Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Cu(I)- and Au(I)-Catalyzed Regioselective Oxidations of Diynes: Divergent Synthesis of N-Heterocycles

Wen-Bo Shen,*[a] Ting-Ting Zhang,[a] Meng Zhang,[a] Jing-Jing Wu,[b] Xiao-Lei Jiang,[a] Guang-Xin Ru,*[a] Guang-Qin Gao,[a] and Xiu-Hong Zhu[a]

[a]College of Sciences and College of Forestry, Henan Agricultural University, Zhengzhou 450002, China

[b]Department of Library, Qingdao Agricultural University, Qingdao 266109, China

Content	Page Number
General Information	S2
More Reaction Condition and Mechanism Studies	S3
Preparation of Starting Materials	S5
General Procedure: Copper Catalysis and Gold Catalysis	S7
Synthetic Applications	S39
X-Ray Crystallographic Data	S42
NMR Spectra	S45

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.

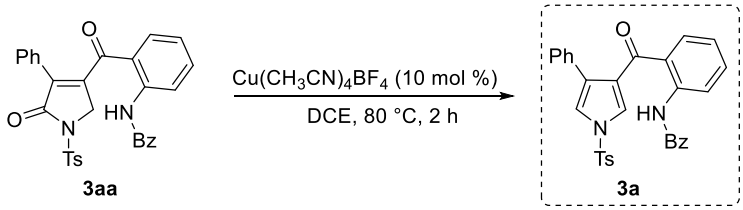
^{1}H NMR spectra were recorded on a Bruker AV-400 spectrometer in chloroform-d_3. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data is being reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, brs = broad singlet, coupling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

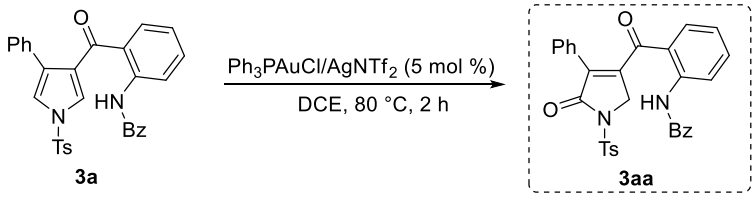
1. **3a** and **3aa** could not be converted to each other:

3aa could not be converted into **3a** under Cu catalysis: only **3aa** was recoveried.



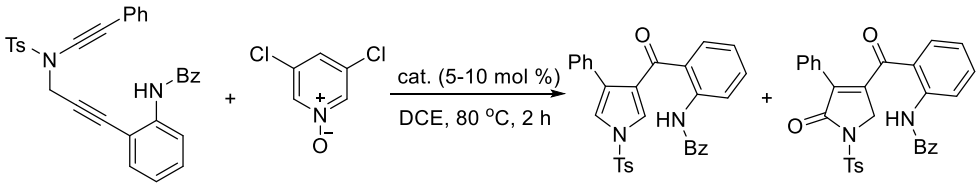
3aa **3a**

3a could not be converted into **3aa** under Au catalysis: only **3a** was recoveried.



3a **3aa**

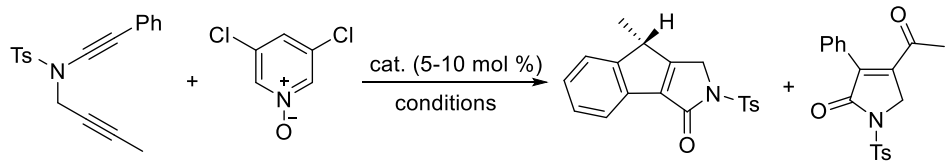
2. Other noble metals such as IPrAuCl/$AgNTf_2$, XPhosAuCl/$AgNTf_2$ and $AgNTf_2$, and Brønsted acids did not catalyze this reaction. These reactions only gave a complicated mixture of products.



1a **2a** (1.5 equiv) **3a** **3aa**

Entry	Cat. (*x* mol %)	Oxidant	*T* (°C)	Yield [%]	
				3a	**3aa**
1	$IPrAuCl/AgNTf_2$ (5)	**2a**	80	11	68
2	XPhosAuCl/$AgNTf_2$ (5)	**2a**	80	25	33
3	$AgNTf_2$ (5)	**2a**	80	33	18
4	MsOH (10)	**2a**	80	<1	<1
5	TsOH (10)	**2a**	80	<1	<1
6	CF_3COOH (10)	**2a**	80	<1	<1
7	TfOH (10)	**2a**	80	<1	<1
8	$HNTf_2$ (10)	**2a**	80	<1	<1

3. Optimization of reaction conditions for the oxidative cyclization of diyne **4a**, please see as followed:[a]

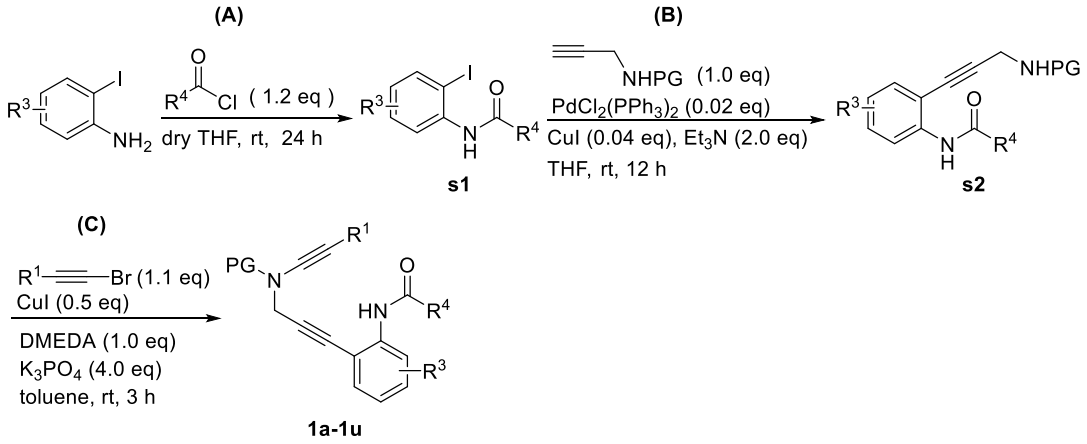


4a **2a** (1.2 equiv) **5a** **5aa**

Entry	Cat. (*x* mol %)	Reaction conditions	Yield [%][b]	
			5a	**5aa**
1	$Cu(CH_3CN)_4BF_4$ (10)	DCE, 80 °C, 12 h	7	16
2	$Cu(CH_3CN)_4PF_6$ (10)	DCE, 80 °C, 4.5 h	12	14
3	CuOTf (10)	DCE, 80 °C, 25 h	8	10
4	$Cu(OTf)_2$ (10)	DCE, 80 °C, 6.5 h	10	20
5	$Ph_3PAuCl/AgNTf_2$ (5)	DCE, 80 °C, 2 h	28	5
6	$Ph_3PAuCl/AgNTf_2$ (5)	PhCl, 80 °C, 1.5 h	71	12
7	$Ph_3PAuCl/AgNTf_2$ (5)	$PhCF_3$, 80 °C, 1.5 h	78	10
8	$Ph_3PAuCl/AgNTf_2$ (5)	TCE, 80 °C, 1.5 h	63	14
9	$Ph_3PAuCl/AgNTf_2$ (5)	$PhCF_3$, 60 °C, 1.5 h	78	11
10	$IPrAuCl/AgNTf_2$ (5)	$PhCF_3$, 60 °C, 1.0 h	67	9
11	$XPhosAuCl/AgNTf_2$ (5)	$PhCF_3$, 60 °C, 1.0 h	51	6
12[c]	**$Ph_3PAuCl/AgNTf_2$ (5)**	**$PhCF_3$, 60 °C, 1.0 h**	**80**	**5**

[a] Reaction conditions: **4a** (0.1 mmol), **2a** (0.12 mmol), catalyst (5-10 mol %), 0.05 M, in vials. [b] Measured by ^1H NMR using diethyl phthalate as the internal standard. [c] 10 mol % NaBARF was added.

Representative synthetic procedures for the preparation of amide-tethered diynes 1a-1u:



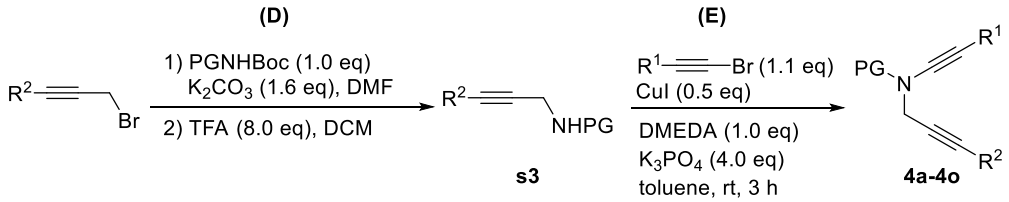
(A): Acyl chloride (12.0 mmol) was slowly added to a solution of 2-iodoaniline (10.0 mmol) in 20.0 mL dry THF at room temperature via dropping funnel. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. The reaction typically took 24 h. Upon completion, EtOAc (30 mL) was added, and the mixture was washed with 5% $NaHCO_3$, brine, dried over $MgSO_4$, and concentrated under reduced pressure to yield the crude iodobenzene **s1**, which was then used in the next step without purification.[1]

(B): Add $Pd(PPh_3)_2Cl_2$ (0.2 mmol, 140.4 mg), CuI (0.4 mmol, 76.0 mg) and triethylamine (20.0 mmol, 2020.0 mg) to a solution of the *N*-sulfonyl propargyl amine (10.0 mmol) and iodobenzene **s1** (10.0 mmol) in THF (30.0 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 12 h. Upon completion, the reaction crude was filtered through a Celite plug and concentrated under vacuum, and the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford the desired substrates **s2**.[2]

(C): To a mixture of **s2** (3.0 mmol), K_3PO_4 (12.0 mmol, 2544.0 mg), CuI (1.5 mmol, 285.0 mg), and DMEDA (3.0 mmol, 264.0 mg) in the reaction vial was added a solution of a respective brominated alkyne (3.3 mmol) in toluene. The reaction mixture was

stirred at room temperature and the progress of the reaction was monitored by TLC. The reaction typically took 3 h. Upon completion, the reaction crude was filtered through a Celite plug and concentrated under vacuum, and the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford the desired enynamide substrates **1a-1u**.[2]

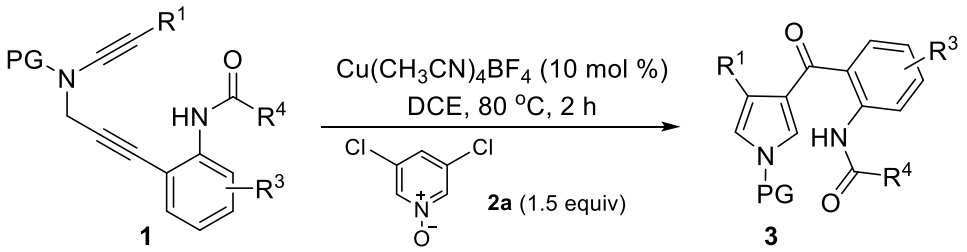
Representative synthetic procedures for the preparation of diynes 4a-4o:



(D): Add propargyl bromide (10.0 mmol) to a solution of the PGNHBoc (10.0 mmol) and potassium carbonate (16.0 mmol, 2208.0 mg) in DMF (15.0 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 3 h. Upon completion, the reaction crude was filtered through a Celite plug and concentrated under vacuum, and the residue was added into a solution of the trifluoroacetic acid (80.0 mmol, 9120.0 mg) in DCM (15.0 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 12 h. Upon completion, the reaction crude was concentrated under vacuum, and the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford the desired substrates **s3**.[3]

(E): To a mixture of **s3** (3.0 mmol), K_3PO_4 (12.0 mmol, 2544.0 mg), CuI (1.5 mmol, 285.0 mg), and DMEDA (3.0 mmol, 264.0 mg) in the reaction vial was added a solution of a respective brominated alkyne (3.3 mmol) in toluene. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. The reaction typically took 3 h. Upon completion, the reaction crude was filtered through a Celite plug and concentrated under vacuum, and the residue was purified by

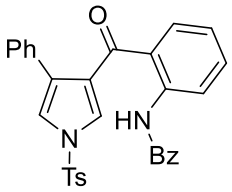
chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford the desired enynamide substrates **4a**-**4o**.[2]



General procedure for the synthesis of pyrroles 3:

3,5-Dichloropyridine *N*-oxide **2a** (0.3 mmol, 49.2 mg) and $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg) were added in this order to the amide-tethered diynes **1** (0.2 mmol) in DCE (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 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 product **3**.

***N*-(2-(4-phenyl-1-tosyl-1*H*-pyrrole-3-carbonyl)phenyl)benzamide (3a)**



3a

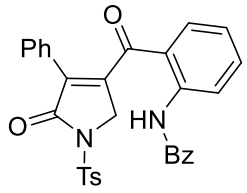
The reaction was conducted with *N*-(2-(3-((4-methyl-*N*-(phenylethynyl)phenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1a**, 0.2 mmol, 101.0 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.3 mmol, 49.2 mg), and $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg) in DCE (4.0 mL) at 80 °C (80 °C, heating mantle temperature).

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **3a** (81.8 mg, 79%) as a pale yellow oil.

The reaction was conducted with *N*-(2-(3-((4-methyl-*N*-(phenylethynyl)phenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1a**, 1.0 mmol, 505.0 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 1.5 mmol, 246.0 mg), and $Cu(CH_3CN)_4BF_4$ (0.1 mmol, 31.5 mg) in DCE (20.0 mL) at 80 ^oC (80 °C, oil bath temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **3a** (369.9 mg, 71%) as a pale yellow oil.

^1H NMR (400 MHz, $CDCl_3$) δ 11.85 (s, 1H), 8.81 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.59 (t, *J* = 7.9 Hz, 1H), 7.52 – 7.42 (m, 4H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.30 – 7.24 (m, 6H), 7.05 (t, *J* = 7.6 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 166.0, 146.2, 140.7, 134.8(4), 134.8(0), 134.5, 133.5, 132.2, 132.0, 130.4, 130.0, 128.7, 128.5, 128.1, 127.5, 127.4(1), 127.3(8), 126.6, 126.2, 124.2, 122.4, 121.2, 119.1, 21.7; IR (neat): 3284 (br), 2924, 1727, 1678, 1603, 1581, 1494, 1448, 1377, 1305, 1189, 1174, 1067, 906, 669; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{25}N_2O_4S$ 521.1530, found 521.1524.

_N_-(2-(5-oxo-4-phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrole-3-carbonyl)phenyl)benzamide (3aa)

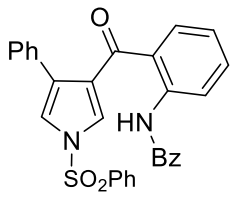


3aa

^1H NMR (400 MHz, $CDCl_3$) δ 11.33 (s, 1H), 8.04 (d, *J* = 7.3 Hz, 1H), 7.21 – 7.15 (m, 4H), 6.73 – 6.58 (m, 5H), 6.50 – 6.32 (m, 7H), 5.97 (d, *J* = 6.7 Hz, 1H), 3.93 (s, 2H), 1.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 166.2, 166.1, 147.6, 145.7, 142.2, 137.1, 136.0, 134.7, 134.3, 133.3, 132.4, 129.9, 129.0, 128.9, 128.6, 128.4, 127.5, 122.7, 120.8, 119.7, 50.7, 21.7; IR (neat): 3284 (br), 2924, 1727, 1683, 1624, 1582, 1494, 1449, 1367,

1241, 1183, 1158, 1090, 965, 665; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{25}N_2O_5S$ 537.1479, found 537.1477.

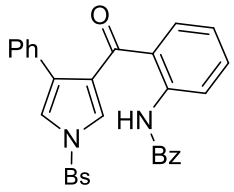
_N_-(2-(4-phenyl-1-(phenylsulfonyl)-1_H_-pyrrole-3-carbonyl)phenyl)benzamide (3b)



3b

The reaction was conducted with *N*-(2-(3-(*N*-(phenylethynyl)phenylsulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1b**, 0.2 mmol, 98.2 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.3 mmol, 49.2 mg), and $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg) in DCE (4.0 mL) at 80 °C (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **3b** (86.0 mg, 85%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.87 (s, 1H), 8.82 (d, *J* = 8.4 Hz, 1H), 8.03 – 7.95 (m, 4H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.66 – 7.42 (m, 8H), 7.32 – 7.25 (m, 6H), 7.05 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 166.0, 140.8, 137.9, 134.9, 134.7, 134.4, 133.6, 132.1, 132.0, 130.1, 129.8, 128.7, 128.5, 128.1, 127.5, 127.4, 127.3, 126.8, 126.1, 124.1, 122.4, 121.2, 119.1; IR (neat): 3280 (br), 2924, 1727, 1678, 1629, 1581, 1525, 1448, 1378, 1304, 1174, 1090, 1068, 755, 605; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{30}H_{23}N_2O_4S$ 507.1373, found 507.1370.

_N_-(2-(1-((4-bromophenyl)sulfonyl)-4-phenyl-1_H_-pyrrole-3-carbonyl)phenyl)benzamide (3c)

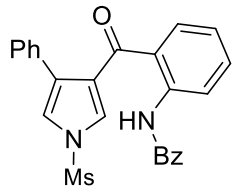


3c

The reaction was conducted with *N*-(2-(3-((4-bromo-*N*-(phenylethynyl)phenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1c**, 0.2 mmol, 113.8 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.3 mmol, 49.2 mg), and $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg) in DCE (4.0 mL) at 80 °C (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **3c** (68.4 mg, 58%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.85 (s, 1H), 8.81 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 2H), 7.81 (d, *J* = 7.0 Hz, 2H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.70 (d, *J* = 7.1 Hz, 2H), 7.59 (t, *J* = 7.9 Hz, 1H), 7.53 – 7.43 (m, 4H), 7.29 – 7.26 (m, 6H), 7.05 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 166.0, 140.8, 136.8, 134.9, 134.4, 133.5, 133.2, 132.0, 131.9, 130.5, 130.3, 128.8, 128.7, 128.5, 128.1, 127.7, 127.4, 127.2, 125.9, 124.1, 122.5, 121.3, 118.9; IR (neat): 3311 (br), 2925, 1728, 1679, 1603, 1580, 1448, 1392, 1305, 1265, 1185, 1067, 1009, 906, 745; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{30}H_{22}BrN_2O_4S$ 585.0478, found 585.0474.

***N*-(2-(1-(methylsulfonyl)-4-phenyl-1*H*-pyrrole-3-carbonyl)phenyl)benzamide (3d)**



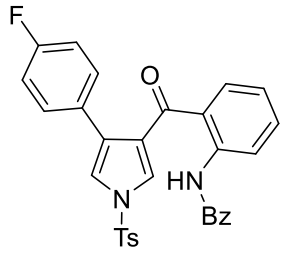
3d

The reaction was conducted with *N*-(2-(3-(*N*-(phenylethynyl)methylsulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1d**, 0.2 mmol, 85.7 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.3 mmol, 49.2 mg), and $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg) in DCE (4.0 mL) at 80 °C (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **3d** (64.9 mg, 73%) as a yellow solid (mp 236-238 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.93 (s, 1H), 8.84 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 7.3 Hz, 2H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.60 – 7.45 (m, 5H), 7.32 – 7.25 (m, 6H), 7.03 (t, *J* = 7.6

Hz, 1H), 3.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 165.9, 140.9, 135.0, 134.5, 133.6, 132.0(2), 131.9(9), 130.2, 128.8, 128.6, 128.1, 127.7, 127.4, 127.0, 125.6, 123.9, 122.4, 121.2, 118.8, 43.3; IR (neat): 3265 (br), 2926, 1670, 1602, 1581, 1529, 1508, 1447, 1361, 1226, ,1173, 1156, 1071, 904, 699; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{25}H_{21}N_2O_4S$ 445.1217, found 445.1208.

_N_-(2-(4-(4-fluorophenyl)-1-tosyl-1_H_-pyrrole-3-carbonyl)phenyl)benzamide (3e)

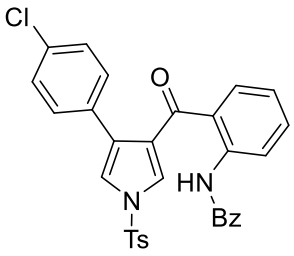


3e

The reaction was conducted with *N*-(2-(3-(*N*-((4-fluorophenyl)ethynyl)methylsulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1e**, 0.2 mmol, 104.6 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.3 mmol, 49.2 mg), and $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg) in DCE (4.0 mL) at 80 °C (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **3e** (99.9 mg, 92%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.78 (s, 1H), 8.80 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 7.9 Hz, 2H), 7.83 (d, *J* = 8.2 Hz, 2H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.61 (t, *J* = 7.9 Hz, 1H), 7.53 – 7.43 (m, 4H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.26 – 7.23 (m, 3H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.01 – 6.96 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 166.0, 162.2 (d, *J* = 245.0 Hz), 146.2, 140.7, 134.9, 134.8, 134.4, 133.4, 132.0, 130.4, 129.8 (d, *J* = 8.0 Hz), 129.0, 128.7, 128.3 (d, *J* = 3.0 Hz), 127.4, 126.4, 124.3, 122.5, 121.4, 119.1, 115.5 (d, *J* = 22.0 Hz), 21.7; IR (neat): 3285 (br), 2924, 1727, 1681, 1602, 1581, 1511, 1448, 1377, 1295, 1175, 1069, 1007, 967, 668; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{24}FN_2O_4S$ 539.1435, found 539.1425.

_N_-(2-(4-(4-chlorophenyl)-1-tosyl-1_H_-pyrrole-3-carbonyl)phenyl)benzamide (3f)

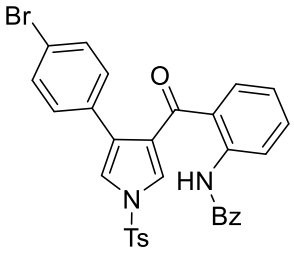


3f

The reaction was conducted with *N*-(2-(3-((*N*-((4-chlorophenyl)ethynyl)-4-methylphenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1f**, 0.2 mmol, 107.8 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.3 mmol, 49.2 mg), and $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg) in DCE (4.0 mL) at 80 ºC (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **3f** (87.1 mg, 79%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.76 (s, 1H), 8.81 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 7.2 Hz, 2H), 7.84 – 7.78 (m, 3H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.52 – 7.44 (m, 4H), 7.35 (d, *J* = 7.7 Hz, 2H), 7.28 – 7.21 (m, 2H), 7.10 (t, *J* = 7.3 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 166.0, 146.3, 140.7, 134.9, 134.7, 134.5, 133.5, 133.4, 132.0, 130.8, 130.5, 129.4, 128.9, 128.8, 128.7, 127.4, 126.6, 126.4, 124.3, 122.6, 121.5, 119.3, 21.7; IR (neat): 3317 (br), 2921, 1679, 1628, 1603, 1581, 1508, 1448, 1382, 1295, 1262, 1174, 1069, 906, 669; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{24}ClN_2O_4S$ 555.1140, found 555.1131.

***N*-(2-(4-(4-bromophenyl)-1-tosyl-1*H*-pyrrole-3-carbonyl)phenyl)benzamide (3g)**

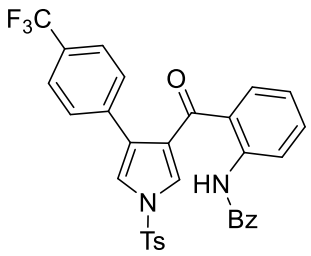


3g

The reaction was conducted with *N*-(2-(3-((*N*-((4-bromophenyl)ethynyl)-4-methylphenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1g**, 0.2 mmol, 116.8 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.3 mmol, 49.2 mg), and $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg) in DCE (4.0 mL) at 80 °C (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **3g** (102.1 mg, 85%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.76 (s, 1H), 8.81 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 7.3 Hz, 2H), 7.84 – 7.78 (m, 3H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.53 – 7.42 (m, 6H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.30 – 7.26 (m, 1H), 7.16 (d, *J* = 7.4 Hz, 2H), 7.10 (t, *J* = 7.6 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9, 166.0, 146.3, 140.7, 134.9, 134.7, 134.4, 133.4, 132.0, 131.6, 131.2, 130.5, 129.8, 128.9, 128.8, 127.4(2), 127.4(0), 126.6, 126.3, 124.3, 122.6, 121.6, 121.5, 119.3, 21.7; IR (neat): 3287 (br), 2923, 1671, 1623, 1603, 1580, 1509, 1494, 1378, 1297, 1253, 1173, 1069, 904, 664; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{24}BrN_2O_4S$ 599.0635, found 599.0628.

_N_-(2-(1-tosyl-4-(4-(trifluoromethyl)phenyl)-1_H_-pyrrole-3-carbonyl)phenyl)benzamide (3h)

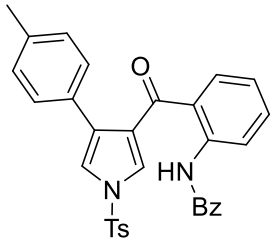


3h

The reaction was conducted with *N*-(2-(3-((4-methyl-*N*-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1h**, 0.2 mmol, 114.6 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.3 mmol, 49.2 mg), and $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg) in DCE (4.0 mL) at 80 °C (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **3h** (88.4 mg, 75%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.73 (s, 1H), 8.81 (d, *J* = 8.3 Hz, 1H), 7.96 (d, *J* = 7.0 Hz, 2H), 7.85 – 7.80 (m, 3H), 7.63 (t, *J* = 7.7 Hz, 1H), 7.57 – 7.35 (m, 11H), 7.11 (t, *J* = 7.5 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 166.0, 146.4, 140.7, 135.0, 134.6, 134.4, 133.3, 132.0, 130.5, 128.8, 128.7, 128.4, 127.5, 127.4, 126.8, 126.3, 125.42 (q, *J* = 3.7 Hz), 124.3, 122.6, 121.5, 119.9, 21.7; IR (neat): 3288 (br), 2926, 1728, 1682, 1627, 1581, 1521, 1494, 1376, 1325, 1265, 1173, 1068, 906, 672; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{32}H_{24}F_3N_2O_4S$ 589.1403, found 589.1395.

_N_-(2-(4-(_p_-tolyl)-1-tosyl-1_H_-pyrrole-3-carbonyl)phenyl)benzamide (3i)

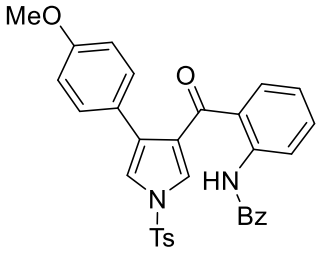


3i

The reaction was conducted with *N*-(2-(3-((4-methyl-*N*-(*p*-tolylethynyl)phenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1i**, 0.2 mmol, 103.8 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.3 mmol, 49.2 mg), and $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg) in DCE (4.0 mL) at 80 °C (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **3i** (77.4 mg, 72%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.83 (s, 1H), 8.81 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 7.4 Hz, 2H), 7.83 – 7.78 (m, 3H), 7.60 (t, *J* = 7.9 Hz, 1H), 7.51 – 7.43 (m, 4H), 7.34 (d, *J* = 7.2 Hz, 2H), 7.27 – 7.26 (m, 1H), 7.18 – 7.16 (m, 2H), 7.10 – 7.06 (m, 3H), 2.42 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 166.0, 146.1, 140.7, 137.3, 134.9, 134.7, 134.5, 133.6, 131.9, 130.4, 130.0, 129.2, 128.7, 127.9, 127.4(4), 127.3(6), 126.6, 126.2, 124.4, 122.5, 121.3, 118.8, 21.7, 21.2; IR (neat): 3279 (br), 2922, 1732, 1679, 1629, 1581, 1517, 1448, 1378, 1305, 1264, 1189, 1069, 967, 618; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{32}H_{27}N_2O_4S$ 535.1686, found 535.1677.

***N*-(2-(4-(4-methoxyphenyl)-1-tosyl-1*H*-pyrrole-3-carbonyl)phenyl)benzamide (3j)**

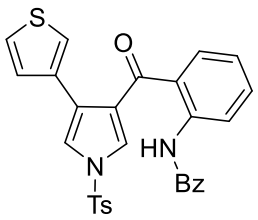


3j

The reaction was conducted with *N*-(2-(3-((*N*-((4-methoxyphenyl)ethynyl)-4-methylphenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1j**, 0.2 mmol, 107.0 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.3 mmol, 49.2 mg), and $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg) in DCE (4.0 mL) at 80 °C (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **3j** (75.3 mg, 68%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.85 (s, 1H), 8.81 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 7.9 Hz, 2H), 7.83 – 7.77 (m, 3H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.51 – 7.45 (m, 4H), 7.34 (d, *J* = 7.3 Hz, 2H), 7.27 – 7.20 (m, 3H), 7.07 (t, *J* = 7.0 Hz, 1H), 6.83 (d, *J* = 6.8 Hz, 2H), 3.78 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 166.0, 159.1, 146.1, 140.7, 134.9, 134.8, 134.5, 133.6, 132.0, 130.4, 129.7, 129.3, 128.7, 127.4(3), 127.3(6), 126.6, 126.2, 124.6, 124.3, 122.5, 121.2, 118.5, 113.9, 55.2, 21.7; IR (neat): 3280 (br), 2925, 1727, 1679, 1628, 1580, 1514, 1493, 1377, 1295, 1249, 1174, 1037, 906, 670; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{32}H_{27}N_2O_5S$ 551.1635, found 551.1625.

***N*-(2-(4-(thiophen-3-yl)-1-tosyl-1*H*-pyrrole-3-carbonyl)phenyl)benzamide (3k)**

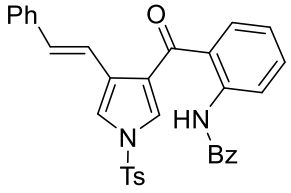


3k

The reaction was conducted with *N*-(2-(3-((4-methyl-*N*-(thiophen-3-ylethynyl)phenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1k**, 0.2 mmol, 102.2 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.3 mmol, 49.2 mg), and $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg) in DCE (4.0 mL) at 80 °C (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **3k** (90.2 mg, 86%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.86 (s, 1H), 8.82 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 7.3 Hz, 2H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.61 (t, *J* = 7.9 Hz, 1H), 7.55 – 7.43 (m, 4H), 7.38 – 7.32 (m, 4H), 7.26 (t, *J* = 3.9 Hz, 1H), 7.10 – 7.07 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 165.9, 146.2, 140.7, 134.8(2), 134.7(5), 134.5, 133.6, 132.3, 132.0, 130.4, 128.8, 127.7, 127.4, 127.3, 126.5, 126.4, 125.6, 124.5, 124.4, 122.7, 122.5, 121.3, 119.0, 21.7; IR (neat): 3284 (br), 2922, 1727, 1680, 1628, 1581, 1524, 1494, 1448, 1327, 1207, 1135, 1070, 969, 666; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{29}H_{23}N_2O_4S_2$ 527.1094, found 527.1083.

_N_-(2-(4-styryl-1-tosyl-1_H_-pyrrole-3-carbonyl)phenyl)benzamide (3l)



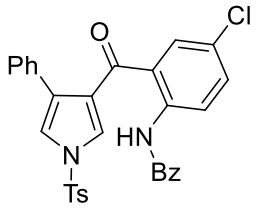
3l

The reaction was conducted with *N*-(2-(3-((4-methyl-*N*-(4-phenylbut-3-en-1-yn-1-yl)phenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1l**, 0.2 mmol, 106.2 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.3 mmol, 49.2 mg), and $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg) in DCE (4.0 mL) at 80 °C (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **3l** (67.2 mg, 61%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.66 (s, 1H), 8.80 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 7.7 Hz, 2H), 7.85 – 7.79 (m, 3H), 7.66 (t, *J* = 7.9 Hz, 1H), 7.53 – 7.41 (m, 7H), 7.36 – 7.26 (m, 6H), 7.19 (t, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 16.5 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 193.9, 165.9, 146.2, 140.2, 137.0, 134.7, 134.5, 134.4, 132.8, 132.0, 130.6, 130.4, 128.8, 128.6, 127.8, 127.5, 127.3(9), 127.3(5), 127.2, 126.5, 126.3, 125.1, 122.7, 121.7, 119.0, 117.5, 21.7; IR (neat): 3318 (br), 2956, 1725, 1679, 1624, 1579, 1521, 1494, 1448, 1378, 1297, 1119, 1068, 967, 672; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{33}H_{27}N_2O_4S$ 547.1686, found 547.1678.

_N_-(4-chloro-2-(4-phenyl-1-tosyl-1_H_-pyrrole-3-carbonyl)phenyl)benzamide (3m)

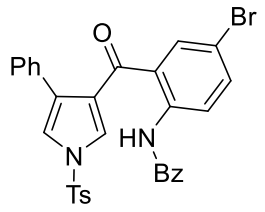


3m

The reaction was conducted with *N*-(4-chloro-2-(3-((4-methyl-*N*-(phenylethynyl)phenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1m**, 0.2 mmol, 107.8 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.3 mmol, 49.2 mg), and $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg) in DCE (4.0 mL) at 80 ºC (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **3m** (61.8 mg, 56%) as a pale yellow oil.

^1H NMR (400 MHz, $CDCl_3$) δ 11.71 (s, 1H), 8.78 (d, *J* = 9.0 Hz, 1H), 7.96 (d, *J* = 7.7 Hz, 2H), 7.86 (d, *J* = 7.2 Hz, 2H), 7.65 – 7.59 (m, 1H), 7.55 – 7.44 (m, 5H), 7.37 (d, *J* = 7.7 Hz, 2H), 7.30 – 7.22 (m, 6H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 165.8, 146.3, 139.2, 134.8, 134.3, 134.2, 132.8, 132.2, 132.0, 130.5, 130.0, 128.8, 128.5, 128.2, 127.6, 127.4, 126.4, 126.2, 125.2, 122.6, 119.3, 21.7; IR (neat): 3287 (br), 2923, 1729, 1683, 1632, 1577, 1510, 1492, 1375, 1287, 1173, 1112, 1067, 967, 669; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{24}ClN_2O_4S$ 555.1140, found 555.1141.

_N_-(4-bromo-2-(4-phenyl-1-tosyl-1_H_-pyrrole-3-carbonyl)phenyl)benzamide (3n)

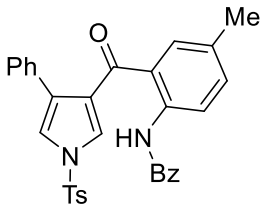


3n

The reaction was conducted with *N*-(4-bromo-2-(3-((4-methyl-*N*-(phenylethynyl)phenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1n**, 0.2 mmol, 116.8 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.3 mmol, 49.2 mg), and $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg) in DCE (4.0 mL) at 80 ^oC (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **3n** (72.3 mg, 60%) as a pale yellow oil.

^1H NMR (400 MHz, $CDCl_3$) δ 11.73 (s, 1H), 8.73 (d, *J* = 9.0 Hz, 1H), 7.96 (d, *J* = 7.2 Hz, 2H), 7.86 (d, *J* = 7.1 Hz, 2H), 7.79 – 7.73 (m, 1H), 7.62 (d, *J* = 8.9 Hz, 1H), 7.56 – 7.44 (m, 4H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.30 – 7.22 (m, 6H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 165.8, 146.3, 139.6, 137.2, 135.7, 134.8, 134.1, 132.2, 132.0, 130.5, 130.0, 128.8, 128.5, 128.2, 127.6, 127.4, 126.4, 126.1, 125.4, 122.8, 119.3, 114.7, 21.7; IR (neat): 3286 (br), 2922, 1729, 1682, 1630, 1597, 1510, 1492 ,1393, 1375, 1295, 1173, 1089, 966, 669; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{24}BrN_2O_4S$ 599.0635, found 599.0636.

***N*-(4-methyl-2-(4-phenyl-1-tosyl-1*H*-pyrrole-3-carbonyl)phenyl)benzamide (3o)**



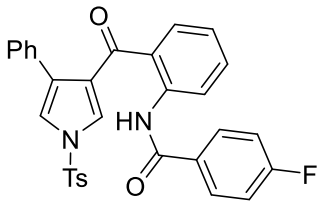
3o

The reaction was conducted with *N*-(4-methyl-2-(3-((4-methyl-*N*-(phenylethynyl)phenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1o**, 0.2 mmol, 103.8 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.3 mmol, 49.2 mg), and $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg) in DCE (4.0 mL) at 80 ^oC (80 °C, heating mantle temperature).

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **3o** (66.3 mg, 62%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.75 (s, 1H), 8.68 (d, *J* = 8.6 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 7.0 Hz, 2H), 7.51 – 7.43 (m, 5H), 7.39 – 7.34 (m, 3H), 7.30 – 7.26 (m, 6H), 2.44 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 165.8, 146.2, 138.3, 135.5, 135.0, 134.6, 133.9, 132.3, 132.0, 131.9, 130.4, 130.0, 128.7, 128.5, 128.1, 127.5, 127.4, 126.8, 126.1, 124.1, 121.2, 119.0, 21.7, 20.7; IR (neat): 3290 (br), 2923, 1727, 1679, 1628, 1590, 1519, 1450, 1371, 1304, 1263, 1188, 1090, 968, 669; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{32}H_{27}N_2O_4S$ 535.1686, found 535.1688.

4-fluoro-*N*-(2-(4-phenyl-1-tosyl-1*H*-pyrrole-3-carbonyl)phenyl)benzamide (3p)

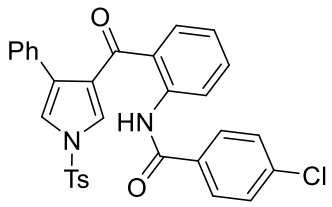


3p

The reaction was conducted with 4-fluoro-*N*-(2-(3-((4-methyl-*N*-(phenylethynyl)phenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1p**, 0.2 mmol, 104.6 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.3 mmol, 49.2 mg), and $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg) in DCE (4.0 mL) at 80 ºC (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **3p** (85.6 mg, 79%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.87 (s, 1H), 8.78 (d, *J* = 8.3 Hz, 1H), 8.01 – 7.98 (m, 2H), 7.84 (d, *J* = 6.8 Hz, 2H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.60 (t, *J* = 7.9 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.35 (d, *J* = 7.4 Hz, 2H), 7.30 – 7.26 (m, 6H), 7.14 – 7.05 (m, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 164.3 (d, *J* = 104.0 Hz), 146.2, 140.7, 134.9, 133.6, 132.2, 130.4, 130.0, 129.9 (d, *J* = 9.0 Hz), 128.5, 128.1, 127.5, 127.4, 126.5, 126.2, 124.1, 122.5, 121.2, 119.2, 115.8 (d, *J* = 22.0 Hz), 21.7; IR (neat): 3324 (br), 2922, 1731, 1680, 1628, 1530, 1504, 1445, 1377, 1293, 1174, 1160, 1067, 967, 669; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{24}FN_2O_4S$ 539.1435, found 539.1436.

4-chloro-*N*-(2-(4-phenyl-1-tosyl-1*H*-pyrrole-3-carbonyl)phenyl)benzamide (3q)

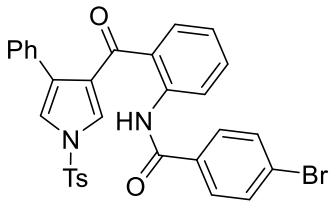


3q

The reaction was conducted with 4-chloro-*N*-(2-(3-((4-methyl-*N*-(phenylethynyl)phenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1q**, 0.2 mmol, 107.8 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.3 mmol, 49.2 mg), and $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg) in DCE (4.0 mL) at 80 ºC (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **3q** (77.8 mg, 70%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.90 (s, 1H), 8.78 (d, *J* = 8.3 Hz, 1H), 7.91 (d, *J* = 6.1 Hz, 2H), 7.85 – 7.79 (m, 3H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.52 – 7.48 (m, 1H), 7.41 (d, *J* = 6.2 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.30 – 7.25 (m, 6H), 7.07 (t, *J* = 6.7 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 164.8, 146.2, 140.6, 138.3, 134.9, 134.8, 133.6, 132.9, 132.2, 130.4, 130.0, 129.0, 128.9, 128.5, 128.1, 127.5, 127.4, 126.5, 126.2, 124.1, 122.6, 121.2, 119.1, 21.7; IR (neat): 3278 (br), 2924, 1732, 1682, 1628, 1594, 1528, 1490, 1378, 1294, 1174, 1067, 1013, 967, 669; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{24}ClN_2O_4S$ 555.1140, found 555.1142.

4-bromo-*N*-(2-(4-phenyl-1-tosyl-1*H*-pyrrole-3-carbonyl)phenyl)benzamide (3r)



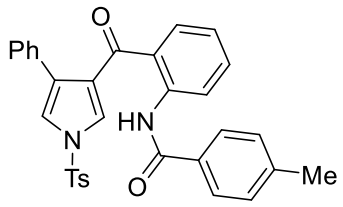
3r

The reaction was conducted with 4-bromo-*N*-(2-(3-((4-methyl-*N*-(phenylethynyl)phenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1r**, 0.2 mmol,

116.8 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.3 mmol, 49.2 mg), and $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg) in DCE (4.0 mL) at 80 °C (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **3r** (71.6 mg, 60%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.90 (s, 1H), 8.78 (d, *J* = 8.3 Hz, 1H), 7.85 – 7.79 (m, 5H), 7.60 (t, *J* = 8.8 Hz, 3H), 7.50 – 7.46 (m, 1H), 7.35 (d, *J* = 7.3 Hz, 2H), 7.30 – 7.26 (m, 6H), 7.08 (t, *J* = 7.1 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 164.9, 146.2, 140.6, 134.9, 134.8, 133.6, 133.3, 132.2, 132.0, 130.4, 130.0, 129.0, 128.5, 128.1, 127.5, 127.4, 126.8, 126.5, 126.2, 124.1, 122.7, 121.2, 119.2, 21.7; IR (neat): 3304 (br), 2920, 1682, 1628, 1584, 1507, 1445, 1383, 1308, 1264, 1189, 1067, 1009, 758, 669; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{24}BrN_2O_4S$ 599.0635, found 599.0634.

4-methyl-*N*-(2-(4-phenyl-1-tosyl-1*H*-pyrrole-3-carbonyl)phenyl)benzamide (3s)



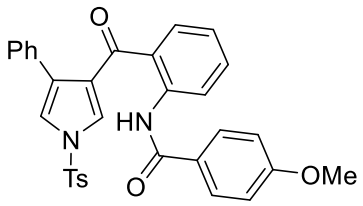
3s

The reaction was conducted with 4-methyl-*N*-(2-(3-((4-methyl-*N*-(phenylethynyl)phenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1s**, 0.2 mmol, 103.8 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.3 mmol, 49.2 mg), and $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg) in DCE (4.0 mL) at 80 °C (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **3s** (90.5 mg, 85%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.82 (s, 1H), 8.81 (d, *J* = 8.4 Hz, 1H), 7.88 – 7.82 (m, 4H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.58 (t, *J* = 7.9 Hz, 1H), 7.47 (d, *J* = 2.2 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.30 – 7.23 (m, 8H), 7.04 (t, *J* = 7.6 Hz, 1H), 2.43 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 166.0, 146.1, 142.5, 140.9, 134.9, 134.8, 133.5, 132.2, 131.7, 130.4, 130.0, 129.4, 128.5, 128.1, 127.5(0), 127.4(7), 127.4, 126.7, 126.1, 124.1, 122.3, 121.2, 119.1, 21.7, 21.5; IR (neat): 3284 (br), 2923, 1731, 1679, 1628, 1581,

1506, 1446, 1377, 1266, 1124, 1067, 1019, 967, 670; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{32}H_{27}N_2O_4S$ 535.1686, found 535.1684.

4-methoxy-*N*-(2-(4-phenyl-1-tosyl-1*H*-pyrrole-3-carbonyl)phenyl)benzamide (3t)

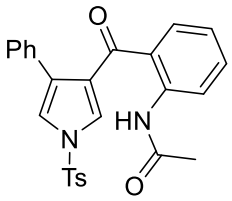


3t

The reaction was conducted with 4-methoxy-*N*-(2-(3-((4-methyl-*N*-(phenylethynyl)phenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1t**, 0.2 mmol, 107.0 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.3 mmol, 49.2 mg), and $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg) in DCE (4.0 mL) at 80 ºC (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **3t** (78.2 mg, 71%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.81 (s, 1H), 8.80 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 8.8 Hz, 2H), 7.83 (d, *J* = 8.2 Hz, 2H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.58 (t, *J* = 7.9 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.30 – 7.26 (m, 6H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 165.5, 162.6, 146.1, 141.0, 134.9, 134.8, 133.6, 132.2, 130.4, 130.0, 129.4, 128.5, 128.1, 127.5, 127.4, 126.8, 126.7, 126.1, 124.0, 122.1, 121.1, 119.1, 113.9, 55.4, 21.7.; IR (neat): 3286 (br), 2925, 1729, 1677, 1626, 1581, 1507, 1446, 1375, 1253, 1114, 1067, 1028, 906, 669; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{32}H_{27}N_2O_5S$ 551.1635, found 551.1633.

***N*-(2-(4-phenyl-1-tosyl-1*H*-pyrrole-3-carbonyl)phenyl)acetamide (3u)**

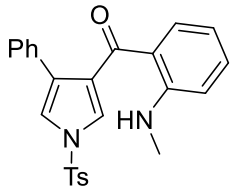


3u

The reaction was conducted with *N*-(2-(3-((4-methyl-*N*-(phenylethynyl)phenyl)sulfonamido)prop-1-yn-1-yl)phenyl)acetamide (**1u**, 0.2 mmol, 88.6 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.3 mmol, 49.2 mg), and $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg) in DCE (4.0 mL) at 80 ^oC (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **3u** (72.3 mg, 78%) as a pale yellow oil.

^1H NMR (400 MHz, $CDCl_3$) δ 10.76 (s, 1H), 8.57 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.43 (d, *J* = 2.3 Hz, 1H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.26 (m, 6H), 7.06 (t, *J* = 7.6 Hz, 1H), 2.45 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 169.2, 146.2, 140.2, 134.9, 134.5, 133.0, 132.2, 130.4, 130.2, 128.5, 128.2, 127.6, 127.4, 126.8, 126.4, 124.2, 122.3, 121.3, 119.3, 25.3, 21.7; IR (neat): 3370 (br), 2924, 1696, 1631, 1596, 1581, 1517, 1448, 1374, 1266, 1173, 1067, 1008, 967, 669; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{26}H_{23}N_2O_4S$ 459.1373, found 459.1370.

(2-(methylamino)phenyl)(4-phenyl-1-tosyl-1*H*-pyrrol-3-yl)methanone (3v)



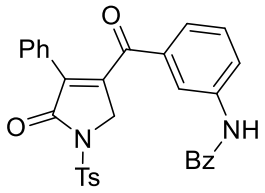
3v

The reaction was conducted with 4-methyl-*N*-(3-(2-(methylamino)phenyl)prop-2-yn-1-yl)-*N*-(phenylethynyl)benzenesulfonamide (**1v**, 0.2 mmol, 88.6 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.3 mmol, 49.2 mg), and $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg) in DCE (4.0 mL) at 80 ^oC (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **3v** (60.6 mg, 70%) as a pale yellow oil.

^1H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.40 – 7.32 (m, 4H), 7.27 – 7.20 (m, 6H), 6.69 (d, *J* = 8.5 Hz, 1H), 6.51 (t, *J* = 7.5 Hz, 1H), 2.88 (d, *J* = 5.0 Hz, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0,

152.5, 145.8, 135.3, 134.8, 132.7, 130.3, 130.0, 128.4, 127.9, 127.2, 123.9, 118.4, 118.3, 113.8, 110.9, 29.3, 21.7; IR (neat): 3370 (br), 2924, 1696, 1631, 1596, 1581, 1517, 1448, 1374, 1266, 1173, 1067, 1008, 967, 669; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{26}H_{23}N_2O_4S$ 459.1373, found 459.1370.

_N_-(3-(5-oxo-4-phenyl-1-tosyl-2,5-dihydro-1_H_-pyrrole-3-carbonyl)phenyl)benzamide (3wa)

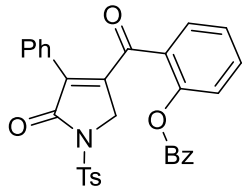


3wa

The reaction was conducted with *N*-(3-(3-((4-methyl-*N*-(phenylethynyl)phenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1w**, 0.2 mmol, 101.0 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.6 mmol, 98.4 mg), $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg) in DCE (4.0 mL) at 80 °C (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) yielded **3wa** (71.0 mg, 66%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.02 (m, 2H), 7.90 (d, *J* = 8.2 Hz, 2H), 7.79 (s, 1H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.45 – 7.30 (m, 4H), 7.24 – 7.19 (m, 5H), 7.14 – 7.03 (m, 3H), 4.76 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 166.8, 165.7, 147.9, 145.7, 138.8, 136.5, 135.0, 134.7, 134.2, 132.1, 129.9, 129.8, 129.6, 129.2, 128.8, 128.6, 128.3(4), 128.2(8), 127.0, 125.8, 125.1, 120.6, 50.8, 21.7; IR (neat): 3358 (br), 2922, 1725, 1653, 1592, 1539, 1483, 1431, 1362, 1327, 1259, 1171, 1089, 668, 583; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{25}N_2O_5S$ 537.1479, found 537.1475.

2-(5-oxo-4-phenyl-1-tosyl-2,5-dihydro-1_H_-pyrrole-3-carbonyl)phenyl benzoate (3xa)

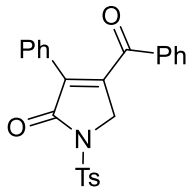


3xa

The reaction was conducted with 2-(3-((4-methyl-*N*-(phenylethynyl)phenyl)sulfonamido)prop-1-yn-1-yl)phenyl benzoate (**1x**, 0.2 mmol, 101.2 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.6 mmol, 98.4 mg), $Cu(CH_3CN)_4BF_4$ (0.02 mmol, 6.3 mg) in DCE (4.0 mL) at 80 °C (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) yielded **3xa** (82.8 mg, 77%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.0 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.68 (t, *J* = 7.0 Hz, 1H), 7.55 – 7.52 (m, 3H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.23 (m, 2H), 7.19 – 7.06 (m, 5H), 4.69 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1, 166.6, 164.8, 149.4, 147.1, 145.5, 137.9, 134.8, 134.4, 134.3, 131.0, 130.0, 129.8, 129.7, 129.6, 129.0, 128.9, 128.5, 128.2, 128.1, 128.0, 125.9, 123.4, 50.2, 21.7; IR (neat): 2920, 1730, 1653, 1600, 1492, 1448, 1368, 1327, 1261, 1189, 1172, 1089, 1058, 964, 668; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{24}NO_6S$ 538.1319, found 538.1318.

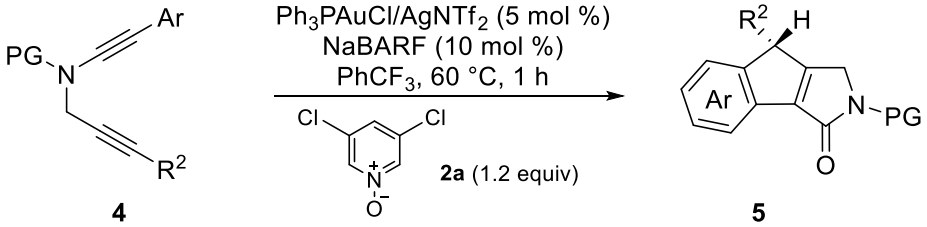
4-benzoyl-3-phenyl-1-tosyl-1,5-dihydro-2*H*-pyrrol-2-one (3ya)



3ya

The reaction was conducted with 4-methyl-*N*-(phenylethynyl)-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (**1y**, 0.2 mmol, 77.0 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.6 mmol, 98.4 mg), and $Cu(CH_3CN)_4PF_6$ (0.02 mmol, 7.5 mg) in DCE (4.0 mL) at 80 °C

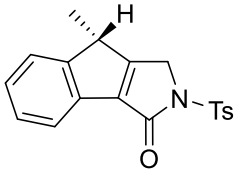
(80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **3ya** (60.3 mg, 72%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.6 Hz, 2H), 7.67 (d, *J* = 7.3 Hz, 2H), 7.46 (t, *J* = 6.8 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 2H), 7.29 – 7.26 (m, 4H), 7.21 – 7.13 (m, 3H), 4.80 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 166.6, 147.6, 145.6, 136.4, 134.8, 134.4, 134.2, 129.9, 129.7, 129.4, 129.2, 128.7, 128.6, 128.4, 128.3, 50.6, 21.7; IR (neat): 2923, 1724, 1653, 1596, 1493, 1448, 1365, 1328, 1254, 1188, 1172, 1115, 1090, 963, 667; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{20}NO_4S$ 418.1108, found 418.1106.



General procedure for the synthesis of dihydroindeno[1,2-*c*]pyrrol-3(2*H*)-ones 5:

3,5-Dichloropyridine *N*-oxide **2a** (0.24 mmol, 39.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and NaBARF (0.02 mmol, 17.7 mg) were added in this order to the diynes **4** (0.2 mmol) in $PhCF_3$ (4.0 mL) at room temperature. The reaction mixture was stirred at 60 °C (60 °C, heating mantle temperature) and the progress of the reaction was monitored by TLC. The reaction typically took 1 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 **5**.

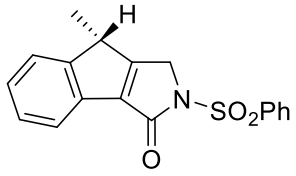
8-methyl-2-tosyl-1,8-dihydroindeno[1,2-*c*]pyrrol-3(2*H*)-one (5a)



5a

The reaction was conducted with *N*-(but-2-yn-1-yl)-4-methyl-*N*-(phenylethynyl)benzenesulfonamide (**4a**, 0.2 mmol, 64.6 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.24 mmol, 39.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and NaBARF (0.02 mmol, 17.7 mg) in $PhCF_3$ (4.0 mL) at 60 ºC (60 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **5a** (48.8 mg, 72%) as a yellow solid (mp 174-176 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.2 Hz, 2H), 7.62 (d, *J* = 6.7 Hz, 1H), 7.42 (d, *J* = 6.3 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 2H), 7.29 – 7.28 (m, 2H), 4.73 (s, 2H), 3.74 (q, *J* = 7.2 Hz, 1H), 2.42 (s, 3H), 1.43 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 163.5, 151.2, 145.0, 139.0, 135.6, 134.3, 129.7, 128.0, 127.3, 126.7, 123.5, 120.9, 49.4, 42.3, 21.6, 15.5; IR (neat): 2922, 1724, 1597, 1362, 1307, 1169, 1132, 1090, 672, 580, 545; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{18}NO_3S$ 340.1002, found 340.1001.

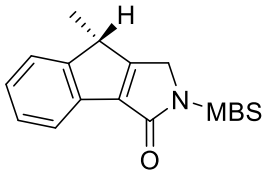
8-methyl-2-(phenylsulfonyl)-1,8-dihydroindeno[1,2-*c*]pyrrol-3(2*H*)-one (5b)



5b

The reaction was conducted with *N*-(but-2-yn-1-yl)-*N*-(phenylethynyl)benzenesulfonamide (**4b**, 0.2 mmol, 61.8 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.24 mmol, 39.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and NaBARF (0.02 mmol, 17.7 mg) in $PhCF_3$ (4.0 mL) at 60 ºC (60 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **5b** (54.0 mg, 83%) as a pale yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.3 Hz, 2H), 7.66 – 7.61 (m, 2H), 7.57 – 7.54 (m, 2H), 7.42 (d, *J* = 6.2 Hz, 1H), 7.31 – 7.26 (m, 2H), 4.74 (s, 2H), 3.75 (q, *J* = 7.2 Hz, 1H), 1.43 (d, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 163.5, 151.2, 138.9, 138.5, 134.2, 133.9, 129.1, 127.9, 127.3, 126.7, 123.5, 120.9, 49.5, 42.3, 15.4; IR (neat): 2930, 1738, 1448, 1360, 1307, 1171, 1134, 1090, 775, 608, 569; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{16}NO_3S$ 326.0845, found 326.0844.

2-((4-methoxyphenyl)sulfonyl)-8-methyl-1,8-dihydroindeno[1,2-*c*]pyrrol-3(2*H*)-one (5c)

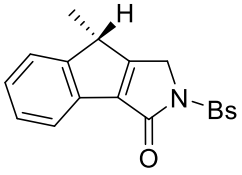


5c

The reaction was conducted with *N*-(but-2-yn-1-yl)-4-methoxy-*N*-(phenylethynyl)benzenesulfonamide (**4c**, 0.2 mmol, 67.8 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.24 mmol, 39.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and NaBARF (0.02 mmol, 17.7 mg) in $PhCF_3$ (4.0 mL) at 60 ºC (60 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **5c** (62.5 mg, 88%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.2 Hz, 2H), 7.62 (d, *J* = 6.8 Hz, 1H), 7.42 (d, *J* = 6.7 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.01 (d, *J* = 7.2 Hz, 2H), 4.73 (s, 2H), 3.86 (s, 3H), 3.75 (q, *J* = 7.1 Hz, 1H), 1.44 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 163.9, 163.6, 151.2, 139.1, 134.4, 130.4, 130.1, 127.4, 126.7, 123.5, 120.9, 114.3, 55.7, 49.4, 42.3, 15.5; IR (neat): 2930, 1721, 1595, 1498, 1359, 1263, 1164, 1091, 675, 580, 554; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{18}NO_4S$ 356.0951, found 356.0950.

2-((4-bromophenyl)sulfonyl)-8-methyl-1,8-dihydroindeno[1,2-*c*]pyrrol-3(2*H*)-one (5d)



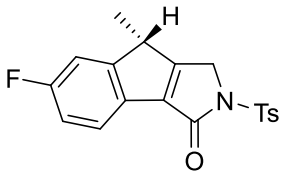
5d

The reaction was conducted with 4-bromo-*N*-(but-2-yn-1-yl)-*N*-(phenylethynyl)benzenesulfonamide (**4d**, 0.2 mmol, 77.6 mg), 3,5-dichloropyridine *N*-

oxide (**2a**, 0.24 mmol, 39.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and NaBARF (0.02 mmol, 17.7 mg) in $PhCF_3$ (4.0 mL) at 60 °C (60 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **5d** (56.6 mg, 70%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.2 Hz, 2H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.54 (d, *J* = 6.8 Hz, 1H), 7.35 (d, *J* = 6.8 Hz, 1H), 7.25 – 7.21 (m, 2H), 4.65 (s, 2H), 3.68 (q, *J* = 7.7 Hz, 1H), 1.36 (d, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 163.5, 151.1, 138.9, 137.5, 134.1, 132.4, 129.5, 129.3, 127.4, 126.8, 123.6, 120.9, 49.5, 42.4, 15.5; IR (neat): 2930, 1736, 1574, 1471, 1364, 1172, 1133, 1068, 744, 616, 572; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{15}BrNO_3S$ 403.9951, found 403.9950.

6-fluoro-8-methyl-2-tosyl-1,8-dihydroindeno[1,2-*c*]pyrrol-3(2*H*)-one (5e)

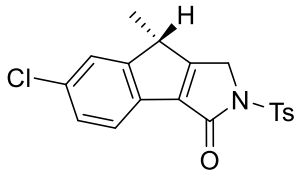


5e

The reaction was conducted with *N*-(but-2-yn-1-yl)-*N*-((4-fluorophenyl)ethynyl)-4-methylbenzenesulfonamide (**4e**, 0.2 mmol, 68.2 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.24 mmol, 39.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and NaBARF (0.02 mmol, 17.7 mg) in $PhCF_3$ (4.0 mL) at 60 °C (60 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **5e** (36.4 mg, 51%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.51 – 7.43 (m, 1H), 7.27 (d, *J* = 7.4 Hz, 2H), 7.06 (d, *J* = 8.6 Hz, 1H), 6.93 (t, *J* = 8.5 Hz, 1H), 4.64 (s, 2H), 3.67 (q, *J* = 7.1 Hz, 1H), 2.35 (s, 3H), 1.36 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 163.4 (d, *J* = 20.0 Hz), 161.0, 153.5 (d, *J* = 8.0 Hz), 145.1, 138.4, 135.6, 130.4 (d, *J* = 2.0 Hz), 129.8, 128.1, 121.8 (d, *J* = 9.0 Hz), 114.3 (d, *J* = 23.0 Hz), 111.7 (d, *J* = 24.0 Hz), 49.3, 42.4, 21.7, 15.5; IR (neat): 2922, 1724, 1598, 1509, 1360, 1307, 1162, 1091, 814, 665, 546; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{17}FNO_3S$ 358.0908, found 358.0907.

6-chloro-8-methyl-2-tosyl-1,8-dihydroindeno[1,2-*c*]pyrrol-3(2*H*)-one (5f)

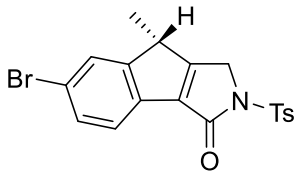


5f

The reaction was conducted with *N*-(but-2-yn-1-yl)-*N*-((4-chlorophenyl)ethynyl)-4-methylbenzenesulfonamide (**4f**, 0.2 mmol, 71.6 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.24 mmol, 39.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and NaBARF (0.02 mmol, 17.7 mg) in $PhCF_3$ (4.0 mL) at 60 ^oC (60 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **5f** (34.4 mg, 46%) as a pale yellow oil.

^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.1 Hz, 2H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.40 – 7.35 (m, 3H), 7.30 – 7.27 (m, 1H), 4.73 (s, 2H), 3.75 (q, *J* = 7.4 Hz, 1H), 2.43 (s, 3H), 1.44 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 163.2, 152.8, 145.2, 138.5, 135.5, 132.8 (9), 132.8 (6), 129.8, 128.1, 127.7, 124.3, 121.7, 49.3, 42.4, 21.7, 15.4; IR (neat): 2927, 1731, 1597, 1440, 1362, 1303, 1170, 1091, 662, 588, 545; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{17}ClNO_3S$ 374.0612, found 374.0611.

6-bromo-8-methyl-2-tosyl-1,8-dihydroindeno[1,2-*c*]pyrrol-3(2*H*)-one (5g)



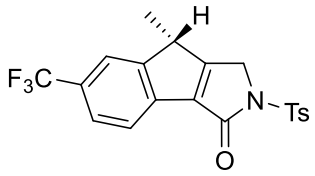
5g

The reaction was conducted with *N*-((4-bromophenyl)ethynyl)-*N*-(but-2-yn-1-yl)-4-methylbenzenesulfonamide (**4g**, 0.2 mmol, 80.4 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.24 mmol, 39.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and NaBARF (0.02 mmol, 17.7 mg) in $PhCF_3$ (4.0 mL) at 60 ^oC (60 °C, heating mantle

temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **5g** (39.3 mg, 47%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.48 (s, 1H), 7.42 – 7.35 (m, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 4.64 (s, 2H), 3.67 (q, *J* = 15.2, 7.6 Hz, 1H), 2.36 (s, 3H), 1.36 (d, *J* = 7.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 163.1, 153.1, 145.2, 138.5, 135.5, 133.3, 130.6, 129.8, 128.1, 127.1, 122.1, 120.9, 49.3, 42.4, 21.7, 15.3; IR (neat): 2925, 1729, 1596, 1462, 1362, 1302, 1169, 1090, 674, 586, 545; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{17}BrNO_3S$ 418.0107, found 418.0105.

8-methyl-2-tosyl-6-(trifluoromethyl)-1,8-dihydroindeno[1,2-*c*]pyrrol-3(2*H*)-one (5h)

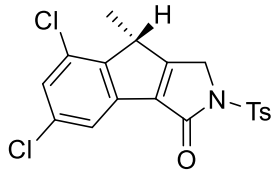


5h

The reaction was conducted with *N*-(but-2-yn-1-yl)-4-methyl-*N*-((4-(trifluoromethyl)phenyl)ethynyl)benzenesulfonamide (**4h**, 0.2 mmol, 78.2 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.24 mmol, 39.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and NaBARF (0.02 mmol, 17.7 mg) in $PhCF_3$ (4.0 mL) at 60 °C (60 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **5h** (59.4 mg, 73%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.58 (s, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 2H), 4.70 (s, 2H), 3.76 (q, *J* = 7.6 Hz, 1H), 2.36 (s, 3H), 1.40 (d, *J* = 7.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 162.9, 151.5, 145.3, 138.5, 137.7, 135.5, 129.8, 128.1, 125.0 (q, *J* = 3.8 Hz), 121.1, 120.5, 120.4, 49.5, 42.6, 21.7, 15.2; IR (neat): 2925, 1734, 1597, 1433, 1361, 1326, 1170, 1090, 672, 610, 577; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{17}F_3NO_3S$ 408.0876, found 408.0875.

5,7-dichloro-8-methyl-2-tosyl-1,8-dihydroindeno[1,2-*c*]pyrrol-3(2*H*)-one (5i)

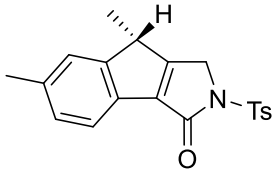


5i

The reaction was conducted with *N*-(but-2-yn-1-yl)-*N*-((3,5-dichlorophenyl)ethynyl)-4-methylbenzenesulfonamide (**4i**, 0.2 mmol, 78.4 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.24 mmol, 39.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and NaBARF (0.02 mmol, 17.7 mg) in $PhCF_3$ (4.0 mL) at 60 ^oC (60 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **5i** (54.7 mg, 67%) as a pale yellow oil.

^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.3 Hz, 2H), 7.45 (s, 1H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.16 (s, 1H), 4.67 (s, 2H), 3.82 (q, *J* = 7.3 Hz, 1H), 2.36 (s, 3H), 1.45 (d, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 162.6, 145.8, 145.3, 137.5, 137.3, 135.3, 134.5, 130.7, 129.8, 128.1, 127.0, 120.0, 49.3, 42.7, 21.7, 13.7; IR (neat): 2921, 1727, 1595, 1422, 1361, 1298, 1170, 1095, 837, 600, 543; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{16}Cl_2NO_3S$ 408.0222, found 408.0223.

6,8-dimethyl-2-tosyl-1,8-dihydroindeno[1,2-*c*]pyrrol-3(2*H*)-one (5j)

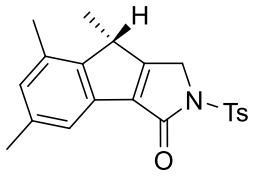


5j

The reaction was conducted with *N*-(but-2-yn-1-yl)-4-methyl-*N*-(*p*-tolylethynyl)benzenesulfonamide (**4j**, 0.2 mmol, 67.4 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.24 mmol, 39.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and NaBARF (0.02 mmol, 17.7 mg) in $PhCF_3$ (4.0 mL) at 60 ^oC (60 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) yielded **5j** (57.2 mg, 81%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.5 Hz, 2H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 2H), 7.23 (s, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 4.70 (s, 2H), 3.70 (q, *J* = 7.4 Hz, 1H), 2.42 (s, 3H), 2.39 (s, 3H), 1.41 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 163.6, 151.5, 144.9, 138.9, 136.7, 135.7, 131.6, 129.7, 128.0, 124.4, 120.5, 49.4, 42.1, 21.6 (3), 21.6 (0), 15.6; IR (neat): 2921, 1731, 1597, 1441, 1359, 1304, 1171, 1090, 820, 674, 584; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{20}NO_3S$ 354.1158, found 354.1156.

5,7,8-trimethyl-2-tosyl-1,8-dihydroindeno[1,2-*c*]pyrrol-3(2*H*)-one (5k)

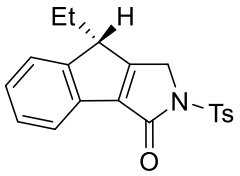


5k

The reaction was conducted with *N*-(but-2-yn-1-yl)-*N*-((3,5-dimethylphenyl)ethynyl)-4-methylbenzenesulfonamide (**4k**, 0.2 mmol, 70.2 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.24 mmol, 39.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and NaBARF (0.02 mmol, 17.7 mg) in $PhCF_3$ (4.0 mL) at 60 ^{o}C (60 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **5k** (52.1 mg, 71%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.7 Hz, 2H), 7.35 – 7.29 (m, 3H), 6.87 (s, 1H), 4.70 (s, 2H), 3.75 (q, *J* = 7.2 Hz, 1H), 2.42 (s, 3H), 2.37 (s, 3H), 2.31 (s, 3H), 1.41 (d, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 163.8, 146.1, 144.9, 138.6, 137.5, 135.7, 134.4, 133.5, 129.7, 129.3, 128.0, 119.3, 49.3, 41.6, 21.6, 21.1, 18.6, 14.7; IR (neat): 2923, 1730, 1597, 1443, 1360, 1170, 1123, 1089, 851, 665, 545; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{22}NO_3S$ 368.1315, found 368.1316.

8-ethyl-2-tosyl-1,8-dihydroindeno[1,2-*c*]pyrrol-3(2*H*)-one (5l)

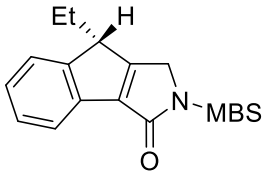


5l

The reaction was conducted with 4-methyl-*N*-(pent-2-yn-1-yl)-*N*-(phenylethynyl)benzenesulfonamide (**4l**, 0.2 mmol, 107.8 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.24 mmol, 39.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and NaBARF (0.02 mmol, 17.7 mg) in $PhCF_3$ (4.0 mL) at 60 ºC (60 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **5l** (56.5 mg, 80%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.6 Hz, 2H), 7.61 (d, *J* = 6.7 Hz, 1H), 7.41 (d, *J* = 6.4 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.29 – 7.22 (m, 2H), 4.76 (d, *J* = 5.5 Hz, 2H), 3.69 (t, *J* = 10.8 Hz, 1H), 2.42 (s, 3H), 2.09 – 2.00 (m, 1H), 1.83 – 1.74 (m, 1H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 163.5, 149.4, 145.0, 139.9, 135.6, 134.9, 129.8, 128.0, 127.4, 126.6, 123.8, 120.9, 50.2, 49.3, 23.7, 21.7, 11.1; IR (neat): 2931, 1728, 1597, 1458, 1360, 1170, 1133, 1091, 776, 671, 544; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{20}NO_3S$ 354.1158, found 354.1159.

8-ethyl-2-((4-methoxyphenyl)sulfonyl)-1,8-dihydroindeno[1,2-*c*]pyrrol-3(2*H*)-one (5m)



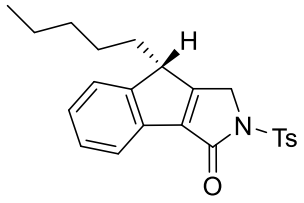
5m

The reaction was conducted with 4-methoxy-*N*-(pent-2-yn-1-yl)-*N*-(phenylethynyl)benzenesulfonamide (**4m**, 0.2 mmol, 70.6 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.24 mmol, 39.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and NaBARF (0.02 mmol, 17.7 mg) in $PhCF_3$ (4.0 mL) at 60 ºC (60 °C, heating

mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **5m** (53.2 mg, 72%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.7 Hz, 2H), 7.62 (d, *J* = 7.3 Hz, 1H), 7.42 (d, *J* = 6.9 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.01 (d, *J* = 7.8 Hz, 2H), 4.81 – 4.70 (m, 2H), 3.86 (s, 3H), 3.69 (t, 1H), 2.10 – 2.03 (m, 1H), 1.84 – 1.77 (m, 1H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 163.9, 163.5, 149.5, 139.9, 134.9, 130.3, 130.0, 127.3, 126.6, 123.8, 120.9, 114.3, 55.7, 50.1, 49.3, 23.7, 11.1; IR (neat): 2923, 1729, 1595, 1458, 1361, 1164, 1134, 1090, 835, 675, 587; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{20}NO_4S$ 370.1108, found 370.1107.

8-pentyl-2-tosyl-1,8-dihydroindeno[1,2-c]pyrrol-3(2H)-one (5n)



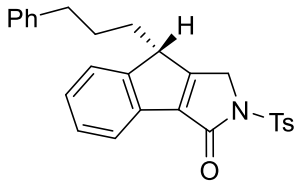
5n

The reaction was conducted with 4-methyl-*N*-(oct-2-yn-1-yl)-*N*-(phenylethynyl)benzenesulfonamide (**4n**, 0.2 mmol, 76.0 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.24 mmol, 39.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and NaBARF (0.02 mmol, 17.7 mg) in $PhCF_3$ (4.0 mL) at 60 ºC (60 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **5n** (58.6 mg, 74%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.5 Hz, 2H), 7.62 (d, *J* = 7.0 Hz, 1H), 7.41 (d, *J* = 6.9 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.29 – 7.26 (m, 2H), 4.81 – 4.70 (m, 2H), 3.73 – 3.70 (m, 1H), 2.43 (s, 3H), 2.01 – 1.94 (m, 1H), 1.74 – 1.68 (m, 1H), 1.31 (s, 6H), 0.94 – 0.83 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 163.5, 149.8, 145.0, 139.7, 135.6, 134.7, 129.8, 128.0, 127.3, 126.6, 123.8, 120.9, 50.2, 48.1, 31.8, 30.6, 26.6, 22.4, 21.7, 14.0; IR (neat): 2927, 1730, 1597, 1457, 1360, 1170,

1133, 1089, 777, 671, 544; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{26}NO_3S$ 396.1628, found 396.1629.

8-(3-phenylpropyl)-2-tosyl-1,8-dihydroindeno[1,2-*c*]pyrrol-3(2*H*)-one (5o)

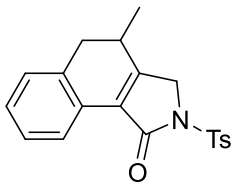


5o

The reaction was conducted with 4-methyl-*N*-(phenylethynyl)-*N*-(6-phenylhex-2-yn-1-yl)benzenesulfonamide (**4o**, 0.2 mmol, 85.6 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.24 mmol, 39.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and NaBARF (0.02 mmol, 17.7 mg) in $PhCF_3$ (4.0 mL) at 60 °C (60 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **5o** (46.2 mg, 52%) as a pale yellow oil.

^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 6.5 Hz, 2H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.30 – 7.13 (m, 8H), 7.05 (d, *J* = 6.3 Hz, 2H), 4.60 (s, 2H), 3.67 – 3.59 (m, 1H), 2.55 (t, *J* = 6.5 Hz, 2H), 2.34 (s, 3H), 1.96 – 1.88 (m, 1H), 1.73 – 1.65 (m, 1H), 1.61 – 1.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 163.4, 149.5, 145.0, 141.3, 139.8, 135.6, 134.7, 129.7, 128.5, 128.3, 128.0, 127.4, 126.6, 126.1, 123.8, 121.0, 50.1, 47.9, 35.7, 29.9, 28.4, 21.6; IR (neat): 2923, 1729, 1598, 1456, 1360, 1170, 1131, 1090, 777, 672, 588; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{27}H_{26}NO_3S$ 444.1628, found 444.1627.

4-methyl-2-tosyl-2,3,4,5-tetrahydro-1H-benzo[e]isoindol-1-one (5pa)

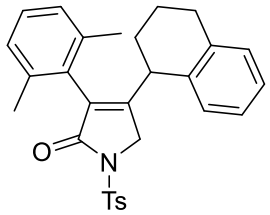


5pa

The reaction was conducted with *N*-(but-2-yn-1-yl)-4-methyl-*N*-(otolylethynyl) benzenesulfonamide (**4p**, 0.2 mmol, 67.4 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.24 mmol, 39.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and NaBARF (0.02 mmol, 17.7 mg) in $PhCF_3$ (4.0 mL) at 60 ^oC (60 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **5pa** (35.4 mg, 50%) as a pale yellow oil.

^1H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.00 (m, 3H), 7.34 (d, *J* = 6.0 Hz, 2H), 7.20 – 7.14 (m, 3H), 4.57 – 4.41 (m, 2H), 3.01 – 2.87 (m, 2H), 2.71 – 2.65 (m, 1H), 2.43 (s, 3H), 1.25 – 1.19 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 158.7, 145.0, 135.6, 134.1, 129.7, 128.6, 128.1, 127.9, 127.4, 127.2, 127.0, 123.7, 50.1, 36.0, 29.4, 21.7, 17.2; IR (neat): 2926, 1721, 1597, 1453, 1362, 1170, 1114, 1090, 783, 671, 587; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{20}NO_3S$ 354.1158, found 354.1160.

3-(2,6-dimethylphenyl)-4-(1,2,3,4-tetrahydronaphthalen-1-yl)-1-tosyl-1,5-dihydro-2*H*-pyrrol-2-one (5qa)



5qa

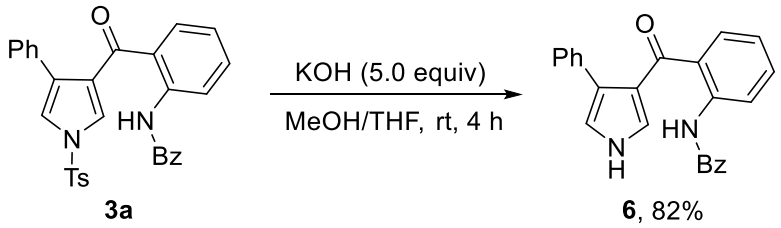
The reaction was conducted with *N*-((2,6-dimethylphenyl)ethynyl)-4-methyl-*N*-(6-phenylhex-2-yn-1-yl)benzenesulfonamide (**4q**, 0.2 mmol, 91.2 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.24 mmol, 39.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and NaBARF (0.02 mmol, 17.7 mg) in $PhCF_3$ (4.0 mL) at 60 ^oC (60 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **5qa** (59.6 mg, 65%) as a pale yellow oil.

^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.33 – 7.29 (m, 4H), 7.19 – 7.10 (m, 3H), 7.04 – 6.99 (m, 2H), 5.85 – 5.77 (m, 1H), 4.63 (s, 2H), 2.80 – 2.77 (m, 2H), 2.62 – 2.57 (m, 2H), 2.43 (s, 3H), 2.07 – 1.99 (m, 2H), 1.91 (s, 6H), 0.96 – 0.83 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 150.2, 145.0, 140.3, 139.7, 137.1, 135.5, 133.9, 129.6,

128.8, 128.6, 128.0, 127.4, 126.4, 121.0, 51.8, 35.3, 32.0, 21.7, 20.0; IR (neat): 2923, 1721, 1596, 1454, 1362, 1171, 1031, 1052, 775, 655, 585; HRMS (ESI) m/z: [M + H]+ calcd for $C_{29}H_{30}NO_3S$ 472.1941, found 472.1944.

Synthetic Applications

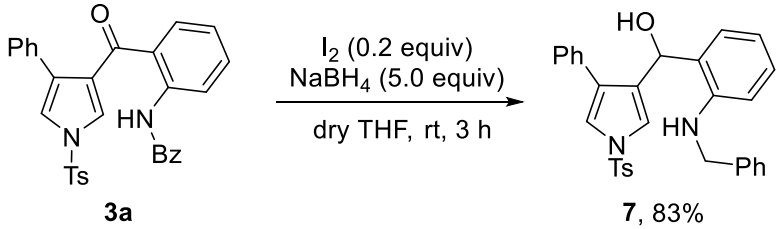
N-(2-(4-phenyl-1*H*-pyrrole-3-carbonyl)phenyl)benzamide (6)



3a **6**, 82%

KOH (1.0 mmol, 56.0 mg) was added to a solution of compound **3a** (0.2 mmol, 73.2 mg) in MeOH/THF (2.0 ml/2.0 ml) at room temperature. The reaction mixture was stirred at 80 ^{o}C (80 °C, heating mantle 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** (60.0 mg, 82% yield, yellow oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.74 (s, 1H), 8.91 (s, 1H), 8.71 (d, *J* = 6.7 Hz, 1H), 7.98 (d, *J* = 6.0 Hz, 2H), 7.80 (d, *J* = 6.9 Hz, 1H), 7.56 – 7.43 (m, 4H), 7.37 – 7.23 (m, 5H), 7.05 – 6.99 (m, 2H), 6.91 – 6.87 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 166.2, 139.7, 134.4, 134.3, 133.4, 133.2, 132.0, 128.7, 128.3(2), 128.2(5), 127.5, 127.1, 126.9, 126.5, 126.3, 122.7, 122.4, 121.5, 118.8; IR (neat): 3278 (br), 2920, 1661, 1600, 1580, 1510, 1492, 1448, 1436, 1383, 1307, 1293, 756, 696; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{19}N_2O_2$ 367.1441, found 367.1440.

(2-(benzylamino)phenyl)(4-phenyl-1-tosyl-1*H*-pyrrol-3-yl)methanol (7)

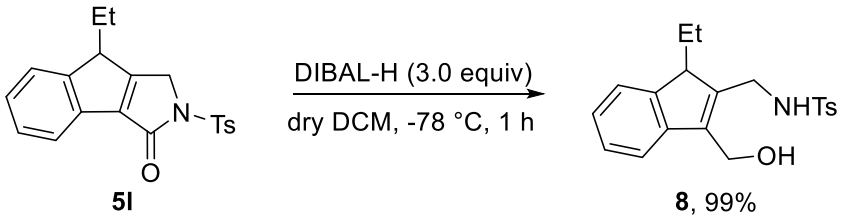


3a **7**, 83%

To a mixture of I_2 (0.04 mmol, 10.2 mg), and $NaBH_4$ (1.0 mmol, 38.0 mg) was added to a solution of the compound **3a** (0.2 mmol, 73.2 mg) in dry THF (4.0 mL) at room

temperature. 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** (84.5 mg, 83% yield, yellow oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.30 – 7.10 (m, 17H), 6.97 (d, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 7.9 Hz, 2H), 5.84 (s, 1H), 4.25 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 145.2, 139.3, 135.8, 133.2, 130.0, 129.2, 129.1, 128.5, 128.3, 127.6, 127.3, 127.0(4), 126.9(9), 126.0, 120.0, 118.6, 116.8, 111.6, 68.2, 47.7, 21.6; IR (neat): 3527 (br), 3405 (br), 2923, 1603, 1584, 1518, 1452, 1371, 1318, 1188, 1172, 1090, 1067, 966, 671; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{29}N_2O_3S$ 509.1893, found 509.1892.

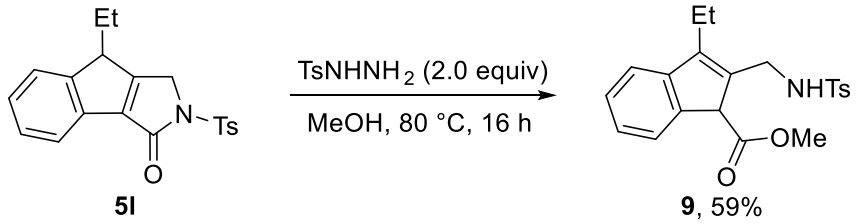
_N_-((1-ethyl-3-(hydroxymethyl)-1_H_-inden-2-yl)methyl)-4-methylbenzenesulfonamide (8)



5l **8**, 99%

DIBAL-H (0.6 mmol, 0.6 mL, 1.0 M) was added dropwise to a solution of compound **5l** (0.2 mmol, 71.4 mg) in dry DCM (4.0 mL) at -78 ^{o}C. The reaction mixture was stirred at -78 ^{o}C 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** (70.7 mg, 99% yield, yellow oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.31 (m, 2H), 7.26 – 7.17 (m, 4H), 5.32 – 5.27 (m, 1H), 4.63 – 4.54 (m, 2H), 4.10 – 4.06 (m, 1H), 3.81 – 3.75 (m, 1H), 3.33 (t, *J* = 5.0 Hz, 1H), 2.39 (s, 3H), 2.01 – 1.95 (m, 1H), 1.74 – 1.67 (m, 2H), 0.50 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 143.5, 143.3, 142.0, 140.0, 136.7, 129.7, 127.1, 126.5, 125.4, 123.0, 119.4, 56.3, 50.5, 39.0, 22.2, 21.5, 8.7; IR (neat): 3480 (br), 3276 (br), 2927, 1721, 1598, 1459, 1324, 1289, 1158, 1093, 814, 661, 550; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{20}H_{23}NNaO_3S$ 380.1291, found 380.1292.

methyl 1-ethyl-2-(((4-methylphenyl)sulfonamido)methyl)-1*H*-indene-3-carboxylate (9)



$TsNHNH_2$ (0.4 mmol, 74.4 mg) was added dropwise to a solution of compound **5l** (0.2 mmol, 71.4 mg) in MeOH (4.0 mL) at room temperature. The reaction mixture was stirred at 80 °C 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 **9** (45.4 mg, 59% yield) as a yellow solid (mp 141-143 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.8 Hz, 2H), 7.49 (d, *J* = 7.4 Hz, 1H), 7.34 – 7.26 (m, 4H), 7.20 (t, *J* = 7.3 Hz, 1H), 5.12 – 5.09 (m, 1H), 4.22 (s, 1H), 4.08 – 4.03 (m, 1H), 3.96 – 3.89 (m, 1H), 3.70 (s, 3H), 2.52 (q, *J* = 7.6 Hz, 2H), 2.40 (s, 3H), 1.14 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 146.6, 144.2, 143.4, 140.1, 136.8, 132.5, 129.6, 127.7, 127.2, 125.8, 123.9, 119.7, 55.4, 52.6, 39.9, 21.5, 18.6, 13.4; IR (neat): 3285 (br), 2922, 1731, 1598, 1434, 1326, 1160, 1092, 1062, 814, 734, 662; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{24}NO_4S$ 386.1421, found 386.1422.

Reference

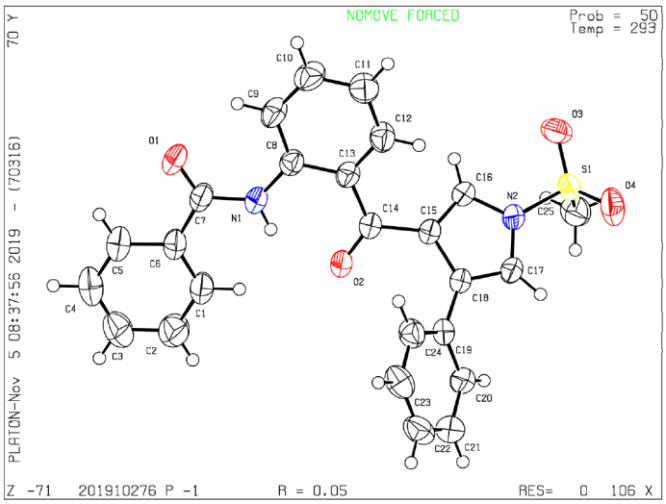
(1) G. Evindar, R. A. Batey, *J. Org. Chem.* 2006, **71**, 1802-1808.

(2) W.-B. Shen, X.-T. Tang, T.-T. Zhang, S.-Y. Liu, J.-M. He, T.-F. Su, *Org. Lett.* 2020, **22**, 6799-6804.

(3) E. Benedetti, A. Simonneau, A. Hours, H. Amouri, A. Penoni, G. Palmisano, M. Malacria, J.-P. Goddard, L. Fensterbank, *Adv. Synth. & Catal.* 2011, **353**, 1908-1912.

***N*-(2-(1-(methylsulfonyl)-4-phenyl-1*H*-pyrrole-3-carbonyl)phenyl)benzamide (3d). CCDC Number = 2049243**

Crystal of **3d** was grown by slow evaporation of hexane/ethyl acetate solution of **3d** 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.



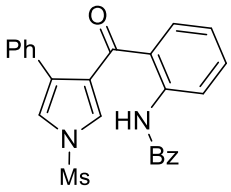


Figure S1. Crystal structure of **3d** with thermal ellipsoids at 50% probability

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

Cell:          a=8.9146(9)       b=11.2178(9)      c=11.8266(7)
               alpha=79.648(6)   beta=70.259(8)    gamma=85.201(7)
Temperature:   293 K

                Calculated                Reported
Volume          1094.72(17)               1094.72(16)
Space group     P -1                      P -1
Hall group      -P 1                      -P 1
Moiety formula  C25 H20 N2 O4 S           C25 H20 N2 O4 S
Sum formula     C25 H20 N2 O4 S           C25 H20 N2 O4 S
Mr              444.49                    444.49
Dx,g cm-3       1.349                     1.348
Z               2                         2
Mu (mm-1)       1.606                     1.606
F000            464.0                     464.0
F000'           466.02
h,k,lmax        10,13,14                  10,13,14
Nref            3917                      3915
Tmin,Tmax       0.825,0.865               0.897,1.000
Tmin'           0.786

Correction method= # Reported T Limits: Tmin=0.897 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.999          Theta(max)= 67.071

R(reflections)= 0.0473( 2885)     wR2(reflections)= 0.1299( 3915)

S = 1.008                 Npar= 290
```

8-methyl-2-tosyl-1,8-dihydroindeno[1,2-*c*]pyrrol-3(2*H*)-one (5a). CCDC Number = 2086108

Crystal of **5a** was grown by slow evaporation of hexane/dichloromethane solution of **5a** 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.

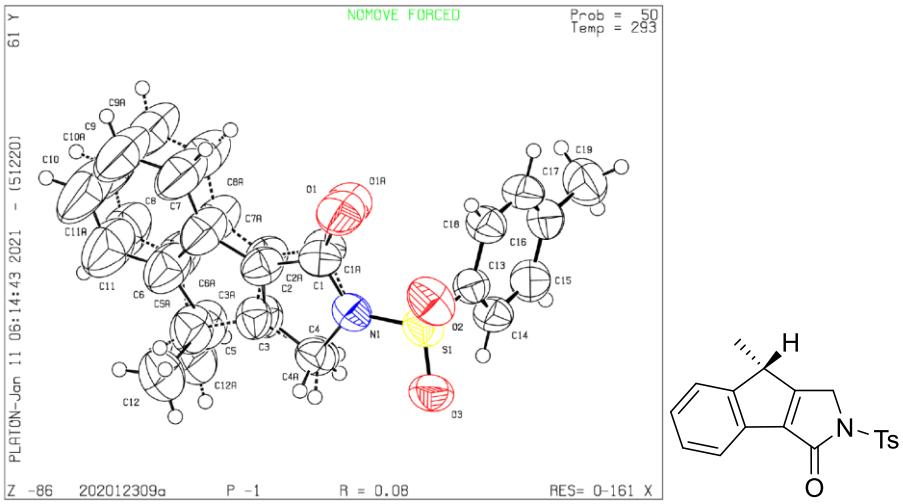


Figure S2. Crystal structure of **5a** with thermal ellipsoids at 50% probability

Bond precision: C-C = 0.0053 A		Wavelength=1.54184
Cell:	a=6.0727(4)	b=12.1141(8) c=12.8850(7)
	alpha=86.689(5)	beta=84.600(5) gamma=79.238(6)
Temperature:	293 K	
	Calculated	Reported
Volume	926.30(10)	926.29(10)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C19 H17 N O3 S [+ solvent]	C19 H17 N O3 S
Sum formula	C19 H17 N O3 S [+ solvent]	C19 H17 N O3 S
Mr	339.40	339.39
Dx,g cm-3	1.217	1.217
Z	2	2
Mu (mm-1)	1.679	1.679
F000	356.0	356.0
F000'	357.67	
h,k,lmax	7,14,15	7,14,15
Nref	3321	3305
Tmin,Tmax	0.785,0.845	0.908,1.000
Tmin'	0.764	

Correction method= # Reported T Limits: Tmin=0.908 Tmax=1.000
AbsCorr = MULTI-SCAN

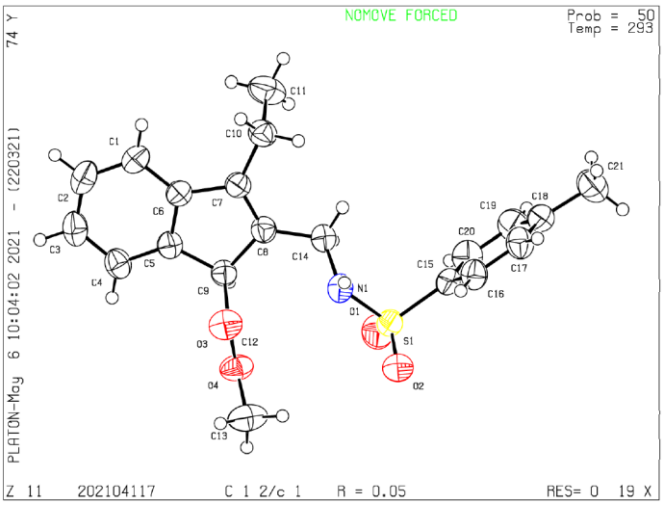
Data completeness= 0.995 Theta(max)= 67.031

R(reflections)= 0.0754(2536) wR2(reflections)= 0.2533(3305)

S = 1.056 Npar= 236

methyl 1-ethyl-2-(((4-methylphenyl)sulfonamido)methyl)-1*H*-indene-3-carboxylate (9). CCDC Number = 2086109

Crystal of **9** was grown by slow evaporation of hexane/dichloromethane solution of **9** 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.



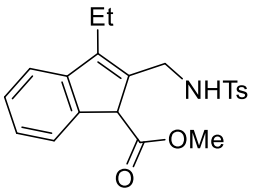


Figure S3. Crystal structure of **9** with thermal ellipsoids at 50% probability

Bond precision: C-C = 0.0034 A		Wavelength=1.54184	
Cell:	a=17.8847(4)	b=9.00834(19)	c=25.4932(6)
	alpha=90	beta=106.905(2)	gamma=90
Temperature:	293 K		

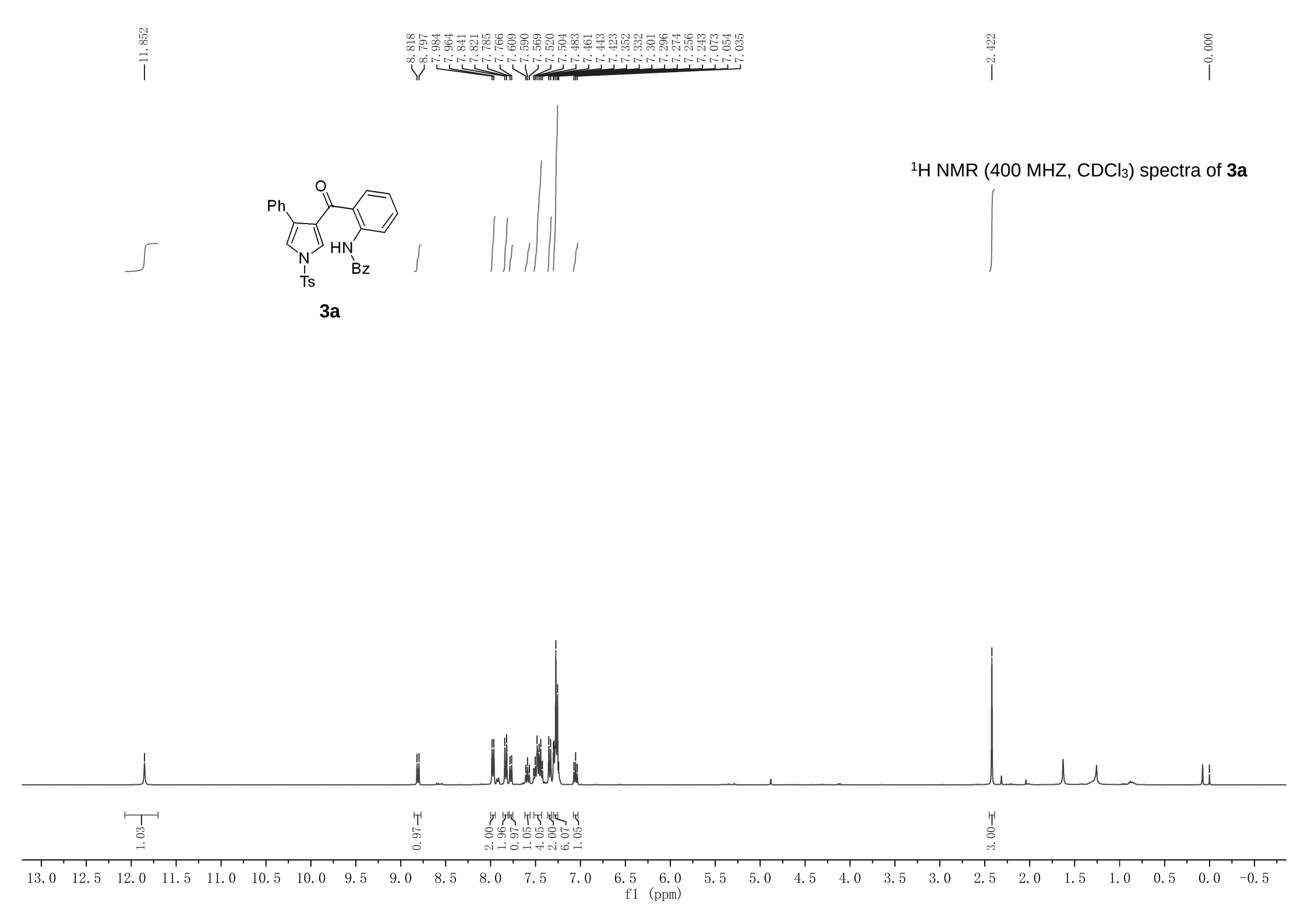
	Calculated	Reported
Volume	3929.77(16)	3929.75(15)
Space group	C 2/c	C 1 2/c 1
Hall group	-C 2yc	-C 2yc
Moiety formula	C21 H23 N O4 S	C21 H23 N O4 S
Sum formula	C21 H23 N O4 S	C21 H23 N O4 S
Mr	385.46	385.46
Dx,g cm-3	1.303	1.303
Z	8	8
Mu (mm-1)	1.682	1.682
F000	1632.0	1632.0
F000'	1639.34	
h,k,lmax	21,11,31	21,10,31
Nref	3777	3716
Tmin,Tmax	0.817,0.889	0.966,1.000
Tmin'	0.790	

Correction method= # Reported T Limits: Tmin=0.966 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.984 Theta(max)= 70.708

R(reflections)= 0.0490(3116) wR2(reflections)= 0.1477(3716)

S = 1.036 Npar= 251

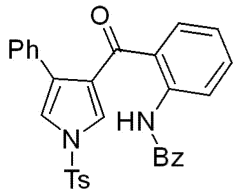


3a

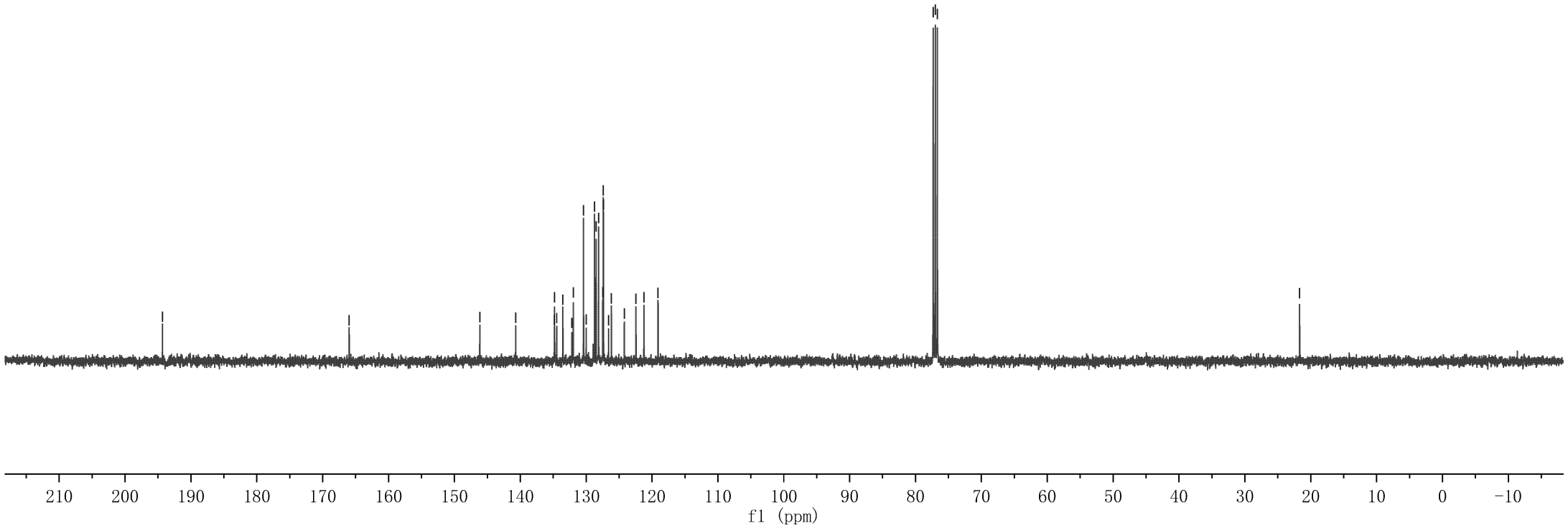
^{1}H NMR (400 MHZ, $CDCl_3$) spectra of **3a**

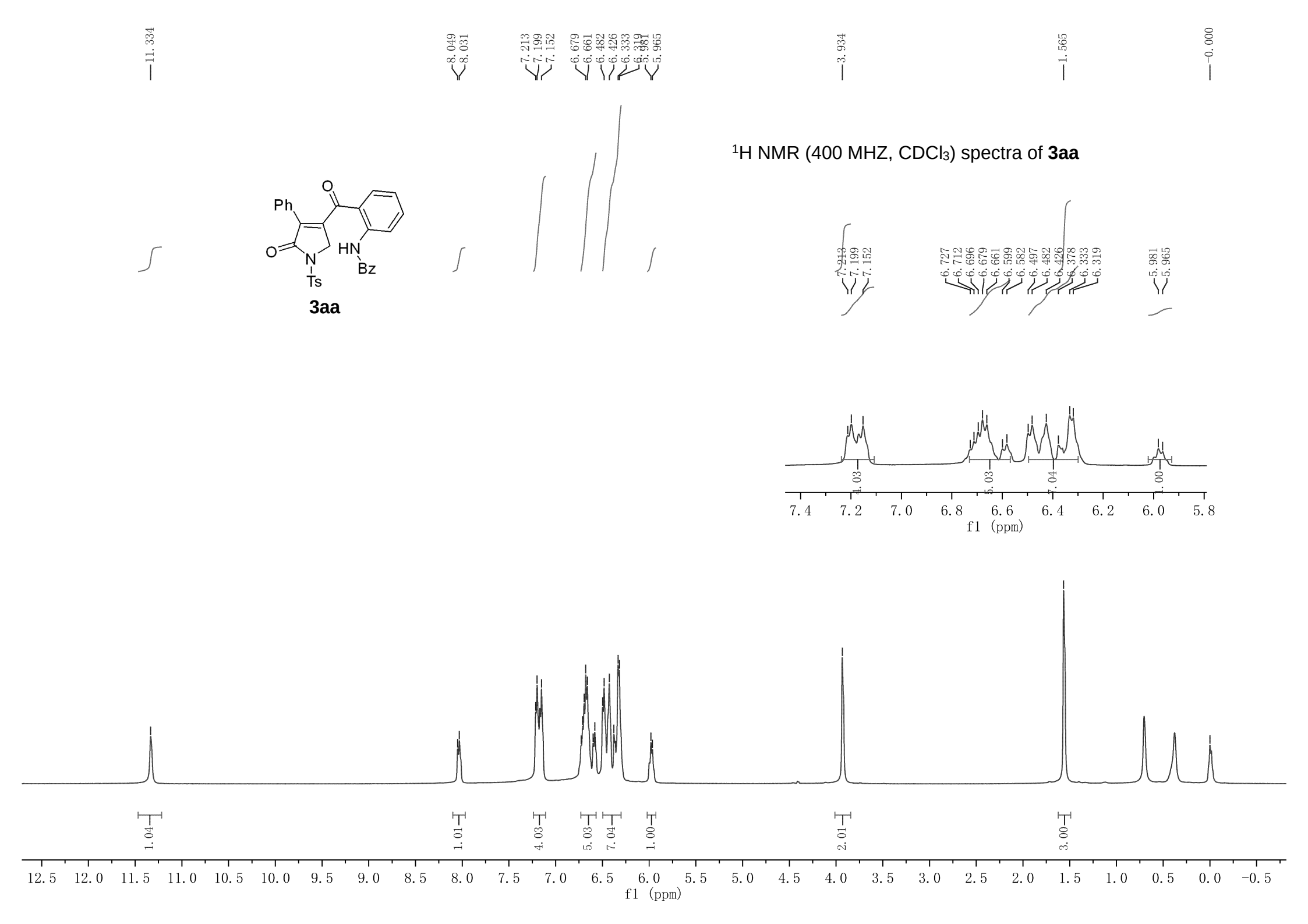
194.32
165.97
146.15
140.70
134.84
134.80
134.47
133.53
132.18
131.95
130.40
129.98
128.72
128.48
128.11
127.49
127.41
127.38
126.60
126.17
124.21
122.44
121.23
119.08
77.32
77.00
76.68
21.69

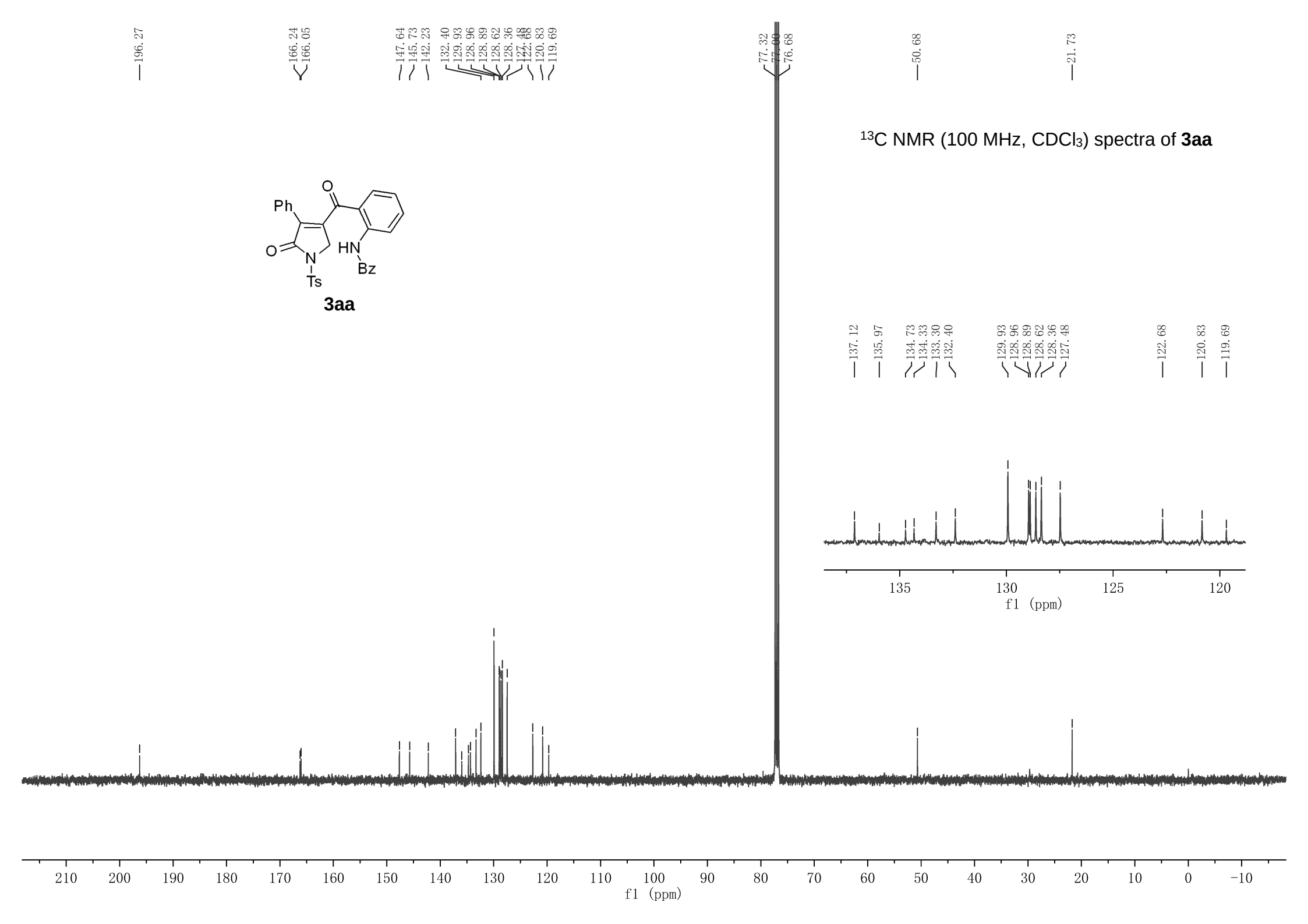
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3a**



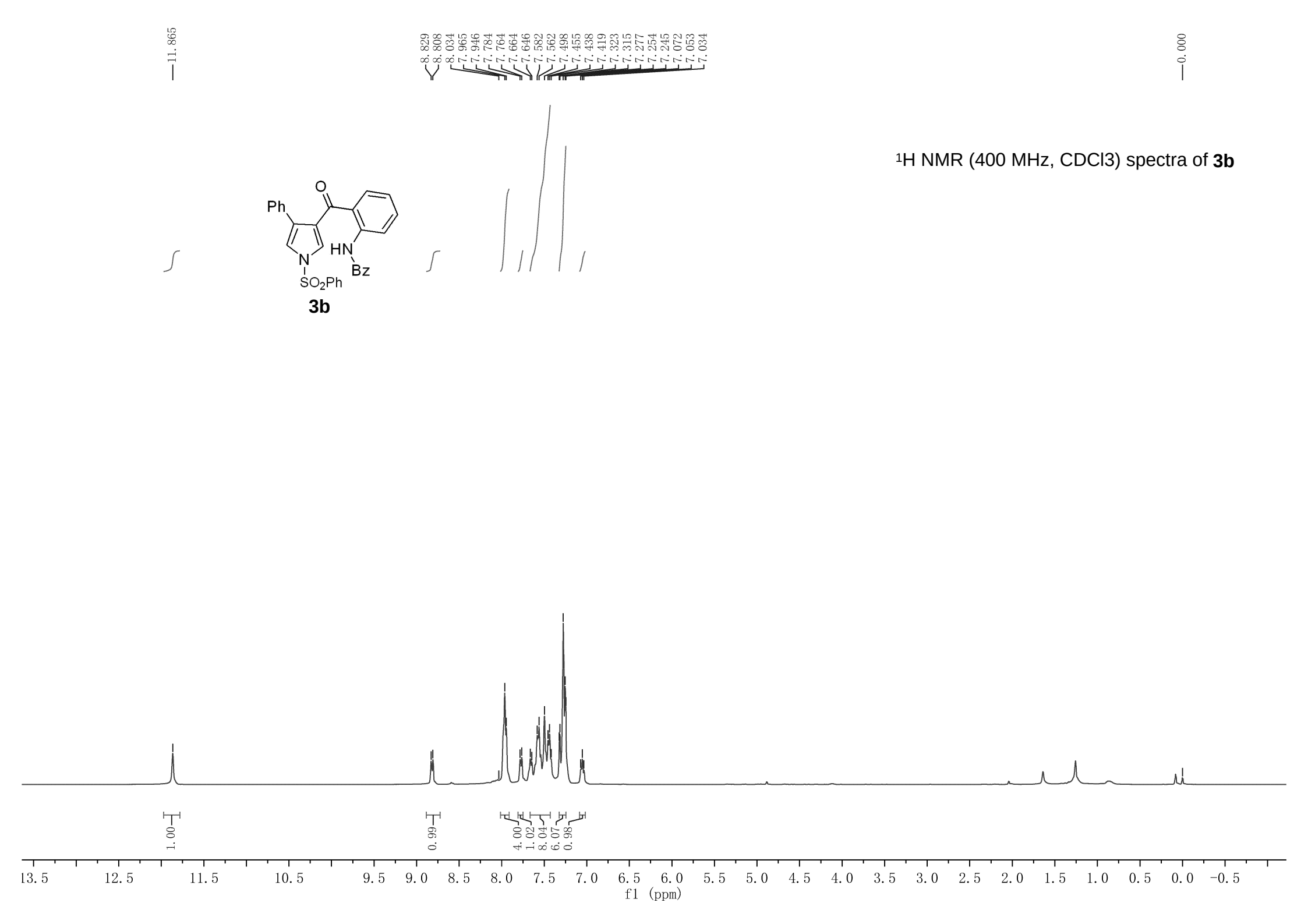
3a




11.334
8.049
8.031
7.213
7.199
7.152
6.679
6.661
6.482
6.426
6.333
6.319
5.981
5.965
3.934
1.565
0.000
Ph
O
O
N
Ts
HN
Bz
3aa
1H NMR (400 MHZ, CDCl3) spectra of 3aa
7.213
7.199
7.152
6.727
6.712
6.696
6.679
6.661
6.599
6.582
6.497
6.482
6.426
6.378
6.333
6.319
5.981
5.965
4.03
5.03
7.04
1.00
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
f1 (ppm)
1.04
1.01
4.03
5.03
7.04
1.00
2.01
3.00
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3aa**

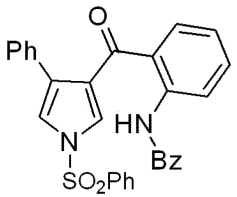


3b

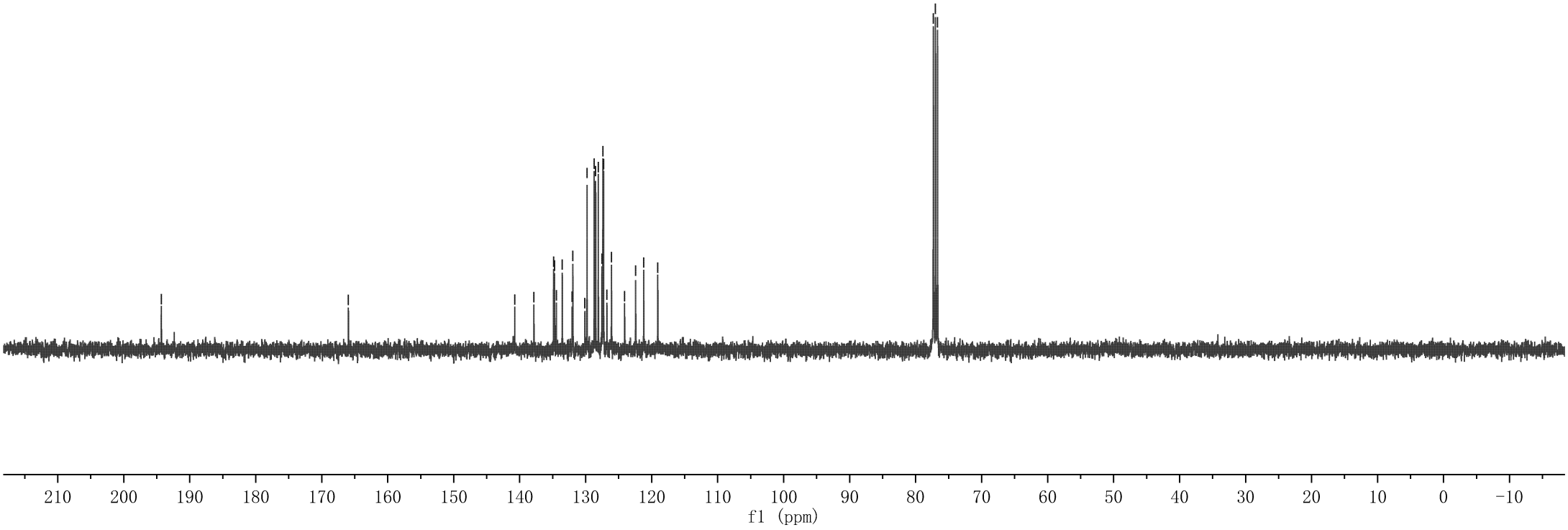
^{1}H NMR (400 MHz, CDCl3) spectra of **3b**

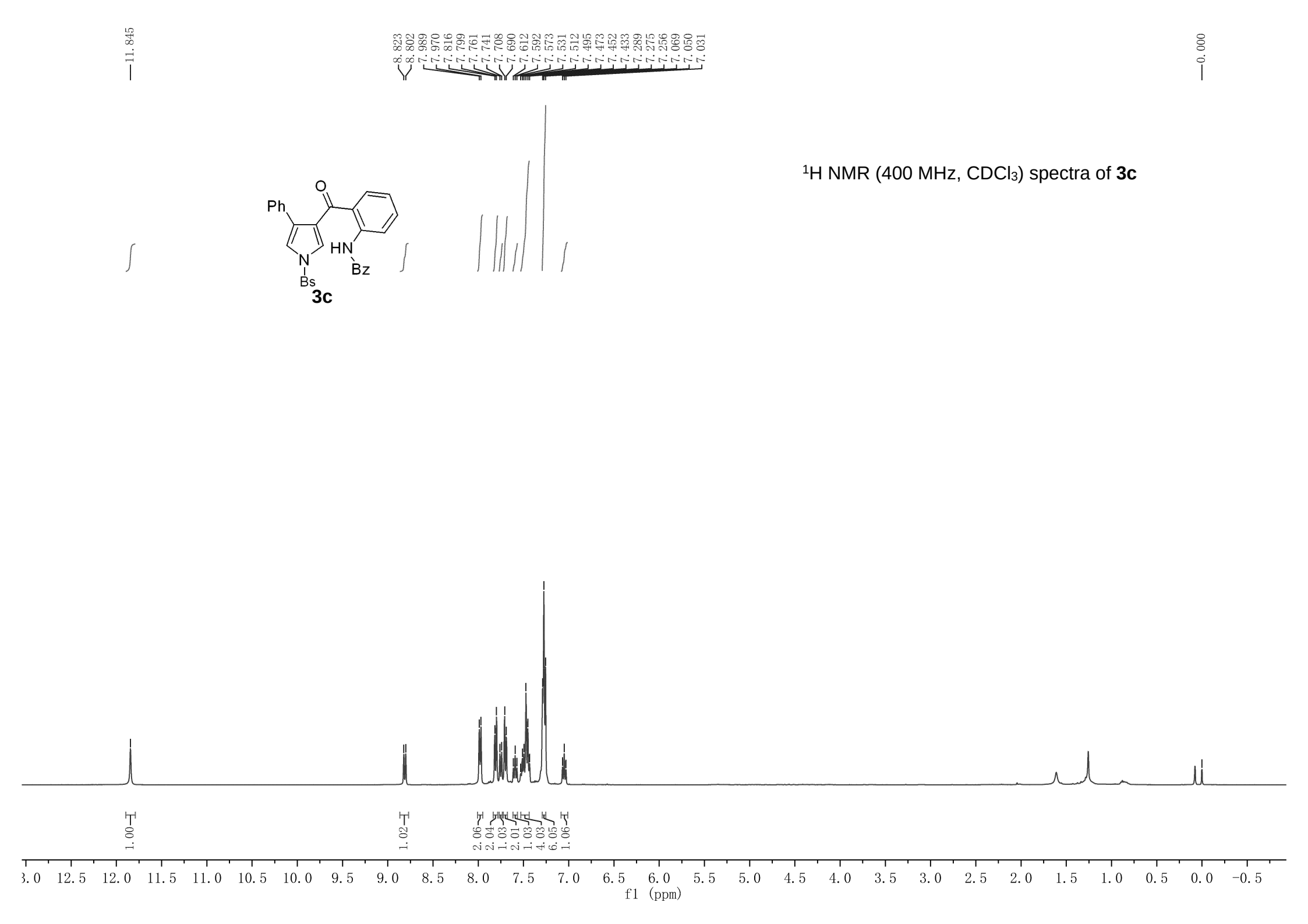
194.31
165.96
140.75
137.85
134.86
134.72
134.44
133.55
132.06
131.95
130.13
129.80
128.71
128.49
128.09
127.54
127.40
127.29
126.78
126.09
124.10
122.43
121.21
119.08
77.32
77.00
76.68

^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3b**



3b

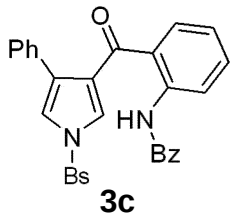




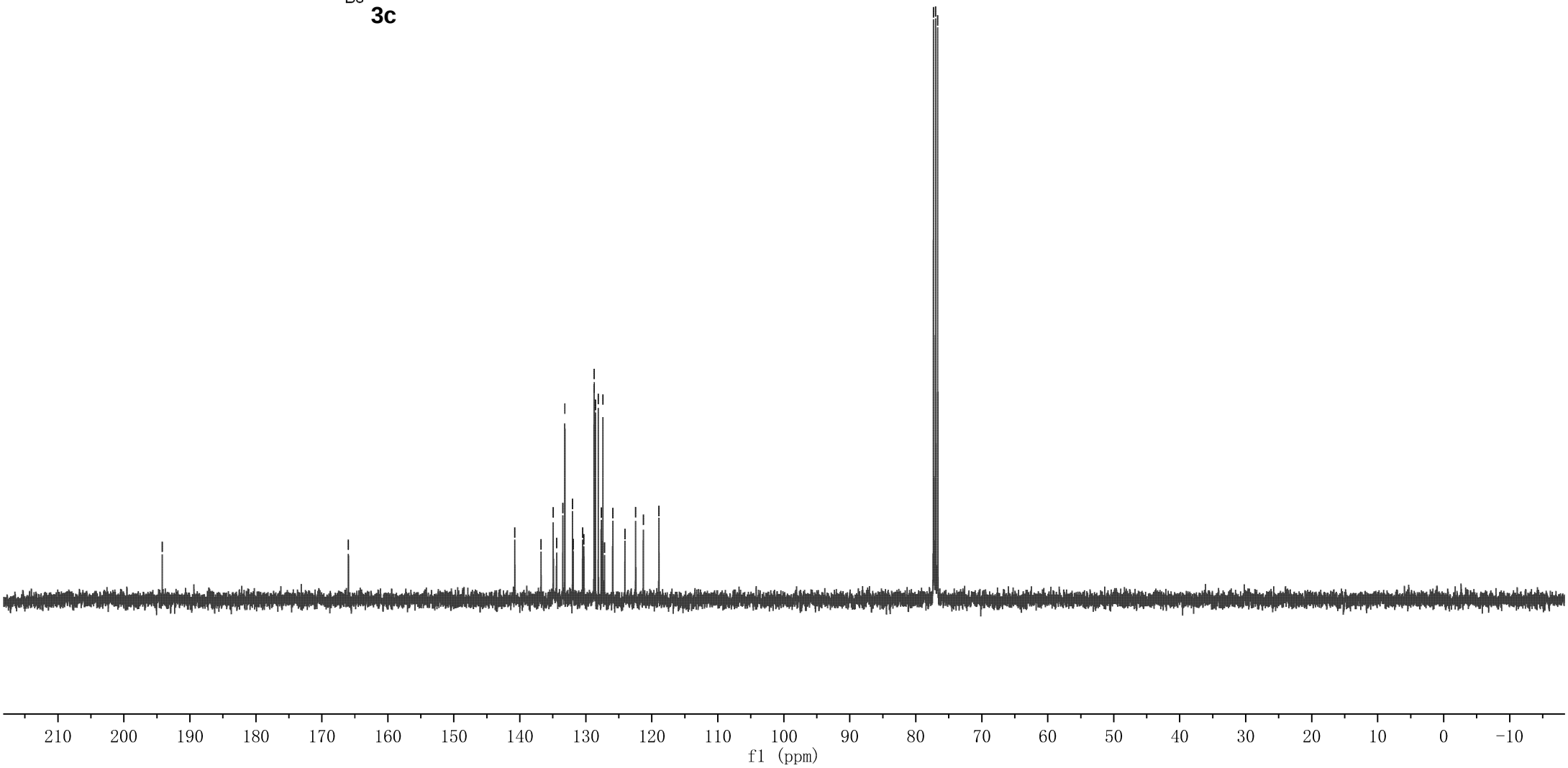
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3c**

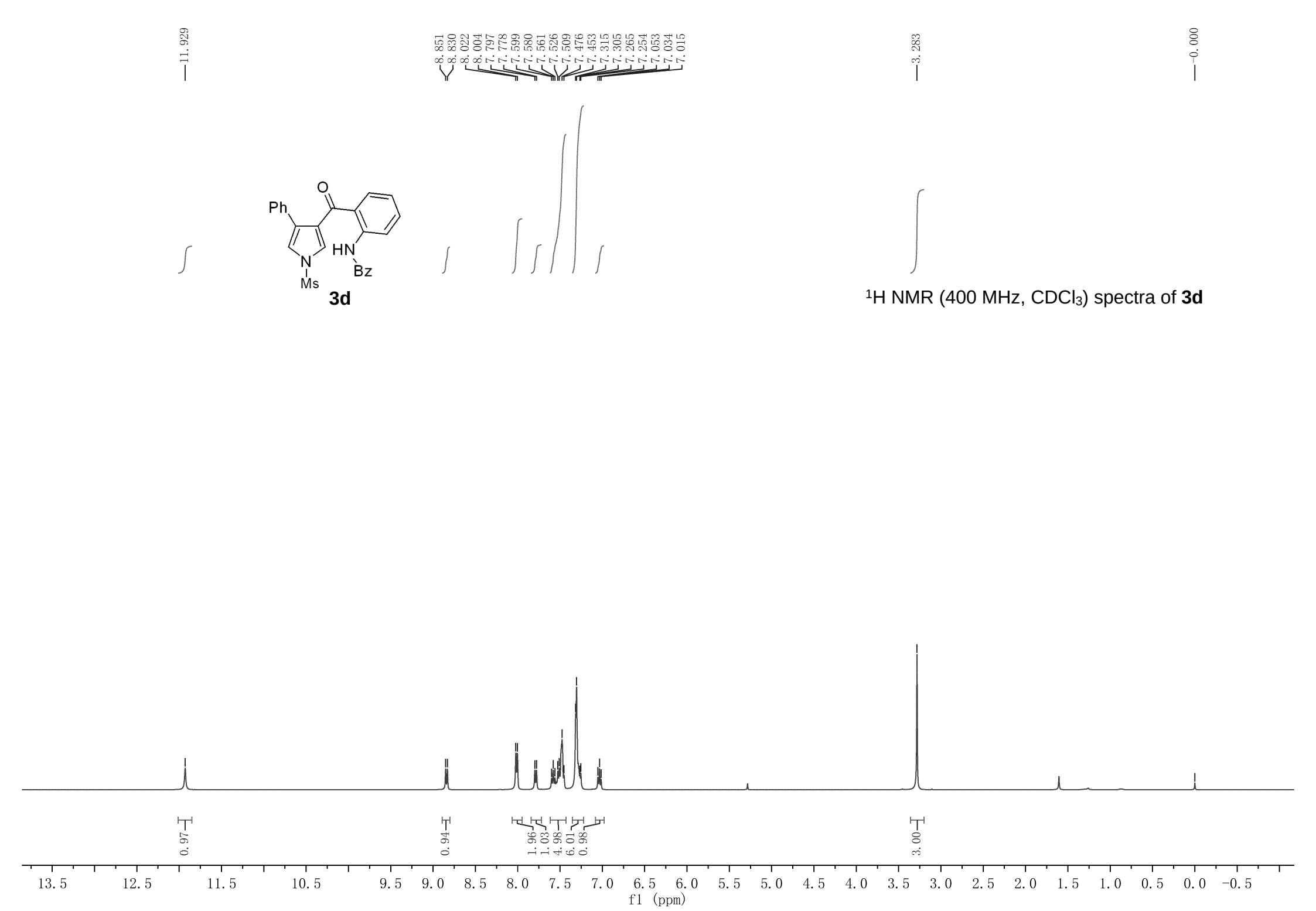
194.18
165.98
140.76
136.78
134.94
134.43
133.49
133.18
132.00
131.91
130.49
130.29
128.75
128.72
128.53
128.11
127.67
127.41
127.17
125.92
124.07
122.45
121.28
118.92
77.32
77.00
76.68

^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3c**



3c

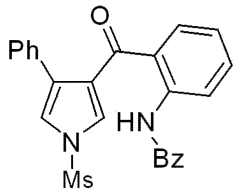




3d

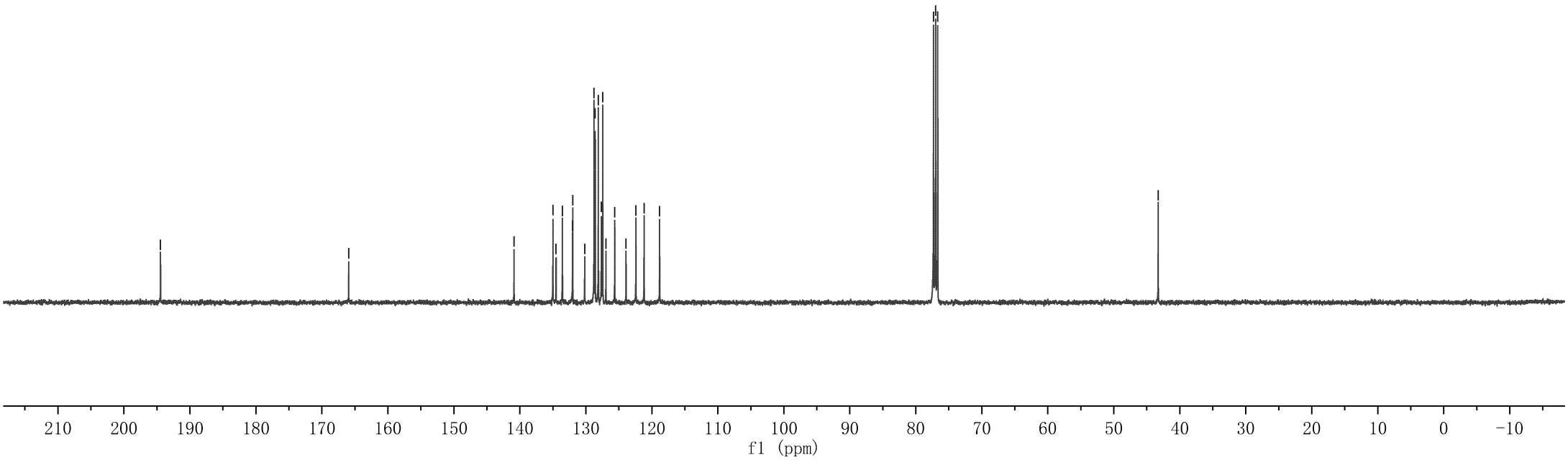
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3d**

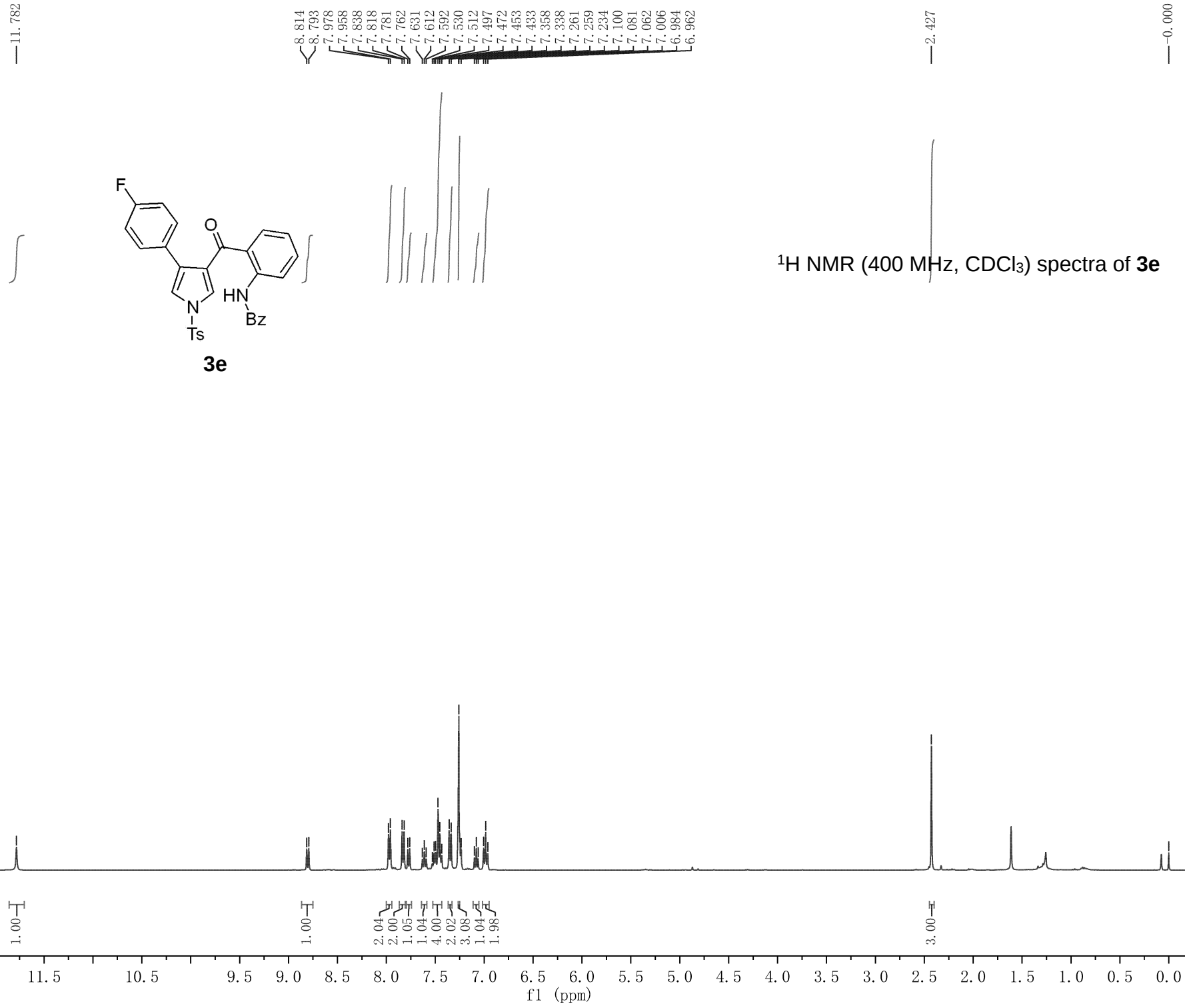
194.46
165.94
140.88
134.99
134.52
133.55
132.02
131.99
130.18
128.76
128.59
128.12
127.66
127.44
126.96
125.62
123.91
122.42
121.18
118.83
77.32
77.00
76.68
43.27



3d

^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3d**



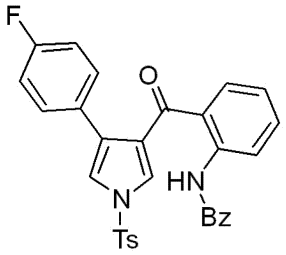


3e

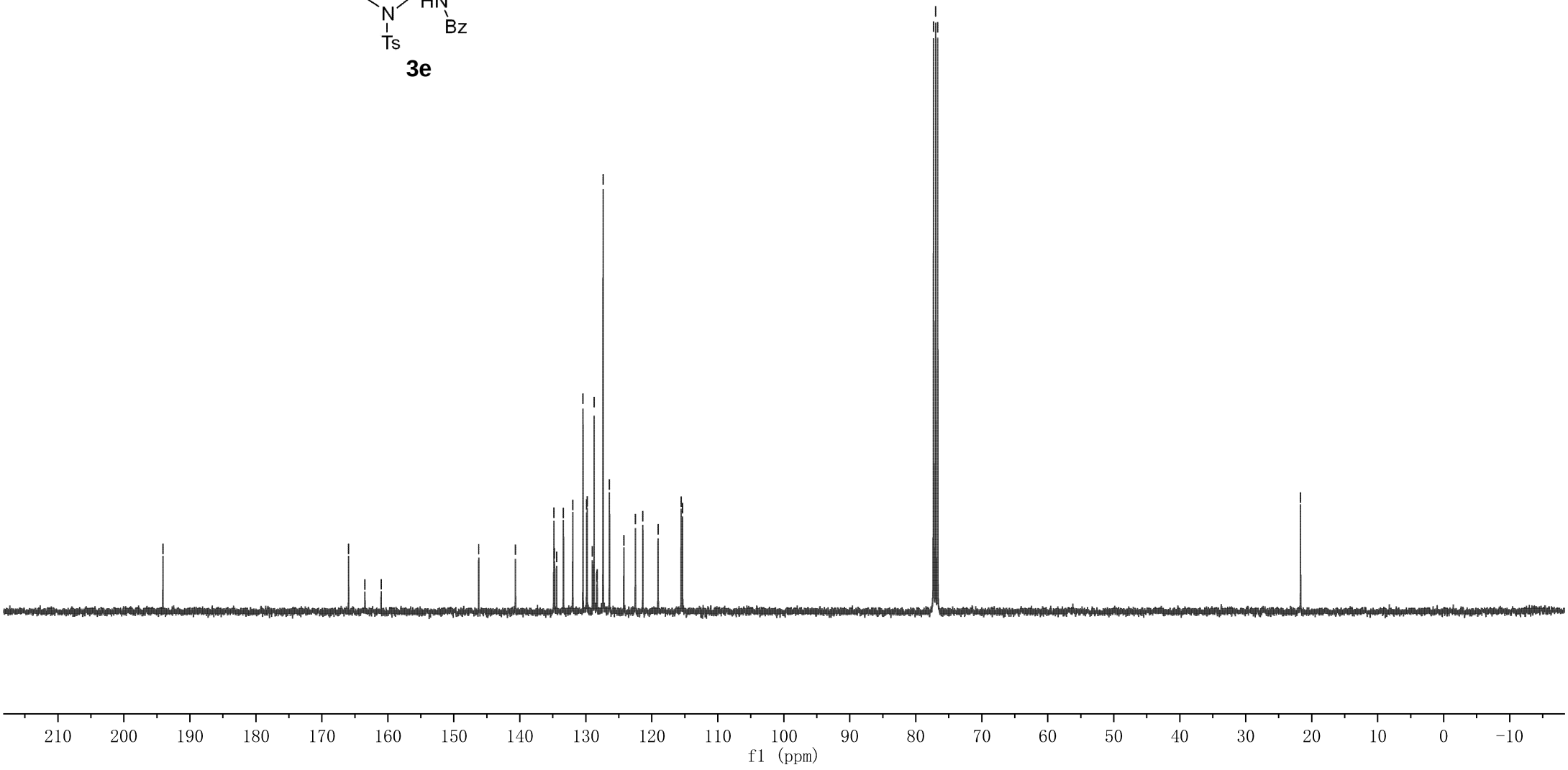
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3e**

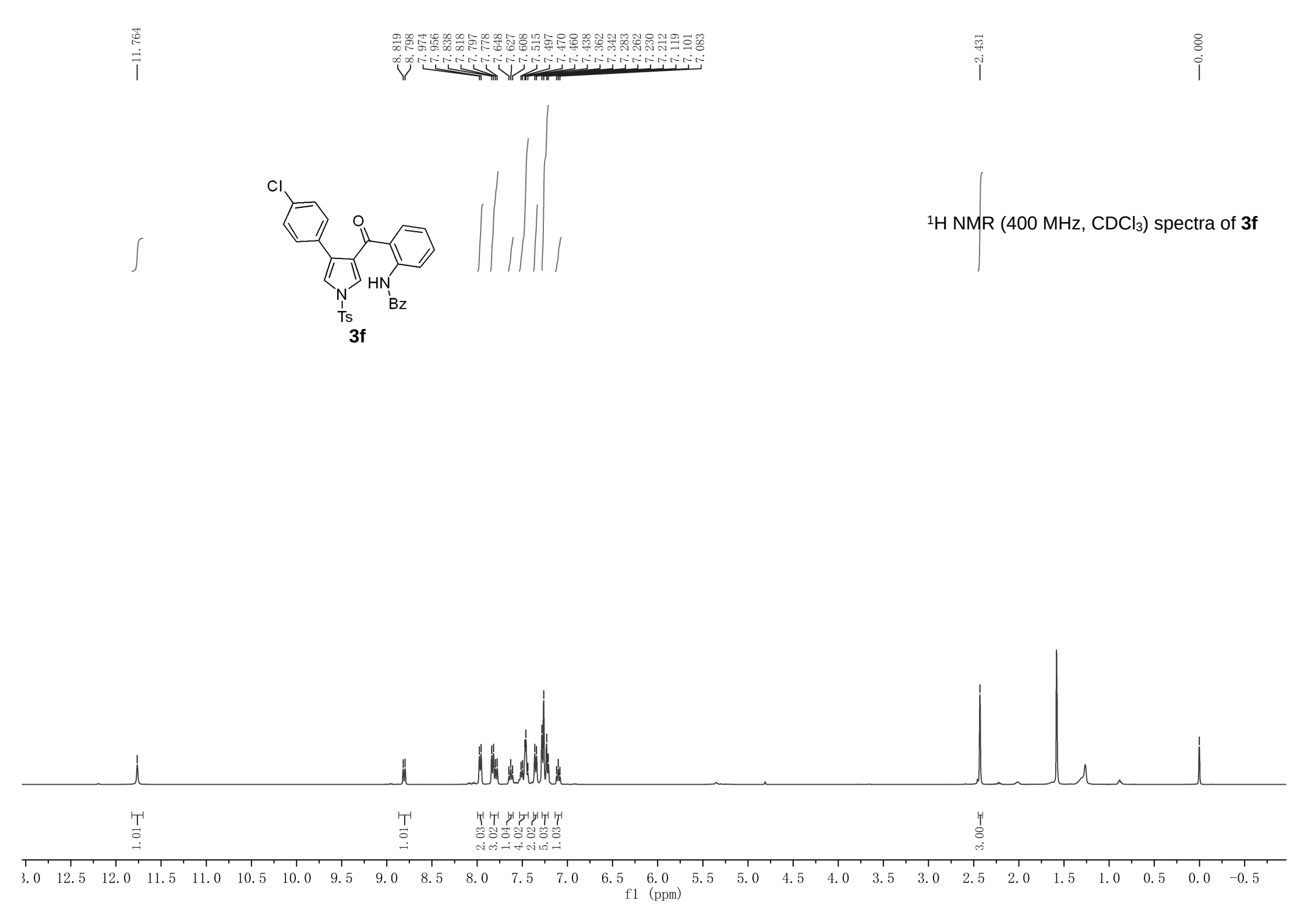
194.09
165.95
163.47
161.02
146.23
140.66
134.85
134.76
134.44
133.40
131.99
130.43
129.87
129.79
129.00
128.74
128.30
128.27
127.39
126.42
124.25
122.49
121.36
119.05
115.56
115.34
77.32
77.00
76.68
21.70

^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3e**

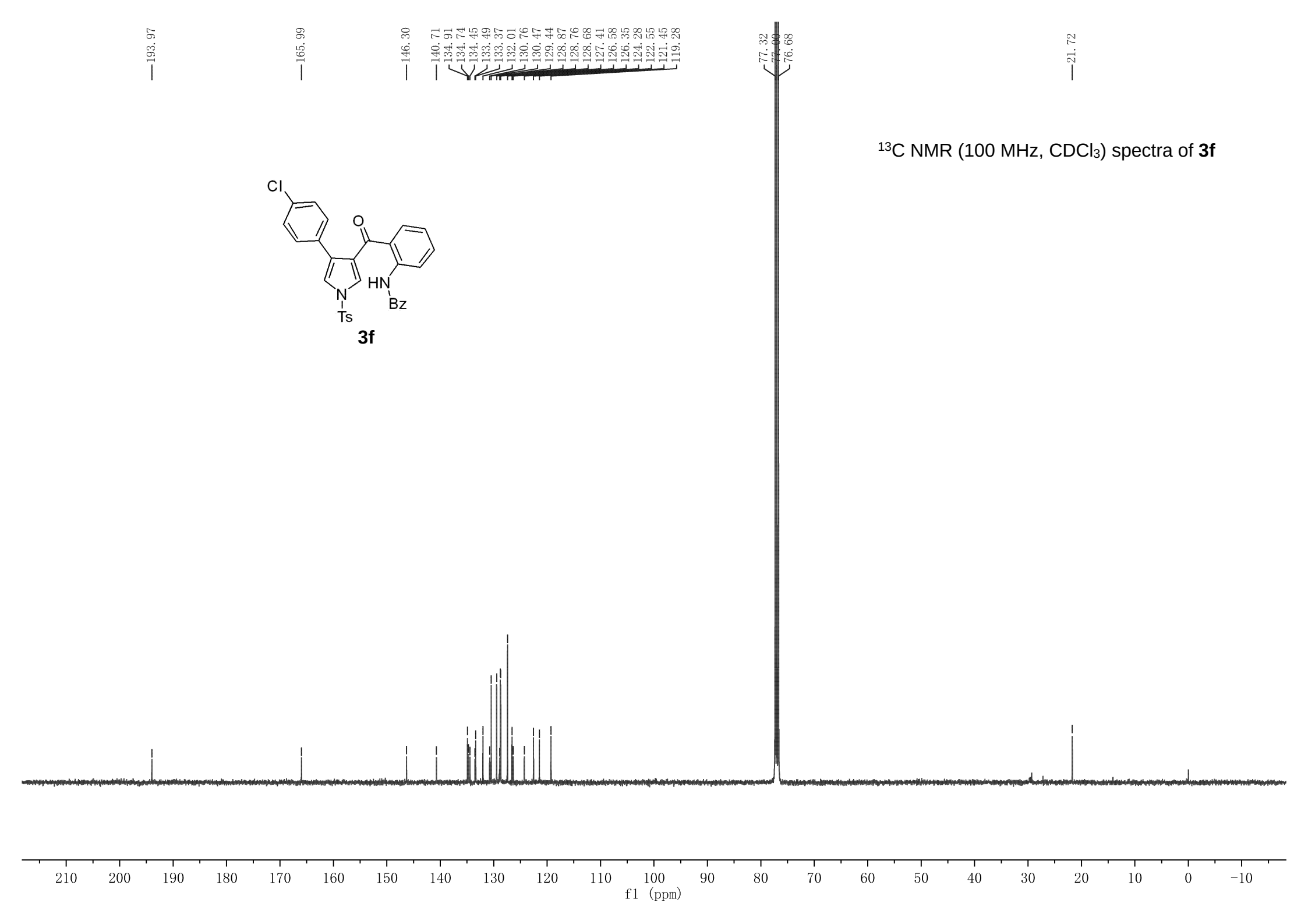


3e

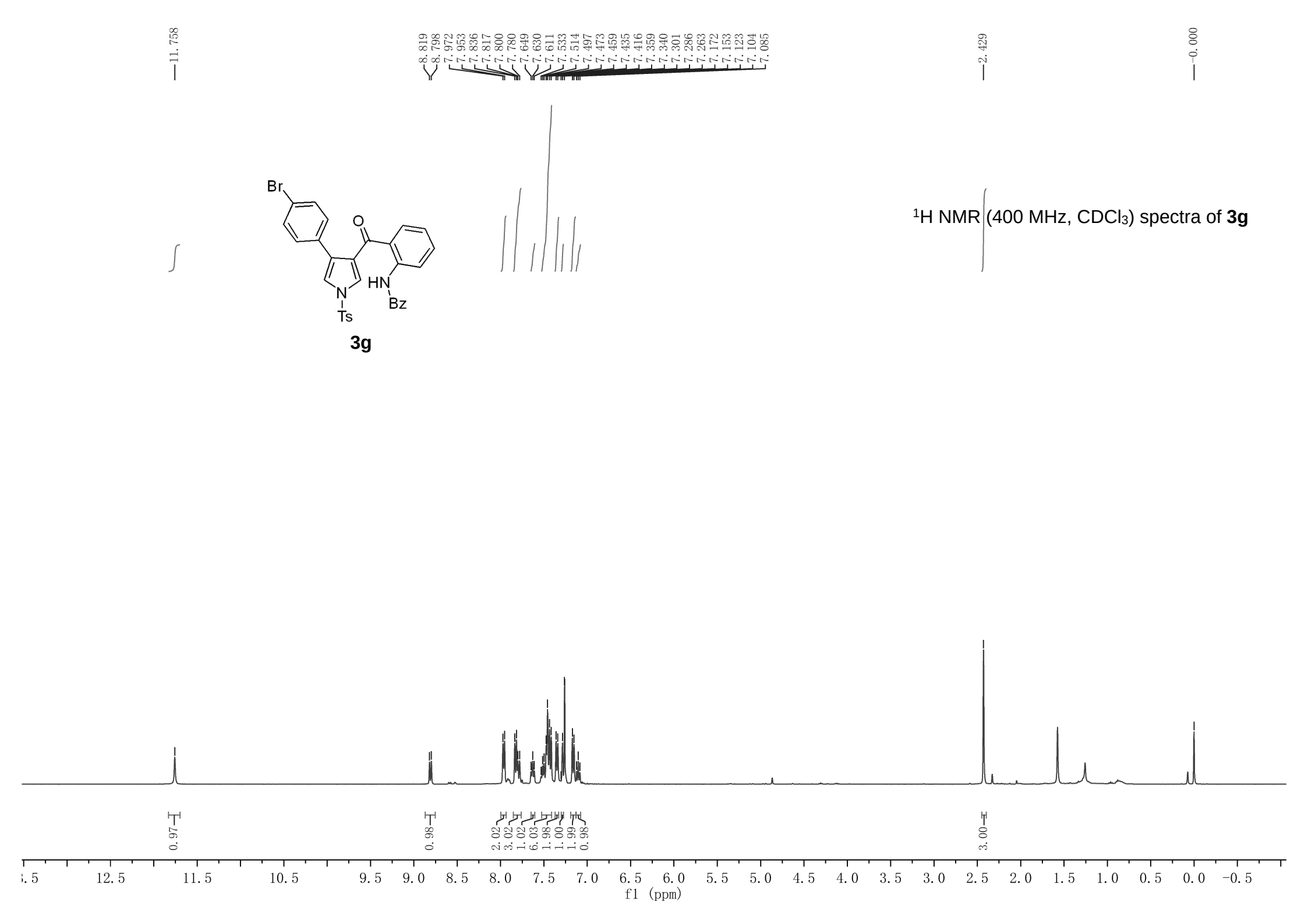




^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3f**

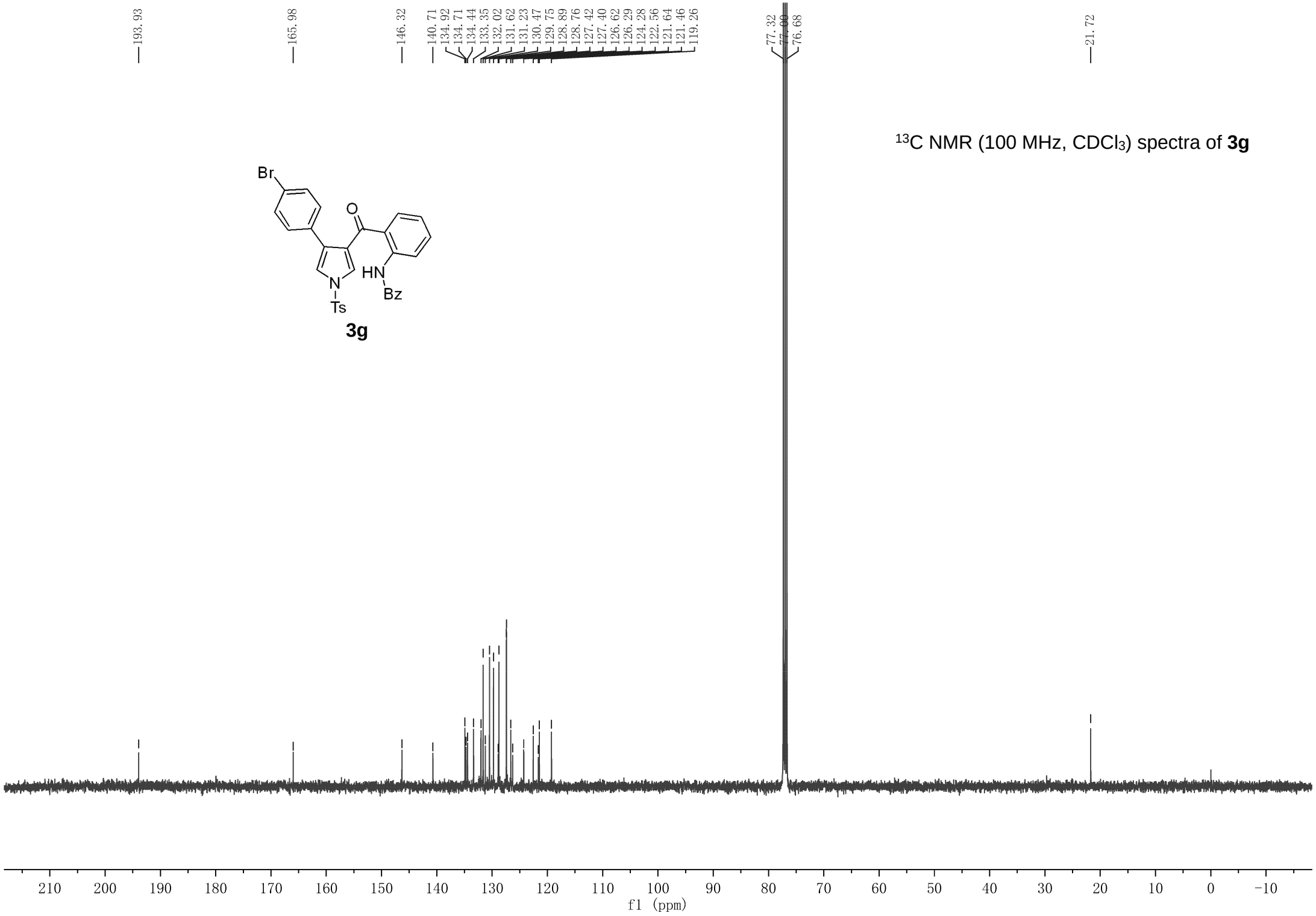


^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3f**

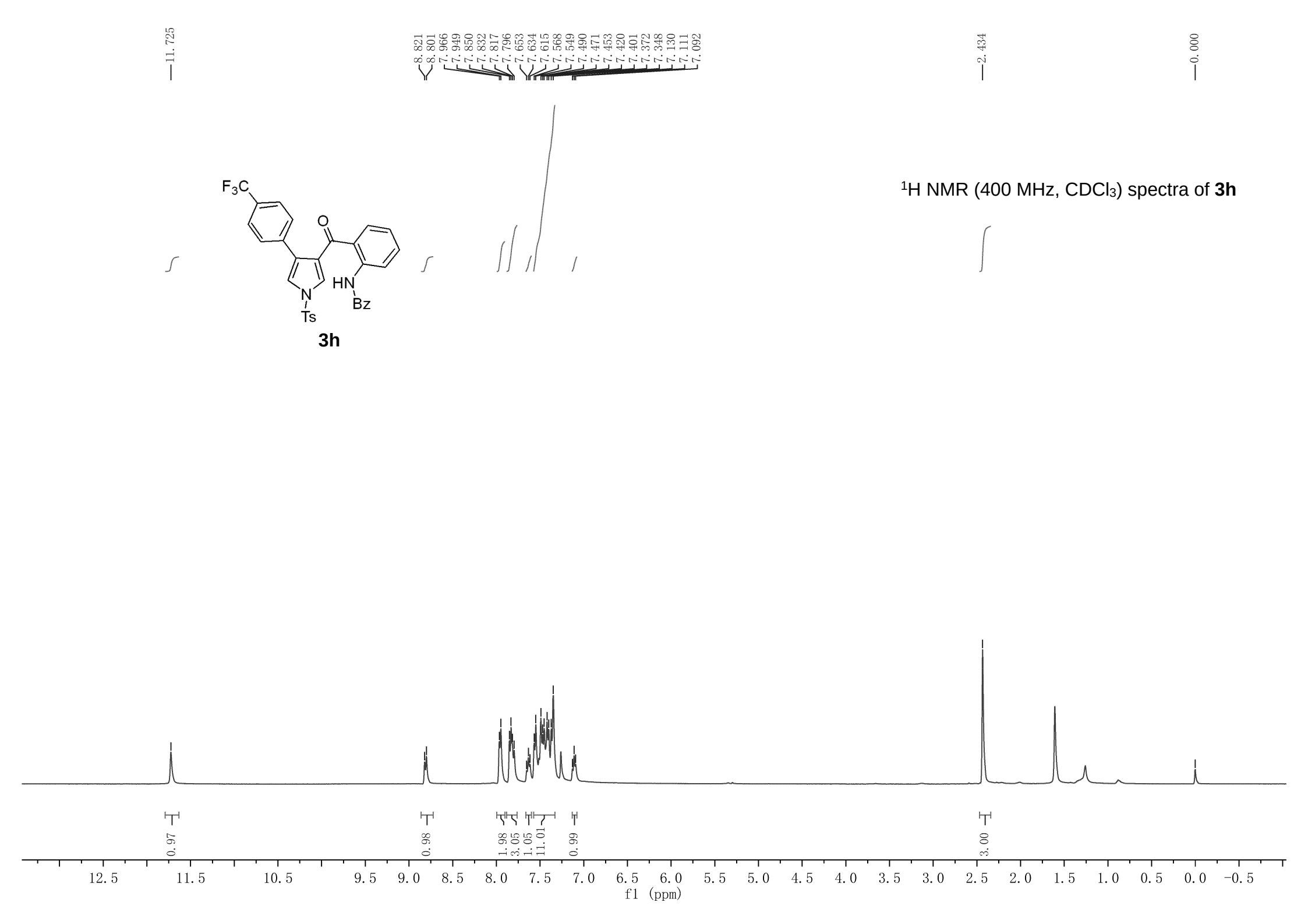


3g

^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3g**

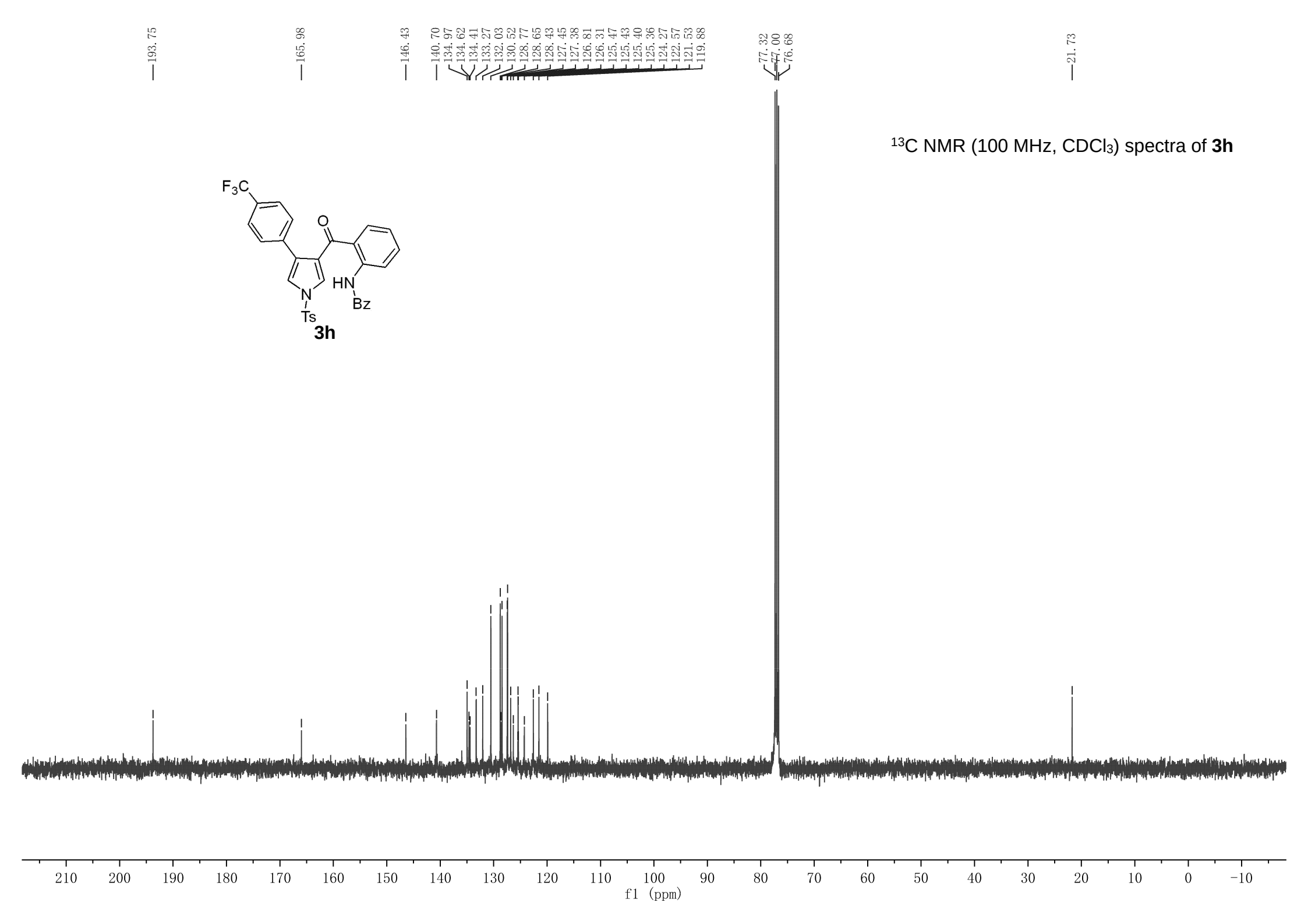


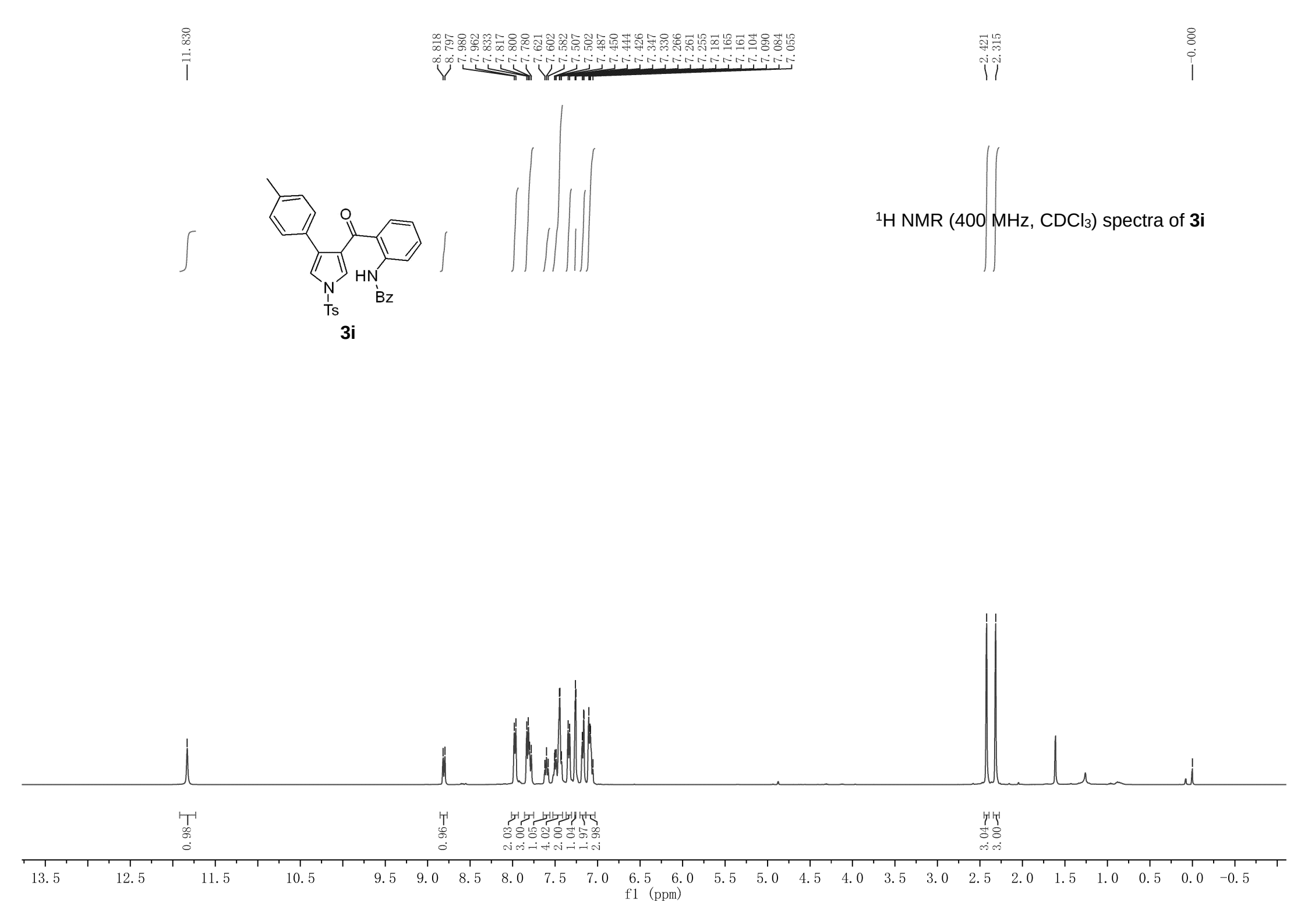
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3g**



3h

^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3h**


193.75
165.98
146.43
140.70
134.97
134.62
134.41
133.27
132.03
130.52
128.77
128.65
128.43
127.45
127.38
126.81
126.31
125.47
125.43
125.40
125.36
124.27
122.57
121.53
119.88
77.32
77.00
76.68
21.73
F3C
O
HN
Bz
N
Ts
3h
13C NMR (100 MHz, CDCl3) spectra of 3h
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)

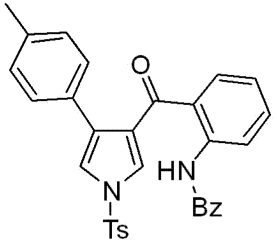


3i

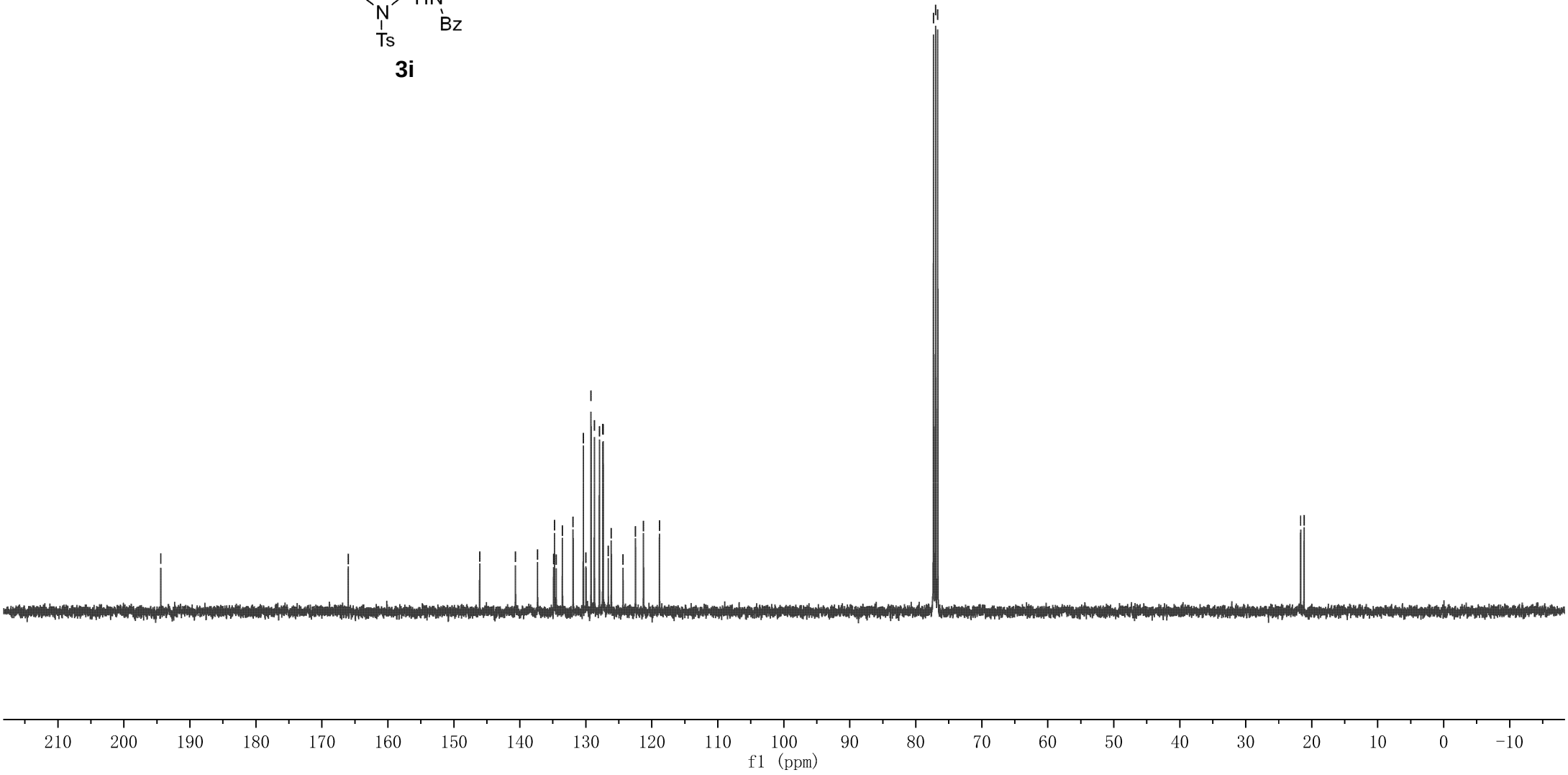
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3i**

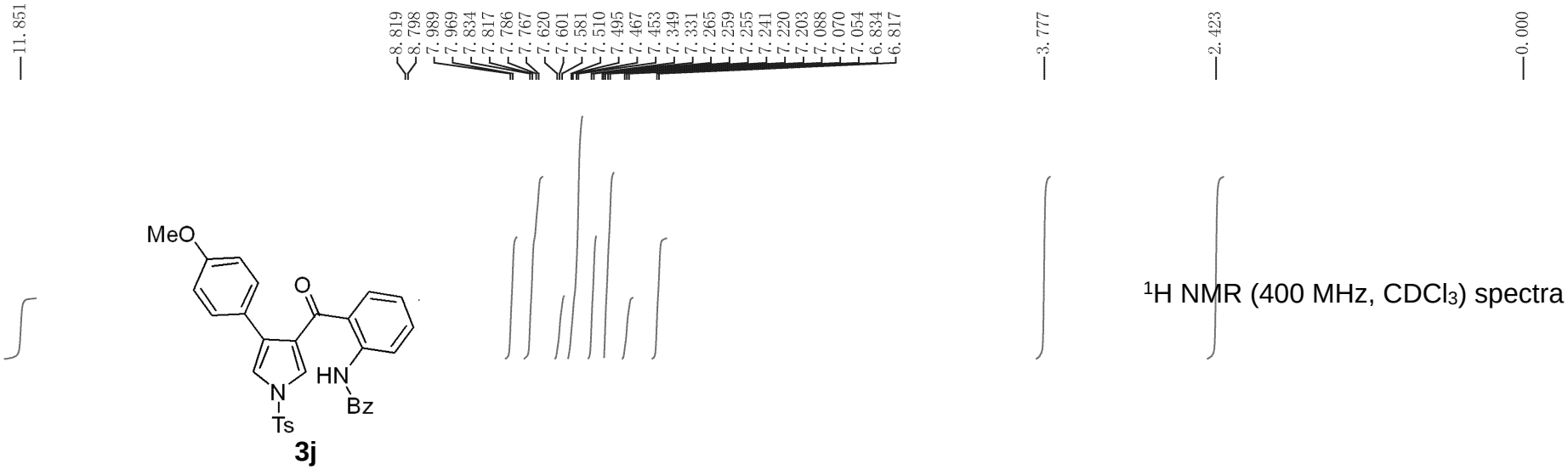
194.41
166.01
146.09
140.67
137.32
134.89
134.74
134.49
133.56
131.93
130.38
129.98
129.21
128.71
127.94
127.44
127.36
126.61
126.15
124.37
122.48
121.26
118.84
77.32
77.00
76.68
21.69
21.16

^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3i**



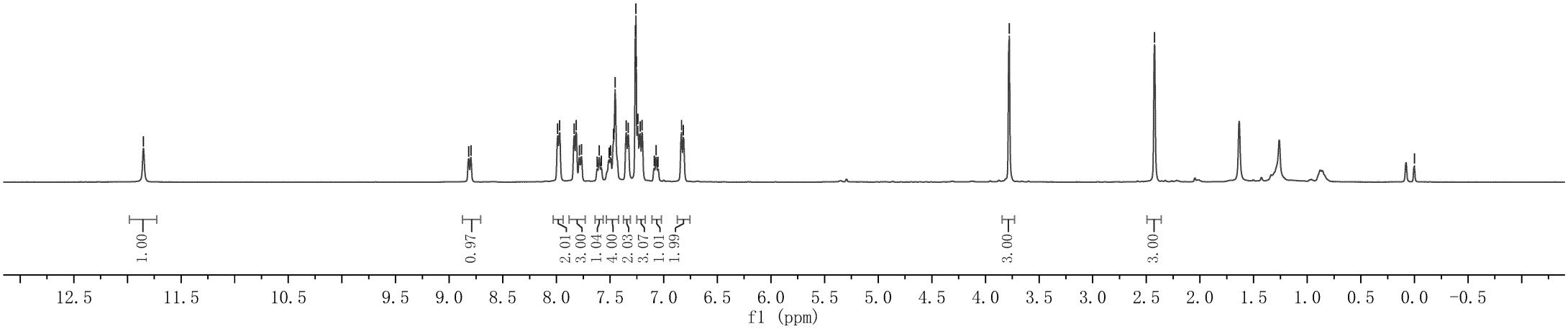
3i





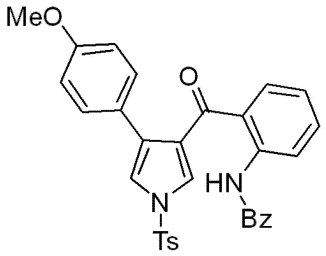
3j

^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3j**

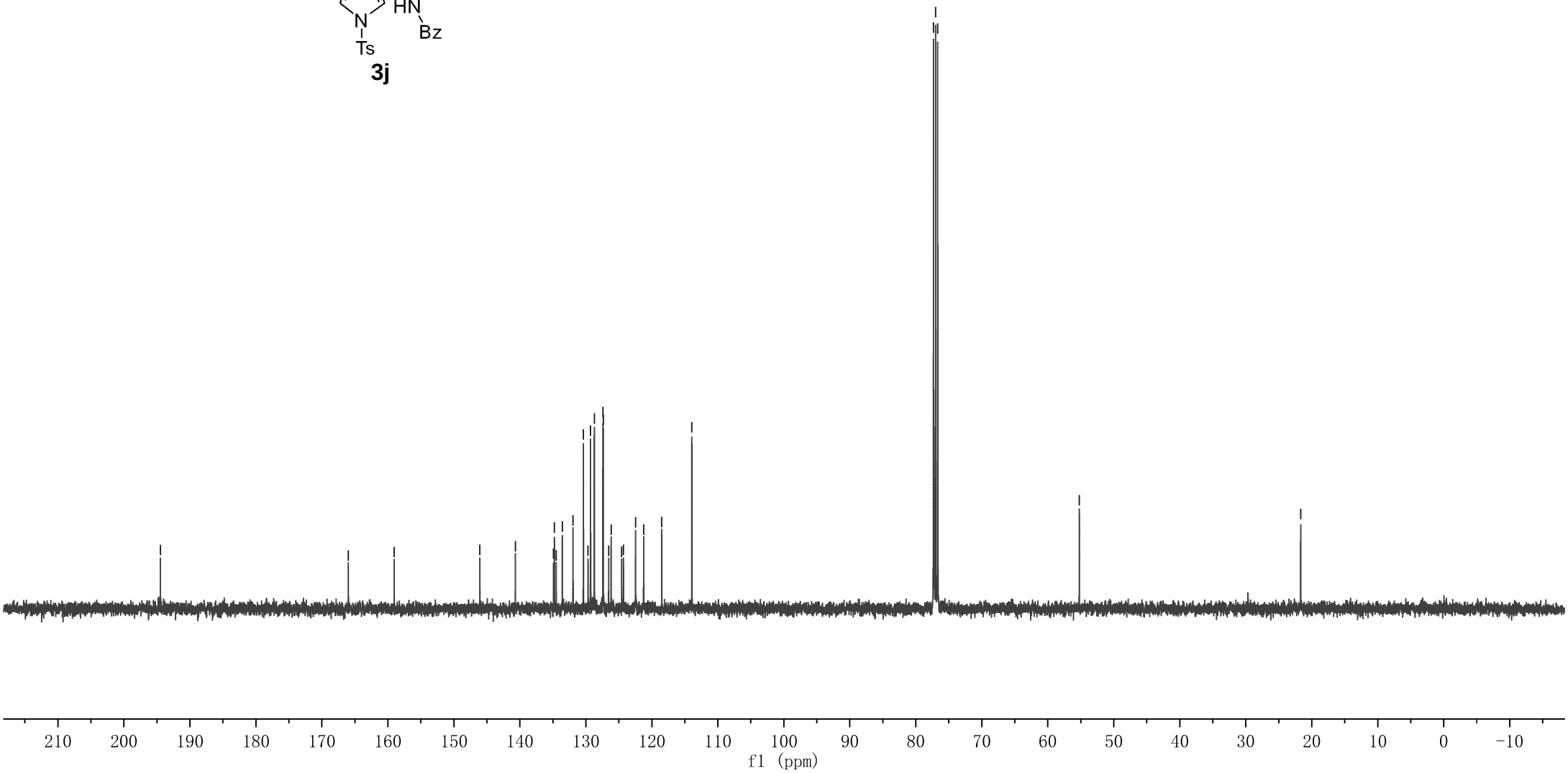


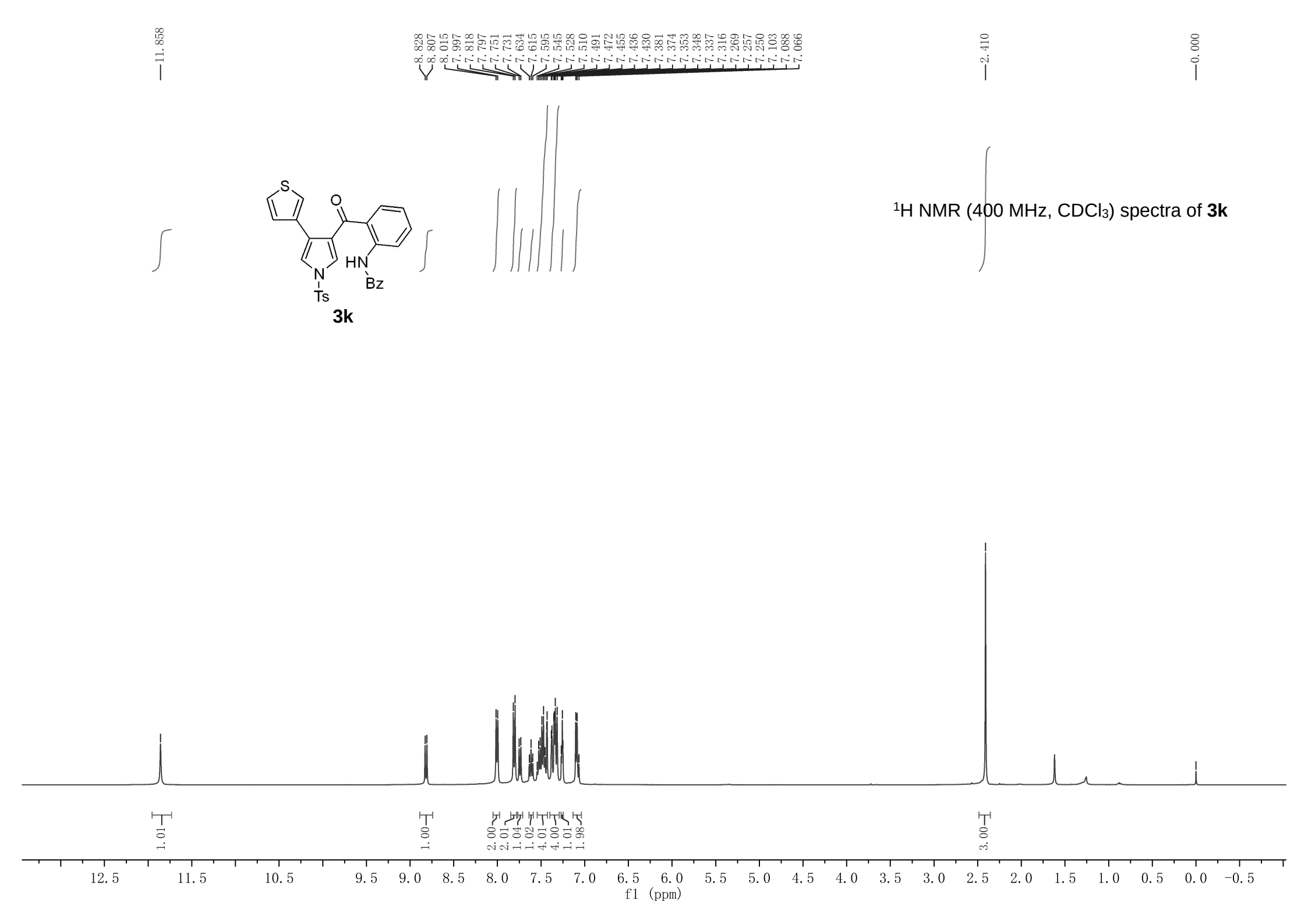
194.47
166.00
159.05
146.07
140.67
134.90
134.76
134.49
133.57
131.95
130.37
129.67
129.29
128.72
127.43
127.36
126.55
126.17
124.58
124.30
122.47
121.24
118.50
113.93
77.32
77.00
76.68
55.22
21.68

^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3j**



3j



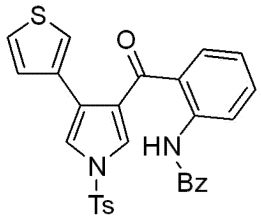


3k

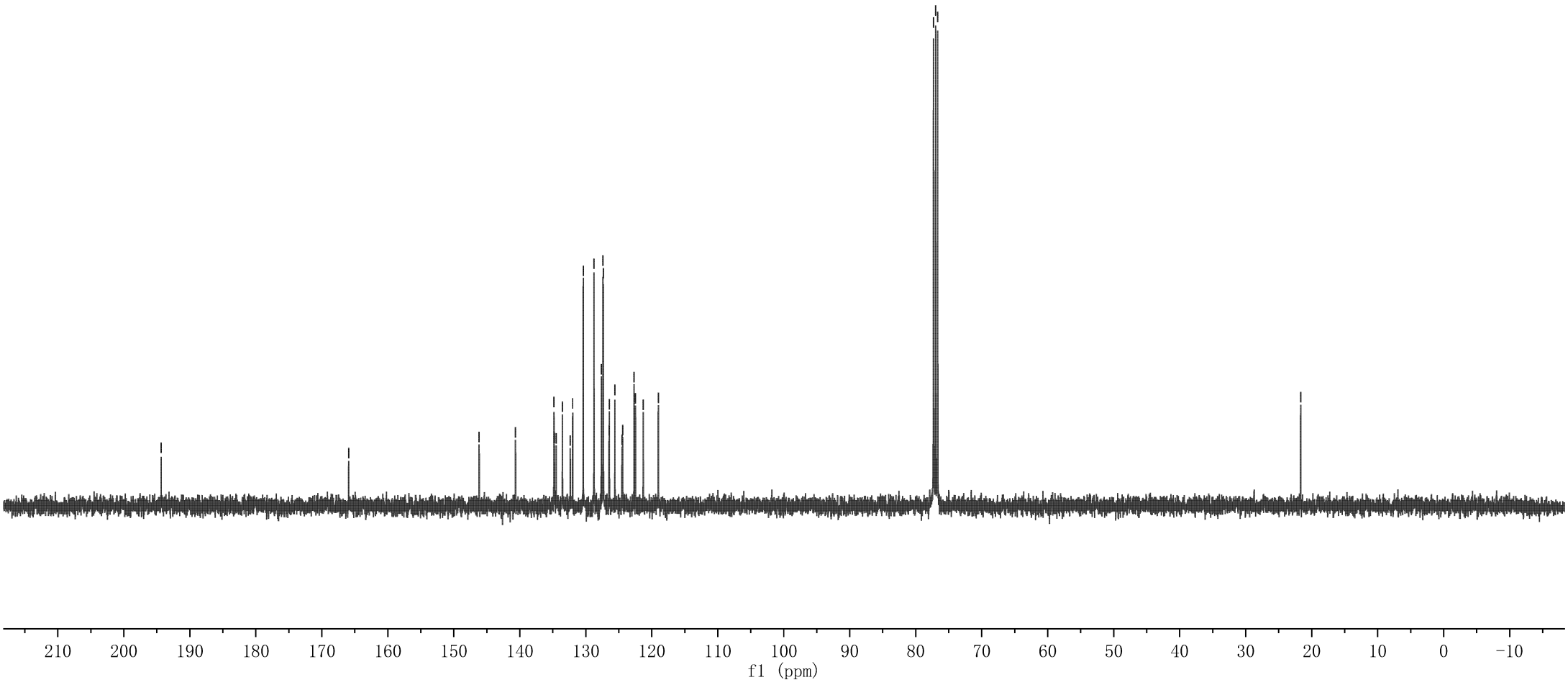
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3k**

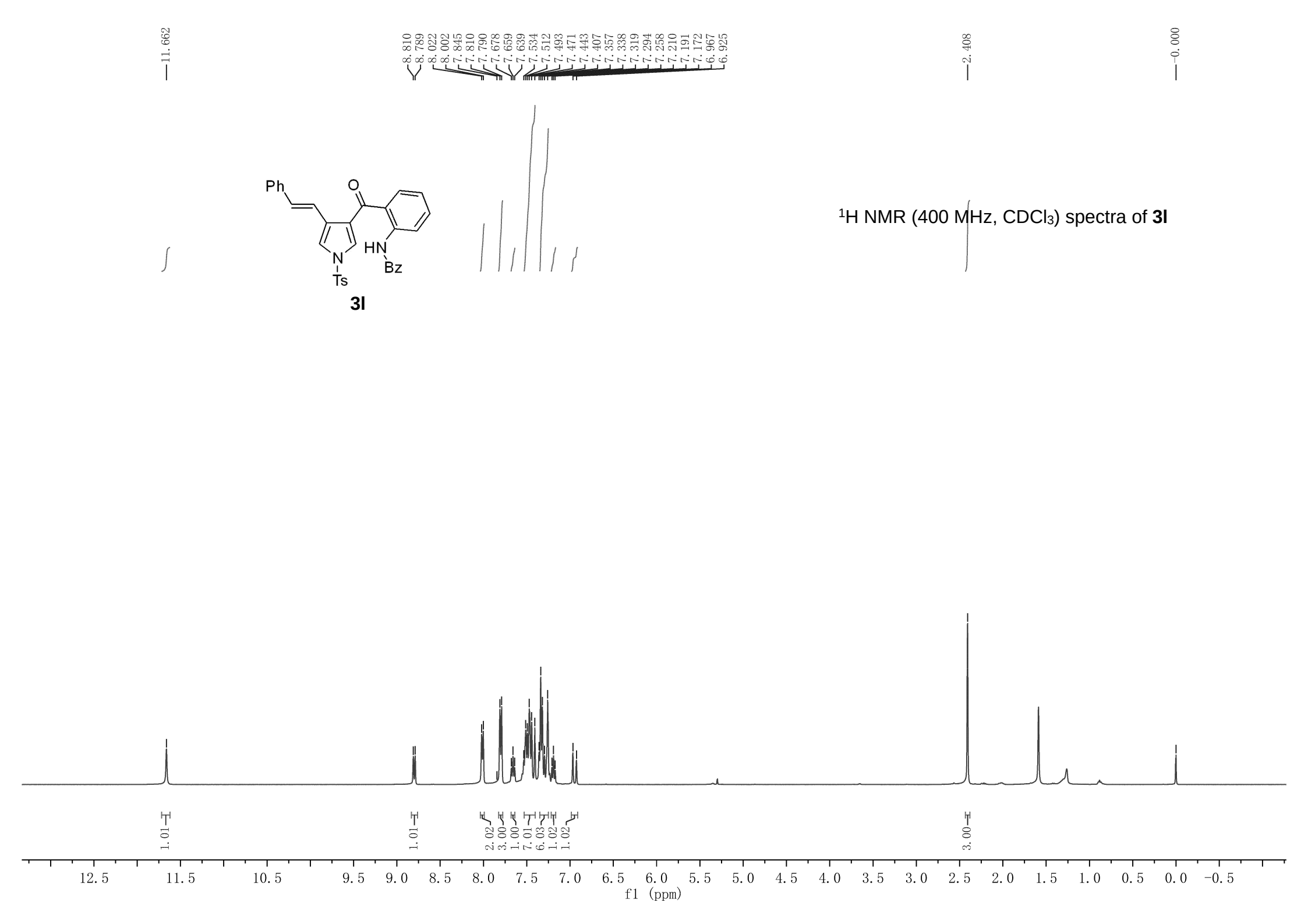
194.35
165.93
146.16
140.65
134.82
134.75
134.49
133.55
132.34
131.99
130.39
128.76
127.65
127.40
127.34
126.48
126.43
125.59
124.52
124.41
122.68
122.47
121.29
119.01
77.32
77.00
76.68
21.68

^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3k**



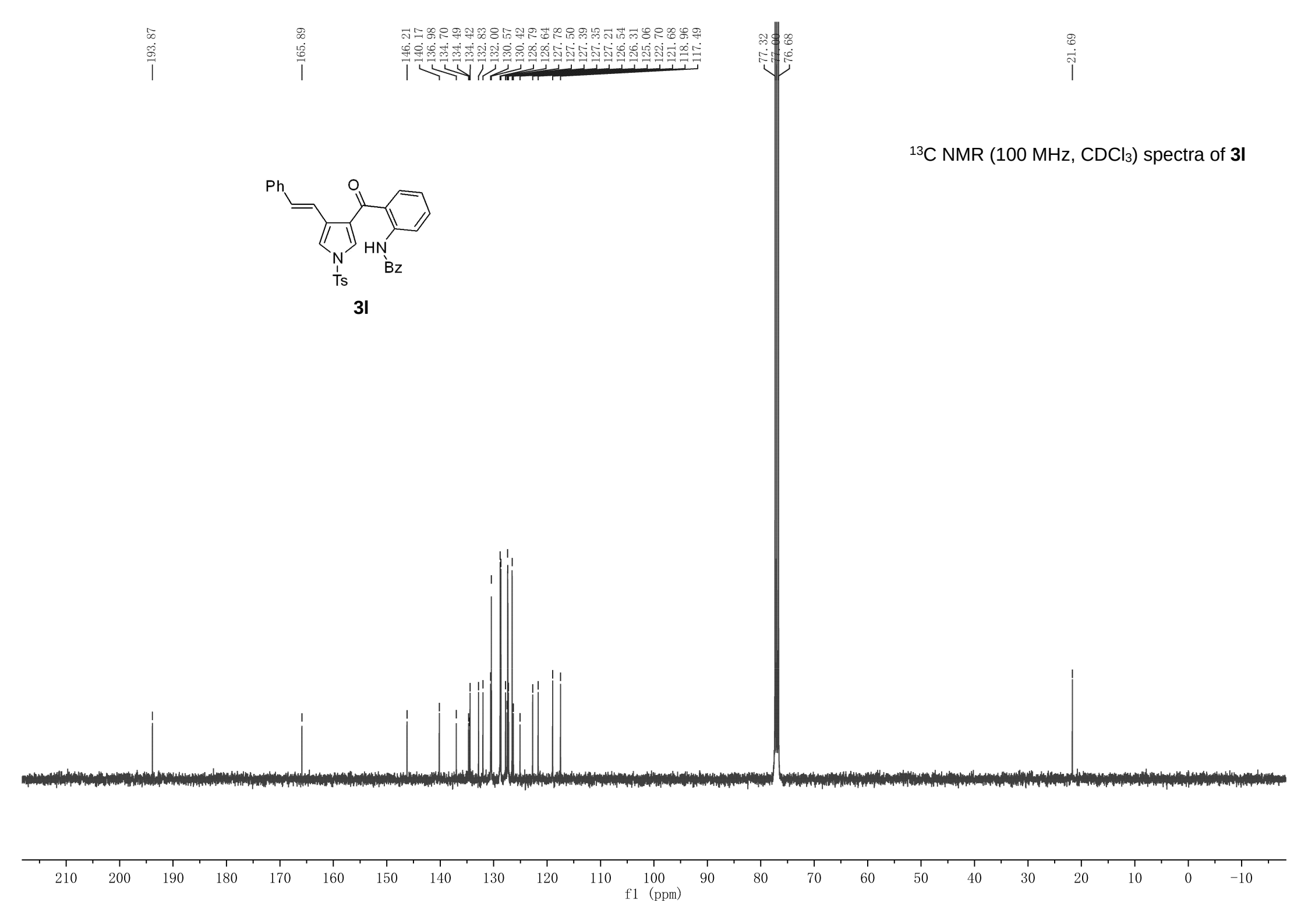
3k

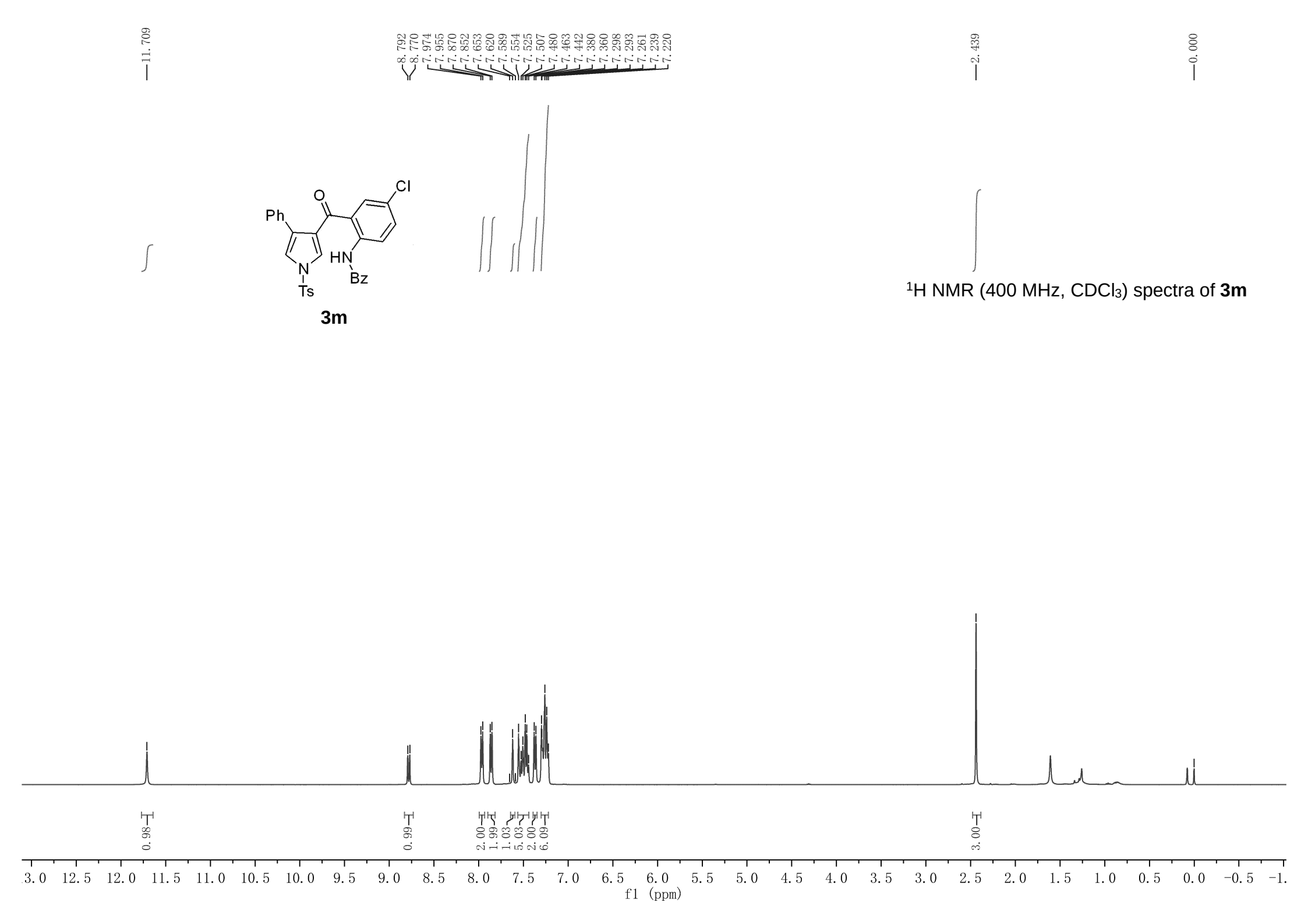




3l

^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3l**


193.87
165.89
146.21
140.17
136.98
134.70
134.49
134.42
132.83
132.00
130.57
130.42
128.79
128.64
127.78
127.50
127.39
127.35
127.21
126.54
126.31
125.06
122.70
121.68
118.96
117.49
77.32
77.00
76.68
21.69
Ph
O
N
Ts
HN
Bz
3l
13C NMR (100 MHz, CDCl3) spectra of 3l
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)

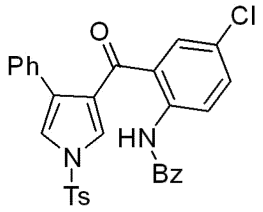


3m

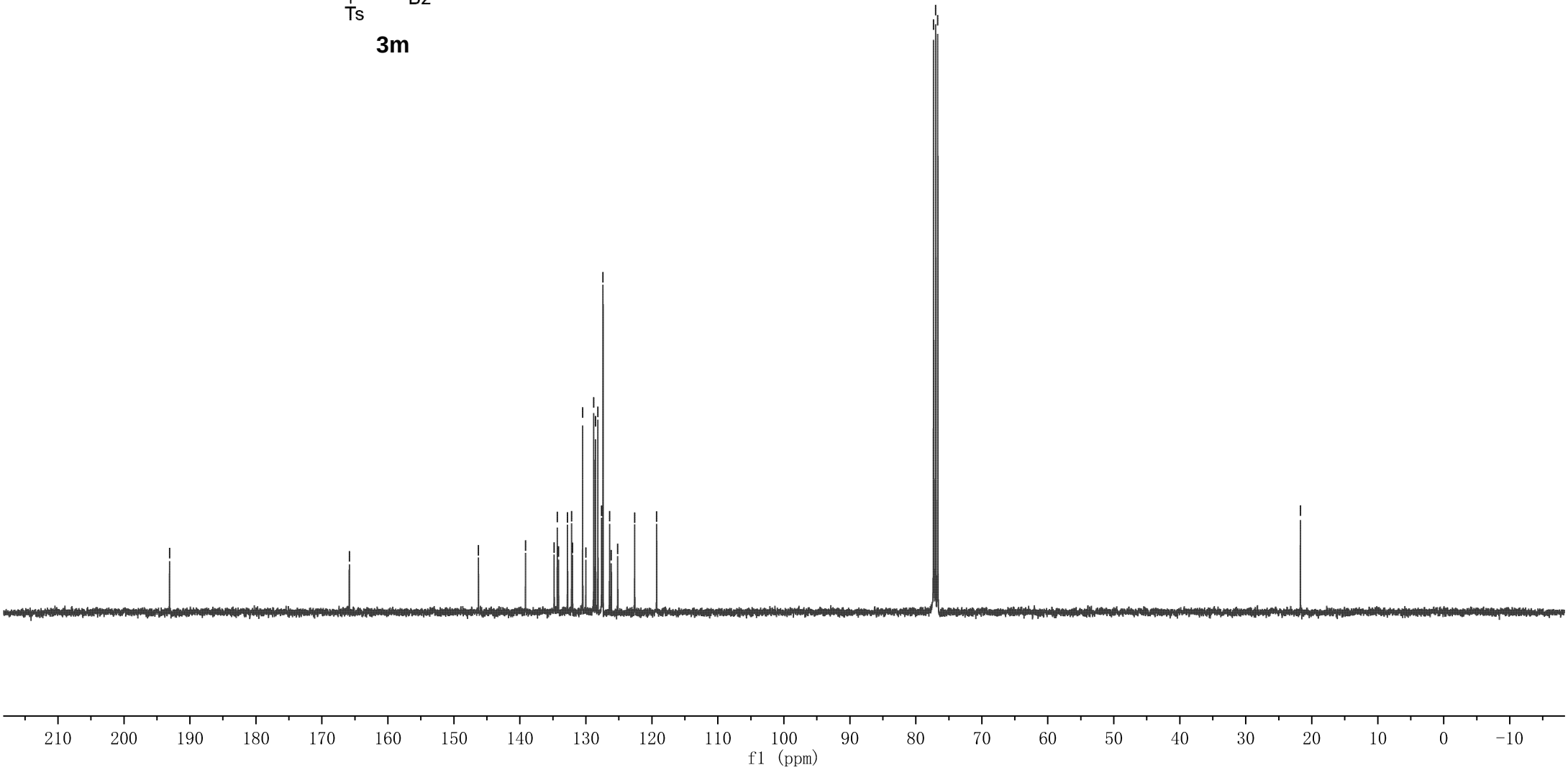
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3m**

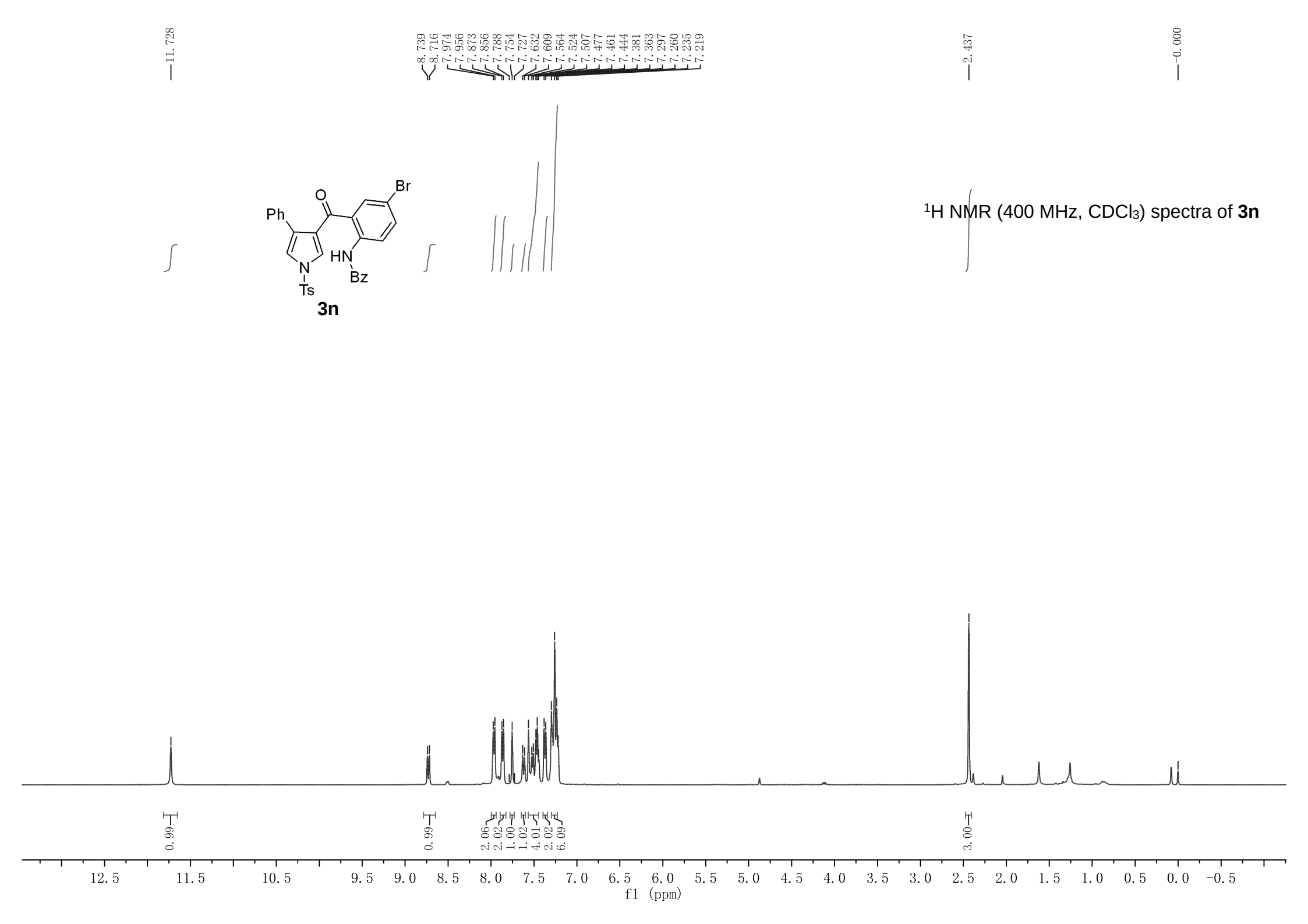
193.09
165.84
146.28
139.15
134.81
134.33
134.15
132.78
132.16
132.02
130.49
130.00
128.80
128.53
128.18
127.62
127.40
126.41
126.15
125.18
122.61
119.28
77.32
77.00
76.68
21.72

^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3m**



3m

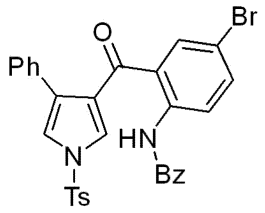




3n

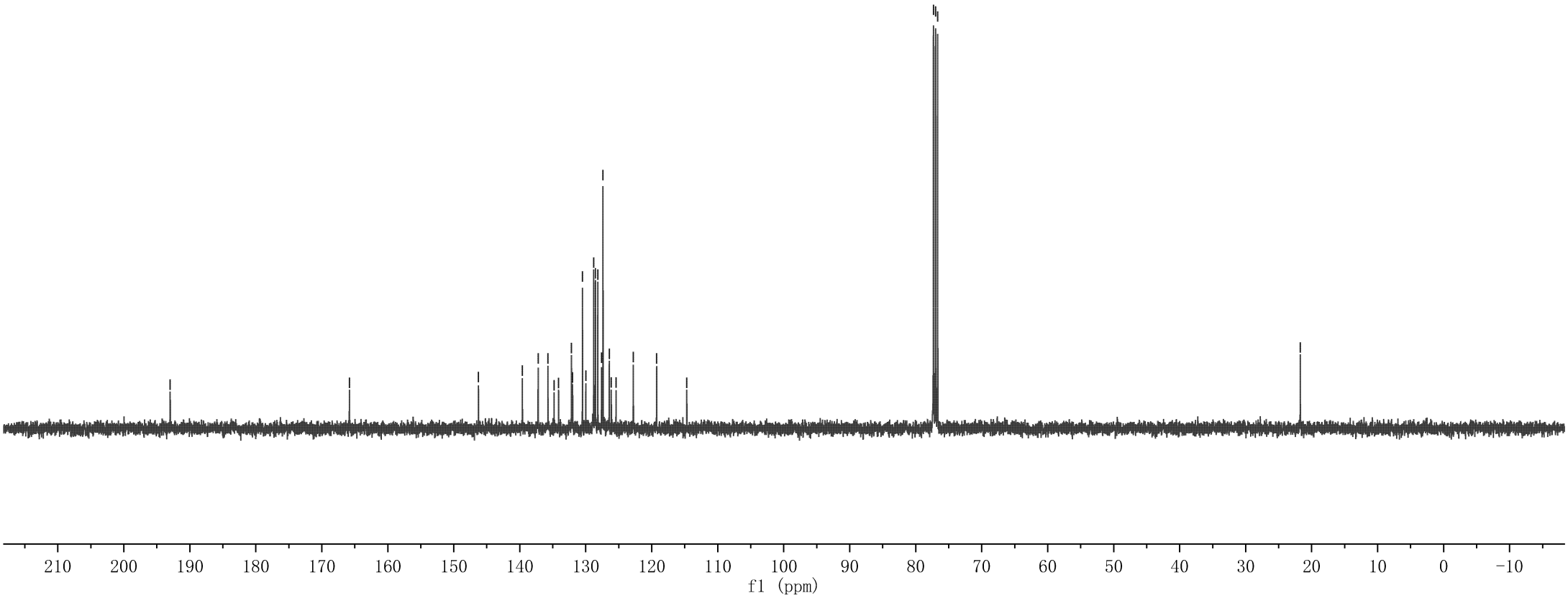
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3n**

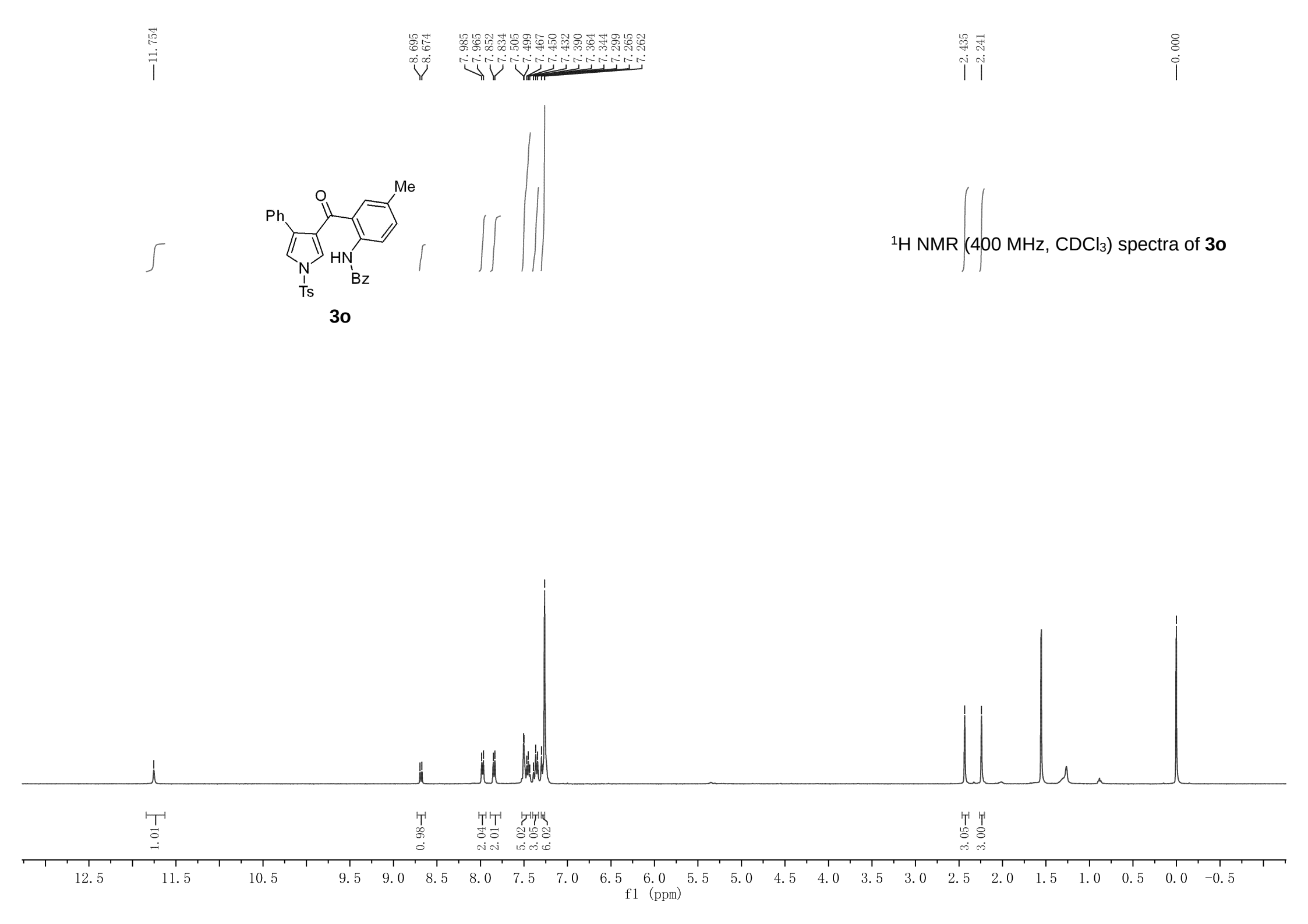
192.97
165.81
146.26
139.61
137.21
135.73
134.79
134.12
132.17
131.99
130.49
129.99
128.79
128.53
128.18
127.60
127.39
126.44
126.13
125.41
122.79
119.25
114.69
77.32
77.00
76.68
21.72



3n

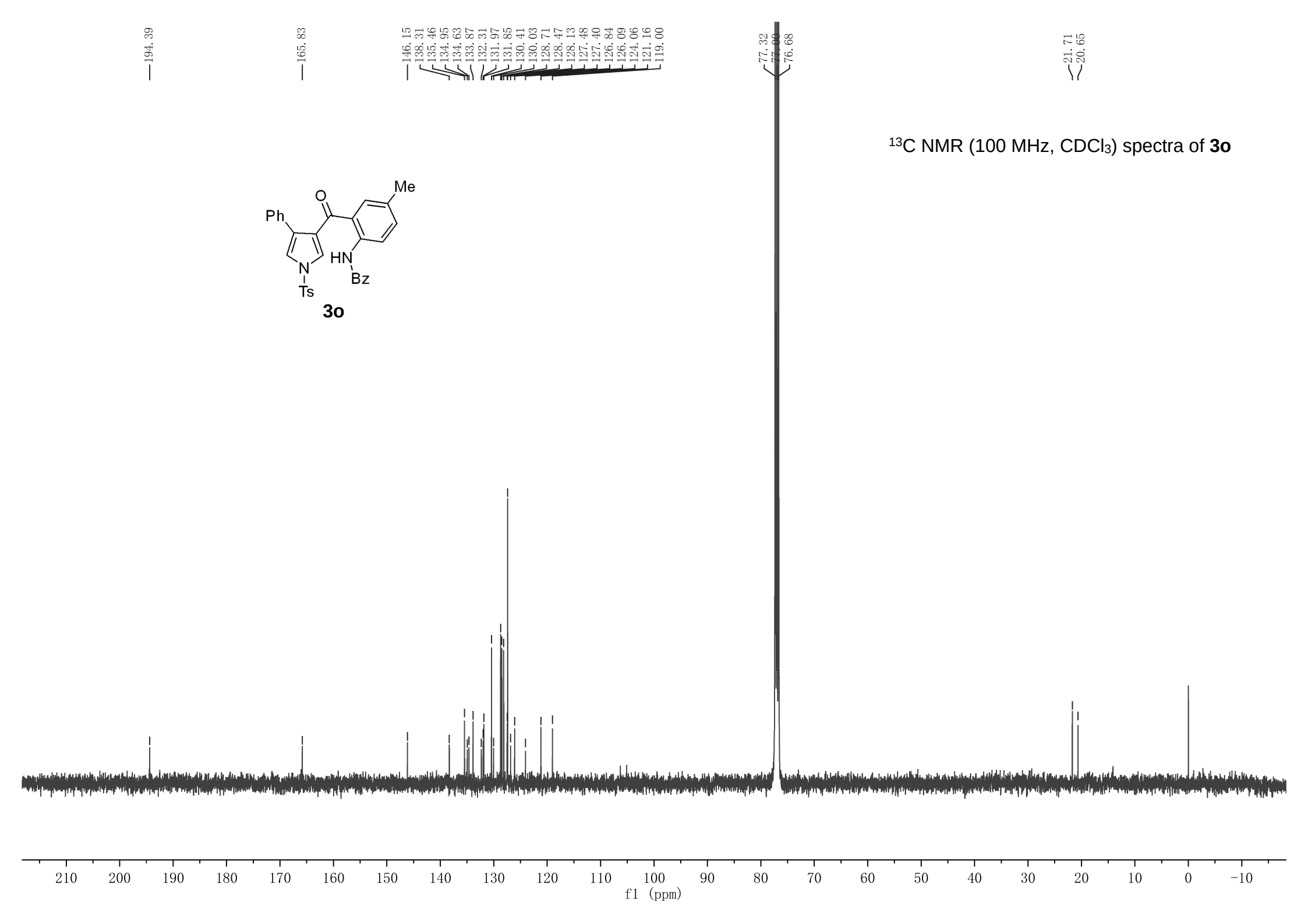
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3n**



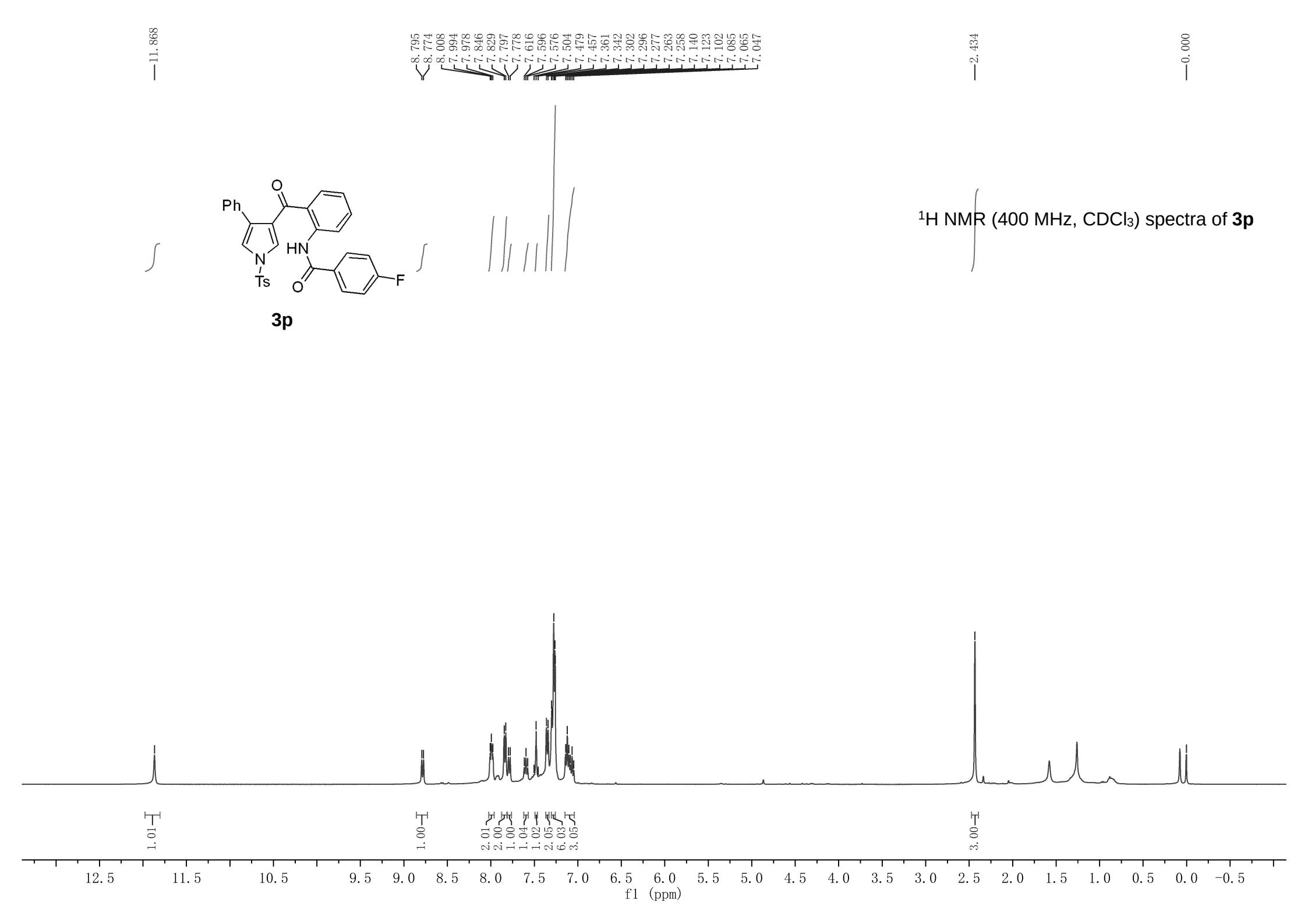


3o

^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3o**

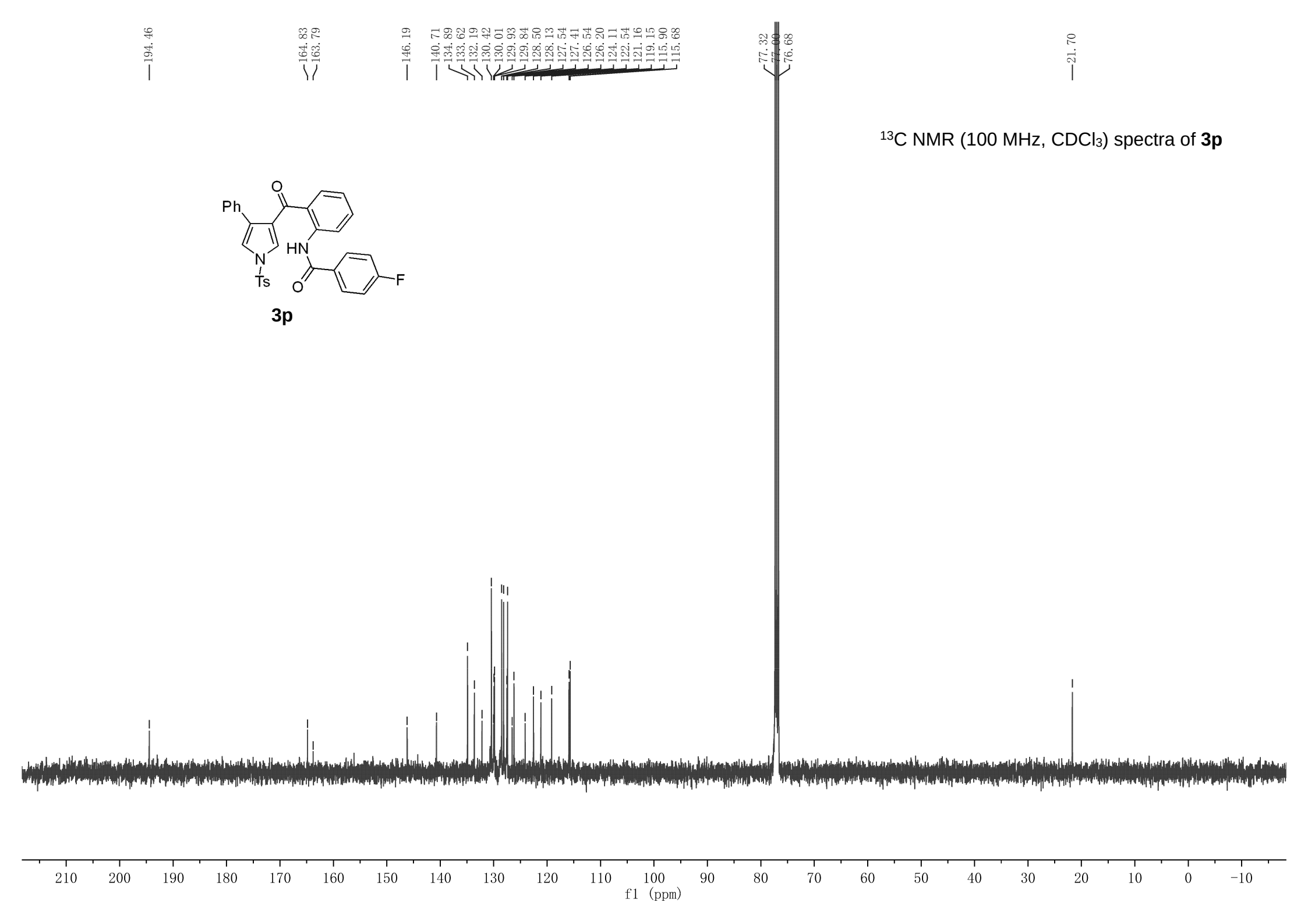


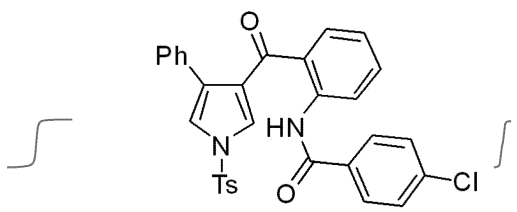
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3o**



3p

^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3p**


194.46
164.83
163.79
146.19
140.71
134.89
133.62
132.19
130.42
130.01
129.93
129.84
128.50
128.13
127.54
127.41
126.54
126.20
124.11
122.54
121.16
119.15
115.90
115.68
77.32
77.00
76.68
21.70
Ph
O
HN
N
Ts
O
F
3p
13C NMR (100 MHz, CDCl3) spectra of 3p
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)

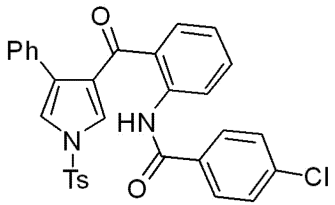


3q

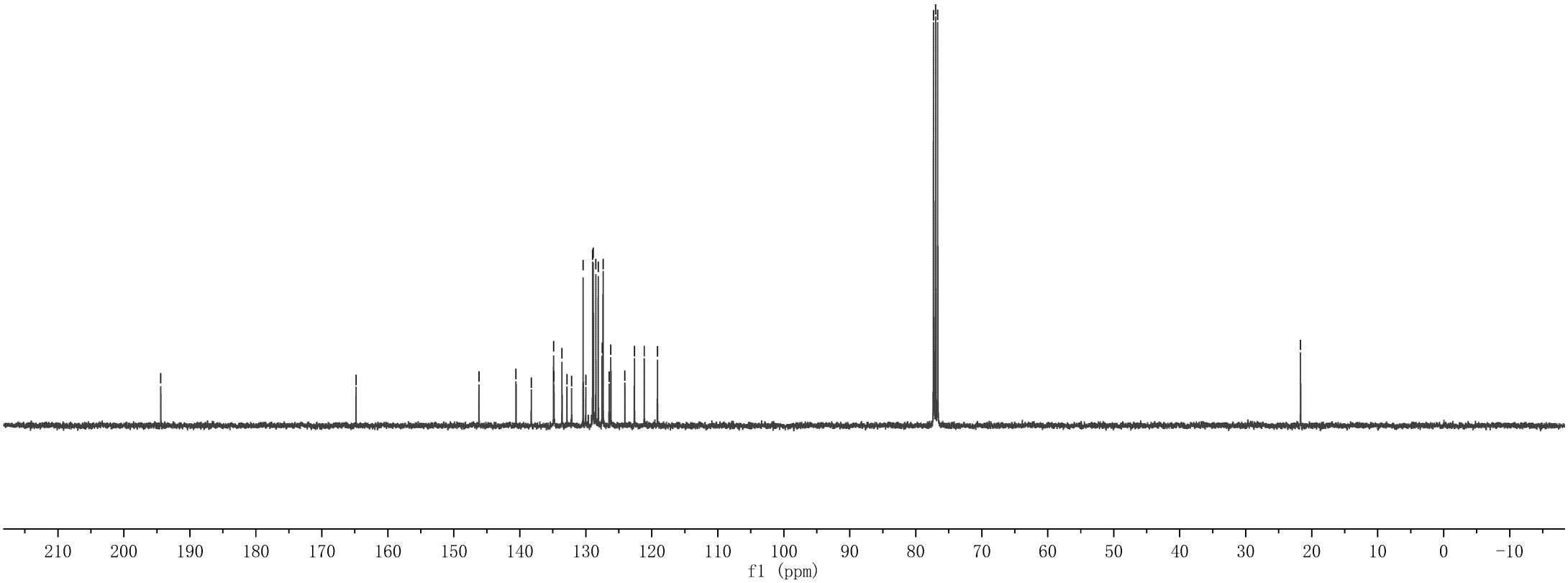
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3q**

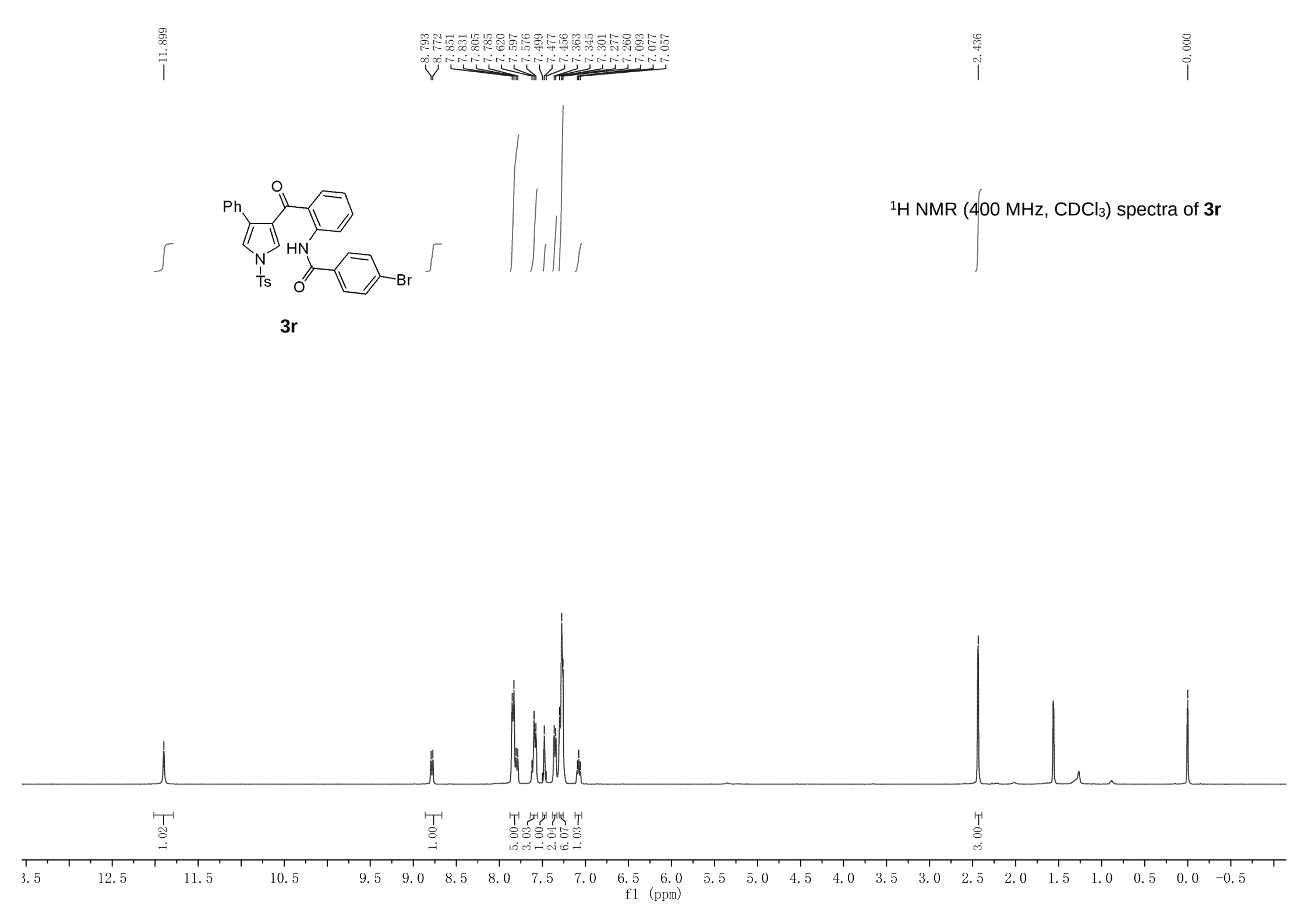
194.41
164.82
146.19
140.58
138.26
134.89
134.83
133.61
132.87
132.15
130.41
130.00
128.97
128.86
128.49
128.12
127.53
127.39
126.47
126.21
124.08
122.63
121.15
119.14
77.32
77.00
76.68
21.69

^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3q**



3q



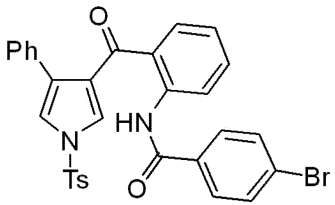


3r

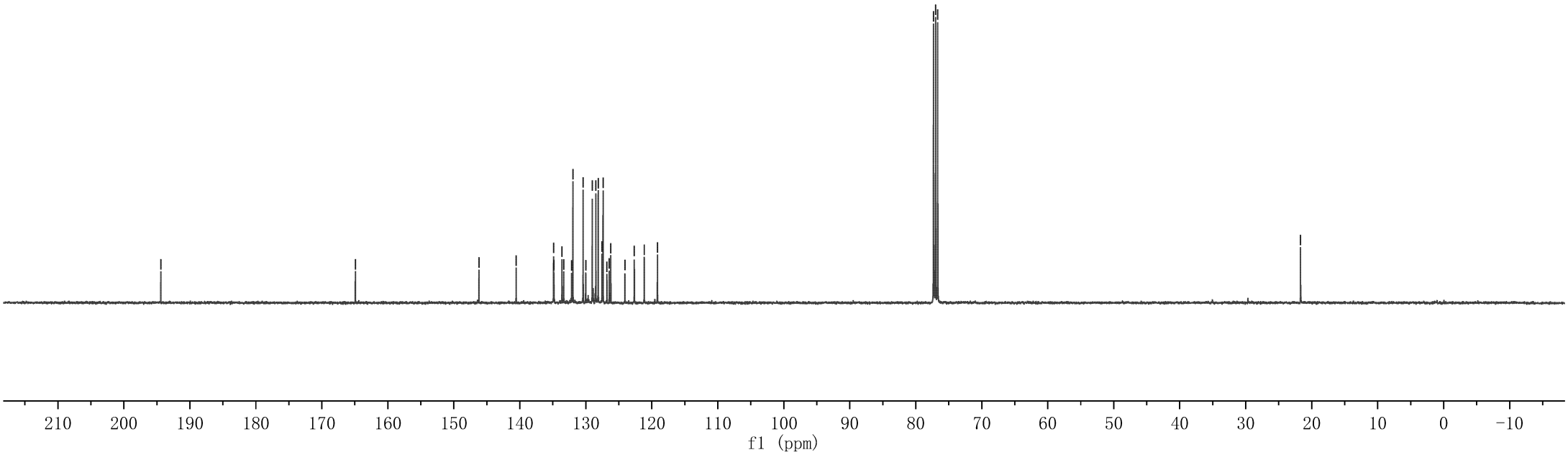
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3r**

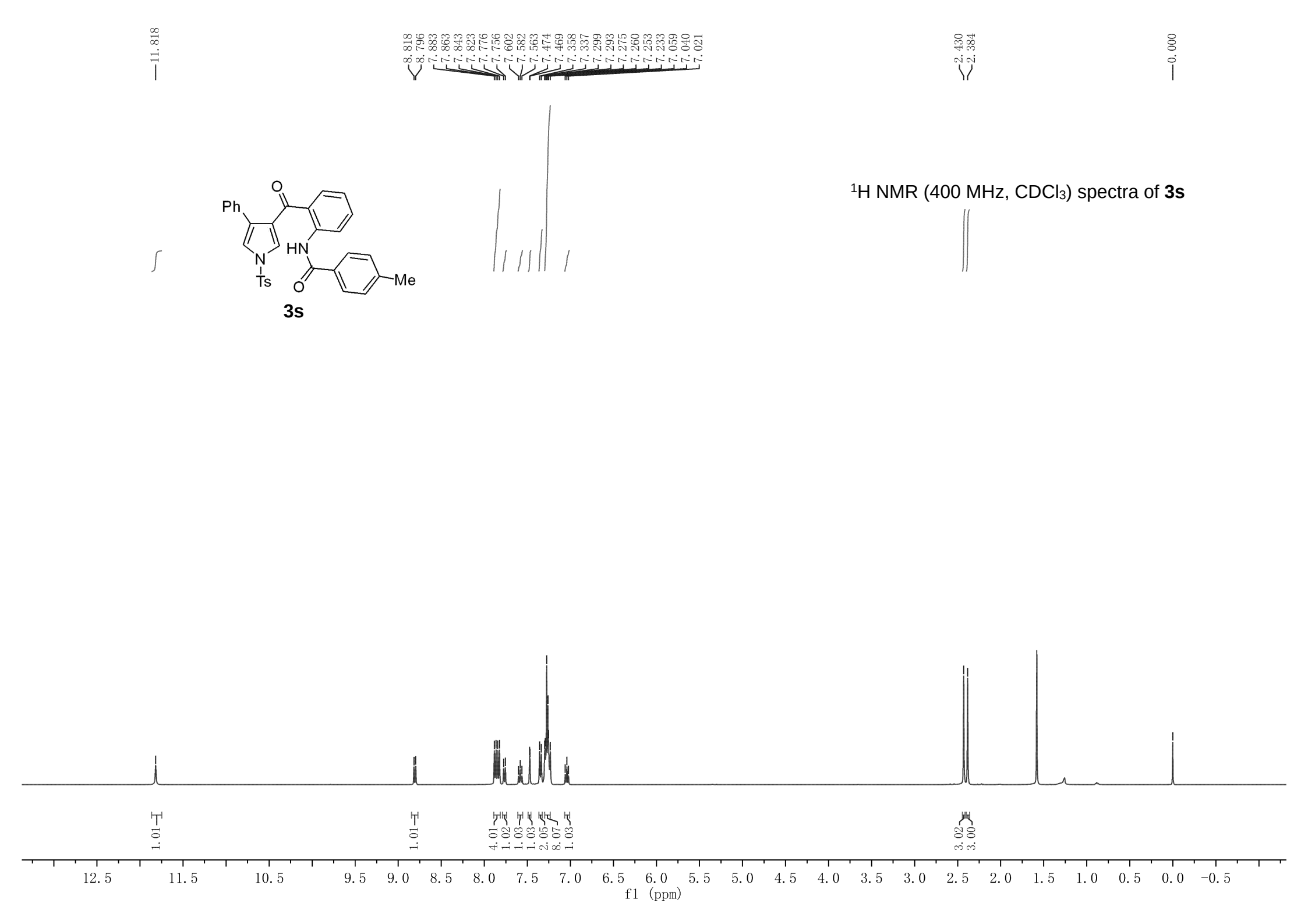
194.40
164.92
146.19
140.56
134.89
134.83
133.61
133.34
132.15
131.96
130.41
130.01
129.02
128.48
128.12
127.53
127.39
126.80
126.46
126.22
124.08
122.65
121.15
119.15
77.32
77.00
76.68
21.70

^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3r**



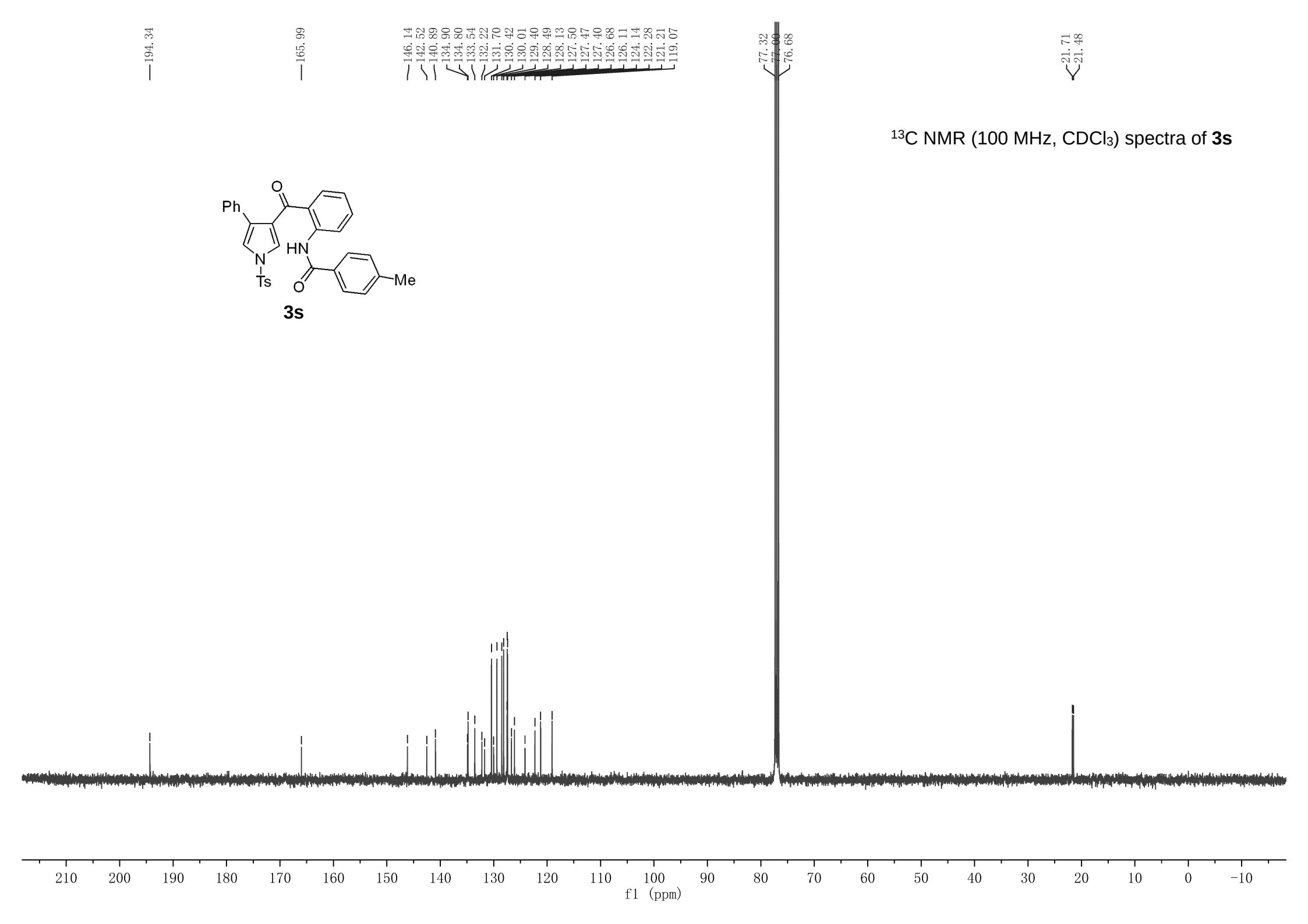
3r



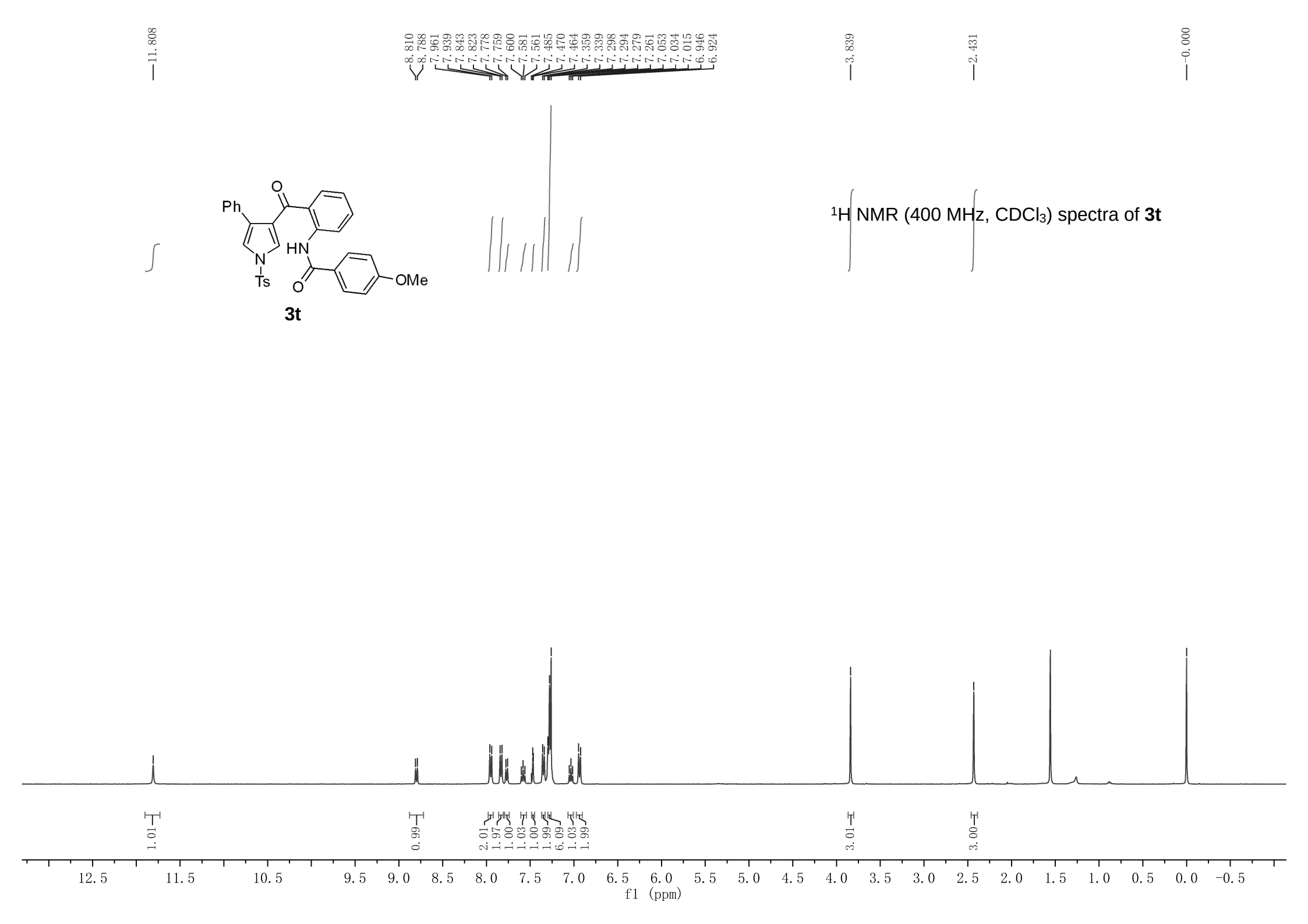


3s

^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3s**



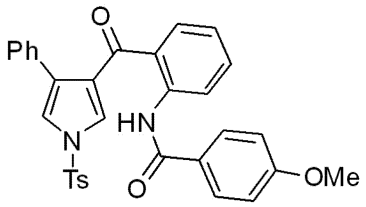
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3s**



3t

^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3t**

^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3t**



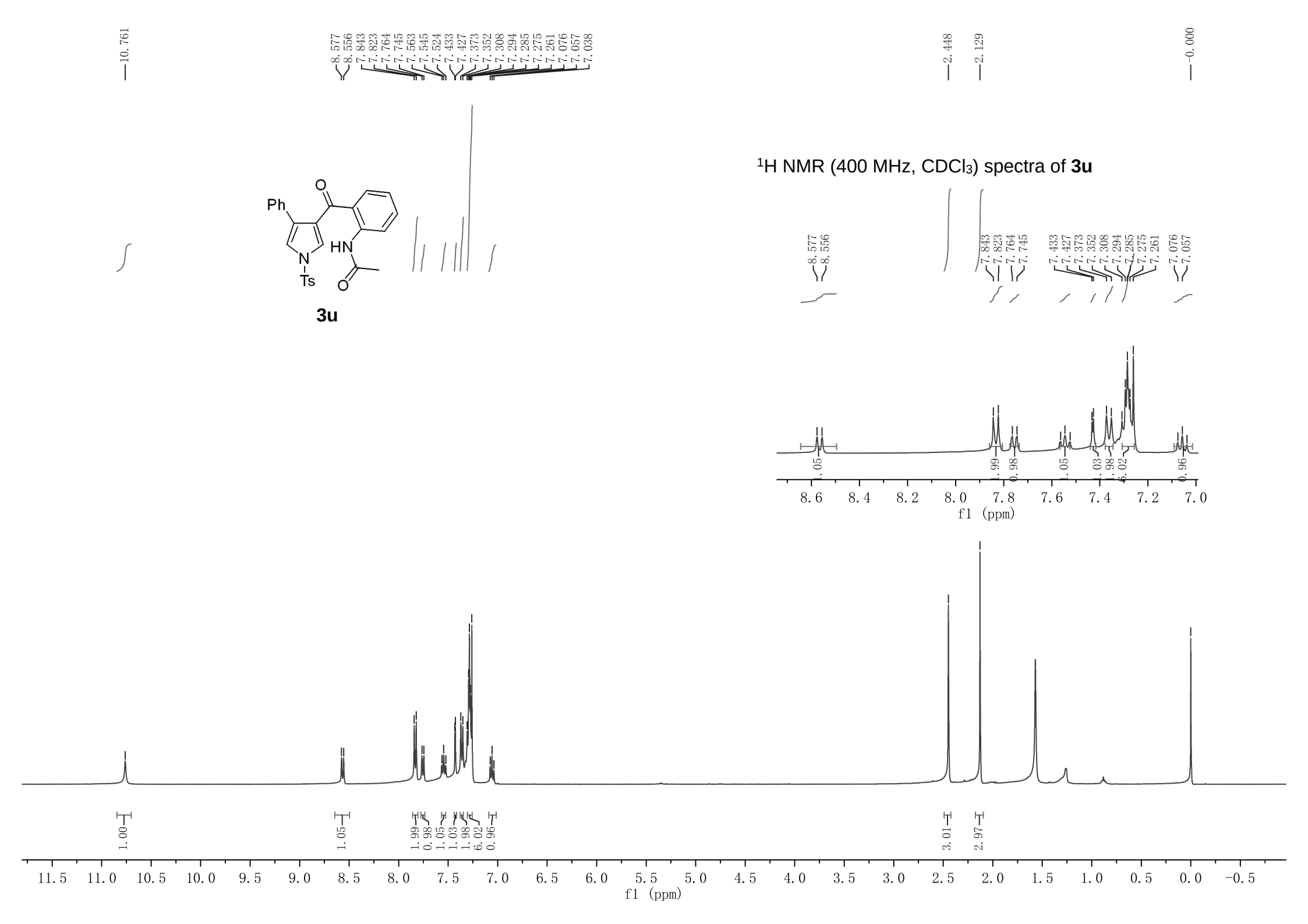
3t

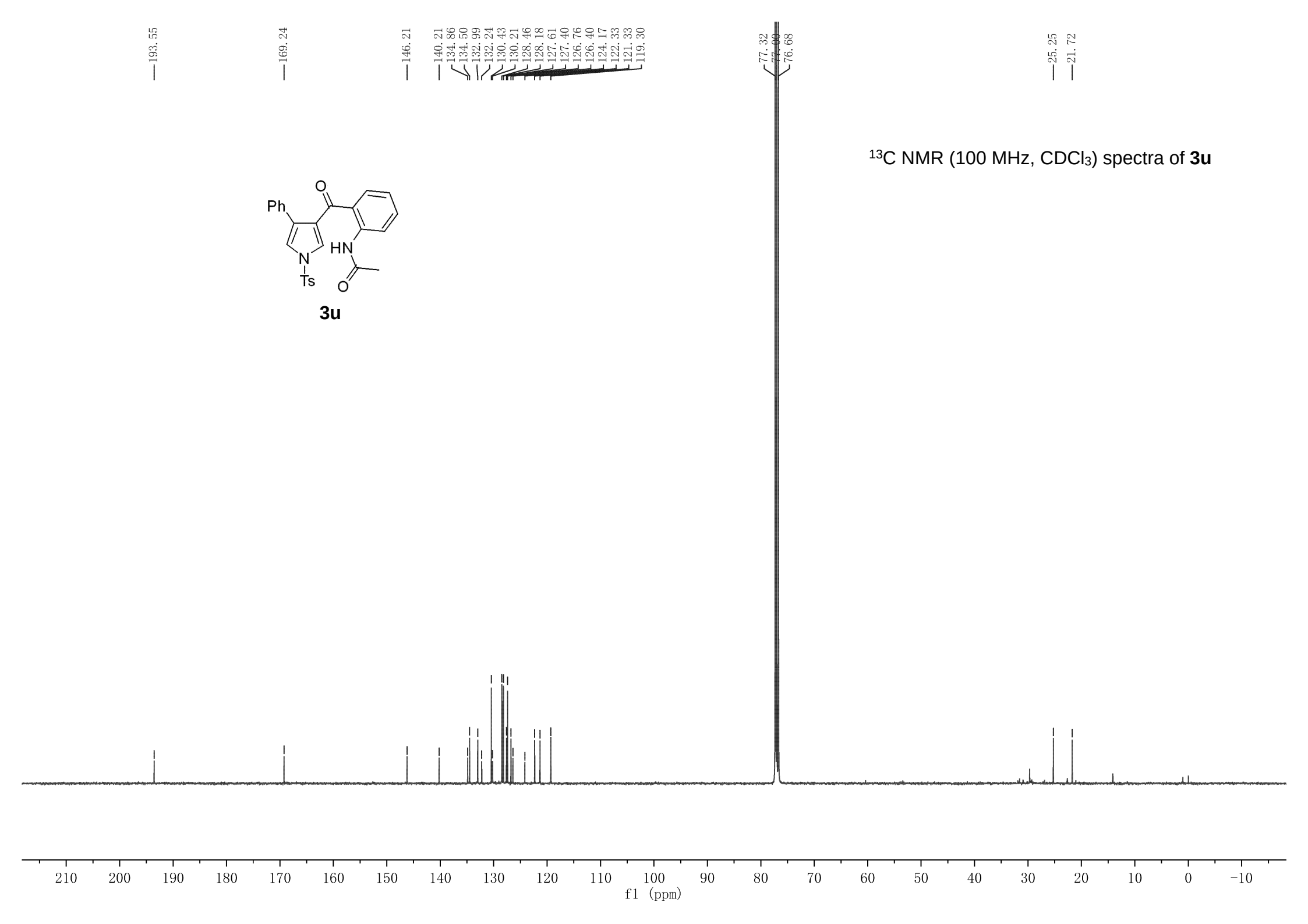
194.38
165.50
162.58
146.13
141.04
133.55
130.40
129.38
128.48
128.12
127.47
127.38
126.10
122.13
121.12
113.92
77.32
77.00
76.68
55.40
21.69

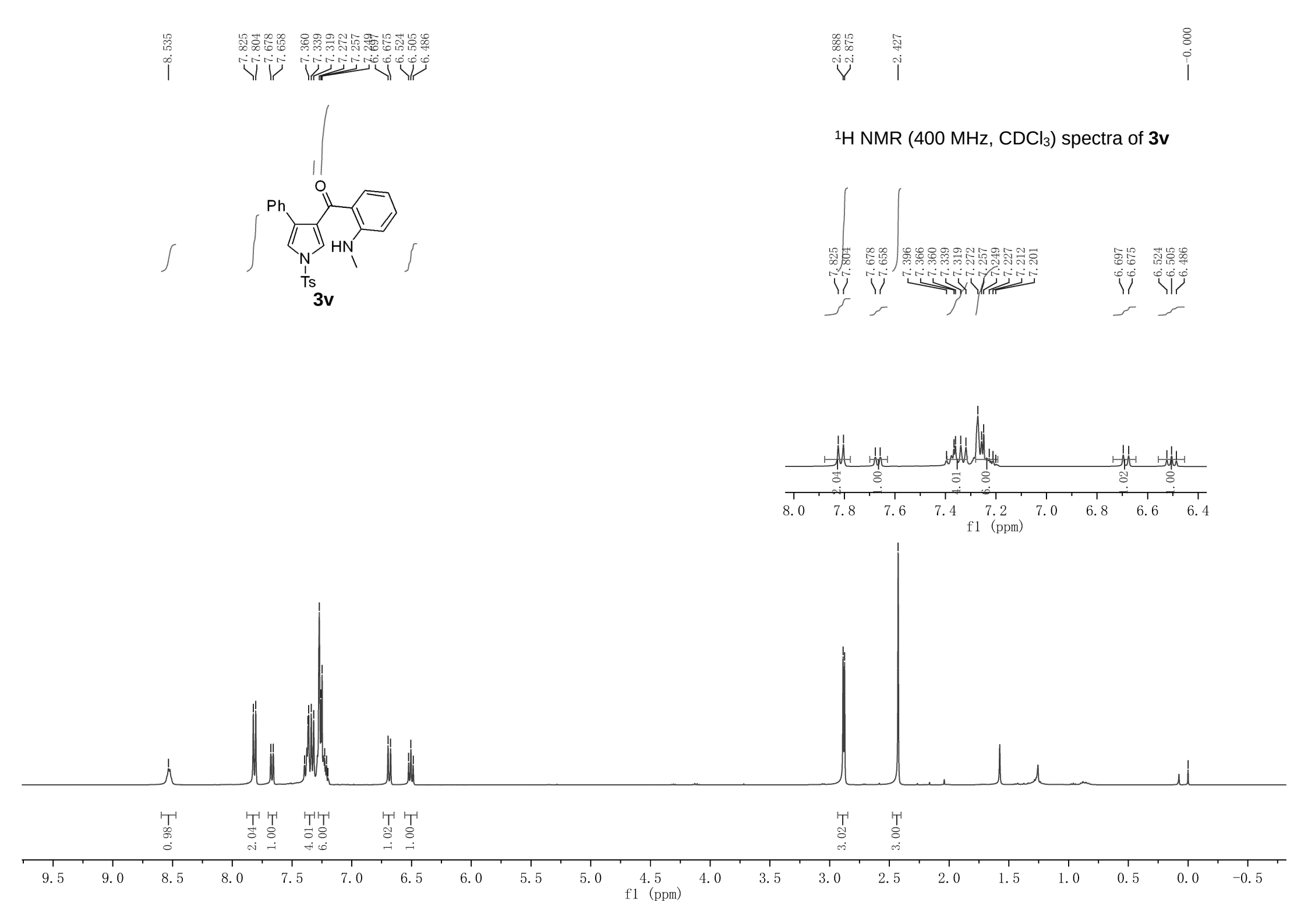
134.89
134.81
133.55
132.22
130.40
129.99
129.38
128.48
128.12
127.47
127.38
126.78
126.68
126.10
124.01
122.13
121.12
119.06
113.92

132 128 124 120 116
f1 (ppm)

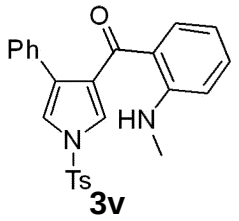
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


10.761
8.577
8.556
7.843
7.823
7.764
7.745
7.563
7.545
7.524
7.433
7.427
7.373
7.352
7.308
7.294
7.285
7.275
7.261
7.076
7.057
7.038
2.448
2.129
-0.000
Ph
O
HN
N
Ts
O
3u
1H NMR (400 MHz, CDCl3) spectra of 3u
f1 (ppm)
f1 (ppm)


193.55
169.24
146.21
140.21
134.86
134.50
132.99
132.24
130.43
130.21
128.46
128.18
127.61
127.40
126.76
126.40
124.17
122.33
121.33
119.30
77.32
77.00
76.68
25.25
21.72
Ph
O
HN
N
Ts
O
3u
13C NMR (100 MHz, CDCl3) spectra of 3u
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)

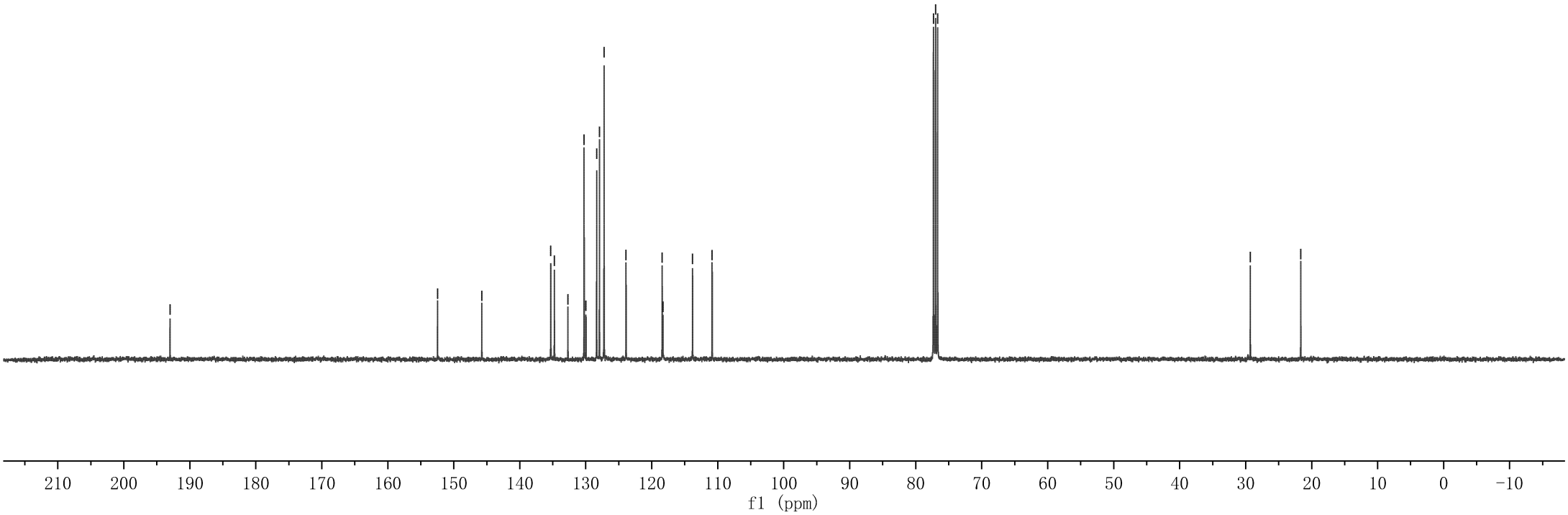

8.535
7.825
7.804
7.678
7.658
7.360
7.339
7.319
7.272
7.257
7.249
6.697
6.675
6.524
6.505
6.486
2.888
2.875
2.427
0.000
Ph
O
HN
N
Ts
3v
1H NMR (400 MHz, CDCl3) spectra of 3v
7.396
7.366
7.360
7.339
7.319
7.272
7.257
7.249
7.227
7.212
7.201
2.04
1.00
4.01
6.00
1.02
1.00
f1 (ppm)
0.98
2.04
1.00
4.01
6.00
1.02
1.00
3.02
3.00
f1 (ppm)

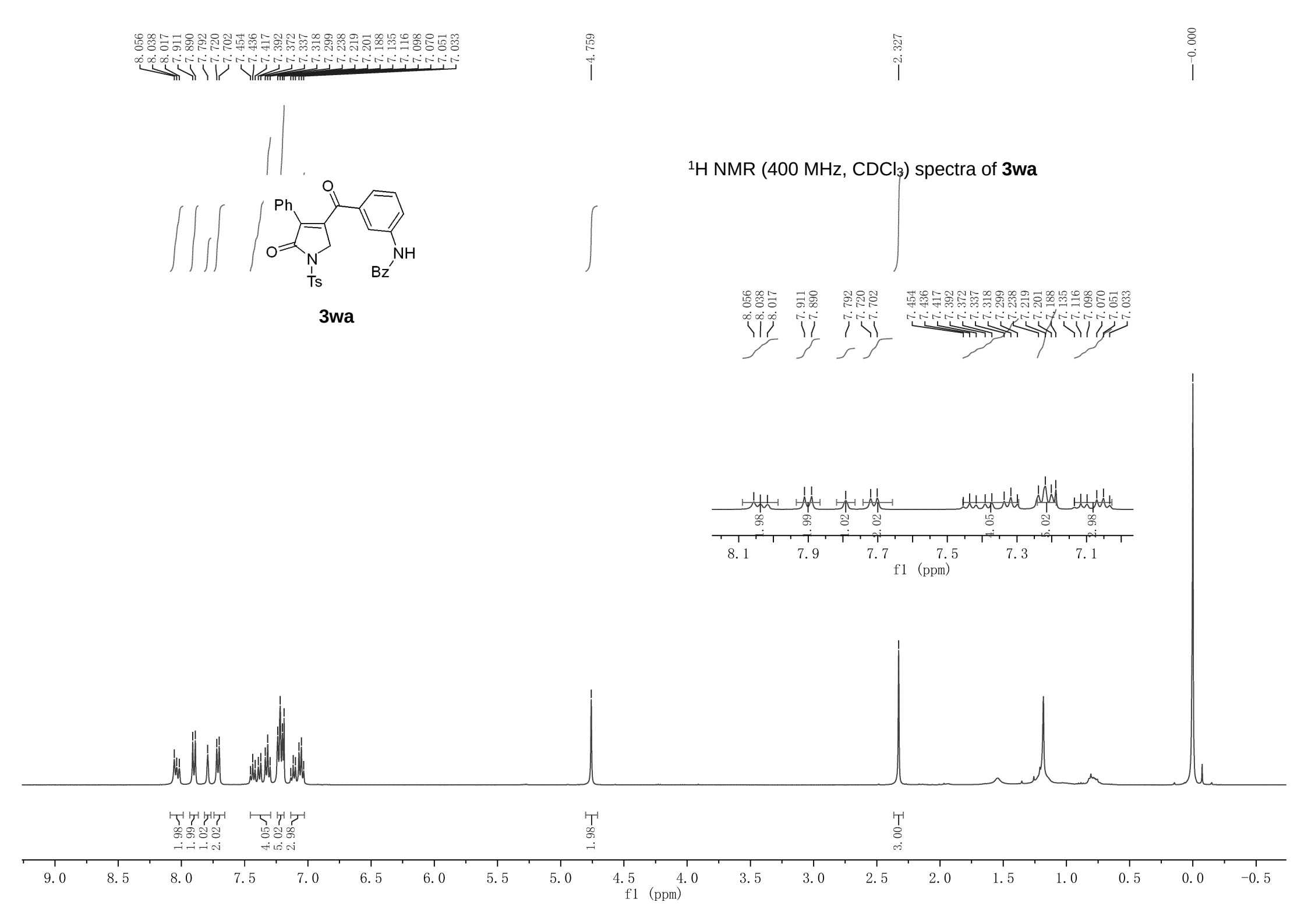
193.00
152.46
145.75
135.30
134.75
132.70
130.25
129.97
128.35
127.93
127.22
123.90
118.42
118.30
113.81
110.85
77.32
77.00
76.68
29.30
21.65



3v

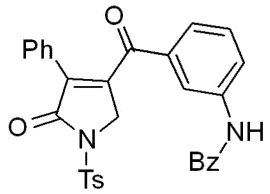
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3v**



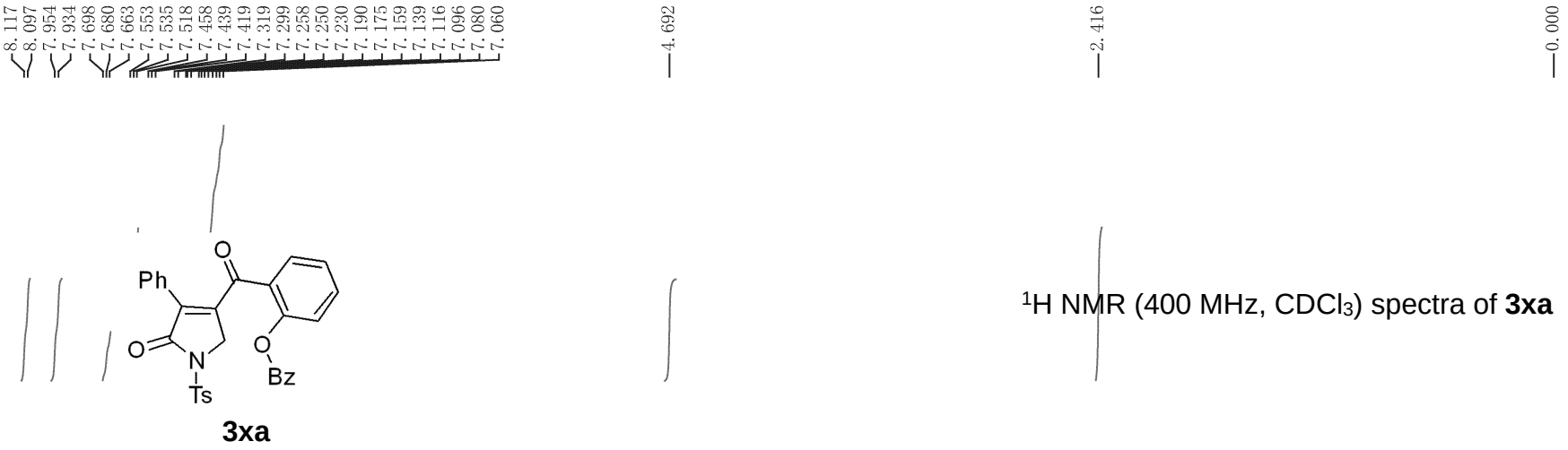

8.056
8.038
8.017
7.911
7.890
7.792
7.720
7.702
7.454
7.436
7.417
7.392
7.372
7.337
7.318
7.299
7.238
7.219
7.201
7.188
7.135
7.116
7.098
7.070
7.051
7.033
4.759
2.327
0.000
Ph
O
O
N
Ts
NH
Bz
3wa
1H NMR (400 MHz, CDCl3) spectra of 3wa
1.98
1.99
1.02
2.02
4.05
5.02
2.98
1.98
3.00
f1 (ppm)

192.06
166.77
165.70
147.91
145.65
138.78
136.50
134.96
134.71
134.20
132.13
129.89
129.83
129.64
129.18
128.75
128.61
128.34
128.28
127.04
125.83
125.08
120.63
77.32
77.00
76.68
50.78
21.68

^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3wa**

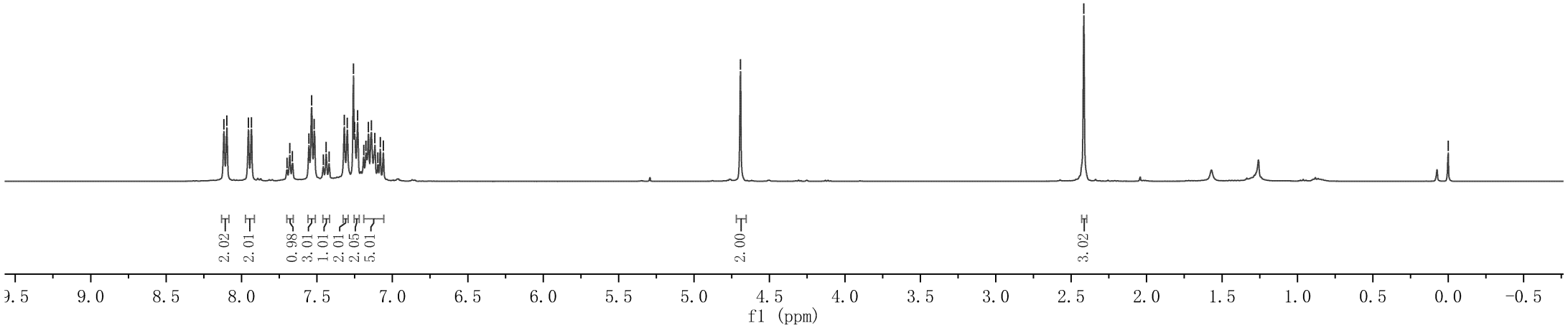


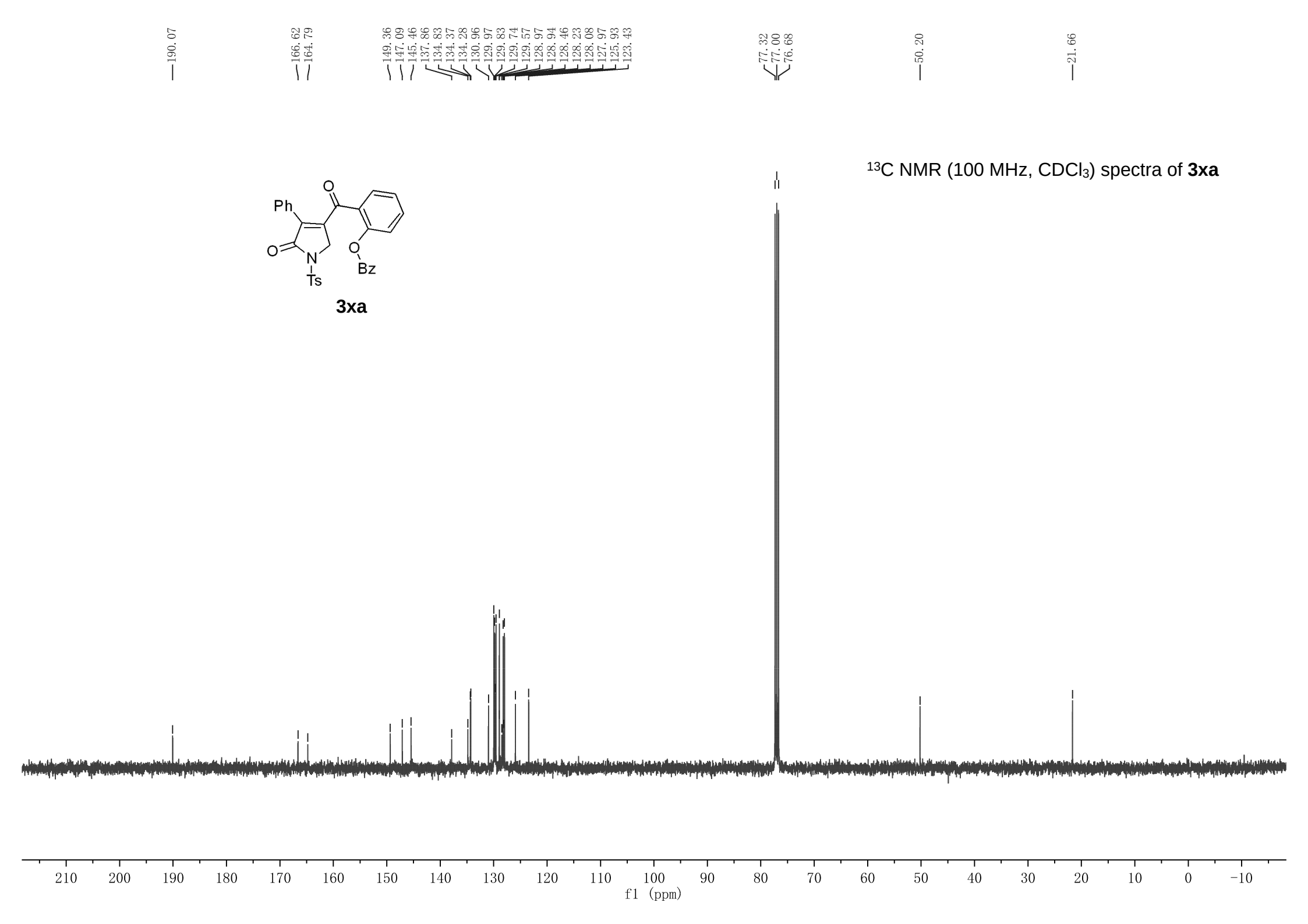
3wa

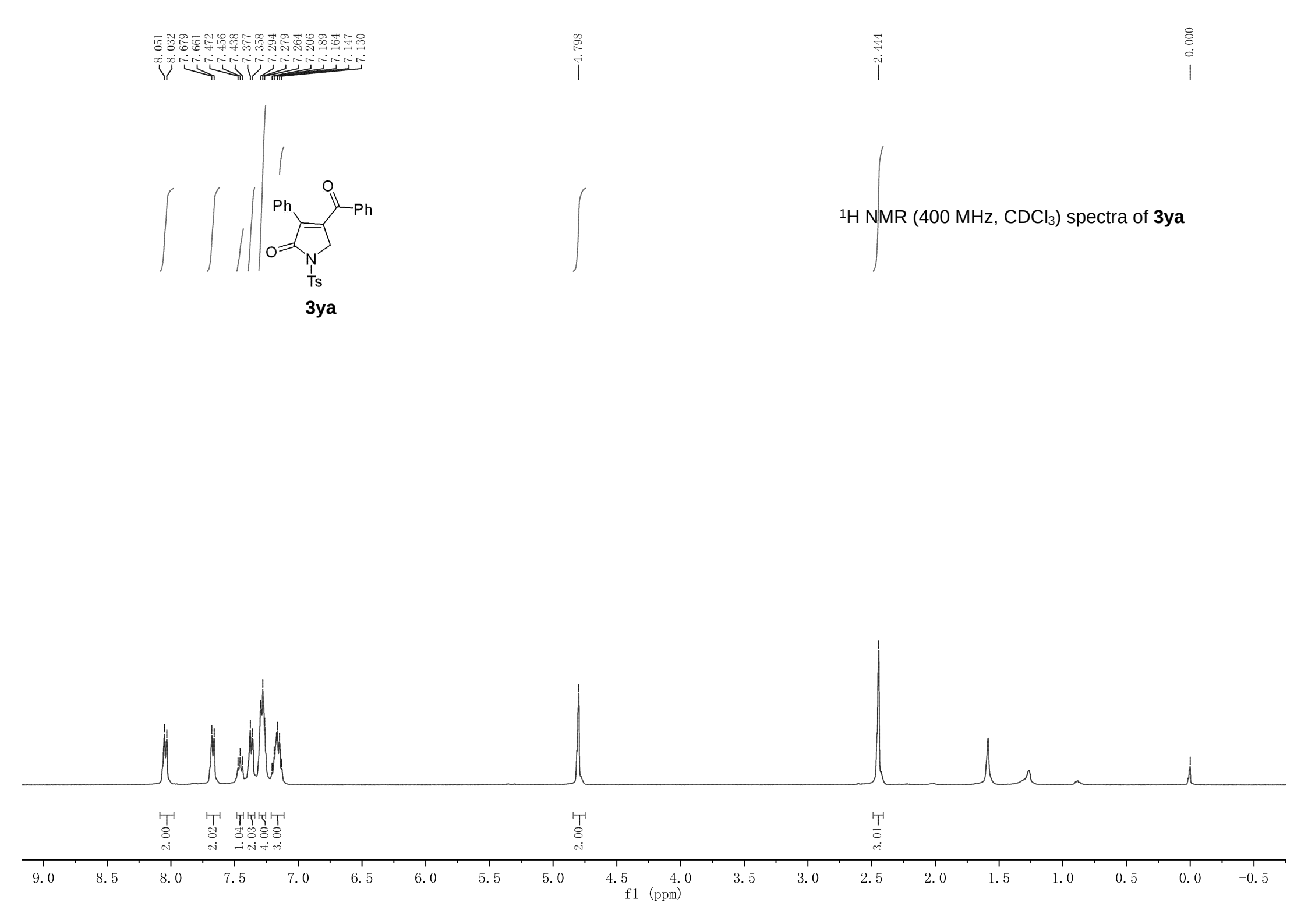


3xa

^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3xa**

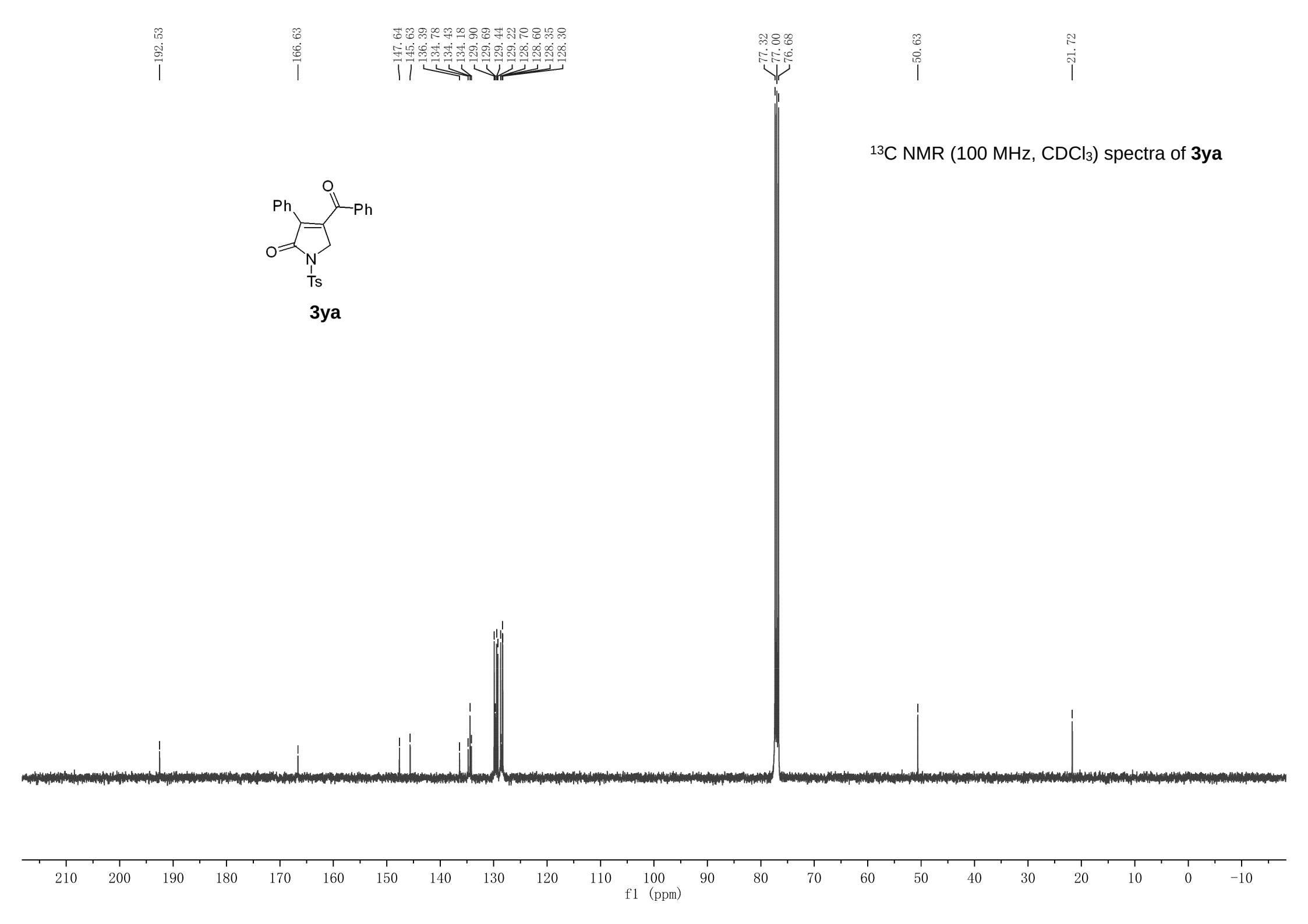


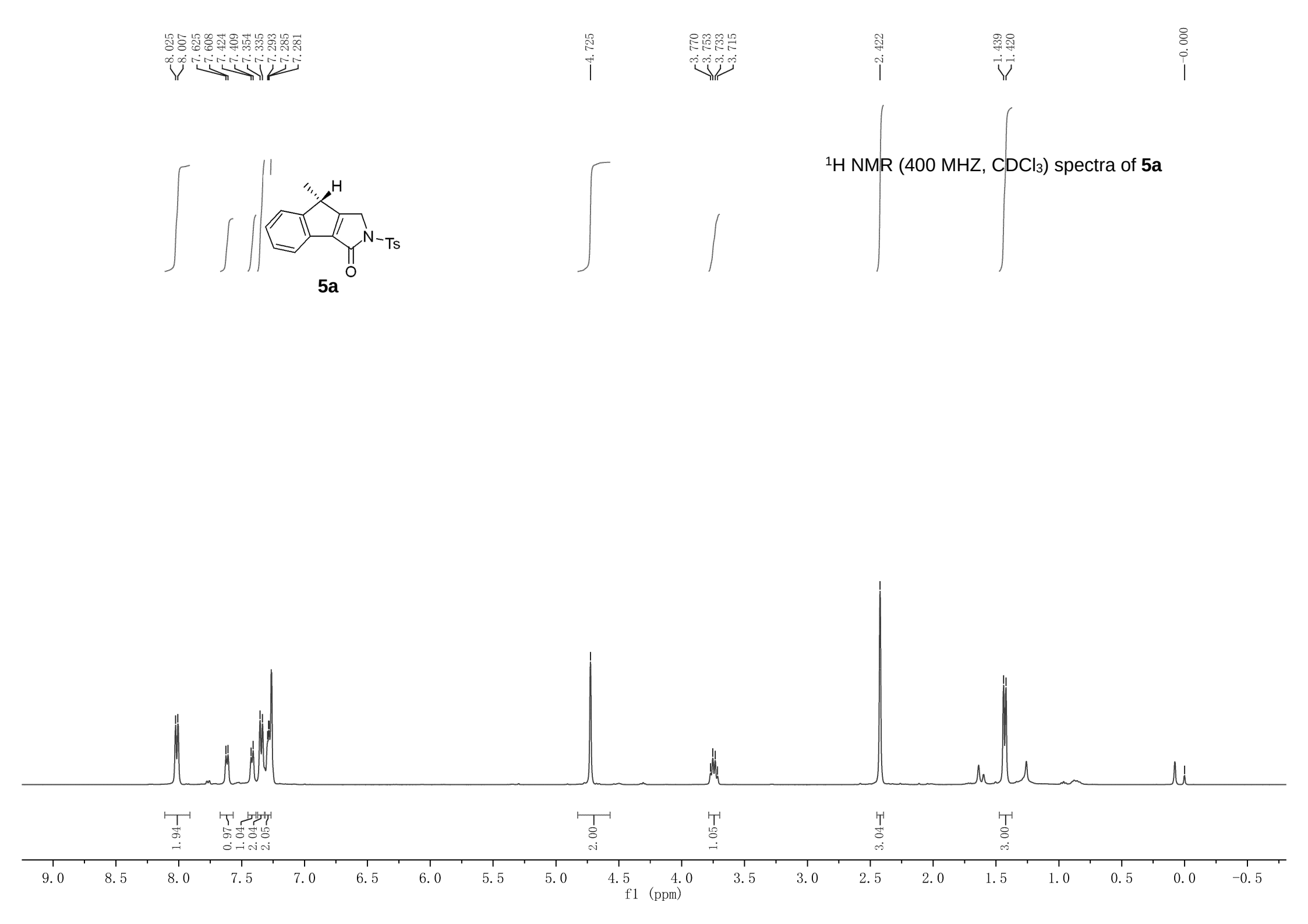

190.07
166.62
164.79
149.36
147.09
145.46
137.86
134.83
134.37
134.28
130.96
129.97
129.83
129.74
129.57
128.97
128.94
128.46
128.23
128.08
127.97
125.93
123.43
77.32
77.00
76.68
50.20
21.66
Ph
O
O
N
Ts
O
Bz
3xa
13C NMR (100 MHz, CDCl3) spectra of 3xa
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



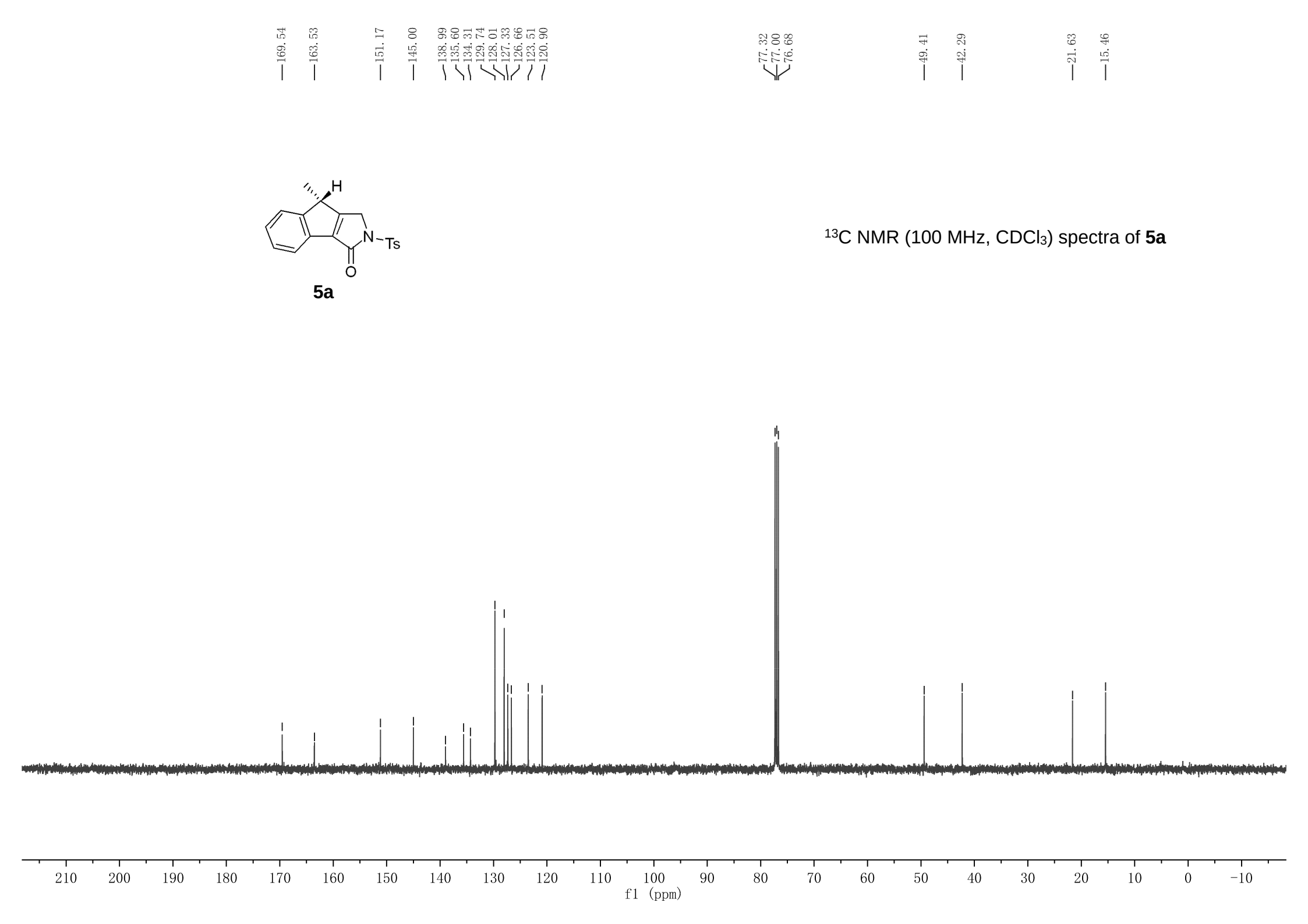
3ya

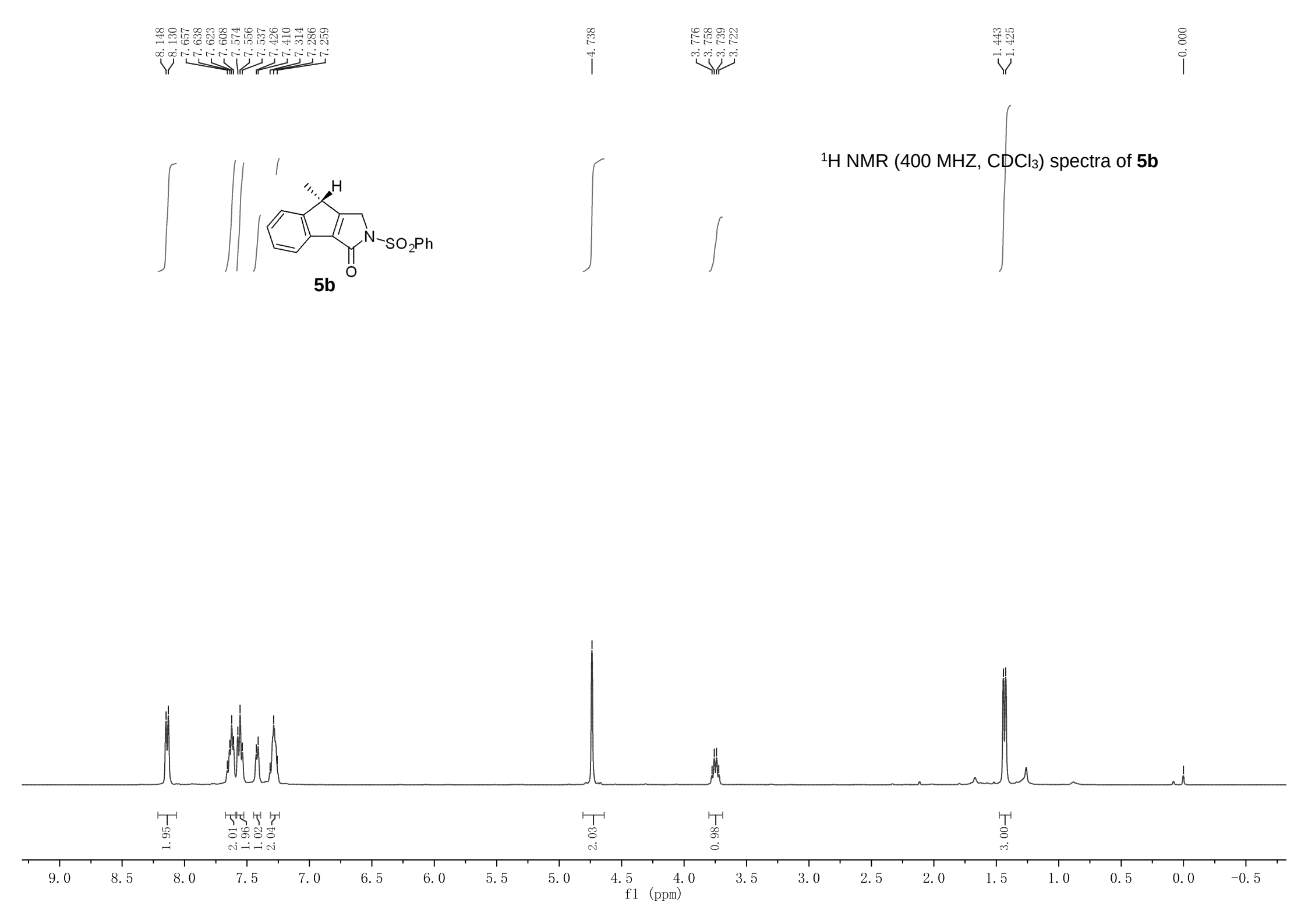
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ya**


192.53
166.63
147.64
145.63
136.39
134.78
134.43
134.18
129.90
129.69
129.44
129.22
128.70
128.60
128.35
128.30
77.32
77.00
76.68
50.63
21.72
Ph
O
Ph
O
N
Ts
3ya
13C NMR (100 MHz, CDCl3) spectra of 3ya
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)

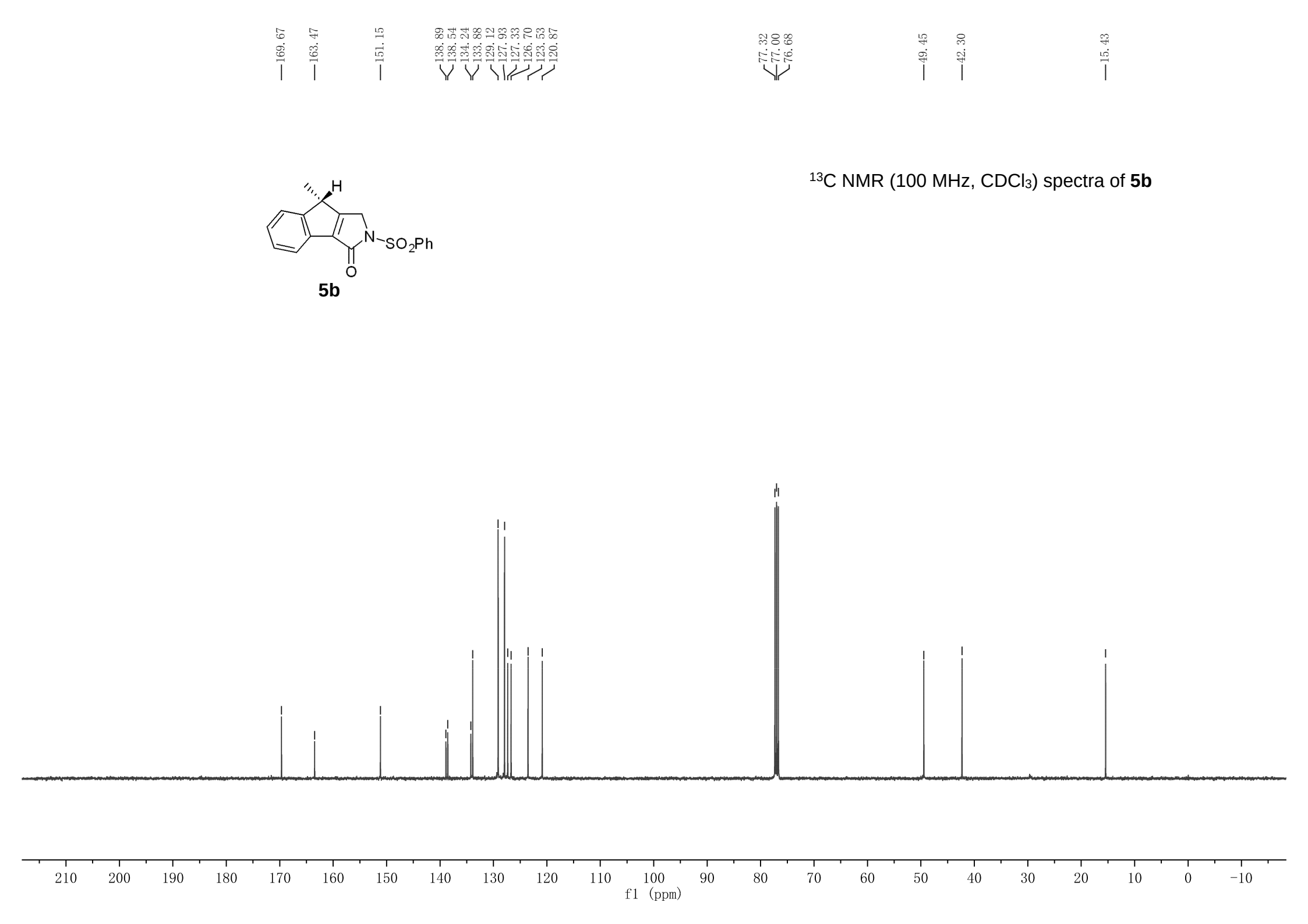


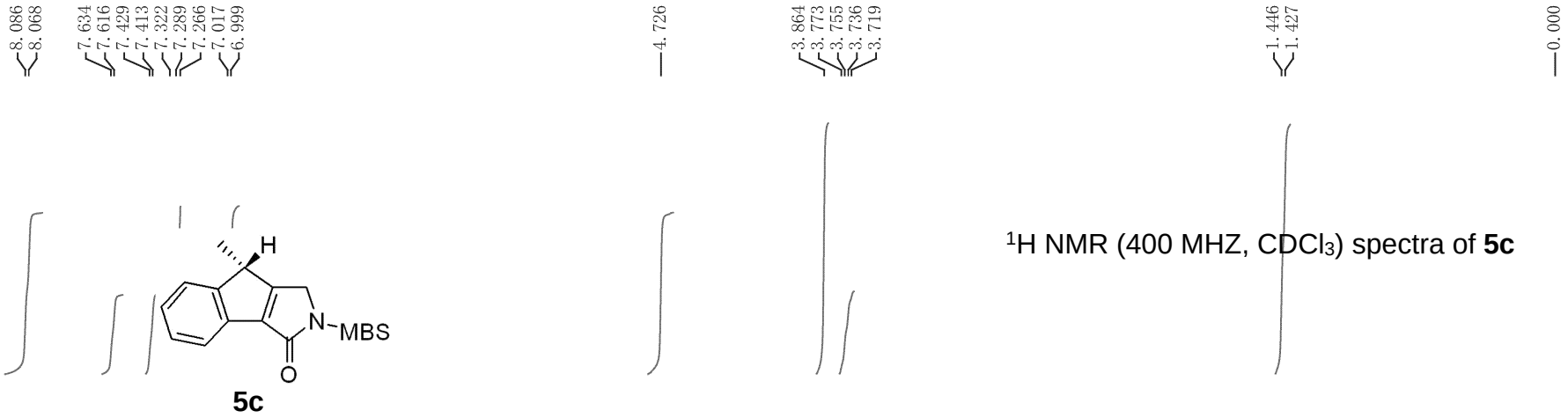
^{1}H NMR (400 MHZ, $CDCl_3$) spectra of **5a**


169.54
163.53
151.17
145.00
138.99
135.60
134.31
129.74
128.01
127.33
126.66
123.51
120.90
77.32
77.00
76.68
49.41
42.29
21.63
15.46
H
N
Ts
O
5a
13C NMR (100 MHz, CDCl3) spectra of 5a
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)



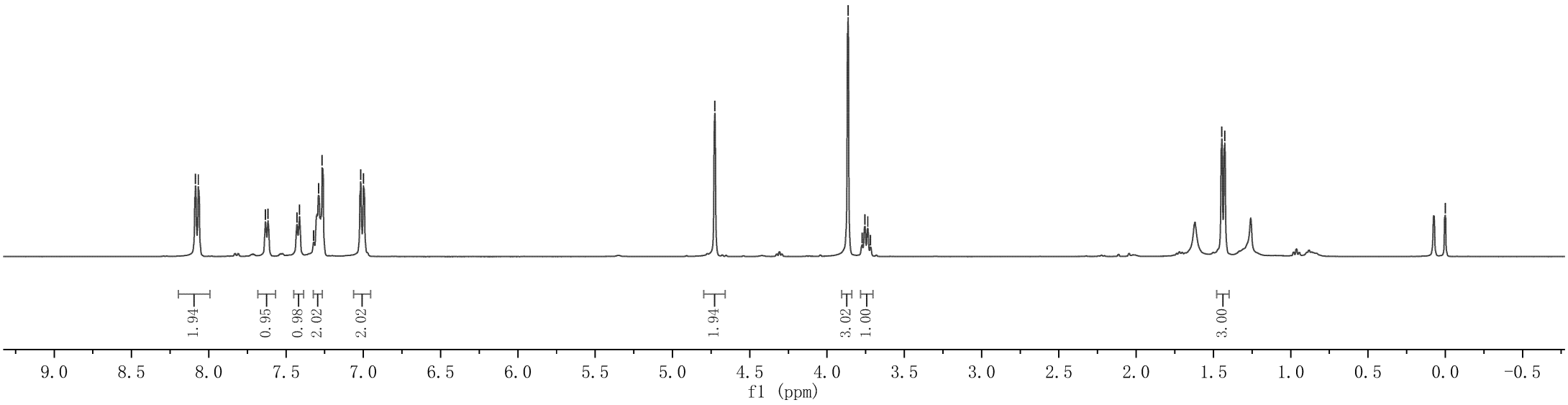
^{1}H NMR (400 MHZ, $CDCl_3$) spectra of **5b**

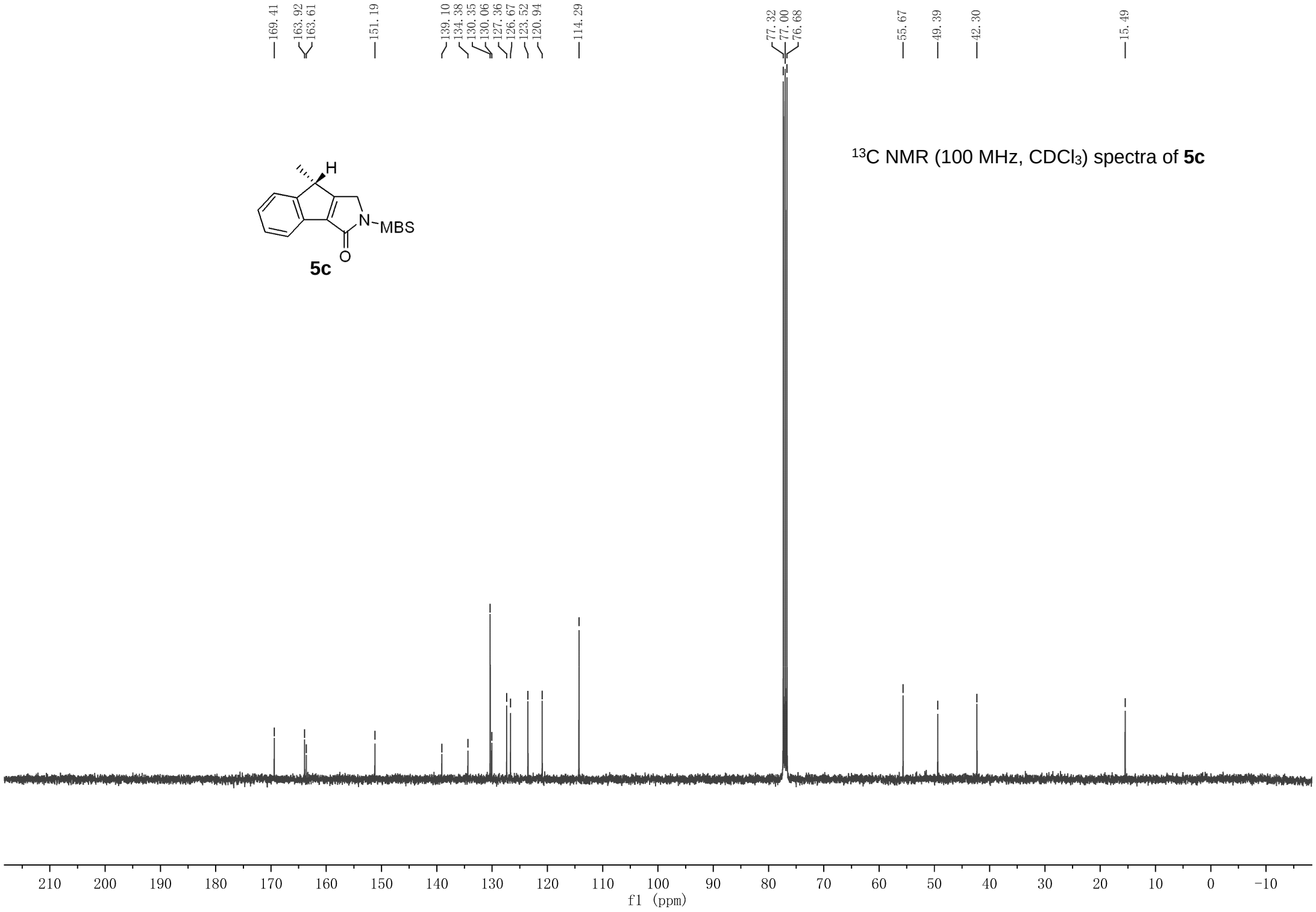

169.67
163.47
151.15
138.89
138.54
134.24
133.88
129.12
127.93
127.33
126.70
123.53
120.87
77.32
77.00
76.68
49.45
42.30
15.43
H
N
SO2Ph
O
5b
13C NMR (100 MHz, CDCl3) spectra of 5b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

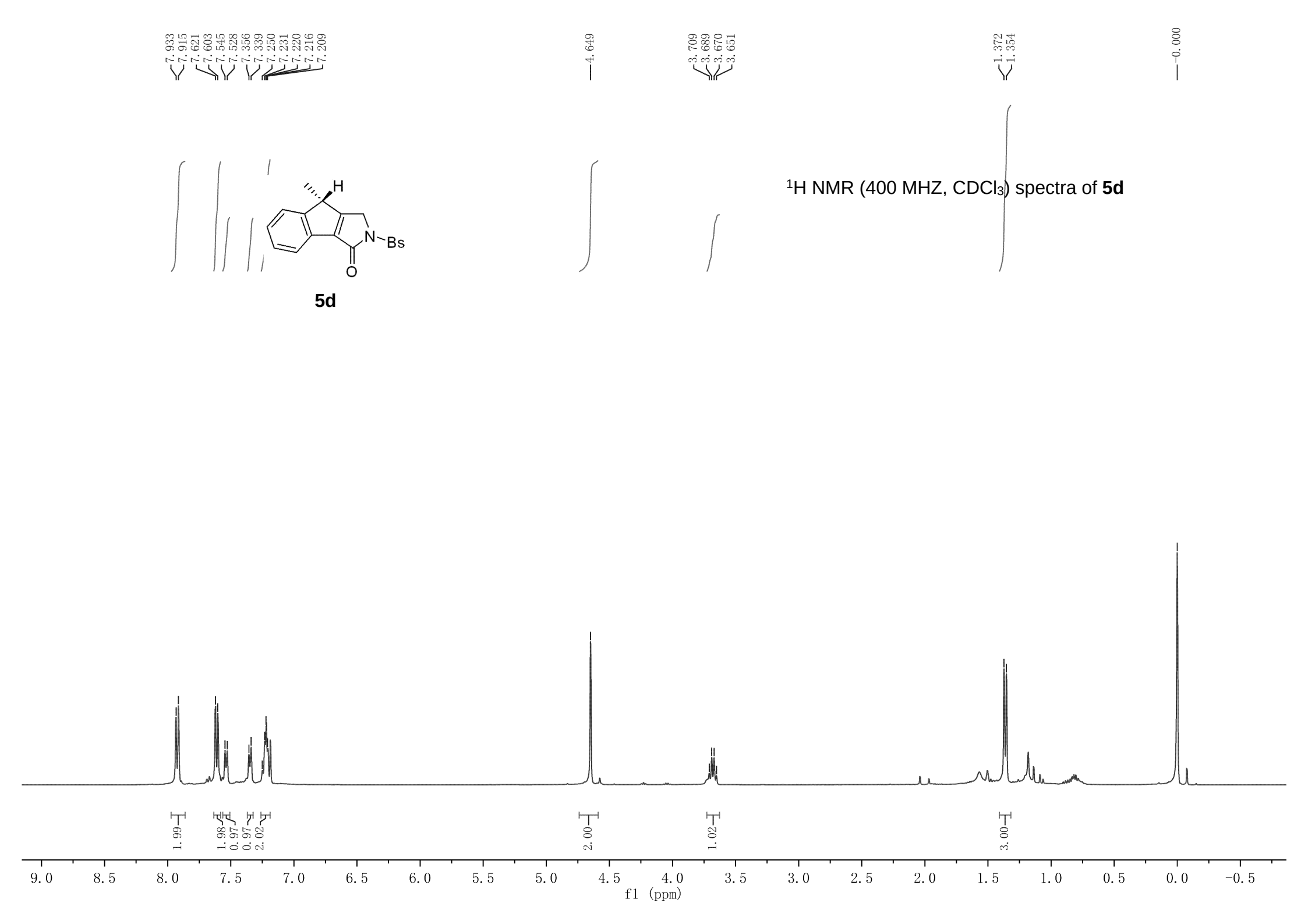


5c

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



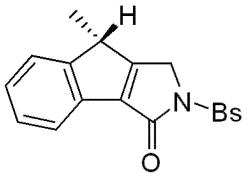

169.41
163.92
163.61
151.19
139.10
134.38
130.35
130.06
127.36
126.67
123.52
120.94
114.29
77.32
77.00
76.68
55.67
49.39
42.30
15.49
H
N
MBS
O
5c
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **5c**
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



5d

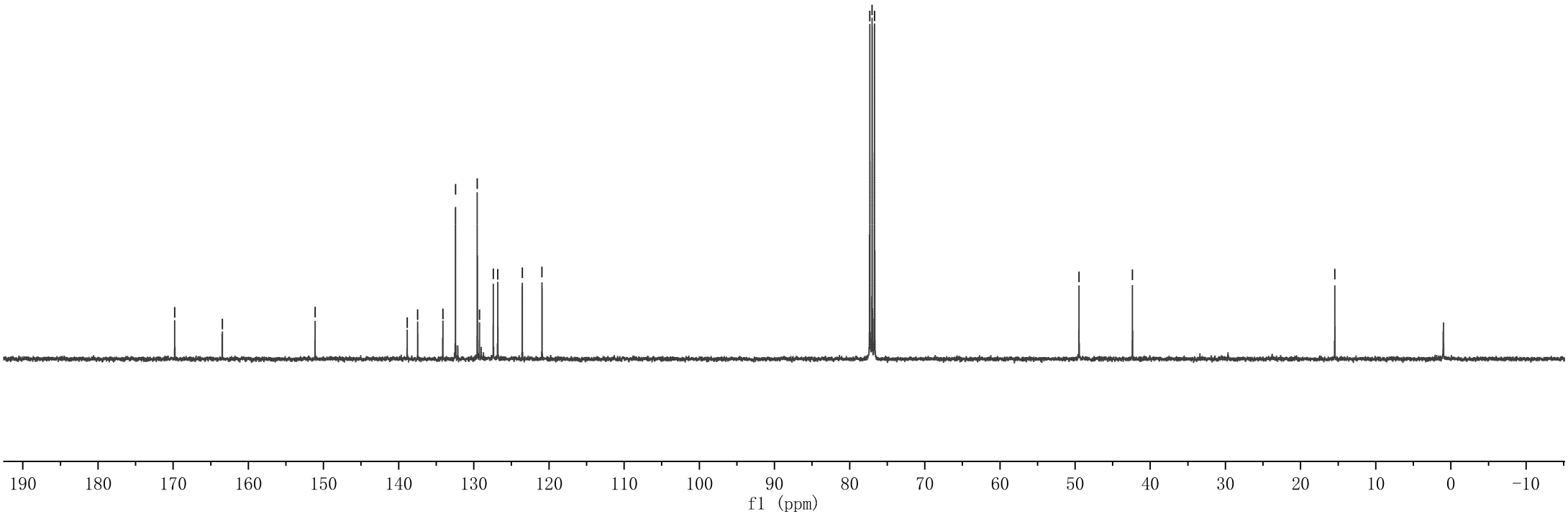
^{1}H NMR (400 MHZ, $CDCl_3$) spectra of **5d**

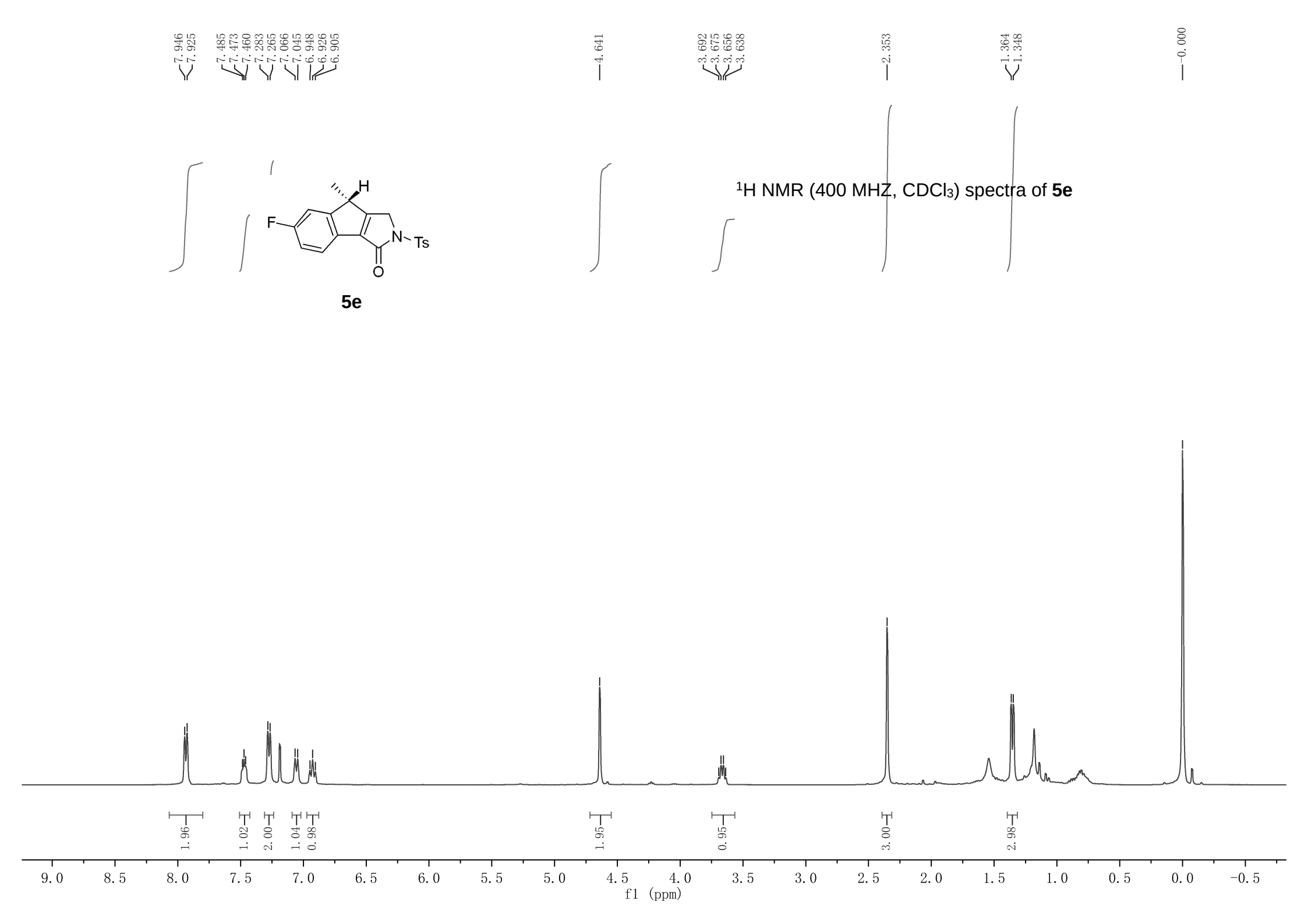
169.79
163.47
151.12
138.86
137.47
134.12
132.44
129.54
129.25
127.41
126.82
123.56
120.93
77.32
77.00
76.68
49.48
42.37
15.45



5d

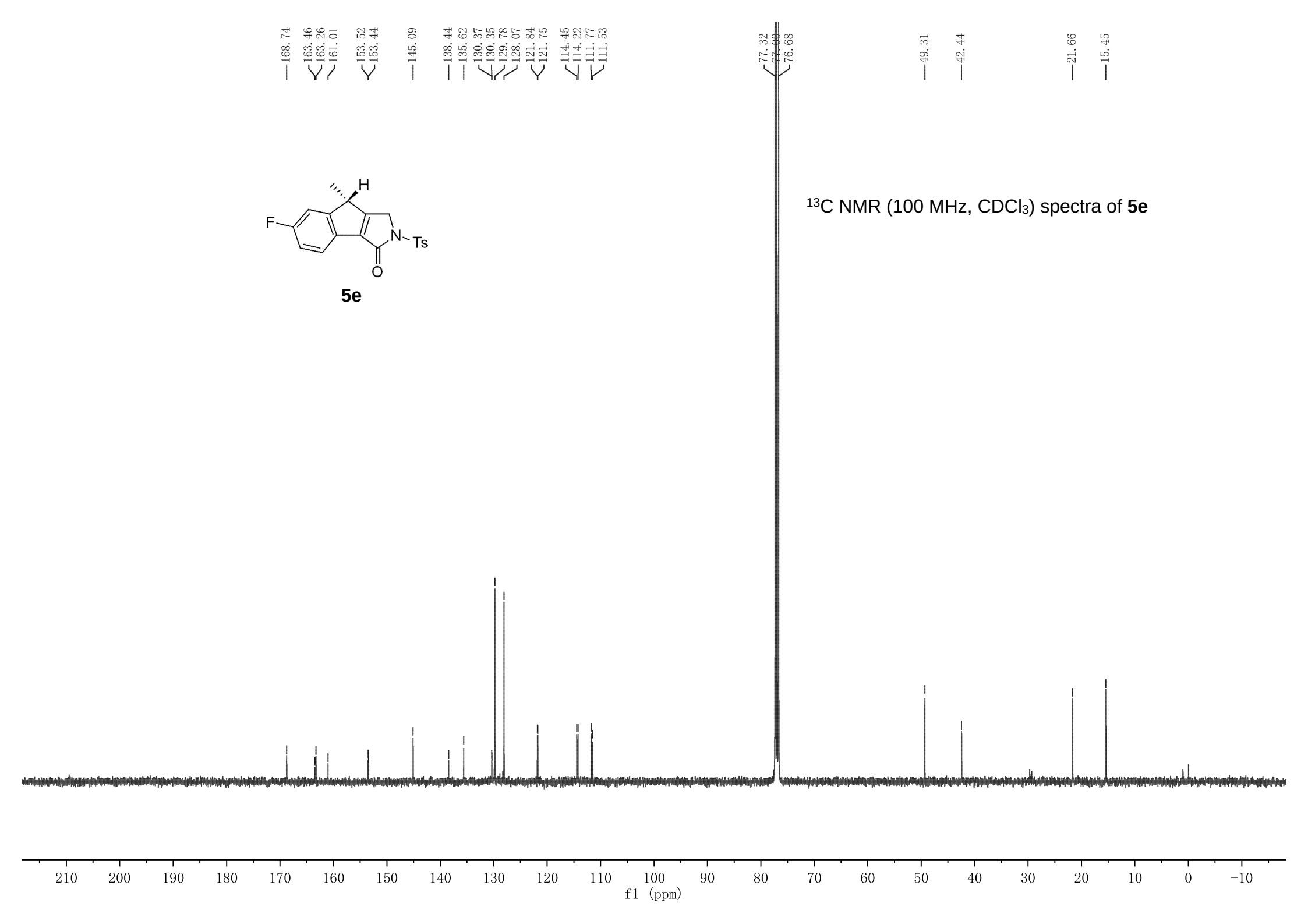
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **5d**



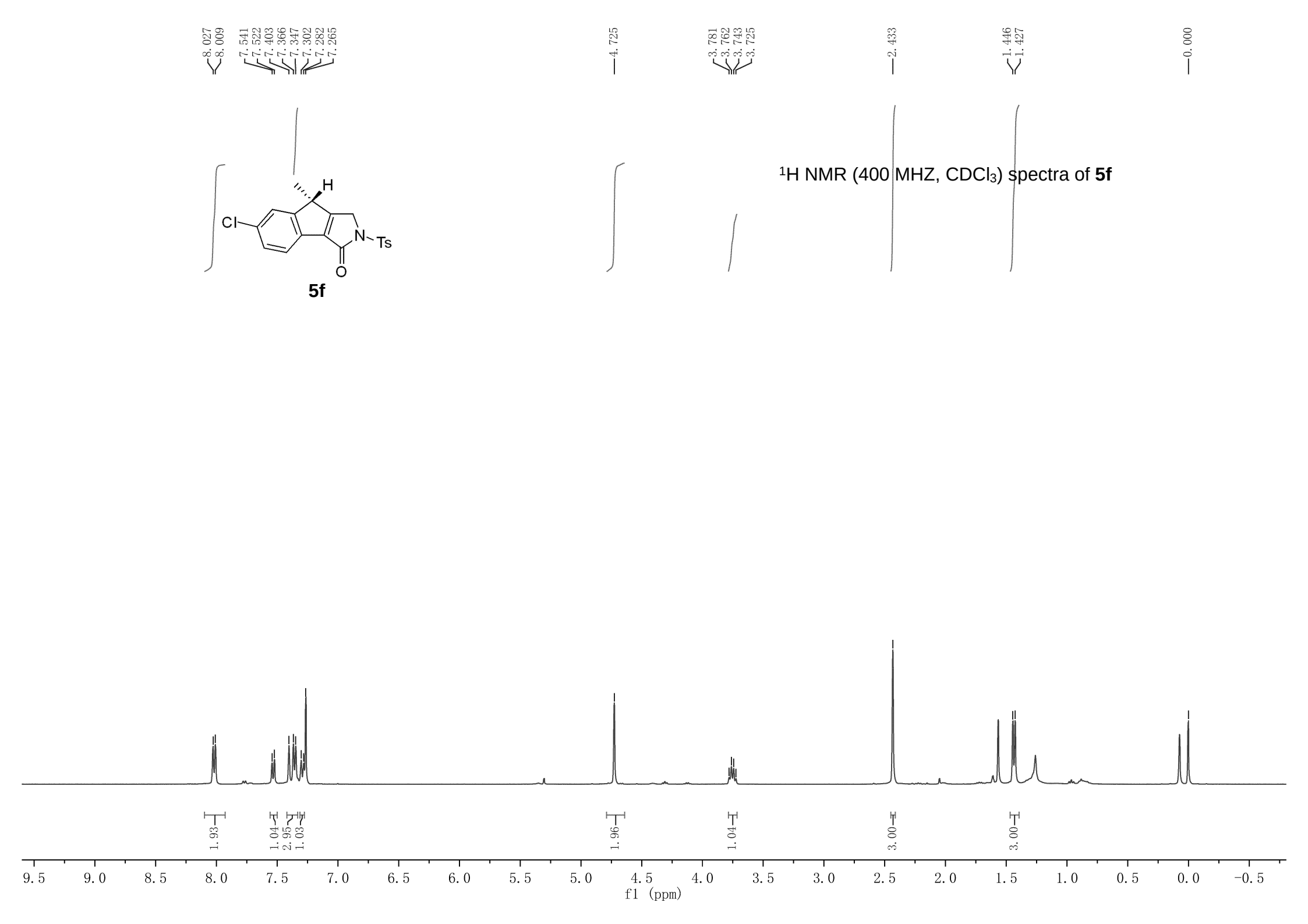


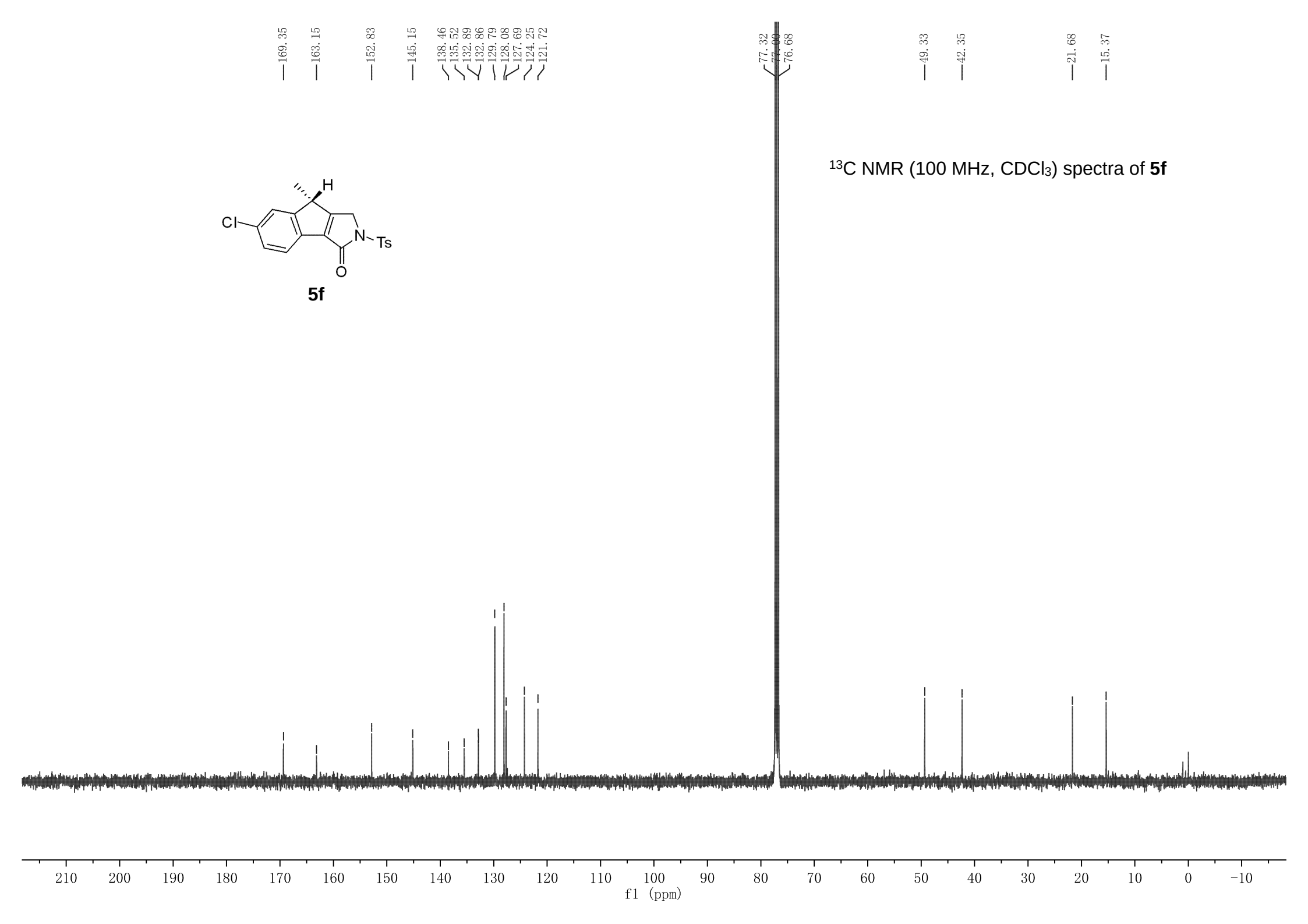
5e

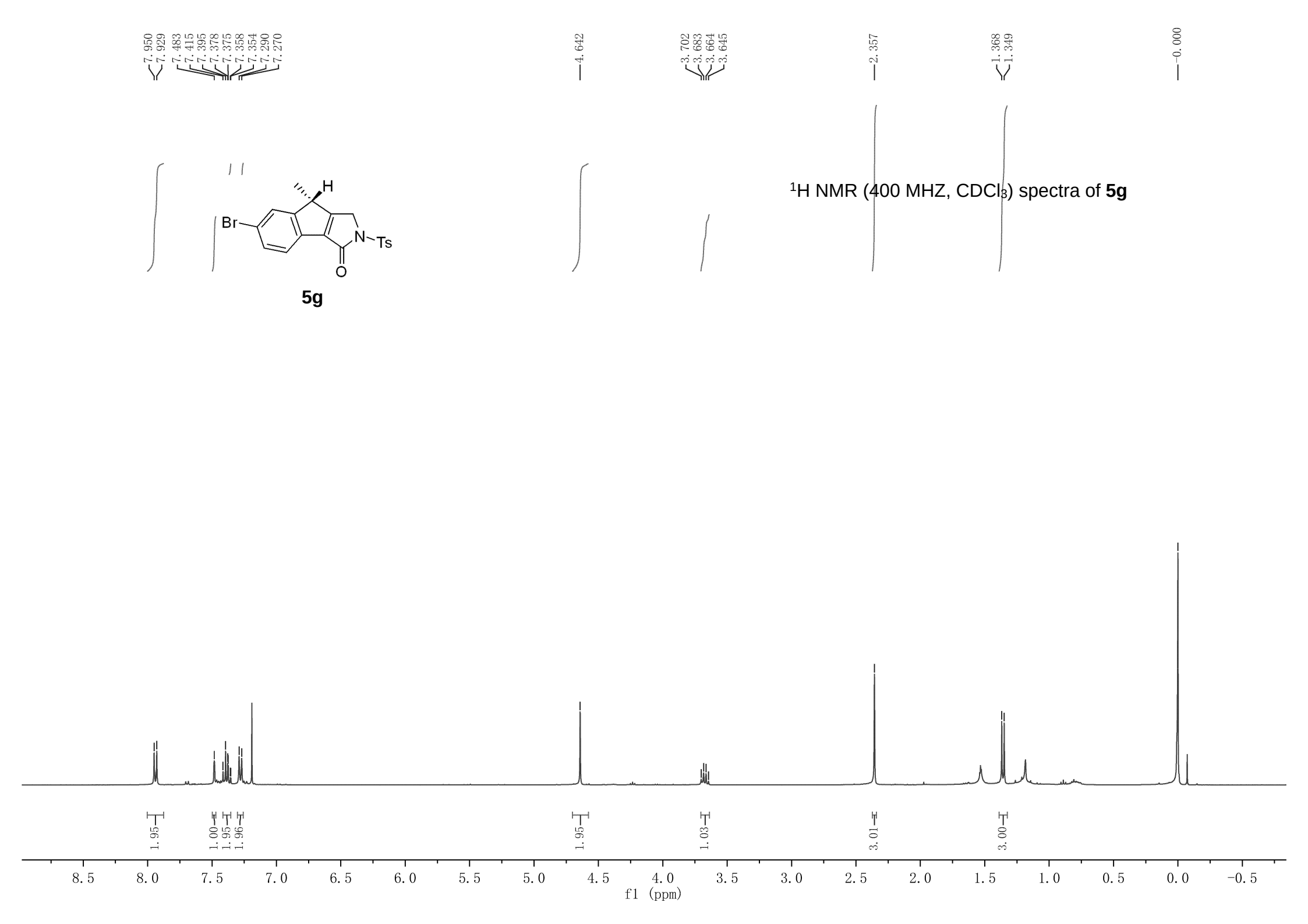
^{1}H NMR (400 MHZ, $CDCl_3$) spectra of **5e**



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

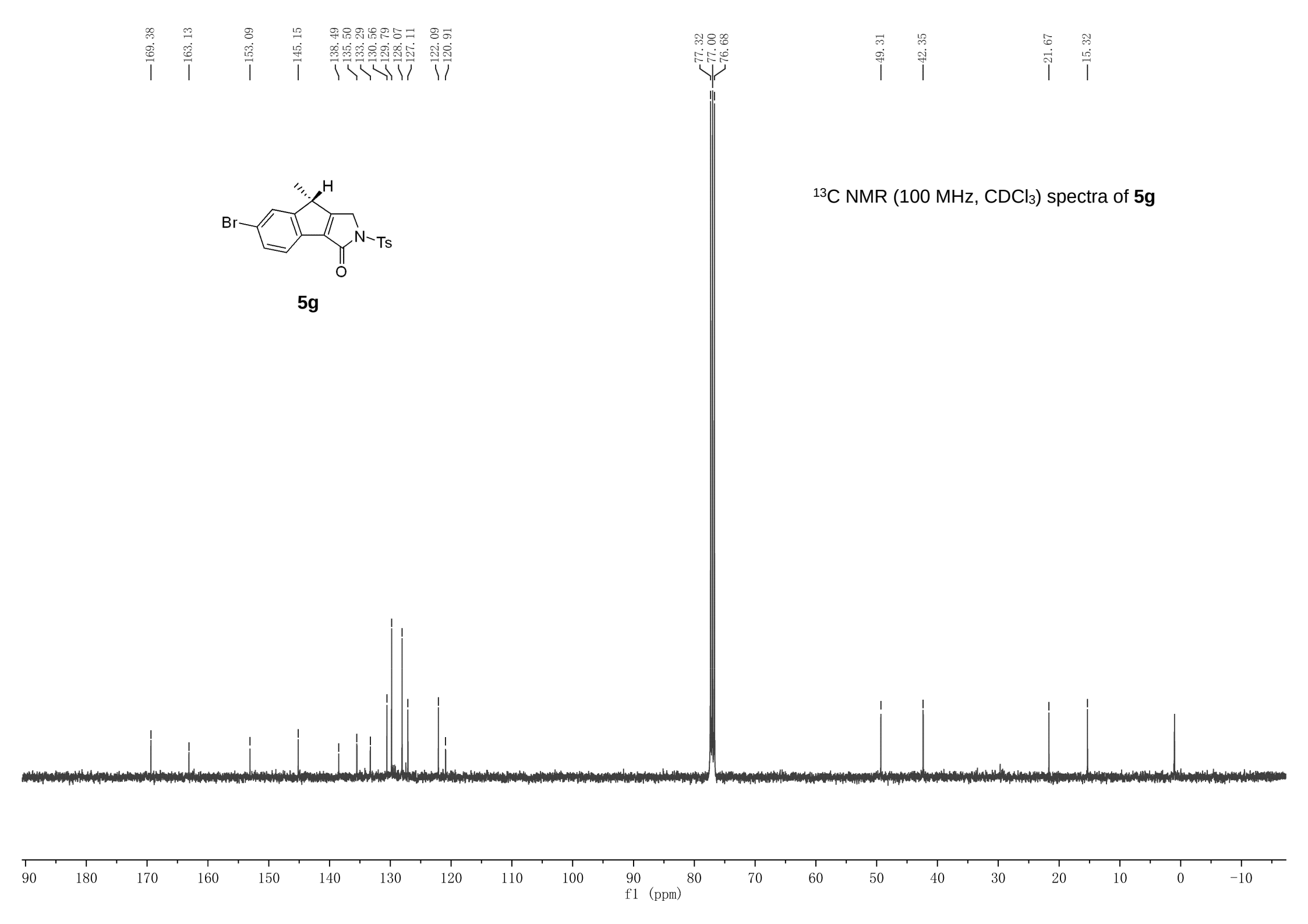

8.027
8.009
7.541
7.522
7.403
7.366
7.347
7.302
7.282
7.265
4.725
3.781
3.762
3.743
3.725
2.433
1.446
1.427
0.000
H
Cl
N
Ts
O
5f
1H NMR (400 MHZ, CDCl3) spectra of 5f
1.93
1.04
2.95
1.03
1.96
1.04
3.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


169.35
163.15
152.83
145.15
138.46
135.52
132.89
132.86
129.79
128.08
127.69
124.25
121.72
77.32
77.00
76.68
49.33
42.35
21.68
15.37
H
Cl
N
Ts
O
5f
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **5f**
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)

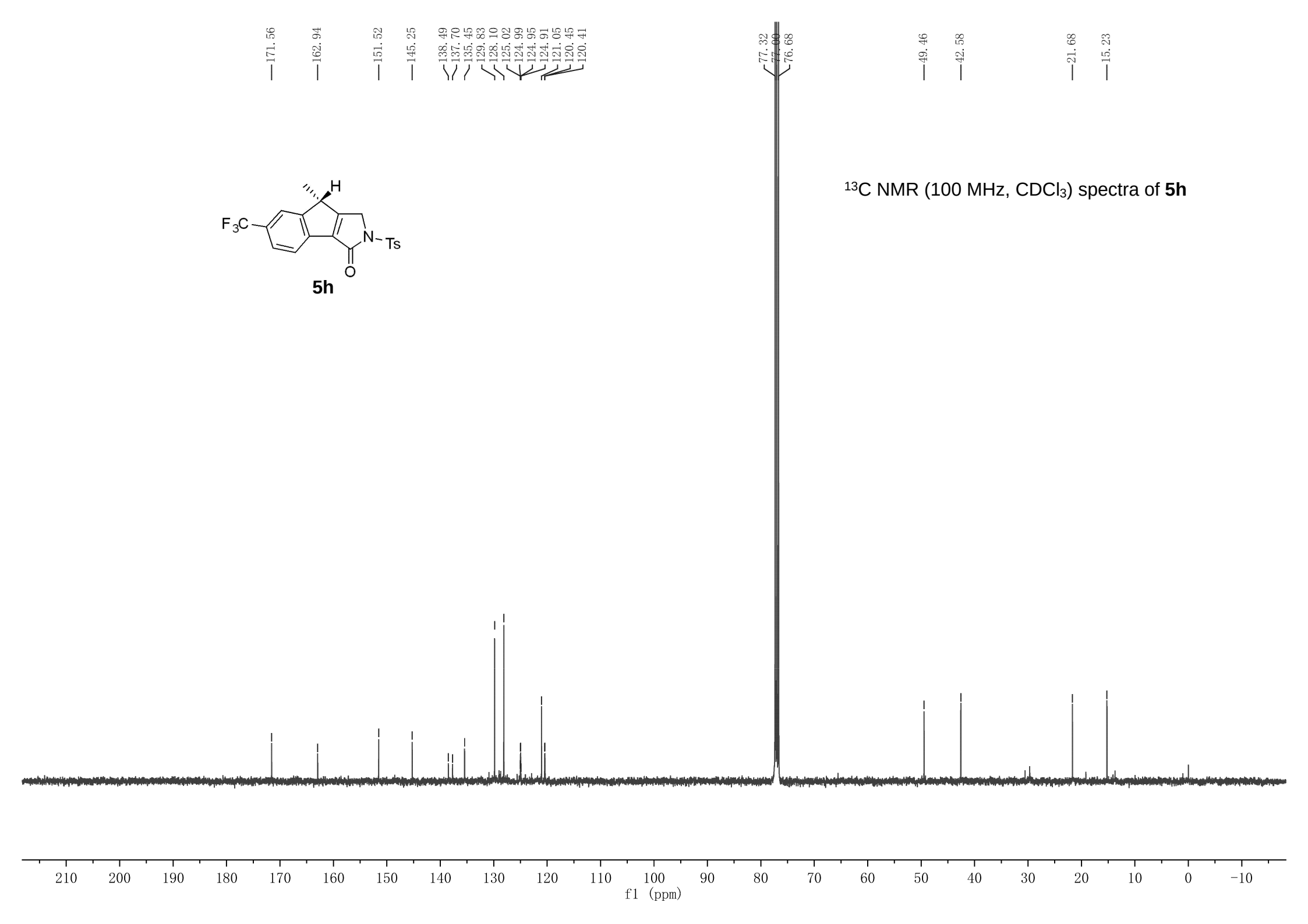


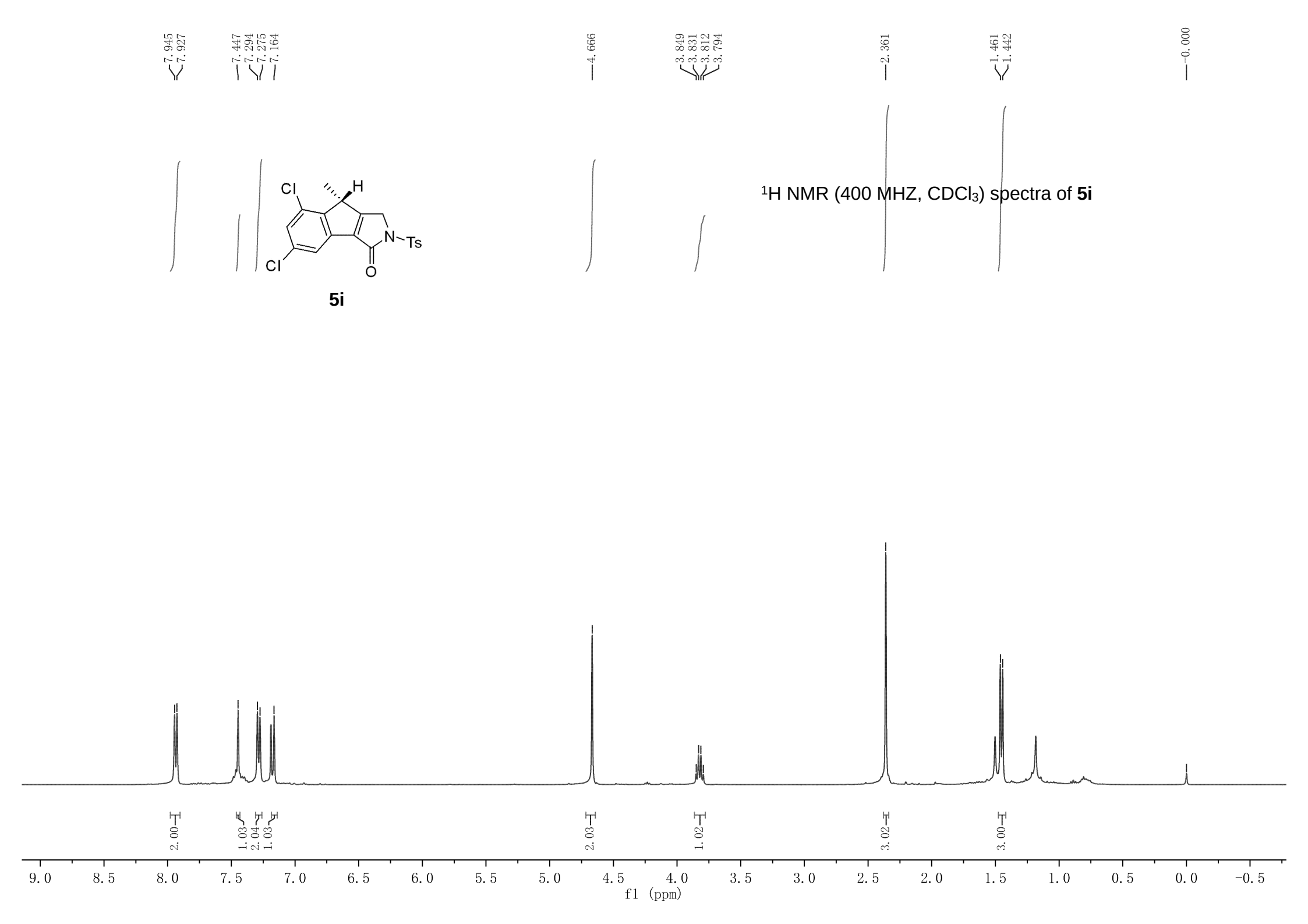
5g

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


169.38
163.13
153.09
145.15
138.49
135.50
133.29
130.56
129.79
128.07
127.11
122.09
120.91
77.32
77.00
76.68
49.31
42.35
21.67
15.32
Br
H
N
Ts
O
5g
13C NMR (100 MHz, CDCl3) spectra of 5g
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.957
7.936
7.645
7.626
7.583
7.524
7.504
7.295
7.275
4.699
3.785
3.766
3.747
3.728
2.358
1.415
1.395
0.000
H
F3C
N
Ts
O
5h
1H NMR (400 MHZ, CDCl3) spectra of 5h
1.94
1.00
0.98
1.03
2.01
1.92
0.96
3.05
3.00
f1 (ppm)

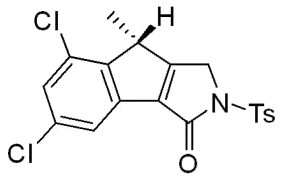

171.56
162.94
151.52
145.25
138.49
137.70
135.45
129.83
128.10
125.02
124.99
124.95
124.91
121.05
120.45
120.41
77.32
77.00
76.68
49.46
42.58
21.68
15.23
H
F3C
N
Ts
O
5h
13C NMR (100 MHz, CDCl3) spectra of 5h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)



5i

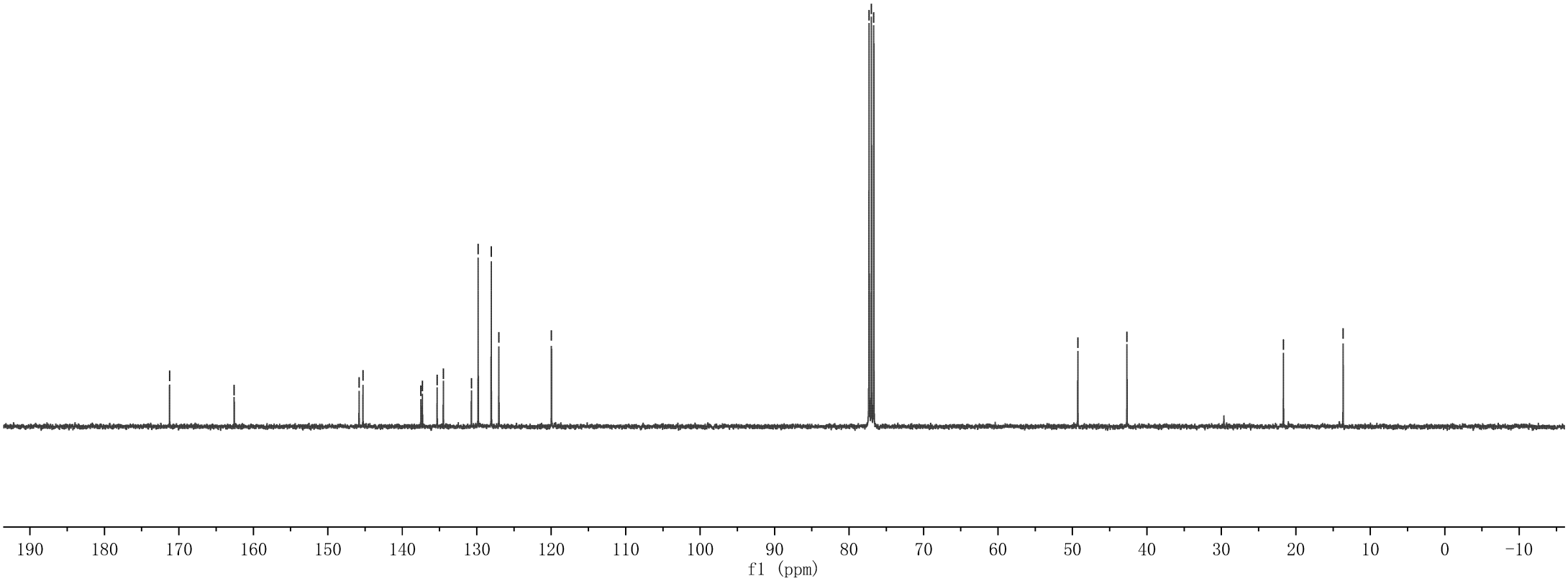
^{1}H NMR (400 MHZ, $CDCl_3$) spectra of **5i**

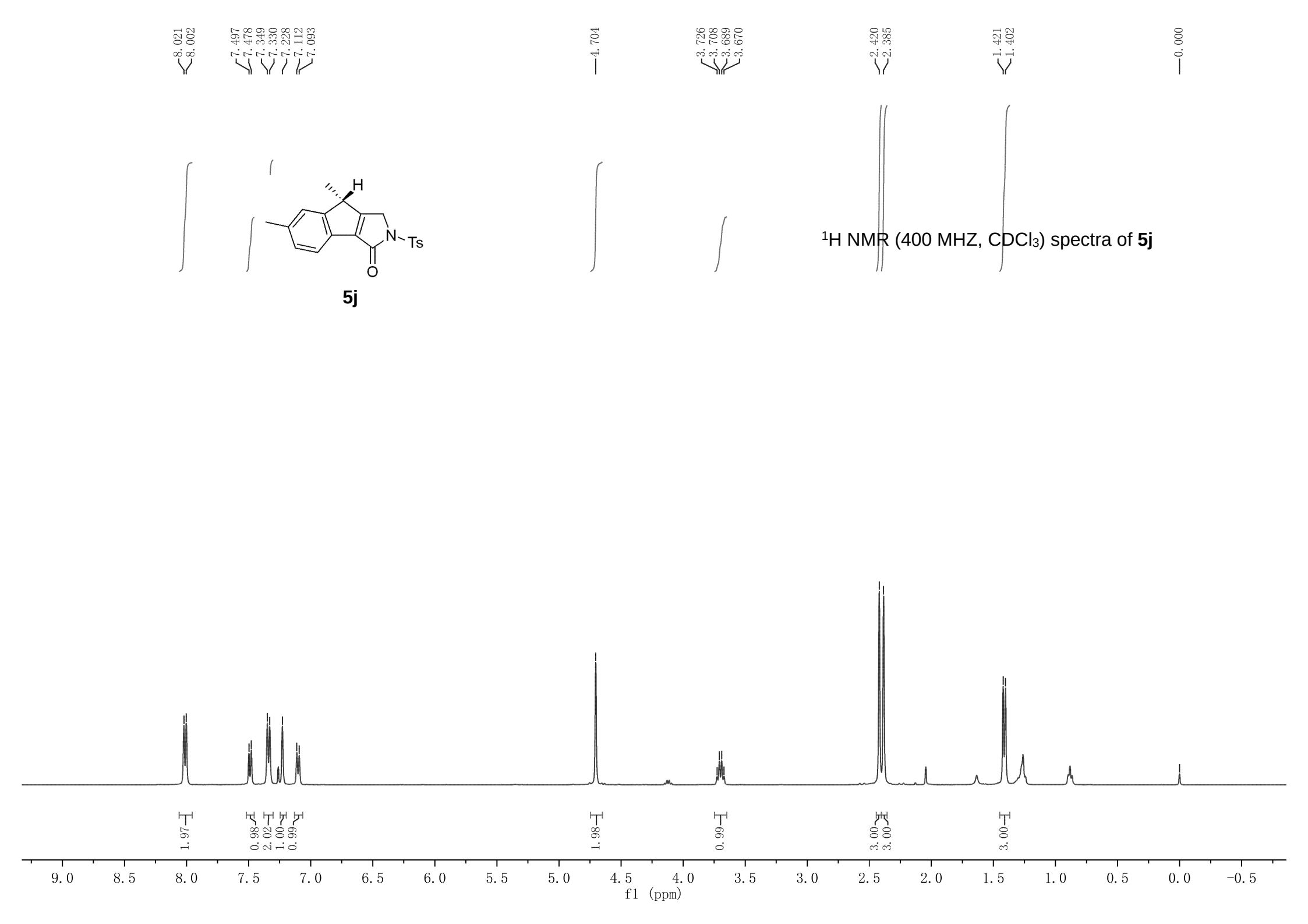
171.26
162.57
145.80
145.28
137.50
137.29
135.32
134.49
130.72
129.81
128.05
127.03
119.97
77.32
77.00
76.68
49.28
42.68
21.67
13.65



5i

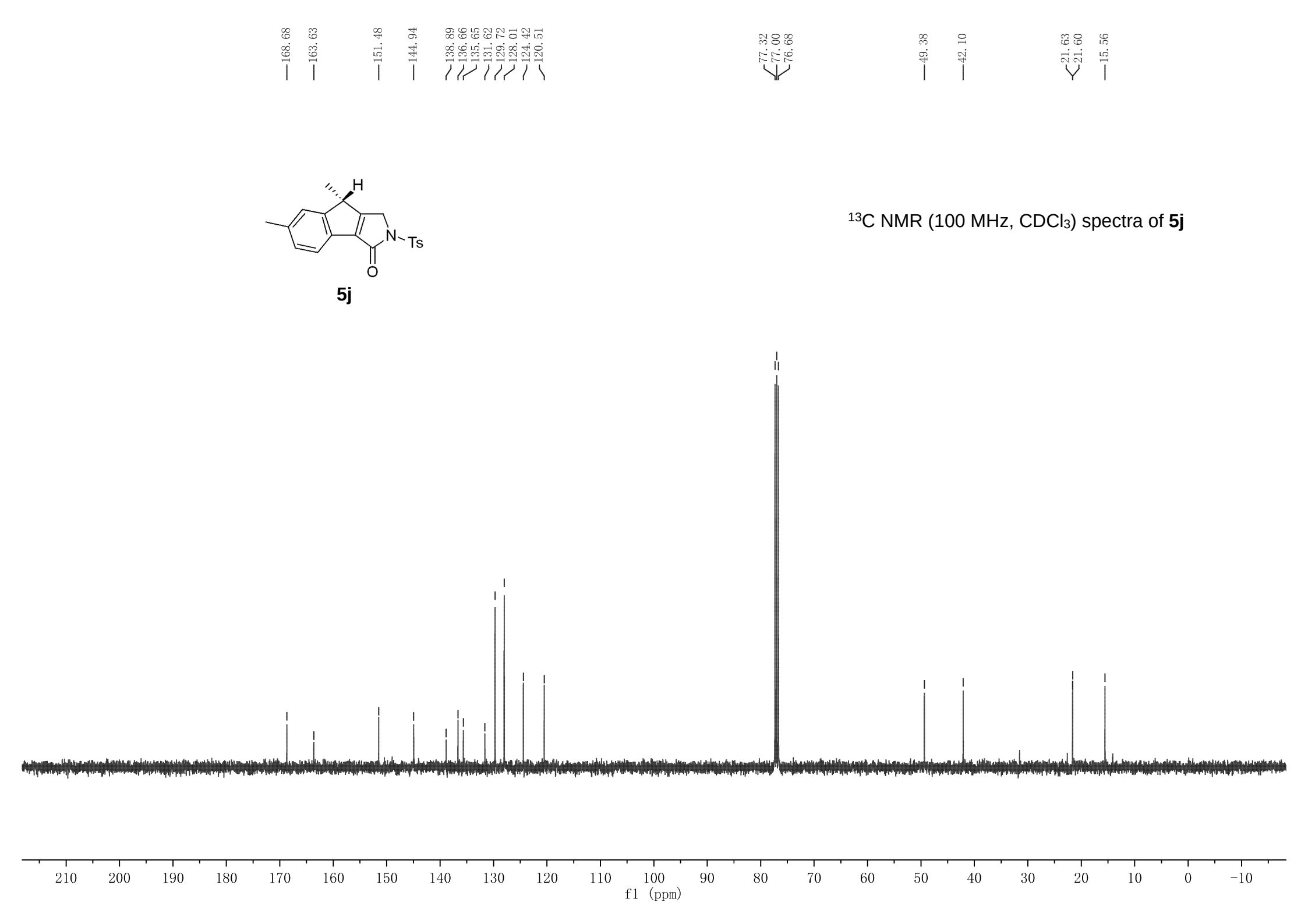
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **5i**

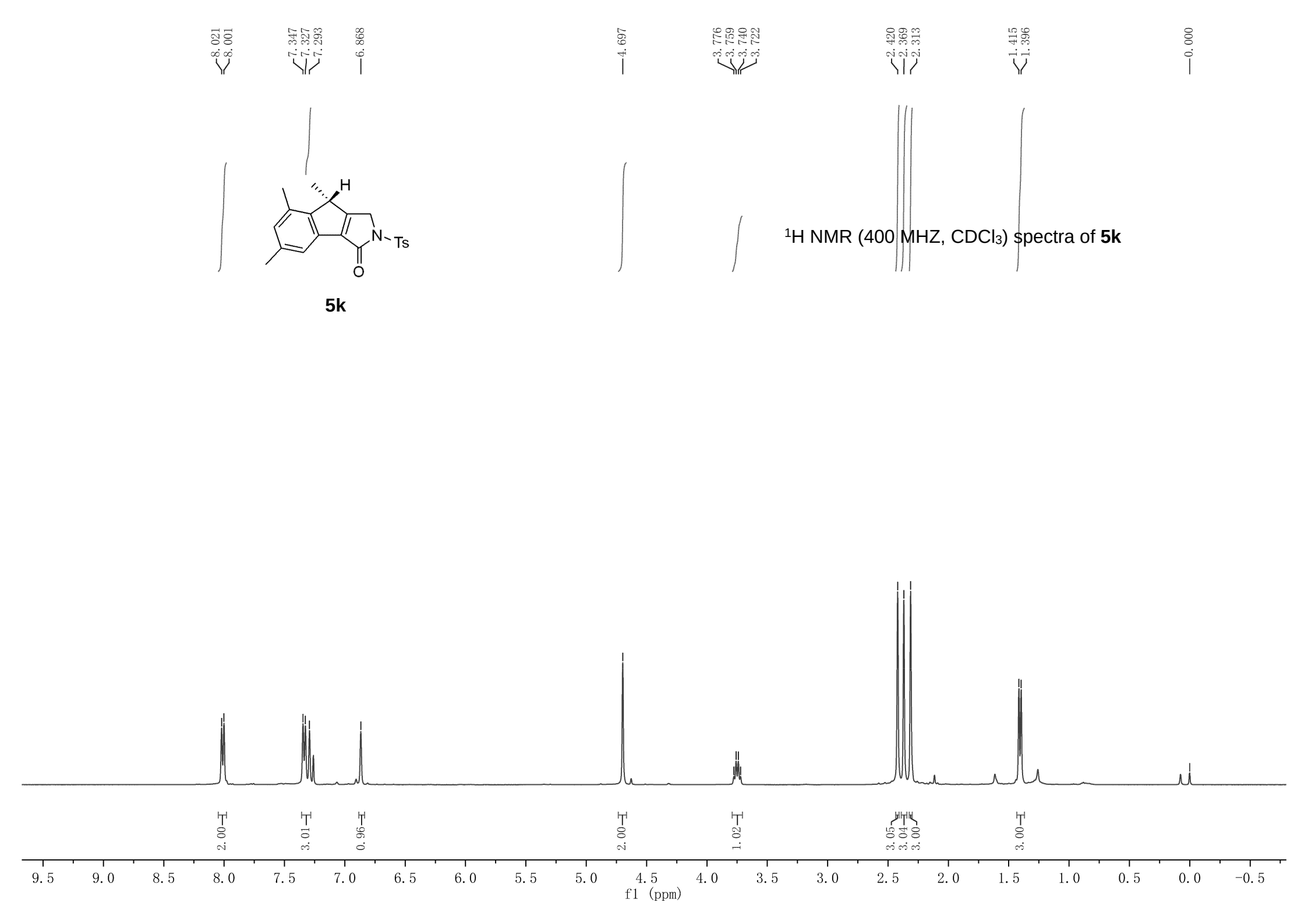




5j

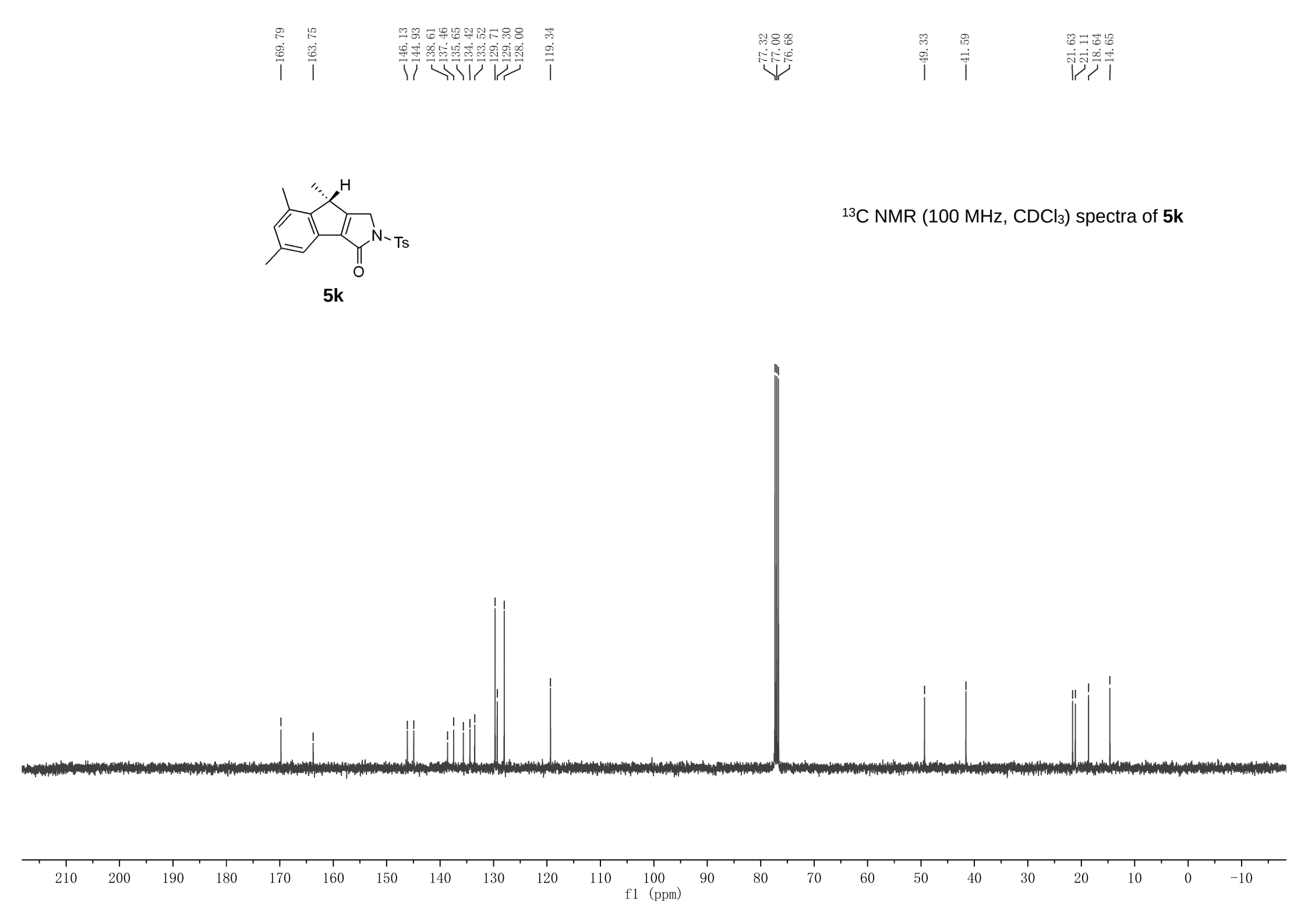
^{1}H NMR (400 MHZ, $CDCl_3$) spectra of **5j**

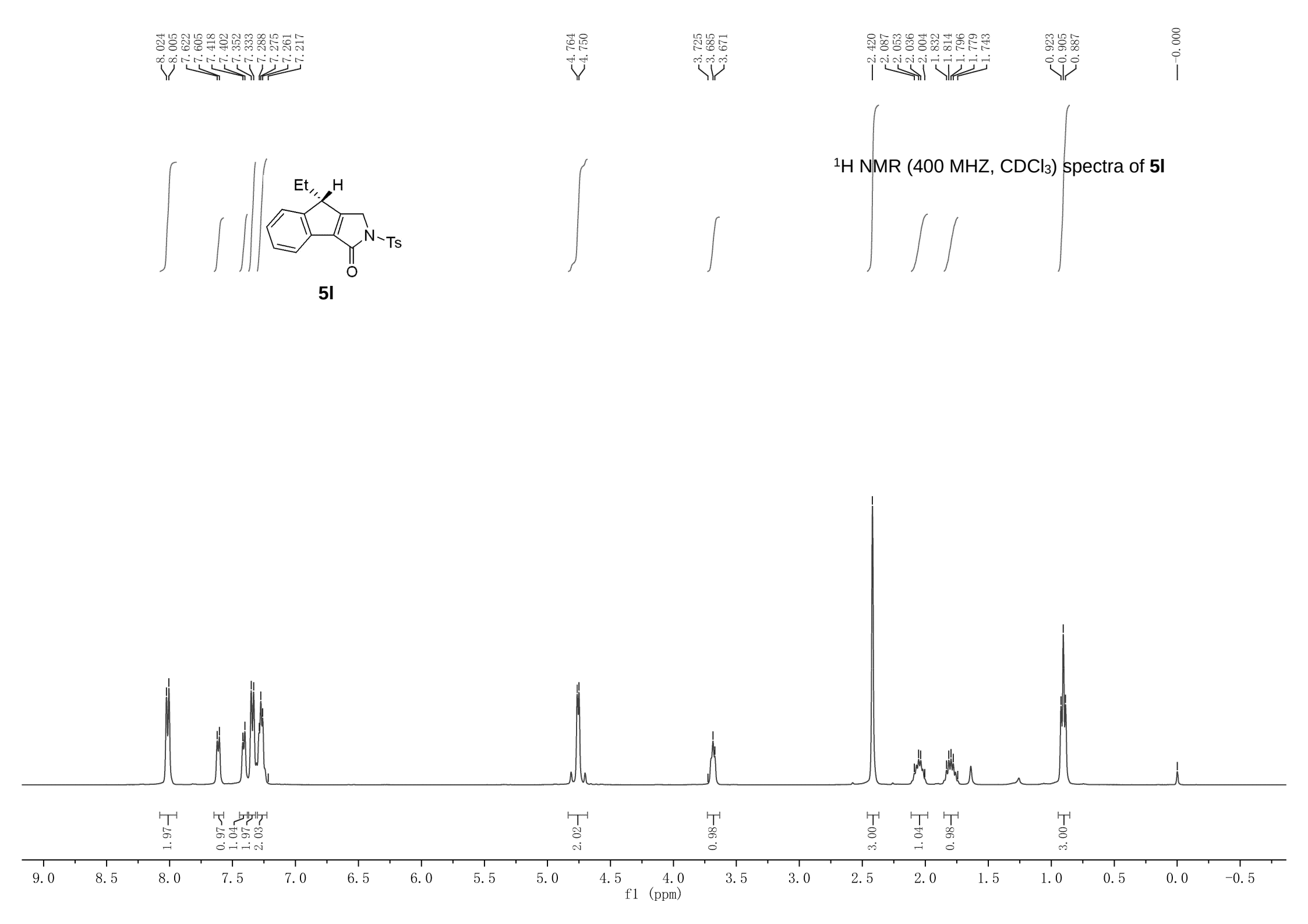

168.68
163.63
151.48
144.94
138.89
136.66
135.65
131.62
129.72
128.01
124.42
120.51
77.32
77.00
76.68
49.38
42.10
21.63
21.60
15.56
H
N
Ts
O
5j
13C NMR (100 MHz, CDCl3) spectra of 5j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)



5k

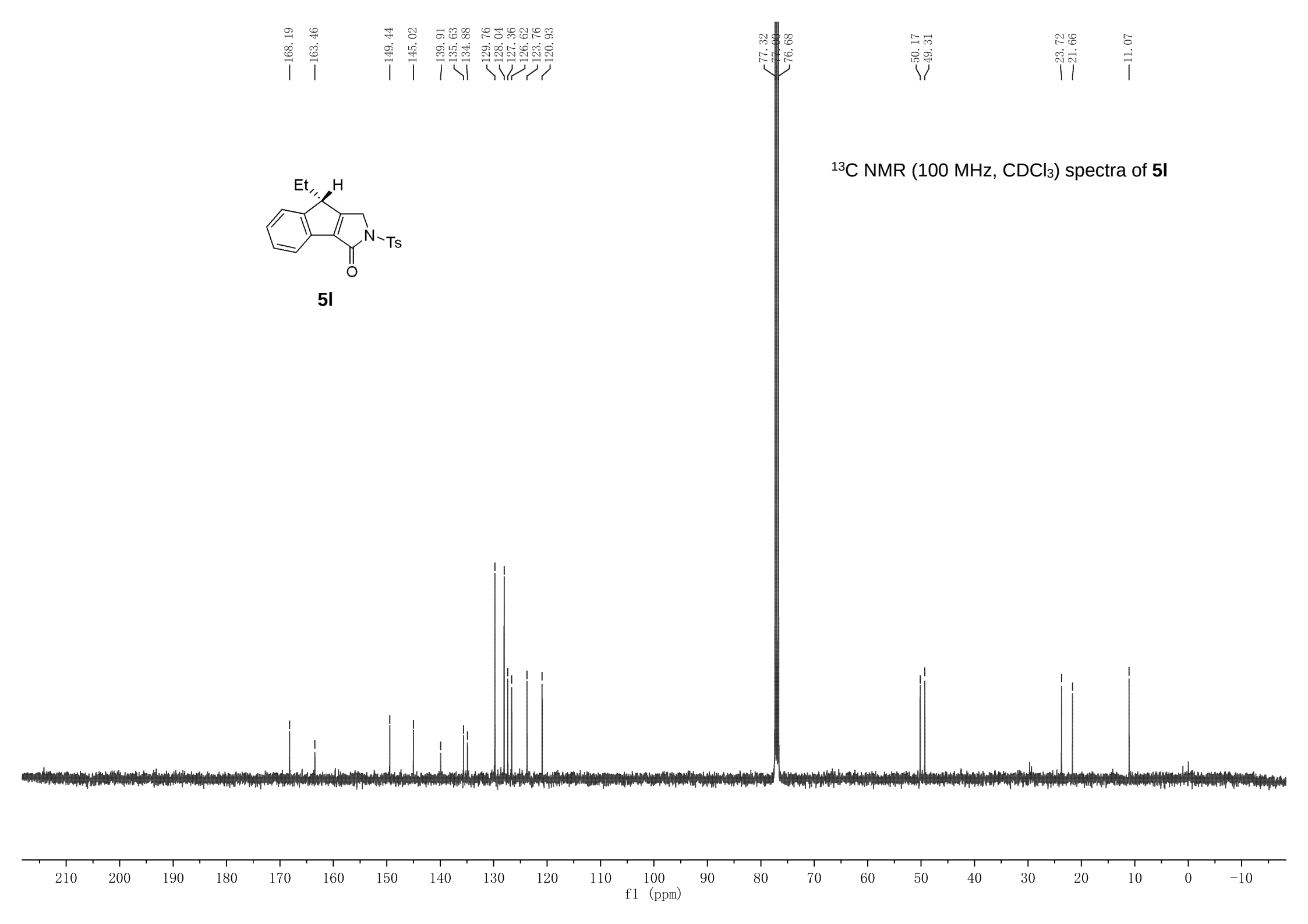
^{1}H NMR (400 MHZ, $CDCl_3$) spectra of **5k**

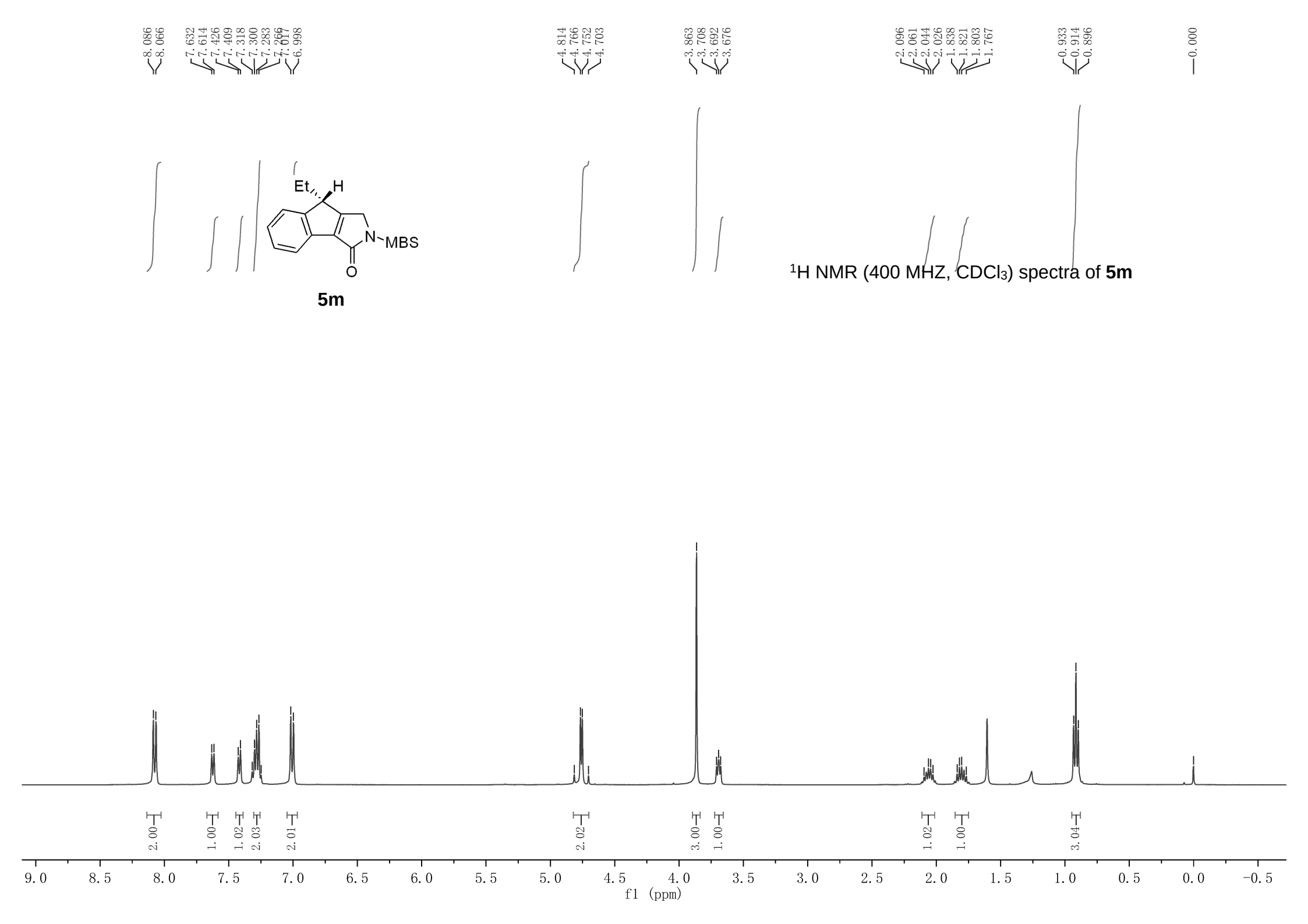

169.79
163.75
146.13
144.93
138.61
137.46
135.65
134.42
133.52
129.71
129.30
128.00
119.34
77.32
77.00
76.68
49.33
41.59
21.63
21.11
18.64
14.65
H
N
Ts
O
5k
13C NMR (100 MHz, CDCl3) spectra of 5k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)



5l

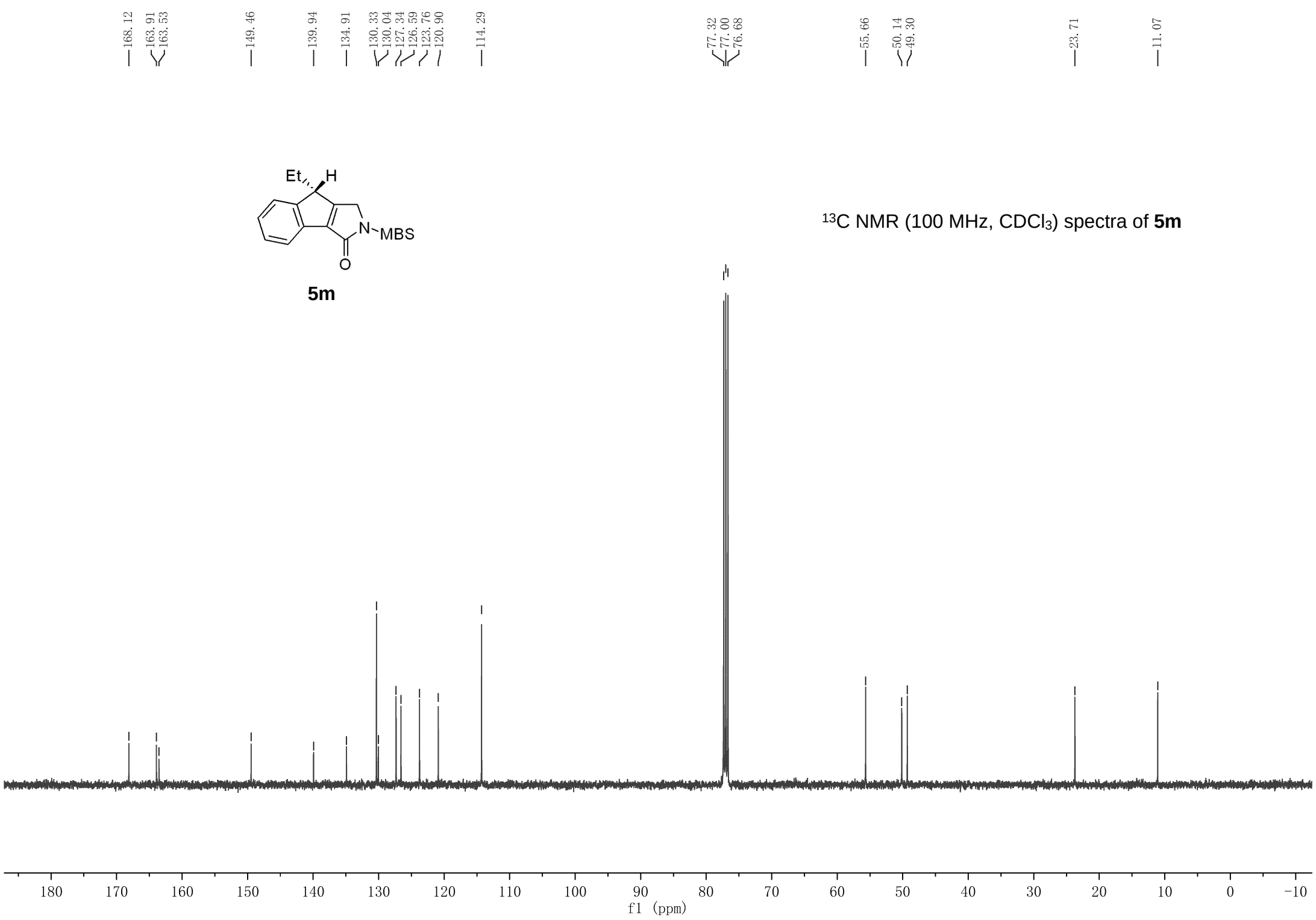
^{1}H NMR (400 MHZ, $CDCl_3$) spectra of **5l**

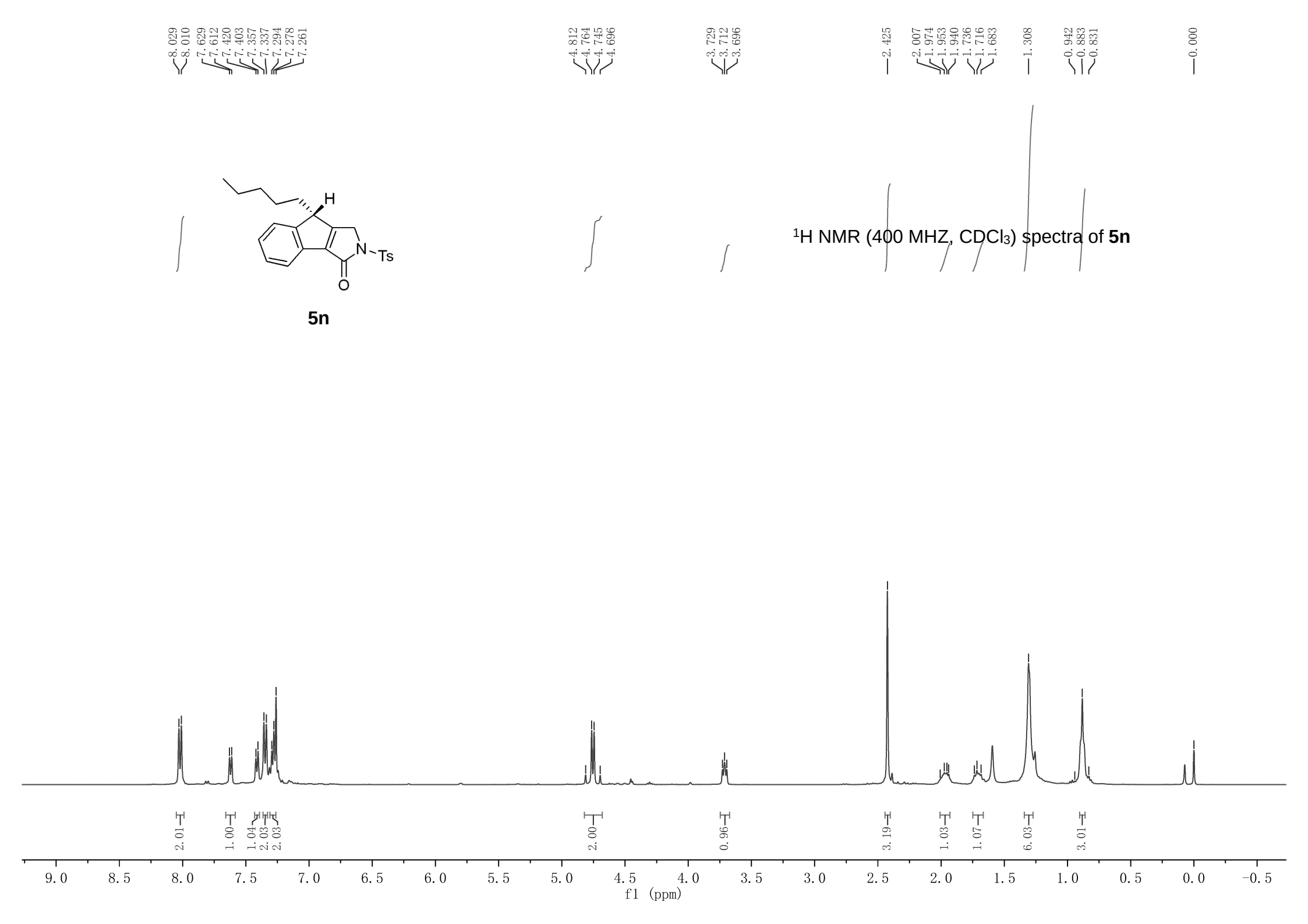

168.19
163.46
149.44
145.02
139.91
135.63
134.88
129.76
128.04
127.36
126.62
123.76
120.93
77.32
77.00
76.68
50.17
49.31
23.72
21.66
11.07
Et
H
N
Ts
O
5l
13C NMR (100 MHz, CDCl3) spectra of 5l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



5m

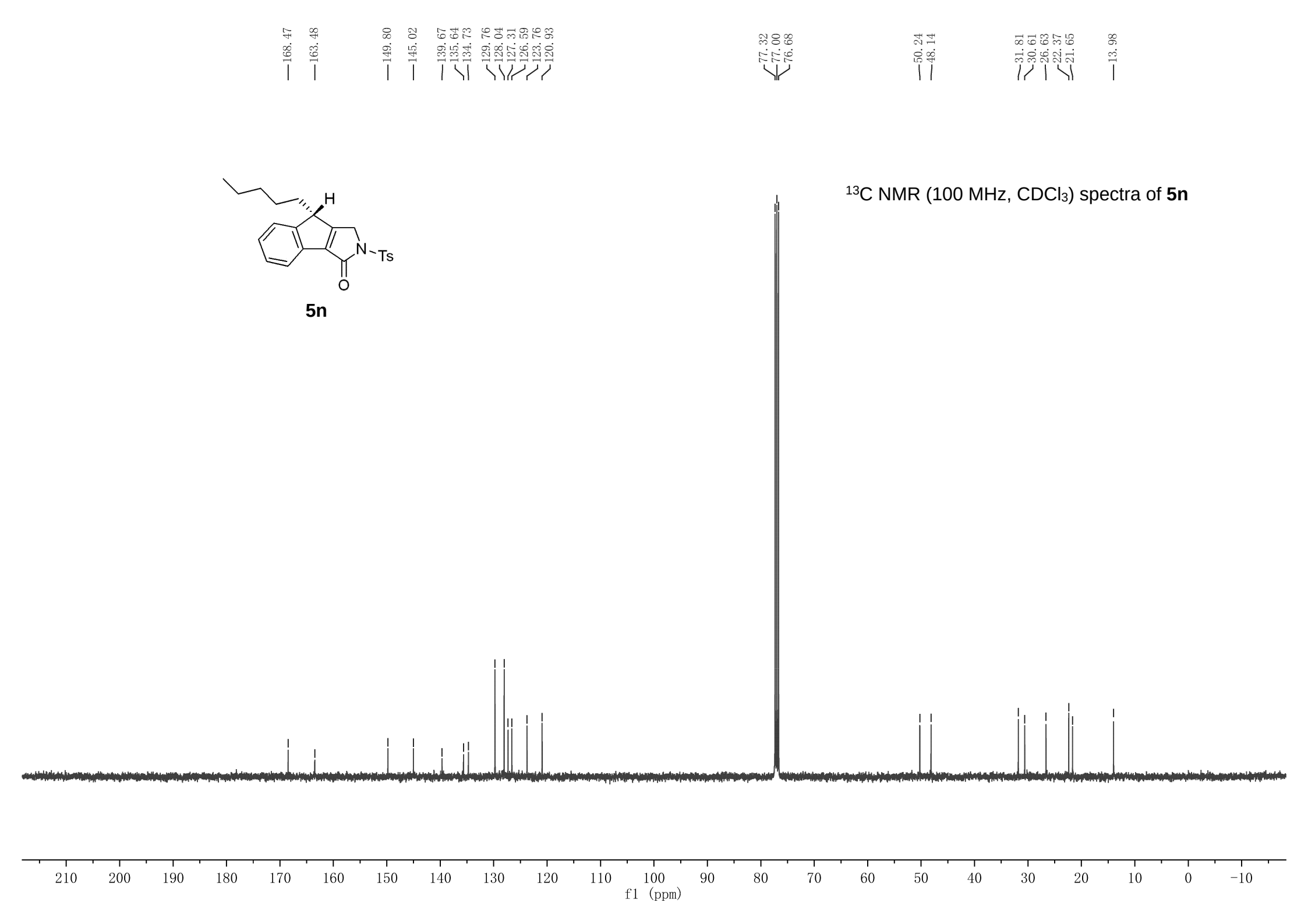
^{1}H NMR (400 MHZ, $CDCl_3$) spectra of **5m**

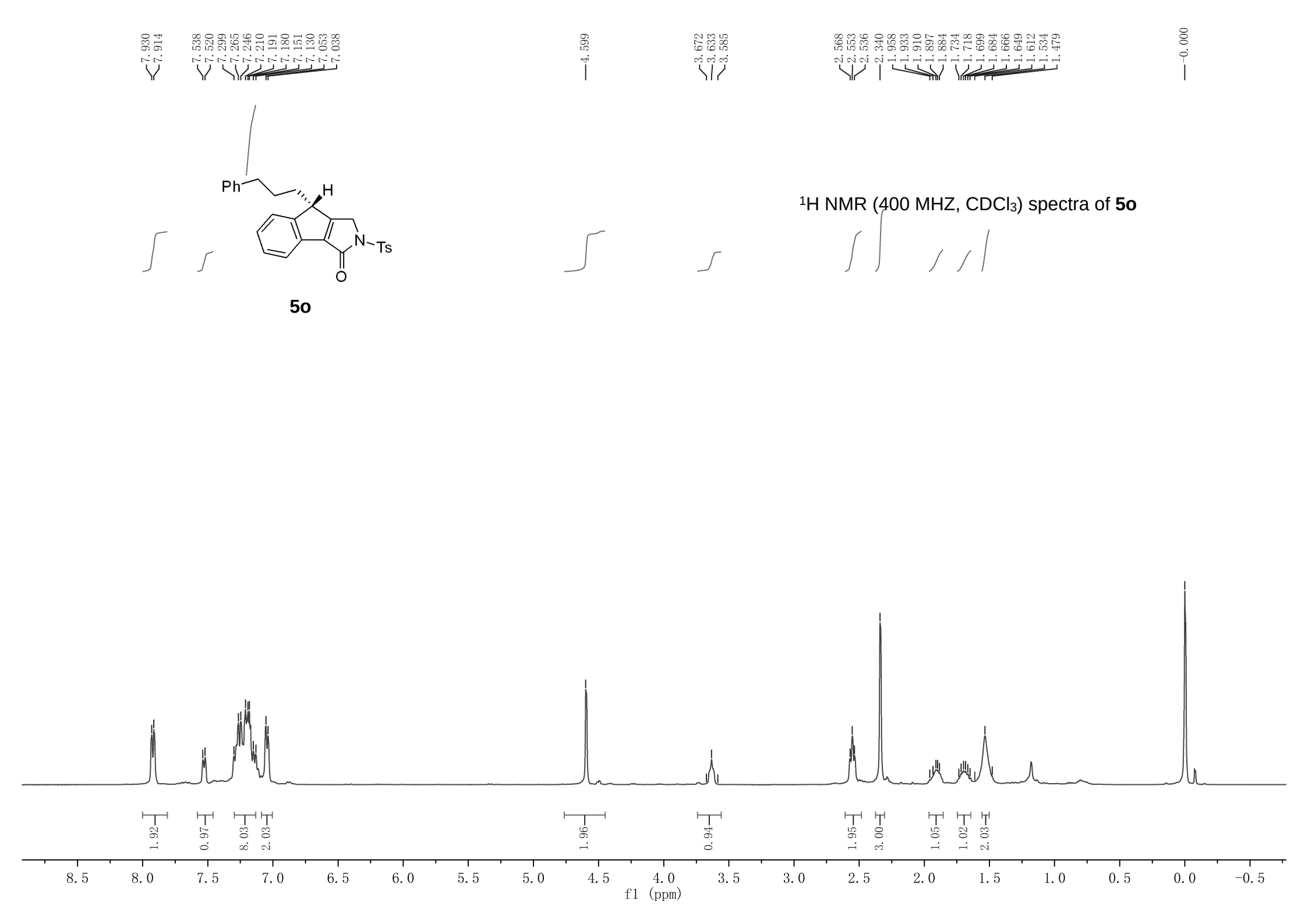

168.12
163.91
163.53
149.46
139.94
134.91
130.33
130.04
127.34
126.59
123.76
120.90
114.29
77.32
77.00
76.68
55.66
50.14
49.30
23.71
11.07
Et
H
N
MBS
O
5m
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **5m**
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



5n

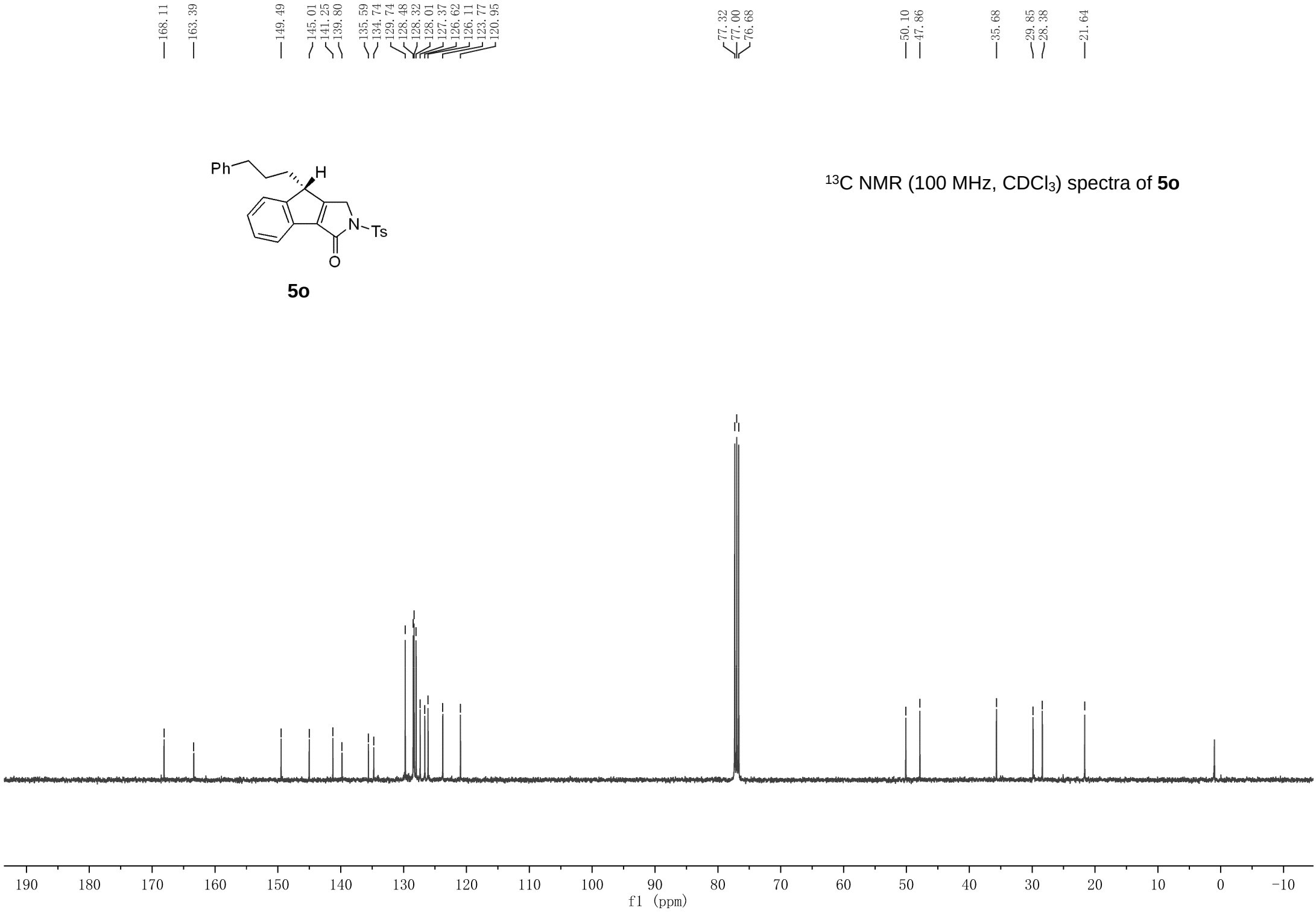
^{1}H NMR (400 MHZ, $CDCl_3$) spectra of **5n**


168.47
163.48
149.80
145.02
139.67
135.64
134.73
129.76
128.04
127.31
126.59
123.76
120.93
77.32
77.00
76.68
50.24
48.14
31.81
30.61
26.63
22.37
21.65
13.98
H
N
Ts
O
5n
13C NMR (100 MHz, CDCl3) spectra of 5n
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)



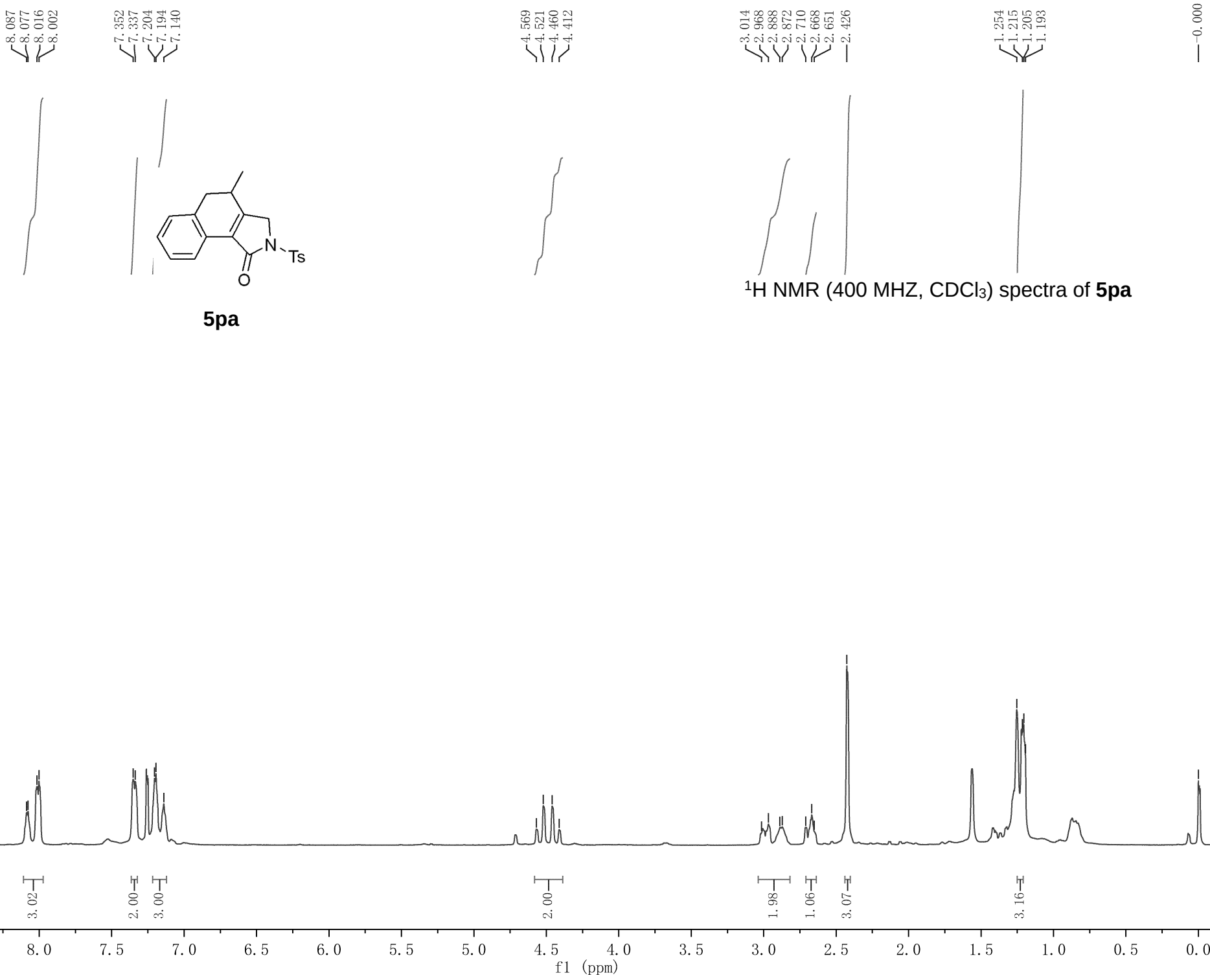
5o

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



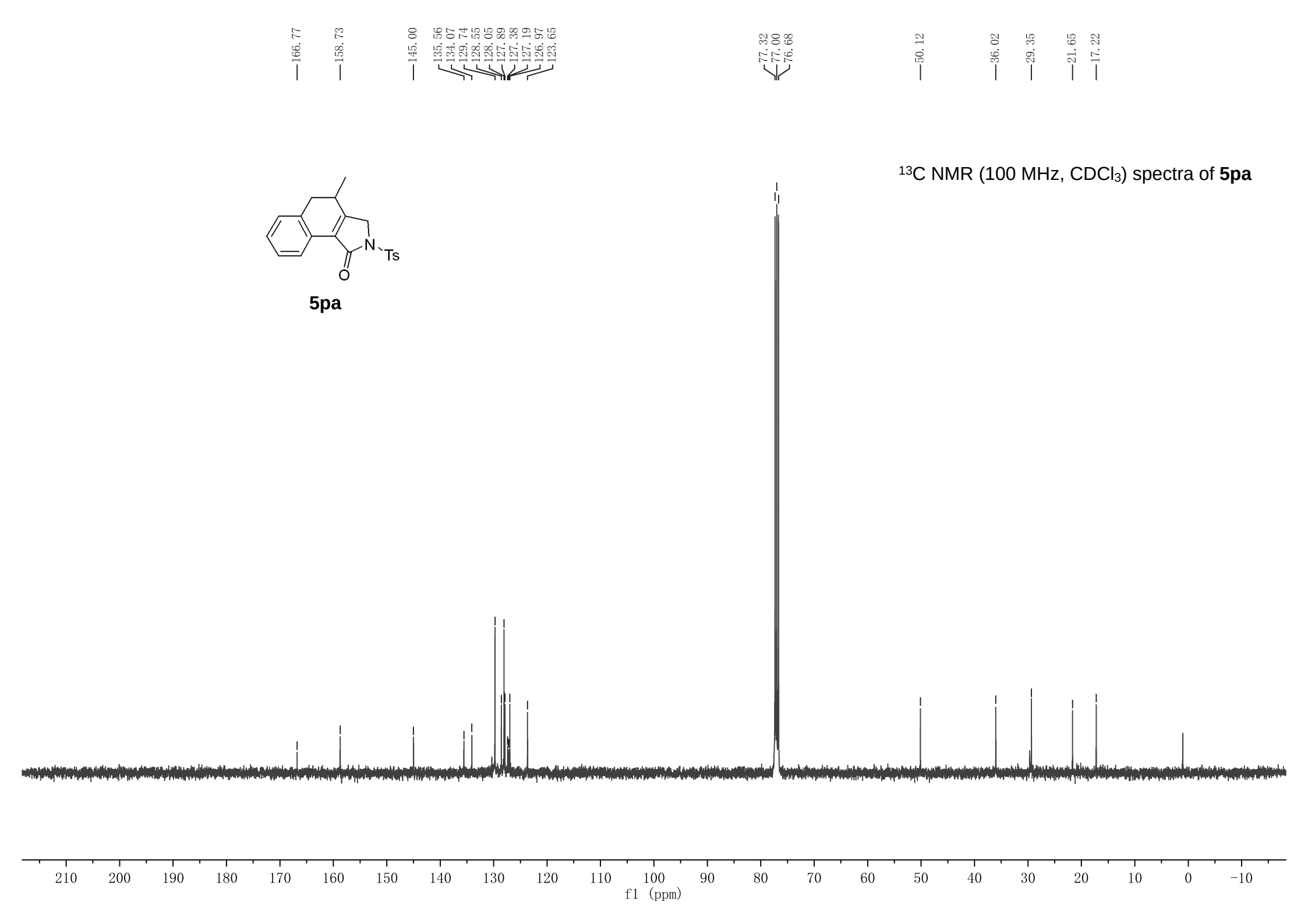
5o

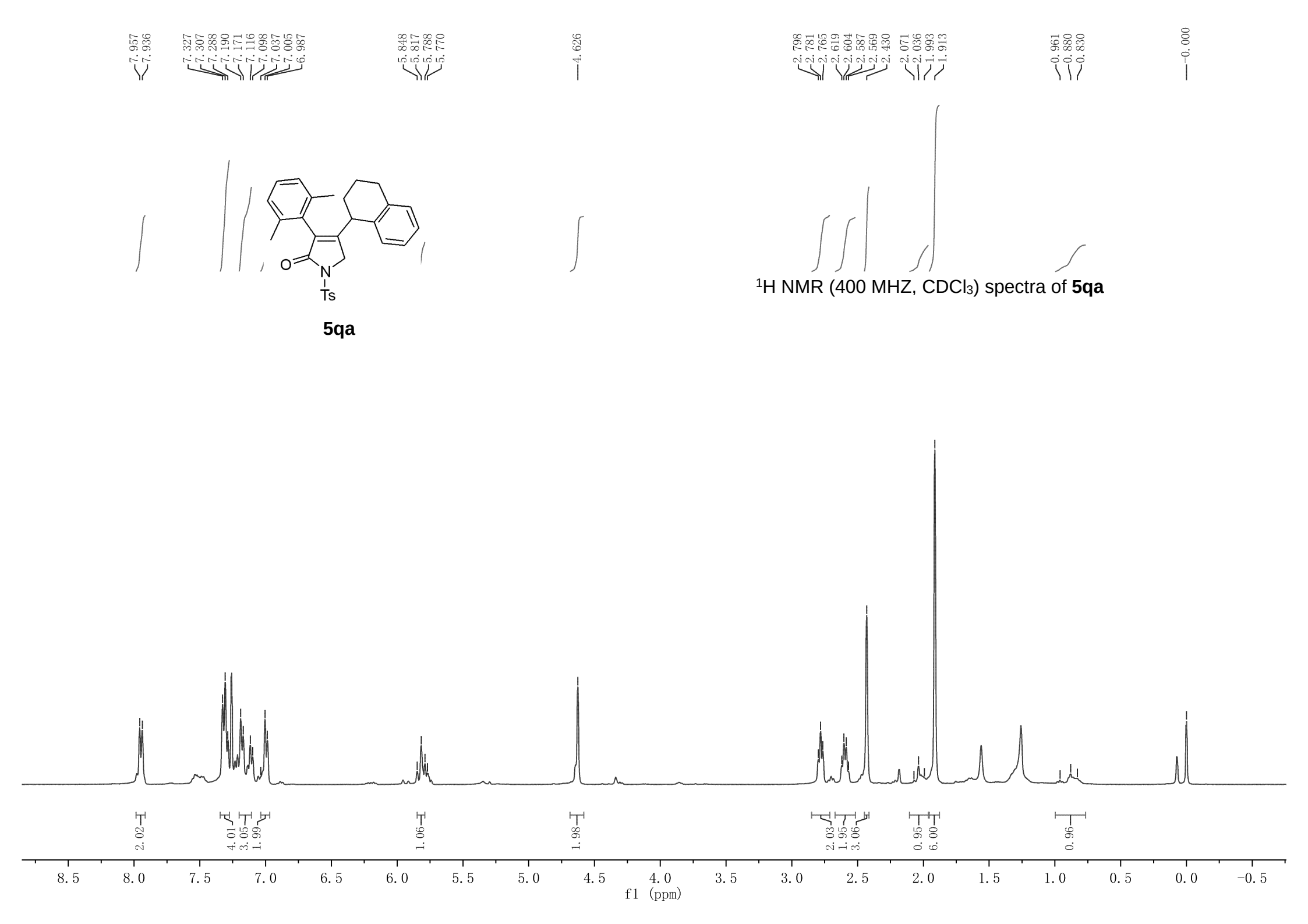
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **5o**



5pa

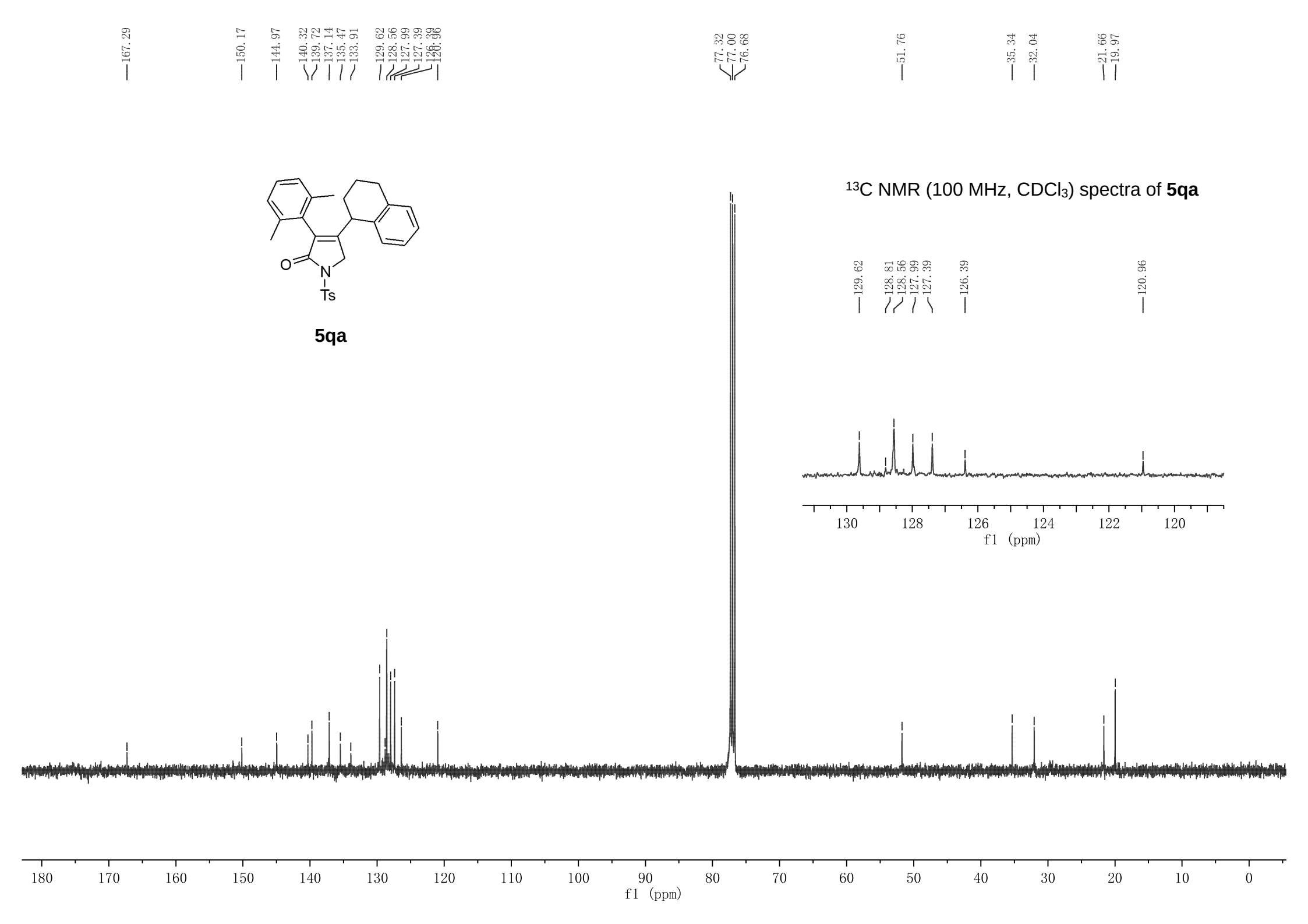
^{1}H NMR (400 MHZ, $CDCl_3$) spectra of **5pa**

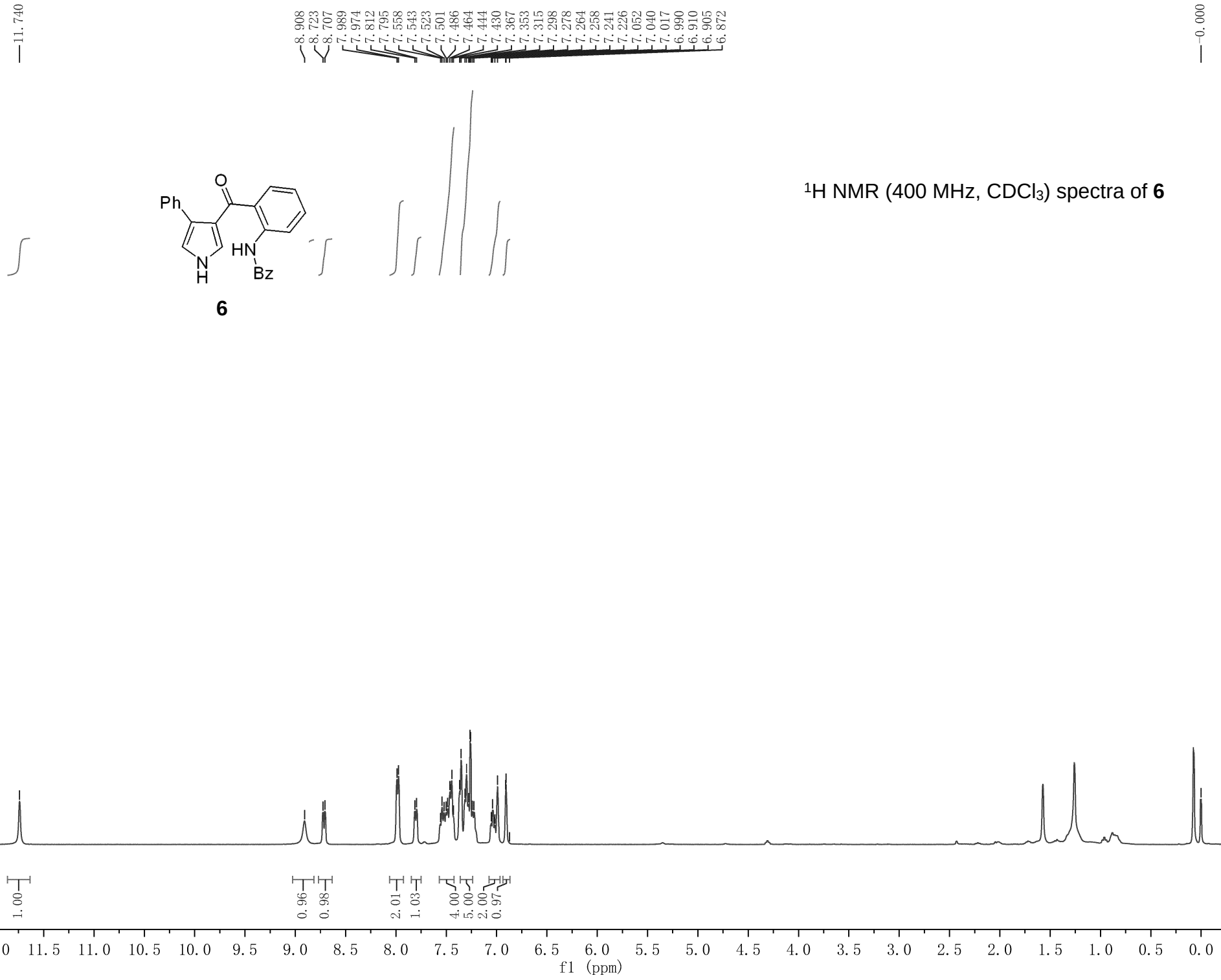

166.77
158.73
145.00
135.56
134.07
129.74
128.55
128.05
127.89
127.38
127.19
126.97
123.65
77.32
77.00
76.68
50.12
36.02
29.35
21.65
17.22
N
Ts
O
5pa
13C NMR (100 MHz, CDCl3) spectra of 5pa
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



5qa

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

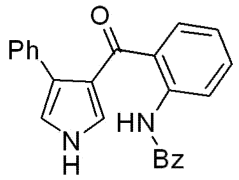

167.29
150.17
144.97
140.32
139.72
137.14
135.47
133.91
129.62
128.56
127.99
127.39
126.39
120.96
77.32
77.00
76.68
51.76
35.34
32.04
21.66
19.97
O
N
Ts
5qa
13C NMR (100 MHz, CDCl3) spectra of 5qa
129.62
128.81
128.56
127.99
127.39
126.39
120.96
130
128
126
124
122
120
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



6

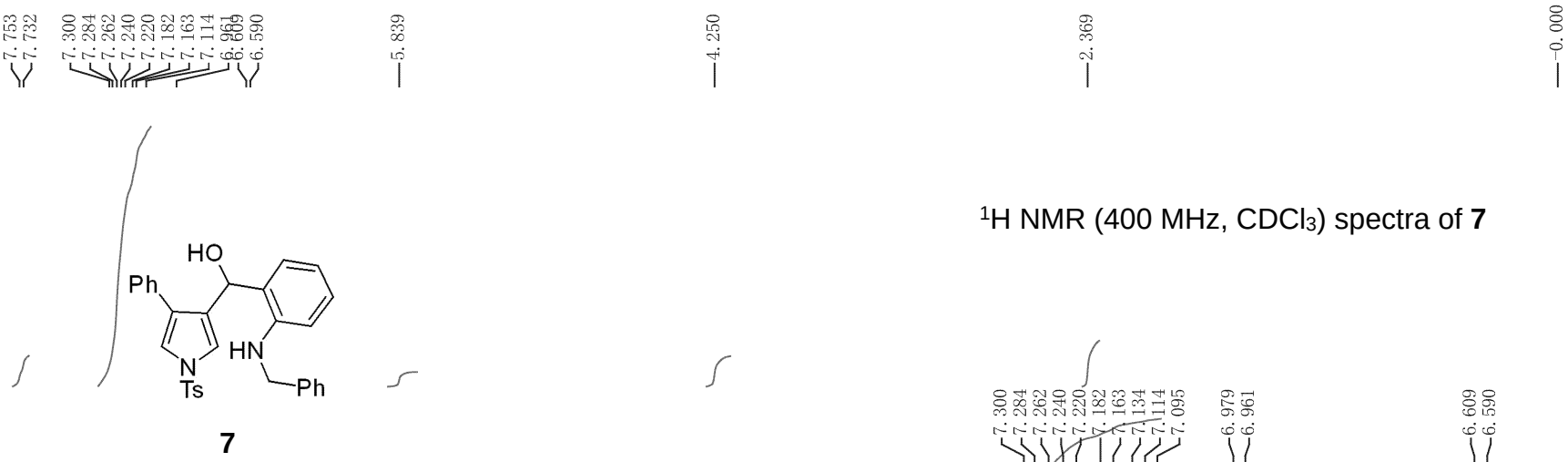
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **6**

194.48
166.21
139.71
134.43
134.30
133.36
133.15
131.95
128.73
128.32
128.25
127.45
127.12
126.94
126.45
126.29
122.69
122.43
121.45
118.79
77.32
77.00
76.68



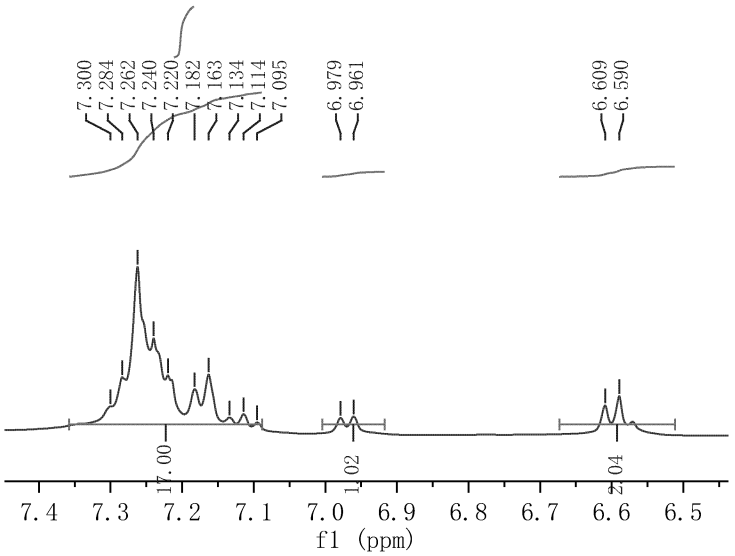
6

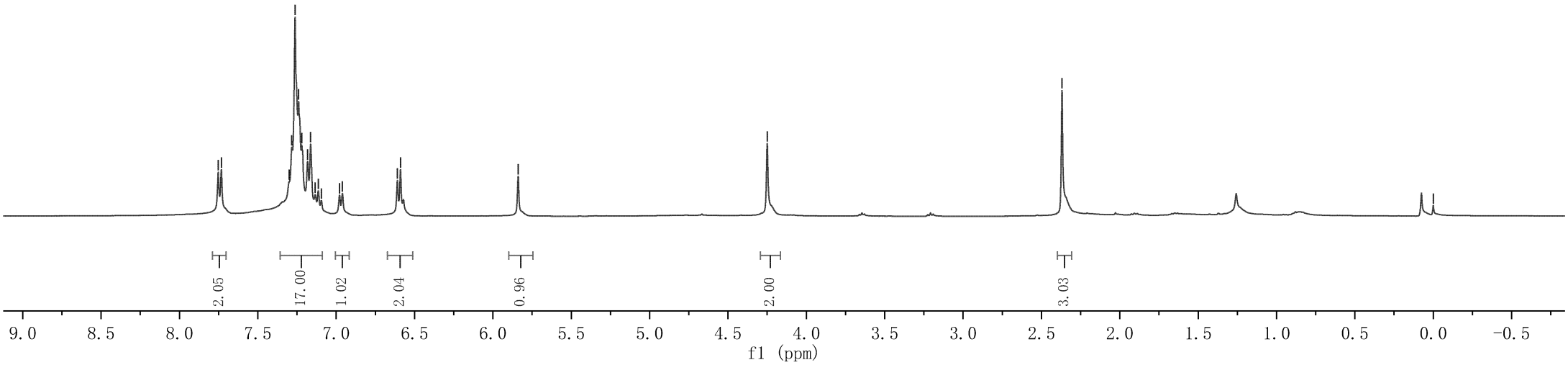
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **6**

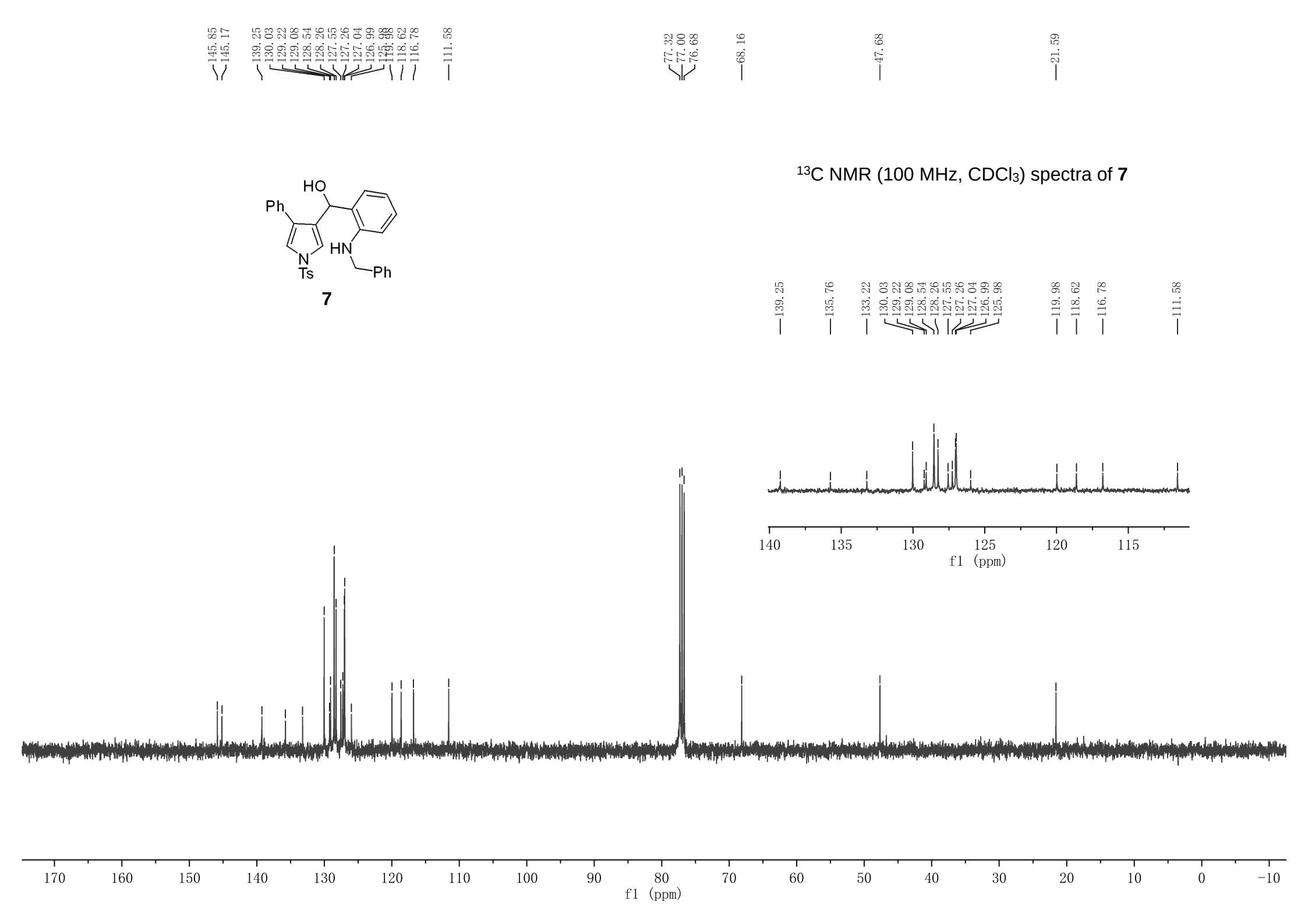


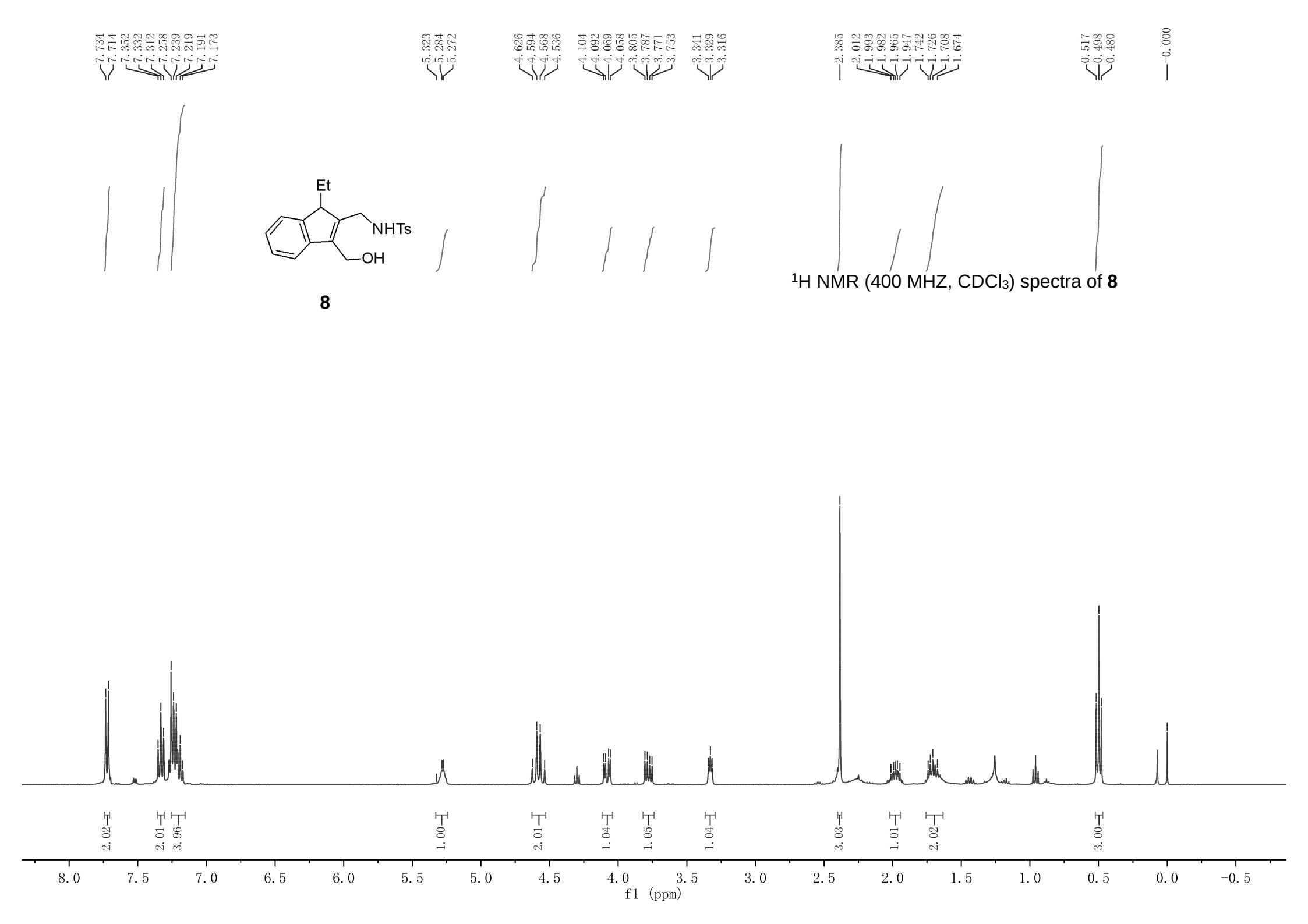
7

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






145.85
145.17
139.25
130.03
129.22
129.08
128.54
128.26
127.55
127.26
127.04
126.99
125.98
119.98
118.62
116.78
111.58
77.32
77.00
76.68
68.16
47.68
21.59
HO
Ph
HN
N
Ts
Ph
7
13C NMR (100 MHz, CDCl3) spectra of 7
139.25
135.76
133.22
130.03
129.22
129.08
128.54
128.26
127.55
127.26
127.04
126.99
125.98
119.98
118.62
116.78
111.58
140
135
130
125
120
115
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

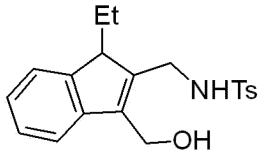


8

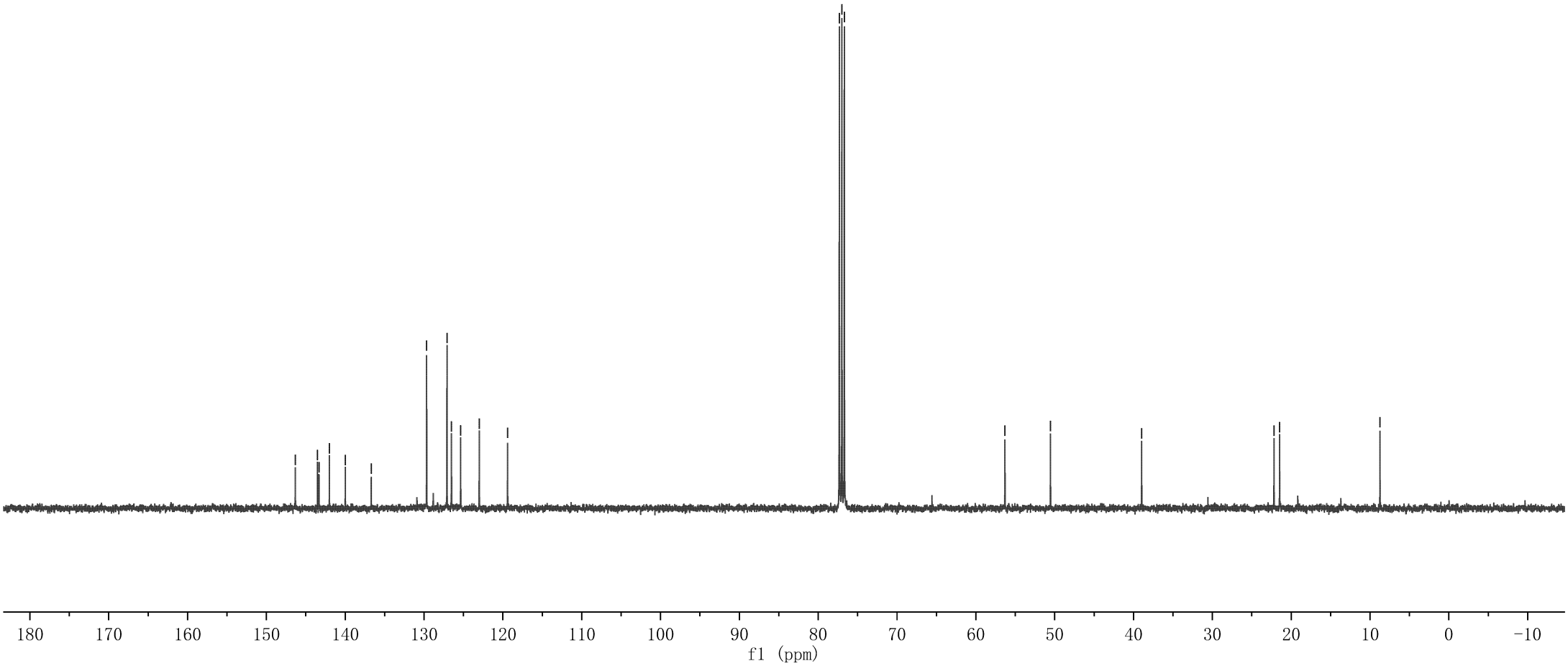
^{1}H NMR (400 MHZ, $CDCl_3$) spectra of **8**

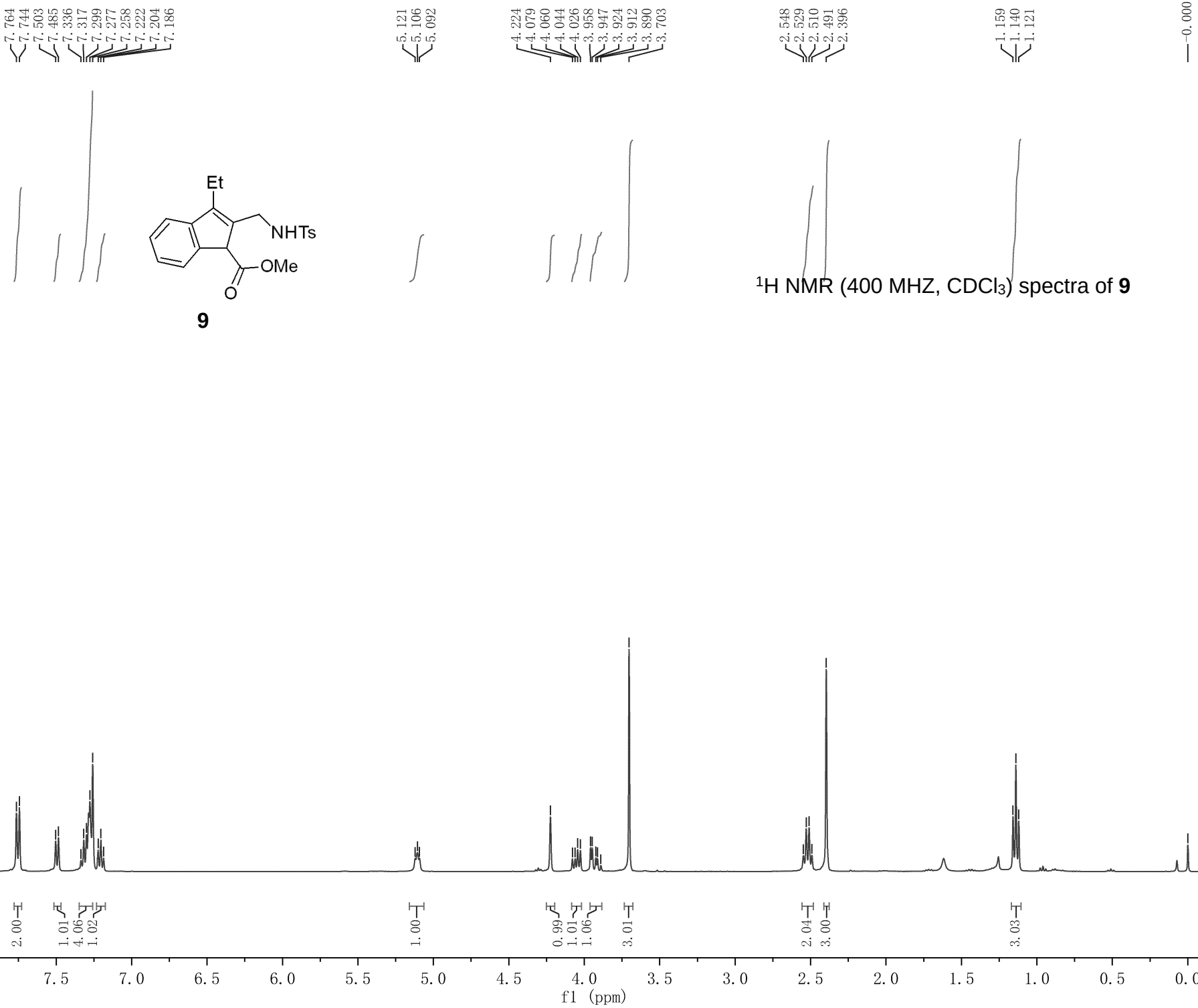
146.33
143.51
143.33
142.00
139.99
136.70
129.67
127.09
126.52
125.36
123.00
119.40
77.32
77.00
76.68
56.31
50.54
38.97
22.18
21.47
8.74

^{13}C NMR (100 MHz, CDCl3) spectra of 8



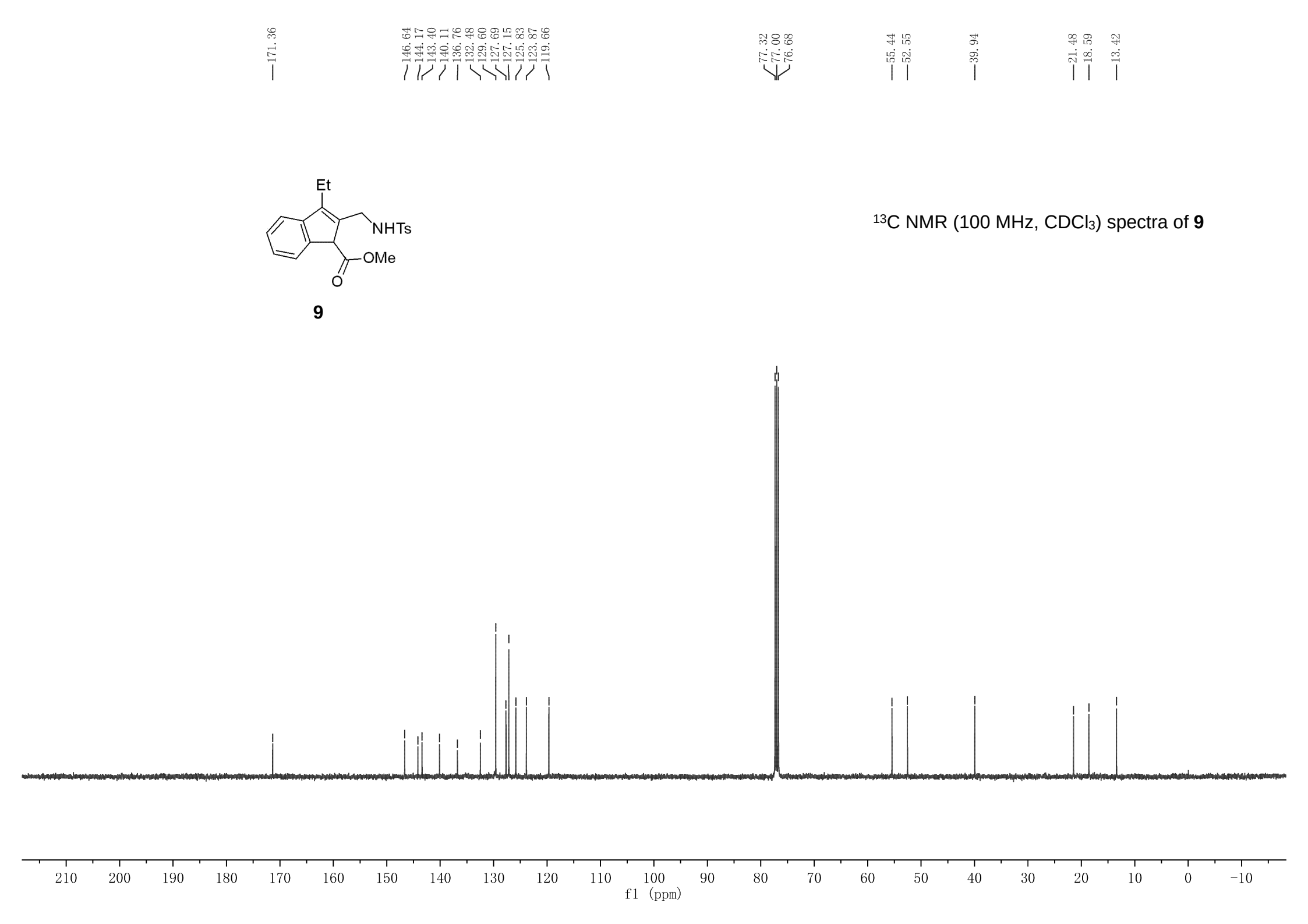
8





9

^{1}H NMR (400 MHZ, $CDCl_3$) spectra of **9**


171.36
146.64
144.17
143.40
140.11
136.76
132.48
129.60
127.69
127.15
125.83
123.87
119.66
77.32
77.00
76.68
55.44
52.55
39.94
21.48
18.59
13.42
Et
NHTs
OMe
O
9
13C NMR (100 MHz, CDCl3) spectra of 9
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)