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Electronic Supplementary Information for

Phosphine-Catalyzed Divergent Reactivity of Alkynoates with Acid Anhydrides: Chemo- and Stereoselective Synthesis of Polysubstituted Olefins and Dienes

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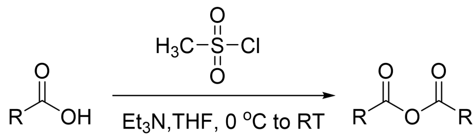
I. General Information

Unless otherwise noted, all reactions were carried out in nitrogen atmosphere under anhydrous conditions. Solvents were purified prior to use according to standard procedures. ^{1}H NMR, ^{13}C NMR spectra were recorded on a Bruker AV-III400 (400 MHz) spectrometer. ^{1}H and ^{13}C NMR spectra were recorded in benzene-d$_6$ (δ 7.16) or $CDCl_3$(δ 7.26) with tetramethylsilane (TMS) as the internal standard. Column chromatography was performed on silica gel (200-300 mesh) using a mixture of petroleum ether/ethyl acetate as eluant. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br s (broad singlet). HRMS spectra were acquired in ESI mode with the mass analyzer of TOF used. All the commercially available reagents were used without any purification. Some of alkyl acid anhydrides and acyl chlorides were prepared according to the known procedures.[1-9]

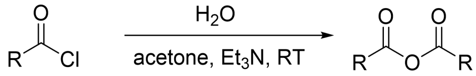
II. General Procedures for the Synthesis of Anhydrides 2

Method A:



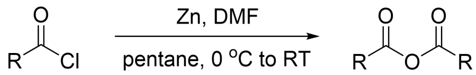
The anhydrides **2** were synthesized according to a known procedure. Triethylamine (3.4 equiv.) in THF (0.30 M) was added dropwise to a THF solution (0.34 M) containing organic acid (2.0 equiv.) and methanesulfonyl chloride (1.1 equiv.) at 0 °C. The resulting mixture was stirred for 12 h and concentrated in vacuo. The mixture was extracted with saturated $NaHCO_3$ solution and ethyl acetate for three times, and the combined organic phase was washed with brine, dried over $MgSO_4$, filtered and concentrated to obtain the anhydride.

Method B:



Prepared according to a known procedure. Acid chloride (5.0 mmol) and water (2.5 mmol) were mixed in acetone (5 mL). The resulting mixture was then slowly added triethylamine (5.0 mmol) over 2 minutes. After the completion of the reaction as monitored by TLC, the precipitated triethylamine hydrochloride was filtered off. Then, the solid triethylamine hydrochloride was washed with (5 mL × 3) acetone. The combined solutions were evaporated under vacuum to give the product.

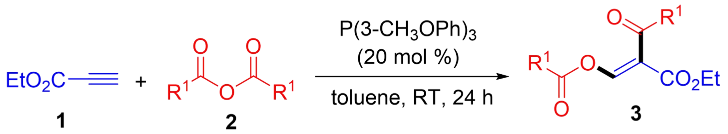
Method C:



A procedure from the literature was used. Under argon and at 0 °C, acid chloride (4.0 mmol) was added dropwise to a suspension of zinc powder (144.0 mg, 2.2 mmol) in pentane (4.0 mL) and anhydrous DMF (0.6 mL, 8.0 mmol). The resulting mixture was warmed to room temperature and stirred for 20 h. The mixture was then filtered on a pad of flash silica eluting with pentane / Et_2O. Removal of the solvents in vacuo furnished the corresponding anhydrides.

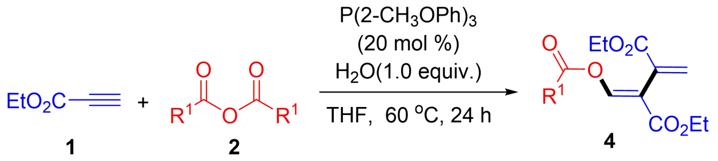
III. Typical Procedure for the Phosphine-Catalyzed Reactions of Alkynoates with Anhydrides

Produce A: typical procedure for the synthesis polysubstituted olefins 3



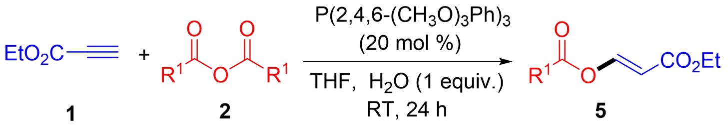
Under argon atmosphere, to a 10 mL Schlenk tube was added propiolate **1** (0.20 mmol), acid anhydride **2** (0.30 mmol), P(3-$CH_3OPh)_3$ (14.1 mg, 20 mol %) and toluene (2.0 mL). The resulting reaction mixture was stirred at room temperature for 24 h. The solvent was removed on a rotary evaporator under reduced pressure and the residue was subjected to column chromatography isolation on silica gel by gradient elution with petroleum ether / ethyl acetate (20:1-5:1) to give the product polysubstituted olefine **3**.

Produce B: typical procedure for the synthesis of conjugated dienes 4



Under argon atmosphere, propiolate **1** (0.40 mmol), acid anhydride **2** (0.20 mmol), P(2-$CH_3OPh)_3$ (14.1 mg, 20 mol %) , H_2O (5.0 µL, 1.0 equiv) and THF (2.0 mL) were added to a 10 mL Schlenk tube. The resulting reaction mixture was stirred at 60 °C for 24 h. The solvent was removed on a rotary evaporator under reduced pressure and the residue was subjected to column chromatography isolation on silica gel by gradient elution with petroleum ether / ethyl acetate (30:1-4:1) to give the product conjugated diene **4**.

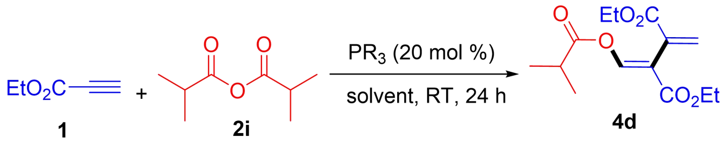
Produce C: typical procedure for the synthesis of vinyl esters 5



Also under argon atmosphere, ethyl propiolate **1** (0.30 mmol), acid anhydride **2** (0.20 mmol), P(2,4,6-$(CH_3O)_3Ph)_3$ (21.3 mg, 20 mol %), H_2O (5.0 µL, 1.0 equiv.) and THF (2.0 mL) were added to a 10 mL Schlenk tube. The resulting reaction mixture was stirred at room temperature for 24 h. The solvent was removed on a rotary evaporator under reduced pressure and the residue was subjected to column chromatography isolation on silica gel by gradient elution with petroleum ether / ethyl acetate (40:1-10:1) to give the product vinyl esters **5**.

IV. Survey of the Reaction Conditions

Table S1. Survey of conditions for the synthesis of conjugated dienes 4[a]

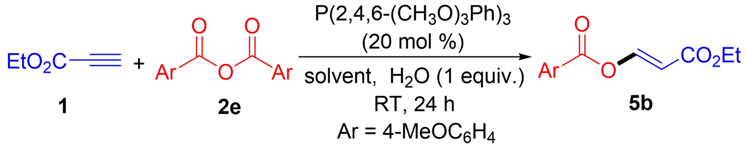


Entry	PR_3	Solvent	Yield of **4d** (%)[b]
1	PPh_3	Toluene	20
2	$PMePh_2$	Toluene	10
3	P(4-$ClC_6H_4)_3$	Toluene	10
4	P(2-$CH_3OC_6H_4)_3$	Toluene	22

5	$P(3\text{-}CH_3OC_6H_4)_3$	Toluene	12
6	$P(4\text{-}CH_3OC_6H_4)_3$	Toluene	13
7	PBu_3	Toluene	11
8	$P(2,4,6\text{-}(CH_3O)_3C_6H_2)_3$	Toluene	Trace
9	$P(3,5\text{-}(CH_3O)_2C_6H_3)_3$	Toluene	Trace
10	$P(2\text{-}CH_3OC_6H_4)_3$	1,4-Dioxane	20
11	$P(2\text{-}CH_3OC_6H_4)_3$	DMF	17
12	$P(2\text{-}CH_3OC_6H_4)_3$	THF	24
13	$P(2\text{-}CH_3OC_6H_4)_3$	C_2H_5OH	-
14	$P(2\text{-}CH_3OC_6H_4)_3$	THF	38^{c}
15	$P(2\text{-}CH_3OC_6H_4)_3$	THF	26^{d}
16	$P(2\text{-}CH_3OC_6H_4)_3$	THF	26^{e}
17	$P(2\text{-}CH_3OC_6H_4)_3$	THF	$47^{c,f}$

[a] Reaction conditions: ethyl propiolate **1** (0.4 mmol), isobutyric anhydride **2i** (0.2 mmol), PR_3 (20 mol %), solvent (2.0 mL), RT, 24 h. [b] Isolated yield based on **2i**. [c] H_2O (0.2 mmol) was added. [d] PhOH (0.2 mmol) was added. [e] CH_3OH (0.2 mmol) was added. [f] Conducted at 60 °C instead of RT.

Table S2. Survey of conditions for synthesis of the vinyl esters 5[a]

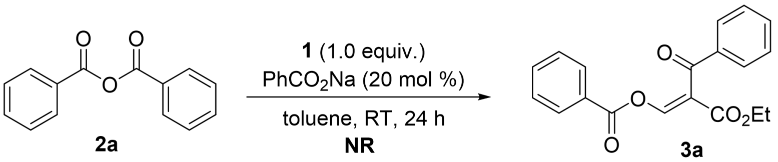


Entry	PR_3	Solvent	Yield of **5b** (%)[b]
1	PPh_3	Toluene	28
2	$PMePh_2$	Toluene	18
3	$P(4\text{-}ClC_6H_4)_3$	Toluene	25
4	$P(2\text{-}CH_3OC_6H_4)_3$	Toluene	21
5	$P(3\text{-}CH_3OC_6H_4)_3$	Toluene	22
6	$P(4\text{-}CH_3OC_6H_4)_3$	Toluene	21
7	$P(3,5\text{-}(CH_3O)_2C_6H_3)_3$	Toluene	28
8	$P(2,4,6\text{-}(CH_3O)_3C_6H_2)_3$	Toluene	47
9	PBu_3	Toluene	17
10	$P(2,4,6\text{-}(CH_3O)_3C_6H_2)_3$	THF	61
11	$P(2,4,6\text{-}(CH_3O)_3C_6H_2)_3$	1,4-Dioxane	59

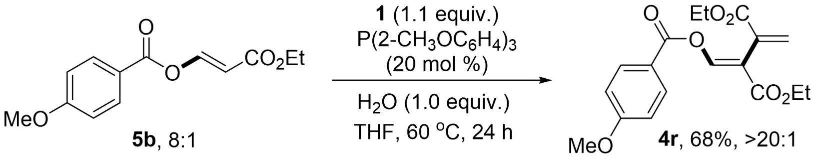
12	P(2,4,6-$CH_3OC_6H_2$)$_3$	CH_2Cl_2	35
13	P(2,4,6-$CH_3OC_6H_4$)$_3$	CH_3CN	53
14	P(2,4,6-(CH_3O)$_3C_6H_2$)$_3$	THF	79[c]
15	P(2,4,6-(CH_3O)$_3C_6H_2$)$_3$	THF	90[d]
16	P(2,4,6-(CH_3O)$_3C_6H_2$)$_3$	THF	64[e]

[a] Reaction conditions: ethyl propiolate **1** (0.3 mmol), 4-methoxybenzoic anhydride **2e** (0.2 mmol), PR_3 (20 mol %), solvent (2.0 mL), RT, 24 h. [b] Isolated yield based on **2e** and dr 8:1. [c] H_2O (0.1 mmol) was added. [d] H_2O (0.2 mmol) was added. [e] Ethyl propiolate **1** (0.2 mmol) and 4-methoxybenzoic anhydride **2e** (0.3 mmol) were used.

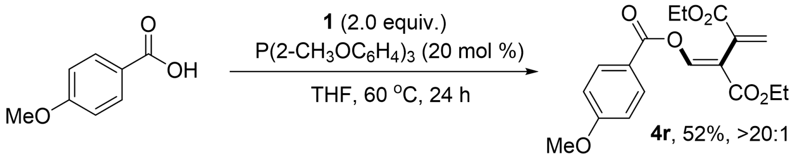
V. Control Experiments for Mechanistic Investigation



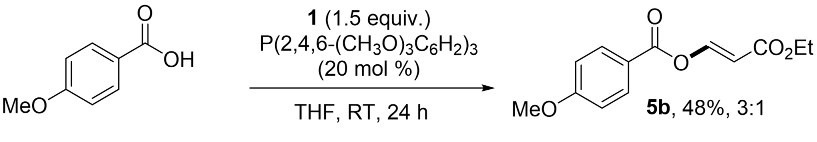
Under argon atmosphere, ethyl propiolate **1** (0.20 mmol), benzoic anhydride **2a** (67.9 mg, 0.30 mmol), toluene (2.0 mL) and $PhCO_2Na$ (8.7 mg, 20 mol %) were added to a 10 mL Schlenk tube. The resulting reaction mixture was stirred at room temperature for 24 h, and no reaction occurred according to TLC detection.



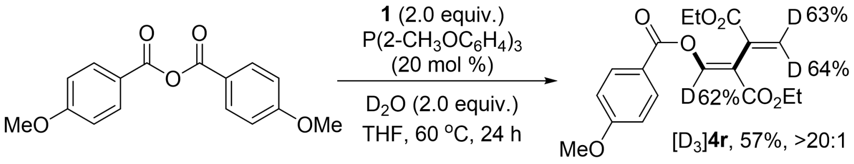
Under argon atmosphere, 3-ethoxy-3-oxoprop-1-en-1-yl 4-methoxybenzoate **5b** (50.0 mg, 0.20 mmol), ethyl propiolate **1** (22.0 µL, 0.22 mmol), P(2-CH_3OPh)$_3$ (14.1 mg, 20 mol %), H_2O (5.0 µL, 1.0 equiv.) and THF (2.0 mL) were added to a 10 mL Schlenk tube. The resulting reaction mixture was stirred at 60 °C for 24 h. The solvent was removed on a rotary evaporator under reduced pressure and the residue was subjected to column chromatography isolation to give the product **4r** in 68 % yiled with dr > 20:1.



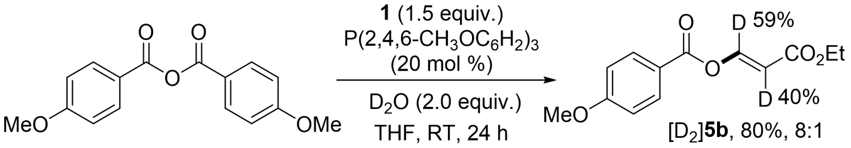
In argon atmosphere, ethyl propiolate **1** (40.0 µL, 0.40 mmol), 4-methoxybenzoic acid (30.4 mg, 0.20 mmol), P(2-CH_3OPh)$_3$ (14.1 mg, 20 mol %) and THF (2.0 mL) were added to a 10 mL Schlenk tube. The resulting reaction mixture was stirred at 60 °C for 24 h. The solvent was removed on a rotary evaporator under reduced pressure and the residue was subjected to column chromatography isolation to give the product **4r** in 52% yield with dr >20:1.



In argon atmosphere, ethyl propiolate **1** (30.0 µL, 0.30 mmol), 4-methoxybenzoic acid (30.4 mg, 0.20 mmol), P(2,4,6-(CH_3O)$_3$Ph)$_3$ (21.3 mg, 20 mol %) and THF (2.0 mL) were added to a 10 mL Schlenk tube. The resulting reaction mixture was then stirred at room temperature for 24 h. The solvent was removed on a rotary evaporator under reduced pressure and the residue was subjected to column chromatography isolation to give the product **5b** in 48% yield with dr 3:1

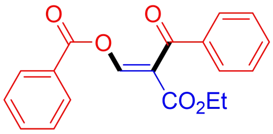


In argon atmosphere, ethyl propiolate **1** (40.0 μL, 0.40 mmol), 4-methoxybenzoic anhydride **2e** (57.3 mg, 0.20 mmol), P(2-$CH_3OPh)_3$ (14.1 mg, 20 mol %), D_2O (10.0 μL, 2.0 equiv.) and THF (2.0 mL) were added to a 10 mL Schlenk tube. The resulting reaction mixture was stirred at 60 ºC for 24 h. The solvent was removed on a rotary evaporator under reduced pressure and the residue was subjected to column chromatography isolation to give the product **[**D_3**]4r** in 57% yield with dr > 20:1.

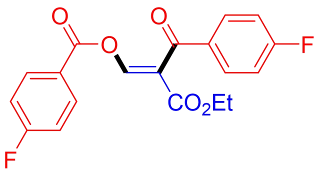


In the argon atmosphere, ethyl propiolate **1** (30.0 μL, 0.30 mmol), 4-methoxybenzoic anhydride **2e** (57.3 mg, 0.20 mmol), P(2,4,6-$(CH_3O)_3Ph)_3$ (21.3 mg, 20 mol %), D_2O (10.0 μL, 2.0 equiv.) and THF (2.0 mL) were added to a 10 mL Schlenk tube. The resulting reaction mixture was then stirred at room temperature for 24 h. The solvent was removed on a rotary evaporator under reduced pressure and the residue was subjected to column chromatography isolation to give the product **[**D_2**]5b** in 80% yield with dr 8:1.

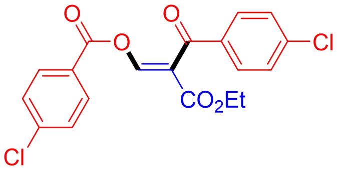
VI. Analytical Data for Compounds 3, 4, and 5



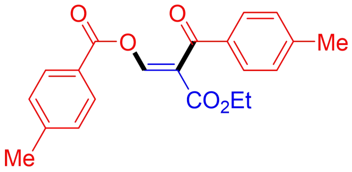
3a (63%,40.8 mg, dr > 20:1), Scheme 2; prepared according to the Produce A. Ethyl propiolate **1** (20.0 μL, 0.2 mmol) and benzoic anhydride **2a** (67.9 mg, 0.3 mmol) were employed to give **3a** in 63% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (20:1-10:1). A white solid, mp: 76-78 ºC. ^{1}H NMR (400 MHz, C_6D_6) δ 8.98 (s, 1H), 7.95 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.64 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.07 (t, *J* = 7.3 Hz, 1H), 7.00 (t, *J* = 7.3 Hz, 2H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.73 (dd, *J* = 10.8, 4.8 Hz, 2H), 3.92 (q, *J* = 7.1 Hz, 2H), 0.81 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 190.3, 164.2, 161.8, 147.2, 137.5, 134.3, 133.5, 130.5, 129.4, 129.0, 128.7, 127.5, 119.2, 61.3, 14.0 ppm. HRMS(ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{16}NaO_5$ 347.0890; found 347.0895.



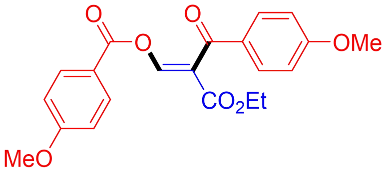
3b (56%, 40.3 mg, dr = 7:1), Scheme 2; prepared according to the Produce A. Ethyl propiolate **1** (20.0 μL, 0.2 mmol) and 4-fluorobenzoic anhydride **2b** (78.7 mg, 0.3 mmol) were employed to give **3b** in 56% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (20:1-10:1). A white solid, mp: 89-91 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 2H), 6.68 (d, *J* = 8.6 Hz, 2H), 3.92 (dd, *J* = 14.4, 7.2 Hz, 2H), 0.82 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ188.7, 166.7 (d, *J* = 256.5 Hz), 166.3 (d, *J* = 255.2 Hz), 164.0, 160.7, 147.2, 133.8 (d, *J* = 2.8 Hz), 133.2 (d, *J* = 9.8 Hz), 132.1 (d, *J* = 9.4 Hz), 123.5 (d, *J* = 2.9 Hz), 118.9, 116.1 (d, *J* = 22.1 Hz), 116.0 (d, *J* = 22.3 Hz), 61.4, 14.0 ppm. HRMS(ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{14}F_2NaO_5$ 383.0702; found 383.0694.



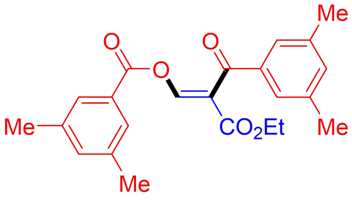
3c (48%, 37.6 mg, dr = 10:1), Scheme 2; prepared according to the Produce A. Ethyl propiolate **1** (20.0 µL, 0.2 mmol) and 4-chlorobenzoic anhydride **2c** (88.5 mg, 0.3 mmol) were employed to give **3c** in 48% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (20:1-10:1). A white solid, mp: 104-105 ºC. ^1H NMR (400 MHz, C_6D_6) δ 8.86 (s, 1H), 7.65 (d, *J* = 8.7 Hz, 2H), 7.34 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 2H), 6.68 (d, *J* = 8.8 Hz, 2H), 3.92 (q, *J* = 7.1 Hz, 2H), 0.82 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 189.0, 163.9, 160.9, 147.2, 141.1, 140.2, 135.7, 131.7, 130.8, 129.3, 129.2, 125.6, 118.9, 61.5, 14.0 ppm. HRMS(ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{14}Cl_2NaO_5$ 415.0110; found 415.0134.



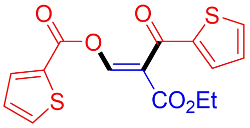
3d (51%, 35.9 mg, dr = 11:1), Scheme 2; prepared according to the Produce A. Ethyl propiolate **1** (20.0 µL, 0.2 mmol) and 4-methylbenzoic anhydride **2d** (76.3 mg, 0.3 mmol) were employed to give **3d** in 51% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (20:1-10:1). A white solid, mp: 91-93 ºC. ^1H NMR (400 MHz, C_6D_6) δ 9.03 (s, 1H), 8.08 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 6.85 (d, *J* = 7.9 Hz, 2H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 2H), 3.94 (q, *J* = 7.1 Hz, 2H), 1.91 (s, 3H), 1.78 (s, 3H), 0.83 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 190.0, 172.4, 164.4, 161.9, 147.1, 145.3, 144.3, 135.2, 130.7, 129.7, 129.5, 124.9, 119.3, 61.2, 21.4, 21.4, 14.0 ppm. HRMS(ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{20}NaO_5$ 357.1203; found 357.1184.



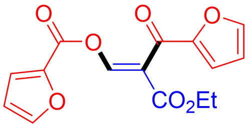
3e (41%, 31.5 mg, dr = 13:1), Scheme 2; prepared according to the Produce A. Ethyl propiolate **1** (20.0 µL, 0.2 mmol) and 4-methoxybenzoic anhydride **2e** (85.9 mg, 0.3 mmol) were employed to give **3e** in 41% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (20:1-5:1). A white solid, mp: 78-80 ºC. ^1H NMR (400 MHz, C_6D_6) δ 9.11 (s, 1H), 8.03 (d, *J* = 8.9 Hz, 2H), 7.76 (d, *J* = 9.0 Hz, 2H), 6.58 (d, *J* = 8.9 Hz, 2H), 6.29 (d, *J* = 9.0 Hz, 2H), 3.96 (q, *J* = 7.1 Hz, 2H), 3.07 (s, 3H), 2.97 (s, 3H), 0.84 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 189.0, 164.7, 164.5, 161.6, 147.0, 132.9, 131.9, 114.3, 114.2, 61.2, 54.9, 54.8, 14.1 ppm. HRMS(ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{20}NaO_7$ 407.1101; found 407.1101.



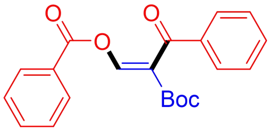
3f (63%, 47.9 mg, dr = 9:1), Scheme 2; prepared according to the Produce A. Ethyl propiolate **1** (20.0 μL, 0.2 mmol) and 3,5-dimethylbenzoic anhydride **2f** (82.3 mg, 0.3 mmol) were employed to give **3f** in 63% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (20:1-5:1). A white solid, mp: 110-112 °C. ^{1}H NMR (400 MHz, C_6D_6) δ 9.09 (s, 1H), 7.78 (d, J = 6.8 Hz, 2H), 7.38 (d, J = 7.0 Hz, 2H), 6.80 (s, 1H), 6.66 (s, 1H), 3.98 (m, 2H), 1.98 (s, 6H), 1.83 (s, 6H), 0.88 (m, 3H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 190.5, 164.5, 162.1, 147.2, 138.6, 138.5, 137.9, 136.2, 135.3, 128.4, 127.5, 127.5, 119.5, 61.3, 21.0, 20.7, 14.0 ppm. HRMS(ESI) m/z: [M + Na]$^+$ Calcd for $C_{23}H_{24}NaO_5$ 403.1516; found 403.1521.



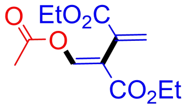
3g (68%, 45.7 mg, dr = 10:1), Scheme 2; prepared according to the Produce A. Ethyl propiolate **1** (20.0 μL, 0.2 mmol) and thiophene-2-carboxylic anhydride **2g** (71.5 mg, 0.3 mmol) were employed to give **3g** in 68% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (10:1-5:1). A white solid, mp: 120 °C. ^{1}H NMR (400 MHz, C_6D_6) δ 8.86 (s, 1H), 7.60 (d, J = 8.4 Hz, 1H), 7.33 (d, J = 3.6 Hz, 1H), 6.91 (d, J = 8.4 Hz, 1H), 6.61 (d, J = 4.8 Hz, 1H), 6.46 (t, J = 4.1 Hz, 1H), 6.23 (t, J = 4.2 Hz, 1H), 3.93 (q, J = 7.1 Hz, 2H), 0.83 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 182.1, 163.8, 161.5, 157.1, 146.7, 141.0, 136.0, 135.1, 134.7, 134.3, 132.0, 129.3, 119.2, 61.4, 14.0 ppm. HRMS(ESI) m/z: [M + Na]$^+$ Calcd for $C_{15}H_{12}S_2NaO_5$ 359.0018; found 359.0019.



3h (66%, 40.1 mg, dr = 20:1), Scheme 2; prepared according to the Produce A. Ethyl propiolate **1** (20.0 μL, 0.2 mmol) and furan-2-carboxylic anhydride **2h** (61.9 mg, 0.3 mmol) were employed to give **3h** in 66% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (10:1-5:1). A white solid, mp: 107-109 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 6.97 (d, J = 3.5 Hz, 1H), 6.87 (d, J = 0.9 Hz, 1H), 6.73 (s, 1H), 6.69 (d, J = 3.6 Hz, 1H), 5.87 (dd, J = 3.6, 1.7 Hz, 1H), 5.64 (dd, J = 3.6, 1.7 Hz, 1H), 3.99 (q, J = 7.1 Hz, 2H), 0.89 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.3, 163.9, 153.3, 153.2, 148.3, 147.0, 146.9, 142.1, 121.5, 118.8, 112.5, 112.3, 61.3, 14.0 ppm. HRMS(ESI) m/z: [M + H]$^+$ Calcd for $C_{15}H_{13}O_7$ 305.0656; found 305.0654.

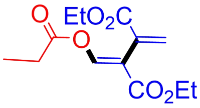


3i (54%, 38.0 mg, dr > 10:1), Scheme 2; prepared according to the Produce A. *Tert*-butyl propiolate (26.3 μL, 0.2 mmol) and benzoic anhydride **2a** (67.9 mg, 0.3 mmol) were employed to give **3i** in 54% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (30:1-10:1). A colorless oil. ^{1}H NMR (400 MHz, C_6D_6) δ 8.95 (s, 1H), 7.96 (dd, J = 8.2, 1.3 Hz, 2H), 7.71 (dd, J = 8.3, 1.2 Hz, 2H), 7.05 (dd, J = 15.6, 7.3 Hz, 3H), 6.92 (t, J = 7.5 Hz, 1H), 6.75 (t, J = 7.8 Hz, 2H), 1.25 (s, 9H) ppm. ^{13}C (101 MHz, C_6D_6) δ 190.1, 163.1, 161.5, 146.5, 137.4, 133.8, 132.9, 130.2, 128.9, 128.5, 128.3, 127.2, 120.2, 81.6, 27.5 ppm. HRMS(ESI) m/z: [M + Na]$^+$ Calcd for $C_{21}H_{20}NaO_5$ 375.1203; found 375.1203.

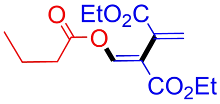


4a (43%, 22.0 mg, dr = 20:1), Scheme 4; prepared according to the Produce B. Ethyl propiolate **1** (40.0 μL, 0.4 mmol), H_2O (5.0 μL, 1.0 equiv.) and acetic anhydride **2i** (18.9 μL, 0.2 mmol) were employed to give **4a** in 43%

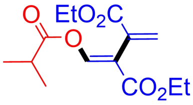
yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (30:1-4:1). A colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 6.69 (d, *J* = 1.6 Hz, 1H), 5.62 (d, *J* = 1.5 Hz, 1H), 4.08 (qd, *J* = 7.1, 5.1 Hz, 4H), 1.41 (s, 3H), 1.00 (td, *J* = 7.1, 5.9 Hz, 6H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 166.1, 165.7, 165.6, 145.2, 133.5, 129.9, 115.6, 61.0, 60.9, 19.6, 14.2, 14.0 ppm. HRMS(ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{17}O_6$ 257.1020; found 257.1025.



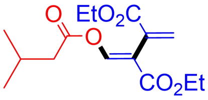
4b (41%, 22.2 mg, dr > 20:1), Scheme 4; prepared according to the Produce B. Ethyl propiolate **1** (40.0 μL, 0.4 mmol), H_2O (5.0 μL, 1.0 equiv.) and propionic anhydride **2j** (25.6 μL, 0.2 mmol) were employed to give **4b** in 41% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (30:1-4:1). A colorless oil. ^{1}H NMR (400 MHz, C_6D_6) δ 8.70 (d, *J* = 1.8 Hz, 1H), 6.61 (s, 1H), 5.57 (d, *J* = 1.4 Hz, 1H), 4.01 (m, 4H), 1.73 (q, *J* = 7.5 Hz, 2H), 0.93 (q, *J* = 7.2 Hz, 6H), 0.69 (t, *J* = 7.5 Hz, 3H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 169.7, 165.7, 165.6, 145.3, 133.6, 129.9, 115.5, 61.0, 60.9, 26.9, 14.2, 14.1, 8.4 ppm. HRMS(ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{18}NaO_6$ 293.0996; found 293.0984.



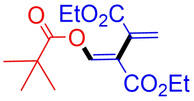
4c (46%, 26.1 mg, dr = 20:1), Scheme 4; prepared according to the Produce B. Ethyl propiolate **1** (40.0 μL, 0.4 mmol), H_2O (5.0 μL, 1.0 equiv.) and butyric anhydride **2k** (32.7 μL, 0.2 mmol) were employed to give **4c** in 46% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (30:1-4:1). A colorless oil. ^{1}H NMR (400 MHz, C_6D_6) δ 8.71 (d, *J* = 4.1 Hz, 1H), 6.62 (t, *J* = 1.6 Hz, 1H), 5.59 (d, *J* = 1.4 Hz, 1H), 4.01 (m, 4H), 1.78 (t, *J* = 7.3 Hz, 2H), 1.26 (m, 2H), 0.93 (q, *J* = 7.0 Hz, 6H), 0.59 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 168.9, 165.7, 165.6, 145.3, 133.6, 129.9, 115.5, 61.0, 60.9, 35.3, 17.9, 14.2, 14.1, 13.3 ppm. HRMS(ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{20}NaO_6$ 307.1152; found 307.1165.



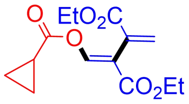
4d (47%, 26.7 mg, dr > 20:1), Scheme 4; prepared according to the Produce B. Ethyl propiolate **1** (40.0 μL, 0.4 mmol), H_2O (5.0 μL, 1.0 equiv.) and isobutyric anhydride **2l** (32.4 μL, 0.2 mmol) were employed to give **4d** in 47% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (30:1-4:1). A colorless oil. ^{1}H NMR (400 MHz, C_6D_6) δ 8.68 (s, 1H), 6.60 (s, 1H), 5.57 (s, 1H), 4.07 – 3.91 (m, 4H), 2.09 (dt, *J* = 13.9, 7.0 Hz, 1H), 0.93 (q, *J* = 6.9 Hz, 6H), 0.81 (d, *J* = 7.0 Hz, 6H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 172.2, 165.7, 165.6, 145.5, 133.6, 129.8, 115.6, 61.0, 60.9, 33.8, 18.2, 14.2, 14.1 ppm. HRMS(ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{20}NaO_6$ 307.1152; found 307.1153.



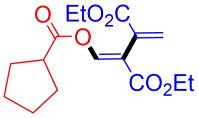
4e (41%, 24.5 mg, dr > 20:1), Scheme 4; prepared according to the Produce B. Ethyl propiolate **1** (40.0 μL, 0.4 mmol), H_2O (5.0 μL, 1.0 equiv.) and 3-methylbutanoic anhydride **2m** (39.0 μL, 0.2 mmol) were employed to give **4e** in 41% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (30:1-4:1). A colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 6.74 (d, *J* = 1.3 Hz, 1H), 5.70 (d, *J* = 1.1 Hz, 1H), 4.11 (m, 4H), 1.94 (m, 1H), 1.88 (m, 2H), 1.04 (q, *J* = 7.0 Hz, 6H), 0.75 (d, *J* = 6.4 Hz, 6H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 168.3, 165.7, 165.6, 145.3, 133.7, 129.9, 115.6, 61.0, 60.9, 42.3, 25.3, 22.0, 14.2, 14.1 ppm. HRMS(ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{22}NaO_6$ 321.1309; found 321.1301.



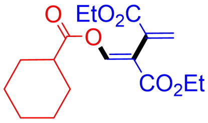
4f (64%, 38.2 mg, dr > 20:1), Scheme 4; prepared according to the Produce B. Ethyl propiolate **1** (40.0 μL, 0.4 mmol), H_2O (5.0 μL, 1.0 equiv.) and pivalic anhydride **2n** (38.9 μL, 0.2 mmol) were employed to give **4f** in 64% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (30:1-4:1). A colorless oil. ^{1}H NMR (400 MHz, C_6D_6) δ 8.68 (s, 1H), 6.59 (d, *J* = 1.5 Hz, 1H), 5.57 (d, *J* = 1.5 Hz, 1H), 3.99 (qd, *J* = 7.1, 5.4 Hz, 4H), 0.92 (m, 15H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 173.6, 165.7, 165.6, 145.6, 133.7, 129.7, 115.7, 61.0, 60.9, 38.9, 26.5, 14.2, 14.1 ppm. HRMS(ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{22}NaO_6$ 321.1309; found 321.1319.



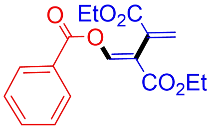
4g (53%, 29.9 mg, dr > 20:1), Scheme 4; prepared according to the Produce B. Ethyl propiolate **1** (40.0 μL, 0.4 mmol), H_2O (5.0 μL, 1.0 equiv.) and cyclopropanecarboxylic anhydride **2o** (27.7 μL, 0.2 mmol) were employed to give **4g** in 53% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (30:1-4:1). A colorless oil. ^{1}H NMR (400 MHz, C_6D_6) δ 8.70 (s, 1H), 6.62 (d, *J* = 1.6 Hz, 1H), 5.58 (d, *J* = 1.5 Hz, 1H), 3.99 (dq, *J* = 14.2, 7.1 Hz, 4H), 1.10 (dd, *J* = 12.5, 4.5 Hz, 1H), 0.92 (dt, *J* = 13.3, 7.1 Hz, 6H), 0.82 – 0.71 (m, 2H), 0.28 (dd, *J* = 8.0, 3.2 Hz, 2H). ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 170.4, 165.7, 165.6, 145.4, 133.6, 129.9, 115.3, 61.0, 60.9, 14.1, 12.7, 9.7, 9.0 ppm. HRMS(ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{18}NaO_6$ 305.0996; found 305.1003.



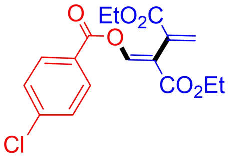
4h (45%, 27.9 mg, dr > 20:1), Scheme 4; prepared according to the Produce B. Ethyl propiolate **1** (40.0 μL, 0.4 mmol), H_2O (5.0 μL, 1.0 equiv.) and cyclopentanecarboxylic anhydride **2p** (42.1 μL, 0.2 mmol) were employed to give **4h** in 45% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (30:1-4:1). A colorless oil. ^{1}H NMR (400 MHz, C_6D_6) δ 8.72 (s, 1H), 6.62 (d, *J* = 1.2 Hz, 1H), 5.60 (d, *J* = 1.1 Hz, 1H), 4.00 (m, 4H), 2.33 (p, *J* = 7.9 Hz, 1H), 1.59 (td, *J* = 14.5, 7.4 Hz, 2H), 1.47 (m, 2H), 1.37 (dd, *J* = 9.2, 5.9 Hz, 2H), 1.18 (dd, *J* = 6.8, 4.2 Hz, 2H), 0.93 (q, *J* = 7.0 Hz, 6H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 171.9, 165.8, 165.6, 145.7, 133.7, 129.8, 115.5, 61.0, 60.9, 43.5, 30.1, 29.7, 26.0, 25.8, 14.2, 14.1 ppm. HRMS(ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{22}NaO_6$ 333.1309; found 333.1319.



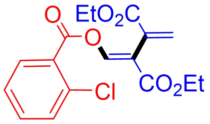
4i (42%, 27.2 mg, dr > 20:1), Scheme 4; prepared according to the Produce B. Ethyl propiolate **1** (40.0 μL, 0.4 mmol), H_2O (5.0 μL, 1.0 equiv.) and cyclohexanecarboxylic anhydride **2q** (45.4 μL, 0.2 mmol) were employed to give **4i** in 42% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (30:1-4:1). A colorless oil. ^{1}H NMR (400 MHz, C_6D_6) δ 8.78 (s, 1H), 6.63 (d, *J* = 1.5 Hz, 1H), 5.61 (d, *J* = 1.5 Hz, 1H), 4.02 (m, 4H), 1.95 (tt, *J* = 11.0, 3.7 Hz, 1H), 1.81 (d, *J* = 14.4 Hz, 1H), 1.64 (d, *J* = 12.9 Hz, 2H), 1.48 (m, 1H), 1.42 (m, 2H), 1.26 (m, 3H), 0.93 (dt, *J* = 15.6, 7.8 Hz, 7H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 171.1, 165.7, 165.6, 145.6, 133.7, 129.8, 115.6, 61.0, 60.9, 42.6, 29.2, 28.5, 25.7, 25.5, 25.2, 14.2, 14.1 ppm. HRMS(ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{24}NaO_6$ 347.1465; found 347.1458.



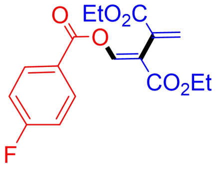
4j (71%, 45.2 mg, dr = 20:1), Scheme 4; prepared according to the Produce B. Ethyl propiolate **1** (40.0 μL, 0.4 mmol), H_2O (5.0 μL, 1.0 equiv.) and benzoic anhydride **2a** (45.3 mg, 0.2 mmol) were employed to give **4j** in 71% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (30:1-4:1). A white solid. mp: 61 °C. ^{1}H NMR (400 MHz, C_6D_6) δ 8.88 (s, 1H), 7.92 (d, *J* = 7.1 Hz, 2H), 7.03 (dd, *J* = 11.4, 7.6 Hz, 1H), 6.93 (t, *J* = 7.7 Hz, 2H), 6.66 (d, *J* = 1.5 Hz, 1H), 5.64 (d, *J* = 1.5 Hz, 1H), 4.02 (q, *J* = 7.1 Hz, 4H), 0.94 (dd, *J* = 13.3, 7.1 Hz, 6H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 172.6, 165.8, 165.6, 162.1, 145.5, 134.2, 133.8, 130.51, 130.49, 130.1, 128.8, 128.6, 116.3, 61.14, 61.01, 14.2, 14.1 ppm. HRMS(ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{18}NaO_6$ 341.0991; found 341.0996.



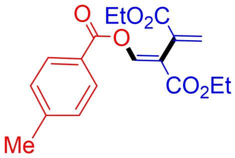
4k (61%, 43.0 mg, dr > 20:1), Scheme 4; prepared according to the Produce B. Ethyl propiolate **1** (40.0 μL, 0.4 mmol), H_2O (5.0 μL, 1.0 equiv.) and 4-chlorobenzoic anhydride **2c** (59.0 mg, 0.2 mmol) were employed to give **4k** in 61% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (30:1-10:1). A white solid. mp: 63-65 °C. ^{1}H NMR (400 MHz, C_6D_6) δ 8.82 (s, 1H), 7.61 (m, 2H), 6.85 (m, 2H), 6.66 (d, *J* = 1.5 Hz, 1H), 5.60 (d, *J* = 1.5 Hz, 1H), 4.02 (q, *J* = 7.2 Hz, 4H), 0.94 (td, *J* = 7.1, 4.7 Hz, 6H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 165.6, 165.4, 161.3, 145.2, 141.7, 140.8, 133.8, 132.3, 131.8, 130.0, 129.2, 126.5, 116.6, 61.2, 61.1, 14.2, 14.1 ppm. HRMS(ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{17}ClNaO_6$ 375.0606; found 375.0596.



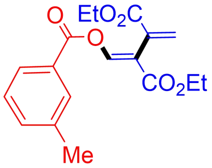
4l (70%, 49.3 mg, dr = 5:1), Scheme 4; prepared according to the Produce B. Ethyl propiolate **1** (40.0 μL, 0.4 mmol), H_2O (5.0 μL, 1.0 equiv.) and 2-chlorobenzoic anhydride **2t** (59.0 mg, 0.2 mmol) were employed to give **4l** in 70% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (20:1- 4:1). A white solid. mp: 62 °C. ^{1}H NMR (400 MHz, C_6D_6) δ 8.84 (s, 1H), 7.54 (dd, *J* = 7.7, 1.8 Hz, 1H), 6.97 (dd, *J* = 7.9, 1.1 Hz, 1H), 6.64 (tdd, *J* = 12.5, 7.5, 1.5 Hz, 3H), 5.62 (d, *J* = 1.5 Hz, 1H), 4.01 (dd, *J* = 7.1, 5.5 Hz, 4H), 0.93 (dt, *J* = 8.9, 7.1 Hz, 6H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 165.5, 165.5, 160.7, 145.2, 136.7, 135.3, 133.8, 133.5, 132.4, 131.6, 130.3, 126.7, 116.8, 61.1, 61.0, 14.2, 14.1 ppm. HRMS(ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{17}ClNaO_6$ 375.0606; found 375.0620.



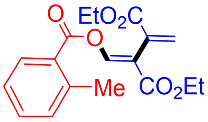
4m (77%, 51.8 mg, dr = 11:1), Scheme 4; prepared according to the Produce B. Ethyl propiolate **1** (40.0 μL, 0.4 mmol), H_2O (5.0 μL, 1.0 equiv.) and 4-fluorobenzoic anhydride **2b** (52.4 mg, 0.2 mmol) were employed to give **4m** in 77% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (30:1- 4:1). A colorless oil. ^{1}H NMR (400 MHz, C_6D_6) δ 8.85 (s, 1H), 7.71 (dd, *J* = 8.8, 5.4 Hz, 2H), 6.66 (d, *J* = 1.4 Hz, 1H), 6.51 (t, *J* = 8.6 Hz, 2H), 5.61 (d, *J* = 1.4 Hz, 1H), 4.02 (qd, *J* = 7.1, 1.6 Hz, 4H), 0.93 (td, *J* = 7.1, 3.9 Hz, 6H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 166.6 (d, *J* = 255.7 Hz), 165.7, 165.5, 161.1, 145.2, 133.8, 133.1 (d, *J* = 9.6 Hz), 130.0, 124.3 (d, *J* = 2.9 Hz), 116.4, 116.0 (d, *J* = 22.3 Hz), 61.1, 61.0, 14.2, 14.1 ppm. HRMS(ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{17}FNaO_6$ 359.0901; found 359.0907.



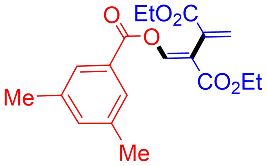
4n (83%, 55.1 mg, dr > 20:1), Scheme 4; prepared according to the Produce B. Ethyl propiolate **1** (40.0 µL, 0.4 mmol), H_2O (5.0 µL, 1.0 equiv.) and 4-methylbenzoic anhydride **2d** (50.9 mg, 0.2 mmol) were employed to give **4n** in 83% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (30:1-4:1). A white solid. mp: 120-122 ºC. ^{1}H NMR (400 MHz, C_6D_6) δ 8.93 (s, 1H), 7.91 (d, *J* = 8.2 Hz, 2H), 6.77 (d, *J* = 8.0 Hz, 2H), 6.69 (d, *J* = 1.5 Hz, 1H), 5.67 (d, *J* = 1.5 Hz, 1H), 4.02 (qd, *J* = 7.1, 1.4 Hz, 4H), 1.89 (s, 3H), 0.93 (td, *J* = 7.1, 4.9 Hz, 6H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 165.8, 165.6, 162.2, 145.6, 145.3, 144.4, 133.9, 130.6, 130.0, 129.7, 129.4, 125.5, 116.0, 61.1, 61.0, 21.5, 14.2, 14.1 ppm. HRMS(ESI) m/z: [M + Na]$^+$ Calcd for $C_{18}H_{20}NaO_6$ 355.1152; found 355.1151.



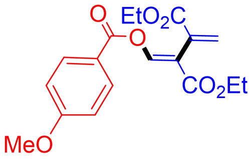
4o (77%, 51.2 mg, dr = 20:1), Scheme 4; prepared according to the Produce B. Ethyl propiolate **1** (40.0 µL, 0.4 mmol), H_2O (5.0 µL, 1.0 equiv.) and 3-methylbenzoic anhydride **2r** (50.9 mg, 0.2 mmol) were employed to give **4o** in 77% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (30:1-4:1). A white solid. mp: 108-110 ºC. ^{1}H NMR (400 MHz, C_6D_6) δ 8.92 (s, 1H), 7.80 (d, *J* = 5.5 Hz, 2H), 6.95 – 6.87 (m, 2H), 6.68 (d, *J* = 1.4 Hz, 1H), 5.67 (d, *J* = 1.5 Hz, 1H), 4.02 (qd, *J* = 7.1, 2.2 Hz, 4H), 1.92 (s, 3H), 0.93 (dd, *J* = 14.9, 7.2 Hz, 6H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 165.8, 165.6, 162.3, 145.5, 138.8, 135.1, 133.9, 131.2 130.0, 128.8, 128.2, 127.7, 116.2, 61.1, 61.0, 20.9, 14.2, 14.1 ppm. HRMS(ESI) m/z: [M + Na]$^+$ Calcd for $C_{18}H_{20}NaO_6$ 355.1152; found 355.1158.



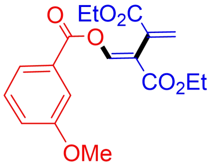
4p (65%, 43.2 mg, dr > 20:1), Scheme 4; prepared according to the Produce B. Ethyl propiolate **1** (40.0 µL, 0.4 mmol), H_2O (5.0 µL, 1.0 equiv.) and 2-methylbenzoic anhydride **2s** (50.9 mg, 0.2 mmol) were employed to give **4p** in 65% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (30:1-4:1). A white solid. mp: 102-104 ºC. ^{1}H NMR (400 MHz, C_6D_6) δ 8.90 (s, 1H), 7.86(m, 1H), 6.99 (td, *J* = 7.5, 1.2 Hz, 1H), 6.84 (dd, *J* = 12.1, 7.7 Hz, 2H), 6.64 (d, *J* = 1.5 Hz, 1H), 5.64 (d, *J* = 1.5 Hz, 1H), 4.02 (qd, *J* = 7.1, 3.6 Hz, 4H), 2.46 (s, 3H), 0.94 (dt, *J* = 8.7, 7.1 Hz, 6H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 165.68, 165.66, 162.3, 145.6, 142.5, 134.0, 133.4, 132.2, 131.5, 130.0, 127.0, 126.2, 115.9, 61.1, 60.9, 22.1, 14.2, 14.1 ppm. HRMS(ESI) m/z: [M + Na]$^+$ Calcd for $C_{18}H_{20}NaO_6$ 355.1152; found 355.1152.



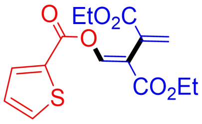
4q (58%, 40.2 mg, dr > 20:1), Scheme 4; prepared according to the Produce B. Ethyl propiolate **1** (40.0 µL, 0.4 mmol), H_2O (5.0 µL, 1.0 equiv.) and 3,5-dimethylbenzoic anhydride **2f** (54.9 mg, 0.2 mmol) were employed to give **4q** in 58% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (30:1-5:1). A white solid. mp: 95-97 ºC. ^{1}H NMR (400 MHz, C_6D_6) δ 8.96 (s, 1H), 7.69 (s, 2H), 6.74 (s, 1H), 6.70 (d, *J* = 1.4 Hz, 1H), 5.69 (d, *J* = 1.4 Hz, 1H), 4.01 (dd, *J* = 7.1, 3.9 Hz, 4H), 1.94 (s, 6H), 0.92 (dt, *J* = 8.8, 7.1 Hz, 6H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 165.8, 165.6, 162.5, 145.7, 138.6, 136.1, 133.9, 129.9, 116.1, 61.1, 61.0, 20.9, 14.2, 14.1 ppm. HRMS(ESI) m/z: [M + Na]$^+$ Calcd for $C_{19}H_{22}NaO_6$ 369.1309; found 369.1318.



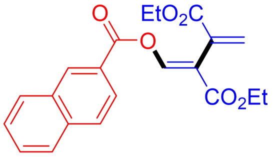
4r (59%, 41.1 mg, dr > 20:1), Scheme 4; prepared according to the Produce B. Ethyl propiolate **1** (40.0 µL, 0.4 mmol), H_2O (5.0 µL, 1.0 equiv.) and 4-methoxybenzoic anhydride **2e** (57.3 mg, 0.2 mmol) were employed to give **4r** in 59% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (20:1-5:1). A colorless oil. ^{1}H NMR (400 MHz, C_6D_6) δ 8.93 (s, 1H), 7.94 (d, J = 8.9 Hz, 2H), 6.70 (d, J = 1.6 Hz, 1H), 6.53 (d, J = 8.9 Hz, 2H), 5.70 (d, J = 1.6 Hz, 1H), 4.02 (qd, J = 7.1, 3.1 Hz, 4H), 3.16 (s, 3H), 0.94 (td, J = 7.1, 4.2 Hz, 6H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 165.9, 165.7, 164.8, 161.8, 145.7, 133.9, 132.8, 129.9, 120.3, 115.7, 114.3, 61.1, 60.9, 55.1, 14.2, 14.1 ppm. HRMS(ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{20}NaO_7$ 371.1101; found 371.1099.



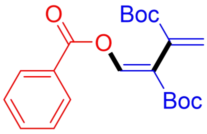
4s (62%, 43.2 mg, dr = 20:1), Scheme 4; prepared according to the Produce B. Ethyl propiolate **1** (40.0 µL, 0.4 mmol), H_2O (5.0 µL, 1.0 equiv.) and 3-methoxybenzoic anhydride **2u** (57.3 mg, 0.2 mmol) were employed to give **4s** in 62% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (30:1- 10:1). A white solid. mp: 69-71 ºC. ^{1}H NMR (400 MHz, C_6D_6) δ 8.89 (s, 1H), 7.62-7.58 (m, 1H), 7.57-7.54 (m, 1H), 6.89 (t, J = 7.9 Hz, 1H), 6.81 (ddd, J = 8.3, 2.6, 1.0 Hz, 1H), 6.65 (d, J = 1.5 Hz, 1H), 5.66 (d, J = 1.5 Hz, 1H), 4.01 (qd, J = 7.1, 1.7 Hz, 4H), 3.20 (s, 3H), 0.92 (q, J = 7.1 Hz, 6H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 165.8, 165.5, 162.1, 160.2, 145.4, 133.8, 130.0, 129.5, 128.2, 122.9, 121.3, 116.3, 114.7, 61.1, 61.0, 54.9, 14.2, 14.1 ppm. HRMS(ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{20}NaO_6$ 371.1101; found 371.1100.



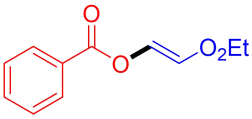
4t (68%, 44.1 mg, dr > 20:1), Scheme 4; prepared according to the Produce B. Ethyl propiolate **1** (40.0 µL, 0.4 mmol), H_2O (5.0 µL, 1.0 equiv.) and thiophene-2-carboxylic anhydride **2g** (47.7 mg, 0.2 mmol) were employed to give **4t** in 68% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (20:1-5:1). A white solid. mp: 72-74 ºC. ^{1}H NMR (400 MHz, C_6D_6) δ 8.80 (s, 1H), 7.53 (dd, J = 3.8, 1.1 Hz, 1H), 6.78 – 6.68 (m, 2H), 6.39 (dd, J = 4.9, 3.9 Hz, 1H), 5.65 (d, J = 1.5 Hz, 1H), 4.01 (dq, J = 14.2, 7.1 Hz, 4H), 0.93 (td, J = 7.1, 2.8 Hz, 6H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 165.7, 165.5, 157.6, 145.0, 135.6, 134.6, 133.6, 131.3, 130.1, 128.2,116.2, 61.1, 61.0, 14.2, 14.1 ppm. HRMS(ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{16}SNaO_6$ 347.0560; found 347.0570.



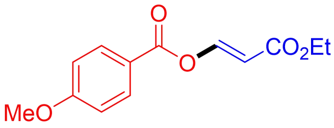
4u (70%, 51.5 mg, dr > 20:1), Scheme 4; prepared according to the Produce B. Ethyl propiolate **1** (40.0 µL, 0.4 mmol), H_2O (5.0 µL, 1.0 equiv.) and 2-naphthoic anhydride **2v** (67.3 mg, 0.2 mmol) were employed to give **4u** in 70% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (30:1-4:1). A white solid. mp: 76 ºC. ^{1}H NMR (400 MHz, C_6D_6) δ 8.99 (s, 1H), 8.55 (s, 1H), 8.00 (dd, J = 8.6, 1.6 Hz, 1H), 7.44 (m, 2H), 7.13 – 7.07 (m, 1H), 6.76 (d, J = 1.4 Hz, 1H), 5.72 (d, J = 1.4 Hz, 1H), 4.04 (q, J = 7.0 Hz, 4H), 0.94 (dt, J = 10.7, 7.1 Hz, 6H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 165.9, 165.6, 162.3, 145.6, 142.1, 136.3, 133.9, 132.9, 132.7, 130.1, 129.9, 129.1, 128.9, 127.1, 125.9, 125.4, 116.3, 61.1, 61.0, 14.2, 14.1 ppm. HRMS(ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{20}NaO_6$ 391.1152; found 391.1143.



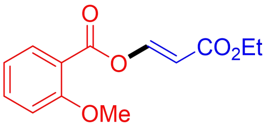
4v (31%, 23.2 mg, dr > 20:1), Scheme 4; prepared according to the Produce B. *Tert*-butyl propiolate (53.3 μL, 0.4 mmol) and benzoic anhydride **2a** (45.3 mg, 0.2 mmol) were employed to give **4v** in 70% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (20:1-10:1). A colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.95 (dd, J = 8.4, 1.3 Hz, 2H), 7.54 (t, J = 7.5 Hz, 1H), 7.38 (t, J = 7.8 Hz, 2H), 6.46 (d, J = 1.6 Hz, 1H), 5.69 (d, J = 1.6 Hz, 1H), 1.40 (d, J = 14.9 Hz, 18H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 163.9, 161.3, 143.2, 133.3, 129.3, 128.2, 127.8, 126.9, 116.3, 80.4, 80.2, 27.1, 27.0 ppm. HRMS(ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{26}NaO_6$ 397.1622; found 397.1631.



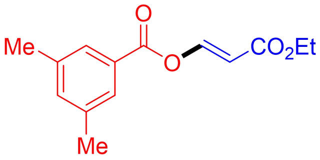
5a (77%, 32.0 mg, dr = 6:1), Scheme 5; prepared according to the Produce C. Ethyl propiolate **1** (30.0 μL, 0.3 mmol), H_2O (5.0 μL, 1.0 equiv.) and benzoic anhydride **2a** (45.3 mg, 0.2 mmol) were employed to give **5a** in 77% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (40:1-10:1). A colorless oil. ^{1}H NMR (400 MHz, C_6D_6) δ 8.75 (d, J = 12.5 Hz, 1H), 7.88 (d, J = 7.1 Hz, 2H), 7.07 (t, J = 7.4 Hz, 1H), 6.94 (t, J = 7.7 Hz, 2H), 5.87 (d, J = 12.5 Hz, 1H), 4.01 (q, J = 7.1 Hz, 2H), 0.95 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 165.7, 162.5, 149.8, 134.1, 130.5, 128.7, 128.2, 106.7, 60.4, 14.2 ppm. HRMS(ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{12}NaO_4$ 243.0628; found 243.0635.



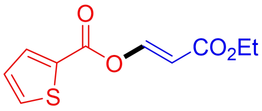
5b (90%, 45.0 mg, dr = 8:1), Scheme 5; prepared according to the Produce C. Ethyl propiolate **1** (30.0 μL, 0.3 mmol), H_2O (5.0 μL, 1.0 equiv.) and 4-methoxybenzoic anhydride **2e** (57.3 mg, 0.2 mmol) were employed to give **5b** in 90% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (40:1-10:1). A white solid. mp: 80 - 82 °C. ^{1}H NMR (400 MHz, C_6D_6) δ 8.83 (d, J = 12.6 Hz, 1H), 7.91 (d, J = 9.0 Hz, 2H), 6.54 (d, J = 9.0 Hz, 2H), 5.90 (d, J = 12.6 Hz, 1H), 4.01 (q, J = 7.1 Hz, 2H), 3.13 (s, 3H), 0.96 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 165.9, 164.7, 162.2, 150.1, 132.8, 120.4, 114.2, 106.2, 60.3, 55.0, 14.3 ppm. HRMS(ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{14}NaO_5$ 273.0733; found 273.0722.



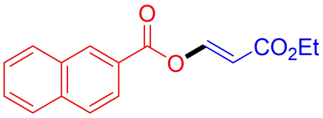
5c (84%, 42.0 mg, dr > 20:1), Scheme 5; prepared according to the Produce C. Ethyl propiolate **1** (30.0 μL, 0.3 mmol), H_2O (5.0 μL, 1.0 equiv.) and 2-methoxybenzoic anhydride **2w** (57.3 mg, 0.2 mmol) were employed to give **5c** in 84% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (40:1-10:1). A white solid. mp: 72 - 74 °C. ^{1}H NMR (400 MHz, C_6D_6) δ 8.85 (d, J = 12.5 Hz, 1H), 7.72 (dd, J = 7.8, 1.8 Hz, 1H), 7.05 (ddd, J = 8.6, 7.4, 1.8 Hz, 1H), 6.62 (td, J = 7.8, 0.9 Hz, 1H), 6.37 (d, J = 8.4 Hz, 1H), 5.90 (d, J = 12.6 Hz, 1H), 3.99 (q, J = 7.1 Hz, 2H), 3.22 (s, 3H), 0.94 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 165.9, 161.5, 160.5, 150.2, 134.8, 132.6, 120.2, 117.9, 112.3, 106.2, 60.3, 55.4, 14.2 ppm. HRMS(ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{14}NaO_5$ 273.0733; found 273.0730.



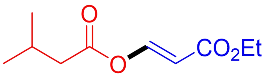
5d (98%, 48.6 mg, dr = 6:1), Scheme 5; prepared according to the Produce C. Ethyl propiolate **1** (30.0 μL, 0.3 mmol), H_2O (5.0 μL, 1.0 equiv.) and 3,5-dimethylbenzoic anhydride **2f** (54.9 mg, 0.2 mmol) were employed to give **5d** in 98% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (40:1-10:1). A white solid. mp: 75 °C. ^{1}H NMR (400 MHz, C_6D_6) δ 8.57 (d, *J* = 12.6 Hz, 1H), 7.42 (s, 1H), 6.91 (s, 1H), 6.54 (s, 1H), 5.64 (d, *J* = 12.6 Hz, 1H), 3.77(m, 2H), 1.73 (d, *J* = 0.4 Hz, 6H), 0.71 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 164.6, 161.6, 148.8, 137.3, 134.9, 127.5, 127.2, 105.3, 59.2, 19.7, 13.1 ppm. HRMS(ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{16}NaO_4$ 271.0941; found 271.0953.



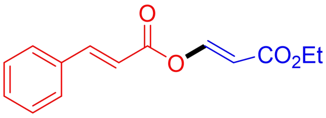
5e (64%, 28.9 mg, dr = 5:1), Scheme 5; prepared according to the Produce C. Ethyl propiolate **1** (30.0 μL, 0.3 mmol), H_2O (5.0 μL, 1.0 equiv.) and thiophene-2-carboxylic anhydride **2g** (47.7 mg, 0.2 mmol) were employed to give **5e** in 64% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (40:1-10:1). A white solid. mp: 62 - 64 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 12.5 Hz, 1H), 7.96 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.71 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.18 (dd, *J* = 4.9, 3.8 Hz, 1H), 5.88 (d, *J* = 12.5 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 153.2, 135.4, 127.7, 121.6, 87.0, 81.5, 62.5, 61.4, 14.0 ppm. HRMS(ESI) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{10}SNaO_4$ 249.0192; found 249.0197.



5f (70%, 37.8 mg, dr = 9:1), Scheme 5; prepared according to the Produce C. Ethyl propiolate **1** (30.0 μL, 0.3 mmol), H_2O (5.0 μL, 1.0 equiv.) and 2-naphthoic anhydride **2v** (67.3 mg, 0.2 mmol) were employed to give **5f** in 70% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (40:1-10:1). A white solid. mp: 82 - 84 °C. ^{1}H NMR (400 MHz, C_6D_6) δ 8.83 (d, *J* = 12.5 Hz, 1H), 8.49 (s, 1H), 8.00 -7.91 (m, 1H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.47-7.42 (m, 2H), 7.20 (t, *J* = 7.5 Hz, 1H), 5.93 (d, *J* = 12.6 Hz, 1H), 4.03 (q, *J* = 7.2 Hz, 2H), 0.97 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 162.8, 149.9, 136.3, 132.9, 132.6, 129.7, 129.3, 128.9, 127.9, 127.2, 125.4, 125.2, 106.5, 60.6, 14.3 ppm. HRMS(ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{14}NaO_4$ 293.0784; found 293.0785.



5g (53%, 21.2 mg, dr > 20:1), Scheme 5; prepared according to the Produce C. Ethyl propiolate **1** (30.0 μL, 0.3 mmol), H_2O (5.0 μL, 1.0 equiv.) and 3-methylbutanoic anhydride **2m** (39.0 μL, 0.2 mmol) were employed to give **5g** in 53% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (40:1-10:1). A colorless oil. ^{1}H NMR (400 MHz, C_6D_6) δ 8.65 (d, *J* = 12.6 Hz, 1H), 5.81 (d, *J* = 12.6 Hz, 1H), 4.00 (q, *J* = 7.1 Hz, 2H), 1.82 (dd, *J* = 13.0, 6.5 Hz, 1H), 1.76 (d, *J* = 6.4 Hz, 2H), 0.94 (t, *J* = 7.1 Hz, 3H), 0.67 (d, *J* = 6.4 Hz, 6H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 168.5, 165.8, 149.6, 106.0, 60.4, 42.3, 25.3, 22.0, 14.2 ppm. HRMS(ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_{17}O_4$ 201.1121; found 201.1129.



5h (75%, 36.9 mg, dr > 20:1), Scheme 5; prepared according to the Produce C. Ethyl propiolate **1** (30.0 μL, 0.3 mmol), H_2O (5.0 μL, 1.0 equiv.) and cinnamic anhydride **2x** (55.6 mg, 0.2 mmol) were employed to give **5h** in

75% yield by column chromatography isolation on silica gel via gradient elution with petroleum ether / ethyl acetate (40:1-10:1). A white solid. mp: 63 - 65 °C. ^{1}H NMR (400 MHz, C_6D_6) δ 8.80 (d, *J* = 12.6 Hz, 1H), 7.64 (d, *J* = 16.0 Hz, 1H), 7.05 – 6.88 (m, 5H), 6.10 (d, *J* = 16.0 Hz, 1H), 5.91 (d, *J* = 12.6 Hz, 1H), 4.03 (q, *J* = 7.1 Hz, 2H), 0.96 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, C_6D_6) δ 165.8, 162.5, 149.9, 148.2, 134.1, 131.0, 129.0, 128.7, 115.7, 106.2, 60.4, 14.3 ppm. HRMS(ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{14}NaO_4$ 269.0784; found 269.0790.

VII. ORTEP Drawings for 3b, 4k, 5b

Table S3. Crystal data and structure refinement for 3b (ellipsoids at 50% probability)

Tips: hexane and ethyl acetate were used for the crystal growth.

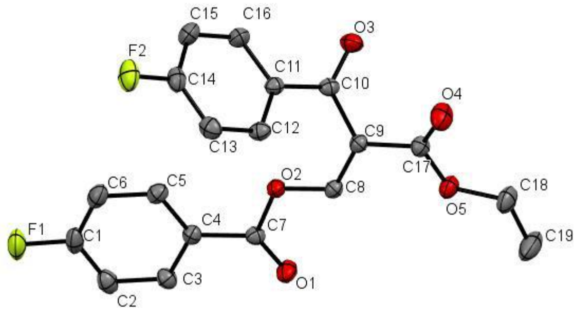


Figure S1. X-ray Crystal Structure of **3b**

Identification code	**3b**
Empirical formula	$C_{19}H_{14}F_2O_5$
Formula weight	360.30
Temperature	113.15 K
Crystal system, Space group	orthorhombic, Pna21
Unit cell dimensions	a=7.2621(2) Å, α=90°
	b=14.5996(4) Å, β=90°
	c=15.7127(5) Å, γ=90°
Volume	1665.92(8) Å^3
Z, Calculated density	4, 1.437 g/cm^3
Absorption coefficient	0.118 mm^{-1}
F(000)	744.0
Crystal size	0.23 × 0.2 × 0.14 mm^3
Radiation	MoK α (λ = 0.71073)
2Θ range for data collection	5.186 to 65.81°
Limiting indices	$-10 \leq h \leq 10$, $-22 \leq k \leq 21$, $-23 \leq l \leq 23$
Reflections collected/unique	23672/5790 [Rint = 0.0466, Rsigma = 0.0352]
Data/restraints/parameters	5790/1/237
Goodness-of-fit on F2	1.023
Final R indexes [I>=2σ (I)]	R1 = 0.0385, wR2 = 0.0925
Final R indexes [all data]	R1 = 0.0443, wR2 = 0.0965
Largest diff. peak/hole	0.30/-0.25 e Å^{-3}
Flack parameter	-0.3(3)
CCDC	2133581

Table S4. Crystal data and structure refinement for 4k (ellipsoids at 50% probability)

Tips: hexane and ethyl acetate were used for the crystal growth.

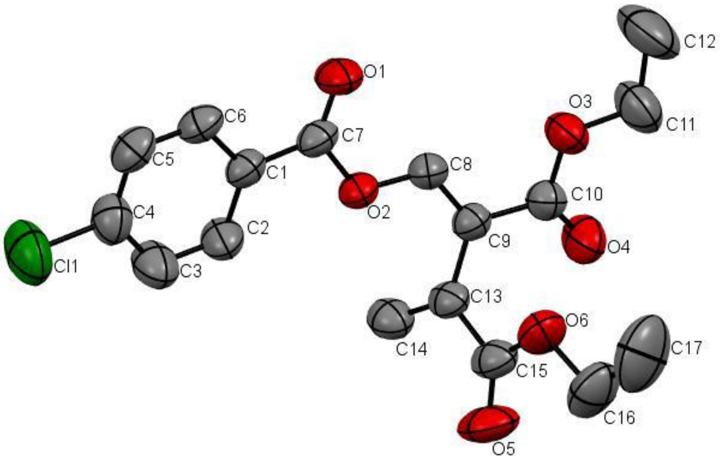


Figure S2. X-ray Crystal Structure of **4k**

Identification code	**4k**
Empirical formula	$C_{17}H_{17}ClO_6$
Formula weight	352.75
Temperature	300.85(10) K
Crystal system, Space group	triclinic, P-1
Unit cell dimensions	a=7.7704(5) Å, α=91.269(5)°
	b=10.7352(7) Å, β=97.889(5)°
	c=10.8707(7) Å, γ=90.643(5)°
Volume	897.90(10) Å^3
Z, Calculated density	2, 1.305 g/cm^3
Absorption coefficient	0.240 mm^{-1}
F(000)	368.0
Crystal size	0.25 × 0.21 × 0.15
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection	3.784 to 61.814°
Limiting indices	$-10 \leq h \leq 9$, $-15 \leq k \leq 13$, $-13 \leq l \leq 15$
Reflections collected/unique	12562, 4507 [Rint = 0.0267, Rsigma = 0.0325]
Data/restraints/parameters	4507/24/246
Goodness-of-fit on F2	1.044
Final R indexes [I>=2σ (I)]	R1 = 0.0498, wR2 = 0.1386
Final R indexes [all data]	R1 = 0.0920, wR2 = 0.1583
Largest diff. peak/hole	0.26/-0.33 e Å^{-3}
CCDC	2143069

Table S5. Crystal data and structure refinement for 5b (ellipsoids at 50% probability)

Tips: hexane and ethyl acetate were used for the crystal growth.

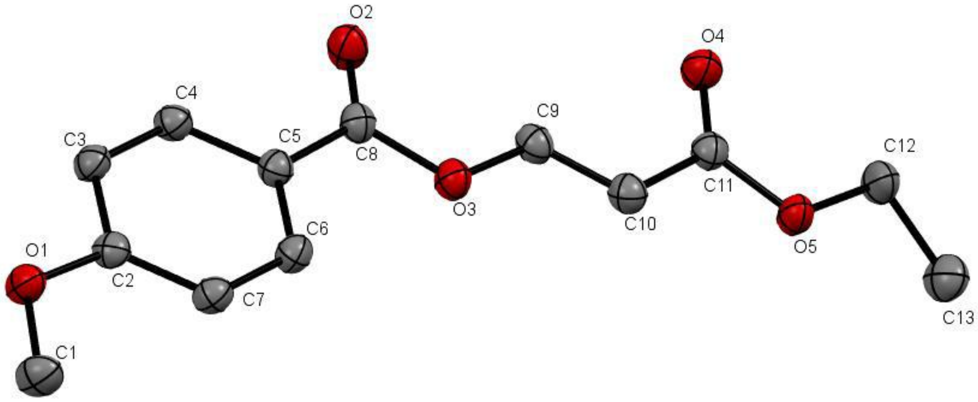


Figure S3. X-ray Crystal Structure of **5b**

Identification code	**5b**
Empirical formula	$C_{13}H_{14}O_5$
Formula weight	250.24
Temperature	113.15 K
Crystal system, Space group	triclinic, P-1
Unit cell dimensions	a=8.4627(5) Å, α=79.025(5)°
	b=8.5873(4) Å, β=66.995(6)°
	c=9.3807(7) Å, γ=77.883(5)°
Volume	609.05(7) Å^3
Z, Calculated density	2, 1.365 g/cm^3
Absorption coefficient	0.105 mm^{-1}
F(000)	264.0
Crystal size	0.24 × 0.22 × 0.17
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	4.752 to 65.818°
Limiting indices	$-12 \leq h \leq 12$, $-12 \leq k \leq 11$, $-13 \leq l \leq 14$
Reflections collected/unique	9172, 4079 [Rint = 0.0293, Rsigma = 0.0375]
Data/restraints/parameters	4079/0/166
Goodness-of-fit on F2	1.045
Final R indexes [I>=2σ (I)]	R1 = 0.0479, wR2 = 0.1217
Final R indexes [all data]	R1 = 0.0649, wR2 = 0.1370
Largest diff. peak/hole	0.34/-0.25 e Å^{-3}
CCDC	2132379

VIII. Supplementary References

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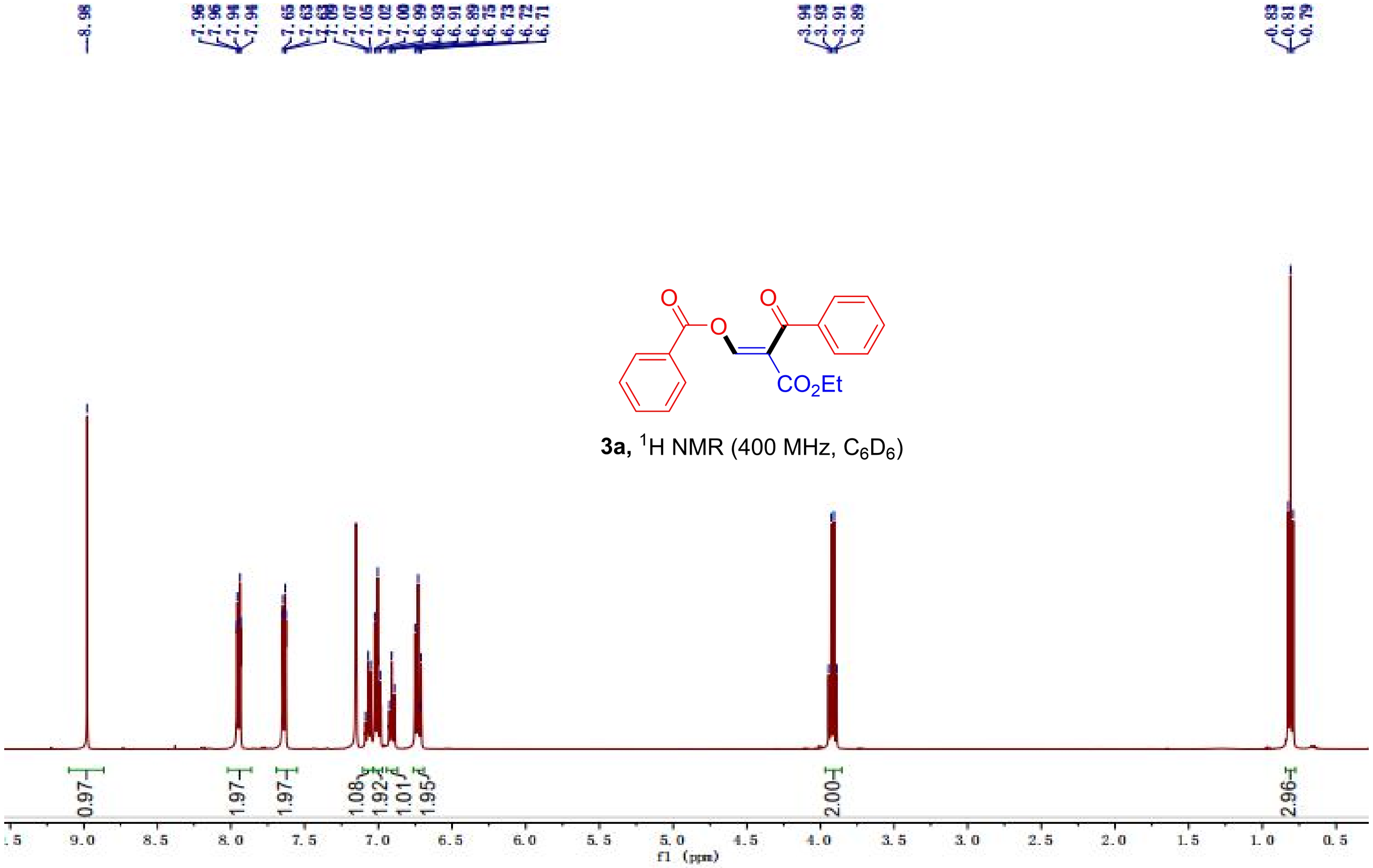
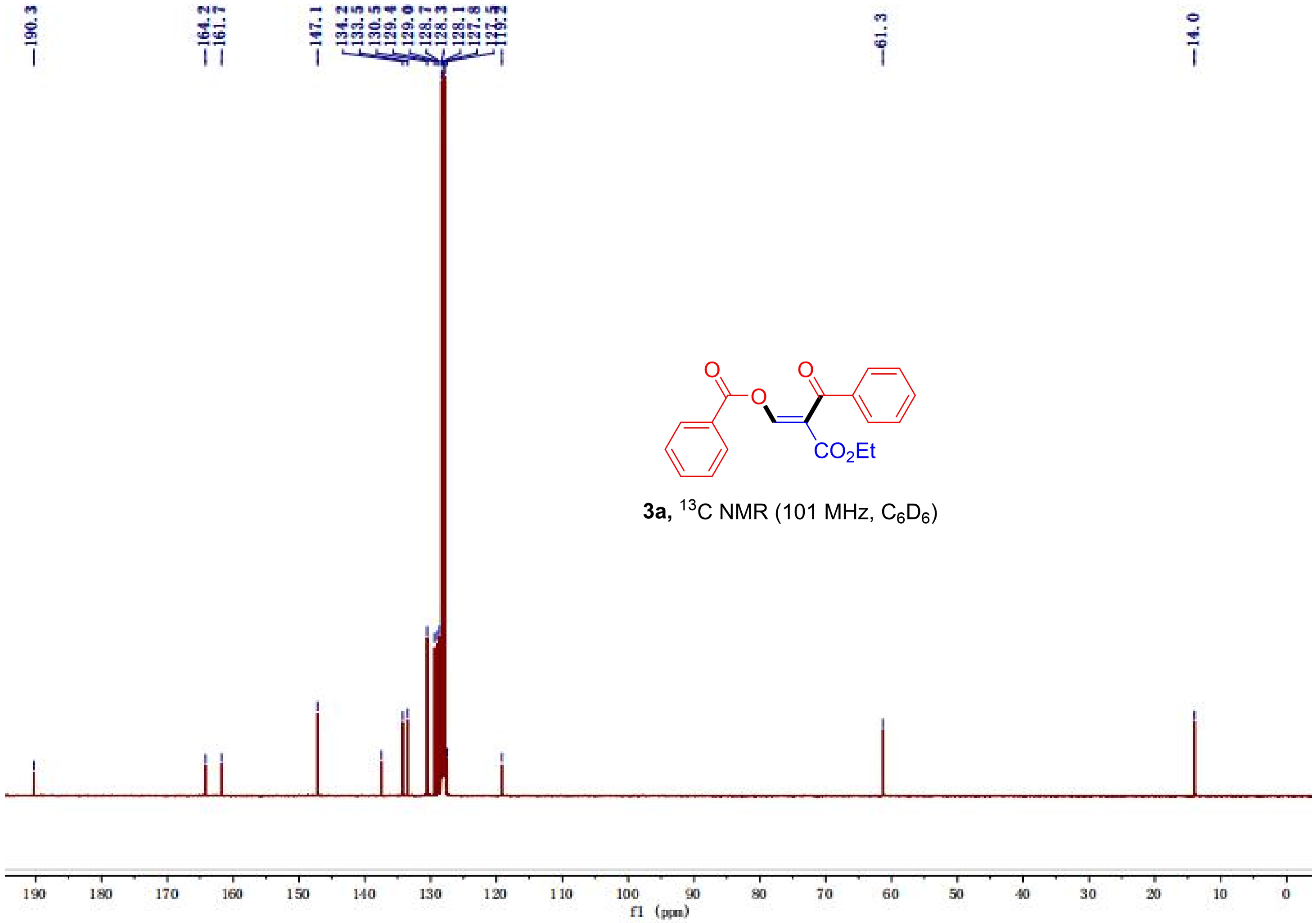
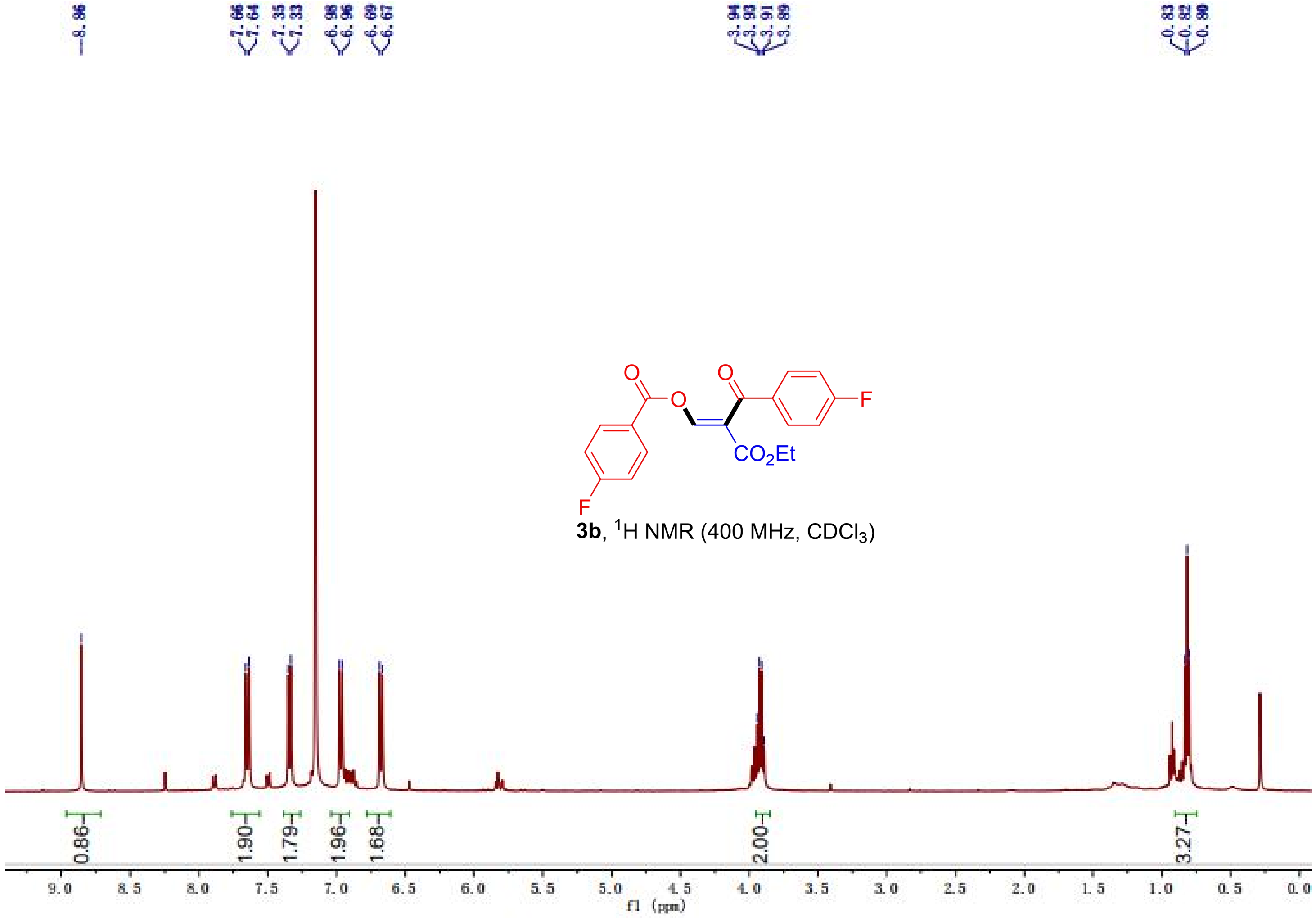
IX. ^{1}H and ^{13}C NMR Spectra for Compounds 3, 4, and 5



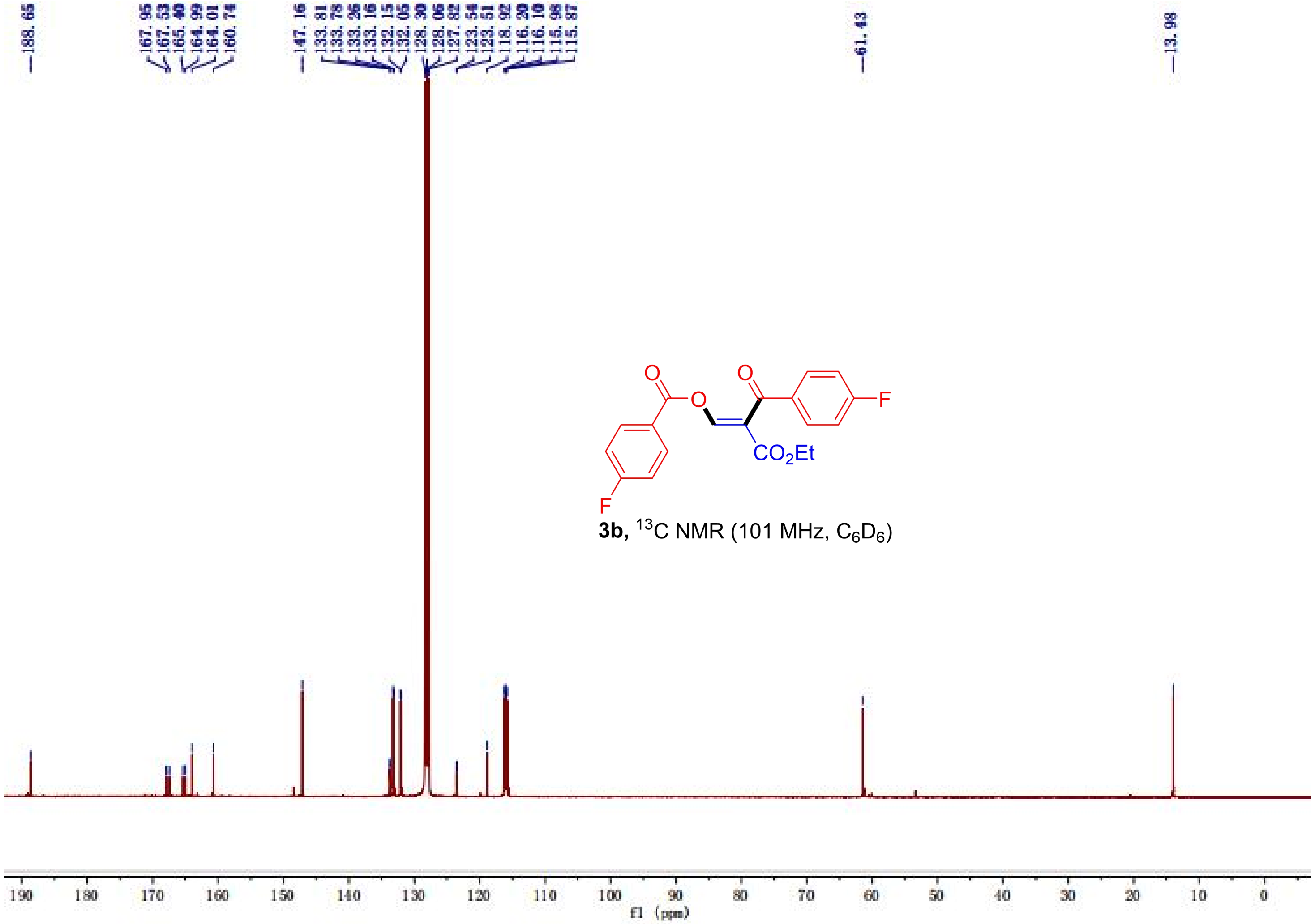
3a, ^{1}H NMR (400 MHz, C_6D_6)



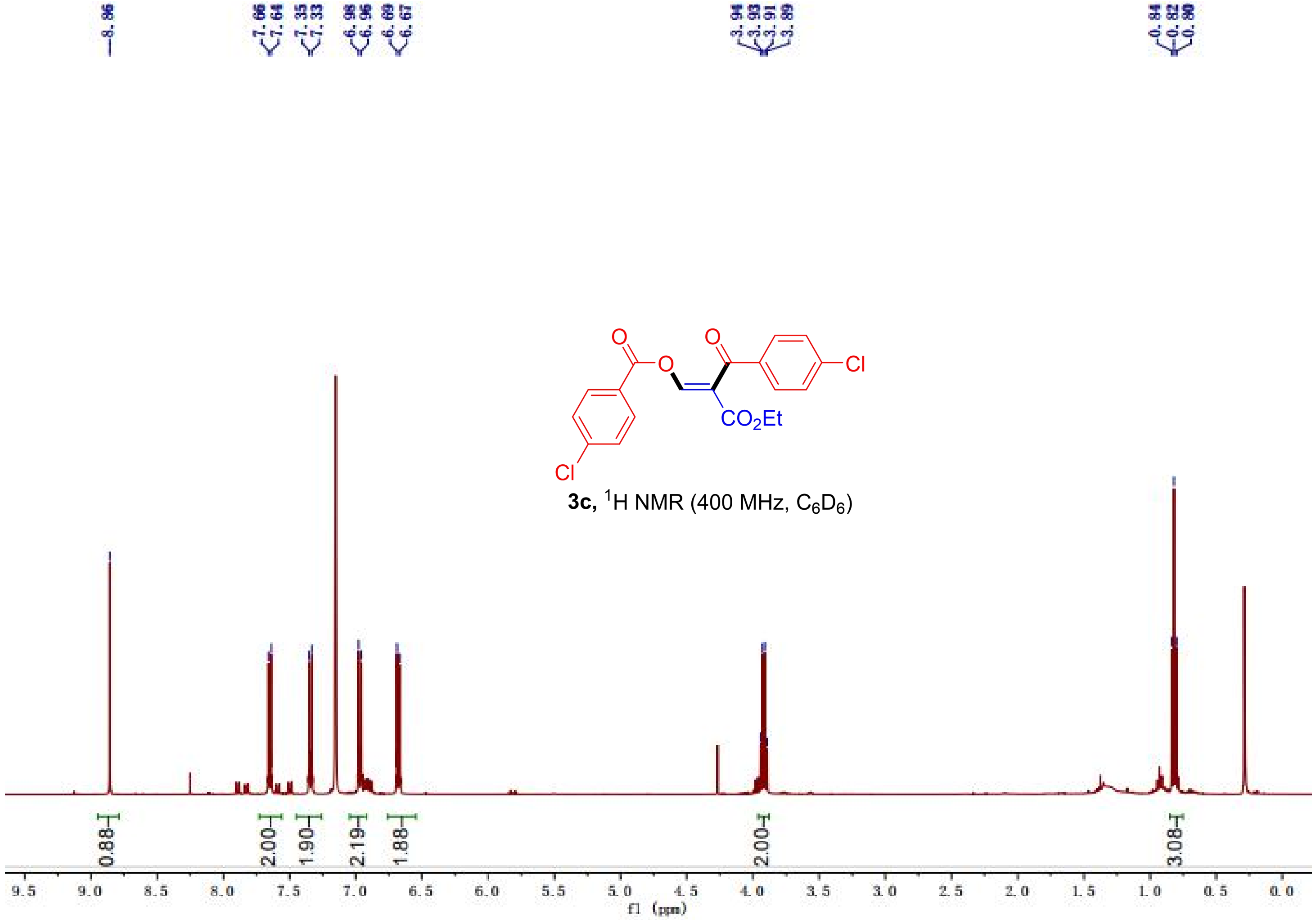
3a, ^{13}C NMR (101 MHz, C_6D_6)



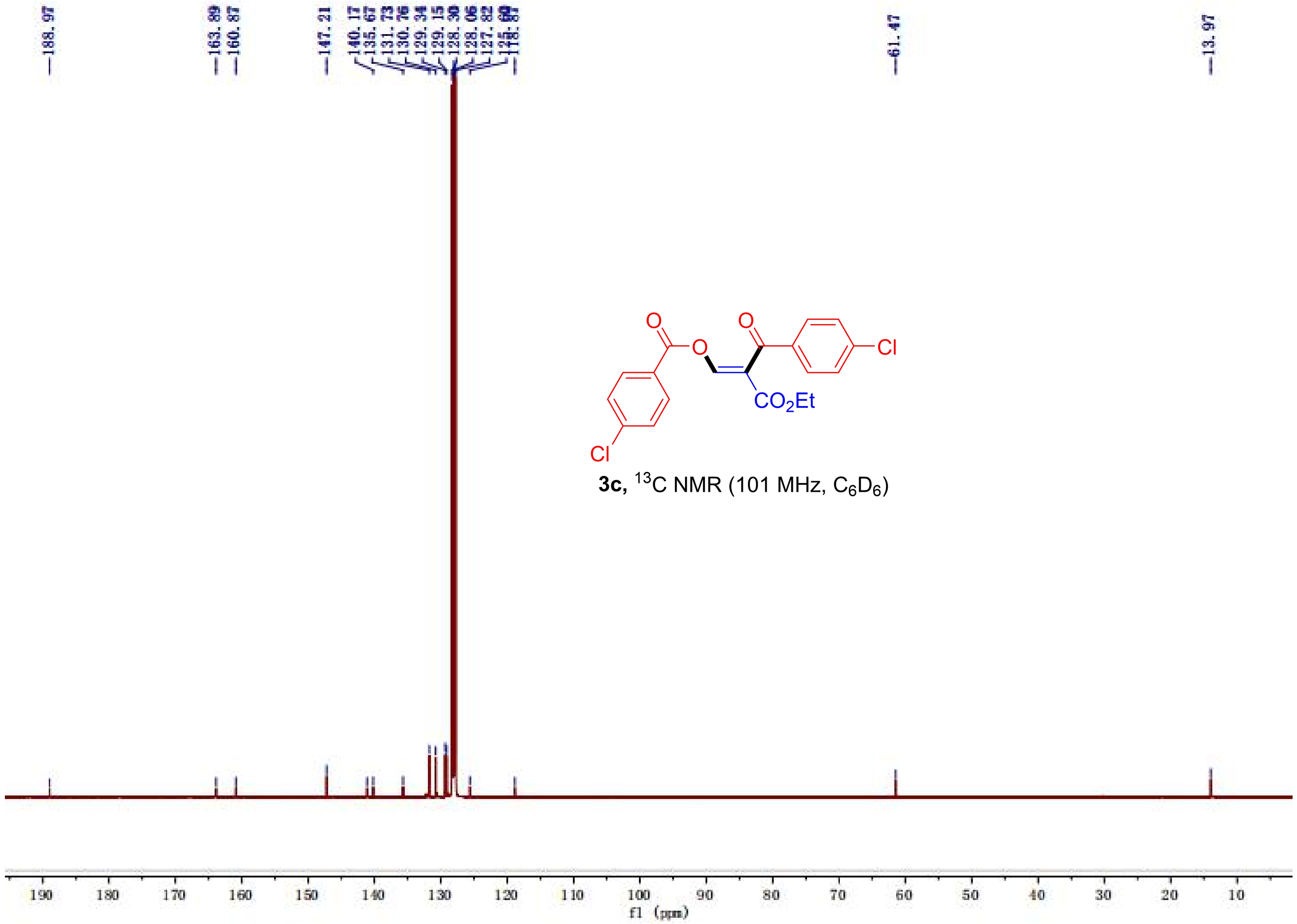
3b, ^{1}H NMR (400 MHz, CDCl$_3$)



3b, ^{13}C NMR (101 MHz, C_6D_6)



3c, ^{1}H NMR (400 MHz, C_6D_6)



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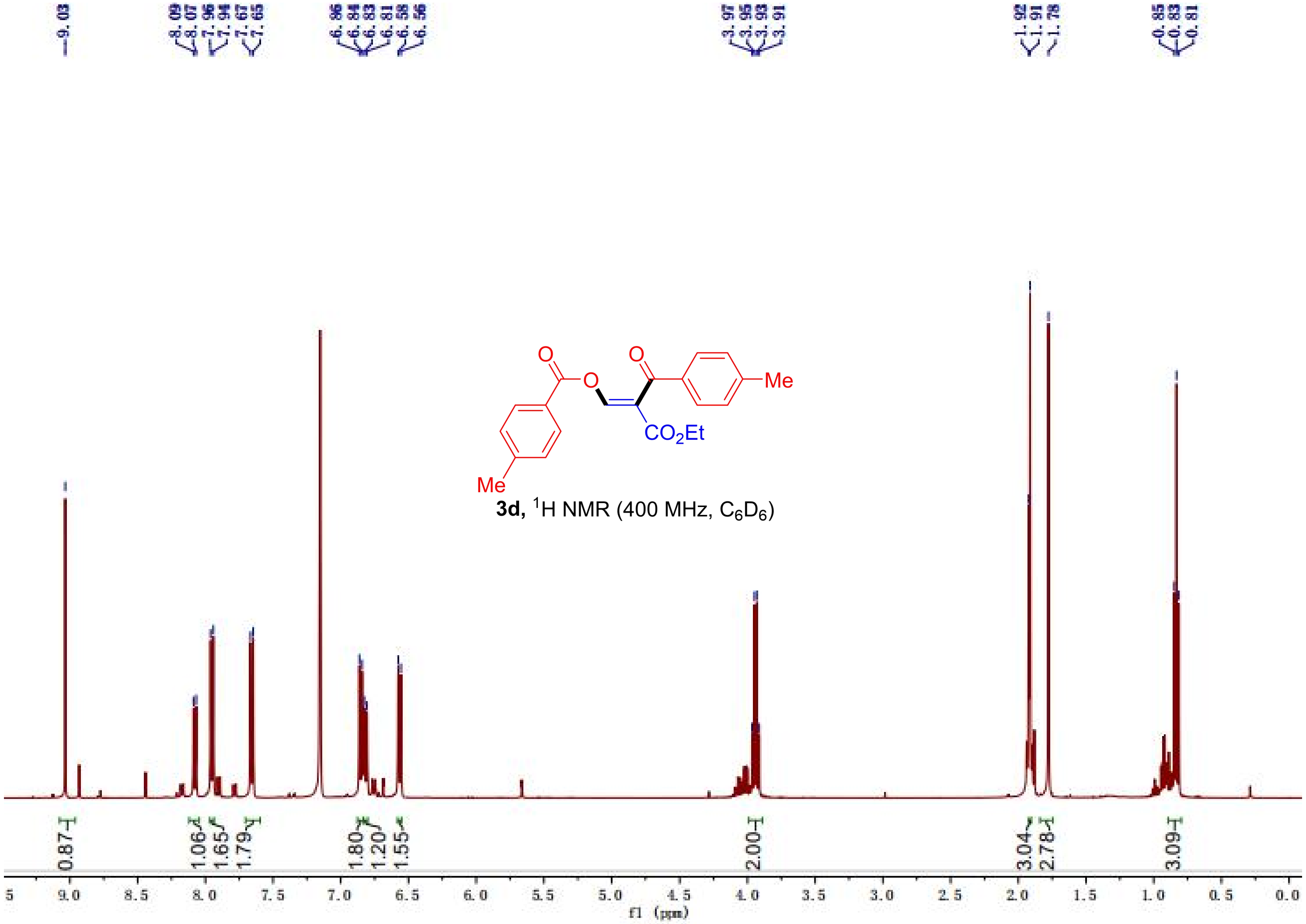

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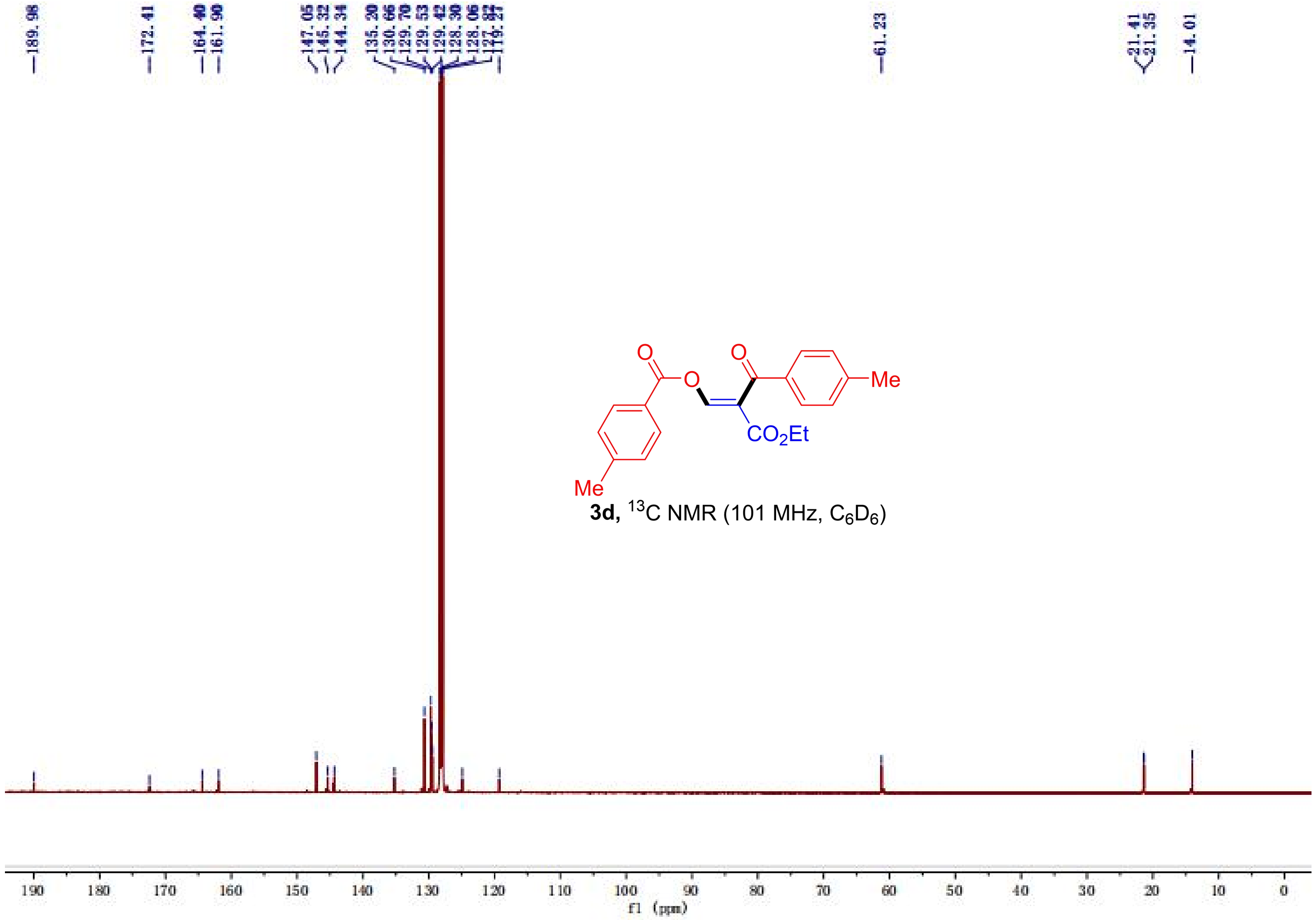

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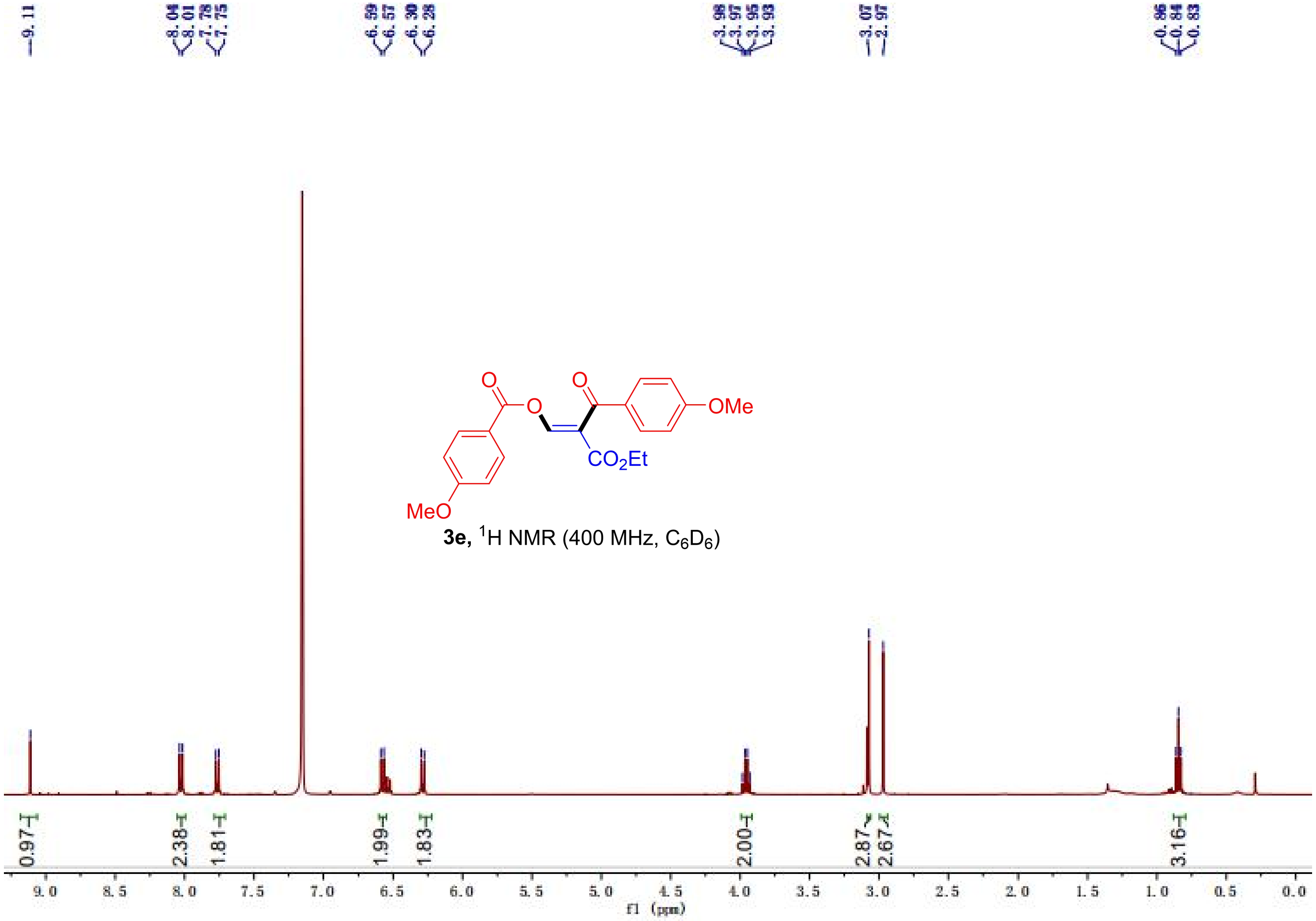

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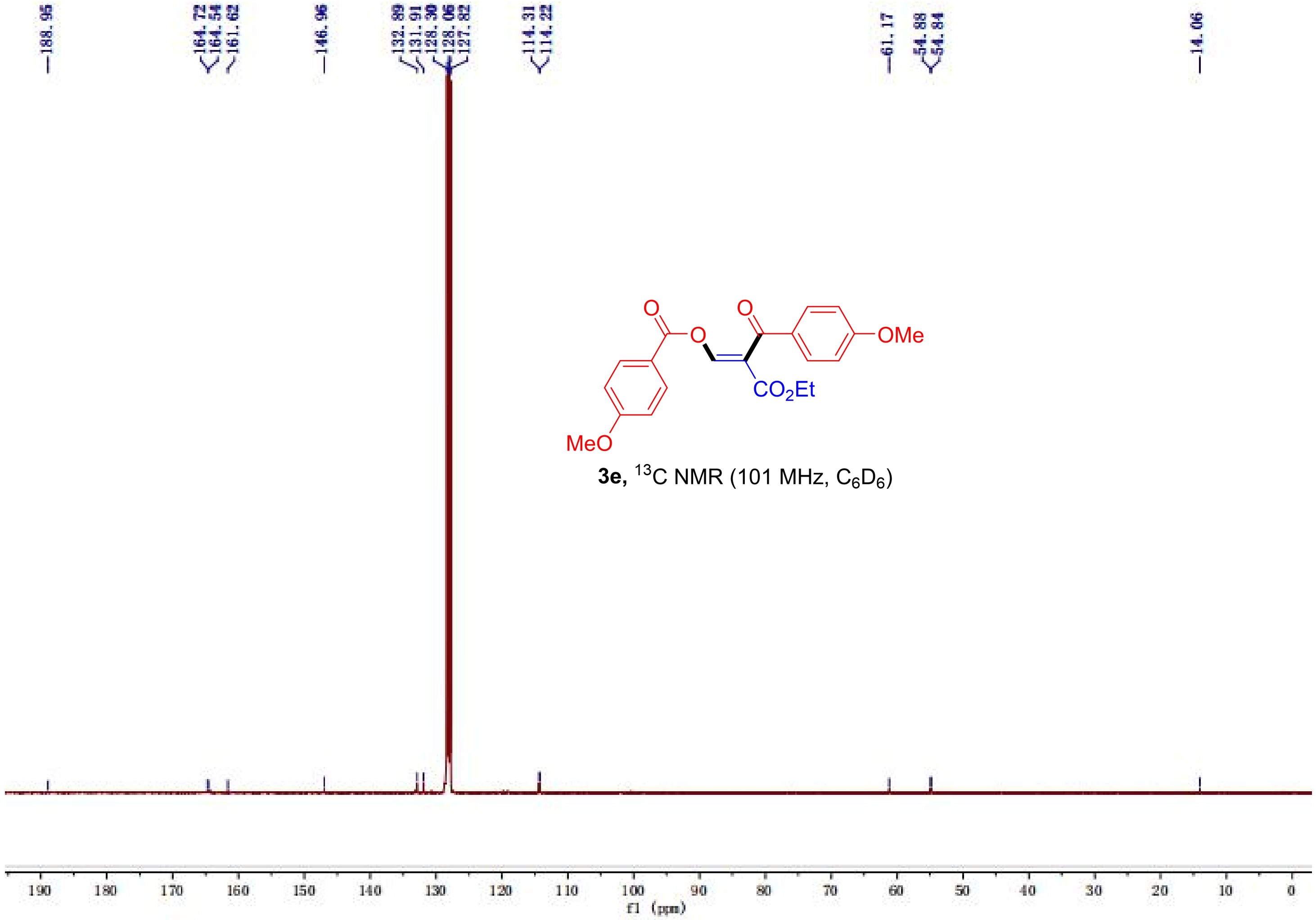

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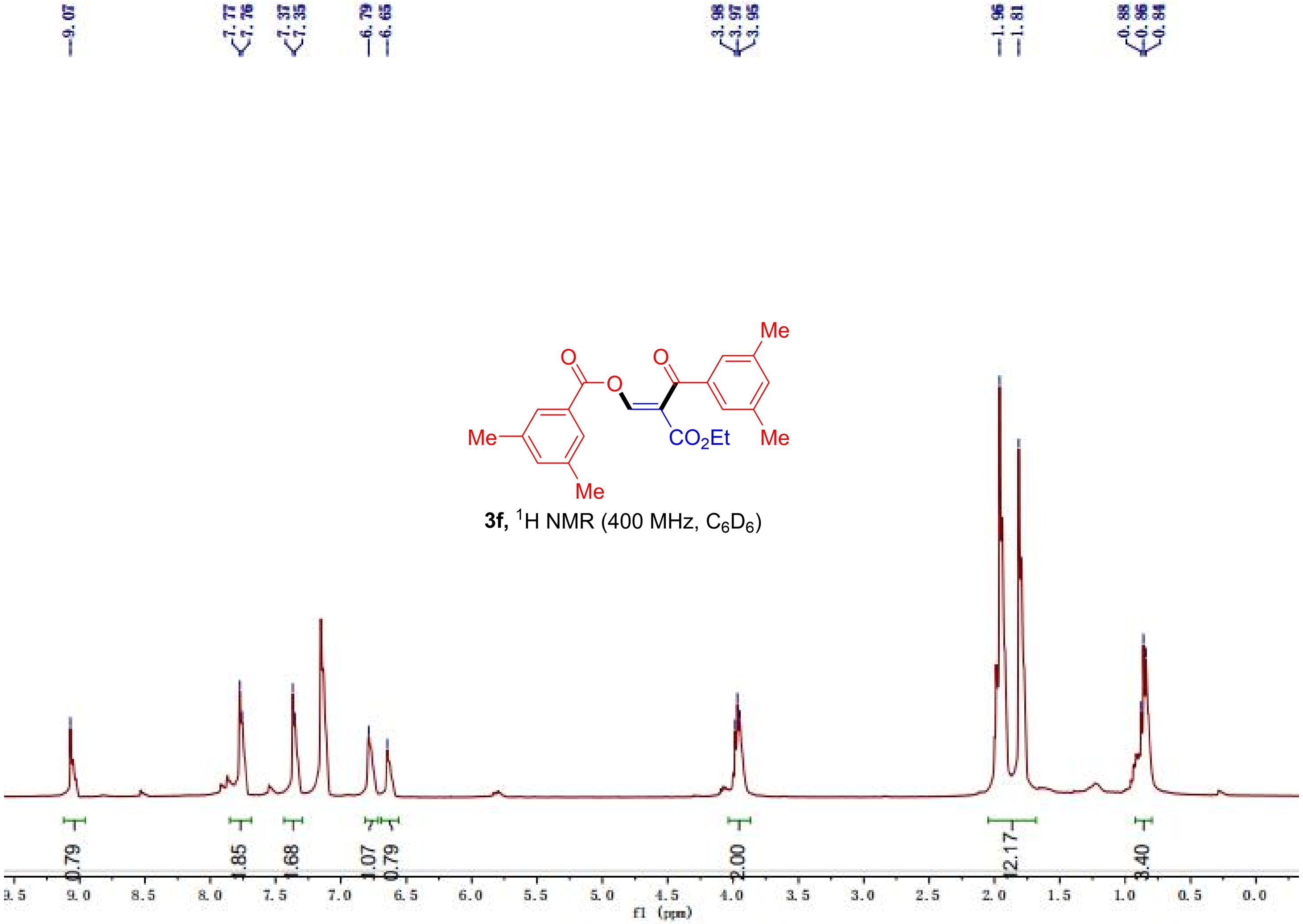

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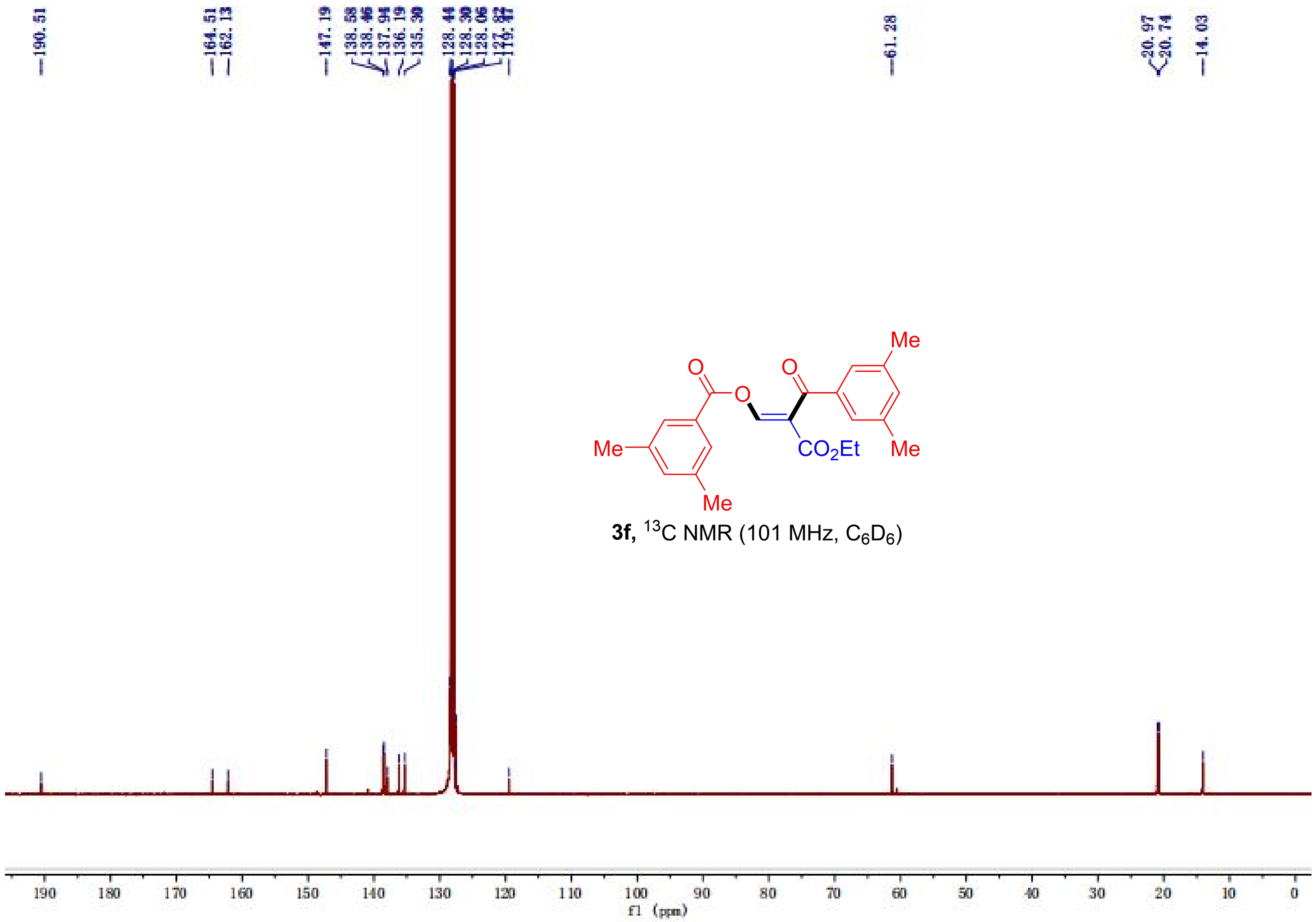

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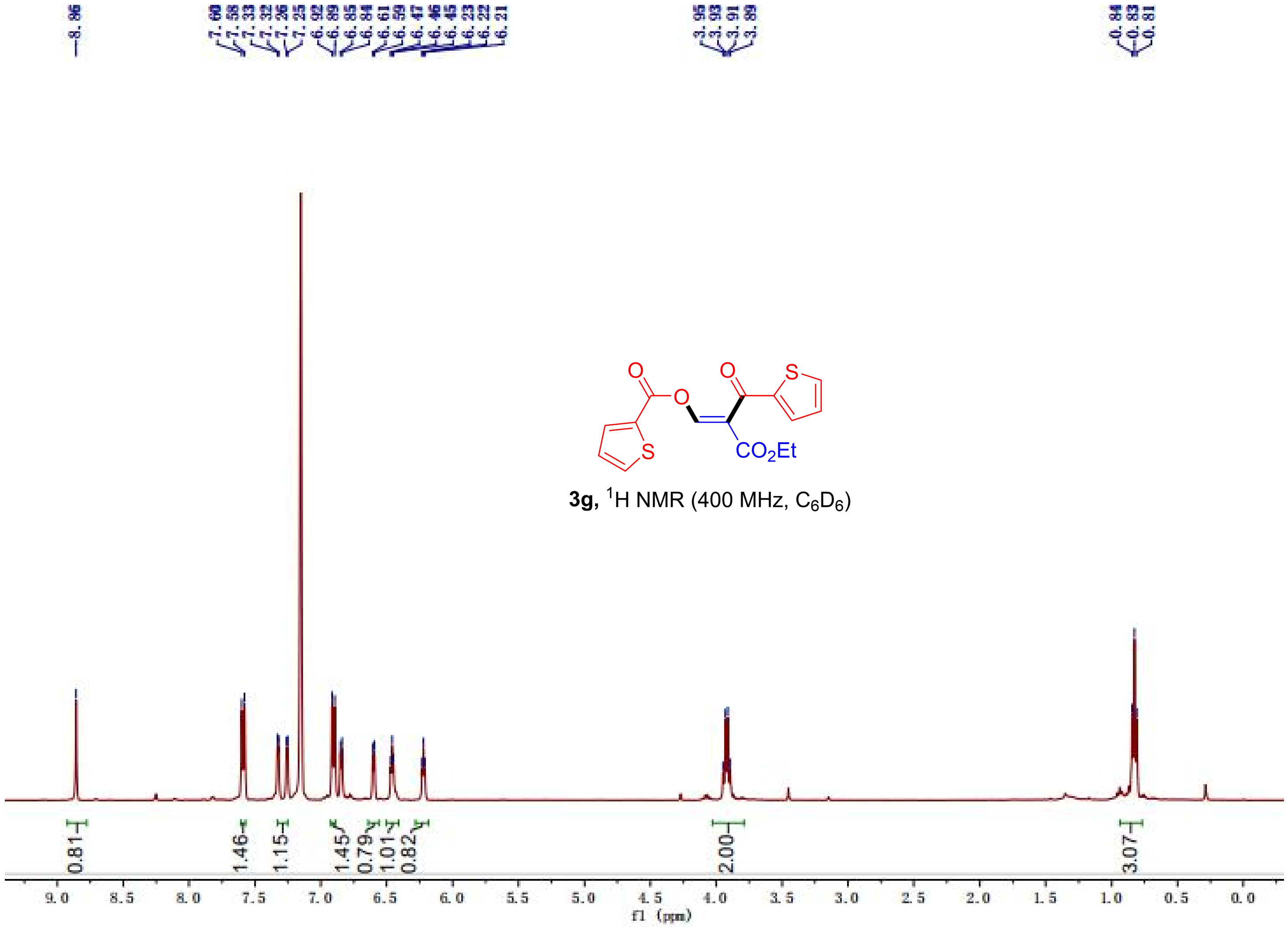
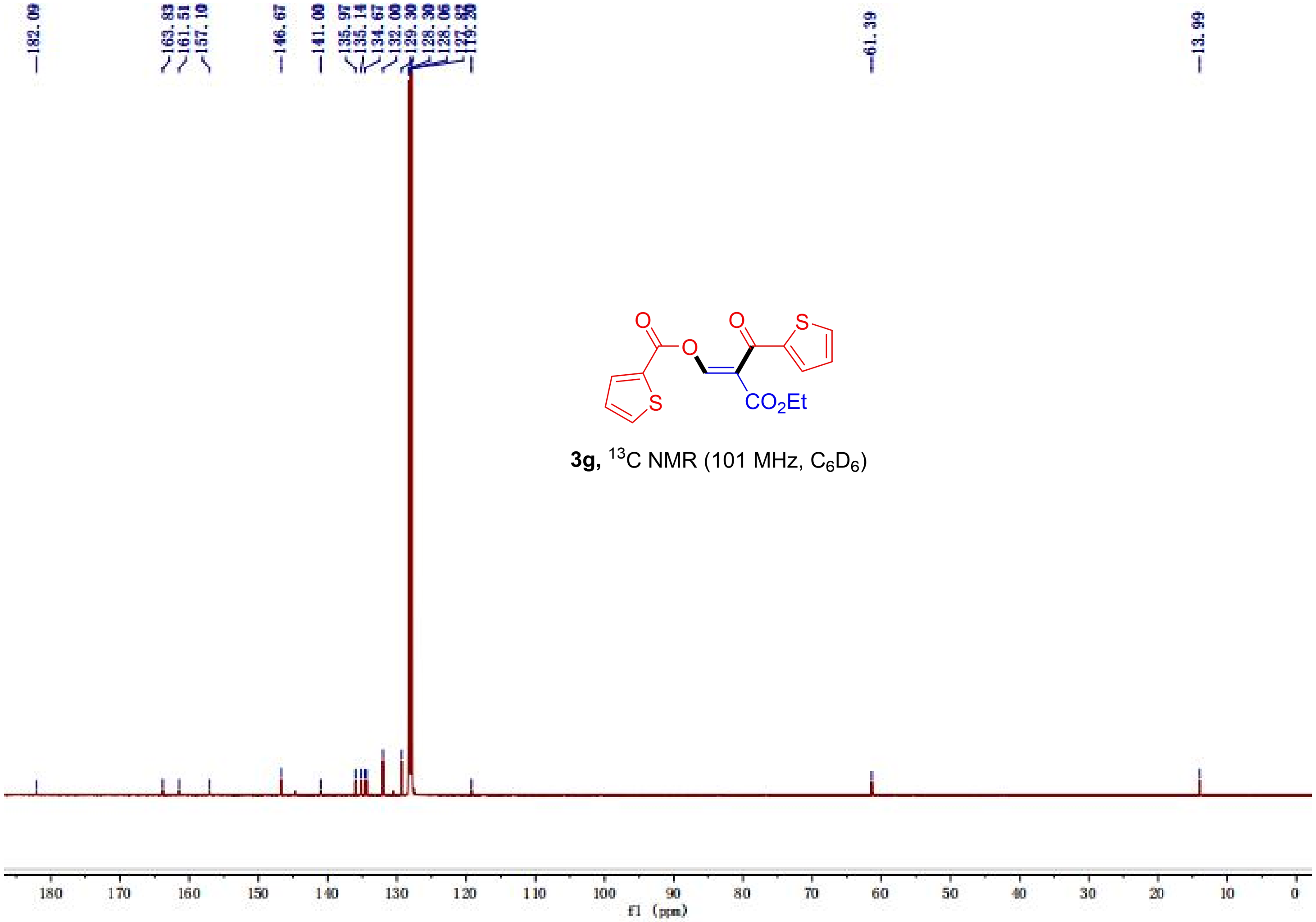


3g, ^{1}H NMR (400 MHz, C_6D_6)



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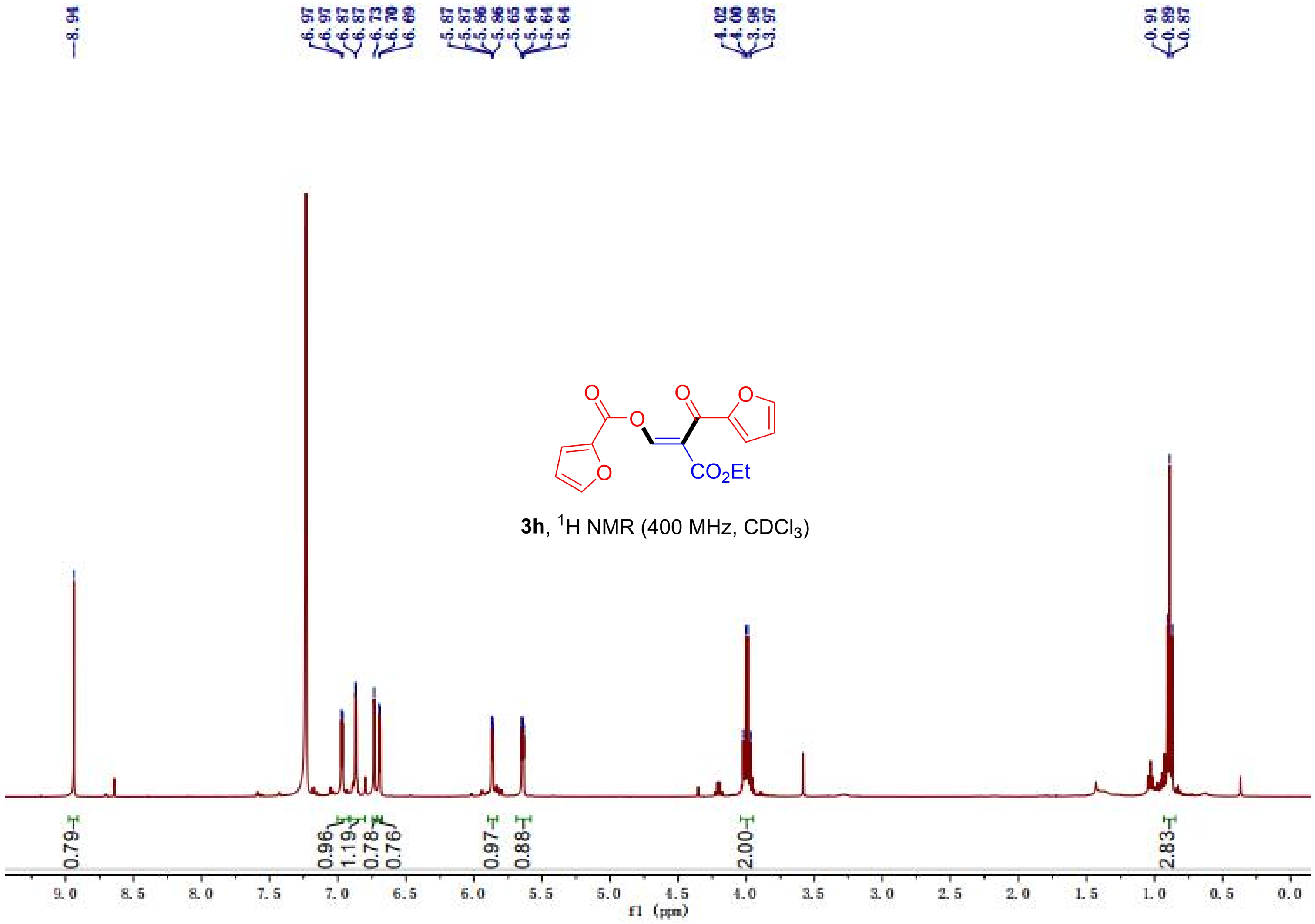

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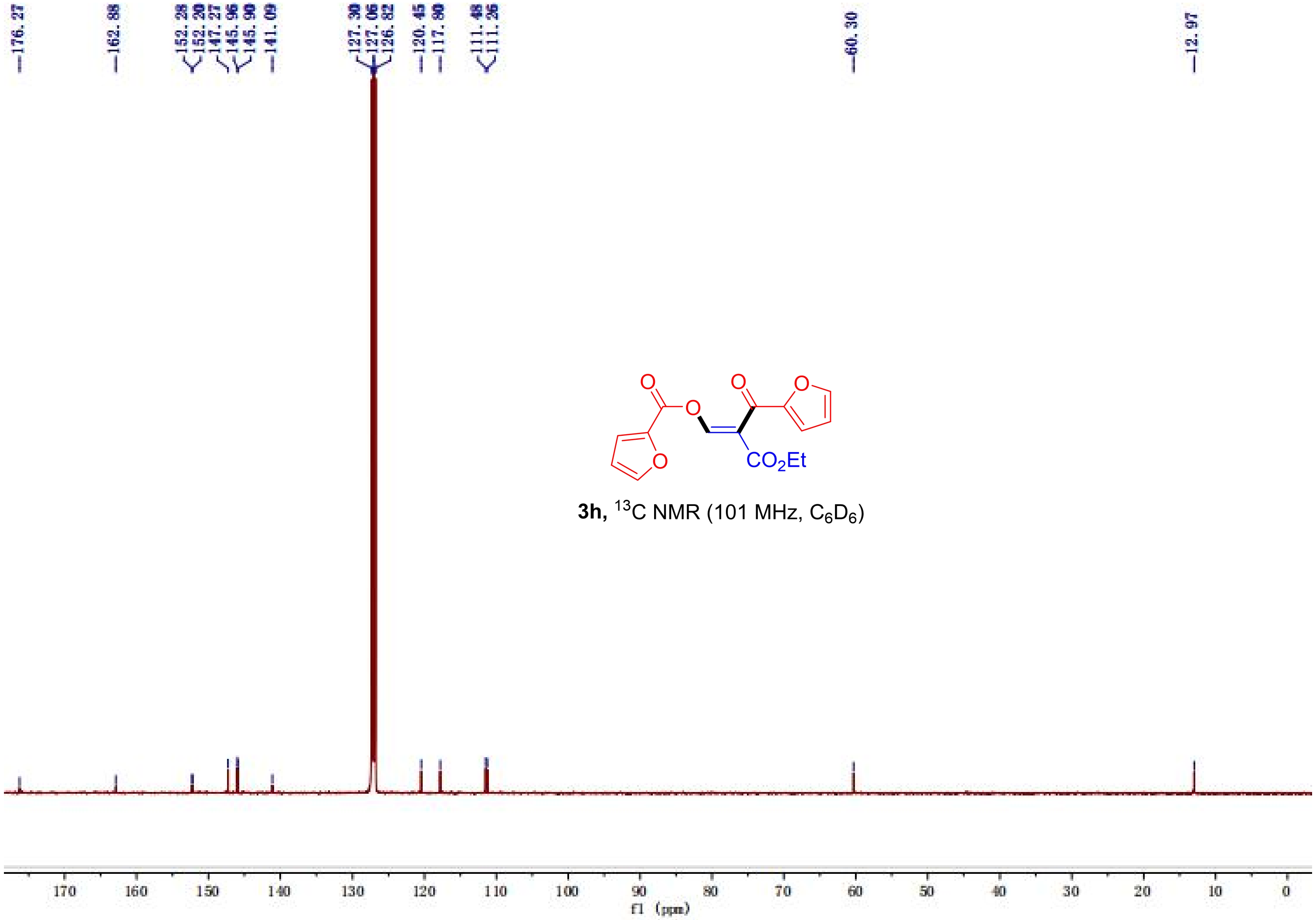
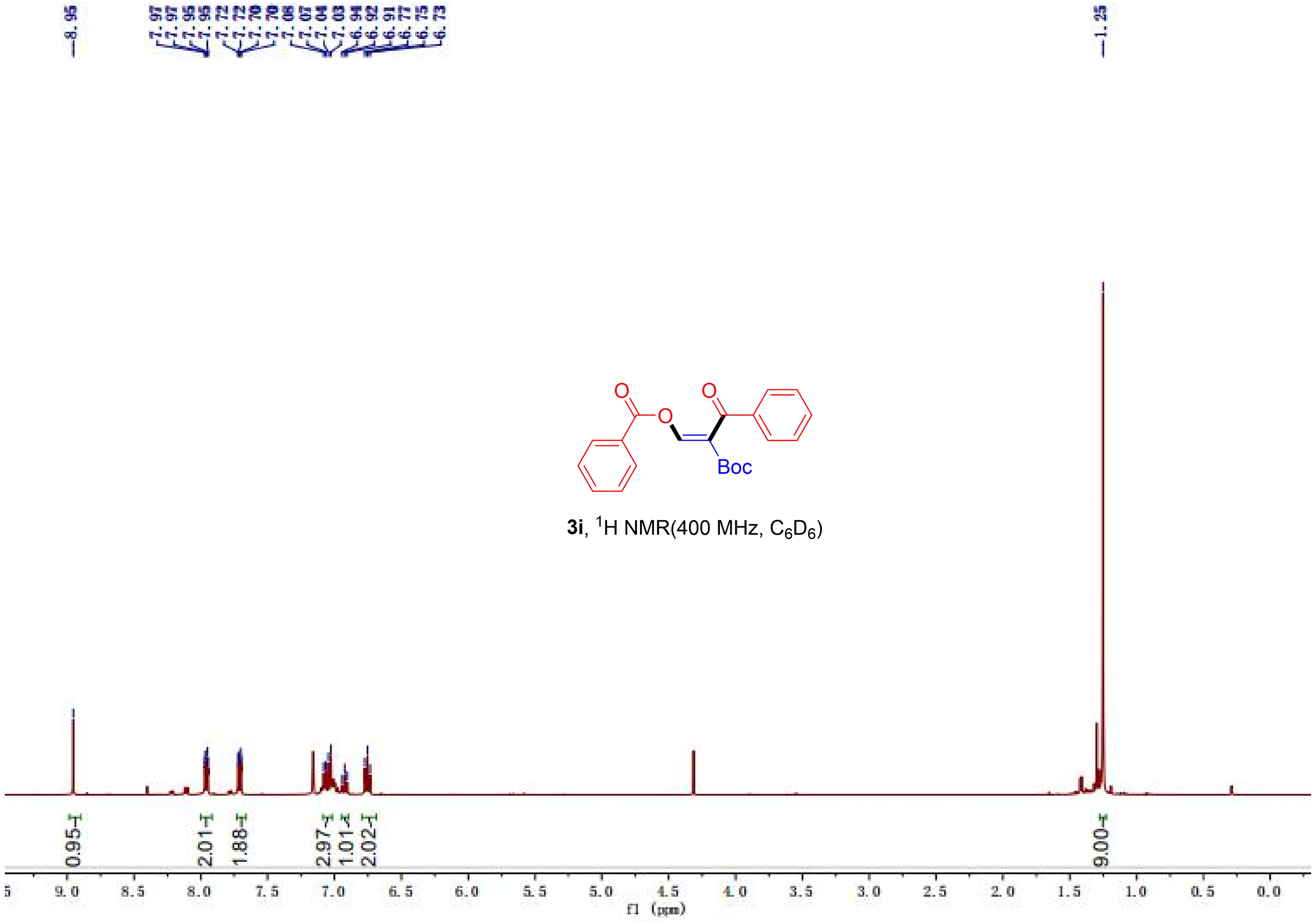


3h, ^{13}C NMR (101 MHz, C_6D_6)



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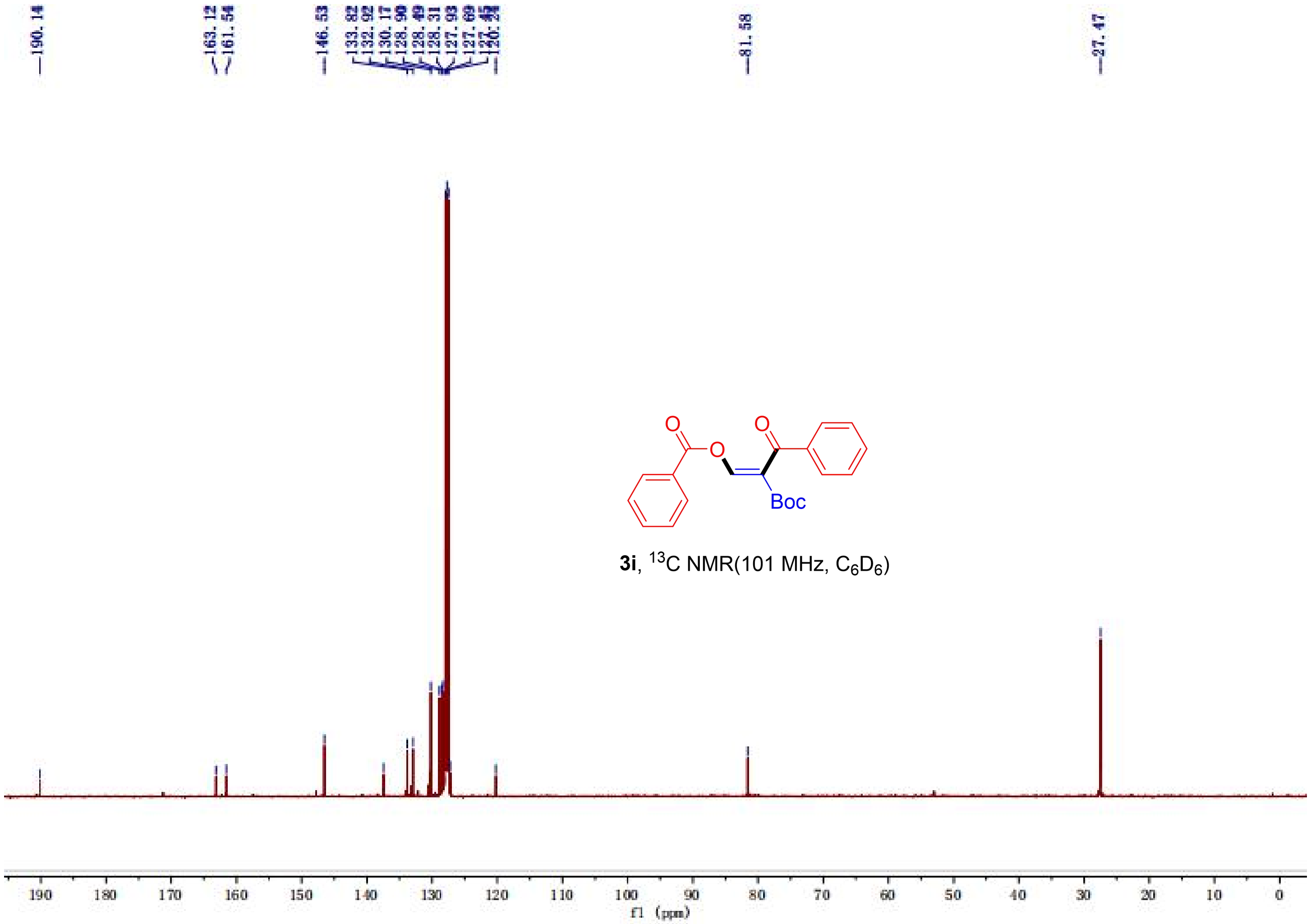

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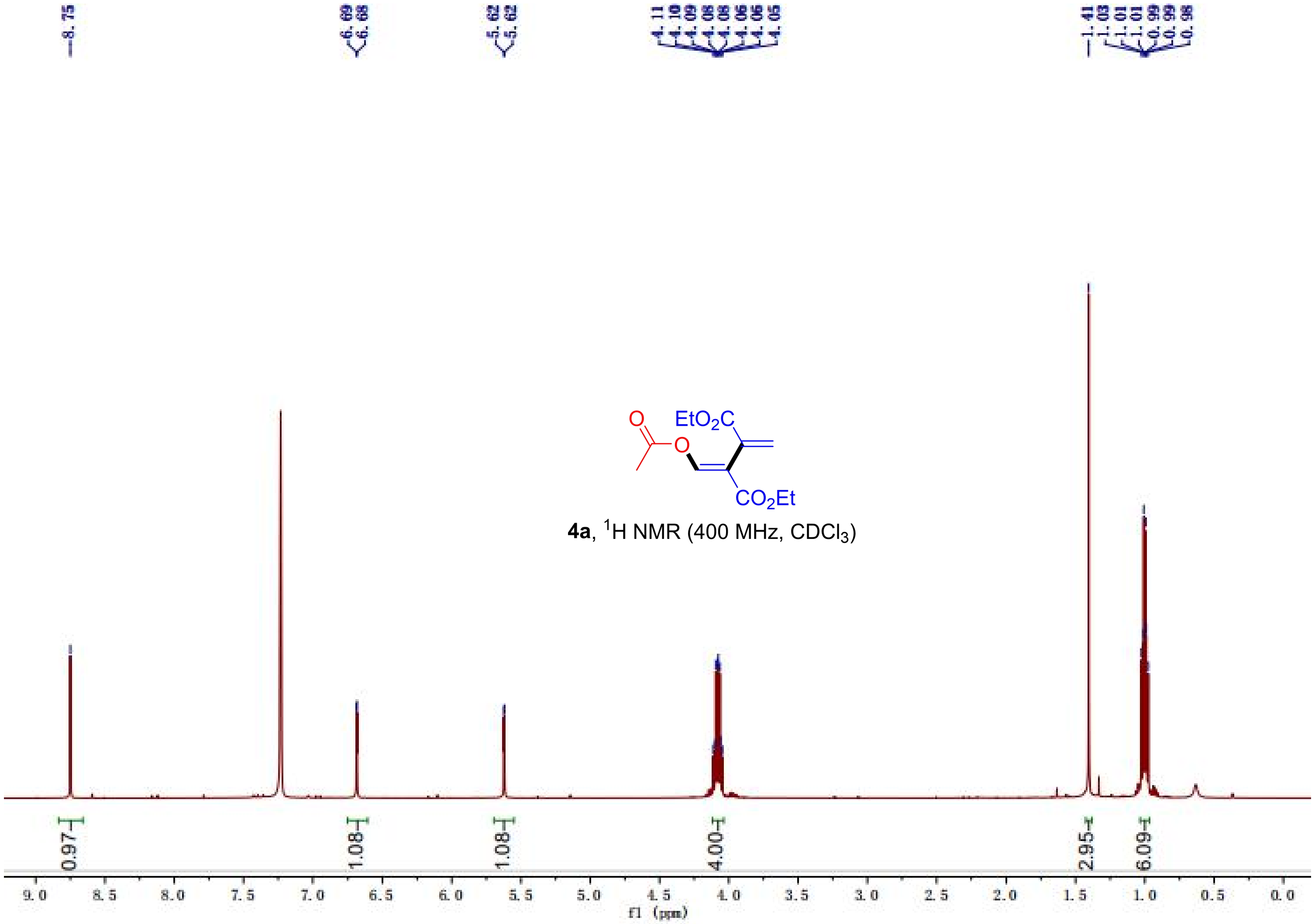
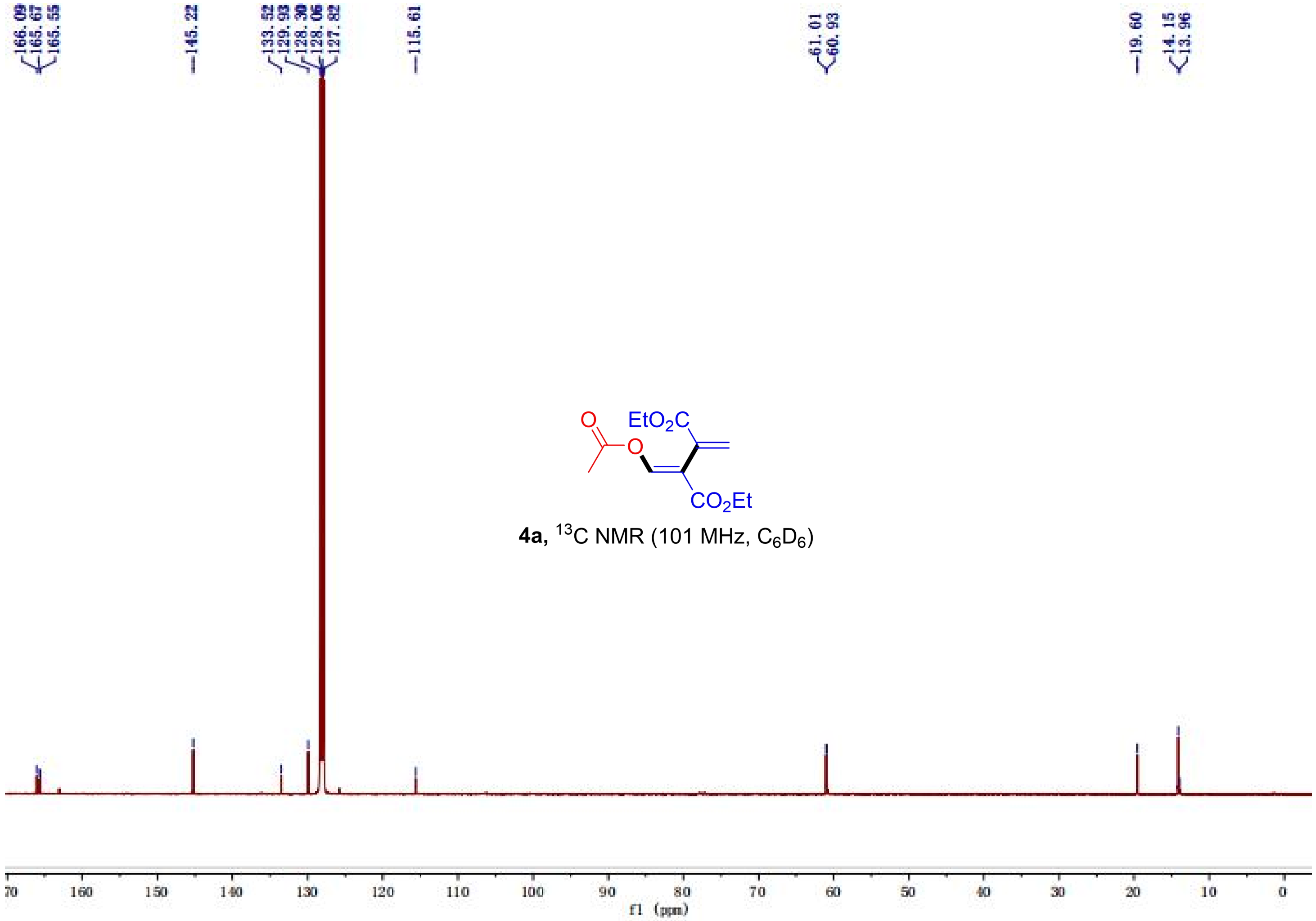


4a, ^1H NMR (400 MHz, $CDCl_3$)



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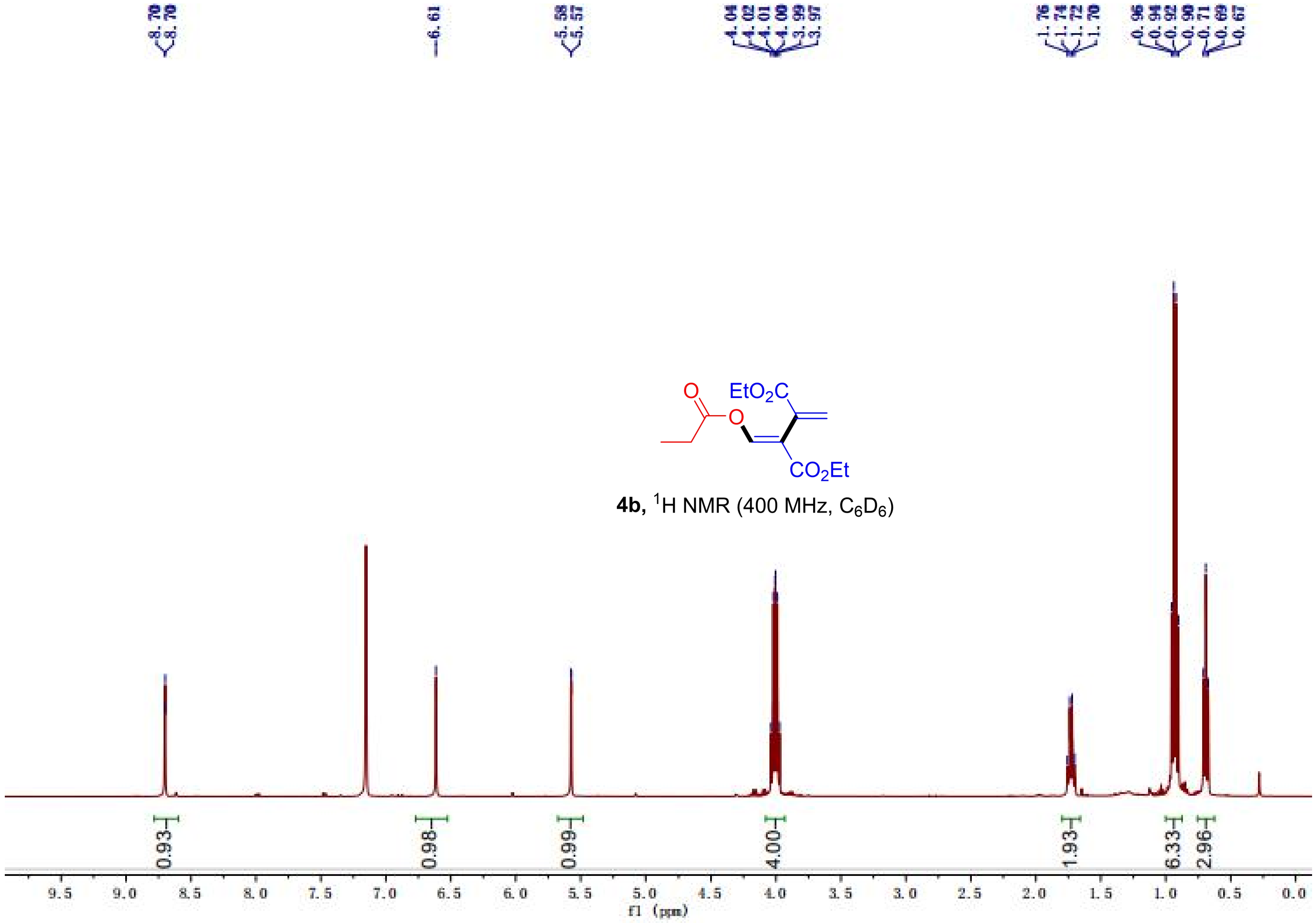
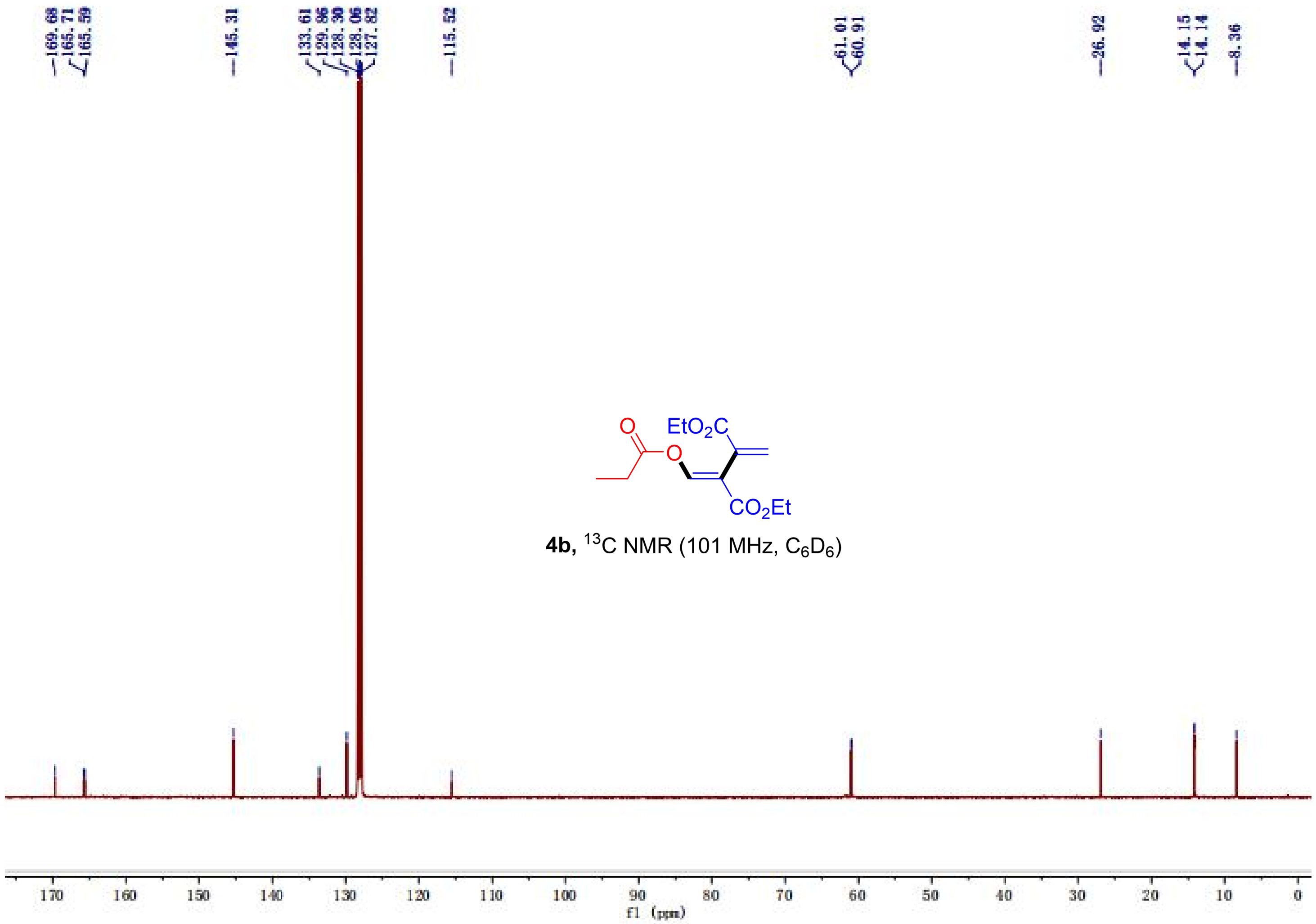
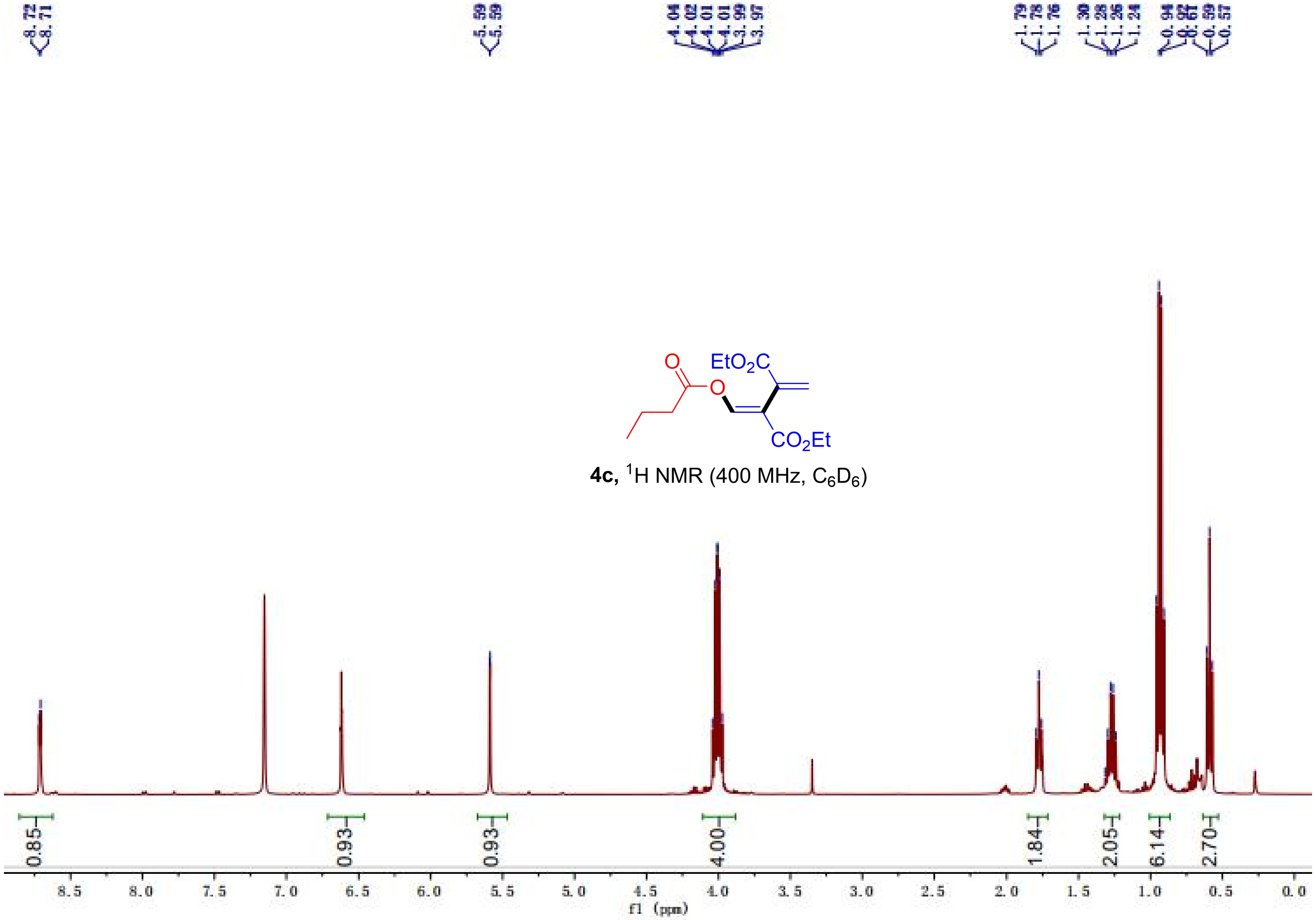


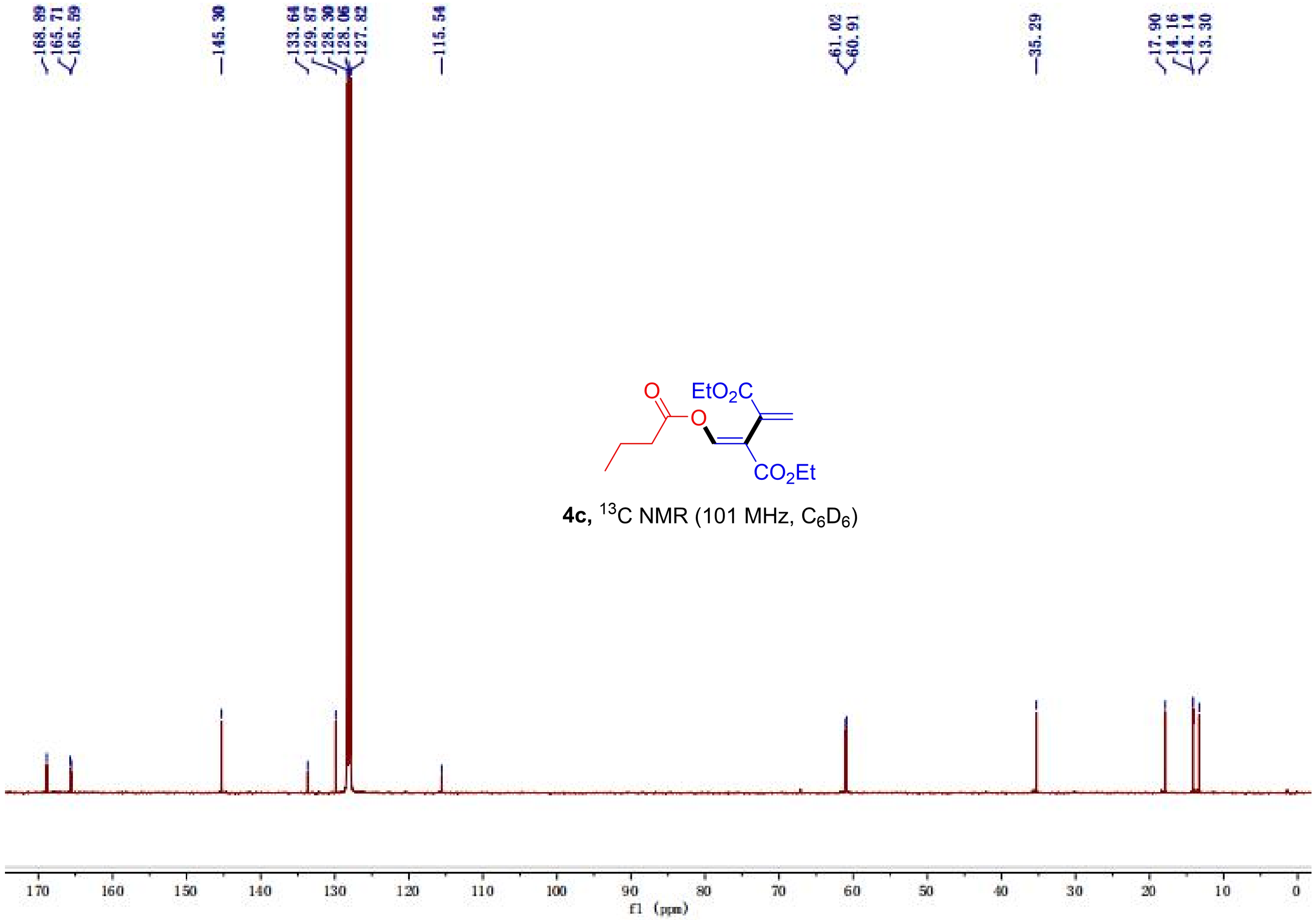
4b, ^{1}H NMR (400 MHz, C_6D_6)



4b, ^{13}C NMR (101 MHz, C_6D_6)



4c, ^{1}H NMR (400 MHz, C_6D_6)



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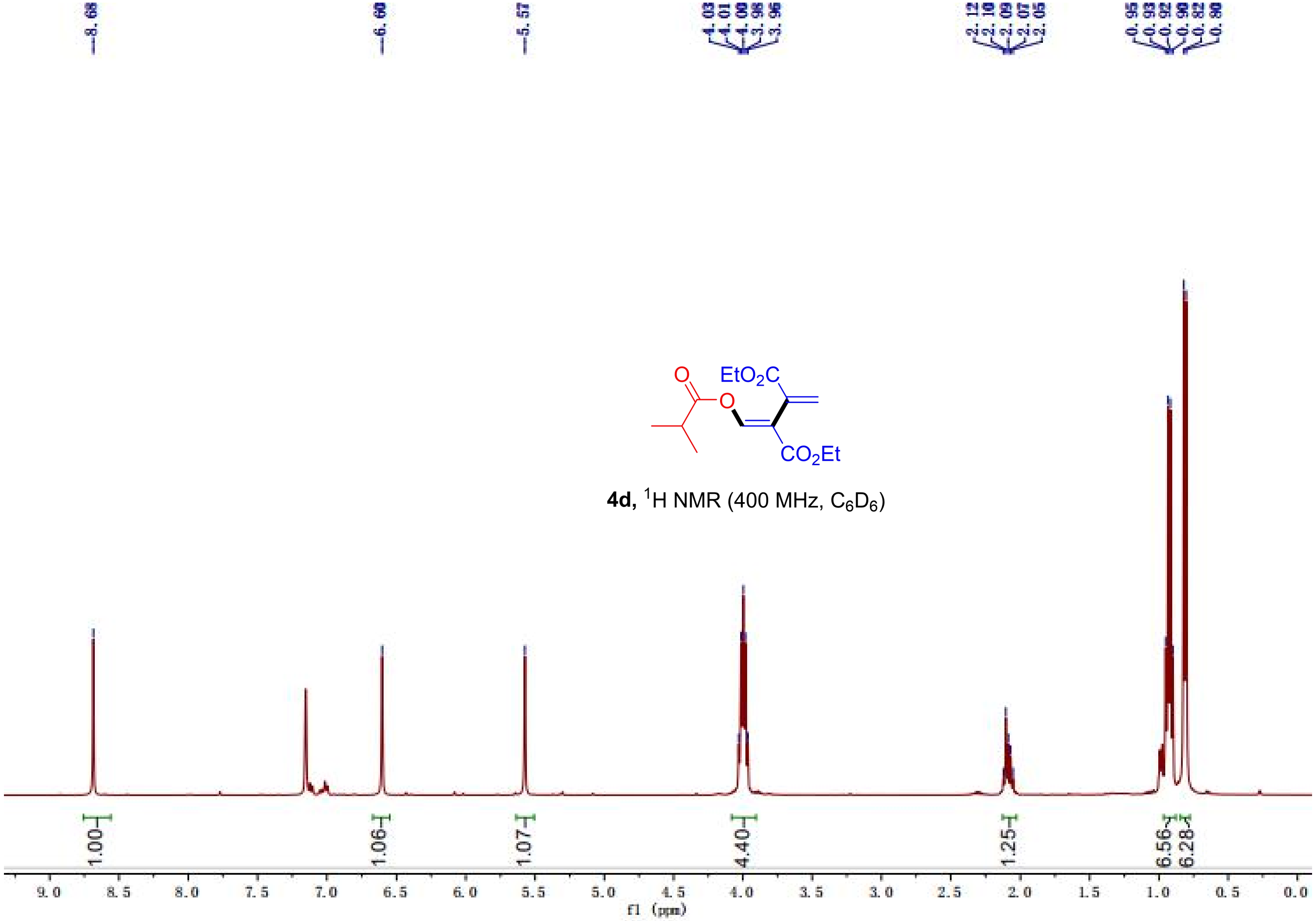
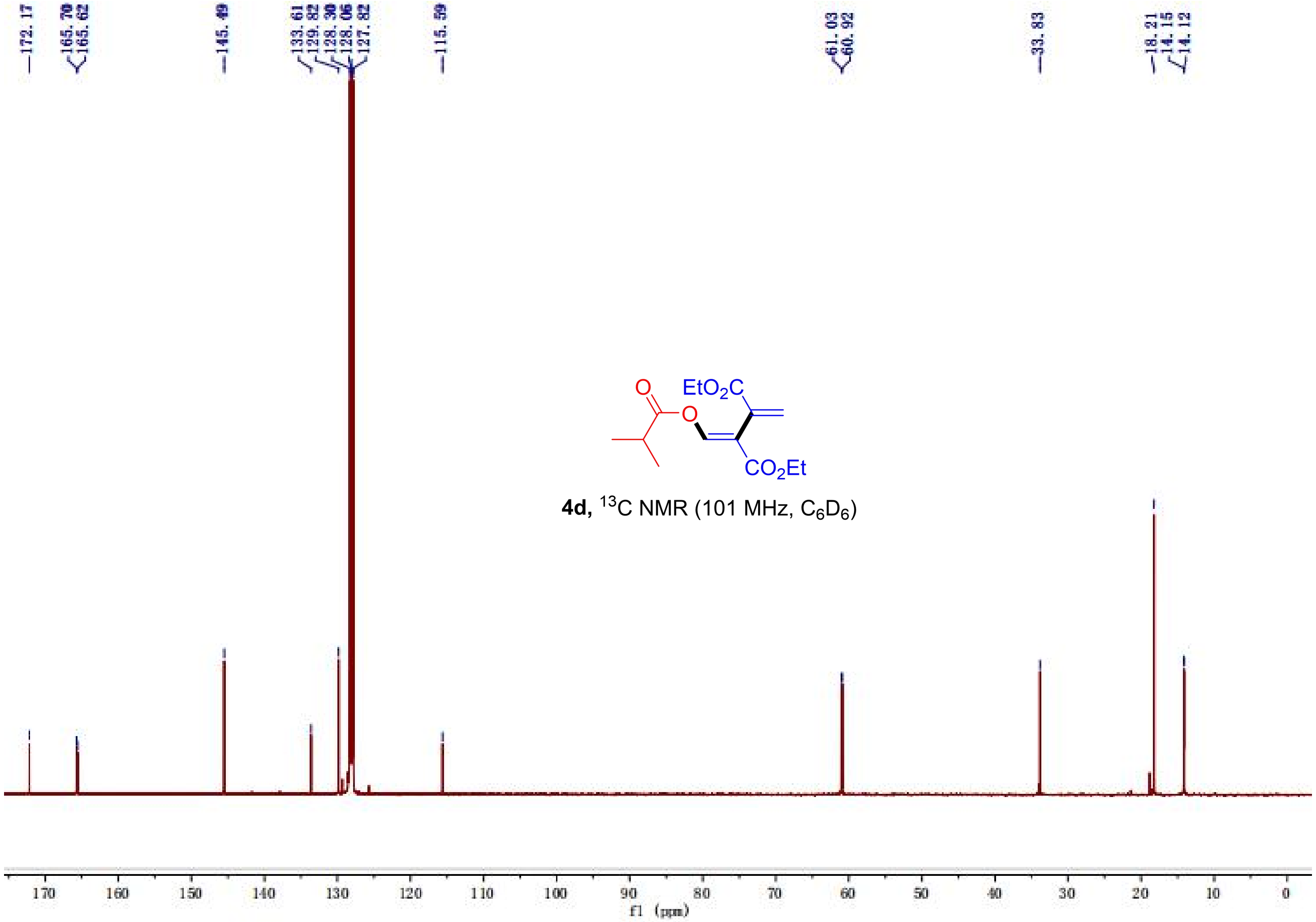
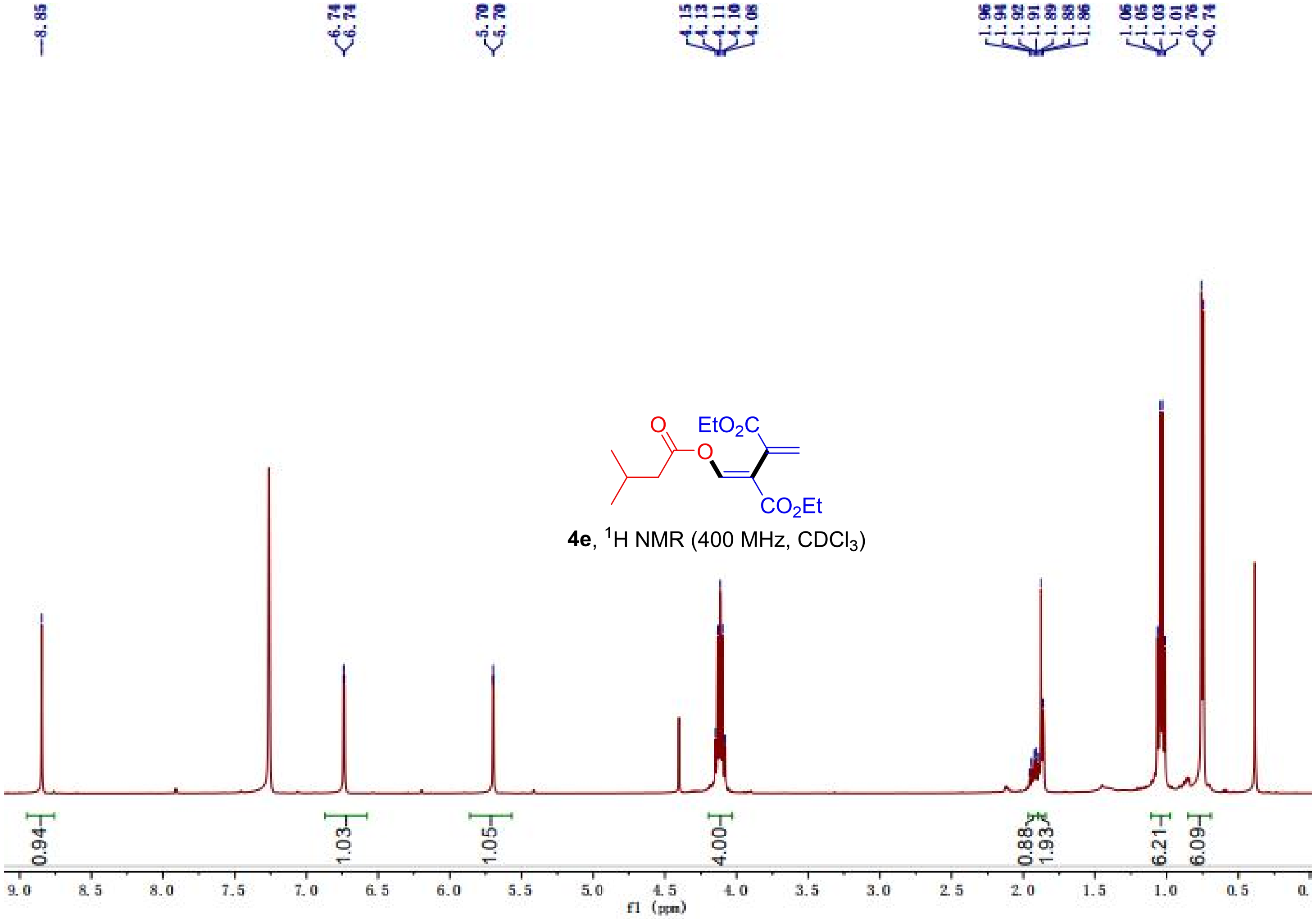


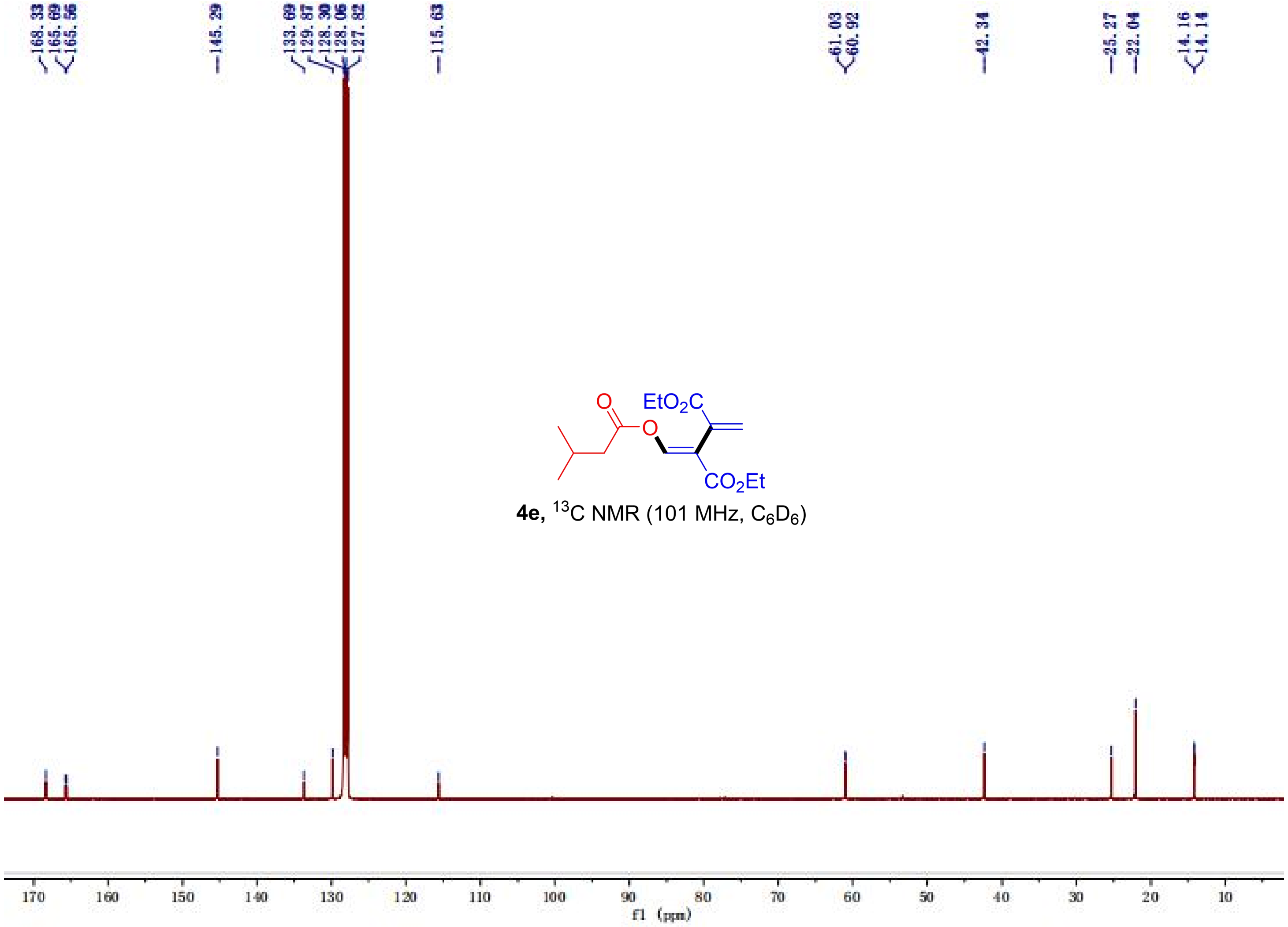
4d, ^{1}H NMR (400 MHz, C_6D_6)



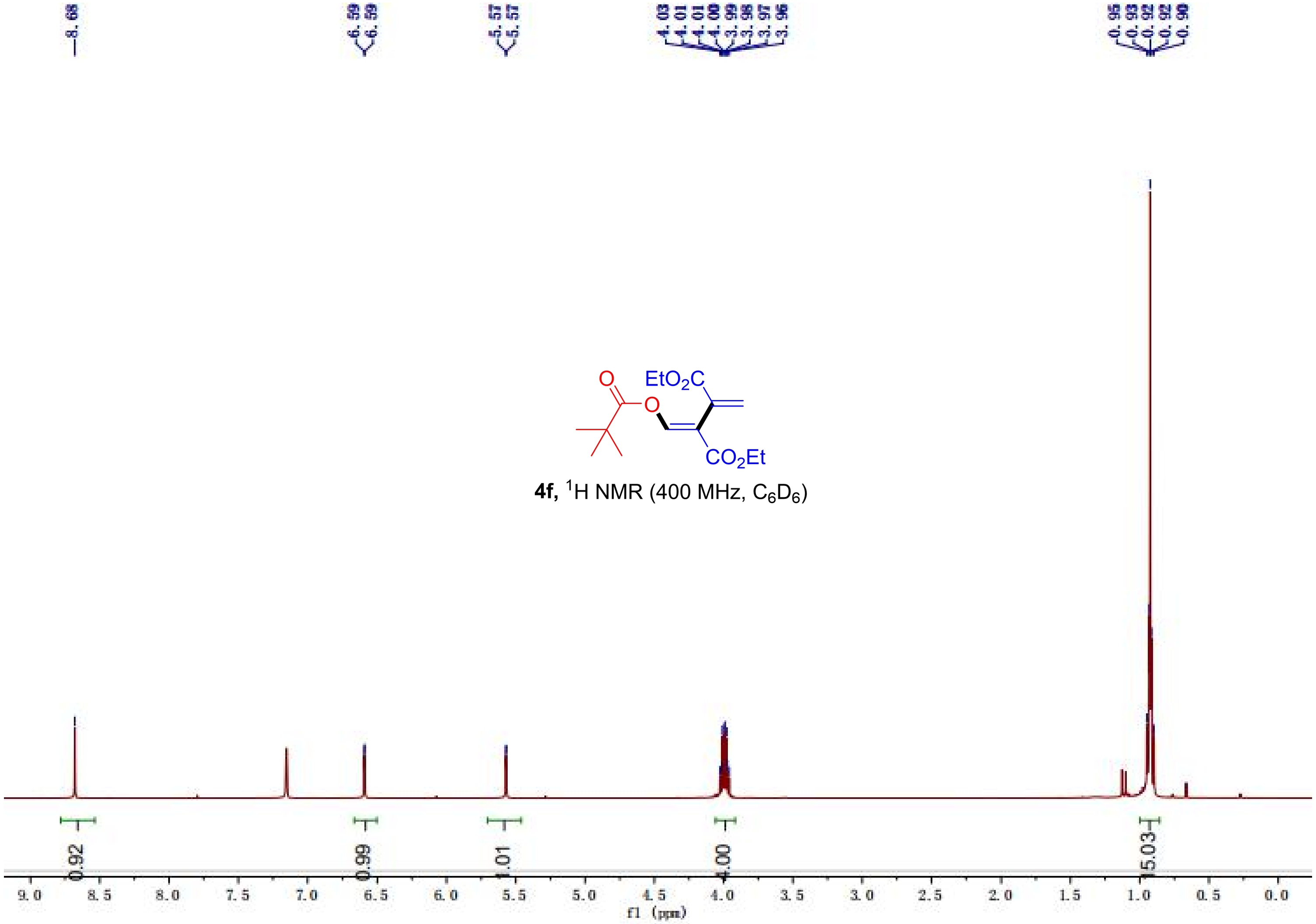
4d, ^{13}C NMR (101 MHz, C_6D_6)



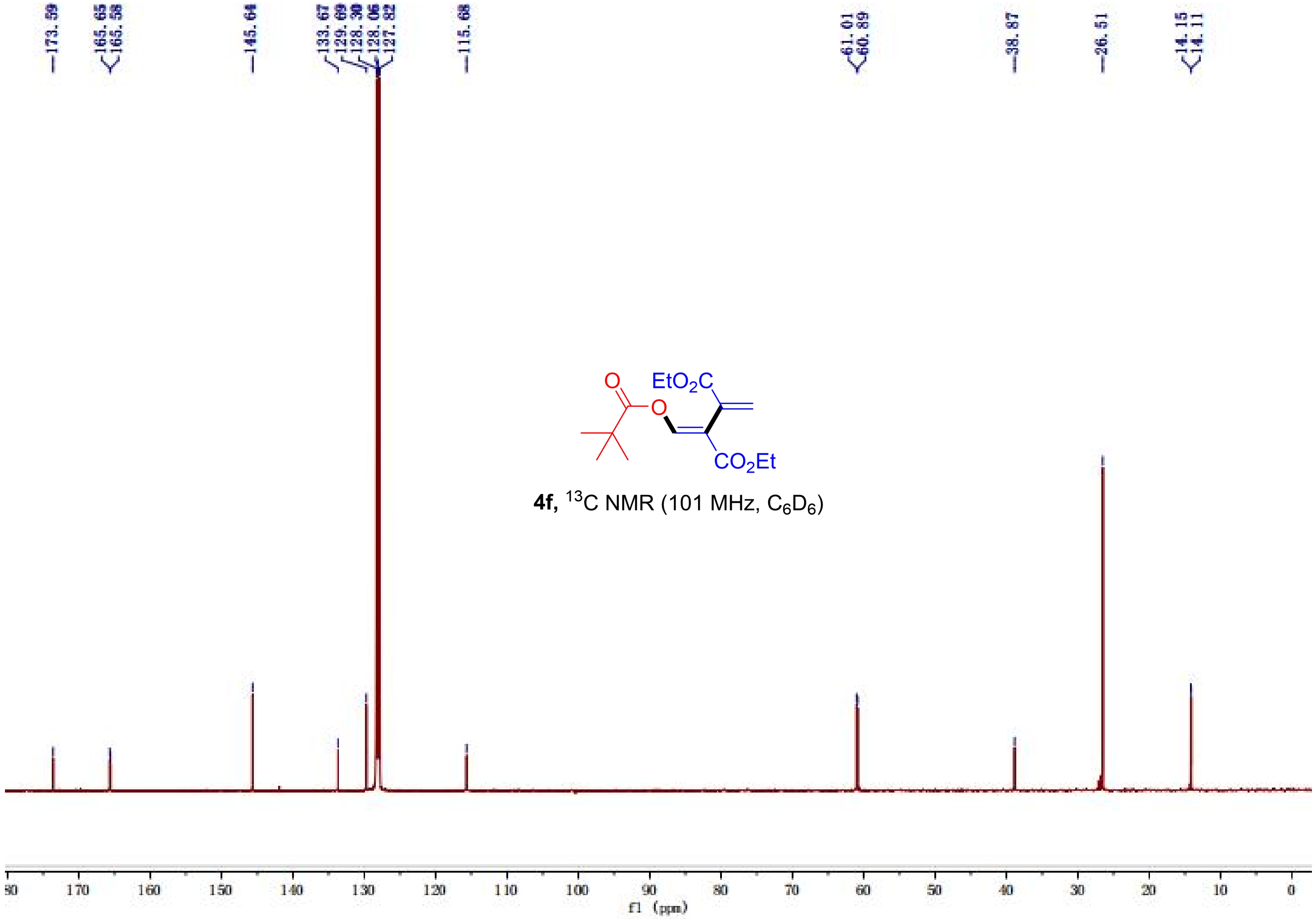
4e, ^{1}H NMR (400 MHz, $CDCl_3$)



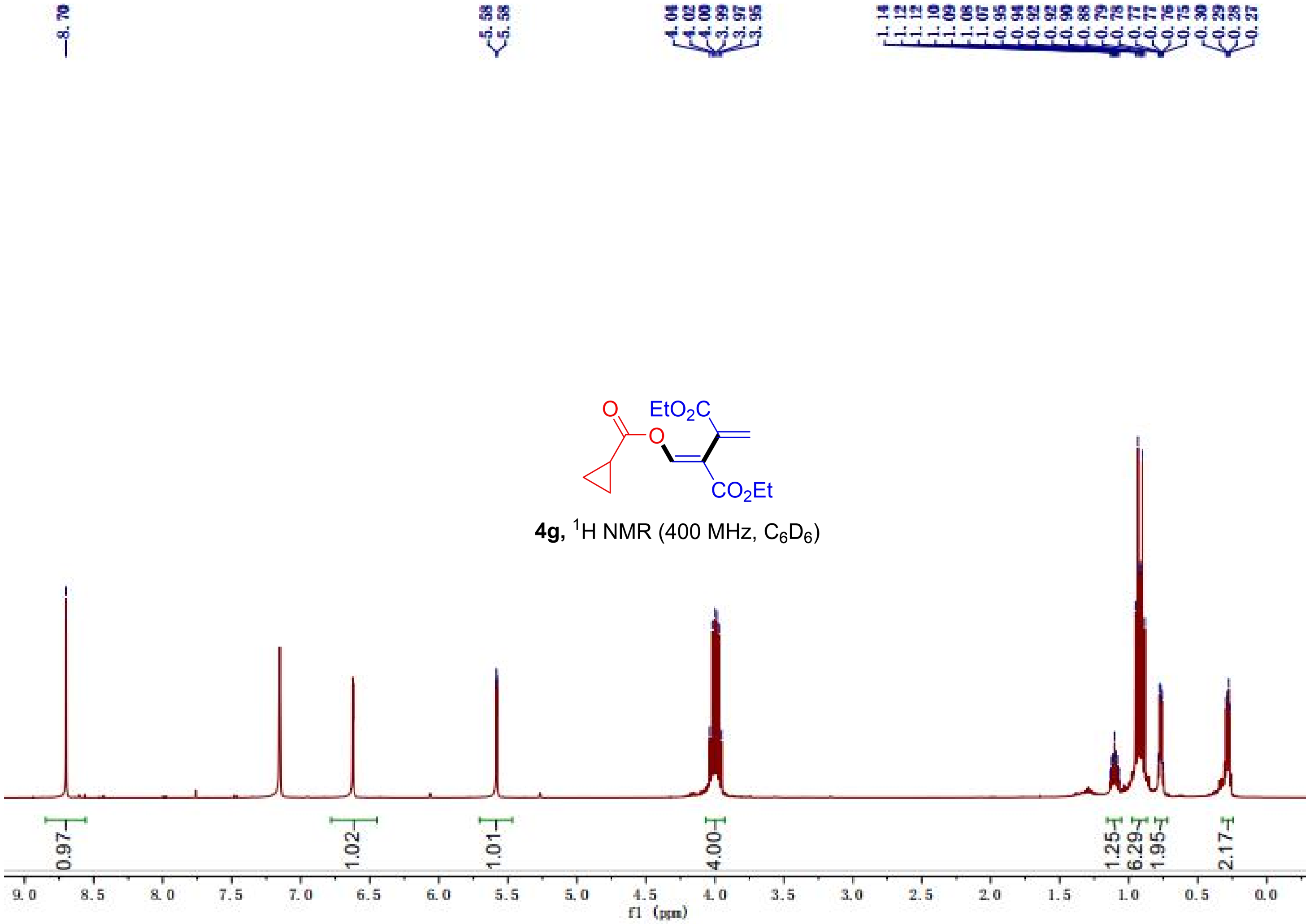
4e, ^{13}C NMR (101 MHz, C_6D_6)



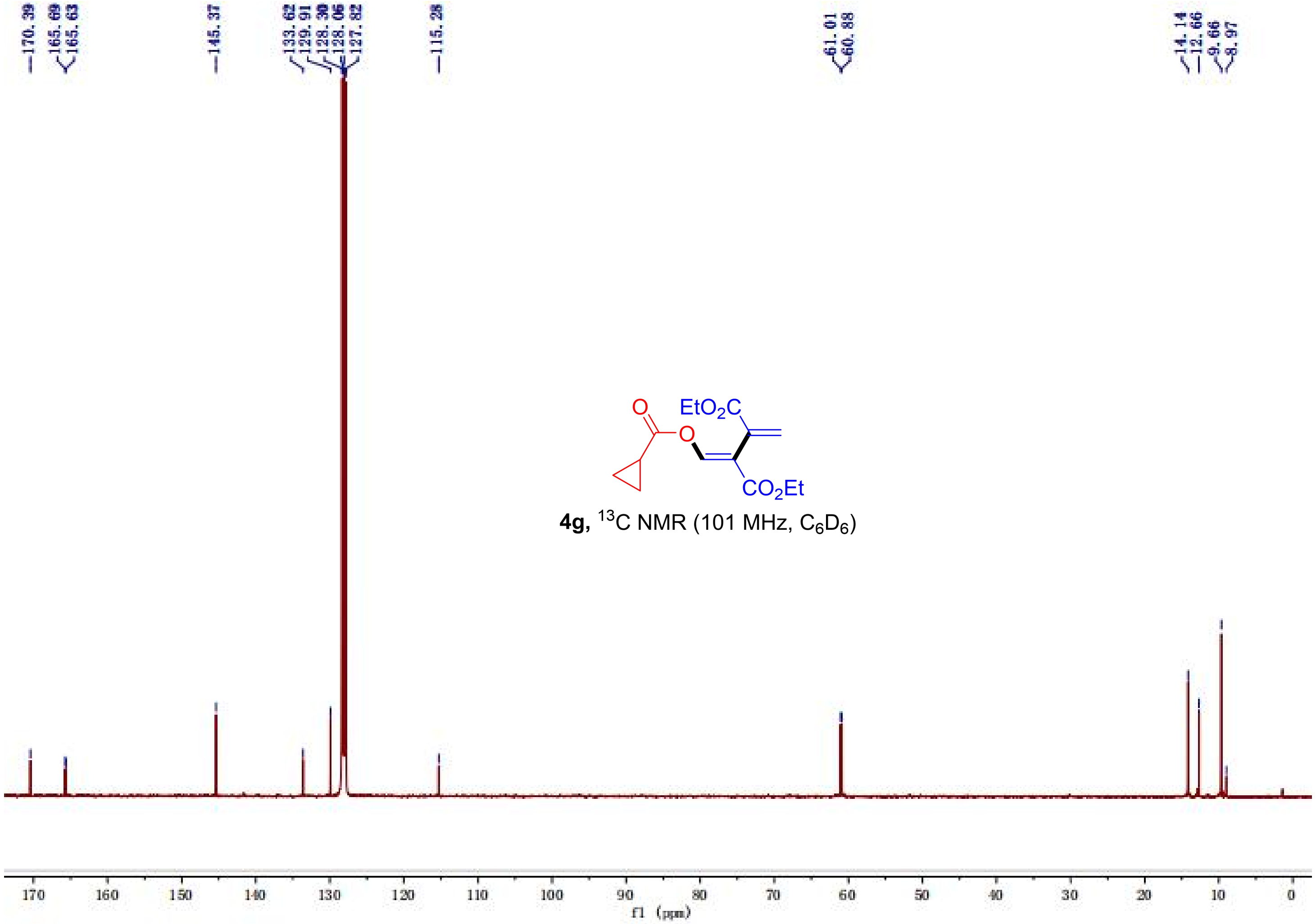
4f, ^{1}H NMR (400 MHz, C_6D_6)



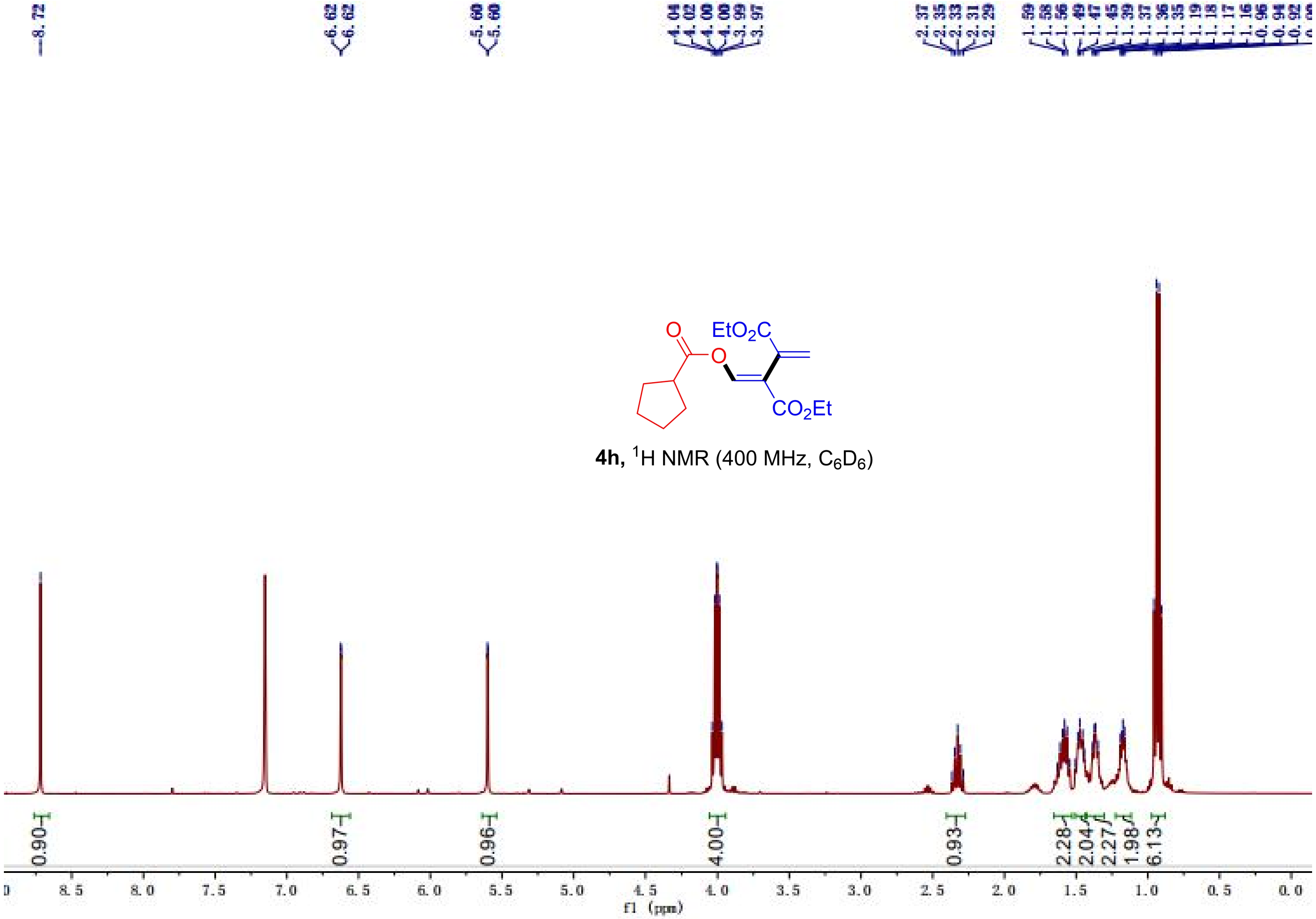
4f, ^{13}C NMR (101 MHz, C_6D_6)



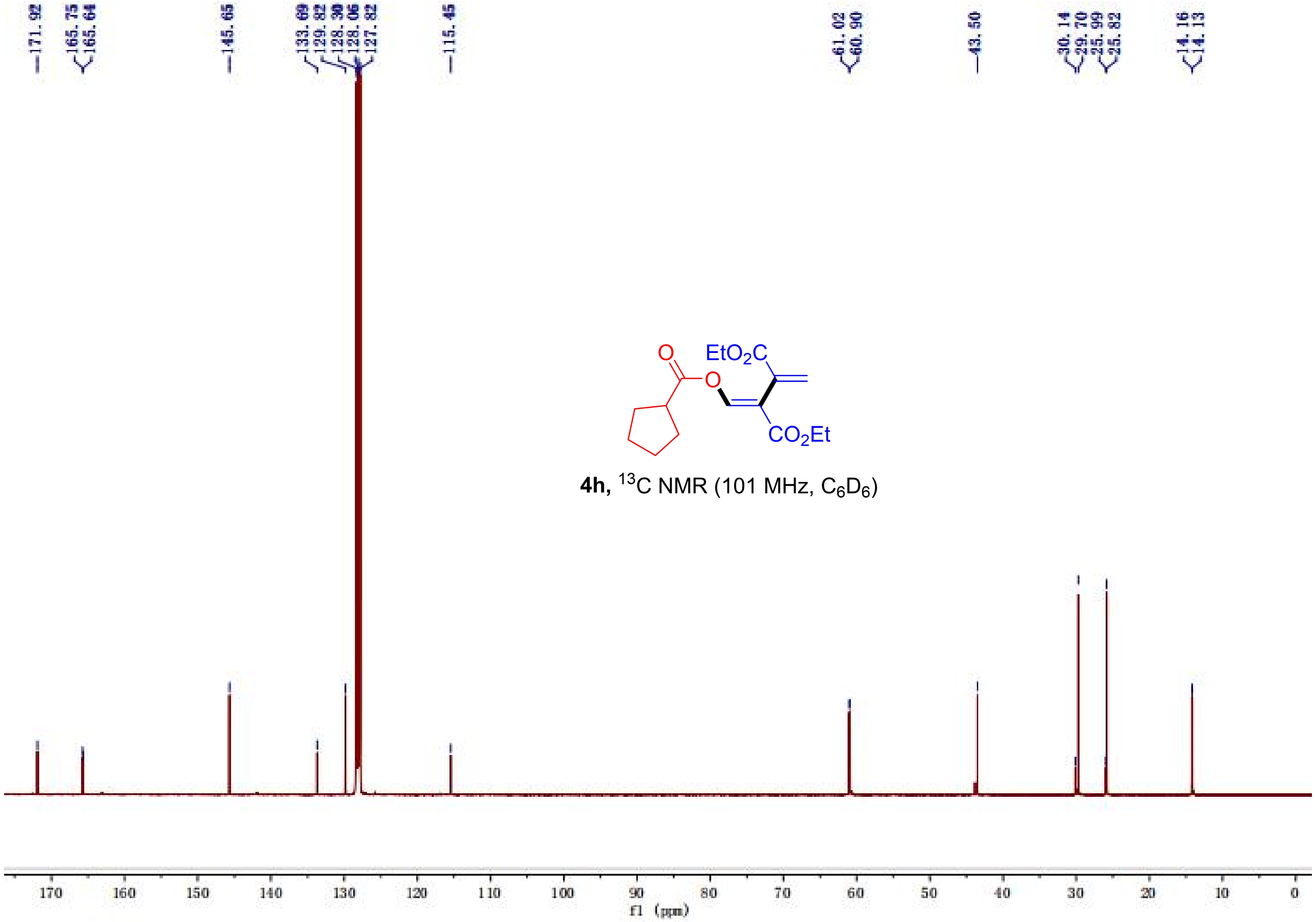
4g, ^{1}H NMR (400 MHz, C_6D_6)



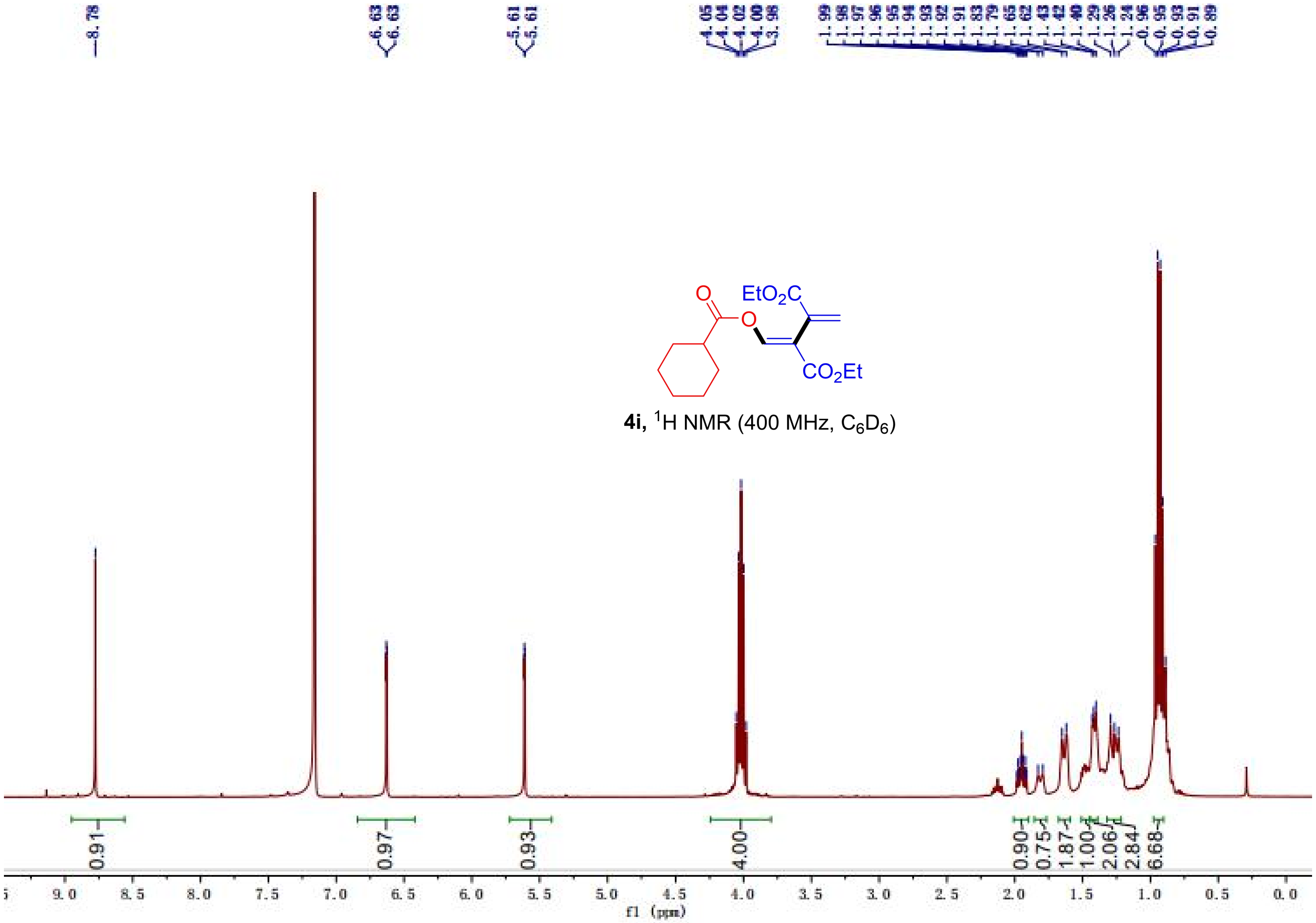
4g, ^{13}C NMR (101 MHz, C_6D_6)



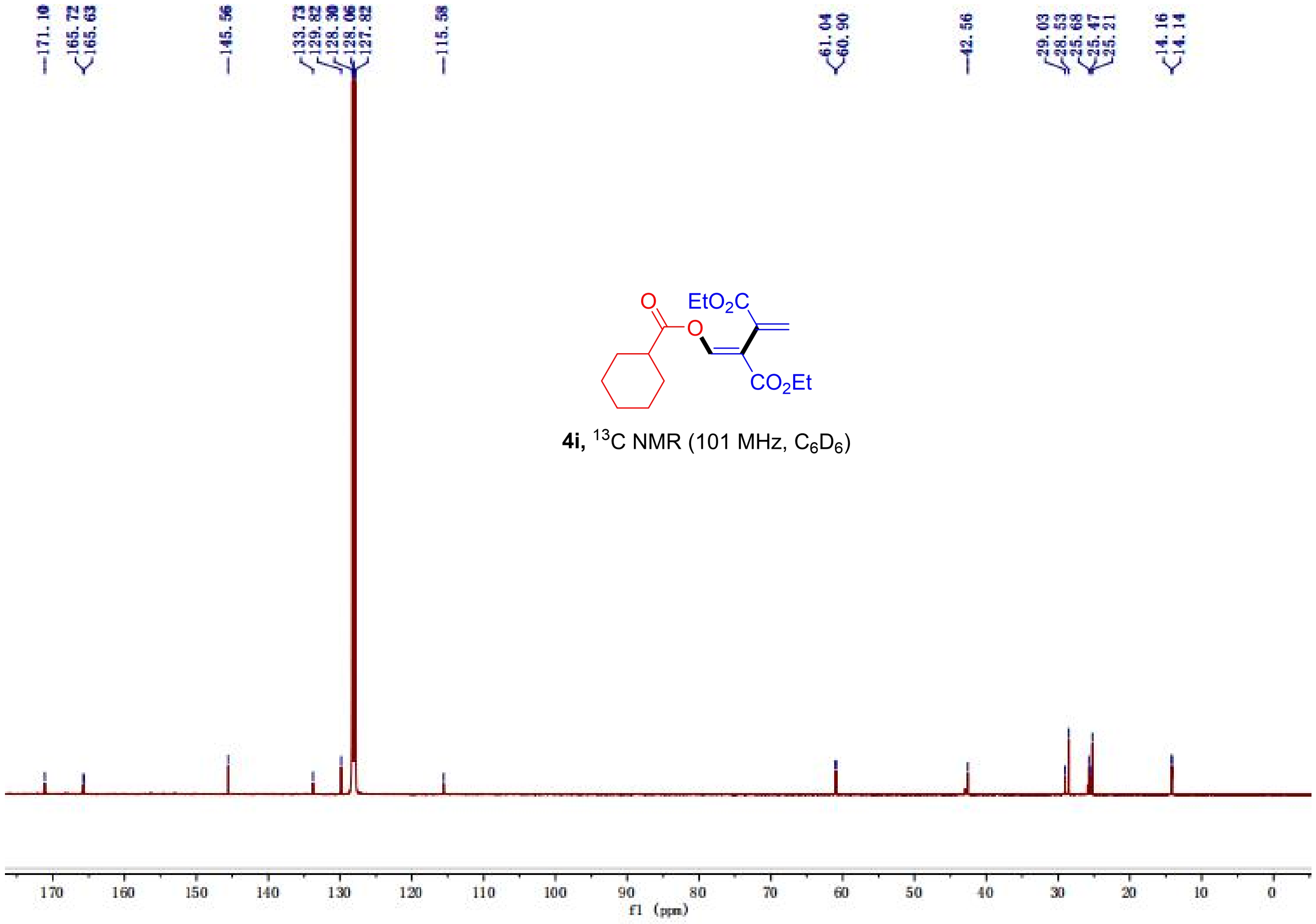
4h, ^{1}H NMR (400 MHz, C_6D_6)



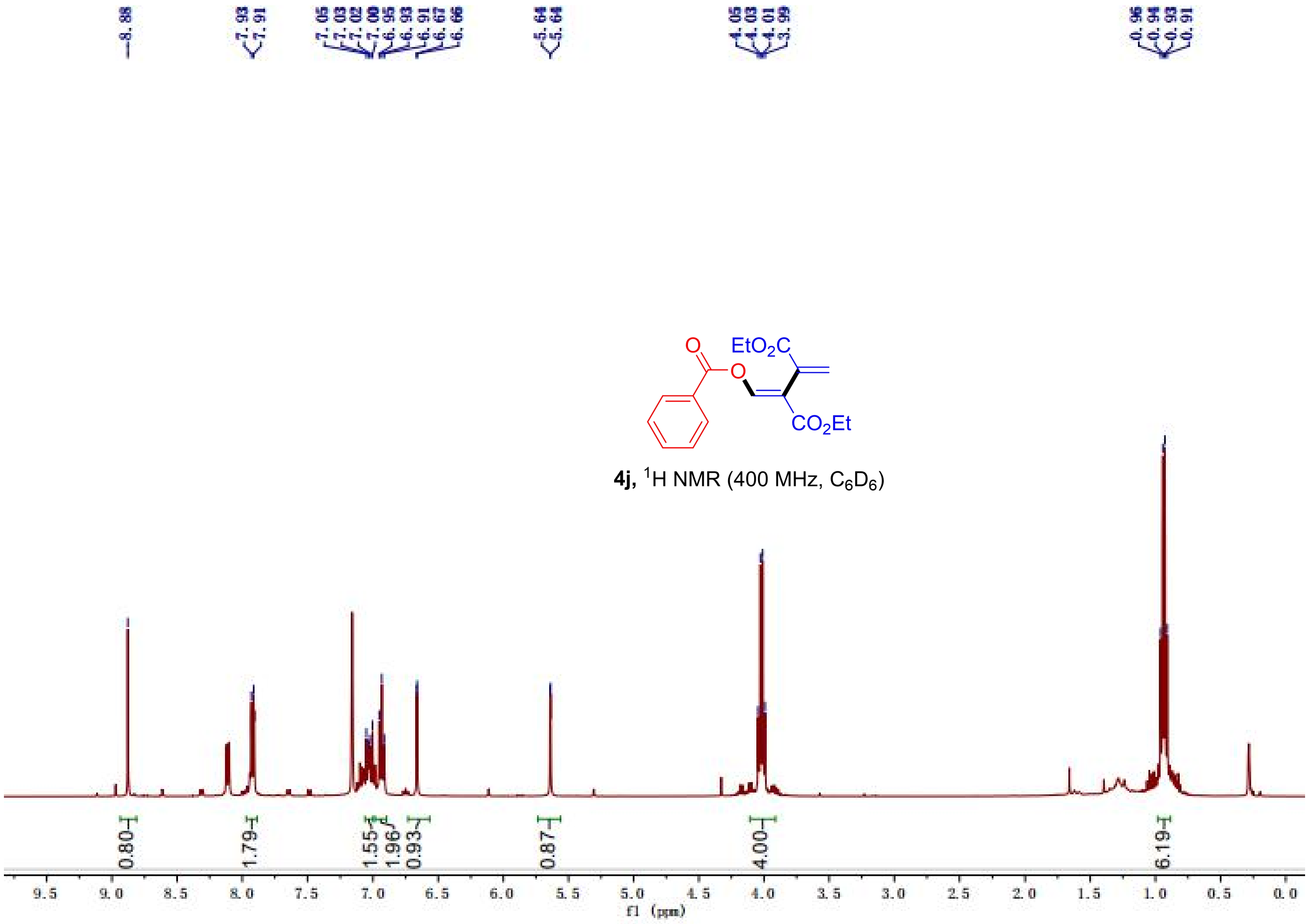
4h, ^{13}C NMR (101 MHz, C_6D_6)



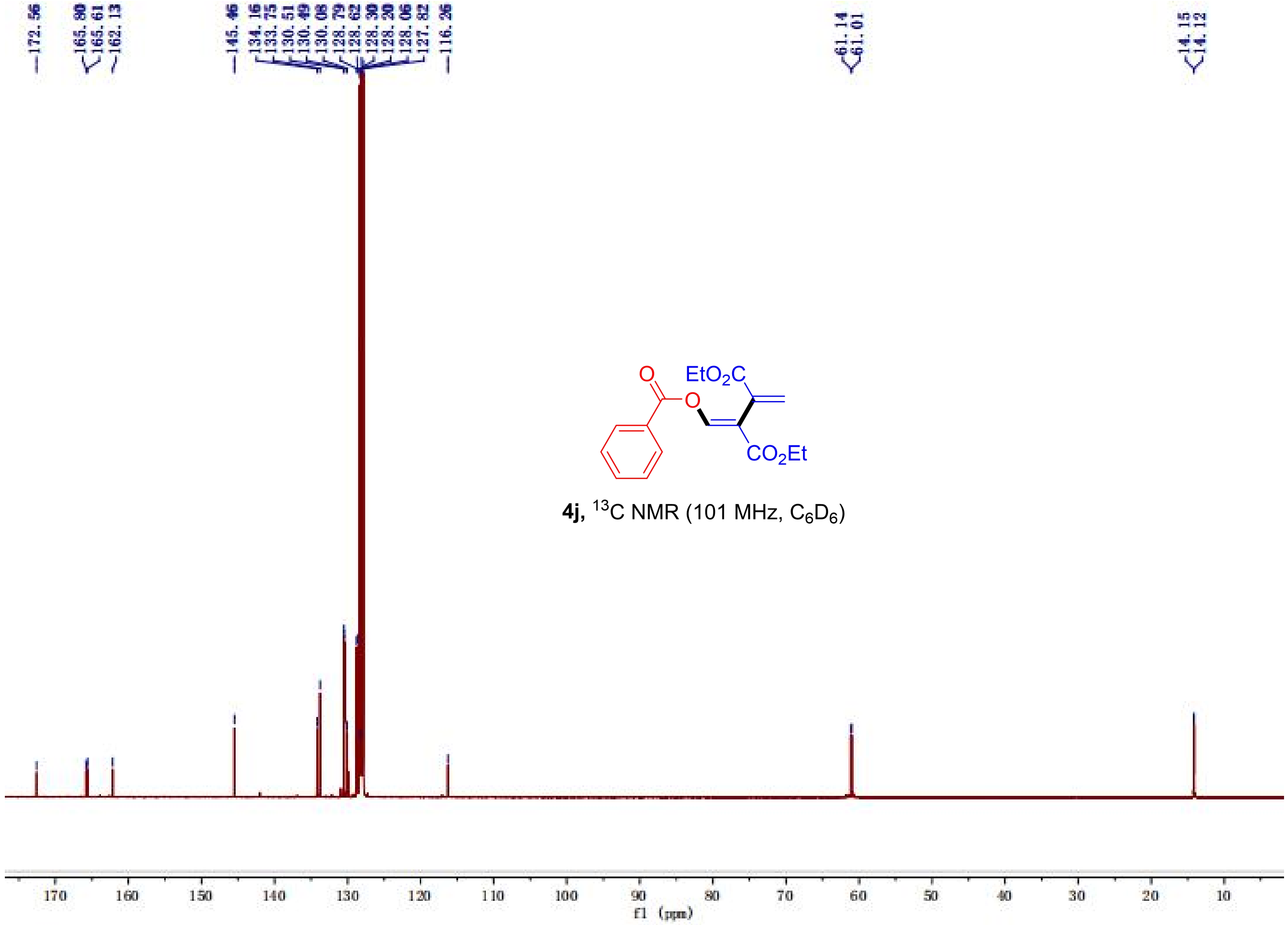
4i, ^{1}H NMR (400 MHz, C_6D_6)



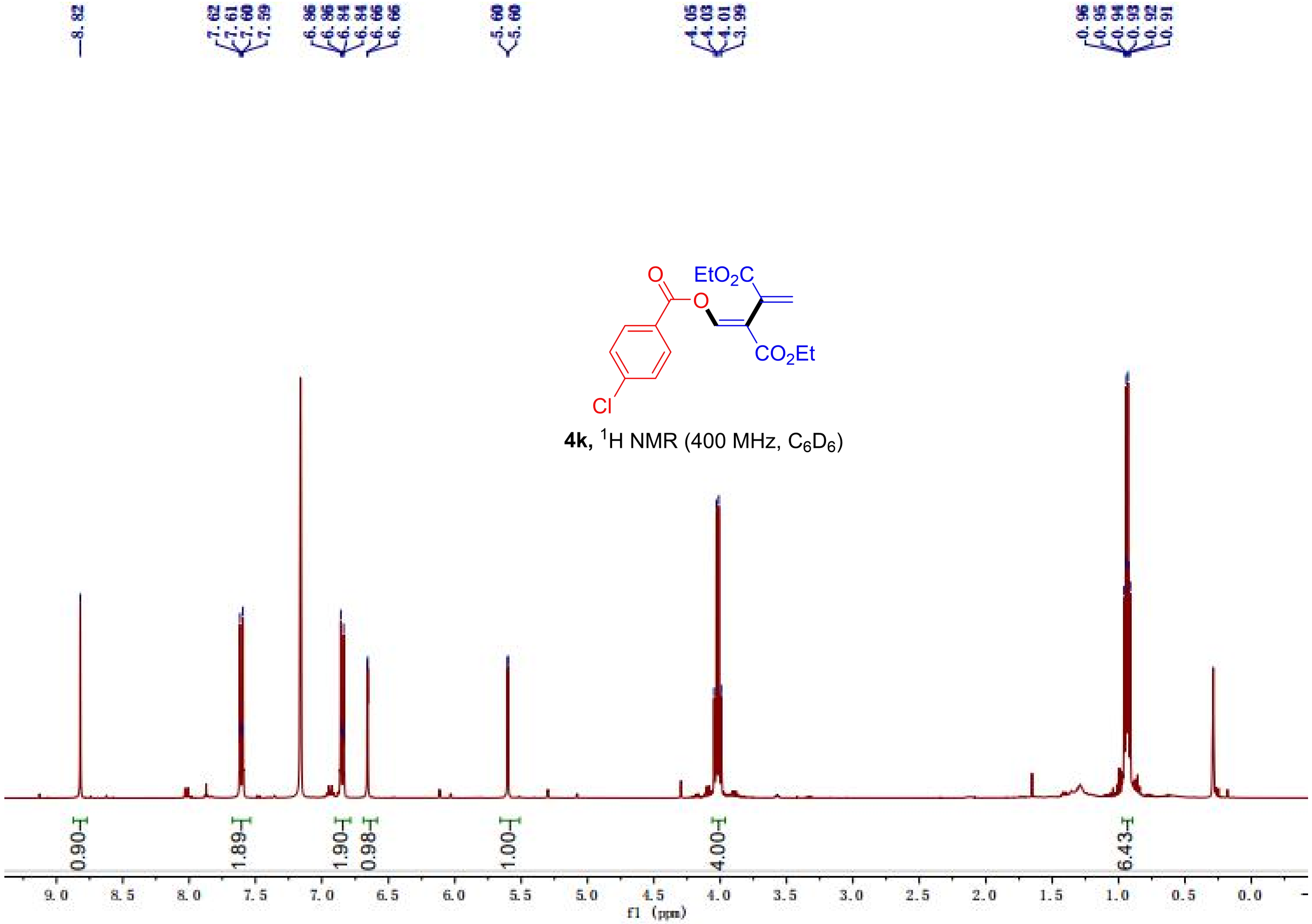
4i, ^{13}C NMR (101 MHz, C_6D_6)



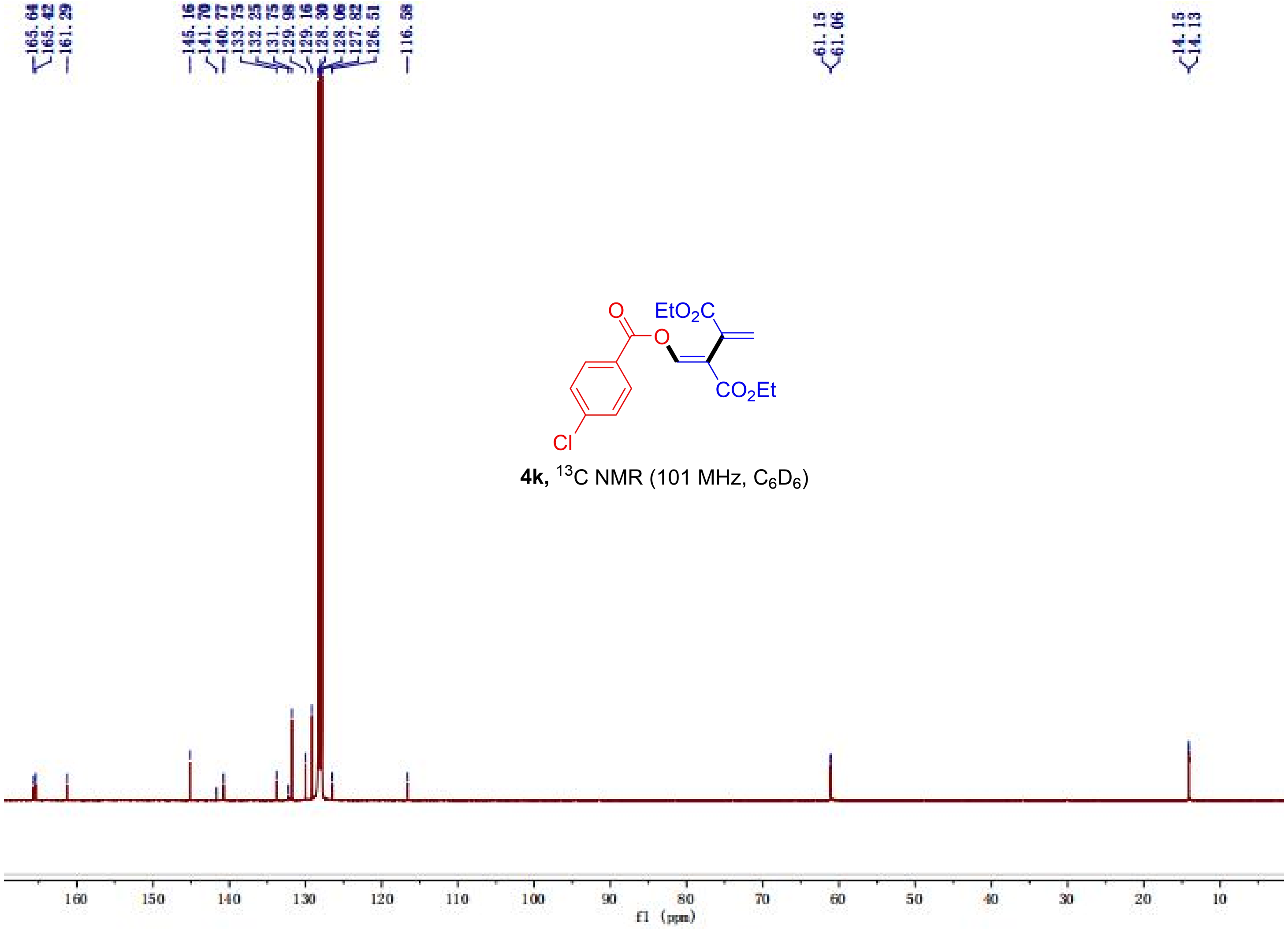
4j, ^{1}H NMR (400 MHz, C_6D_6)



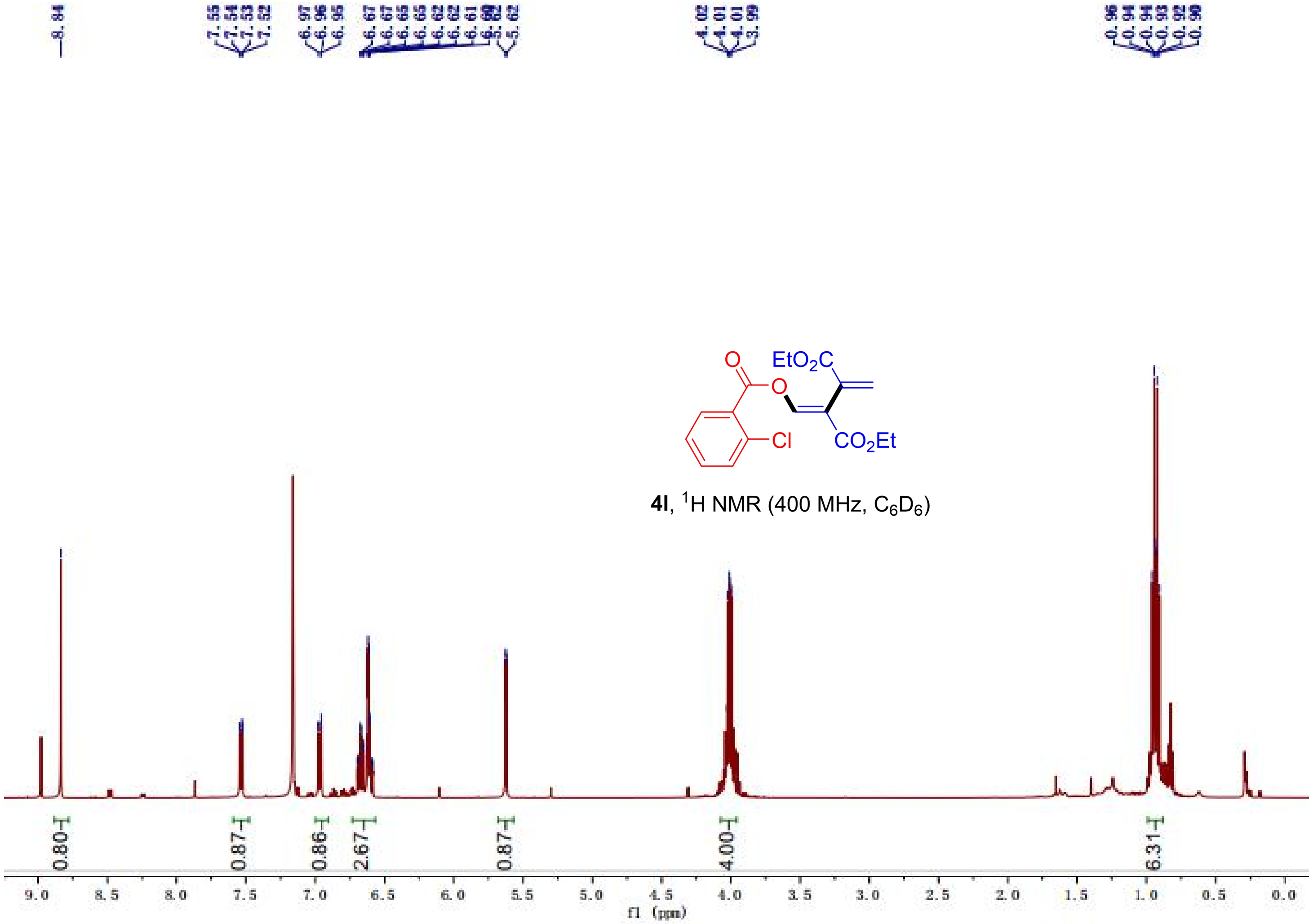
4j, ^{13}C NMR (101 MHz, C_6D_6)



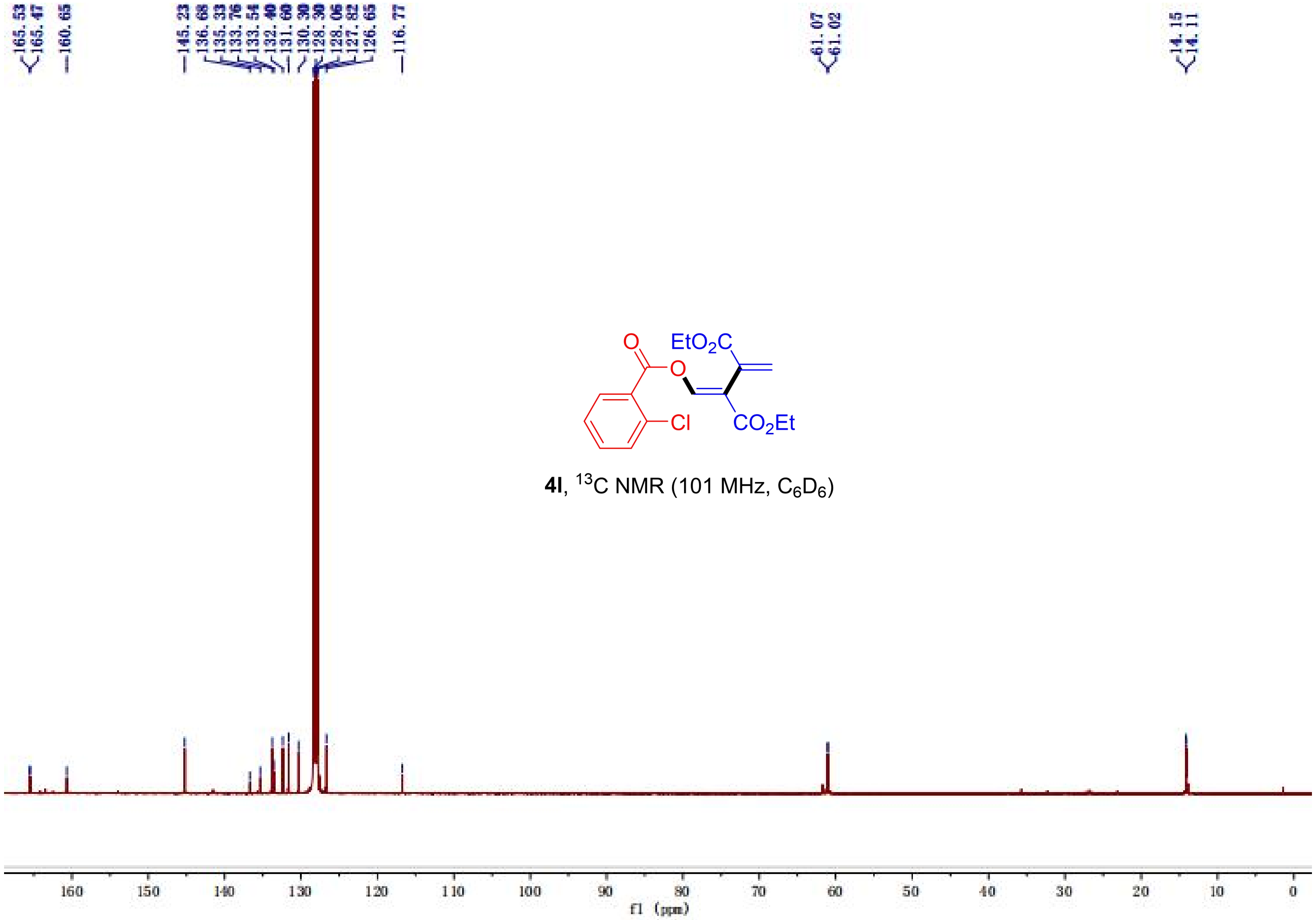
4k, ^{1}H NMR (400 MHz, C_6D_6)



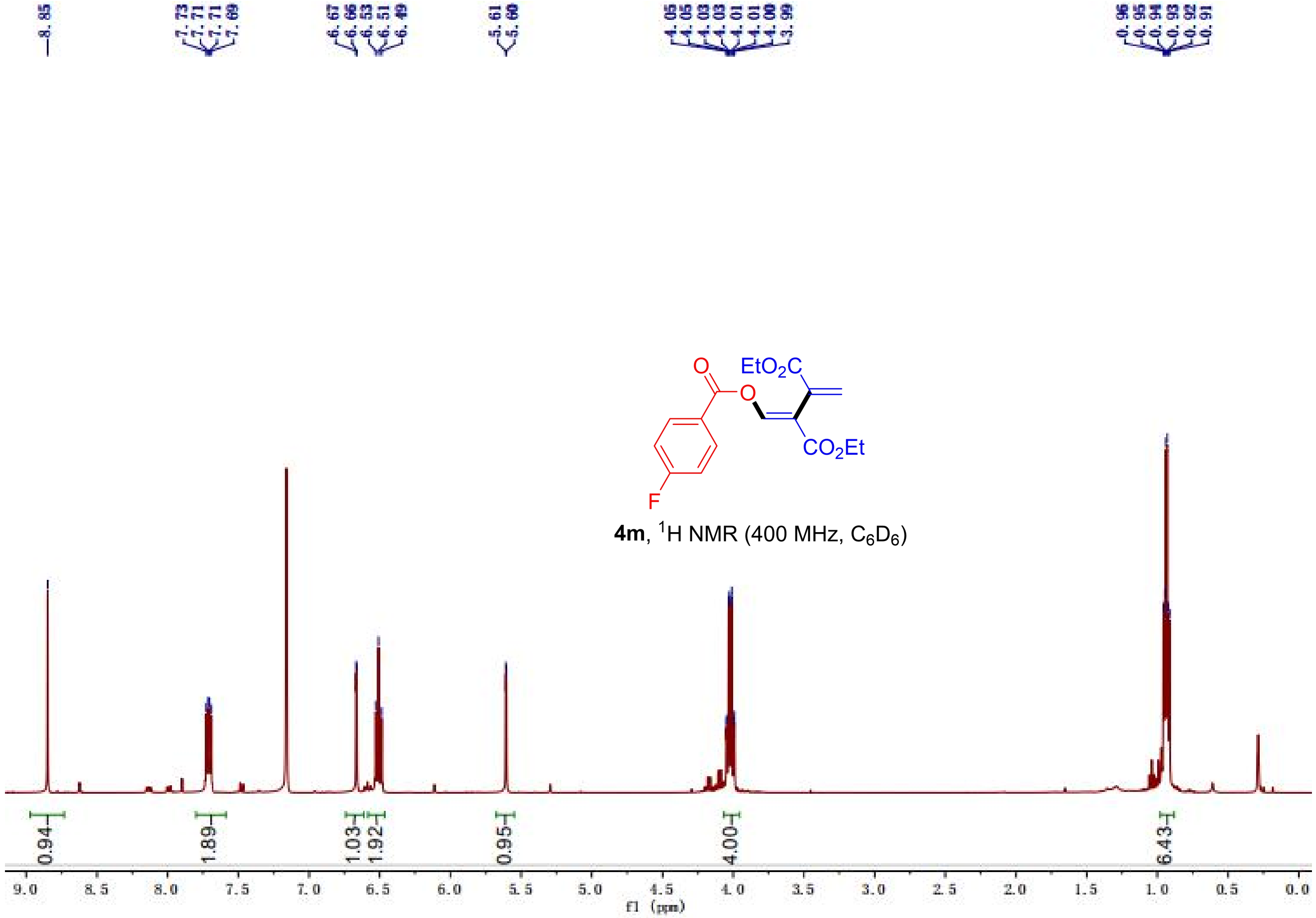
4k, ^{13}C NMR (101 MHz, C_6D_6)



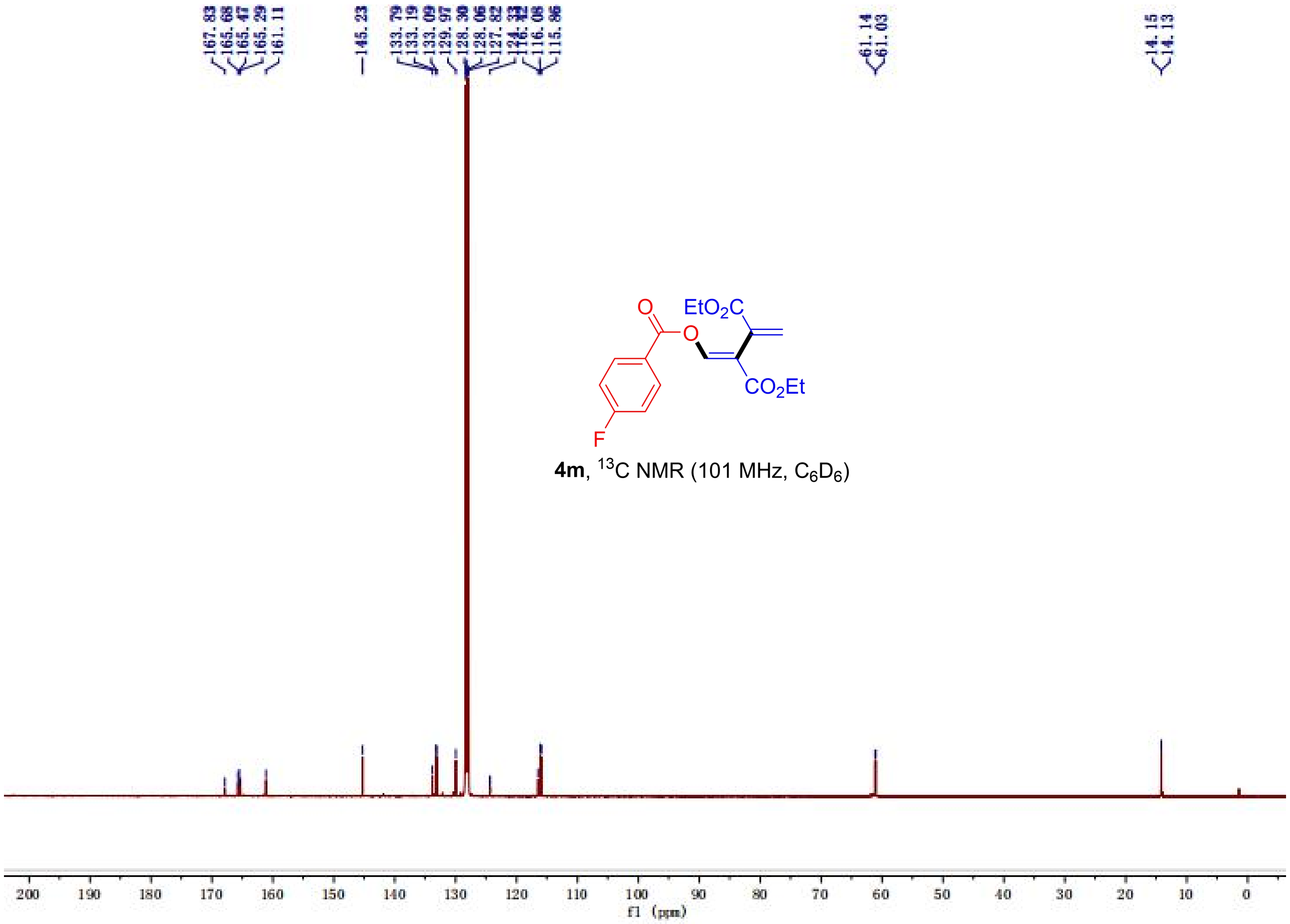
4l, ^{1}H NMR (400 MHz, C_6D_6)



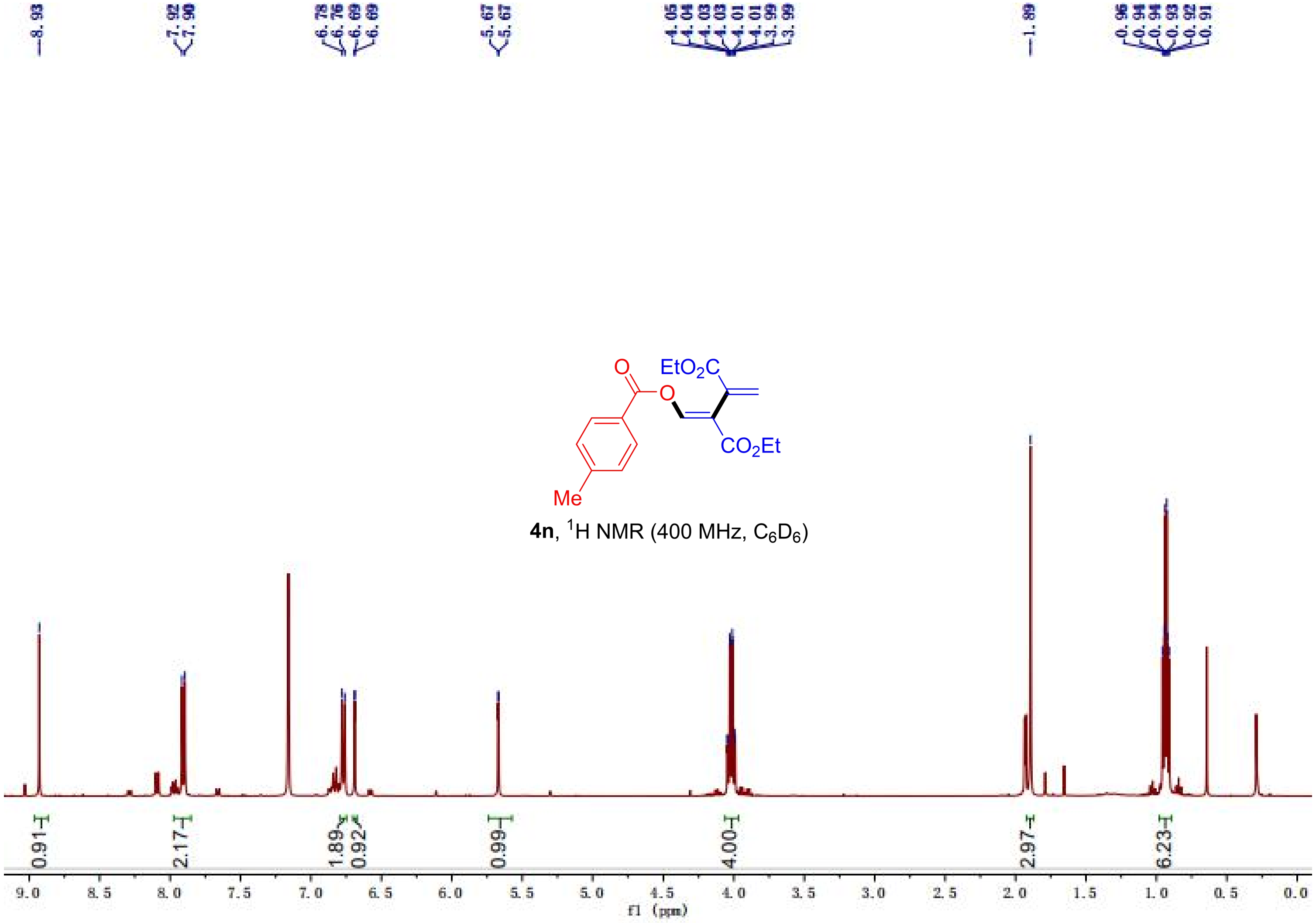
4l, ^{13}C NMR (101 MHz, C_6D_6)



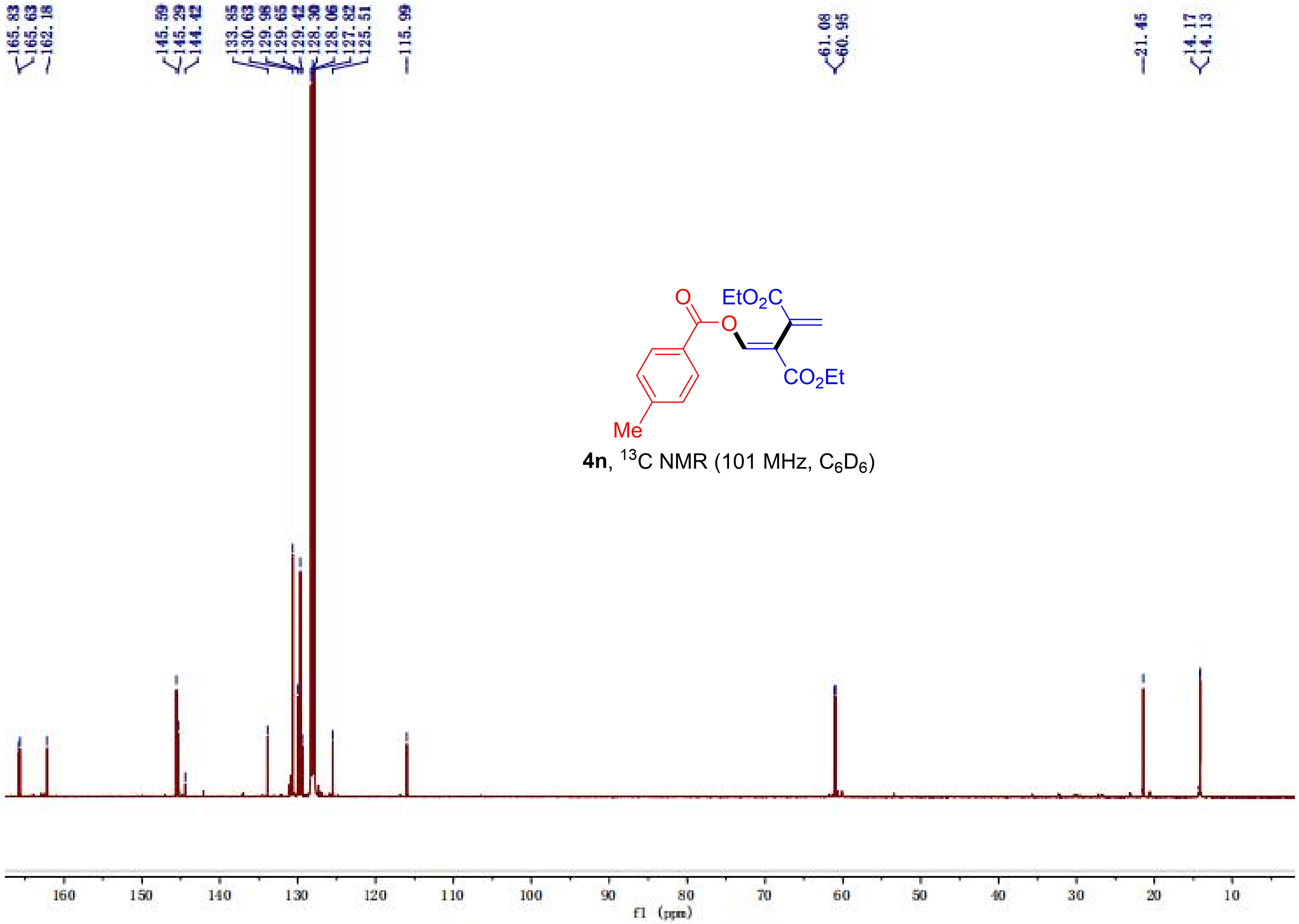
4m, ^{1}H NMR (400 MHz, C_6D_6)



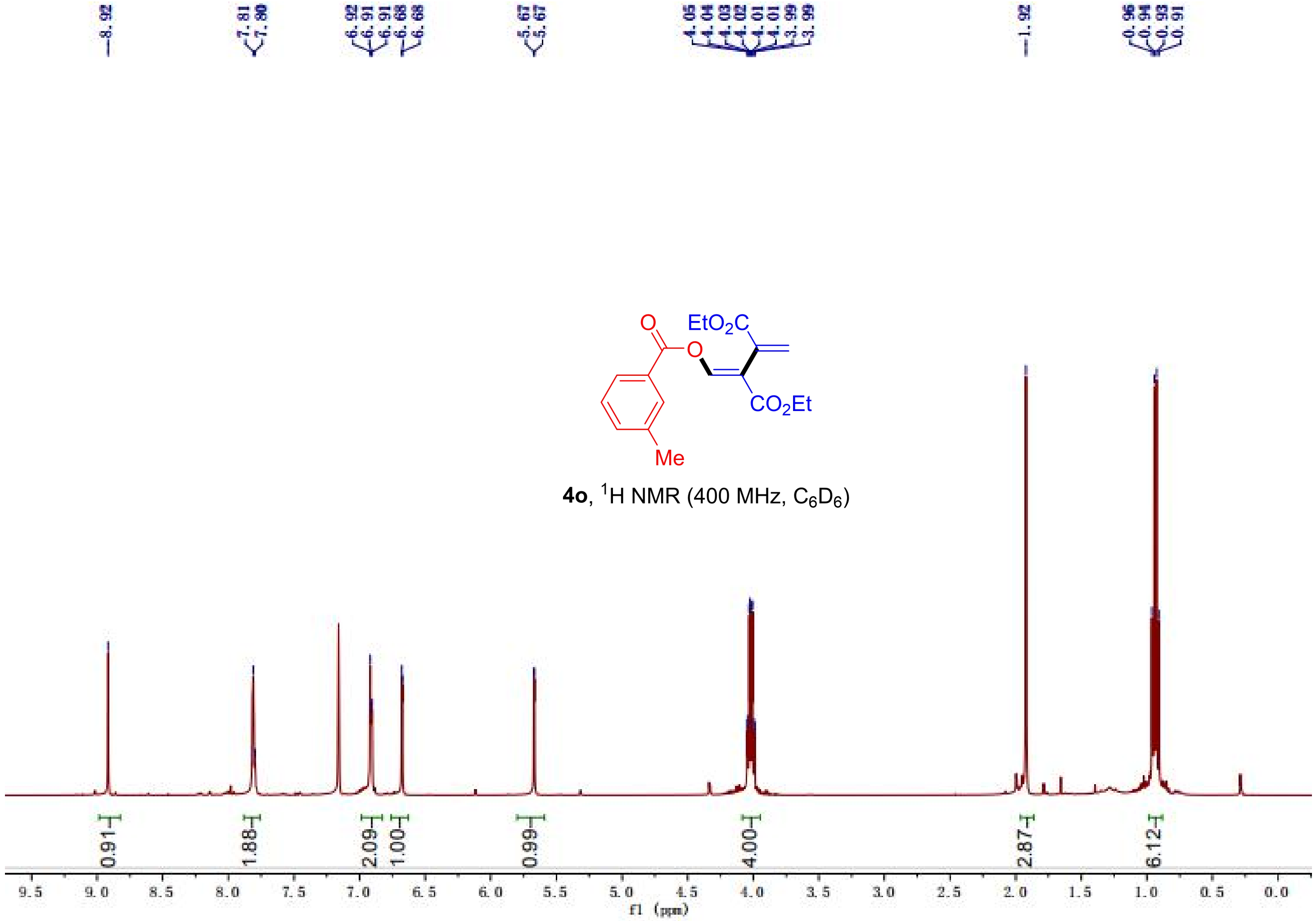
4m, ^{13}C NMR (101 MHz, C_6D_6)



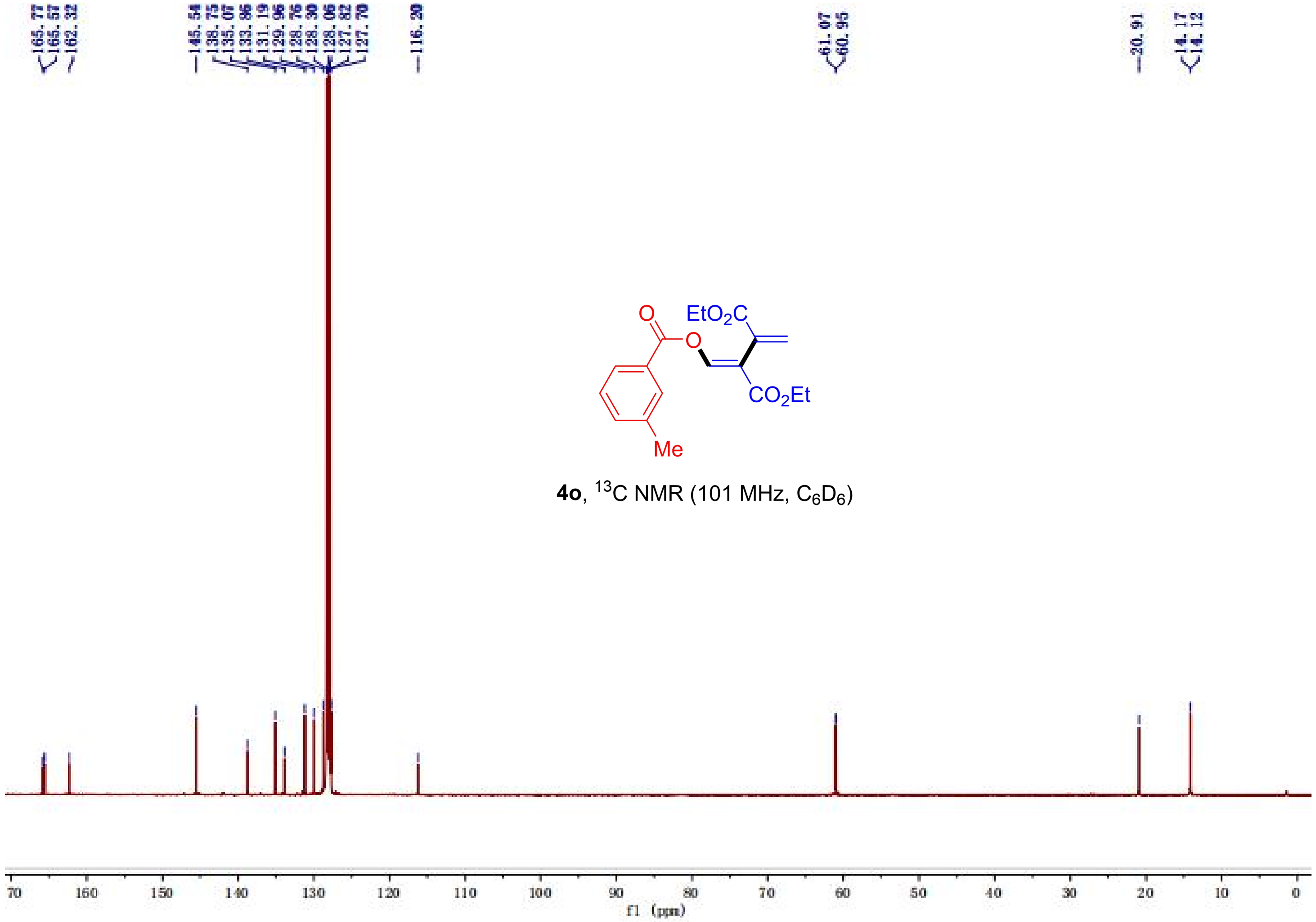
4n, ^{1}H NMR (400 MHz, C_6D_6)



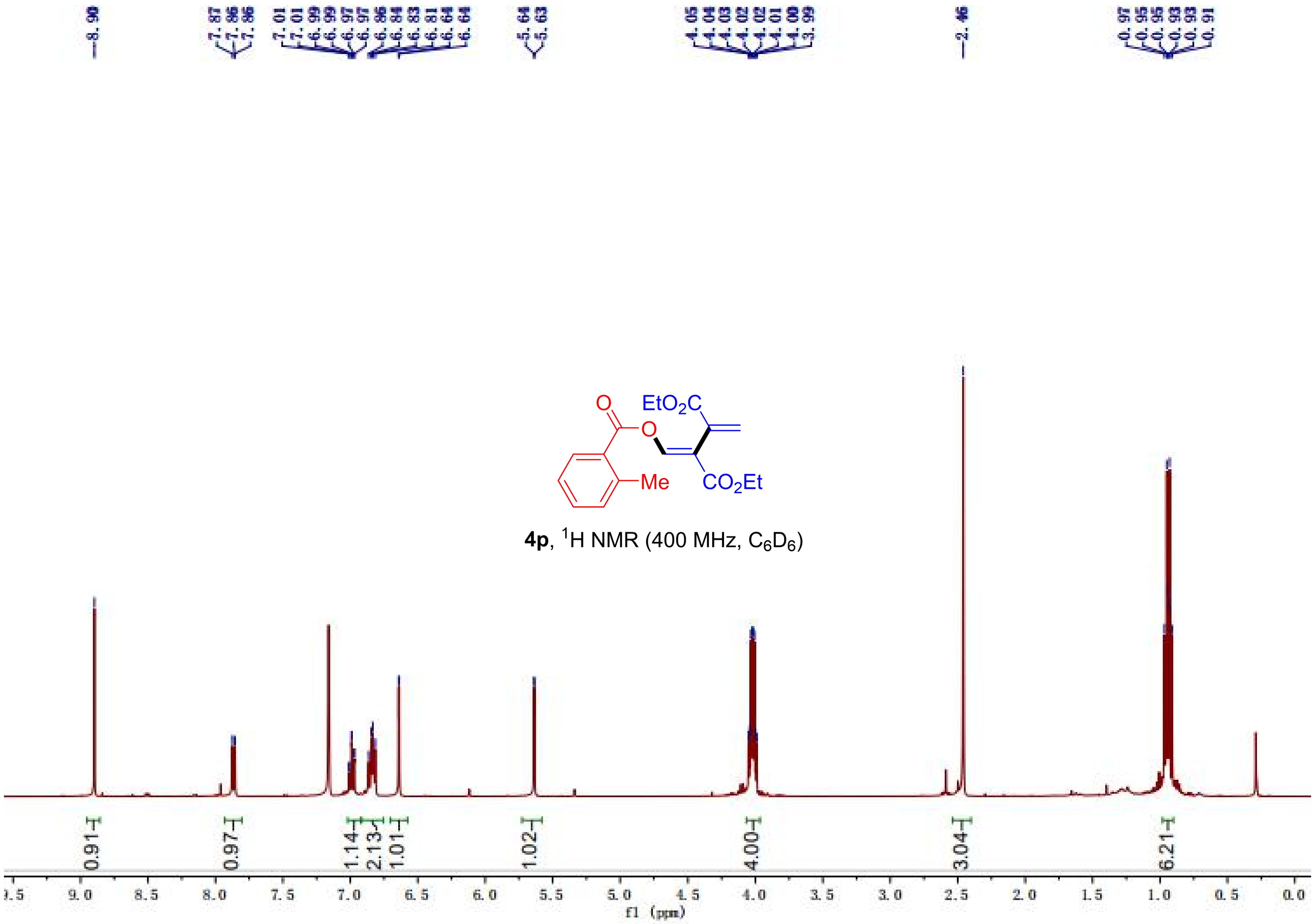
4n, ^{13}C NMR (101 MHz, C_6D_6)



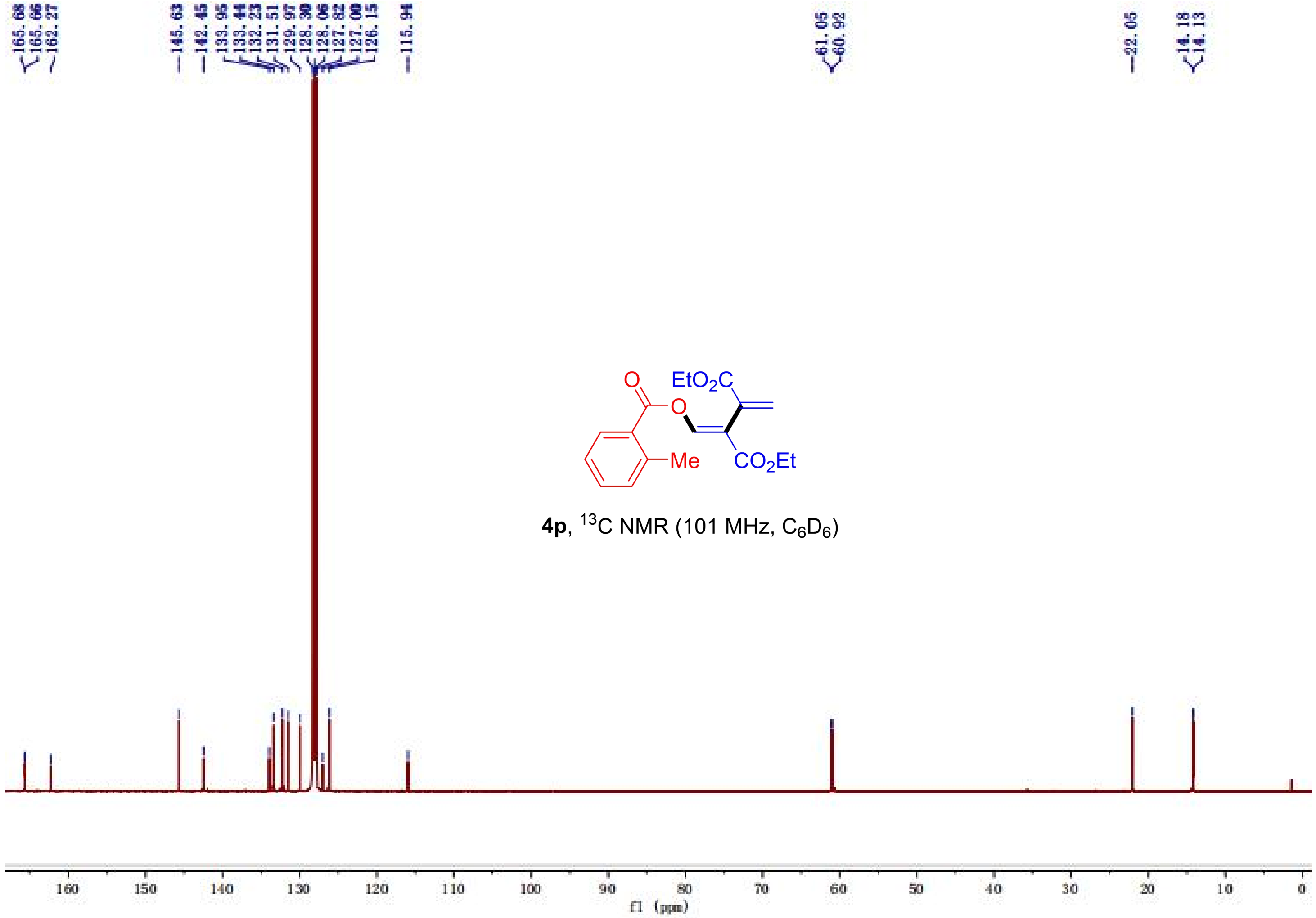
4o, ^{1}H NMR (400 MHz, C_6D_6)



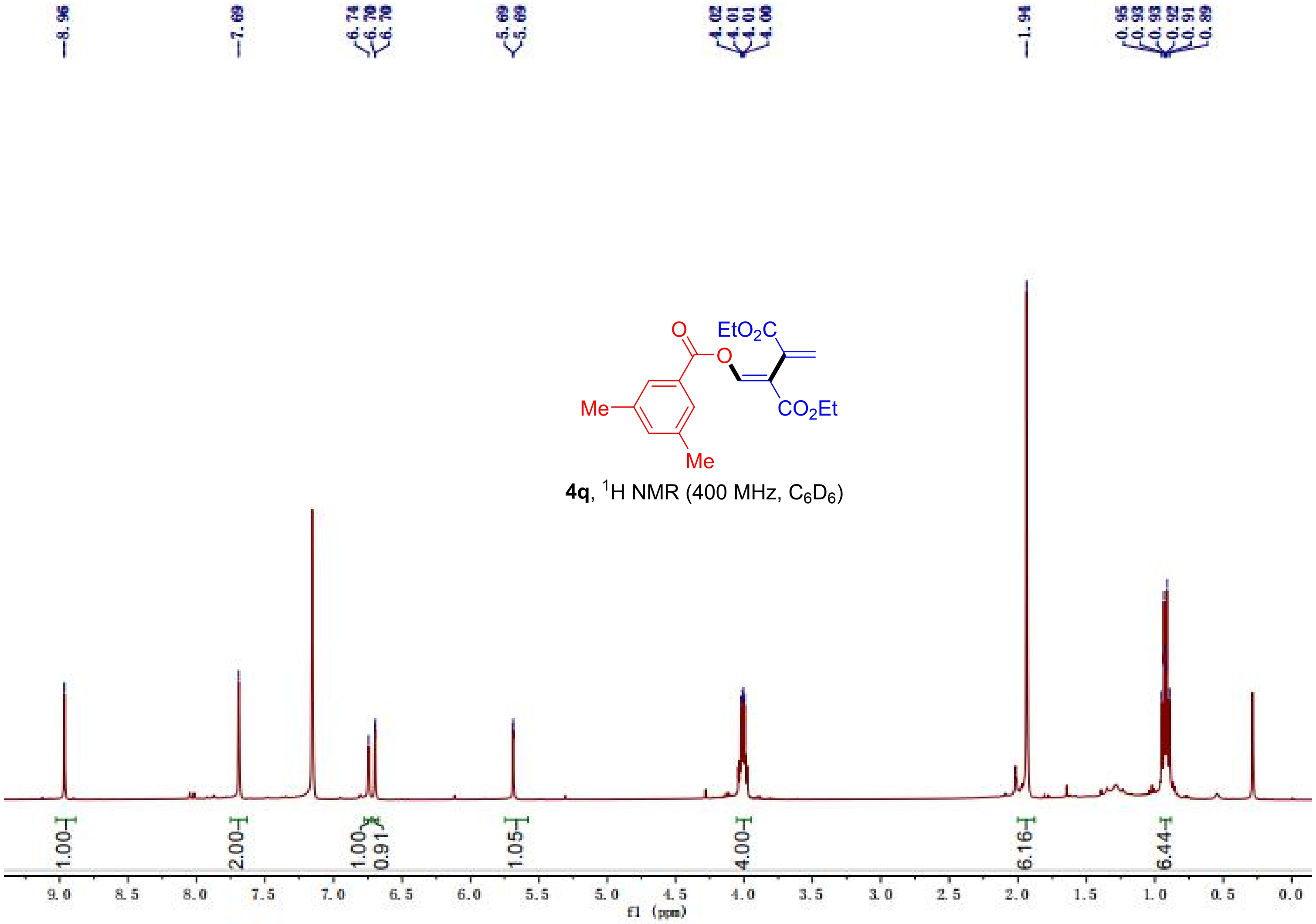
4o, ^{13}C NMR (101 MHz, C_6D_6)



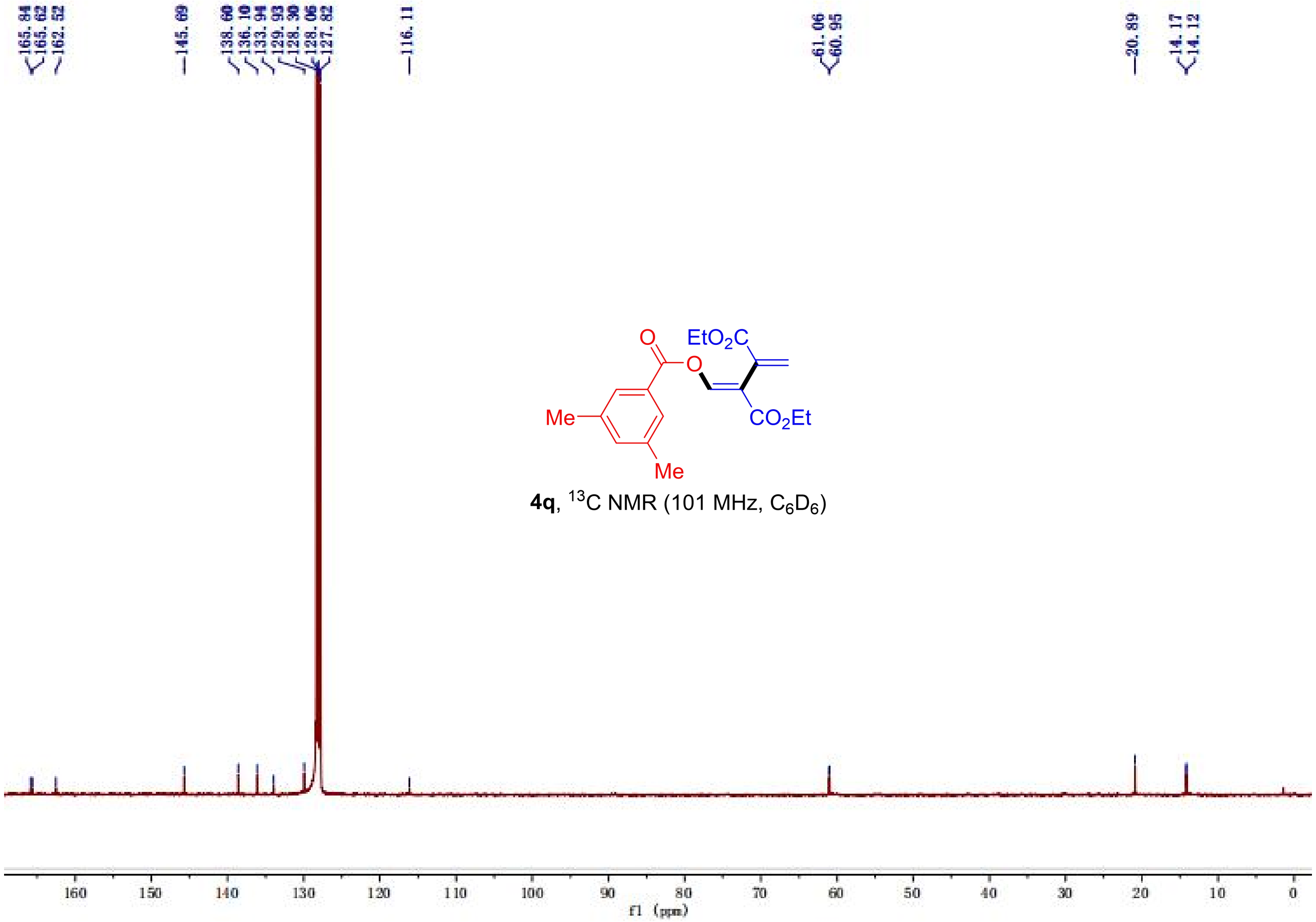
4p, ^{1}H NMR (400 MHz, C_6D_6)



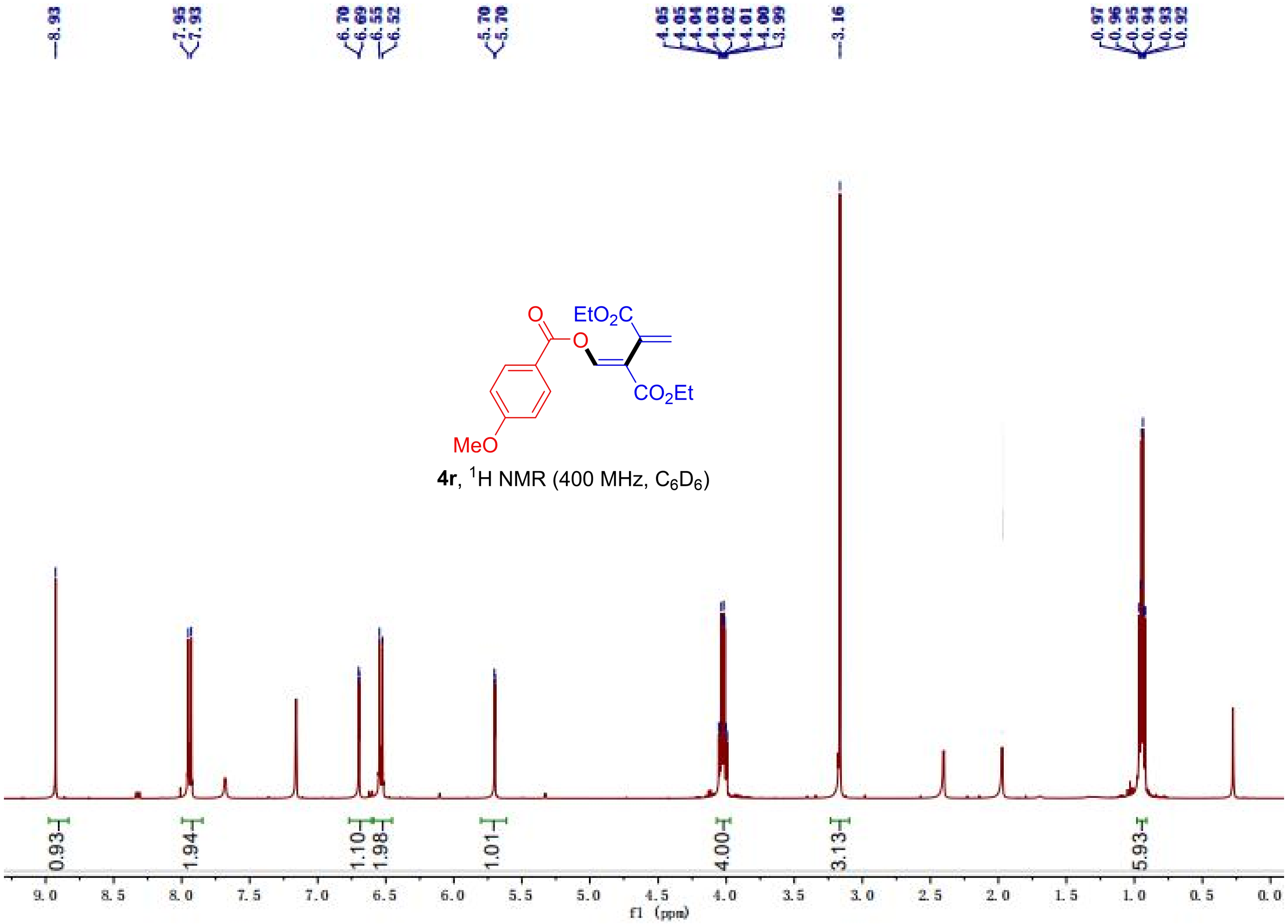
4p, ^{13}C NMR (101 MHz, C_6D_6)



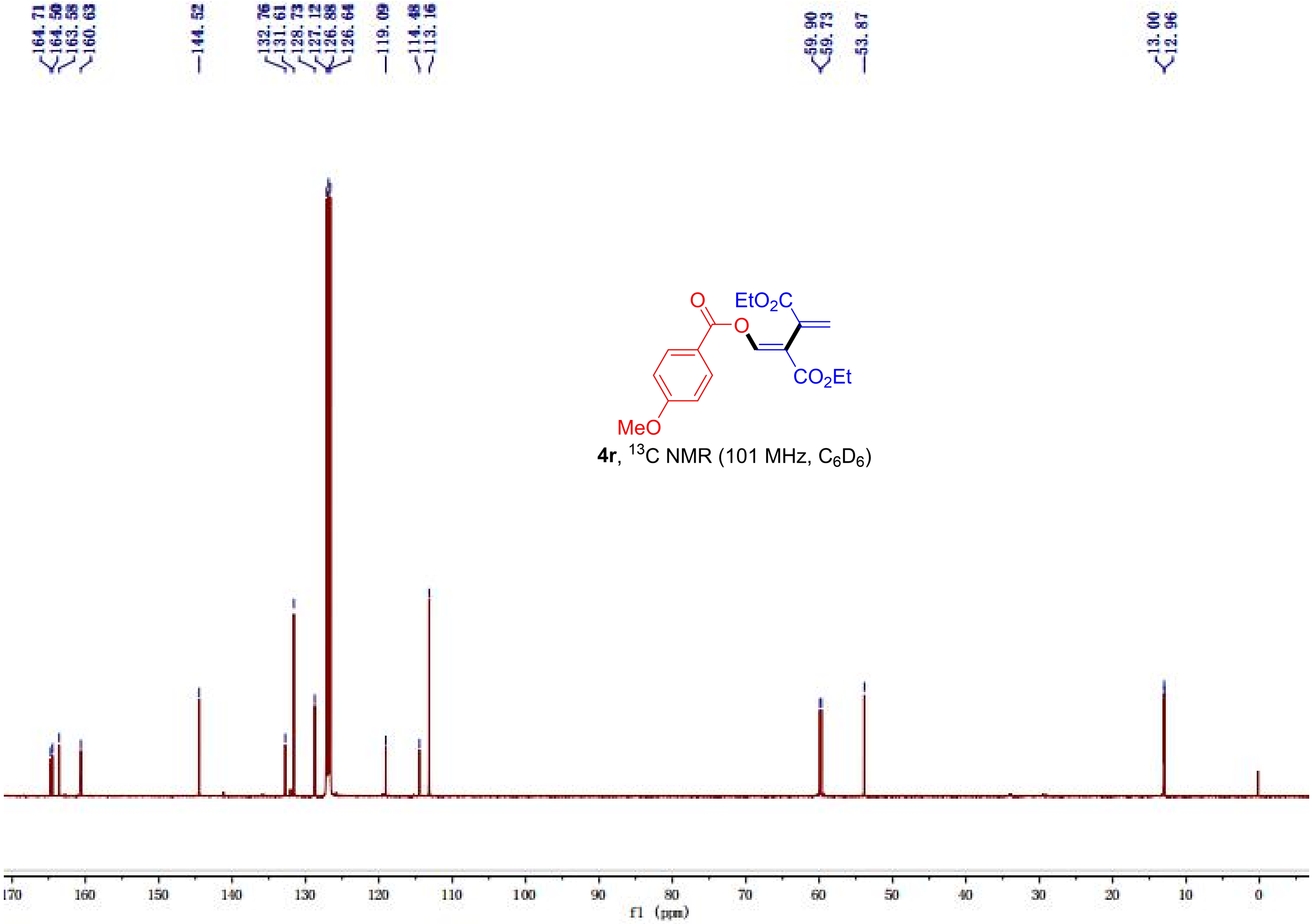
4q, ^{1}H NMR (400 MHz, C_6D_6)



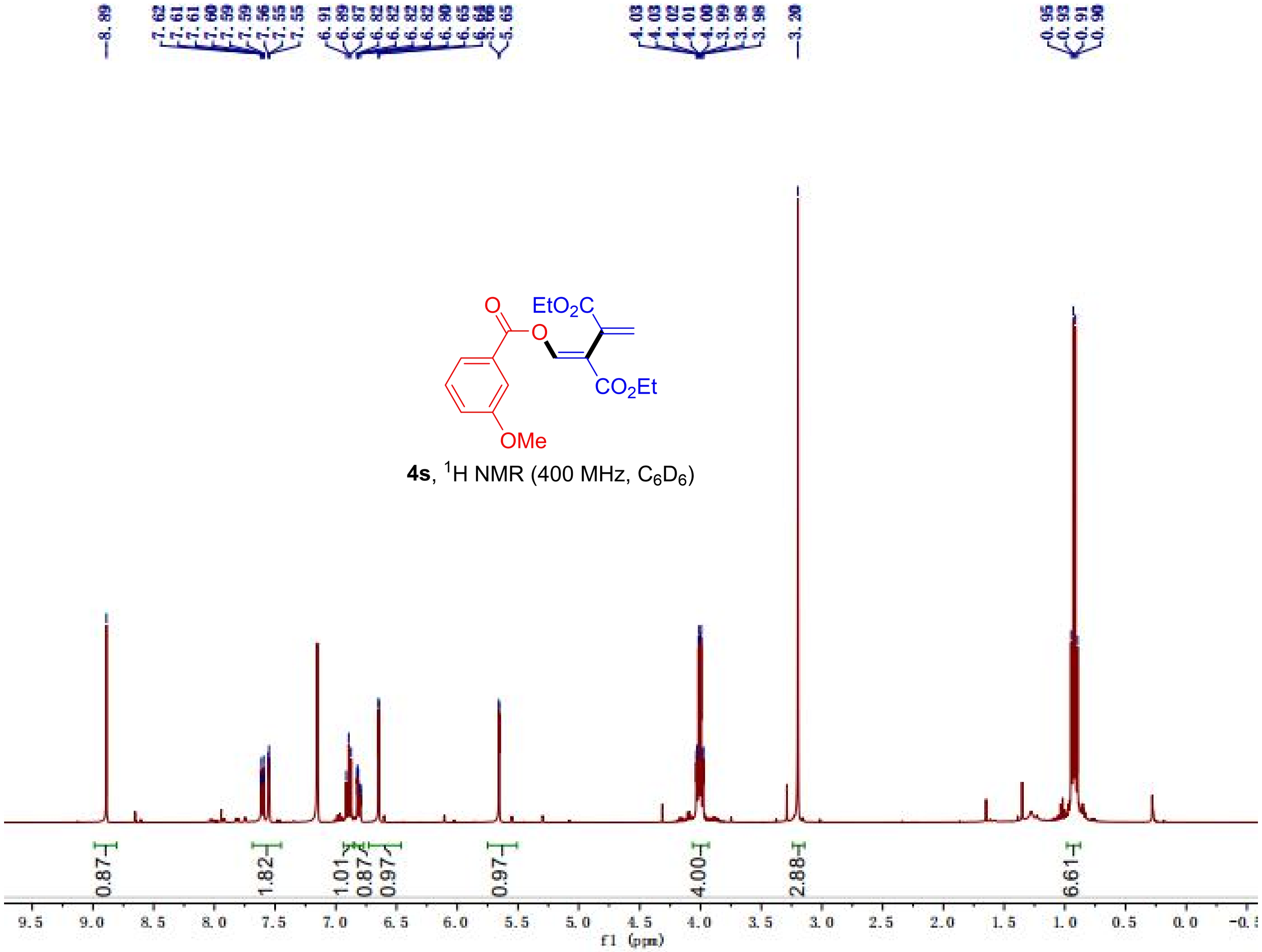
4q, ^{13}C NMR (101 MHz, C_6D_6)



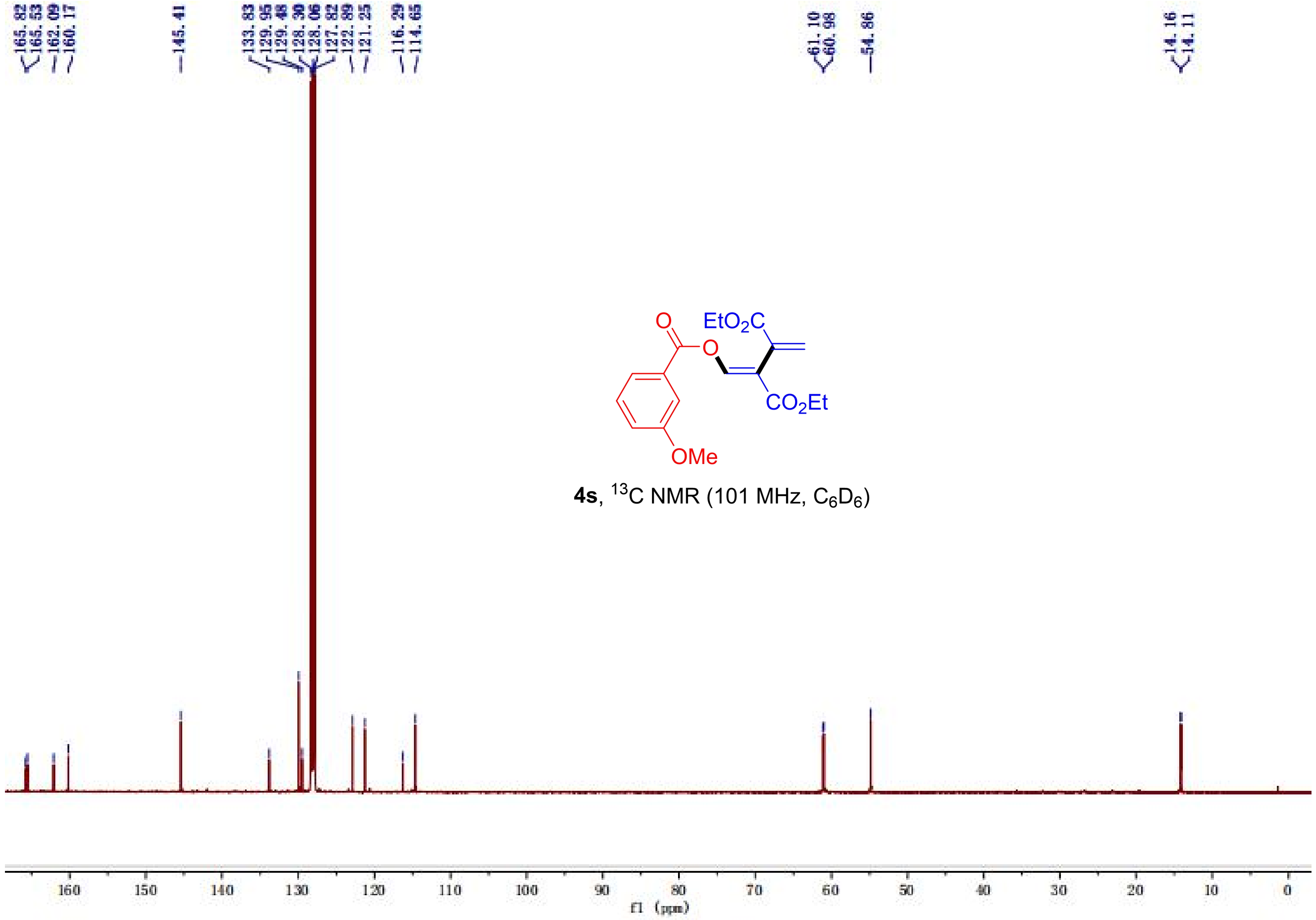
4r, ^1H NMR (400 MHz, C_6D_6)



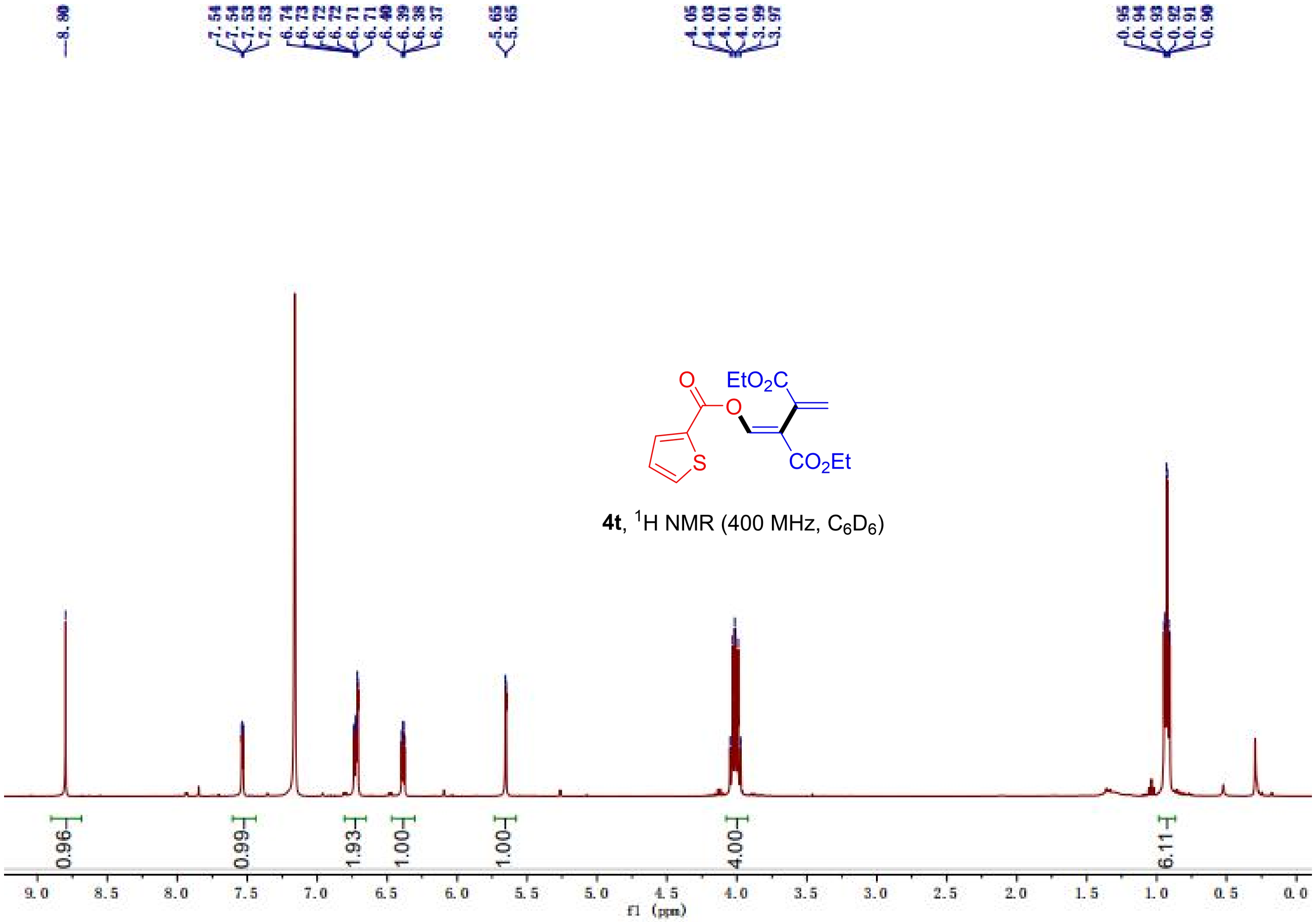
4r, ^{13}C NMR (101 MHz, C_6D_6)



4s, ^{1}H NMR (400 MHz, C_6D_6)



4s, ^{13}C NMR (101 MHz, C_6D_6)



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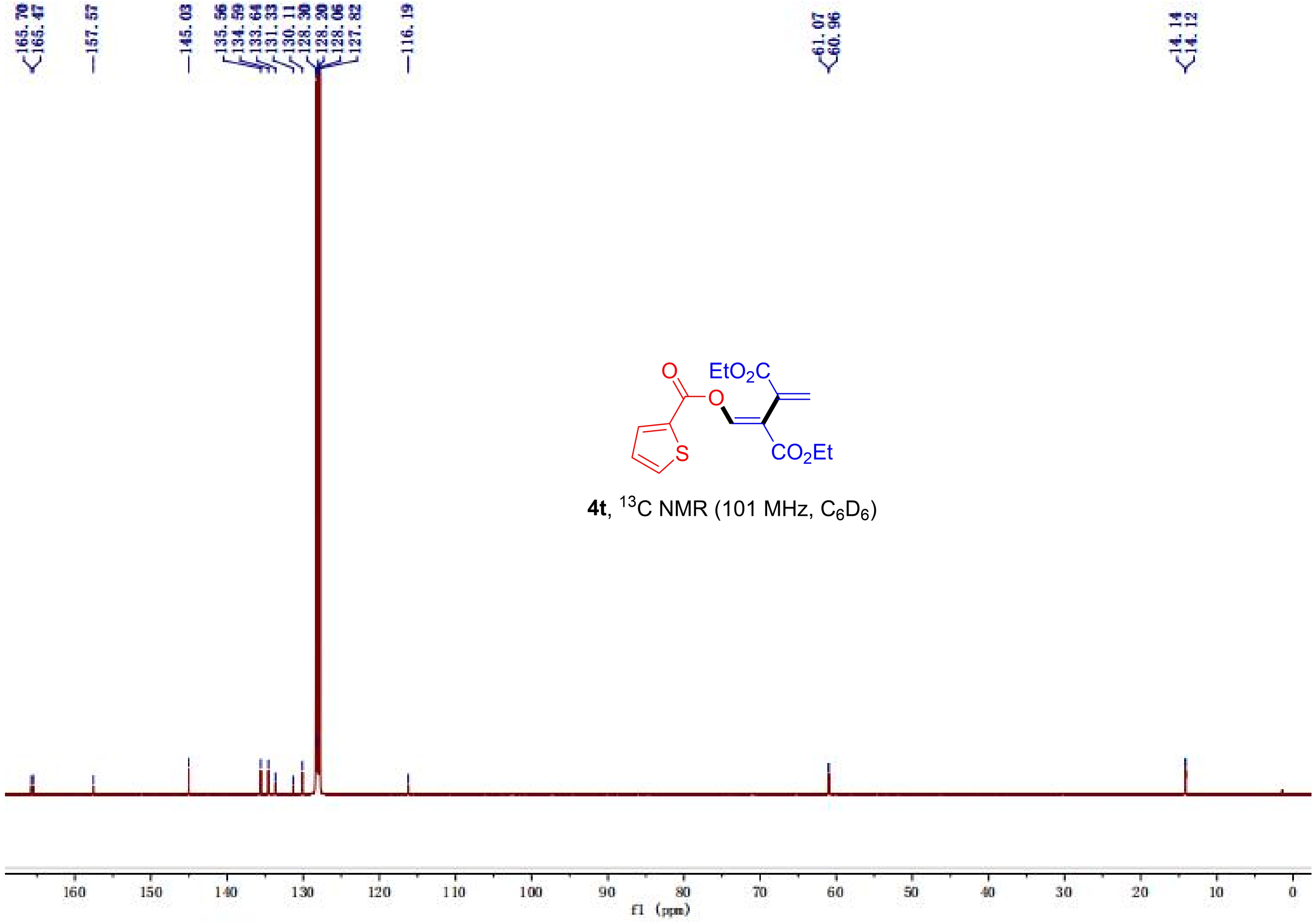
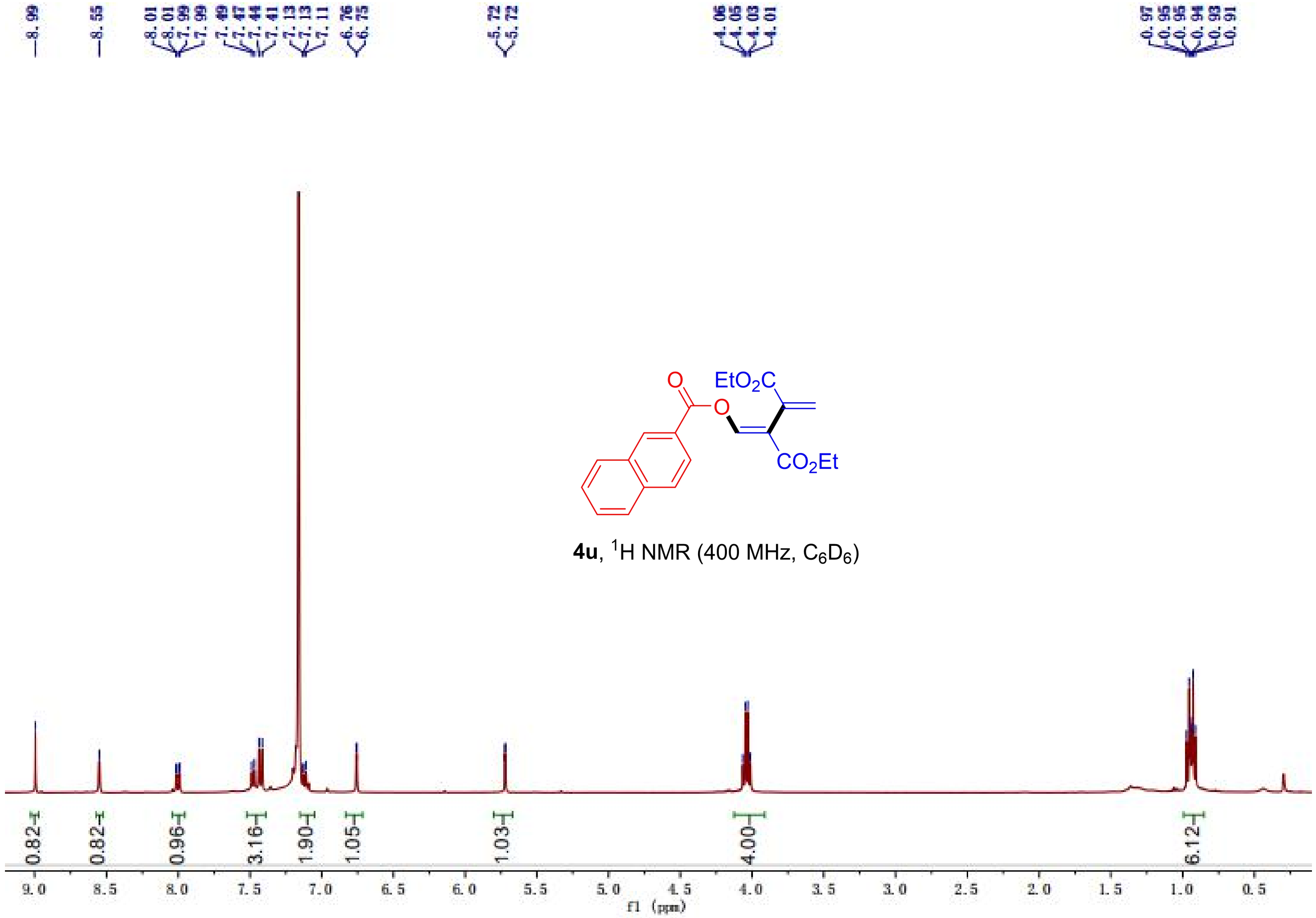
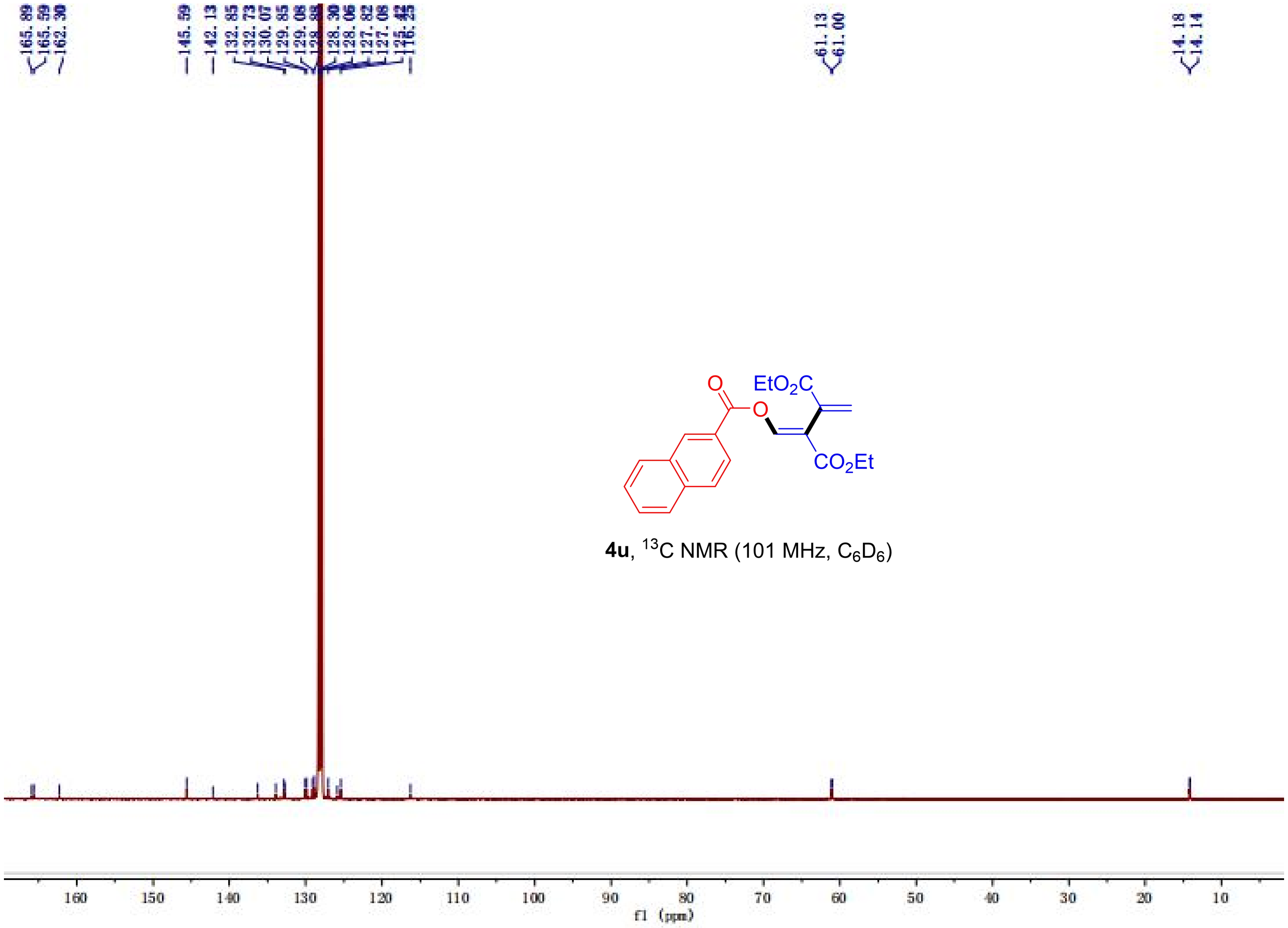


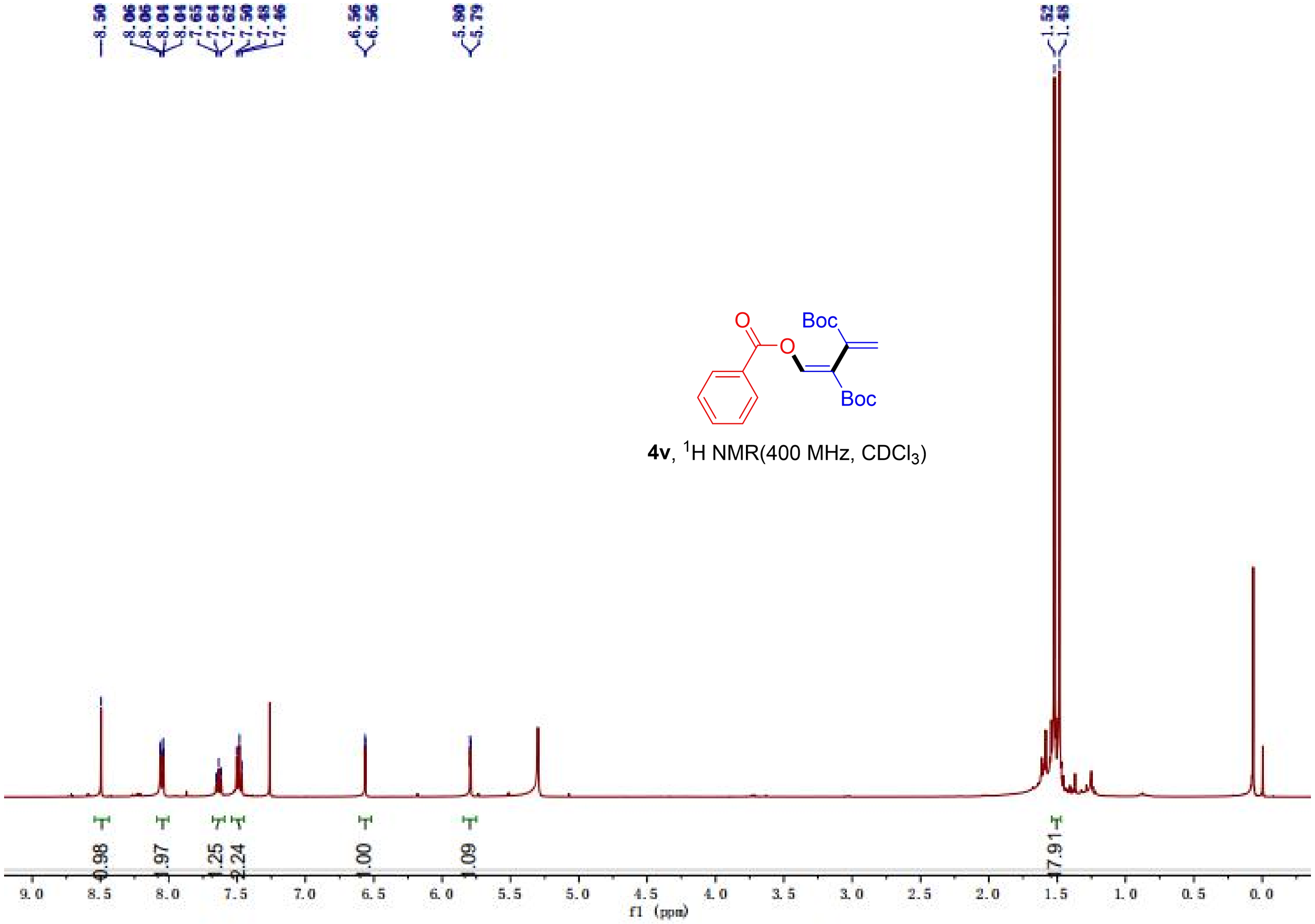
4t, ^{13}C NMR (101 MHz, C_6D_6)



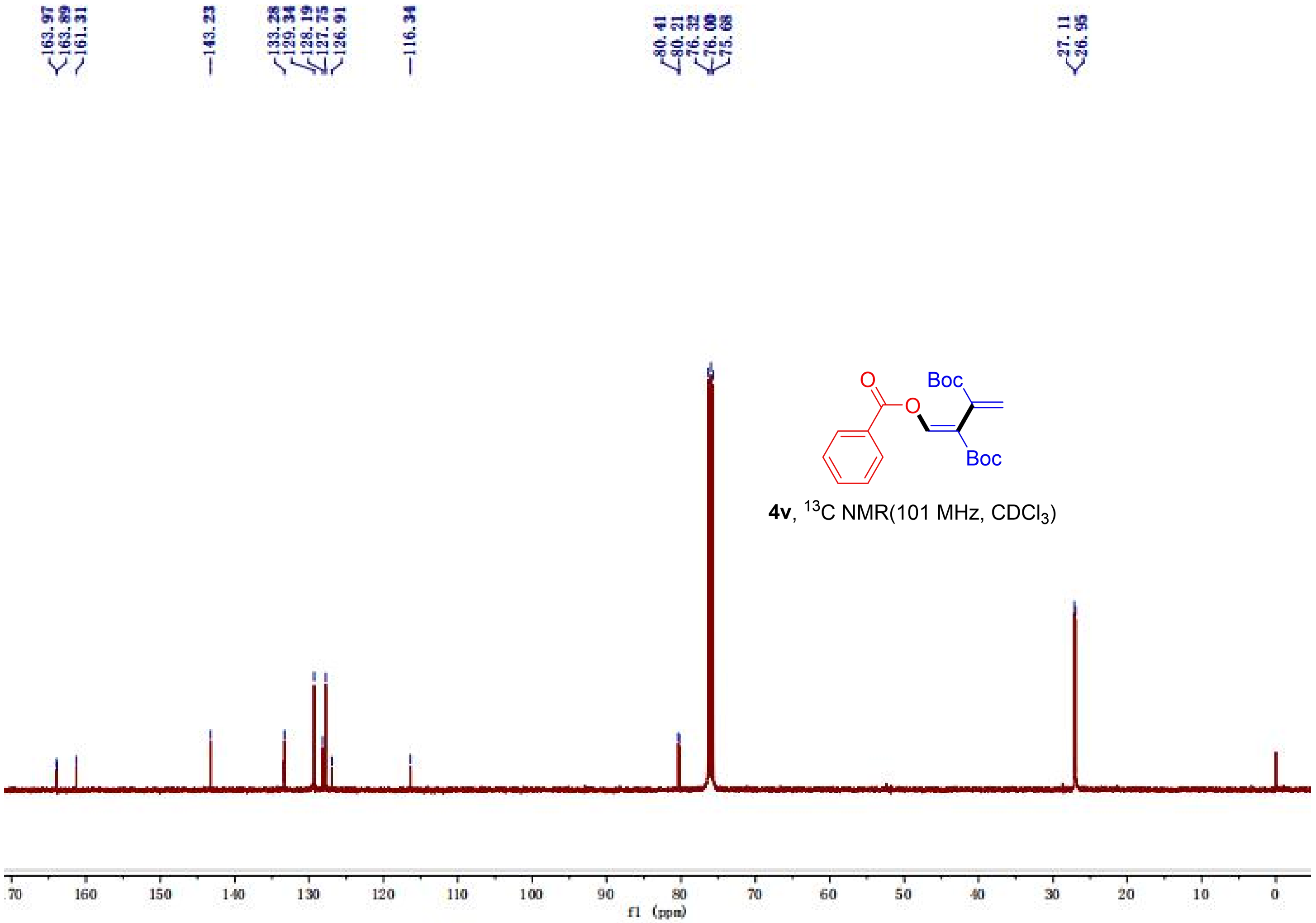
4u, ^{1}H NMR (400 MHz, C_6D_6)



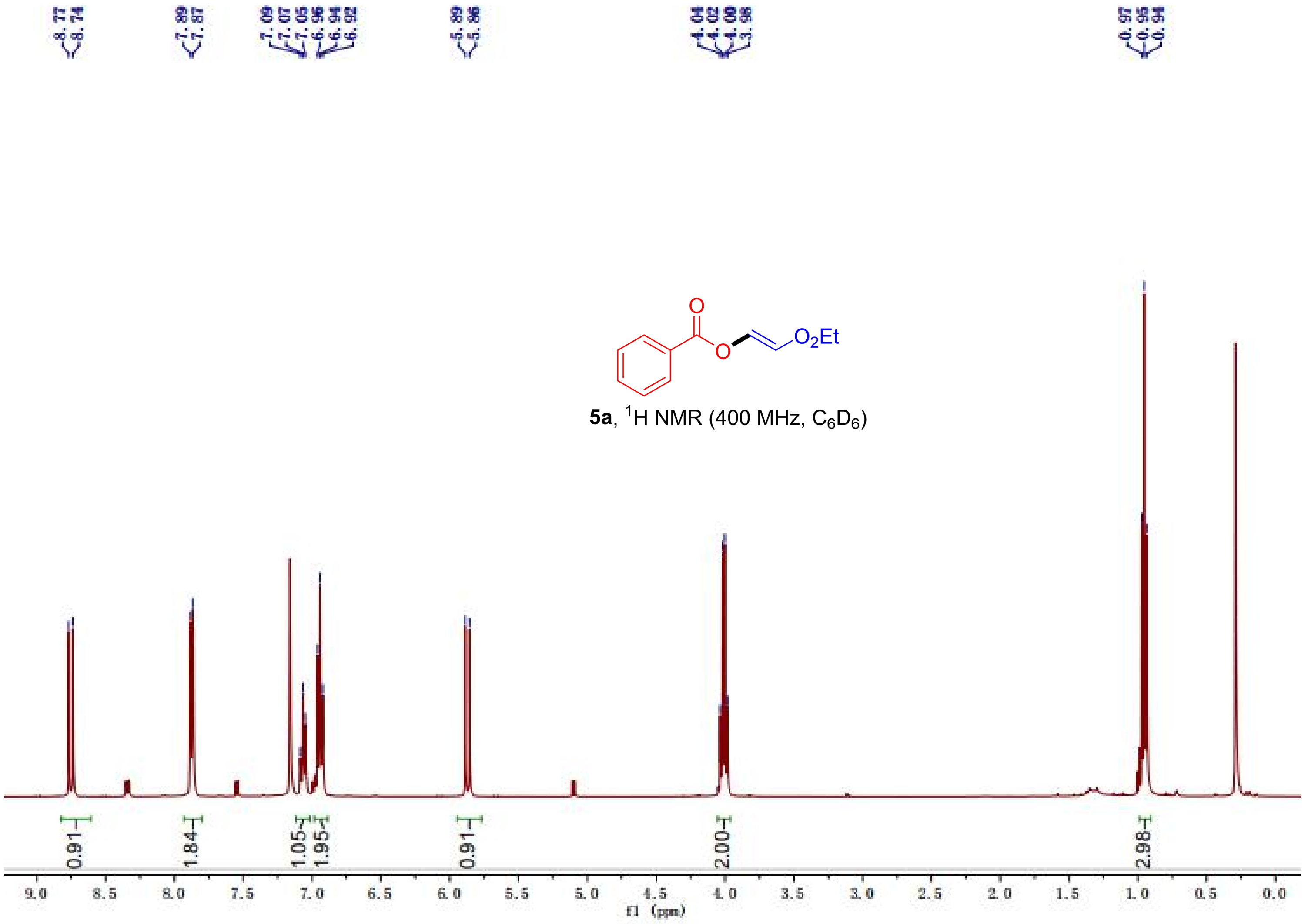
4u, ^{13}C NMR (101 MHz, C_6D_6)



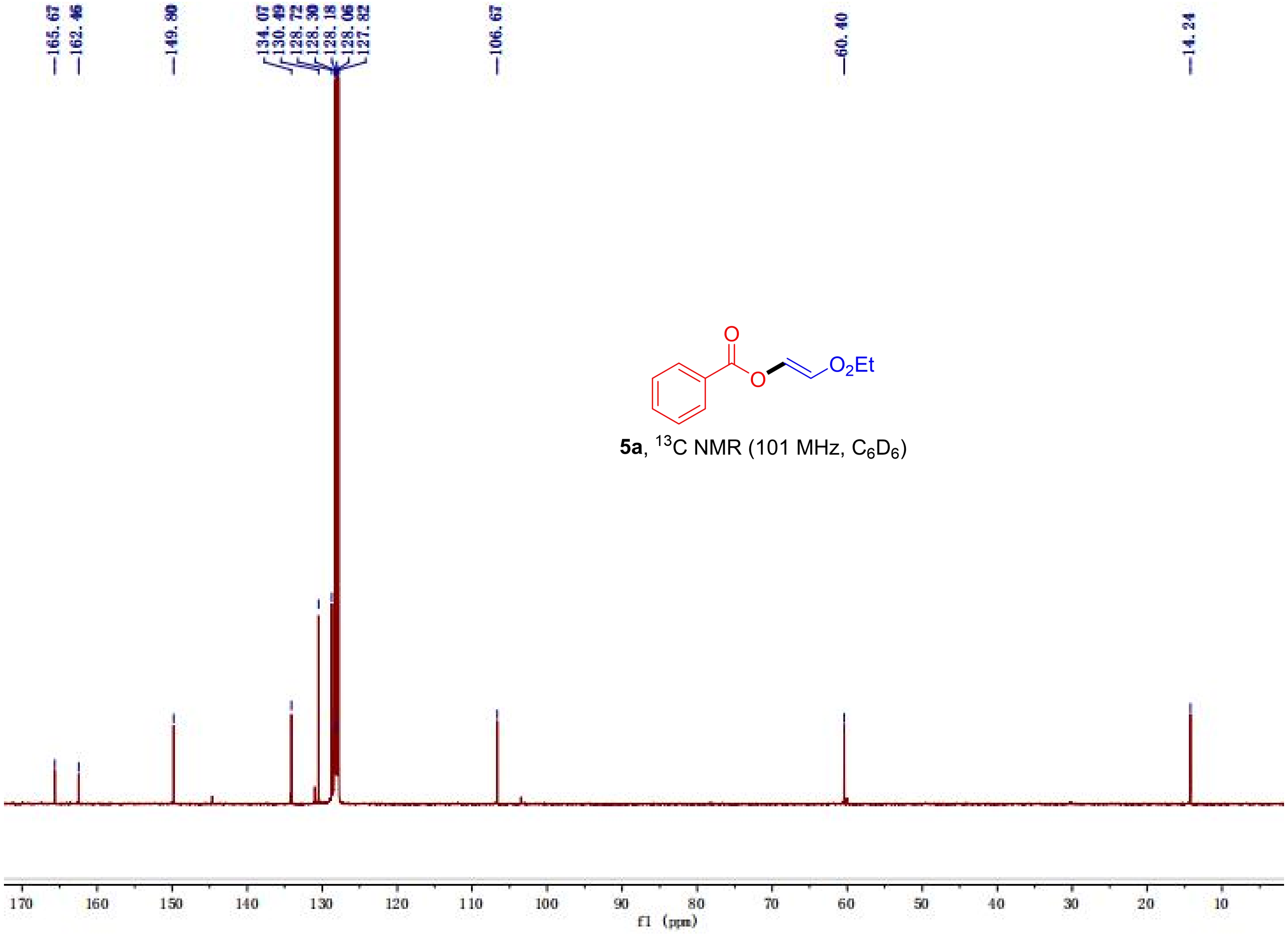
4v, ^{1}H NMR(400 MHz, CDCl$_3$)



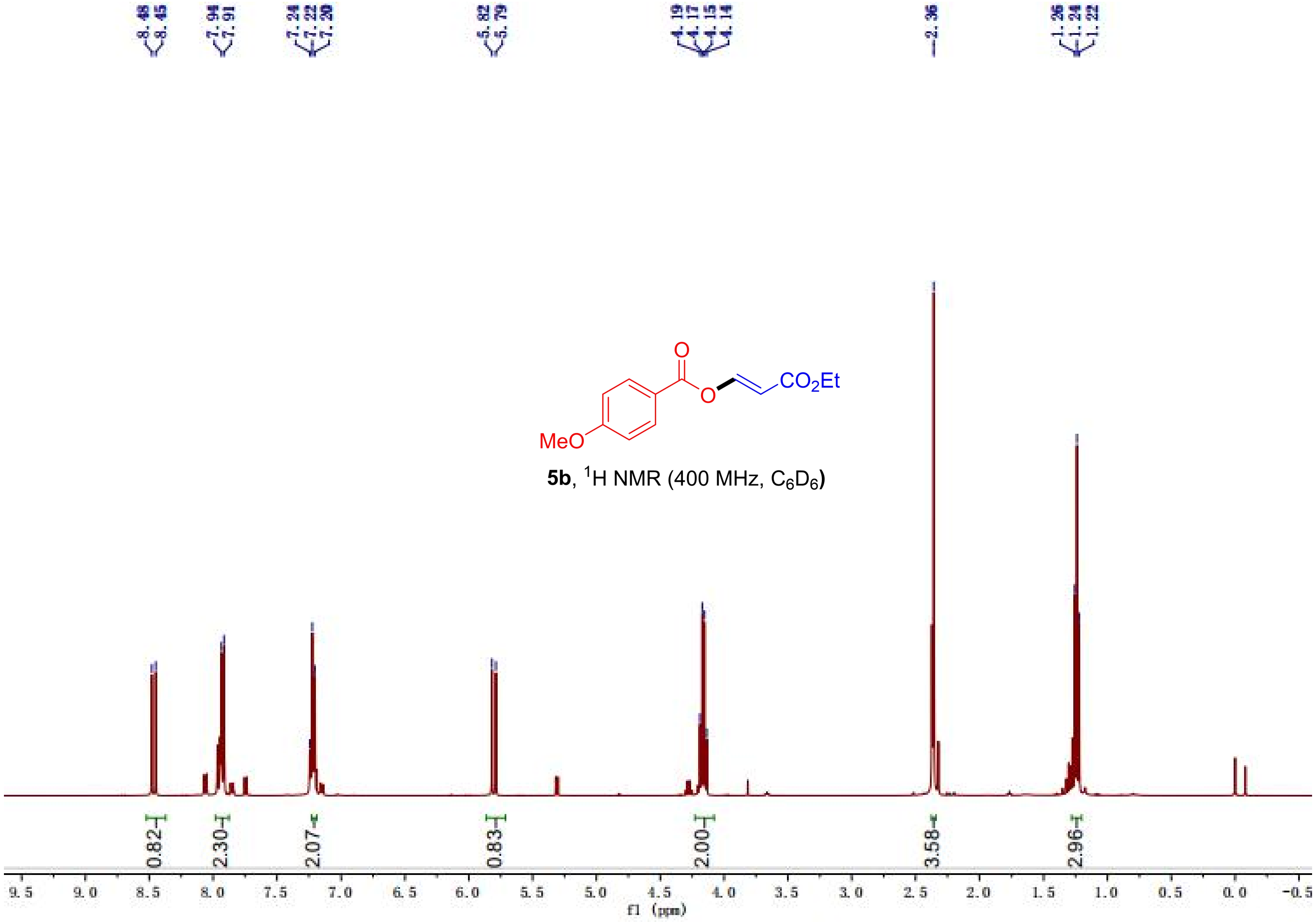
4v, ^{13}C NMR(101 MHz, CDCl$_3$)



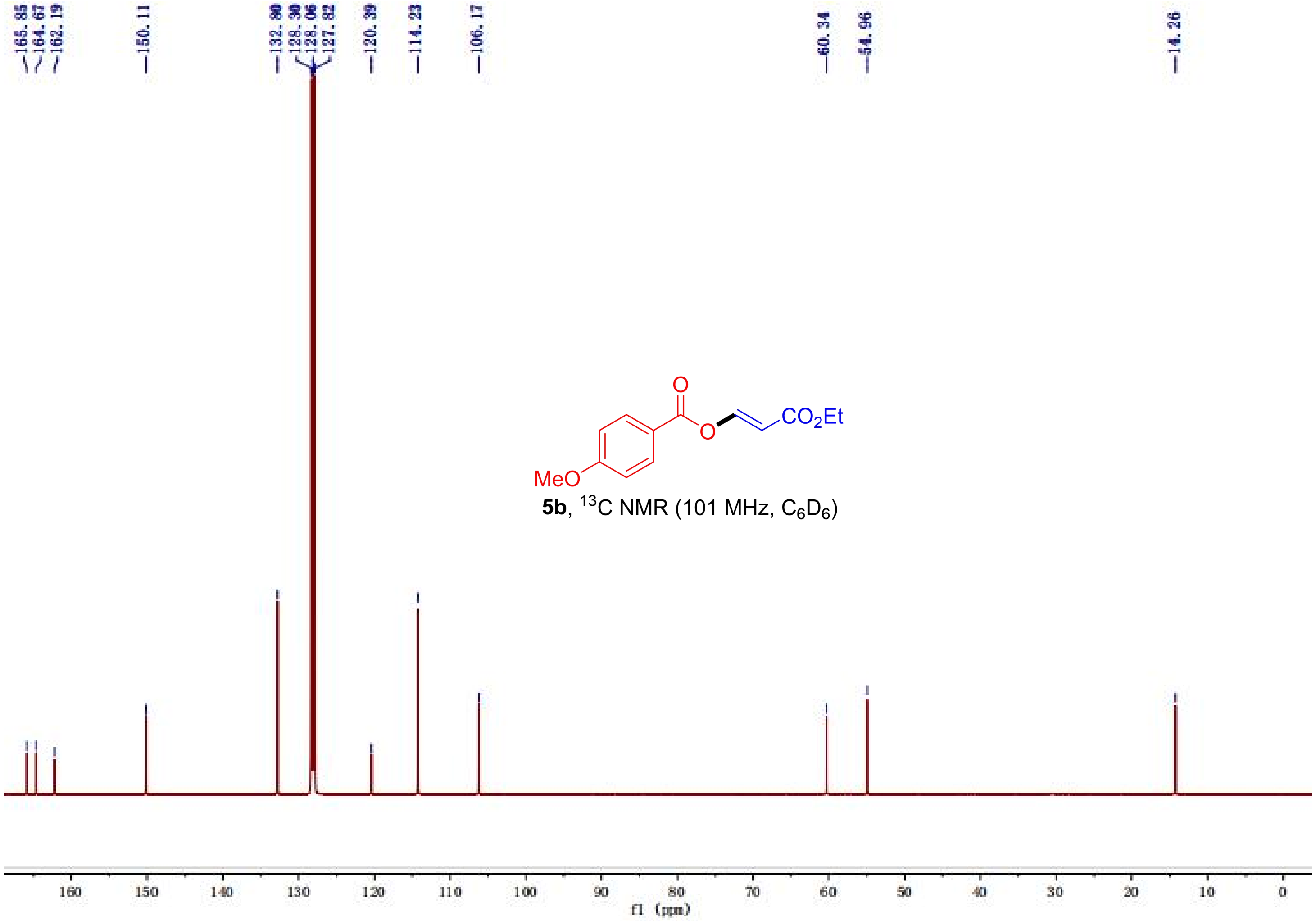
5a, ^{1}H NMR (400 MHz, C_6D_6)



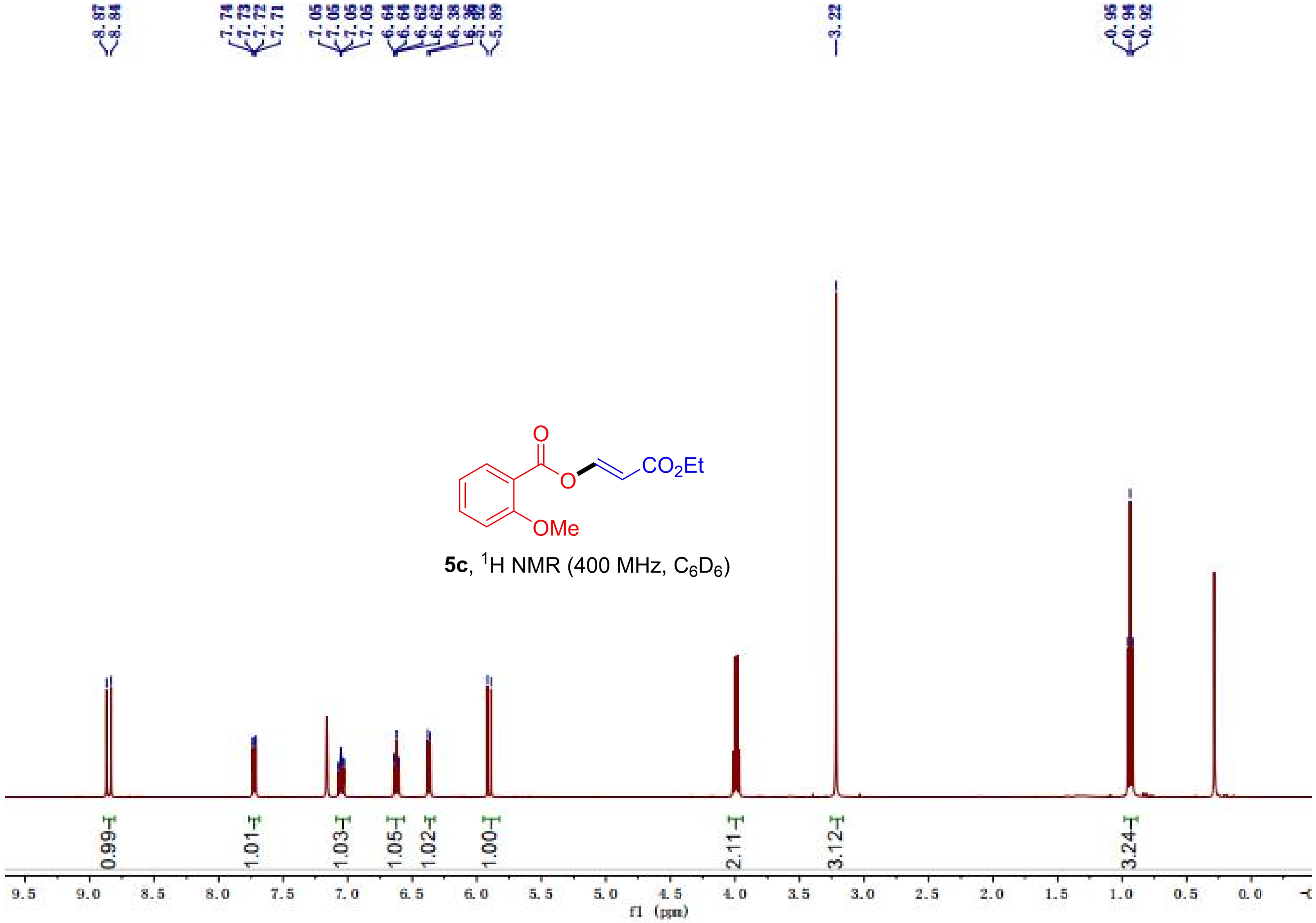
5a, ^{13}C NMR (101 MHz, C_6D_6)



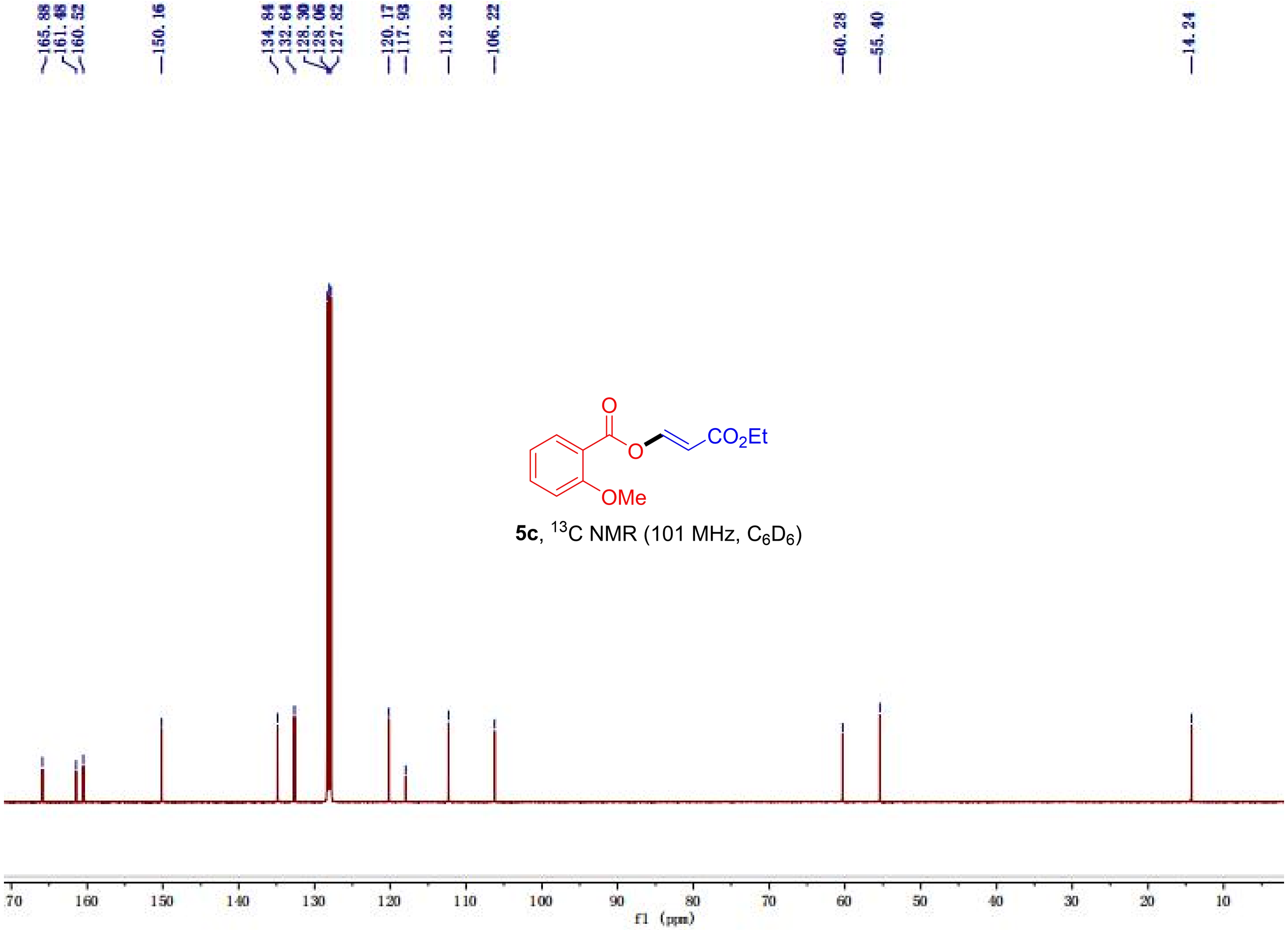
5b, ^{1}H NMR (400 MHz, C_6D_6)



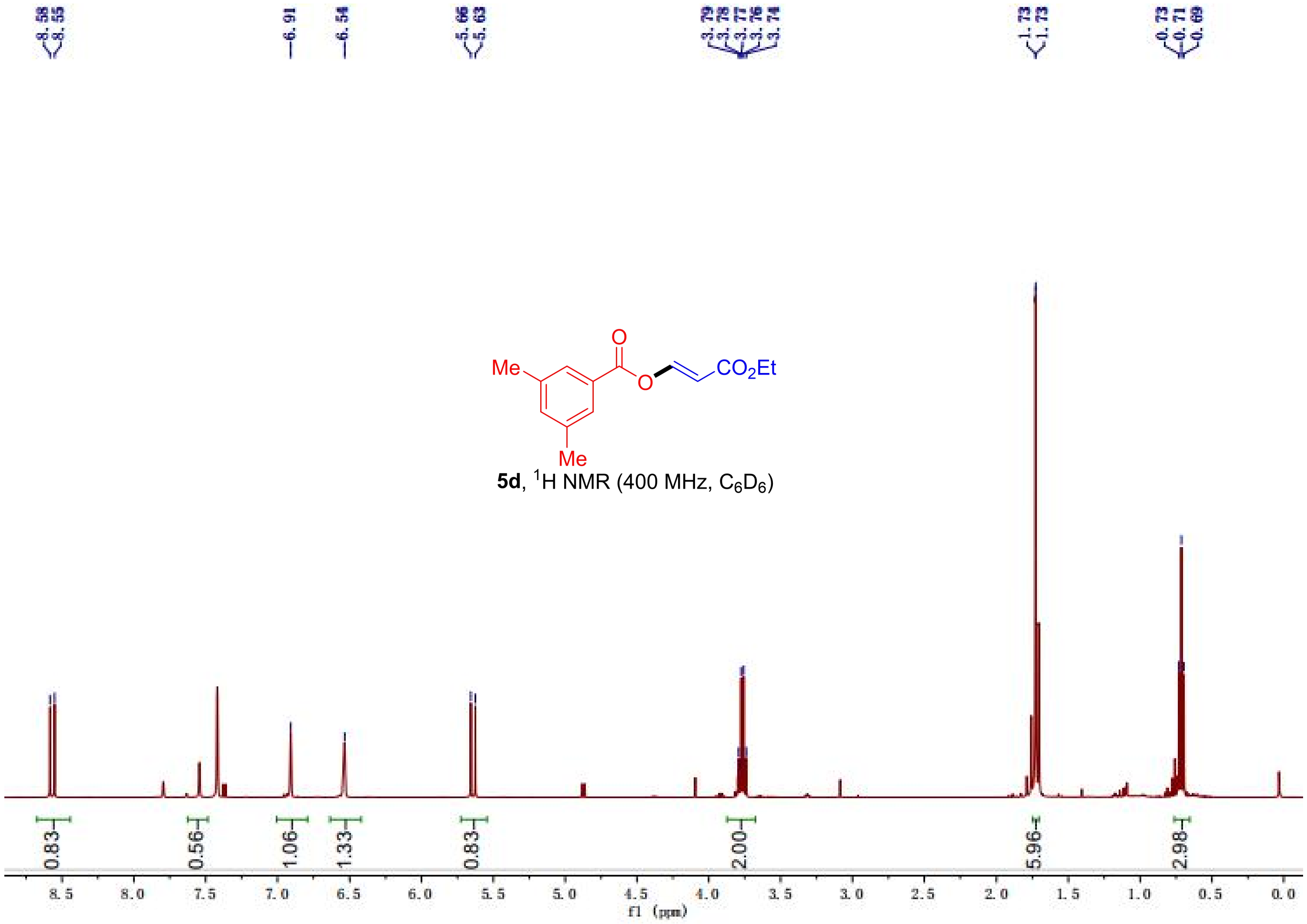
5b, ^{13}C NMR (101 MHz, C_6D_6)



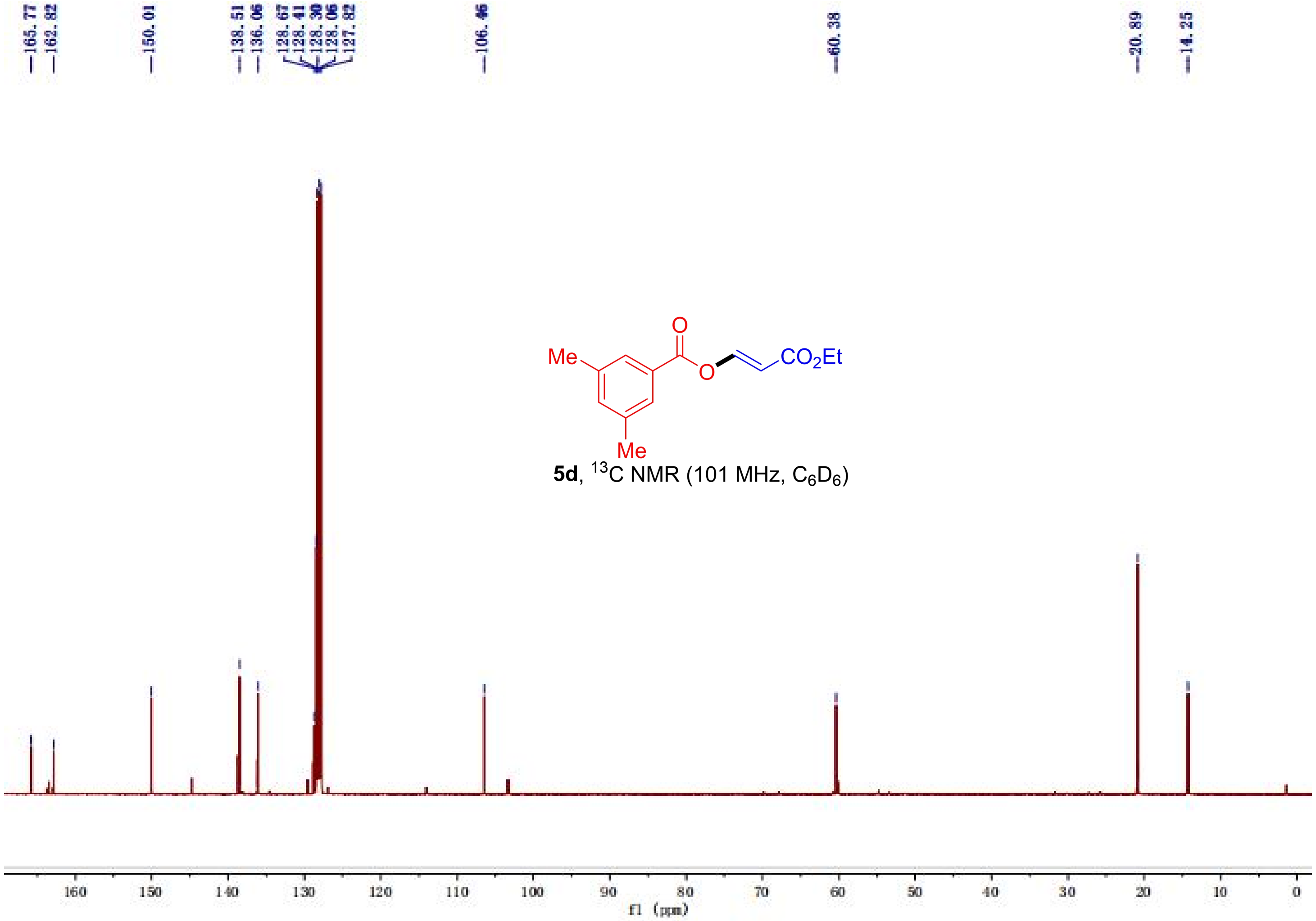
5c, ^{1}H NMR (400 MHz, C_6D_6)



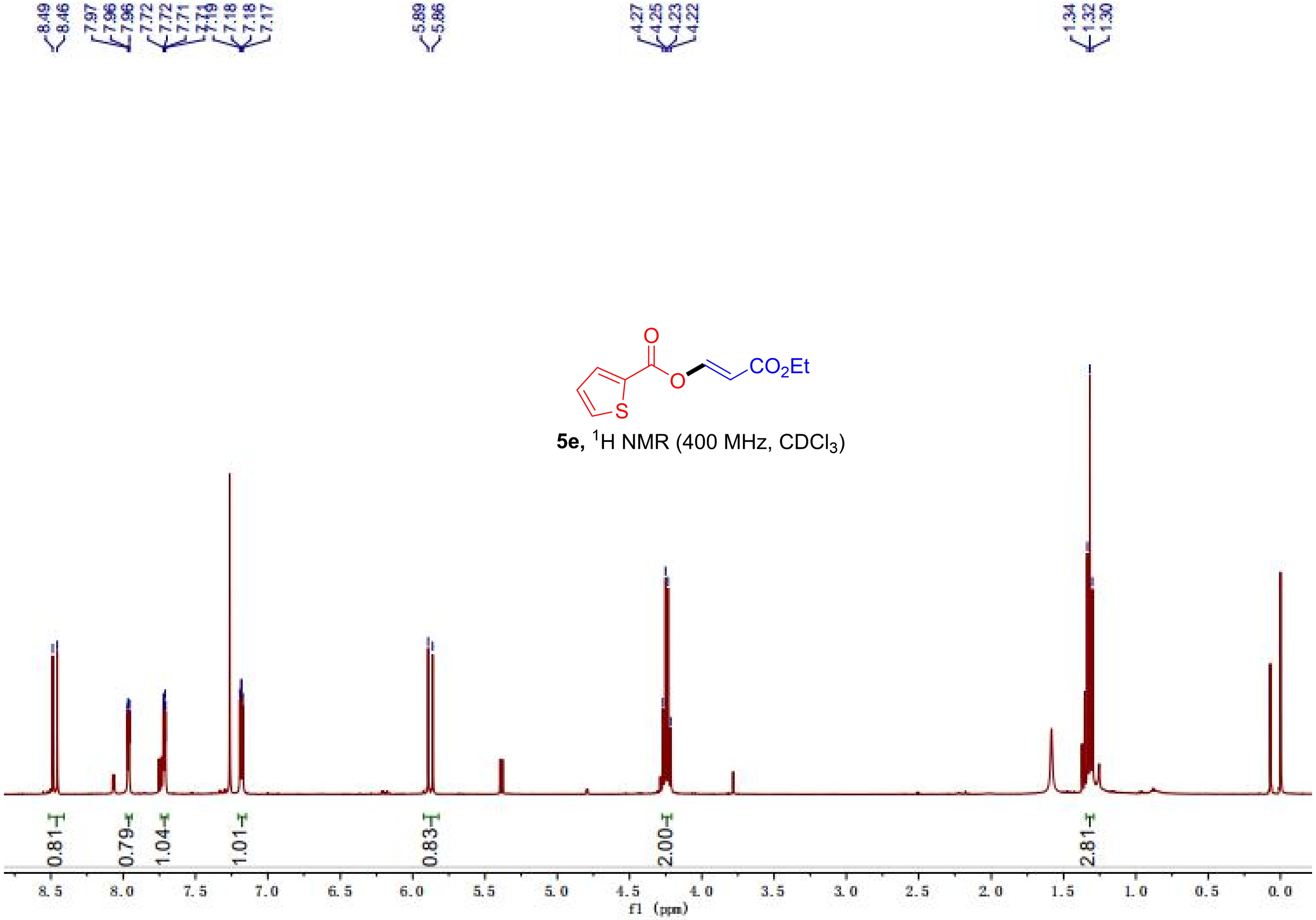
5c, ^{13}C NMR (101 MHz, C_6D_6)



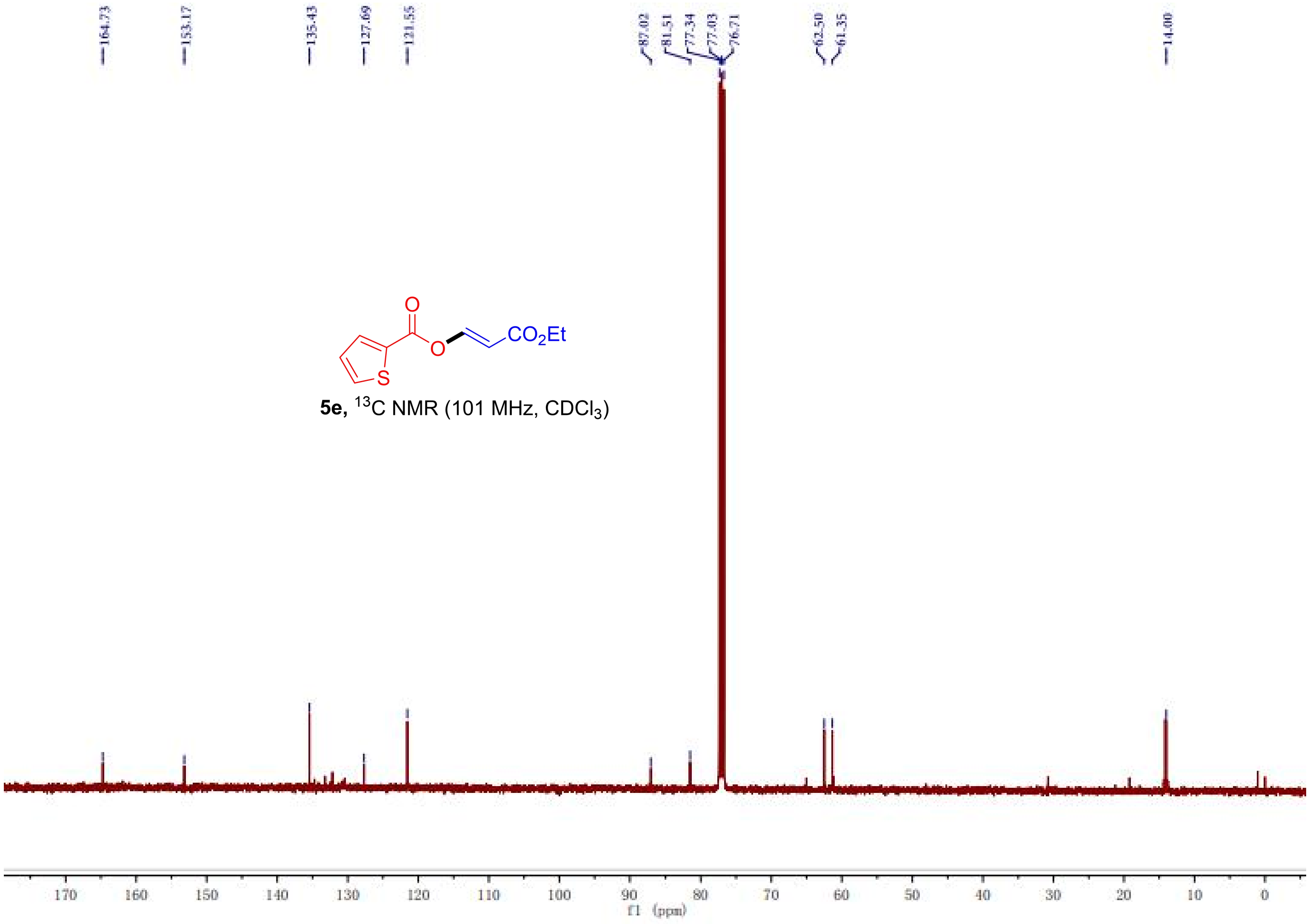
5d, ^{1}H NMR (400 MHz, C_6D_6)



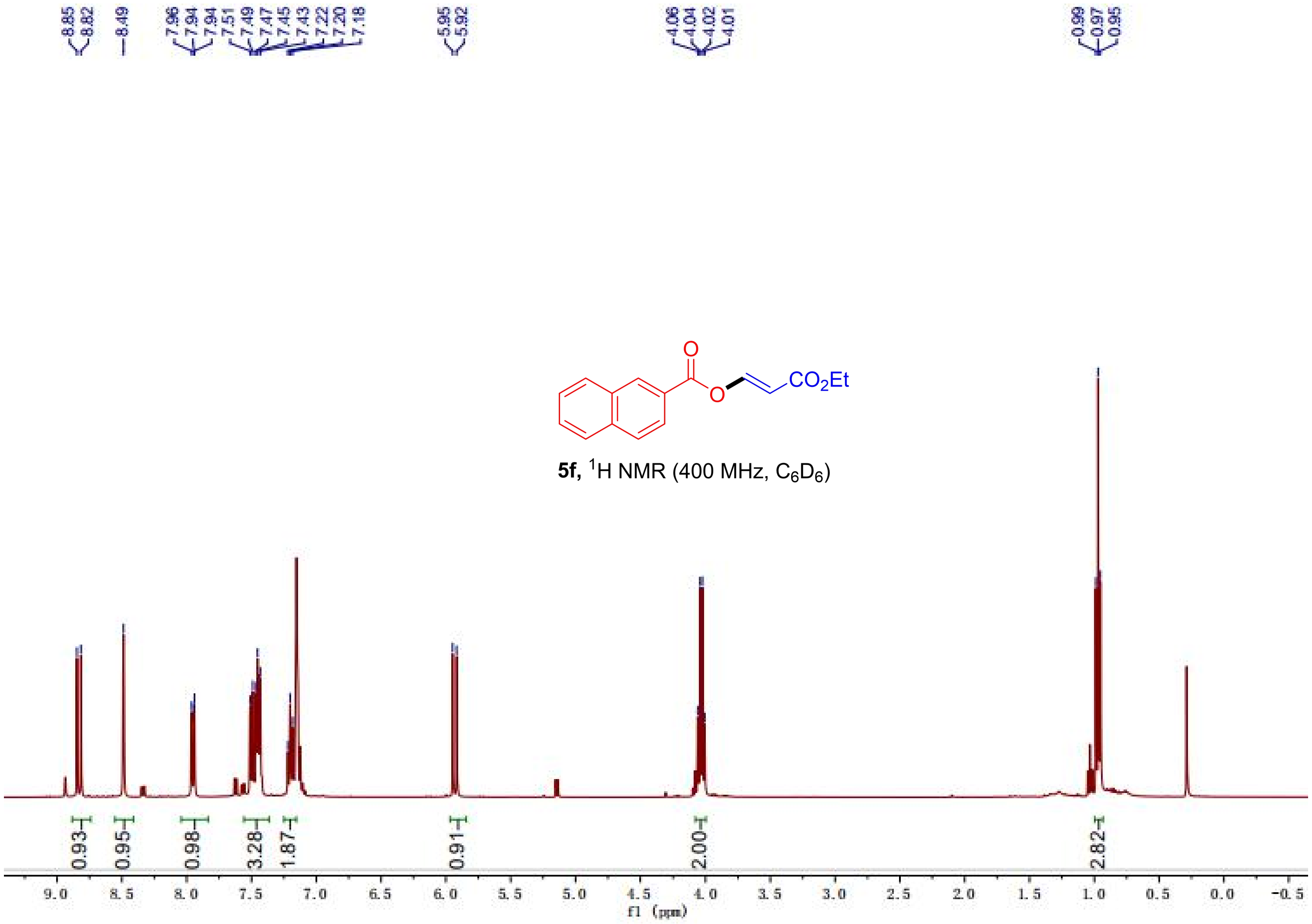
5d, ^{13}C NMR (101 MHz, C_6D_6)



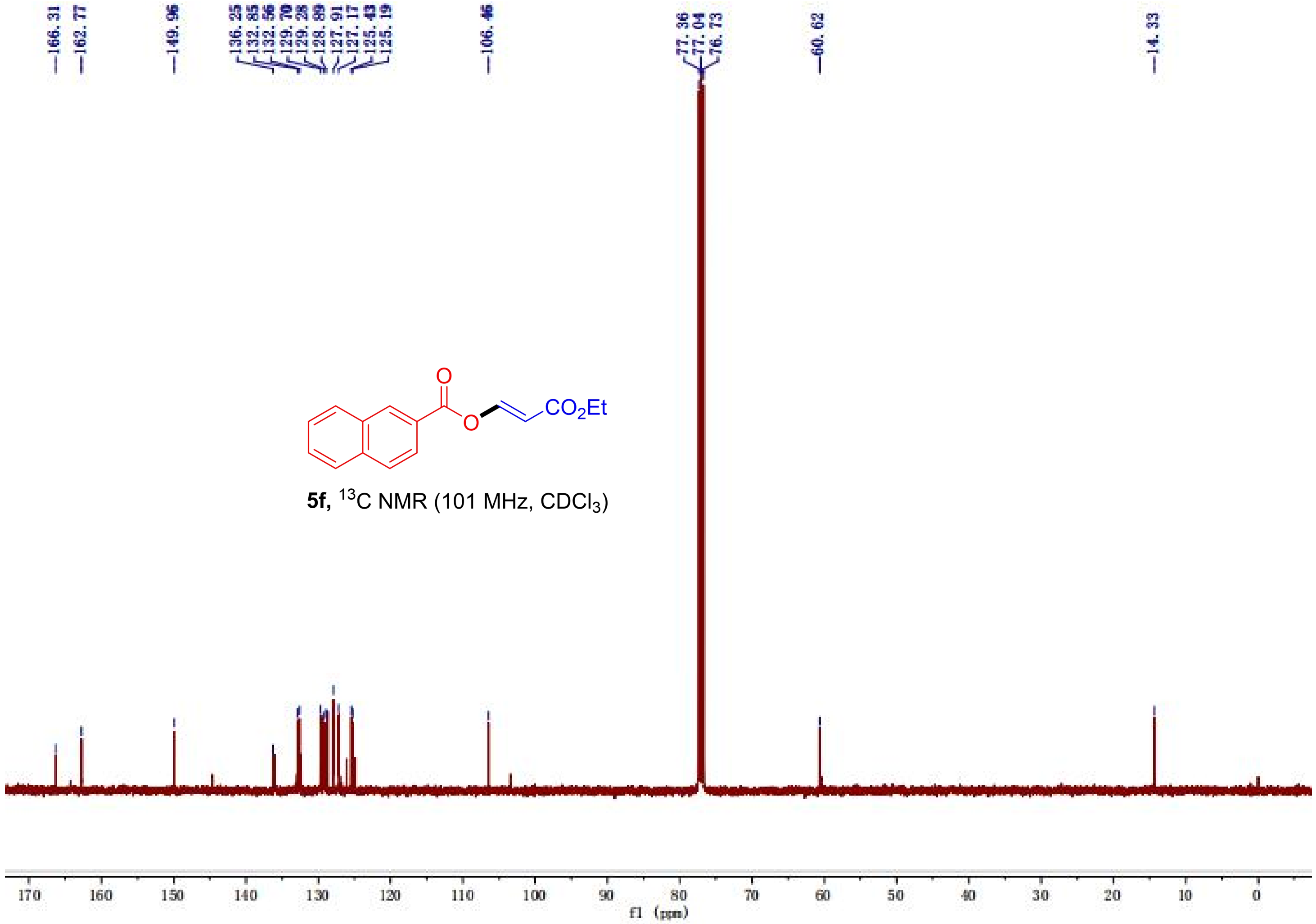
5e, ^{1}H NMR (400 MHz, $CDCl_3$)



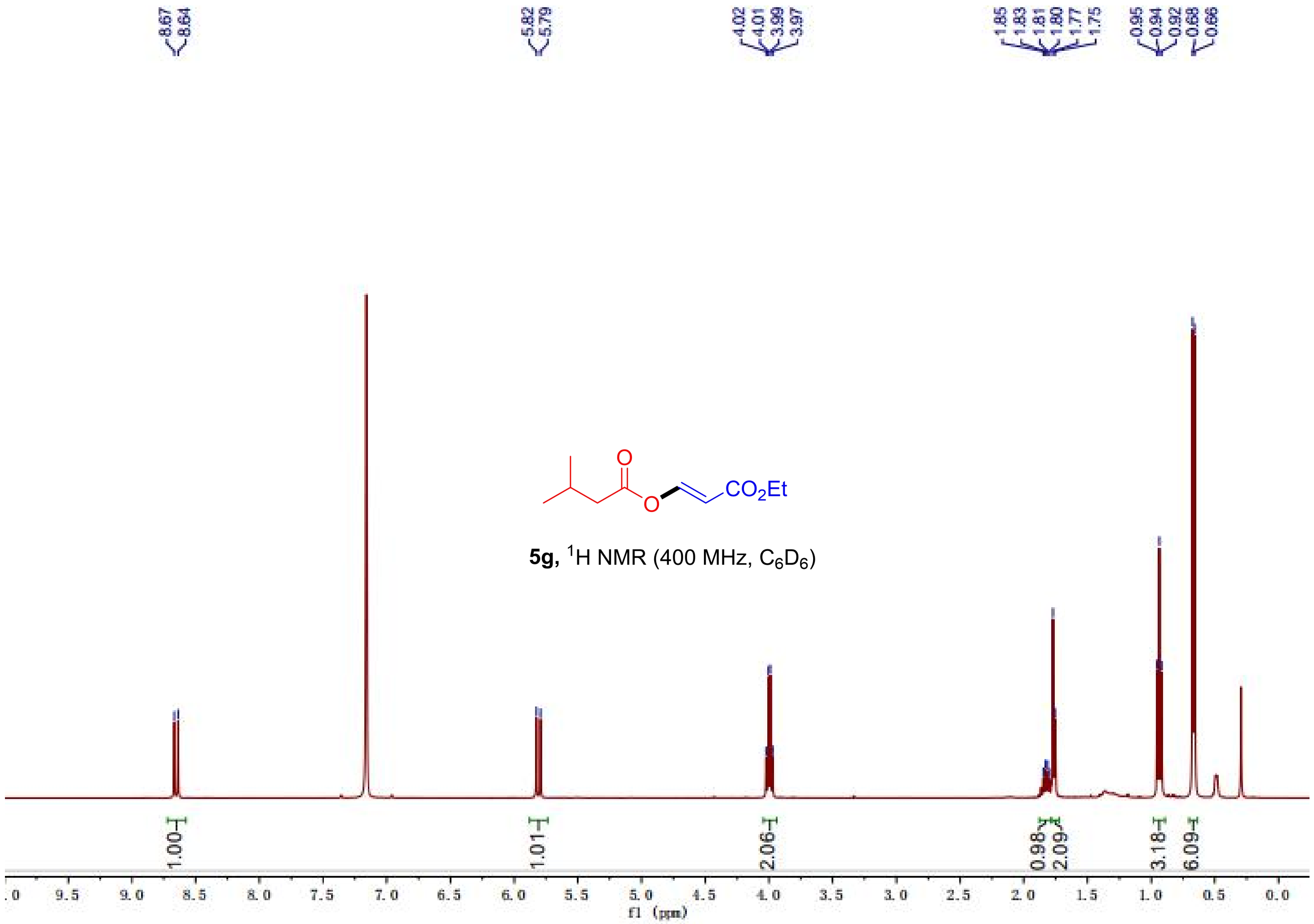
5e, ^{13}C NMR (101 MHz, CDCl$_3$)



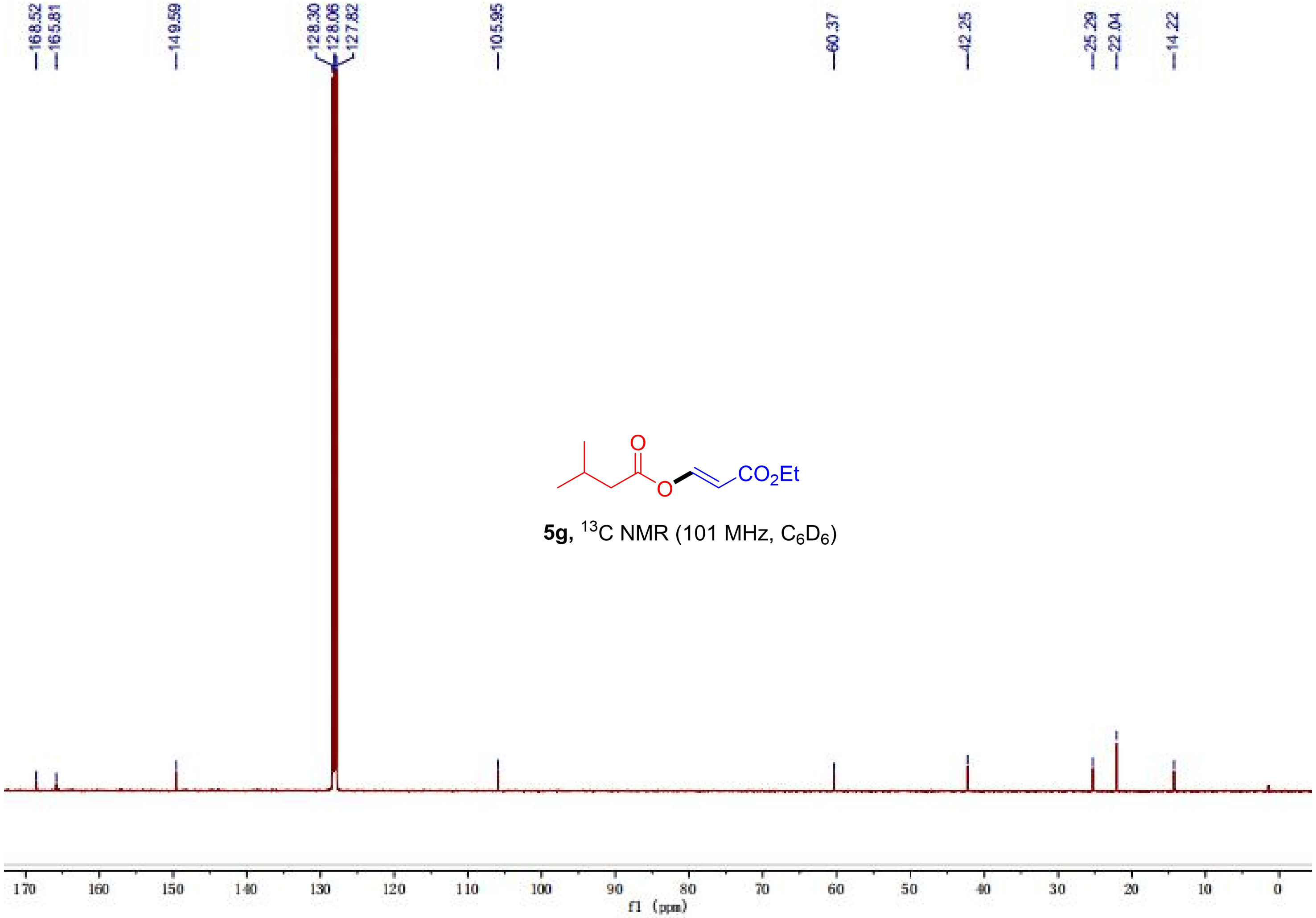
5f, ^{1}H NMR (400 MHz, C_6D_6)



5f, ^{13}C NMR (101 MHz, CDCl$_3$)



5g, ^{1}H NMR (400 MHz, C_6D_6)



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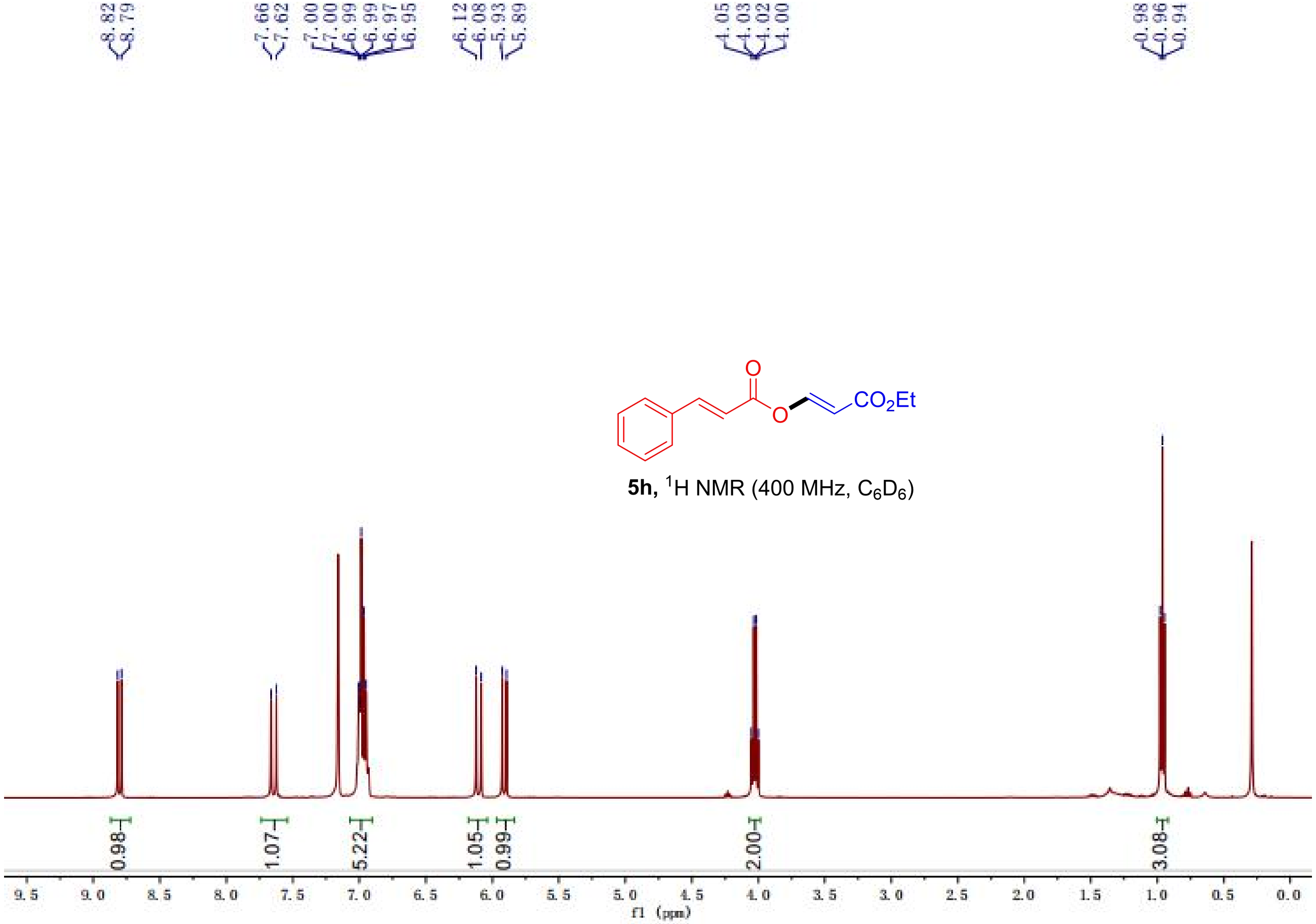

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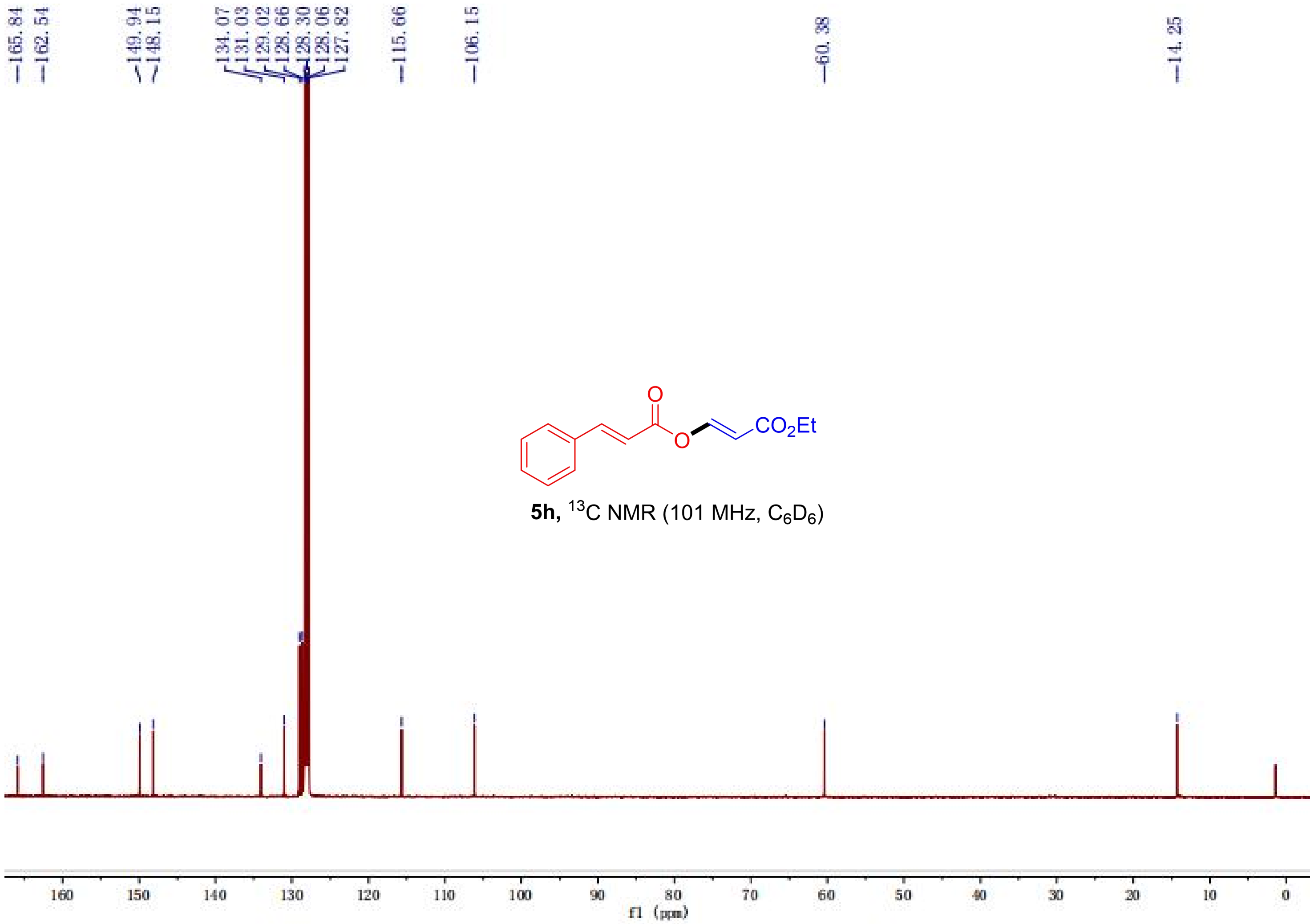

5h, ^{13}C NMR (101 MHz, C_6D_6)