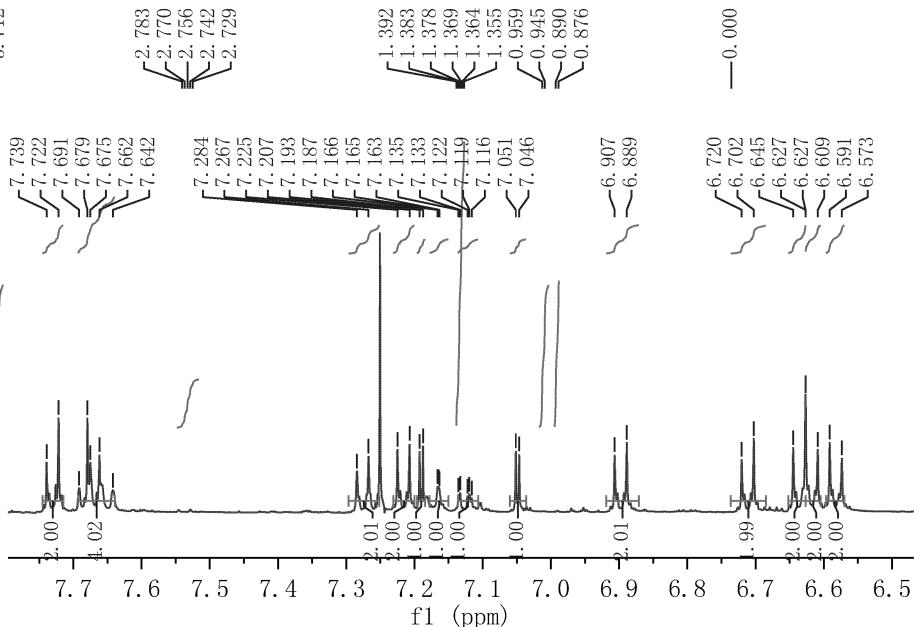
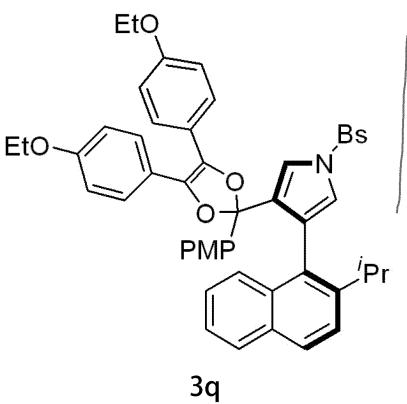
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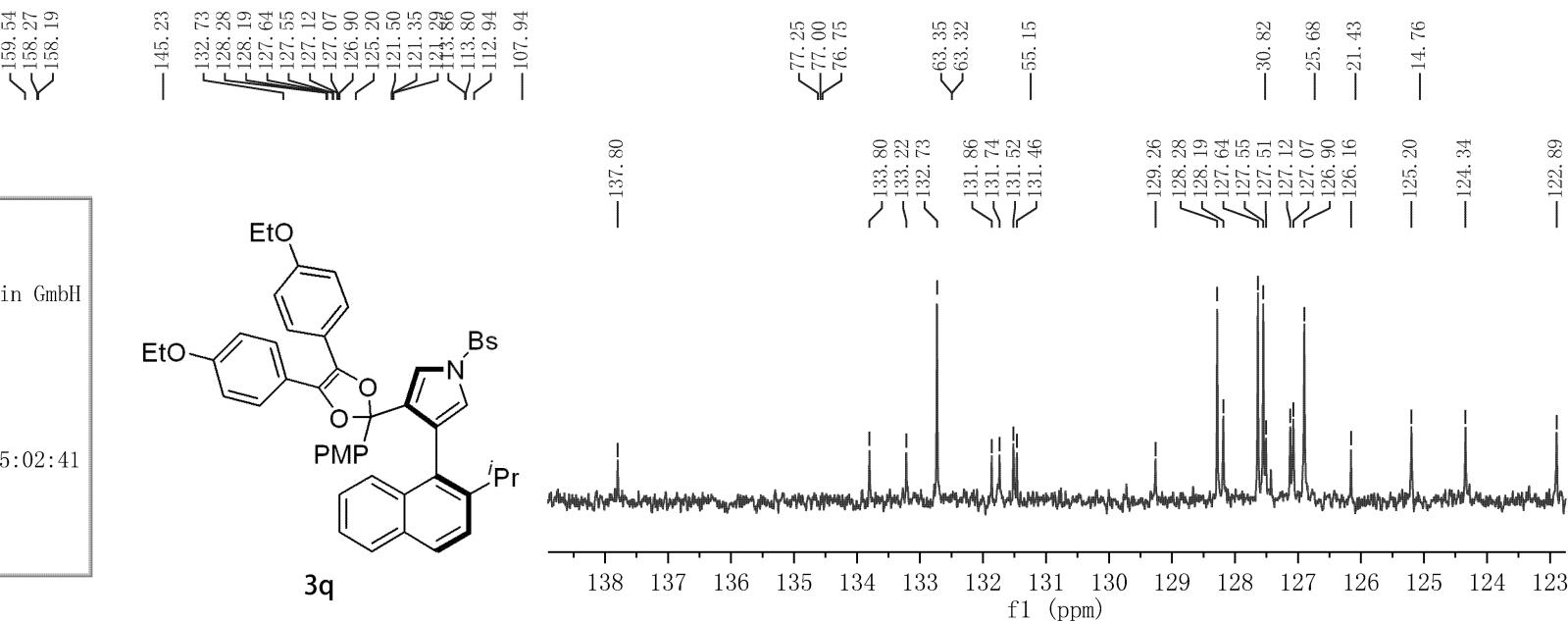
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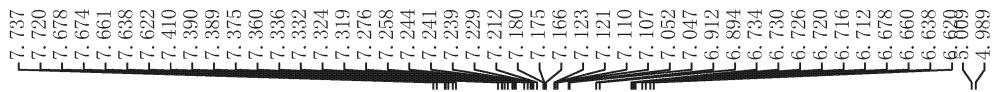


Parameter	Value
1 Title	WGI-1-12-H-2
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	299.3
5 Number of Scans	18
6 Acquisition Time	3.1719
7 Acquisition Date	2023-09-19T14:59:11
8 Spectrometer Frequency	500.17
9 Spectral Width	10330.6

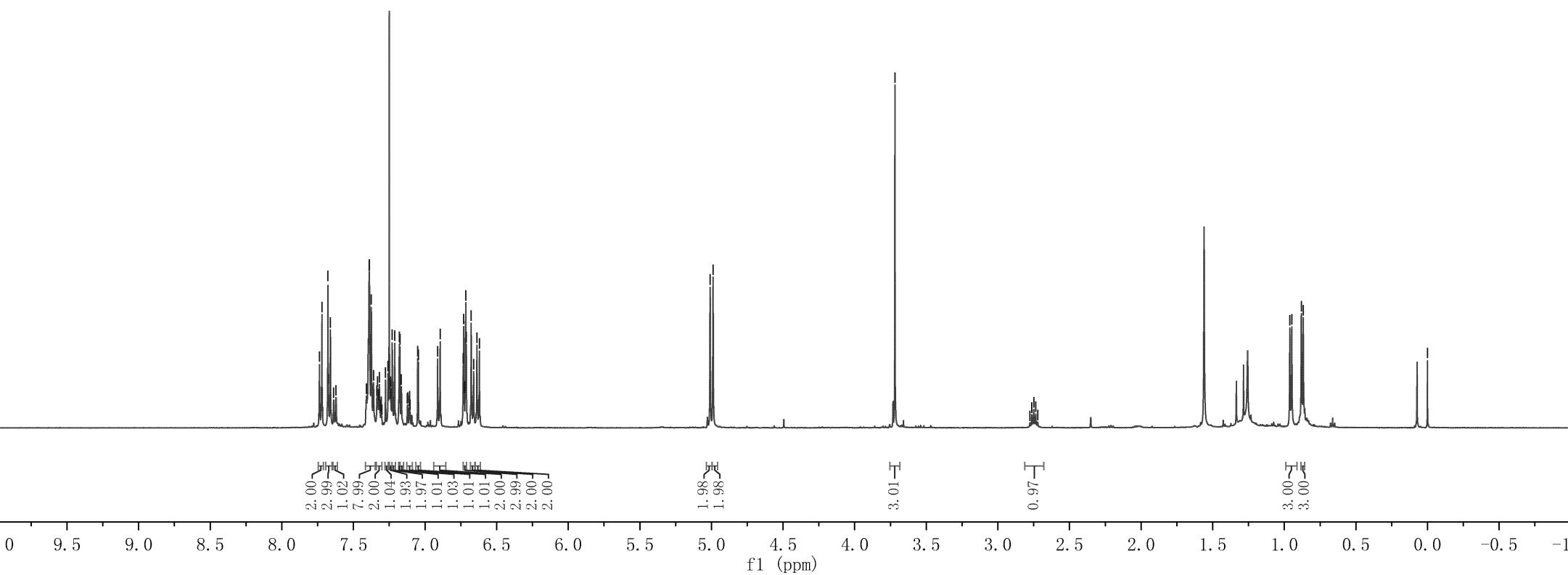
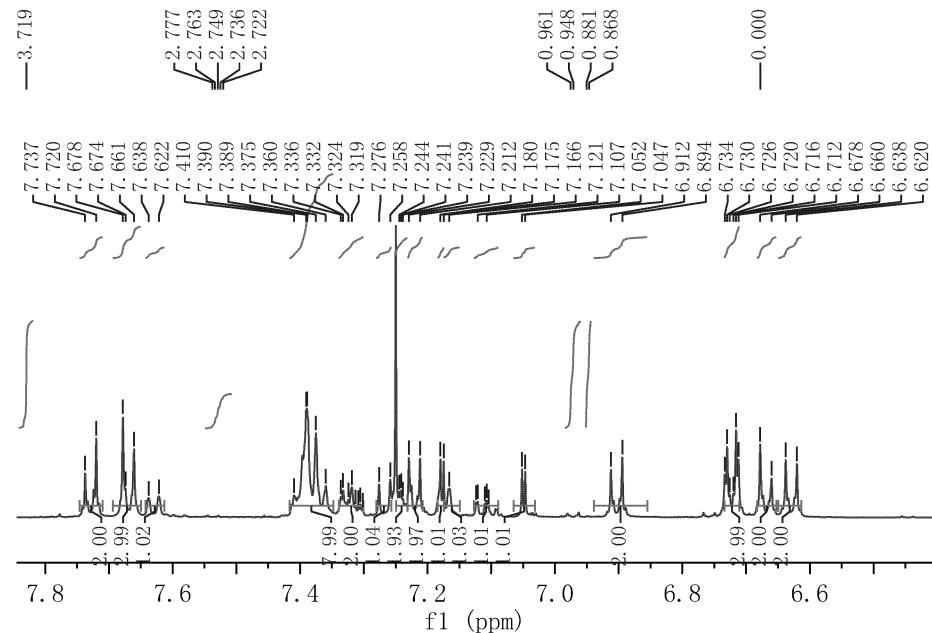
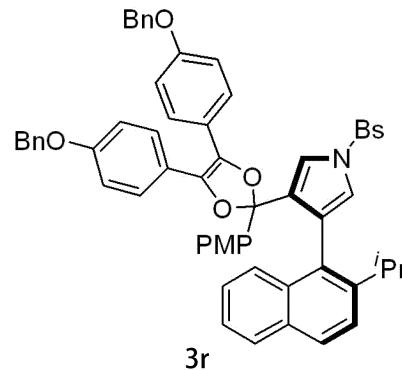


Parameter	Value
1 Title	WGH-1-12-C-2
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	299.4
5 Number of Scans	137
6 Acquisition Time	1.1010
7 Acquisition Date	2023-09-19T15:02:41
8 Spectrometer Frequency	125.77
9 Spectral Width	29761.9





Parameter	Value
1 Title	WGH-1-11
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	299.2
5 Number of Scans	11
6 Acquisition Time	3.1719
7 Acquisition Date	2023-09-18T14:28:46
8 Spectrometer Frequency	500.17
9 Spectral Width	10330.6



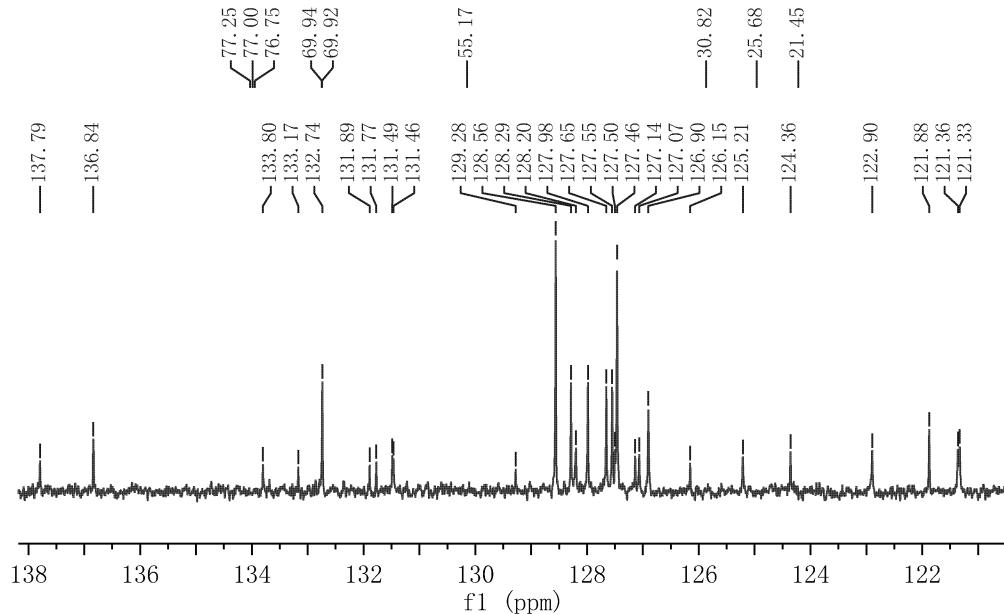
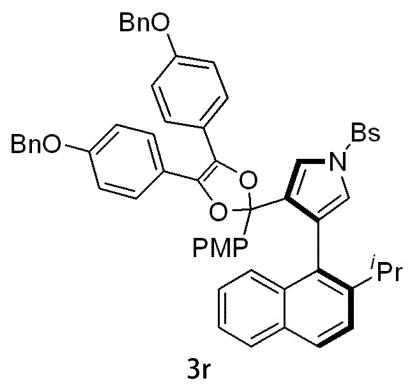
Parameter	Value
1 Title	WGH-1-11-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	299.3
5 Number of Scans	164
6 Acquisition Time	1.1010
7 Acquisition Date	2023-09-18T14:32:01
8 Spectrometer Frequency	125.77
9 Spectral Width	29761.9

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—158.11
—158.03

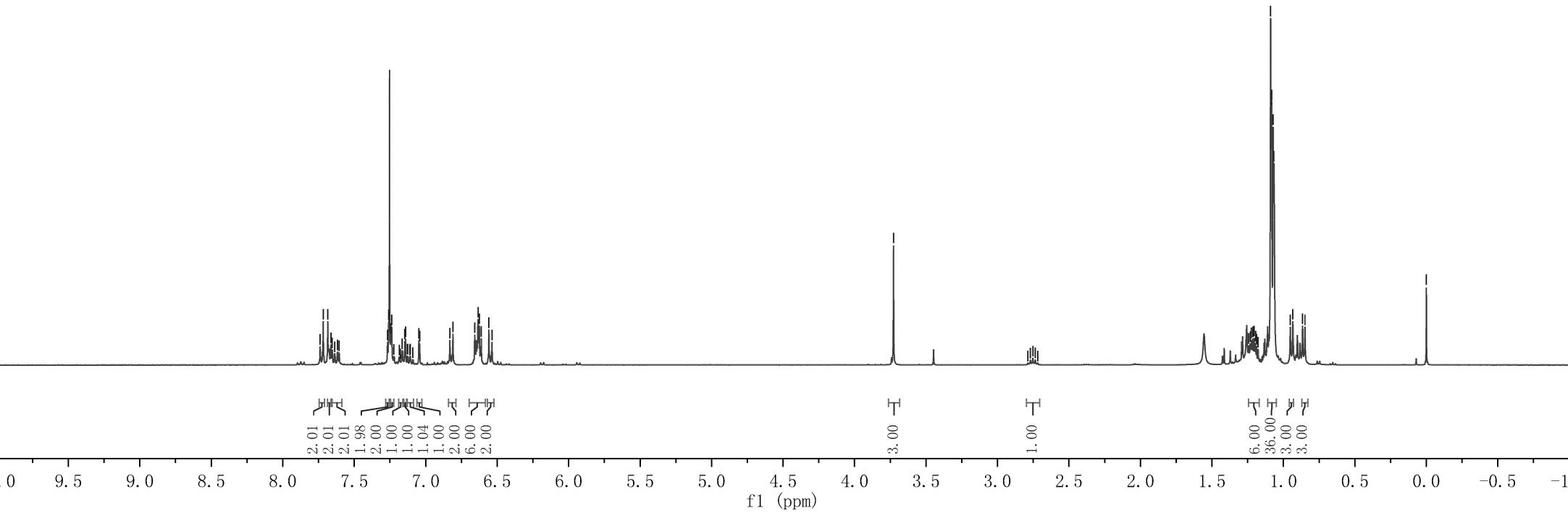
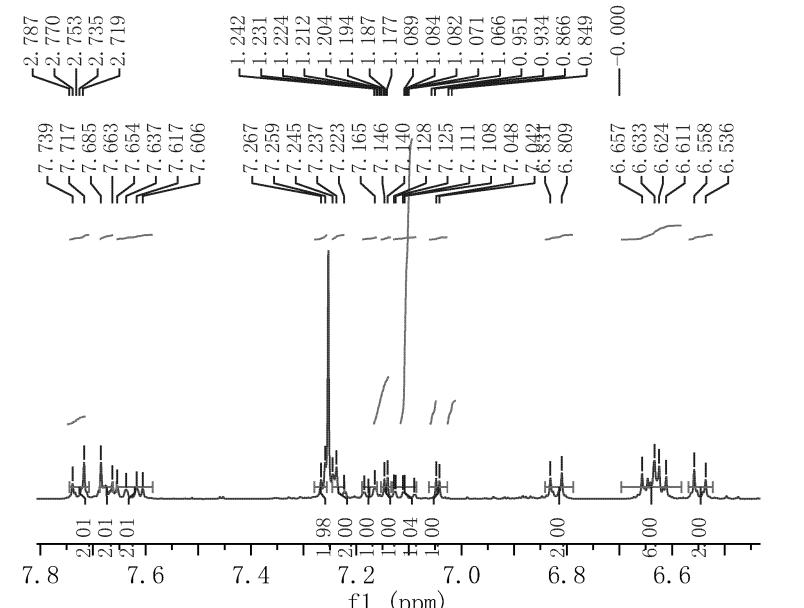
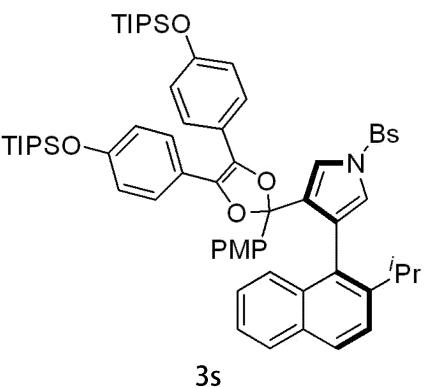
—145.21

—136.84
—132.74
—128.56
—128.29
—128.20
—127.98
—127.65
—127.55
—127.46
—126.90
—121.88
—124.30
—114.23
—112.97

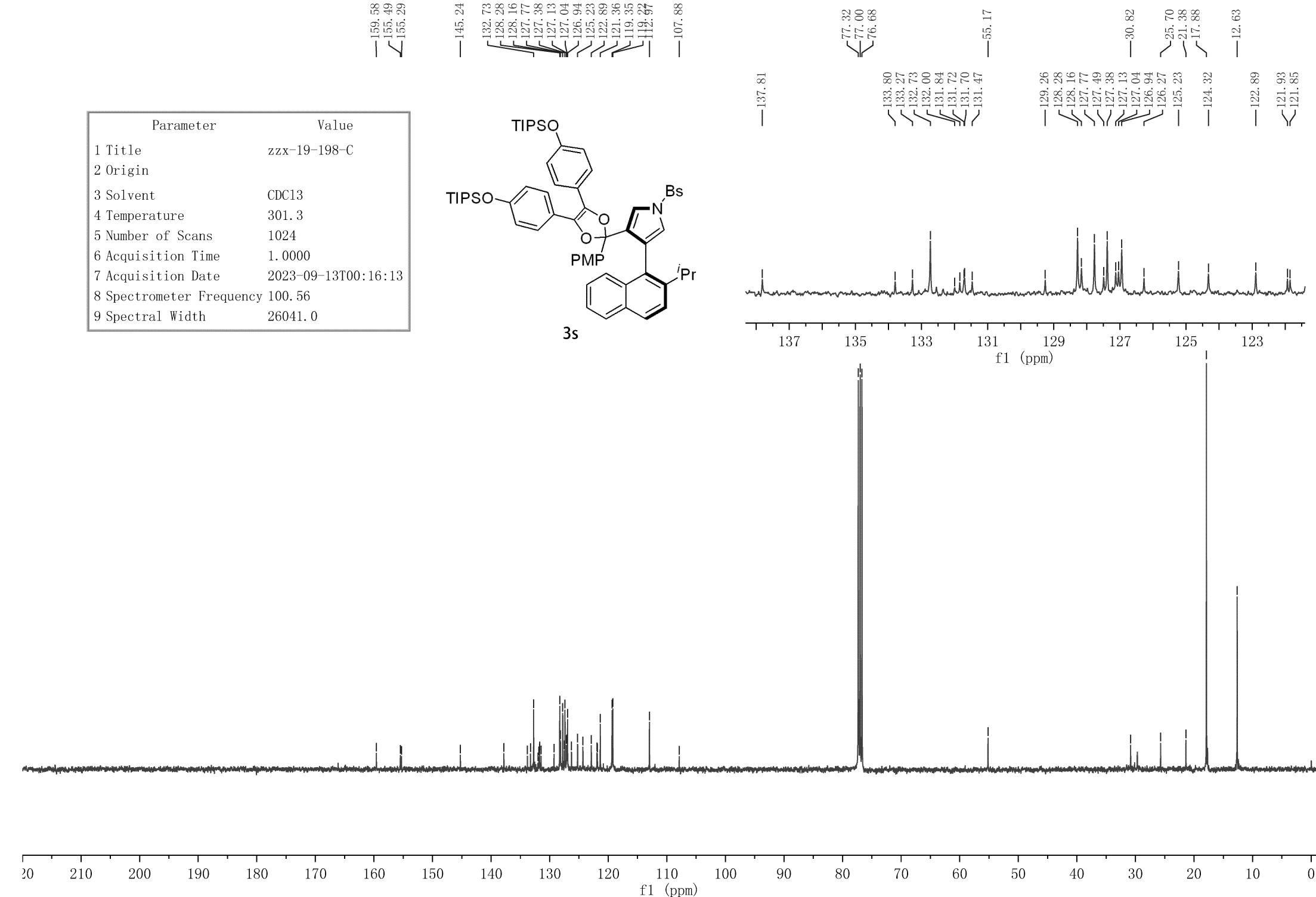
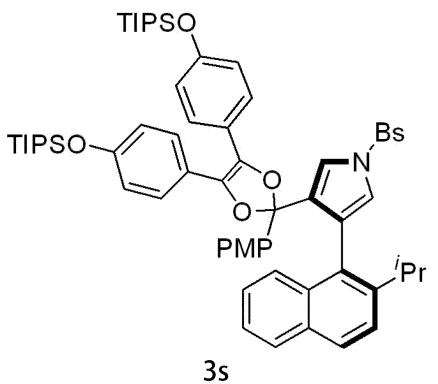
—108.02

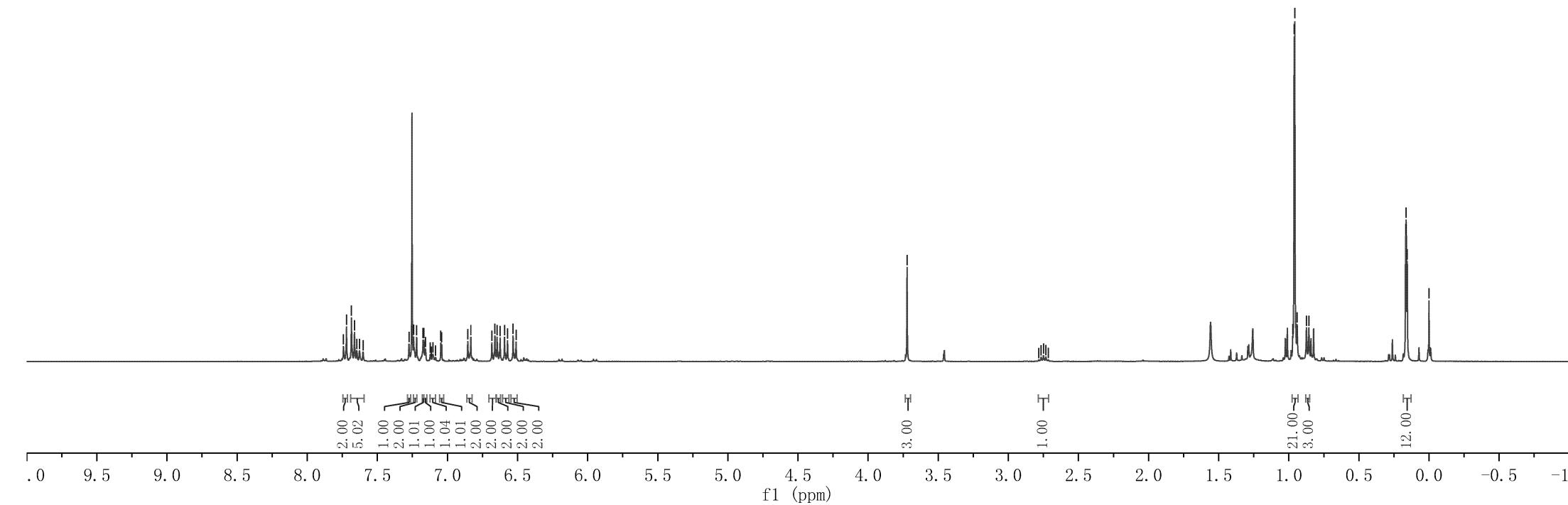
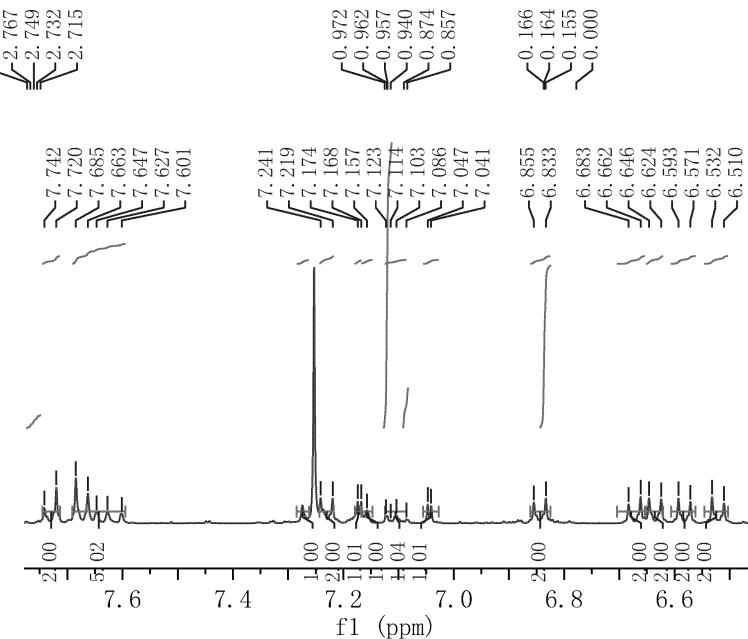
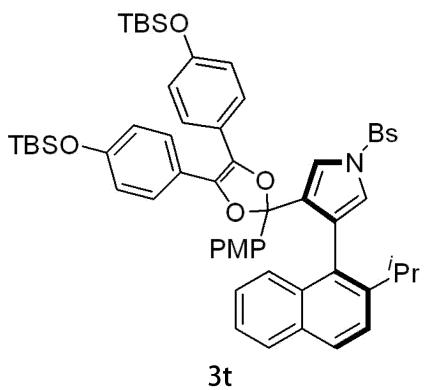
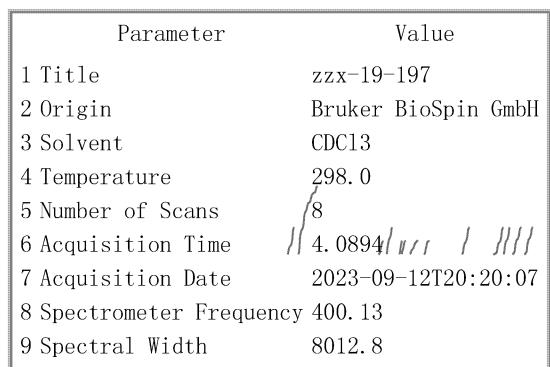


Parameter	Value
1 Title	zzx-19-198
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.0
5 Number of Scans	6
6 Acquisition Time	4/0894 <i>hrs</i> <i>s</i>
7 Acquisition Date	2023-09-12T20:24:03
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8



Parameter	Value
1 Title	zzx-19-198-C
2 Origin	
3 Solvent	CDC13
4 Temperature	301.3
5 Number of Scans	1024
6 Acquisition Time	1.0000
7 Acquisition Date	2023-09-13T00:16:13
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0





Parameter	Value
1 Title	zzx-19-197-C
2 Origin	
3 Solvent	CDCl ₃
4 Temperature	301.2
5 Number of Scans	1024
6 Acquisition Time	1.0000
7 Acquisition Date	2023-09-12T23:38:19
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

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—155.07
—154.93

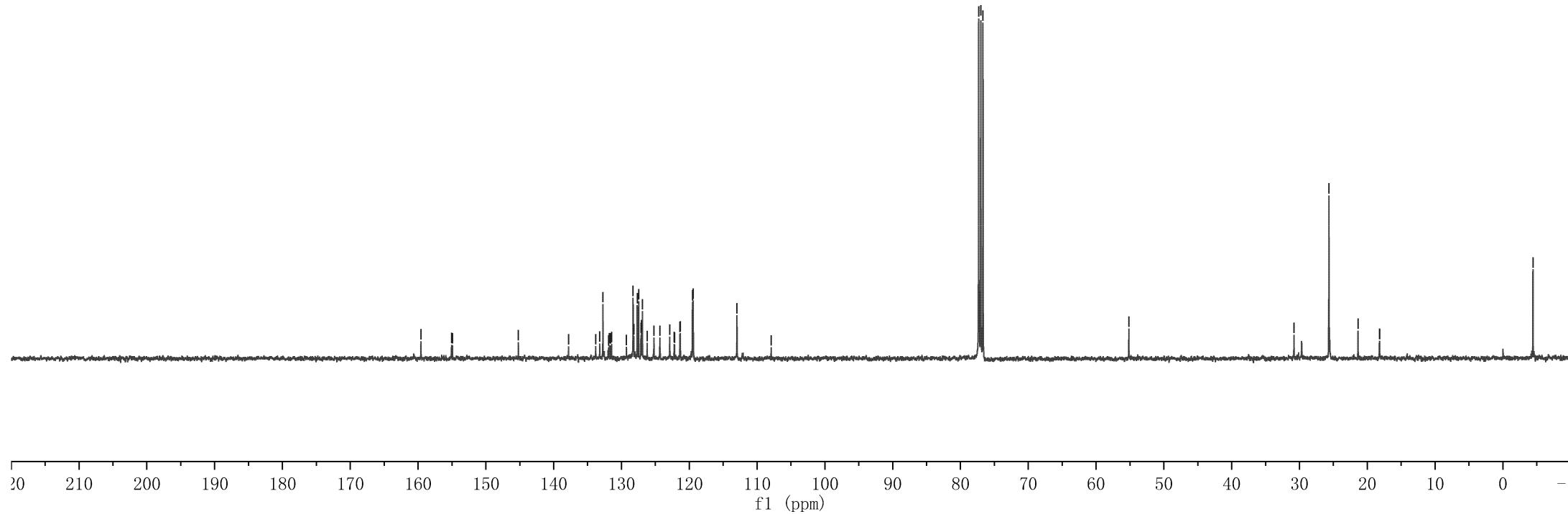
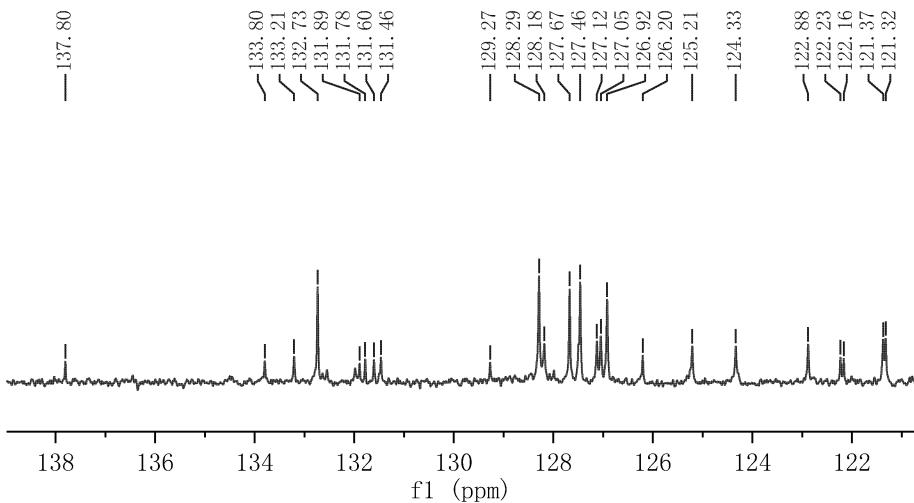
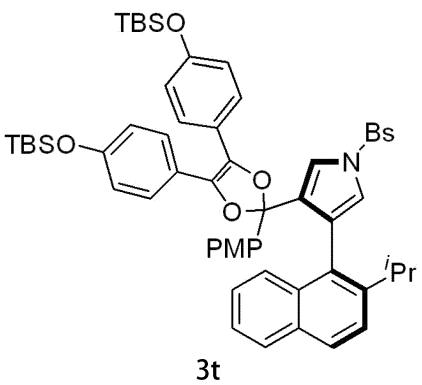
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—127.46
—127.12
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—126.92
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—121.32
—119.53
—112.42
—107.92

—137.80
—77.32
—77.00
—76.68

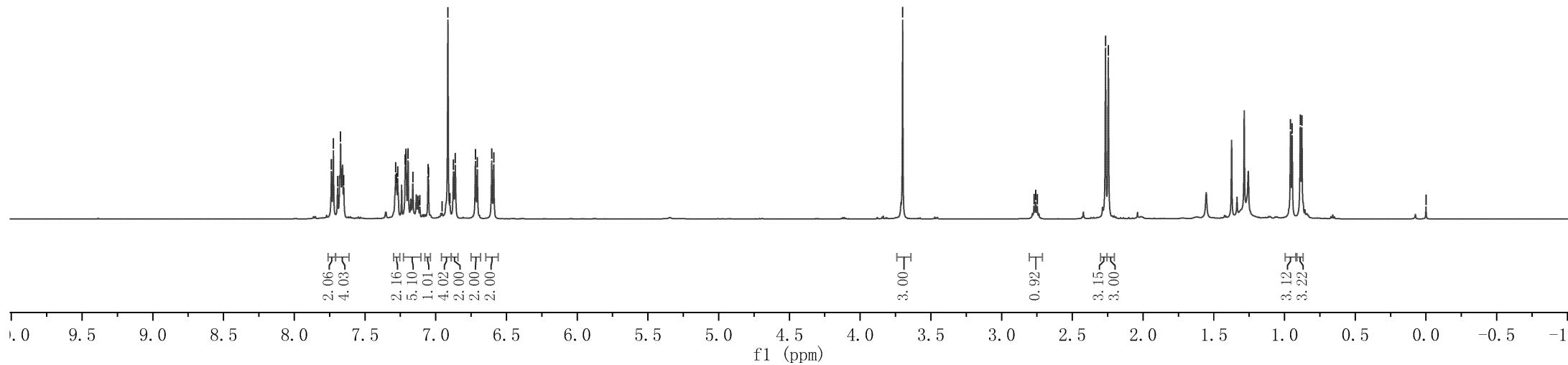
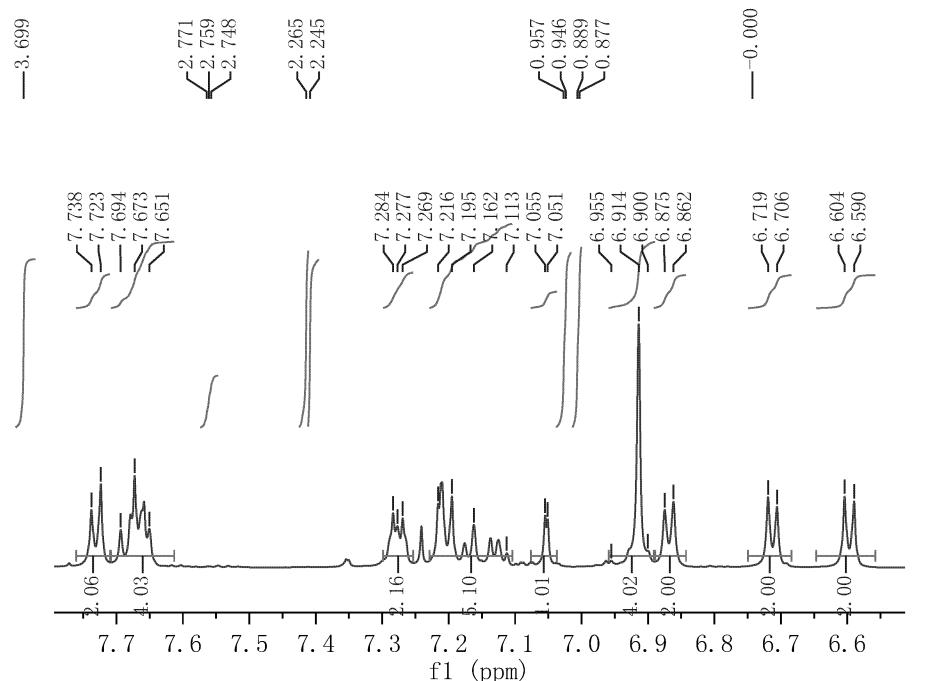
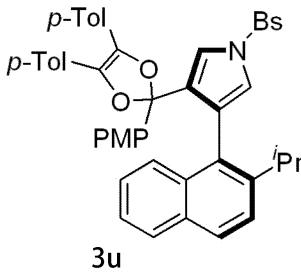
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—131.46

—129.27
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—127.46
—127.12
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—126.92
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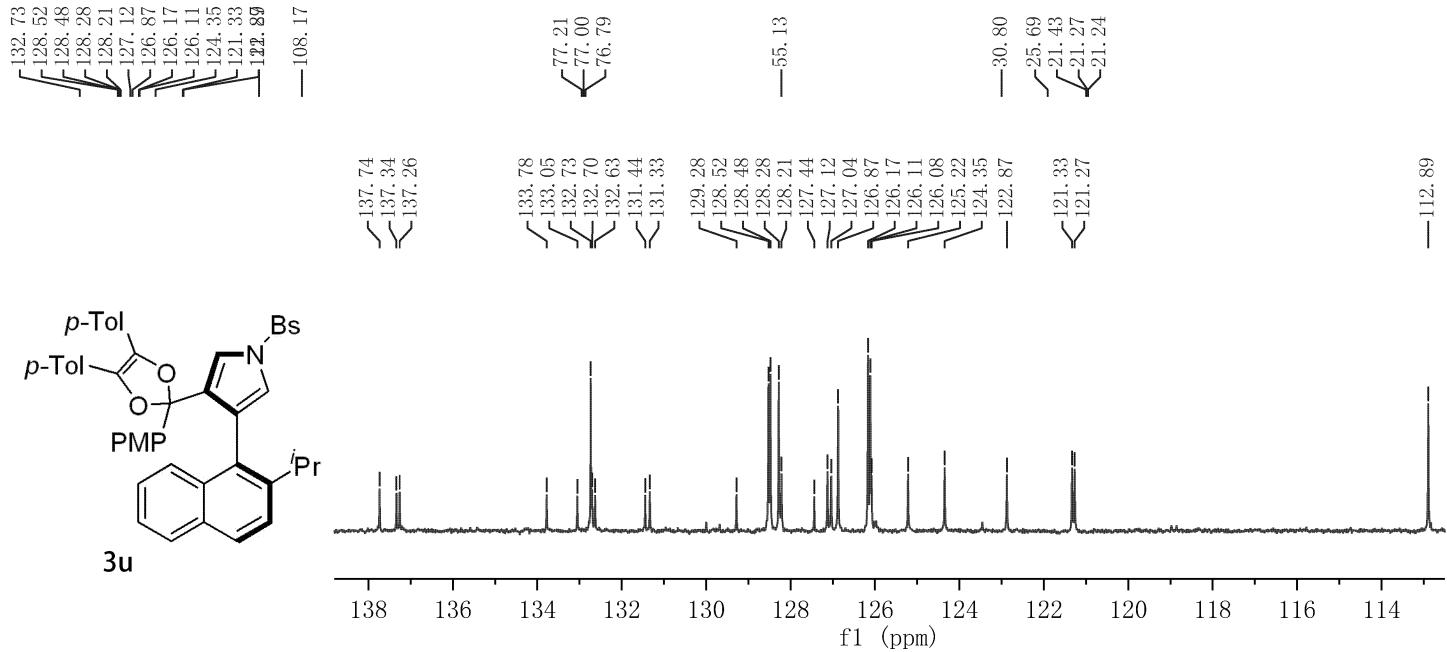
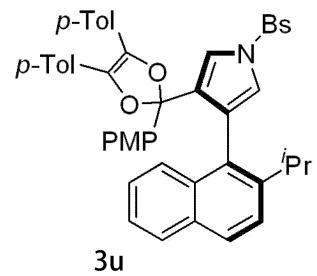
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—121.32

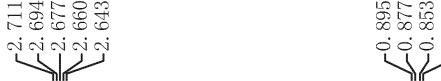


Parameter	Value
1 Title	CYB-4
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDC13
4 Temperature	298.0
5 Number of Scans	19
6 Acquisition Time	2.7263
7 Acquisition Date	2022-11-18T15:08:12
8 Spectrometer Frequency	600.13
9 Spectral Width	12019.2

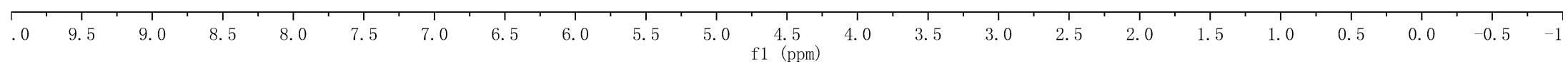
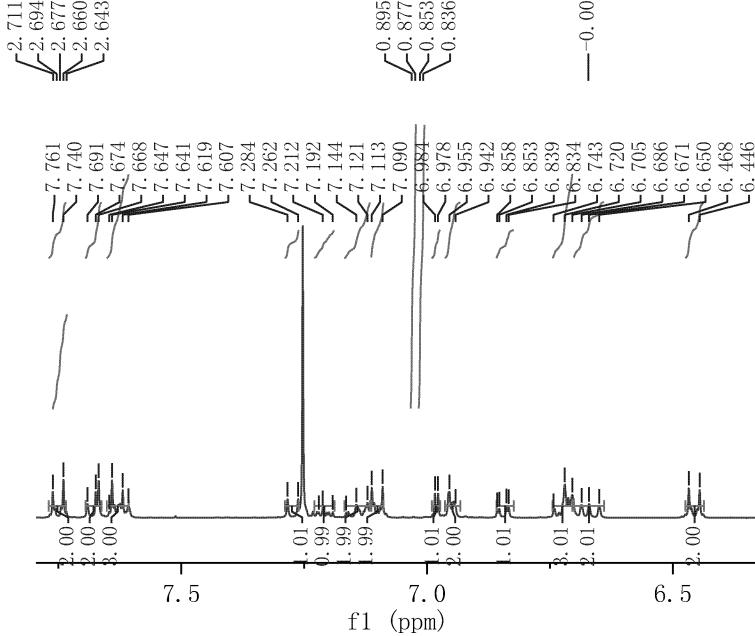
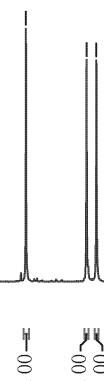
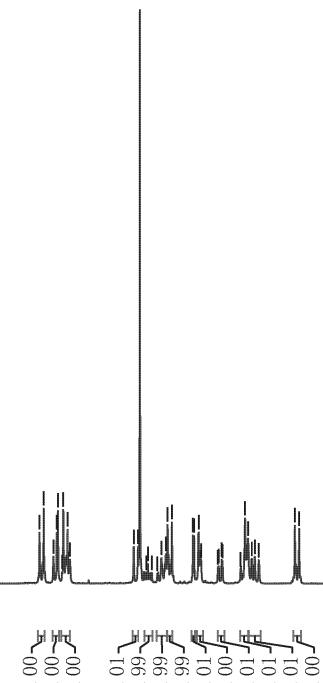
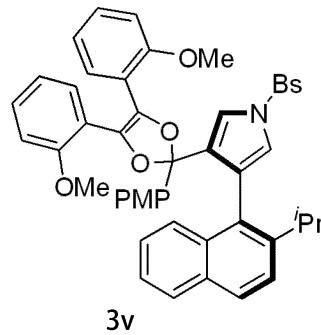


Parameter	Value
1 Title	CYB-4
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	298.0
5 Number of Scans	41
6 Acquisition Time	0.9044
7 Acquisition Date	2022-11-18T15:11:43
8 Spectrometer Frequency	150.90
9 Spectral Width	36231.9





Parameter	Value
1 Title	ZYJ-1-7-2
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	298.0
5 Number of Scans	4
6 Acquisition Time	4.0894
7 Acquisition Date	2023-09-14T11:29:28
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8



Parameter	Value
1 Title	ZYJ-1-7-2-C
2 Origin	
3 Solvent	CDCl ₃
4 Temperature	301.2
5 Number of Scans	800
6 Acquisition Time	1.0000
7 Acquisition Date	2023-09-14T15:10:53
8 Spectrometer Frequency	100.56
9 Spectral Width	26041.0

~159.19
~156.59
~156.41

-145.26

132.63
129.12
128.89
128.70
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125.11
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110.25
108.50

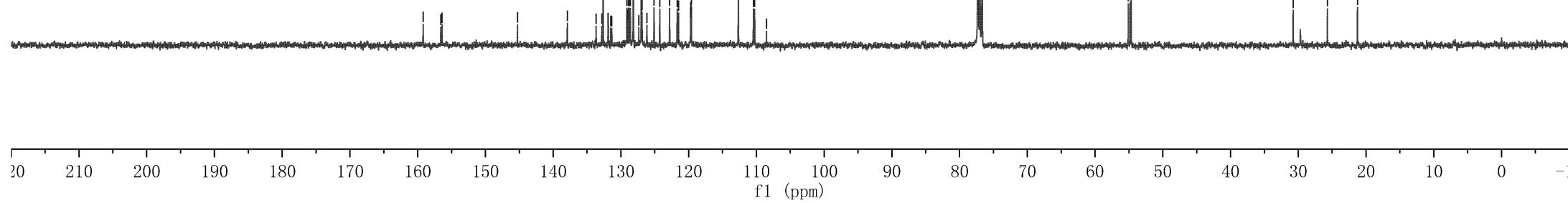
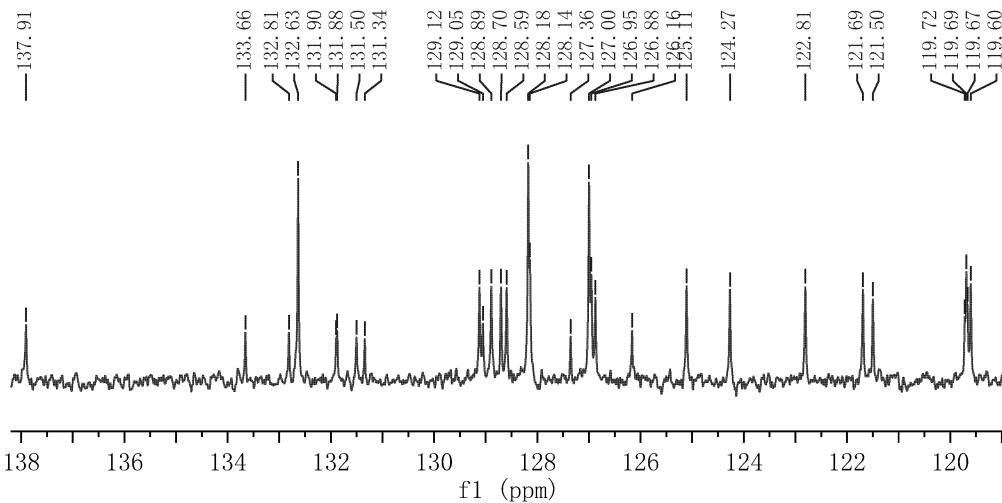
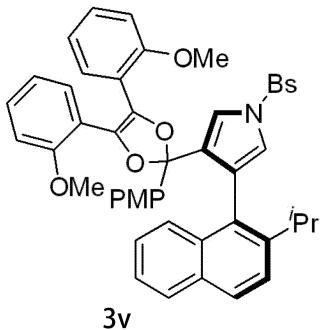
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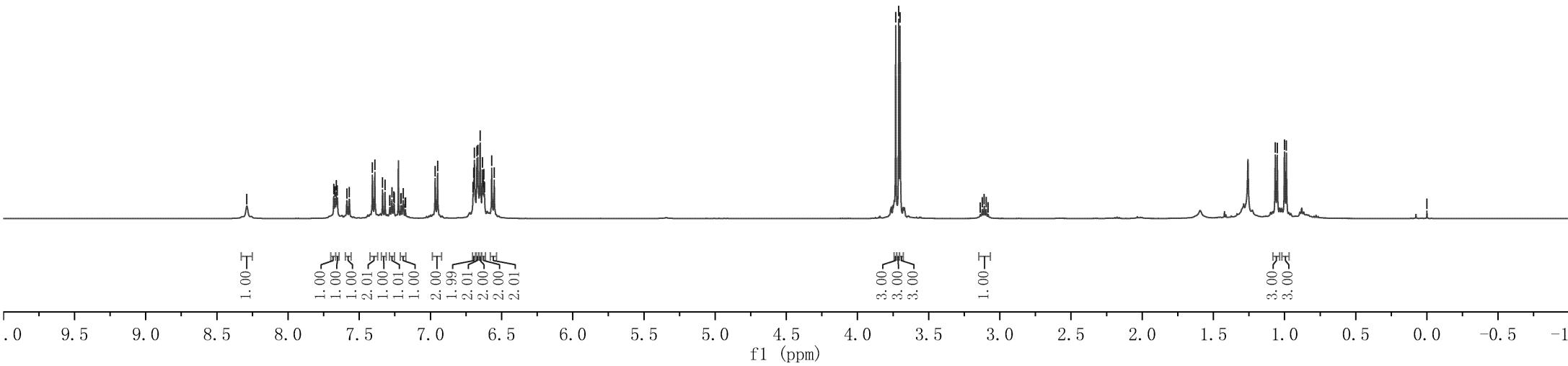
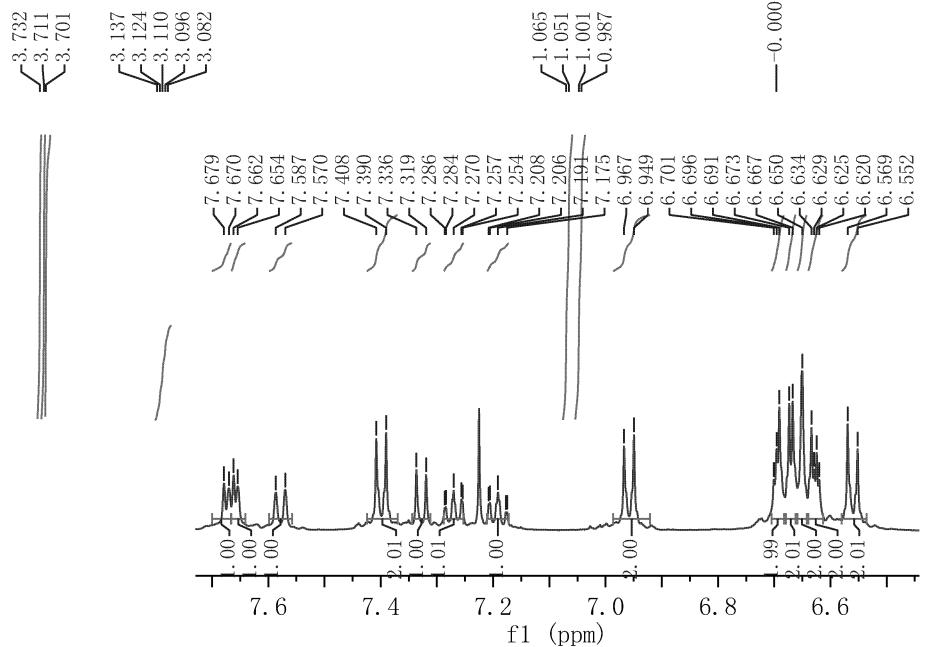
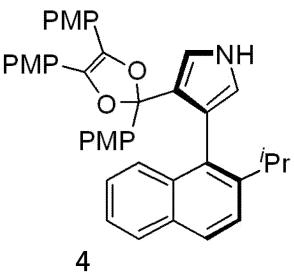
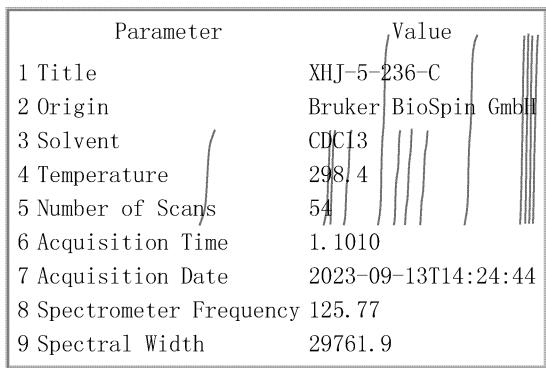
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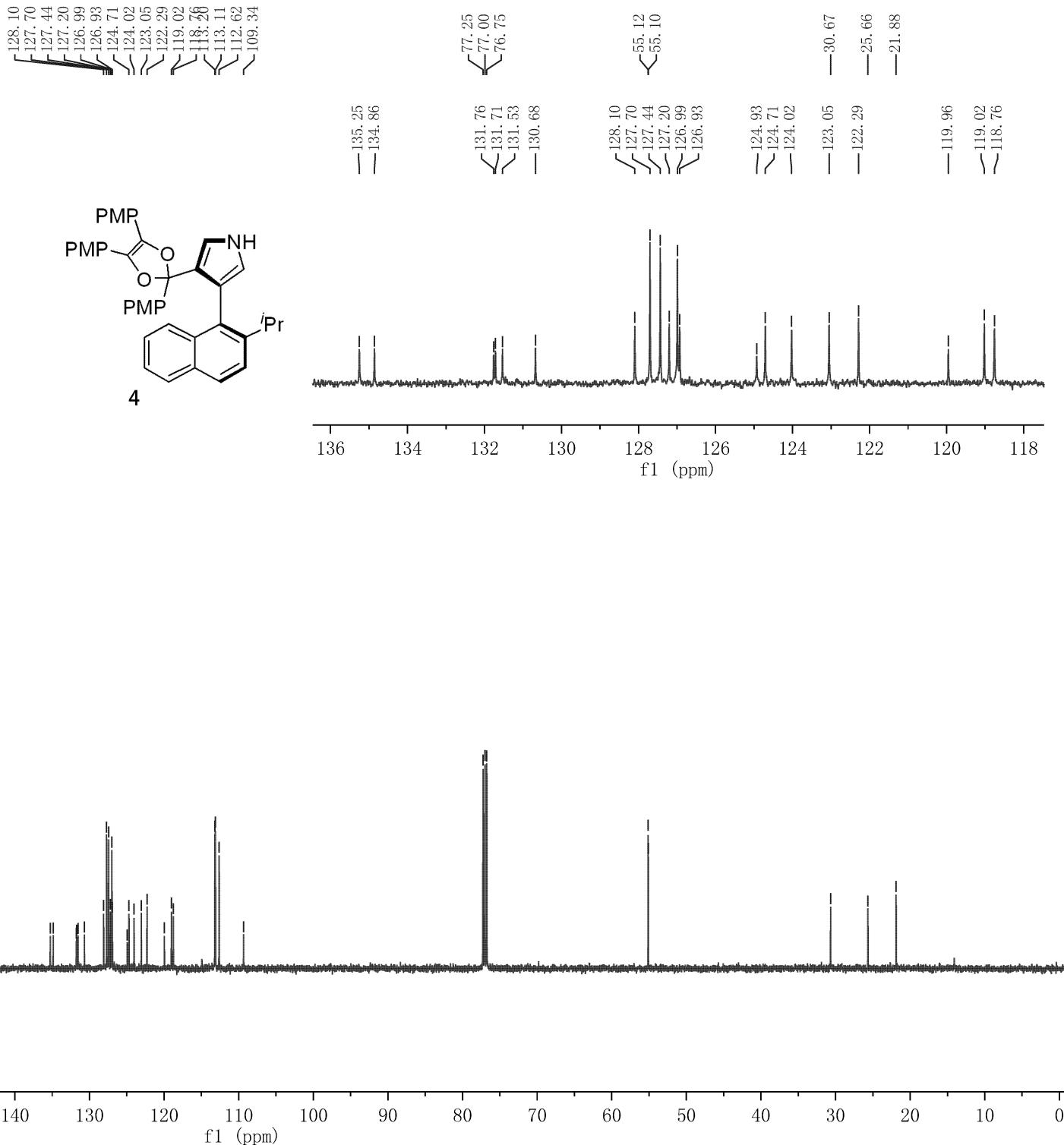
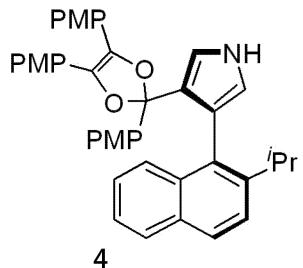
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121.69
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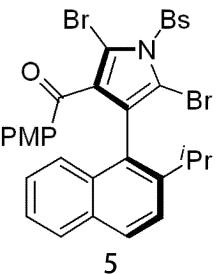
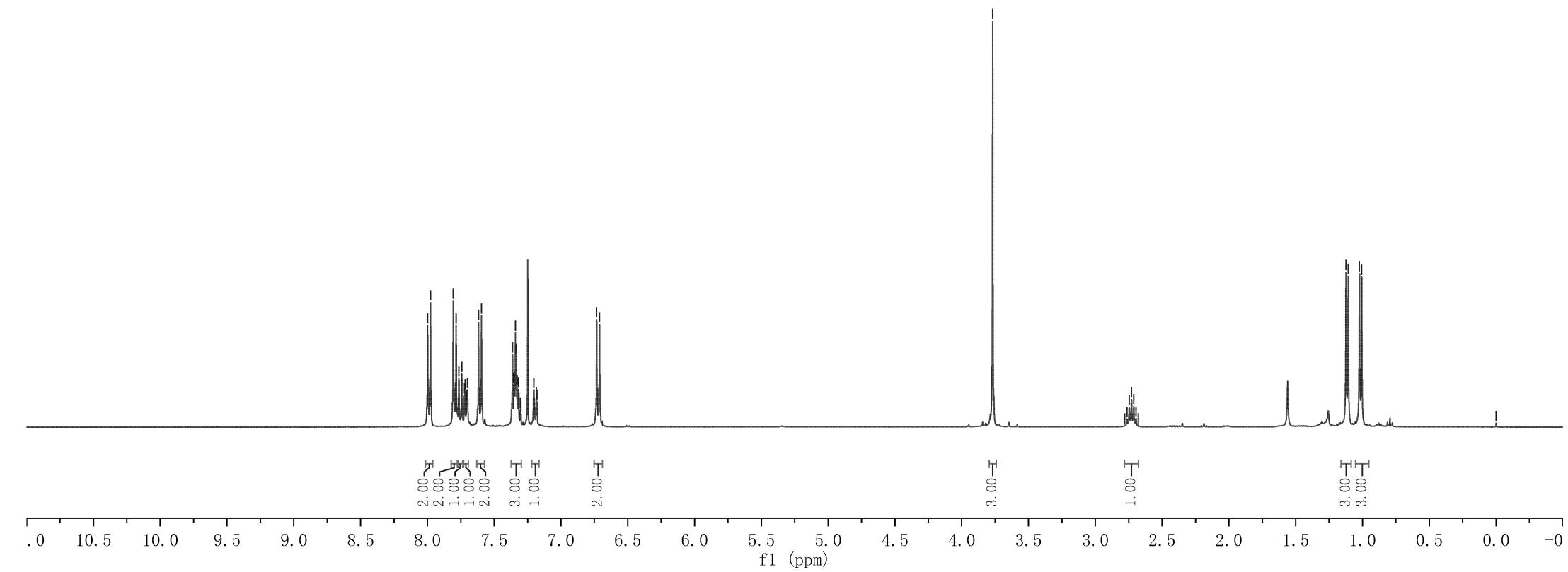
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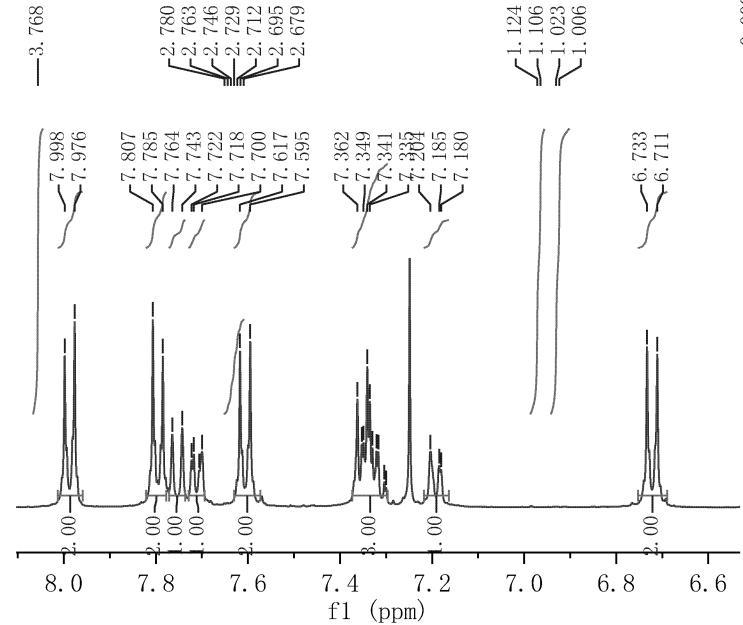


Parameter	Value
1 Title	XHJ-5-236-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDC13
4 Temperature	298.4
5 Number of Scans	54
6 Acquisition Time	1.1010
7 Acquisition Date	2023-09-13T14:24:44
8 Spectrometer Frequency	125.77
9 Spectral Width	29761.9





Parameter	Value
1 Title	XHJ-6-82-H
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	298.0
5 Number of Scans	11
6 Acquisition Time	4.0894
7 Acquisition Date	2023-10-24T21:30:00
8 Spectrometer Frequency	400.13
9 Spectral Width	8012.8



—188.24

—163.98

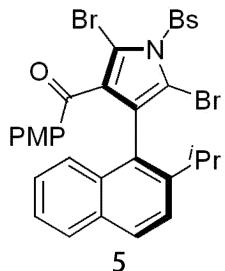
—145.86
—132.89
—132.11
—132.03
—131.77
—129.77
—129.47
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—128.00
—126.18
—125.33
—125.08
—125.05
—123.66

—105.87
—103.01

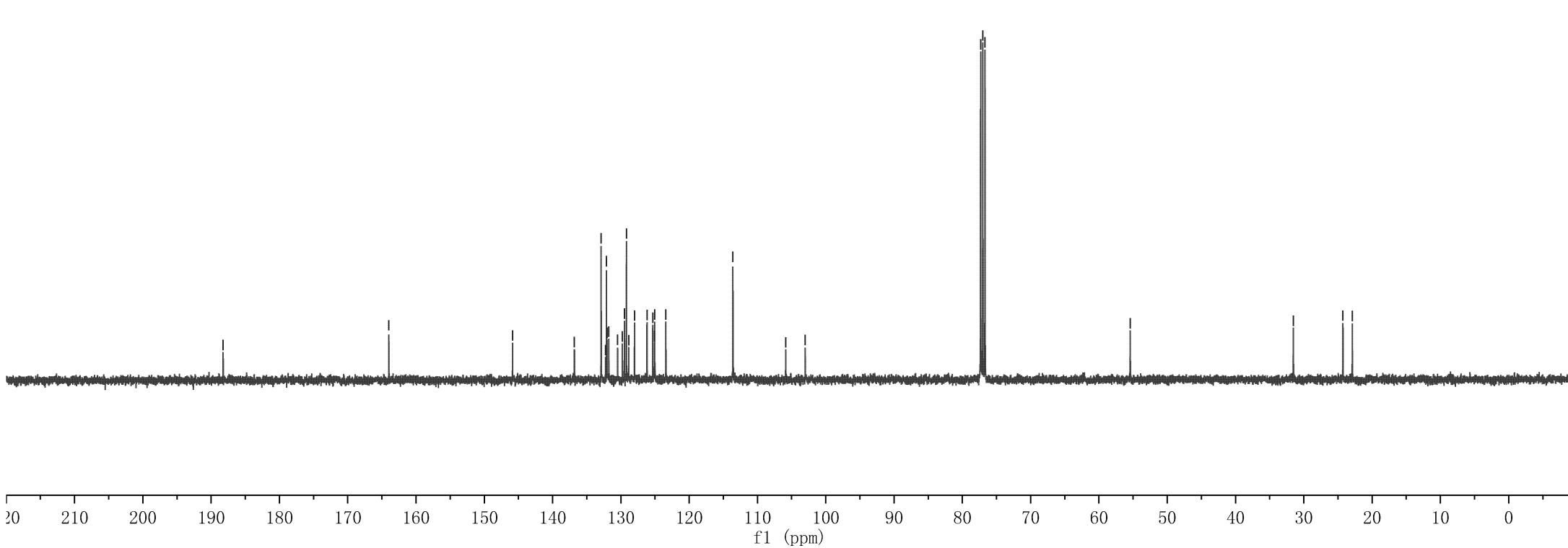
—77.32
—77.00
—76.68

—136.81
—132.89
—132.26
—132.11
—132.03
—131.77
—130.48
—129.77
—129.47
—129.19
—128.84
—128.00
—31.53
—126.18
—125.33
—125.08
—24.27
—22.89

Parameter	Value
1 Title	XHJ-6-82-C
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl ₃
4 Temperature	300.0
5 Number of Scans	101
6 Acquisition Time	1.3631
7 Acquisition Date	2023-10-24T21:31:39
8 Spectrometer Frequency	100.61
9 Spectral Width	24038.5



5





Parameter	Value
1 Title	XIJ-6-87-H
2 Origin	Bruker Biospin GmbH
3 Solvent	CDC13
4 Temperature	300.0
5 Number of Scans	15
6 Acquisition Time	3.1719
7 Acquisition Date	2023-10-27T16:28:37
8 Spectrometer Frequency	500.17
9 Spectral Width	10330.6

