Supporting Information

Visible Light-Driven [3+3] Annulation Reaction of 2*H*-Azirines with Huisgen Zwitterions and Synthesis of 1,2,4-Triazines

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1. General information

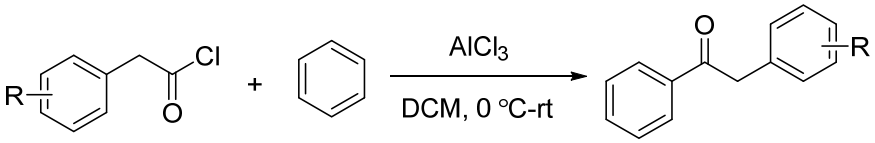
Unless otherwise stated, all reactions were carried out under nitrogen atmosphere/anhydrous conditions. Commercially available chemicals were directly used without further purification. Anhydrous solvents were distilled by conventional procedures prior to use. Flash column chromatography was performed on silica gel (200–300 mesh) using a mixture of petroleum ether (PE)/ethyl acetate (EA) or methanol/ethyl acetate as the eluent. ^{1}H, ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6. High resolution mass spectra were acquired in the ESI mode with the mass analyzer of TOF. Light sources include 10W/460 nm blue light LED, 3W/365nm UV LED and 15W/550nm green light LED, which are commercially available.

2. Experimental procedures

2.1 Synthesis of ketones.[1-4]

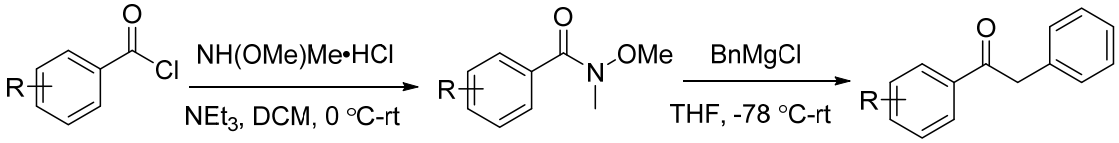
Commercially unavailable ketones, which were used in the synthesis of *2H*-azirines, were prepared according to the reported methods in literature.[1-4] The representative procedures are described below.

To a mixture of phenylacetyl chloride (7.5 g, 50 mmol) and substituted arene (70 mmol) in DCM (50 mL) was slowly added anhydrous aluminum chloride (8.0 g, 60 mmol) portionwise at 0 ºC. After the addition, the resulting mixture was stirred at room temperature overnight until phenylacetyl chloride was completely consumed. It was then poured onto an ice-water mixture (50 mL) with vigorous stirring. The organic layer was separated, washed with brine (30 mL) and dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated *in vacuo* on a rotary evaporator. The crude product was purified by column chromatography on silica gel to give the corresponding substituted ketones.



Following above procedure, different substituted ketones were also prepared from substituted phenylacetyl chloride and benzene.

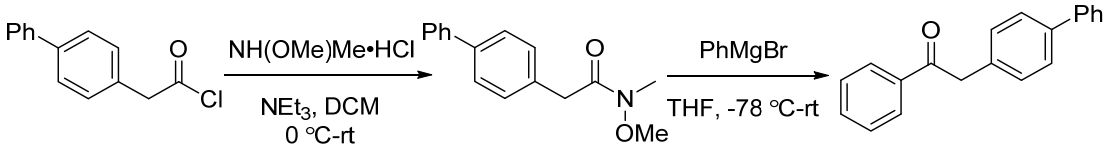
Some specific ketones were prepared by the following procedures.



R = 2-Me, 3-Me, 4-CF_3

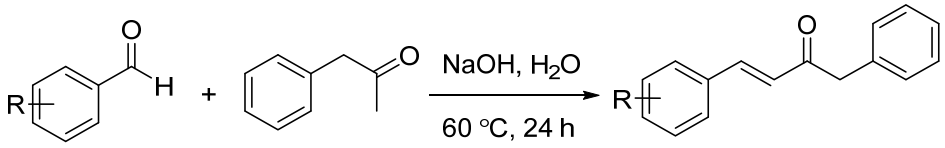
To a stirred suspension of *N*-methoxymethylamine hydrochloride (0.976 g, 10 mmol) in DCM (25 ml) was slowly added triethylamine (2.8 ml, 20 mmol) at 0 °C. Benzoyl chloride (1.16 ml, 10 mmol) was then added dropwise to the mixture. The resultant was then warmed to room temperature and stirred for 2 h before quenching with saturated aqueous $NaHCO_3$ solution (20 mL). The organic phase was separated and washed with 1*M* HCl (5 ml), and brine (20 ml), respectively, and dried over Na_2SO_4. After filtration, the filtrate was concentrated *in vacuo* on a rotary evaporator to give the crude *N*-methoxy-*N*-methylbenzamide.

To a solution of above *N*-methoxy-*N*-methylacetamide (4 mmol) in anhydrous THF (20 mL) was dropwise added benzylmagnesium chloride (6 mL, 6 mmol, 1 *M* in THF) at -78 °C under nitrogen atmosphere. The mixture was stirred for 2 h at the low temperature and then slowly warmed to room temperature. TLC indicated that the amide was consumed, the reaction mixture was then diluted with ethyl acetate (20 mL), washed with water (20 mL) and brine (20 mL). The organic layer was collected and concentrated on a rotary evaporator. The residue was isolated by flash column chromatography on silica gel to give the corresponding ketones shown in above equation.



Following above procedure, 4-phenyl substituted ketone was prepared in 78% yield from 2-([1,1'-biphenyl]-4-yl) acetyl chloride

The unsaturated ketones were prepared by the following procedure.

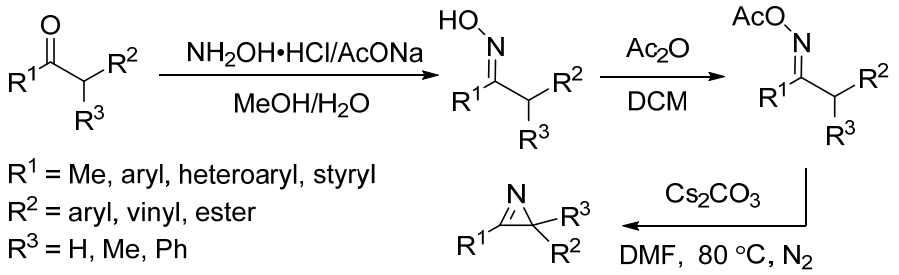


R = H, 4-Me, 4-Cl

Sodium hydroxide (75 mg, 1.85 mmol) was dissolved in water (35 mL) and the aqueous solution was mixed with substituted benzaldehyde (7.2 mmol) and phenylacetone (0.94 g, 7.0 mmol). The resulting mixture was heated at 60 °C with stirring for 24 h. After cooling to room temperature, DCM (100 mL) was added to the reaction mixture with vigorous stirring. The organic layer was collected and the aqueous layer was extracted twice with DCM (30 mL×2). The combined organic layers were washed with brine (20 mL) and dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure on a rotary evaporator, and the residue was subjected to flash column chromatography to afford pure ketones.

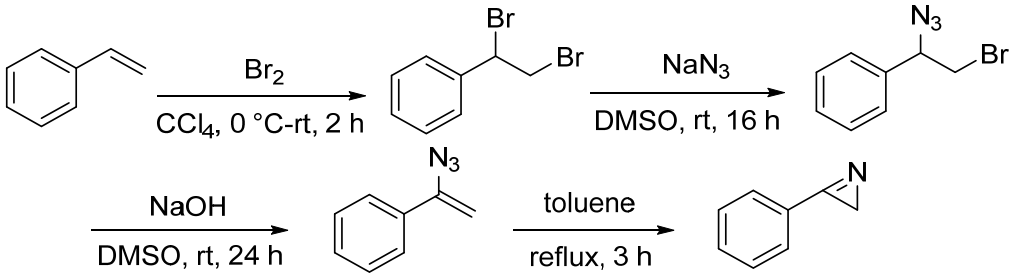
2.2 Synthesis of 2*H*-azirines.[5-7]

Substituted *2H*-azirines used in this work were prepared by the following typical procedures according to the literature[5-7].



Method A: A mixture of ketone (5 mmol), $NH_2OH·HCl$ (0.695 g, 10 mmol) and NaOAc (1.36 g, 10 mmol) in $MeOH/H_2O$ was stirred at ambient temperature for 12 h. After consumption of the ketone (detected by TLC), the solvent was then removed under reduced pressure, and the residue was then extracted with ethyl acetate (25 mL× 2). The combined ethyl acetate layers were washed with saturated $NaHCO_3$ aqueous solution (10 mL) and brine (10 mL). The organic layer was dried over anhydrous Na_2SO_4. After filtration, the filtrate was evaporated under reduced pressure to afford crude ketoximes. The ketoximes were used for the next step without further purification. A mixture of the ketoxime and acetic anhydride (2.0 equiv.) was stirred in DCM at room temperature for 12 h while TLC indicated the reaction was complete. The reaction mixture was diluted with DCM (25 mL) and washed with water (20 mL× 2). The organic layer was dried over anhydrous Na_2SO_4. After filtration and concentration, the crude product was purified by flash column chromatography to afford the corresponding ketoxime acetate.

A mixture of ketoxime acetate (2 mmol) and Cs_2CO_3 (1.30 g, 4 mmol) in DMF (10 mL) was stirred at 80 °C under N_2. After consumption of the ketoxime acetate (TLC monitored), the reaction mixture was cooled to room temperature and filtered. The filter cake was washed twice with ethyl acetate (10 mL × 2). The combined filtrates were washed twice with brine (10 mL × 2) and dried over anhydrous Na_2SO_4. After filtration and concentration, the residue was purified by flash column chromatography on silica gel to afford the desired azirines.

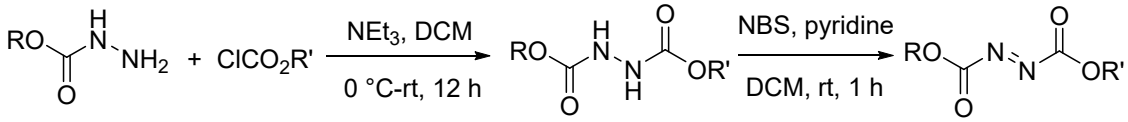


Method B: To a cooled solution of styrene (1.3g, 12.5 mol) in CCl_4 (10 mL) in an ice bath was slowly added a solution of bromine (0.7 mL, 12.5 mmol) in CCl_4 (10 mL). The resulting mixture was then stirred at rt for 2 h, and then the solvent was removed on a rotary evaporator. The crystalline dibromide was obtained and washed twice with cooled petroleum ether (5 mL × 2). To a solution of the prepared dibromide (2.95 g, 11 mmol) in DMSO (20 mL), sodium azide (1.25 g, 19 mmol) was slowly added with stirring over 1h. The mixture became thick as the expected azido bromide precipitated, and was stirred overnight at rt. A solution of sodium hydroxide (0.5 g, 12 mmol) in water (1.0 mL) was then added, and the resulting mixture was stirred at rt for additional 24 h. Then the mixture was poured into 2% sodium bicarbonate aqueous solution (50 mL) and extracted twice with DCM (20 ml × 2). The combined extracts were washed with water (10 mL × 2), dried over

Na_2SO_4. After filtration and removal of solvent, an oily residue was obtained and was subjected to column chromatographic isolation to give a yellow oil, which was dissolved in toluene (25 mL). The toluene solution was refluxed for 3 h and then cooled to room temperature. After work-up and flash column chromatography, the mono-substituted azirine was collected in 52% overall yield.

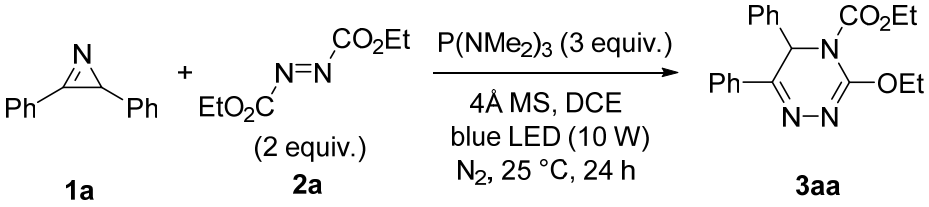
2.3 Synthesis of asymmetric azocarboxylates 2.[8]

Following the route below, asymmetric azocarboxylates **2** were prepared by the reported procedure.[8]



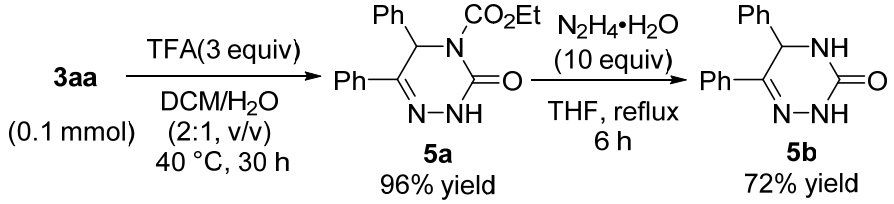
R = Bn, *t*-Bu R' = Bn, *i*-Pr, Et

2.4 Typical procedure of visible light-driven [3+3] annulation reaction.



A Schlenk tube was charged with azirine **1a** (19 mg, 0.1 mmol), azocarboxylate **2a** (40 mg, 0.2 mmol), 4Å MS sieves (10 mg) and dichloroethane (1.0 mL). The tube was then immersed in an ice bath and HMPT (55 mg, 0.3 mmol) was added dropwise by a microsyringe. After being stirred for 10 min, the tube was warmed up to room temperature. It was then placed under the irradiation of the blue LED light until **1a** was completely consumed (for 24 h, monitored by TLC). After removal of the solvent on a rotary evaporator, the residue was subjected to flash column chromatographic isolation (eluent: petroleum ether/ethyl acetate 15:1, V/V) to give product **3aa** (31 mg, yield 90%).

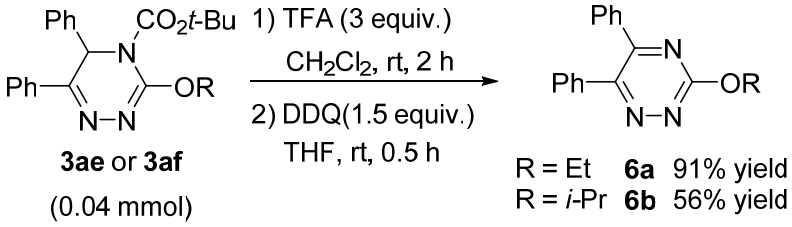
2.5 Transformations of selected products 3



Conversion of 3aa into dihydro-1,2,4-triazin-3(*2H*)-ones 5 (Scheme 3, a): To a solution of **3aa** (35 mg, 0.1 mmol) in DCM/H_2O (3 mL, V/V=2:1) was added trifluoroacetic acid (0.4 mL, 0.3 mmol) at 0 ºC. After being stirred for 10 min, the mixture was warmed up to 40 °C and stirred for 30 h. After being cooled to rt, DCM (20 mL) was added into it, followed by addition of saturated aqueous $NaHCO_3$ (5 mL) with vigorous stirring. The organic layer was separated and washed with brine (5 mL), and dried over Na_2SO_4. After filtration and concentration, the residue was subjected to flash

column chromatography (eluent: petroleum ether/ethyl acetate 8:1, V/V) to give **5a** (33 mg, 96% yield).

To a solution of **5a** (55 mg, 0.16 mmol) in THF (1 mL) was added hydrazine monohydrate (80 mg, 1.6 mmol, 10 equiv.). The resulting mixture was heated to reflux for 6 h. After removal of volatile components on a rotary evaporator, the crude product was purified by flash column chromatography (eluent: petroleum ether/ethyl acetate 1:5, V/V) to give **5b** (29 mg, 72% yield).



3ae or **3af**
(0.04 mmol)

R = Et **6a** 91% yield
R = *i*-Pr **6b** 56% yield

Transformation into 1,2,4-triazines 6 (Scheme 3, b): To a solution of **3ae** (16 mg, 0.04 mmol) in DCM (1.0 mL) was added trifluoroacetic acid (0.2 mL, 0.15 mmol) by a microsyringe. The resulting mixture was stirred at rt for 2 h. It was then mixed with saturated $NaHCO_3$ aqueous solution (5 mL) with vigorous stirring. The resulting mixture was extracted with DCM (5 mL×3) and the combined organic layers were dried over Na_2SO_4. After filtration and concentration, the crude product (12 mg) was directly used in the next step.

The above crude product was dissolved in THF (1 mL), followed by addition of DDQ (18 mg, 0.08 mmol, 2 equiv.). The resultant was stirred at rt for 30 min. After concentration and isolation by column chromatography (eluent: petroleum ether/ethyl acetate 10:1, V/V), triazine **6a** (10 mg, 91% yield) was obtained.

Following the same procedure, triazine **6b** (7 mg, 56% yield) was also prepared from **3af** (17 mg, 0.04 mmol).

3. Mechanistic studies

3.1 The inhibition experiment (Scheme 4, a)

Scheme 4, (a)

(0.1 mmol) (0.2 mmol)

3aa

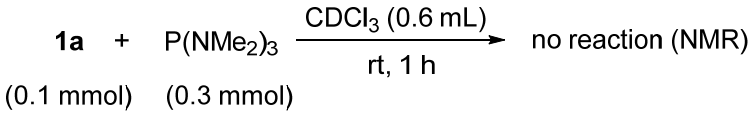
x = 0.15, 45% yield
0.3, 18% yield

To a mixture of **1a** (19 mg, 0.1 mmol), **2a** (40 mg, 0.2 mmol), 4Å MS sieves (10 mg) and dichloroethane (1.0 mL), HMPT (55 mg, 0.3 mmol) was dropwise added at 0 °C with stirring by a microsyringe. After being stirred at the same temperature for 10 min, the reaction mixture was warmed up to rt and TEMPO (23 mg, 0.15 mmol) was added into it. The resulting mixture was irradiated under blue LED light with stirring for 24 h. After removal of the solvent under reduced pressure, the annulation product **3aa** (15 mg, 45% yield) was collected by flash column chromatography (eluent: petroleum ether/ethyl acetate 15:1, V/V). Similarly, when the loading

amount of TEMPO was increased to 0.3 mmol, product **3aa** was collected in 18% yield.

3.2 NMR monitoring on the reaction of 1a and HMPT (Scheme 4, b)

Scheme 4, (b)



In an NMR tube, to a solution of **1a** (0.1 mmol) in $CDCl_3$ (0.6 mL) was added HMPT (0.3 mmol) at rt, and the resulting mixture was stirred at rt for 1 h. The reaction was then monitored by ^1H NMR spectroscopy (Figure S1, b). Compared to the ^1H NMR spectrum of **1a** (Figure S1, a), the ^1H NMR spectrum (Figure S1, b) of the reaction mixture clearly illustrated that no reaction occurred between **1a** and HMPT under above conditions.

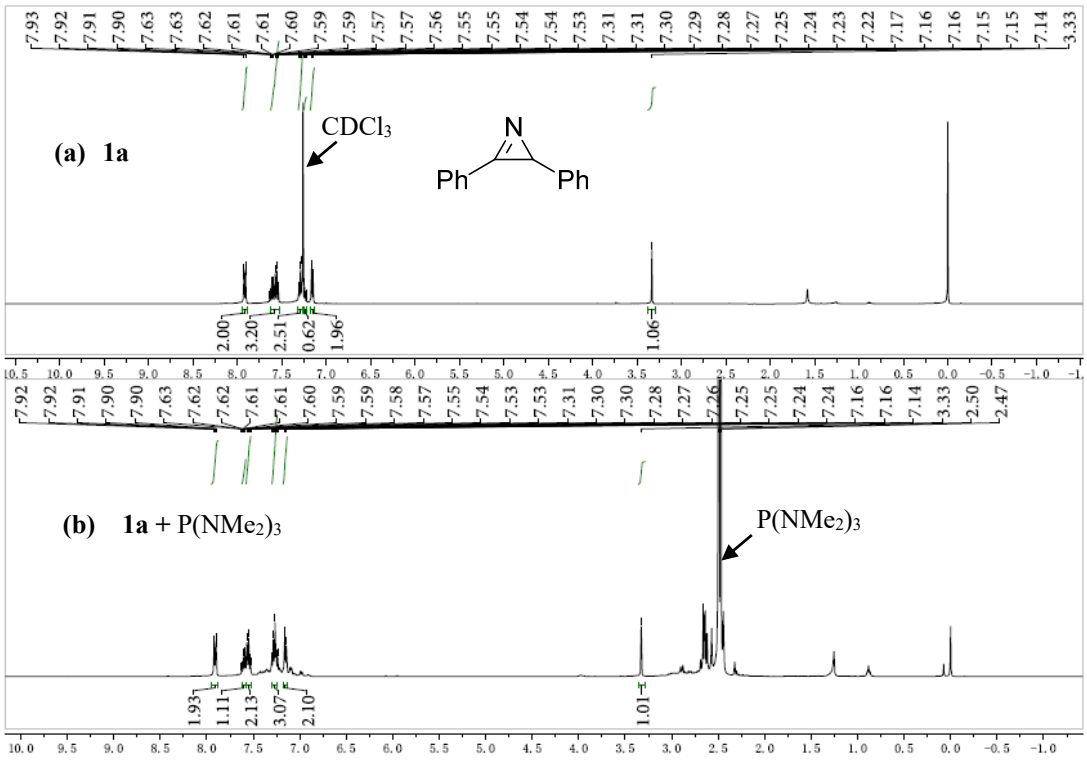
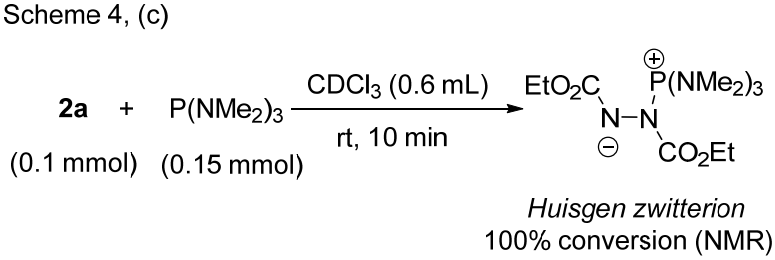


Figure S1. ^1H NMR spectra of **1a** and the reaction mixture of (**1a** + **HMPT**)

3.3 NMR monitoring on formation of Huisgen zwitterion (Scheme 4, c)

Scheme 4, (c)



In an NMR tube, to a solution of **2a** (0.1 mmol) in $CDCl_3$ (0.6 mL) was added HMPT (0.15 mmol) at rt, and the resulting mixture was stirred for 10 min, and then was monitored by NMR spectroscopy (Figures S2, S3). Compared to the ^1H NMR spectrum of **2a** (Figure S2, a), the ^1H NMR spectrum

of the reaction mixture (Figure S2, b) clearly indicated that the expected Huisgen zwitterion was formed in 100% conversion with substrate **2a** completely consumed. This result was also confirmed by the ^{31}P NMR measurement. The ^{31}P NMR spectrum of the reaction mixture (Figure S3, b) indicated that the predominant components only included excessive HMPT (δ_P 121.6 ppm) and the formed Huisgen zwitterion (δ_P 40.1 ppm).

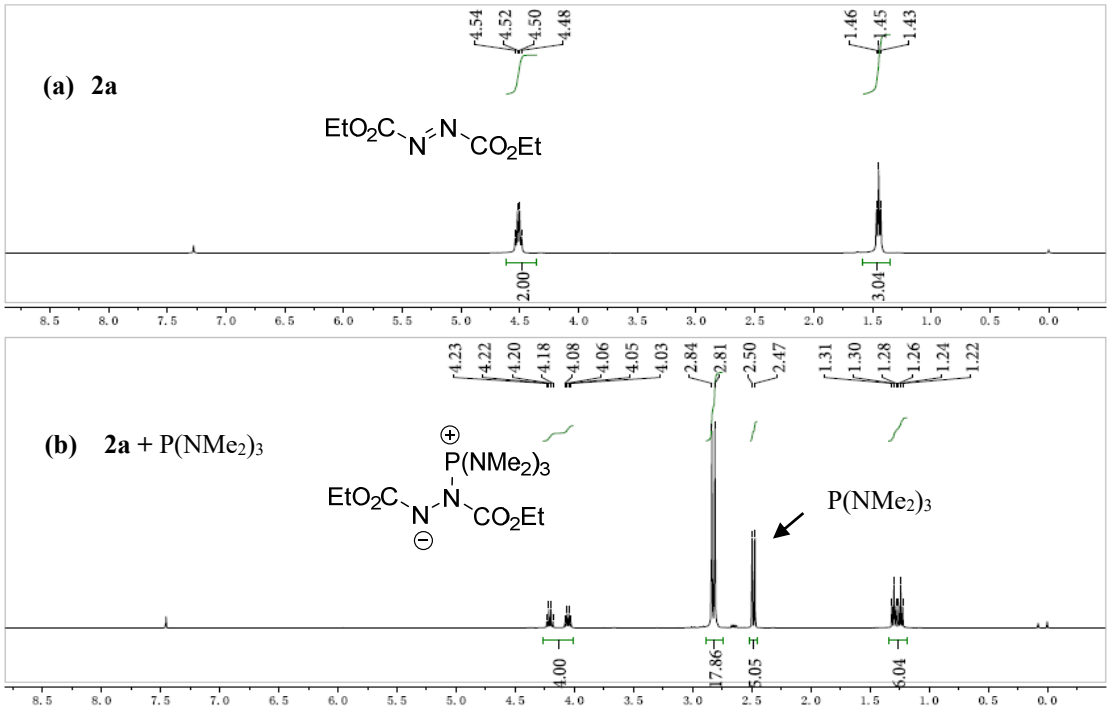


Figure S2. ^{1}H NMR spectra of **2a** and the reaction mixture of (**2a** + **HMPT**)

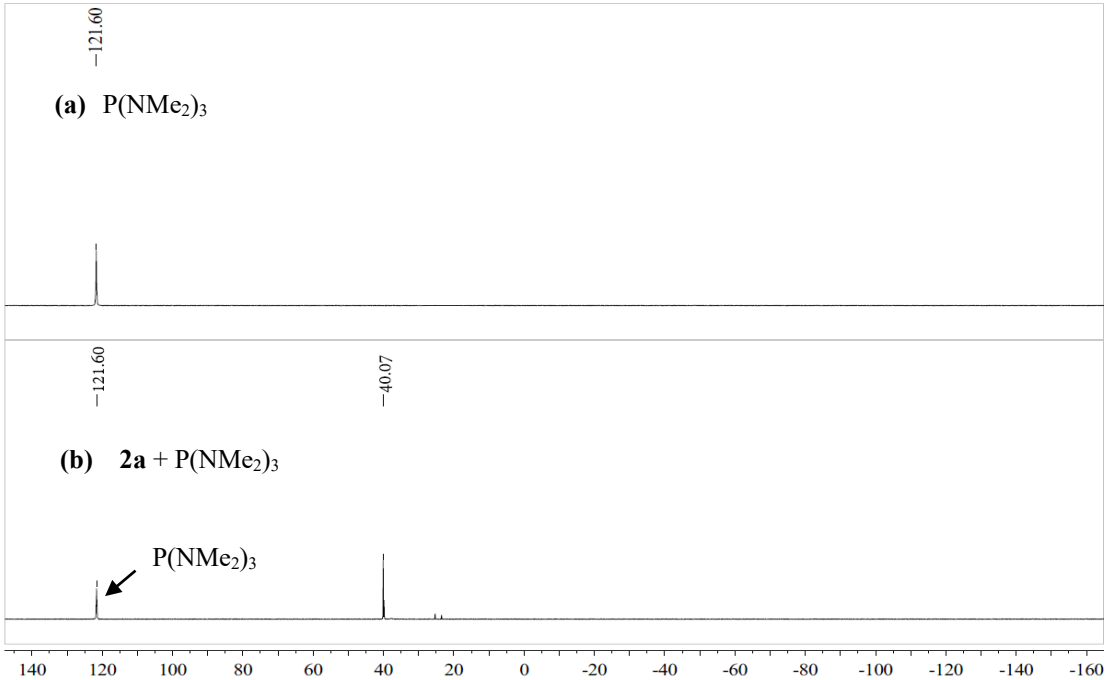
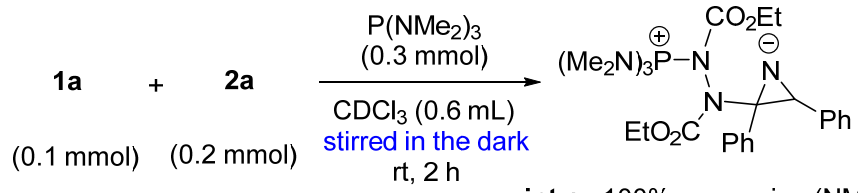


Figure S3. ^{31}P NMR spectra of HMPT and the reaction mixture of (**2a** + **HMPT**)

3.4 The dark reaction of azirine 1a, 2a and HMPT (Scheme 4, d)

Scheme 4, (d)



int-a 100% conversion (NMR)

HRMS-ESI (m/z $[M+H]^+$= 531.2848)

To a mixture of **1a** (0.1 mmol) and **2a** (0.2 mmol) in $CDCl_3$ (0.6 mL) in an NMR tube was added HMPT (0.3 mmol) at rt. The NMR tube was wrapped with aluminum foil to avoid light. The resulting mixture was stirred at rt in the dark for 2 h, and then was monitored by NMR spectroscopy (Figure S4, S5). At the beginning (ca. 10 min), ^1H and ^{31}P NMR spectra (Figure S4, a and Figure S5, a) clearly showed that the reaction mixture predominantly contained azirine **1a**, Huisgen zwitterion and excessive HMPT. Also, the ^{31}P NMR spectrum (Figure S4, b) indicated that a new phosphorus-containing species (δ_P 40.2 ppm) was formed in a small amount. After stirred at rt for 2 h in the dark, the NMR measurements of the reaction mixture (Figure S4, b and Figure S5, b) unveiled that the azirine **1a** was completely consumed (Figure S4, a) and the amount of the new species was accordingly increased (Figure S5, b). At 2 h, the reaction mixture predominantly contained the new species, excessive Huisgen zwitterion and HMPT (Figure S5, b). The follow-up HRMS measurement disclosed that the new species could be a 1:1 adduct of azirine **1a** and Huisgen zwitterion. Also, its ^{31}P NMR chemical shift (δ_P 40.2 ppm) indicated that the adduct contained a tetra-coordinated phosphorus. According to the above spectroscopic data, a structure named as **int-a** was presumably assigned for this adduct.

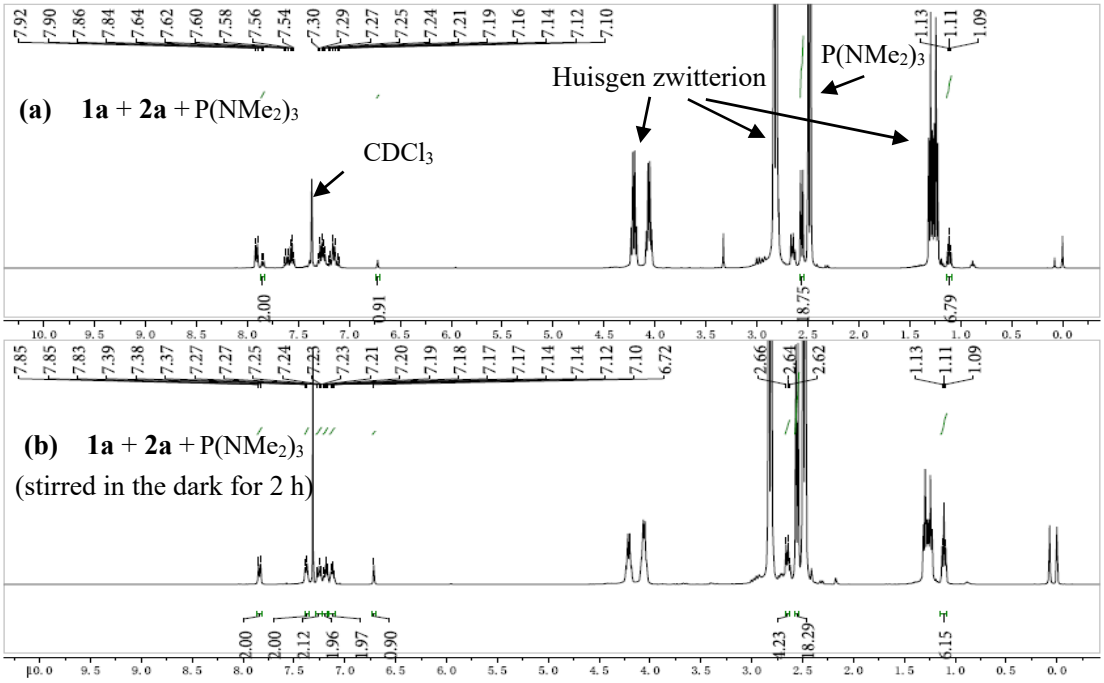


Figure S4. ^1H NMR spectra of the reaction mixture of **1a** + **2a** + HMPT at the beginning (ca. 10 min) and at 2 h

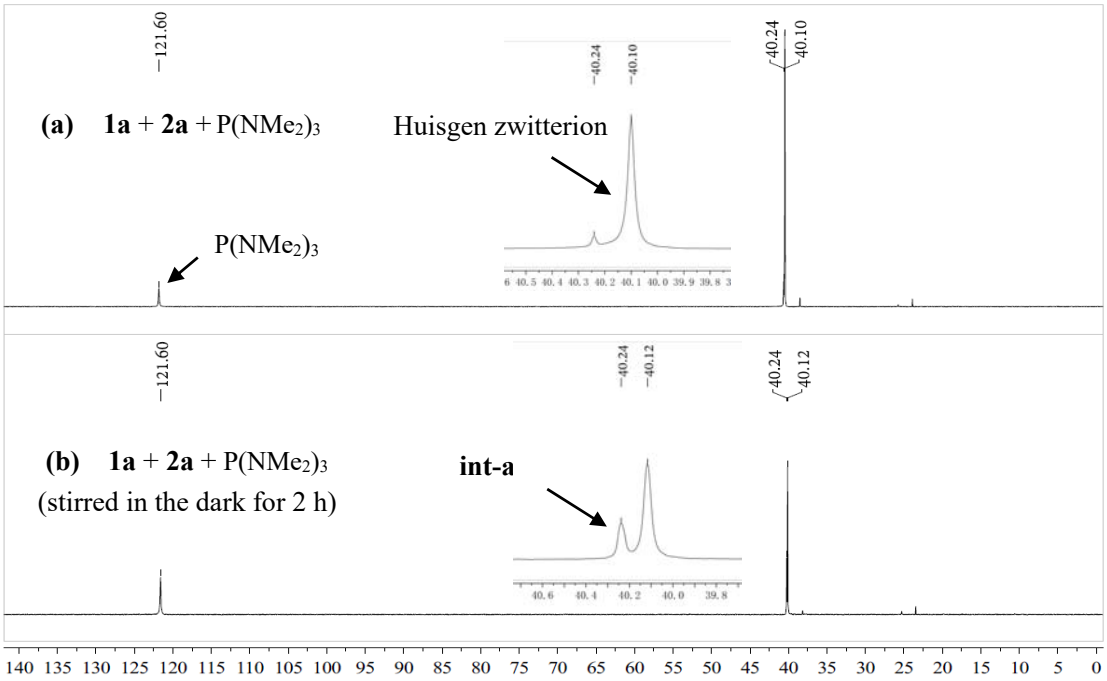
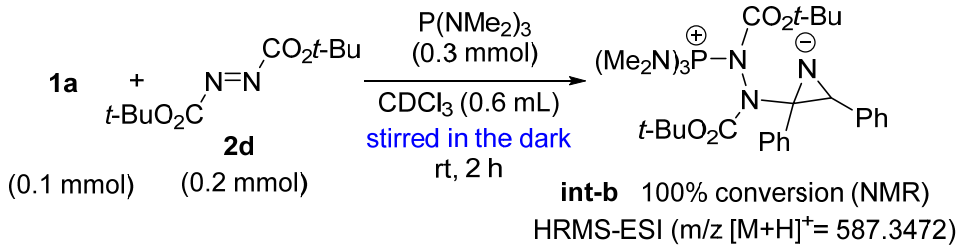


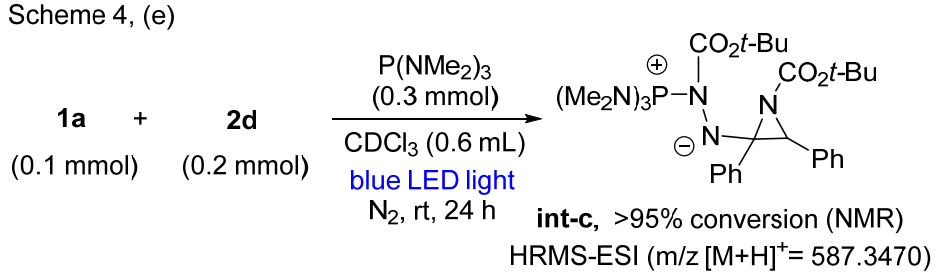
Figure S5. ^{31}P NMR spectra of the reaction mixture of **1a** + **2a** + HMPT at the beginning (ca. 10 min) and at 2 h

3.5 The dark and light reactions of azirine 1a, 2d and HMPT (Scheme 4, d, e)

Scheme 4, (d)



Scheme 4, (e)



Following the above procedures, the reaction of azirine **1a** (0.1 mmol), azodicarboxylate **2d** (0.2 mmol) and HMPT (0.3 mmol) in $CDCl_3$ (0.6 mL) was run in an NMR tube and measured by NMR spectroscopy and HRMS. The NMR measurements (Figures S6 and S7) and HRMS confirmed that azirine **1a** readily reacted with the in situ generated Huisgen zwitterion from **2d** and HMPT at rt in the dark to give an adduct **int-b** in 100% conversion after 2 h.

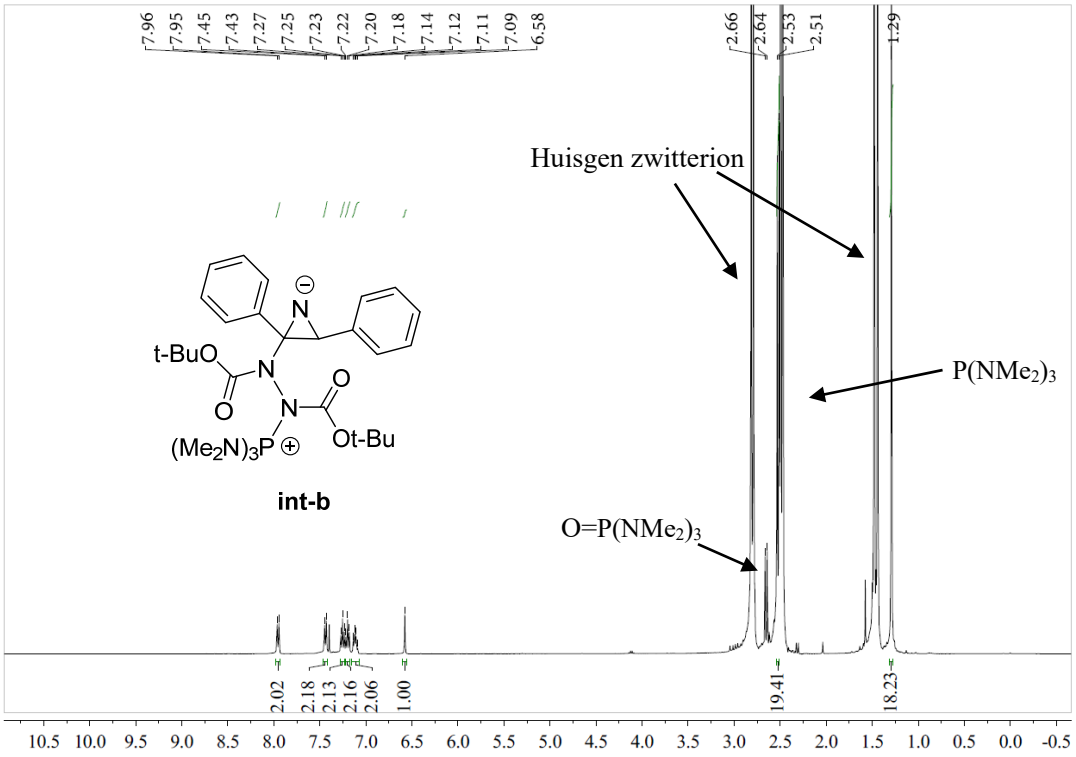


Figure S6. ^{1}H NMR spectrum of the reaction mixture of **1a** + **2d** + HMPT after being stirred in the dark for 2 h.

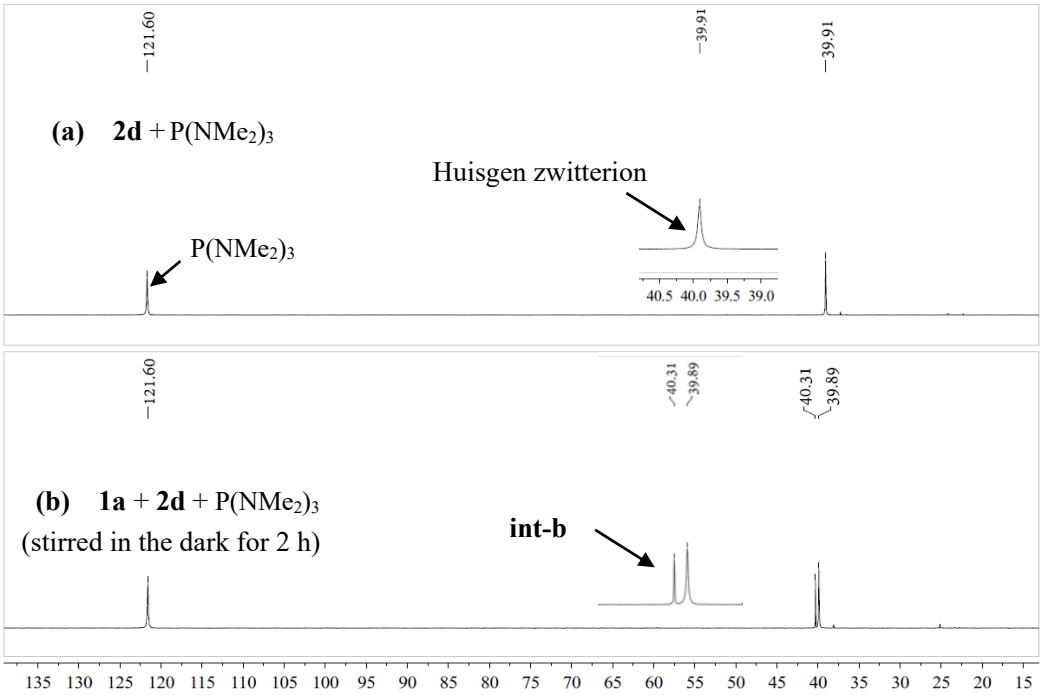


Figure S7. ^{31}P NMR spectra of the reaction mixture of **1a** + **2d** + HMPT at the beginning (ca. 10 min) and at 2 h

Next, the above reaction mixture of **1a** and **2d** was irradiated at rt under the blue LED light for 24 h. The NMR measurements indicated that, under the irradiation of the blue light, the adduct **int-b** was transformed into another phosphorus-containing species (δ_P 36.3 ppm) in > 95% conversion

(by ^{31}P NMR assay) instead of the annulation product **3ad** (Figures S8 and S9). Also, this new species has almost identical m/z value as that of the adduct **int-b** in the HRMS measurement.

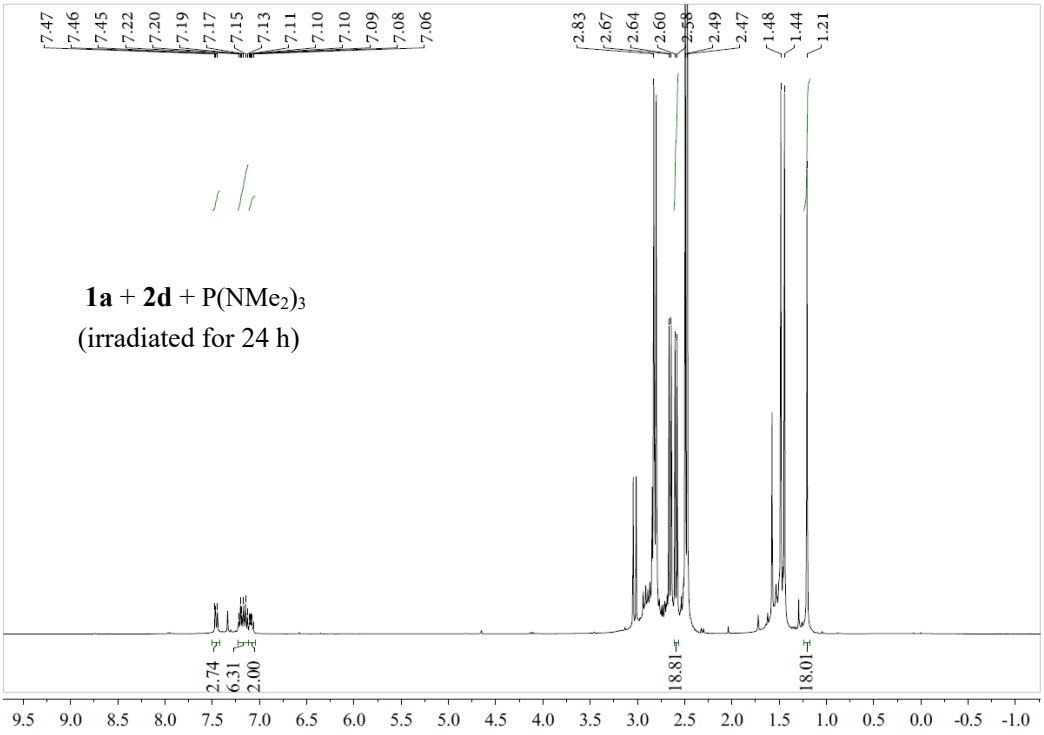


Figure S8. ^{1}H NMR spectrum of the reaction mixture of **1a** + **2d** + HMPT after being irradiated for 24 h

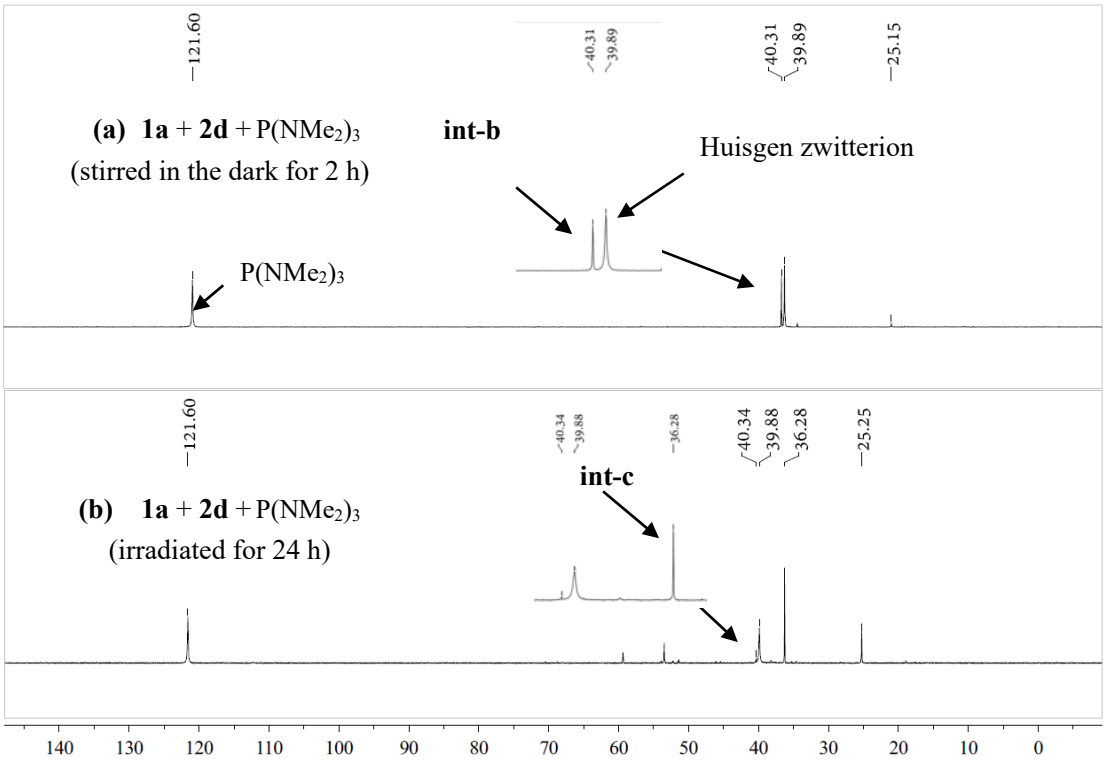


Figure S9. ^{31}P NMR spectra of the reaction mixture of **1a** + **2d** + HMPT after being stirred in the dark for 2 h (a) and after being irradiated under the blue light for 24 h (b)

In order to determine the possible structure of this new species, we performed several ^{13}C NMR measurements. Firstly, the ^{13}C NMR spectrum of the in situ generated Huisgen zwitterion from **2d** (0.2 mmol) and HMPT (0.3 mmol) was measured as a reference and assigned according to the the previous report (Figure 10). [9]

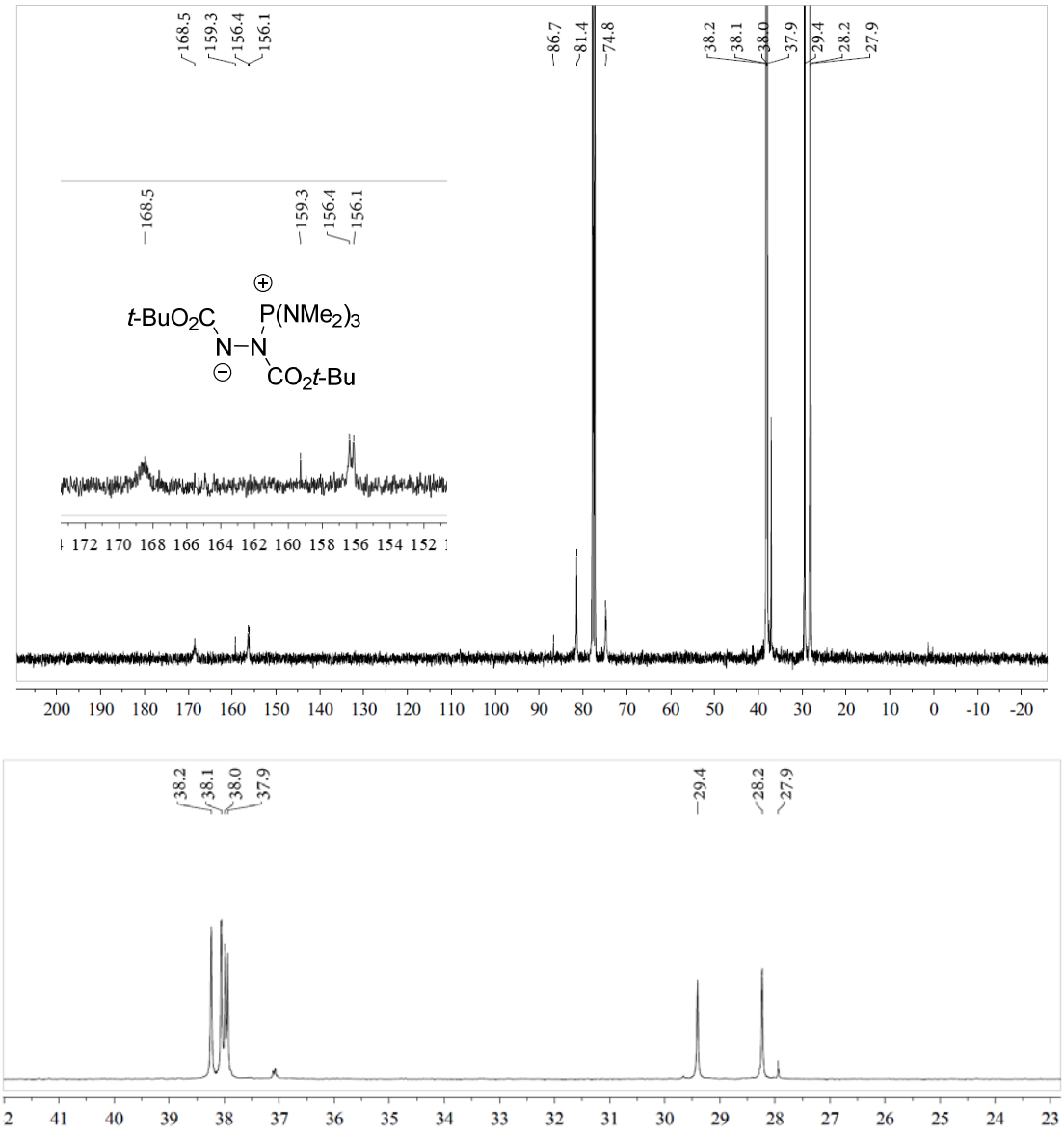


Figure S10. ^{13}C NMR spectrum of the Huisgen zwitterion from **2d** + HMPT

HMPT: ^{13}C NMR (101 MHz, $CDCl_3$) δ 38.1 (d, J = 25.5 Hz);

DTBAD (**2d**): ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 86.7, 27.9;

Huisgen zwitterion (**2d** + **HMPT**): ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5 (br s), 156.3 (d, J = 25.9 Hz), 81.4, 74.8, 38.0 (d, J = 11.8 Hz), 29.4, 28.2.

Next, the sample of the adduct **int-c** from the experiment Scheme 4, (d) and the sample of the new species from the experiment Scheme 4, (e) were measured by ^{13}C NMR spectroscopy (Figures S11 and S12). By comparing with the reference, the ^{13}C NMR spectra for **int-b** and the new species were assigned. Based on all NMR measurements and HRMS results, we assigned the possible structure of the new species (**int-c**) as shown in Scheme 4, (e). As shown in Figure S11, the signals

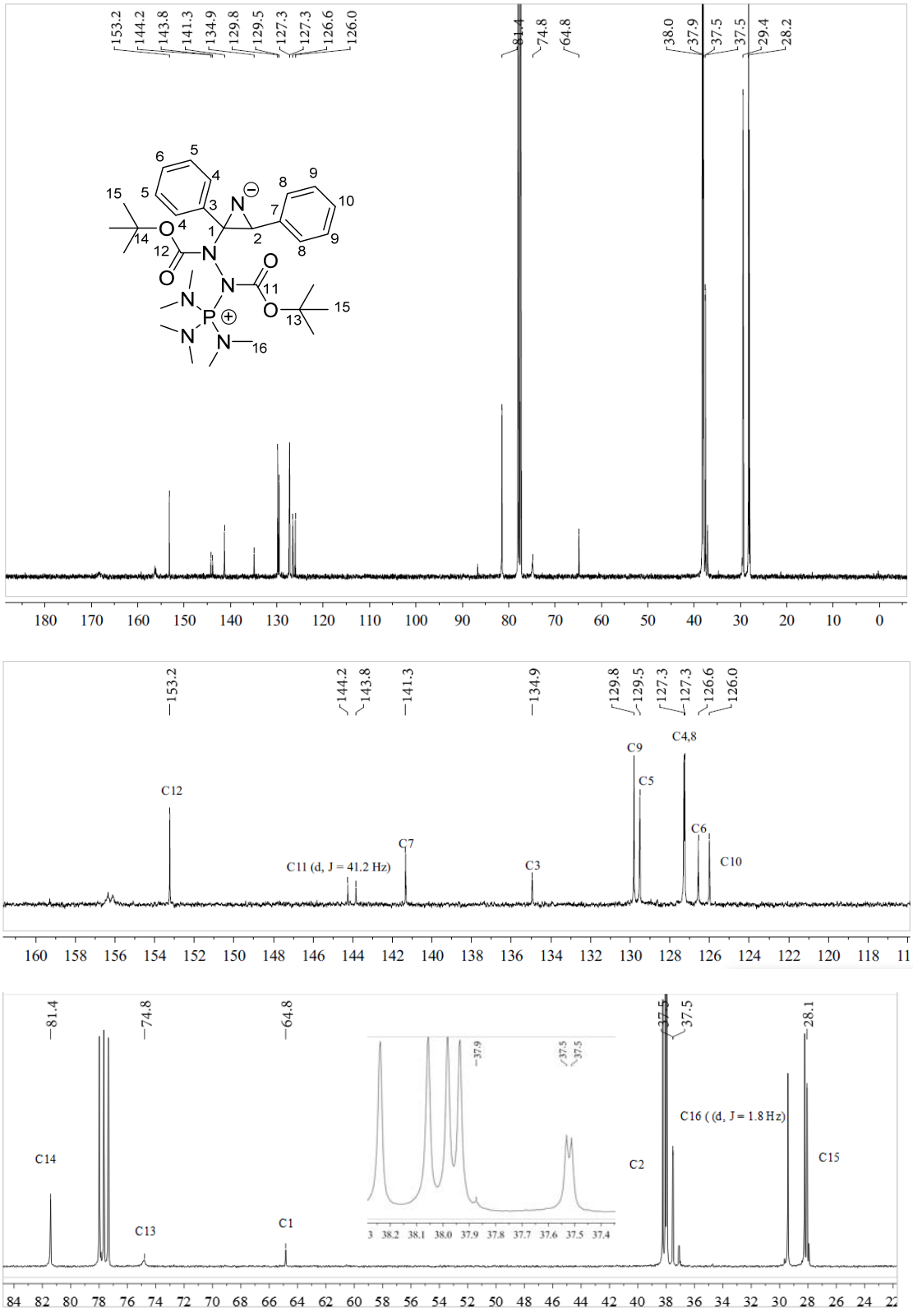


Figure S11. ^{13}C NMR spectrum of the reaction mixture of **1a** + **2d** + HMPT after being stirred in the dark for 2 h

are assigned according to the structure of **int-b** as follows. Singlet peak (153.2 ppm) and doublet peak (144.0 ppm) are assigned to the carbonyl carbon C12 and C11, respectively. Considering the different chemical environments of C3 and C7, the lower peak at 134.9 ppm is assigned to C3. The

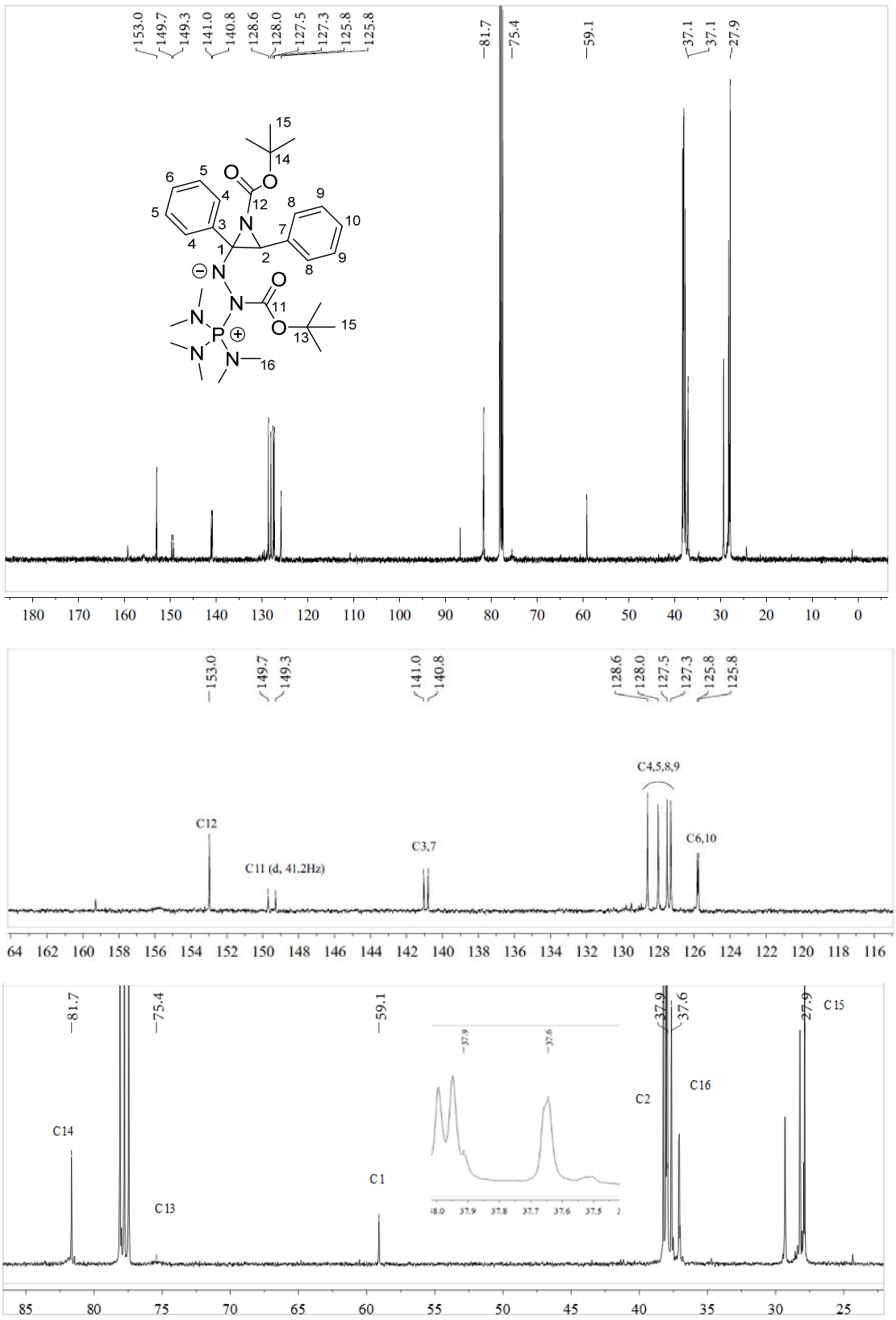


Figure S12. ^{13}C NMR spectrum of the reaction mixture of **1a** + **2d** + HMPT after being irradiated under the blue light for 24 h

signals from 126.0 ppm to 129.8 ppm are assigned to other carbons of phenyl groups. The peaks at 74.8 ppm and 81.4 ppm belong to C13 and C14 from the *tert*-butyl groups. Doublet peak at 37.5

ppm is in accordance with the environment of C16 and singlet peak at upfield 37.5 ppm comes from C15. Lastly, C1, C2 from the aziridine ring appears at 64.8 ppm and 37.9 ppm, respectively.

In Figure S12, the ^{13}C NMR signals of the species **int-c** are shown, which illustrates the NMR spectra of this solution after irradiation. Compared with the ^{13}C NMR spectrum of **int-b** (Figure S11), the main differences come from the signals of C1, C3 and C11. C1 moves upfield from 64.8 ppm to 59.1 ppm; C3 moves downfield from 134.9 to 141.0 ppm; C11 moves downfield from 144.0 to 149.5 ppm.

3.6 Light on/off experiments on the reaction of 1a, 2a and HMPT

The light on/off control experiments were performed according to the following typical procedure. To a mixture of **2a** (0.1 mmol) and HMPT (0.15 mmol) in $CDCl_3$ (0.6 mL) in an NMR tube, azirine **1a** (0.05 mmol) was added at rt. The resulting mixture was stirred at rt in the dark for 1 h and then monitored by NMR spectroscopy. Then the reaction was stirred under the irradiation of the blue light for 0.5 h and monitored again by NMR spectroscopy. ^1H NMR spectrum (Figure S13) showed that a diagnostic signal at 6.45 ppm for annulation product **3aa** appeared. Again, the reaction mixture was stirred in the dark again for 2 h, and monitored by NMR spectroscopy. The ^1H NMR spectrum (Figure S14) showed that the intensity of the signal at 6.45 ppm did not increase at all after the reaction was stirred without light irradiation for 2 h. This result clearly shows that the annulation reaction requires a constant light irradiation.

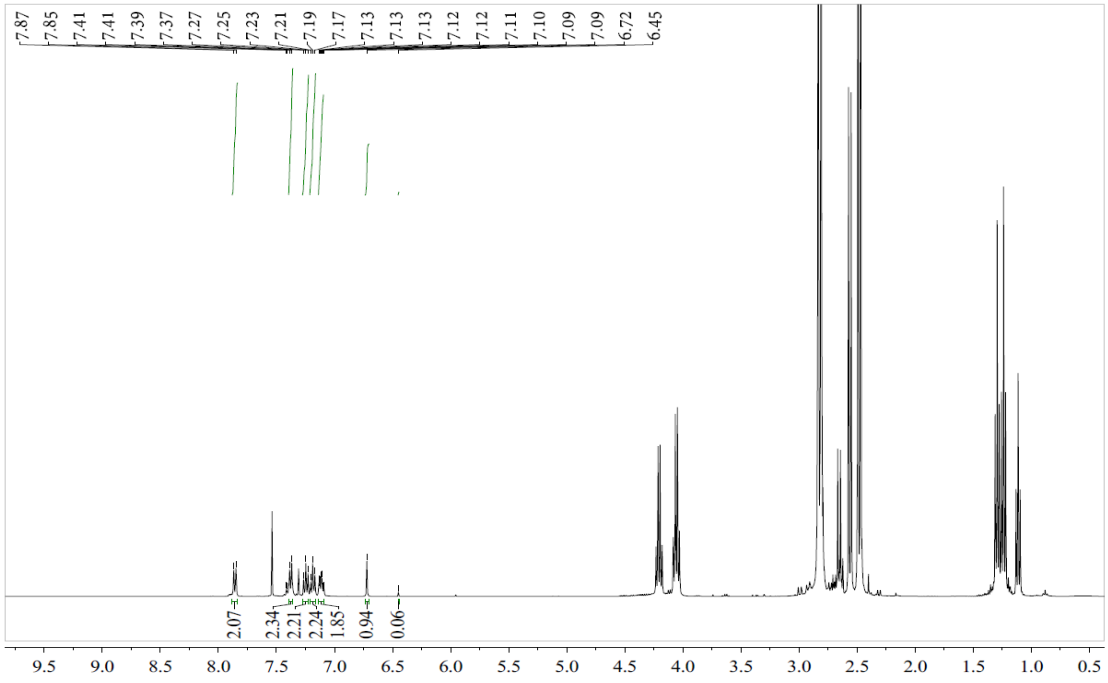


Figure S13. ^1H NMR spectrum of the reaction mixture after being stirred in the dark for 1 h followed by being irradiated for 0.5 h

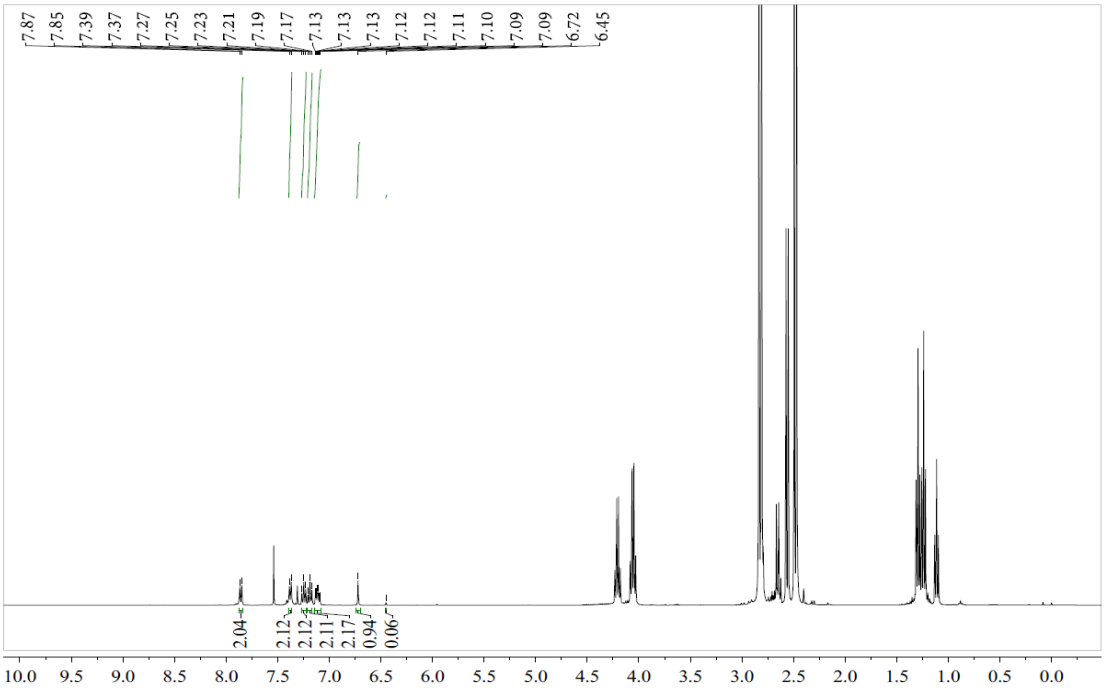
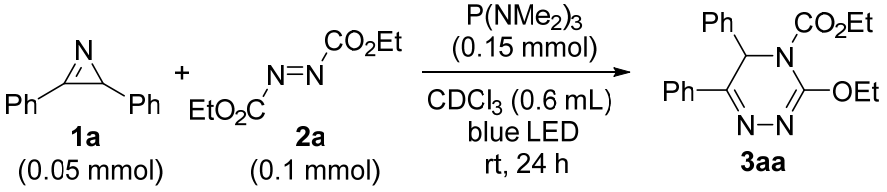


Figure S14. ^{1}H NMR spectrum of the reaction mixture after the light was turned off for 2 h

3.7 NMR tracking experiment on the reaction of 1a, 2a and HMPT



As shown in above equation, the annulation of azirine **1a** (0.05 mmol), azodicarboxylate **2a** (0.1 mmol) and HMPT (0.15 mmol) in $CDCl_3$ (0.6 mL) was run in an NMR tube and was continuously monitored by ^{1}H and ^{31}P NMR measurements for over 20 h. The stacked spectra are shown in Figures S15 and S16. This NMR tracking experiment clearly reveals the interchanges occur in the annulation among reactants, intermediates, and product. As shown in the stacked ^{1}H NMR spectra (Figure S15), the decline of the diagnostic signal at 3.30 ppm from **1a** (C2-H) clearly reveals that azirine **1a** was consumed in about 2 h; in contrast, the complete conversion of **int-a** into product **3aa** took about 20 h. The stacked ^{31}P NMR spectra (Figure S16) also clearly reveal how the phosphorus-containing components interchanged in the reaction.

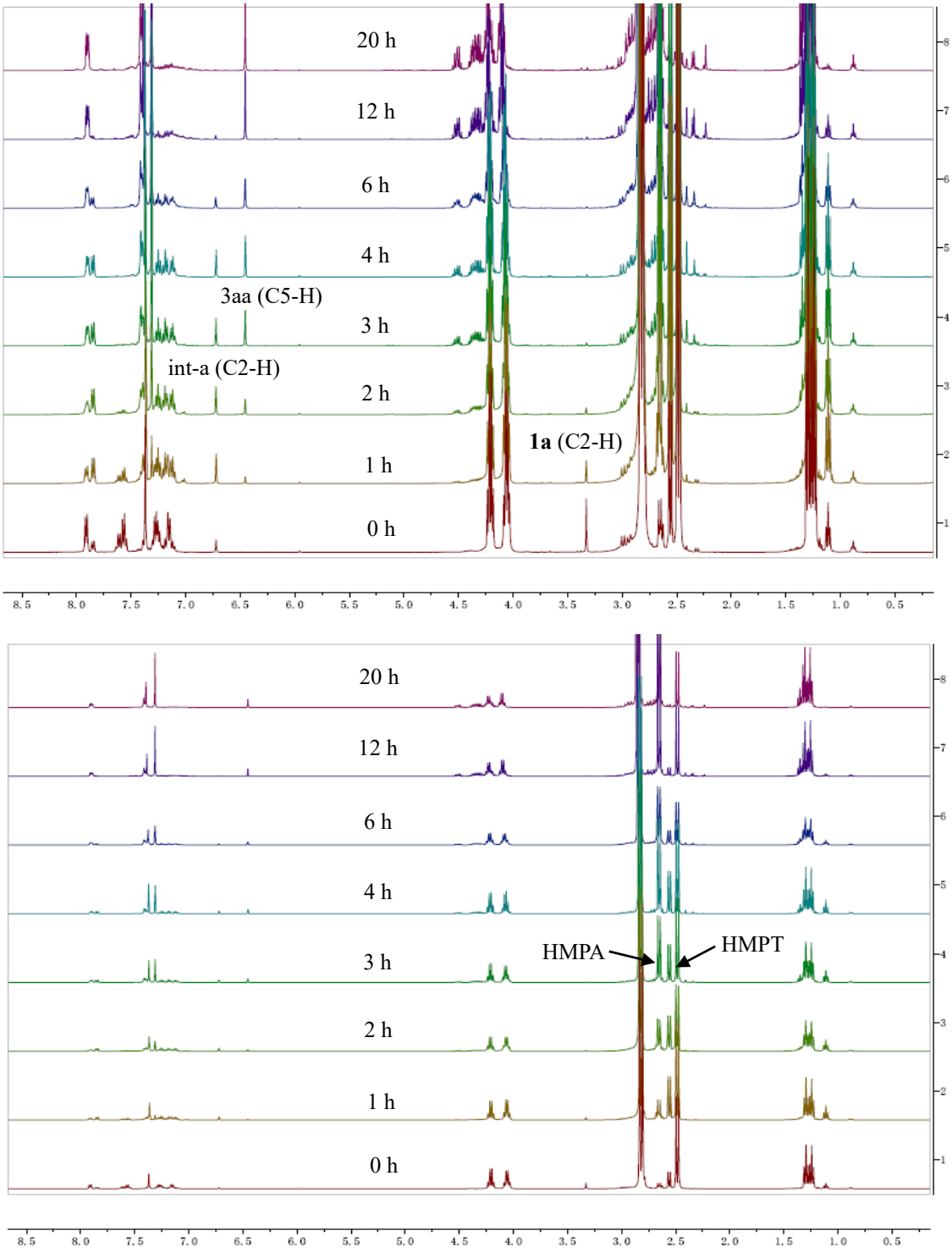


Figure S15. The stacked ^{1}H NMR spectra of the reaction mixture at different time

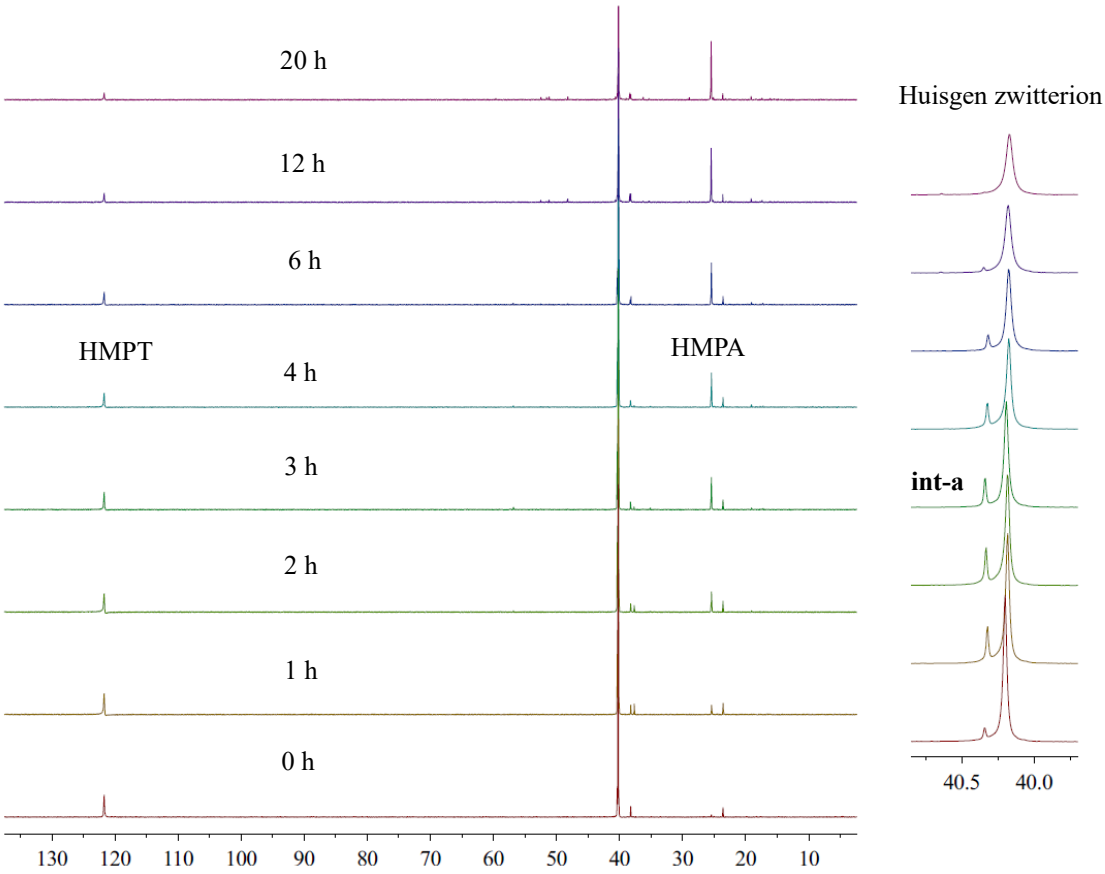


Figure S16. The stacked ^{31}P NMR spectra of the reaction mixture at different time

3.8 UV/VIS absorption experiments

A series of UV-Visible light absorption experiments were performed and the corresponding UV-Vis absorption spectra are illustrated in Figure S17-18. Generally, the test samples were prepared at the same concentrations at those in the reaction of **1a**, **2a** and HMPT under the standard conditions, namely, **1a** at 0.1 *M*, **2a** at 0.2 *M*, and HMPT at 0.3 *M* in DCE. As shown in Figure S17, the azirine **1a** (sample 1) and the in situ generated Huisgen zwitterion from **2a** and HMPT (sample 2) did not have obvious absorption in the visible wavelength range (Figure S17, red and green curves). In contrast, the in situ generated adduct **int-a** from **1a**, **2a** and HMPT (sample 3) elicited an obvious and broad absorption band in the visible region (Figure S17, black curve). The intensity of this absorption band increased significantly and peaked at 505 nm after the sample 3 was irradiated under blue LED light for 1 h (Figure S17, pink curve). This visible absorption is corroborated with the color change from pale yellow (at the beginning) to violet (after 1 h) observed in the reaction. To rule out the possibility that the absorption band would come from product **3aa**, a solution of isolated **3aa** in DCE (sample 5) was also tested. As shown in Figure S18, product **3aa** did not have appreciable absorption in the visible region.

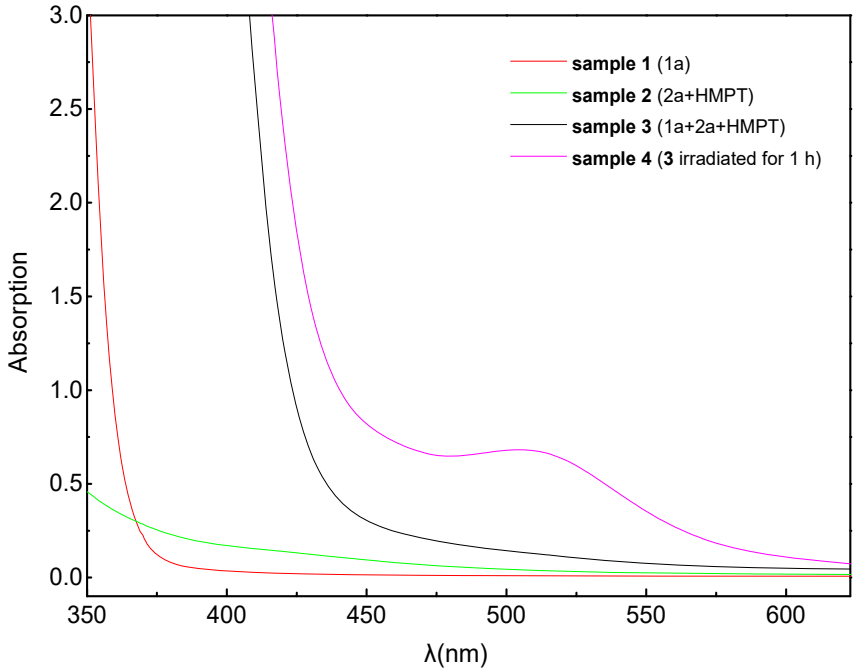


Figure S17. UV-VIS Absorption Spectra of reaction components

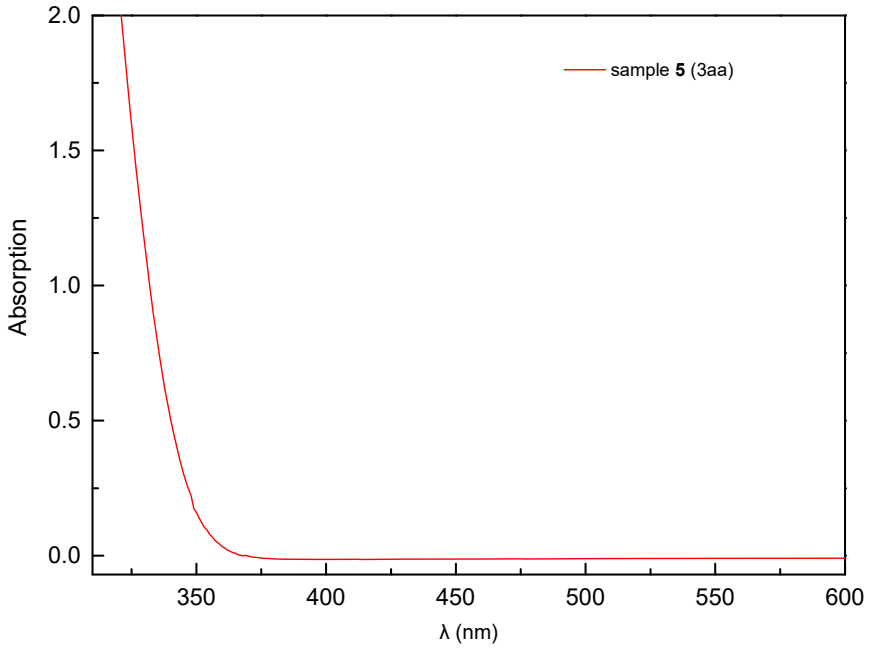


Figure S18. UV-VIS Absorption Spectrum of **3aa**

3.9 EPR experiments

To investigate the inhibition effect of TEMPO on the annulation reaction, we tested the relative consumption of TEMPO in the reaction. In a 10 mL volumetric flask, TEMPO (234 mg, 1.5 mmol) was added and followed by addition of solvent DCE to make a TEMPO stock solution. From this stock solution, each 2.0 mL of the solution was transferred into three 5 mL-vials, respectively. Into vial #1 and vial #2, **1a** (30 mg, 0.2 mmol), **2a** (68 mg, 0.4 mmol), HMPT (65 mg, 0.4 mmol) were respectively added. Then, vial #1 and vial #3 (only contained TEMPO solution) were irradiated at rt for 24 h by the blue LED light. Vial #2 was kept at rt in the dark for 24 h. At this point of time, 0.3 mL of each solution was respectively taken from vials #1-3 and diluted with DCE (25 mL) to prepare EPR samples (**1**, **2** and **3**). As shown in Figure S19, the EPR spectra from all samples **1**-**3** only gave the signal from the TEMPO. However, the intensity of the signal from sample **1** (prepared from the solution in vial #1) was lowered by 11% while it was compared with the signals from samples **2** and **3**. This result indicated that TEMPO was partially consumed in the inhibition experiment (Scheme 4, a). The consumption of TEMPO should be attributed to quenching possible radical intermediates in the annulation reaction.

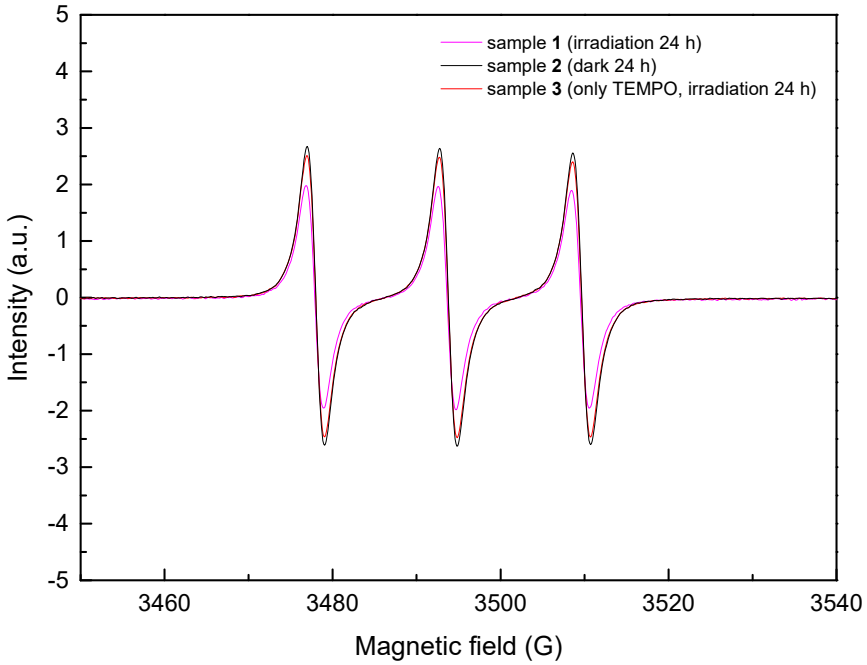
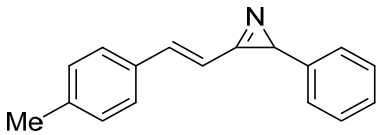


Figure S19. EPR spectra of TEMPO samples at the same initial concentration.

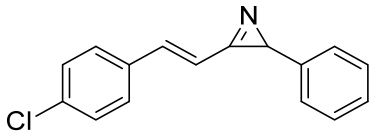
4. Characterization data for new compounds.



(*E*)-3-(4-Methylstyryl)-2-phenyl-2*H*-azirine (1m)

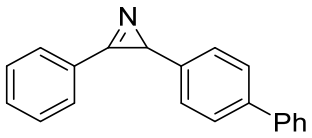
Colorless oil. 161 mg, 35% overall yield (PE:EA=100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J*

= 7.3 Hz, 2H), 7.34 – 7.26 (m, 3H), 7.24 – 7.20 (m, 3H), 7.19 – 7.13 (m, 3H), 3.15 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 147.7, 141.2, 140.0, 131.8, 129.8, 128.2, 128.2, 126.9, 126.1, 110.2, 33.5, 21.5. HRMS-ESI: calcd. for $C_{17}H_{15}N$ $[M+H]^+$ 234.1283, found 234.1286.



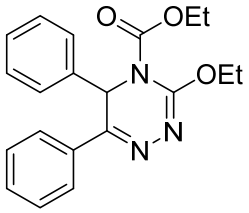
(*E*)-3-(4-Chlorostyryl)-2-phenyl-2*H*-azirine (1n)

Light yellow oil. 210 mg, 40% overall yield (PE:EA=100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.45 (m, 2H), 7.40 – 7.36 (m, 2H), 7.33 – 7.19 (m, 5H), 7.18 – 7.12 (m, 2H), 3.16 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 146.1, 140.7, 136.6, 132.9, 129.3, 128.3, 127.1, 126.1, 111.9, 33.7. HRMS-ESI: calcd. for $C_{16}H_{12}N$ $[M+H]^+$ 254.0737, found 254.0738.



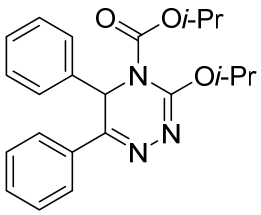
2-([1,1'-Biphenyl]-4-yl)-3-phenyl-2*H*-azirine (1v)

White solid. m.p. 128.8–130.0 ºC. 17.7 mg, 33% overall yield (PE:EA=100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.91 (m, 2H), 7.62 – 7.59 (m, 1H), 7.58 – 7.54 (m, 4H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.35 – 7.30 (m, 1H), 7.26 – 7.22 (m, 2H), 3.37 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 140.8, 140.1, 140.0, 133.3, 130.0, 129.3, 128.8, 127.2, 127.1, 127.0, 126.6, 124.1, 34.3. HRMS-ESI: calcd. for $C_{20}H_{15}N$ $[M+H]^+$ 270.1283, found 270.1281.



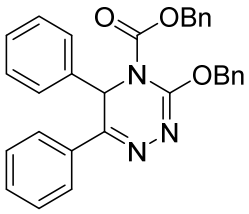
Ethyl 3-ethoxy-5,6-diphenyl-1,2,4-triazine-4(5*H*)-carboxylate (3aa)

Colorless oil. 31 mg, 90% yield (PE:EA=15:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.88 (m, 2H), 7.42 – 7.38 (m, 3H), 7.31 (s, 5H), 6.45 (s, 1H), 4.52 (dq, *J* = 10.6, 7.1 Hz, 1H), 4.43 – 4.26 (m, 2H), 1.34 (t, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 152.9, 148.4, 134.7, 134.1, 130.4, 129.0, 128.9, 128.8, 127.7, 126.7, 64.8, 63.7, 52.8, 14.2. HRMS-ESI: calcd. for $C_{20}H_{21}N_3O_3$ $[M+H]^+$ 352.1661, found 352.1661.



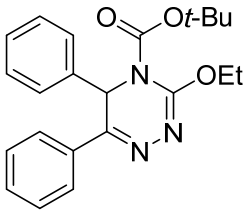
Isopropyl 3-isopropoxy-5,6-diphenyl-1,2,4-triazine-4(5*H*)-carboxylate (3ab)

Colorless oil. 37 mg, 97% yield (PE:EA=20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.88 (m, 2H), 7.43 – 7.37 (m, 3H), 7.34 – 7.27 (m, 5H), 6.43 (s, 1H), 5.34 (hept, *J* = 6.2 Hz, 1H), 5.06 (hept, *J* = 6.2 Hz, 1H), 1.35 (dd, *J* = 6.2, 3.6 Hz, 6H), 1.30 (d, *J* = 6.2 Hz, 3H), 1.25 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 152.6, 148.0, 134.8, 134.1, 130.4, 128.9, 128.83, 128.76, 127.7, 126.6, 72.4, 72.0, 52.6, 22.0, 21.89, 21.86, 21.6. HRMS-ESI: calcd. for $C_{22}H_{25}N_3O_3$ $[M+H]^+$ 380.1974, found 380.1971.



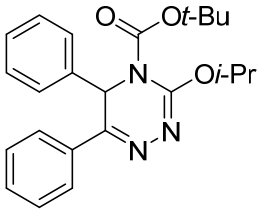
Benzyl 3-(benzyloxy)-5,6-diphenyl-1,2,4-triazine-4(5*H*)-carboxylate (3ac)

White oil. 33 mg, 70% yield (PE:EA=20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.77 (m, 2H), 7.45 – 7.37 (m, 4H), 7.36 – 7.27 (m, 10H), 7.25 – 7.17 (m, 4H), 6.51 (s, 1H), 5.45 (d, *J* = 12.3 Hz, 1H), 5.31 – 5.20 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 152.8, 148.1, 135.3, 134.7, 134.4, 133.9, 130.6, 129.1, 129.0, 128.8, 128.65, 128.62, 128.44, 128.38, 128.1, 127.7, 126.7, 70.4, 69.5, 53.0. HRMS-ESI: calcd. for $C_{30}H_{25}N_3O_3$ $[M+H]^+$ 476.1974, found 476.1968.



***tert*-Butyl 3-ethoxy-5,6-diphenyl-1,2,4-triazine-4(5*H*)-carboxylate (3ae)**

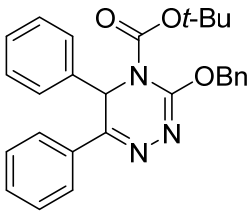
Colorless oil. 33 mg, 87% yield (PE:EA=15:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.90 (m, 2H), 7.42 – 7.36 (m, 3H), 7.35 – 7.23 (m, 5H), 6.41 (s, 1H), 4.50 (dq, *J* = 10.6, 7.1 Hz, 1H), 4.33 (dq, *J* = 10.6, 7.1 Hz, 1H), 1.53 (s, 9H), 1.32 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 151.4, 148.9, 135.0, 134.2, 130.4, 129.0, 128.8, 128.7, 127.7, 126.6, 83.7, 64.5, 52.2, 28.1, 14.3. HRMS-ESI: calcd. for $C_{22}H_{25}N_3O_3$ $[M+H]^+$ 380.1974, found 380.1969.



***tert*-Butyl 3-isopropoxy-5,6-diphenyl-1,2,4-triazine-4(5*H*)-carboxylate (3af)**

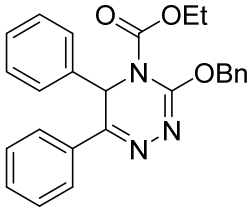
White solid. m.p. 160.0–161.1 ºC. 36 mg, 93% yield (PE:EA=20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.89 (m, 2H), 7.41 – 7.38 (m, 3H), 7.34 – 7.27 (m, 5H), 6.41 (s, 1H), 5.34 (hept, *J* = 6.0 Hz, 1H), 1.52 (s, 9H), 1.35 (d, *J* = 6.2 Hz, 3H), 1.23 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$)

δ 155.0, 151.6, 148.3, 135.1, 134.2, 130.3, 128.9, 128.8, 128.7, 127.7, 126.6, 83.7, 71.9, 52.1, 28.2, 21.9, 21.6. HRMS-ESI: calcd. for $C_{23}H_{27}N_3O_3$ $[M+H]^+$ 394.2131, found 394.2129.



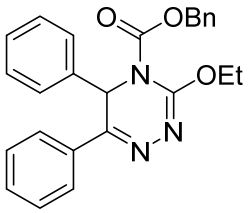
***tert*-Butyl 3-(benzyloxy)-5,6-diphenyl-1,2,4-triazine-4(5*H*)-carboxylate (3ag)**

White solid. m.p. 121.9–123.5 ºC. 31 mg, 71% yield (PE:EA=10:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.87 (m, 2H), 7.43 – 7.38 (m, 3H), 7.37 – 7.28 (m, 10H), 6.43 (s, 1H), 5.48 (d, *J* = 12.2 Hz, 1H), 5.32 (d, *J* = 12.2 Hz, 1H), 1.42 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 151.3, 148.9, 135.6, 134.9, 134.1, 130.4, 129.0, 128.84, 128.74, 128.3, 128.2, 128.1, 127.7, 126.7, 84.0, 70.0, 52.4, 28.0. HRMS-ESI: calcd. for $C_{27}H_{27}N_3O_3$ $[M+H]^+$ 442.2131, found 442.2130.



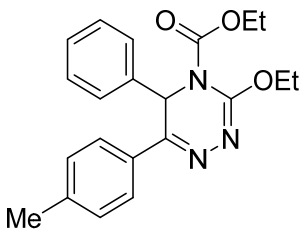
Benzyl 3-ethoxy-5,6-diphenyl-1,2,4-triazine-4(5*H*)-carboxylate (3ah)

Colorless oil. 11 mg, 30% yield (PE:EA=20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.84 (m, 2H), 7.38 – 7.26 (m, 13H), 6.43 (s, 1H), 5.49 (d, *J* = 12.3 Hz, 1H), 5.24 (d, *J* = 12.3 Hz, 1H), 4.24 (qd, *J* = 7.2, 2.6 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 152.8, 148.3, 135.6, 134.5, 134.0, 130.6, 129.04, 128.98, 128.8, 128.4, 128.2, 128.0, 127.7, 126.7, 70.2, 63.9, 52.9, 14.2. HRMS-ESI: calcd. for $C_{25}H_{23}N_3O_3$ $[M+H]^+$ 414.1818, found 414.1820.



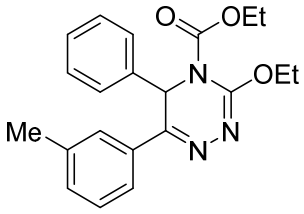
Ethyl 3-(benzyloxy)-5,6-diphenyl-1,2,4-triazine-4(5*H*)-carboxylate (3ah')

Colorless oil. 9 mg, 23% yield (PE:EA=15:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.87 (m, 2H), 7.46 – 7.37 (m, 8H), 7.33 (s, 5H), 6.50 (s, 1H), 5.37 (d, *J* = 12.2 Hz, 1H), 5.25 (d, *J* = 12.2 Hz, 1H), 4.56 – 4.44 (m, 1H), 4.42 – 4.33 (m, 1H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 152.8, 148.2, 134.9, 134.5, 134.0, 130.5, 129.04, 128.99, 128.8, 128.6, 128.6, 128.1, 127.7, 126.7, 69.3, 64.9, 52.9, 14.1. HRMS-ESI: calcd. for $C_{25}H_{23}N_3O_3$ $[M+H]^+$ 414.1818, found 414.1818.



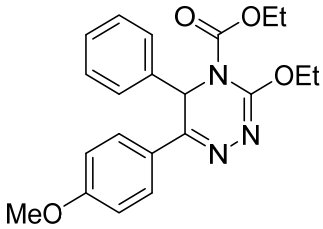
Ethyl 3-ethoxy-5-phenyl-6-(*p*-tolyl)-1,2,4-triazine-4(5*H*)-carboxylate (3ba)

Colorless oil. 26 mg, 71% yield (PE:EA=10:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.30 (s, 5H), 7.21 (d, *J* = 8.2 Hz, 2H), 6.44 (s, 1H), 4.50 (dq, *J* = 10.6, 7.1 Hz, 1H), 4.41 – 4.25 (m, 3H), 2.36 (s, 3H), 1.49 – 1.10 (m, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 152.9, 148.3, 140.9, 134.7, 131.3, 129.5, 129.0, 128.8, 127.6, 126.6, 64.8, 63.7, 52.7, 21.4, 14.2. HRMS-ESI: calcd. for $C_{21}H_{23}N_3O_3$ $[M+H]^+$ 366.1818, found 366.1817.



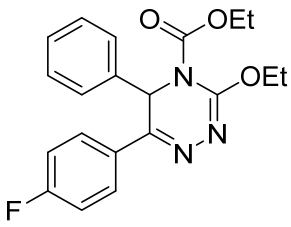
Ethyl 3-ethoxy-5-phenyl-6-(*m*-tolyl)-1,2,4-triazine-4(5*H*)-carboxylate (3ca)

Colorless oil. 29 mg, 80% yield (PE:EA=10:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.74 (m, 1H), 7.65 (d, *J* = 7.7 Hz, 1H), 7.30 (s, 5H), 7.26 (s, 1H), 7.22 (d, *J* = 7.7 Hz, 1H), 6.45 (s, 1H), 4.56 – 4.46 (m, 1H), 4.40 – 4.25 (m, 3H), 2.36 (s, 3H), 1.42 – 1.22 (m, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 152.9, 148.4, 138.5, 134.7, 134.0, 131.3, 128.9, 129.0, 128.7, 127.6, 127.2, 123.8, 64.7, 63.7, 52.7, 21.4, 14.2. HRMS-ESI: calcd. for $C_{21}H_{23}N_3O_3$ $[M+H]^+$ 366.1818, found 366.1818.



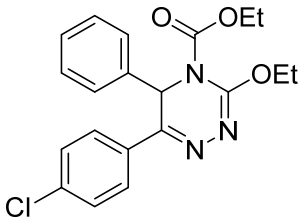
Ethyl 3-ethoxy-6-(4-methoxyphenyl)-5-phenyl-1,2,4-triazine-4(5*H*)-carboxylate (3da)

Colorless oil. 24 mg, 62% yield (PE:EA=5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.82 (m, 2H), 7.30 (s, 5H), 6.95 – 6.88 (m, 2H), 6.43 (s, 1H), 4.50 (dq, *J* = 10.6, 7.1 Hz, 1H), 4.40 – 4.26 (m, 3H), 3.82 (s, 3H), 1.38 – 1.27 (m, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 154.7, 152.9, 148.3, 134.7, 129.0, 128.9, 128.3, 127.7, 114.2, 64.7, 63.7, 55.4, 52.8, 14.2. HRMS-ESI: calcd. for $C_{21}H_{23}N_3O_4$ $[M+H]^+$ 382.1767, found 382.1768.



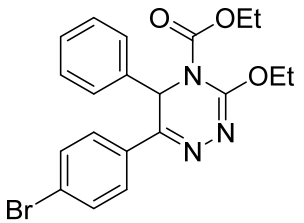
Ethyl 3-ethoxy-6-(4-fluorophenyl)-5-phenyl-1,2,4-triazine-4(5*H*)-carboxylate (3ea)

Colorless oil. 21 mg, 57% yield (PE:EA=10:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.83 (m, 2H), 7.35 – 7.28 (m, 5H), 7.08 (t, *J* = 8.6 Hz, 2H), 6.41 (s, 1H), 4.51 (dq, *J* = 10.6, 7.1 Hz, 1H), 4.42 – 4.24 (m, 3H), 1.43 – 1.21 (m, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ164.1 (d, *J* = 251.4 Hz), 154.0, 152.9, 148.4, 134.4, 130.3 (d, *J* = 2.82 Hz), 129.09, 129.07, 128.6 (d, *J* = 8.6 Hz), 127.7, 115.9 (d, *J* = 21.9 Hz), 64.9, 63.8, 52.8, 14.2. HRMS-ESI: calcd. for $C_{20}H_{20}FN_3O_3$ $[M+H]^+$ 370.1567, found 370.1562.



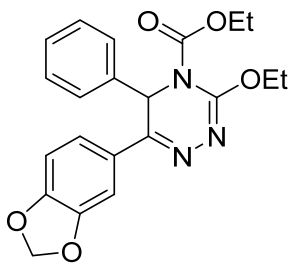
Ethyl 3-ethoxy-6-(4-chlorophenyl)-5-phenyl-1,2,4-triazine-4(5*H*)-carboxylate (3fa)

Colorless oil. 29 mg, 75% yield (PE:EA=10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.82 (m, 2H), 7.38 – 7.36 (m, 2H), 7.33 – 7.28 (m, 5H), 6.39 (s, 1H), 4.51 (dq, *J* = 10.6, 7.1 Hz, 1H), 4.38– 4.30 (m, 3H), 1.36 – 1.30 (m, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 152.9, 148.4, 136.6, 134.4, 132.5, 129.1, 129.0, 127.9, 127.6, 64.9, 63.9, 52.7, 14.2. HRMS-ESI: calcd. for $C_{20}H_{20}ClN_3O_3$ $[M+H]^+$ 386.1271, found 386.1267.



Ethyl 6-(4-bromophenyl)-3-ethoxy-5-phenyl-1,2,4-triazine-4(5*H*)-carboxylate (3ga)

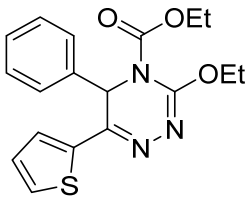
Colorless oil. 36 mg, 84% yield (PE:EA=10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.27 (m, 5H), 6.39 (s, 1H), 4.52 (dq, *J* = 10.4, 6.8 Hz, 1H), 4.42 – 4.25 (m, 3H), 1.40 – 1.29 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1, 152.8, 148.4, 134.4, 133.0, 132.0, 129.1, 128.1, 127.6, 125.0, 64.9, 63.9, 52.6, 14.2. HRMS-ESI: calcd. for $C_{20}H_{20}BrN_3O_3$ $[M+H]^+$ 430.0766, found 430.0759.



Ethyl 6-(benzo[d][1,3]dioxol-5-yl)-3-ethoxy-5-phenyl-1,2,4-triazine-4(5H)-carboxylate (3ia)

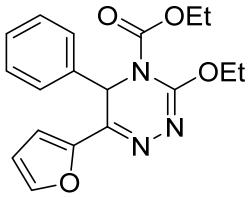
Colorless oil. 24 mg, 60% yield (PE:EA=7:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 1.7 Hz, 1H),

7.23 (s, 5H), 7.20 – 7.17 (m, 1H), 6.71 (d, *J* = 8.2 Hz, 1H), 6.31 (s, 1H), 5.92 (s, 2H), 4.42 (dq, *J* = 10.6, 7.1 Hz, 1H), 4.32 – 4.19 (m, 3H), 1.25 (dt, *J* = 7.1 Hz, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4, 151.9, 148.7, 147.3, 147.3, 133.7, 128.0, 127.9, 127.5, 126.6, 120.6, 107.1, 105.6, 100.5, 63.7, 62.70, 51.9, 13.2. HRMS-ESI: calcd. for $C_{21}H_{21}N_3O_5$ $[M+H]^+$ 396.1559, found 396.1558.



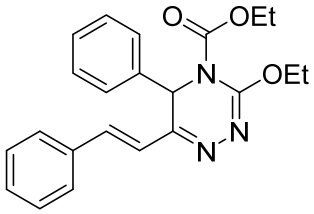
Ethyl 3-ethoxy-5-phenyl-6-(thiophen-2-yl)-1,2,4-triazine-4(5*H*)-carboxylate (3ja)

Colorless oil. 28 mg, 80% yield (PE:EA=10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.35 – 7.29 (m, 6H), 7.02 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.37 (s, 1H), 4.49 (dq, *J* = 10.6, 7.1 Hz, 1H), 4.40 – 4.26 (m, 3H), 1.38 – 1.23 (m, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 152.8, 151.0, 148.4, 139.3, 134.6, 129.6, 129.02, 128.98, 128.0, 127.6, 127.5, 64.9, 63.8, 53.7, 14.2. HRMS-ESI: calcd. for $C_{18}H_{19}N_3O_3S$ $[M+H]^+$ 358.1225, found 358.1223.



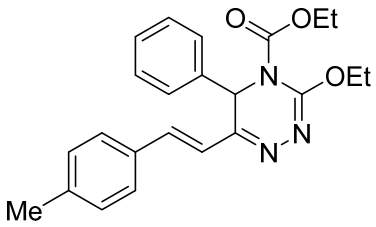
Ethyl 3-ethoxy-6-(furan-2-yl)-5-phenyl-1,2,4-triazine-4(5*H*)-carboxylate (3ka)

Colorless oil. 22 mg, 65% yield (PE:EA=5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 1.8, 0.7 Hz, 1H), 7.33 (s, 5H), 7.09 (d, *J* = 3.5 Hz, 1H), 6.53 (dd, *J* = 3.5, 1.8 Hz, 1H), 6.41 (s, 1H), 4.53 (dq, *J* = 10.6, 7.1 Hz, 1H), 4.45 – 4.26 (m, 3H), 1.35 (q, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.7, 149.1, 148.2, 147.8, 144.7, 134.8, 128.9, 128.8, 127.3, 112.3, 111.9, 64.9, 63.8, 52.5, 14.2. HRMS-ESI: calcd. for $C_{18}H_{19}N_3O_4$ $[M+H]^+$ 342.1454, found 342.1453.



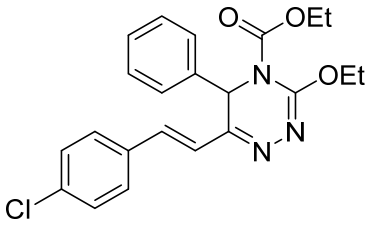
Ethyl (*E*)-3-ethoxy-5-phenyl-6-styryl-1,2,4-triazine-4(5*H*)-carboxylate (3la)

Colorless oil. 28 mg, 76% yield (PE:EA=8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 2H), 7.41 – 7.31 (m, 8H), 7.25 (d, *J* = 16.7 Hz, 1H), 7.01 (d, *J* = 16.7 Hz, 1H), 6.32 (s, 1H), 4.52 (dq, *J* = 10.7, 7.1 Hz, 1H), 4.43 – 4.29 (m, 3H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 152.9, 148.4, 136.8, 135.5, 134.6, 129.3, 129.0, 128.9, 128.8, 127.41, 127.38, 124.6, 65.0, 63.9, 52.1, 14.20, 14.16. HRMS-ESI: calcd. for $C_{22}H_{23}N_3O_3$ $[M+H]^+$ 378.1818, found 378.1816.



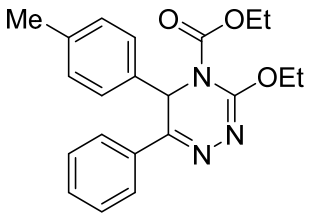
Ethyl (*E*)-3-ethoxy-6-(4-methylstyryl)-5-phenyl-1,2,4-triazine-4(5*H*)-carboxylate (3ma)

Colorless oil. 21 mg, 53% yield (PE:EA=5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.1 Hz, 2H), 7.35 – 7.29 (m, 5H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.98 (d, *J* = 16.6 Hz, 1H), 6.31 (s, 1H), 4.56 – 4.44 (m, 1H), 4.41 – 4.27 (m, 3H), 2.35 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 153.0, 148.2, 139.4, 136.3, 134.8, 132.9, 129.5, 129.0, 128.8, 127.4, 127.3, 124.0, 64.8, 63.8, 52.1, 21.4, 14.2. HRMS-ESI: calcd. for $C_{23}H_{25}N_3O_3$ $[M+H]^+$ 392.1974, found 392.1970.



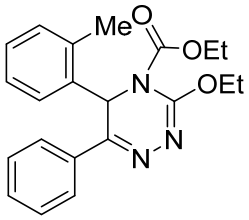
Ethyl (*E*)-6-(4-chlorostyryl)-3-ethoxy-5-phenyl-1,2,4-triazine-4(5*H*)-carboxylate (3na)

Colorless oil. 23 mg, 58% yield (PE:EA=5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 2H), 7.35 – 7.29 (m, 7H), 7.14 (d, *J* = 16.7 Hz, 1H), 6.90 (d, *J* = 16.7 Hz, 1H), 6.24 (s, 1H), 4.54 – 4.45 (m, 1H), 4.41 – 4.25 (m, 3H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 151.9, 147.2, 133.9, 133.7, 133.6, 133.1, 128.0, 127.9, 127.4, 126.4, 124.5, 63.9, 62.8, 51.0, 13.2, 13.1. HRMS-ESI: calcd. for $C_{22}H_{22}ClN_3O_3$ $[M+H]^+$ 412.1428, found 412.1426.



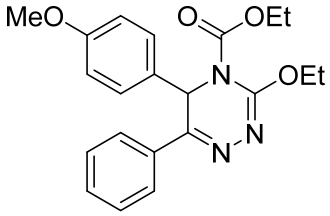
Ethyl 3-ethoxy-6-phenyl-5-(*p*-tolyl)-1,2,4-triazine-4(5*H*)-carboxylate (3oa)

Colorless oil. 26 mg, 73% yield (PE:EA=10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.90 (m, 2H), 7.45 – 7.38 (m, 3H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 6.43 (s, 1H), 4.54 (dq, *J* = 10.5, 7.1 Hz, 1H), 4.43 – 4.28 (m, 3H), 2.33 (s, 3H), 1.36 (q, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 152.9, 148.4, 138.9, 134.1, 131.7, 130.4, 129.7, 128.7, 127.7, 126.6, 64.8, 63.7, 52.7, 21.2, 14.2. HRMS-ESI: calcd. for $C_{21}H_{23}N_3O_3$ $[M+H]^+$ 366.1818, found 366.1815.



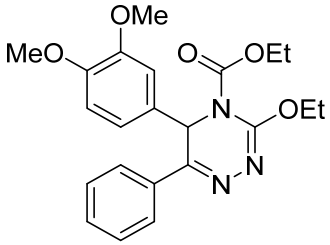
Ethyl 3-ethoxy-6-phenyl-5-(*o*-tolyl)-1,2,4-triazine-4(5*H*)-carboxylate (3pa)

Colorless oil. 27 mg, 74% yield (PE:EA=10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.81 (m, 2H), 7.41 (dd, *J* = 5.0, 2.0 Hz, 3H), 7.27 – 7.22 (m, 2H), 7.10 – 7.04 (m, 1H), 7.02 – 6.98 (m, 1H), 6.62 (s, 1H), 4.55 (dq, *J* = 10.7, 7.1 Hz, 1H), 4.45 – 4.22 (m, 3H), 2.65 (s, 3H), 1.37 – 1.31 (m, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 152.9, 148.9, 137.1, 133.9, 131.4, 131.3, 130.5, 129.3, 128.8, 128.6, 126.6, 126.5, 64.8, 63.7, 50.9, 19.4, 14.2. HRMS-ESI: calcd. for $C_{21}H_{23}N_3O_3$ $[M+H]^+$ 366.1818, found 366.1816.



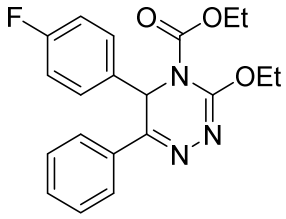
Ethyl 3-ethoxy-5-(4-methoxyphenyl)-6-phenyl-1,2,4-triazine-4(5*H*)-carboxylate (3qa)

Colorless oil. 25 mg, 65% yield (PE:EA=5:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.78 (m, 2H), 7.44 – 7.36 (m, 3H), 7.27 – 7.22 (m, 3H), 6.91 – 6.76 (m, 2H), 6.39 (s, 1H), 4.61 – 4.44 (m, 1H), 4.44 – 4.15 (m, 3H), 3.76 (s, 3H), 1.33 (q, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 155.2, 152.9, 148.4, 134.0, 130.4, 129.2, 128.7, 126.6, 114.4, 64.8, 63.7, 55.2, 52.5, 14.2. HRMS-ESI: calcd. for $C_{21}H_{23}N_3O_4$ $[M+H]^+$ 382.1767, found 382.1765.



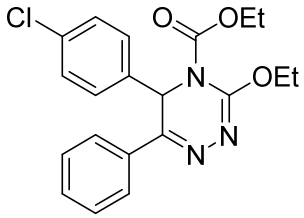
Ethyl 5-(3,4-dimethoxyphenyl)-3-ethoxy-6-phenyl-1,2,4-triazine-4(5*H*)-carboxylate (3ra)

Colorless oil. 25 mg, 62% yield (PE:EA=5:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.87 (m, 2H), 7.43 – 7.37 (m, 3H), 6.88 (d, *J* = 1.9 Hz, 1H), 6.84 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.76 (d, *J* = 8.3 Hz, 1H), 6.38 (s, 1H), 4.60 – 4.48 (m, 1H), 4.46 – 4.37 (m, 1H), 4.37 – 4.26 (m, 2H), 3.84 (s, 3H), 3.83 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1, 151.9, 148.5, 148.3, 147.4, 133.0, 129.4, 128.5, 127.7, 125.6, 119.4, 110.1, 109.6, 63.7, 62.7, 54.9, 54.8, 51.8, 13.2, 13.2. HRMS-ESI: calcd. for $C_{22}H_{25}N_3O_5$ $[M+H]^+$ 412.1872, found 412.1872.



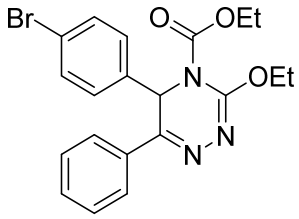
Ethyl 3-ethoxy-5-(4-fluorophenyl)-6-phenyl-1,2,4-triazine-4(5*H*)-carboxylate (3sa)

Colorless oil. 28 mg, 76% yield (PE:EA=10:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.80 (m, 2H), 7.44 – 7.37 (m, 3H), 7.34 – 7.27 (m, 2H), 6.99 (t, *J* = 8.7 Hz, 2H), 6.42 (s, 1H), 4.52 (dq, *J* = 10.6, 7.1 Hz, 1H), 4.42 – 4.26 (m, 3H), 1.34 (q, *J* = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0 (d, *J* = 248.2 Hz), 154.8, 152.9, 148.3, 133.8, 130.6, 130.45 (d, *J* = 3.1 Hz), 129.68 (d, *J* = 8.5 Hz), 128.8, 126.6, 116.0 (d, *J* = 21.7 Hz), 64.9, 63.8, 52.0, 14.2. HRMS-ESI: calcd. for $C_{20}H_{20}FN_3O_3$ $[M+H]^+$ 370.1567, found 370.1564.



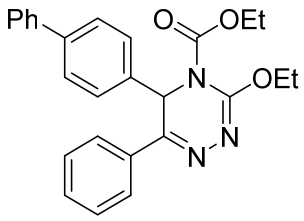
Ethyl 5-(4-chlorophenyl)-3-ethoxy-6-phenyl-1,2,4-triazine-4(5*H*)-carboxylate (3ta)

Colorless oil. 32 mg, 84% yield (PE:EA=10:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.82 (m, 2H), 7.45 – 7.37 (m, 3H), 7.34 – 7.22 (m, 5H), 6.41 (s, 1H), 4.57 – 4.47 (m, 1H), 4.41 – 4.28 (m, 3H), 1.50 – 1.17 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 152.9, 148.3, 135.0, 133.8, 133.1, 130.7, 129.3, 129.2, 128.9, 126.6, 65.0, 63.9, 52.0, 14.22, 14.20. HRMS-ESI: calcd. for $C_{20}H_{20}ClN_3O_3$ $[M+H]^+$ 386.1271, found 386.1268.



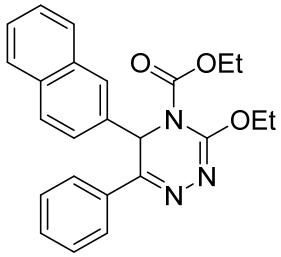
Ethyl 5-(4-bromophenyl)-3-ethoxy-6-phenyl-1,2,4-triazine-4(5*H*)-carboxylate (3ua)

Colorless oil. 27 mg, 63% yield (PE:EA=10:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.82 (m, 2H), 7.47 – 7.36 (m, 5H), 7.19 (dd, *J* = 8.5, 2.1 Hz, 2H), 6.39 (s, 1H), 4.57 – 4.47 (m, 1H), 4.42 – 4.26 (m, 3H), 1.37 – 1.30 (m, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 152.9, 148.2, 133.8, 133.6, 132.2, 130.6, 129.4, 128.9, 126.6, 123.2, 64.9, 63.9, 52.1, 14.2. HRMS-ESI: calcd. for $C_{20}H_{20}BrN_3O_3$ $[M+H]^+$ 430.0766, found 430.0764.



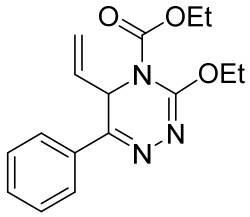
Ethyl 5-([1,1'-biphenyl]-4-yl)-3-ethoxy-6-phenyl-1,2,4-triazine-4(5*H*)-carboxylate (3va)

Colorless oil. 22 mg, 51% yield (PE:EA=10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.84 (m, 2H), 7.55 – 7.51 (m, 4H), 7.44 – 7.32 (m, 8H), 6.50 (s, 1H), 4.56 (dq, *J* = 10.6, 7.1 Hz, 1H), 4.45 – 4.27 (m, 3H), 1.35 (q, *J* = 7.1 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 152.9, 148.4, 141.8, 140.3, 134.0, 133.6, 130.5, 128.8, 128.1, 127.7, 127.6, 127.1, 126.7, 126.1, 64.9, 63.8, 52.6, 14.2. HRMS-ESI: calcd. for $C_{26}H_{25}N_3O_3$ $[M+H]^+$ 428.1974, found 428.1972.



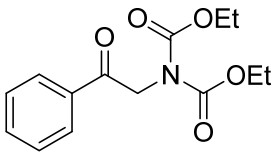
Ethyl 3-ethoxy-5-(naphthalen-2-yl)-6-phenyl-1,2,4-triazine-4(5*H*)-carboxylate (3xa)

Pale yellow oil. 23 mg, 57% yield (PE:EA=10:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.93 (m, 2H), 7.86 – 7.79 (m, 2H), 7.78 – 7.74 (m, 1H), 7.70 – 7.67 (m, 1H), 7.54 – 7.44 (m, 3H), 7.43 – 7.38 (m, 3H), 6.62 (s, 1H), 4.53 (dq, *J* = 10.6, 7.1 Hz, 1H), 4.41 – 4.29 (m, 3H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 153.0, 148.3, 134.1, 133.4, 133.1, 131.8, 130.5, 129.1, 128.8, 128.3, 127.6, 127.2, 126.7, 126.4, 125.3, 64.8, 63.8, 53.0, 14.2, 14.2. HRMS-ESI: calcd. for $C_{24}H_{23}N_3O_3$ $[M+H]^+$ 402.1818, found 402.1820.



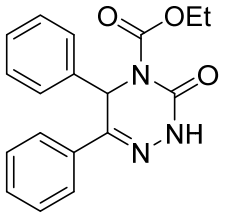
Ethyl 3-ethoxy-6-phenyl-5-vinyl-1,2,4-triazine-4(5*H*)-carboxylate (3ya)

Colorless oil. 1 mg, trace. (PE:EA = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.91 (m, 2H), 7.49 – 7.43 (m, 3H), 5.91 (d, *J* = 4.8 Hz, 1H), 5.74 (ddd, J = 17.2, 10.4, 4.8 Hz, 2H), 5.34 (dd, J = 10.4, 1.1 Hz, 1H), 5.26 (dd, *J* = 17.2, 1.1 Hz, 1H), 4.64 – 4.58 (m, 2H), 4.38 – 4.28 (m, 2H), 1.43 (t, J = 7.1 Hz, 3H), 1.34 (t, *J* = 7.0 Hz, 3H). HRMS-ESI: calcd. for $C_{16}H_{19}N_3O_3$ $[M+H]^+$ 324.1324, found 324.1322.



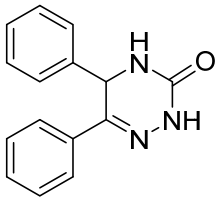
Imidodicarbonic acid, 2-oxo-2-phenylethyl-, 1,3-diethyl ester (4a)

Colorless oil. 23 mg, 85% yield (PE:EA=10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.67 – 7.62 (m, 1H), 7.57 – 7.48 (m, 2H), 5.17 (s, 2H), 4.30 (q, *J* = 7.1 Hz, 4H), 1.32 (t, *J* = 7.1 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 152.3, 133.8, 132.7, 127.8, 126.9, 62.4, 51.2, 13.1. HRMS-ESI: calcd. for $C_{14}H_{17}NO_5$ $[M+H]^+$ 280.1185, found 280.1188.



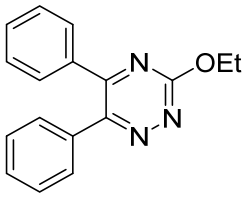
Ethyl 3-oxo-5,6-diphenyl-2,5-dihydro-1,2,4-triazine-4(3*H*)-carboxylate (5a)

White solid. m.p. 189.7–190.6 °C. 33 mg, 96% yield (PE:EA=5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (br s, 1H), 7.83 – 7.69 (m, 2H), 7.45 – 7.37 (m, 5H), 7.35 – 7.29 (m, 3H), 6.63 (s, 1H), 4.48 – 4.32 (m, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4, 148.9, 147.9, 135.0, 133.1, 130.4, 129.2, 129.1, 128.9, 127.5, 126.1, 64.3, 55.5, 14.3. HRMS-ESI: calcd. for $C_{18}H_{17}N_3O_3$ $[M+Na]^+$ 346.1168, found 346.1167.



5,6-Diphenyl-4,5-dihydro-1,2,4-triazin-3(2*H*)-one (5b)

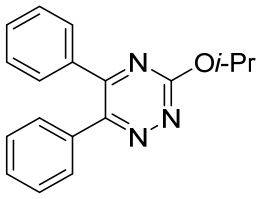
White solid. m.p. 224.6–226.0 °C. 29 mg, 72% yield (PE:EA=1:8). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.24 (br s, 1H), 8.02 (br s, 1H), 7.72 (d, 2H), 7.50 – 7.11 (m, 8H), 5.71 (d, *J* = 2.6 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 151.8, 143.7, 141.0, 134.5, 129.5, 129.4, 129.0, 128.5, 127.4, 126.1, 53.9. HRMS-ESI: calcd. for $C_{15}H_{13}N_3O$ $[M+H]^+$ 252.1137, found 252.1135.



3-Ethoxy-5,6-diphenyl-1,2,4-triazine (6a)[10]

Colorless solid. 10 mg, 91% yield (PE:EA=15:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.52 (m,

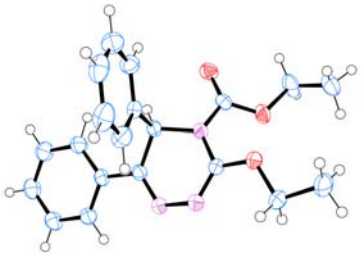
2H), 7.50 – 7.47 (m, 2H), 7.46 – 7.30 (m, 6H), 4.72 (q, J = 7.1 Hz, 2H), 1.55 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.95, 158.5, 153.4, 135.5, 135.3, 130.8, 129.8, 129.3, 129.1, 128.5, 128.4, 64.8, 14.5. HRMS-ESI: calcd. for $C_{17}H_{15}N_3O$ $[M+H]^+$ 278.1293, found 278.1294.



3-Isopropoxy-5,6-diphenyl-1,2,4-triazine (6b)[11]

Pale yellow solid. 15 mg, 56% yield (PE:EA=15:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 2H), 7.51 – 7.46 (m, 2H), 7.44 – 7.40 (m, 1H), 7.39 – 7.29 (m, 5H), 5.62 (p, J = 6.2 Hz, 1H), 1.53 (d, J = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 158.5, 153.1, 135.6, 135.3, 130.8, 129.8, 129.3, 129.0, 128.5, 128.4, 72.0, 21.9. HRMS-ESI: calcd. for $C_{18}H_{17}N_3O$ $[M+H]^+$ 292.1450, found 292.1456.

5. ORTEP drawings



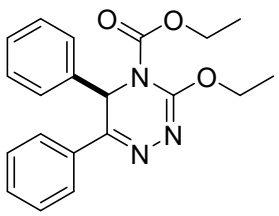
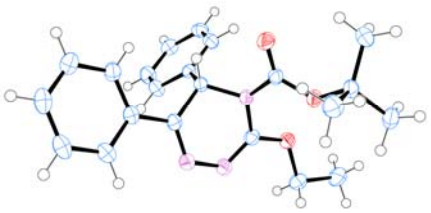


Table 1. Crystal data and structure refinement for 3aa (CCDC 1997893)

Identification code	**3aa**
Empirical formula	$C_{20}H_{21}N_3O_3$
Formula weight	351.40
Temperature/K	113(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	P2(1)/n
a/Å	11.184(2)
b/Å	9.4457(19)
c/Å	17.793(4)
α/°	90
β/°	106.40(3)
γ/°	90
Volume/$Å^3$	1803.2(7)
Z	4
$\rho_{calc}Mg/cm^3$	1.294
Absorption coefficient /mm^{-1}	0.089
F(000)	744
Crystal size/mm^3	0.200 x 0.180 x 0.120
Theta range for data collection /°	2.464 to 27.914
Limiting indices	-14<=h<=14, -12<=k<=12, -23<=l<=22
Reflections collected / unique	17640 / 4299 [R(int) = 0.0439]
Completeness to theta = 25.242	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1 and 0.8777
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4299/0/237
Goodness-of-fit on F^2	1.084
Final R indexes [I>=2σ (I)]	R_1 = 0.0521, wR_2 = 0.1309
Final R indexes [all data]	R_1 = 0.0655, wR_2 = 0.1408
Extinction coefficient	n/a
Largest diff. peak/hole / e $Å^{-3}$	0.211/-0.240



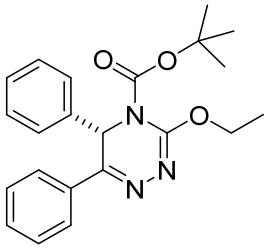
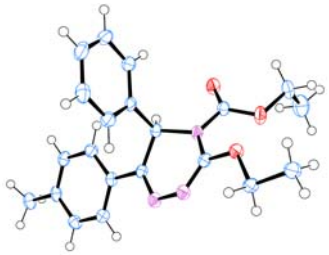


Table 2. Crystal data and structure refinement for 3ae (CCDC 1997894)

Identification code	**3ae**
Empirical formula	$C_{22}H_{25}N_3O_3$
Formula weight	379.45
Temperature/K	113(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	P2(1)/c
a/Å	10.229(2)
b/Å	25.970(5)
c/Å	8.0314(16)
α/°	90
β/°	109.33(3)
γ/°	90
Volume/Å^3	2013.1(8)
Z	4
ρ_{calc}/Mg/m^3	1.252
Absorption coefficient /mm^{-1}	0.084
F(000)	808
Crystal size/mm^3	0.200 x 0.180 x 0.120
Theta range for data collection /°	2.110 to 27.896
Limiting indices	-13<=h<=13, -34<=k<=27, -10<=l<=10
Reflections collected / unique	16735 / 4797 [R(int) = 0.0480]
Completeness to theta = 25.242	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1 and 0.9033
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4797 / 0 / 257
Goodness-of-fit on F^2	1.084
Final R indexes [I>=2σ (I)]	R_1 = 0.0575, wR_2 = 0.1274
Final R indexes [all data]	R_1 = 0.0749, wR_2 = 0.1383
Extinction coefficient	n/a
Largest diff. peak/hole / e Å^{-3}	0.189/-0.285



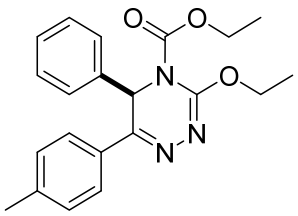


Table 3. Crystal data and structure refinement for 3ba (CCDC 1997895)

Identification code	**3ba**
Empirical formula	$C_{21}H_{23}N_3O_3$
Formula weight	365.42
Temperature/K	113(2) K
Wavelength	0.71073 A
Crystal system	Triclinic
Space group	P-1
a/Å	8.5924(17)
b/Å	10.775(2)
c/Å	11.247(2)
α/°	105.66(3)
β/°	103.08(3)
γ/°	101.25(3)
Volume/Å^3	939.6(4)
Z	2
ρ_{calc}/Mg/m^3	1.292
Absorption coefficient /mm^{-1}	0.088
F(000)	388
Crystal size/mm^3	0.200 x 0.180 x 0.120
Theta range for data collection /°	1.968 to 27.860
Limiting indices	-11<=h<=11, -14<=k<=14, -14<=l<=14
Reflections collected / unique	11190 / 4440 [R(int) = 0.0378]
Completeness to theta = 25.242	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1 and 0.8130
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4440 / 0 / 247
Goodness-of-fit on F^2	1.008
Final R indexes [I>=2σ (I)]	R_1 = 0.0511, wR_2 = 0.1159
Final R indexes [all data]	R_1 = 0.0766, wR_2 = 0.1295
Extinction coefficient	n/a
Largest diff. peak/hole / e Å^{-3}	0.222/-0.302

6. References

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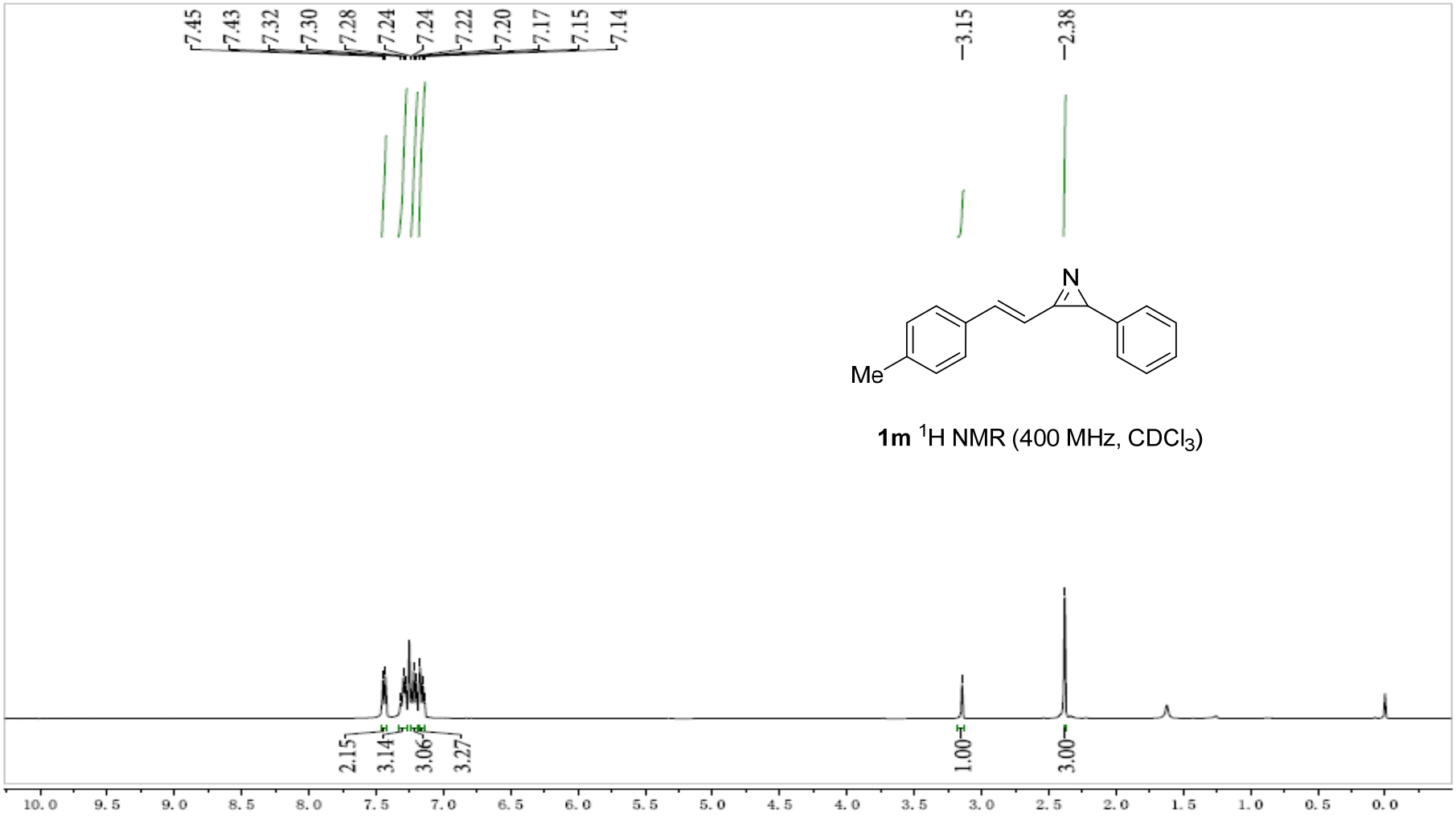
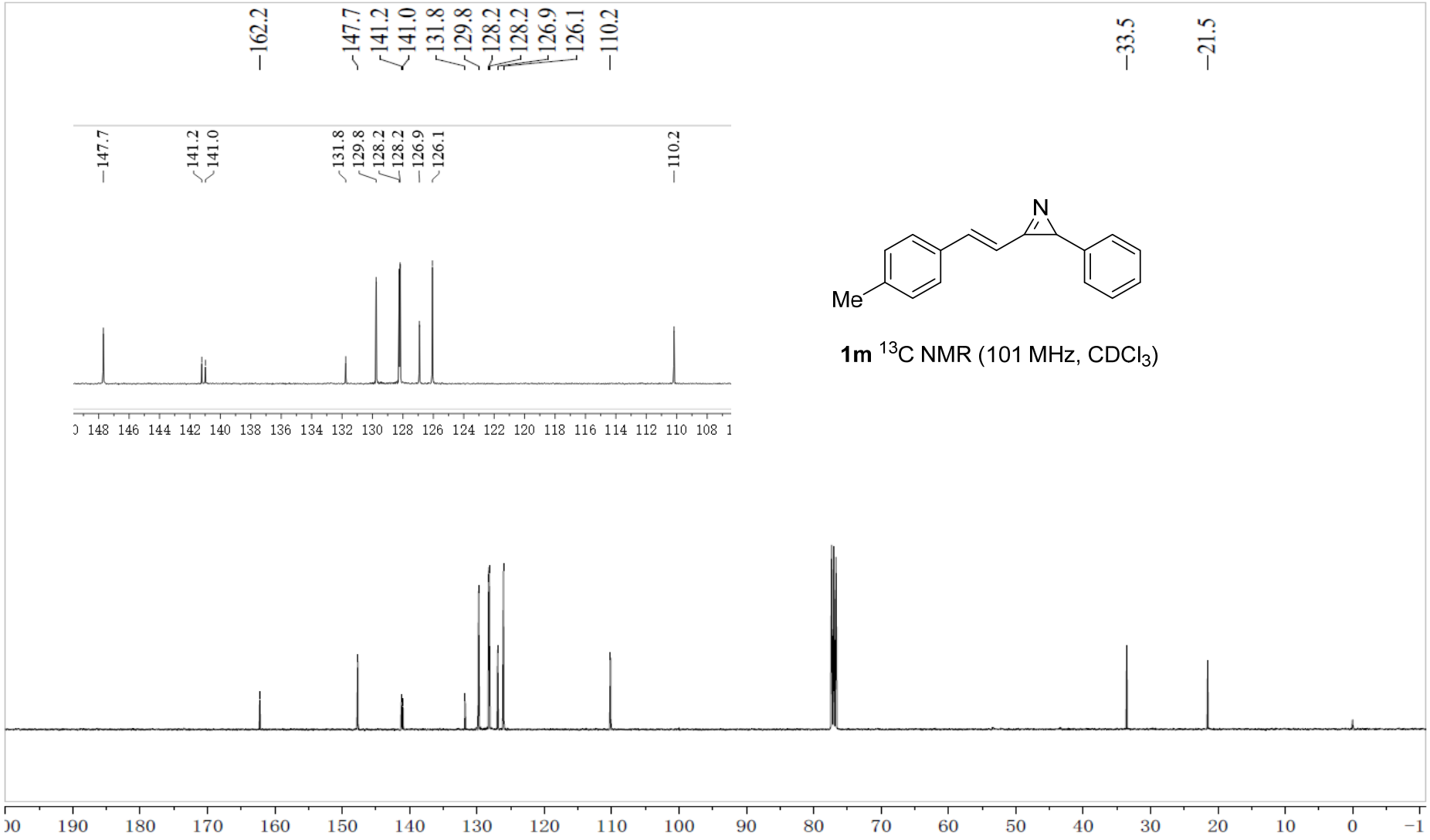
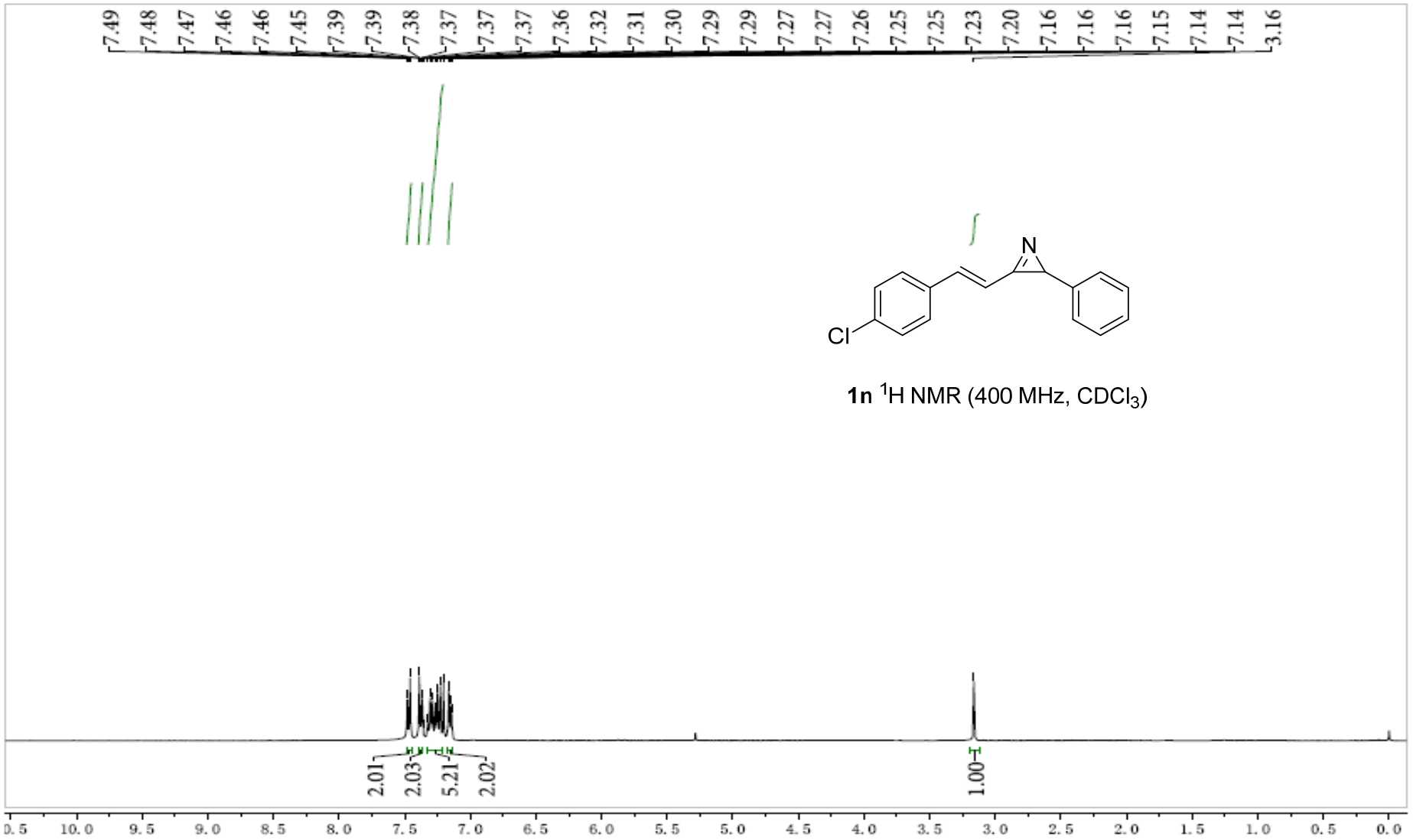
7. NMR spectra for new compounds



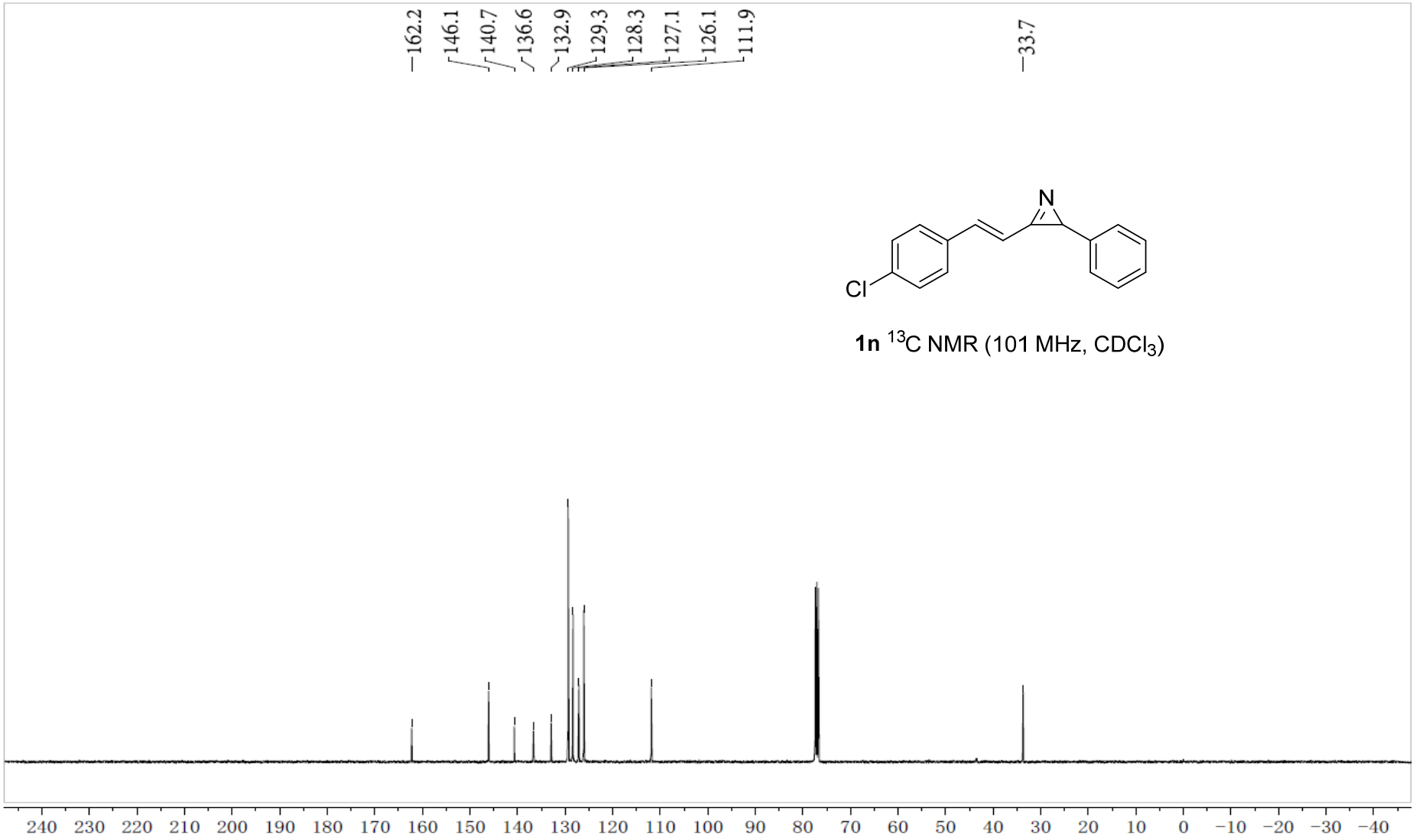
1m ^{1}H NMR (400 MHz, $CDCl_3$)



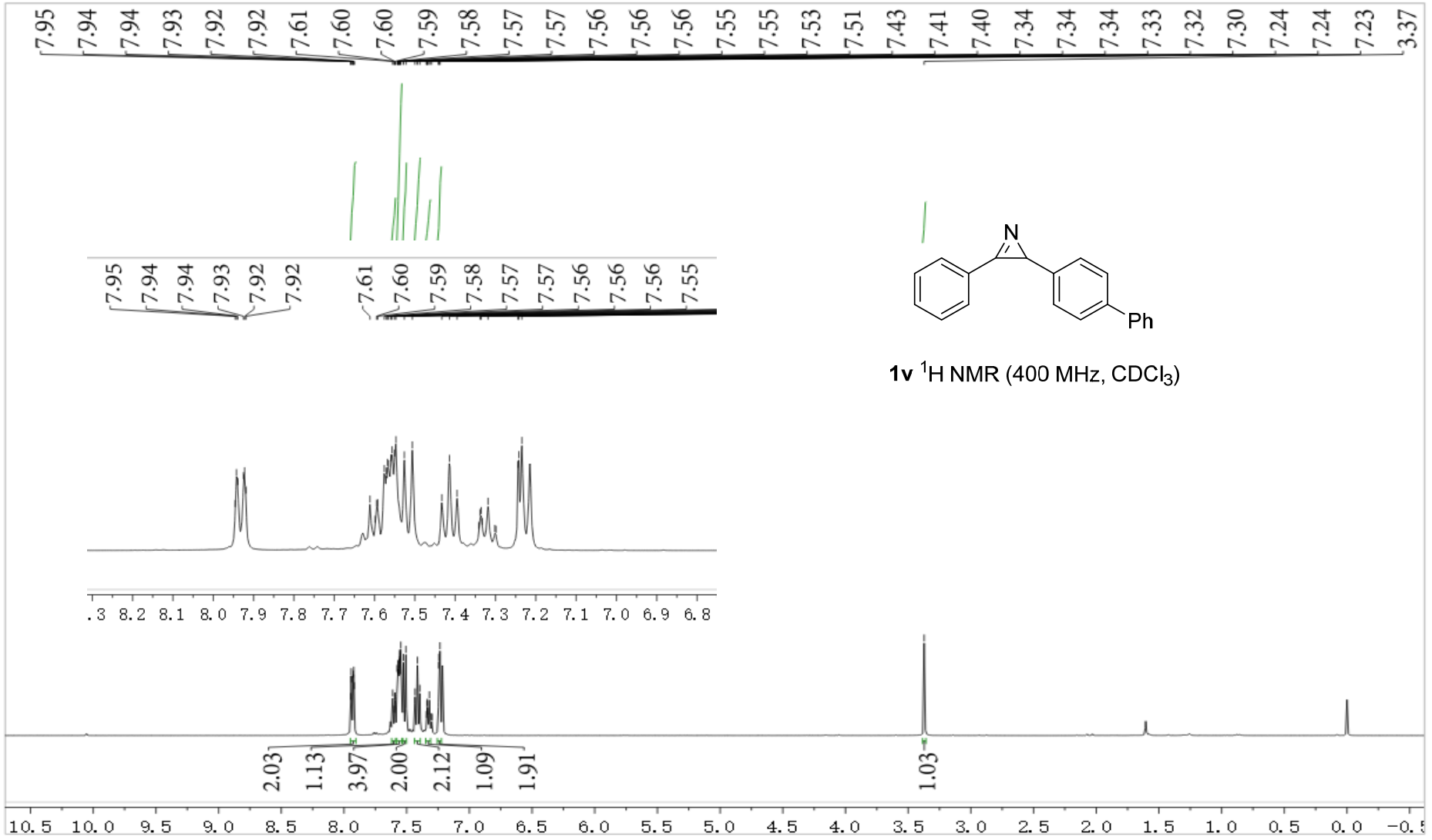
1m ^{13}C NMR (101 MHz, $CDCl_3$)



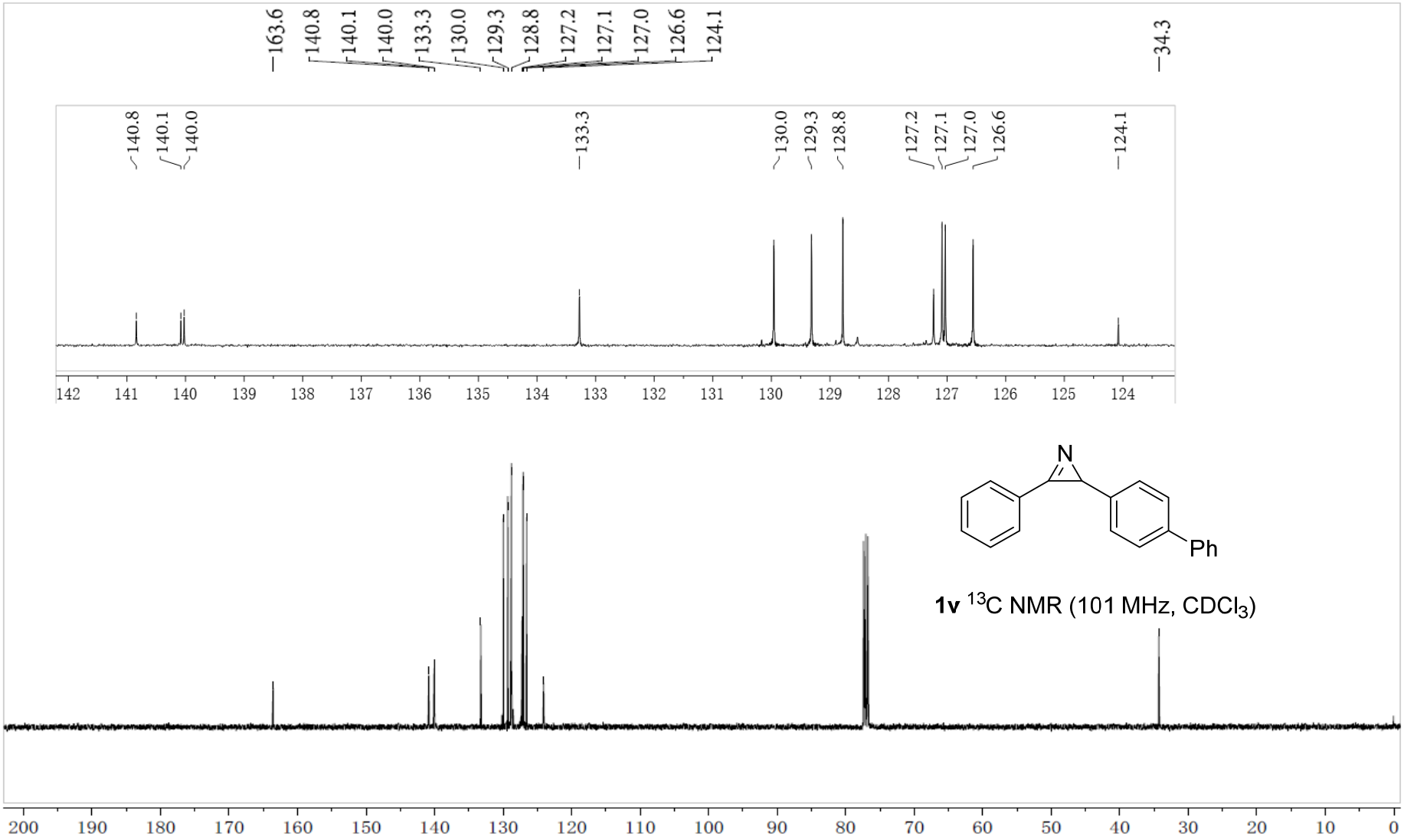
1n ^{1}H NMR (400 MHz, $CDCl_3$)



1n ^{13}C NMR (101 MHz, $CDCl_3$)



1v ^{1}H NMR (400 MHz, $CDCl_3$)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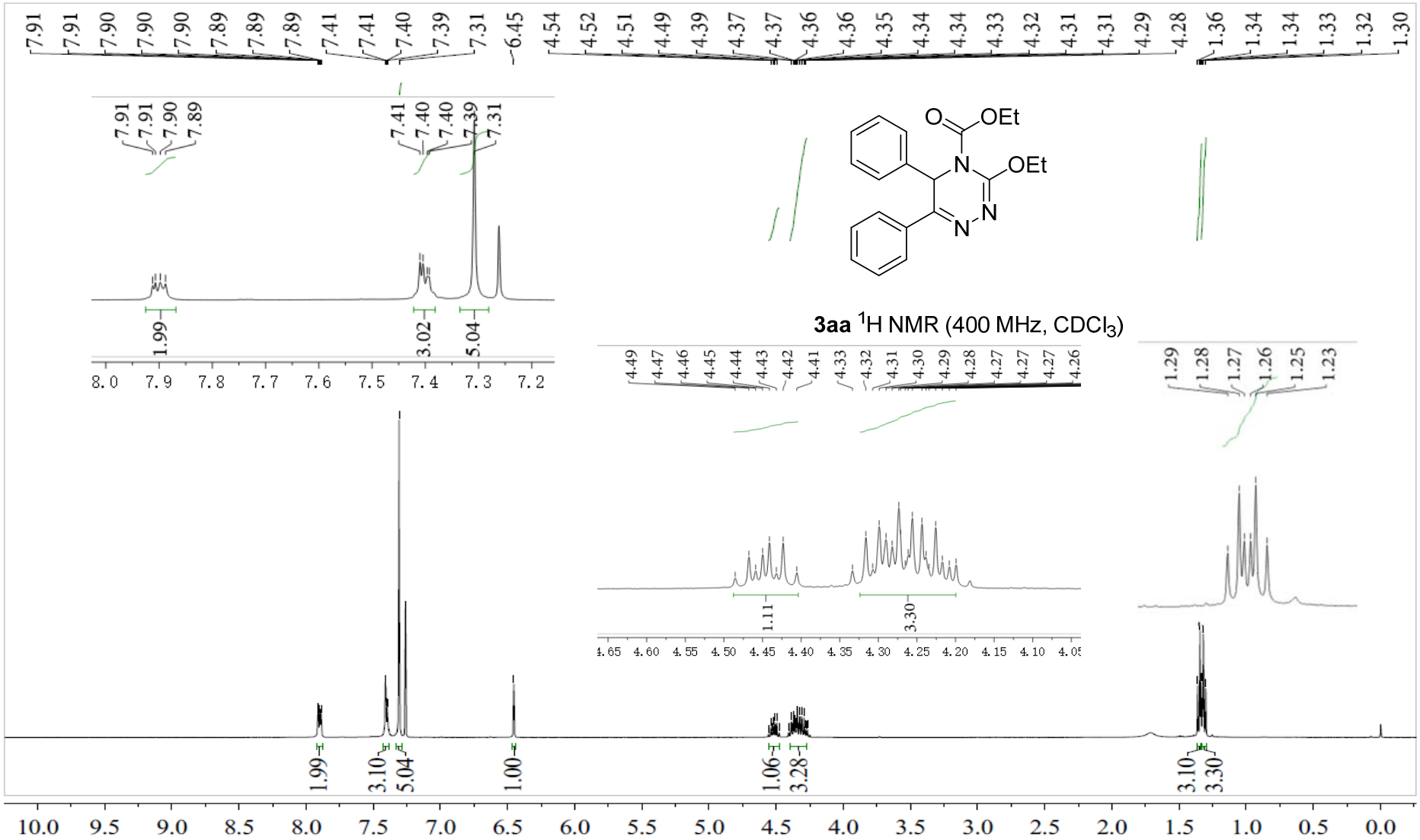
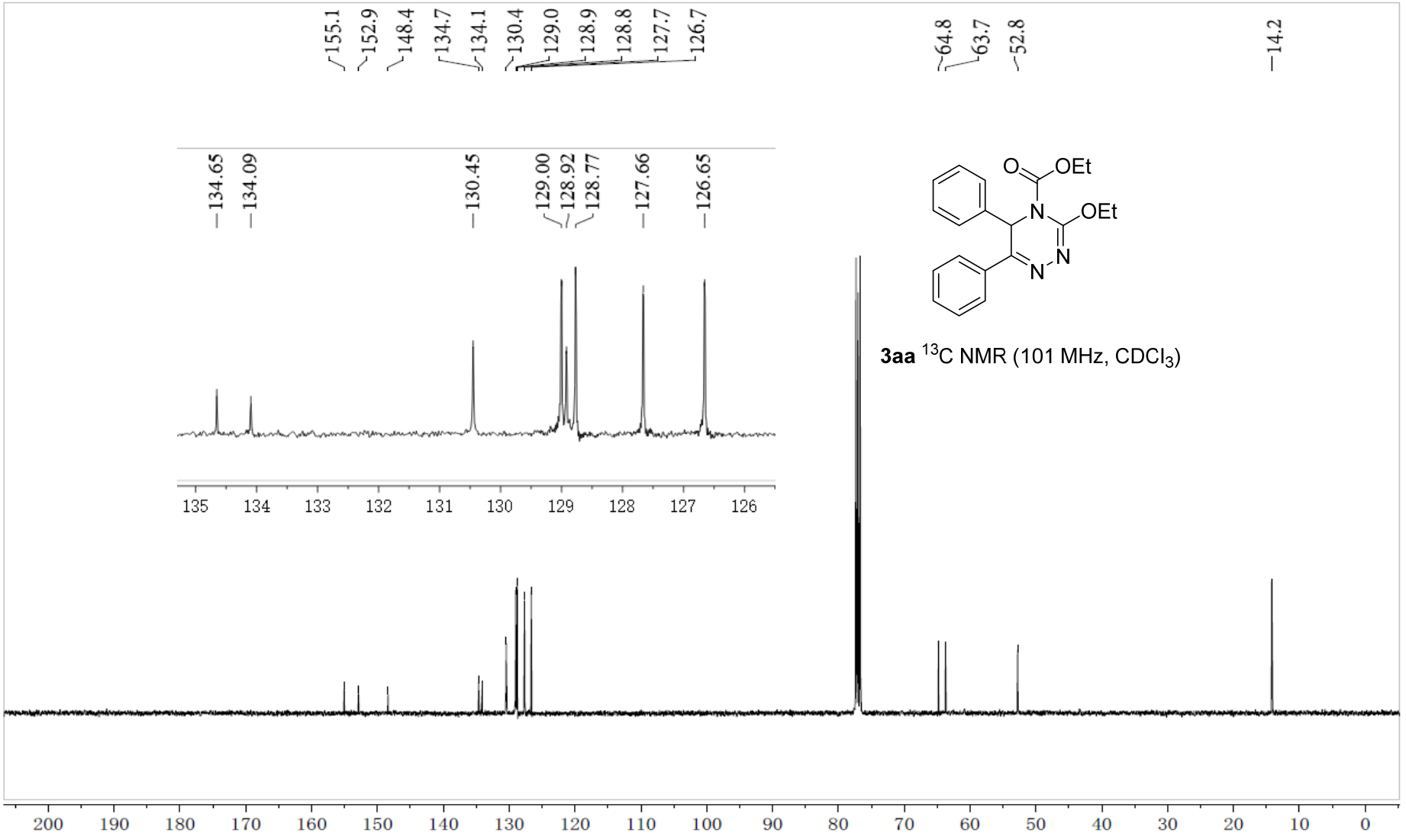
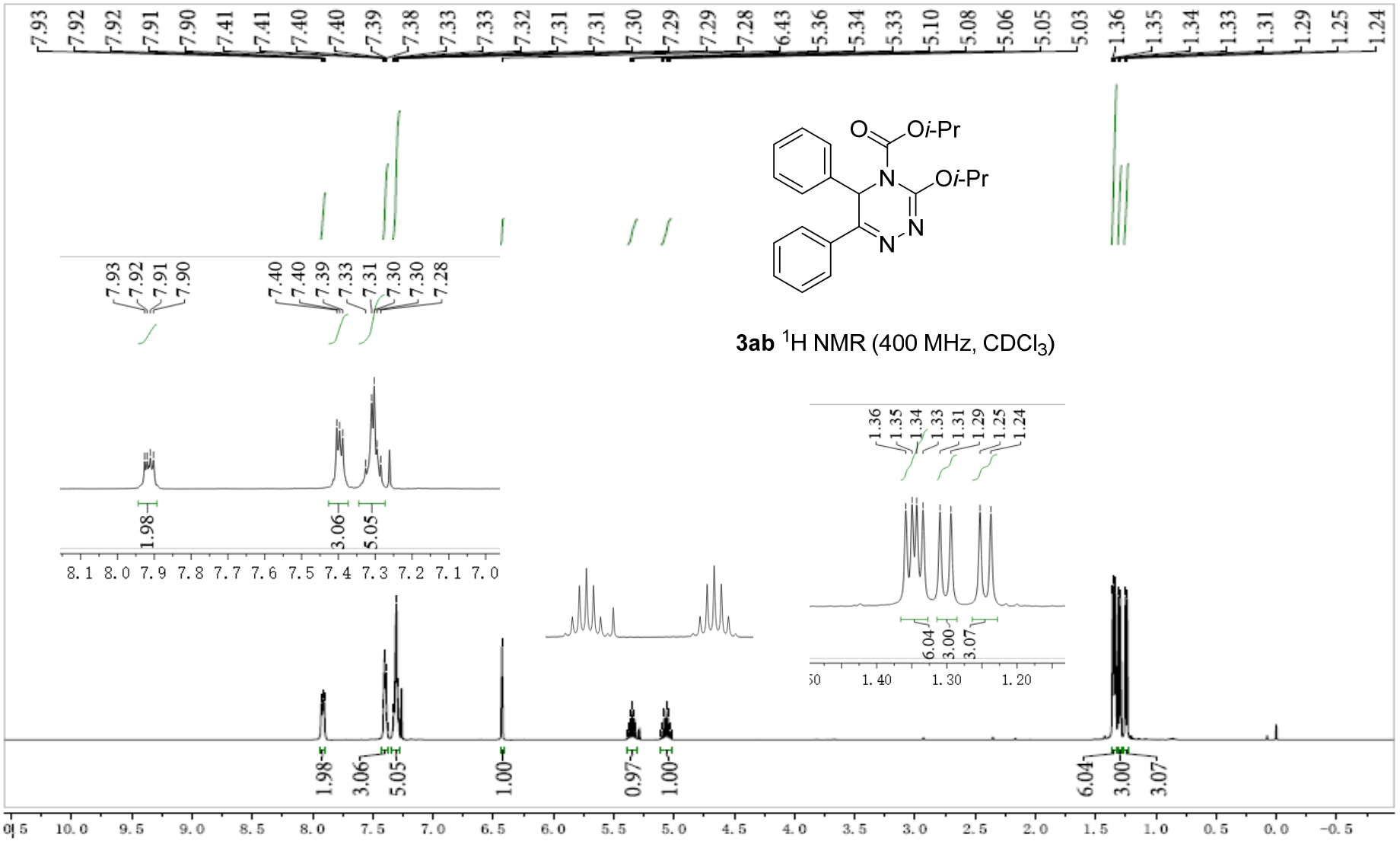
140.8
140.1
140.0
133.3
130.0
129.3
128.8
127.2
127.1
127.0
126.6
124.1
34.3
N
Ph
1v ^{13}C NMR (101 MHz, $CDCl_3$)

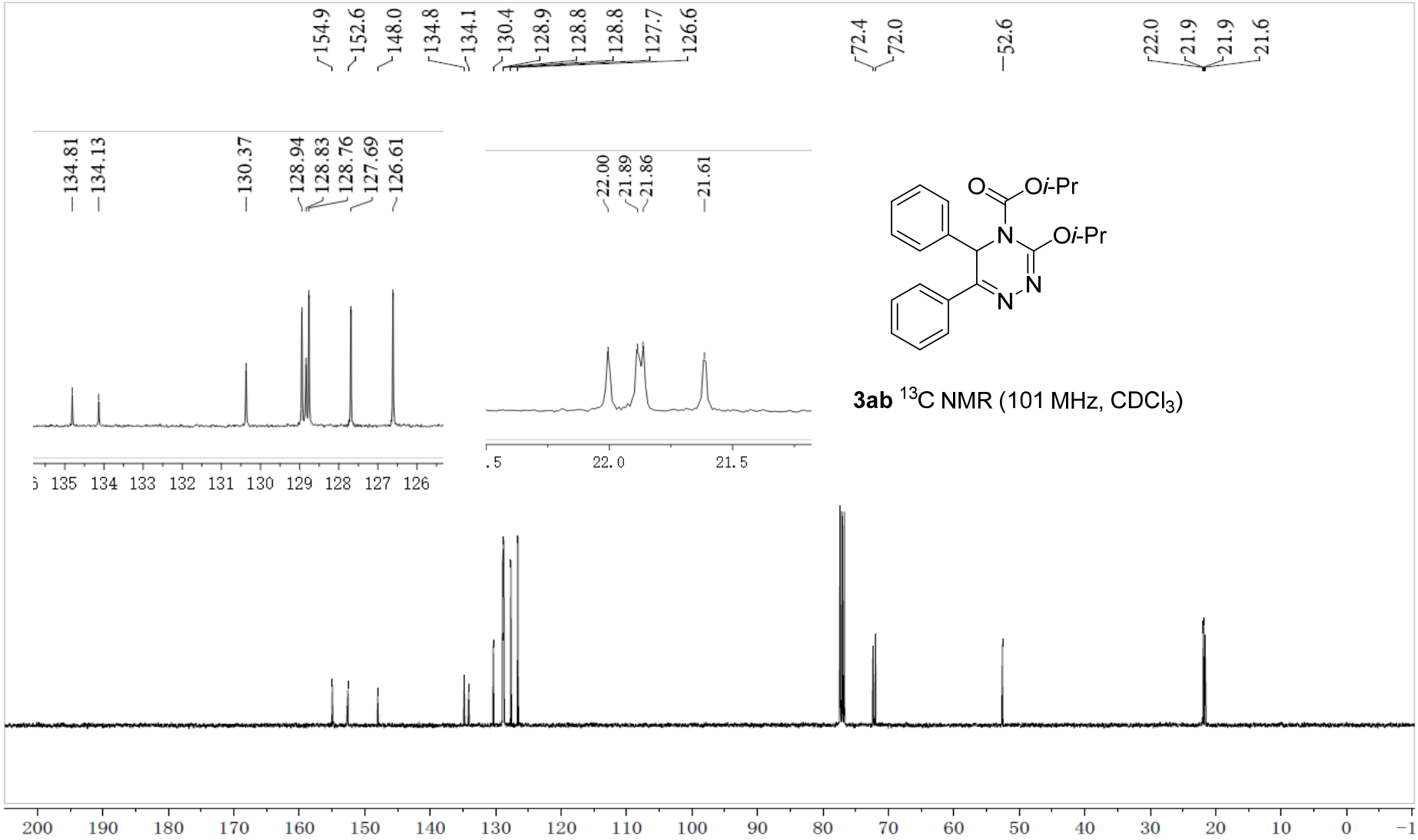

O
OEt
N
OEt
N
N
3aa ^{1}H NMR (400 MHz, $CDCl_3$)



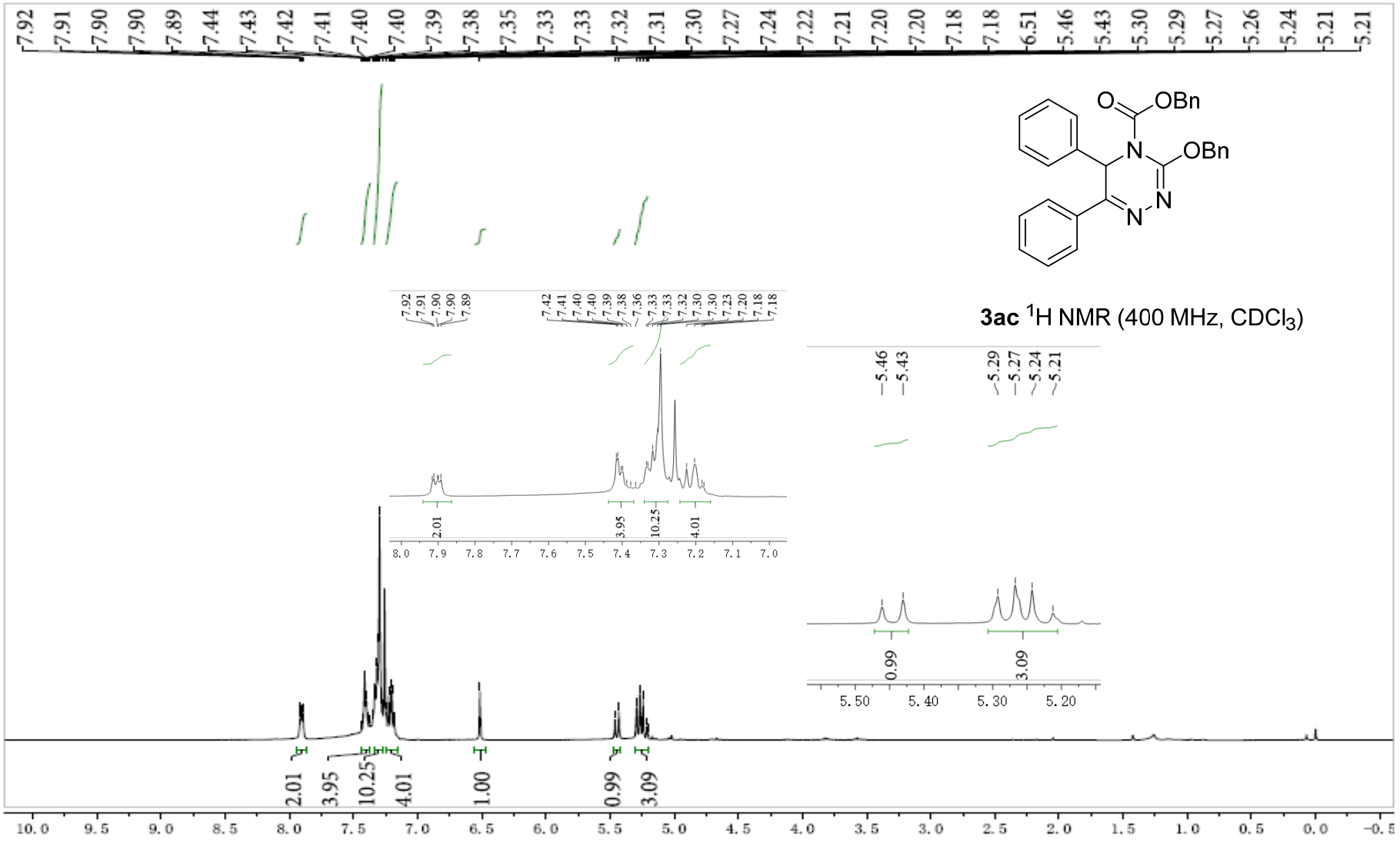
3aa ^{13}C NMR (101 MHz, $CDCl_3$)

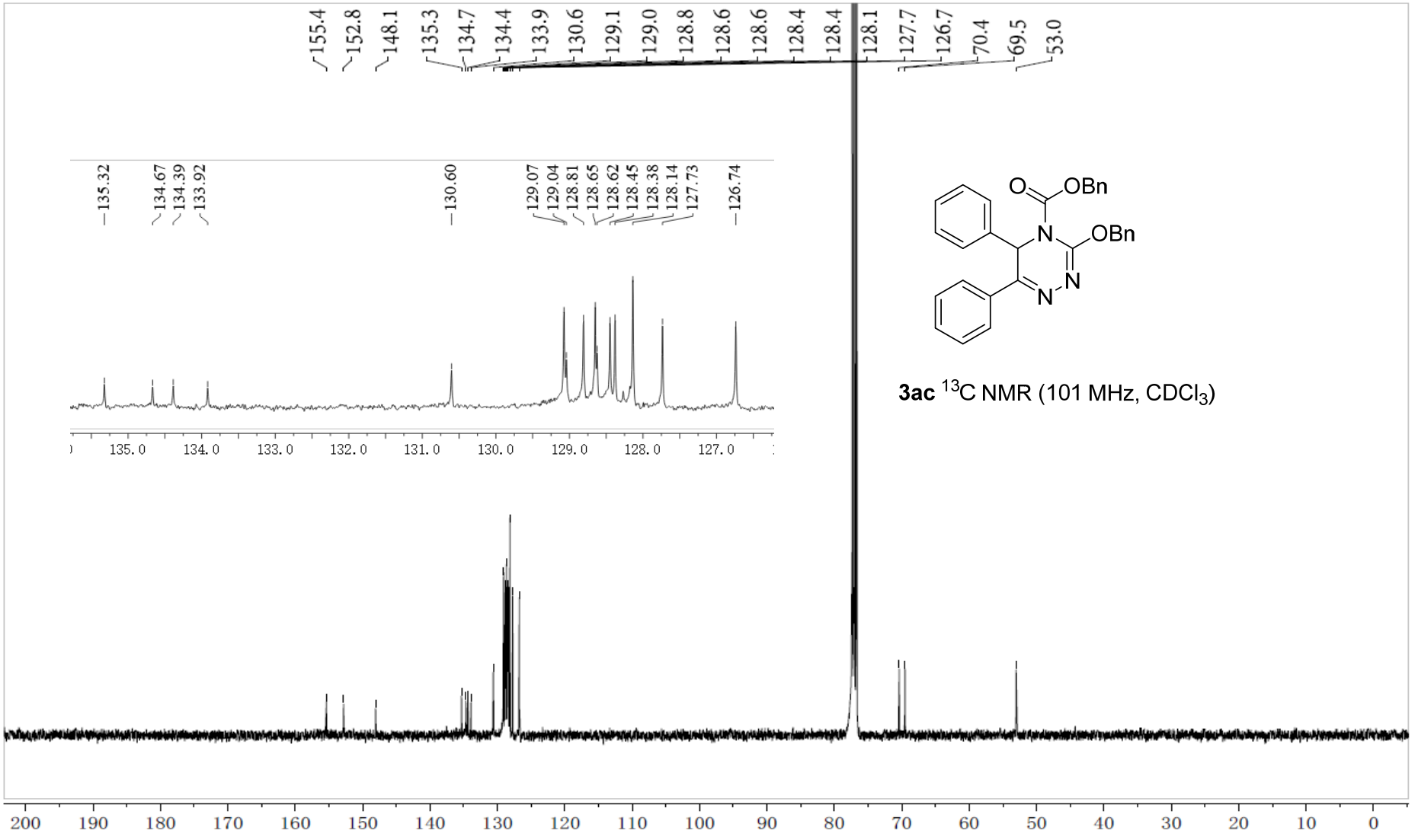


3ab ^{1}H NMR (400 MHz, $CDCl_3$)

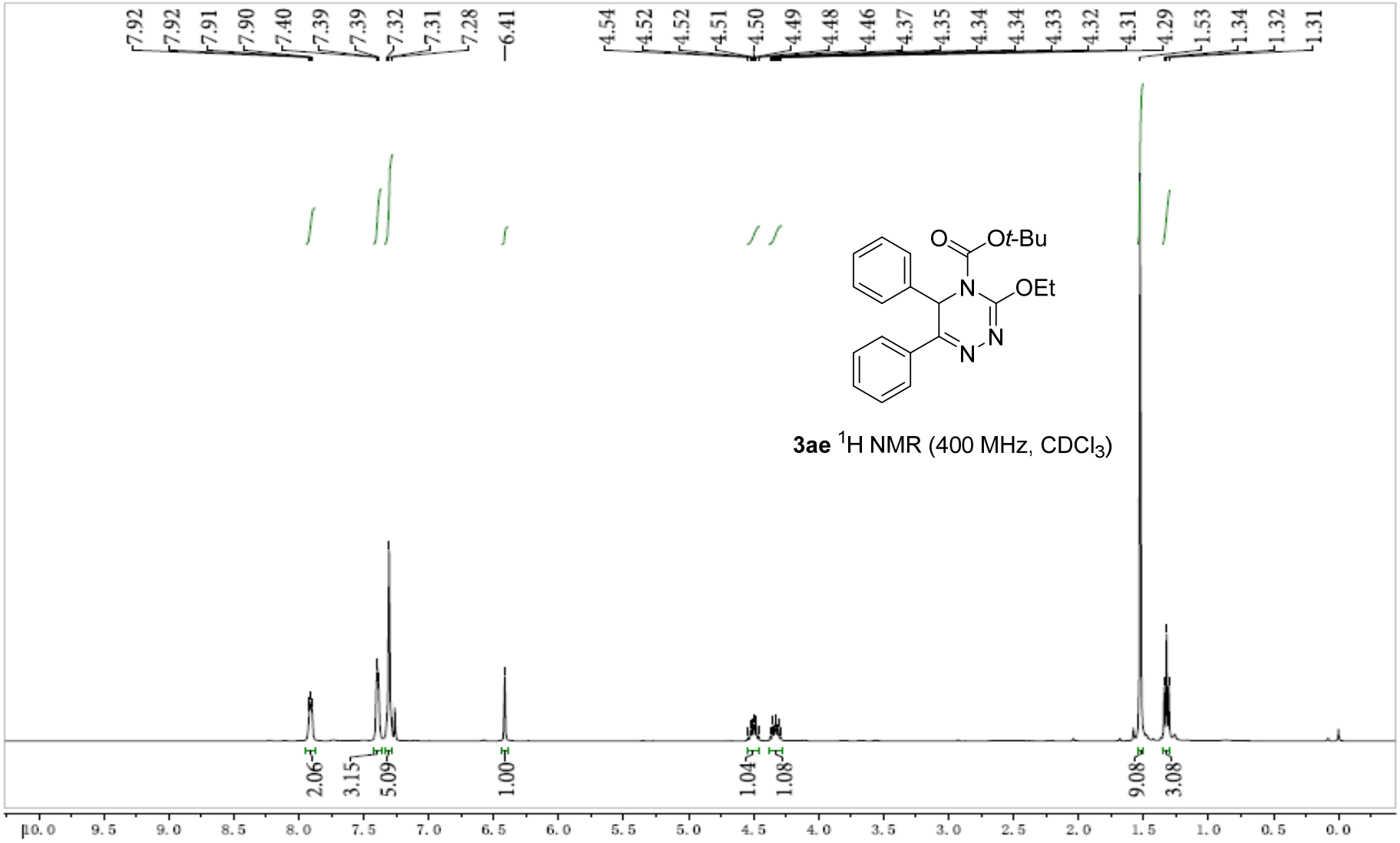


3ab ^{13}C NMR (101 MHz, $CDCl_3$)

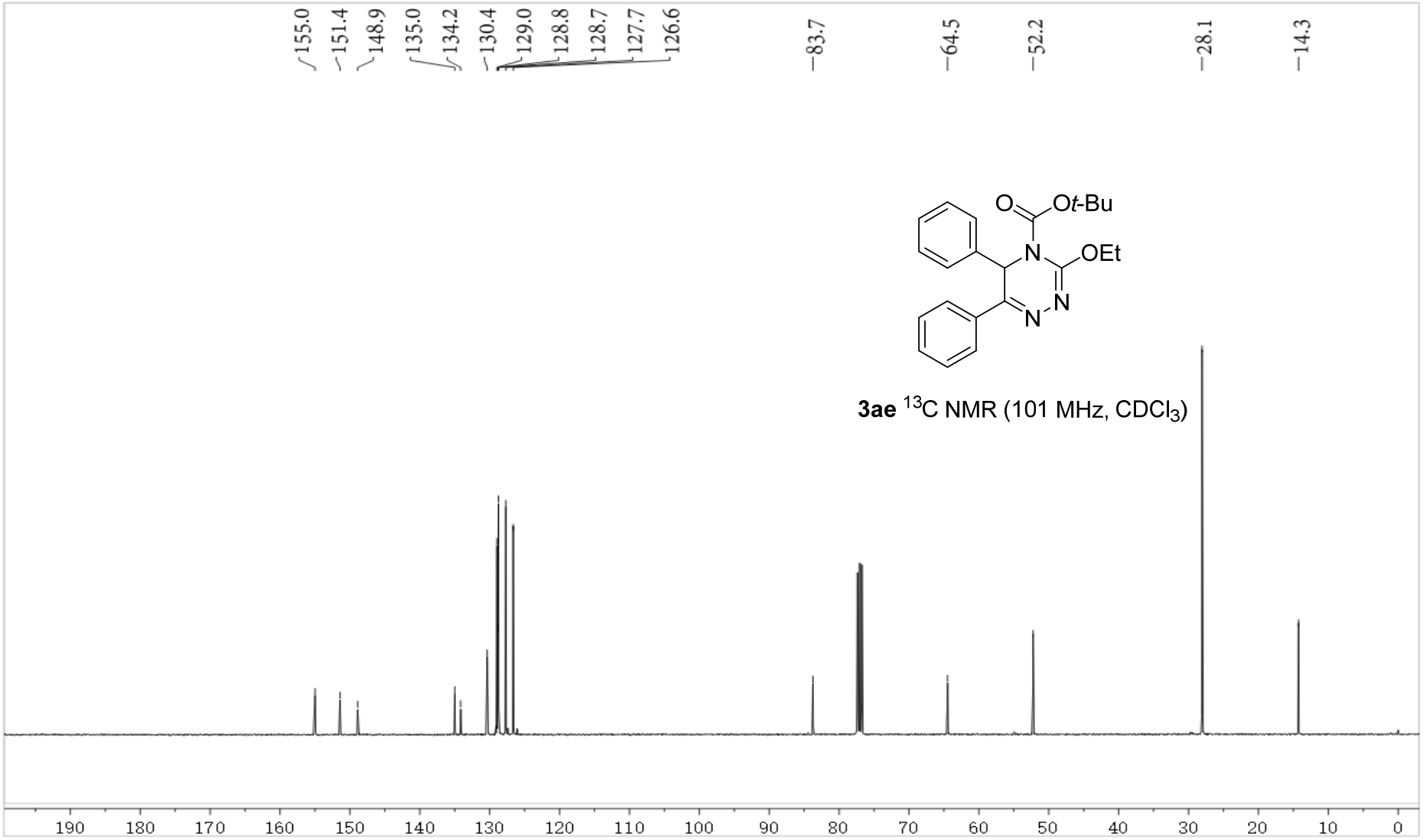

O
OBn
N
OBn
N
N
3ac 1H NMR (400 MHz, CDCl3)



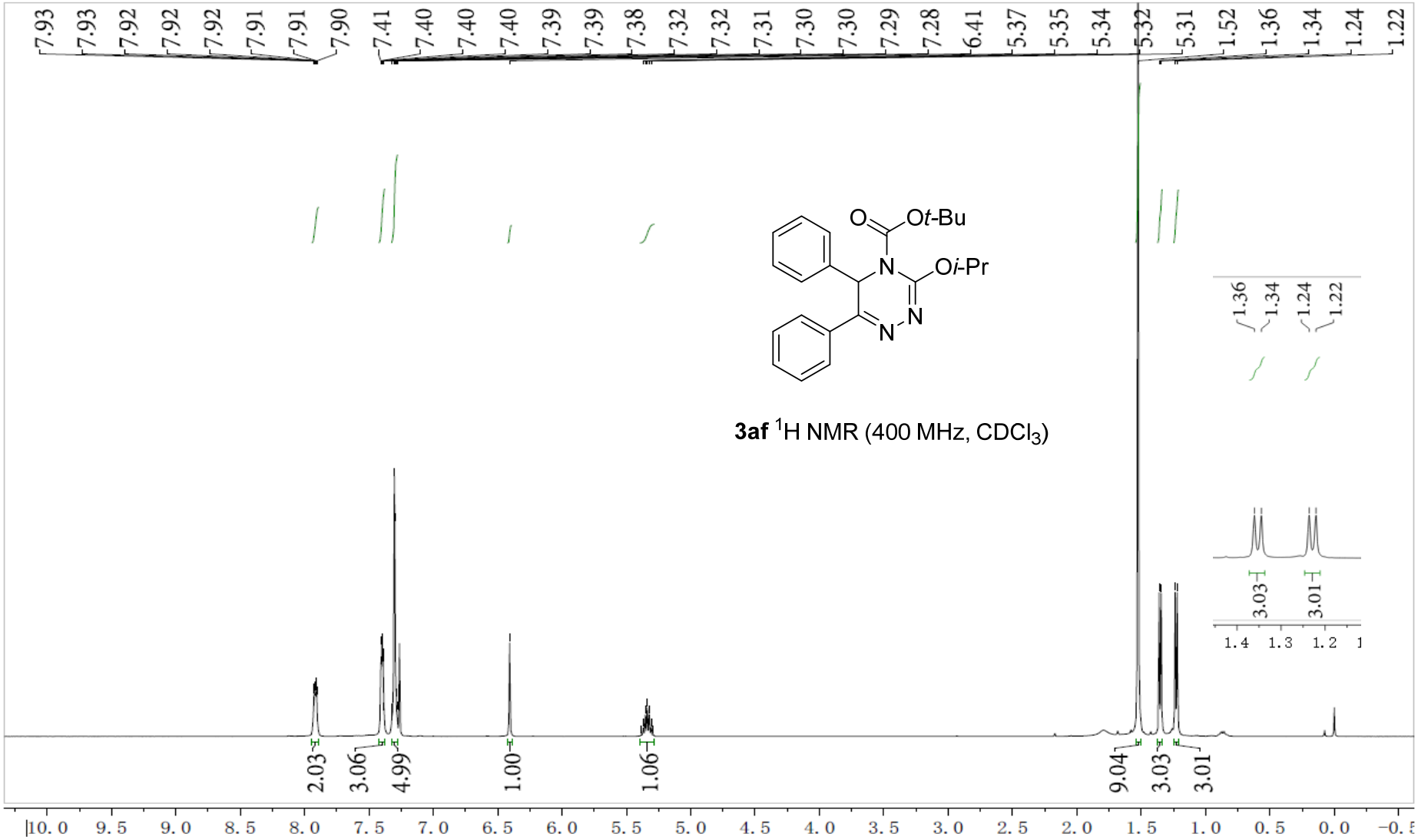
3ac ^{13}C NMR (101 MHz, $CDCl_3$)



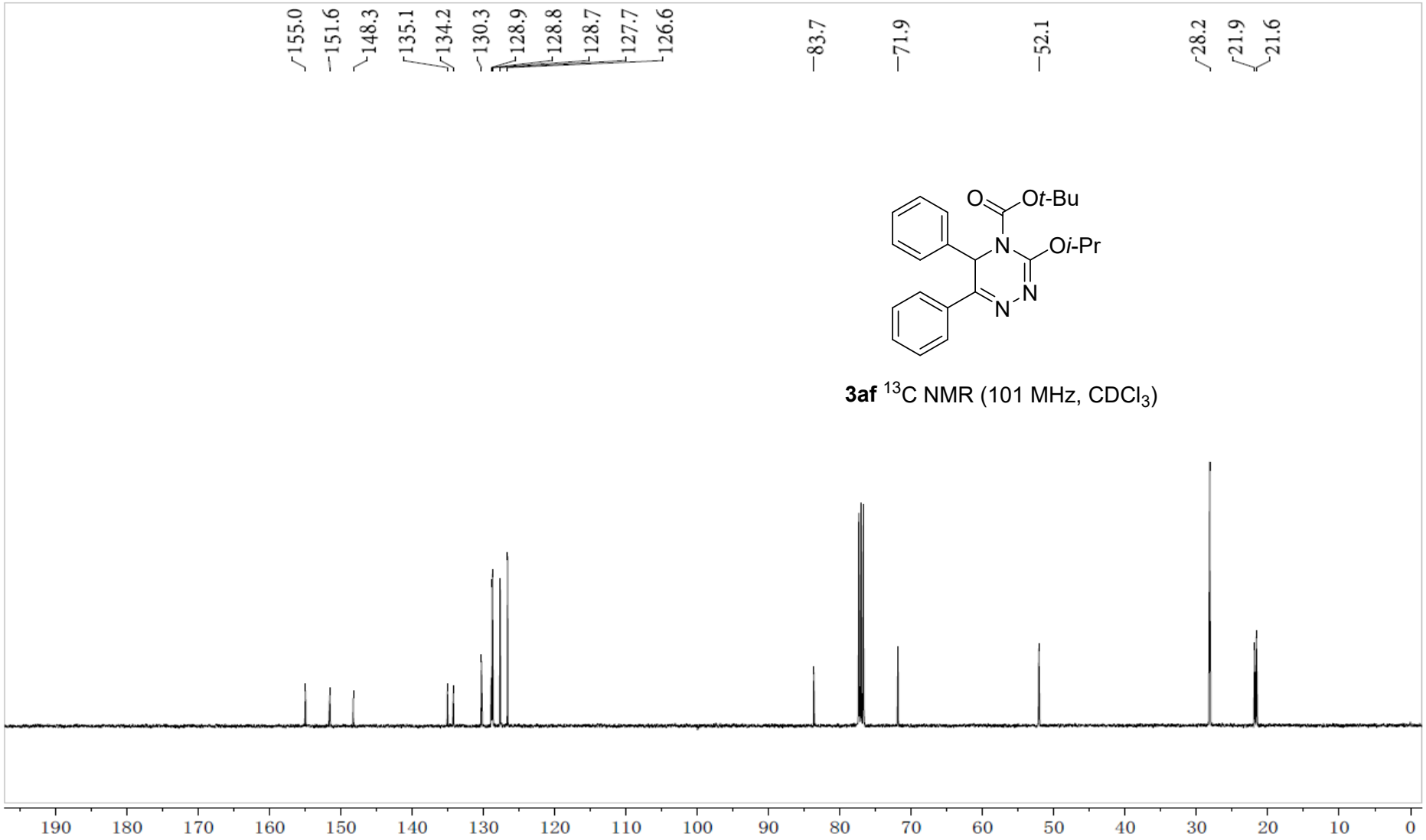
3ae ^{1}H NMR (400 MHz, $CDCl_3$)



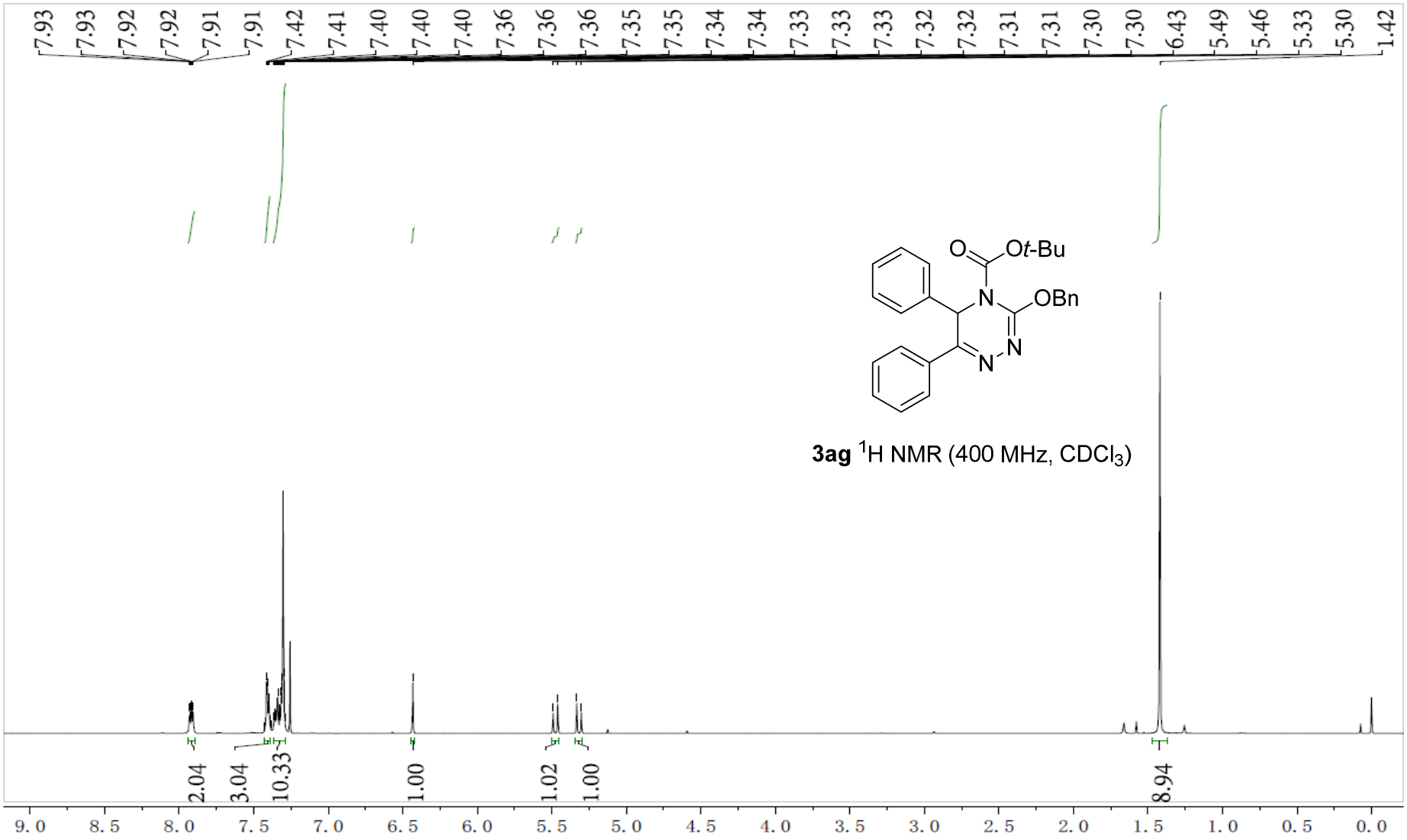
3ae ^{13}C NMR (101 MHz, $CDCl_3$)



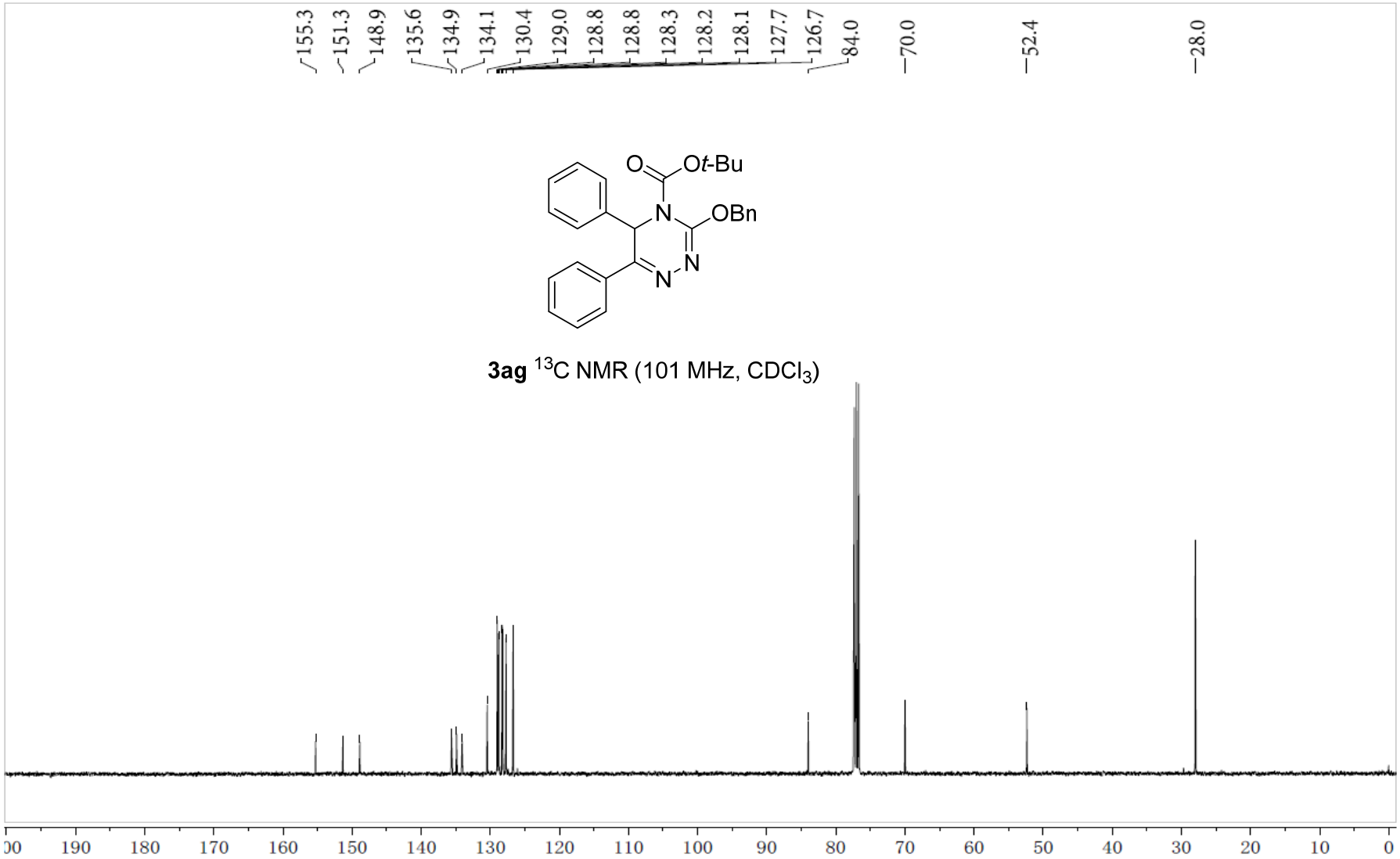
3af ^{1}H NMR (400 MHz, $CDCl_3$)



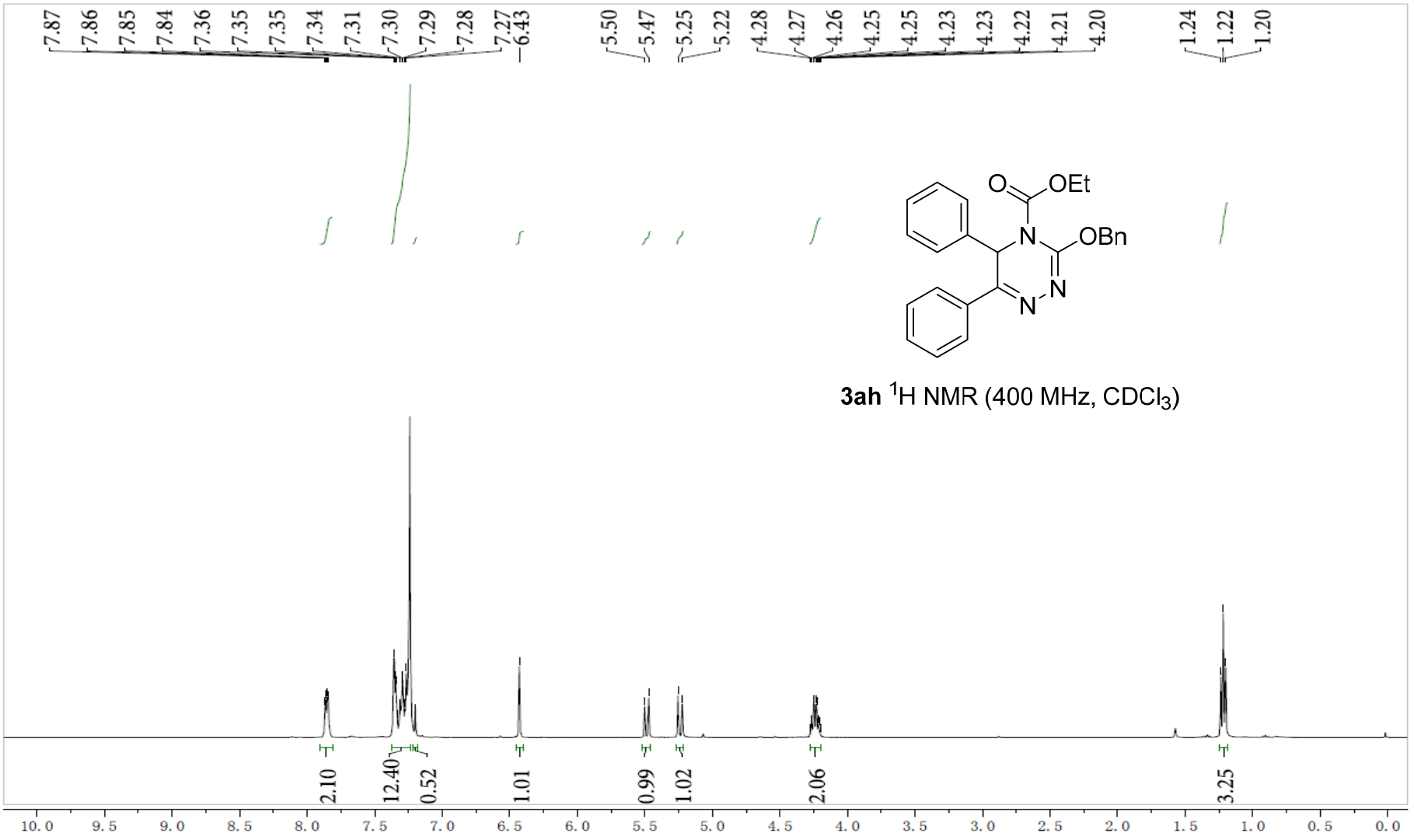
3af ^{13}C NMR (101 MHz, $CDCl_3$)



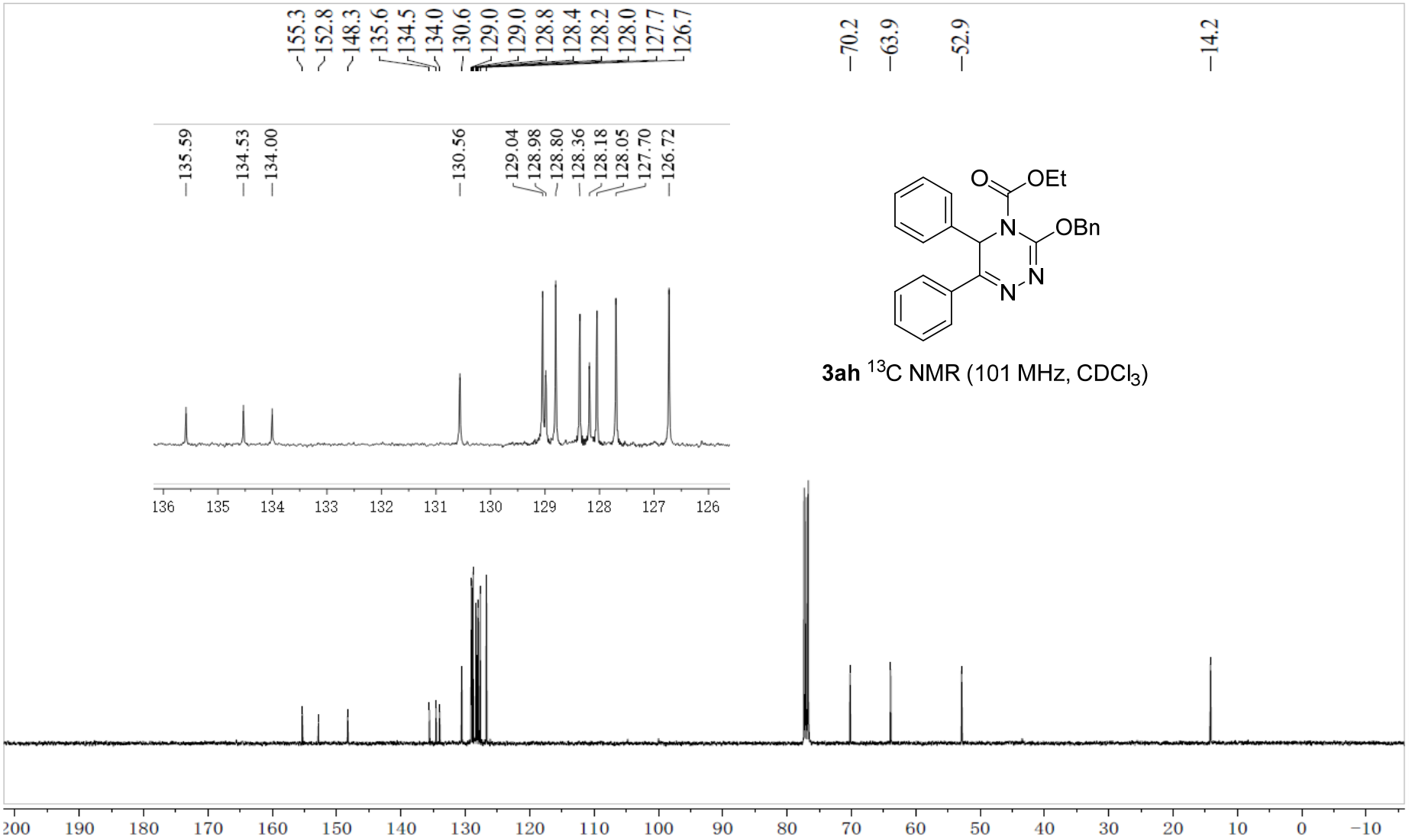
3ag ^{1}H NMR (400 MHz, $CDCl_3$)



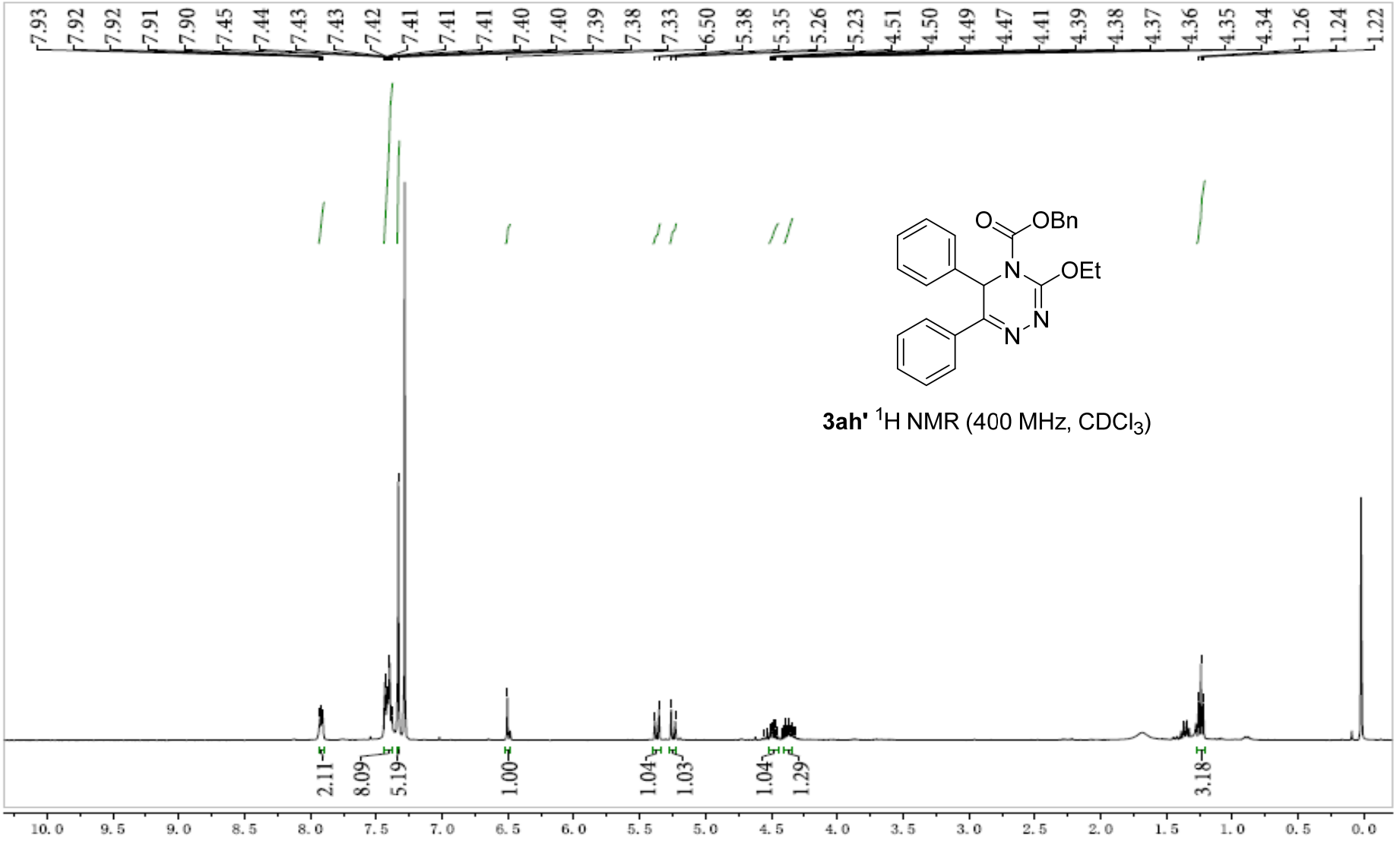
3ag ^{13}C NMR (101 MHz, $CDCl_3$)



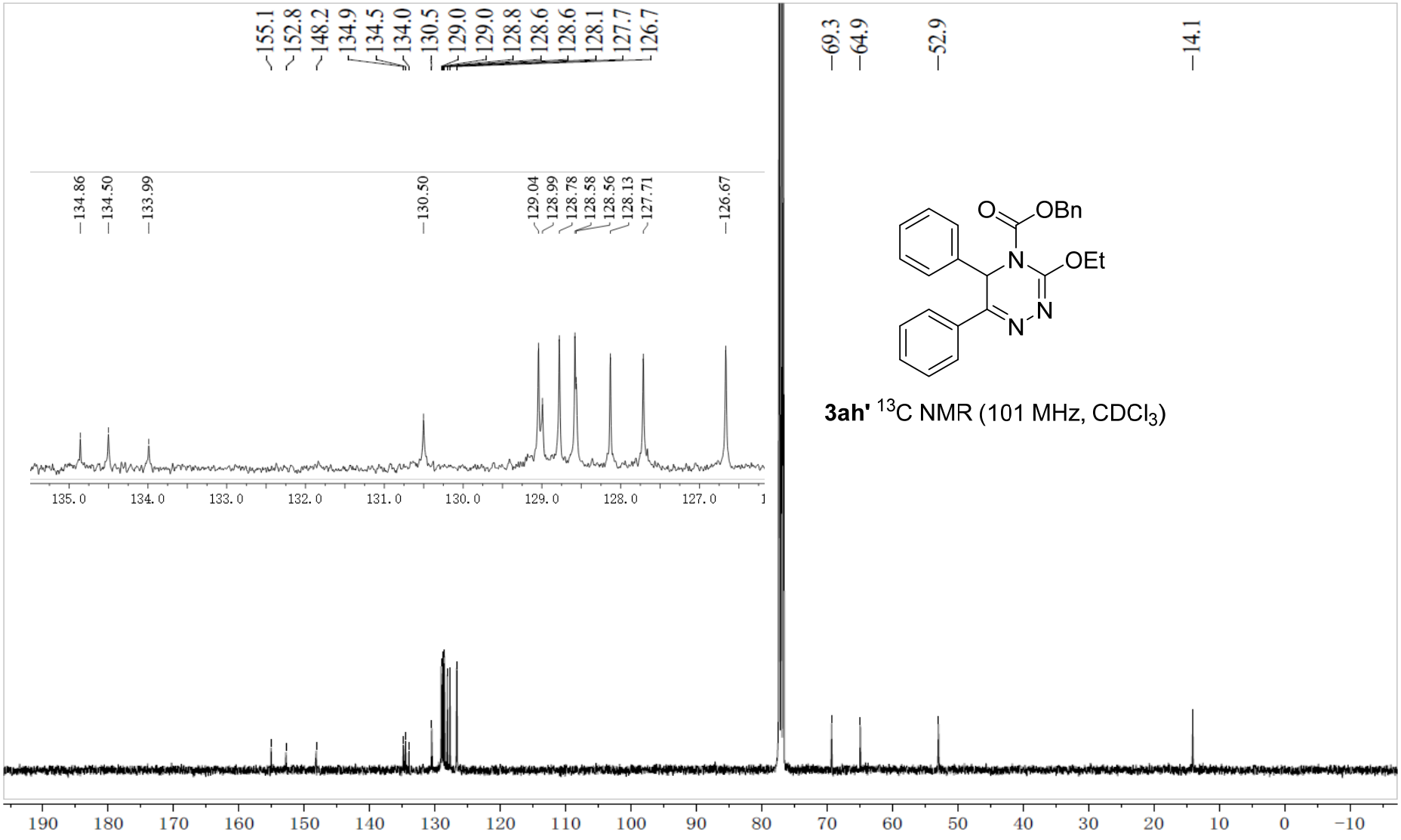
3ah ^{1}H NMR (400 MHz, $CDCl_3$)



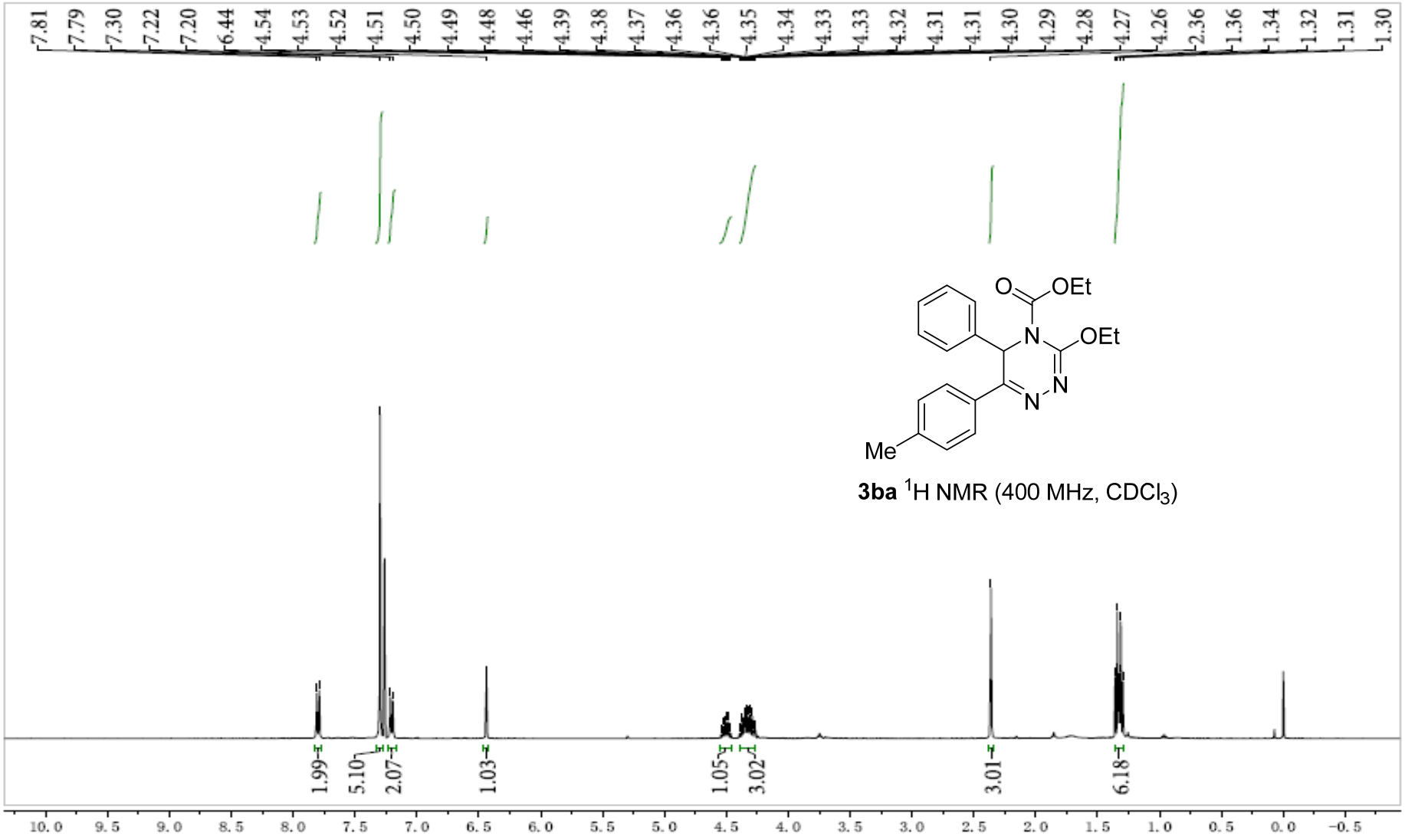
3ah ^{13}C NMR (101 MHz, $CDCl_3$)



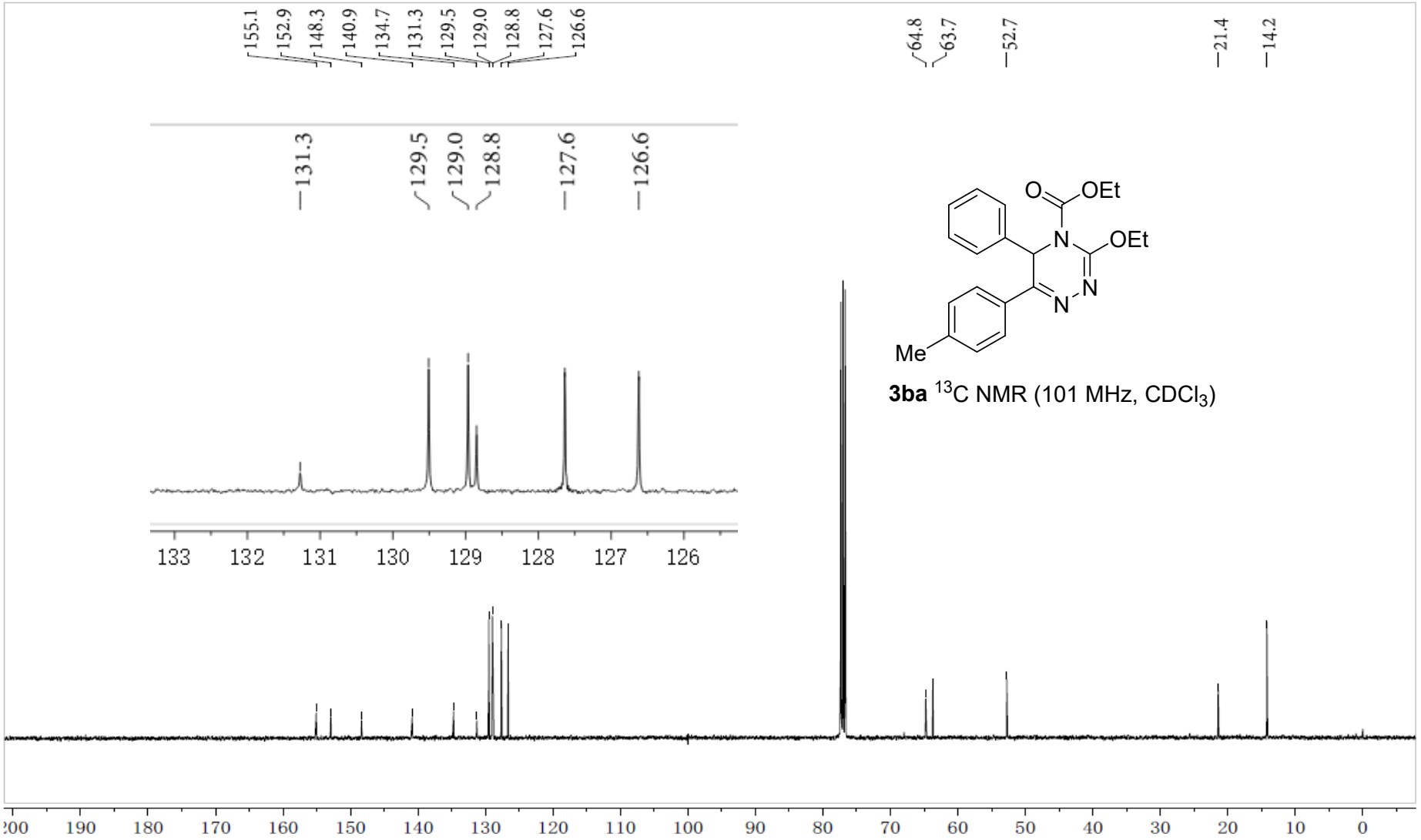
3ah' ^{1}H NMR (400 MHz, $CDCl_3$)



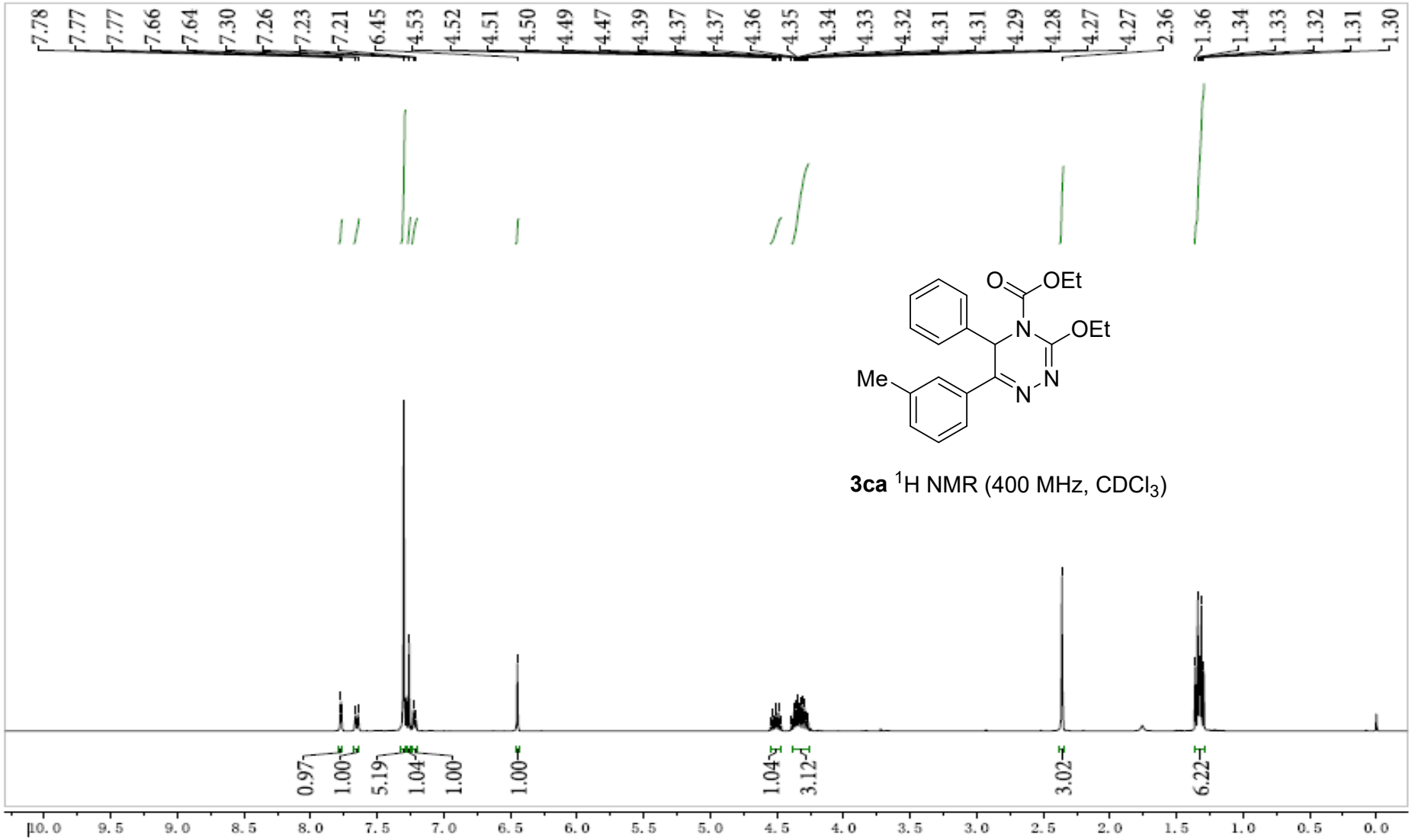
3ah' ^{13}C NMR (101 MHz, $CDCl_3$)



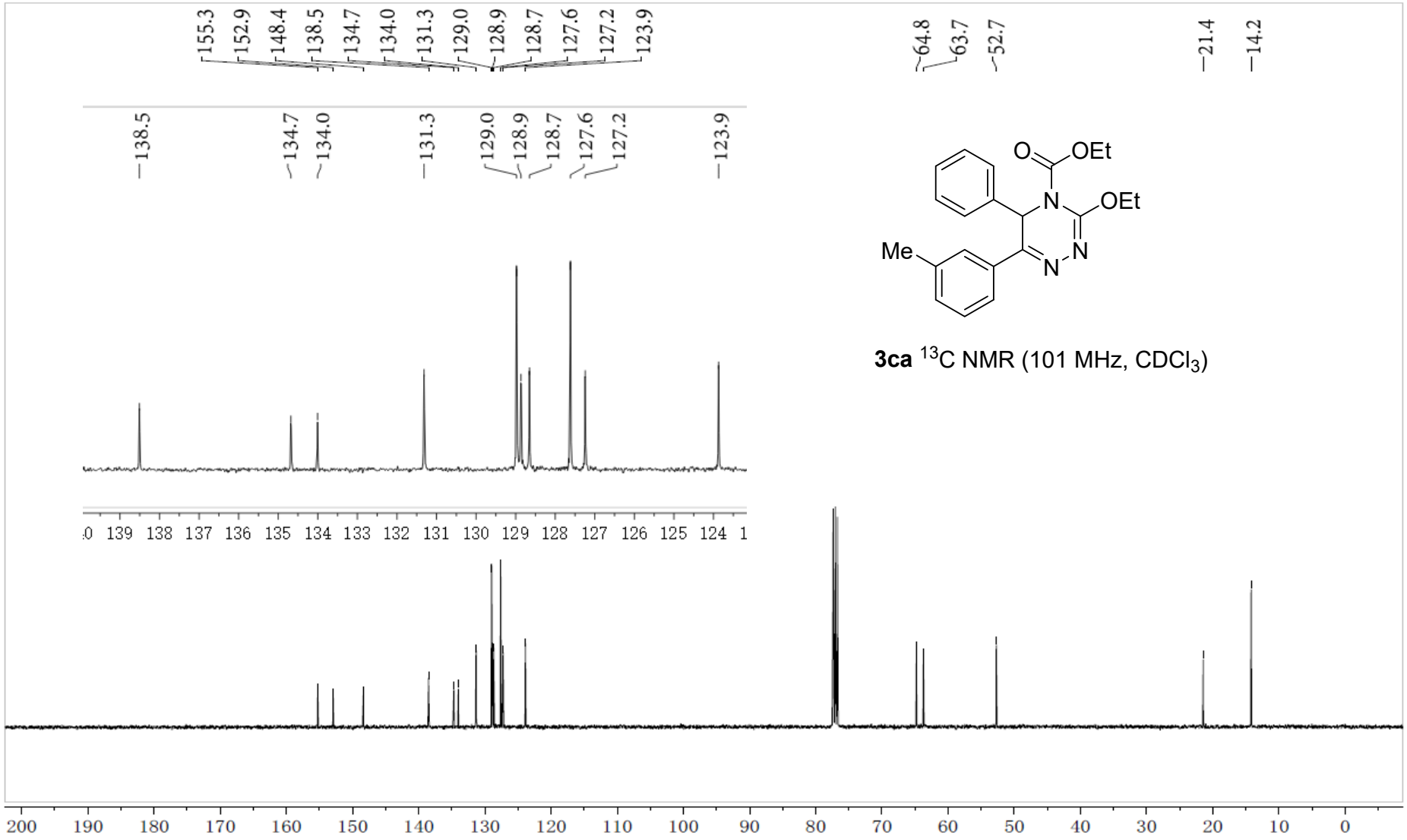
3ba ^{1}H NMR (400 MHz, $CDCl_3$)

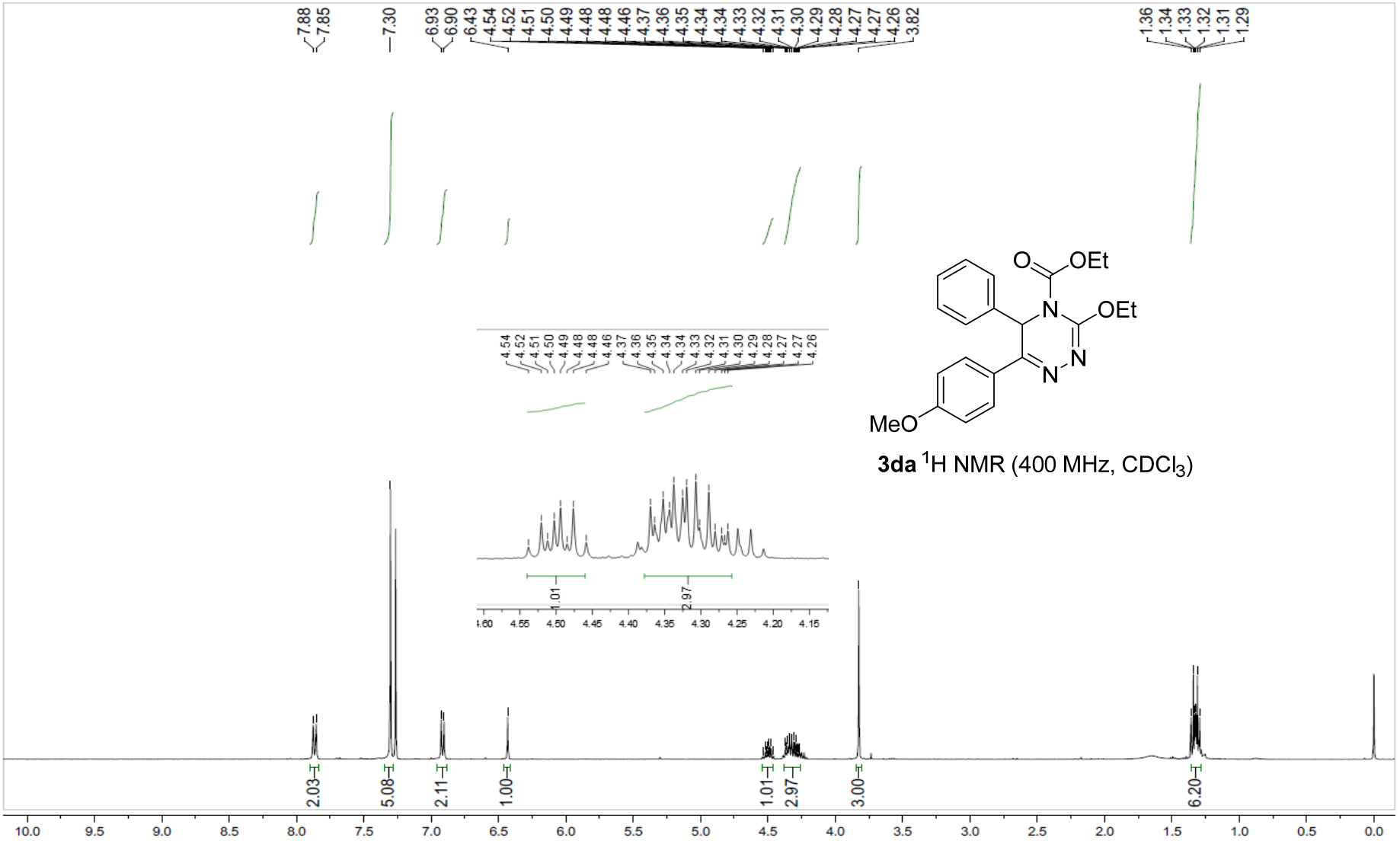


3ba ^{13}C NMR (101 MHz, $CDCl_3$)

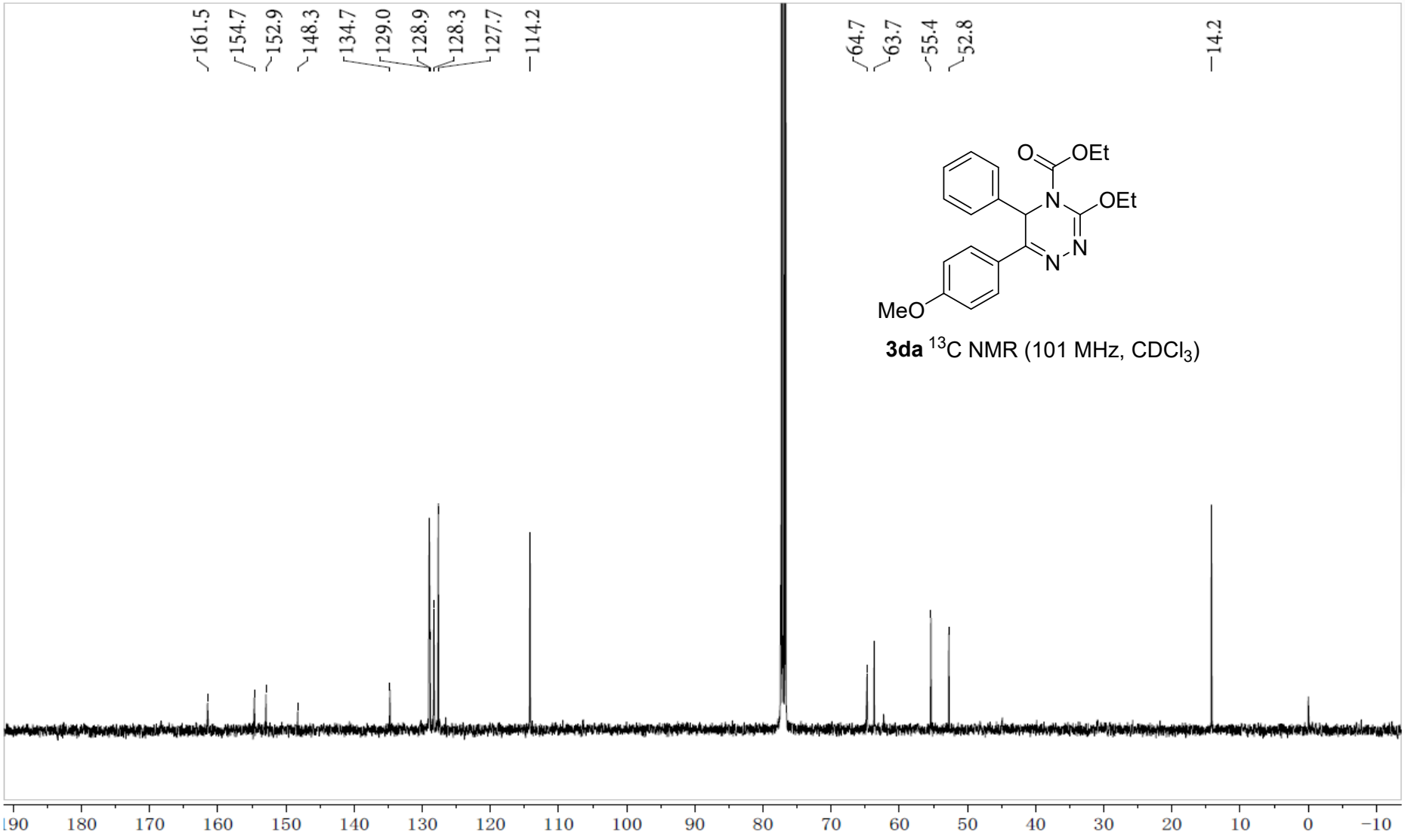


3ca ^{1}H NMR (400 MHz, $CDCl_3$)

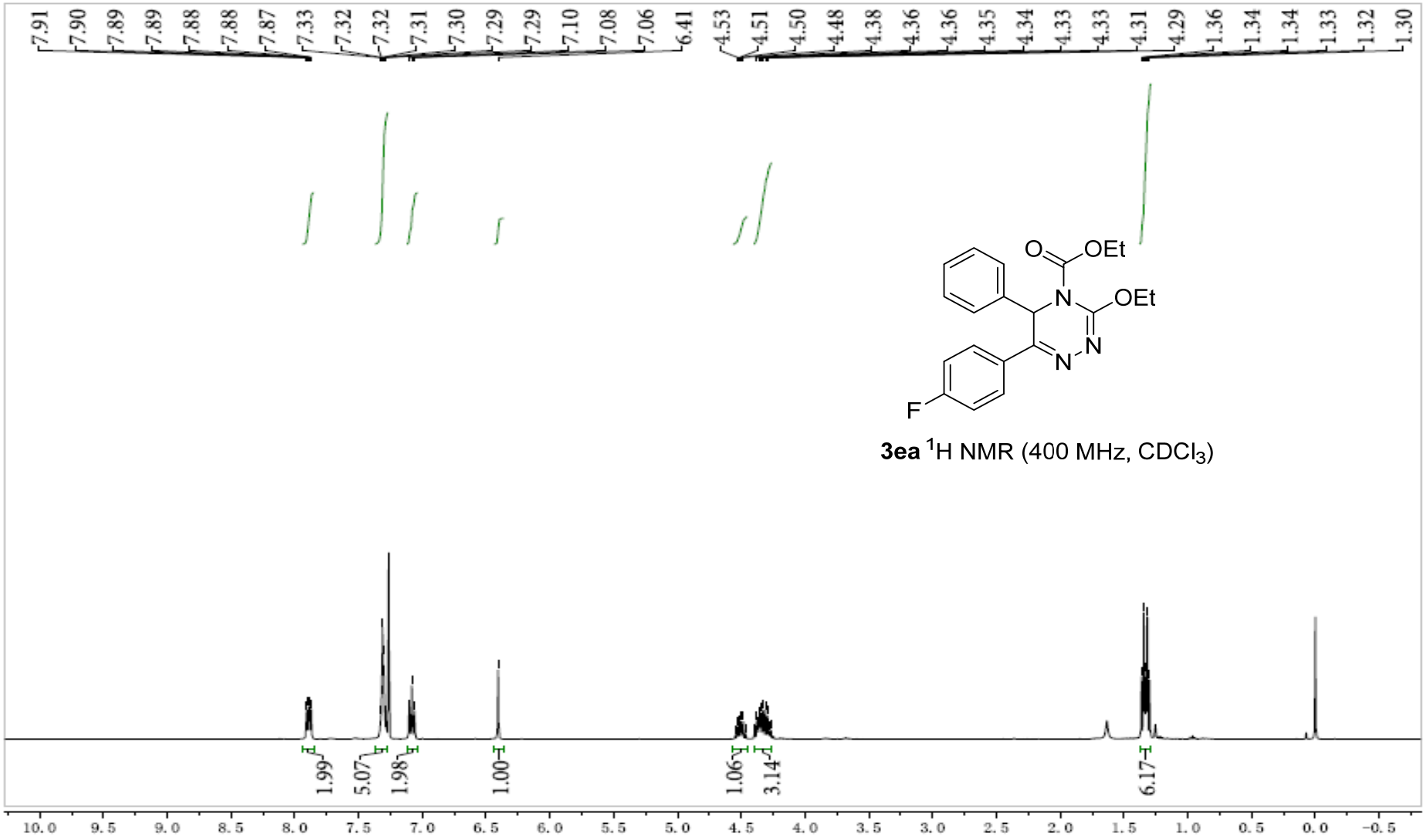

155.3
152.9
148.4
138.5
134.7
134.0
131.3
129.0
128.9
128.7
127.6
127.2
123.9
64.8
63.7
52.7
21.4
14.2
O
OEt
N
OEt
Me
N
N
3ca 13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



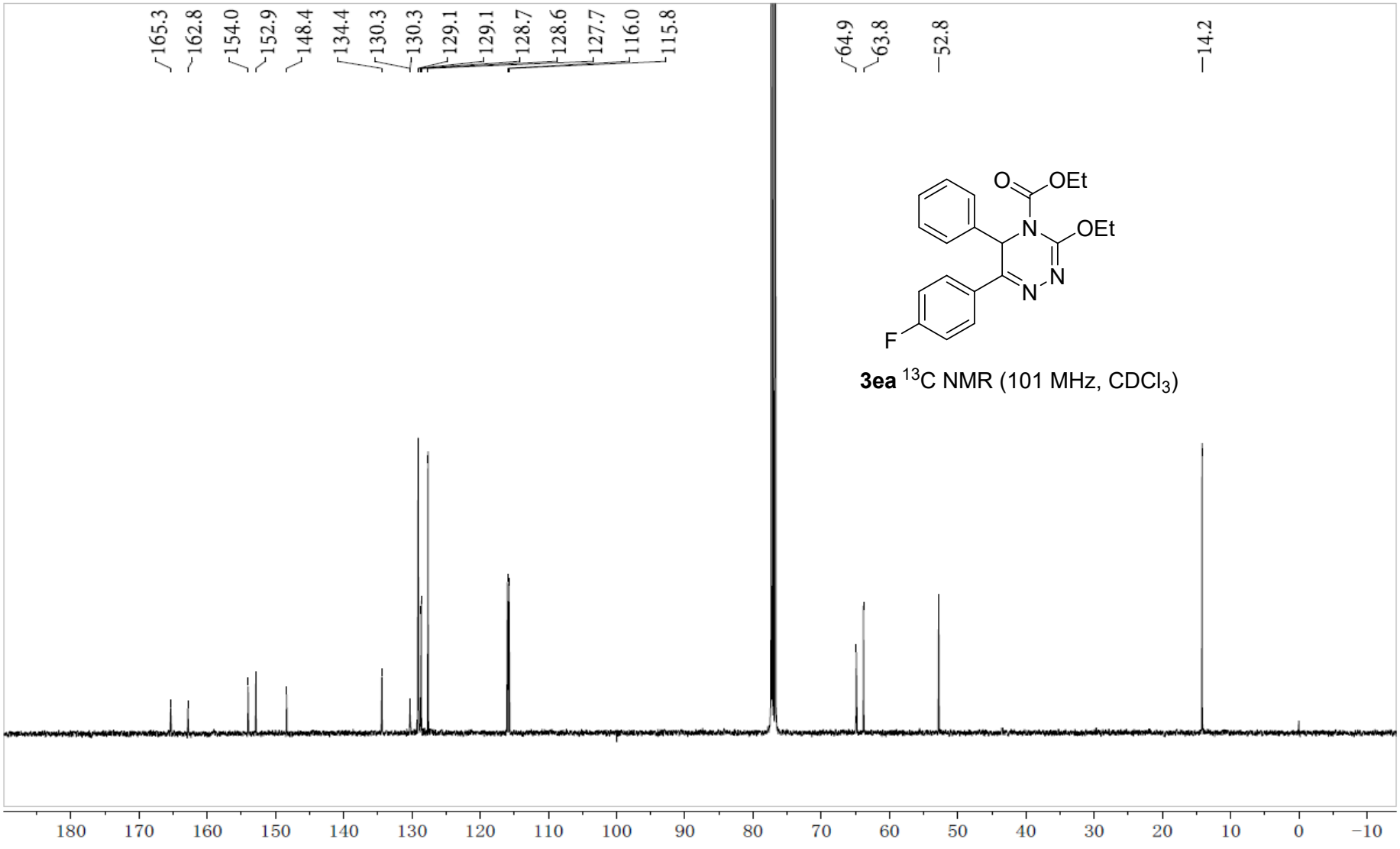
3da ^{1}H NMR (400 MHz, $CDCl_3$)



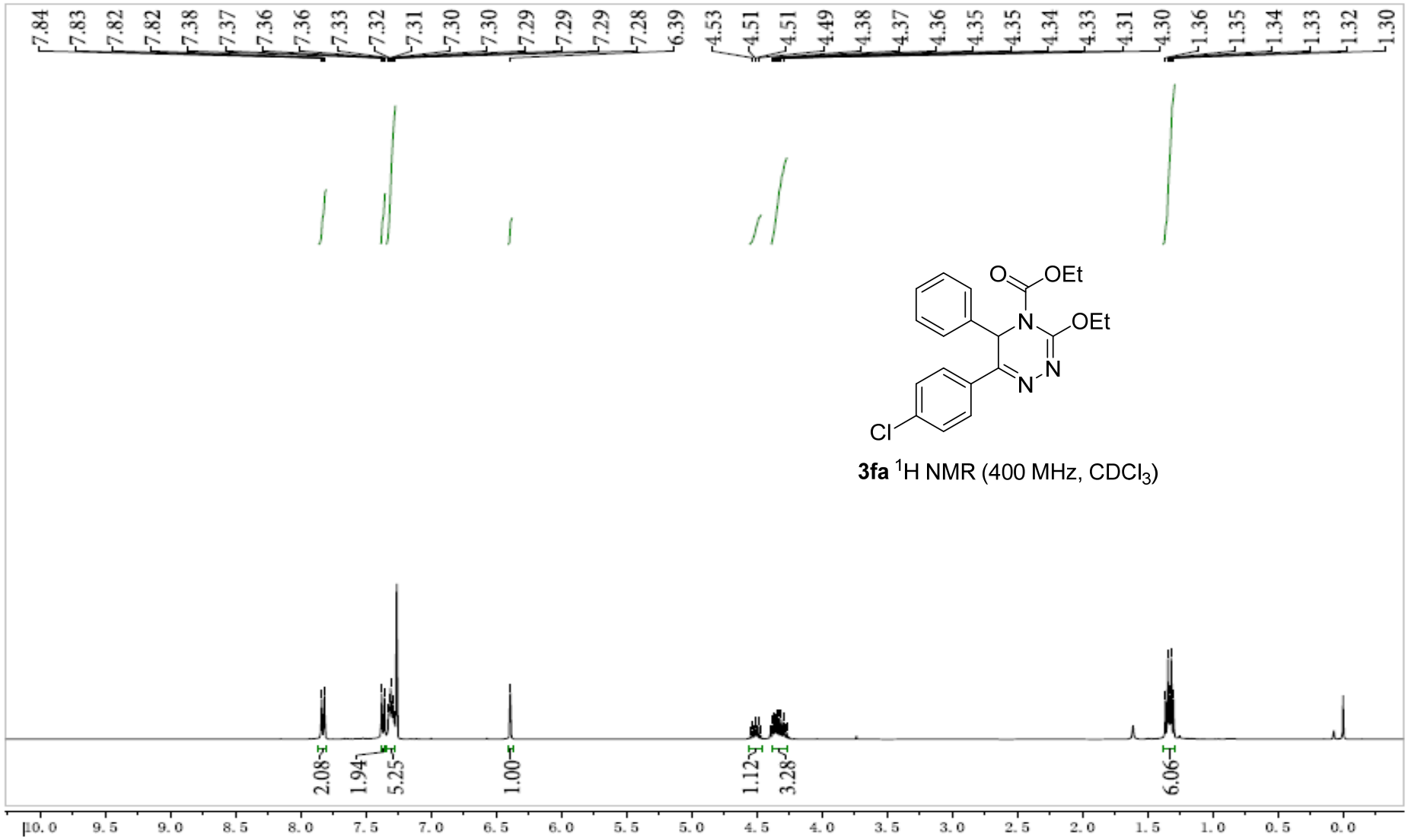
3da ^{13}C NMR (101 MHz, $CDCl_3$)



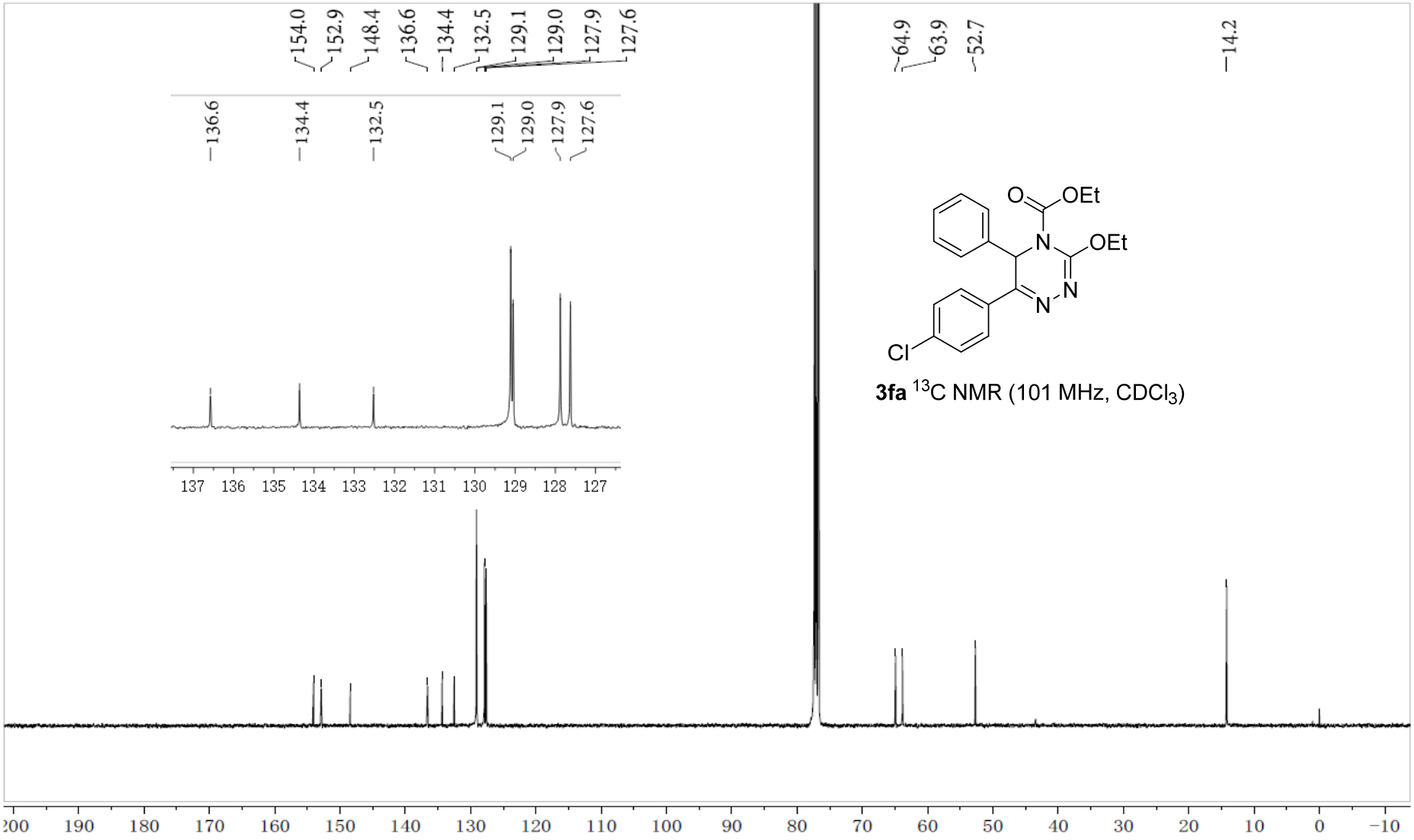
3ea ^{1}H NMR (400 MHz, $CDCl_3$)



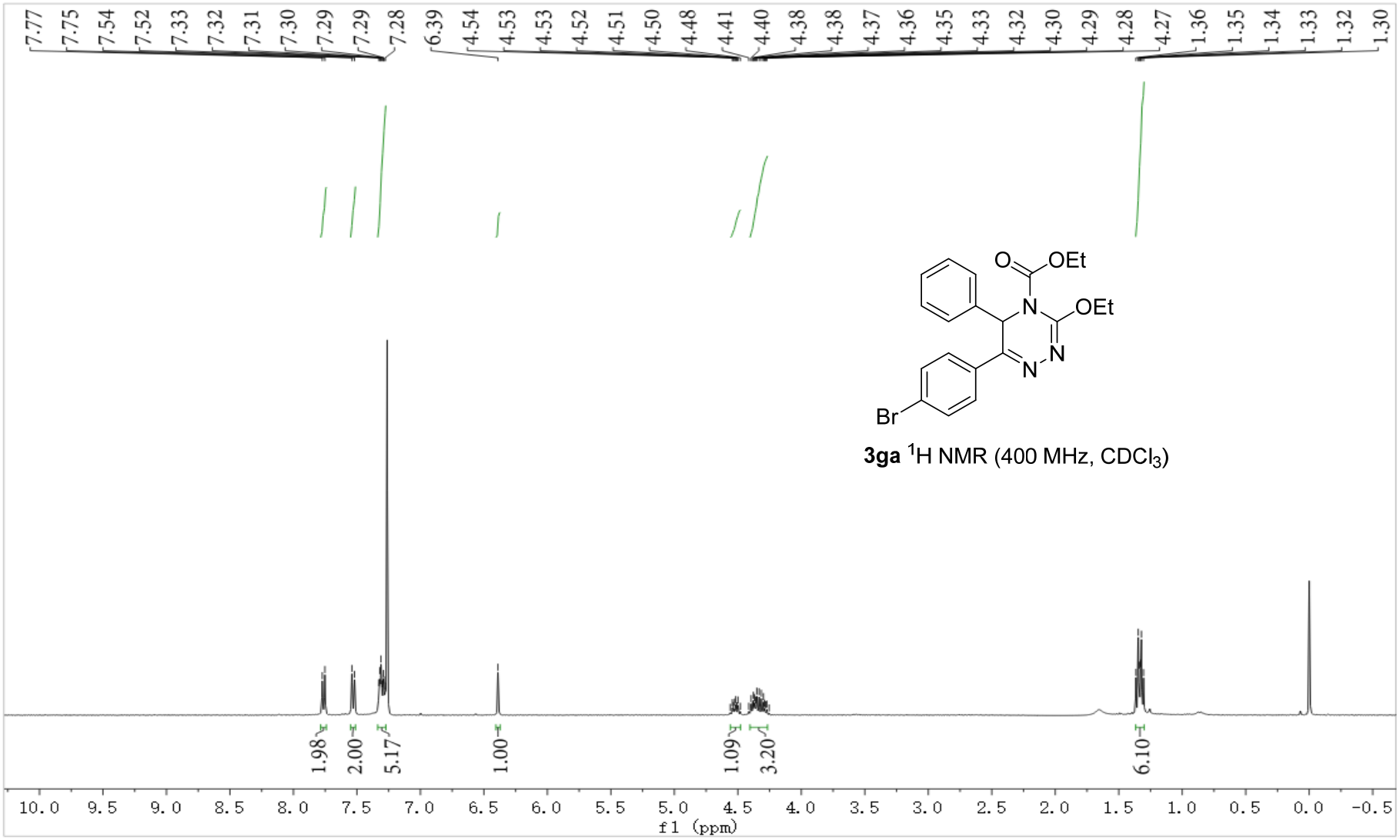
3ea ^{13}C NMR (101 MHz, $CDCl_3$)



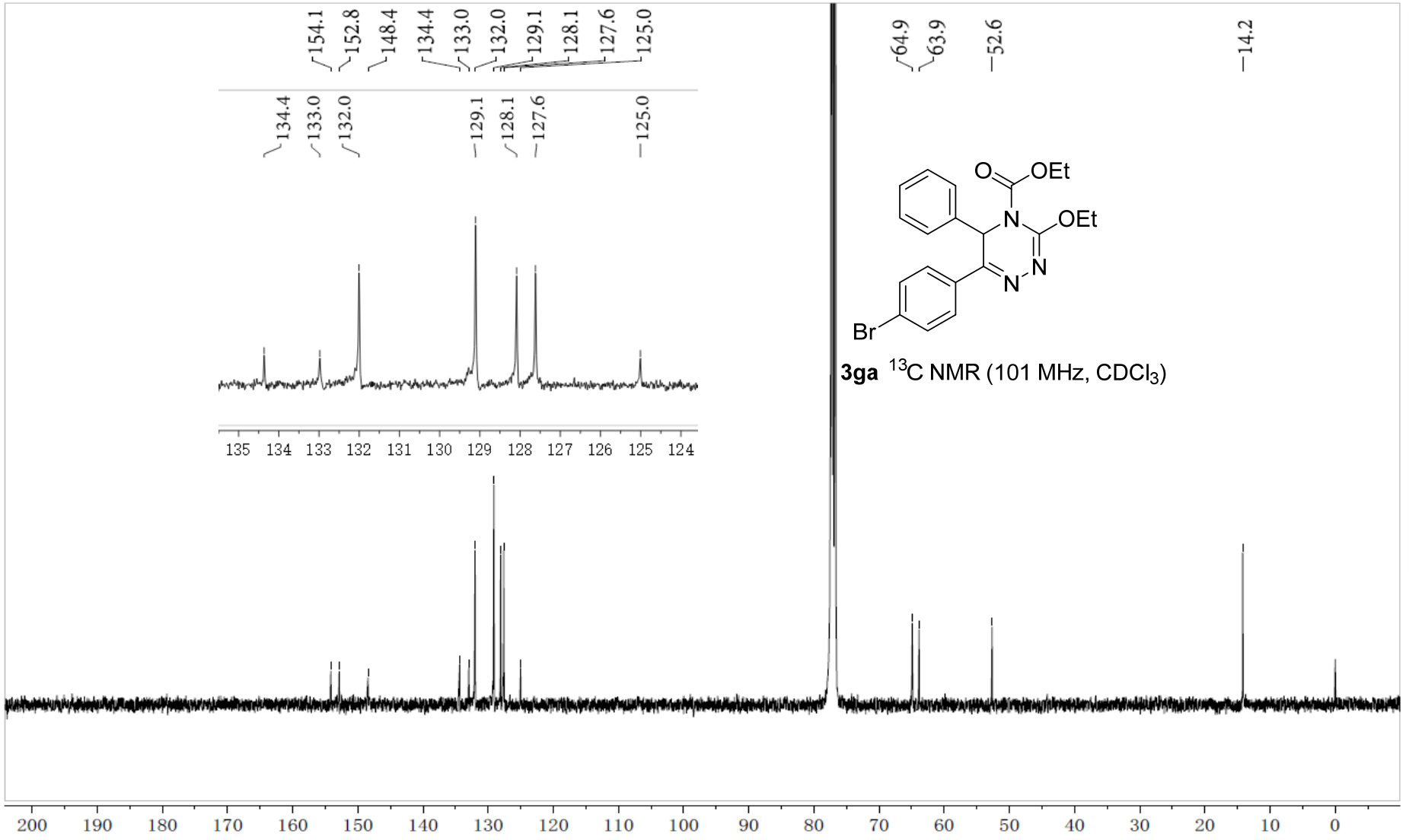
3fa ^{1}H NMR (400 MHz, $CDCl_3$)



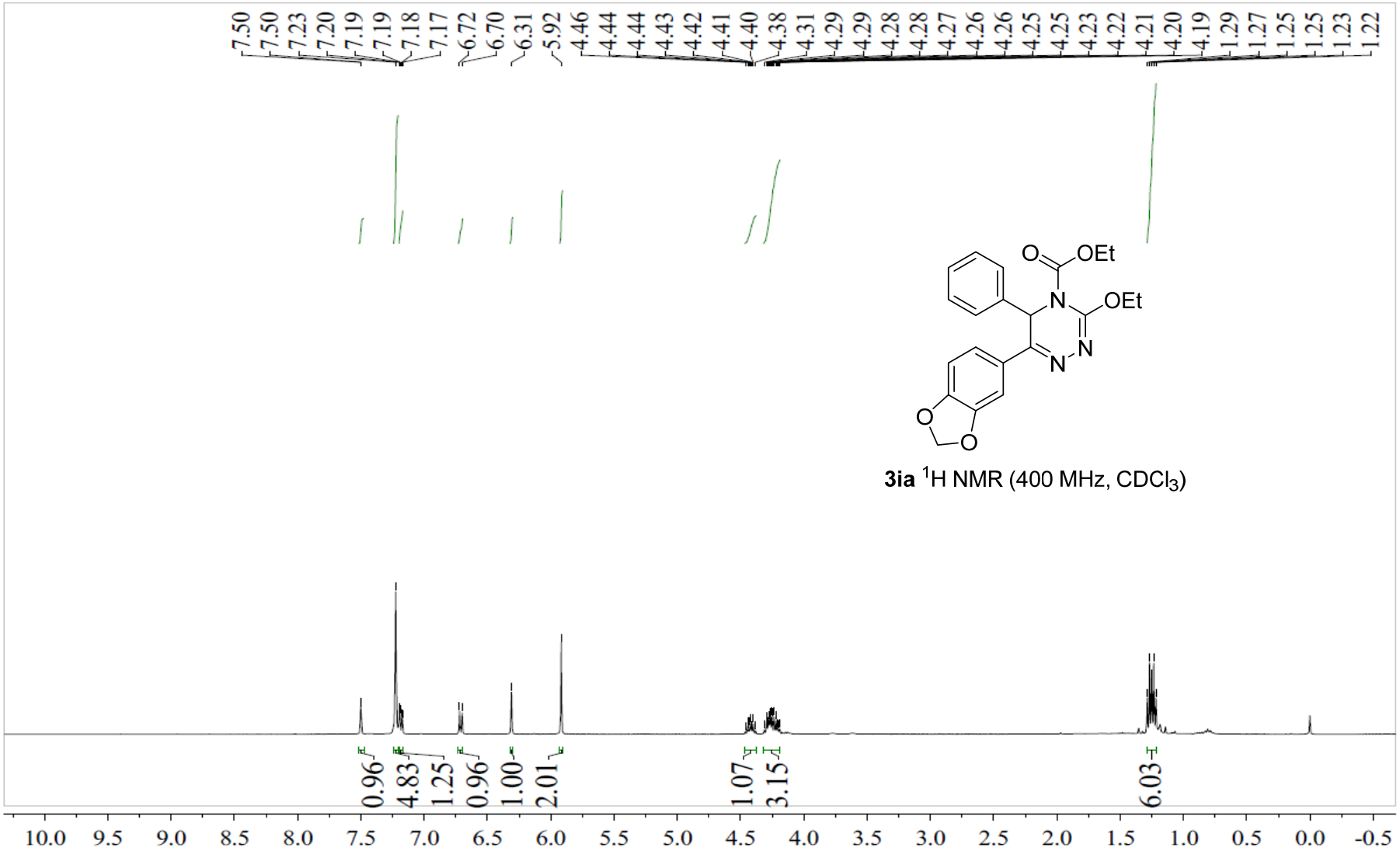
3fa ^{13}C NMR (101 MHz, $CDCl_3$)



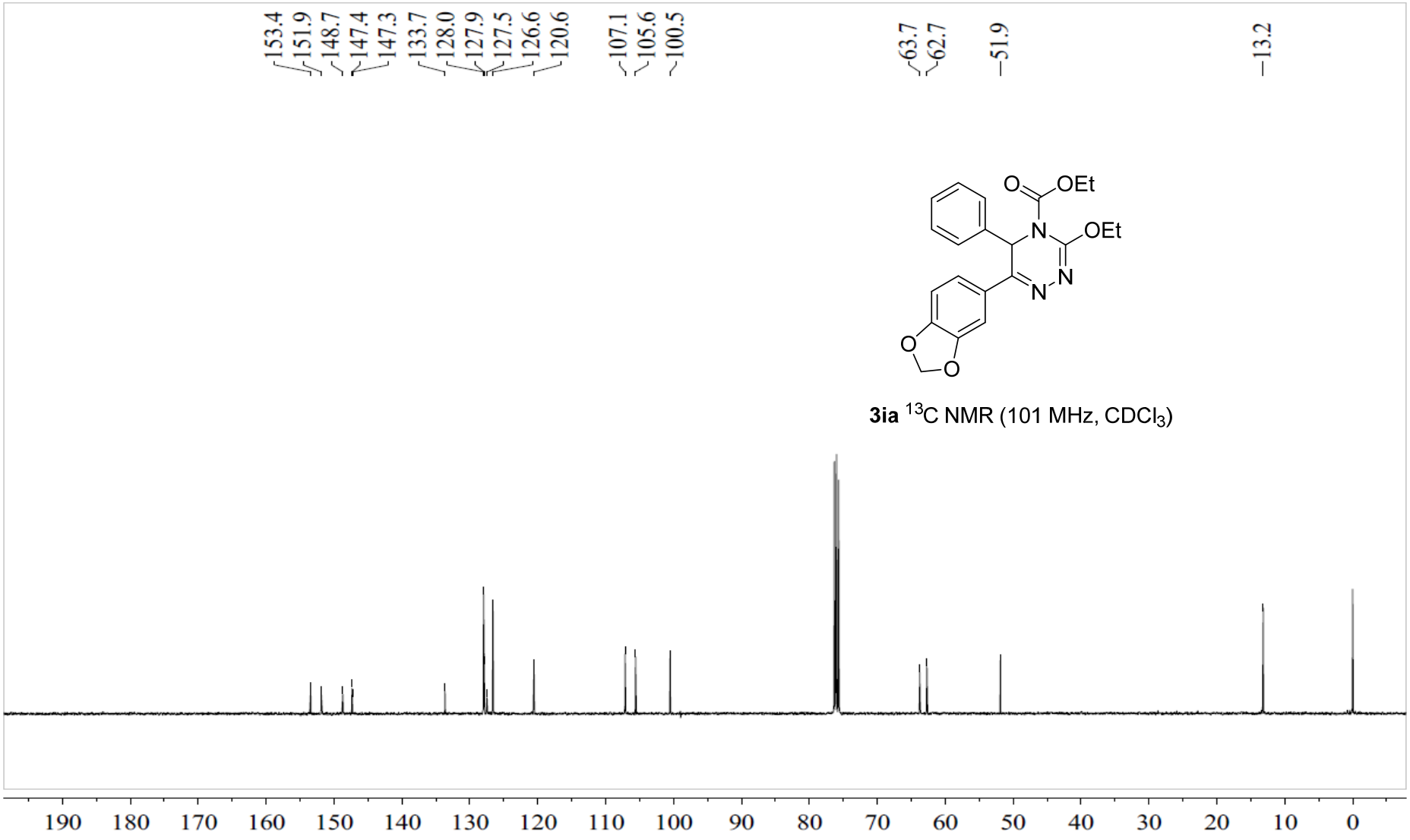
3ga ^{1}H NMR (400 MHz, $CDCl_3$)



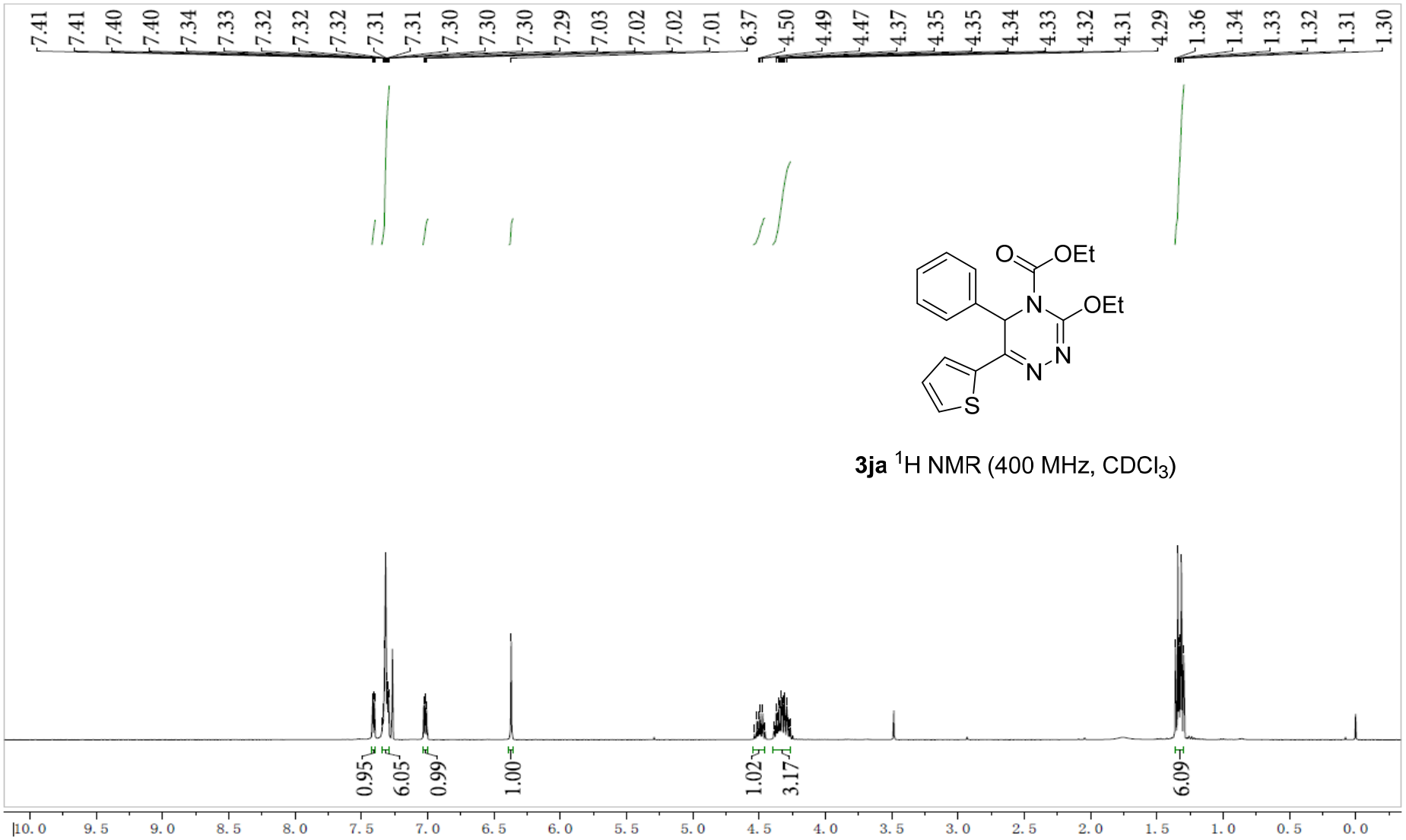
3ga ^{13}C NMR (101 MHz, $CDCl_3$)



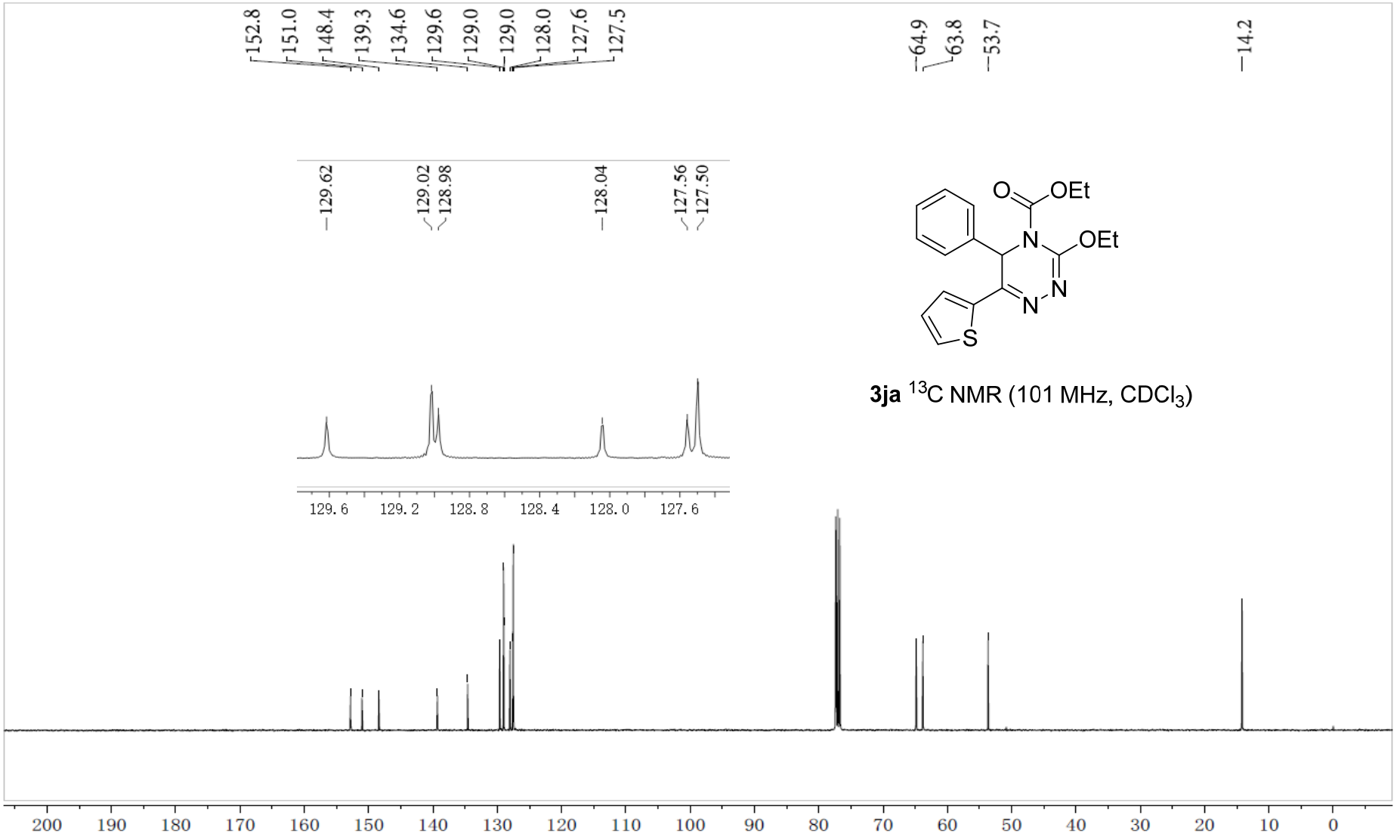
3ia ^{1}H NMR (400 MHz, $CDCl_3$)



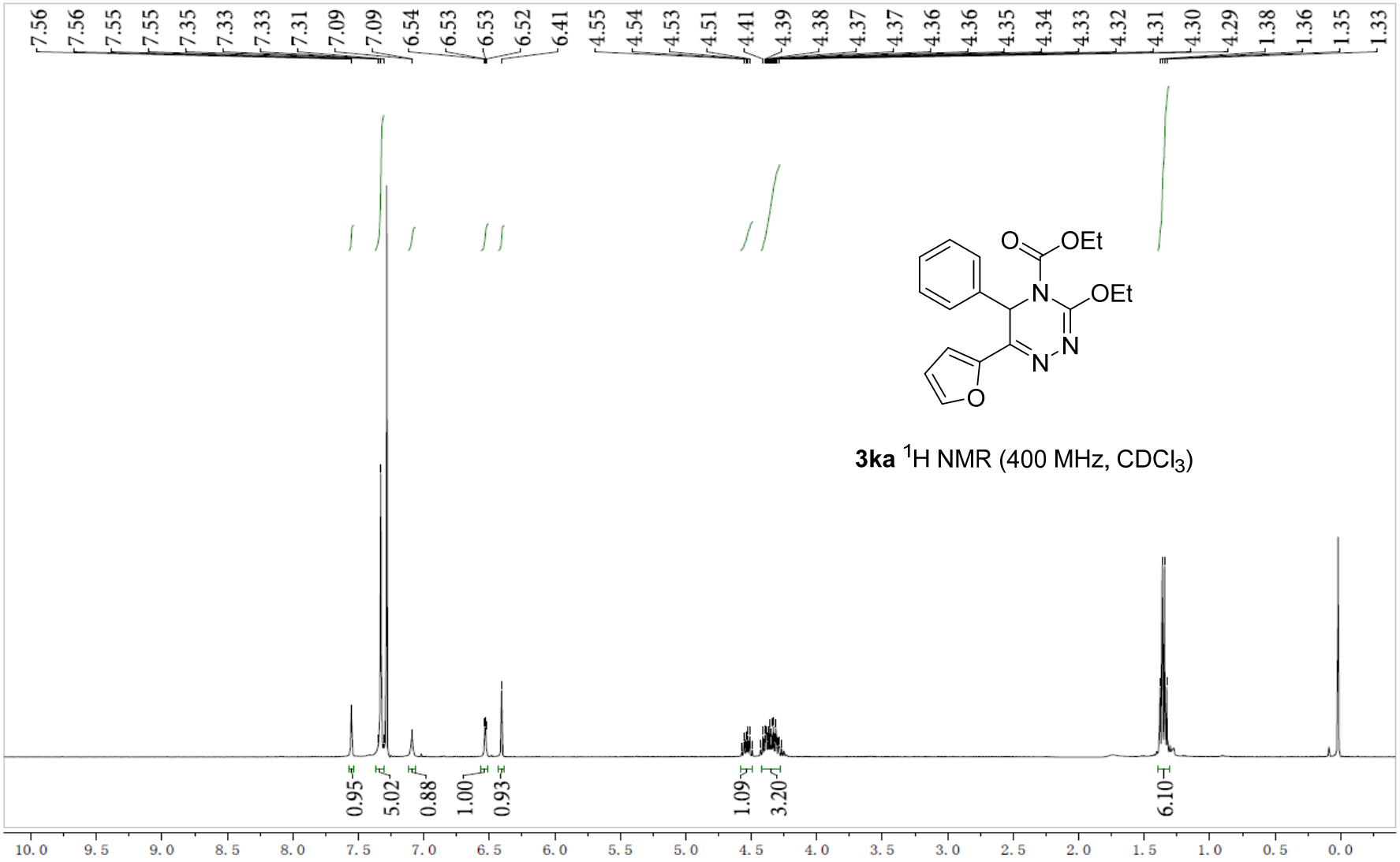
3ia ^{13}C NMR (101 MHz, $CDCl_3$)



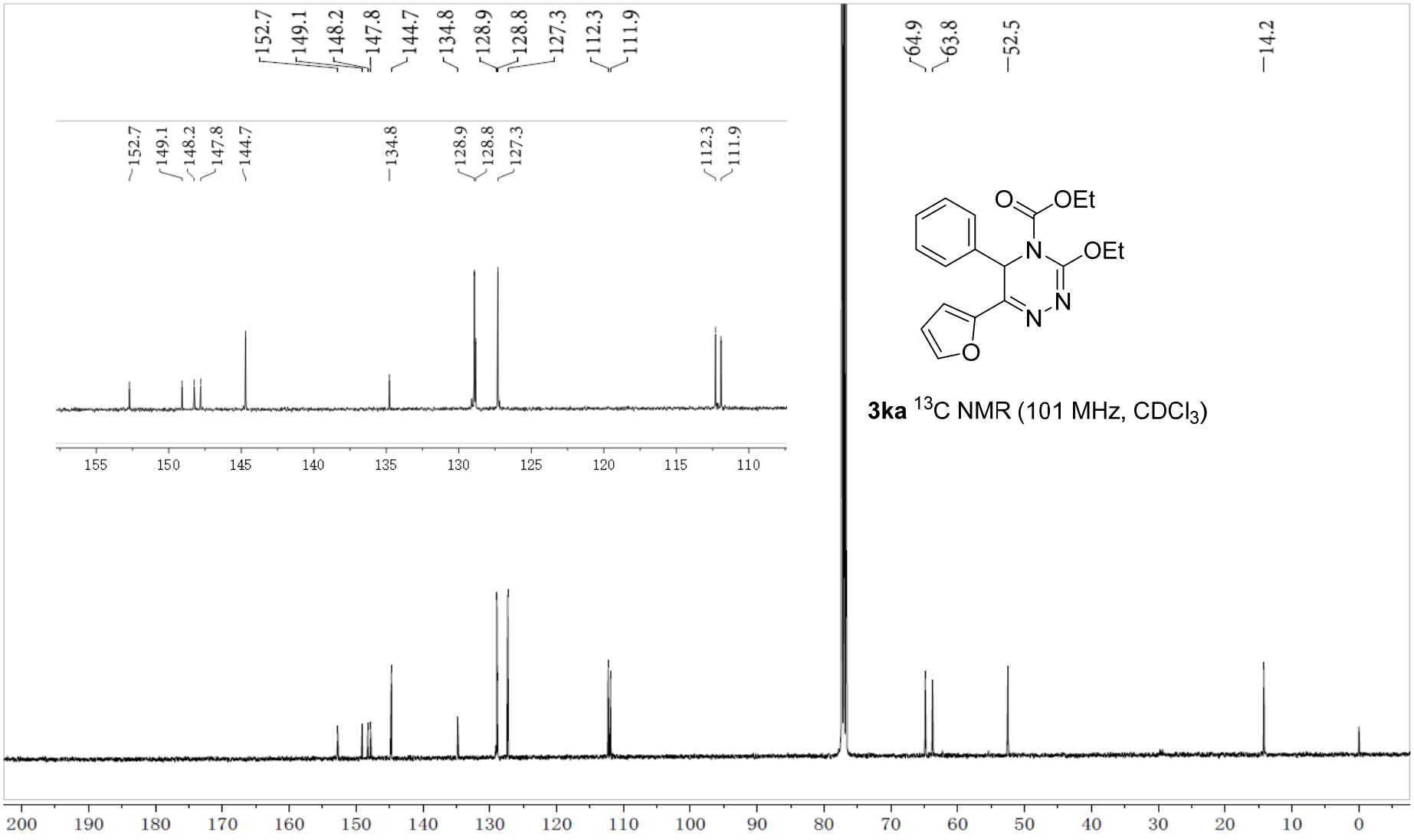
3ja ^{1}H NMR (400 MHz, $CDCl_3$)



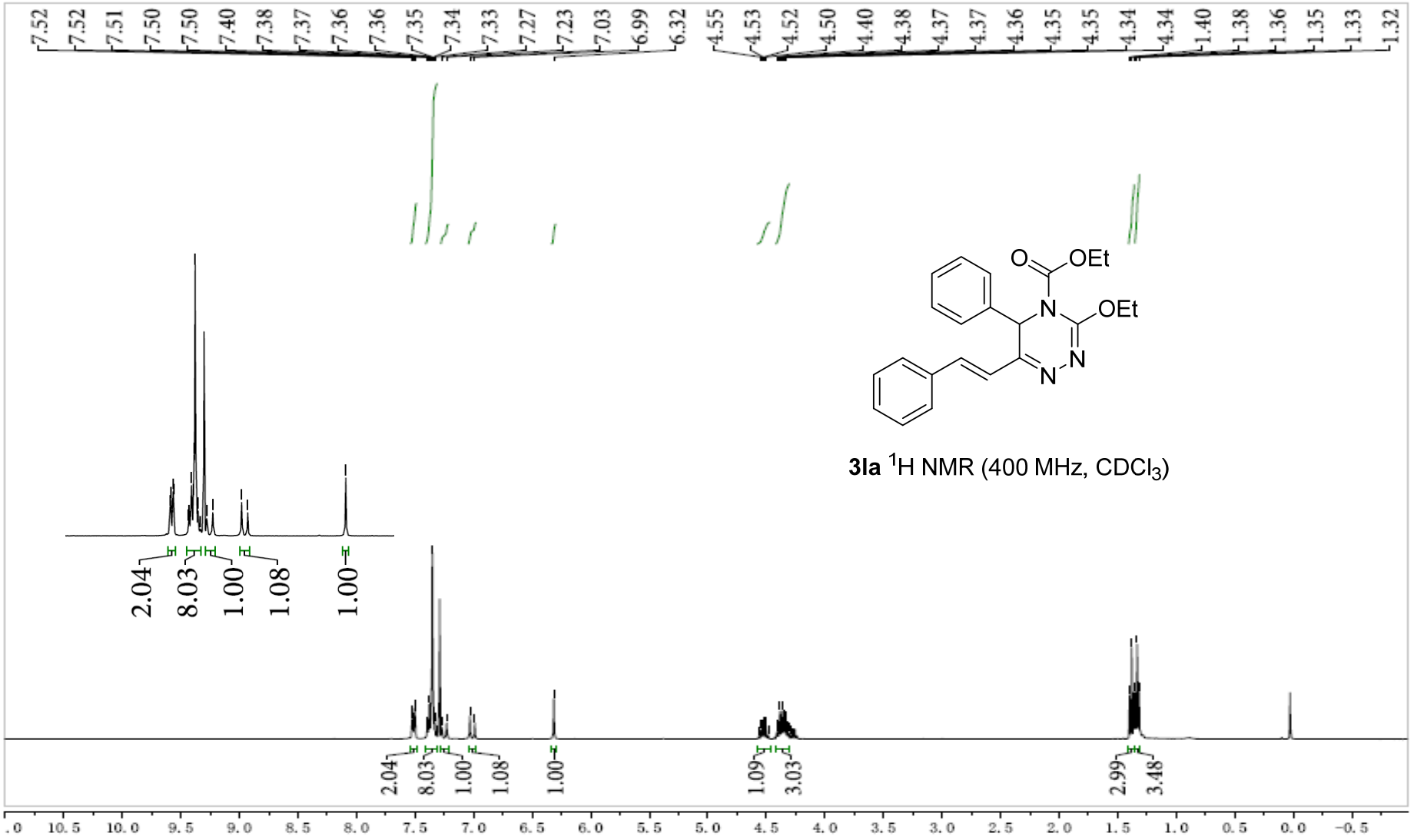
3ja ^{13}C NMR (101 MHz, $CDCl_3$)



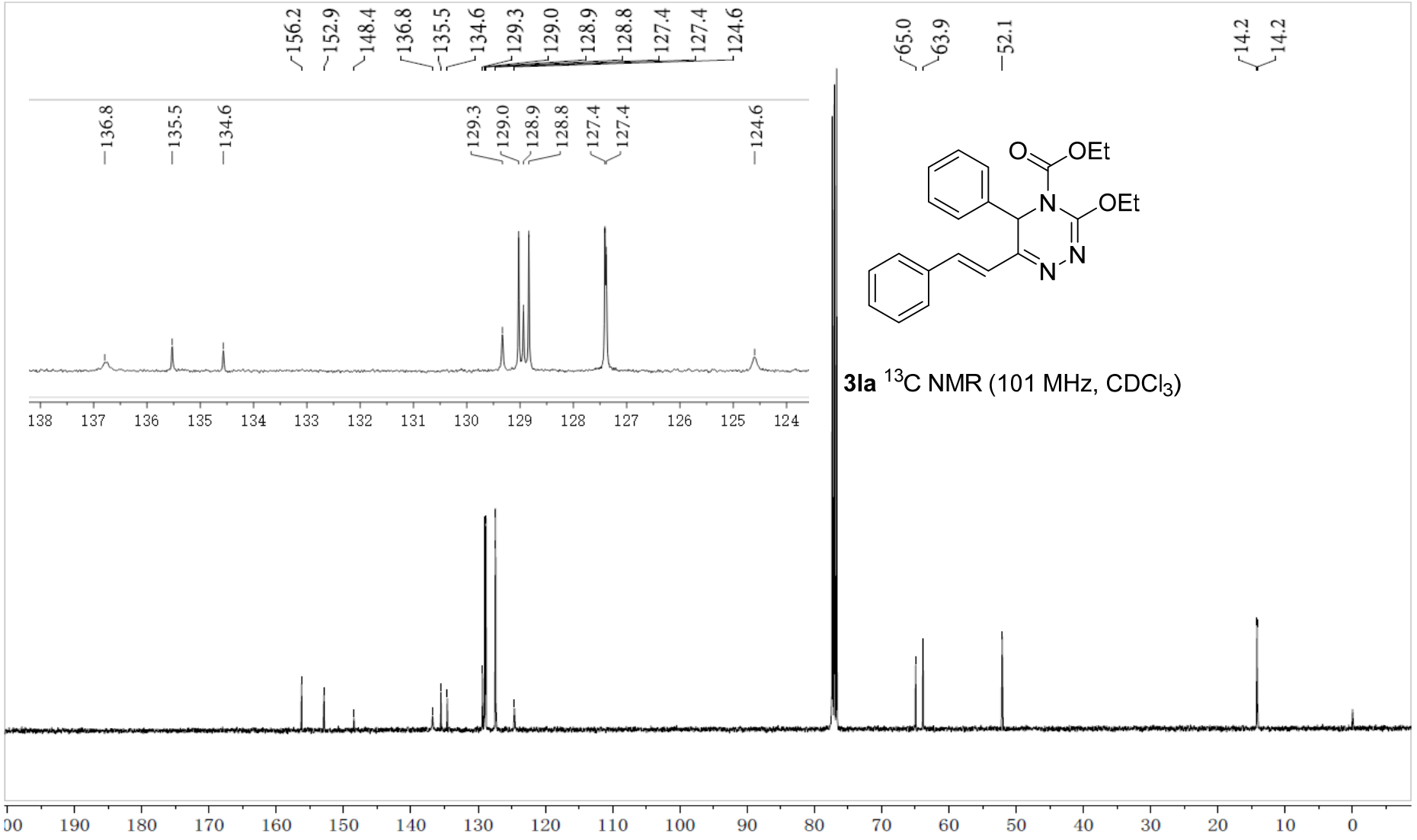
3ka ^{1}H NMR (400 MHz, $CDCl_3$)



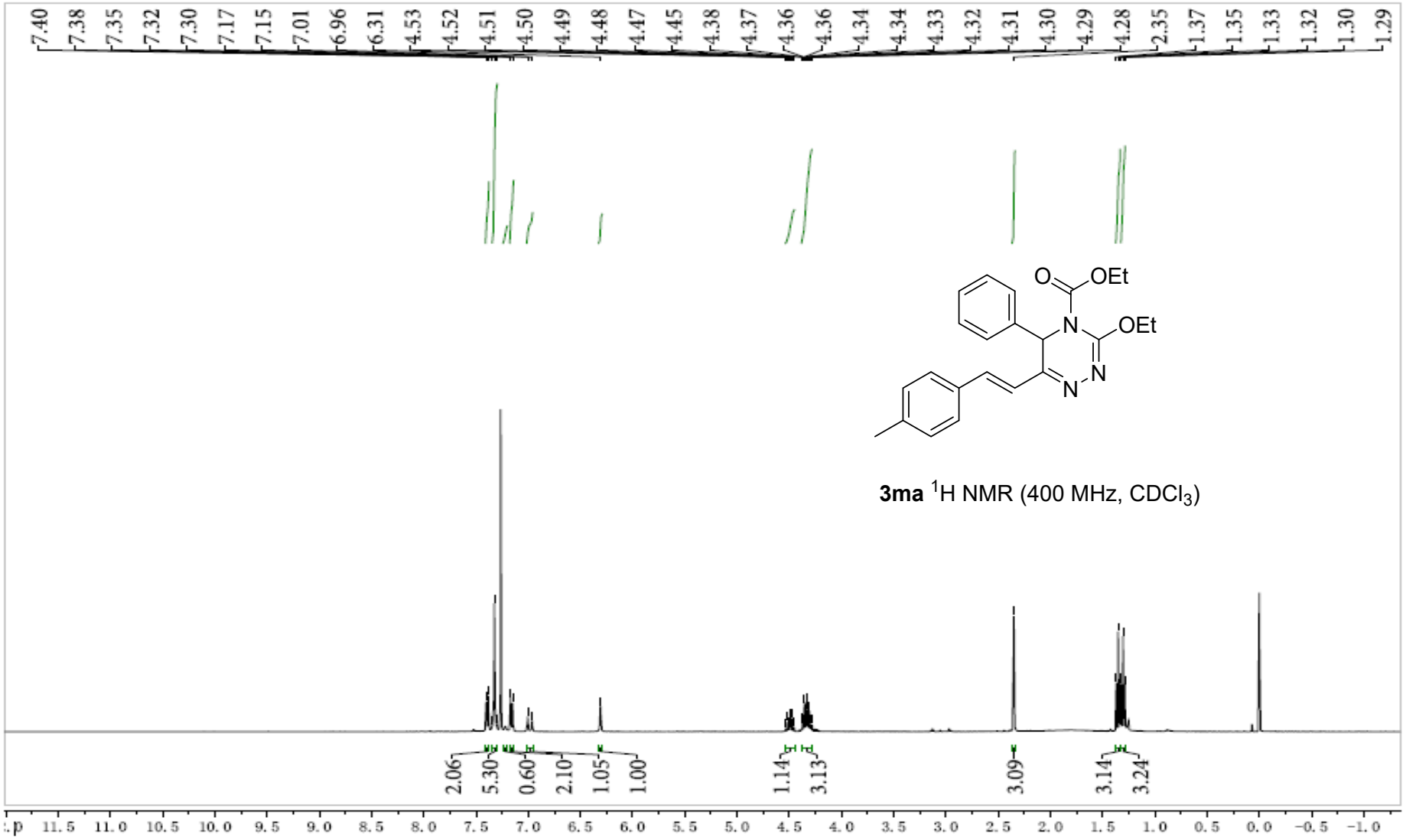
3ka ^{13}C NMR (101 MHz, $CDCl_3$)



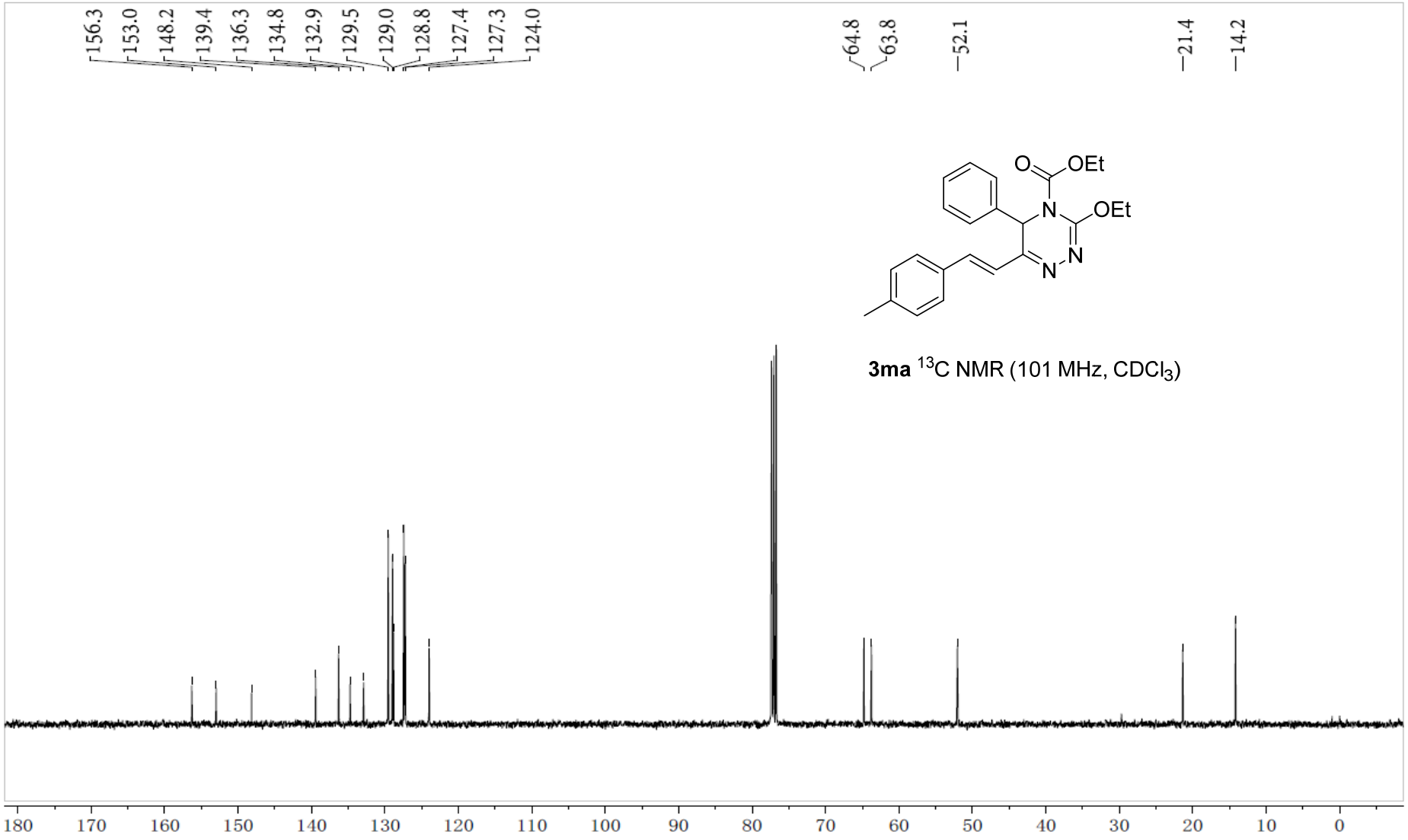
3la ^{1}H NMR (400 MHz, $CDCl_3$)



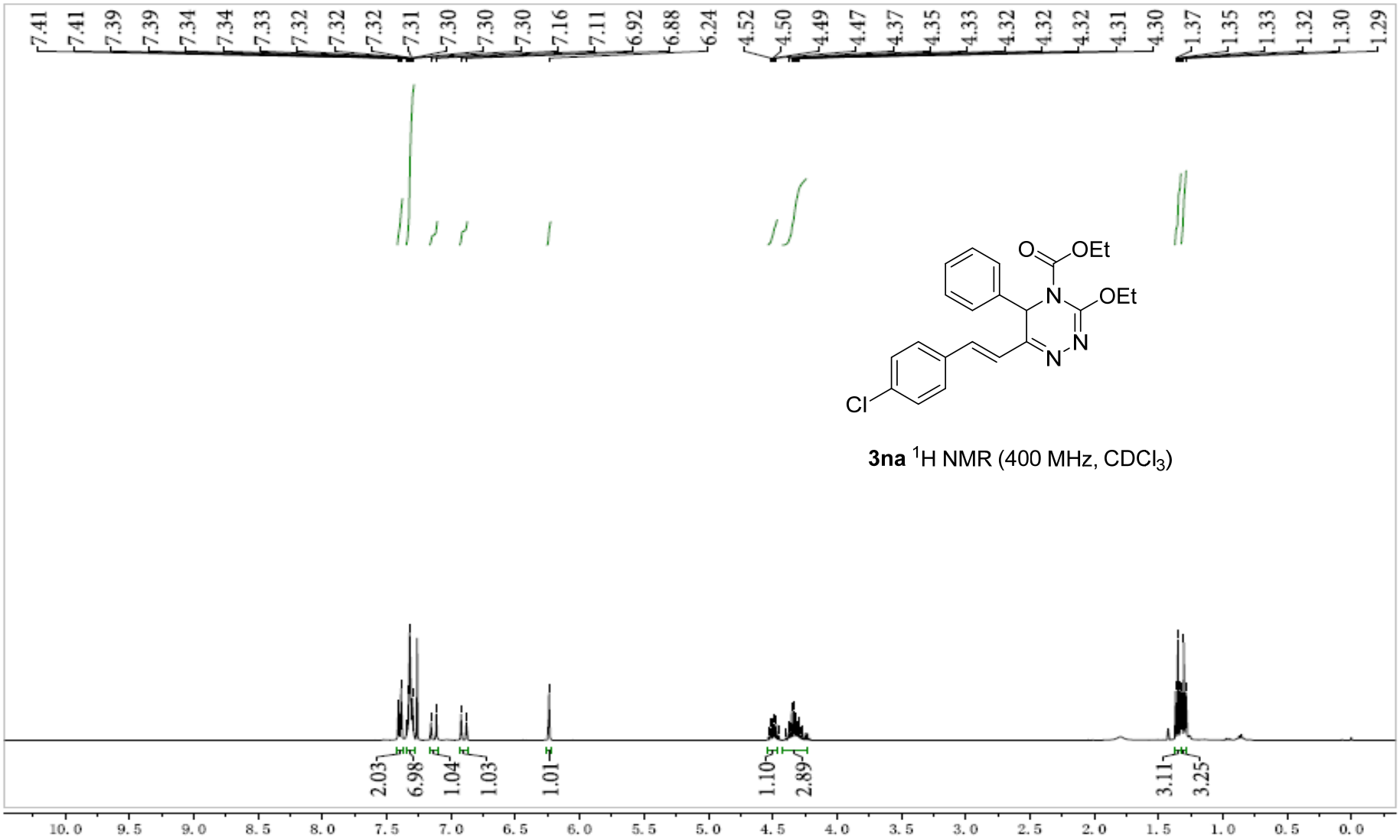
3la ^{13}C NMR (101 MHz, $CDCl_3$)



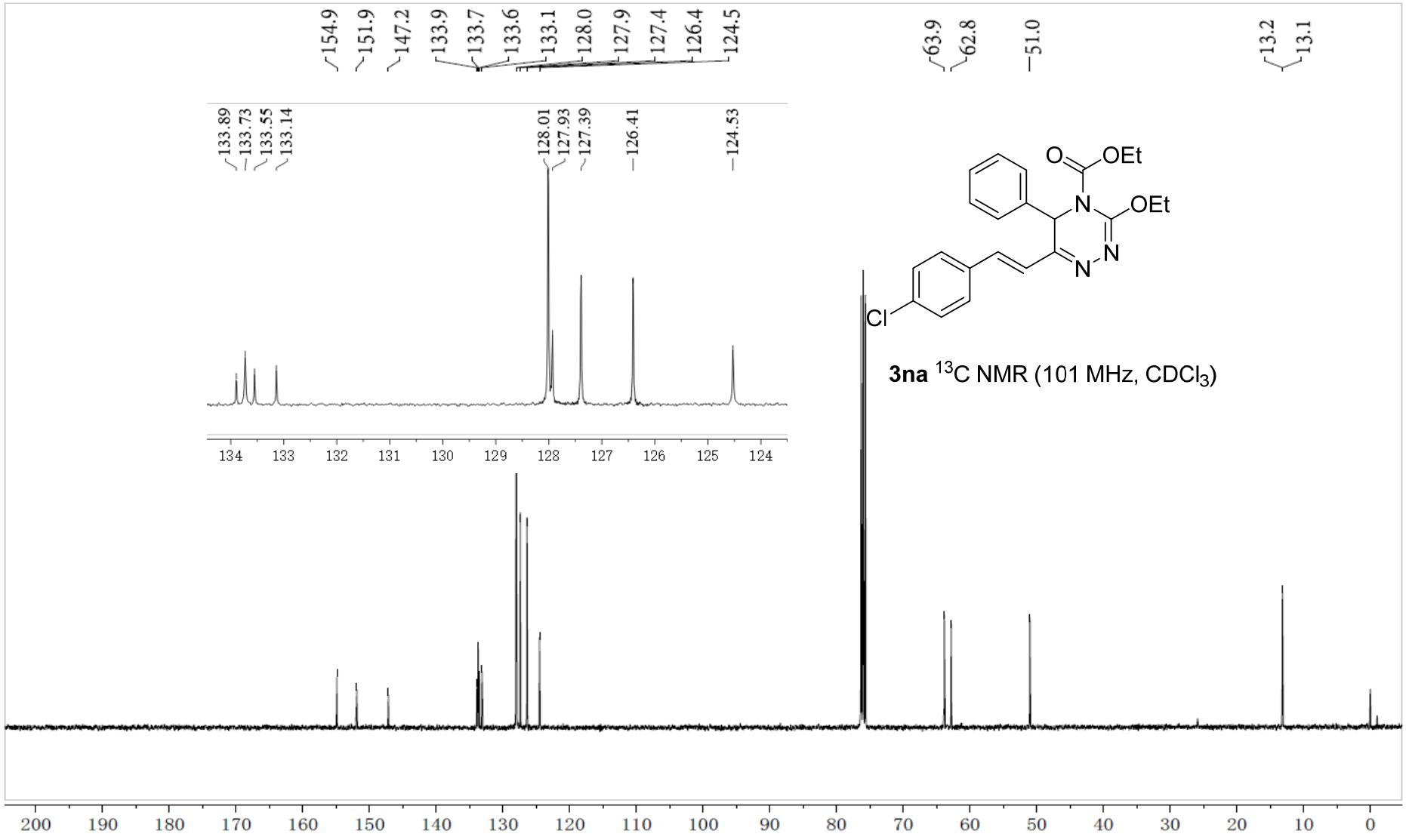
3ma ^{1}H NMR (400 MHz, $CDCl_3$)



3ma ^{13}C NMR (101 MHz, $CDCl_3$)



3na ^{1}H NMR (400 MHz, $CDCl_3$)


154.9
151.9
147.2
133.9
133.7
133.6
133.1
128.0
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127.4
126.4
124.5
63.9
62.8
51.0
13.2
13.1
133.89
133.73
133.55
133.14
128.01
127.93
127.39
126.41
124.53
O
OEt
N
OEt
N
N
Cl
3na 13C NMR (101 MHz, CDCl3)
134
133
132
131
130
129
128
127
126
125
124
200
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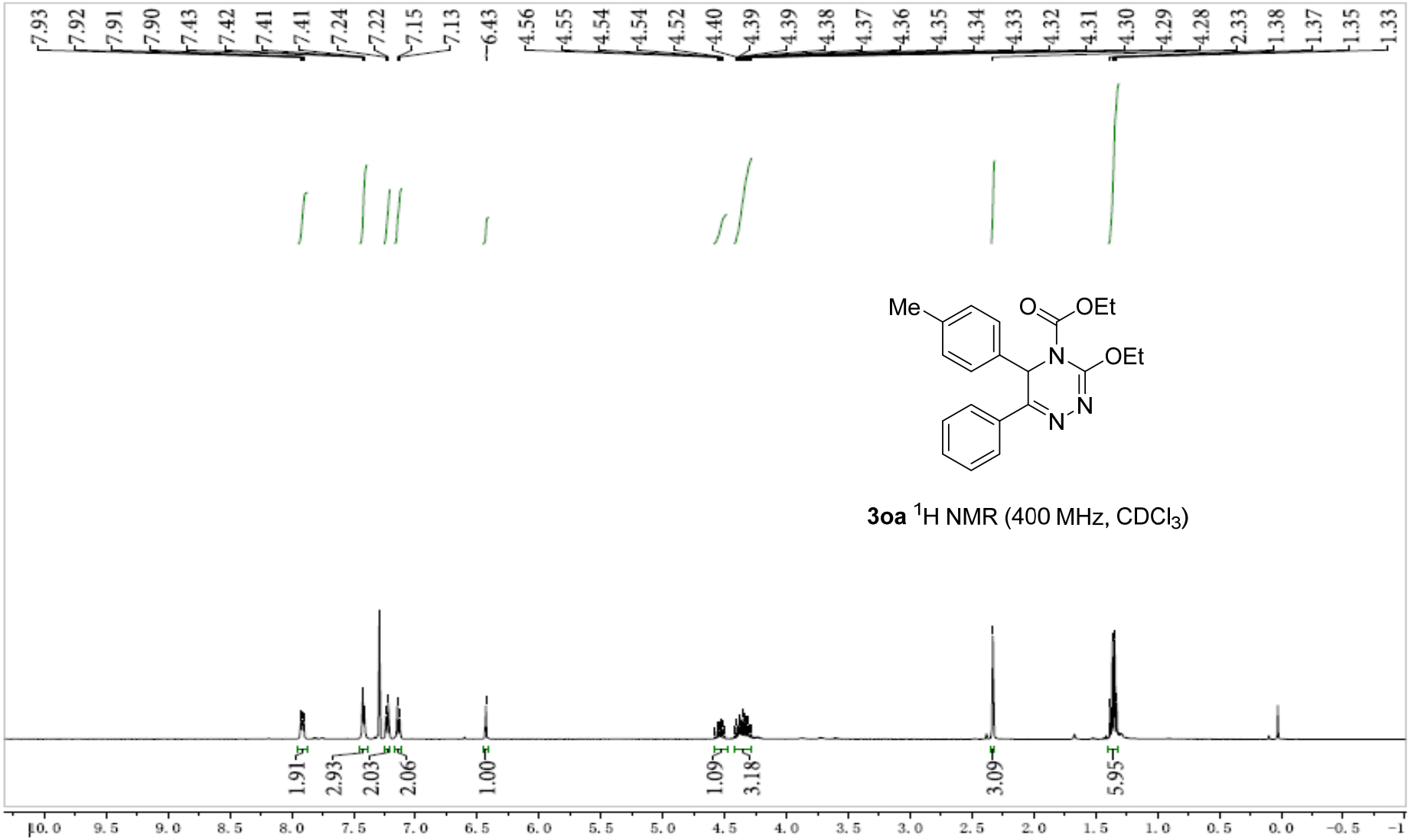
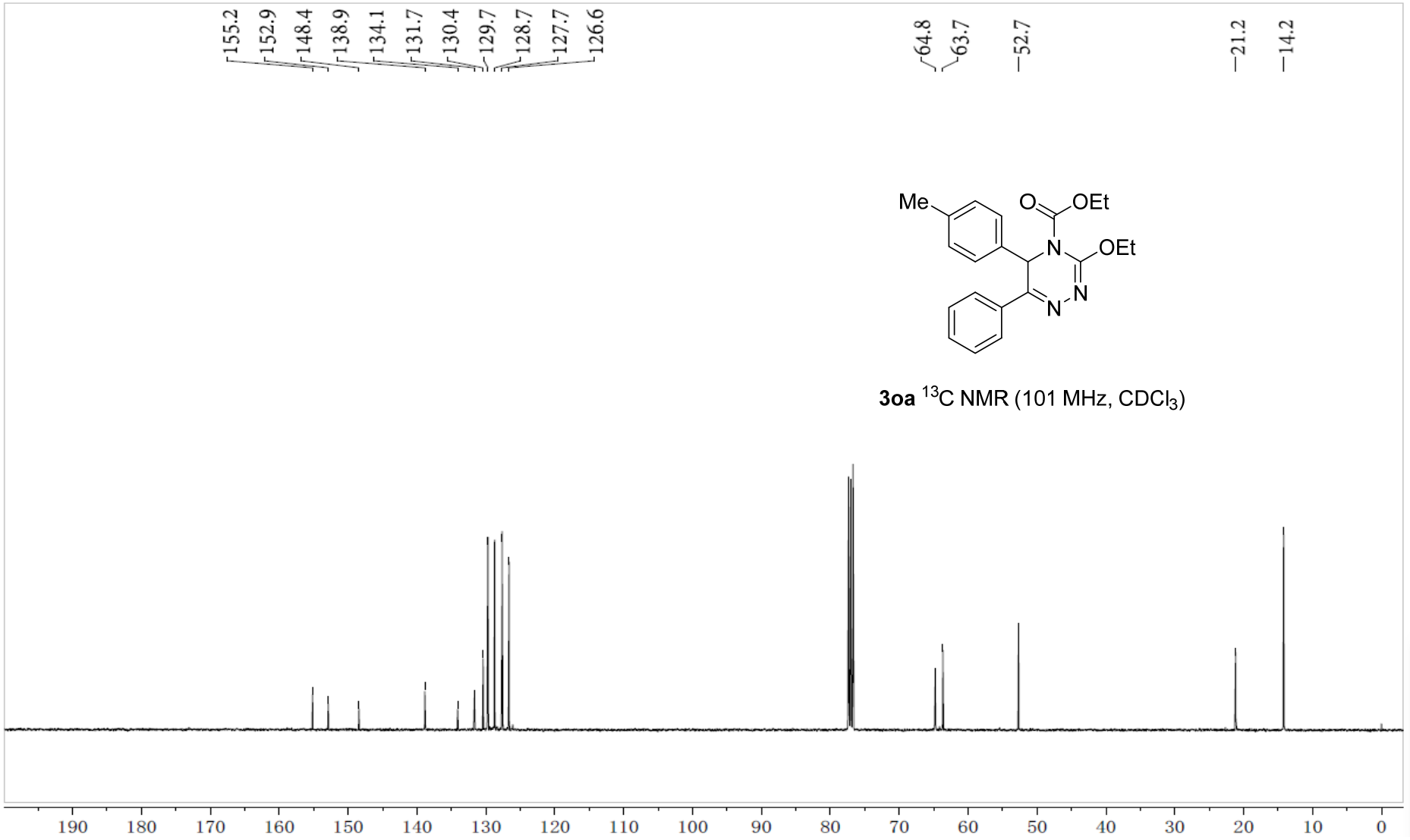
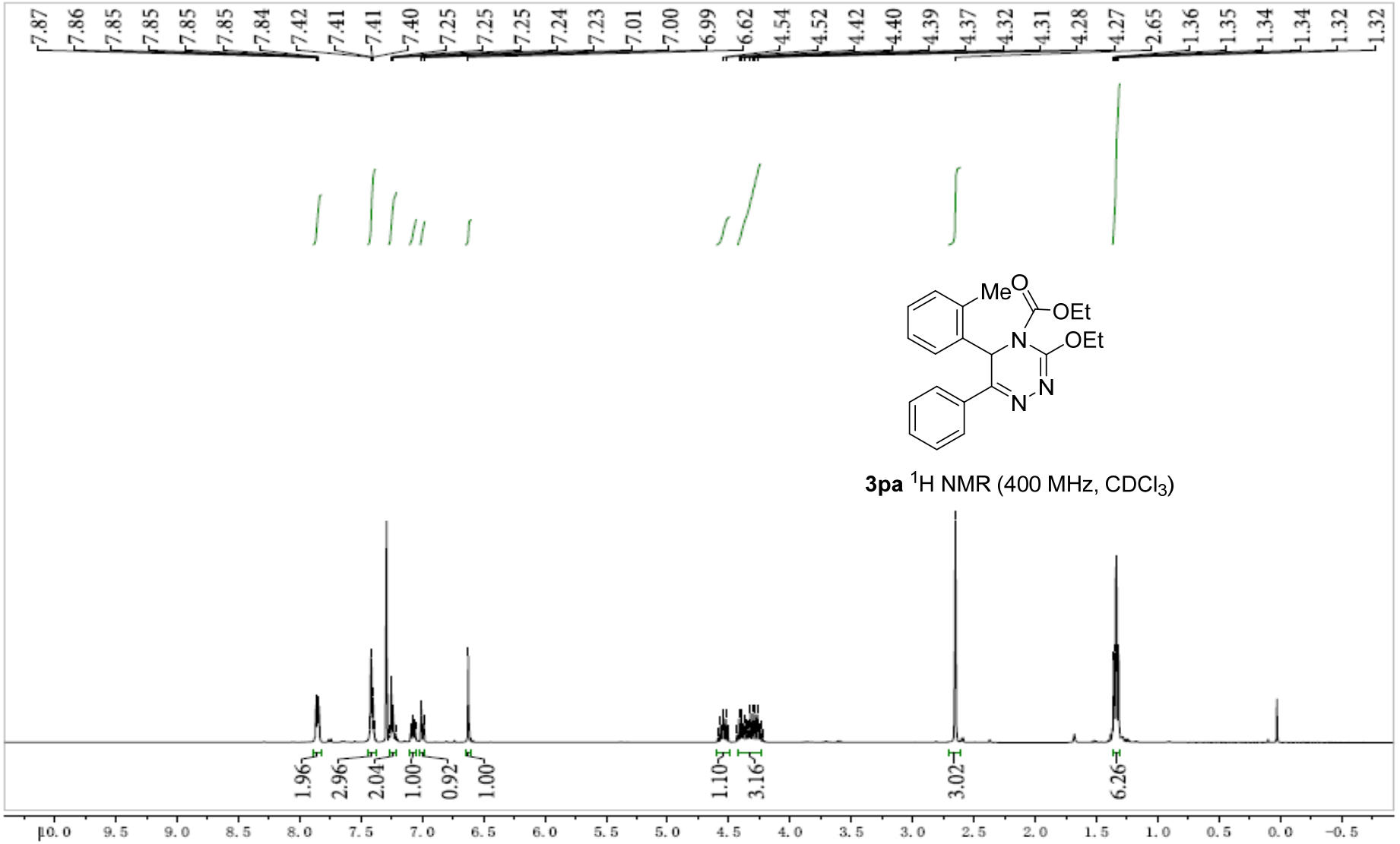
90
80
70
60
50
40
30
20
10
0



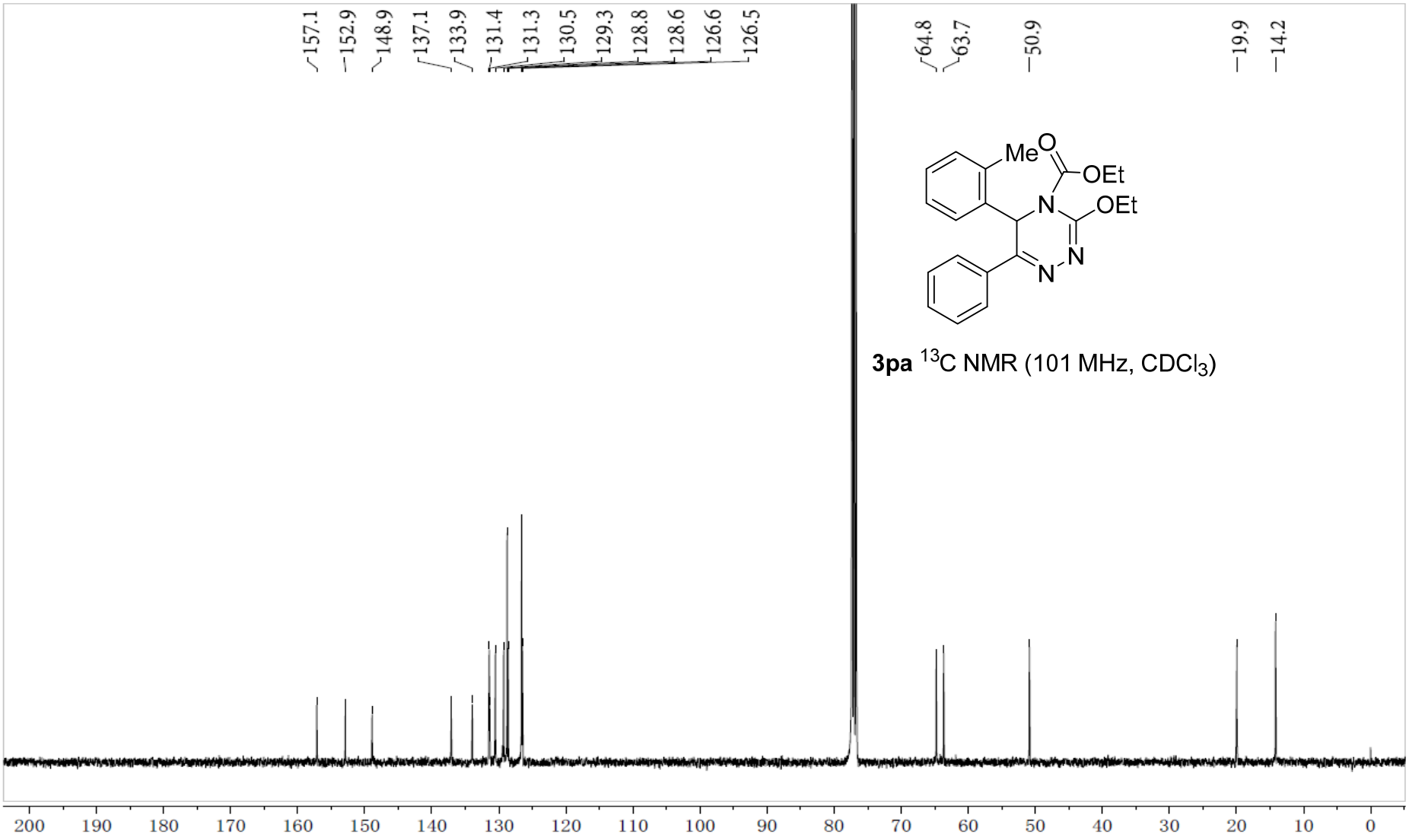
3oa ^{1}H NMR (400 MHz, $CDCl_3$)



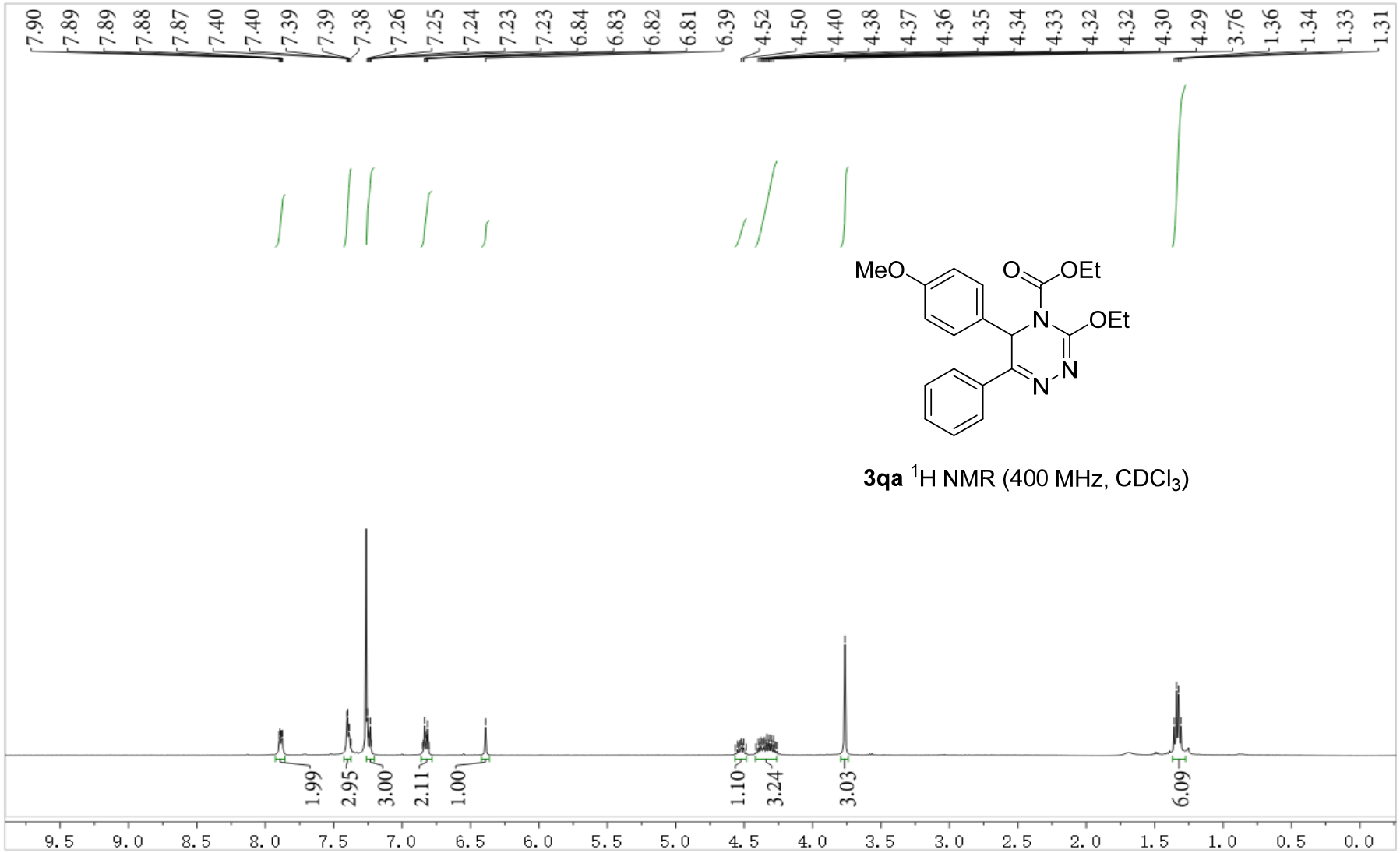
3oa ^{13}C NMR (101 MHz, $CDCl_3$)



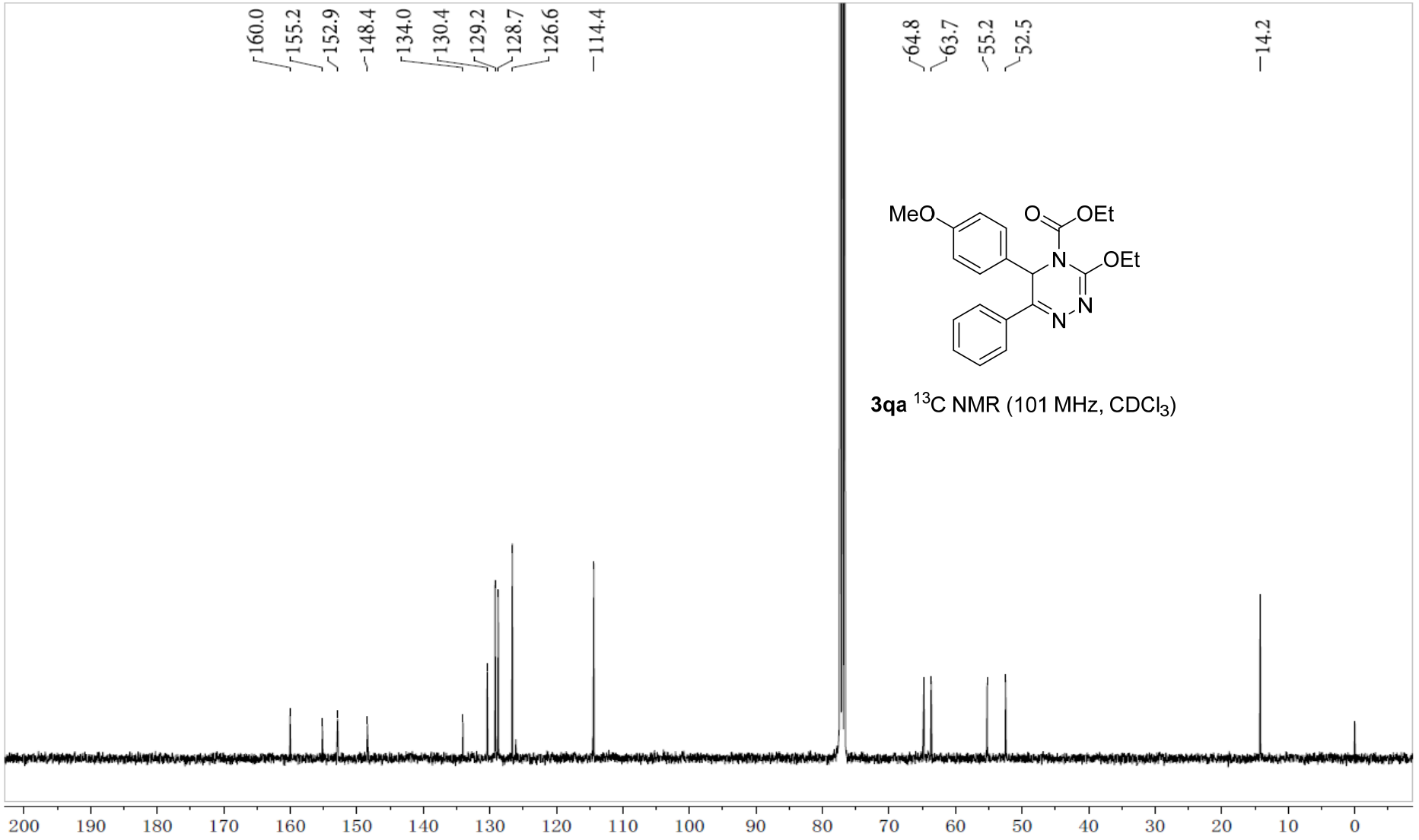
3pa ^{1}H NMR (400 MHz, $CDCl_3$)



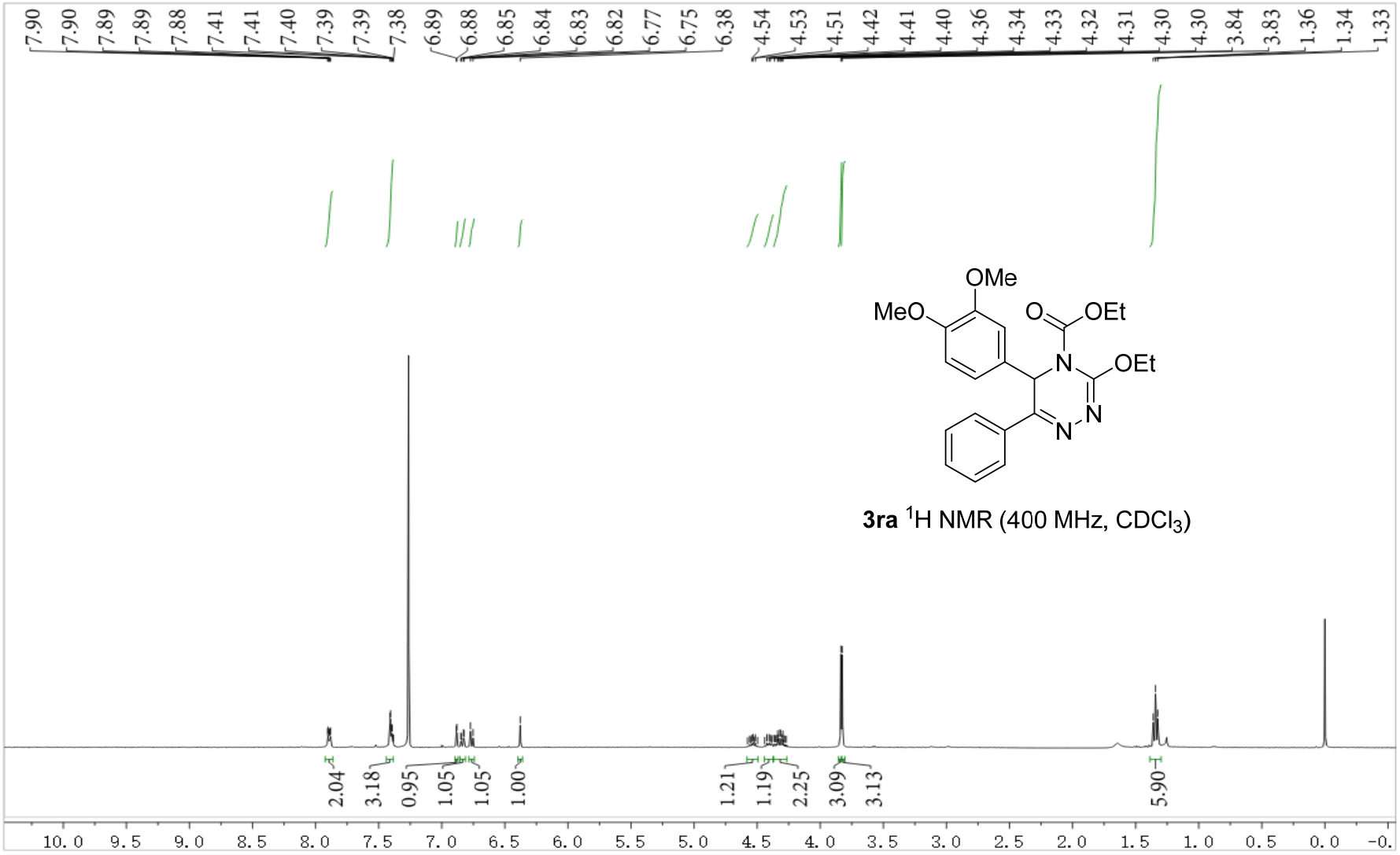
3pa ^{13}C NMR (101 MHz, $CDCl_3$)



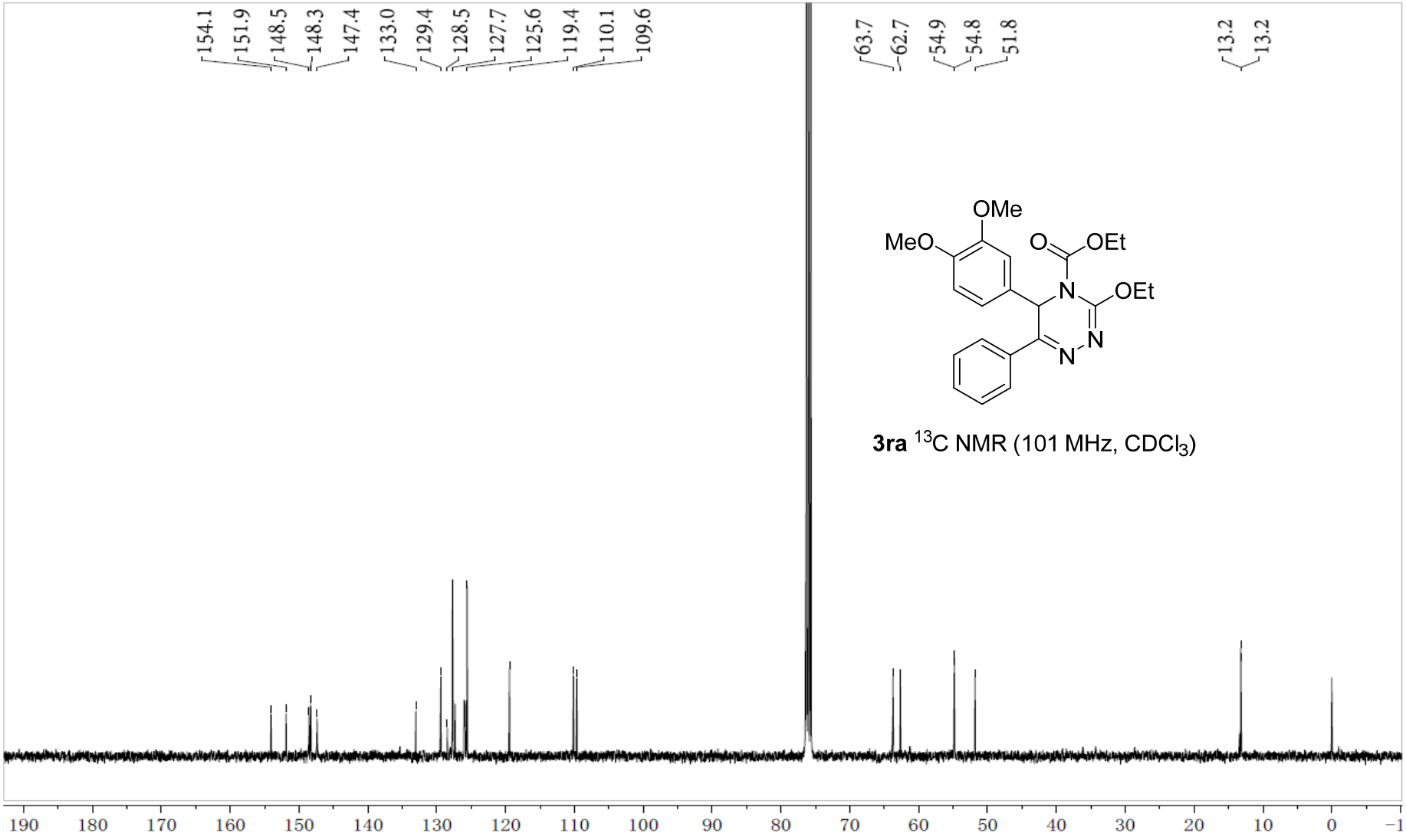
3qa ^{1}H NMR (400 MHz, $CDCl_3$)



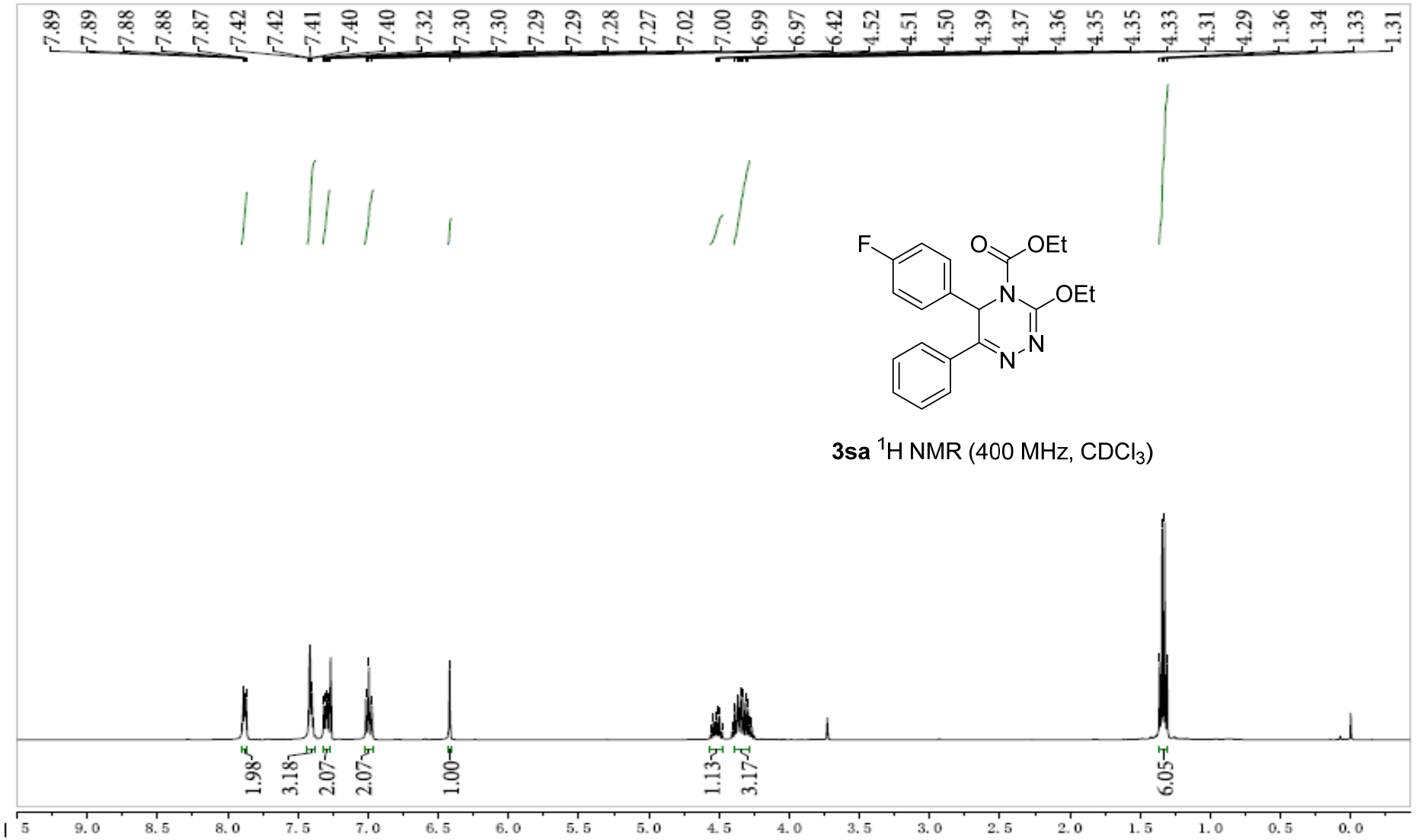
3qa ^{13}C NMR (101 MHz, $CDCl_3$)



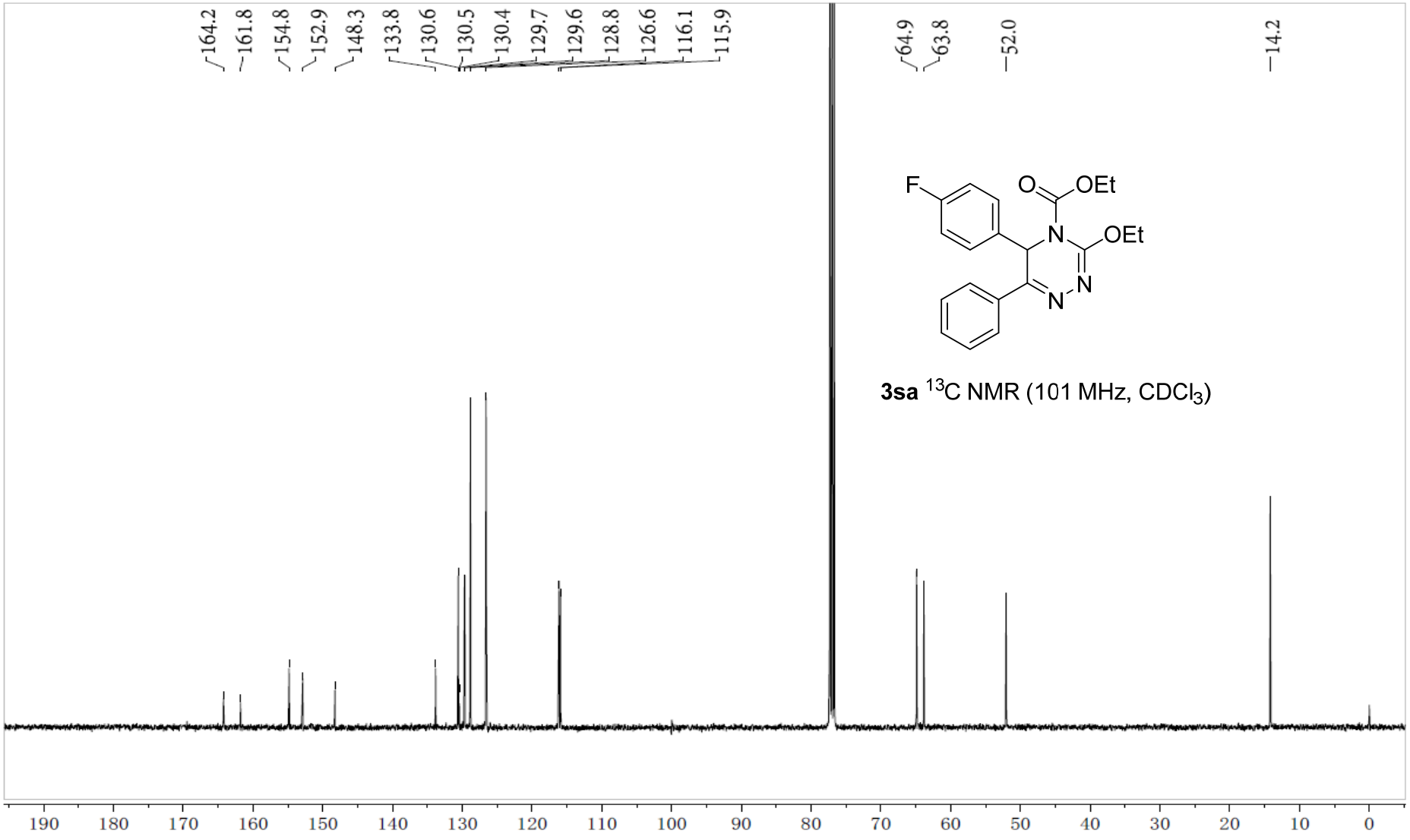
3ra ^{1}H NMR (400 MHz, $CDCl_3$)



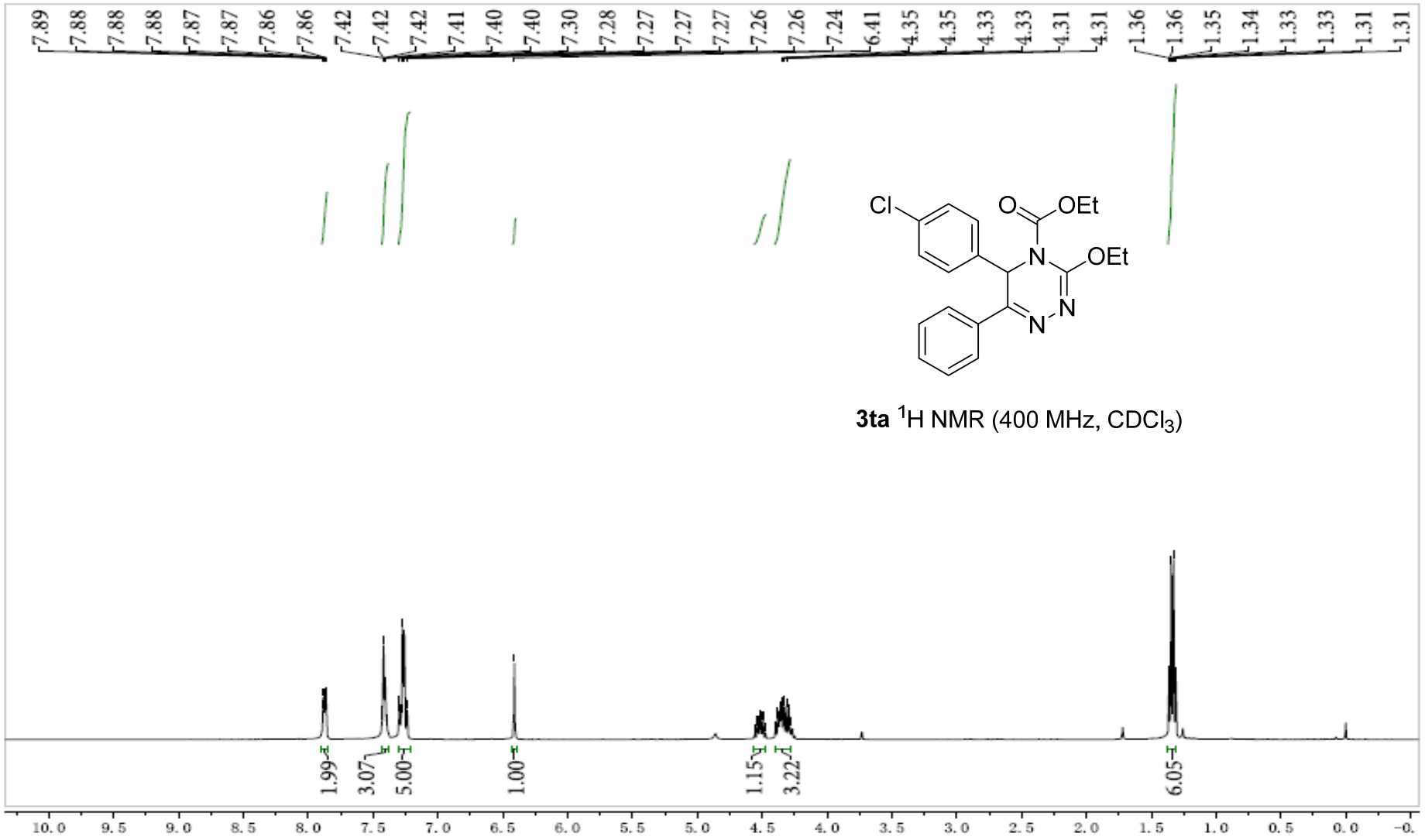
3ra ^{13}C NMR (101 MHz, $CDCl_3$)



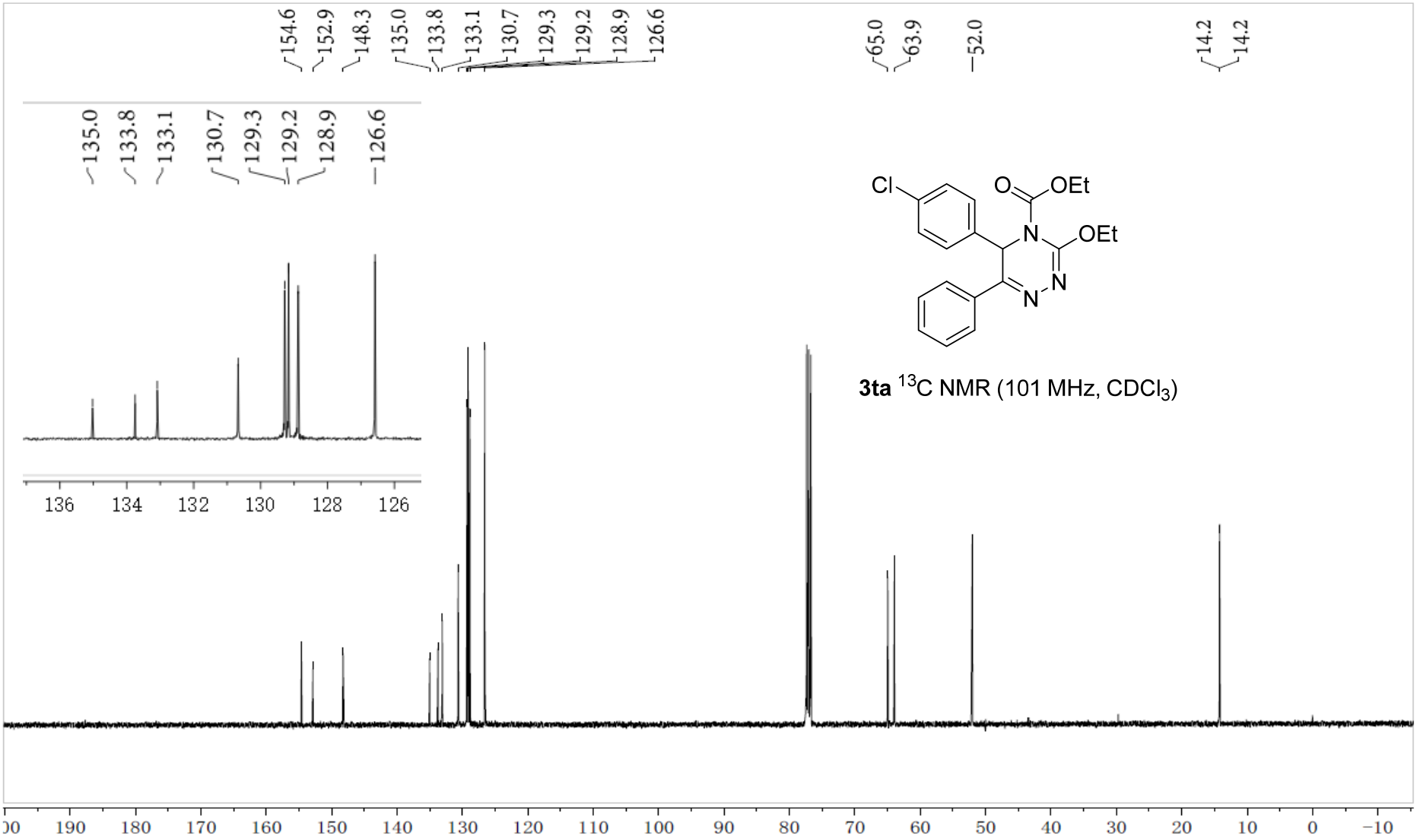
3sa ^{1}H NMR (400 MHz, $CDCl_3$)



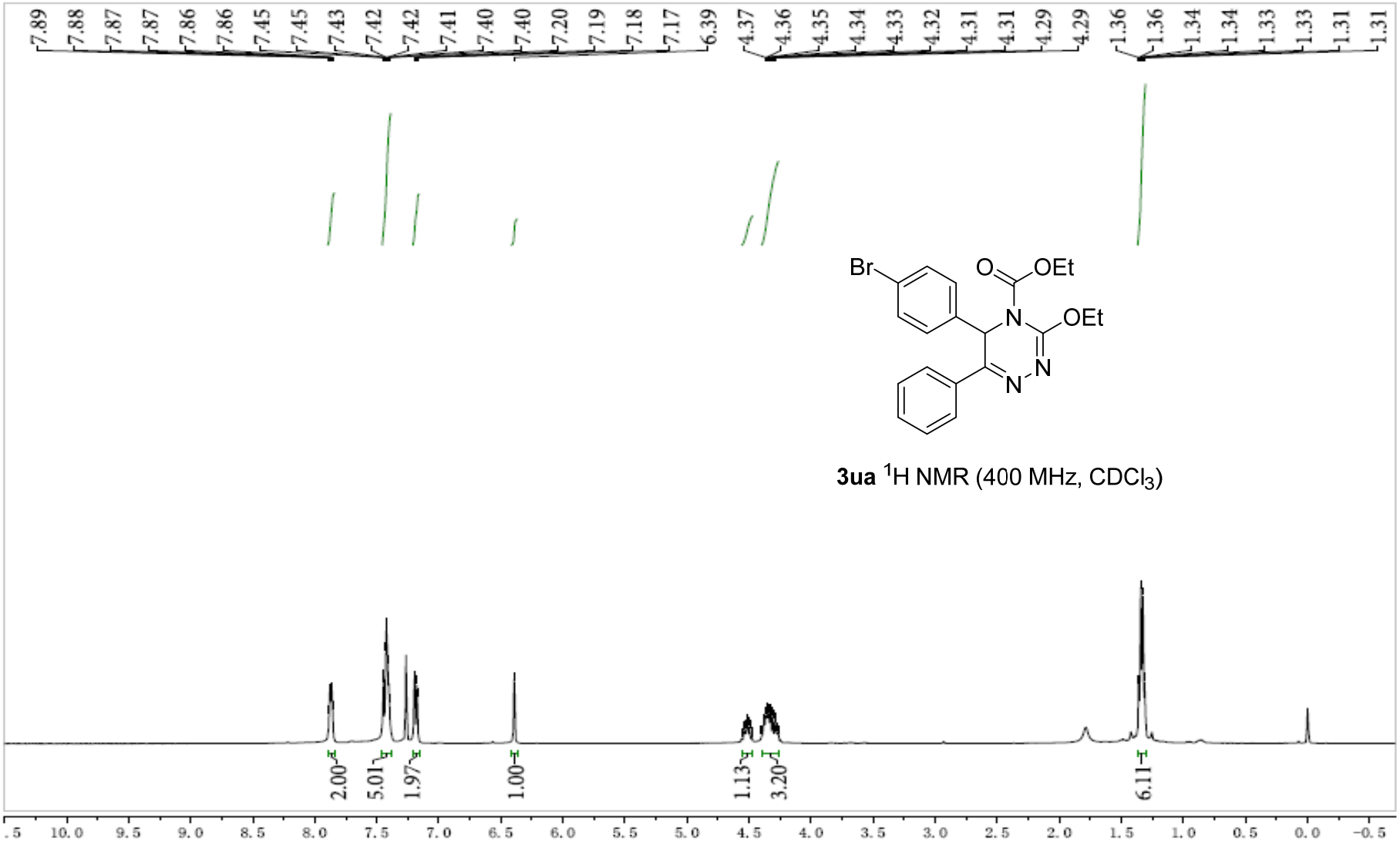
3sa ^{13}C NMR (101 MHz, $CDCl_3$)



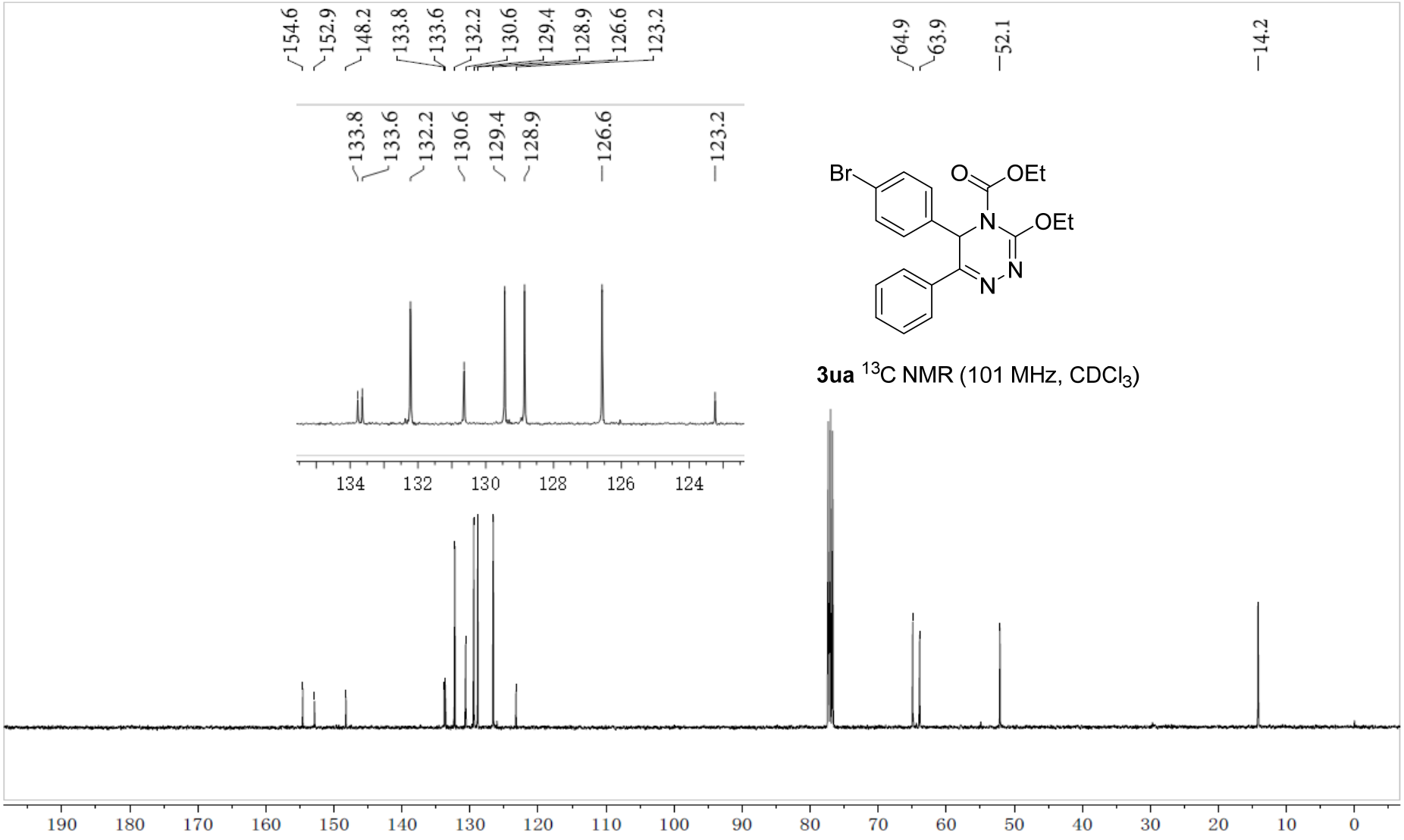
3ta ^{1}H NMR (400 MHz, $CDCl_3$)



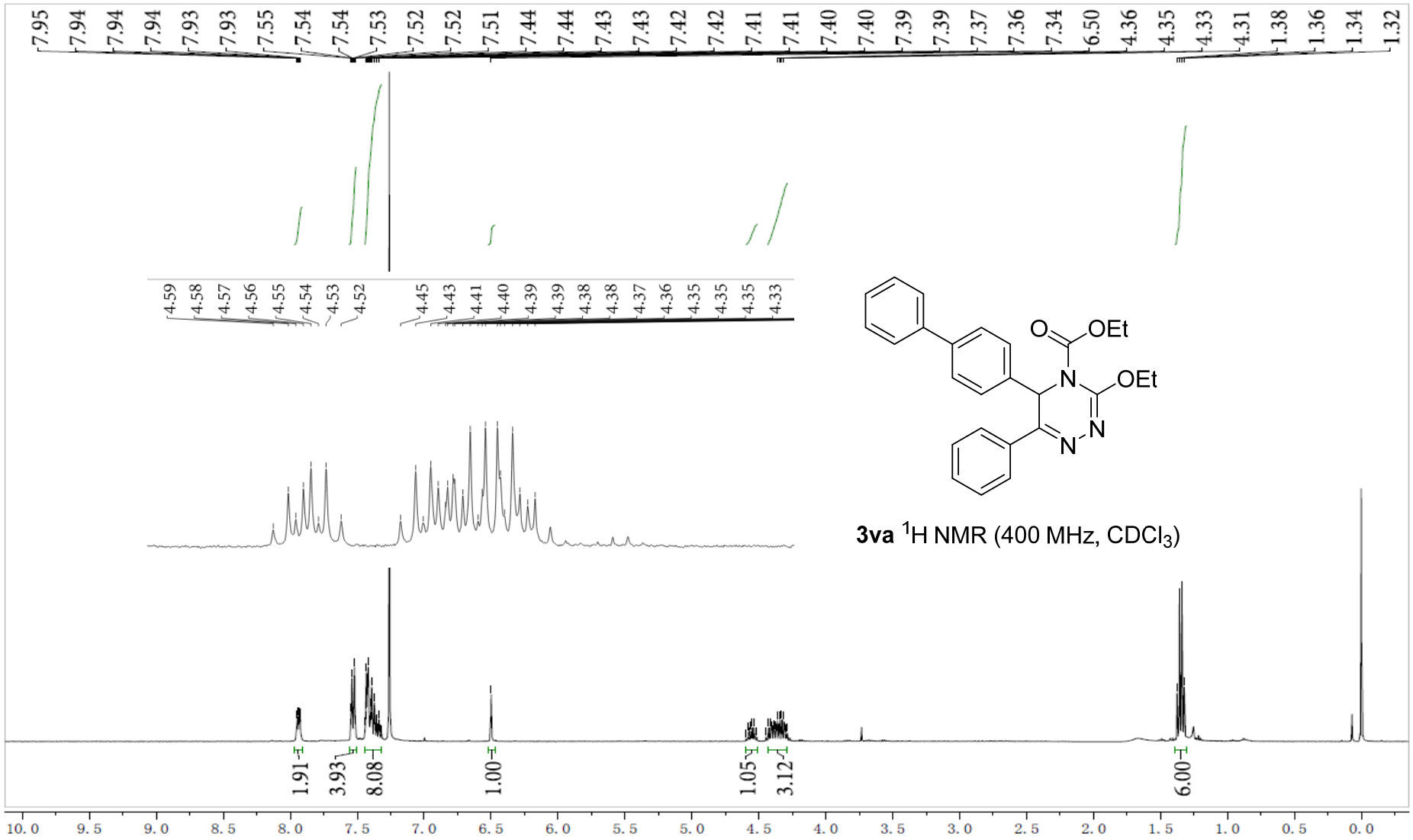
3ta ^{13}C NMR (101 MHz, $CDCl_3$)



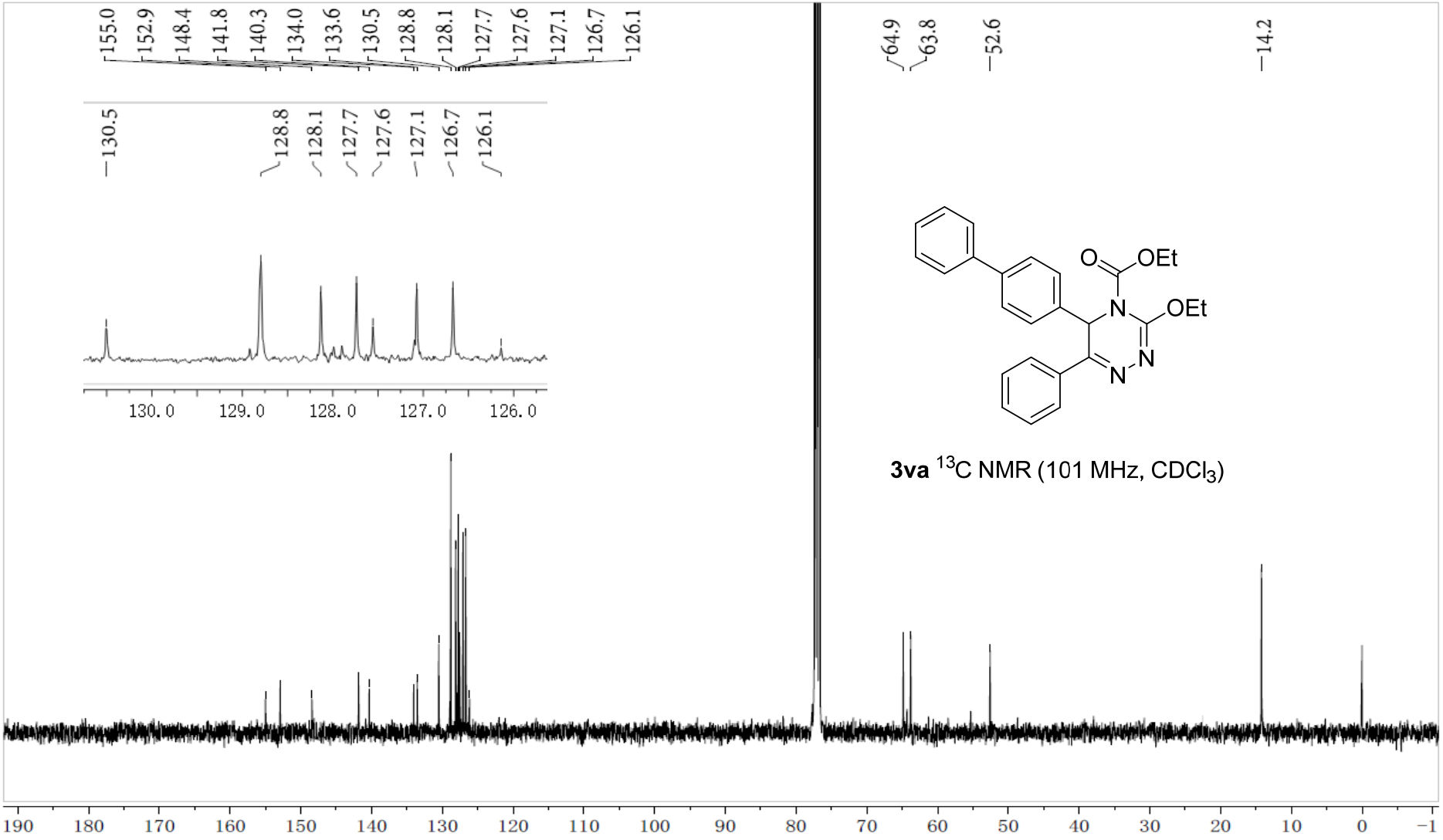
3ua ^{1}H NMR (400 MHz, $CDCl_3$)



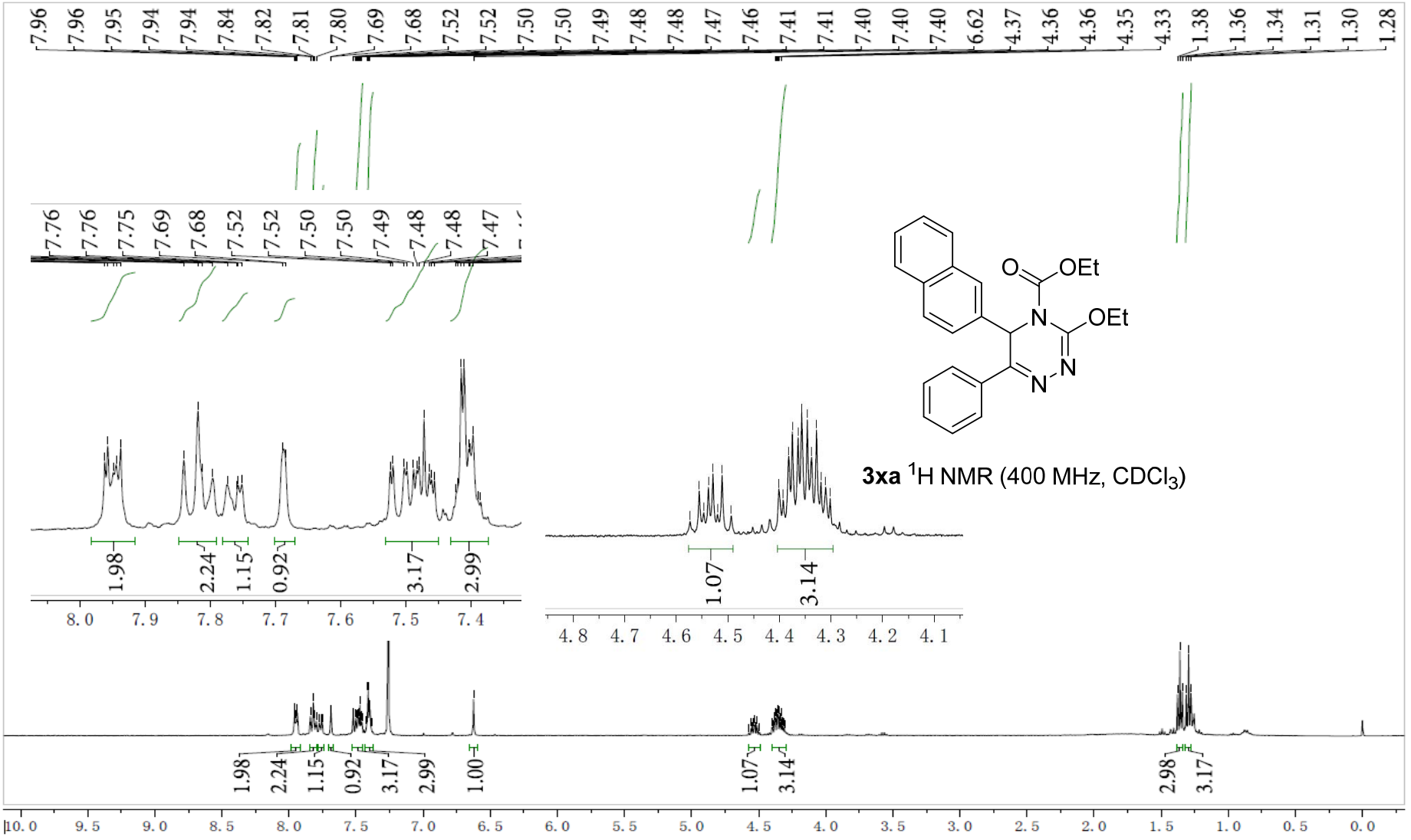
3ua ^{13}C NMR (101 MHz, $CDCl_3$)



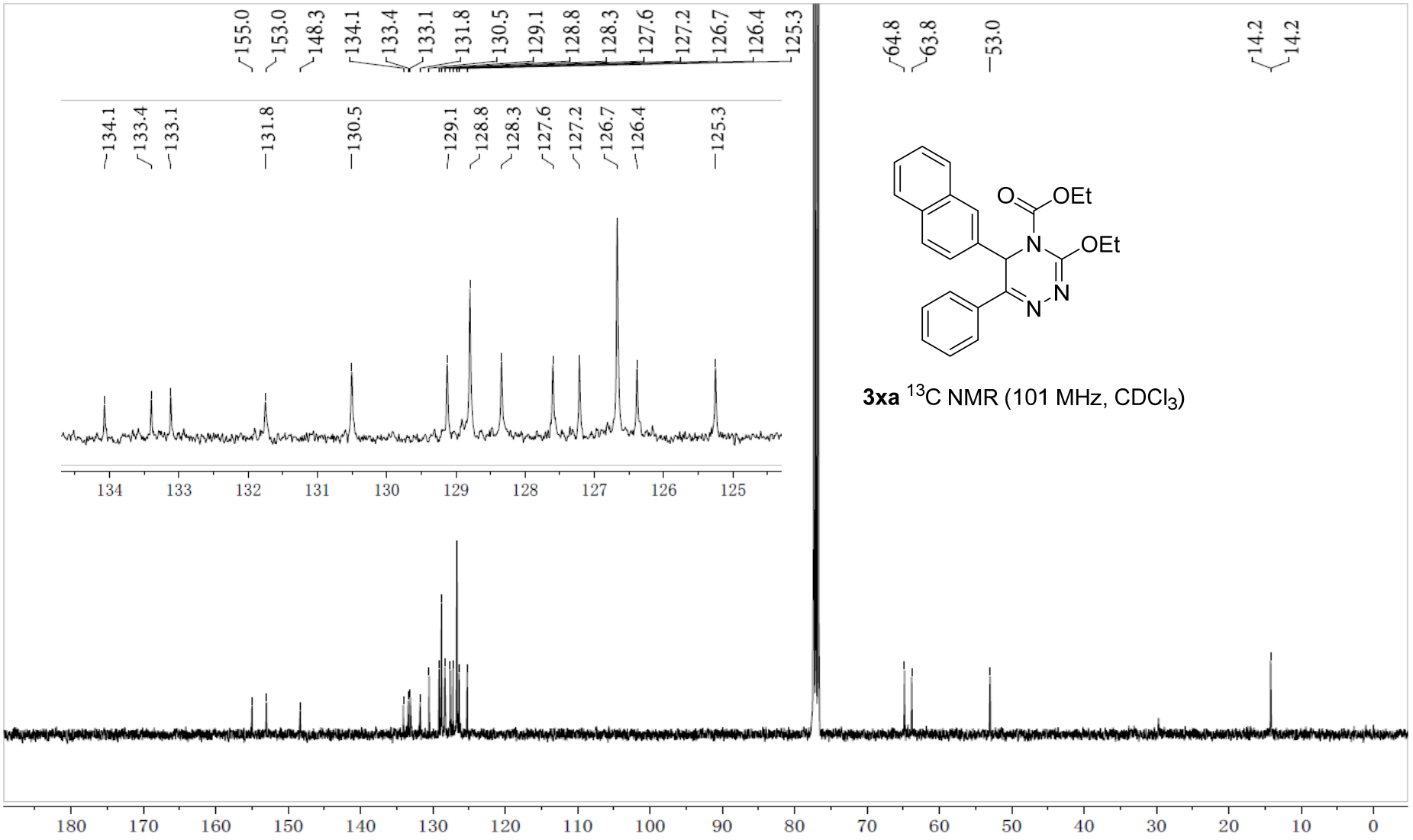
3va ^{1}H NMR (400 MHz, $CDCl_3$)



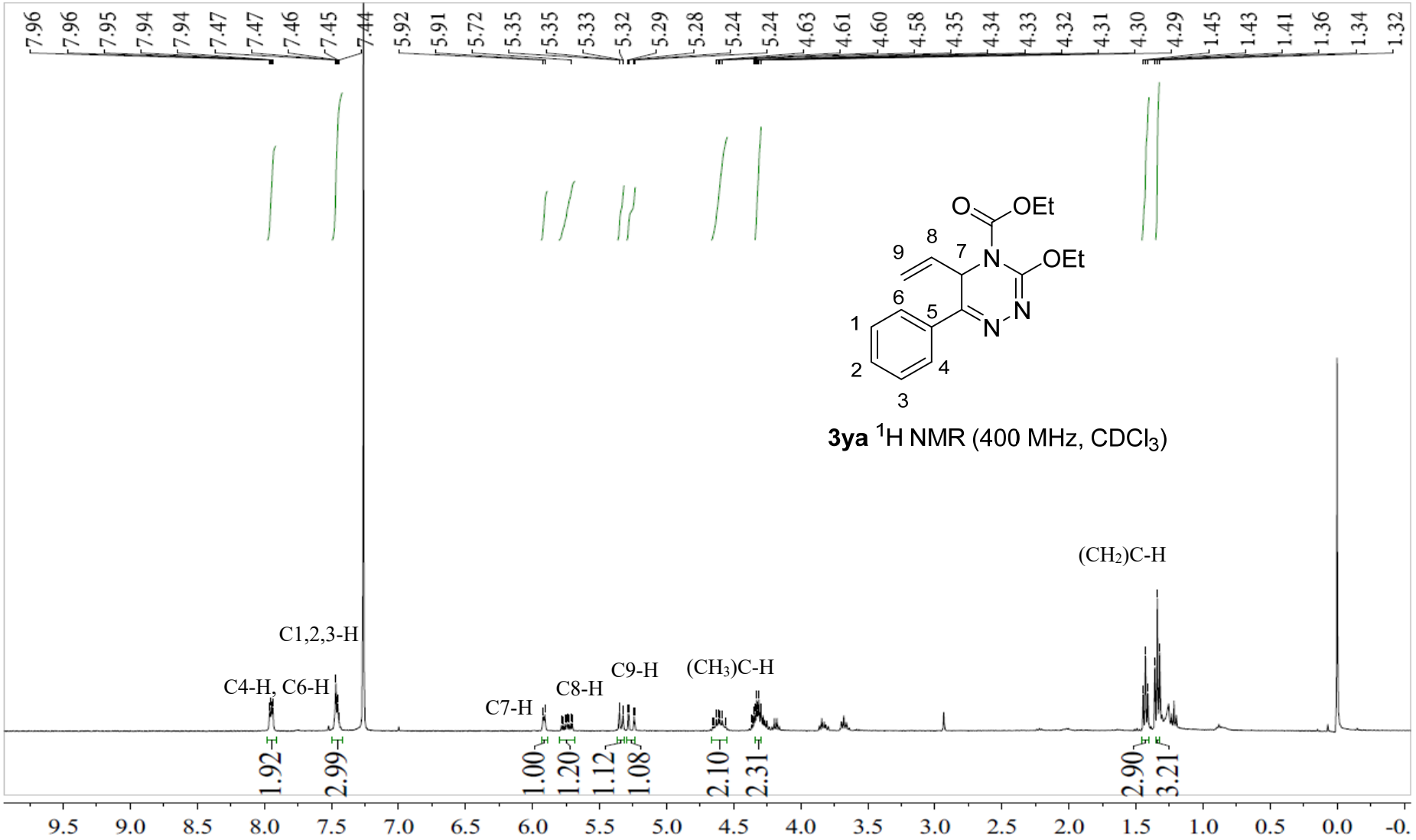
3va ^{13}C NMR (101 MHz, $CDCl_3$)



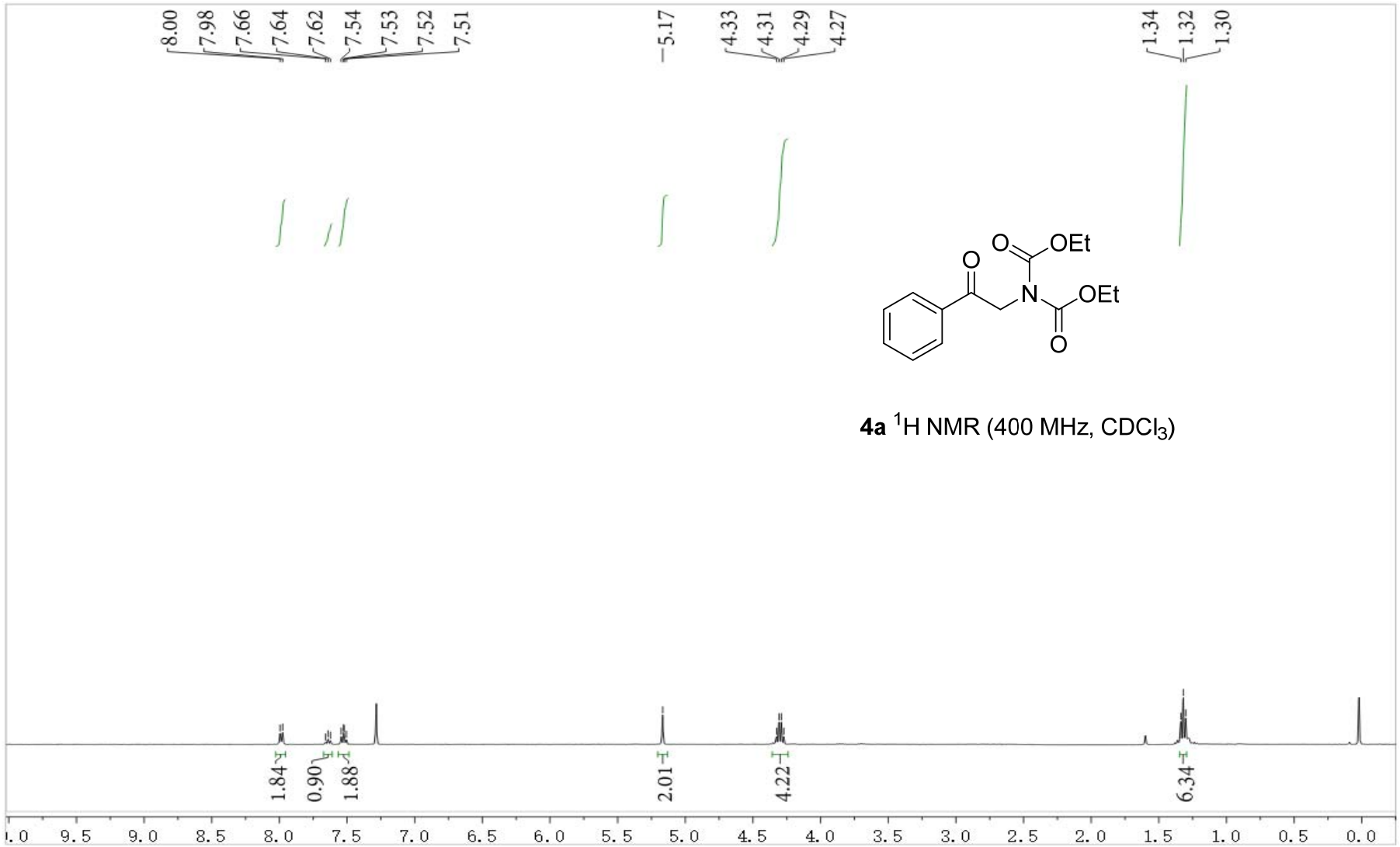
3xa ^{1}H NMR (400 MHz, $CDCl_3$)



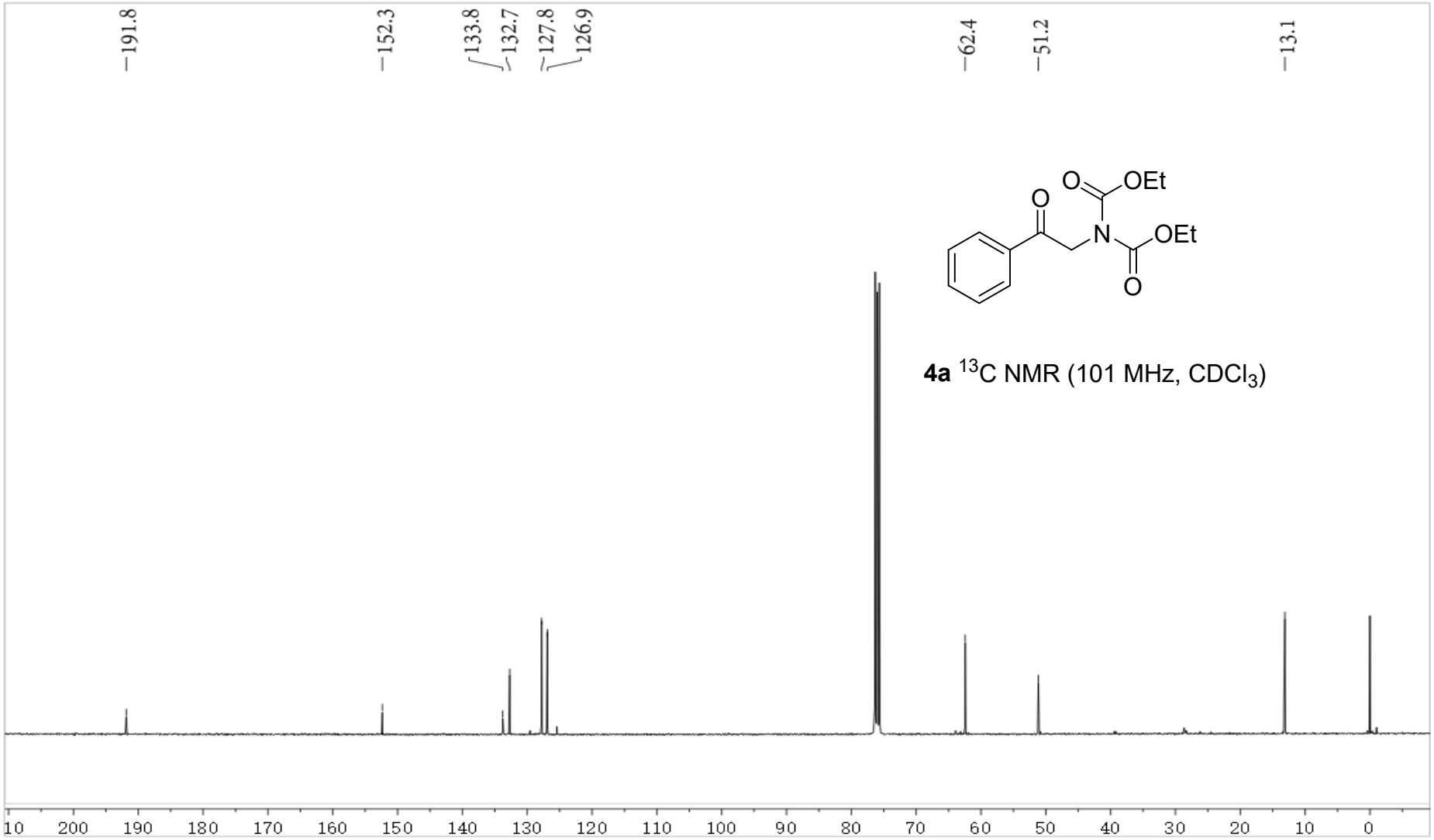
3xa ^{13}C NMR (101 MHz, $CDCl_3$)



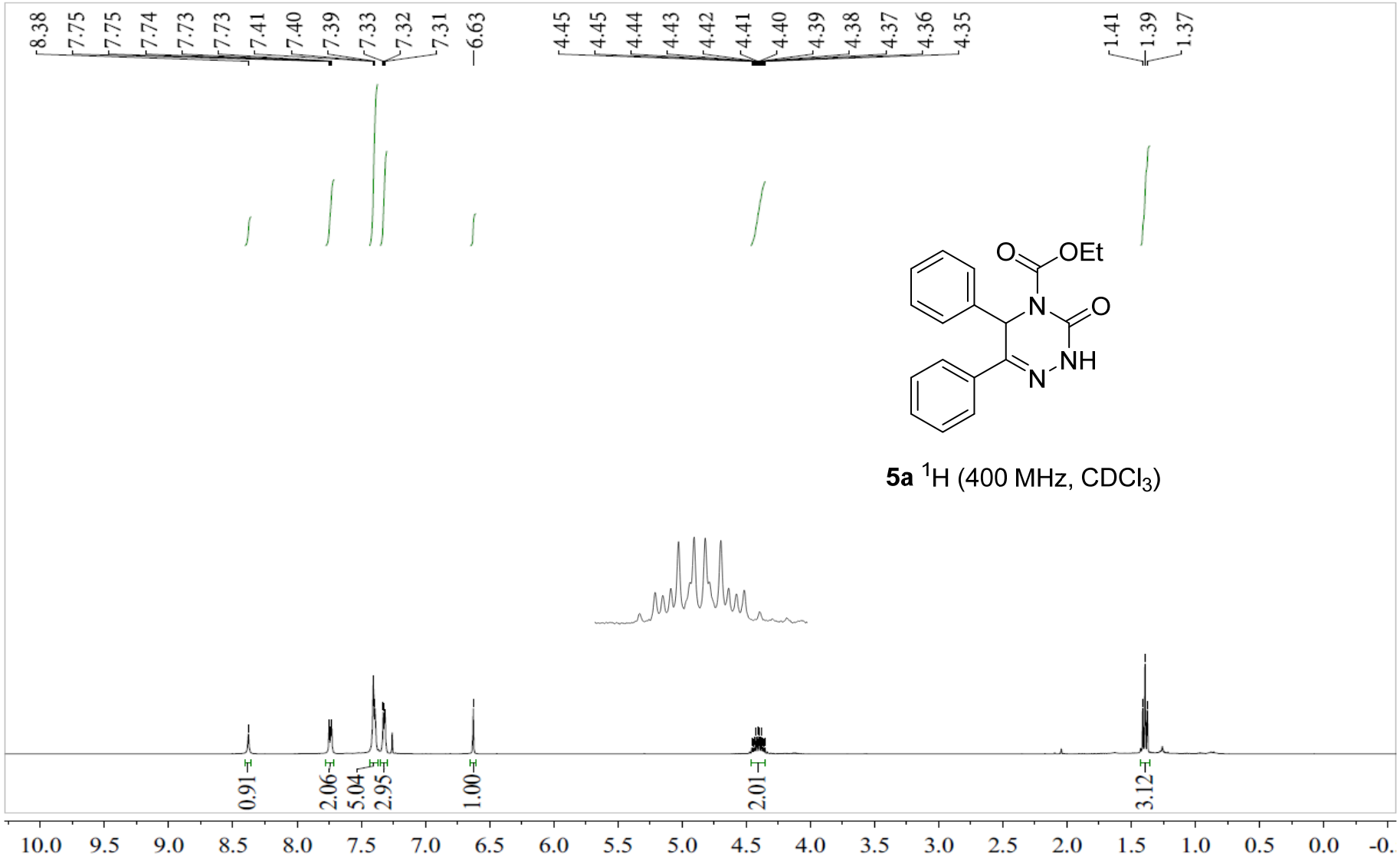
3ya ^{1}H NMR (400 MHz, $CDCl_3$)



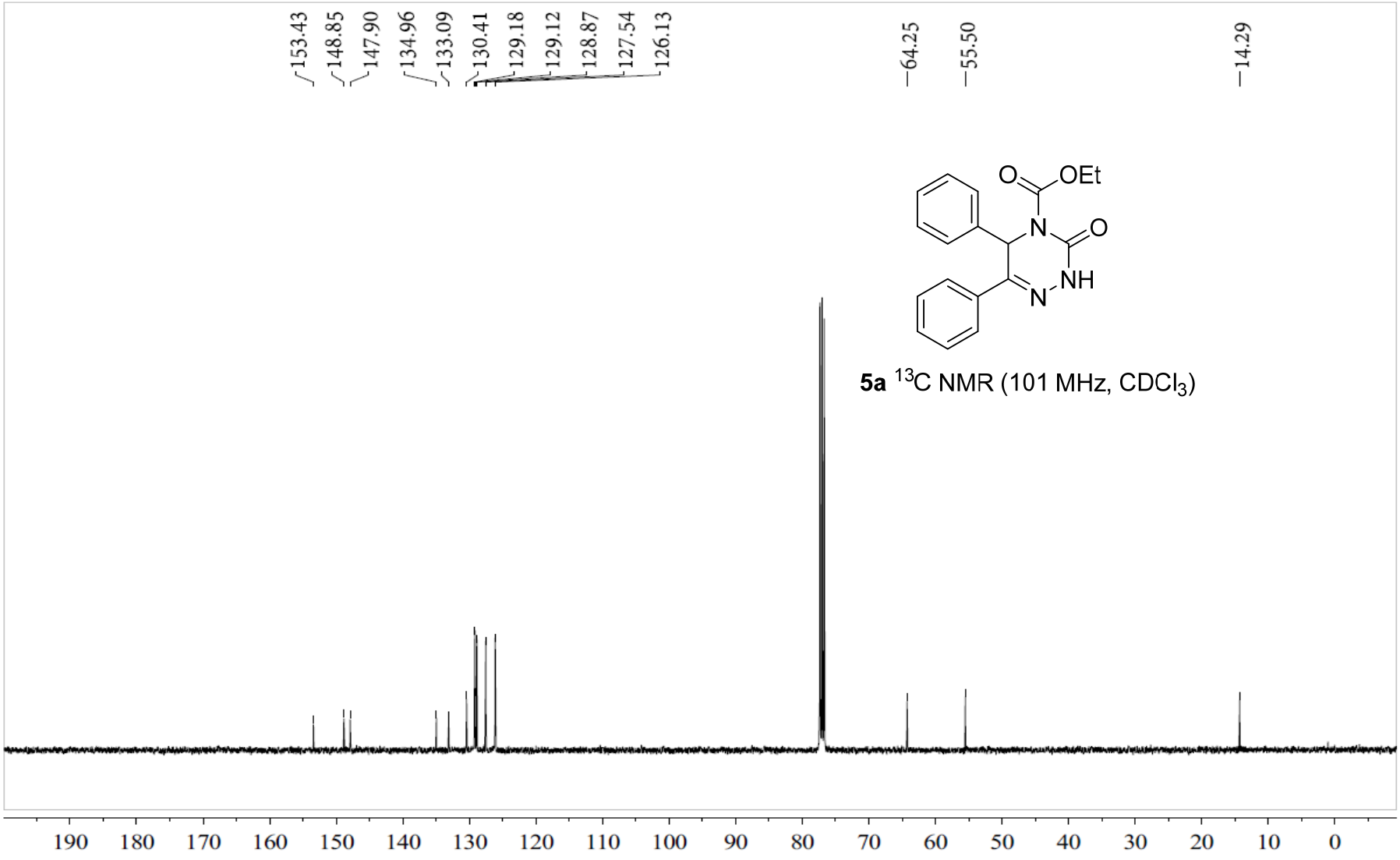
4a ^{1}H NMR (400 MHz, $CDCl_3$)



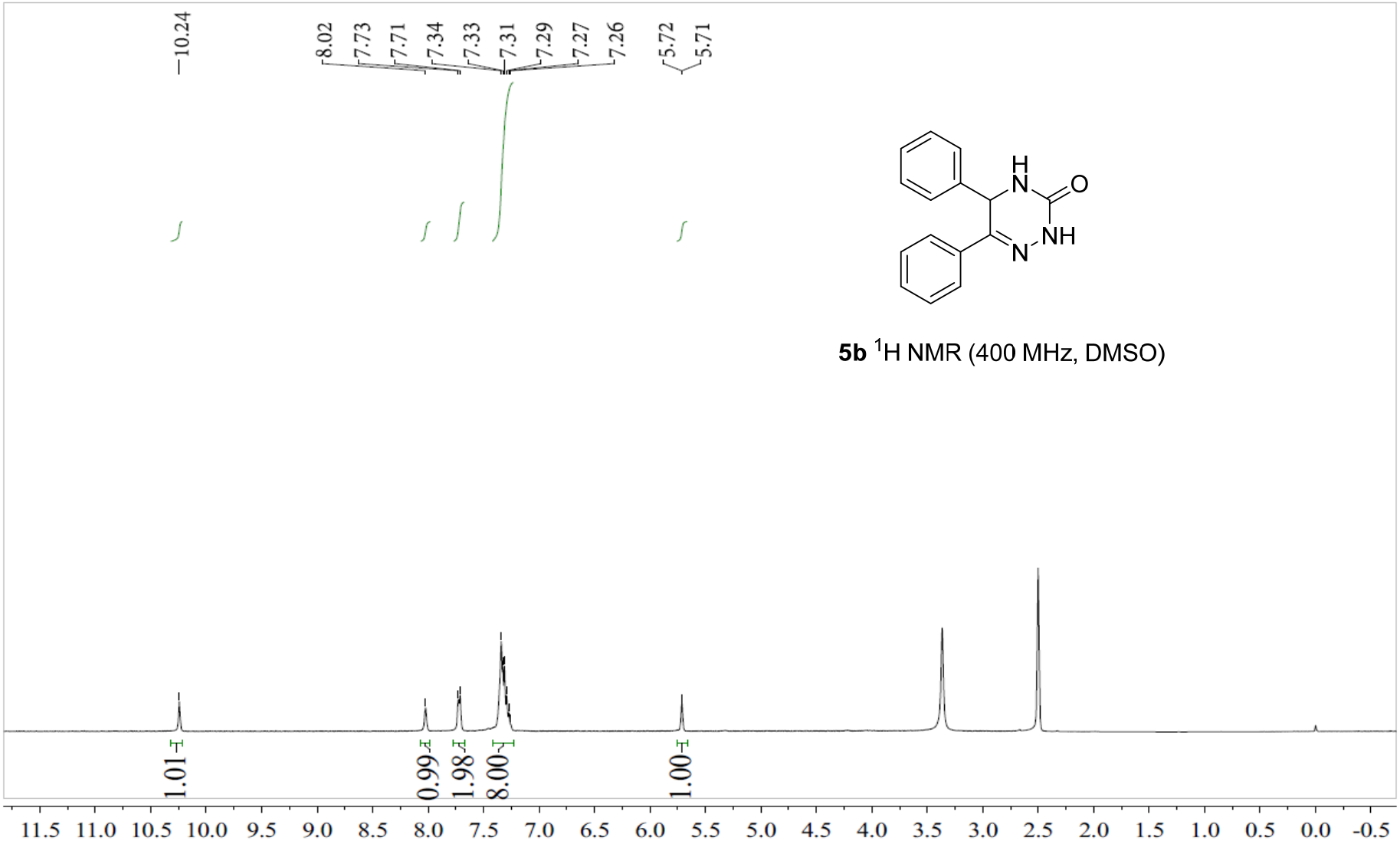
4a ^{13}C NMR (101 MHz, $CDCl_3$)



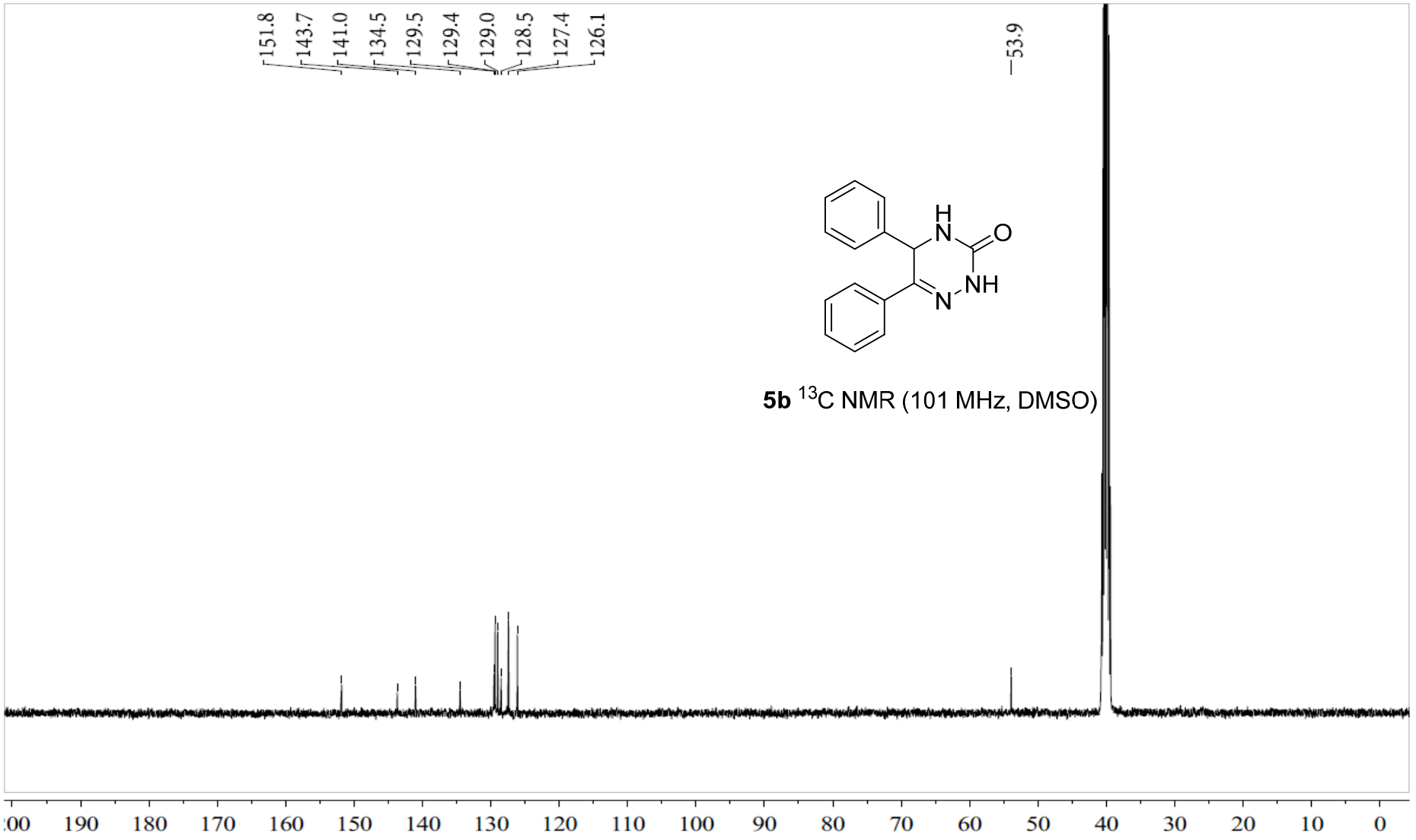
5a ^{1}H (400 MHz, $CDCl_3$)



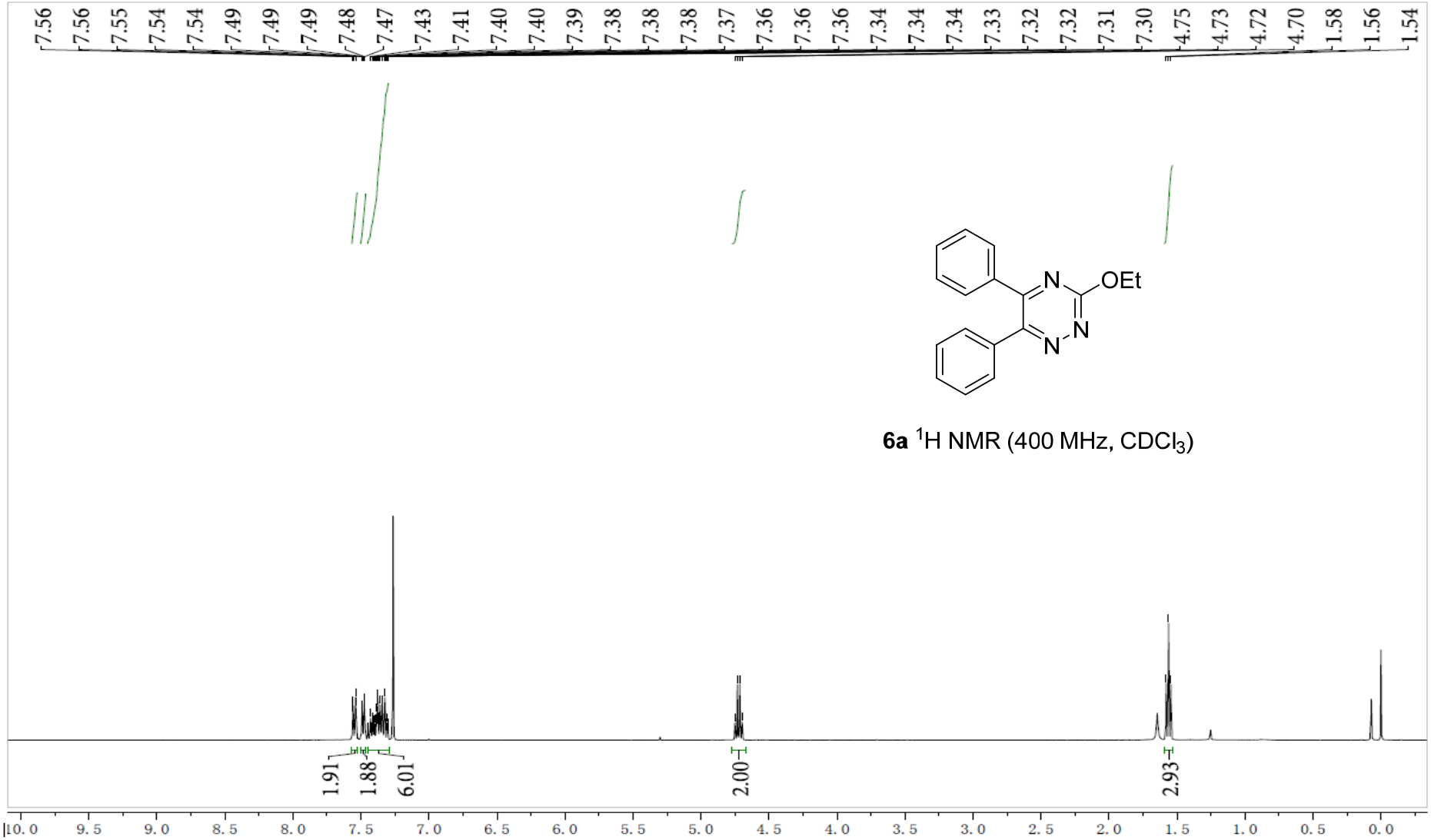
5a ^{13}C NMR (101 MHz, $CDCl_3$)



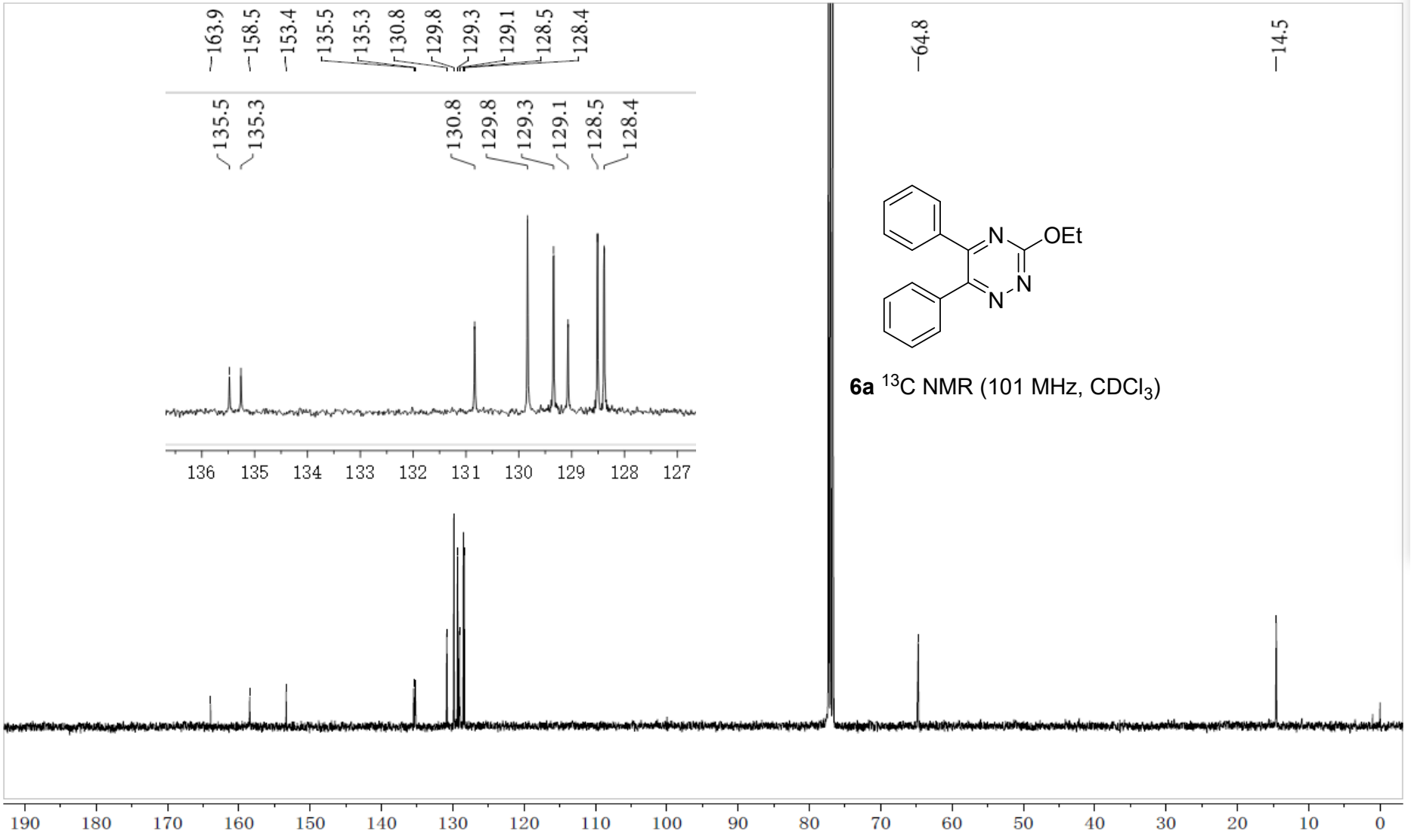
5b ^{1}H NMR (400 MHz, DMSO)



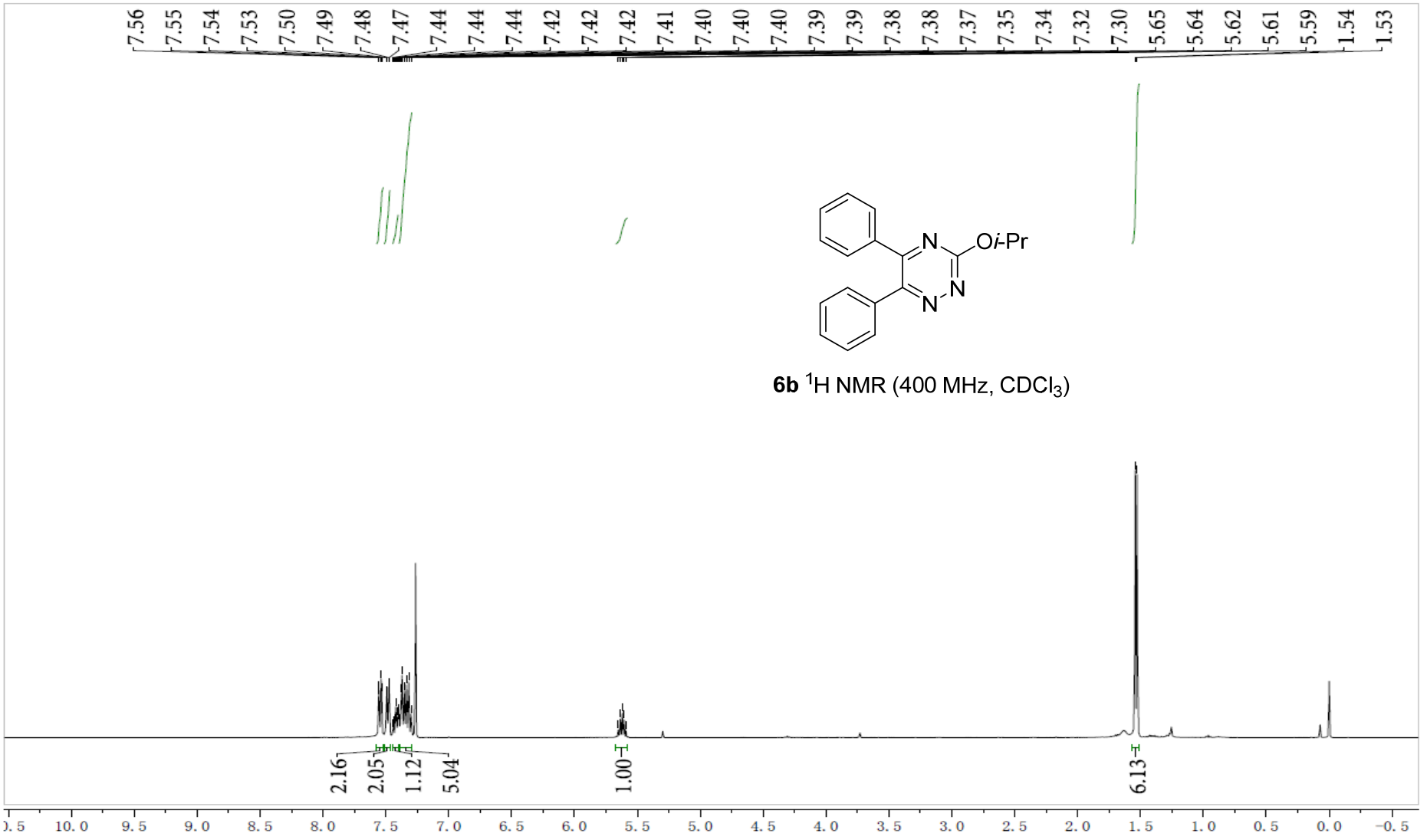
5b ^{13}C NMR (101 MHz, DMSO)



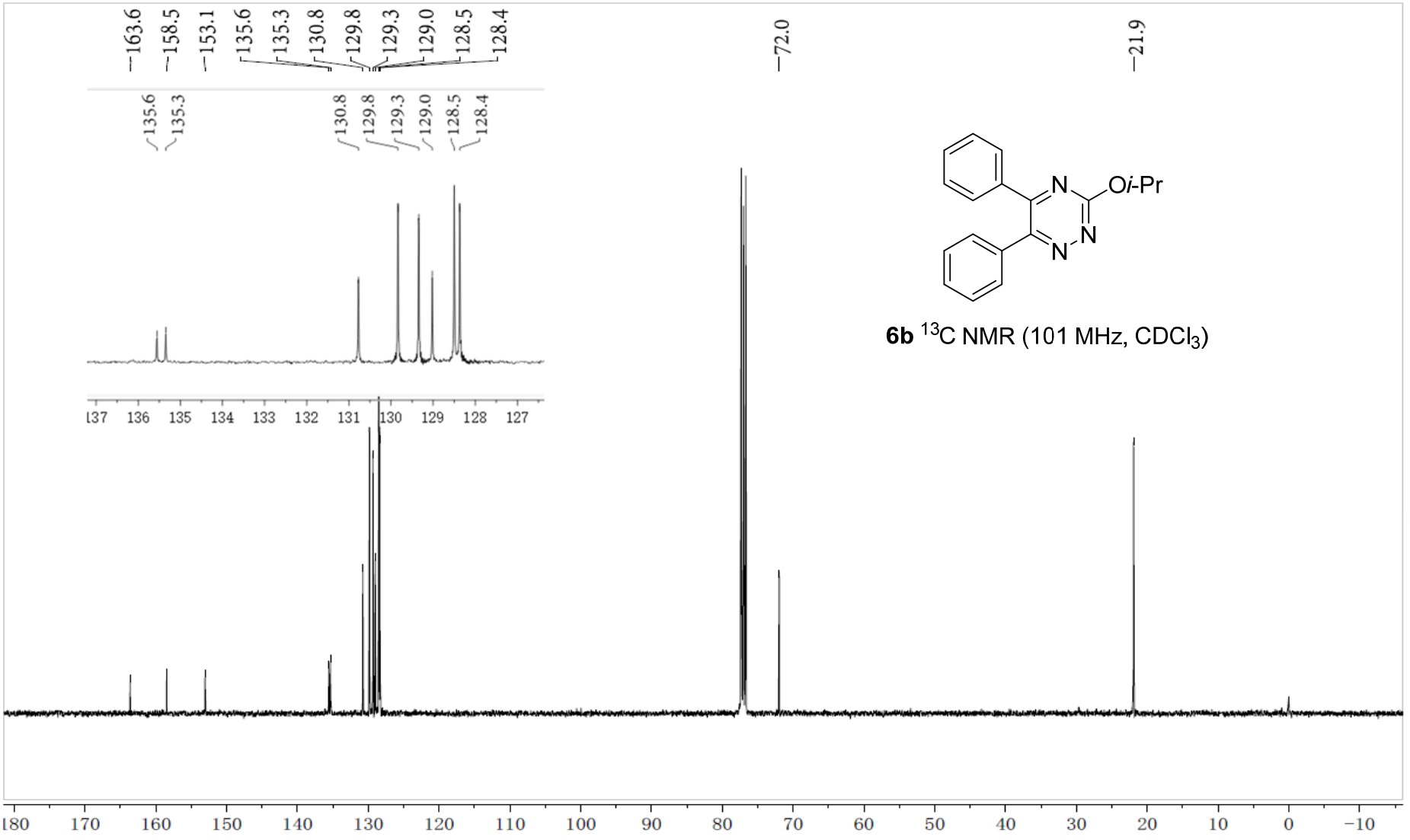
6a ^{1}H NMR (400 MHz, $CDCl_3$)



6a ^{13}C NMR (101 MHz, $CDCl_3$)



6b ^{1}H NMR (400 MHz, $CDCl_3$)



6b ^{13}C NMR (101 MHz, $CDCl_3$)