Supporting Information

Synthesis of 1-Benzylisoindoline and 1-Benzyl-Tetrahydroisoquinoline through Nucleophilic Addition of Organozinc Reagents to *N,O*-acetals

Rui-Jun Ma,[a,b] Jian-Ting Sun,[a] Chang-Hong Liu,[a] Ling Chen,[a] Chang-Mei Si[a,*] and Bang-Guo Wei[a,*]

[a] *Department of Natural Medicine, School of Pharmacy, Fudan University, 826 Zhangheng Road, Shanghai 201203, China*

[b] *Center for Gastrointestinal Endoscopy, Shanxi Provincial People's Hospital, 29 ShuangTa Road, TaiYuan 030012,China*

Email: sicm@fudan.edu.cn; bgwei1974@fudan.edu.cn

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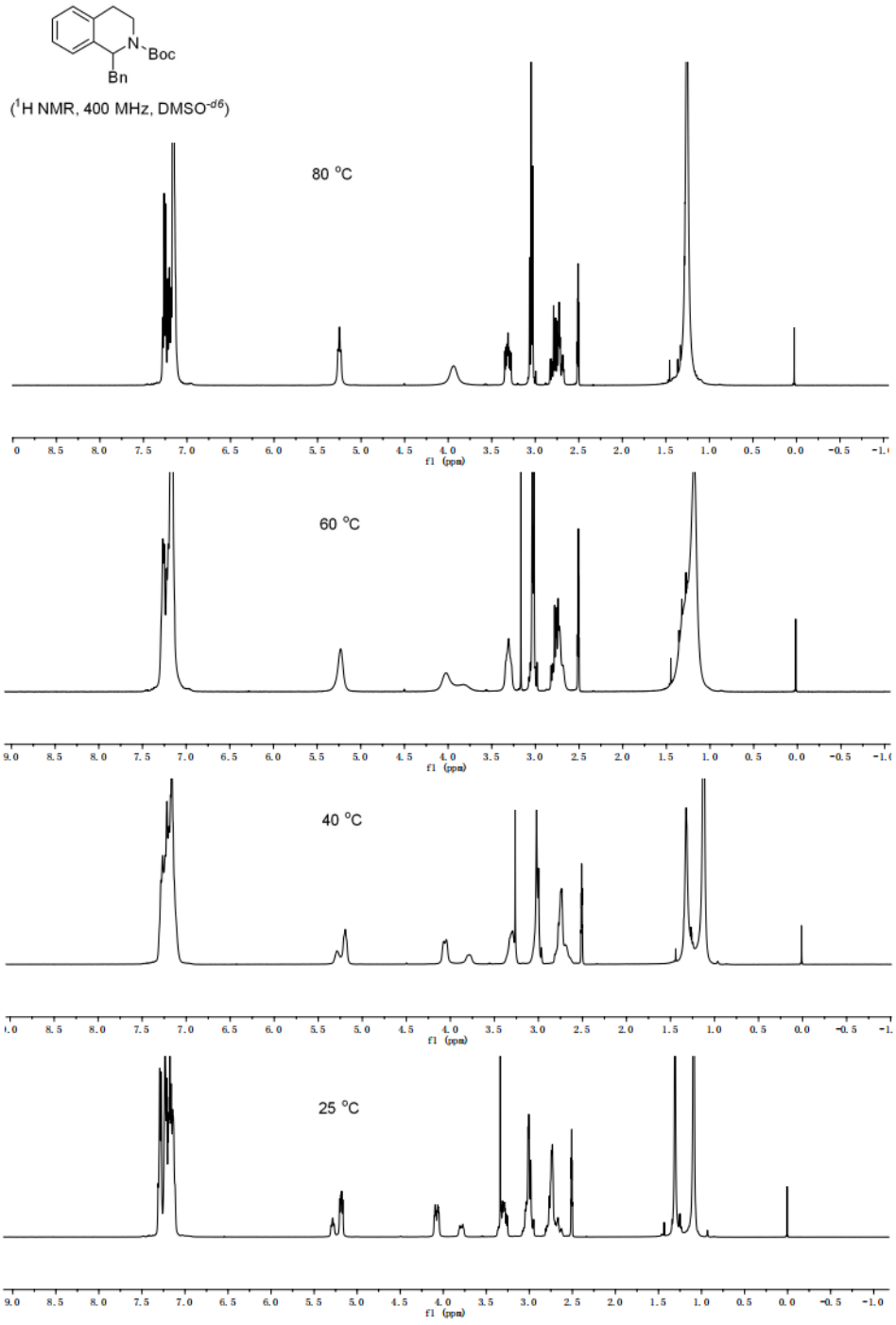
I. NMR spectra of compound 9a at different temperatures



Rotational isomerism exist in the NMR spectrums of the compound **8** and **9**. For the existence of this rotation isomerism, we conducted a NMR spectrum test of the compound **9a** at different temperatures. According to the spectrums, it can be seen that when the temperature continues to rise, the fissures cause by the rotational isomerization continue to decrease. And when the temperature rises to 80 °C, the fissures on the ^{1}H NMR spectrum disappeared.

II. The synthetic details data for the substrates 12a-12f and 13.

General Procedure for the Synthesis of 12 and 13. To a solution of **10/11** (2.0 mmol) in dry THF (10 mL) was added DMAP (0.2 mmol) and Boc_2O (5.0 mmol). After being stirred at room temperature for 12 h, the mixture was quenched with NH_4Cl and extracted with EtOAc (30 mL×3). The combined organic layers were washed with brine, dried over $MgSO_4$, filtrated and concentrated. The residue was purified by flash chromatography on silica gel (PE/EA=5:1) to give the desired product **12/13**.

***tert*-Butyl 1-oxoisoindoline-2-carboxylate 12a.** Light-Yellow solid (457 mg, 98%); m.p. 121-123°C; IR (film): ν_{max} 2979, 1780, 1743, 1393, 1300, 1276, 1151, 1102, 945, 843 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94-7.85 (m, 1H), 7.67-7.59 (m, 1H), 7.52-7.46 (m, 2H), 4.76 (s, 2H), 1.61 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz,$CDCl_3$) δ 166.7, 150.4, 140.7, 133.6, 131.5, 128.5, 125.0, 123.1, 83.2, 49.2, 28.2 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M + Na]^+$ Calcd for $C_{13}H_{15}NO_3Na^+$: 256.0944, found: 256.0945.

***tert*-Butyl 4-bromo-1-oxoisoindoline-2-carboxylate 12b.** Colourless oil (618 mg, 99%); IR (film): ν_{max} 2979, 1785, 1473, 1394, 1327, 1257, 1157, 954, 819, 726 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.98-7.85 (m, 1H), 7.84-7.75 (m, 1H), 7.45-7.38 (m, 1H), 4.67 (s, 2H), 1.62 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.7, 150.1, 141.1, 136.4, 133.5, 130.4, 124.0, 118.0, 83.6, 49.8, 28.2 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M + Na]^+$ Calcd for $C_{13}H_{14}BrNO_3Na^+$: 334.0049, 336.0029, found: 334.0050, 336.0028.

***tert*-Butyl 6-bromo-1-oxoisoindoline-2-carboxylate 12c.** White solid (605 mg, 97%); m.p. 145-147°C; IR (film): ν_{max} 2977, 1717, 1448, 1395, 1324, 1262, 1213, 1158, 778, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.10-8.00 (m, 1H), 7.80-7.70 (m, 1H), 7.40-7.30 (m, 1H), 4.72 (s, 2H), 1.60 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.2, 150.2, 139.3, 136.7, 133.6, 128.1, 124.8, 122.7, 83.7, 49.0, 28.2 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M + Na]^+$ Calcd for $C_{13}H_{14}BrNO_3Na^+$: 334.0049, 336.0029, found: 334.0048, 336.0027.

***tert*-Butyl 5-chloro-1-oxoisoindoline-2-carboxylate 12d.** White solid (519 mg, 97%); m.p. 118-120°C; IR (film): ν_{max} 2976, 1730, 1477, 1363, 1305, 1204, 1182, 1154, 856, 792 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86-7.80 (m, 1H), 7.50-7.42 (m, 2H), 4.75 (s, 2H), 1.60 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.6, 150.3, 142.2, 140.1, 130.1, 129.4, 126.3, 123.6, 83.6, 48.8, 28.2 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M + Na]^+$ Calcd for $C_{13}H_{14}ClNO_3Na^+$: 290.0554, found: 290.0558.

***tert*-Butyl 4-methoxy-1-oxoisoindoline-2-carboxylate 12e.** White solid (484 mg, 92%); m.p. 128-130°C; IR (film): ν_{max} 2970, 1779, 1713, 1497, 1364, 1290, 1154, 1073, 970, 774 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55-7.45 (m,1H), 7.43-7.38 (m, 1H), 7.11-7.05 (m, 1H), 4.68 (s, 2H), 3.93 (s, 3H), 1.60 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.9, 154.5, 150.5, 133.1, 130.2, 129.3, 116.8, 114.4, 83.2, 55.7, 47.2, 28.3 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{18}NO_4^+$: 264.1230, found: 264.1232.

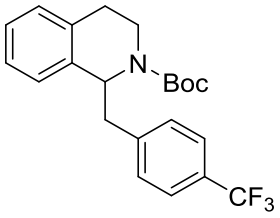
***tert*-Butyl 6-methoxy-1-oxoisoindoline-2-carboxylate 12f.** White solid (484 mg, 92%); m.p. 135-137°C; IR (film): ν_{max} 2975, 1772, 1710, 1496, 1456, 1363, 1203, 1023, 981, 776 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.31 (m, 2H), 7.22-7.17 (m, 1H), 4.69 (s, 2H), 3.86 (s, 3H), 1.60 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.9, 160.2, 150.3, 133.0, 132.7, 123.9, 122.5, 106.9, 83.1, 55.7, 48.8, 28.1 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{17}NO_4Na^+$: 286.1050, found: 286.1052.

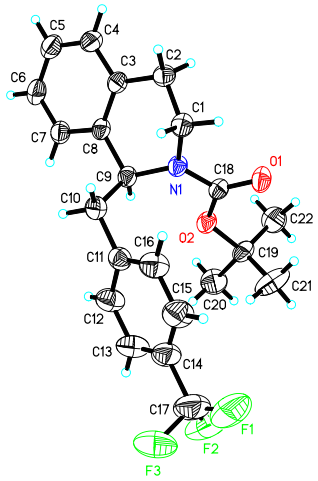
***tert*-Butyl 1-oxo-3,4-dihydroisoquinoline-2(1H)-carboxylate 13.** White solid (470 mg, 95%); m.p. 73-75 °C; IR (film): ν_{max} 2978, 1783, 1390, 1327, 1267, 1155, 947, 853 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.20-8.12 (m, 1H), 7.50-7.45 (m, 1H), 7.39-7.31 (m, 1H), 7.24-7.18 (m, 1H), 4.03-3.96 (m, 2H), 3.04-2.97 (m, 2H), 1.59 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR

(100 MHz, $CDCl_3$) δ 164.1, 153.3, 139.6, 132.9, 129.7, 129.4, 127.3, 127.3, 83.3, 44.5, 28.4, 28.2 ppm; HRMS (ESI-Orbitrap) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{17}NO_3Na^+$: 270.2832, found: 270.2832.

III. X-Ray Structure of 9i

ORTEP drawing of the X-ray crystallographic structure of **9i**





CCDC 2011532. For detailed crystallographic data, please refer to the Cambridge Crystallographic Data Centre at http://ccdc.cam.ac.uk.

Table 1. Crystal data and structure refinement for **9i**.

Identification code	**9i**	
Empirical formula	C22 H24 F3 N O2	
Formula weight	391.42	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 18.7943(14) Å	α= 90 °.
	b = 11.2236(8) Å	β= 95.655(2) °.
	c = 9.8308(8) Å	γ = 90 °.
Volume	2063.6(3) $Å^3$	

Z	4
Density (calculated)	1.260 Mg/m^3
Absorption coefficient	0.098 mm^{-1}
F(000)	824
Crystal size	0.200 x 0.160 x 0.120 mm^3
Theta range for data collection	2.762 to 25.999 °.
Index ranges	-21<=h<=23, -13<=k<=13, -12<=l<=12
Reflections collected	30521
Independent reflections	4041 [R(int) = 0.0326]
Completeness to theta = 25.242 °	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6406
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4041 / 36 / 284
Goodness-of-fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0469, wR2 = 0.1159
R indices (all data)	R1 = 0.0670, wR2 = 0.1317
Extinction coefficient	0.037(4)
Largest diff. peak and hole	0.196 and -0.126 e.$Å^{-3}$

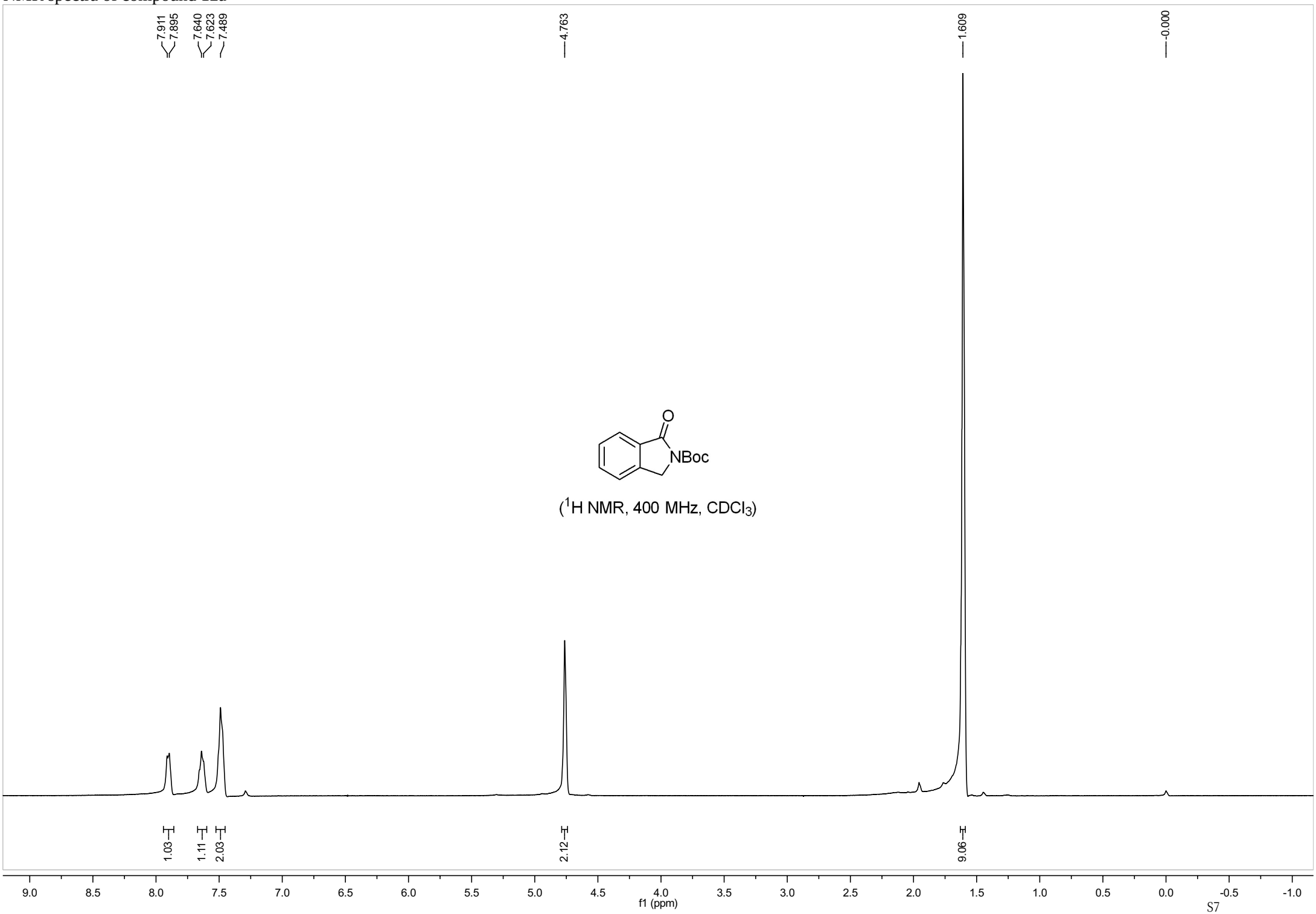
Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for dd20068. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	1706(1)	4004(1)	8581(1)	68(1)
O(2)	2236(1)	5455(1)	7434(1)	61(1)
N(1)	1669(1)	3971(1)	6272(1)	52(1)
C(1)	1253(1)	2865(1)	6144(2)	60(1)
C(2)	530(1)	3096(2)	5382(2)	64(1)
C(3)	566(1)	3888(1)	4155(2)	55(1)
C(4)	-23(1)	3991(2)	3184(2)	68(1)
C(5)	-11(1)	4716(2)	2065(2)	74(1)
C(6)	592(1)	5358(2)	1884(2)	72(1)
C(7)	1180(1)	5275(2)	2828(2)	63(1)

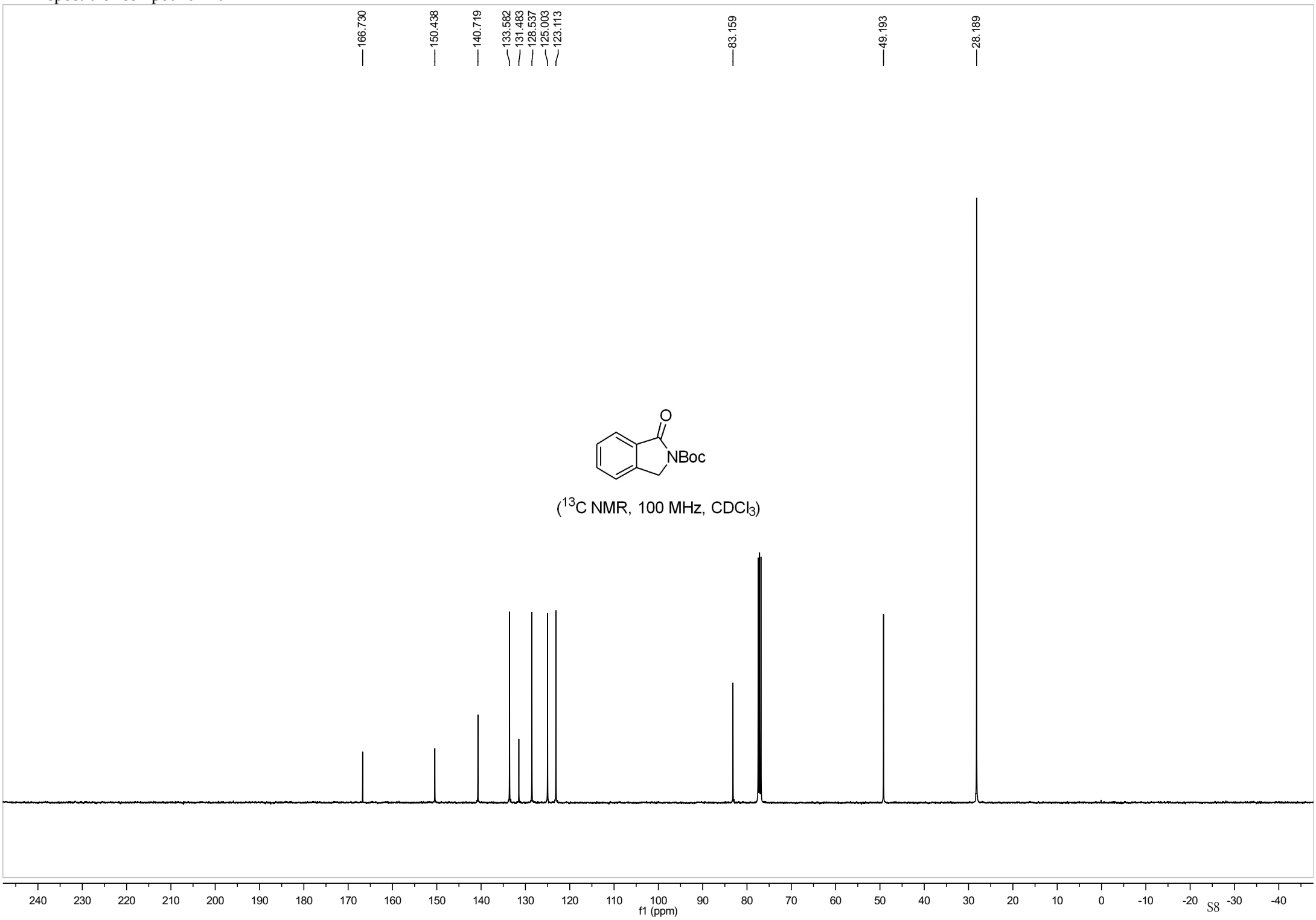
C(8)	1174(1)	4548(1)	3977(2)	52(1)
C(9)	1839(1)	4498(1)	4985(1)	52(1)
C(10)	2445(1)	3817(2)	4372(2)	67(1)
C(11)	3127(1)	3770(2)	5304(2)	63(1)
C(12)	3640(1)	4644(2)	5280(2)	83(1)
C(13)	4261(1)	4605(2)	6155(3)	96(1)
C(14)	4383(1)	3683(2)	7054(2)	88(1)
C(15)	3883(1)	2813(2)	7097(3)	96(1)
C(16)	3260(1)	2853(2)	6226(2)	82(1)
C(17)	5056(2)	3632(4)	7995(4)	132(1)
C(18)	1860(1)	4439(1)	7520(2)	51(1)
C(19)	2524(1)	6091(2)	8666(2)	64(1)
C(20)	2928(1)	7102(2)	8082(2)	101(1)
C(21)	3016(2)	5306(2)	9571(3)	120(1)
C(22)	1916(1)	6574(2)	9394(2)	90(1)
F(1)	5079(4)	2852(8)	8929(9)	185(2)
F(2)	5221(4)	4741(8)	8561(9)	185(2)
F(3)	5617(3)	3491(10)	7265(7)	184(2)
F(1')	5377(3)	2557(7)	7941(9)	189(2)
F(2')	4937(3)	3752(9)	9300(7)	174(2)
F(3')	5528(3)	4390(9)	7739(9)	185(2)

IV. Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectrum

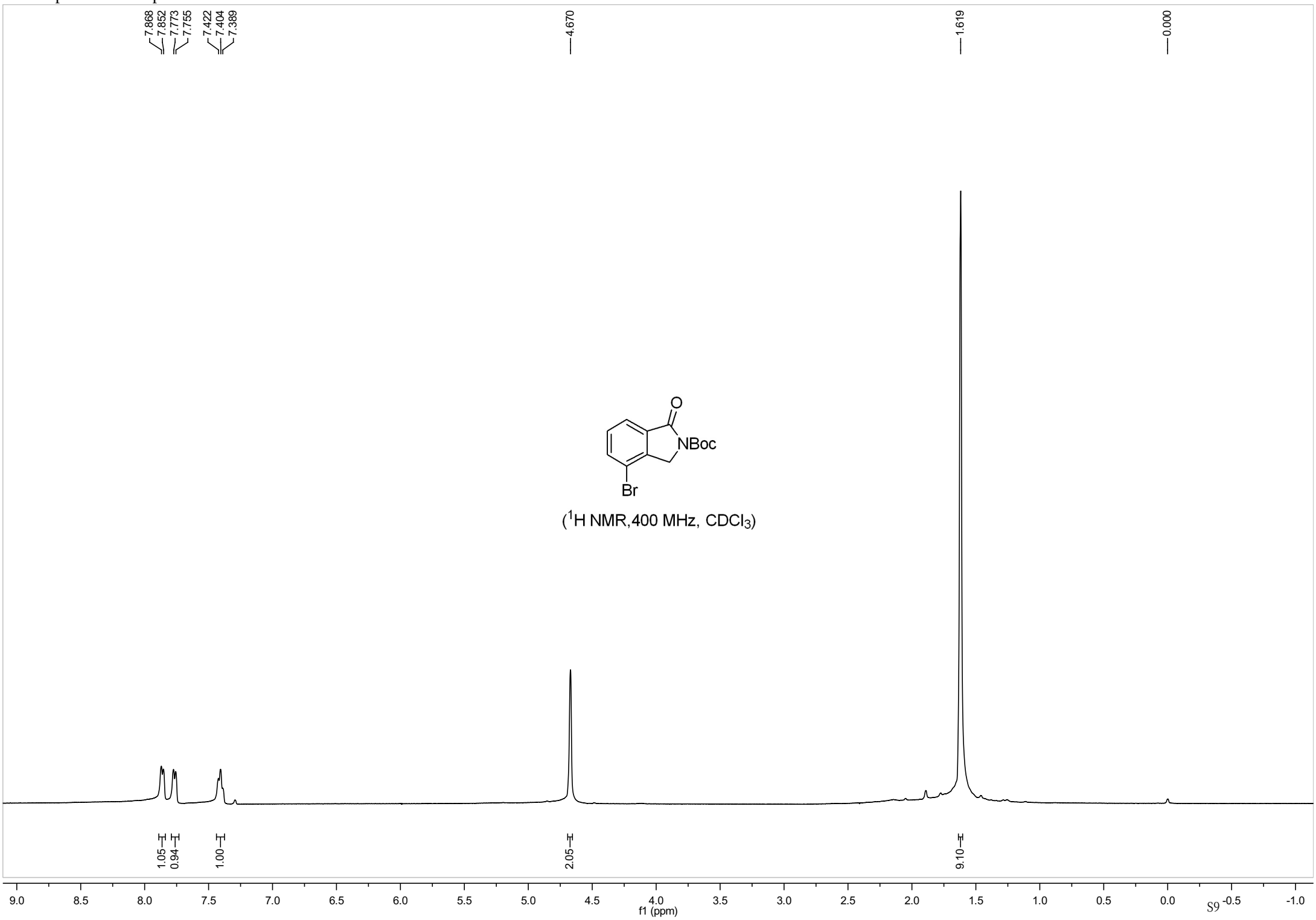
NMR spectra of compound 12a



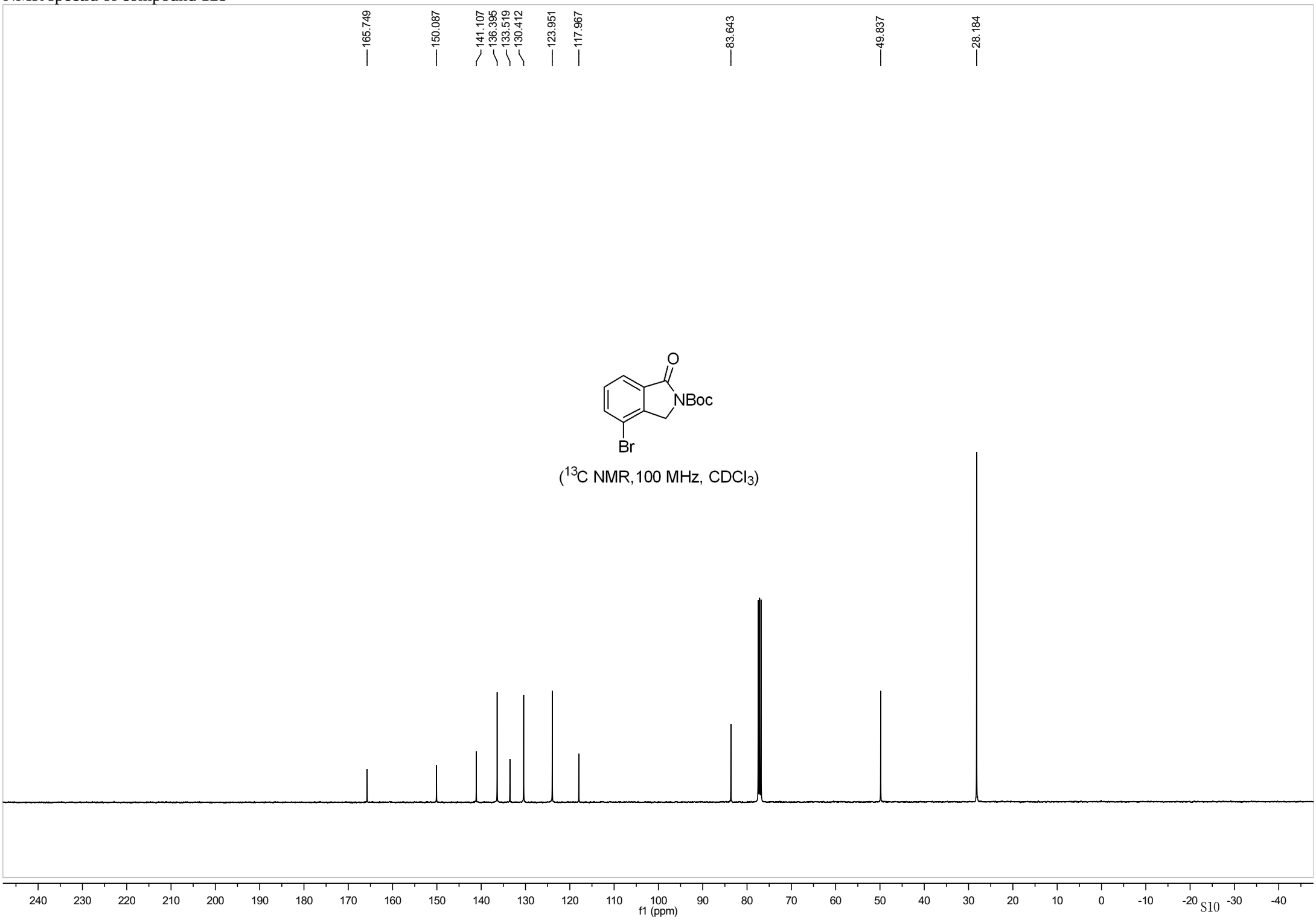
NMR spectra of compound 12a



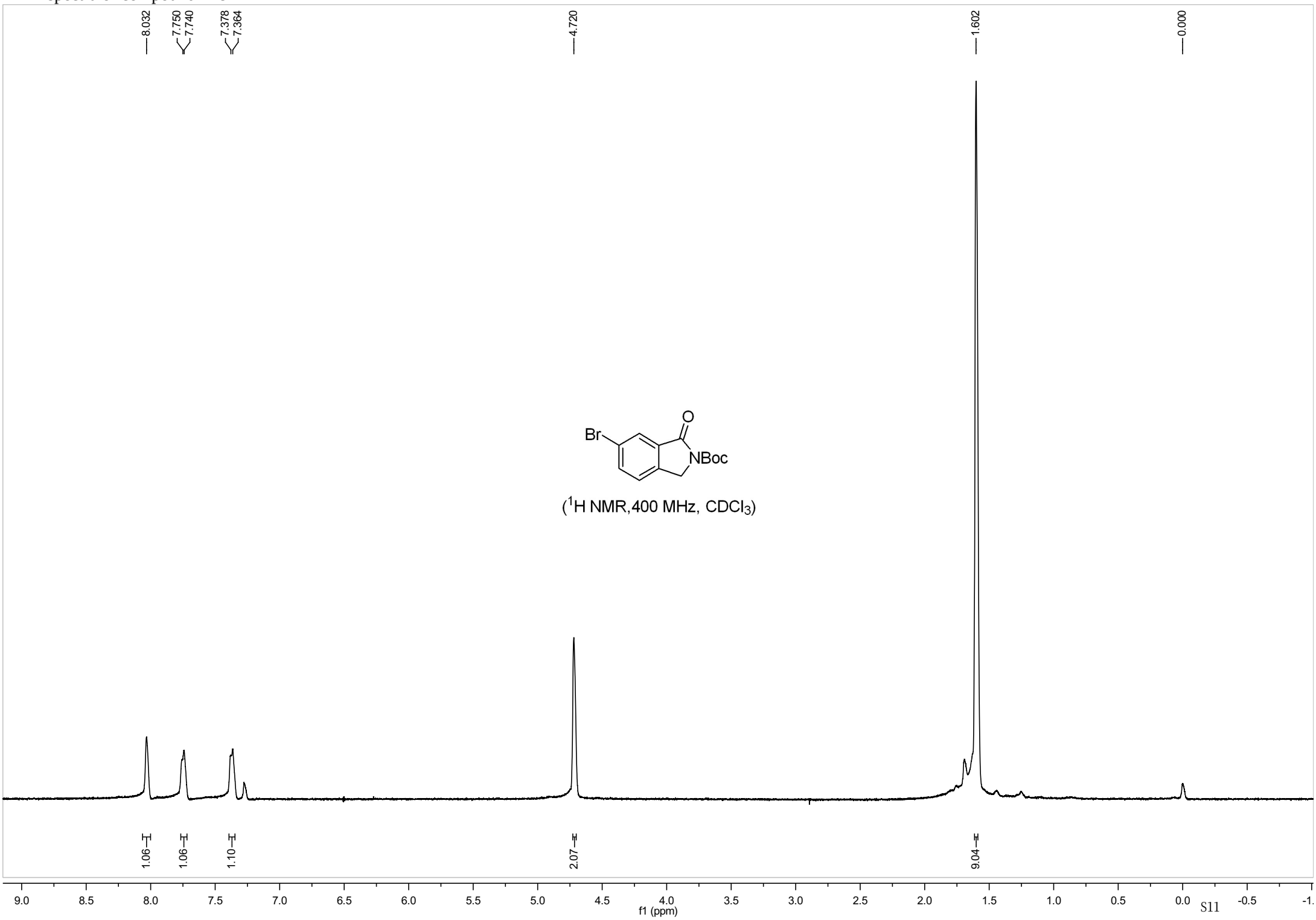
NMR spectra of compound 12b



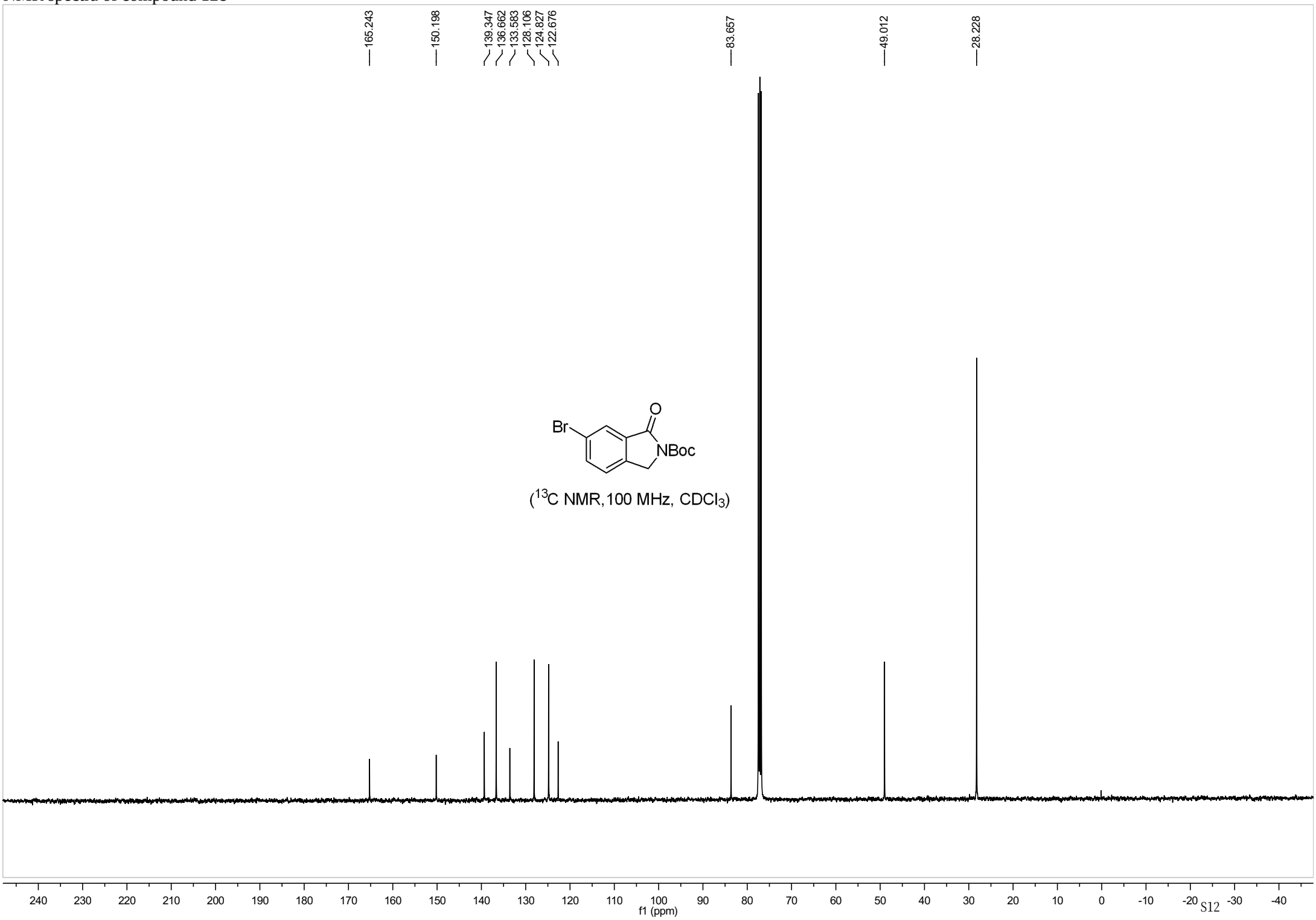
NMR spectra of compound 12b



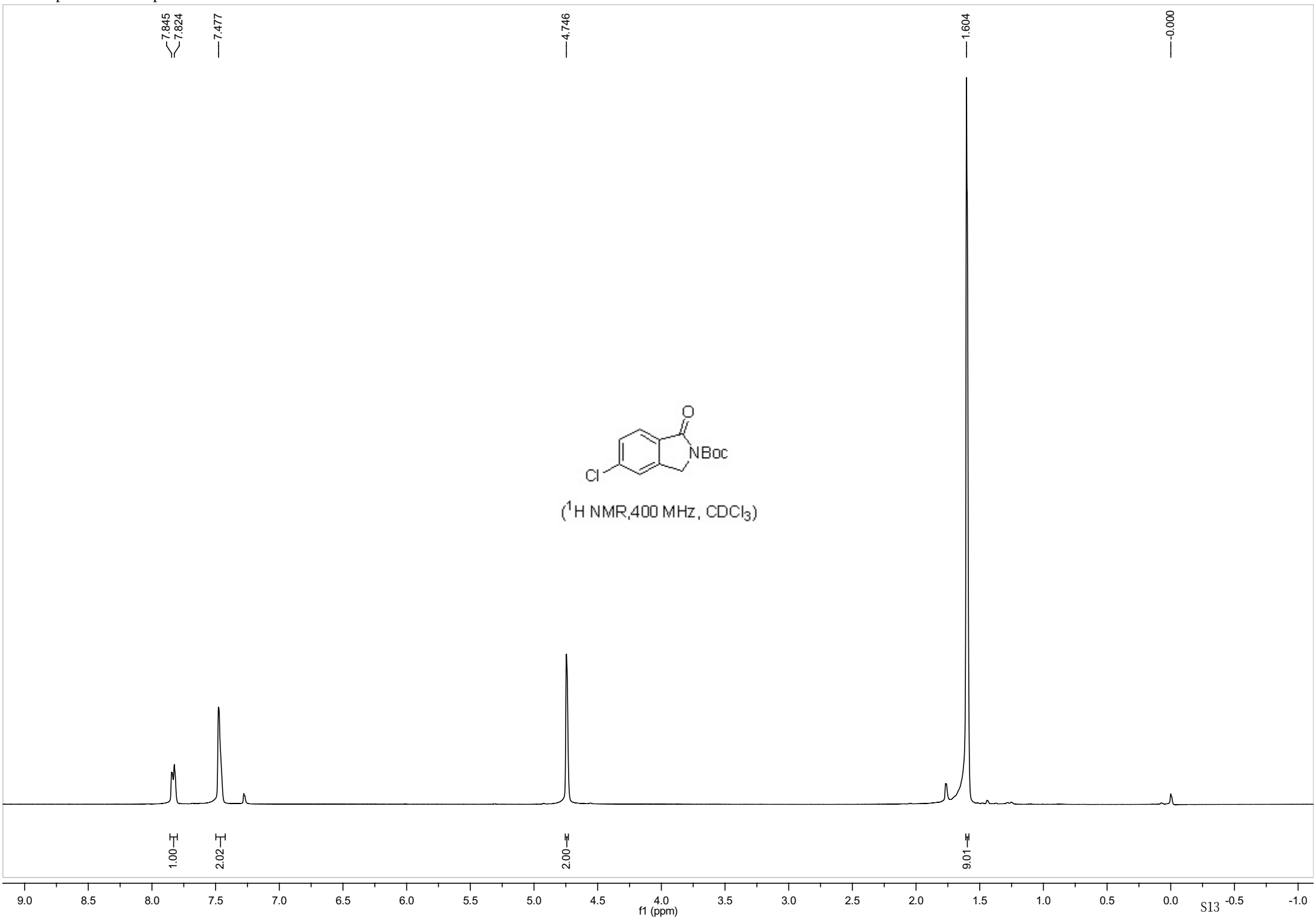
NMR spectra of compound 12c



NMR spectra of compound 12c



NMR spectra of compound 12d



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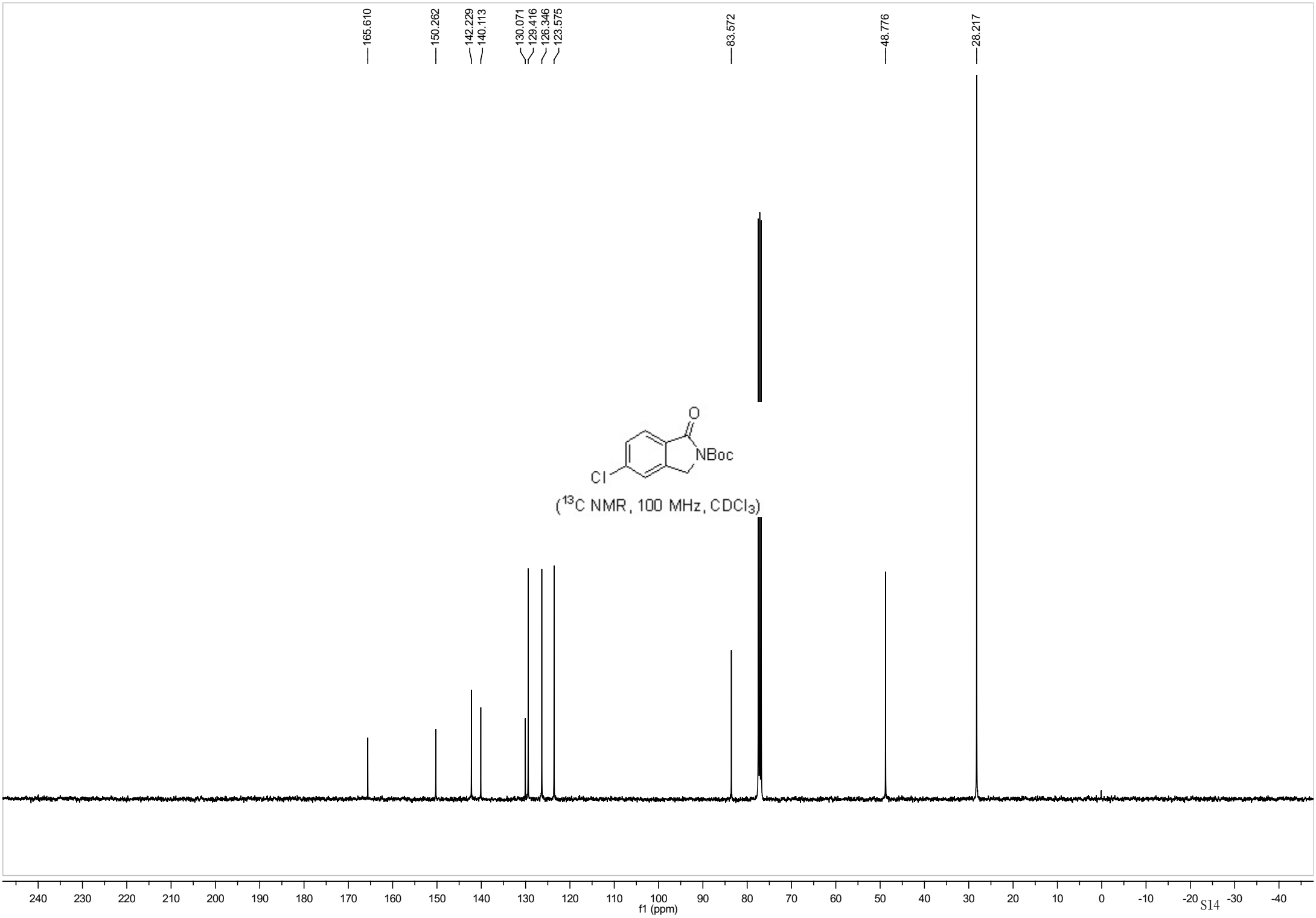

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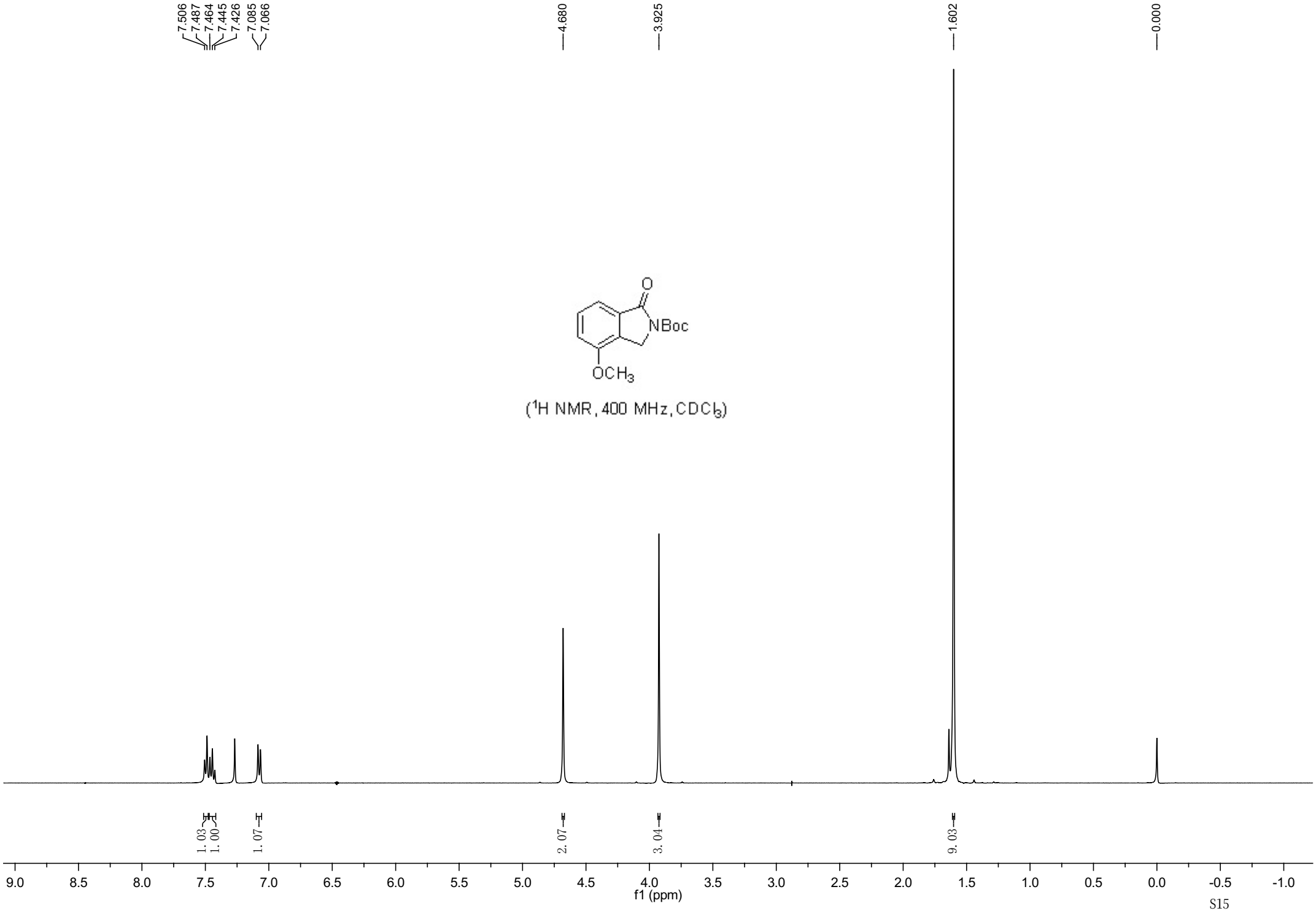

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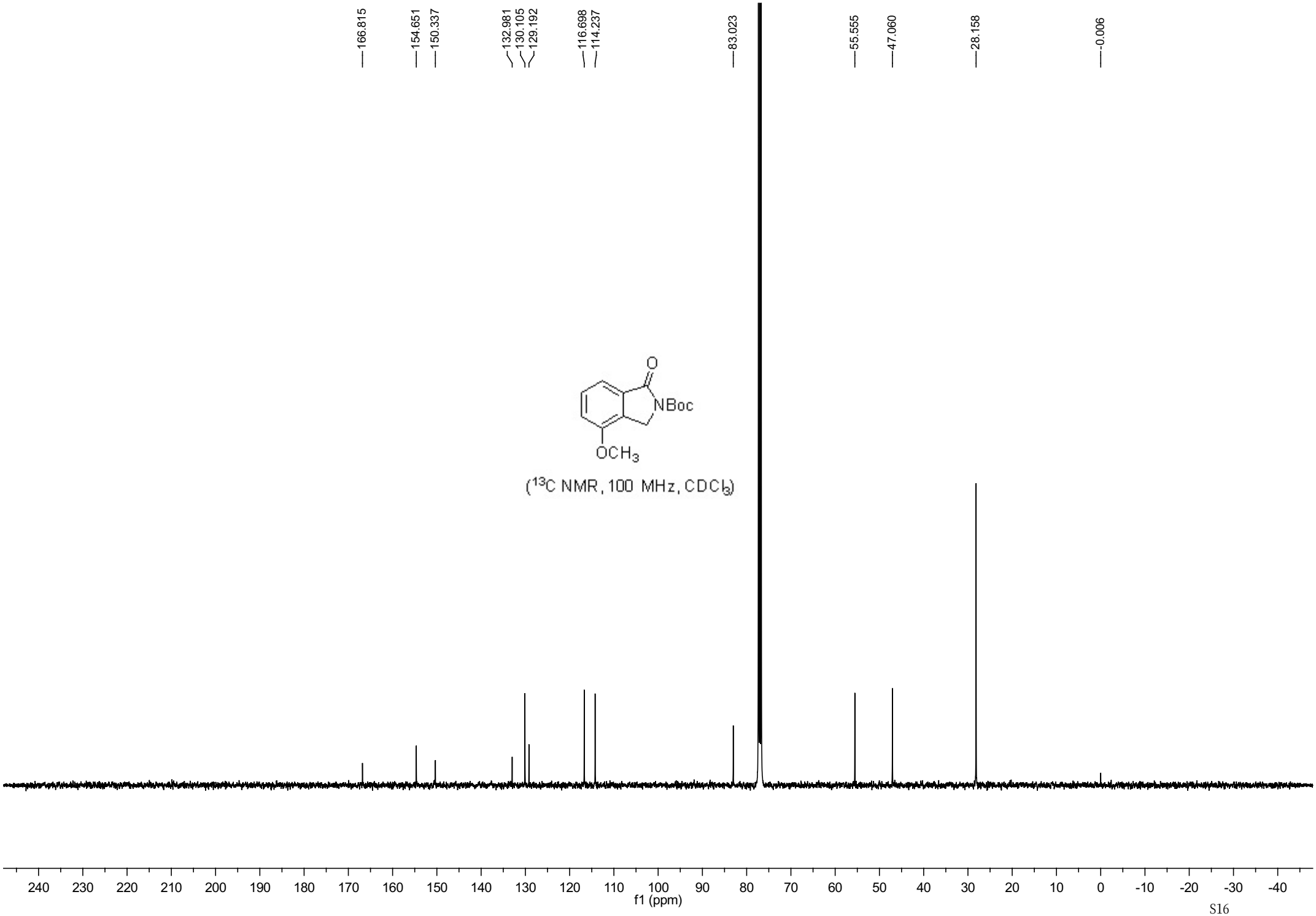
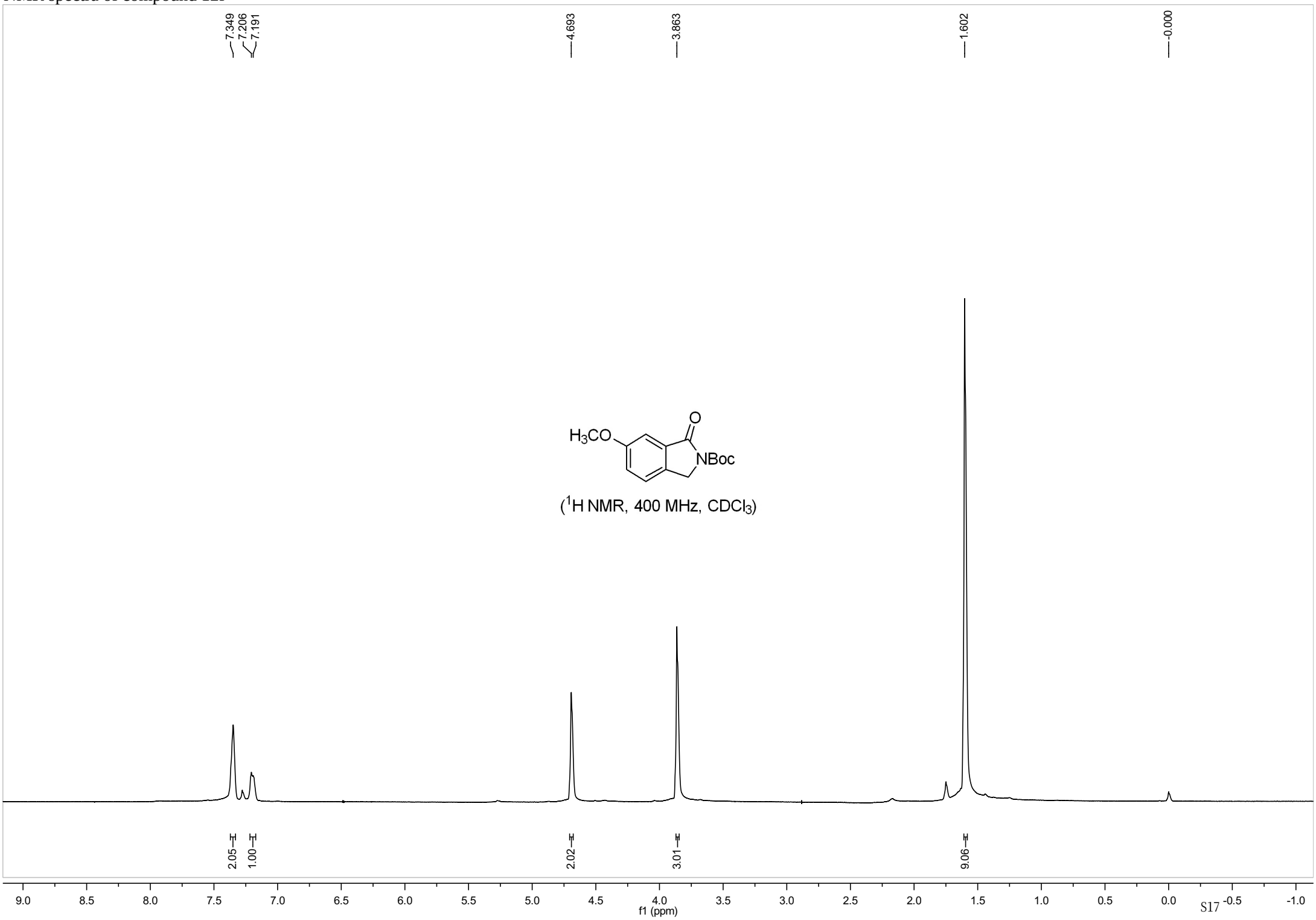
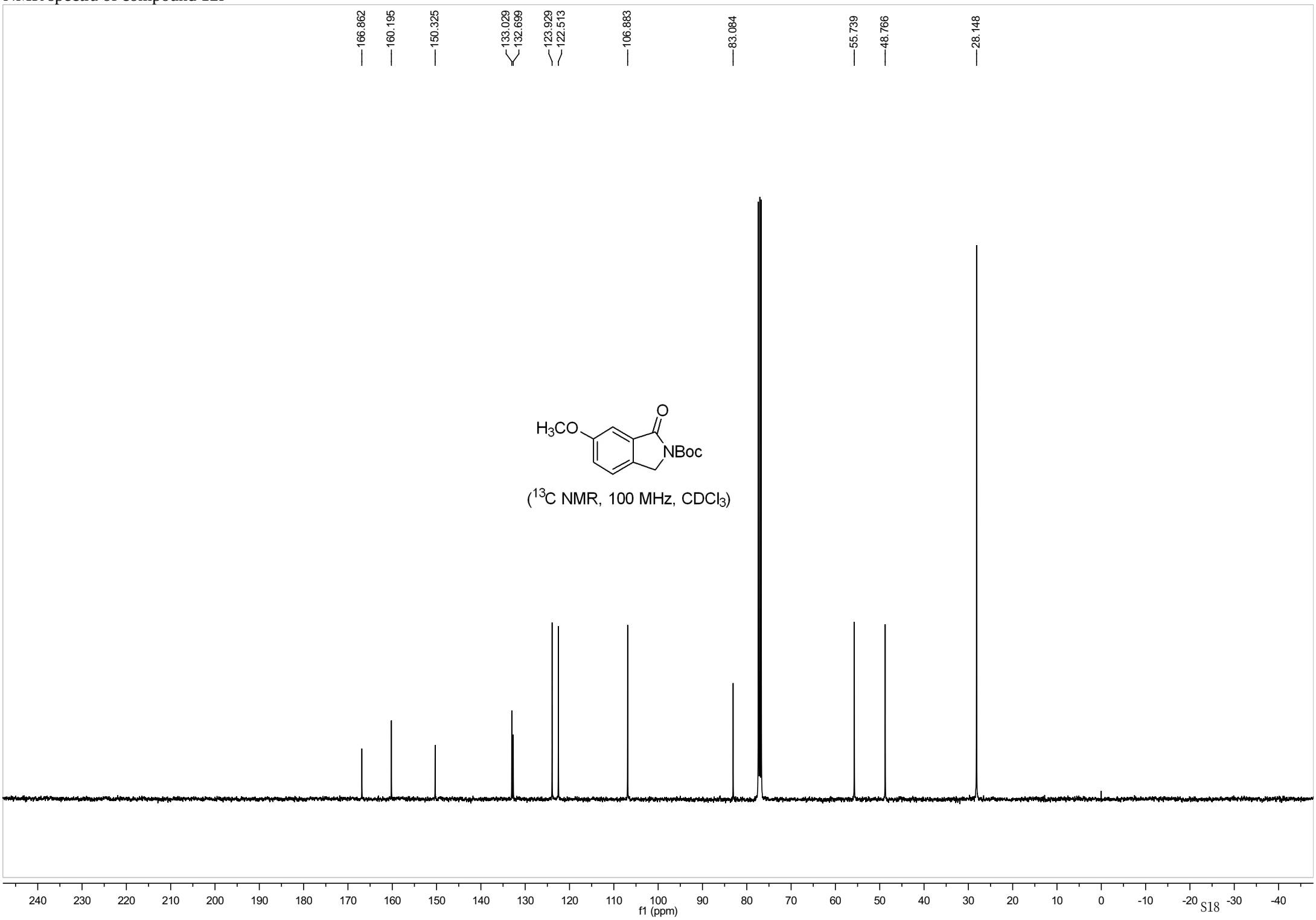


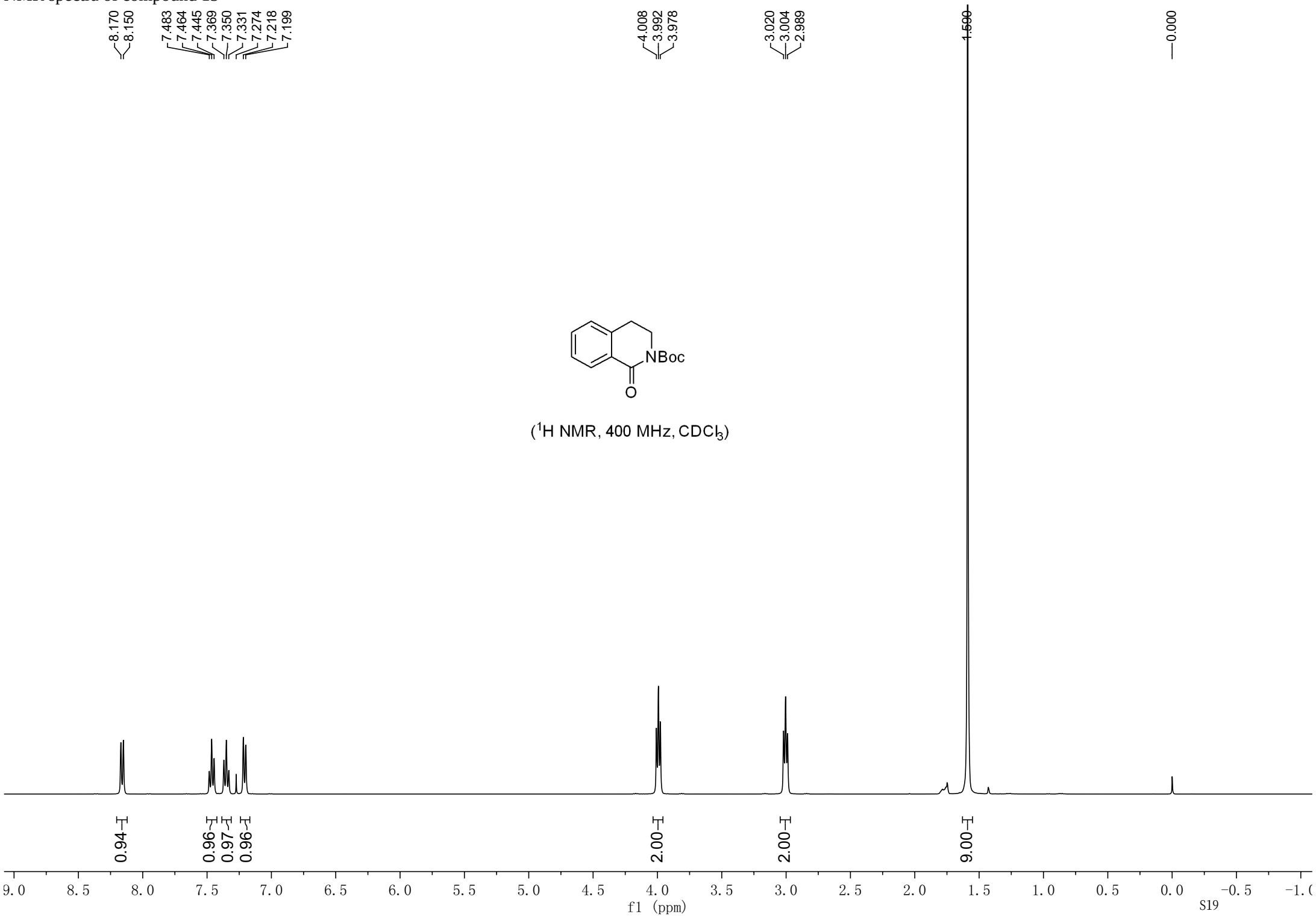
NMR spectra of compound 12f



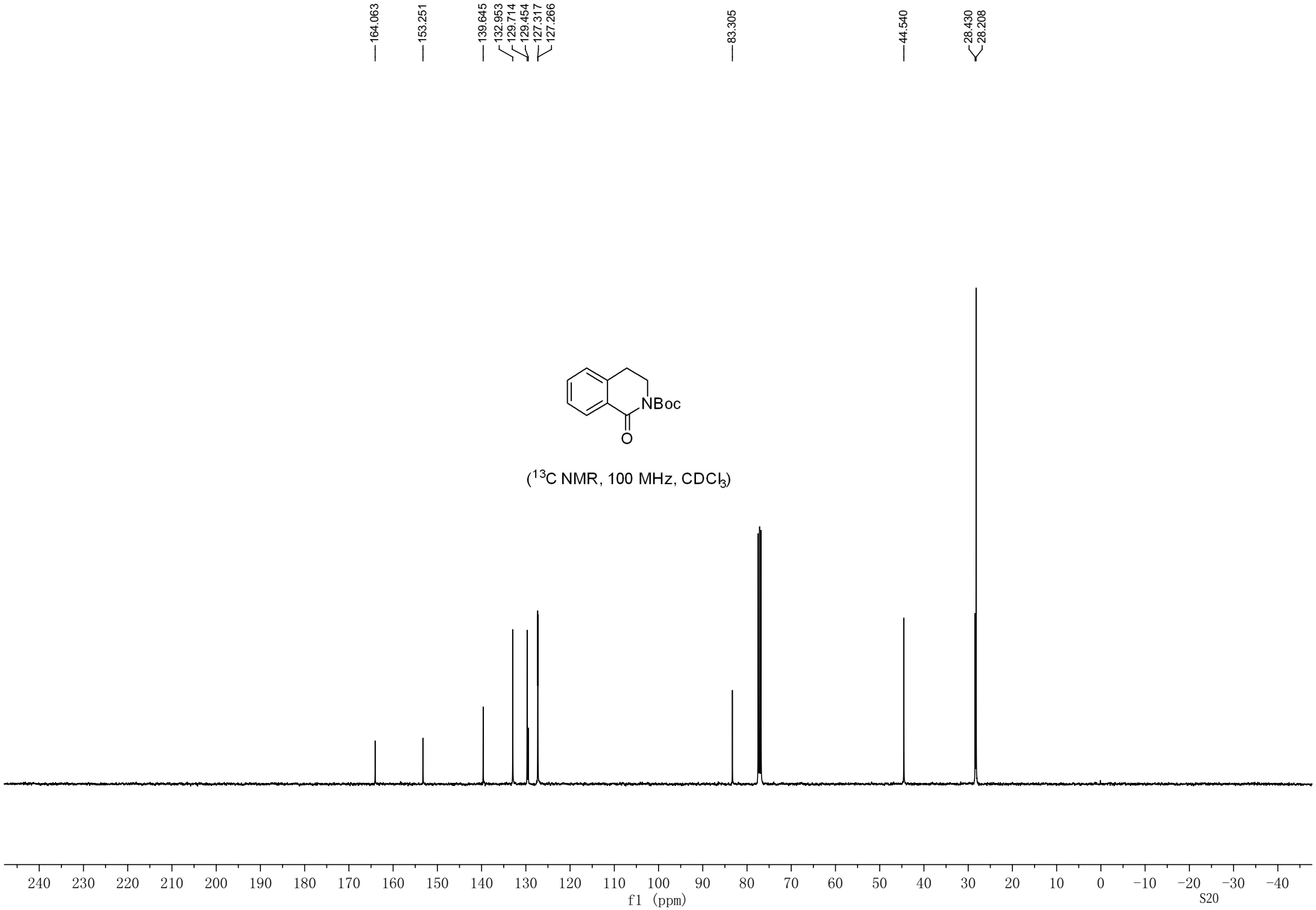
NMR spectra of compound 12f



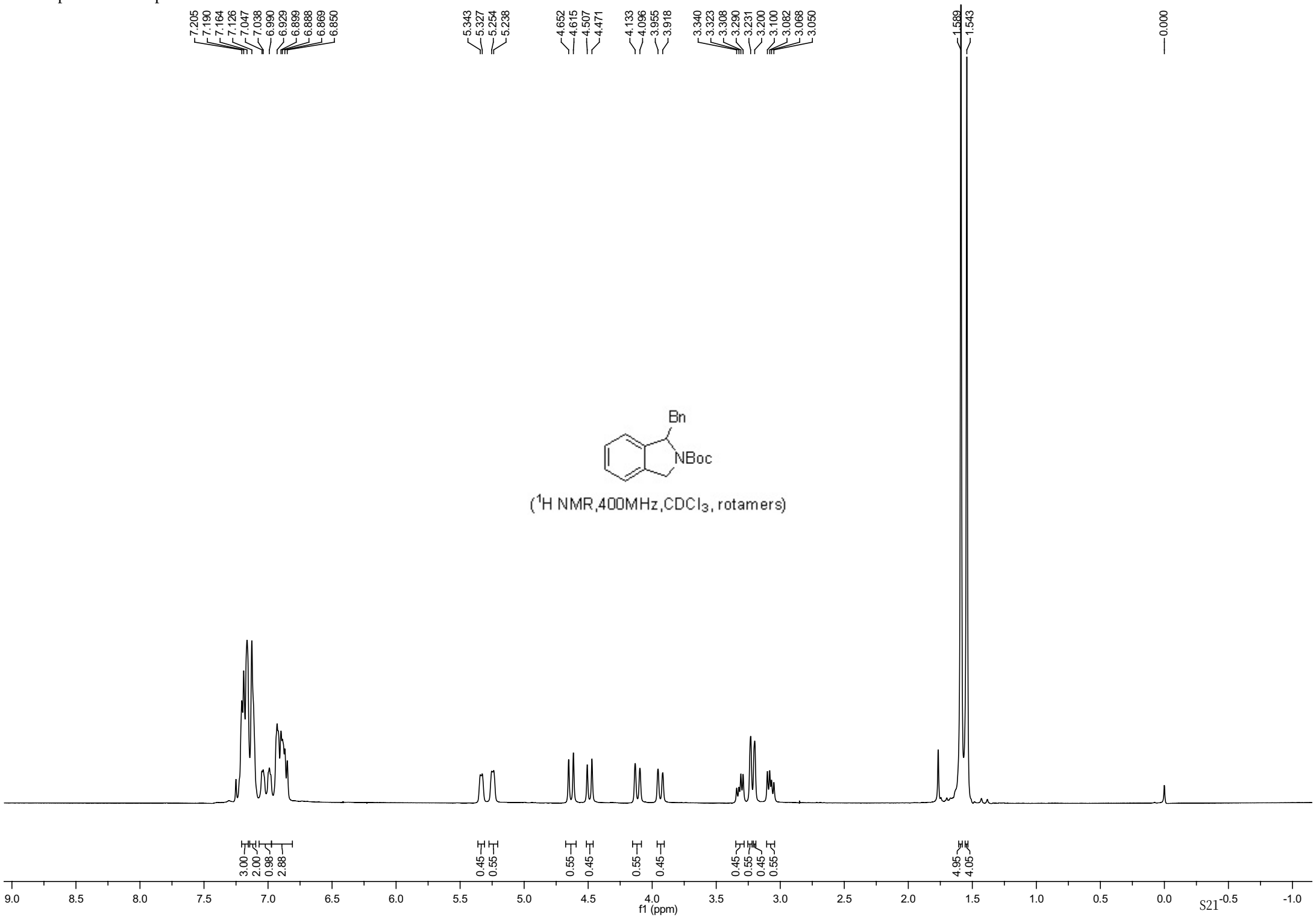
NMR spectra of compound 13



NMR spectra of compound 13



NMR spectra of compound 8a



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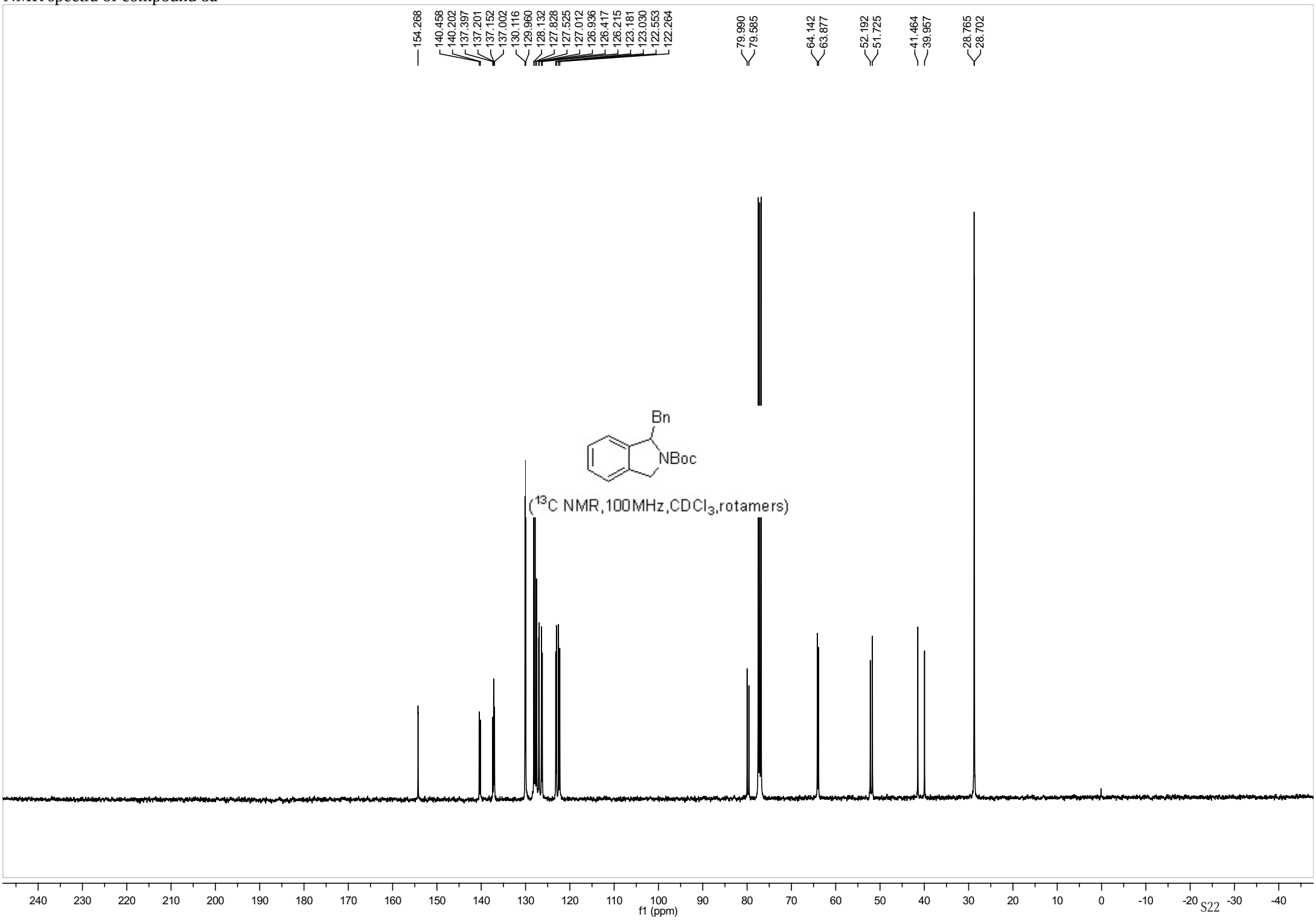
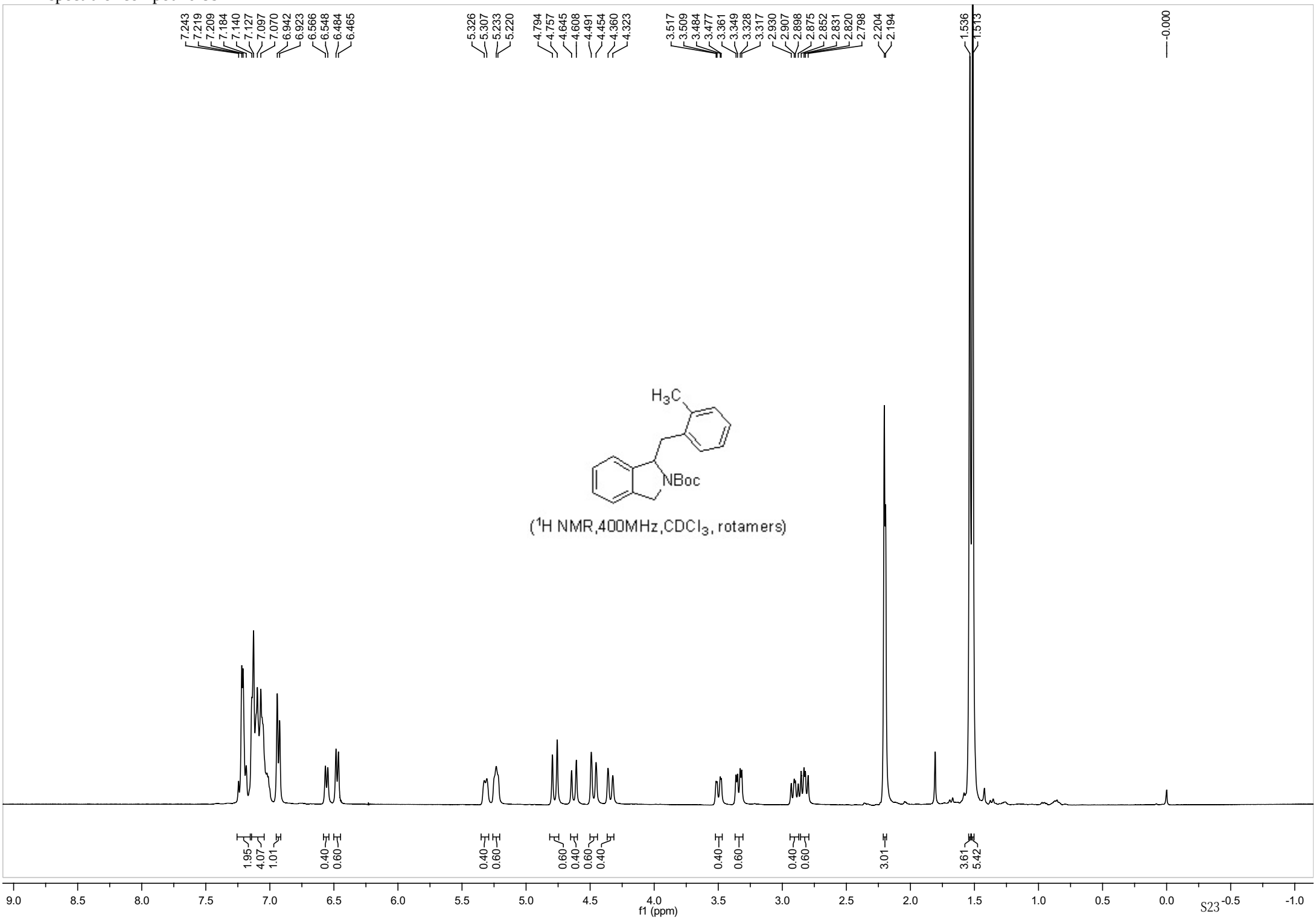


NMR spectra of compound 8b



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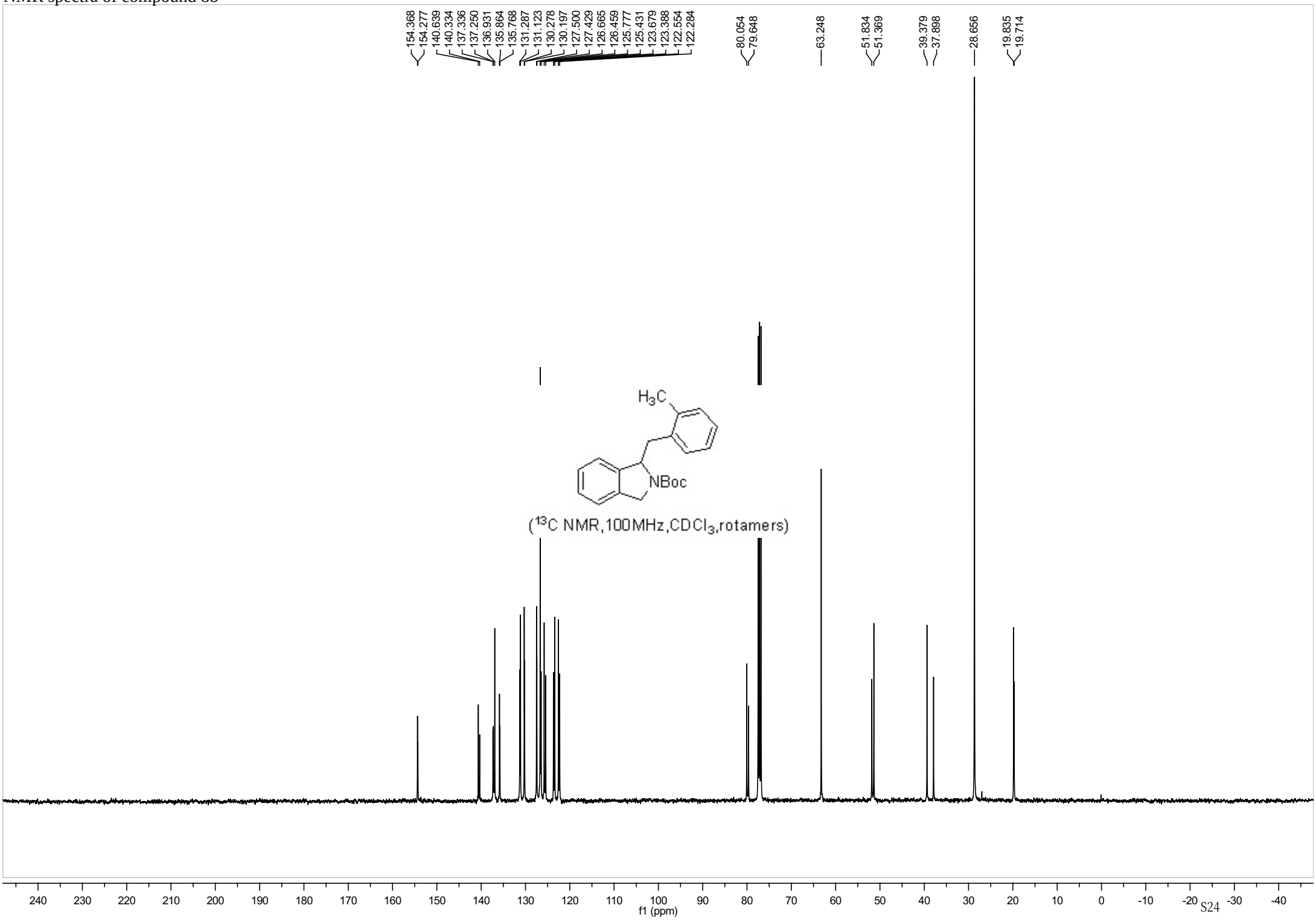
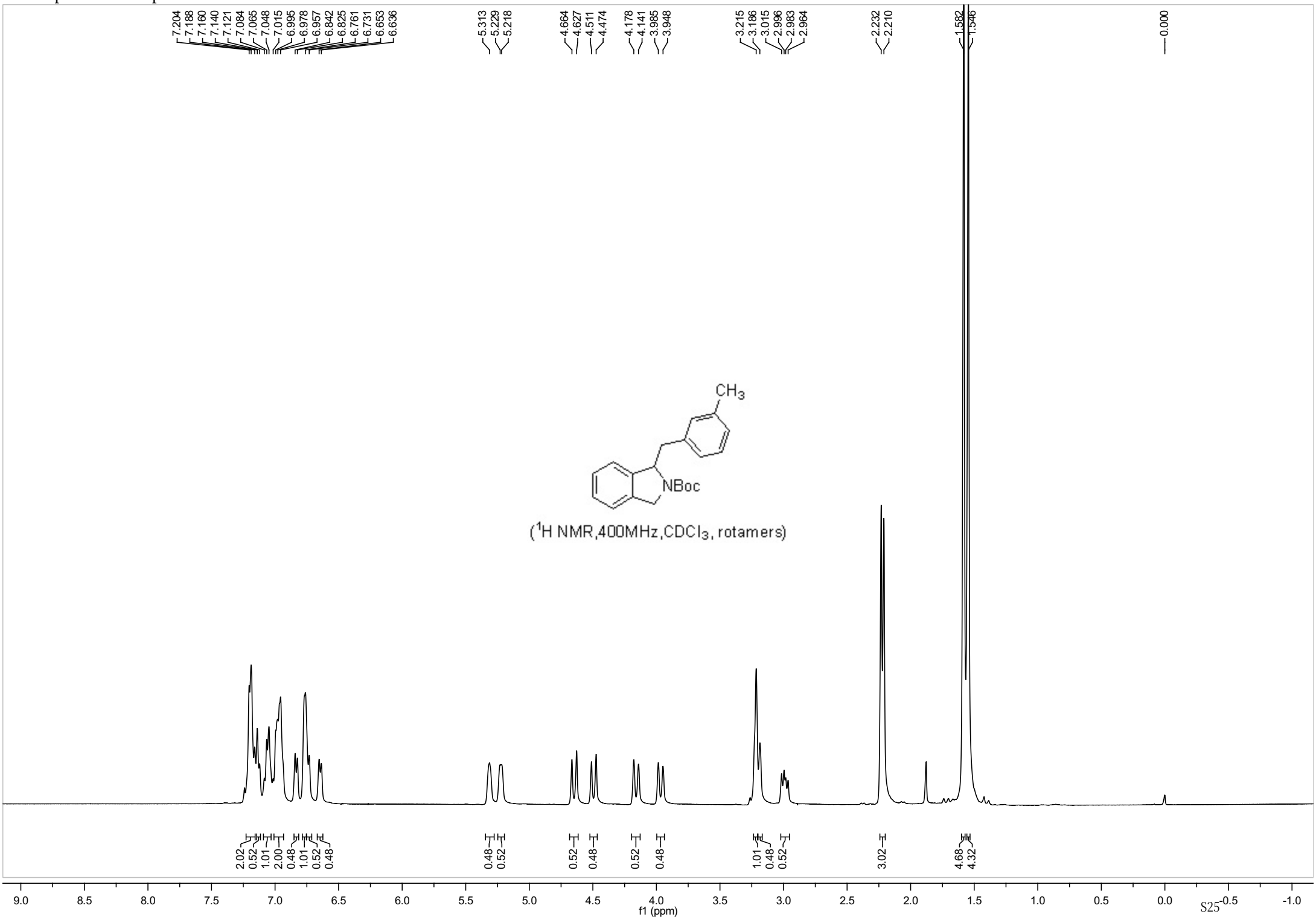
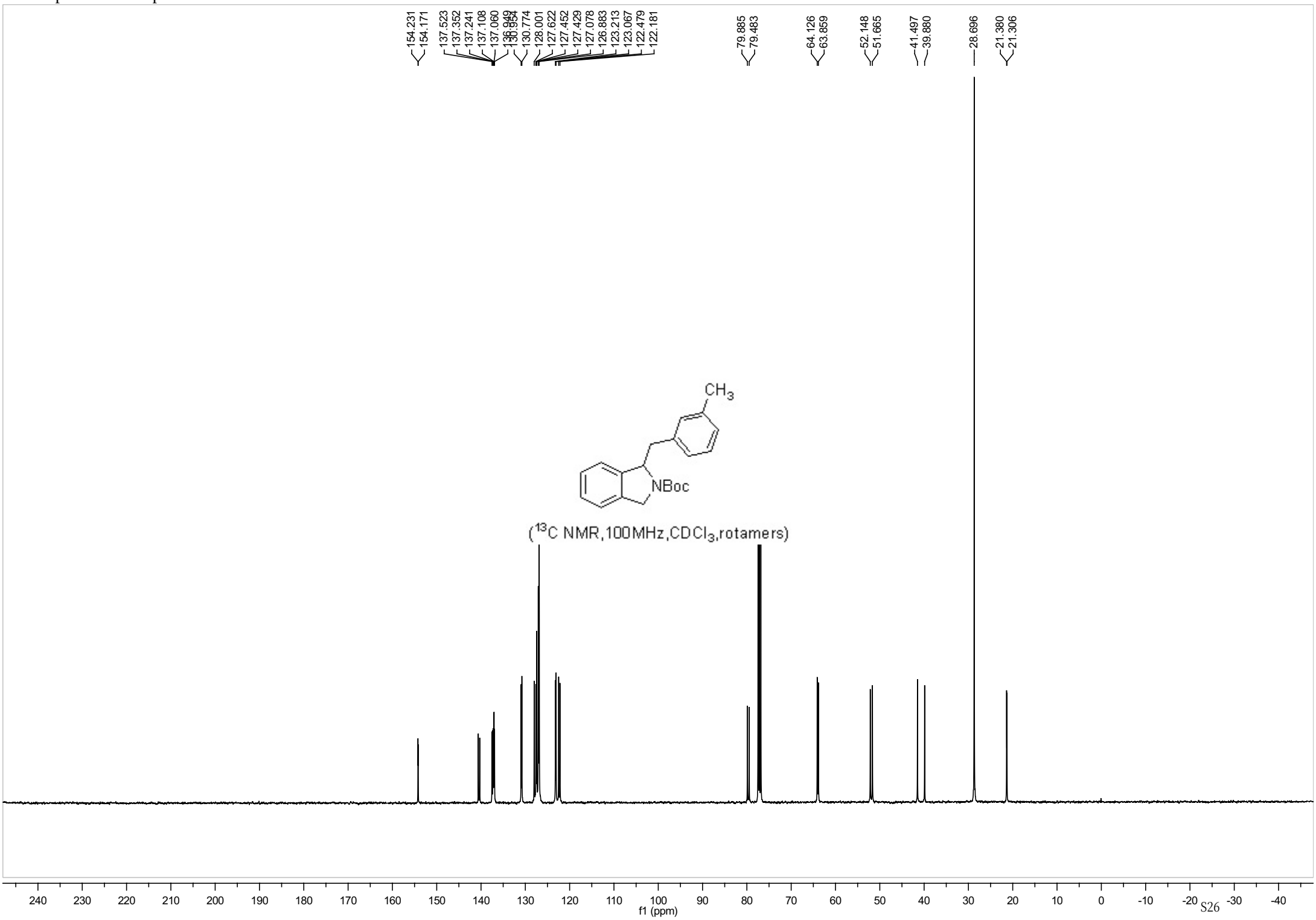


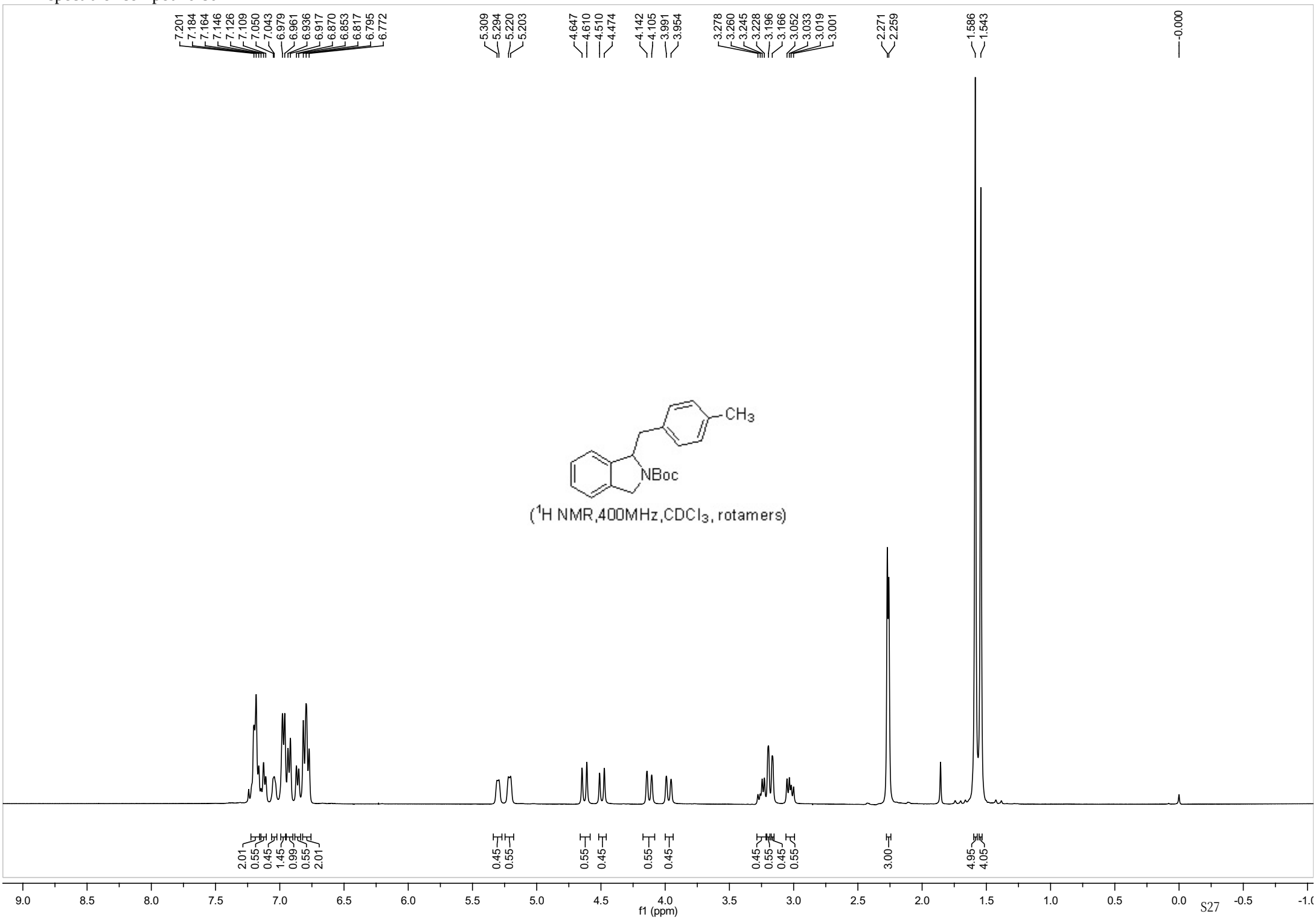
NMR spectra of compound 8c



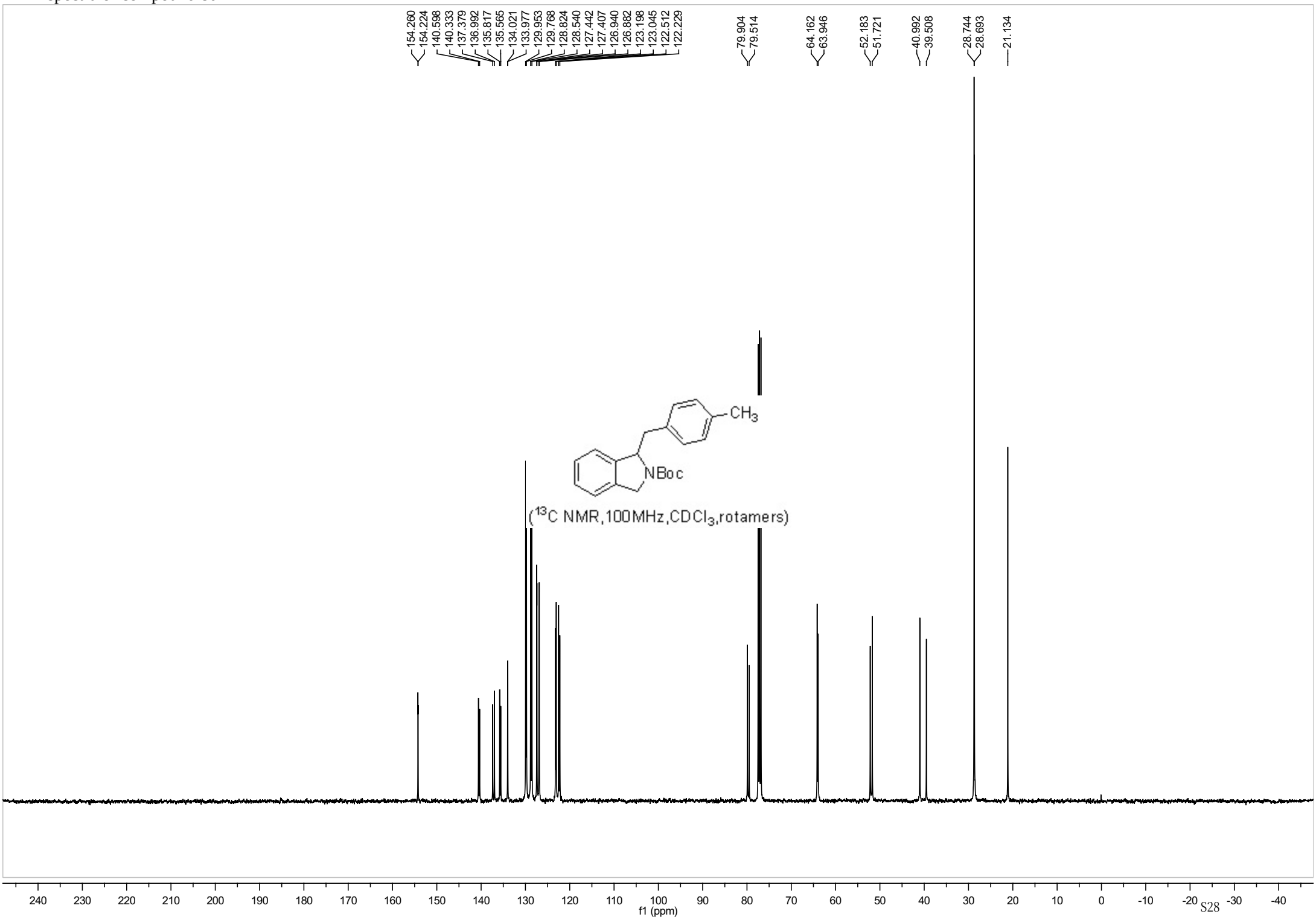
NMR spectra of compound 8c



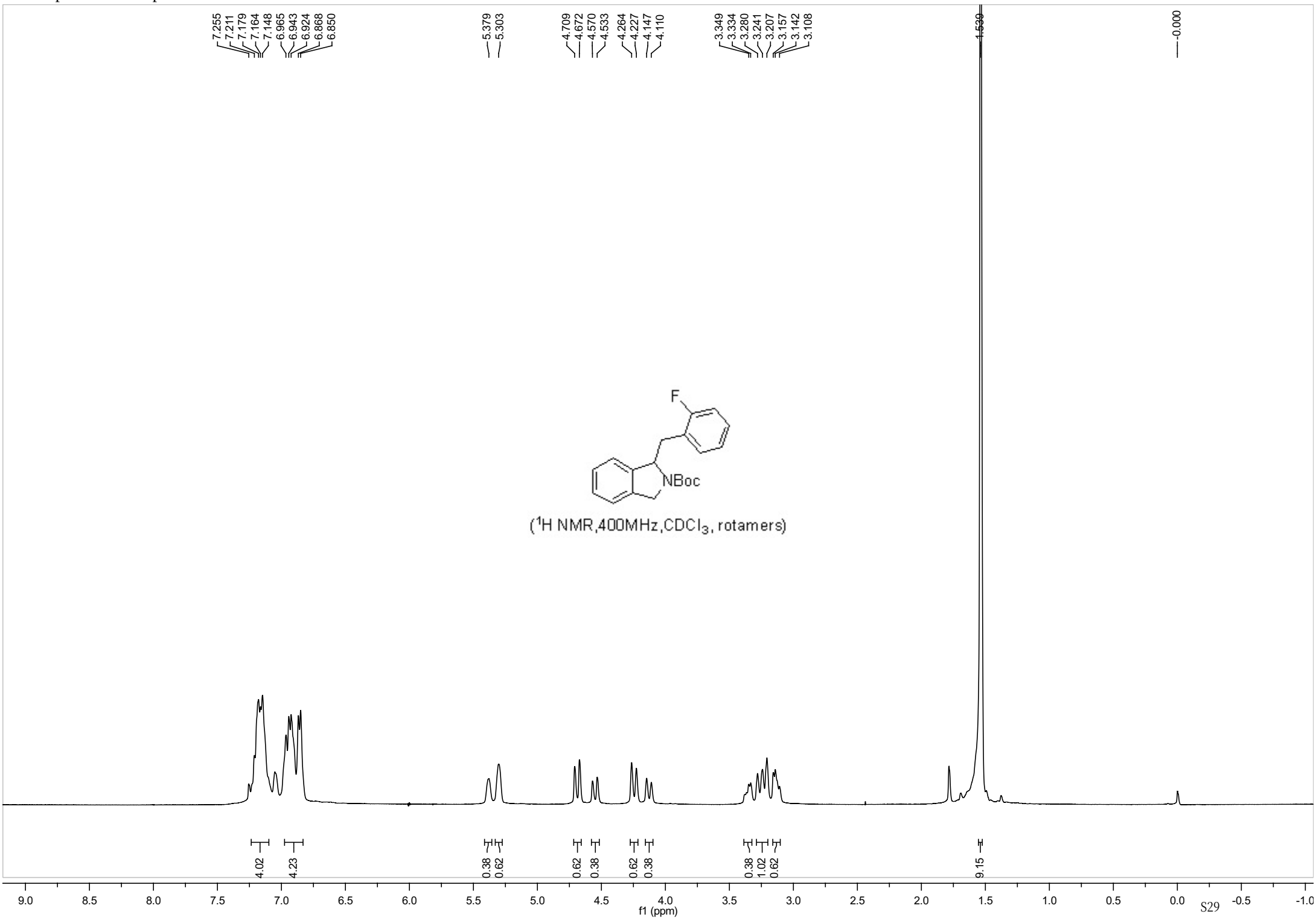
NMR spectra of compound 8d



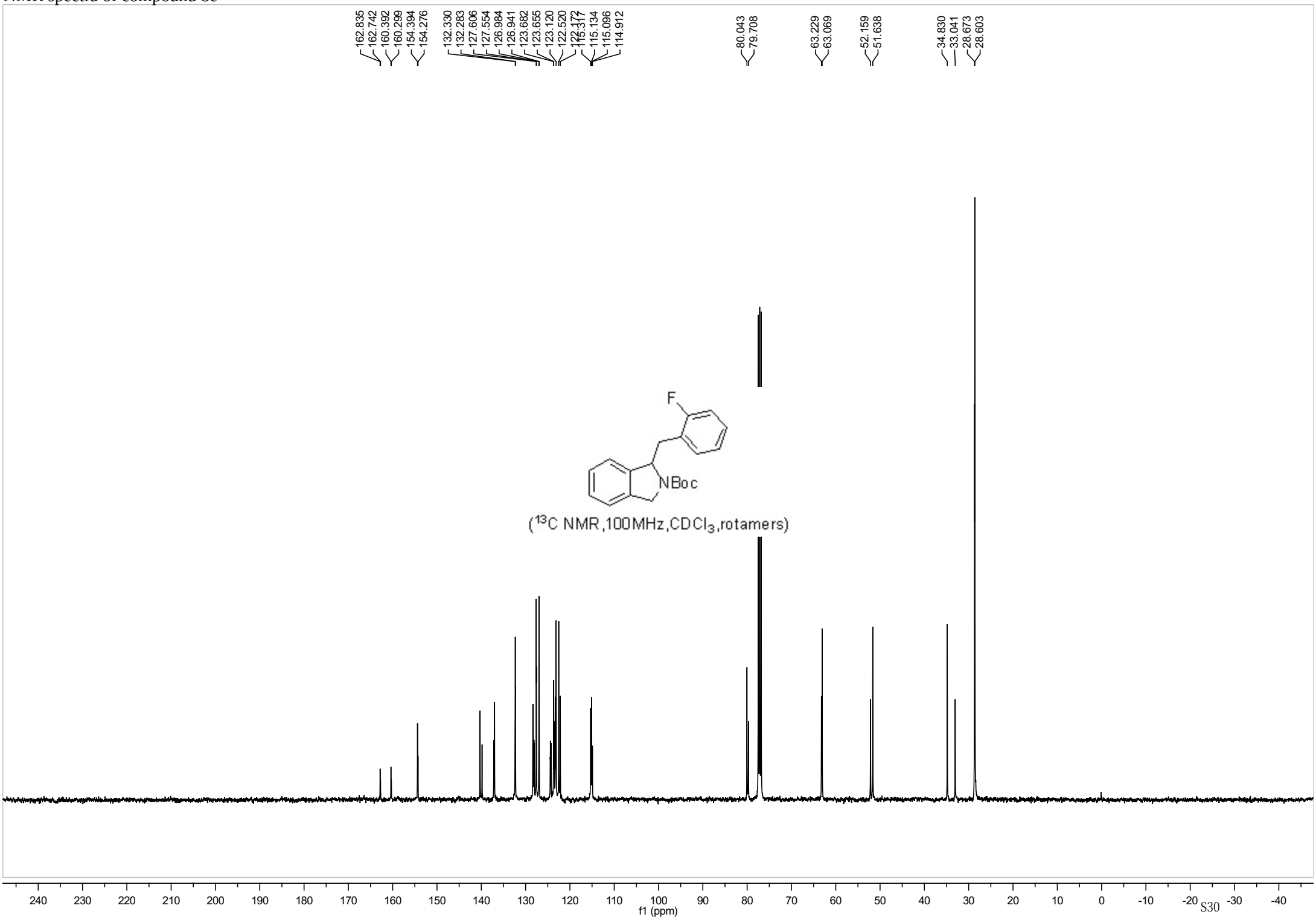
NMR spectra of compound 8d



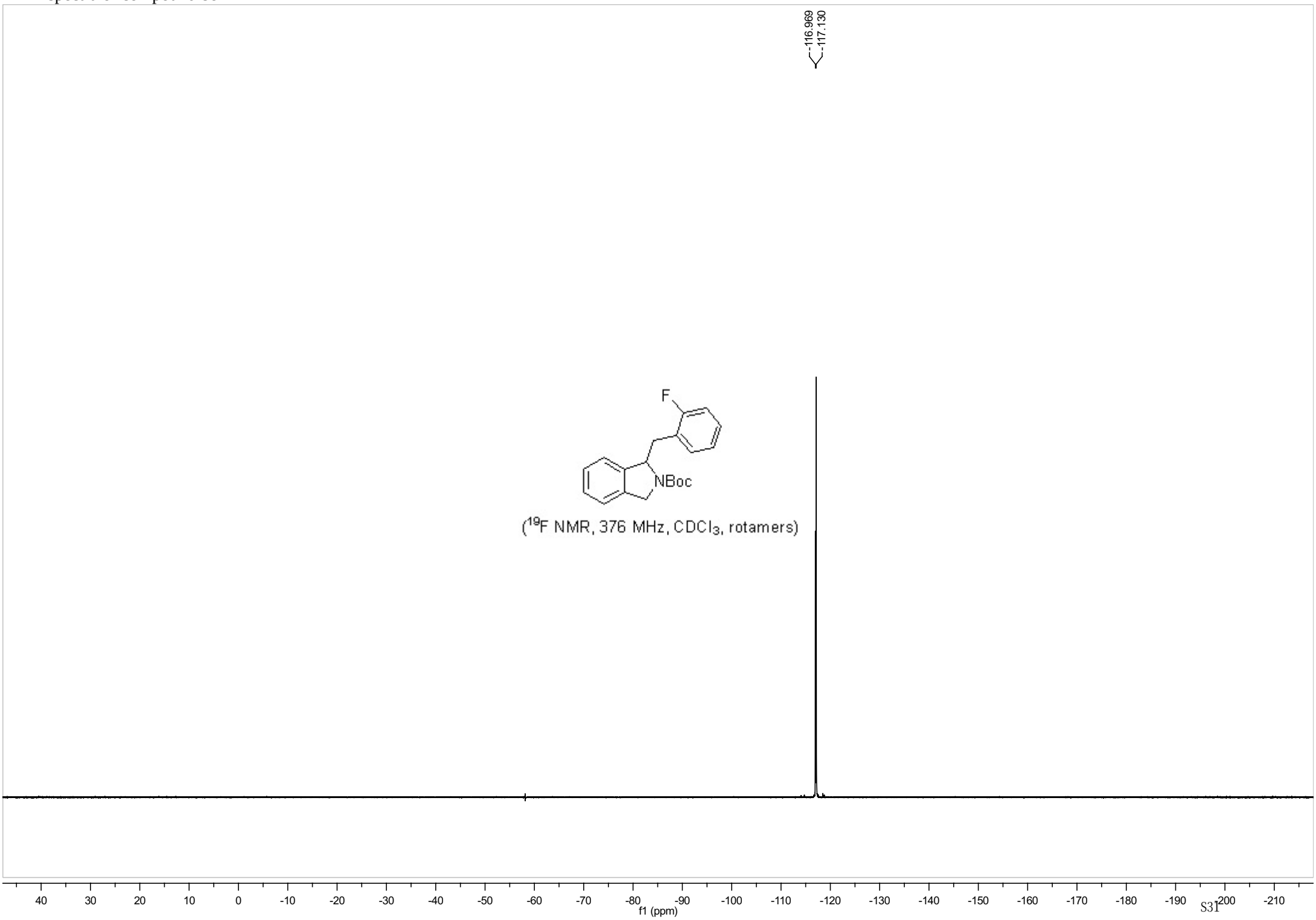
NMR spectra of compound 8e



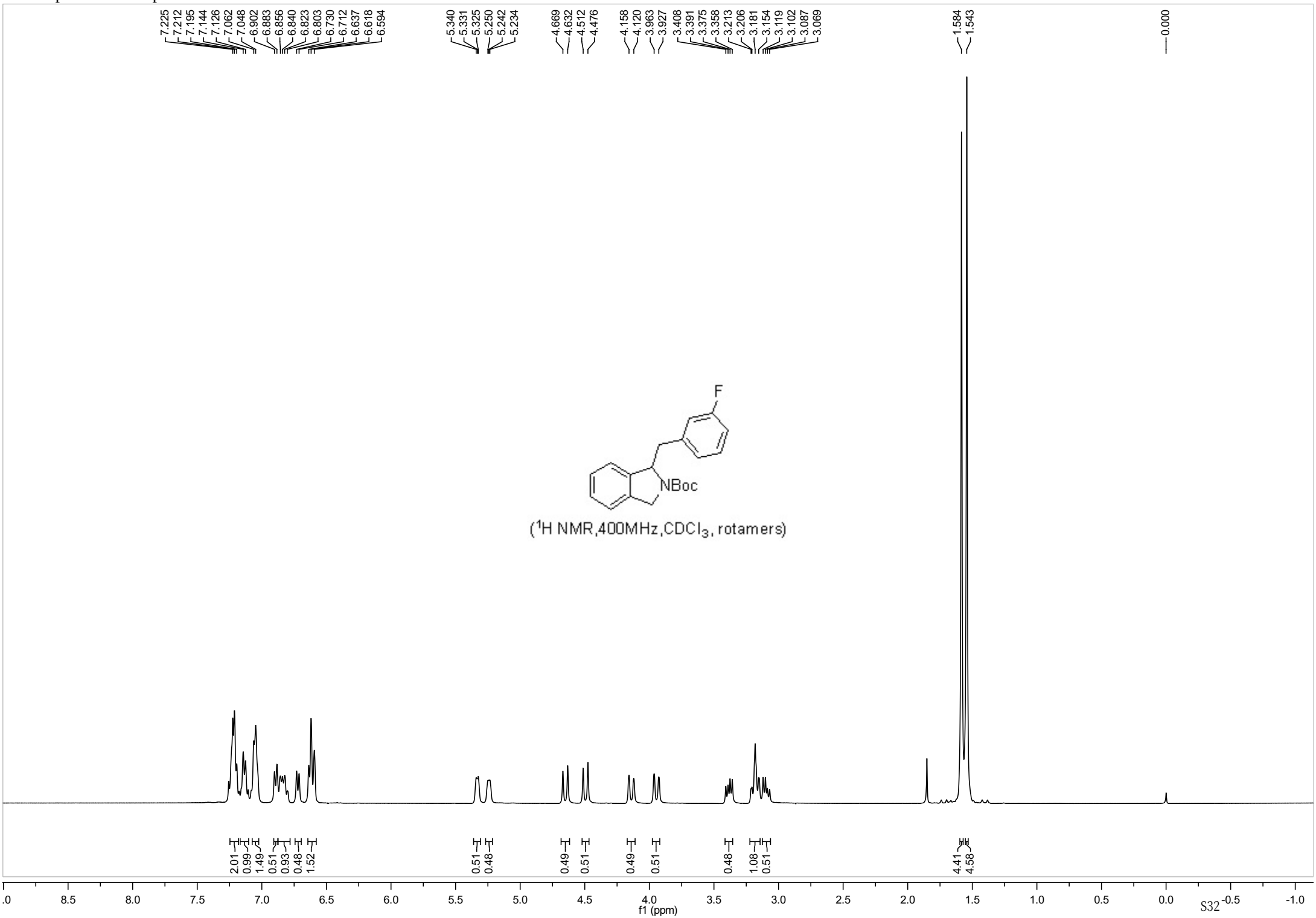
NMR spectra of compound 8e



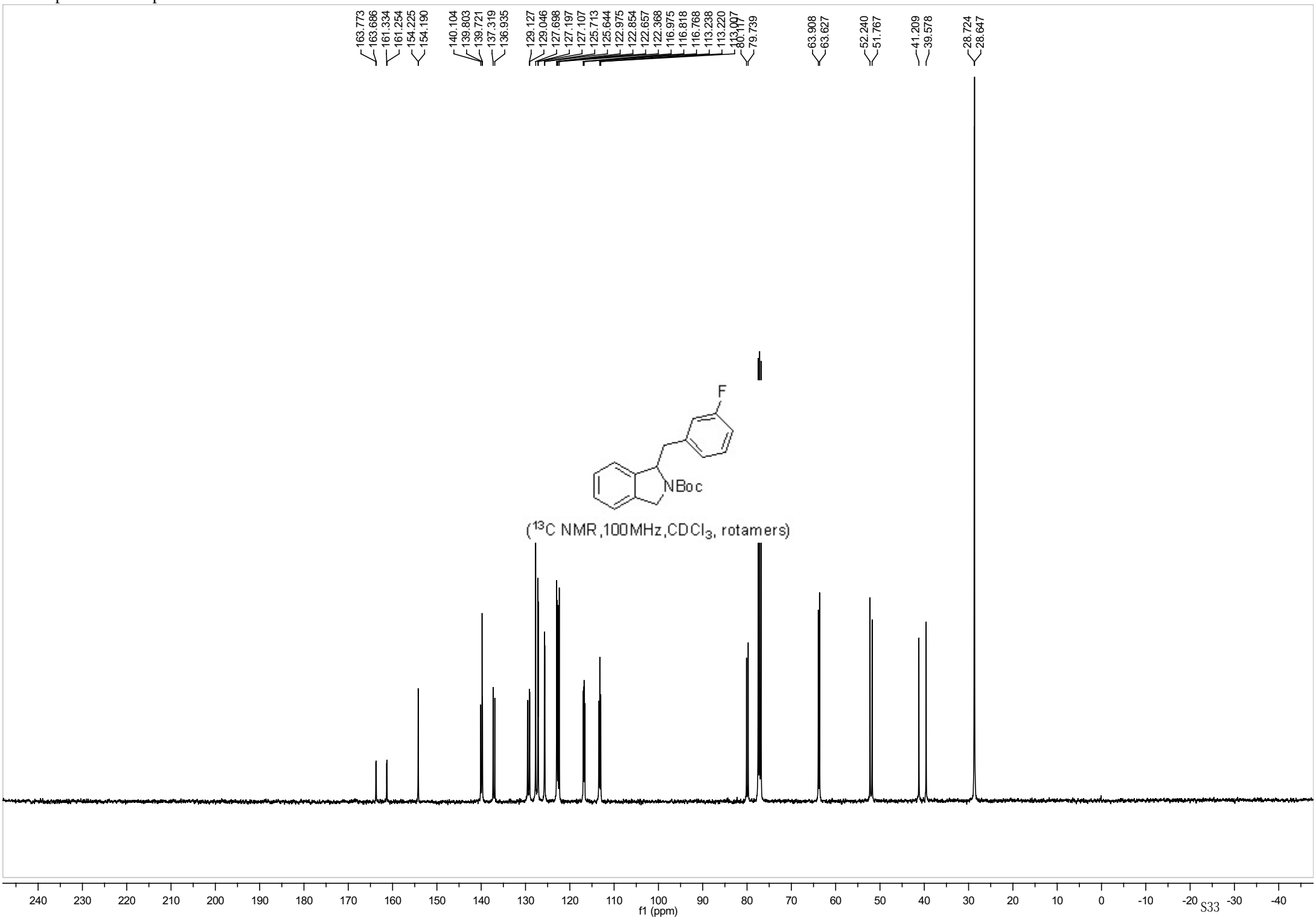
NMR spectra of compound 8e



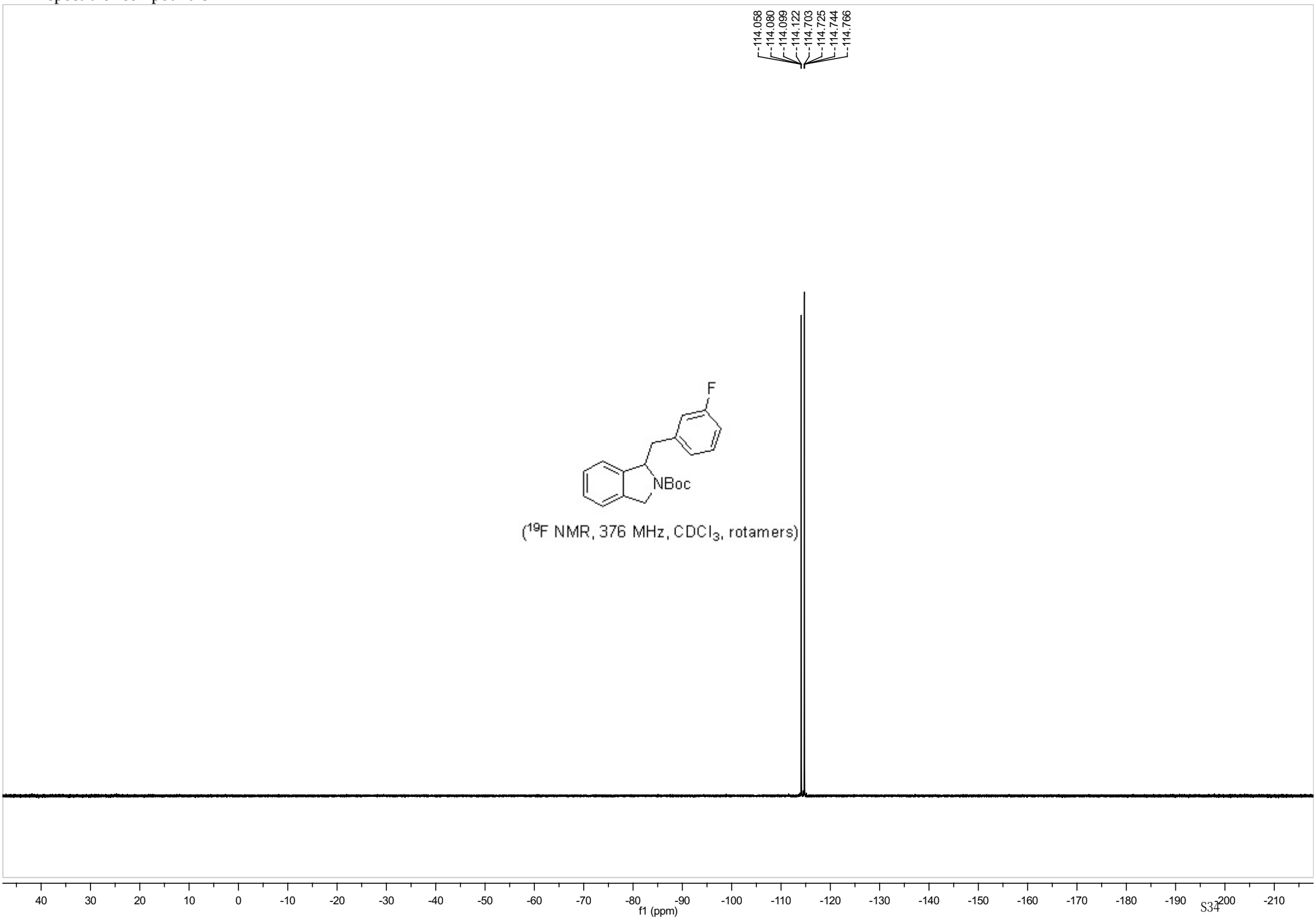
NMR spectra of compound 8f



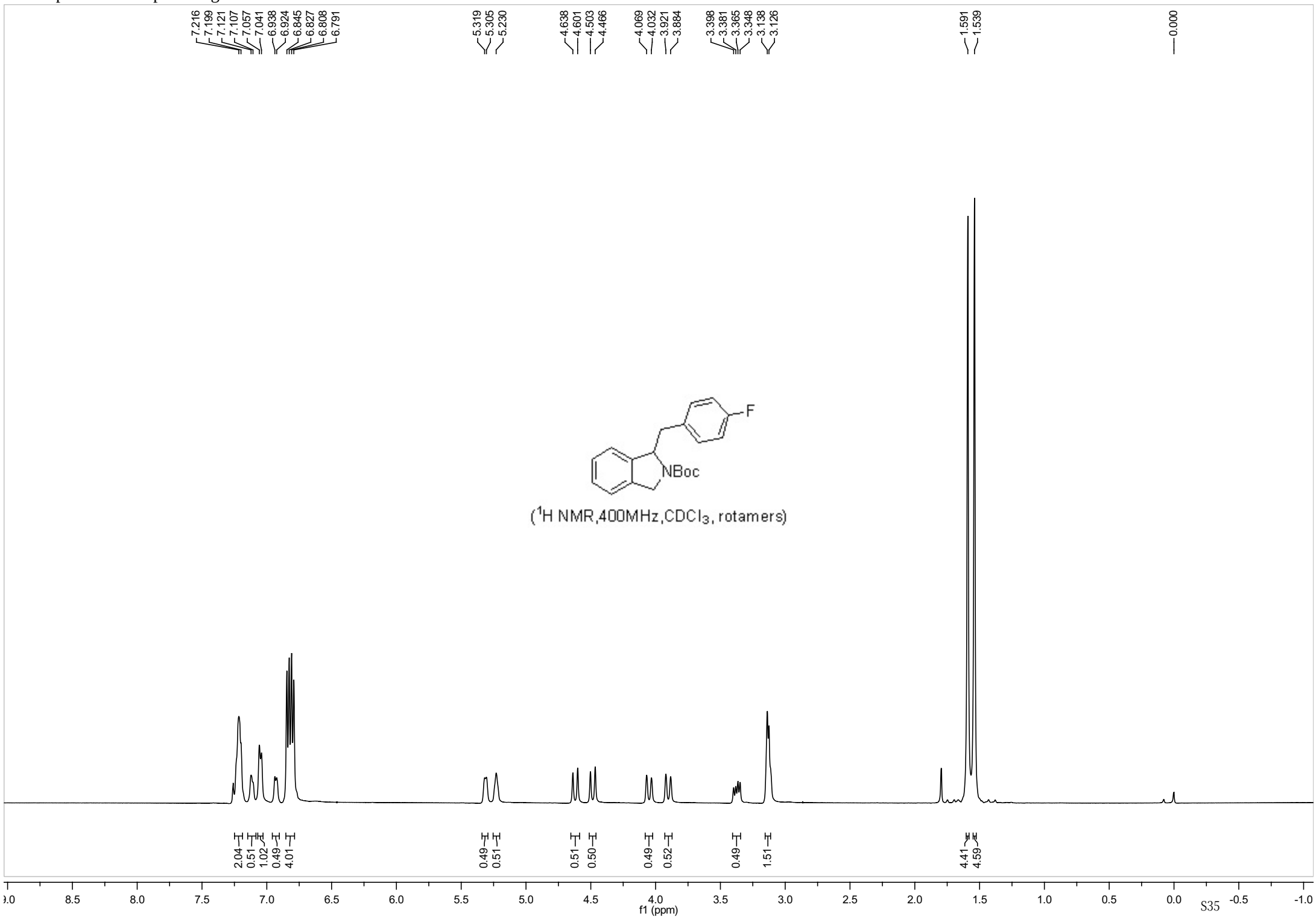
NMR spectra of compound 8f



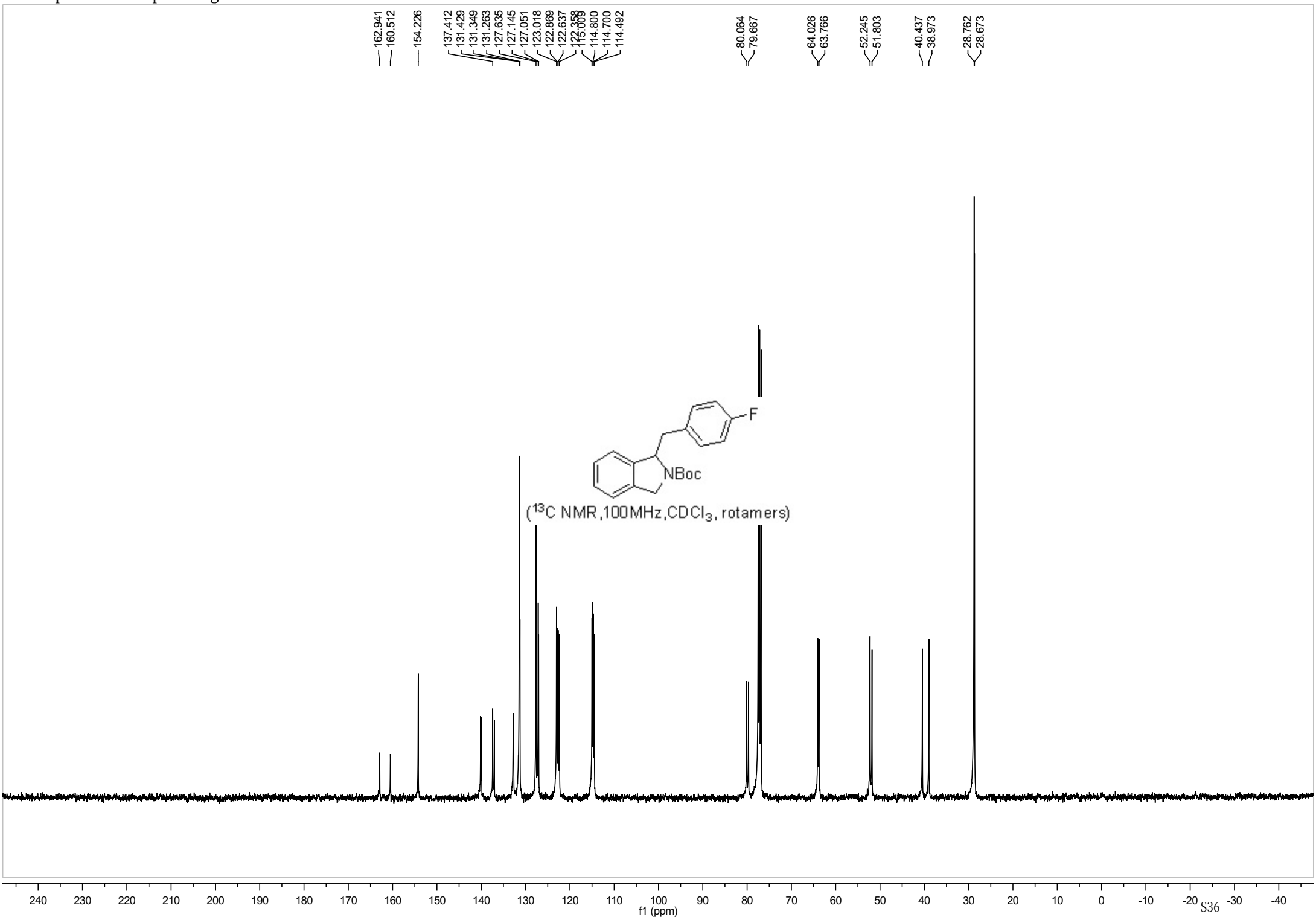
NMR spectra of compound 8f



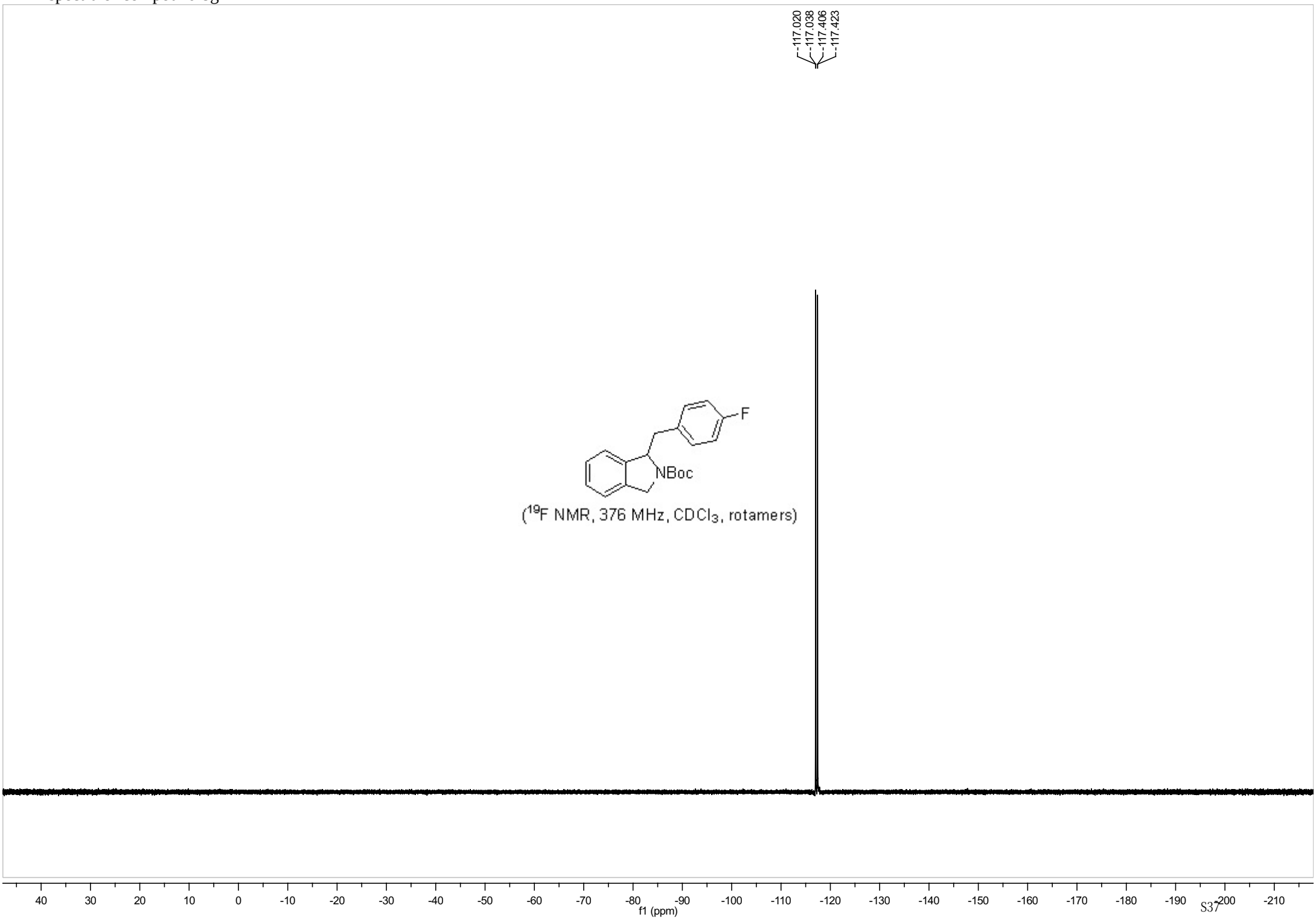
NMR spectra of compound 8g



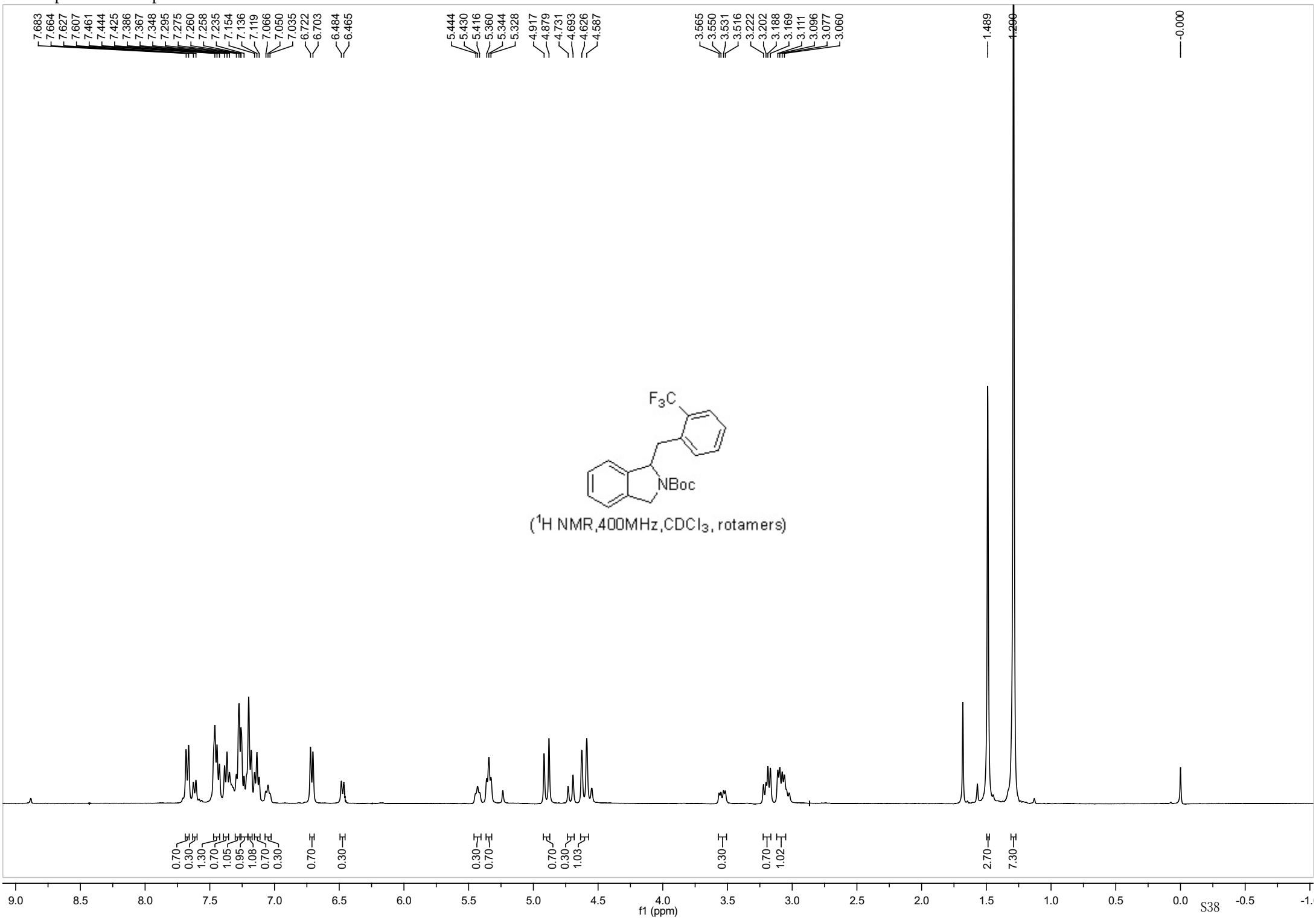
NMR spectra of compound 8g



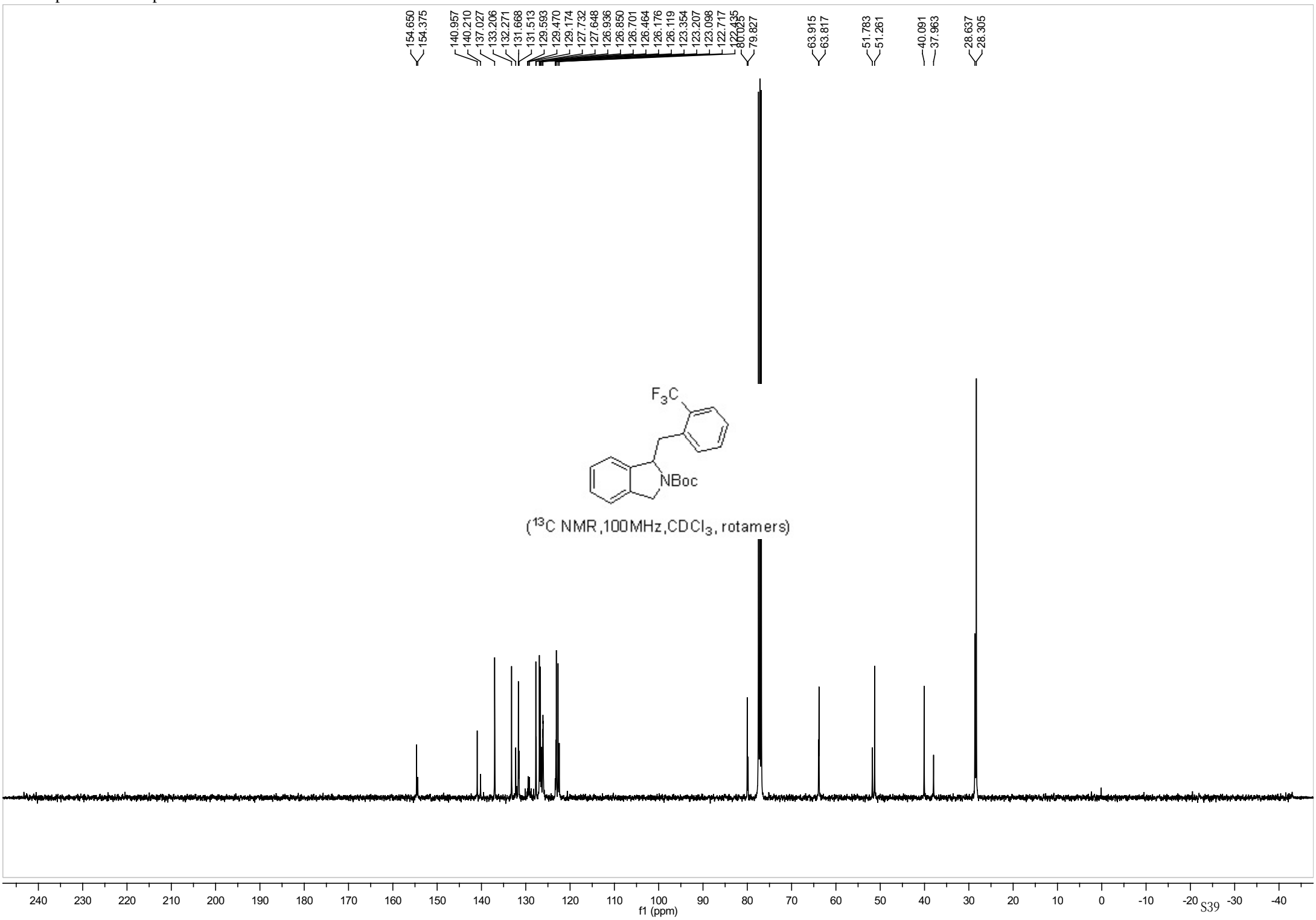
NMR spectra of compound 8g



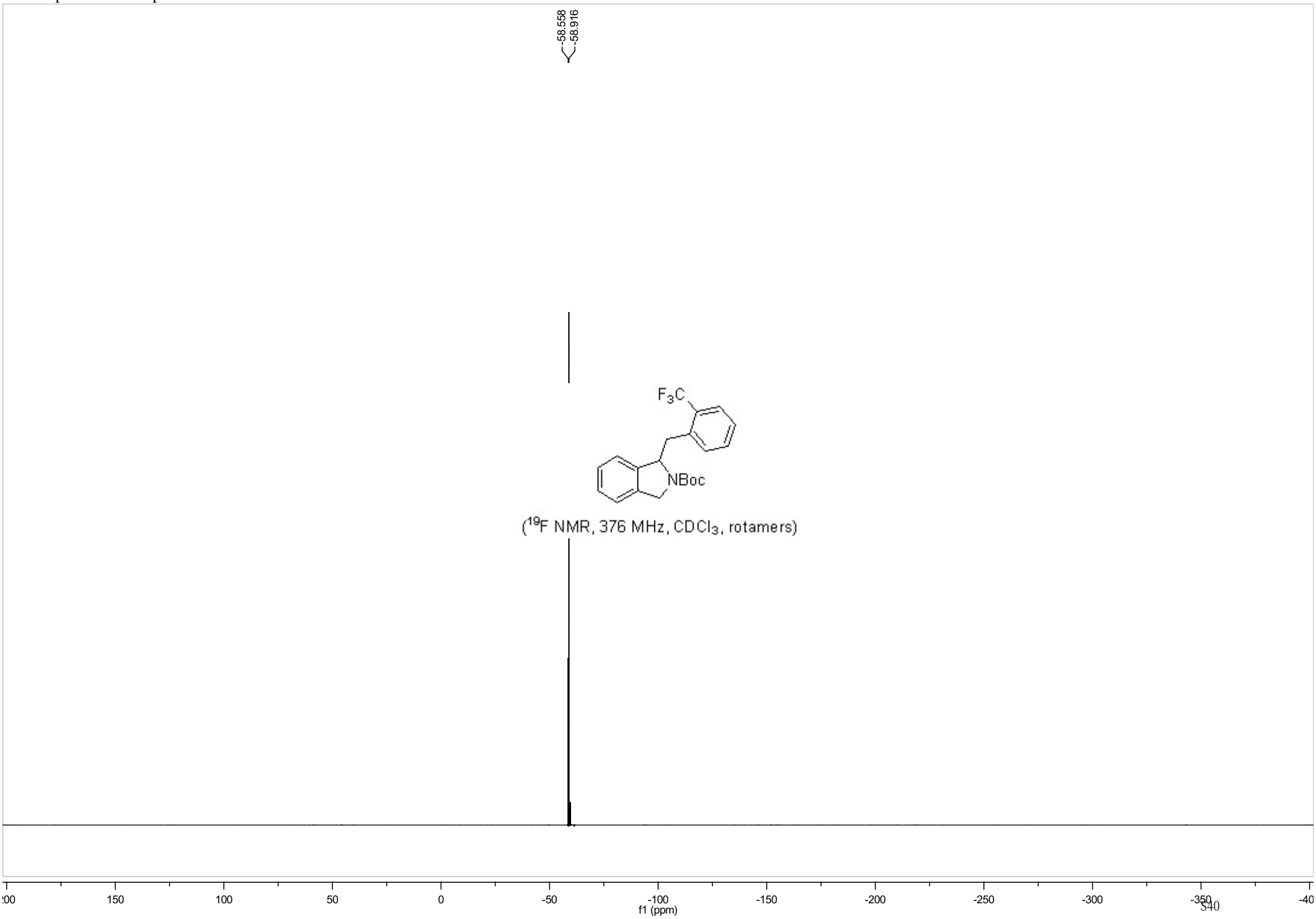
NMR spectra of compound 8h



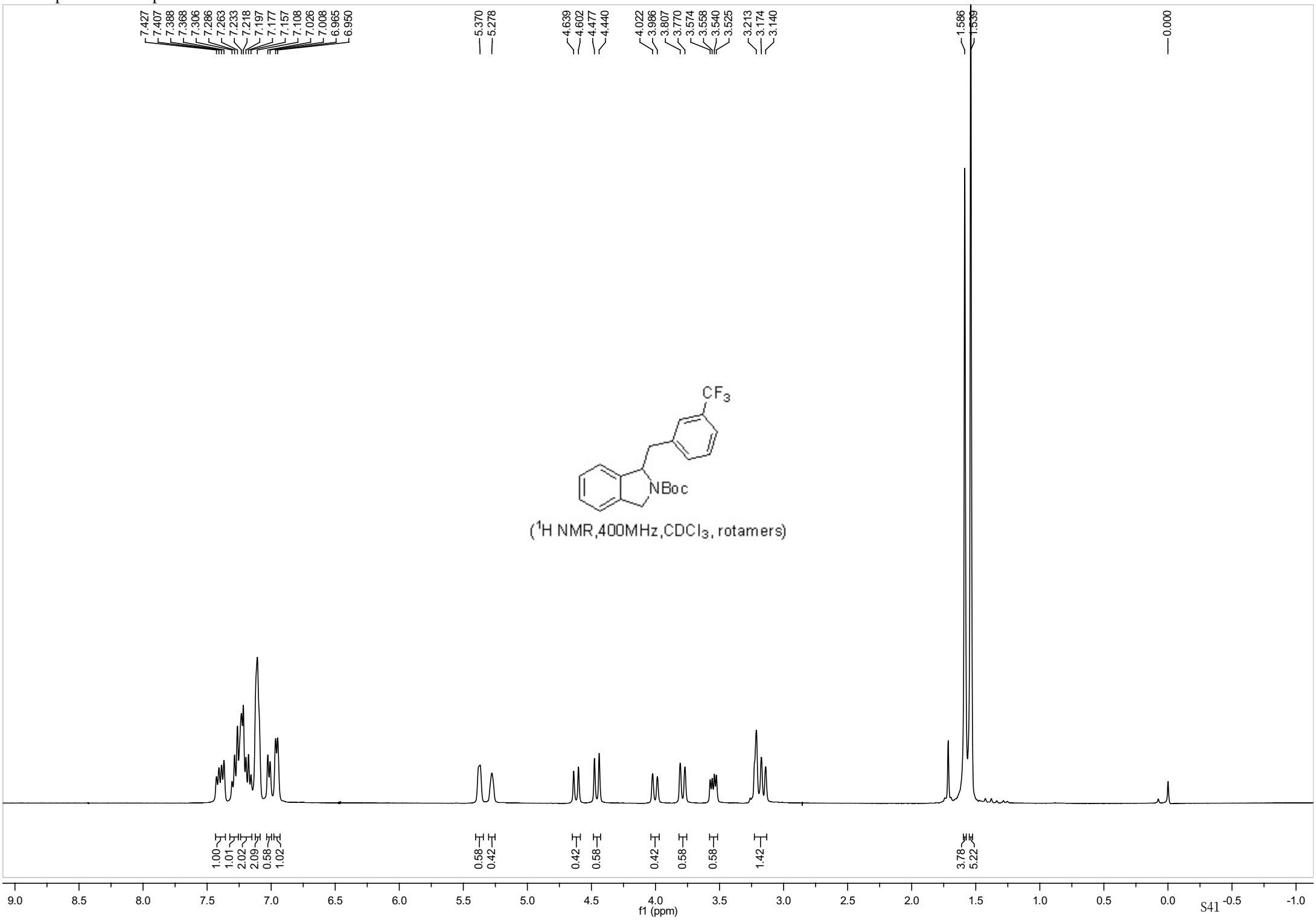
NMR spectra of compound 8h



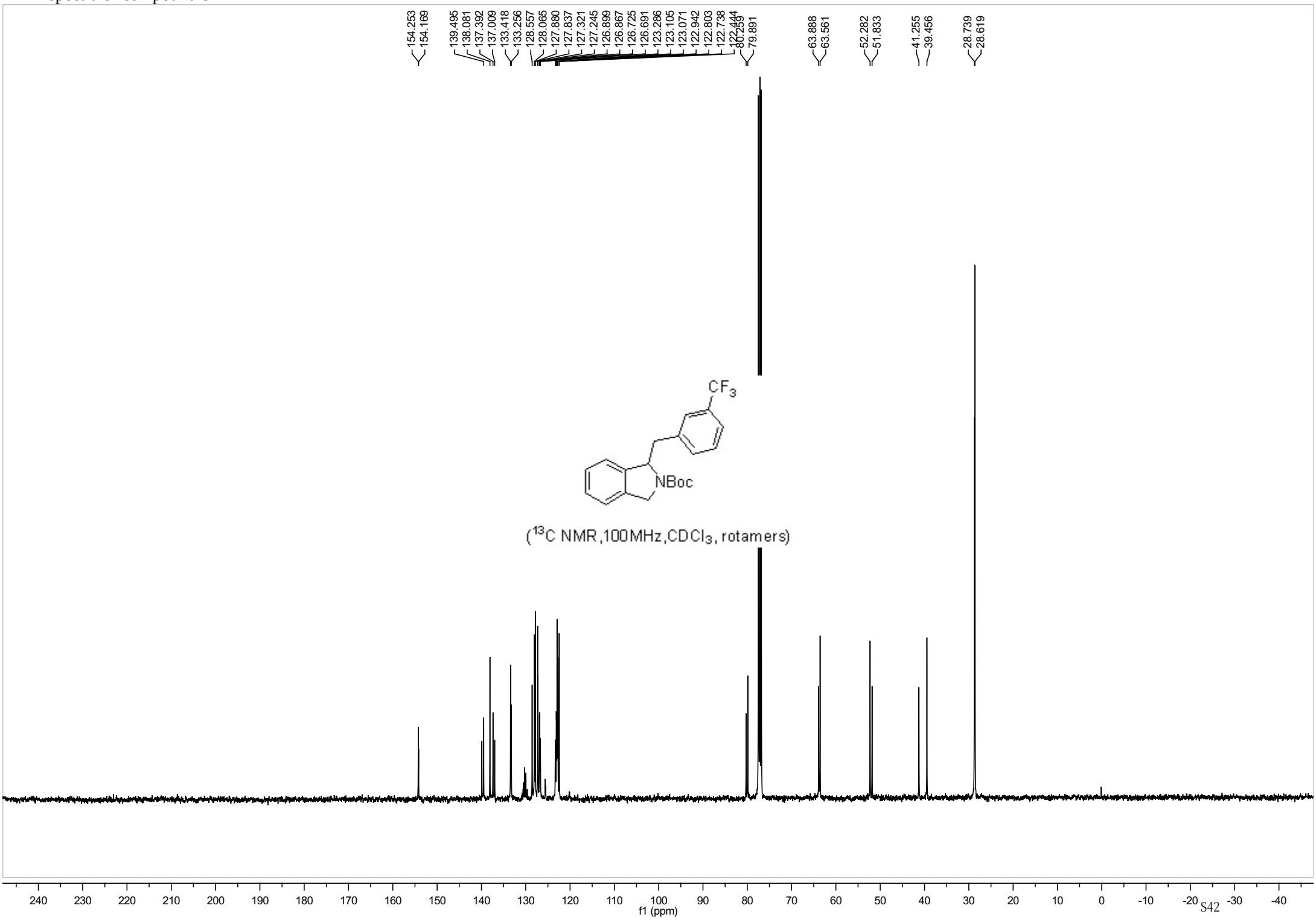
NMR spectra of compound 8h



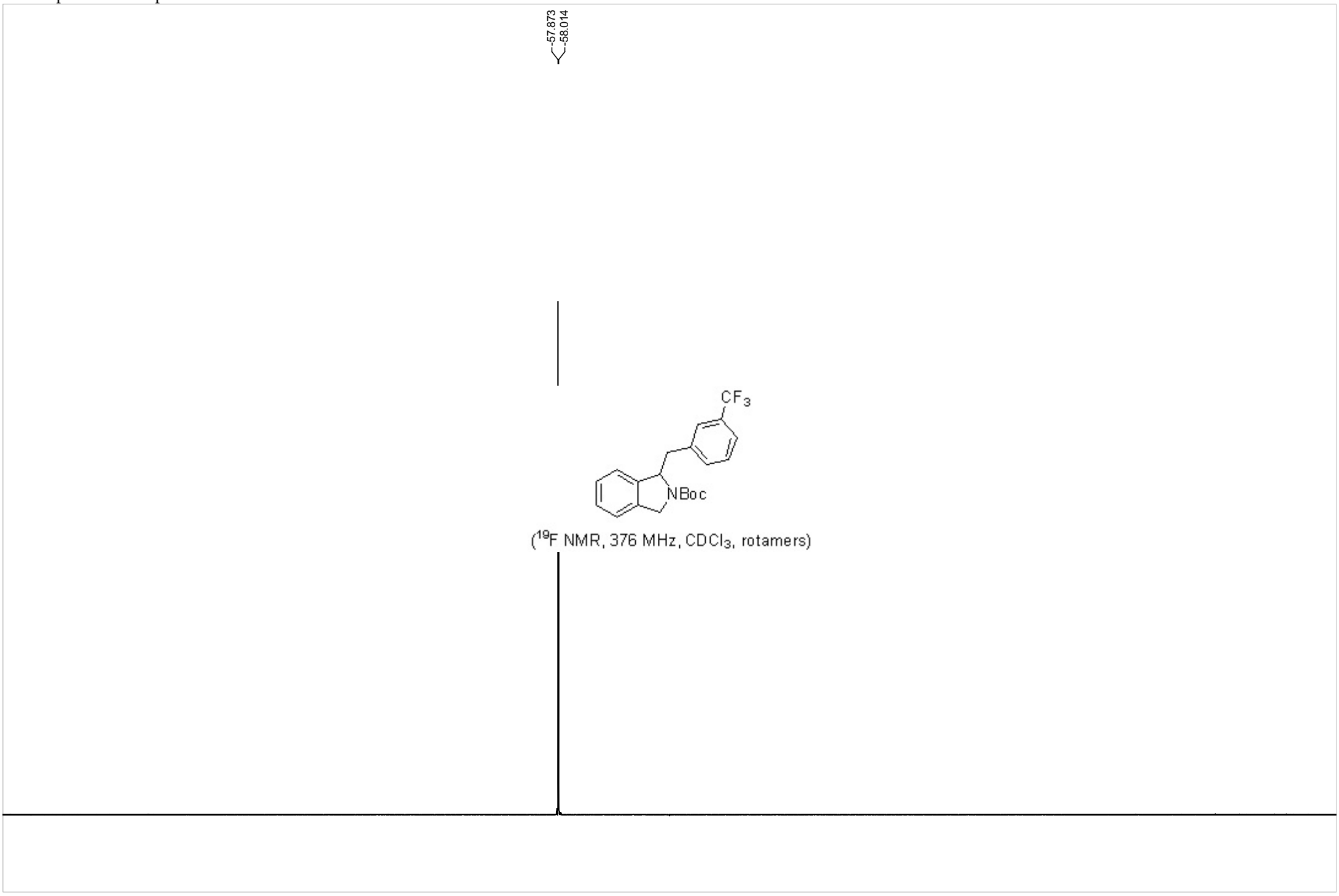
NMR spectra of compound 8i



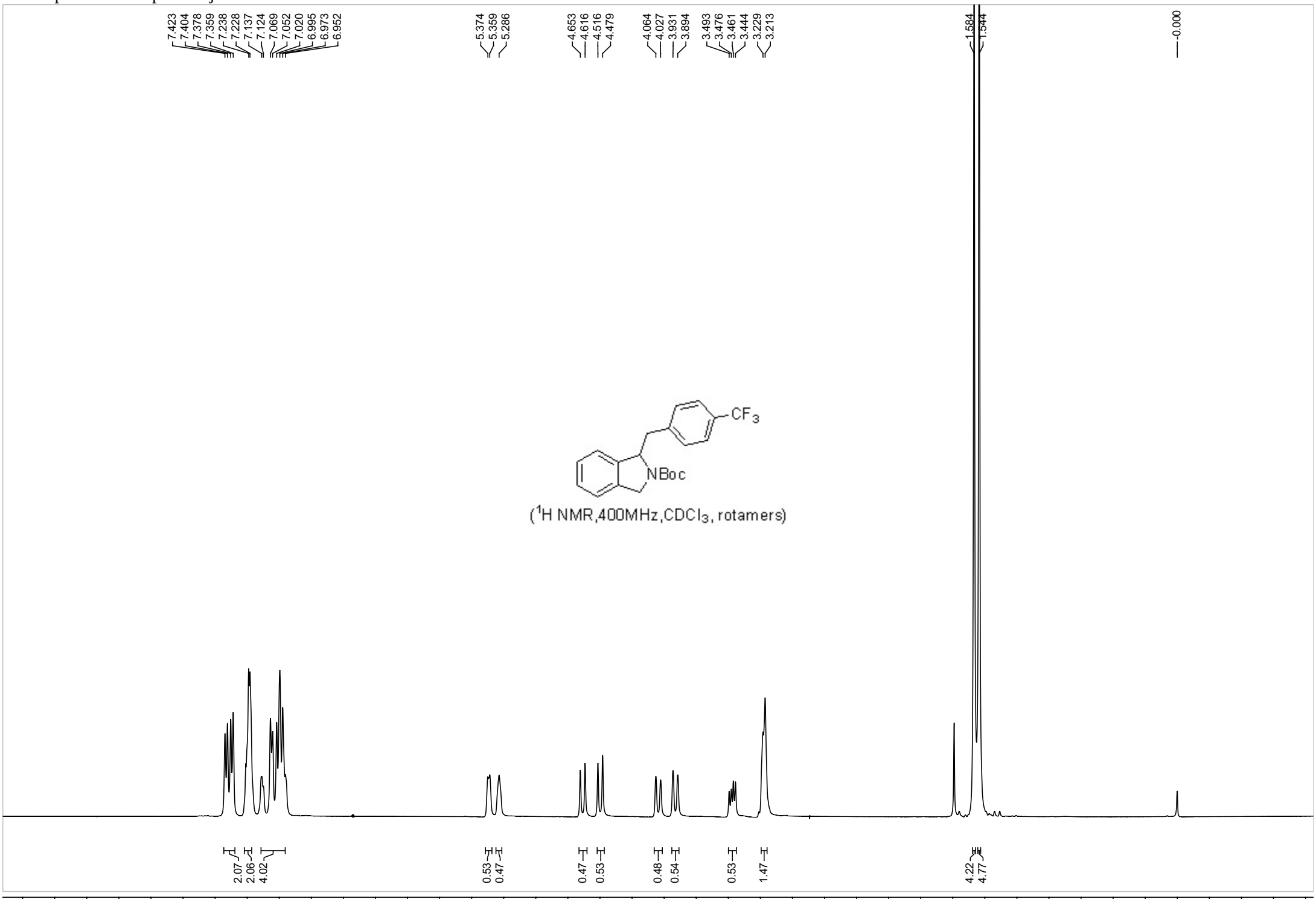
NMR spectra of compound 8i



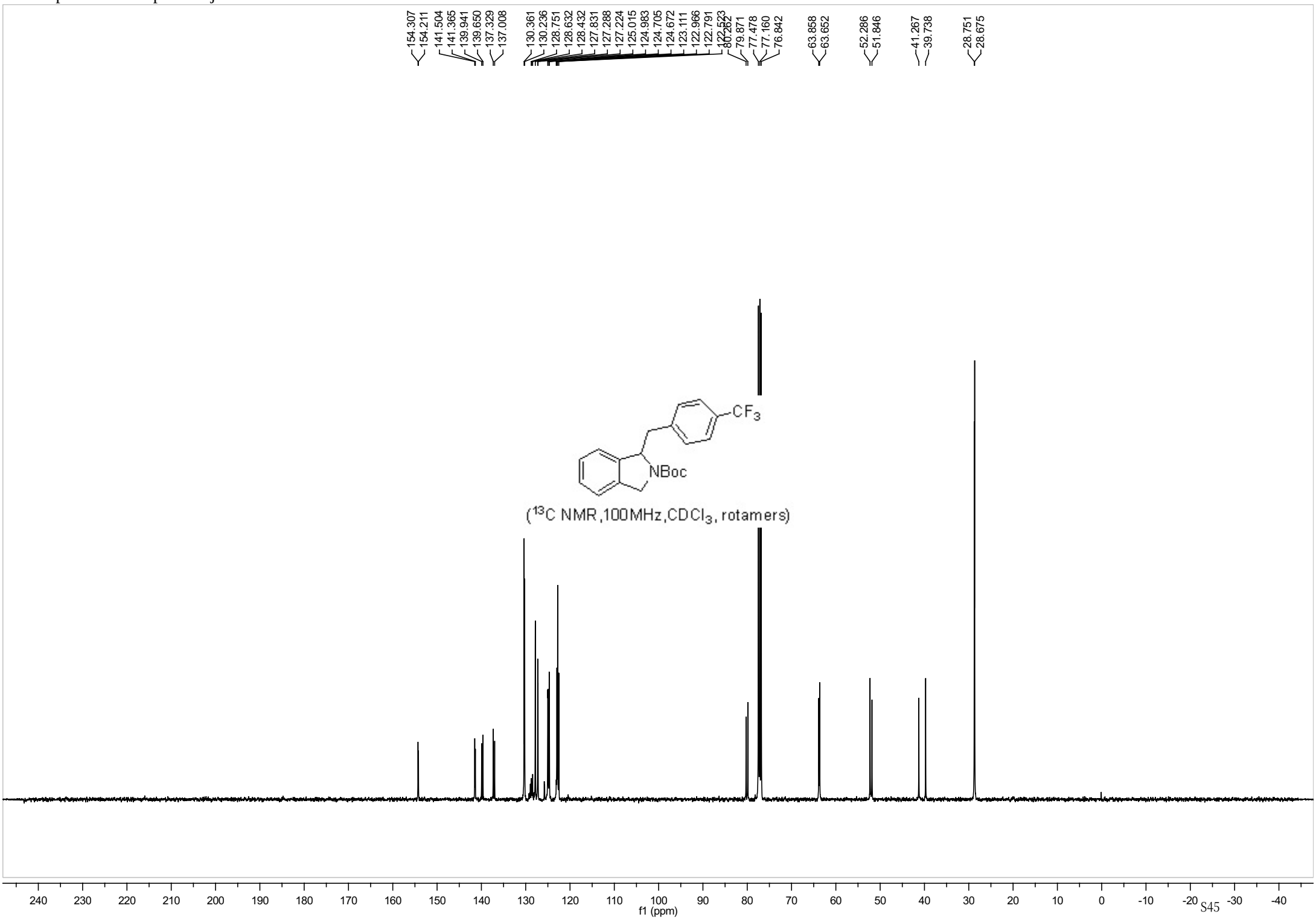
NMR spectra of compound 8i



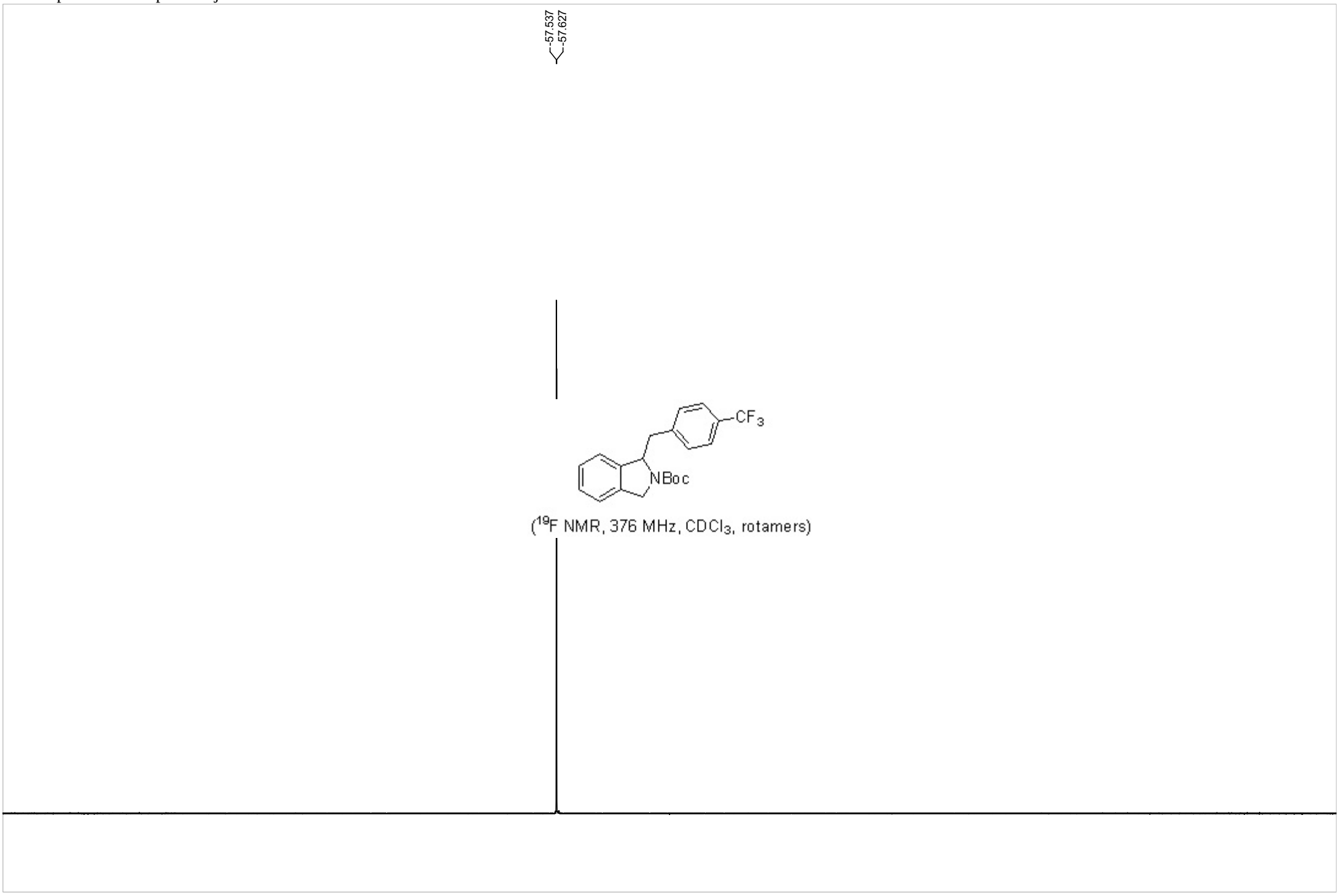
NMR spectra of compound 8j



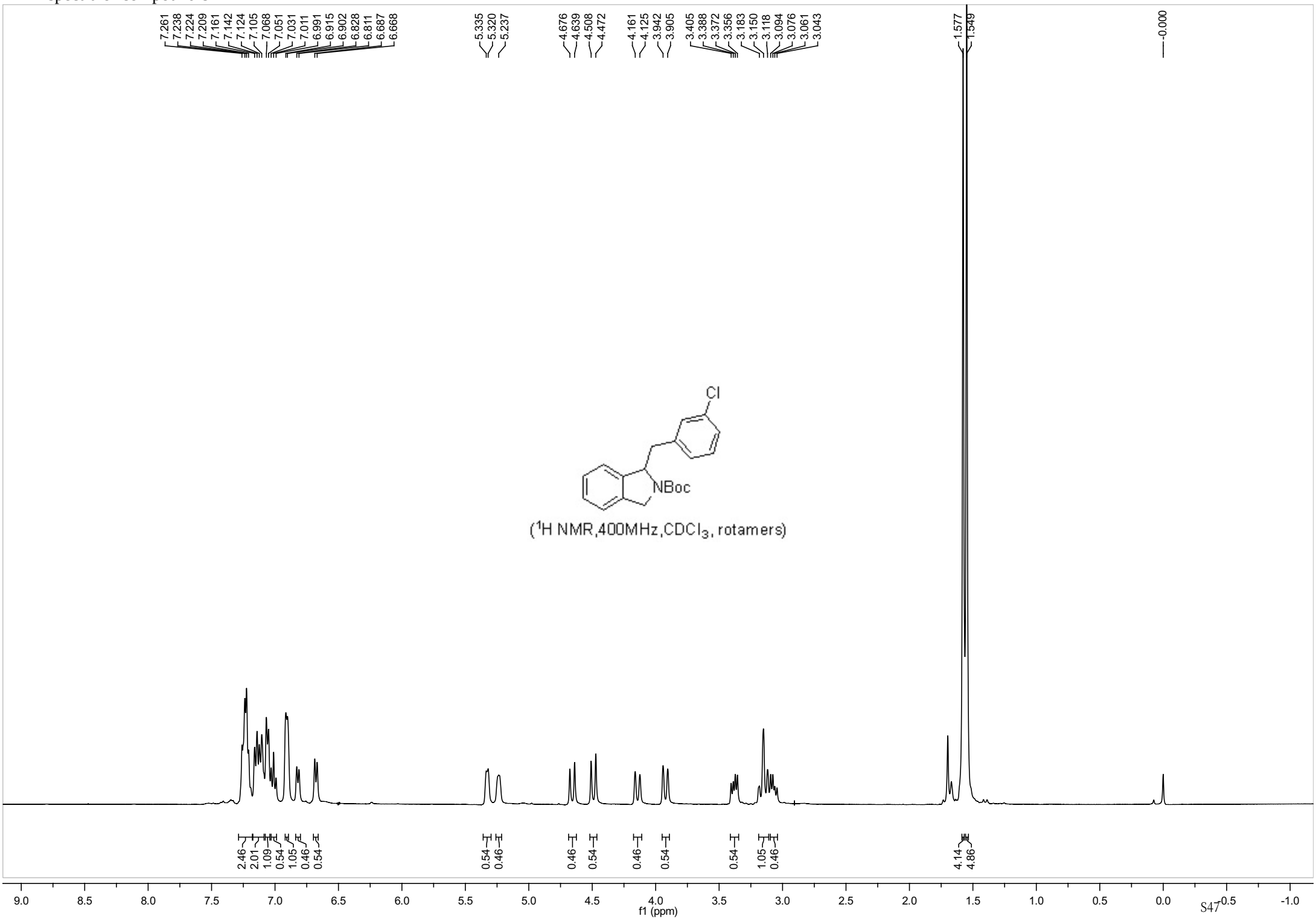
NMR spectra of compound 8j



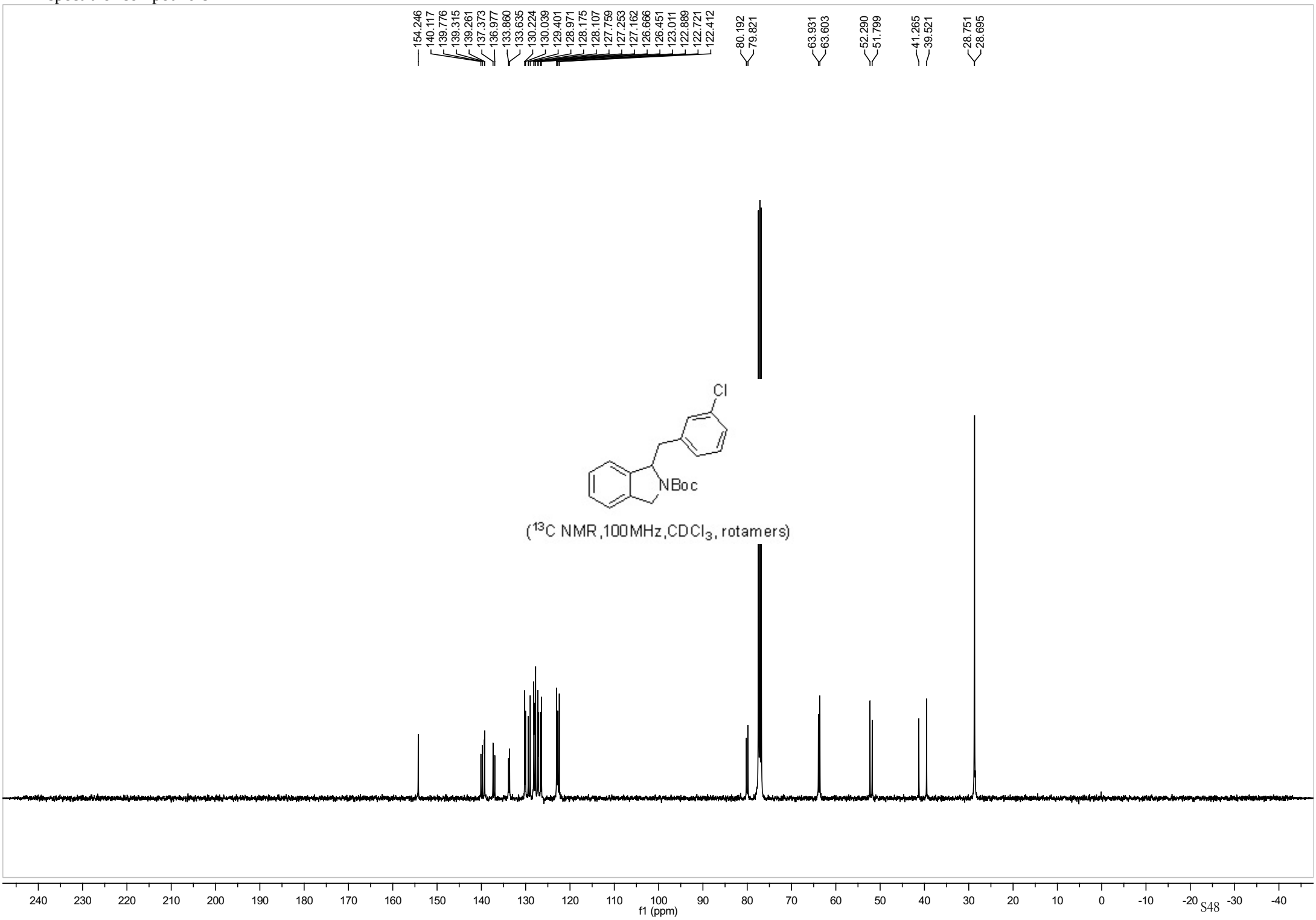
NMR spectra of compound 8j



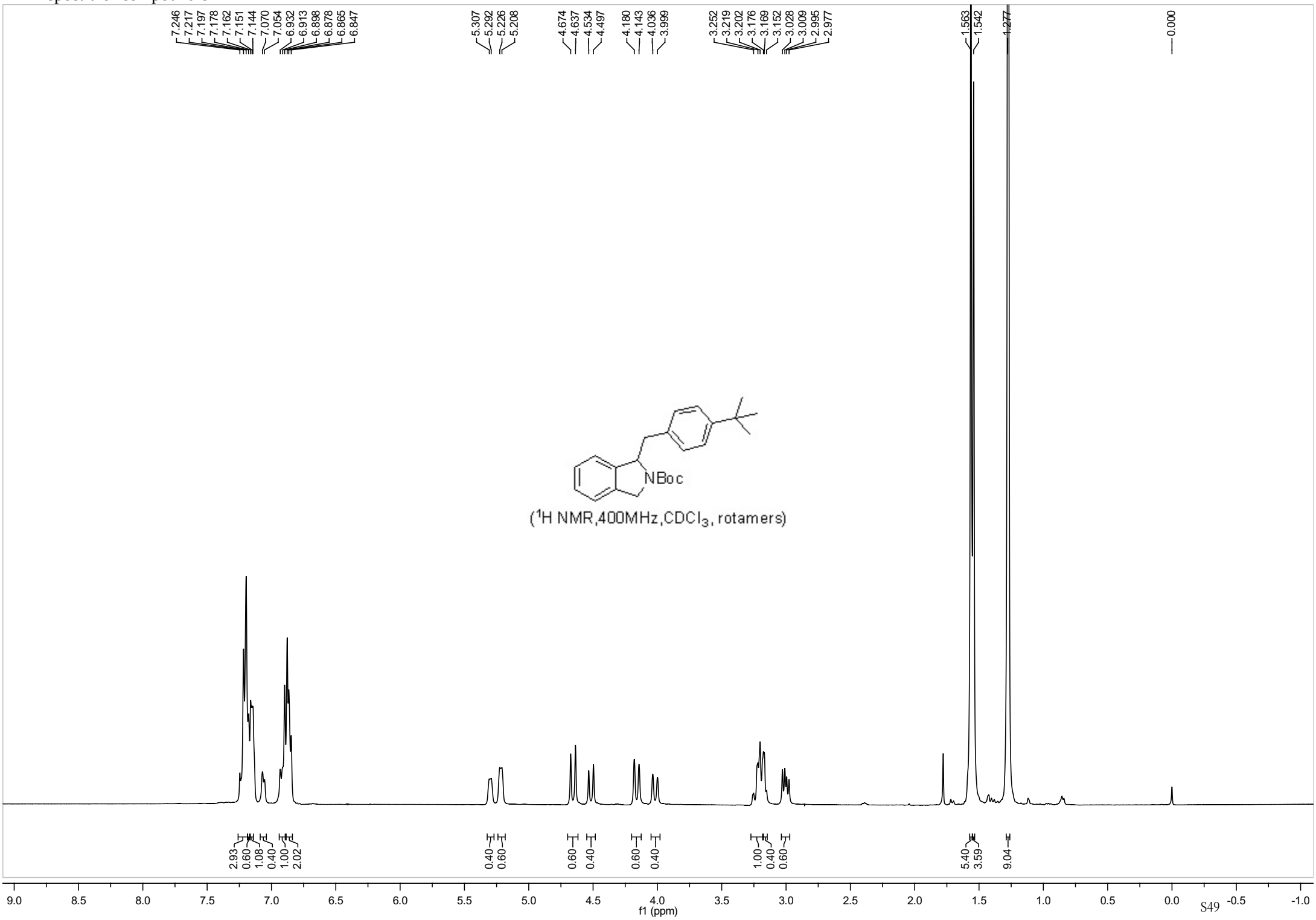
NMR spectra of compound 8k



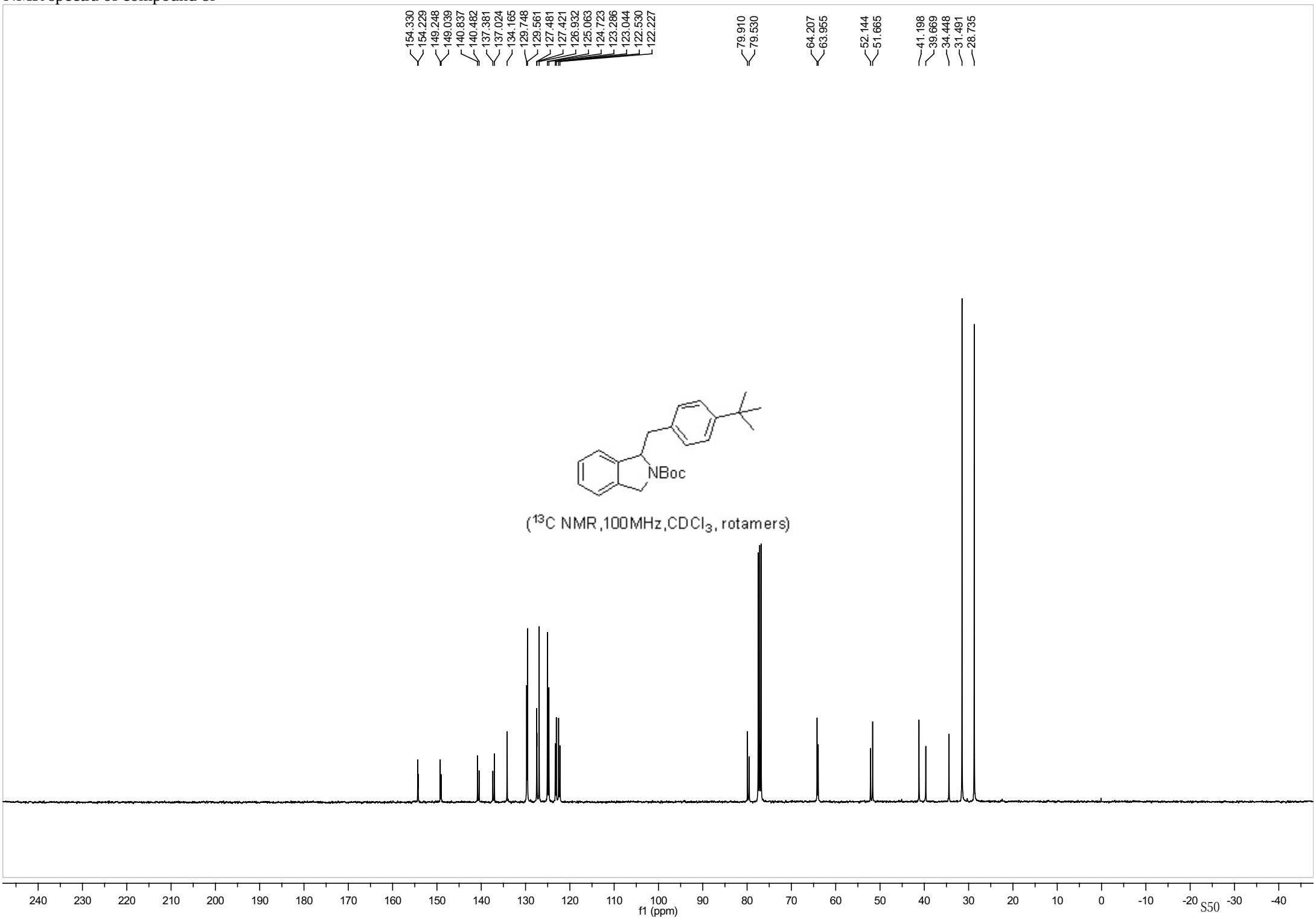
NMR spectra of compound 8k



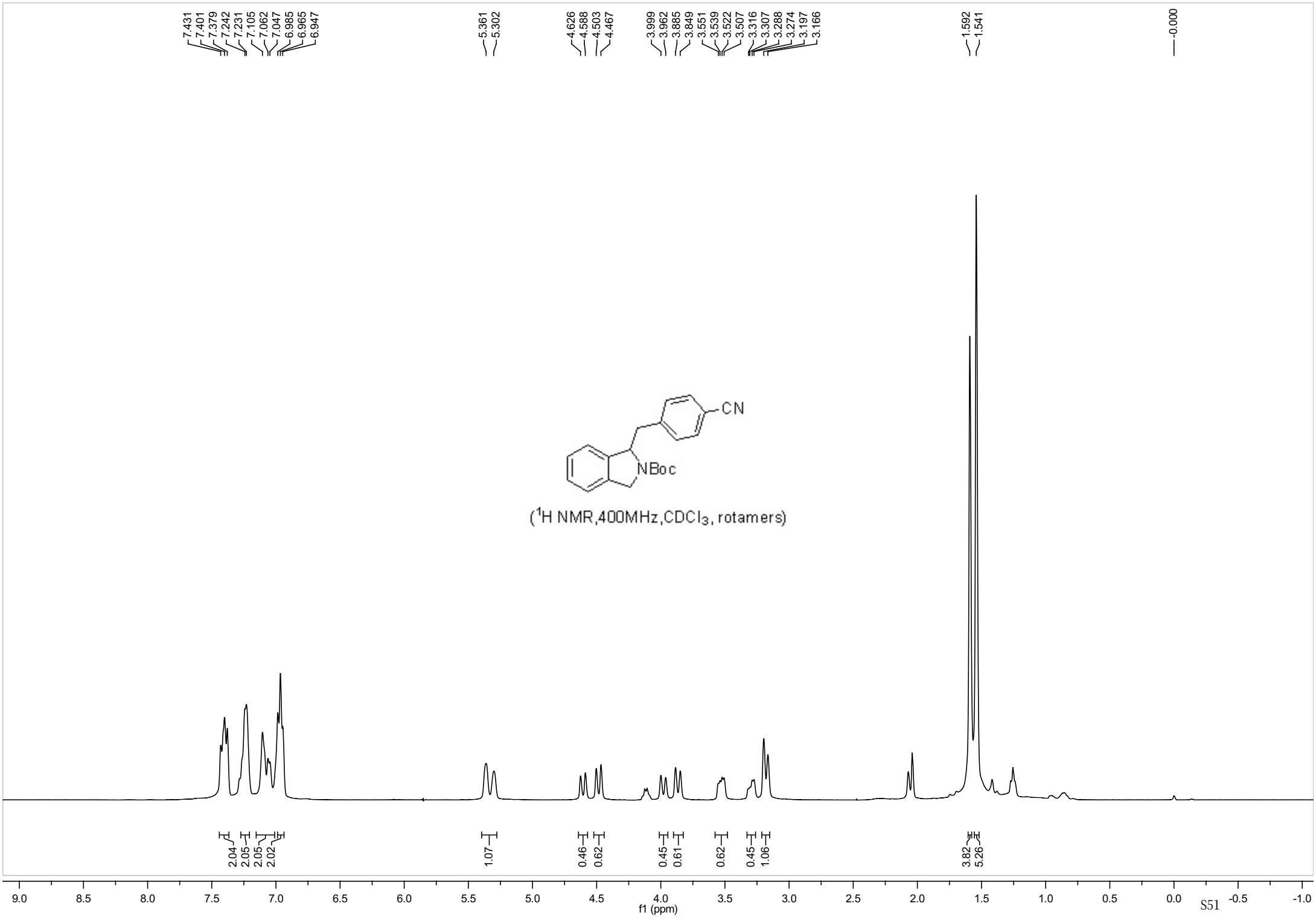
NMR spectra of compound 8l



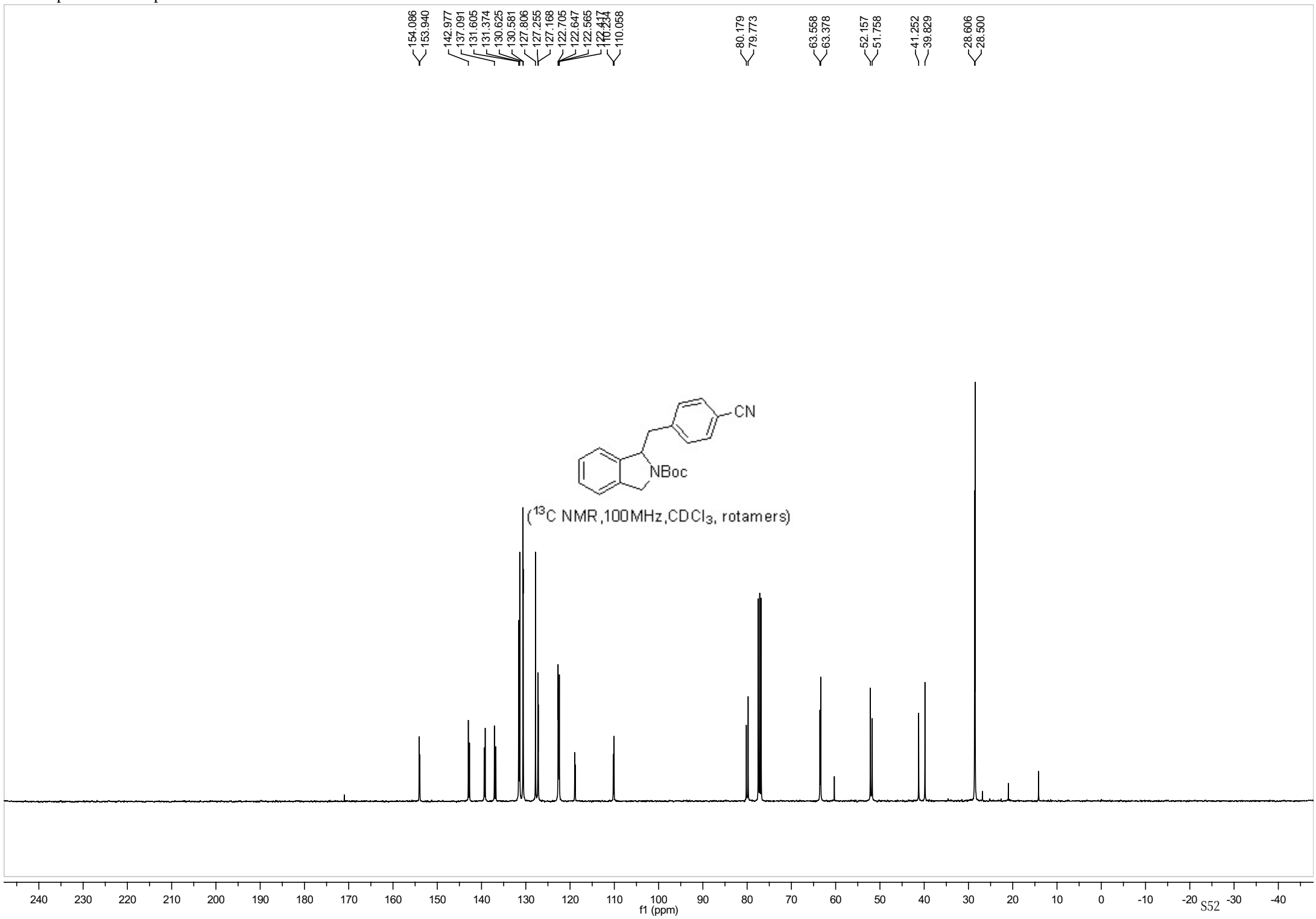
NMR spectra of compound 8l



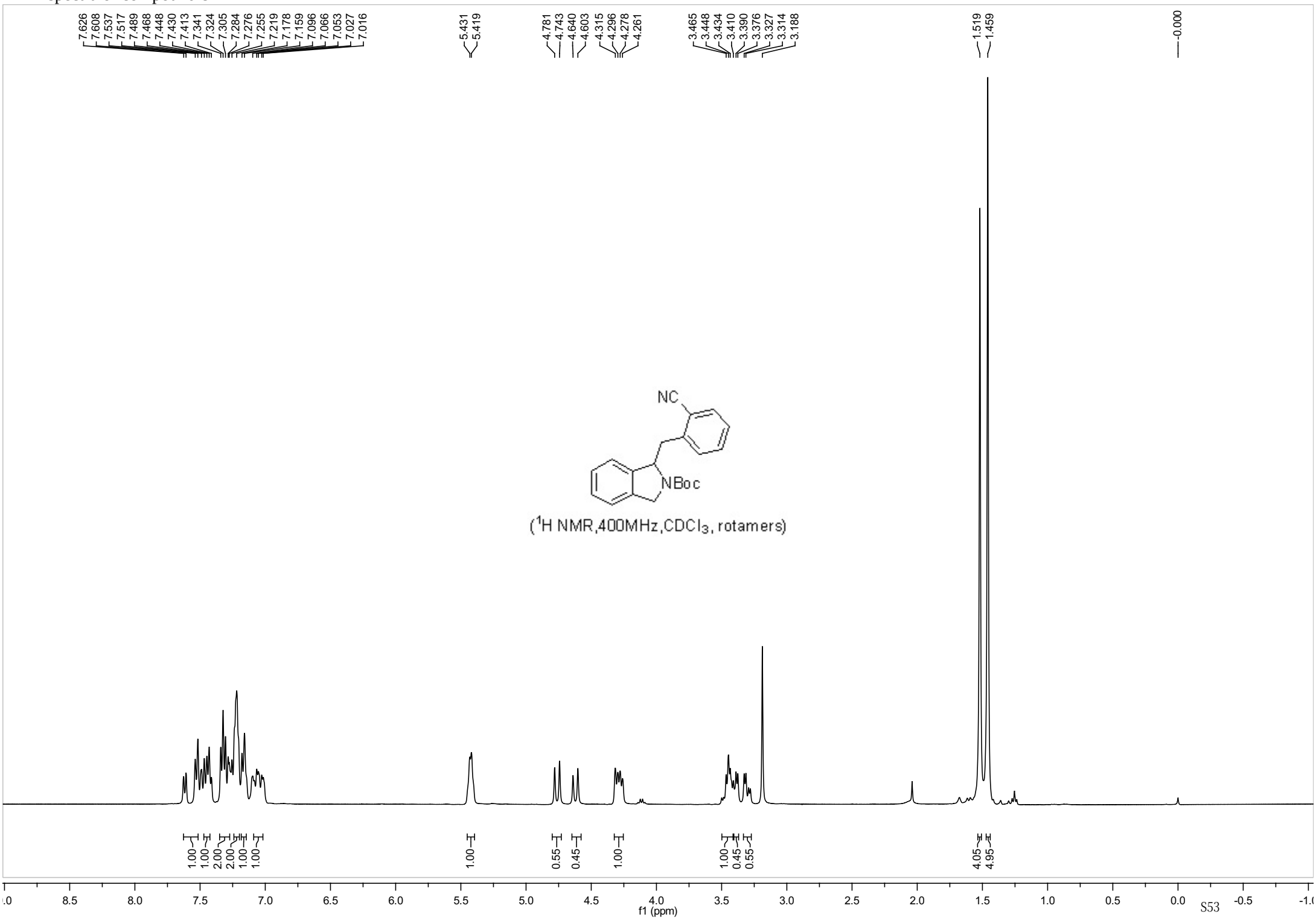
NMR spectra of compound 8m



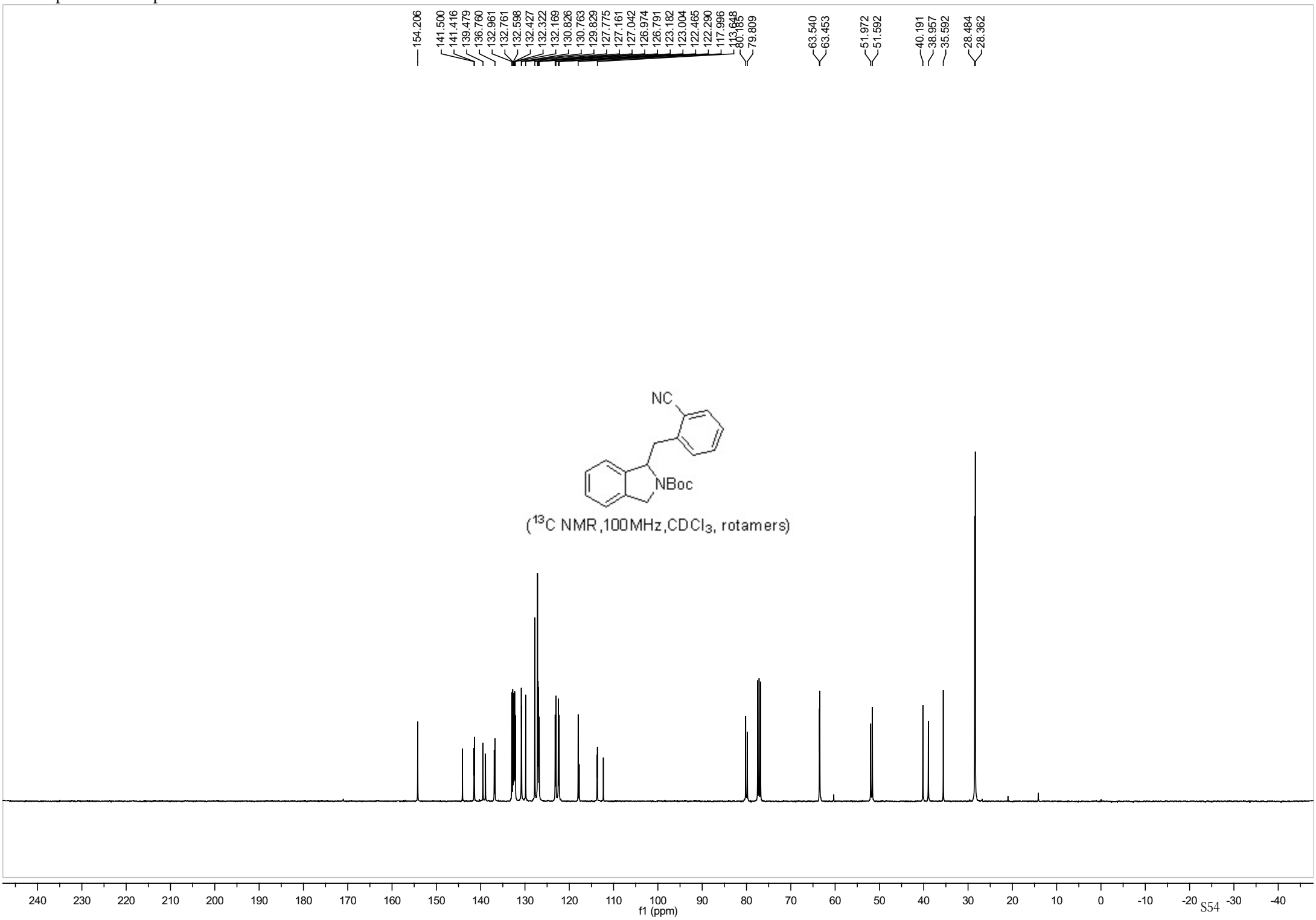
NMR spectra of compound 8m



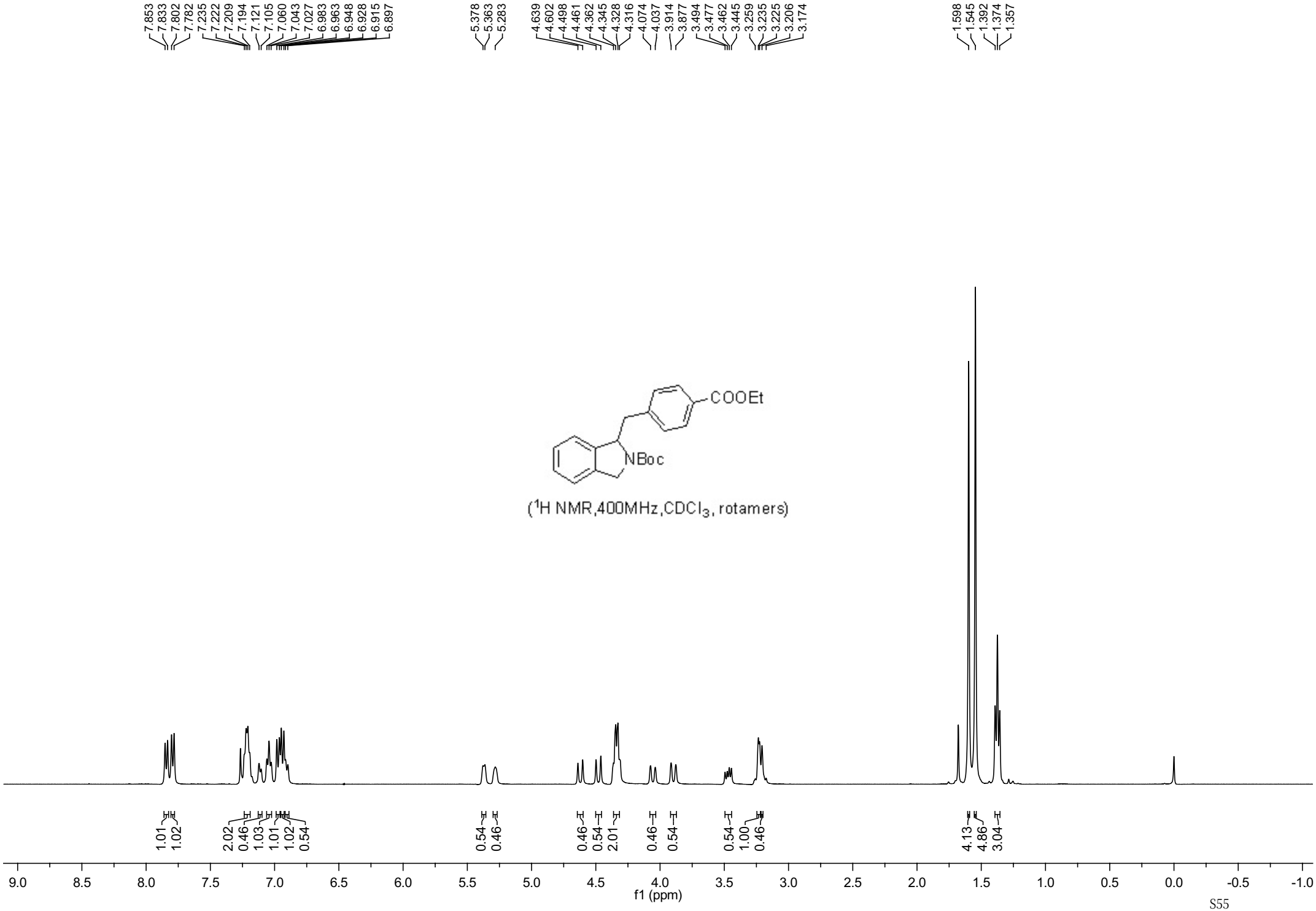
NMR spectra of compound 8n



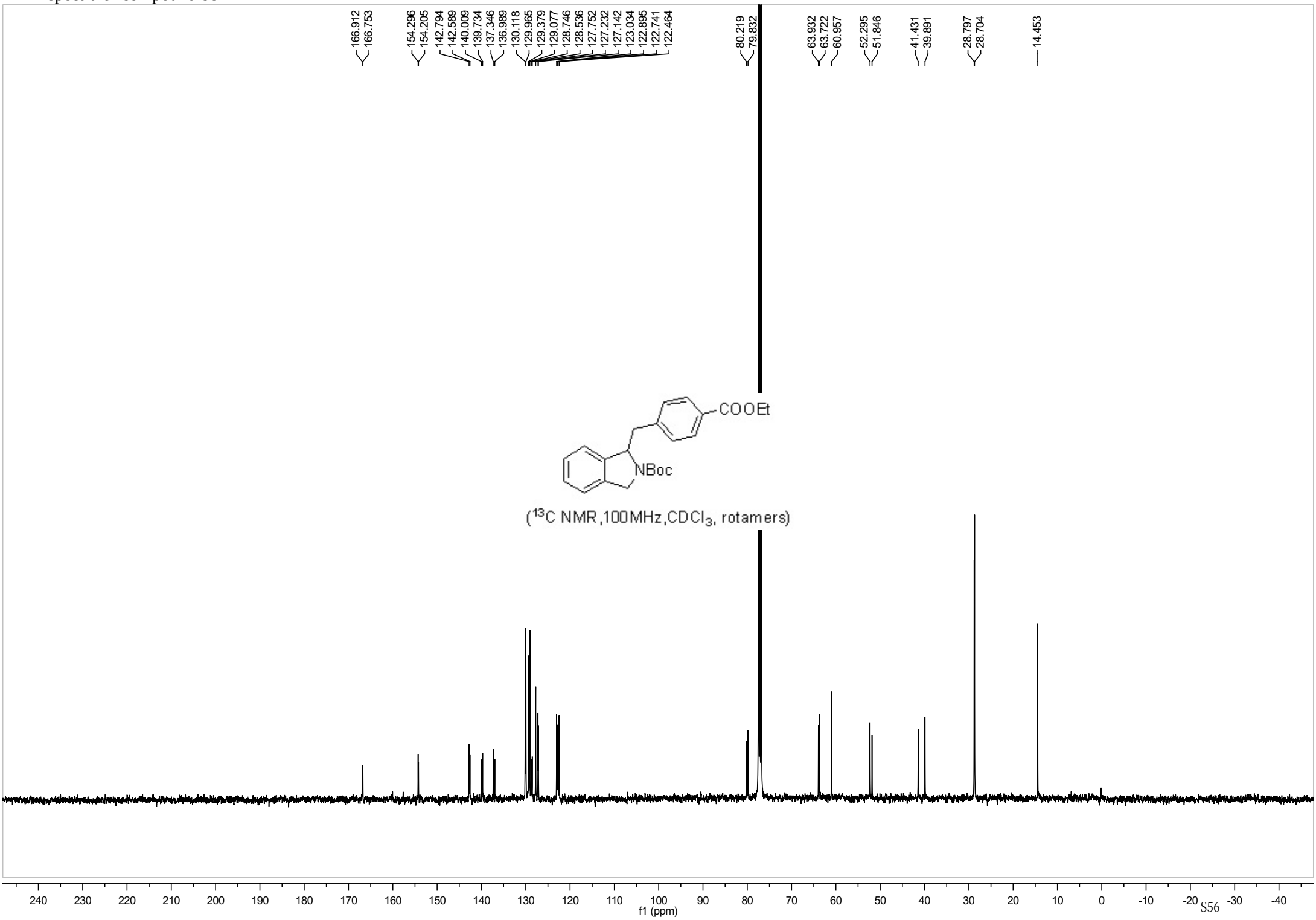
NMR spectra of compound 8n



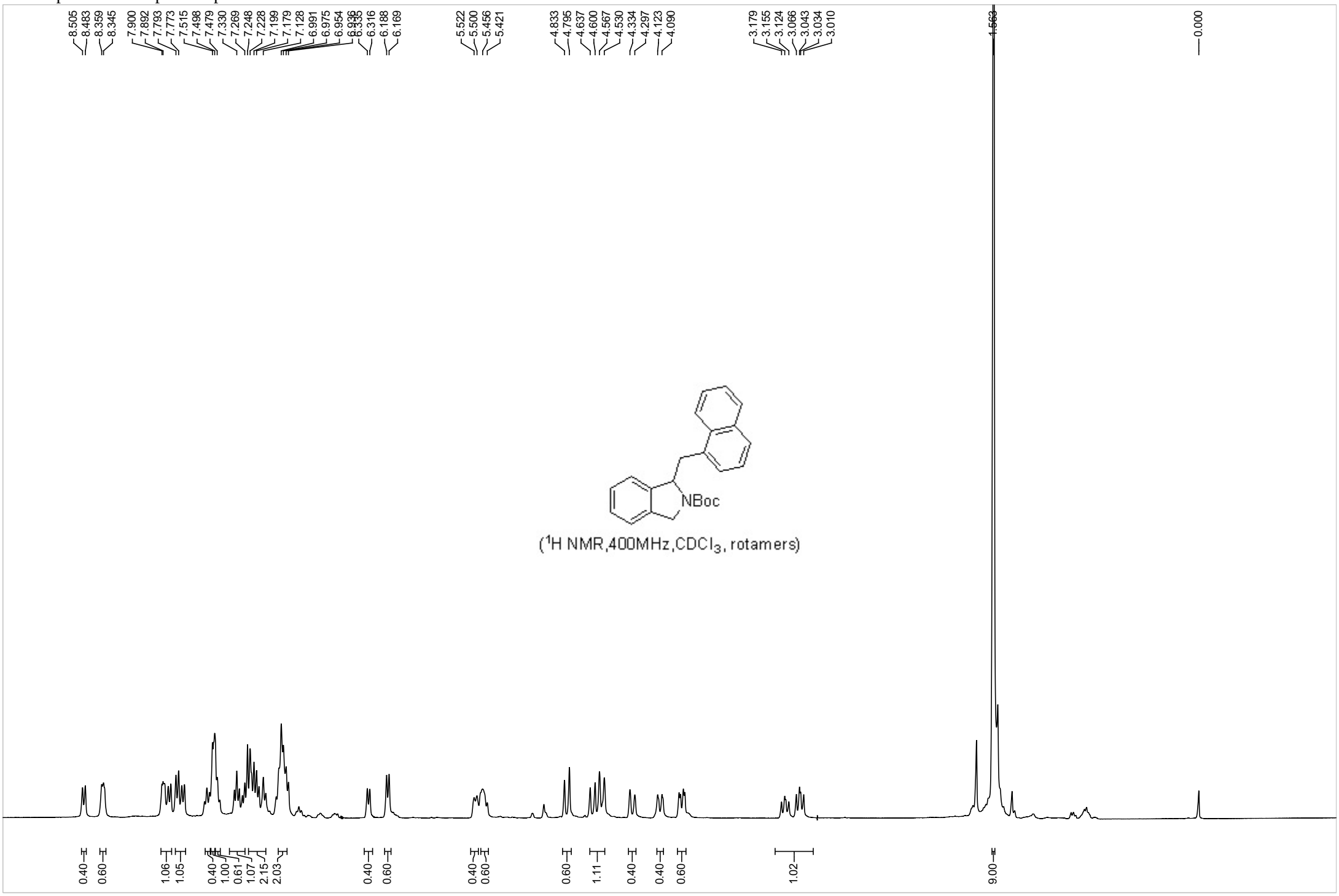
NMR spectra of compound 8o



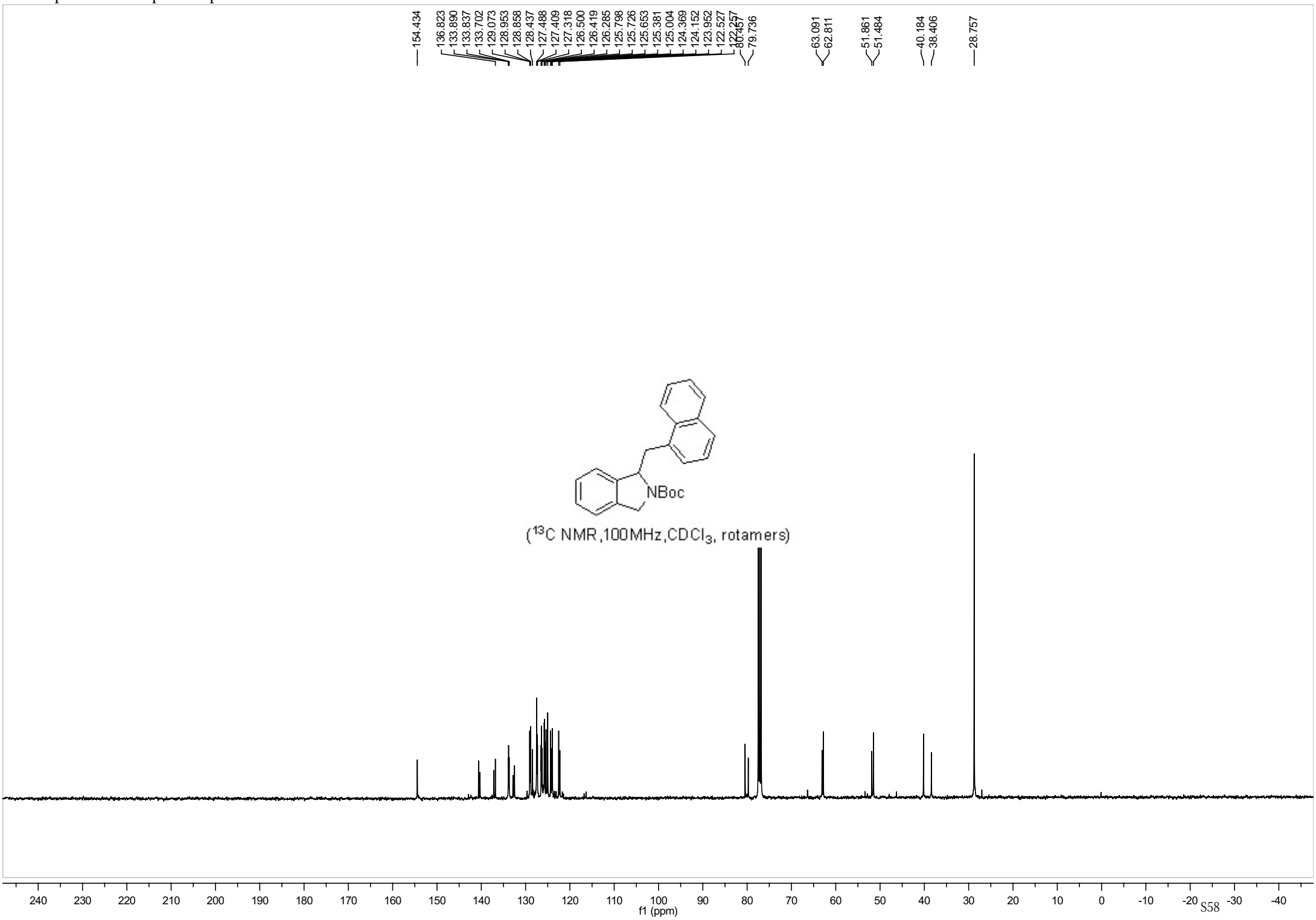
NMR spectra of compound 8o



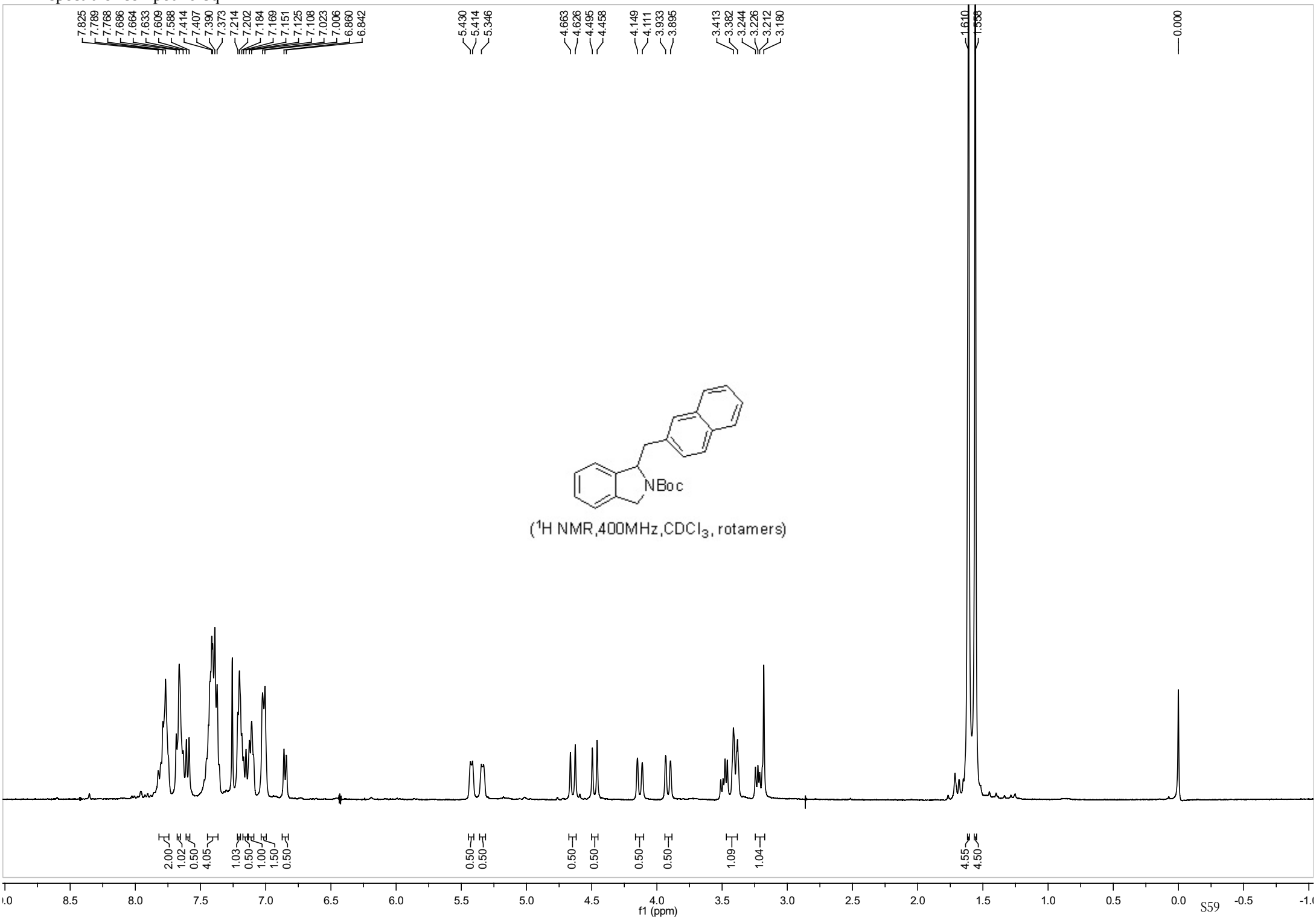
NMR spectra of compound 8p



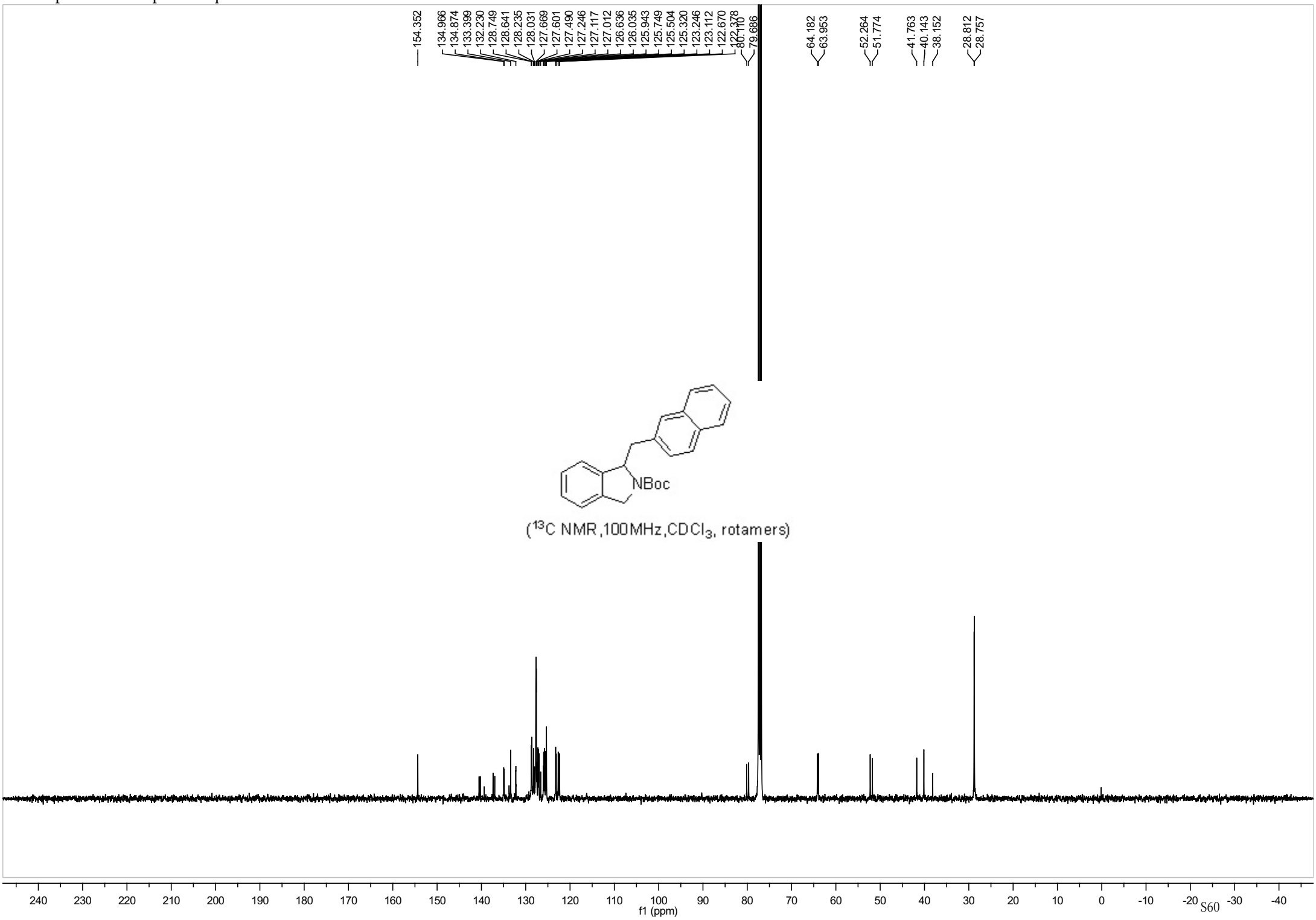
NMR spectra of compound 8p



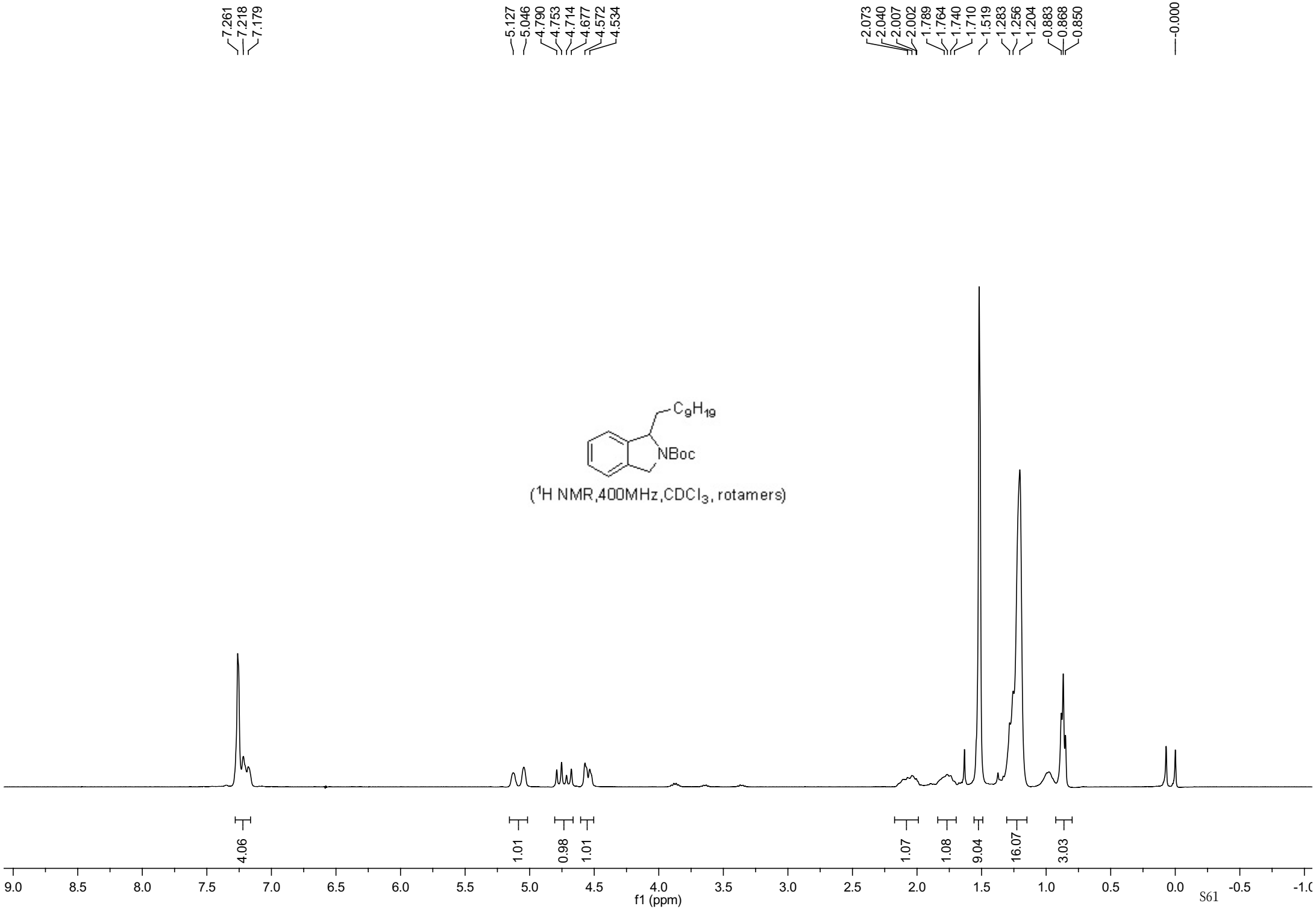
NMR spectra of compound 8q



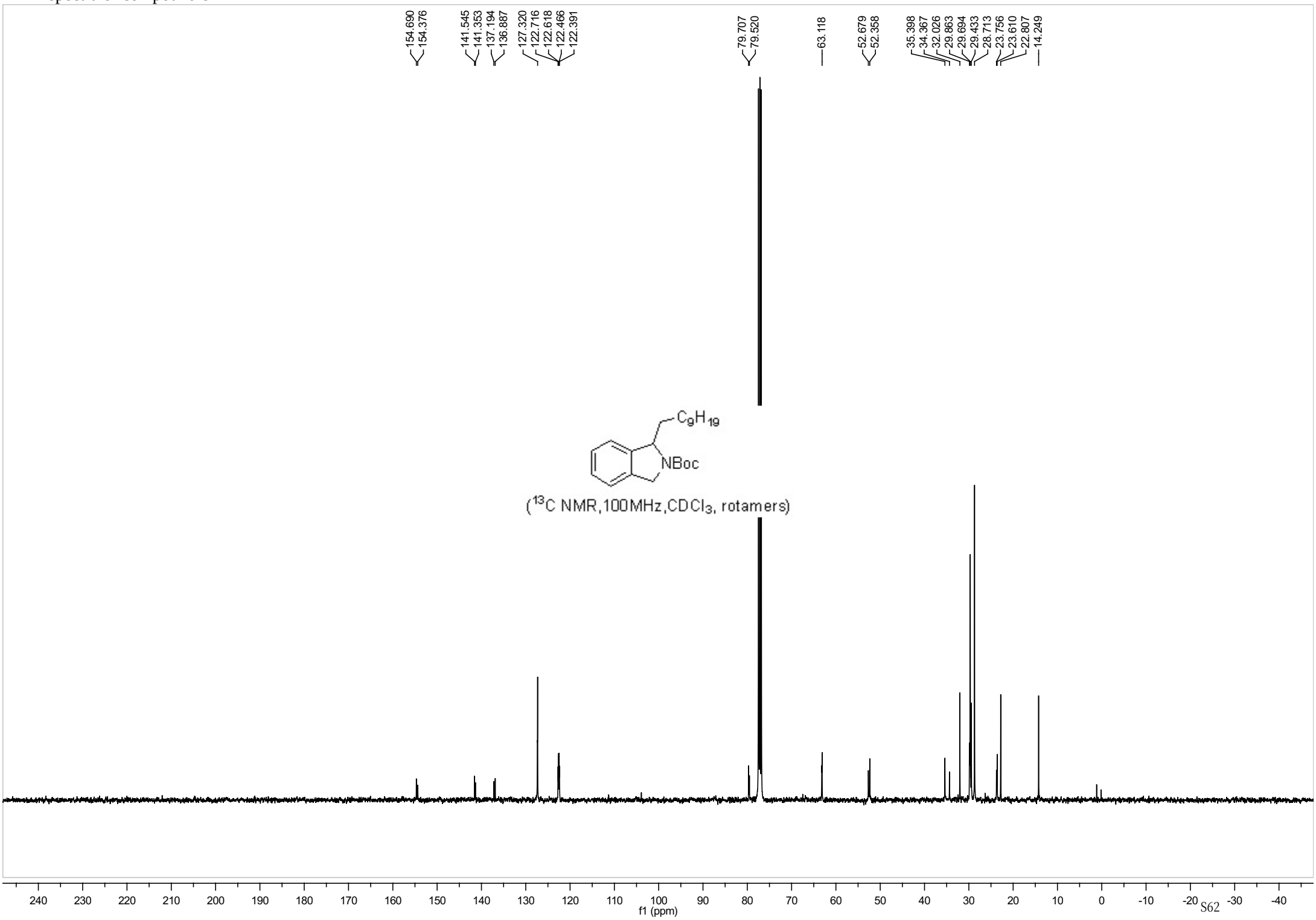
NMR spectra of compound 8q



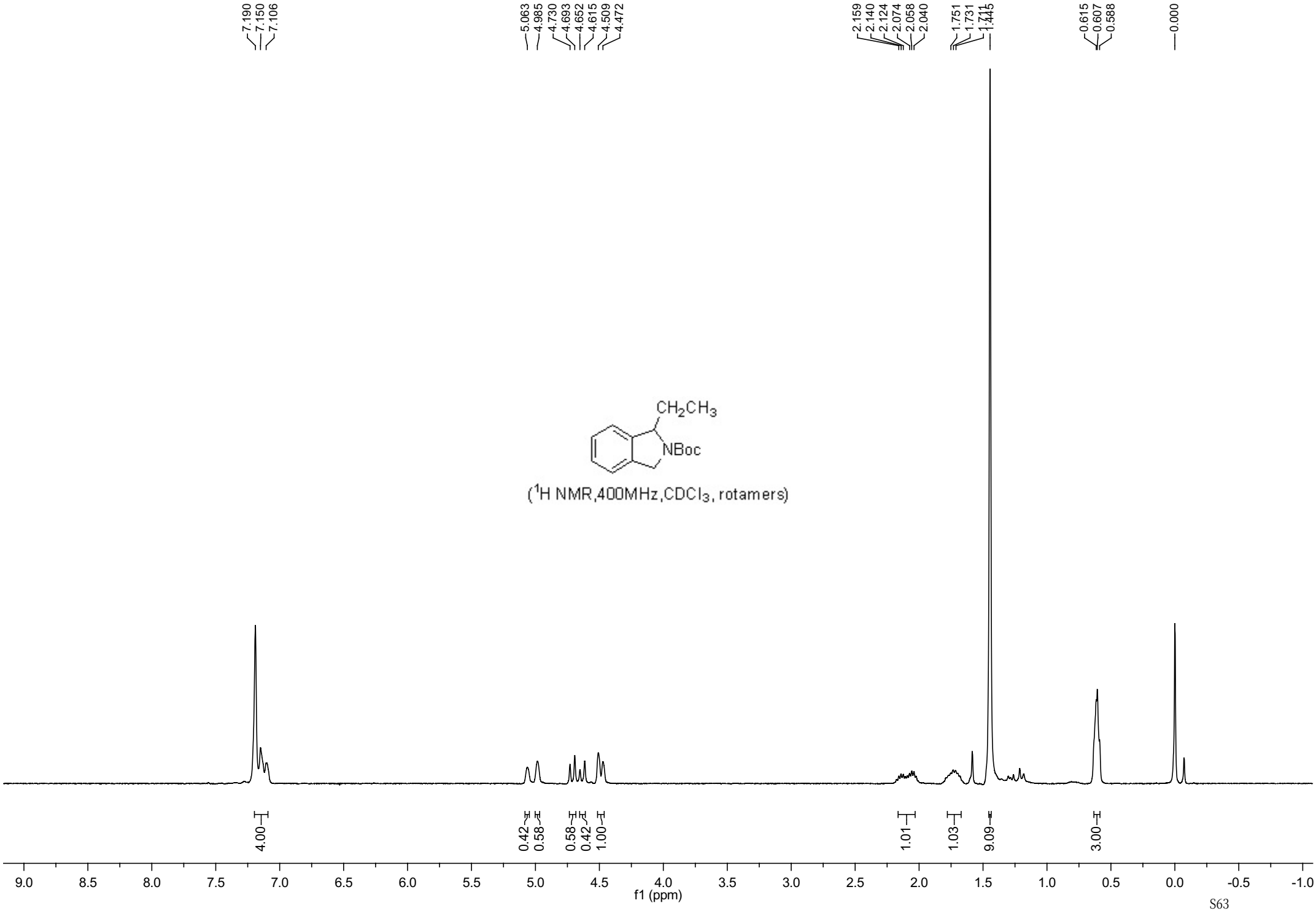
NMR spectra of compound 8r



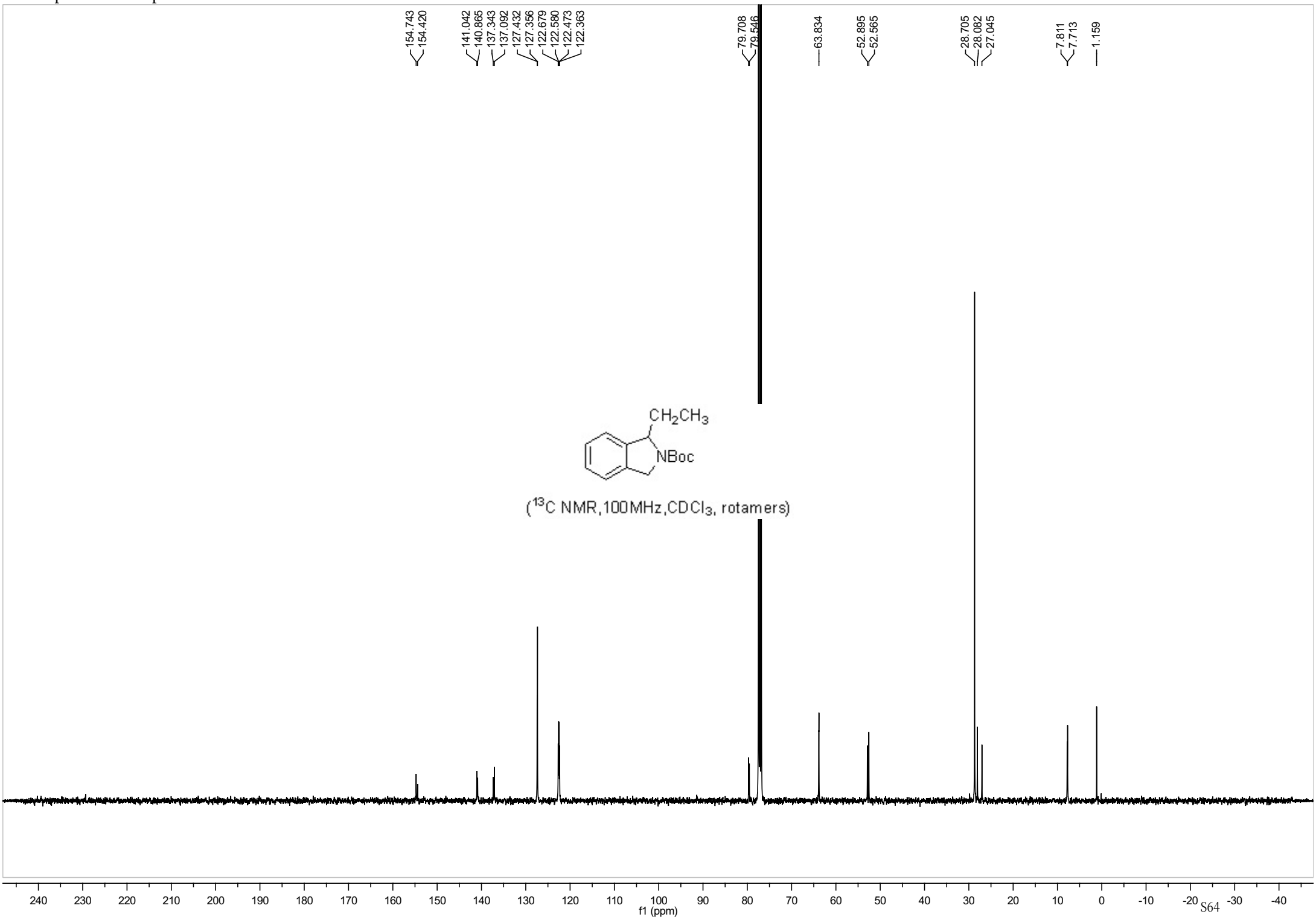
NMR spectra of compound 8r



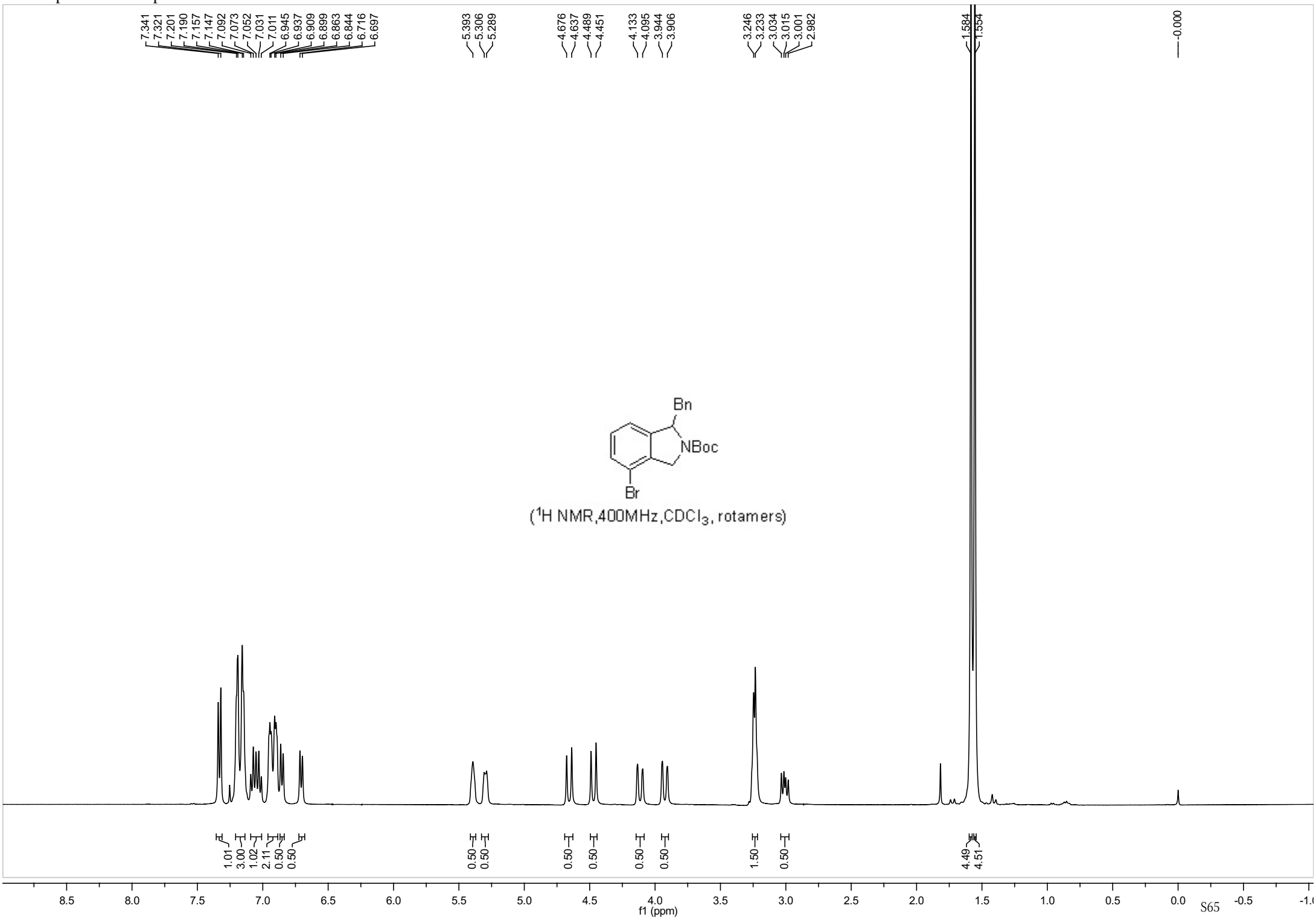
NMR spectra of compound 8s



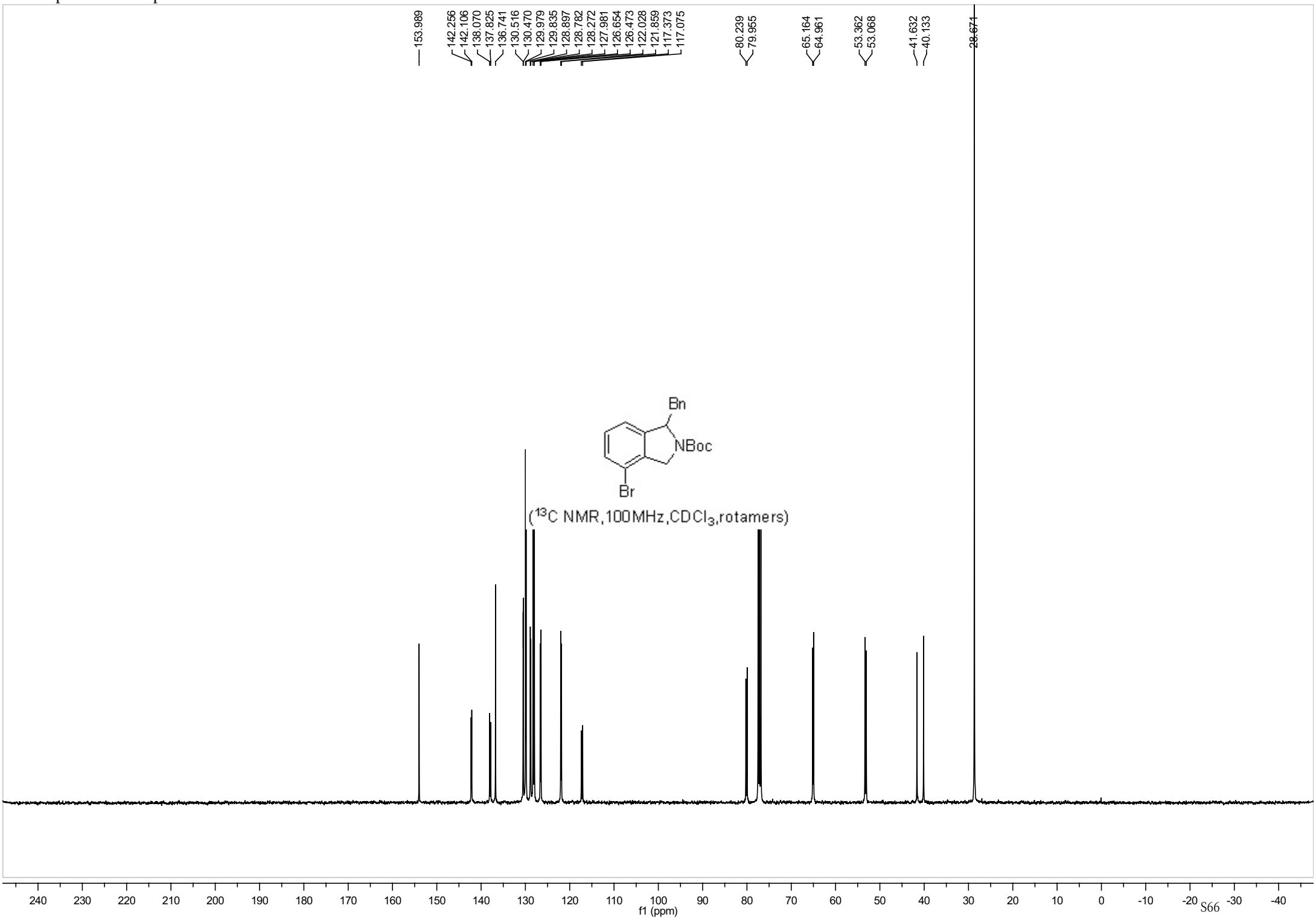
NMR spectra of compound 8s



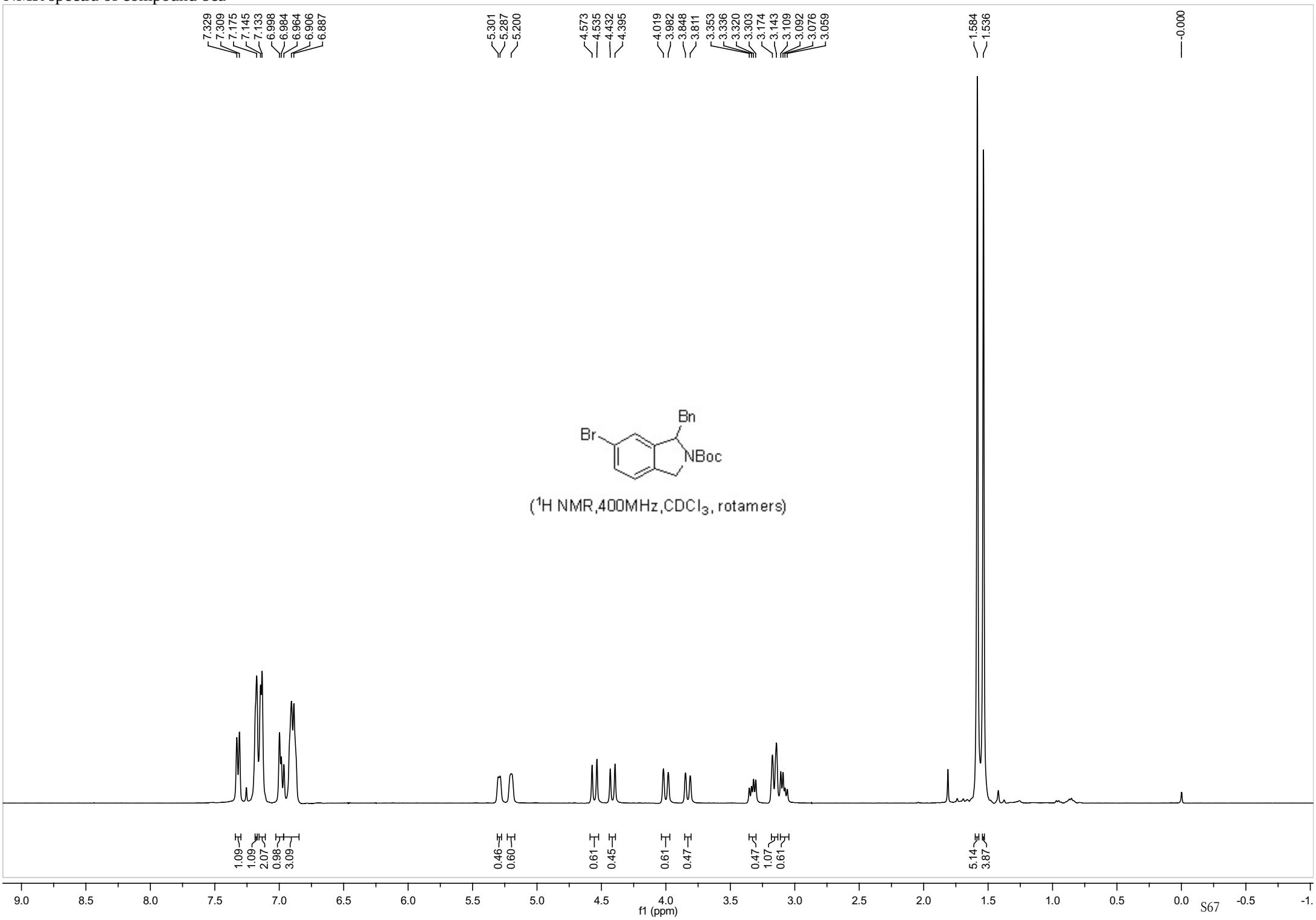
NMR spectra of compound 8ba



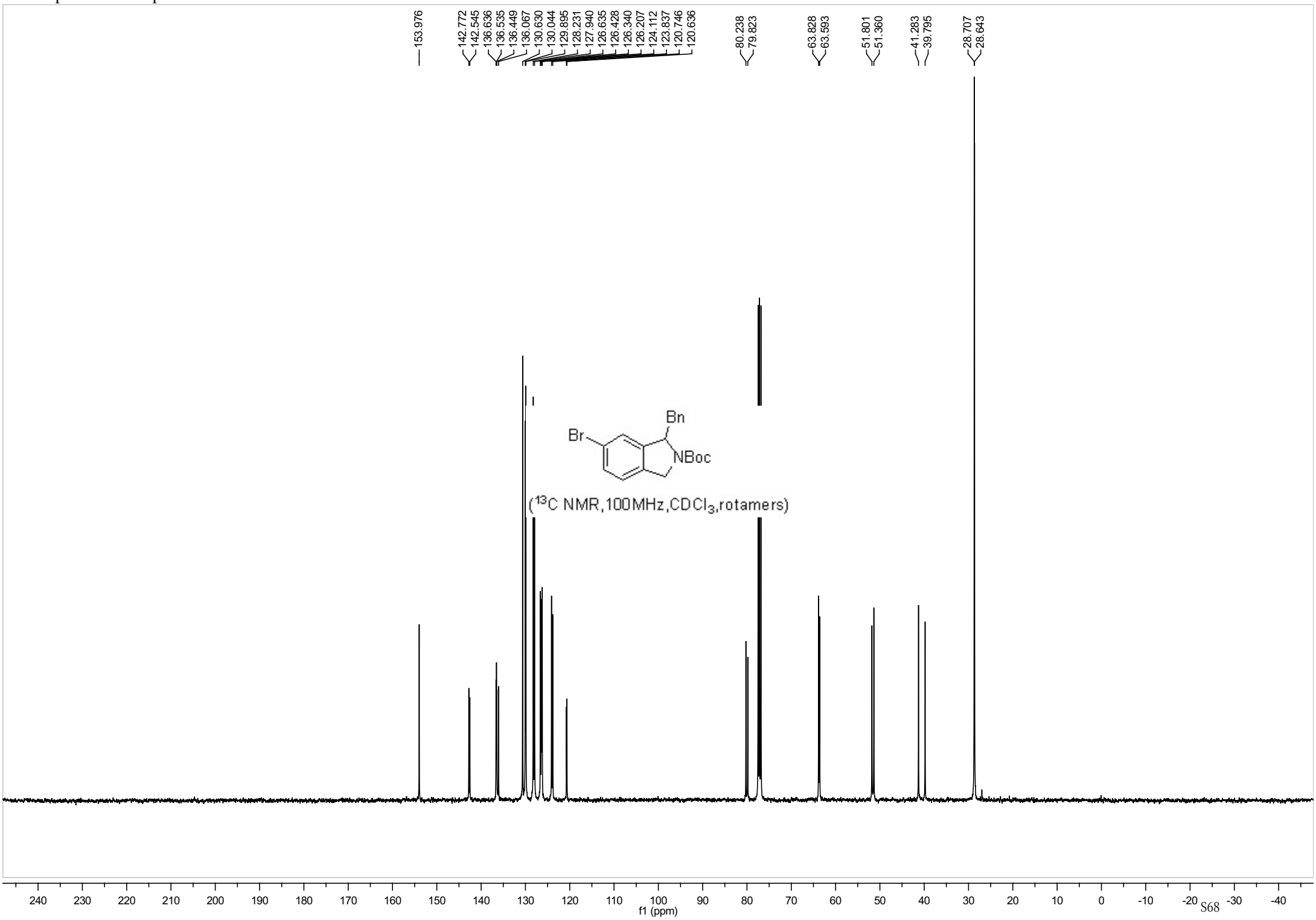
NMR spectra of compound 8ba



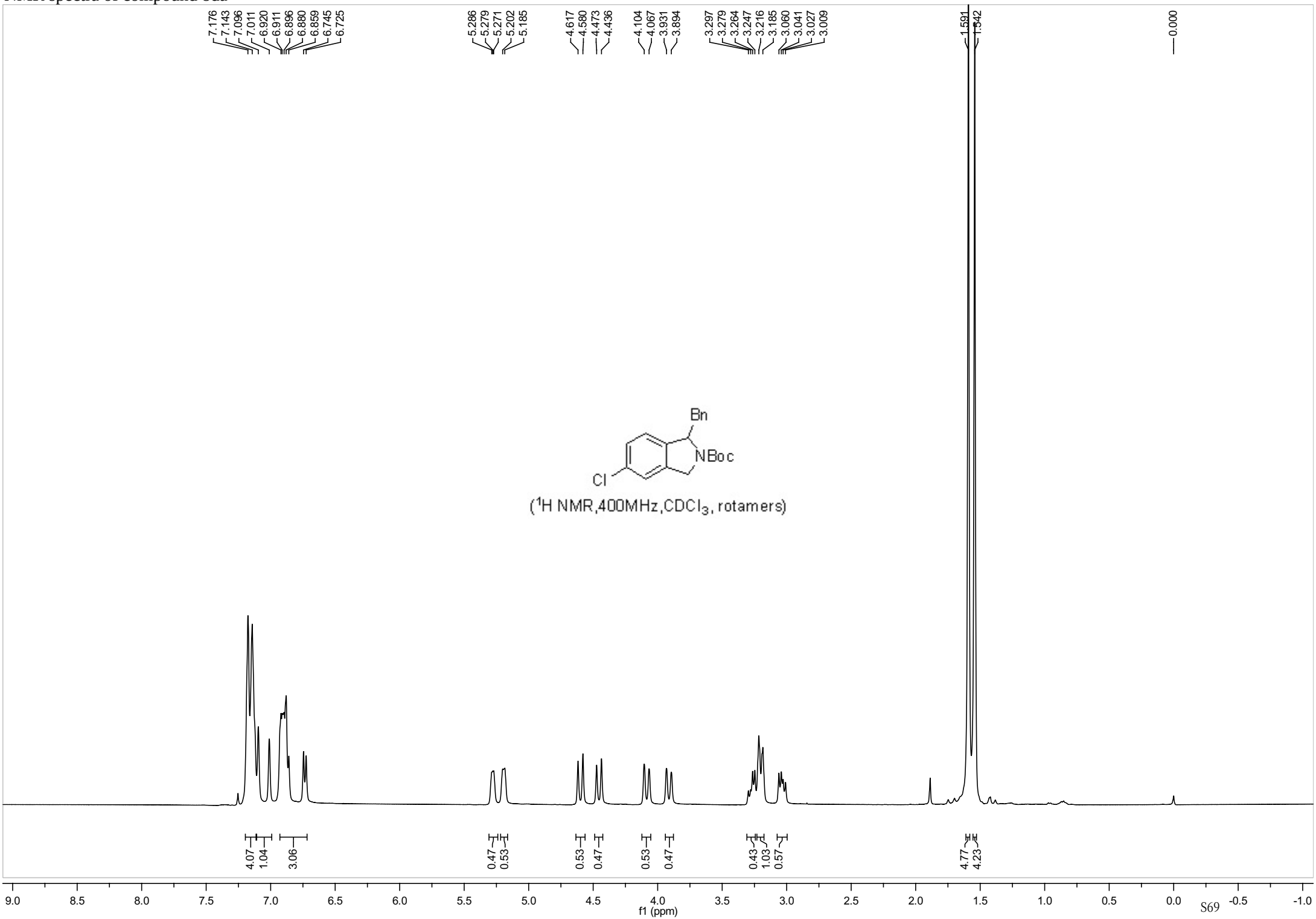
NMR spectra of compound 8ca



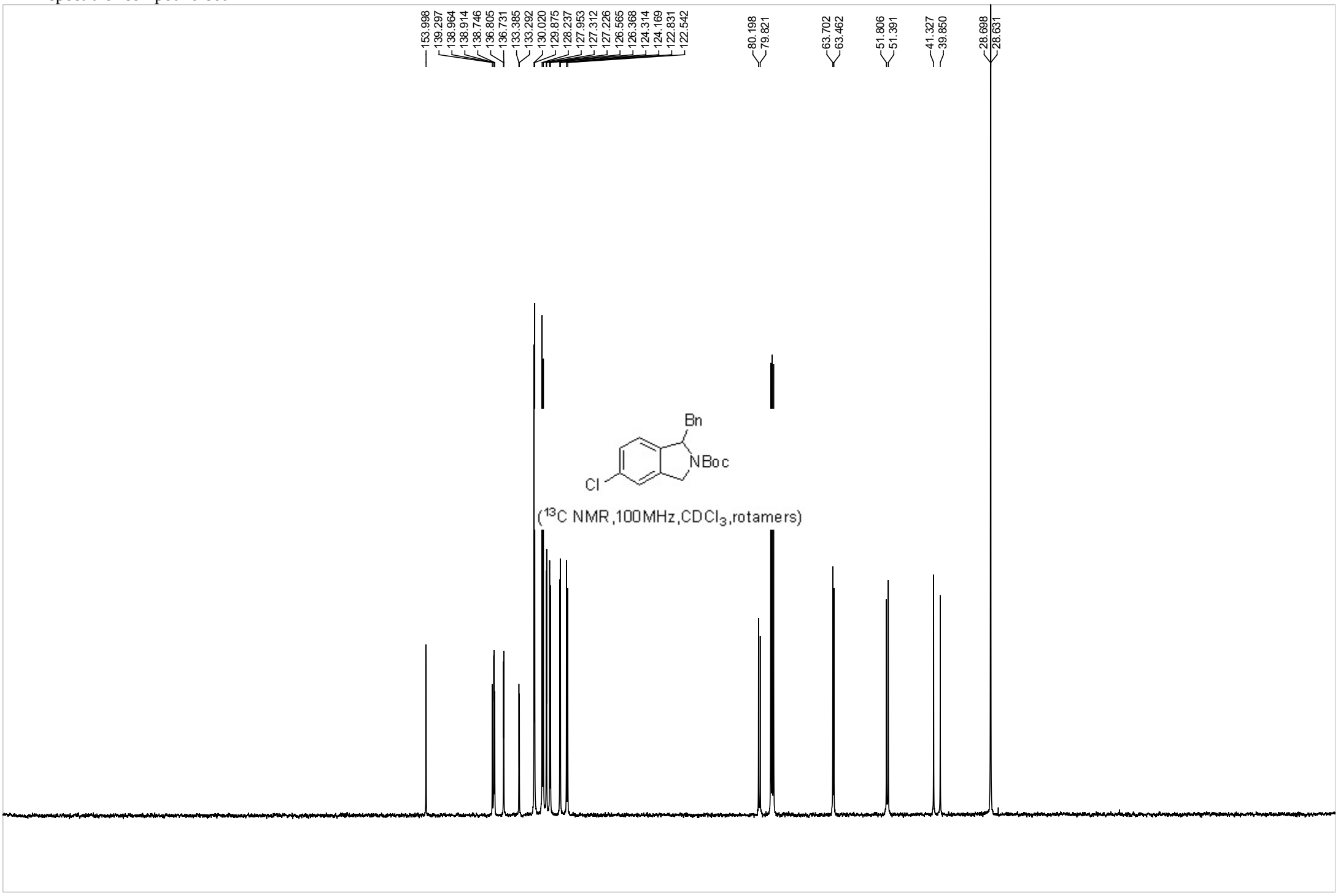
NMR spectra of compound 8ca



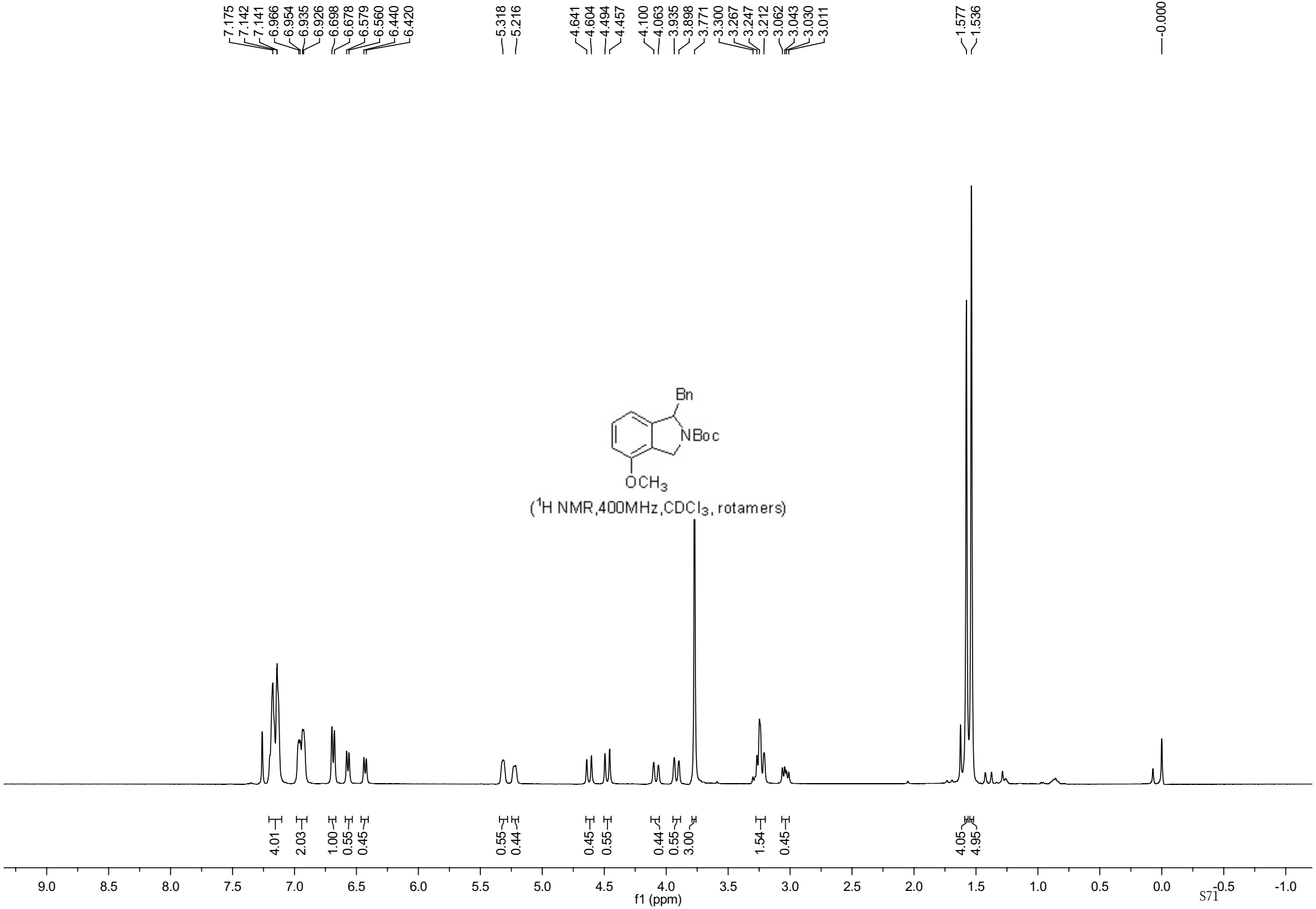
NMR spectra of compound 8da



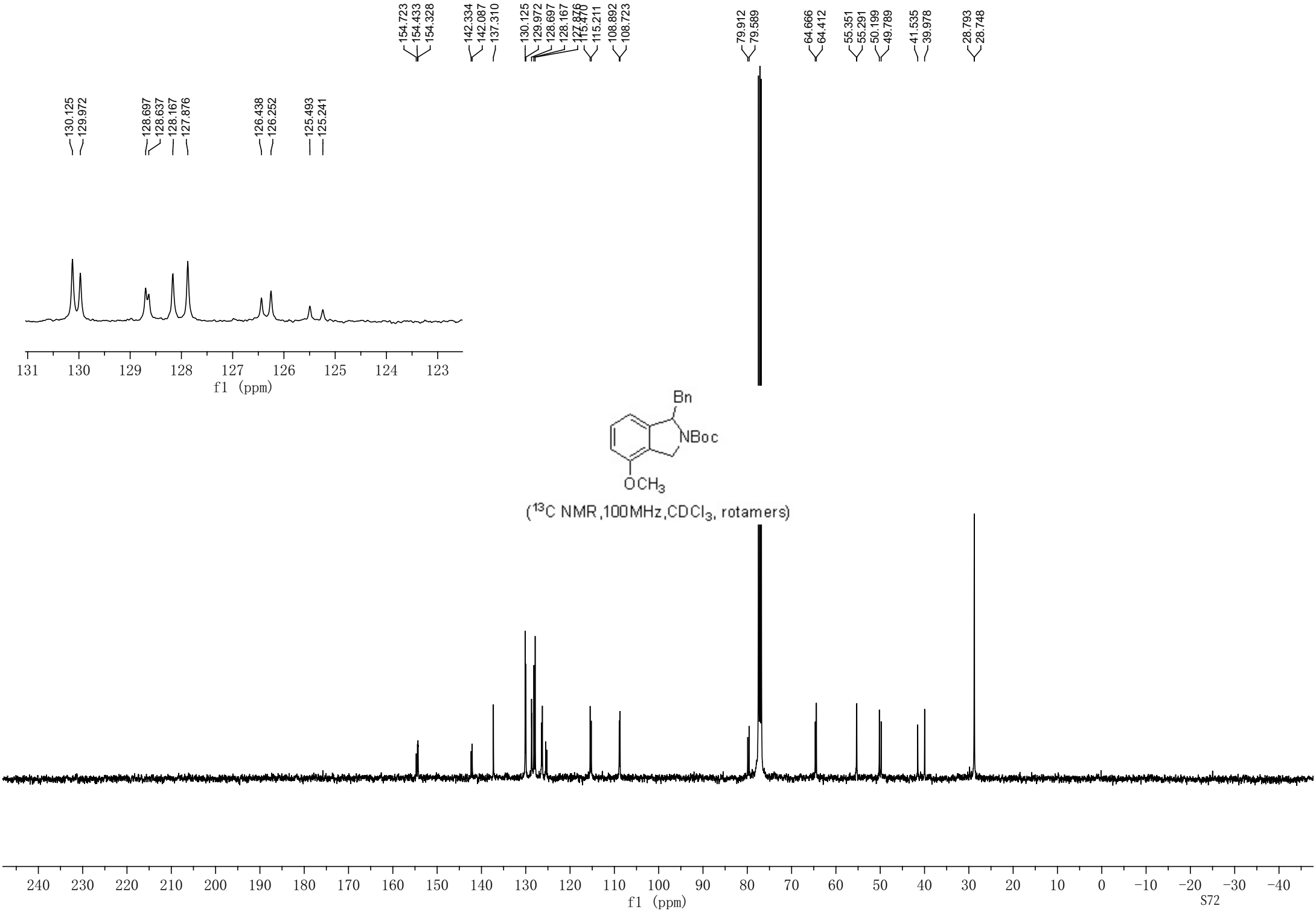
NMR spectra of compound 8da



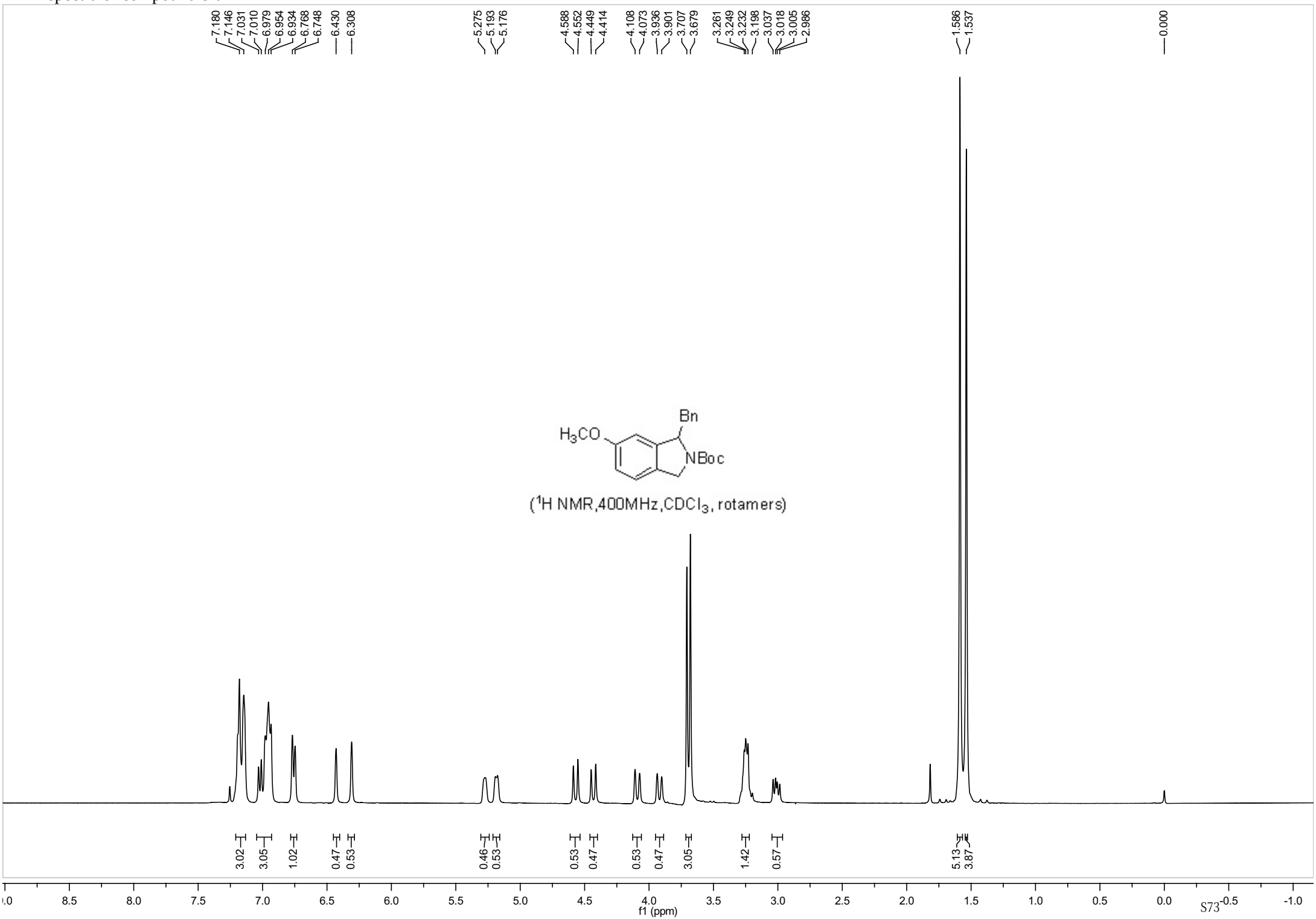
NMR spectra of compound 8ea



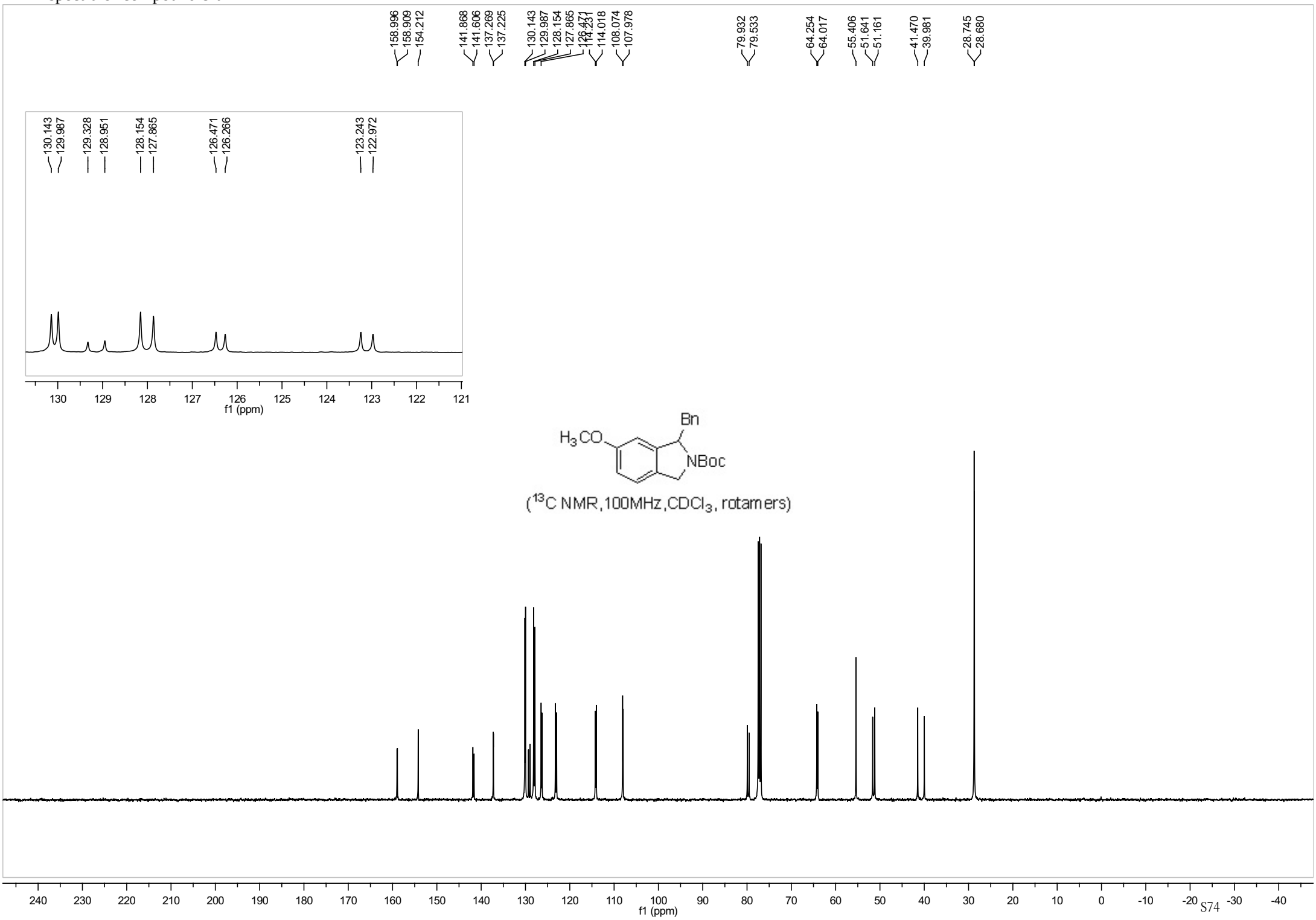
NMR spectra of compound 8ea



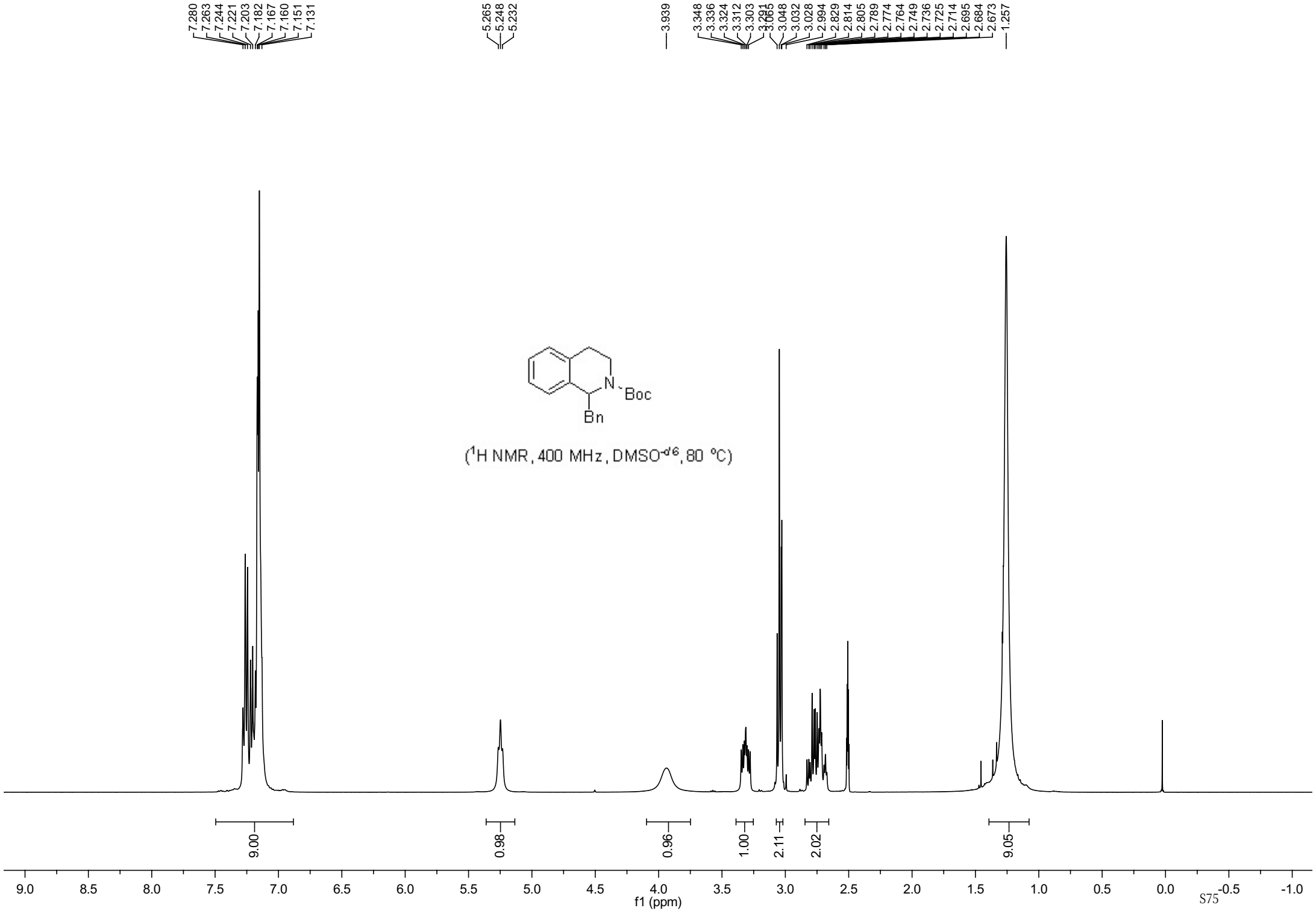
NMR spectra of compound 8fa



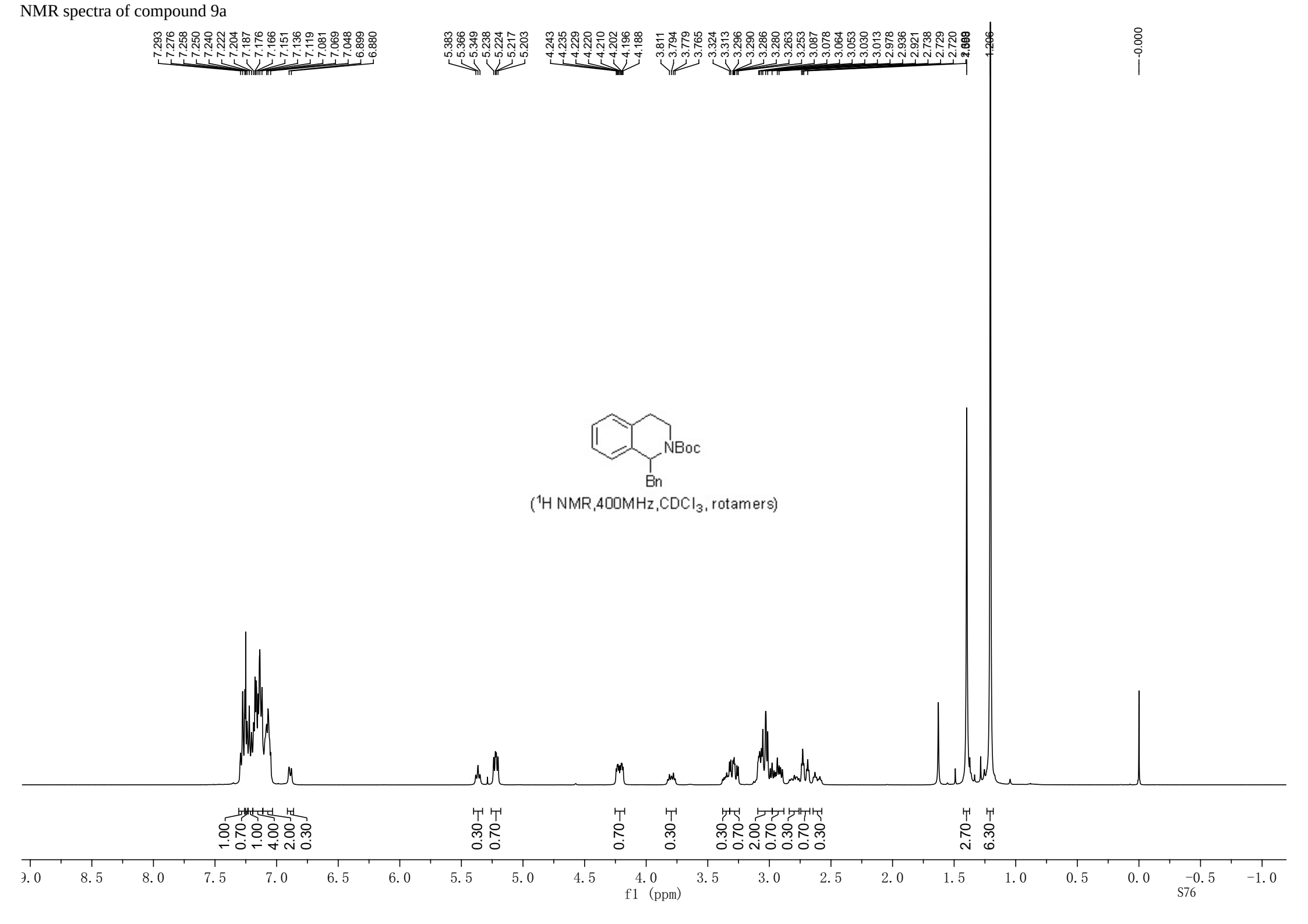
NMR spectra of compound 8fa



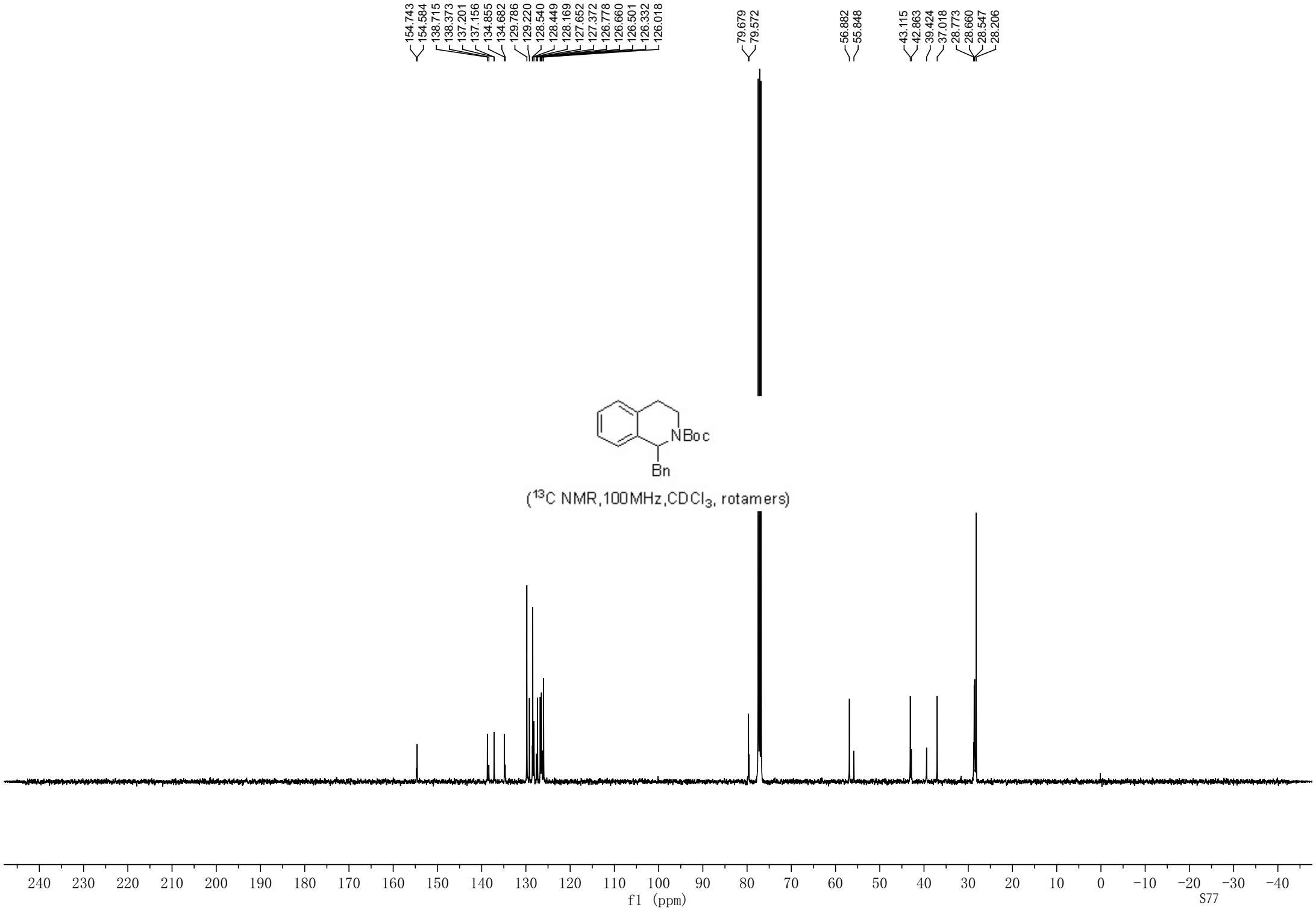
NMR spectra of compound 9a



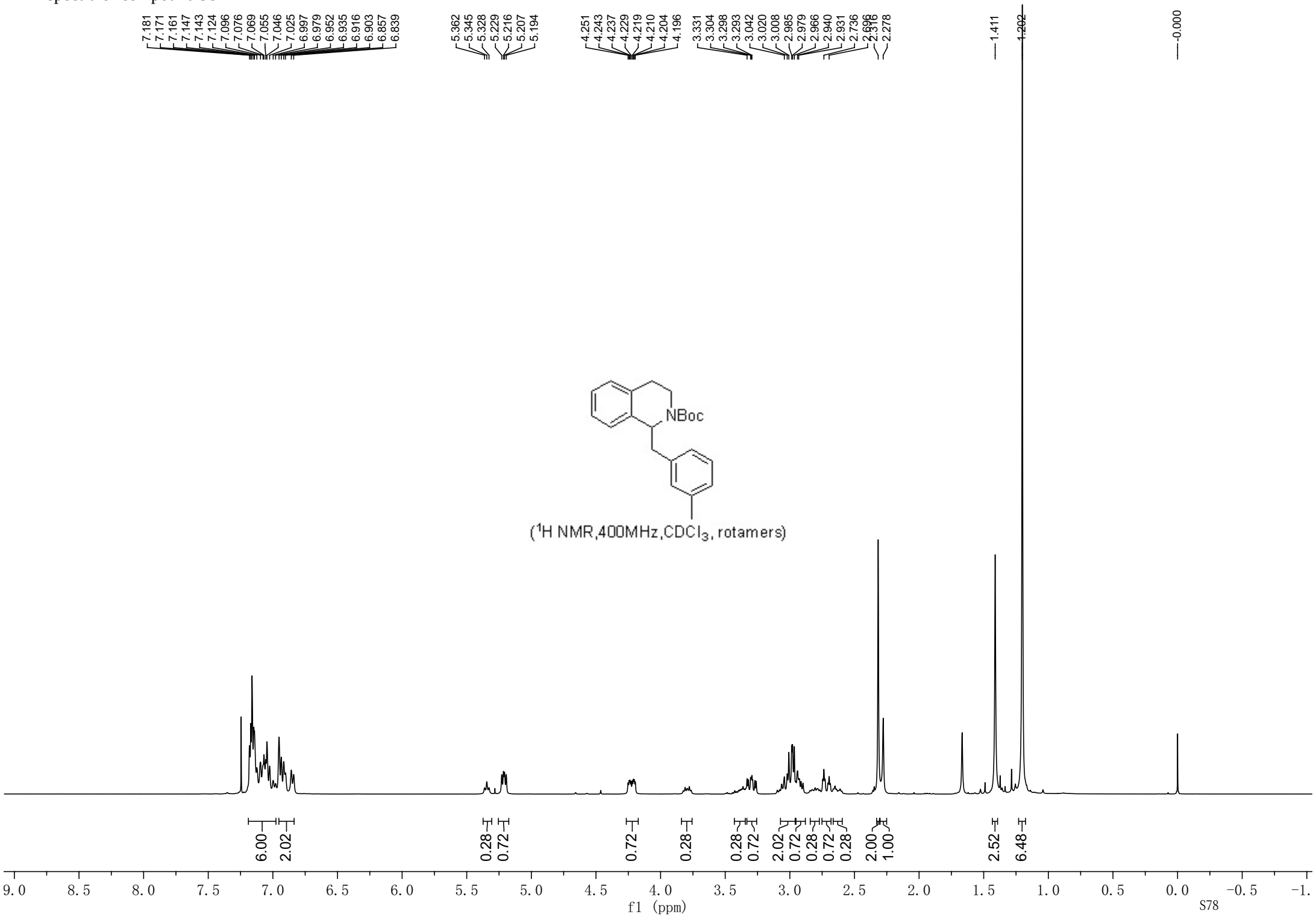
NMR spectra of compound 9a



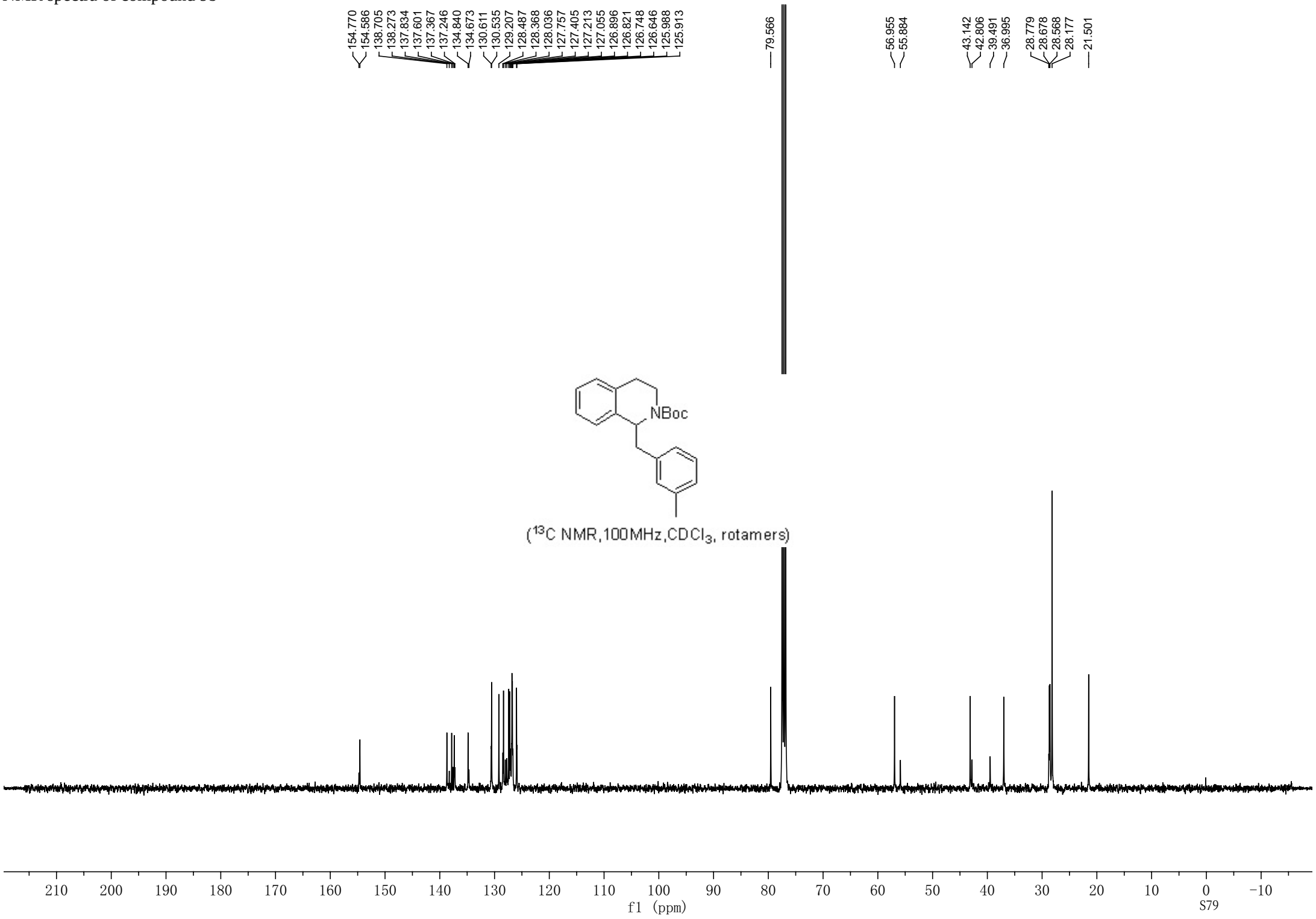
NMR spectra of compound 9a



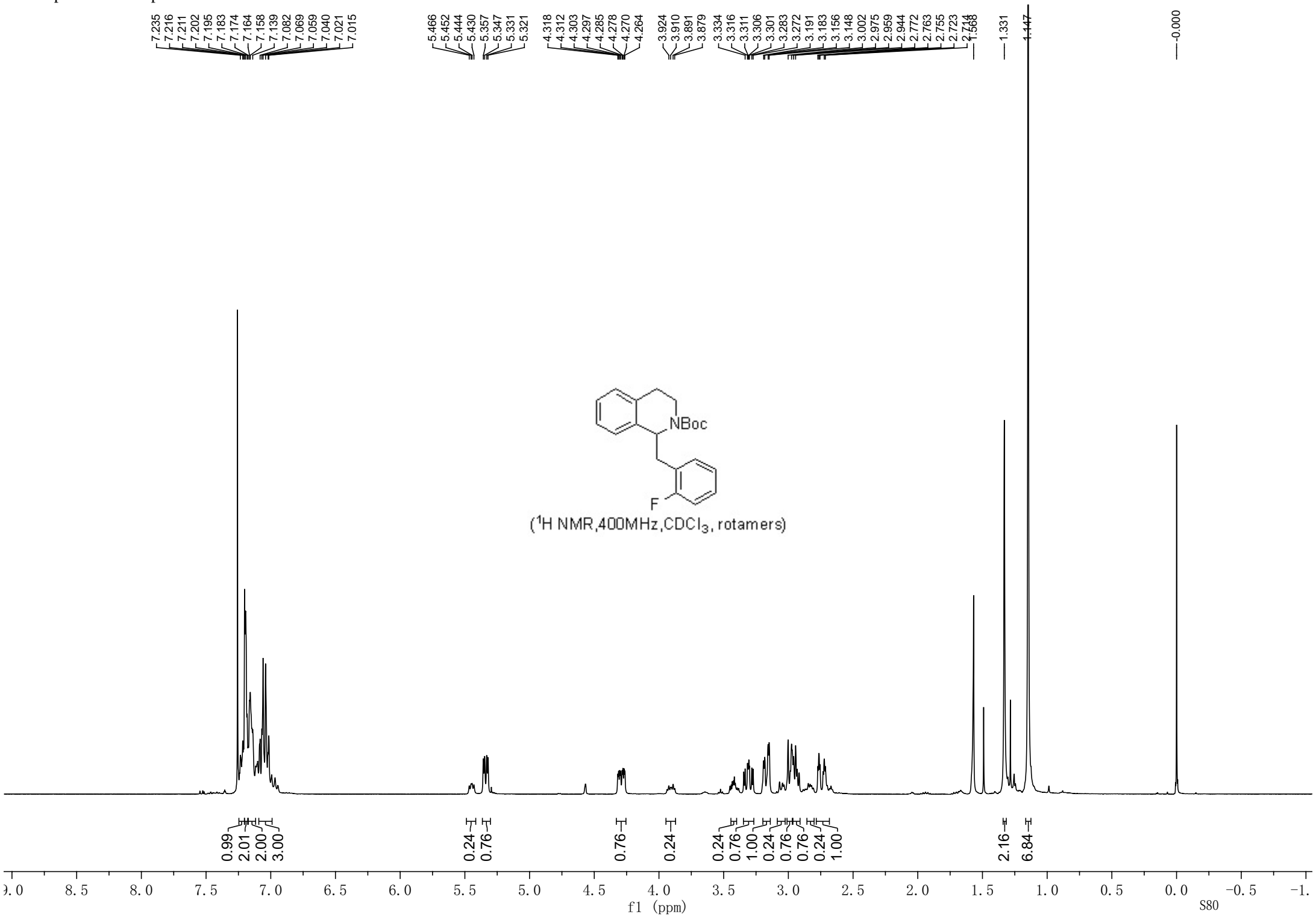
NMR spectra of compound 9b



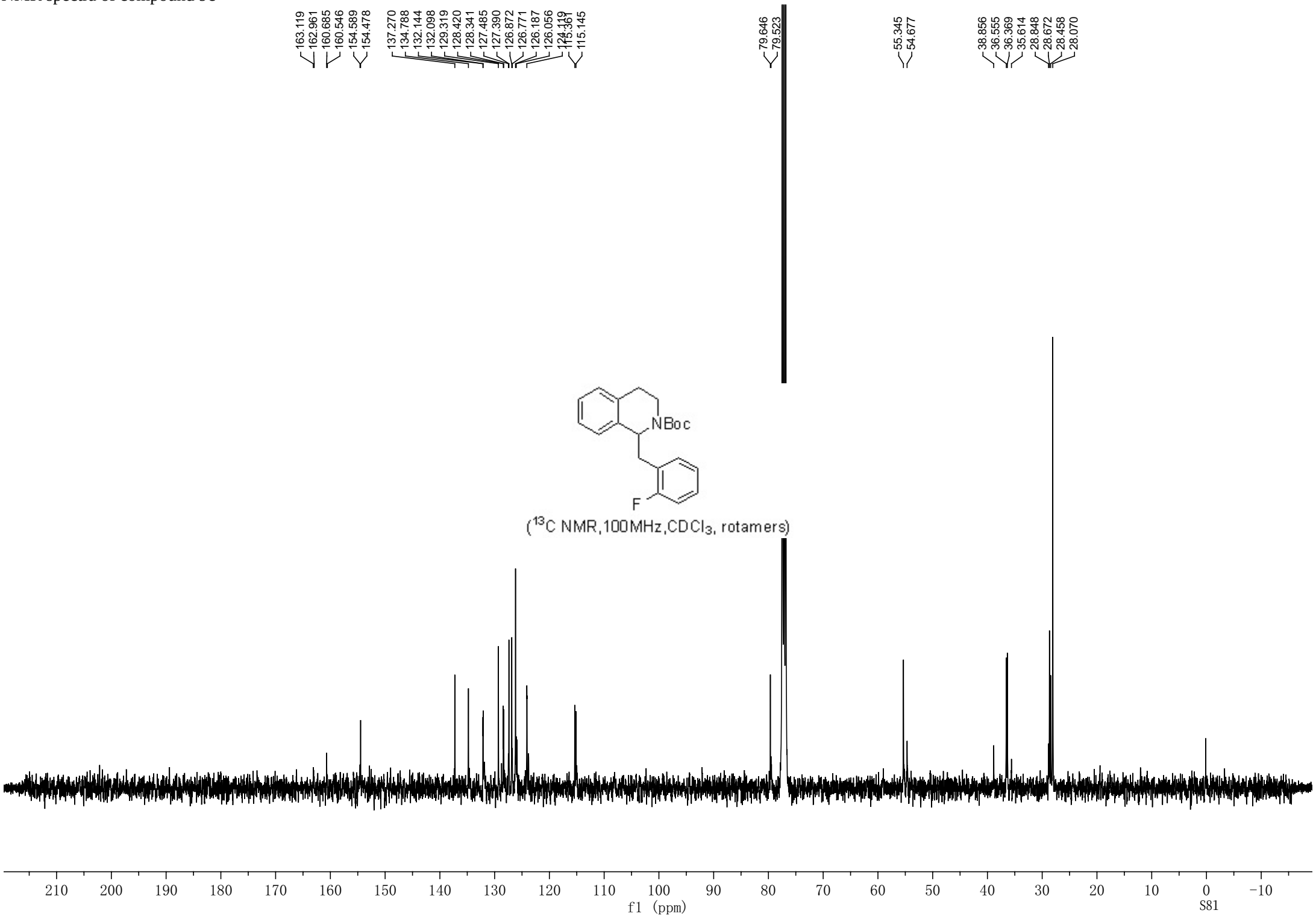
NMR spectra of compound 9b



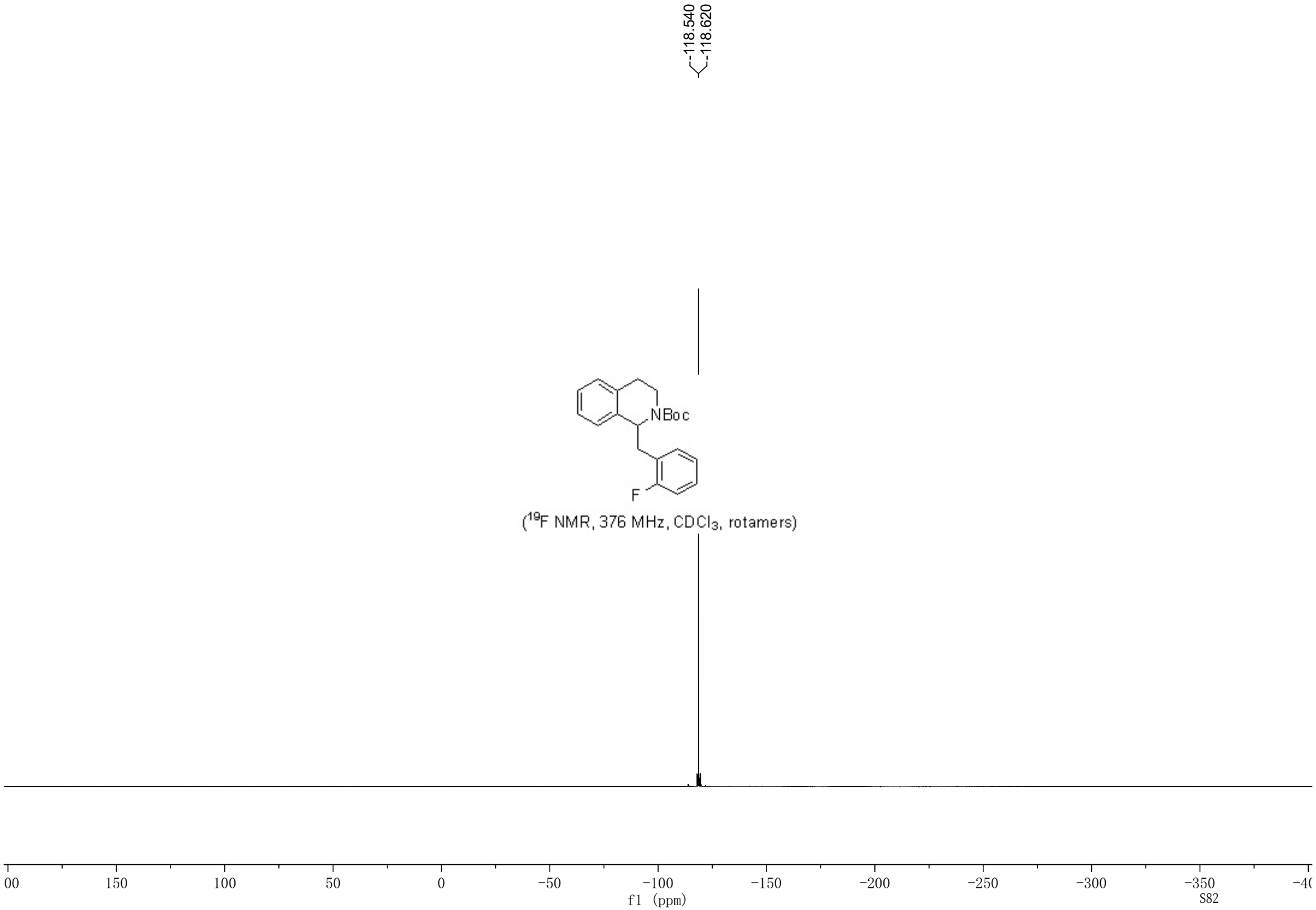
NMR spectra of compound 9c



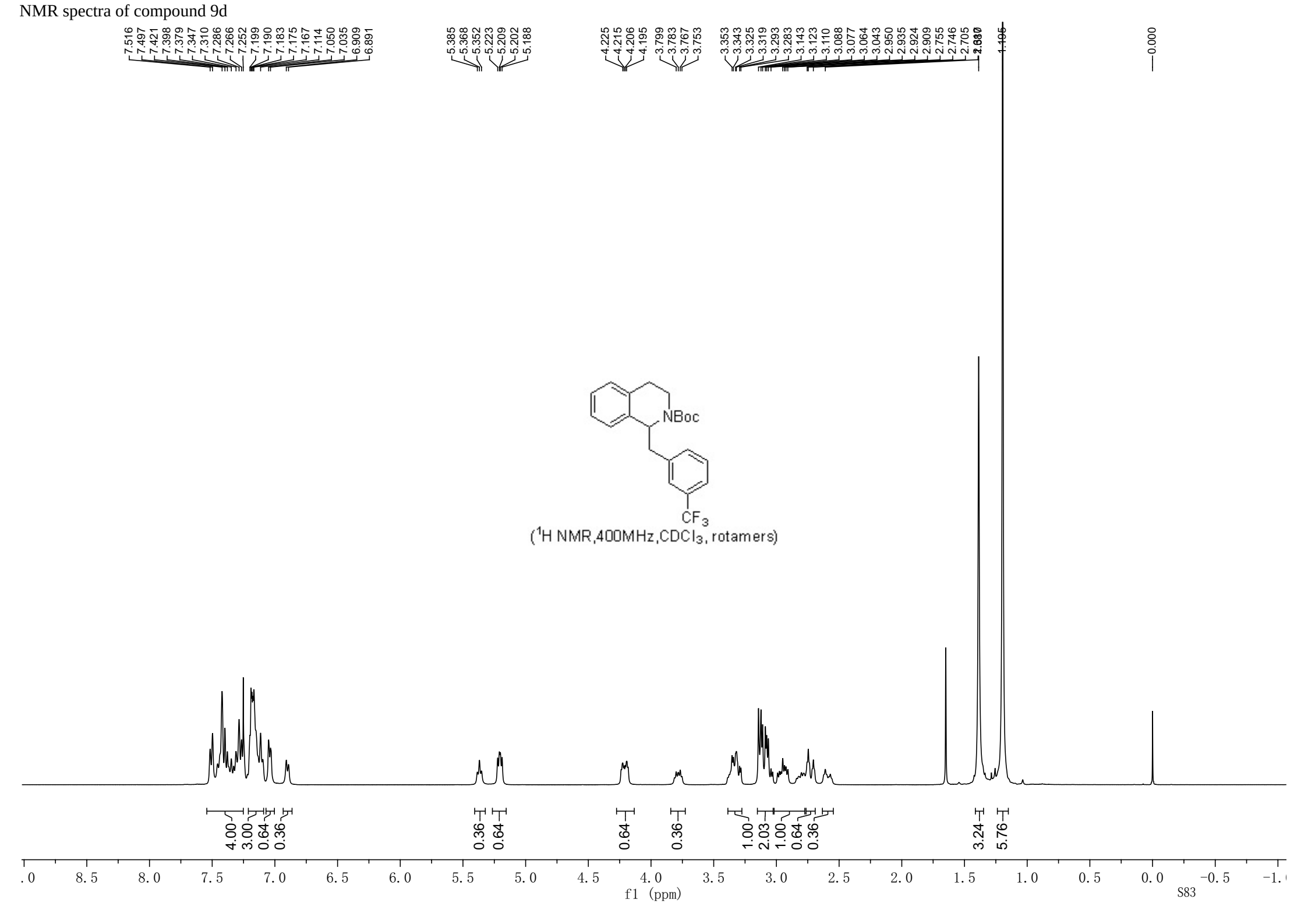
NMR spectra of compound 9c



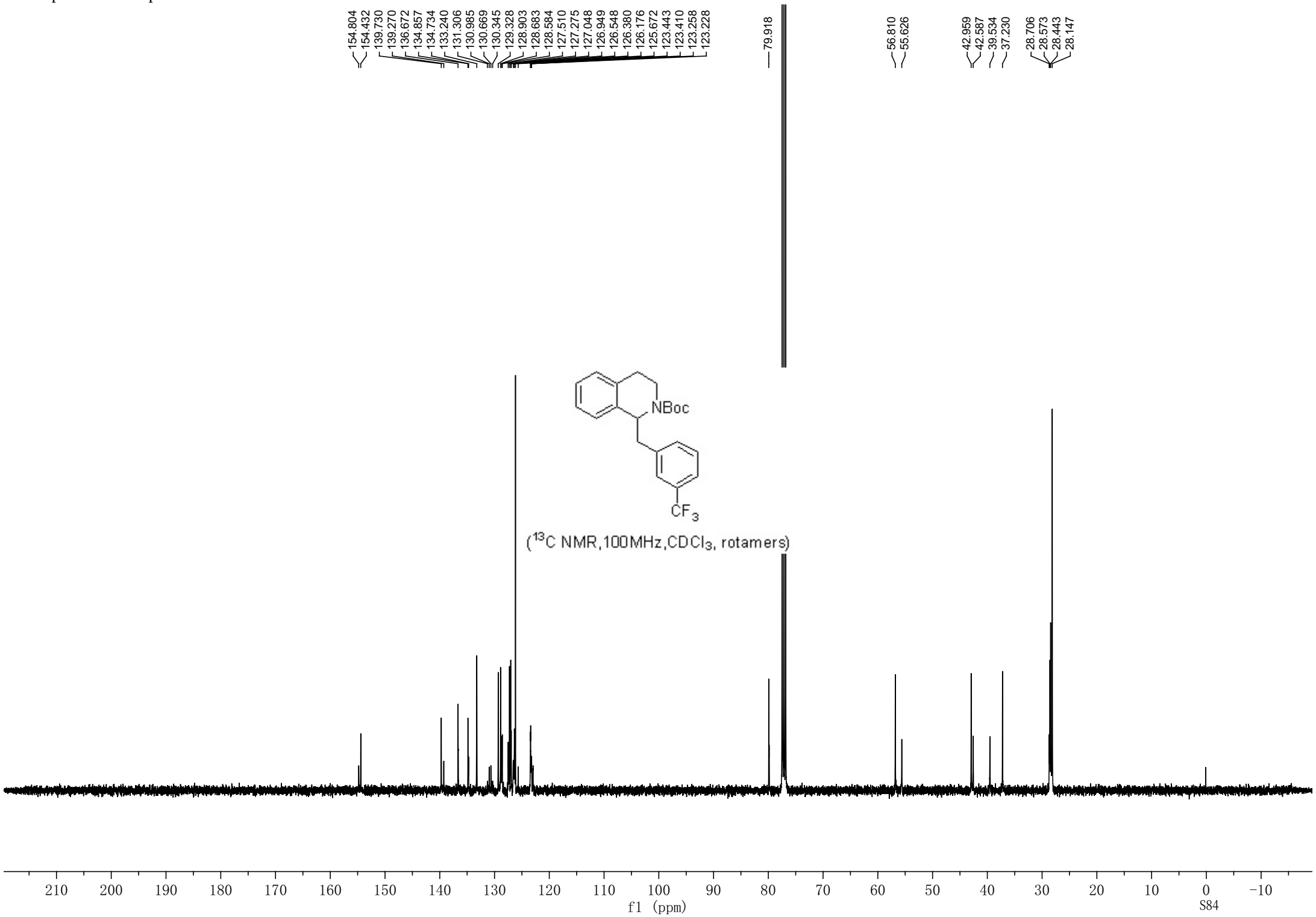
NMR spectra of compound 9c



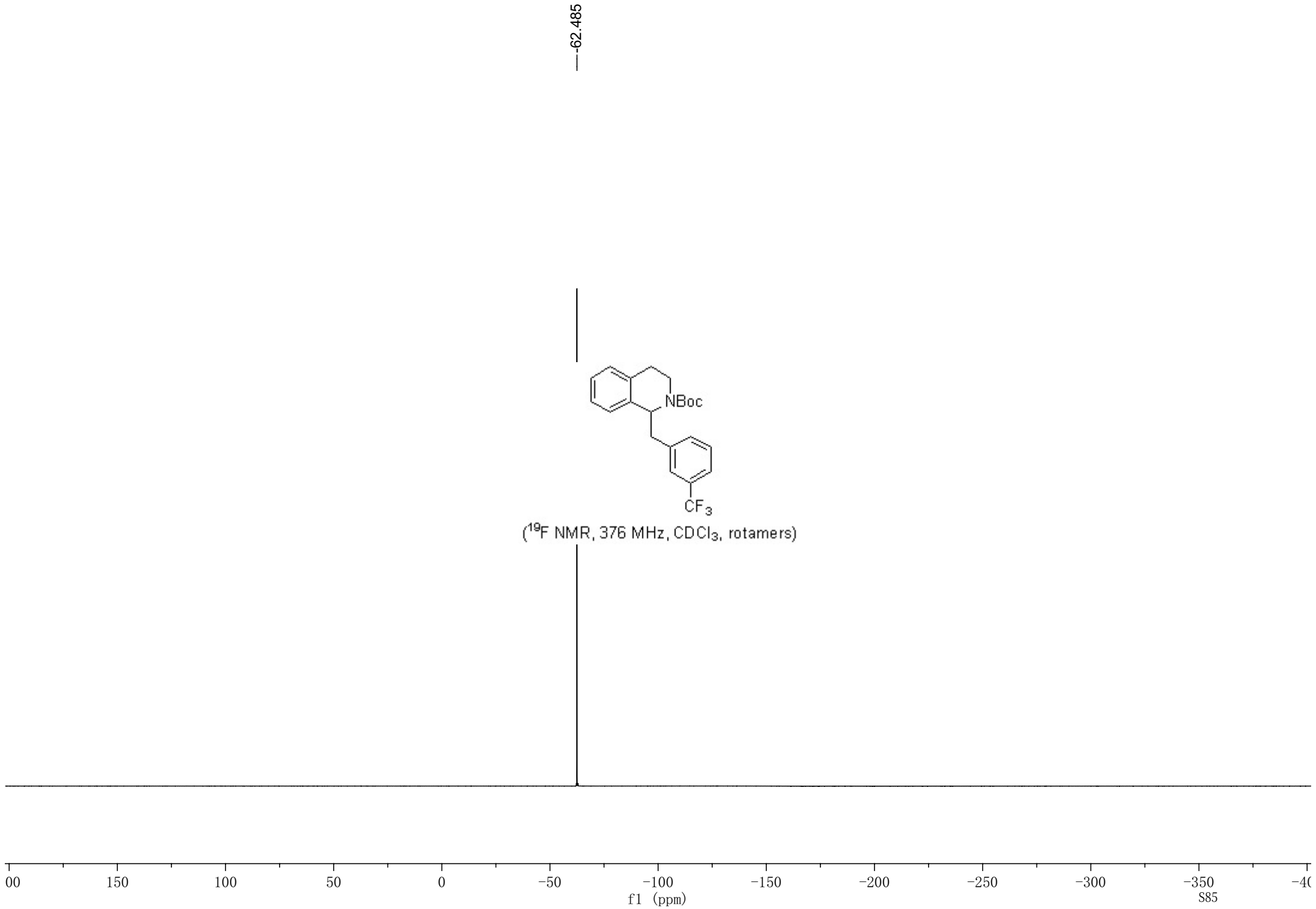
NMR spectra of compound 9d



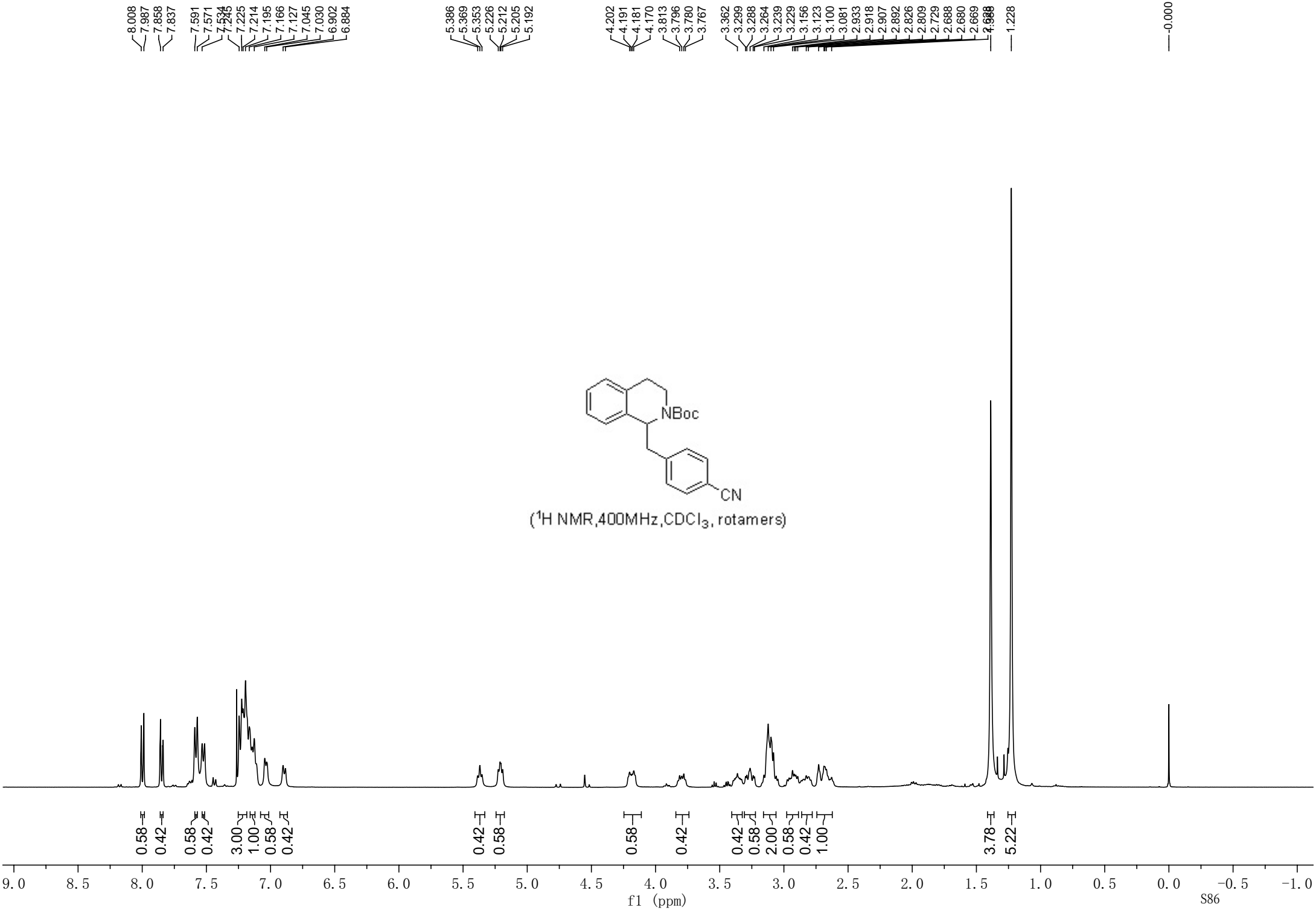
NMR spectra of compound 9d



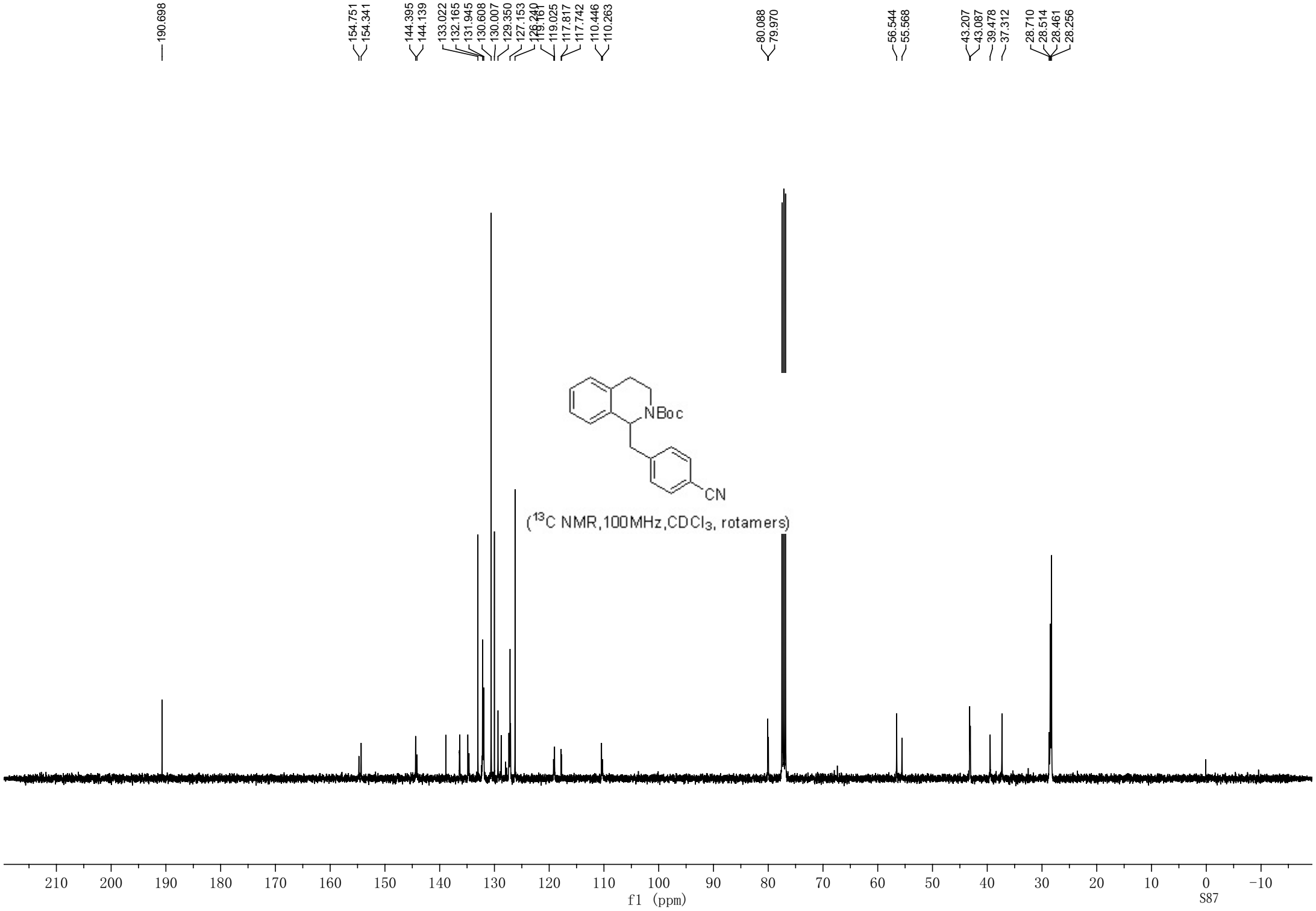
NMR spectra of compound 9d



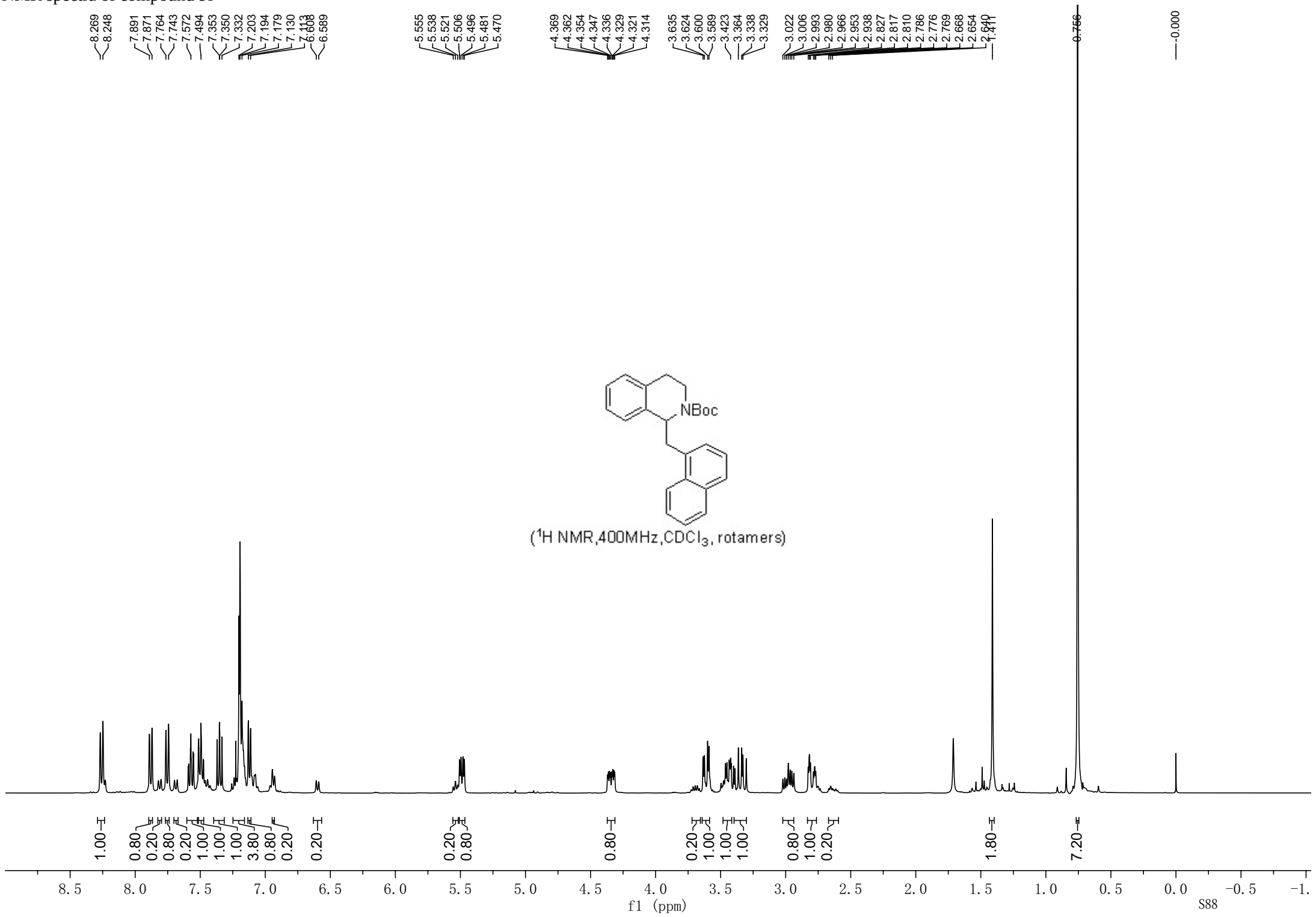
NMR spectra of compound 9e



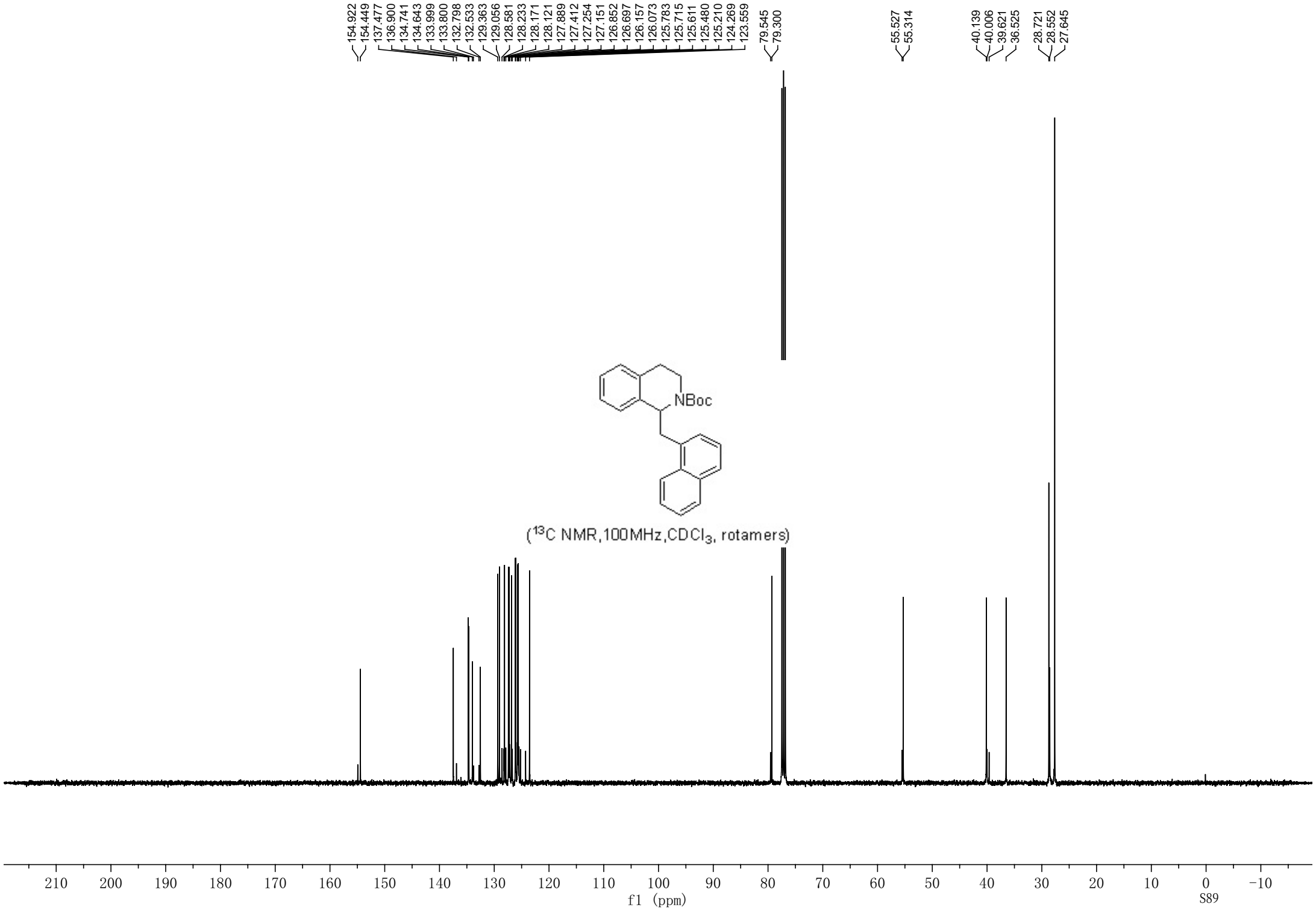
NMR spectra of compound 9e



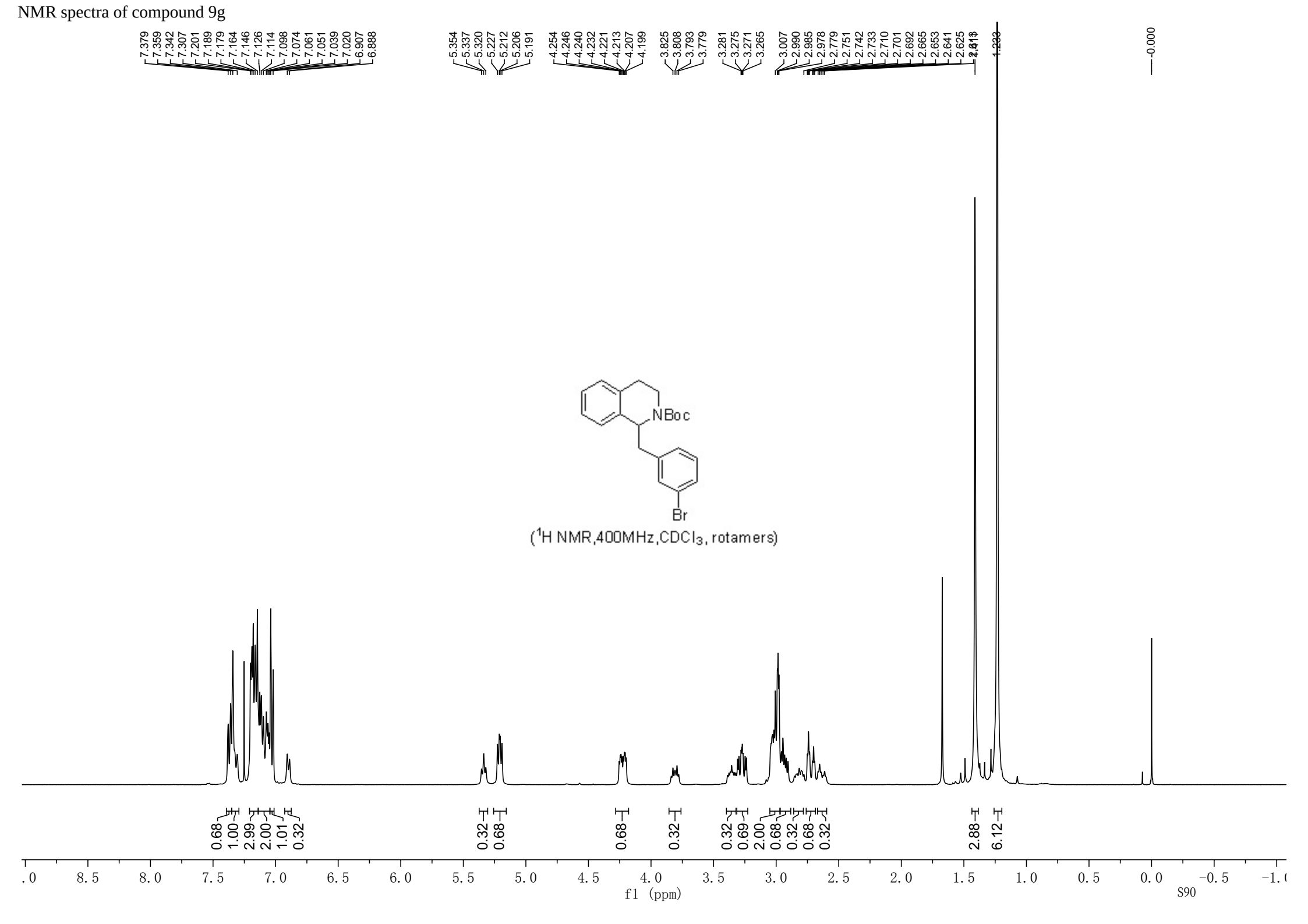
NMR spectra of compound 9f



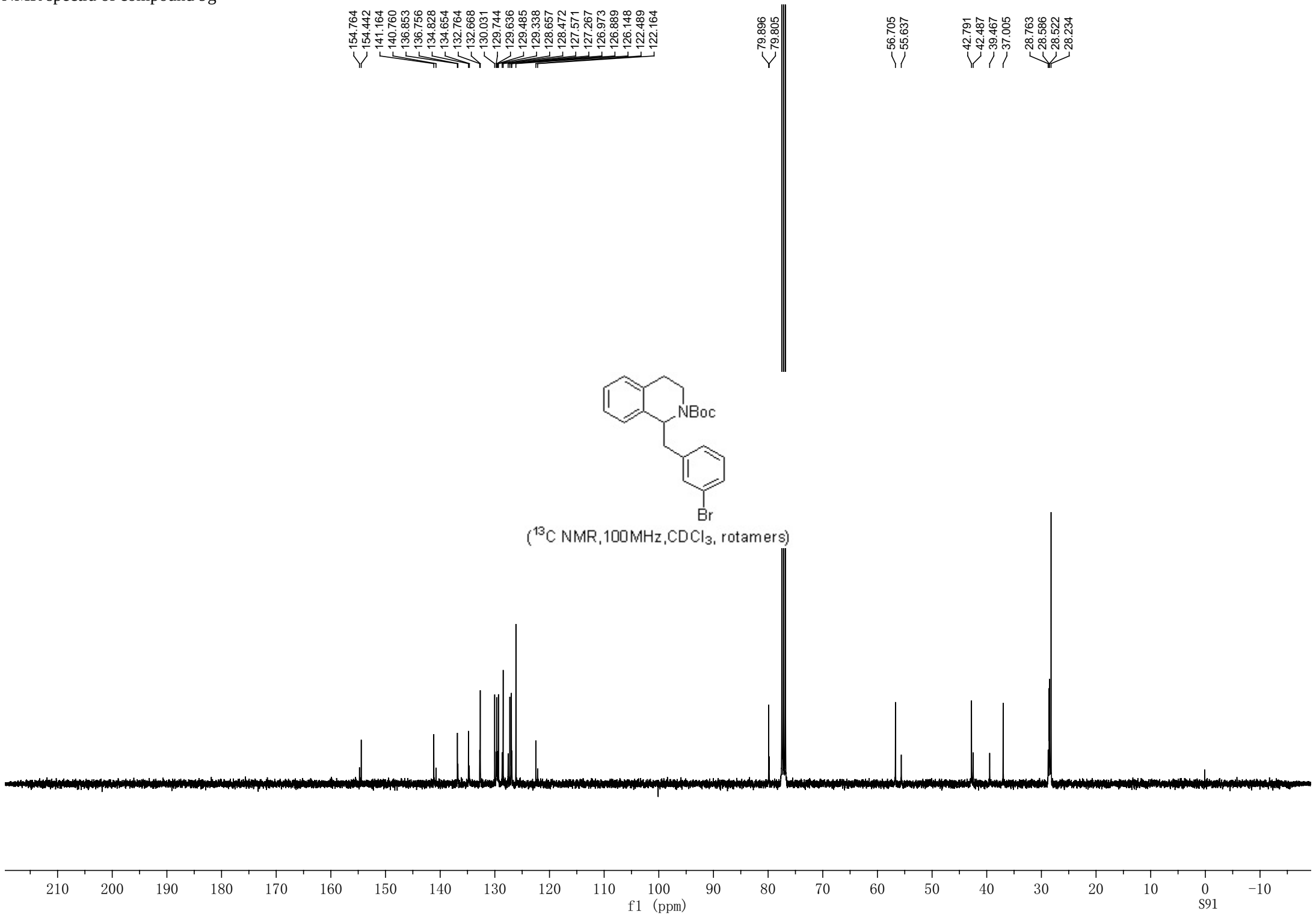
NMR spectra of compound 9f



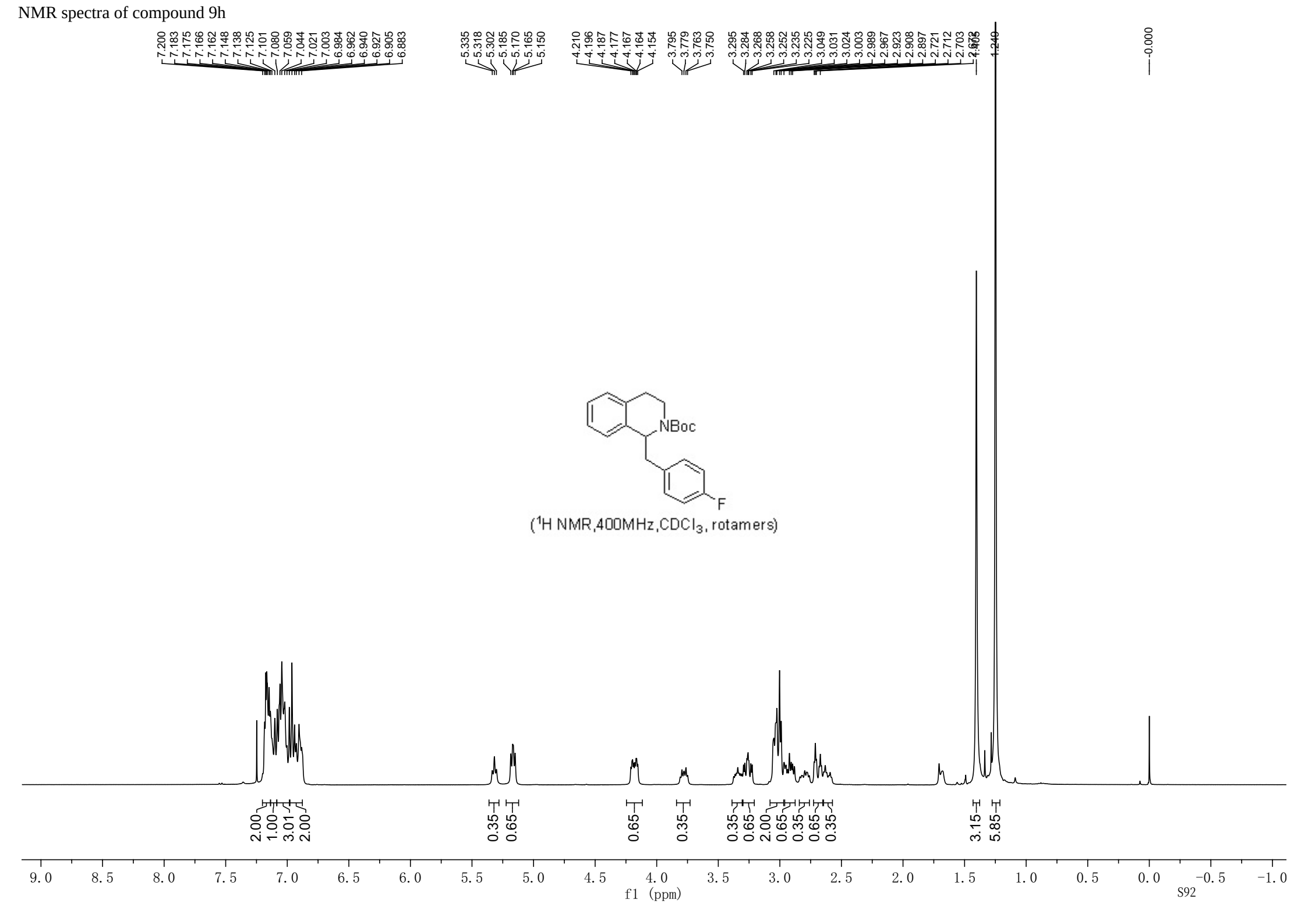
NMR spectra of compound 9g



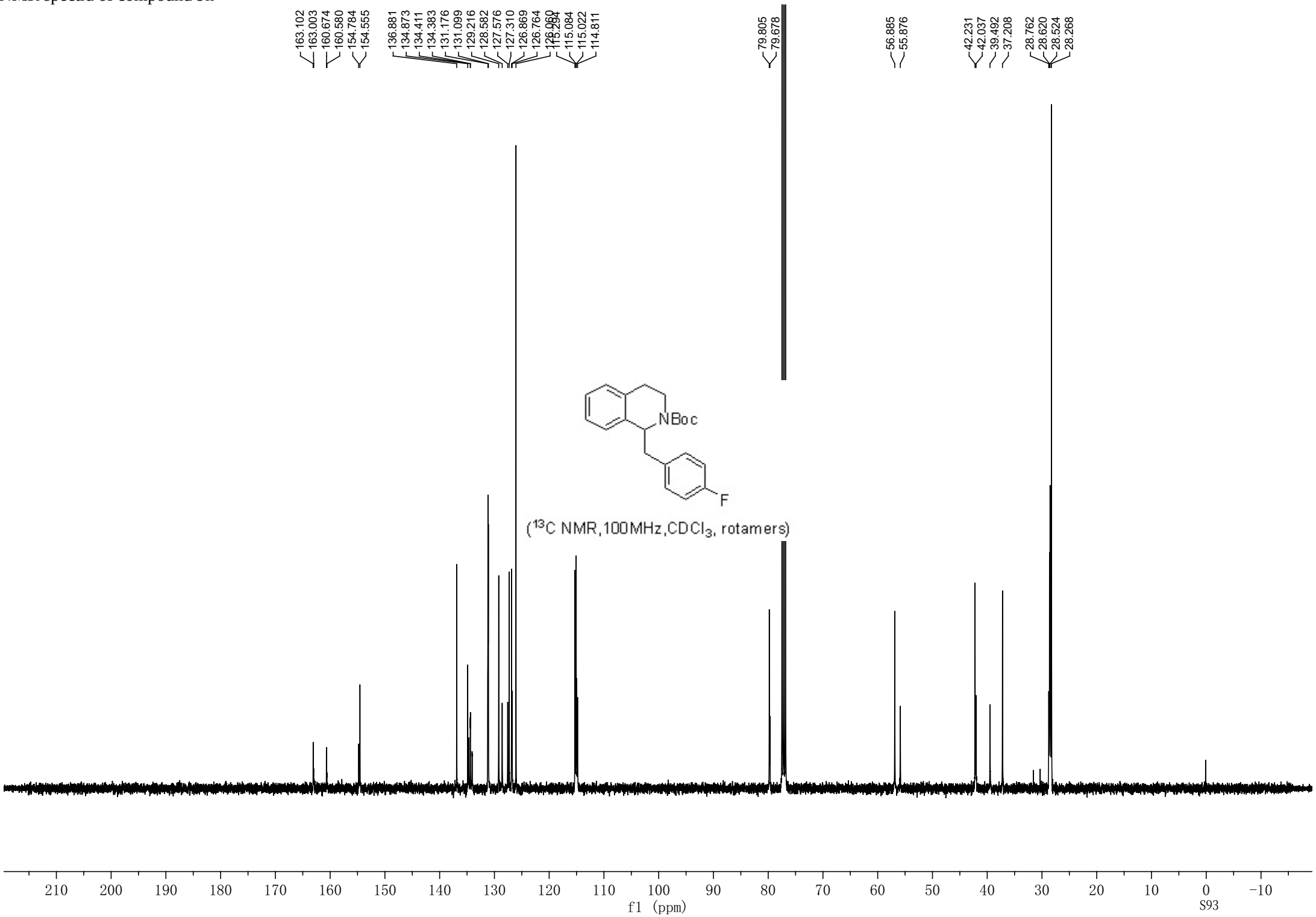
NMR spectra of compound 9g



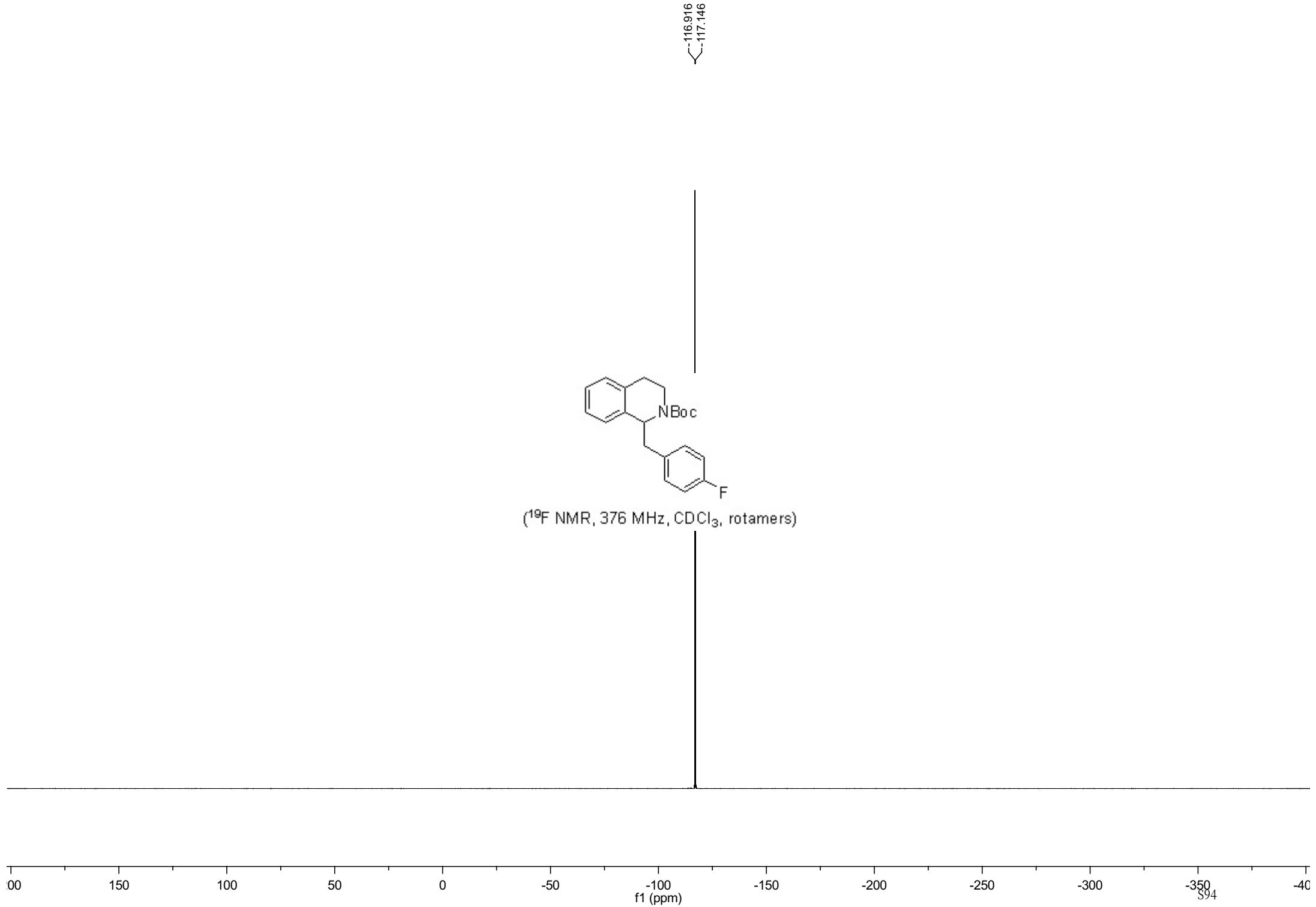
NMR spectra of compound 9h



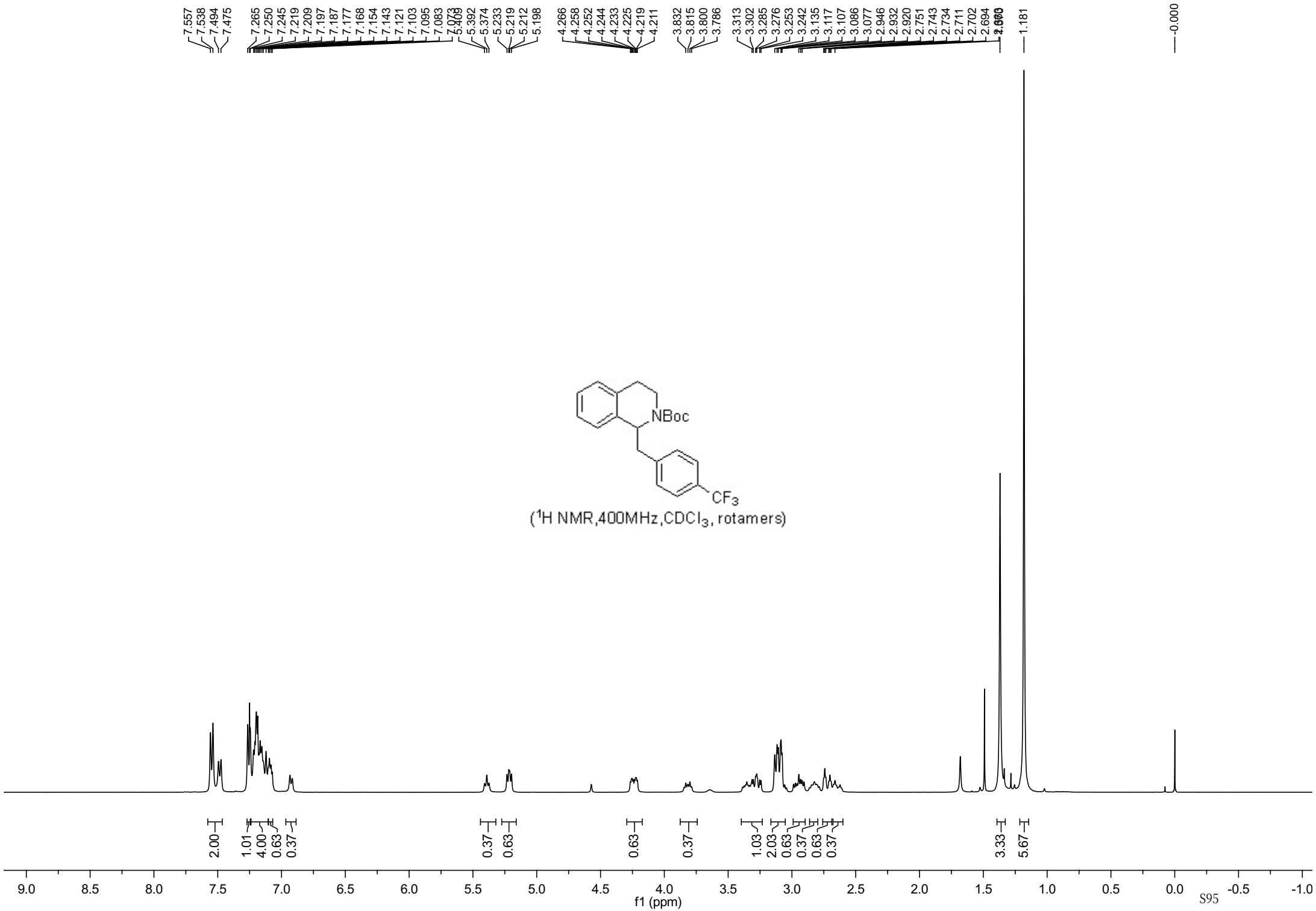
NMR spectra of compound 9h



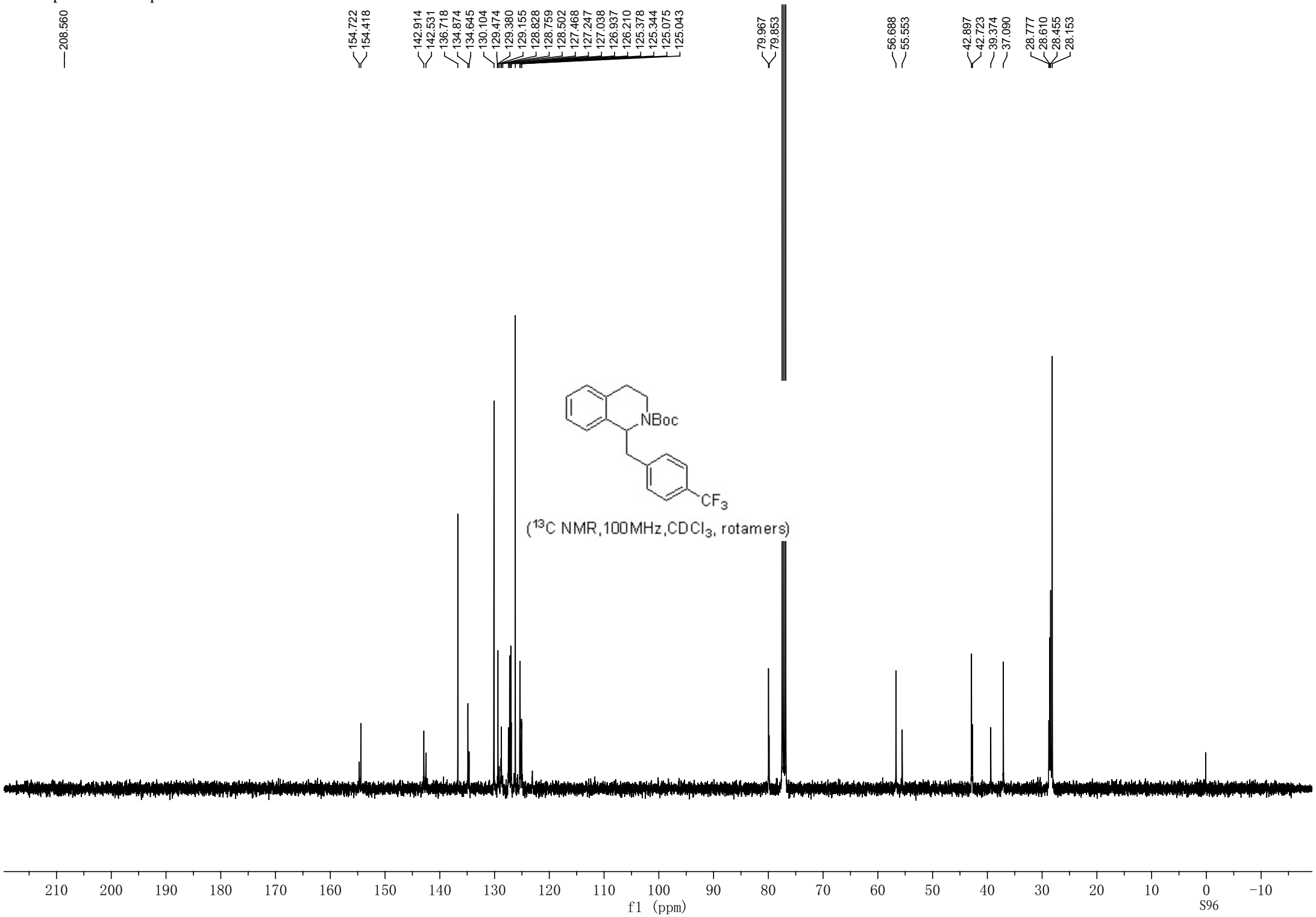
NMR spectra of compound 9h



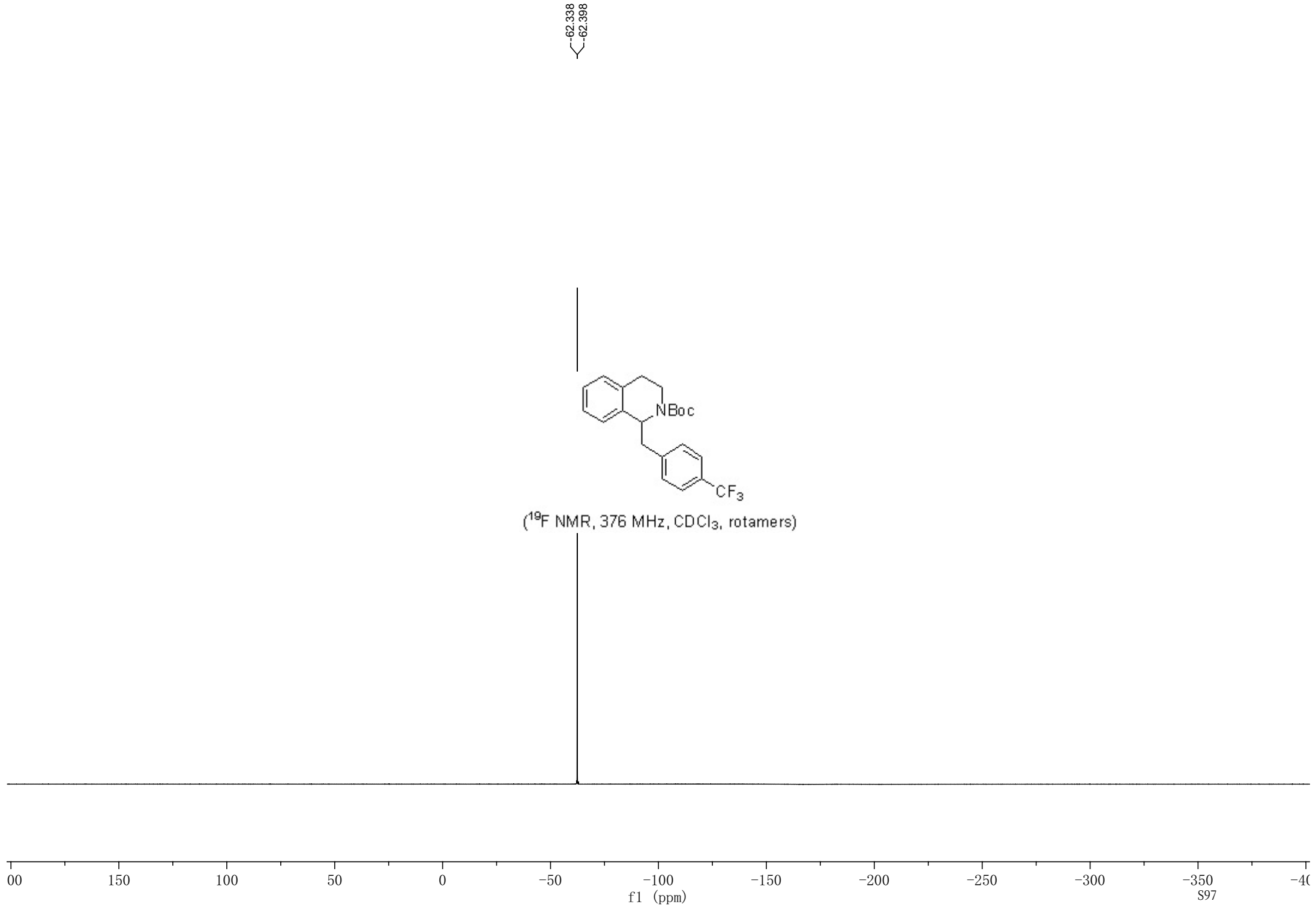
NMR spectra of compound 9i



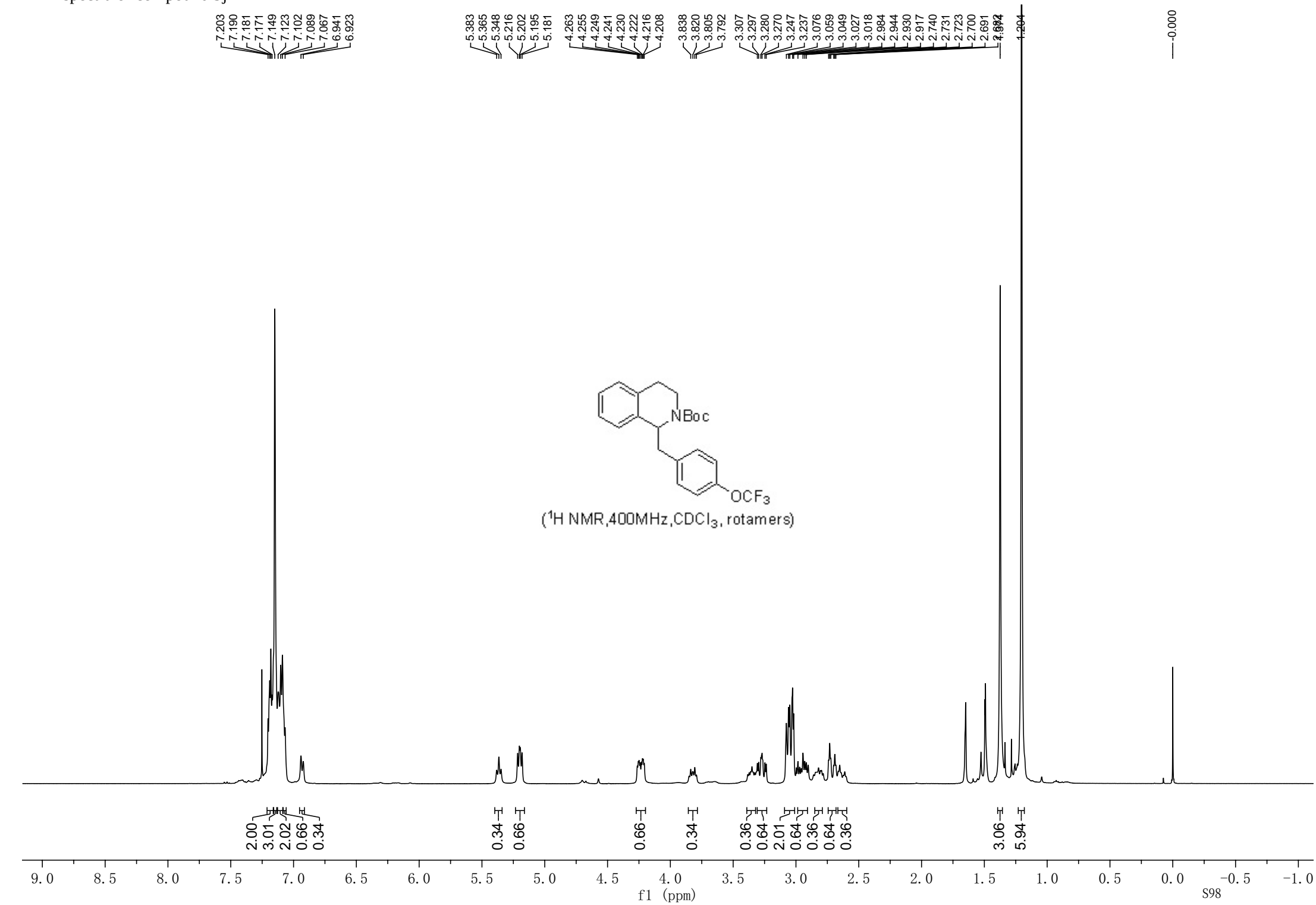
NMR spectra of compound 9i



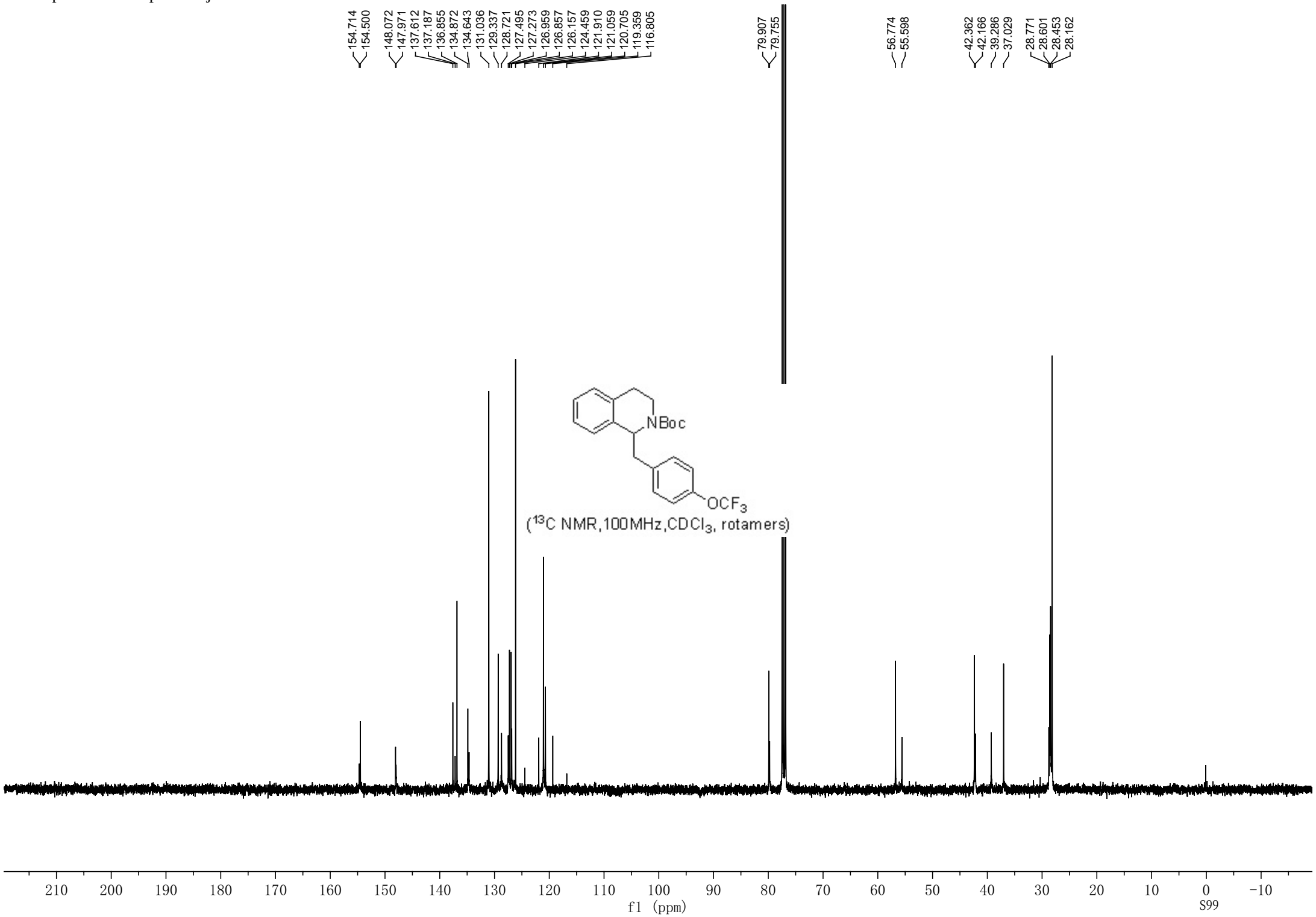
NMR spectra of compound 9i



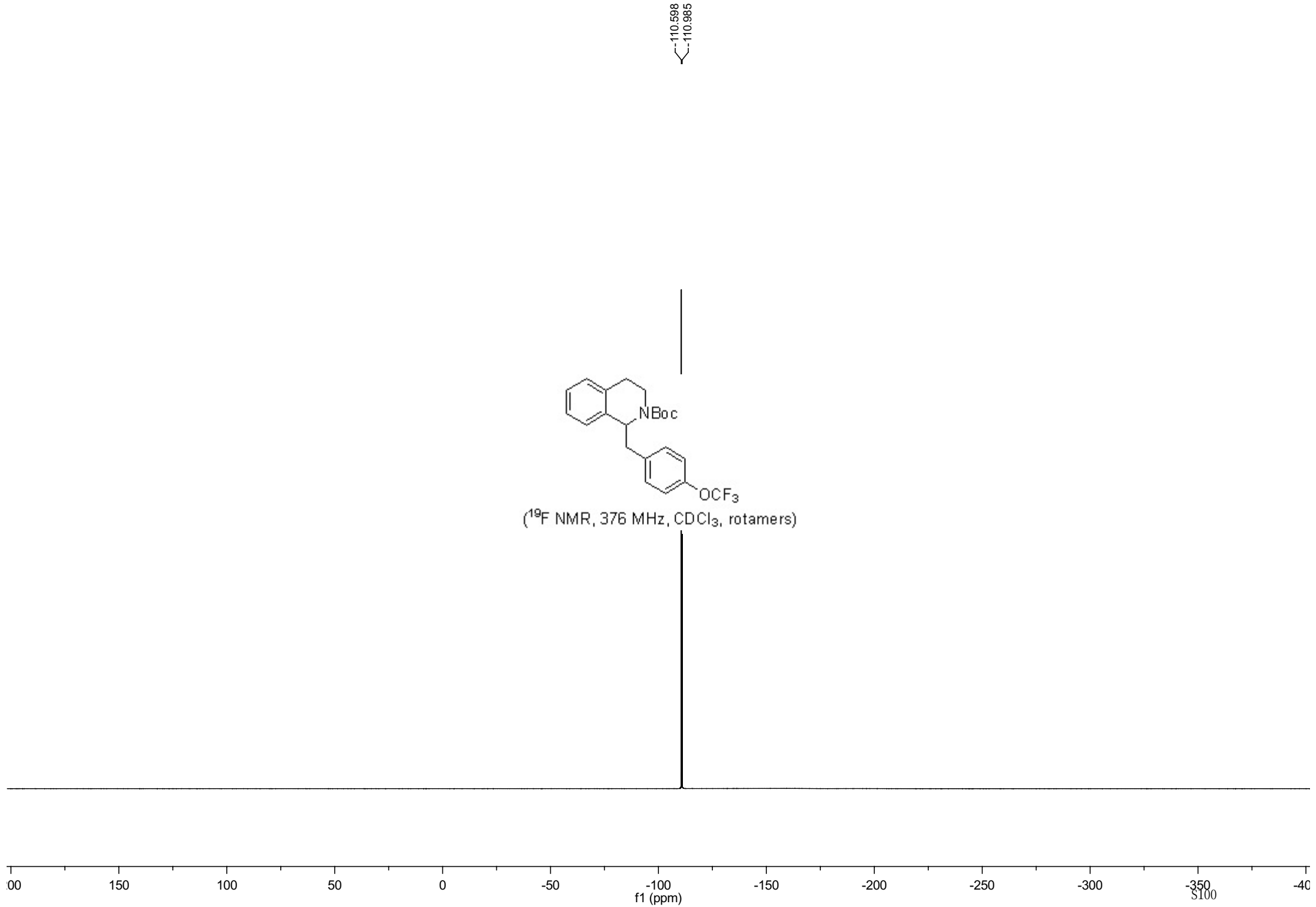
NMR spectra of compound 9j



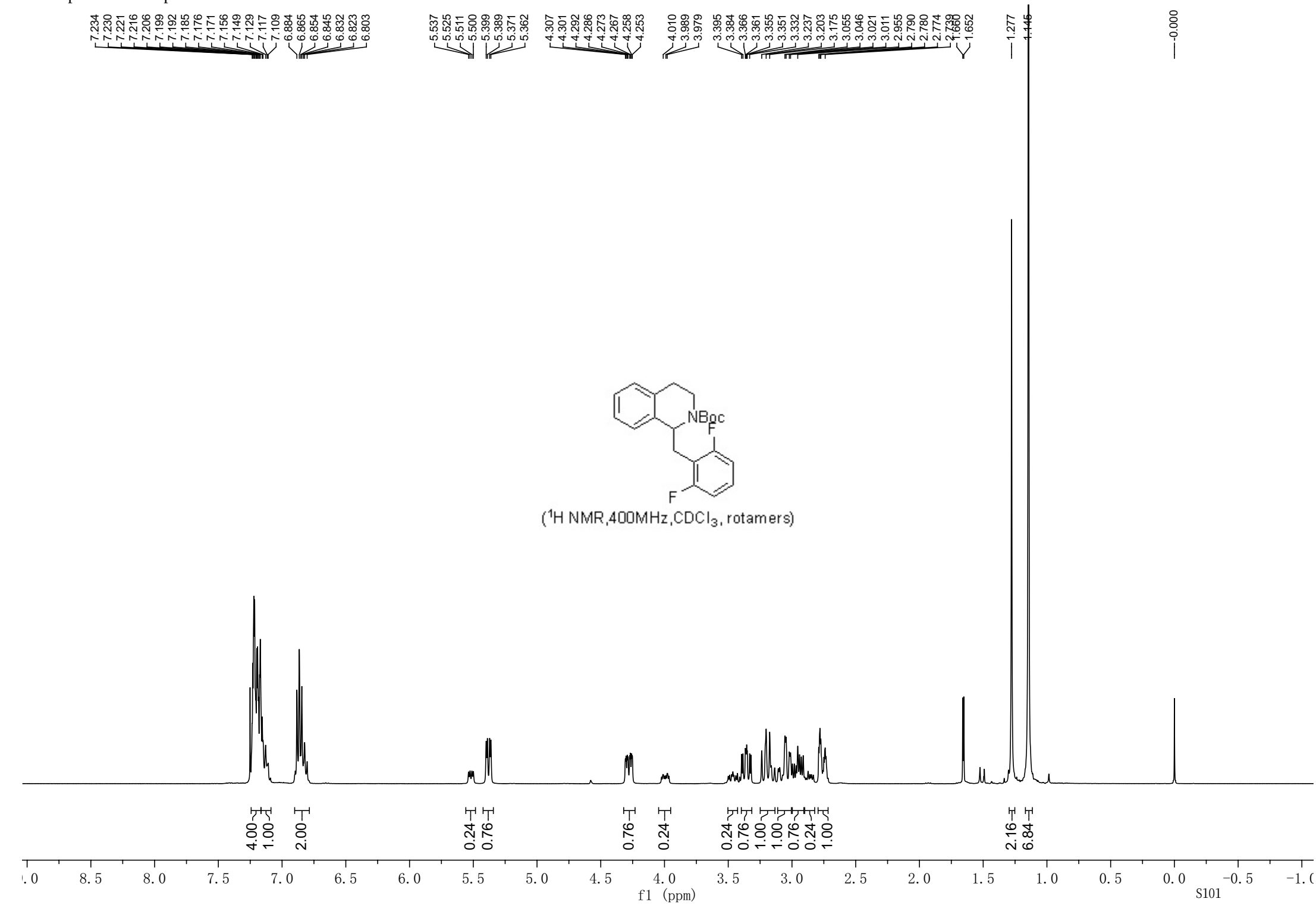
NMR spectra of compound 9j



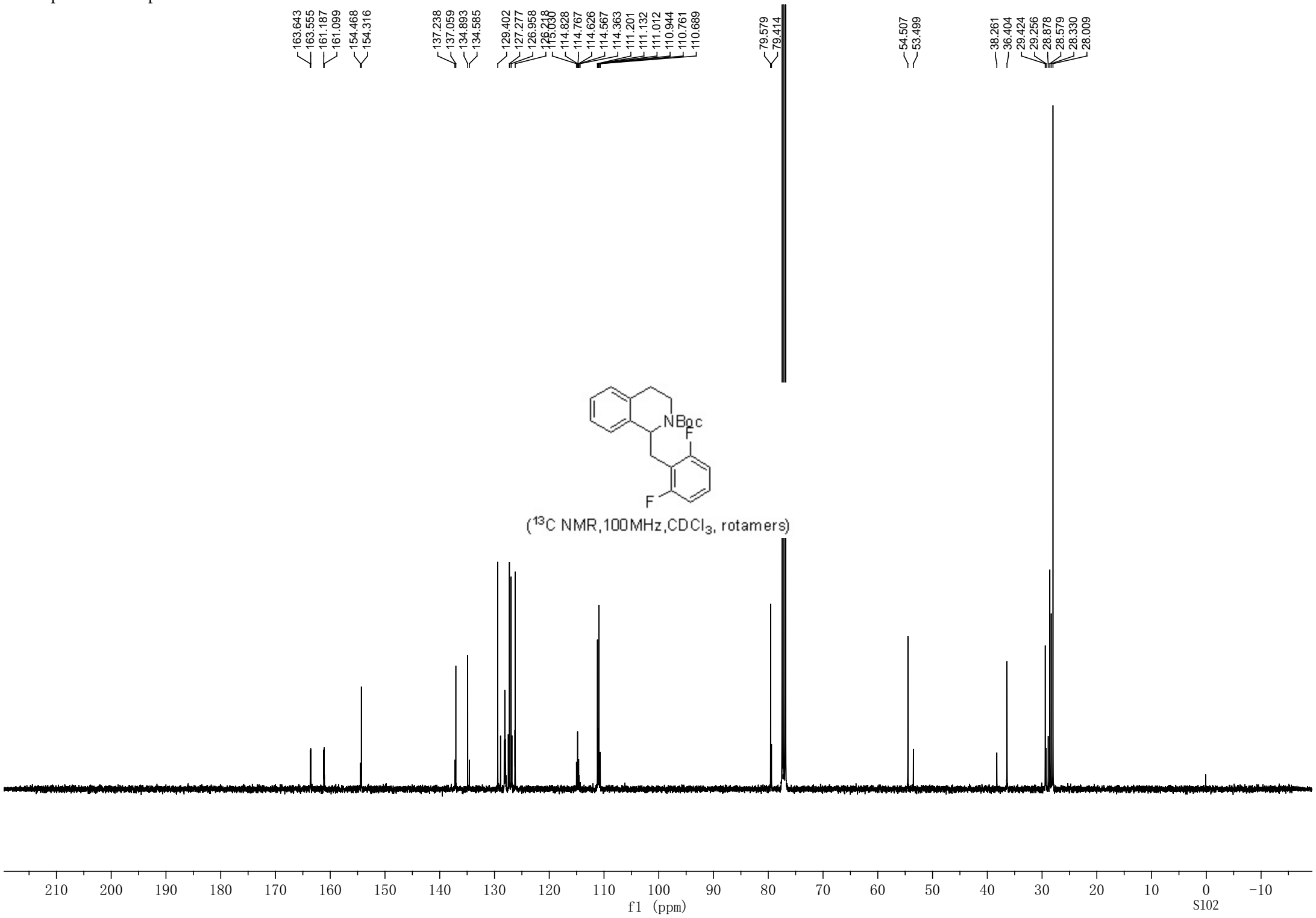
NMR spectra of compound 9j



NMR spectra of compound 9k

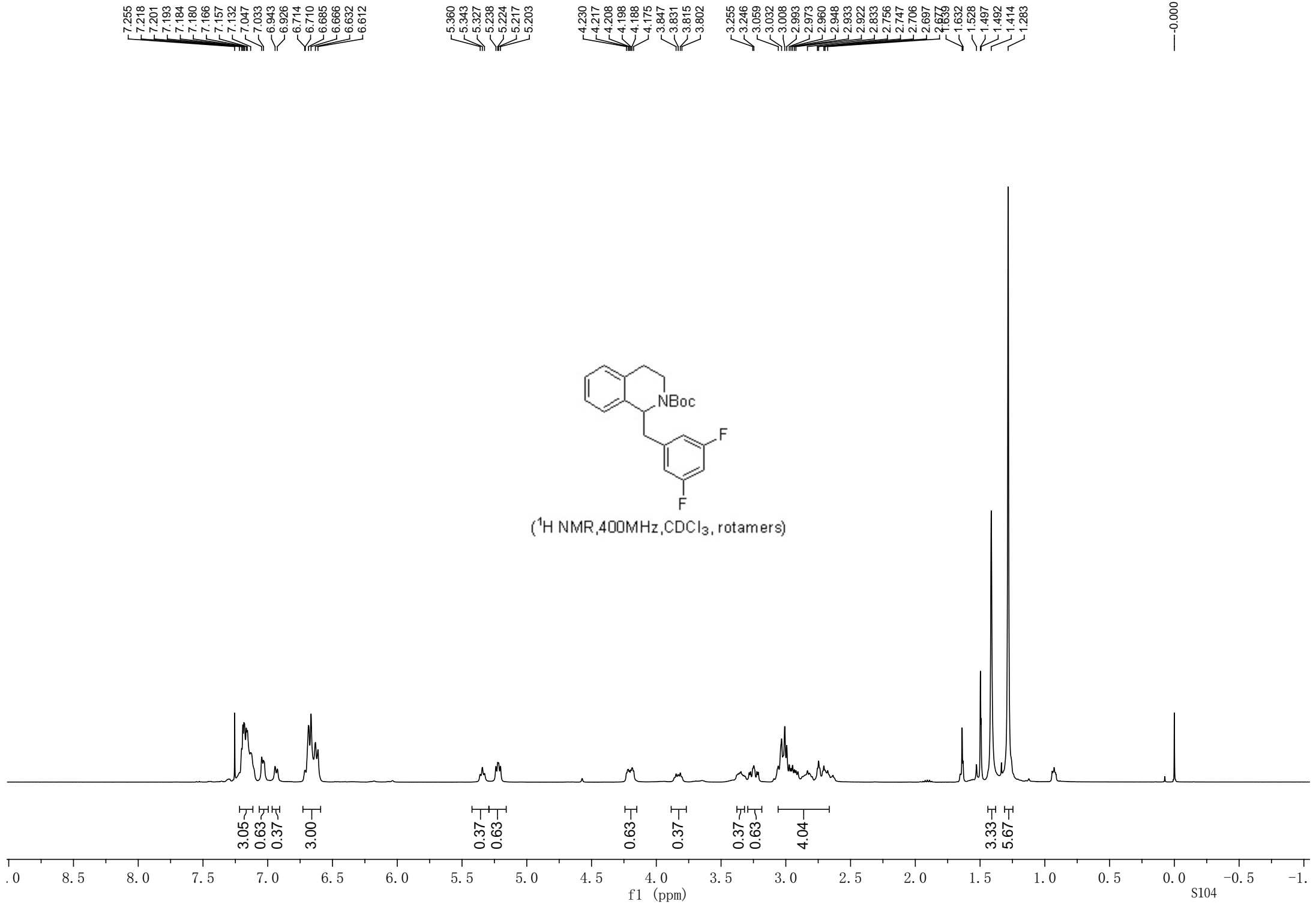


NMR spectra of compound 9k

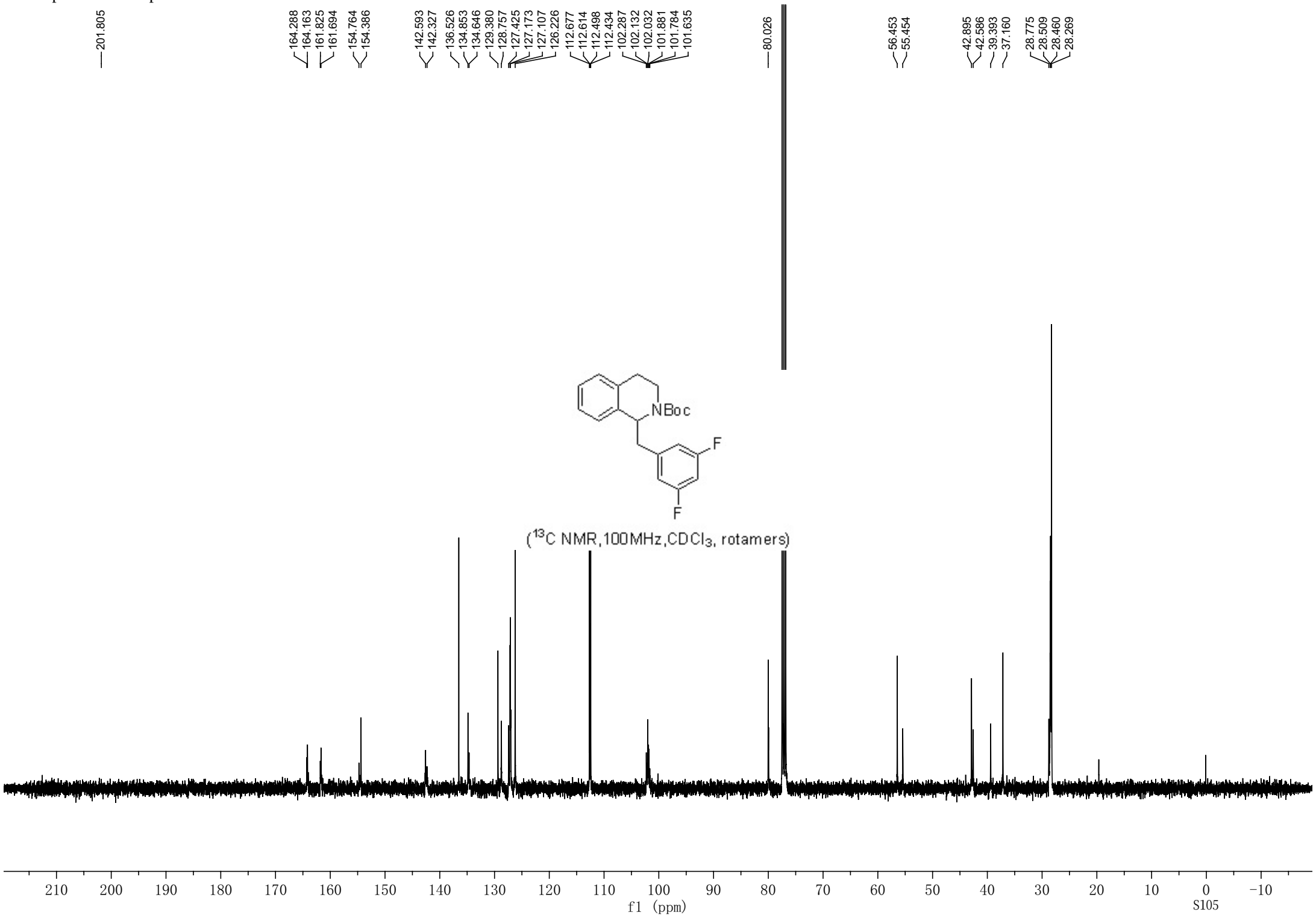


NMR spectra of compound 9k

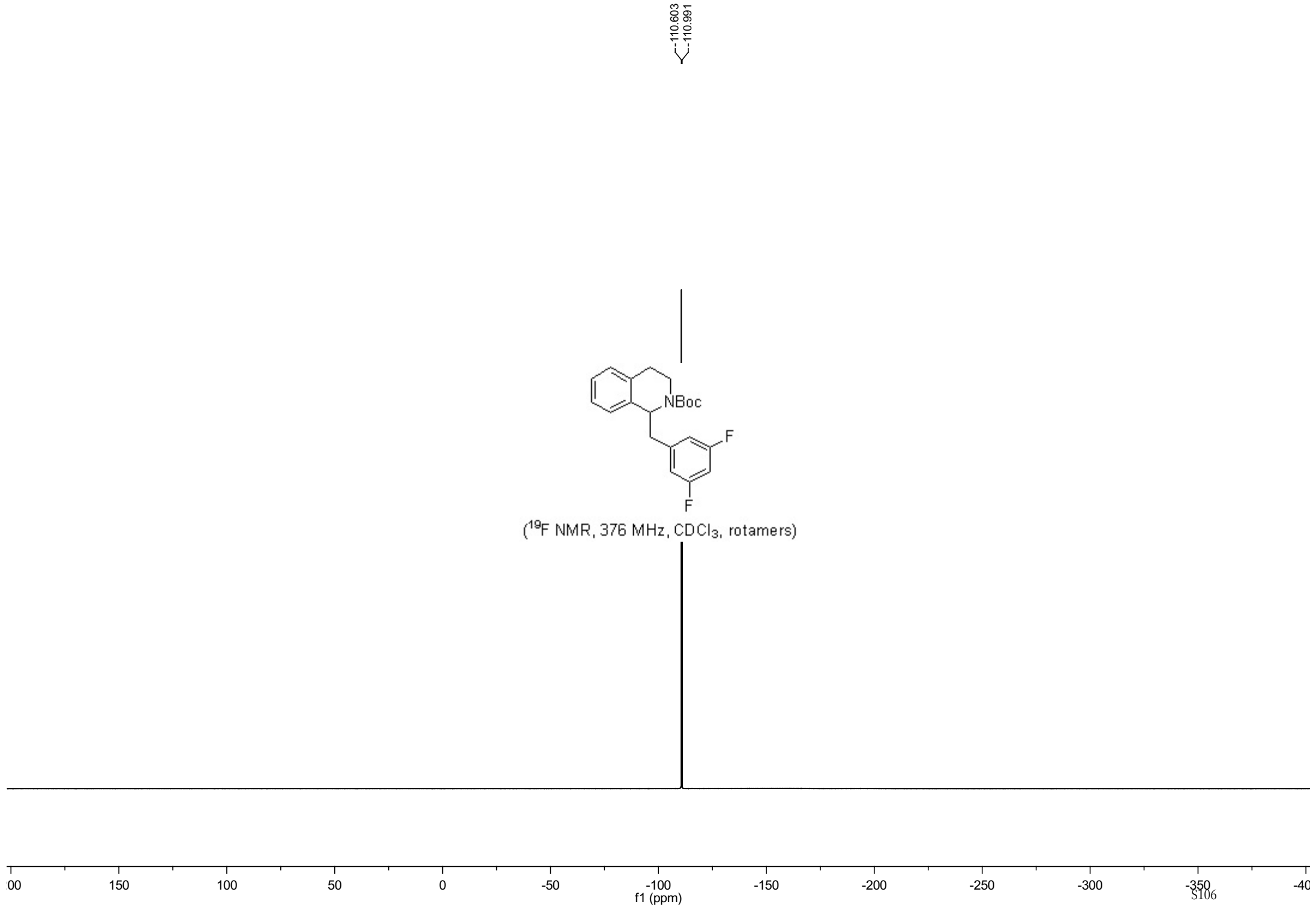
NMR spectra of compound 9l



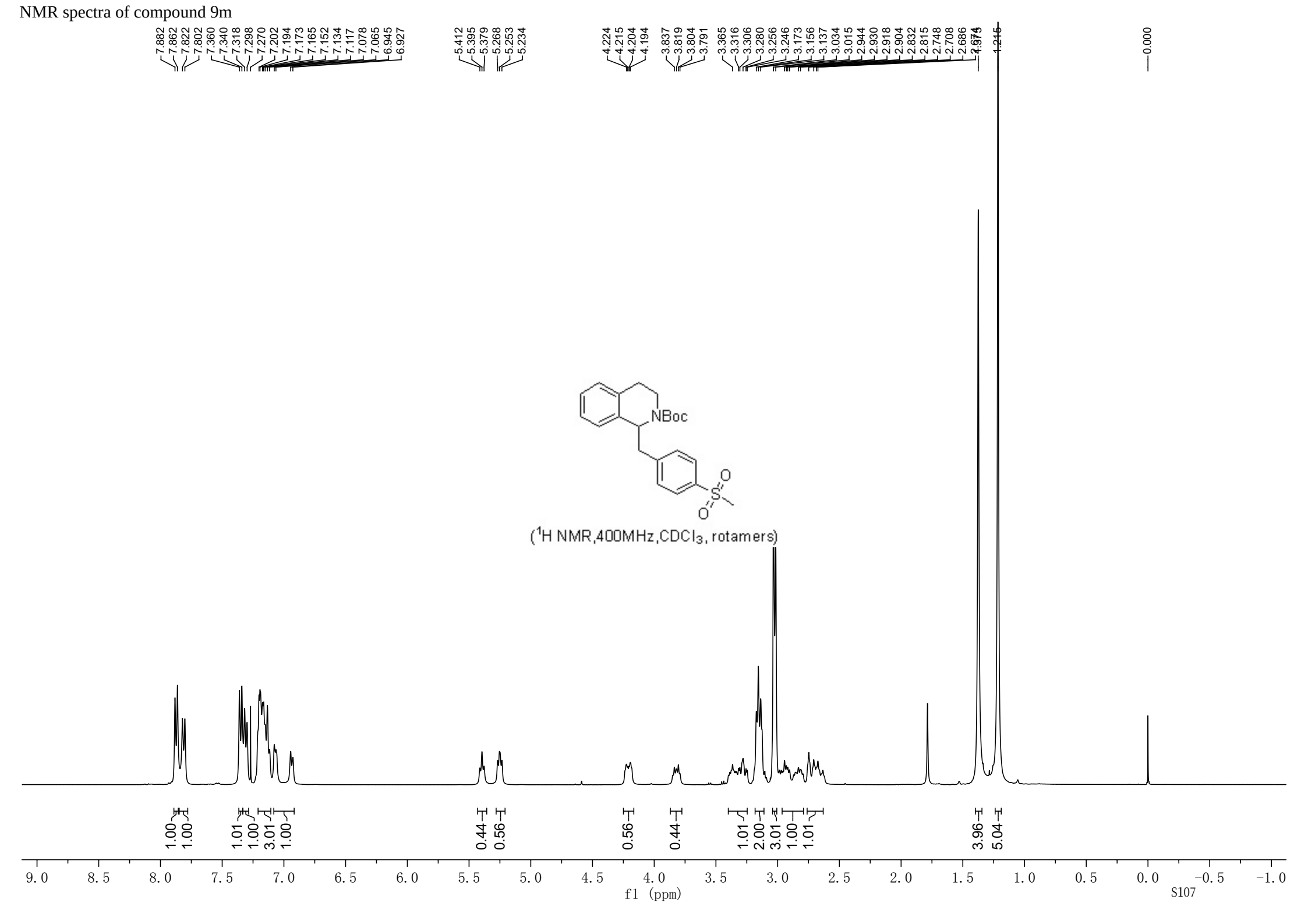
NMR spectra of compound 9l



NMR spectra of compound 9l



NMR spectra of compound 9m



NMR spectra of compound 9m