Supporting Information

Diverse Synthesis of Fused Polyheterocyclic Compounds via [3 + 2] Cycloaddition of in Situ Generated Heteroaromatic *N*-Ylides and Electron-Deficient Olefins

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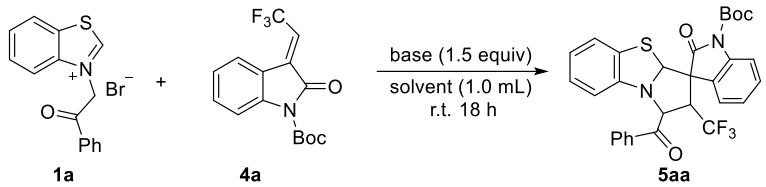
1. Optimization of the [3 + 2] cycloaddition reaction of benzothiazolium salt with other olefinic dipolarophiles

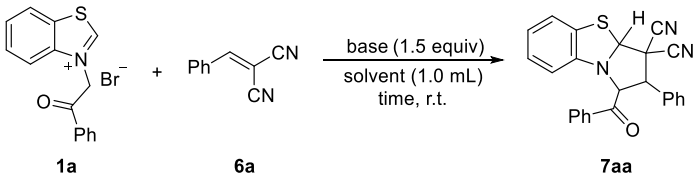
Table S1 Optimization of reaction conditions for the [3 + 2] cycloaddition reaction between benzothiazolium salt and 3-trifluoroethylidene oxindole[a]



entry	base	solvent	yield[b]
1	Cs_2CO_3	DCM	95
2	K_3PO_4	DCM	51
4	DIPEA	DCM	85
5	TEA	DCM	69
6	Cs_2CO_3	Toluene	84
7	Cs_2CO_3	DCE	88
8	Cs_2CO_3	MeCN	71
9	Cs_2CO_3	THF	86

[a]The reaction was carried out with **1a** (0.15 mmol), **4a** (0.10 mmol), base (0.15 mmol) in solvent (1.0 mL) at room temperature for indicated time. [b]Isolated yield.

Table S2 Optimization of reaction conditions for the [3 + 2] cycloaddition reaction of benzothiazolium salt with benzylidenemalononitrile [a]



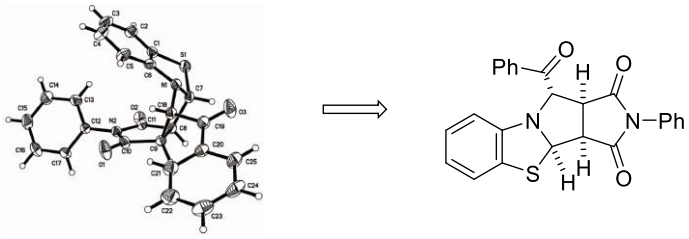
entry	base	solvent	time (h)	yield (%)[b]
1	Cs_2CO_3	THF	3	45
2	Cs_2CO_3	MeCN	2	43
3	Cs_2CO_3	toluene	24	12
4	Cs_2CO_3	EtOH	24	n.d.
5	Cs_2CO_3	$CHCl_3$	3	9
6	Cs_2CO_3	2-MeTHF	24	25
7	Cs_2CO_3	1,4-dioxane	3	46
8	Cs_2CO_3	DME	3	51
9	Cs_2CO_3	MTBE	3	32
10	K_3PO_4	DME	3	44
11	K_2CO_3	DME	3	94
12	Na_2CO_3	DME	3	93
13	Li_2CO_3	DME	3	n.d.

14	$NaHCO_3$	DME	3	72
15	NaOH	DME	3	25
16	DIPEA	DME	3	71
17	TEA	DME	3	95
18[c]	TEA	DME	3	72

[a] The reaction was carried out with **1a** (0.15 mmol), **6a** (0.10 mmol), base (0.15 mmol) in solvent (1.0 mL) at room temperature for indicated time. [b] Isolated yield. [c] 2.0 mL 1,2-dimethoxyethane (DME) was used.

2. X-ray crystal structure of 3aa

Single crystals of compound **3aa** were prepared through dissolving the sample in mixture solvent of EtOH at room temperature and crystalizing by slow evaporation of solvent. A suitable crystal was selected for structure determination on an 'Oxford Gemini E' diffractometer. The crystal was kept at 293 K during data collection. Using Olex2[1], the structure was solved with the ShelXT[2] structure solution program using Intrinsic Phasing and refined with the ShelXL[3] refinement package using Least Squares minimisation.



3aa (CCDC 2193494)

ORTEP of **3aa** (at the 50% probability level)

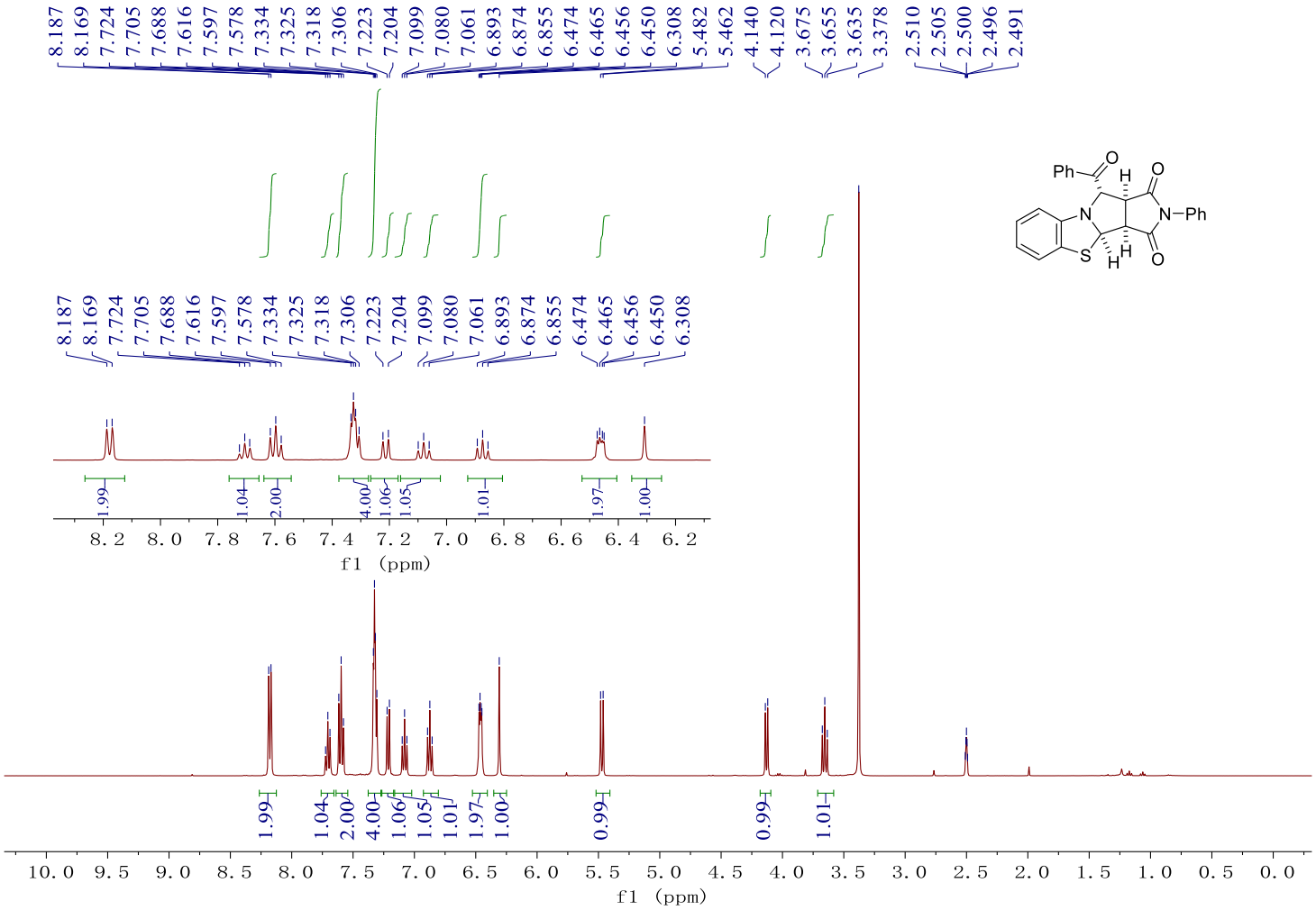
Identification code	**3aa**
Empirical formula	$C_{25}H_{18}N_2O_3S$
Formula weight	426.47
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.4876(6)
b/Å	8.2188(4)
c/Å	23.8232(9)
α/°	90
β/°	101.322(4)
γ/°	90
Volume/Å^3	2013.49(18)
Z	4
ρ_{calc}g/cm^3	1.407
μ/mm^{-1}	1.686

F(000)	888.0
Crystal size/mm^3	0.12 × 0.1 × 0.09
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.57 to 134.16
Index ranges	$-12 \leq h \leq 10$, $-9 \leq k \leq 6$, $-26 \leq l \leq 28$
Reflections collected	7242
Independent reflections	3593 [R_{int} = 0.0337, R_{sigma} = 0.0476]
Data/restraints/parameters	3593/0/280
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0477, wR_2 = 0.1282
Final R indexes [all data]	R_1 = 0.0600, wR_2 = 0.1426
Largest diff. peak/hole / e Å^{-3}	0.23/-0.28

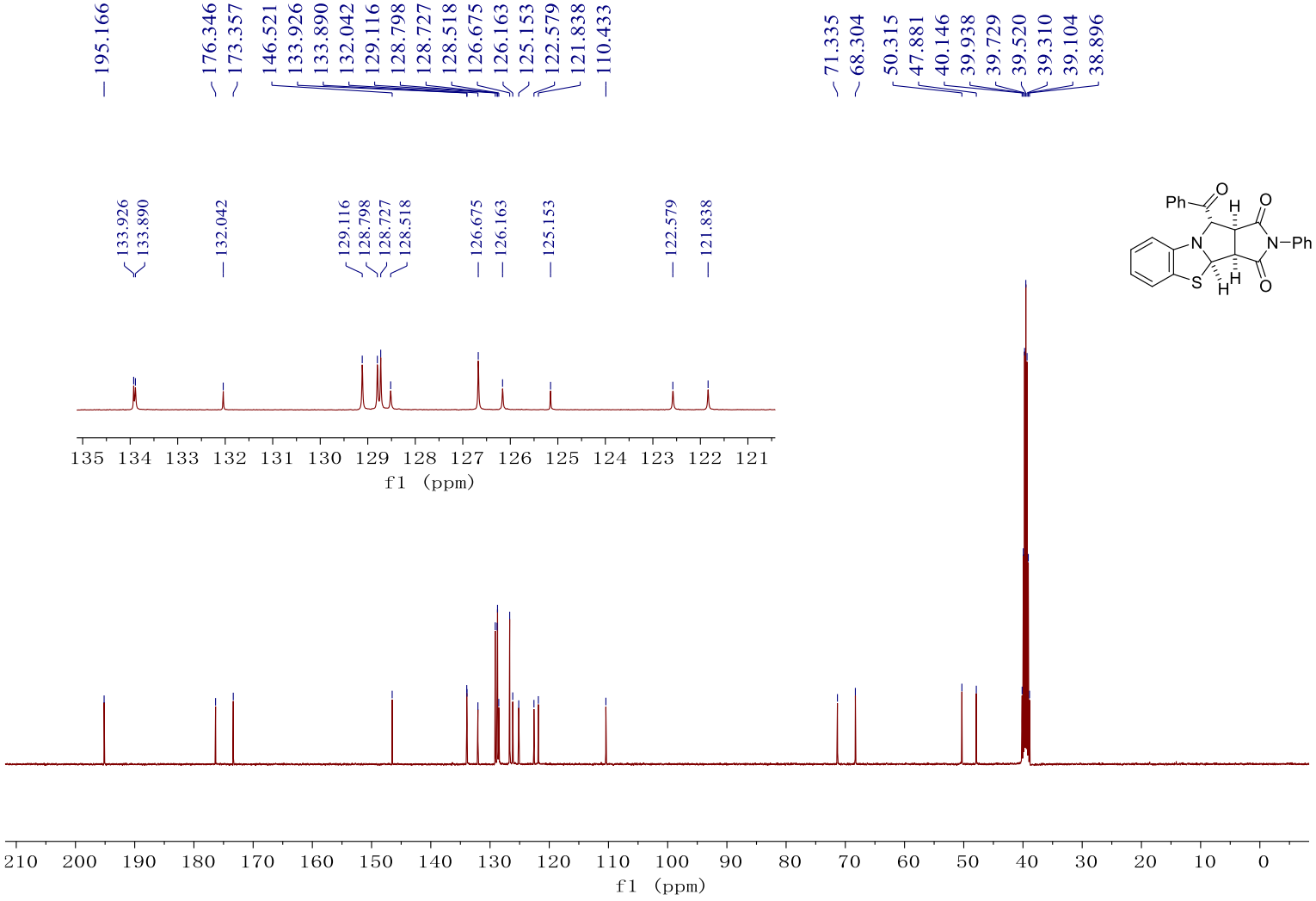
1. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J, Howard, J. A. K; Puschmann, H. *J. Appl. Cryst.*, **2009**, *42*, 339-341.
2. Sheldrick, G. M. *Acta Cryst*. **2015**, A71, 3-8.
3. Sheldrick, G. M. *Acta Cryst.* **2015**, C71, 3-8.

3. ^{1}H, ^{13}C NMR for compounds 3, 5, and 7

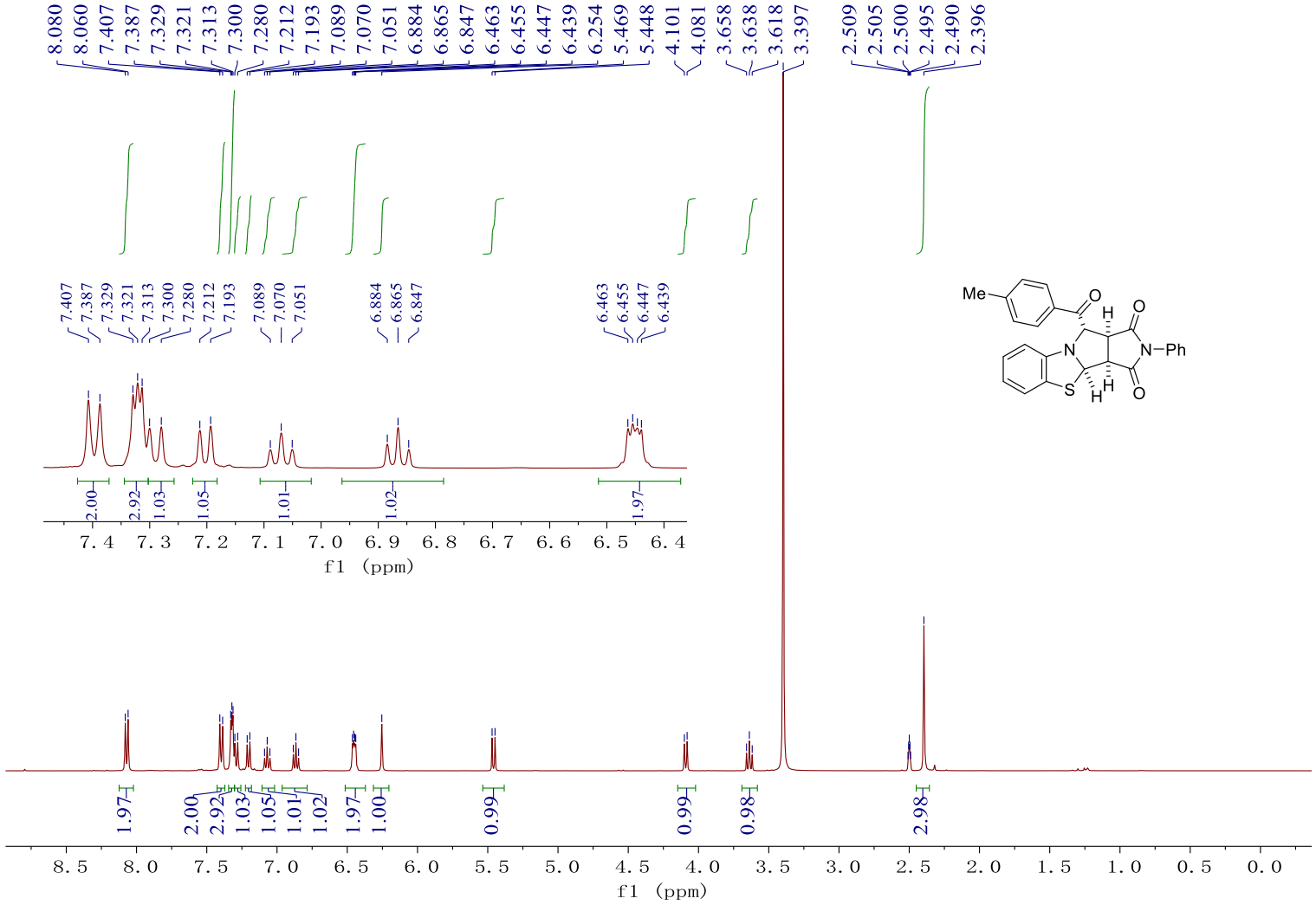
^{1}H NMR (400 MHz, $CDCl_3$) of **3aa**



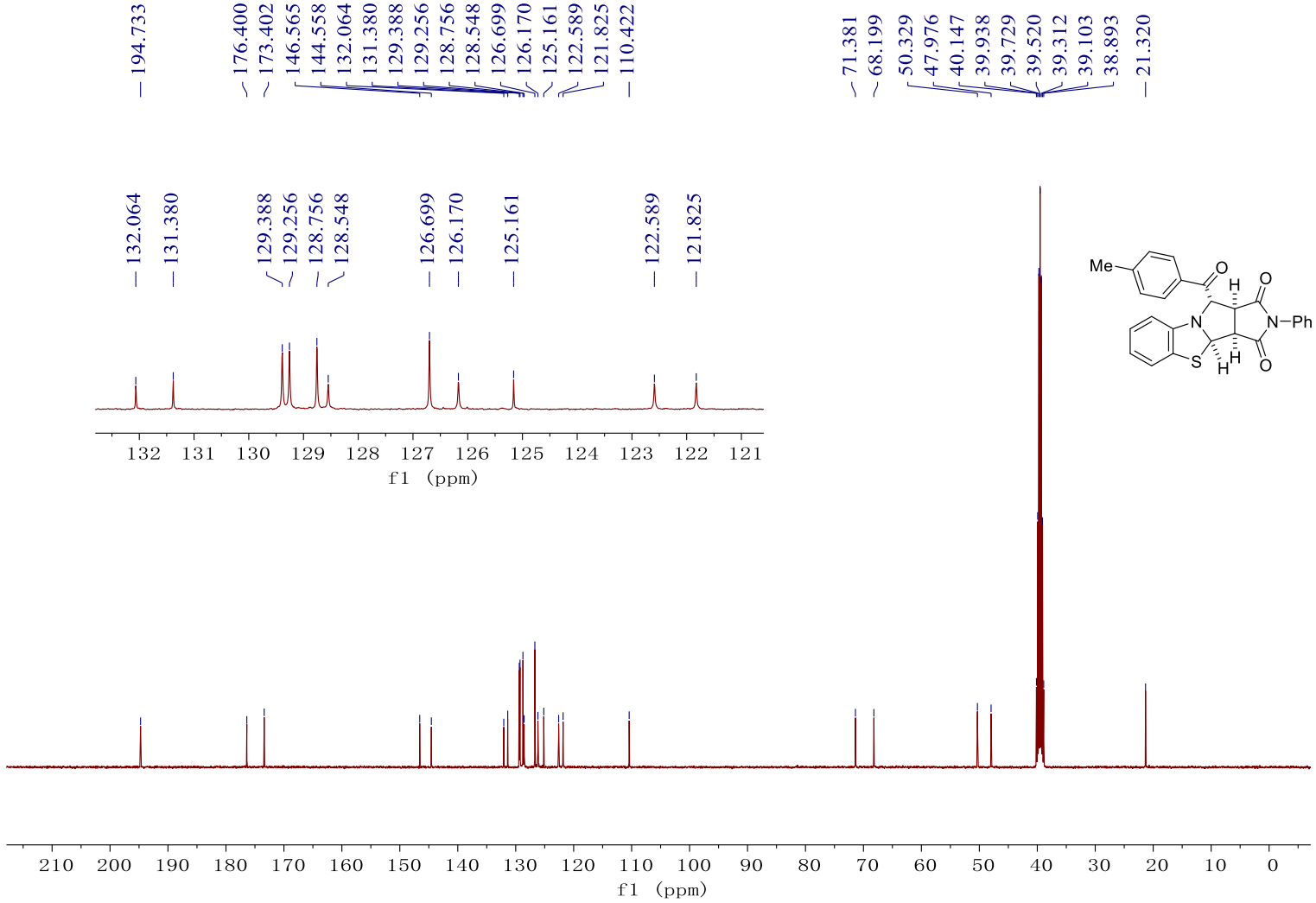
^{13}C NMR (101 MHz, $CDCl_3$) of **3aa**



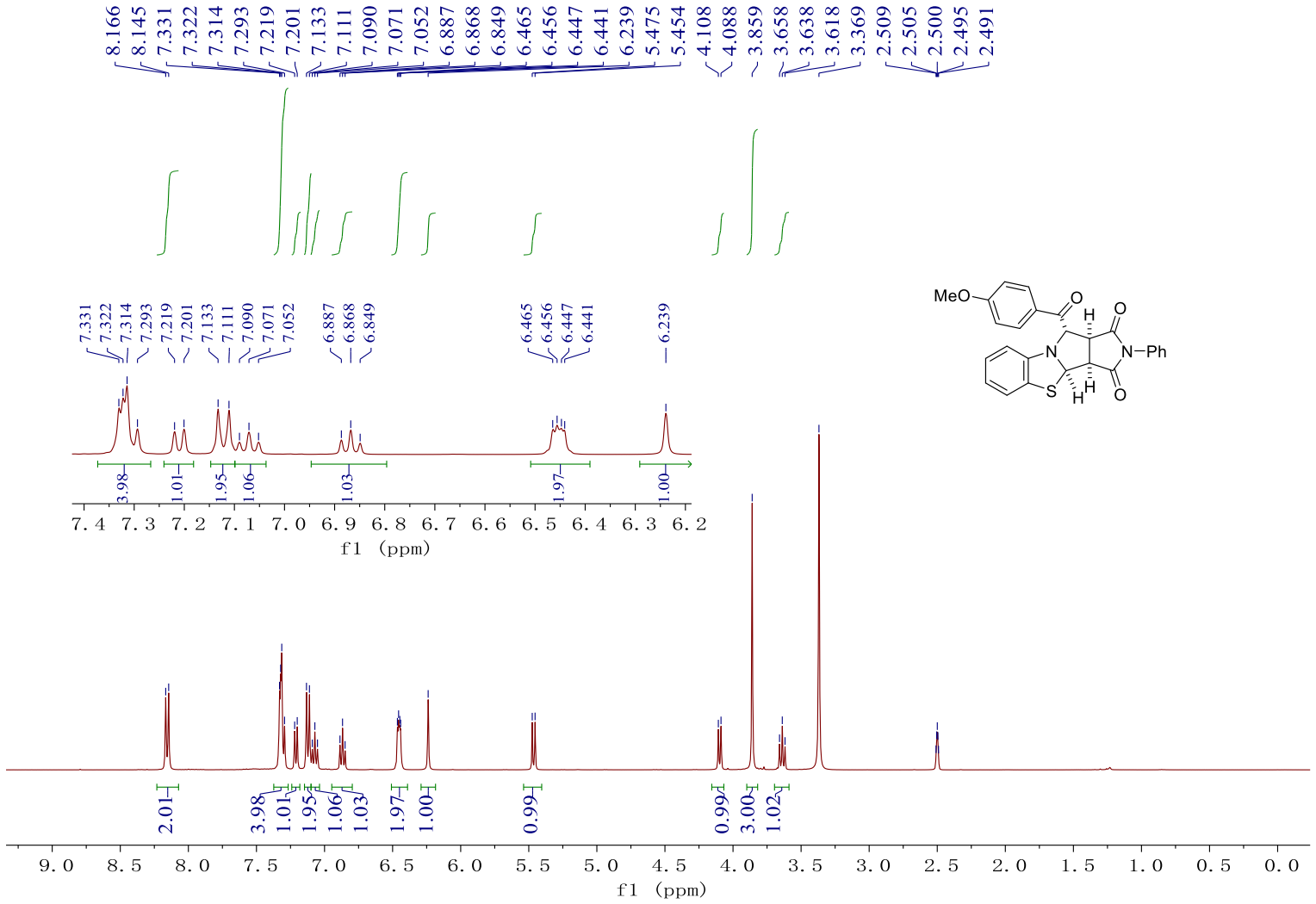
^{1}H NMR (400 MHz, $CDCl_3$) of **3ba**



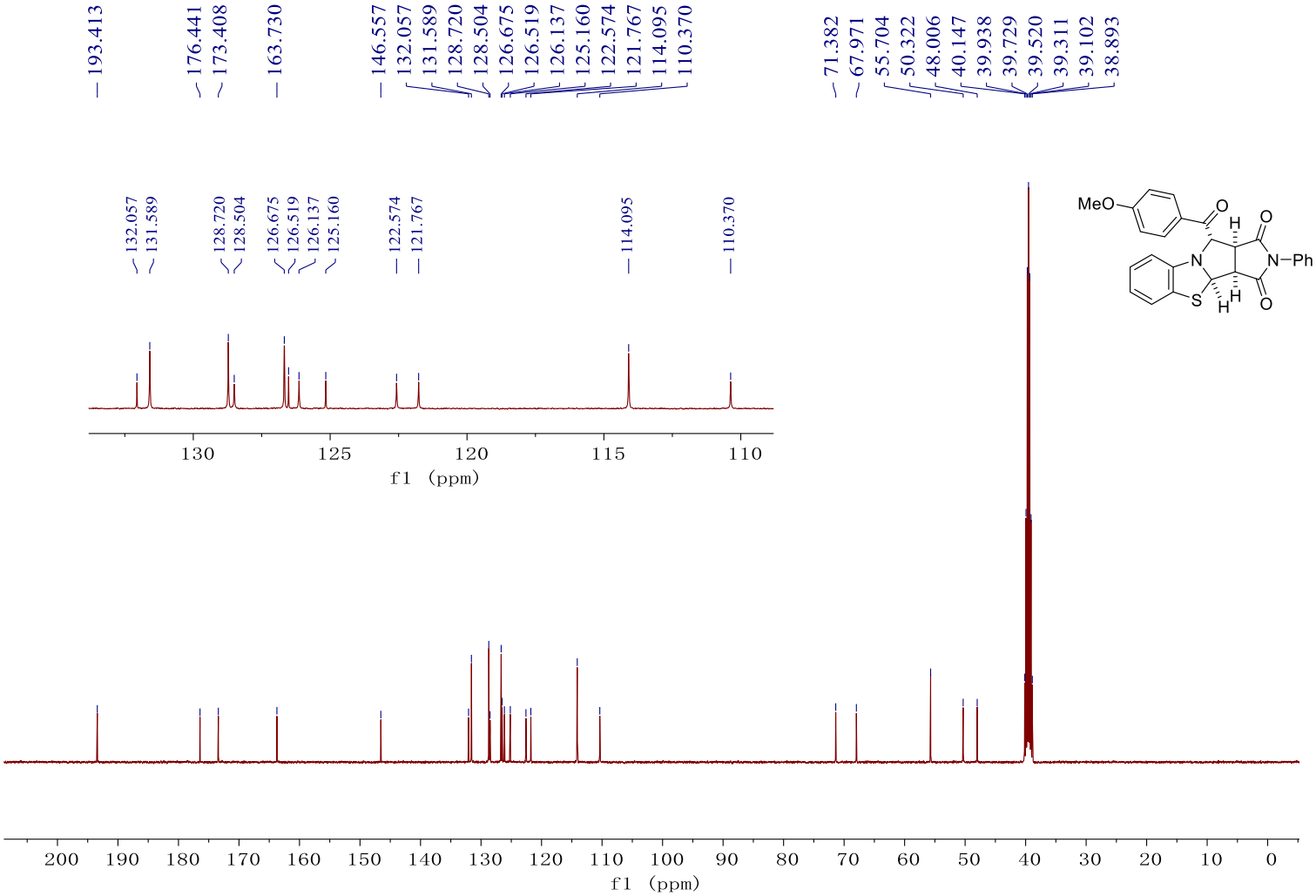
^{13}C NMR (101 MHz, $CDCl_3$) of **3ba**



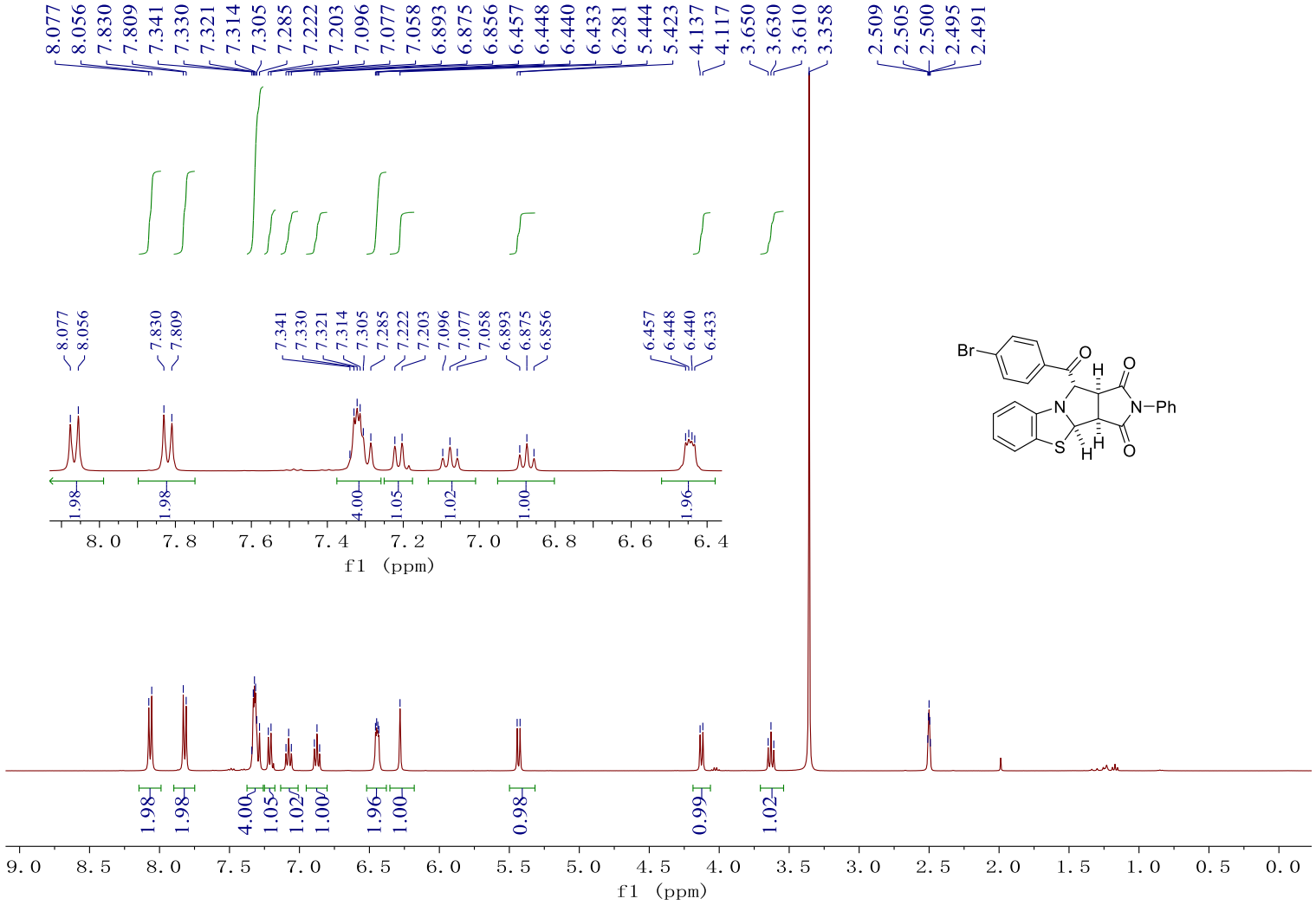
^{1}H NMR (400 MHz, $CDCl_3$) of **3ca**



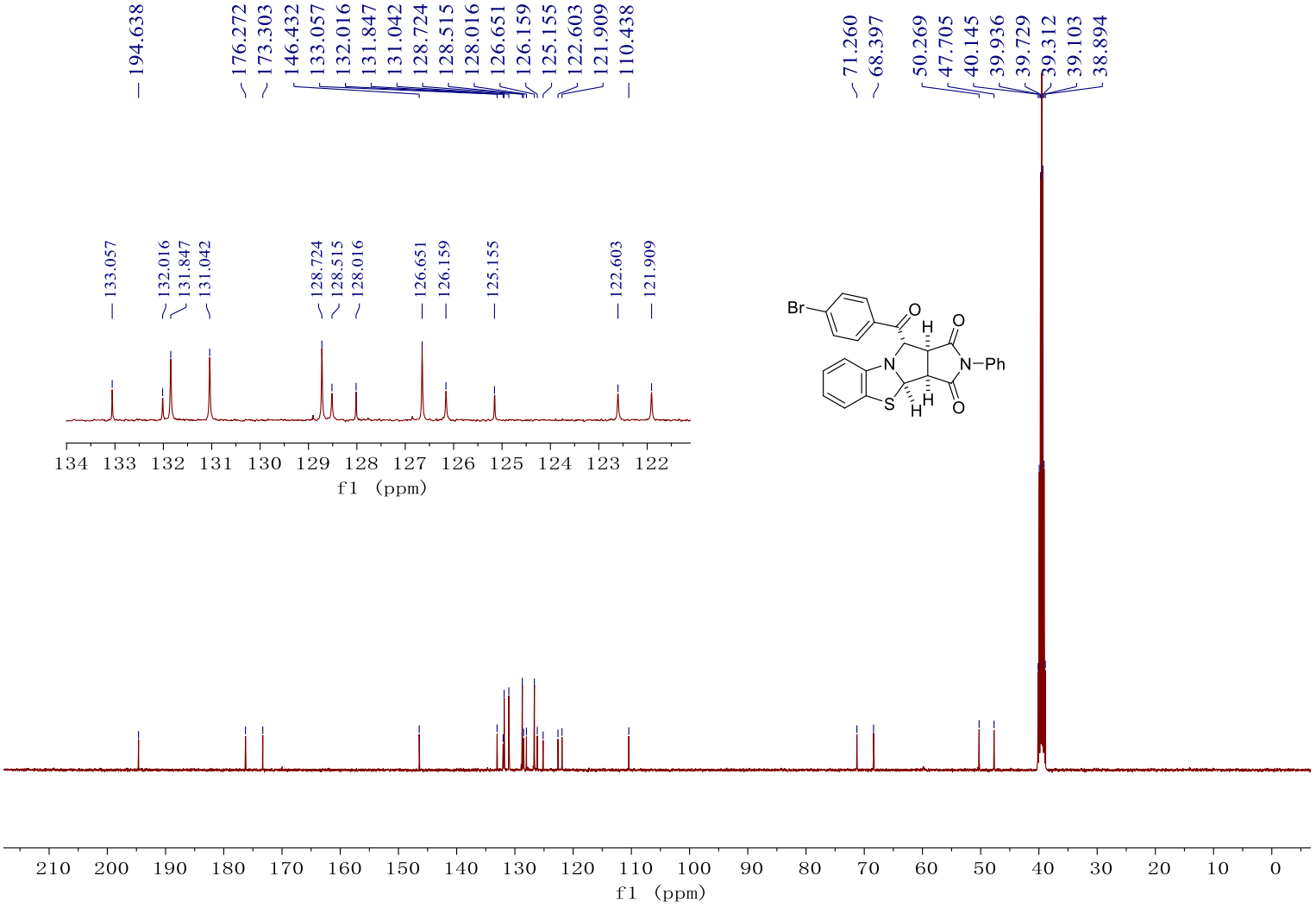
^{13}C NMR (101 MHz, $CDCl_3$) of **3ca**



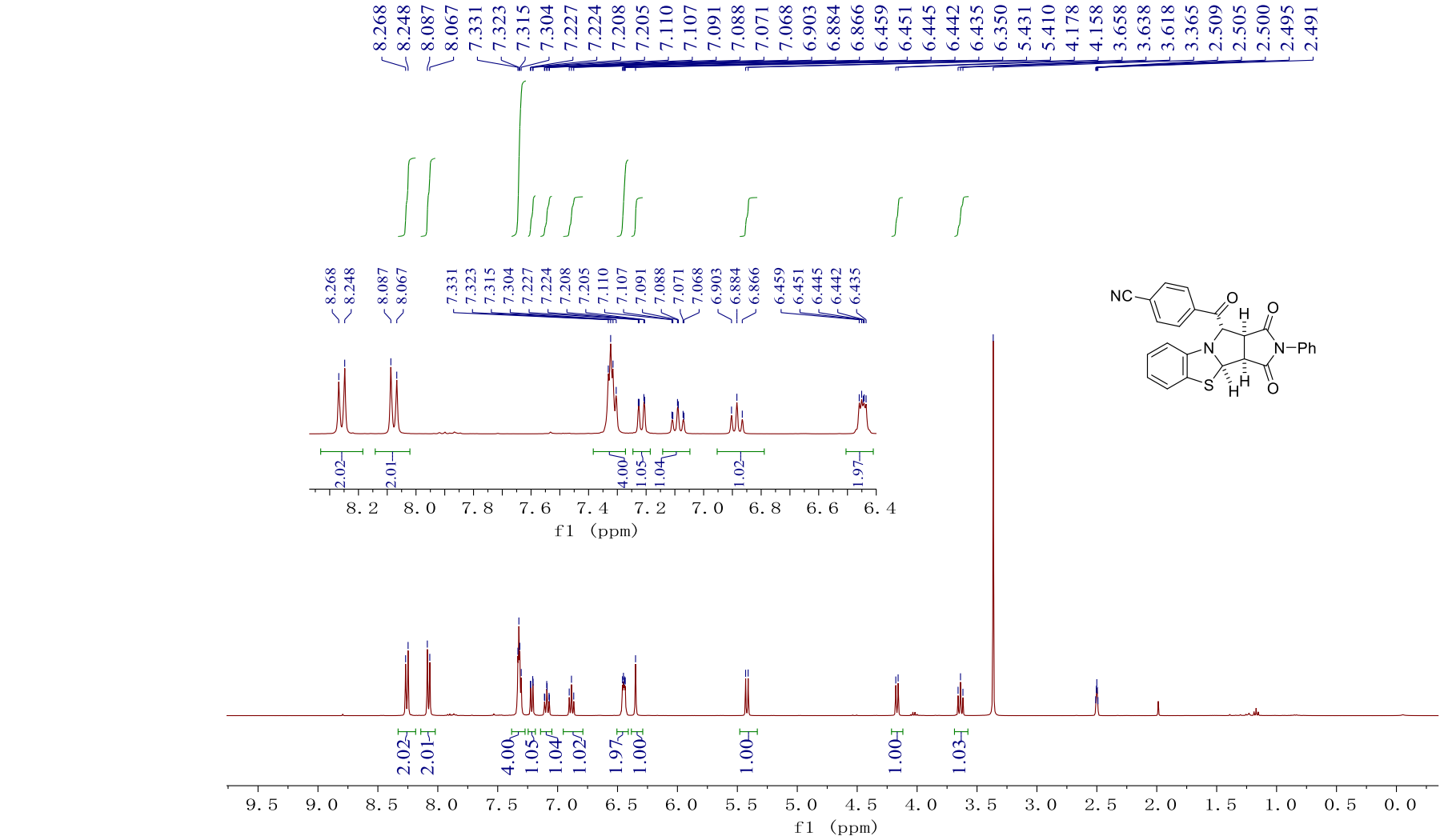
^{1}H NMR (400 MHz, $CDCl_3$) of **3da**



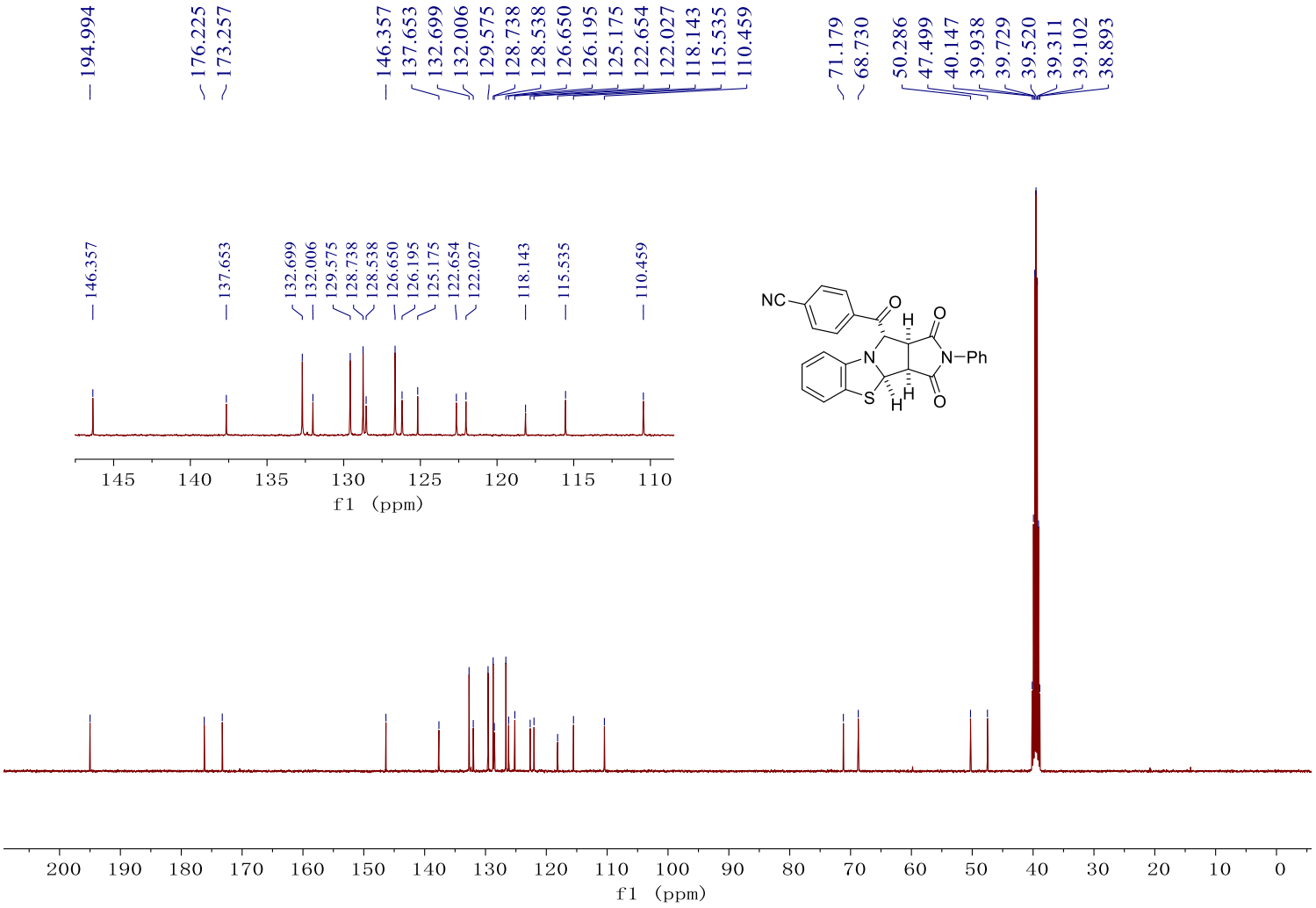
^{13}C NMR (101 MHz, $CDCl_3$) of **3da**



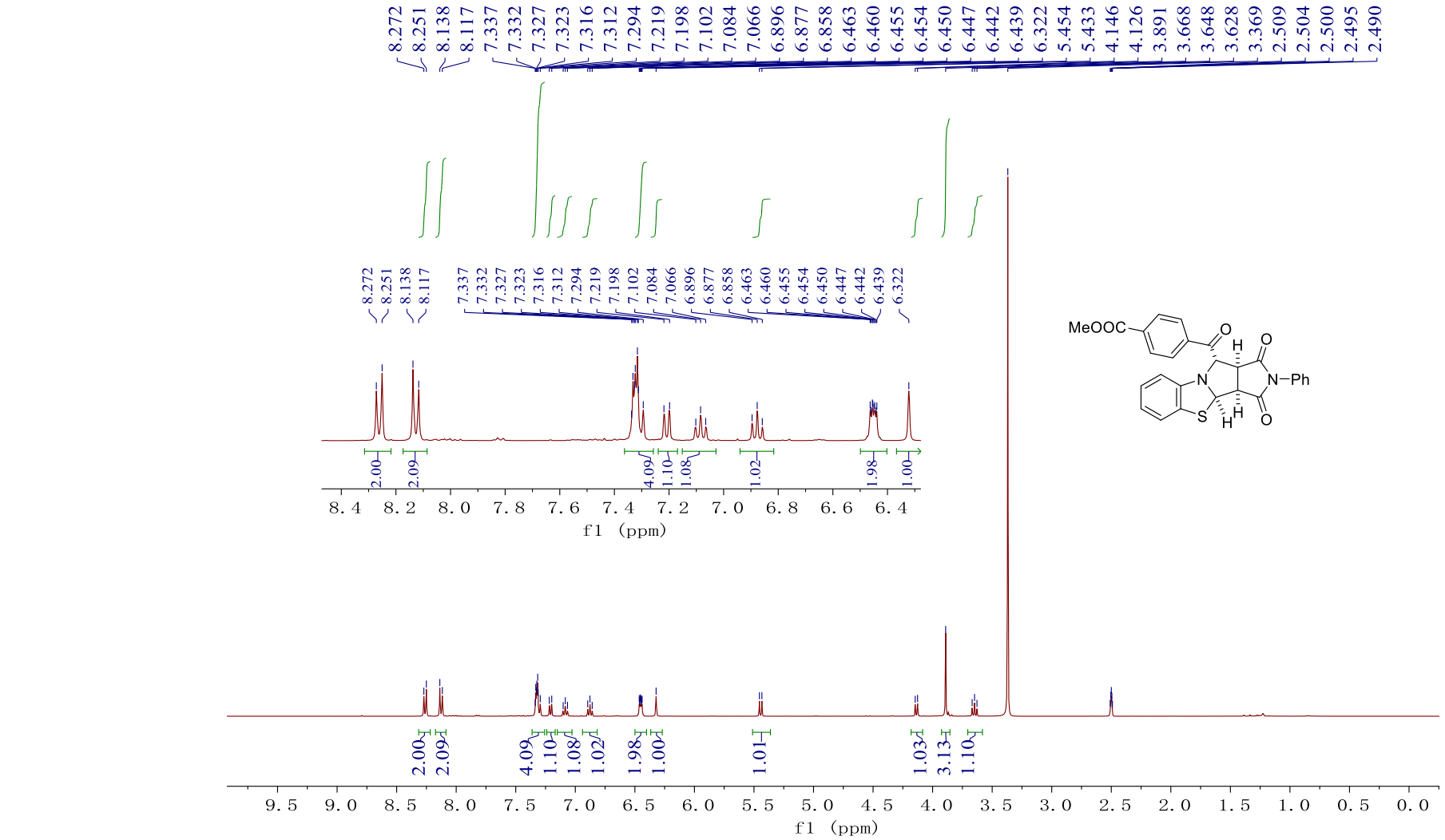
^{1}H NMR (400 MHz, $CDCl_3$) of **3ea**



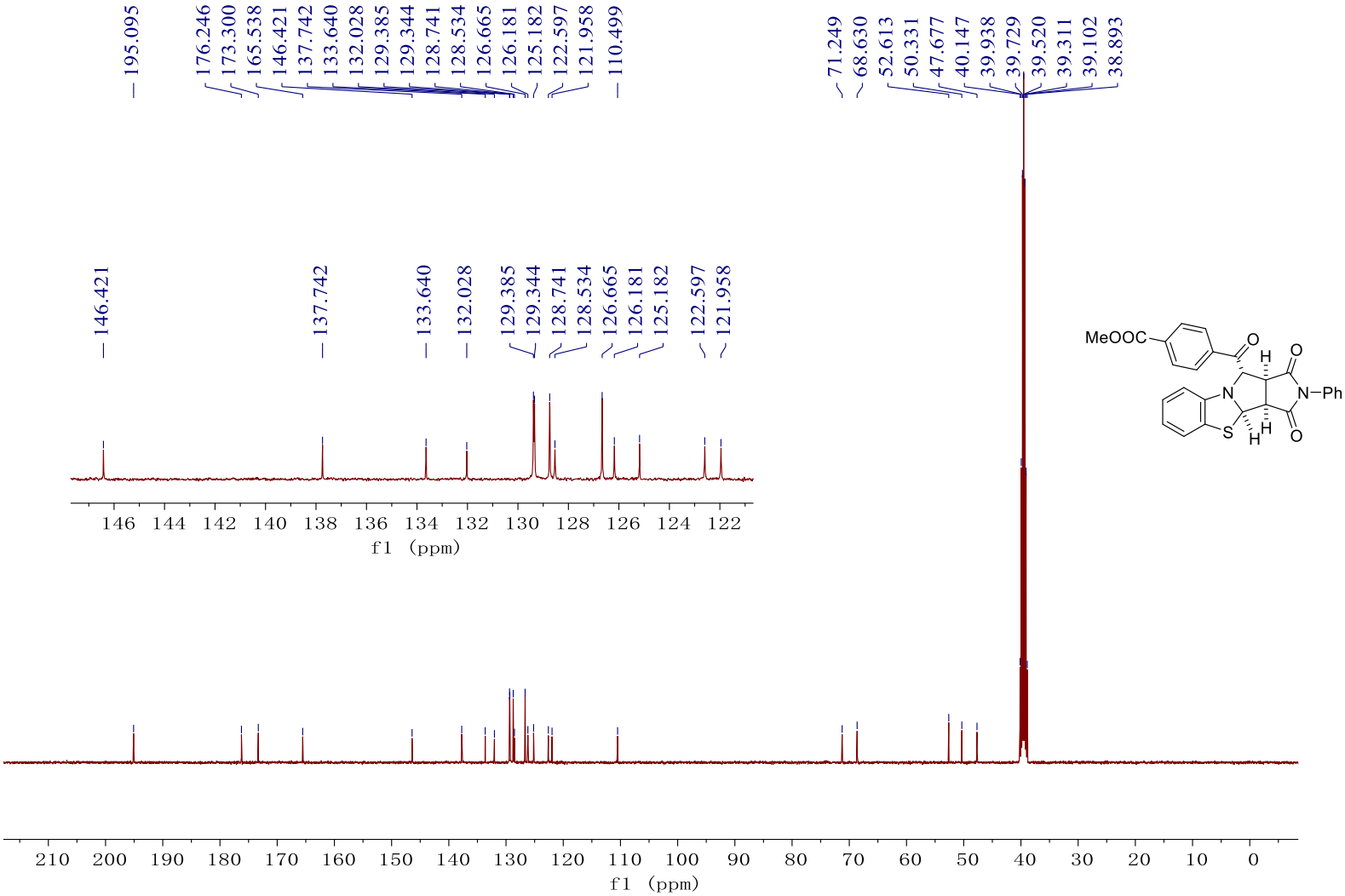
^{13}C NMR (101 MHz, $CDCl_3$) of **3ea**



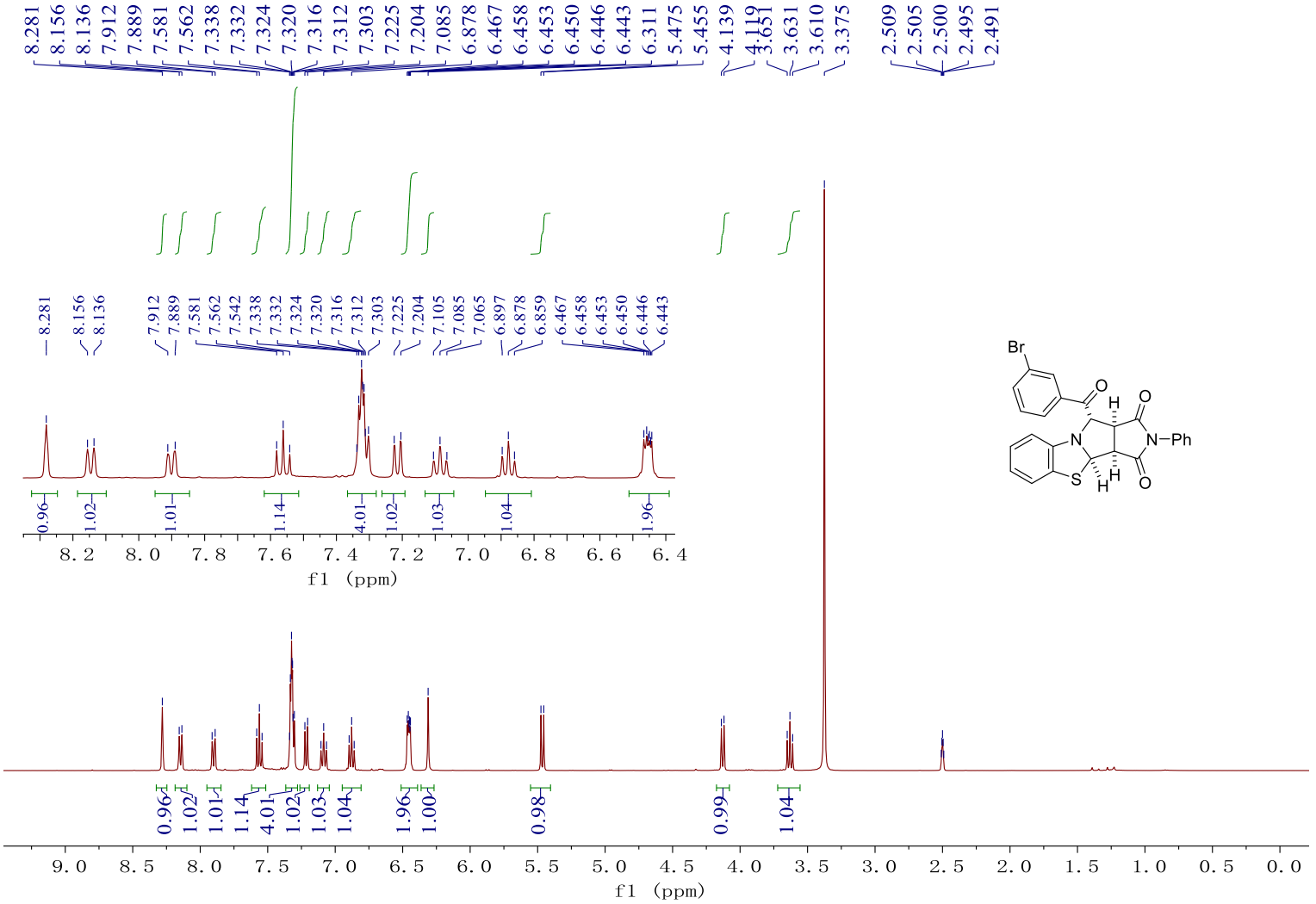
^{1}H NMR (400 MHz, $CDCl_3$) of **3fa**



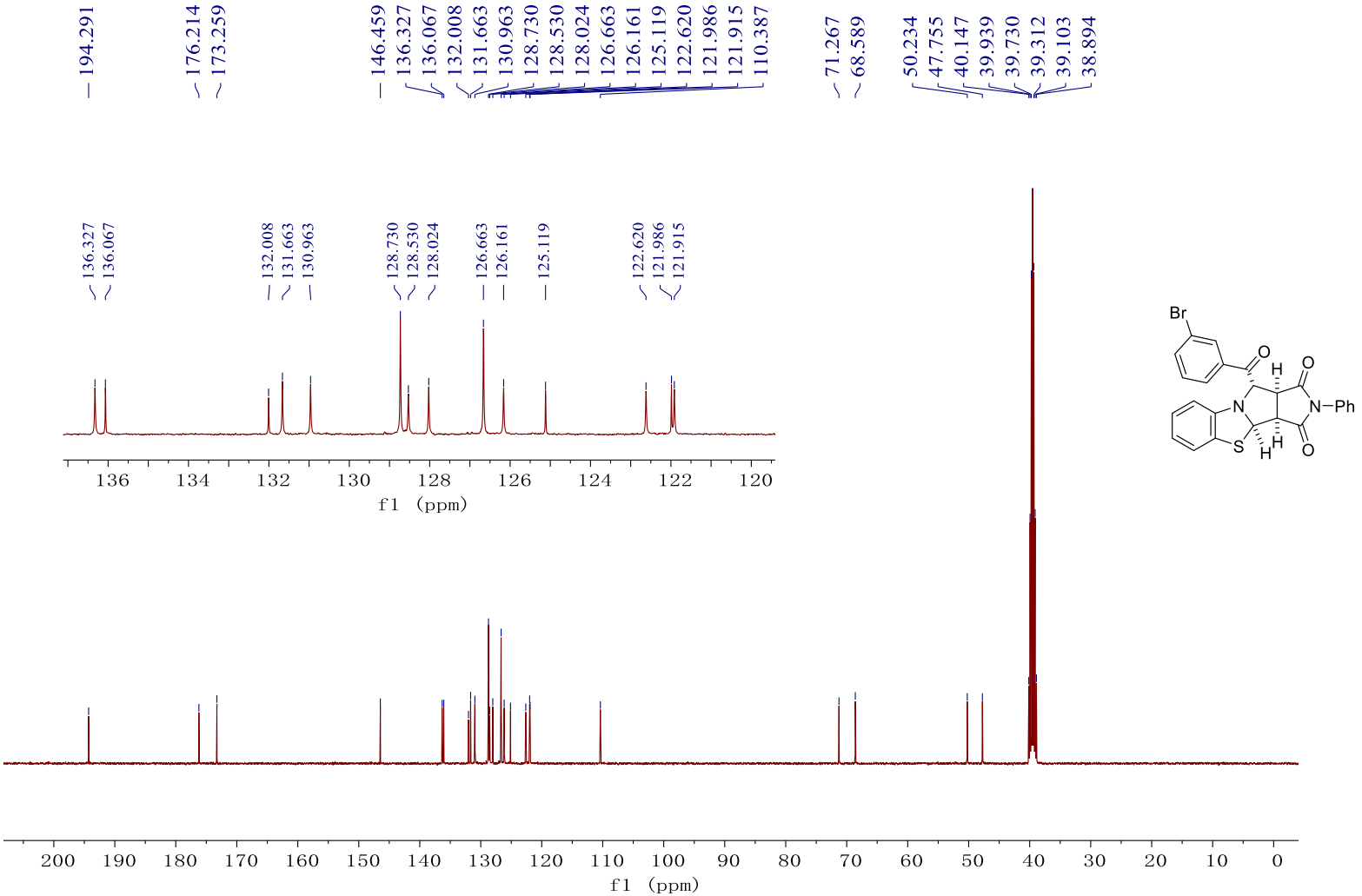
^{13}C NMR (101 MHz, $CDCl_3$) of **3fa**



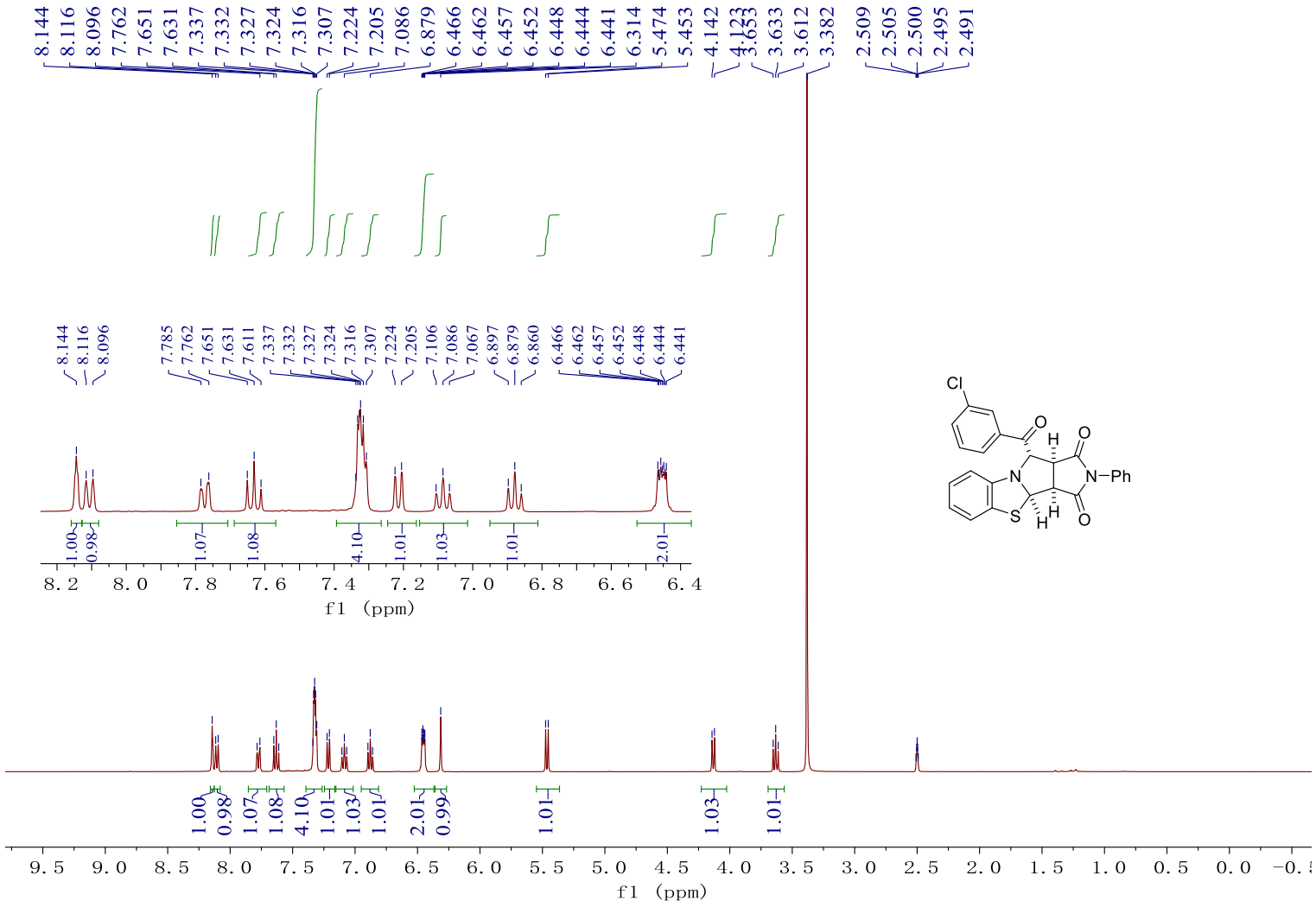
^{1}H NMR (400 MHz, $CDCl_3$) of **3ga**



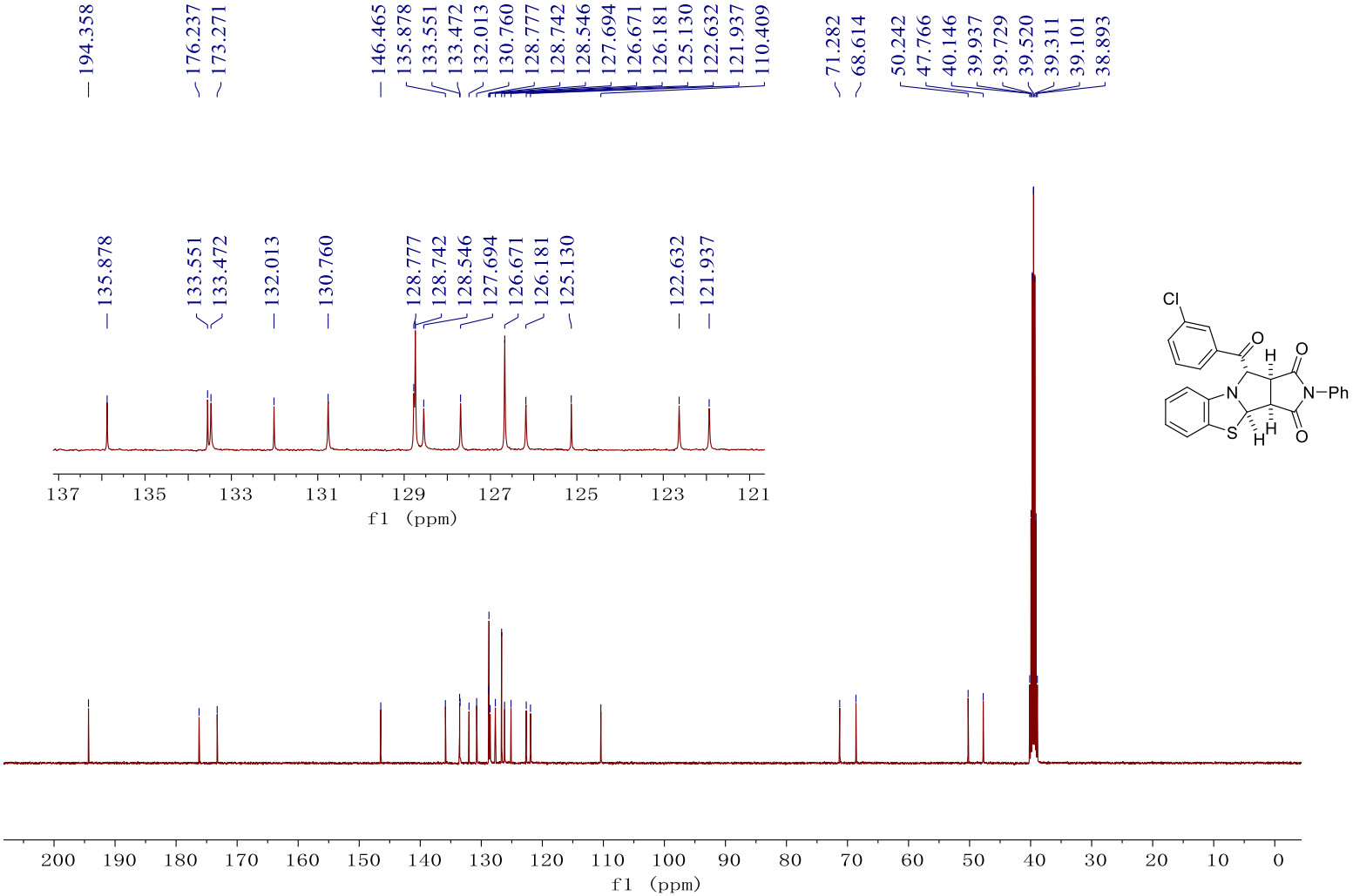
^{13}C NMR (101 MHz, $CDCl_3$) of **3ga**



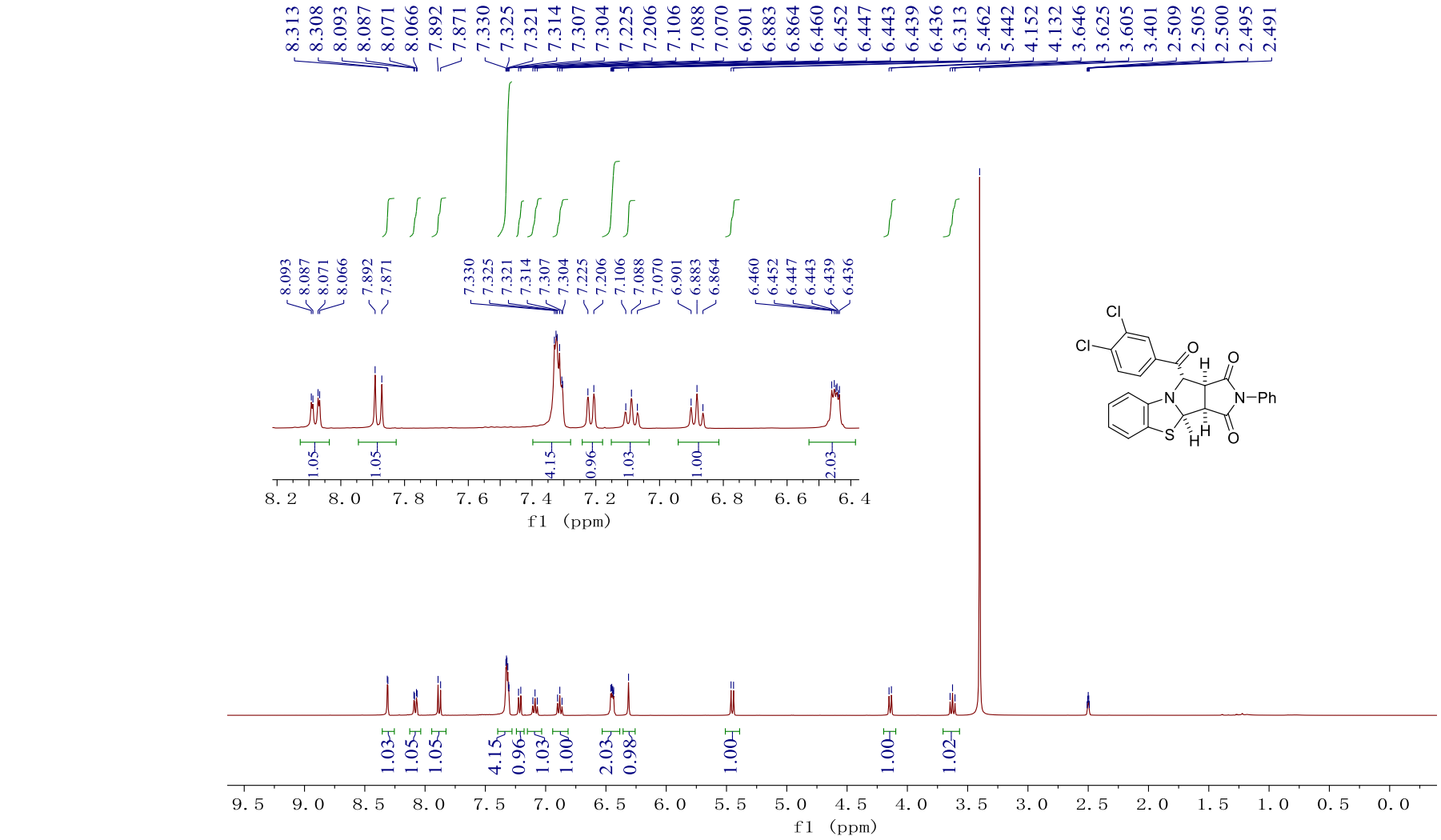
^{1}H NMR (400 MHz, $CDCl_3$) of **3ha**



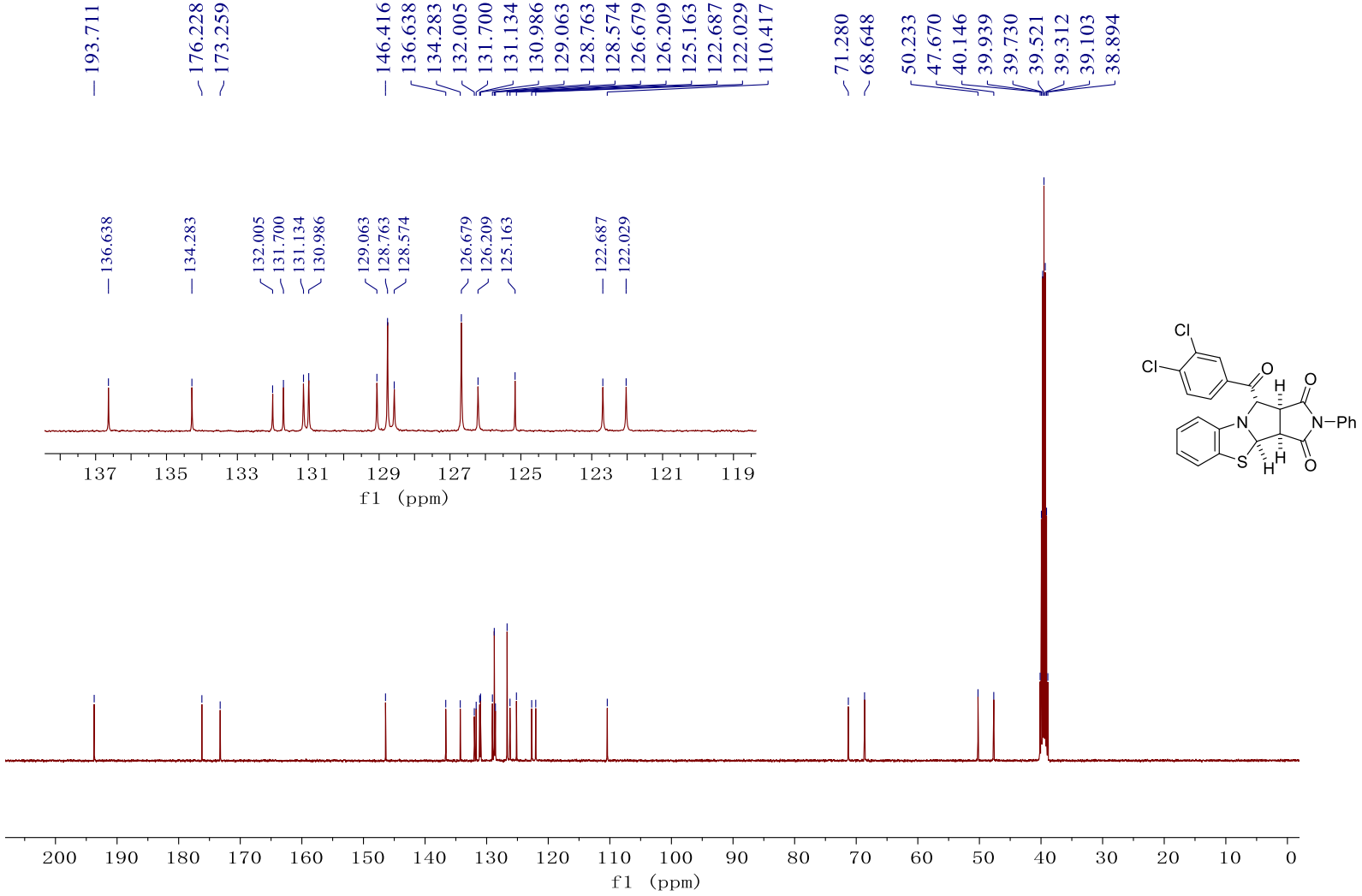
^{13}C NMR (101 MHz, $CDCl_3$) of **3ha**



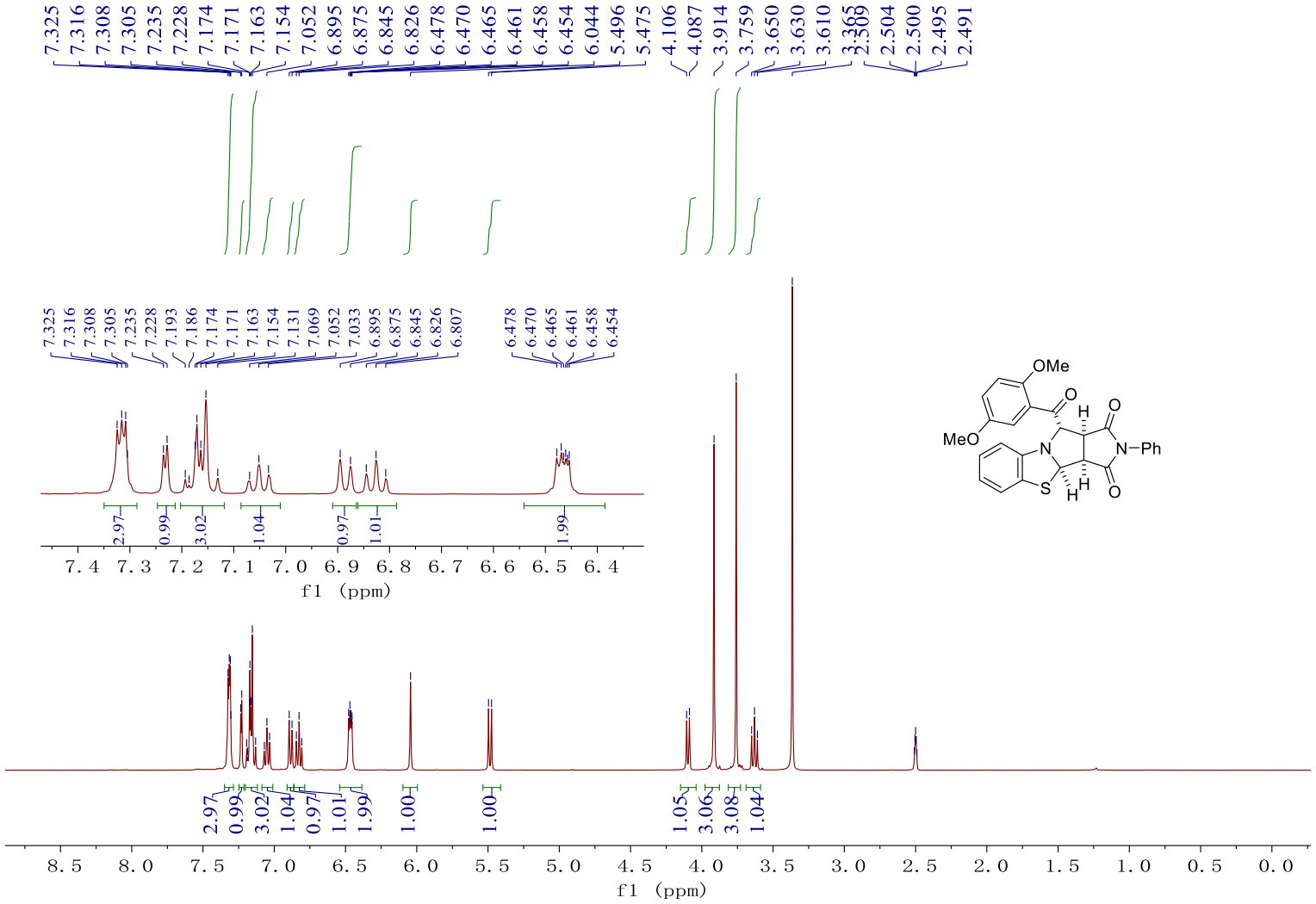
^{1}H NMR (400 MHz, $CDCl_3$) of **3ia**



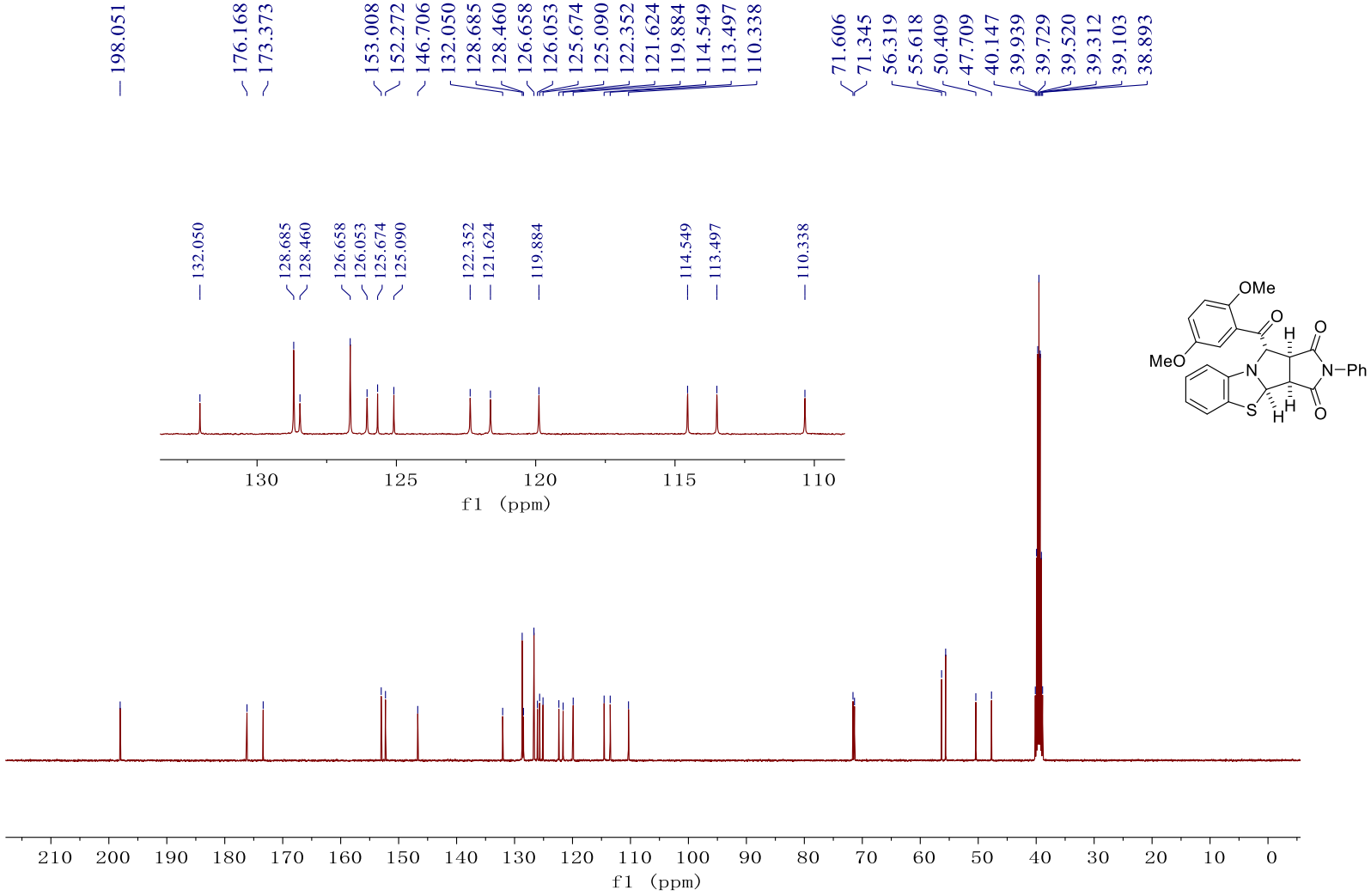
^{13}C NMR (101 MHz, $CDCl_3$) of **3ia**



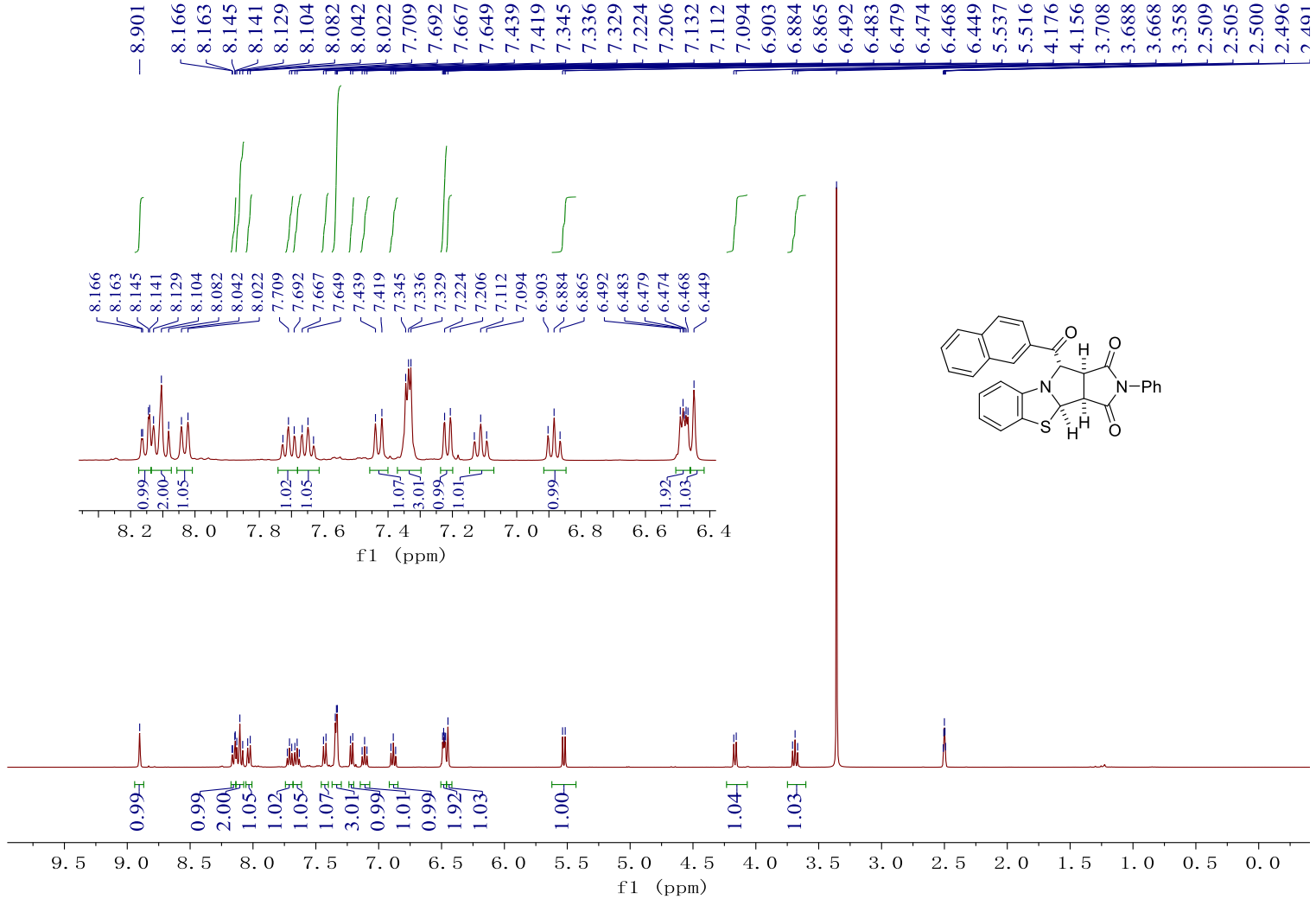
^{1}H NMR (400 MHz, $CDCl_3$) of **3ja**



^{13}C NMR (101 MHz, $CDCl_3$) of **3ja**



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



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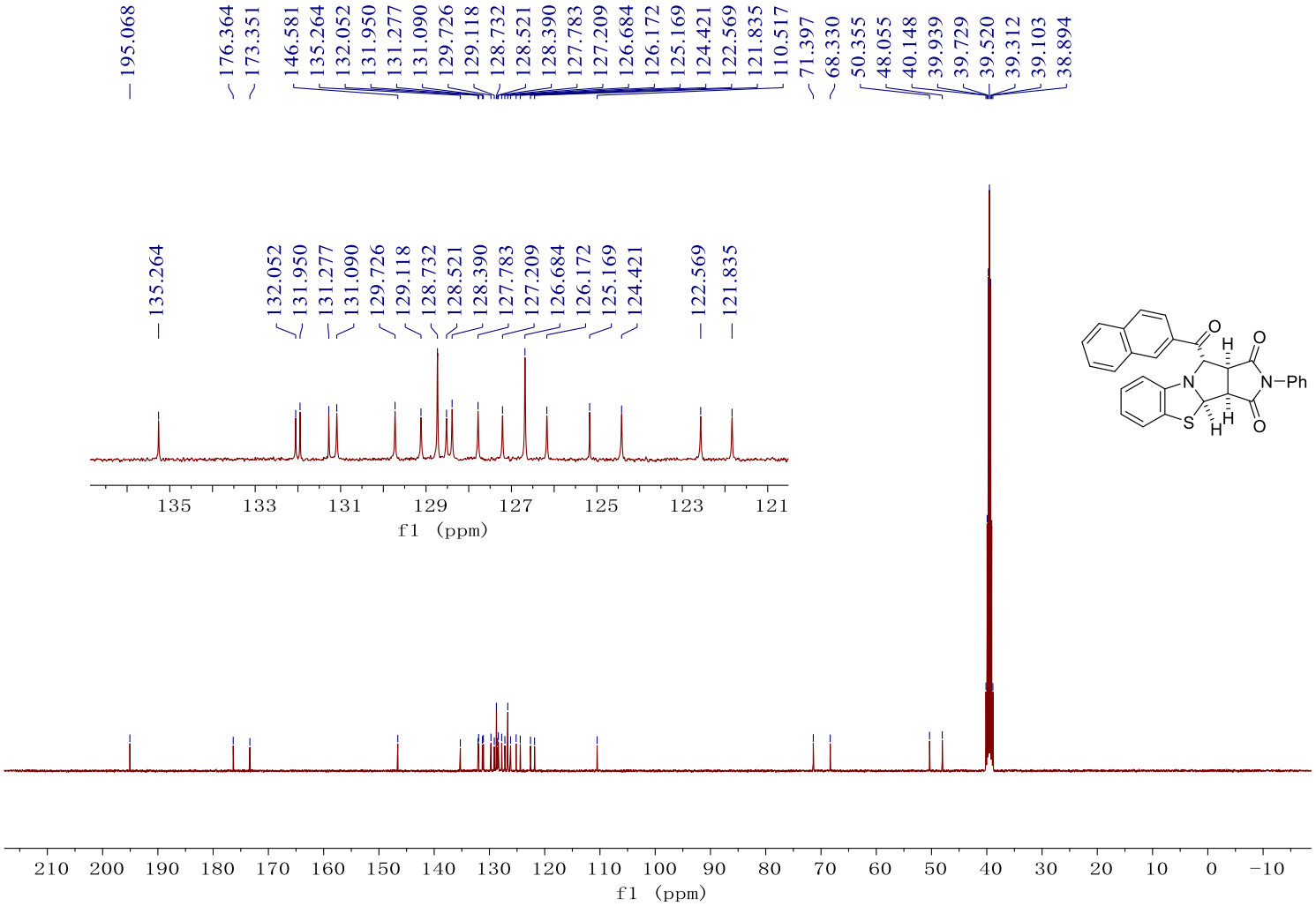
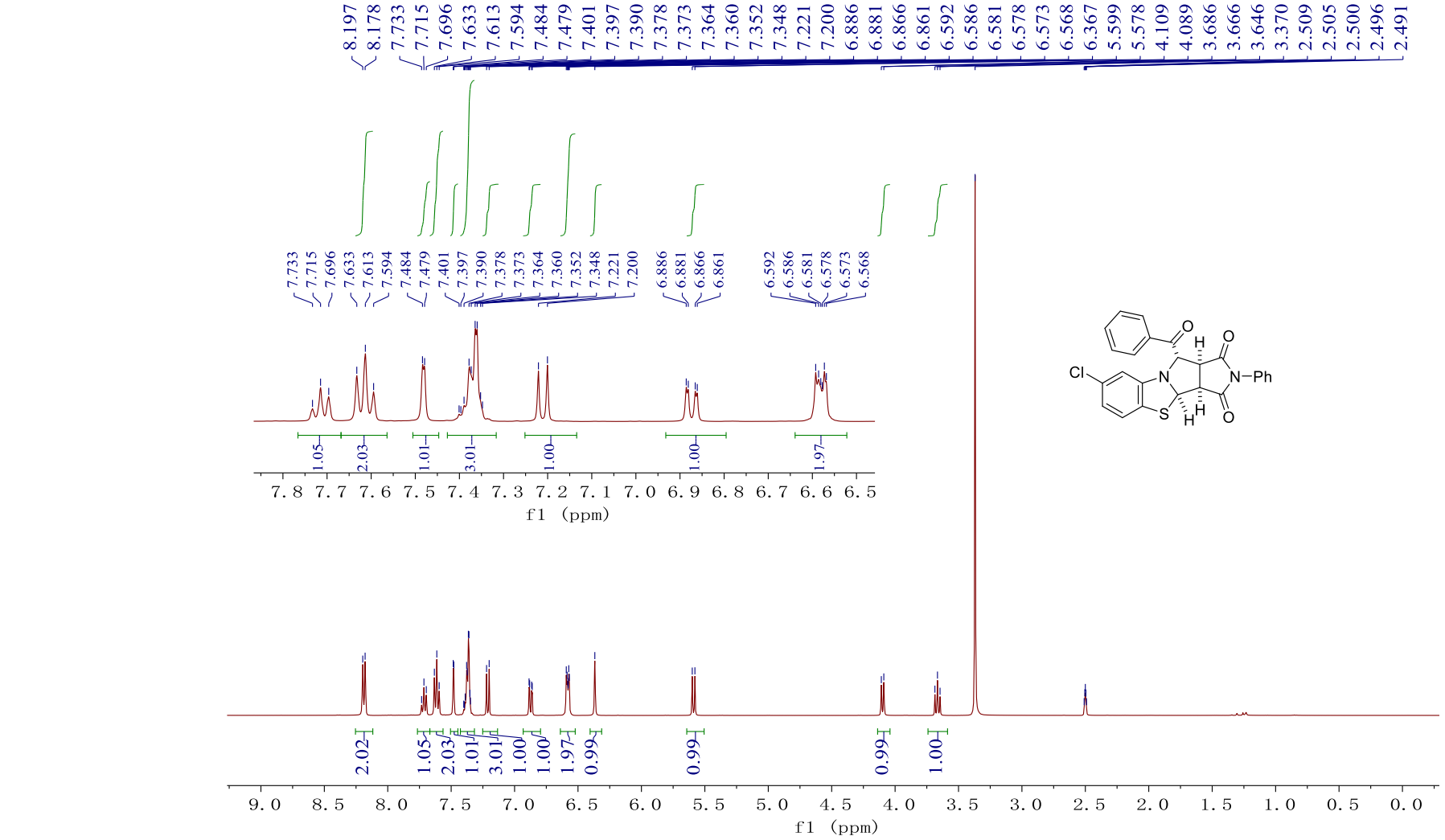


^{1}H NMR (400 MHz, $CDCl_3$) of **3la**



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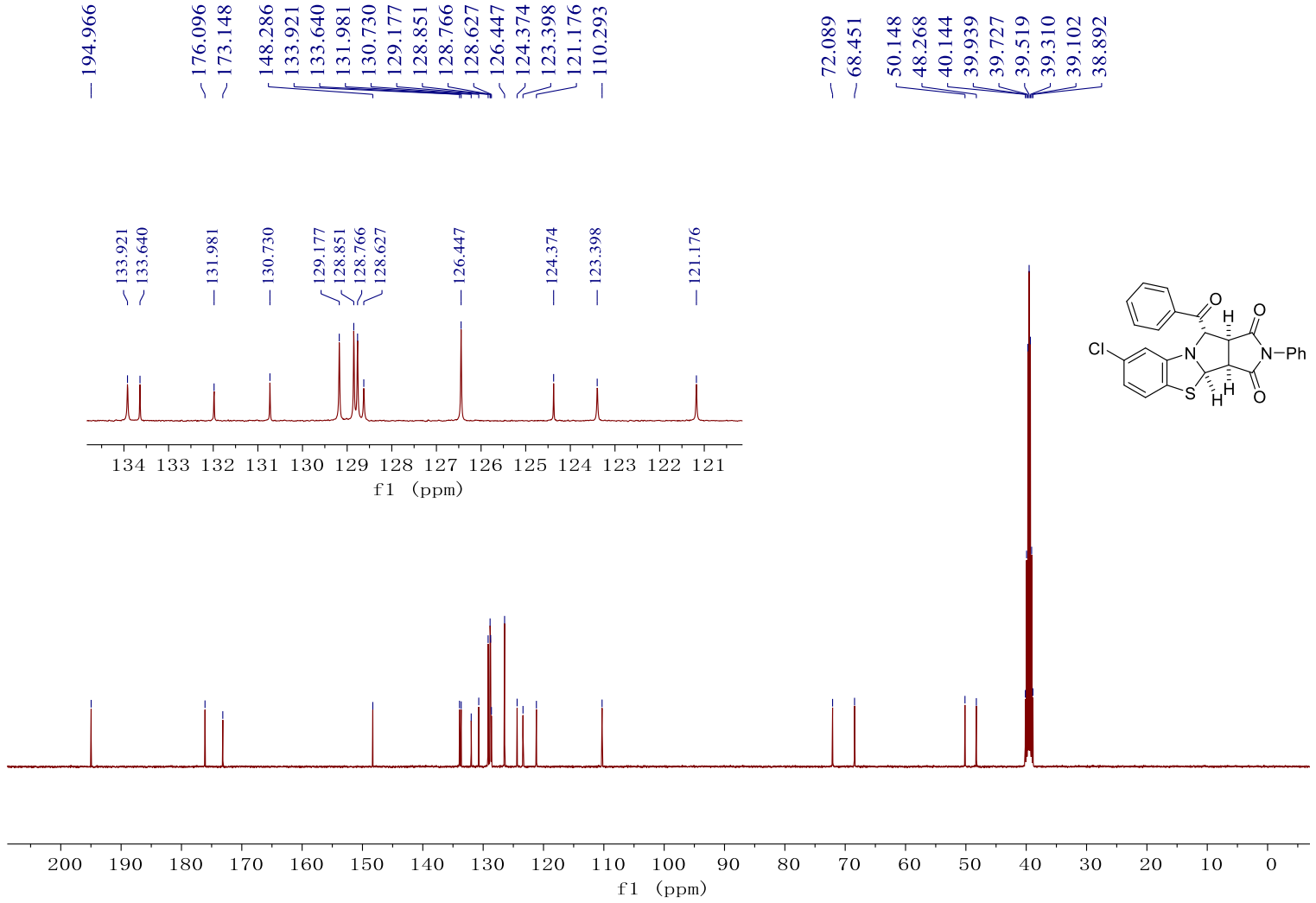
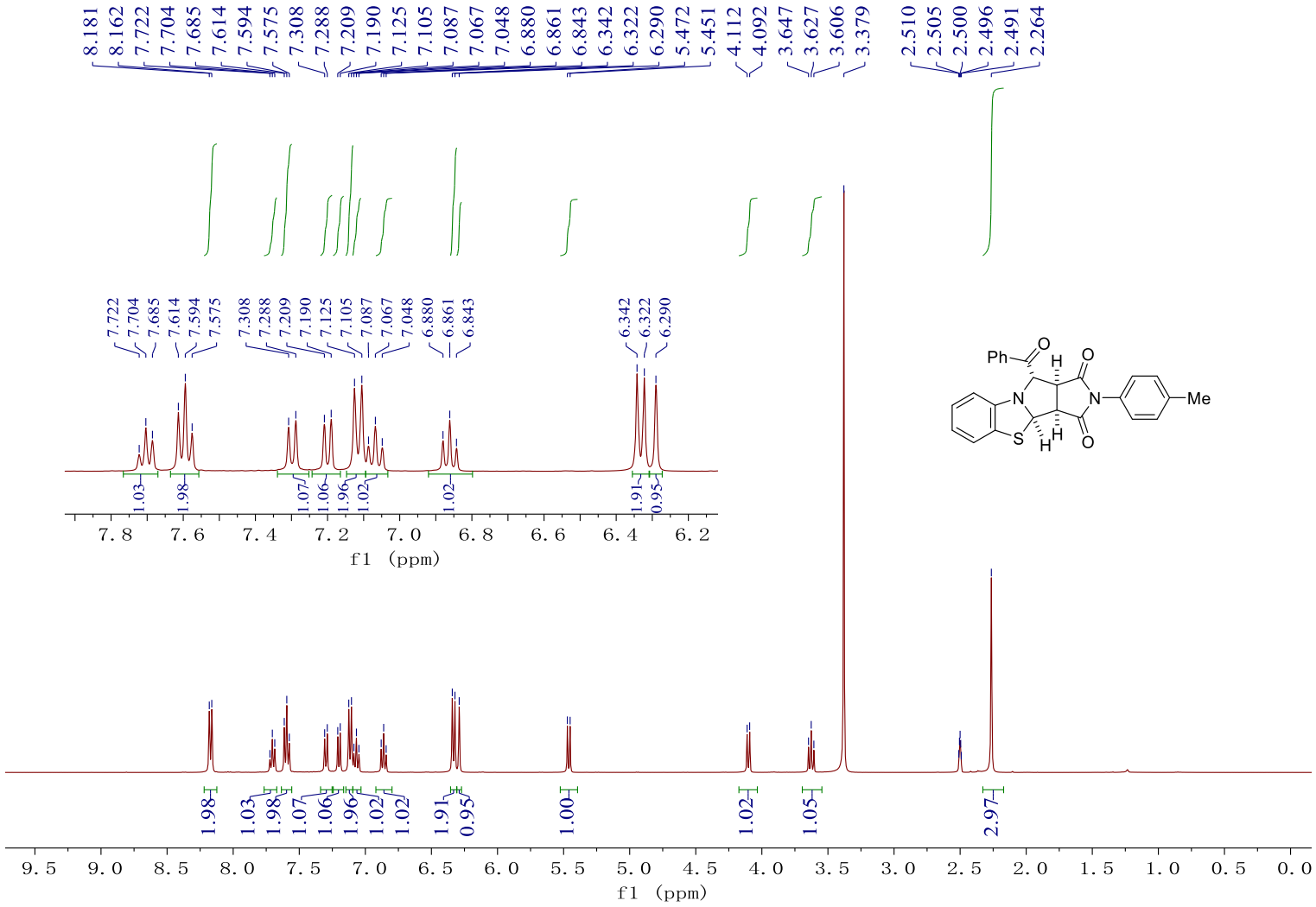
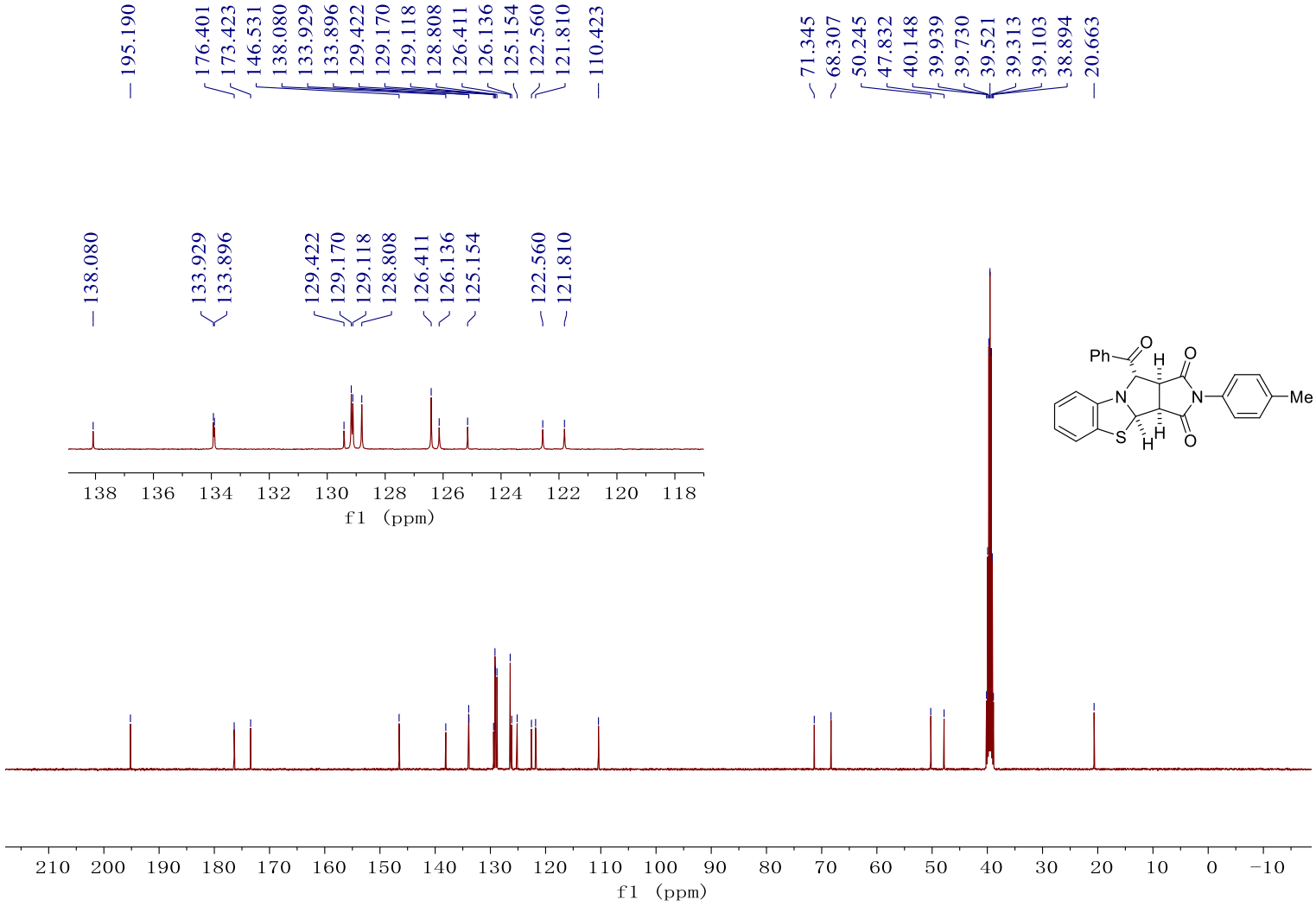


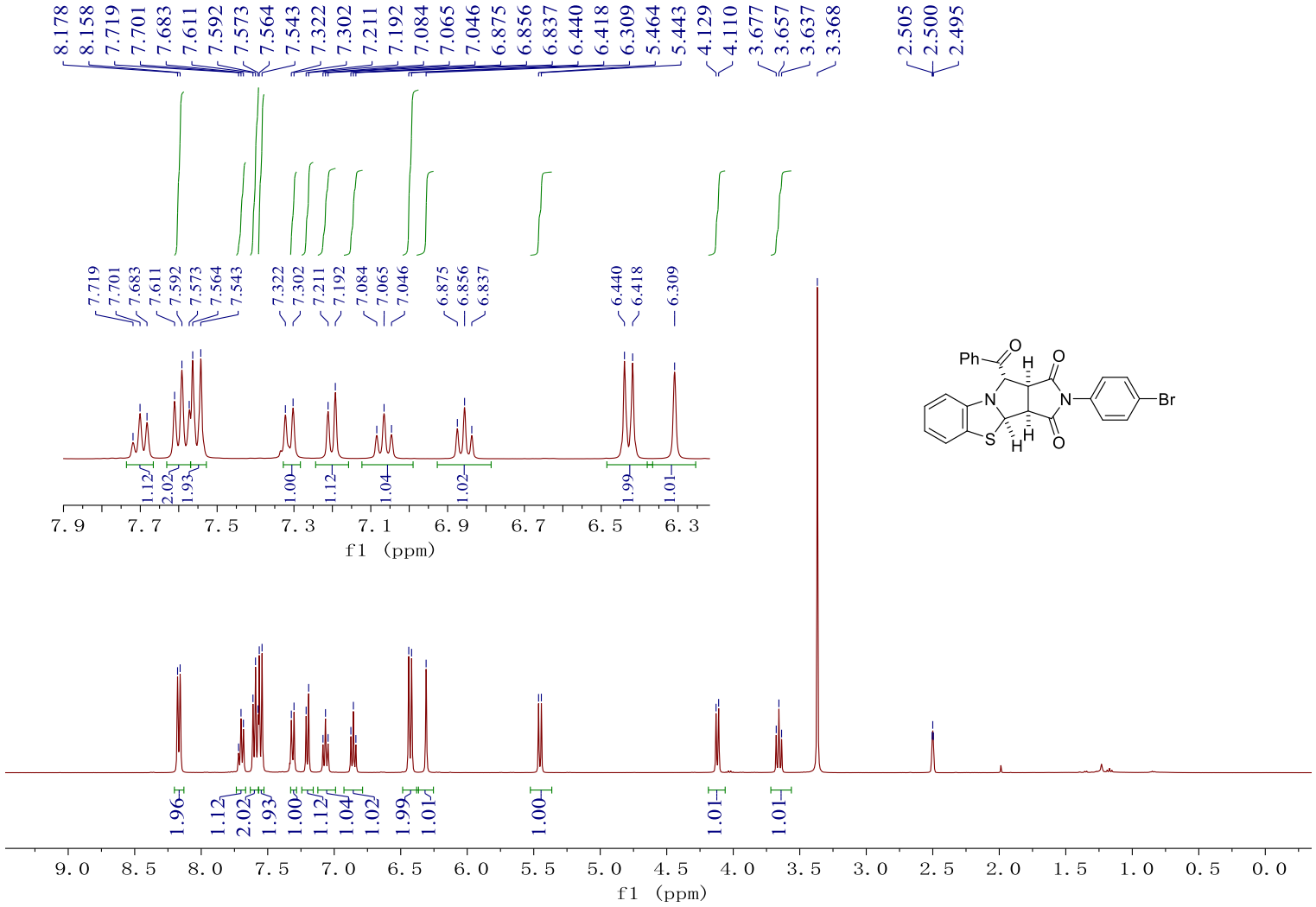
^{1}H NMR (400 MHz, $CDCl_3$) of **3ab**



^{13}C NMR (101 MHz, $CDCl_3$) of **3ab**



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



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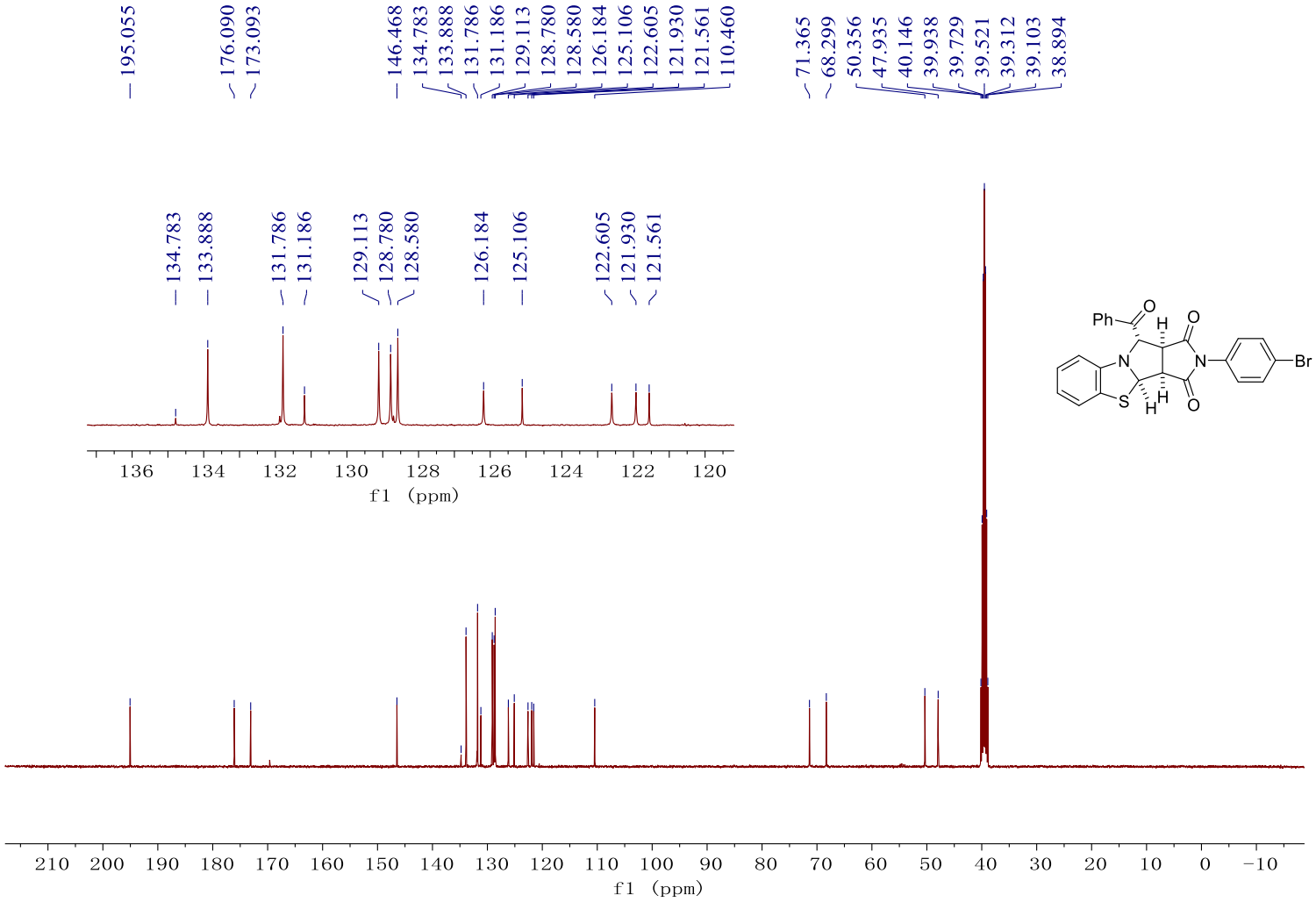

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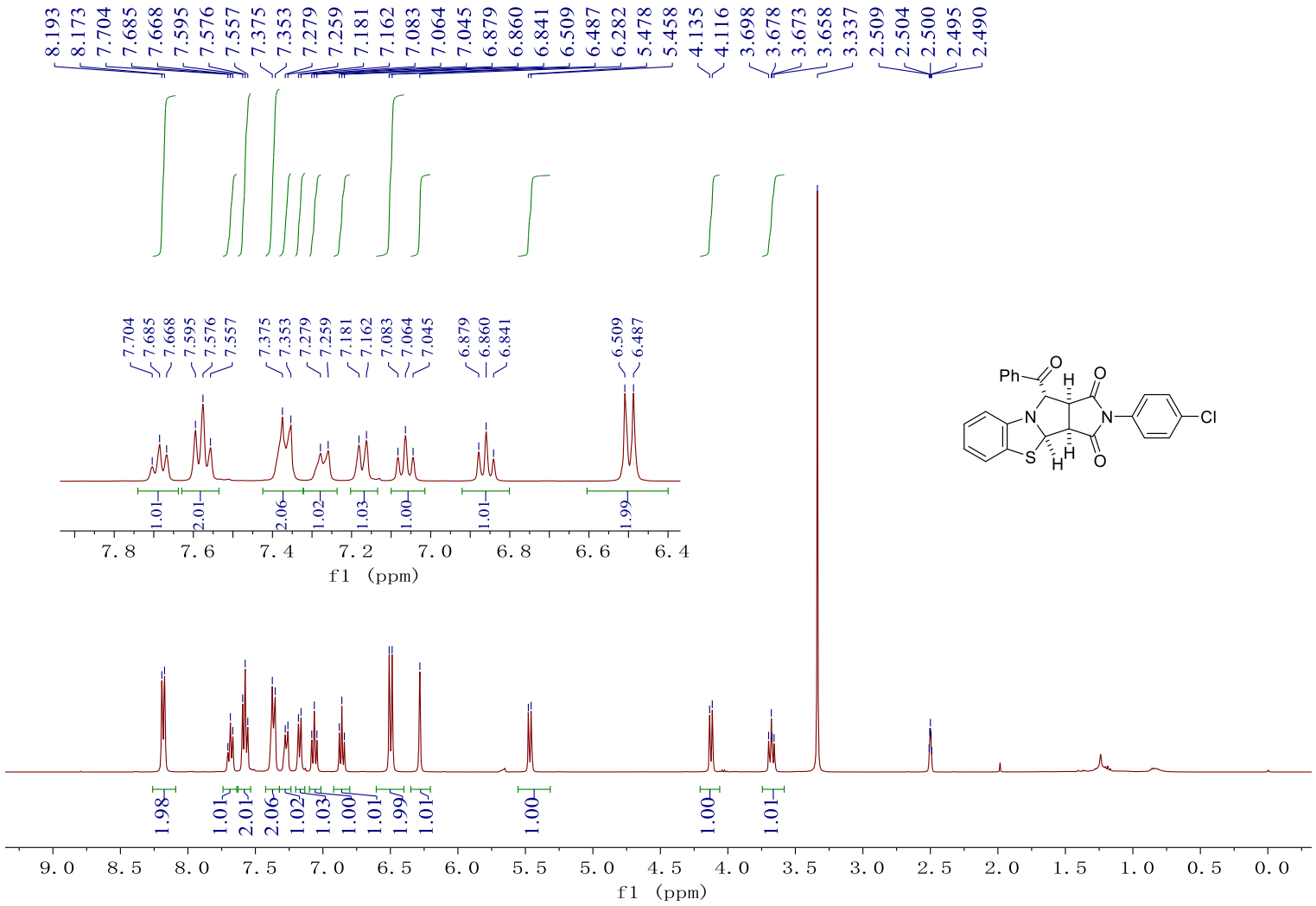

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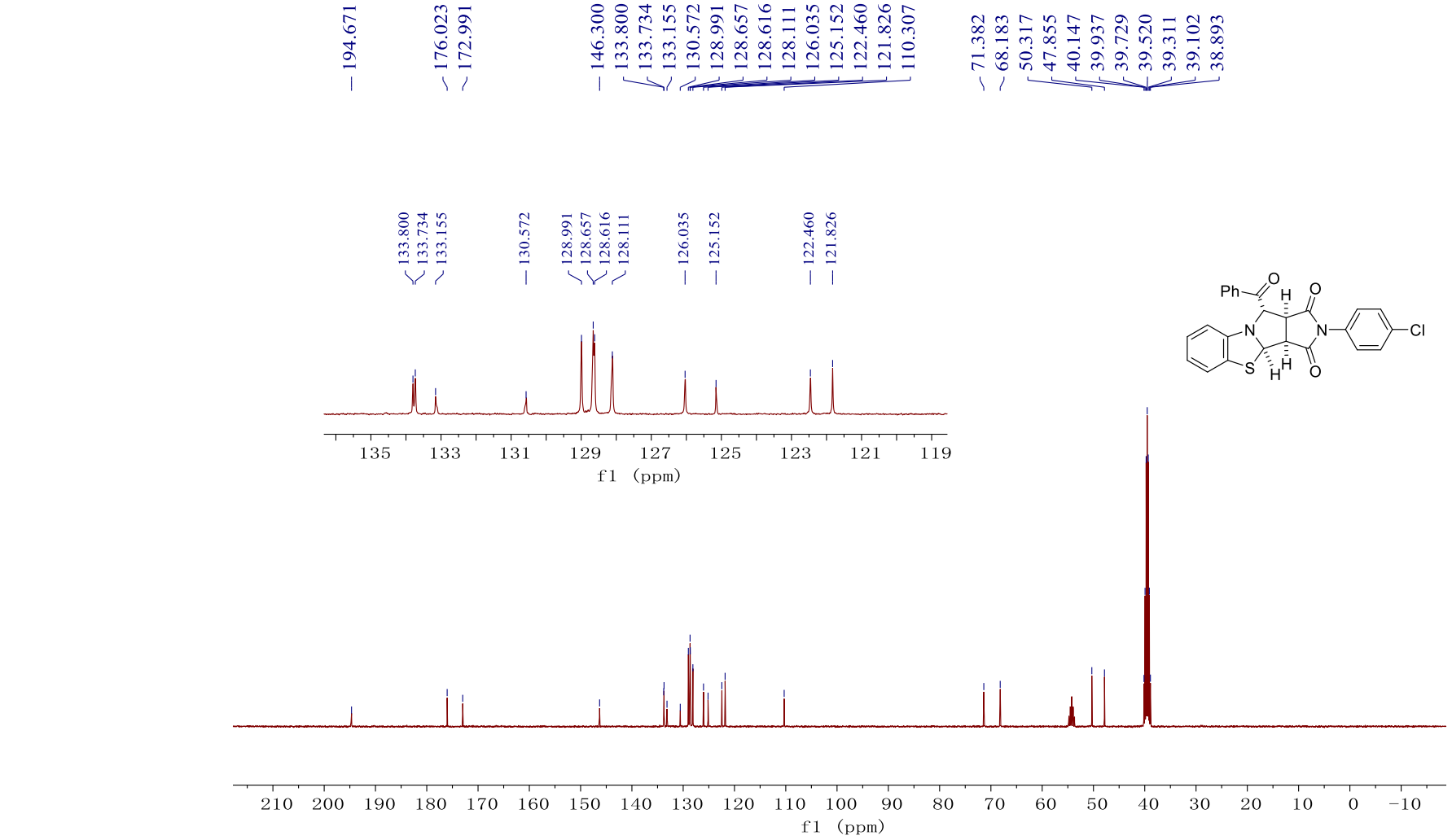

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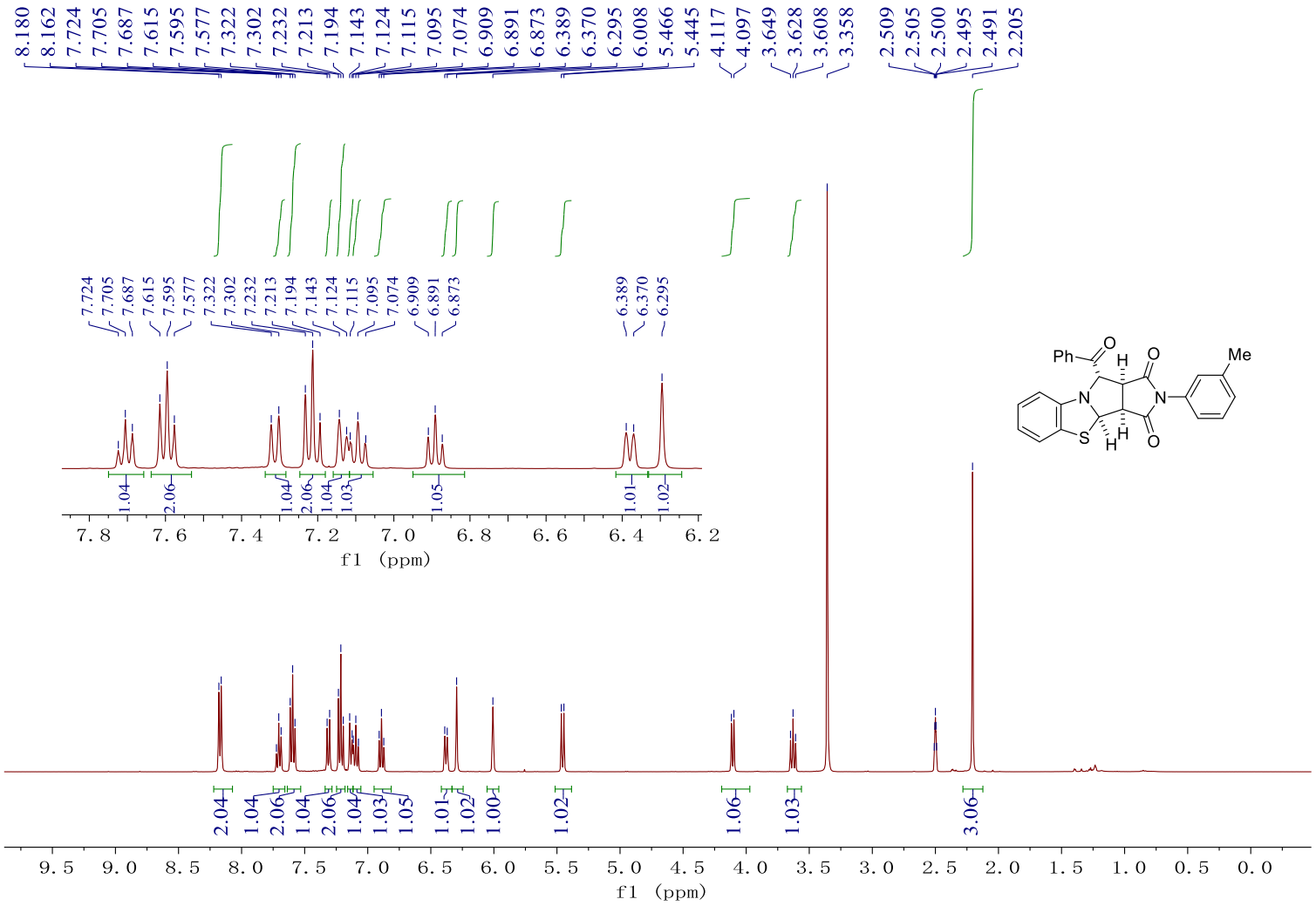

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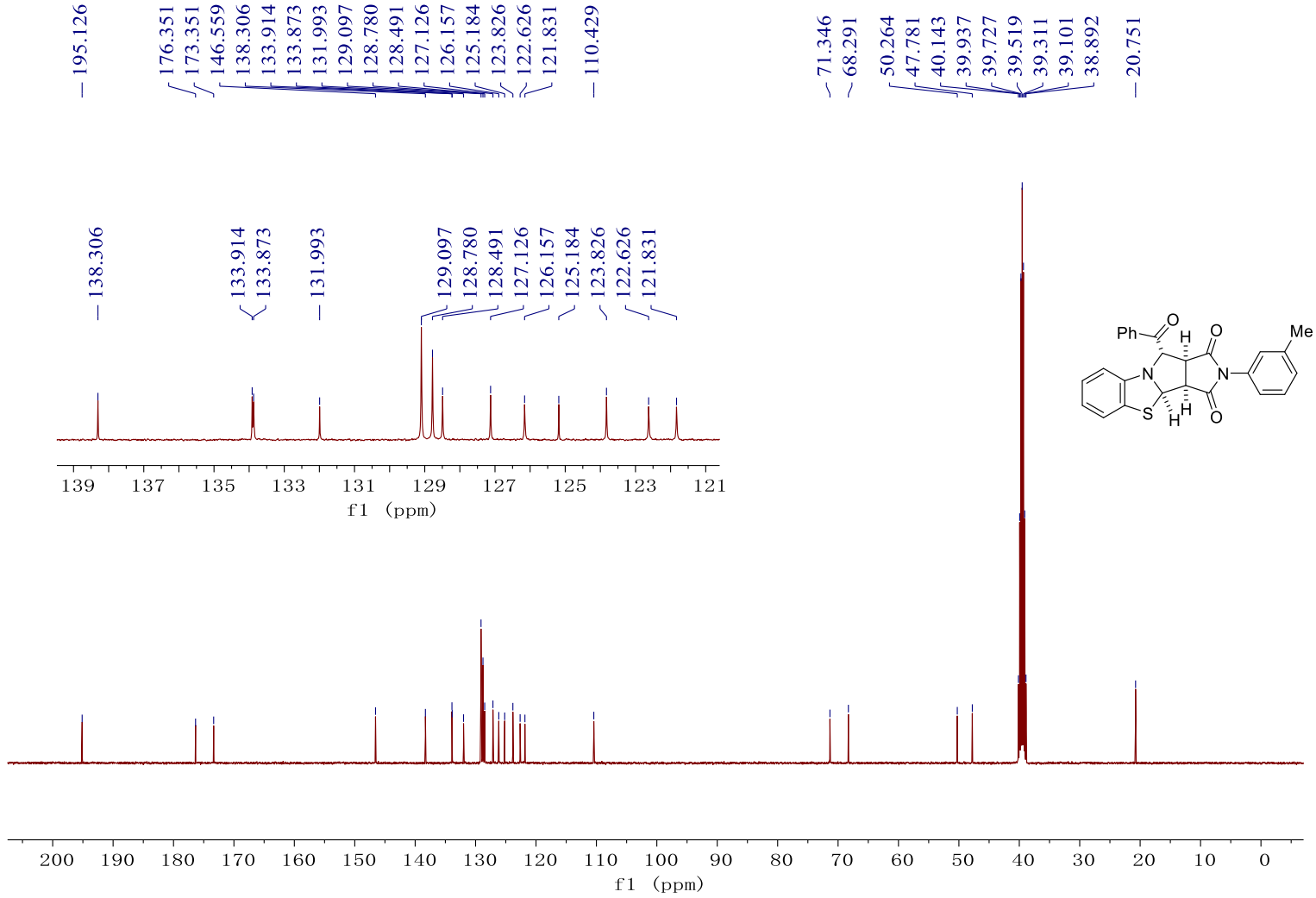

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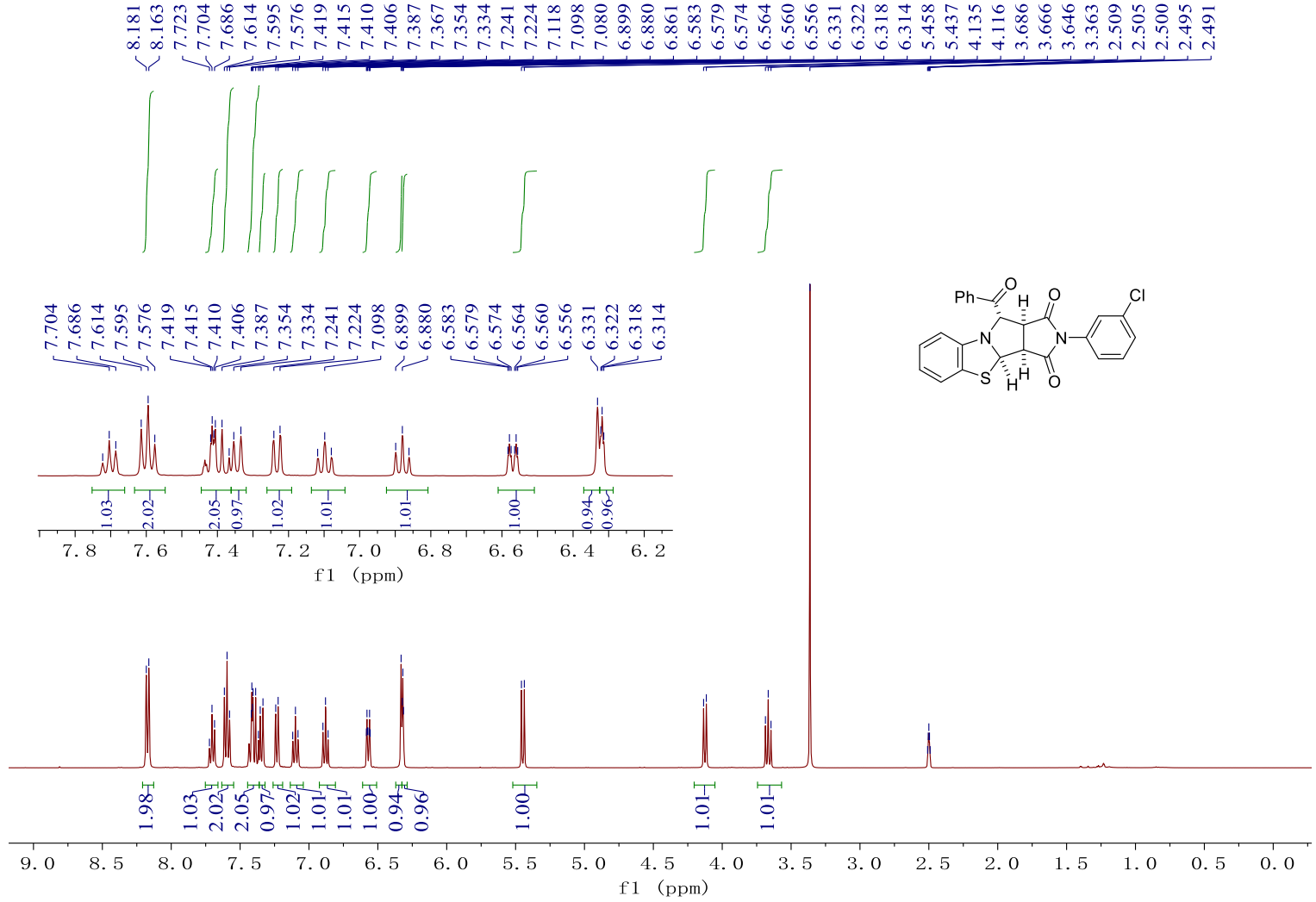
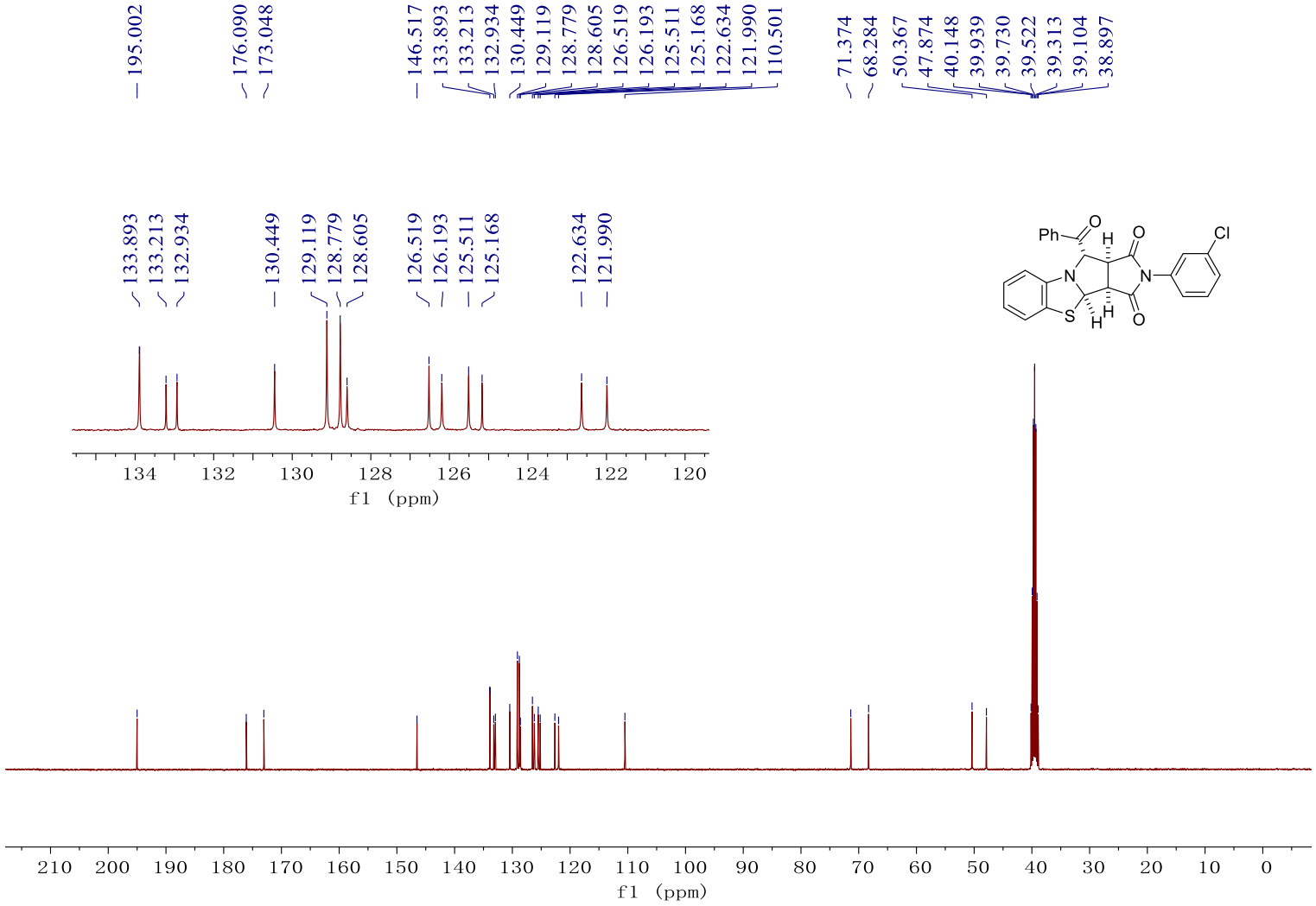


^{13}C NMR (101 MHz, $CDCl_3$) of **3af**



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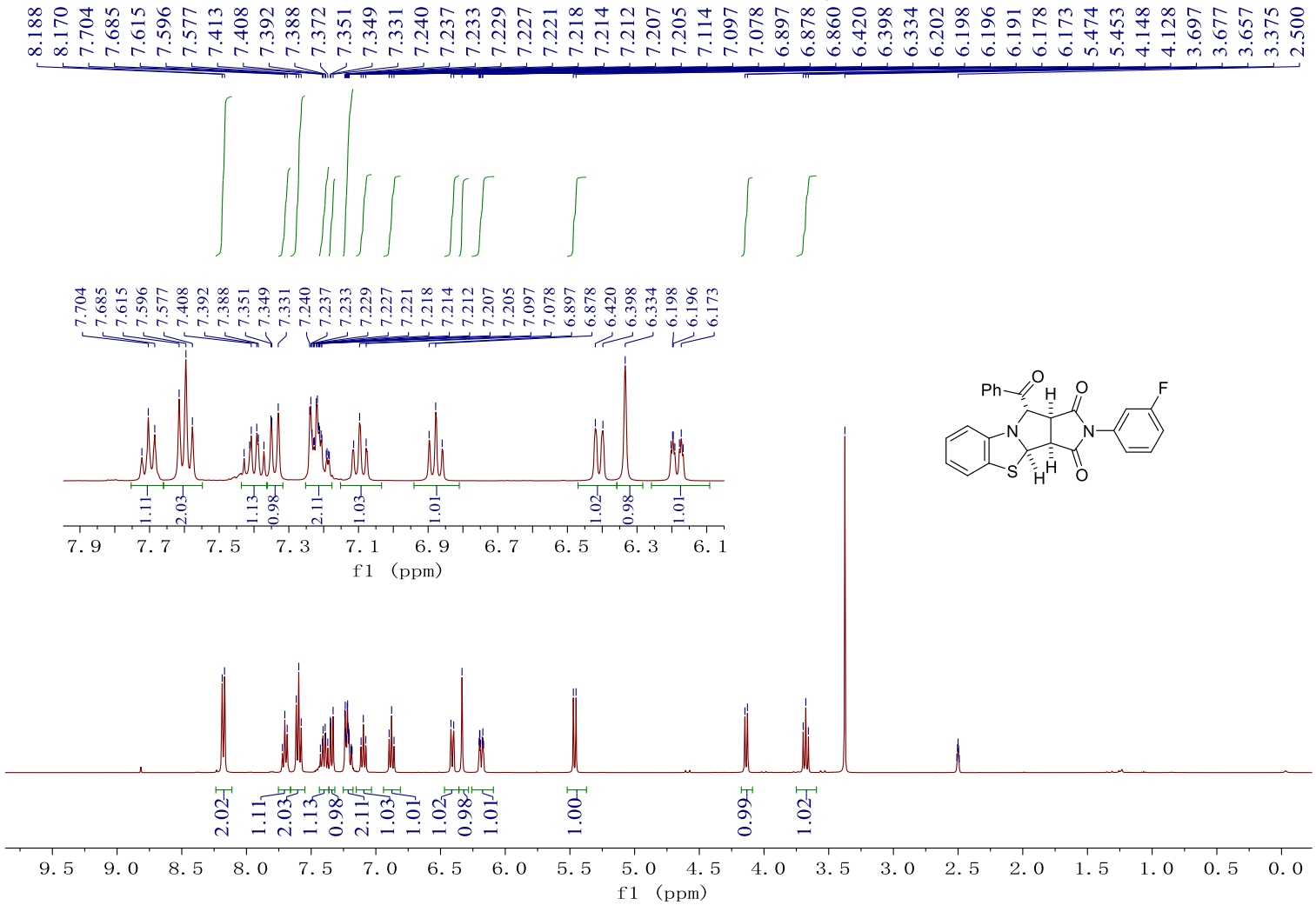
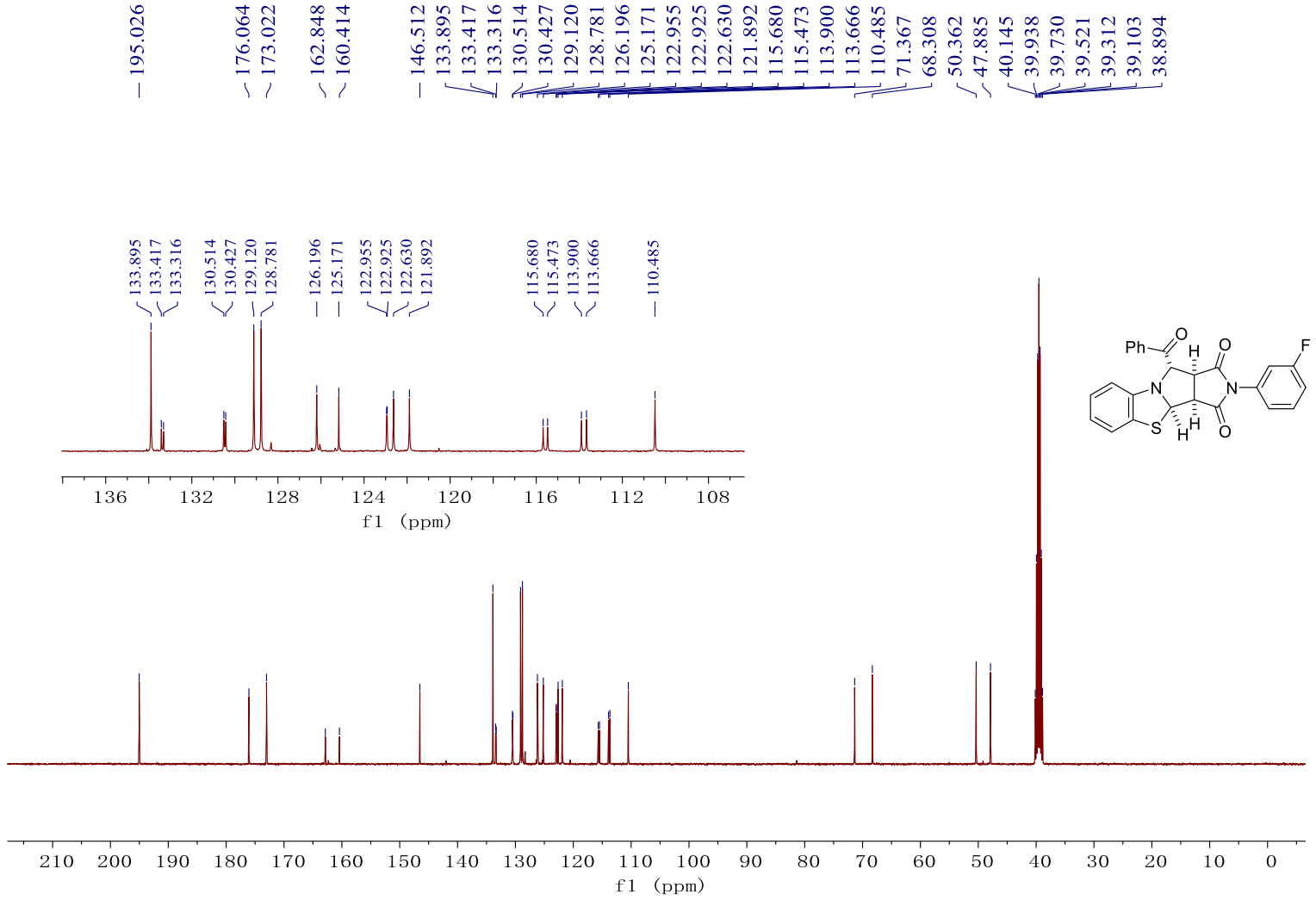
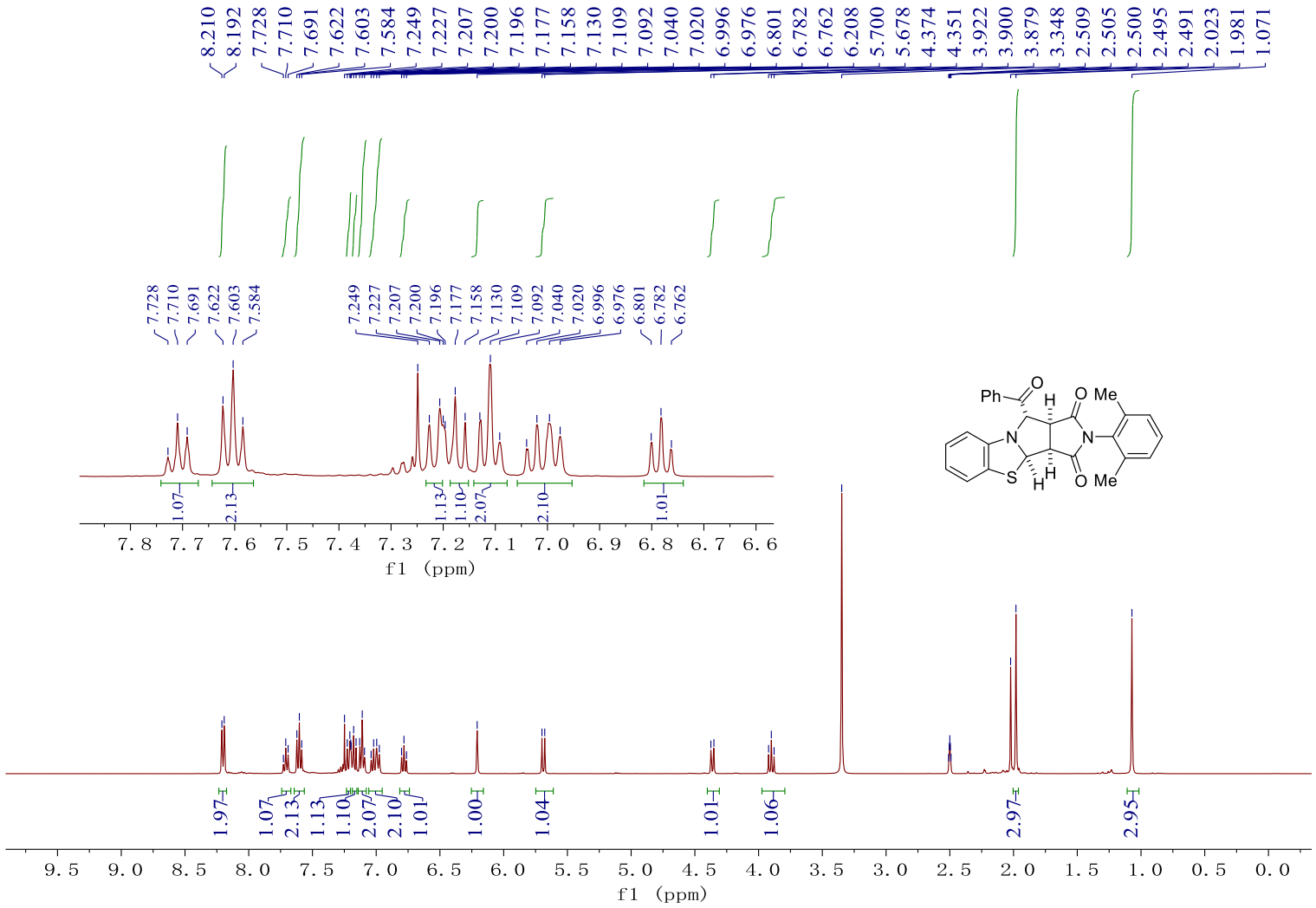


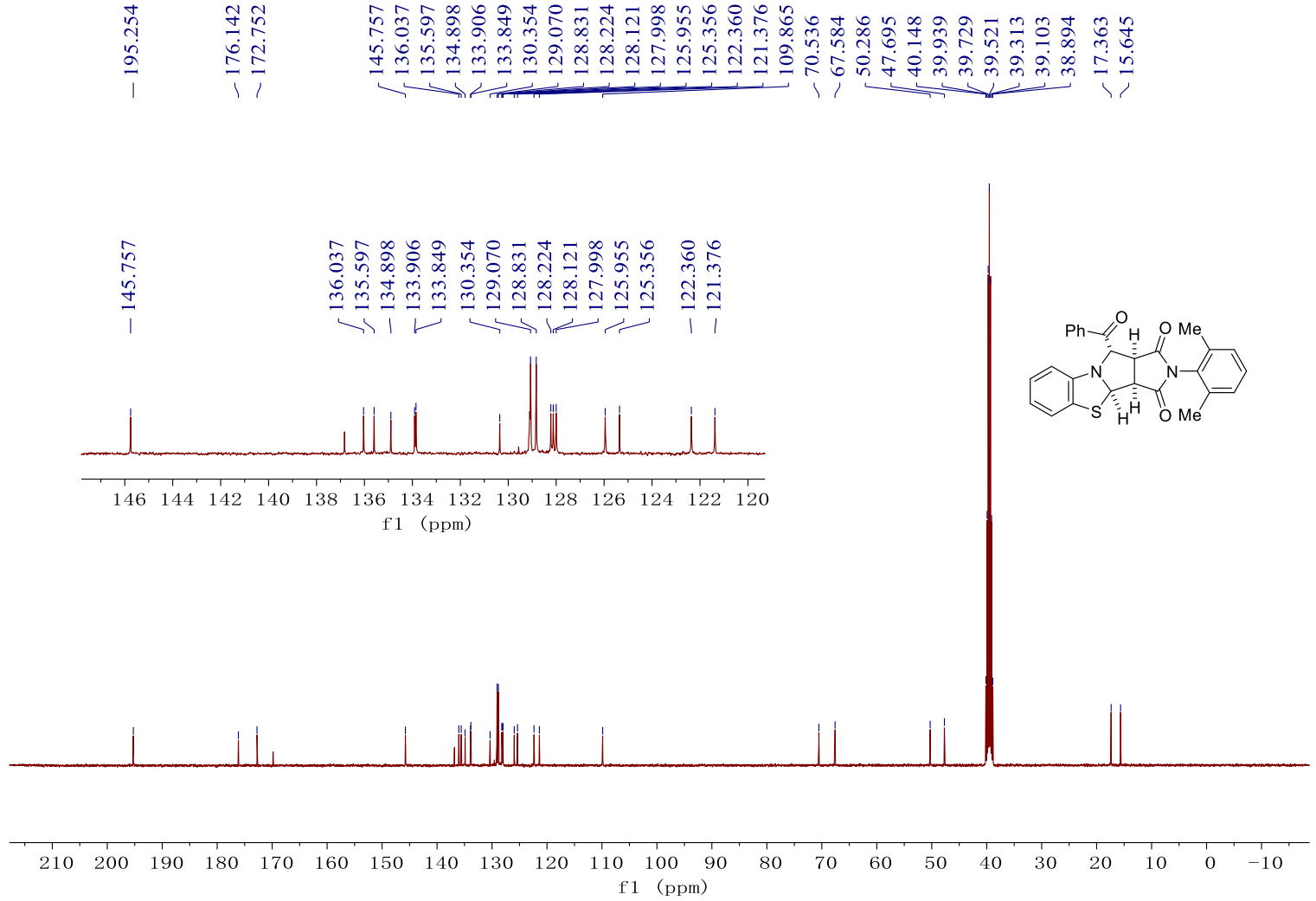
^{13}C NMR (101 MHz, $CDCl_3$) of **3ag**



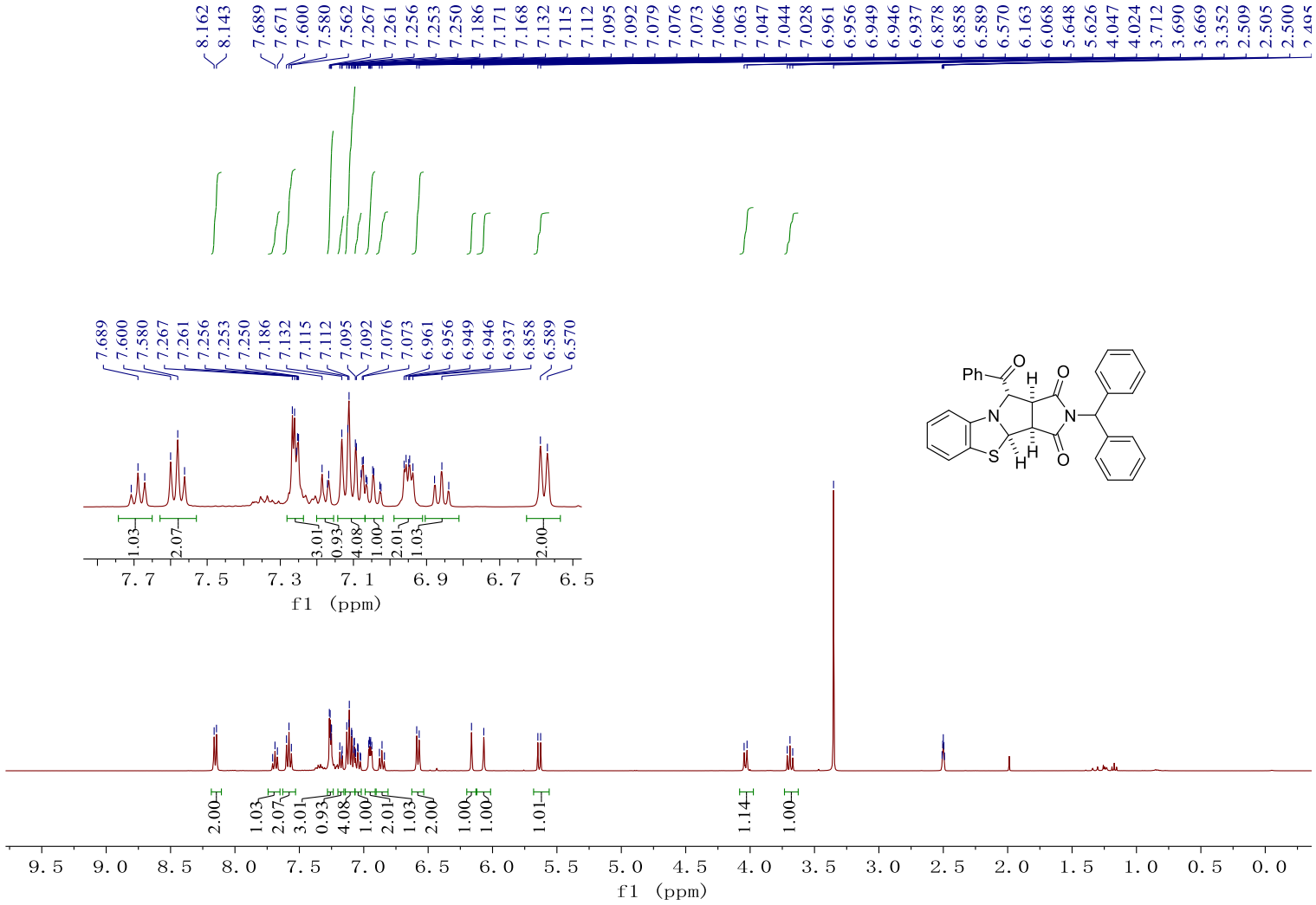
^{1}H NMR (400 MHz, $CDCl_3$) of **3ah**



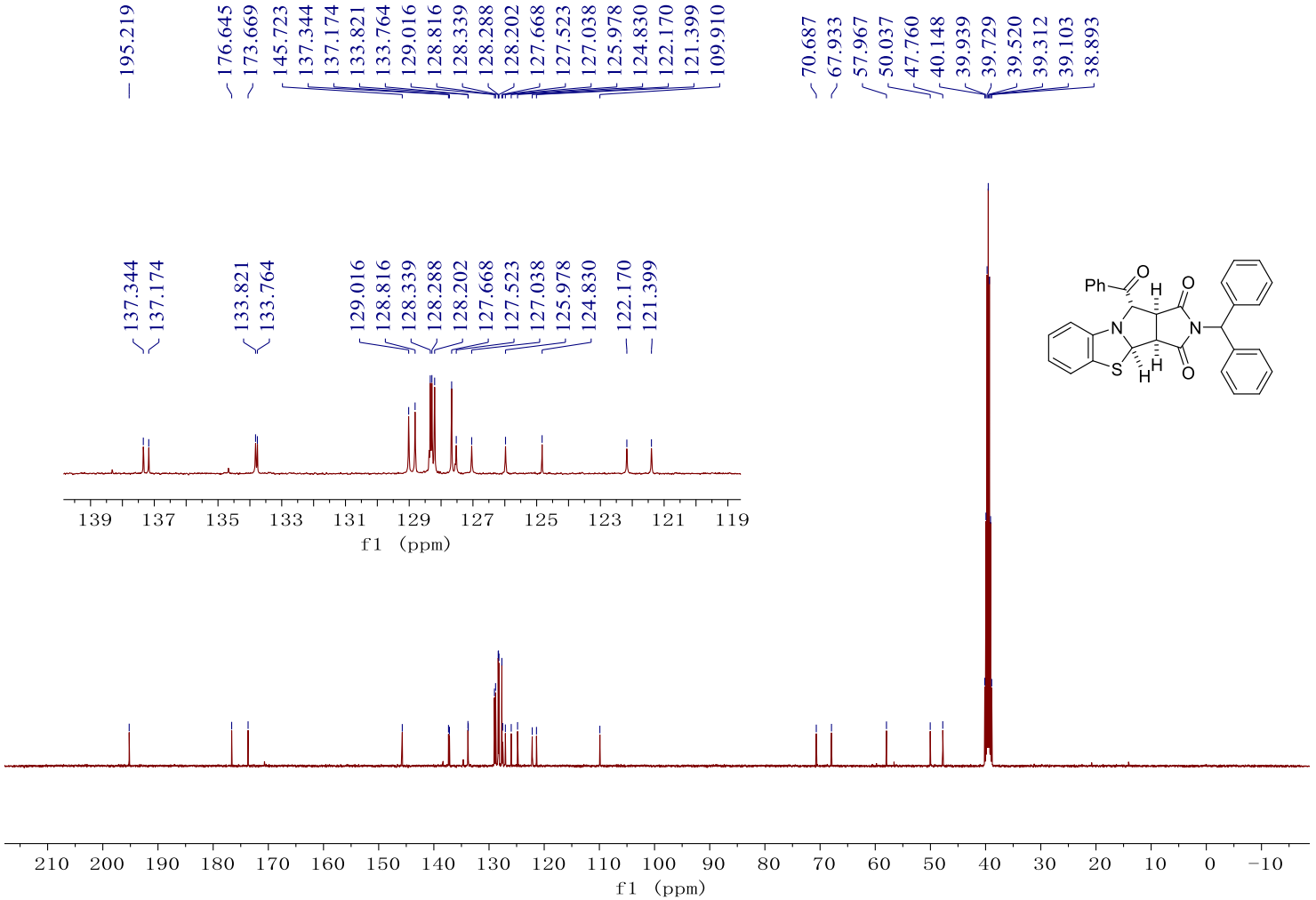
^{13}C NMR (101 MHz, $CDCl_3$) of **3ah**



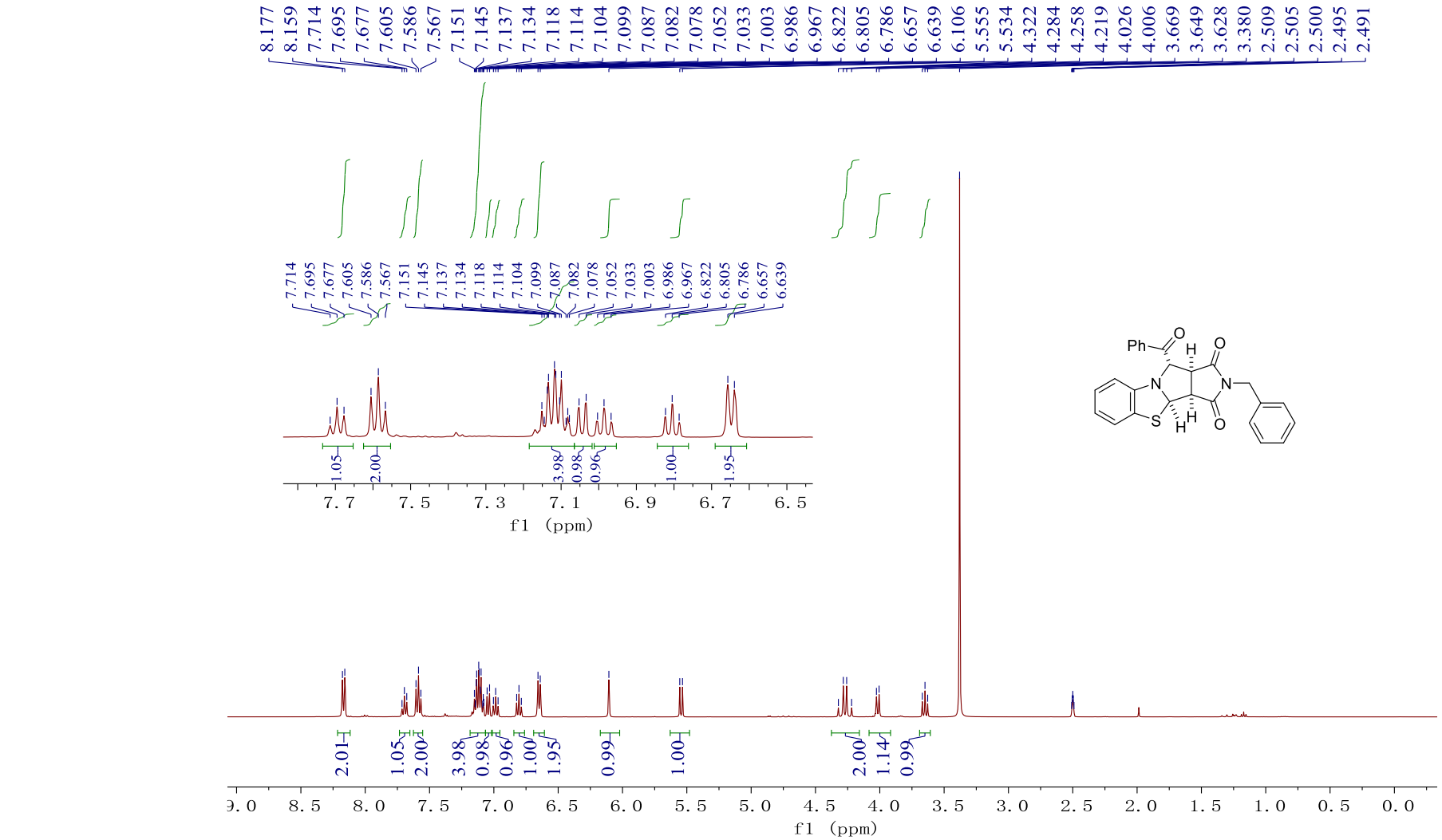
^{1}H NMR (400 MHz, $CDCl_3$) of **3ai**



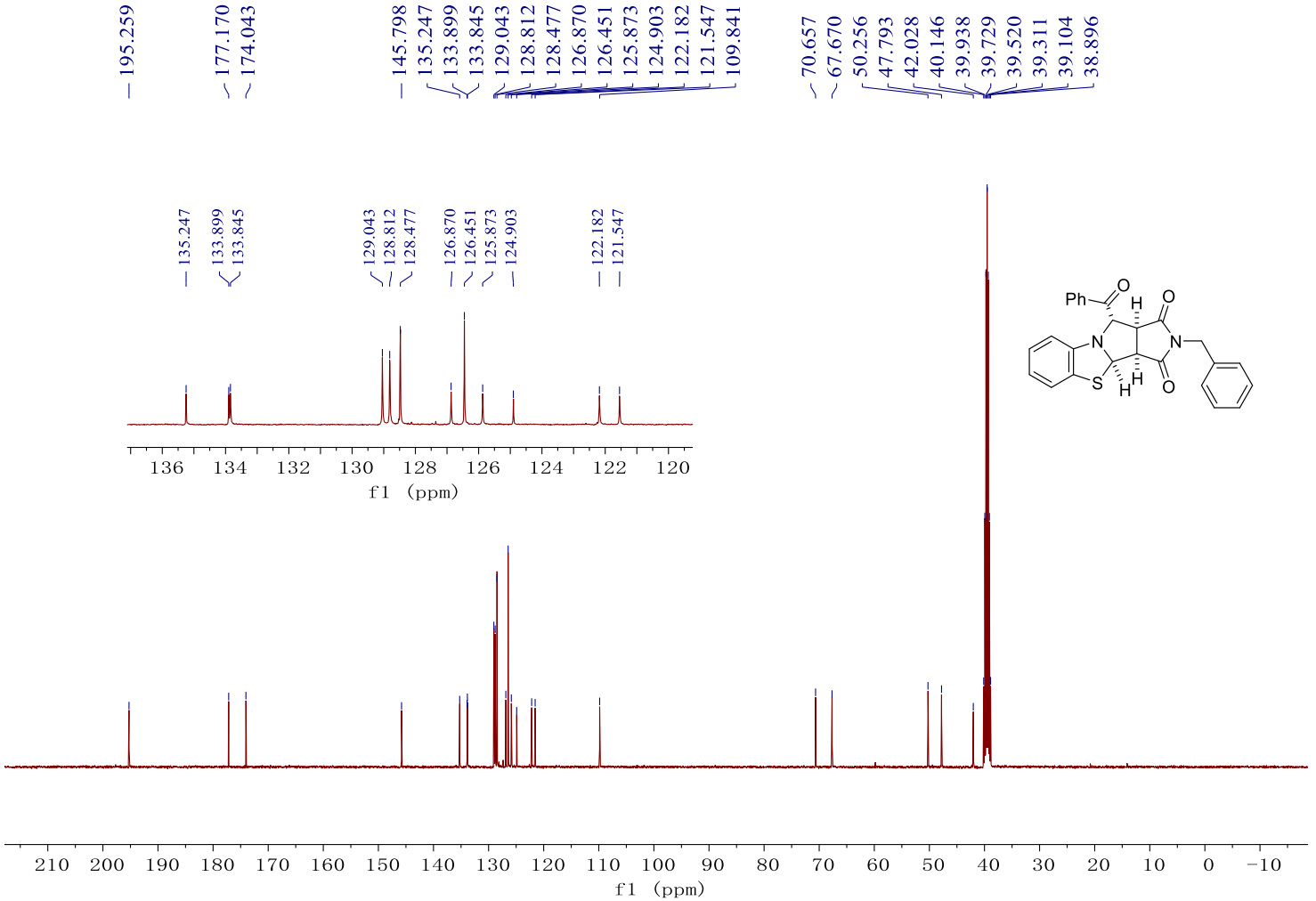
^{13}C NMR (101 MHz, $CDCl_3$) of **3ai**



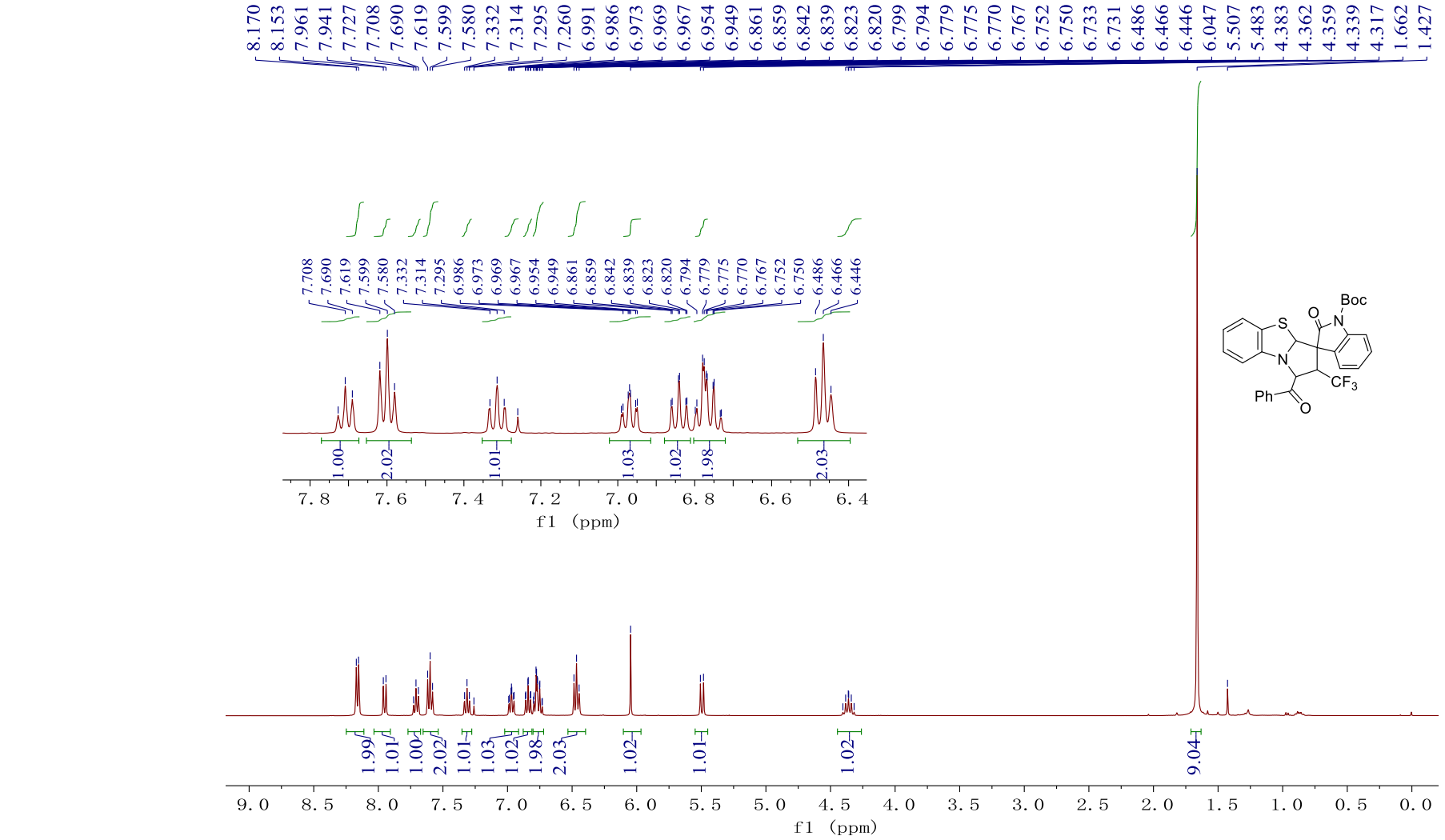
^{1}H NMR (400 MHz, $CDCl_3$) of **3aj**



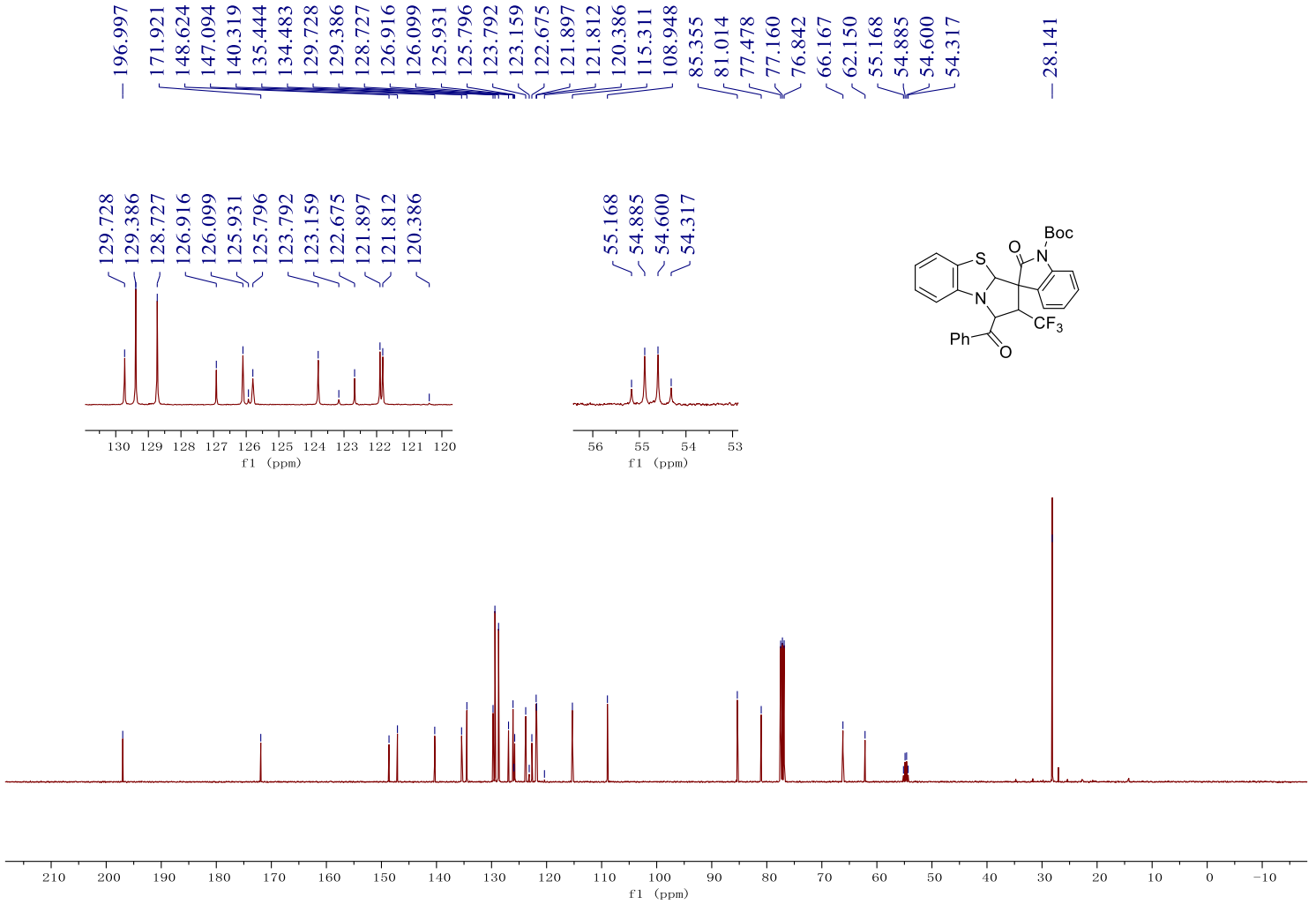
^{13}C NMR (101 MHz, $CDCl_3$) of **3aj**



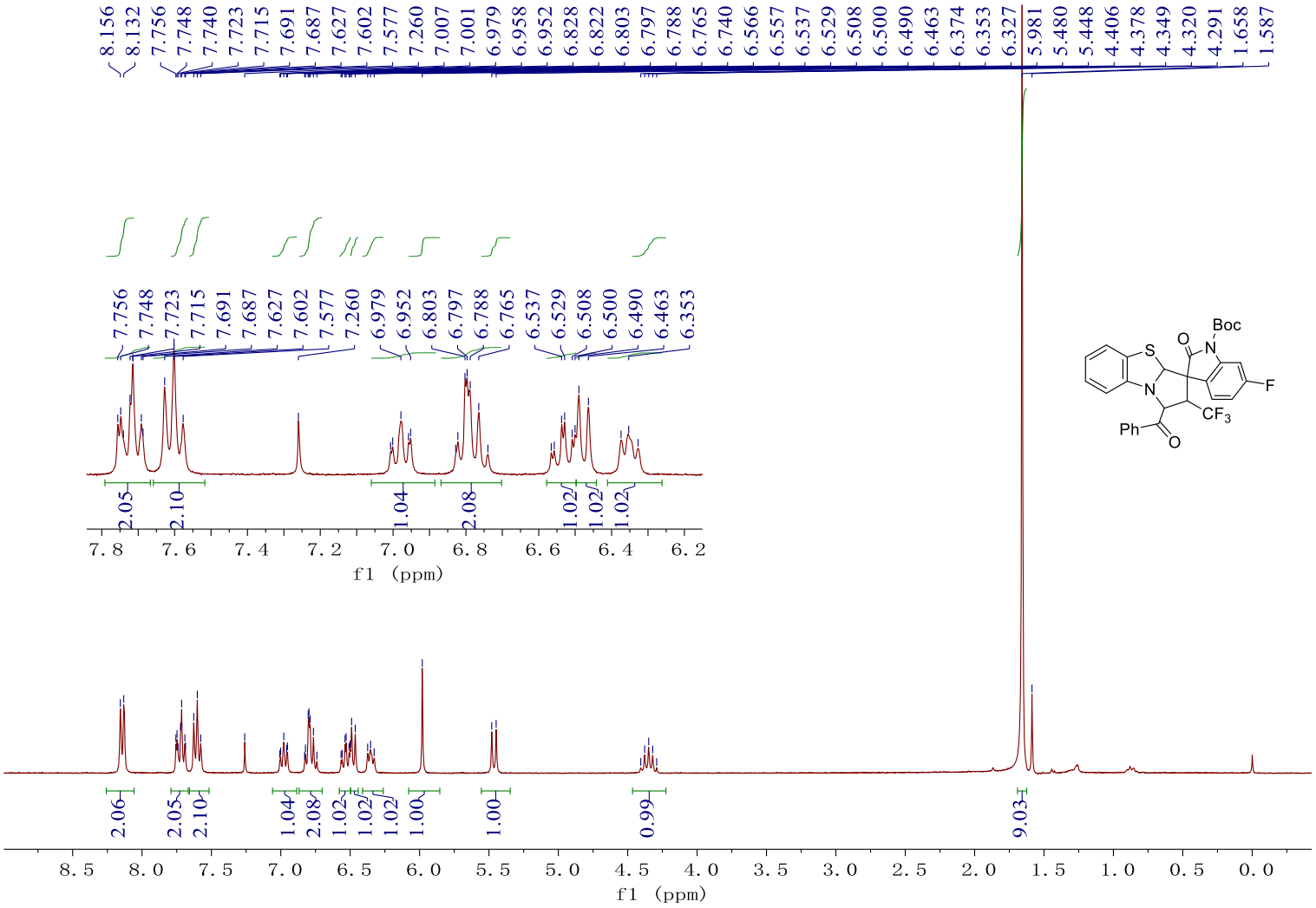
^{1}H NMR (400 MHz, $CDCl_3$) of **5aa**



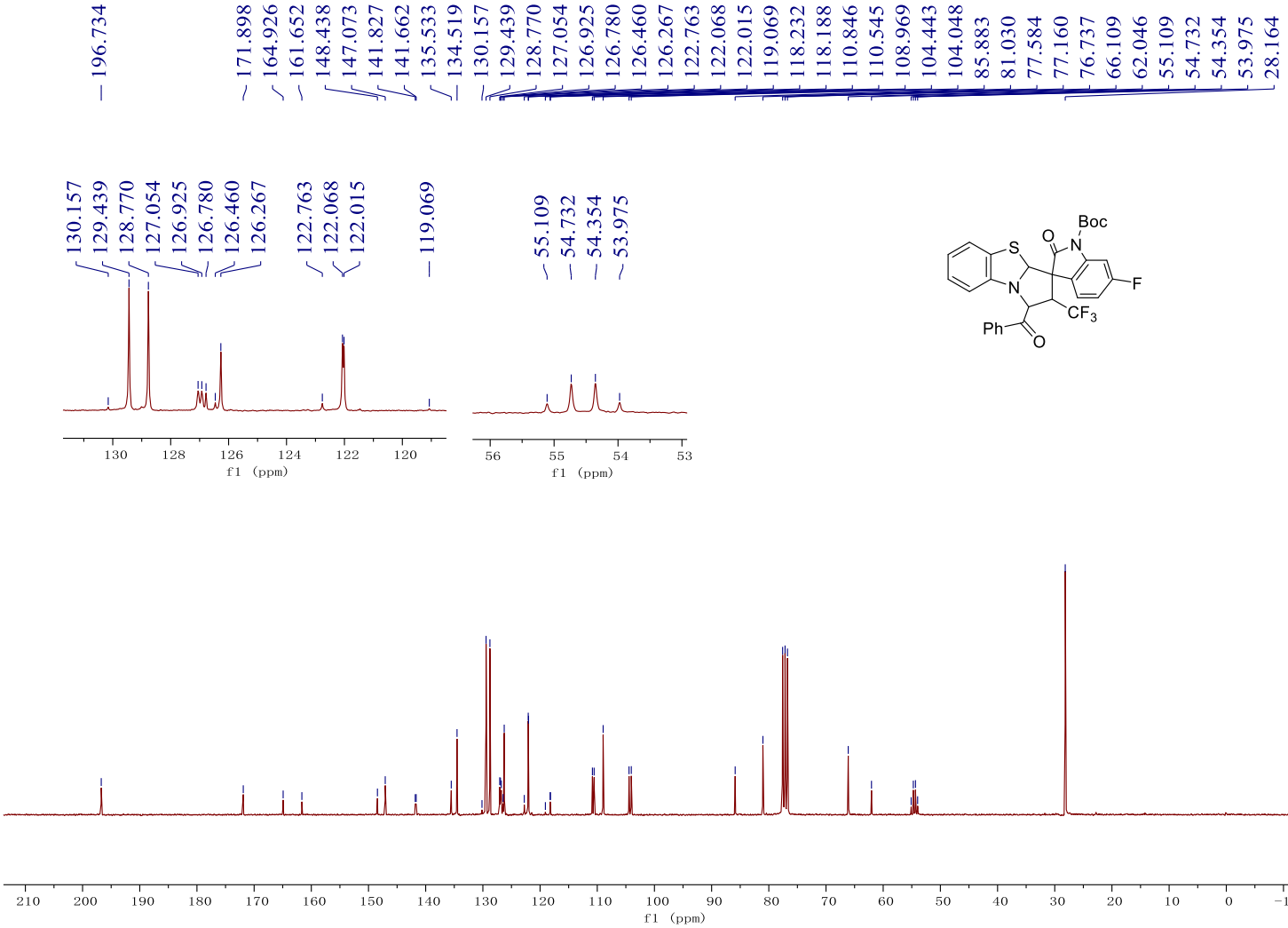
^{13}C NMR (101 MHz, $CDCl_3$) of **5aa**



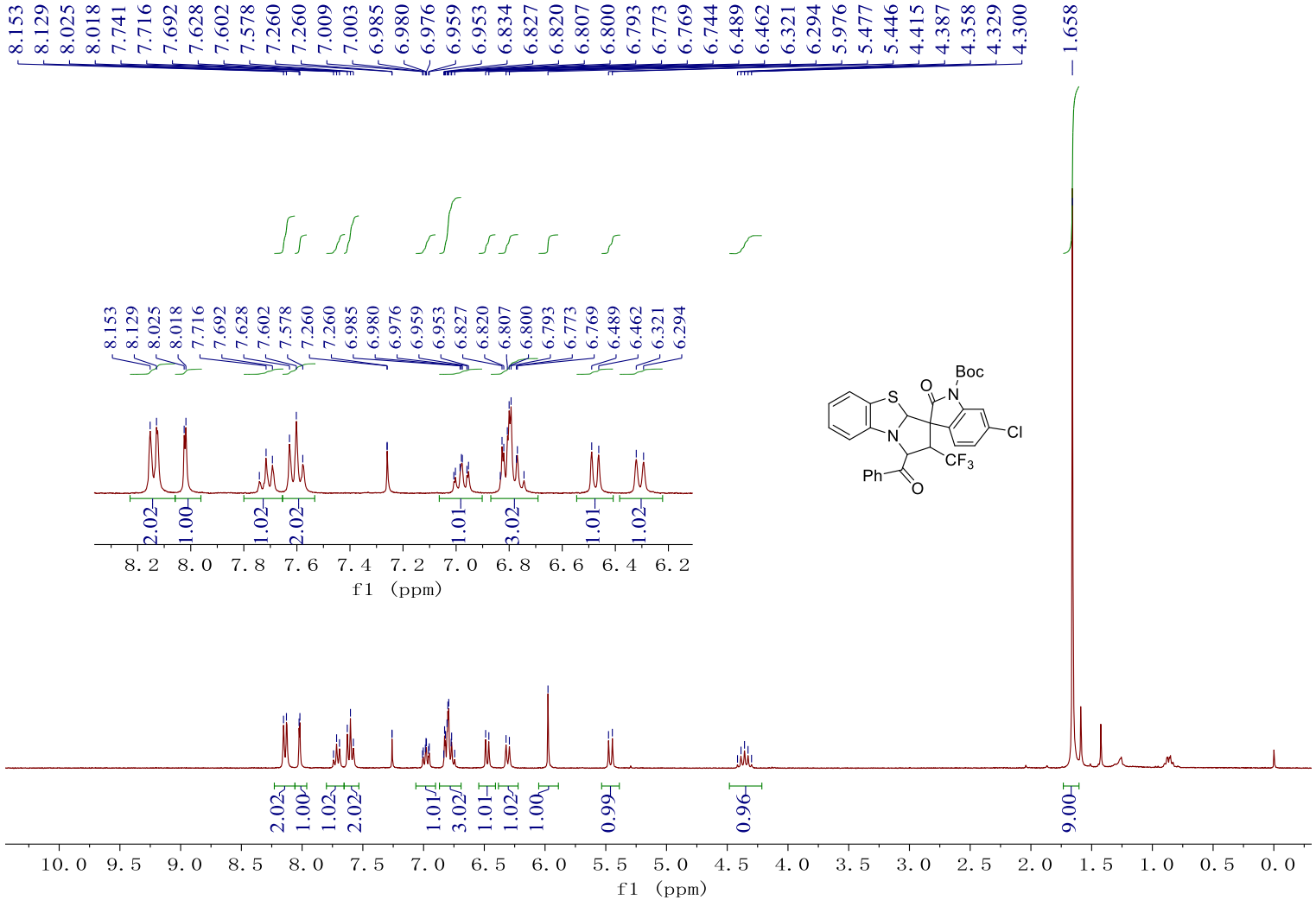
^{1}H NMR (300 MHz, $CDCl_3$) of **5ab**



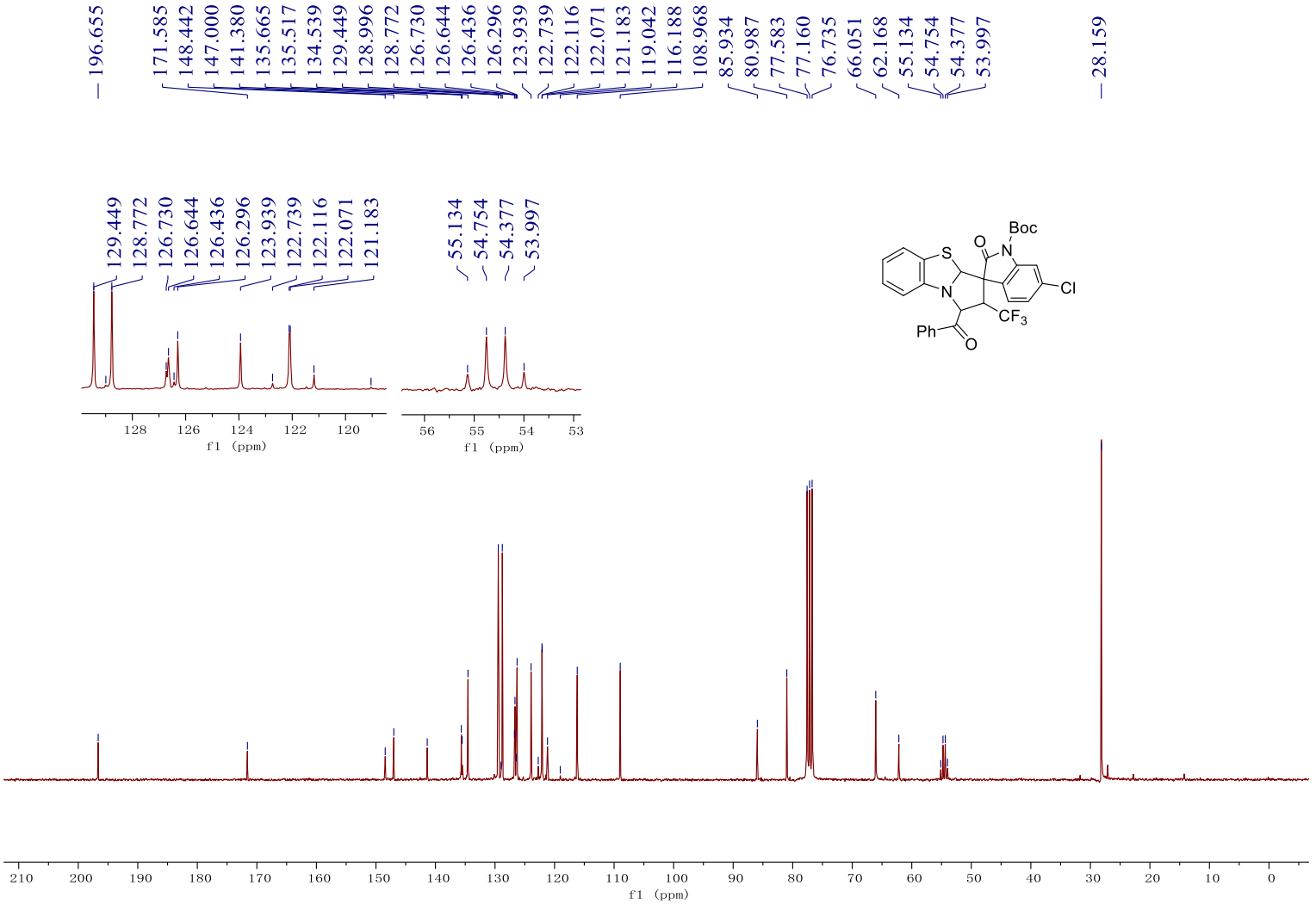
^{13}C NMR (75 MHz, $CDCl_3$) of **5ab**



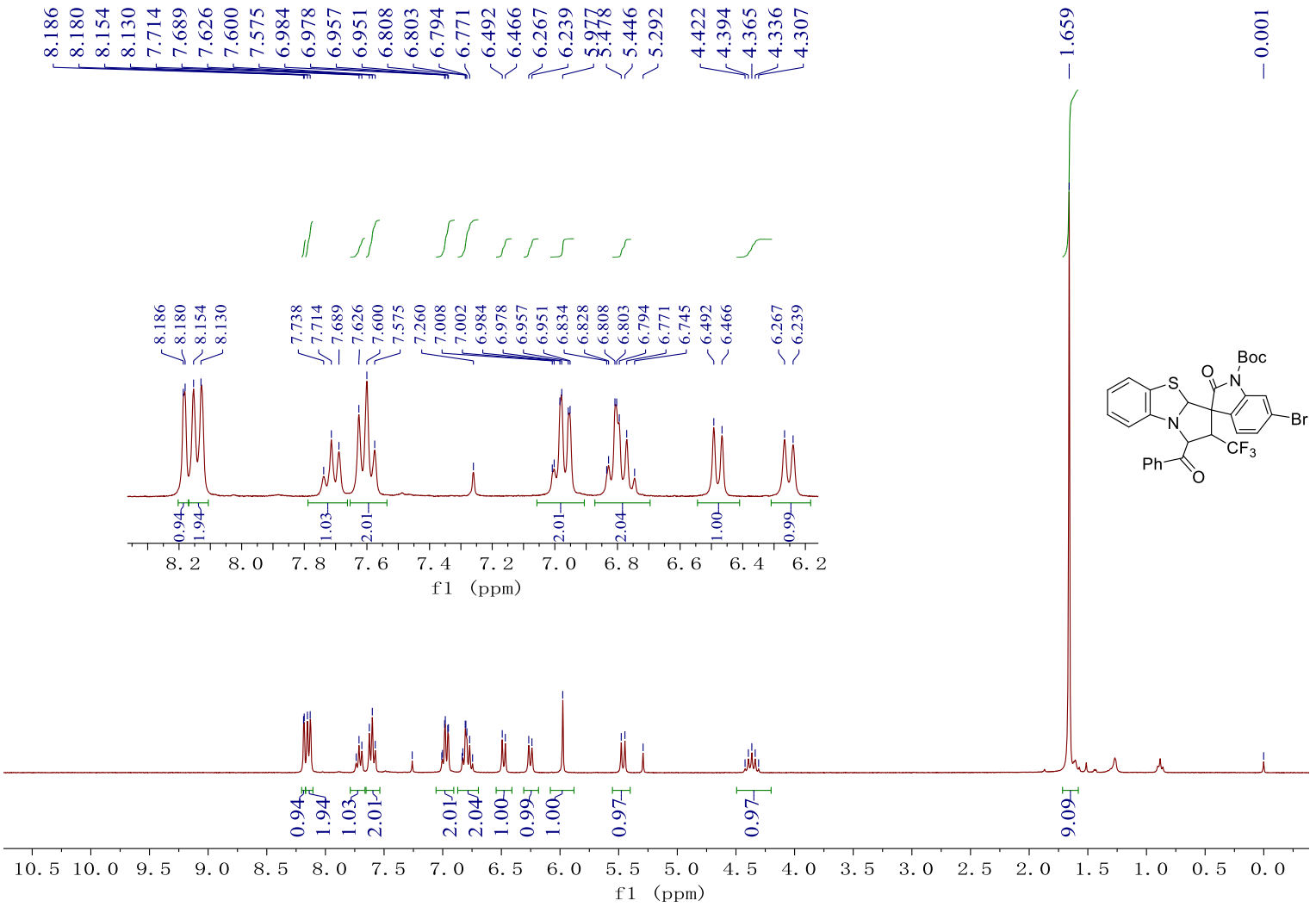
^{1}H NMR (300 MHz, $CDCl_3$) of **5ac**



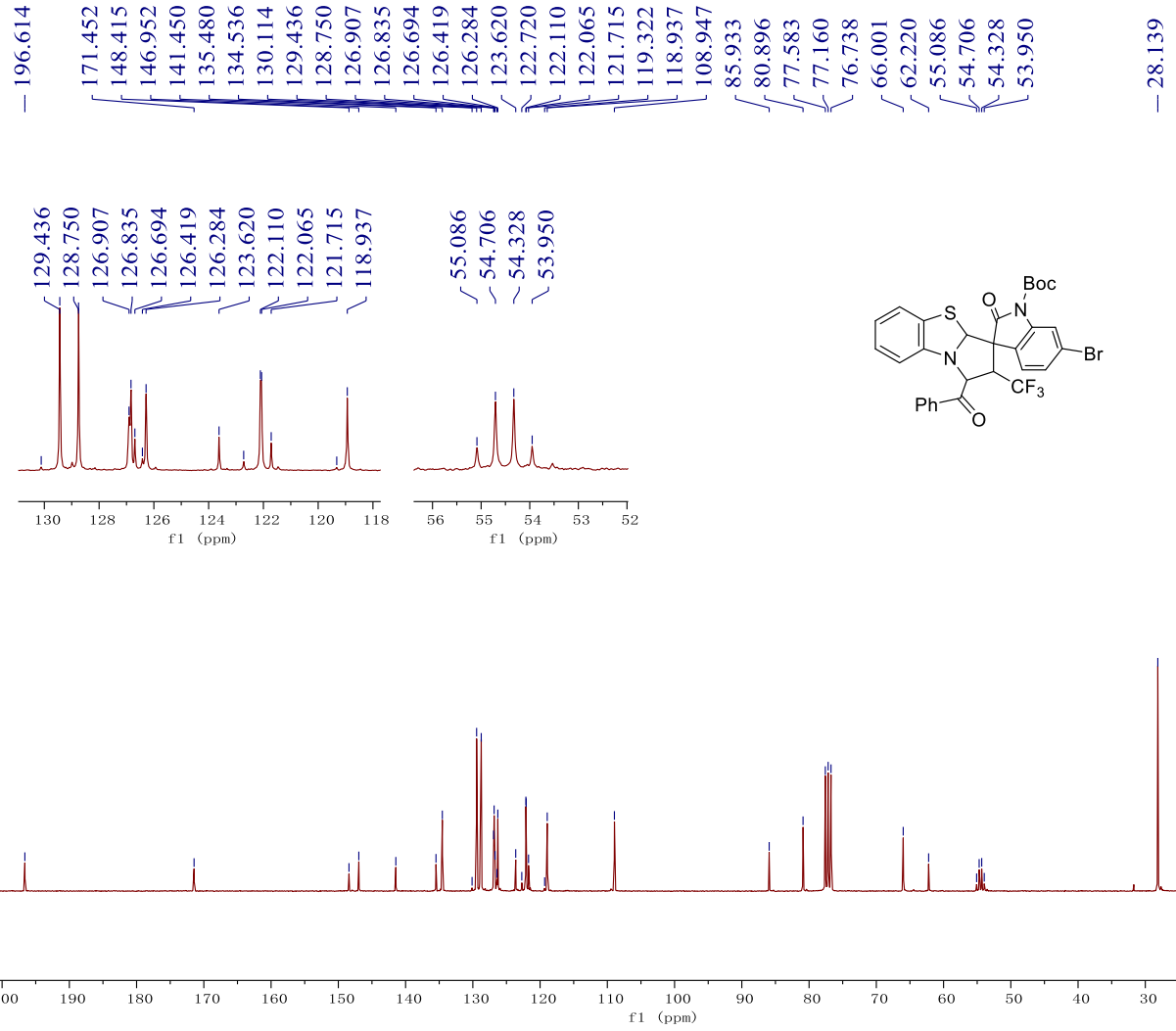
^{13}C NMR (75 MHz, $CDCl_3$) of **5ac**



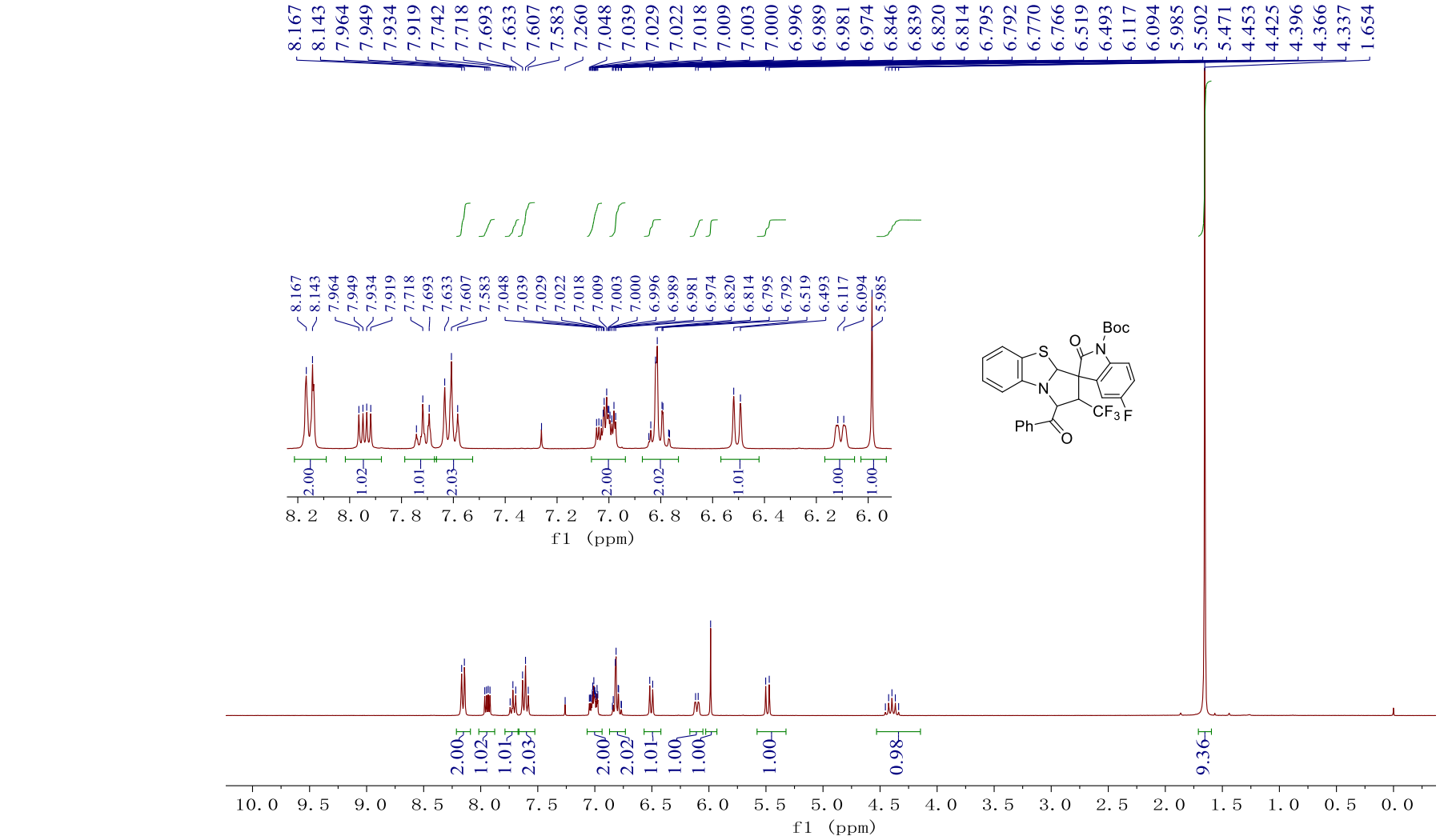
^{1}H NMR (300 MHz, $CDCl_3$) of **5ad**



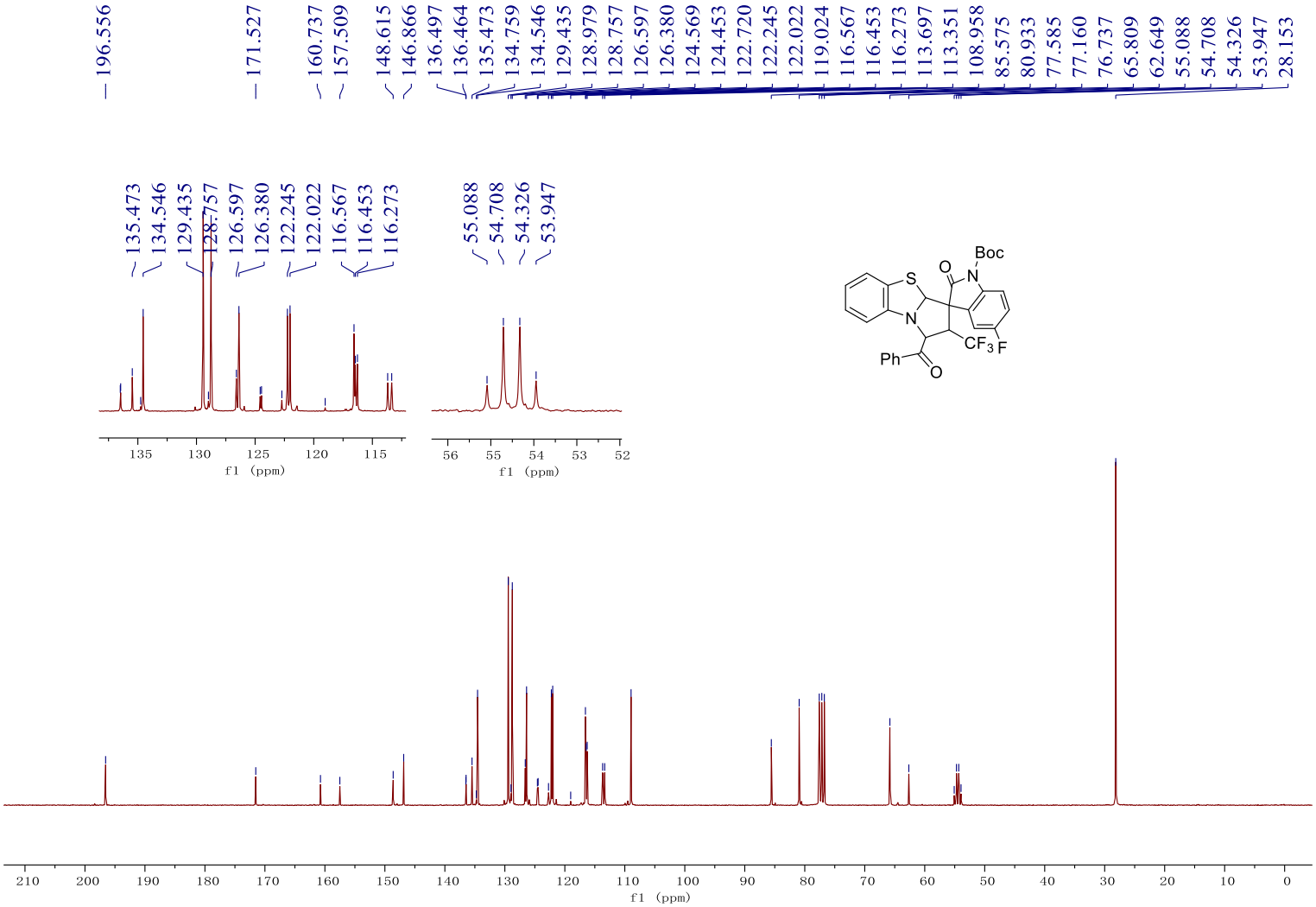
^{13}C NMR (75 MHz, $CDCl_3$) of **5ad**



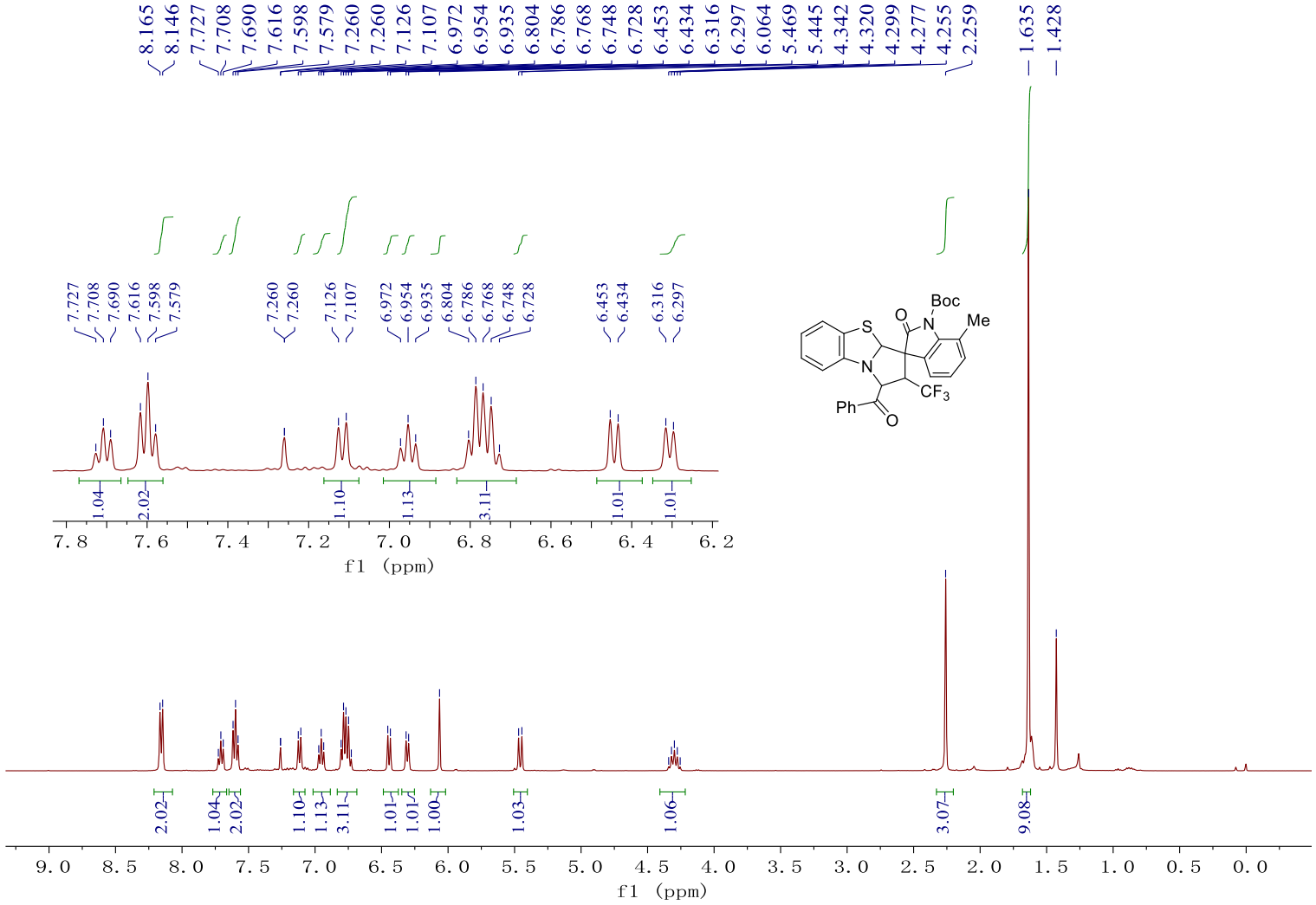
^{1}H NMR (300 MHz, $CDCl_3$) of **5ae**



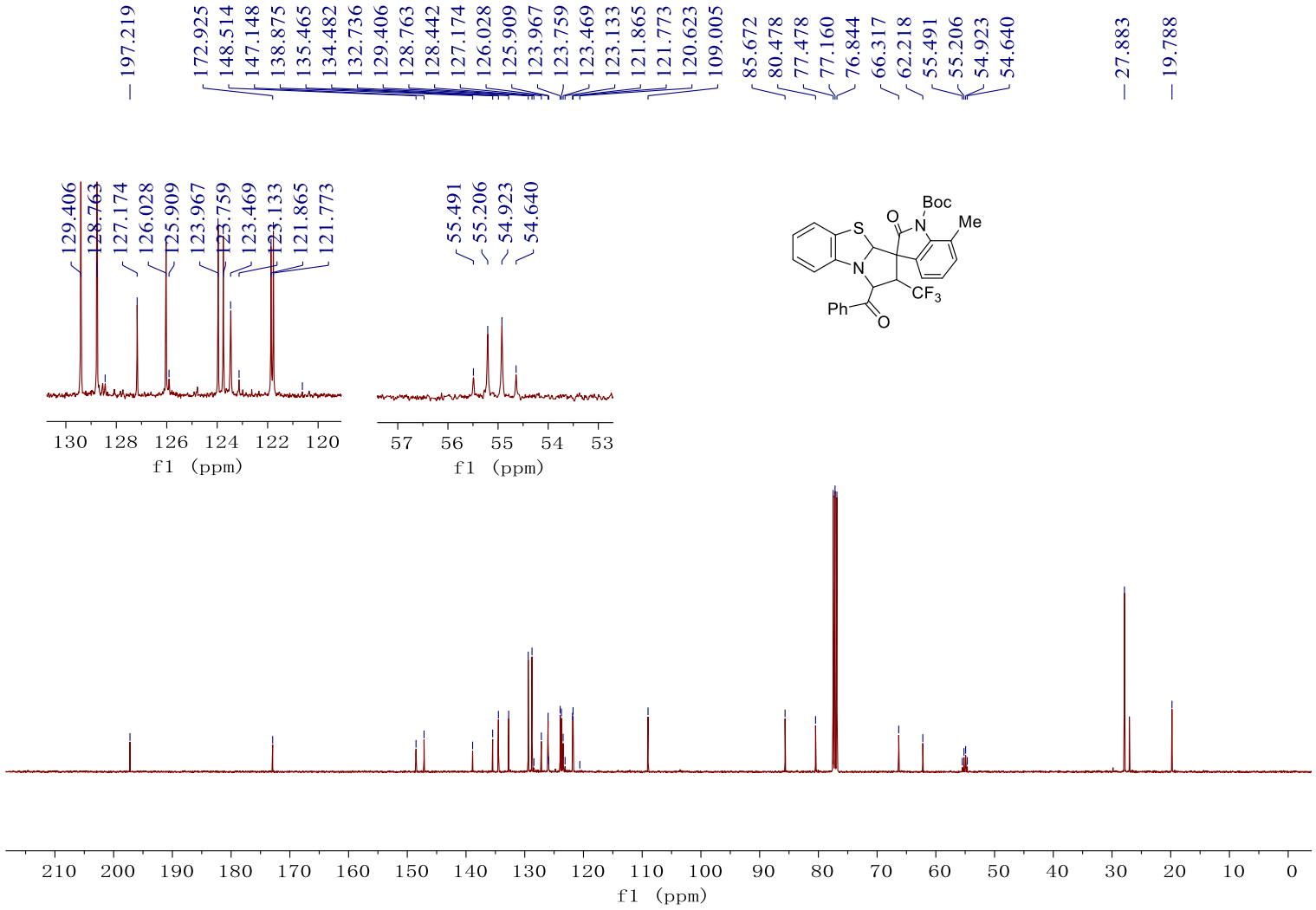
^{13}C NMR (75 MHz, $CDCl_3$) of **5ae**



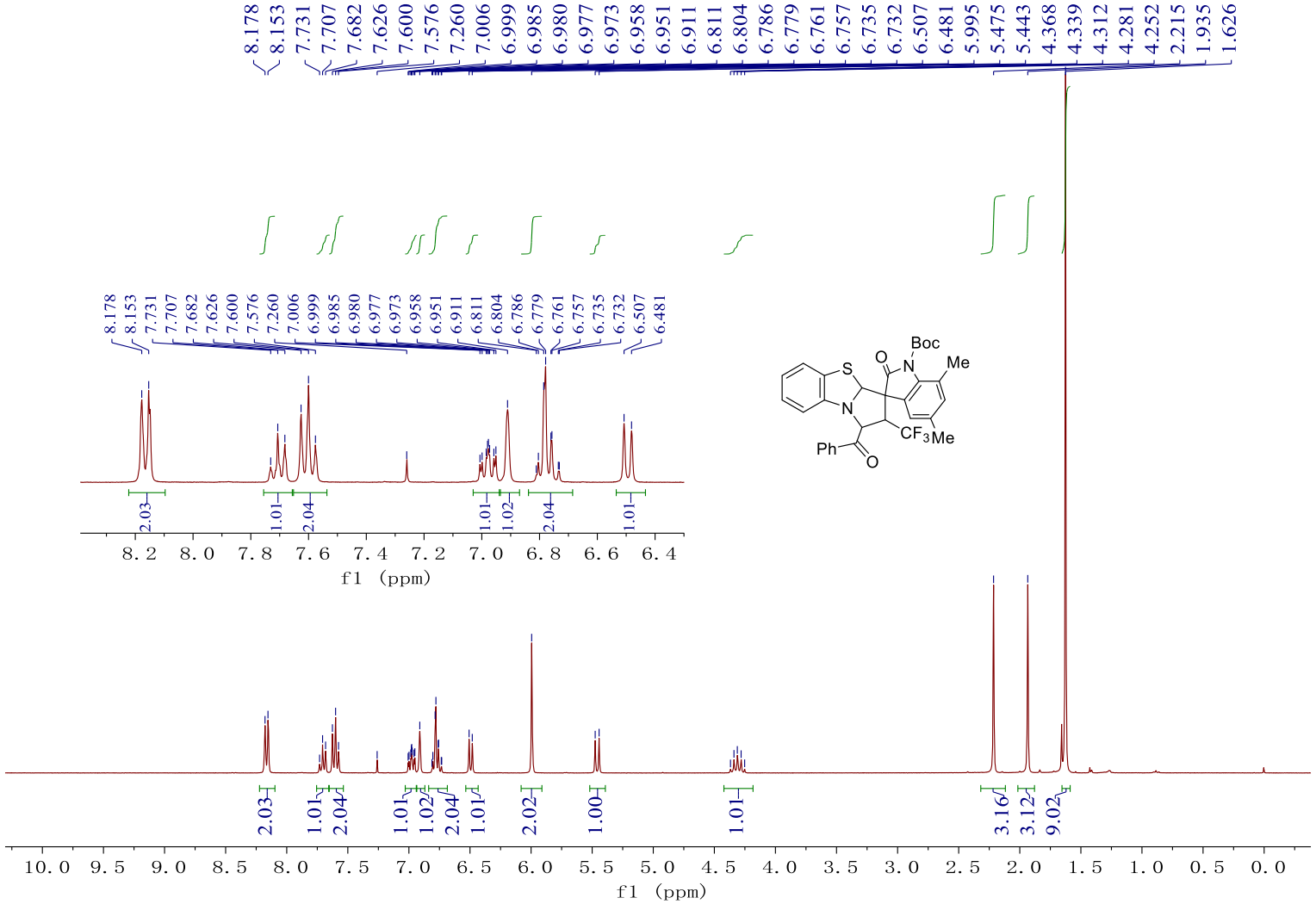
^{1}H NMR (400 MHz, $CDCl_3$) of **5af**



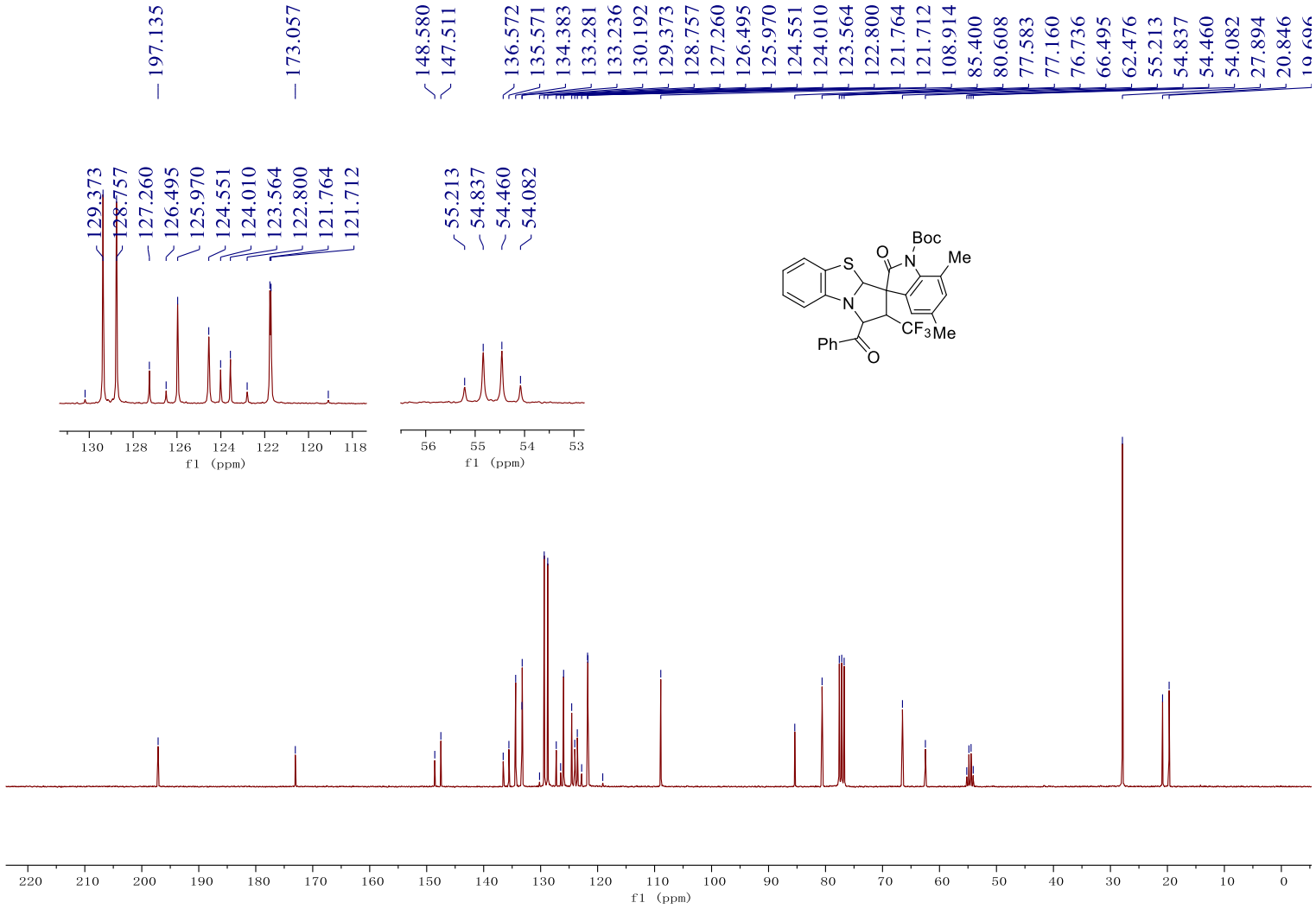
^{13}C NMR (101 MHz, $CDCl_3$) of **5af**



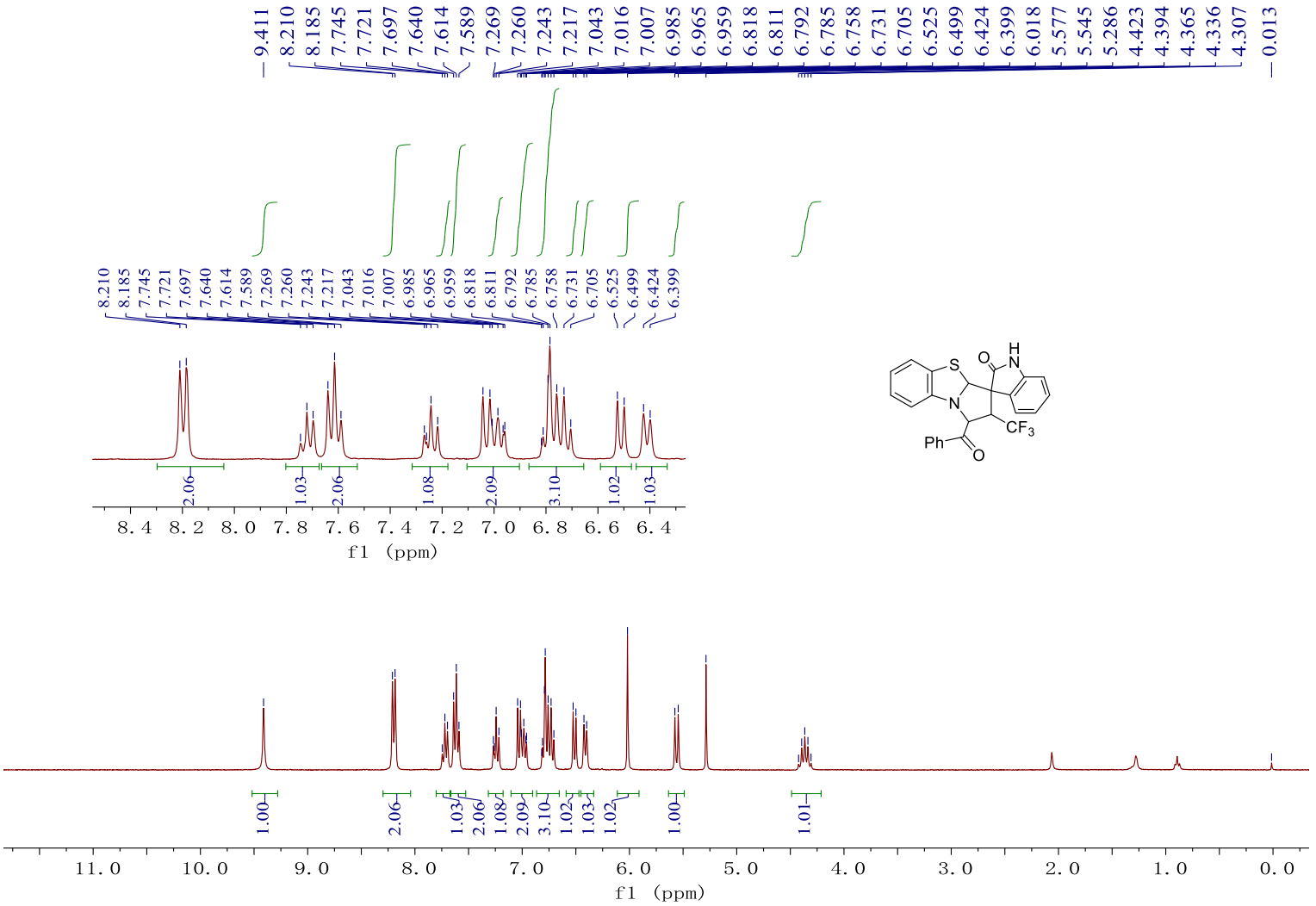
^{1}H NMR (300 MHz, $CDCl_3$) of **5ag**



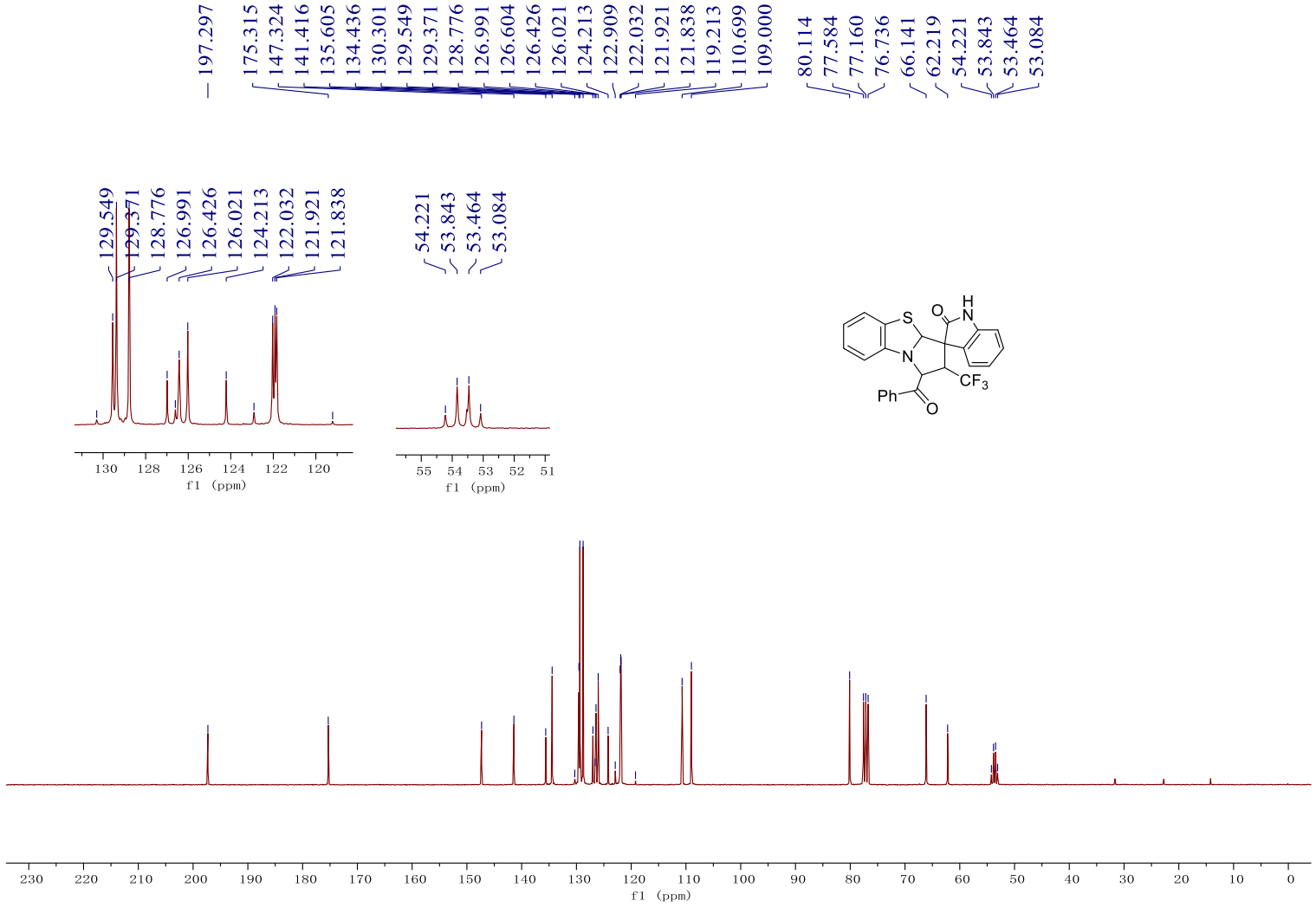
^{13}C NMR (75 MHz, $CDCl_3$) of **5ag**



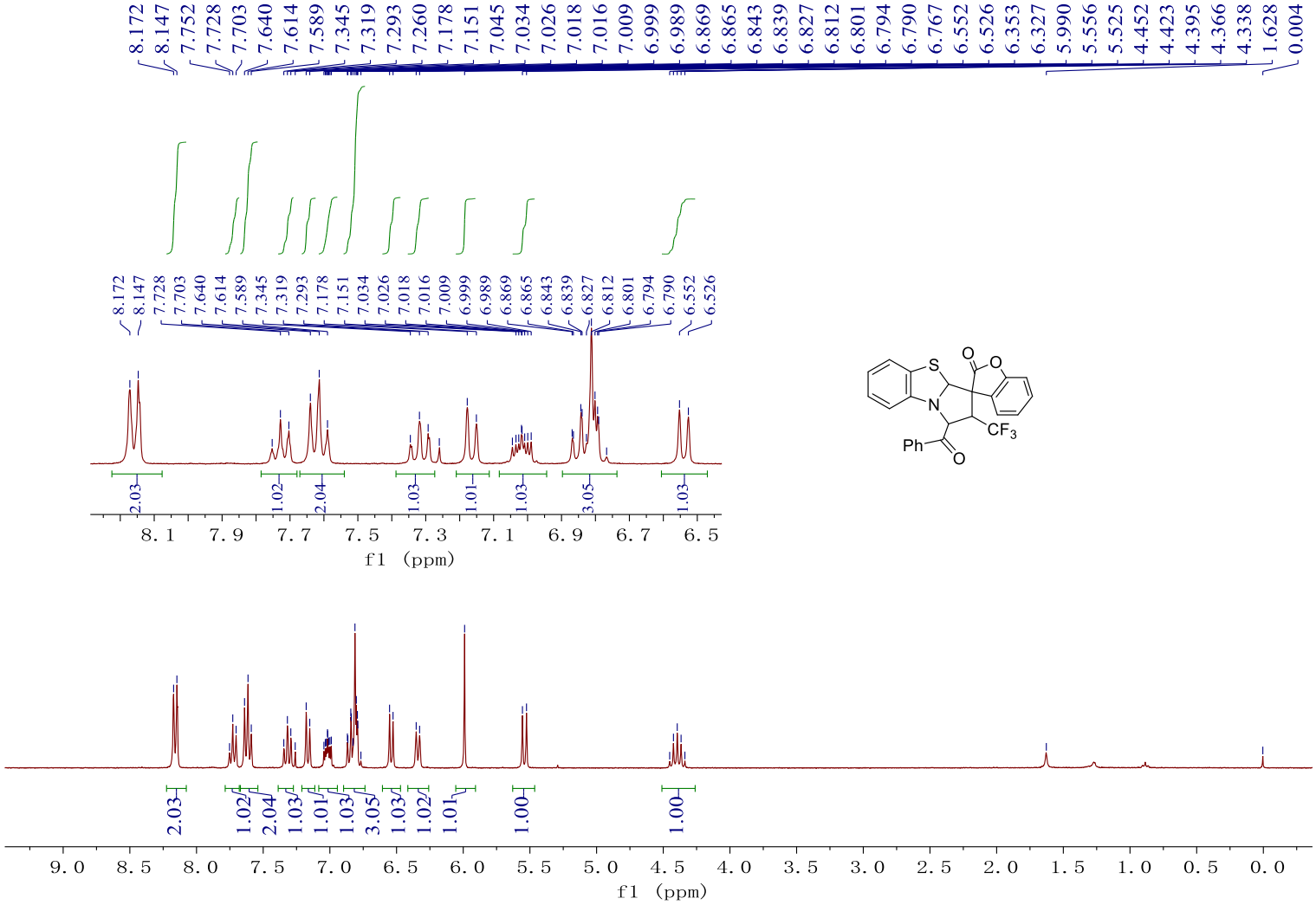
^{1}H NMR (300 MHz, $CDCl_3$) of **5ah**



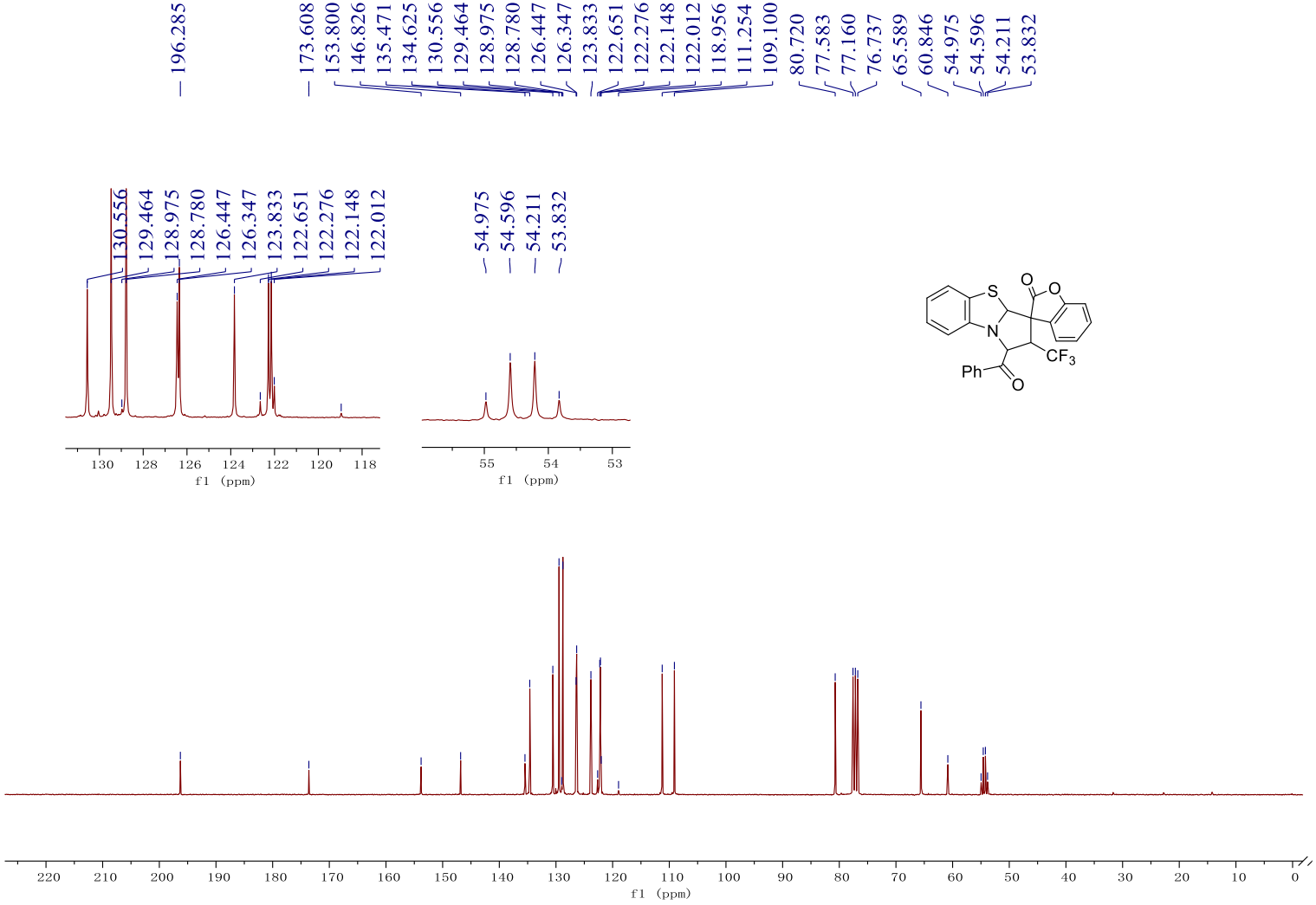
^{13}C NMR (75 MHz, $CDCl_3$) of **5ah**



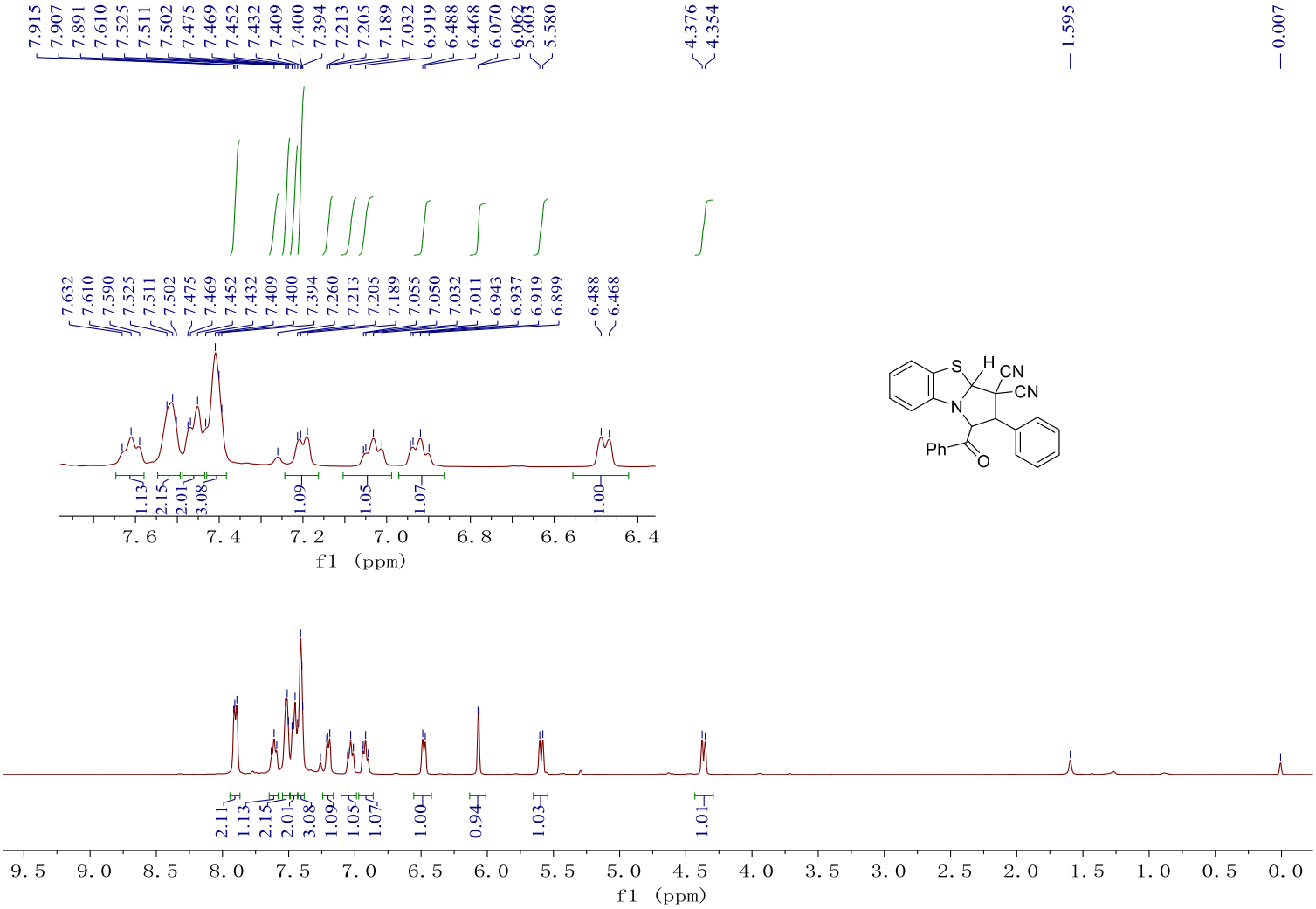
^{1}H NMR (300 MHz, $CDCl_3$) of **5ai**



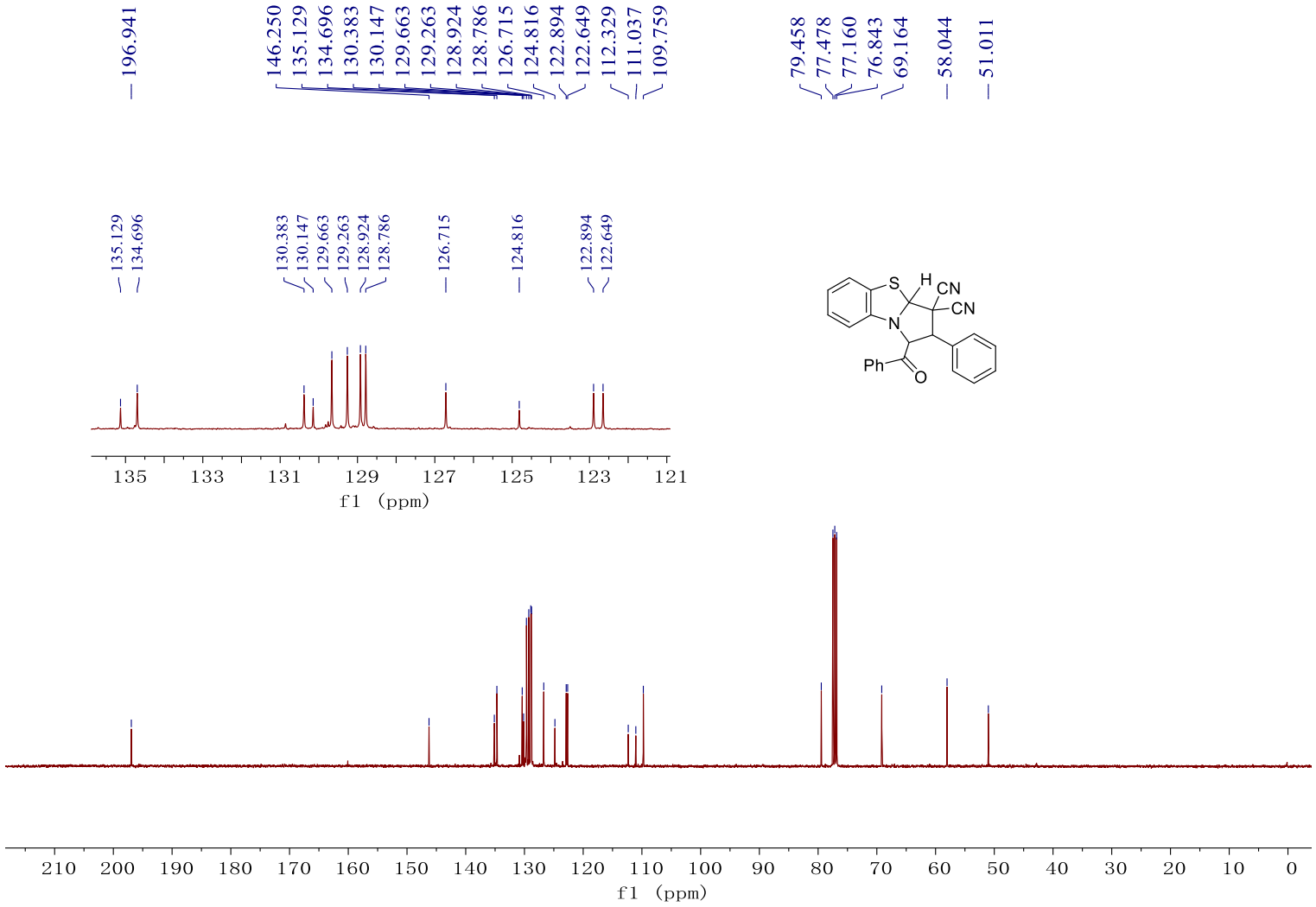
^{13}C NMR (75 MHz, $CDCl_3$) of **5ai**



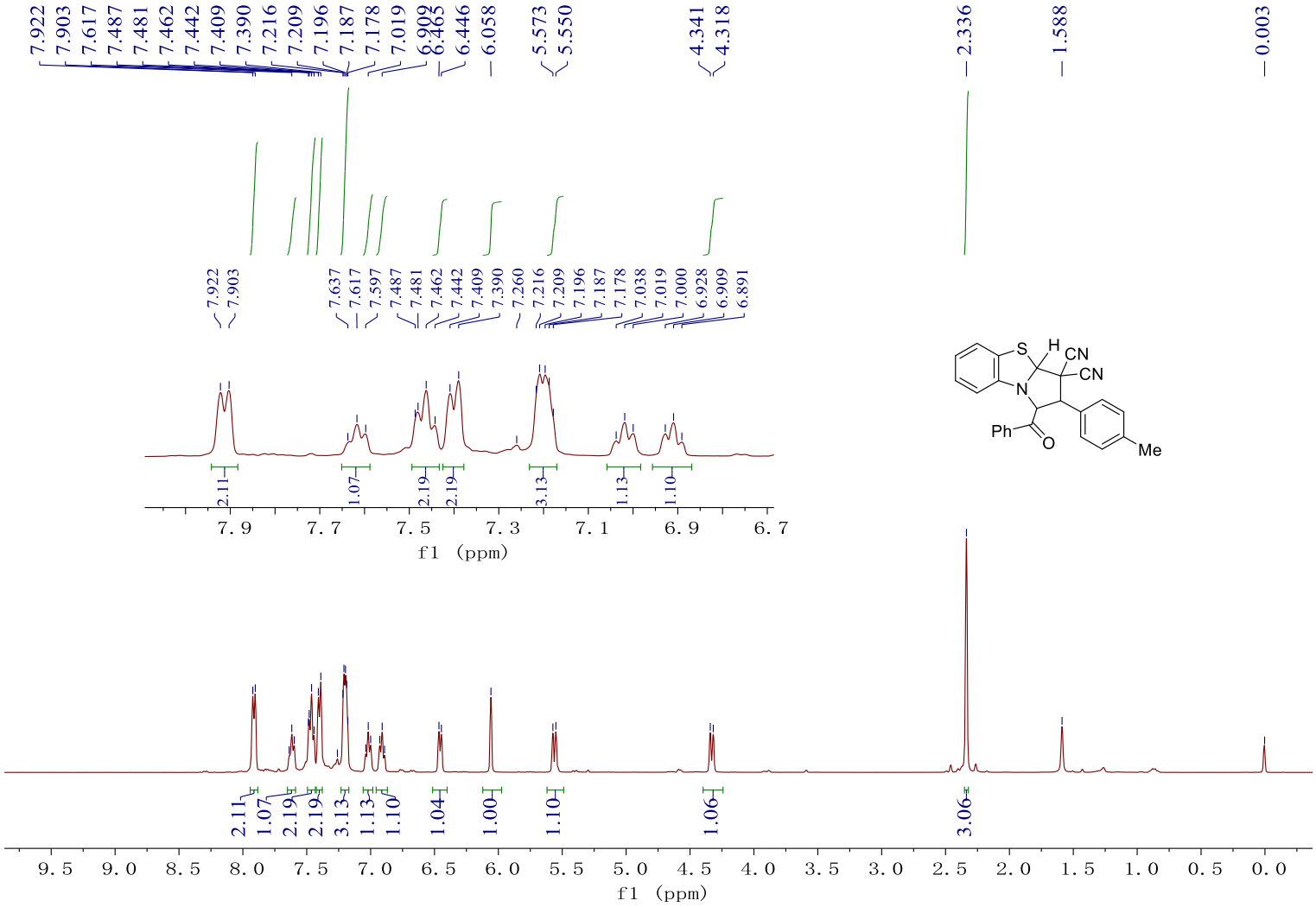
^{1}H NMR (400 MHz, $CDCl_3$) of **7aa**



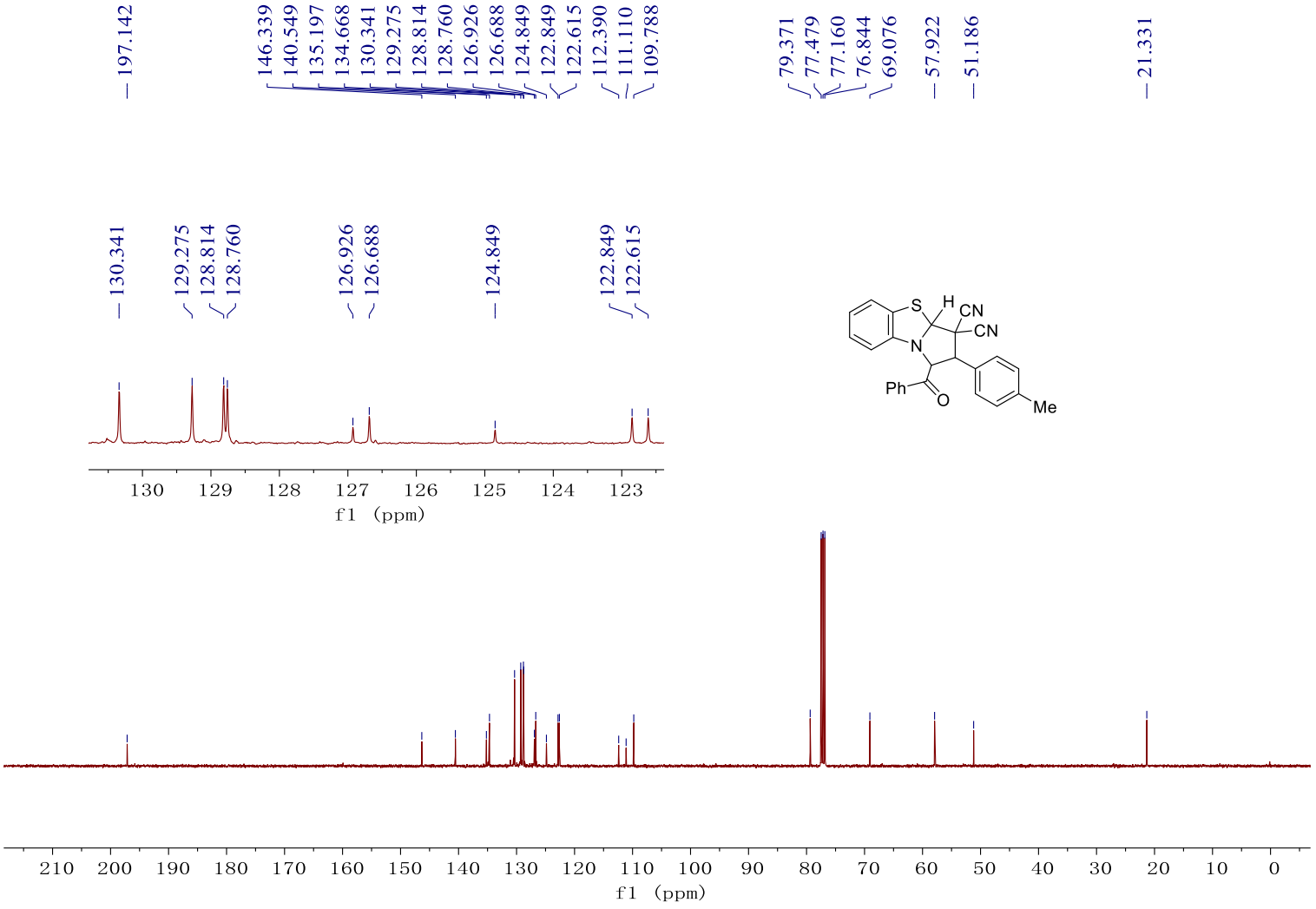
^{13}C NMR (101 MHz, $CDCl_3$) of **7aa**



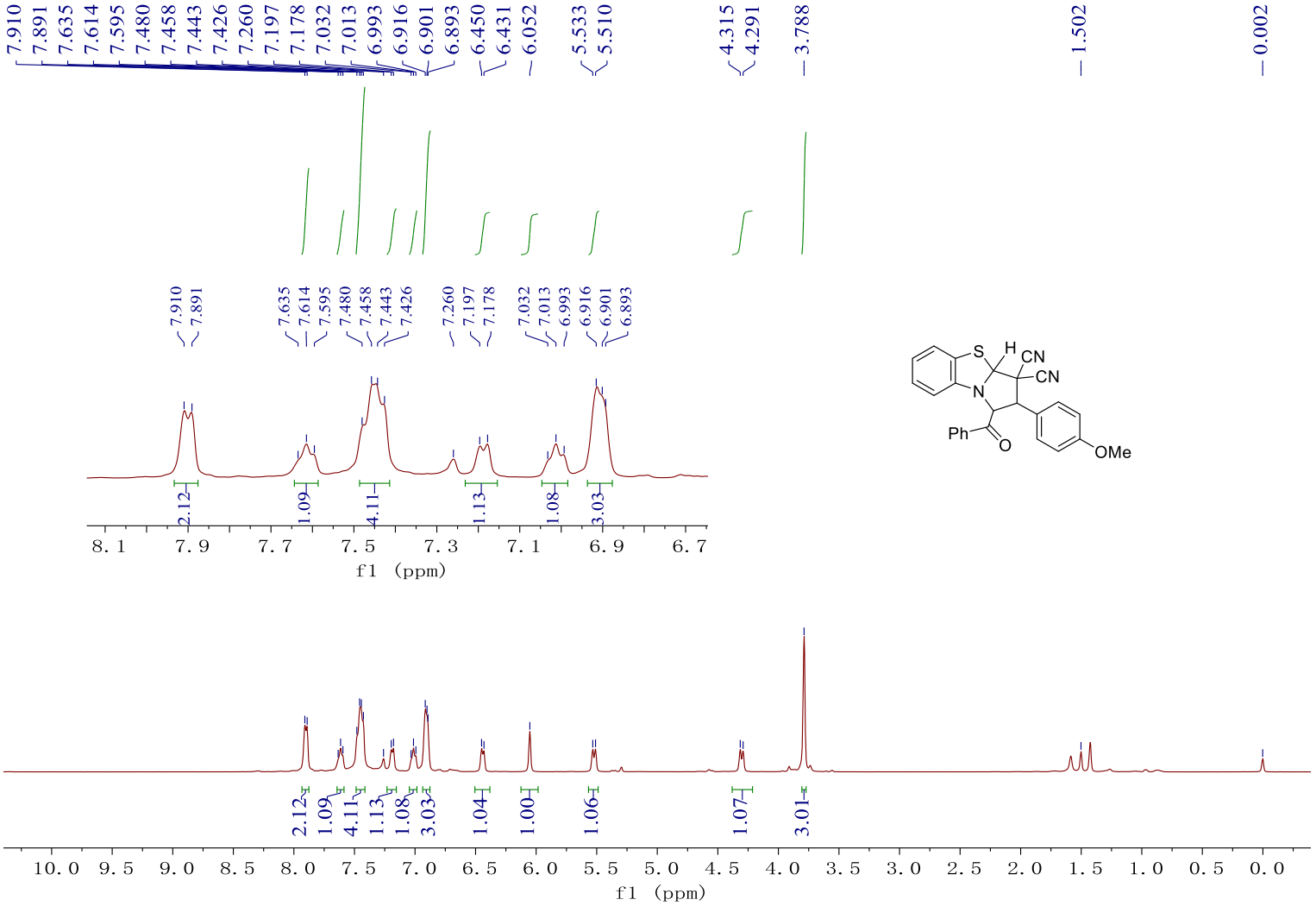
^{1}H NMR (400 MHz, $CDCl_3$) of **7ab**



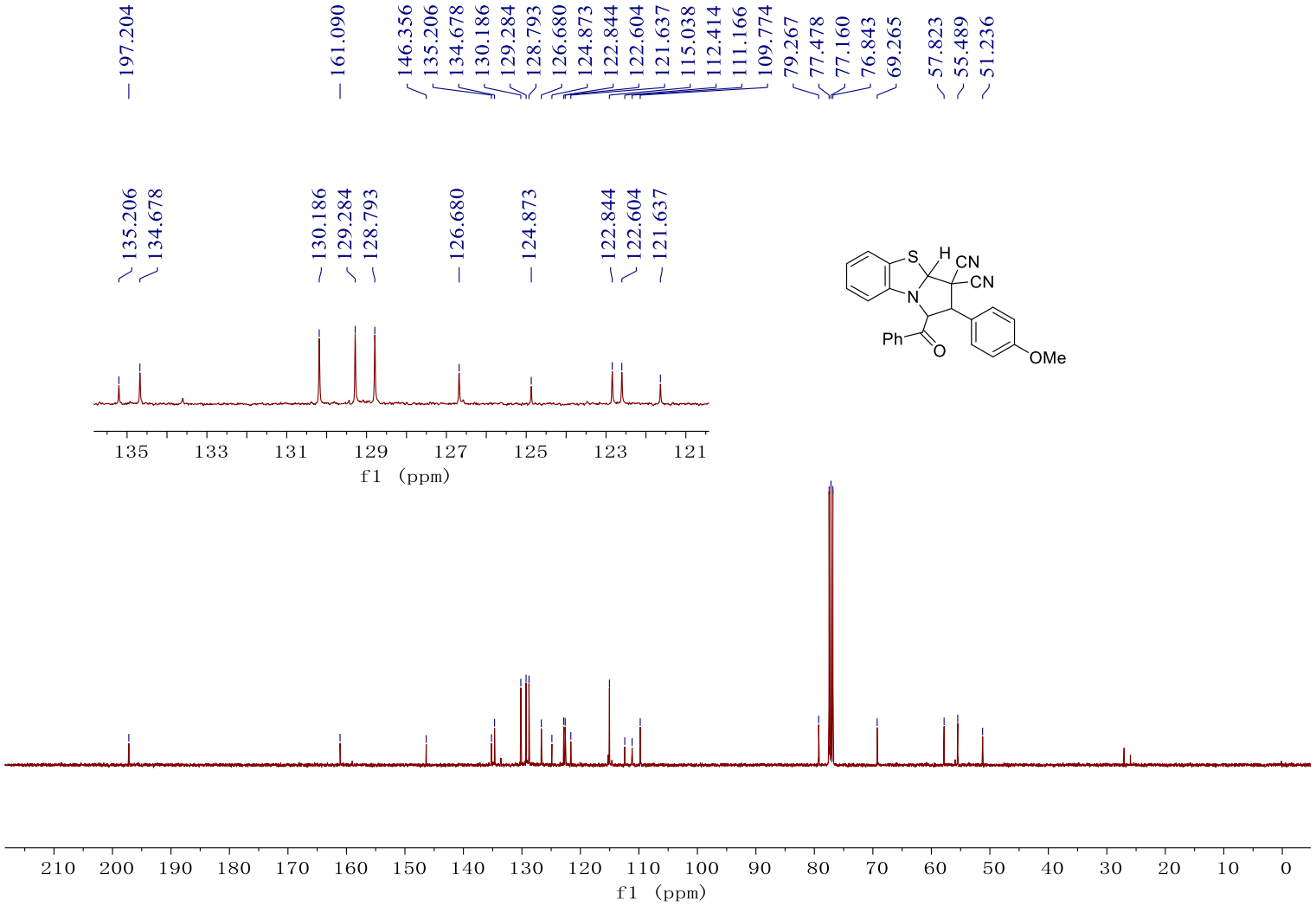
^{13}C NMR (101 MHz, $CDCl_3$) of **7ab**



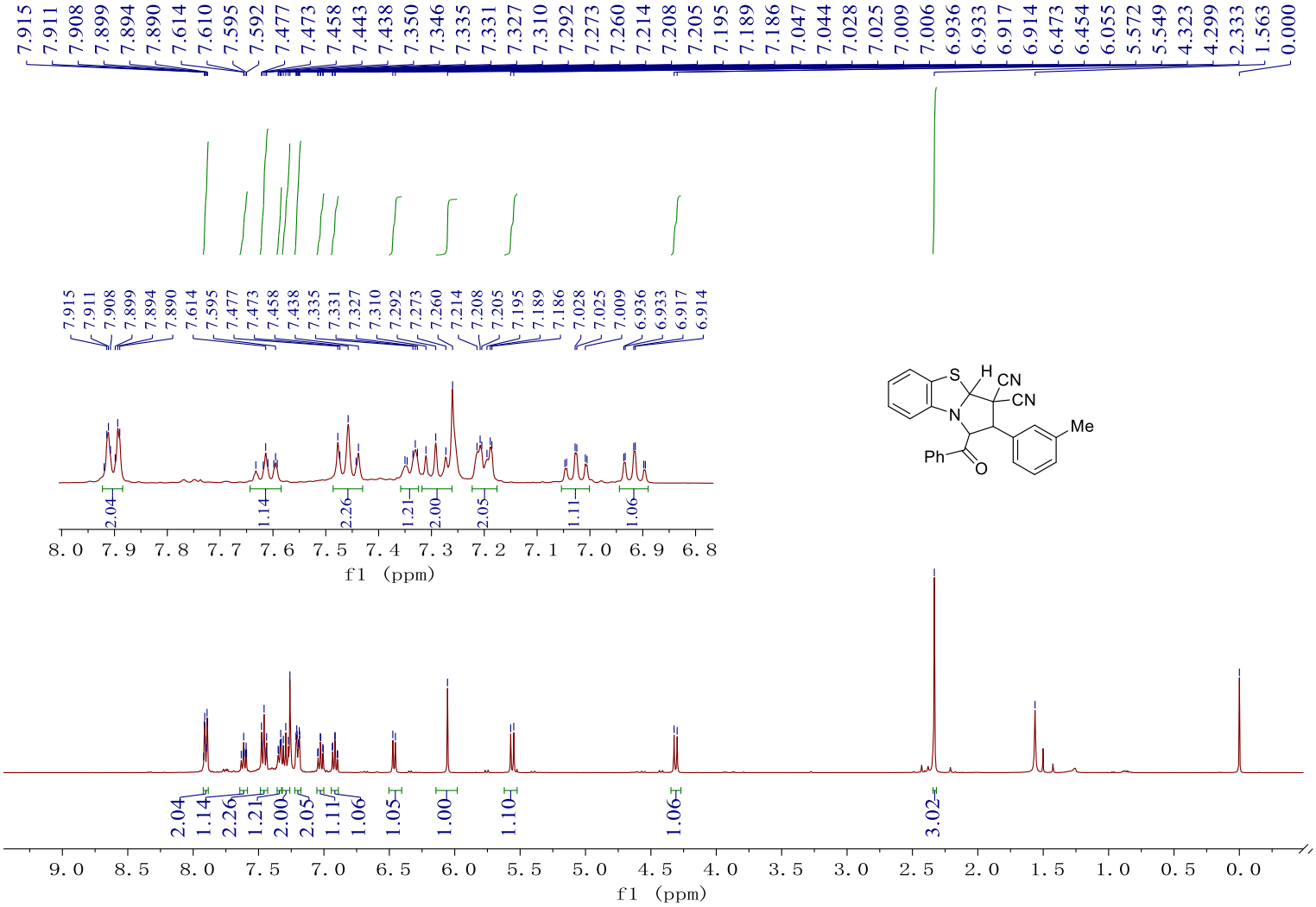
^{1}H NMR (400 MHz, $CDCl_3$) of **7ac**



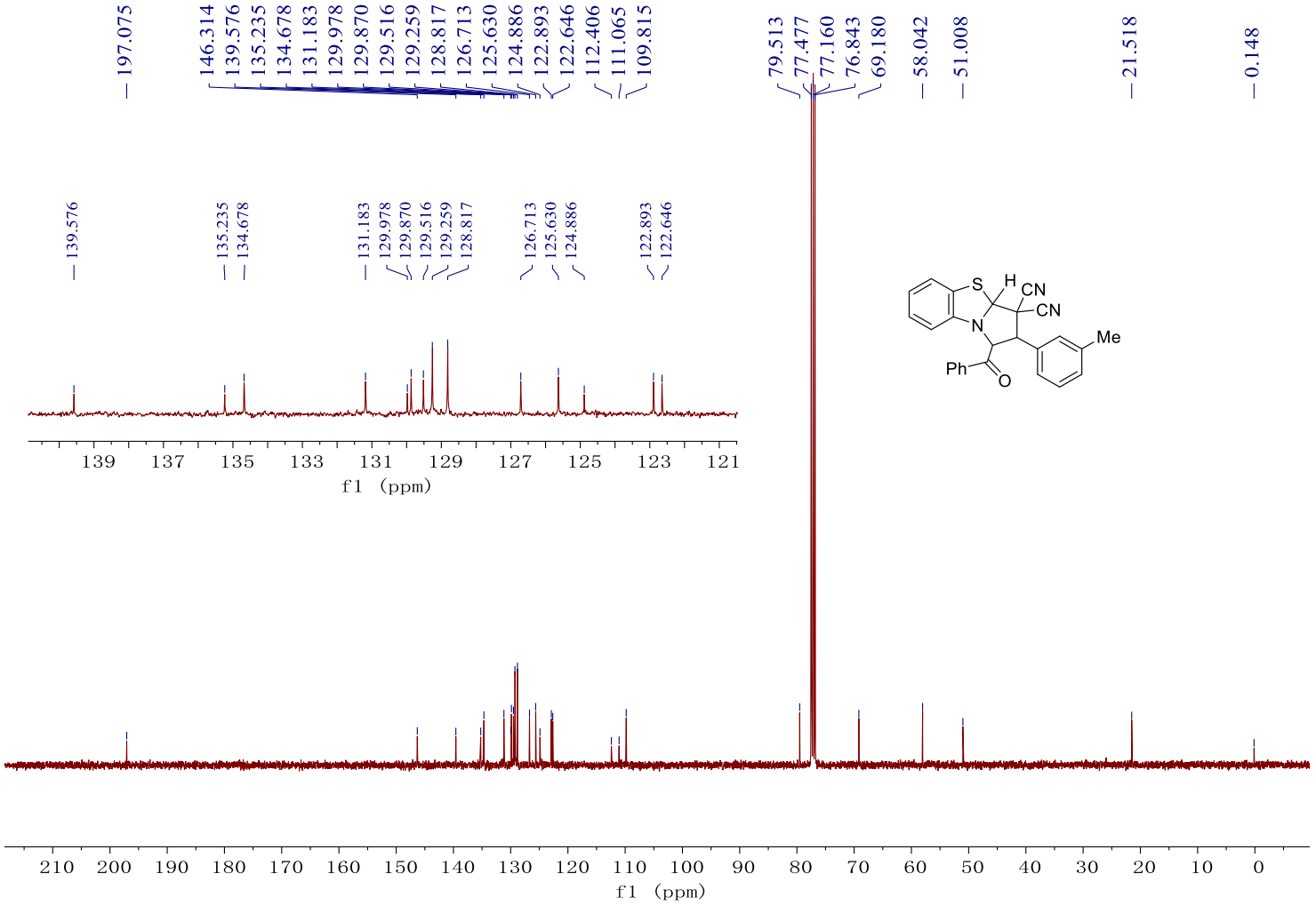
^{13}C NMR (101 MHz, $CDCl_3$) of **7ac**



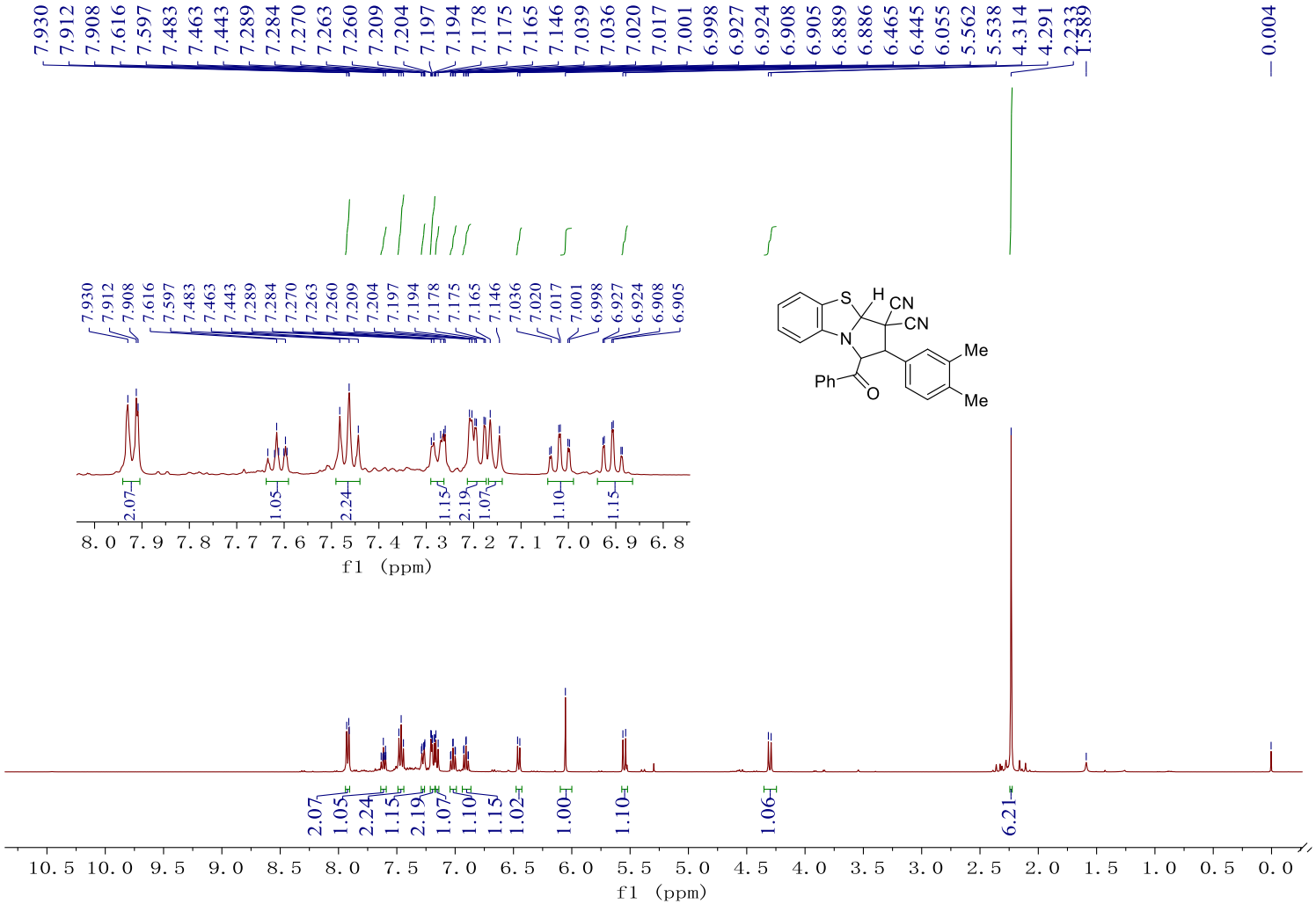
^{1}H NMR (400 MHz, $CDCl_3$) of **7ad**



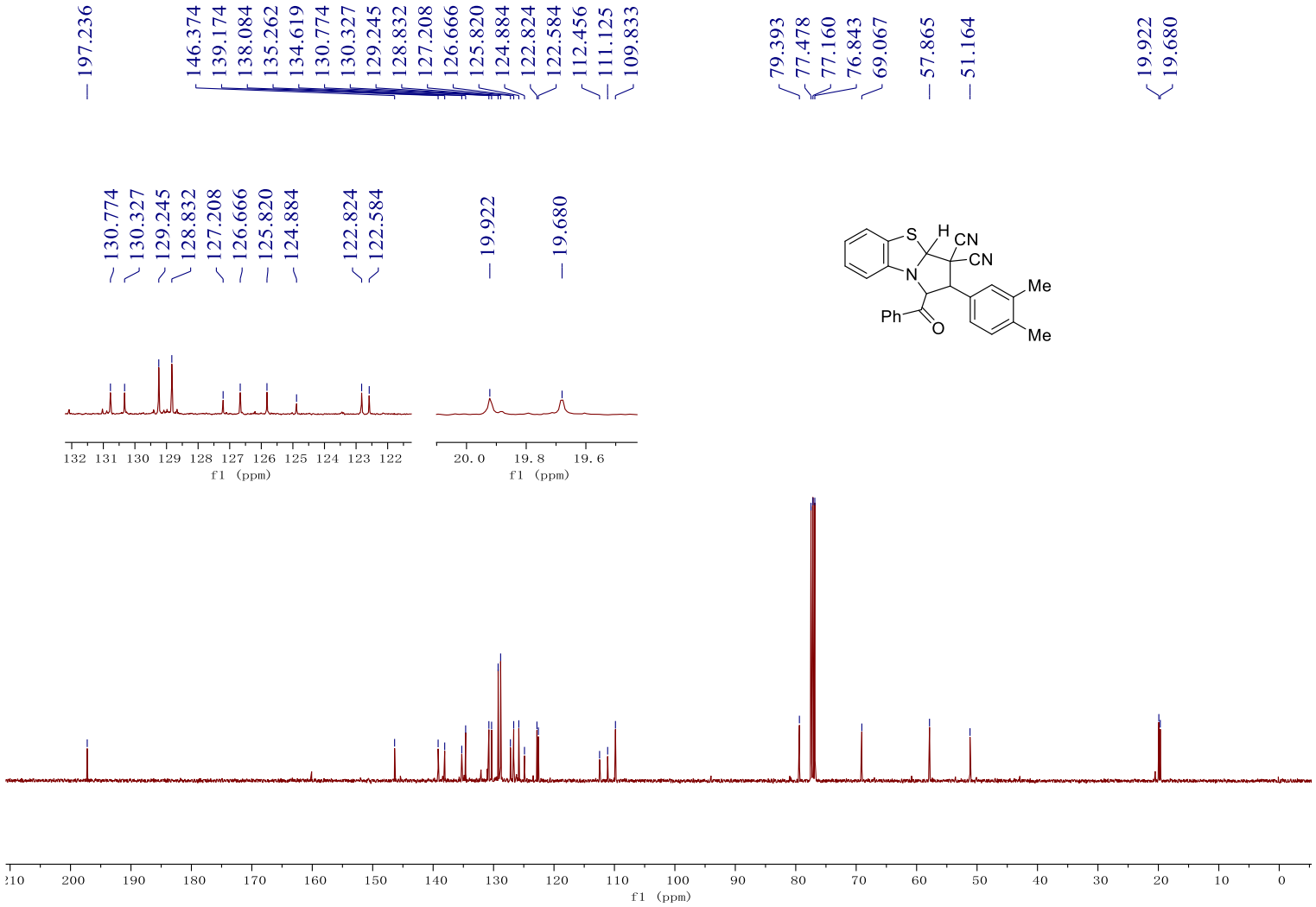
^{13}C NMR (101 MHz, $CDCl_3$) of **7ad**



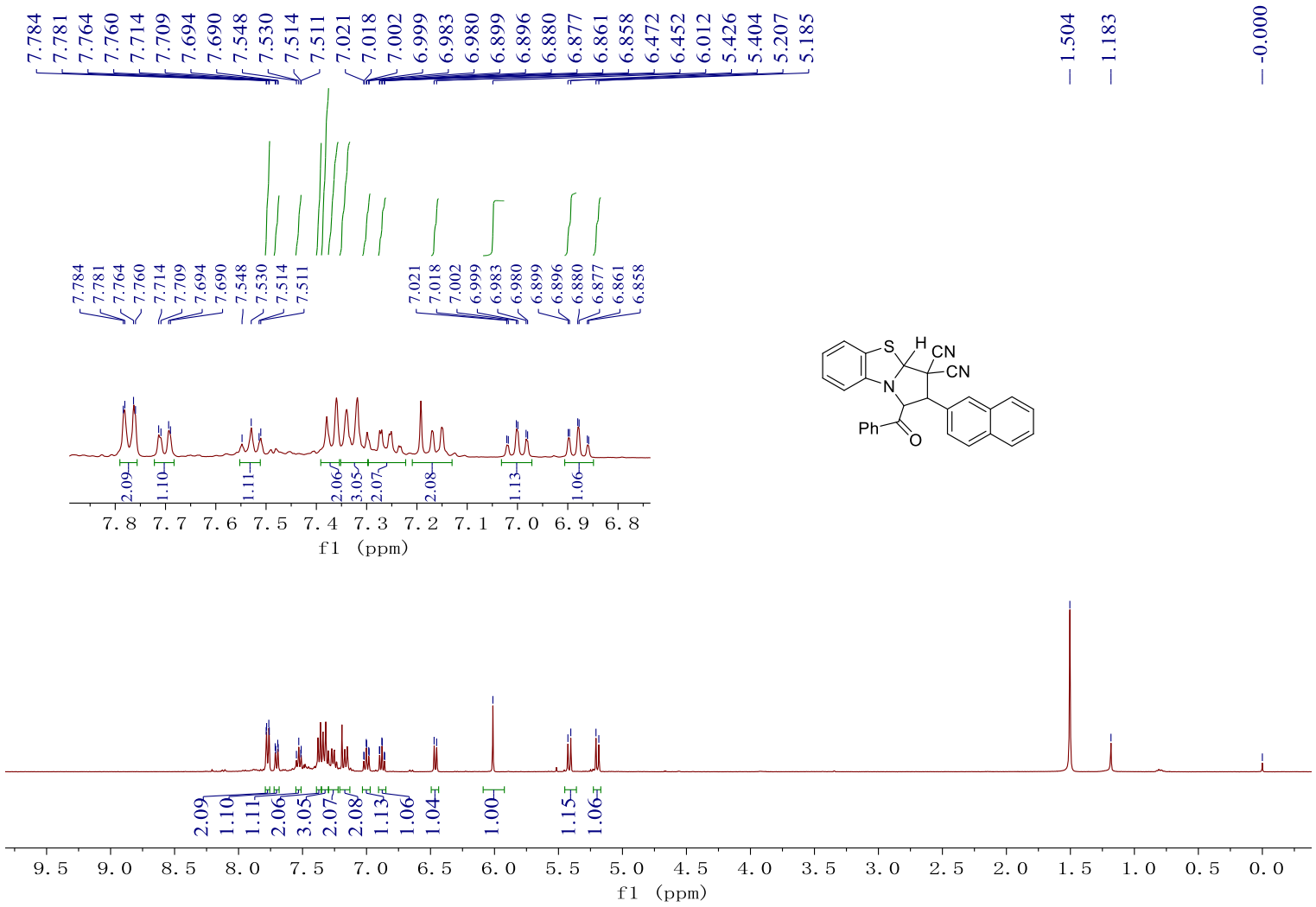
^{1}H NMR (400 MHz, $CDCl_3$) of **7ae**



^{13}C NMR (101 MHz, $CDCl_3$) of **7ae**



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



^{13}C NMR (101 MHz, $CDCl_3$) of **7af**