Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Copper Catalyzed Dearomatization by Michael-Type Addition of Indolyl Ynones: Divergent Synthesis of Functionalized Spiroindoles and Cyclopenta[*c*]quinolin-3-ones

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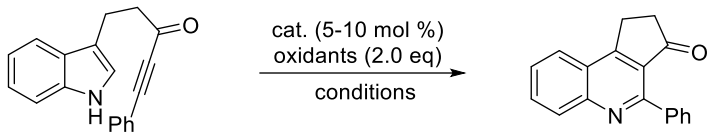
General Information. Ethyl acetate (ACS grade), hexanes (ACS grade) and anhydrous 1,2-dichloroethane (ACS grade) were obtained commercially and used without further purification. Methylene chloride, tetrahydrofuran and diethyl ether were purified according to standard methods unless otherwise noted. Commercially available reagents were used without further purification. 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 iS 10 spectrometer as thin film and are reported in reciprocal centimeter (cm^{-1}). Mass spectra were recorded with Micromass Q-Exactive Focus mass spectrometer using electron spray ionization.

^{1}H NMR spectra were recorded on a Bruker AV-400 spectrometer in chloroform-d_3. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data is being reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, brs = broad singlet, coupling constant(s) in Hz, integration).

^{13}C NMR spectra were recorded on on a Bruker AV-400 spectrometer in chloroform-d_3. Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard.

More Reaction Condition and Mechanism Studies

1. Optimization of reaction conditions for the skeletal rearrangement of indolyl ynone **3a**, please see as followed:[a]

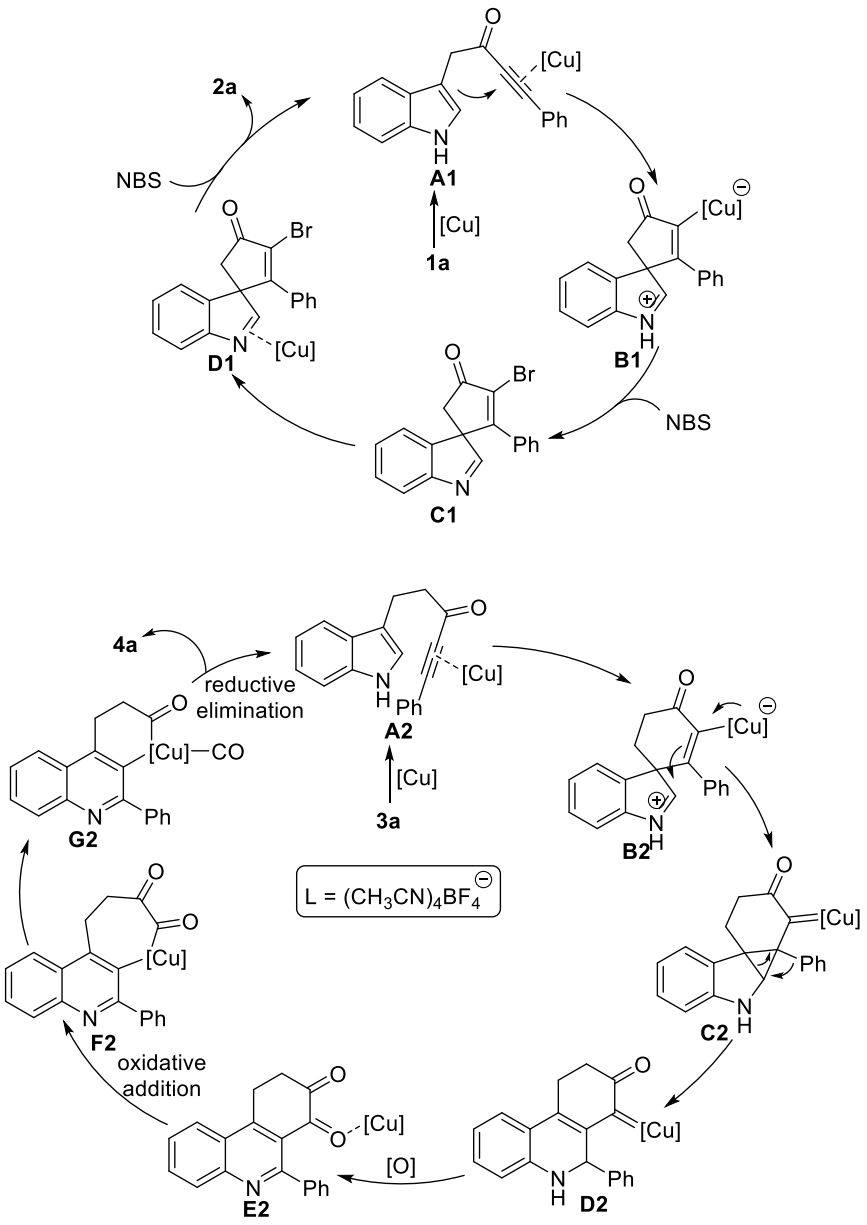


3a **4a**

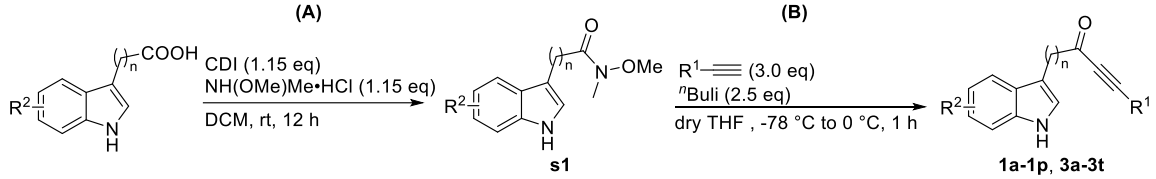
Entry	Cat. (*x* mol %)	Oxidant	Conditions	Yield [%][b]
1	$Cu(CH_3CN)_4PF_6$ (10)	-	DCE, 80 °C, 7 h	37
2	$Cu(CH_3CN)_4BF_4$ (10)	-	DCE, 80 °C, 6 h	42
3	CuOTf (10)	-	DCE, 80 °C, 7 h	24
4	$Cu(PPh_3)_3Br$ (10)	-	DCE, 80 °C, 12 h	<1
5	$Cu(OTf)_2$ (10)	-	DCE, 80 °C, 11 h	31
6	$Cu(hfacac)_2$ (10)	-	DCE, 80 °C, 11 h	38
7	$Zn(OTf)_2$ (10)	-	DCE, 80 °C, 12 h	<1
8	$Y(OTf)_3$ (10)	-	DCE, 80 °C, 12 h	<1
9	$Sc(OTf)_3$ (10)	-	DCE, 80 °C, 12 h	<1
10	$Ph_3PAuCl/AgNTf_2$ (5)	-	DCE, 80 °C, 12 h	<1
11	$[Rh(CO)_2Cl]_2$ (5)	-	DCE, 80 °C, 12 h	<1
12	$Cu(CH_3CN)_4BF_4$ (10)	-	toluene, 80 °C, 12 h	38
13	$Cu(CH_3CN)_4BF_4$ (10)	-	MeCN, 80 °C, 12 h	47
14	$Cu(CH_3CN)_4BF_4$ (10)	MnO_2	MeCN, 80 °C, 12 h	<1
15	$Cu(CH_3CN)_4BF_4$ (10)	$PhI(OAc)_2$	MeCN, 80 °C, 10 h	50
16	$Cu(CH_3CN)_4BF_4$ (10)	TBHP	MeCN, 80 °C, 15 h	60
17	$Cu(CH_3CN)_4BF_4$ (10)	TBHP	MeCN, 60 °C, 17 h	55
18[c]	**$Cu(CH_3CN)_4BF_4$ (10)**	**TBHP**	**MeCN, 80 °C, 10 h**	**66**

[a] Reaction conditions: **1a** (0.1 mmol), oxidant (0.2 mmol), catalyst (5-10 mol %), 0.05 M, 80 °C, in vials. [b] Measured by ^1H NMR using diethyl phthalate as the internal standard. [c] 10 mol % NaBARF was added.

2. Plausible reaction mechanism for the formation of **2a** and **4a**:

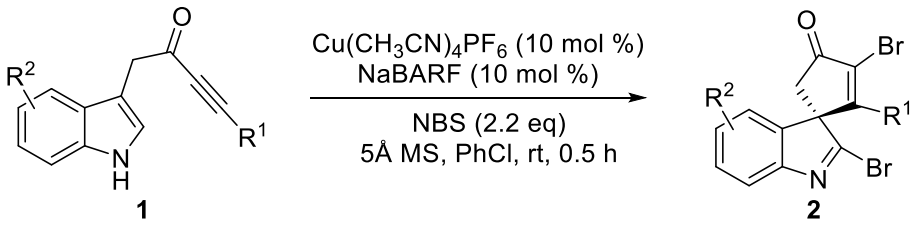


Representative synthetic procedures for the preparation of indolyl ynones 1a-1p and 3a-3t:



(A): CDI (1863.0 mg, 11.5 mmol) was slowly added to a solution of indole carboxylic acid (10.0 mmol) in 20.0 mL DCM at room temperature. The reaction mixture was stirred at room temperature for 0.5 h, after which NH(OMe)Me·HCl (1121.3 mg, 11.5 mmol) was added and the progress of the reaction was monitored by TLC. The reaction typically took 12 h. Upon completion, the crude reaction mixture was then poured into water (20 mL) and basified to pH 10 with 2 M NaOH, extracted with EtOAc (3 × 30 mL) and washed with 10% HCl (15 mL). The organic phases were combined and then dried over anhydrous $MgSO_4$, concentrated under reduced pressure to yield the crude amide products **s1**, which was then used in the next step without purification.[1]

(B): Add ^{n}BuLi (10.0 mL, 25 mmol, 2.5 M in hexane) to a stirred solution of alkyne (30 mmol) in dry THF (20.0 mL) at −78 °C under Ar dropwise. The mixture was stirred for 0.5 h at −78 °C and then compounds **s1** were added. The reaction mixture was warmed to room temperature and was stirred at room temperature and the progress of the reaction was monitored by TLC. The reaction typically took 1 h. Upon completion, the reaction was quenched by the addition of sat. aq. NH_4Cl (20 mL). The organic phases were separated and the aqueous phases was extracted with EtOAc (3 × 20 mL). The organic phases were combined and dried over anhydrous $MgSO_4$, concentrated under reduced pressure. The residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford the desired indolyl ynone substrates **1a-1p** and **3a-3t**.[2]

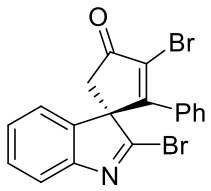


General procedure for the synthesis of dibromo-substituted spiroindoles 2:

NBS (0.44 mmol, 76.6 mg), $Cu(CH_3CN)_4PF_6$ (0.02 mmol, 7.5 mg), NaBARF (0.02 mmol, 17.7 mg), and 5Å molecular sieves (40 mg) were added in this order to the indolyl ynones **1** (0.2 mmol) in PhCl (4.0 mL) at room temperature. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. The reaction

typically took 0.5 h. Upon completion, the mixture was then concentrated and the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford the desired products **2**.

2',3-dibromo-2-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-one (2a)



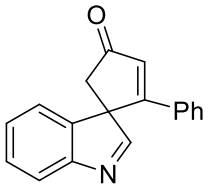
2a

The reaction was conducted with 1-(1*H*-indol-3-yl)-4-phenylbut-3-yn-2-one (**1a**, 0.2 mmol, 51.8 mg), NBS (0.44 mmol, 76.6 mg), $Cu(CH_3CN)_4PF_6$ (0.02 mmol, 7.5 mg), NaBARF (0.02 mmol, 17.7 mg), and 5Å molecular sieves (40 mg) in PhCl (4.0 mL) at room temperature. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **2a** (64.2 mg, 77%) as a yellow solid (mp 179-181 °C).

The reaction was conducted with 1-(1*H*-indol-3-yl)-4-phenylbut-3-yn-2-one (**1a**, 4.0 mmol, 1036.0 mg), NBS (8.8 mmol, 1548.8 mg), $Cu(CH_3CN)_4PF_6$ (0.4 mmol, 14.9 mg), NaBARF (0.2 mmol, 177.2 mg), and 5Å molecular sieves (400 mg) in PhCl (40.0 mL) at room temperature. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **2a** (1117.6 mg, 67%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.7 Hz, 1H), 7.43 – 7.40 (m, 1H), 7.34 – 7.29 (m, 3H), 7.23 – 7.20 (m, 2H), 6.95 (d, *J* = 7.6 Hz, 2H), 3.14 (d, *J* = 18.7 Hz, 1H), 2.90 (d, *J* = 18.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 166.8, 163.7, 154.1, 139.2, 131.3, 130.6, 129.8, 128.5, 127.5, 126.9, 126.8, 122.2, 121.3, 70.3, 41.9; IR (neat): 2924, 1725, 1539, 1454, 1267, 939, 771, 746, 704; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{12}Br_2NO$ 415.9280, found 415.9282.

2-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-one (2aa)

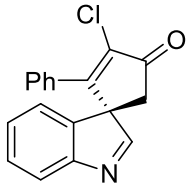


2aa

The reaction was conducted with 1-(1*H*-indol-3-yl)-4-phenylbut-3-yn-2-one (**1a**, 0.2 mmol, 51.8 mg), $Cu(CH_3CN)_4PF_6$ (0.02 mmol, 7.5 mg), NaBARF (0.02 mmol, 17.7 mg), and 5Å molecular sieves (40 mg) in PhCl (4.0 mL) at room temperature. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **2aa** (43.0 mg, 83%) as a pale yellow oil.

The data of **2aa** was reported in previous literature.[3] ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.31 – 7.24 (m, 3H), 7.20 – 7.16 (m, 2H), 6.98 (d, *J* = 7.7 Hz, 2H), 6.85 (s, 1H), 3.05 (d, *J* = 18.7 Hz, 1H), 2.68 (d, *J* = 18.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.2, 174.0, 171.9, 154.8, 140.8, 132.4, 131.3, 130.7, 129.0, 128.8, 127.6, 126.7, 122.1, 121.5, 65.9, 42.3.

3-chloro-2-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-one (2aba)



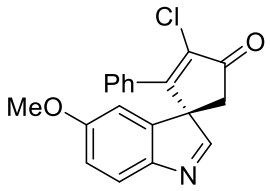
2aba

The reaction was conducted with 1-(1*H*-indol-3-yl)-4-phenylbut-3-yn-2-one (**1a**, 0.2 mmol, 51.8 mg), $CuCl_2$ (0.12 mmol, 16.1 mg), and 5Å molecular sieves (40 mg) in PhCl (4.0 mL) at room temperature. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **2aba** (48.2 mg, 82%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.42 – 7.38 (m, 1H), 7.33 – 7.27 (m, 3H), 7.21 – 7.17 (m, 2H), 6.92 (d, *J* = 7.6 Hz, 2H), 3.24 (d, *J* = 18.8 Hz, 1H), 2.94 (d, *J* = 18.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1, 174.5, 171.5, 155.2, 138.6, 133.5, 130.2, 129.4, 128.3, 127.6, 126.4, 121.9, 121.8, 105.1, 68.8, 38.7; IR (neat):

2921, 2200, 1729, 1601, 1459, 1275, 968, 744, 698; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{13}ClNO$ 294.0680, found 294.0675.

3-chloro-5'-methoxy-2-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-one (2abb)

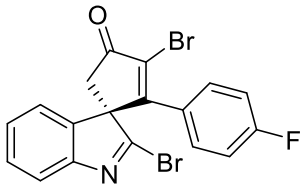


2abb

The reaction was conducted with 1-(5-methoxy-1*H*-indol-3-yl)-4-phenylbut-3-yn-2-one (**1p**, 0.2 mmol, 57.8 mg), $CuCl_2$ (0.12 mmol, 16.1 mg), and 5Å molecular sieves (40 mg) in PhCl (4.0 mL) at room temperature. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **2abb** (48.6 mg, 75%) as a yellow solid (mp 164-166 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.57 (d, *J* = 8.5 Hz, 1H), 7.32 – 7.20 (m, 3H), 7.07 (d, *J* = 7.9 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.82 (s, 1H), 3.80 (s, 3H), 3.12 (d, *J* = 18.9 Hz, 1H), 2.79 (d, *J* = 18.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 170.1, 164.1, 159.8, 148.7, 141.1, 133.0, 131.0, 130.7, 128.5, 127.0, 122.6, 114.3, 107.8, 64.9, 55.8, 40.0; IR (neat): 2924, 2847, 1720, 1590, 1470, 1280, 1027, 976, 746; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{15}ClNO_2$ 324.0786, found 324.0783.

2',3-dibromo-2-(4-fluorophenyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (2b)



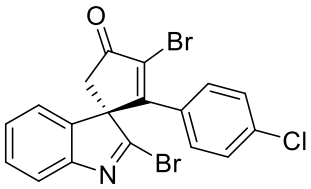
2b

The reaction was conducted with 4-(4-fluorophenyl)-1-(1*H*-indol-3-yl)but-3-yn-2-one (**1b**, 0.2 mmol, 55.4 mg), NBS (0.44 mmol, 76.6 mg), $Cu(CH_3CN)_4PF_6$ (0.02 mmol, 7.5 mg), NaBARF (0.02 mmol, 17.7 mg), and 5Å molecular sieves (40 mg) in PhCl (4.0 mL)

at room temperature. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **2b** (52.2 mg, 60%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.7 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.34 (d, *J* = 4.3 Hz, 2H), 6.98 – 6.90 (m, 4H), 3.14 (d, *J* = 18.7 Hz, 1H), 2.90 (d, *J* = 18.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 165.6, 163.7 (d, *J* = 252.0 Hz), 163.6, 154.1, 139.1, 129.9, 129.3 (d, *J* = 9.0 Hz), 127.7, 127.2 (d, *J* = 3.0 Hz), 127.0, 122.1, 121.4, 115.9 (d, *J* = 22.0 Hz), 70.3, 41.9; IR (neat): 2923, 1732, 1618, 1505, 1472, 1232, 1158, 951, 673; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{11}Br_2FNO$ 433.9186, found 433.9190.

2',3-dibromo-2-(4-chlorophenyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (2c)

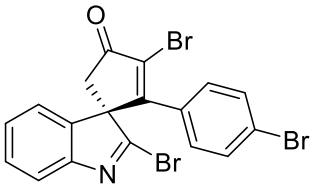


2c

The reaction was conducted with 4-(4-chlorophenyl)-1-(1*H*-indol-3-yl)but-3-yn-2-one (**1c**, 0.2 mmol, 58.8 mg), NBS (0.44 mmol, 76.6 mg), $Cu(CH_3CN)_4PF_6$ (0.02 mmol, 7.5 mg), NaBARF (0.02 mmol, 17.7 mg), and 5Å molecular sieves (40 mg) in PhCl (4.0 mL) at room temperature. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **2c** (59.7 mg, 66%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.6 Hz, 1H), 7.45 – 7.42 (m, 1H), 7.34 (d, *J* = 3.0 Hz, 2H), 7.20 (d, *J* = 7.2 Hz, 2H), 6.89 (d, *J* = 7.2 Hz, 2H), 3.14 (d, *J* = 18.7 Hz, 1H), 2.90 (d, *J* = 18.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 165.4, 163.4, 154.1, 138.9, 136.8, 130.0, 129.6, 128.9, 128.4, 127.7, 127.3, 122.1, 121.4, 70.2, 41.8; IR (neat): 2917, 1720, 1538, 1485, 1096, 1010, 937, 769, 721; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{11}Br_2ClNO$ 451.8870, found 451.8898.

2',3-dibromo-2-(4-bromophenyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (2d)

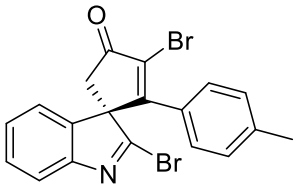


2d

The reaction was conducted with 4-(4-bromophenyl)-1-(1*H*-indol-3-yl)but-3-yn-2-one (**1d**, 0.2 mmol, 67.6 mg), NBS (0.44 mmol, 76.6 mg), $Cu(CH_3CN)_4PF_6$ (0.02 mmol, 7.5 mg), NaBARF (0.02 mmol, 17.7 mg), and 5Å molecular sieves (40 mg) in PhCl (4.0 mL) at room temperature. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **2d** (79.4 mg, 80%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.7 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.37 – 7.33 (m, 4H), 6.82 (d, *J* = 8.5 Hz, 2H), 3.14 (d, *J* = 18.7 Hz, 1H), 2.90 (d, *J* = 18.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 165.5, 163.4, 154.1, 138.9, 131.9, 130.1, 130.0, 128.5, 127.7, 127.3, 125.2, 122.1, 121.4, 70.2, 41.8; IR (neat): 3069, 1715, 1596, 1538, 1450, 1198, 1070, 934, 775; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{11}Br_3NO$ 495.8385, found 493.8395.

2',3-dibromo-2-(*p*-tolyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (2e)



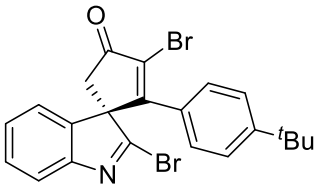
2e

The reaction was conducted with 1-(1*H*-indol-3-yl)-4-(*p*-tolyl)but-3-yn-2-one (**1e**, 0.2 mmol, 54.6 mg), NBS (0.44 mmol, 76.6 mg), $Cu(CH_3CN)_4PF_6$ (0.02 mmol, 7.5 mg), NaBARF (0.02 mmol, 17.7 mg), and 5Å molecular sieves (40 mg) in PhCl (4.0 mL) at room temperature. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **2e** (63.8 mg, 74%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.7 Hz, 1H), 7.44 – 7.40 (m, 1H), 7.32 (d, *J* = 4.2 Hz, 2H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.87 (d, *J* = 8.2 Hz, 2H), 3.12 (d, *J* = 18.6 Hz, 1H),

2.87 (d, J = 18.6 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 166.7, 164.1, 154.0, 141.2, 139.5, 129.7, 129.3, 128.4, 127.6, 127.0, 126.1, 122.2, 121.2, 70.3, 42.0, 21.4; IR (neat): 2924, 1717, 1609, 1541, 1502, 1453, 1269, 934, 766; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{14}Br_2NO$ 429.9437, found 429.9446.

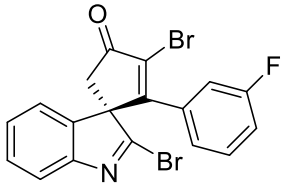
2',3-dibromo-2-(4-(*tert*-butyl)phenyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (2f)



2f

The reaction was conducted with 4-(4-(*tert*-butyl)phenyl)-1-(1*H*-indol-3-yl)but-3-yn-2-one (**1f**, 0.2 mmol, 63.0 mg), NBS (0.44 mmol, 76.6 mg), $Cu(CH_3CN)_4PF_6$ (0.02 mmol, 7.5 mg), NaBARF (0.02 mmol, 17.7 mg), and 5Å molecular sieves (40 mg) in PhCl (4.0 mL) at room temperature. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **2f** (71.9 mg, 76%) as a pale yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.7 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.33 (d, J = 4.2 Hz, 2H), 7.22 (d, J = 8.3 Hz, 2H), 6.92 (d, J = 8.3 Hz, 2H), 3.12 (d, J = 18.6 Hz, 1H), 2.86 (d, J = 18.6 Hz, 1H), 1.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 166.4, 164.2, 154.3, 154.0, 139.8, 129.7, 128.3, 127.6, 126.9, 126.0, 125.5, 122.1, 121.3, 70.2, 42.2, 34.8, 31.0; IR (neat): 2958, 1723, 1604, 1538, 1459, 1269, 1201, 934, 763; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{20}Br_2NO$ 471.9906, found 471.9907.

2',3-dibromo-2-(3-fluorophenyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (2g)

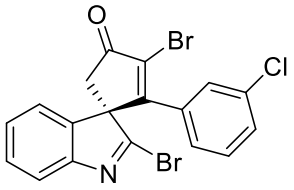


2g

The reaction was conducted with 4-(3-fluorophenyl)-1-(1*H*-indol-3-yl)but-3-yn-2-one (**1g**, 0.2 mmol, 55.4 mg), NBS (0.44 mmol, 76.6 mg), $Cu(CH_3CN)_4PF_6$ (0.02 mmol, 7.5 mg), NaBARF (0.02 mmol, 17.7 mg), and 5Å molecular sieves (40 mg) in PhCl (4.0 mL) at room temperature. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **2g** (68.7 mg, 79%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.7 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.35 (d, *J* = 4.4 Hz, 2H), 7.23 – 7.18 (m, 1H), 7.01 (t, *J* = 8.3 Hz, 1H), 6.72 (d, *J* = 7.7 Hz, 1H), 6.65 (d, *J* = 9.6 Hz, 1H), 3.15 (d, *J* = 18.7 Hz, 1H), 2.91 (d, *J* = 18.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 165.2 (d, *J* = 2.0 Hz), 163.2, 162.1 (d, *J* = 246.0 Hz), 154.1, 138.8, 133.0 (d, *J* = 8.0 Hz), 130.4, 130.3, 130.0, 127.7, 127.6, 122.7 (d, *J* = 3.0 Hz), 122.1, 121.4, 117.6 (d, *J* = 20.0 Hz), 114.2 (d, *J* = 23.0 Hz), 70.2, 41.8; IR (neat): 2924, 1729, 1595, 1470, 1391, 1130, 1073, 956, 763; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{11}Br_2FNO$ 435.9166, found 435.9179.

2',3-dibromo-2-(3-chlorophenyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (2h)



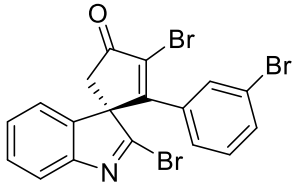
2h

The reaction was conducted with 4-(3-chlorophenyl)-1-(1*H*-indol-3-yl)but-3-yn-2-one (**1h**, 0.2 mmol, 58.8 mg), NBS (0.44 mmol, 76.6 mg), $Cu(CH_3CN)_4PF_6$ (0.02 mmol, 7.5 mg), NaBARF (0.02 mmol, 17.7 mg), and 5Å molecular sieves (40 mg) in PhCl (4.0 mL) at room temperature. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **2h** (75.0 mg, 83%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.4 Hz, 1H), 7.46 – 7.43 (m, 1H), 7.38 – 7.35 (m, 2H), 7.27 – 7.26 (m, 1H), 7.15 (t, *J* = 7.9 Hz, 1H), 6.92 (s, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 3.15 (d, *J* = 18.7 Hz, 1H), 2.91 (d, *J* = 18.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 165.2, 163.1, 154.1, 138.7, 134.5, 132.8, 130.6, 130.0, 129.9, 127.7, 127.1, 125.0,

122.1, 121.4, 70.2, 41.7; IR (neat): 2921, 1726, 1541, 1453, 1257, 1192, 1073, 931, 760; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{11}Br_2ClNO$ 451.8870, found 451.8875.

2',3-dibromo-2-(3-bromophenyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (2i)

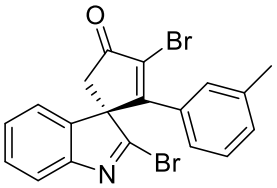


2i

The reaction was conducted with 4-(3-bromophenyl)-1-(1*H*-indol-3-yl)but-3-yn-2-one (**1i**, 0.2 mmol, 67.6 mg), NBS (0.44 mmol, 76.6 mg), $Cu(CH_3CN)_4PF_6$ (0.02 mmol, 7.5 mg), NaBARF (0.02 mmol, 17.7 mg), and 5Å molecular sieves (40 mg) in PhCl (4.0 mL) at room temperature. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **2i** (64.5 mg, 65%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.7 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.36 (d, *J* = 4.8 Hz, 2H), 7.11 – 7.07 (m, 2H), 6.83 (d, *J* = 7.7 Hz, 1H), 3.15 (d, *J* = 18.7 Hz, 1H), 2.92 (d, *J* = 18.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 165.0, 163.2, 154.1, 138.6, 133.5, 133.0, 130.1, 130.0, 129.9, 127.7, 125.4, 122.4, 122.2, 121.4, 70.2, 41.6; IR (neat): 2924, 1729, 1541, 1584, 1448, 1255, 1067, 937, 761; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{11}Br_3NO$ 495.8365, found 495.8376.

2',3-dibromo-2-(*m*-tolyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (2j)



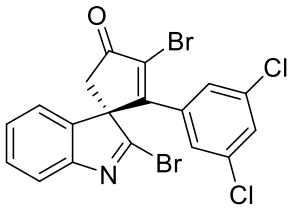
2j

The reaction was conducted with 1-(1*H*-indol-3-yl)-4-(*m*-tolyl)but-3-yn-2-one (**1j**, 0.2 mmol, 54.6 mg), NBS (0.44 mmol, 76.6 mg), $Cu(CH_3CN)_4PF_6$ (0.02 mmol, 7.5 mg), NaBARF (0.02 mmol, 17.7 mg), and 5Å molecular sieves (40 mg) in PhCl (4.0 mL) at

room temperature. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **2j** (55.2 mg, 64%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.7 Hz, 1H), 7.44 – 7.40 (m, 1H), 7.35 – 7.31 (m, 2H), 7.13 – 7.07 (m, 2H), 6.73 – 6.70 (m, 2H), 3.13 (d, *J* = 18.6 Hz, 1H), 2.89 (d, *J* = 18.7 Hz, 1H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 167.1, 163.8, 154.1, 139.3, 138.2, 131.4, 131.2, 129.7, 128.4, 127.5, 127.4, 126.6, 124.0, 122.2, 121.2, 70.3, 41.9, 21.3; IR (neat): 2918, 1723, 1592, 1536, 1450, 1394, 1229, 934, 755; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{14}Br_2NO$ 429.9437, found 429.9442.

2',3-dibromo-2-(3,5-dichlorophenyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (2k)

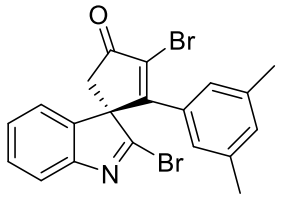


2k

The reaction was conducted with 4-(3,5-dichlorophenyl)-1-(1*H*-indol-3-yl)but-3-yn-2-one (**1k**, 0.2 mmol, 65.6 mg), NBS (0.44 mmol, 76.6 mg), $Cu(CH_3CN)_4PF_6$ (0.02 mmol, 7.5 mg), NaBARF (0.02 mmol, 17.7 mg), and 5Å molecular sieves (40 mg) in PhCl (4.0 mL) at room temperature. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **2k** (59.3 mg, 61%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.41 – 7.35 (m, 2H), 7.32 – 7.30 (m, 1H), 6.75 (s, 2H), 3.16 (d, *J* = 18.8 Hz, 1H), 2.93 (d, *J* = 18.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 163.8, 162.7, 154.2, 138.2, 135.3, 133.8, 130.5, 130.3, 128.5, 127.8, 125.3, 122.1, 121.5, 70.1, 41.5; IR (neat): 2921, 1732, 1578, 1538, 1453, 1263, 1121, 937, 761; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{10}Br_2Cl_2NO$ 483.8501, found 483.8507.

2',3-dibromo-2-(3,5-dimethylphenyl)spiro[cyclopentane-1,3'-indol]-2-en-4-one (2l)

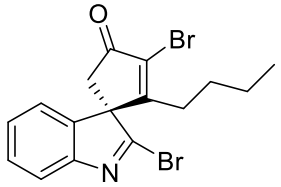


2l

The reaction was conducted with 4-(3,5-dimethylphenyl)-1-(1*H*-indol-3-yl)but-3-yn-2-one (**1l**, 0.2 mmol, 57.4 mg), NBS (0.44 mmol, 76.6 mg), $Cu(CH_3CN)_4PF_6$ (0.02 mmol, 7.5 mg), NaBARF (0.02 mmol, 17.7 mg), and 5Å molecular sieves (40 mg) in PhCl (4.0 mL) at room temperature. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **2l** (65.9 mg, 74%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.7 Hz, 1H), 7.44 – 7.40 (m, 1H), 7.34 – 7.31 (m, 2H), 6.92 (s, 1H), 6.51 (s, 2H), 3.12 (d, *J* = 18.7 Hz, 1H), 2.89 (d, *J* = 18.6 Hz, 1H), 2.14 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 167.3, 163.9, 154.2, 139.4, 138.0, 132.3, 131.1, 129.7, 127.4, 126.3, 124.5, 122.2, 121.1, 70.4, 41.8, 21.2; IR (neat): 2918, 1729, 1590, 1541, 1453, 1235, 1175, 934, 732; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{16}Br_2NO$ 443.9593, found 443.9605.

2',3-dibromo-2-butylspiro[cyclopentane-1,3'-indol]-2-en-4-one (2m)



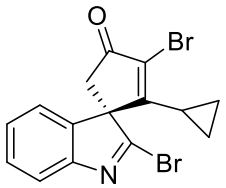
2m

The reaction was conducted with 1-(1*H*-indol-3-yl)oct-3-yn-2-one (**1m**, 0.2 mmol, 47.8 mg), NBS (0.44 mmol, 76.6 mg), $Cu(CH_3CN)_4PF_6$ (0.02 mmol, 7.5 mg), NaBARF (0.02 mmol, 17.7 mg), and 5Å molecular sieves (40 mg) in PhCl (4.0 mL) at room temperature. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **2m** (60.3 mg, 76%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 2.99 (d, *J* = 18.7 Hz, 1H), 2.78 (d, *J* = 18.7 Hz,

1H), 2.07 – 2.00 (m, 1H), 1.94 – 1.88 (m, 1H), 1.34 – 1.26 (m, 1H), 1.21 – 1.09 (m, 3H), 0.73 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 171.9, 163.9, 154.2, 138.8, 129.7, 127.3, 126.9, 122.3, 121.1, 70.3, 41.2, 29.2, 28.8, 22.8, 13.3; IR (neat): 2955, 1723, 1612, 1473, 1326, 1201, 1096, 948, 752; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{16}Br_2NO$ 395.9593, found 395.9596.

2',3-dibromo-2-cyclopropylspiro[cyclopentane-1,3'-indol]-2-en-4-one (2n)

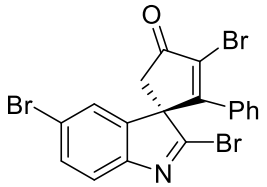


2n

The reaction was conducted with 4-cyclopropyl-1-(1*H*-indol-3-yl)but-3-yn-2-one (**1n**, 0.2 mmol, 44.6 mg), NBS (0.44 mmol, 76.6 mg), $Cu(CH_3CN)_4PF_6$ (0.02 mmol, 7.5 mg), NaBARF (0.02 mmol, 17.7 mg), and 5Å molecular sieves (40 mg) in PhCl (4.0 mL) at room temperature. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **2n** (59.4 mg, 78%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.7 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.29 – 7.25 (m, 1H), 2.94 (d, *J* = 18.7 Hz, 1H), 2.71 (d, *J* = 18.7 Hz, 1H), 1.31 – 1.25 (m, 1H), 1.18 – 1.11 (m, 1H), 1.04 – 0.97 (m, 1H), 0.94 – 0.87 (m, 1H), 0.84 – 0.79 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 171.6, 164.6, 154.0, 139.5, 129.7, 127.5, 122.4, 122.2, 121.2, 70.4, 41.3, 13.1, 9.2, 8.0; IR (neat): 2915, 1720, 1595, 1533, 1450, 1229, 1076, 934, 763; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{12}Br_2NO$ 379.9280, found 379.9287.

2',3,5'-tribromo-2-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-one (2o)

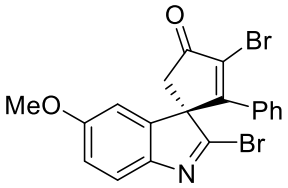


2o

The reaction was conducted with 1-(5-bromo-1*H*-indol-3-yl)-4-phenylbut-3-yn-2-one (**1o**, 0.2 mmol, 67.6 mg), NBS (0.44 mmol, 76.6 mg), $Cu(CH_3CN)_4PF_6$ (0.02 mmol, 7.5 mg), NaBARF (0.02 mmol, 17.7 mg), and 5Å molecular sieves (40 mg) in PhCl (4.0 mL) at room temperature. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **2o** (78.4 mg, 79%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.3 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.28 – 7.24 (m, 2H), 6.99 (d, *J* = 7.8 Hz, 2H), 3.13 (d, *J* = 18.6 Hz, 1H), 2.89 (d, *J* = 18.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 165.9, 164.1, 152.9, 141.3, 133.0, 131.0, 130.8, 128.7, 127.3, 126.9, 125.5, 122.5, 121.4, 70.5, 41.9; IR (neat): 2921, 1726, 1615, 1549, 1473, 1388, 1209, 948, 690; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{11}Br_3NO$ 493.8385, found 493.8388.

2',3-dibromo-5'-methoxy-2-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-one (2p)

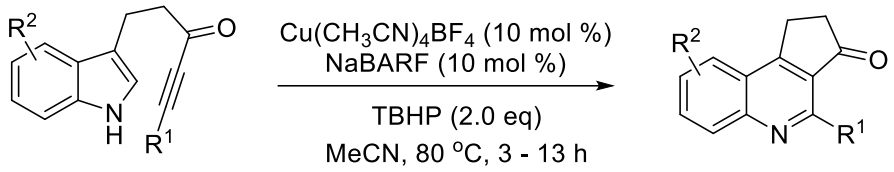


2p

The reaction was conducted with 1-(5-methoxy-1*H*-indol-3-yl)-4-phenylbut-3-yn-2-one (**1p**, 0.2 mmol, 57.8 mg), NBS (0.44 mmol, 76.6 mg), $Cu(CH_3CN)_4PF_6$ (0.02 mmol, 7.5 mg), NaBARF (0.02 mmol, 17.7 mg), and 5Å molecular sieves (40 mg) in PhCl (4.0 mL) at room temperature. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **2p** (76.9 mg, 86%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.5 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.27 – 7.22 (m, 2H), 7.00 (d, *J* = 7.6 Hz, 2H), 6.92 – 6.86 (m, 2H), 3.82 (s, 3H), 3.14 (d, *J* = 18.7 Hz, 1H), 2.87 (d, *J* = 18.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 166.8,

160.3, 159.5, 147.7, 140.8, 131.3, 130.7, 128.5, 127.0, 126.7, 121.8, 114.5, 108.4, 70.3, 55.9, 42.2; IR (neat): 2932, 1720, 1604, 1536, 1470, 1289, 1209, 951, 735; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{14}Br_2NO_2$ 445.9386, found 445.9387.

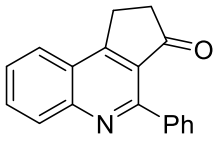


3 **4**

General procedure for the synthesis of cyclopenta[*c*]quinolin-3-ones 4:

TBHP (0.4 mmol, 36.0 mg), $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg), and NaBARF (0.02 mmol, 17.7 mg) were added in this order to the indolyl ynones **3** (0.2 mmol) in MeCN (4.0 mL) at room temperature. The reaction mixture was stirred at 80 °C (80 °C, heating mantle temperature) and the progress of the reaction was monitored by TLC. The reaction typically took 2 - 13 h. Upon completion, the mixture was then concentrated and the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford the desired products **4**.

4-phenyl-1,2-dihydro-3*H*-cyclopenta[*c*]quinolin-3-one (4a)



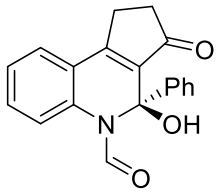
4a

The reaction was conducted with 5-(1*H*-indol-3-yl)-1-phenylpent-1-yn-3-one (**3a**, 0.2 mmol, 54.6 mg), TBHP (0.4 mmol, 36.0 mg), $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg), and NaBARF (0.02 mmol, 17.7 mg) in MeCN (4.0 mL) at 80 °C (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **4a** (33.2 mg, 64%) as a yellow solid (mp 197-199 °C).

The reaction was conducted with 5-(1*H*-indol-3-yl)-1-phenylpent-1-yn-3-one (**3a**, 6.0 mmol, 1638.0 mg), TBHP (12.0 mmol, 1080.0 mg), $Cu(CH_3CN)_4BF_4$ (0.6 mmol, 189.0 mg), and NaBARF (0.3 mmol, 265.8 mg) in MeCN (60.0 mL) at 80 °C. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **4a** (1024.2 mg, 66%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.89 – 7.81 (m, 3H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.58 – 7.48 (m, 3H), 3.47 – 3.44 (m, 2H), 2.87 – 2.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.5, 166.8, 157.1, 149.1, 137.6, 132.7, 130.3, 129.7, 129.3, 127.8, 127.5, 127.2, 125.0, 123.7, 36.4, 23.7; IR (neat): 2918, 1708, 1615, 1550, 1411, 1195, 1076, 772, 695; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{14}NO$ 260.1070, found 260.1070.

4-hydroxy-3-oxo-4-phenyl-1,2,3,4-tetrahydro-5*H*-cyclopenta[*c*]quinoline-5-carbaldehyde (4aa)

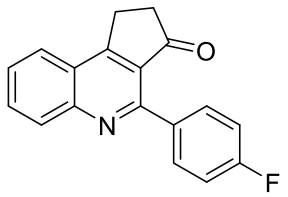


4aa

The reaction was conducted with 5-(1*H*-indol-3-yl)-1-phenylpent-1-yn-3-one (**3a**, 0.2 mmol, 54.6 mg), TBHP (0.4 mmol, 36.0 mg), $PdCl_2$ (0.02 mmol, 3.6 mg), $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg), and NaBARF (0.02 mmol, 17.7 mg) in MeCN (4.0 mL) at 80 °C (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1) yielded **4aa** (52.5 mg, 86%) as a yellow solid (mp 171-173 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 7.54 – 7.45 (m, 4H), 7.33 – 7.23 (m, 5H), 3.06 – 2.77 (m, 3H), 2.66 – 2.53 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 143.4, 136.7, 134.5, 134.4, 133.2, 129.5, 128.8, 128.7, 128.5, 125.3, 124.9, 124.6, 120.5, 35.2, 23.9; IR (neat): 3392(br), 2930, 2853, 2203, 1700, 1641, 1463, 1382, 1195, 761; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{19}H_{16}NO_3$ 328.0944, found 328.0941.

4-(4-fluorophenyl)-1,2-dihydro-3*H*-cyclopenta[*c*]quinolin-3-one (4b)

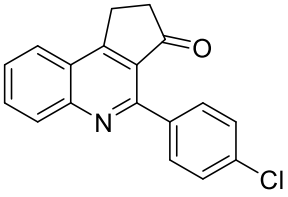


4b

The reaction was conducted with 1-(4-fluorophenyl)-5-(1*H*-indol-3-yl)pent-1-yn-3-one (**3b**, 0.2 mmol, 58.2 mg), TBHP (0.4 mmol, 36.0 mg), $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg), and NaBARF (0.02 mmol, 17.7 mg) in MeCN (4.0 mL) at 80 ^oC (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **4b** (41.6 mg, 75%) as a pale yellow oil.

^1H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 8.2 Hz, 1H), 7.92 – 7.83 (m, 3H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 8.5 Hz, 2H), 3.52 – 3.49 (m, 2H), 2.91 – 2.88 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.7, 167.1, 163.7 (d, *J* = 248.0 Hz), 156.0, 149.1, 133.7 (d, *J* = 4.0 Hz), 132.9, 131.9 (d, *J* = 9.0 Hz), 130.3, 127.4, 125.0, 123.8, 114.9 (d, *J* = 22.0 Hz), 36.5, 23.8; IR (neat): 2913, 1706, 1615, 1556, 1402, 1198, 1076, 843, 763; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{13}FNO$ 278.0976, found 278.0974.

4-(4-chlorophenyl)-1,2-dihydro-3*H*-cyclopenta[*c*]quinolin-3-one (4c)



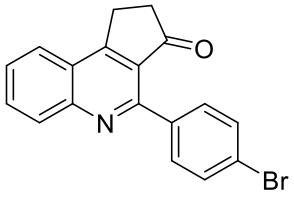
4c

The reaction was conducted with 1-(4-chlorophenyl)-5-(1*H*-indol-3-yl)pent-1-yn-3-one (**3c**, 0.2 mmol, 61.6 mg), TBHP (0.4 mmol, 36.0 mg), $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg), and NaBARF (0.02 mmol, 17.7 mg) in MeCN (4.0 mL) at 80 ^oC (80 °C, heating

mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **4c** (42.9 mg, 73%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 5.4 Hz, 1H), 8.06 (d, *J* = 5.4 Hz, 1H), 7.90 (t, *J* = 6.1 Hz, 1H), 7.80 – 7.77 (m, 2H), 7.70 – 7.66 (m, 1H), 7.47 – 7.44 (m, 2H), 3.50 – 3.48 (m, 2H), 2.89 – 2.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.6, 167.1, 155.8, 149.1, 136.1, 135.6, 132.9, 131.3, 130.3, 128.1, 127.5, 127.4, 125.1, 123.8, 36.4, 23.8; IR (neat): 2924, 1703, 1612, 1544, 1419, 1272, 1087, 834, 749; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{13}ClNO$ 294.0680, found 294.0677.

4-(4-bromophenyl)-1,2-dihydro-3*H*-cyclopenta[*c*]quinolin-3-one (4d)

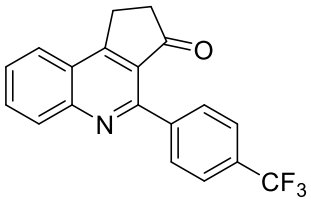


4d

The reaction was conducted with 1-(4-bromophenyl)-5-(1*H*-indol-3-yl)pent-1-yn-3-one (**3d**, 0.2 mmol, 70.4 mg), TBHP (0.4 mmol, 36.0 mg), $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg), and NaBARF (0.02 mmol, 17.7 mg) in MeCN (4.0 mL) at 80 ºC (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **4d** (44.6 mg, 66%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 8.1 Hz, 1H), 7.91 (t, *J* = 7.6 Hz, 1H), 7.74 – 7.62 (m, 5H), 3.52 – 3.50 (m, 2H), 2.90 – 2.88 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.6, 167.1, 155.9, 149.1, 136.5, 132.9, 131.5, 131.0, 130.3, 127.6, 127.4, 125.1, 124.1, 123.8, 36.5, 23.8; IR (neat): 2918, 1712, 1612, 1553, 1408, 1195, 1073, 945, 758; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{13}BrNO$ 338.0175, found 338.0171.

4-(4-(trifluoromethyl)phenyl)-1,2-dihydro-3*H*-cyclopenta[*c*]quinolin-3-one (4e)

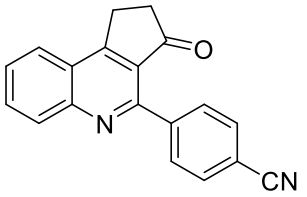


4e

The reaction was conducted with 5-(1*H*-indol-3-yl)-1-(4-(trifluoromethyl)phenyl)pent-1-yn-3-one (**3e**, 0.2 mmol, 68.2 mg), TBHP (0.4 mmol, 36.0 mg), $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg), and NaBARF (0.02 mmol, 17.7 mg) in MeCN (4.0 mL) at 80 ºC (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **4e** (41.9 mg, 64%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 8.1 Hz, 1H), 7.95 – 7.91 (m, 3H), 7.76 – 7.69 (m, 3H), 3.54 – 3.51 (m, 2H), 2.92 – 2.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.5, 167.1, 155.5, 149.1, 141.1, 133.0, 130.4, 130.2, 127.8, 127.4, 125.2, 124.8 (q, *J* = 3.7 Hz), 123.9, 36.4, 23.9; IR (neat): 2918, 1715, 1553, 1411, 1323, 1107, 1059, 849, 761; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{13}F_3NO$ 328.0944, found 328.0940.

4-(3-oxo-2,3-dihydro-1*H*-cyclopenta[*c*]quinolin-4-yl)benzonitrile (4f)



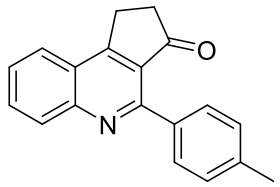
4f

The reaction was conducted with 4-(5-(1*H*-indol-3-yl)-3-oxopent-1-yn-1-yl)benzonitrile (**3f**, 0.2 mmol, 59.6 mg), TBHP (0.4 mmol, 36.0 mg), $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg), and NaBARF (0.02 mmol, 17.7 mg) in MeCN (4.0 mL) at 80 ºC (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **4f** (47.7 mg, 84%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.3 Hz, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 7.95 – 7.93 (m, 3H), 7.78 – 7.72 (m, 3H), 3.54 – 3.52 (m, 2H), 2.92 – 2.90 (m, 2H); ^{13}C NMR

(100 MHz, $CDCl_3$) δ 203.5, 167.2, 154.8, 149.0, 142.0, 133.2, 131.6, 130.6, 130.4, 128.1, 125.3, 123.9, 118.9, 112.8, 36.4, 23.9; IR (neat): 2913, 2223, 1703, 1612, 1547, 1410, 1272, 846, 763; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{13}N_2O$ 285.1022, found 285.1020.

4-(*p*-tolyl)-1,2-dihydro-3*H*-cyclopenta[*c*]quinolin-3-one (4g)

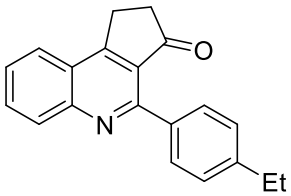


4g

The reaction was conducted with 5-(1*H*-indol-3-yl)-1-(*p*-tolyl)pent-1-yn-3-one (**3g**, 0.2 mmol, 57.4 mg), TBHP (0.4 mmol, 36.0 mg), $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg), and NaBARF (0.02 mmol, 17.7 mg) in MeCN (4.0 mL) at 80 °C (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **4g** (43.1 mg, 79%) as a pale yellow oil.

^1H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.1 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.88 (t, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 6.2 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.30 (d, *J* = 6.6 Hz, 2H), 3.49 – 3.47 (m, 2H), 2.88 – 2.87 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.7, 166.8, 157.2, 149.2, 139.4, 134.8, 132.7, 130.3, 129.7, 128.6, 127.5, 127.1, 124.9, 123.8, 36.5, 23.7, 21.5; IR (neat): 2918, 2853, 1715, 1612, 1550, 1408, 1181, 812, 755; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{16}NO$ 274.1226, found 274.1223.

4-(4-ethylphenyl)-1,2-dihydro-3*H*-cyclopenta[*c*]quinolin-3-one (4h)

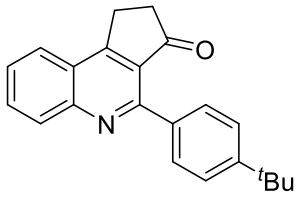


4h

The reaction was conducted with 1-(4-ethylphenyl)-5-(1*H*-indol-3-yl)pent-1-yn-3-one (**3h**, 0.2 mmol, 60.2 mg), TBHP (0.4 mmol, 36.0 mg), $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg), and NaBARF (0.02 mmol, 17.7 mg) in MeCN (4.0 mL) at 80 °C (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **4h** (39.0 mg, 68%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 8.1 Hz, 1H), 7.88 (t, *J* = 7.7 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 3.49 – 3.47 (m, 2H), 2.89 – 2.86 (m, 2H), 2.74 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.6, 166.8, 157.2, 149.2, 145.7, 135.1, 132.6, 130.3, 129.8, 127.5, 127.4, 127.1, 124.9, 123.7, 36.5, 28.8, 23.7, 15.4; IR (neat): 2918, 2251, 1712, 1615, 1550, 1414, 1263, 908, 729; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{18}NO$ 288.1383, found 288.1380.

4-(4-(*tert*-butyl)phenyl)-1,2-dihydro-3*H*-cyclopenta[*c*]quinolin-3-one (4i)

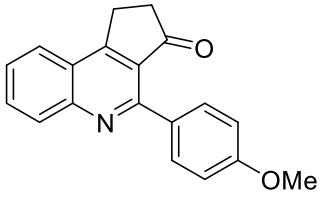


4i

The reaction was conducted with 1-(4-(*tert*-butyl)phenyl)-5-(1*H*-indol-3-yl)pent-1-yn-3-one (**3i**, 0.2 mmol, 65.8 mg), TBHP (0.4 mmol, 36.0 mg), $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg), and NaBARF (0.02 mmol, 17.7 mg) in MeCN (4.0 mL) at 80 °C (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **4i** (40.0 mg, 63%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.2 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.87 (t, *J* = 7.5 Hz, 1H), 7.80 (d, *J* = 7.1 Hz, 2H), 7.64 (t, *J* = 7.3 Hz, 1H), 7.52 (d, *J* = 7.1 Hz, 2H), 3.48 – 3.46 (m, 2H), 2.88 – 2.86 (m, 2H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.7, 166.8, 157.1, 152.4, 149.2, 134.8, 132.6, 130.3, 129.5, 127.5, 127.1, 124.9, 123.7, 36.5, 34.7, 31.3, 23.7; IR (neat): 2958, 2319, 1709, 1615, 1544, 1402, 1198, 942, 752; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{22}NO$ 316.1696, found 316.1692.

4-(4-methoxyphenyl)-1,2-dihydro-3*H*-cyclopenta[*c*]quinolin-3-one (4j)

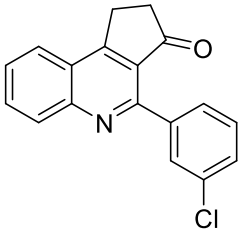


4j

The reaction was conducted with 5-(1*H*-indol-3-yl)-1-(4-methoxyphenyl)pent-1-yn-3-one (**3j**, 0.2 mmol, 60.6 mg), TBHP (0.4 mmol, 36.0 mg), $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg), and NaBARF (0.02 mmol, 17.7 mg) in MeCN (4.0 mL) at 80 ºC (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **4j** (39.9 mg, 69%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.5 Hz, 1H), 8.06 (d, *J* = 8.2 Hz, 1H), 7.90 – 7.83 (m, 3H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 8.5 Hz, 2H), 3.89 (s, 3H), 3.51 – 3.48 (m, 2H), 2.91 – 2.88 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.8, 167.0, 160.8, 156.8, 149.2, 132.7, 131.5, 130.2, 127.4, 127.0, 124.8, 123.8, 113.4, 55.3, 36.5, 23.7; IR (neat): 2918, 2191, 1706, 1607, 1248, 1172, 1025, 837, 755; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{16}NO_2$ 290.1176, found 290.1172.

4-(3-chlorophenyl)-1,2-dihydro-3H-cyclopenta[c]quinolin-3-one (4k)

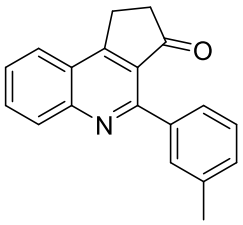


4k

The reaction was conducted with 1-(3-chlorophenyl)-5-(1*H*-indol-3-yl)pent-1-yn-3-one (**3k**, 0.2 mmol, 61.6 mg), TBHP (0.4 mmol, 36.0 mg), $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg), and NaBARF (0.02 mmol, 17.7 mg) in MeCN (4.0 mL) at 80 ºC (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **4k** (40.0 mg, 68%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 8.2 Hz, 1H), 7.91 (t, *J* = 7.7 Hz, 1H), 7.84 (s, 1H), 7.69 (t, *J* = 8.0 Hz, 2H), 7.46 – 7.39 (m, 2H), 3.51 – 3.49 (m, 2H), 2.90 – 2.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.4, 167.0, 155.5, 149.0, 139.3, 133.8, 132.9, 130.3, 129.8, 129.4, 129.0, 128.2, 127.6, 127.4, 125.2, 123.8, 36.4, 23.8; IR (neat): 2921, 2850, 1703, 1615, 1416, 1198, 1081, 877, 758; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{13}ClNO$ 294.0680, found 294.0676.

4-(*m*-tolyl)-1,2-dihydro-3*H*-cyclopenta[*c*]quinolin-3-one (4l)

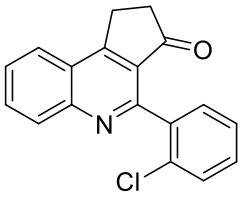


4l

The reaction was conducted with 5-(1*H*-indol-3-yl)-1-(*m*-tolyl)pent-1-yn-3-one (**3l**, 0.2 mmol, 57.4 mg), TBHP (0.4 mmol, 36.0 mg), $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg), and NaBARF (0.02 mmol, 17.7 mg) in MeCN (4.0 mL) at 80 °C (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **4l** (34.9 mg, 64%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 8.2 Hz, 1H), 7.89 (t, *J* = 7.7 Hz, 1H), 7.68 – 7.57 (m, 3H), 7.38 (t, *J* = 6.9 Hz, 1H), 7.30 – 7.26 (m, 1H), 3.51 – 3.49 (m, 2H), 2.89 – 2.87 (m, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.6, 166.8, 157.4, 149.1, 137.6, 137.5, 132.7, 130.3, 130.2, 130.1, 127.7, 127.6, 127.2, 127.1, 125.0, 123.8, 36.5, 23.8, 21.5; IR (neat): 2921, 2181, 1715, 1615, 1556, 1408, 1181, 1033, 755; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{16}NO$ 274.1226, found 274.1224.

4-(2-chlorophenyl)-1,2-dihydro-3*H*-cyclopenta[*c*]quinolin-3-one (4m)

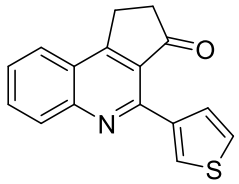


4m

The reaction was conducted with 1-(2-chlorophenyl)-5-(1*H*-indol-3-yl)pent-1-yn-3-one (**3m**, 0.2 mmol, 61.6 mg), TBHP (0.4 mmol, 36.0 mg), $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg), and NaBARF (0.02 mmol, 17.7 mg) in MeCN (4.0 mL) at 80 °C (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **4m** (39.4 mg, 67%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.3 Hz, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 7.92 (t, *J* = 7.6 Hz, 1H), 7.72 (t, *J* = 7.4 Hz, 1H), 7.50 – 7.40 (m, 4H), 3.59 – 3.46 (m, 2H), 2.92 – 2.79 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 165.4, 154.6, 149.1, 137.4, 133.1, 132.7, 130.4, 130.2, 130.0, 129.2, 128.8, 127.8, 126.8, 125.6, 124.0, 36.2, 23.9; IR (neat): 2921, 2850, 1712, 1612, 1556, 1431, 1027, 945, 752; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{13}ClNO$ 294.0680, found 294.0678.

4-(thiophen-3-yl)-1,2-dihydro-3*H*-cyclopenta[*c*]quinolin-3-one (4n)



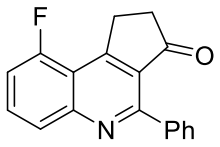
4n

The reaction was conducted with 5-(1*H*-indol-3-yl)-1-(thiophen-3-yl)pent-1-yn-3-one (**3n**, 0.2 mmol, 55.8 mg), TBHP (0.4 mmol, 36.0 mg), $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg), and NaBARF (0.02 mmol, 17.7 mg) in MeCN (4.0 mL) at 80 °C (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **4n** (36.0 mg, 68%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.89 – 7.84 (m, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.41 – 7.36 (m, 1H), 3.46 – 3.44 (m, 2H), 2.90 – 2.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.1, 167.2, 151.5, 149.1,

139.5, 132.7, 130.1, 129.3, 129.0, 127.5, 127.1, 124.8, 124.3, 123.7, 36.5, 23.8; IR (neat): 3111, 2915, 1700, 1558, 1436, 1311, 1181, 871, 756; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{12}NOS$ 266.0634, found 266.0632.

9-fluoro-4-phenyl-1,2-dihydro-3*H*-cyclopenta[*c*]quinolin-3-one (4o)

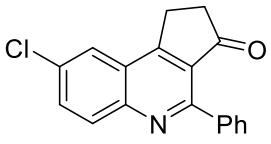


4o

The reaction was conducted with 5-(4-fluoro-1*H*-indol-3-yl)-1-phenylpent-1-yn-3-one (**3o**, 0.2 mmol, 58.2 mg), TBHP (0.4 mmol, 36.0 mg), $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg), and NaBARF (0.02 mmol, 17.7 mg) in MeCN (4.0 mL) at 80 °C (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **4o** (30.5 mg, 55%) as a pale yellow oil.

^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.79 – 7.74 (m, 3H), 7.55 – 7.49 (m, 3H), 7.29 (t, *J* = 9.3 Hz, 1H), 3.76 – 3.65 (m, 2H), 2.85 – 2.83 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.1, 165.0, 160.7, 158.2 (d, *J* = 4.0 Hz), 150.3 (d, *J* = 2.0 Hz), 137.3, 132.3 (d, *J* = 9.0 Hz), 129.8, 129.6, 128.2, 128.1, 127.9, 126.2 (d, *J* = 4.0 Hz), 116.1 (d, *J* = 14.0 Hz), 111.8 (d, *J* = 20.0 Hz), 36.4 (d, *J* = 2.8 Hz), 27.0 (d, *J* = 7.5 Hz); IR (neat): 2924, 2850, 1712, 1624, 1575, 1391, 1192, 1021, 780; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{13}FNO$ 278.0976, found 278.0974.

8-chloro-4-phenyl-1,2-dihydro-3*H*-cyclopenta[*c*]quinolin-3-one (4p)



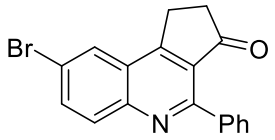
4p

The reaction was conducted with 5-(5-chloro-1*H*-indol-3-yl)-1-phenylpent-1-yn-3-one (**3p**, 0.2 mmol, 61.6 mg), TBHP (0.4 mmol, 36.0 mg), $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3

mg), and NaBARF (0.02 mmol, 17.7 mg) in MeCN (4.0 mL) at 80 ºC (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **4p** (45.3 mg, 77%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (t, *J* = 9.1 Hz, 1H), 8.04 (d, *J* = 7.2 Hz, 1H), 7.88 – 7.76 (m, 3H), 7.57 – 7.51 (m, 3H), 3.51 – 3.41 (m, 2H), 2.93 – 2.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.2, 165.9, 157.4, 147.5, 137.3, 133.4, 133.2, 131.9, 129.8, 129.6, 128.2, 127.9, 125.8, 122.8, 36.4, 23.7; IR (neat): 2921, 2850, 1712, 1547, 1487, 1385, 1183, 834, 712; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{13}ClNO$ 294.0680, found 294.0678.

8-bromo-4-phenyl-1,2-dihydro-3*H*-cyclopenta[*c*]quinolin-3-one (4q)

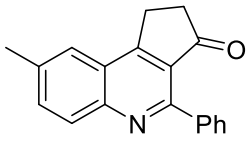


4q

The reaction was conducted with 5-(5-bromo-1*H*-indol-3-yl)-1-phenylpent-1-yn-3-one (**3q**, 0.2 mmol, 70.4 mg), TBHP (0.4 mmol, 36.0 mg), $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg), and NaBARF (0.02 mmol, 17.7 mg) in MeCN (4.0 mL) at 80 ºC (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **4q** (45.3 mg, 67%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.18 (m, 1H), 8.11 – 8.07 (m, 1H), 7.95 – 7.92 (m, 1H), 7.86 – 7.80 (m, 2H), 7.55 – 7.48 (m, 3H), 3.45 – 3.42 (m, 2H), 2.90 – 2.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.1, 165.7, 157.5, 147.7, 137.3, 135.9, 132.0, 129.8, 129.6, 128.2, 127.9, 126.3, 126.1, 121.3, 36.4, 23.7; IR (neat): 3924, 2847, 1715, 1544, 1385, 1181, 954, 840, 698; HRMS (ESI) m/z: [M + H]+ calcd for $C_{18}H_{13}BrNO$ 338.0175, found 338.0173.

8-methyl-4-phenyl-1,2-dihydro-3*H*-cyclopenta[*c*]quinolin-3-one (4r)

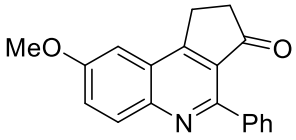


4r

The reaction was conducted with 5-(5-methyl-1*H*-indol-3-yl)-1-phenylpent-1-yn-3-one (**3r**, 0.2 mmol, 57.4 mg), TBHP (0.4 mmol, 36.0 mg), $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg), and NaBARF (0.02 mmol, 17.7 mg) in MeCN (4.0 mL) at 80 ºC (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **4r** (33.3 mg, 61%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.6 Hz, 1H), 7.82 – 7.80 (m, 3H), 7.72 (d, *J* = 8.6 Hz, 1H), 7.51 – 7.47 (m, 3H), 3.46 – 3.43 (m, 2H), 2.88 – 2.85 (m, 2H), 2.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.7, 166.1, 156.2, 147.6, 137.8, 137.4, 134.9, 130.0, 129.7, 129.2, 127.8, 127.5, 125.0, 122.7, 36.5, 23.7, 21.7; IR (neat): 2918, 2200, 1717, 1561, 1436, 1172, 1072, 826, 692; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{16}NO$ 274.1226, found 274.1225.

8-methoxy-4-phenyl-1,2-dihydro-3*H*-cyclopenta[*c*]quinolin-3-one (4s)



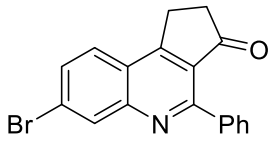
4s

The reaction was conducted with 5-(5-methoxy-1*H*-indol-3-yl)-1-phenylpent-1-yn-3-one (**3s**, 0.2 mmol, 60.6 mg), TBHP (0.4 mmol, 36.0 mg), $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg), and NaBARF (0.02 mmol, 17.7 mg) in MeCN (4.0 mL) at 80 ºC (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **4s** (43.4 mg, 75%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 9.2 Hz, 1H), 7.79 (d, *J* = 7.0 Hz, 2H), 7.53 – 7.47 (m, 4H), 7.21 (d, *J* = 2.4 Hz, 1H), 3.98 (s, 3H), 3.41 – 3.38 (m, 2H), 2.87 – 2.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.8, 165.1, 158.4, 154.6, 145.0, 137.8, 131.7, 129.7, 129.0, 127.8, 127.5, 126.0, 124.7, 101.6, 55.7, 36.5, 23.8; IR (neat): 2921, 2847,

1706, 1558, 1405, 1218, 1027, 832, 689; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{16}NO_2$ 290.1176, found 290.1172.

7-bromo-4-phenyl-1,2-dihydro-3*H*-cyclopenta[*c*]quinolin-3-one (4t)



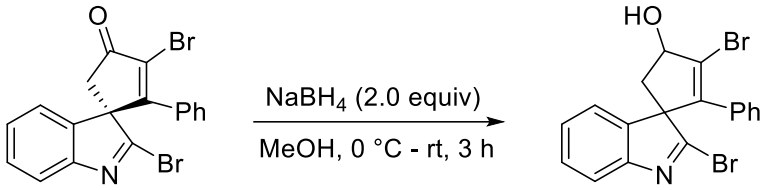
4t

The reaction was conducted with 5-(6-bromo-1*H*-indol-3-yl)-1-phenylpent-1-yn-3-one (**3t**, 0.2 mmol, 70.4 mg), TBHP (0.4 mmol, 36.0 mg), $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg), and NaBARF (0.02 mmol, 17.7 mg) in MeCN (4.0 mL) at 80 ºC (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **4t** (58.1 mg, 86%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.89 (d, *J* = 6.6 Hz, 1H), 7.81 – 7.80 (m, 2H), 7.72 (d, *J* = 8.6 Hz, 1H), 7.58 – 7.49 (m, 3H), 3.46 – 3.44 (m, 2H), 2.87 – 2.85 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.1, 166.7, 158.2, 149.6, 137.2, 132.7, 130.8, 129.8, 129.7, 127.9, 127.8, 127.3, 125.0, 123.7, 36.4, 23.7; IR (neat): 2924, 2847, 1715, 1601, 1547, 1408, 1073, 899, 692; HRMS (ESI) m/z: [M + H]+ calcd for $C_{18}H_{13}BrNO$ 338.0175, found 338.0173.

Synthetic Applications

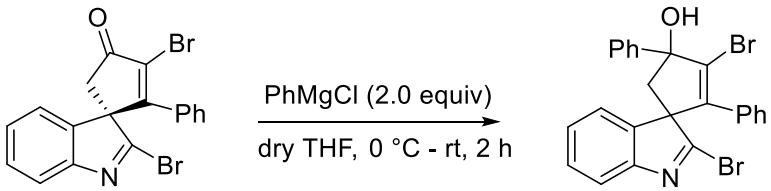
2',3-dibromo-2-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-ol (5)



2a **5**, 66%

$NaBH_4$ (0.4 mmol, 15.2 mg) was added to a solution of compound **2a** (0.2 mmol, 83.4 mg) in MeOH at 0 °C. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. Upon completion, the mixture was then concentrated and the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford the desired product **5** (55.3 mg, 66% yield, yellow oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.6 Hz, 1H), 7.39 – 7.30 (m, 3H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.16 – 7.12 (m, 2H), 6.81 (d, *J* = 7.5 Hz, 2H), 5.27 (t, *J* = 6.3 Hz, 1H), 2.69 – 2.55 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 153.5, 141.7, 141.3, 132.0, 129.1, 128.9, 128.2, 127.5, 126.9, 122.0, 120.9, 78.1, 74.1, 41.7; IR (neat): 3239(br), 2924, 2245, 1712, 1618, 1470, 1326, 1192, 752, 692; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{14}Br_2NO$ 417.9437, found 417.9443.

2',3-dibromo-2,4-diphenylspiro[cyclopentane-1,3'-indol]-2-en-4-ol (6)

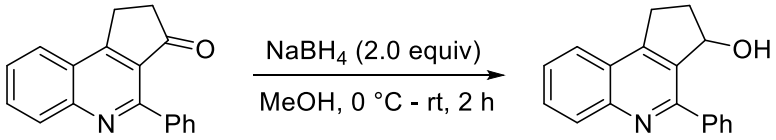


2a **6**, 72%

PhMgCl (0.4 mL, 0.4 mmol, 1.0 M in THF) was added to a solution of the compound **2a** (0.2 mmol, 83.4 mg) in dry THF (4.0 mL) at 0 °C. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. Upon completion, the mixture was then concentrated and the residue was purified by

chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford the desired product **6** (71.3 mg, 72% yield, yellow oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.51 – 7.47 (m, 2H), 7.43 – 7.14 (m, 8H), 6.97 (d, *J* = 8.0 Hz, 2H), 3.06 (d, *J* = 15.1 Hz, 1H), 2.98 (s, 1H), 2.83 (d, *J* = 15.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 153.7, 144.5, 142.8, 141.4, 132.6, 132.1, 129.0, 128.9, 128.7, 128.1, 128.0, 127.9, 126.9, 125.6, 122.5, 120.7, 87.0, 74.8, 48.8; IR (neat): 3228(br), 3057, 2921, 1706, 1612, 1470, 1317, 1218, 749, 692; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{18}Br_2NO$ 493.9750, found 493.9769.

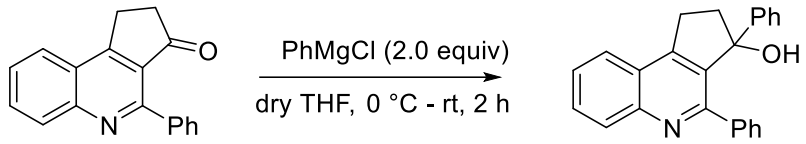
4-phenyl-2,3-dihydro-1*H*-cyclopenta[*c*]quinolin-3-ol (7)



4a **7**, 97%

$NaBH_4$ (0.4 mmol, 15.2 mg) was added dropwise to a solution of compound **4a** (0.2 mmol, 51.8 mg) in MeOH (4.0 mL) at 0 ^{o}C. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. Upon completion, the mixture was then concentrated and the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford the desired product **7** (50.6 mg, 97% yield, yellow oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 6.9 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.55 – 7.43 (m, 4H), 5.58 (d, *J* = 4.7 Hz, 1H), 3.49 – 3.41 (m, 1H), 3.24 – 3.16 (m, 1H), 2.54 – 2.45 (m, 1H), 2.33 (s, 1H), 2.22 – 2.16 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 152.1, 148.1, 139.8, 135.7, 129.9, 129.6, 128.8(2), 128.7(9), 128.7, 126.4, 125.1, 124.3, 75.6, 34.7, 28.5; IR (neat): 3347(br), 3061, 2927, 2240, 1583, 1496, 1357, 1044, 891, 695; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{16}NO$ 262.1226, found 262.1225.

3,4-diphenyl-2,3-dihydro-1*H*-cyclopenta[*c*]quinolin-3-ol (8)



4a **8**, 99%

PhMgCl (0.4 mL, 0.4 mmol, 1.0 M in THF) was added dropwise to a solution of compound **4a** (0.2 mmol, 51.8 mg) in dry THF (4.0 mL) at 0 °C. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. Upon completion, the mixture was then concentrated and the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford the desired product **8** (66.7 mg, 99% yield, yellow oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.25 – 7.18 (m, 8H), 7.10 (d, *J* = 7.8 Hz, 2H), 3.49 – 3.42 (m, 1H), 3.30 – 3.22 (m, 1H), 2.67 – 2.53 (m, 2H), 2.47 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 151.5, 147.8, 147.3, 139.6, 138.0, 130.0, 129.7, 128.6, 128.3(3), 128.2(6), 128.1, 126.8, 126.7, 124.9, 124.6, 124.2, 86.5, 45.1, 27.4; IR (neat): 3361(br), 3063, 2924, 1956, 1737, 1578, 1490, 1050, 763, 698; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{20}NO$ 338.1539, found 338.1537.

Reference

(1) D. Dagoneau, Q. Wang, J. Zhu, *Chem. Eur. J.* 2020, **26**, 4866-4873.

(2) P. Fedoseev, E. Van der Eycken, *Chem. Commun.* 2017, **53**, 7732-7735.

(3) M. J. James, J. D. Cuthbertson, P. O'Brien, R. J. K. Taylor, W. P. Unsworth, *Angew. Chem. Int. Ed.* 2015, **54**, 7640 –7643.

2',3-dibromo-2-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-one (2a). CCDC Number = 2132356

Crystal of **2a** was grown by slow evaporation of hexane/ethyl acetate solution of **2a** at room temperature (25 °C). X-ray diffraction data was collected at 293 K on a Rigaku Gemini E diffractometer with graded-multilayer focused CuK(alpha) X-rays.

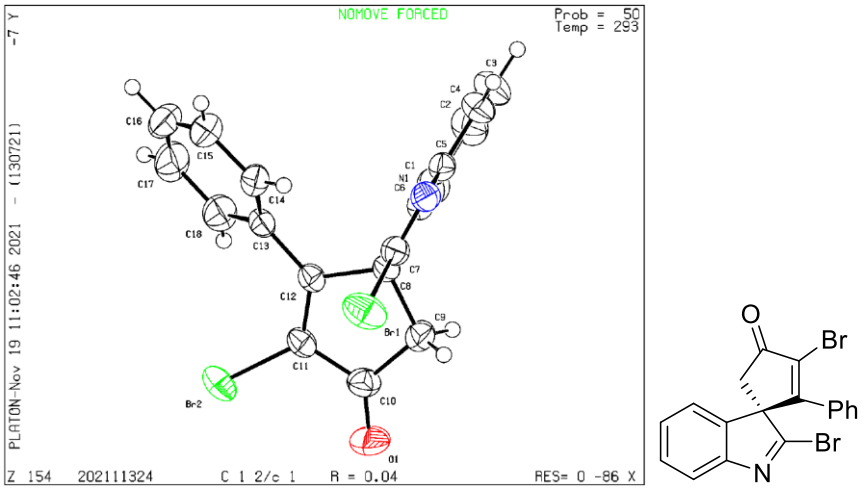


Figure S1. Crystal structure of **2a** with thermal ellipsoids at 50% probability

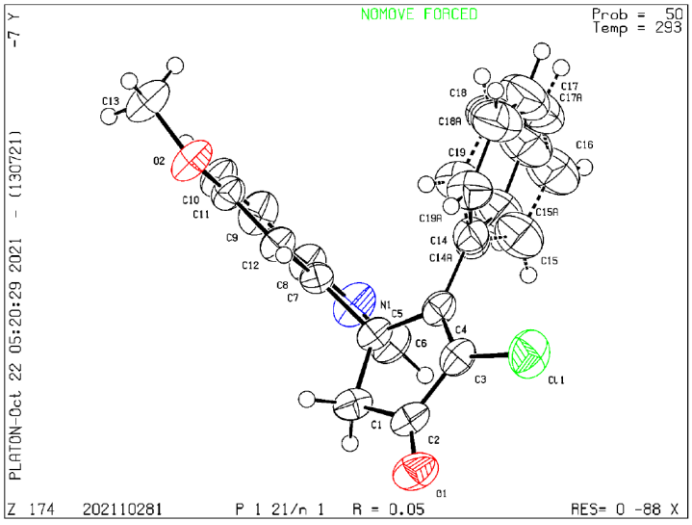
---

```
Bond precision:   C-C = 0.0049 A          Wavelength=1.54184

Cell:             a=14.2057(2)     b=10.32140(14)      c=21.0985(3)
                  alpha=90         beta=95.5952(14)    gamma=90
Temperature:      293 K

                  Calculated                Reported
Volume            3078.78(7)                3078.78(8)
Space group       C 2/c                     C 1 2/c 1
Hall group        -C 2yc                    -C 2yc
Moiety formula    C18 H11 Br2 N O           C18 H11 Br2 N O
Sum formula       C18 H11 Br2 N O           C18 H11 Br2 N O
Mr                417.08                    417.10
Dx,g cm-3         1.800                     1.800
Z                 8                         8
Mu (mm-1)         6.679                     6.679
F000              1632.0                    1632.0
F000'             1624.30
h,k,lmax          16,12,25                  16,12,25
Nref              2756                      2753
Tmin,Tmax         0.435,0.548               0.735,1.000
Tmin'             0.374

Correction method= # Reported T Limits: Tmin=0.735 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.999          Theta(max)= 67.077

R(reflections)= 0.0353( 2472)                wR2(reflections)=
                                             0.1010( 2753)
S = 1.074                 Npar= 200
```

3-chloro-5'-methoxy-2-phenylspiro[cyclopentane-1,3'-indol]-2-en-4-one (2abb).

CCDC Number = 2132359

Crystal of **2abb** was grown by slow evaporation of hexane/dichloromethane solution of **2abb** at room temperature (25 °C). X-ray diffraction data was collected at 293 K on a Rigaku Gemini E diffractometer with graded-multilayer focused CuK(alpha) X-rays.



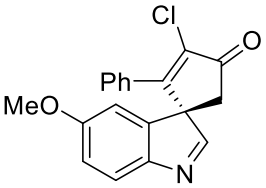


Figure S2. Crystal structure of **2abb** with thermal ellipsoids at 50% probability

---

```
Bond precision:   C-C = 0.0031 A          Wavelength=1.54184

Cell:             a=15.4499(5)     b=6.48001(16)       c=16.3247(5)
                  alpha=90         beta=100.667(3)     gamma=90
Temperature:      293 K

                  Calculated                Reported
Volume            1606.11(8)                1606.11(8)
Space group       P 21/n                    P 1 21/n 1
Hall group        -P 2yn                    -P 2yn
Moiety formula    C19 H14 Cl N O2           C19 H14 Cl N O2
Sum formula       C19 H14 Cl N O2           C19 H14 Cl N O2
Mr                323.76                    323.76
Dx,g cm-3         1.339                     1.339
Z                 4                         4
Mu (mm-1)         2.176                     2.176
F000              672.0                     672.0
F000'             675.27
h,k,lmax          18,7,19                   18,7,19
Nref              2868                      2867
Tmin,Tmax         0.728,0.804               0.968,1.000
Tmin'             0.658

Correction method= # Reported T Limits: Tmin=0.968 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.000          Theta(max)= 67.054

R(reflections)= 0.0459( 2220)                wR2(reflections)=
                                             0.1333( 2867)
S = 1.040                 Npar= 204
```

4-phenyl-1,2-dihydro-3*H*-cyclopenta[*c*]quinolin-3-one (4a). CCDC Number = 2132360

Crystal of **4a** was grown by slow evaporation of hexane/dichloromethane solution of **4a** at room temperature (25 °C). X-ray diffraction data was collected at 293 K on a Rigaku Gemini E diffractometer with graded-multilayer focused CuK(alpha) X-rays.

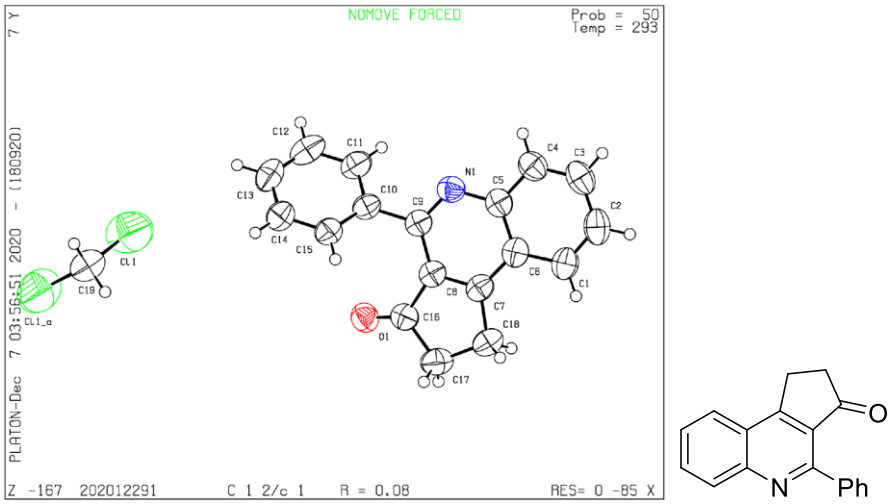


Figure S3. Crystal structure of **4a** with thermal ellipsoids at 50% probability

---

```
Bond precision:  C-C = 0.0066 A          Wavelength=1.54184

Cell:           a=30.272(3)    b=7.2755(2)          c=19.6366(18)
                alpha=90       beta=136.530(17)     gamma=90
Temperature:    293 K

                Calculated                Reported
Volume          2975.4(10)                2975.4(8)
Space group     C 2/c                     C 1 2/c 1
Hall group      -C 2yc                    -C 2yc
Moiety formula  2(C18 H13 N O), C H2 Cl2  2(C18 H13 N O), C H2 Cl2
Sum formula     C37 H28 Cl2 N2 O2         C37 H28 Cl2 N2 O2
Mr              603.51                    603.51
Dx,g cm-3       1.347                     1.347
Z               4                         4
Mu (mm-1)       2.256                     2.256
F000            1256.0                    1256.0
F000'           1262.09
h,k,lmax        36,8,23                   36,8,23
Nref            2668                      2665
Tmin,Tmax       0.719,0.835               0.773,1.000
Tmin'           0.607

Correction method= # Reported T Limits: Tmin=0.773 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.999          Theta(max)= 67.066

R(reflections)= 0.0774( 1929)     wR2(reflections)= 0.2391( 2665)

S = 1.049                 Npar= 195
```

4-hydroxy-3-oxo-4-phenyl-1,2,3,4-tetrahydro-5*H*-cyclopenta[*c*]quinoline-5-carbaldehyde (4aa). CCDC Number = 2132361

Crystal of **4aa** was grown by slow evaporation of hexane/dichloromethane solution of **4aa** at room temperature (25 °C). X-ray diffraction data was collected at 293 K on a Rigaku Gemini E diffractometer with graded-multilayer focused CuK(alpha) X-rays.

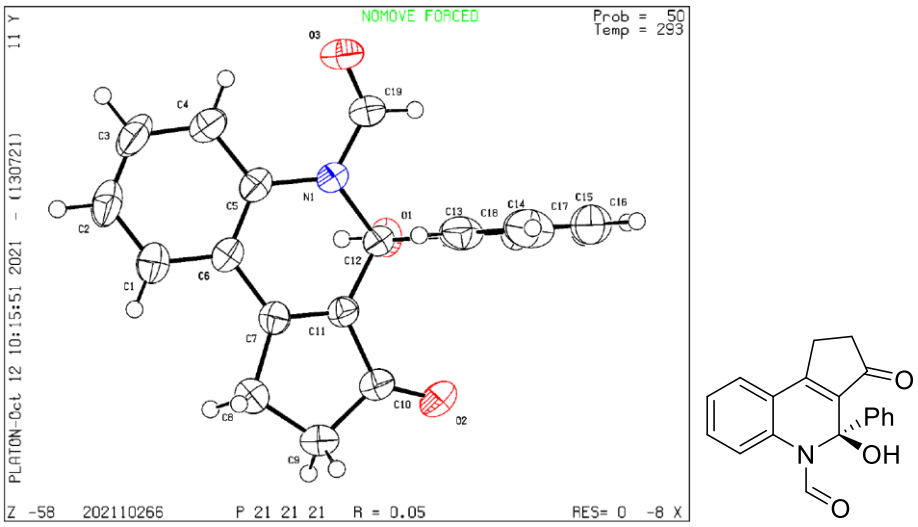


Figure S4. Crystal structure of **4aa** with thermal ellipsoids at 50% probability

---

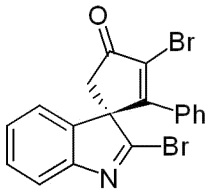
```
Bond precision:   C-C = 0.0051 A          Wavelength=1.54184

Cell:             a=9.0229(4)     b=10.3734(4)     c=15.9971(11)
                  alpha=90        beta=90          gamma=90
Temperature:      293 K

                 Calculated                Reported
Volume           1497.30(14)               1497.31(14)
Space group      P 21 21 21                P 21 21 21
Hall group       P 2ac 2ab                 P 2ac 2ab
Moiety formula   C19 H15 N O3              C19 H15 N O3
Sum formula      C19 H15 N O3              C19 H15 N O3
Mr               305.32                    305.32
Dx,g cm-3        1.354                     1.354
Z                4                         4
Mu (mm-1)        0.749                     0.749
F000             640.0                     640.0
F000'            642.00
h,k,lmax         10,12,19                  10,12,19
Nref             2674[ 1552]               2676
Tmin,Tmax        0.900,0.928               0.907,1.000
Tmin'            0.900

Correction method= # Reported T Limits: Tmin=0.907 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.72/1.00        Theta(max)= 67.068

R(reflections)= 0.0453( 2389)                wR2(reflections)=
                                             0.1192( 2676)
S = 1.052                  Npar= 212
```

2a

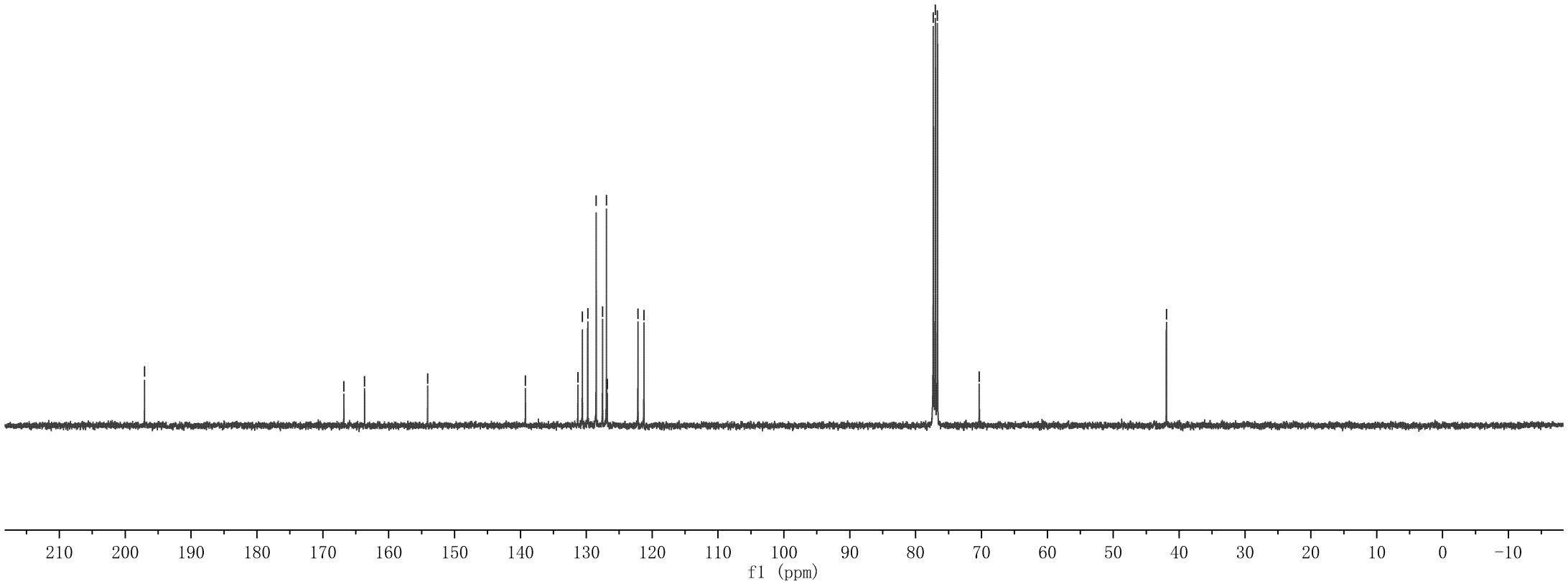
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **2a**

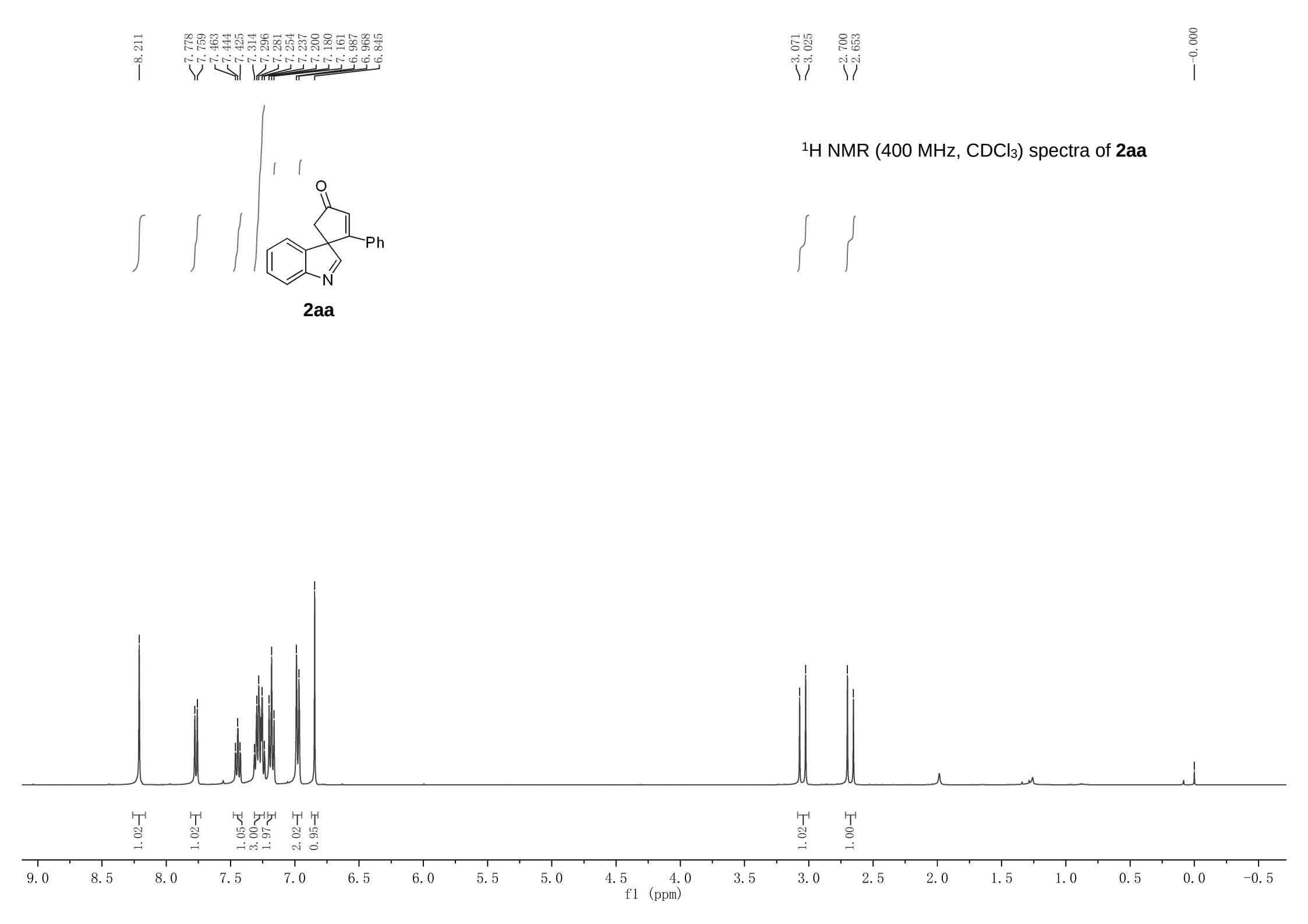
197.06
166.80
163.66
154.09
139.24
131.27
130.60
129.78
128.49
127.53
126.93
126.81
122.16
121.25
77.32
77.00
76.68
70.34
41.93

^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2a**



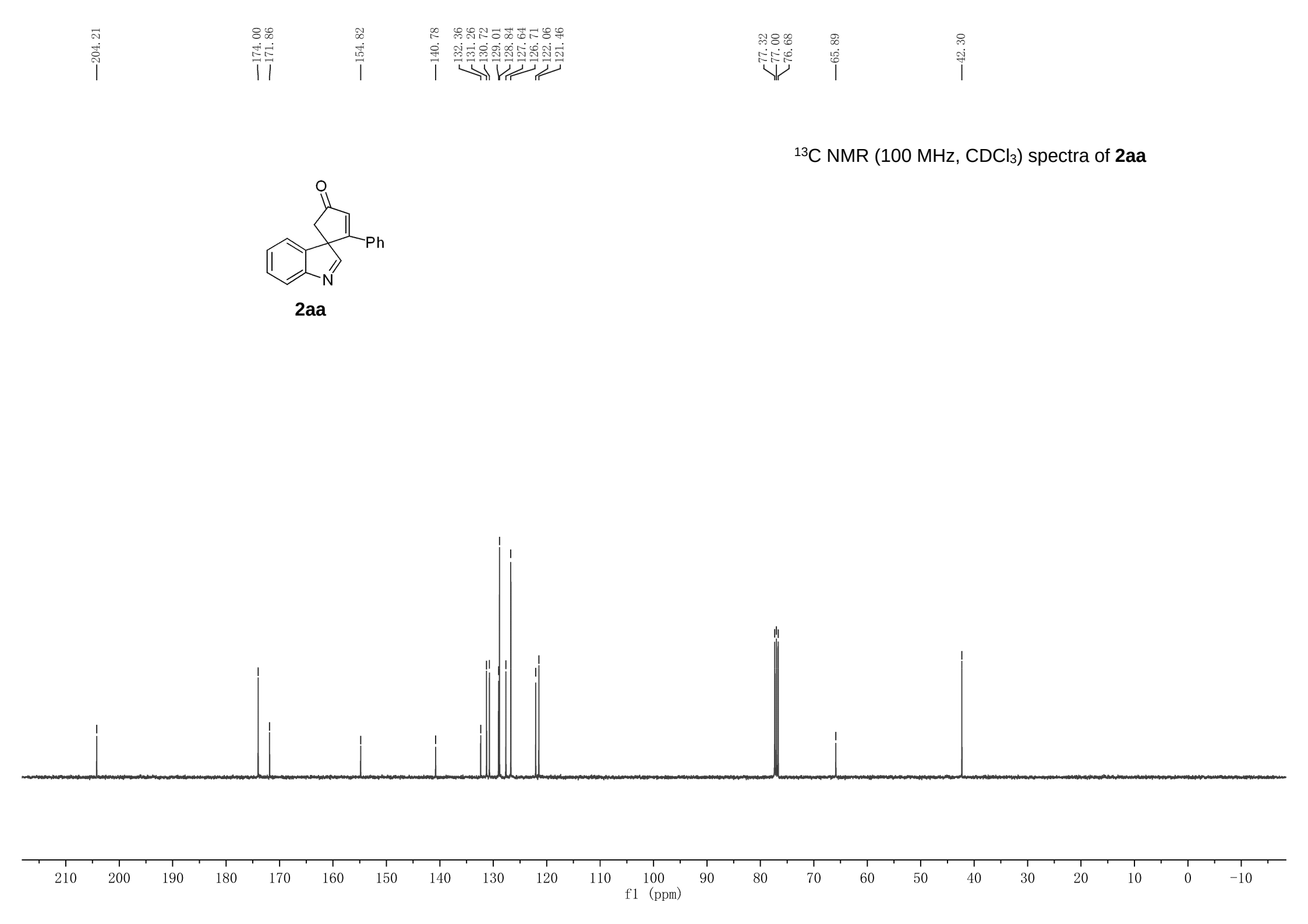
2a



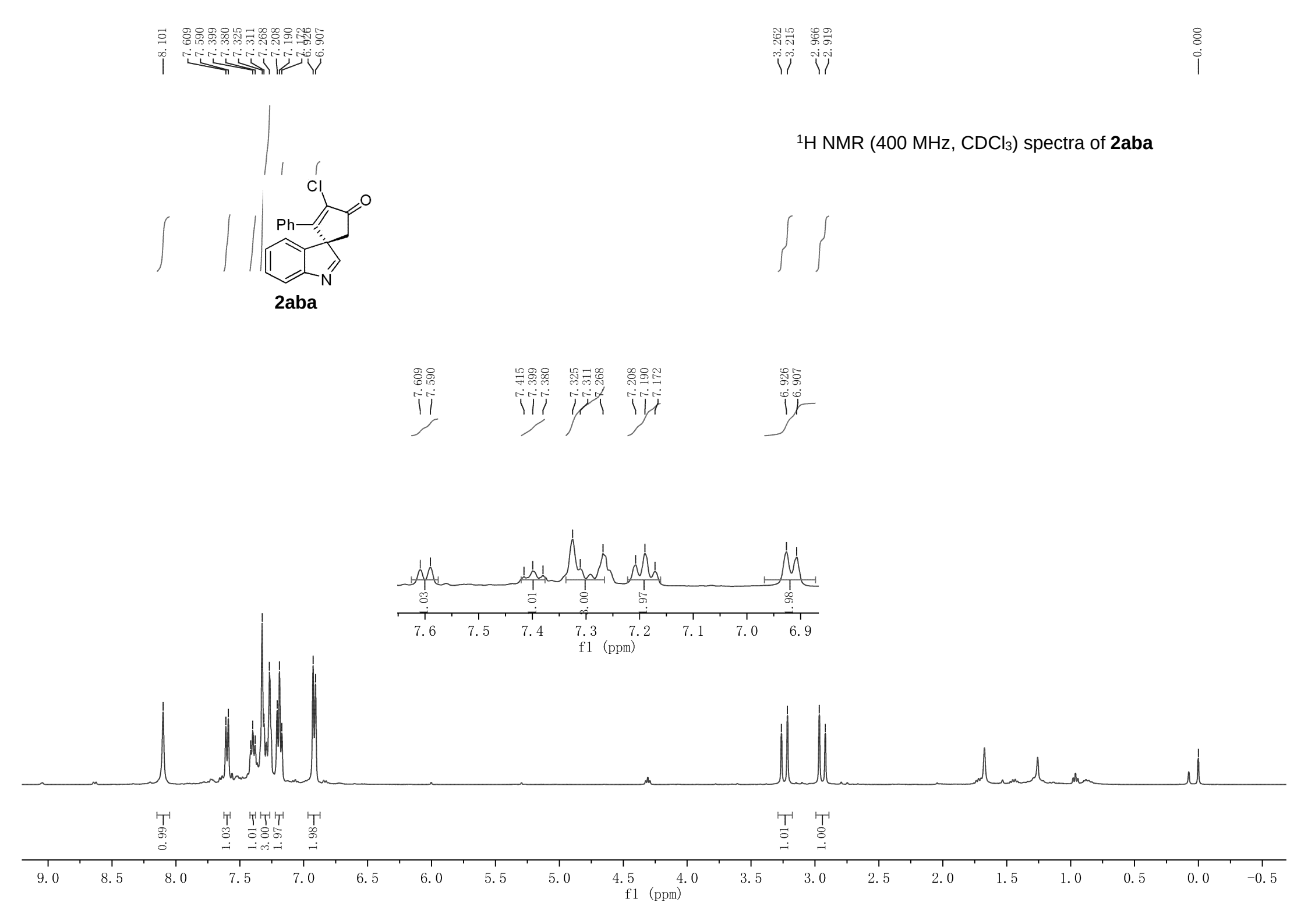


2aa

^{1}H NMR (400 MHz, $CDCl_3$) spectra of **2aa**



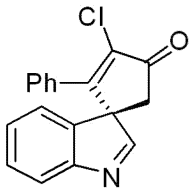
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2aa**



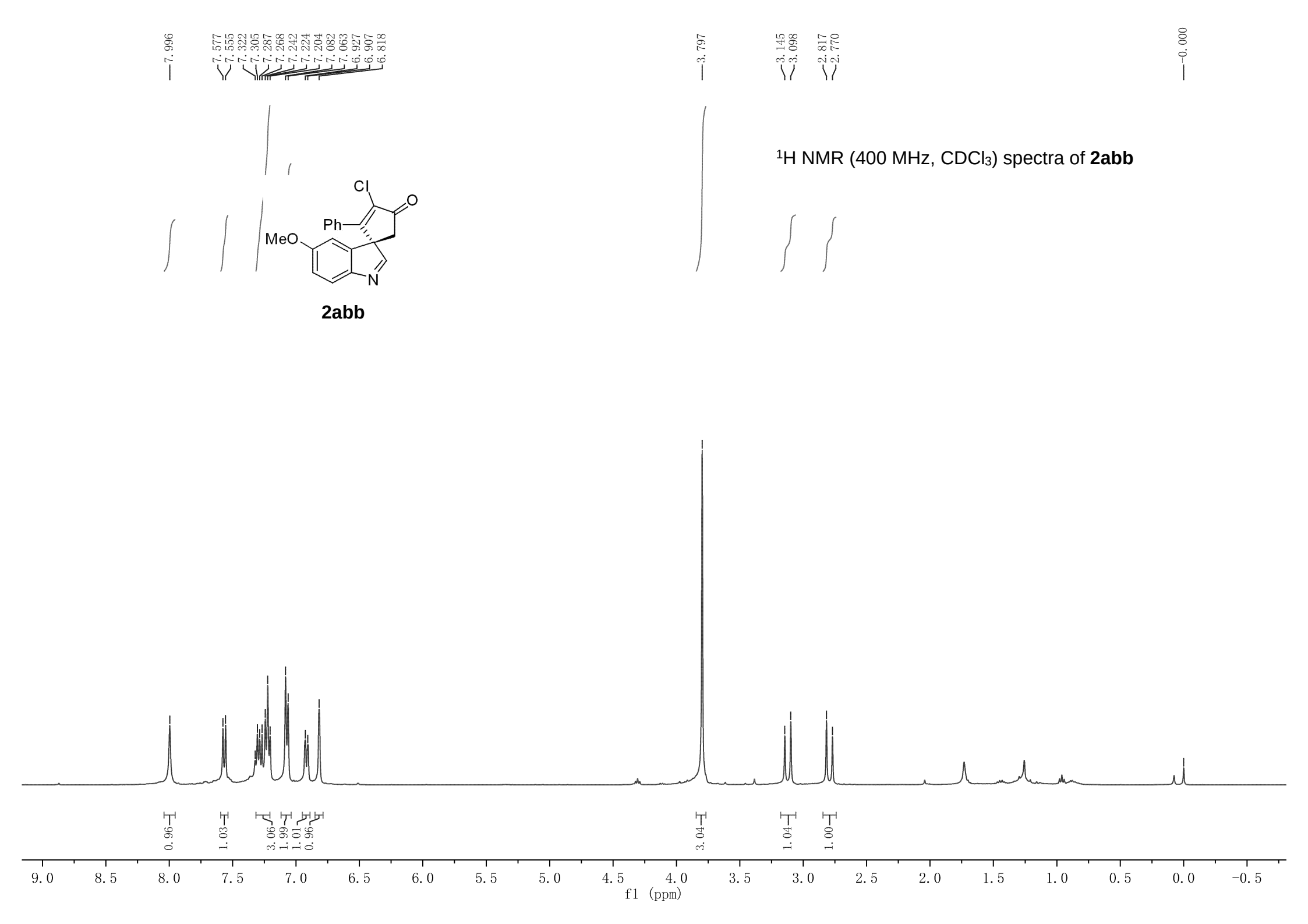
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **2aba**

200.11
174.54
171.47
155.17
138.63
133.51
130.21
129.35
128.34
127.60
126.42
121.92
121.76
105.12
77.32
77.00
76.68
68.83
38.73

^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2aba**



2aba

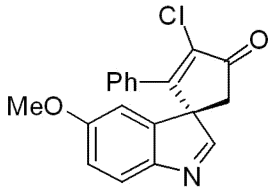


2abb

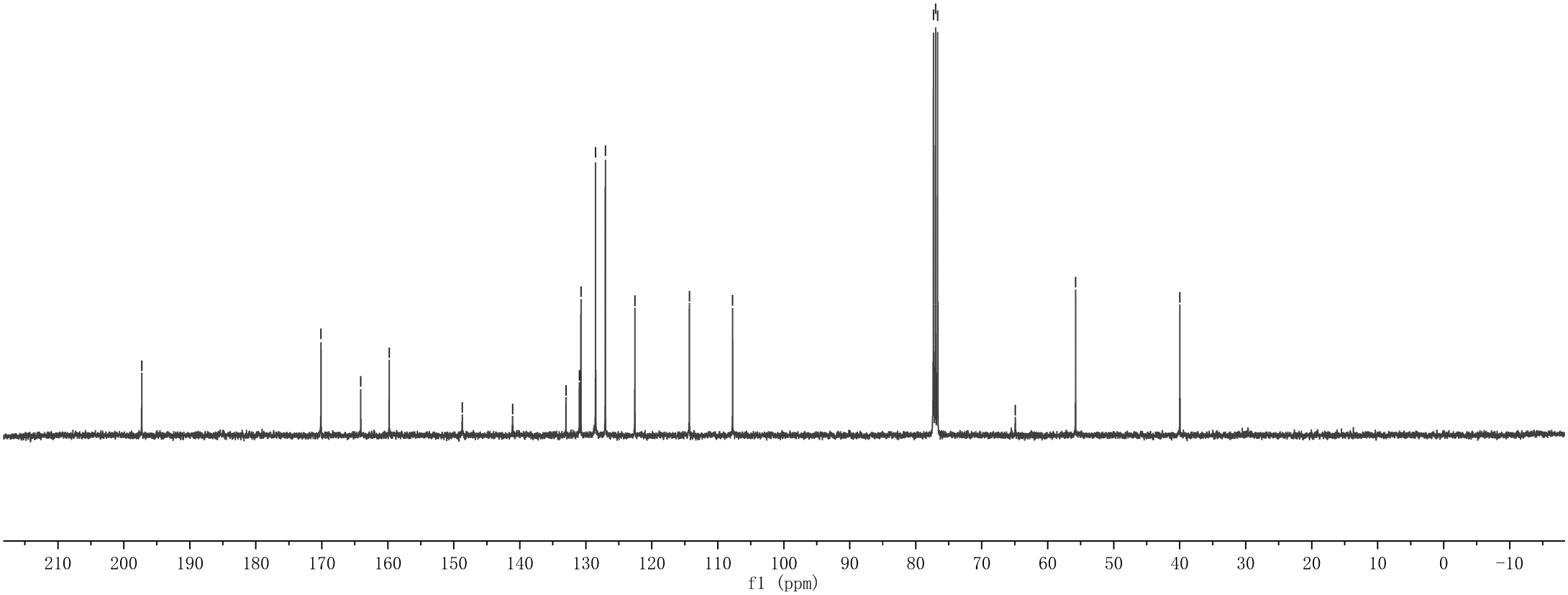
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **2abb**

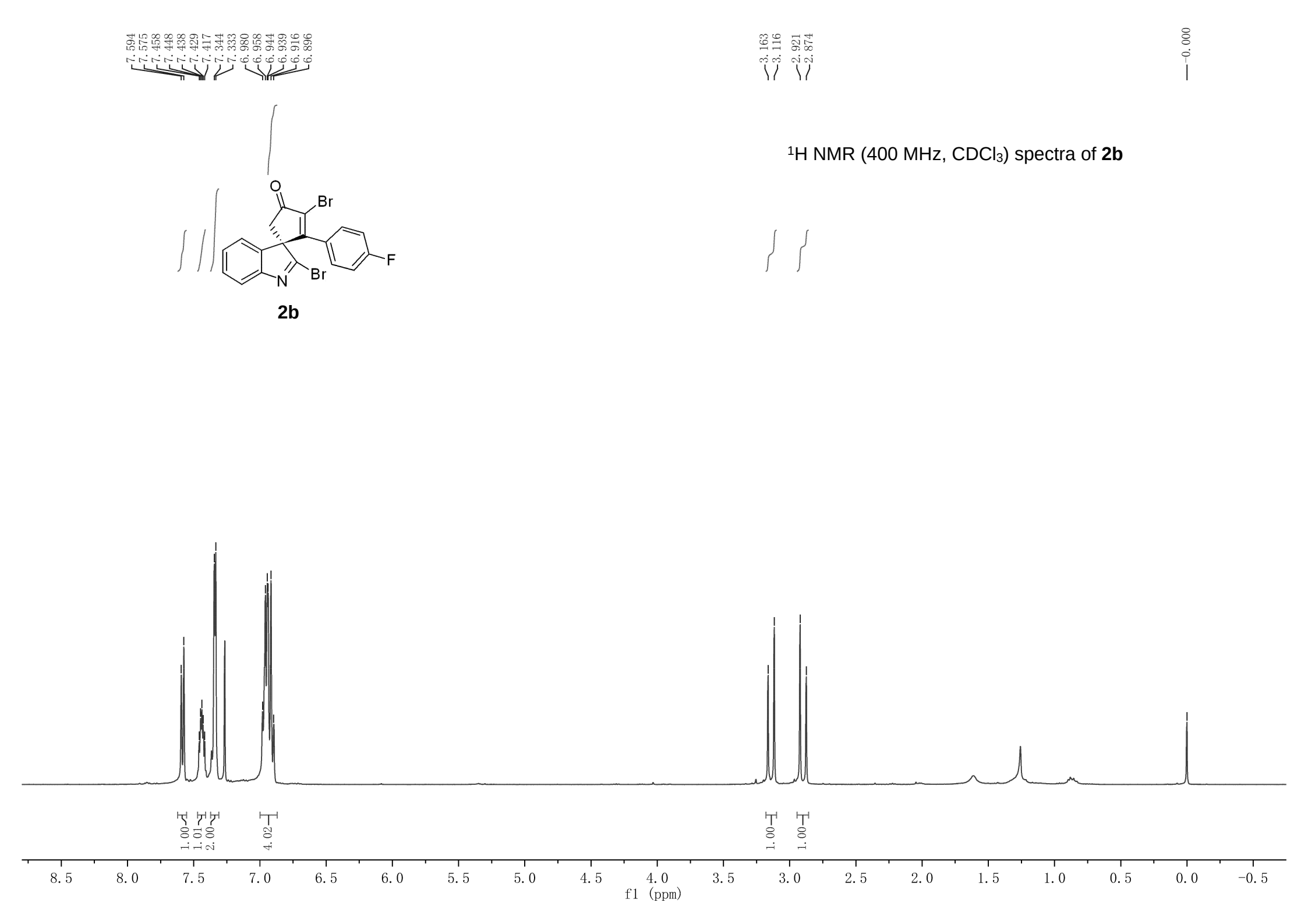
197.29
170.13
164.10
159.79
148.71
141.09
133.00
130.98
130.73
128.52
127.04
122.56
114.30
107.75
77.32
77.00
76.68
64.92
55.78
39.98

^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2abb**



2abb



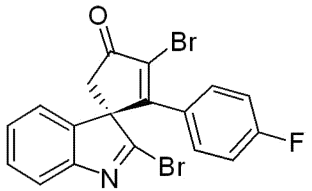


2b

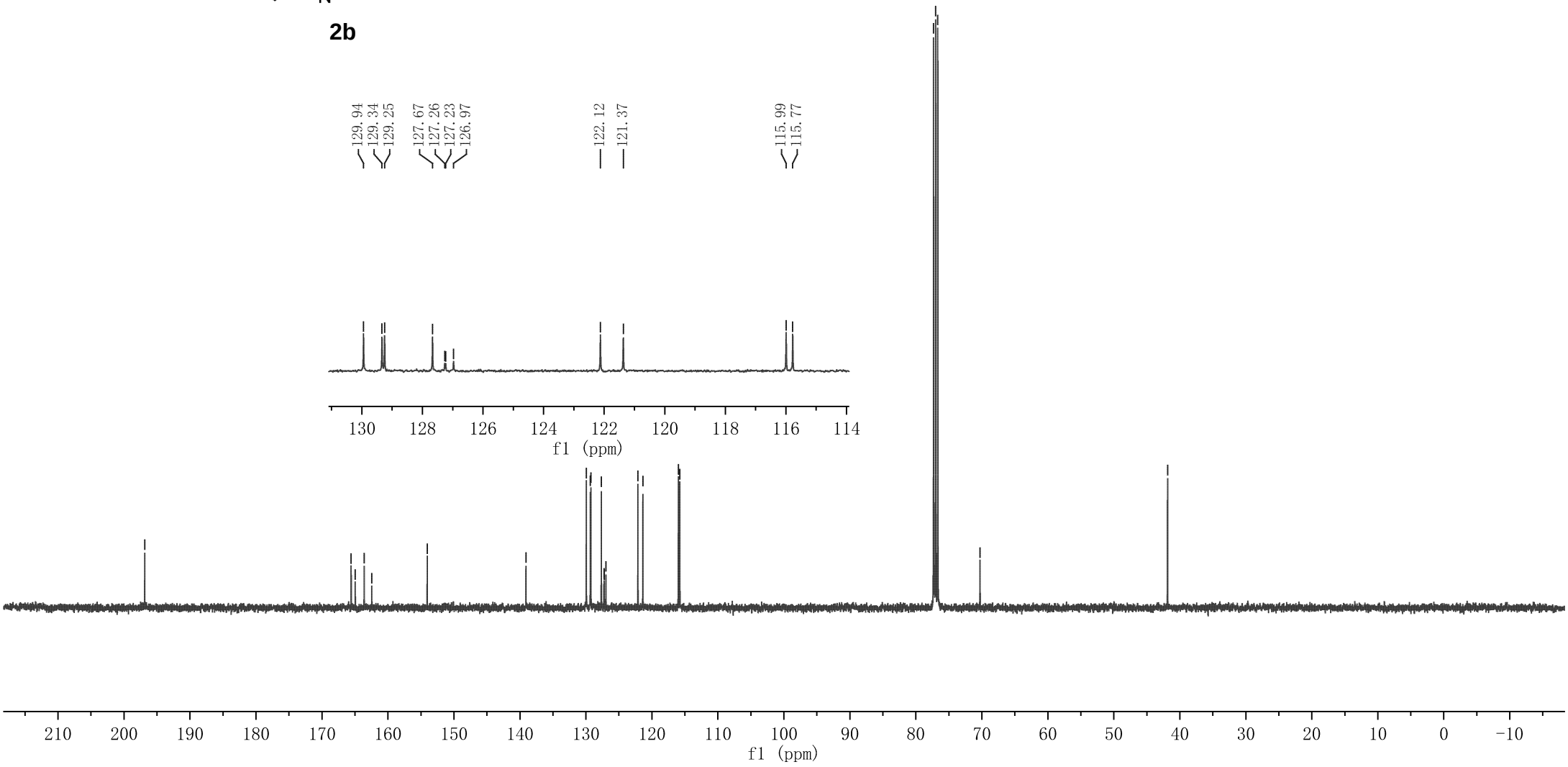
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **2b**

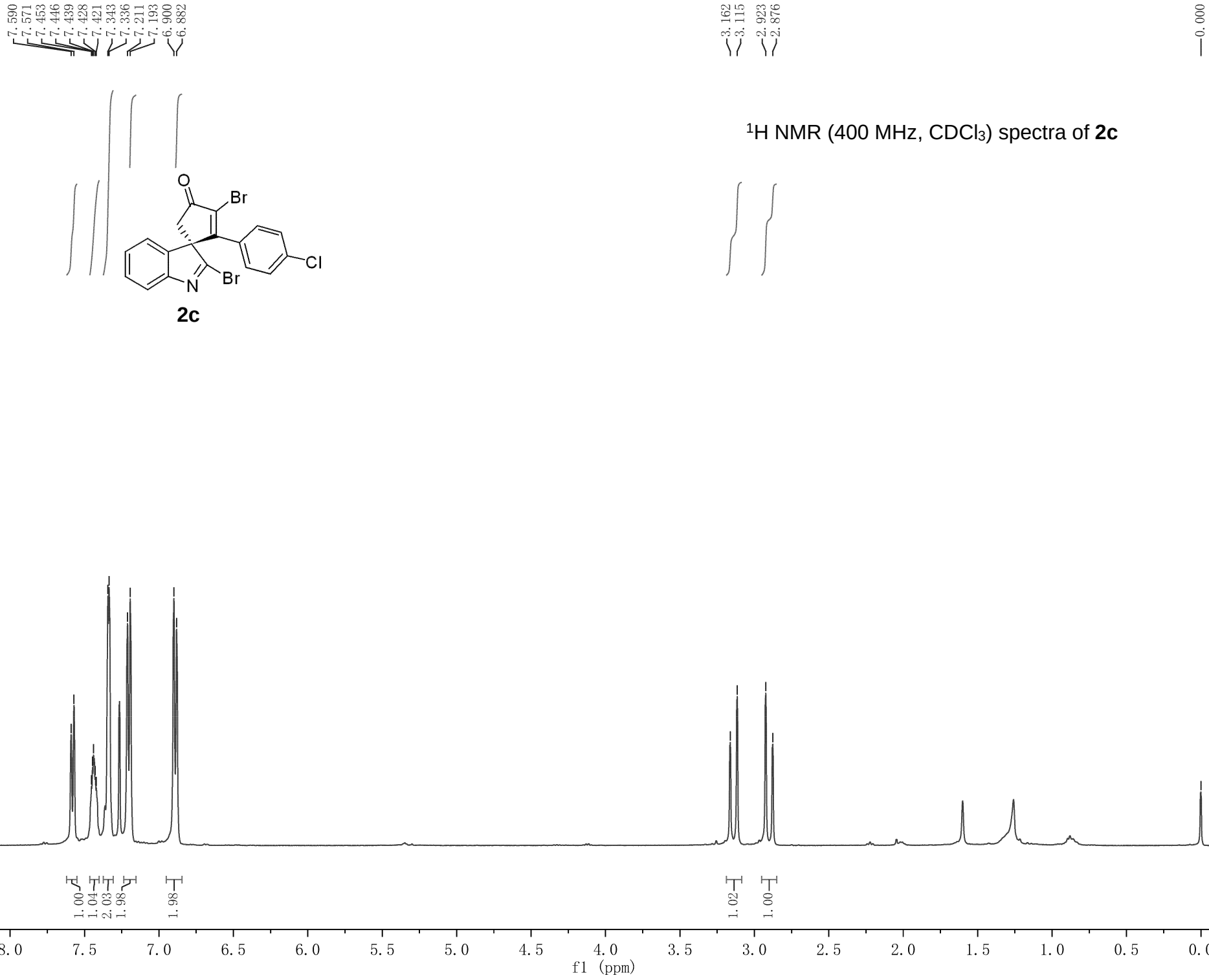
196.86
165.58
164.96
163.60
162.44
154.05
139.09
129.94
129.34
129.25
127.67
127.26
127.23
126.97
122.12
121.37
115.99
115.77
77.32
77.00
76.68
70.28
41.86

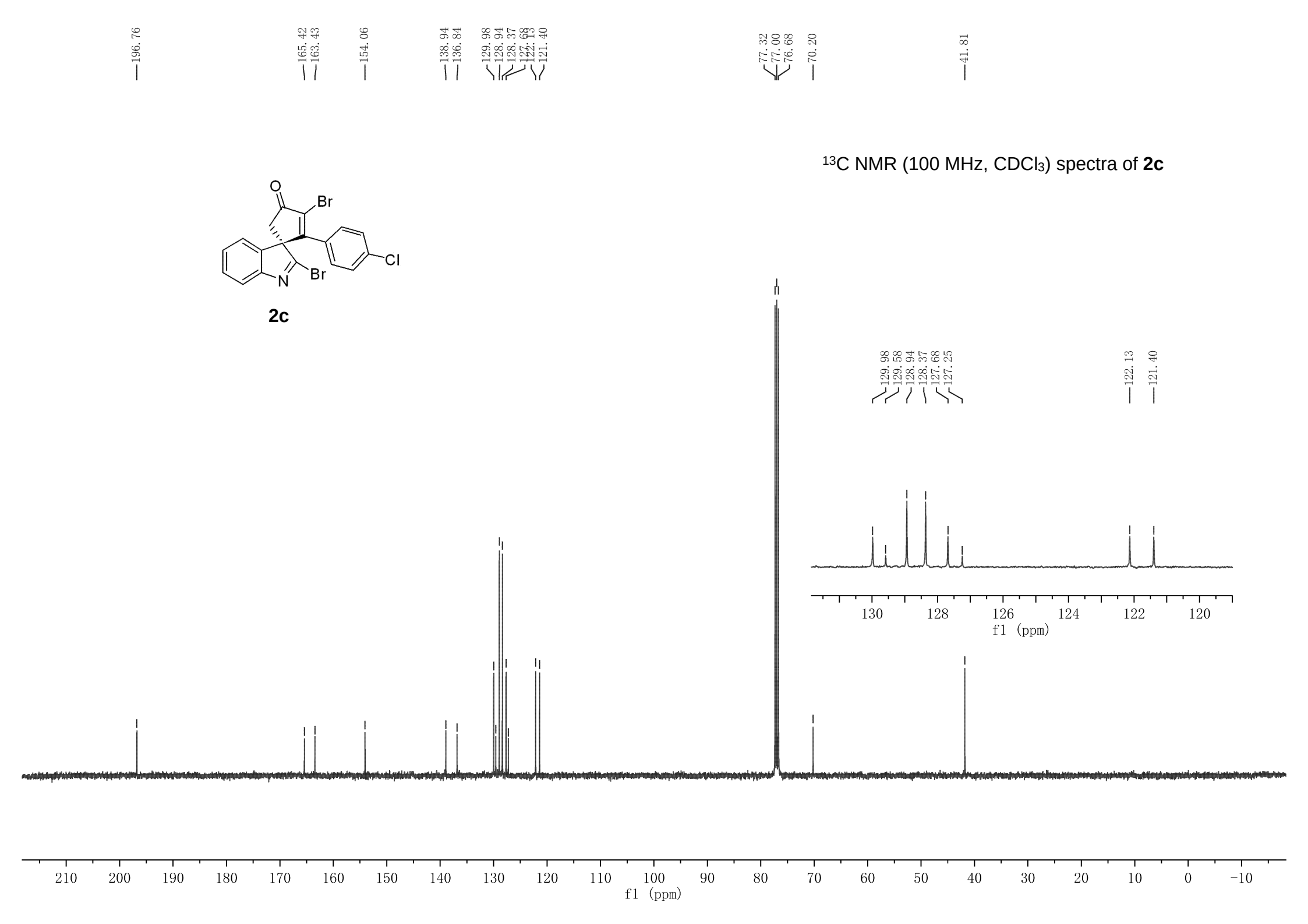
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2b**



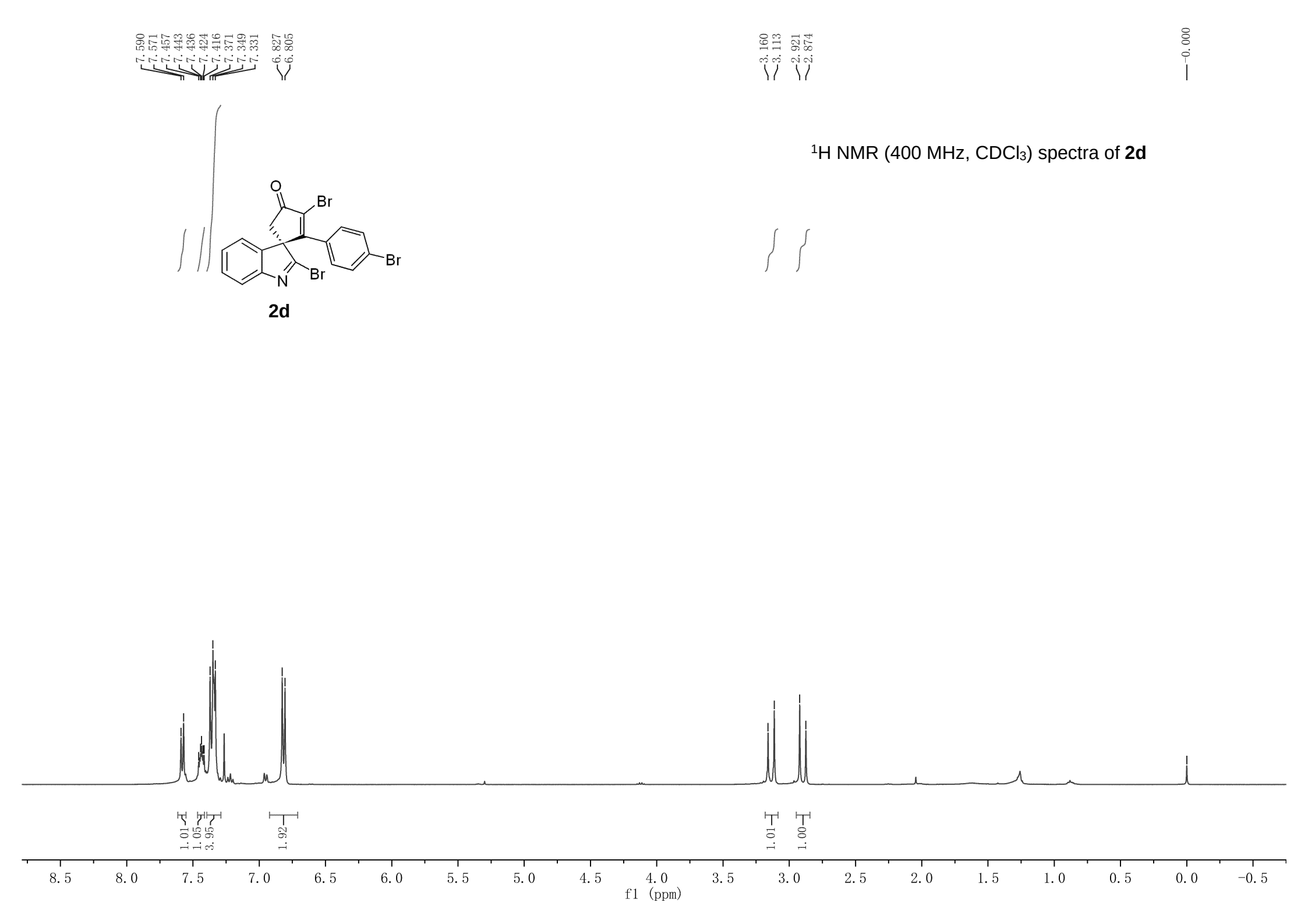
2b



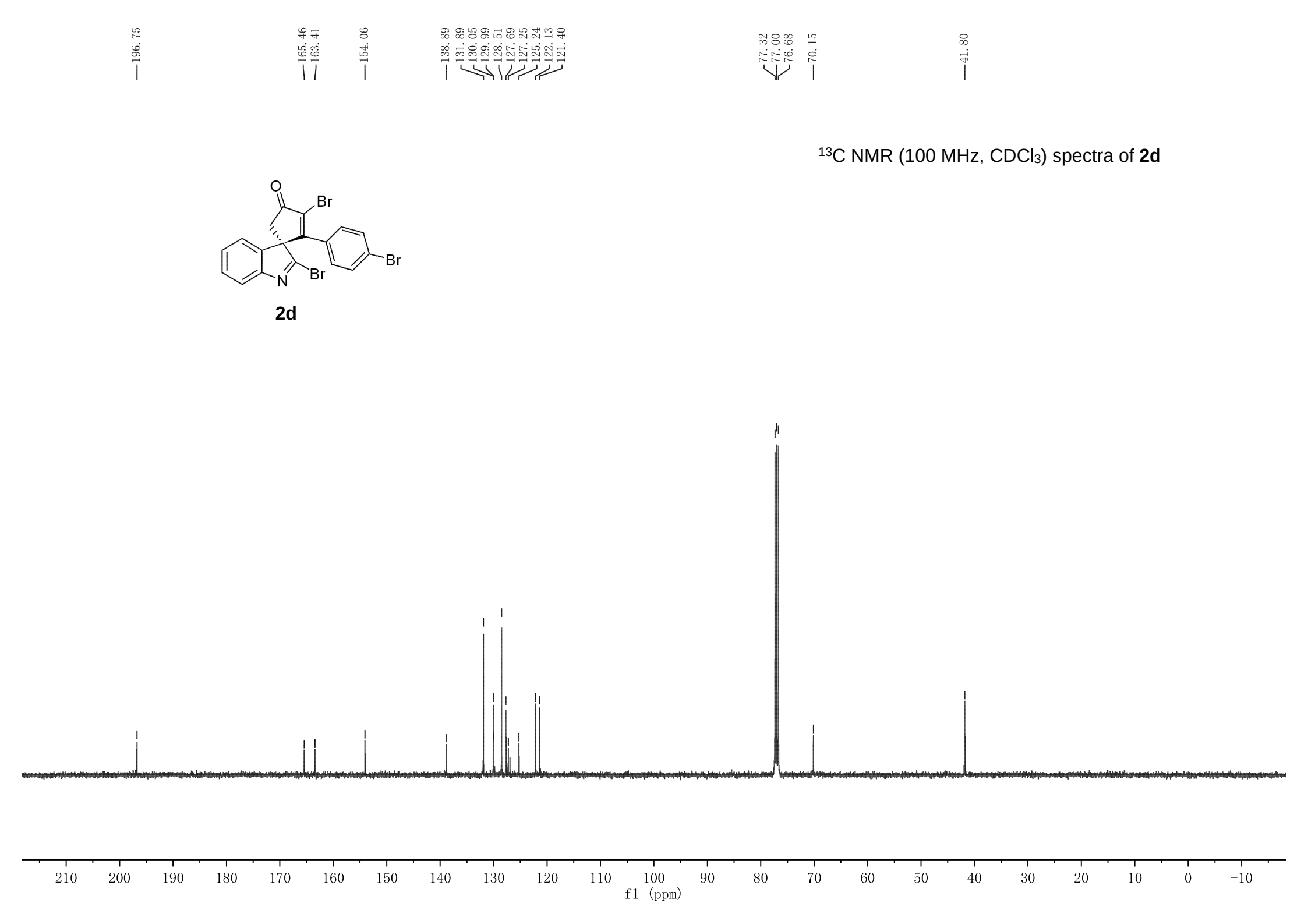

7.590
7.571
7.453
7.446
7.439
7.428
7.421
7.343
7.336
7.211
7.193
6.900
6.882
3.162
3.115
2.923
2.876
0.000
O
Br
Cl
Br
N
2c
1H NMR (400 MHz, CDCl3) spectra of 2c
1.00
1.04
2.03
1.98
1.98
1.02
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

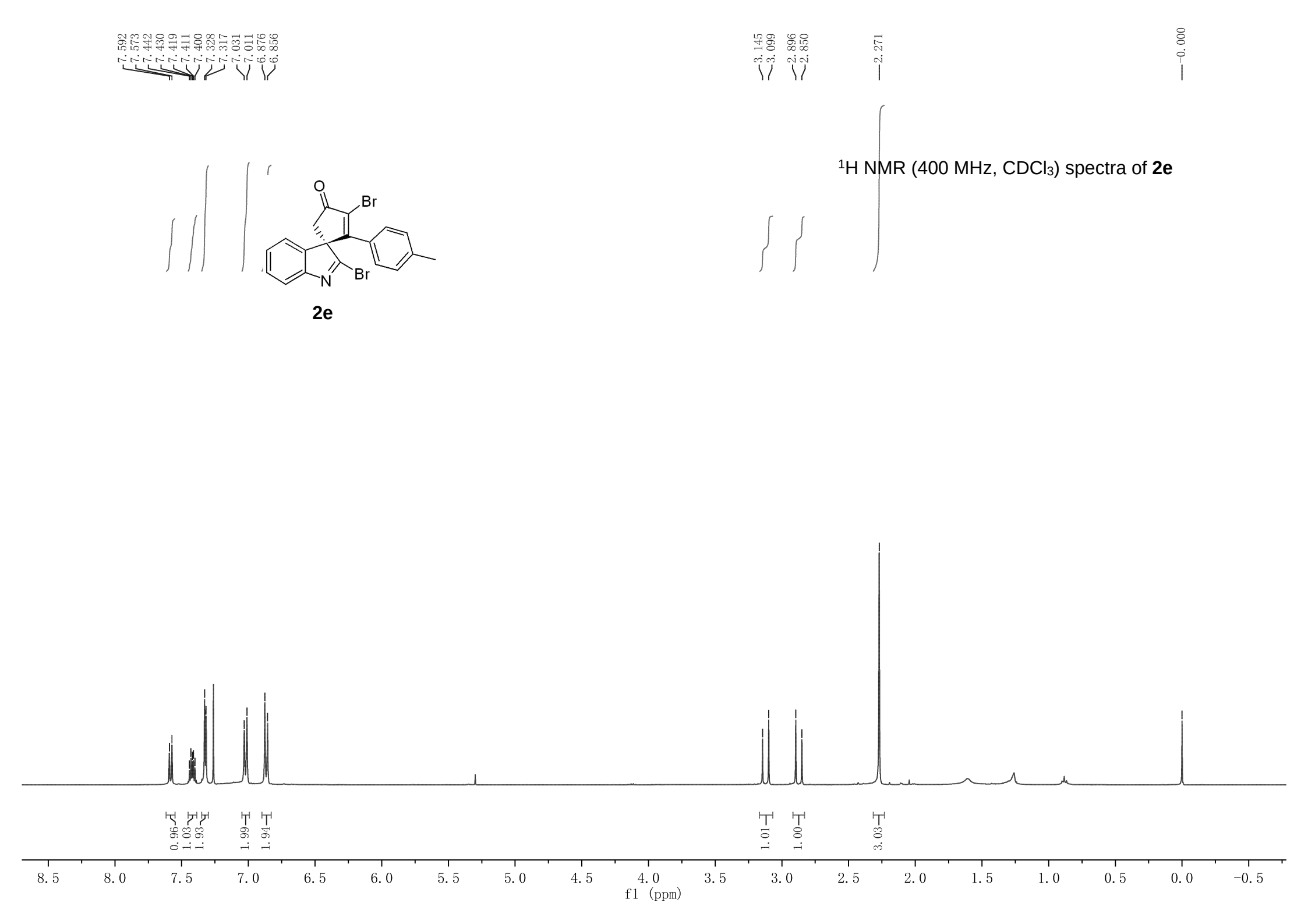


^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2c**

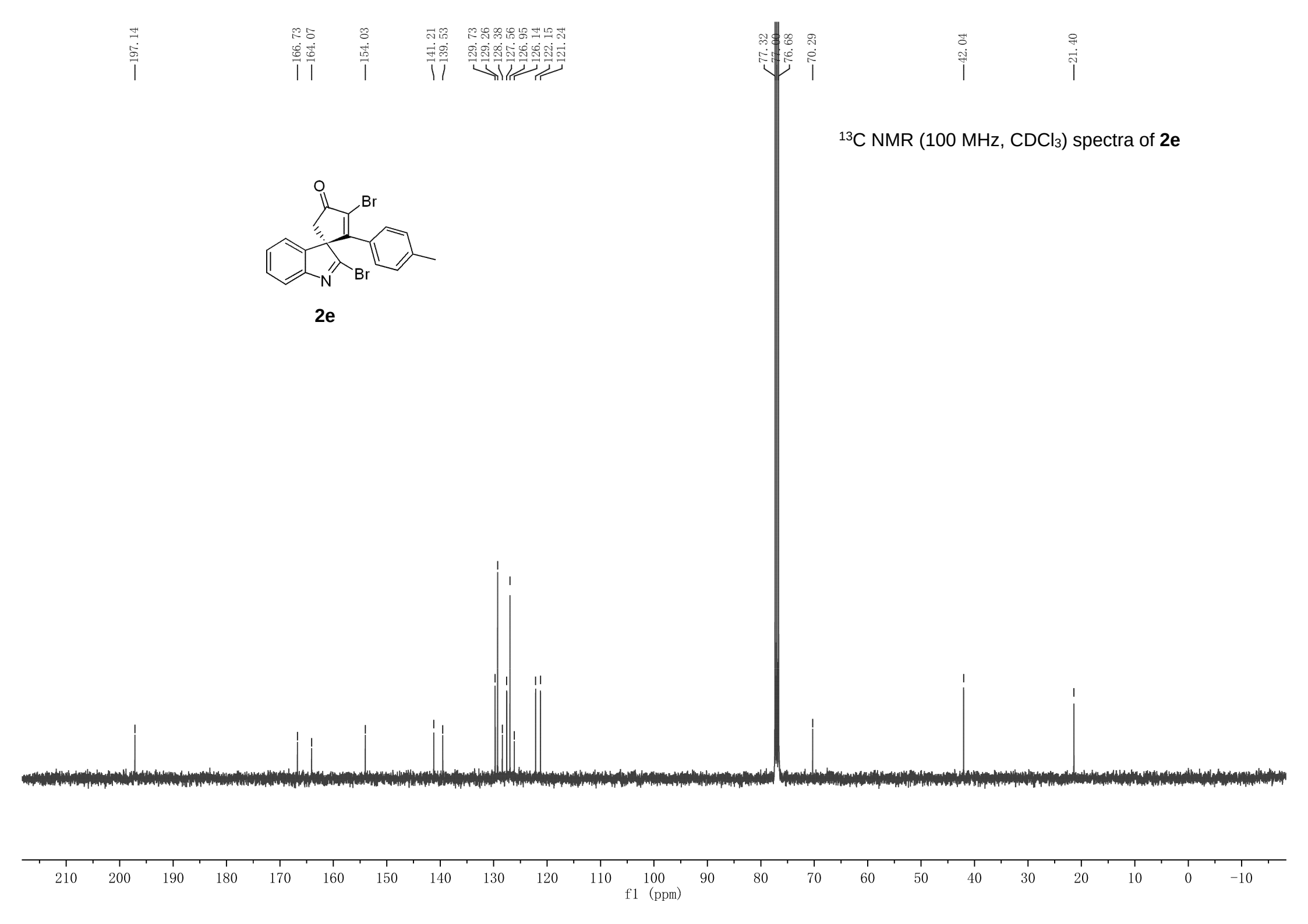


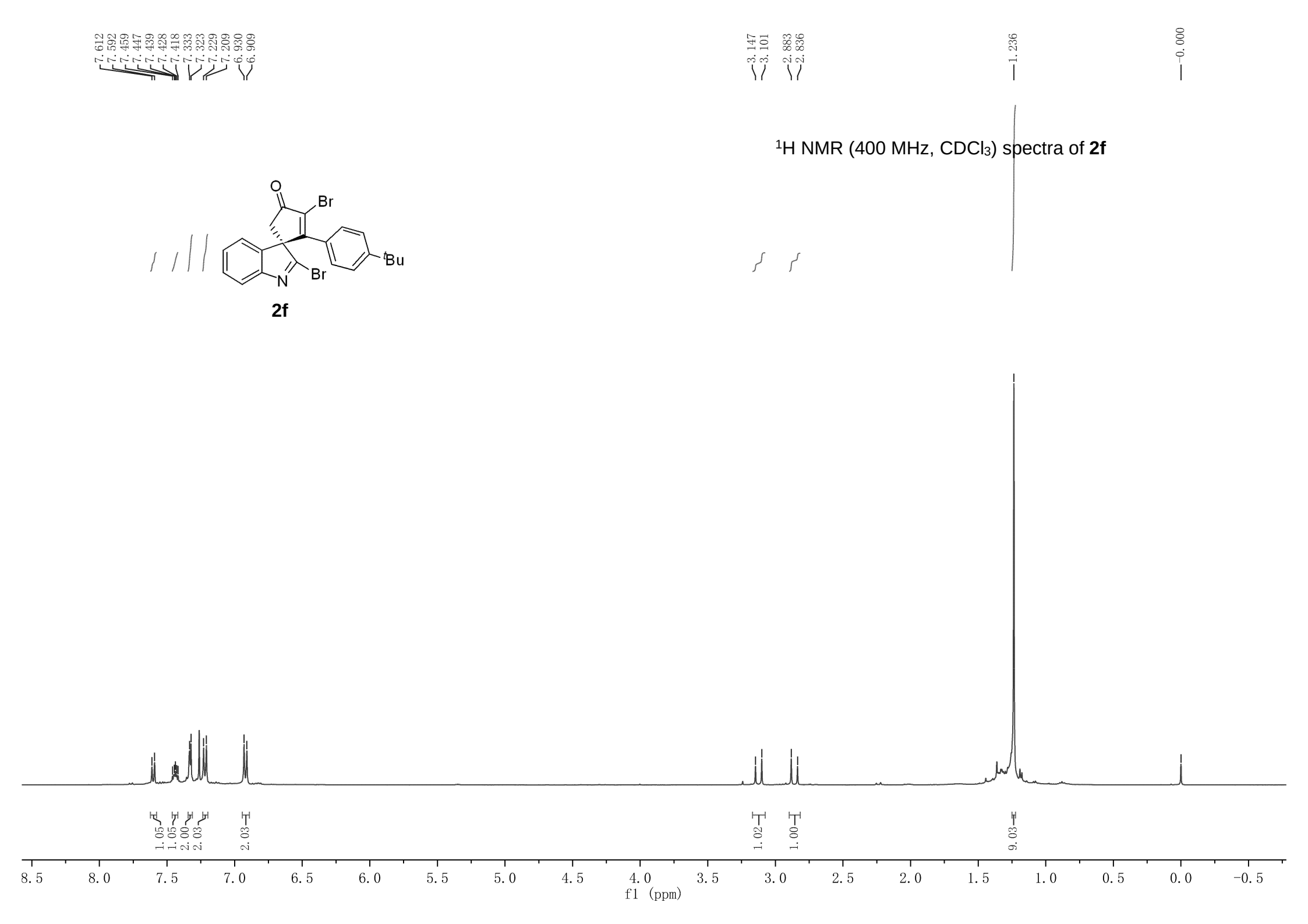
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **2d**


196.75
165.46
163.41
154.06
138.89
131.89
130.05
129.99
128.51
127.69
127.25
125.24
122.13
121.40
77.32
77.00
76.68
70.15
41.80
O
Br
Br
Br
N
2d
13C NMR (100 MHz, CDCl3) spectra of 2d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

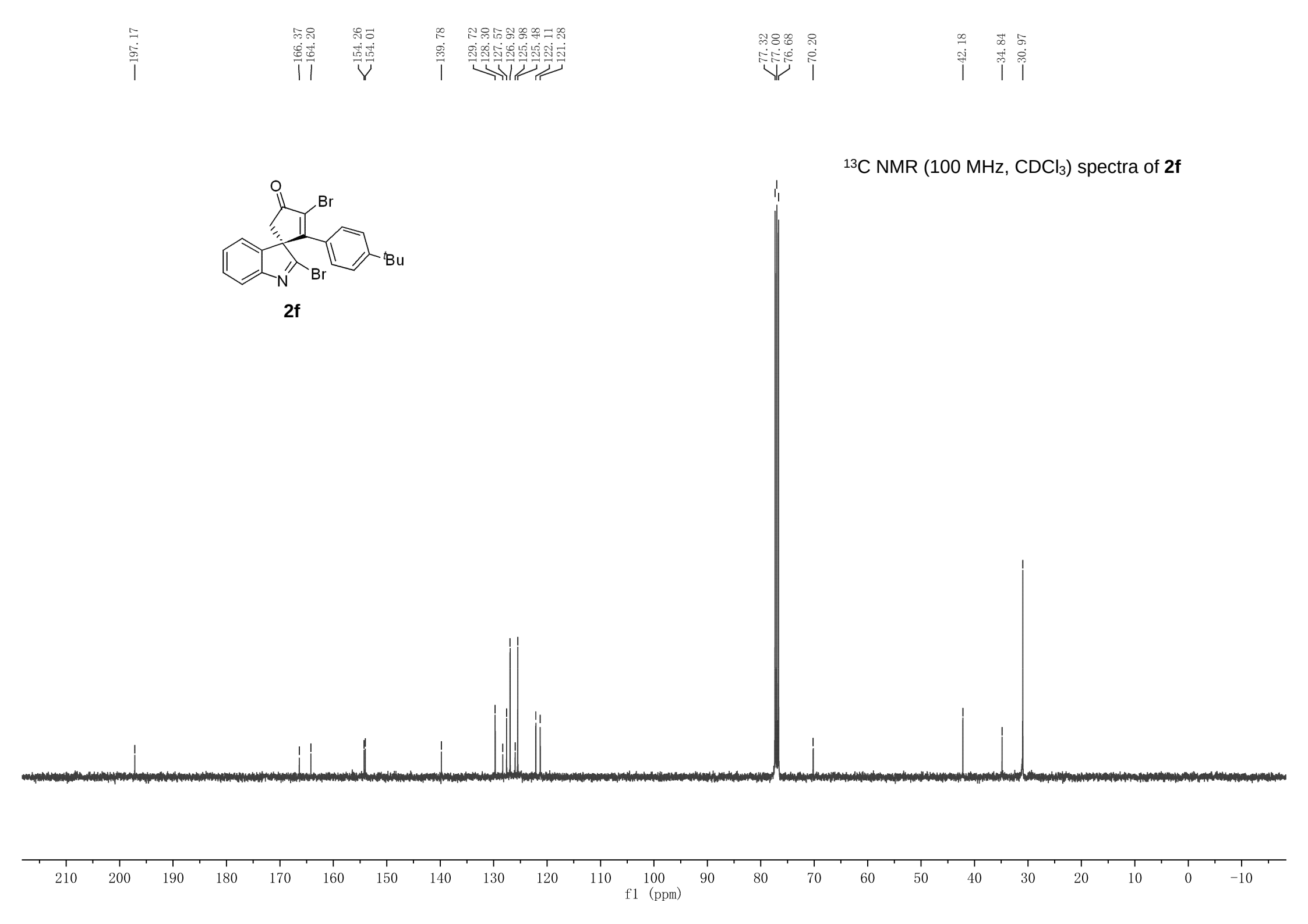


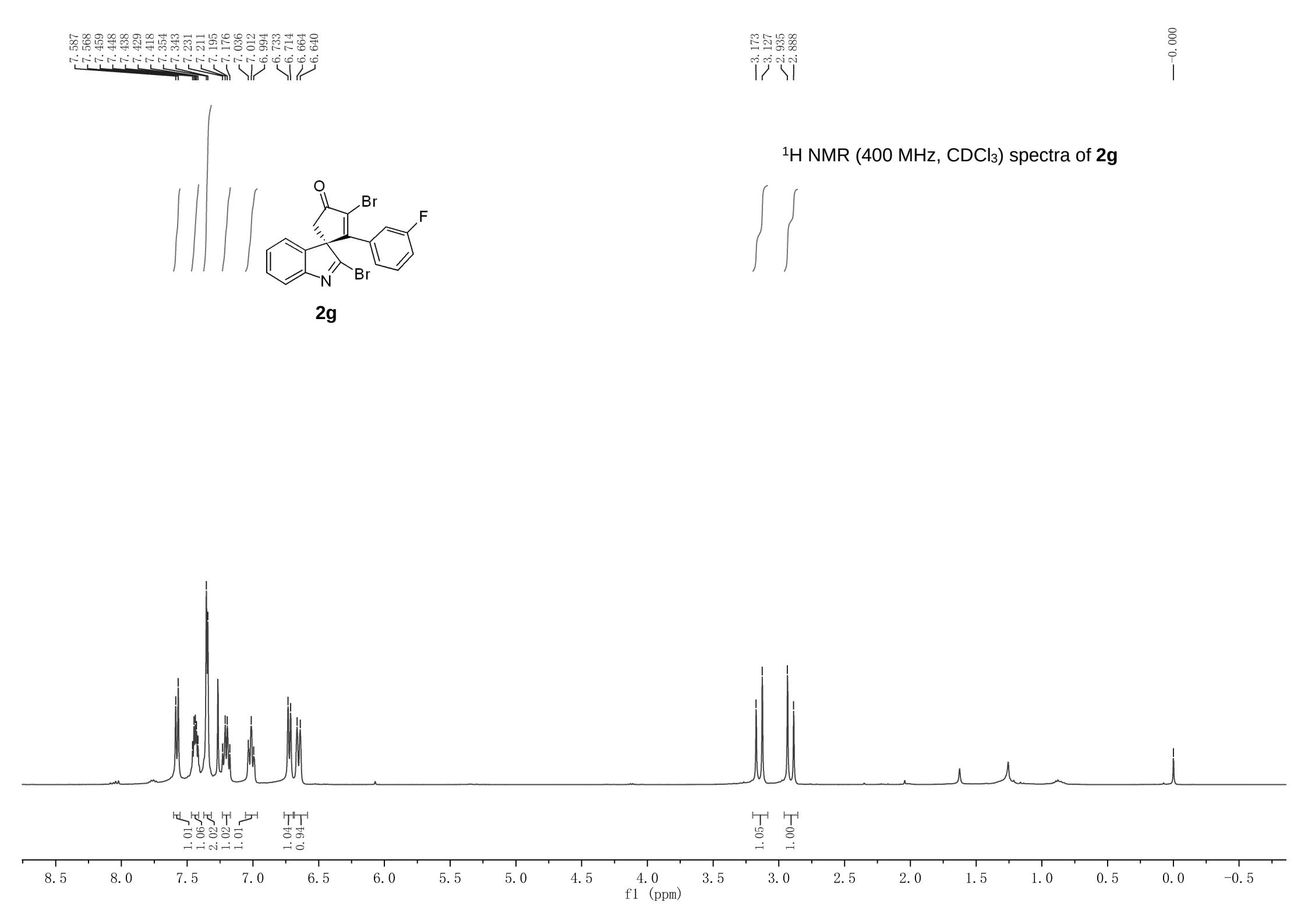
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **2e**


197.14
166.73
164.07
154.03
141.21
139.53
129.73
129.26
128.38
127.56
126.95
126.14
122.15
121.24
77.32
77.00
76.68
70.29
42.04
21.40
O
Br
Br
N
2e
13C NMR (100 MHz, CDCl3) spectra of 2e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



^{1}H NMR (400 MHz, $CDCl_3$) spectra of **2f**

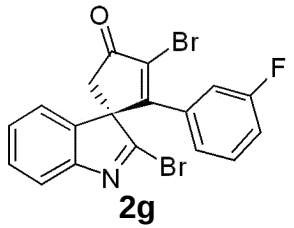

197.17
166.37
164.20
154.26
154.01
139.78
129.72
128.30
127.57
126.92
125.98
125.48
122.11
121.28
77.32
77.00
76.68
70.20
42.18
34.84
30.97
O
Br
Br
N
tBu
2f
13C NMR (100 MHz, CDCl3) spectra of 2f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



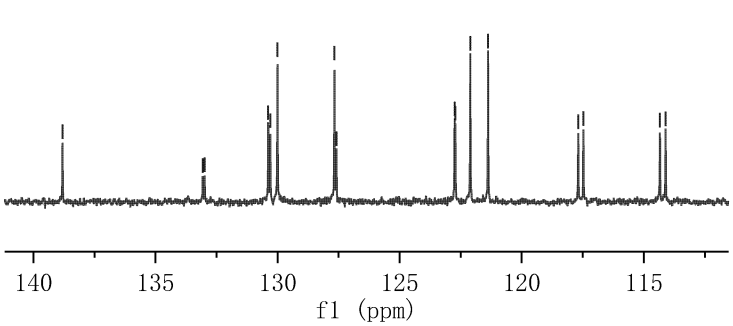
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **2g**

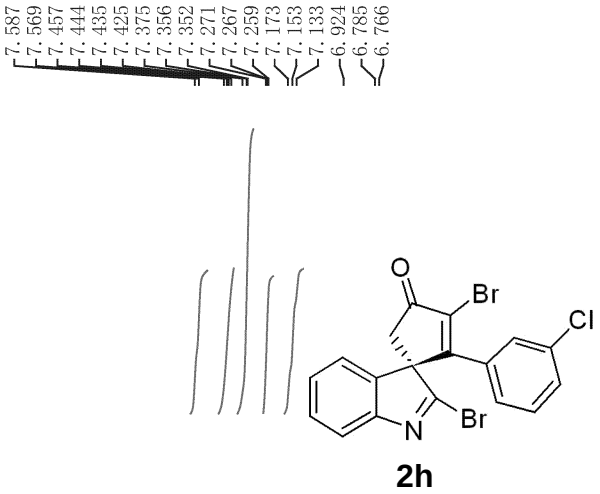
196.78
165.23
165.21
163.37
163.21
160.91
154.06
138.81
130.38
130.30
130.00
127.67
127.59
122.75
122.72
122.11
121.38
117.68
117.48
114.34
114.11
77.32
77.00
76.68
70.22
41.76

^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2g**



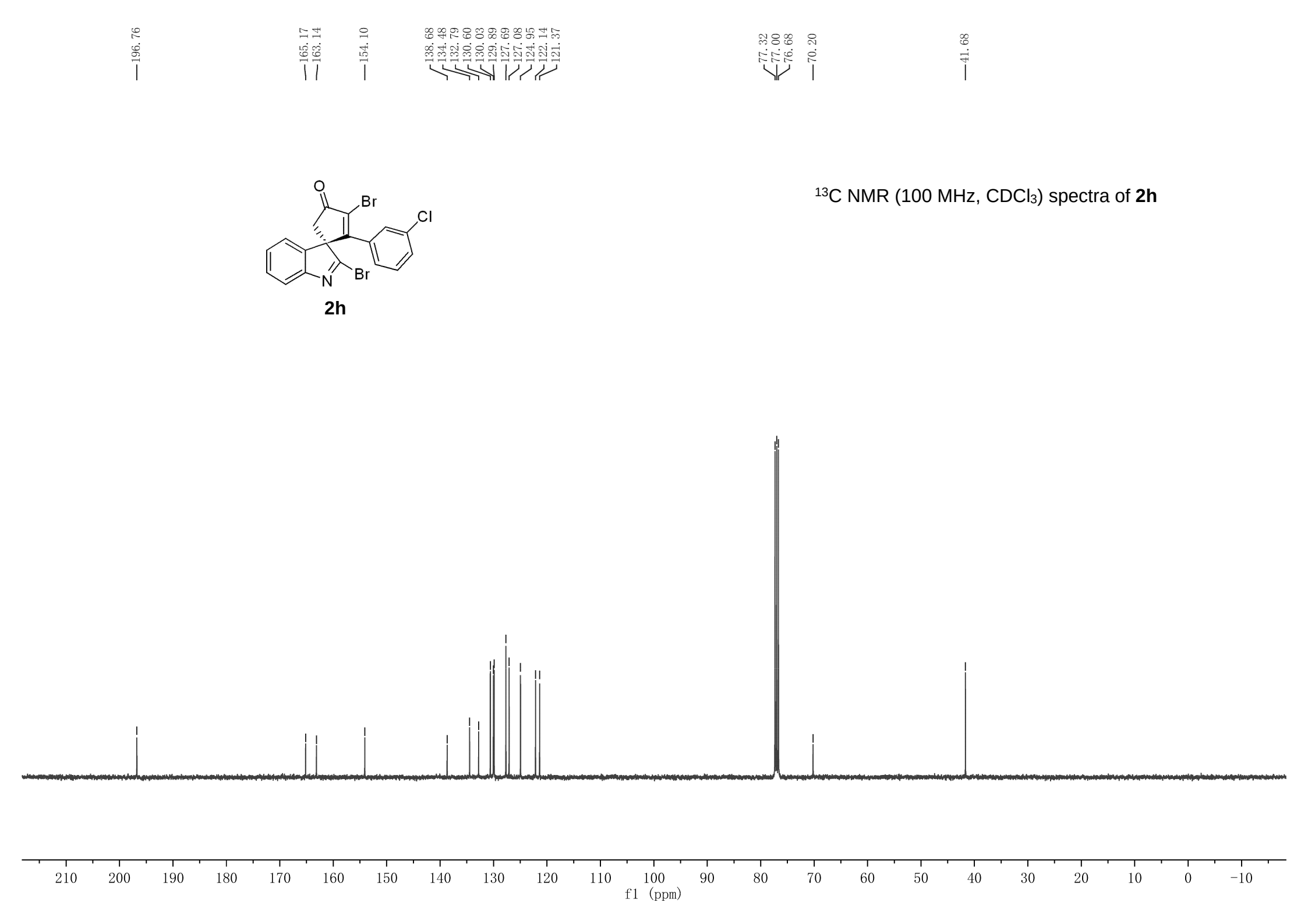
2g

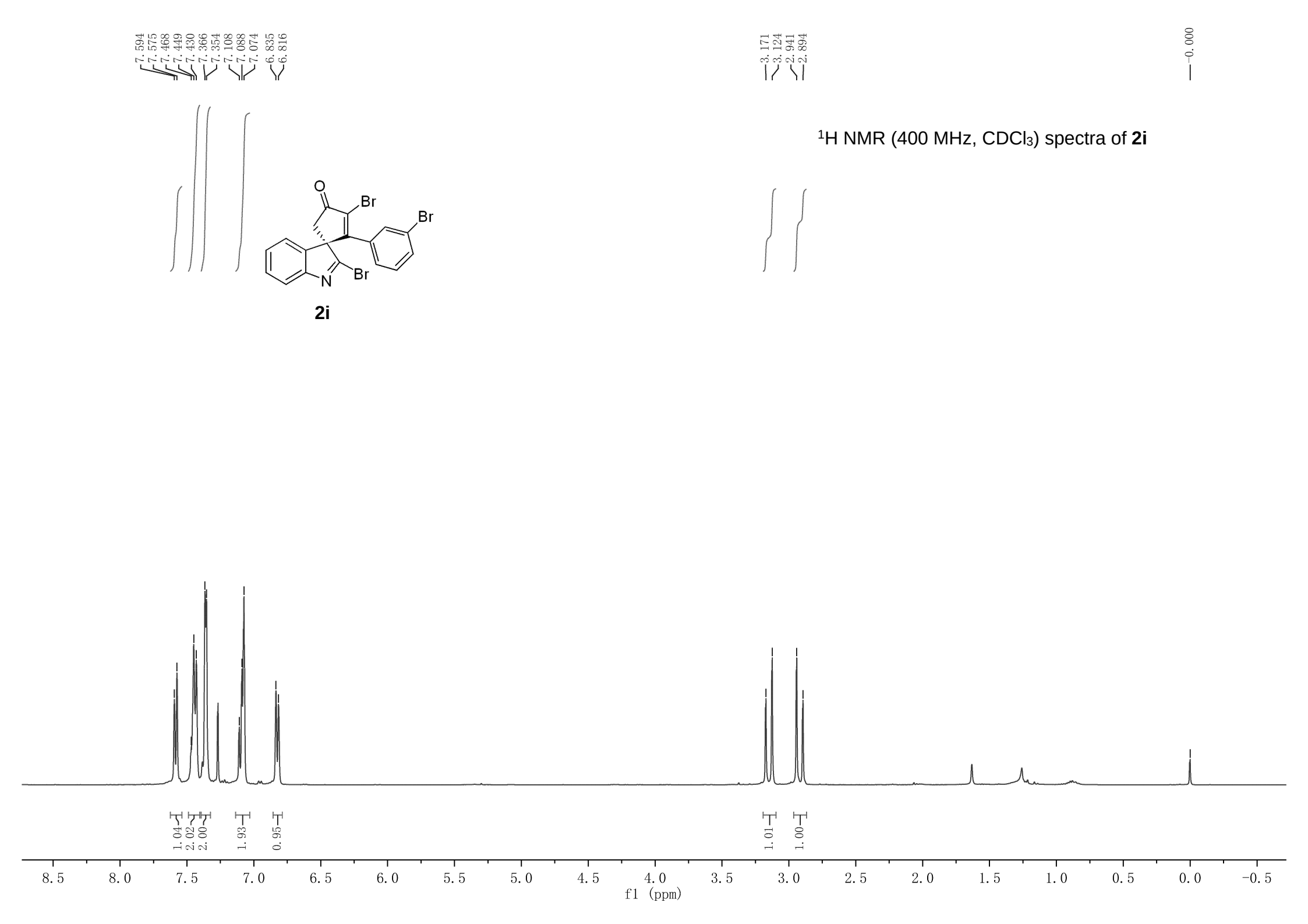




2h

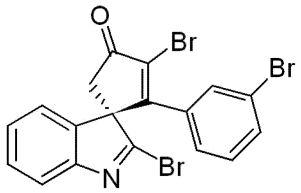
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **2h**


196.76
165.17
163.14
154.10
138.68
134.48
132.79
130.60
130.03
129.89
127.69
127.08
124.95
122.14
121.37
77.32
77.00
76.68
70.20
41.68
O
Br
Cl
Br
N
2h
13C NMR (100 MHz, CDCl3) spectra of 2h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

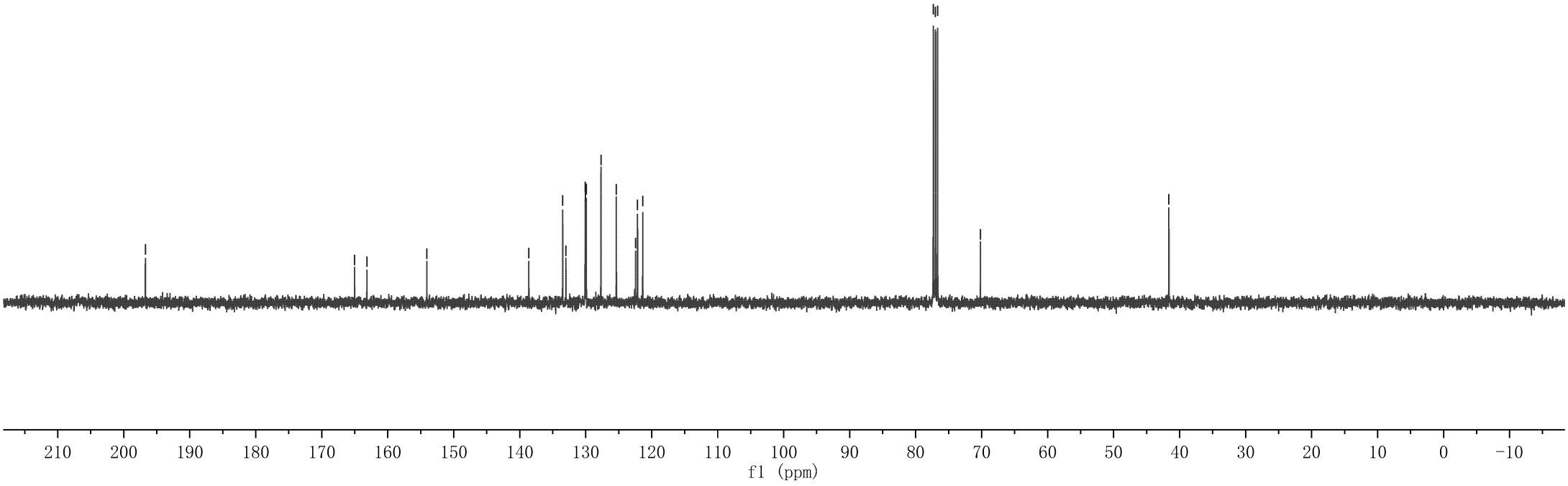

7.594
7.575
7.468
7.449
7.430
7.366
7.354
7.108
7.088
7.074
6.835
6.816
3.171
3.124
2.941
2.894
0.000
O
Br
Br
Br
N
2i
1H NMR (400 MHz, CDCl3) spectra of 2i
1.04
2.02
2.00
1.93
0.95
1.01
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

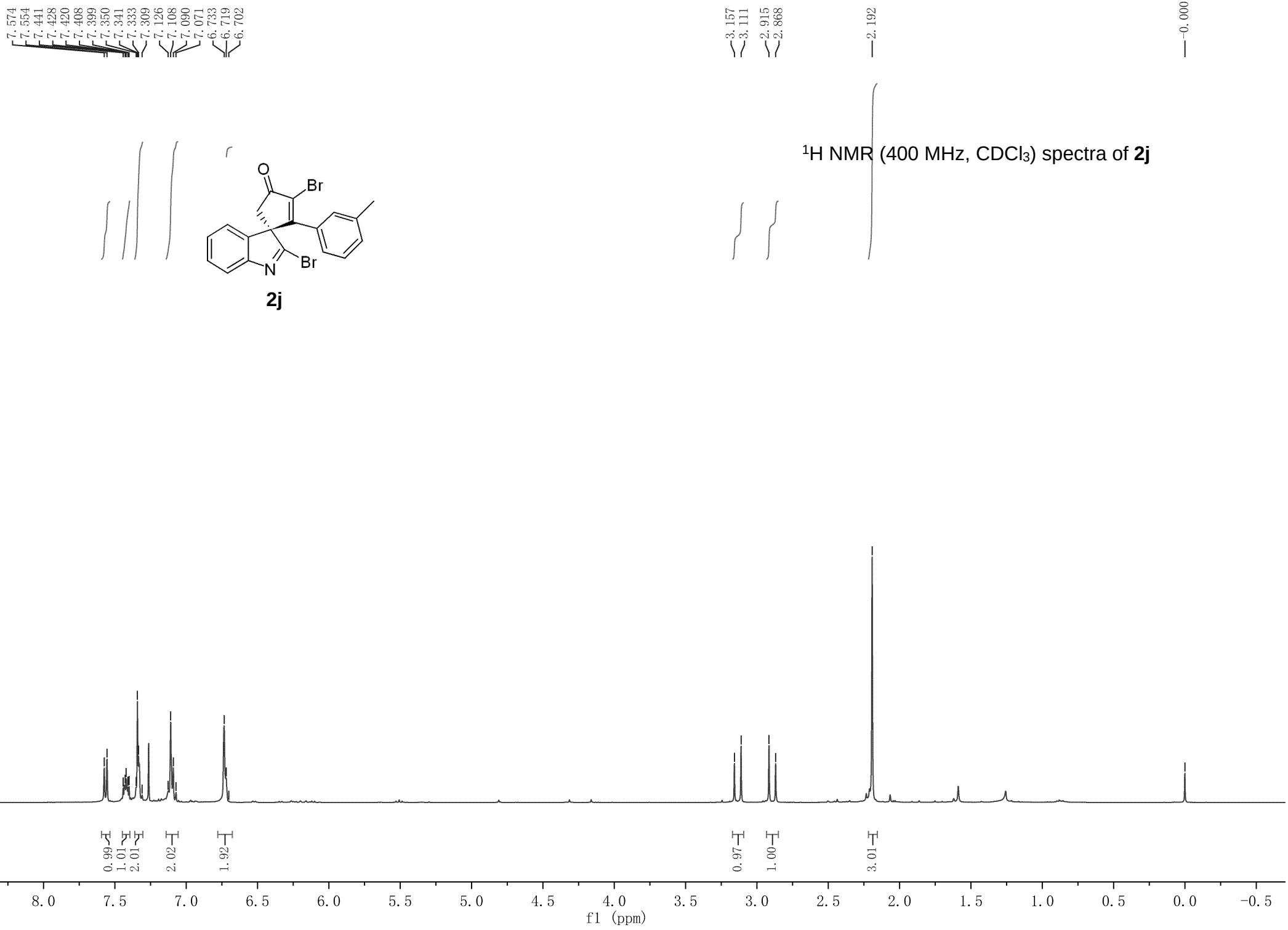
196.72
165.02
163.16
154.07
138.62
133.48
132.99
130.08
130.03
129.91
127.69
125.36
122.44
122.15
121.36
77.32
77.00
76.68
70.18
41.63

^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2i**



2i



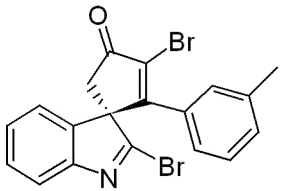


2j

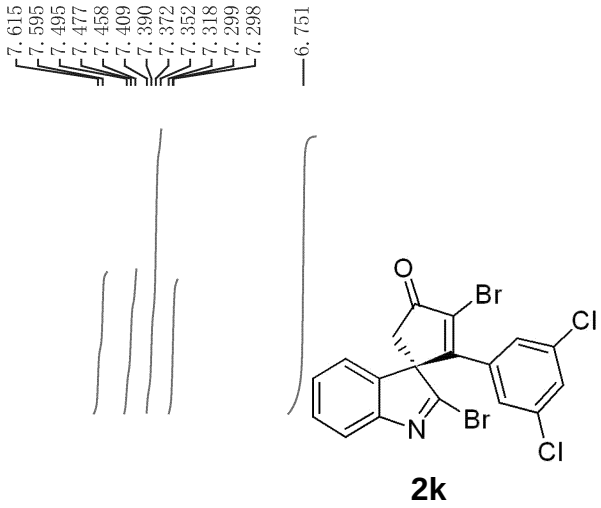
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **2j**

197.19
167.07
163.76
154.13
139.32
138.18
131.41
131.18
129.73
128.37
127.49
127.42
126.57
124.00
122.19
121.16
77.32
77.00
76.68
70.34
41.87
21.30

^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2j**

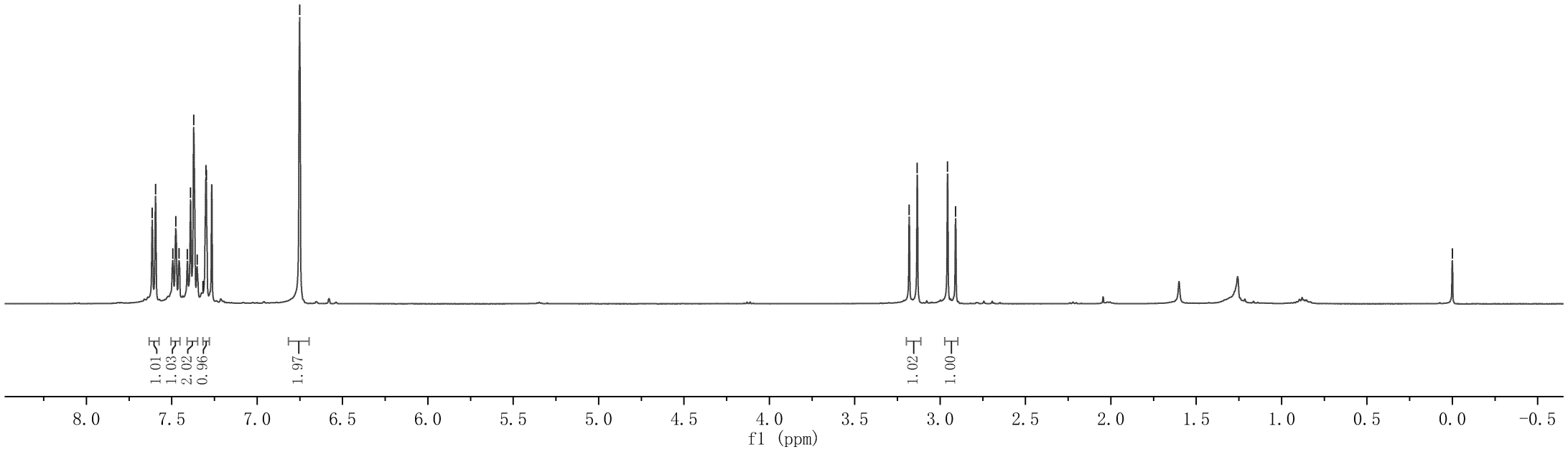


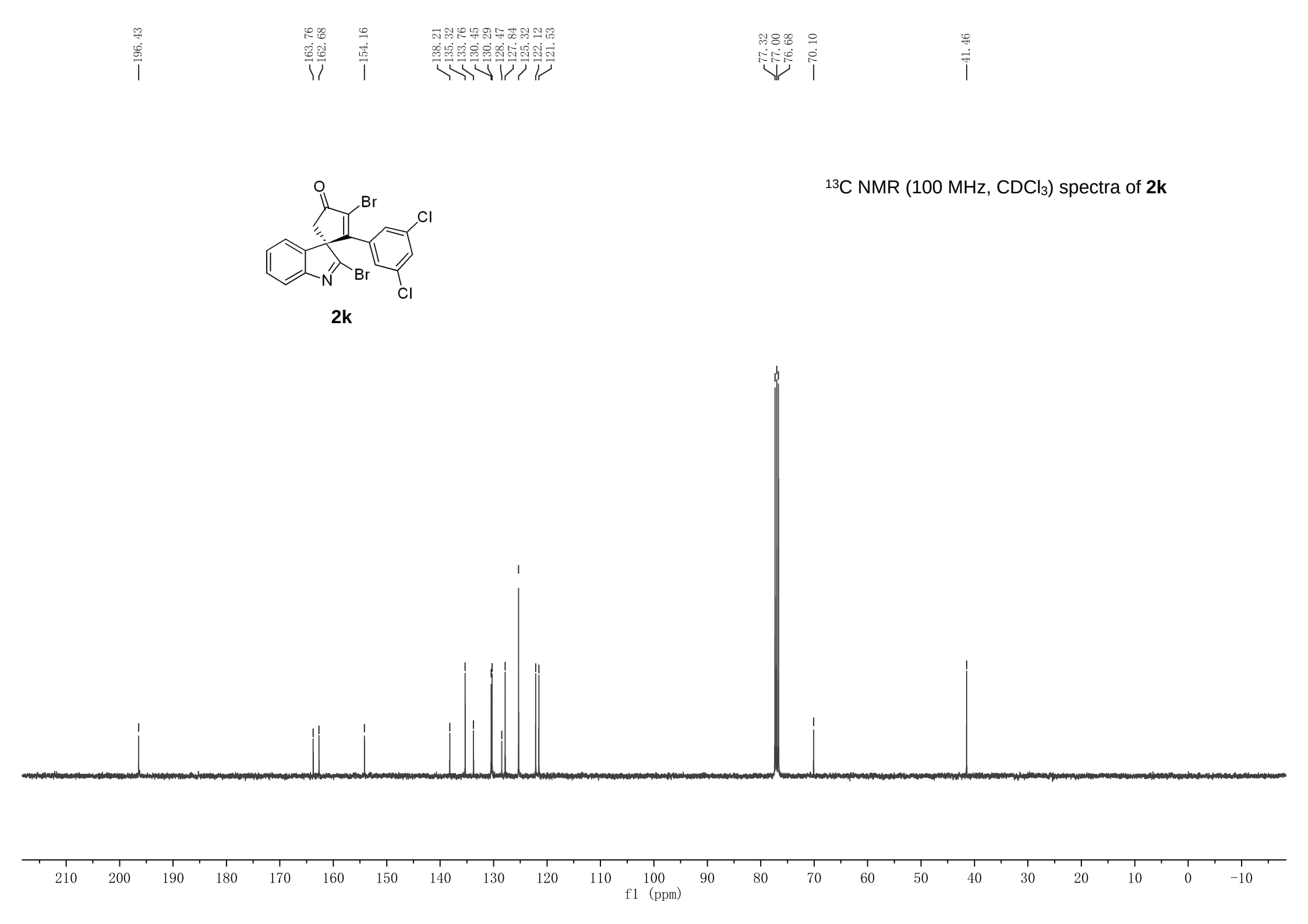
2j

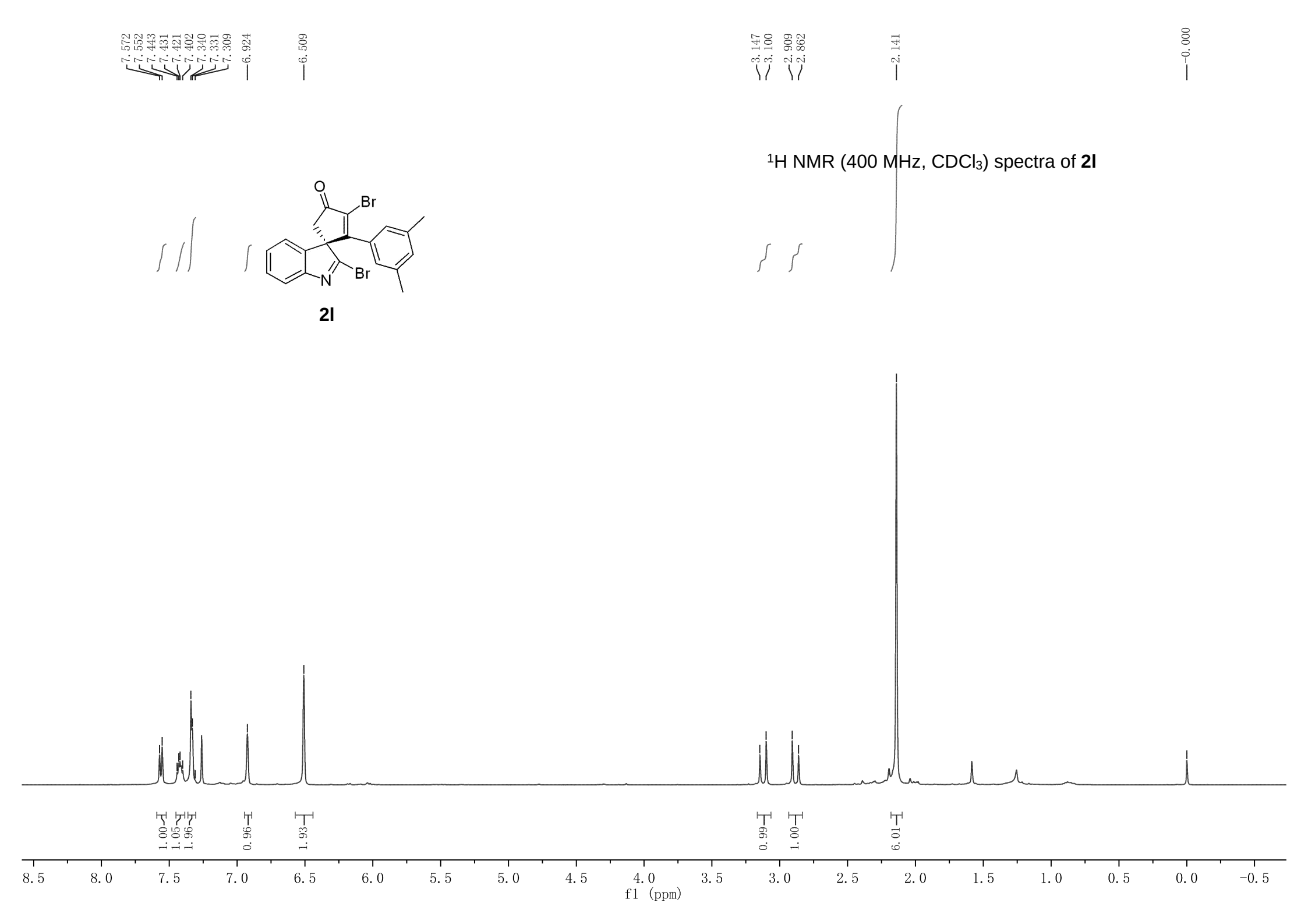


2k

^{1}H NMR (400 MHz, $CDCl_3$) spectra of **2k**

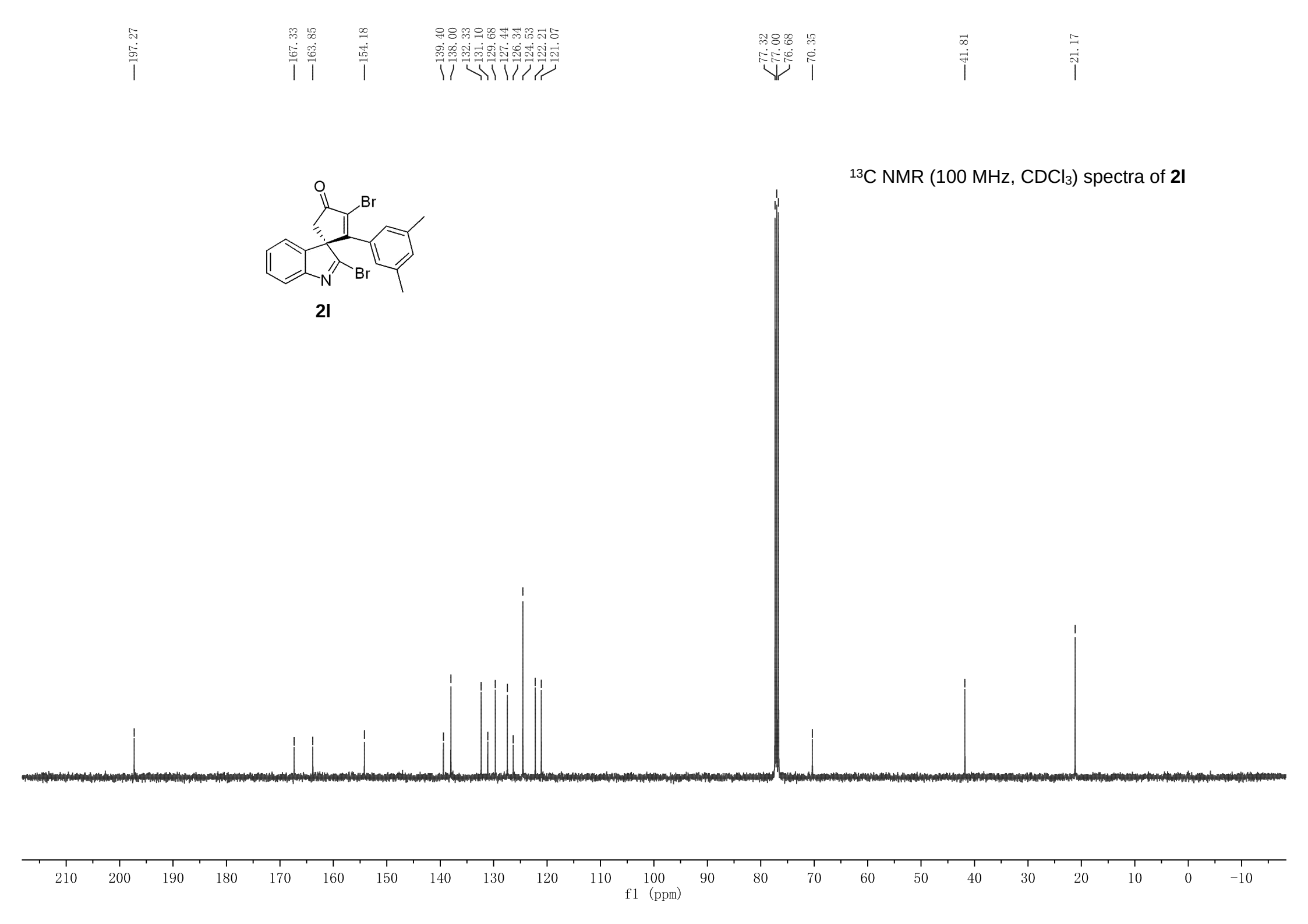


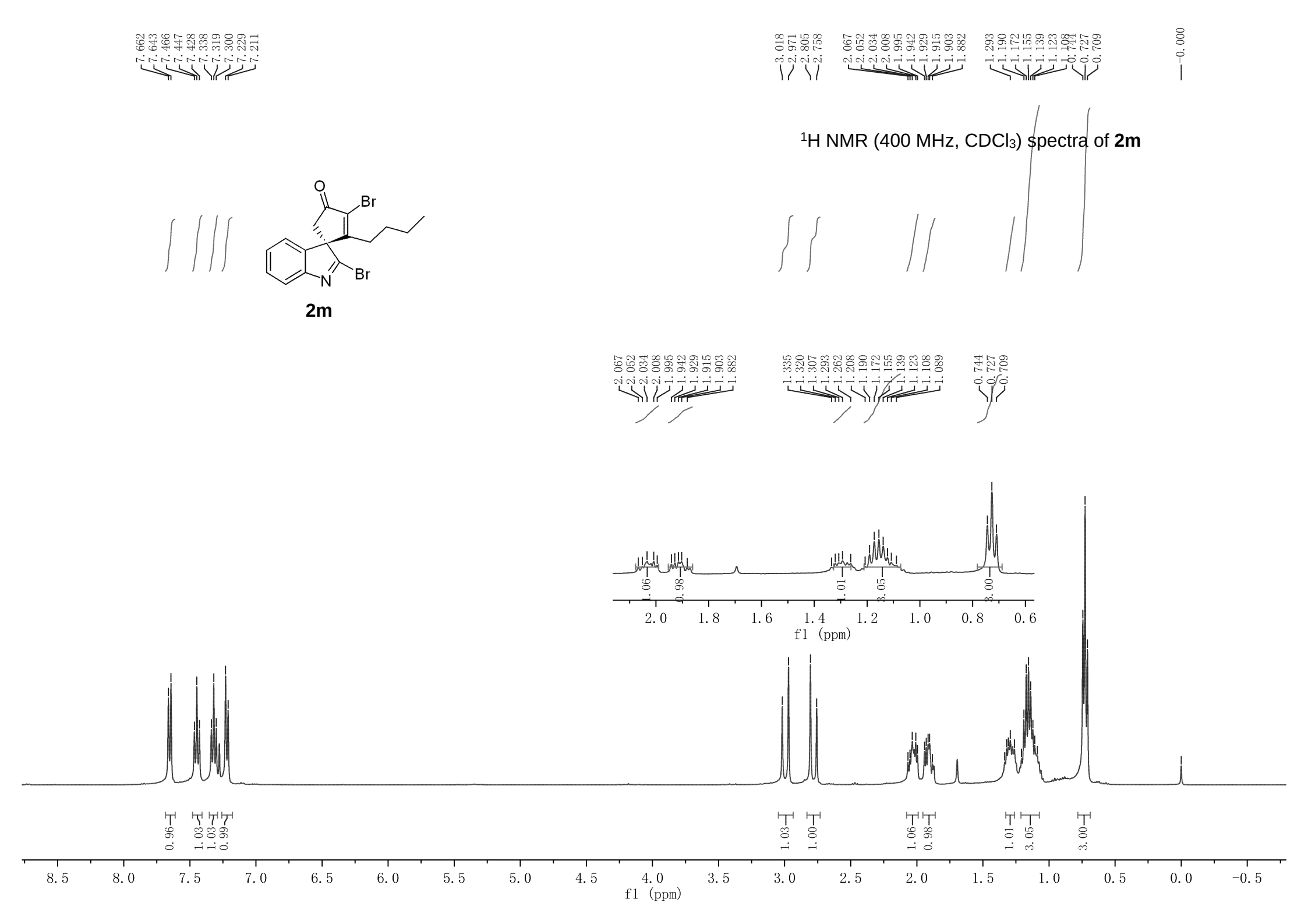

196.43
163.76
162.68
154.16
138.21
135.32
133.76
130.45
130.29
128.47
127.84
125.32
122.12
121.53
77.32
77.00
76.68
70.10
41.46
O
Br
Cl
N
Br
Cl
2k
13C NMR (100 MHz, CDCl3) spectra of 2k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

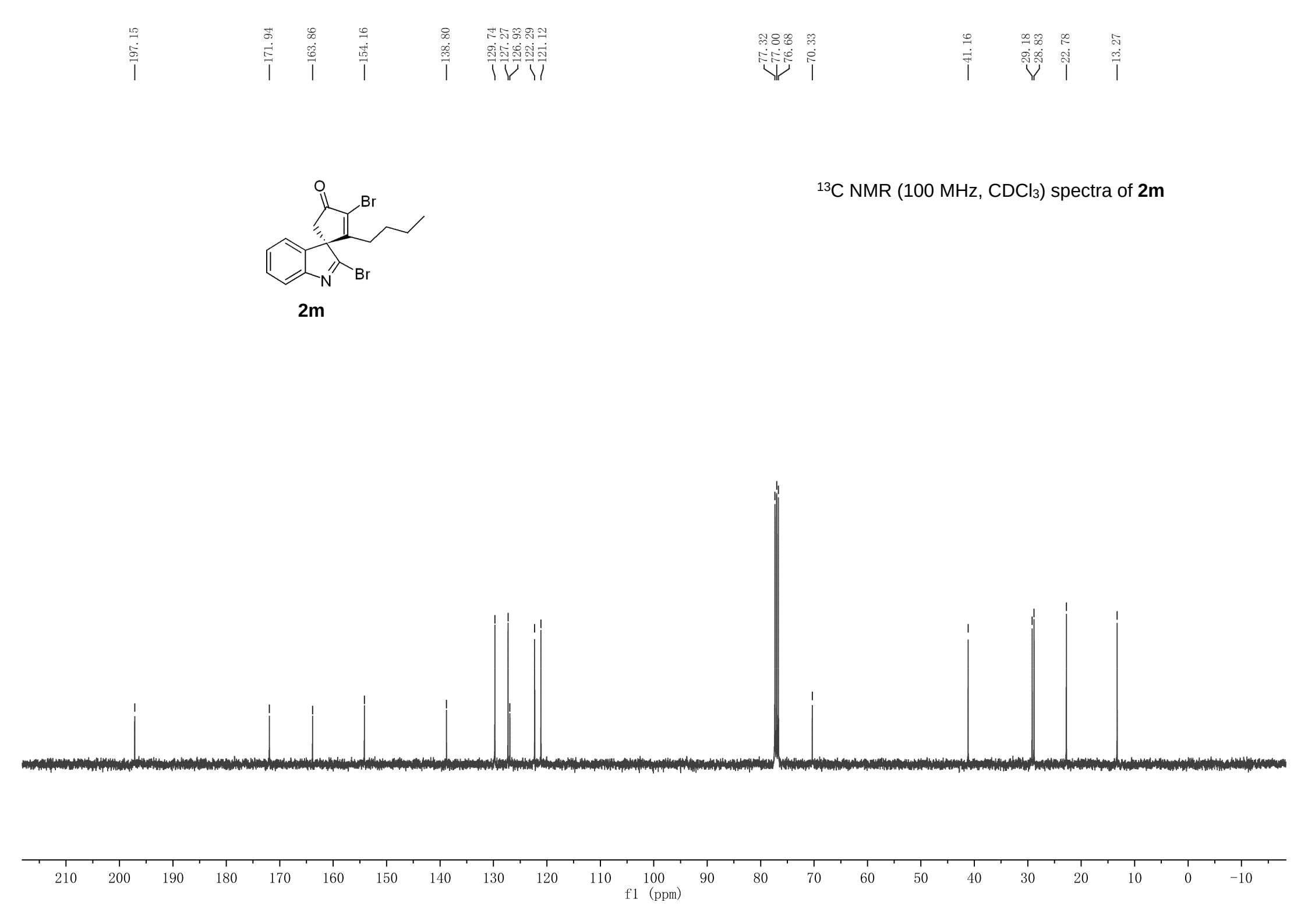


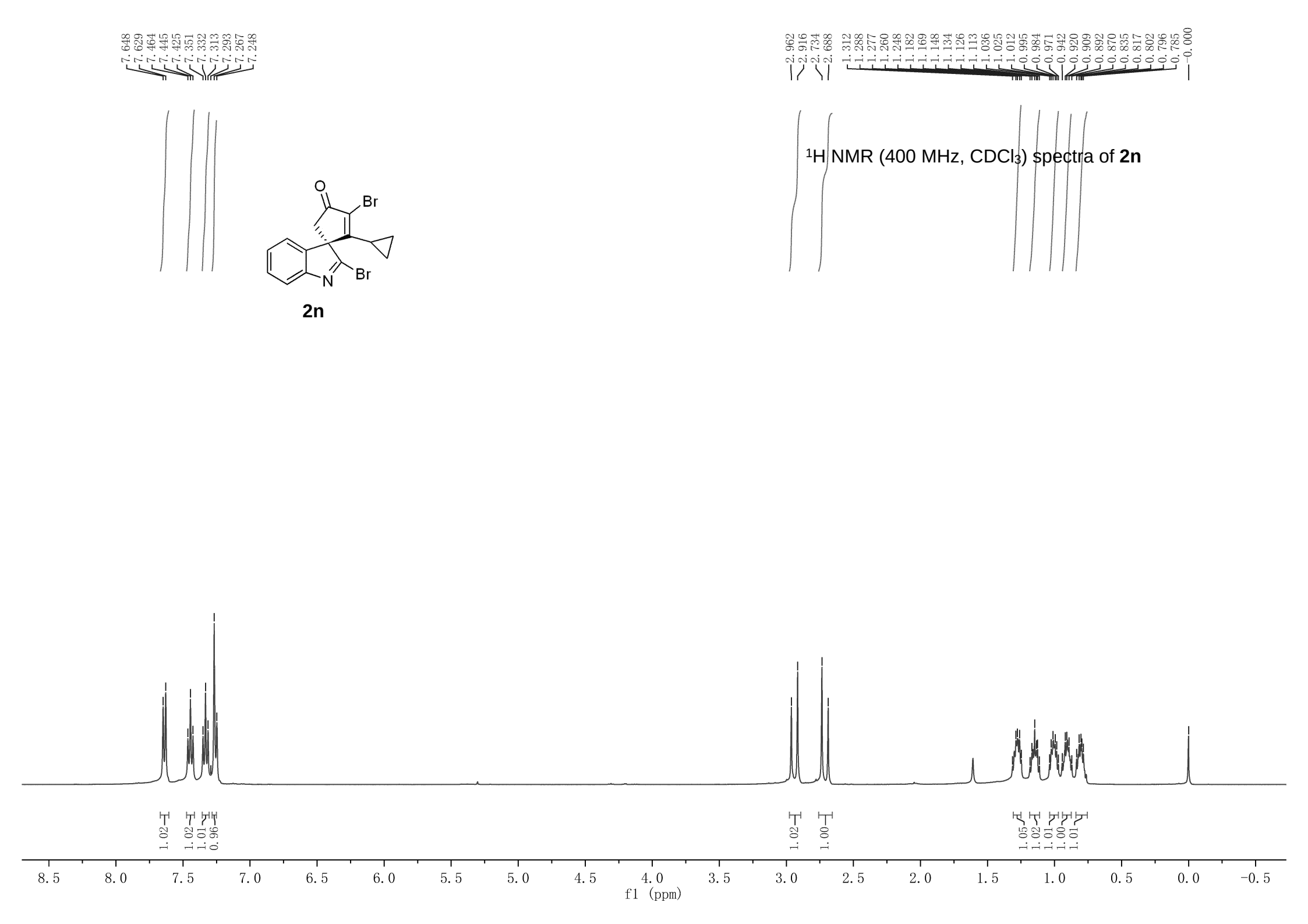
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **2l**

2l


197.27
167.33
163.85
154.18
139.40
138.00
132.33
131.10
129.68
127.44
126.34
124.53
122.21
121.07
77.32
77.00
76.68
70.35
41.81
21.17
O
Br
Br
N
2l
13C NMR (100 MHz, CDCl3) spectra of 2l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

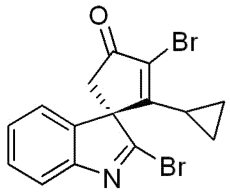

7.662
7.643
7.466
7.447
7.428
7.338
7.319
7.300
7.229
7.211
3.018
2.971
2.805
2.758
2.067
2.052
2.034
2.008
1.995
1.942
1.929
1.915
1.903
1.882
1.293
1.190
1.172
1.155
1.139
1.123
1.108
0.744
0.727
0.709
-0.000
O
Br
Br
N
2m
1H NMR (400 MHz, CDCl3) spectra of 2m
2.067
2.052
2.034
2.008
1.995
1.942
1.929
1.915
1.903
1.882
1.335
1.320
1.307
1.293
1.262
1.208
1.190
1.172
1.155
1.139
1.123
1.108
1.089
0.744
0.727
0.709
1.06
0.98
1.01
3.05
3.00
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
f1 (ppm)
0.96
1.03
1.03
0.99
1.03
1.00
1.06
0.98
1.01
3.05
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


197.15
171.94
163.86
154.16
138.80
129.74
127.27
126.93
122.29
121.12
77.32
77.00
76.68
70.33
41.16
29.18
28.83
22.78
13.27
O
Br
Br
N
2m
13C NMR (100 MHz, CDCl3) spectra of 2m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

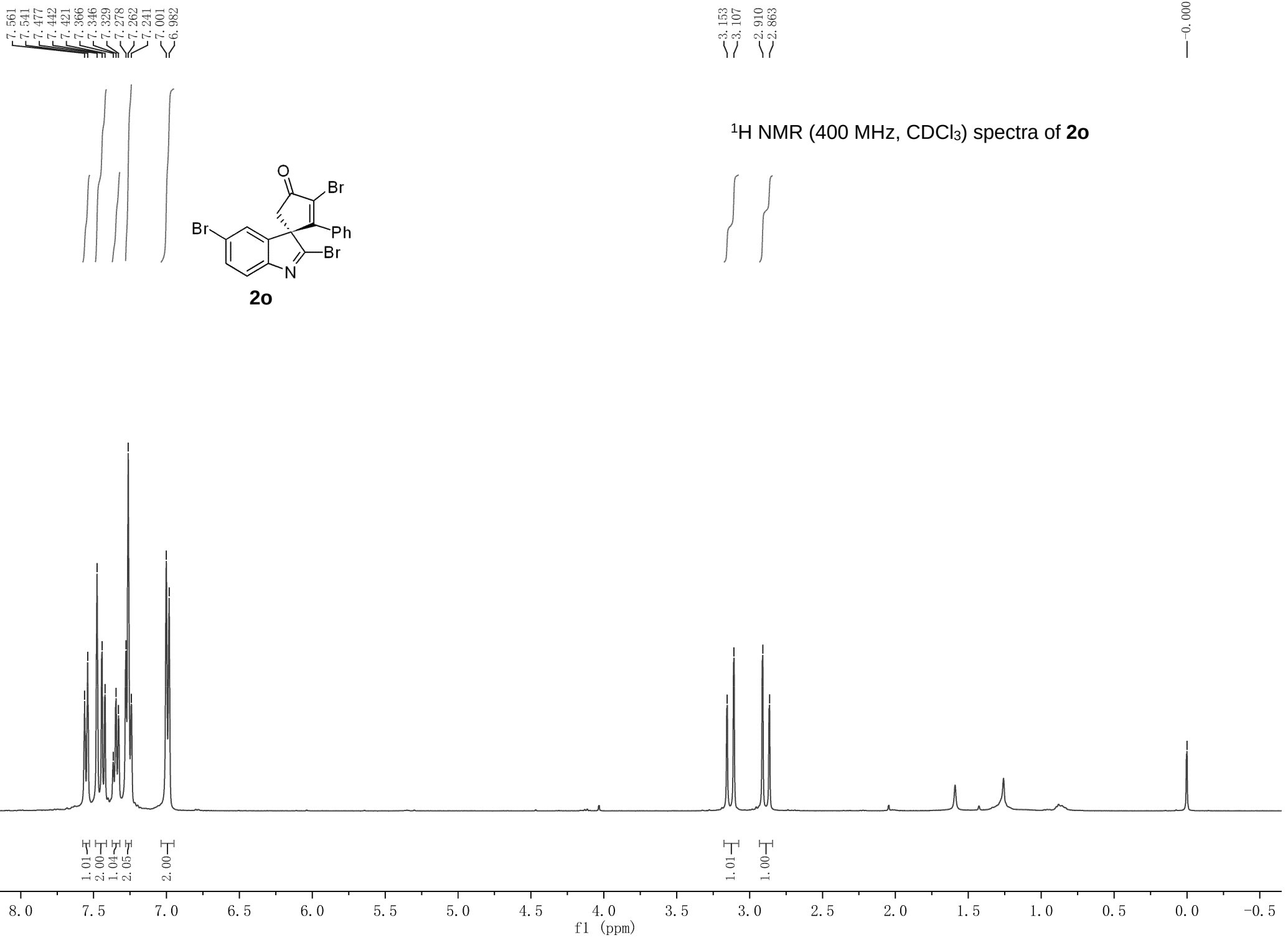

7.648
7.629
7.464
7.445
7.425
7.351
7.332
7.313
7.293
7.267
7.248
2.962
2.916
2.734
2.688
1.312
1.288
1.277
1.260
1.248
1.182
1.169
1.148
1.134
1.126
1.113
1.036
1.025
1.012
0.995
0.984
0.971
0.942
0.920
0.909
0.892
0.870
0.835
0.817
0.802
0.796
0.785
-0.000
O
Br
Br
N
2n
1H NMR (400 MHz, CDCl3) spectra of 2n
1.02
1.02
1.01
0.96
1.02
1.00
1.05
1.02
1.01
1.00
1.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

196.71
171.59
164.59
153.98
139.50
129.72
127.50
122.41
122.19
121.19
77.32
77.00
76.68
70.44
41.34
13.11
9.23
8.01

^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2n**

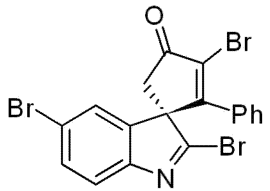


2n

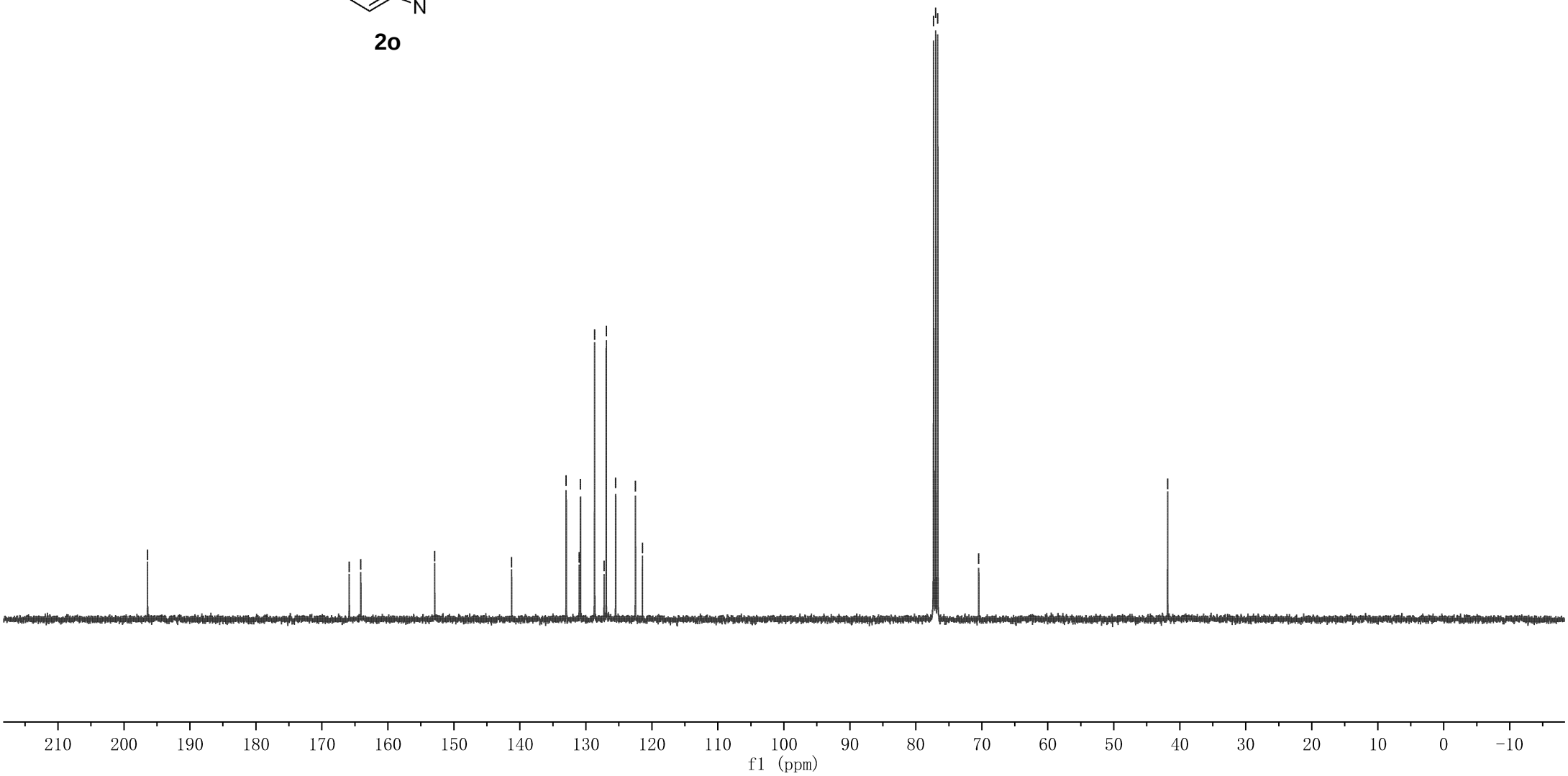

7.561
7.541
7.477
7.442
7.421
7.366
7.346
7.329
7.278
7.262
7.241
7.001
6.982
3.153
3.107
2.910
2.863
0.000
O
Br
Br
Ph
Br
N
2o
1H NMR (400 MHz, CDCl3) spectra of 2o
1.01
2.00
1.04
2.05
2.00
1.01
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

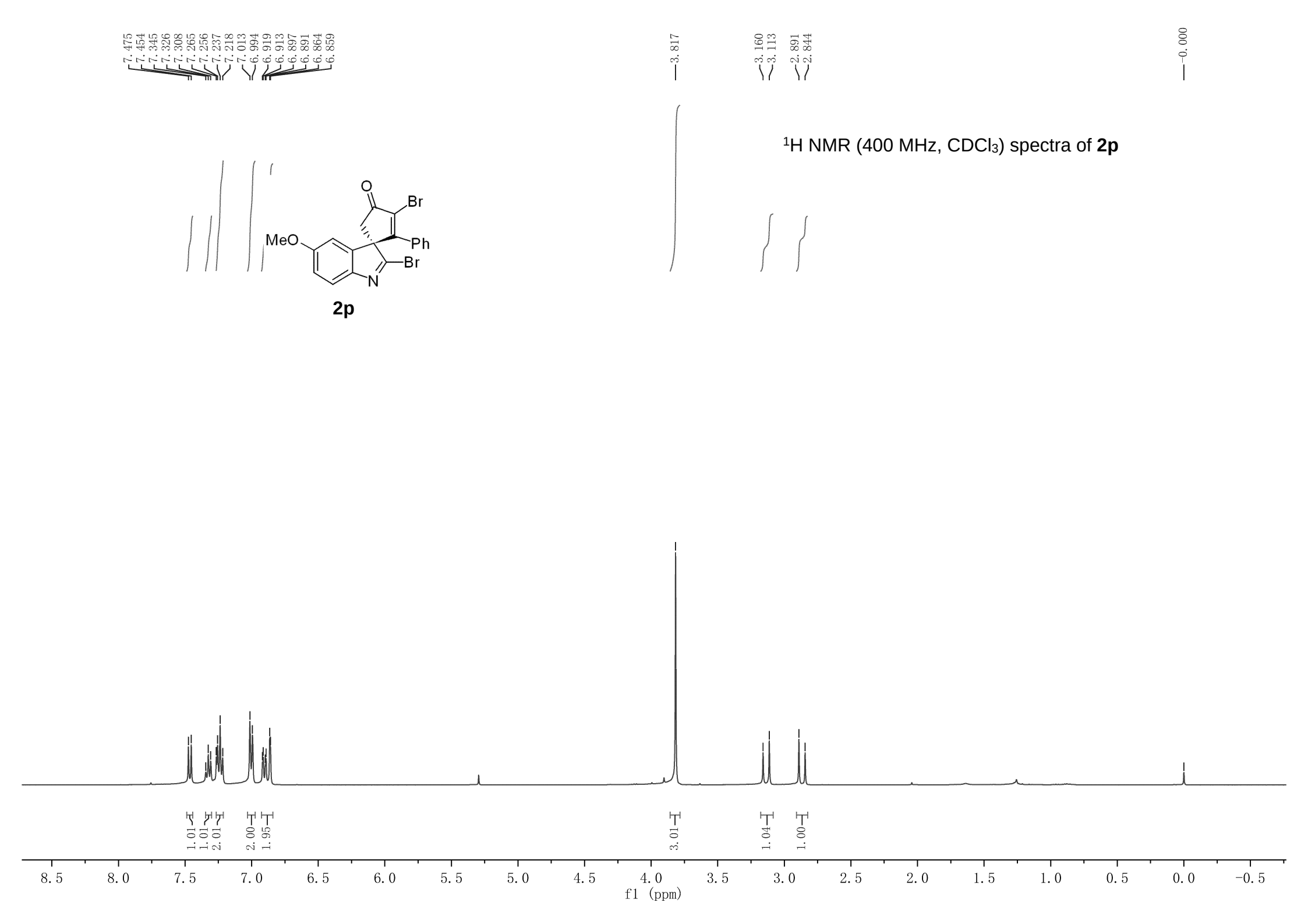
196.42
165.86
164.11
152.91
141.25
132.98
131.01
130.82
128.68
127.25
126.91
125.48
122.49
121.43
77.32
77.00
76.68
70.47
41.85

^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2o**



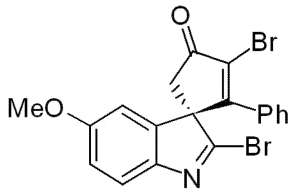
2o



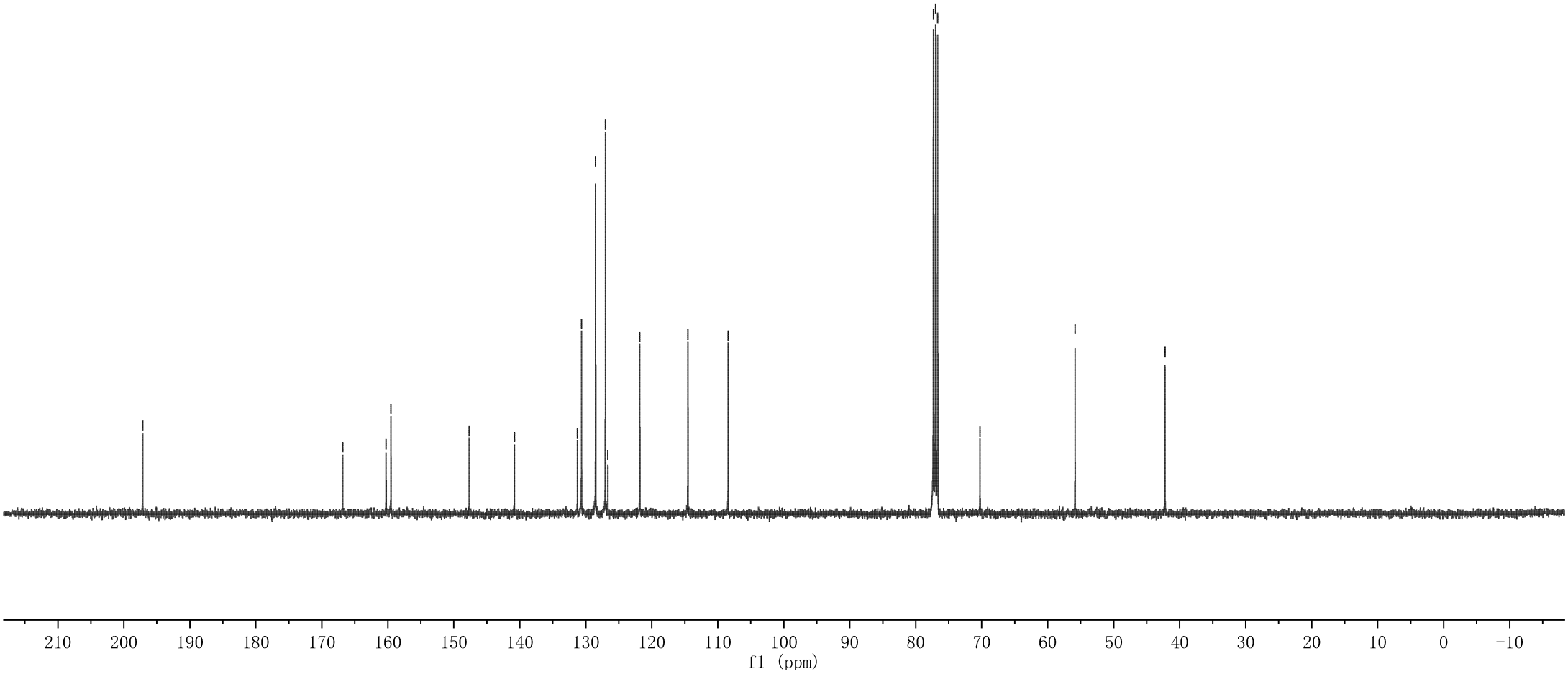

7.475
7.454
7.345
7.326
7.308
7.265
7.256
7.237
7.218
7.013
6.994
6.919
6.913
6.897
6.891
6.864
6.859
3.817
3.160
3.113
2.891
2.844
0.000
O
Br
MeO
Ph
Br
N
2p
1H NMR (400 MHz, CDCl3) spectra of 2p
1.01
1.01
2.01
2.00
1.95
3.01
1.04
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

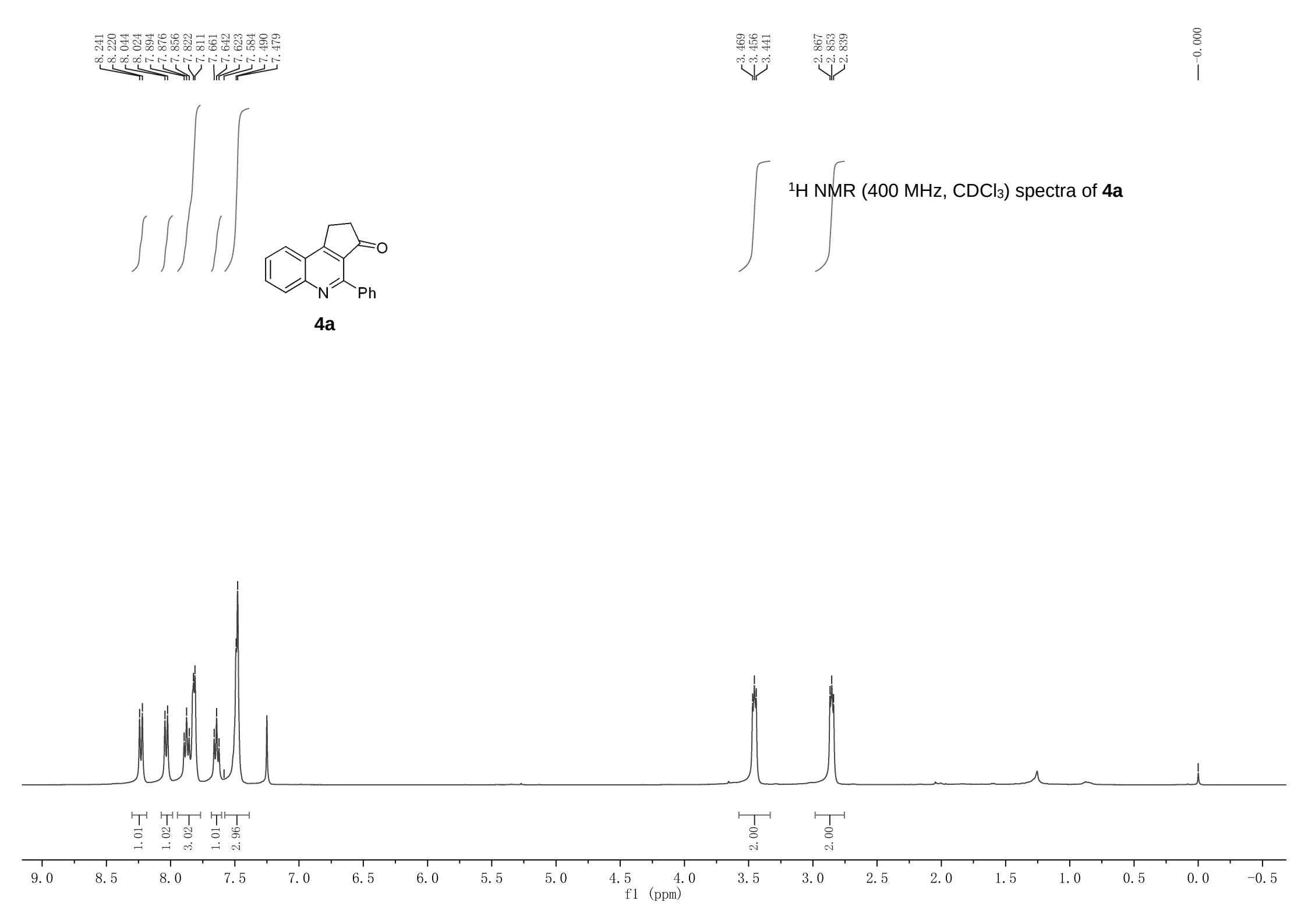
197.15
166.84
160.26
159.53
147.66
140.82
131.27
130.65
128.51
127.02
126.66
121.82
114.52
108.41
77.32
77.00
76.68
70.26
55.85
42.23

^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2p**



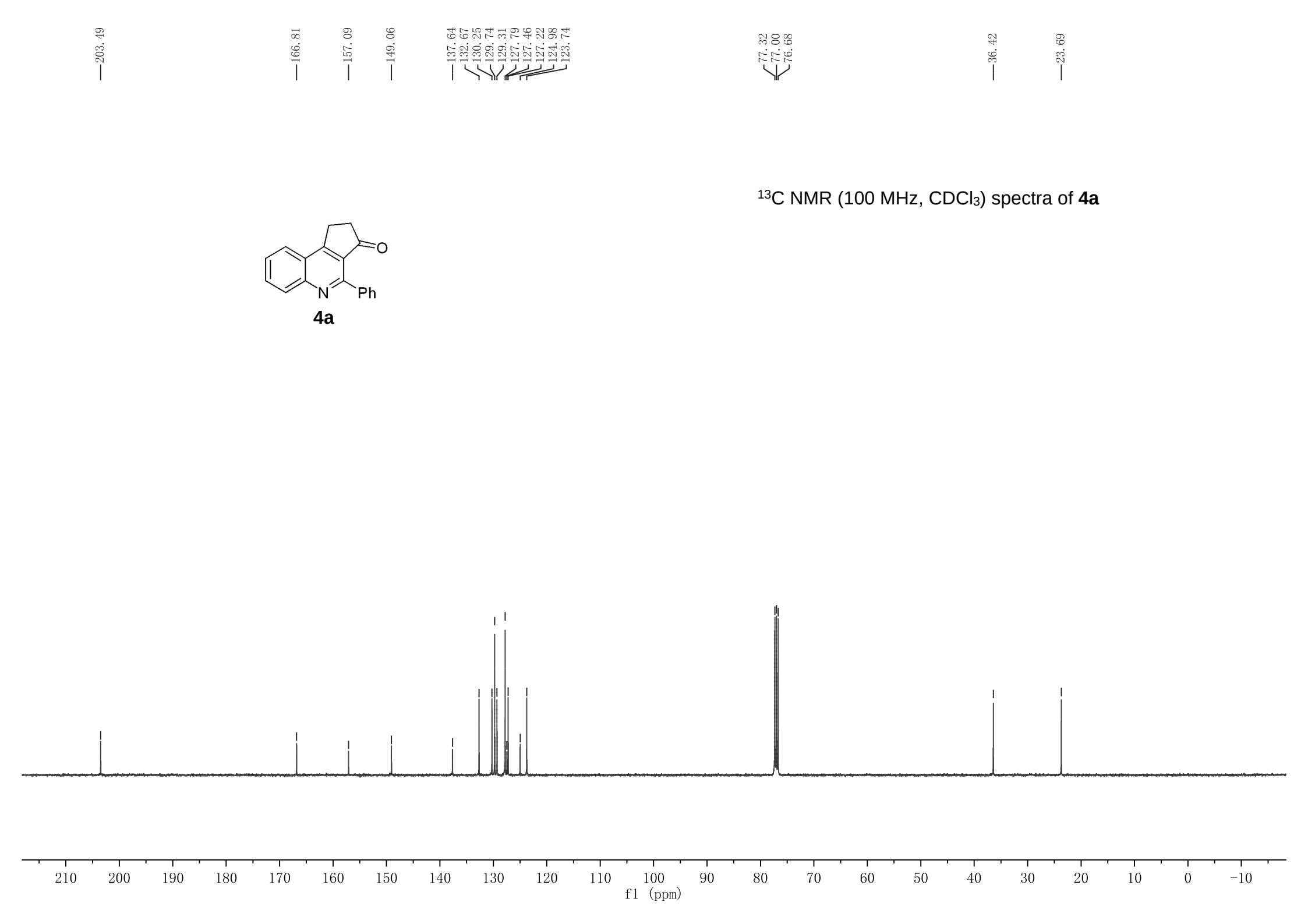
2p



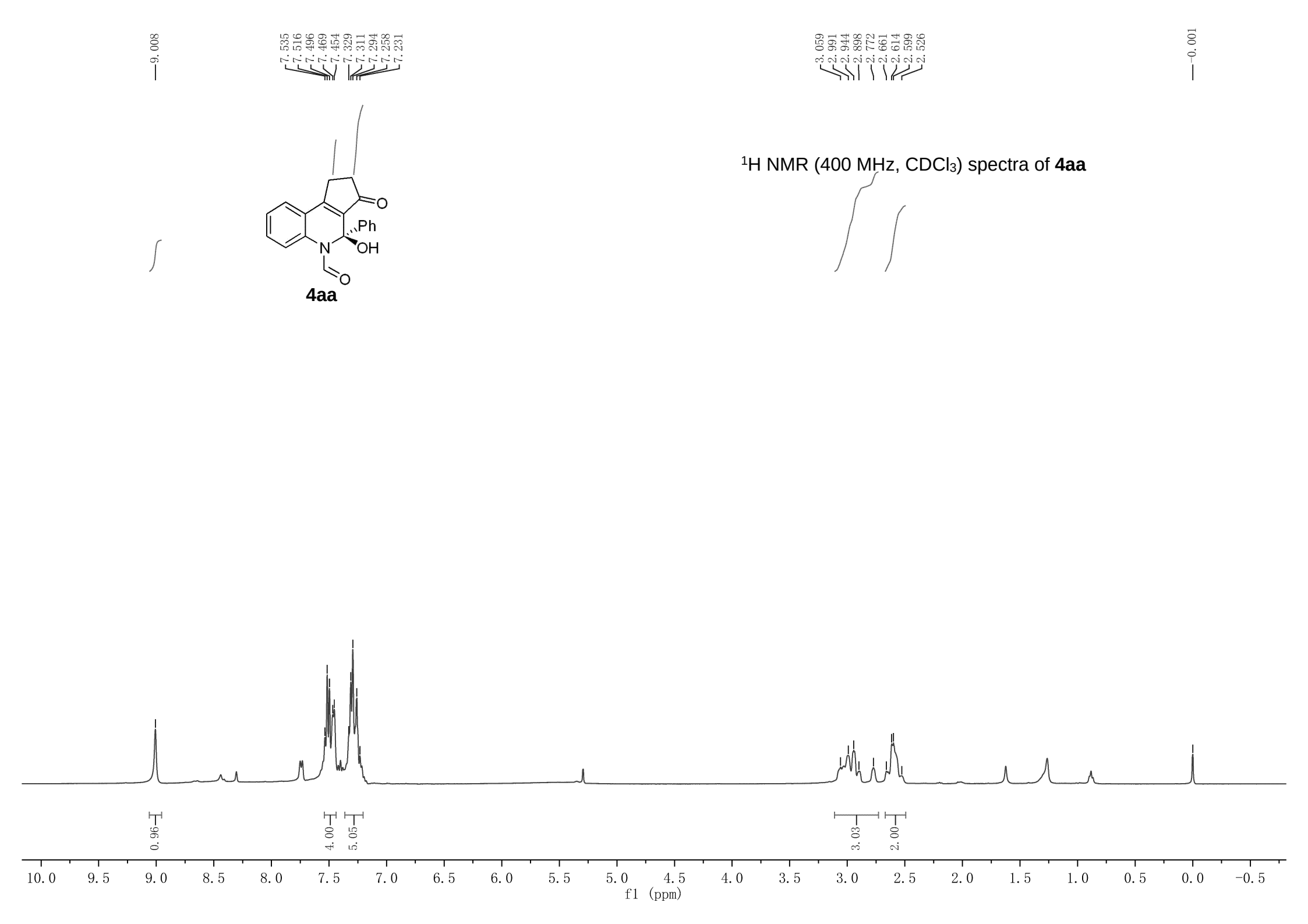


4a

^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4a**

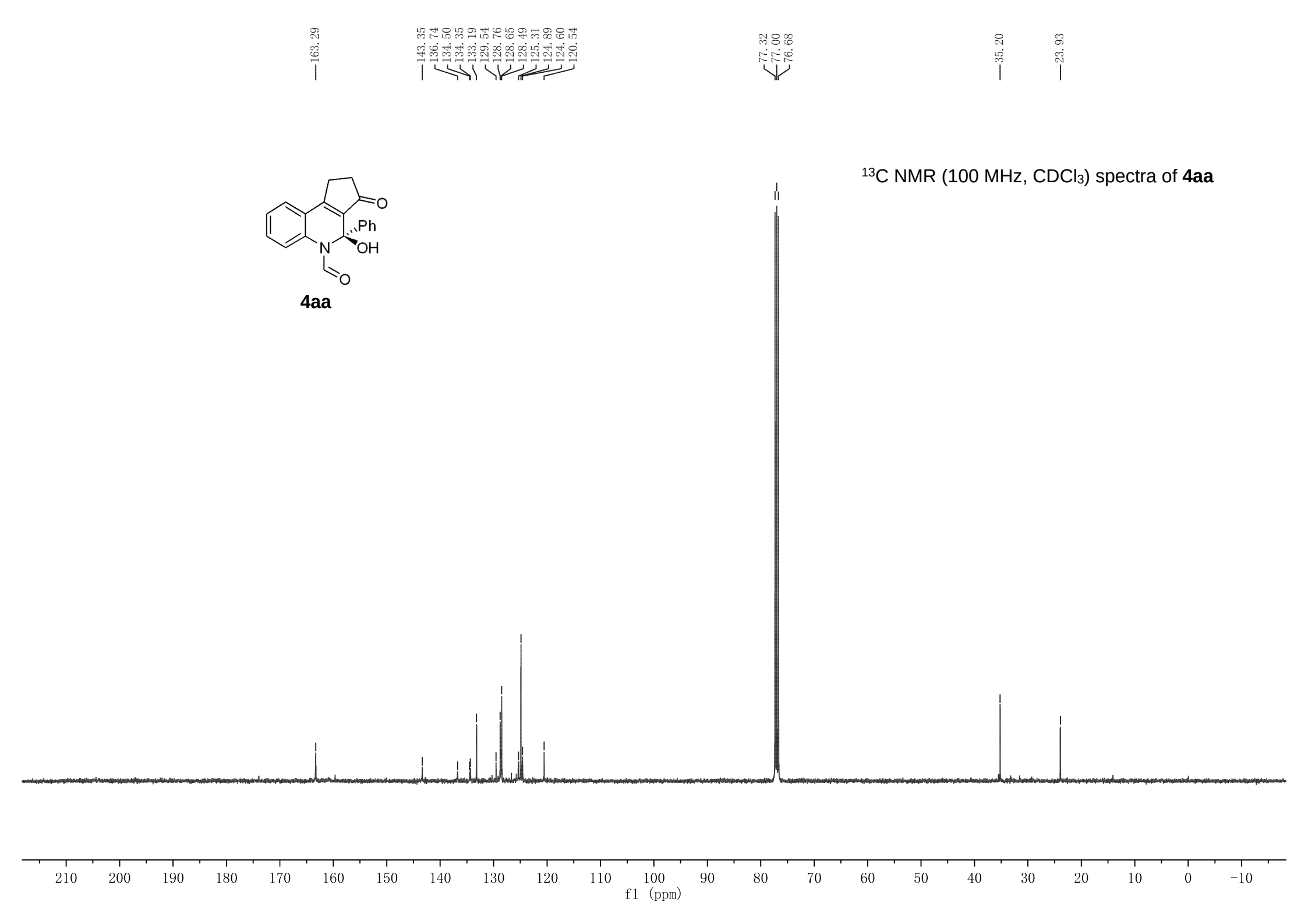


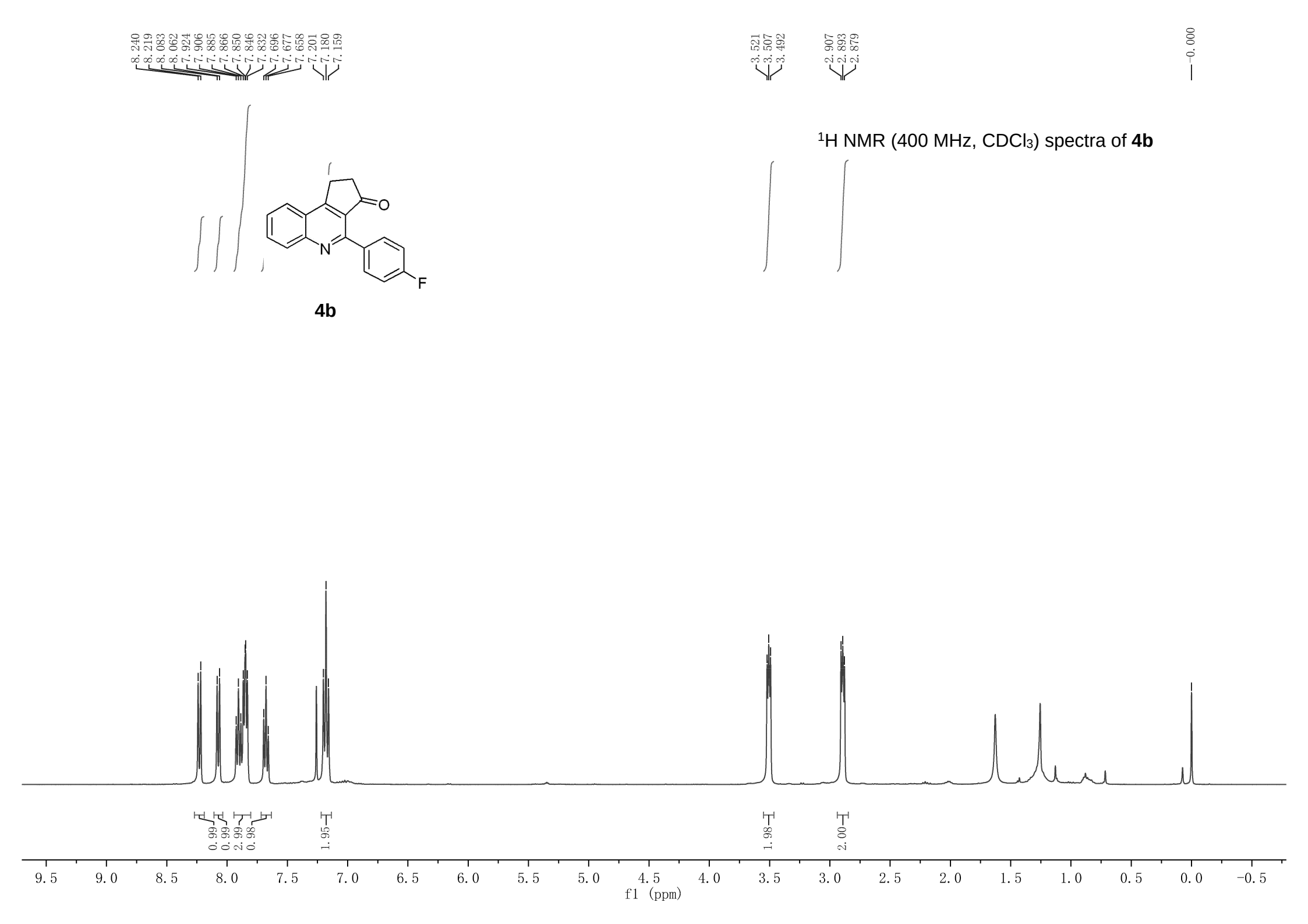
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4a**



4aa

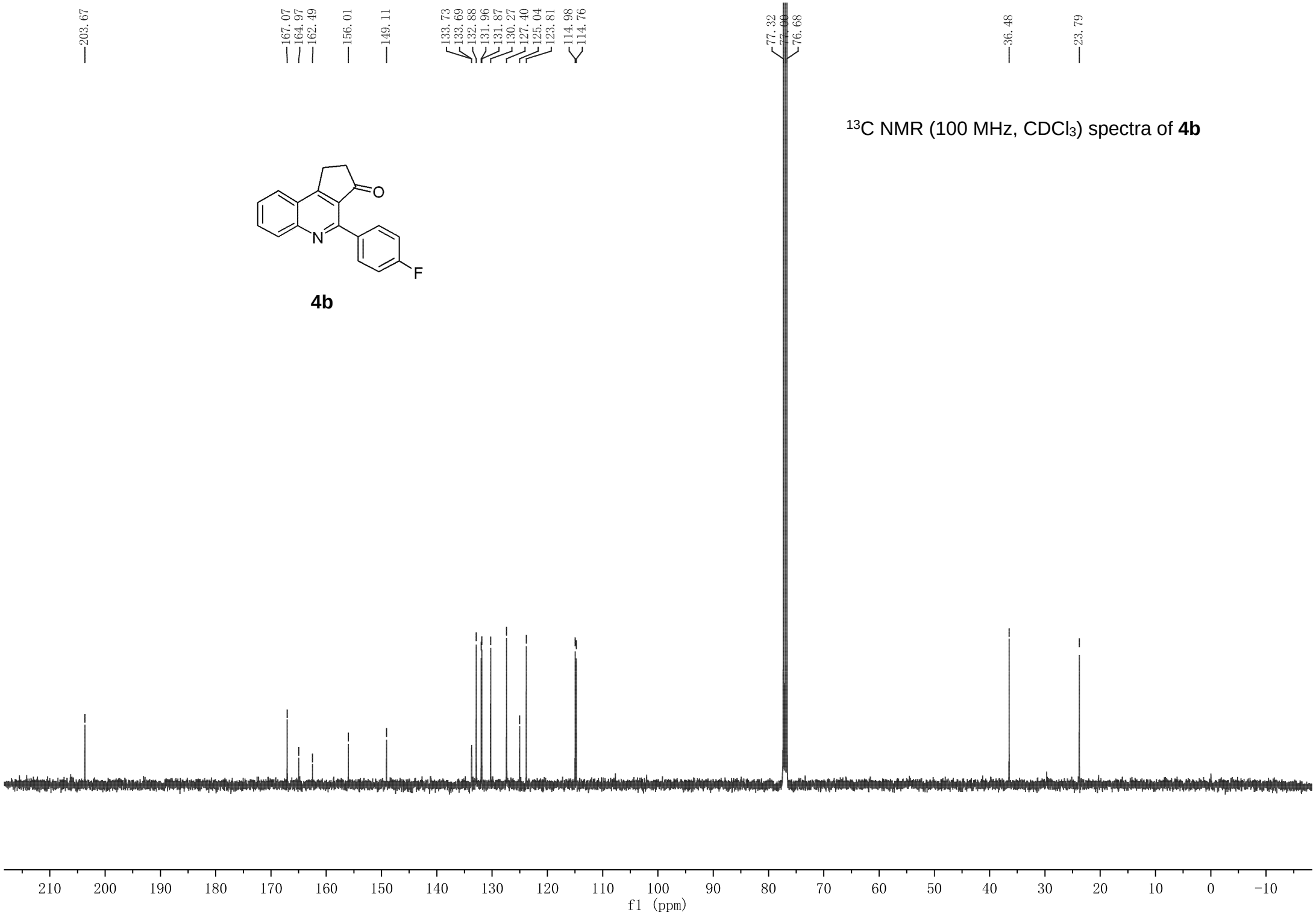
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4aa**

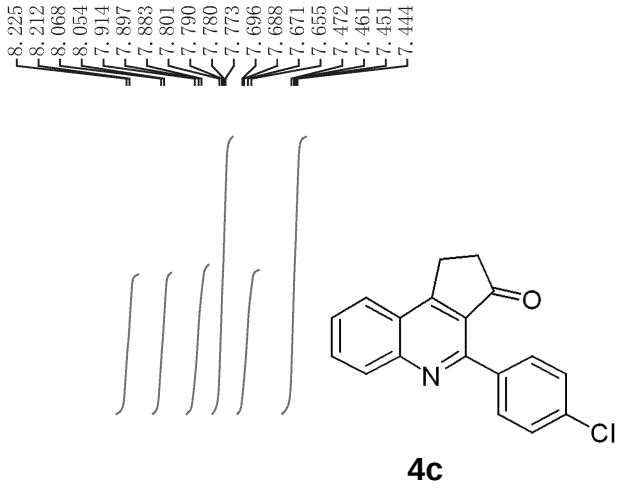

163.29
143.35
136.74
134.50
134.35
133.19
129.54
128.76
128.65
128.49
125.31
124.89
124.60
120.54
77.32
77.00
76.68
35.20
23.93
O
Ph
OH
N
O
4aa
13C NMR (100 MHz, CDCl3) spectra of 4aa
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



4b

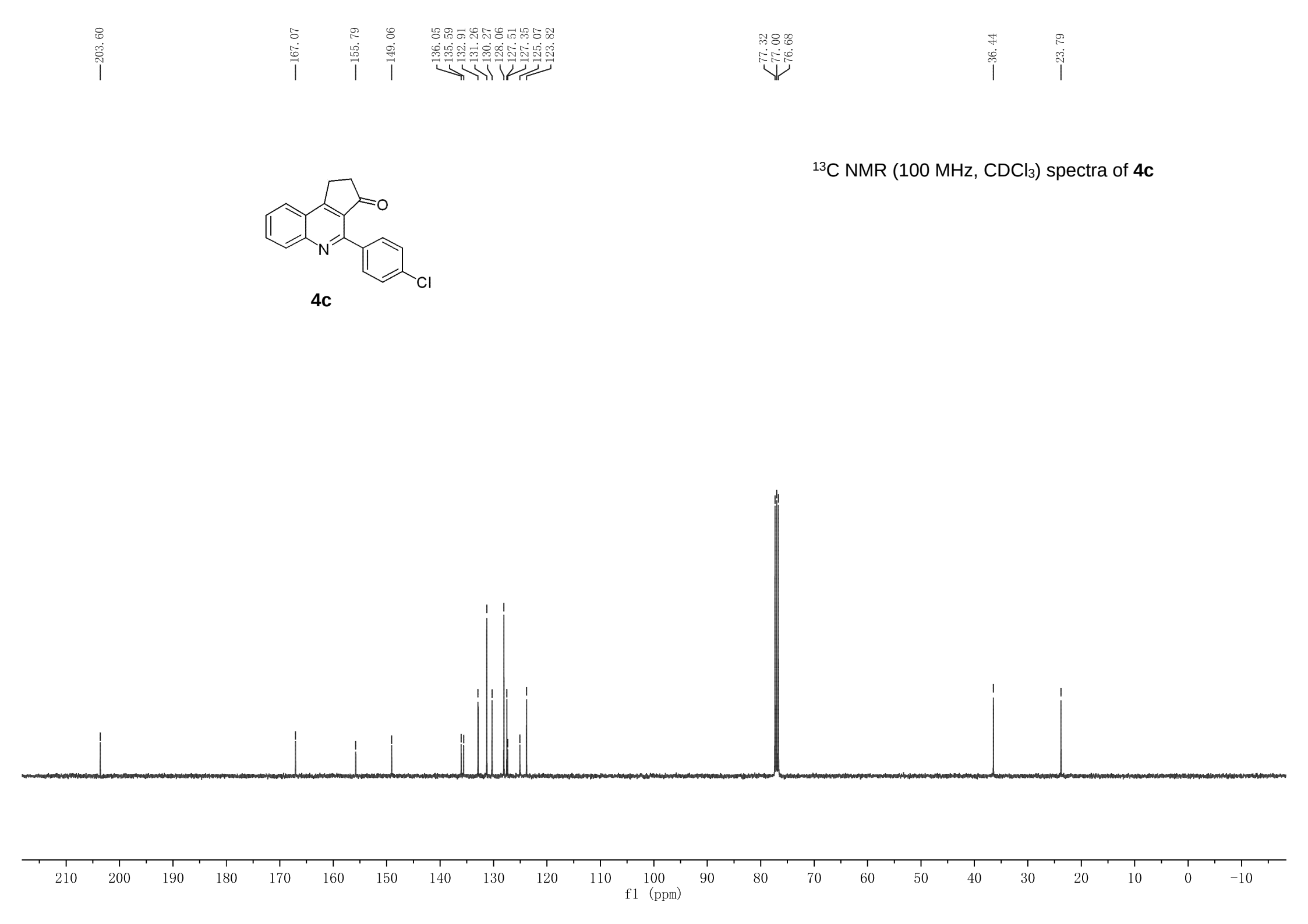
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4b**

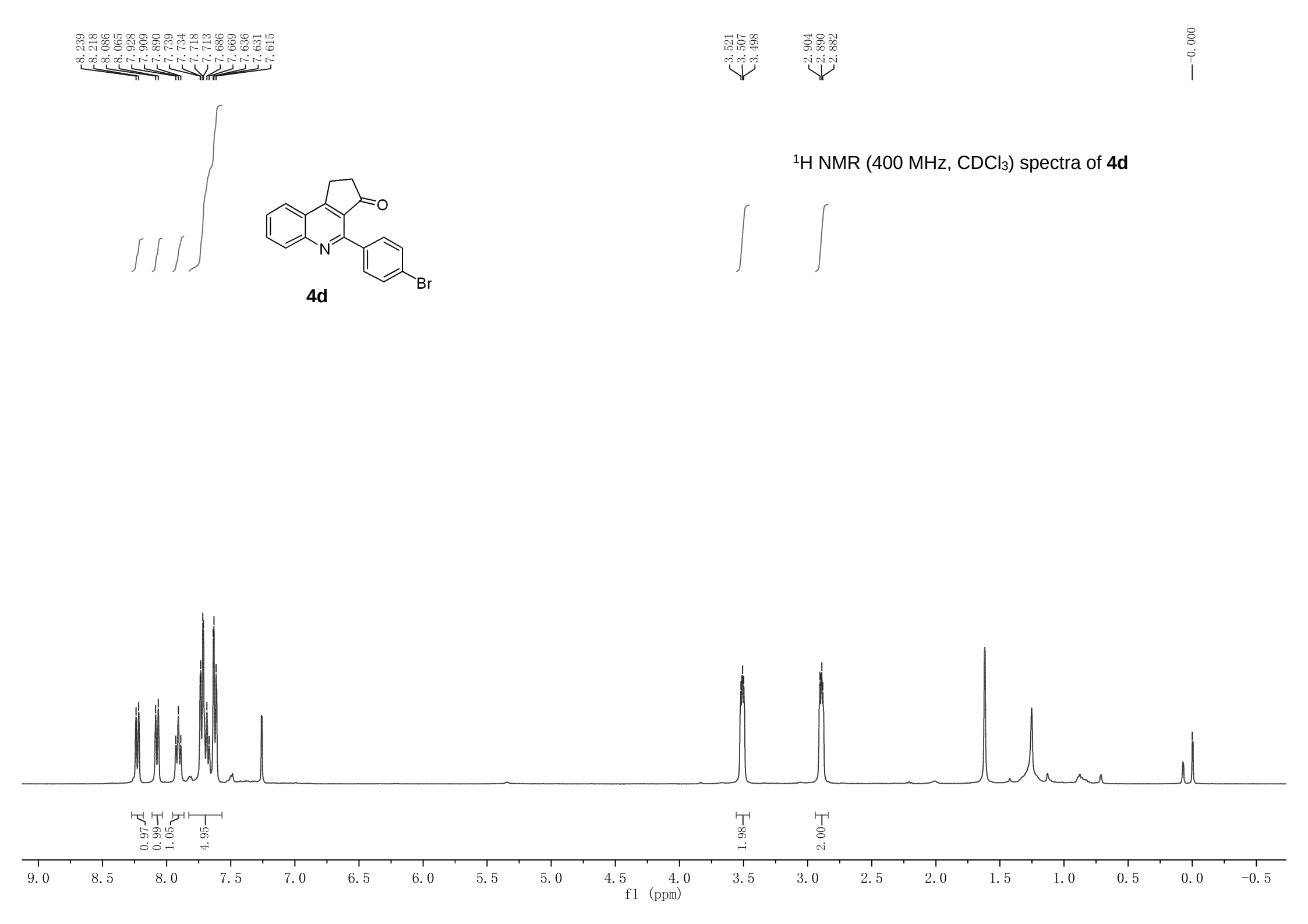

203.67
167.07
164.97
162.49
156.01
149.11
133.73
133.69
132.88
131.96
131.87
130.27
127.40
125.04
123.81
114.98
114.76
77.32
77.00
76.68
36.48
23.79
O
N
F
4b
13C NMR (100 MHz, CDCl3) spectra of 4b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



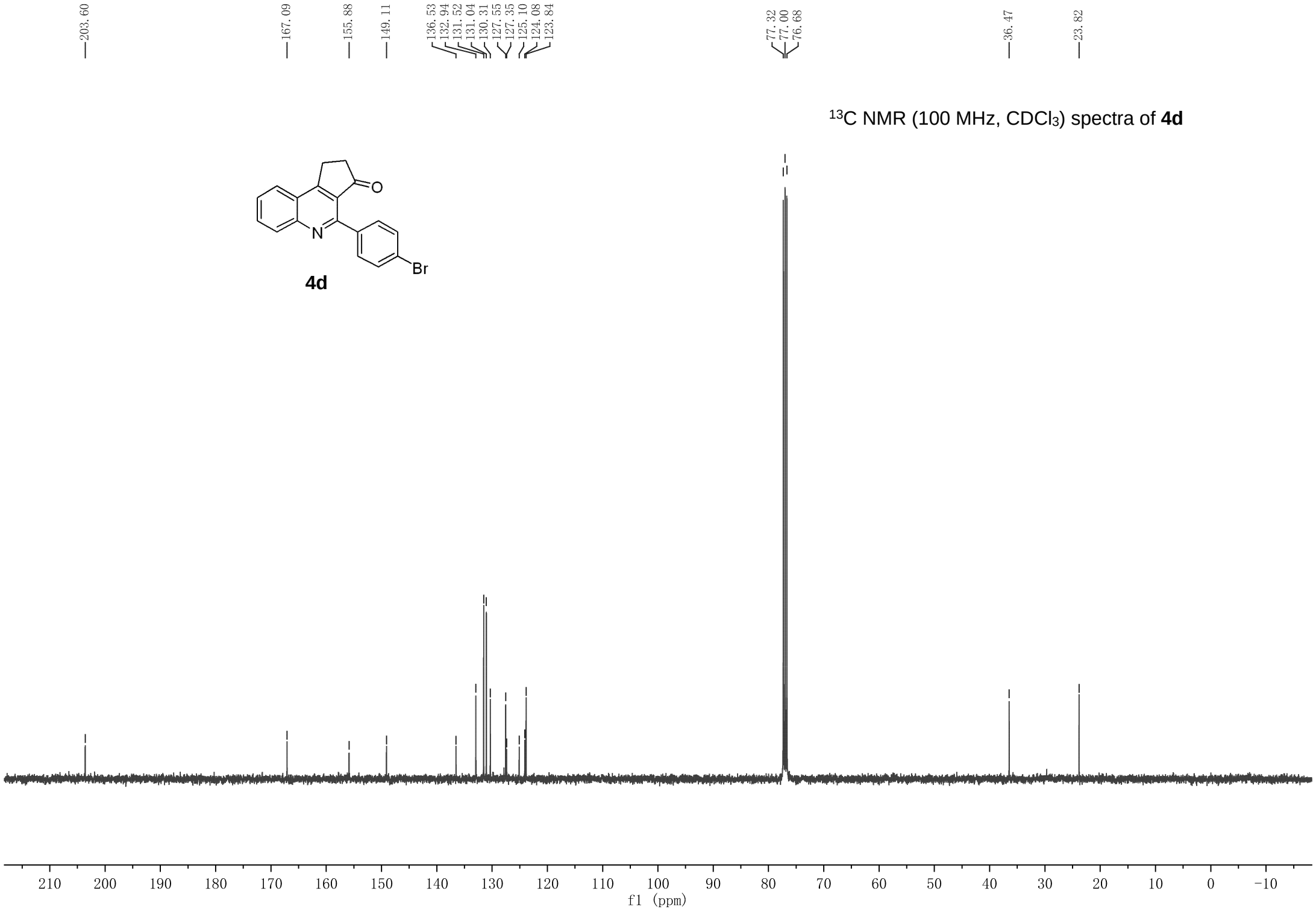
4c

^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4c**

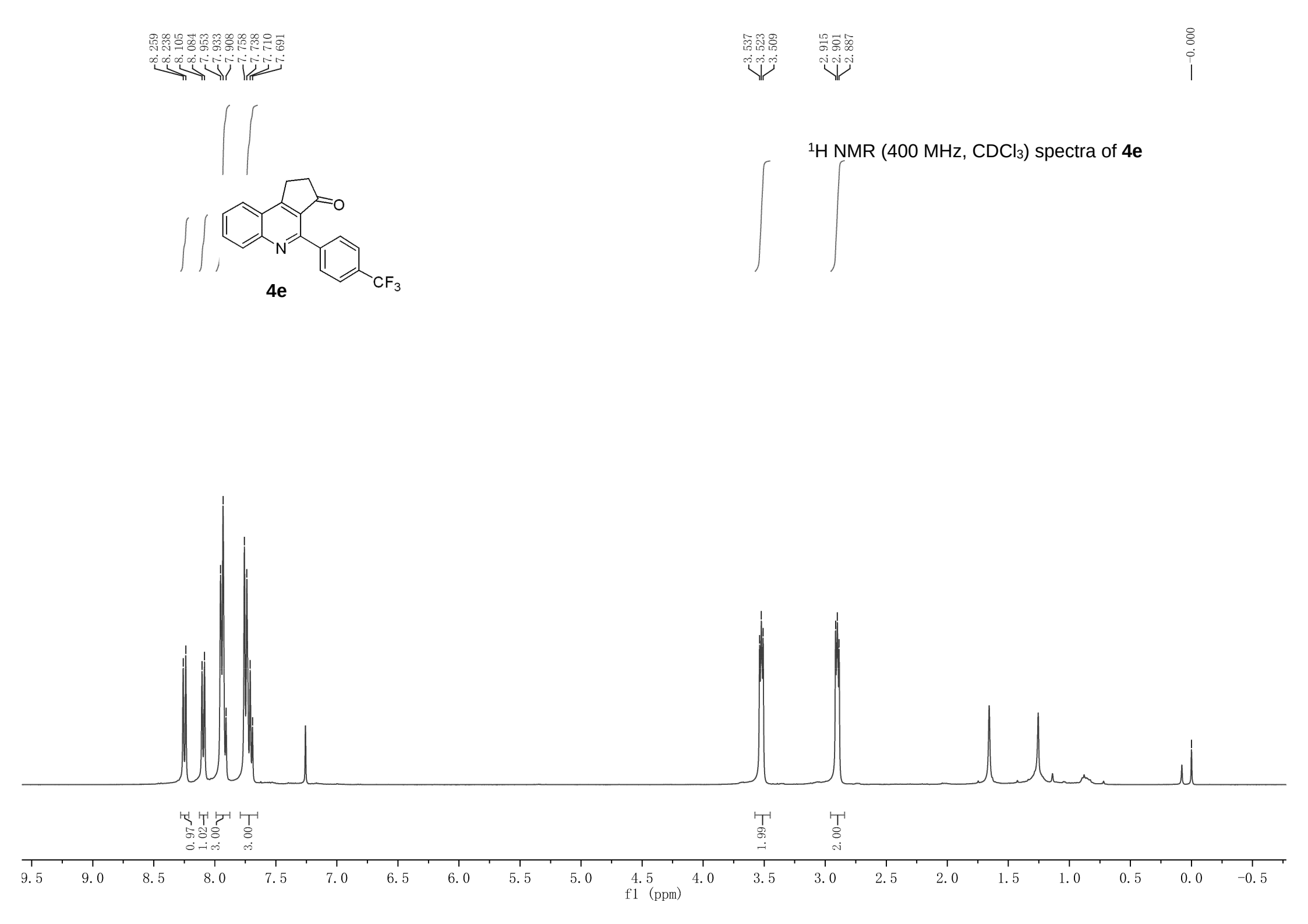

203.60
167.07
155.79
149.06
136.05
135.59
132.91
131.26
130.27
128.06
127.51
127.35
125.07
123.82
77.32
77.00
76.68
36.44
23.79
O
N
Cl
4c
13C NMR (100 MHz, CDCl3) spectra of 4c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

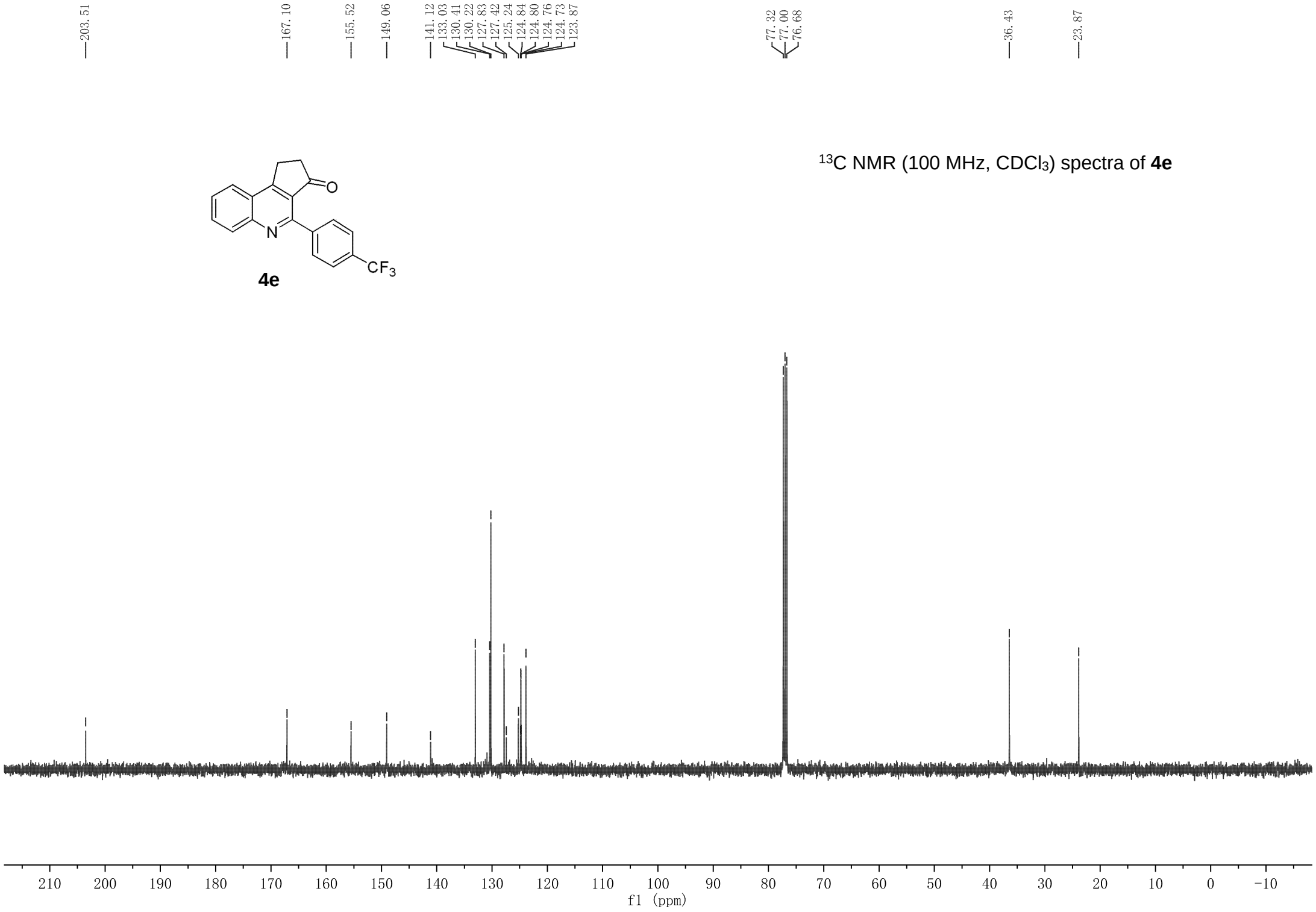


^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4d**

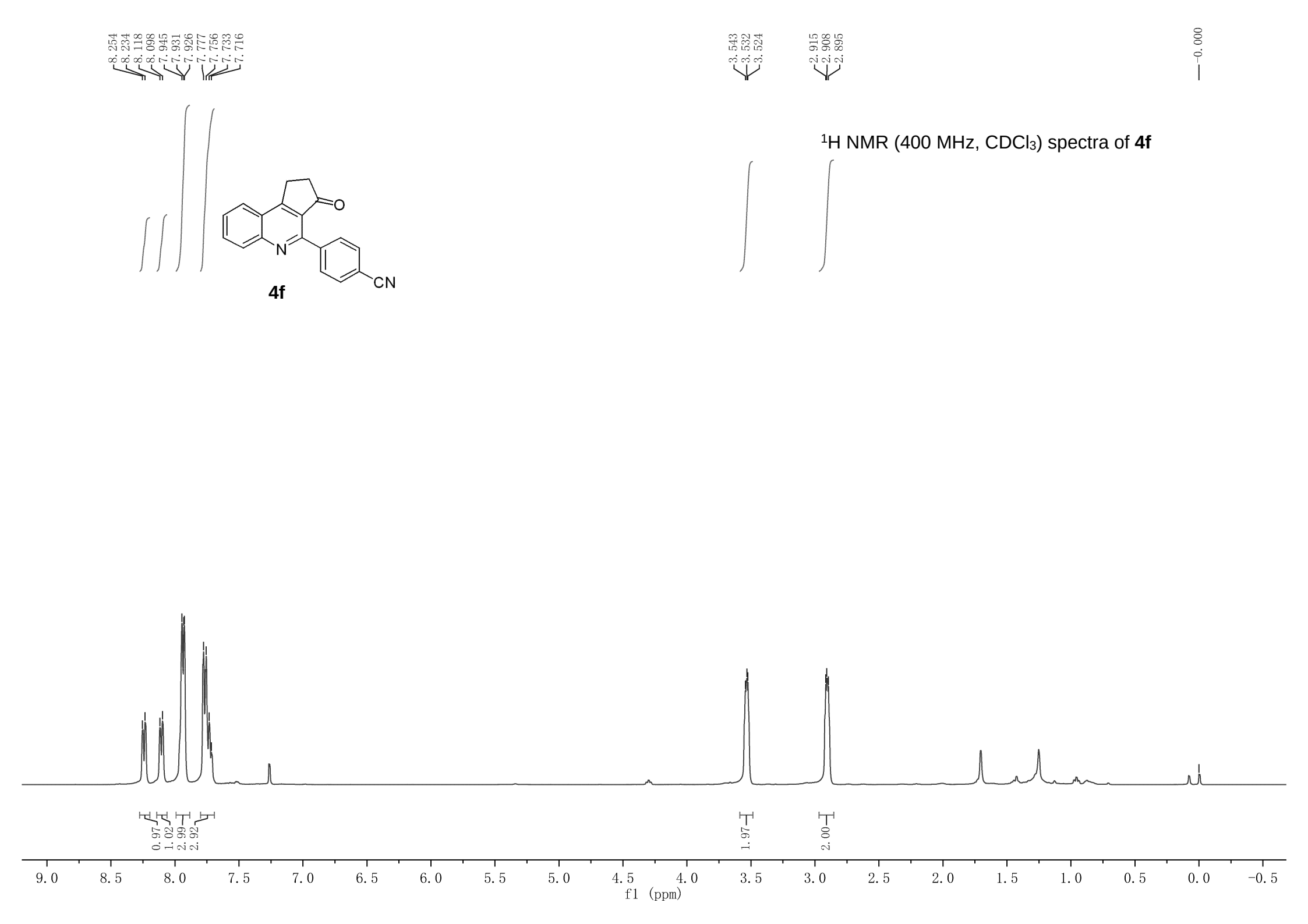


^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4d**

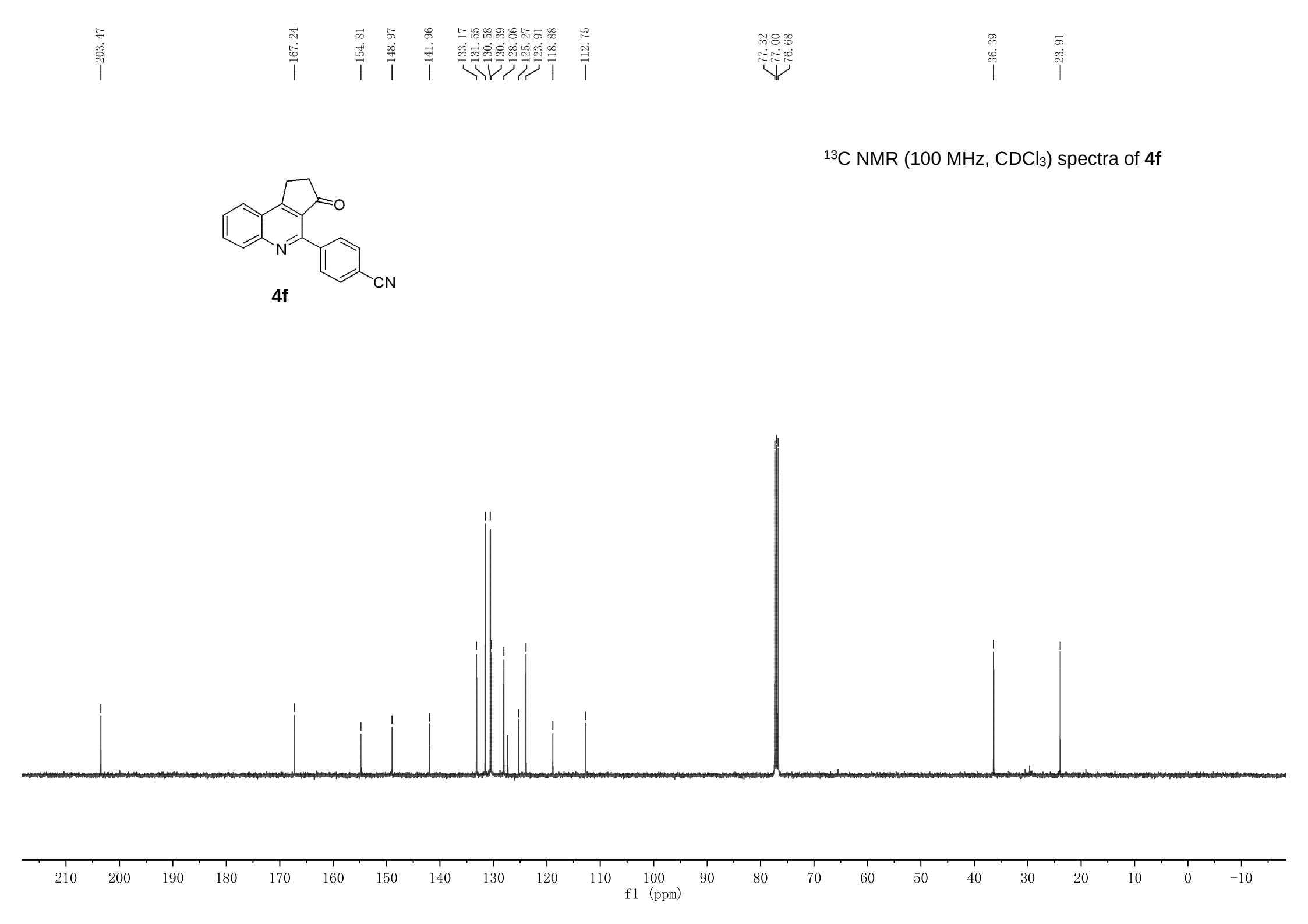

8.259
8.238
8.105
8.084
7.953
7.933
7.908
7.758
7.738
7.710
7.691
3.537
3.523
3.509
2.915
2.901
2.887
0.000
O
N
CF3
4e
1H NMR (400 MHz, CDCl3) spectra of 4e
0.97
1.02
3.00
3.00
1.99
2.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



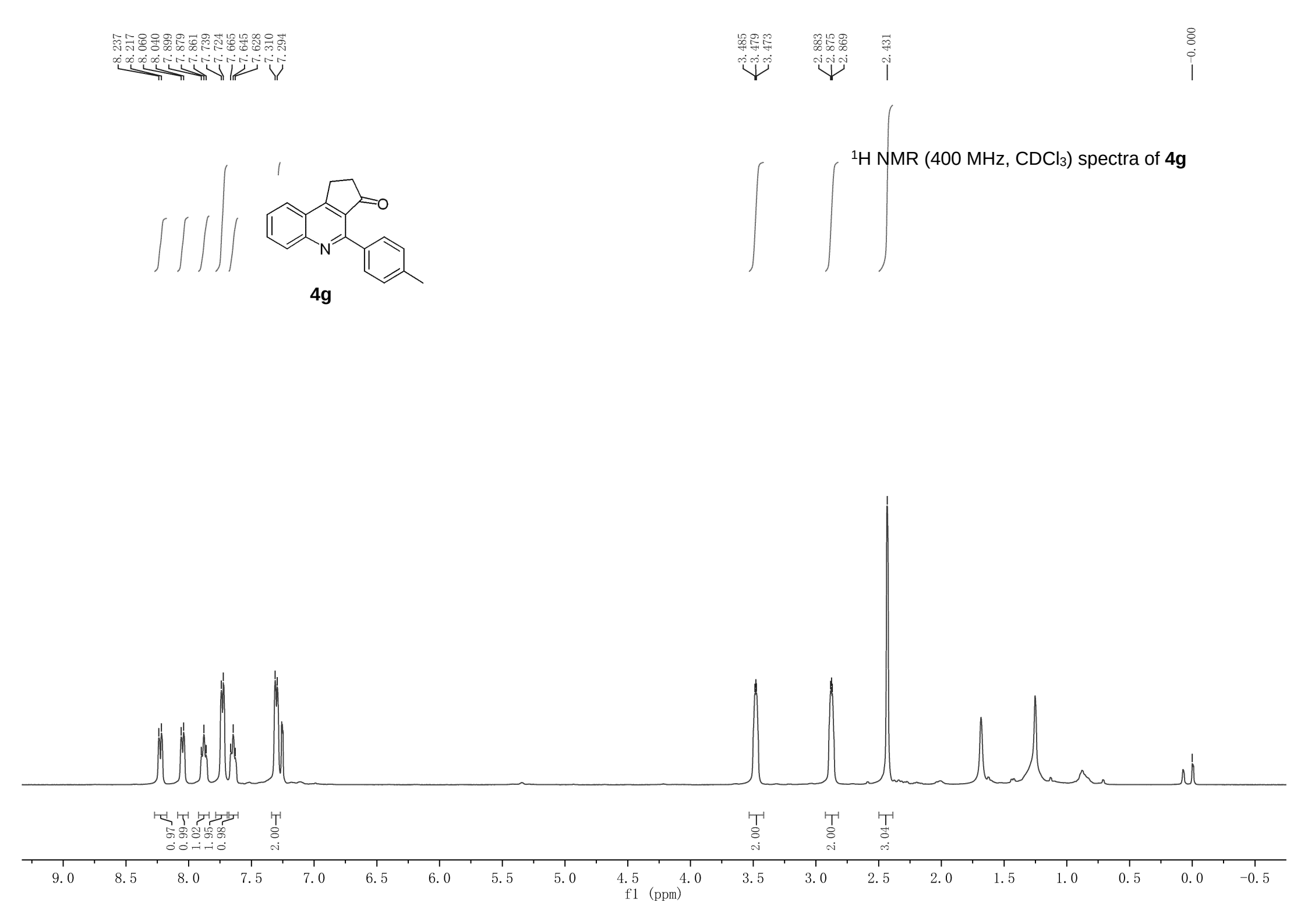
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4e**



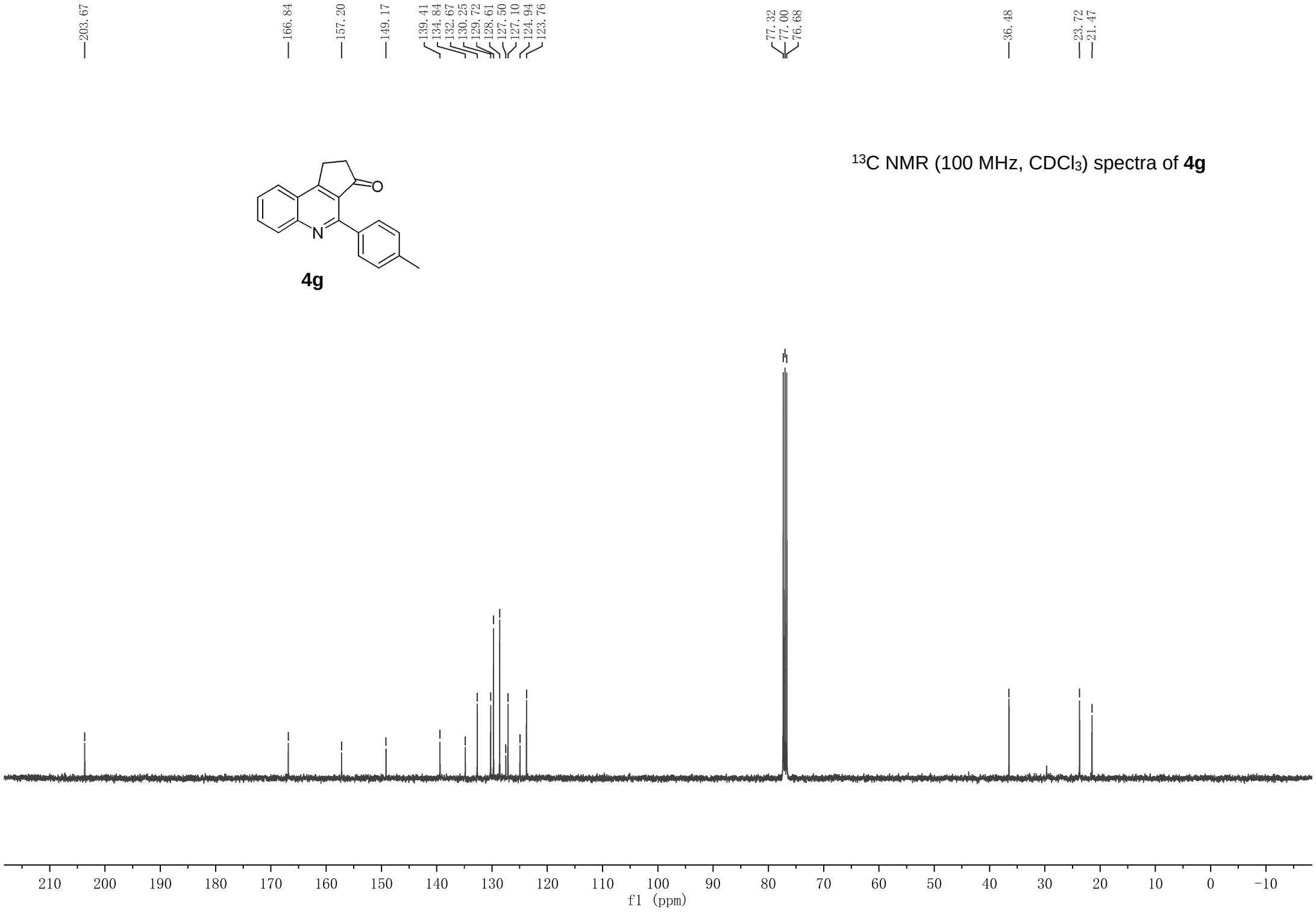
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4f**



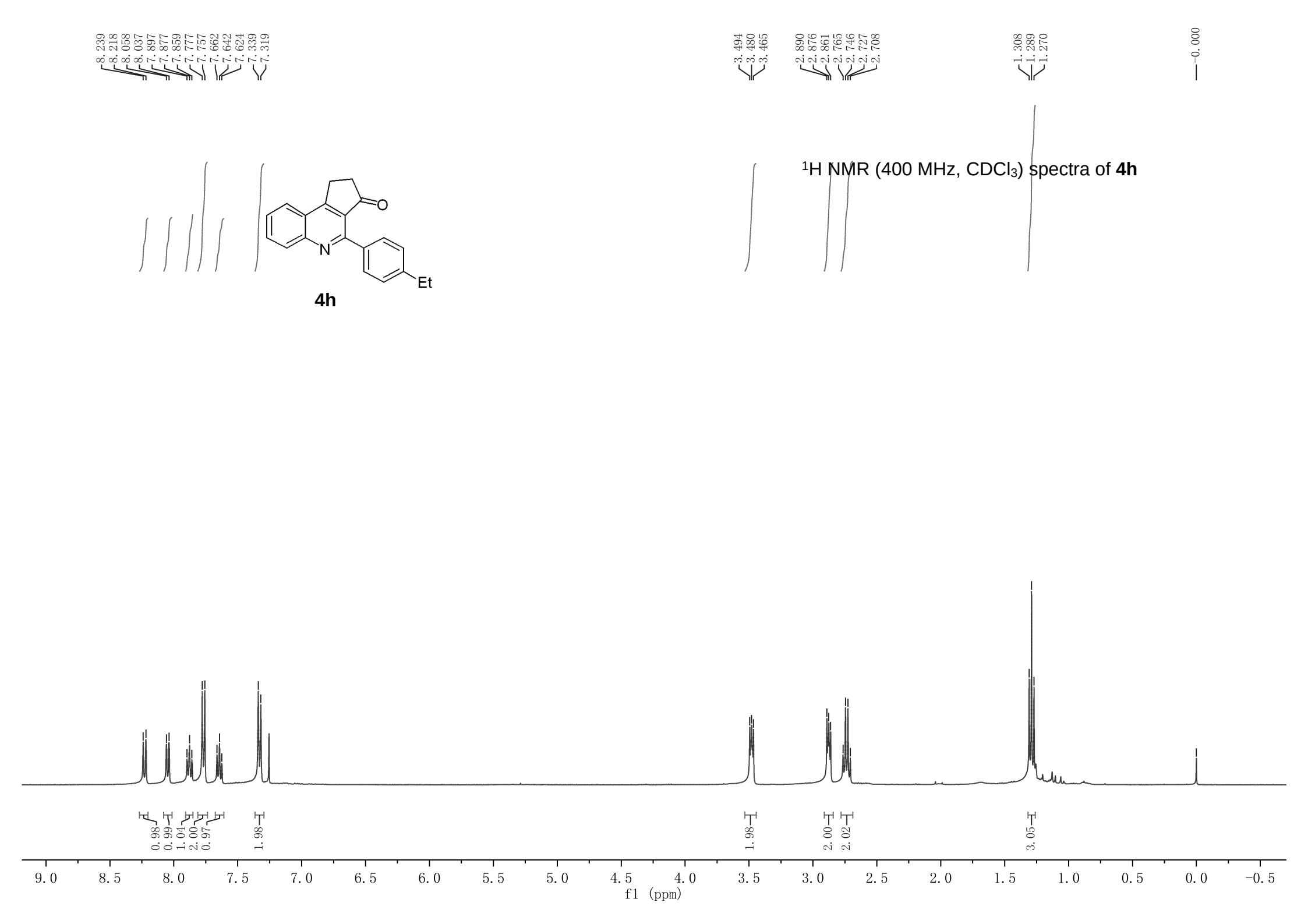
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4f**



^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4g**

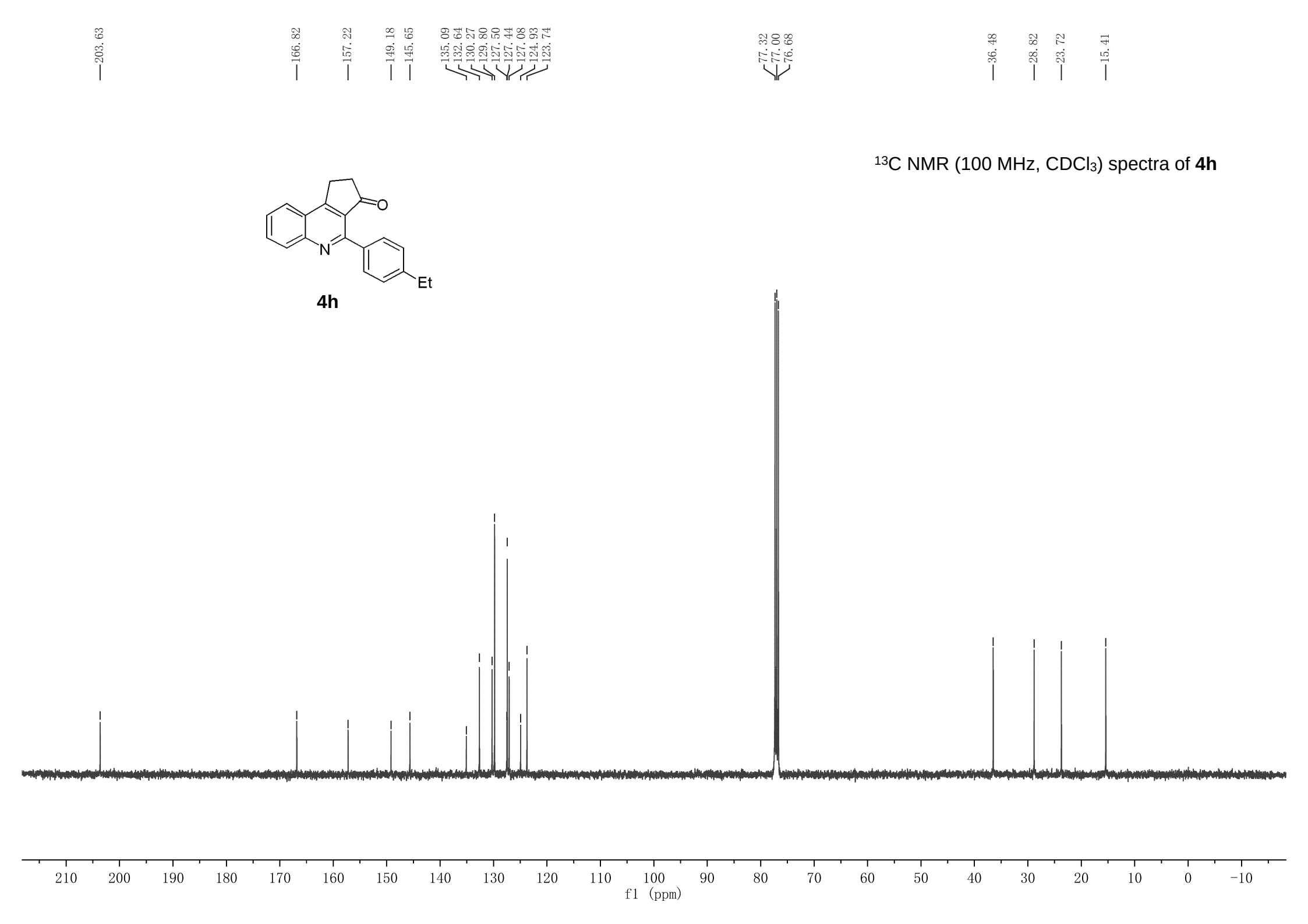


^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4g**

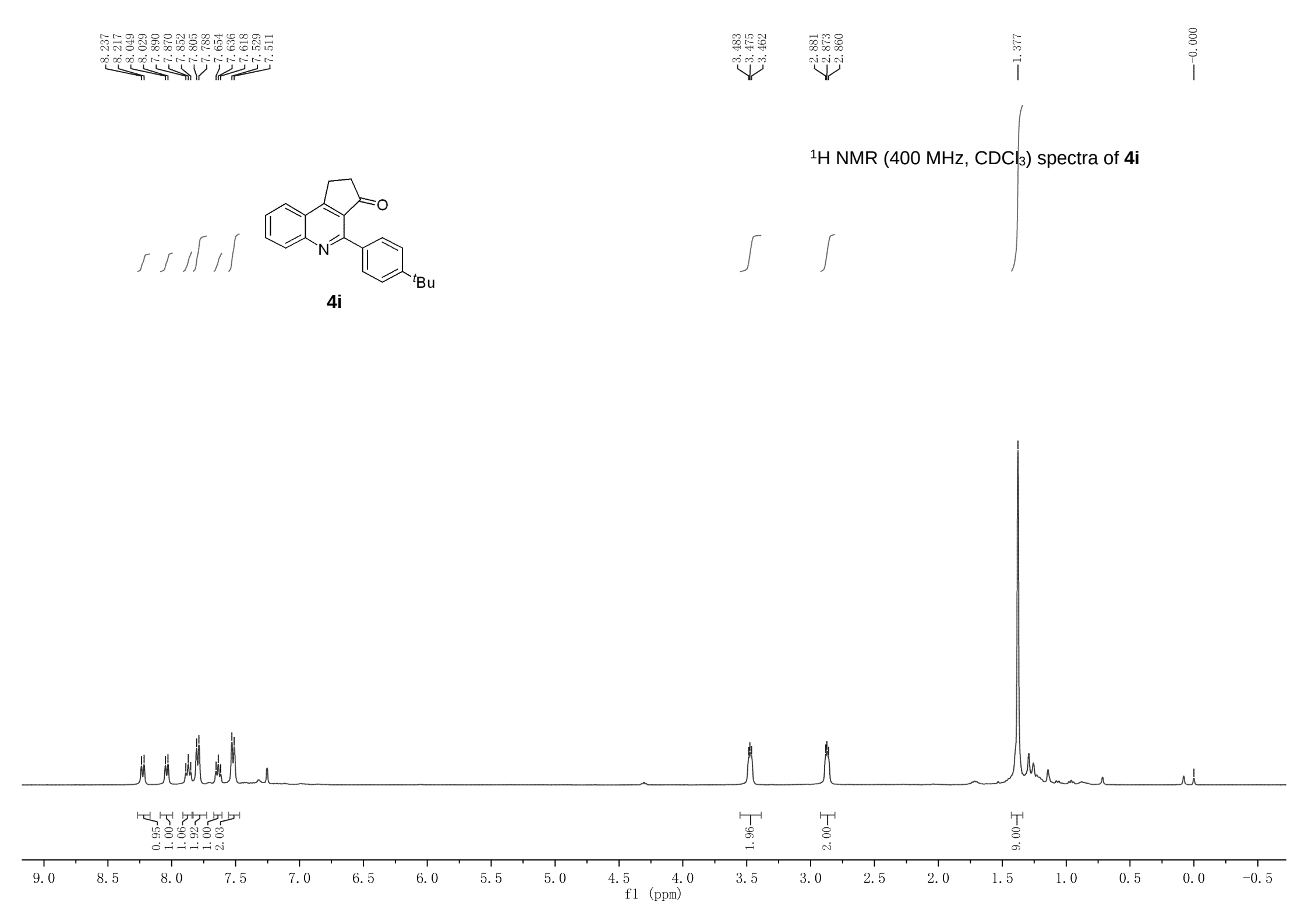


4h

^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4h**

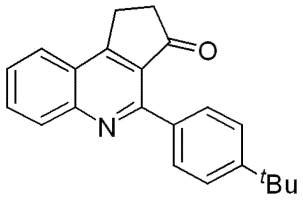


^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4h**



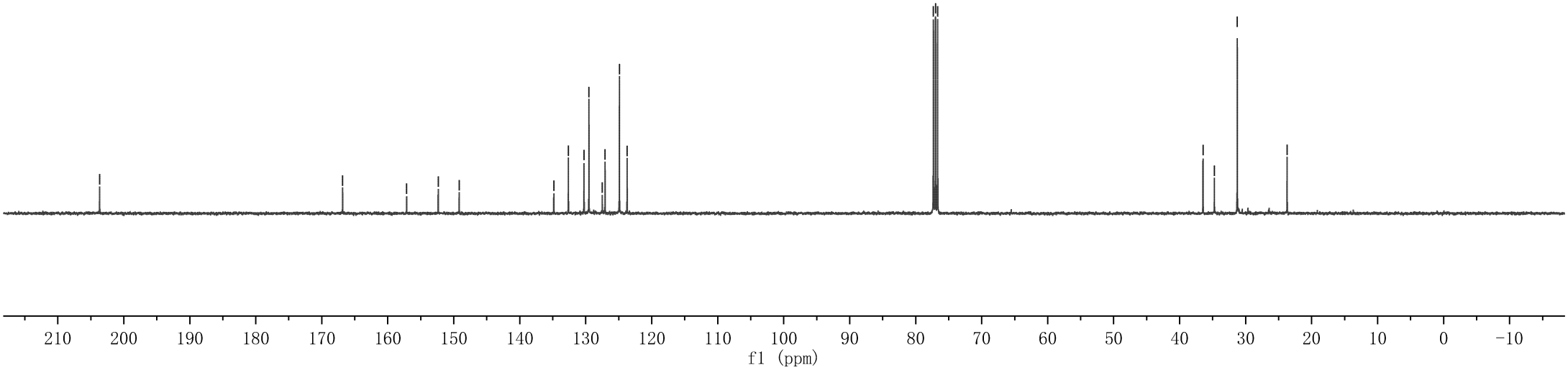
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4i**

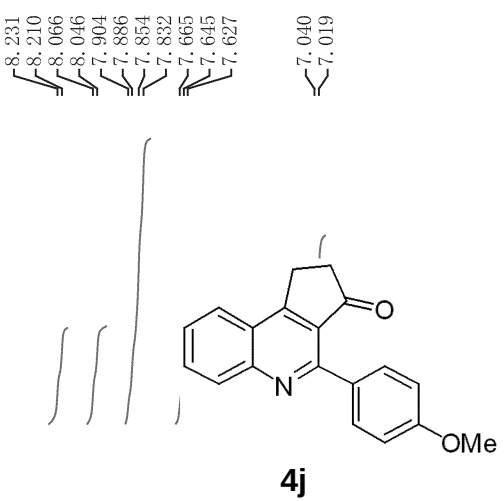
203.66
166.84
157.14
152.35
149.18
134.84
132.63
130.26
129.51
127.49
127.07
124.90
123.73
77.32
77.00
76.68
36.46
34.74
31.27
23.72



4i

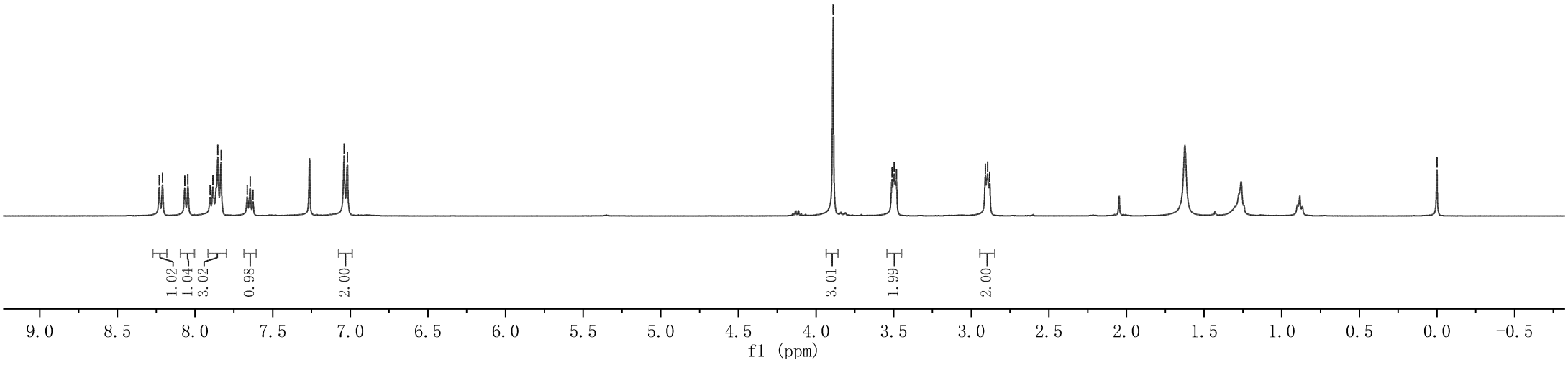
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4i**

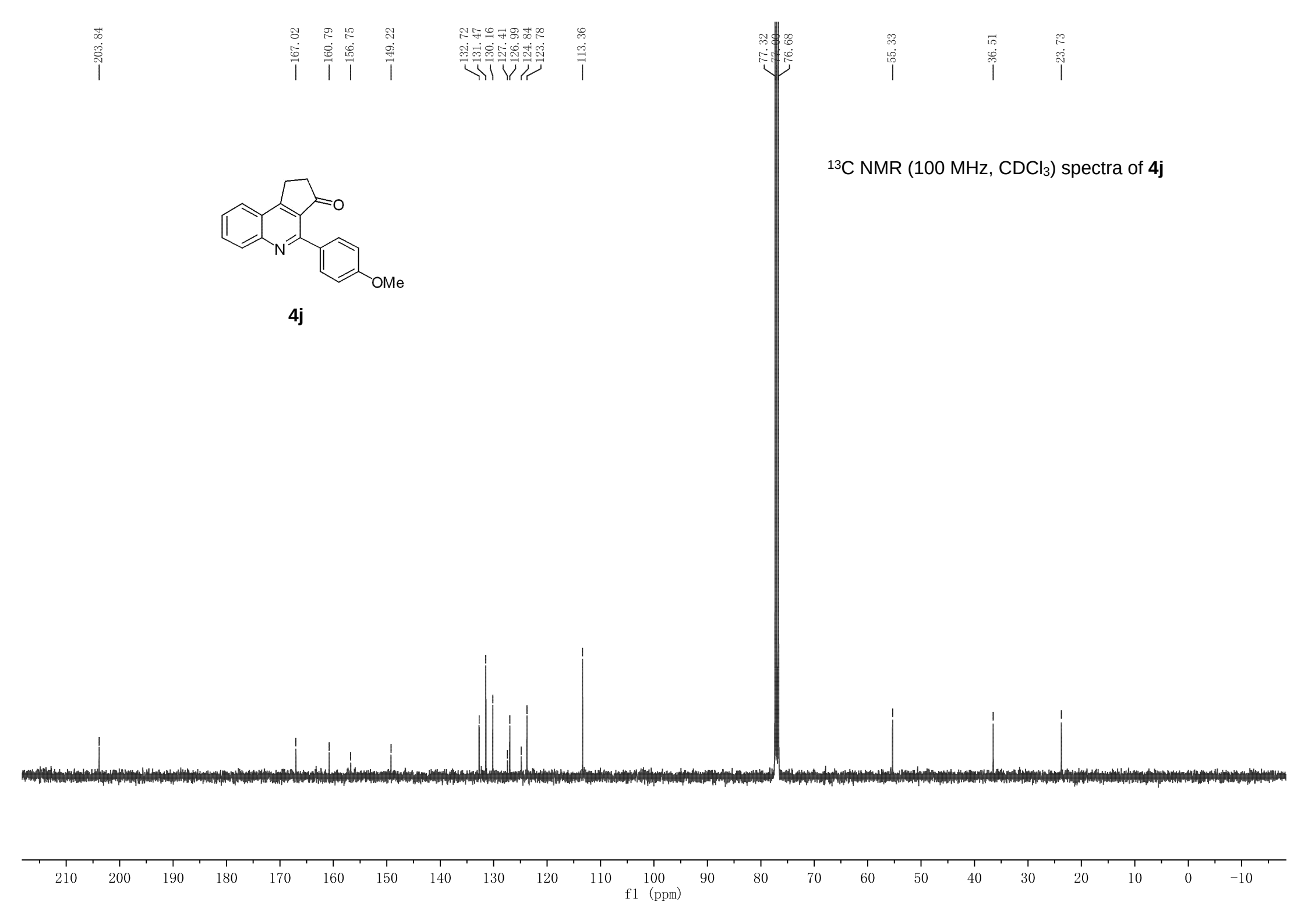


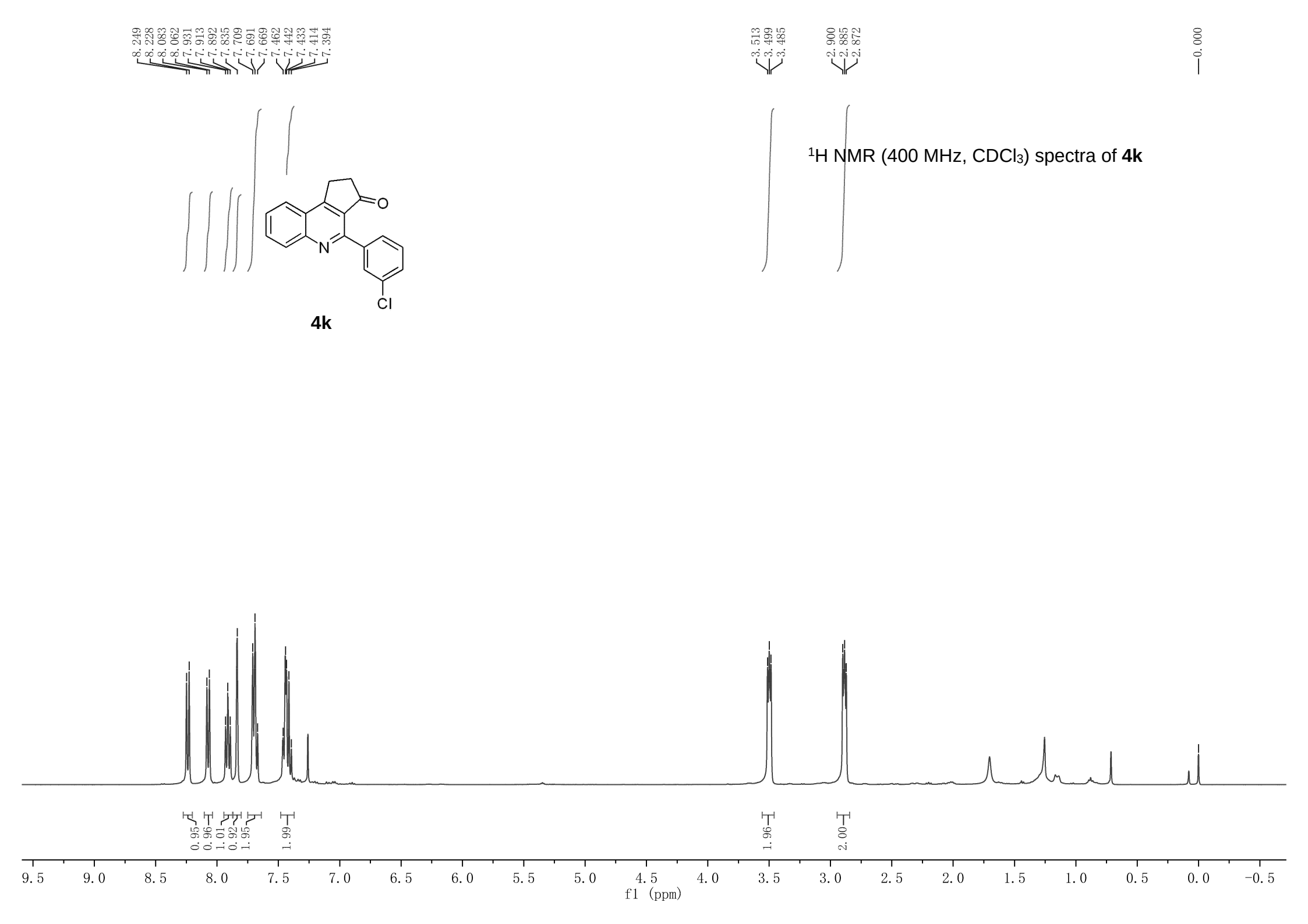


4j

^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4j**

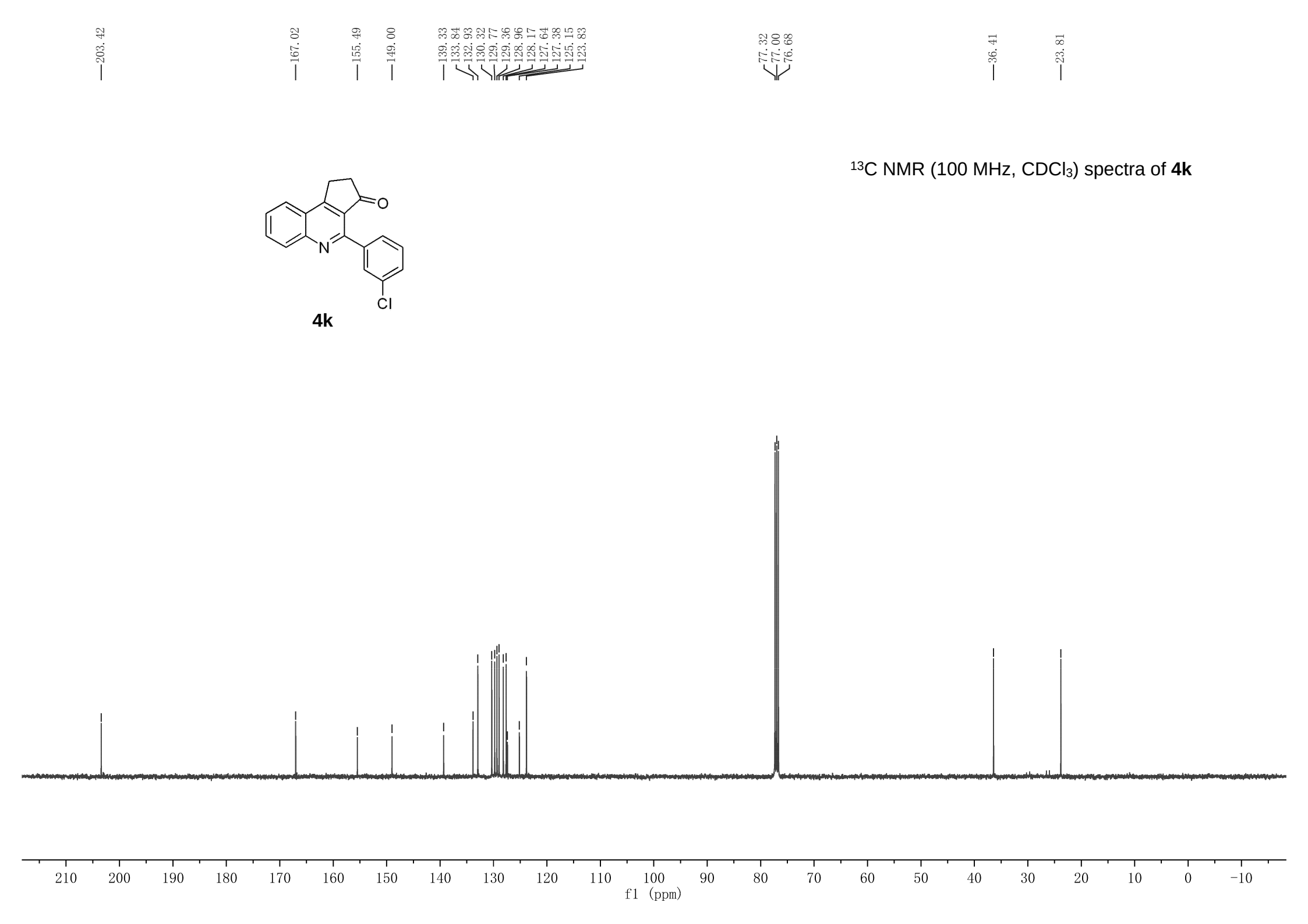



203.84
167.02
160.79
156.75
149.22
132.72
131.47
130.16
127.41
126.99
124.84
123.78
113.36
77.32
77.00
76.68
55.33
36.51
23.73
O
N
OMe
4j
13C NMR (100 MHz, CDCl3) spectra of 4j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

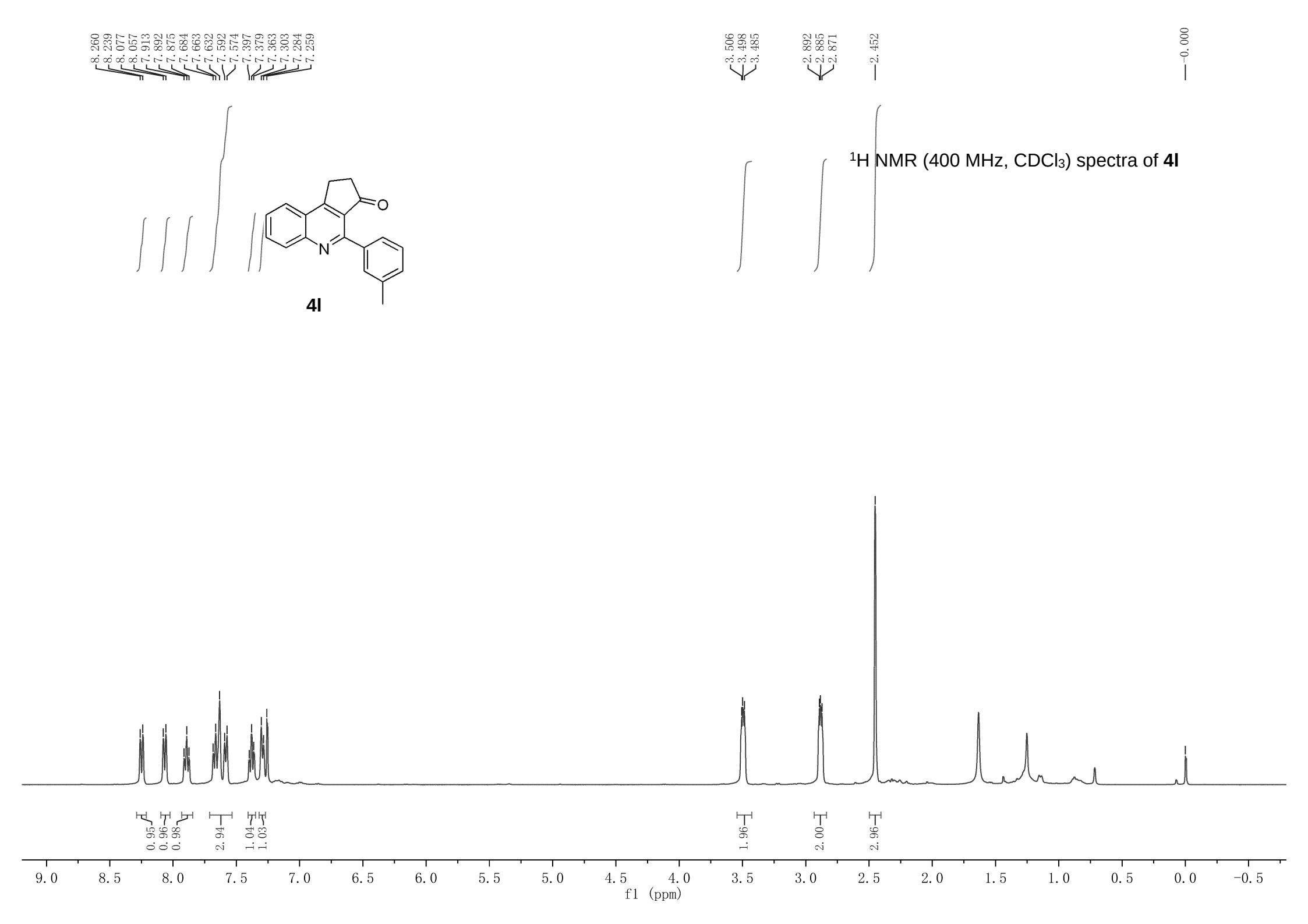


4k

^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4k**

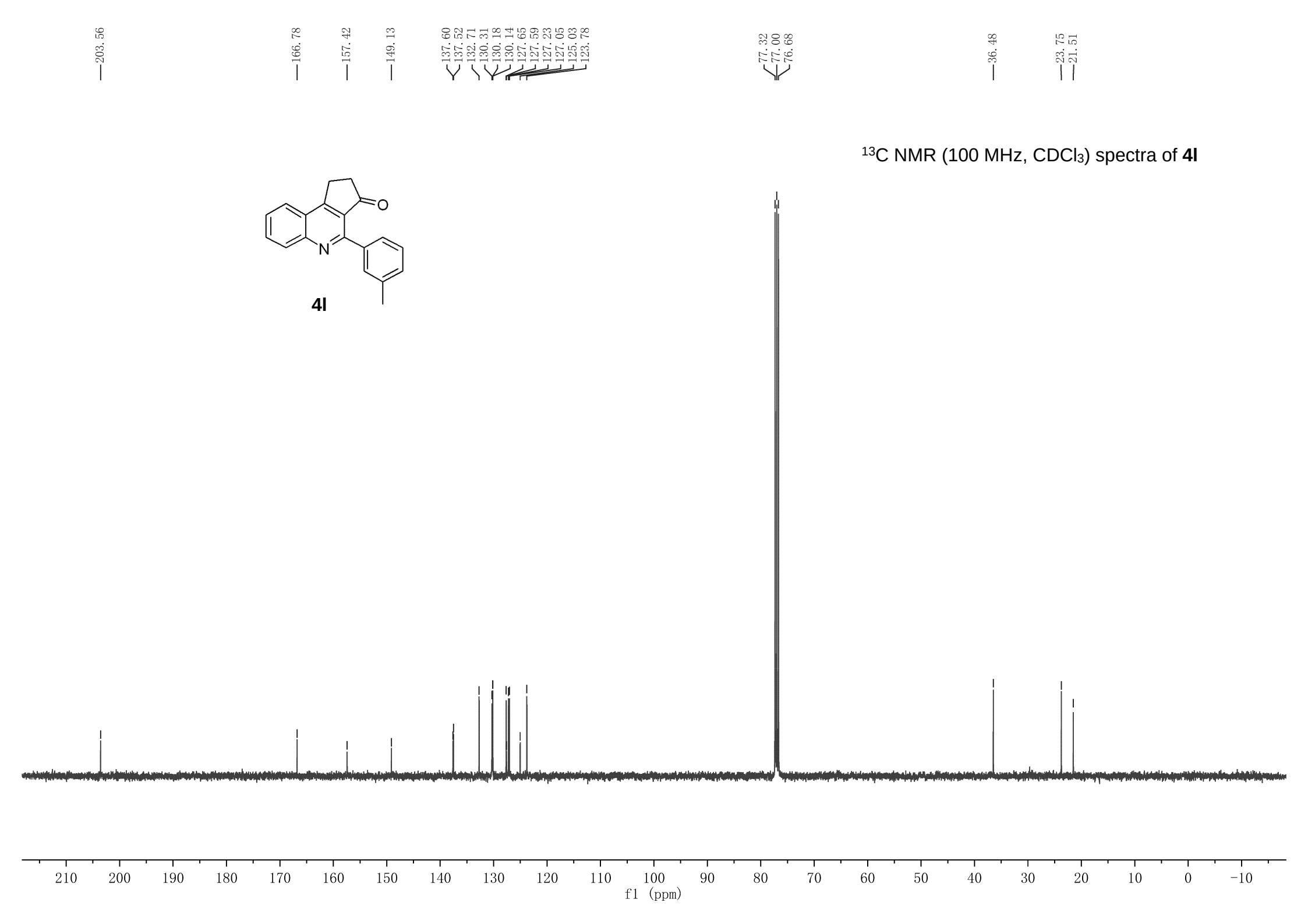


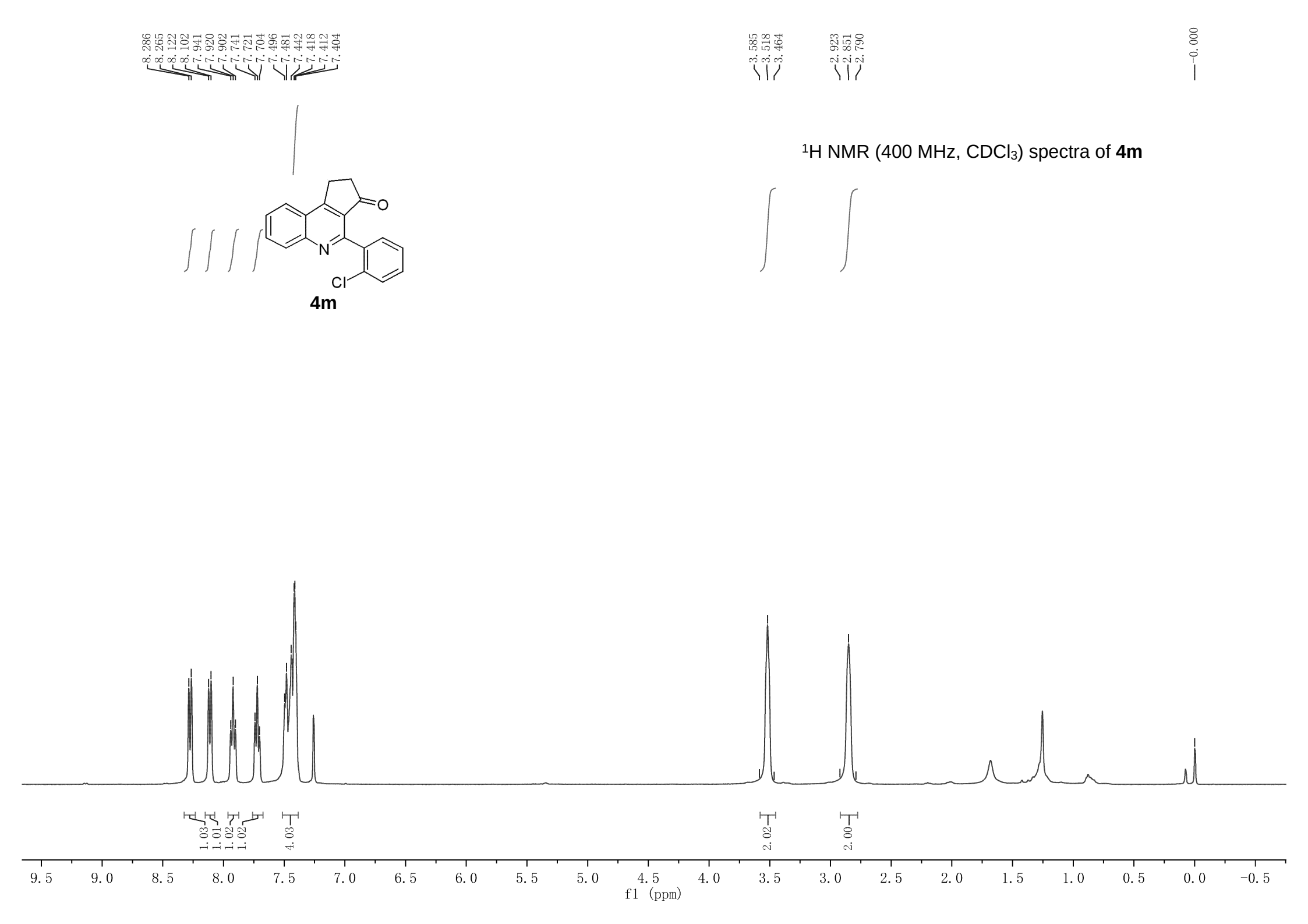
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4k**

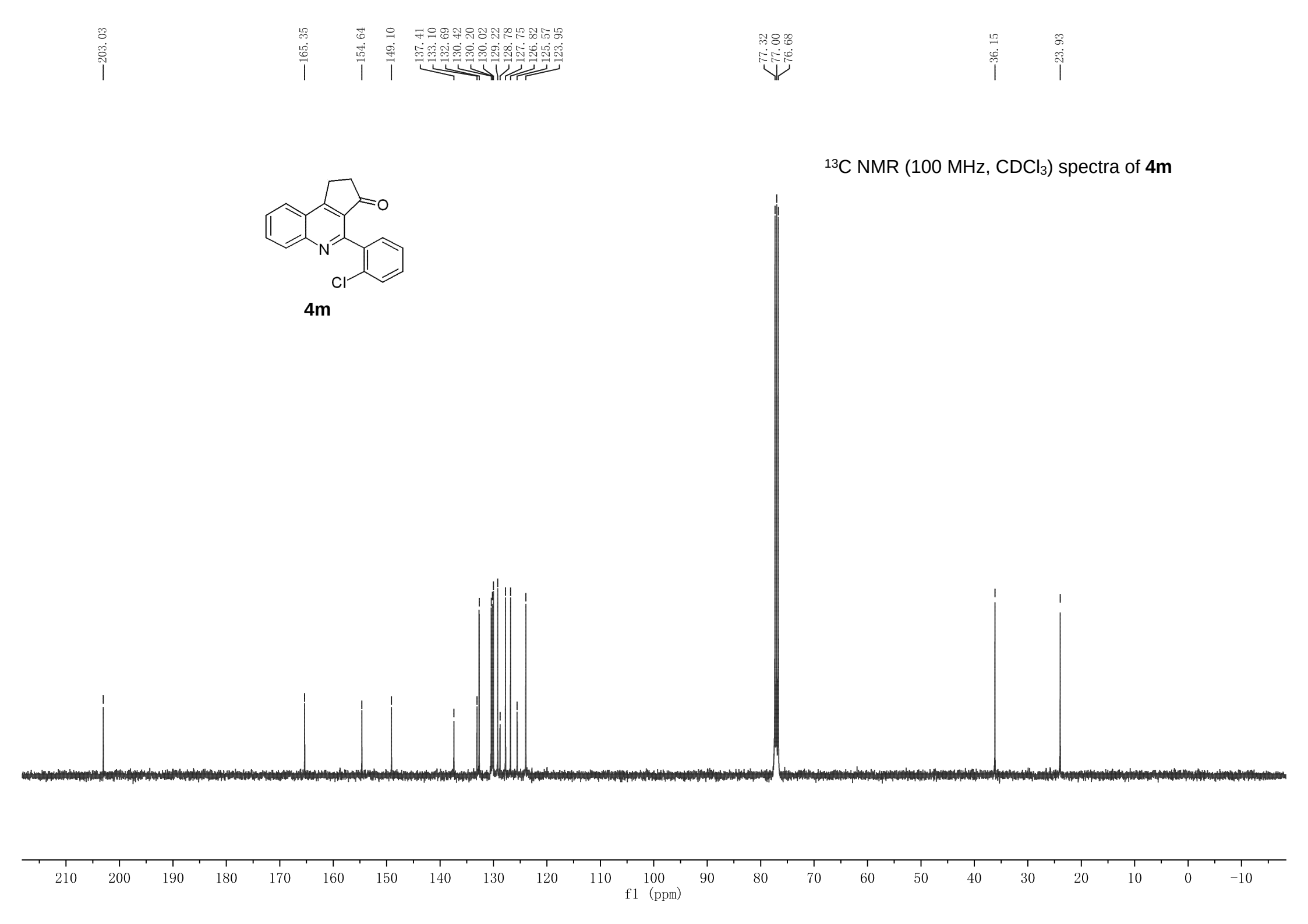


4l

^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4l**

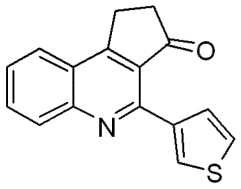

203.56
166.78
157.42
149.13
137.60
137.52
132.71
130.31
130.18
130.14
127.65
127.59
127.23
127.05
125.03
123.78
77.32
77.00
76.68
36.48
23.75
21.51
O
N
4l
13C NMR (100 MHz, CDCl3) spectra of 4l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.286
8.265
8.122
8.102
7.941
7.920
7.902
7.741
7.721
7.704
7.496
7.481
7.442
7.418
7.412
7.404
3.585
3.518
3.464
2.923
2.851
2.790
0.000
O
N
Cl
4m
1H NMR (400 MHz, CDCl3) spectra of 4m
1.03
1.01
1.02
1.02
4.03
2.02
2.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


203.03
165.35
154.64
149.10
137.41
133.10
132.69
130.42
130.20
130.02
129.22
128.78
127.75
126.82
125.57
123.95
77.32
77.00
76.68
36.15
23.93
O
N
Cl
4m
13C NMR (100 MHz, CDCl3) spectra of 4m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

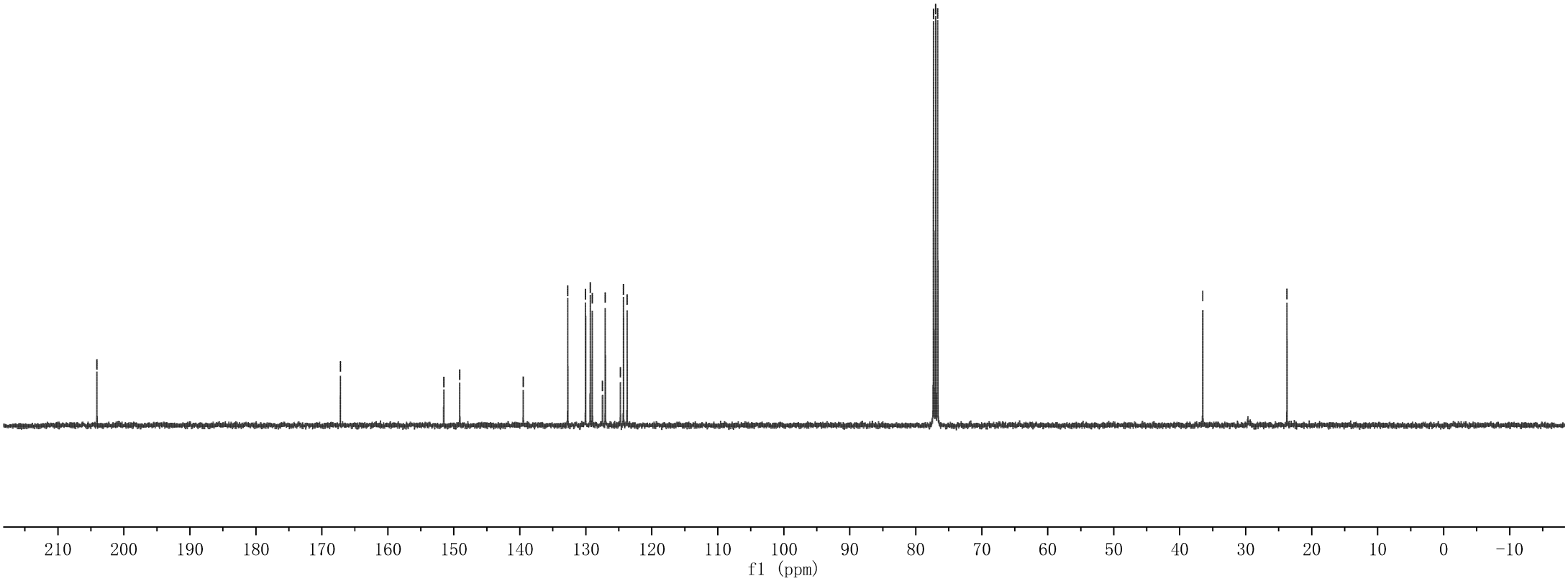
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4n**

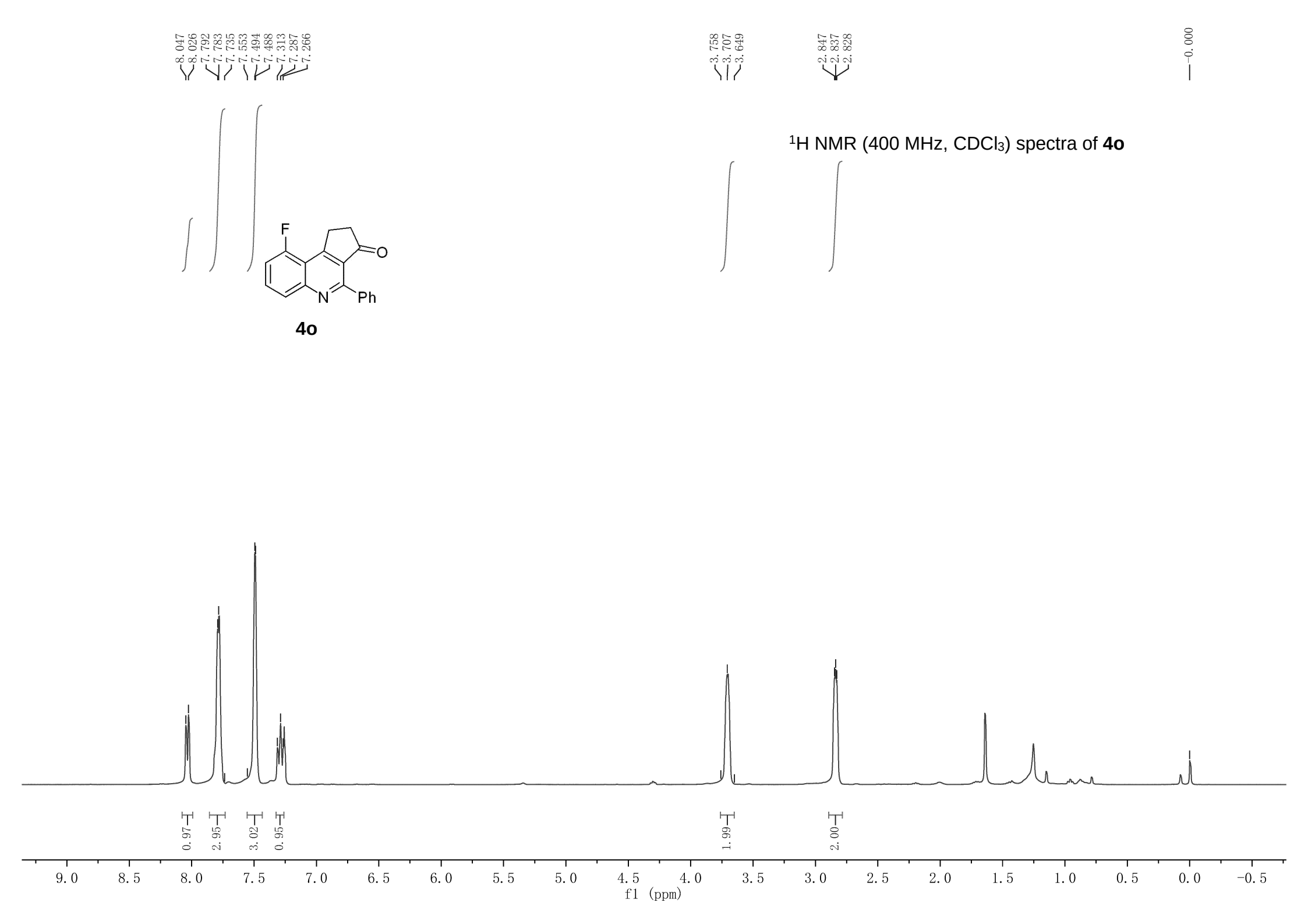
204.09
167.19
151.52
149.10
139.48
132.74
130.05
129.33
129.02
127.46
127.05
124.75
124.29
123.74
77.32
77.00
76.68
36.51
23.75



4n

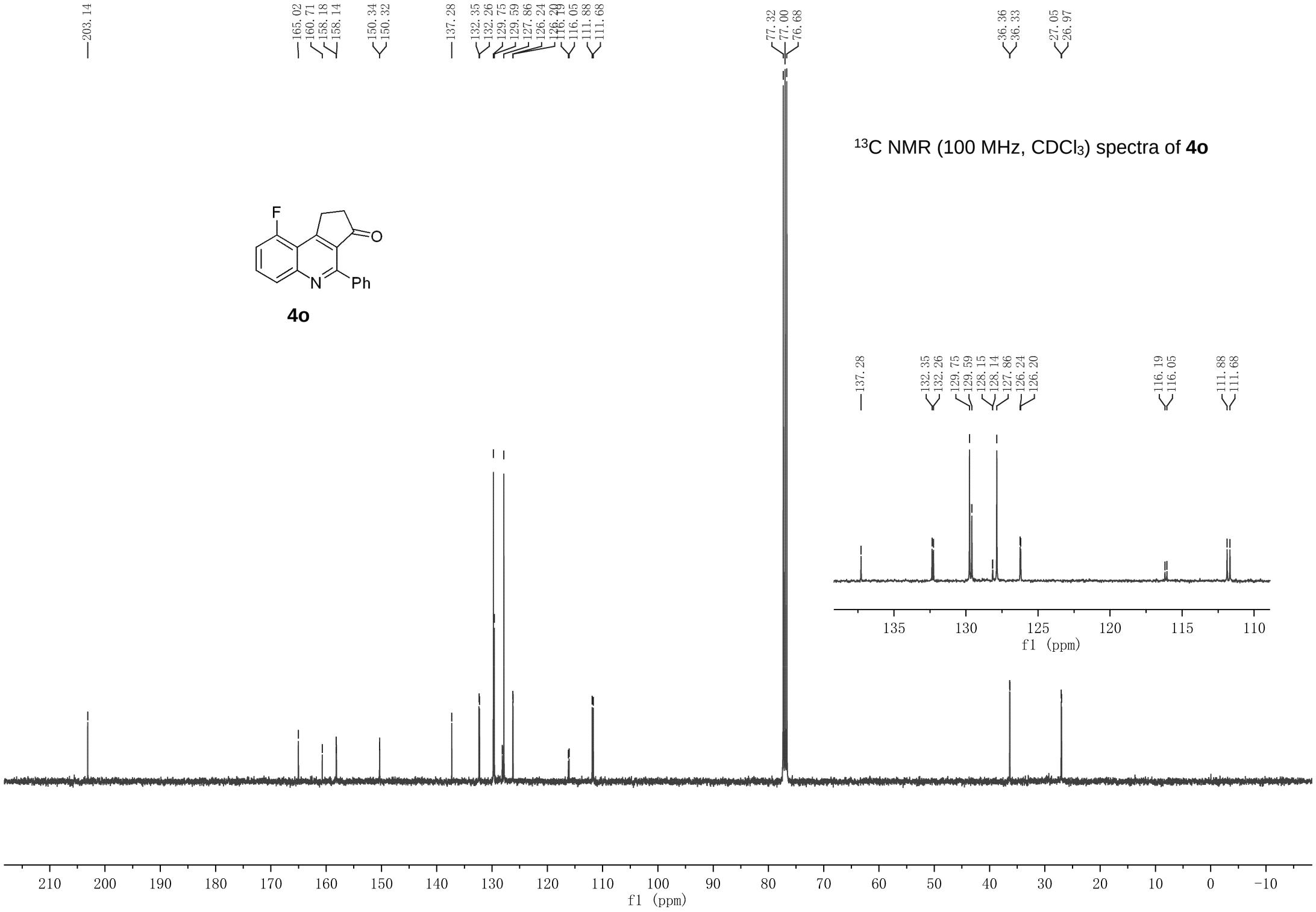
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4n**



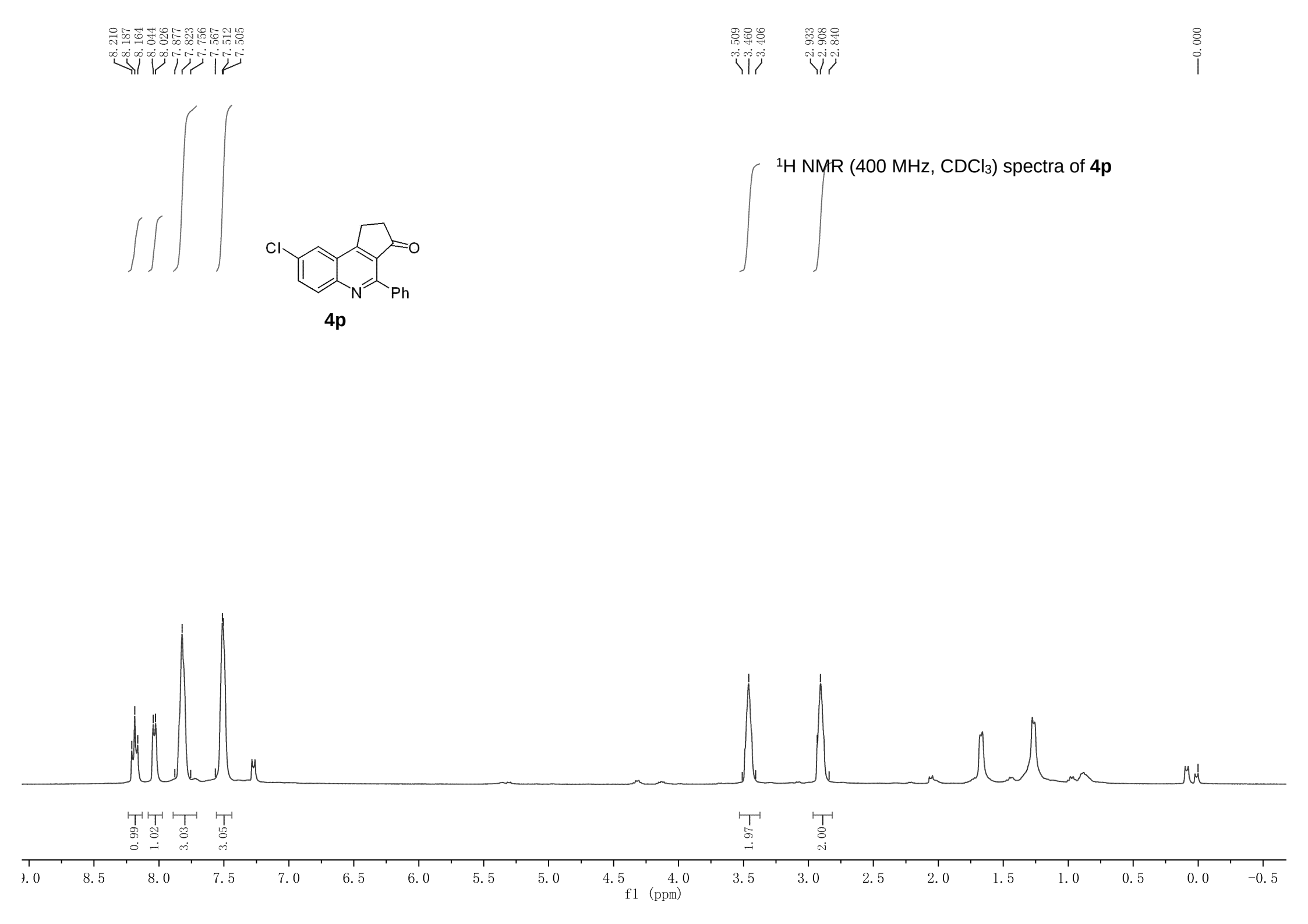


4o

^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4o**



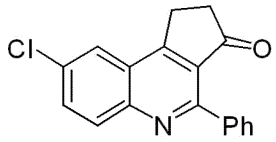
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4o**



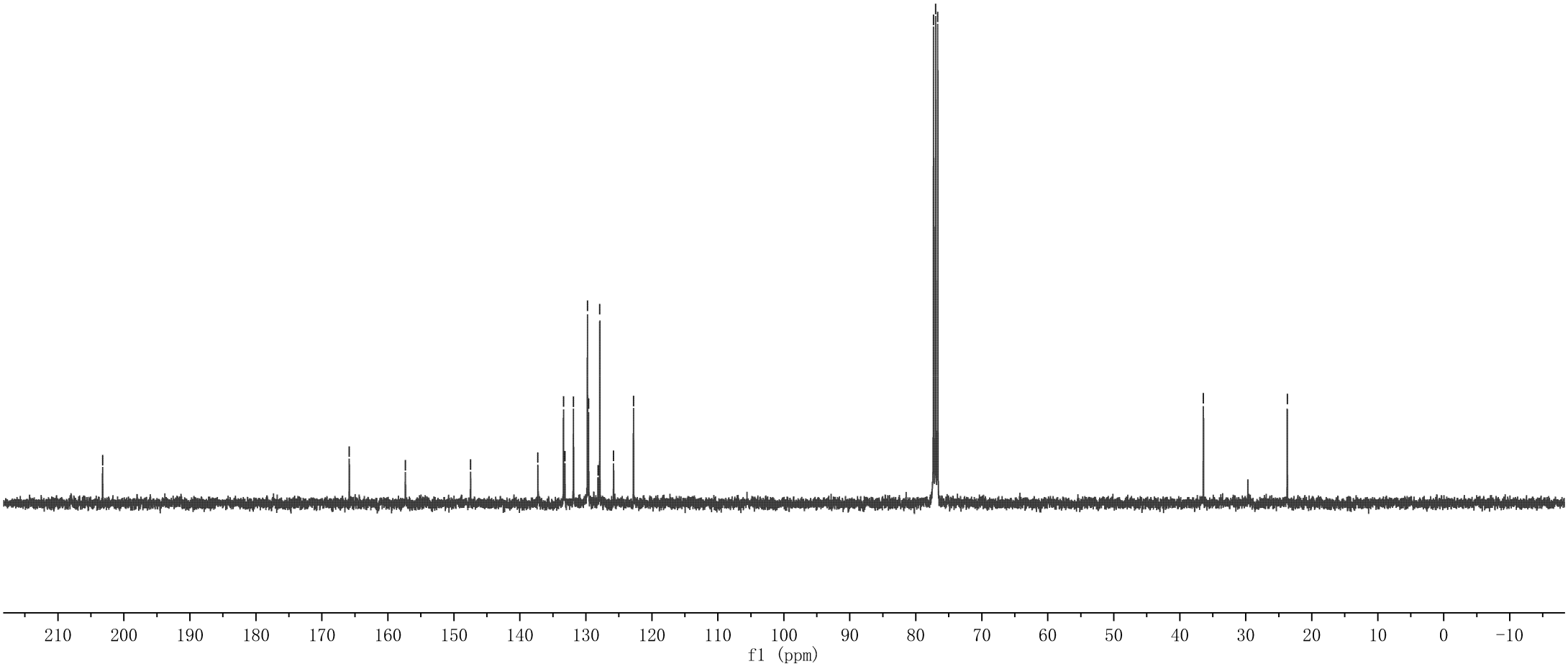
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4p**

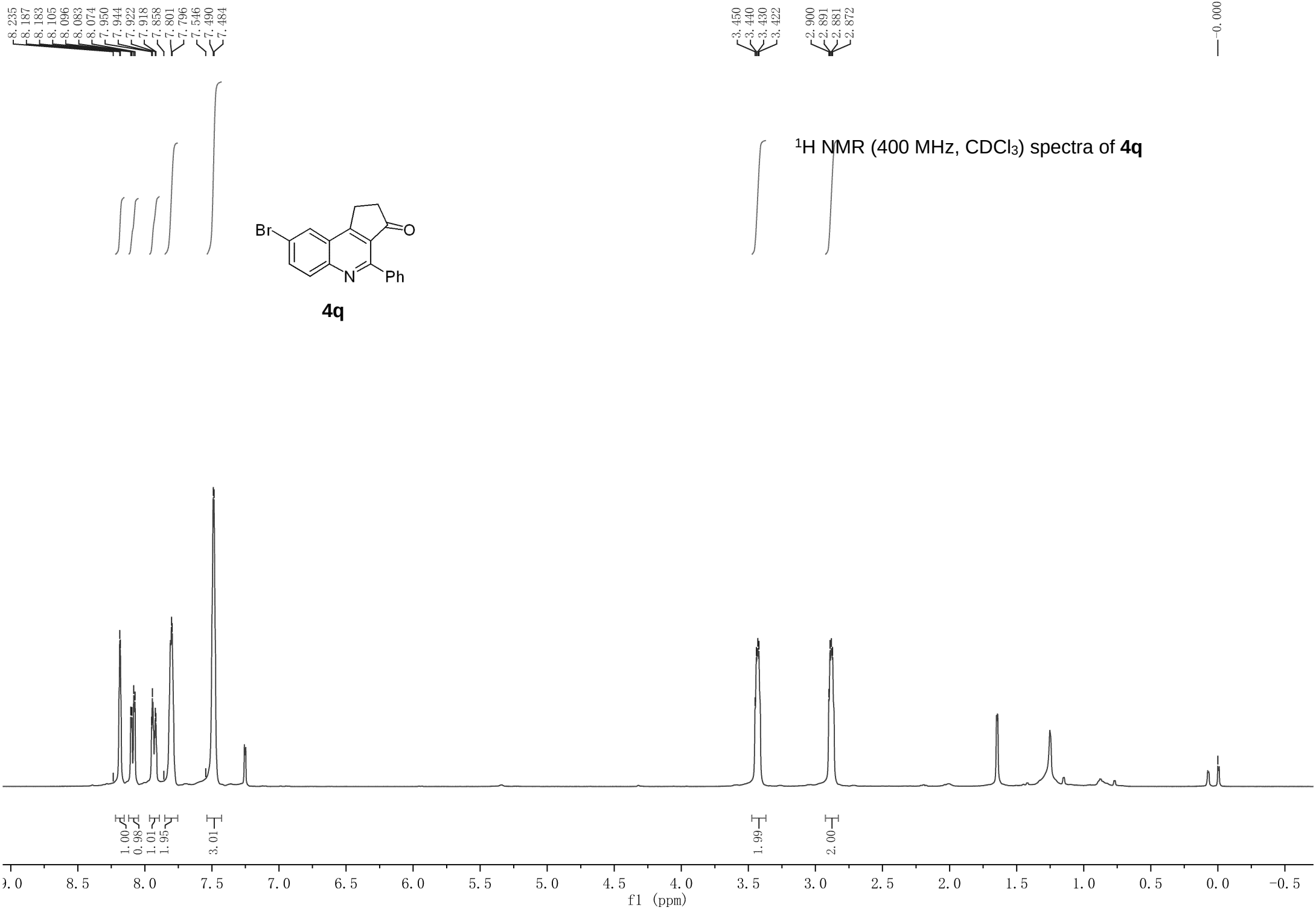
203.23
165.85
157.36
147.46
137.27
133.39
133.17
131.88
129.75
129.58
128.16
127.89
125.80
122.77
77.32
77.00
76.68
36.43
23.71

^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4p**



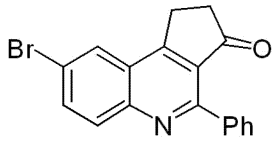
4p



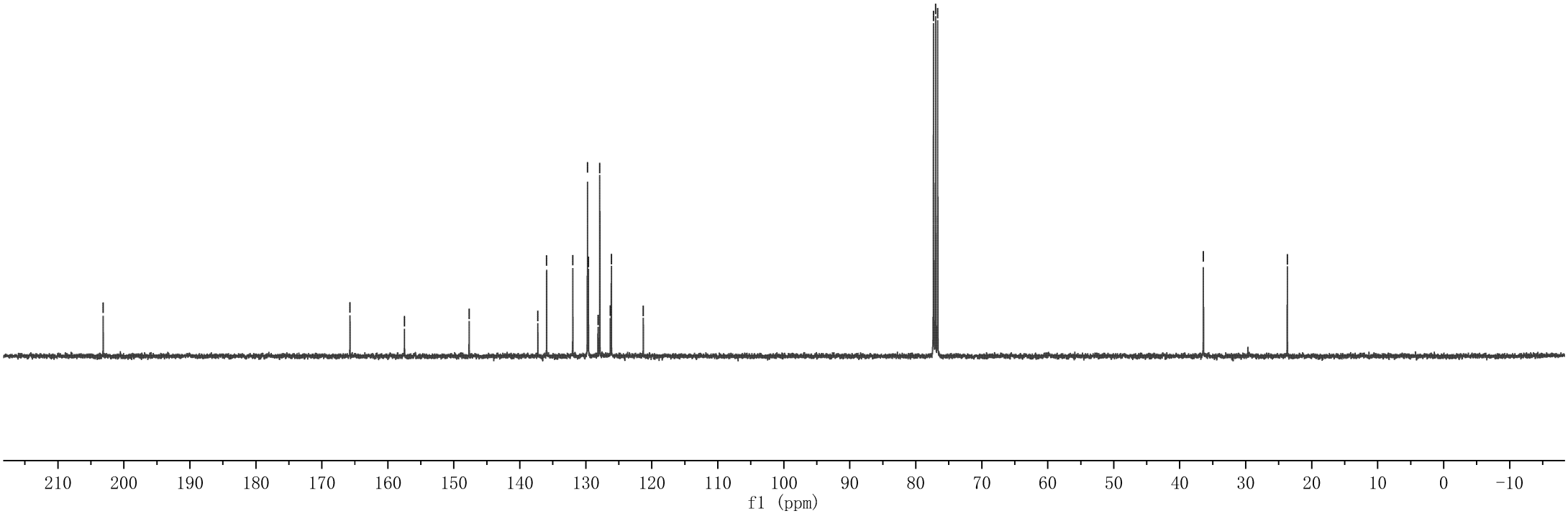

8.235
8.187
8.183
8.105
8.096
8.083
8.074
7.950
7.944
7.922
7.918
7.858
7.801
7.796
7.546
7.490
7.484
3.450
3.440
3.430
3.422
2.900
2.891
2.881
2.872
0.000
Br
O
N
Ph
4q
1H NMR (400 MHz, CDCl3) spectra of 4q
1.00
0.98
1.01
1.95
3.01
1.99
2.00
f1 (ppm)

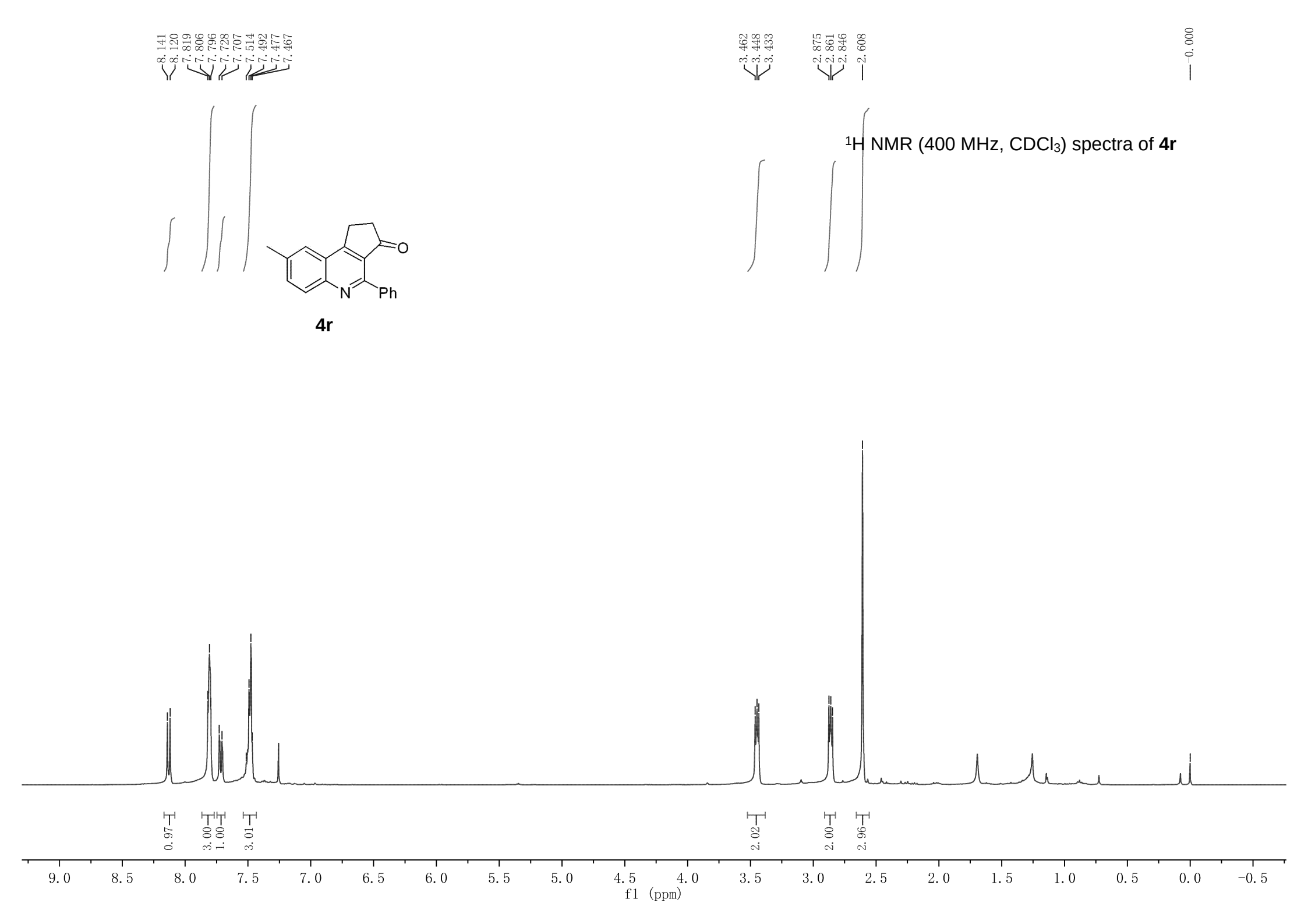
203.14
165.74
157.48
147.68
137.27
135.94
131.97
129.75
129.60
128.15
127.89
126.28
126.13
121.29
77.32
77.00
76.68
36.42
23.70

^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4q**



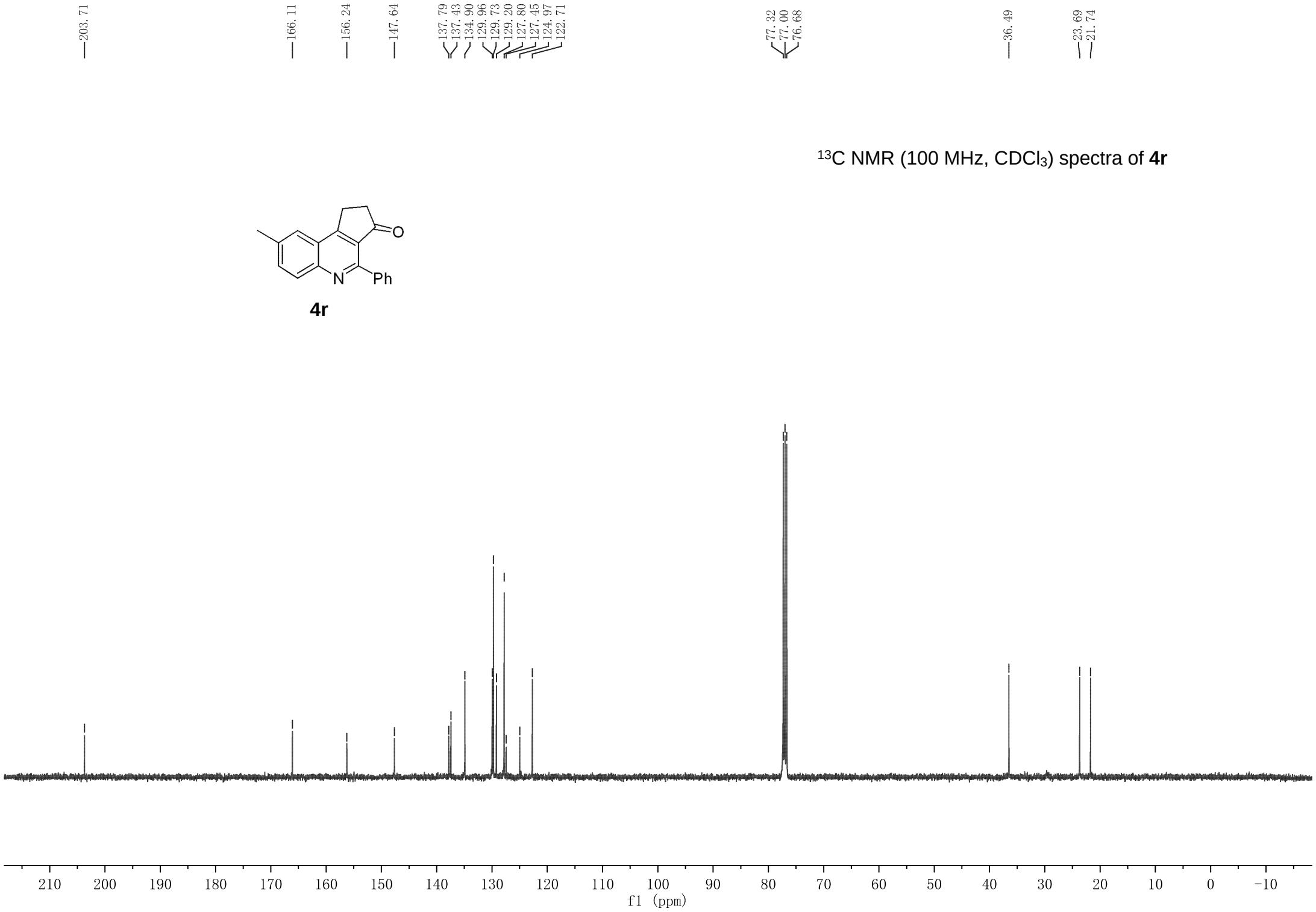
4q



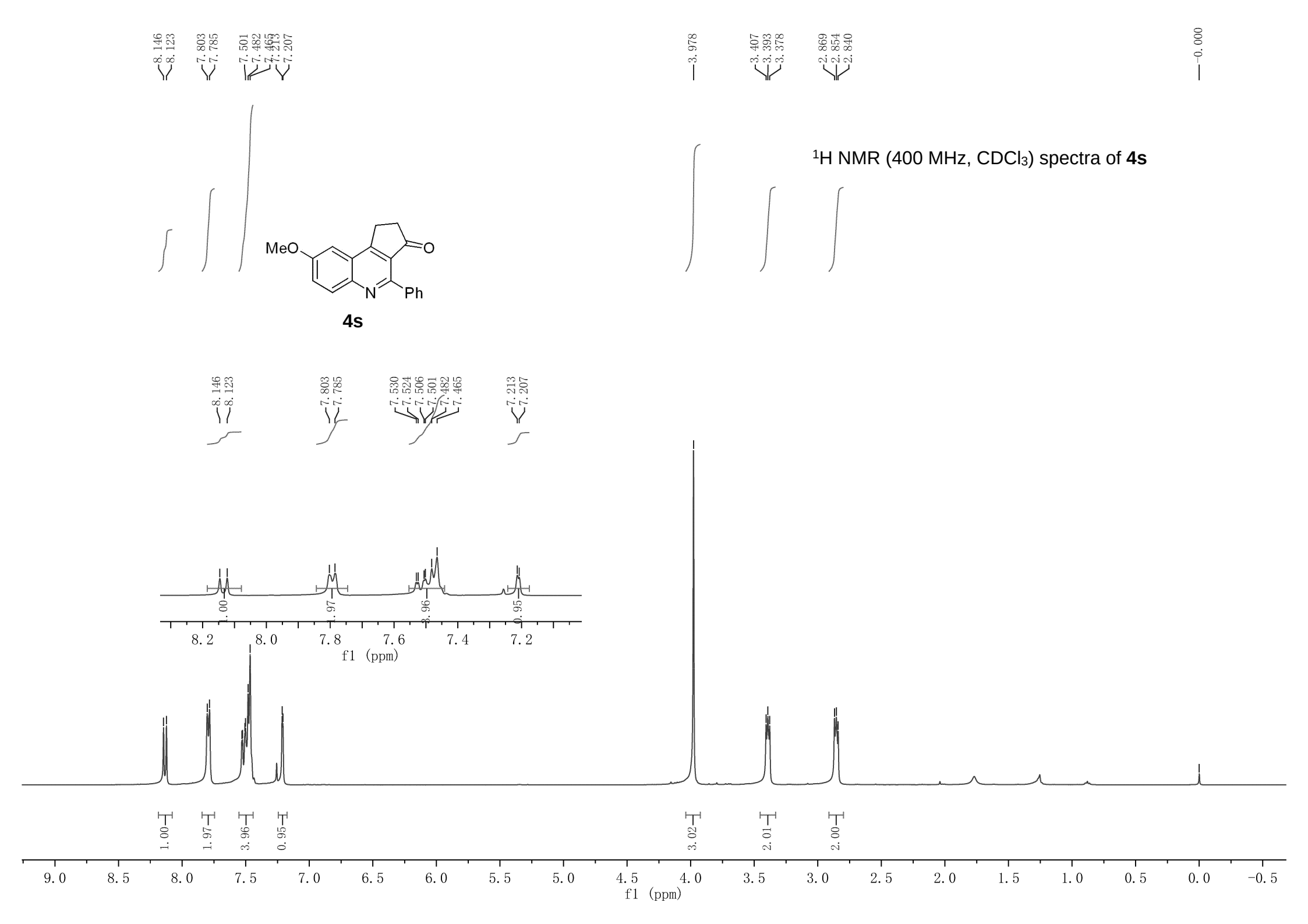


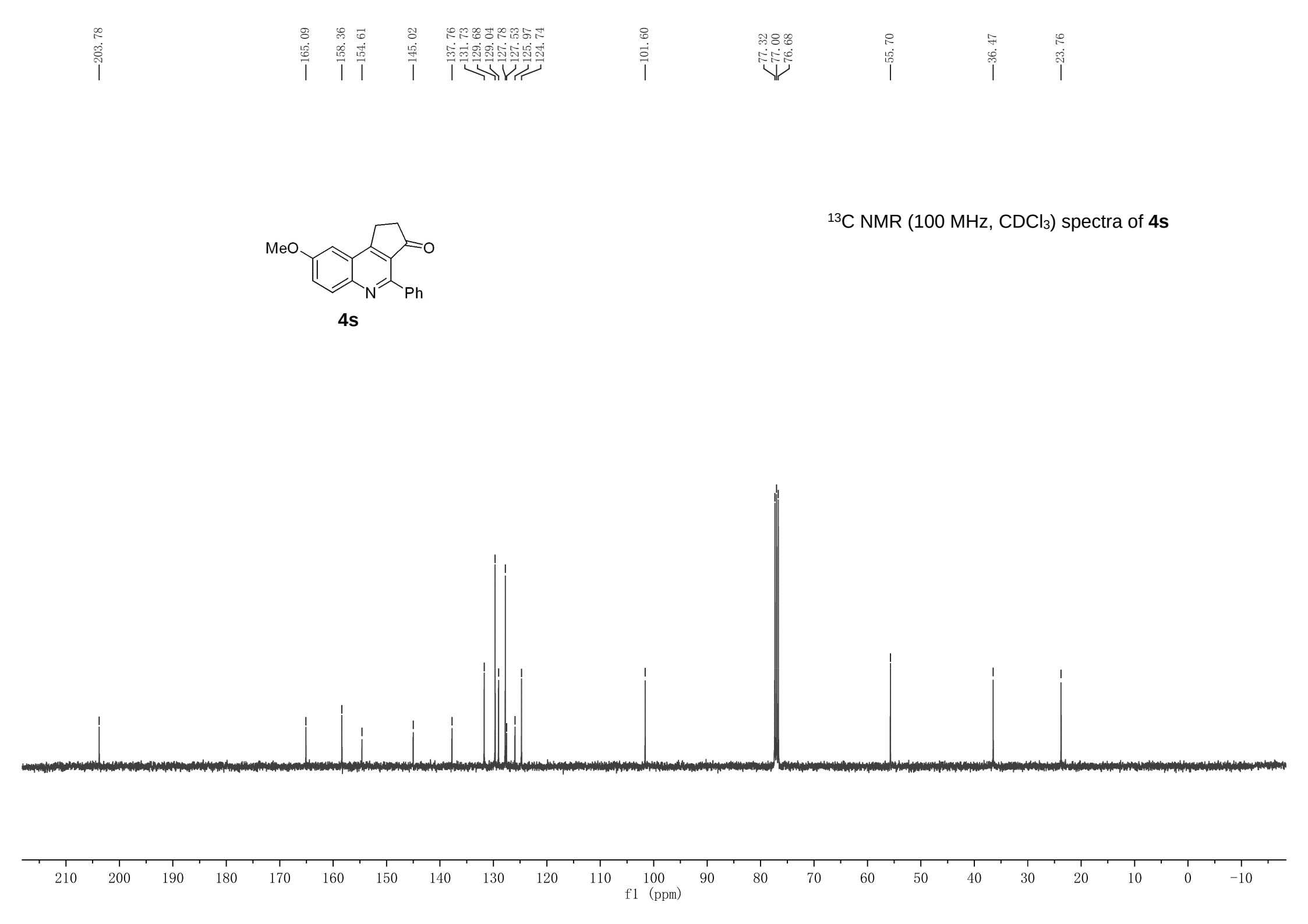
4r

^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4r**

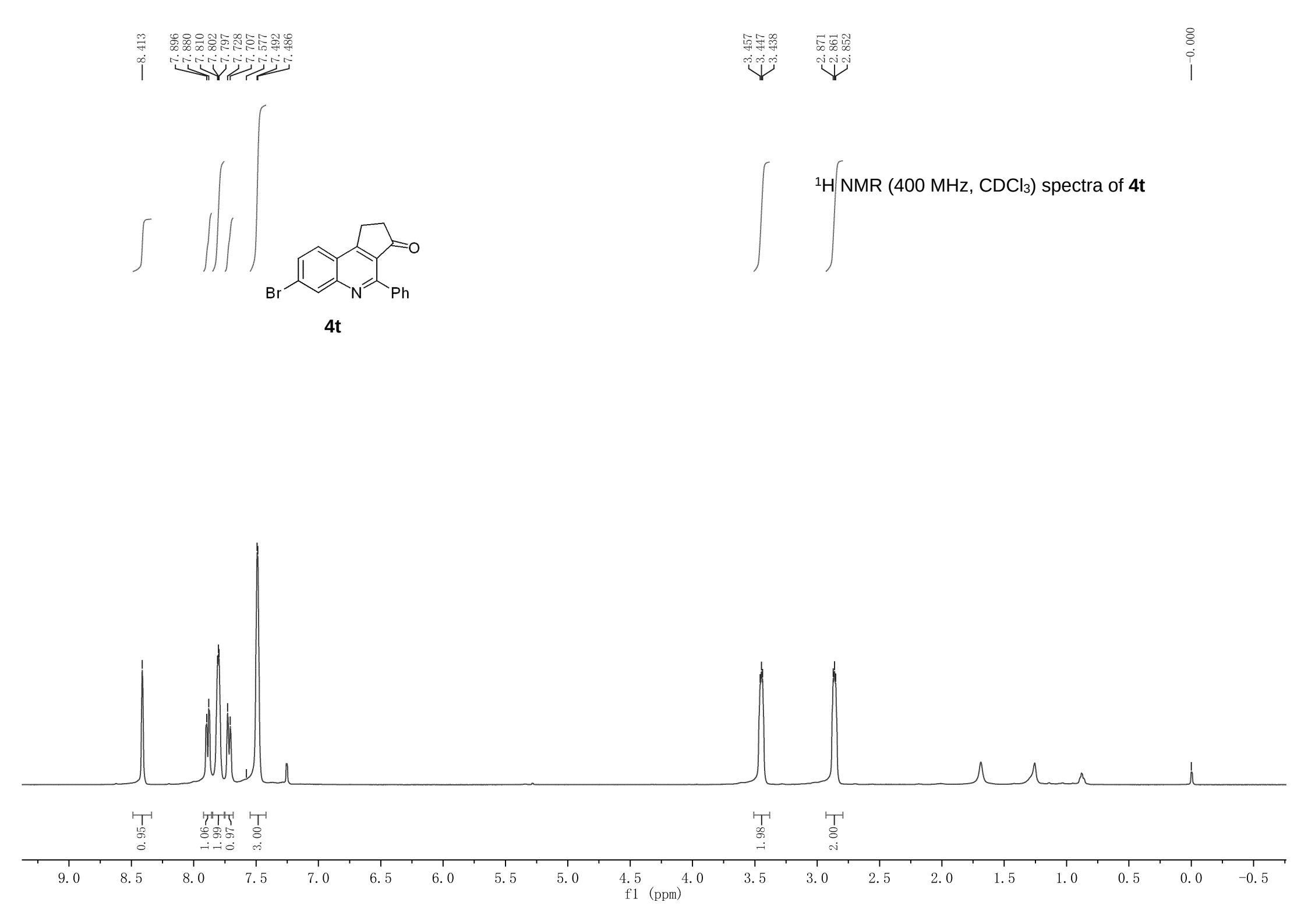


^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4r**


8.146
8.123
7.803
7.785
7.501
7.482
7.465
7.213
7.207
3.978
3.407
3.393
3.378
2.869
2.854
2.840
0.000
MeO
O
N
Ph
4s
1H NMR (400 MHz, CDCl3) spectra of 4s
7.530
7.524
7.506
1.00
1.97
3.96
0.95
3.02
2.01
2.00
f1 (ppm)



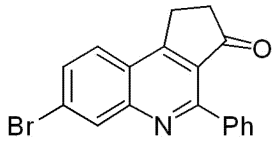
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4s**



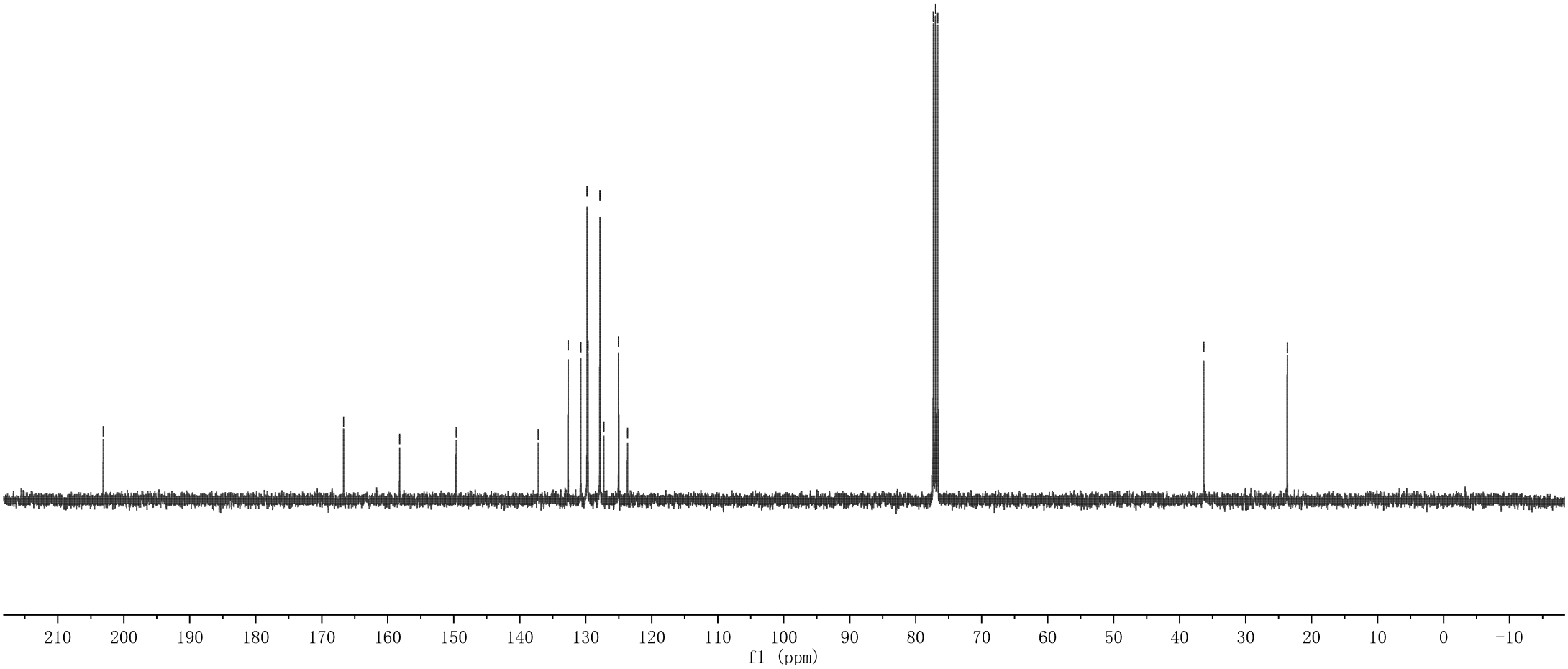
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **4t**

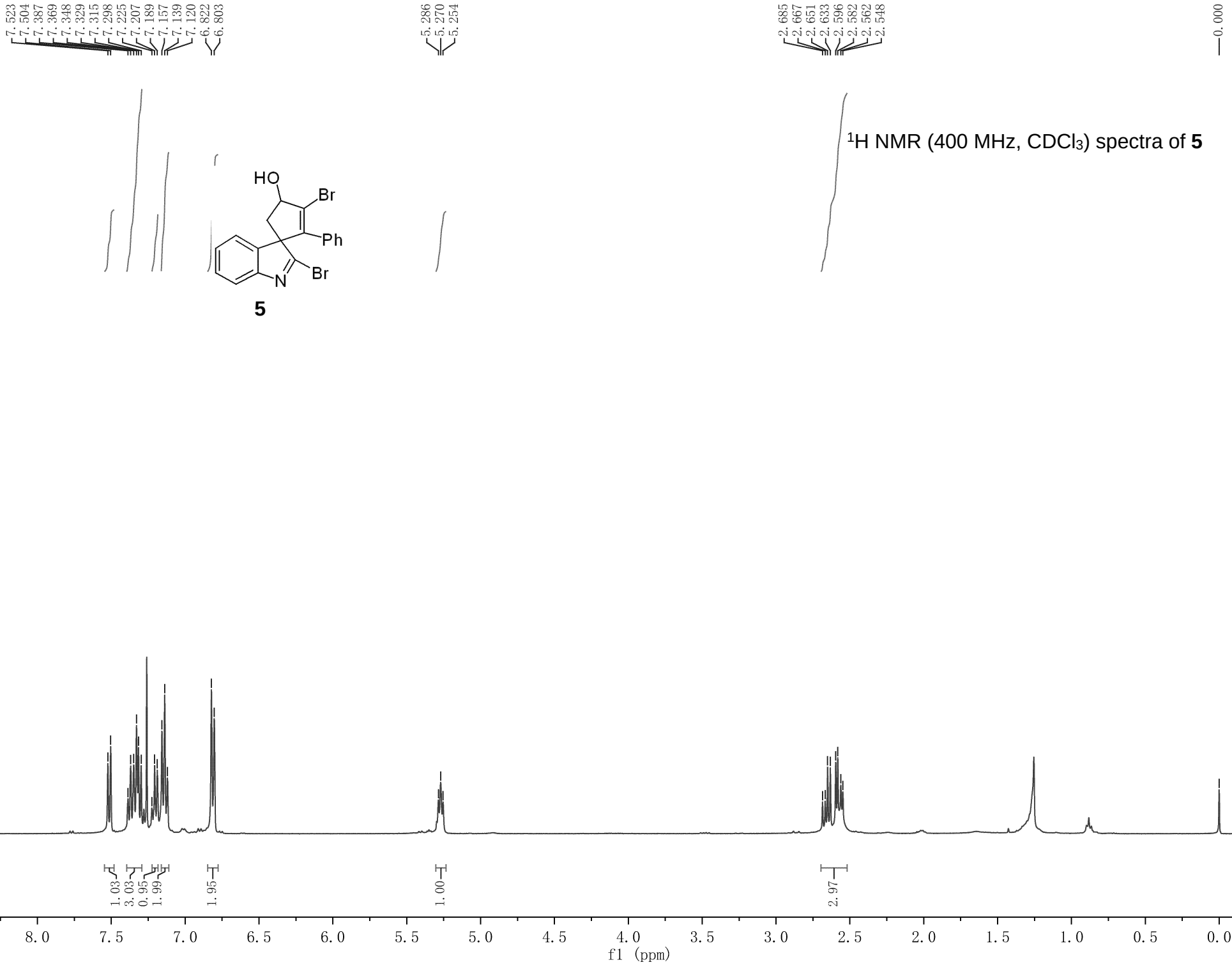
203.11
166.69
158.20
149.63
137.19
132.67
130.75
129.79
129.66
127.85
127.75
127.27
125.02
123.67
77.32
77.00
76.68
36.35
23.69

^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4t**



4t



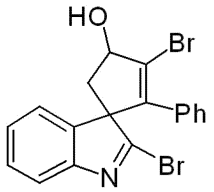


5

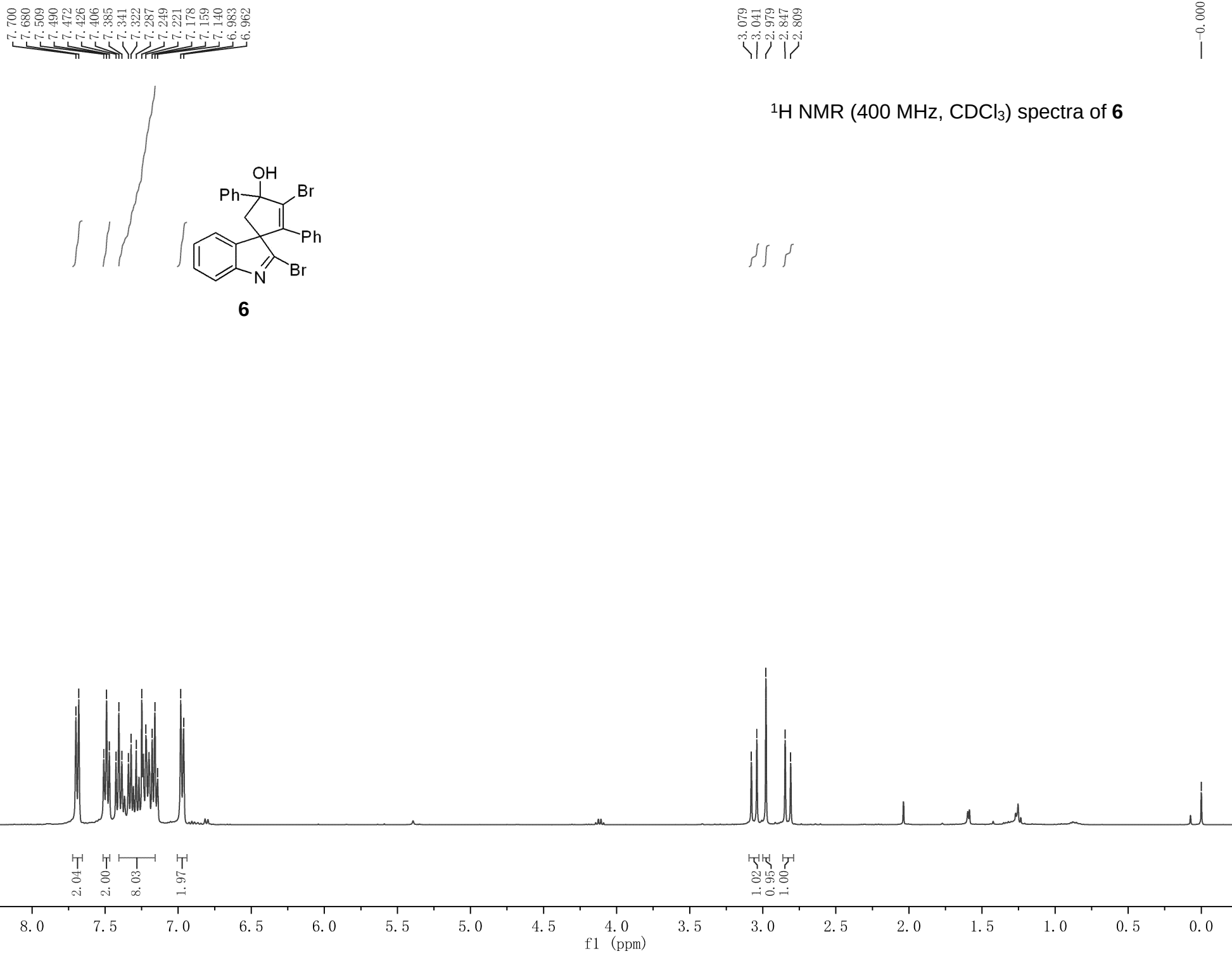
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **5**

166.31
153.47
141.72
141.30
132.00
129.06
128.85
128.18
127.52
126.94
121.95
120.92
78.10
77.32
77.00
76.68
74.11
41.68

^{13}C NMR (100 MHz, $CDCl_3$) spectra of **5**



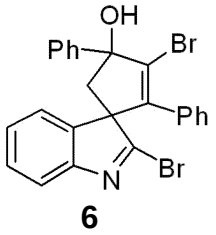
5



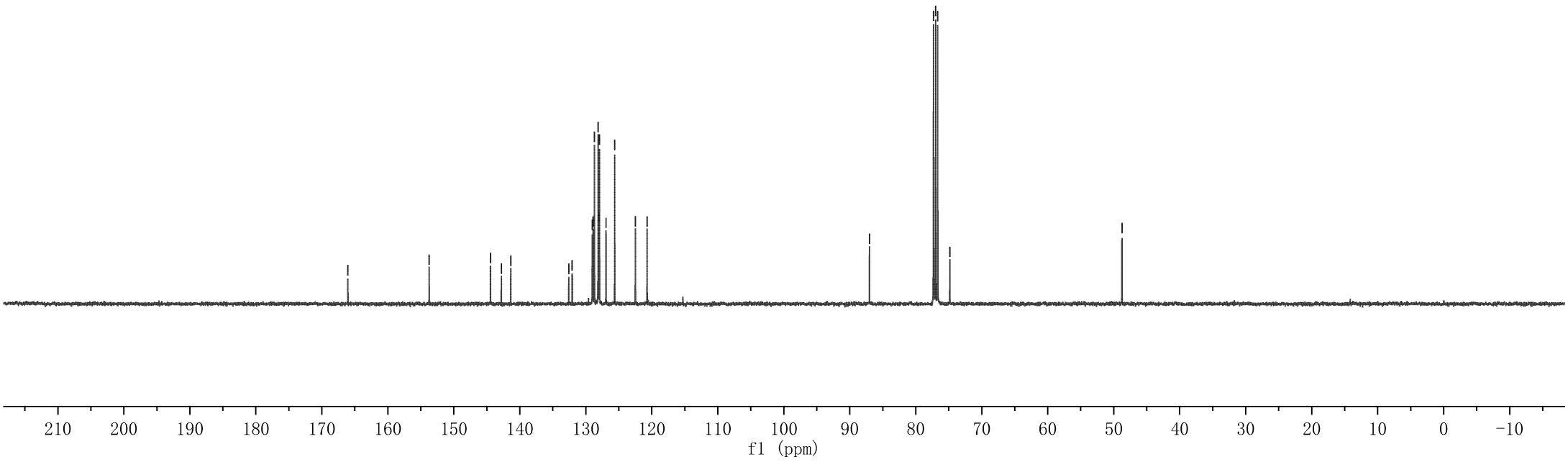
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **6**

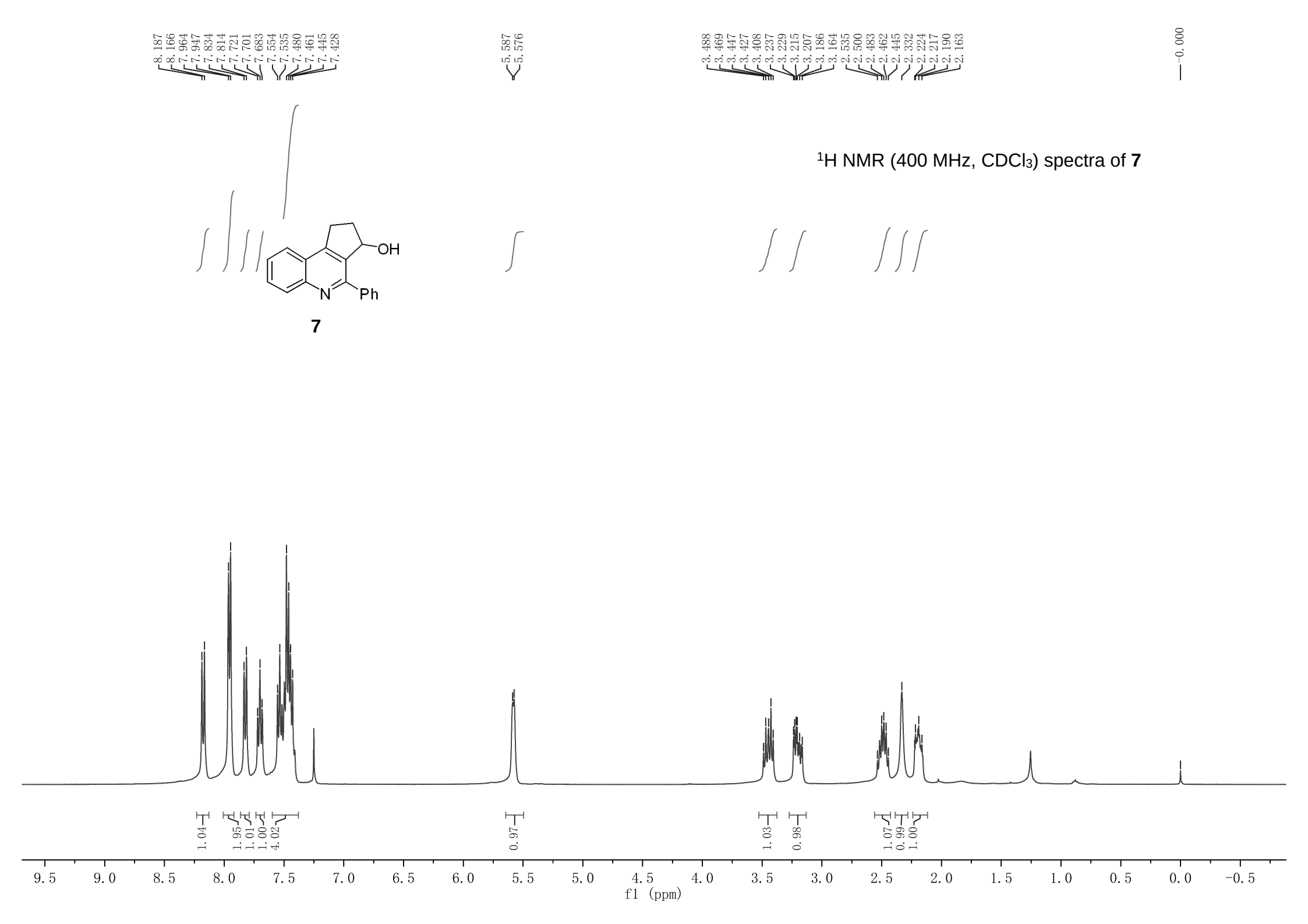
166.05
153.74
144.45
142.80
141.37
132.58
132.07
129.02
128.90
128.70
128.14
128.01
127.93
126.94
125.62
122.49
120.71
87.02
77.32
77.00
76.68
74.84
48.75

^{13}C NMR (100 MHz, $CDCl_3$) spectra of **6**



6

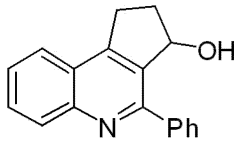




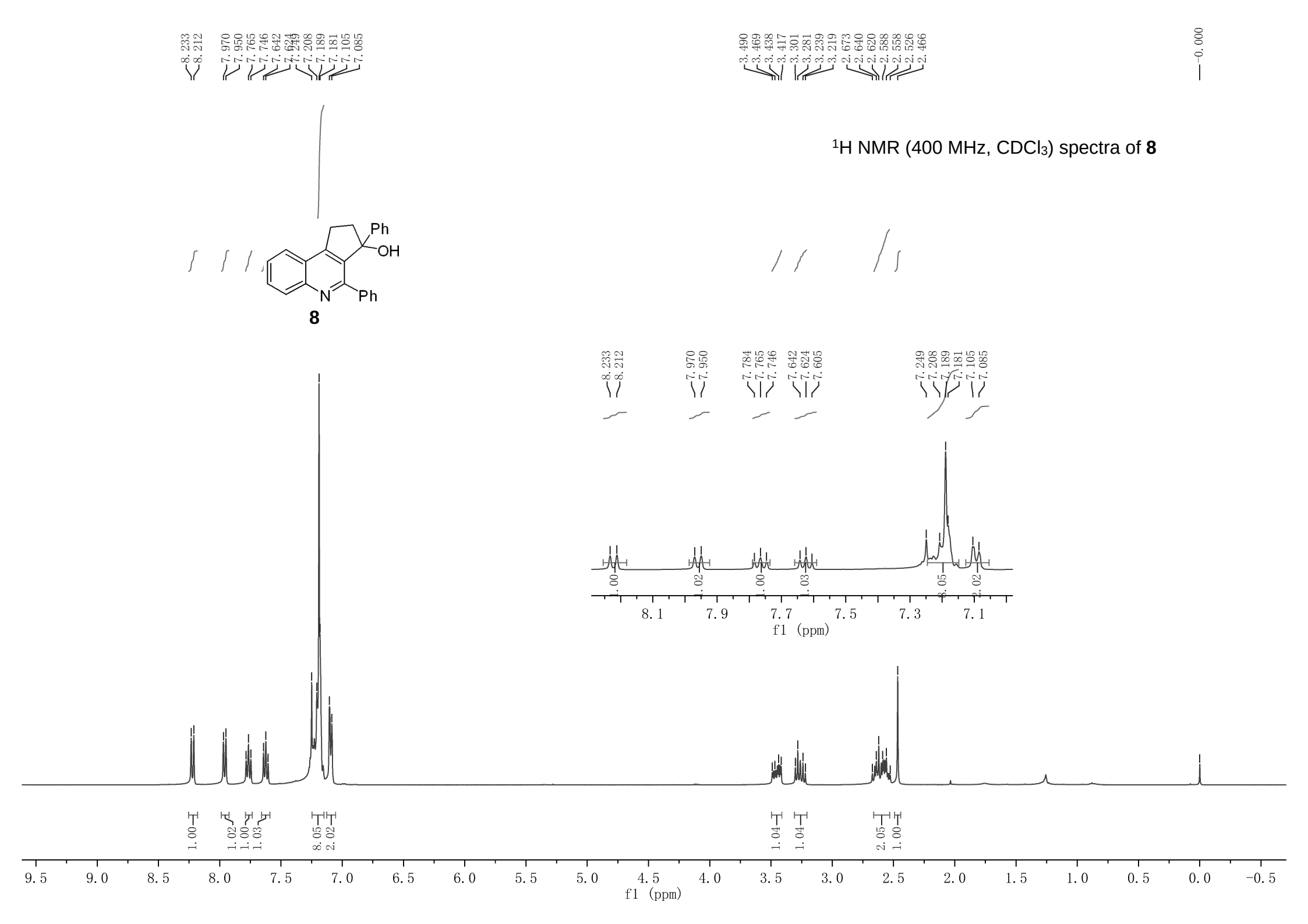
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **7**

7

^{13}C NMR (100 MHz, $CDCl_3$) spectra of **7**



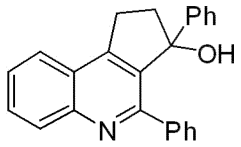
7



^{1}H NMR (400 MHz, $CDCl_3$) spectra of **8**

157.14
151.54
147.75
147.27
139.59
137.97
129.97
129.72
128.60
128.33
128.26
128.11
126.84
126.73
124.93
124.60
124.20
86.46
77.32
77.00
76.68
45.12
27.39

^{13}C NMR (100 MHz, $CDCl_3$) spectra of **8**



8