Supplementary Information

Diastereoselective synthesis of benzazocines by $Zn(OTf)_2$-catalyzed (4+4) cyclocondensation of multisubstituted donor-acceptor cyclopropanes with anthranils

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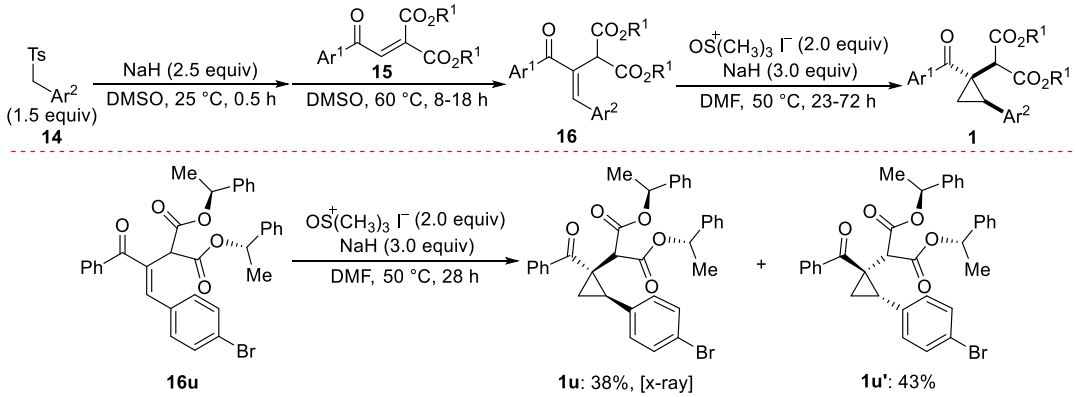
Contents

1. General information

All reactions between the D–A cyclopropanes **1** with anthranils **2** were carried out with flame-dried Schlenk-type glassware using a Schlenk line. The cyclopropanes **1** were prepared according to the related literature.[1] Anthranils **2** are known products and prepared according to the related literature.[2] All other reagents were purchased from commercial suppliers and purified by standard techniques, and the purified solvents were stored over activated molecular sieves 4Å. Flash column chromatography was performed using silica gel (200–400 mesh). Thin-layer chromatography (TLC) was performed on silica gel plates (HSGF 254). Visualization of the developed chromatogram was performed by UV light, staining with iodine (dispersed in silica gel), or by $KMnO_4$ stain. ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) and ^{19}F NMR (470) spectra were recorded in $CDCl_3$. Data for $^{13}C\{^1H\}$ NMR were recorded with broad-band proton decoupling technique. The NMR data of compound **12** was acquired at –50 °C. Structural assignments for compounds **11** and **13** were made with additional information from gCOSY, gHSQC experiments. All chemical shifts (δ) are given in ppm relative to TMS (δ = 0 ppm) as internal standard. Data are reported as follows: chemical shift, multiplicity, coupling constants and integration. Melting points were uncorrected. High resolution mass spectral (HRMS) data were obtained with an ionization mode of APCI/ESI and a TOF analyzer.

2. Experimental procedures

2.1 General procedures for the preparation of cyclopropanes 1[1]



Aryl *p*-tolyl sulfones **14**[3a], 2-aroylmethylenemalonates **15**[3b] were prepared according to related literatures.

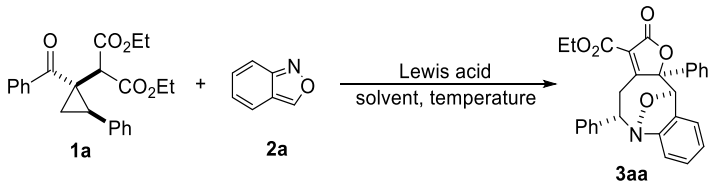
Under an argon atmosphere, to an oven-dried Schlenk tube containing a magnetic stirring bar was added **14** (4.5 mmol, 1.5 equiv)**,** 60% NaH (0.3 g, 7.5 mmol, 2.5 equiv), and DMSO (20 mL). The mixture was stirred at r.t about 30 mins, then **15** (3 mmol, 1 equiv) was added. The resulting mixture was stirred at 60 °C in metal sand bath until the disappearance of **15** as monitored by TLC. Then the reaction mixture was cooled down to room temperature and quenched with saturated NH_4Cl (30 mL). The resulting mixture was extracted with ethyl acetate (100 mL × 3). The organic layer was washed with brine (20 mL × 3), and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by chromatography on silica gel

to afford the product **16**.

Under an argon atmosphere, to an oven-dried Schlenk tube containing a magnetic stirring bar was added **16** (2 mmol, 1 equiv), trimethylsulfoxonium iodide (0.88 g, 4 mmol, 2 equiv), 60% sodium hydride (0.24 g, 6 mmol, 3 equiv), DMF (20 mL). The above mixture was stirred at 50 °C in metal sand bath until the disappearance of **16** as monitored by TLC. The reaction mixture was cooled down to room temperature and quenched with saturated NH_4Cl (30 mL). The resulting mixture was extracted with ethyl acetate (100 mL × 3). The organic layer was washed with brine (20 mL × 3), and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by chromatography on silica gel to afford the cyclopropanes **1**. For the preparation of enantioenriched products **1u** and **1u'**, commercial enantioenriched (*S*)-1-phenylethanol (98% ee) was used.

2.2 Optimization of the (4+4) cyclocondensation reaction conditions

Table S1 Optimization of reaction conditions for the (4+4) annulation of the D-A cyclopropane **1a** with anthranils[a]



entry	**2a** (equiv)	LA (*x* mol %)	solvent	temperature (°C)	time (days)	yield[b](%)
1	2.0	no	1,2-DCE	25	7	NR
2	2.0	no	1,2-DCE	60	7	NR
3	2.0	no	1,2-DCE	90	7	complicated
4	2.0	$Sc(OTf)_3$ (5)	1,2-DCE	25	7	NR
5	2.0	$Sc(OTf)_3$ (5)	1,2-DCE	40	7	NR
6	2.0	$Sc(OTf)_3$ (5)	1,2-DCE	60	7	13
7	2.0	$Y(OTf)_3$ (5)	1,2-DCE	60	7	15
8	2.0	$La(OTf)_3$ (5)	1,2-DCE	60	7	24
9	2.0	$Sm(OTf)_3$ (5)	1,2-DCE	60	7	trace
10	2.0	$Er(OTf)_3$ (5)	1,2-DCE	60	7	15
11	2.0	$Yb(OTf)_3$ (5)	1,2-DCE	60	7	11
12	2.0	$Mg(OTf)_2$ (5)	1,2-DCE	60	7	complicated
13	2.0	$Al(OTf)_3$ (5)	1,2-DCE	60	7	complicated
14	2.0	$Fe(OTf)_3$ (5)	1,2-DCE	60	7	complicated
15	2.0	$Cu(OTf)_2$ (5)	1,2-DCE	60	7	trace
16	2.0	$Zn(OTf)_2$ (5)	1,2-DCE	60	7	28
17	2.0	$Sn(OTf)_2$ (5)	1,2-DCE	60	7	16
18	2.0	$BF_3 \cdot Et_2O$ (5)	1,2-DCE	60	7	NR
19	2.0	$AlCl_3$ (5)	1,2-DCE	60	7	complicated
20	2.0	$FeCl_3$ (5)	1,2-DCE	60	7	complicated
21	2.0	$MgBr_2$ (5)	1,2-DCE	60	7	complicated
22	2.0	MgI_2 (5)	1,2-DCE	60	7	complicated
23	2.0	CaI_2 (5)	1,2-DCE	60	7	trace
24	2.0	$La(OTf)_3$ (5)	1,2-DCE	80	4	37
25	2.0	$La(OTf)_3$ (5)	1,2-DCE	90	2.5	53
26	2.0	$La(OTf)_3$ (5)	1,2-DCE	100	2	49

27	2.0	$Zn(OTf)_2$ (5)	1,2-DCE	80	4	58
28	2.0	$Zn(OTf)_2$ (5)	1,2-DCE	90	2.5	65
29	2.0	$Zn(OTf)_2$ (5)	1,2-DCE	100	2	57
30	2.0	$Zn(OTf)_2$ (10)	1,2-DCE	90	2.5	55
31	2.0	$Zn(OTf)_2$ (2)	1,2-DCE	90	2.5	80
32[c]	2.0	$Zn(OTf)_2$ (2)	1,2-DCE	90	2.5	80 (0.95 g)
33	2.0	$Zn(OTf)_2$ (1)	1,2-DCE	90	2.5	74
34	2.0	$Zn(OTf)_2$ (2)	DCM	reflux	2.5	NR
35	2.0	$Zn(OTf)_2$ (2)	DMSO	90	2.5	NR
36	2.0	$Zn(OTf)_2$ (2)	ethyl ether	reflux	2.5	NR
37	2.0	$Zn(OTf)_2$ (2)	dioxane	90	2.5	62
38	2.0	$Zn(OTf)_2$ (2)	THF	reflux	2.5	45
39	2.0	$Zn(OTf)_2$ (2)	toluene	90	2.5	65
40	3.0	$Zn(OTf)_2$ (2)	1,2-DCE	90	2.5	87
41	4.0	$Zn(OTf)_2$ (2)	1,2-DCE	90	2.5	96
42[d]	4.0	$Zn(OTf)_2$ (2)	1,2-DCE	90	2.5	98 (1.34 g)
43	4.0	$La(OTf)_3$ (2)	1,2-DCE	90	2.5	61
44	4.0	$Sc(OTf)_3$ (2)	1,2-DCE	90	2.5	25
45	4.0	$Sn(OTf)_2$ (2)	1,2-DCE	90	2.5	10

[a]The reaction was conducted with 0.1 mmol of **1a** in 1 mL of solvent. [b]Isolated yields. [c]Run with 2.63 mmol of **1a**. [d]Run with 3 mmol of **1a**.

2.3 General procedure for the synthesis of products 3

Under an argon atmosphere, to an oven-dried Schlenk tube containing a magnetic stirring bar was added cyclopropanes **1** (0.2 mmol, 1 equiv), anthranils **2** (0.8 mmol, 4 equiv), 1,2-DCE (2 mL) and $Zn(OTf)_2$ (1.45 mg, 0.004 mmol, 2 mol%). The reaction mixture was stirred at 90 °C in metal sand bath for 2.5 days. After the reaction was finished, the organic solvent was removed under reduced pressure. Then the crude mixture was purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 5/1) to furnish the desired products **3**.

2.4 Procedure for the preparation of 3aa on gram-scale

Under an argon atmosphere, to an oven-dried Schlenk tube containing a magnetic stirring bar was added cyclopropane **1a** (1.14 g, 3 mmol, 1 equiv), anthranil **2a** (1.428 g, 12 mmol, 4 equiv), 1,2-DCE (40 mL) and $Zn(OTf)_2$ (21.8 mg, 0.06 mmol, 2 mol%). The reaction mixture was stirred at 90 °C in metal sand bath for 2.5 days. After the reaction was finished, the organic solvent was removed under reduced pressure. Then the crude mixture was purified by column chromatography (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 5/1) to furnish the desired products **3aa** in 98% yield (1.34 g, 2.95 mmol).

2.5 Procedure for the reduction of 3aa

Under an argon atmosphere, the cycloadduct **3aa** (415 mg, 0.91 mmol) was dissolved in THF (20 mL), and cooled down to 0 °C, and then $LiAlH_4$ (104 mg, 2.73 mmol, 3 equiv) was added into the solution. The reaction mixture was stirred at room temperature. When the cycloadduct **3aa** disappeared (monitored by TLC),

the reaction mixture was quenched with H_2O and NaOH, and then passed over a plug of celite with 50 mL of MeOH. The filtrate was removed under reduced pressure and the residue was purified by silica gel column chromatography (eluting with petroleum ether/ethyl acetate (v/v): 6/1) to give the desired product **4** in 80% yield (332.2 mg, 0.73 mmol).

2.6 Procedure for the reductive N–O bond cleavage of 4[4]

The compound **4** (45.6 mg, 0.1 mmol, 1 equiv) and dichloromethane (1 mL) were added into a reaction flask with stirring bar. Zinc dust (130 mg, 2.00 mmol, 20 equiv) and acetic acid (1 mL) were sequentially added in to the flask. Then the reaction mixture was stirred at 25 °C. When **4** disappeared (monitored by TLC), the reaction mixture was passed over a plug of celite with 15 mL of ethyl acetate. The filtrate was removed under reduced pressure and the residue was purified by silica gel column chromatography (eluting with petroleum ether/ethyl acetate (v/v): 5/1) to give the product **5** in 25% yield (11.5 mg, 0.025 mmol) and product **6** in 50% yield (21.9 mg, 0.05 mmol).

The compound **4** (45.6 mg, 0.1 mmol, 1 equiv), MeOH (1 mL) and H_2O (1 mL) were added into a reaction flask with stirring bar. Zinc dust (130 mg, 2.00 mmol, 20 equiv) and acetic acid (1 mL) were sequentially added into the flask. Then the reaction mixture was stirred at room temperature. When **4** disappeared (monitored by TLC), the reaction mixture was passed over a plug of celite with 15 mL of ethyl acetate. The filtrate was removed under reduced pressure and the residue was purified by silica gel column chromatography (eluting with petroleum ether/ethyl acetate (v/v): 5/1) to give the product **5** in 80% yield (36.6 mg, 0.08 mmol) and product **6** in 15% yield (6.7 mg, 0.015 mmol).

2.7 Procedure for the decarboxylation of 4

A mixture of compound **4** (332 mg, 0.73 mmol, 1 equiv) and NaCl (342 mg, 5.84 mmol, 8 equiv) in DMSO (5 mL) and water (0.5 mL) was heated at 100 °C under an argon atmosphere for 24 hours. After completion of the reaction, the mixture was cooled down to room temperature, diluted with water (30 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with brine (30 mL), dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure, and the residue was purified by column chromatography (eluting with petroleum ether/ethyl acetate (v/v): 5/1) to afford the desired product **7** in 89% yield (251.5 mg, 0.66 mmol).

2.8 Procedure for the reductive N–O bond cleavage of 7[4]

The compound **7** (38.3 mg, 0.1 mmol, 1 equiv) and dichloromethane (1 mL) were added into a reaction flask with stirring bar. Zinc dust (130 mg, 2.00 mmol, 20 equiv) and acetic acid (1 mL) were sequentially added in to the flask. Then the reaction mixture was stirred at room temperature. When **7** disappeared

(monitored by TLC, about 24 hours), the reaction mixture was passed over a plug of celite with 15 mL of ethyl acetate. The filtrate was removed under reduced pressure and the residue was purified by silica gel column chromatography (eluting with petroleum ether/ethyl acetate (v/v): 5/1) to give the product **8** in 35% yield (13.5 mg, 0.035 mmol) and product **9** in 50% yield (18.5 mg, 0.05 mmol).

The compound **7** (38.3 mg, 0.1 mmol, 1 equiv), MeOH (1 mL) and H_2O (1 mL) were added into a reaction flask with stirring bar. Zinc dust (130 mg, 2.00 mmol, 20 equiv) and acetic acid (1 mL) were sequentially added in to the flask. Then the reaction mixture was stirred at room temperature. When **7** disappeared (monitored by TLC, about 3 hours), the reaction mixture was passed over a plug of celite with 15 mL of ethyl acetate. The filtrate was removed under reduced pressure and the residue was purified by silica gel column chromatography (eluting with petroleum ether/ethyl acetate (v/v): 5/1) to give the product **8** in 85% yield (32.7 mg, 0.085 mmol) and product **9** in 8% yield (3 mg, 0.008 mmol).

2.9 Procedure for the reduction of 7

Under an argon atmosphere, the compound **7** (126.4 mg, 0.33 mmol, 1 equiv) was dissolved in THF (5 mL), and cooled at 0 °C, and then $LiAlH_4$ (50.2 mg, 1.32 mmol, 4 equiv) was added into the reaction mixture. The reaction mixture was stirred at room temperature. When the compound **7** disappeared (monitored by TLC), the reaction mixture was quenched with H_2O and NaOH, and then passed over a plug of celite with 30 mL of MeOH. The filtrate was removed under reduced pressure and the residue was purified by silica gel column chromatography (eluting with petroleum ether/ethyl acetate (v/v): 2/1) to give the desired product **10** in 94% yield (120 mg, 0.31 mmol).

2.10 Procedure for the cycloetherification of 10

Under an argon atmosphere, to an ice-cooled solution of diol **10** (120 mg, 0.31 mmol, 1 equiv) in THF (5 mL) was added NaH (24.8 mg 60% dispersion in mineral oil, 0.62 mmol, 2 equiv). The resultant suspension was stirred for 10 min before the addition of MsCl (70.7 mg, 0.62 mmol, 2 equiv). Then the reaction mixture was stirred at 25 ºC for 12 h before being quenched by the addition of H_2O. The residue was dissolved in 10 mL of CH_2Cl_2 and 10 mL of H_2O and the aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with brine solution (30 mL), dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (eluting with petroleum ether/ethyl acetate (v/v): 8/1) to afford the desired product **11** in 90% yield (103.3 mg, 0.28 mmol).

2.11 Procedure for the reductive N–O bond cleavage and acetylation of 11

Under an argon atmosphere, the product **11** (103.3 mg, 0.28 mmol, 1 equiv) and dichloromethane (5 mL) were added into an oven-dried reaction flask with stirring bar. Zinc dust (364 mg, 5.60 mmol, 20 equiv) and

acetic acid (5 mL) were sequentially added in to the flask. Then the reaction mixture was stirred at room temperature. When **11** disappeared (monitored by TLC), the reaction mixture was passed over a plug of celite with 15 mL of ethyl acetate. The filtrate was removed under reduced pressure and the residue was purified by silica gel column chromatography (eluting with petroleum ether/ethyl acetate (v/v): 4/1) to give the product **12** in 86% yield (90 mg, 0.24 mmol).

The product **12** (18.6 mg, 0.05 mmol, 1 equiv) was dissolved in DCM (1 mL), then Et_3N (10.2 mg, 0.1 mmol, 2 equiv) and Ac_2O (10.1 mg, 0.1 mmol, 2 equiv) was added into the solution. The reaction mixture was stirred at room temperature. When **12** disappeared (monitored by TLC), the reaction mixture was extracted with ethyl acetate, the organic layer was washed with 5% aqueous solution of NaOH and water, and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by silica gel column chromatography (eluting with petroleum ether/ethyl acetate (v/v): 6/1) to give the desired product **13** in 76% yield (15.9 mg, 0.038 mmol).

3. X-Ray crystal structure and details of compounds 3aa, 6, 12, 13, 1u and 3ua

The single crystals of **3aa**, **6, 12, 13, 1u** and **3ua** suitable for X-ray crystallographic analysis were obtained by recrystallization from a mixed solvent of dichloromethane and petroleum ether. The single crystal X-ray diffraction data for the five compounds were collected on a Bruker APEX-II CCD diffractometer with graphite monchromated Mo Kα radiation (λ = 0.71073 Å) for **3aa**, **6, 12, 13, 1u** and **3ua**. Saint program and SADABS program carried out the data integration. The structure was solved by a direct method and refined on F2 using SHELXTL suite of program. All non-hydrogen atoms were anisotropically refined by full-matrix least squares methods. All hydrogen atoms were geometrically generated and isotropically refined using a riding model. The details of the X-ray data collection, structure solution and structure refinements are given in **Table S4, Table S5** and **Table S6**.

Table S4 Crystallographic data and structural refinement details for compounds **3aa** and **6**.

Compound	**3aa**	**6**
Formula	$C_{28}H_{23}NO_5$	$C_{28}H_{25}NO_4$
Formula weight	453.47	439.52
Temperature/K	293	293
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a, Å	11.9433(10)	9.838(4)
b, Å	12.3276(10)	11.101(4)
c, Å	20.1320(17)	11.425(4)
α, deg	75.060(1)	97.664(5)
β, deg	81.142(1)	97.936(5)
γ, deg	75.914(1)	110.262(4)
Volume/Å^3	2764.6(4)	1137.1(7)

Z	4	2
μ/mm^{-1}	0.075	0.086
θ range for data collection, deg	2.1 to 25.0	1.8 to 27.5
Reflections collected	27603	9787
Unique reflections/R_{int}	9696 / R(int) = 0.1373	4981 / R(int) = 0.027
Goodness-of-fit on F^2	1.030	1.08
R, R_w [I > 2σ(I)]	0.0722, 0.2479	0.0552, 0.1543
Residual ρ/(e·Å^{-3})	0.38, –0.33	0.28, –0.31
CCDC	2309776	2309777

Table S5 Crystallographic data and structural refinement details for compounds **12** and **13**.

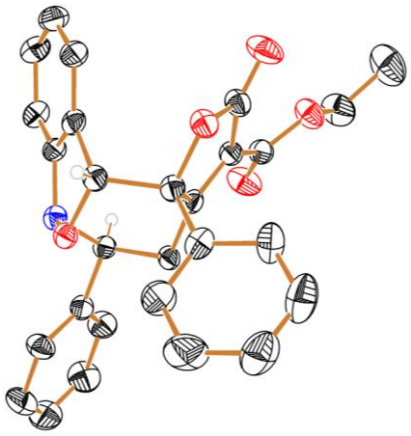
Compound	**12**	**13**
Formula	$C_{25}H_{25}NO_2$	$C_{27}H_{27}NO_3$
Formula weight	371.46	413.49
Temperature/K	293	273
Crystal system	orthorhombic	triclinic
Space group	Pca21	P-1
a, Å	11.3577(14)	10.0943(6)
b, Å	12.6655(16)	12.4294(8)
c, Å	27.035(3)	18.1764(13)
α, deg	90	85.359(2)
β, deg	90	80.756(2)
γ, deg	90	85.323(2)
Volume/Å^3	3889.0(8)	2238.1(3)
Z	8	4
μ/mm^{-1}	0.080	0.079
θ range for data collection, deg	1.5 to 27.5	2.6 to 25.0
Reflections collected	32590	80513
Unique reflections/R_{int}	8633 / R(int) = 0.036	7849 / R(int) = 0.160
Goodness-of-fit on F^2	1.03	1.07
R, R_w [I > 2σ(I)]	0.0501, 0.1386	0.0573, 0.1538
Residual ρ/(e·Å^{-3})	0.37, –0.21	0.32, –0.34
CCDC	2309778	2309779

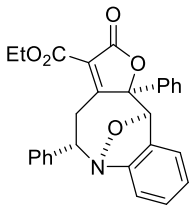
Table S6 Crystallographic data and structural refinement details for compounds **1u** and **3ua**.

Compound	**1u**	**3ua**
Formula	$C_{35}H_{31}BrO_5$	$C_{34}H_{26}BrNO_5$
Formula weight	611.51	608.47
Temperature/K	273	273
Crystal system	trigonal	orthorhombic
Space group	$P3_121$	$P2_12_12_1$
a, Å	11.5209(2)	10.4122(6)
b, Å	11.5209(2)	13.8828(10)
c, Å	40.4128(12)	19.5704(13)
α, deg	90	90
β, deg	90	90
γ, deg	120	90
Volume/Å^3	4645.4(2)	2828.9(3)

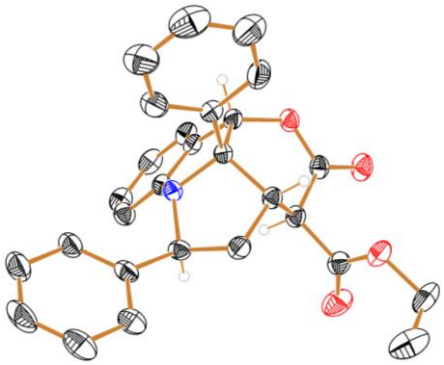
Z	6	4
μ/mm^{-1}	2.129	1.497
θ range for data collection, deg	4.4 to 68.4	2.5 to 25.0
Reflections collected	104615	79600
Unique reflections/R_{int}	5495 / R(int) = 0.094	4978 / R(int) = 0.0907
Goodness-of-fit on F^2	1.08	1.054
R, R_w [I > 2σ(I)]	0.0550, 0.1437	0.0369, 0.0759
Residual ρ/(e·Å^{-3})	0.70, –0.78	0.15, –0.42
Flack x	0.080(6)	–0.006(4)
CCDC	2349182	2349183

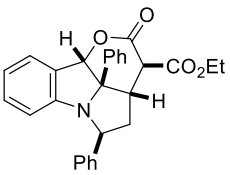
Figure S1 X-ray structure (30 % probability ellipsoids) of **3aa**, **6, 12, 13, 1u** and **3ua**





Compound 3aa





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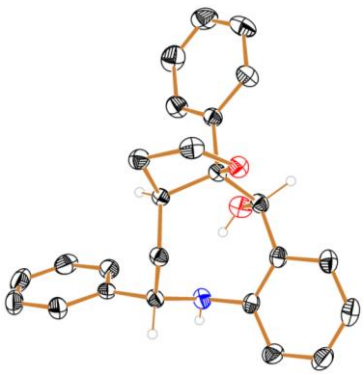

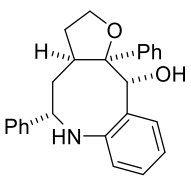

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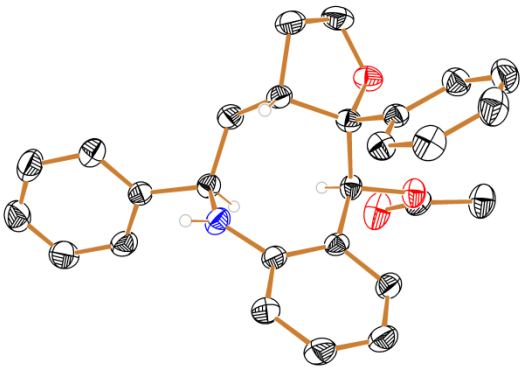
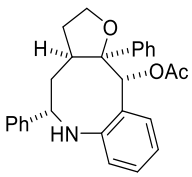
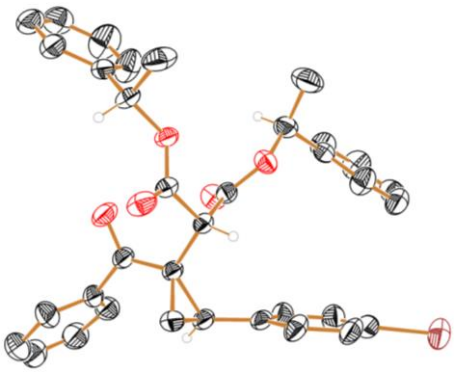
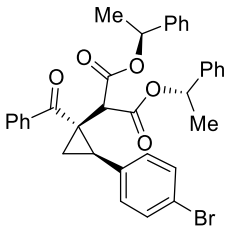


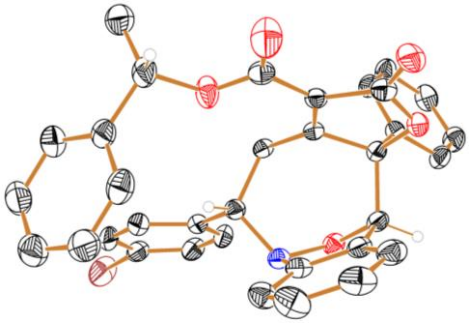


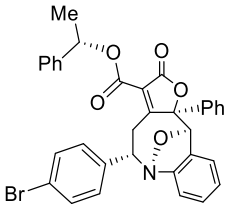
Compound 13





Compound 1u





Compound 3ua

4. References

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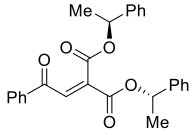
3. (a) Chang, M.-Y.; Chen, Y.-C.; Chan, C.-K. One-pot synthesis of multifunctionalized cyclopropanes. *Tetrahedron* **2014**, *70*, 2257–2263. (b) Qi, C.; Chen, W.; Yang, G. Catalyst-free Synthesis of Aroylmethylidene Malonates via Two-step in One Pot. *Chin. J. Syn. Chem.* **2021**, *29*, 969–974.
4. Singh, R. R.; Skaria, M.; Chen, L.-Y.; Cheng, M.-J.; Liu, R.-S. Gold-catalyzed (4+3)-annulations of 2-alkenyl-1-alkynylbenzenes with anthranils with alkyne-dependent chemoselectivity: skeletal rearrangement *versus* non-rearrangement. *Chem. Sci.* **2019**, *10*, 1201–1206.

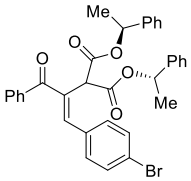
5. Characterization data of compounds

5.1 Characterization data of cyclopropanes 1

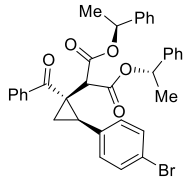
All the cyclopropanes **1** were prepared as previously described.[1] The characterizing data for the new substrate **1u** and the related compounds (**15u**, **16u** and **1u′**) are as follows:



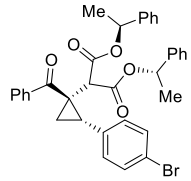
Bis((*S*)-1-phenylethyl) 2-(2-oxo-2-phenylethylidene)malonate (**15u**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1) to afford a yellow oil in 65% yield (1400.4 mg). $[\alpha]_D^{23}$= –40.08 (*c* 0.4, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.87 (s, 1H), 7.68 – 7.60 (m, 1H), 7.54 – 7.47 (m, 2H), 7.39 – 7.24 (m, 10H), 6.13 (q, *J* = 6.5 Hz, 1H), 6.02 (q, *J* = 6.6 Hz, 1H), 1.61 (d, *J* = 6.6 Hz, 3H), 1.58 (d, *J* = 6.6 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 189.1, 163.8, 162.1, 140.6, 140.4, 136.4, 136.02, 135.98, 134.2, 128.91, 128.89, 128.6, 128.4, 128.1, 128.0, 126.5, 126.0, 74.8, 74.2, 22.1, 21.0. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{24}O_5Na$ 451.1516, found 451.1513.



Bis((*S*)-1-phenylethyl) 2-((*E*)-1-(4-bromophenyl)-3-oxo-3-phenylprop-1-en-2-yl)malon- ate (**16u**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 6/1) to afford a yellow oil in 56% yield (999.6 mg). $[\alpha]_D^{23}$= –38.21 (*c* 0.4, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.89 – 7.81 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.55 – 7.46 (m, 4H), 7.41 – 7.31 (m, 11H), 7.25 (d, *J* = 8.3 Hz, 2H), 6.14 – 5.98 (m, 2H), 4.89 (s, 1H), 1.620 (d, *J* = 6.6 Hz, 3H), 1.618 (d, *J* = 6.6 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 196.0, 166.5, 166.4, 143.0, 140.9, 140.5, 137.2, 134.9, 132.9, 132.1, 131.9, 130.2, 129.7, 128.3, 128.2, 127.9, 127.8, 126.3, 126.0, 123.5, 74.18, 74.17, 51.6, 21.8, 21.5. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{29}BrO_5Na$ 619.1091, found 619.1092.

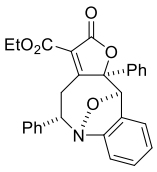


Bis((*S*)-1-phenylethyl) 2-((1*S*,2*R*)-1-benzoyl-2-(4-bromophenyl)cyclopropyl)malonate **(1u).** Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 10/1) to afford a white solid in 38% yield (462 mg). Mp: 120 – 121 °C. $[\alpha]_D^{23}$= –26.11 (*c* 0.4, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 6.6 Hz, 2H), 7.47 – 7.30 (m, 11H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 6.9 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 5.96 (q, *J* = 6.5 Hz, 1H), 5.86 (q, *J* = 6.6 Hz, 1H), 3.08 – 2.98 (m, 1H), 2.85 (s, 1H), 1.98 – 1.83 (m, 1H), 1.72 – 1.66 (m, 1H), 1.60 (d, *J* = 6.5 Hz, 3H), 1.46 (d, *J* = 6.6 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 202.3, 167.9, 167.3, 140.9, 140.6, 137.4, 134.1, 131.6, 130.8, 130.6, 128.48, 128.45, 128.1, 128.0, 127.8, 127.4, 126.3, 126.1, 121.4, 73.8, 73.5, 53.2, 37.8, 27.9, 21.9, 21.2, 16.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{35}H_{32}BrO_5$ 611.1428, found 611.1427.

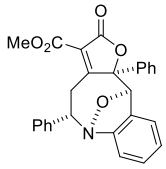


Bis((*S*)-1-phenylethyl) 2-((1*R*,2*S*)-1-benzoyl-2-(4-bromophenyl)cyclopropyl)malonate **(1u′).** Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 10/1) to afford a yellow oil in 43% yield (526.8 mg). $[\alpha]_D^{23}$= –66.79 (*c* 0.4, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.54 (m, 2H), 7.52 – 7.46 (m, 1H), 7.46 – 7.38 (m, 4H), 7.38 – 7.28 (m, 5H), 7.27 – 7.19 (m, 3H), 7.16 – 7.06 (m, 4H), 5.85 (q, *J* = 6.6 Hz, 1H), 5.77 (q, *J* = 6.6 Hz, 1H), 3.15 – 3.06 (m, 1H), 2.75 (s, 1H), 1.96 – 1.87 (m, 1H), 1.68 – 1.62 (m, 1H), 1.42 (d, *J* = 6.6 Hz, 3H), 1.35 (d, *J* = 6.6 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 202.4, 168.0, 167.2, 141.3, 140.3, 137.7, 134.3, 131.7, 130.8, 130.6, 128.5, 128.3, 128.2, 128.1, 127.7, 127.5, 126.7, 125.9, 121.4, 74.2, 73.7, 53.3, 38.3, 27.4, 21.8, 21.1, 16.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{35}H_{32}BrO_5$ 611.1428, found 611.1427.

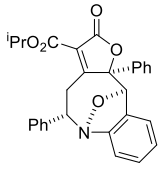
5.2 Characterization data of products 3



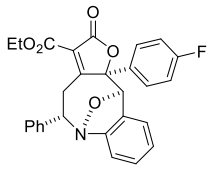
Ethyl 2-oxo-5,11a-diphenyl-4,5,11,11a-tetrahydro-2*H*-6,11-epoxybenzo[*b*]furo[2,3-*e*]azocine-3-carboxylate (**3aa**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 10/1) to afford a white solid in 96% yield (87.1 mg). Mp: 182 – 183 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, J = 7.8 Hz, 2H), 7.53 (d, J = 7.8 Hz, 2H), 7.50 – 7.37 (m, 5H), 7.36 – 7.28 (m, 3H), 7.10 (t, J = 7.4 Hz, 1H), 6.90 (d, J = 7.8 Hz, 1H), 6.03 (s, 1H), 4.52 (dd, J = 10.3, 5.6 Hz, 1H), 4.34 – 4.21 (m, 2H), 3.53 (dd, J = 12.1, 5.4 Hz, 1H), 3.04 – 2.95 (m, 1H), 1.33 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 174.9, 167.5, 160.5, 151.2, 142.5, 135.0, 130.3, 129.6, 129.2, 128.9, 127.7, 126.8, 126.3, 126.1, 124.68, 124.66, 120.8, 112.0, 88.1, 83.0, 68.3, 61.7, 34.7, 14.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{24}NO_5$ 454.1649, found 454.1650.



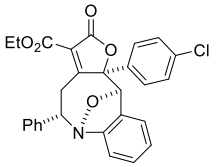
Methyl 2-oxo-5,11a-diphenyl-4,5,11,11a-tetrahydro-2*H*-6,11-epoxybenzo[*b*]furo[2,3-*e*]azocine-3-carboxylate (**3ba**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 10/1) to afford a white solid in 94% yield (82.5 mg). Mp: 204 – 205 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 – 7.61 (m, 2H), 7.55 (d, J = 7.3 Hz, 2H), 7.51 – 7.38 (m, 5H), 7.36 – 7.27 (m, 3H), 7.09 (t, J = 7.5 Hz, 1H), 6.91 (d, J = 7.8 Hz, 1H), 6.03 (s, 1H), 4.54 (dd, J = 10.4, 5.5 Hz, 1H), 3.82 (s, 3H), 3.57 (dd, J = 12.0, 5.6 Hz, 1H), 3.01 (dd, J = 11.9, 10.6 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 176.0, 167.4, 161.0, 151.2, 142.4, 134.9, 130.3, 129.6, 129.2, 128.8, 127.6, 126.7, 126.2, 126.1, 124.6, 120.4, 112.0, 88.2, 82.9, 68.2, 52.5, 34.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{22}NO_5$ 440.1492, found 440.1498.



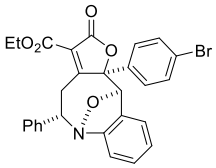
Isopropyl 2-oxo-5,11a-diphenyl-4,5,11,11a-tetrahydro-2*H*-6,11-epoxybenzo[*b*]furo[2,3-*e*]azocine-3-carboxylate (**3ca**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 10/1) to afford a white solid in 96% yield (89.7 mg). Mp: 190 – 191 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.62 (m, 2H), 7.54 (d, J = 7.8 Hz, 2H), 7.50 – 7.38 (m, 5H), 7.38 – 7.27 (m, 3H), 7.15 – 7.05 (m, 1H), 6.90 (d, J = 7.8 Hz, 1H), 6.03 (s, 1H), 5.21 – 5.07 (m, 1H), 4.53 (dd, J = 10.3, 5.7 Hz, 1H), 3.51 (dd, J = 12.2, 5.7 Hz, 1H), 2.99 (dd, J = 12.0, 10.6 Hz, 1H), 1.31 (d, J = 6.3 Hz, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 173.5, 167.4, 159.8, 151.2, 142.5, 135.0, 130.1, 129.5, 129.1, 128.8, 127.6, 126.8, 126.2, 126.0, 124.65, 124.60, 121.1, 111.8, 87.9, 82.9, 69.4, 68.2, 34.6, 21.86, 21.81. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{29}H_{26}NO_5$ 468.1805, found 468.1803.



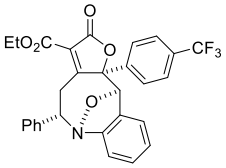
Ethyl 11a-(4-fluorophenyl)-2-oxo-5-phenyl-4,5,11,11a-tetrahydro-2*H*-6,11-epoxybenzo[*b*]furo[2,3-*e*]azocine-3-carboxylate (**3da**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 10/1) to afford a white solid in 86% yield (81.0 mg). Mp: 185 – 186 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 – 7.62 (m, 2H), 7.53 (d, J = 7.3 Hz, 2H), 7.47 – 7.39 (m, 2H), 7.37 – 7.28 (m, 3H), 7.21 – 7.05 (m, 3H), 6.91 (d, J = 7.9 Hz, 1H), 5.98 (s, 1H), 4.53 (dd, J = 10.4, 5.6 Hz, 1H), 4.35 – 4.20 (m, 2H), 3.55 (dd, J = 12.1, 5.6 Hz, 1H), 2.95 (dd, J = 12.1, 10.5 Hz, 1H), 1.33 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 174.5, 167.2, 163.2 (d, $^1J_{FC}$ = 250.0 Hz), 160.3, 151.2, 142.4, 130.9 (d, $^4J_{FC}$ = 3.1 Hz), 130.4, 128.9, 128.3 (d, $^3J_{FC}$ = 8.4 Hz), 127.7, 126.6, 126.0, 124.7, 124.6, 120.8, 116.2 (d, $^2J_{FC}$ = 21.7 Hz), 112.0, 87.6, 83.0, 68.2, 61.7, 34.6, 14.1. ^{19}F NMR (470 MHz, $CDCl_3$) δ –111.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{23}FNO_5$ 472.1555, found 472.1562.



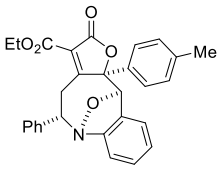
Ethyl 11a-(4-chlorophenyl)-2-oxo-5-phenyl-4,5,11,11a-tetrahydro-2*H*-6,11-epoxybenzo[*b*]furo[2,3-*e*]azocine-3-carboxylate (**3ea**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 10/1) to afford a white solid in 80% yield (77.9 mg). Mp: 194 – 195 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 – 7.58 (m, 2H), 7.56 – 7.49 (m, 2H), 7.47 – 7.38 (m, 4H), 7.36 – 7.28 (m, 3H), 7.14 – 7.05 (m, 1H), 6.90 (d, J = 8.1 Hz, 1H), 5.96 (s, 1H), 4.52 (dd, J = 10.4, 5.6 Hz, 1H), 4.35 – 4.19 (m, 2H), 3.55 (dd, J = 12.1, 5.6 Hz, 1H), 2.94 (dd, J = 12.1, 10.4 Hz, 1H), 1.33 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 174.3, 167.1, 160.3, 151.1, 142.3, 135.8, 133.6, 130.4, 129.4, 128.9, 127.73, 127.71, 126.5, 126.0, 124.7, 124.6, 120.9, 112.0, 87.5, 82.9, 68.2, 61.7, 34.6, 14.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{23}ClNO_5$ 488.1259 found 488.1257.



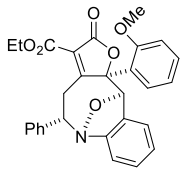
Ethyl 11a-(4-bromophenyl)-2-oxo-5-phenyl-4,5,11,11a-tetrahydro-2*H*-6,11-epoxybenzo[*b*]furo[2,3-*e*]azocine-3-carboxylate (**3fa**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 10/1) to afford a white solid in 76% yield (80.7 mg). Mp: 212 – 213 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.49 (m, 6H), 7.45 – 7.38 (m, 2H), 7.37 – 7.28 (m, 3H), 7.10 (t, J = 7.3 Hz, 1H), 6.90 (d, J = 8.1 Hz, 1H), 5.95 (s, 1H), 4.52 (dd, J = 10.4, 5.6 Hz, 1H), 4.34 – 4.20 (m, 2H), 3.54 (dd, J = 12.1, 5.6 Hz, 1H), 2.94 (dd, J = 12.0, 10.5 Hz, 1H), 1.33 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 174.3, 167.1, 160.3, 151.2, 142.3, 134.2, 132.4, 130.4, 128.9, 128.0, 127.8, 126.5, 126.0, 124.7, 124.6, 124.0, 120.9, 112.0, 87.6, 82.9, 68.2, 61.7, 34.6, 14.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{23}BrNO_5$ 532.0754, found 532.0753.



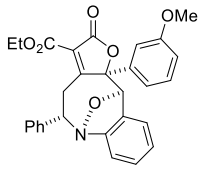
Ethyl 2-oxo-5-phenyl-11a-(4-(trifluoromethyl)phenyl)-4,5,11,11a-tetrahydro-2*H*-6,11-epoxy-benzo[*b*]furo[2,3-*e*]azocine-3-carboxylate (**3ga**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 10/1) to afford a white solid in 96% yield (100.0 mg). Mp: 200 – 201 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, J = 8.2 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H), 7.54 (d, J = 7.5 Hz, 2H), 7.48 – 7.38 (m, 2H), 7.37 – 7.27 (m, 3H), 7.17 – 7.04 (m, 1H), 6.91 (d, J = 8.0 Hz, 1H), 5.98 (s, 1H), 4.55 (dd, J = 10.2, 5.6 Hz, 1H), 4.39 – 4.13 (m, 2H), 3.57 (dd, J = 12.1, 5.6 Hz, 1H), 3.05 – 2.81 (m, 1H), 1.33 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 173.9, 167.0, 160.2, 151.2, 142.2, 139.3, 131.8 (q, $^2J_{FC}$ = 32.9 Hz), 130.5, 128.9, 127.8, 126.8, 126.3, 126.2 (q, $^3J_{FC}$ = 3.2 Hz), 126.0, 124.8, 124.6, 123.6 (q, $^1J_{FC}$ = 272.8 Hz), 121.2, 112.0, 87.4, 83.0, 68.2, 61.8, 34.6, 14.1. ^{19}F NMR (470 MHz, $CDCl_3$) δ –62.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{29}H_{23}F_3NO_5$ 522.1523, found 522.1516.



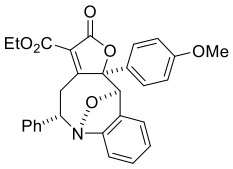
Ethyl 2-oxo-5-phenyl-11a-(*p*-tolyl)-4,5,11,11a-tetrahydro-2*H*-6,11-epoxybenzo[*b*]furo[2,3-*e*]azocine-3-carboxylate (**3ha**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 10/1) to afford a white solid in 96% yield (89.7 mg). Mp: 205 – 206 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 4H), 7.45 – 7.37 (m, 2H), 7.35 – 7.22 (m, 5H), 7.13 – 7.05 (m, 1H), 6.90 (d, J = 7.8 Hz, 1H), 6.01 (s, 1H), 4.51 (dd, J = 10.4, 5.6 Hz, 1H), 4.34 – 4.20 (m, 2H), 3.52 (dd, J = 12.1, 5.6 Hz, 1H), 2.99 (dd, J = 12.0, 10.5 Hz, 1H), 2.37 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 175.0, 167.6, 160.5, 151.2, 142.5, 139.7, 131.9, 130.2, 129.9, 128.8, 127.7, 126.9, 126.2, 126.1, 124.6, 120.7, 112.0, 88.1, 82.9, 68.3, 61.6, 34.6, 21.2, 14.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{29}H_{26}NO_5$ 468.1805, found 468.1804.



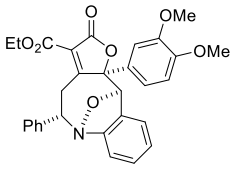
Ethyl 11a-(2-methoxyphenyl)-2-oxo-5-phenyl-4,5,11,11a-tetrahydro-2*H*-6,11-epoxybenzo[*b*]furo[2,3-*e*]azocine-3-carboxylate (**3ia**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 10/1) to afford a white solid in 95% yield (91.7 mg). Mp: 180 – 181 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (dd, J = 7.8, 1.1 Hz, 1H), 7.49 (d, J = 7.6 Hz, 2H), 7.45 – 7.34 (m, 3H), 7.33 – 7.24 (m, 3H), 7.17 – 7.04 (m, 2H), 6.89 (d, J = 8.0 Hz, 2H), 6.19 (s, 1H), 4.51 (dd, J = 10.3, 5.7 Hz, 1H), 4.35 – 4.20 (m, 2H), 3.66 (s, 3H), 3.54 (dd, J = 12.0, 5.7 Hz, 1H), 2.87 (dd, J = 11.8, 10.7 Hz, 1H), 1.33 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 173.2, 168.0, 160.8, 158.8, 151.6, 142.6, 131.2, 130.0, 128.9, 128.7, 127.5, 126.8, 126.1, 124.70, 124.65, 122.1, 121.8, 120.9, 112.3, 111.9, 87.2, 81.9, 67.9, 61.2, 55.6, 34.7, 14.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{29}H_{26}NO_6$ 484.1755, found 484.1747.



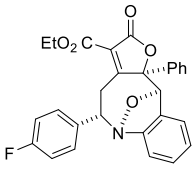
Ethyl 11a-(3-methoxyphenyl)-2-oxo-5-phenyl-4,5,11,11a-tetrahydro-2*H*-6,11-epoxybenzo[*b*]furo[2,3-*e*]azocine-3-carboxylate (**3ja**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 10/1) to afford a white solid in 93% yield (89.6 mg). Mp: 190 – 191 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, J = 7.3 Hz, 2H), 7.47 – 7.23 (m, 7H), 7.22 – 7.14 (m, 1H), 7.13 – 7.05 (m, 1H), 6.99 – 6.92 (m, 1H), 6.90 (d, J = 7.8 Hz, 1H), 6.00 (s, 1H), 4.52 (dd, J = 10.4, 5.6 Hz, 1H), 4.34 – 4.19 (m, 2H), 3.82 (s, 3H), 3.54 (dd, J = 12.1, 5.6 Hz, 1H), 3.04 (dd, J = 12.1, 10.5 Hz, 1H), 1.33 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 174.8, 167.4, 160.4, 160.1, 151.2, 142.5, 136.5, 130.3, 128.8, 127.7, 126.8, 126.1, 124.66, 124.63, 120.7, 118.4, 114.8, 112.2, 112.0, 87.9, 83.0, 68.2, 61.6, 55.4, 34.7, 14.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{29}H_{26}NO_6$ 484.1755, found 484.1754.



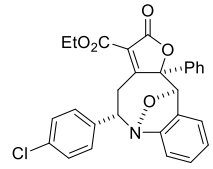
Ethyl 11a-(4-methoxyphenyl)-2-oxo-5-phenyl-4,5,11,11a-tetrahydro-2*H*-6,11-epoxybenzo[*b*]furo[2,3-*e*]azocine-3-carboxylate (**3ka**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 10/1) to afford a white solid in 95% yield (91.8 mg). Mp: 182 – 183 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.48 (m, 4H), 7.46 – 7.37 (m, 2H), 7.35 – 7.27 (m, 3H), 7.09 (t, J = 7.4 Hz, 1H), 7.00 – 6.94 (m, 2H), 6.90 (d, J = 7.8 Hz, 1H), 6.00 (s, 1H), 4.52 (dd, J = 10.4, 5.6 Hz, 1H), 4.35 – 4.19 (m, 2H), 3.82 (s, 3H), 3.53 (dd, J = 12.0, 5.6 Hz, 1H), 2.98 (dd, J = 11.9, 10.6 Hz, 1H), 1.33 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 175.0, 167.4, 160.5, 160.4, 151.2, 142.5, 130.2, 128.8, 127.7, 127.6, 126.9, 126.6, 126.0, 124.6, 120.6, 114.5, 111.9, 88.0, 82.9, 68.2, 61.6, 55.4, 34.6, 14.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{29}H_{26}NO_6$ 484.1755, found 484.1752.



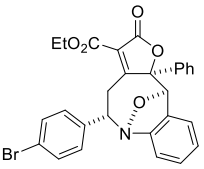
Ethyl 11a-(3,4-dimethoxyphenyl)-2-oxo-5-phenyl-4,5,11,11a-tetrahydro-2*H*-6,11-epoxybenzo[*b*]furo[2,3-*e*]azocine-3-carboxylate **(3la).** Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 10/1) to afford a white solid in 95% yield (97.5 mg). Mp: 176 – 177 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, J = 7.4 Hz, 2H), 7.45 – 7.36 (m, 2H), 7.36 – 7.26 (m, 4H), 7.13 – 7.03 (m, 2H), 6.99 – 6.84 (m, 2H), 5.97 (s, 1H), 4.52 (dd, J = 10.3, 5.6 Hz, 1H), 4.35 – 4.20 (m, 2H), 3.89 (s, 3H), 3.87 (s, 3H), 3.54 (dd, J = 12.1, 5.7 Hz, 1H), 3.04 (dd, J = 11.8, 10.7 Hz, 1H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 175.0, 167.5, 160.4, 151.1, 149.9, 149.3, 142.5, 130.2, 128.8, 127.6, 127.1, 126.8, 126.0, 124.6, 120.4, 119.0, 111.9, 111.3, 109.0, 88.0, 83.2, 68.1, 61.6, 56.0, 55.9, 34.6, 14.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{30}H_{28}NO_7$ 514.1860, found 514.1862.



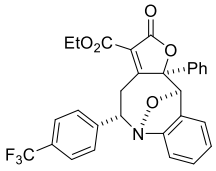
Ethyl 5-(4-fluorophenyl)-2-oxo-11a-phenyl-4,5,11,11a-tetrahydro-2*H*-6,11-epoxybenzo[*b*]furo[2,3-*e*]azocine-3-carboxylate (**3ma**)**.** Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 10/1) to afford a white solid in 93% yield (87.5 mg). Mp: 170 – 171 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 – 7.61 (m, 2H), 7.54 – 7.40 (m, 5H), 7.36 – 7.28 (m, 2H), 7.16 – 7.03 (m, 3H), 6.89 (d, J = 7.8 Hz, 1H), 6.02 (s, 1H), 4.51 (dd, J = 10.4, 5.6 Hz, 1H), 4.34 – 4.19 (m, 2H), 3.51 (dd, J = 12.1, 5.6 Hz, 1H), 2.94 (dd, J = 12.0, 10.5 Hz, 1H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 174.7, 167.4, 162.2 (d, $^{1}J_{FC}$ = 246.3 Hz), 160.5, 151.1, 138.3 (d, $^{4}J_{FC}$ = 3.1 Hz), 134.9, 130.3, 129.7, 129.2, 127.8 (d, $^{3}J_{FC}$ = 8.1 Hz), 126.8, 126.2, 124.8, 124.7, 120.9, 115.7 (d, $^{2}J_{FC}$ = 21.5 Hz), 112.0, 88.0, 83.0, 67.6, 61.7, 34.7, 14.2. ^{19}F NMR (470 MHz, $CDCl_3$) δ –114.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{23}FNO_5$ 472.1555, found 472.1546.



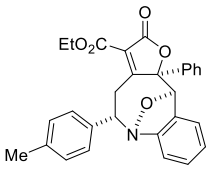
Ethyl 5-(4-chlorophenyl)-2-oxo-11a-phenyl-4,5,11,11a-tetrahydro-2H-6,11-epoxybenzo[b]furo[2,3-e]azocine-3-carboxylate (**3na**)**.** Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 10/1) to afford a white solid in 94% yield (91.5 mg). Mp: 196 – 197 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 – 7.59 (m, 2H), 7.51 – 7.40 (m, 5H), 7.40 – 7.35 (m, 2H), 7.35 – 7.28 (m, 2H), 7.15 – 7.06 (m, 1H), 6.89 (d, J = 7.8 Hz, 1H), 6.02 (s, 1H), 4.51 (dd, J = 10.4, 5.6 Hz, 1H), 4.34 – 4.18 (m, 2H), 3.52 (dd, J = 12.1, 5.6 Hz, 1H), 2.93 (dd, J = 12.0, 10.5 Hz, 1H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 174.6, 167.3, 160.5, 151.0, 141.0, 134.9, 133.5, 130.4, 129.7, 129.3, 129.0, 127.5, 126.8, 126.2, 124.8, 124.7, 120.9, 112.0, 88.0, 83.0, 67.6, 61.7, 34.5, 14.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{23}ClNO_5$ 488.1259, found 488.1254.



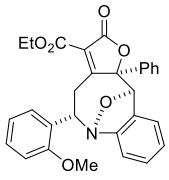
Ethyl 5-(4-bromophenyl)-2-oxo-11a-phenyl-4,5,11,11a-tetrahydro-2*H*-6,11-epoxybenzo[*b*]furo[2,3-*e*]azocine-3-carboxylate (**3oa**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 10/1) to afford a white solid in 91% yield (100.3 mg). Mp: 205 – 206 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.58 (m, 2H), 7.58 – 7.50 (m, 2H), 7.50 – 7.37 (m, 5H), 7.37 – 7.28 (m, 2H), 7.16 – 7.07 (m, 1H), 6.89 (d, J = 7.8 Hz, 1H), 6.02 (s, 1H), 4.49 (dd, J = 10.4, 5.6 Hz, 1H), 4.34 – 4.19 (m, 2H), 3.52 (dd, J = 12.1, 5.6 Hz, 1H), 2.92 (dd, J = 12.0, 10.5 Hz, 1H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.6, 167.3, 160.5, 151.0, 141.5, 134.9, 131.9, 130.4, 129.7, 129.3, 127.9, 126.8, 126.2, 124.8, 124.7, 121.6, 121.0, 112.0, 88.0, 83.0, 67.6, 61.7, 34.4, 14.2. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{22}BrNO_5Na$ 554.0574, found 554.0569.



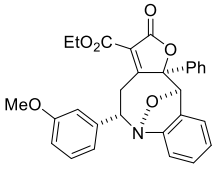
Ethyl 2-oxo-11a-phenyl-5-(4-(trifluoromethyl)phenyl)-4,5,11,11a-tetrahydro-2*H*-6,11-epoxybenzo[*b*]furo[2,3-*e*]azocine-3-carboxylate (**3pa**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 10/1) to afford a white solid in 90% yield (93.7 mg). Mp: 193 – 194 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.58 (m, 6H), 7.52 – 7.39 (m, 3H), 7.38 – 7.29 (m, 2H), 7.17 – 7.07 (m, 1H), 6.89 (d, J = 7.8 Hz, 1H), 6.04 (s, 1H), 4.59 (dd, J = 10.4, 5.6 Hz, 1H), 4.36 – 4.20 (m, 2H), 3.56 (dd, J = 12.1, 5.6 Hz, 1H), 2.93 (dd, J = 12.0, 10.5 Hz, 1H), 1.33 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 174.4, 167.2, 160.5, 150.9, 146.3, 134.8, 130.4, 130.0 (q, $^{2}J_{FC}$ = 32.5 Hz), 129.7, 129.3, 126.8, 126.6, 126.2, 125.8 (q, $^{3}J_{FC}$ = 3.7 Hz), 124.9, 124.8, 124.0 (q, $^{1}J_{FC}$ = 272.0 Hz), 121.1, 112.0, 88.0, 83.1, 67.7, 61.8, 34.3, 14.2. ^{19}F NMR (470 MHz, $CDCl_3$) δ –62.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{29}H_{23}F_3NO_5$ 522.1523, found 522.1530.



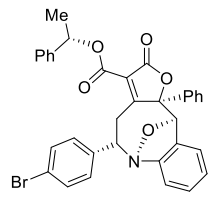
Ethyl 2-oxo-11a-phenyl-5-(*p*-tolyl)-4,5,11,11a-tetrahydro-2*H*-6,11-epoxybenzo[*b*]furo [2,3-*e*]azocine-3-carboxylate (**3qa**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 10/1) to afford a white solid in 95% yield (88.6 mg). Mp: 192 – 193 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.62 (m, 2H), 7.52 – 7.38 (m, 5H), 7.36 – 7.28 (m, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.14 – 7.05 (m, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.02 (s, 1H), 4.50 (dd, *J* = 10.4, 5.6 Hz, 1H), 4.34 – 4.20 (m, 2H), 3.52 (dd, *J* = 12.1, 5.6 Hz, 1H), 2.99 (dd, *J* = 12.0, 10.5 Hz, 1H), 2.37 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 174.9, 167.5, 160.4, 151.3, 139.6, 137.4, 135.0, 130.2, 129.6, 129.5, 129.2, 126.8, 126.2, 126.0, 124.61, 124.57, 120.7, 111.9, 88.0, 82.9, 68.1, 61.6, 34.7, 21.1, 14.2. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{29}H_{26}NO_5$ 468.1805, found 468.1810.



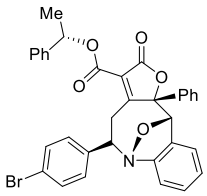
Ethyl 5-(2-methoxyphenyl)-2-oxo-11a-phenyl-4,5,11,11a-tetrahydro-2*H*-6,11-epoxybenzo[*b*] furo[2,3-*e*]azocine-3-carboxylate (**3ra**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 10/1) to afford a white solid in 45% yield (43.5 mg). Mp: 195 – 196 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.71 – 7.62 (m, 2H), 7.49 – 7.38 (m, 3H), 7.36 – 7.26 (m, 3H), 7.13 – 7.03 (m, 2H), 6.96 – 6.86 (m, 2H), 6.02 (s, 1H), 4.93 (dd, *J* = 10.2, 5.7 Hz, 1H), 4.38 – 4.28 (m, 1H), 4.28 – 4.19 (m, 1H), 3.88 (s, 3H), 3.67 (dd, *J* = 12.0, 5.7 Hz, 1H), 2.84 (dd, *J* = 12.0, 10.2 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 174.2, 167.8, 160.3, 155.5, 151.2, 135.2, 130.9, 130.1, 129.5, 129.1, 128.8, 127.5, 126.9, 126.3, 124.52, 124.49, 121.3, 121.0, 112.2, 110.3, 88.2, 82.8, 62.6, 61.4, 55.4, 32.2, 14.1. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{29}H_{26}NO_6$ 484.1755, found 484.1752.



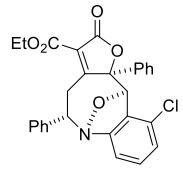
Ethyl 5-(3-methoxyphenyl)-2-oxo-11a-phenyl-4,5,11,11a-tetrahydro-2*H*-6,11-epoxybenzo [*b*]furo[2,3-*e*]azocine-3-carboxylate (**3sa**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 10/1) to afford a white solid in 95% yield (91.6 mg). Mp: 183 – 184 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 – 7.62 (m, 2H), 7.51 – 7.39 (m, 3H), 7.38 – 7.27 (m, 3H), 7.17 – 7.05 (m, 3H), 6.95 – 6.83 (m, 2H), 6.01 (s, 1H), 4.50 (dd, *J* = 10.4, 5.6 Hz, 1H), 4.35 – 4.19 (m, 2H), 3.85 (s, 3H), 3.53 (dd, *J* = 12.1, 5.6 Hz, 1H), 2.99 (dd, *J* = 12.0, 10.4 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 174.7, 167.4, 160.4, 160.0, 151.2, 144.0, 135.0, 130.2, 129.9, 129.6, 129.2, 126.8, 126.2, 124.6, 120.8, 118.3, 112.9, 111.96, 111.95, 88.0, 82.9, 68.1, 61.6, 55.3, 34.5, 14.2. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{29}H_{26}NO_6$ 484.1755, found 484.1750.



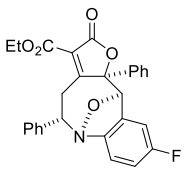
(*S*)-1-phenylethyl (5*S*, 6*R*, 11*R*, 11a*R*)-5-(4-bromophenyl)-2-oxo-11a-phenyl-4,5,11,11a-tetrahydro-2H-6,11-epoxybenzo[b]furo[2, 3-e]azocine-3-carboxylate (**3ua**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 10/1) to afford a white solid in 63% yield (38 mg). Mp: 156 – 157 °C. $[\alpha]_D^{23}$ = –63.58 (*c* 0.4, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 – 7.62 (m, 2H), 7.53 – 7.43 (m, 5H), 7.41 – 7.29 (m, 7H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.16 – 7.12 (m, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 6.03 (s, 1H), 6.01 (q, *J* = 6.6 Hz, 1H), 4.32 (dd, *J* = 10.4, 5.7 Hz, 1H), 3.47 (dd, *J* = 12.1, 5.7 Hz, 1H), 2.89 (dd, *J* = 12.0, 10.5 Hz, 1H), 1.62 (d, *J* = 6.6 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 173.7, 167.2, 159.4, 150.9, 141.3, 140.3, 134.8, 131.8, 130.2, 129.6, 129.2, 128.7, 128.4, 127.8, 126.8, 126.4, 126.2, 124.81, 124.77, 121.6, 120.8, 111.8, 87.9, 83.0, 73.8, 67.4, 34.3, 21.6. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{34}H_{27}NBrO_5$ 608.1067, found 608.1073.



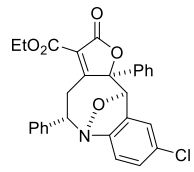
(*S*)-1-phenylethyl (5*R*, 6*S*, 11*S*, 11a*S*)-5-(4-bromophenyl)-2-oxo-11a-phenyl-4,5,11,11a-tetrahydro-2H-6,11-epoxybenzo[b]furo[2, 3-e]azocine-3-carboxylate (**3ua′**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 10/1) to afford a yellow oil in 29% yield (17.8 mg). $[\alpha]_D^{23}$= –40.84 (*c* 0.4, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.68 – 7.63 (m, 2H), 7.51 – 7.43 (m, 5H), 7.41 – 7.33 (m, 6H), 7.25 (t, *J* = 7.3 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.03 (s, 1H), 5.99 (q, *J* = 6.6 Hz, 1H), 4.37 (dd, *J* = 10.3, 5.8 Hz, 1H), 3.40 (dd, *J* = 12.1, 5.8 Hz, 1H), 2.85 (dd, *J* = 12.0, 10.5 Hz, 1H), 1.61 (t, *J* = 6.6 Hz, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 173.7, 167.2, 159.6, 150.9, 141.3, 140.6, 134.8, 131.8, 130.2, 129.7, 129.2, 128.7, 128.2, 127.8, 126.8, 126.2, 126.1, 124.8, 121.5, 121.1, 111.8, 88.0, 83.0, 73.9, 67.2, 34.2, 21.8. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{34}H_{27}NBrO_5$ 608.1067, found 608.1073.



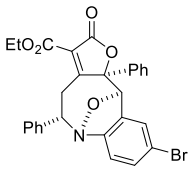
Ethyl 7-chloro-2-oxo-5,11a-diphenyl-4,5,11,11a-tetrahydro-2*H*-6,11-epoxybenzo[*b*]furo[2,3-*e*]azocine-3-carboxylate (**3ab**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 10/1) to afford a white solid in 74% yield (72.0 mg). Mp: 175 – 176 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.62 (m, 2H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.49 – 7.39 (m, 5H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.23 (t, *J* = 7.9 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 6.18 (s, 1H), 4.64 (dd, *J* = 10.4, 5.6 Hz, 1H), 4.38 – 4.23 (m, 2H), 3.61 (dd, *J* = 12.1, 5.6 Hz, 1H), 3.03 (dd, *J* = 12.0, 10.6 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 174.3, 166.4, 160.6, 152.6, 141.9, 134.9, 131.6, 130.4, 129.6, 129.2, 128.9, 127.8, 126.1, 126.0, 125.7, 124.8, 121.2, 110.1, 88.9, 83.2, 67.9, 61.8, 34.6, 14.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{23}ClNO_5$ 488.1259, found 488.1262.



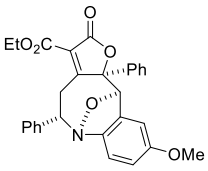
Ethyl 9-fluoro-2-oxo-5,11a-diphenyl-4,5,11,11a-tetrahydro-2*H*-6,11-epoxybenzo[*b*]furo[2,3-*e*]azocine-3-carboxylate (**3ac**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 10/1) to afford a white solid in 88% yield (82.8 mg). Mp: 187 – 188 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.72 – 7.59 (m, 2H), 7.51 (d, *J* = 7.2 Hz, 2H), 7.49 – 7.37 (m, 5H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.09 – 6.96 (m, 2H), 6.89 – 6.81 (m, 1H), 5.99 (s, 1H), 4.48 (dd, *J* = 10.5, 5.5 Hz, 1H), 4.37 – 4.23 (m, 2H), 3.54 (dd, *J* = 12.1, 5.5 Hz, 1H), 2.99 (dd, *J* = 12.1, 10.5 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 174.8, 167.2, 160.5, 159.8 (d, $^1J_{FC}$ = 244.6 Hz), 147.4, 142.3, 134.8, 129.7, 129.3, 128.9, 128.8 (d, $^3J_{FC}$ = 8.9 Hz), 127.8, 126.2, 126.0, 120.9, 117.3 (d, $^2J_{FC}$ = 24.2 Hz), 113.0 (d, $^3J_{FC}$ = 8.8 Hz), 112.2 (d, $^2J_{FC}$ = 25.6 Hz), 87.8, 82.9, 68.7, 61.8, 34.6, 14.2. ^{19}F NMR (470 MHz, $CDCl_3$) δ –117.7. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{23}FNO_5$ 472.1555, found 472.1546.



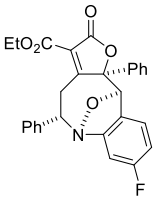
Ethyl 9-chloro-2-oxo-5,11a-diphenyl-4,5,11,11a-tetrahydro-2*H*-6,11-epoxybenzo[*b*]furo[2,3-*e*]azocine-3-carboxylate (**3ad**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 10/1) to afford a white solid in 87% yield (84.6 mg). Mp: 192 – 193 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.59 (m, 2H), 7.55 – 7.38 (m, 7H), 7.36 – 7.26 (m, 3H), 6.83 (d, *J* = 8.3 Hz, 1H), 5.99 (s, 1H), 4.51 (dd, *J* = 10.5, 5.5 Hz, 1H), 4.38 – 4.22 (m, 2H), 3.53 (dd, *J* = 12.2, 5.5 Hz, 1H), 2.99 (dd, *J* = 12.1, 10.5 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 174.5, 167.1, 160.5, 149.9, 142.1, 134.8, 130.4, 129.9, 129.7, 129.3, 128.9, 128.8, 127.8, 126.1, 126.0, 124.8, 121.2, 113.0, 87.7, 82.9, 68.7, 61.9, 34.6, 14.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{23}ClNO_5$ 488.1259, found 488.1250.



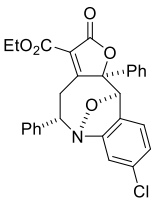
Ethyl 9-bromo-2-oxo-5,11a-diphenyl-4,5,11,11a-tetrahydro-2*H*-6,11-epoxybenzo[*b*]furo [2,3-*e*]azocine-3-carboxylate (**3ae**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 10/1) to afford a white solid in 85% yield (91.4 mg). Mp: 214 – 215 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 – 7.59 (m, 2H), 7.55 – 7.37 (m, 9H), 7.36 – 7.29 (m, 1H), 6.78 (d, J = 8.3 Hz, 1H), 5.99 (s, 1H), 4.51 (dd, J = 10.4, 5.5 Hz, 1H), 4.38 – 4.23 (m, 2H), 3.53 (dd, J = 12.2, 5.5 Hz, 1H), 2.99 (dd, J = 12.1, 10.5 Hz, 1H), 1.35 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 174.4, 167.0, 160.5, 150.4, 142.1, 134.8, 133.2, 129.7, 129.3, 129.1, 128.9, 127.8, 127.7, 126.1, 126.0, 121.2, 117.1, 113.4, 87.7, 82.9, 68.6, 61.9, 34.6, 14.2. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_{28}H_{22}BrNO_5Na$ 554.0574, found 554.0579.



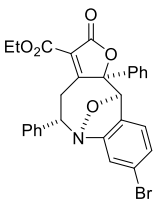
Ethyl 9-methoxy-2-oxo-5,11a-diphenyl-4,5,11,11a-tetrahydro-2*H*-6,11-epoxybenzo[*b*] furo[2,3-*e*]azocine-3-carboxylate (**3af**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 10/1) to afford a white solid in 80% yield (77.3 mg). Mp: 179 – 180 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, J = 7.5 Hz, 2H), 7.52 (d, J = 7.5 Hz, 2H), 7.50 – 7.36 (m, 5H), 7.31 (t, J = 7.4 Hz, 1H), 6.90 – 6.76 (m, 3H), 5.97 (s, 1H), 4.43 (dd, J = 10.4, 5.5 Hz, 1H), 4.38 – 4.20 (m, 2H), 3.79 (s, 3H), 3.50 (dd, J = 12.1, 5.6 Hz, 1H), 2.98 (dd, J = 11.7, 10.8 Hz, 1H), 1.35 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 175.0, 167.7, 160.5, 157.1, 144.5, 142.7, 135.0, 129.6, 129.2, 128.8, 128.2, 127.6, 126.2, 126.1, 120.3, 117.1, 112.9, 109.2, 88.1, 83.0, 68.5, 61.7, 55.9, 34.6, 14.2. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{29}H_{26}NO_6$ 484.1755, found 484.1761.



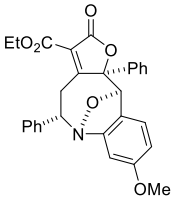
Ethyl 8-fluoro-2-oxo-5,11a-diphenyl-4,5,11,11a-tetrahydro-2*H*-6,11-epoxybenzo[*b*]furo [2,3-*e*]azocine-3-carboxylate (**3ag**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 10/1) to afford a white solid in 89% yield (83.8 mg). Mp: 196 – 197 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.59 (m, 2H), 7.51 (d, J = 7.2 Hz, 2H), 7.50 – 7.38 (m, 5H), 7.33 (t, J = 7.4 Hz, 1H), 7.30 – 7.23 (m, 1H), 6.85 – 6.75 (m, 1H), 6.62 (dd, J = 8.5, 2.2 Hz, 1H), 5.99 (s, 1H), 4.52 (dd, J = 10.4, 5.6 Hz, 1H), 4.39 – 4.23 (m, 2H), 3.56 (dd, J = 12.1, 5.6 Hz, 1H), 3.00 (dd, J = 12.1, 10.5 Hz, 1H), 1.36 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 174.6, 167.3, 164.1 (d, $^1J_{FC}$ = 248.3 Hz), 160.4, 153.1 (d, $^3J_{FC}$ = 11.3 Hz), 142.0, 134.8, 129.7, 129.3, 128.9, 127.8, 126.2, 126.0, 125.7 (d, $^3J_{FC}$ = 10.1 Hz), 122.4, 121.2, 111.7 (d, $^2J_{FC}$ = 23.3 Hz), 100.2 (d, $^2J_{FC}$ = 26.9 Hz), 88.0, 82.8, 68.2, 61.8, 34.6, 14.2. ^{19}F NMR (470 MHz, $CDCl_3$) δ –110.1. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{28}H_{23}FNO_5$ 472.1555, found 472.1554.



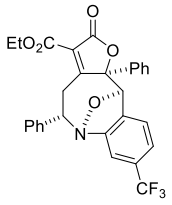
Ethyl 8-chloro-2-oxo-5,11a-diphenyl-4,5,11,11a-tetrahydro-2*H*-6,11-epoxybenzo[*b*]furo[2,3-*e*] azocine-3-carboxylate (**3ah**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 10/1) to afford a white solid in 87% yield (84.7 mg). Mp: 193 – 194 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 – 7.59 (m, 2H), 7.56 – 7.36 (m, 7H), 7.36 – 7.30 (m, 1H), 7.24 (d, J = 8.1 Hz, 1H), 7.07 (dd, J = 8.0, 1.8 Hz, 1H), 6.90 (d, J = 1.8 Hz, 1H), 6.00 (s, 1H), 4.50 (dd, J = 10.5, 5.5 Hz, 1H), 4.38 – 4.25 (m, 2H), 3.56 (dd, J = 12.2, 5.6 Hz, 1H), 3.00 (dd, J = 12.1, 10.5 Hz, 1H), 1.36 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 174.6, 167.3, 160.4, 152.7, 141.9, 136.2, 134.8, 129.7, 129.3, 128.9, 127.8, 126.2, 126.0, 125.6, 125.4, 124.9, 121.2, 112.6, 87.9, 82.9, 68.5, 61.9, 34.6, 14.2. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{28}H_{23}ClNO_5$ 488.1259, found 488.1260.



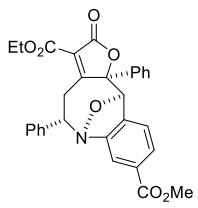
Ethyl 8-bromo-2-oxo-5,11a-diphenyl-4,5,11,11a-tetrahydro-2*H*-6,11-epoxybenzo[*b*]furo[2,3-*e*]azocine-3-carboxylate (**3ai**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 10/1) to afford a white solid in 92% yield (97.7 mg). Mp: 200 – 201 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, J = 7.7 Hz, 2H), 7.55 – 7.38 (m, 7H), 7.32 (t, J = 7.4 Hz, 1H), 7.25 – 7.14 (m, 2H), 7.06 (s, 1H), 5.98 (s, 1H), 4.50 (dd, J = 10.4, 5.5 Hz, 1H), 4.39 – 4.24 (m, 2H), 3.57 (dd, J = 12.1, 5.5 Hz, 1H), 3.05 – 2.94 (m, 1H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.5, 167.3, 160.4, 152.8, 141.9, 134.7, 129.7, 129.3, 128.9, 127.8, 127.7, 126.2, 126.0, 125.8, 123.9, 121.2, 115.4, 87.8, 82.9, 68.5, 61.9, 34.6, 14.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{23}BrNO_5$ 532.0754, found 532.0749.



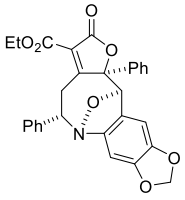
Ethyl 8-methoxy-2-oxo-5,11a-diphenyl-4,5,11,11a-tetrahydro-2*H*-6,11-epoxybenzo[*b*]furo[2,3-*e*]azocine-3-carboxylate (**3aj**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 10/1) to afford a white solid in 84% yield (81.1 mg). Mp: 190 – 191 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, J = 7.3 Hz, 2H), 7.53 (d, J = 7.5 Hz, 2H), 7.49 – 7.36 (m, 5H), 7.32 (t, J = 7.3 Hz, 1H), 7.21 (d, J = 8.3 Hz, 1H), 6.68 – 6.56 (m, 1H), 6.43 (s, 1H), 5.95 (s, 1H), 4.52 (dd, J = 10.3, 5.5 Hz, 1H), 4.39 – 4.20 (m, 2H), 3.78 (s, 3H), 3.54 (dd, J = 12.0, 5.5 Hz, 1H), 3.06 – 2.93 (m, 1H), 1.35 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 175.1, 167.6, 161.6, 160.5, 153.0, 142.5, 135.1, 129.5, 129.2, 128.8, 127.7, 126.2, 126.1, 125.1, 120.9, 118.8, 110.0, 98.4, 88.3, 82.9, 68.2, 61.6, 55.6, 34.6, 14.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{29}H_{26}NO_6$ 484.1755, found 484.1749.



Ethyl 2-oxo-5,11a-diphenyl-8-(trifluoromethyl)-4,5,11,11a-tetrahydro-2*H*-6,11-epoxybenzo[*b*]furo[2,3-*e*]azocine-3-carboxylate (**3ak**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 10/1) to afford a white solid in 86% yield (89.6 mg). Mp: 186 – 187 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, J = 7.0 Hz, 2H), 7.59 – 7.29 (m, 10H), 7.13 (s, 1H), 6.08 (s, 1H), 4.56 (dd, J = 10.3, 5.5 Hz, 1H), 4.38 – 4.19 (m, 2H), 3.58 (dd, J = 12.2, 5.6 Hz, 1H), 3.09 – 2.94 (m, 1H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 174.2, 167.1, 160.3, 152.0, 141.7, 134.5, 132.9 (q, $^2J_{FC}$ = 32.7 Hz), 130.9, 129.8, 129.4, 129.0, 127.9, 126.1, 126.0, 125.2, 123.6 (q, $^1J_{FC}$ = 272.5 Hz), 121.8 (q, $^3J_{FC}$ = 3.5 Hz), 121.3, 109.1, 87.6, 82.8, 68.5, 61.9, 34.6, 14.1. ^{19}F NMR (470 MHz, $CDCl_3$) δ –62.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{29}H_{23}F_3NO_5$ 522.1523, found 522.1525.

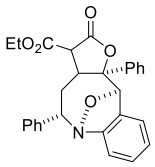


3-Ethyl 8-methyl 2-oxo-5,11a-diphenyl-4,5,11,11a-tetrahydro-2*H*-6,11-epoxybenzo[*b*]furo[2,3-*e*]azocine-3,8-dicarboxylate (**3al**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 10/1) to afford a white solid in 96% yield (98.1 mg). Mp: 213 – 214 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.74 (m, 1H), 7.69 – 7.61 (m, 2H), 7.60 – 7.51 (m, 3H), 7.51 – 7.36 (m, 6H), 7.32 (t, J = 7.4 Hz, 1H), 6.06 (s, 1H), 4.56 (dd, J = 10.5, 5.5 Hz, 1H), 4.35 – 4.19 (m, 2H), 3.91 (s, 3H), 3.57 (dd, J = 12.2, 5.5 Hz, 1H), 3.02 (dd, J = 12.1, 10.6 Hz, 1H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 174.5, 167.1, 166.0, 160.2, 151.7, 142.0, 134.7, 132.4, 131.8, 129.7, 129.3, 128.8, 127.8, 126.3, 126.1, 126.0, 124.6, 120.9, 113.0, 87.7, 82.8, 68.6, 61.8, 52.4, 34.5, 14.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{30}H_{26}NO_7$ 512.1704, found 512.1708.

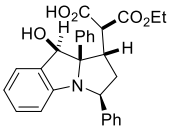


Ethyl 2-oxo-5,12a-diphenyl-4,5,12,12a-tetrahydro-2*H*-6,12-epoxy[1,3]dioxolo[4',5':4,5]benzo[1,2-*b*]furo[2,3-*e*]azocine-3-carboxylate (**3an**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 10/1) to afford a white solid in 85% yield (82.8 mg). Mp: 163 – 164 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 – 7.59 (m, 2H), 7.54 – 7.38 (m, 7H), 7.31 (t, *J* = 7.4 Hz, 1H), 6.74 (s, 1H), 6.40 (s, 1H), 6.00 (d, *J* = 1.2 Hz, 1H), 5.97 (d, *J* = 1.2 Hz, 1H), 5.88 (s, 1H), 4.41 (dd, *J* = 10.5, 5.4 Hz, 1H), 4.38 – 4.25 (m, 2H), 3.52 (dd, *J* = 12.1, 5.4 Hz, 1H), 3.00 (dd, *J* = 11.9, 10.7 Hz, 1H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 175.3, 167.7, 160.6, 149.6, 145.8, 145.0, 142.5, 135.0, 129.6, 129.2, 128.8, 127.6, 126.2, 126.0, 120.6, 118.3, 104.7, 102.1, 94.5, 88.4, 83.2, 68.0, 61.7, 34.6, 14.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{29}H_{24}NO_7$ 498.1547, found 498.1556.

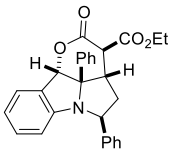
5.3 Characterization data of transformation products



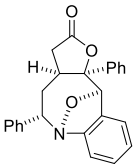
Ethyl 2-oxo-5,11a-diphenyl-3,3a,4,5,11,11a-hexahydro-2*H*-6,11-epoxybenzo[*b*]furo[2,3-*e*]azocine-3-carboxylate (**4**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 15/1 – 10/1) to afford a white solid in 80% yield (332.2 mg). Mp: 123 – 124 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.65 (m, 2H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.49 – 7.32(m, 8H), 7.24 – 7.18 (m, 1H), 7.04 (d, *J* = 7.7 Hz, 1H), 5.65 (s, 1H), 4.53 (dd, *J* = 9.3, 4.0 Hz, 1H), 4.08 – 3.95 (m, 2H), 3.30 – 3.20 (m, 1H), 2.62 – 2.52 (m, 1H), 2.50 (d, *J* = 10.3 Hz, 1H), 2.06 – 1.93 (m, 1H), 1.13 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 170.5, 166.5, 151.6, 142.8, 142.0, 130.4, 130.1, 128.9, 128.8, 128.5, 127.5, 126.4, 125.6, 125.3, 124.7, 112.5, 88.1, 87.4, 73.4, 62.2, 51.2, 49.8, 32.4, 13.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{26}NO_5$ 456.1805, found 456.1811.



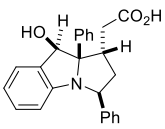
3-Ethoxy-2-(9-hydroxy-3,9a-diphenyl-2,3,9,9a-tetrahydro-1*H*-pyrolo[1,2-*a*]indol-1-yl)-3-oxopropanoic acid (**5**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 5/1 – 2/1) to afford a white solid in 80% yield (36.6 mg in MeOH), 25% yield (11.5 mg in DCM). Mp: 139 – 140 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.79 (m, 2H), 7.47 (d, *J* = 7.4 Hz, 2H), 7.43 – 7.35 (m, 4H), 7.34 – 7.27 (m, 3H), 7.18 (t, *J* = 7.7 Hz, 1H), 6.93 – 6.86 (m, 1H), 6.56 (d, *J* = 7.9 Hz, 1H), 5.66 (s, 1H), 4.57 (dd, *J* = 11.6, 5.9 Hz, 1H), 4.30 – 4.16 (m, 2H), 3.73 – 3.64 (m, 1H), 3.56 (d, *J* = 11.1 Hz, 1H), 2.22 – 2.14 (m, 1H), 2.13 – 2.04 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 171.0, 168.3, 153.6, 143.3, 141.0, 130.8, 130.7, 128.7, 128.4, 128.0, 127.7, 127.3, 126.7, 126.2, 121.1, 110.7, 84.4, 75.7, 66.2, 62.1, 51.9, 47.2, 40.4, 14.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{28}NO_5$ 458.1962, found 458.1969.



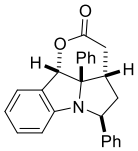
Ethyl 2-oxo-3a1,5-diphenyl-3,3a,3a1,4,5,10b-hexahydro-2*H*-benzo[*b*]pyrano[4,3,2-*gh*]pyrrolizine-3-carboxylate (**6**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 10/1 – 8/1) to afford a white solid in 15% yield (6.7 mg in MeOH), 50% yield (21.9 mg in DCM). Mp: 181 – 182 °C**.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.5 Hz, 2H), 7.52 – 7.27 (m, 10H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 5.75 (s, 1H), 4.67 (dd, *J* = 10.9, 6.9 Hz, 1H), 4.40 – 4.23 (m, 2H), 3.48 – 3.36 (m, 1H), 3.02 (d, *J* = 13.1 Hz, 1H), 2.46 – 2.36 (m, 1H), 2.32 – 2.19 (m, 1H), 1.33 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 168.4, 167.5, 154.6, 144.8, 142.5, 131.7, 129.0, 128.8, 127.9, 127.4, 126.5, 125.8, 125.6, 125.1, 121.9, 111.1, 87.5, 78.9, 68.2, 62.1, 48.9, 46.6, 39.1, 14.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{26}NO_4$ 440.1856, found 440.1861.



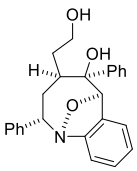
5,11a-Diphenyl-3,3a,4,5,11,11a-hexahydro-2*H*-6,11-epoxybenzo[*b*]furo[2,3-*e*]azocin-2-one (**7**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 10/1) to afford a white solid in 89% yield (251.5 mg). Mp: 228 – 229 °C**.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, J = 7.7 Hz, 2H), 7.59 – 7.27 (m, 10H), 7.26 – 7.18 (m, 1H), 7.05 (d, J = 7.8 Hz, 1H), 5.44 (s, 1H), 4.57 (s, 1H), 2.99 – 2.85 (m, 1H), 2.51 – 2.39 (m, 1H), 2.15 – 1.99 (m, 1H), 1.94 – 1.73 (m, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 175.8, 149.8, 144.2, 139.8, 132.8, 129.4, 128.9, 128.7, 128.1, 127.2, 127.0, 125.6, 125.5, 124.0, 113.3, 89.8, 87.3, 72.5, 43.6, 36.2, 32.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{22}NO_3$ 384.1594, found 384.1589.



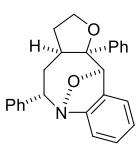
2-(9-Hydroxy-3,9a-diphenyl-2,3,9,9a-tetrahydro-1*H*-pyrrolo[1,2-*a*]indol-1-yl)acetic acid (**8**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 5/1 – 2/1) to afford a white solid in 85% yield (32.7 mg in MeOH), 35% yield (13.5 mg in DCM). Mp: 121 – 122 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, J = 7.3 Hz, 2H), 7.47 (d, J = 7.7 Hz, 2H), 7.40 – 7.17 (m, 8H), 6.89 (t, J = 7.3 Hz, 1H), 6.67 (d, J = 7.9 Hz, 1H), 5.55 (s, 1H), 4.52 (dd, J = 10.7, 6.8 Hz, 1H), 3.35 – 3.22 (m, 1H), 2.66 (dd, J = 16.4, 5.6 Hz, 1H), 2.46 – 2.36 (m, 1H), 2.16 (dd, J = 16.4, 9.0 Hz, 1H), 2.11 – 2.01 (m, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 177.6, 155.2, 143.5, 141.2, 131.0, 130.7, 128.5, 128.3, 127.7, 127.4, 127.0, 126.5, 125.7, 121.0, 110.6, 84.5, 75.5, 66.3, 44.3, 40.8, 34.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{24}NO_3$ 386.1751, found 386.1750.



3a1,5-Diphenyl-3,3a,3a1,4,5,10b-hexahydro-2*H*-benzo[*b*]pyrano[4,3,2-*gh*]pyrrolizin-2-one (**9**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 10/1 – 6/1) to afford a white solid in 8% yield (3 mg in MeOH), 50% yield (18.5 mg in DCM). Mp: 158 – 159 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J = 8.2 Hz, 2H), 7.48 (d, J = 7.6 Hz, 2H), 7.45 – 7.39 (m, 2H), 7.39 – 7.22 (m, 6H), 6.94 (t, J = 7.4 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H), 5.74 (s, 1H), 4.68 (dd, J = 10.7, 7.0 Hz, 1H), 3.12 – 2.99 (m, 1H), 2.57 (dd, J = 15.7, 4.2 Hz, 1H), 2.48 (dd, J = 13.2, 7.0 Hz, 1H), 2.29 – 2.16 (m, 1H), 2.03 (dd, J = 15.7, 13.8 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 171.8, 155.2, 145.4, 143.0, 131.3, 128.81, 128.75, 127.6, 127.2, 126.5, 126.0, 125.7, 125.6, 121.6, 110.8, 87.6, 79.6, 68.6, 43.9, 40.0, 32.9. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{22}NO_2$ 368.1645, found 368.1641.

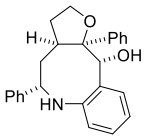


4-(2-Hydroxyethyl)-2,5-diphenyl-3,4,5,6-tetrahydro-2*H*-1,6-epoxybenzo[*b*]azocin-5-ol (**10**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 5/1 – 2/1) to afford a white solid in 94% yield (120 mg). Mp: 178 – 179 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, J = 7.2 Hz, 2H), 7.59 – 7.41 (m, 5H), 7.40 – 7.30 (m, 4H), 7.25 – 7.16 (m, 2H), 7.06 (d, J = 7.8 Hz, 1H), 5.33 (s, 1H), 4.51 (s, 1H), 3.38 – 3.24 (m, 1H), 3.21 – 3.08 (m, 1H), 3.03 – 2.80 (m, 1H), 2.57 – 2.43 (m, 1H), 2.05 – 1.91 (m, 1H), 1.80 – 1.48 (m, 2H), 1.24 – 1.15 (m, 1H), 1.14 – 1.03 (m, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 149.6, 148.2, 140.7, 134.3, 128.8, 128.5, 128.4, 127.1, 126.9, 126.8, 124.9, 124.8, 124.7, 113.6, 90.0, 79.6, 72.1, 59.9, 40.8, 33.0, 29.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{26}NO_3$ 388.1907, found 388.1900.

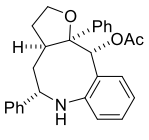


5,11a-Diphenyl-3,3a,4,5,11,11a-hexahydro-2*H*-6,11-epoxybenzo[*b*]furo[2,3-*e*]azocine (**11**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 10/1 – 8/1) to afford a white solid in 90% yield (33.1 mg). Mp: 177 – 178 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.73 (m, 2H), 7.57 – 7.44 (m, 5H), 7.39 – 7.28 (m, 4H), 7.25 – 7.16 (m, 2H), 7.03 (d, J = 7.8 Hz, 1H), 5.26 (s, 1H), 4.57 – 4.46 (m, 1H), 4.12 – 4.01 (m, 1H), 3.93 – 3.81 (m, 1H), 2.78 – 2.66

(m, 1H), 2.16 – 2.03 (m, 1H), 1.93 – 1.83 (m, 1H), 1.82 – 1.71 (m, 1H), 1.24 – 1.12 (m, 1H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 150.2, 148.6, 141.1, 135.0, 128.47, 128.45, 128.3, 127.2, 126.9, 126.8, 125.4, 124.7, 124.6, 113.1, 90.2, 88.8, 73.0, 68.7, 47.0, 32.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{24}NO_2$ 370.1802, found 370.1808.



5,11a-Diphenyl-2,3,3a,4,5,6,11,11a-octahydrobenzo[*b*]furo[2,3-*e*]azocin-11-ol (**12**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 8/1 – 6/1) to afford a white solid in 86% yield (90 mg). Mp: 176 – 177 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.80 (brs, 1H), 7.87 – 7.71 (m, 1H), 7.65 (d, J = 7.6 Hz, 2H), 7.61 – 7.50 (m, 3H), 7.50 – 7.28 (m, 7H), 7.07 (d, J = 7.5 Hz, 1H), 4.62 (brs, 1H), 4.46 (brs, 1H), 3.88 – 3.59 (m, 3H), 2.84 – 2.69 (m, 1H), 2.26 – 2.11 (m, 1H), 1.61 – 1.49 (m, 1H), 1.20 – 1.11 (m, 1H), 0.95 – 0.78 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.8, 143.6, 141.8, 137.5, 131.0, 128.7, 128.3, 128.0, 127.4, 126.8, 126.6, 126.2, 125.5, 124.8, 91.1, 80.2, 65.2, 63.9, 37.0, 35.4, 34.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{26}NO_2$ 372.1958, found 372.1967.

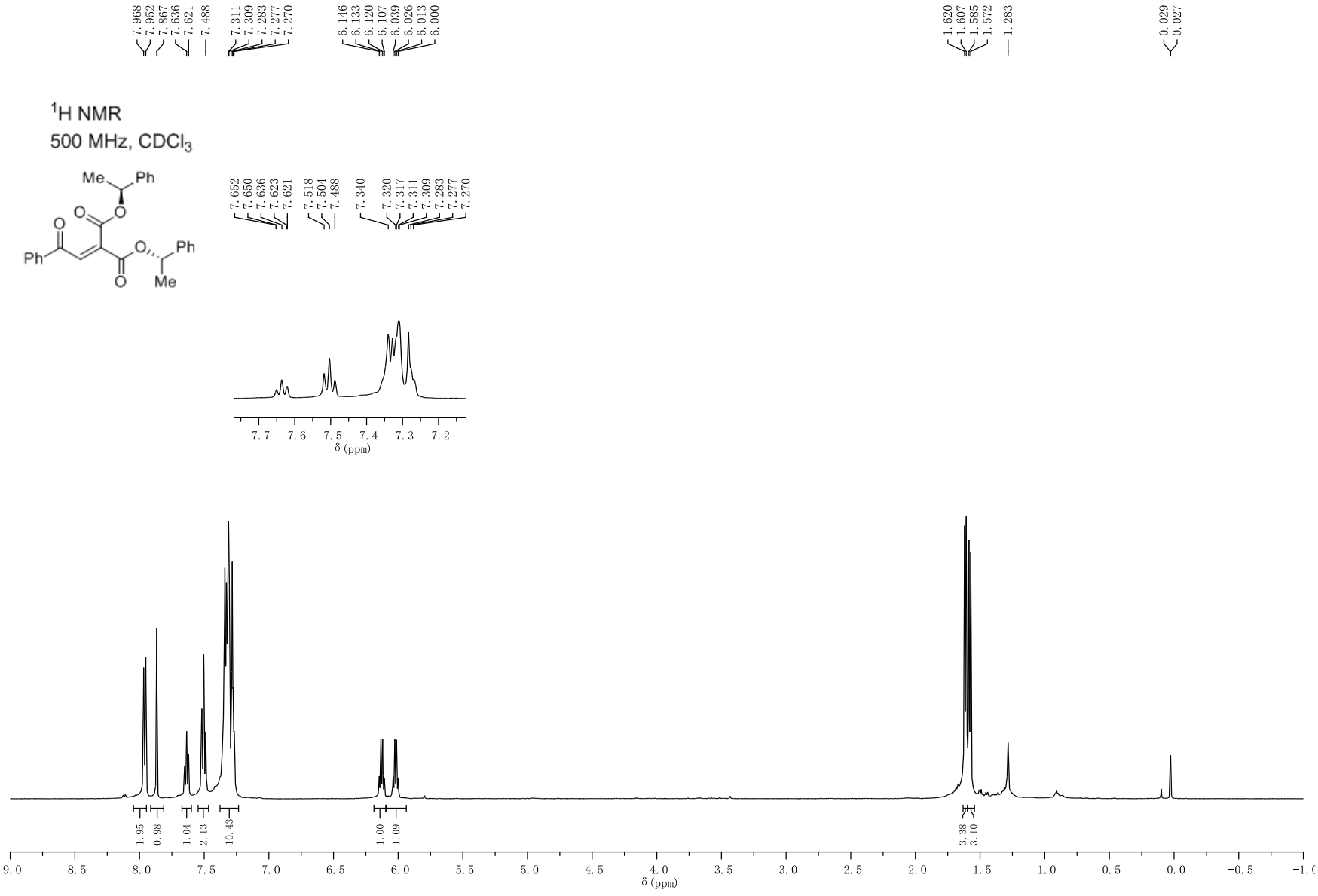


5,11a-diphenyl-2,3,3a,4,5,6,11,11a-octahydrobenzo[b]furo[2,3-e]azocin-11-yl acetate (**13**). Purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate (v/v): 6/1) to afford a white solid in 76% yield (15.9 mg). Mp: 182 – 183 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.38 (m, 4H), 7.38 – 7.30 (m, 1H), 7.24 – 7.04 (m, 6H), 7.04 – 6.95 (m, 1H), 6.67 – 6.39 (m, 3H), 5.17 – 4.98 (m, 1H), 4.09 – 3.86 (m, 2H), 3.85 – 3.73 (m, 1H), 3.26 – 3.09 (m, 1H), 2.62 – 2.51 (m, 1H), 2.14 (s, 3H), 2.09 – 1.96 (m, 1H), 1.92 – 1.80 (m, 1H), 1.80 – 1.69 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9, 145.7, 144.8, 140.4, 129.0, 128.8, 128.2, 127.6, 127.2, 126.9, 126.8, 126.7, 119.5, 119.2, 90.2, 74.3, 64.5, 58.4, 42.7, 39.4, 32.4, 21.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{28}NO_3$ 414.2064, found 414.2072.

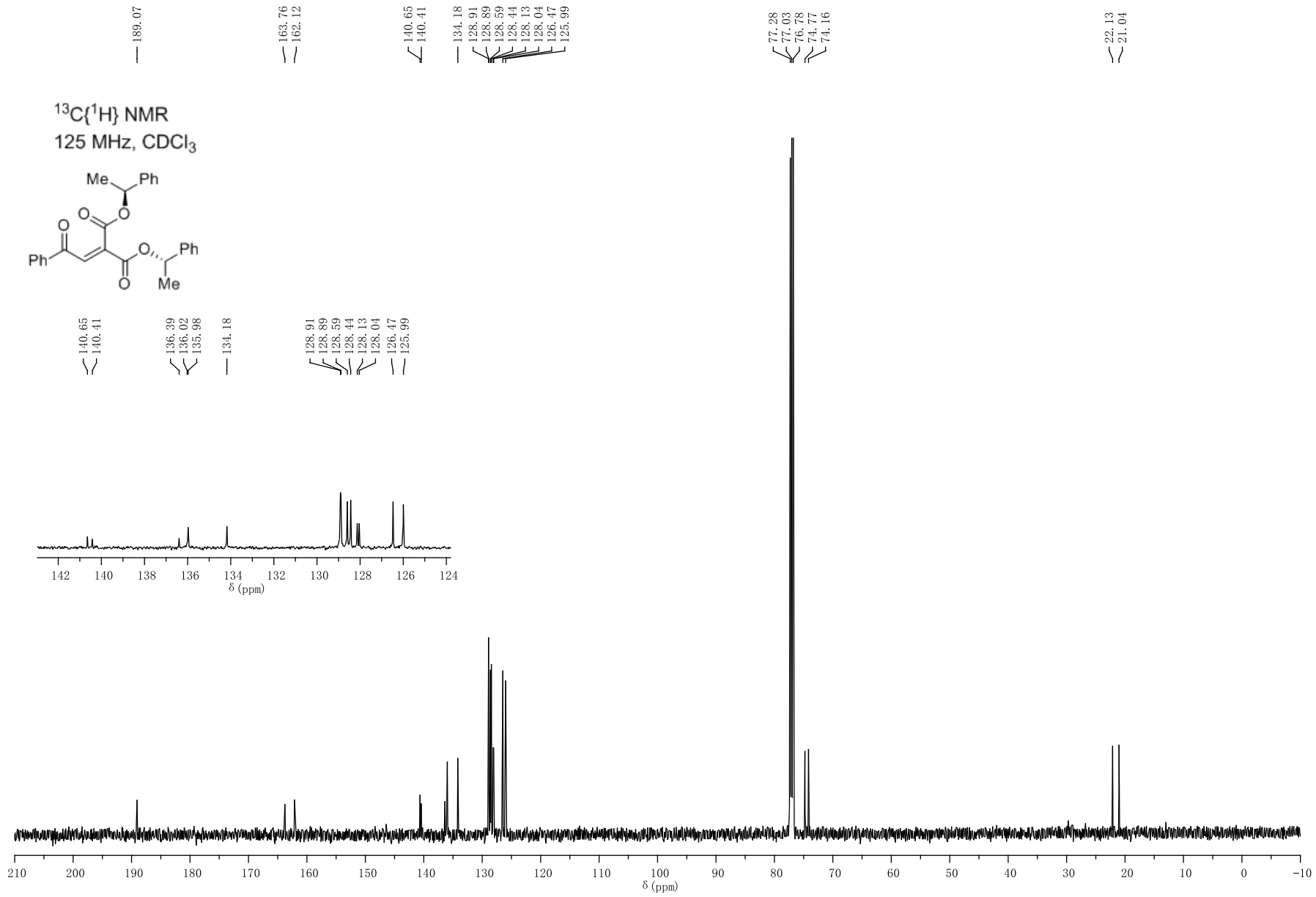
6. Copies of NMR spectra for compounds

6.1 Copies of NMR spectra for compounds 15u, 16u, 1u and 1u′

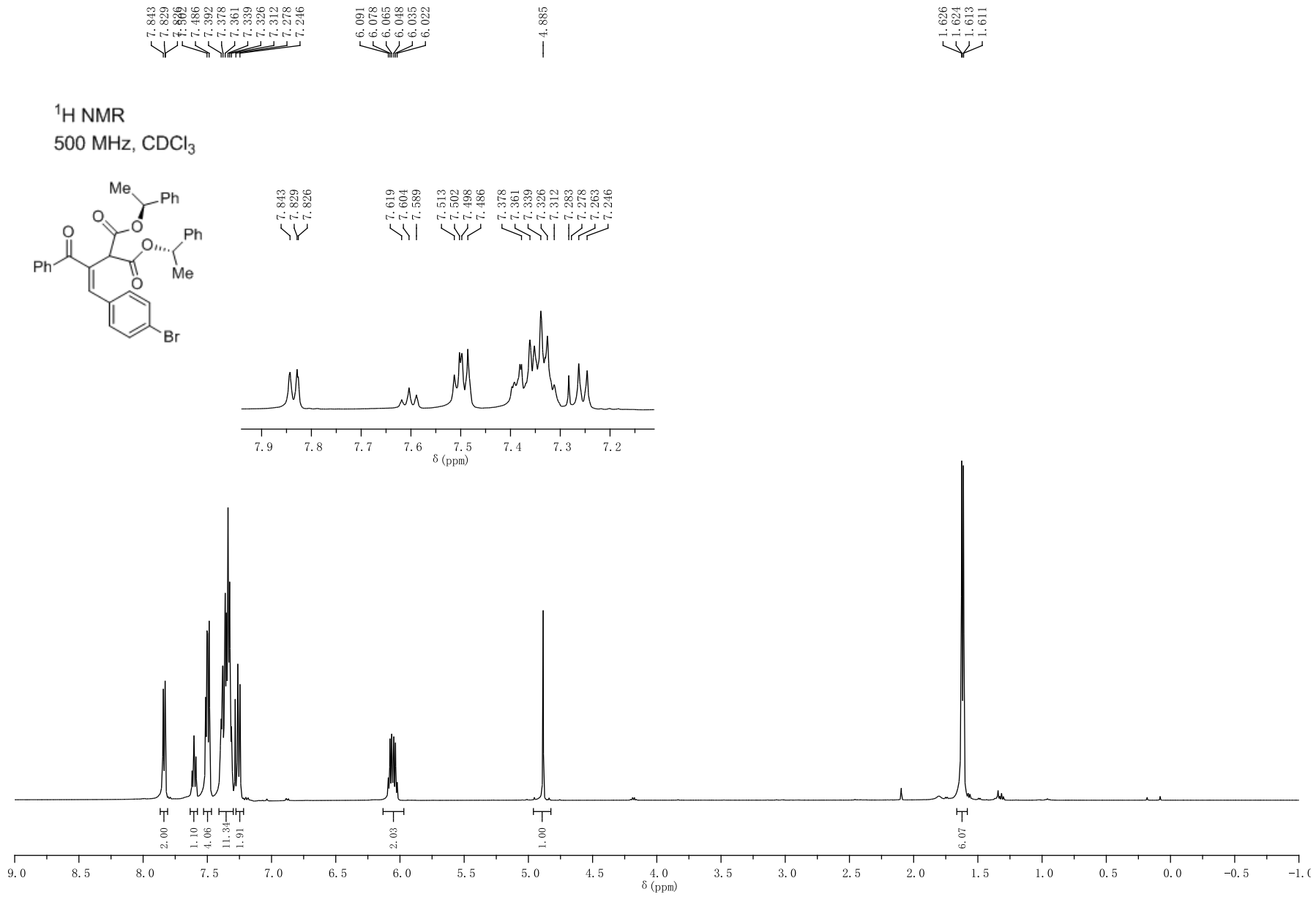
Compound 15u



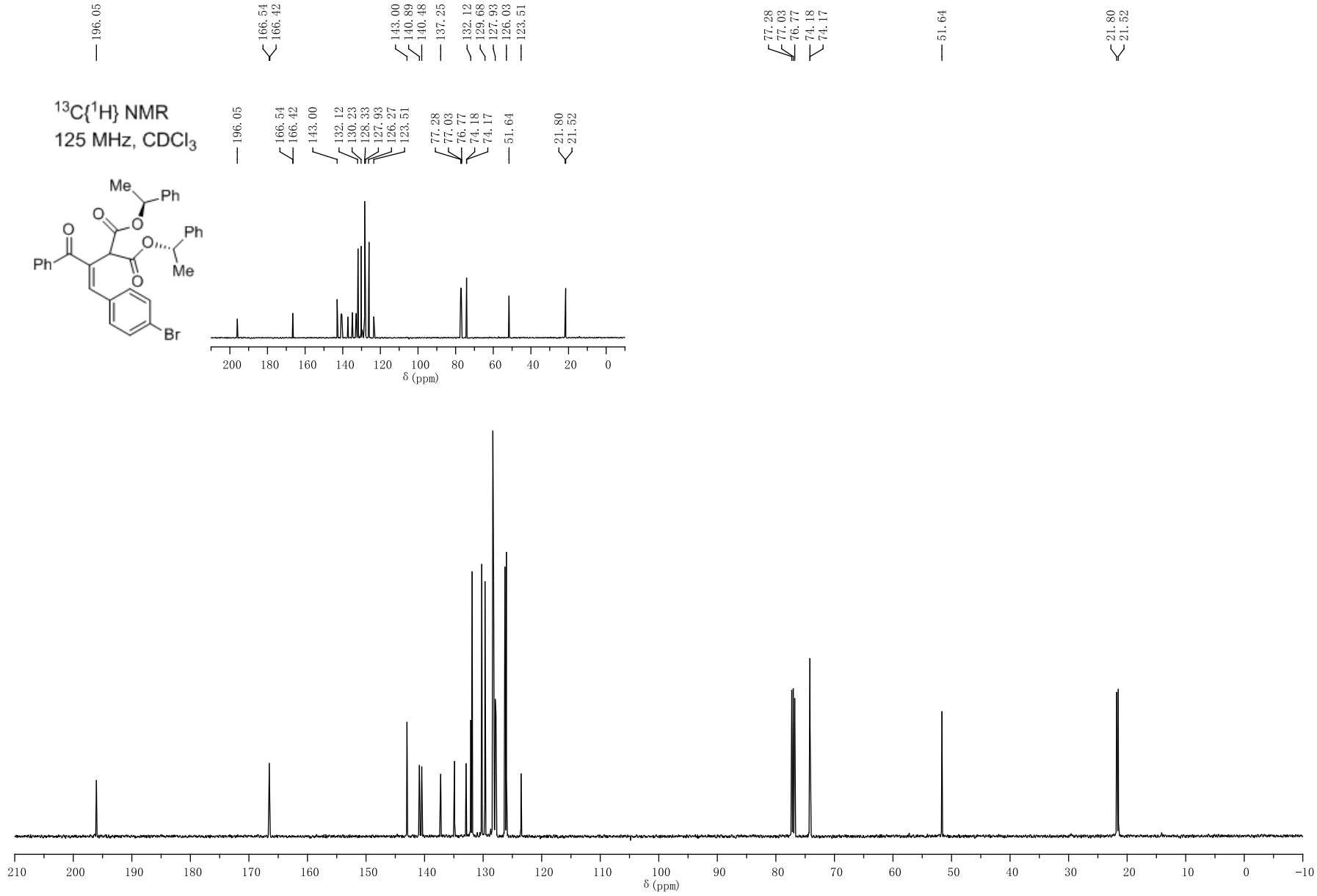
Compound 15u



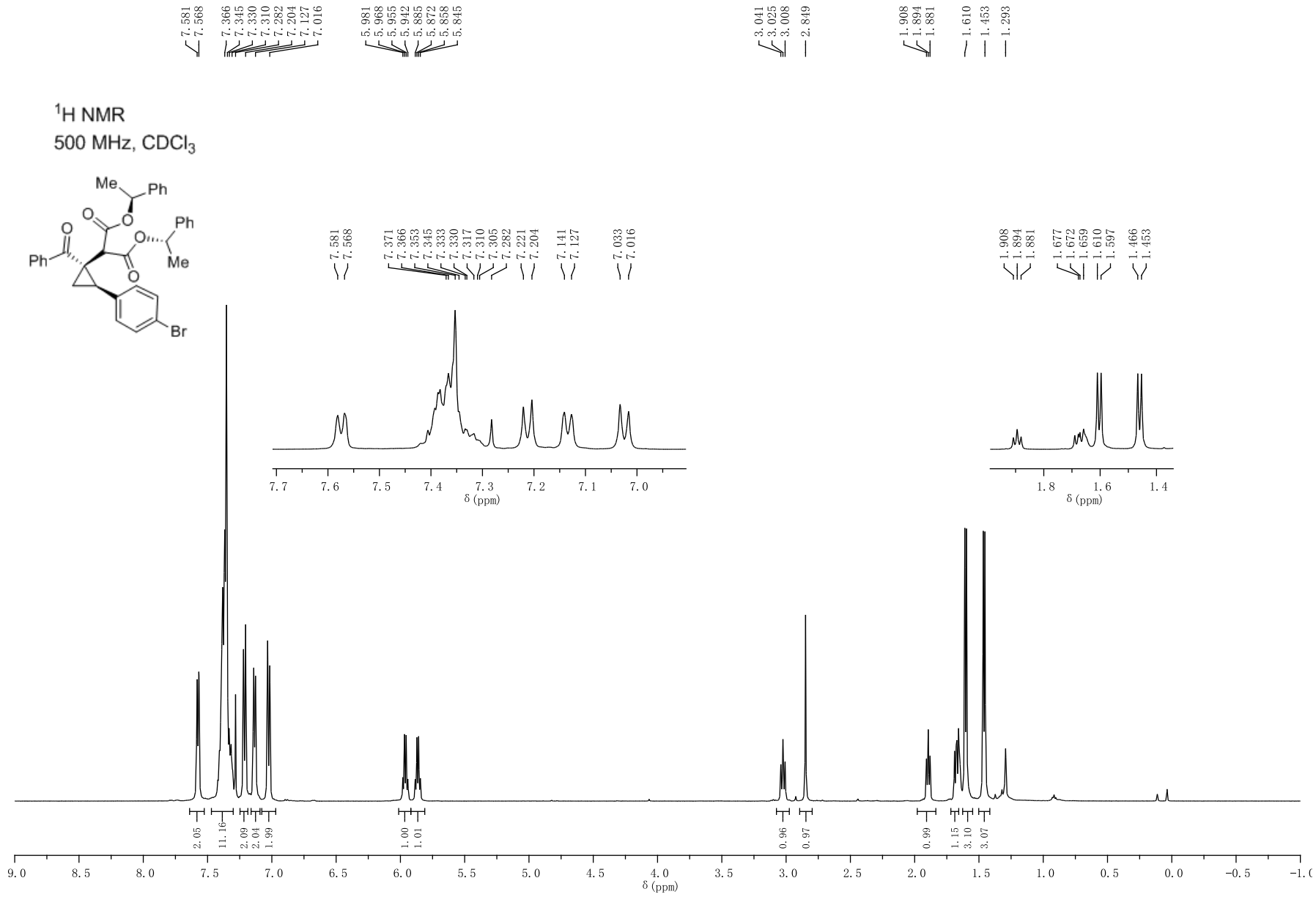
Compound 16u



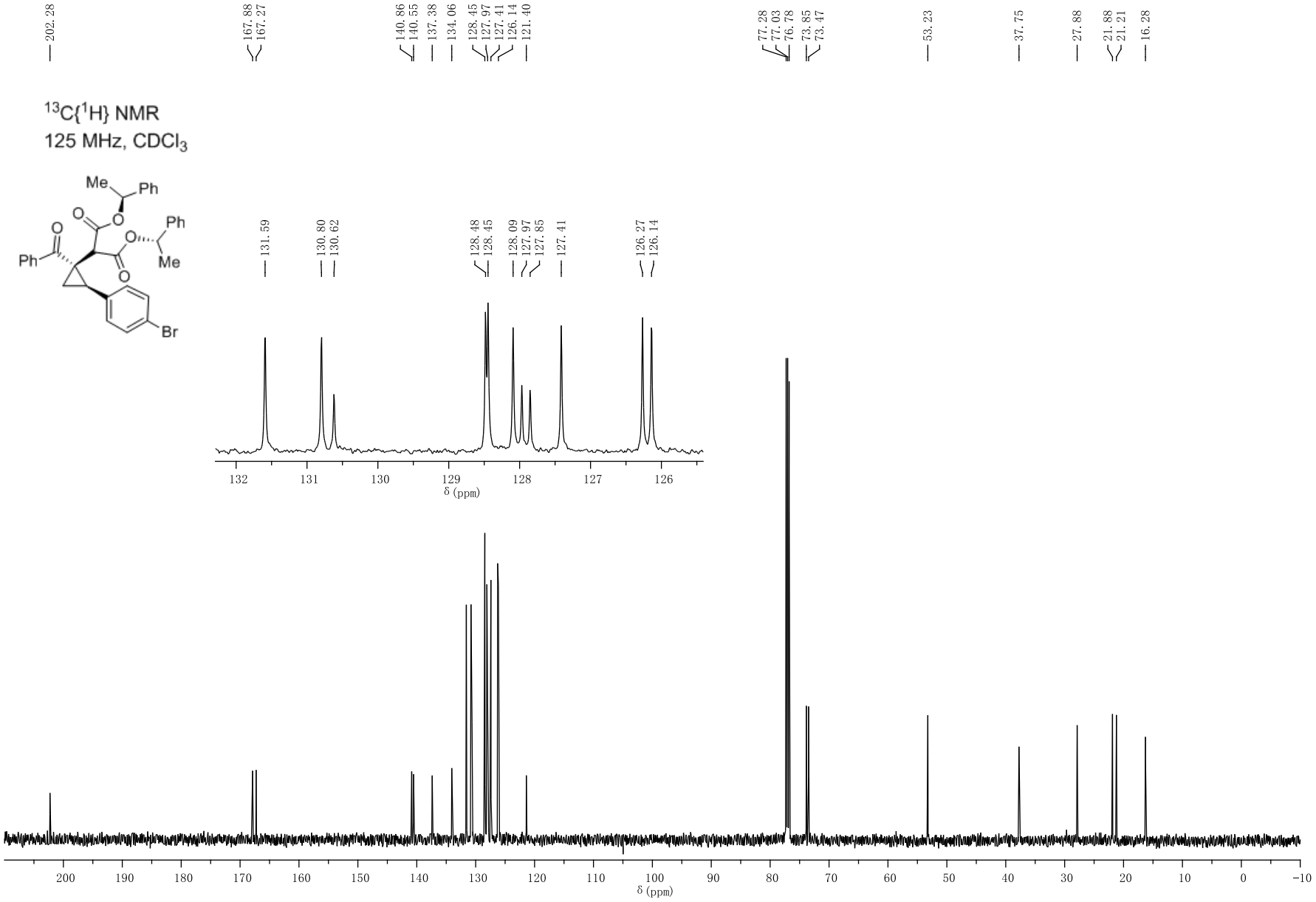
Compound 16u



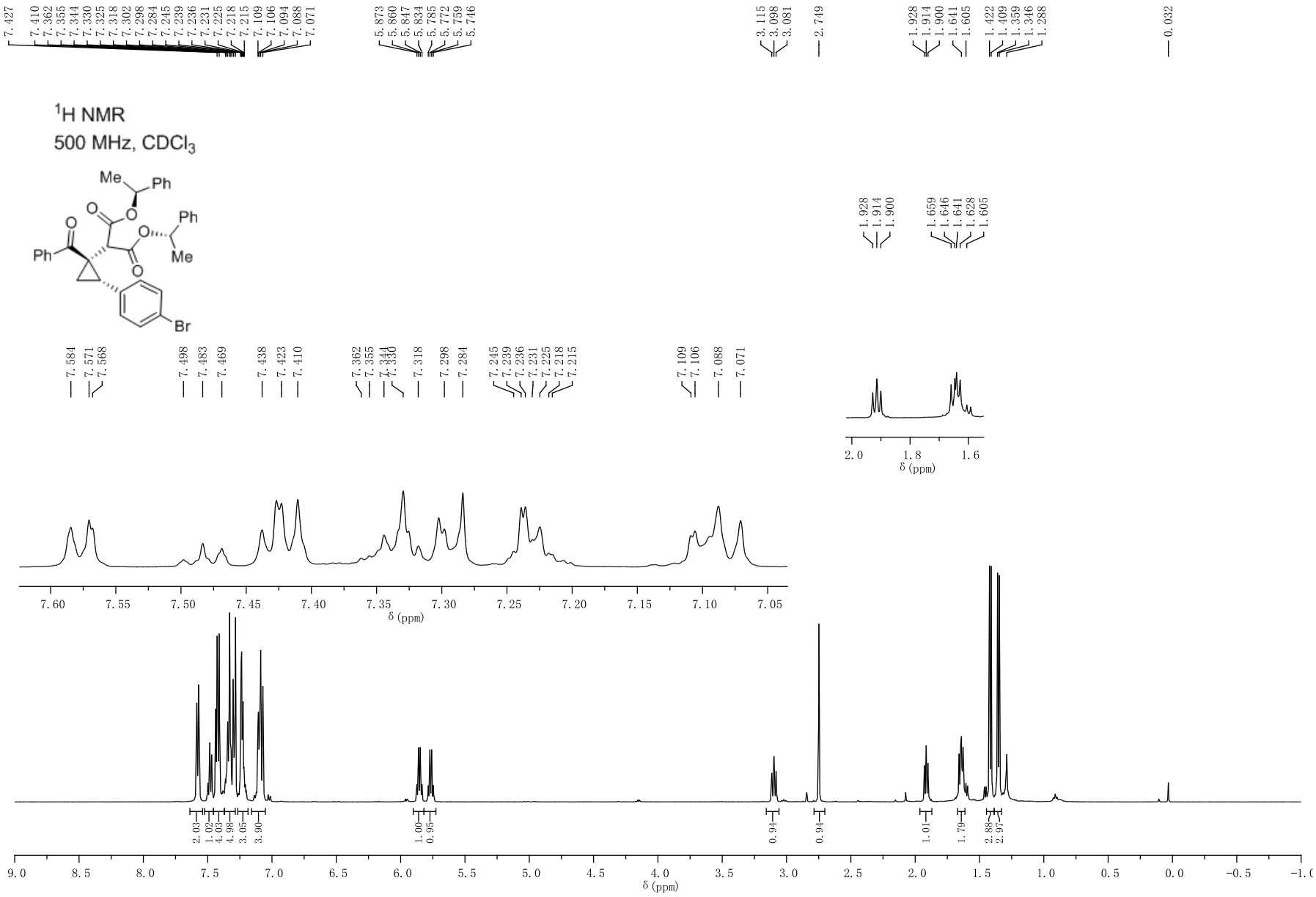
Compound 1u


7.581
7.568
7.366
7.345
7.330
7.310
7.282
7.204
7.127
7.016
5.981
5.968
5.955
5.942
5.885
5.872
5.858
5.845
3.041
3.025
3.008
2.849
1.908
1.894
1.881
1.610
1.453
1.293
1H NMR
500 MHz, CDCl3
Me
Ph
O
O
Ph
O
Me
Ph
O
Br
δ (ppm)
2.05
11.16
2.09
2.04
1.99
1.00
1.01
0.96
0.97
0.99
1.15
3.10
3.07

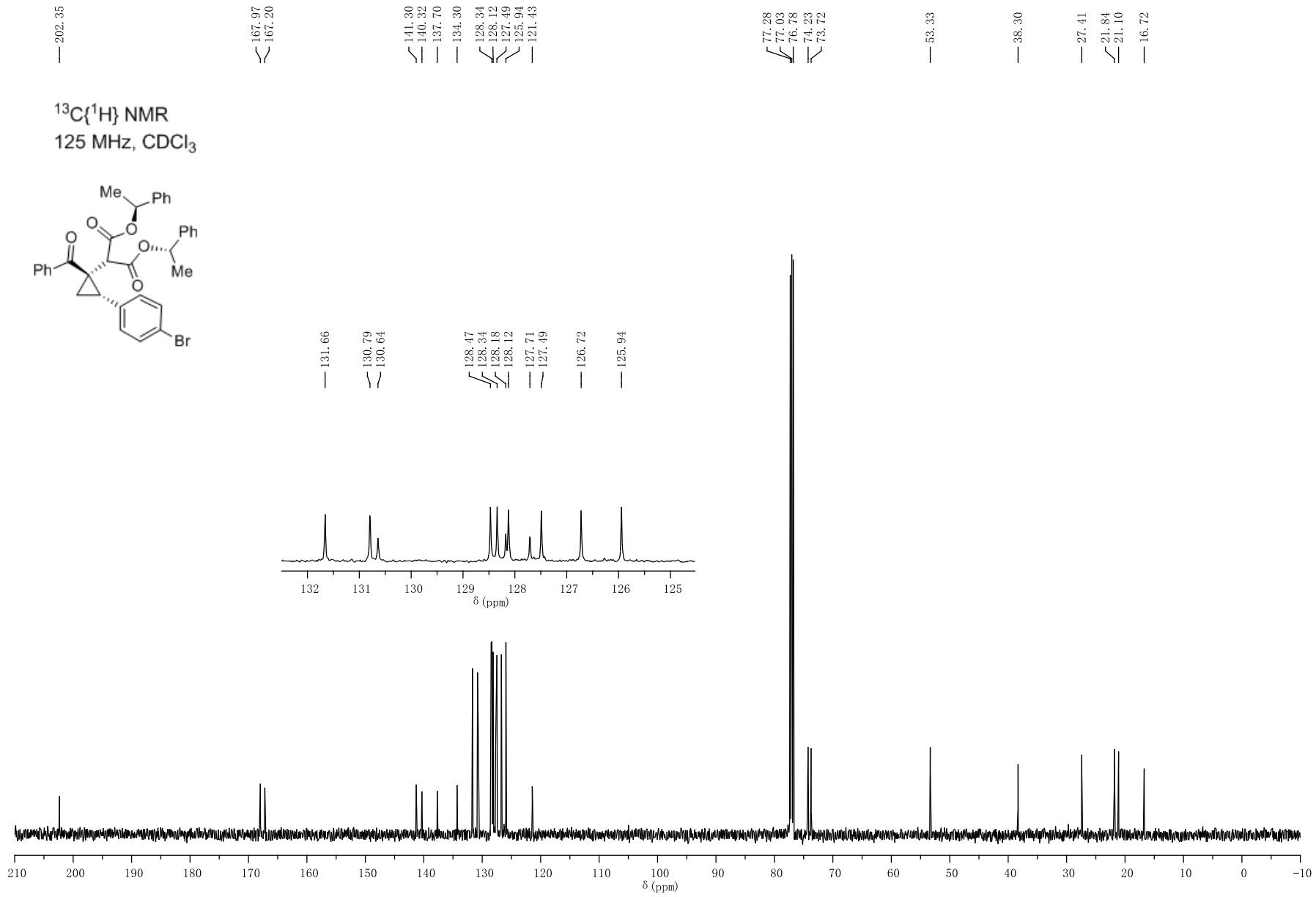
Compound 1u


202.28
167.88
167.27
140.86
140.55
137.38
134.06
128.45
127.97
127.41
126.14
121.40
77.28
77.03
76.78
73.85
73.47
53.23
37.75
27.88
21.88
21.21
16.28
13C{1H} NMR
125 MHz, CDCl3
Me
Ph
O
O
Ph
O
Me
Ph
O
O
Br
131.59
130.80
130.62
128.48
128.45
128.09
127.97
127.85
127.41
126.27
126.14
132
131
130
129
128
127
126
δ (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
δ (ppm)

Compound 1u′

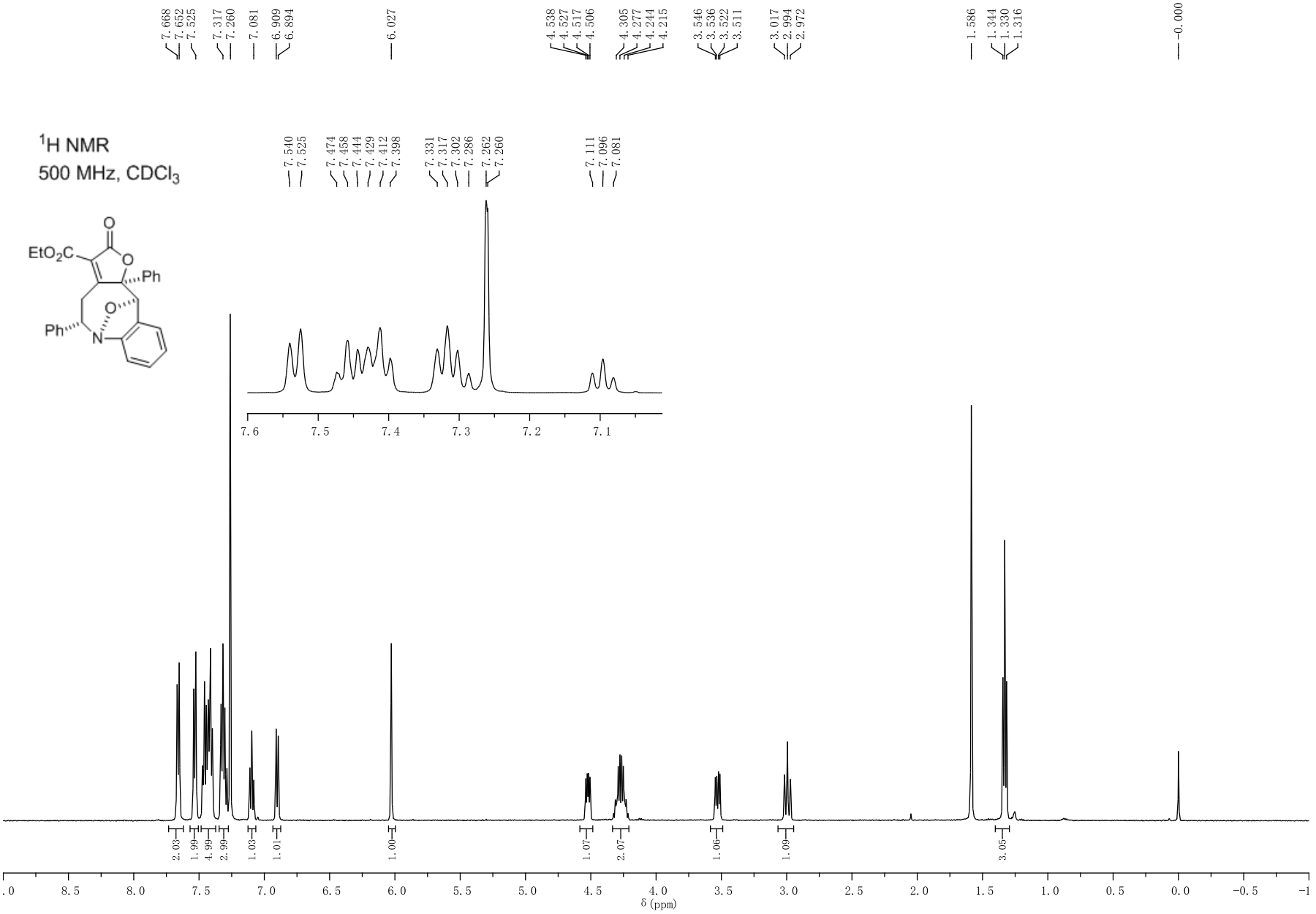

7.427 7.410 7.362 7.355 7.344 7.330 7.325 7.318 7.302 7.298 7.284 7.245 7.239 7.236 7.231 7.225 7.218 7.215 7.109 7.106 7.094 7.088 7.071
5.873 5.860 5.847 5.834 5.785 5.772 5.759 5.746
3.115 3.098 3.081
2.749
1.928 1.914 1.900 1.659 1.646 1.641 1.628 1.605 1.422 1.409 1.359 1.346 1.288
0.032
1H NMR
500 MHz, CDCl3
Me Ph O O Ph O Me O Ph O Br
7.584 7.571 7.568 7.498 7.483 7.469 7.438 7.423 7.410 7.362 7.355 7.344 7.330 7.318 7.298 7.284 7.245 7.239 7.236 7.231 7.225 7.218 7.215 7.109 7.106 7.088 7.071
δ (ppm)
2.03 1.02 4.03 4.98 3.05 3.90 1.00 0.95 0.94 0.94 1.01 1.79 2.88 2.97
δ (ppm)

Compound 1u′

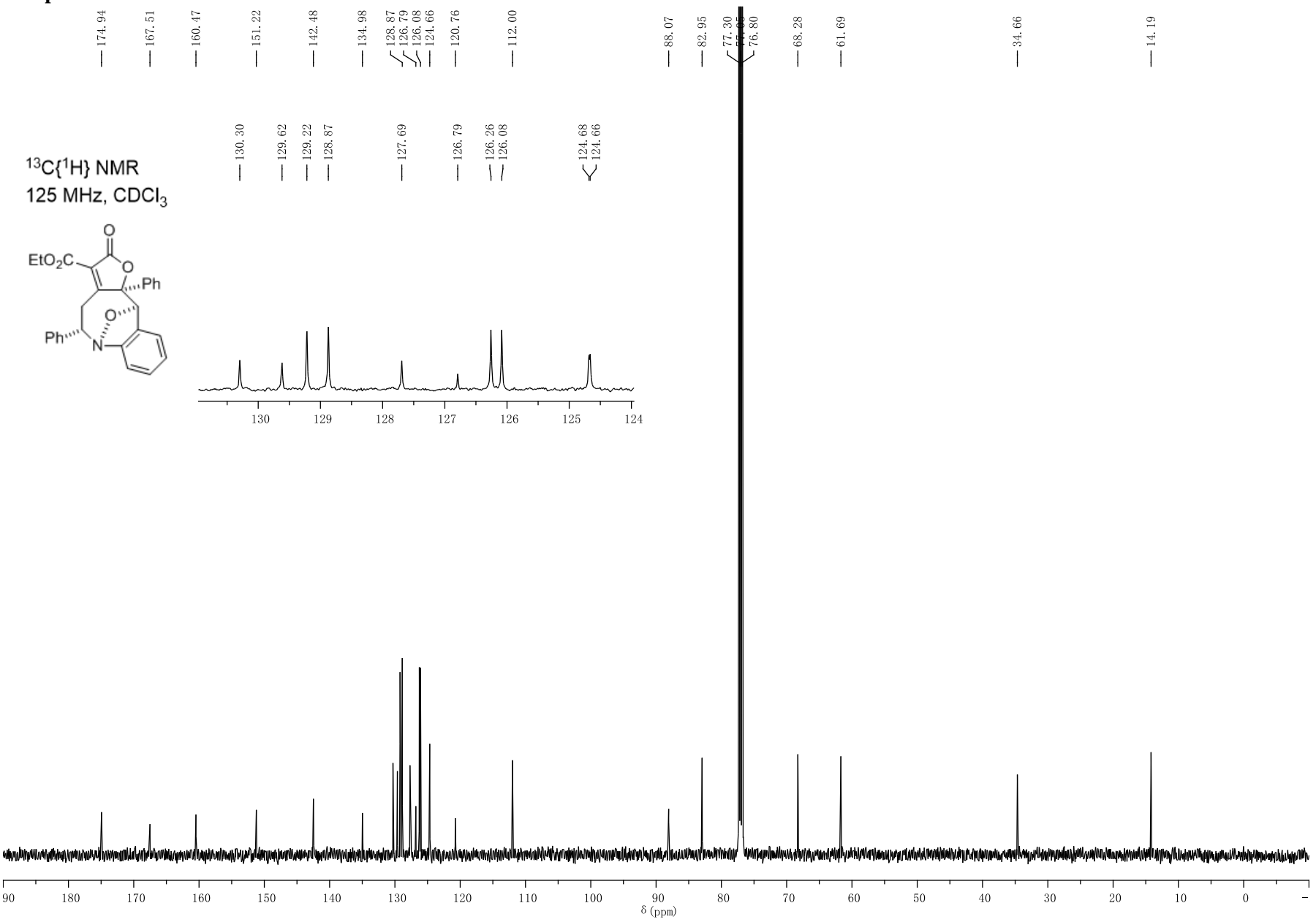

202.35
167.97
167.20
141.30
140.32
137.70
134.30
128.34
128.12
127.49
125.94
121.43
77.28
77.03
76.78
74.23
73.72
53.33
38.30
27.41
21.84
21.10
16.72
13C{1H} NMR
125 MHz, CDCl3
Me
Ph
O
O
Ph
O
O
Ph
Me
O
Br
131.66
130.79
130.64
128.47
128.34
128.18
128.12
127.71
127.49
126.72
125.94
δ (ppm)
δ (ppm)

6.2 Copies of NMR spectra for products 3

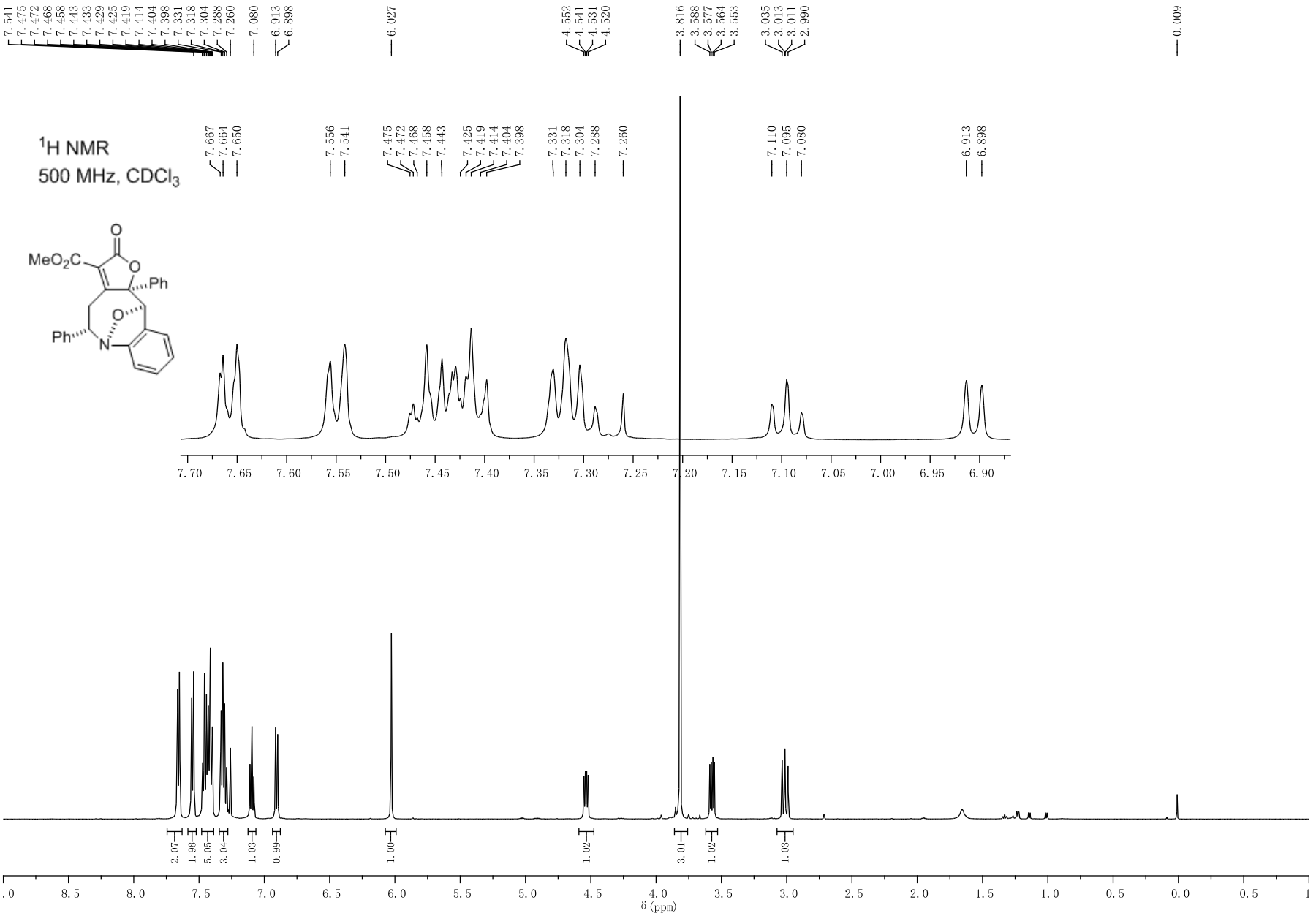
Compound 3aa



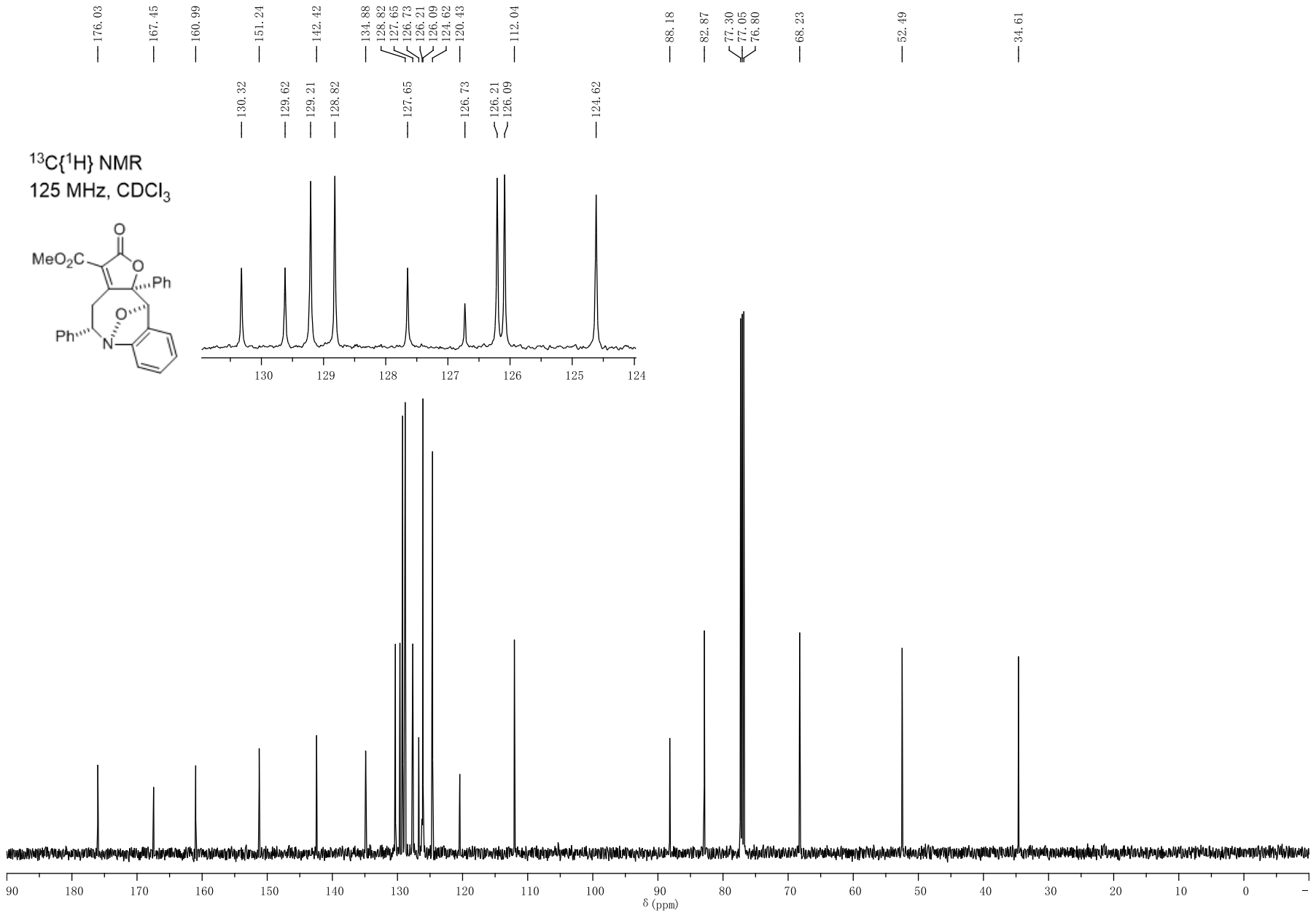
Compound 3aa



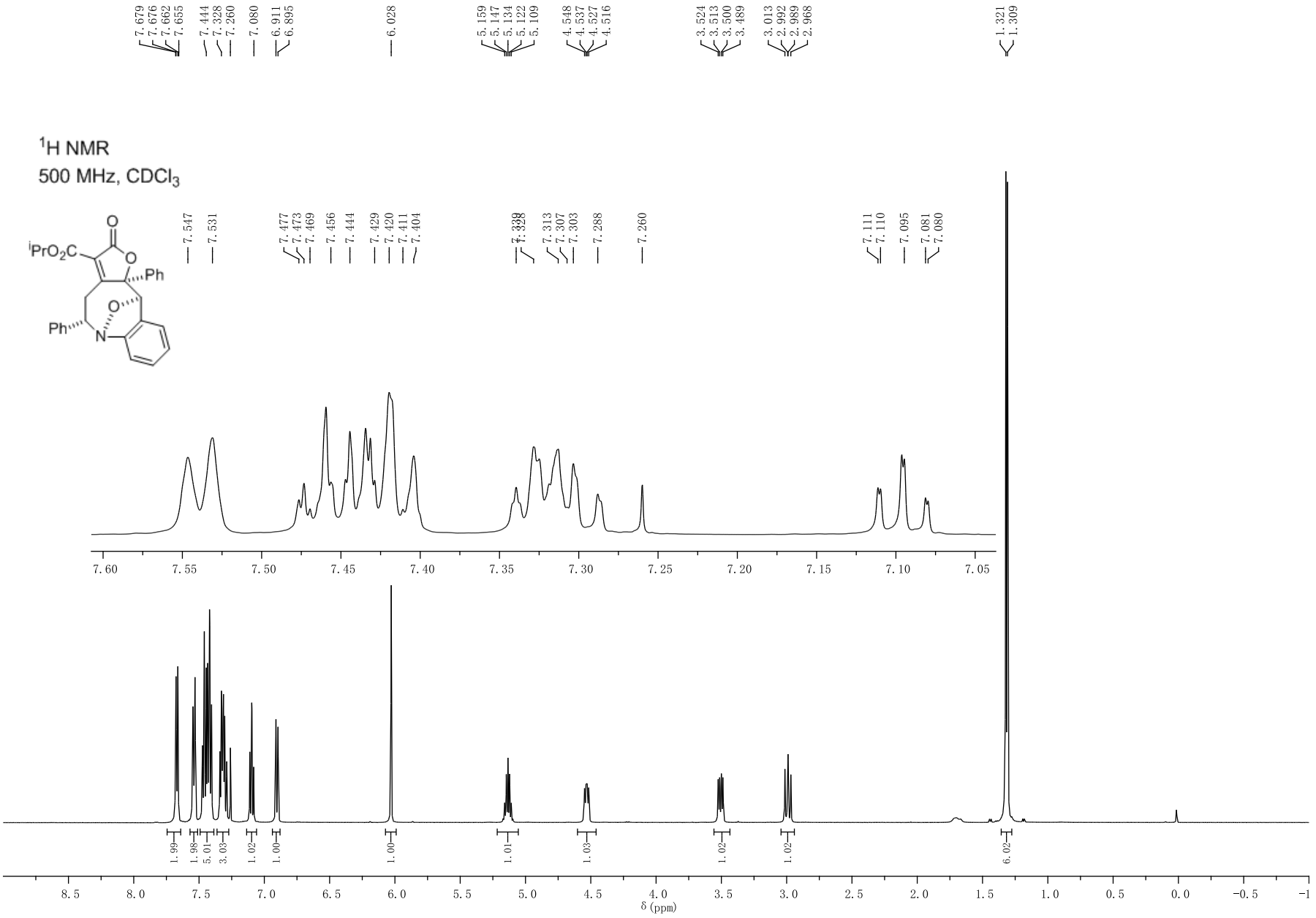
Compound 3ba



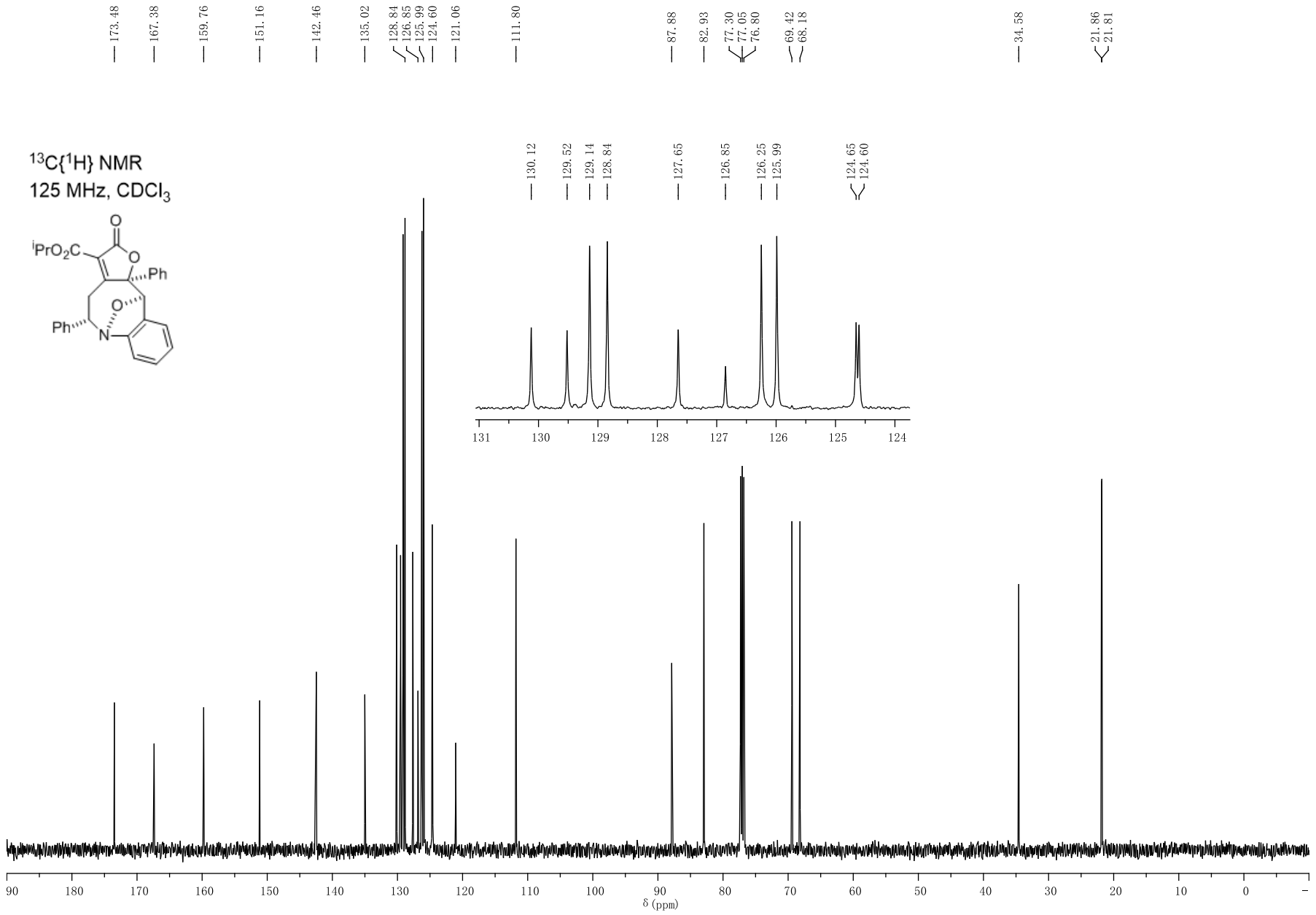
Compound 3ba



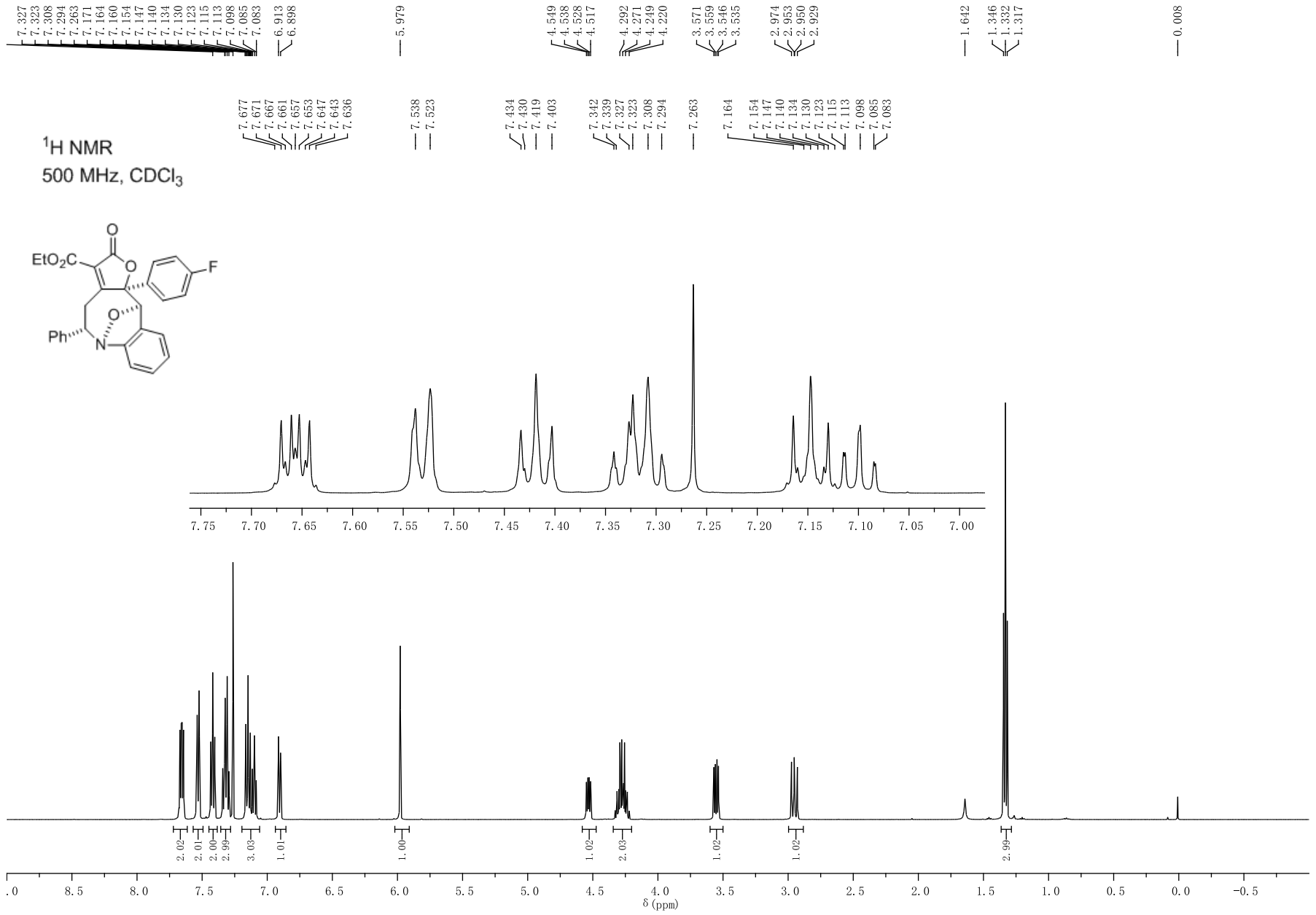
Compound 3ca



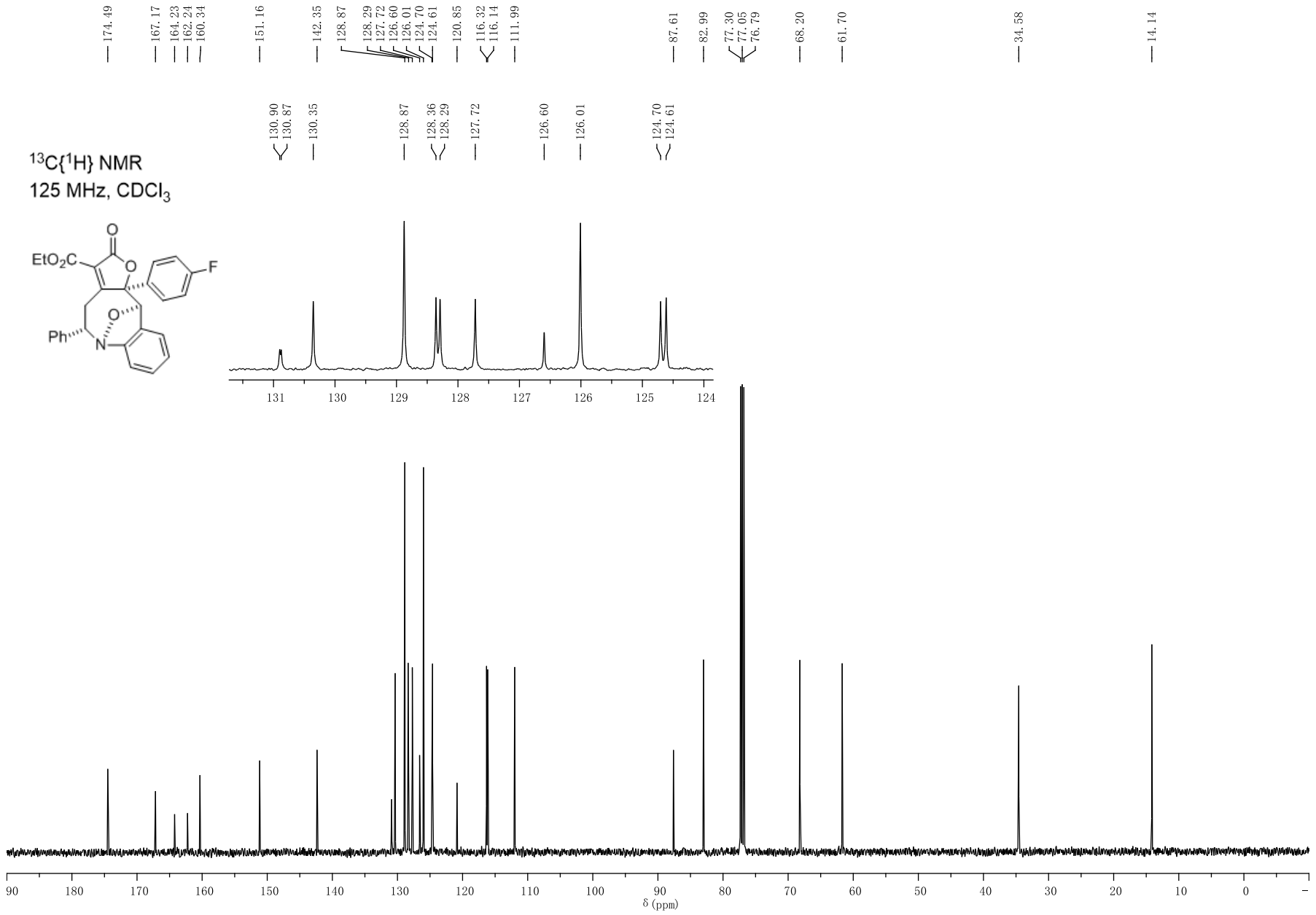
Compound 3ca



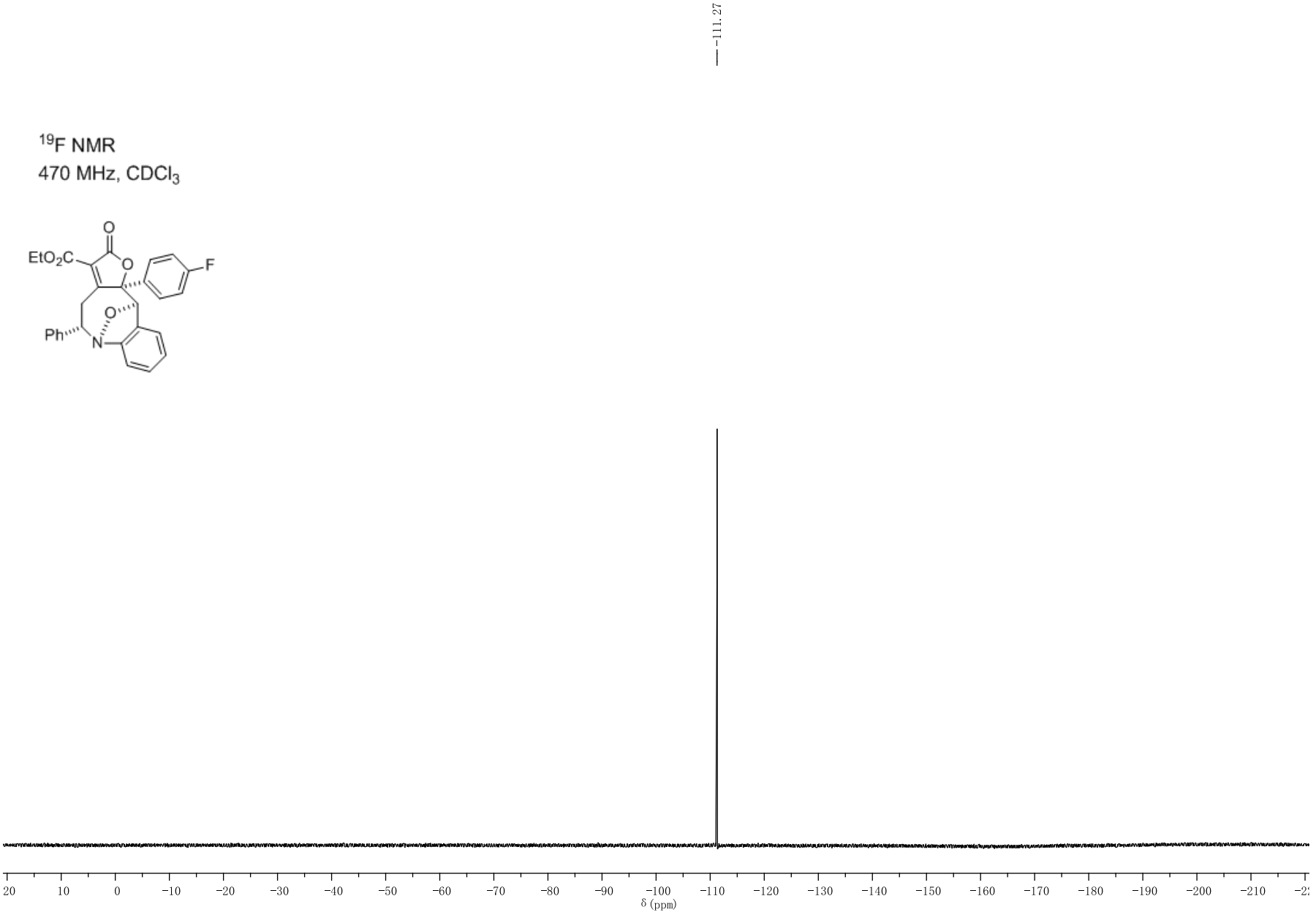
Compound 3da



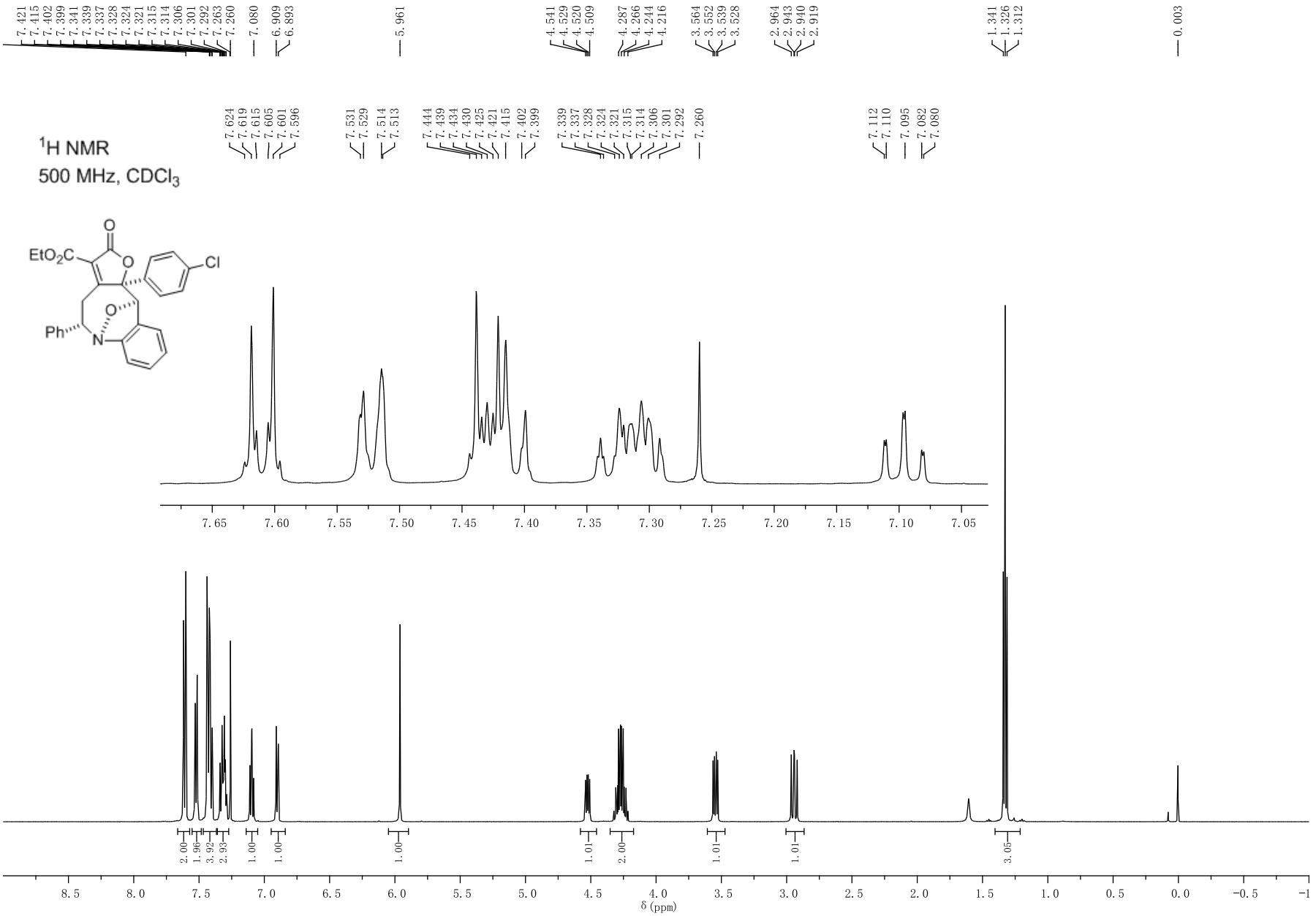
Compound 3da



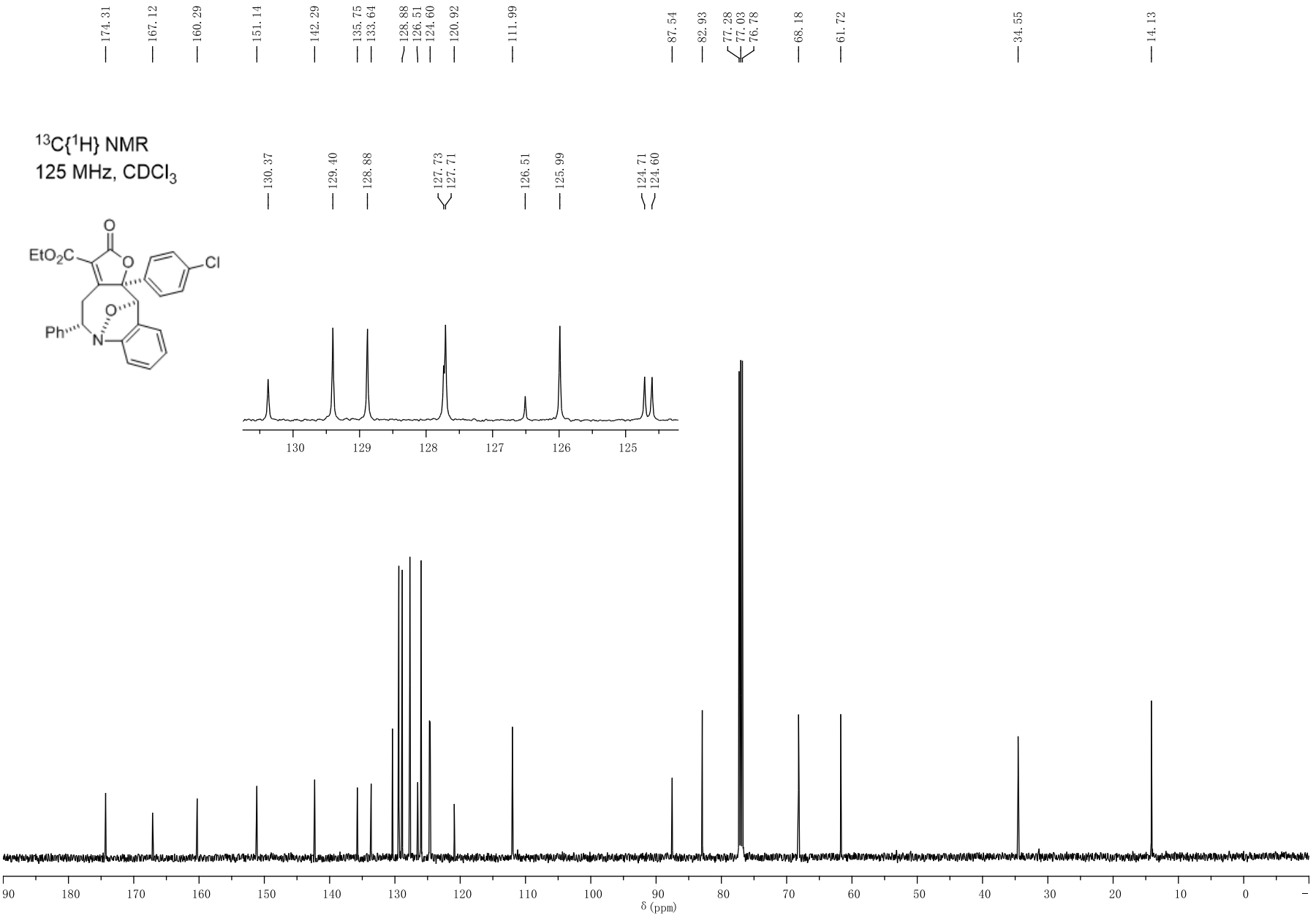
Compound 3da



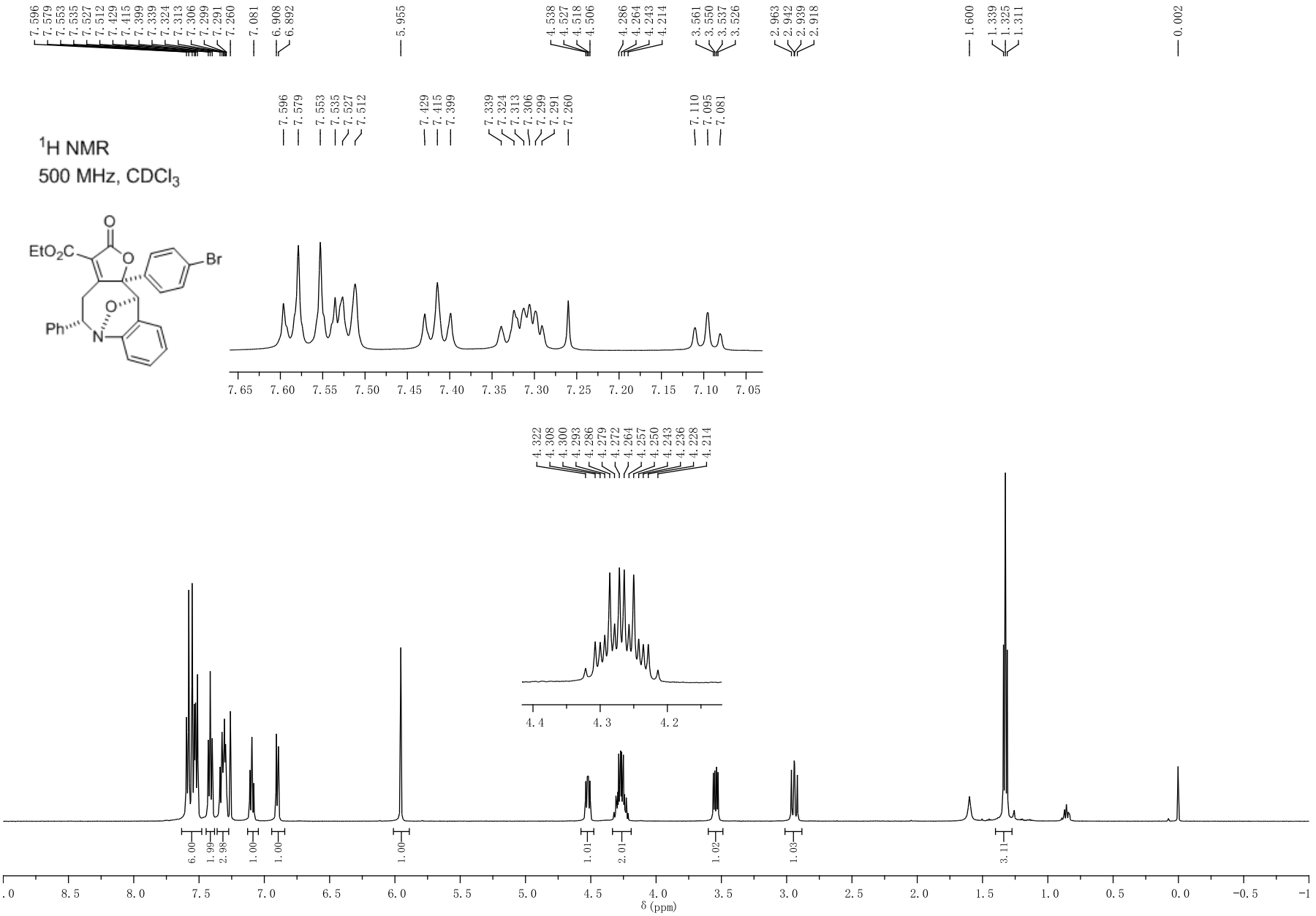
Compound 3ea



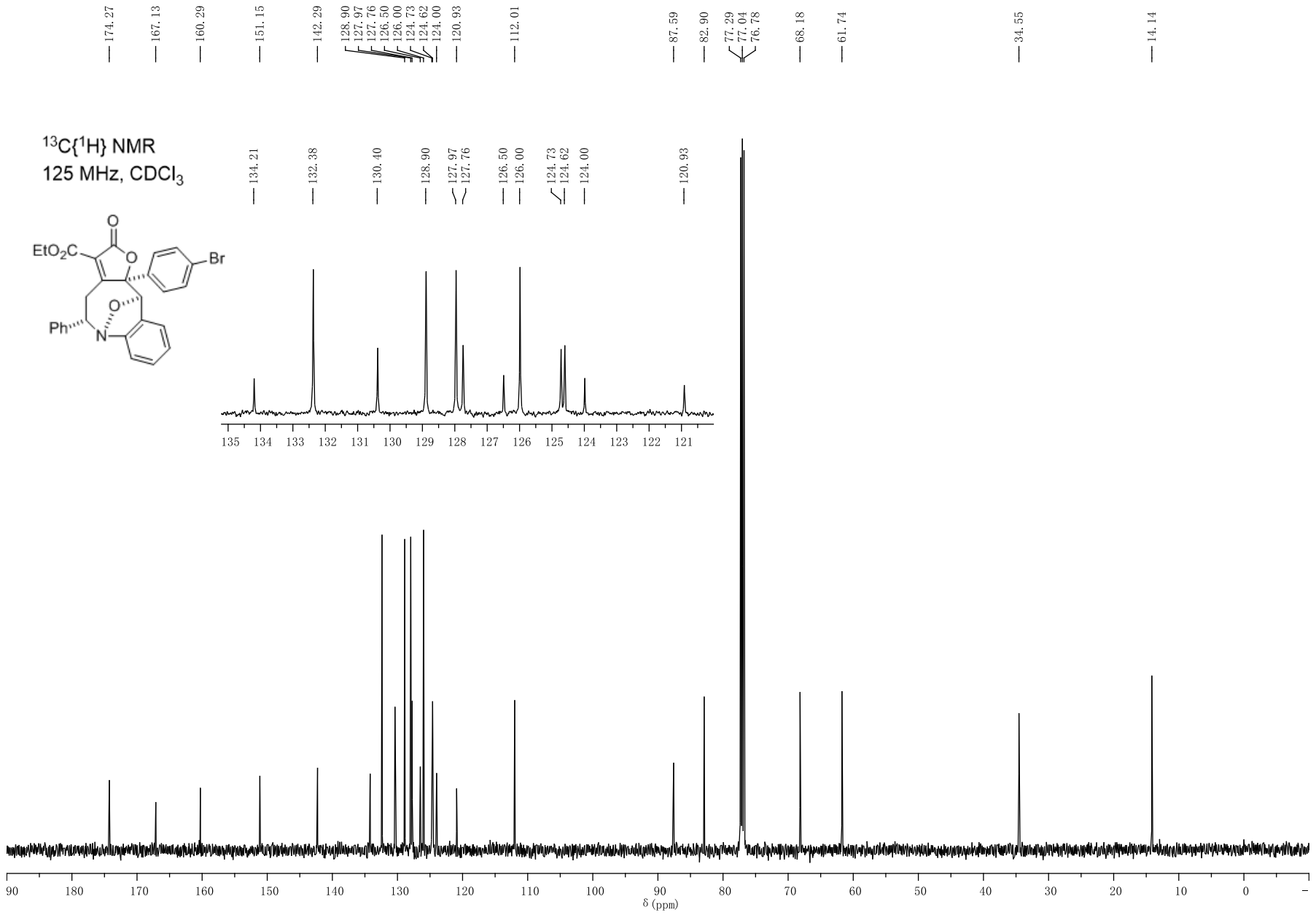
Compound 3ea



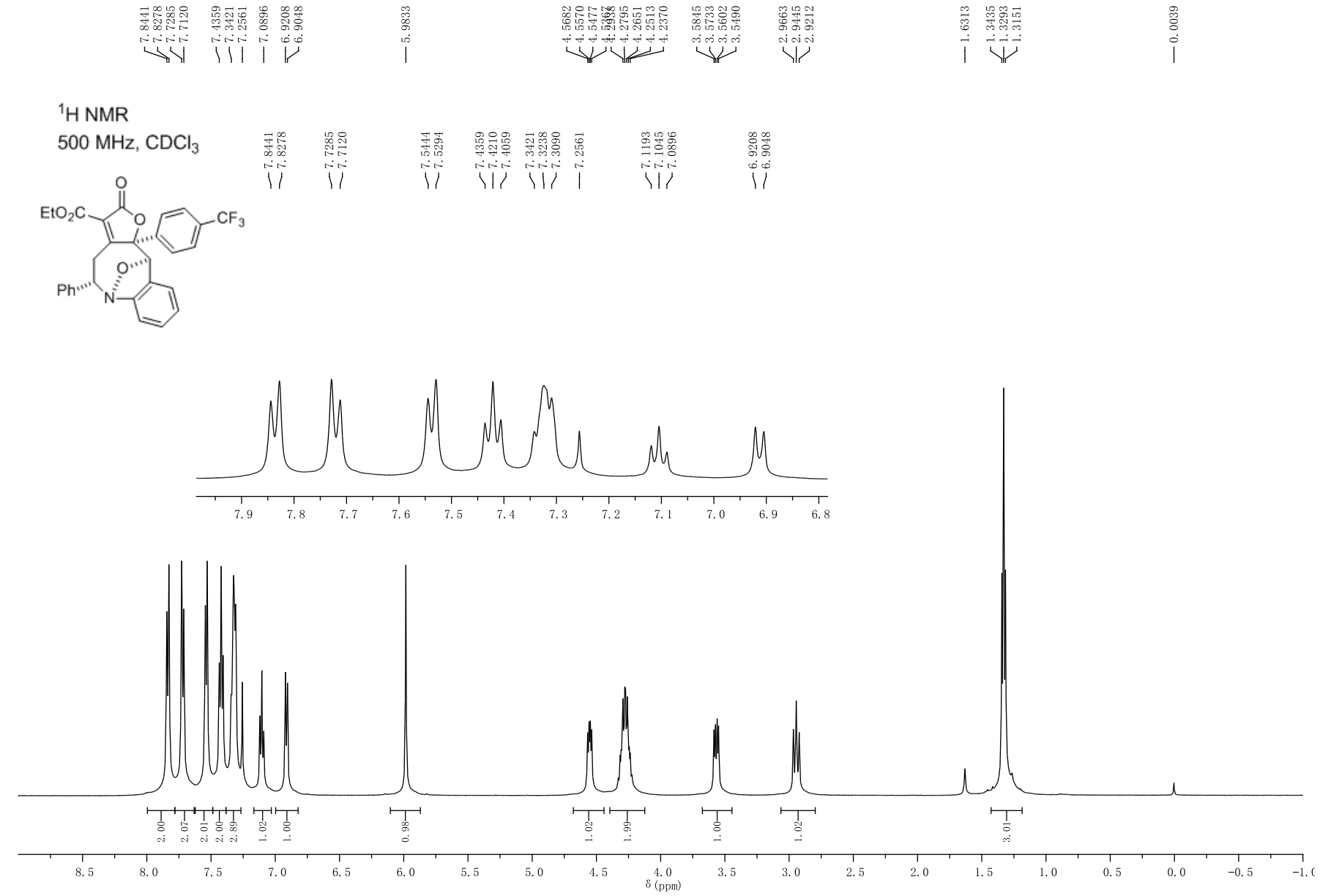
Compound 3fa



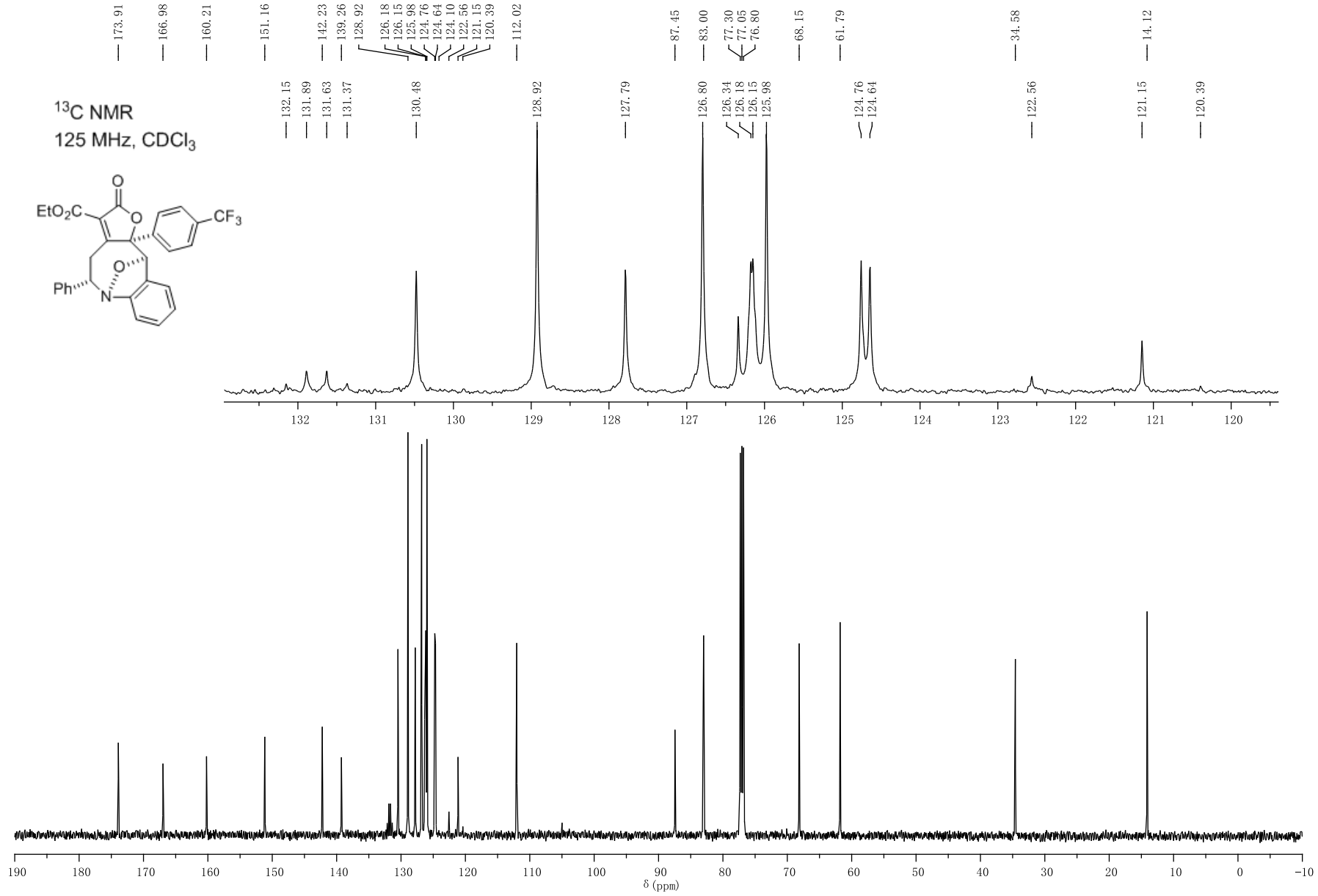
Compound 3fa



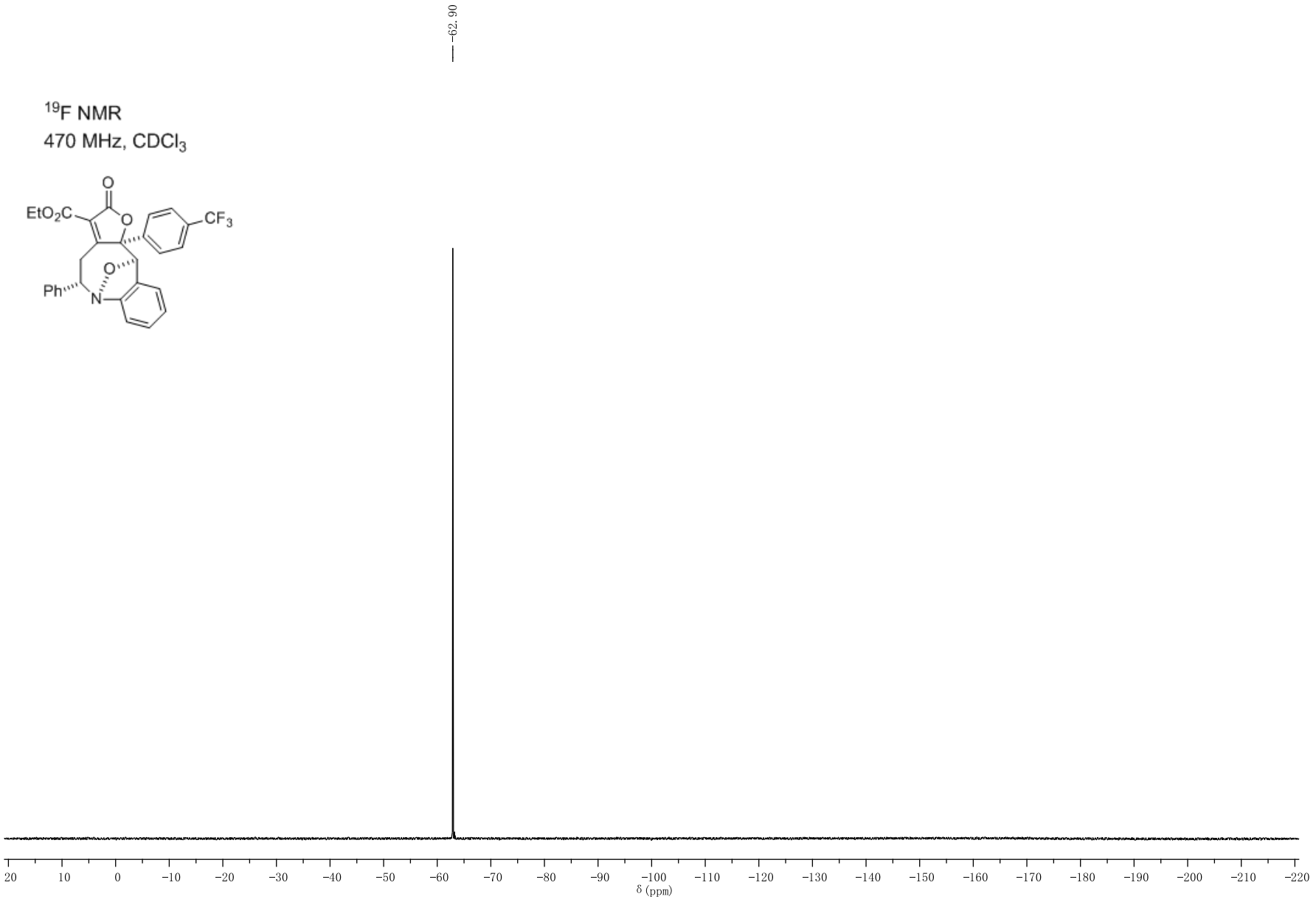
Compound 3ga



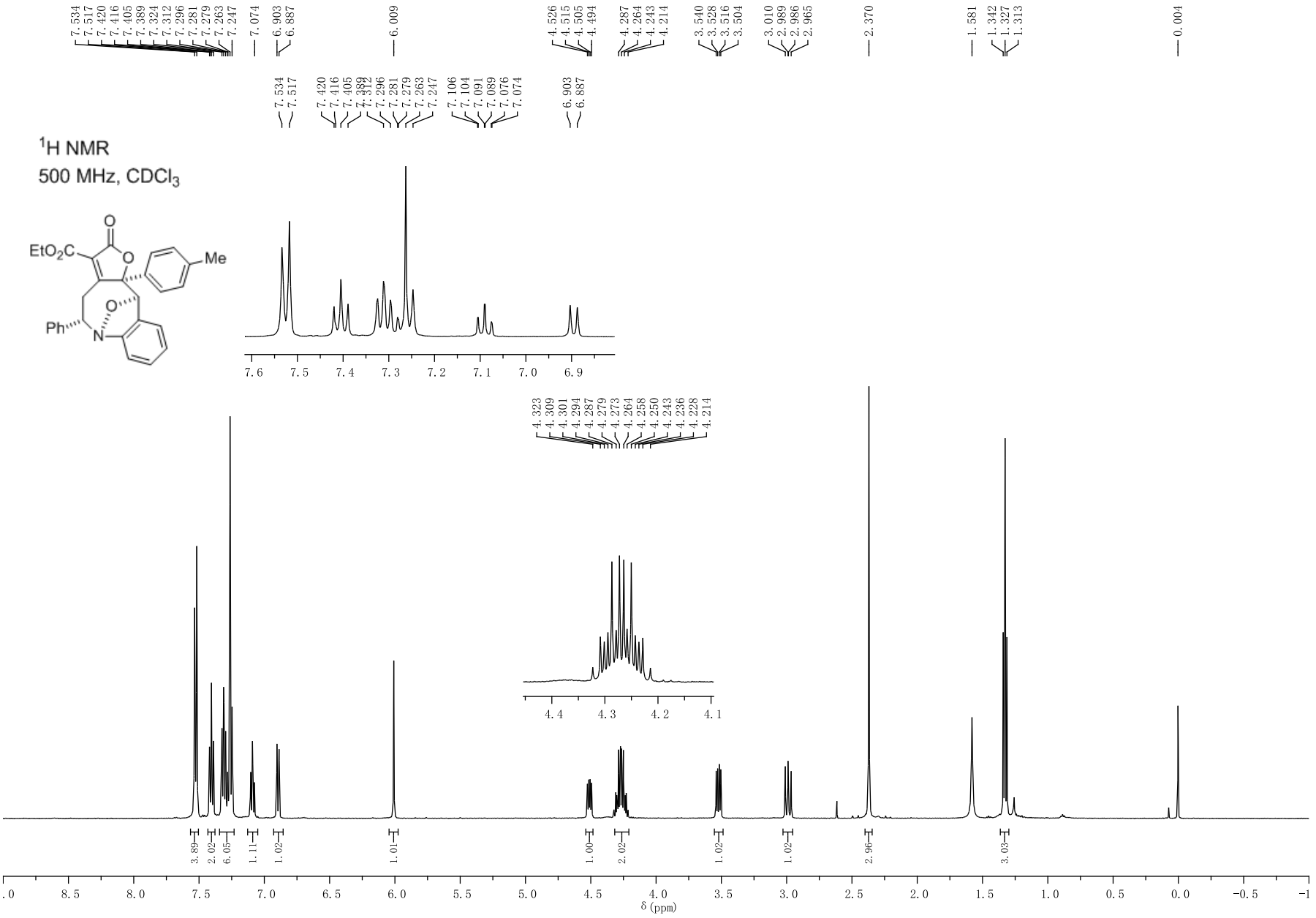
Compound 3ga



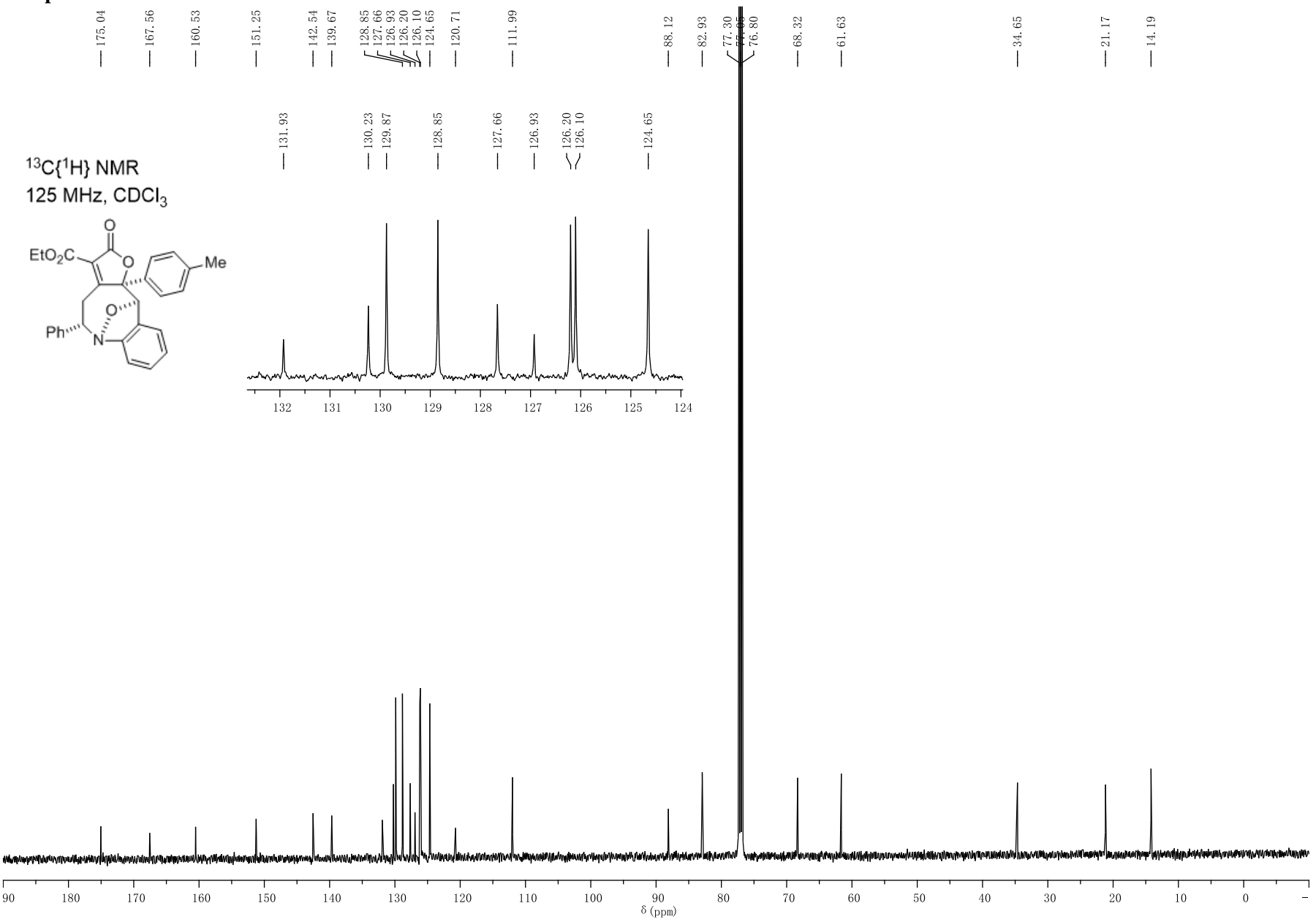
Compound 3ga



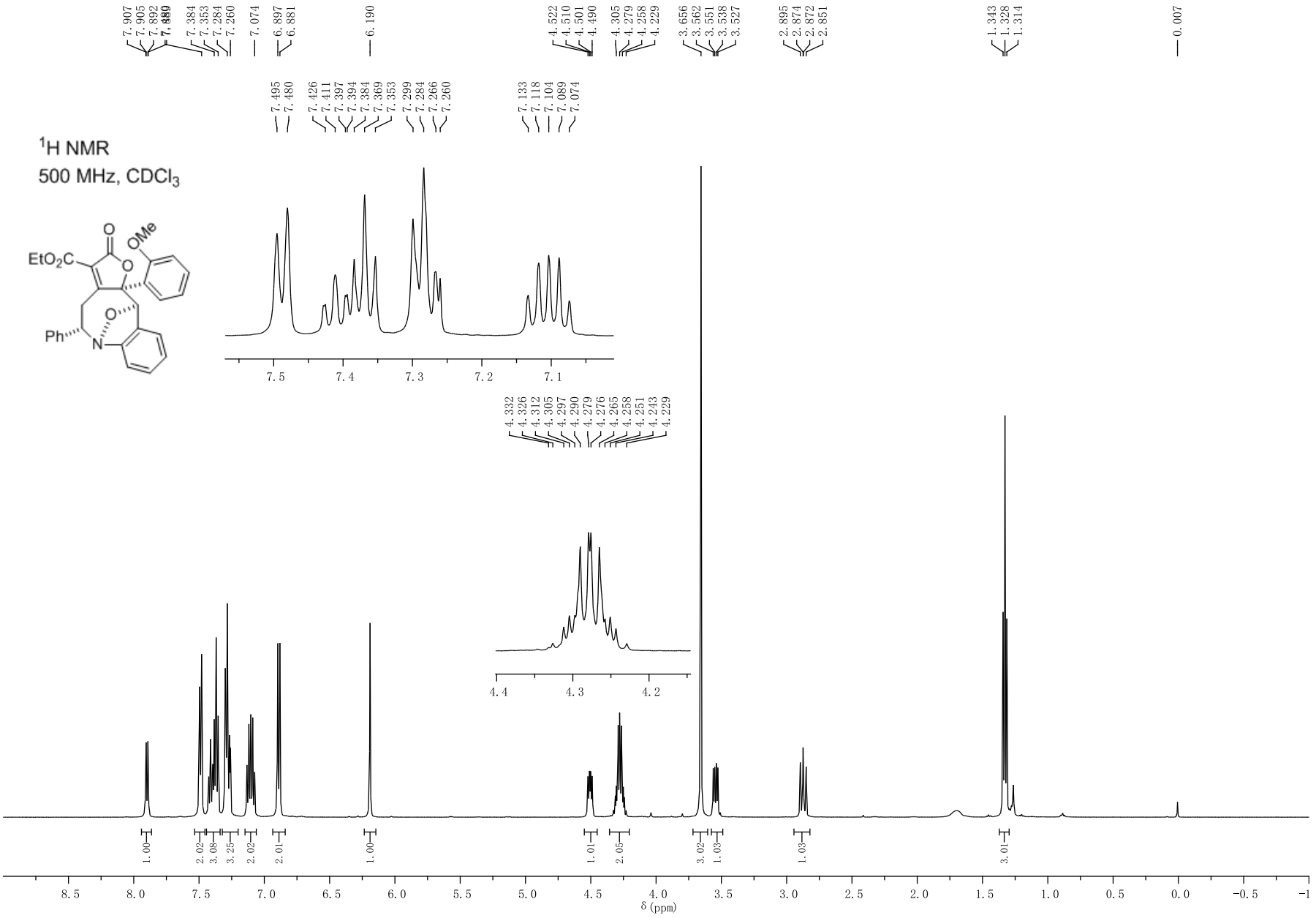
Compound 3ha



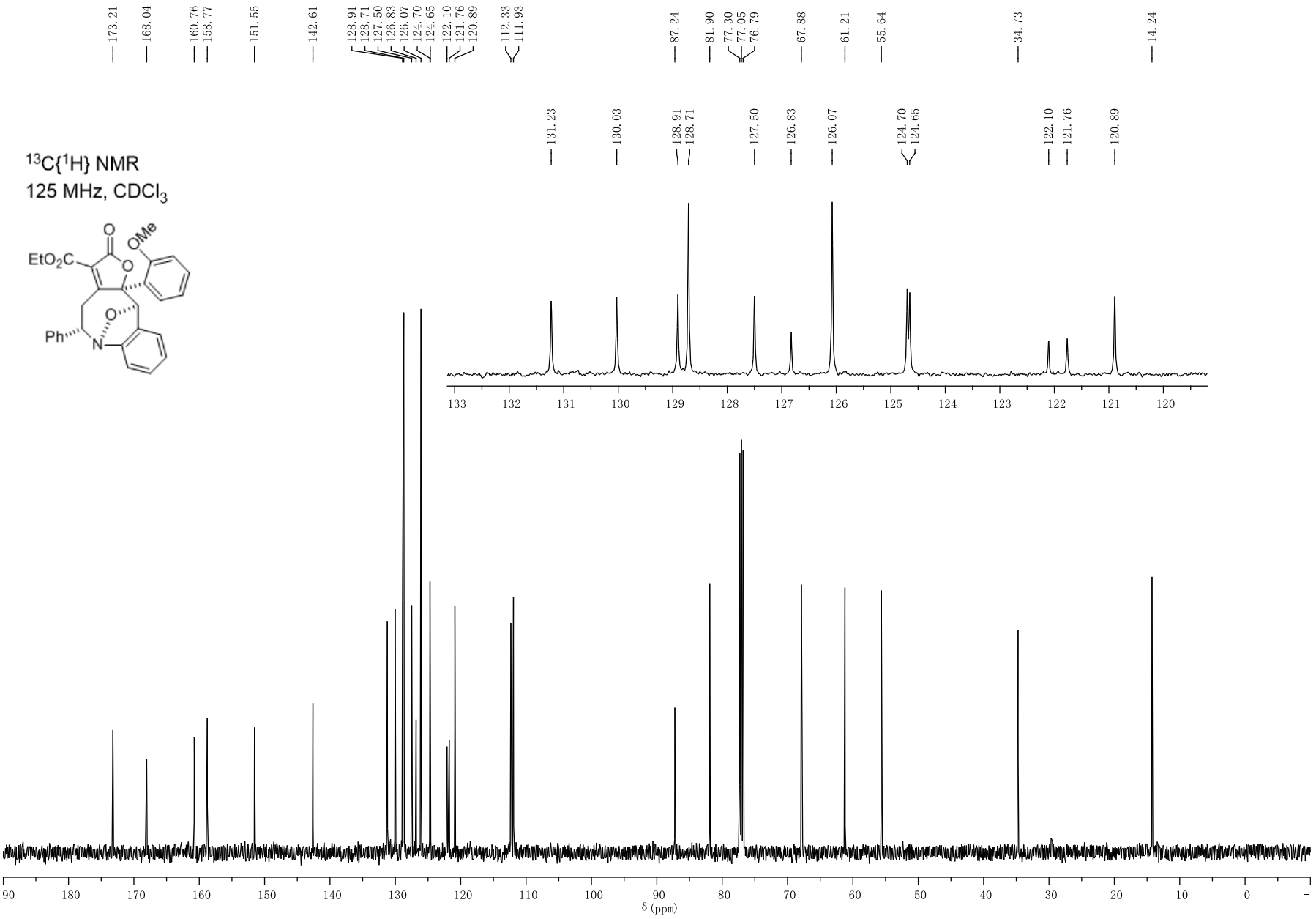
Compound 3ha



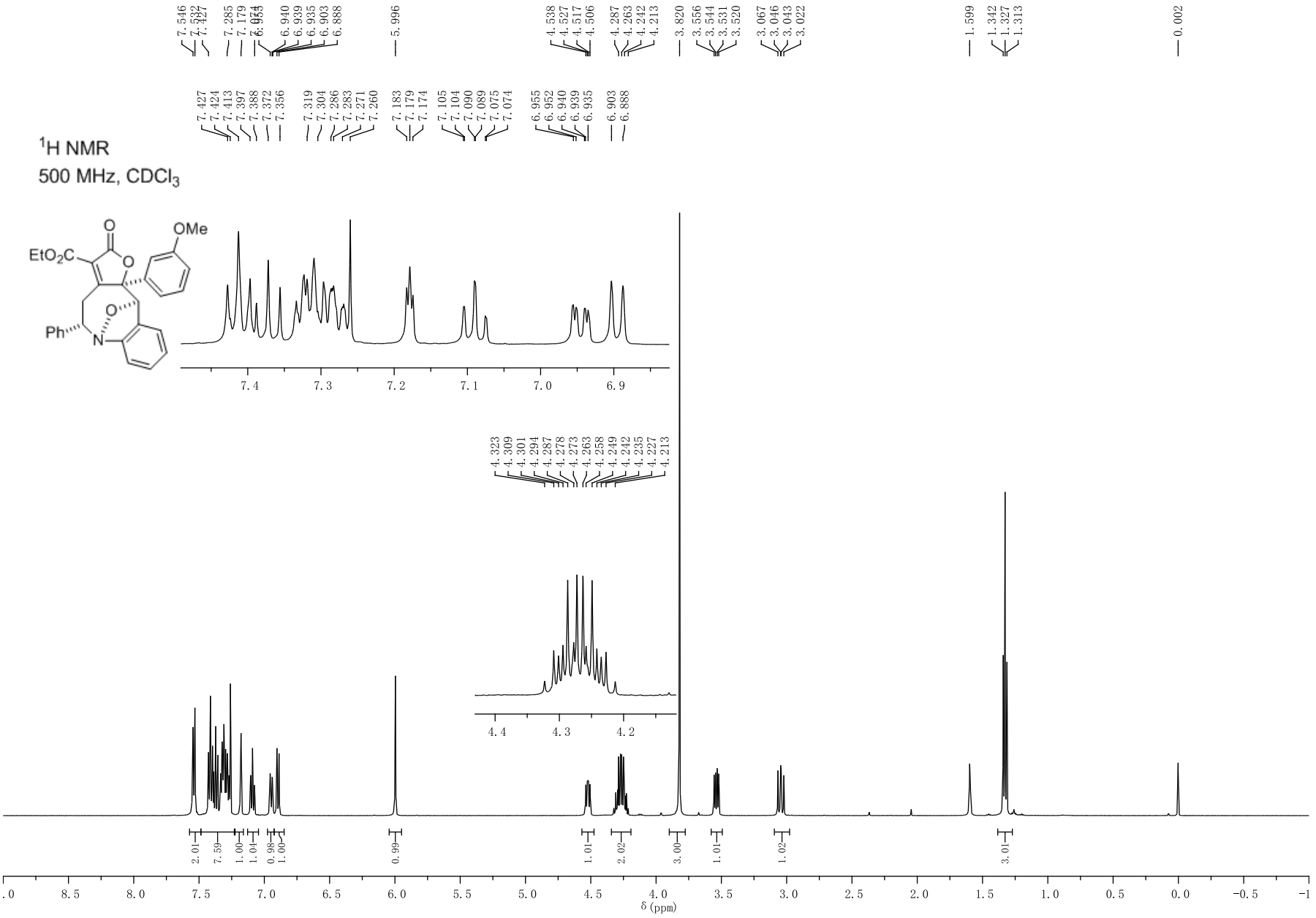
Compound 3ia



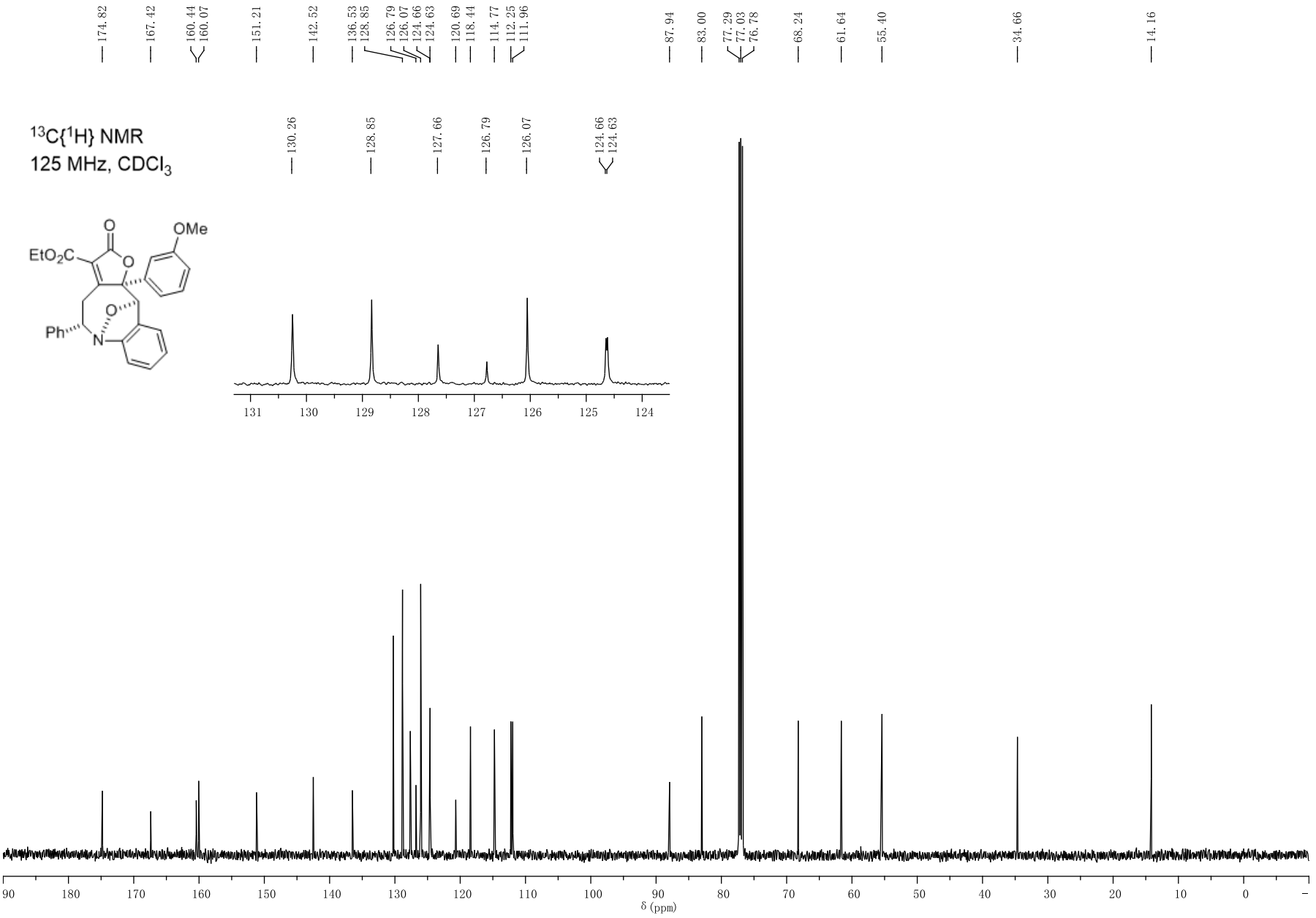
Compound 3ia



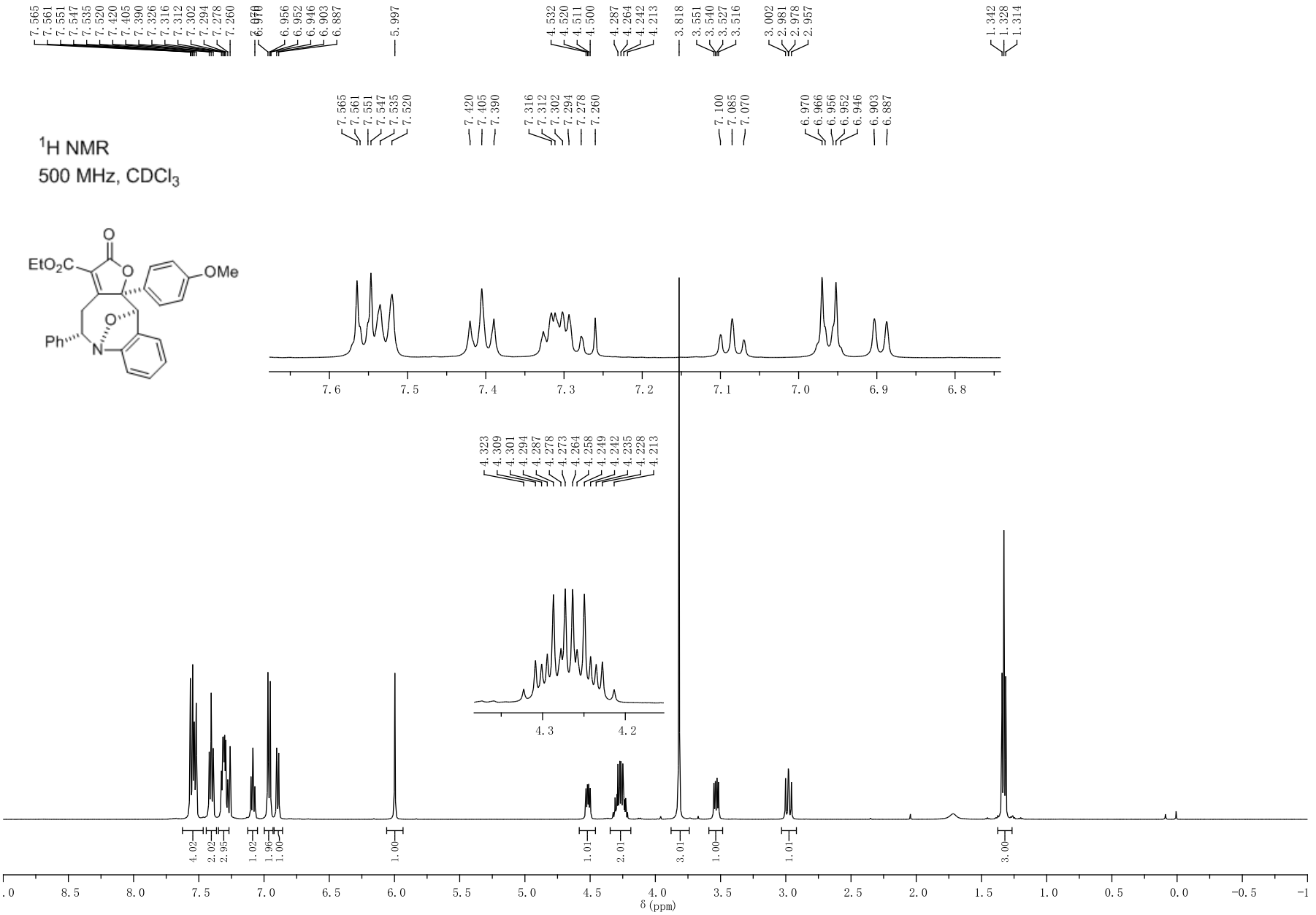
Compound 3ja



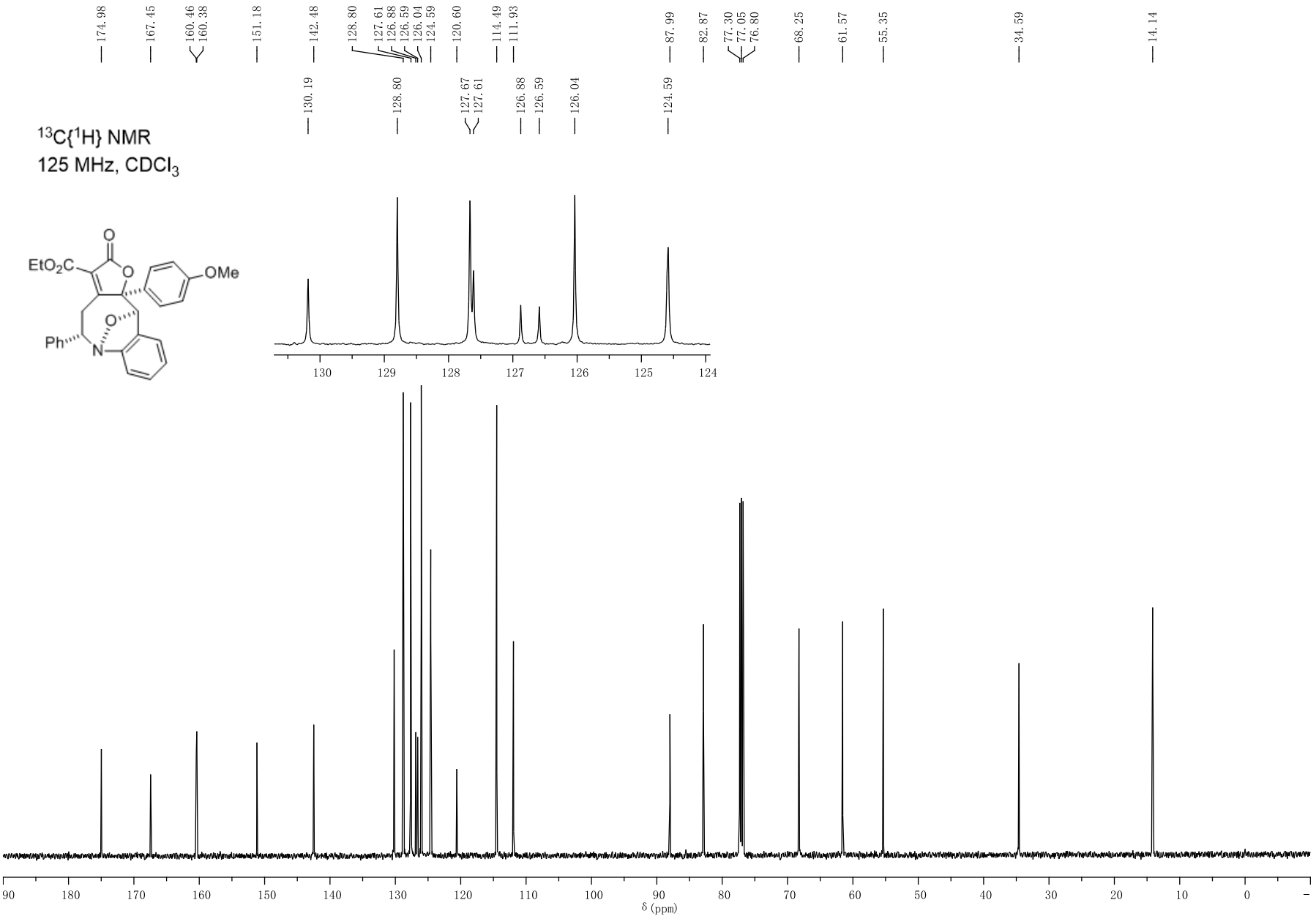
Compound 3ja



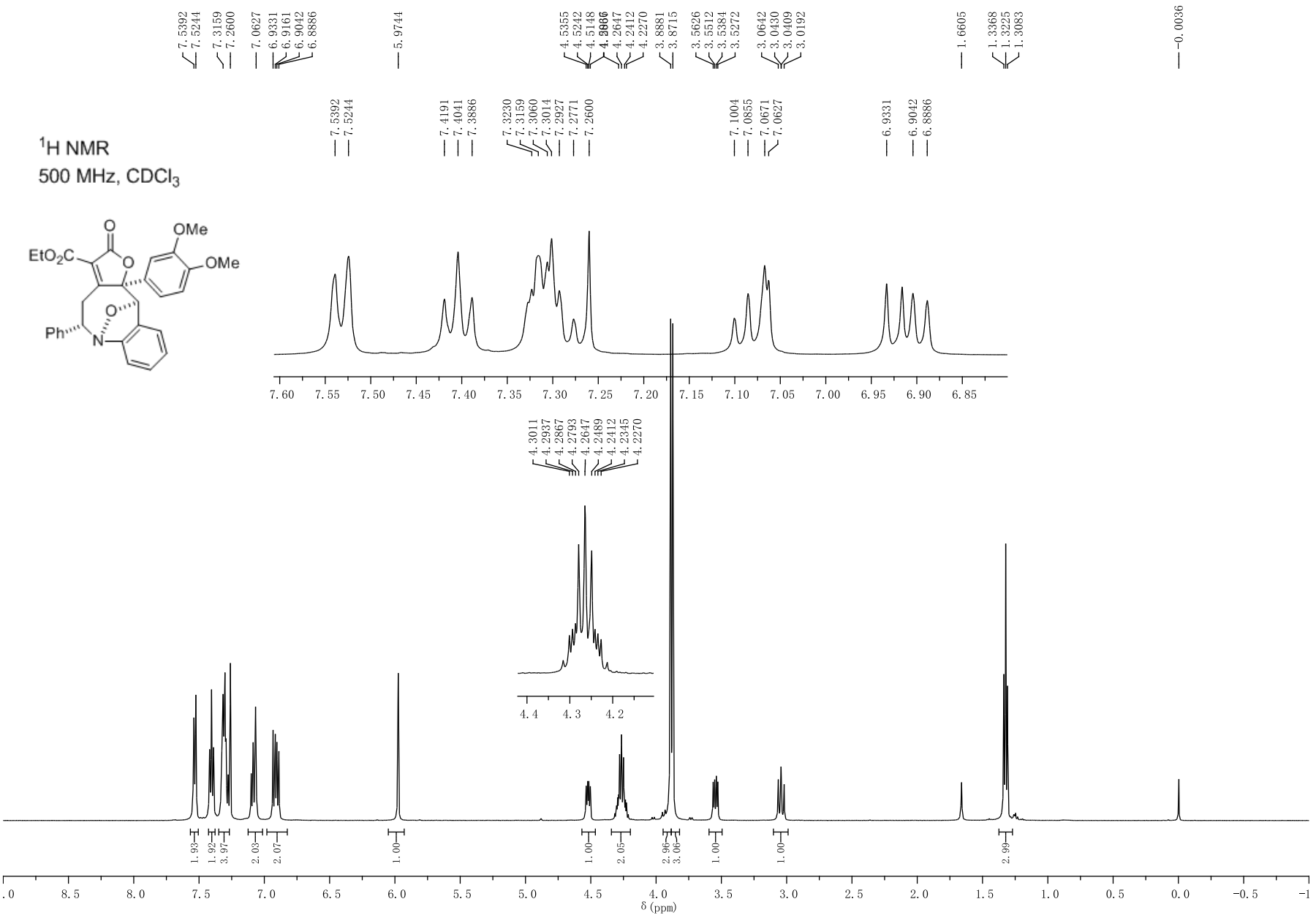
Compound 3ka



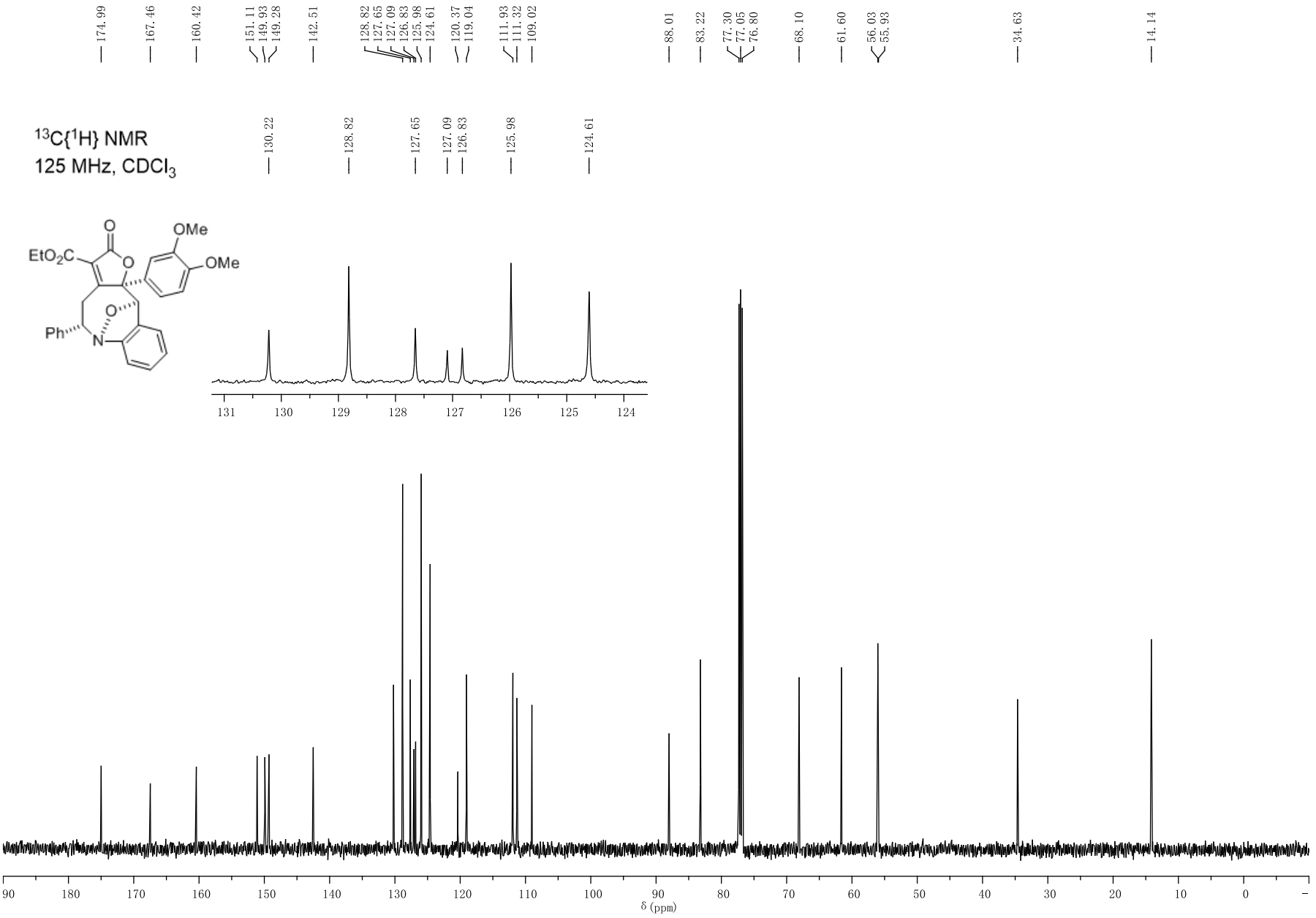
Compound 3ka



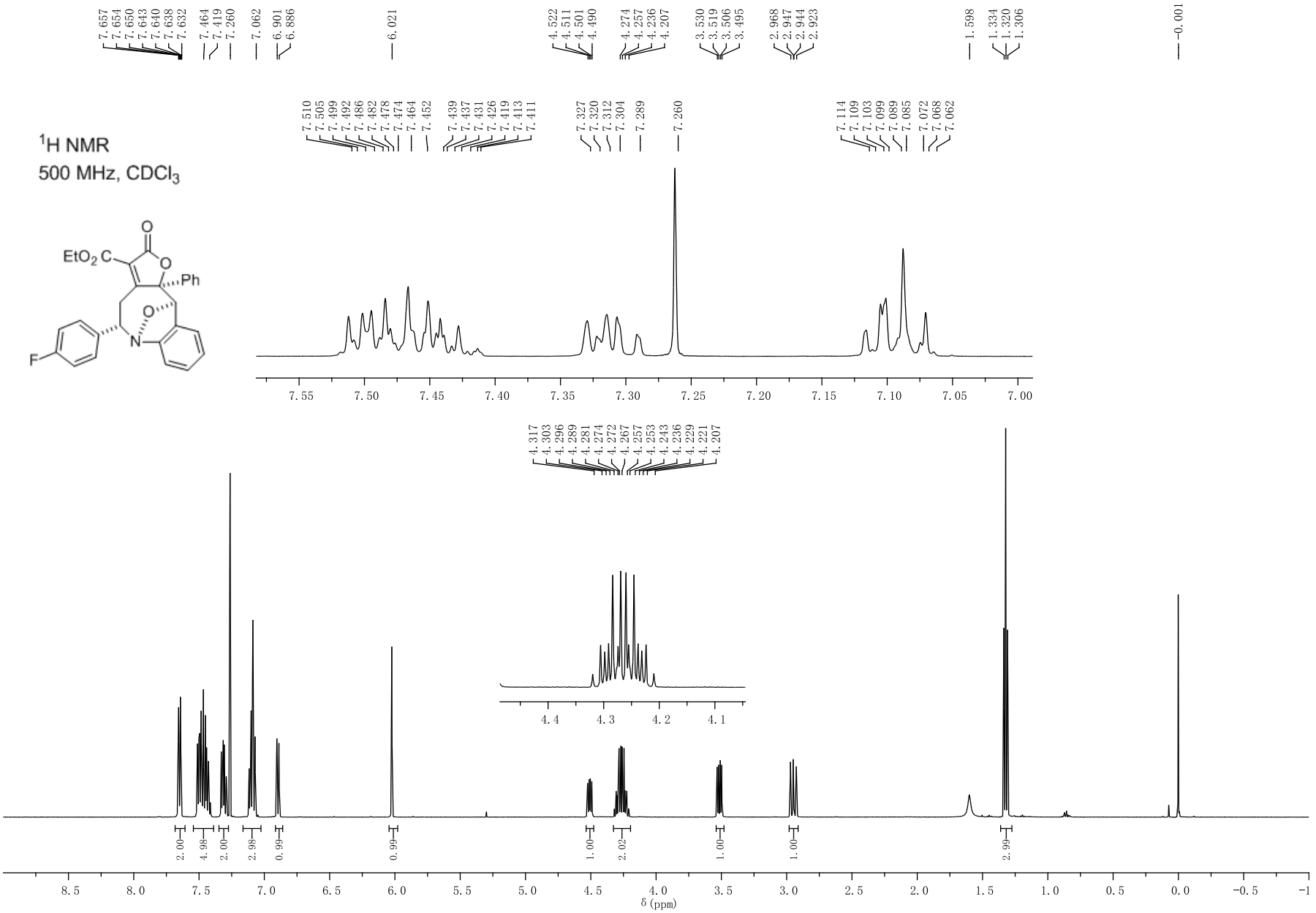
Compound 3la



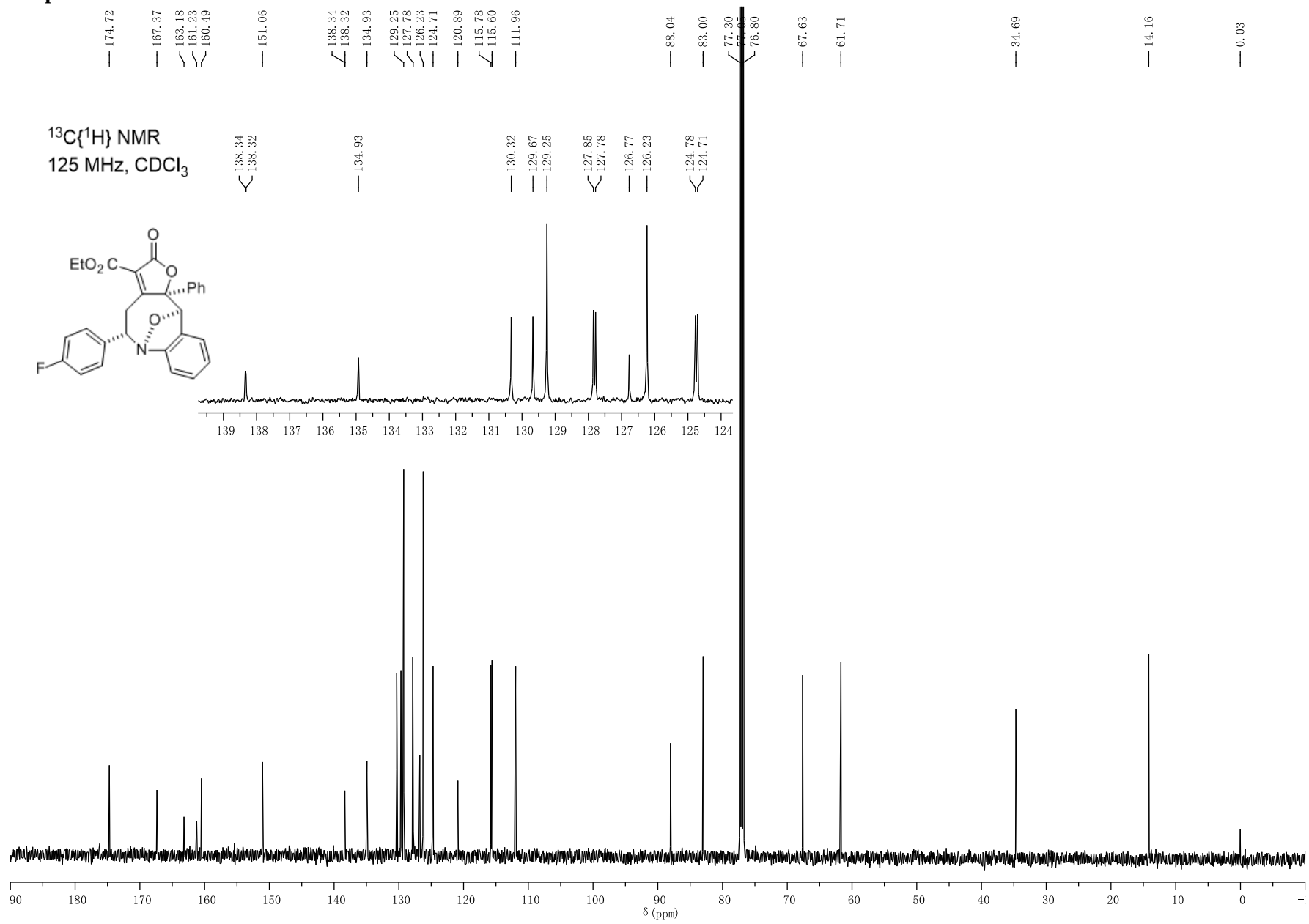
Compound 3la



Compound 3ma

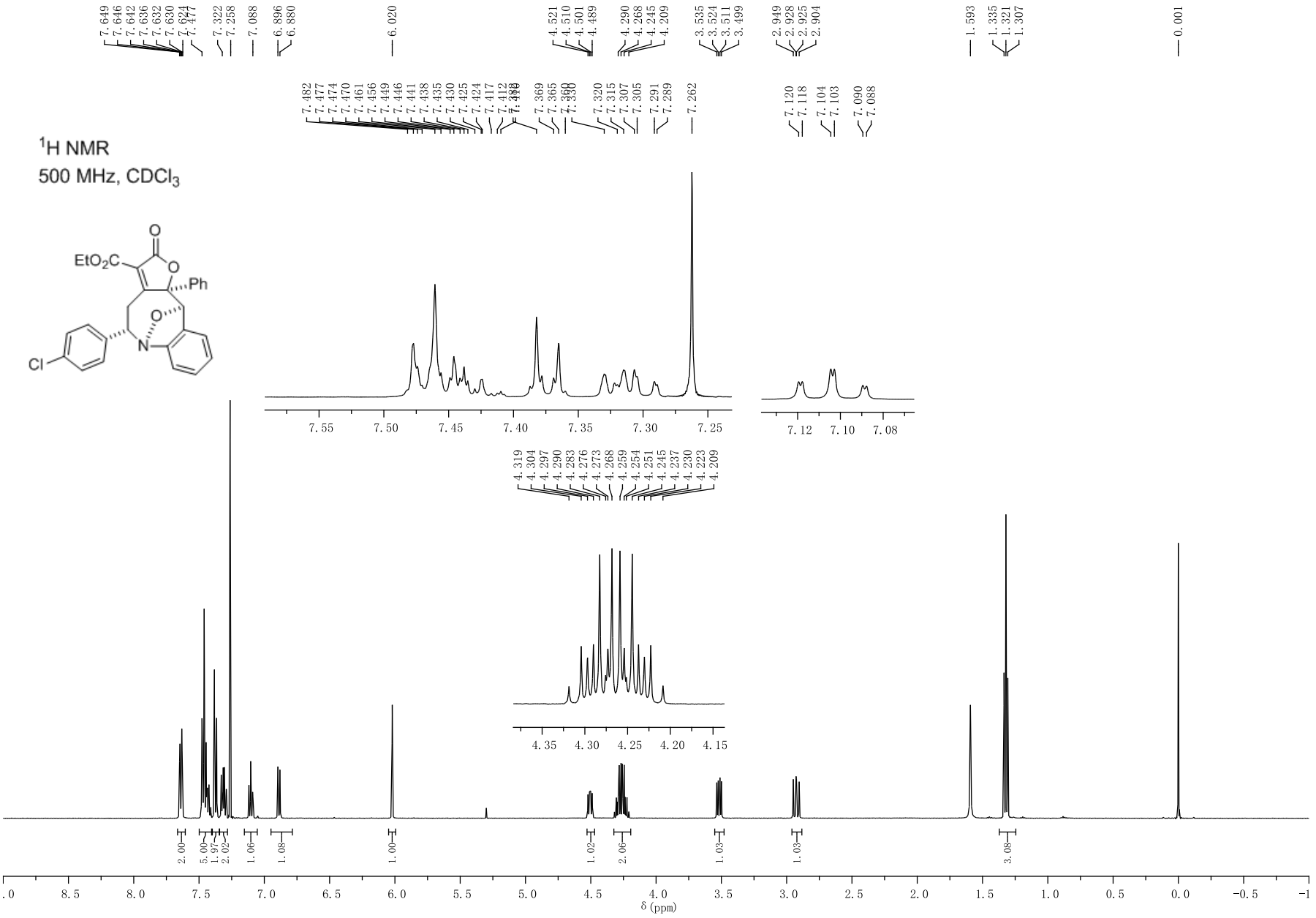


Compound 3ma

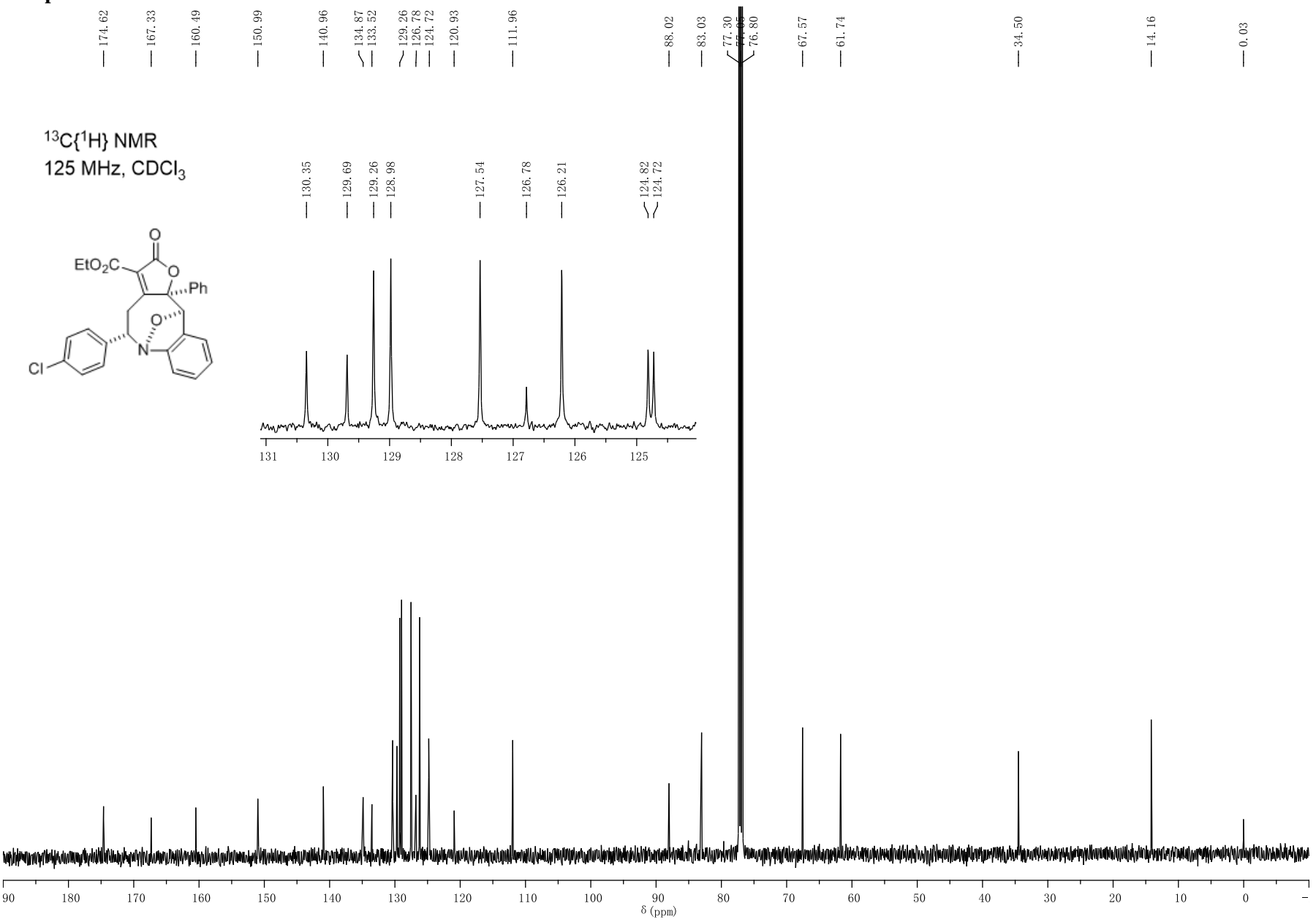


Compound 3ma

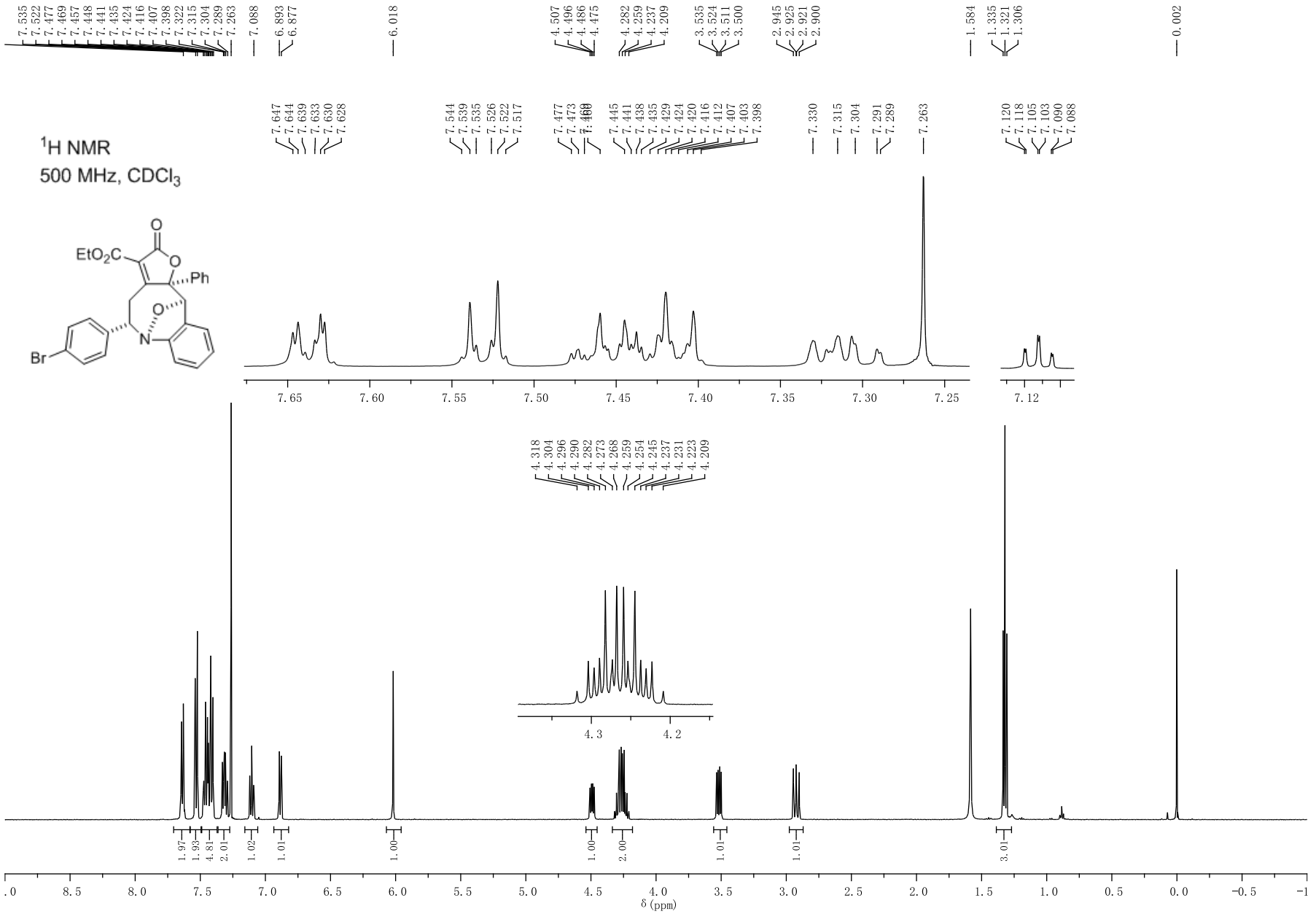
Compound 3na



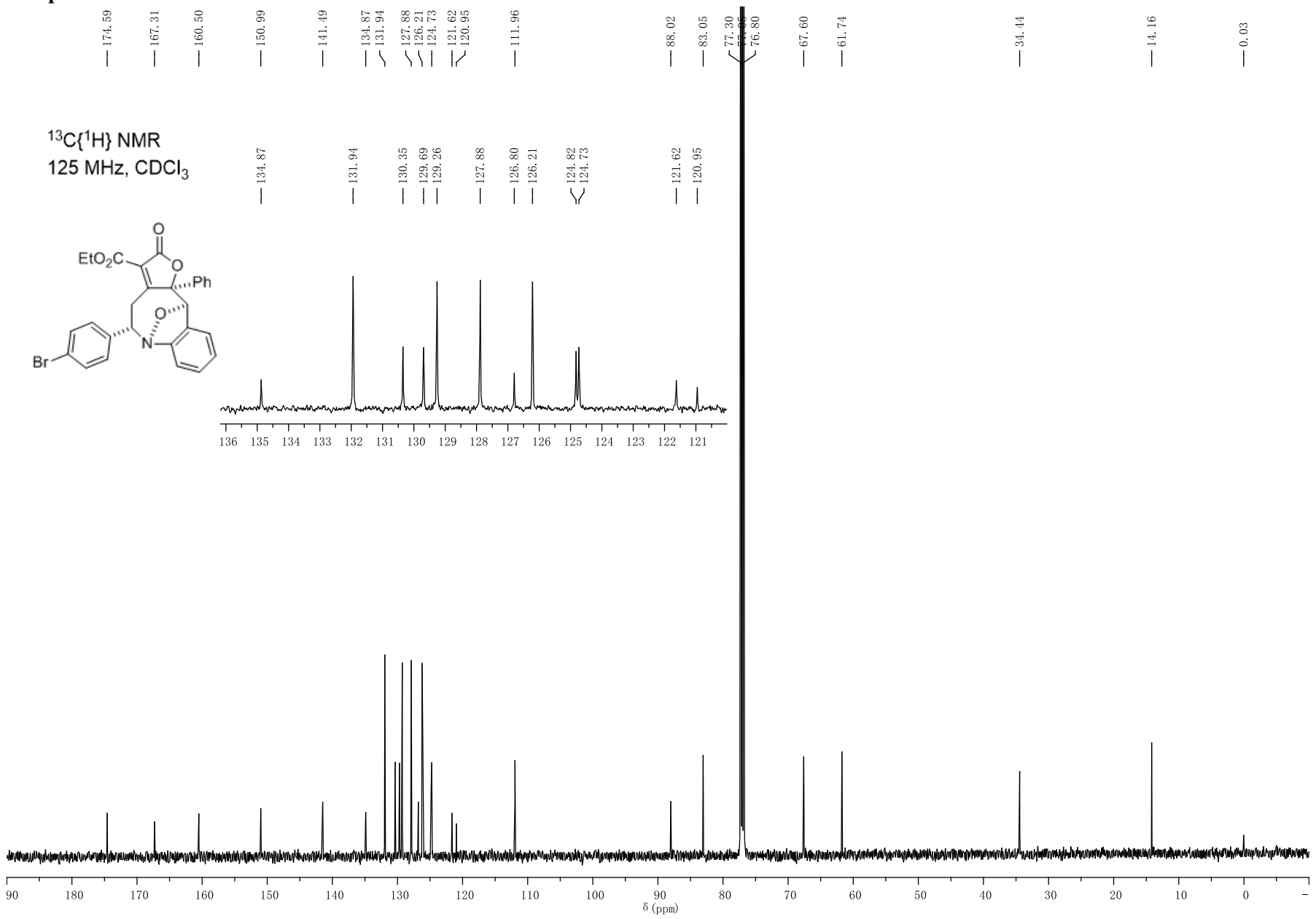
Compound 3na



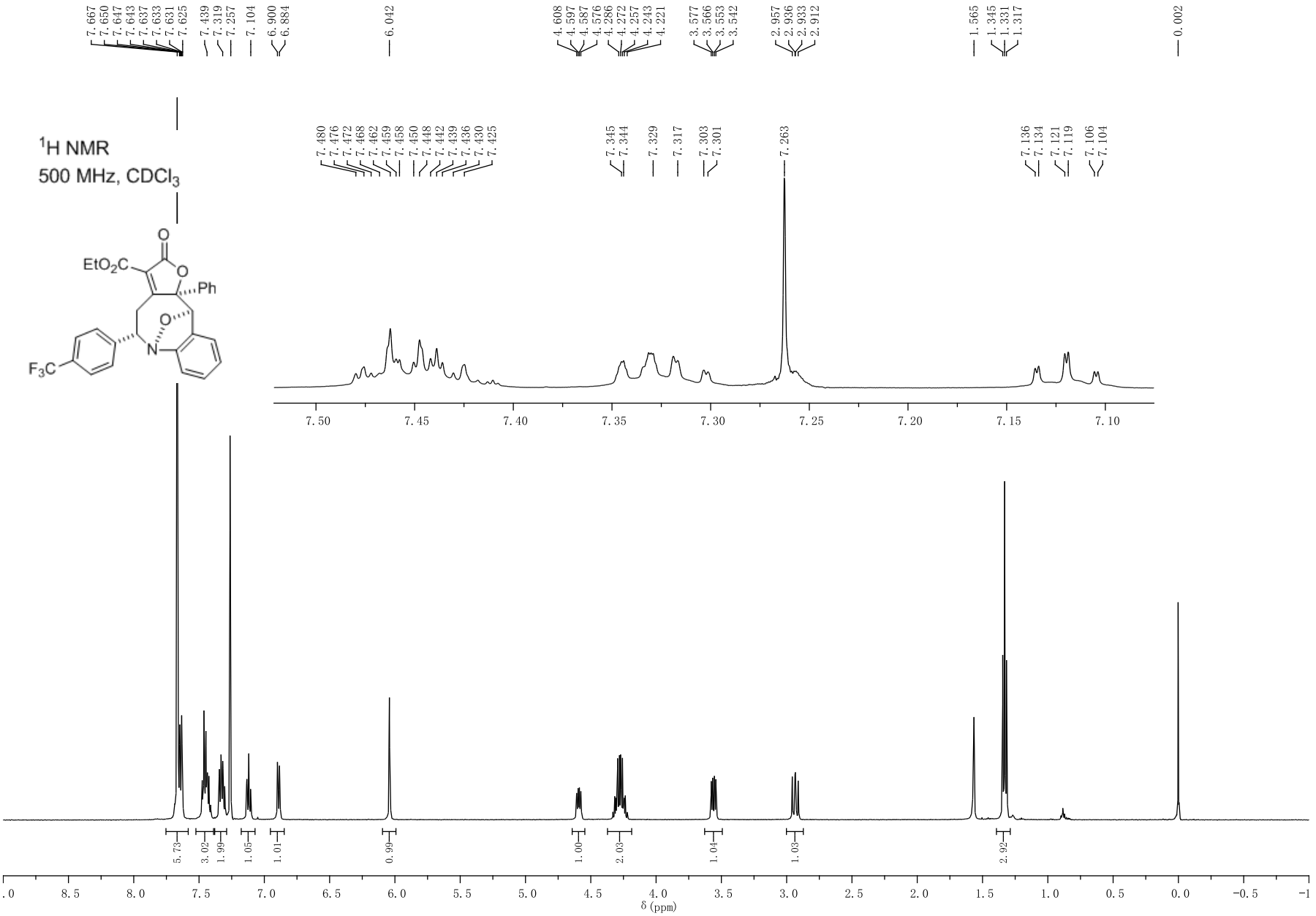
Compound 3oa



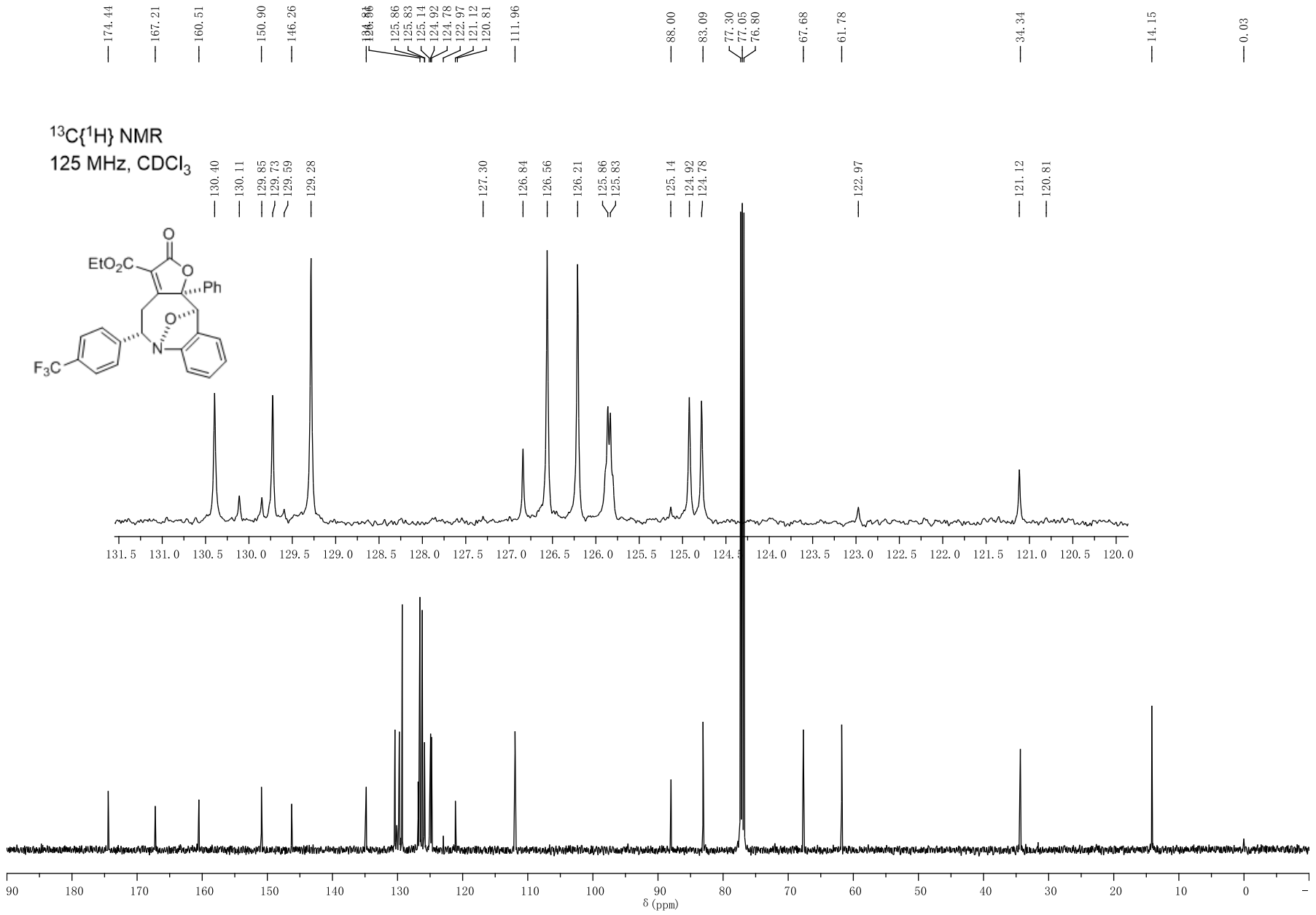
Compound 3oa



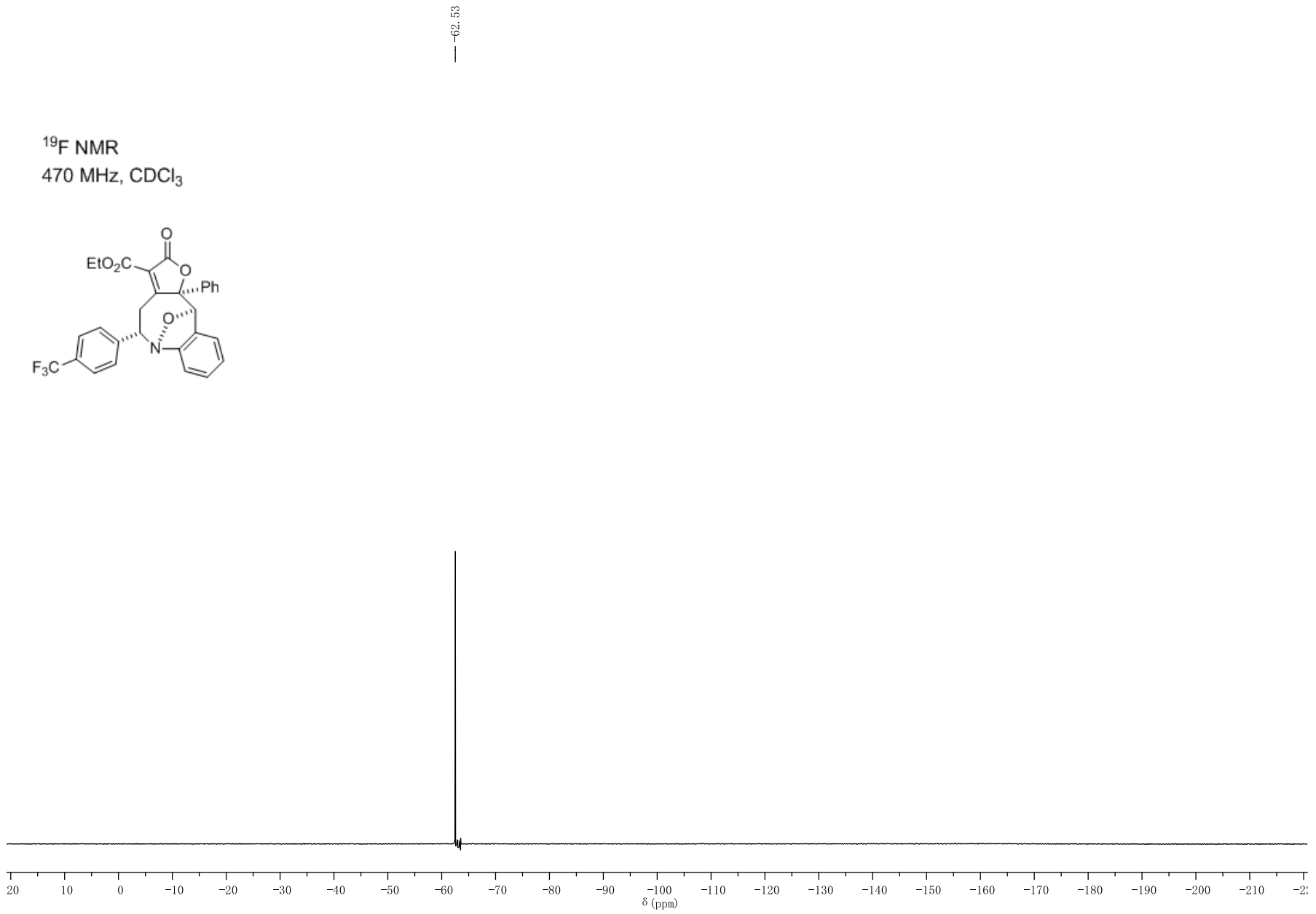
Compound 3pa



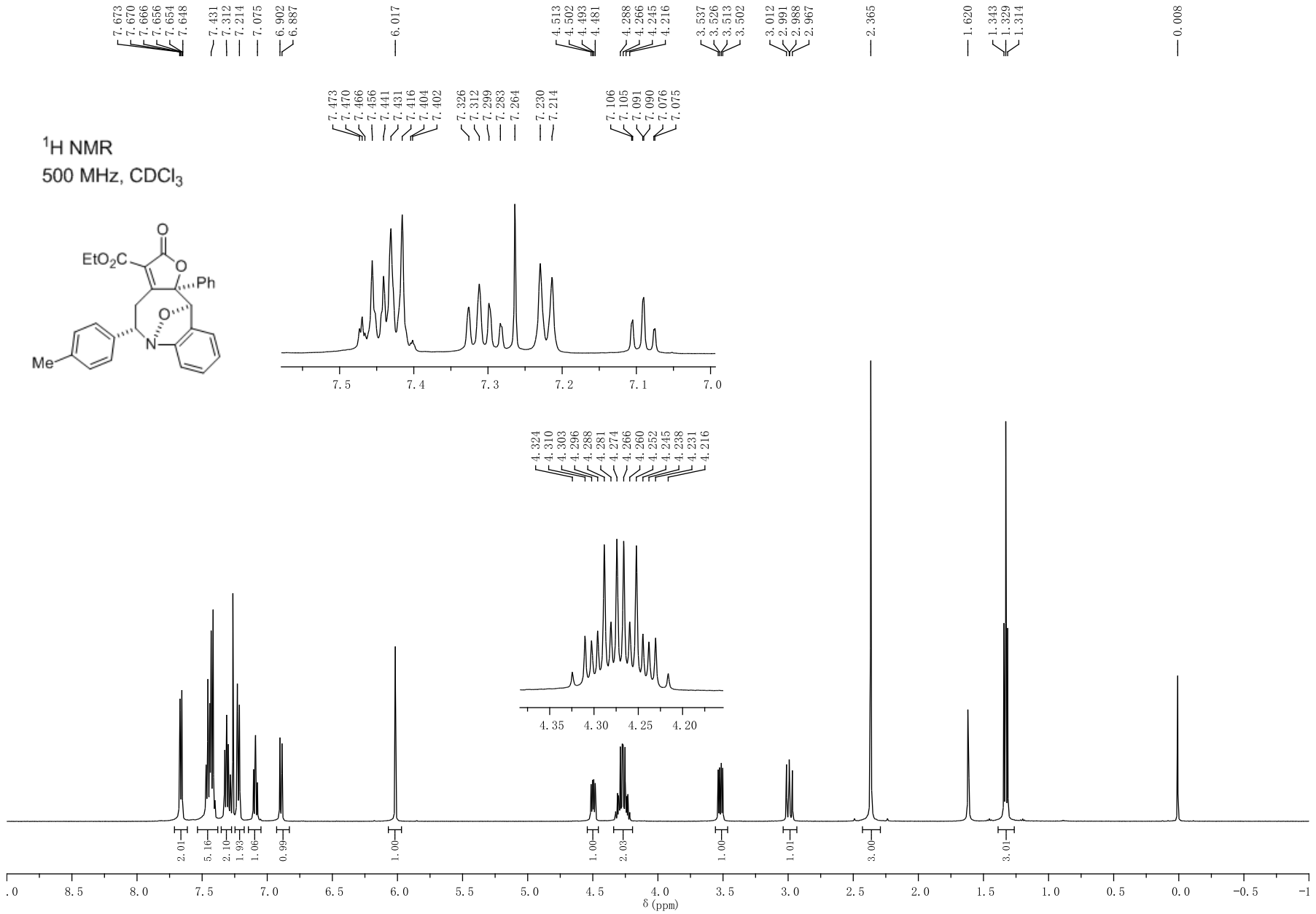
Compound 3pa



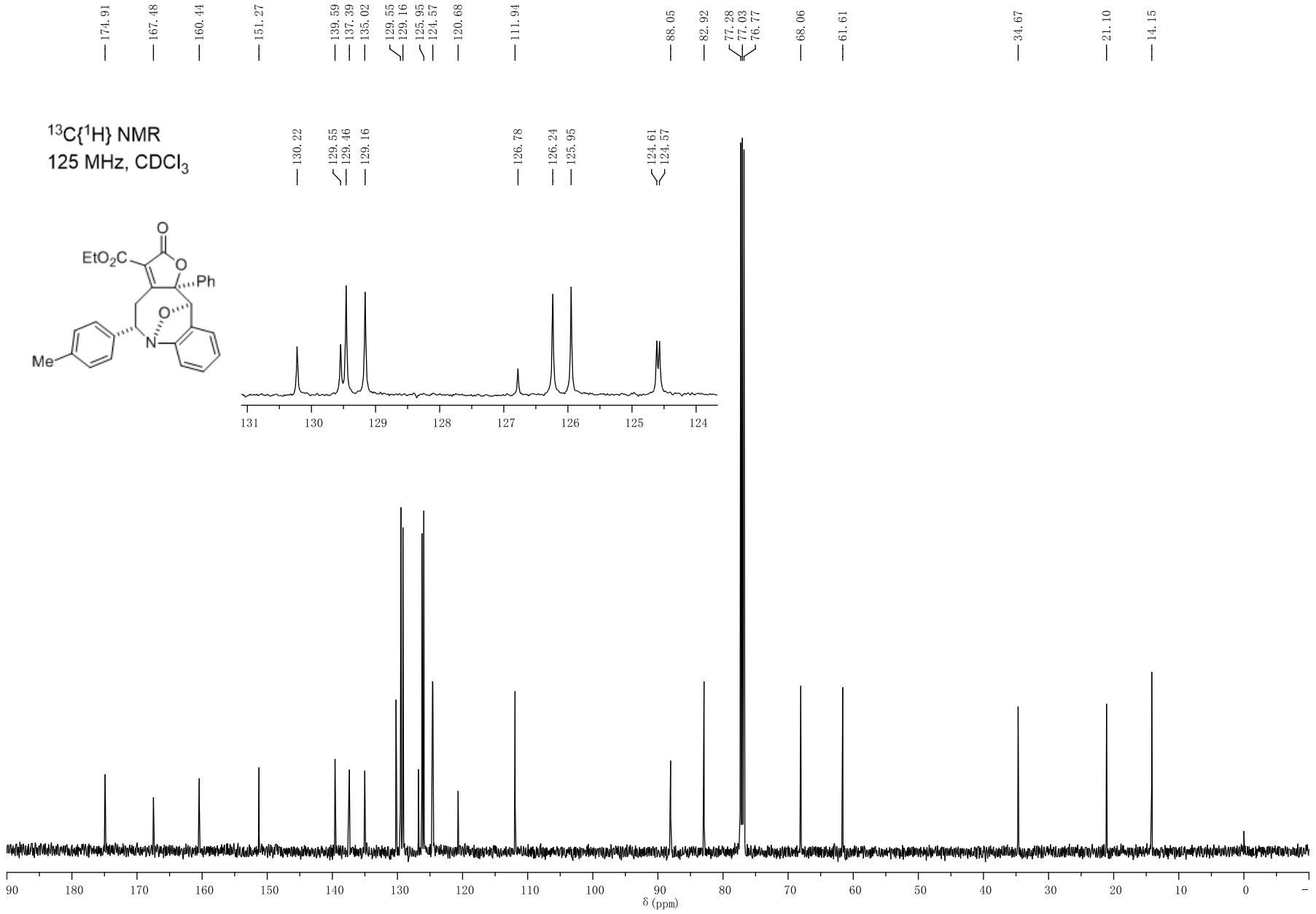
Compound 3pa



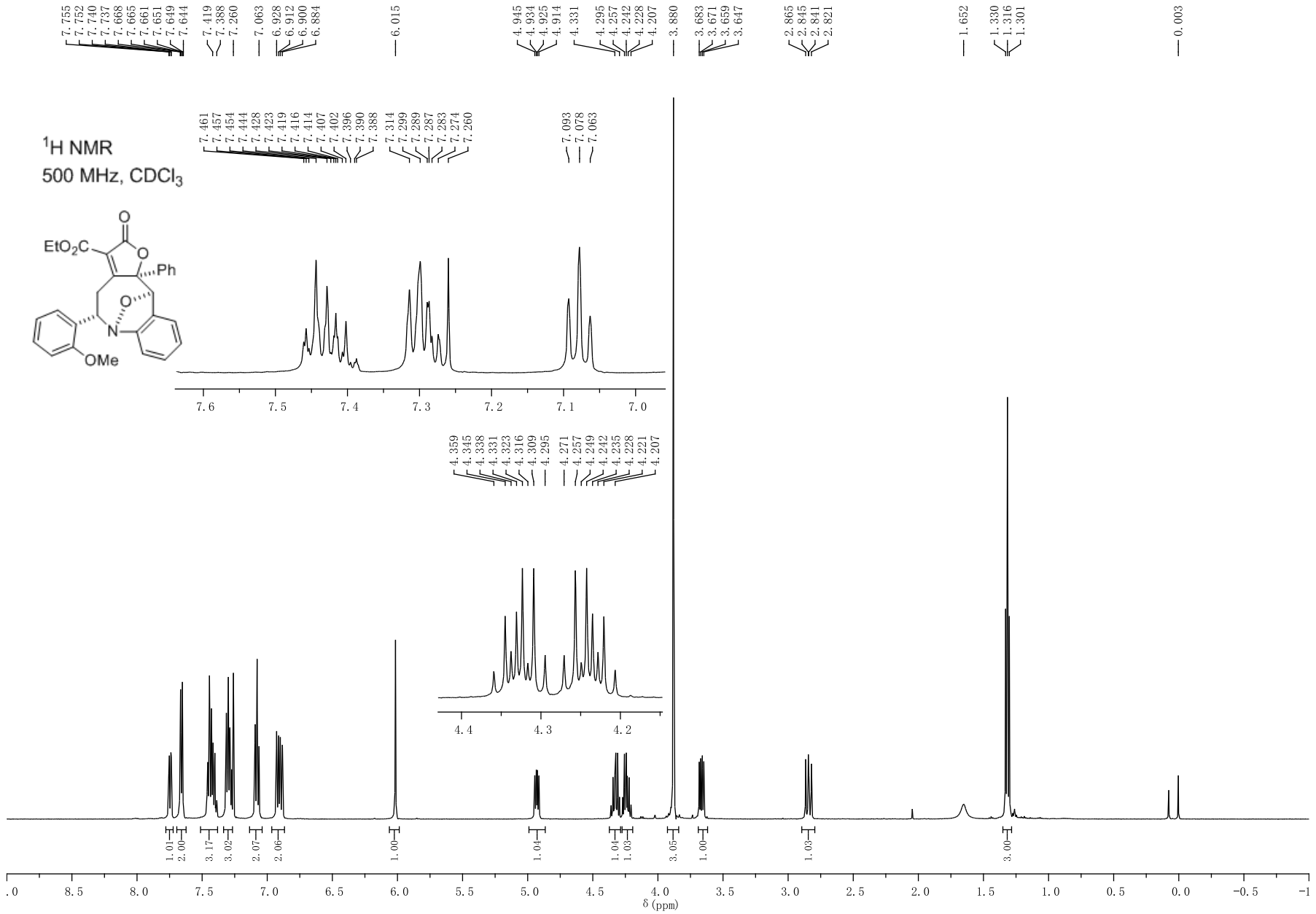
Compound 3qa



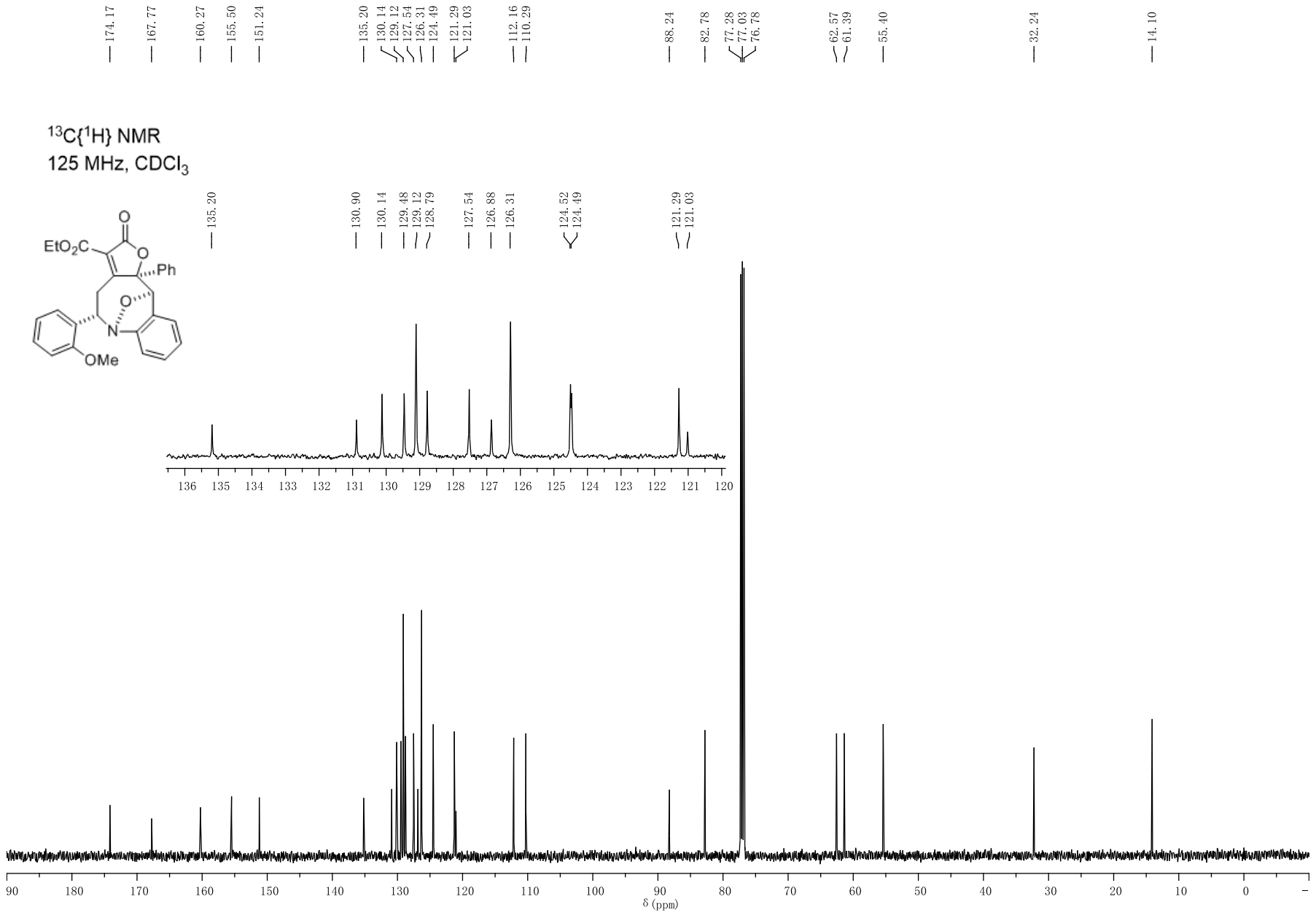
Compound 3qa



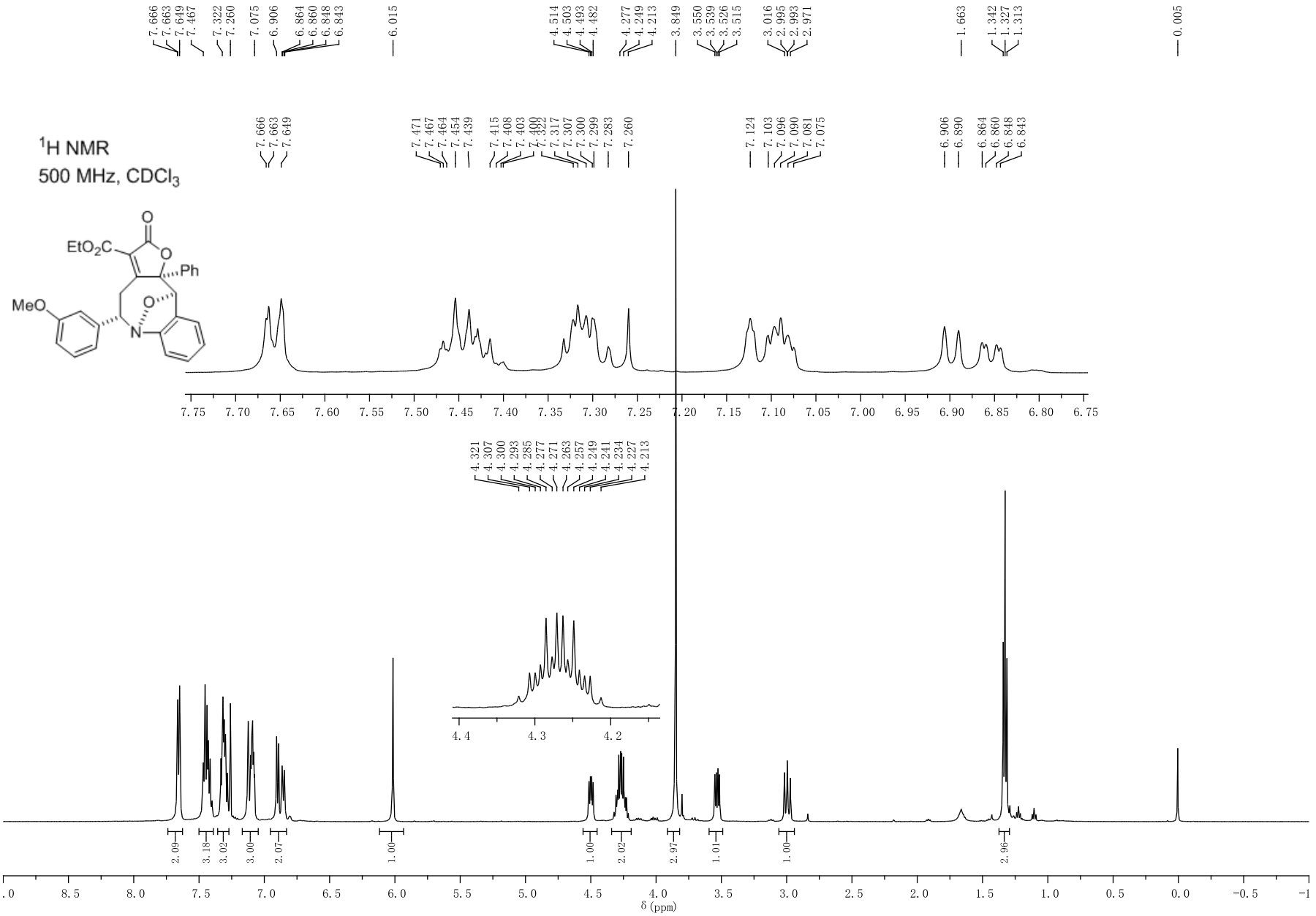
Compound 3ra



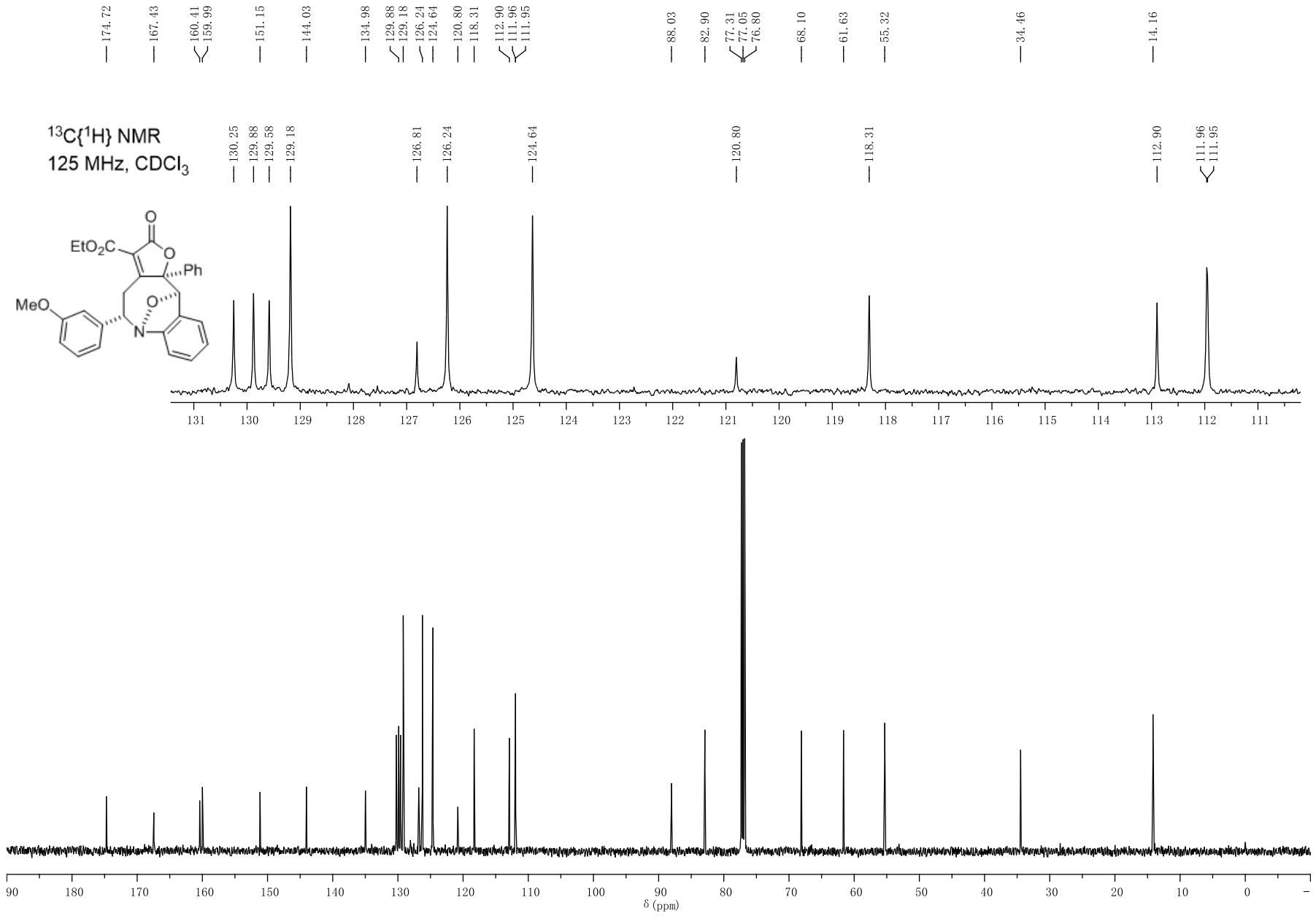
Compound 3ra



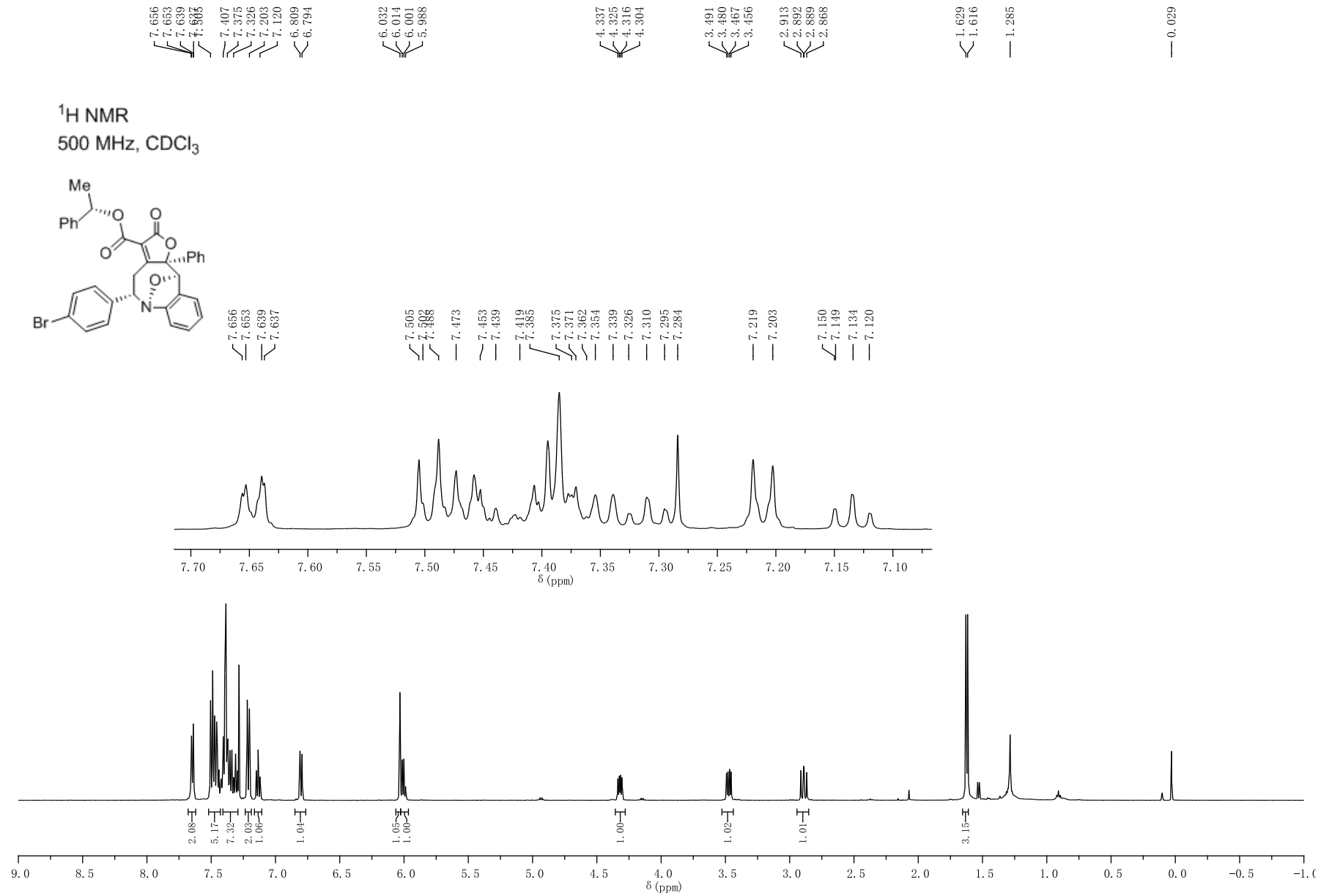
Compound 3sa



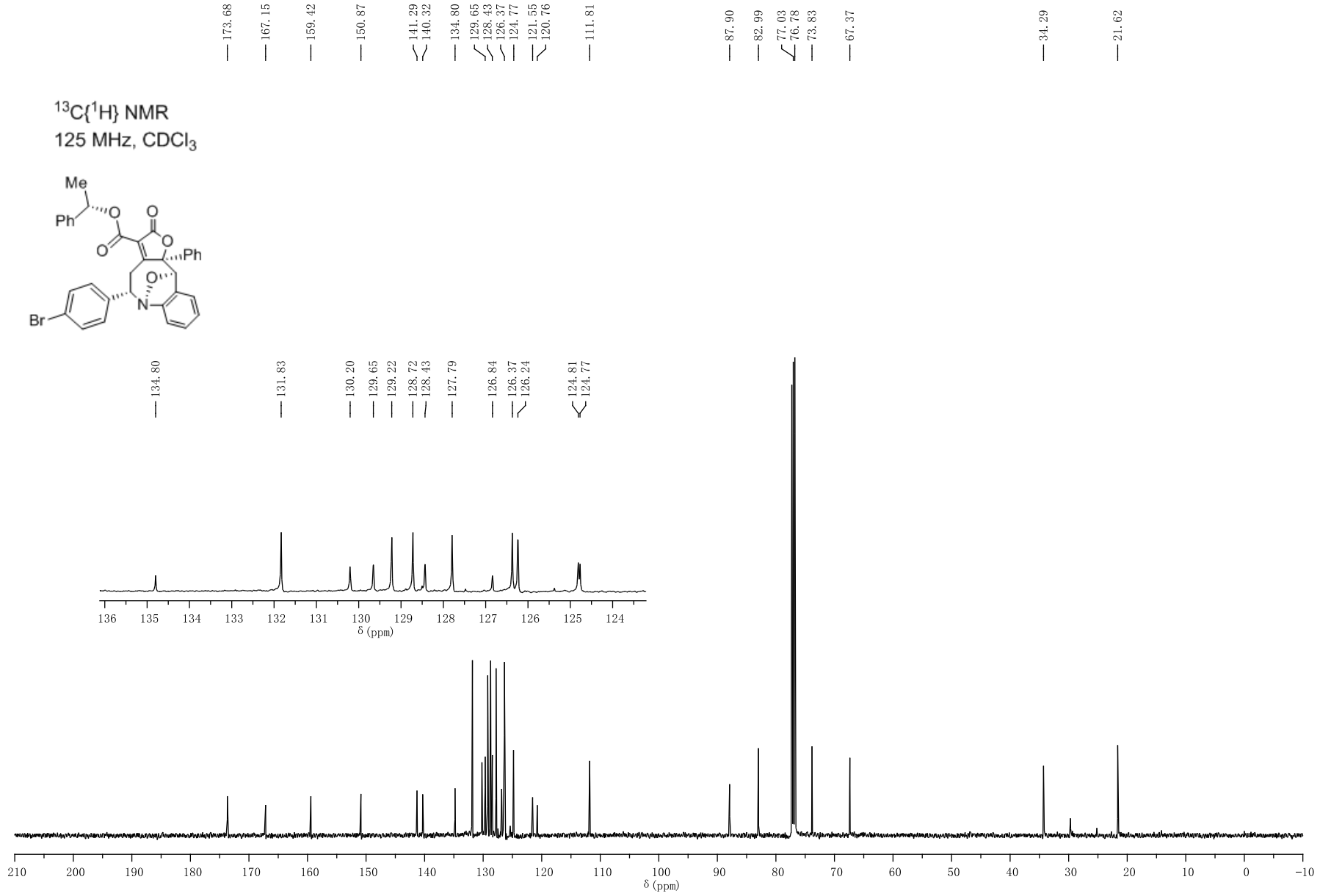
Compound 3sa



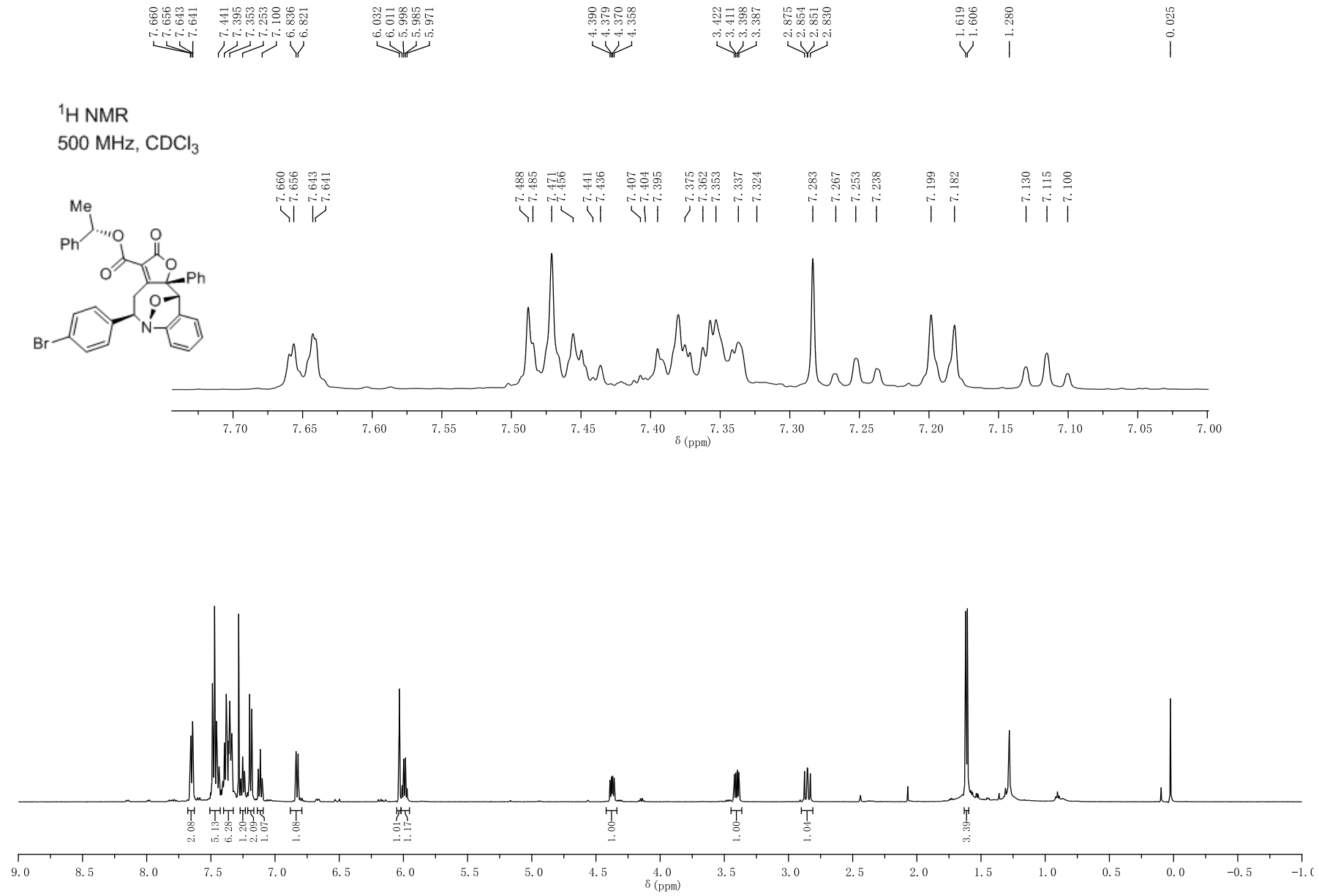
Compound 3ua



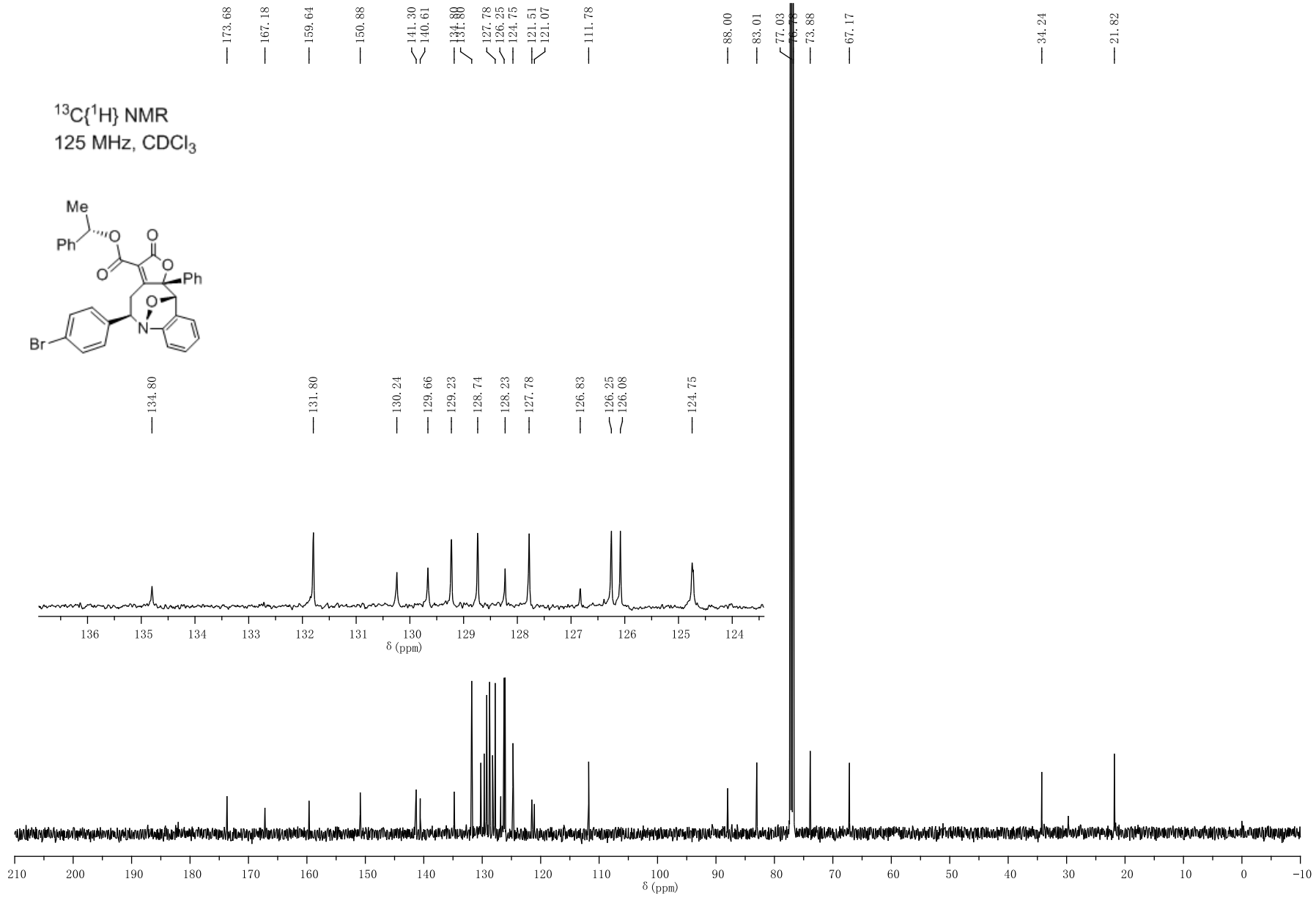
Compound 3ua



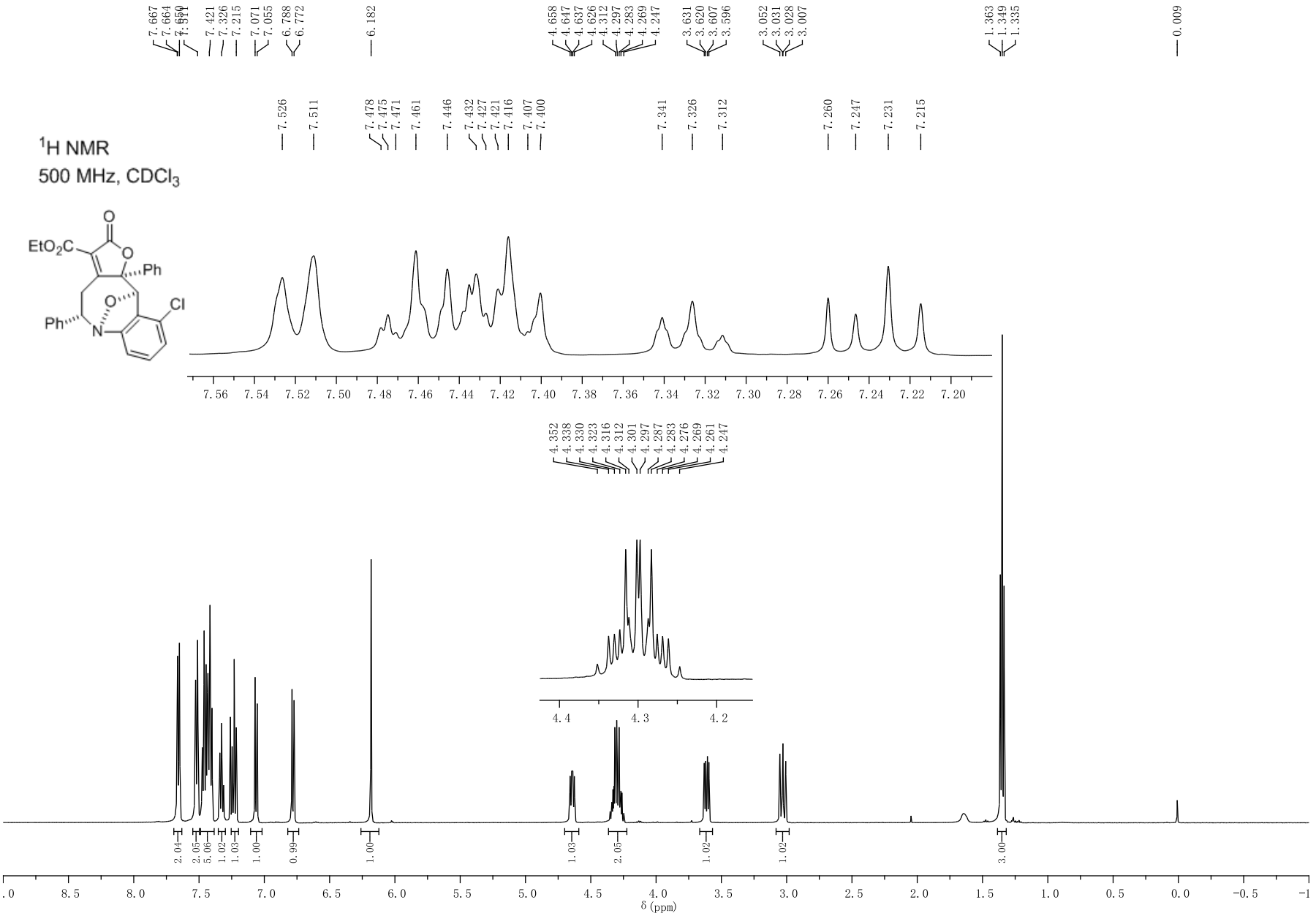
Compound 3ua′



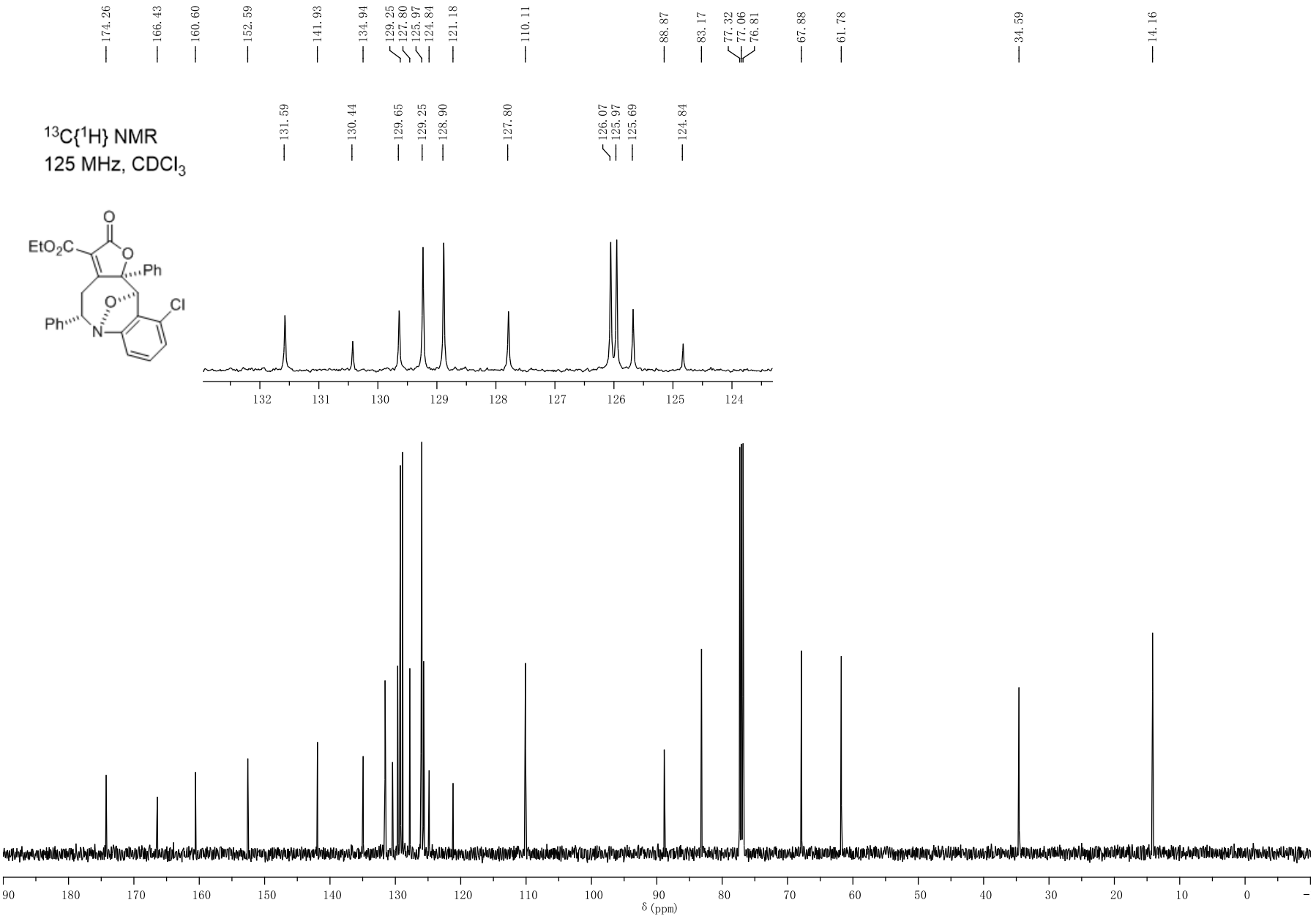
Compound 3ua′



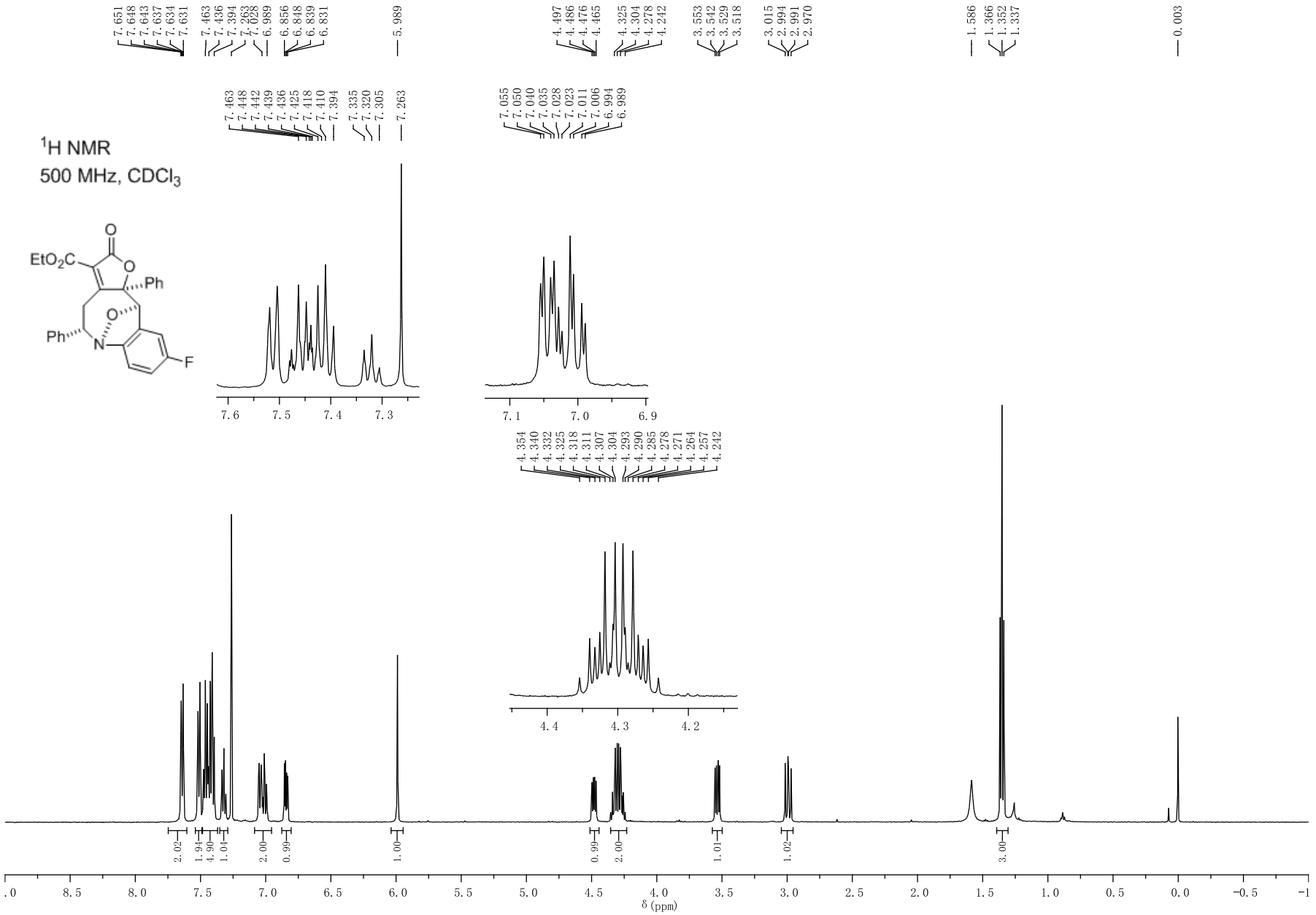
Compound 3ab



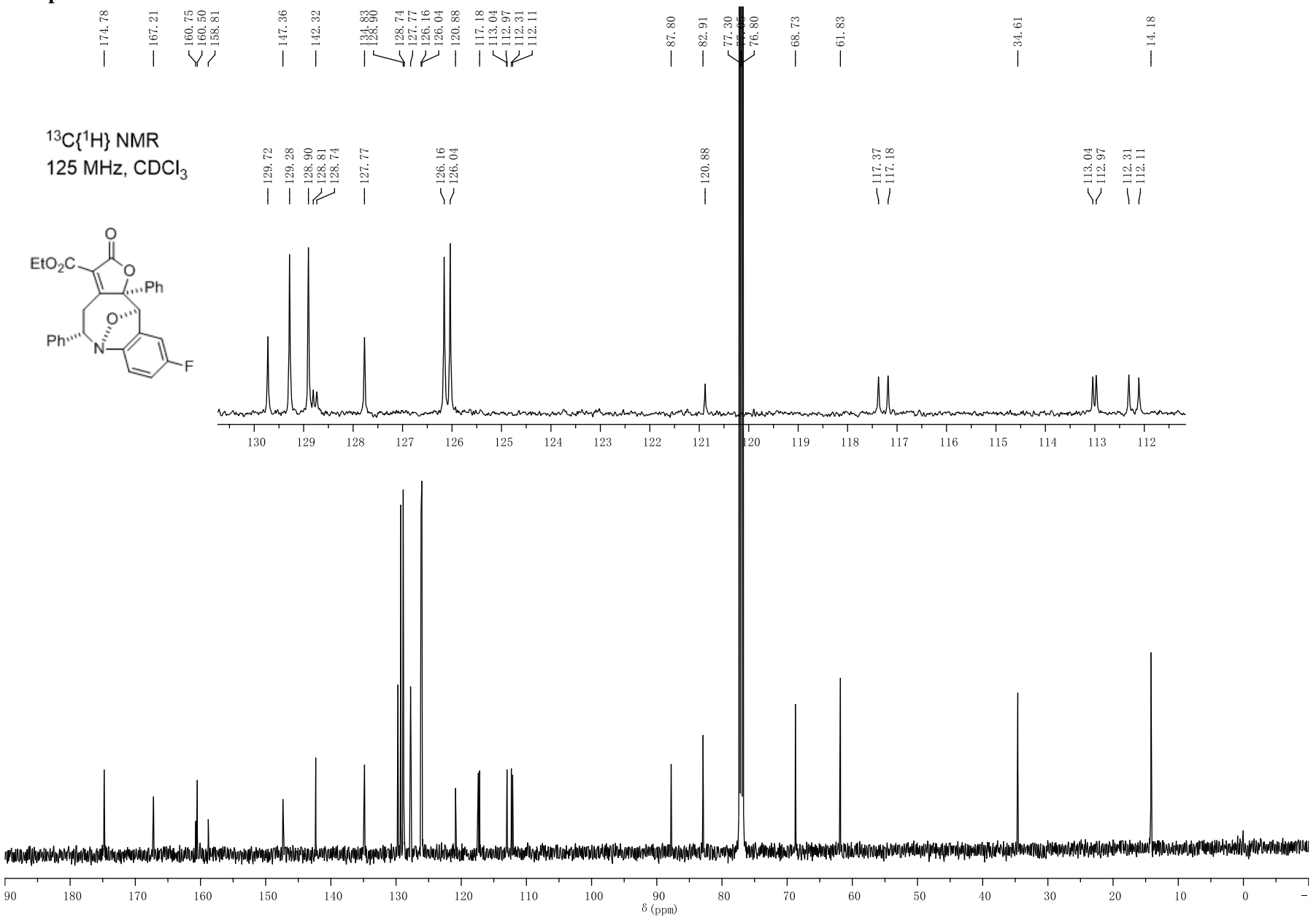
Compound 3ab



Compound 3ac

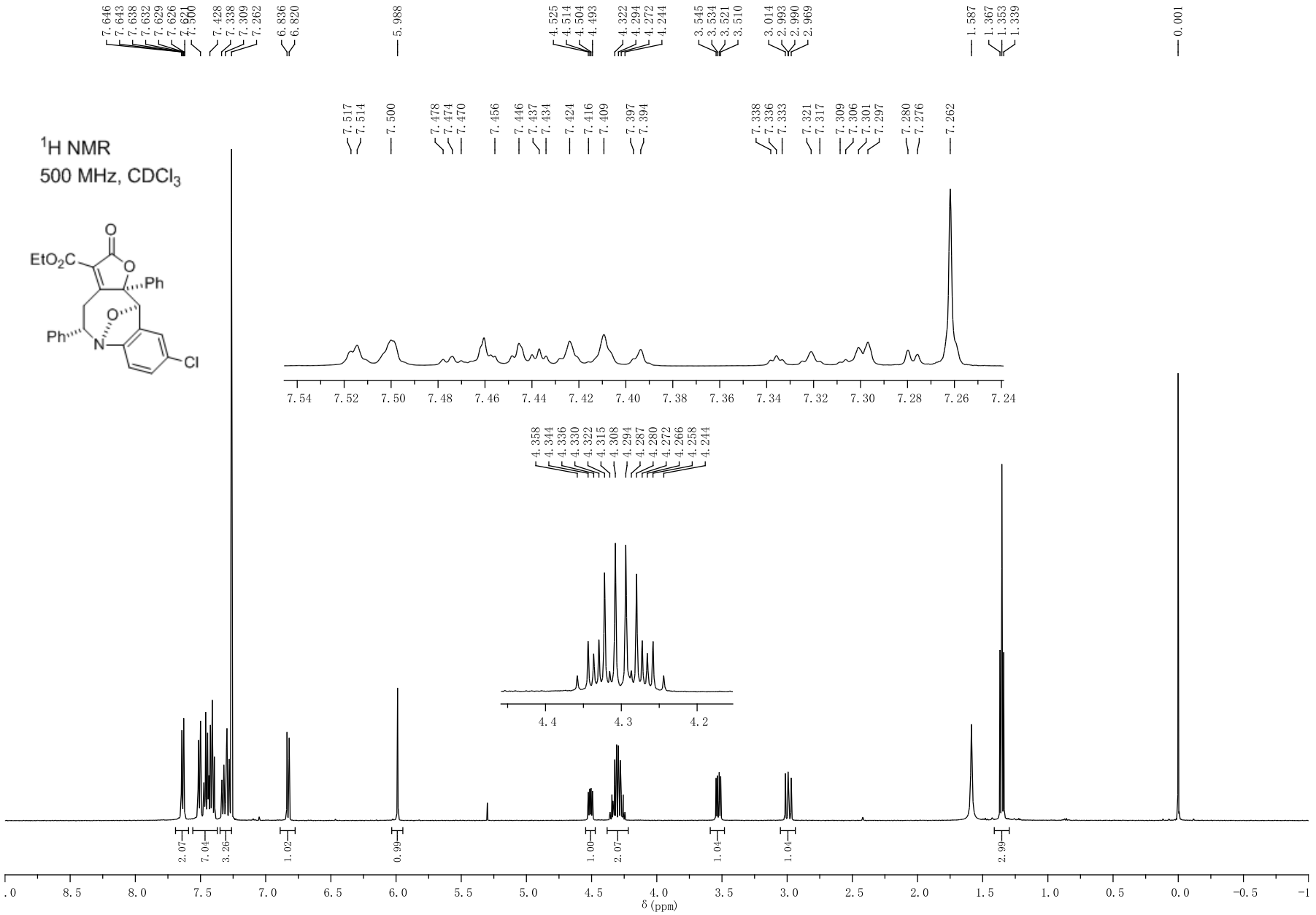


Compound 3ac

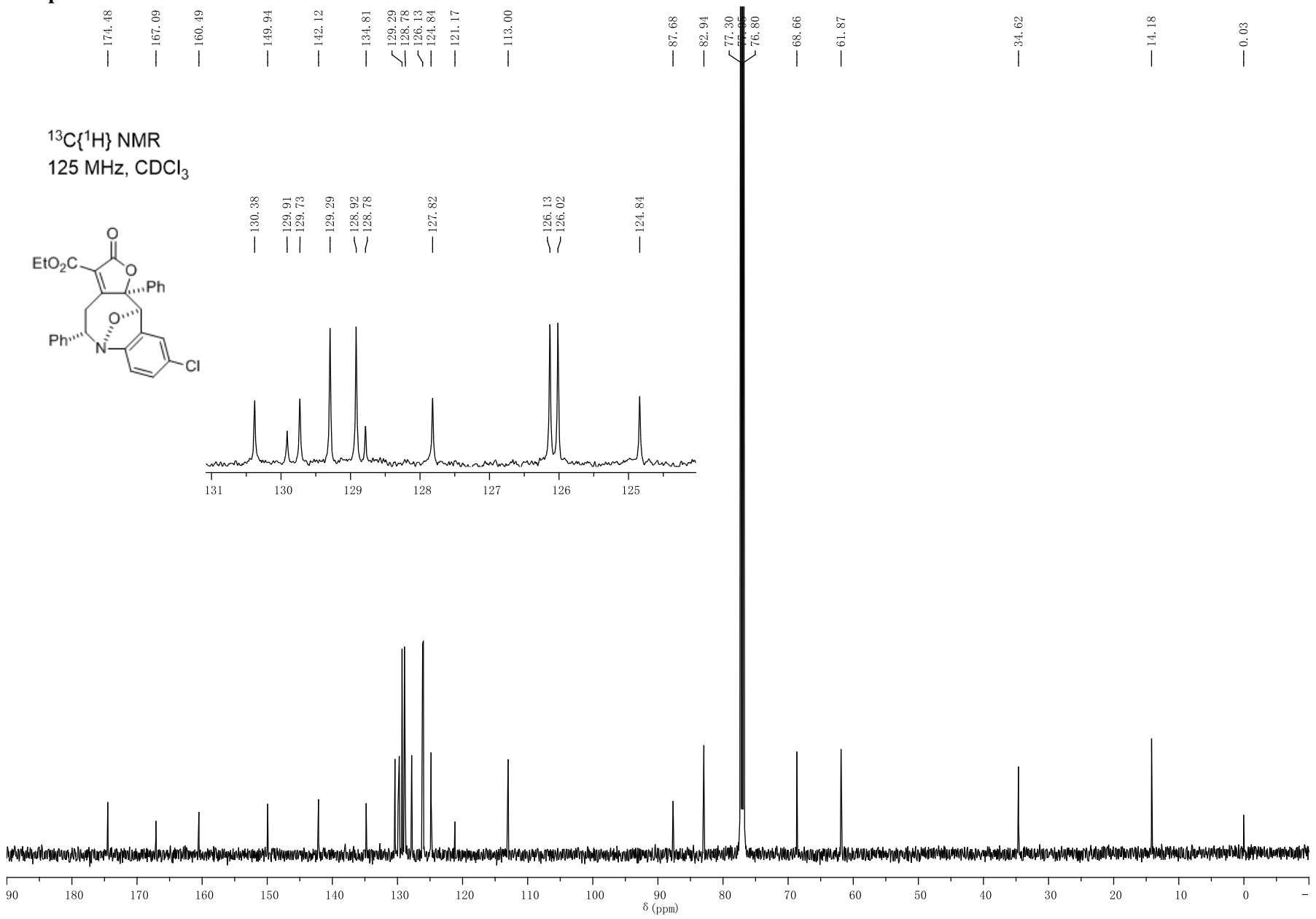


Compound 3ac

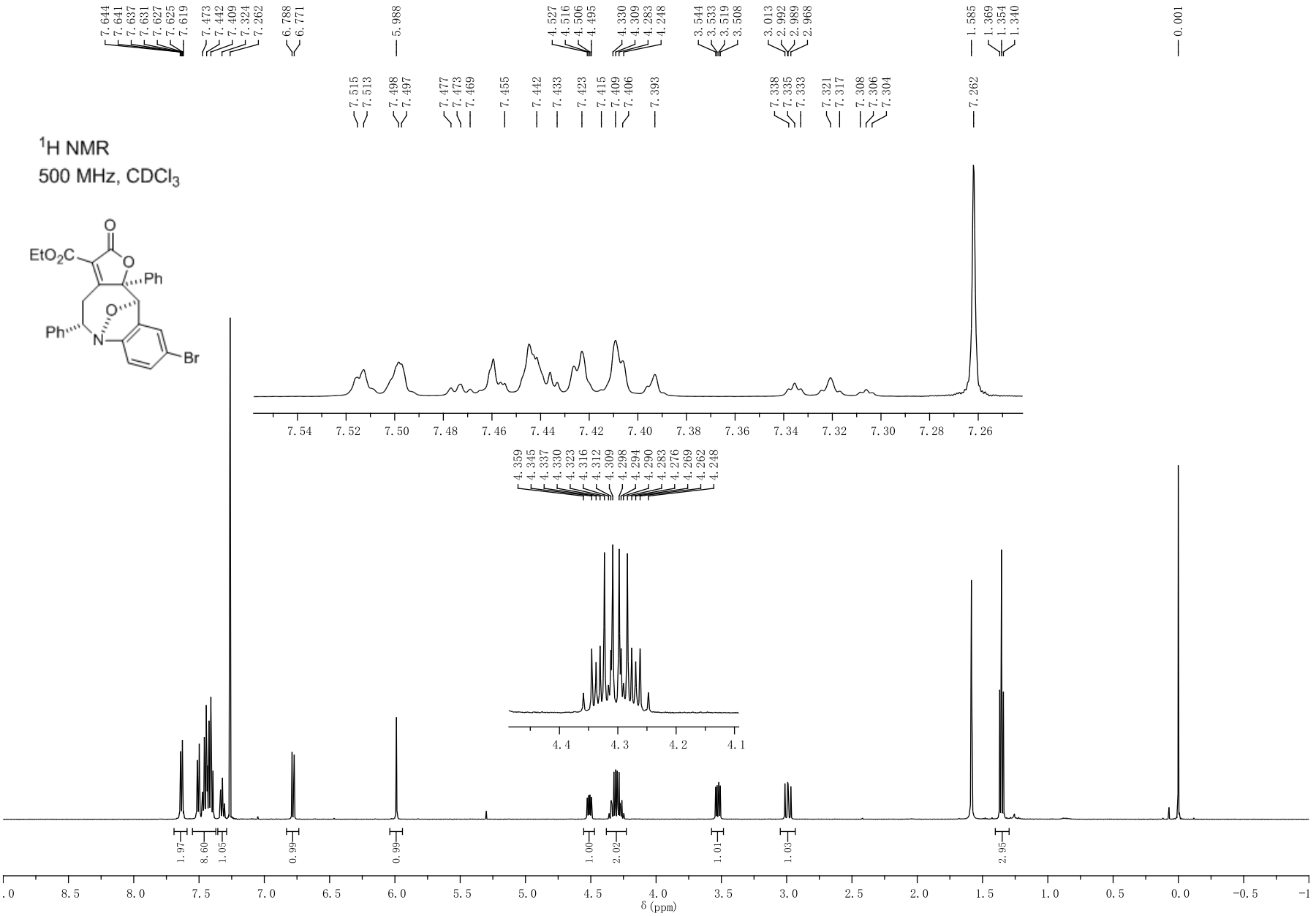
Compound 3ad



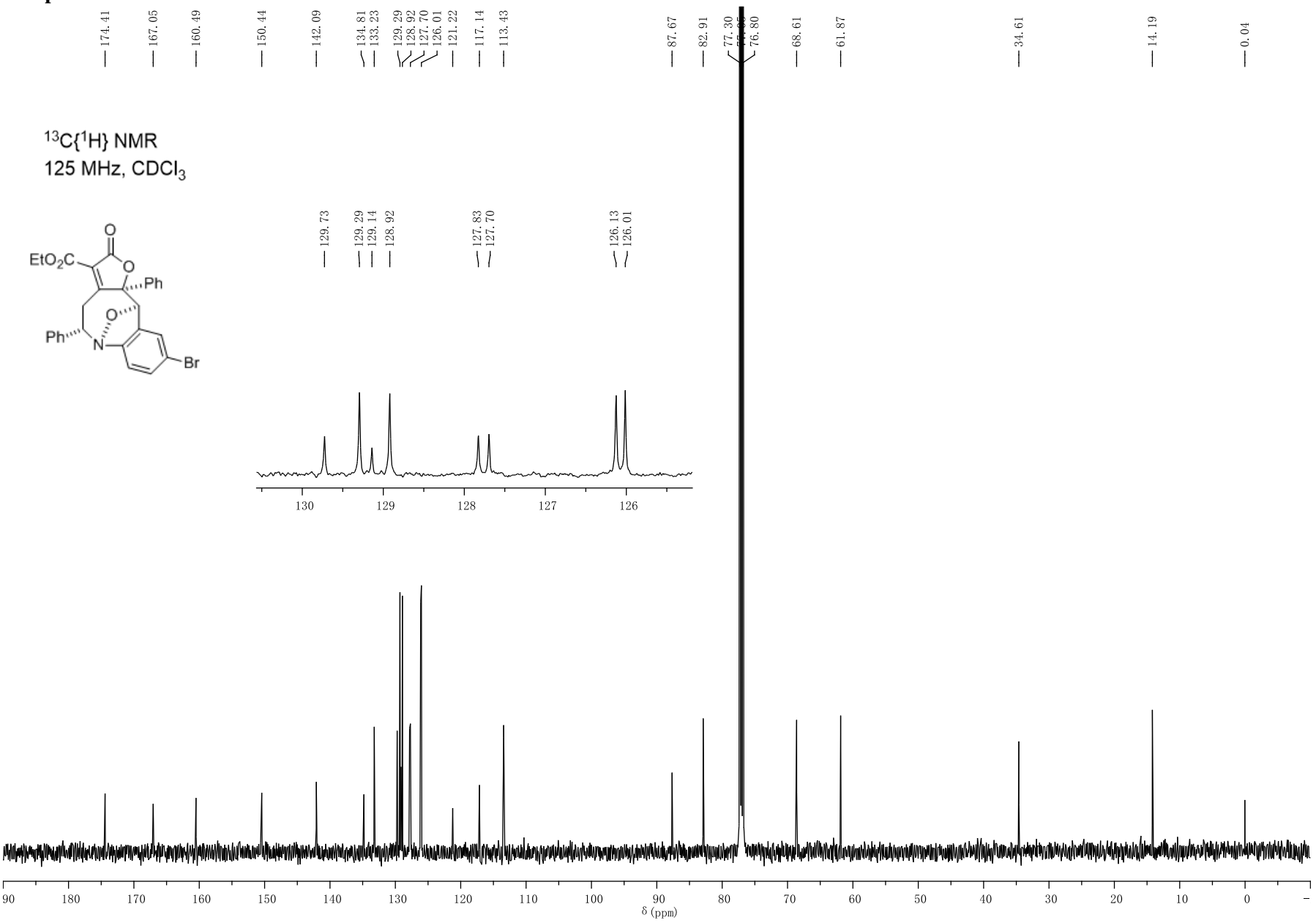
Compound 3ad



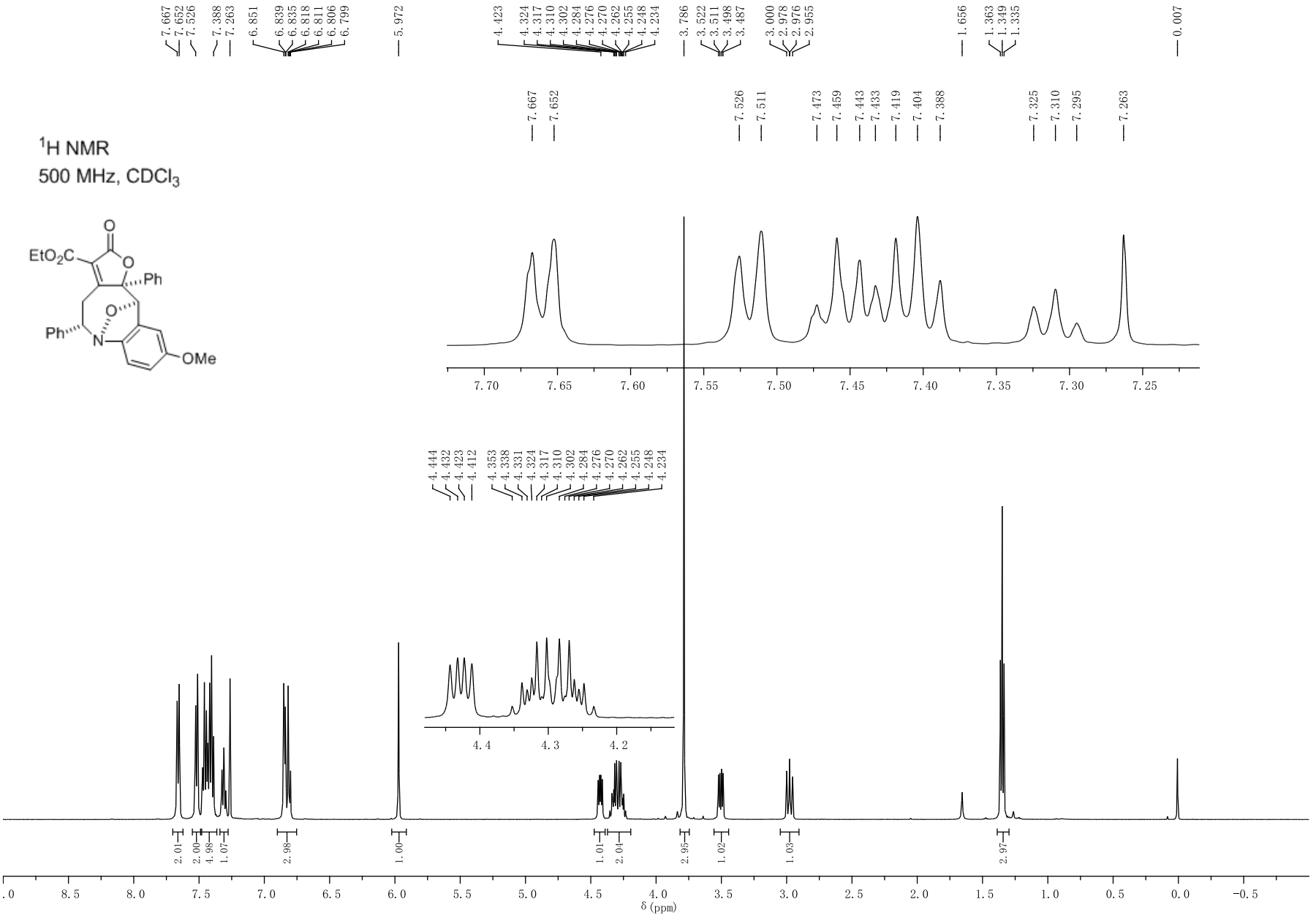
Compound 3ae



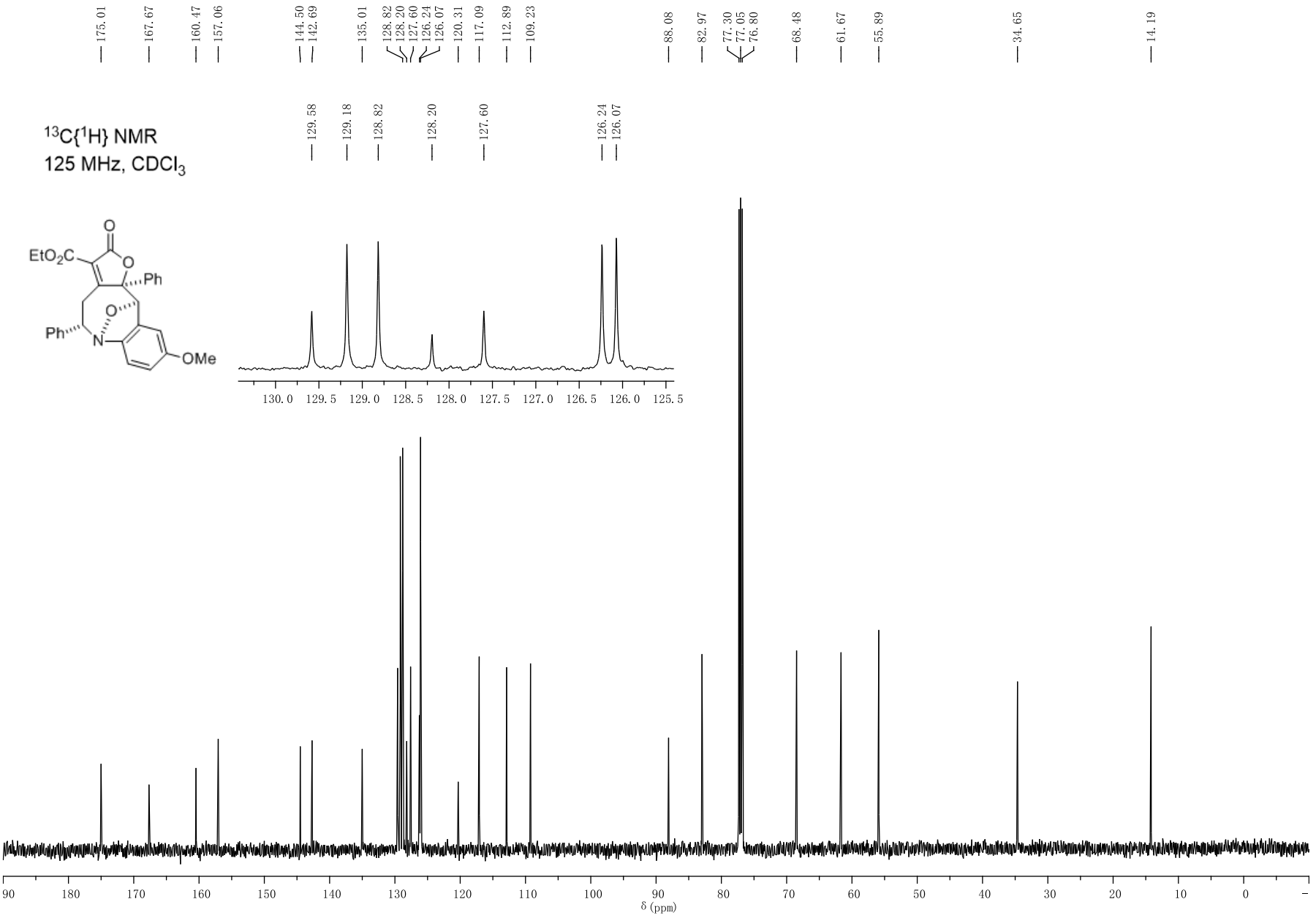
Compound 3ae



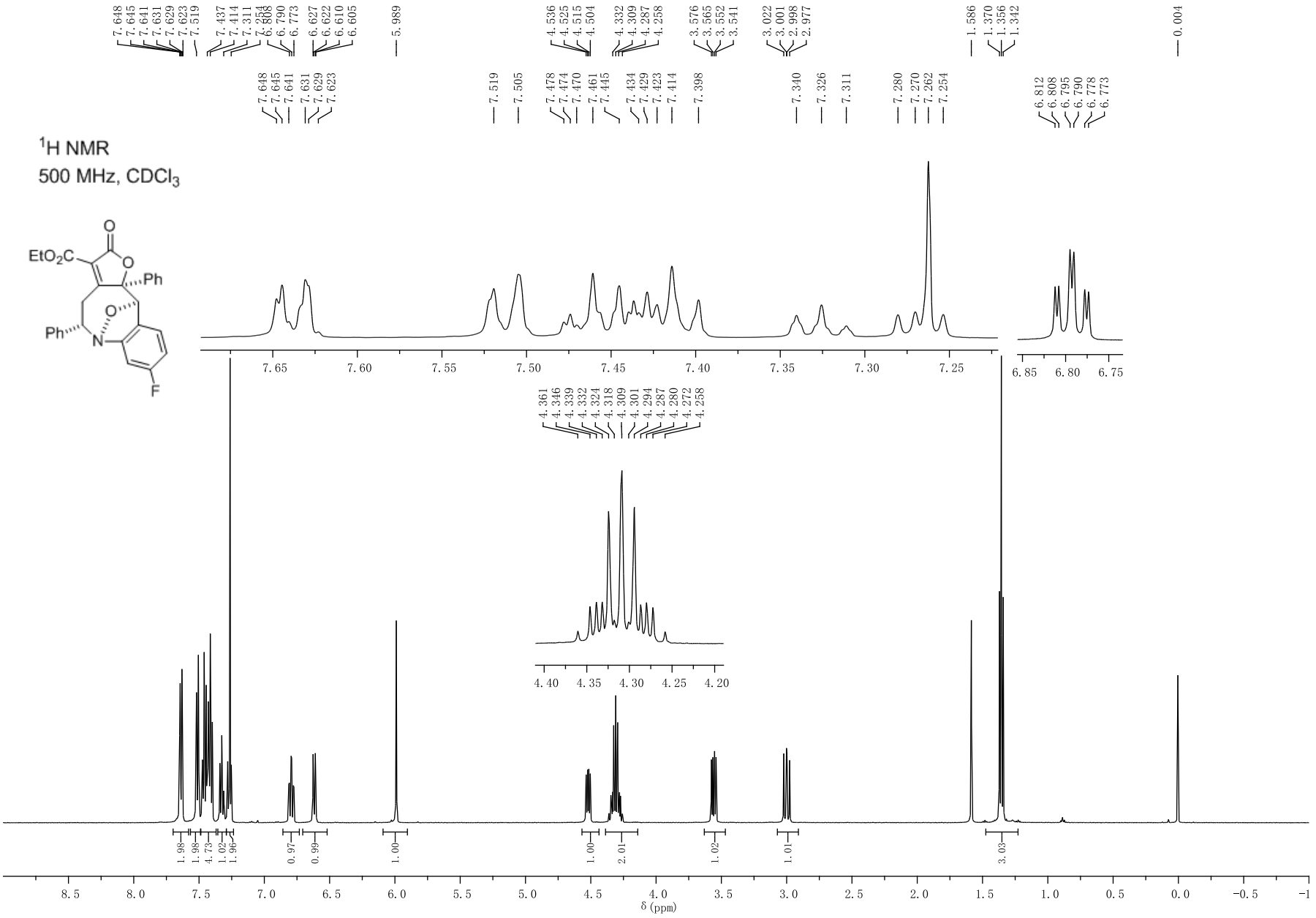
Compound 3af



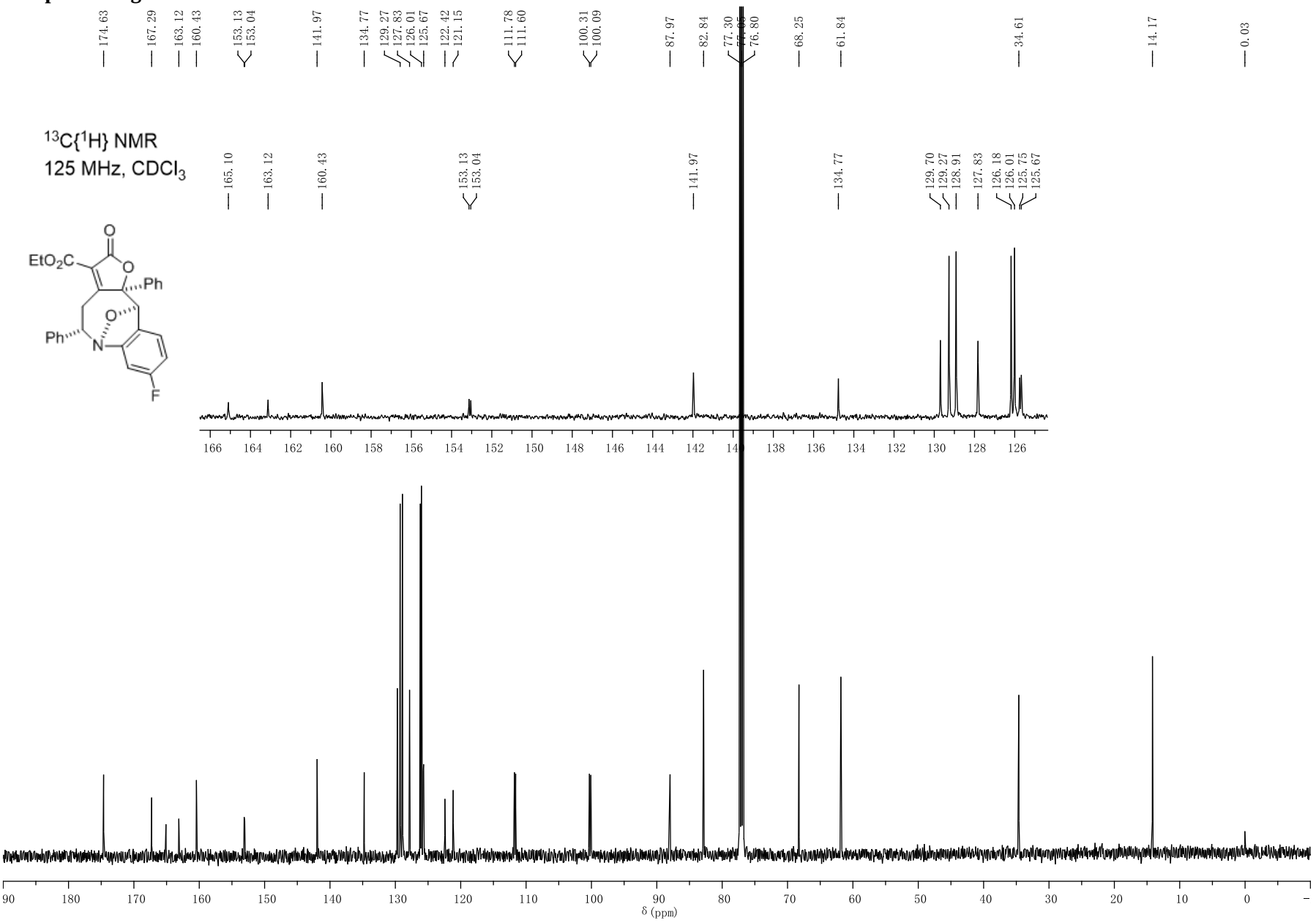
Compound 3af



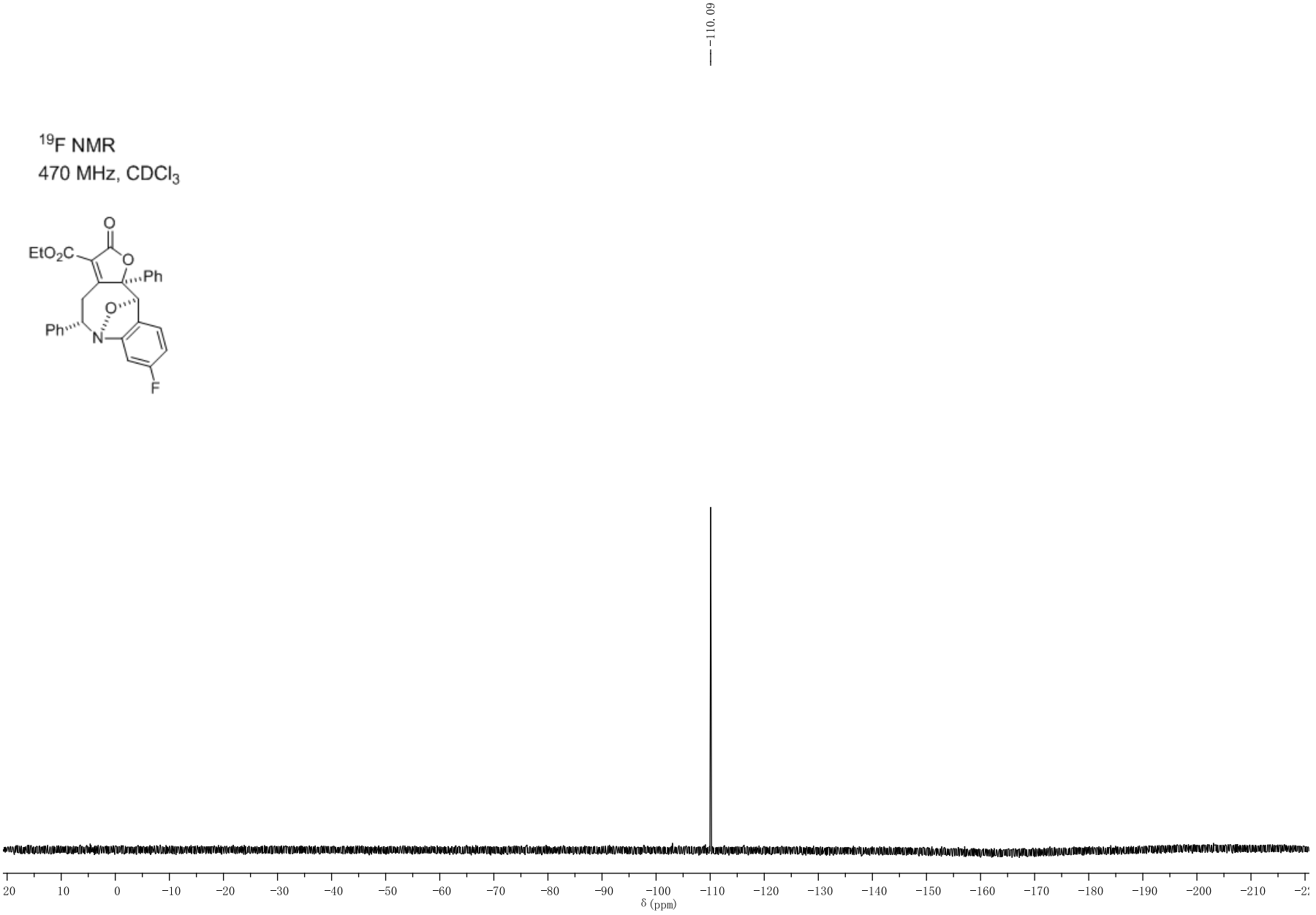
Compound 3ag



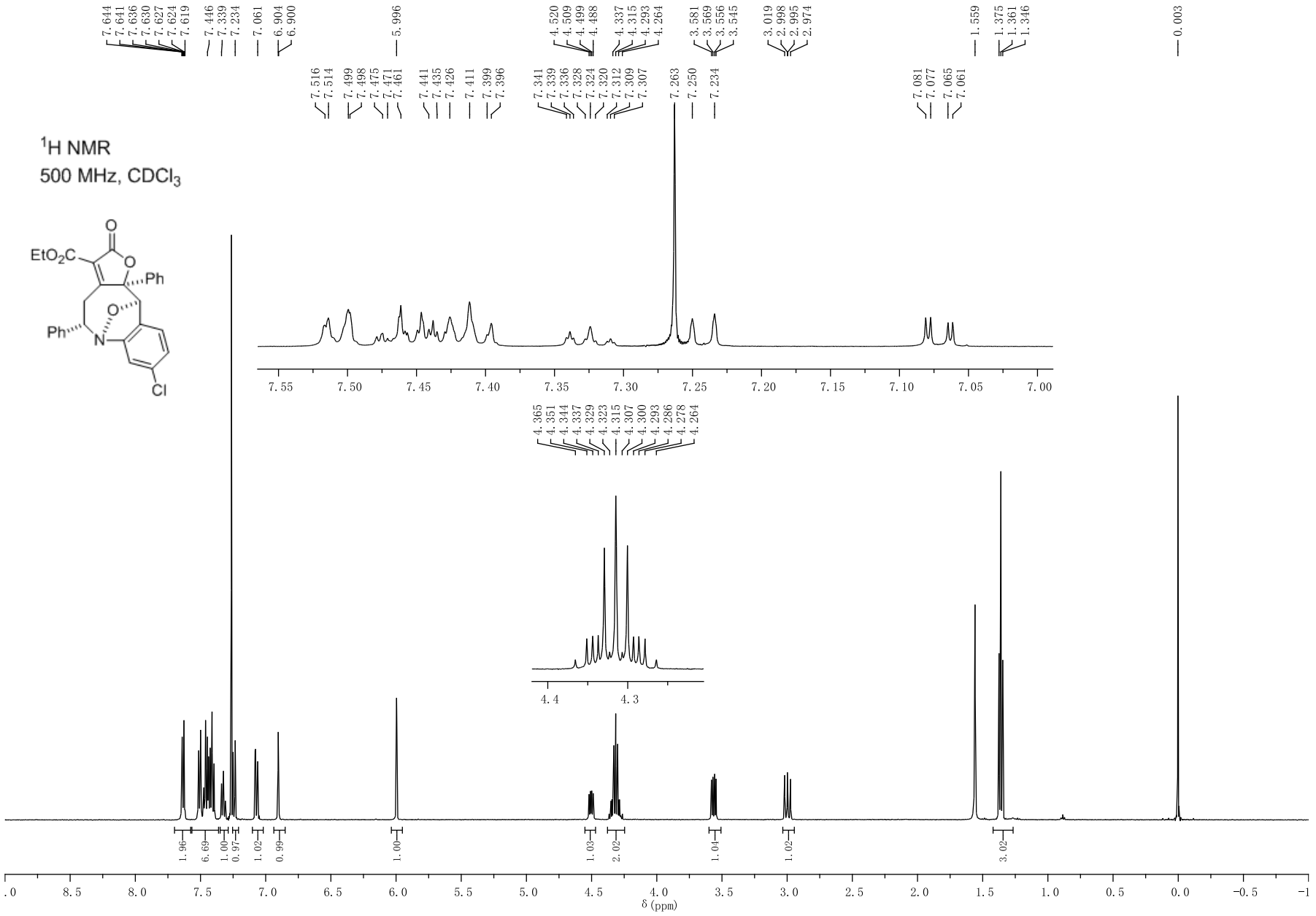
Compound 3ag



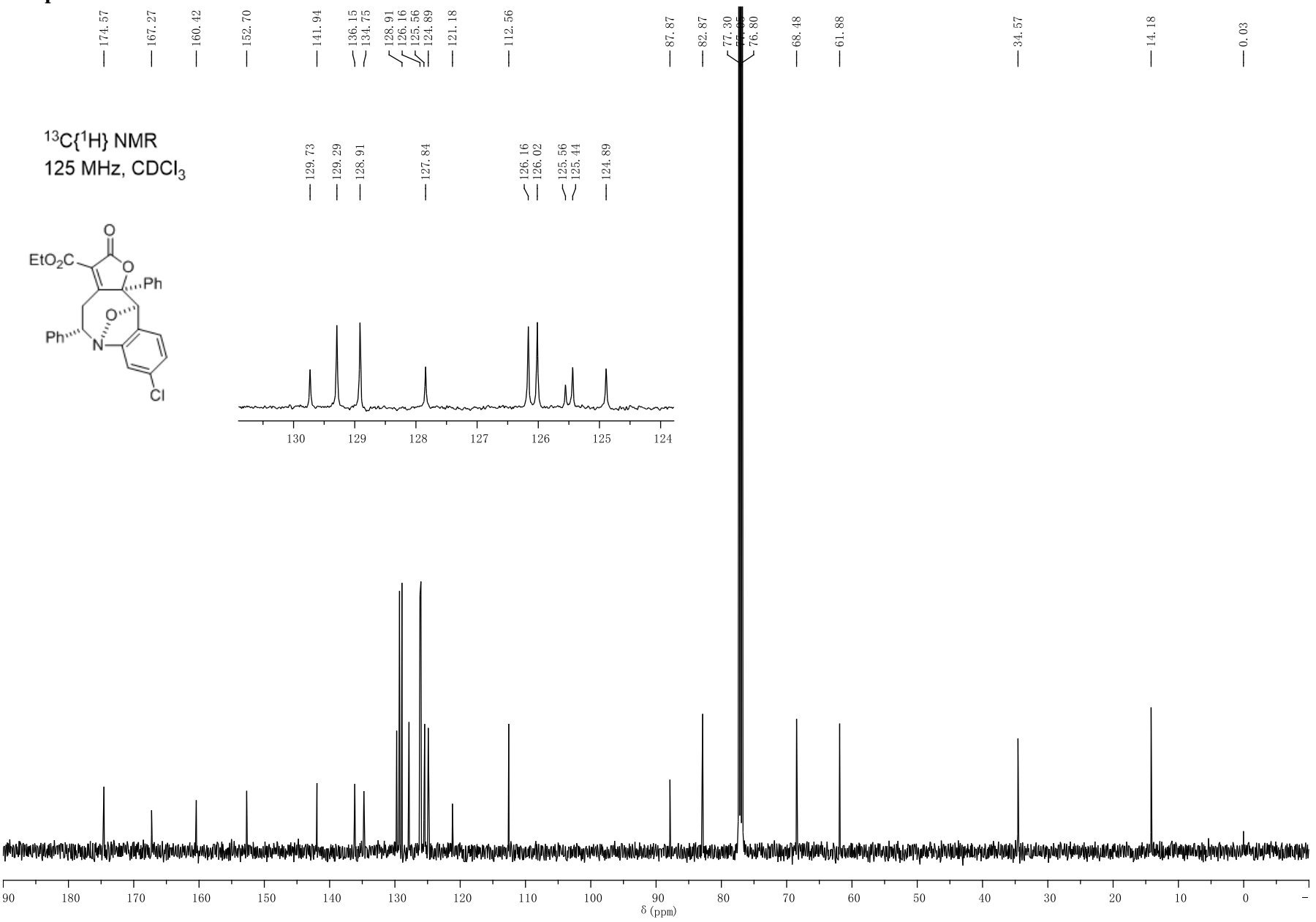
Compound 3ag



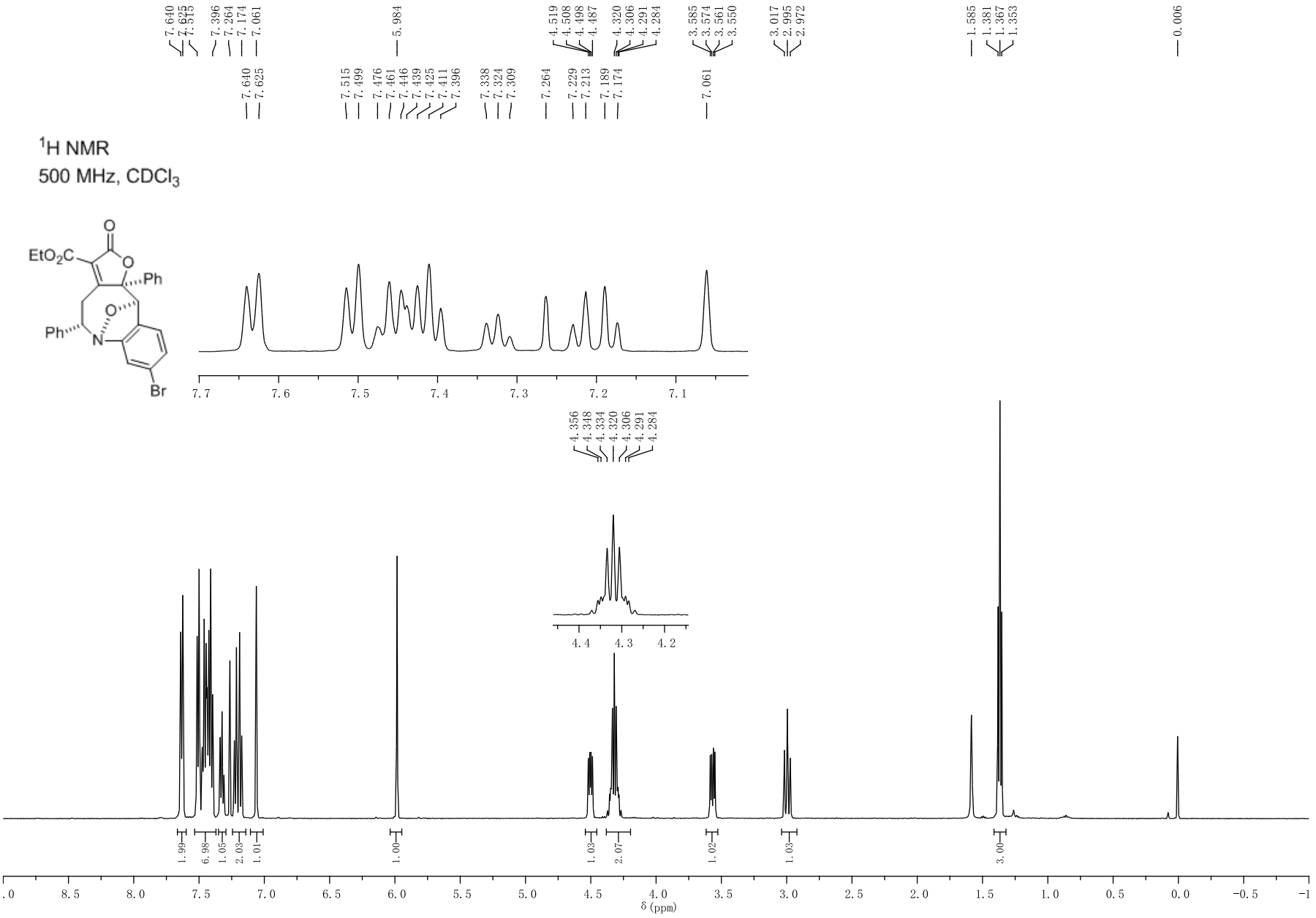
Compound 3ah



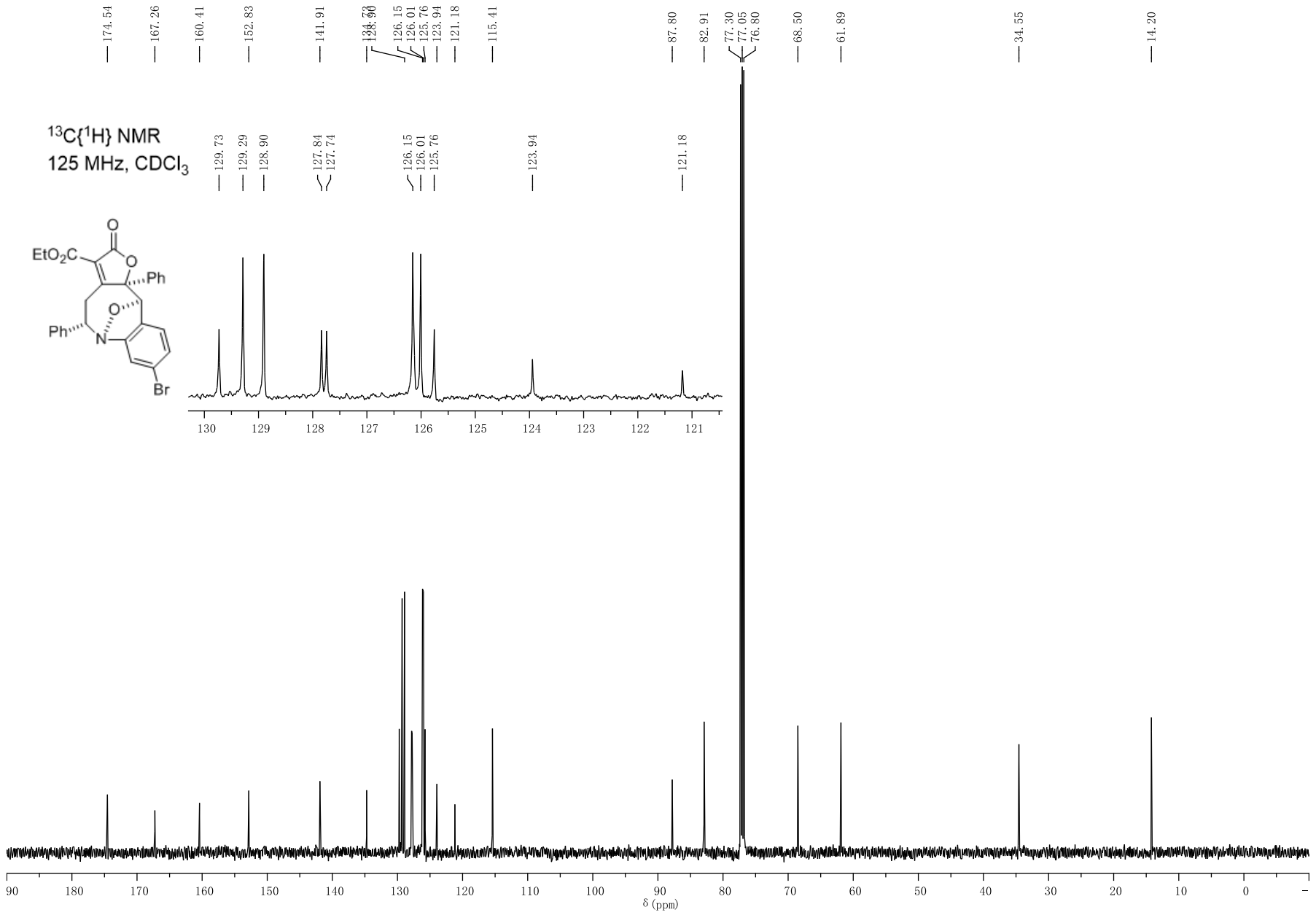
Compound 3ah



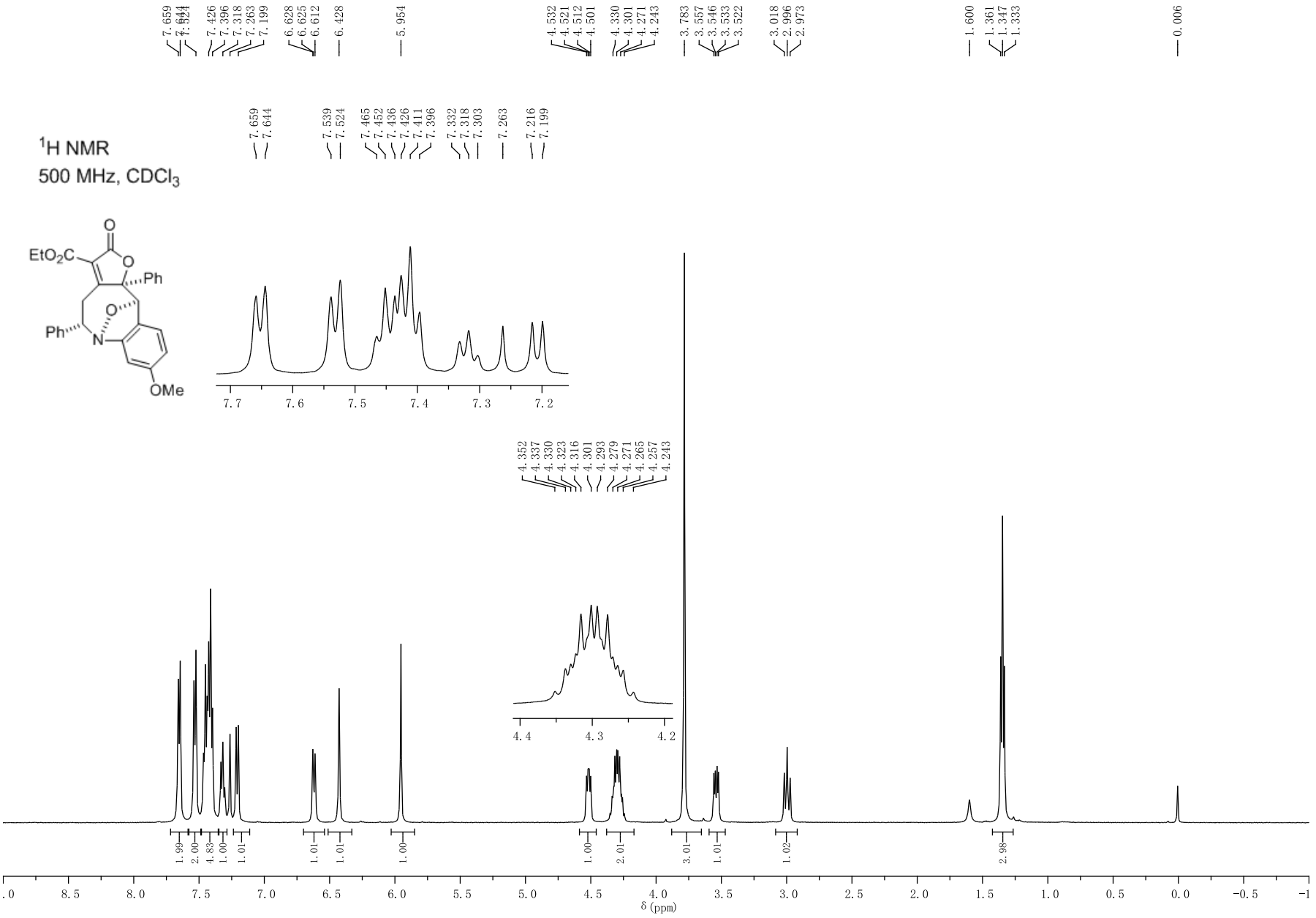
Compound 3ai



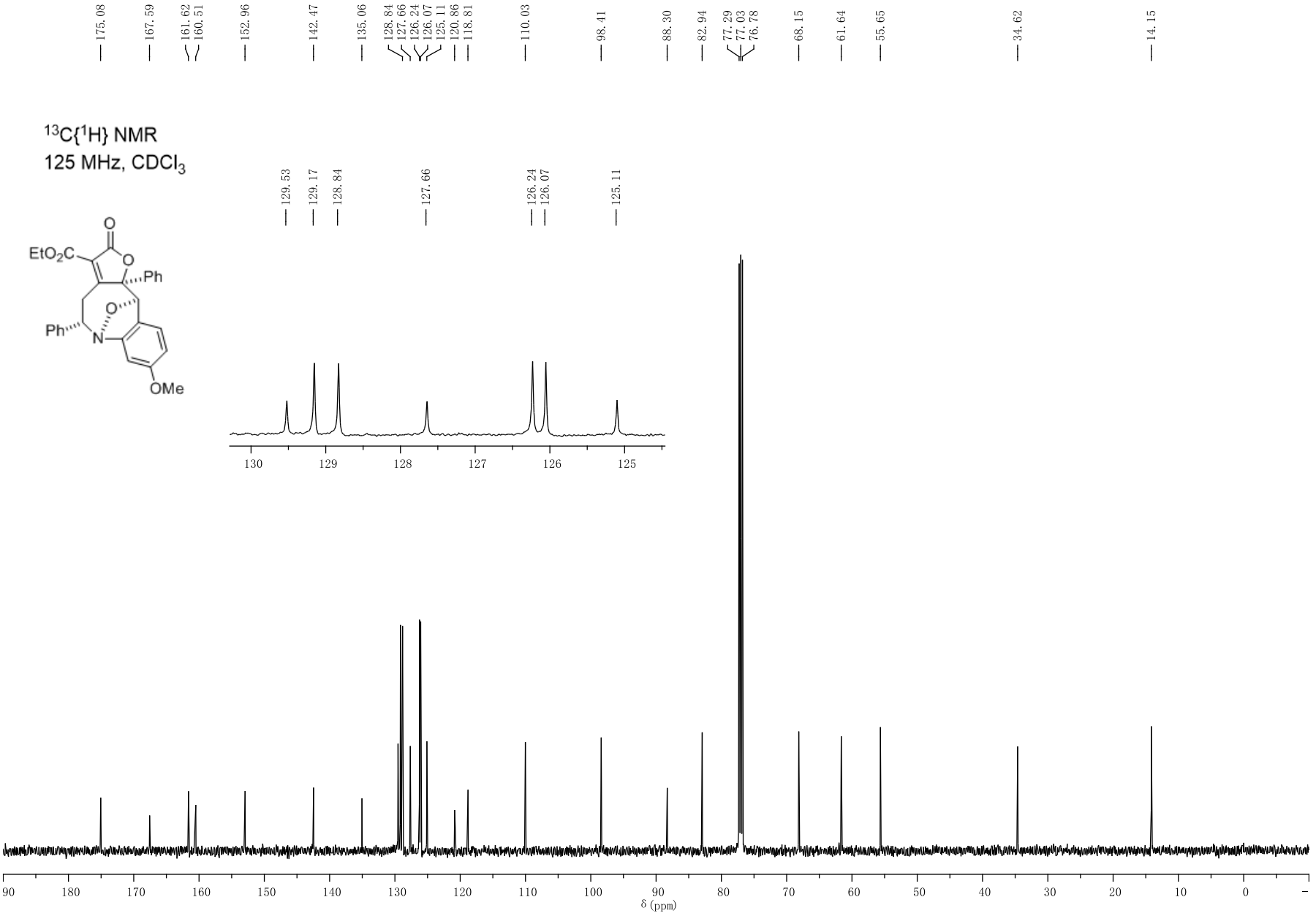
Compound 3ai



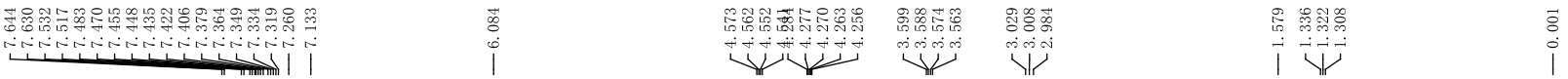
Compound 3aj



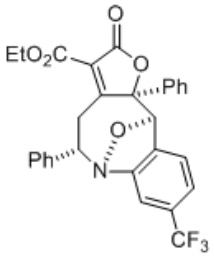
Compound 3aj

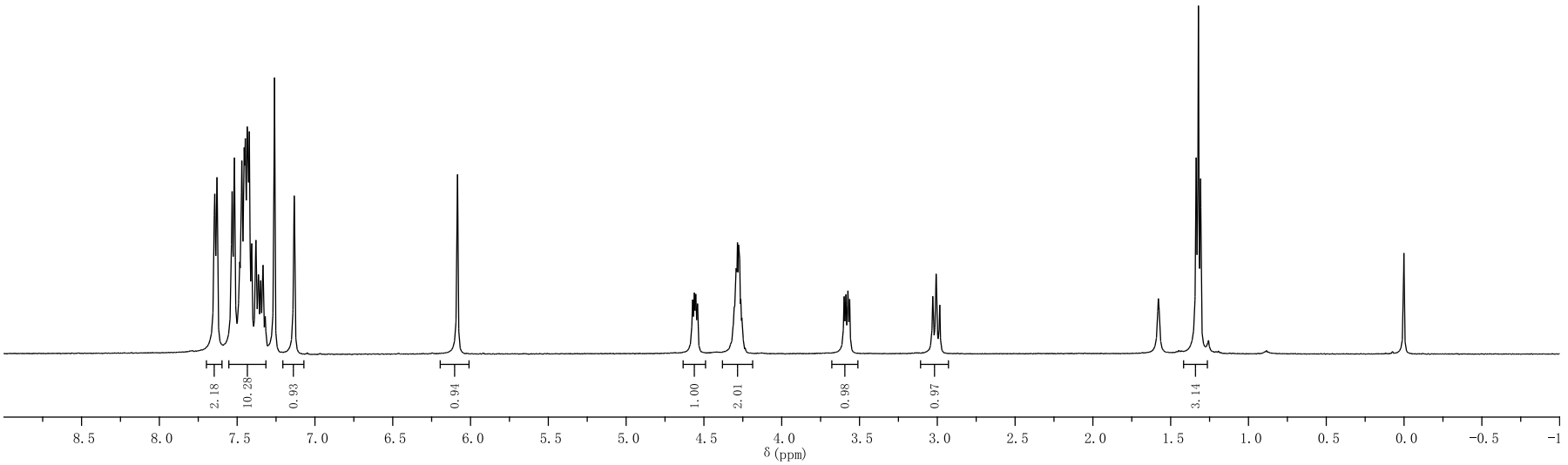


Compound 3ak

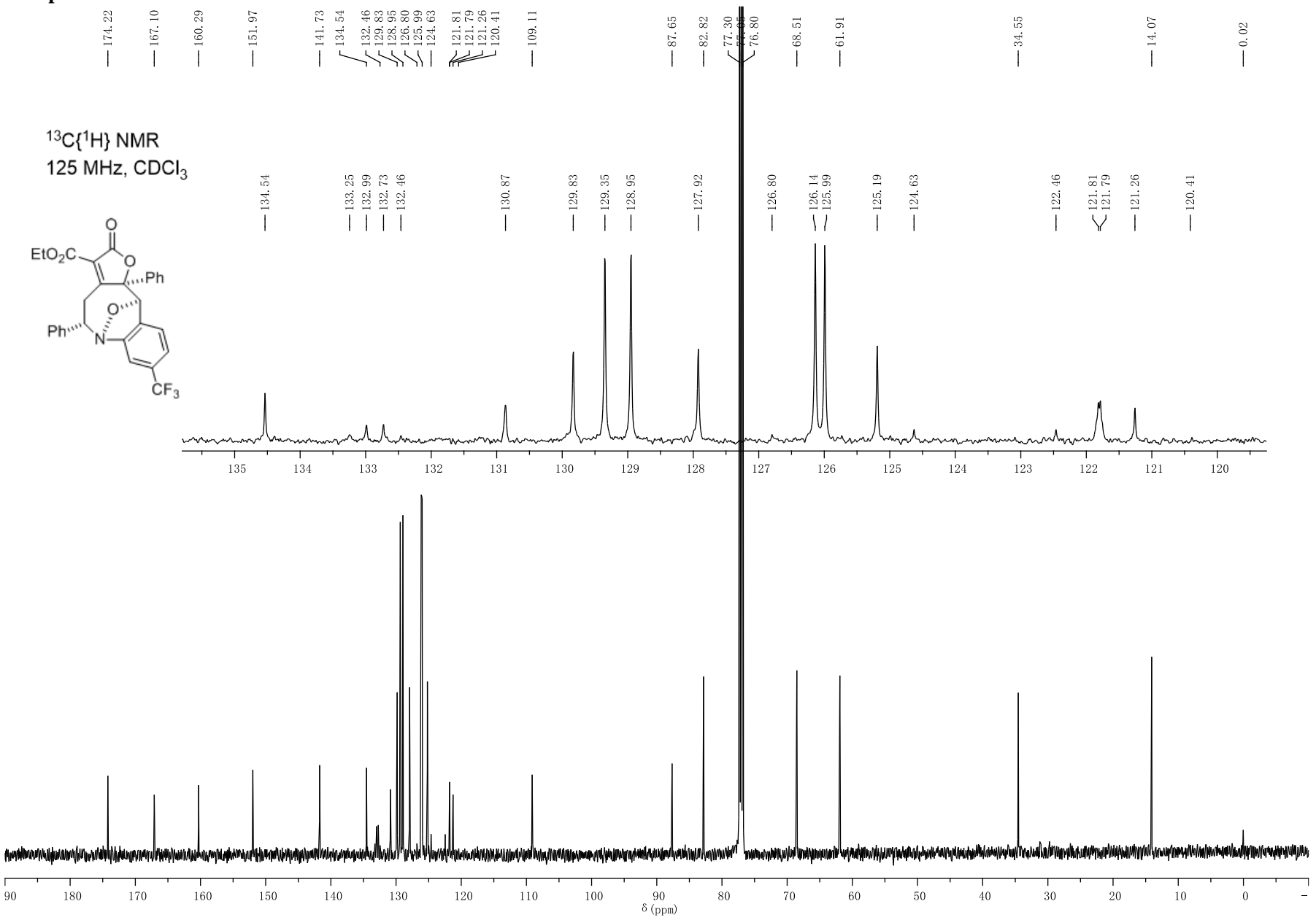


^{1}H NMR
500 MHz, $CDCl_3$

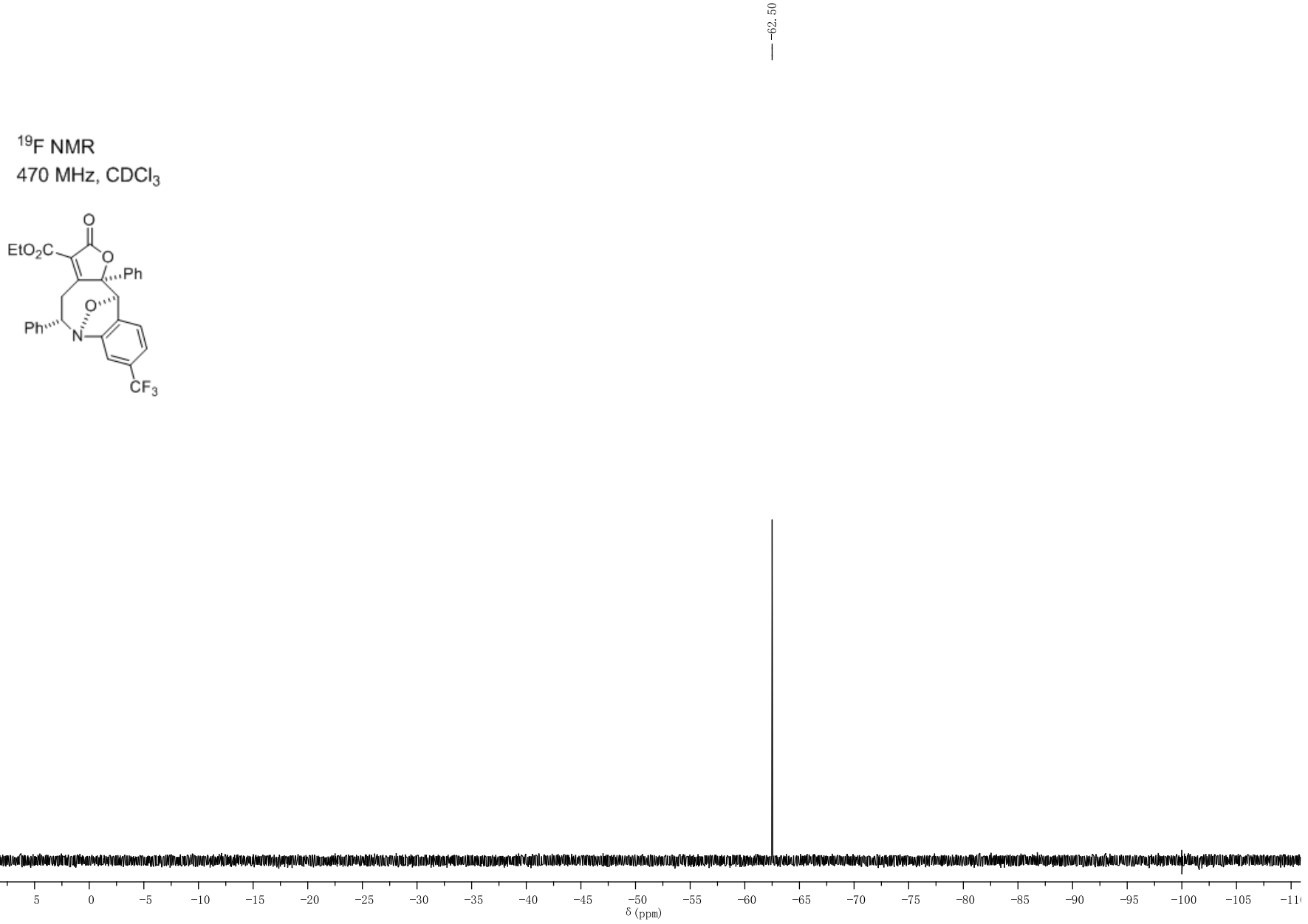




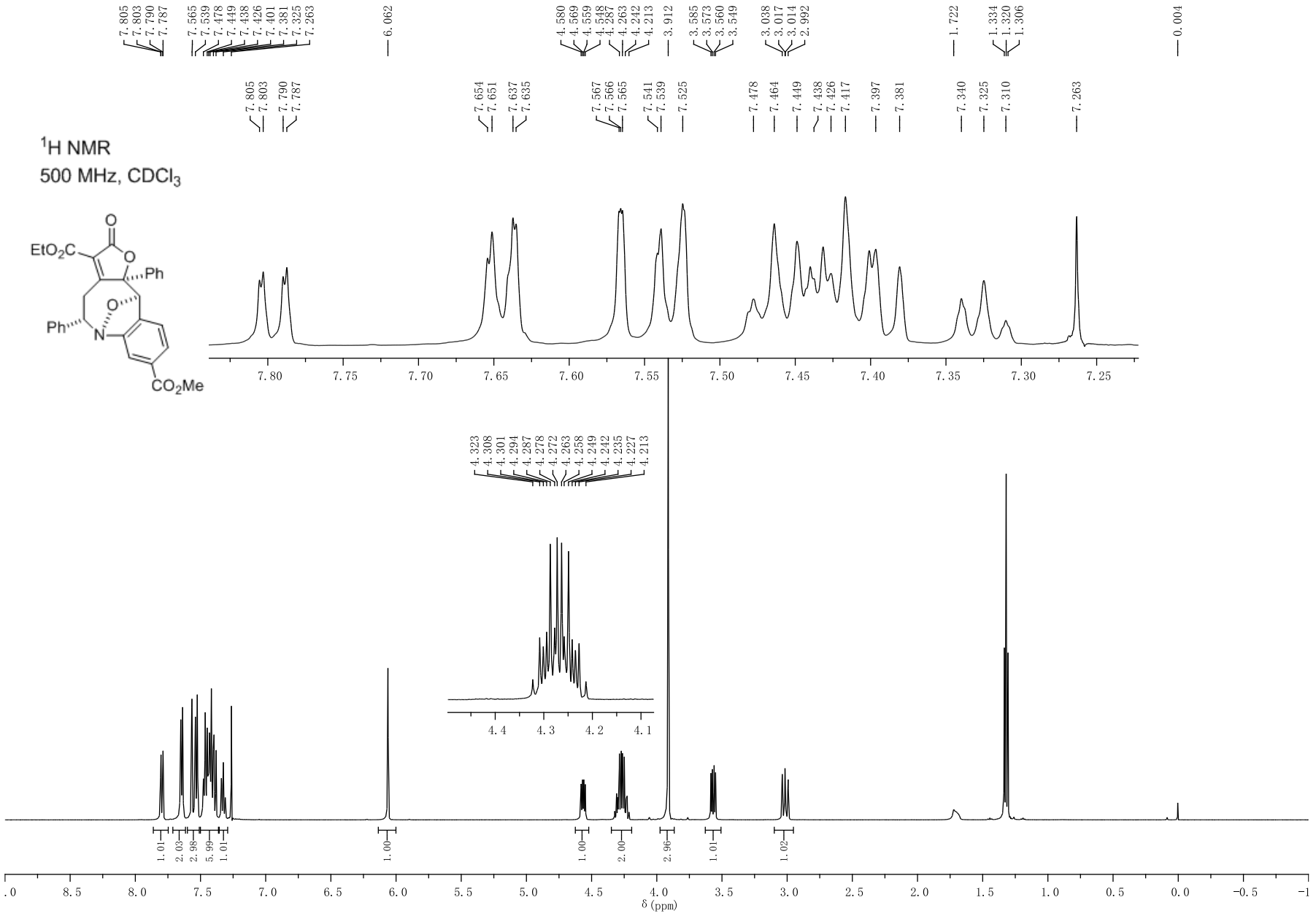
Compound 3ak



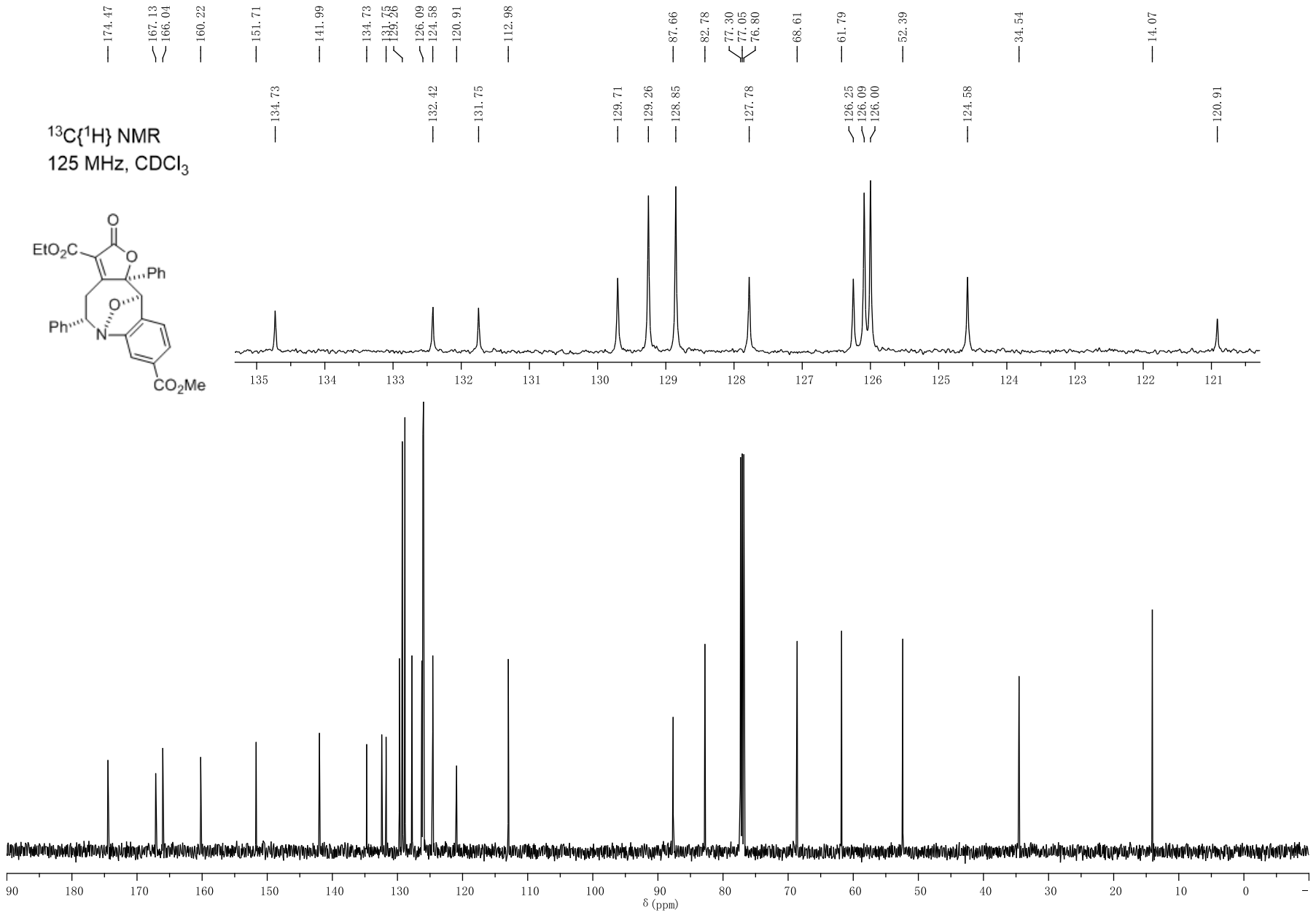
Compound 3ak



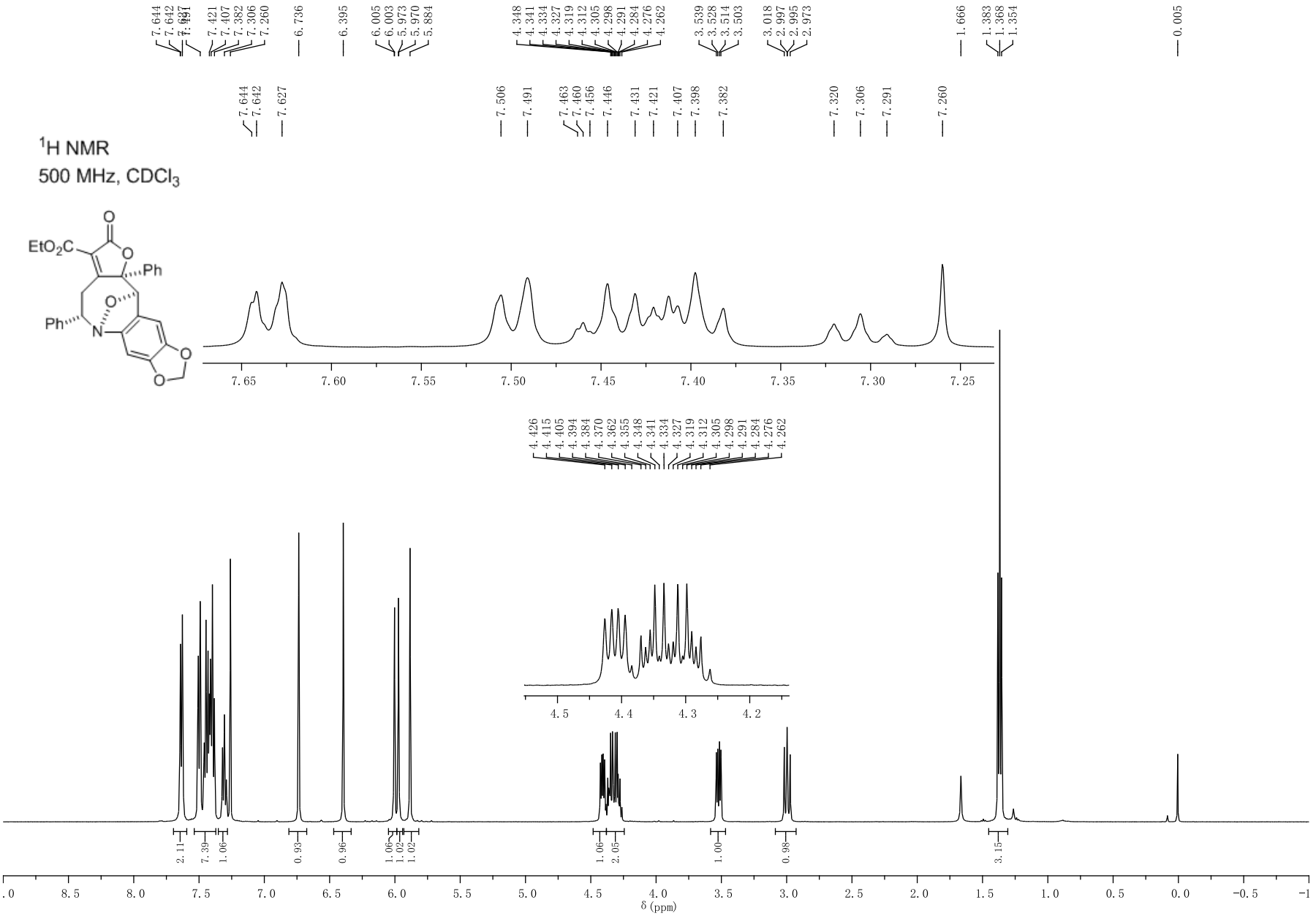
Compound 3al



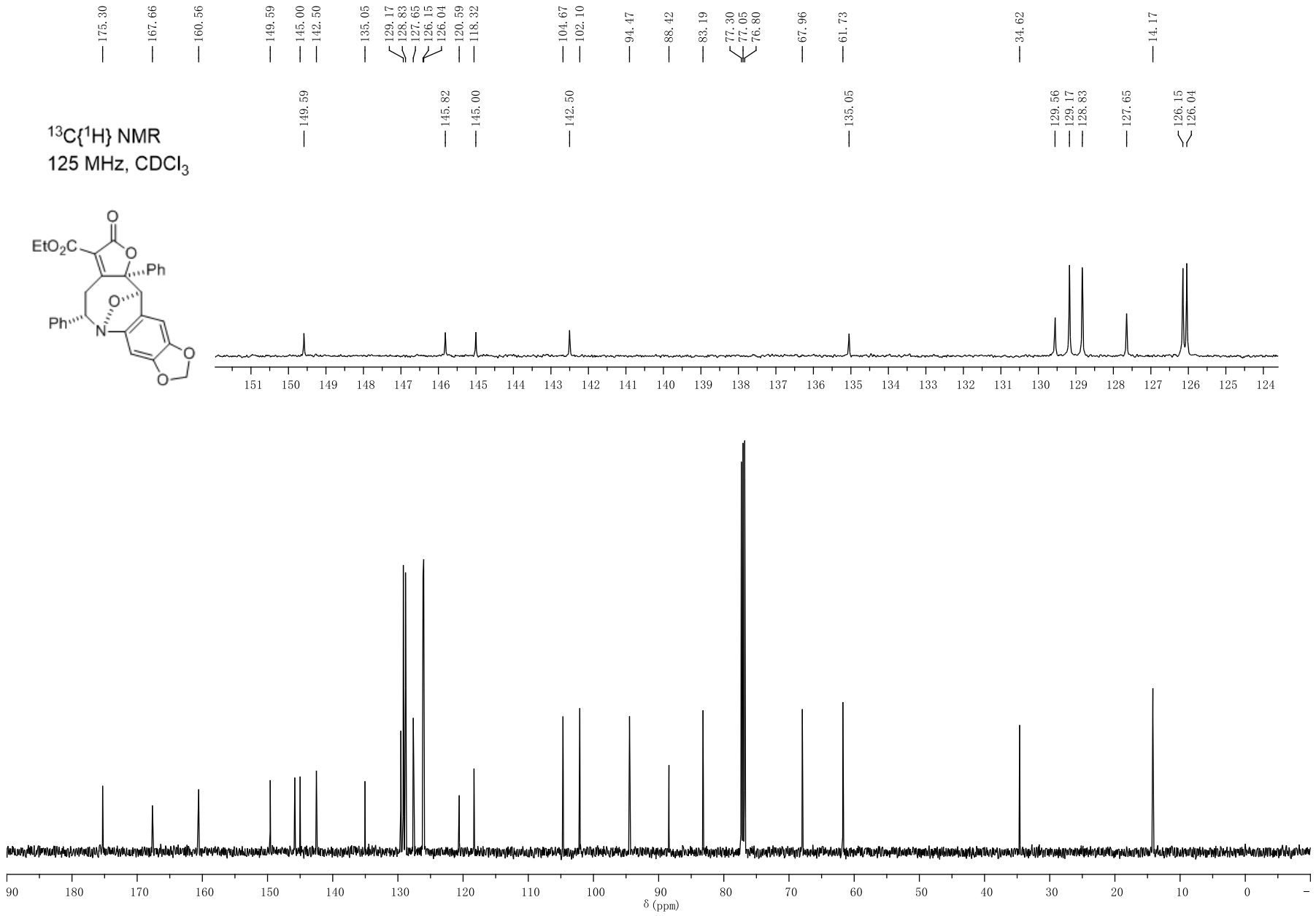
Compound 3al



Compound 3an

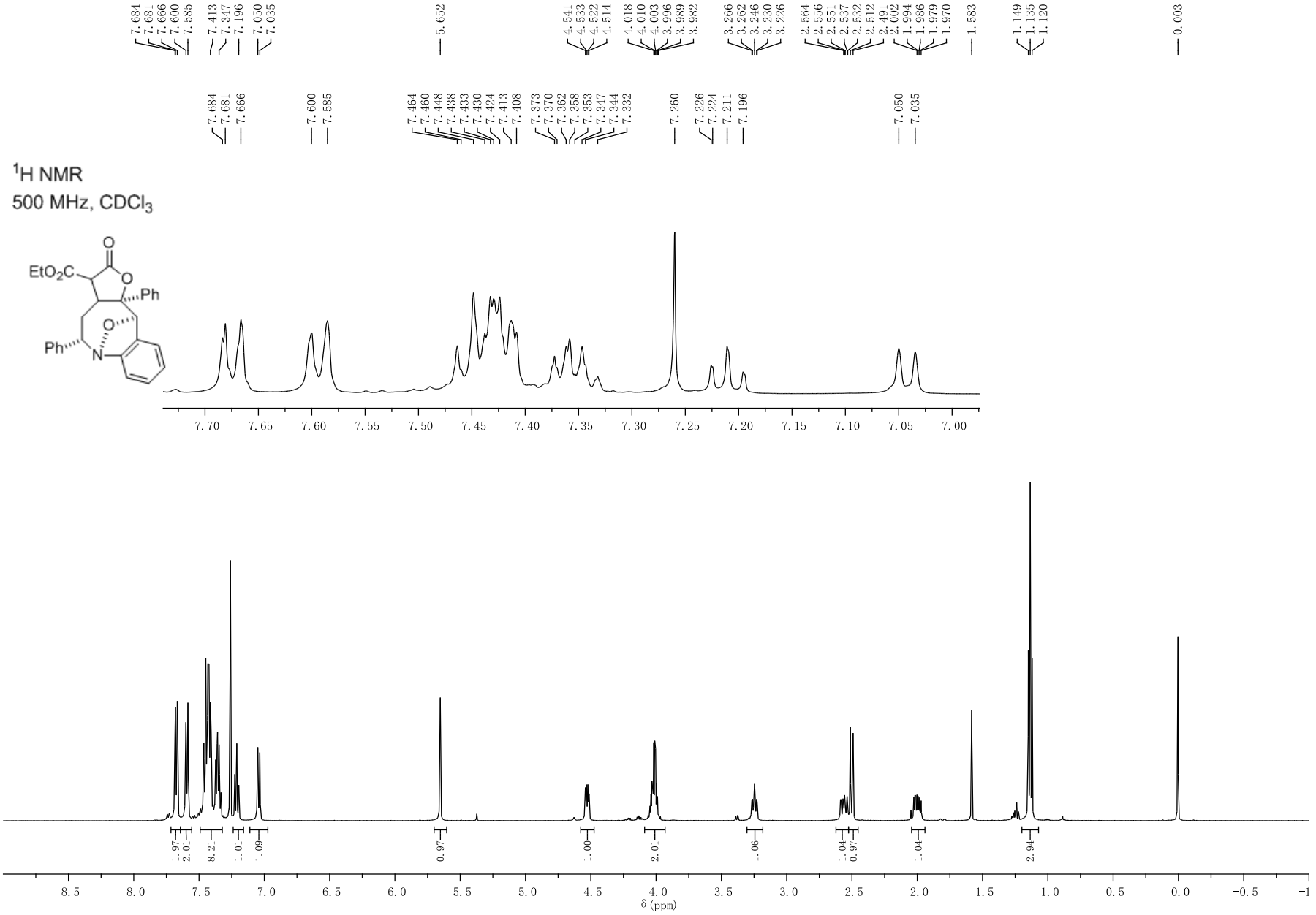


Compound 3an

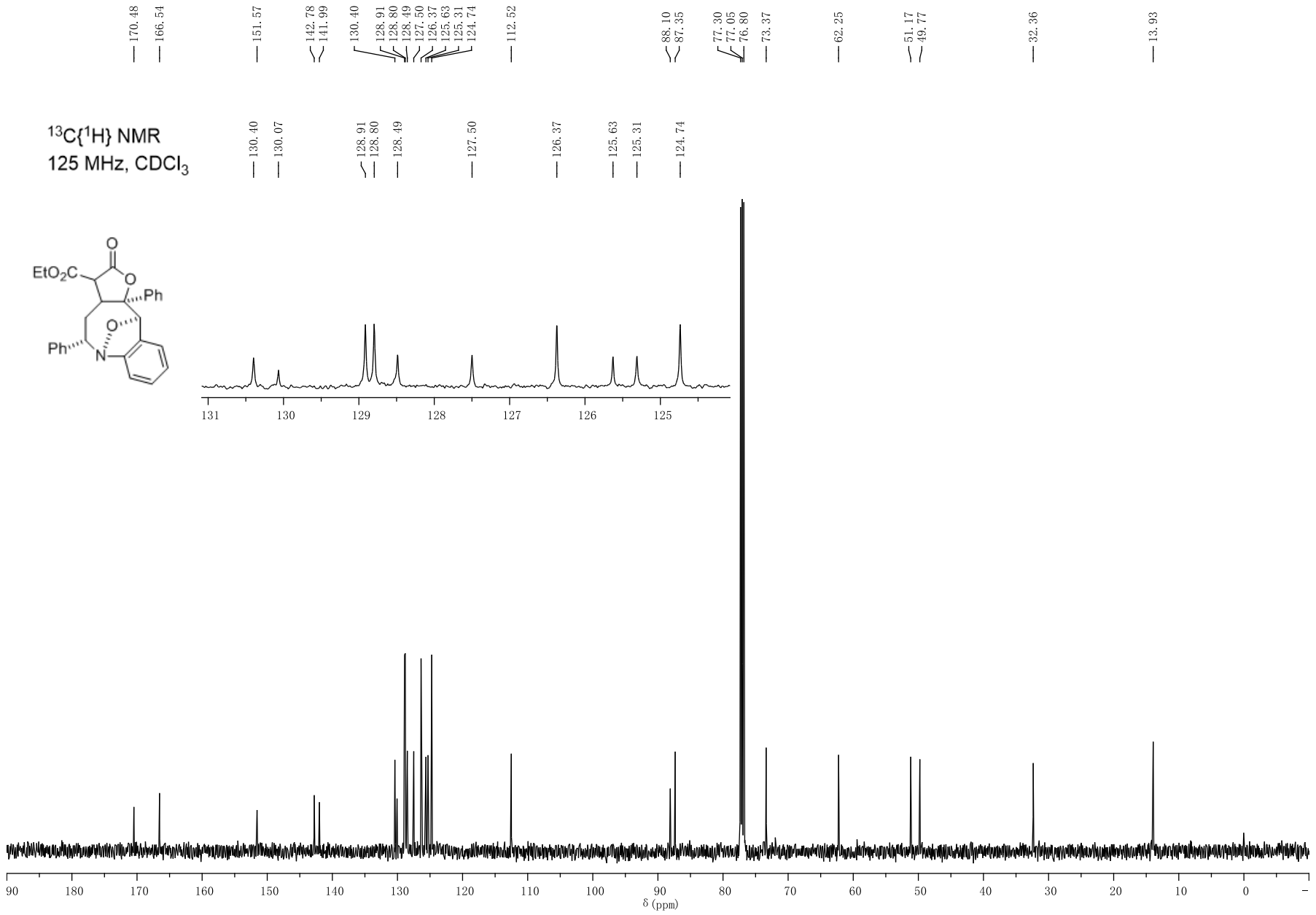


6.3 Copies of NMR spectra for transformation products

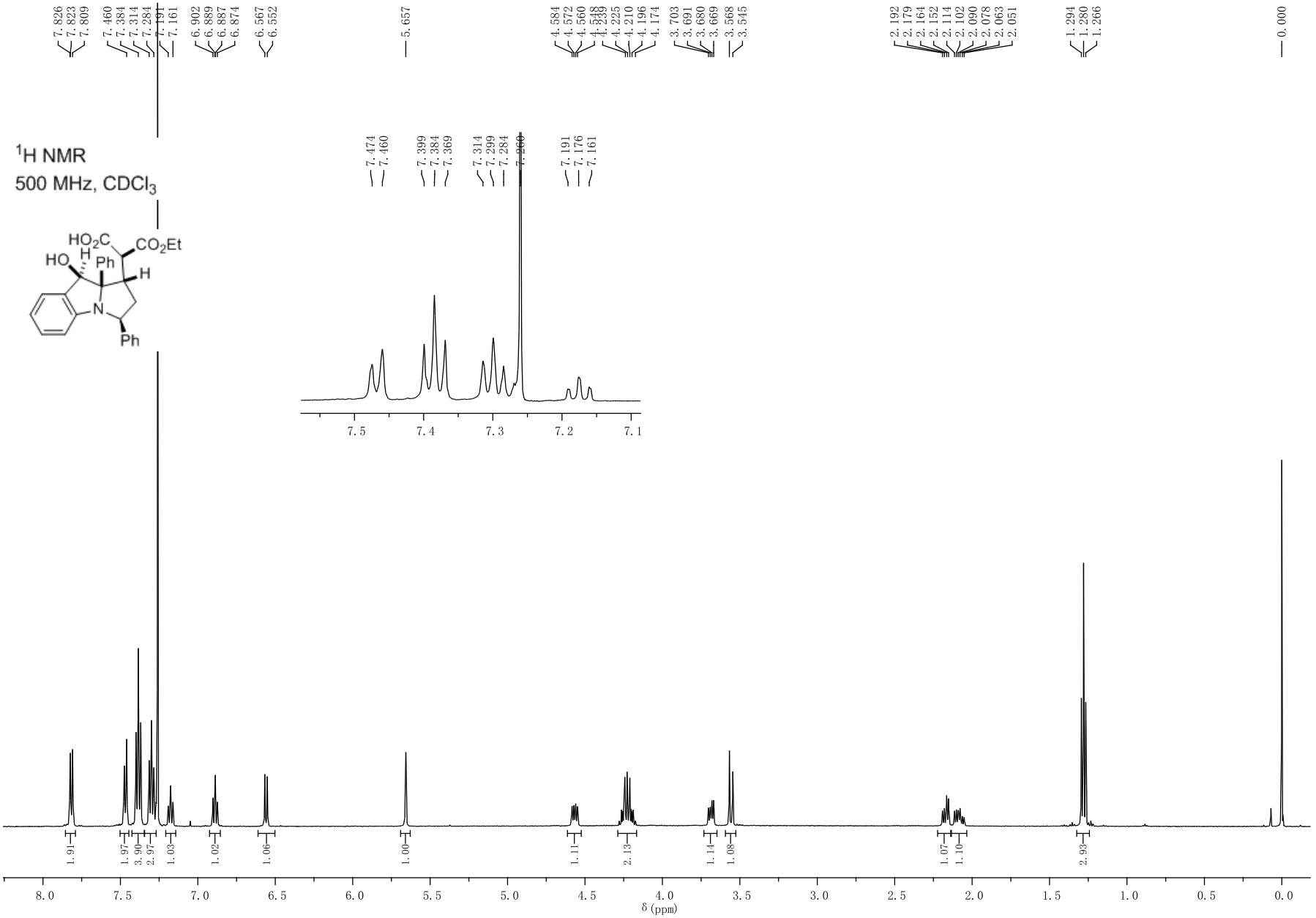
Compound 4



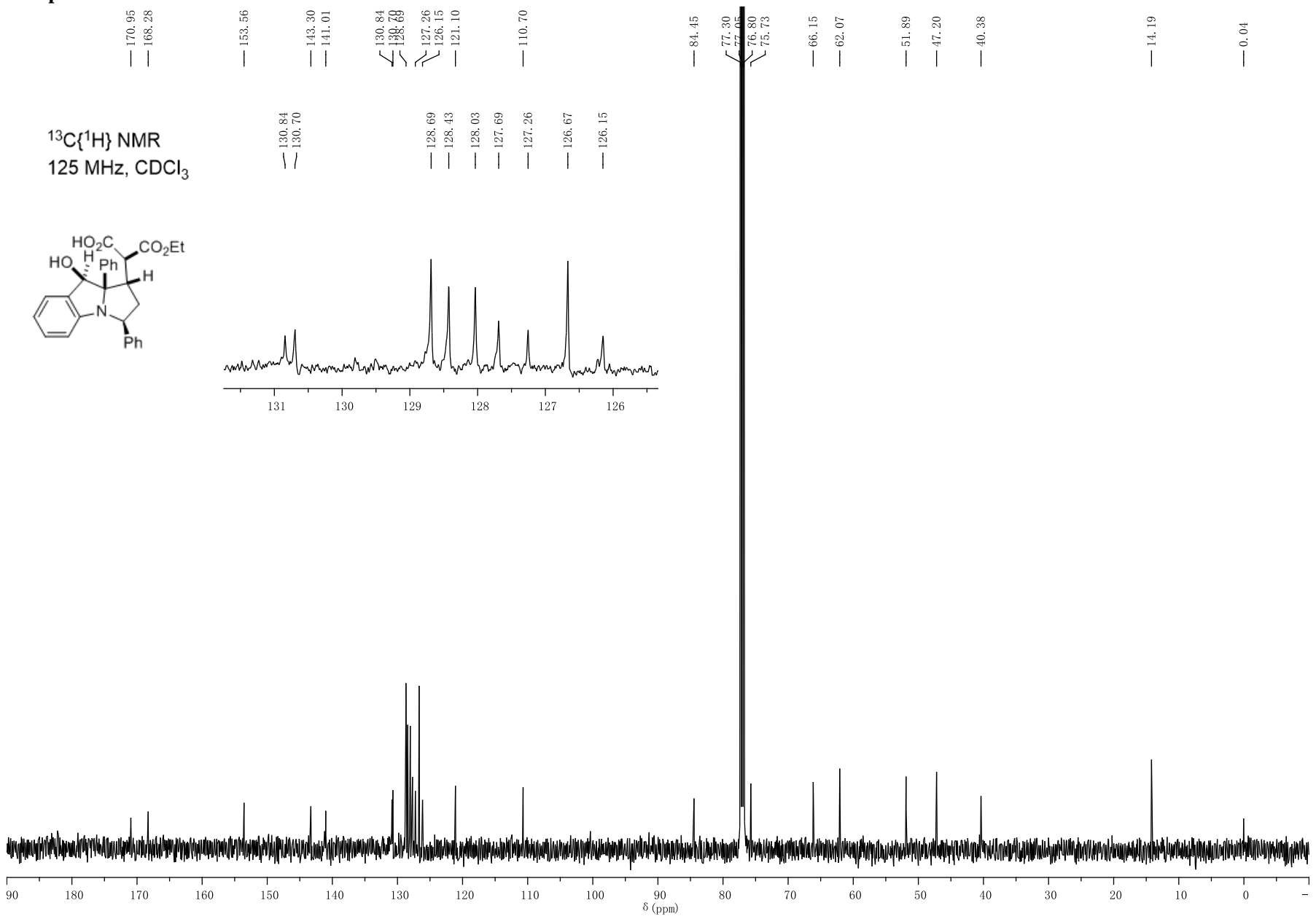
Compound 4


170.48
166.54
151.57
142.78
141.99
130.40
128.91
128.80
128.49
127.50
126.37
125.63
125.31
124.74
112.52
88.10
87.35
77.30
77.05
76.80
73.37
62.25
51.17
49.77
32.36
13.93
13C{1H} NMR
125 MHz, CDCl3
130.40
130.07
128.91
128.80
128.49
127.50
126.37
125.63
125.31
124.74
EtO2C
O
O
Ph
O
Ph
N
131
130
129
128
127
126
125
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

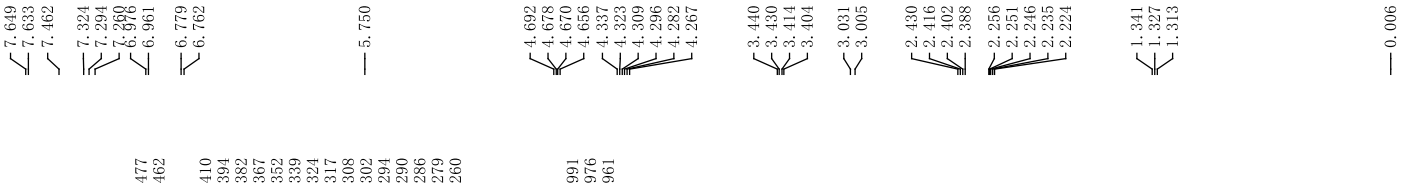
Compound 5


7.826
7.823
7.809
7.460
7.384
7.314
7.284
7.191
7.161
6.902
6.889
6.887
6.874
6.567
6.552
5.657
4.584
4.572
4.560
4.548
4.239
4.225
4.210
4.196
4.174
3.703
3.691
3.680
3.669
3.568
3.545
2.192
2.179
2.164
2.152
2.114
2.102
2.090
2.078
2.063
2.051
1.294
1.280
1.266
0.000
^{1}H NMR
500 MHz, CDCl$_3$
HO$_2$C
CO$_2$Et
HO
H
Ph
H
N
Ph
7.474
7.460
7.399
7.384
7.369
7.314
7.299
7.284
7.260
7.191
7.176
7.161
7.5
7.4
7.3
7.2
7.1
1.91
1.97
3.90
2.97
1.03
1.02
1.06
1.00
1.11
2.13
1.14
1.08
1.07
1.10
2.93
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
δ (ppm)

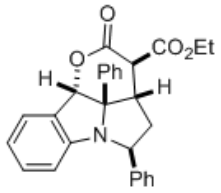
Compound 5

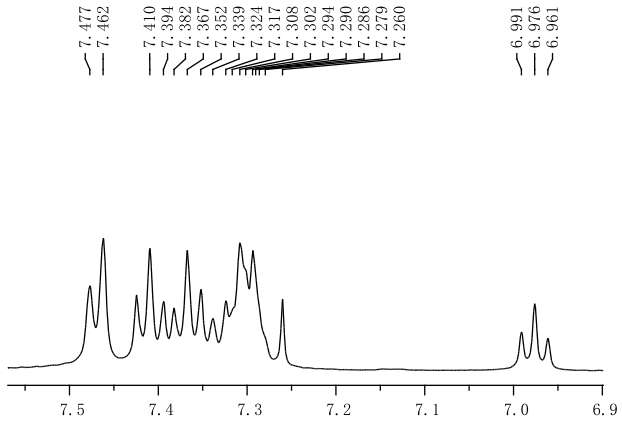

170.95
168.28
153.56
143.30
141.01
130.84
130.70
128.69
128.43
128.03
127.69
127.26
126.67
126.15
121.10
110.70
84.45
77.30
77.05
76.80
75.73
66.15
62.07
51.89
47.20
40.38
14.19
0.04
13C{1H} NMR
125 MHz, CDCl3
HO2C
CO2Et
HO
H
Ph
H
N
Ph
δ (ppm)

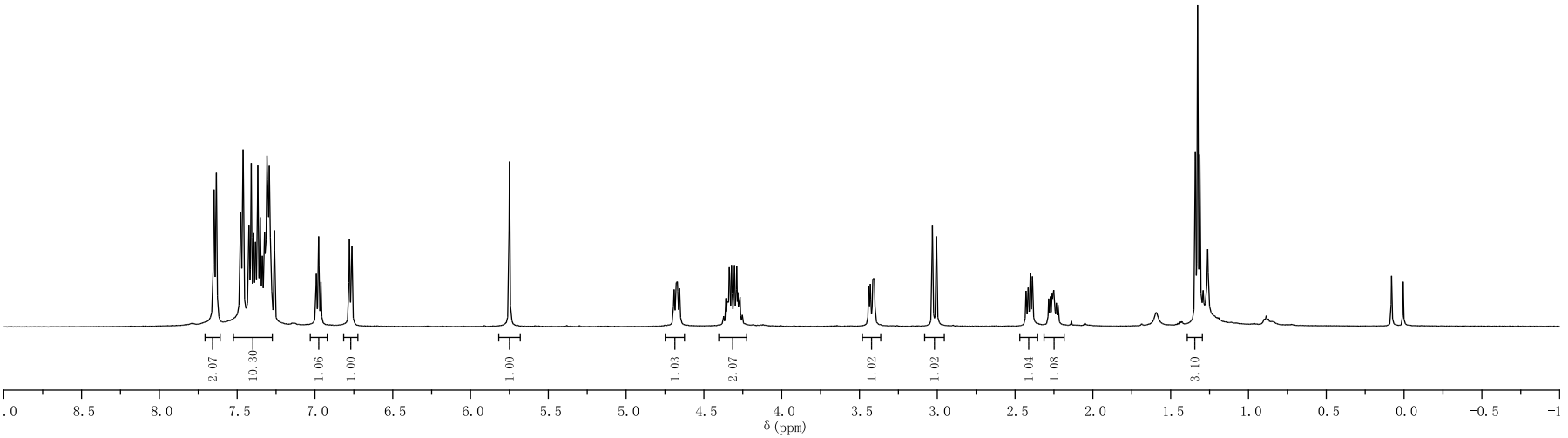
Compound 6



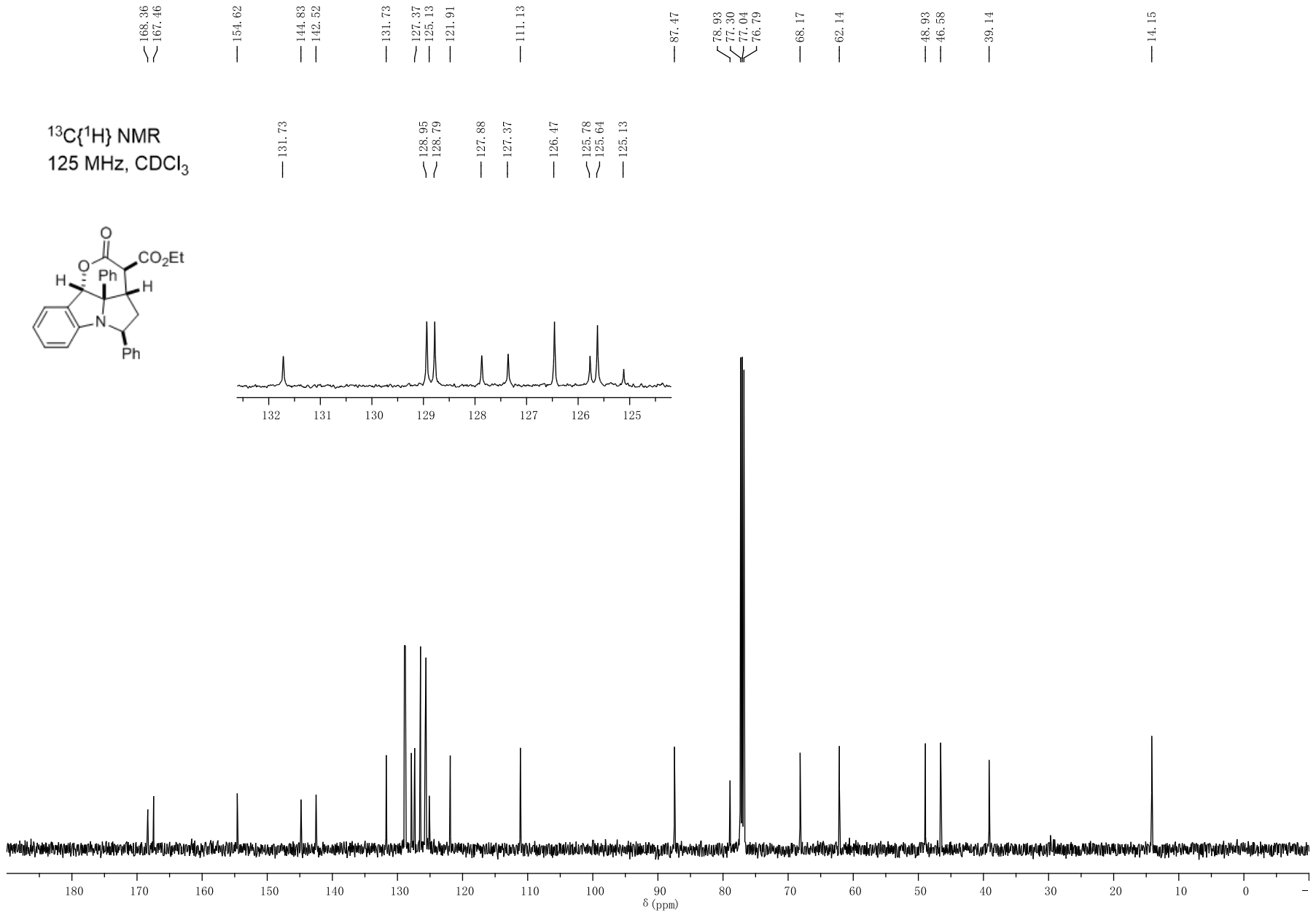
^{1}H NMR
500 MHz, $CDCl_3$



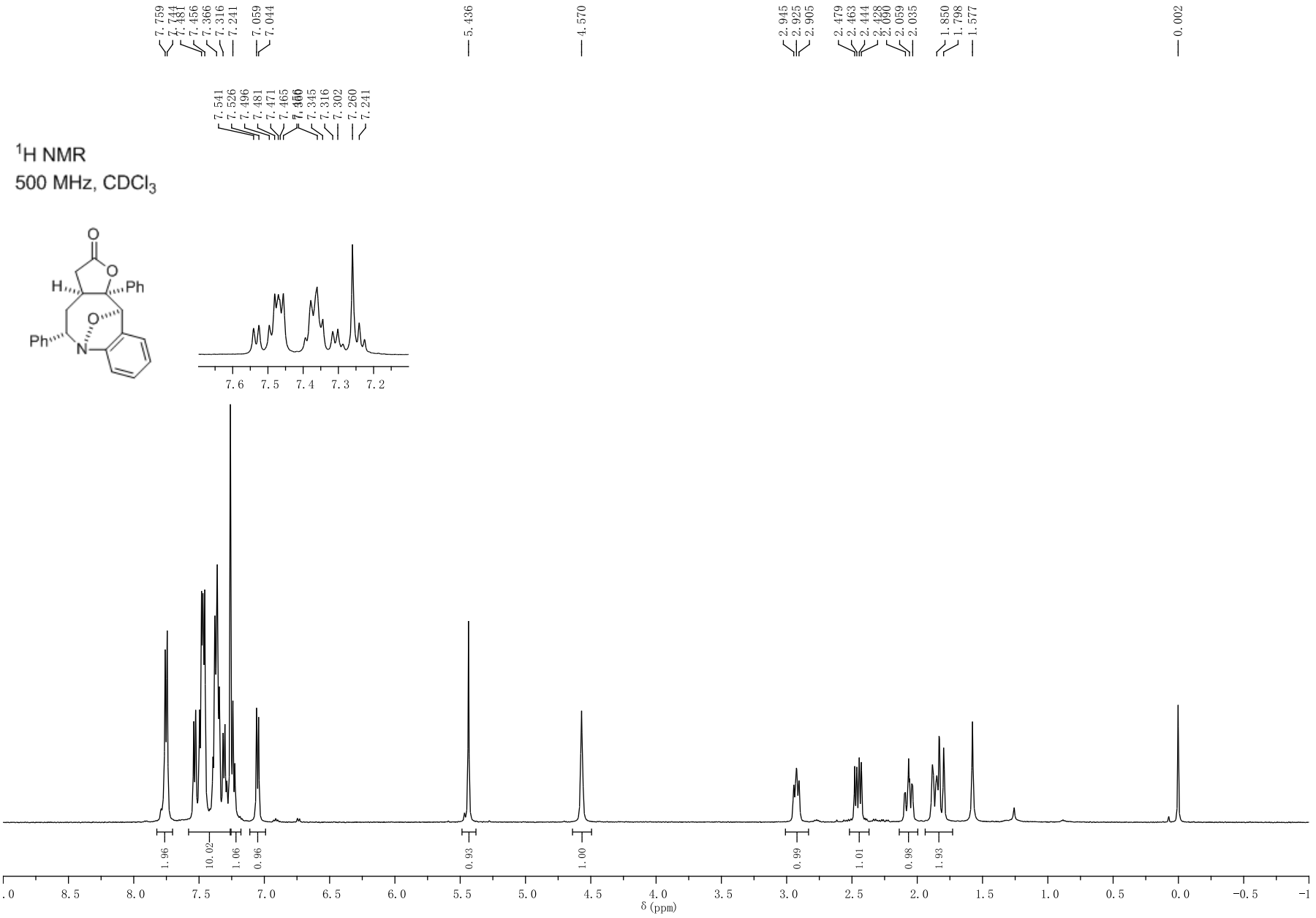




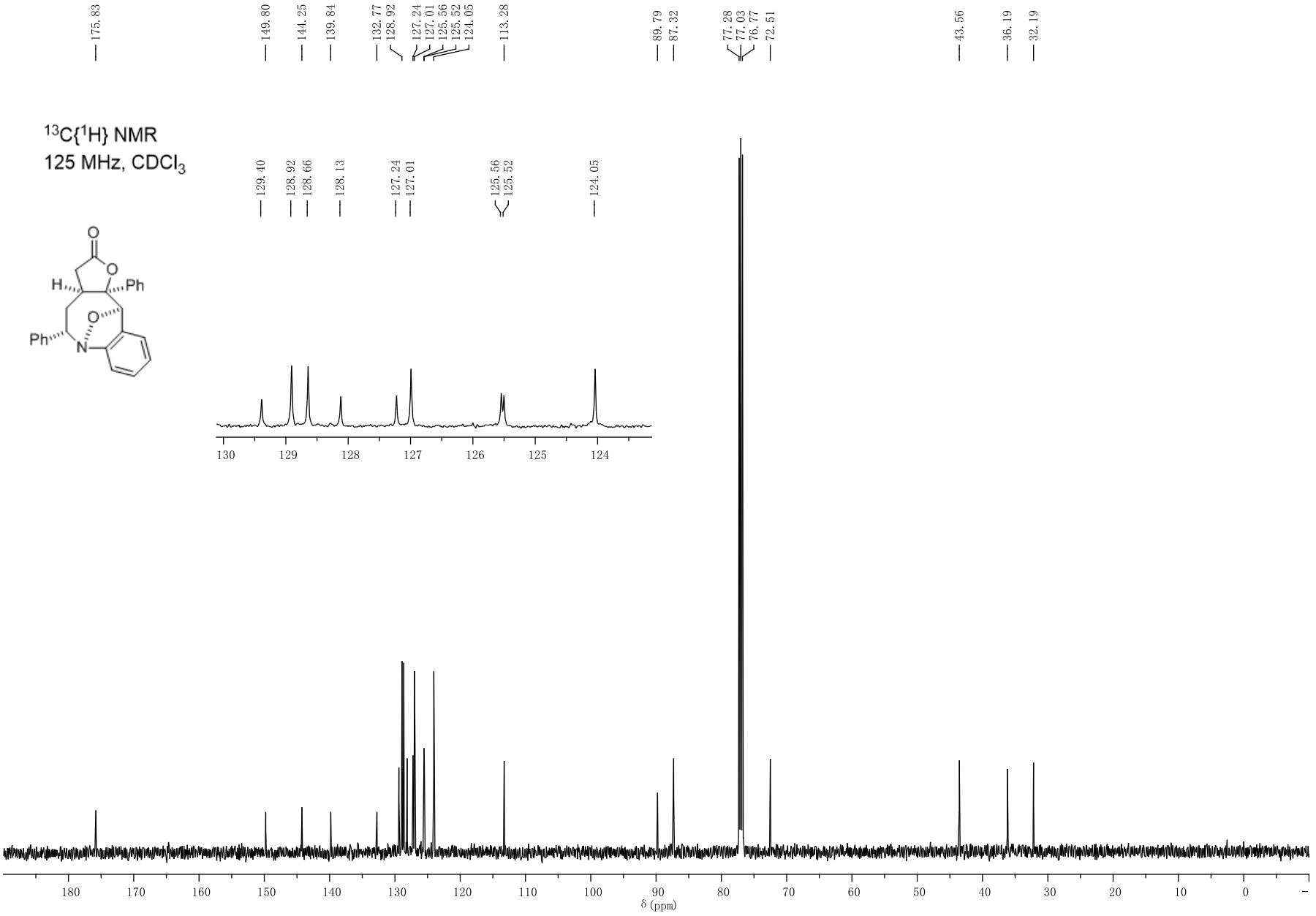
Compound 6


168.36
167.46
154.62
144.83
142.52
131.73
127.37
125.13
121.91
111.13
87.47
78.93
77.30
77.04
76.79
68.17
62.14
48.93
46.58
39.14
14.15
13C{1H} NMR
125 MHz, CDCl3
131.73
128.95
128.79
127.88
127.37
126.47
125.78
125.64
125.13
O
O
CO2Et
H
Ph
H
N
Ph
δ (ppm)

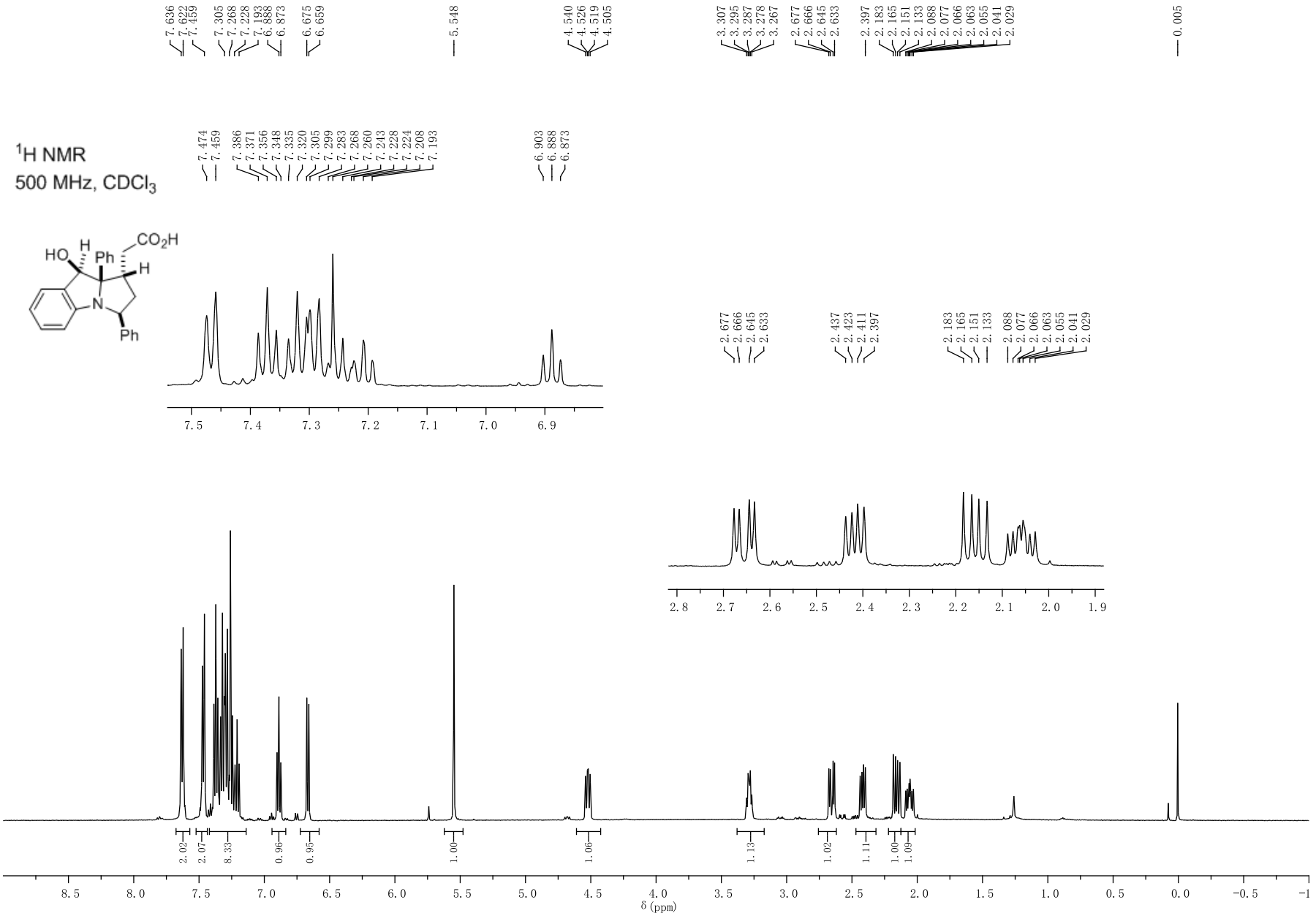
Compound 7


7.759
7.744
7.481
7.456
7.366
7.316
7.241
7.059
7.044
5.436
4.570
2.945
2.925
2.905
2.479
2.463
2.444
2.428
2.090
2.059
2.035
1.850
1.798
1.577
0.002
7.541
7.526
7.496
7.481
7.471
7.465
7.345
7.316
7.302
7.260
7.241
1H NMR
500 MHz, CDCl3
O
O
H
Ph
O
Ph
N
7.6
7.5
7.4
7.3
7.2
1.96
10.02
1.06
0.96
0.93
1.00
0.99
1.01
0.98
1.93
δ (ppm)

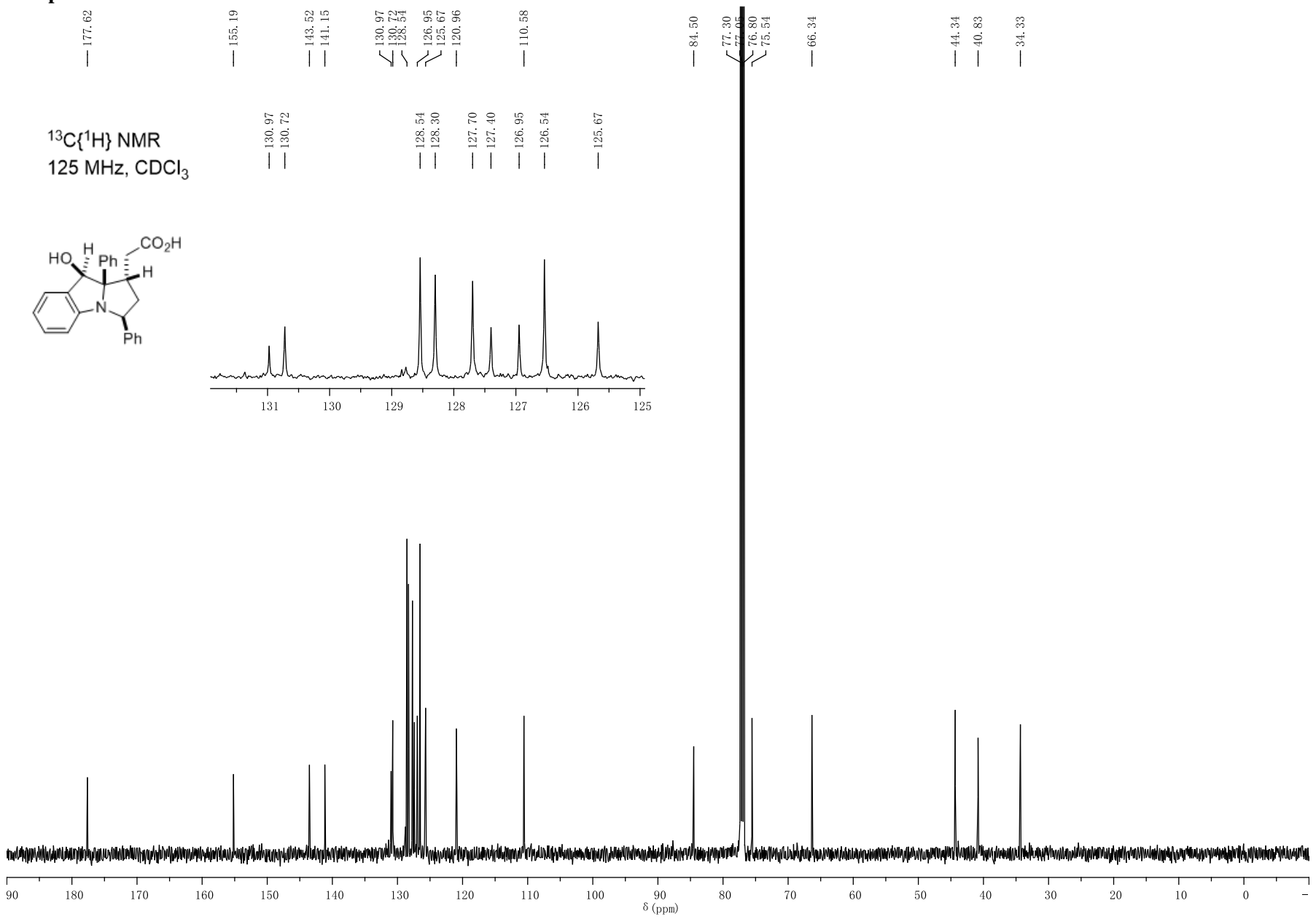
Compound 7


175.83
149.80
144.25
139.84
132.77
128.92
127.24
127.01
125.56
125.52
124.05
113.28
89.79
87.32
77.28
77.03
76.77
72.51
43.56
36.19
32.19
13C{1H} NMR
125 MHz, CDCl3
129.40
128.92
128.66
128.13
127.24
127.01
125.56
125.52
124.05
O
O
H
Ph
O
Ph
N
δ (ppm)

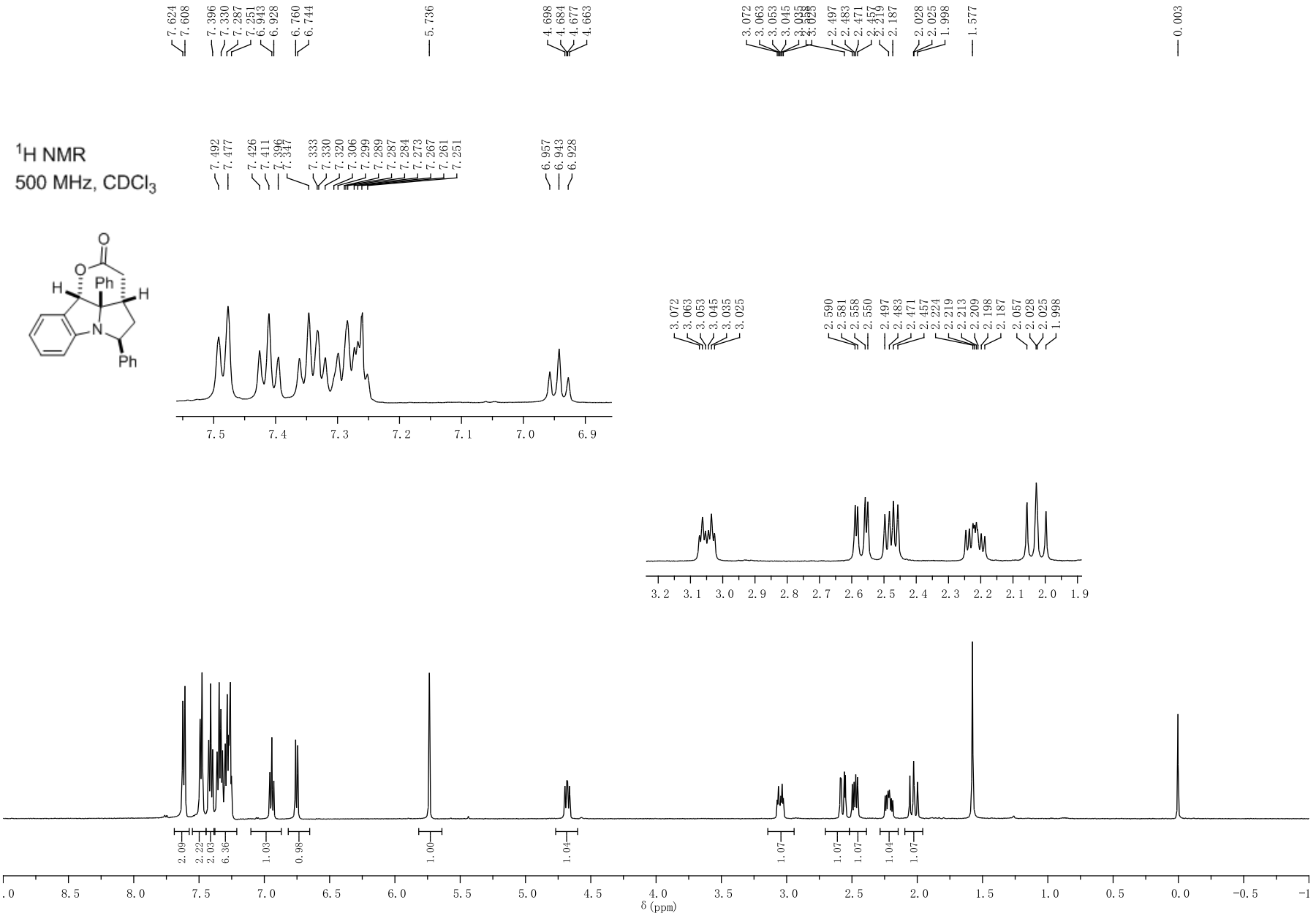
Compound 8


7.636
7.622
7.459
7.305
7.268
7.228
7.193
6.888
6.873
6.675
6.659
5.548
4.540
4.526
4.519
4.505
3.307
3.295
3.287
3.278
3.267
2.677
2.666
2.645
2.633
2.397
2.183
2.165
2.151
2.133
2.088
2.077
2.066
2.063
2.055
2.041
2.029
0.005
1H NMR
500 MHz, CDCl3
7.474
7.459
7.386
7.371
7.356
7.348
7.335
7.320
7.305
7.299
7.283
7.268
7.260
7.243
7.228
7.224
7.208
7.193
6.903
6.888
6.873
HO
H
Ph
CO2H
H
N
Ph
2.677
2.666
2.645
2.633
2.437
2.423
2.411
2.397
2.183
2.165
2.151
2.133
2.088
2.077
2.066
2.063
2.055
2.041
2.029
2.02
2.07
8.33
0.96
0.95
1.00
1.06
1.13
1.02
1.11
1.00
1.09
δ (ppm)

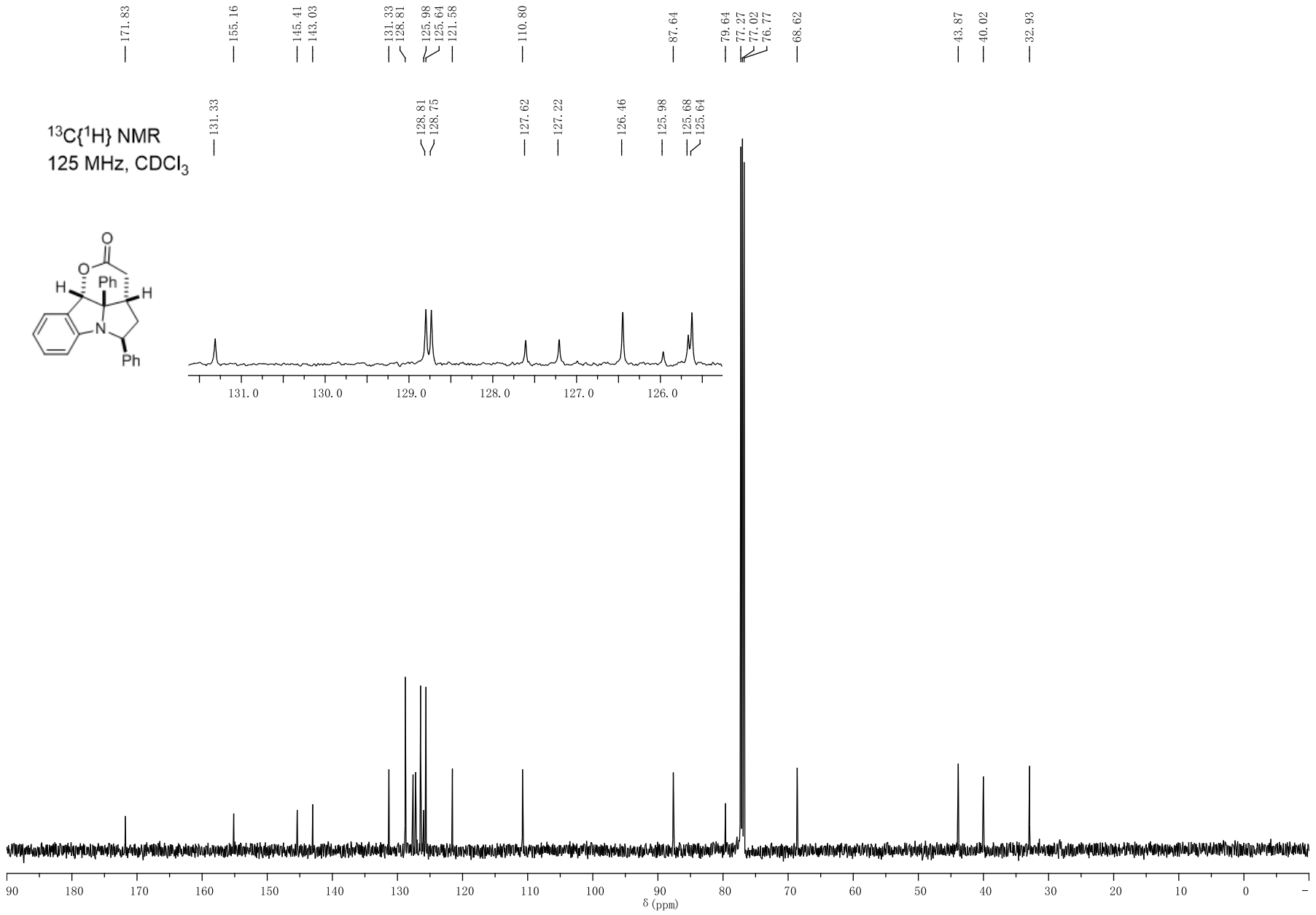
Compound 8


177.62
155.19
143.52
141.15
130.97
130.72
128.54
126.95
125.67
120.96
110.58
84.50
77.30
76.80
75.54
66.34
44.34
40.83
34.33
$^{13}C\{^{1}H\}$ NMR
125 MHz, $CDCl_3$
130.97
130.72
128.54
128.30
127.70
127.40
126.95
126.54
125.67
HO
H
Ph
CO_2H
H
N
Ph
131
130
129
128
127
126
125
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

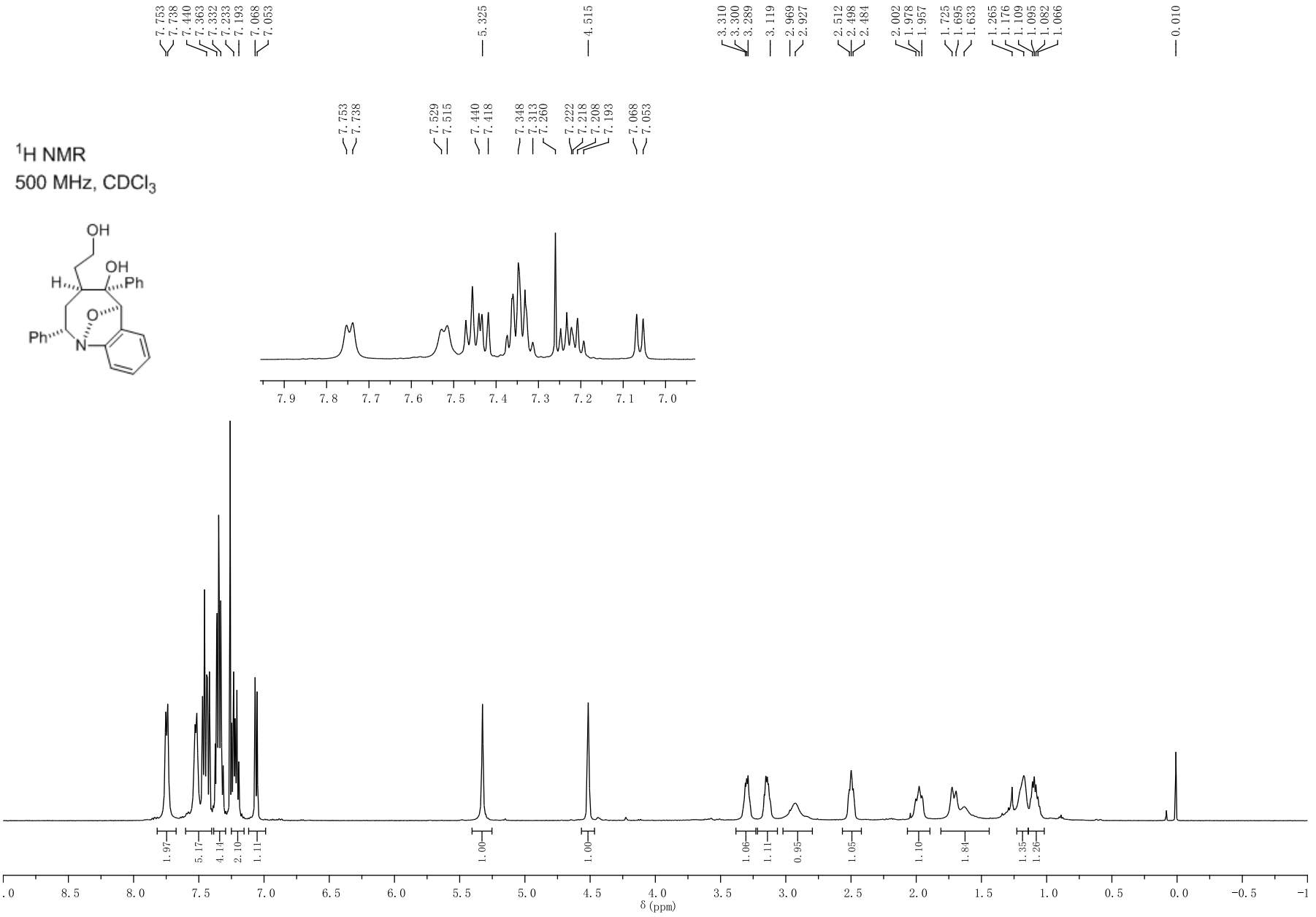
Compound 9


7.624
7.608
7.396
7.330
7.287
7.251
6.943
6.928
6.760
6.744
5.736
4.698
4.684
4.677
4.663
3.072
3.063
3.053
3.045
3.035
2.497
2.483
2.471
2.457
2.187
2.028
2.025
1.998
1.577
0.003
1H NMR
500 MHz, CDCl3
7.492
7.477
7.426
7.411
7.396
7.347
7.333
7.330
7.320
7.306
7.299
7.289
7.287
7.284
7.273
7.267
7.261
7.251
6.957
6.943
6.928
O
O
H
Ph
H
N
Ph
3.072
3.063
3.053
3.045
3.035
3.025
2.590
2.581
2.558
2.550
2.497
2.483
2.471
2.457
2.224
2.219
2.213
2.209
2.198
2.187
2.057
2.028
2.025
1.998
7.5
7.4
7.3
7.2
7.1
7.0
6.9
3.2
3.1
3.0
2.9
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
2.09
2.22
2.03
6.36
1.03
0.98
1.00
1.04
1.07
1.07
1.07
1.04
1.07
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
δ (ppm)

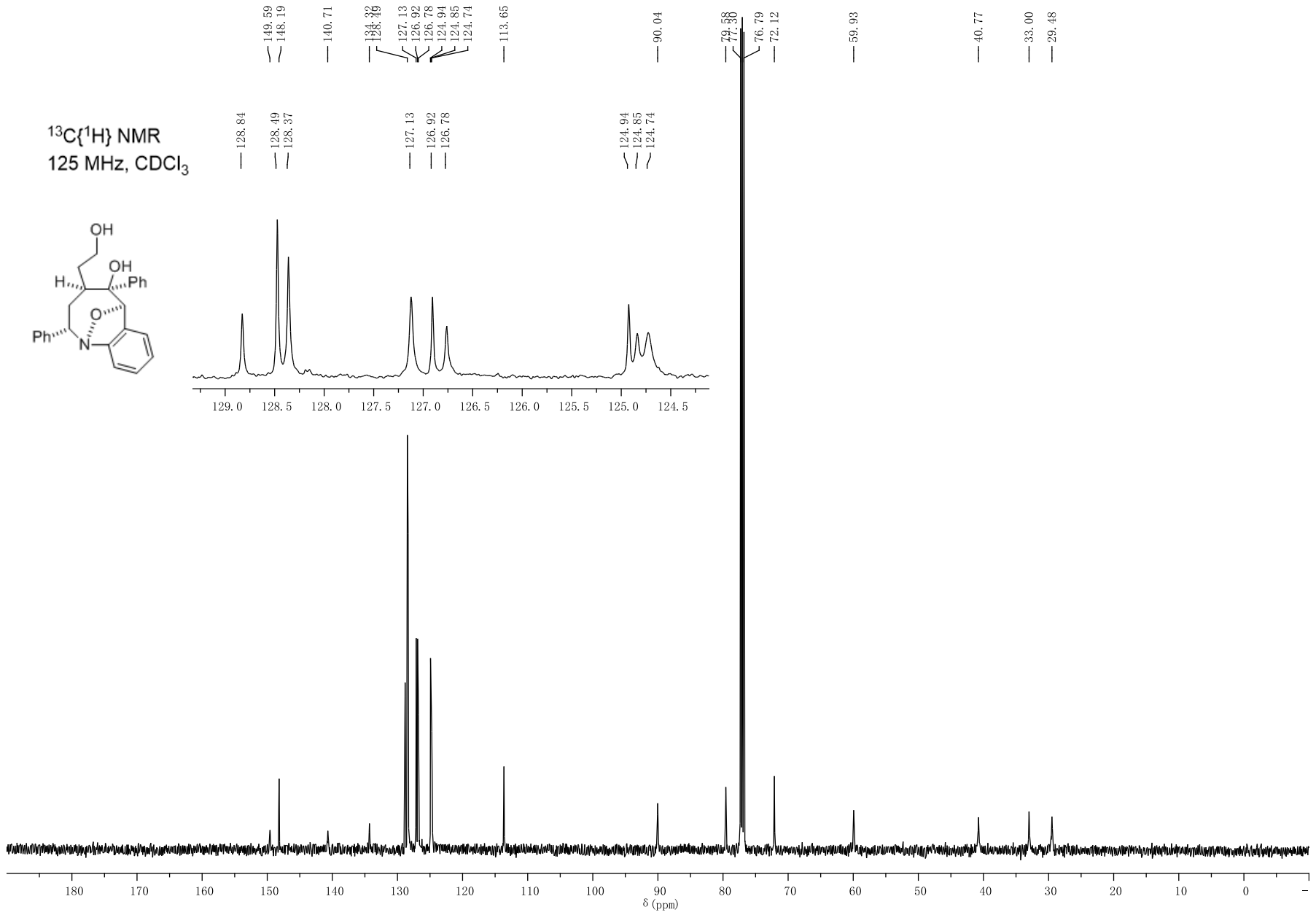
Compound 9


171.83
155.16
145.41
143.03
131.33
128.81
125.98
125.64
121.58
110.80
87.64
79.64
77.27
77.02
76.77
68.62
43.87
40.02
32.93
131.33
128.81
128.75
127.62
127.22
126.46
125.98
125.68
125.64
13C{1H} NMR
125 MHz, CDCl3
O
O
H
Ph
H
N
Ph
131.0
130.0
129.0
128.0
127.0
126.0
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

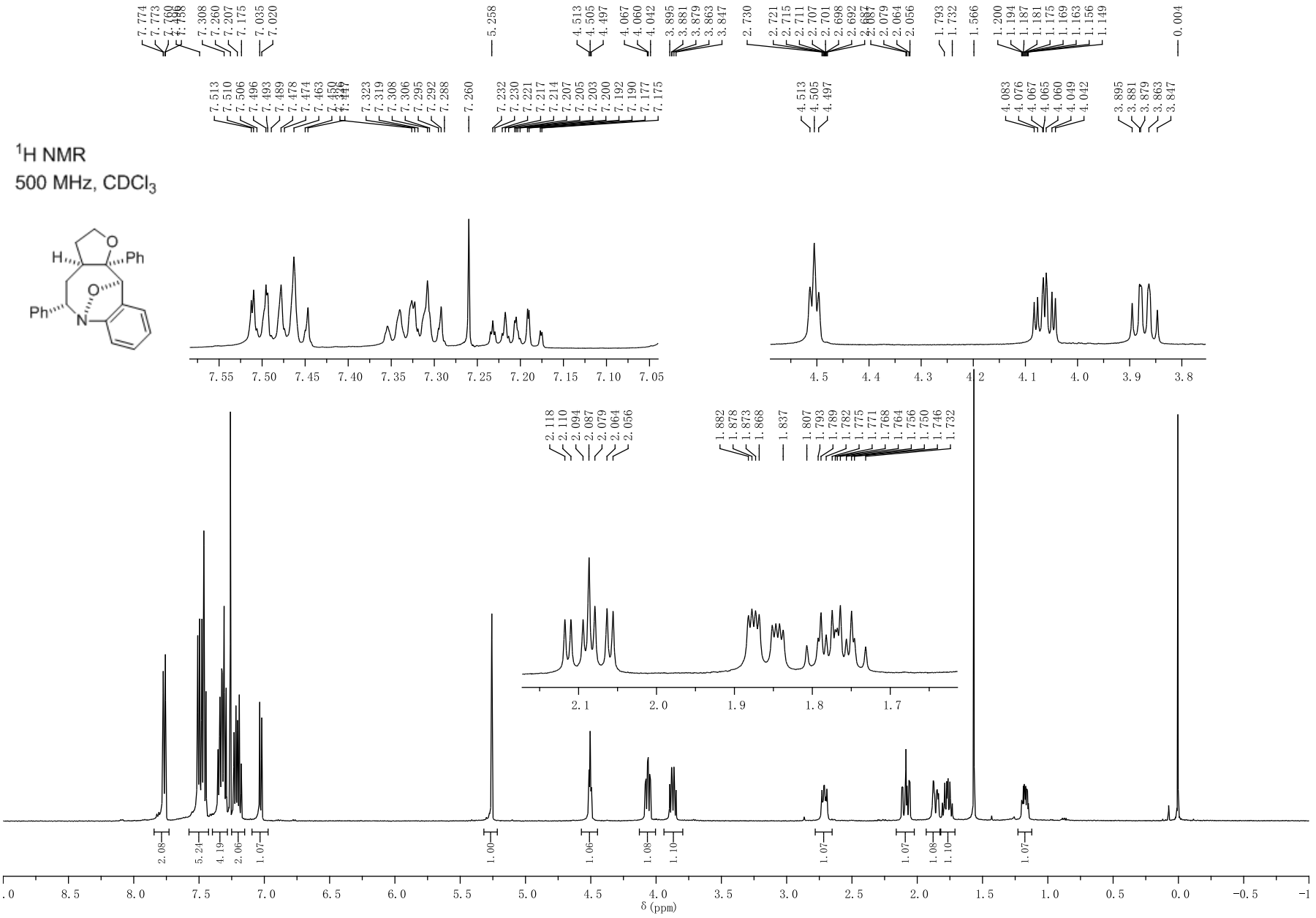
Compound 10


7.753
7.738
7.440
7.363
7.332
7.233
7.193
7.068
7.053
5.325
4.515
3.310
3.300
3.289
3.119
2.969
2.927
2.512
2.498
2.484
2.002
1.978
1.957
1.725
1.695
1.633
1.265
1.176
1.109
1.095
1.082
1.066
0.010
1H NMR
500 MHz, CDCl3
OH
OH
H
Ph
O
Ph
N
δ (ppm)

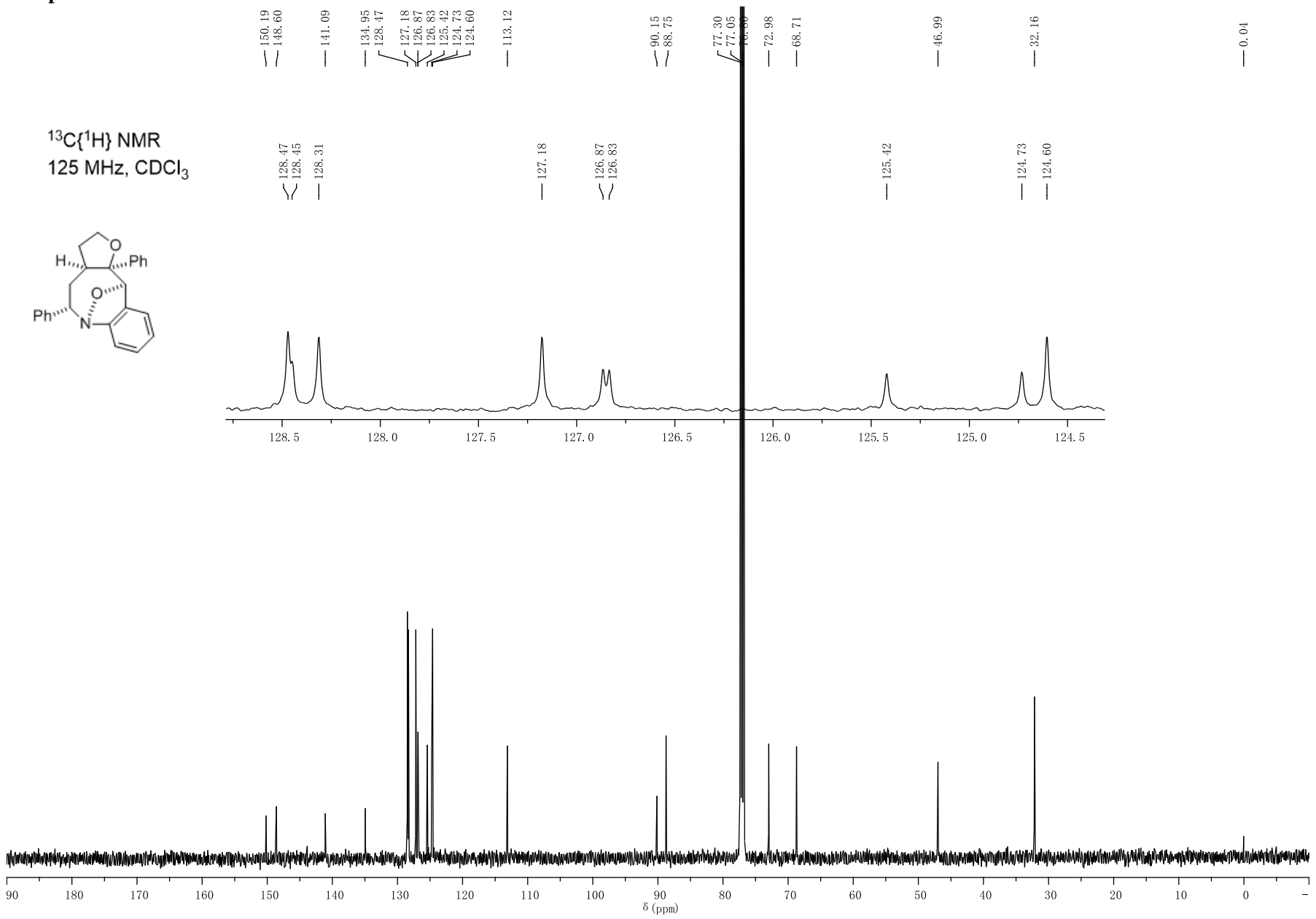
Compound 10


149.59
148.19
140.71
134.32
128.49
127.13
126.92
126.78
124.94
124.85
124.74
113.65
90.04
79.58
77.30
76.79
72.12
59.93
40.77
33.00
29.48
$^{13}C\{^{1}H\}$ NMR
125 MHz, $CDCl_3$
128.84
128.49
128.37
127.13
126.92
126.78
124.94
124.85
124.74
OH
OH
H
Ph
O
Ph
N
δ (ppm)

Compound 11

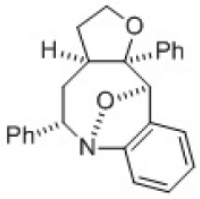


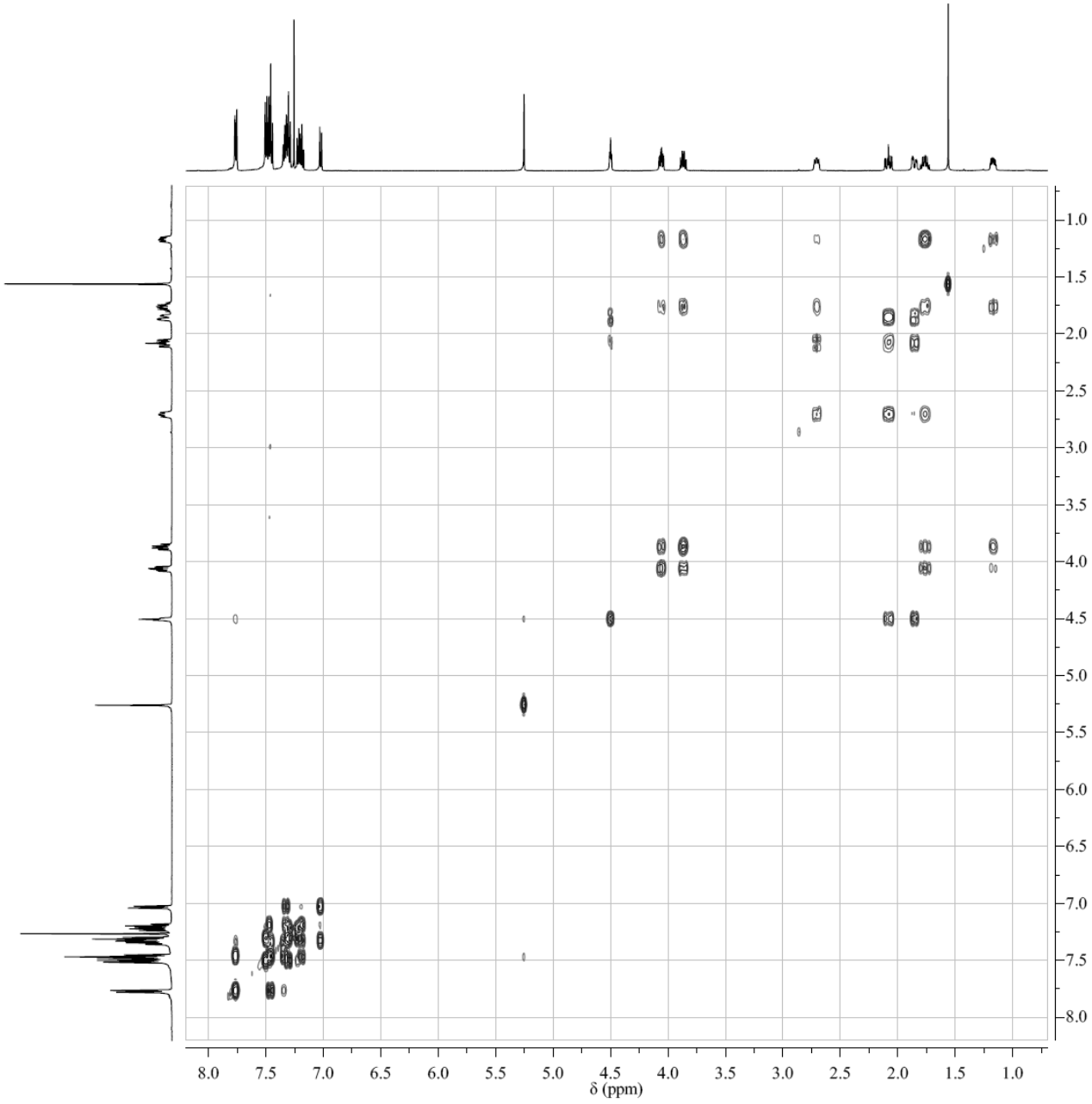
Compound 11


150.19
148.60
141.09
134.95
128.47
127.18
126.87
126.83
125.42
124.73
124.60
113.12
90.15
88.75
77.30
77.05
72.98
68.71
46.99
32.16
0.04
13C{1H} NMR
125 MHz, CDCl3
128.47
128.45
128.31
127.18
126.87
126.83
125.42
124.73
124.60
H
O
Ph
O
Ph
N
δ (ppm)

Compound 11

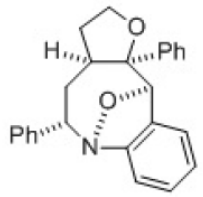
2D COSY NMR
500 MHz, $CDCl_3$

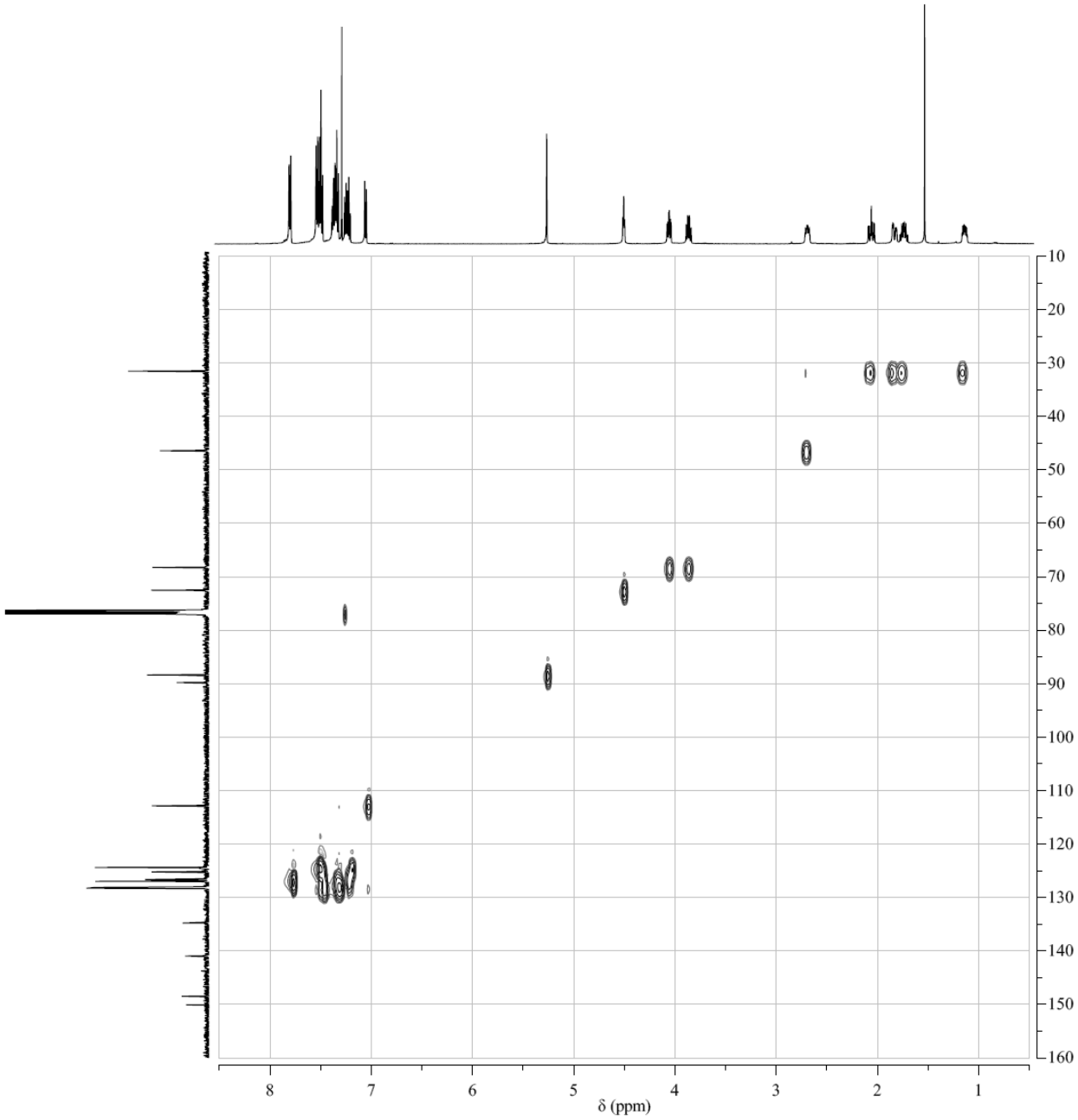




Compound 11

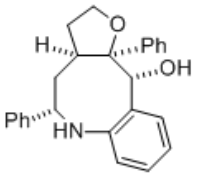
2D HSQC NMR
500 MHz, $CDCl_3$

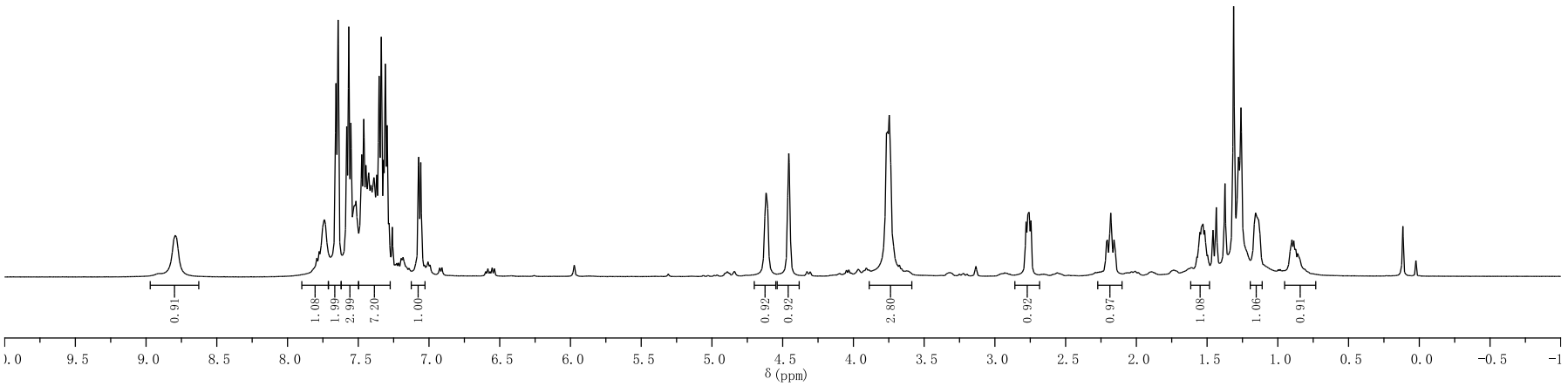




Compound 12 (–50 °C)

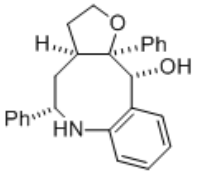
^{1}H NMR
500 MHz, $CDCl_3$

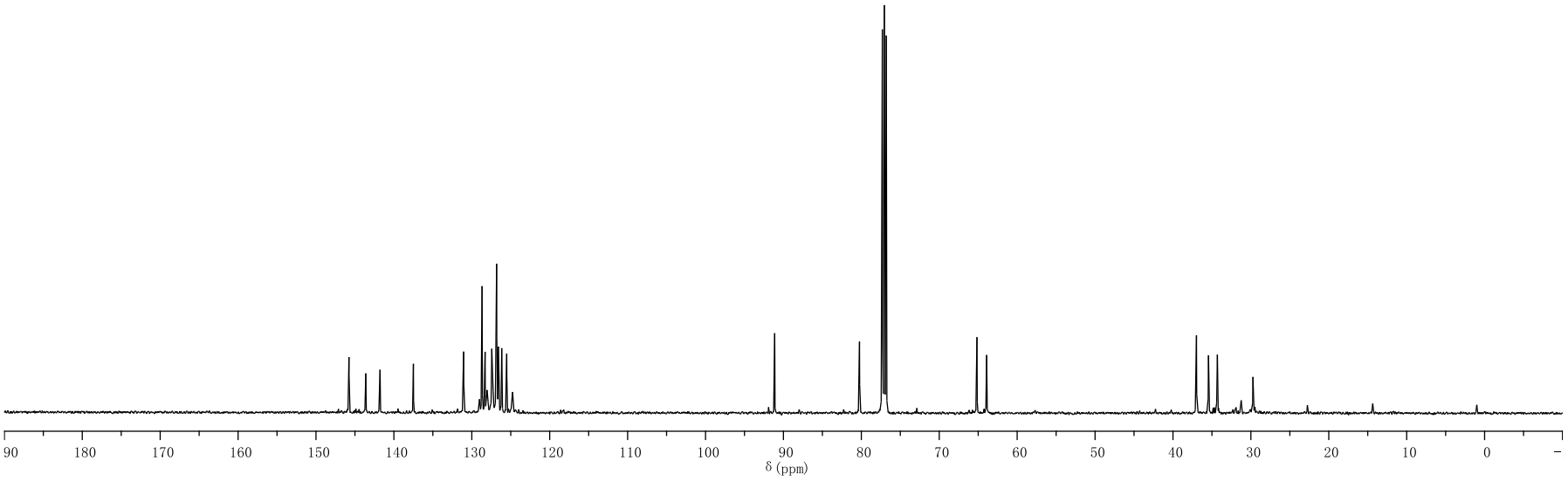




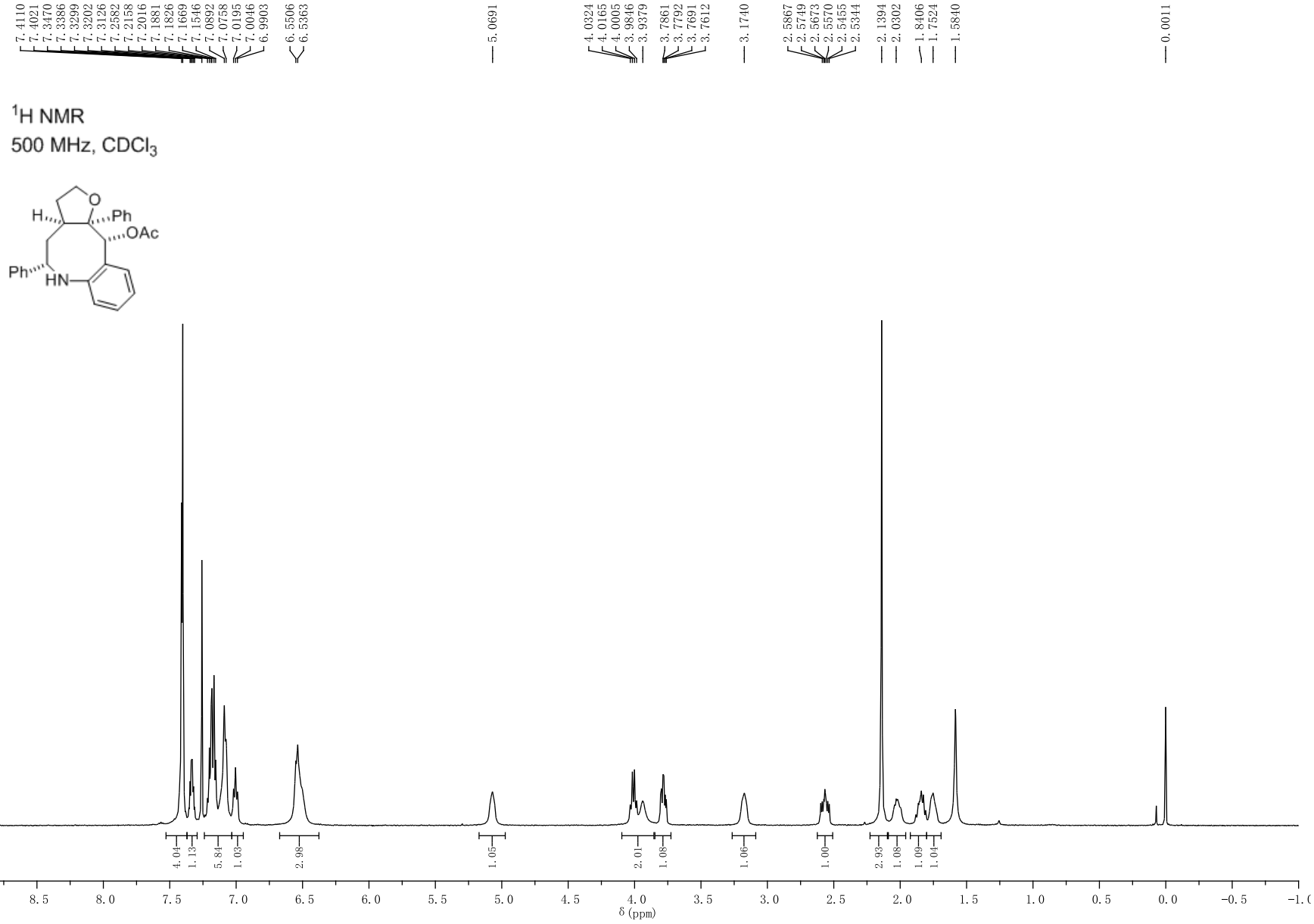
Compound 12 (–50 °C)

$^{13}C\{^{1}H\}$ NMR
125 MHz, $CDCl_3$

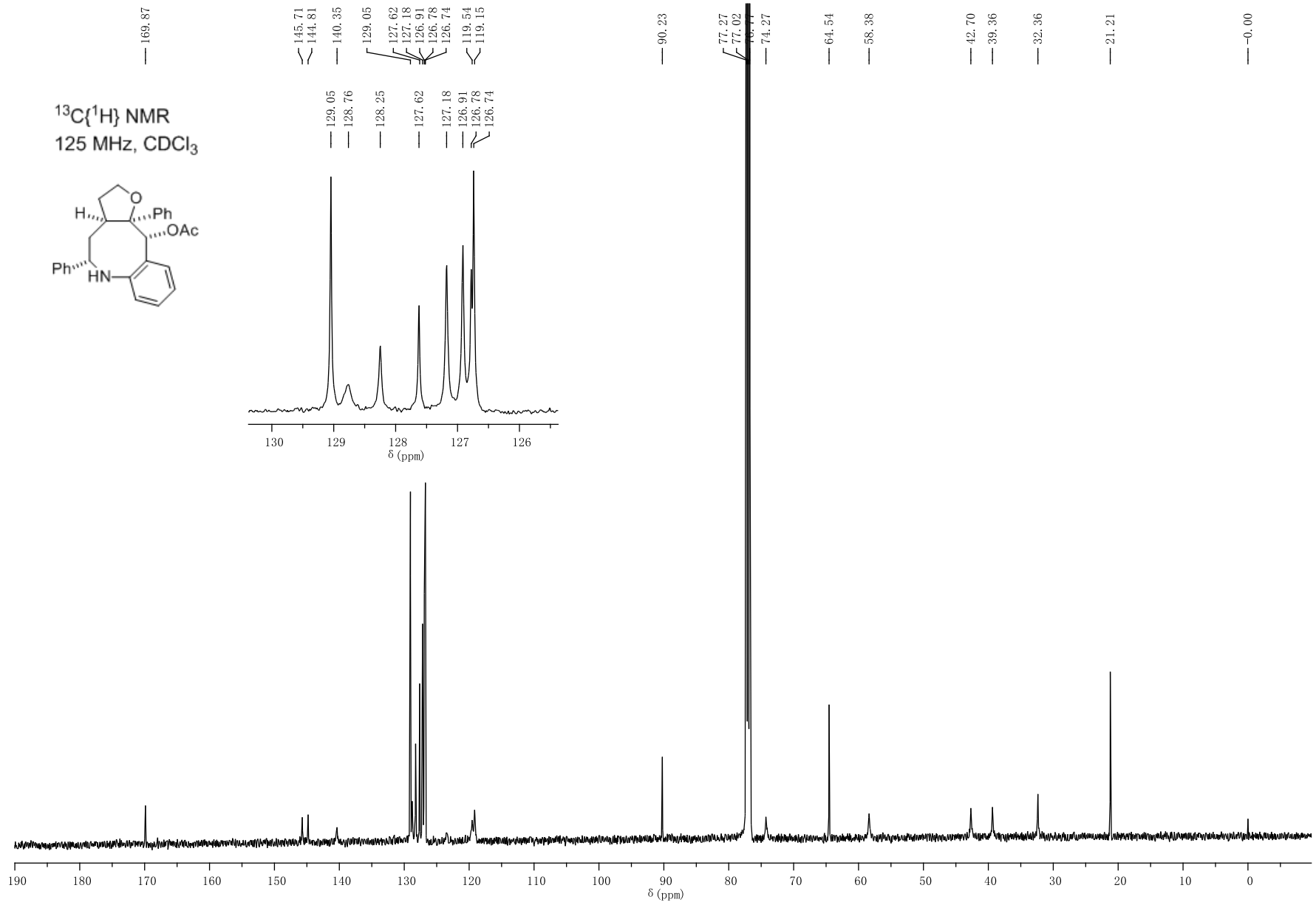




Compound 13

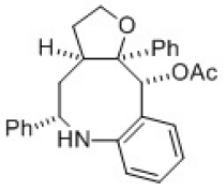

7.4110
7.4021
7.3470
7.3386
7.3299
7.3202
7.3126
7.2582
7.2158
7.2016
7.1881
7.1826
7.1669
7.1546
7.0892
7.0758
7.0195
7.0046
6.9903
6.5506
6.5363
5.0691
4.0324
4.0165
4.0005
3.9846
3.9379
3.7861
3.7792
3.7691
3.7612
3.1740
2.5867
2.5749
2.5673
2.5570
2.5455
2.5344
2.1394
2.0302
1.8406
1.7524
1.5840
0.0011
1H NMR
500 MHz, CDCl3
H
O
Ph
OAc
Ph
HN
4.04
1.13
5.84
1.03
2.98
1.05
2.01
1.08
1.06
1.00
2.93
1.08
1.09
1.04
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
δ (ppm)

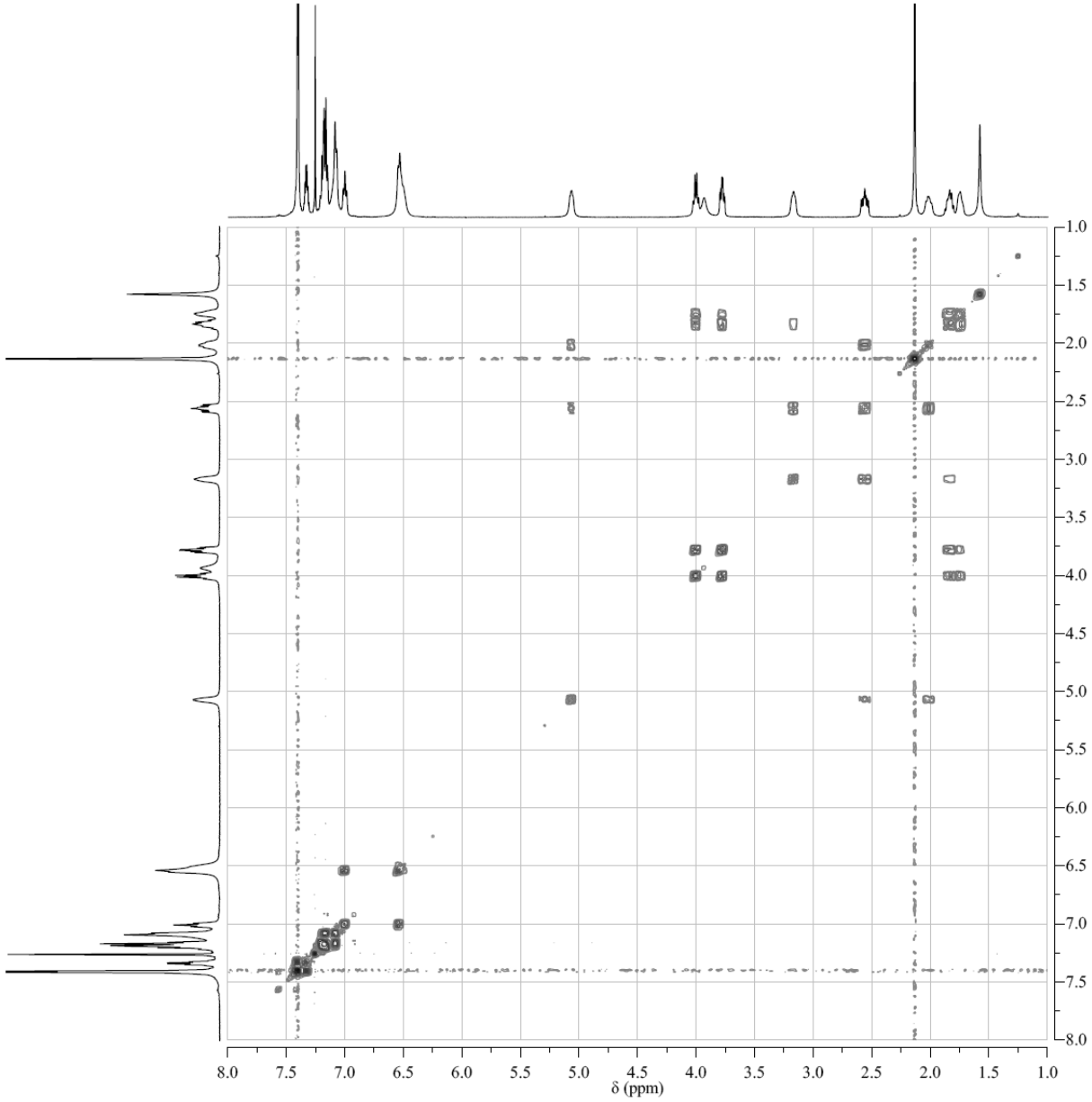
Compound 13


169.87
145.71
144.81
140.35
129.05
127.62
127.18
126.91
126.78
126.74
119.54
119.15
90.23
77.27
77.02
74.27
64.54
58.38
42.70
39.36
32.36
21.21
0.00
13C{1H} NMR
125 MHz, CDCl3
H
O
Ph
OAc
Ph
HN
δ (ppm)

Compound 13

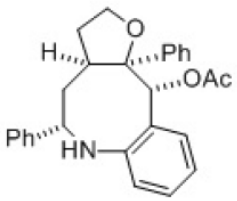
2D COSY NMR
500 MHz, $CDCl_3$

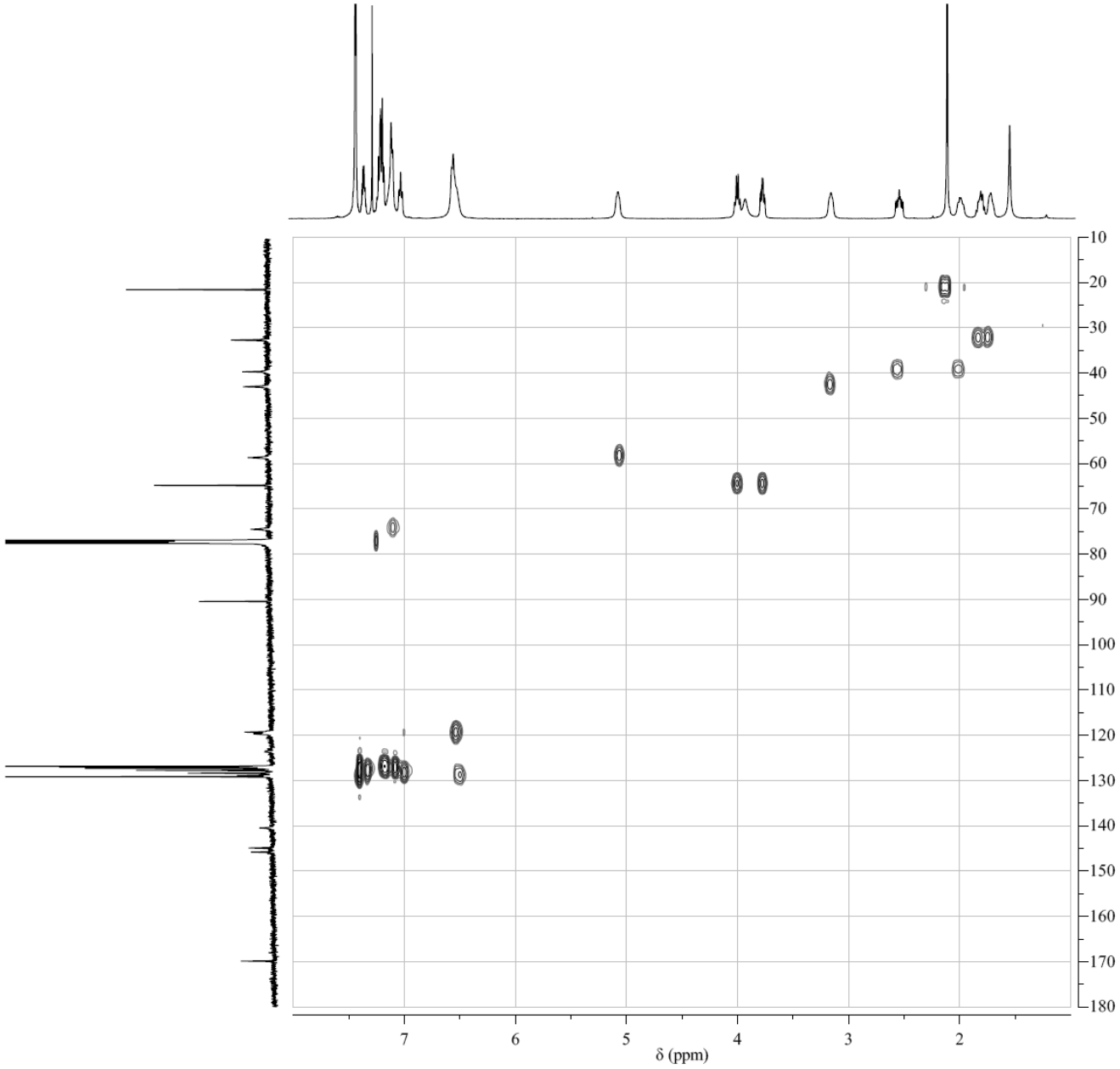




Compound 13

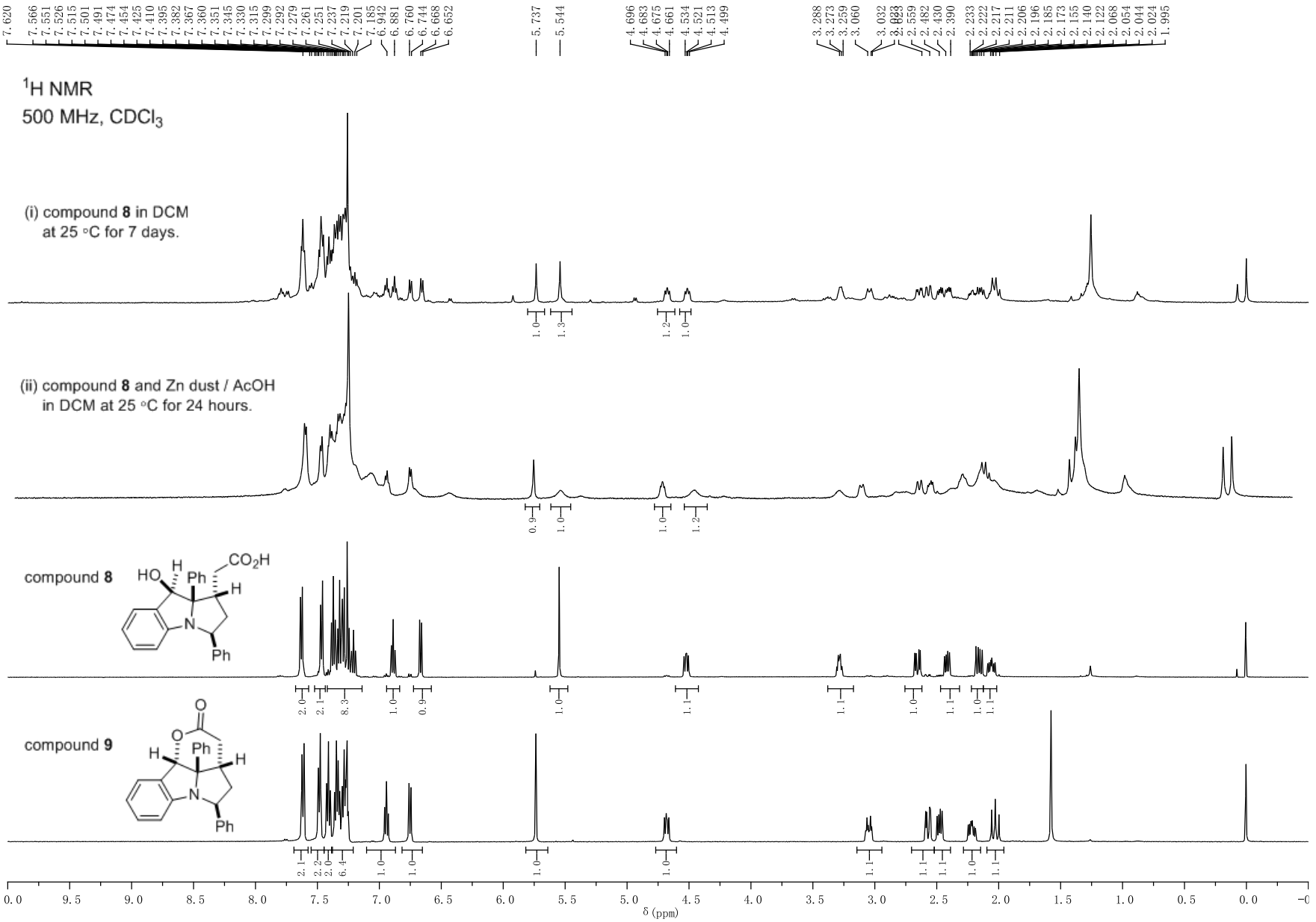
2D HSQC NMR
500 MHz, $CDCl_3$



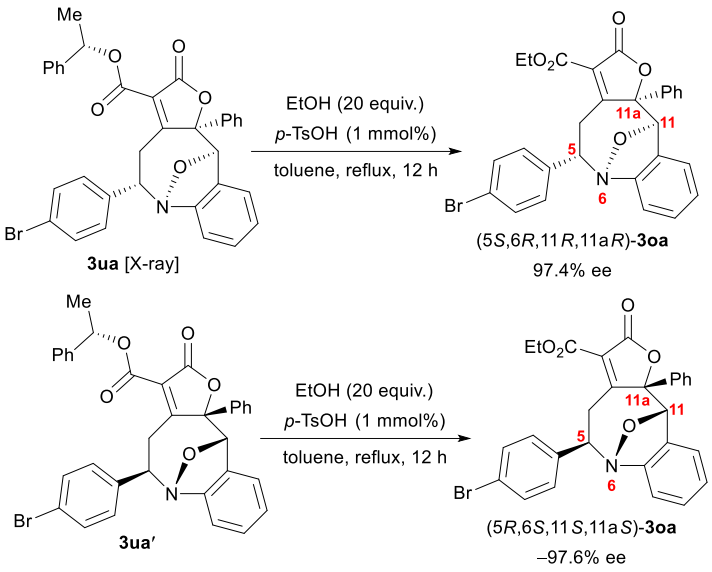


7. Studies on the conversion of compound 8 to compound 9

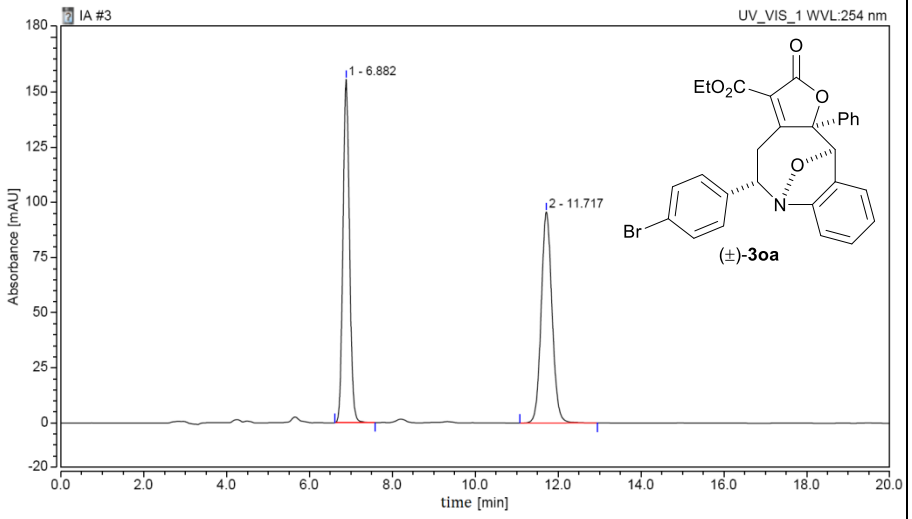
Figure S2 ^{1}H NMR Studies on the conversion of compound 8 to compound 9



8. Determination of the structure of 3ua′ by transesterification and by comparison of HPLC

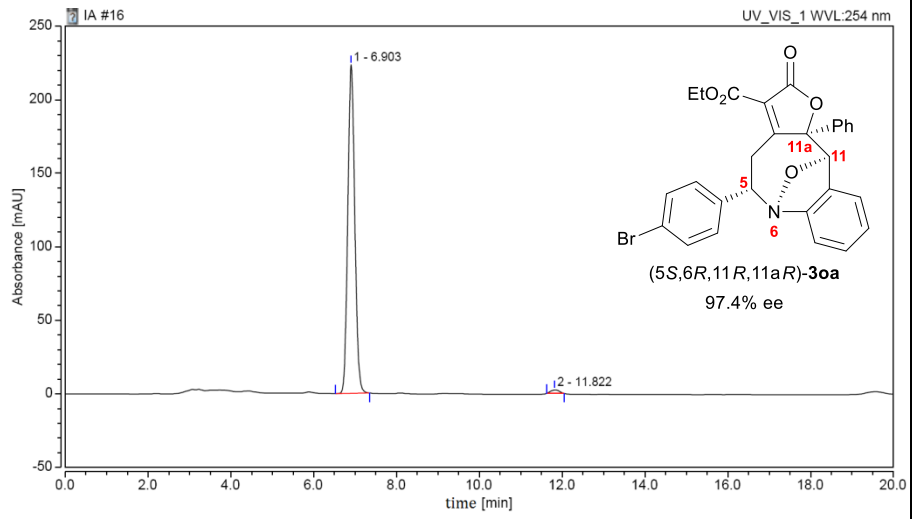


HPLC (Daicel CHIRALPAK IA column, isopropanol/*n*-hexane = 30/70, flow rate = 1.0 mL/min, λ = 254 nm)



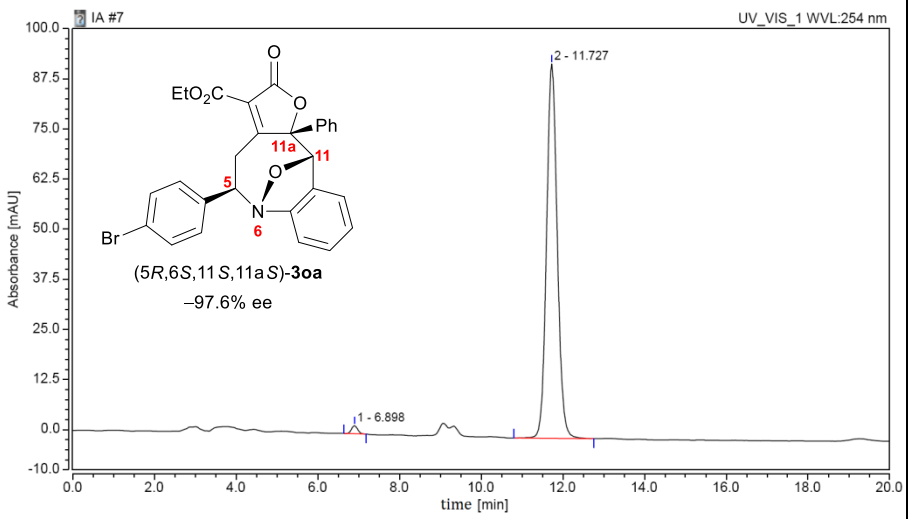
Area Percent Report

Peak	RetTime	Area [mAU]	Height	Area%
1	6.882	28.336	155.757	49.39
2	11.717	29.033	95.728	50.61



Area Percent Report

Peak	RetTime	Area [mAU]	Height	Area%
1	6.903	43.635	223.469	98.71
2	11.822	0.572	2.437	1.29



Area Percent Report

Peak	RetTime	Area [mAU]	Height	Area%
1	6.898	0.350	2.030	1.21
2	11.727	28.440	93.436	98.79