Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Cobalt-catalyzed modular assembling toward multi-functionalized furan derivatives

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1. General Information

All reactions were performed under an atmosphere of nitrogen using standard Schlenk techniques, unless otherwise indicated. All commercial reagents were used without further purification, unless otherwise noted. Reactions were monitored by thin layer chromatography (TLC) analysis. TLC plates were viewed under UV light and stained with potassium permanganate. Yields refer to products isolated after purification by column chromatography, unless otherwise stated. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Bruker AV-400 (400 MHz) and JEOL-500 (500 MHz) spectrometers. NMR samples were dissolved in $CDCl_3$ (unless specified otherwise) and chemical shifts are reported in ppm referenced to residual nondeuterated solvent. IR spectra were obtained from Thermo Scientific NICOLET 380 FT-IR (KCl card). HRMS were obtained on an Exactive Plus LC-MS (ESI) mass spectrometer with the use of quadrupole analyzer.

2. General Procedures

General Procedure 1 (GP 1) - *Syntheses of dihydronfurans or tri-substituted furans*.

A flame-dried Schlenk tube equipped with a stir bar was added **Co(salen) A** (10 mol%), corresponding β-dione (0.4 mmol), NFSI (0.3 mmol), unsaturated alkenes or terminal-alkynes (0.2 mmol) and anhydrous ethyl acetate (0.2 M) under an nitrogen atmosphere. The reaction mixture was kept stirring at 60 ºC (oil bath). When the reaction was complete as suggested by TLC, the reaction mixture was directly concentrated by rotary evaporation. The furans were isolated by silica column chromatography (typically 5-10% of ethyl acetate in petroleum ether).

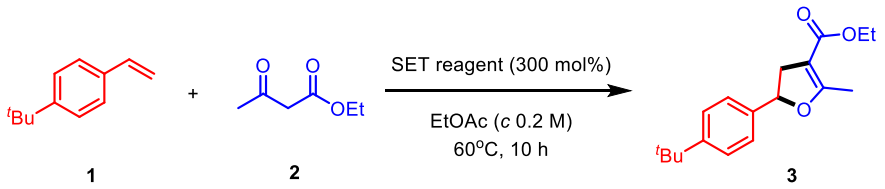
General Procedure 2 (GP 2) - *Syntheses of tetra-substituted furans.*

A flame-dried Schlenk tube equipped with a stir bar was added **Co(salen) G** (10 mol%), 1,3-cyclohexanedione (0.4 mmol), NFSI (0.3 mmol), internal-alkynes (0.2 mmol), sodium bicarbonate (0.4 mmol) and anhydrous acetonitrile (0.05 M) under an nitrogen atmosphere. The reaction mixture was kept stirring at 60 ºC (oil bath). When the reaction was complete as suggested by TLC, the reaction mixture was directly concentrated by rotary evaporation. The tetra-substituted furans were isolated by silica column chromatography (typically 5-10% of ethyl acetate in petroleum ether).

3. Screening of other oxidants than NFSI

Some oxidants have been shown to display a strong background reaction in a similar kind of cycloaddition, among which are ceric ammonium nitrate (*J. Org. Chem.* **1991**, *56*, 4772-4778; *Synthesis* **2011**, *15*, 2466-2470), $Mn(OAc)_3{\cdot}2H_2O$ (*Org. Lett.* **2014**, *16*, 5992-5995; *J. Org. Chem.* **2005**, *70*, 3859-3863.), $K_2S_2O_8$ (*Synthesis* **2015**, *47*, 3191-3197.), and Ag_2CO_3 (*Tetrahedron Lett.* **1997***, 38*, 2095-2098; *J. Am. Chem. Soc.* **2012**, *134*, 5766-5769.).

We then screened other commonly used SET reagents in this transformation, including TBHP, $Cu(OAc)_2$, $PhI(OAc)_2$, and oxygen. Unfortunately, none of the above SET reagents were as effective as NFSI in the current transformation.



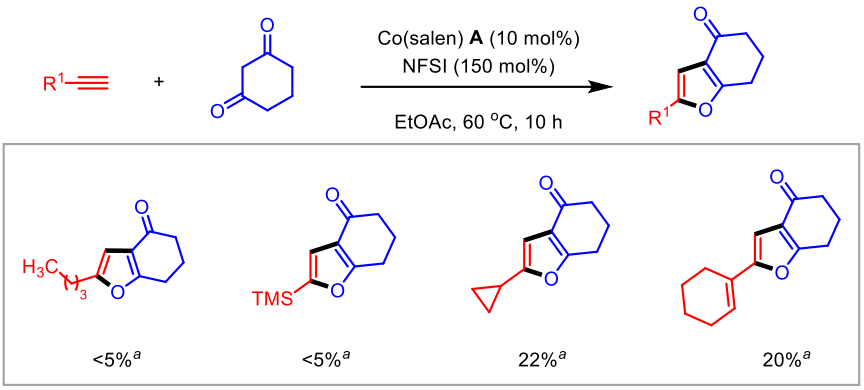
1 2 3

entry	variation from standard conditions	yield (%)[b]
1	TBHP	N.D.
2	$Cu(OAc)_2$	N.D.
3	$PhI(OAc)_2$	<5
4	O_2 (1 atm)	N.D.

[a] Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), and SET reagent (300 mol%) in EtOAc (*c* 0.2 M) at 60 °C for 10 h under a N_2 atmosphere. [b] Yields determined by ^1H NMR analysis using CH_2Br_2 as the internal standard.

4. Unsucessful substrates

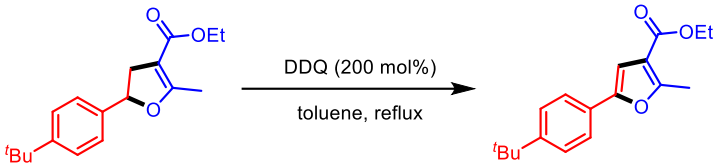
Under the current reaction conditions, the aliphatic alkyne and ethynyltrimethylsilane merely afforded any desired cycloaddition products. The reactions of ethynylcyclopropane and enyne substrate (1-ethynylcyclohex-1-ene) were also sluggish and thus only afforded very low reaction yields. Starting materials were recovered in most of these reactions, which accounts for the mass balance.



[a] Yields determined by 1H NMR analysis using CH_2Br_2 as the internal standard.

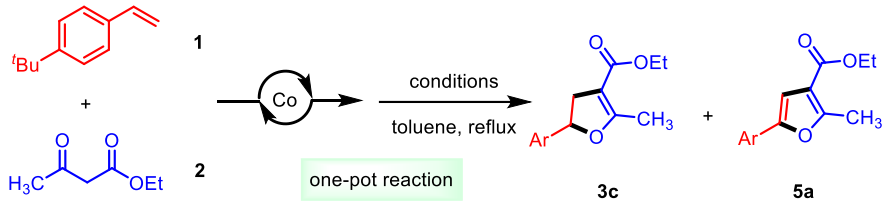
5. Oxidation of dihydrofuran to furan

Following the literature procedure (*Org. Lett.* **2017**, *19*, 3043-3046; *Tetrahedron Lett.* **2003**, *44*, 7937-7940.), we found the dihydrofuran (**3c**) underwent the oxidation with 2 equiv. of DDQ to afford the desired furan (**5a**) in a 35% yield.



3c **5a**, 35%

We then tried the one-pot transformation, *i.e.*, first Co-catalyzed dihydrofuran formation and then oxidation as follows. Despite the generation of 14% of desired furan (**5a**), most of the dihydrofuran (**3c**) was recovered (entry 1). Neither the extra addition of Fe or Cu catalysts (entries 2-4) nor the use of oxygen as the oxidant (entry 5) could improve the reaction results. We speculate further extensive optimization of reaction conditions is necessary to achieve good efficiency of this one-pot transformation.

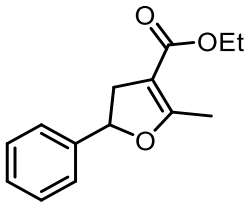


3c **5a**

entry	conditions	**3c** (%)[a]	**5a** (%)[a]
1	DDQ (200 mol%)	40	14
2	$FeCl_3$ (10 mol%) DDQ (200 mol%)	trace	trace
3	$FeCl_2$ (10 mol%) DDQ (200 mol%)	20	10
4	$Cu(OAc)_2$ (10 mol%) DDQ (200 mol%)	42	trace
5	$Cu(OAc)_2$ (10 mol%) O_2 (1 atm)	64	trace

[a] Yields determined by 1H NMR analysis using CH_2Br_2 as the internal standard.

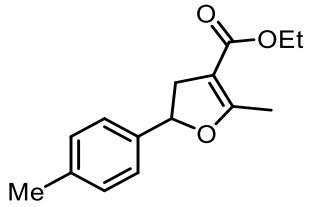
6. Characterization of products



Ethyl-2-methyl-5-phenyl-4,5-dihydrofuran-3-carboxylate[1] (3a)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 34.0 mg (73% yield) of the desired product as yellow liquid.

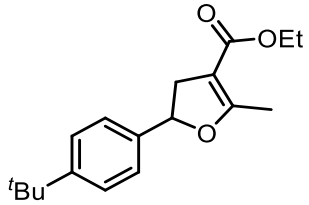
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.28 (m, 5H), 5.59 (dd, *J* = 10.7, 8.4 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.37 – 3.30 (m, 1H), 2.95 – 2.88 (m, 1H), 2.29 (t, *J* = 1.3 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H).



Ethyl-2-methyl-5-(p-tolyl)-4,5-dihydrofuran-3-carboxylate[1] (3b)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 38.9 mg (79% yield) of the desired product as yellow liquid.

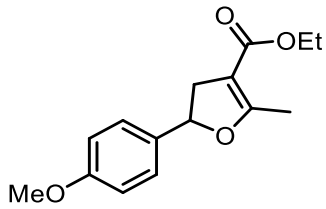
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.55 (dd, *J* = 10.6, 8.5 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.34 – 3.27 (m, 1H), 2.94 – 2.88 (m, 1H), 2.35 (s, 3H), 2.27 (t, *J* = 1.4 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H).



Ethyl-5-(4-(tert-butyl)phenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate[1] (3c)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 46.6 mg (81% yield) of the desired product as yellow liquid.

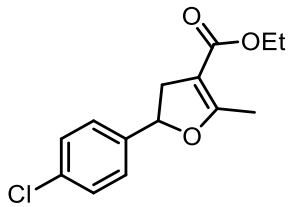
^{1}H NMR (500 MHz, Chloroform-d) δ 7.40 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 5.57 (dd, *J* = 10.7, 8.4 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.34 – 3.25 (m, 1H), 3.02 – 2.85 (m, 1H), 2.28 (s, 3H), 1.32 (s, 9H), 1.28 (t, *J* = 7.1 Hz, 3H).



Ethyl-5-(4-methoxyphenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate[1] (3d)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 43.6 mg (83% yield) of the desired product as yellow liquid.

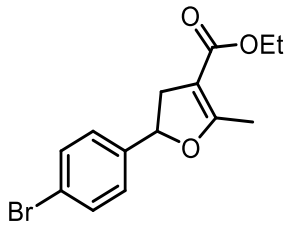
^{1}H NMR (500 MHz, Chloroform-d) δ 7.27 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 5.53 (dd, *J* = 10.5, 8.6 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 3.34 – 3.22 (m, 1H), 2.96 – 2.86 (m, 1H), 2.26 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H).



Ethyl-5-(4-chlorophenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate[1] (3e)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 36.8 mg (69% yield) of the desired product as yellow liquid.

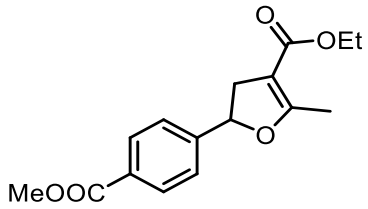
^{1}H NMR (500 MHz, Chloroform-d) δ 7.36 – 7.32 (m, 2H), 7.28 – 7.24 (m, 2H), 5.55 (dd, *J* = 10.7, 8.3 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.37 – 3.28 (m, 1H), 2.91 – 2.81 (m, 1H), 2.27 (t, *J* = 1.6 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H).



Ethyl-5-(4-bromophenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (3f)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 44.8 mg (72% yield) of the desired product as yellow liquid.

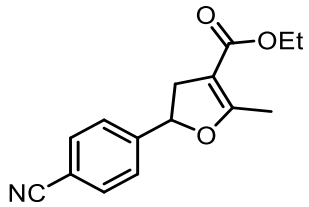
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 5.53 (dd, *J* = 10.6, 8.3 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.39 – 3.24 (m, 1H), 2.89 – 2.79 (m, 1H), 2.27 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 167.4, 165.8, 140.6, 131.7, 127.3, 122.0, 101.7, 82.2, 59.6, 38.0, 14.4, 14.0. **IR** (neat, cm^{-1}): 2980 (m), 1691 (m), 1648 (s), 1221 (m), 822 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{14}H_{16}BrO_3$: 311.0277; Found: 311.0271.



Ethyl-5-(4-(methoxycarbonyl)phenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (3g)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 27.5mg (47% yield) of the desired product as yellow liquid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 5.63 (dd, *J* = 10.7, 8.4 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.92 (s, 3H), 3.60 – 3.26 (m, 1H), 2.86 – 2.81 (m, 1H), 2.30 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 167.5, 166.7, 165.8, 146.6, 130.0, 129.8, 125.4, 101.8, 82.3, 59.6, 52.2, 38.1, 14.4, 14.0. **IR** (neat, cm^{-1}): 2981 (m), 1720 (s) 1696 (m), 1649 (s), 1220 (m), 761 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{16}H_{19}O_5$: 291.1227; Found: 291.1224.

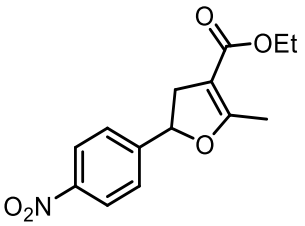


Ethyl-5-(4-cyanophenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (3h)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 22.6 mg 44% yield) of the desired product as yellow liquid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 5.62 (dd, *J* = 10.8, 8.1 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.44 – 3.34 (m, 1H), 2.86 – 2.79 (m, 1H), 2.29 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 167.3, 165.6, 146.9, 132.5, 126.1, 118.5, 111.8, 101.8, 81.7, 59.7, 38.1, 14.4, 13.9. **IR** (neat, cm^{-1}): 2980 (m),

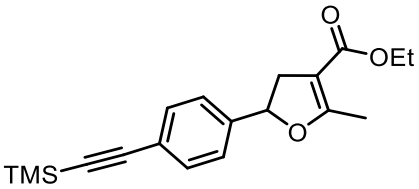
1691 (m), 1648 (s), 1219 (m), 835 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{15}H_{16}NO_3$: 258.1125; Found: 258.1126.



Ethyl-2-methyl-5-(4-nitrophenyl)-4,5-dihydrofuran-3-carboxylate (3i)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 34.9 mg (63% yield) of the desired product as yellow liquid.

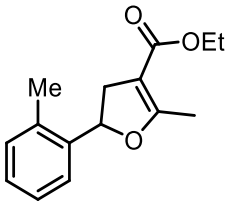
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.23 (d, *J* = 8.7 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 5.67 (dd, *J* = 10.9, 8.1 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.48 – 3.36 (m, 1H), 2.89 – 2.80 (m, 1H), 2.30 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 167.2, 165.5, 148.8, 147.5, 126.1, 123.9, 101.8, 81.4, 59.7, 38.2, 14.4, 14.0. **IR** (neat, cm^{-1}): 2980 (m), 1692 (m), 1650 (s), 1218 (m), 852 (m); **HRMS (ESI)** m/z: $[M+ Na]^+$ Calcd. for $C_{14}H_{15}NO_5Na$: 300.0842; Found: 300.0844.



Ethyl-2-methyl-5-(4-((trimethylsilyl)ethynyl)phenyl)-4,5-dihydrofuran-3-carboxylate (3j)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 44.0 mg (67% yield) of the desired product as yellow liquid.

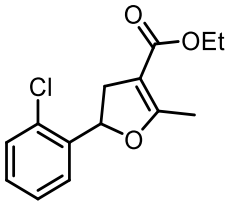
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 5.56 (dd, *J* = 10.7, 8.5 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.39 – 3.27 (m, 1H), 2.88 – 2.80 (m, 1H), 2.28 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.25 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 167.5, 165.9, 141.8, 132.2, 125.4, 122.9, 104.6, 101.7, 94.5, 82.6, 59.6, 38.0, 14.4, 14.0, -0.1. **IR** (neat, cm^{-1}): 2962 (m), 1701 (s), 1650 (m), 1222 (m), 864 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{19}H_{25}O_3Si$: 329.1567; Found: 329.1568.



Ethyl-2-methyl-5-(o-tolyl)-4,5-dihydrofuran-3-carboxylate (3k)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 37.8 mg (77% yield) of the desired product as yellow liquid.

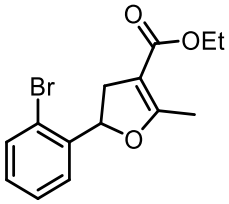
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.29 (m, 1H), 7.24 – 7.14 (m, 3H), 5.77 (dd, *J* = 10.8, 8.4 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.41 – 3.27 (m, 1H), 2.84 – 2.70 (m, 1H), 2.38 – 2.27 (m, 6H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 167.7, 166.1, 139.8, 134.1, 130.6, 127.7, 126.2, 124.5, 101.6, 80.7, 59.5, 37.3, 19.1, 14.4, 14.1. **IR** (neat, cm^{-1}): 2978 (m), 1696 (m), 1648 (s), 1222 (m), 757 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{15}H_{19}O_3$: 247.1329; Found: 247.1324.



Ethyl-5-(2-chlorophenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (3l)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 36.7 mg (69% yield) of the desired product as yellow liquid.

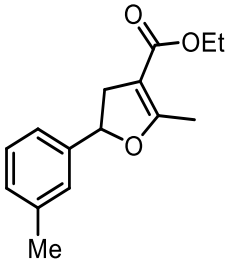
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.35 (m, 2H), 7.31 – 7.21 (m, 2H), 5.89 (dd, *J* = 10.9, 7.7 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.58 – 3.49 (m, 1H), 2.79 – 2.68 (m, 1H), 2.33 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 167.4, 165.9, 139.6, 131.2, 129.6, 128.9, 127.0, 125.9, 101.8, 79.9, 59.6, 37.5, 14.4, 13.9. **IR** (neat, cm^{-1}): 2980 (m), 1690 (s), 1649 (m), 1203 (m), 771 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{14}H_{16}ClO_3$: 267.0782; Found: 267.0782.



Ethyl-5-(2-bromophenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (3m)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 43.7 mg (70% yield) of the desired product as yellow liquid.

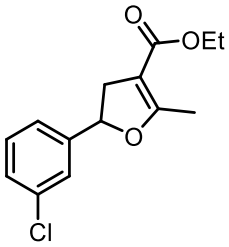
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.48 (m, 1H), 7.39 – 7.28 (m, 2H), 7.20 – 7.13 (m, 1H), 5.85 (dd, *J* = 10.9, 7.6 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.64 – 3.42 (m, 1H), 2.82 – 2.60 (m, 1H), 2.34 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 167.5, 165.9, 141.2, 132.8, 129.1, 127.6, 126.1, 120.8, 101.7, 81.8, 59.6, 37.6, 14.4, 14.0. **IR** (neat, cm^{-1}): 2978(m), 1695 (m), 1652 (s), 1220 (m), 751 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{14}H_{16}BrO_3$: 311.0277; Found: 311.0273.



Ethyl-2-methyl-5-(m-tolyl)-4,5-dihydrofuran-3-carboxylate (3n)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 36.3 mg (74% yield) of the desired product as yellow liquid.

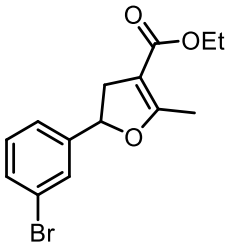
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.27 (m, 1H), 7.22 – 7.10 (m, 3H), 5.57 (dd, *J* = 10.7, 8.4 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.40 – 3.25 (m, 1H), 3.00 – 2.87 (m, 1H), 2.38 (s, 3H), 2.30 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 167.6, 166.1, 141.4, 138.4, 128.9, 128.6, 126.3, 122.8, 101.7, 83.2, 59.5, 37.9, 21.4, 14.5, 14.1. **IR** (neat, cm^{-1}): 2980 (m), 1697 (s), 1648 (m), 1222 (m), 787 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{15}H_{19}O_3$: 247.1329; Found: 247.1327.



Ethyl-5-(3-chlorophenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (3o)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 38.4 mg (72% yield) of the desired product as yellow liquid.

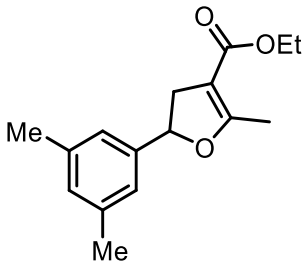
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 (m, 3H), 7.24 – 7.15 (m, 1H), 5.55 (dd, *J* = 10.7, 8.2 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.41 – 3.26 (m, 1H), 2.92 – 2.80 (m, 1H), 2.29 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 167.4, 165.9, 143.7, 134.6, 130.0, 128.2, 125.7, 123.7, 101.7, 82.1, 59.6, 38.1, 14.4, 14.0. **IR** (neat, cm^{-1}): 2982 (m), 1730 (s), 1650 (s), 1224 (m), 787 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{14}H_{16}ClO_3$: 267.0782; Found: 267.0782.



Ethyl-5-(3-bromophenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (3p)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 44.7 mg (72% yield) of the desired product as yellow liquid.

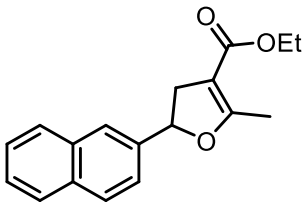
^{1}H NMR (400 MHz, Chloroform-d) δ 7.50 (s, 1H), 7.47 – 7.38 (m, 1H), 7.25 – 7.13 (m, 2H), 5.57 (dd, *J* = 10.8, 8.2 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.41 – 3.31 (m, 1H), 2.98 – 2.85 (m, 1H), 2.31 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-d) δ 167.5, 165.9, 144.0, 131.2, 130.4, 128.7, 124.3, 122.9, 101.8, 82.1, 59.7, 38.2, 14.5, 14.1. **IR** (neat, cm^{-1}): 2981 (m), 1691 (m), 1651 (s), 1223 (m), 784 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{14}H_{16}BrO_3$: 311.0277; Found: 311.0267.



Ethyl-5-(3,5-dimethylphenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (3q)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 37.7 mg (72% yield) of the desired product as yellow liquid.

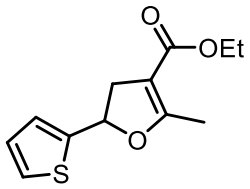
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.95 (m, 3H), 5.52 (dd, *J* = 10.6, 8.7 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.35 – 3.22 (m, 1H), 2.96 – 2.87 (m, 1H), 2.32 (s, 6H), 2.29 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 167.7, 166.1, 141.3, 138.3, 129.8, 123.5, 101.7, 83.3, 59.5, 37.8, 21.3, 14.4, 14.1. **IR** (neat, cm^{-1}): 2979 (m), 1697 (s), 1647 (m), 1221 (m), 818 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{16}H_{21}O_3$: 261.1485; Found: 261.1484.



Ethyl-2-methyl-5-(naphthalen-2-yl)-4,5-dihydrofuran-3-carboxylate (3r)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 39.6 mg (70% yield) of the desired product as yellow liquid.

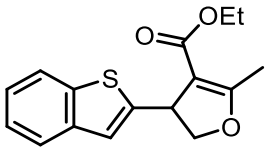
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.81 (m, 3H), 7.77 (s, 1H), 7.55 – 7.41 (m, 3H), 5.76 (dd, *J* = 10.5, 8.5 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.48 – 3.31 (m, 1H), 3.07 – 2.92 (m, 1H), 2.34 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 167.7, 166.1, 138.7, 133.1, 128.8, 128.0, 127.7, 126.4, 126.2, 124.6, 123.5, 101.8, 83.3, 59.6, 38.0, 14.4, 14.1. **IR** (neat, cm^{-1}): 2976 (m), 1693 (m), 1648 (s), 1221 (m), 818 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{18}H_{19}O_3$: 283.1329; Found: 283.1326.



Ethyl-2-methyl-5-(thiophen-3-yl)-4,5-dihydrofuran-3-carboxylate (3s)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 28.3 mg (59% yield) of the desired product as yellow liquid.

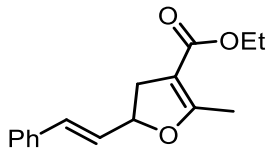
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.33 – 7.29 (m, 1H), 7.16 – 7.05 (m, 1H), 7.02 – 6.95 (m, 1H), 5.79 (dd, *J* = 10.2, 8.3 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.41 – 3.26 (m, 1H), 3.13 – 3.00 (m, 1H), 2.24 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H).**^{13}C NMR** (126 MHz, Chloroform-*d*) δ 167.1, 165.9, 144.1, 126.9, 125.8, 125.3, 101.8, 78.8, 59.6, 38.0, 14.4, 14.1. **IR** (neat, cm^{-1}): 2979 (m), 1694 (s), 1647 (m), 1218 (m), 703 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{12}H_{15}SO_3$: 239.0736; Found: 239.0734.



Ethyl-4-(benzo[b]thiophen-2-yl)-2-methyl-4,5-dihydrofuran-3-carboxylate (3t)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 44.9 mg (78% yield) of the desired product as yellow liquid.

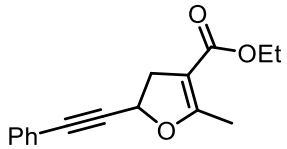
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.85 – 7.76 (m, 1H), 7.76 – 7.72 (m, 1H), 7.39 – 7.30 (m, 2H), 7.28 (s, 1H), 5.87 (dd, *J* = 10.3, 7.7 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.43 – 3.32 (m, 1H), 3.22 – 3.04 (m, 1H), 2.28 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 167.0, 165.7, 144.8, 139.6, 139.1, 124.6, 124.4, 123.7, 122.4, 121.4, 101.9, 79.2, 59.6, 37.8, 14.4, 14.0. **IR** (neat, cm^{-1}): 2980 (m), 1691 (s), 1647 (m), 1227 (m), 726 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{16}H_{17}SO_3$: 289.0893; Found: 289.0891.



Ethyl-(E)-2-methyl-5-styryl-4,5-dihydrofuran-3-carboxylate (3u)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 32.1mg (62% yield) of the desired product as yellow liquid.

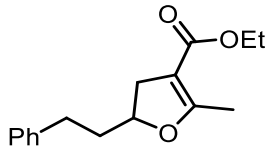
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.42 – 7.38 (m, 2H), 7.36 – 7.31 (m, 2H), 7.29 – 7.23 (m, 1H), 6.62 (d, *J* = 15.8 Hz, 1H), 6.27 (dd, *J* = 15.8, 7.3 Hz, 1H), 5.23 – 5.19 (m, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.30 – 3.07 (m, 1H), 2.89 – 2.66 (m, 1H), 2.24 (t, *J* = 1.6 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 167.5, 166.1, 136.1, 132.3, 128.6, 128.1, 127.9, 126.7, 101.8, 82.6, 59.5, 35.9, 14.5, 14.1. **IR** (neat, cm^{-1}): 2981 (m), 1692 (s), 1646 (m), 1221 (m), 748 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{16}H_{19}O_3$: 259.1329; Found: 259.1328.



Ethyl-2-methyl-5-(phenylethynyl)-4,5-dihydrofuran-3-carboxylate (3v)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 28.3 mg (55% yield) of the desired product as yellow liquid.

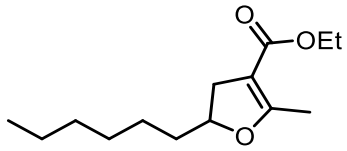
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.47 – 7.43 (m, 2H), 7.35 – 7.28 (m, 3H), 5.41 (dd, *J* = 10.6, 8.1 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.31 – 3.18 (m, 1H), 3.12 – 3.05 (m, 1H), 2.24 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 167.0, 165.7, 131.8, 128.8, 128.3, 122.0, 101.9, 86.9, 86.4, 71.1, 59.6, 37.6, 14.4, 14.1. **IR** (neat, cm^{-1}): 2983 (m), 1719 (s), 1670 (m), 1220 (m), 758 (m); **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd. for $C_{16}H_{16}O_3Na$: 279.0992; Found: 279.0992.



Ethyl-2-methyl-5-phenethyl-4,5-dihydrofuran-3-carboxylate (3w)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 17.9 mg (34% yield) of the desired product as yellow liquid.

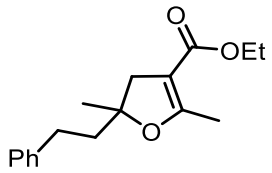
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.36 – 7.24 (m, 2H), 7.20 (d, *J* = 6.7 Hz, 3H), 4.65 – 4.56 (m, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.97 (m, 1H), 2.84 – 2.62 (m, 2H), 2.57 (m, 1H), 2.19 (s, 3H), 2.12 – 1.97 (m, 1H), 1.95 – 1.80 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 167.8, 166.4, 141.2, 128.43, 128.40, 125.9, 101.6, 81.5, 59.4, 37.7, 35.2, 31.3, 14.4, 14.2. **IR** (neat, cm^{-1}): 2981 (m), 1731 (s), 1643 (m), 1228 (m), 700 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{16}H_{21}O_3$: 261.1485; Found: 261.1480.



Ethyl-5-hexyl-2-methyl-4,5-dihydrofuran-3-carboxylate (3x)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 15.5 mg (32% yield) of the desired product as yellow liquid.

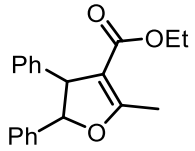
^{1}H NMR (500 MHz, Chloroform-*d*) δ 4.67 – 4.51 (m, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.04 – 2.85 (m, 1H), 2.57 – 2.44 (m, 1H), 2.17 (s, 3H), 1.79 – 1.66 (m, 1H), 1.56 – 1.51 (m, 1H), 1.47 – 1.36 (m, 2H), 1.35 – 1.31 (m, 2H), 1.29 – 1.27 (m, 3H), 1.27 – 1.25. (m, 2H), 1.25 – 1.21 (m, 2H), 0.88 (t, *J* = 6.8 Hz, 3H).**^{13}C NMR** (126 MHz, Chloroform-*d*) δ 167.8, 166.5, 101.5, 82.6, 59.4, 36.1, 35.2, 31.7, 29.1, 24.9, 22.6, 14.5, 14.2, 14.1. **IR** (neat, cm^{-1}): 2955 (m), 1698 (s), 1646 (m), 1225 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{14}H_{25}O_3$: 241.1798; Found: 241.1795.



Ethyl-2,5-dimethyl-5-phenethyl-4,5-dihydrofuran-3-carboxylate (3y)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 16.7 mg (30% yield) of the desired product as yellow liquid.

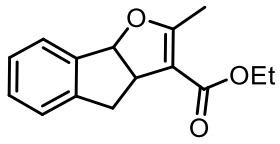
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 (d, *J* = 7.5 Hz, 2H), 7.18 – 7.07 (m, 3H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.79 (d, *J* = 14.4 Hz, 1H), 2.70 – 2.50 (m, 3H), 2.15 (s, 3H), 1.96 – 1.84 (m, 2H), 1.36 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.8, 166.4, 141.8, 128.4, 128.3, 125.9, 101.1, 87.7, 59.4, 43.0, 40.8, 30.1, 26.8, 14.5, 14.3. **IR** (neat, cm^{-1}): 2929 (m), 1697 (s), 1644 (m), 1259 (m), 700 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{17}H_{23}O_3$: 275.1642; Found: 275.1642.



Ethyl-2-methyl-4,5-diphenyl-4,5-dihydrofuran-3-carboxylate[2] (3z)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 24.9 mg (40% yield) of the desired product as yellow liquid.

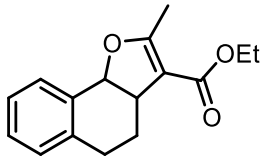
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.19 (m, 10H), 5.44 (d, *J* = 5.8 Hz, 1H), 4.30 (d, *J* = 5.7 Hz, 1H), 4.12 – 3.91 (m, 2H), 2.49 (s, 3H), 1.06 (t, *J* = 7.1 Hz, 3H).



Ethyl-2-methyl-3a,8a-dihydro-8H-indeno[2,1-b]furan-3-carboxylate[1] (3aa)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 36.1 mg (74% yield, >20:1 d.r.) of the desired product as yellow liquid.

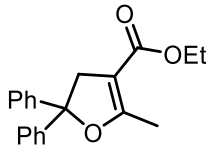
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.40 (m, 1H), 7.38 – 7.32 (m, 1H), 7.30 – 7.27 (m, 2H), 6.02 (d, *J* = 9.2 Hz, 1H), 4.21 (q, *J* = 12.2 Hz, 2H), 4.12 – 4.02 (m, 1H), 3.42 – 3.33 (m, 1H), 3.16 – 3.20 (m, 1H), 2.17 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H).



Ethyl-2-methyl-3a,4,5,9b-tetrahydronaphtho[2,1-b]furan-1-carboxylate[1] (3ab)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 36.2 mg (70% yield, >20:1 d.r.) of the desired product as yellow liquid.

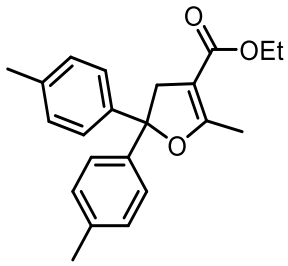
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.48 – 7.40 (m, 1H), 7.28 – 7.23 (m, 2H), 7.21 – 7.15 (m, 1H), 5.42 (d, *J* = 9.2 Hz, 1H), 4.24 – 4.17 (m, 2H), 3.41 – 3.36 (m, 1H), 2.81 – 2.67 (m, 1H), 2.65 – 2.52 (m, 1H), 2.23 (s, 3H), 2.13 – 2.00 (m, 1H), 1.70 – 1.63 (m, 1H), 1.33 (t, *J* = 7.1 Hz, 3H).



Ethyl-2-methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate[1] (3ac)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 34.0 mg (55% yield) of the desired product as yellow liquid.

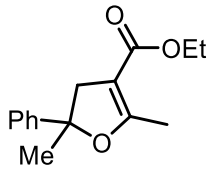
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.38 – 7.34 (m, 4H), 7.33 – 7.30 (m, 4H), 7.30 – 7.27 (m, 2H), 4.15 (d, *J* = 7.1 Hz, 2H), 3.68 – 3.55 (m, 2H), 2.35 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H).



Ethyl-2-methyl-5,5-di-p-tolyl-4,5-dihydrofuran-3-carboxylate (3ad)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 43.2 mg (64% yield) of the desired product as yellow liquid.

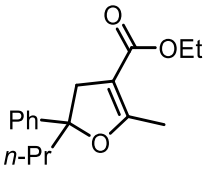
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (d, *J* = 8.0 Hz, 4H), 7.13 (d, *J* = 8.0 Hz, 4H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.60 – 3.53 (m, 2H), 2.34 (t, *J* = 1.6 Hz, 3H), 2.33 (s, 6H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 166.4, 165.9, 142.4, 137.1, 128.9, 125.6, 101.7, 91.5, 59.5, 44.1, 21.0, 14.4, 14.3. **IR** (neat, cm^{-1}): 2978 (m), 1695 (s), 1650 (m), 1230 (m), 814 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{22}H_{25}O_3$: 337.1798; Found: 337.1791.



Ethyl-5-(2-chlorophenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate[1] (3ae)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 33.5 mg (68% yield) of the desired product as yellow liquid.

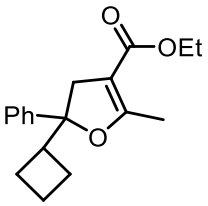
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.46 – 7.32 (m, 4H), 7.28 – 7.19(m, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.15 – 3.02 (m, 2 H),2.98 (s, 3H), 1.68 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H).



Ethyl-2-methyl-5-phenyl-5-propyl-4,5-dihydrofuran-3-carboxylate (3af)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 23.8 mg (43% yield) of the desired product as yellow liquid.

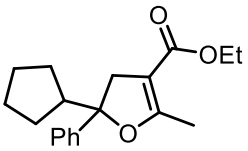
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.30 (m, 4H), 7.27 – 7.21 (m, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.15 – 2.98 (m, 2H), 2.29 (s, 3H), 1.97 – 1.80 (m, 2H), 1.43 – 1.30 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.20 – 1.07 (m, 1H), 0.86 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 166.7, 166.2, 145.8, 128.2, 126.9, 124.6, 101.3, 90.9, 59.4, 45.1, 42.9, 17.0, 14.4, 14.2, 14.2. **IR** (neat, cm^{-1}): 2958 (m), 1697 (s), 1650 (m), 1236 (m), 700 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{17}H_{23}O_3$: 275.1642; Found: 275.1636.



Ethyl-5-cyclobutyl-2-methyl-5-phenyl-4,5-dihydrofuran-3-carboxylate (3ag)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 22.0 mg (38% yield) of the desired product as yellow liquid.

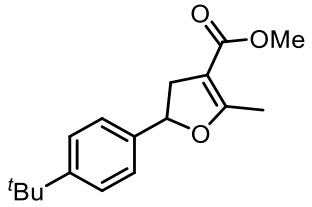
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.36 – 7.30 (m, 4H), 7.27 – 7.21 (m,1H), 4.16 – 4.10 (m, 2H), 3.10 – 2.95 (m, 2H), 2.88 – 2.78 (m, 1H), 2.34 (s, 3H), 2.02 – 1.88 (m, 3H), 1.81 – 1.56 (m, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 167.1, 166.1, 144.9, 128.1, 127.0, 124.6, 101.6, 91.1, 59.4, 45.4, 40.5, 22.5, 22.3, 16.5, 14.4, 14.1. **IR** (neat, cm^{-1}): 2979 (m), 1695 (s), 1649 (m), 1234 (m), 698 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{18}H_{23}O_3$: 287.1642; Found: 287.1637.



Ethyl-5-cyclopentyl-2-methyl-5-phenyl-4,5-dihydrofuran-3-carboxylate (3ah)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 25.8 mg (43% yield) of the desired product as yellow liquid.

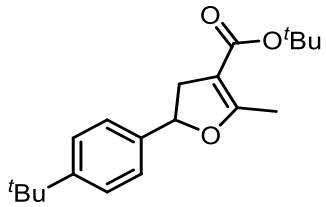
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (m, 4H), 7.27 – 7.20 (m, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.21 (d, *J* = 14.1 Hz, 1H), 3.06 (d, *J* = 14.2 Hz, 1H), 2.49 – 2.38 (m, 1H), 2.29 (s, 3H), 1.75 – 1.30 (m, 8H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 167.2, 166.1, 146.5, 128.1, 126.8, 124.8, 101.5, 92.3, 59.4, 50.9, 41.7, 27.5, 26.8, 25.7, 25.6, 14.4, 14.1. **IR** (neat, cm^{-1}): 2954 (m), 1697 (s), 1650 (m), 1235 (m), 700 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{19}H_{25}O_3$: 301.1798; Found: 301.1795.



Methyl-5-(4-(tert-butyl)phenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate[3] (3ai)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 33.5 mg (61% yield) of the desired product as yellow liquid.

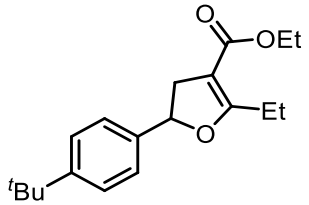
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.41 – 7.32 (m, 2H), 7.36 – 7.27 (m, 2H), 5.57 (dd, *J* = 10.6, 8.3 Hz, 1H), 3.72 (s, 3H), 3.35 – 3.25 (m, 1H), 3.00 – 2.90 (m, 1H), 2.28 (s, 3H), 1.32 (s, 9H).



Tert-butyl-5-(4-(tert-butyl)phenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (3aj)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 32.4 mg (51% yield) of the desired product as yellow liquid.

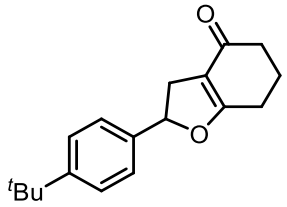
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 5.52 (dd, *J* = 10.5, 8.7 Hz, 1H), 3.29 – 3.22 (m, 1H), 2.94 – 2.86 (m, 1H), 2.23 (s, 3H), 1.49 (s, 9H), 1.32 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 166.4, 165.6, 151.1, 138.6, 125.6, 125.6, 103.2, 82.7, 79.5, 38.1, 34.6, 31.3, 28.4, 14.1. **IR** (neat, cm^{-1}): 2964 (m), 1694 (s), 1651 (m), 1142 (m), 835 (m); **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd. for $C_{20}H_{28}O_3Na$: 339.1931; Found: 339.1930.



Tert-butyl-5-(4-(tert-butyl)phenyl)-2-ethyl-4,5-dihydrofuran-3-carboxylate (3ak)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 30.9 mg (51% yield) of the desired product as yellow liquid.

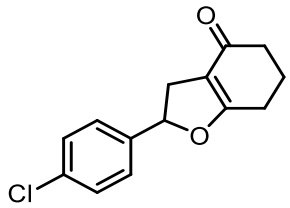
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 5.57 (dd, *J* = 10.7, 8.3 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.32 (dd, *J* = 14.5, 10.9 Hz, 1H), 2.93 (dd, *J* = 14.5, 8.2 Hz, 1H), 2.88 – 2.60 (m, 2H), 1.33 (s, 9H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 172.3, 165.9, 151.0, 138.7, 125.5, 125.4, 100.5, 82.8, 59.3, 38.0, 34.5, 31.3, 21.3, 14.4, 11.2. **IR** (neat, cm^{-1}): 2962 (m), 1672 (s), 1265 (m), 734 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{19}H_{27}O_3$: 303.1955; Found: 303.1952.



2-(4-(tert-butyl)phenyl)-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3al)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 53.0 mg (98% yield) of the desired product as yellow liquid.

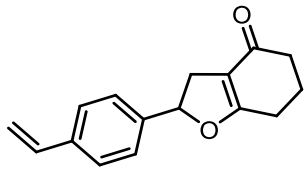
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.48 – 7.37 (m, 2H), 7.36 – 7.25 (m, 2H), 5.73 (dd, *J* = 10.4, 8.1 Hz, 1H), 3.29 – 3.22 (m, 1H), 2.98 – 2.86 (m, 1H), 2.53 – 2.46 (m, 2H), 2.43 – 2.33 (m, 2H), 2.13 – 2.06 (m, 2H), 1.32 (s, 9H).**^{13}C NMR** (126 MHz, Chloroform-*d*) δ 195.4, 177.1, 151.7, 137.4, 125.8, 125.7, 113.1, 86.4, 36.5, 34.6, 33.6, 31.2, 23.9, 21.7. **IR** (neat, cm^{-1}): 2954 (m), 1627 (s), 1227 (m), 826 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{18}H_{23}O_2$: 271.1693; Found: 271.1691.



2-(4-chlorophenyl)-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3am)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 45.8 mg (92% yield) of the desired product as yellow liquid.

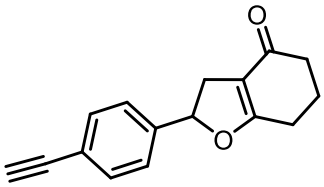
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.39 – 7.34 (m, 2H), 7.31 – 7.24 (m, 2H), 5.72 (dd, *J* = 10.5, 8.0 Hz, 1H), 3.32 – 3.25 (m, 1H), 2.93 – 2.77 (m, 1H), 2.55 – 2.47 (m, 2H), 2.45 – 2.35 (m, 2H), 2.15 – 2.08 (m, 2H).**^{13}C NMR** (126 MHz, Chloroform-*d*) δ 195.3, 176.9, 139.1, 134.3, 128.9, 127.2, 112.9, 85.4, 36.4, 34.0, 23.8, 21.7. **IR** (neat, cm^{-1}): 2946 (m), 1628 (s), 1227 (m), 826 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{14}H_{14}ClO_2$: 249.0677; Found: 249.0675.



2-(4-vinylphenyl)-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3an)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 29.4 mg (61% yield) of the desired product as yellow liquid.

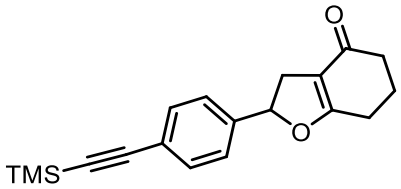
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 7.7 Hz, 2H), 7.32 – 7.24 (m, 2H), 6.71 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.75 (dd, *J* = 18.3, 10.3 Hz, 2H), 5.27 (d, *J* = 10.9 Hz, 1H), 3.38 – 3.14 (m, 1H), 3.08 – 2.78 (m, 1H), 2.51 (t, *J* = 5.6 Hz, 2H), 2.39 (t, *J* = 6.3 Hz, 2H), 2.16 – 2.00 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 195.4, 177.1, 139.9, 137.9, 136.2, 126.6, 126.1, 114.5, 113.0, 86.2, 36.5, 33.9, 23.9, 21.7. **IR** (neat, cm^{-1}): 2922 (m), 1724 (s), 1638 (m), 1269 (m), 730 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{16}H_{17}O_2$: 241.1223; Found: 241.1225.



2-(4-ethynylphenyl)-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3ao)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 26.1 mg (55% yield) of the desired product as yellow liquid.

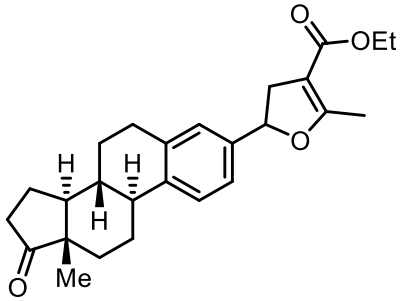
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 9.0 Hz, 2H), 5.74 (dd, *J* = 10.6, 8.0 Hz, 1H), 3.37 – 3.20 (m, 1H), 3.10 (s, 1H), 2.90 – 2.77 (m, 1H), 2.52 (t, *J* = 6.5 Hz, 2H), 2.40 (t, *J* = 6.5 Hz, 2H), 2.10 (p, *J* = 6.4 Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 195.4, 177.0, 141.3, 132.5, 125.7, 122.2, 112.9, 85.7, 83.1, 77.8, 36.4, 34.0, 23.9, 21.7. **IR** (neat, cm^{-1}): 2948 (m), 1630 (s), 1401 (m), 1229 (m), 837 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{16}H_{15}O_2$: 239.1067; Found: 239.1069.



2-(4-((trimethylsilyl)ethynyl)phenyl)-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3ap)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 40.4 mg (65% yield) of the desired product as yellow liquid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 5.72 (dd, *J* = 10.5, 8.1 Hz, 1H), 3.35 – 3.17 (m, 1H), 2.95 – 2.70 (m, 1H), 2.51 (t, *J* = 6.2 Hz, 2H), 2.39 (t, *J* = 6.5 Hz, 2H), 2.09 (p, *J* = 6.4 Hz, 2H), 0.24 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 195.4, 176.9, 140.9, 132.3, 125.6, 123.3, 112.9, 104.4, 94.9, 85.8, 36.5, 34.1, 23.9, 21.7, -0.1. **IR** (neat, cm^{-1}): 2954 (m), 1630 (s), 1505 (m), 1225 (m), 838 (m) 329. **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{19}H_{23}O_2Si$: 311.1462; Found: 311.1465.

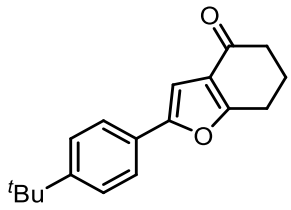


Ethyl-2-methyl-5-((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)-4,5-dihydrofuran-3-carboxylate (3aq)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 40.7 mg (50% yield, 1:1 d.r.) of the desired product as yellow liquid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 8.1 Hz, 1H), 7.12 (d, *J* = 8.1 Hz, 1H), 7.07 (s, 1H), 5.53 (dd, *J* = 10.4, 8.7 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.38 – 3.26 (m, 1H), 2.96 – 2.94 (m, 1H), 2.93 – 2.91 (m, 2H), 2.54 – 2.49 (m, 1H), 2.45 – 2.41 (m, 1H), 2.33 – 2.28 (m, 1H), 2.27 (s, 3H), 2.20 – 2.11 (m, 1H), 2.06 – 2.02 (m, 2H), 2.00 – 1.94 (m, 1H), 1.68 – 1.61 (m, 1H), 1.59 – 1.39 (m, 6H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.91 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 220.8, 167.6, 166.1, 139.83, 139.82, 138.9, 138.85, 136.91, 126.41, 126.38, 125.7, 123.31, 123.27, 101.7, 83.01, 82.99, 59.5, 50.5, 47.9, 44.4, 38.1,

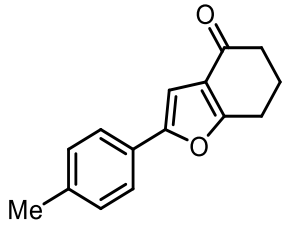
37.7, 35.8, 31.5, 29.42, 29.40, 26.4, 25.7, 21.6, 14.4, 14.1, 13.8. **IR** (neat, cm^{-1}): 2929 (m), 1736 (s), 1693 (m), 1646 (m), 1220 (m), 734 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{26}H_{33}O_4$: 409.2373; Found: 409.2371.



2-(4-(tert-butyl)phenyl)-6,7-dihydrobenzofuran-4(5H)-one[4] (5a)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 40.4 mg (75% yield) of the desired product as yellow solid.

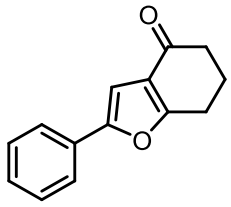
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 6.84 (s, 1H), 2.95 (t, *J* = 6.3 Hz, 2H), 2.53 (t, *J* = 6.3 Hz, 2H), 2.22 (p, *J* = 6.3 Hz, 2H), 1.34 (s, 9H).



2-(p-tolyl)-6,7-dihydrobenzofuran-4(5H)-one[4] (5b)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 31.7 mg (70% yield) of the desired product as yellow solid.

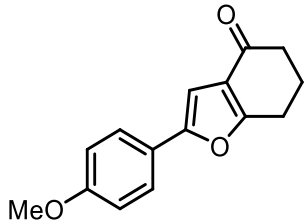
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 6.83 (s, 1H), 2.95 (t, *J* = 6.2 Hz, 2H), 2.56 – 2.49 (m, 2H), 2.37 (s, 3H), 2.25 – 2.17 (m, 2H).



2-phenyl-6,7-dihydrobenzofuran-4(5H)-one[4] (5c)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 25.2 mg (59% yield) of the desired product as yellow solid.

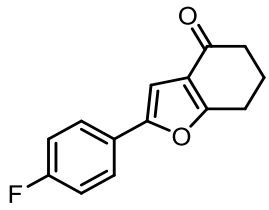
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.69 – 7.63 (m, 2H), 7.45 – 7.36 (m, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 6.89 (s, 1H), 2.96 (t, *J* = 6.3 Hz, 2H), 2.52 (t, *J* = 6.1 Hz, 2H), 2.26 – 2.18 (m, 2H).



2-(4-methoxyphenyl)-6,7-dihydrobenzofuran-4(5H)-one[4] (5d)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 35.4 mg (73% yield) of the desired product as yellow solid.

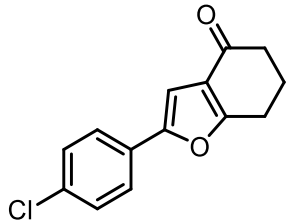
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.74 (s, 1H), 3.83 (s, 3H), 2.94 (t, *J* = 6.1 Hz, 2H), 2.52 (t, *J* = 6.2 Hz, 2H), 2.21 (m, 2H).



2-(4-fluorophenyl)-6,7-dihydrobenzofuran-4(5H)-one[4] (5e)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 28.5 mg (62% yield) of the desired product as yellow solid.

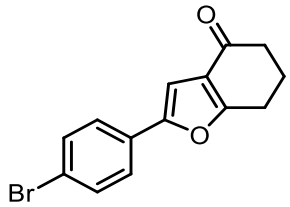
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.56 (m, 2H), 7.09 (t, *J* = 8.6 Hz, 2H), 6.82 (s, 1H), 2.95 (t, *J* = 6.1 Hz, 2H), 2.53 (t, *J* = 6.4 Hz, 2H), 2.23 – 2.16 (m, 2H).



2-(4-chlorophenyl)-6,7-dihydrobenzofuran-4(5H)-one[4] (5f)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 30.8 mg (62% yield) of the desired product as yellow solid.

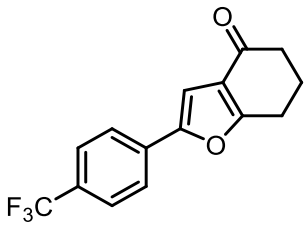
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 6.88 (s, 1H), 2.95 (t, *J* = 6.2 Hz, 2H), 2.53 (t, *J* = 6.4 Hz, 2H), 2.26 – 2.18 (m, 2H).



2-(4-bromophenyl)-6,7-dihydrobenzofuran-4(5H)-one[4] (5g)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 37.3 mg (64% yield) of the desired product as yellow solid.

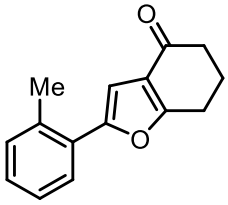
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.00 – 7.41 (m, 4H), 6.89 (s, 1H), 2.95 t, *J* = 6.2 Hz, 2H), 2.53 (t, *J* = 6.4 Hz, 2H), 2.22 (p, *J* = 6.3 Hz, 2H).



2-(4-(trifluoromethyl)phenyl)-6,7-dihydrobenzofuran-4(5H)-one[4] (5h)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 26.2 mg (47% yield) of the desired product as yellow solid.

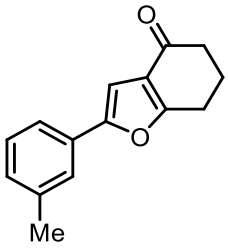
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 7.9 Hz, 2H), 7.65 (d, *J* = 7.9 Hz, 2H), 7.01 (s, 1H), 2.98 (t, *J* = 5.9 Hz, 2H), 2.55 (t, *J* = 5.9 Hz, 2H), 2.32 – 2.13 (m, 2H).



2-(o-tolyl)-6,7-dihydrobenzofuran-4(5H)-one (5i)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 32.2 mg (71% yield) of the desired product as yellow solid.

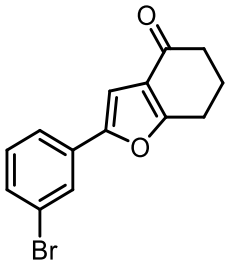
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.73 – 7.65 (m, 1H), 7.28 – 7.22 (m, 3H), 6.79 (s, 1H), 2.96 (t, *J* = 6.3 Hz, 2H), 2.57 – 2.52 (m, 2H), 2.48 (s, 3H), 2.23 (p, *J* = 6.4 Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 194.7, 166.3, 153.6, 134.9, 131.2, 129.0, 128.1, 126.9, 126.0, 122.8, 104.6, 37.6, 23.4, 22.6, 21.9. **IR** (neat, cm^{-1}): 2951 (m), 1676 (s), 1596 (m), 1214 (m), 761 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{15}H_{15}O_2$: 227.1067; Found: 227.1066.



2-(m-tolyl)-6,7-dihydrobenzofuran-4(5H)-one (5j)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 29.4 mg (65% yield) of the desired product as yellow solid.

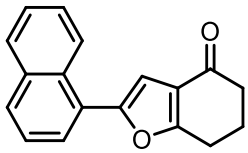
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.49 – 7.44 (m, 2H), 7.28 (t, *J* = 7.7 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 6.87 (s, 1H), 2.96 (t, *J* = 6.3 Hz, 2H), 2.56 – 2.50 (m, 2H), 2.39 (s, 3H), 2.22 (p, *J* = 6.3 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 194.6, 166.6, 154.3, 138.4, 129.6, 128.9, 128.7, 124.5, 122.8, 121.1, 100.7, 37.6, 23.4, 22.6, 21.4. **IR** (neat, cm^{-1}): 2949 (m), 1674 (s), 1611 (m), 1218 (m), 782 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{15}H_{15}O_2$: 227.1067; Found: 227.1066.



2-(3-bromophenyl)-6,7-dihydrobenzofuran-4(5H)-one (5k)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 37.6 mg (65% yield) of the desired product as yellow solid.

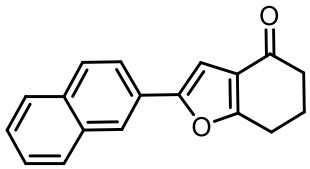
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (s, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 7.1 Hz, 1H), 6.93 (s, 1H), 2.98 (t, *J* = 5.8 Hz, 2H), 2.56 (t, *J* = 5.9 Hz, 2H), 2.41 – 2.00 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 194.2, 166.9, 152.5, 131.6, 130.8, 130.3, 126.8, 122.9, 122.4, 102.0, 37.6, 23.4, 22.5. **IR** (neat, cm^{-1}): 2951 (m), 1676 (s), 1596 (m), 1214 (m), 761 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{14}H_{12}BrO_2$: 291.0015; Found: 291.0016.



2-(naphthalen-1-yl)-6,7-dihydrobenzofuran-4(5H)-one[5] (5l)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 35.0 mg (67% yield) of the desired product as yellow solid.

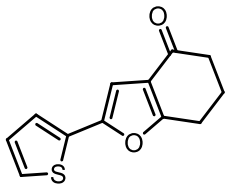
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.34 (d, *J* = 8.0 Hz, 1H), 7.92 – 7.85 (m, 2H), 7.74 (d, *J* = 7.1 Hz, 1H), 7.61 – 7.48 (m, 3H), 7.00 (s, 1H), 3.02 (t, *J* = 6.1 Hz, 2H), 2.59 (t, *J* = 6.3 Hz, 2H), 2.27 (p, *J* = 6.1 Hz, 2H).



2-(naphthalen-2-yl)-6,7-dihydrobenzofuran-4(5H)-one (5m)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 35.8 mg (68% yield) of the desired product as yellow solid.

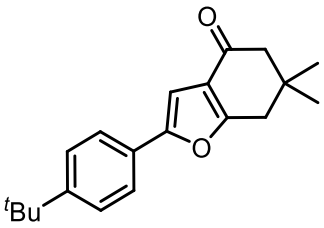
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (s, 1H), 7.89 –7.81 (m, 3H), 7.72 (d, *J* = 8.6 Hz, 1H), 7.49 (p, *J* = 6.7 Hz, 2H), 7.00 (s, 1H), 3.00 (t, *J* = 6.2 Hz, 2H), 2.55 (t, *J* = 6.4 Hz, 2H), 2.24 (p, *J* = 6.3 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 194.4, 166.9, 154.3, 133.3, 132.9, 128.6, 128.2, 127.8, 127.1, 126.7, 126.3, 123.1, 122.6, 122.0, 101.5, 37.6, 23.5, 22.6. **IR** (neat, cm^{-1}): 2949 (m), 1672 (s), 1630 (m), 1232 (m), 748 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{18}H_{15}O_2$: 263.1067; Found: 263.1067.



2-(thiophen-2-yl)-6,7-dihydrobenzofuran-4(5H)-one (5n)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 18.5 mg (42% yield) of the desired product as yellow solid.

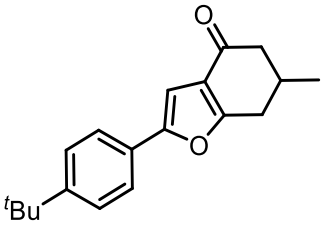
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.21 (m, 2H), 7.09 – 7.01 (m, 1H), 6.72 (s, 1H), 2.93 (t, *J* = 5.9 Hz, 2H), 2.51 (t, *J* = 5.9 Hz, 2H), 2.32 – 2.04 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 194.3, 166.3, 149.7, 132.4, 127.7, 125.1, 123.6, 122.8, 100.8, 37.6, 23.4, 22.5. **IR** (neat, cm^{-1}): 2951 (m), 1673 (s), 1577 (m), 1239 (m), 721 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{12}H_{11}O_2S$: 219.0474; Found: 219.0477.



2-(4-(tert-butyl)phenyl)-6,6-dimethyl-6,7-dihydrobenzofuran-4(5H)-one (5o)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 41.0 mg (69% yield) of the desired product as yellow solid.

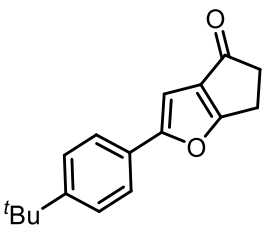
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 6.84 (s, 1H), 2.82 (s, 2H), 2.40 (s, 2H), 1.33 (s, 9H), 1.17 (s, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 194.0, 165.6, 154.7, 151.2, 127.1, 125.7, 123.7, 121.6, 100.1, 52.0, 37.5, 35.3, 34.7, 31.2, 28.6. **IR** (neat, cm^{-1}): 2962 (m), 1672 (s), 1578 (m), 1265 (m), 734 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{20}H_{25}O_2$: 297.1849; Found: 297.1846.



2-(4-(tert-butyl)phenyl)-6-methyl-6,7-dihydrobenzofuran-4(5H)-one (5p)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 41.8 mg (74% yield) of the desired product as yellow solid.

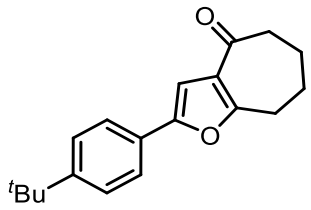
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 6.83 (s, 1H), 3.03 (dd, *J* = 17.0, 4.8 Hz, 1H), 2.66 – 2.54 (m, 2H), 2.53 – 2.42 (m, 1H), 2.28 (dd, *J* = 16.2, 11.3 Hz, 1H), 1.33 (s, 9H), 1.20 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 194.2, 166.1, 154.6, 151.2, 127.1, 125.7, 123.7, 122.5, 100.1, 46.1, 34.7, 31.5, 31.2, 30.8, 21.1. **IR** (neat, cm^{-1}): 2958 (m), 1676 (s), 1578 (m), 1212 (m), 733 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{19}H_{23}O_2$: 283.1693; Found: 283.1688.



2-(4-(tert-butyl)phenyl)-5,6-dihydro-4H-cyclopenta[b]furan-4-one (5q)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 26.1 mg (51% yield) of the desired product as yellow solid.

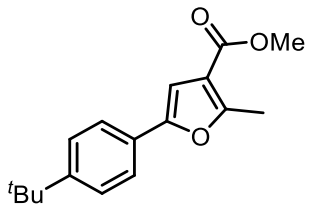
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 6.68 (s, 1H), 3.09 – 3.05 (m, 2H), 3.03 – 2.99 (m, 2H), 1.34 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 195.4, 182.1, 161.8, 151.8, 129.6, 127.2, 125.8, 123.9, 98.6, 41.7, 34.7, 31.2, 22.5. **IR** (neat, cm^{-1}): 2962 (m), 1700 (s), 1590 (m), 1176 (m), 839 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{17}H_{19}O_2$: 255.1380; Found: 255.1378.



2-(4-(tert-butyl)phenyl)-5,6,7,8-tetrahydro-4H-cyclohepta[b]furan-4-one (5r)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 40.2 mg (71% yield) of the desired product as yellow solid.

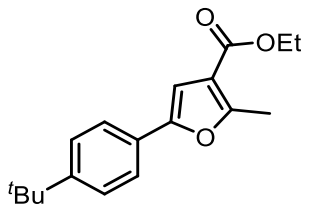
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 6.90 (s, 1H), 3.10 (t, *J* = 6.3 Hz, 2H), 2.83 – 2.70 (m, 2H), 2.13 – 2.01 (m, 2H), 2.01 – 1.89 (m, 2H), 1.33 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 196.8, 161.0, 152.6, 151.0, 127.1, 125.6, 125.3, 123.6, 104.3, 44.5, 34.6, 31.2, 29.8, 24.9, 22.9. **IR** (neat, cm^{-1}): 2959 (m), 1647 (s), 1572 (m), 1201 (m), 840 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{19}H_{23}O_2$: 283.1693; Found: 283.1691.



Methyl-5-(4-(tert-butyl)phenyl)-2-methylfuran-3-carboxylate (5s)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 16.2 mg (30% yield) of the desired product as yellow liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 6.83 (s, 1H), 3.85 (s, 3H), 2.65 (s, 3H), 1.34 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.6, 158.5, 152.0, 150.8, 127.3, 125.6, 123.5, 115.0, 104.7, 51.3, 34.6, 31.2, 13.9. **IR** (neat, cm^{-1}): 2955 (m), 1719 (s), 1606 (m), 1232 (m), 776 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{17}H_{21}O_3$: 273.1485; Found: 273.1487.

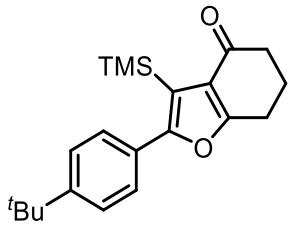


Ethyl-5-(4-(tert-butyl)phenyl)furan-3-carboxylate (5t)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 17.3 mg (30% yield) of the desired product as yellow liquid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 6.83 (s, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.64 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.33 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 164.2, 158.3, 151.9, 150.7, 127.4,

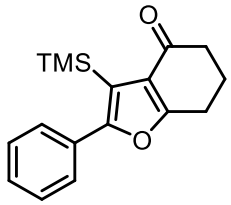
125.6, 123.4, 115.3, 104.8, 60.2, 34.6, 31.2, 14.4, 13.9. **IR** (neat, cm^{-1}): 2961 (m), 1716 (s), 1606 (m), 1231 (m), 775 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{18}H_{23}O_3$: 287.1642; Found: 287.1643.



2-(4-(tert-butyl)phenyl)-3-(trimethylsilyl)-6,7-dihydrobenzofuran-4(5H)-one (5u)

Synthesized according to **GP 2**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 36.1 mg (53% yield) of the desired product as yellow solid.

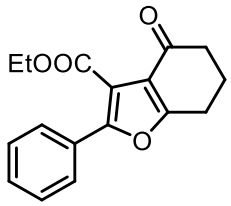
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.30 (m, 4H), 2.90 (t, *J* = 6.2 Hz, 2H), 2.52 (t, *J* = 6.4 Hz, 2H), 2.19 (p, *J* = 6.3 Hz, 2H), 1.35 (s, 9H), 0.14 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 194.7, 167.1, 159.6, 152.2, 129.6, 129.1, 126.2, 124.8, 112.2, 38.3, 34.7, 31.3, 23.5, 22.5, 0.2. **IR** (neat, cm^{-1}): 2954 (m), 1674 (s), 1245 (m), 833 (m); **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd. for $C_{21}H_{28}O_2SiNa$: 363.1751; Found: 363.1750.



2-phenyl-3-(trimethylsilyl)-6,7-dihydrobenzofuran-4(5H)-one (5v)

Synthesized according to **GP 2**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 28.0 mg (49% yield) of the desired product as yellow solid.

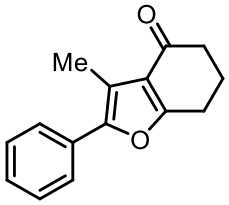
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.34 (m, 5H), 2.91 (t, *J* = 6.3 Hz, 2H), 2.52 (t, *J* = 6.5 Hz, 2H), 2.19 (p, *J* = 6.3 Hz, 2H), 0.14 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 194.6, 167.2, 159.3, 132.0, 129.9, 129.0, 127.8, 126.2, 112.6, 38.3, 23.5, 22.5, 0.1. **IR** (neat, cm^{-1}): 2950 (m), 1674 (s), 1579 (m), 1244 (m), 762 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{17}H_{21}O_2Si$: 285.1305; Found: 285.1303.



Ethyl-4-oxo-2-phenyl-4,5,6,7-tetrahydrobenzofuran-3-carboxylate (5w)

Synthesized according to **GP 2**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 19.2 mg (34% yield) of the desired product as yellow solid.

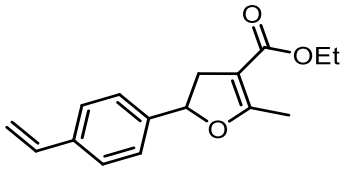
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 7.4 Hz, 2H), 7.46 – 7.30 (m, 3H), 4.40 (q, *J* = 7.1 Hz, 2H), 2.94 (t, *J* = 6.2 Hz, 2H), 2.54 (t, *J* = 6.3 Hz, 2H), 2.22 (p, *J* = 6.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 192.4, 165.7, 164.5, 152.9, 129.2, 128.7, 128.6, 126.5, 120.9, 111.5, 61.8, 38.0, 23.4, 22.3, 13.9. **IR** (neat, cm^{-1}): 2955 (m), 1728 (s), 1683 (m), 1222 (m), 762 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{17}H_{17}O_4$: 285.1121; Found: 285.1119.



3-methyl-2-phenyl-6,7-dihydrobenzofuran-4(5H)-one[6] (5x)

Synthesized according to **GP 2**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 17.3 mg (38% yield) of the desired product as yellow solid.

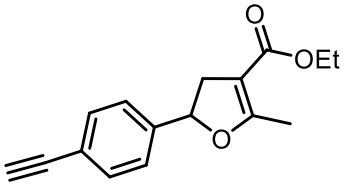
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.62 – 7.58 (m, 2H), 7.46 – 7.39 (m, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 2.92 (t, *J* = 6.3 Hz, 2H), 2.53 – 2.49 (m, 2H), 2.48 (s, 3H), 2.19 (p, *J* = 6.4 Hz, 2H).



Ethyl-2-methyl-5-(4-vinylphenyl)-4,5-dihydrofuran-3-carboxylate (7a)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 30.1 mg (58% yield) of the desired product as yellow liquid.

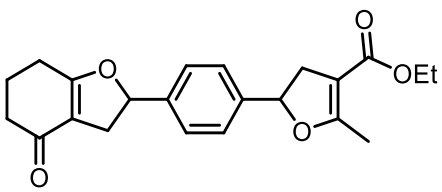
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 6.71 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.75 (d, *J* = 17.6 Hz, 1H), 5.57 (dd, *J* = 10.6, 8.4 Hz, 1H), 5.26 (d, *J* = 10.9 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.32 (ddd, *J* = 14.3, 10.7, 1.4 Hz, 1H), 2.99 – 2.84 (m, 1H), 2.29 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.5, 165.9, 141.0, 137.5, 136.3, 126.4, 125.8, 114.2, 101.7, 82.8, 59.5, 37.9, 14.4, 14.1. **IR** (neat, cm^{-1}): 2979 (m), 1693 (s), 1647 (m), 1221 (m), 840 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{16}H_{19}O_3$: 259.1329; Found: 259.1331.



Ethyl-5-(4-ethynylphenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (7b)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 33.2 mg (65% yield) of the desired product as yellow liquid.

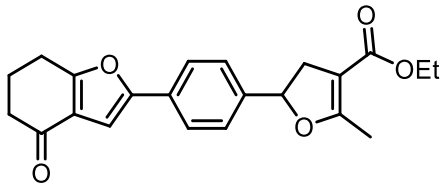
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 5.57 (dd, *J* = 10.6, 8.4 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.45 – 3.27 (m, 1H), 3.08 (s, 1H), 2.94 – 2.74 (m, 1H), 2.28 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 167.5, 165.8, 142.3, 132.4, 125.5, 121.8, 101.7, 83.2, 82.4, 77.5, 59.6, 37.9, 14.4, 14.0. **IR** (neat, cm^{-1}): 2925 (m), 1695 (s), 1649 (s), 1223 (m), 836 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{16}H_{17}O_3$: 257.1172; Found: 257.1173.



Ethyl-2-methyl-5-(4-(4-oxo-2,3,4,5,6,7-hexahydrobenzofuran-2-yl)phenyl)-4,5-dihydrofuran-3-carboxylate (8a)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 2:1) afforded 40.0 mg (54% yield 1:1 d.r.) of the desired product as yellow solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.38 – 7.29 (m, 4H), 5.74 (dd, *J* = 10.4, 8.1 Hz, 1H), 5.58 (dd, *J* = 10.6, 8.4 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.41 – 3.15 (m, 2H), 3.03 – 2.75 (m, 2H), 2.50 (t, *J* = 6.1 Hz, 2H), 2.38 (t, *J* = 6.4 Hz, 2H), 2.27 (s, 3H), 2.08 (p, *J* = 6.3 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 195.4, 176.9, 167.5, 165.9, 141.9, 140.5, 126.2, 126.0, 112.9, 101.7, 85.8, 82.53, 82.52, 59.5, 37.9, 36.4, 33.9, 23.9, 21.7, 14.4, 14.0. **IR** (neat, cm^{-1}): 2945 (m), 1692 (s), 1630 (m), 1224 (m), 763 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{22}H_{25}O_5$: 369.1697; Found: 369.1703.



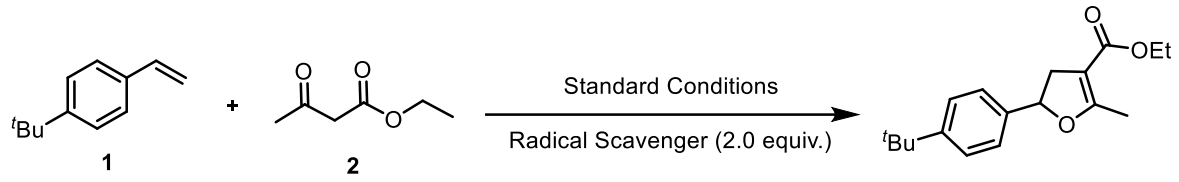
Ethyl-2-methyl-5-(4-(4-oxo-4,5,6,7-tetrahydrobenzofuran-2-yl)phenyl)-4,5-dihydrofuran-3-carboxylate (8b)

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 2:1) afforded 46.3 mg (63% yield) of the desired product as yellow solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 6.89 (s, 1H), 5.59 (dd, *J* = 10.6, 8.4 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.43 – 3.25 (m, 1H), 2.96 (t, *J* = 6.2 Hz, 2H), 2.94 – 2.86 (m, 1H), 2.59 – 2.49 (m, 2H), 2.29 (s, 3H), 2.22 (p, *J* = 6.6 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 194.5, 167.5, 166.8, 165.9, 153.8, 141.3, 129.6, 126.2, 124.2, 122.9, 101.8, 101.2, 82.7, 59.6, 37.9, 37.6, 23.4, 22.5, 14.4, 14.1. **IR** (neat, cm^{-1}): 2951 (m), 1679 (s), 1649 (m), 1222 (m), 836 (m); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{22}H_{23}O_5$: 367.1540; Found: 367.1545.

4. Radical inhibition experiment

TEMPO or BHT were added into the solution of **1** and **2** under standard conditions. The Crude ^1H NMR indicated the addition of radical scavenger completely shut down the reaction and the corresponding yields were given with Br_2CH_2 as the internal standard.



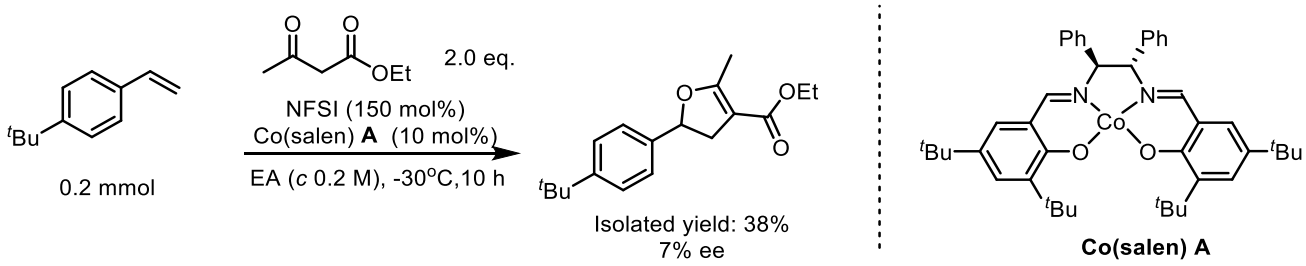
Radical Scavenger	Yield (%)
TEMPO	15
BHT	< 5

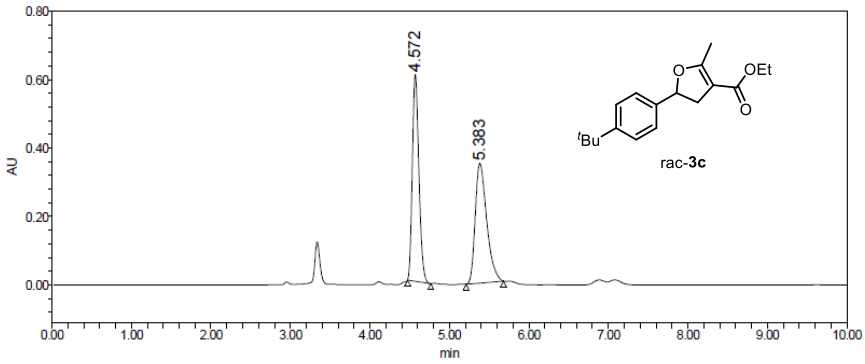
5. Radical inhibition experiment

TEMPO or BHT were added into the solution of **1** and **2** under standard conditions. The Crude ^1H NMR indicated the addition of radical scavenger completely shut down the reaction and the corresponding yields were given with Br_2CH_2 as the internal standard.

7. Co-catalyzed enantiselective dihydrofuran reaction

The preliminary trials of Co-catalyzed enantiselective dihydrofuran reaction were conducted at -30ºC, delivering the desired dihydrofuran product with 7% ee [CHIRALPAK® IG, 5% ^{i}PrOH in hexanes, 1.0 mL/min, 268 nm; t_1 = 4.6 min, t_2 = 5.4 min].

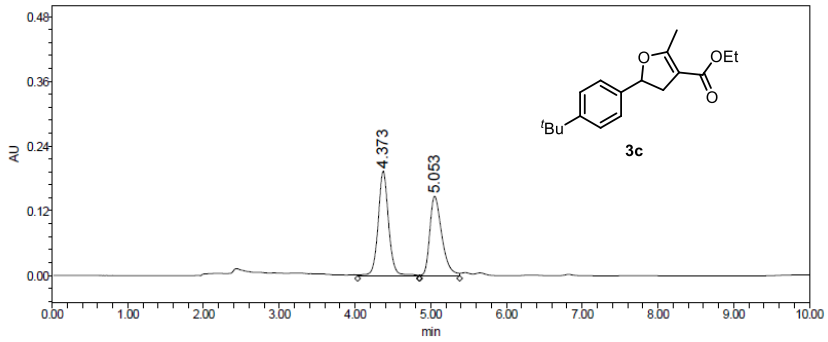




Channel: 2998; Processed Channel: PDA 268.8 纳米 (210-400)纳米; Result Id: 19402; Processing Method: 111222

Processed Channel Descr.: PDA 268.8 纳米 (210-400)纳米

	Processed Channel Descr.	RT	Area	Height	% Area
1	PDA 268.8 纳米 (210-400)纳米	4.572	3451718	603633	49.65
2	PDA 268.8 纳米 (210-400)纳米	5.383	3500219	349765	50.35



Channel: 274.1 纳米; Processed Channel: PDA 274.1 纳米 (210-400)纳米; Result Id: 19477; Processing Method: 1010

Processed Channel Descr.: PDA 274.1 纳米 (210-400)纳米

	Processed Channel Descr.	RT	Area	Height	% Area
1	PDA 274.1 纳米 (210-400)纳米	4.373	1861724	193647	53.38
2	PDA 274.1 纳米 (210-400)纳米	5.053	1625781	147155	46.62

8. References

[1] H. Yi, Z. Liao, G. Zhang, G. Zhang, C. Fan, X. Zhang, E. E. Bunel, C.-W. Pao, J.-F. Lee, A. Lei, *Chem. Eur. J.* **2015**, *21*, 18925-18929.

[2] E. Biçer, M. Yılmaz, E. V. Burgaz, A. T. Pekel, *Helv. Chim. Acta* **2013**, *96*, 135-141.

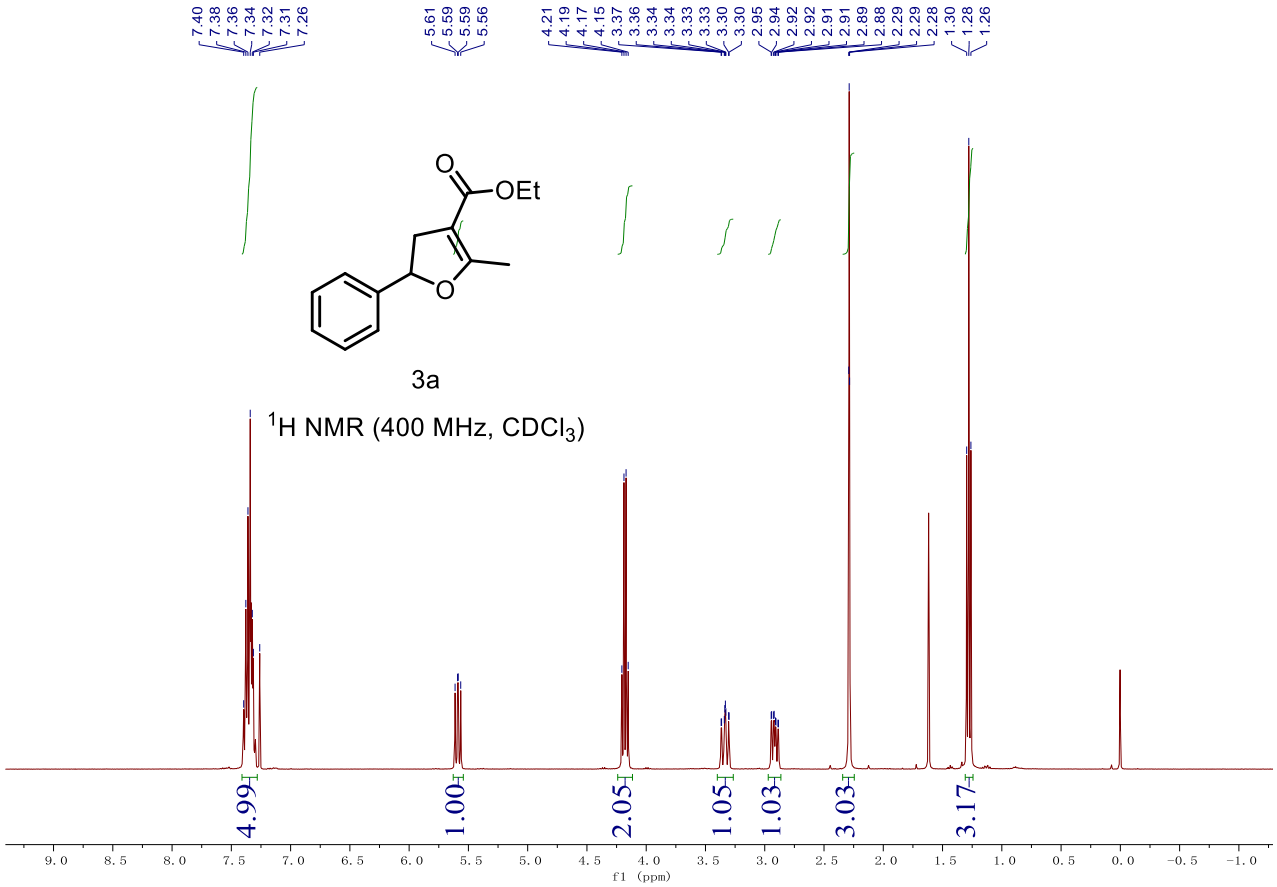
[3] S. Tang, K. Liu, Y. Long, X. Gao, M. Gao, A. Lei, *Org. Lett.* **2015**, *17*, 2404-2407.

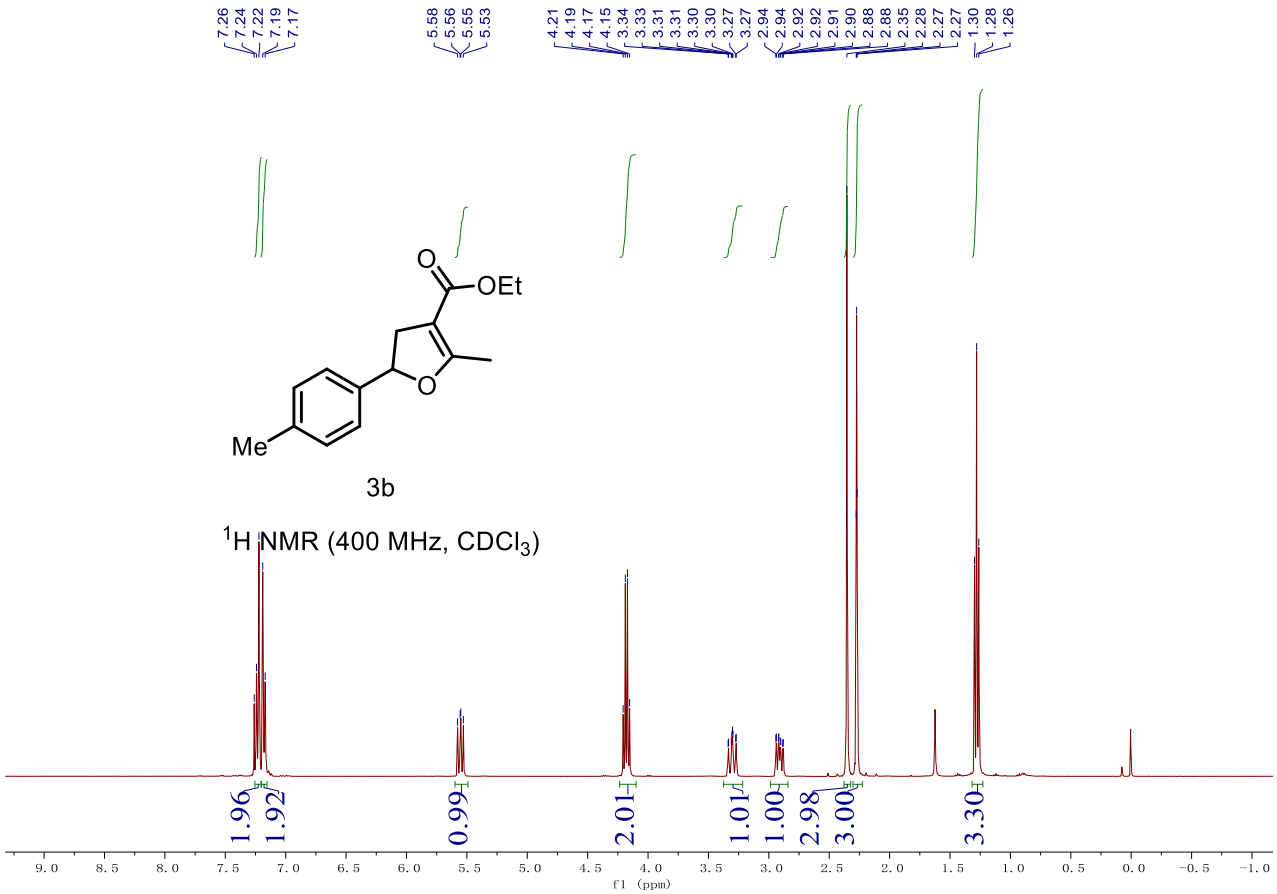
[4] H. Ye, R. Liu, D. Li, Y. Liu, H. Yuan, W. Guo, L. Zhou, X. Cao, H. Tian, J. Shen, P. G. Wang, *Org. Lett.* **2013**, *15*, 18-21.

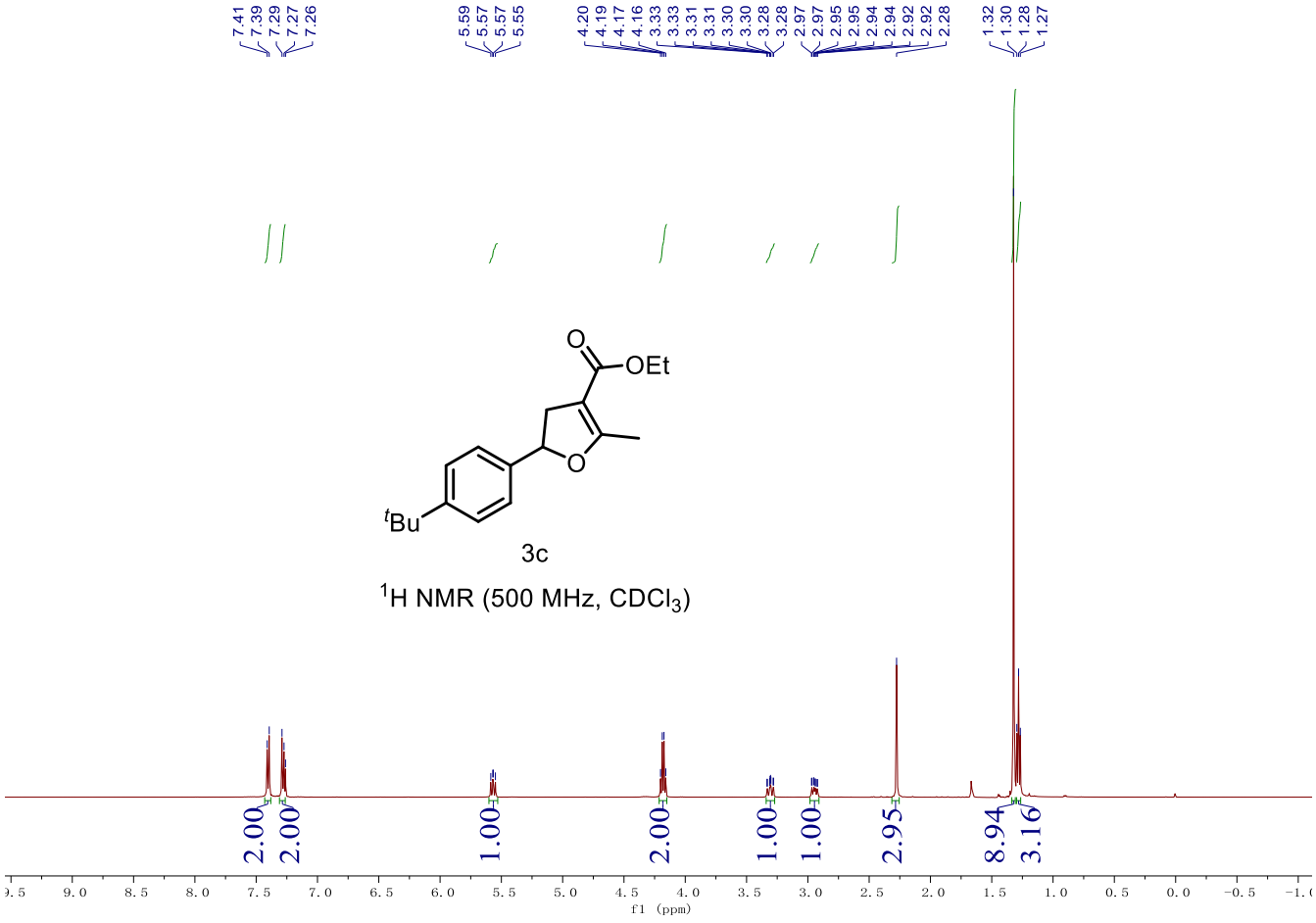
[5] L. Xia, Y. R. Lee, *Eur. J. Org. Chem.* **2014**, *2014*, 3430-3442.

[6] Y.-Y. Han, Y.-Y. Jiao, D. Ren, Z. Hu, S. Shen, S. Yu, *Asian. J. Org. Chem.* **2017**, *6*, 414-417.

9. NMR Spectra

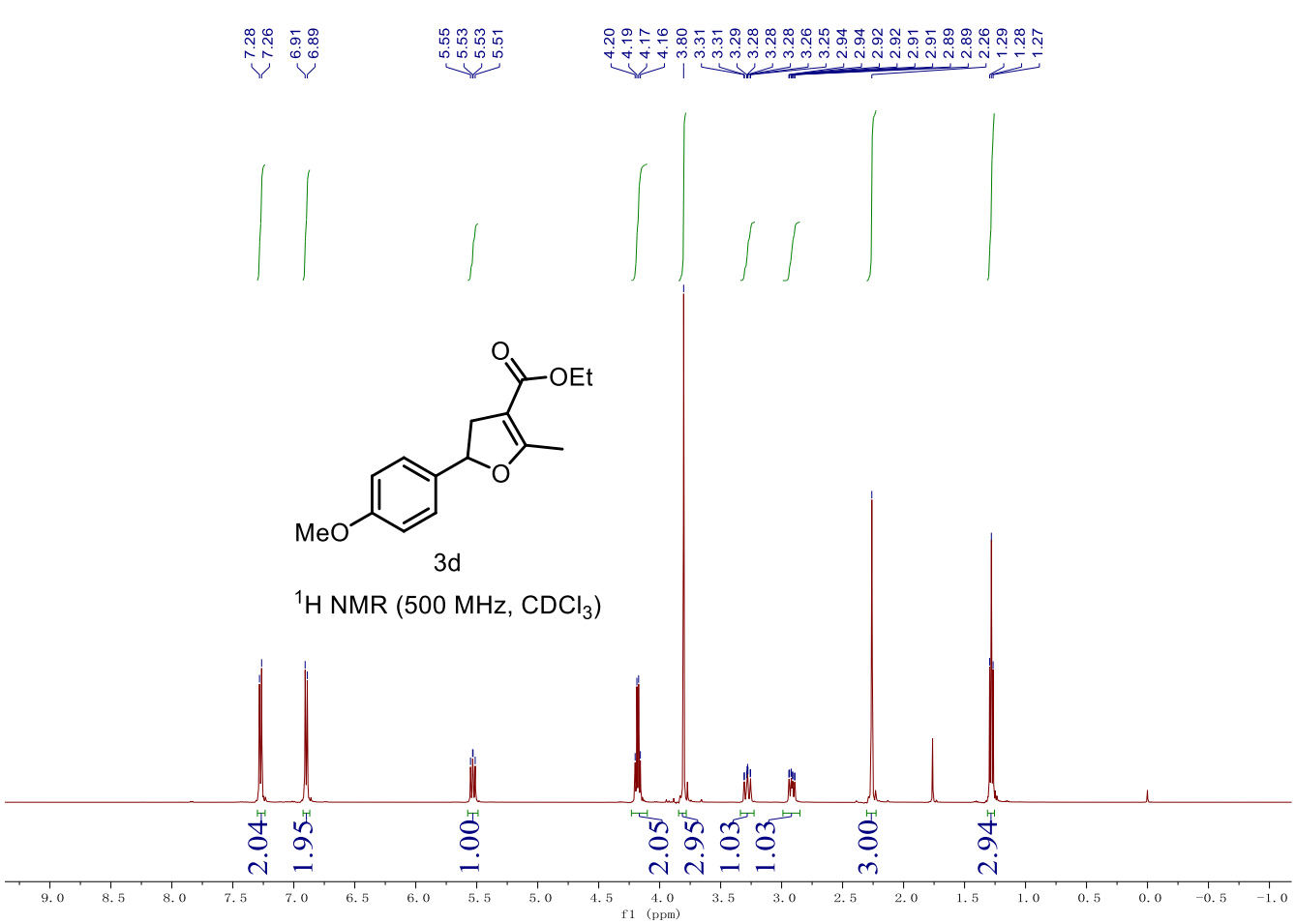






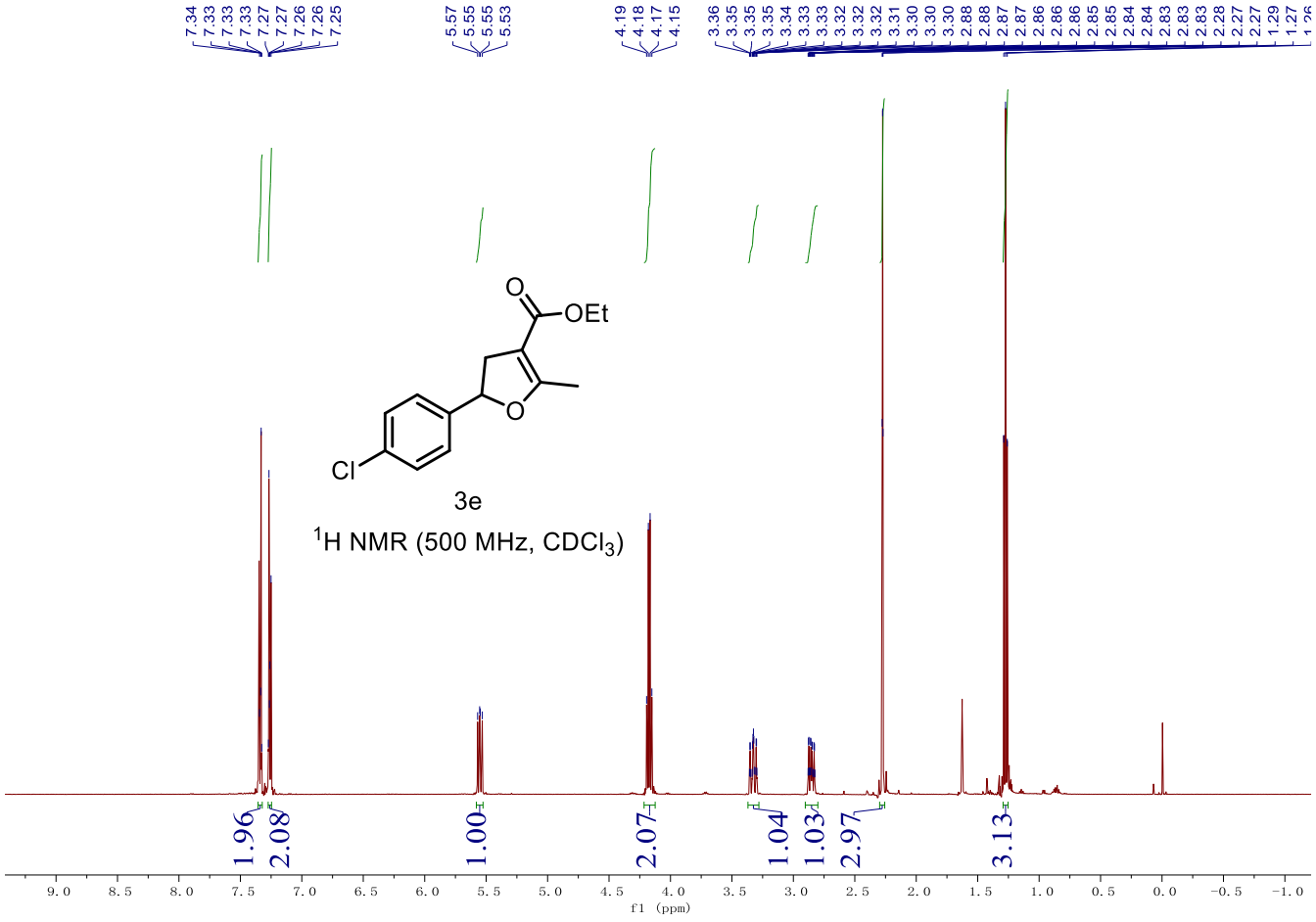
3c

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



3d

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


7.34
7.33
7.33
7.33
7.27
7.27
7.26
7.26
7.25
5.57
5.55
5.55
5.53
4.19
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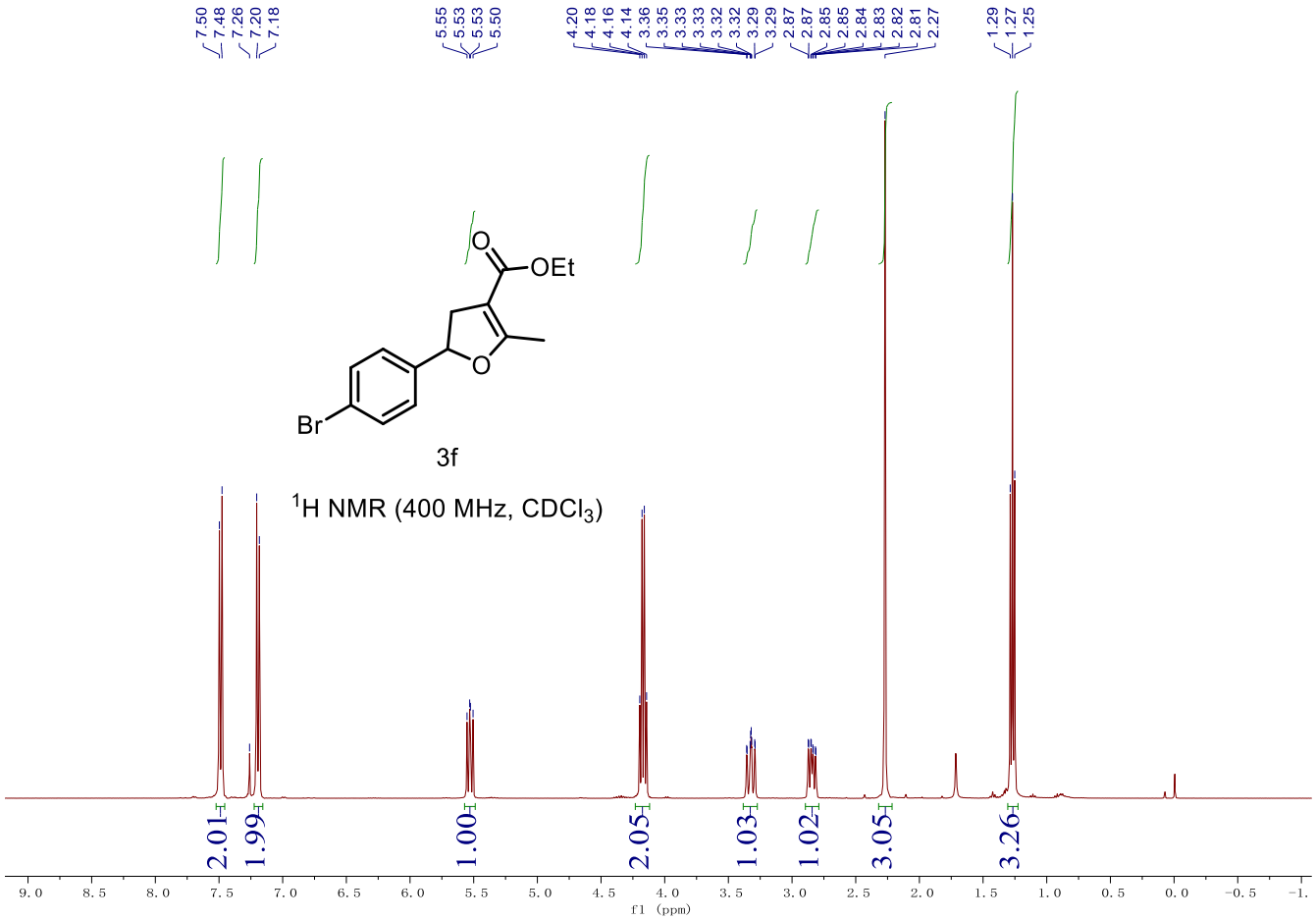
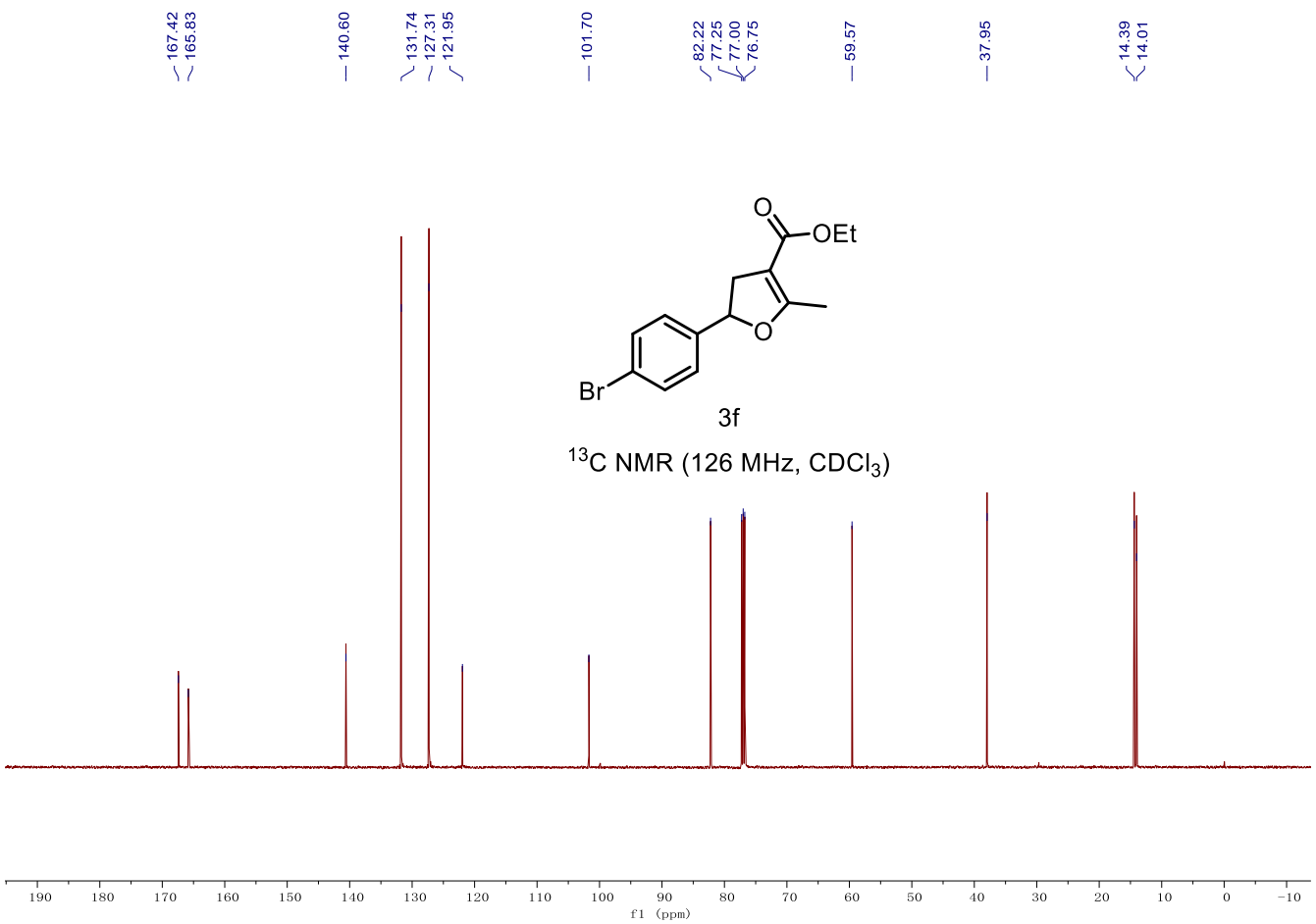
2.85
2.85
2.84
2.84
2.83
2.83
2.83
2.28
2.27
2.27
1.29
1.27
O
OEt
O
Cl
3e
1H NMR (500 MHz, CDCl3)
1.96
2.08
1.00
2.07
1.04
1.03
2.97
3.13
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f1 (ppm)



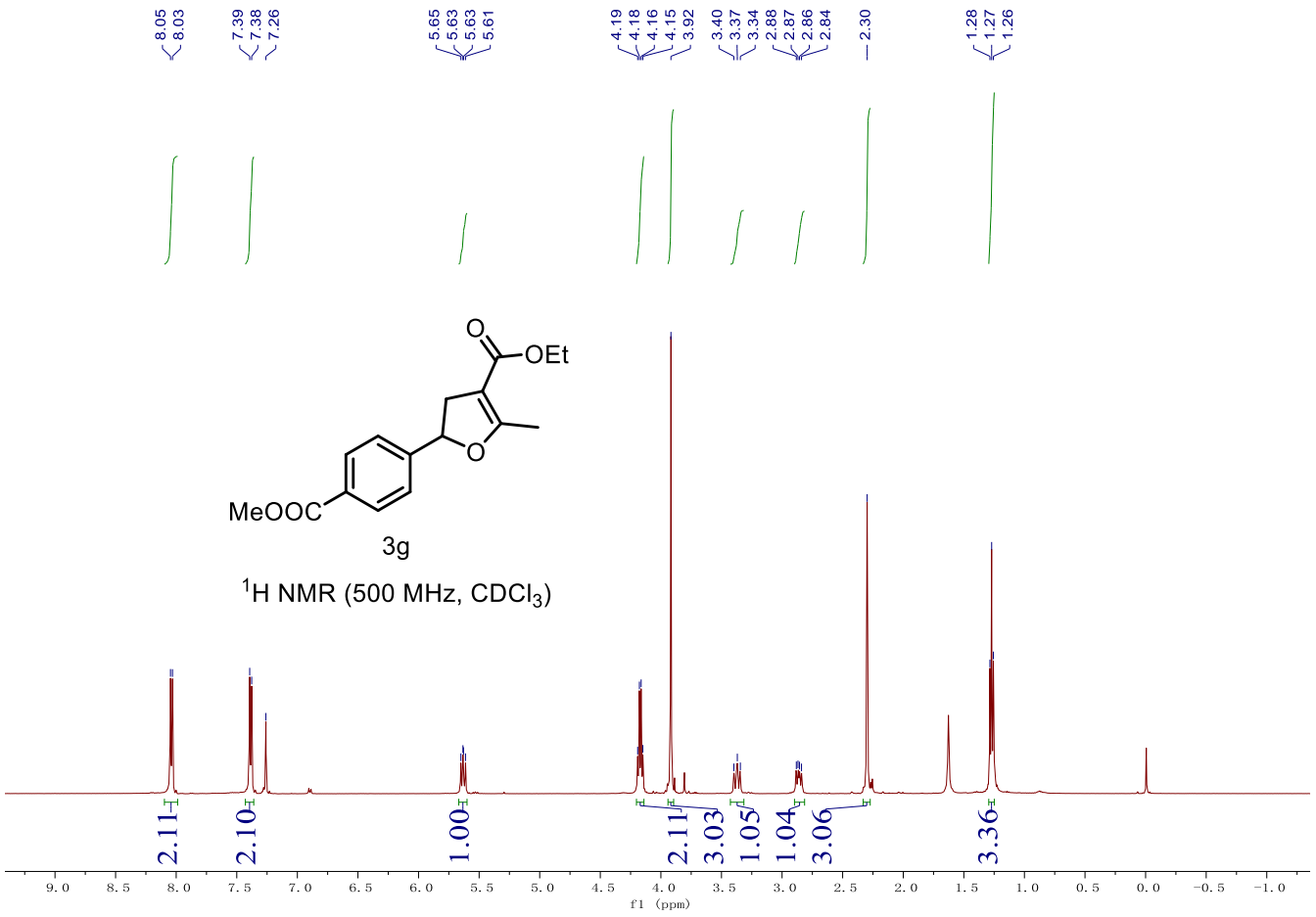
3f

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



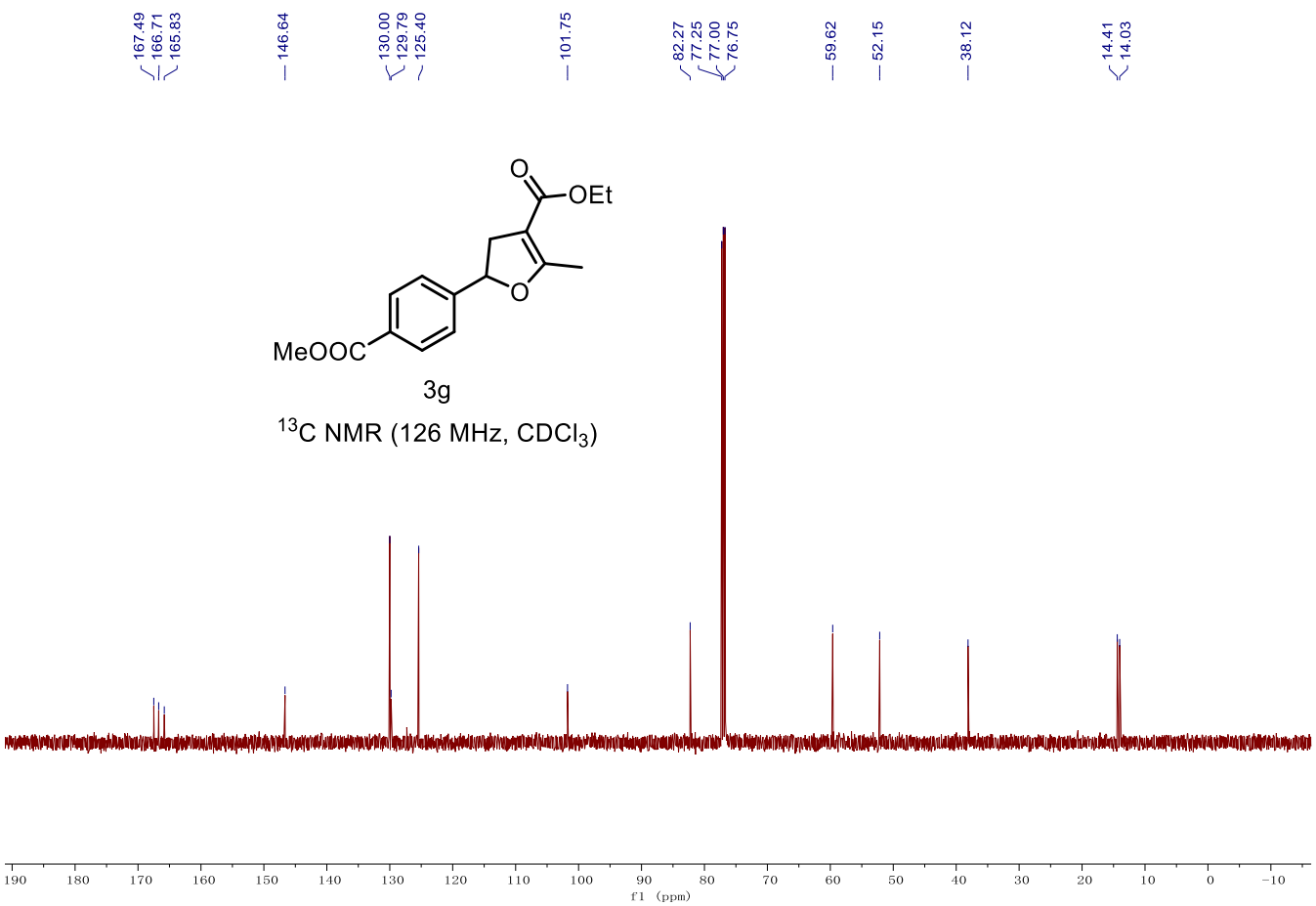
3f

^{13}C NMR (126 MHz, $CDCl_3$)



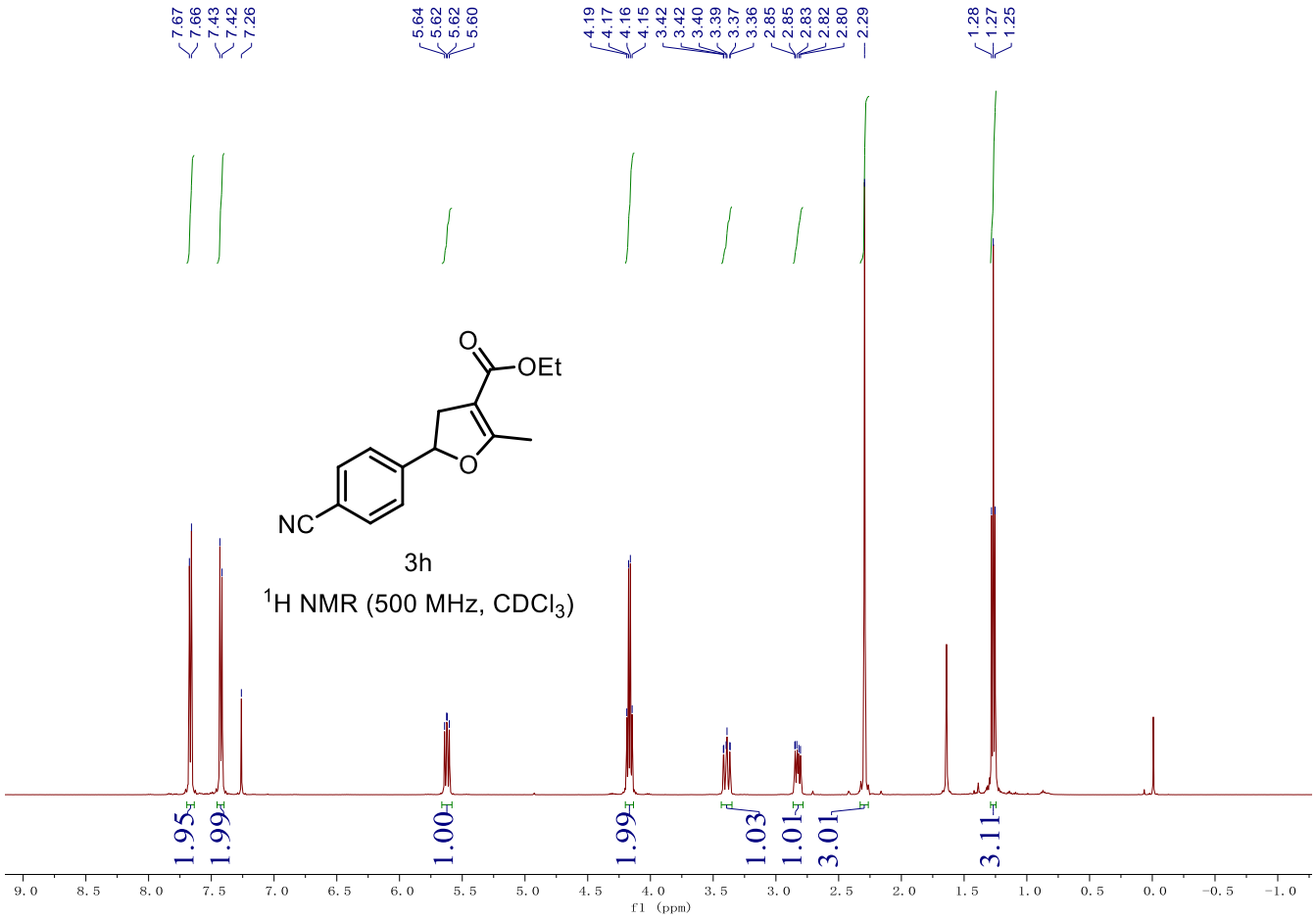
3g

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



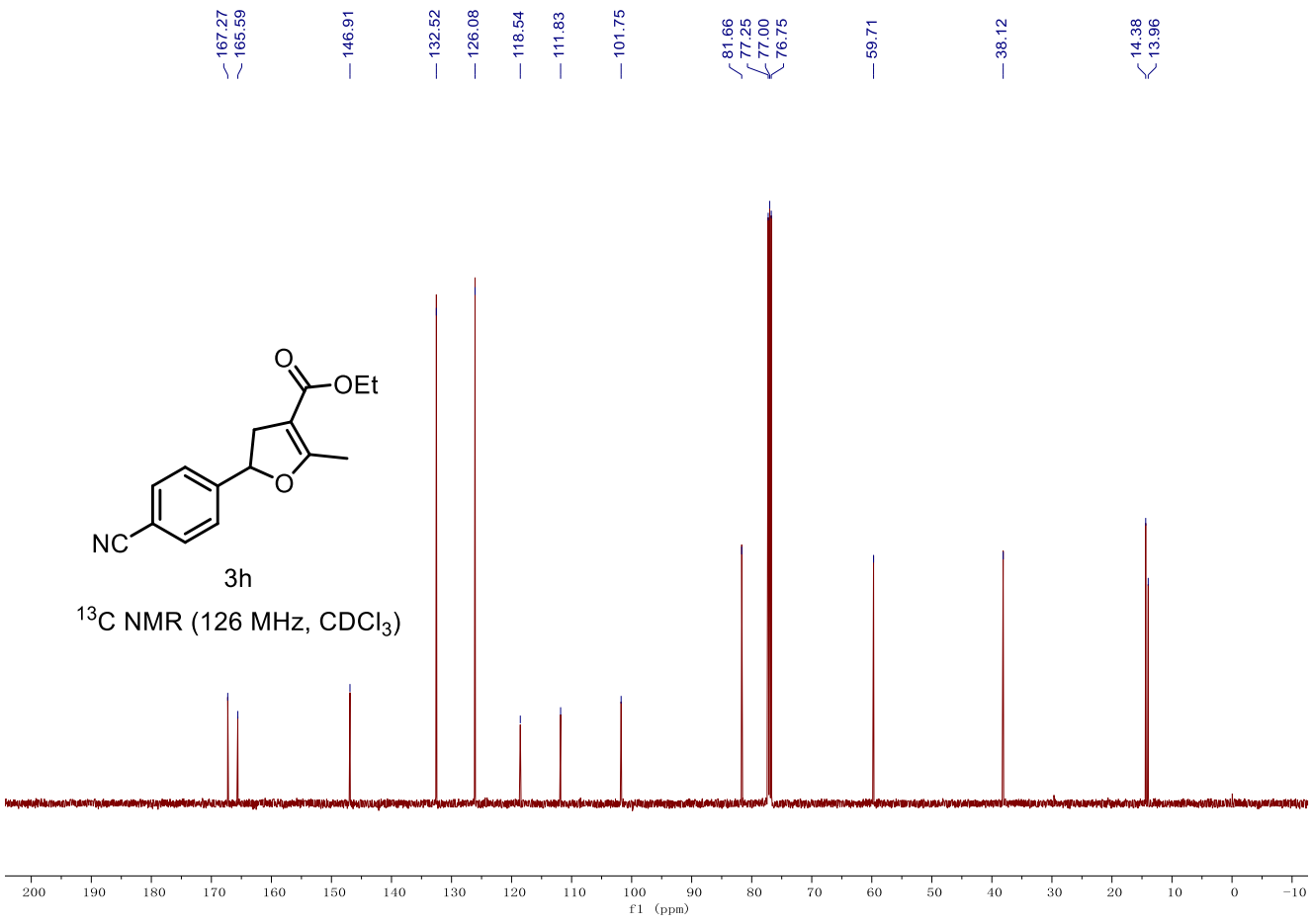
3g

^{13}C NMR (126 MHz, $CDCl_3$)



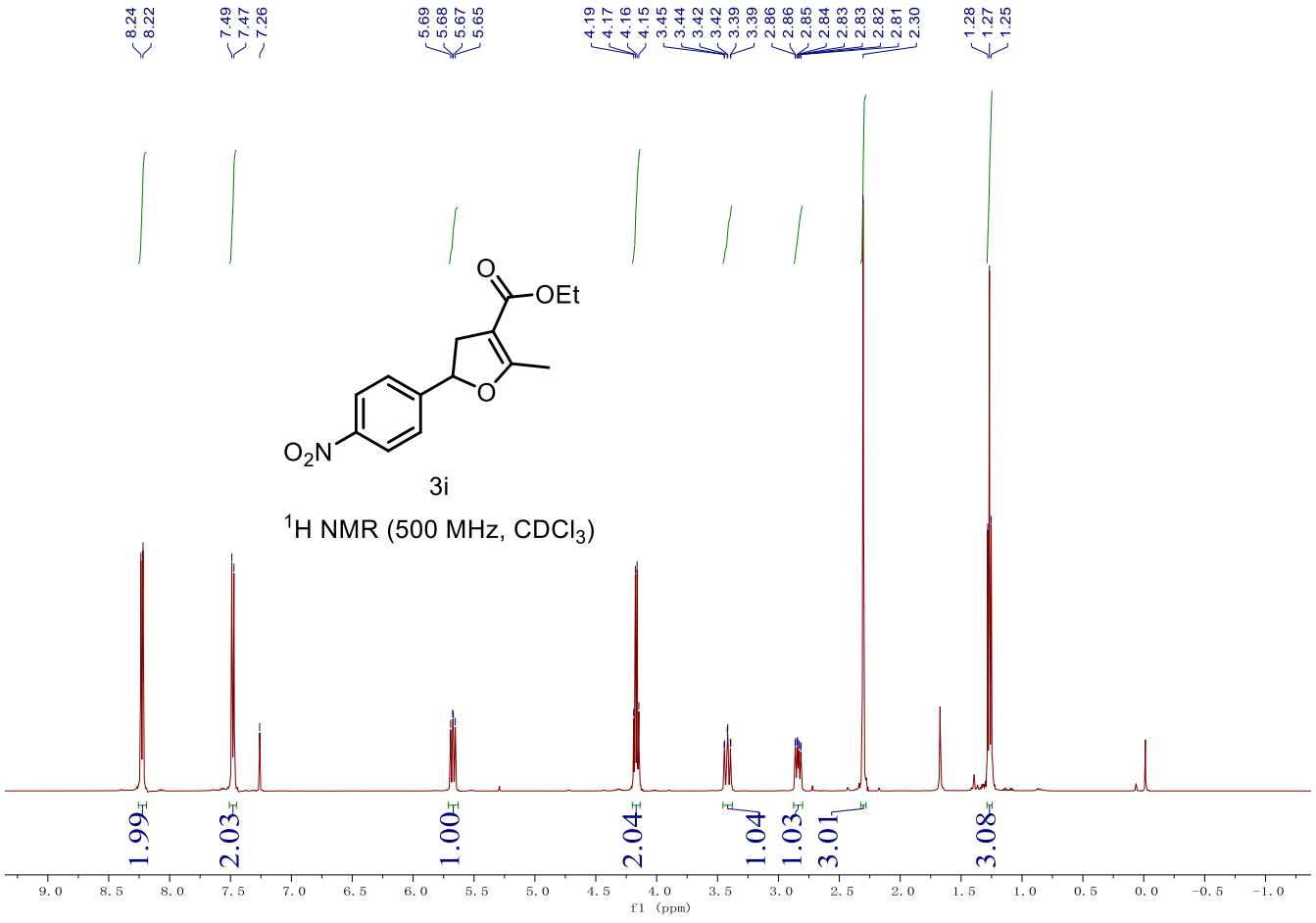
3h

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



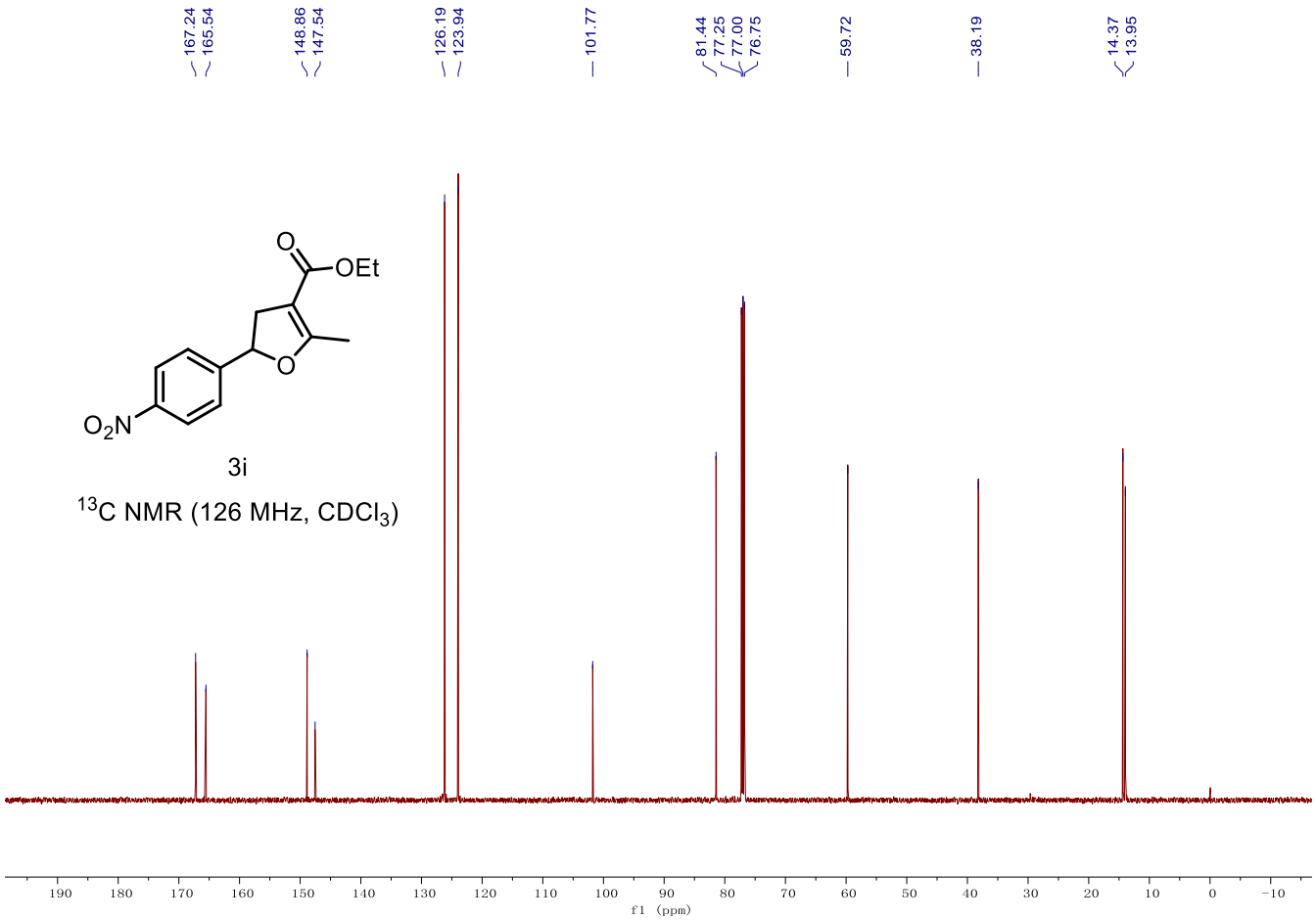
3h

^{13}C NMR (126 MHz, $CDCl_3$)



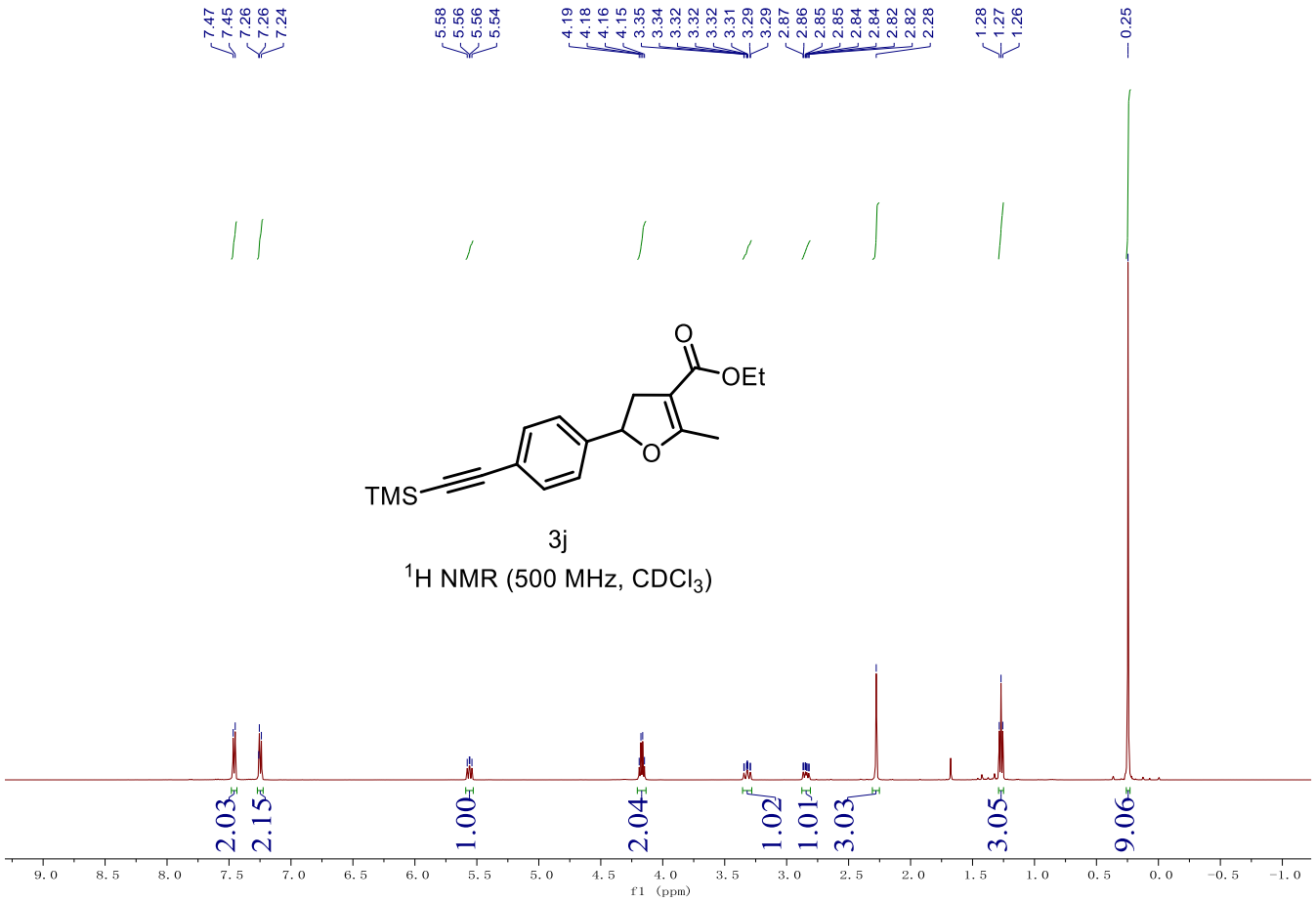
3i

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



3i

^{13}C NMR (126 MHz, $CDCl_3$)



3j

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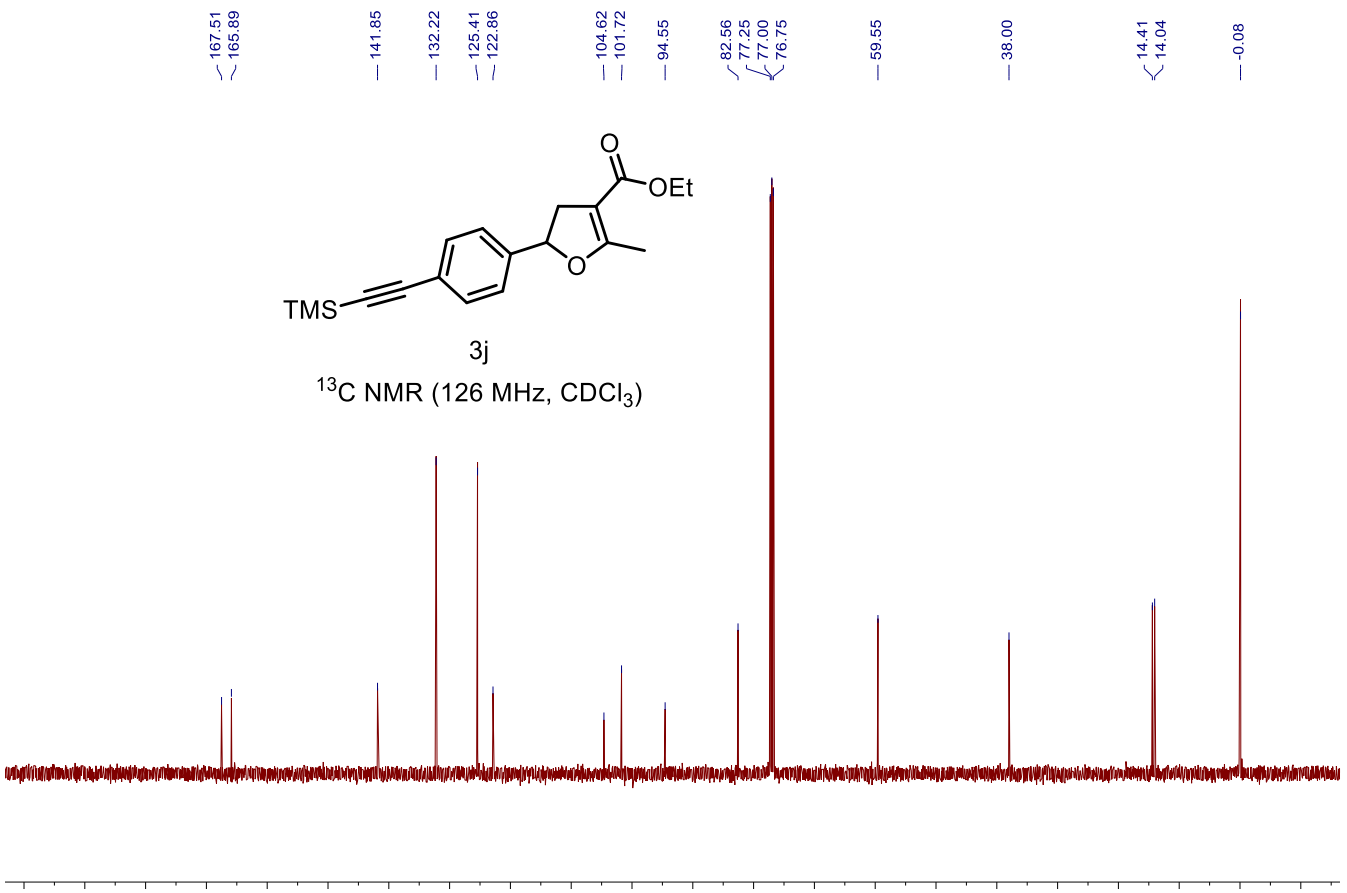
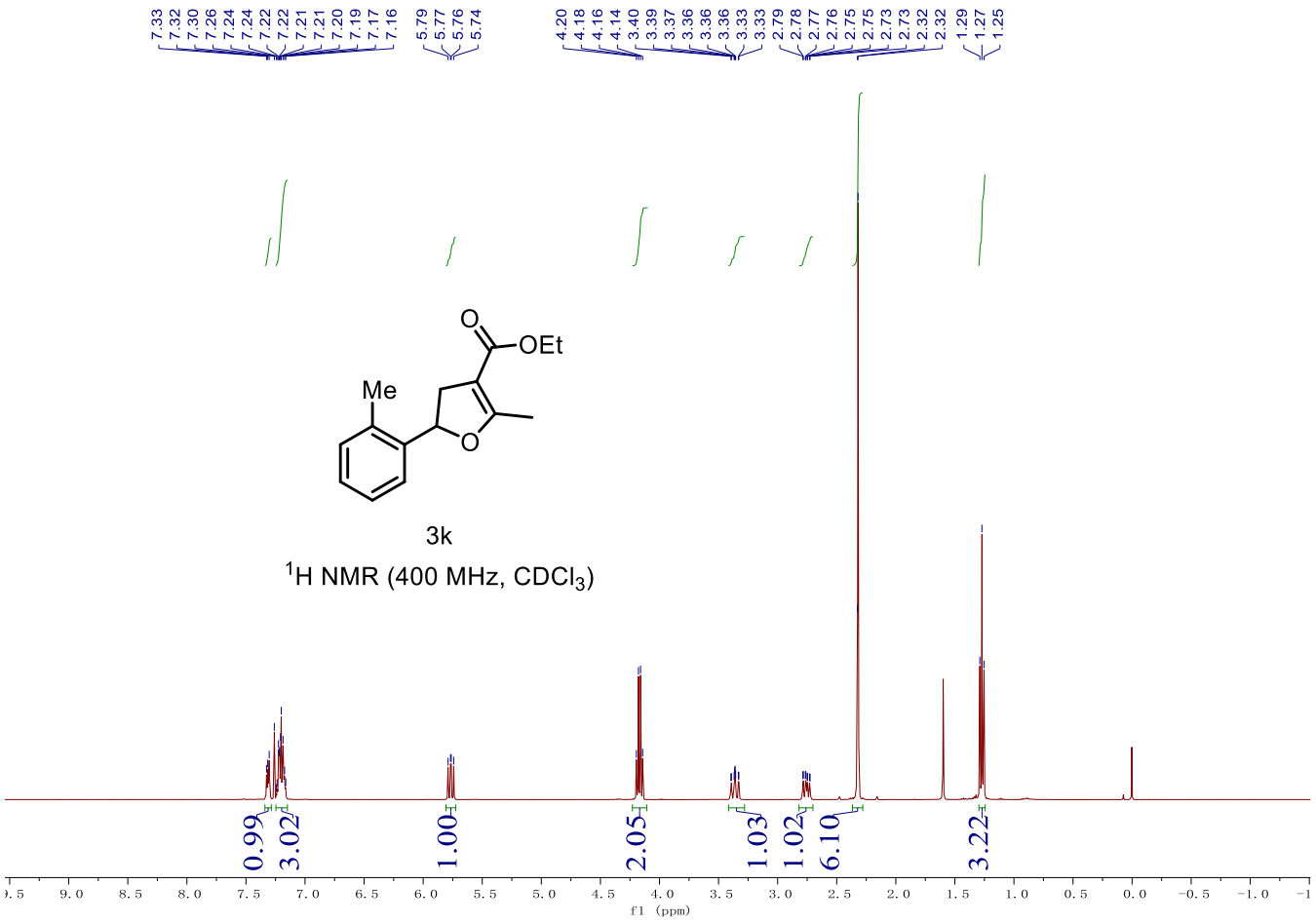


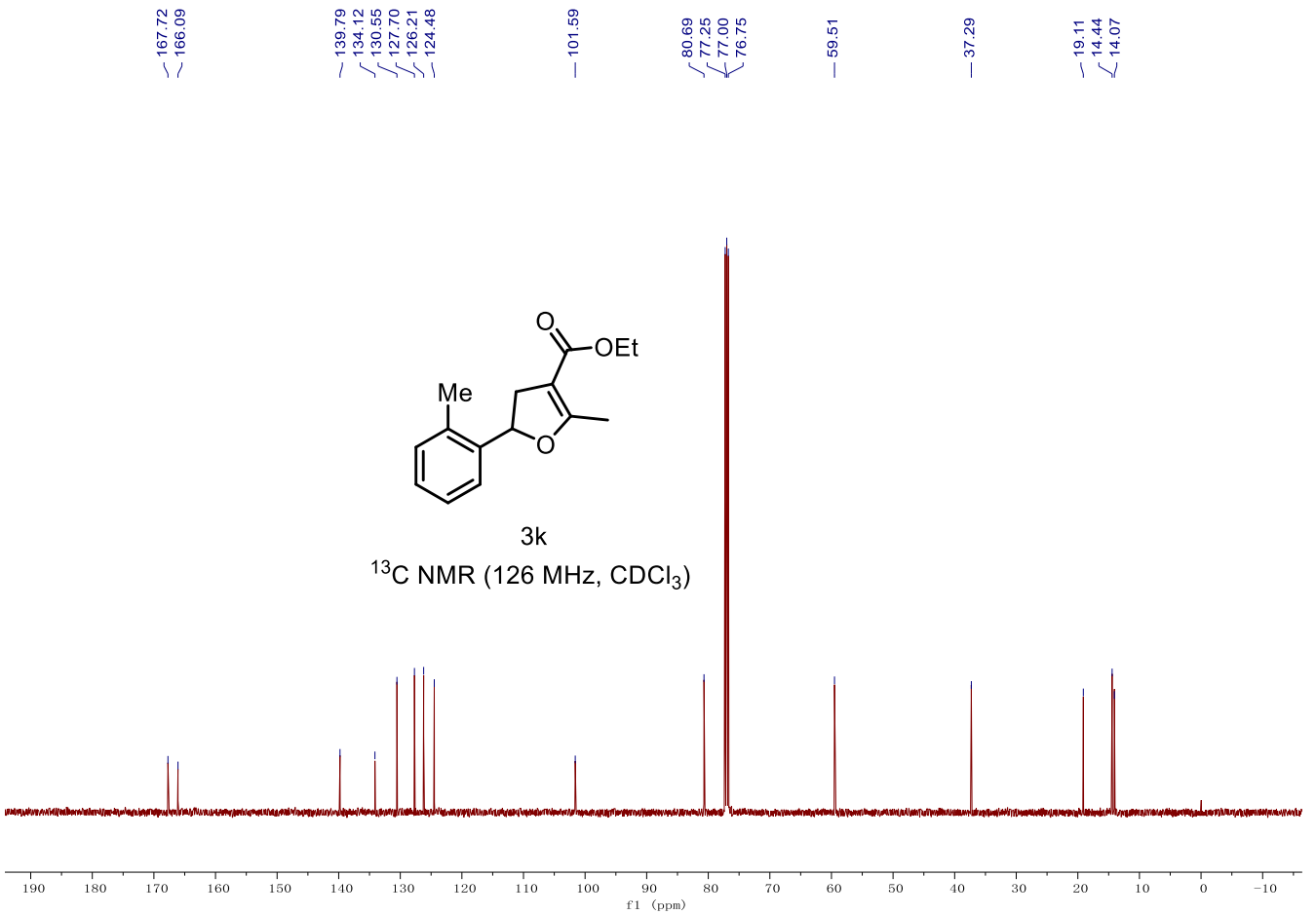
3j

^{13}C NMR (126 MHz, $CDCl_3$)



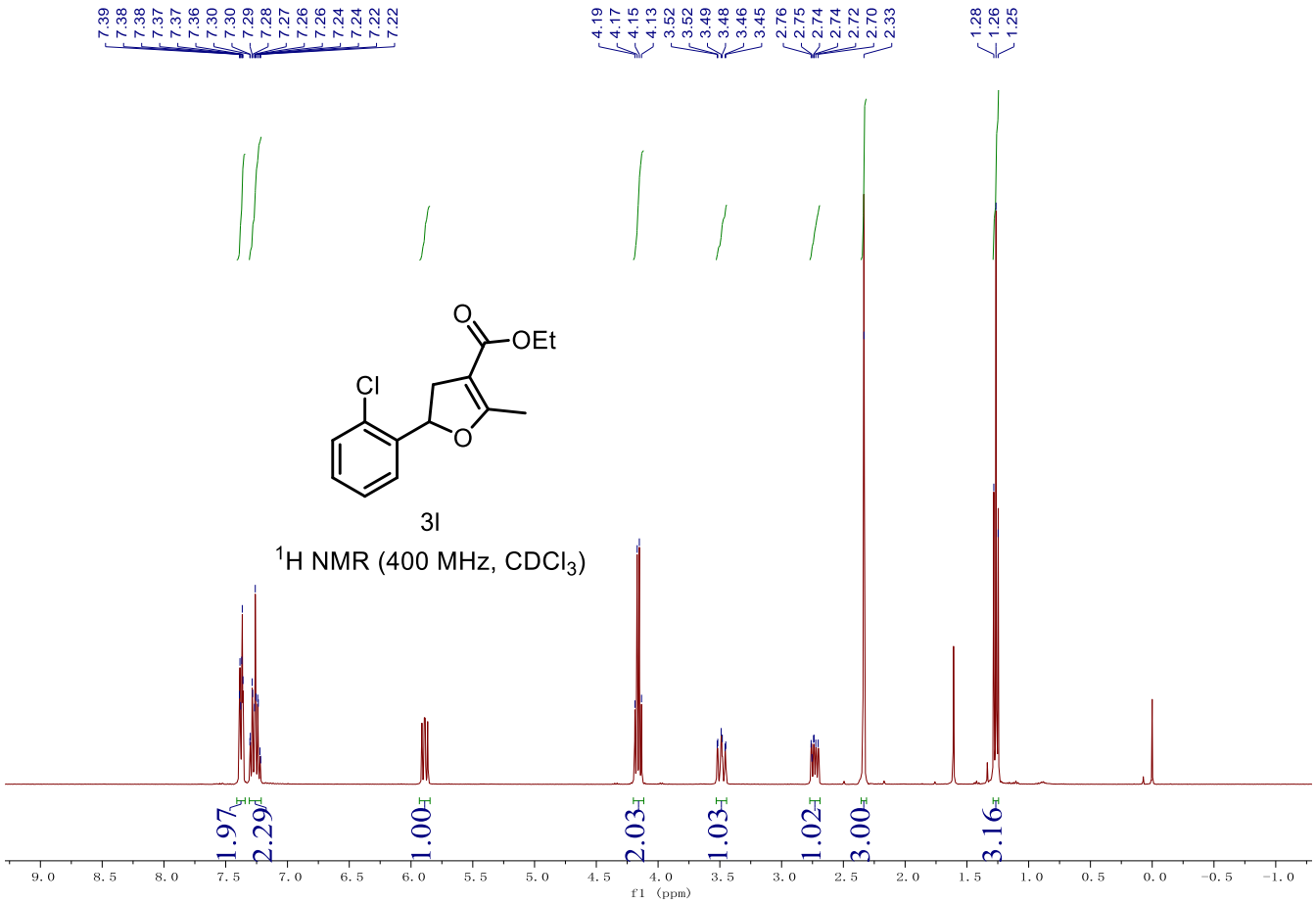
3k

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



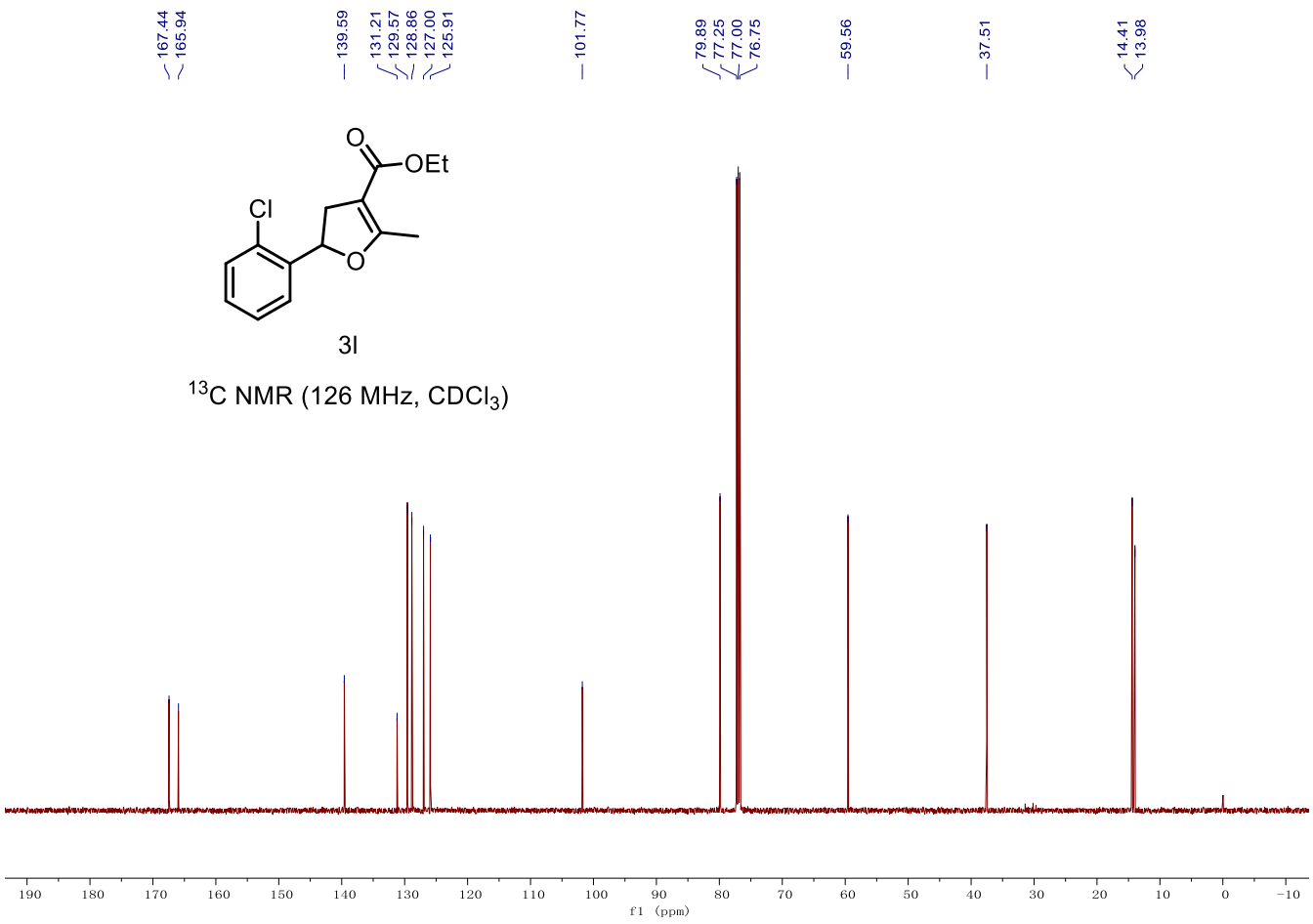
3k

^{13}C NMR (126 MHz, $CDCl_3$)



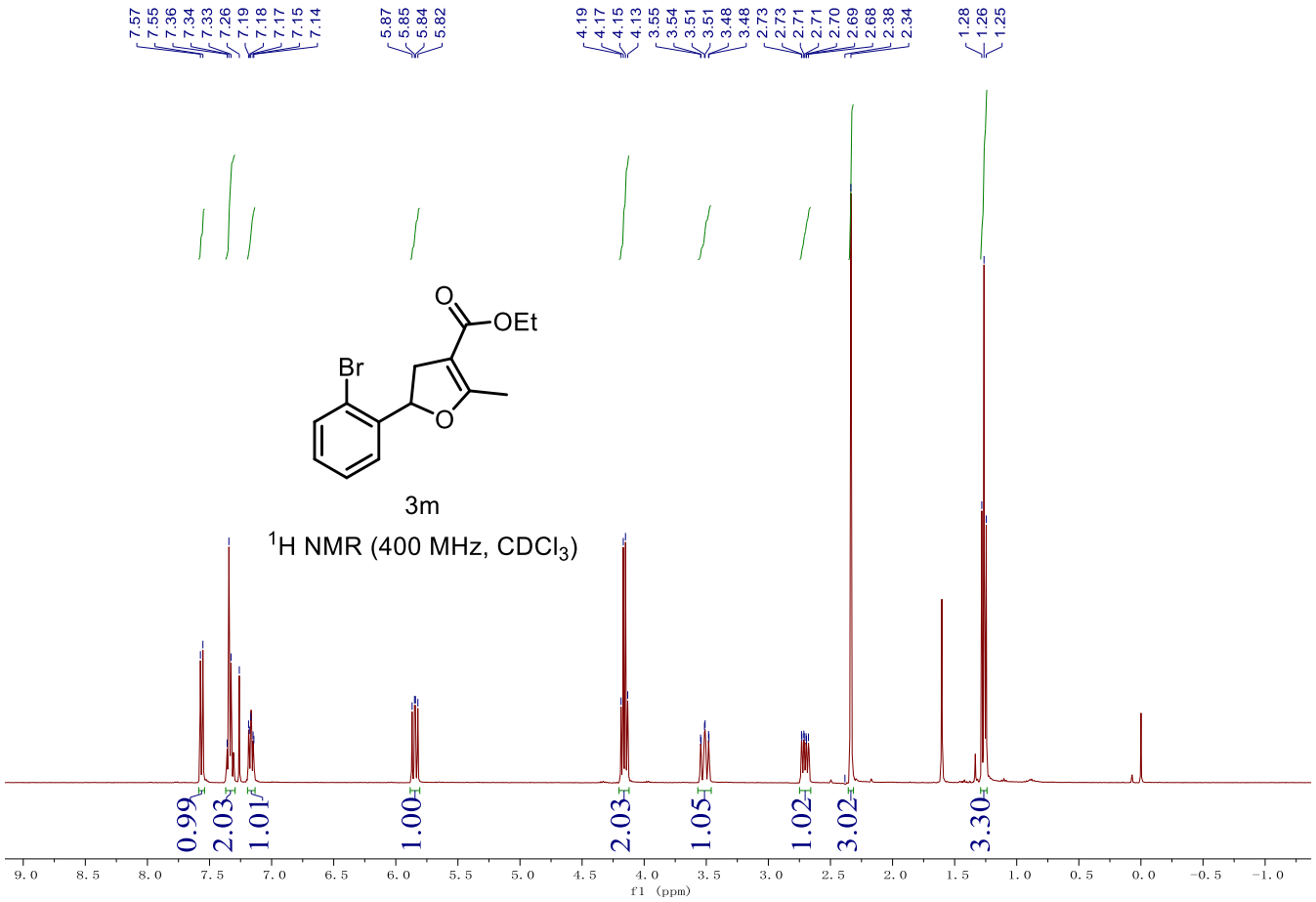
3l

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



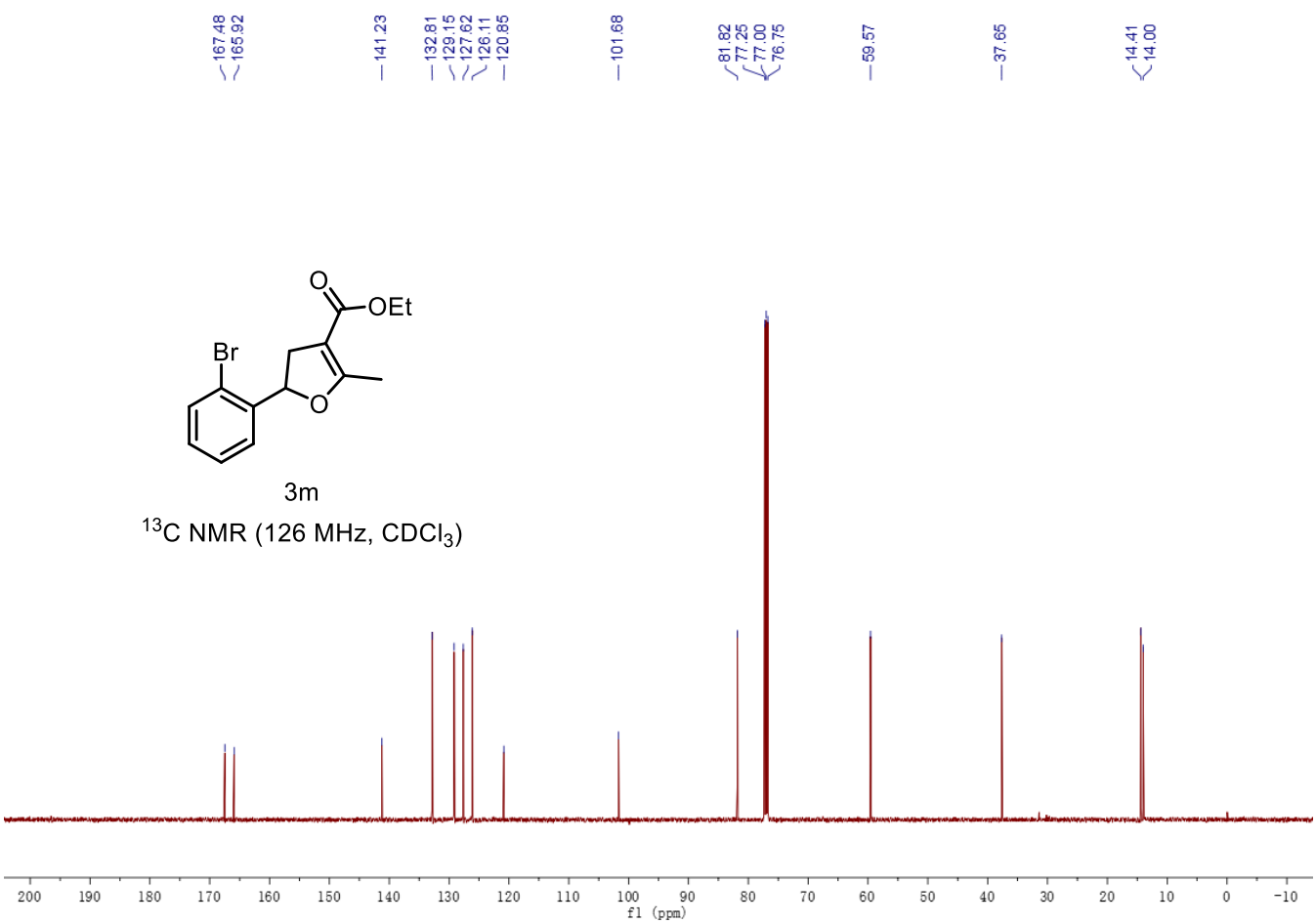
3l

^{13}C NMR (126 MHz, $CDCl_3$)



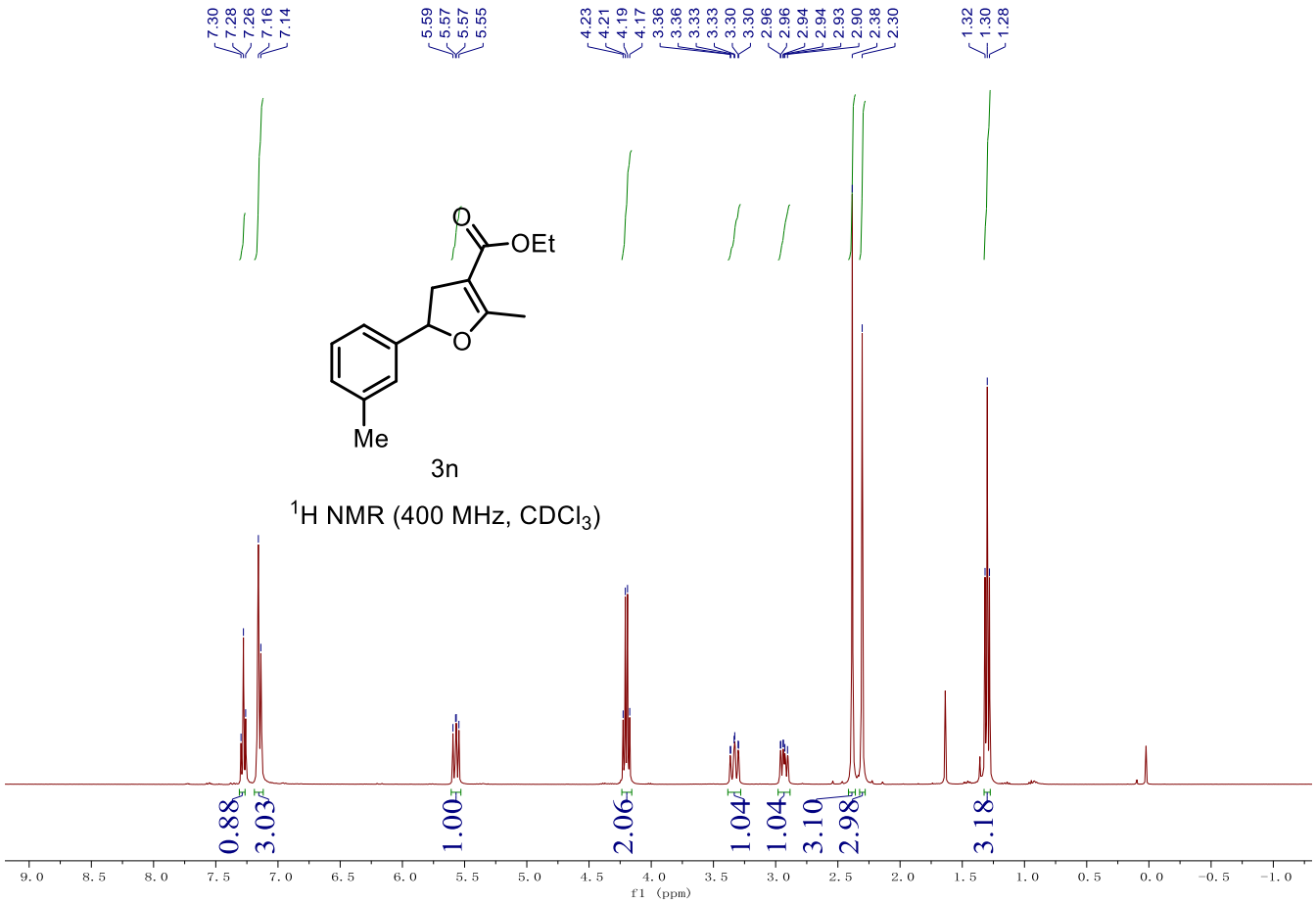
3m

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



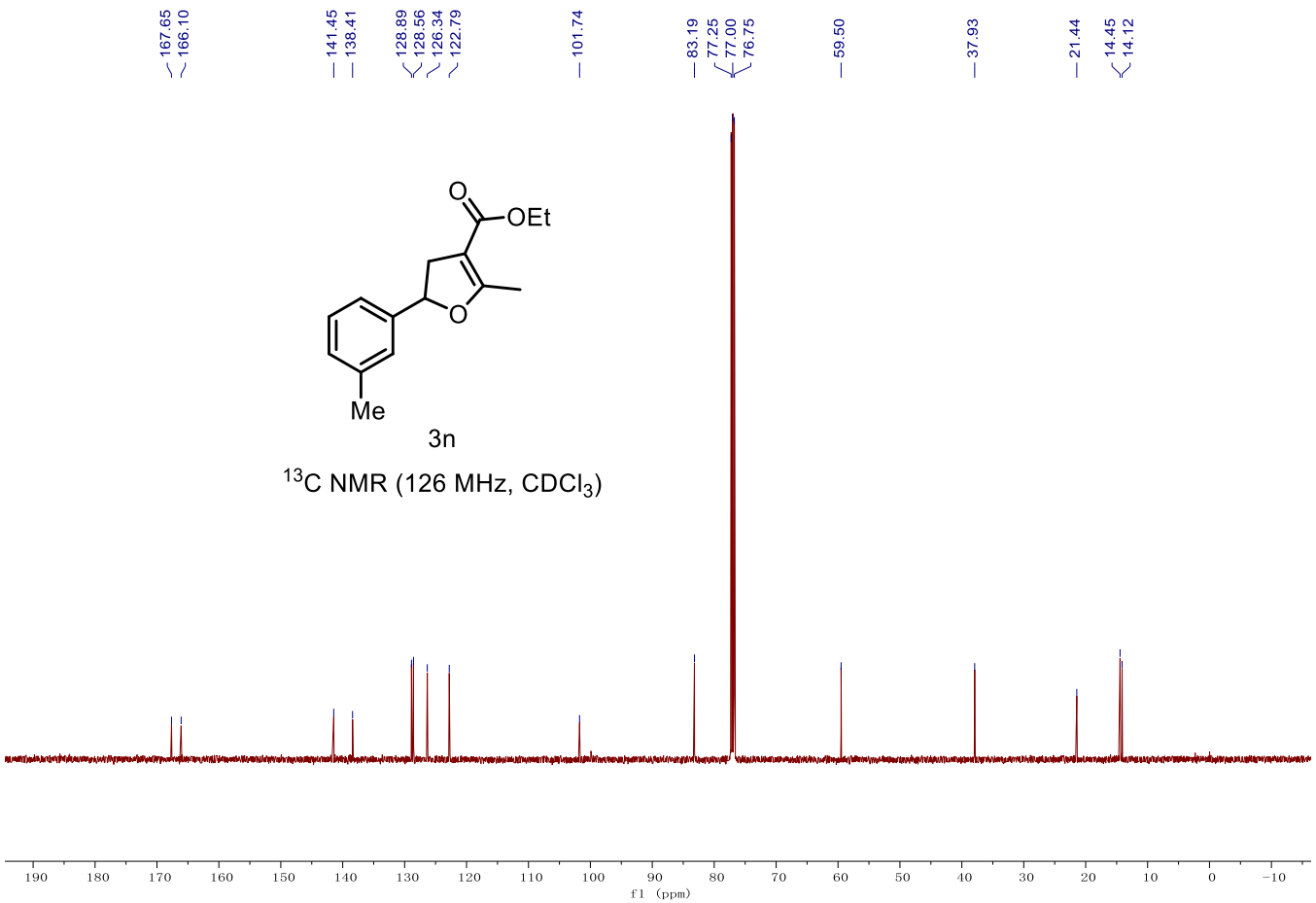
3m

^{13}C NMR (126 MHz, $CDCl_3$)



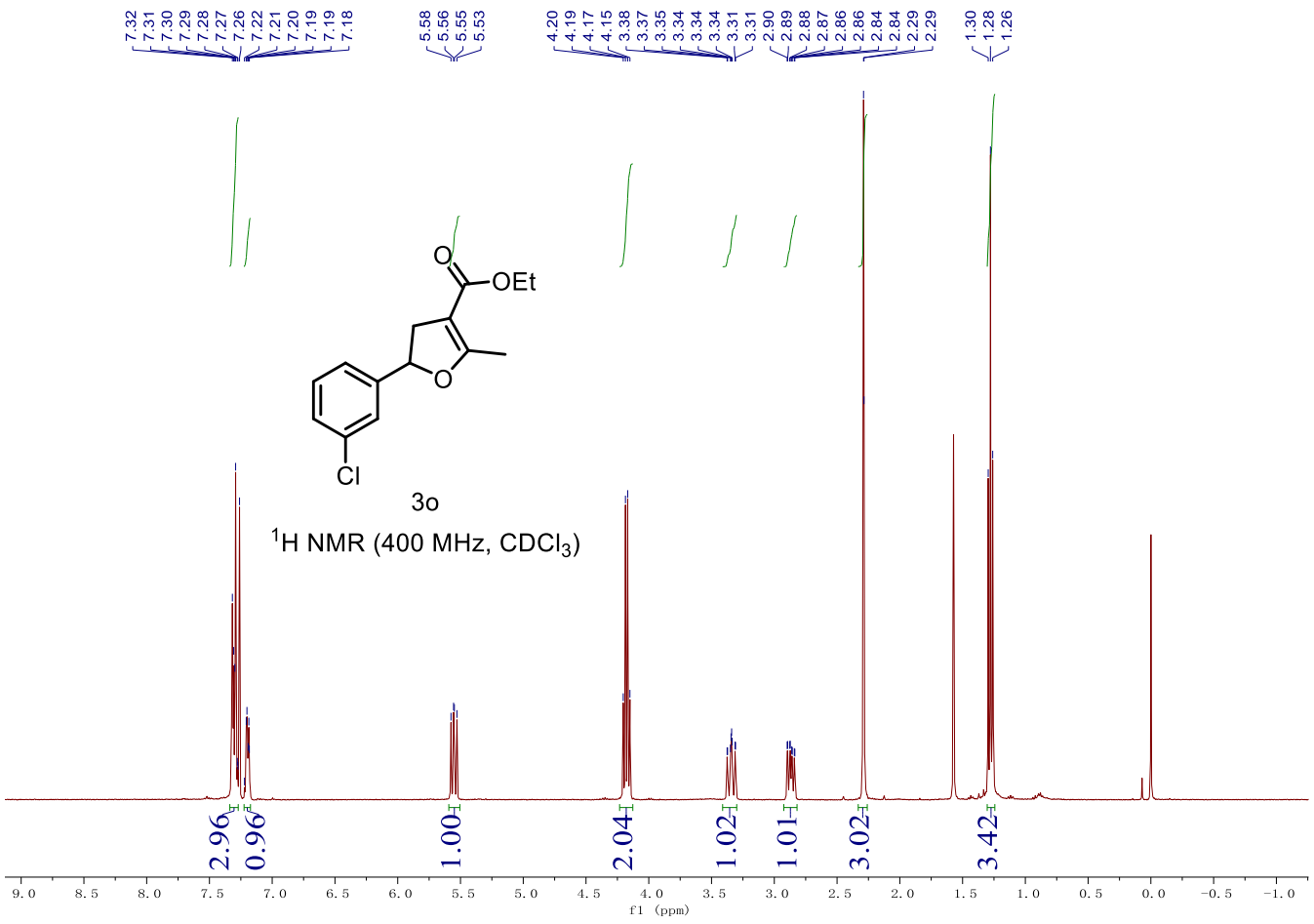
3n

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



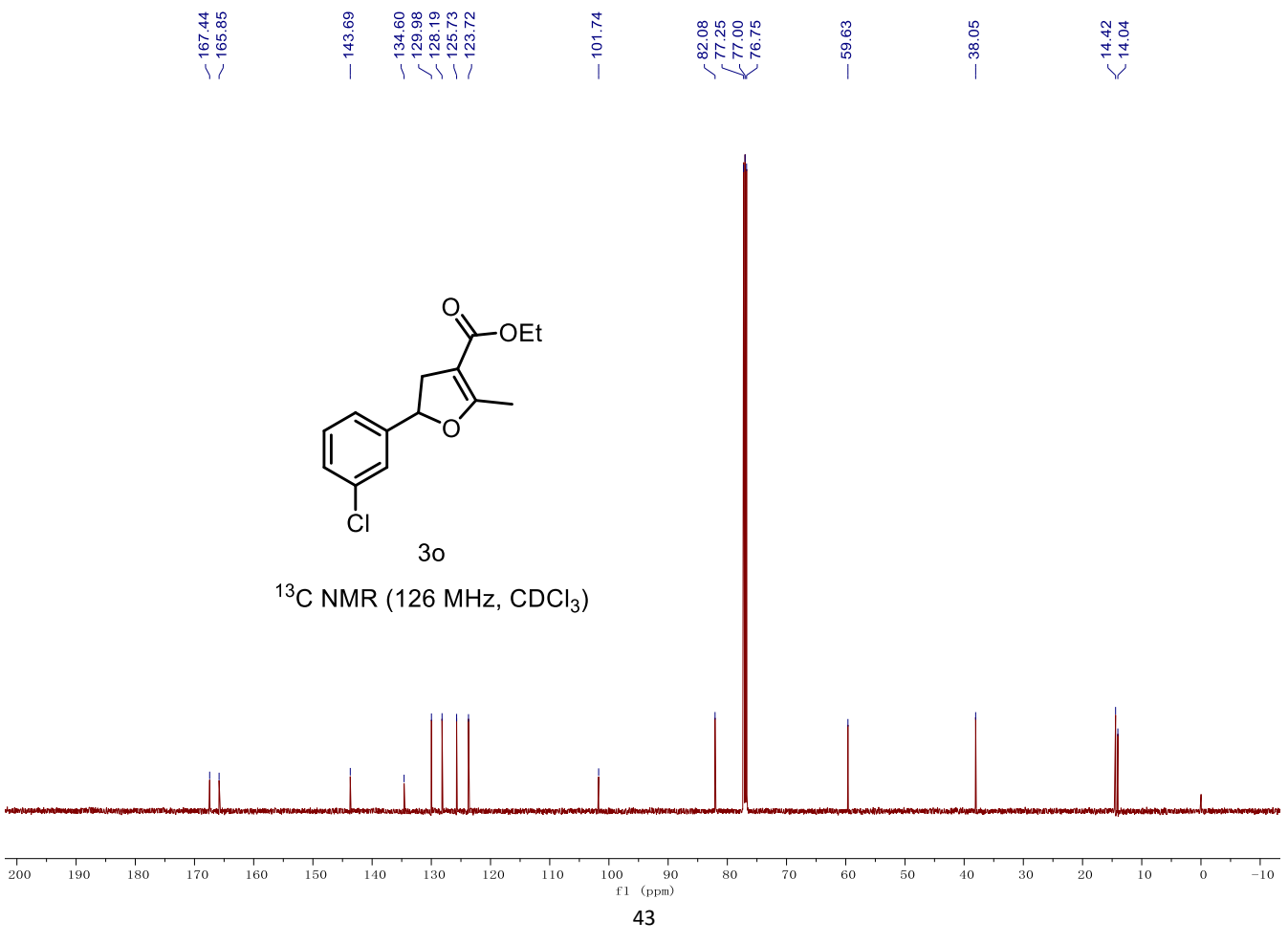
3n

^{13}C NMR (126 MHz, $CDCl_3$)



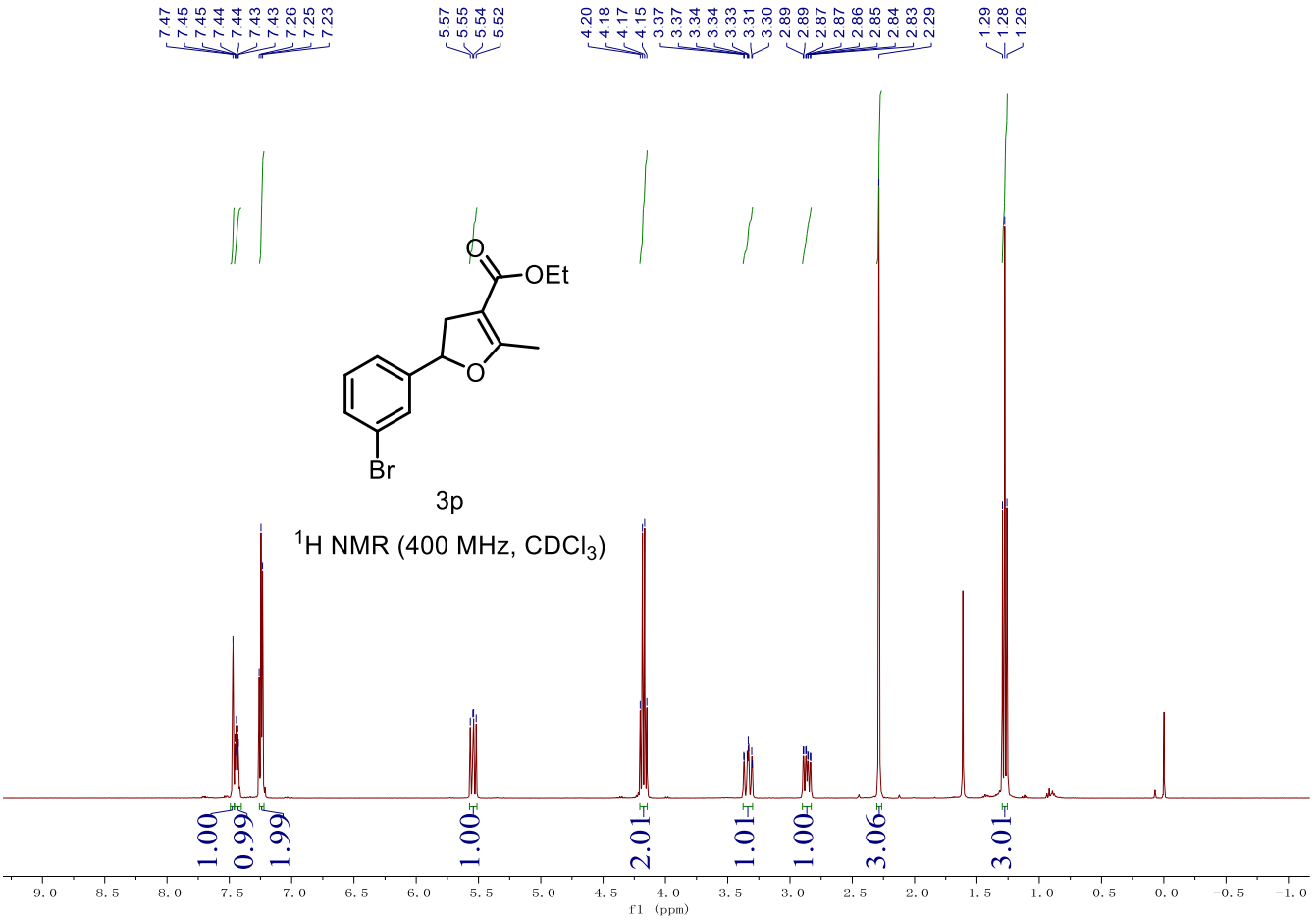
3o

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



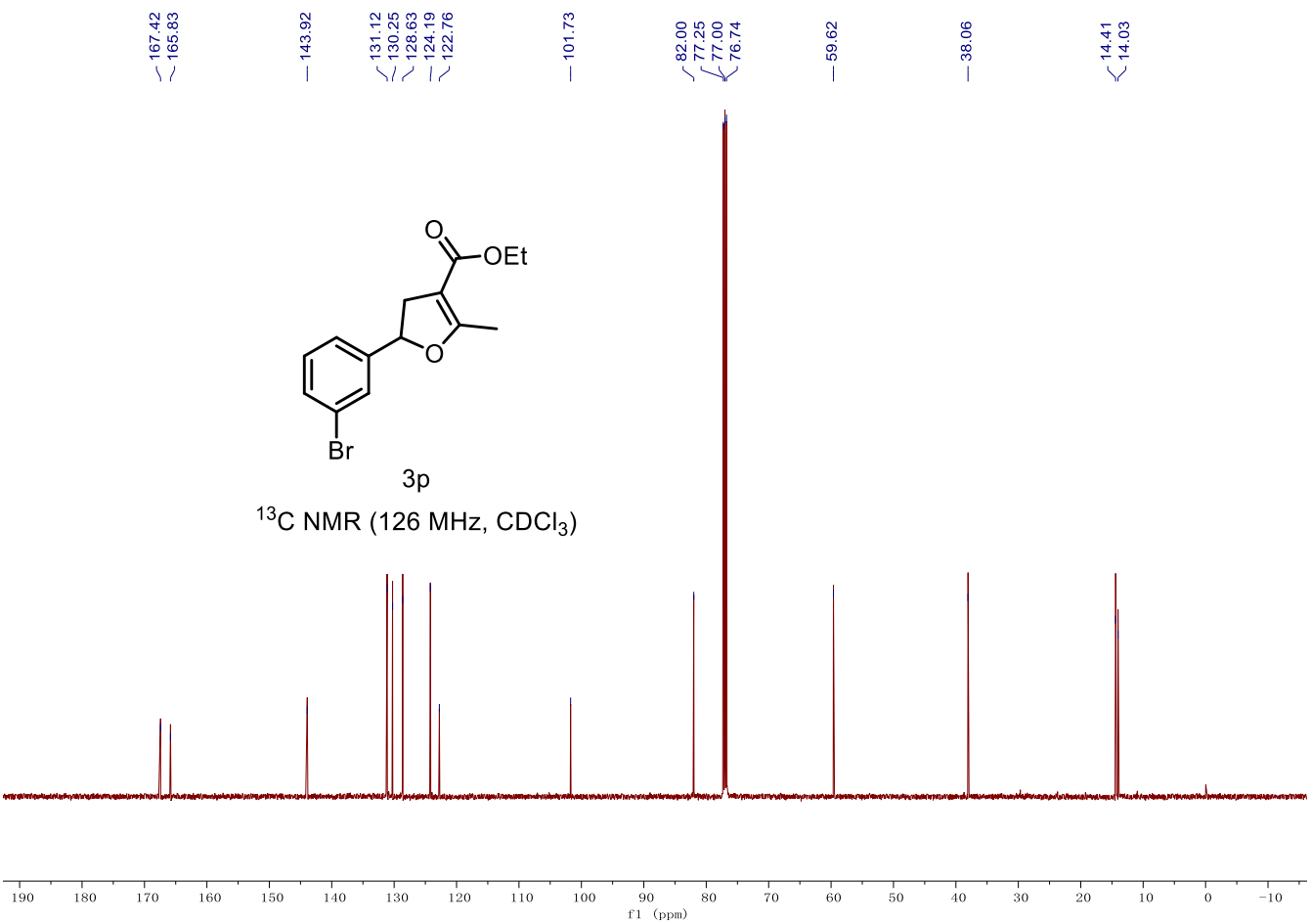
3o

^{13}C NMR (126 MHz, $CDCl_3$)



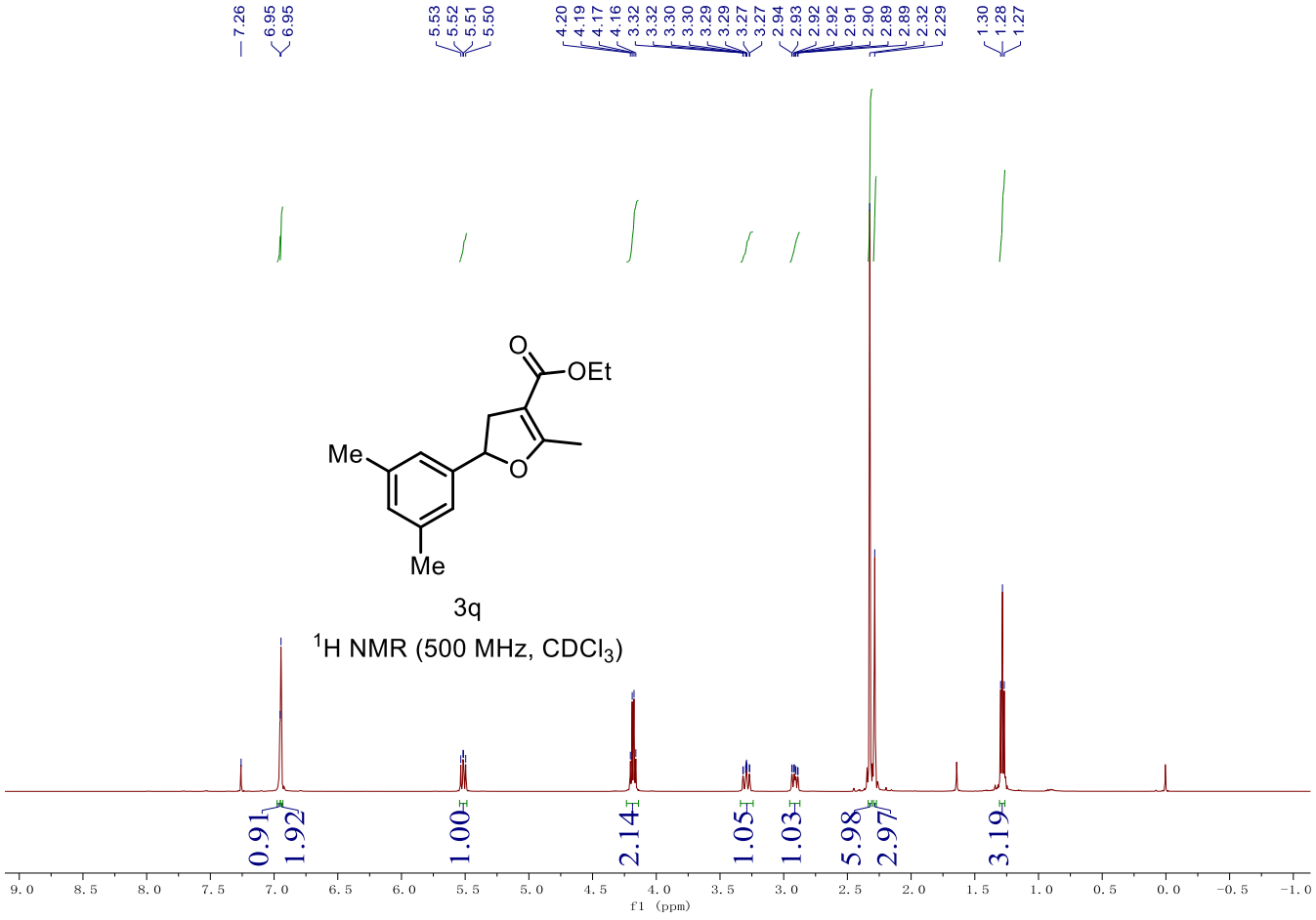
3p

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



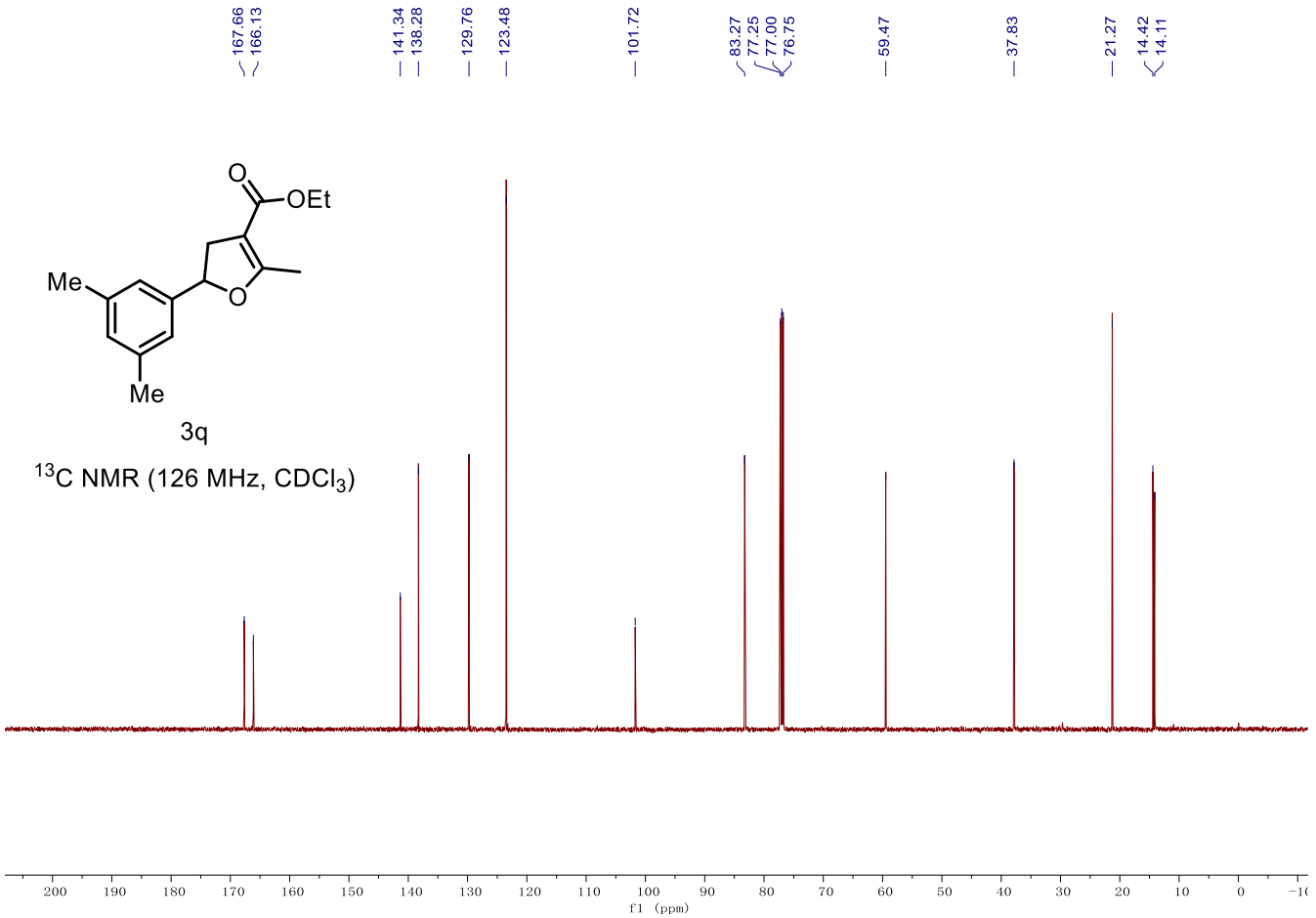
3p

^{13}C NMR (126 MHz, $CDCl_3$)



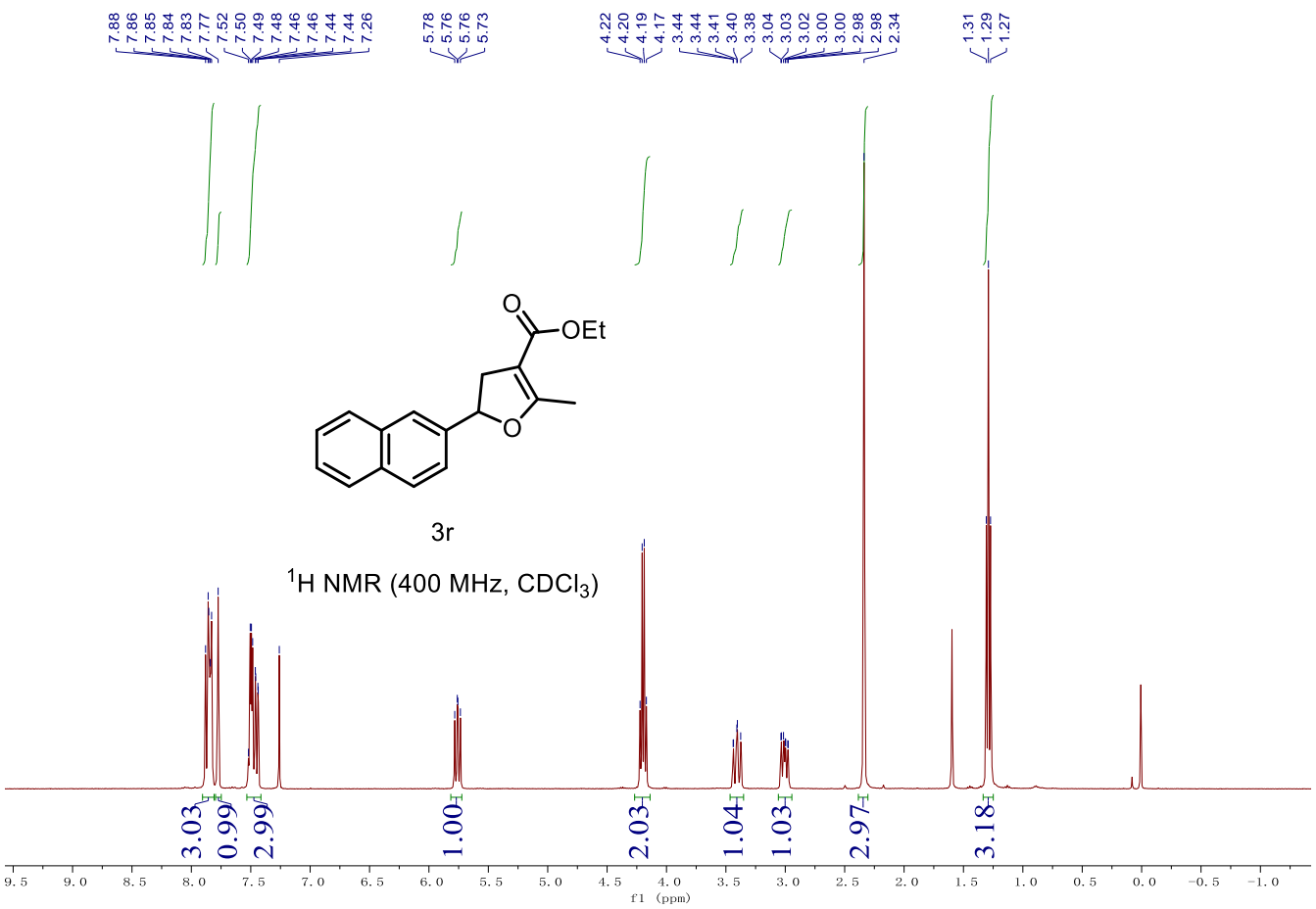
3q

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



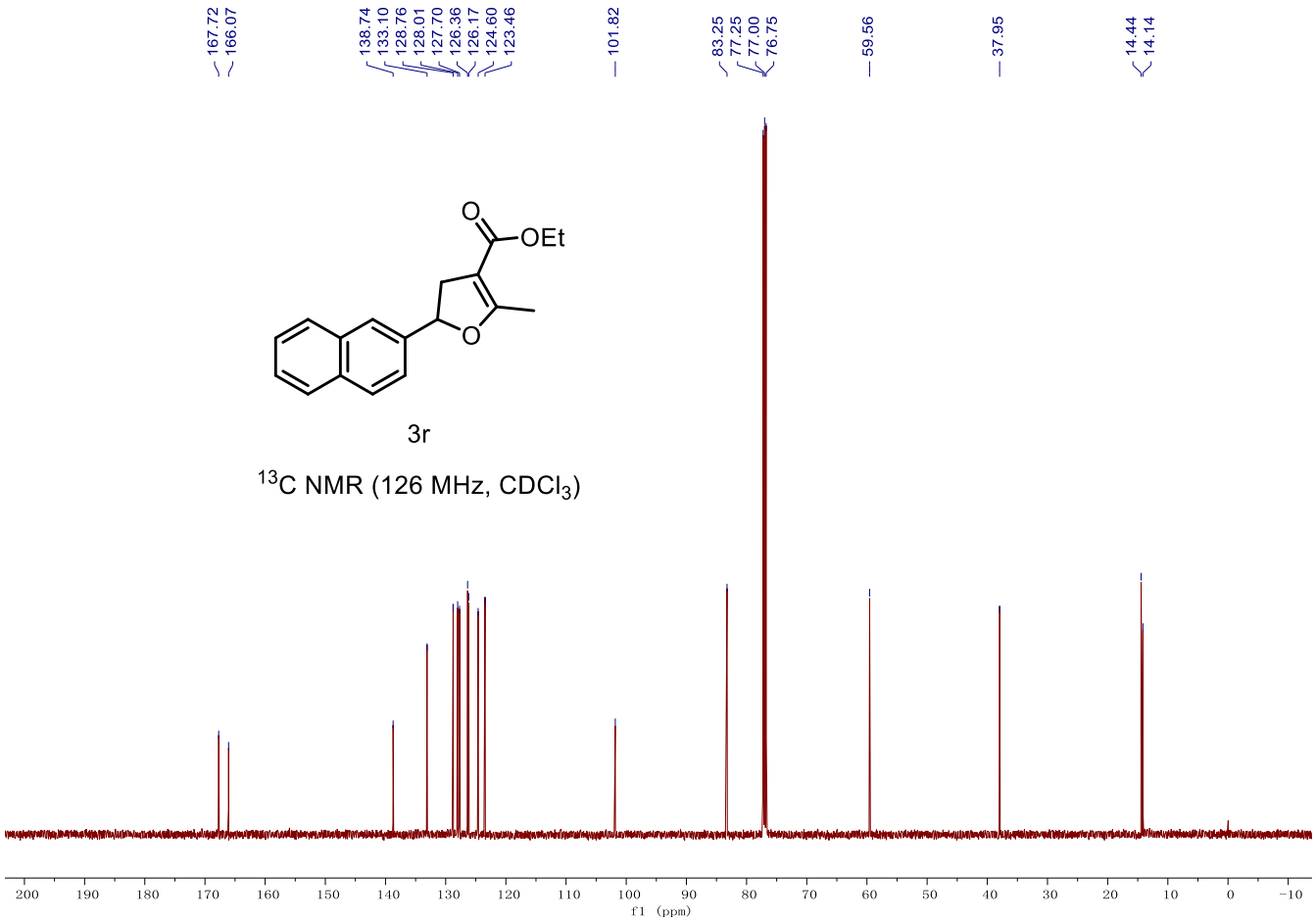
3q

^{13}C NMR (126 MHz, $CDCl_3$)



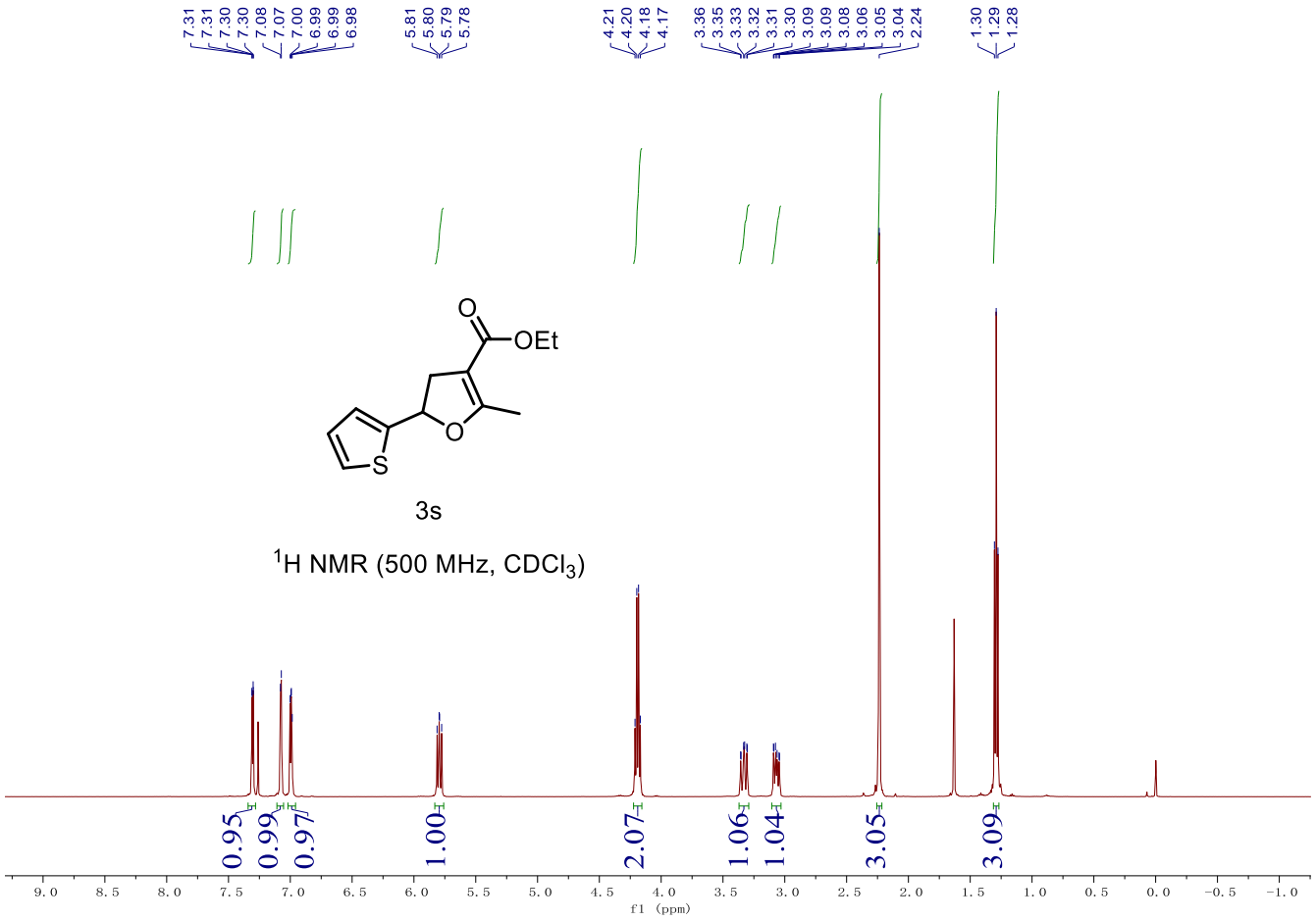
3r

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



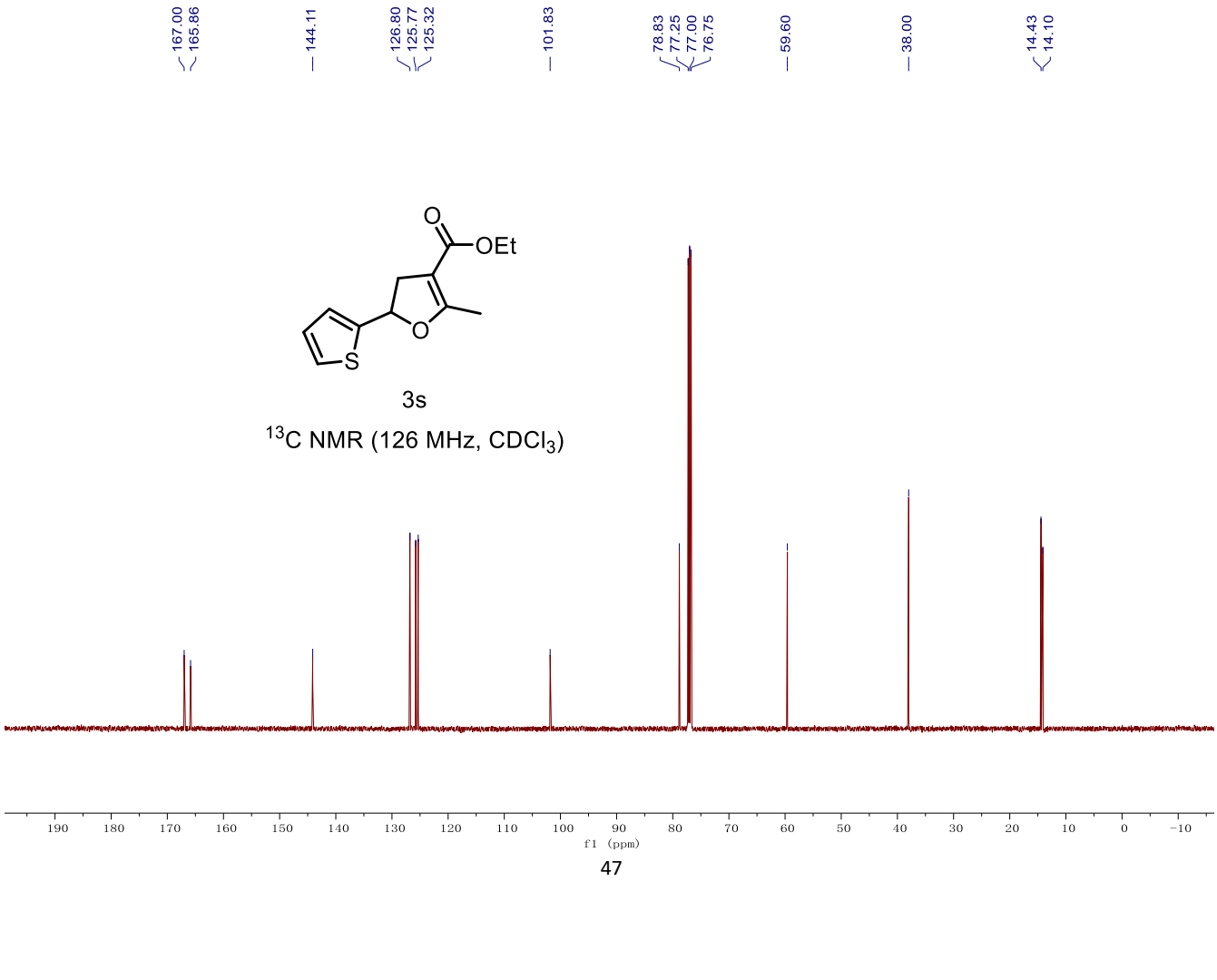
3r

^{13}C NMR (126 MHz, $CDCl_3$)



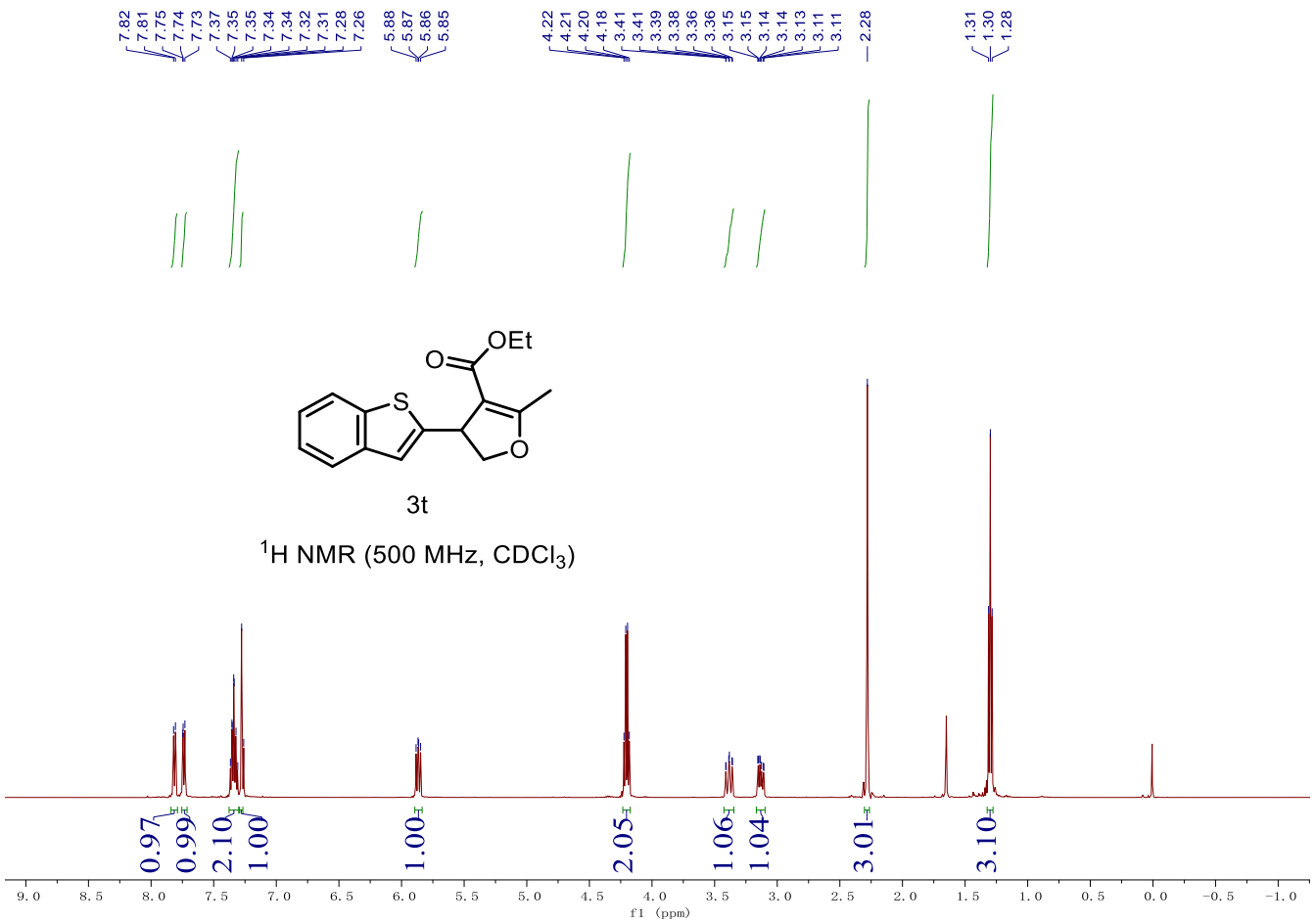
3s

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



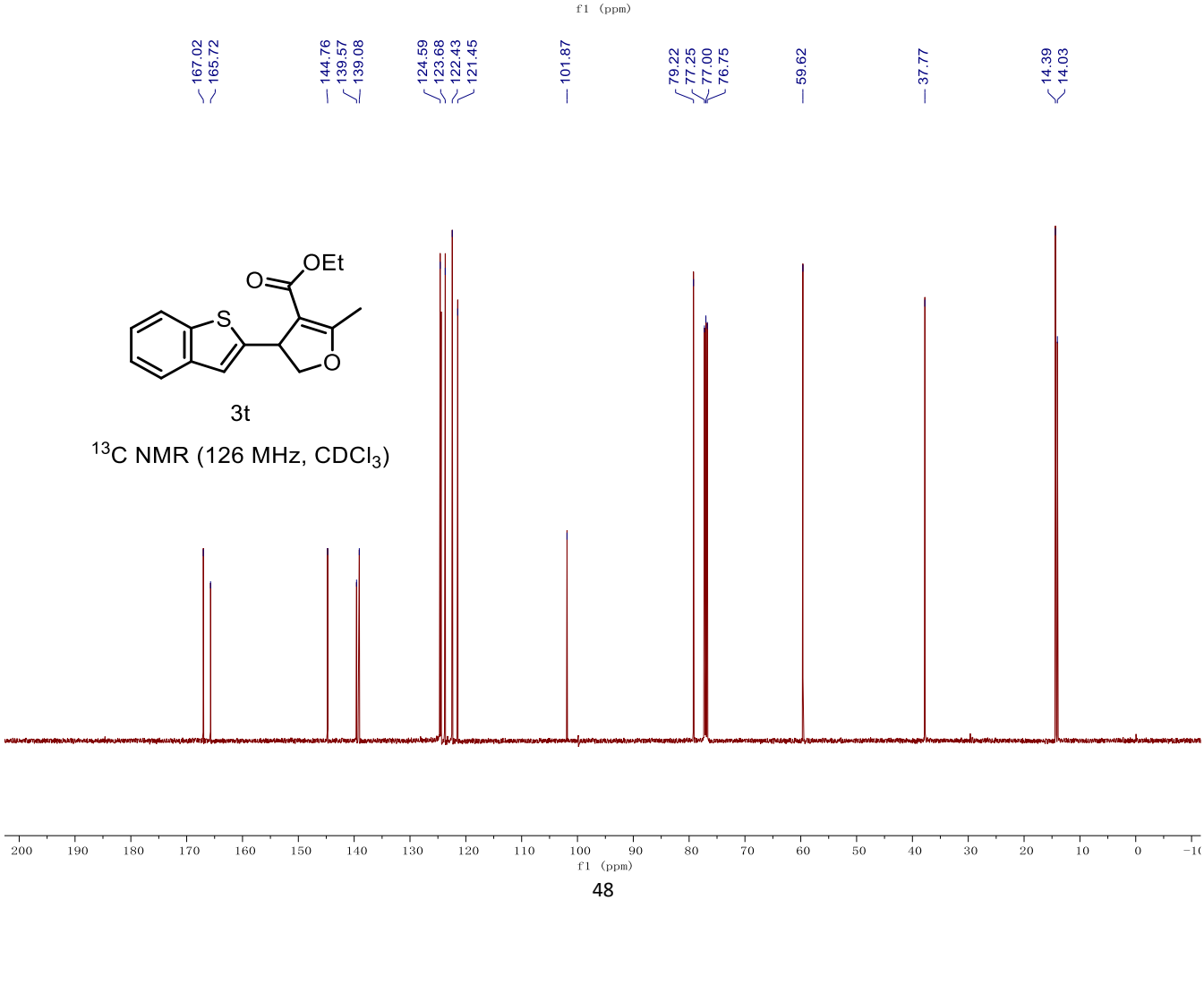
3s

^{13}C NMR (126 MHz, $CDCl_3$)



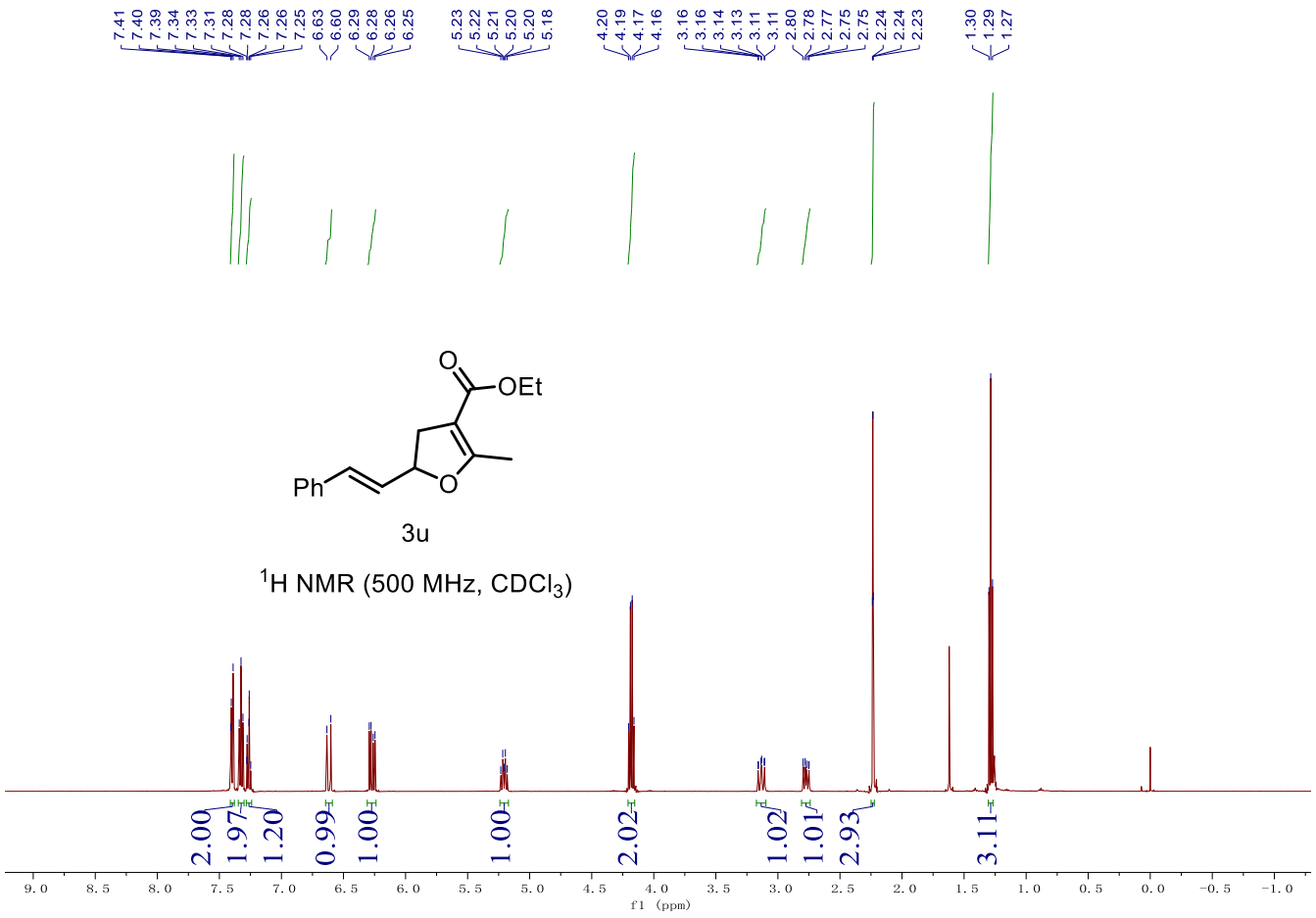
3t

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



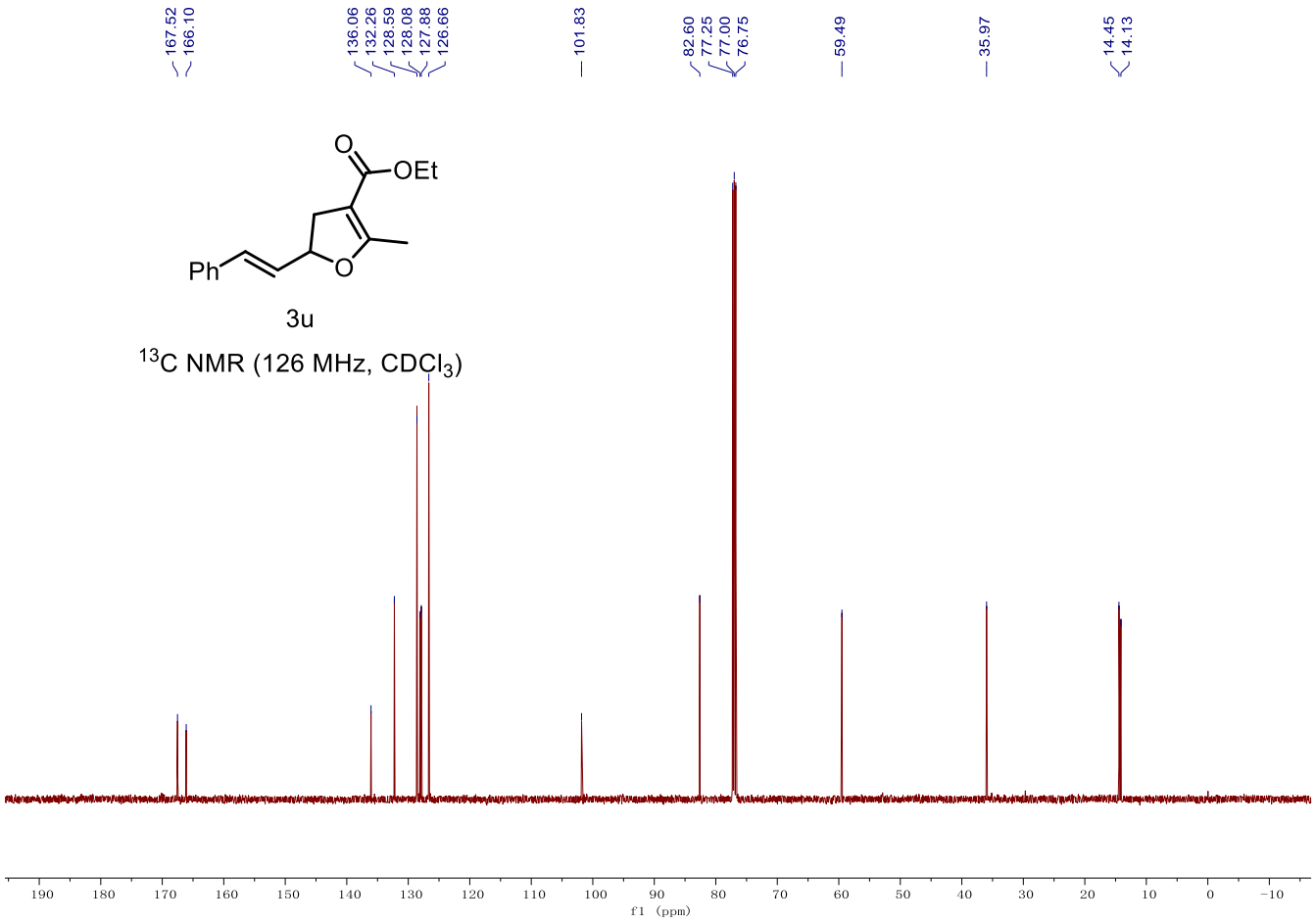
3t

^{13}C NMR (126 MHz, $CDCl_3$)



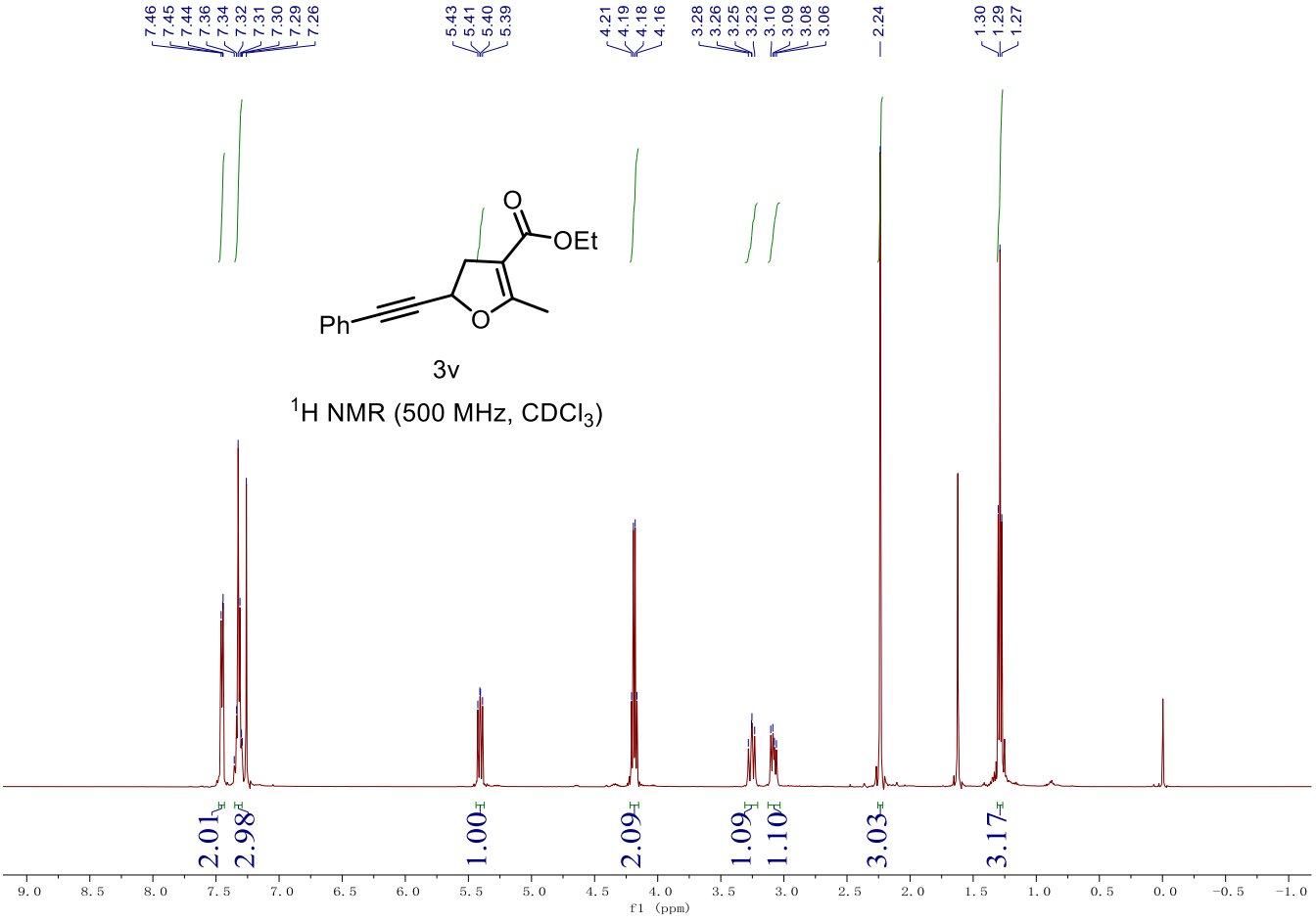
3u

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



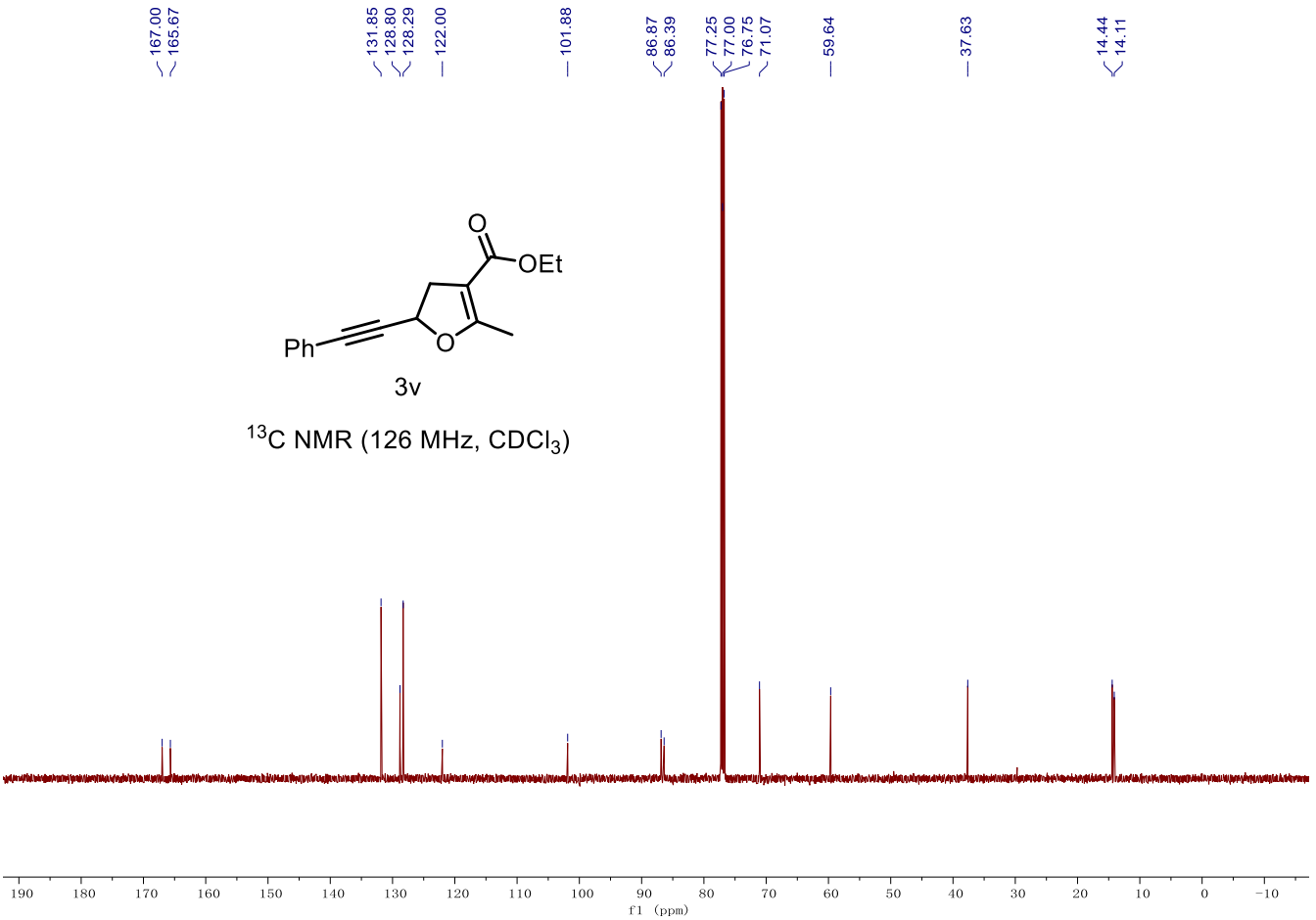
3u

^{13}C NMR (126 MHz, $CDCl_3$)



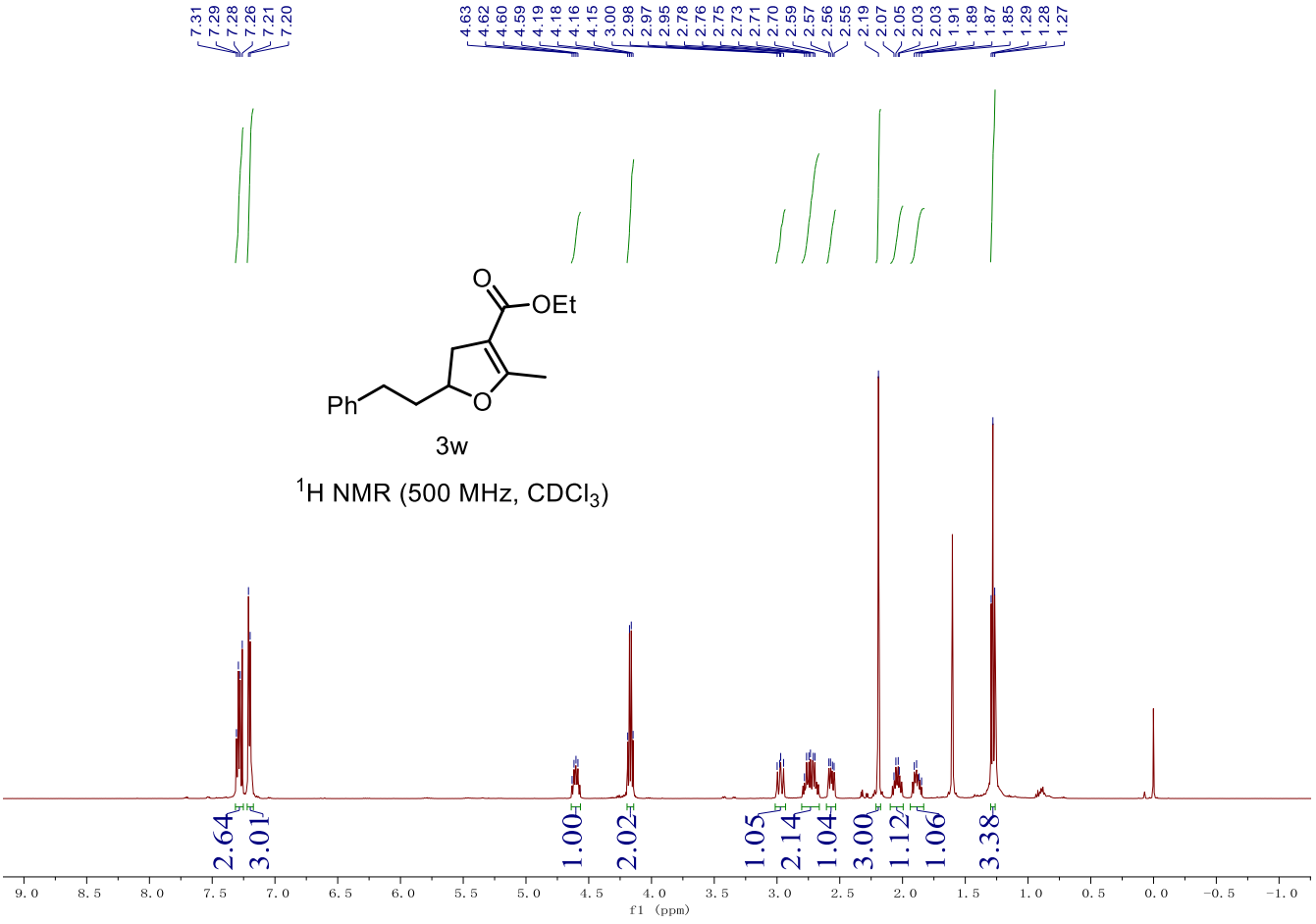
3v

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



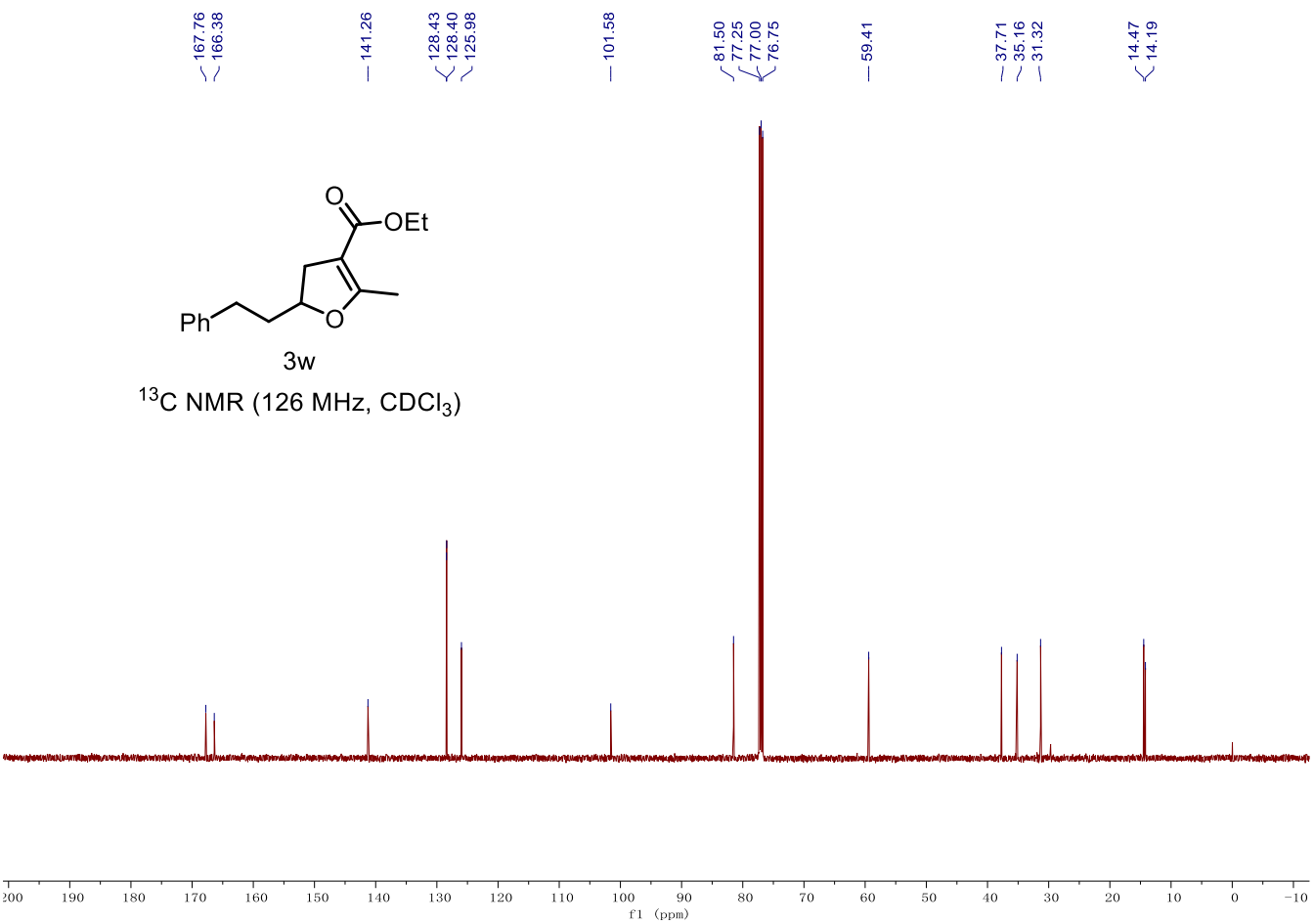
3v

^{13}C NMR (126 MHz, $CDCl_3$)



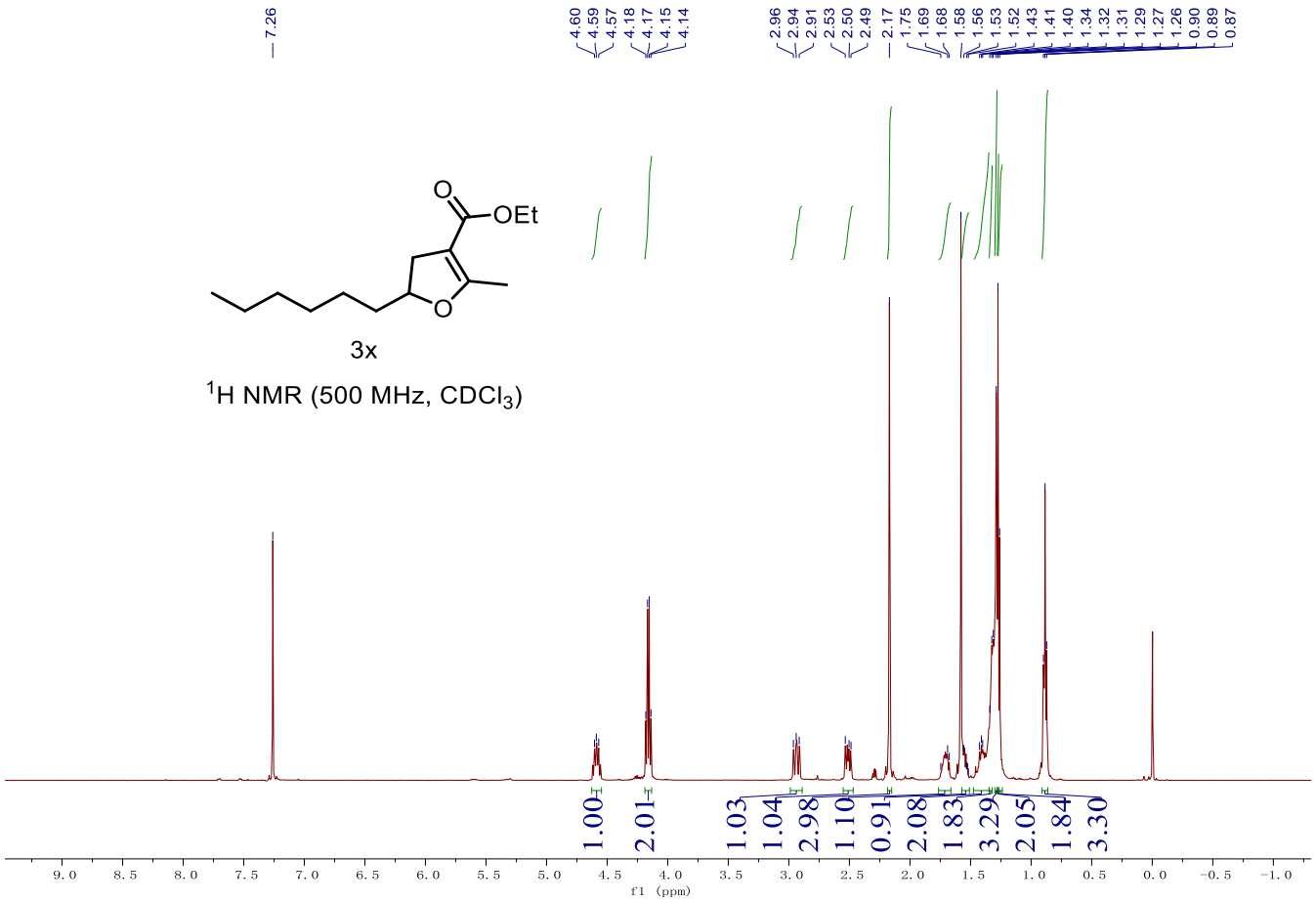
3w

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



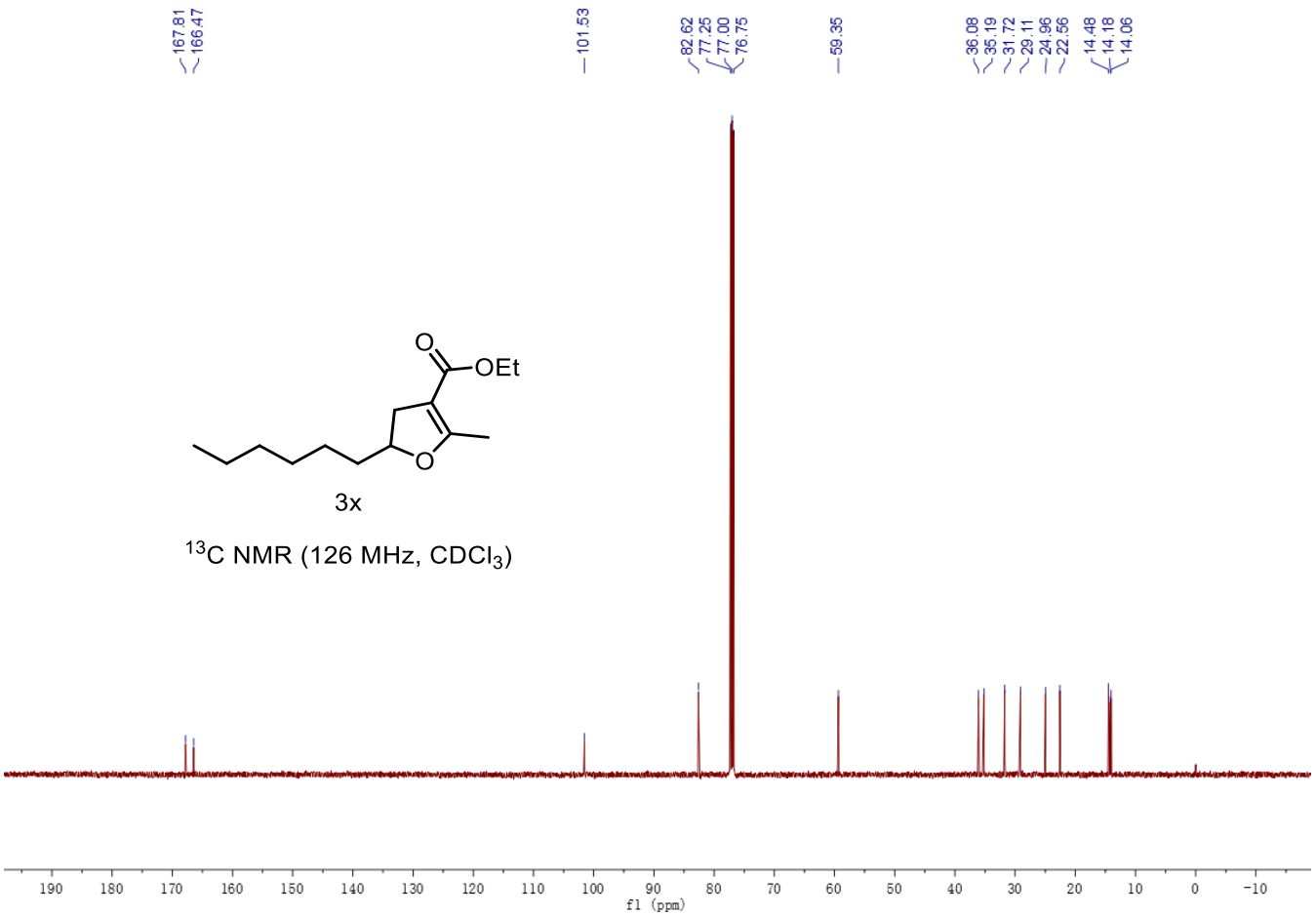
3w

^{13}C NMR (126 MHz, $CDCl_3$)



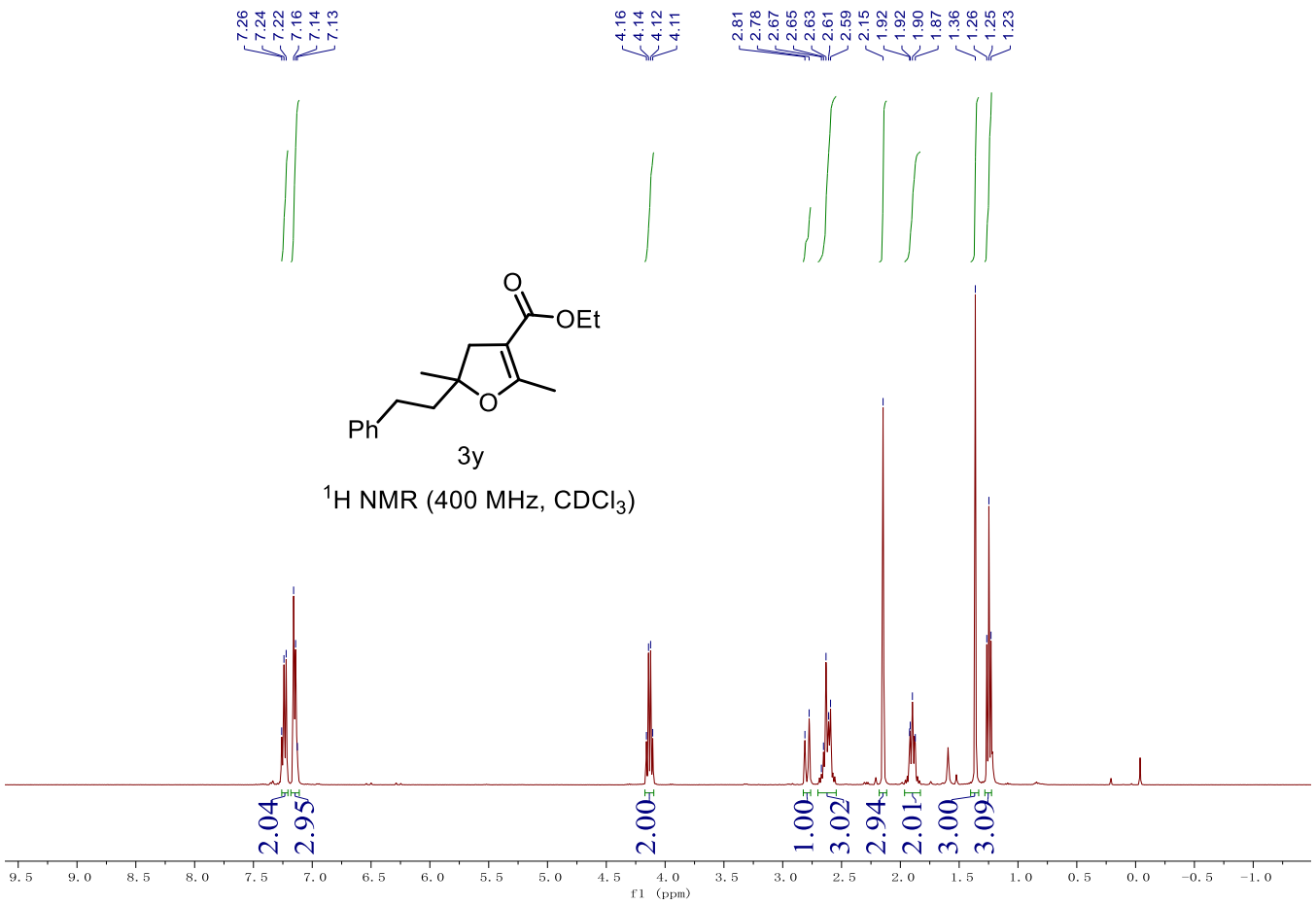
3x

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



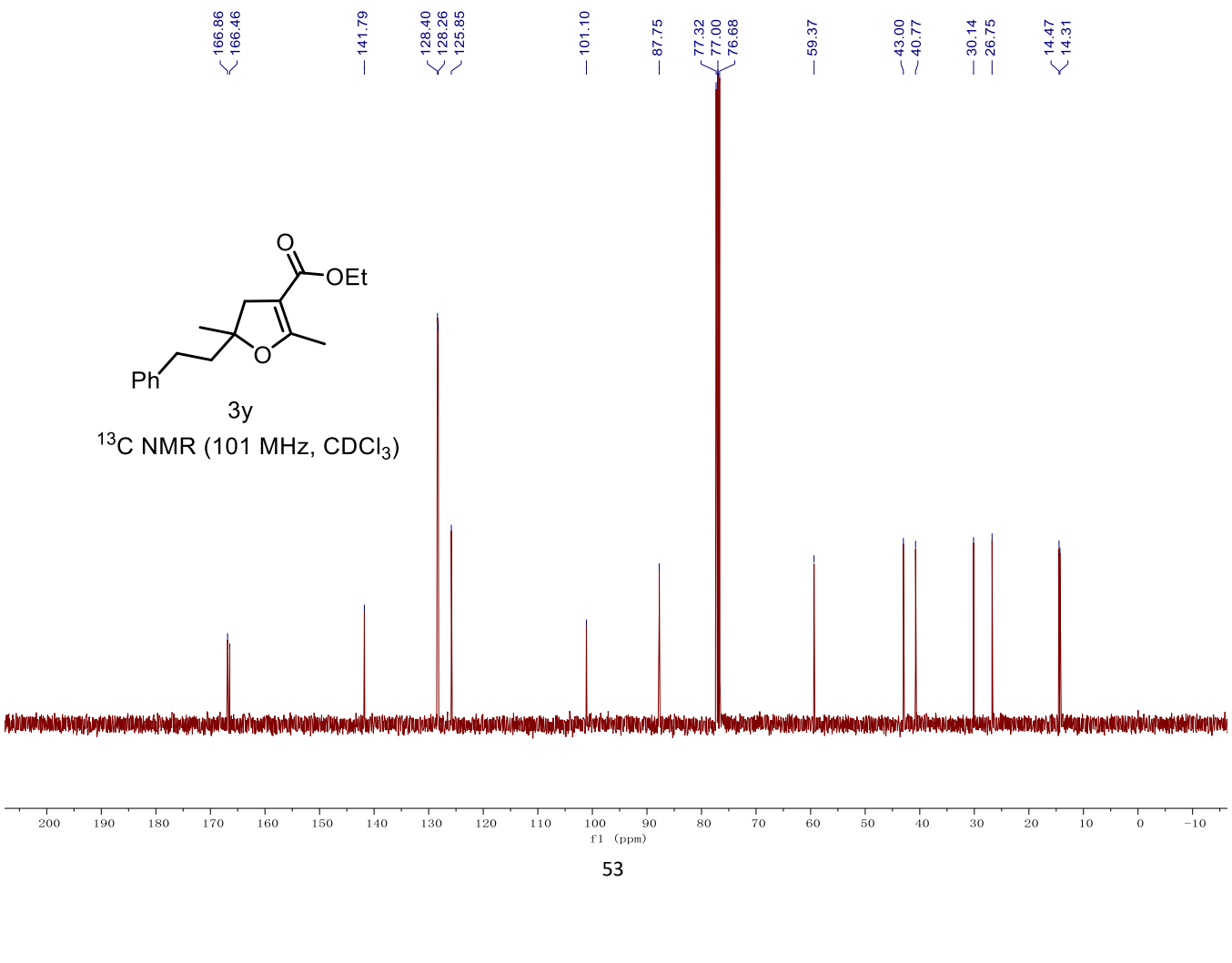
3x

^{13}C NMR (126 MHz, $CDCl_3$)



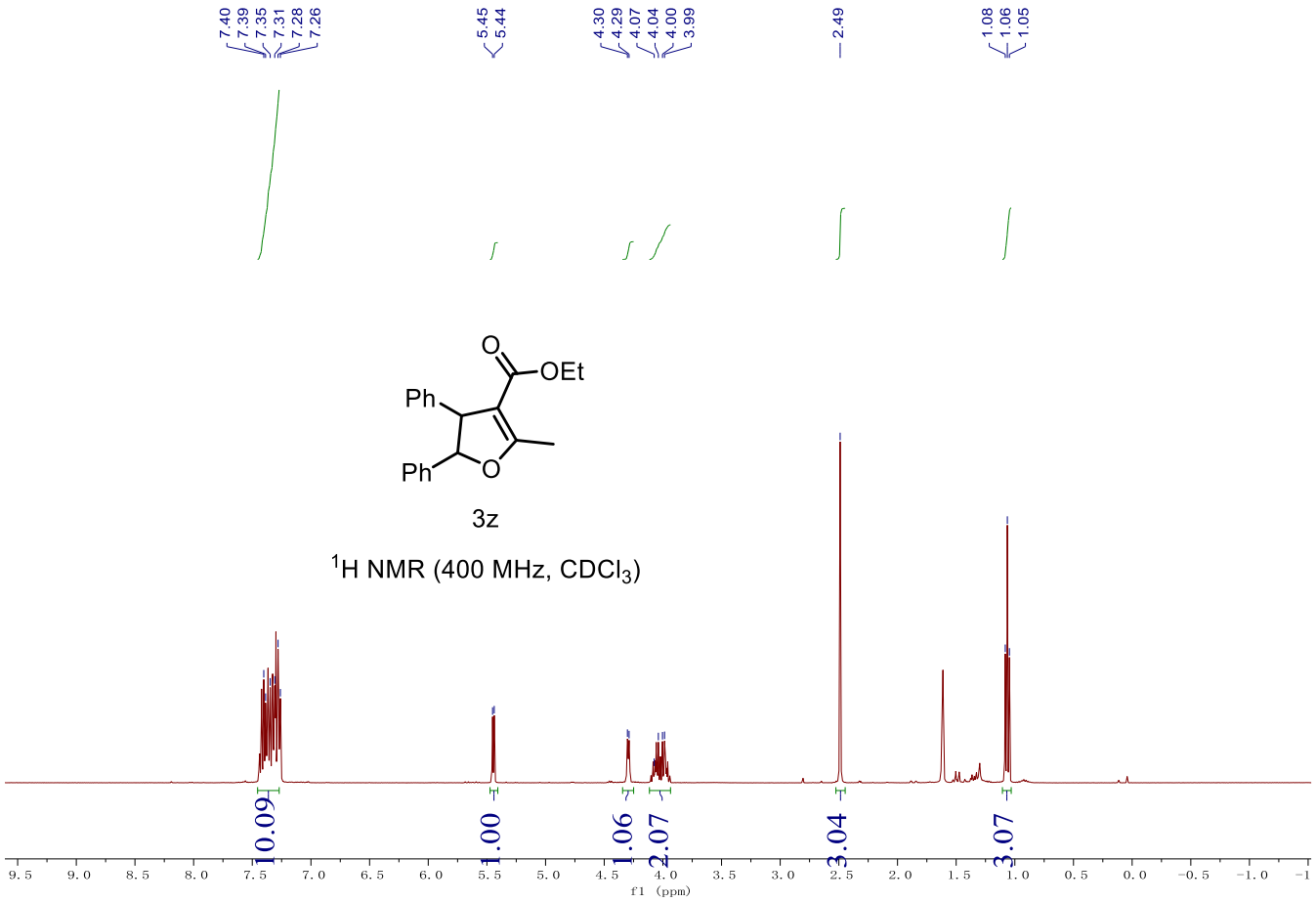
3y

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



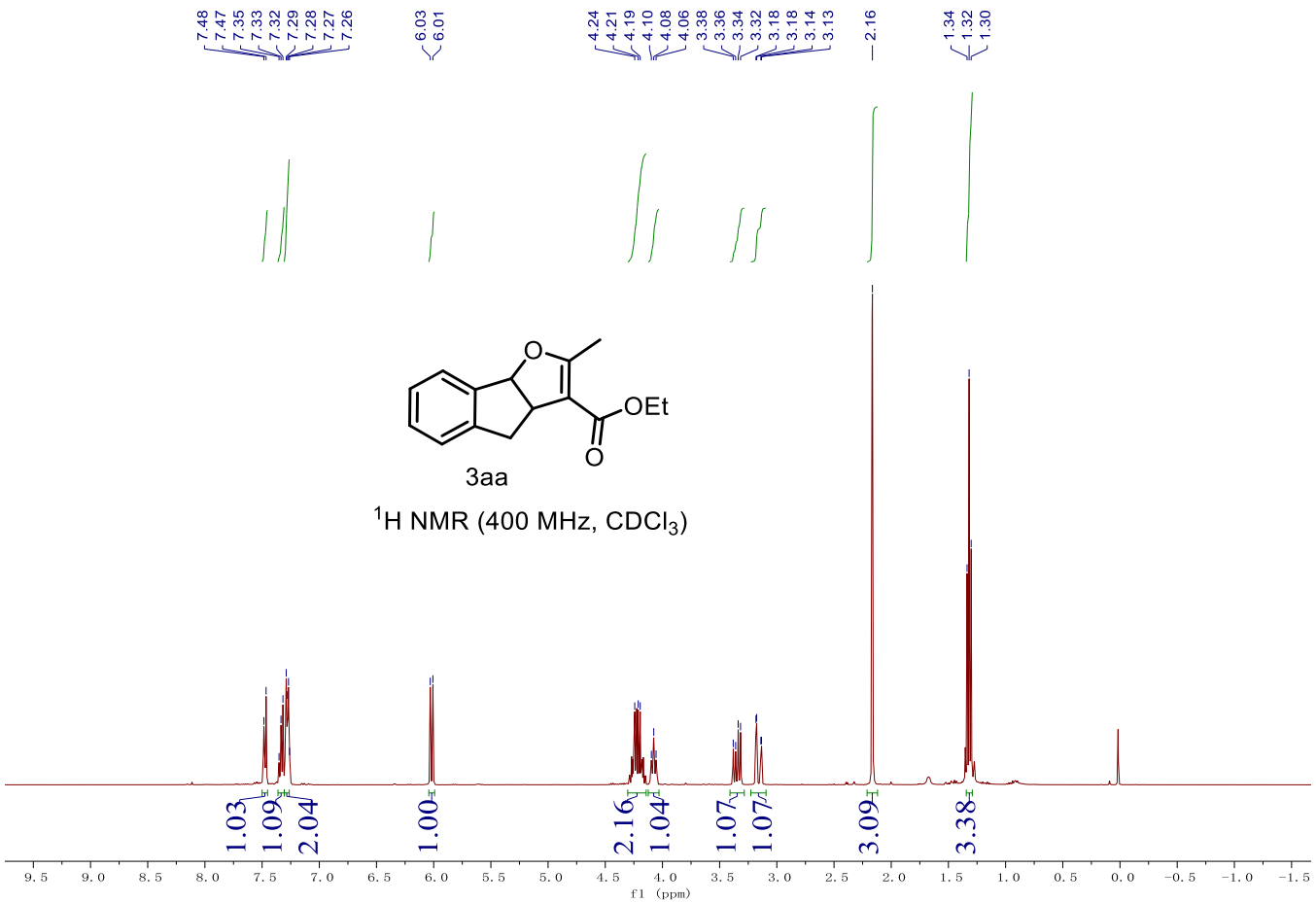
3y

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



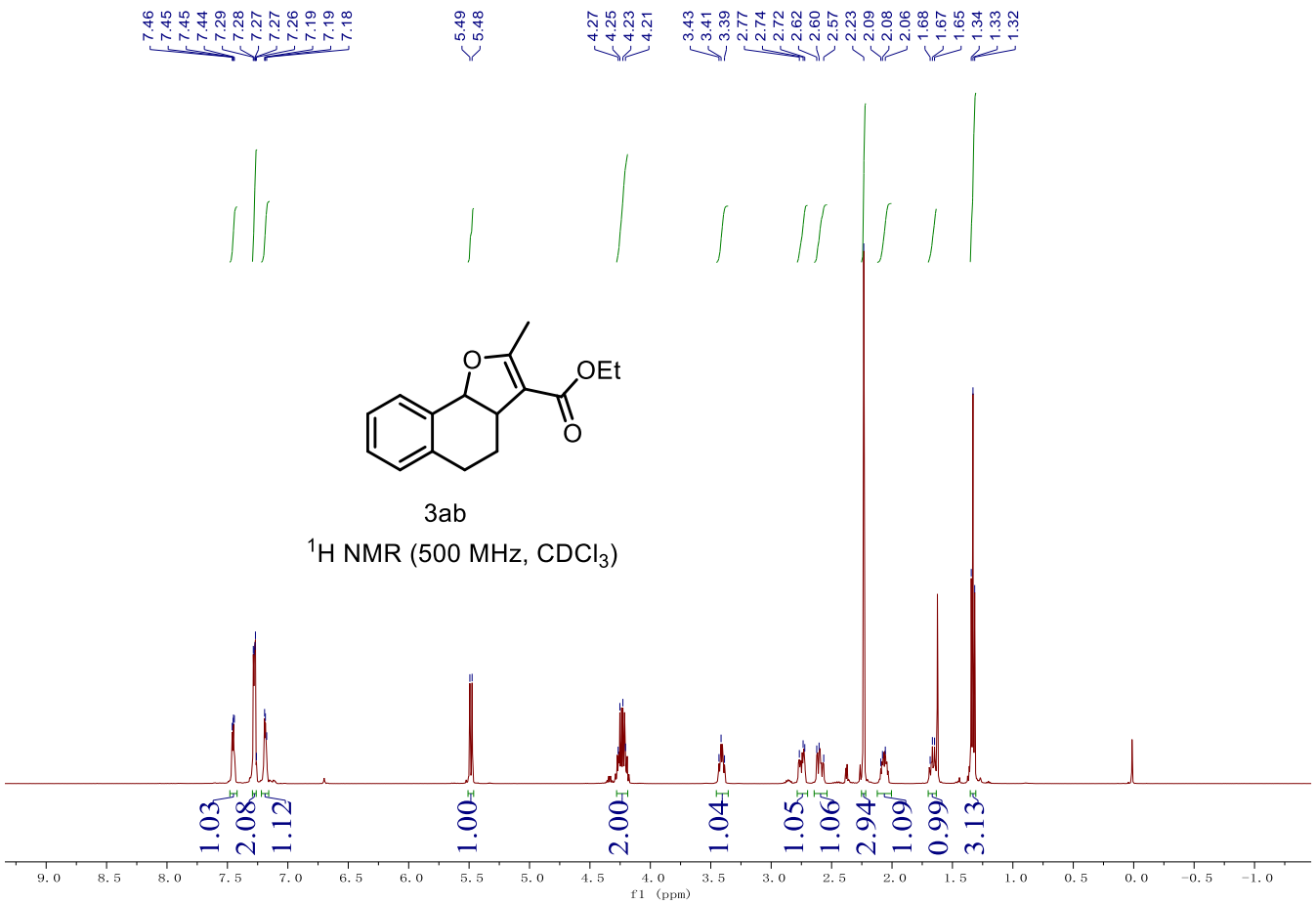
3z

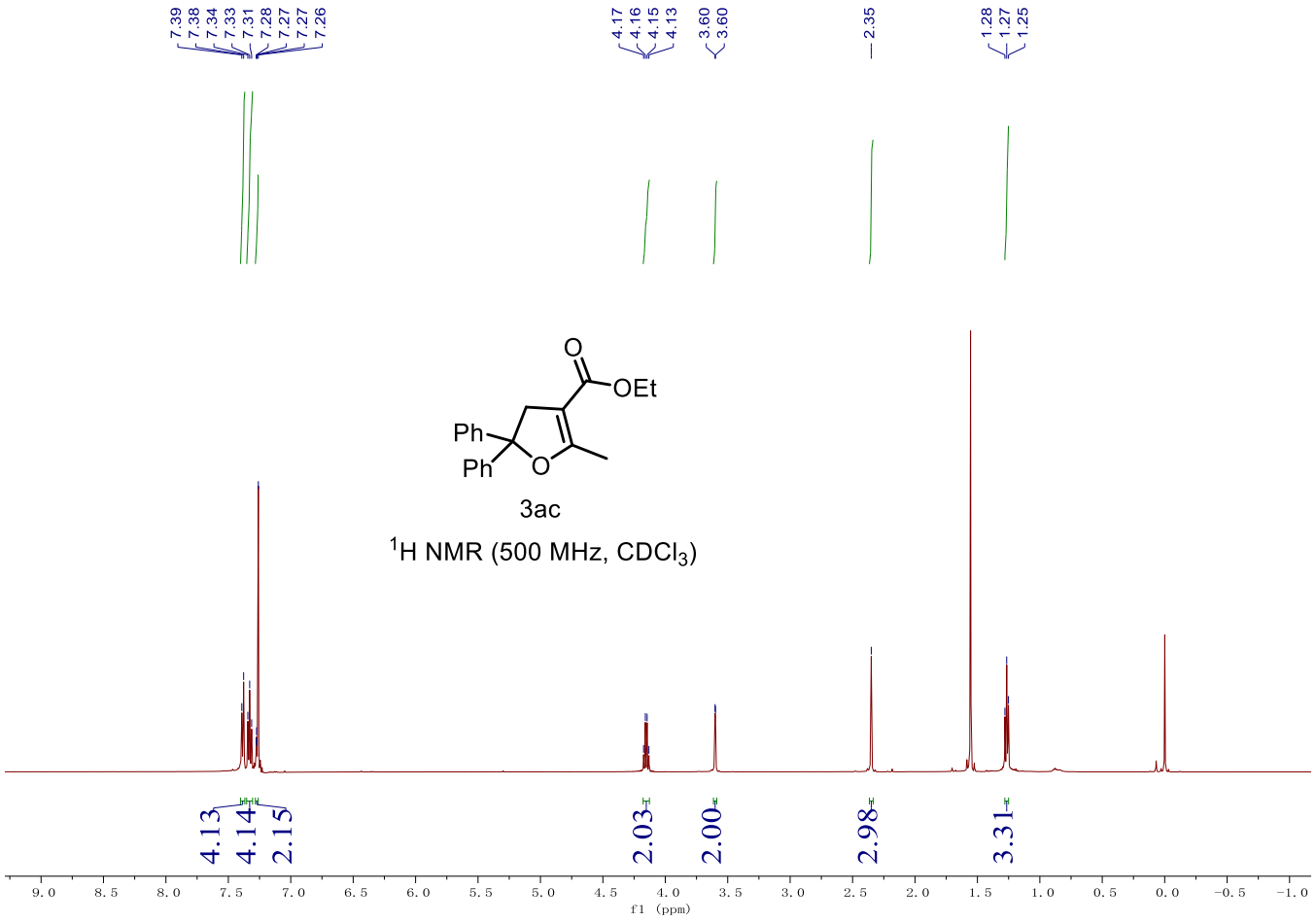
^{1}H NMR (400 MHz, $CDCl_3$)

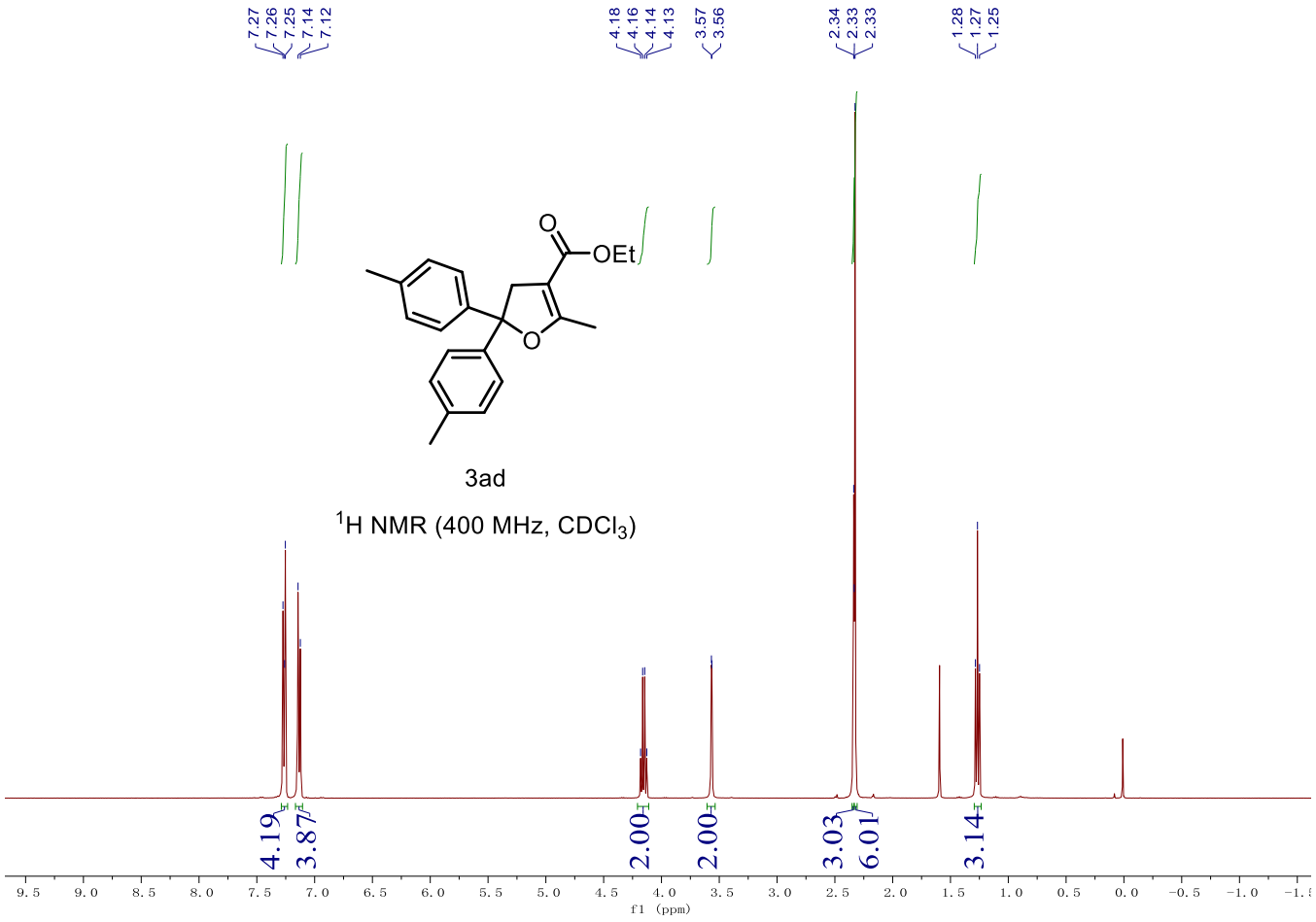


3aa

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

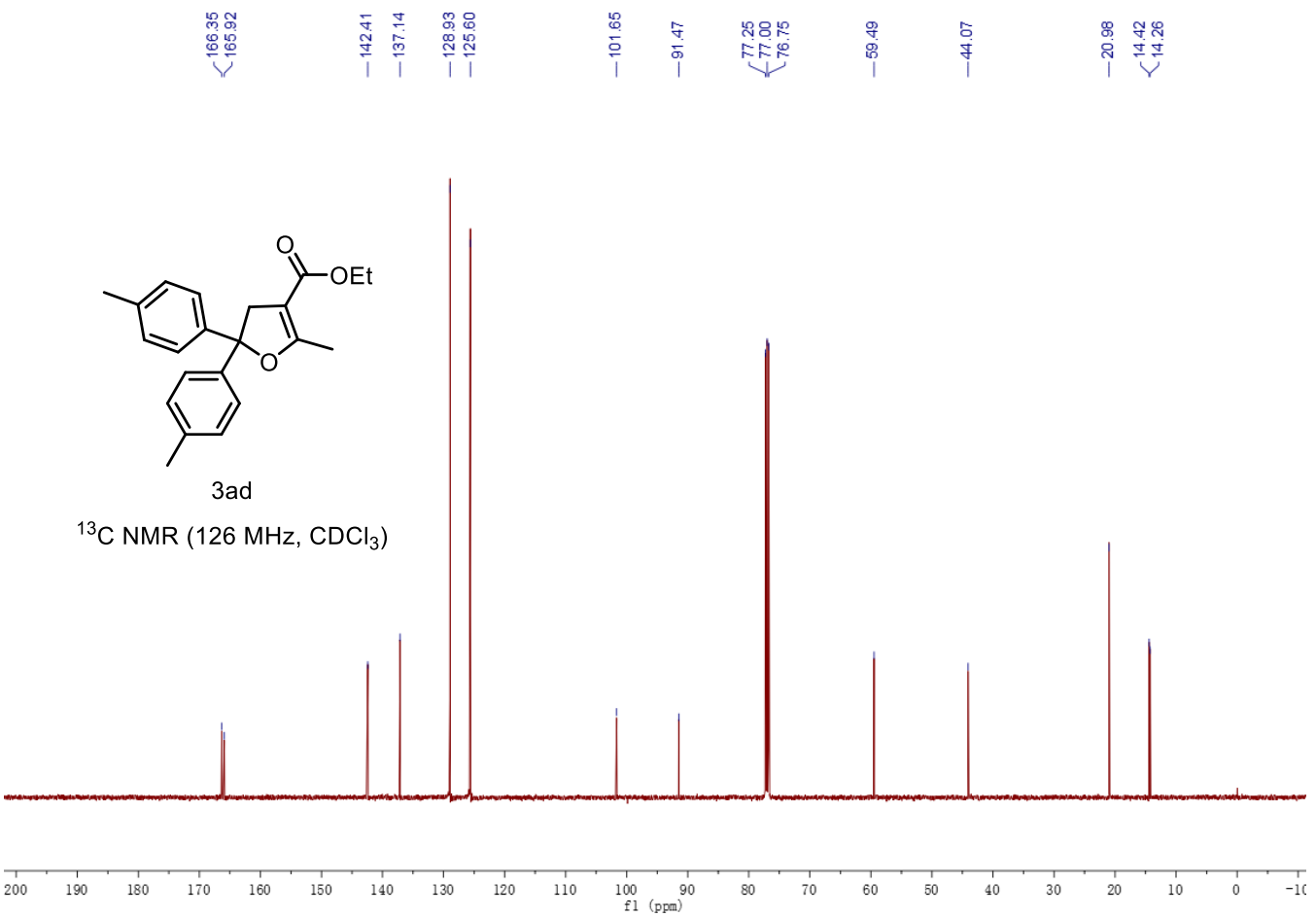

7.46
7.45
7.45
7.44
7.29
7.28
7.27
7.27
7.26
7.19
7.19
7.18
5.49
5.48
4.27
4.25
4.23
4.21
3.43
3.41
3.39
2.77
2.74
2.72
2.62
2.60
2.57
2.23
2.09
2.08
2.06
1.68
1.67
1.65
1.34
1.33
1.32
O
OEt
O
3ab
1H NMR (500 MHz, CDCl3)
1.03
2.08
1.12
1.00
2.00
1.04
1.05
1.06
2.94
1.09
0.99
3.13
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


7.39
7.38
7.34
7.33
7.31
7.28
7.27
7.27
7.26
4.17
4.16
4.15
4.13
3.60
3.60
2.35
1.28
1.27
1.25
O
OEt
Ph
Ph
O
3ac
1H NMR (500 MHz, CDCl3)
4.13
4.14
2.15
2.03
2.00
2.98
3.31
f1 (ppm)



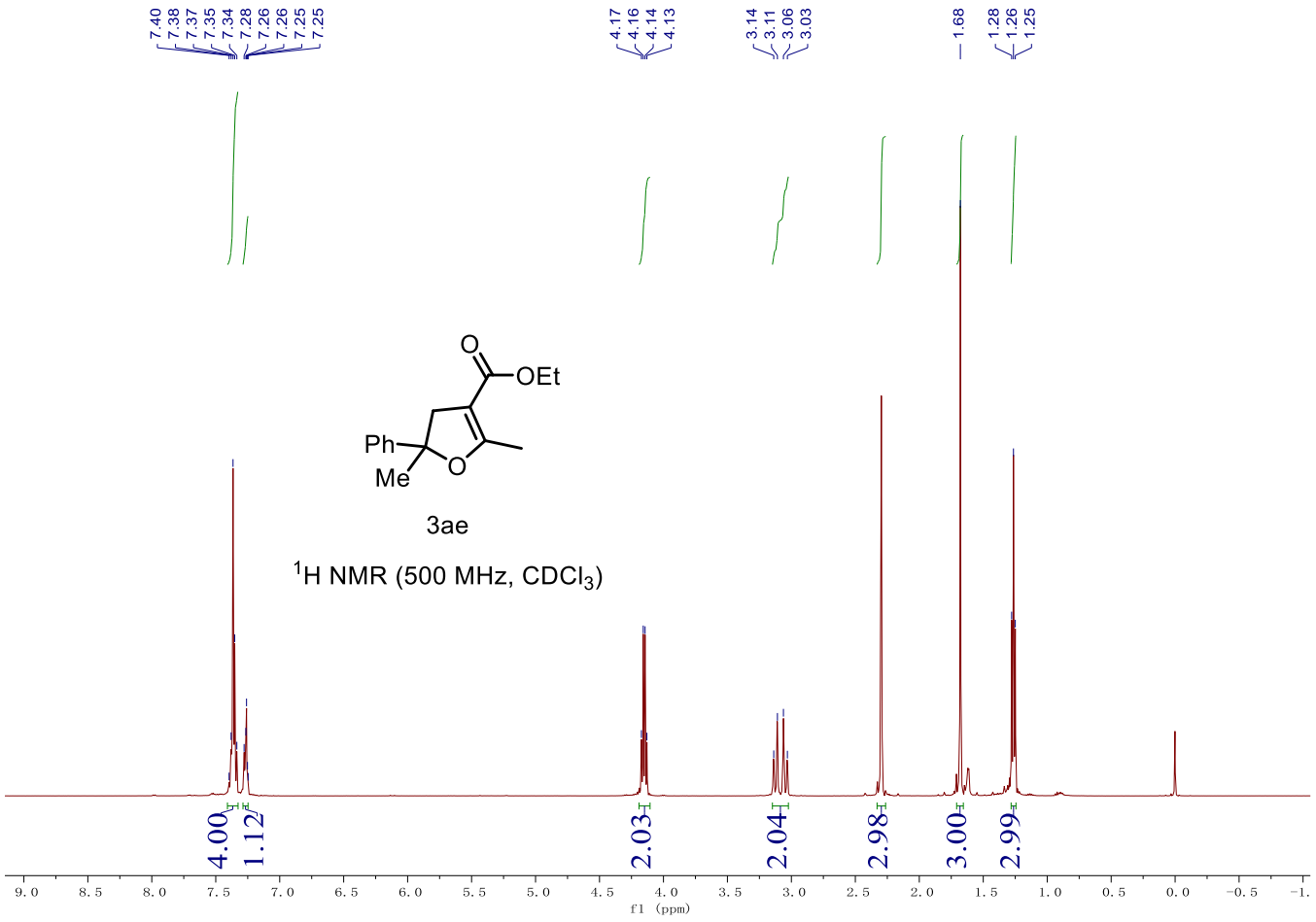
3ad

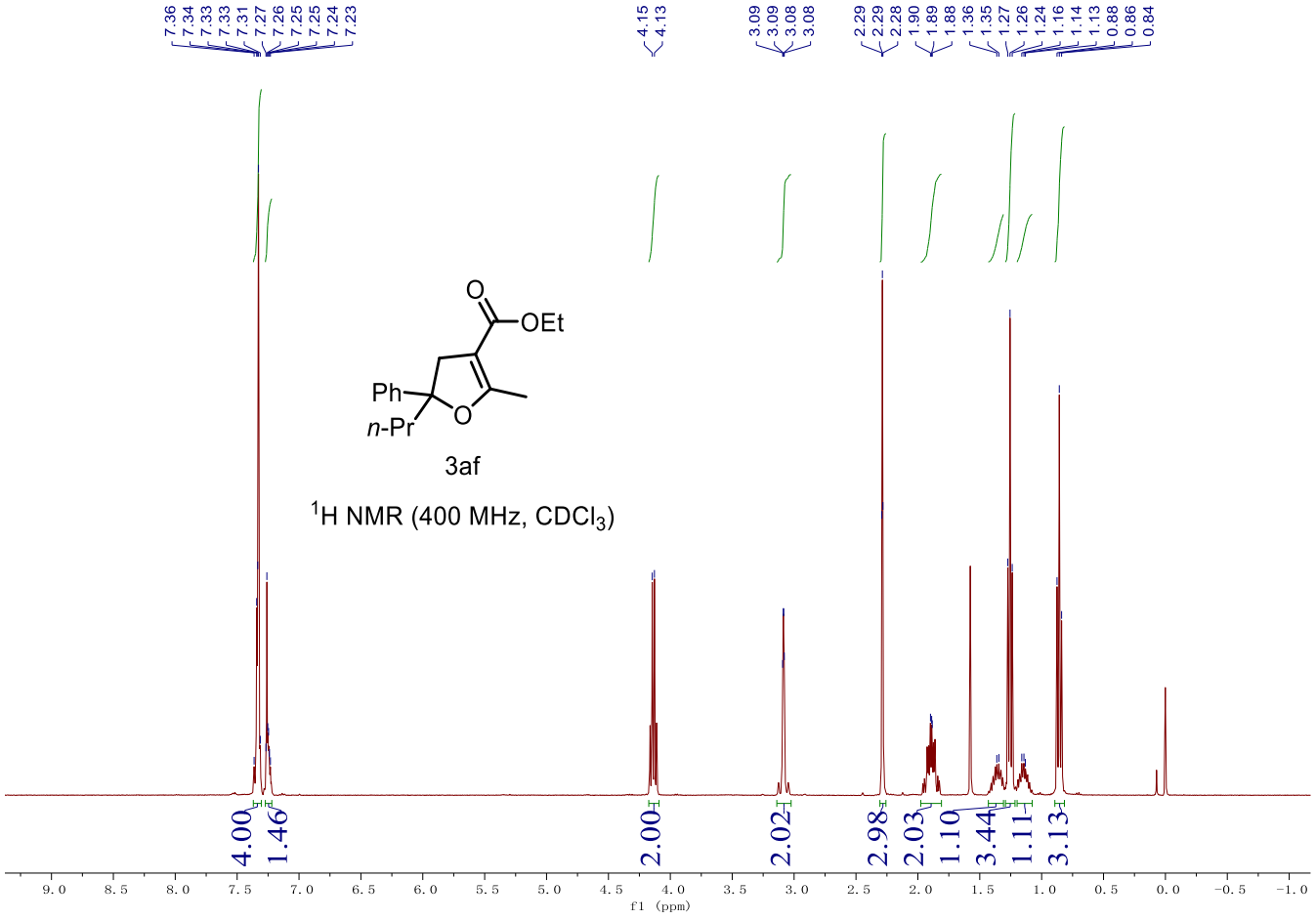
^{1}H NMR (400 MHz, $CDCl_3$)



3ad

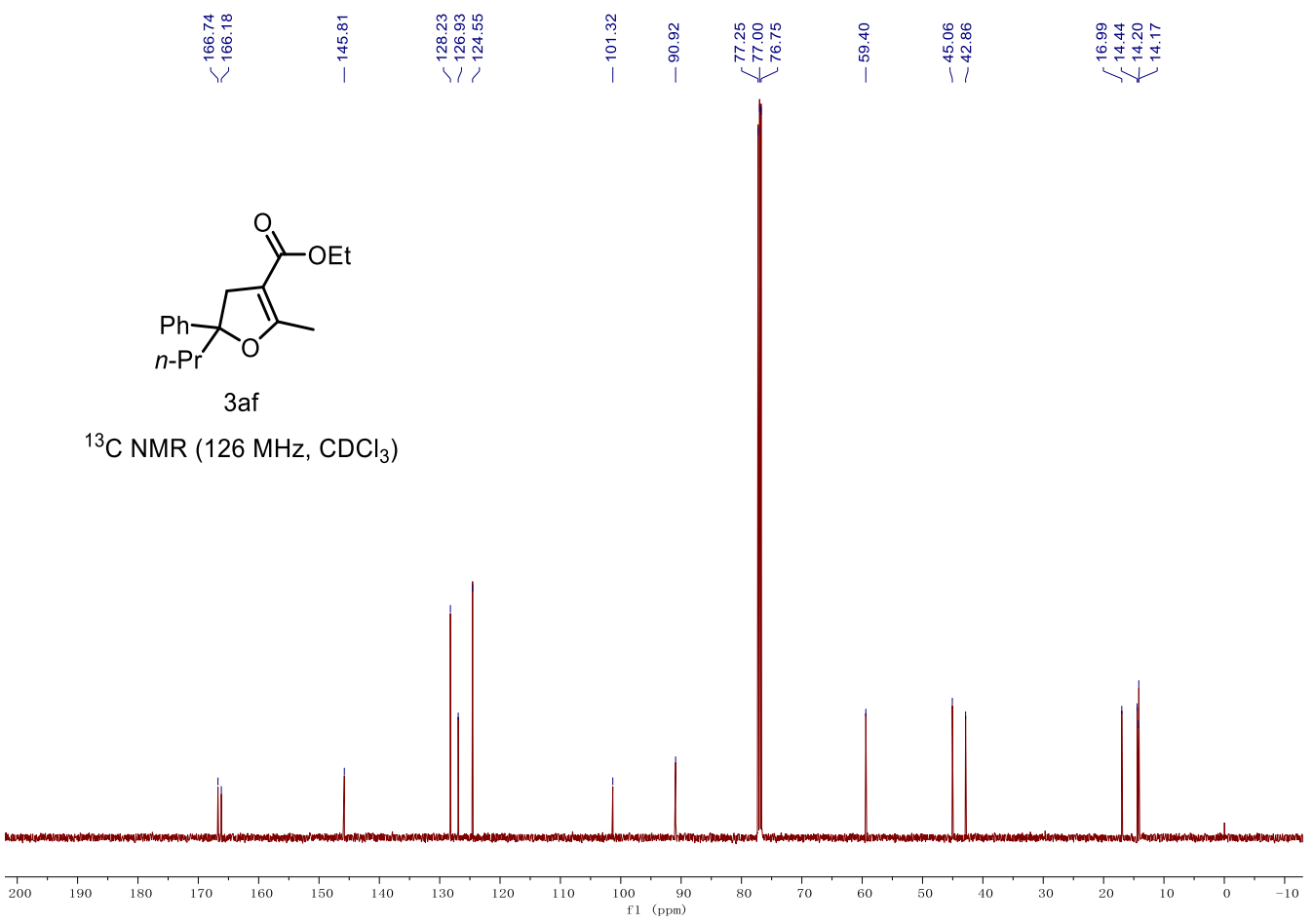
^{13}C NMR (126 MHz, $CDCl_3$)


7.40
7.38
7.37
7.35
7.34
7.28
7.26
7.26
7.25
7.25
4.17
4.16
4.14
4.13
3.14
3.11
3.06
3.03
1.68
1.28
1.26
1.25
O
OEt
Ph
Me
O
3ae
1H NMR (500 MHz, CDCl3)
4.00
1.12
2.03
2.04
2.98
3.00
2.99
f1 (ppm)



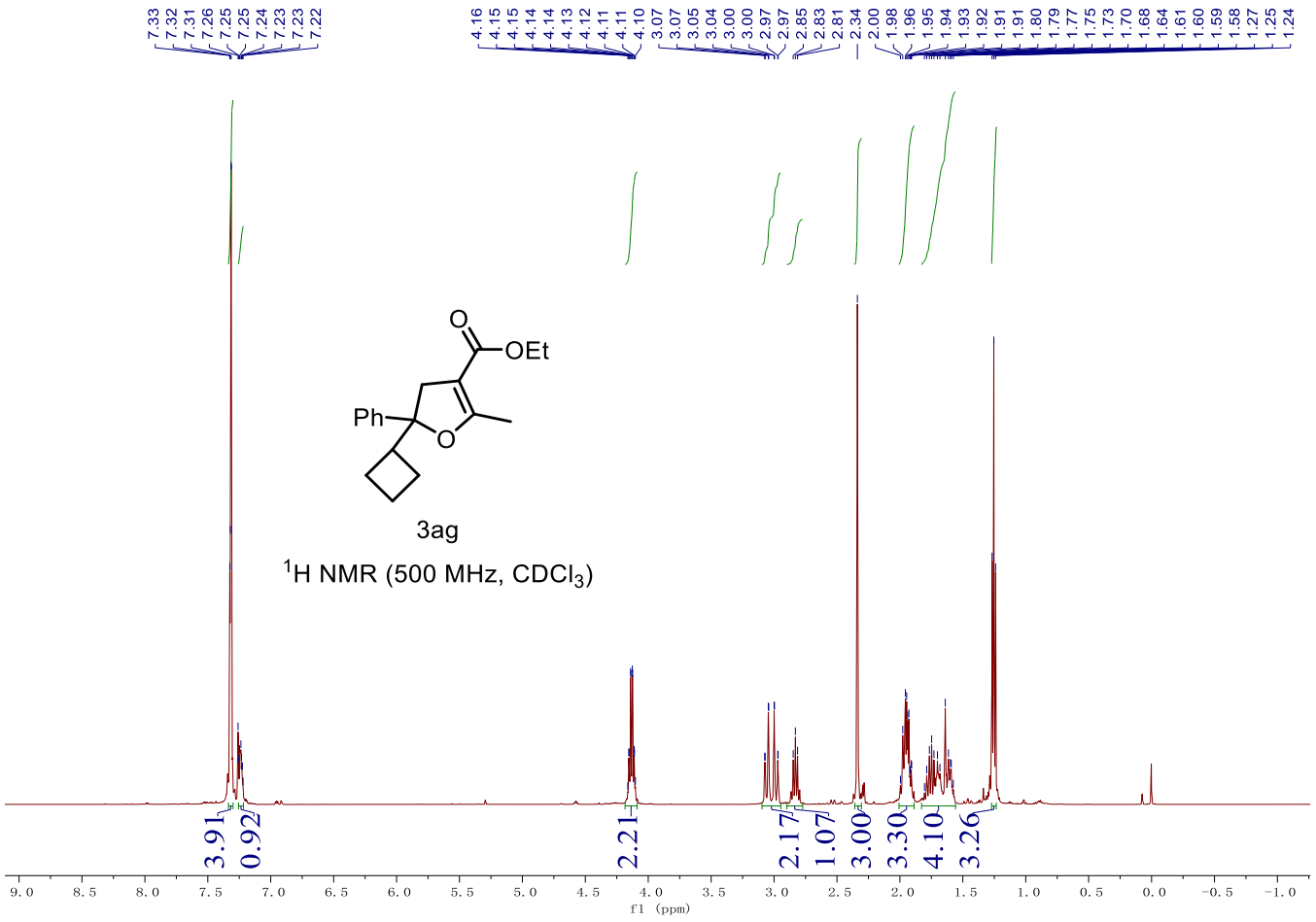
3af

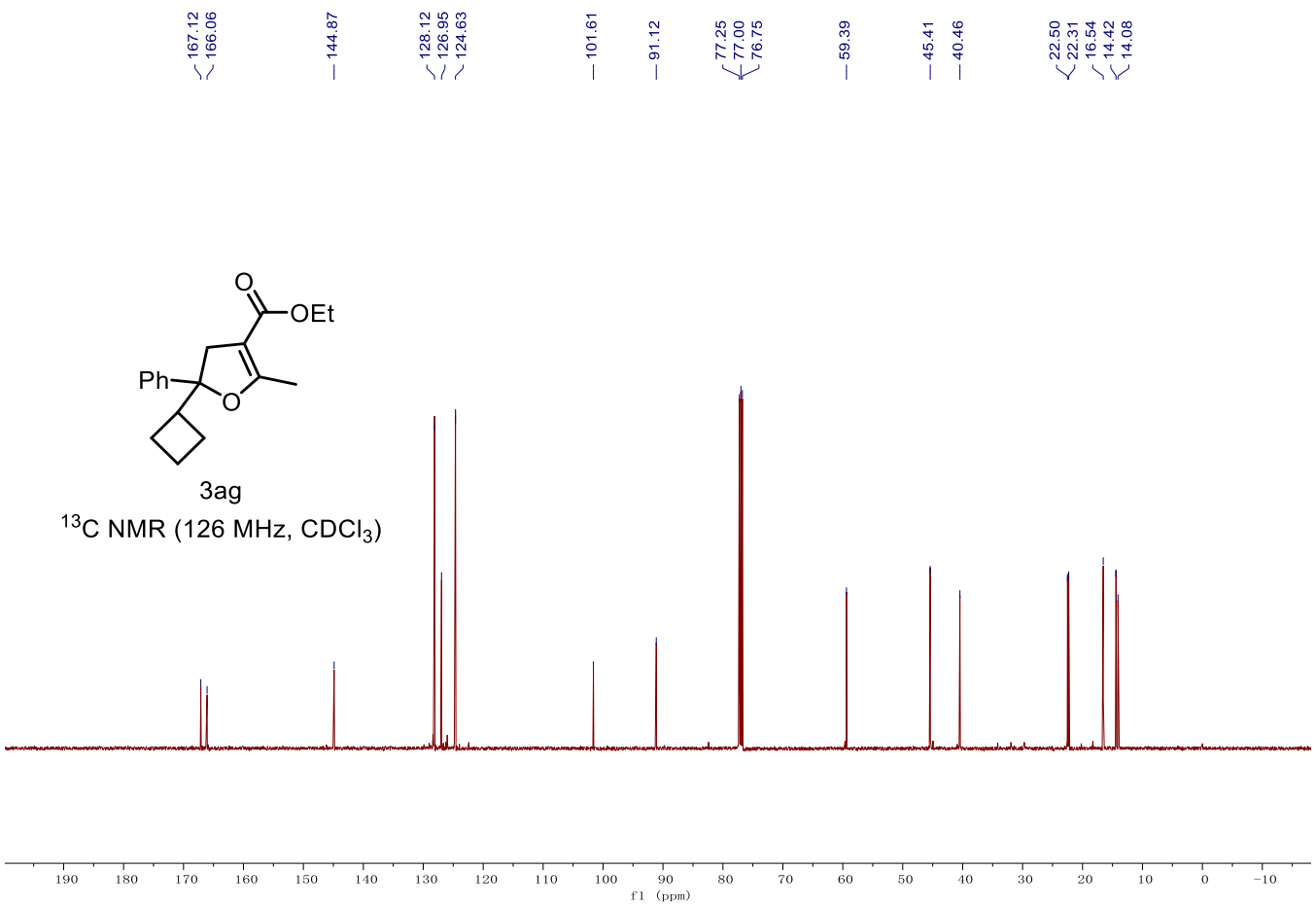
^{1}H NMR (400 MHz, $CDCl_3$)

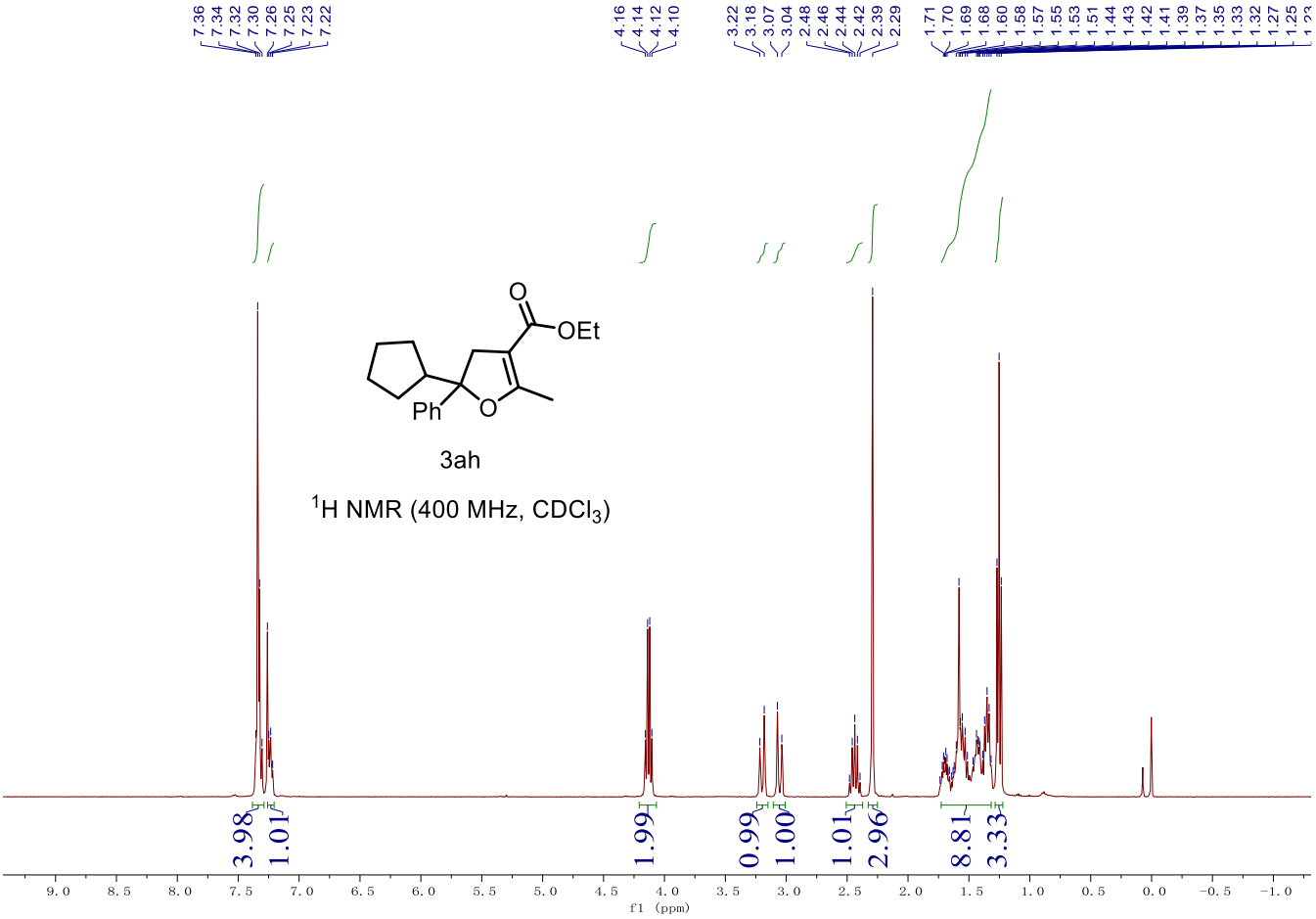


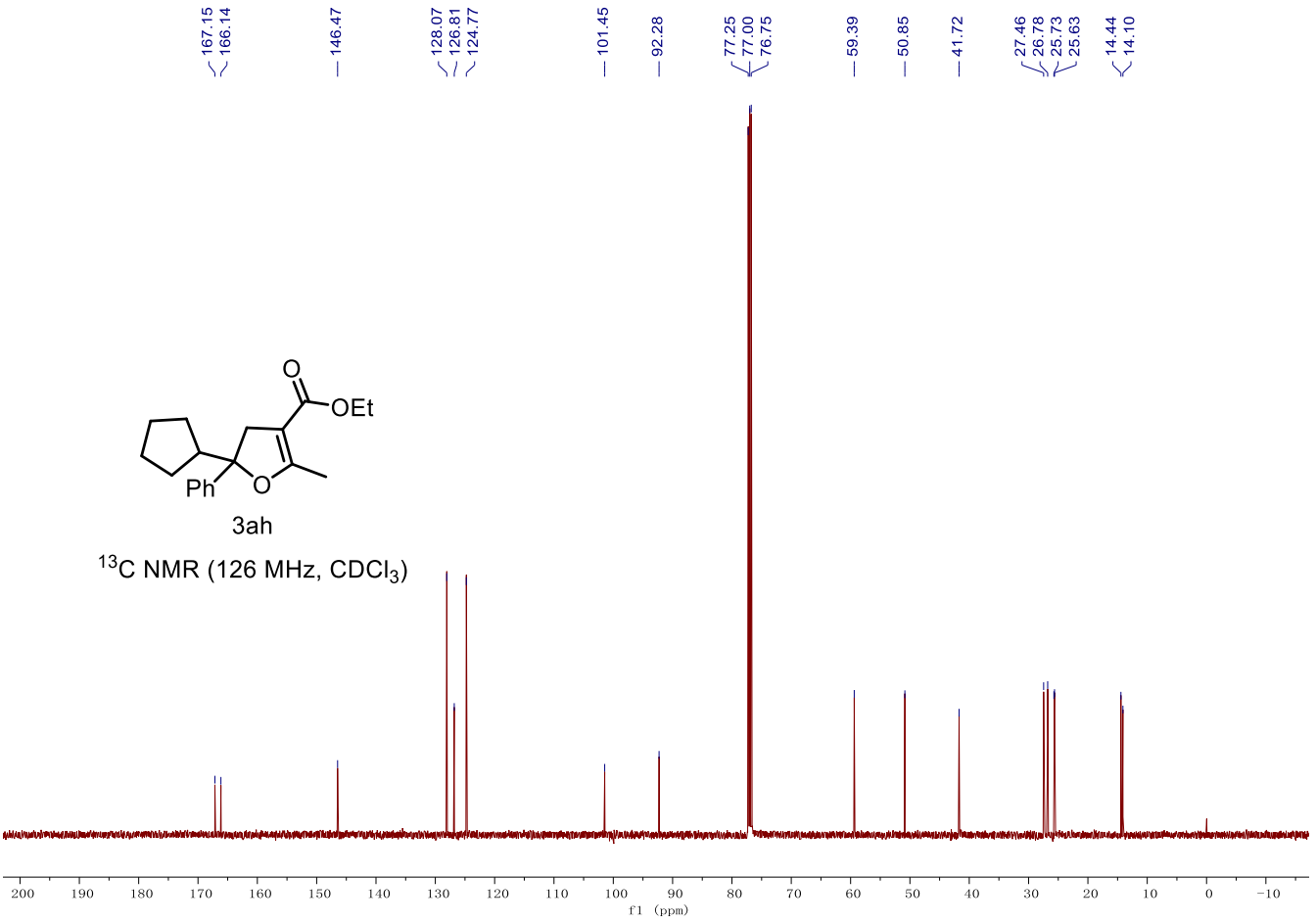
3af

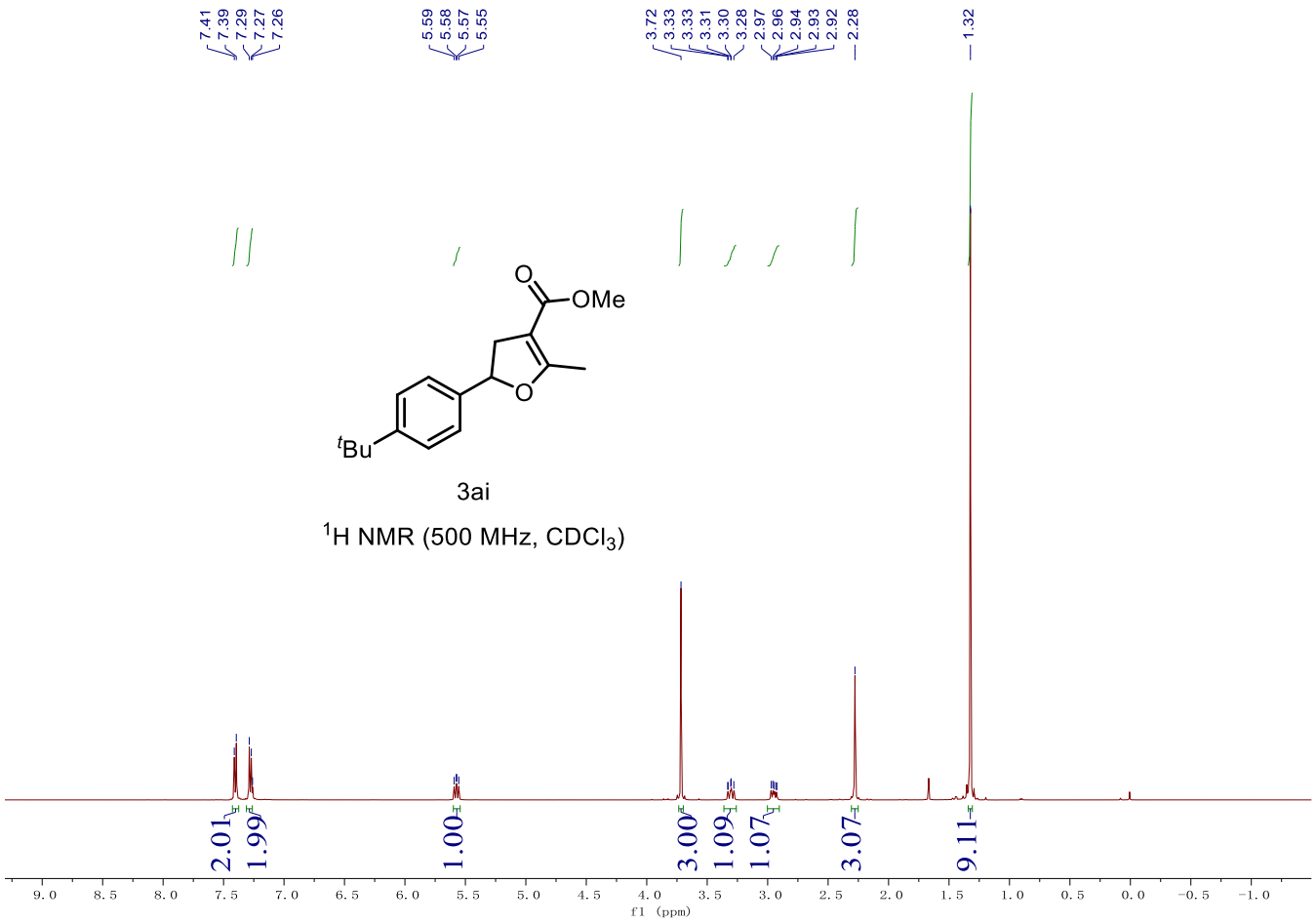
^{13}C NMR (126 MHz, $CDCl_3$)

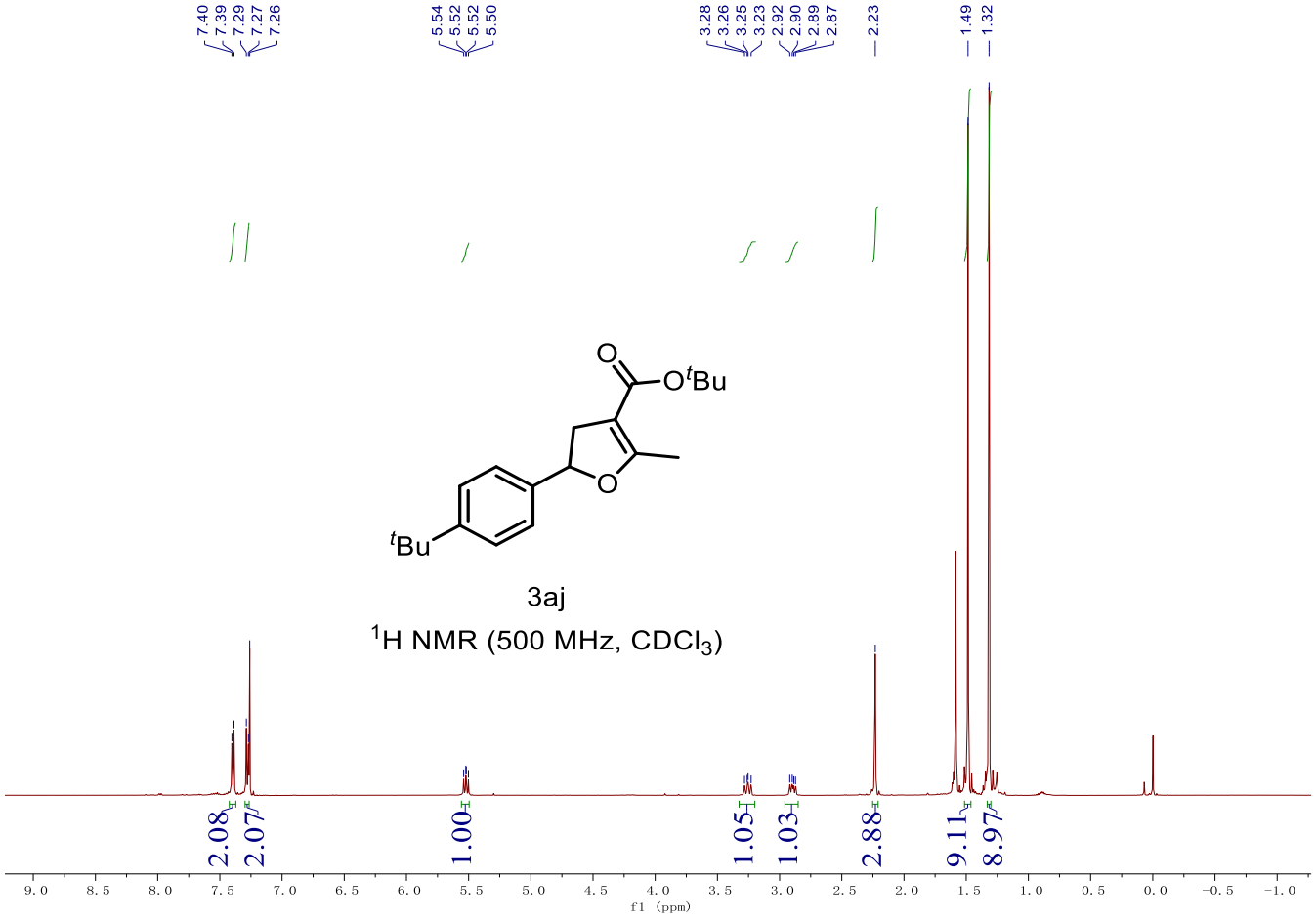

7.33 7.32 7.31 7.26 7.25 7.25 7.24 7.23 7.23 7.22
4.16 4.15 4.15 4.14 4.14 4.13 4.12 4.11 4.11 4.10
3.07 3.05 3.04 3.00 3.00 2.97 2.97 2.85 2.83 2.81
2.34 2.00 1.98 1.96 1.95 1.94 1.93 1.92 1.91 1.91
1.80 1.79 1.77 1.75 1.73 1.70 1.68 1.64 1.61 1.60
1.59 1.58 1.27 1.25 1.24
O
OEt
Ph
O
3ag
1H NMR (500 MHz, CDCl3)
3.91 0.92 2.21 2.17 1.07 3.00 3.30 4.10 3.26
f1 (ppm)


167.12 166.06 144.87 128.12 126.95 124.63 101.61 91.12 77.25 77.00 76.75 59.39 45.41 40.46 22.50 22.31 16.54 14.42 14.08
O
OEt
Ph
O
3ag
13C NMR (126 MHz, CDCl3)
f1 (ppm)


7.36
7.34
7.32
7.30
7.26
7.25
7.23
7.22
4.16
4.14
4.12
4.10
3.22
3.18
3.07
3.04
2.48
2.46
2.44
2.42
2.39
2.29
1.71
1.70
1.69
1.68
1.60
1.58
1.57
1.55
1.53
1.51
1.44
1.43
1.42
1.41
1.39
1.37
1.35
1.33
1.32
1.27
1.25
O
OEt
Ph
O
3ah
1H NMR (400 MHz, CDCl3)
3.98
1.01
1.99
0.99
1.00
1.01
2.96
8.81
3.33
f1 (ppm)

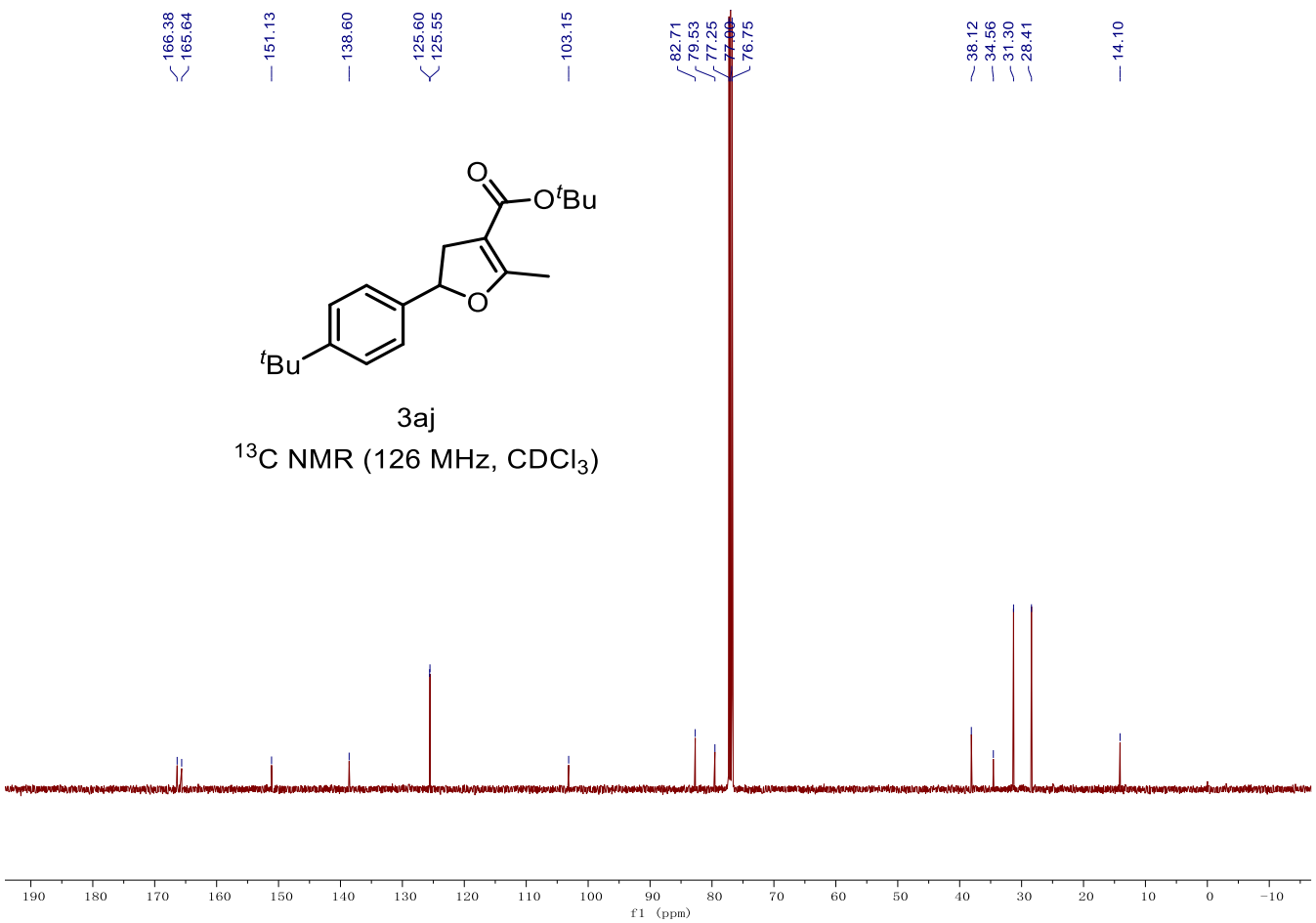

167.15
166.14
146.47
128.07
126.81
124.77
101.45
92.28
77.25
77.00
76.75
59.39
50.85
41.72
27.46
26.78
25.73
25.63
14.44
14.10
O
OEt
Ph
O
3ah
13C NMR (126 MHz, CDCl3)
f1 (ppm)


7.41
7.39
7.29
7.27
7.26
5.59
5.58
5.57
5.55
3.72
3.33
3.33
3.31
3.30
3.28
2.97
2.96
2.94
2.93
2.92
2.28
1.32
O
OMe
O
tBu
3ai
1H NMR (500 MHz, CDCl3)
2.01
1.99
1.00
3.00
1.09
1.07
3.07
9.11
f1 (ppm)



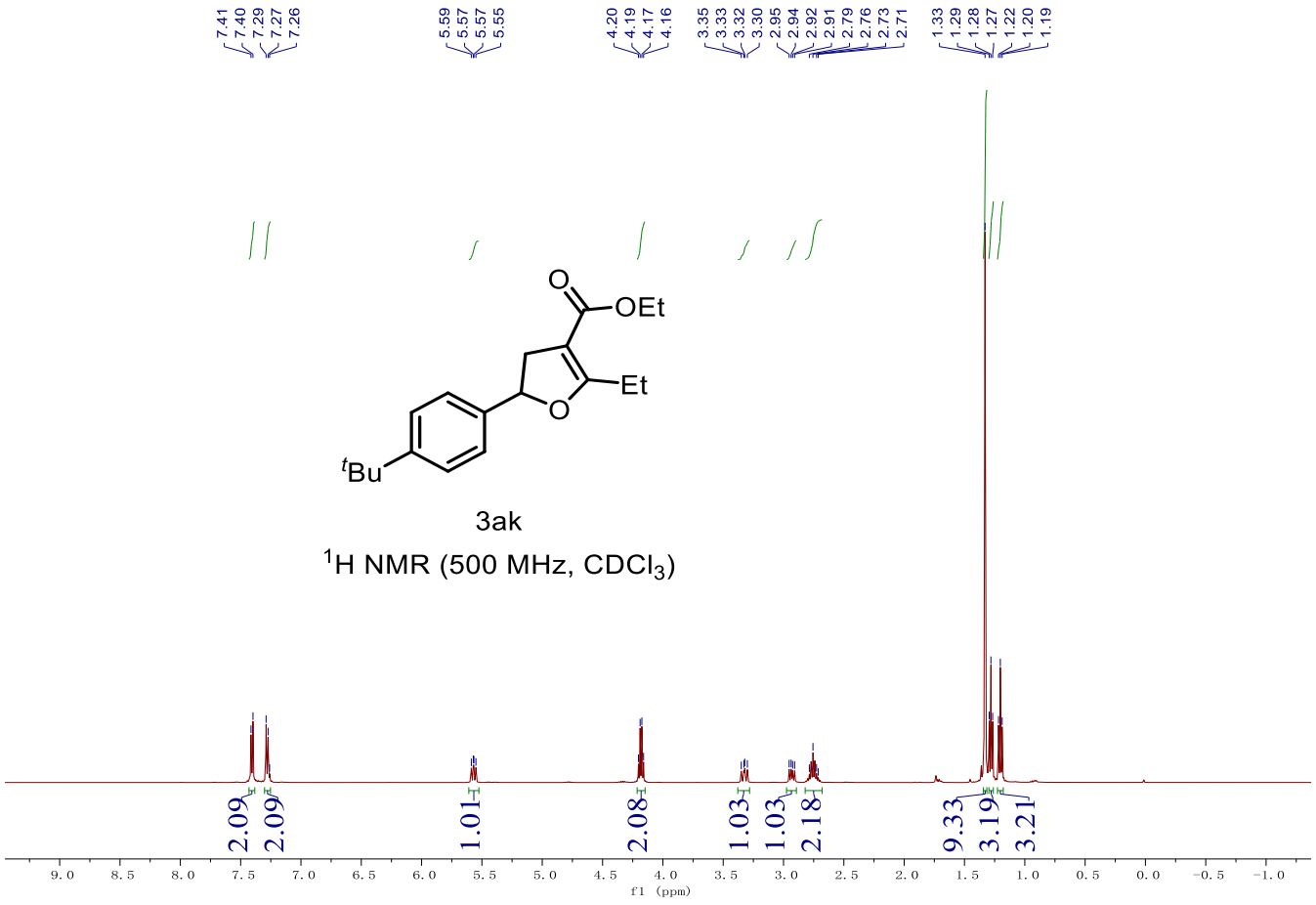
3aj

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



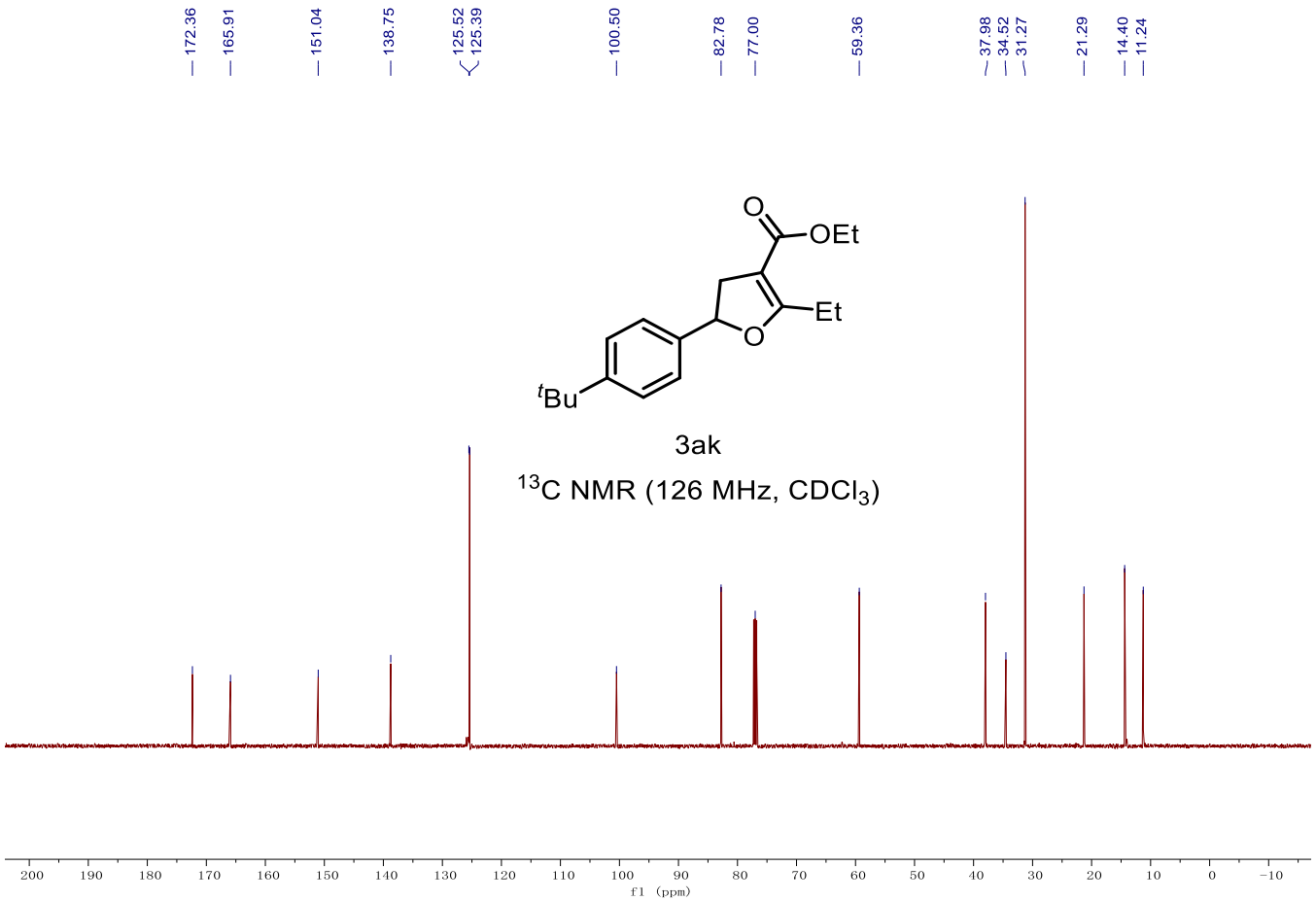
3aj

^{13}C NMR (126 MHz, $CDCl_3$)



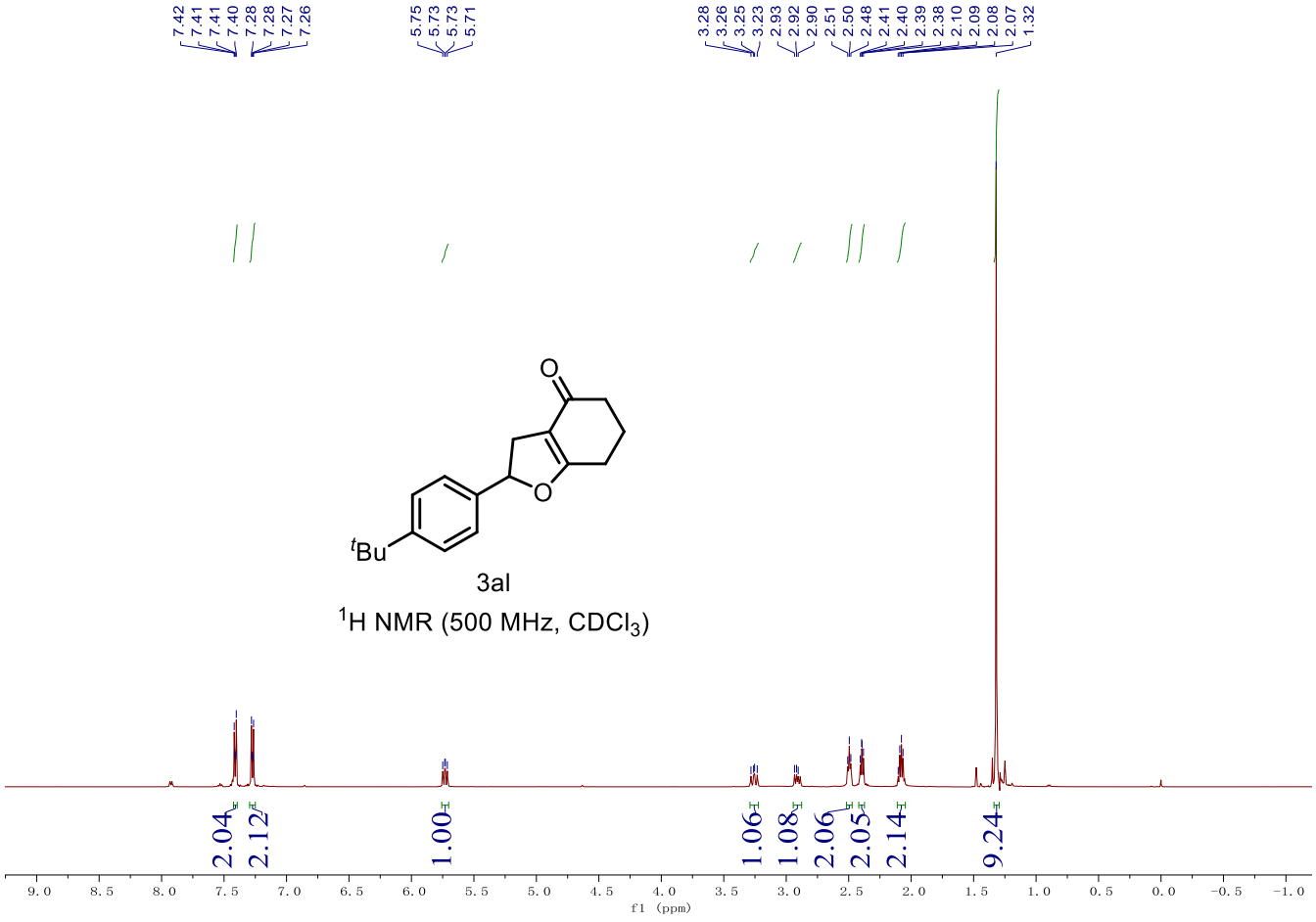
3ak

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



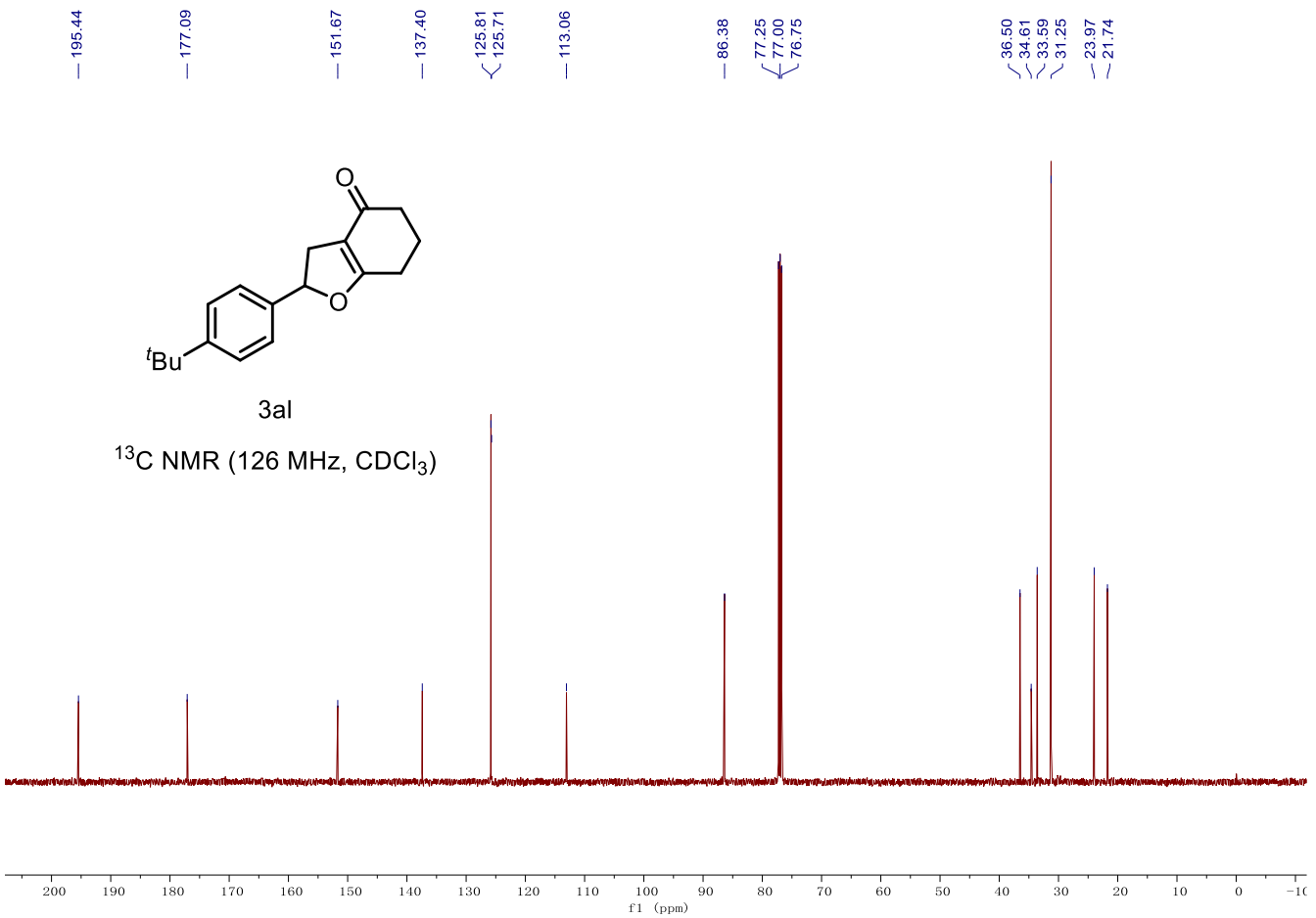
3ak

^{13}C NMR (126 MHz, $CDCl_3$)



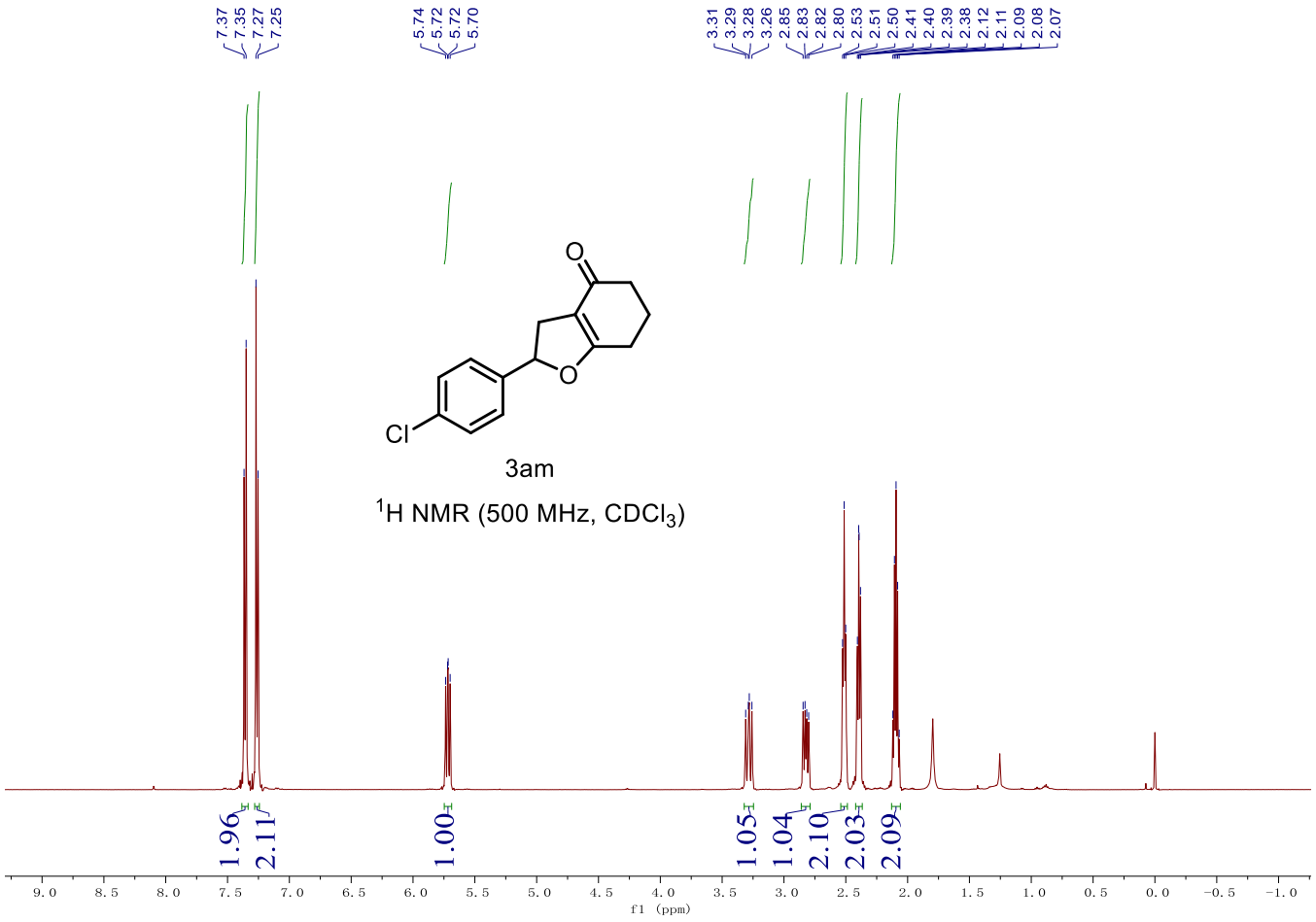
3al

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



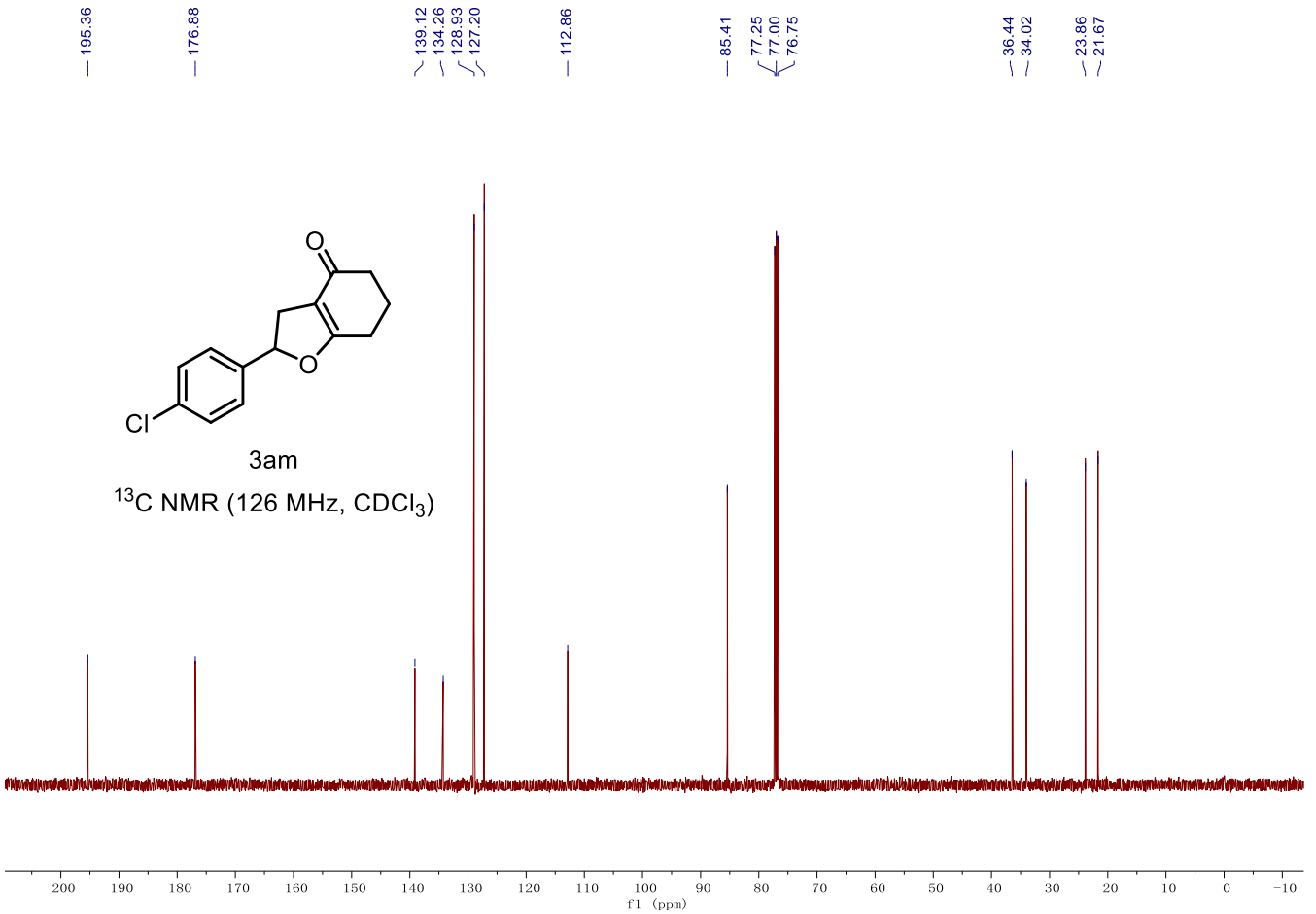
3al

^{13}C NMR (126 MHz, $CDCl_3$)



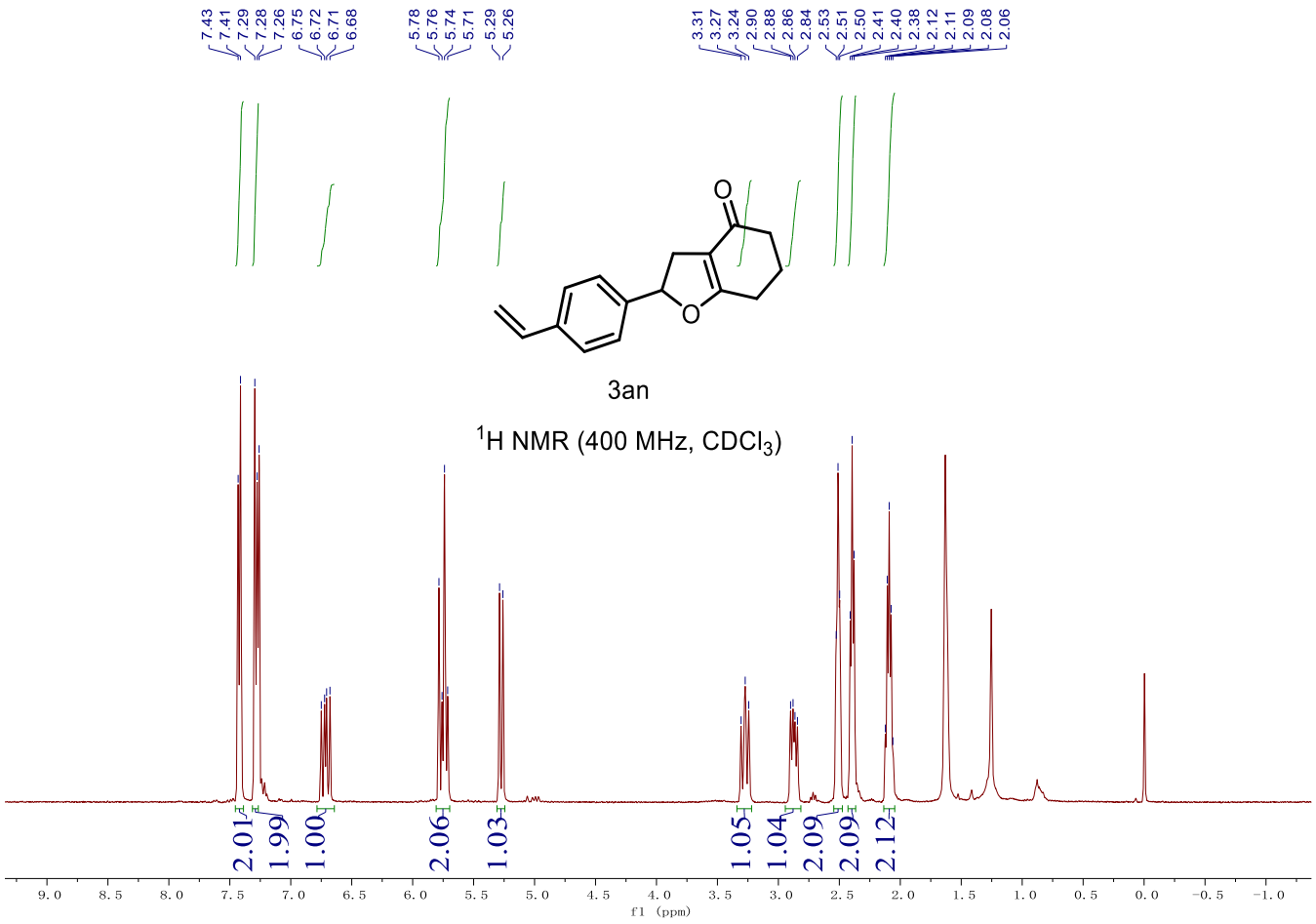
3am

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



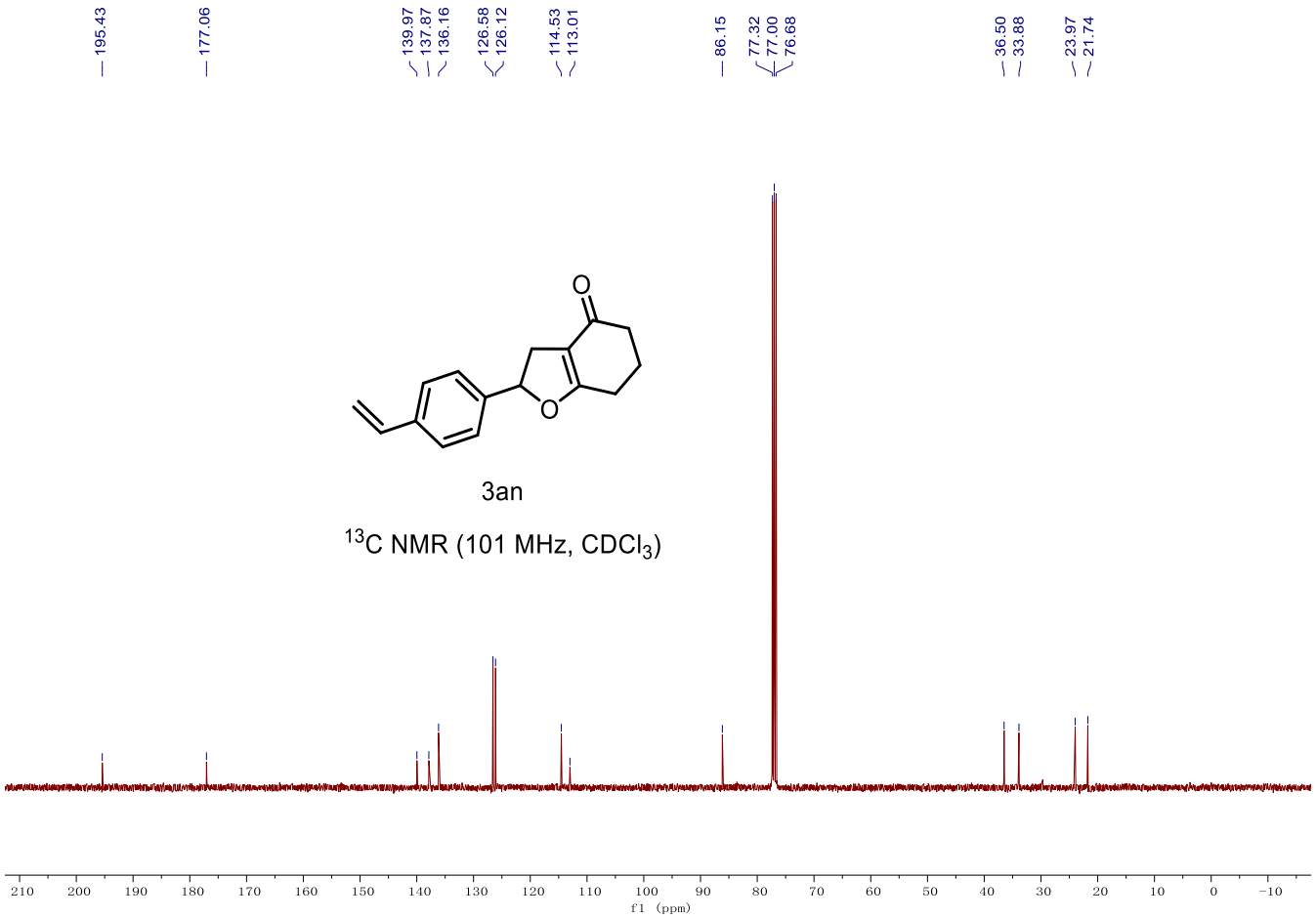
3am

^{13}C NMR (126 MHz, $CDCl_3$)



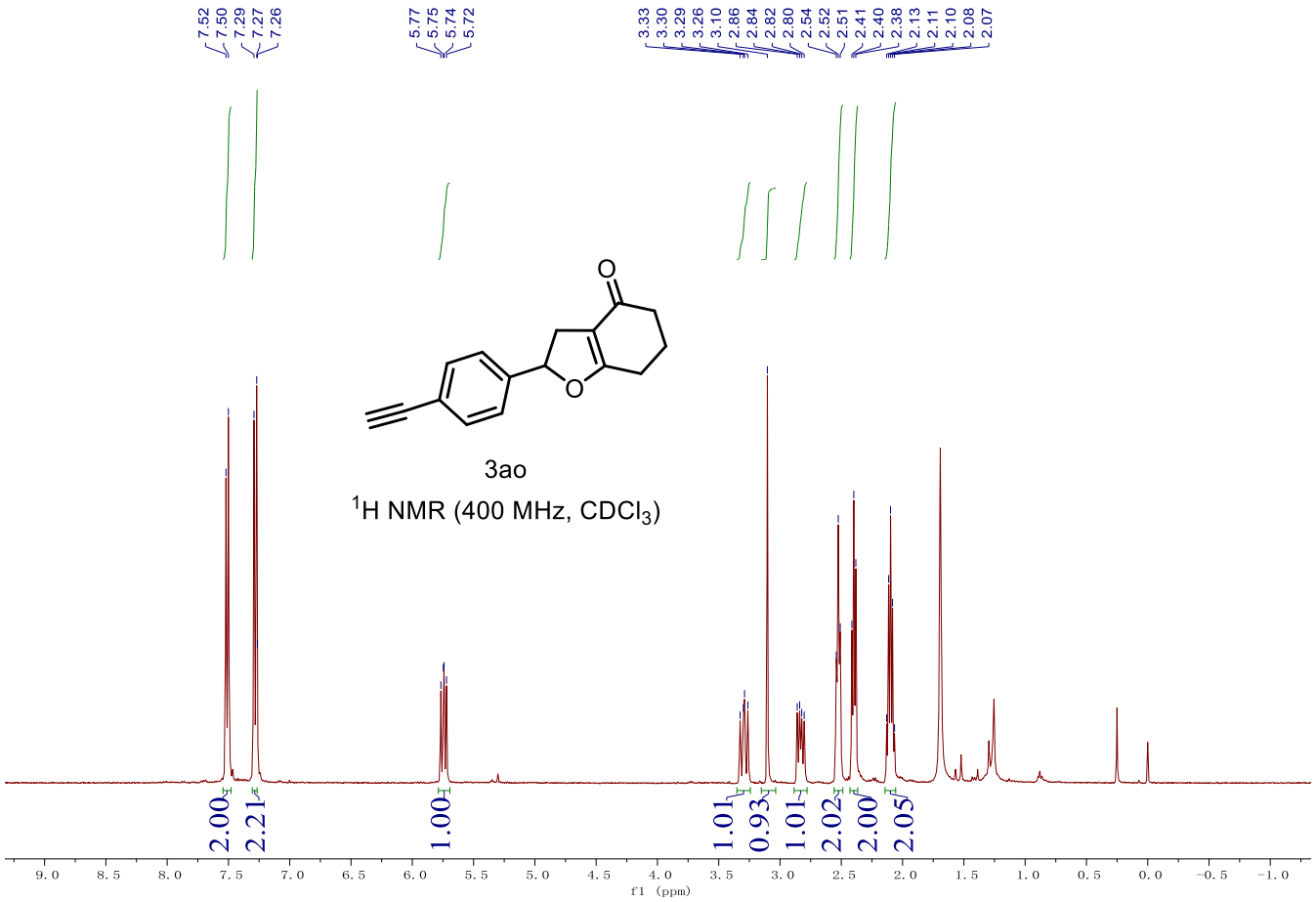
3an

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



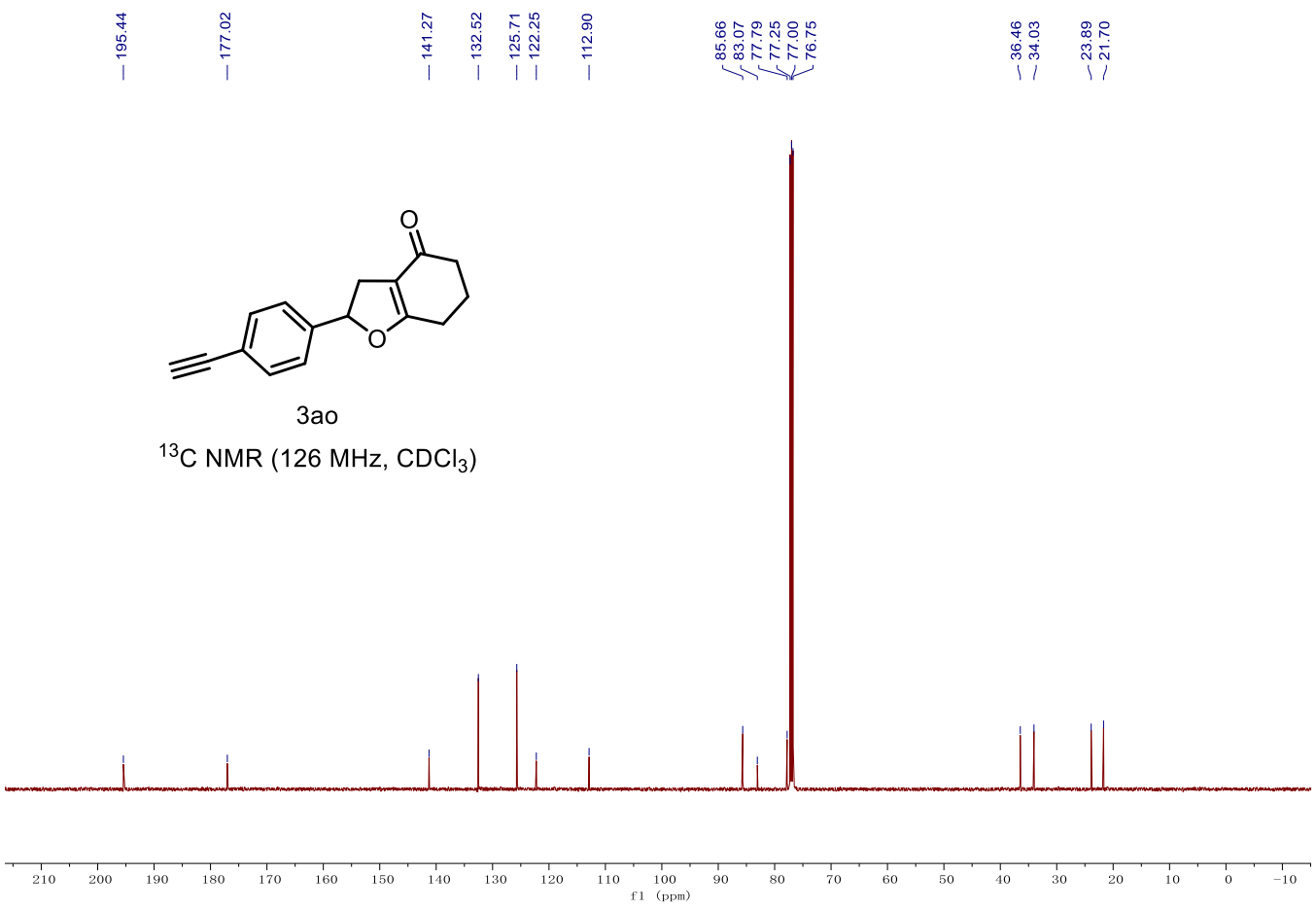
3an

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



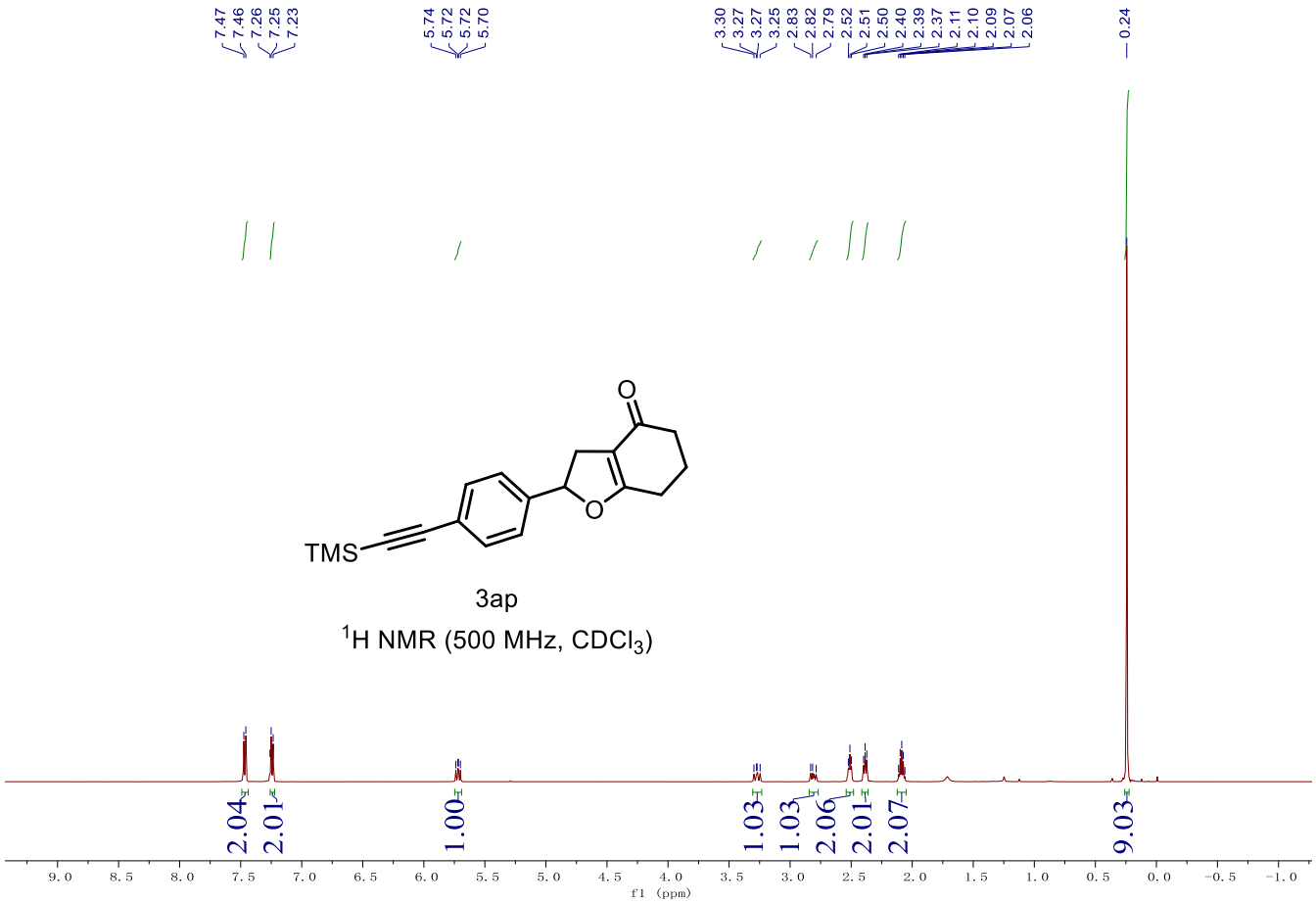
3ao

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



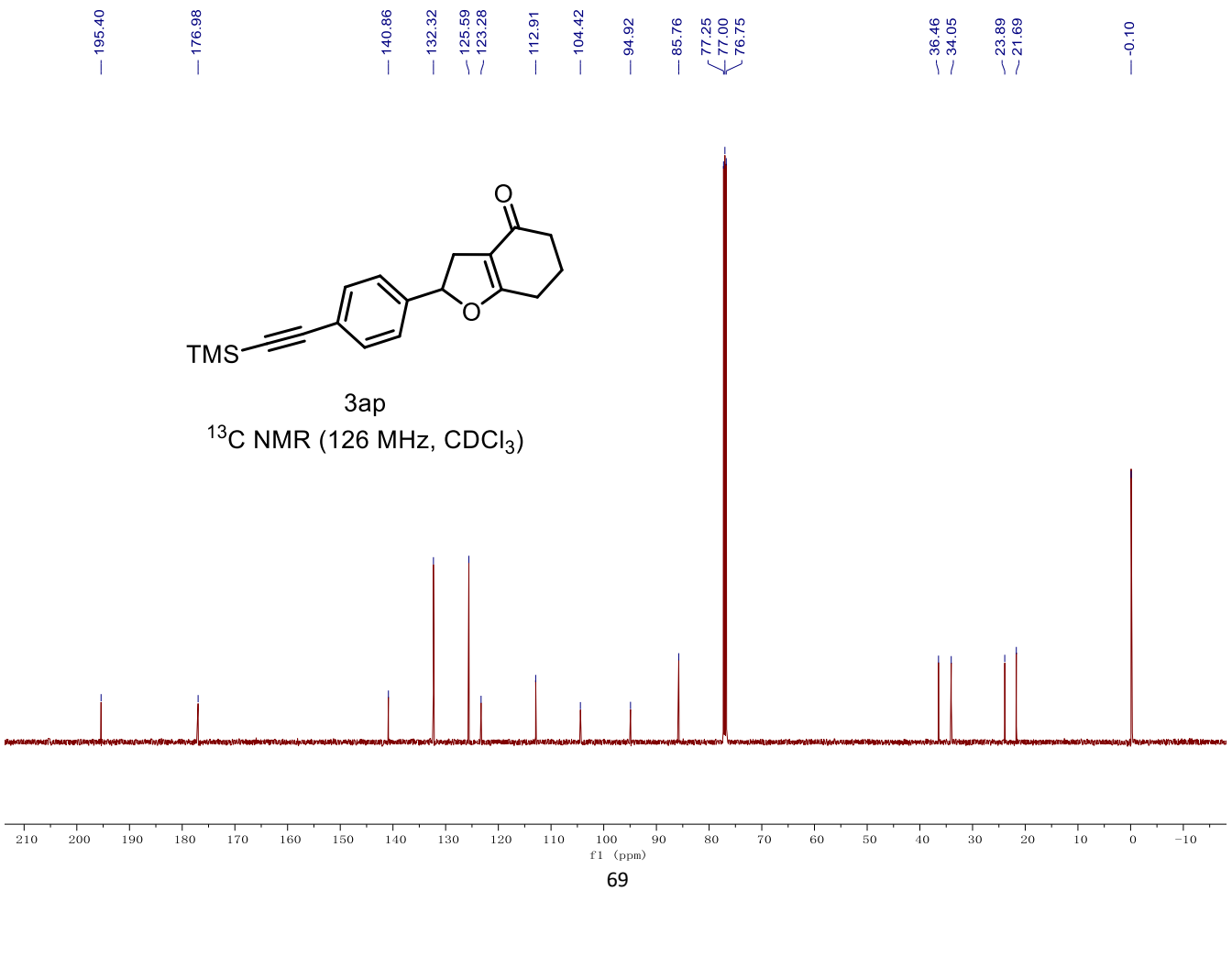
3ao

^{13}C NMR (126 MHz, $CDCl_3$)



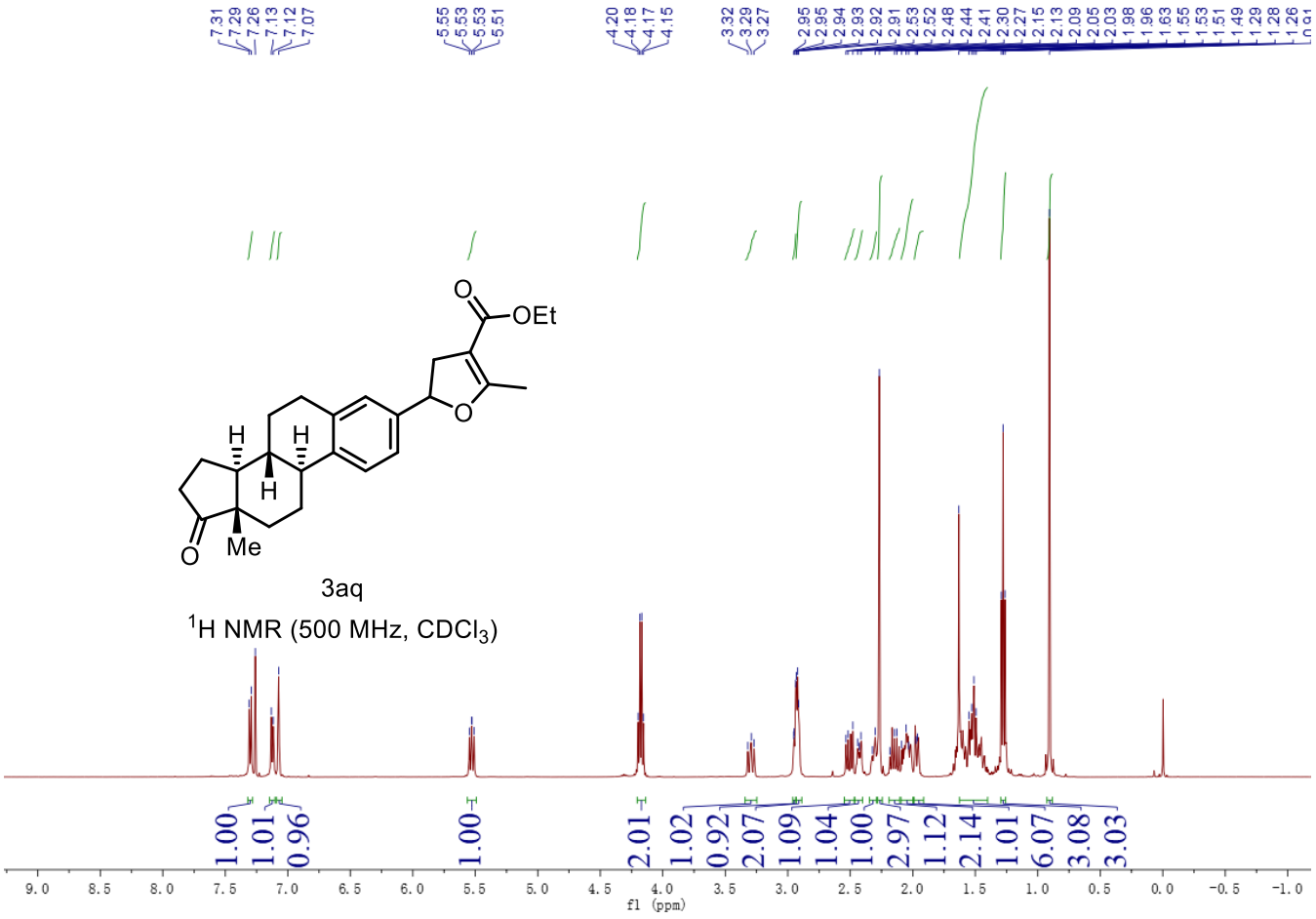
3ap

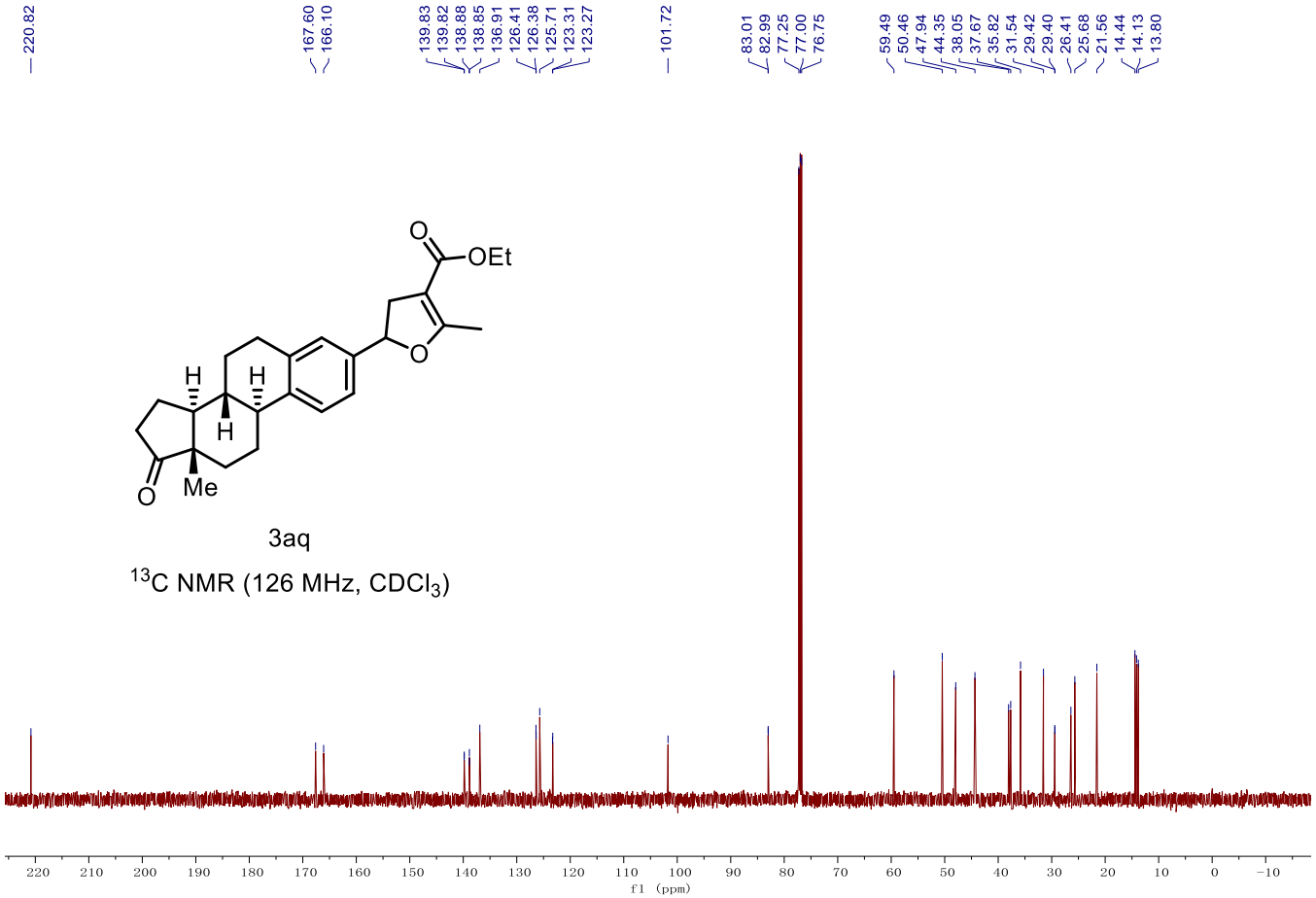
^{1}H NMR (500 MHz, $CDCl_3$)

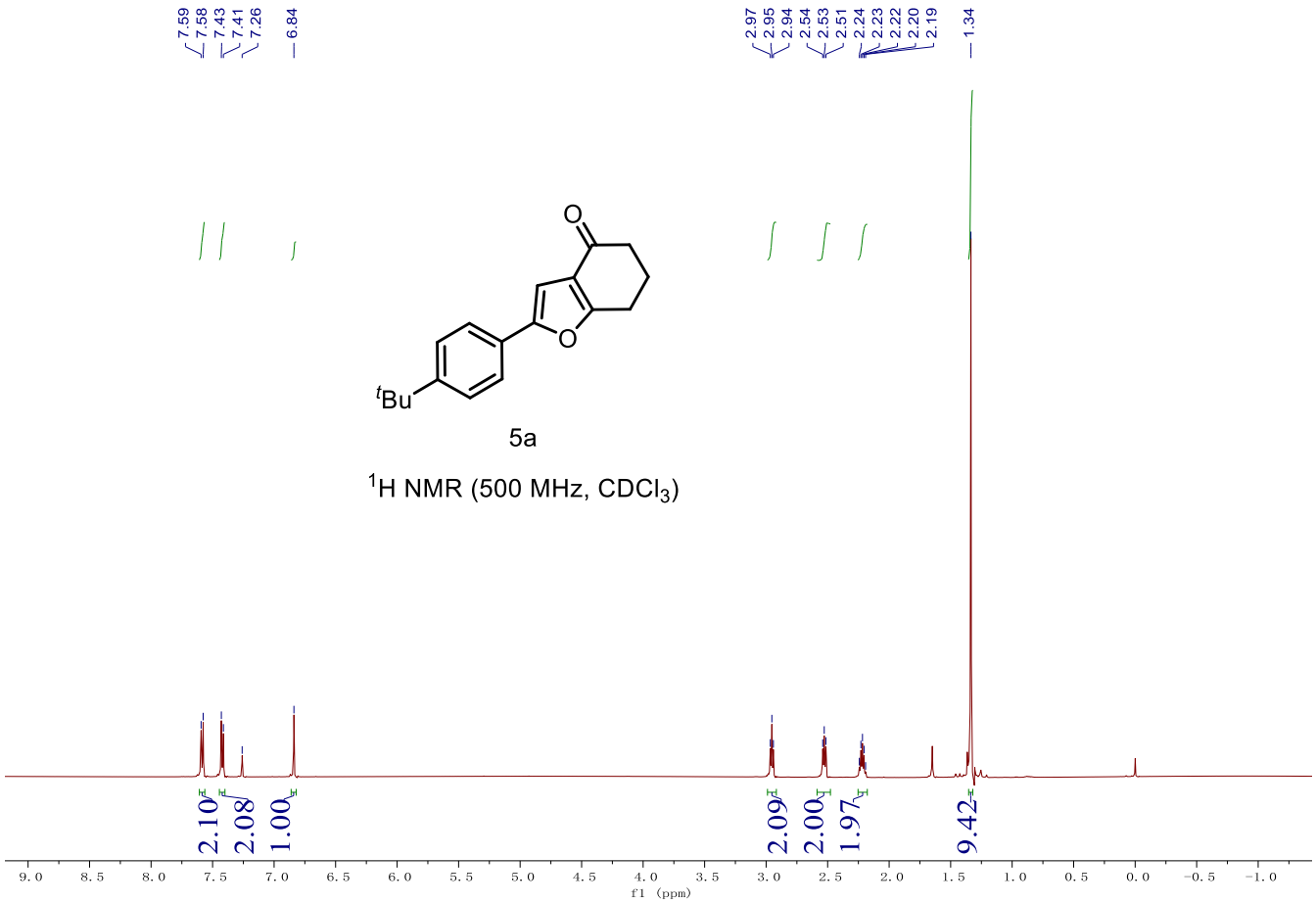


3ap

^{13}C NMR (126 MHz, $CDCl_3$)

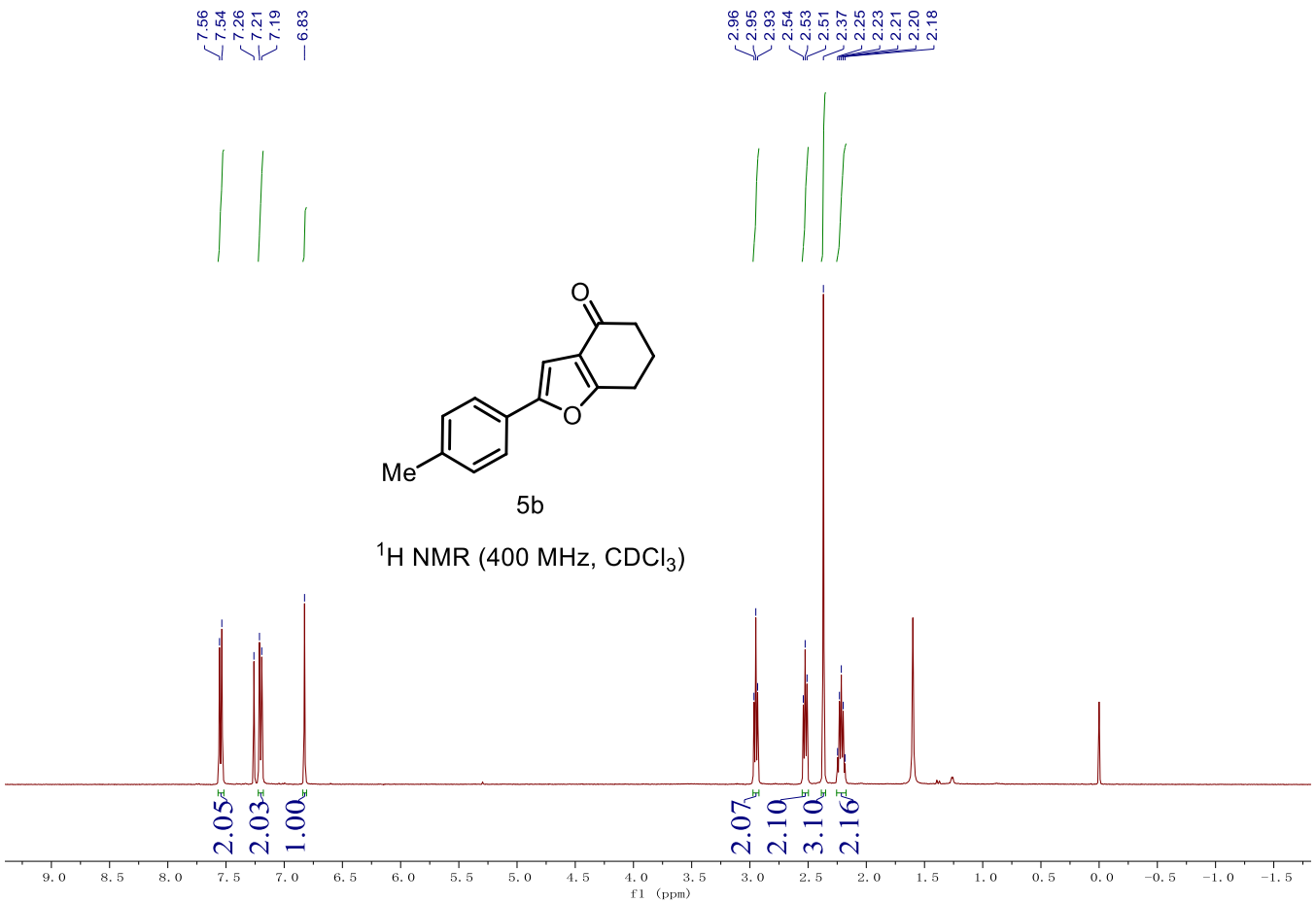

OEt
O
H
H
H
O
Me
3aq
1H NMR (500 MHz, CDCl3)
f1 (ppm)


OEt
O
H
H
H
O
Me
3aq
13C NMR (126 MHz, CDCl3)
f1 (ppm)



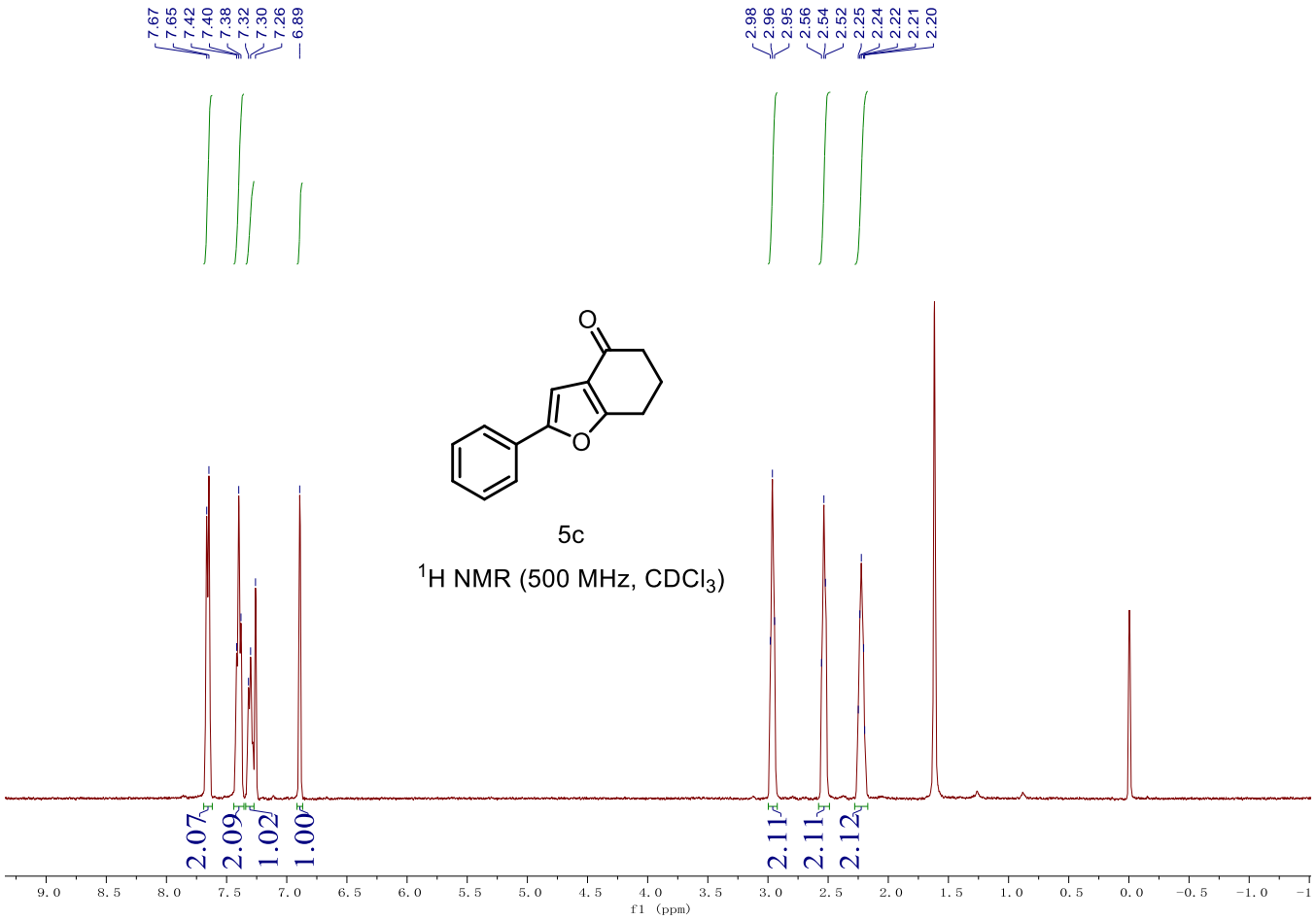
5a

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



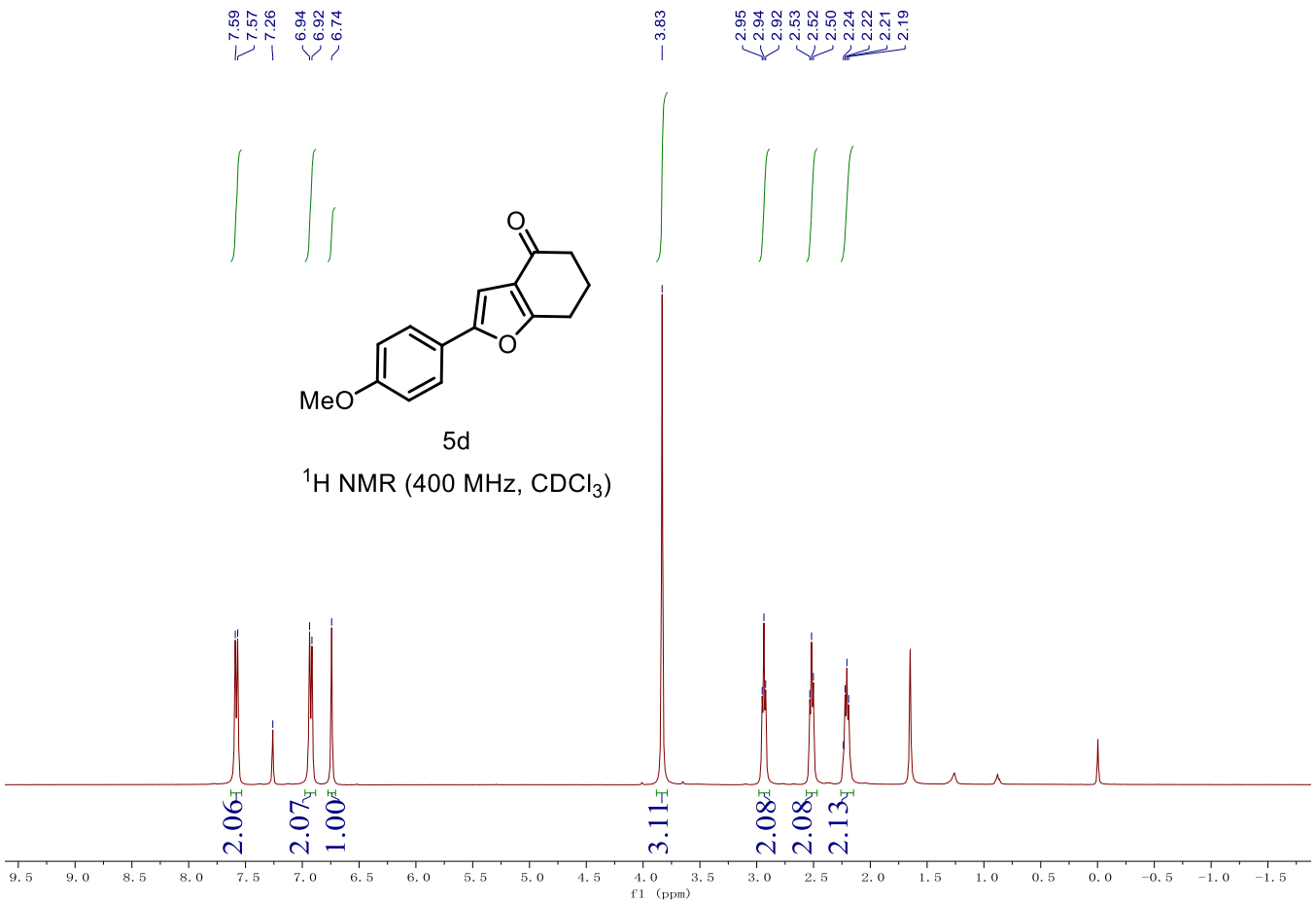
5b

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



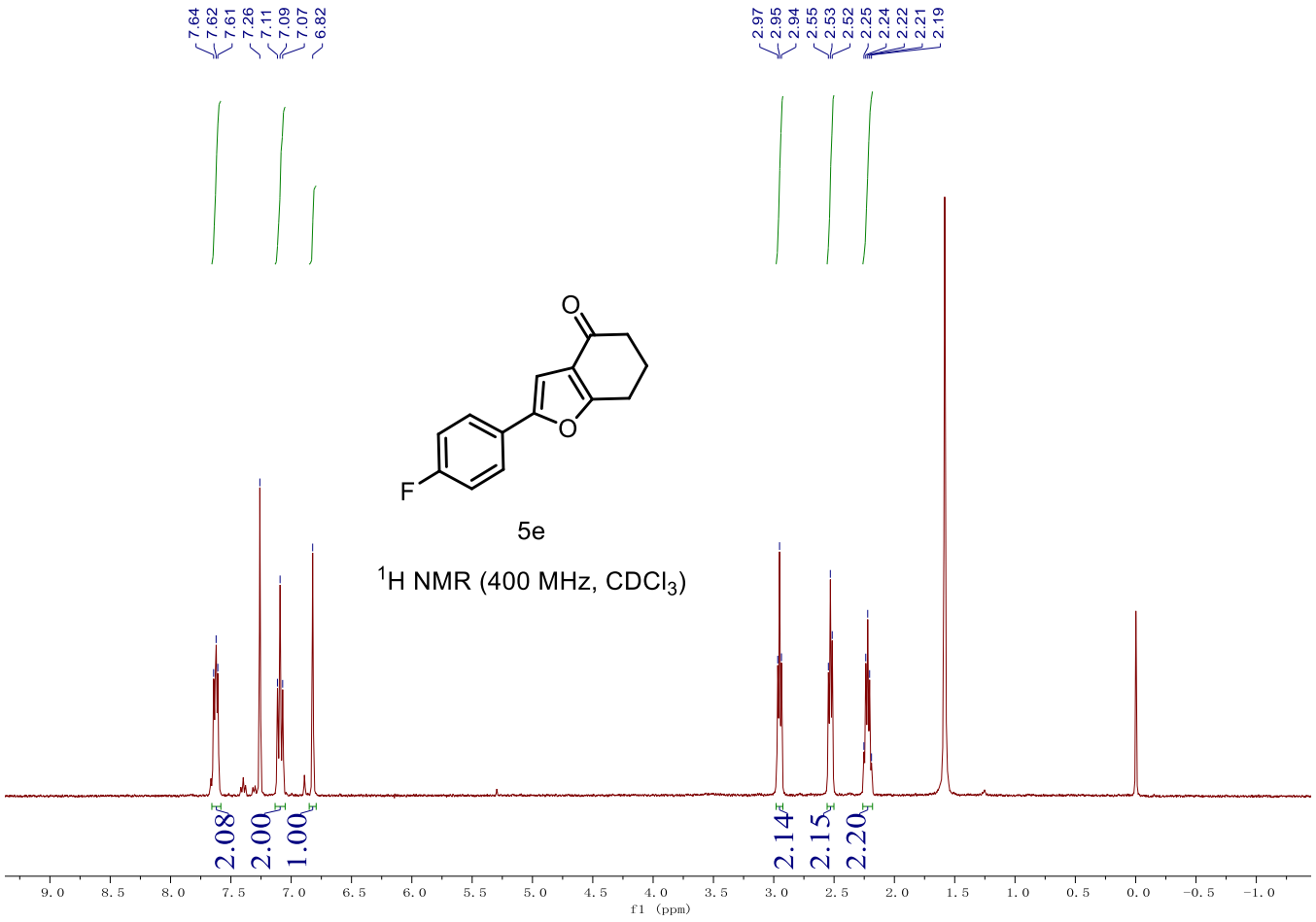
5c

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



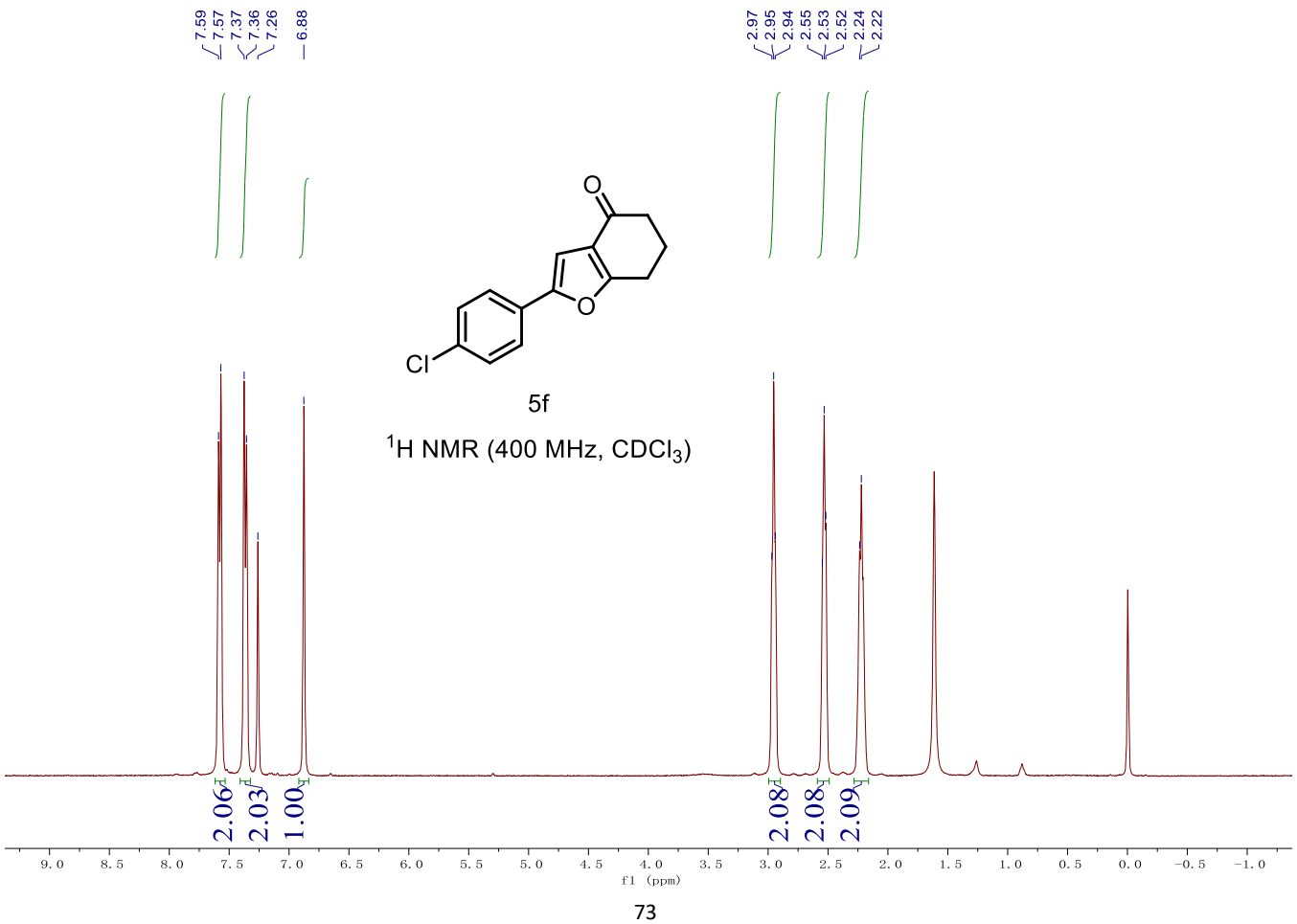
5d

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



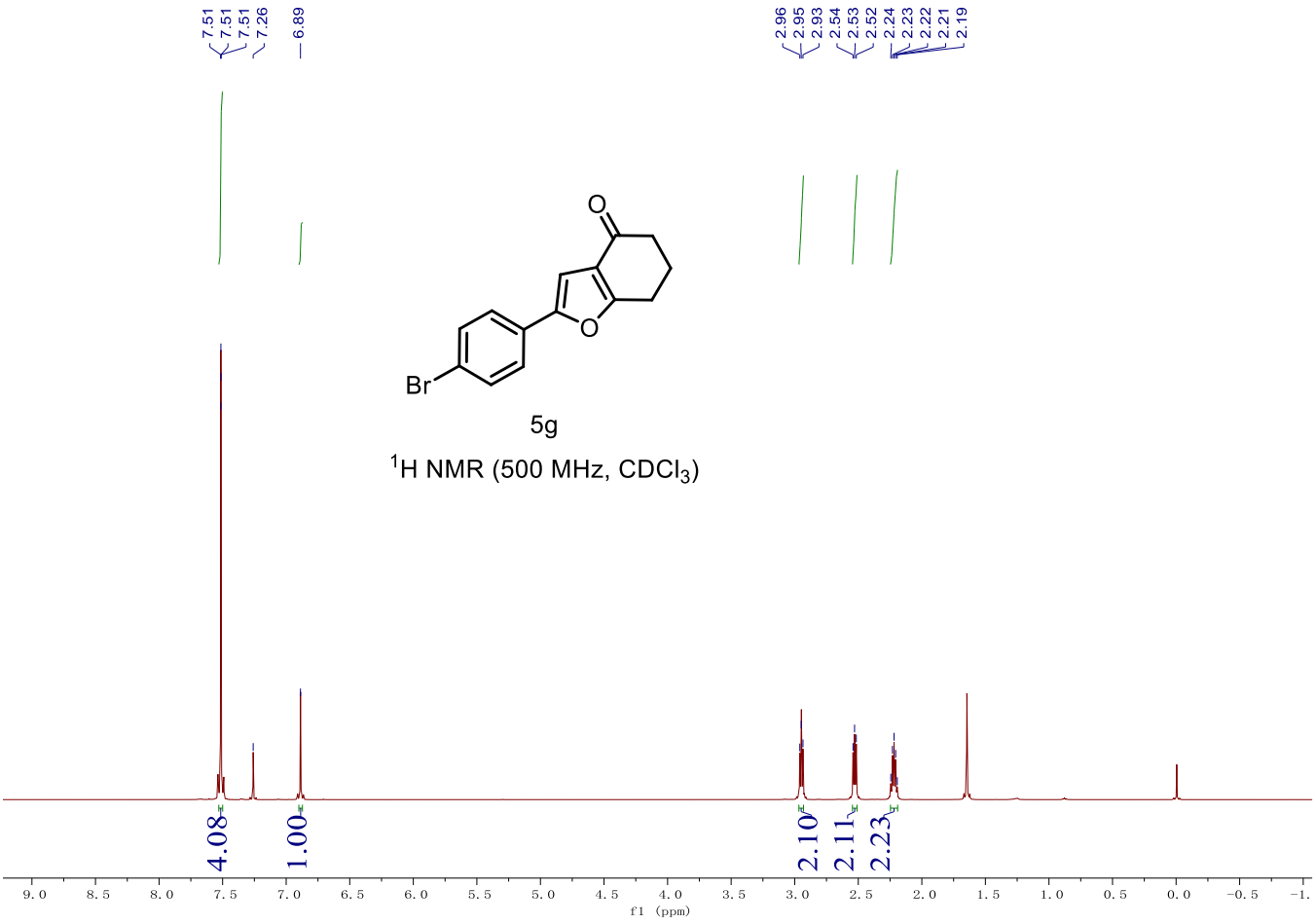
5e

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



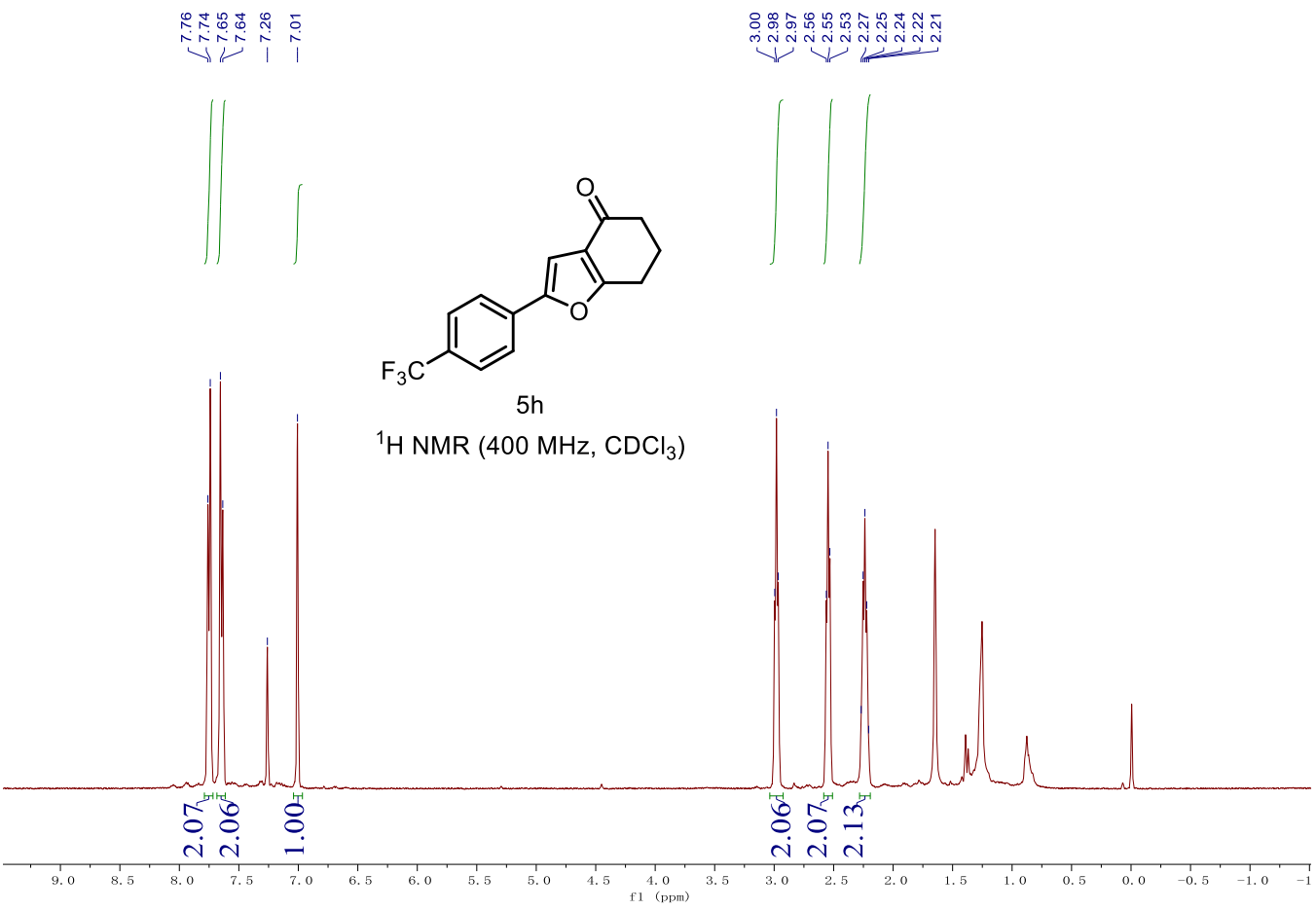
5f

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



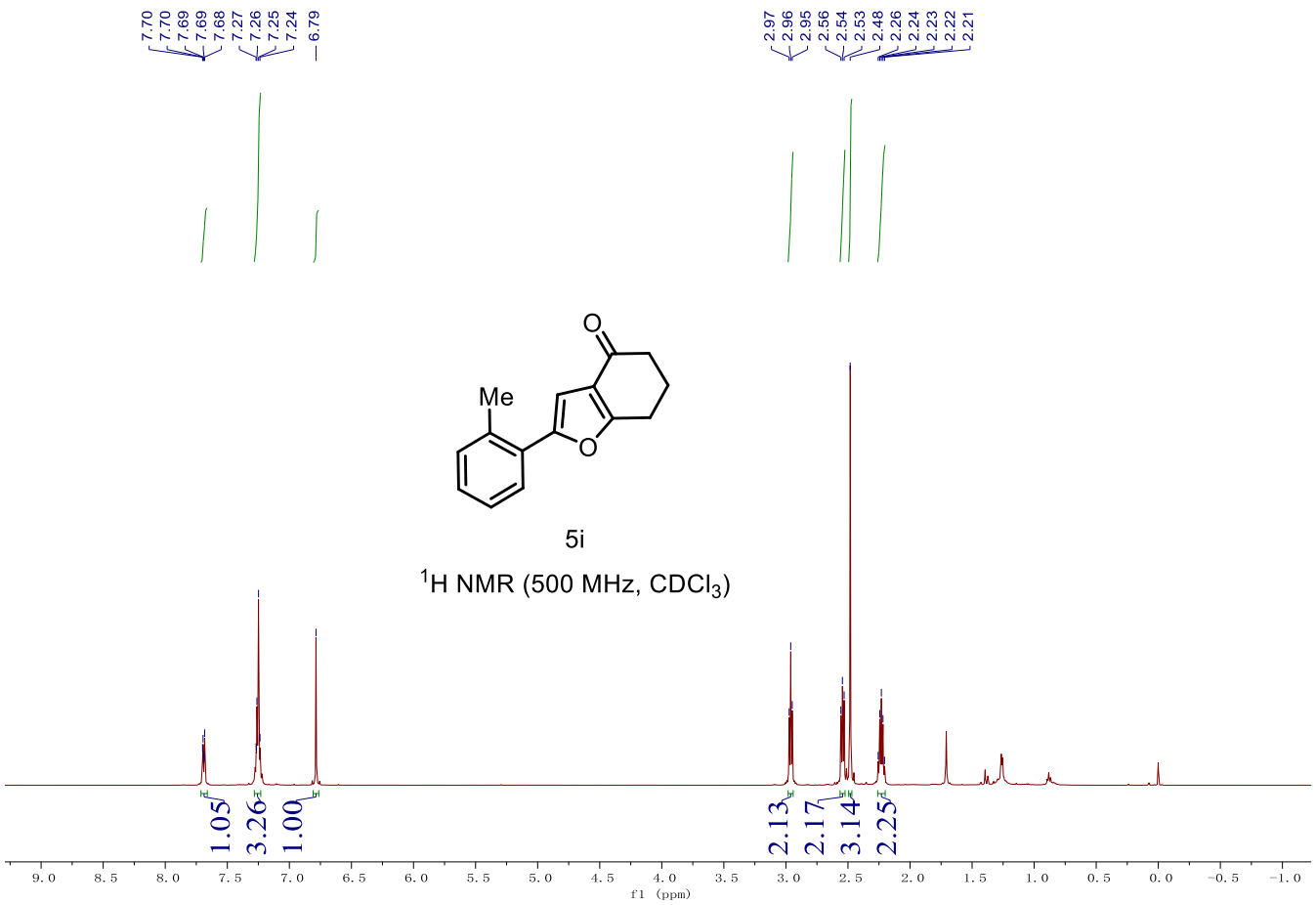
5g

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



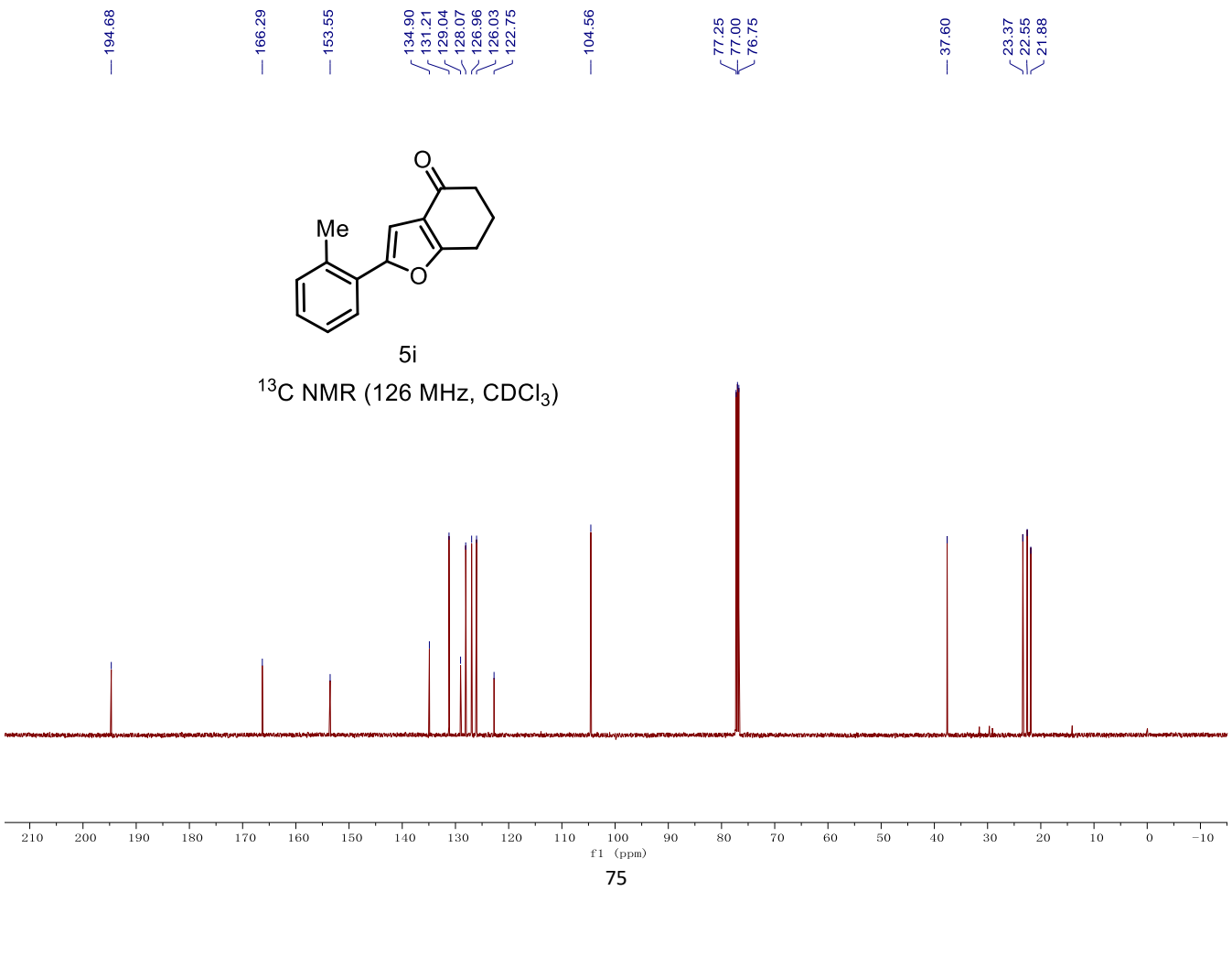
5h

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



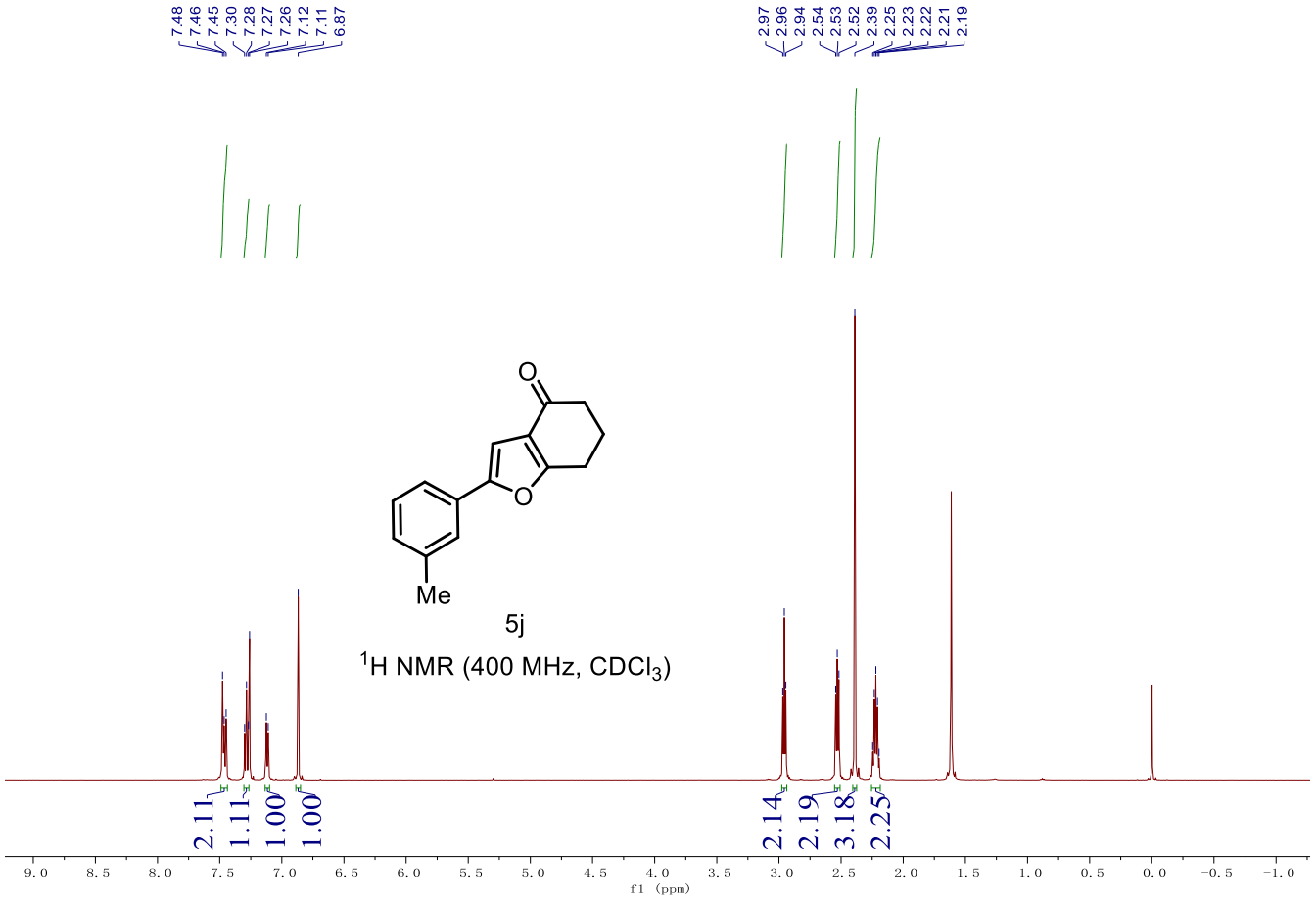
5i

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



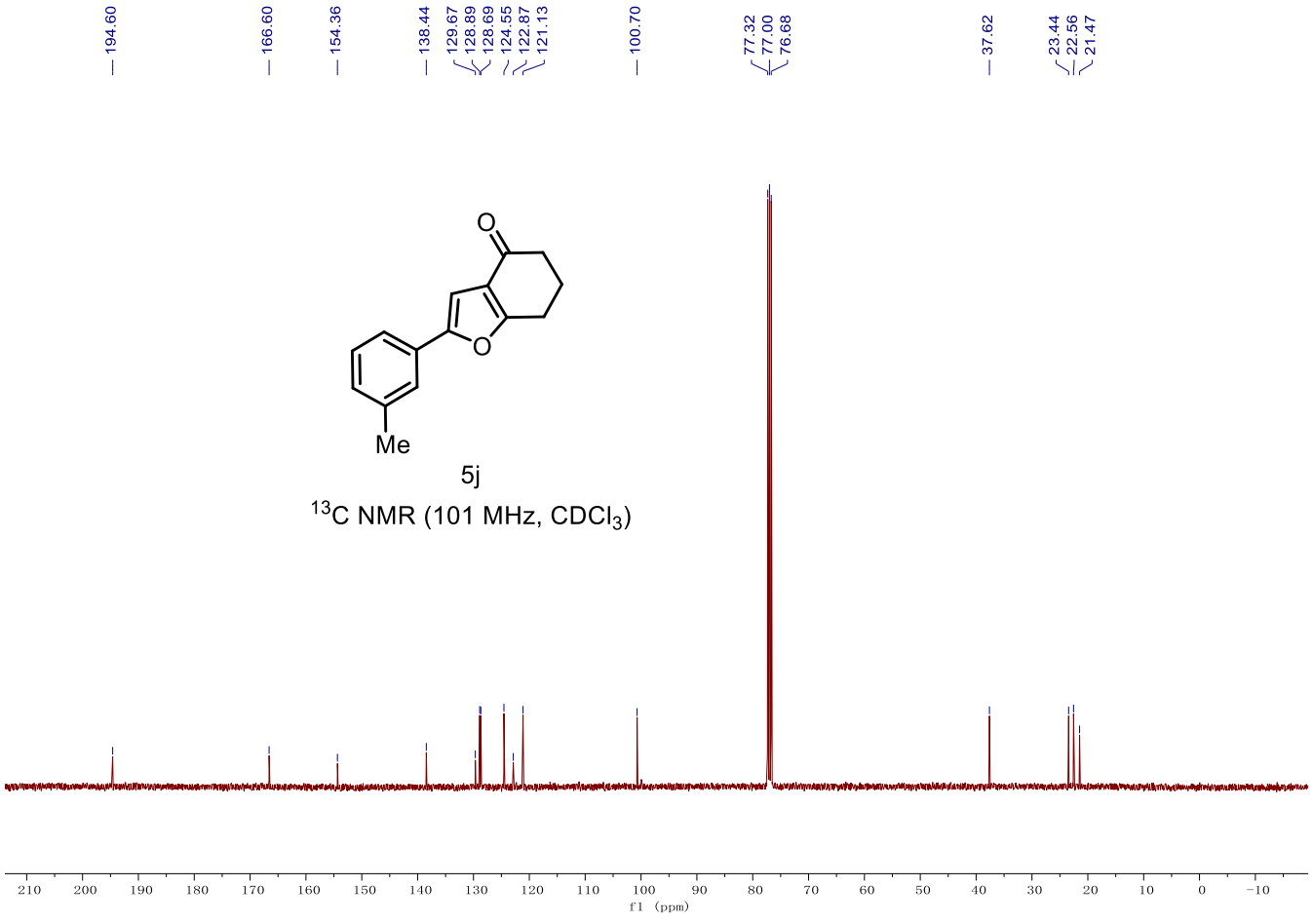
5i

^{13}C NMR (126 MHz, $CDCl_3$)



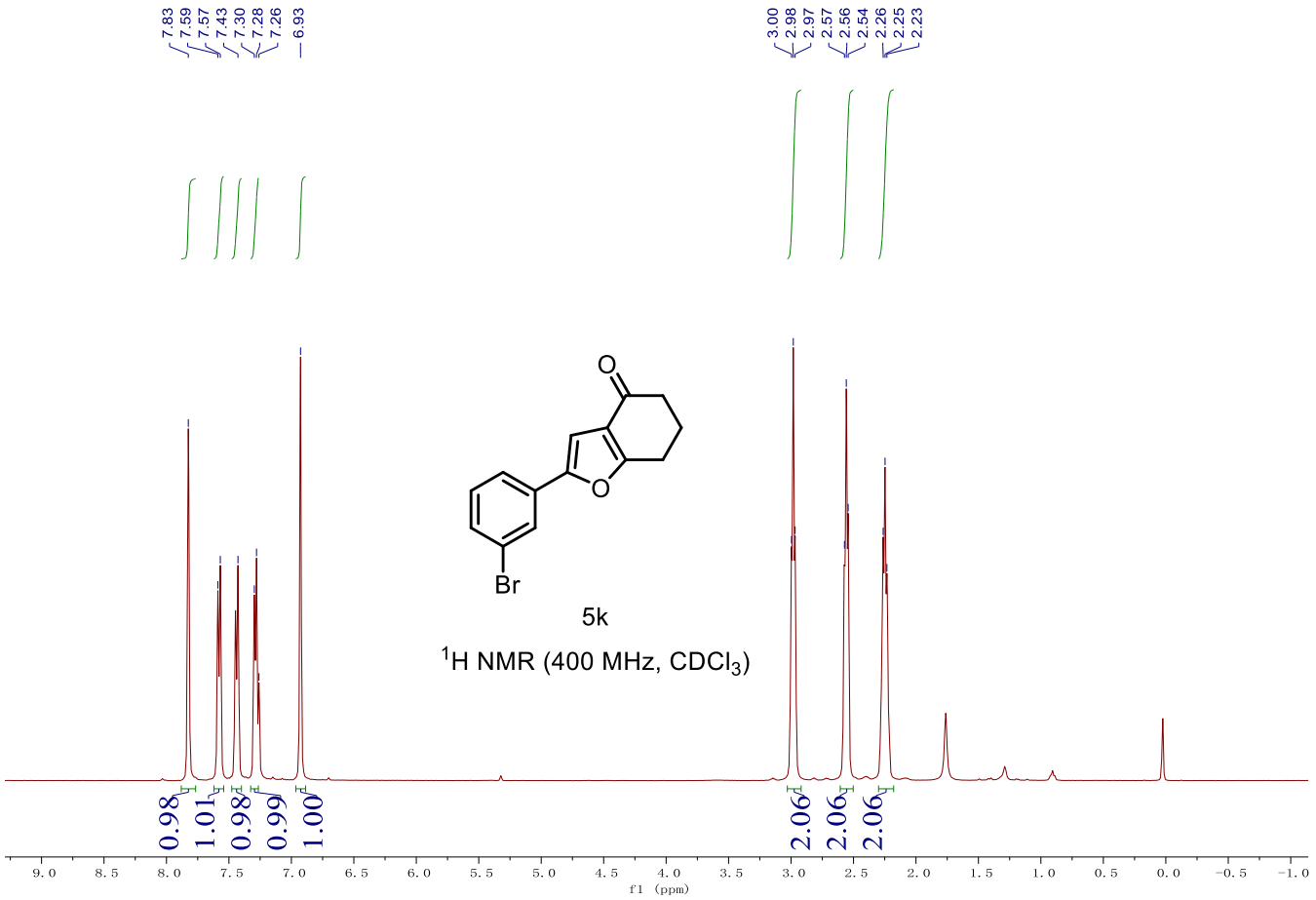
5j

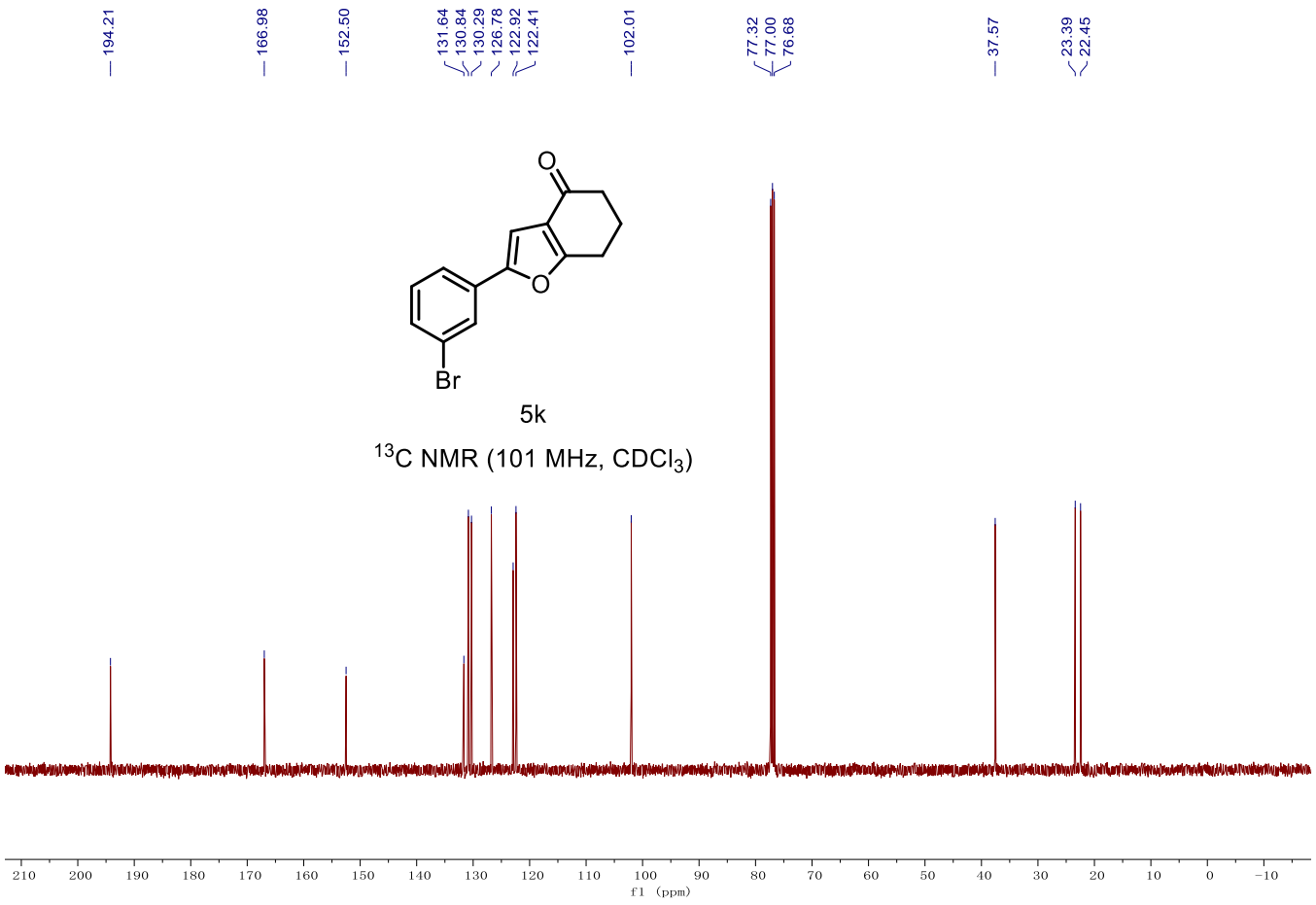
^{1}H NMR (400 MHz, $CDCl_3$)

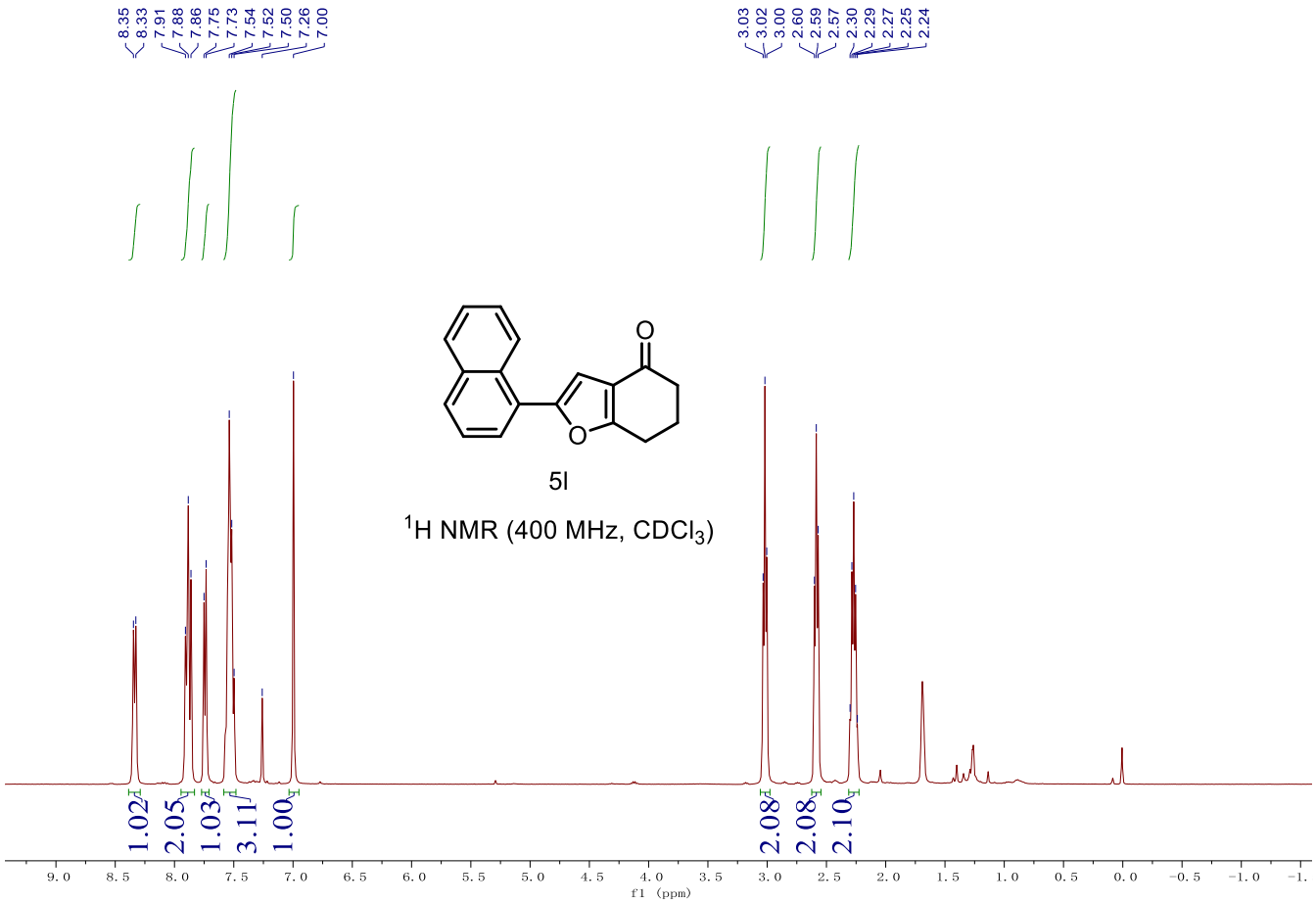


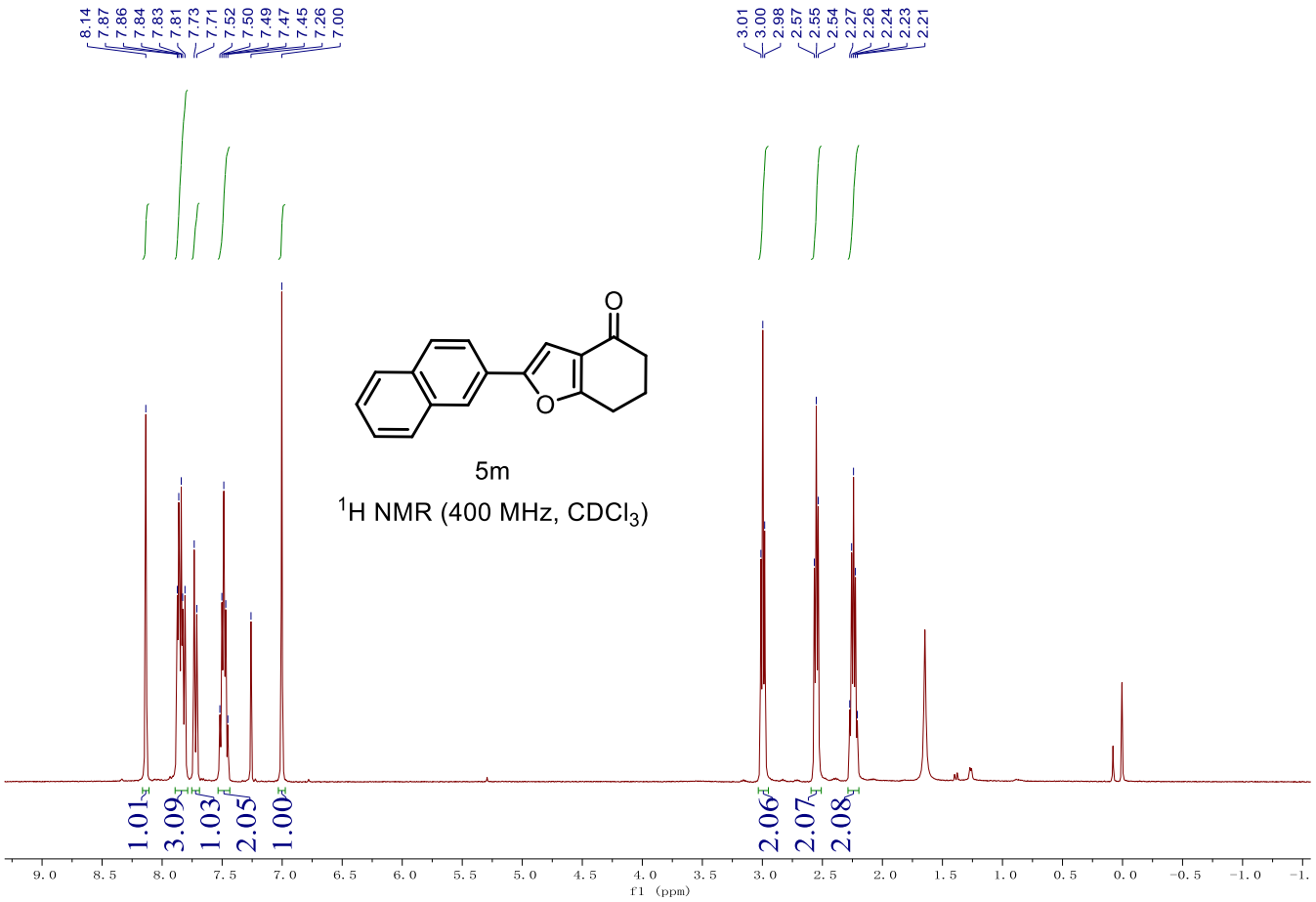
5j

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


7.83
7.59
7.57
7.43
7.30
7.28
7.26
6.93
3.00
2.98
2.97
2.57
2.56
2.54
2.26
2.25
2.23
O
O
Br
5k
^{1}H NMR (400 MHz, CDCl$_3$)
0.98
1.01
0.98
0.99
1.00
2.06
2.06
2.06
f1 (ppm)

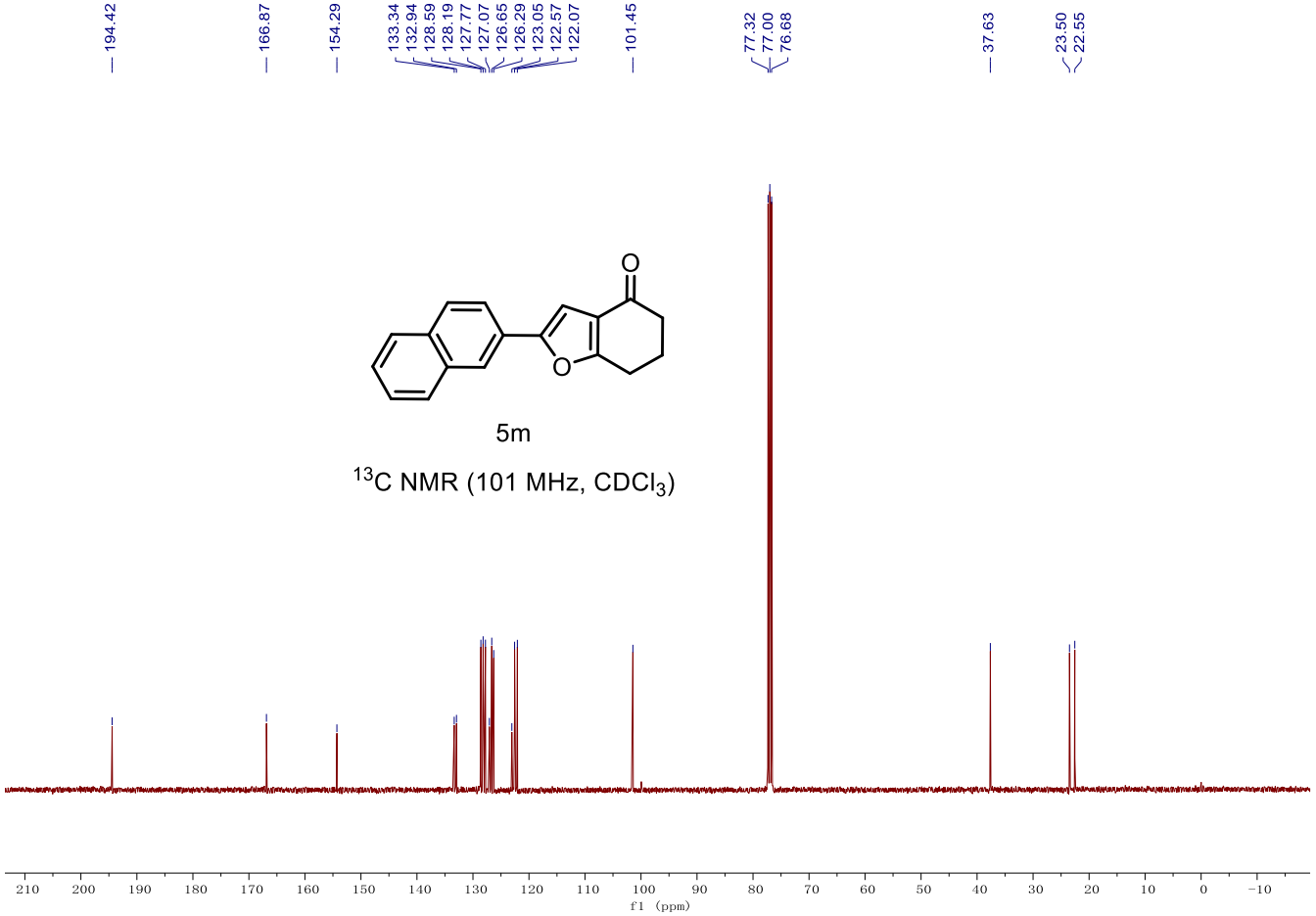

194.21
166.98
152.50
131.64
130.84
130.29
126.78
122.92
122.41
102.01
77.32
77.00
76.68
37.57
23.39
22.45
O
O
Br
5k
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)


8.35
8.33
7.91
7.88
7.86
7.75
7.73
7.54
7.52
7.50
7.26
7.00
3.03
3.02
3.00
2.60
2.59
2.57
2.30
2.29
2.27
2.25
2.24
O
O
5l
^{1}H NMR (400 MHz, $CDCl_3$)
1.02
2.05
1.03
3.11
1.00
2.08
2.08
2.10
f1 (ppm)



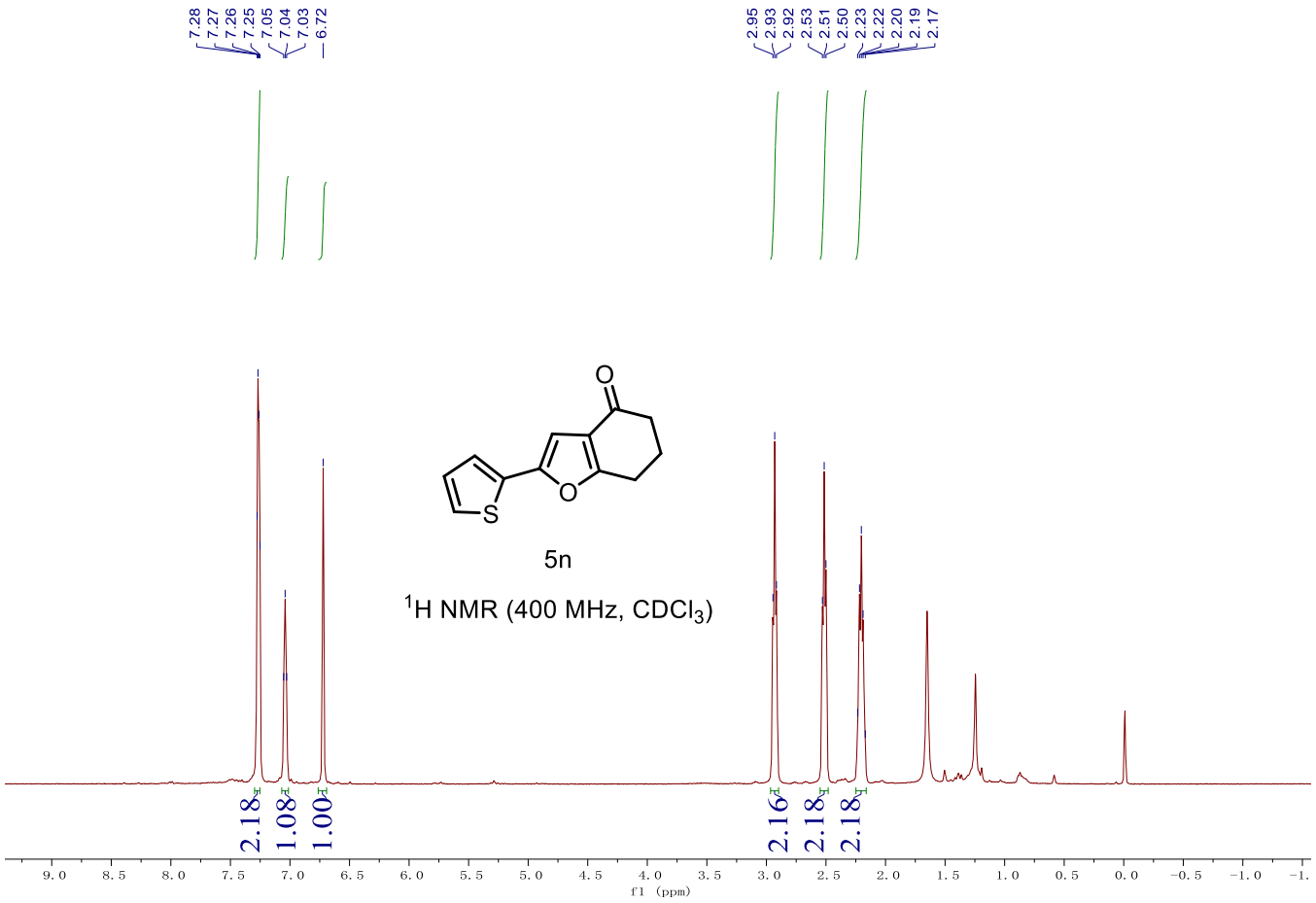
5m

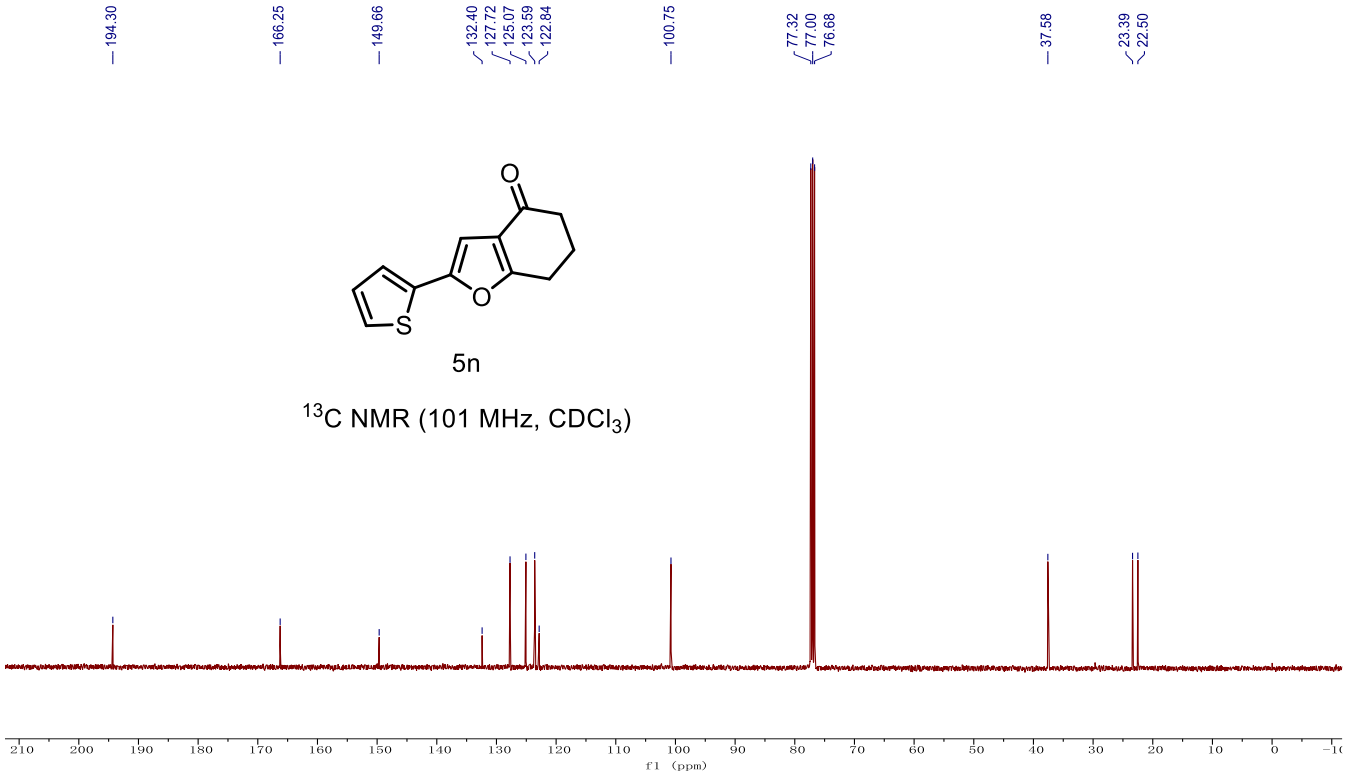
^{1}H NMR (400 MHz, $CDCl_3$)

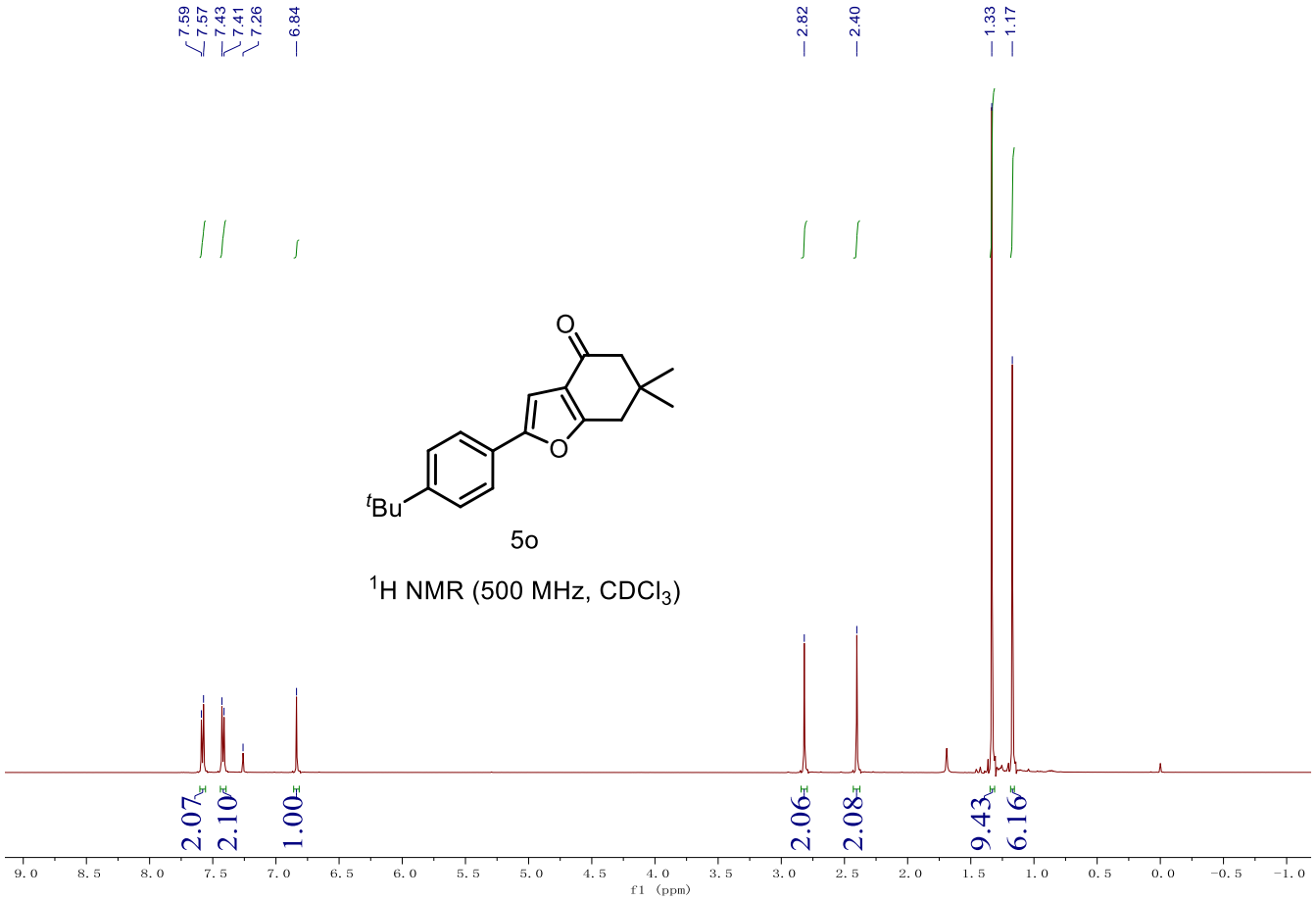


5m

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

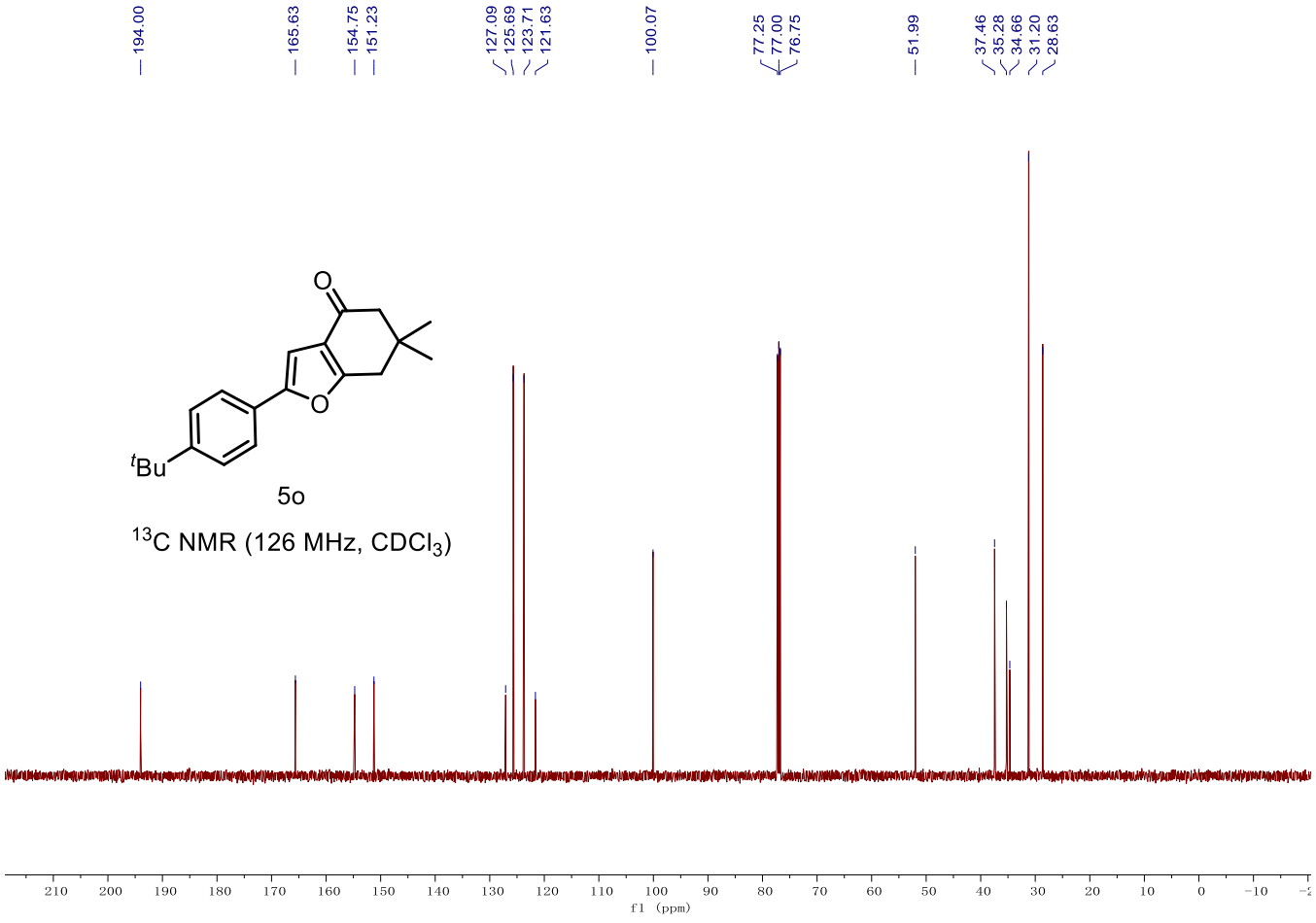

7.28
7.27
7.26
7.25
7.05
7.04
7.03
6.72
2.95
2.93
2.92
2.53
2.51
2.50
2.23
2.22
2.20
2.19
2.17
O
S
O
5n
1H NMR (400 MHz, CDCl3)
2.18
1.08
1.00
2.16
2.18
2.18
f1 (ppm)


194.30
166.25
149.66
132.40
127.72
125.07
123.59
122.84
100.75
77.32
77.00
76.68
37.58
23.39
22.50
O
S
O
5n
13C NMR (101 MHz, CDCl3)
f1 (ppm)



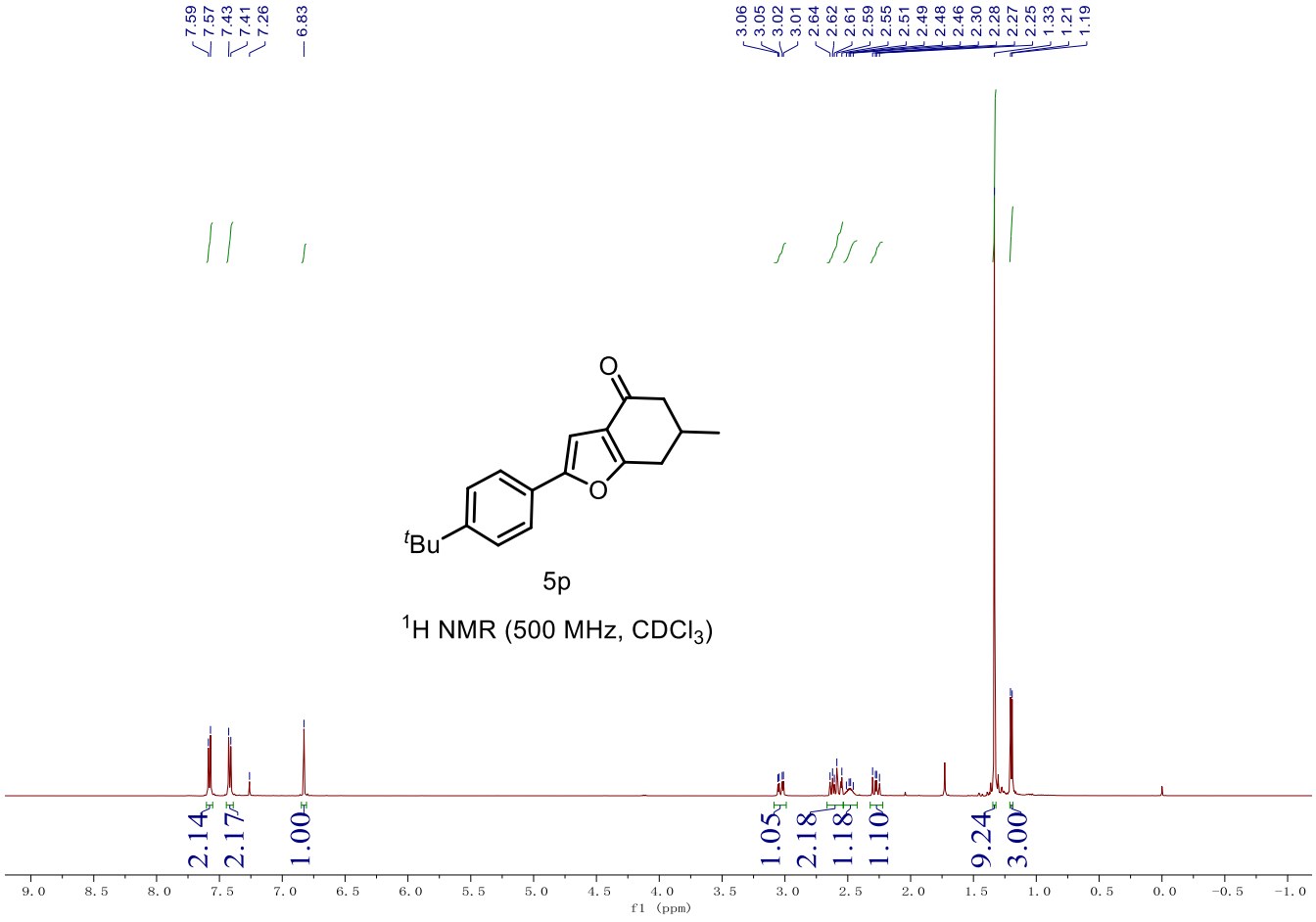
5o

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



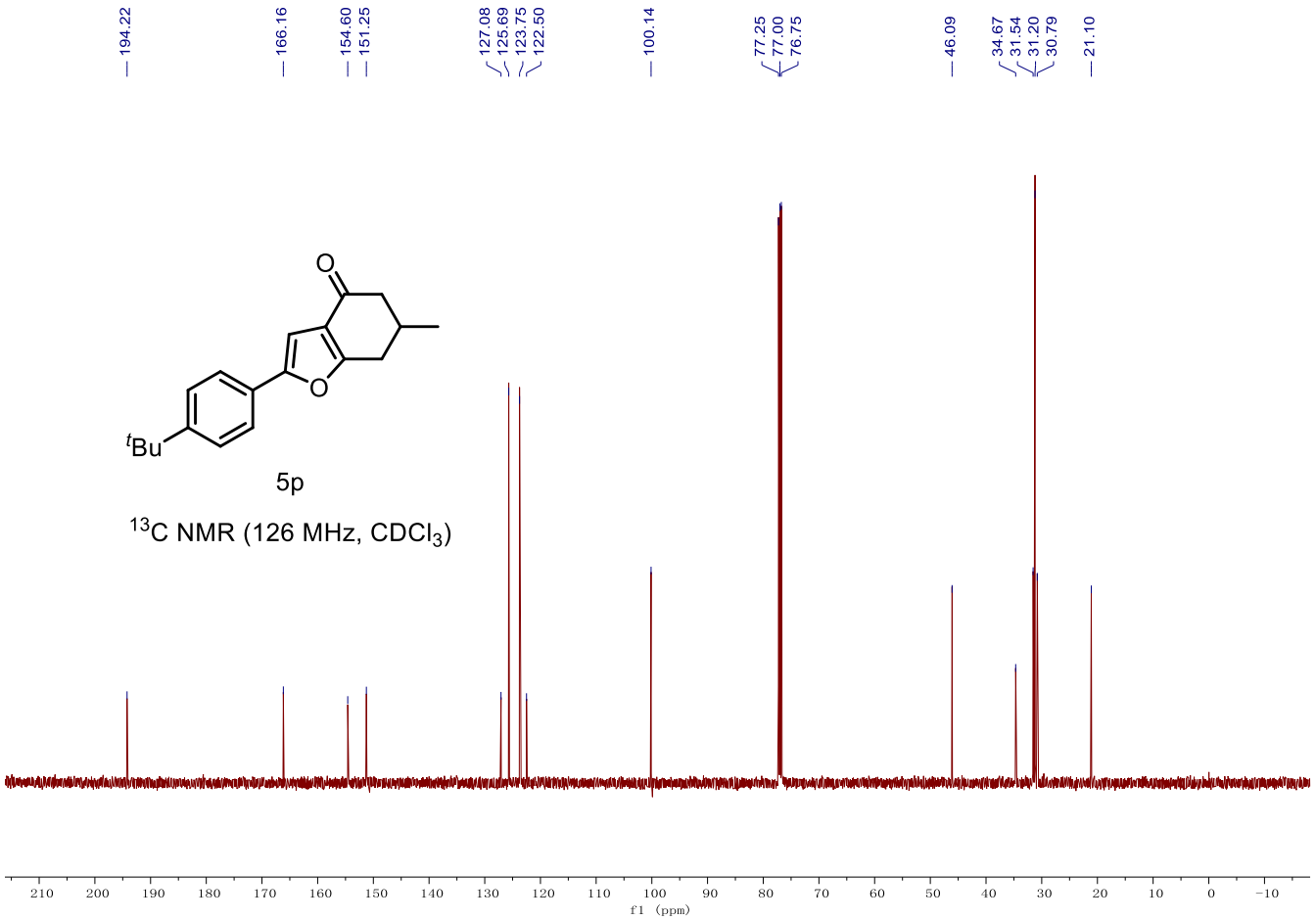
5o

^{13}C NMR (126 MHz, $CDCl_3$)



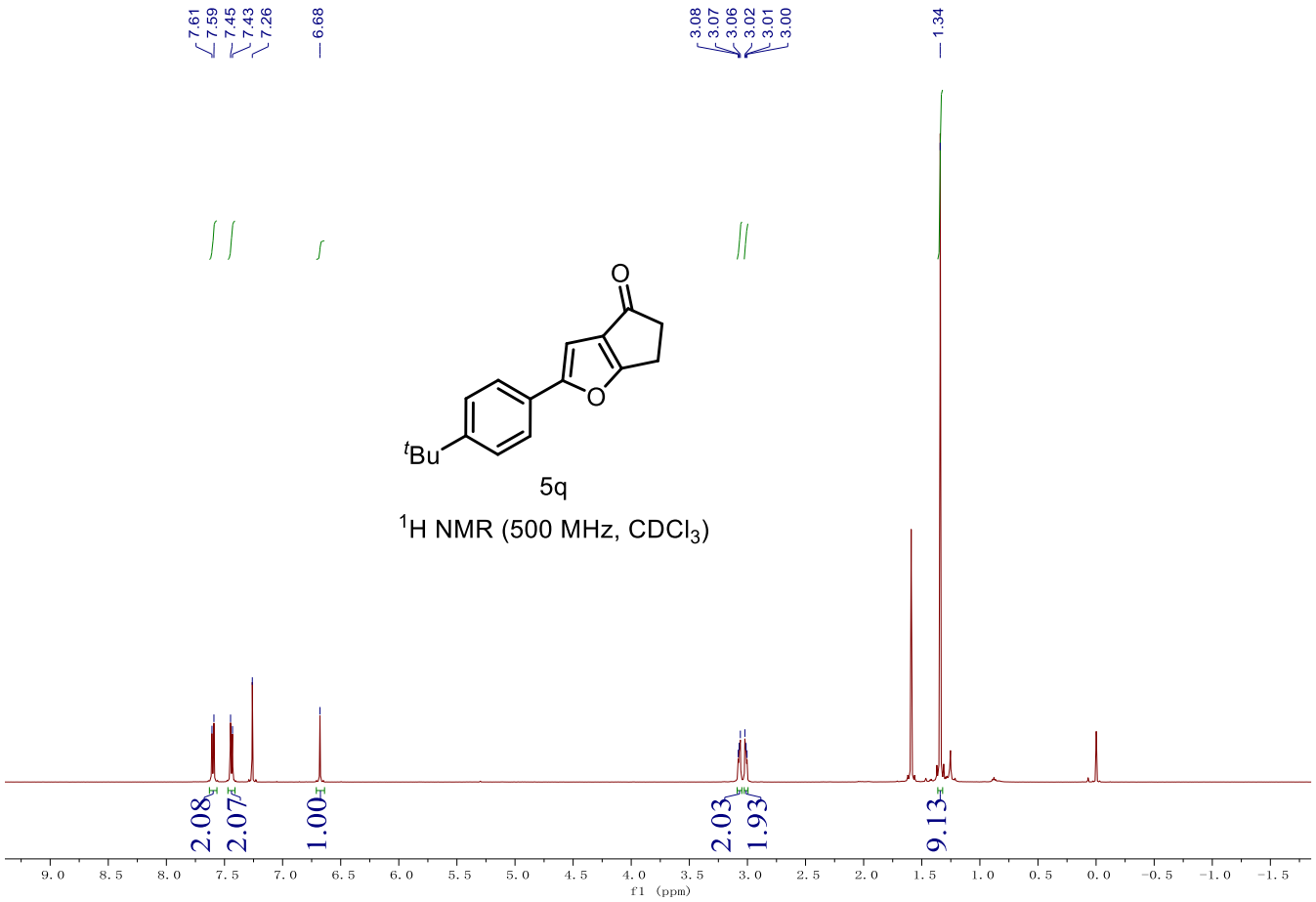
5p

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



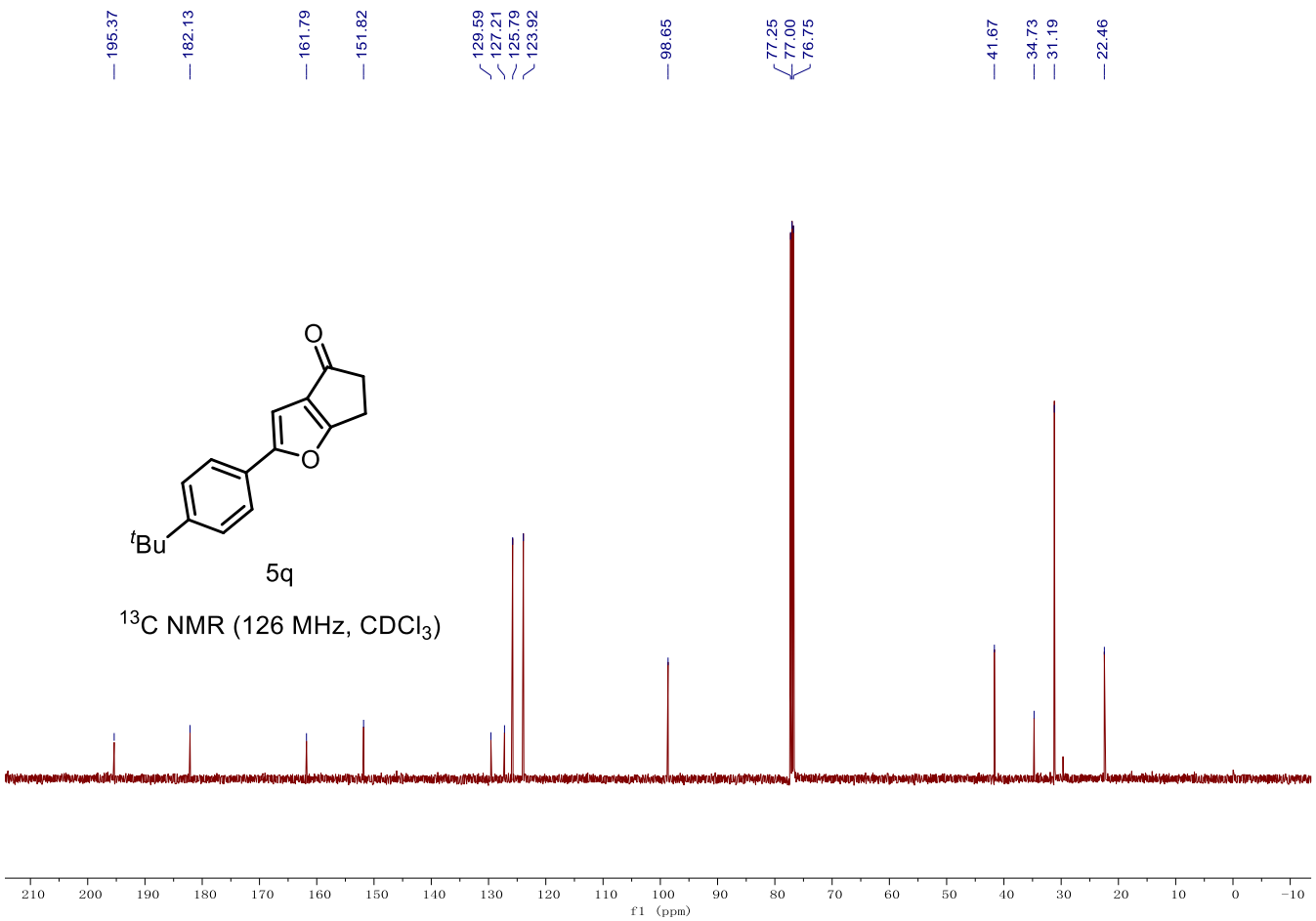
5p

^{13}C NMR (126 MHz, $CDCl_3$)



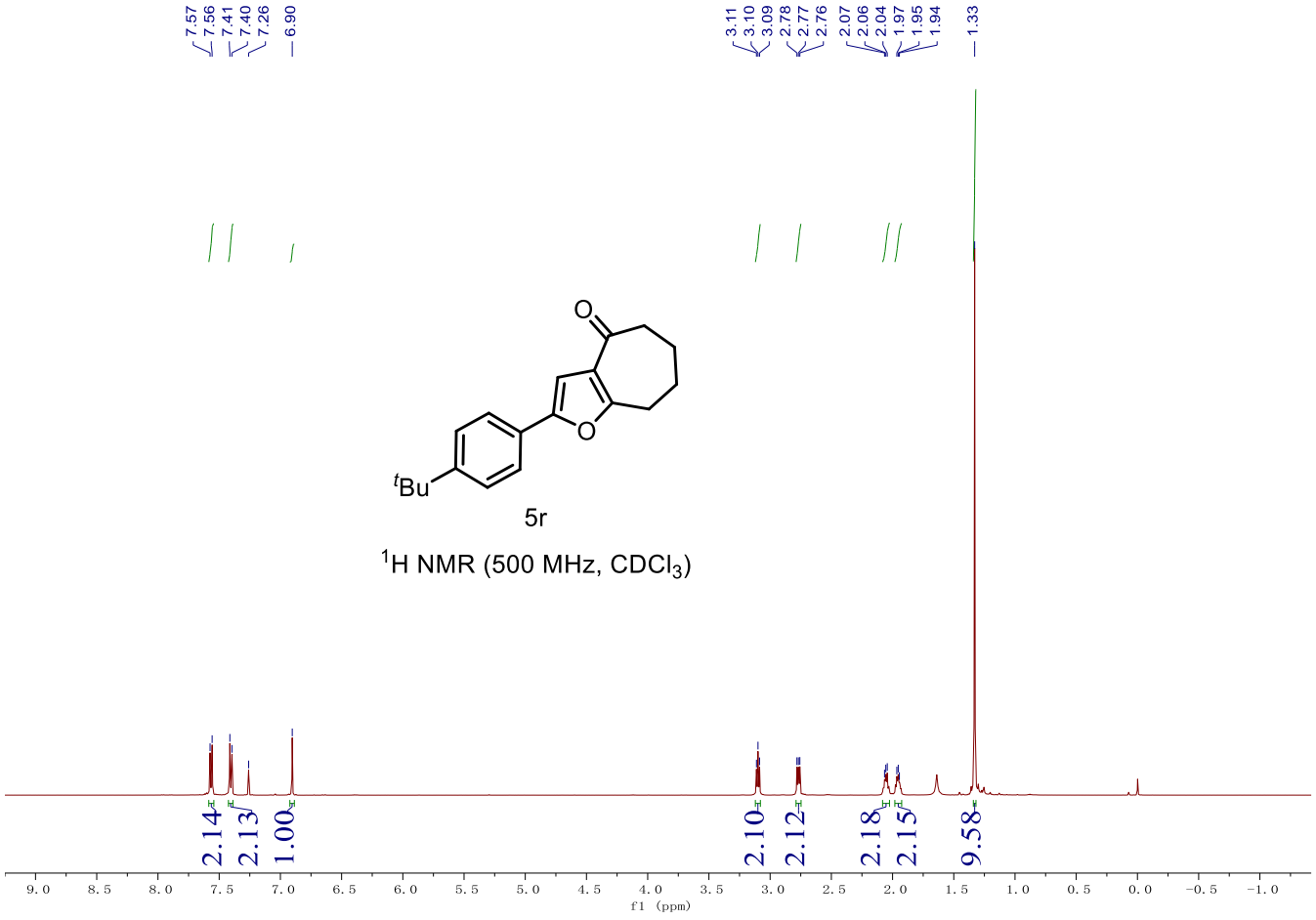
5q

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



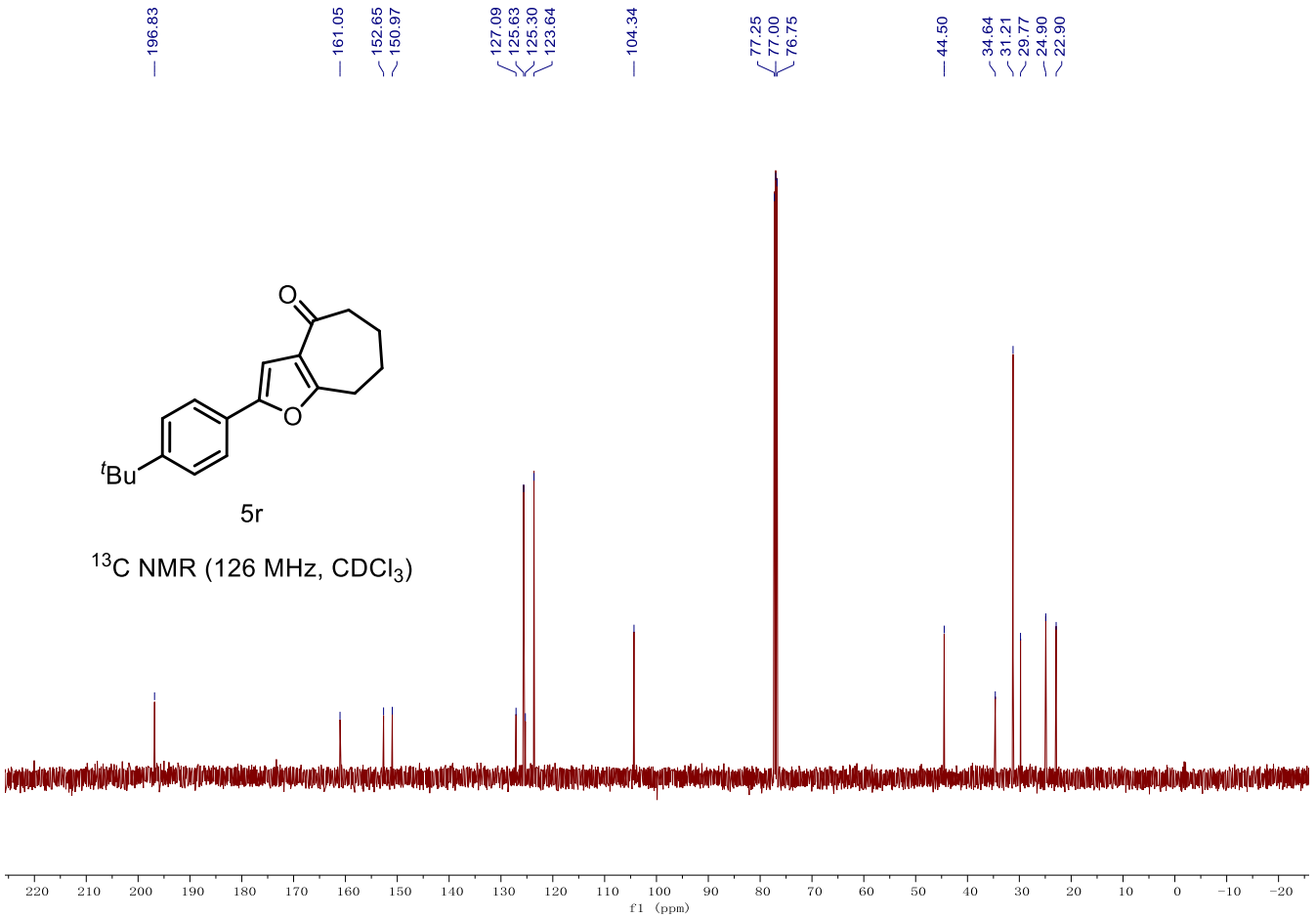
5q

^{13}C NMR (126 MHz, $CDCl_3$)



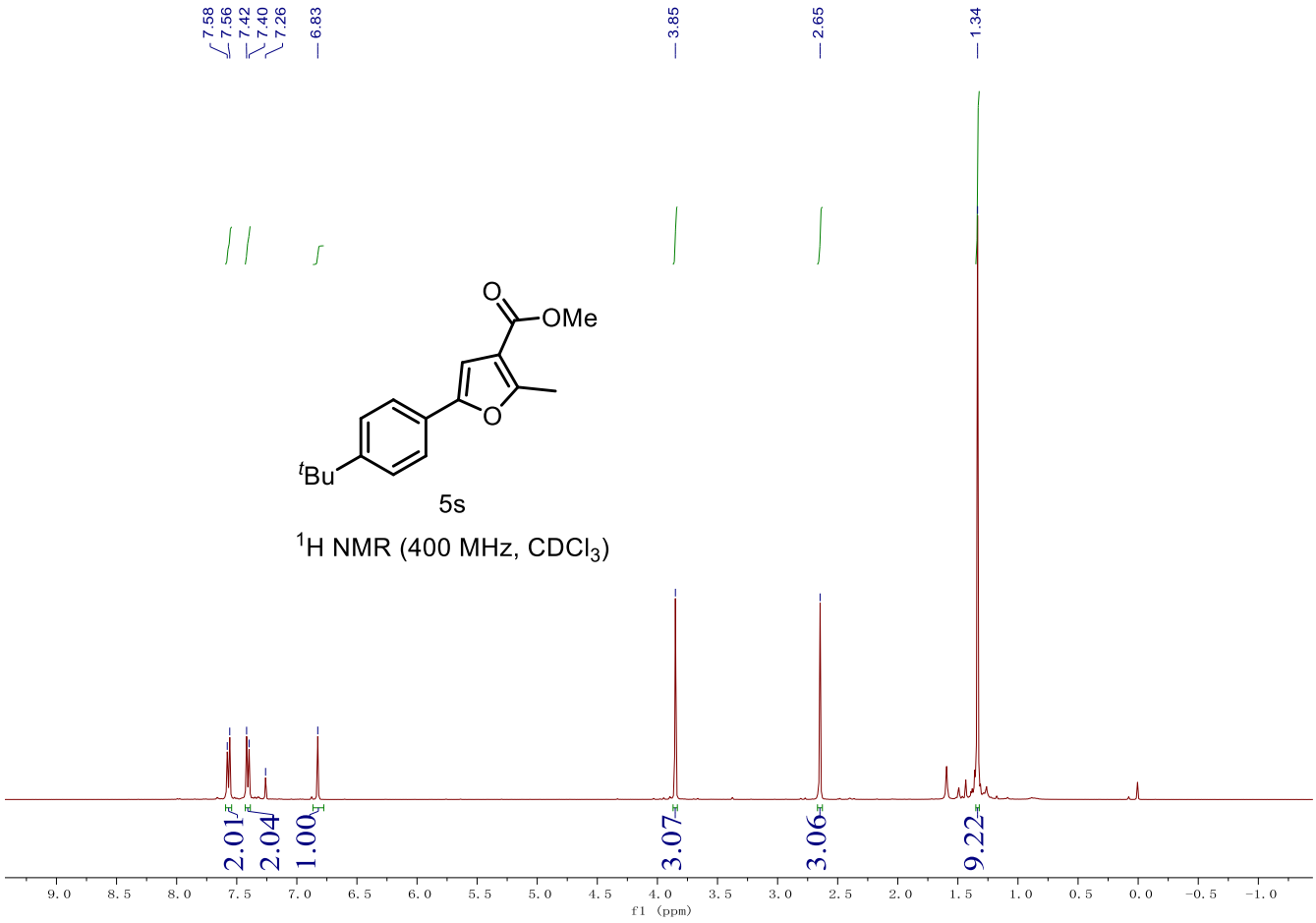
5r

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



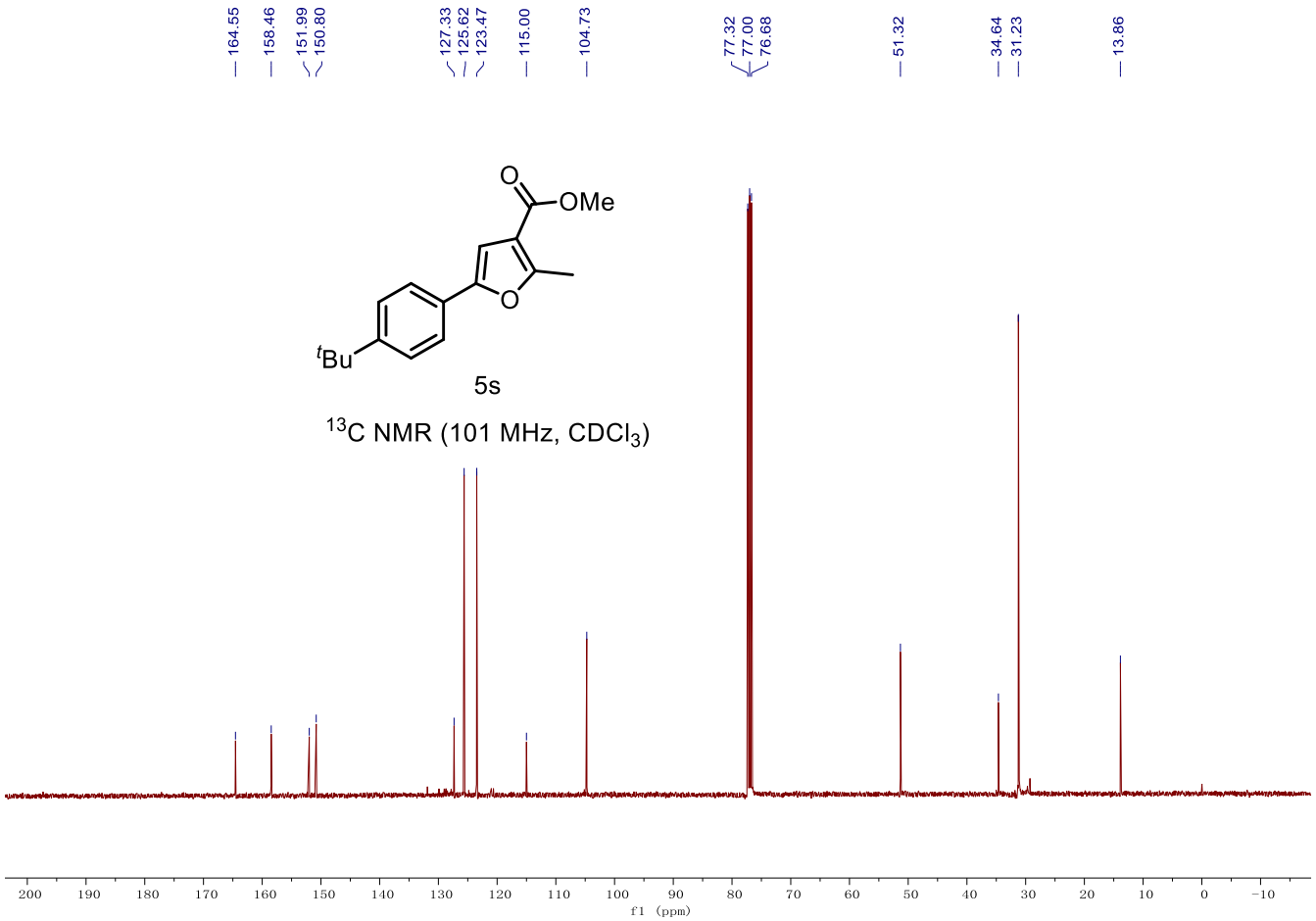
5r

^{13}C NMR (126 MHz, $CDCl_3$)



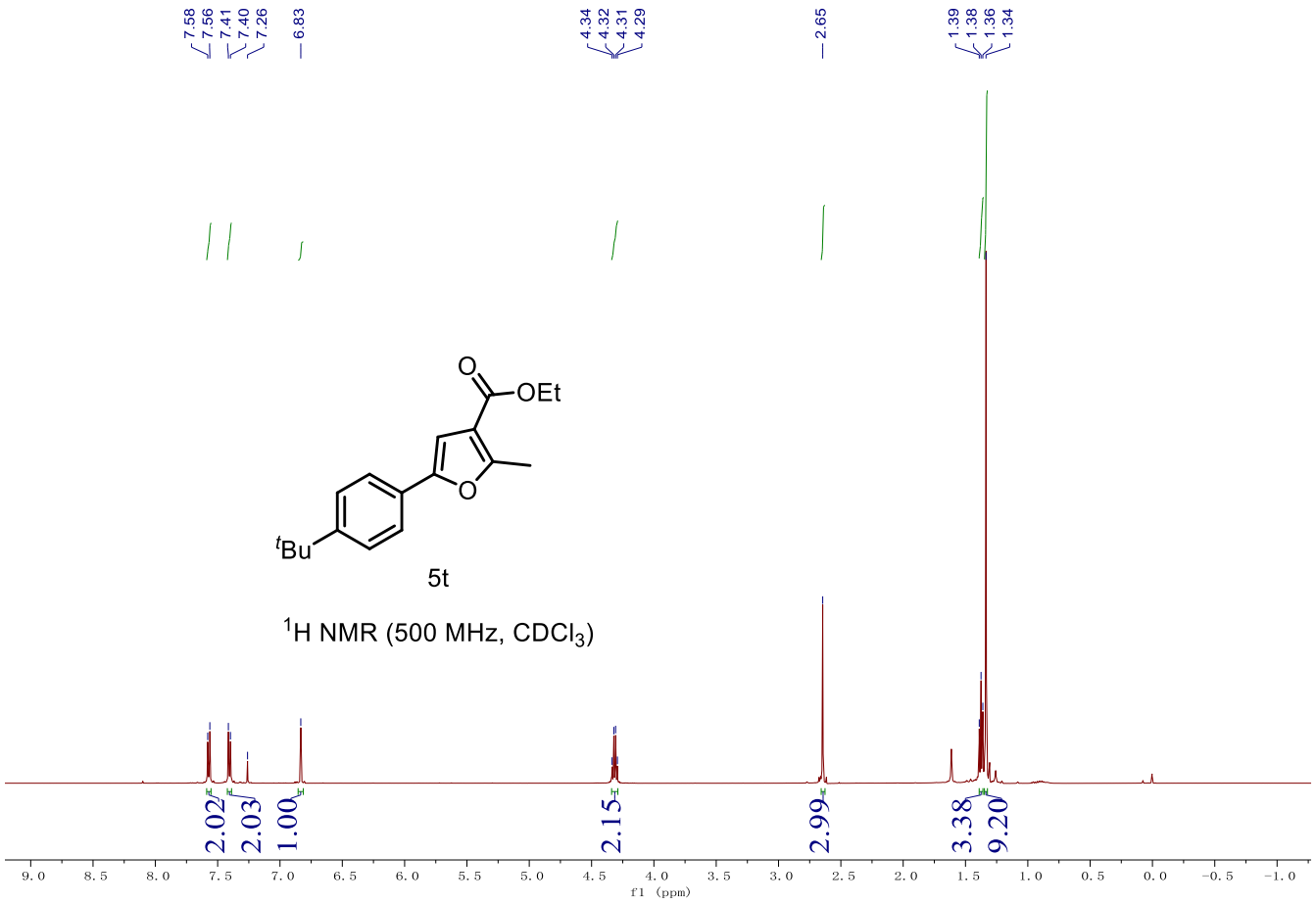
5s

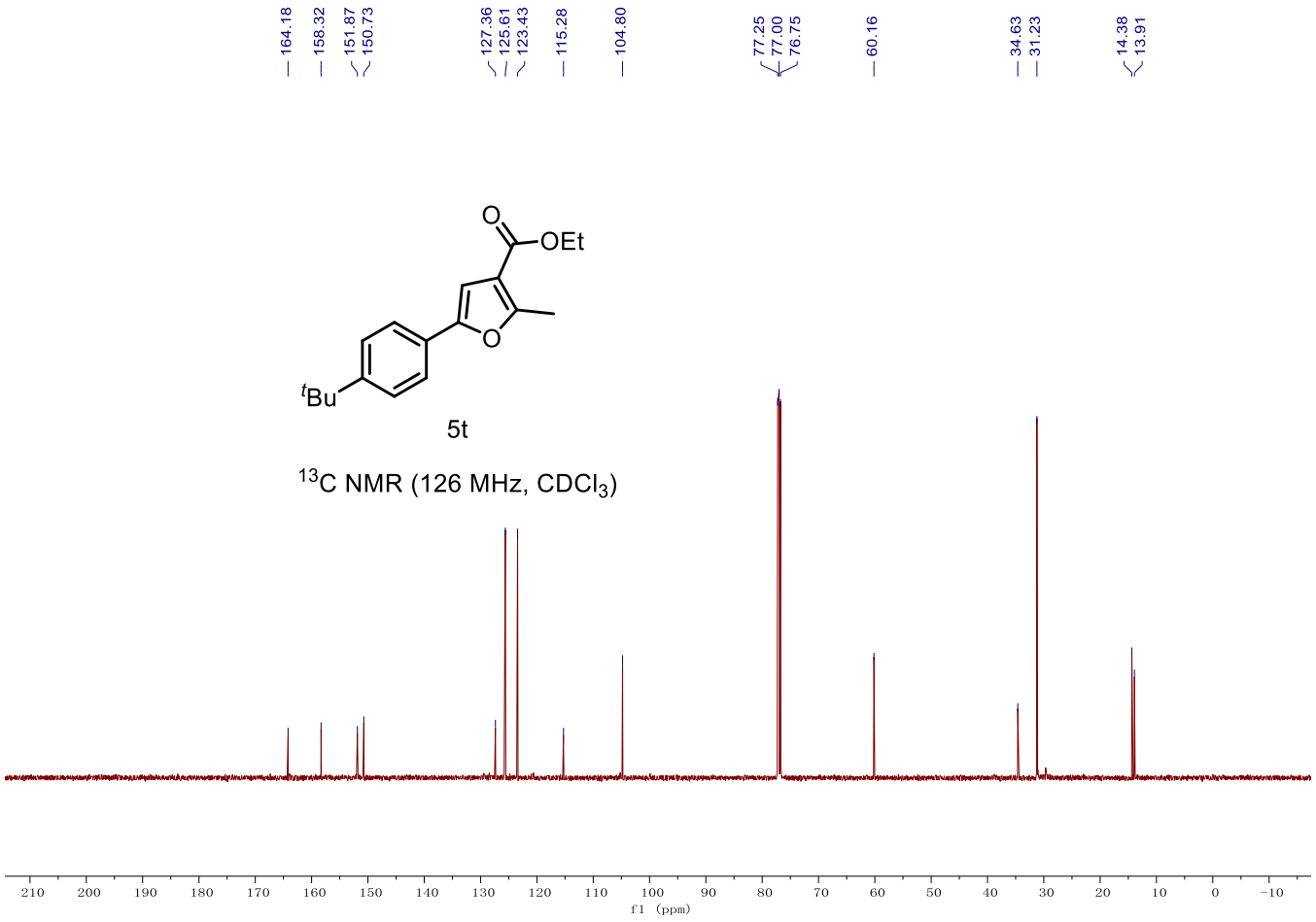
^{1}H NMR (400 MHz, $CDCl_3$)

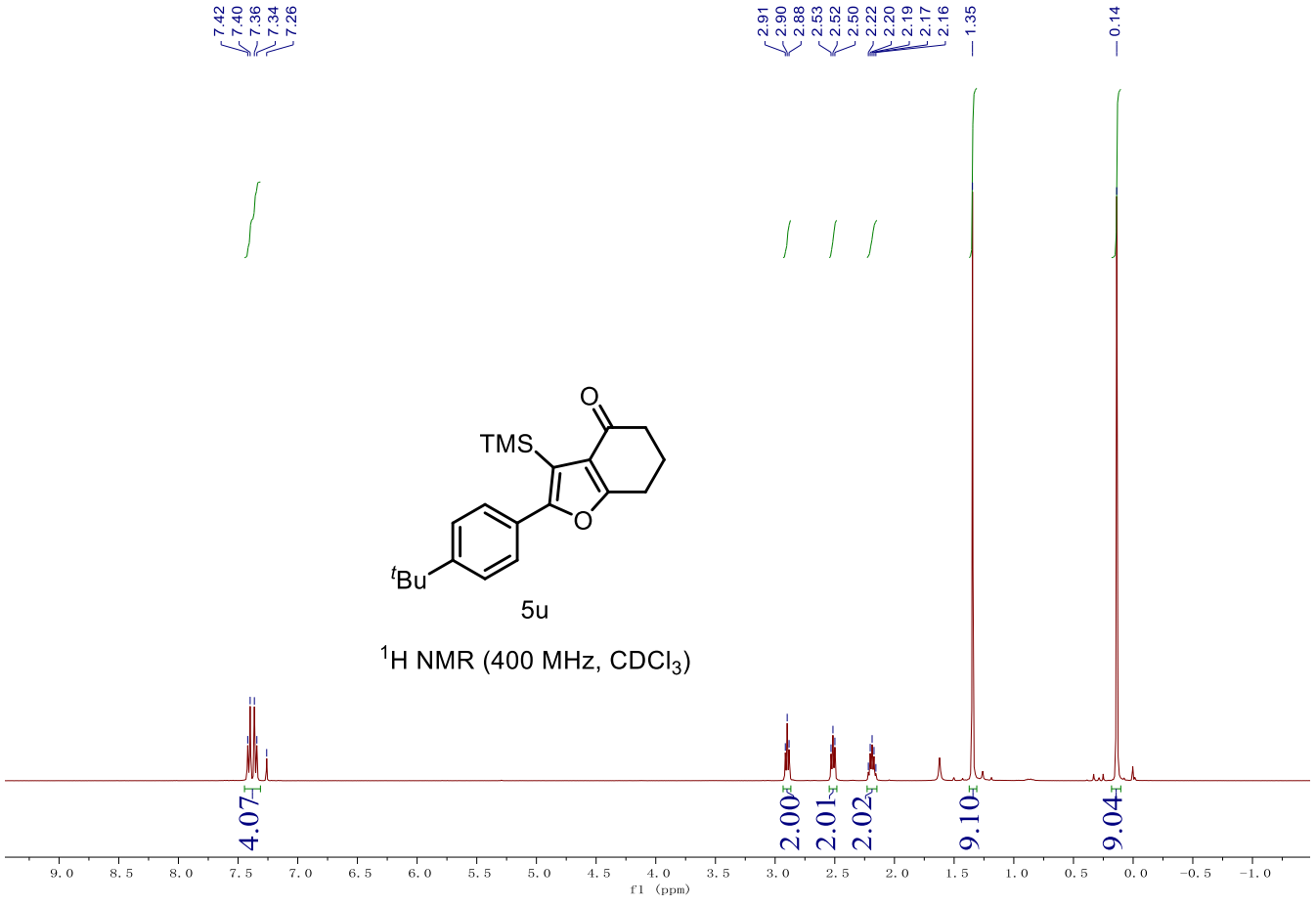


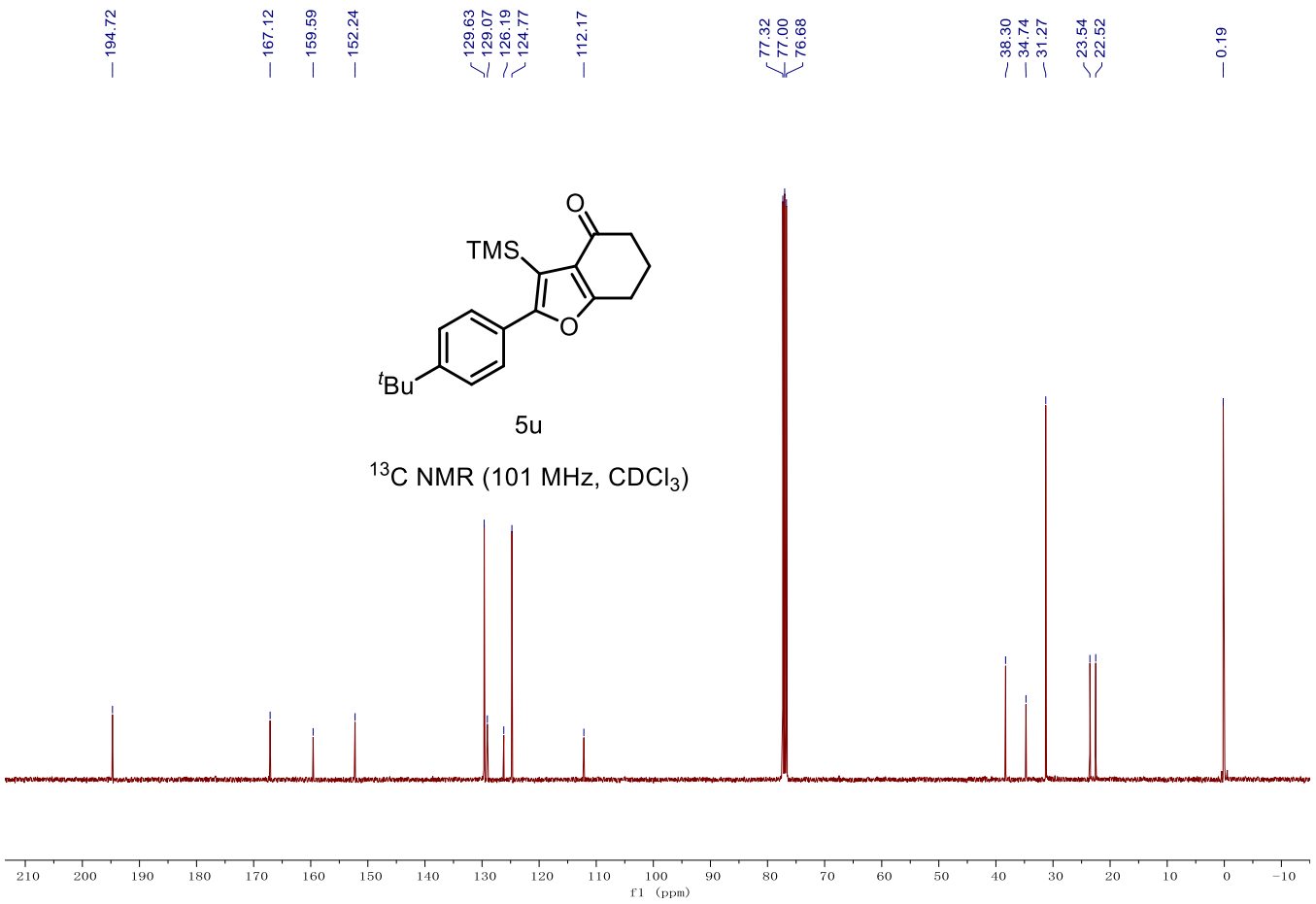
5s

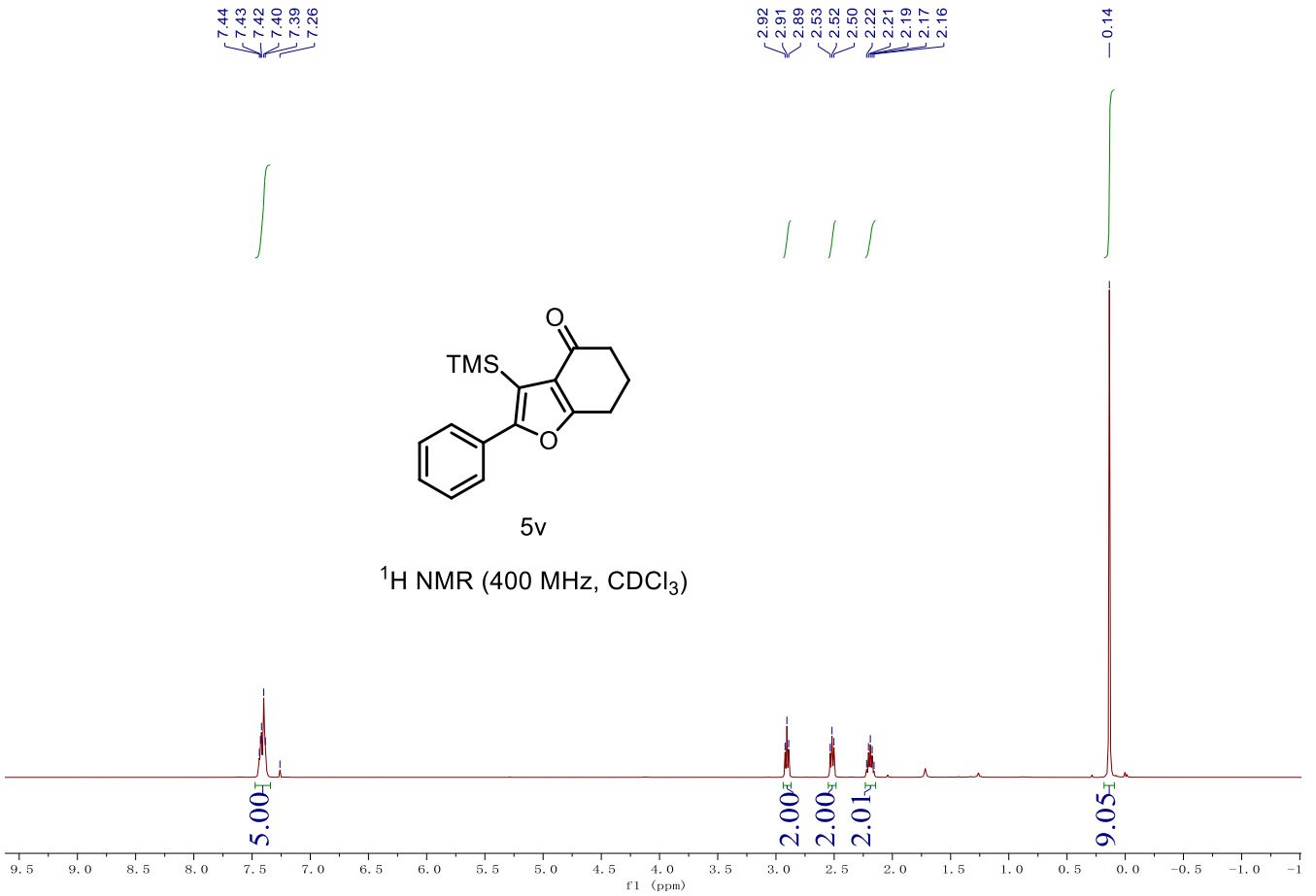
^{13}C NMR (101 MHz, $CDCl_3$)

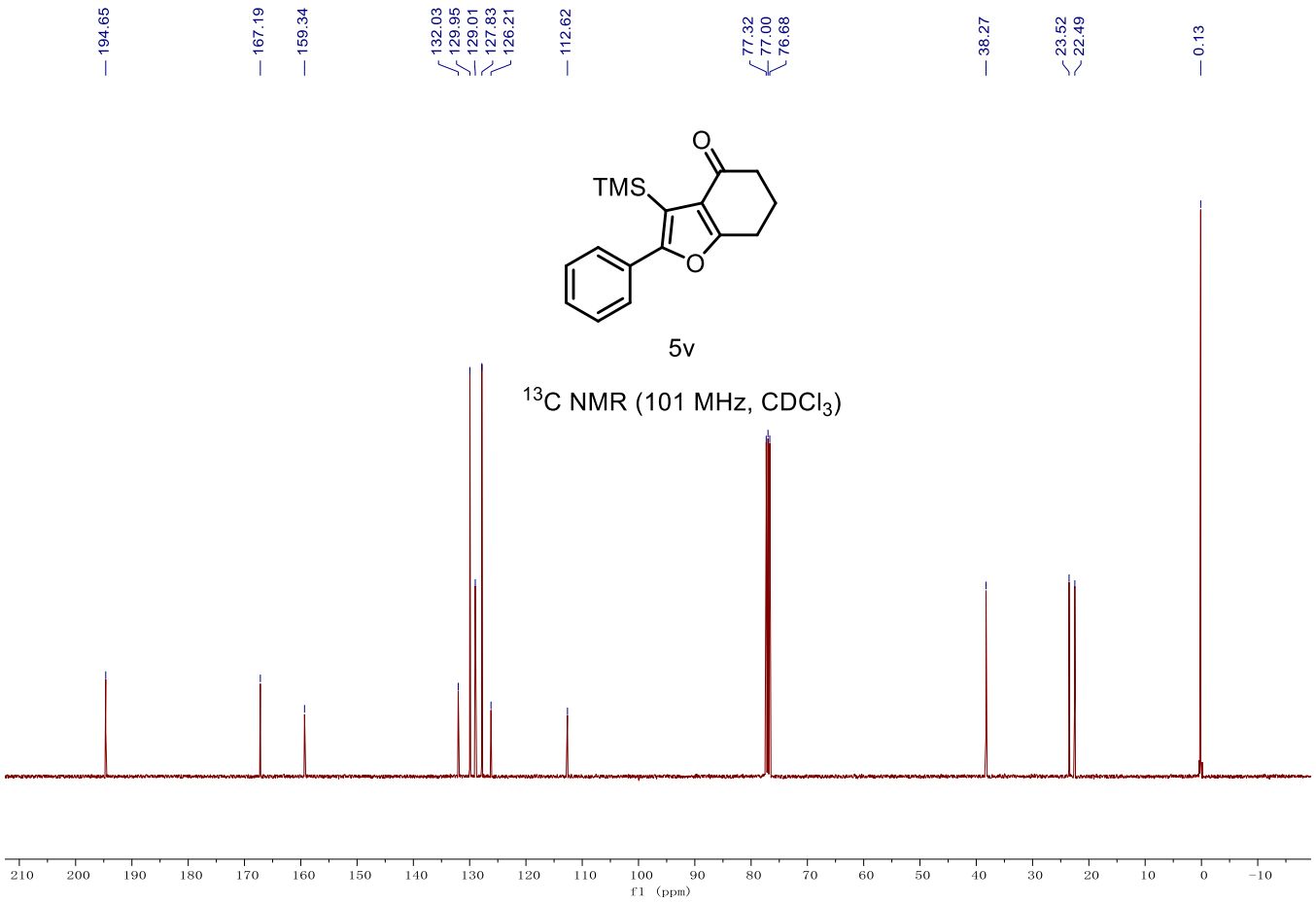

7.58
7.56
7.41
7.40
7.26
6.83
4.34
4.32
4.31
4.29
2.65
1.39
1.38
1.36
1.34
O
OEt
O
tBu
5t
1H NMR (500 MHz, CDCl3)
2.02
2.03
1.00
2.15
2.99
3.38
9.20
f1 (ppm)

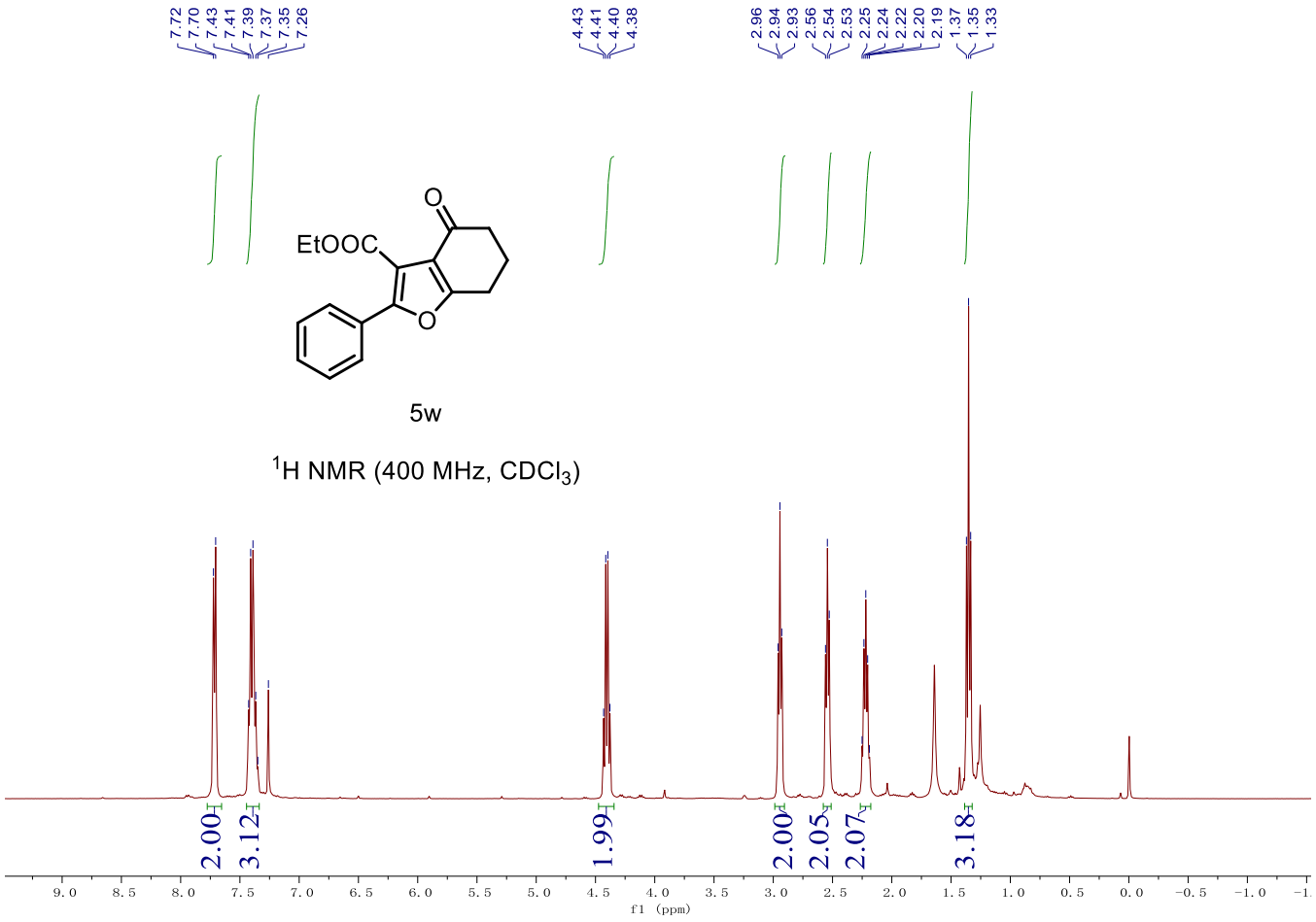

164.18
158.32
151.87
150.73
127.36
125.61
123.43
115.28
104.80
77.25
77.00
76.75
60.16
34.63
31.23
14.38
13.91
O
OEt
O
tBu
5t
13C NMR (126 MHz, CDCl3)
f1 (ppm)


7.42
7.40
7.36
7.34
7.26
2.91
2.90
2.88
2.53
2.52
2.50
2.22
2.20
2.19
2.17
2.16
1.35
0.14
O
TMS
O
tBu
5u
1H NMR (400 MHz, CDCl3)
4.07
2.00
2.01
2.02
9.10
9.04
f1 (ppm)


194.72
167.12
159.59
152.24
129.63
129.07
126.19
124.77
112.17
77.32
77.00
76.68
38.30
34.74
31.27
23.54
22.52
0.19
TMS
O
O
tBu
5u
13C NMR (101 MHz, CDCl3)
f1 (ppm)

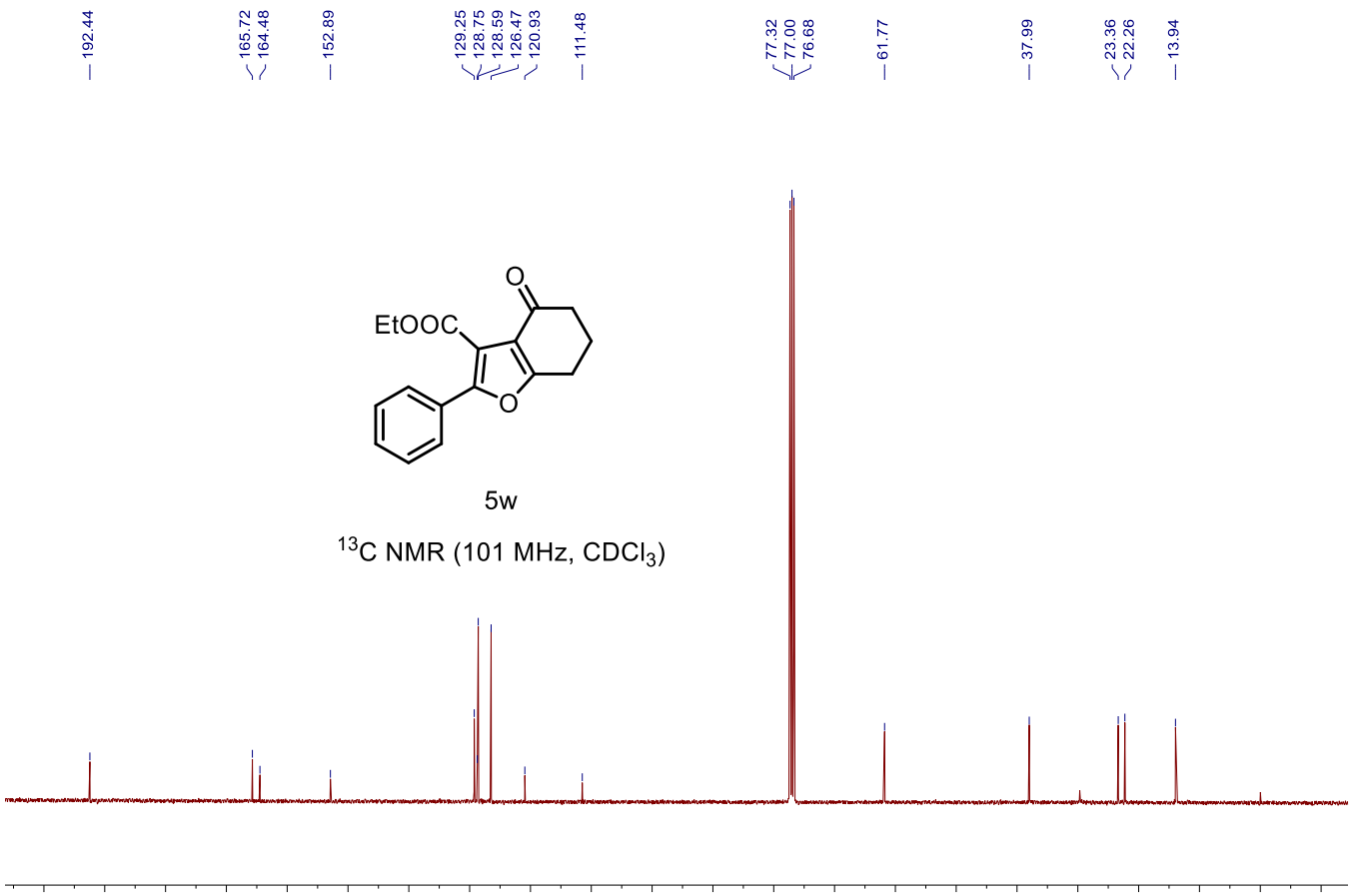

7.44
7.43
7.42
7.40
7.39
7.26
2.92
2.91
2.89
2.53
2.52
2.50
2.22
2.21
2.19
2.17
2.16
0.14
TMS
O
O
5v
1H NMR (400 MHz, CDCl3)
5.00
2.00
2.00
2.01
9.05
f1 (ppm)


194.65
167.19
159.34
132.03
129.95
129.01
127.83
126.21
112.62
77.32
77.00
76.68
38.27
23.52
22.49
0.13
TMS
O
O
5v
^{13}C NMR (101 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



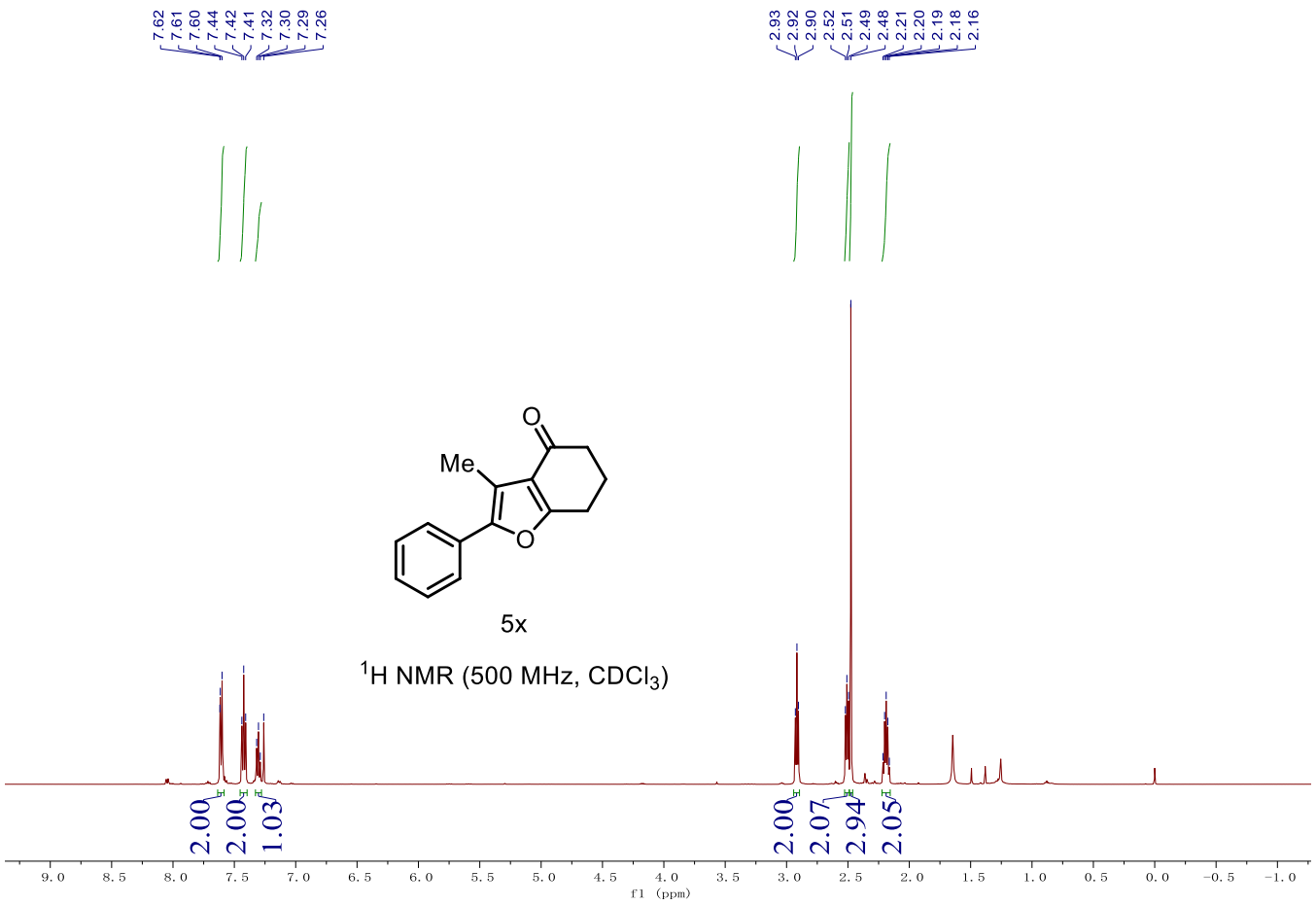
5w

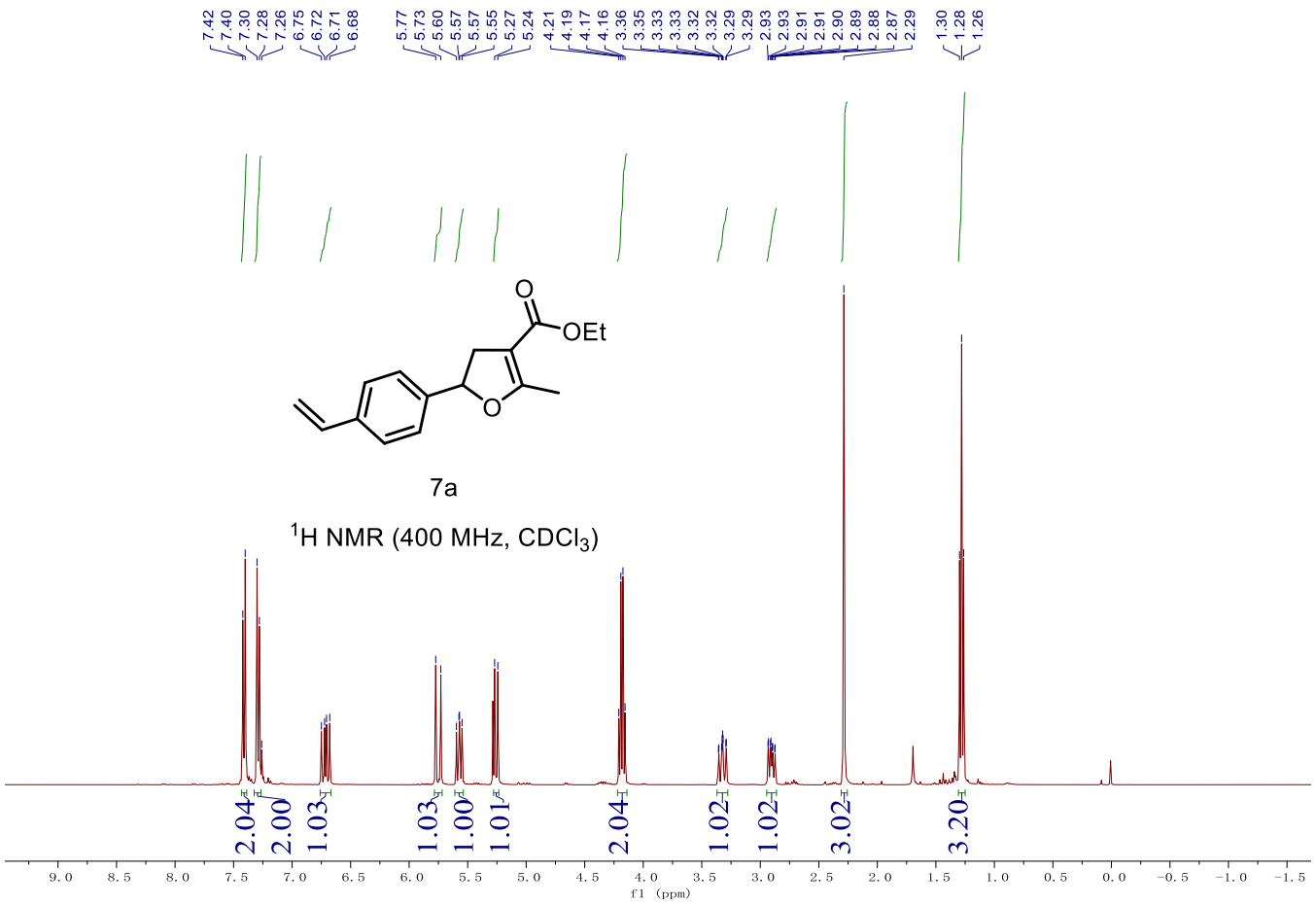
^{1}H NMR (400 MHz, $CDCl_3$)



5w

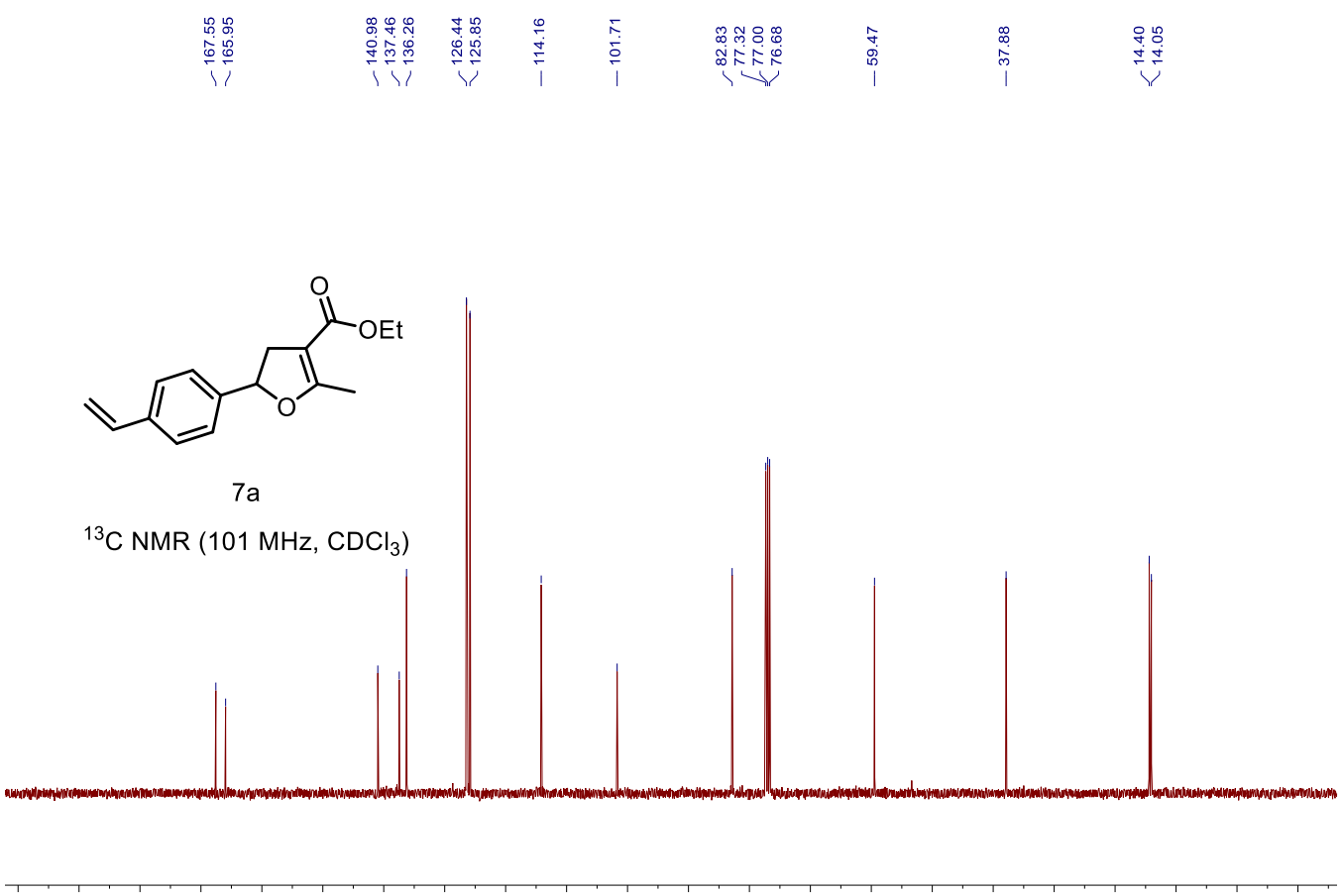
^{13}C NMR (101 MHz, $CDCl_3$)


7.62
7.61
7.60
7.44
7.42
7.41
7.32
7.30
7.29
7.26
2.93
2.92
2.90
2.52
2.51
2.49
2.48
2.21
2.20
2.19
2.18
2.16
O
Me
O
5x
^{1}H NMR (500 MHz, CDCl$_3$)
2.00
2.00
1.03
2.00
2.07
2.94
2.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)



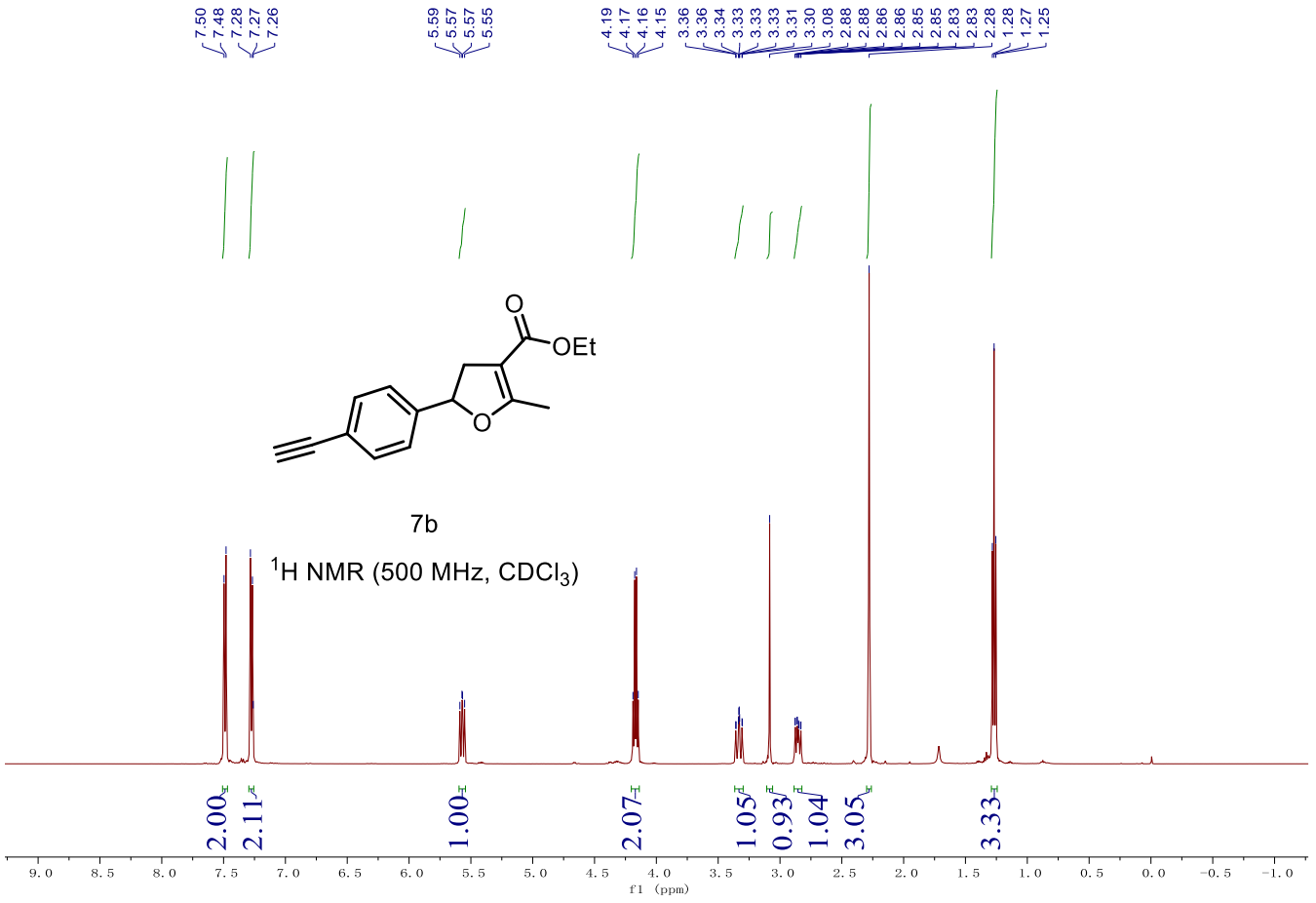
7a

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



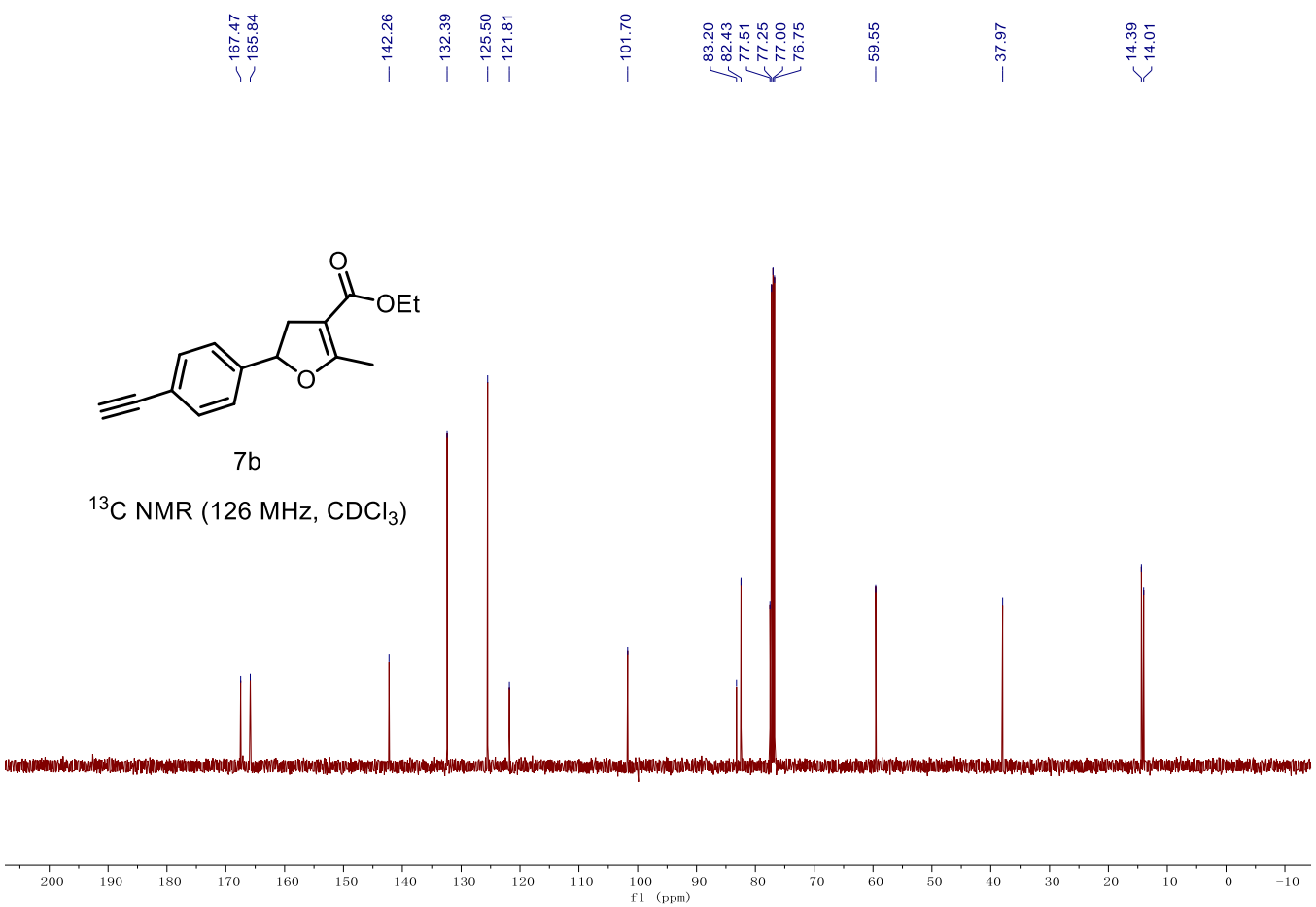
7a

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



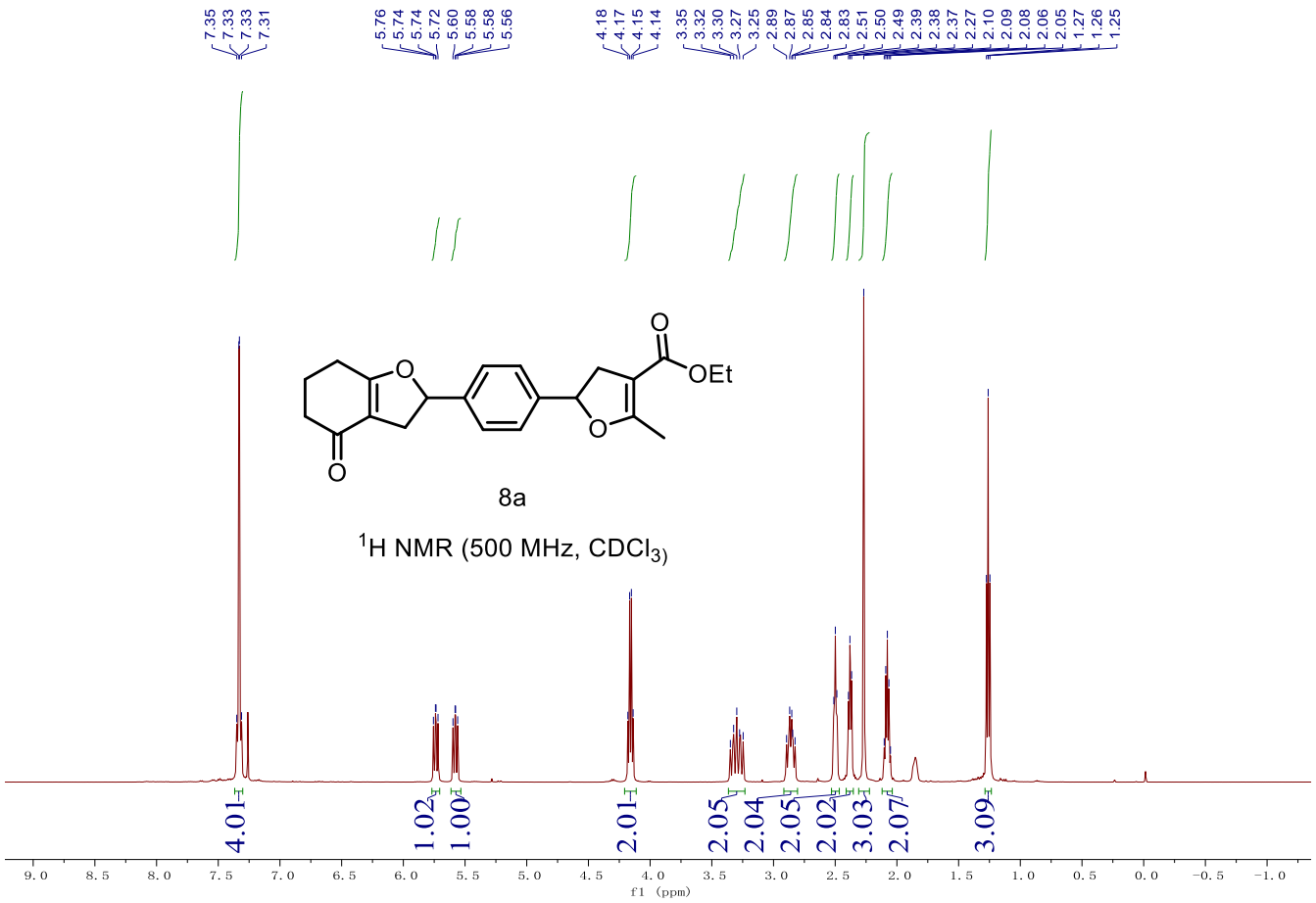
7b

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



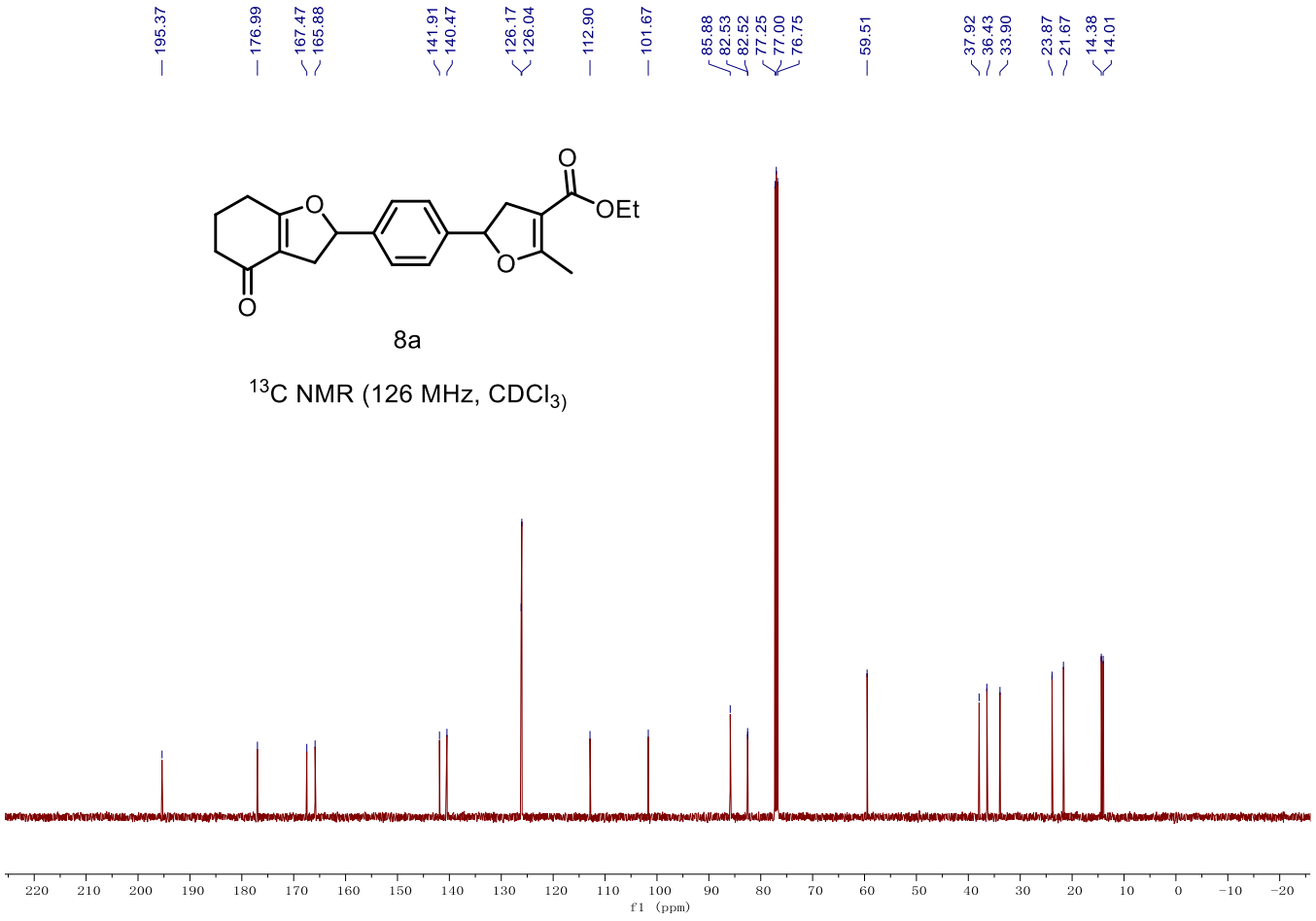
7b

^{13}C NMR (126 MHz, $CDCl_3$)



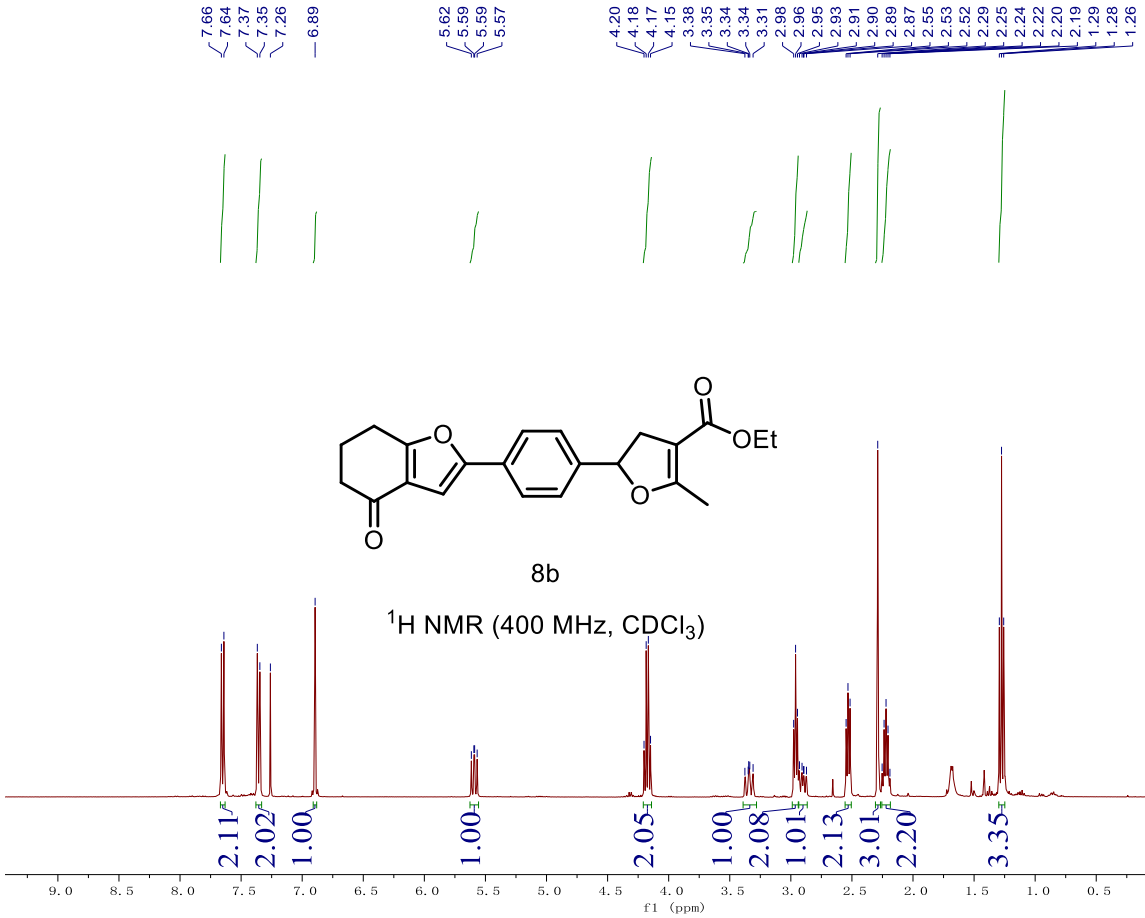
8a

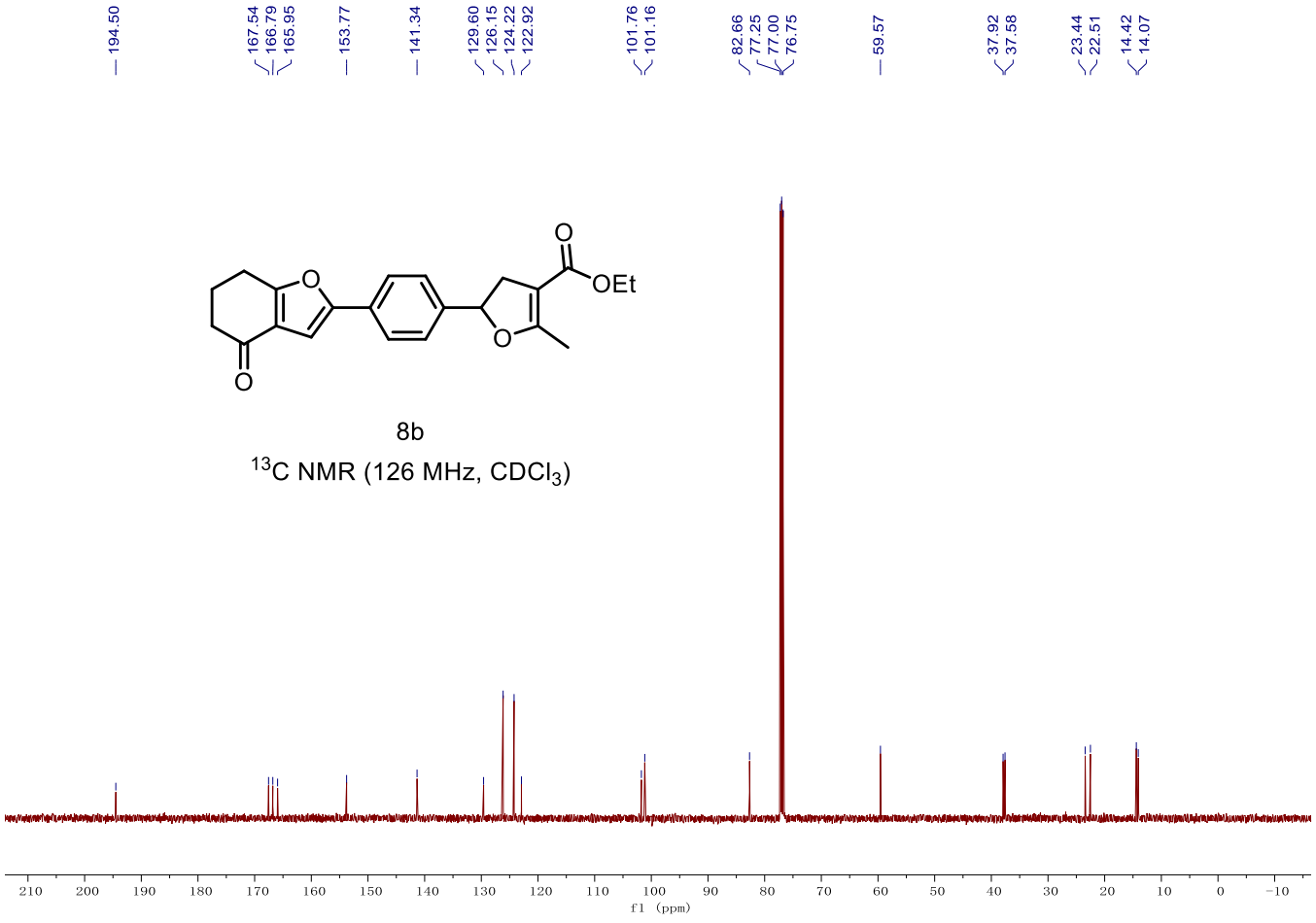
^{1}H NMR (500 MHz, $CDCl_3$)



8a

^{13}C NMR (126 MHz, $CDCl_3$)


7.66
7.64
7.37
7.35
7.26
6.89
5.62
5.59
5.59
5.57
4.20
4.18
4.17
4.15
3.38
3.35
3.34
3.34
3.31
2.98
2.96
2.95
2.93
2.91
2.90
2.89
2.87
2.55
2.53
2.52
2.29
2.25
2.24
2.22
2.20
2.19
1.29
1.28
1.26
O
OEt
O
O
8b
1H NMR (400 MHz, CDCl3)
2.11
2.02
1.00
1.00
2.05
1.00
2.08
1.01
2.13
3.01
2.20
3.35
f1 (ppm)


194.50
167.54
166.79
165.95
153.77
141.34
129.60
126.15
124.22
122.92
101.76
101.16
82.66
77.25
77.00
76.75
59.57
37.92
37.58
23.44
22.51
14.42
14.07
O
OEt
O
O
8b
13C NMR (126 MHz, CDCl3)
f1 (ppm)