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·Supporting Information

for

Palladium-Catalyzed Stereoselective Ring-opening Reaction of Aryl Cyclopropyl Ketones

Yan-Zuo Chen[a,b], Neng Wang[a] , Zong-Rui Hou[a], Xian-Li Zhou[a], Xiaohuan Li*[,a], Feng Gao*[,a], and Ting Jiang*[,b]

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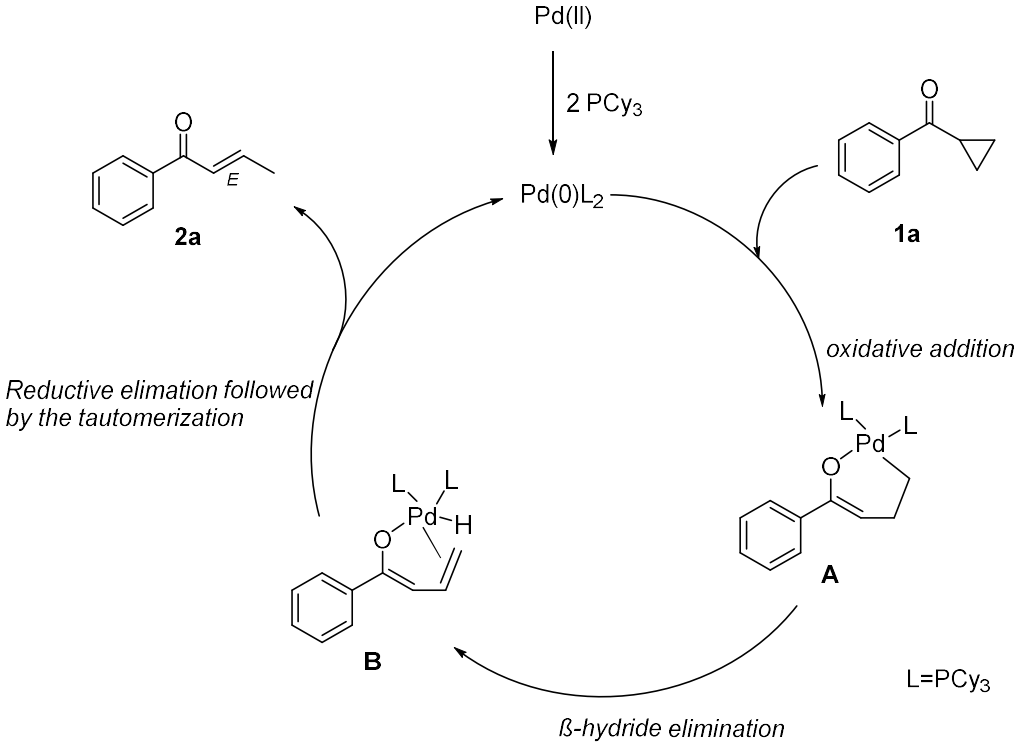
1. Plausible Mechanism

Based on the experimental results and relevant literature, a plausible mechanism was proposed (Scheme S1).[1] Initially, the $Pd^{(II)}$ catalyst is reduced by ligand to generate the active $Pd^{(0)}$ species. Then, oxidative addition of the phenyl cyclopropyl ketone to $Pd^{(0)}$ to afford the palladium-dihydropyran **A**. The *β*-elimination of **A** gives *π*-complex of Palladium-hydride **B**. Finally, reductive elimination followed by the tautomerization gives the (*E*)-1-phenylbut-2-en-1-one and regenerates the $Pd^{(0)}$ species. The tautomerization could happen with Pd assistance.[2] However, the mechanism of Pd assisted tautomerization has more than one possibility.[2b] Since we did not do any experiments to explore the mechanism of tautomerization, the processes were not shown in Scheme S1.

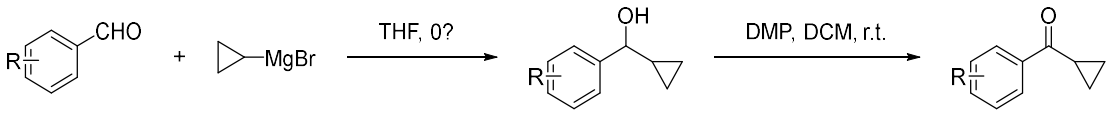


Scheme S1. Proposed catalytic cycle

2. Experimental Sections

2.1 Preparation of phenyl cyclopropyl ketones

The phenyl cyclopropyl ketones **1a-1o** was prepared according to the reported literature.[3]



2.1.1 Preparation of phenyl cyclopropyl(phenyl)methanols

To a 50 mL two-neck round bottom flask, cyclopropylmagnesium bromide (8.0 mmol, 2.0 equiv., 1.0 M in THF) was added. A solution of substituted benzaldehyde (4.0 mmol, 1.0 equiv.) in anhydrous THF (20 mL) was slowly added at 0 ℃ in 30 min. After stirring for 90 min, the reaction mixture was quenched by a saturated NH_4Cl aqueous solution. After extraction with ethyl acetate, the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to give cyclopropyl(phenyl)methanols in quantitative yield, which was used without further purification.

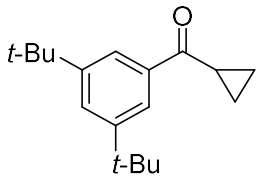
2.1.2 Preparation of phenyl cyclopropyl ketones

To a 100 mL round bottom flask, a solution of cyclopropyl(phenyl)methanols (4.0 mmol, 1.0 equiv.) in DCM (25 mL) were added. Dess-Martin Periodinane (4.8 mmol, 1.2 equiv.) was added in two batches. The reaction mixture was stirred for 15 min, and quenched by 10 mL saturated $NaHCO_3$ aqueous solution and 10mL saturated $Na_2S_2O_3$ aqueous solution, and stirred for another 2h. Then the reaction mixture was extracted with DCM. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica (Ethyl acetate/Petroleum ether = 1/20 to 1/10, v/v) to give the desired phenyl cyclopropyl ketones.

The compounds **1b**[4],**1e**[5], **1f**[4], **1g**[6], **1h**[7], **1l**[4], **1m**[4], **1n**[4], **1p**[8], **1s**[8], **1t**[9] **and 1u**[9] has been reported in the literatures, and was consistent with the literature data. Phenyl

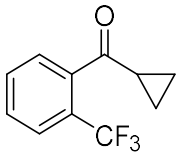
cyclopropyl ketones **1a** are commercially available from TCI, **1d and 1j** are commercially available from Energy Chemical.

cyclopropyl(3,5-di-tert-butylphenyl)methanone (1c)



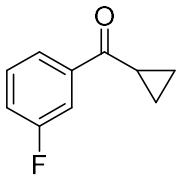
This compound was prepared by the general procedure described above and was obtained as white solid (360 mg, 54% for two steps). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.86 (d, J = 2.1 Hz, 2H), 7.65 (t, J = 2.2 Hz, 1H), 2.69 (m, 1H), 1.37 (s, 18H), 1.24 (p, J = 4.0 Hz, 2H), 1.04 (m, 2H); ^{13}C NMR (150 MHz, Chloroform-*d*) δ 201.5, 600.1, 137.8, 127.0, 122.2, 35.0, 31.4, 17.3, 11.6; HRMS (ESI) *m/z* calculated for $C_{18}H_{27}O$ $[M+H]^+$: 259.2056, found 259.2036.

cyclopropyl(2-(trifluoromethyl)phenyl)methanone (1i)



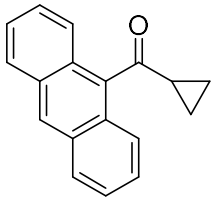
This compound was prepared by the general procedure described above and was obtained as yellow oil (576 mg, 67% for two steps). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.71 (d, J = 7.8 Hz, 1H), 7.61 (t, J = 7.5 Hz, 1H), 7.55 (t, J = 8.0 Hz, 2H), 2.31 (m 1H), 1.33 (p, J = 3.8 Hz, 2H), 1.12 (m, 2H); ^{13}C NMR (150 MHz, Chloroform-*d*) δ 204.7, 140.9 (q, $J_{C\text{-}F}$ = 3.0 Hz), 131.8, 129.9, 127.5, 127.0 (q, $J_{C\text{-}F}$ = 31.5 Hz), 126.6 (q, $J_{C\text{-}F}$ = 4.5 Hz), 123.6 (q, $J_{C\text{-}F}$ = 271.5 Hz), 21.8, 13.1; HRMS (ESI) *m/z* calculated for $C_{11}H_{10}F_3O$ $[M+H]^+$: 215.0678, found 215.0647.

cyclopropyl(3-fluorophenyl)methanone (1k)



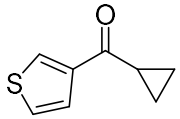
This compound was prepared by the general procedure described above and was obtained as yellow oil (420 mg, 64% for two steps). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.81 (d, J = 7.7, 1.4 Hz, 1H), 7.68 (ddd, J = 9.5, 2.7, 1.6 Hz, 1H), 7.45 (m, 1H), 7.29 – 7.23 (m, 1H), 2.62 (m, 1H), 1.28 – 1.24 (m, 2H), 1.07 (m , 2H); ^{13}C NMR (150 MHz, Chloroform-*d*) δ 199.4, 162.8 (d, J_{C-F} = 97.5 Hz), 140.1(d, J_{C-F} = 6.0 Hz), 130.1 (d, J_{C-F} = 6.0 Hz), 123.7 (d, J_{C-F} = 3.0 Hz), 119.7 (d, J_{C-F} = 21.0 Hz), 114.8 (d, J_{C-F} = 21.0 Hz) , 17.3, 11.9; HRMS (ESI) *m/z* calculated for $C_{10}H_{10}FO$ $[M+H]^+$: 165.0710, found 165.0719.

anthracen-9-yl(cyclopropyl)methanone (1o)



This compound was prepared by the general procedure described above and was obtained as yellow solid (632 mg, 64% for two steps). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.50 (s, 1H), 8.04 (d, J = 8.0 Hz, 2H), 8.00 (d, J = 8.4 Hz, 2H), 7.55 – 7.47 (m, 4H), 2.55 – 2.49 (m, 1H), 1.56 (m, 2H), 1.24 – 1.20 (m, 2H); ^{13}C NMR (150 MHz, Chloroform-*d*) δ 209.7, 136.9, 131.2, 128.7, 128.3, 127.3, 126.6, 125.5, 125.1, 25.1, 13.5; HRMS (ESI) *m/z* calculated for $C_{18}H_{15}O$ $[M+H]^+$: 247.1117, found 247.1127.

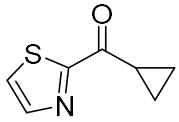
cyclopropyl(thiophen-3-yl)methanone (1q)



This compound was prepared by the general procedure described above and was obtained as colorless oil (525 mg, 69% for two steps). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.12 (dd, J = 3.0, 1.3 Hz, 1H), 7.59 (dd, J = 5.1, 1.4 Hz, 1H), 7.32 (dd, J = 5.1, 2.9

Hz, 1H), 2.51 (m, 1H), 1.21 (p, J = 4.6 Hz, 2H), 1.01 (m, 2H); ^{13}C NMR (150 MHz, Chloroform-*d*) δ 194.7, 143.1, 131.5, 127.0, 126.2, 18.3, 11.3; HRMS (ESI) *m/z* calculated for C_8H_9OS $[M+H]^+$: 153.0369, found 153.0385.

cyclopropyl(thiazol-2-yl)methanone (1r)

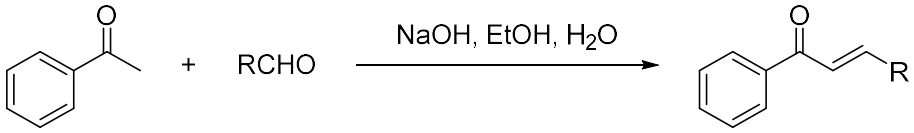


This compound was prepared by the general procedure described above and was obtained as yellow oil (444 mg, 58% for two steps). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.02 (d, J = 3.1 Hz, 1H), 7.67 (d, J = 3.0 Hz, 1H), 3.22 (m, 1H), 1.34 – 1.28 (m, 2H), 1.18 – 1.12 (m, 2H); ^{13}C NMR (150 MHz, Chloroform-*d*) δ 193.7, 167.8, 144.8, 125.9, 17.2, 12.7; HRMS (ESI) *m/z* calculated for C_7H_8NOS $[M+H]^+$: 154.0321, found 154.0338.

2.2 Preparation of cyclopropyl-substituted phenyl ketones

2.2.1 General procedure for the synthesis of chalcones

Method A:

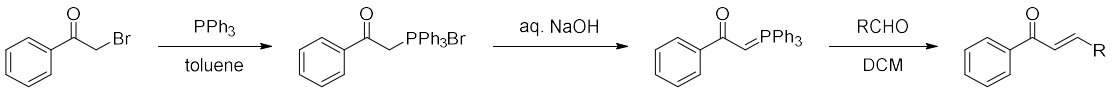


The preparation was according to a previously reported procedure. Acetophenone (5.00 mmol) was dissolved in ethanol (7.5 mL) in a 50 mL round-bottom flask and cooled to 0 ℃, a solution of sodium hydroxide (10.00 mmol) in water (3.0 mL) was added. Then the solution of ethanol (7.5 mL) containing benzaldehyde (5.00 mmol) was added drop wise with stirring over a period of 10 min. The reaction mixture was stirred at room temperature for 12 h until the starting material disappeared by monitored with TLC. Then water was added to the reaction mixture. The mixture was extracted with DCM (15 mL x 3). The combined organic layers were washed with saturated $NaHCO_3$ and

the brine, dried over Na_2SO_4 and evaporated to obtain chalcones derivatives with sufficient purity for the next step.

The chalcones derivatives without additionally noted were prepared according to method A from the reported literature, and was consistent with the literature data.

Method B:



A mixture of 2-bromo-1-phenylethan-1-one (5.00 mmol), triphenylphosphine (5.00 mmol) in toluene (20 mL) was stirred at room temperature for 16 h. The precipitate formed was filtered and washed with toluene. The solid was dissolved in water and the aqueous layer was treated with aqueous sodium hydroxide (10 mL, 1N). It was then extracted with DCM (2 x 20 mL). The combined organic layers were dried over sodium sulfate and to this, aldehyde (5.00 mmol) was added. The mixture was stirred at room temperature. The reaction was monitored by TLC. Upon completion, the dichloromethane was evaporated to get a solid residue. The solid residue was triturated using hexane (50 mL). The solid triphenylphosphine oxide was filtered off and the hexane layer was dried and evaporated to obtain chalcones derivatives with sufficient purity for the next step.

The alkyl-substituted chalcones derivatives were prepared according to method B from the reported literature, and was consistent with the literature data.

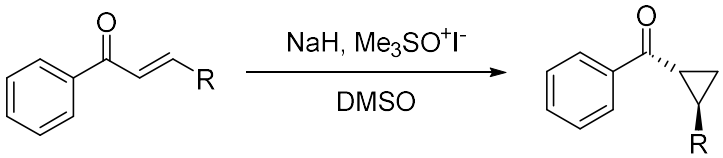
Gram-scale synthesis of compound 2a

To a 250 mL three-neck round-bottom flask equipped with a magnetic stirrer, condenser tube and argon inlet was charged $Pd(OAc)_2$ (0.4 mmol, 90 mg), PCy_3 (0.8 mmol, 224 mg), and 1,4-dioxane (80 mL). The mixture was stirred at room temperature for 1h, and then the phenyl cyclopropyl ketone (8.0 mmol, 1.168g) was added via syringe at room temperature. The mixture was heated to 100 ℃ for 18 h, and was cooled to room temperature. The reaction mixture was diluted with EtOAc, filtered with a celite pad,

and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel, eluting with EtOAc/PE (1:30 ~ 1:10, v/v), to afford the desired product as colorless oil (1.045g, 86%).

1.2.2 General procedure for the synthesis of substituted-cyclopropyl ketones.

The substituted-cyclopropyl ketone **3** was synthesized according the reported methods.[10]



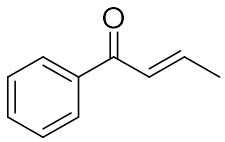
3

A flame-dried 25 mL flask was charged with solid NaH (60% in mineral oil, 96 mg, 2.40 mmol) and trimethylsulfoxonium iodide (528 mg, 2.40 mmol) and the flask was placed under an argon atmosphere. DMSO (10 mL) was then added dropwise to the flask. After hydrogen evolution ceased, the reaction mixture was stirred for an additional 15 min, during which time the solution became clear. Chalcone derivatives (2.00 mmol) was then added in one portion via syringe. The reaction mixture was allowed to stir for 2 h at room temperature. The reaction was then quenched by addition of water, and the mixture extracted three times with EtOAc. The combined organic layers were dried over Na_2SO_4, and volatiles were removed under reduced pressure to yield the crude product as a dark residue. The crude product was purified by flash column chromatography on silica gel, eluting with EtOAc/PE (1:30 ~ 1:10, v/v), to afford the desired products.

The compounds **3a**[10], **3b**[11], **3c**[11] and **3d**[11] have been reported in the literatures. The NMR data of them were consistent with the literature data.

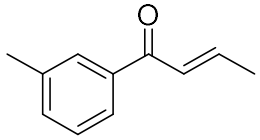
2.3 Characterization data for the products

(*E*)-1-phenylbut-2-en-1-one (2a)



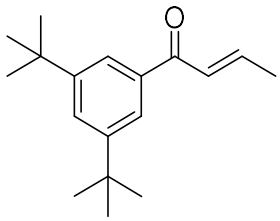
This compound was prepared by the general procedure described above and was obtained as yellow oil (78 mg, 89%). Rf (PE:Et_2O = 10:1): 0.61 ; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 7.6 Hz, 2H), 7.55(t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 6.9 Hz, 2H), 7.07 (dd, *J* = 13.6, 6.8 Hz, 1H), 6.91 (d, *J* = 15.3 Hz, 1H), 2.00 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (150 MHz, Chloroform-*d*) δ 190.8, 145.0, 138.0, 132.6, 128.5, 127.6, 18.6; HRMS (ESI) *m/z* calculated for $C_{10}H_{11}O$ $[M+H]^+$: 147.0804, found 147.0833.

(*E*)-1-(m-tolyl)but-2-en-1-one (2b)



This compound was prepared by the general procedure described above and was obtained as yellow oil (62 mg, 65%). Rf (PE:Et_2O = 10:1): 0.59 ; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.74 (s, 1H), 7.71 (dt, *J* = 6.6, 2.0 Hz, 1H), 7.38 – 7.33 (m, 2H), 7.06 (m, 1H), 6.90 (dd, *J* = 15.3, 1.7 Hz, 1H), 2.41 (s, 3H), 1.99 (dd, *J* = 6.9, 1.7 Hz, 3H); ^{13}C NMR (150 MHz, Chloroform-*d*) δ 191.0, 144.8, 138.3, 138.0, 133.4, 129.1, 128.4, 127.7, 125.7, 21.4, 18.6; HRMS (ESI) *m/z* calculated for $C_{11}H_{13}O$ $[M+H]^+$: 161.0961, found 161.0953.

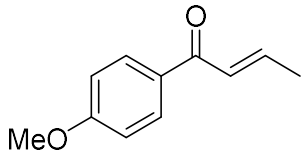
(*E*)-1-(3,5-di-tert-butylphenyl)but-2-en-1-one (2c)



This compound was prepared by the general procedure described above and was obtained as white solid (51 mg, 33%). Rf (PE:EtOAc = 10:1): 0.46 ; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.76 (s, 2H), 7.63 (s, 1H), 7.07 (m, 1H), 6.91 (d, *J* = 15.3 Hz,

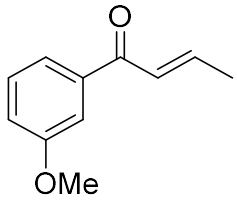
1H), 2.01 (d, *J* = 6.9 Hz, 3H), 1.36 (s, 18H); ^{13}C NMR (150 MHz, Chloroform-*d*) δ 191.6, 151.1, 144.5, 137.6, 128.0, 126.9, 122.7, 35.0, 31.4, 18.6; HRMS (ESI) *m/z* calculated for $C_{18}H_{27}O$ $[M+H]^+$: 259.2056, found 259.2067.

(*E*)-1-(4-methoxyphenyl)but-2-en-1-one (2d)



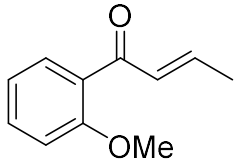
This compound was prepared by the general procedure described above and was obtained as yellow oil (89 mg, 84%). Rf (PE:Et_2O = 10:1): 0.57; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.9 Hz, 2H), 7.05 (m, 1H), 6.95 – 6.89 (m, 3H), 3.86 (s, 3H), 1.98 (dd, *J* = 6.9, 1.7 Hz, 3H); ^{13}C NMR (150 MHz, Chloroform-*d*) δ 189.0, 163.3, 143.9, 130.8, 130.7, 127.2, 113.7, 55.4, 18.5; HRMS (ESI) *m/z* calculated for $C_{11}H_{13}O_2$ $[M+H]^+$: 177.0910, found 177.0923.

(*E*)-1-(3-methoxyphenyl)but-2-en-1-one (2e)



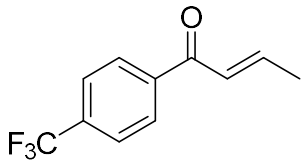
This compound was prepared by the general procedure described above and was obtained as yellow solid (87 mg, 82%). Rf (PE:Et_2O = 10:1): 0.56; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 7.6 Hz, 1H), 7.45 (s, 1H), 7.37 (t, *J* = 8.1 Hz, 1H), 7.13 – 7.02 (m, 2H), 6.89 (d, *J* = 15.4 Hz, 1H), 3.86 (s, 3H), 2.00 (d, *J* = 6.9Hz, 3H); ^{13}C NMR (150 MHz, Chloroform-*d*) δ 190.5, 159.8, 145.1, 139.3, 129.5, 127.6, 121.1, 119.2, 112.8, 55.4, 18.6; HRMS (ESI) *m/z* calculated for $C_{11}H_{13}O_2$ $[M+H]^+$: 177.0910, found 177.0931.

(*E*)-1-(2-methoxyphenyl)but-2-en-1-one (2f)



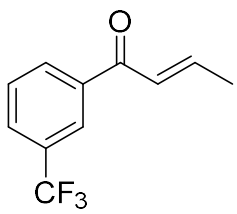
This compound was prepared by the general procedure described above and was obtained as yellow oil (49 mg, 46%). Rf (PE:Et_2O = 10:1): 0.59; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.47 (d, J = 7.5 Hz, 1H), 7.42 (t, J = 7.9 Hz, 1H), 6.99 (m, 1H), 6.95 (d, J = 8.4 Hz, 1H), 6.89 – 6.82 (m, 1H), 6.68 (d, J = 15.4 Hz, 1H), 3.85 (s, 3H), 1.93 (d, J = 6.9 Hz, 3H); ^{13}C NMR (150 MHz, Chloroform-*d*) δ 193.6, 157.8, 144.2, 132.4, 132.3, 130.0, 129.3, 120.5, 111.6, 55.7, 18.4; HRMS (ESI) *m/z* calculated for $C_{11}H_{13}O_2$ $[M+H]^+$: 177.0910, found 177.0917.

(*E*)-1-(4-(trifluoromethyl)phenyl)but-2-en-1-one (2g)



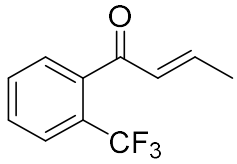
This compound was prepared by the general procedure described above and was obtained as yellow oil (96 mg, 75%). Rf (PE:Et_2O = 10:1): 0.55; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.00 (d, J = 8.5 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 7.11 (m, 1H), 6.87 (dd, J = 15.3, 1.8 Hz, 1H), 2.02 (dd, J = 6.9, 1.8 Hz, 3H); ^{13}C NMR (150 MHz, Chloroform-*d*) δ 189.9, 146.6, 140.8, 133.8 (q, $J_{C\text{-}F}$ = 33.0 Hz), 128.8, 127.3, 125.5 (q, $J_{C\text{-}F}$ = 4.5 Hz), 124.7 (q, $J_{C\text{-}F}$ = 270.0 Hz), 18.7; HRMS (ESI) *m/z* calculated for $C_{11}H_{10}F_3O$ $[M+H]^+$: 215.0648, found 215.0680.

(*E*)-1-(3-(trifluoromethyl)phenyl)but-2-en-1-one (2h)



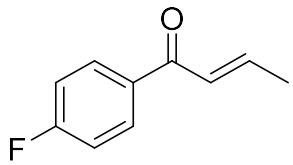
This compound was prepared by the general procedure described above and was obtained as yellow oil (93 mg, 72%). Rf (PE:Et_2O = 10:1): 0.57; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.16 (s, 1H), 8.10 (d, J = 7.9 Hz, 1H), 7.80 (d, J = 7.1 Hz, 1H), 7.60 (t, J = 7.8 Hz, 1H), 7.16 – 7.09 (m, 1H), 6.90 (dd, J = 15.3, 1.7 Hz, 1H), 2.03 (dd, J = 6.9, 1.6 Hz, 3H); ^{13}C NMR (150 MHz, Chloroform-*d*); δ 189.3, 146.6, 138.5, 131.6, 131.1 (q, J_{C-F} = 34.5 Hz), 129.2, 129.1 (q, J_{C-F} = 4.5 Hz), 126.9, 125.4 (q, J_{C-F} = 4.5 Hz), 123.8 (q, J_{C-F} = 270.0 Hz), 18.7, 1.0; ^{19}F NMR (565 MHz, Chloroform-*d*) δ -62.77; HRMS (ESI) *m/z* calculated for $C_{11}H_{10}F_3O$ $[M+H]^+$: 215.0648, found 215.0637.

(*E*)-1-(2-(trifluoromethyl)phenyl)but-2-en-1-one (2i)



This compound was prepared by the general procedure described above and was obtained as yellow oil (58 mg, 45%). Rf (PE:Et_2O = 10:1): 0.58; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.71 (d, J = 7.8 Hz, 1H), 7.57 (dt, J = 24.1, 7.5 Hz, 2H), 7.36 (d, J = 7.5 Hz, 1H), 6.61 – 6.52 (m, 1H), 6.43 (d, J = 15.8 Hz, 1H), 1.95 (d, J = 6.8 Hz, 3H); ^{13}C NMR (150 MHz, Chloroform-*d*) δ 195.3, 149.1, 138.8, 132.7, 131.4, 129.6, 127.8 (q, J_{C-F} =31.5 Hz), 127.4, 126.6 (q, J_{C-F} = 3.0 Hz), 126.3, 124.5, 123.6 (q, J_{C-F} = 273.0 Hz), 18.6; HRMS (ESI) *m/z* calculated for $C_{11}H_{10}F_3O$ $[M+H]^+$: 215.0648, found 215.0656.

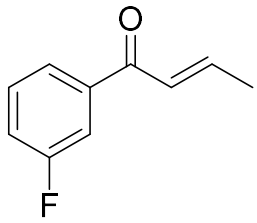
(*E*)-1-(4-fluorophenyl)but-2-en-1-one (2j)



This compound was prepared by the general procedure described above and was obtained as yellow oil (67 mg, 68%); Rf (PE:EtOAc = 10:1): 0.58; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.70 (d, J = 7.7 Hz, 1H), 7.60 (ddd, J = 9.4, 2.7, 1.5 Hz, 1H), 7.44 (td,

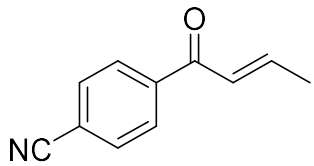
J = 7.9, 5.5 Hz, 1H), 7.27 – 7.22 (m, 1H), 7.10 (m, 1H), 6.86 (dd, *J* = 15.3, 1.7 Hz, 1H), 2.01 (dd, *J* = 6.9, 1.6 Hz, 3H); ^{13}C NMR (150 MHz, Chloroform-*d*) δ 189.0, 165.5 (d, $J_{C\text{-}F}$ = 240.0 Hz), 145.2, 134.2 (d, $J_{C\text{-}F}$ = 2.5 Hz), 131.0 (d, $J_{C\text{-}F}$ = 9.0 Hz), 127.1, 115.7, 115.5, 18.6; HRMS (ESI) *m/z* calculated for $C_{10}H_{10}FO$ $[M+H]^+$: 165.0710, found 165.0723.

(*E*)-1-(3-fluorophenyl)but-2-en-1-one (2k)



This compound was prepared by the general procedure described above and was obtained as yellow oil (71 mg, 72%); Rf (PE:EtOAc = 10:1): 0.58; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 6.5 Hz, 1H), 7.60 (d, *J* = 9.4 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.27 – 7.22 (m, 1H), 7.09 (m, 1H), 6.86 (d, *J* = 15.3 Hz, 1H), 2.01 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (150 MHz, Chloroform-*d*) δ 188.4, 161.8 (d, $J_{C\text{-}F}$ = 247.5 Hz), 145.0, 139.0 (d, $J_{C\text{-}F}$ = 6.0 Hz), 129.1 (d, $J_{C\text{-}F}$ = 6.0 Hz), 126.2, 123.2 (d, $J_{C\text{-}F}$ = 3.0 Hz), 118.6 (d, $J_{C\text{-}F}$ = 21.0 Hz), 114.2 (d, $J_{C\text{-}F}$ = 21.0 Hz), 17.6; HRMS (ESI) *m/z* calculated for $C_{10}H_{10}FO$ $[M+H]^+$: 165.0710, found 165.0736.

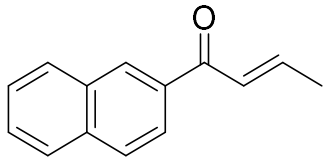
(*E*)-4-(but-2-enoyl)benzonitrile (2l)



This compound was prepared by the general procedure described above and was obtained as yellow solid (69 mg, 67%); Rf (PE:EtOAc = 10:1): 0.52; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.03 – 7.94 (m, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.11 (dq, *J* = 15.4, 6.9 Hz, 1H), 6.85 (dd, *J* = 15.3, 1.7 Hz, 1H), 2.02 (dd, *J* = 6.9, 1.6 Hz, 3H); ^{13}C NMR

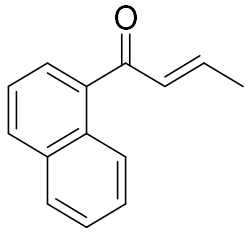
(150 MHz, Chloroform-*d*) δ 189.4, 147.2, 141.2, 132.4, 128.9, 127.0, 118.0, 115.8, 18.8; HRMS (ESI) *m/z* calculated for $C_{11}H_{10}NO$ $[M+H]^+$: 172.0757, found : 172.0776.

(*E*)-1-(naphthalen-2-yl)but-2-en-1-one (2m)



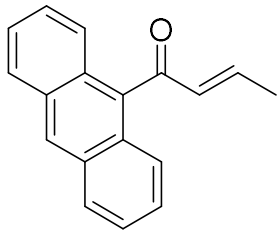
This compound was prepared by the general procedure described above and was obtained as yellow solid (75 mg, 64%); Rf (PE:EtOAc = 10:1): 0.48; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.44 (s, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.89 (dd, *J* = 15.7, 8.4 Hz, 2H), 7.57 (ddd, *J* = 25.7, 8.1, 6.9 Hz, 2H), 7.19 – 7.11 (m, 1H), 7.08 (dd, *J* = 15.3 Hz, 1H), 2.05 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, Chloroform-*d*) δ 190.5, 144.9, 135.4, 135.2, 132.6, 129.9, 129.5, 128.4, 128.3, 127.8, 127.5, 126.7, 124.5, 18.6; HRMS (ESI) *m/z* calculated for $C_{14}H_{13}O$ $[M+H]^+$: 197.0961, found 197.0989.

(*E*)-1-(naphthalen-1-yl)but-2-en-1-one (2n)



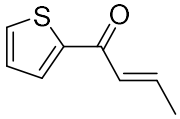
This compound was prepared by the general procedure described above and was obtained as yellow solid (76 mg, 65%); Rf (PE:EtOAc = 10:1): 0.47; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.24 (d, *J* = 8.1 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 1H), 7.91 – 7.86 (m, 1H), 7.65 (d, *J* = 7.0 Hz, 1H), 7.57 – 7.47 (m, 3H), 6.89 – 6.82 (m, 1H), 6.68 (d, *J* = 15.6 Hz, 1H), 1.97 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (150 MHz, Chloroform-*d*) δ 196.1, 146.9, 136.9, 133.8, 132.8, 131.3, 130.5, 128.4, 127.3, 126.9, 126.4, 125.7, 124.4, 18.5; HRMS (ESI) *m/z* calculated for $C_{14}H_{13}O$ $[M+H]^+$: 197.0961, found 197.0957.

(*E*)-1-(anthracen-9-yl)but-2-en-1-one (2o)



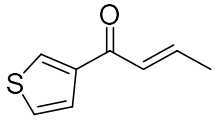
This compound was prepared by the general procedure described above and was obtained as yellow solid (68 mg, 46%); Rf (PE:EtOAc = 10:1): 0.41; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.49 (s, 1H), 8.03 (dd, *J* = 6.2, 3.5 Hz, 2H), 7.86 – 7.81 (m, 2H), 7.50 – 7.44 (m, 4H), 6.69 (dd, *J* = 15.8, 1.1 Hz, 1H), 6.51 – 6.43 (m, 1H), 1.87 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (150 MHz, Chloroform-*d*) δ 200.5, 149.8, 135.0, 134.6, 131.1, 128.6, 128.3, 128.1, 126.4, 125.4, 125.3, 18.6; HRMS (ESI) *m/z* calculated for $C_{18}H_{15}O$ $[M+H]^+$: 247.1117, found $[M+H]^+$: 247.1123.

(*E*)-1-(thiophen-2-yl)but-2-en-1-one (2p)



This compound was prepared by the general procedure described above and was obtained as yellow oil (79 mg, 87%); Rf (PE:EtOAc = 10:1): 0.57; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.64 (dd, *J* = 4.9, 1.2 Hz, 1H), 7.18 – 7.07 (m, 2H), 6.82 (dd, *J* = 15.2, 1.7 Hz, 1H), 1.99 (dd, *J* = 6.9, 1.8 Hz, 3H); ^{13}C NMR (150 MHz, Chloroform-*d*) δ 182.2, 145.1, 144.3, 133.6, 131.8, 128.1, 126.9, 77.4, 77.0, 76.7, 18.5; HRMS (ESI) *m/z* calculated for C_8H_9OS $[M+H]^+$: 153.0369, found 153.0375.

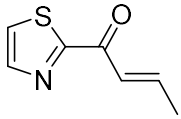
(*E*)-1-(thiophen-3-yl)but-2-en-1-one (2q)



This compound was prepared by the general procedure described above and was obtained as yellow oil (78 mg, 85%); Rf (PE:EtOAc = 10:1): 0.56; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.05 (s, 1H), 7.59 (d, *J* = 5.1 Hz, 1H), 7.33 (s, 1H), 7.09 (m, 1H), 6.80

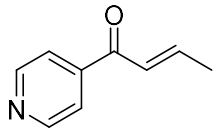
(d, J = 15.3 Hz, 1H), 1.98 (d, J = 6.9 Hz, 3H); ^{13}C NMR (150 MHz, Chloroform-*d*) δ 184.1, 144.2, 142.7, 131.9, 131.8, 128.1, 127.5, 126.3, 77.3, 77.0, 76.7, 18.5; HRMS (ESI) *m/z* calculated for C_8H_9OS $[M+H]^+$: 153.0369, found 153.0359.

(*E*)-1-(thiazol-2-yl)but-2-en-1-one (2r)



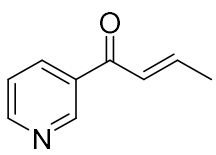
This compound was prepared by the general procedure described above and was obtained as yellow oil (73 mg, 80%); Rf (PE:EtOAc = 10:1): 0.54; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.02 (s, 1H), 7.66 (s, 1H), 7.36 (m, 1H), 7.30 (d, J = 15.5 Hz, 1H), 2.04 (d, J = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, Chloroform-*d*) δ 181.6, 168.4, 146.9, 144.7, 126.2, 126.1, 77.3, 77.0, 76.8, 18.8; HRMS (ESI) *m/z* calculated for C_7H_8NOS $[M+H]^+$: 154.0321, found 154.0356.

(*E*)-1-(pyridin-4-yl)but-2-en-1-one (2s)



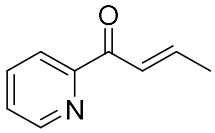
This compound was prepared by the general procedure described above and was obtained as yellow oil (76 mg, 86%); Rf (PE:EtOAc = 10:1): 0.62; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.77 (m, 2H), 7.72 – 7.61 (m, 2H), 7.14 – 7.04 (m, 1H), 6.83 – 6.76 (m, 1H), 2.01 (dd, J = 6.9, 1.6 Hz, 3H); ^{13}C NMR (150 MHz, Chloroform-*d*) δ 190.1, 150.7, 147.6, 144.2, 127.1, 121.6, 77.4, 77.1, 76.7, 18.8; HRMS (ESI) *m/z* calculated for $C_9H_{10}NO$ $[M+H]^+$: 148.0757, found 148.0772.

(*E*)-1-(pyridin-3-yl)but-2-en-1-one (2t)



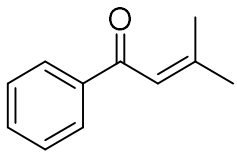
This compound was prepared by the general procedure described above and was obtained as yellow oil (75 mg, 85%); Rf (PE:EtOAc = 10:1): 0.59; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.11 (d, *J* = 1.4 Hz, 1H), 8.75 (dd, *J* = 4.8, 1.8 Hz, 1H), 8.18 (dt, *J* = 8.0, 1.9 Hz, 1H), 7.41 (ddd, *J* = 8.0, 4.8, 1.0 Hz, 1H), 7.11 (m, 1H), 6.86 (dq, *J* = 15.4, 1.6 Hz, 1H), 2.02 (dd, *J* = 6.9, 1.6 Hz, 3H); ^{13}C NMR (150 MHz, Chloroform-*d*) δ 189.4, 153.0, 149.8, 146.6, 135.9, 133.2, 127.2, 123.6, 77.4, 77.0, 76.7, 18.7; HRMS (ESI) *m/z* calculated for $C_9H_{10}NO$ $[M+H]^+$: 148.0757, found 148.0763.

(*E*)-1-(pyridin-2-yl)but-2-en-1-one (2u)



This compound was prepared by the general procedure described above and was obtained as yellow oil (73 mg, 83%); Rf (PE:EtOAc = 10:1): 0.64; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.69 (ddd, *J* = 4.7, 1.8, 0.9 Hz, 1H), 8.10 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.83 (td, *J* = 7.7, 1.7 Hz, 1H), 7.59 (dd, *J* = 15.6, 1.7 Hz, 1H), 7.45 (ddd, *J* = 7.5, 4.7, 1.3 Hz, 1H), 7.28 – 7.20 (m, 1H), 2.02 (dd, *J* = 6.9, 1.7 Hz, 3H); ^{13}C NMR (150 MHz, Chloroform-*d*) δ 189.4, 154.2, 148.8, 145.5, 145.5, 137.0, 126.7, 126.2, 122.9, 77.2, 77.0, 76.8, 18.7; HRMS (ESI) *m/z* calculated for $C_9H_{10}NO$ $[M+H]^+$: 148.0757, found 148.0781.

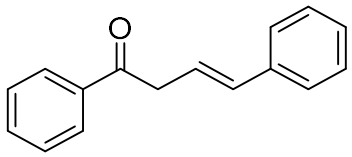
(*E*)-3-methyl-1-phenylbut-2-en-1-one (4a)



This compound was prepared by the general procedure described above and was obtained as yellow oil (22 mg, 23%); Rf (PE:EtOAc = 10:1): 0.61; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.91 (m, 2H), 7.53 – 7.48 (m, 2H), 7.46 – 7.42 (m, 2H), 6.75 (p, *J* = 1.4 Hz, 1H), 2.21 (d, *J* = 1.4 Hz, 3H), 2.02 (d, *J* = 1.4 Hz, 3H); ^{13}C NMR (100

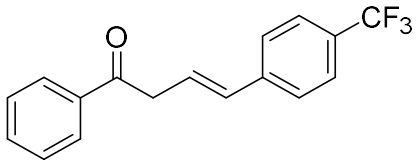
MHz, Chloroform-*d*) δ 191.6, 139.3, 132.3, 128.4, 128.2, 128.1, 121.2, 27.9, 21.1; HRMS (ESI) *m/z* calculated for $C_{11}H_{13}O$ $[M+H]^+$: 161.0961, found 161.0979.

(*E*)-1,4-diphenylbut-3-en-1-one (4b)



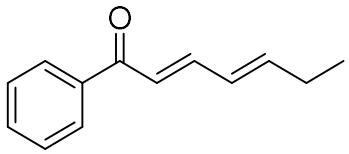
This compound was prepared by the general procedure described above and was obtained as white solid (60 mg, 45%); Rf (PE:EtOAc = 10:1): 0.56; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.03 – 7.99 (m, 2H), 7.60 – 7.56 (m, 1H), 7.51 – 7.47 (m, 2H), 7.40 – 7.37 (m, 2H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 6.58 – 6.53 (m, 1H), 6.48 (dt, *J* = 16.0, 6.7 Hz, 1H), 3.92 (dd, *J* = 6.7, 1.3 Hz, 2H); ^{13}C NMR (150 MHz, Chloroform-*d*) δ 198.0, 137.0, 136.6, 133.6, 133.2, 128.7, 128.5, 128.4, 127.5, 126.3, 122.6, 42.7; HRMS (ESI) *m/z* calculated for $C_{16}H_{15}O$ $[M+H]^+$: 223.1117, found 223.1131.

(*E*)-1-phenyl-4-(4-(trifluoromethyl)phenyl)but-3-en-1-one (4c)



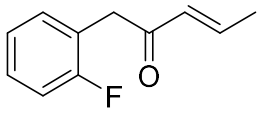
This compound was prepared by the general procedure described above and was obtained as yellow solid (66 mg, 38%); Rf (PE:EtOAc = 10:1): 0.54; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.01 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.52 – 7.46 (m, 4H), 6.64 – 6.55 (m, 2H), 3.95 (d, *J* = 5.5 Hz, 2H); ^{13}C NMR (150 MHz, Chloroform-*d*) δ 197.5, 140.4, 136.5, 133.4, 132.3, 129.4 (q, J_{C-F} = 31.5 Hz), 128.8, 128.3, 126.4, 126.0 (q, J_{C-F} = 270.0 Hz), 125.5 (q, J_{C-F} = 4.5 Hz), 42.5; HRMS (ESI) *m/z* calculated for $C_{17}H_{14}F_3O$ $[M+H]^+$: 291.0991, found 291.0987.

(2*E*,4*E*)-1-phenylhepta-2,4-dien-1-one (4d)



This compound was prepared by the general procedure described above and was obtained as white solid (27 mg, 24%); Rf (PE:EtOAc = 10:1): 0.46; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.94 (dd, J = 8.3, 1.4 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.44 – 7.39 (m, 1H), 6.89 (d, J = 14.9 Hz, 1H), 6.35 – 6.27 (m, 2H), 2.25 (m, 2H), 1.08 (t, J = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, Chloroform-*d*) δ 207.4, 191.0, 147.8, 145.5, 138.3, 132.5, 128.5, 128.4, 128.2, 123.6, 26.2, 12.9; HRMS (ESI) *m/z* calculated for $C_{13}H_{15}O$ $[M+H]^+$: 187.1117, found 187.1131.

(*E*)-1-(2-fluorophenyl)pent-3-en-2-one (4e)



This compound was prepared by the general procedure described above and was obtained as yellow solid (66 mg, 62%); Rf (PE:EtOAc = 10:1) : 0.48; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.26 – 7.21 (m, 1H), 7.20 (t, J = 7.5 Hz, 1H), 7.12 – 7.03 (m, 2H), 7.01 – 6.93 (m, 1H), 6.20 (dd, J = 15.7, 2.1 Hz, 1H), 3.86 (s, 2H), 1.90 (dd, J = 6.9, 2.4 Hz, 3H); ^{13}C NMR (150 MHz, Chloroform-*d*) δ 196.1, 161.0 (d, $J_{C\text{-}F}$ = 244.5 Hz), 143.8, 131.6 (d, $J_{C\text{-}F}$ = 4.5 Hz), 130.8, 128.8 (d, $J_{C\text{-}F}$ = 9.0 Hz), 124.2 (d, $J_{C\text{-}F}$ = 3.0 Hz), 121.9 (d, $J_{C\text{-}F}$ = 16.5 Hz), 115.4 (d, $J_{C\text{-}F}$ = 21.0 Hz), 40.3(d, $J_{C\text{-}F}$ = 2.7 Hz), 18.3; HRMS (ESI) *m/z* calculated for $C_{11}H_{12}FO$ $[M+H]^+$: 179.0867, found 179.0884.

3. Reference

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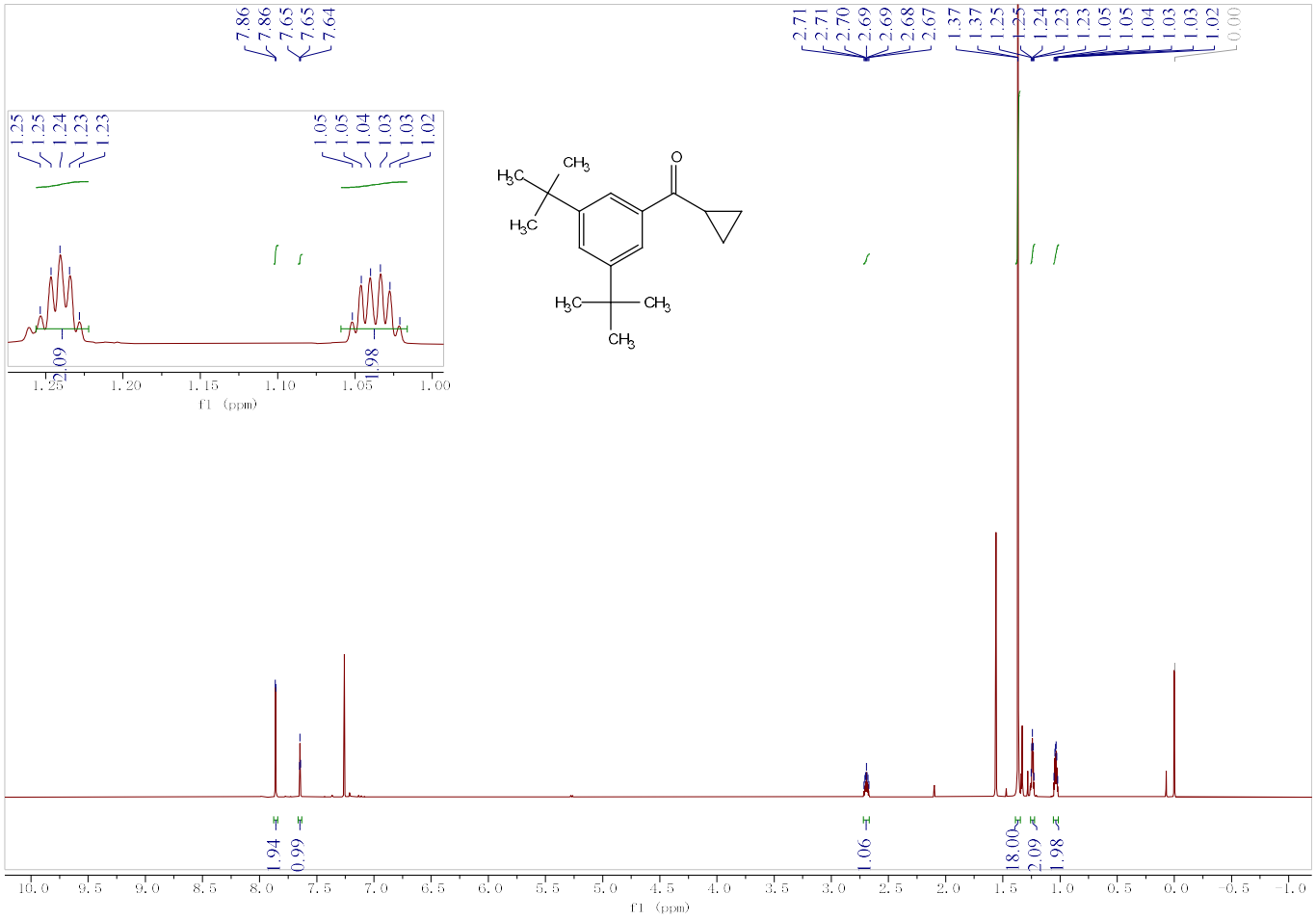
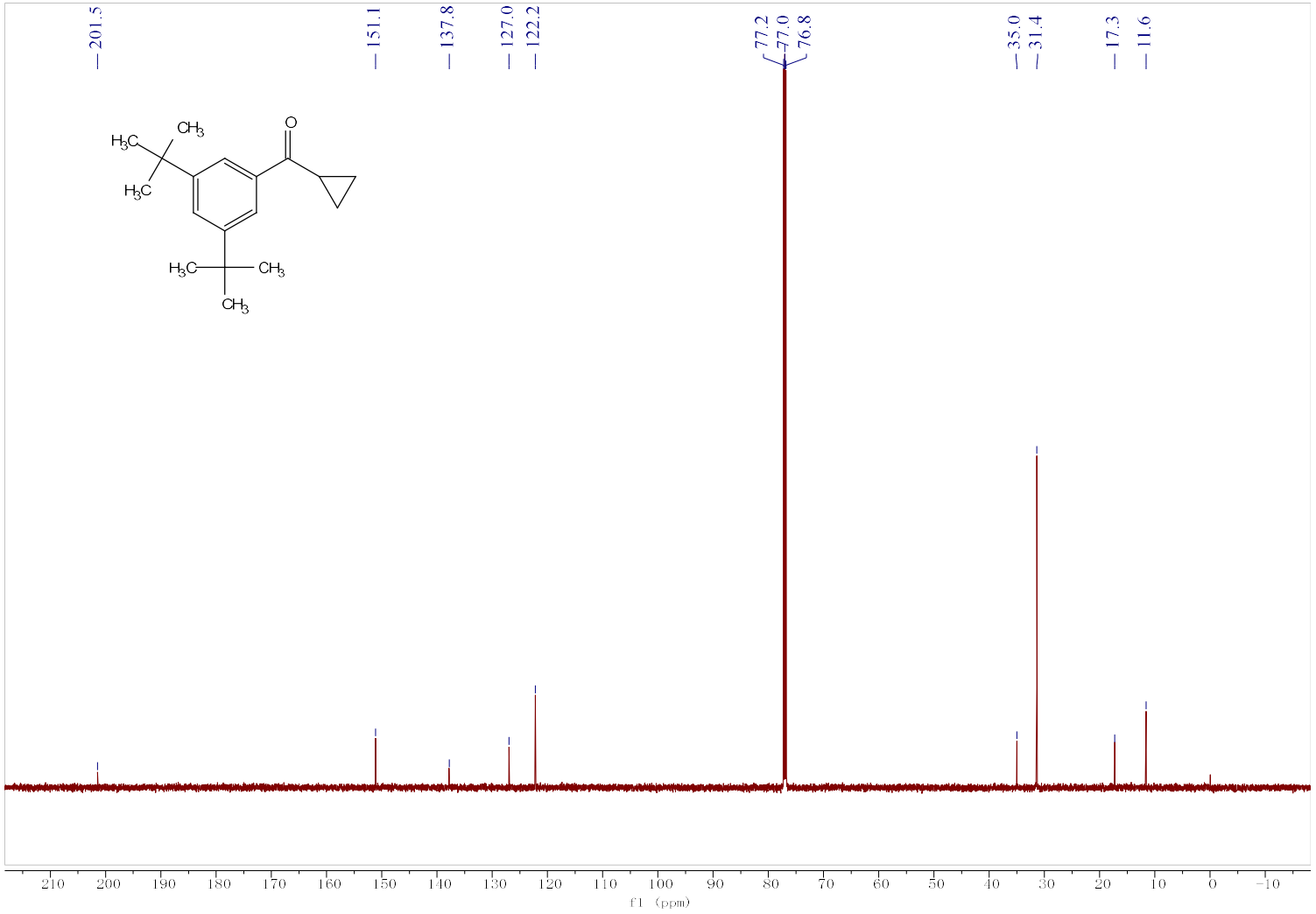
4. Copy of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra

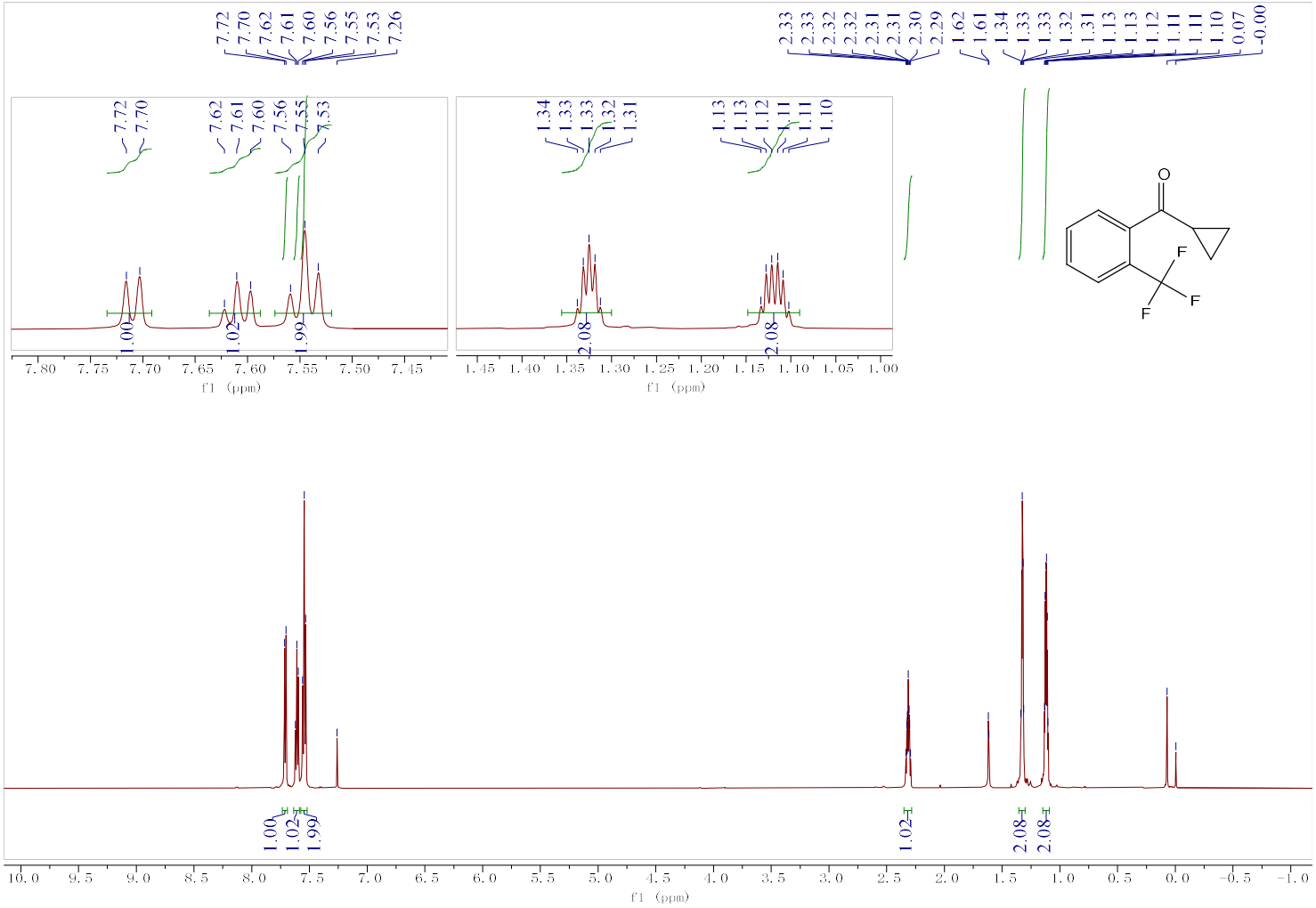
^{1}H NMR Spectrum of 1c (600 MHz, Chloroform-*d*)



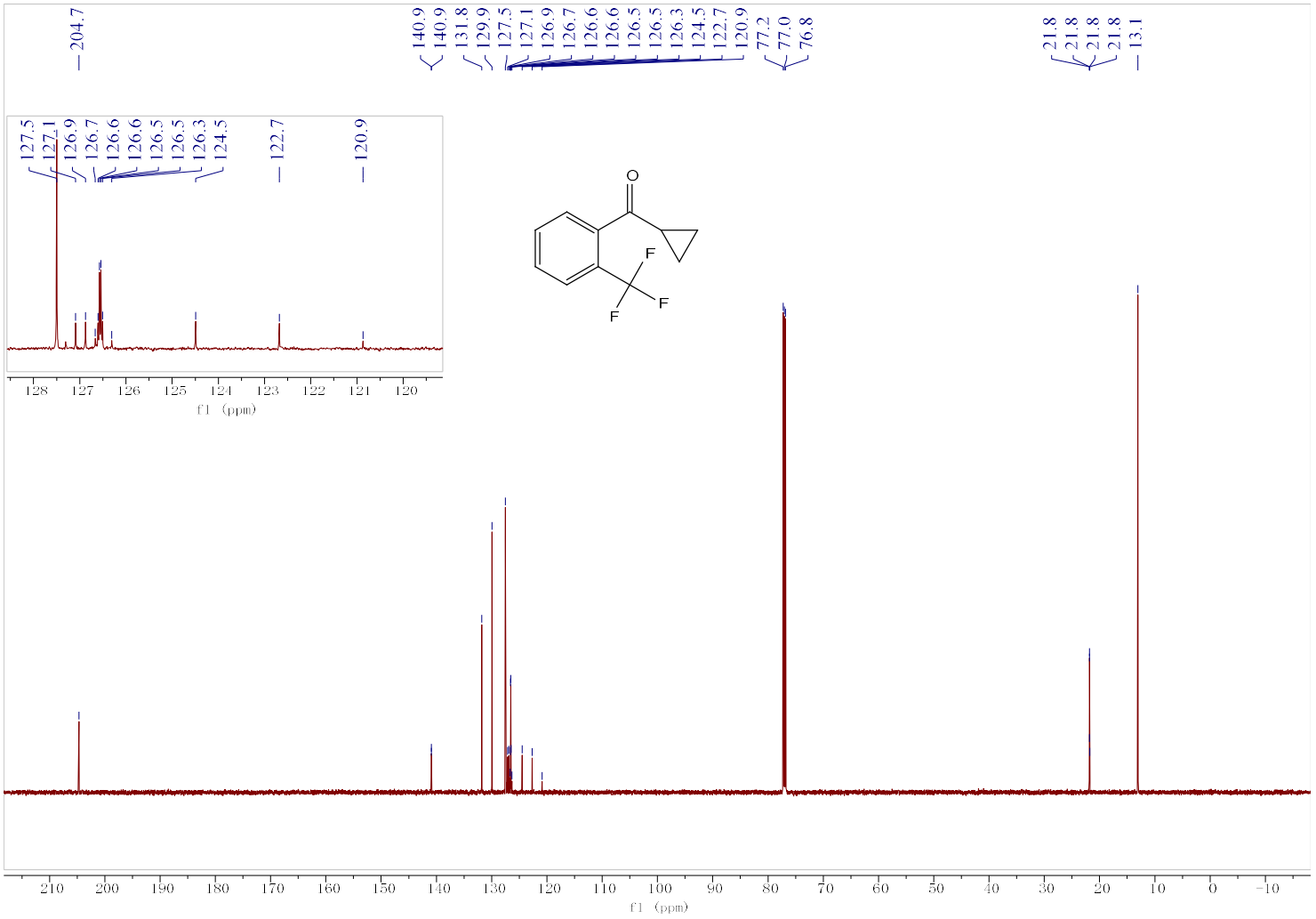
^{13}C NMR Spectrum of 1c (150 MHz, Chloroform-*d*)



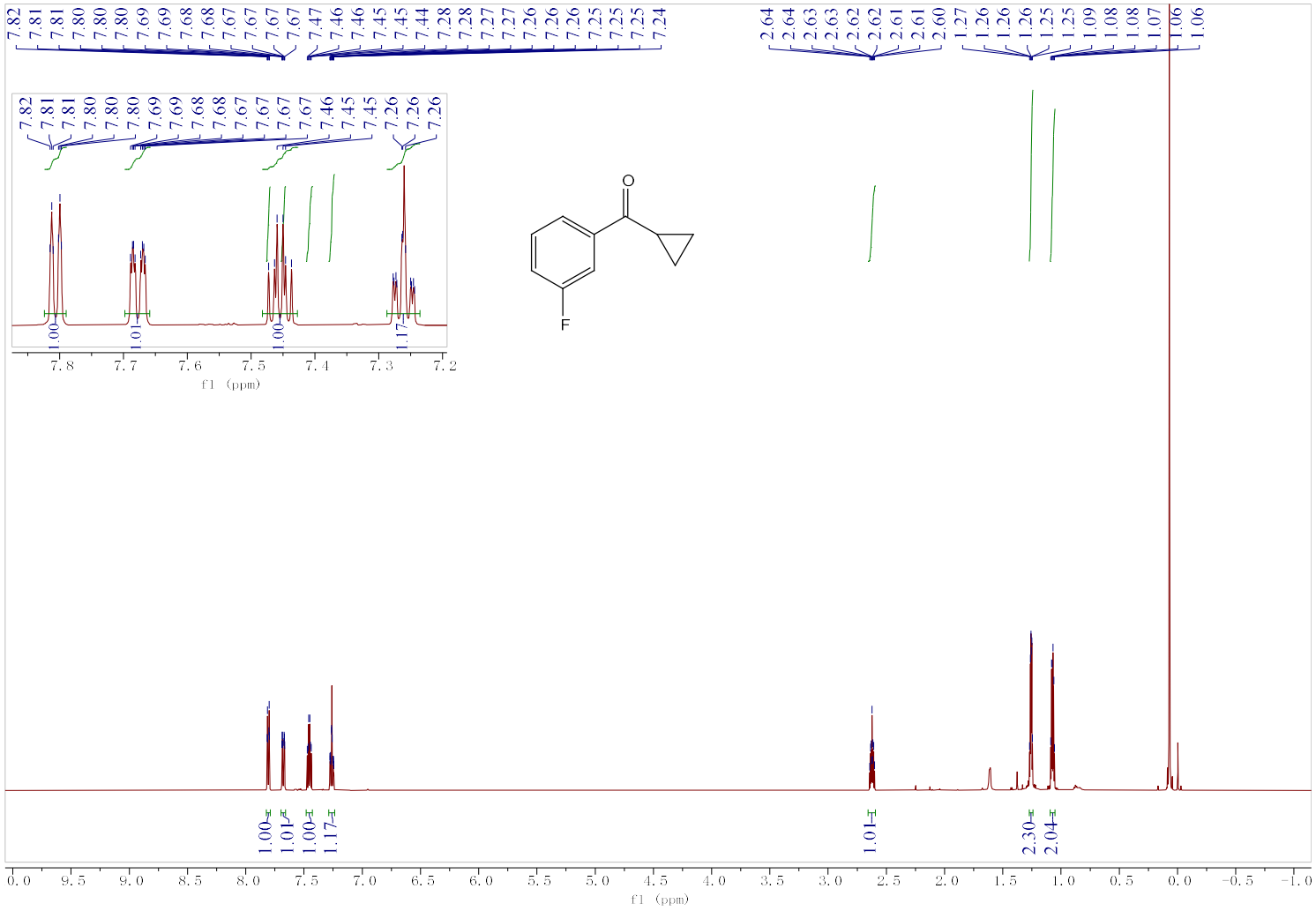
^{1}H NMR Spectrum of 1i (600 MHz, Chloroform-*d*)



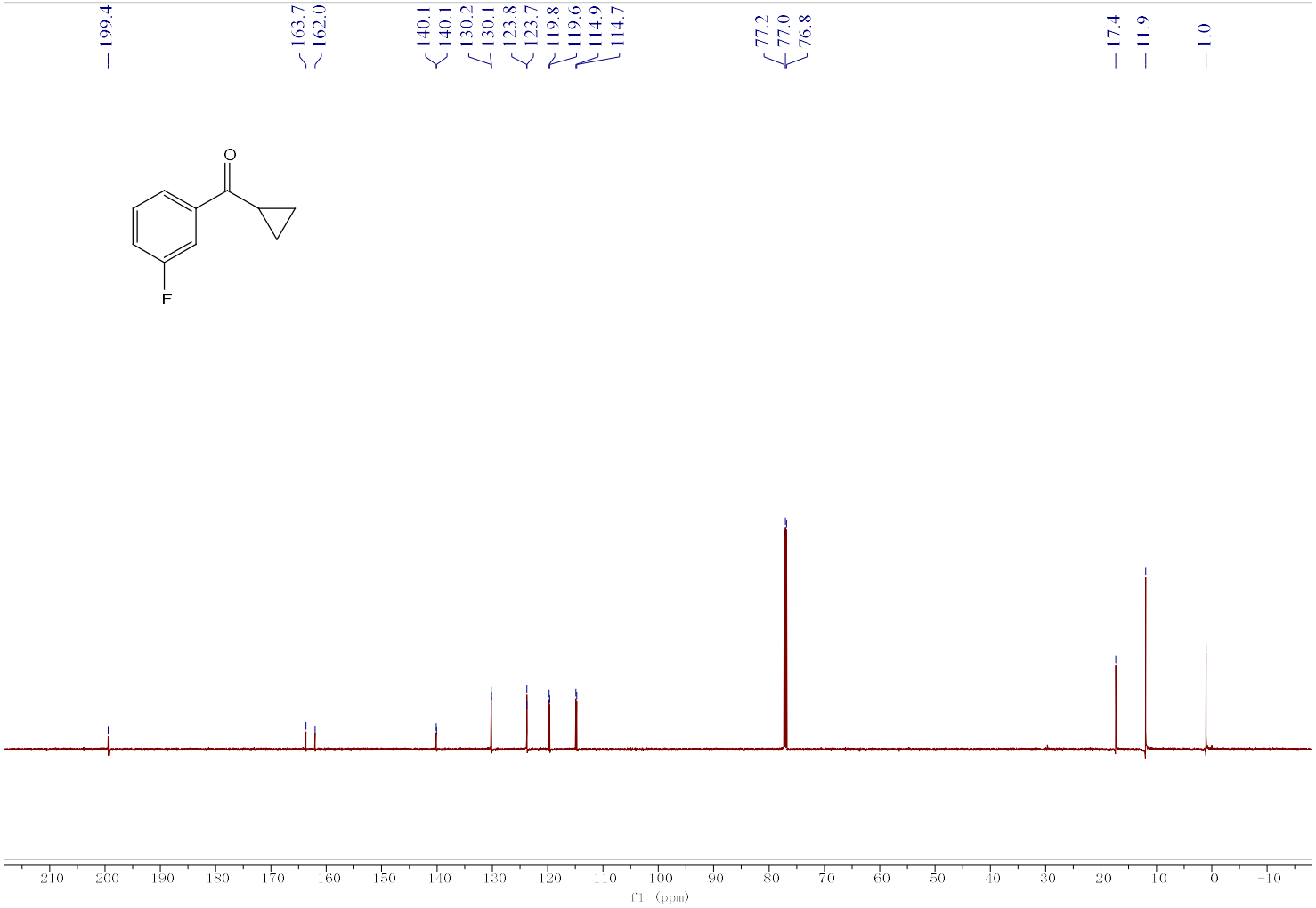
^{13}C NMR Spectrum of 1i (150 MHz, Chloroform-*d*)



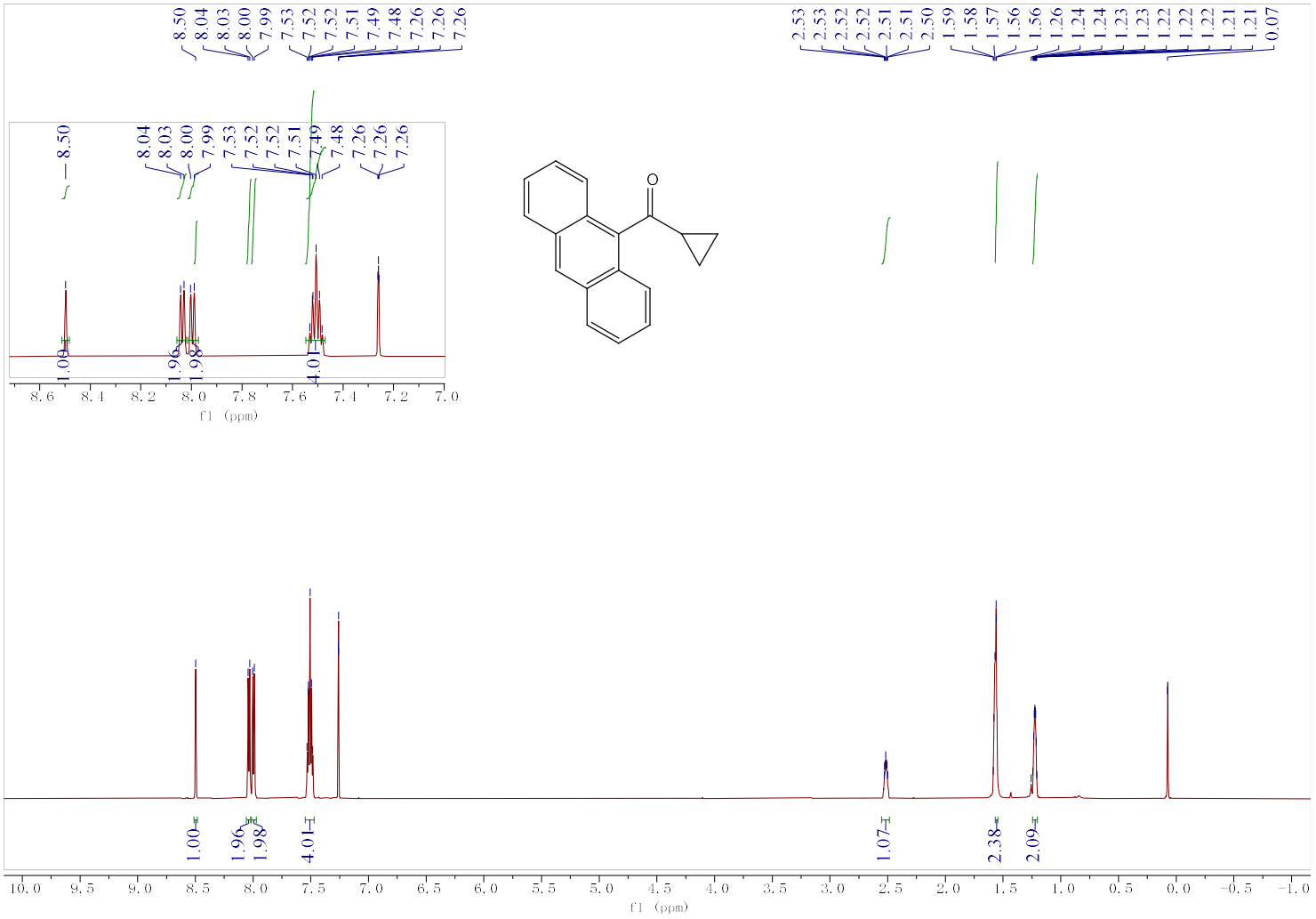
^{1}H NMR Spectrum of 1k (600 MHz, Chloroform-*d*)



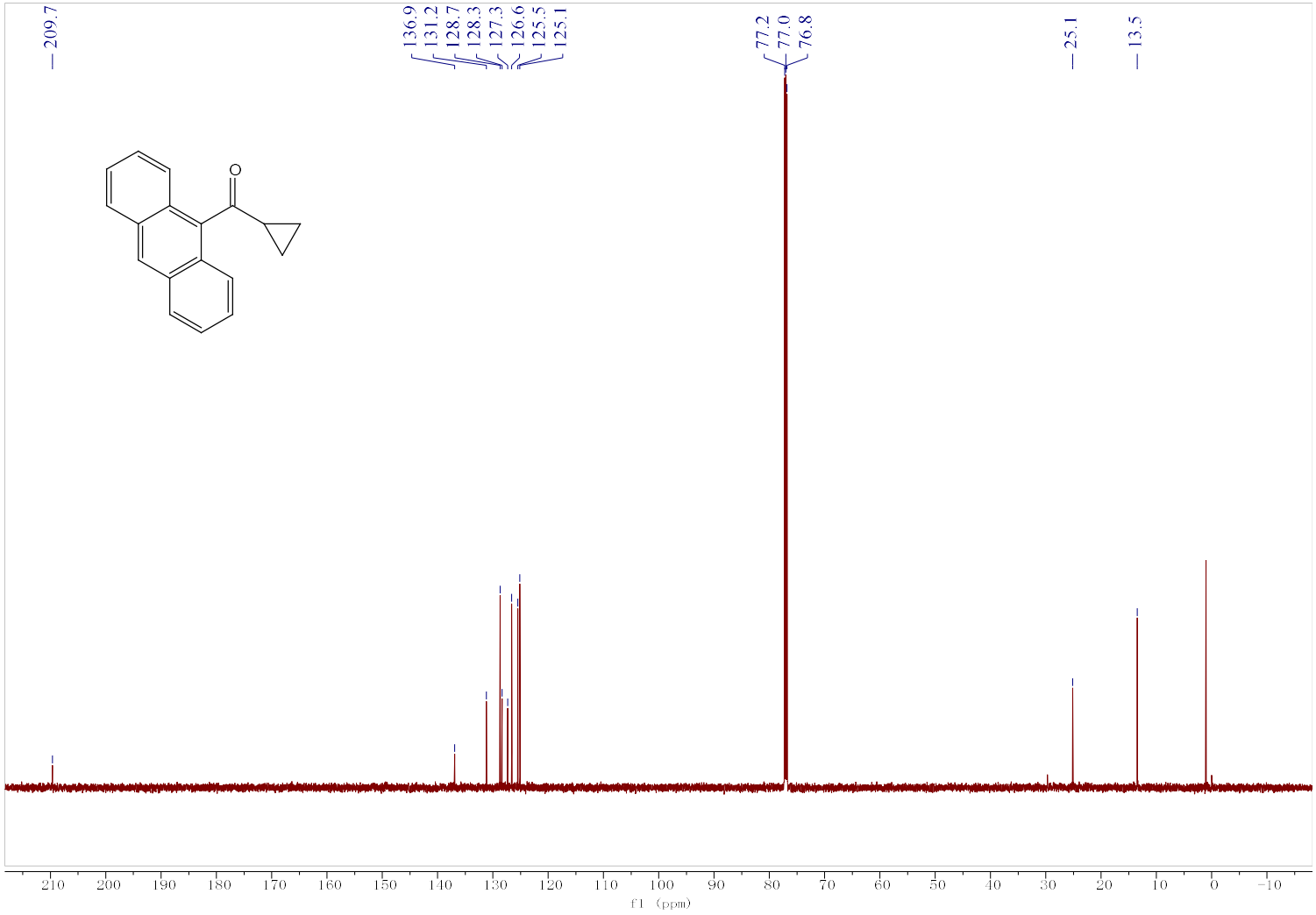
^{13}C NMR Spectrum of 1k (150 MHz, Chloroform-*d*)



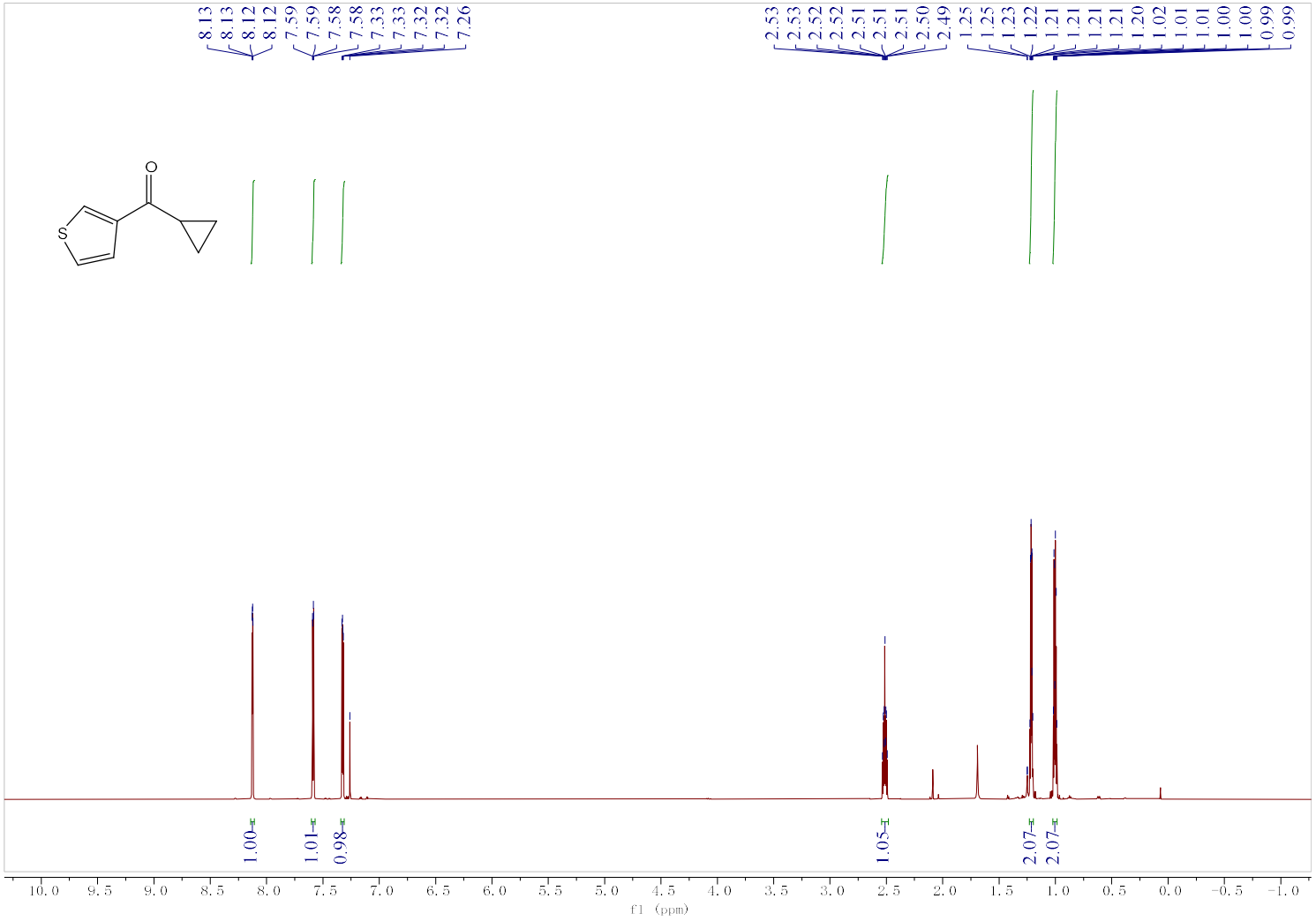
^{1}H NMR Spectrum of 1o (600 MHz, Chloroform-*d*)



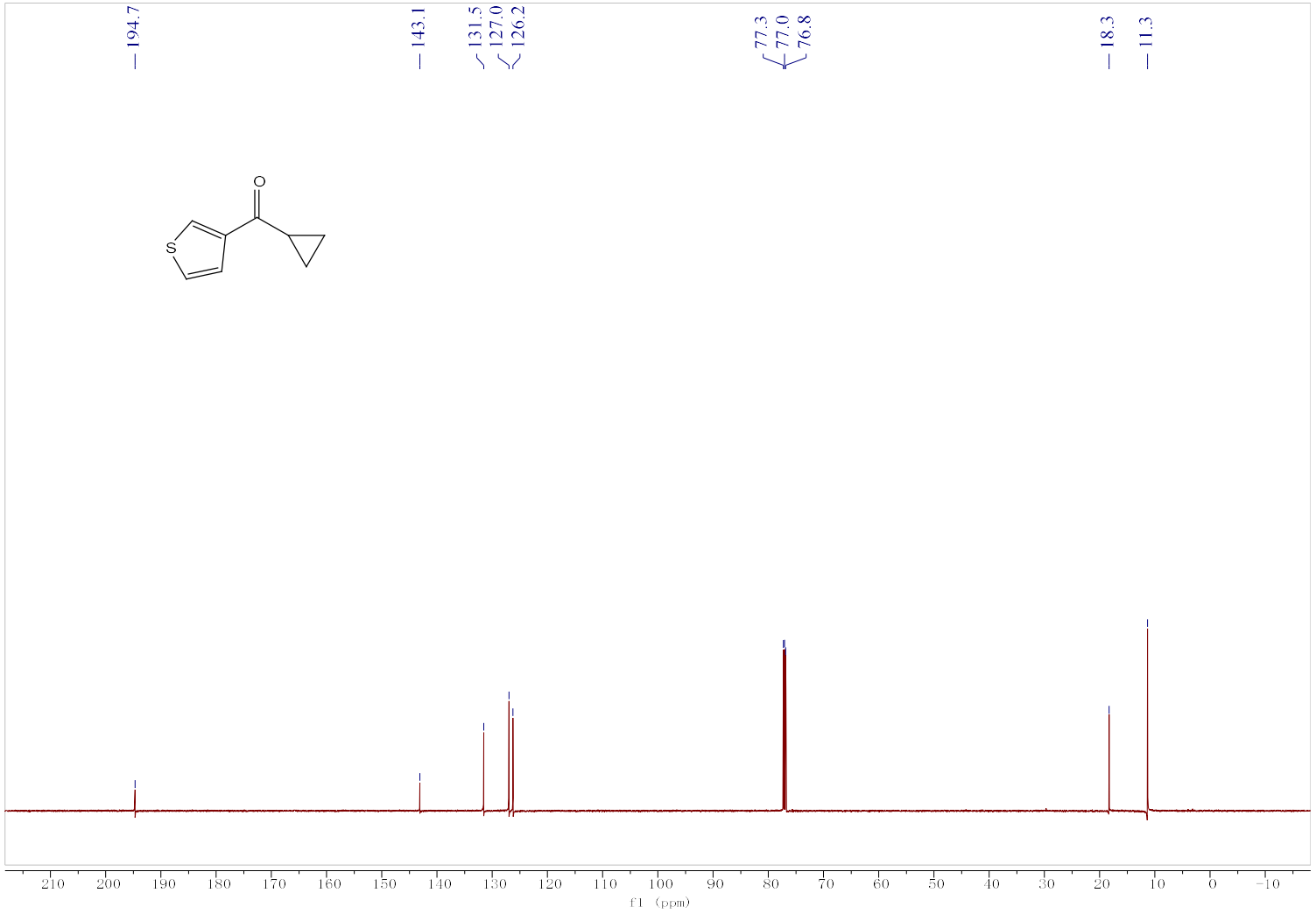
^{13}C NMR Spectrum of 1o (150 MHz, Chloroform-*d*)



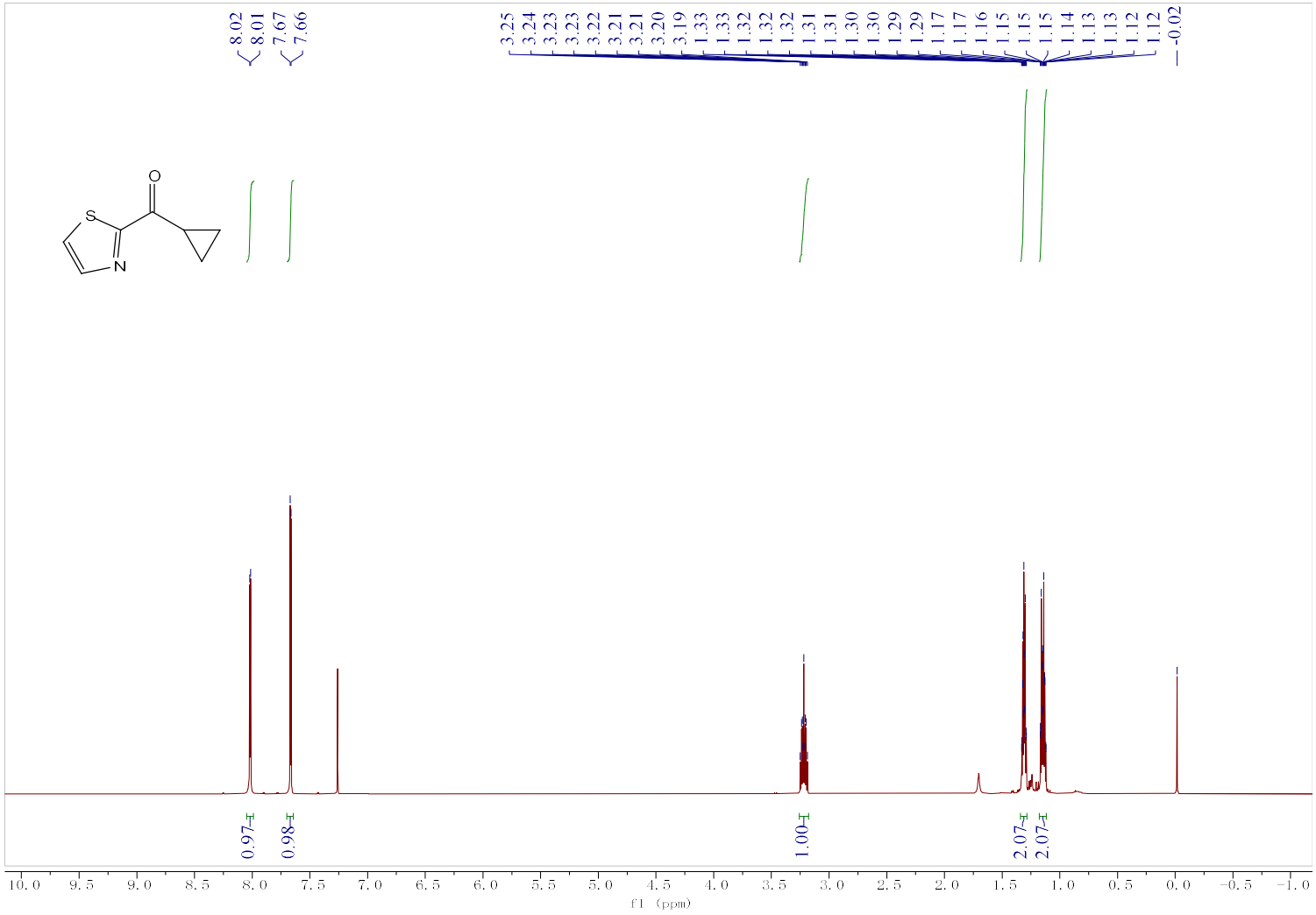
^{1}H NMR Spectrum of 1q (600 MHz, Chloroform-*d*)



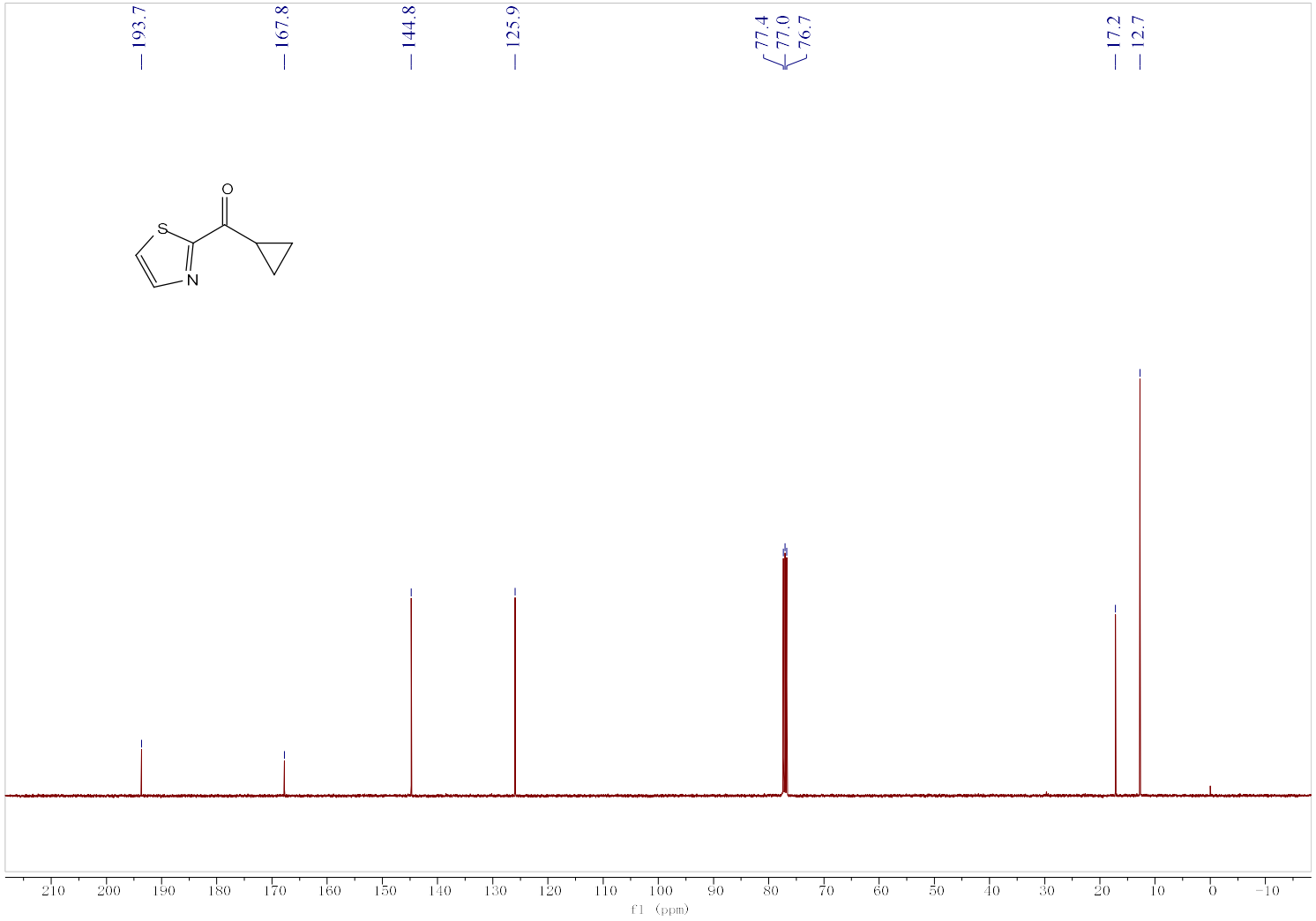
^{13}C NMR Spectrum of 1q (150 MHz, Chloroform-*d*)



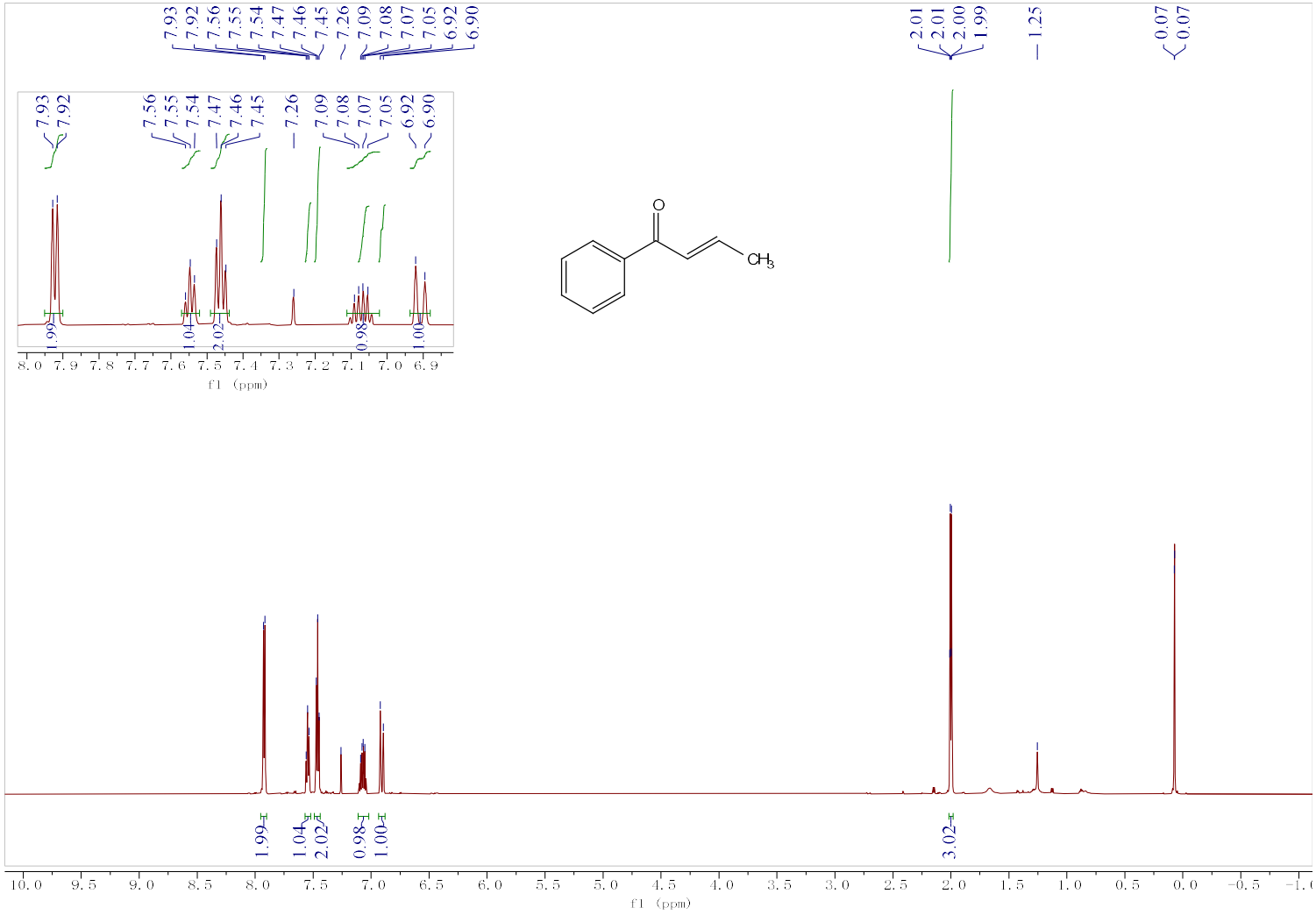
^{1}H NMR Spectrum of 1r (600 MHz, Chloroform-*d*)



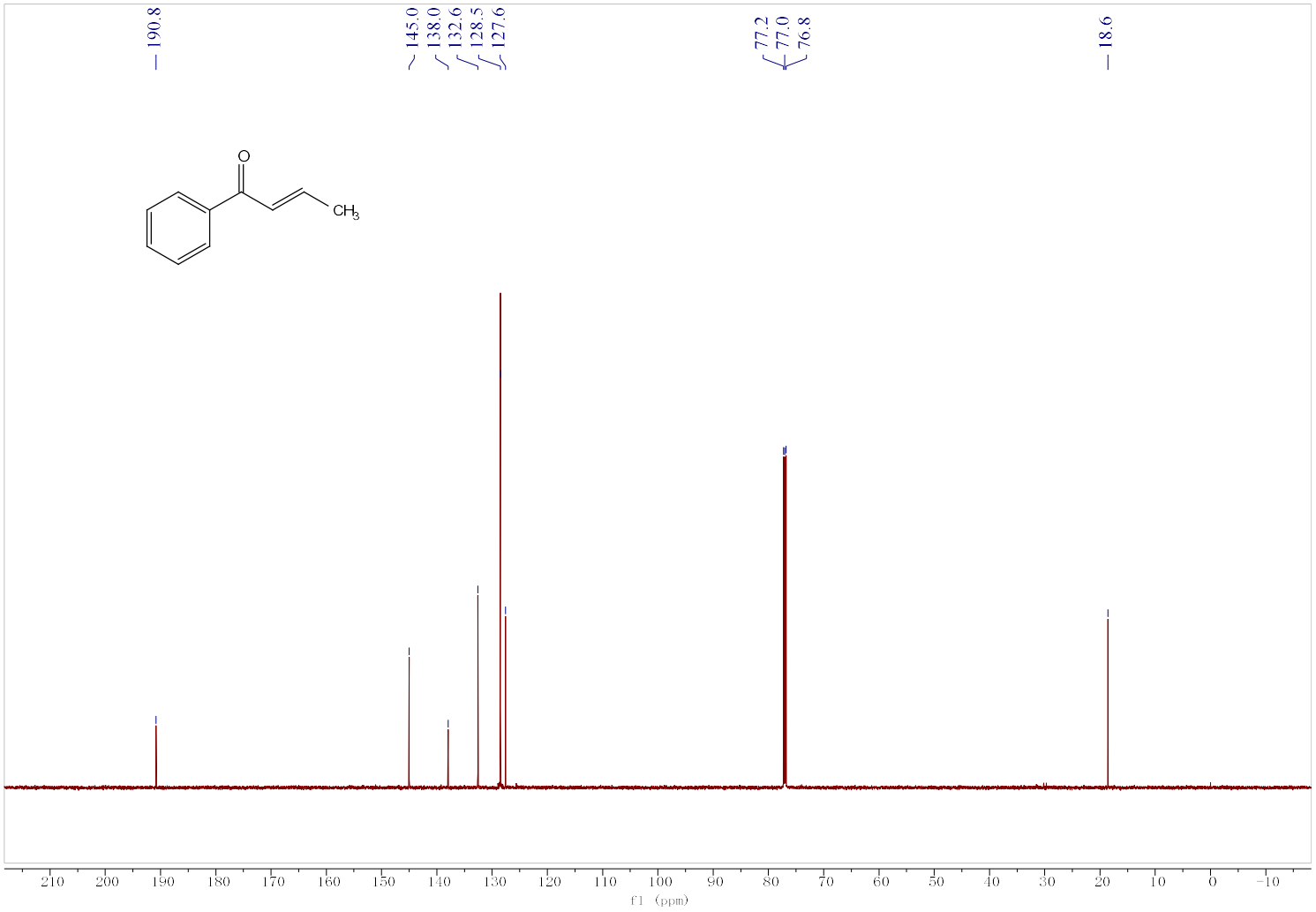
^{13}C NMR Spectrum of 1r (150 MHz, Chloroform-*d*)



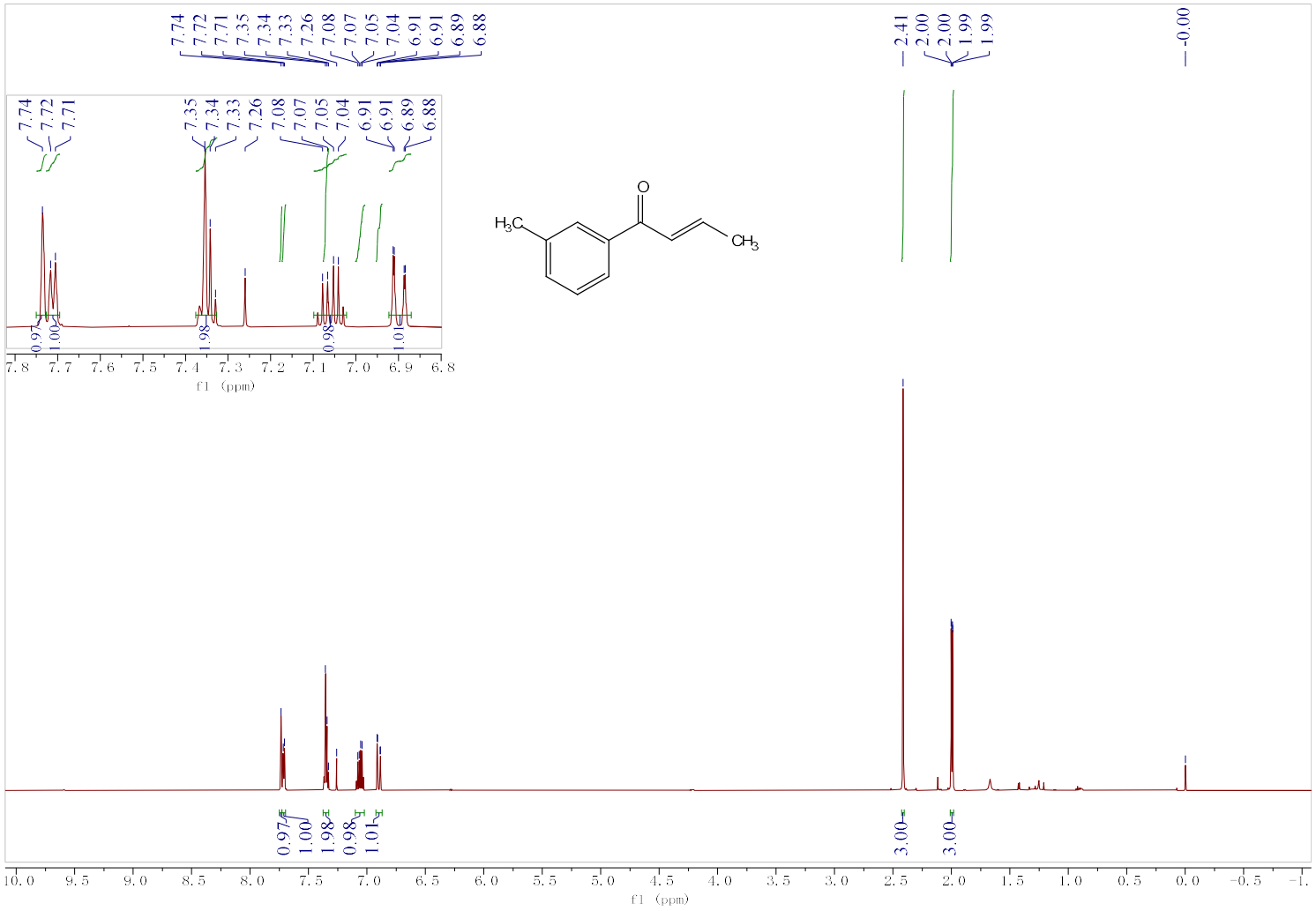
^{1}H NMR Spectrum of 2a (600 MHz, Chloroform-*d*)



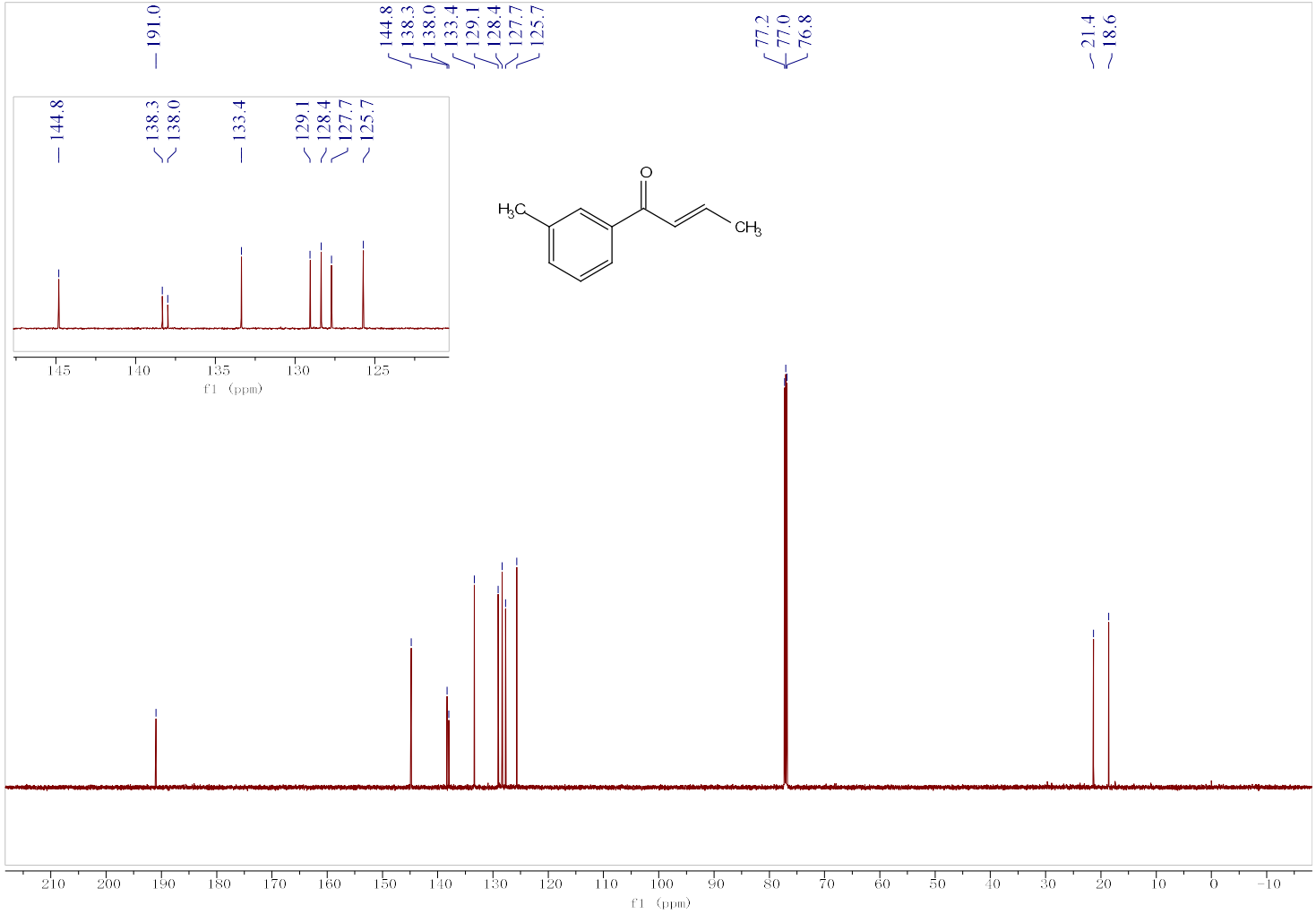
^{13}C NMR Spectrum of 2a (150 MHz, Chloroform-*d*)



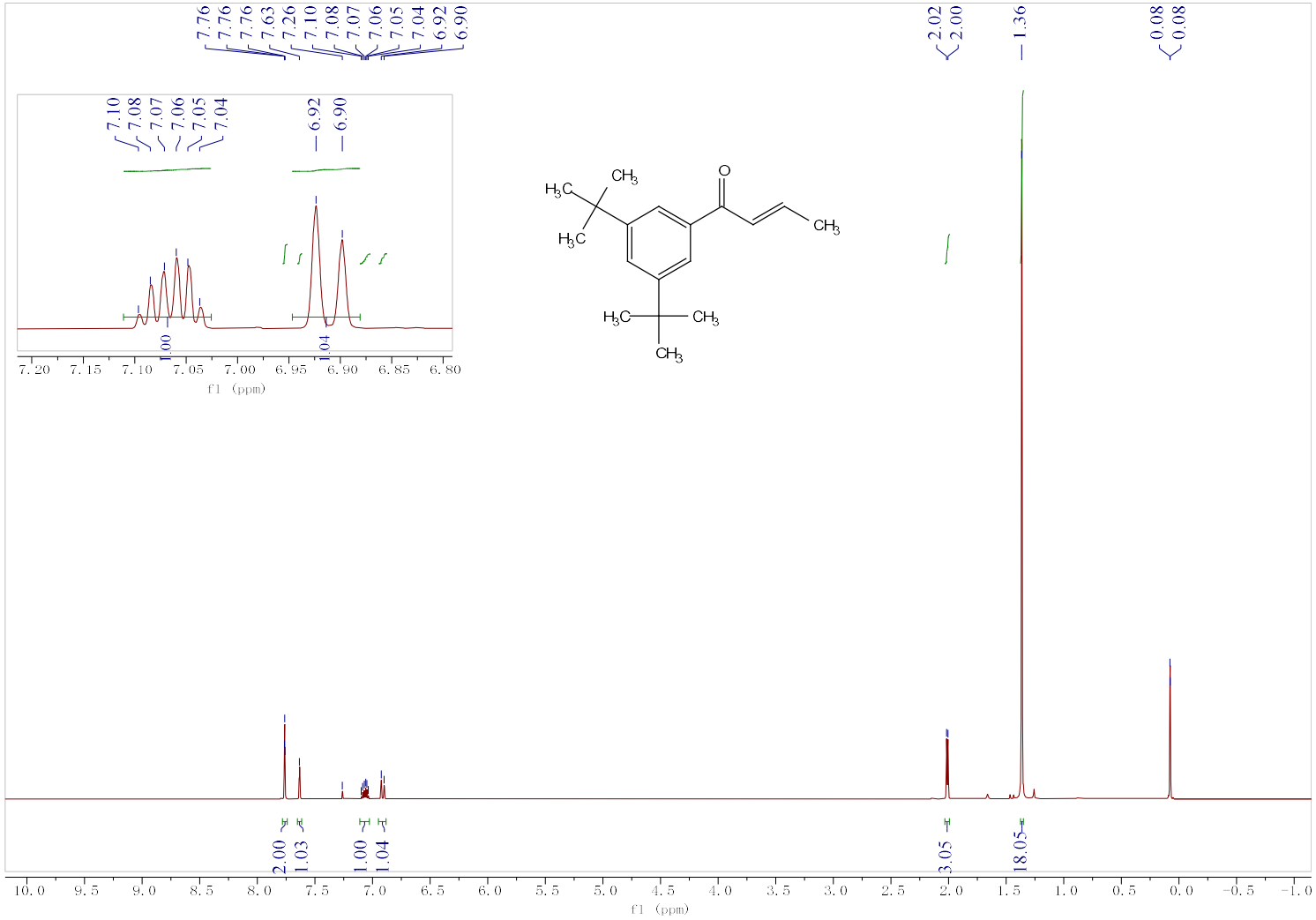
^{1}H NMR Spectrum of 2b (600 MHz, Chloroform-*d*)



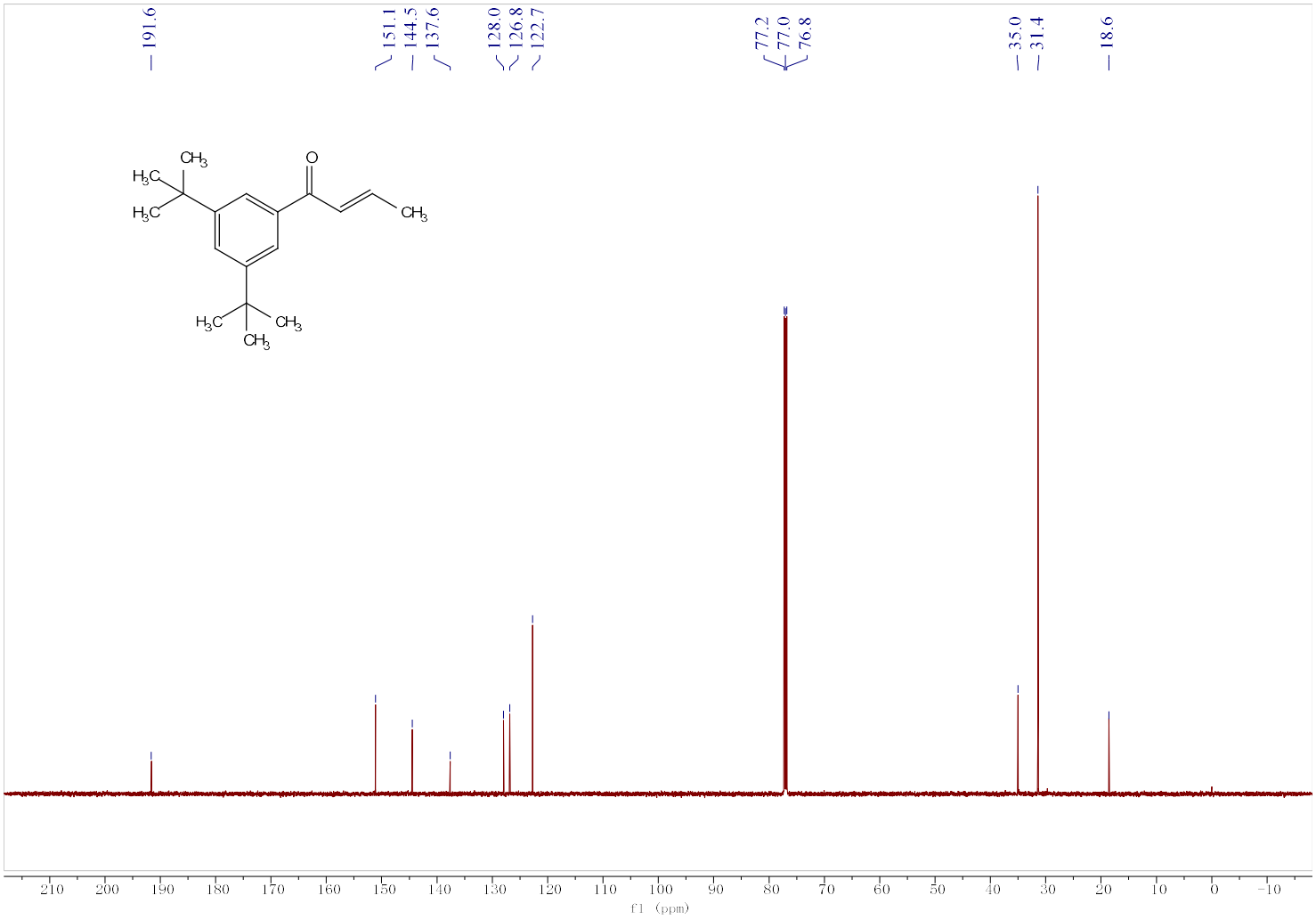
^{13}C NMR Spectrum of 2b (150 MHz, Chloroform-*d*)



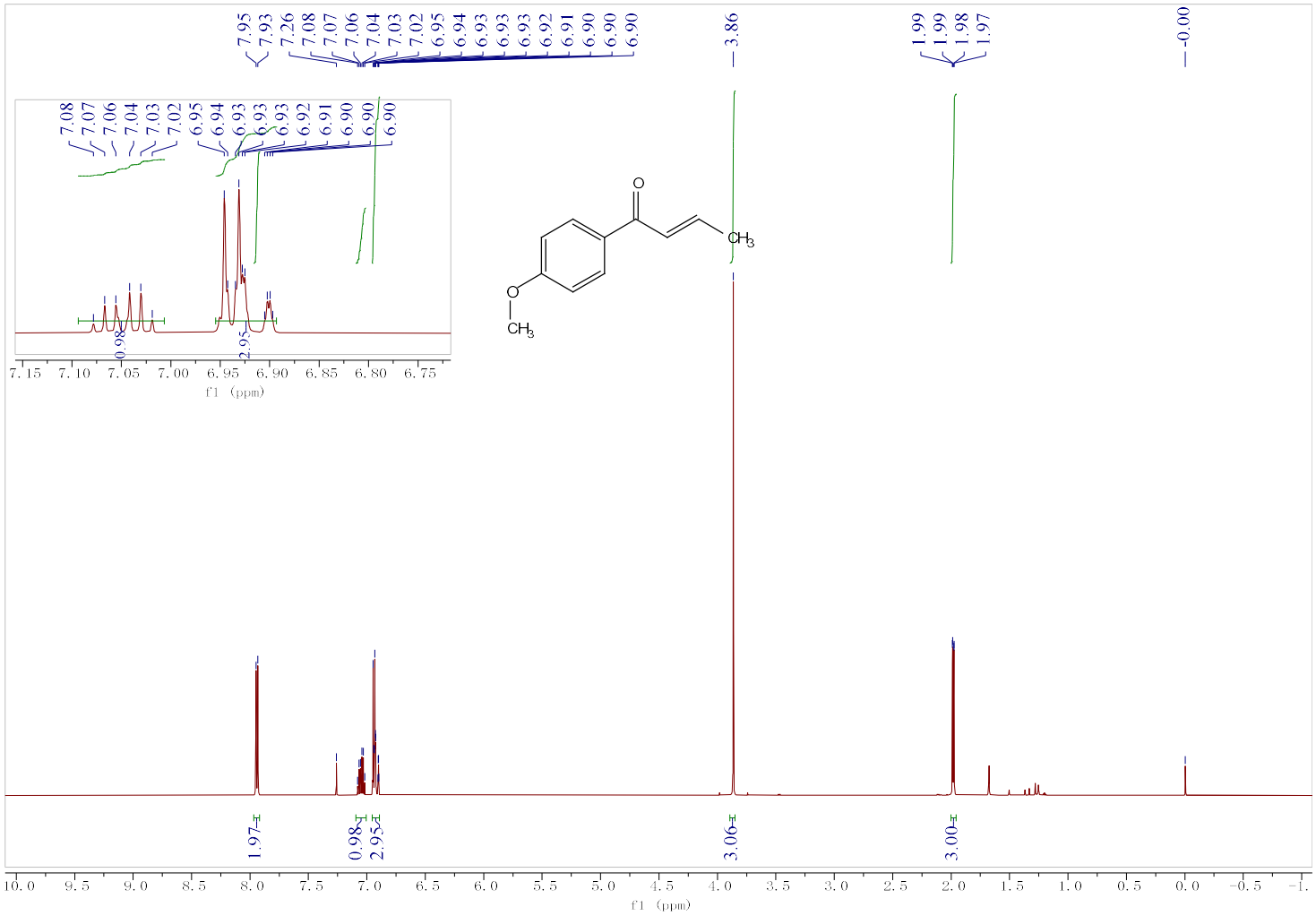
^{1}H NMR Spectrum of 2c (600 MHz, Chloroform-*d*)



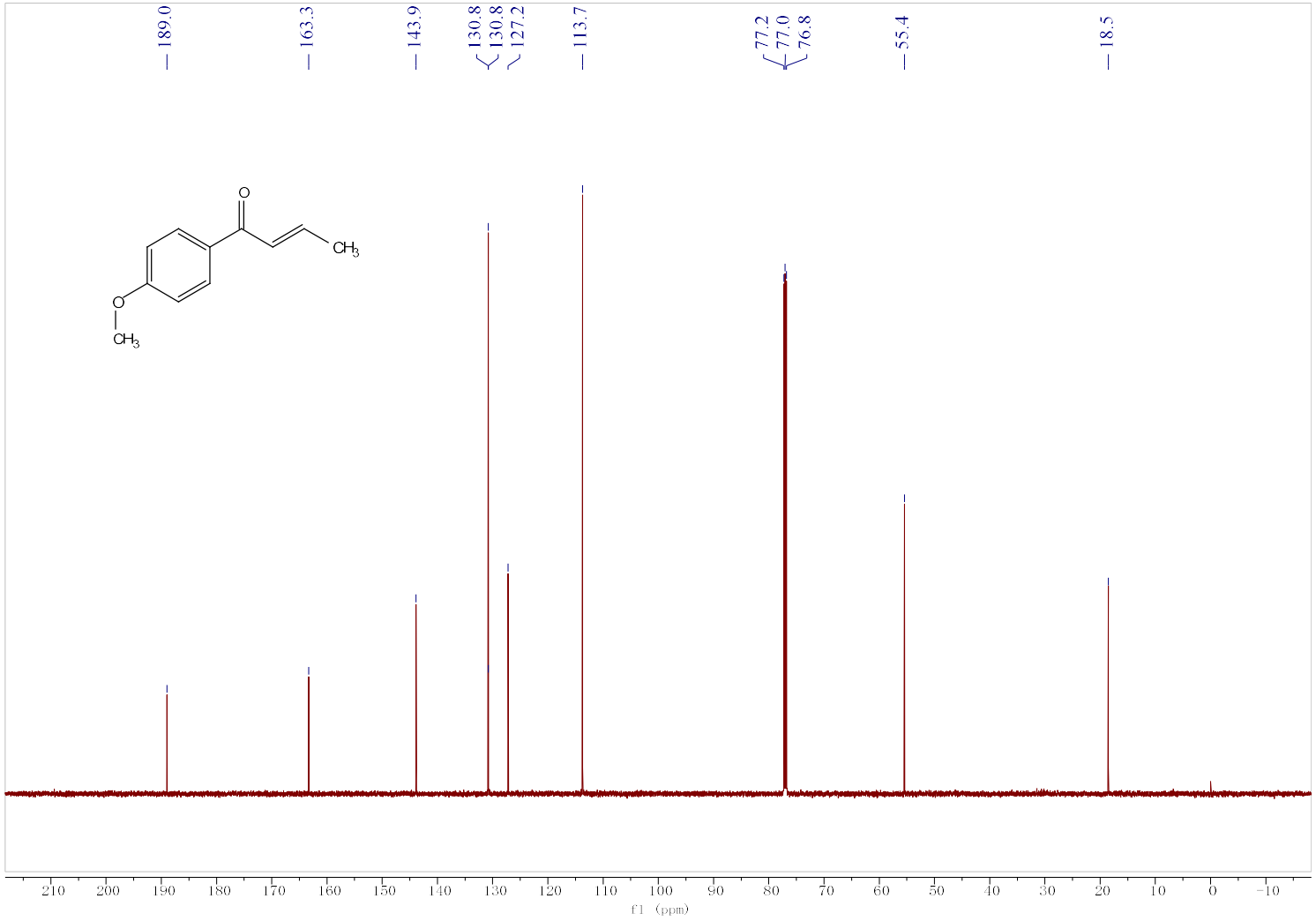
^{13}C NMR Spectrum of 2c (150 MHz, Chloroform-*d*)



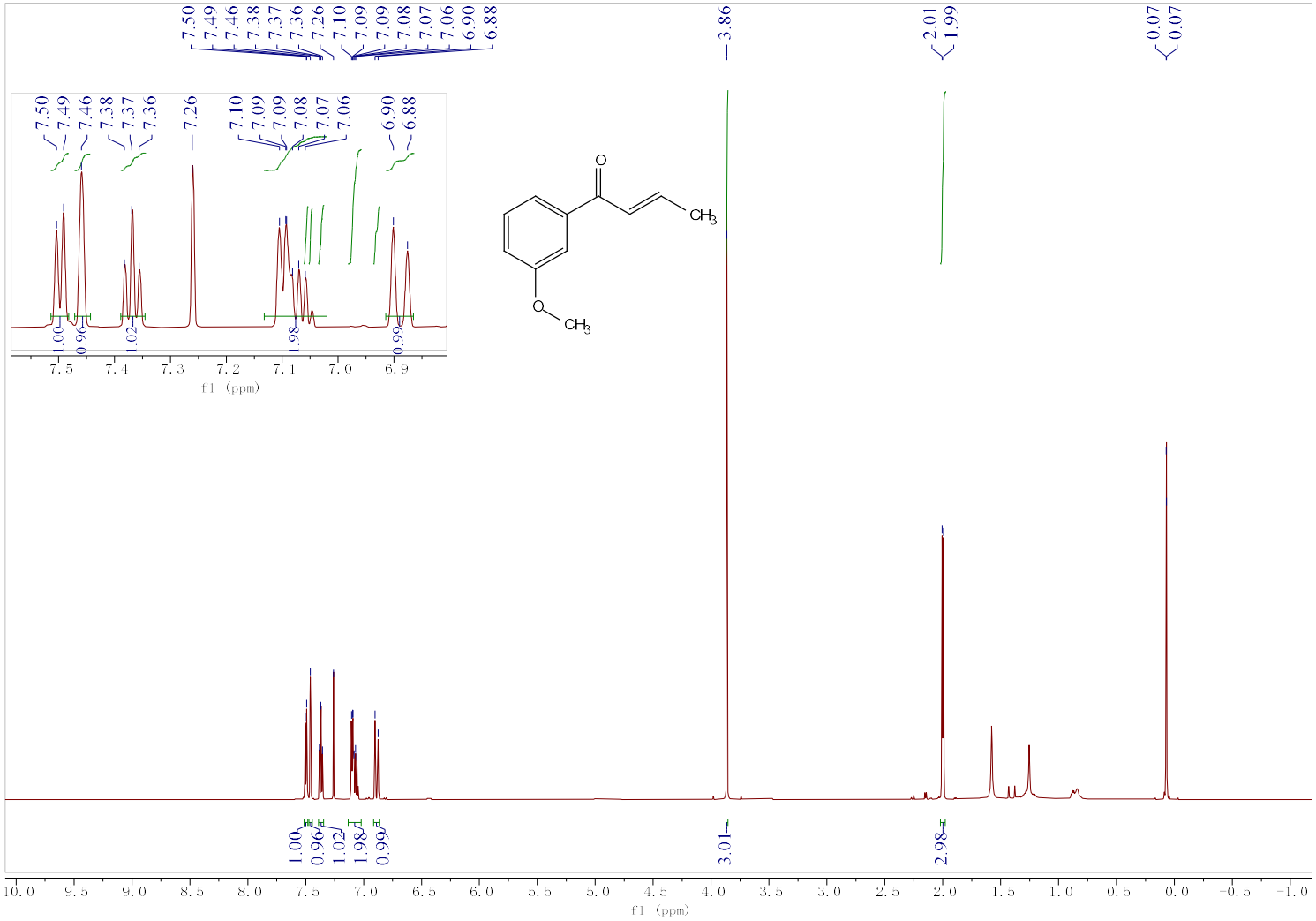
[1]H NMR Spectrum of 2d (600 MHz, Chloroform-*d*)



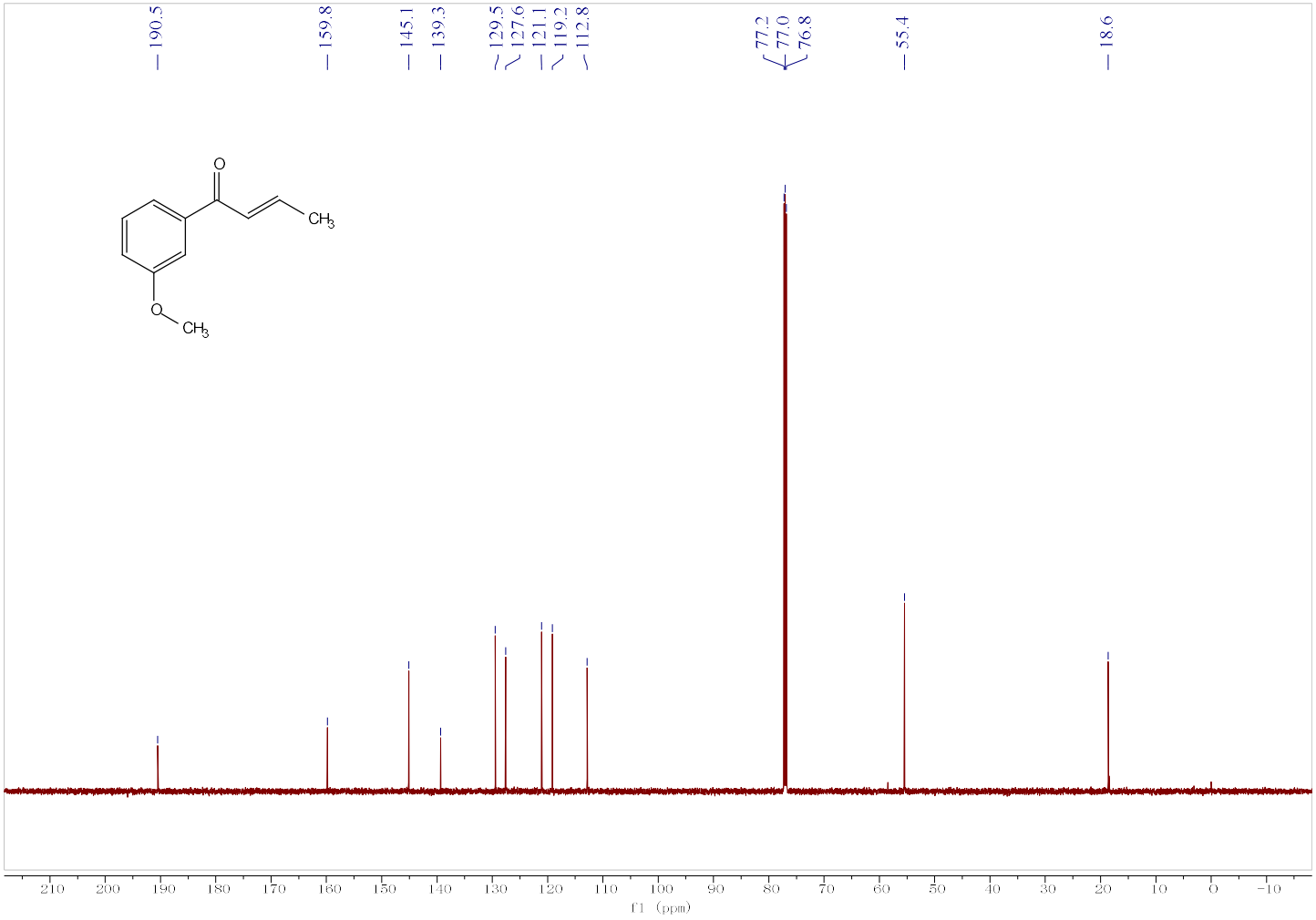
^{13}C NMR Spectrum of 2d (150 MHz, Chloroform-*d*)



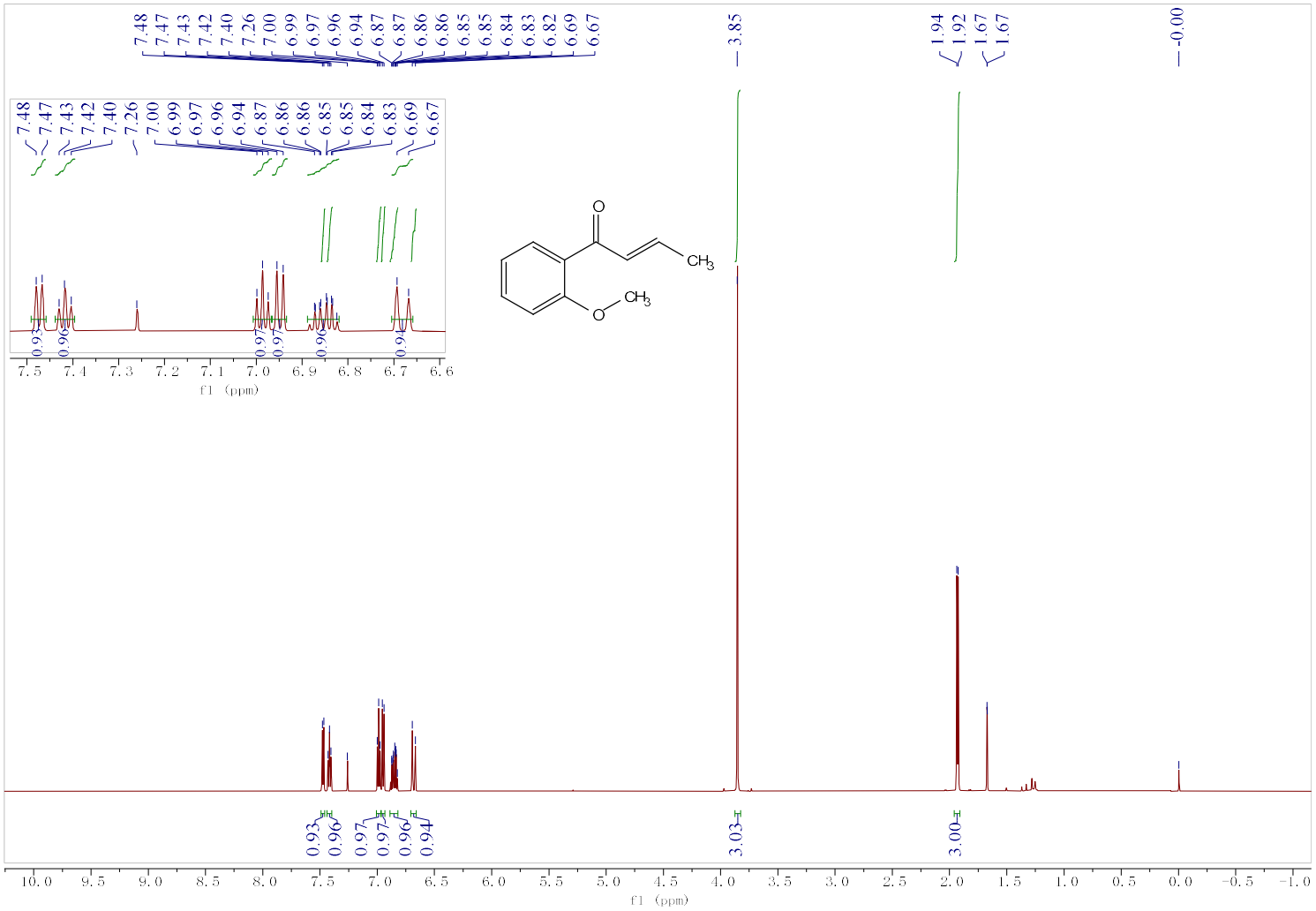
^{1}H NMR Spectrum of 2e (600 MHz, Chloroform-*d*)



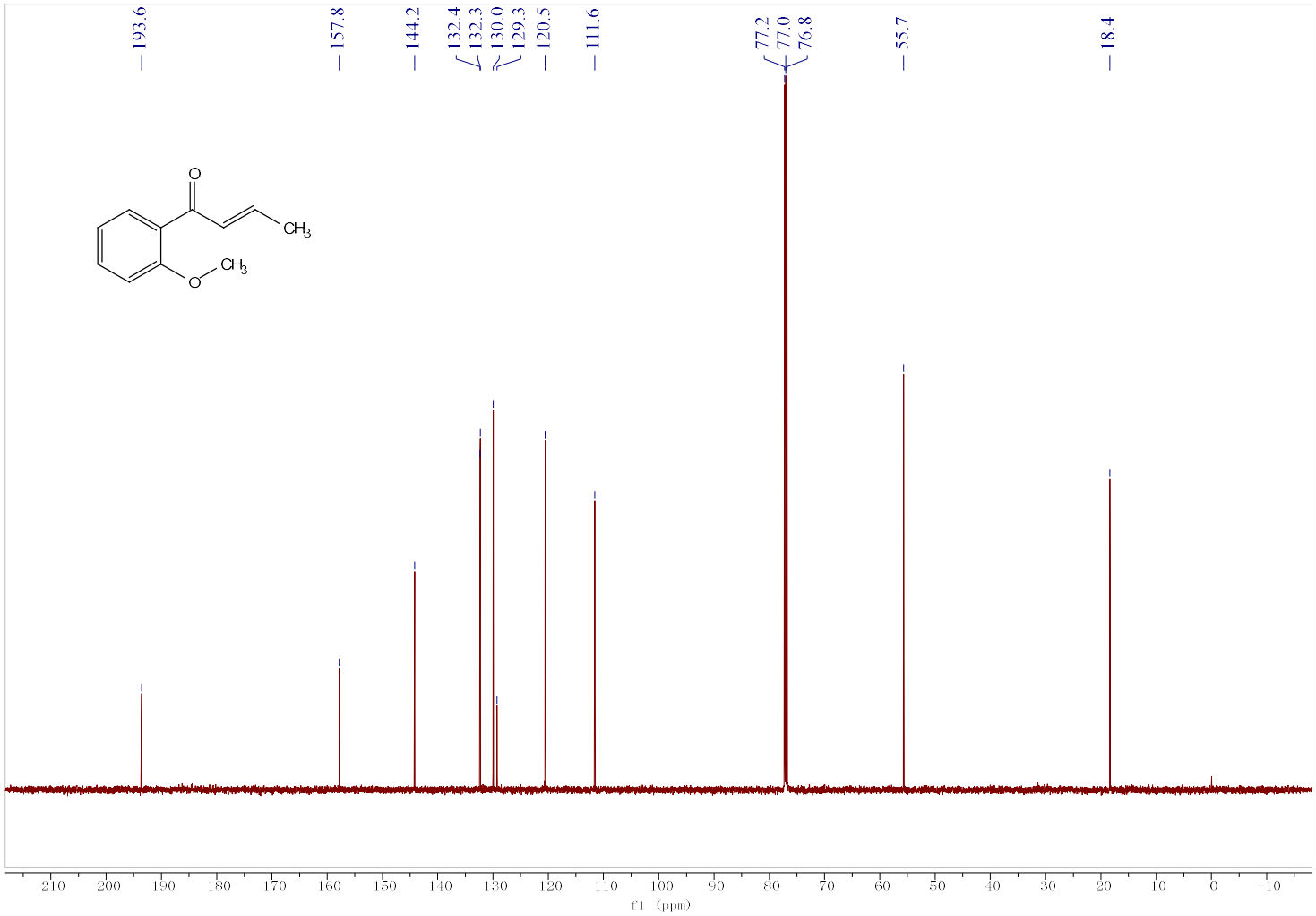
^{13}C NMR Spectrum of 2e (150 MHz, Chloroform-*d*)



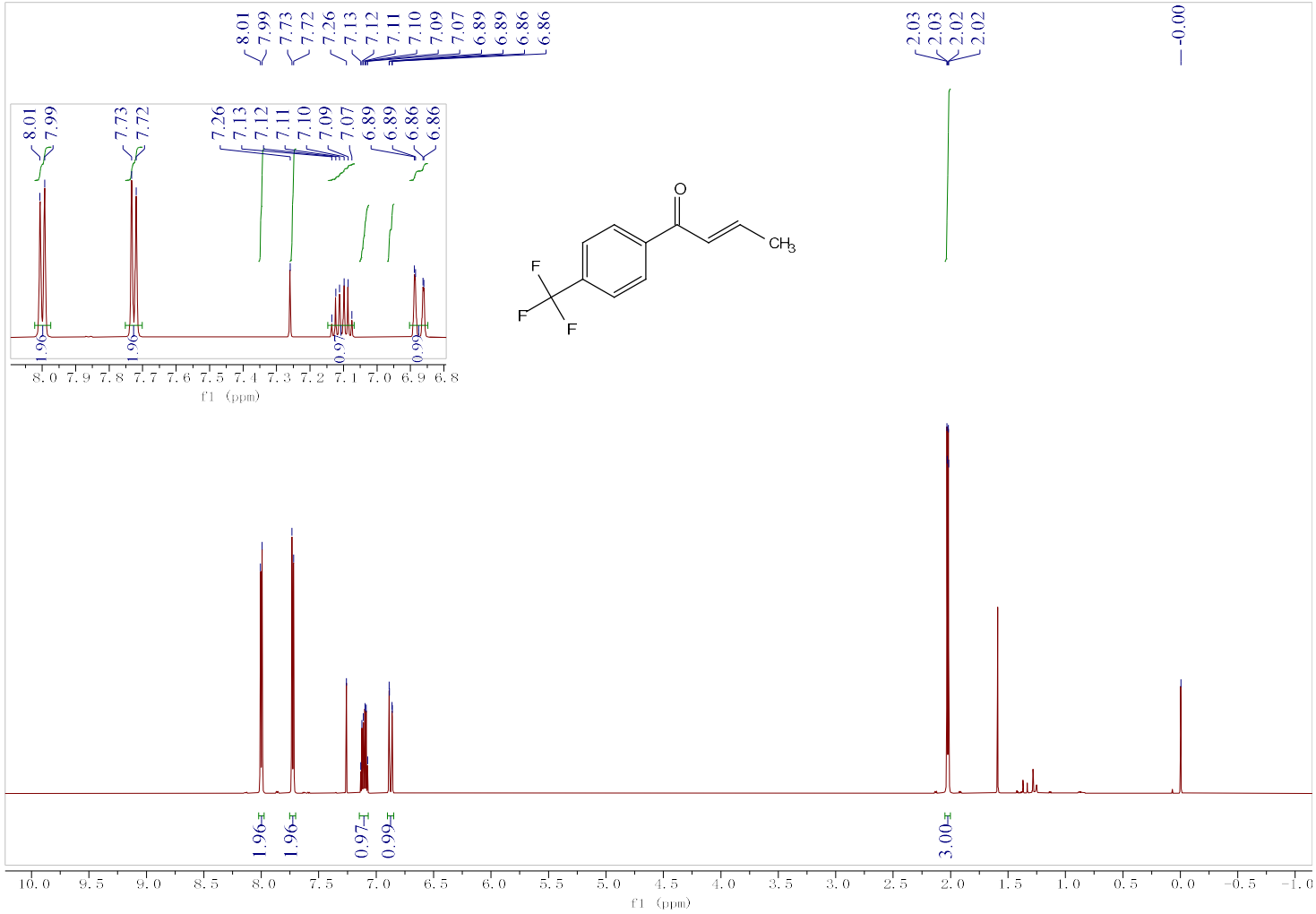
^{1}H NMR Spectrum of 2f (600 MHz, Chloroform-*d*)



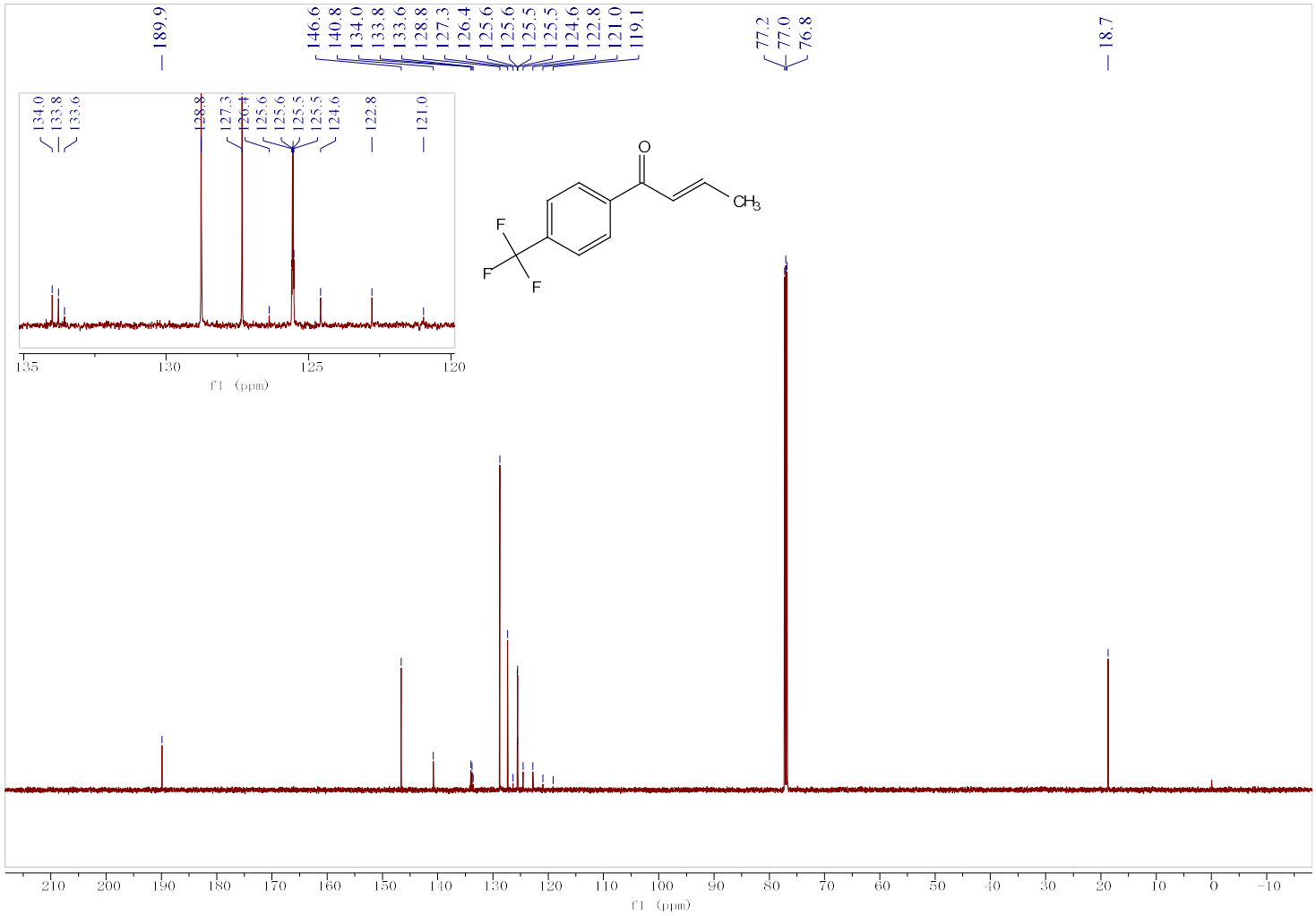
^{13}C NMR Spectrum of 2f (150 MHz, Chloroform-*d*)



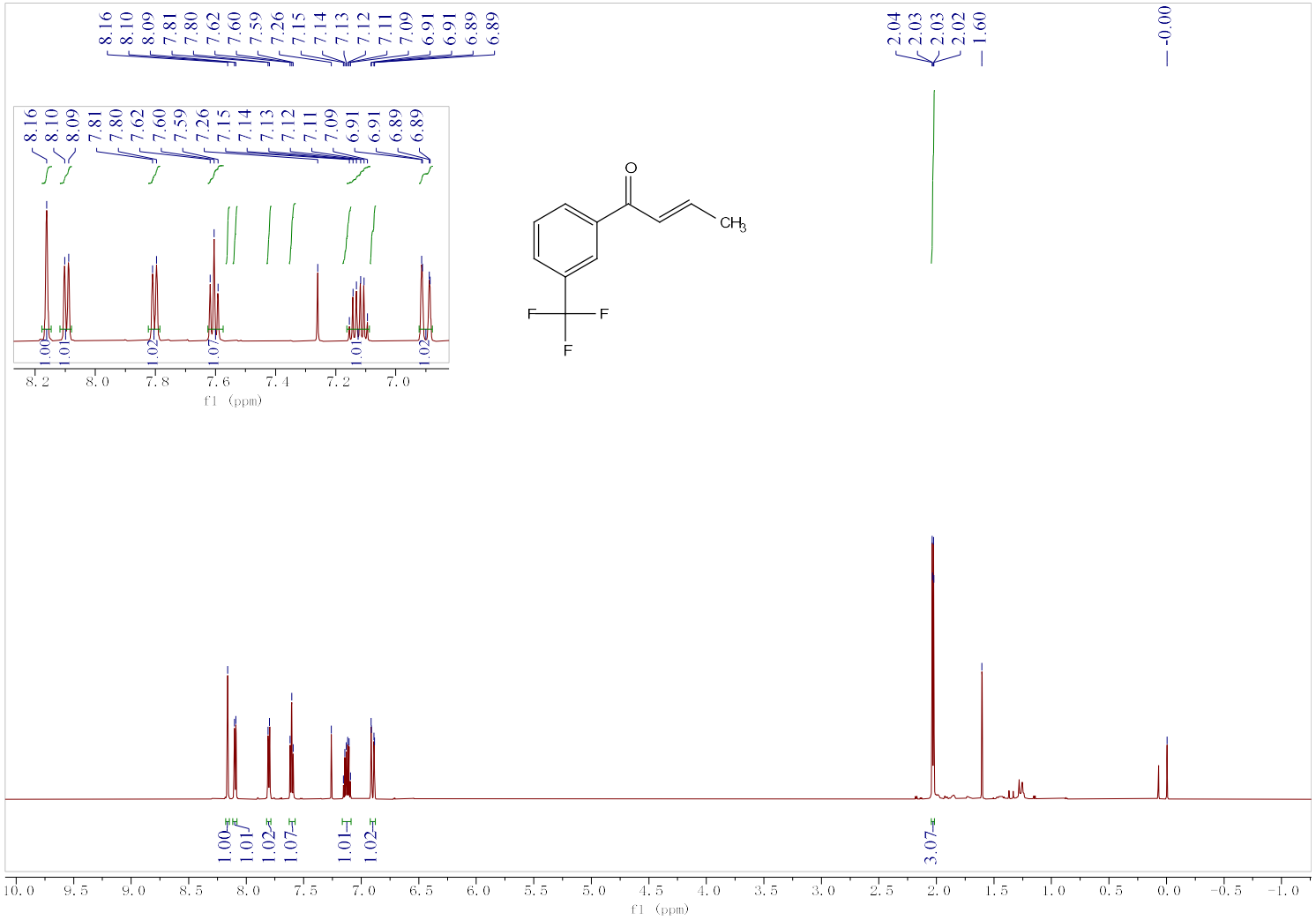
^{1}H NMR Spectrum of 2g (600 MHz, Chloroform-*d*)



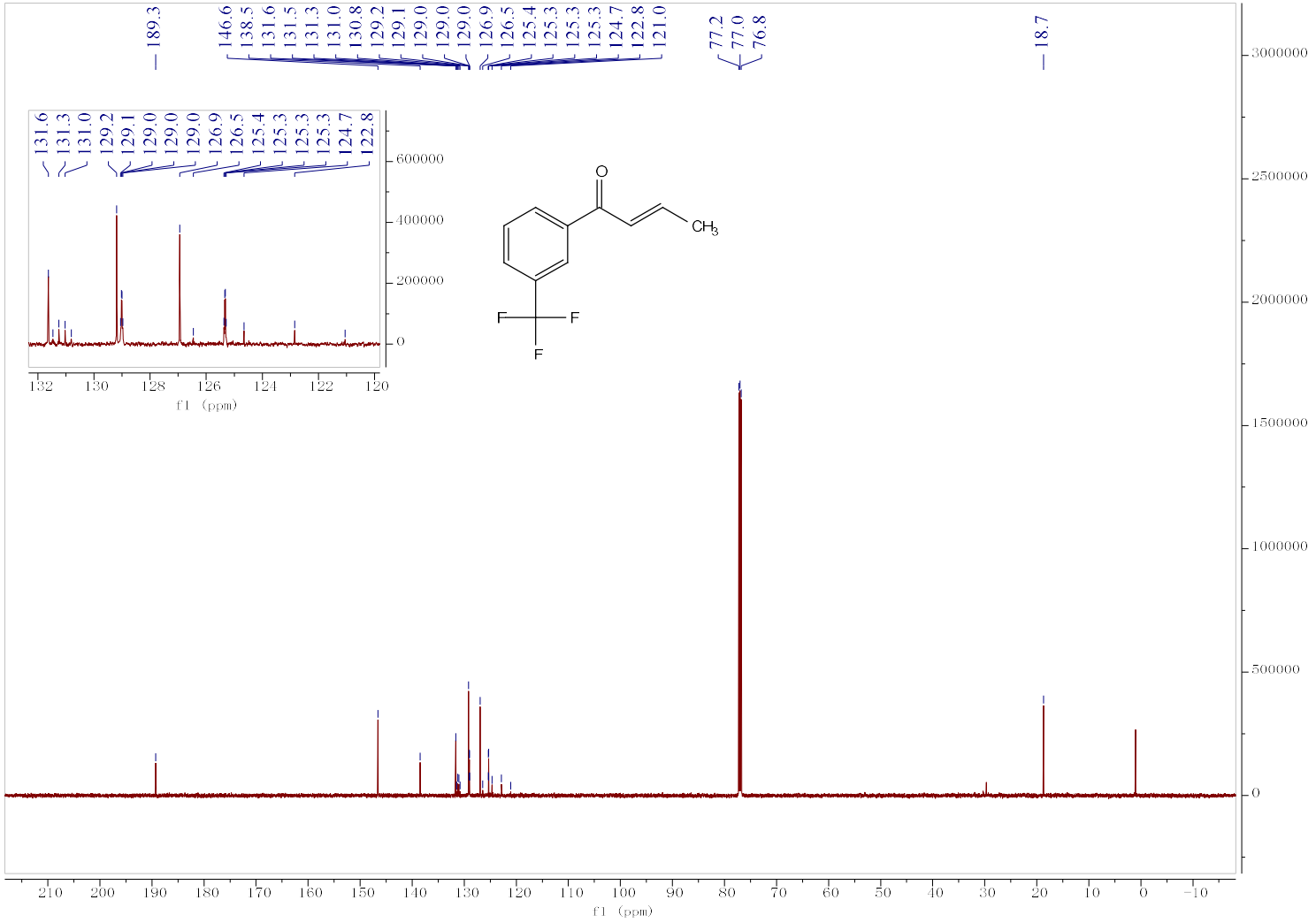
^{13}C NMR Spectrum of 2g (150 MHz, Chloroform-*d*)



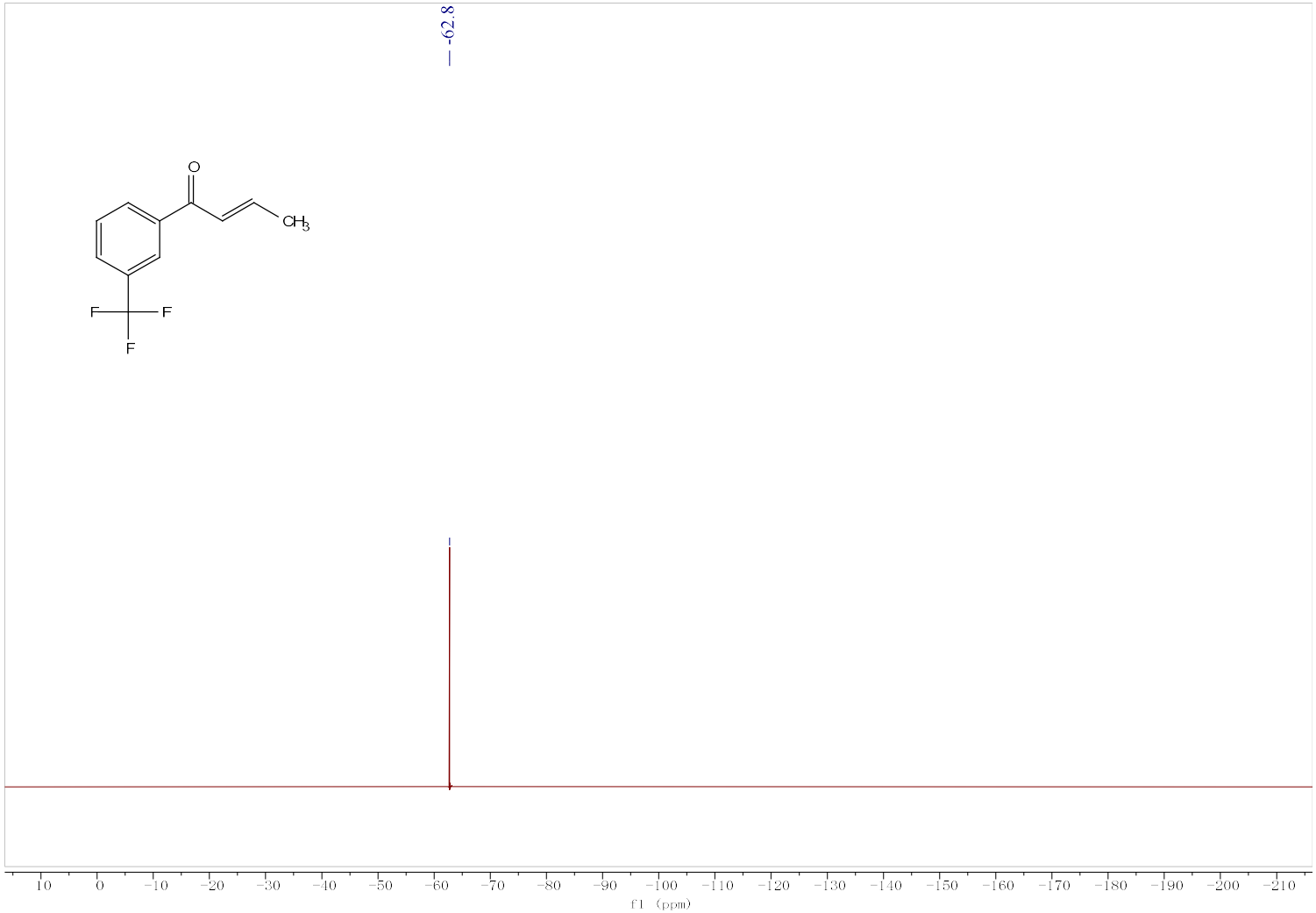
^{1}H NMR Spectrum of 2h (600 MHz, Chloroform-*d*)



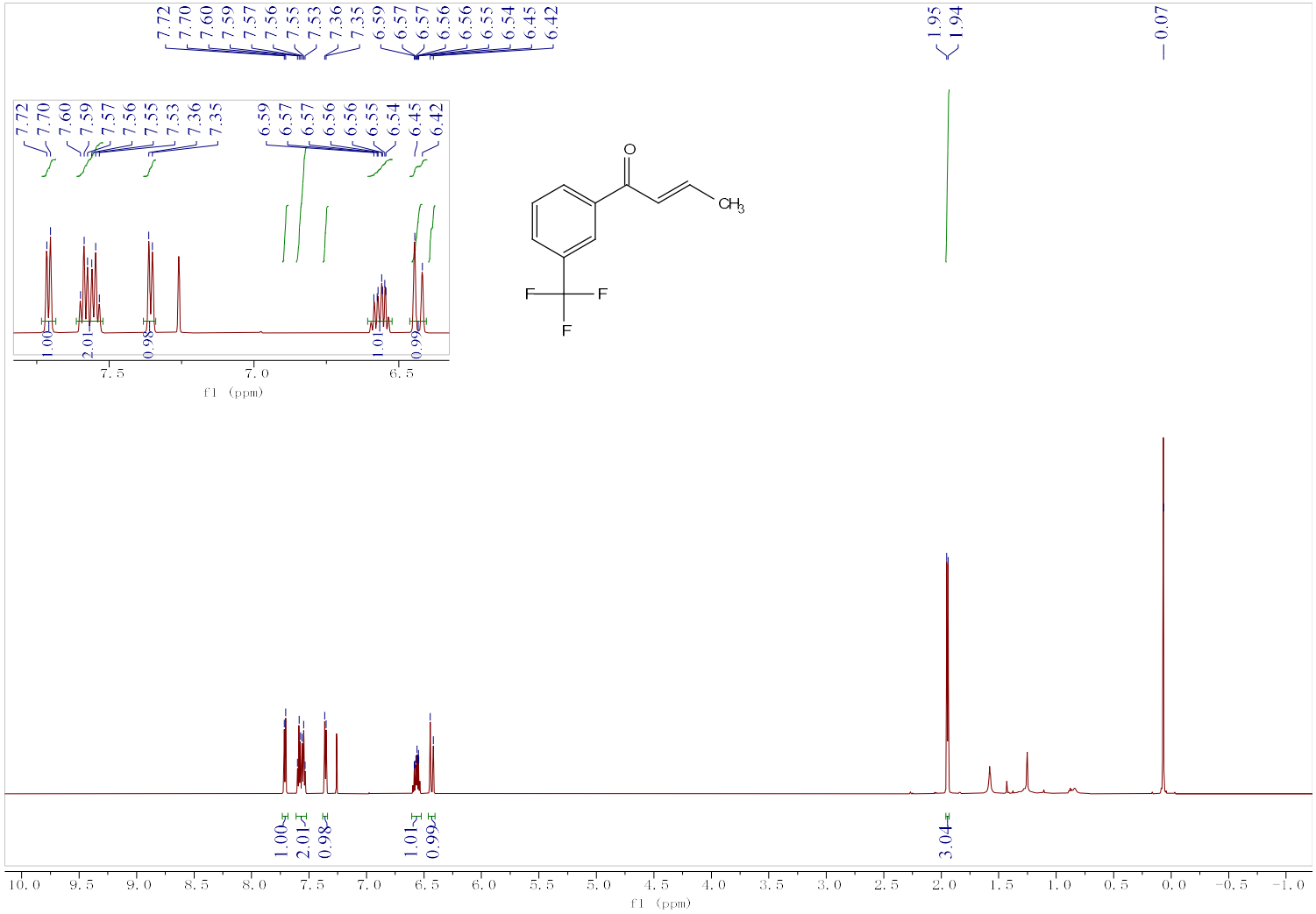
^{13}C NMR Spectrum of 2h (150 MHz, Chloroform-*d*)



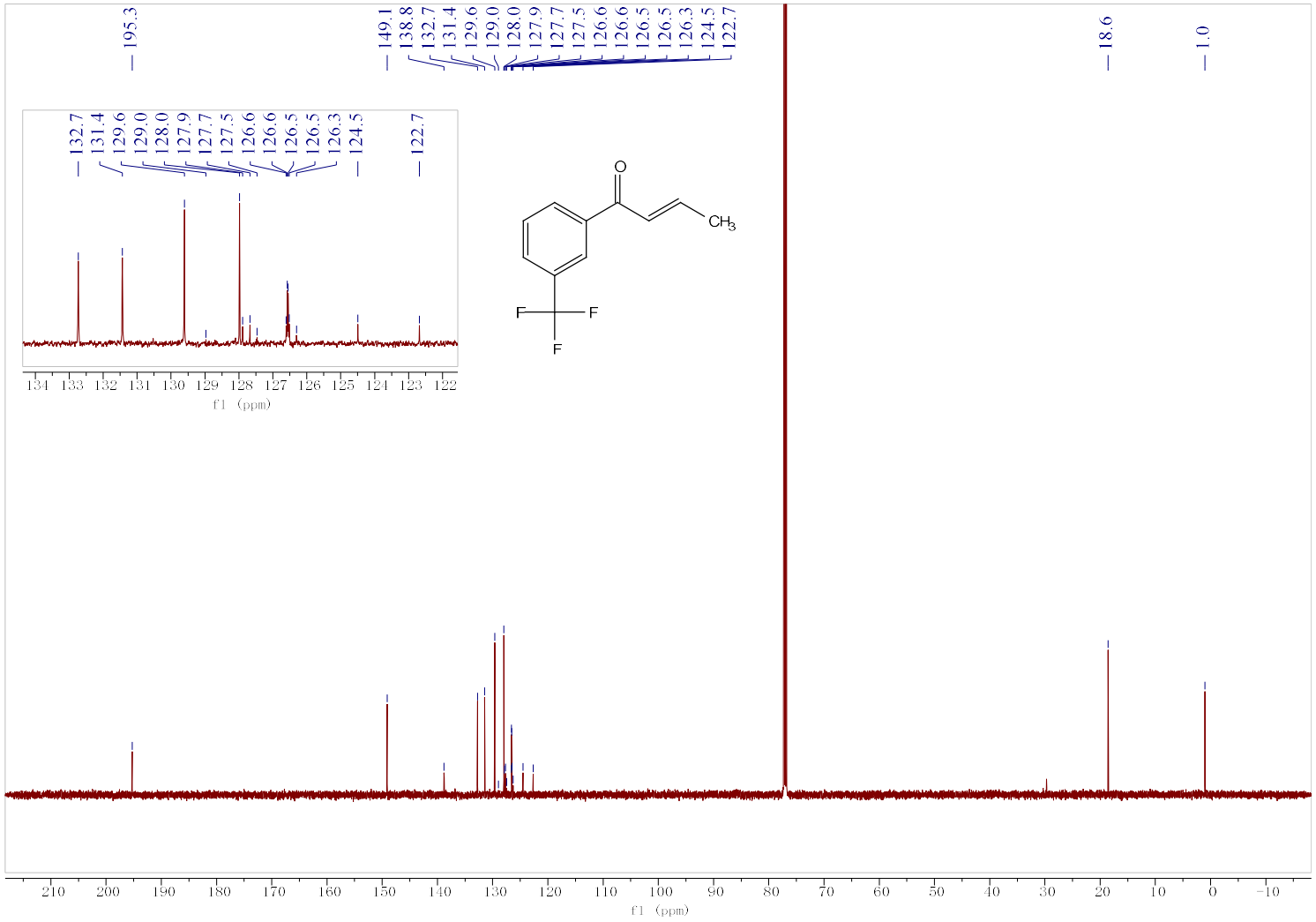
^{19}F NMR Spectrum of 2h (565 MHz, Chloroform-*d*)



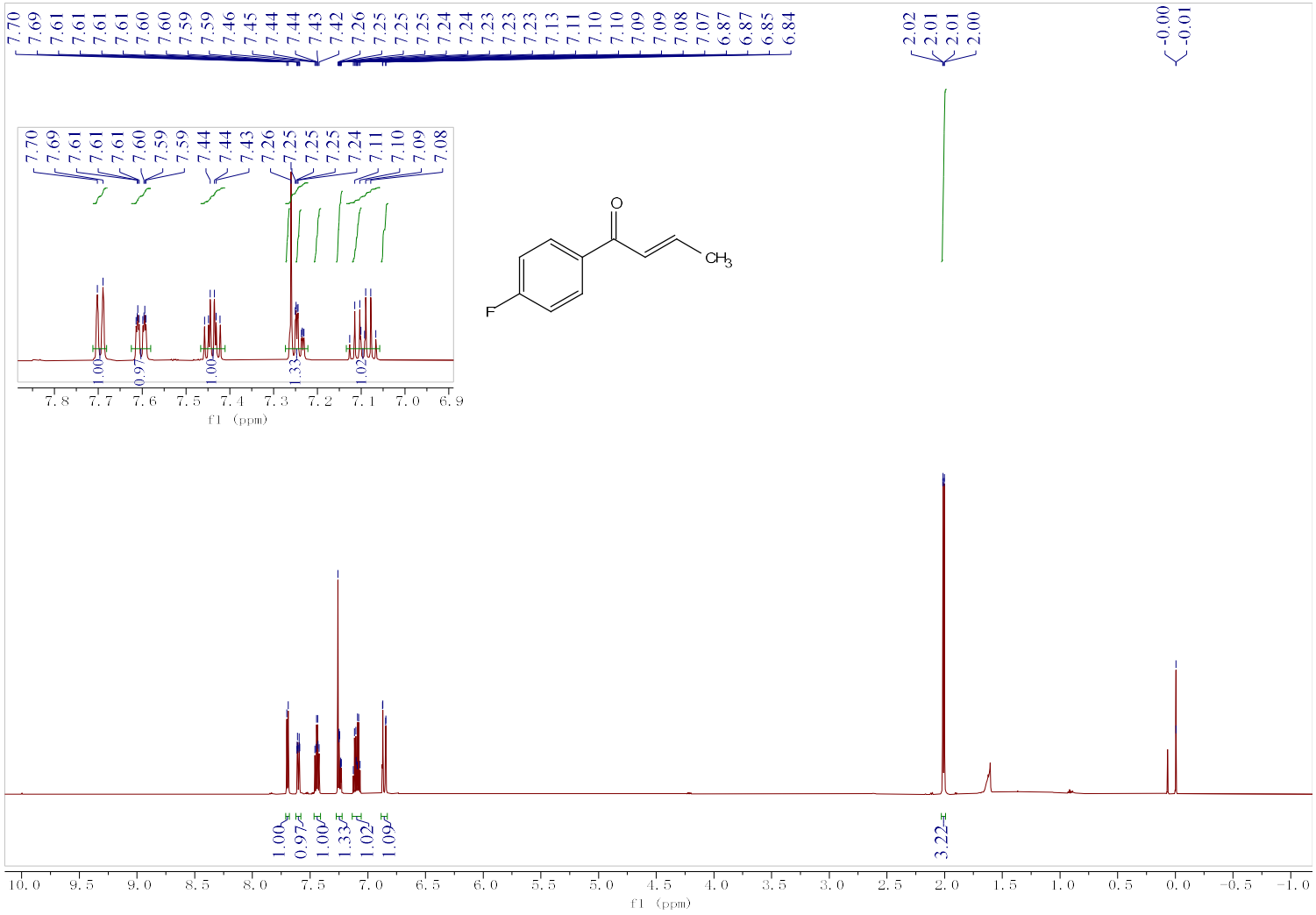
^{1}H NMR Spectrum of 2i (600 MHz, Chloroform-*d*)



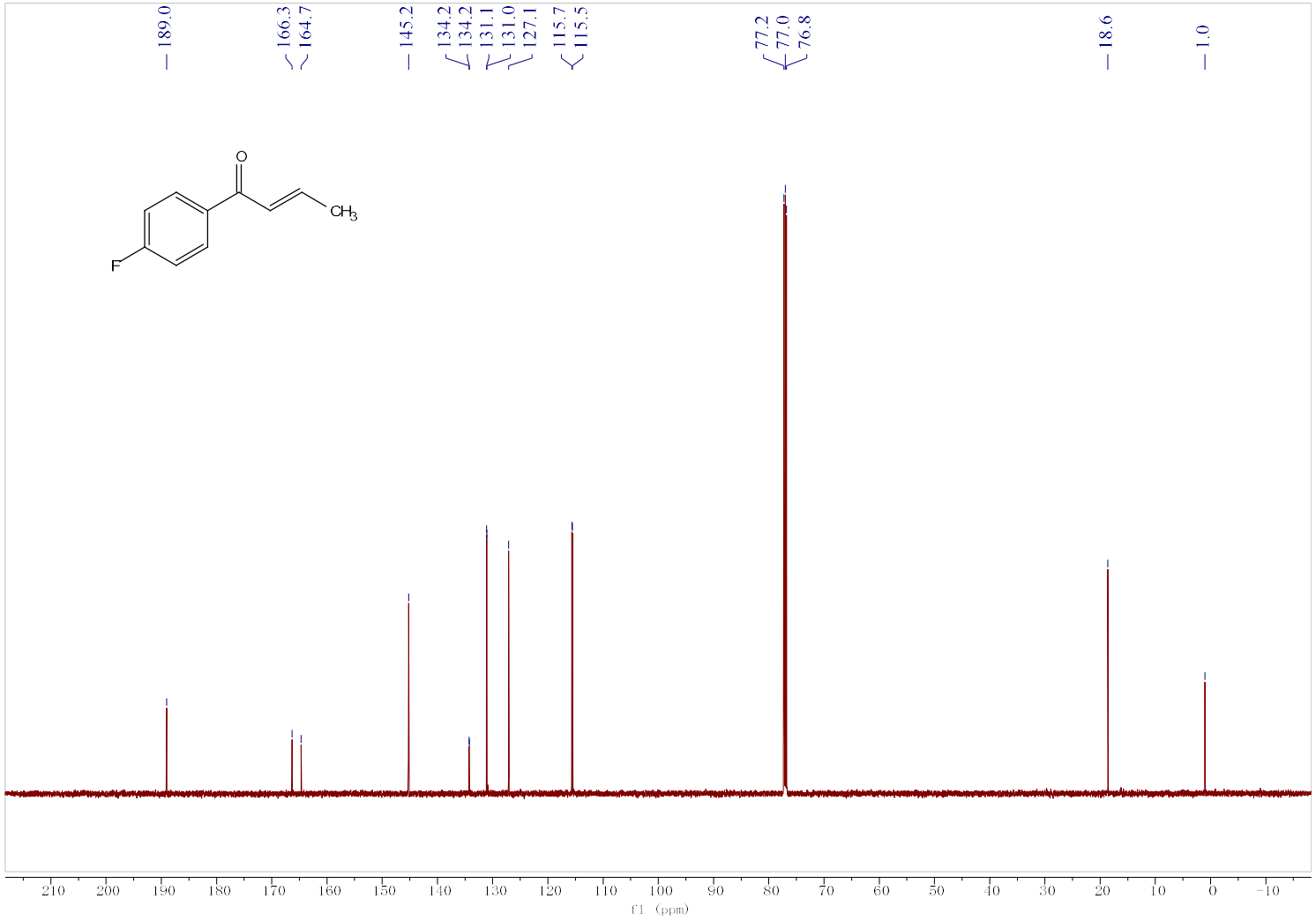
^{13}C NMR Spectrum of 2i (150 MHz, Chloroform-*d*)



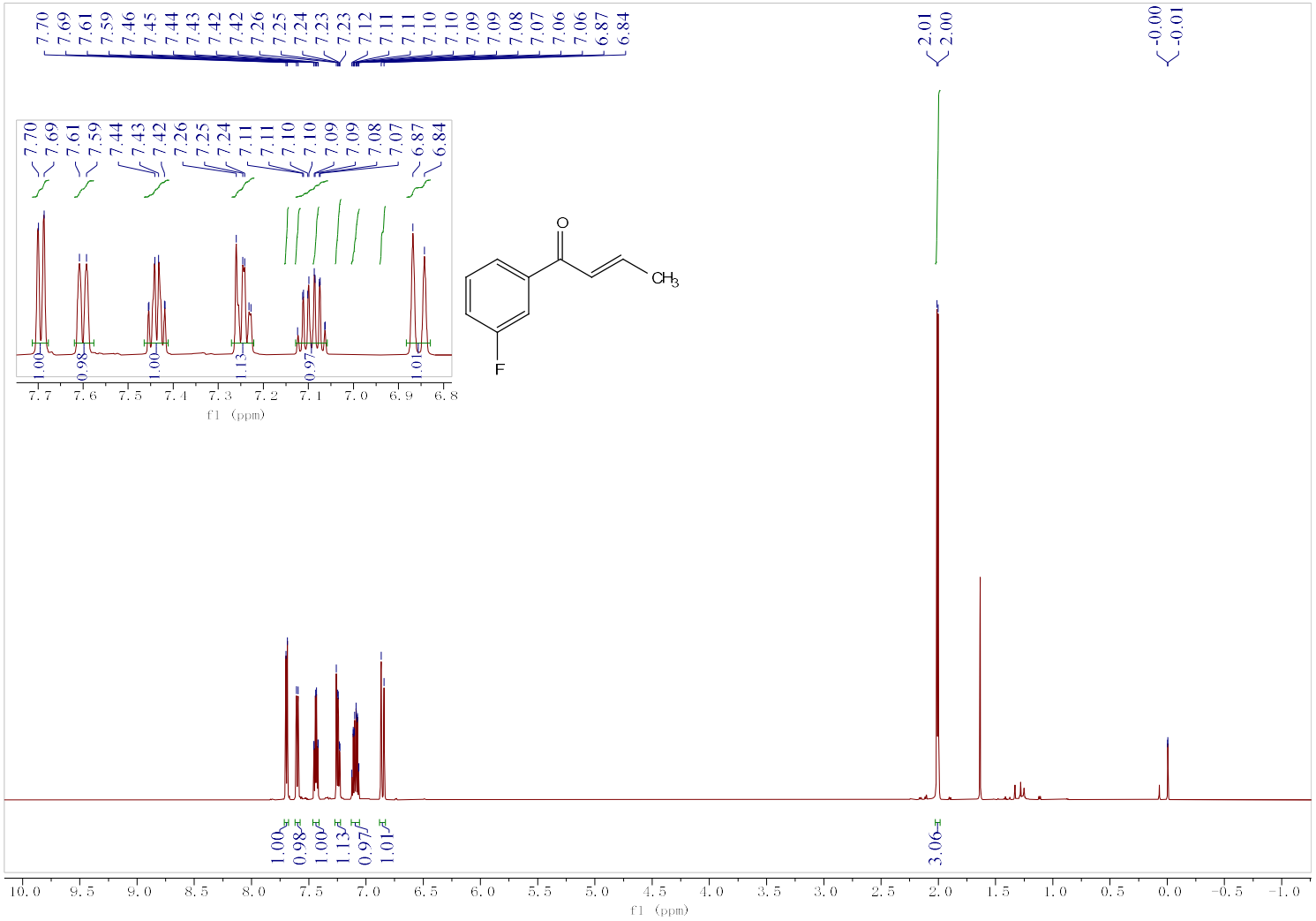
^{1}H NMR Spectrum of 2j (600 MHz, Chloroform-*d*)



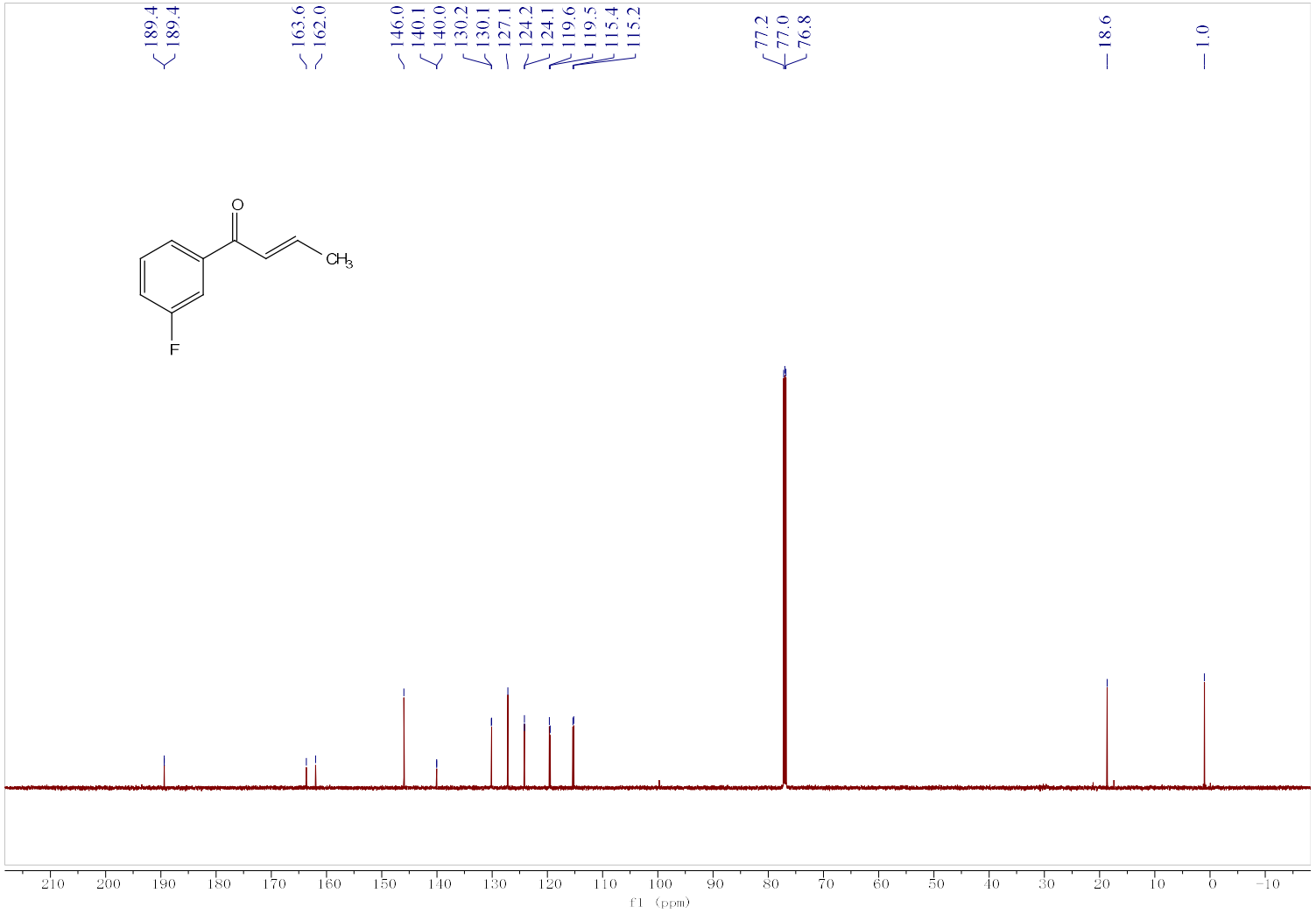
^{13}C NMR Spectrum of 2j (150 MHz, Chloroform-*d*)



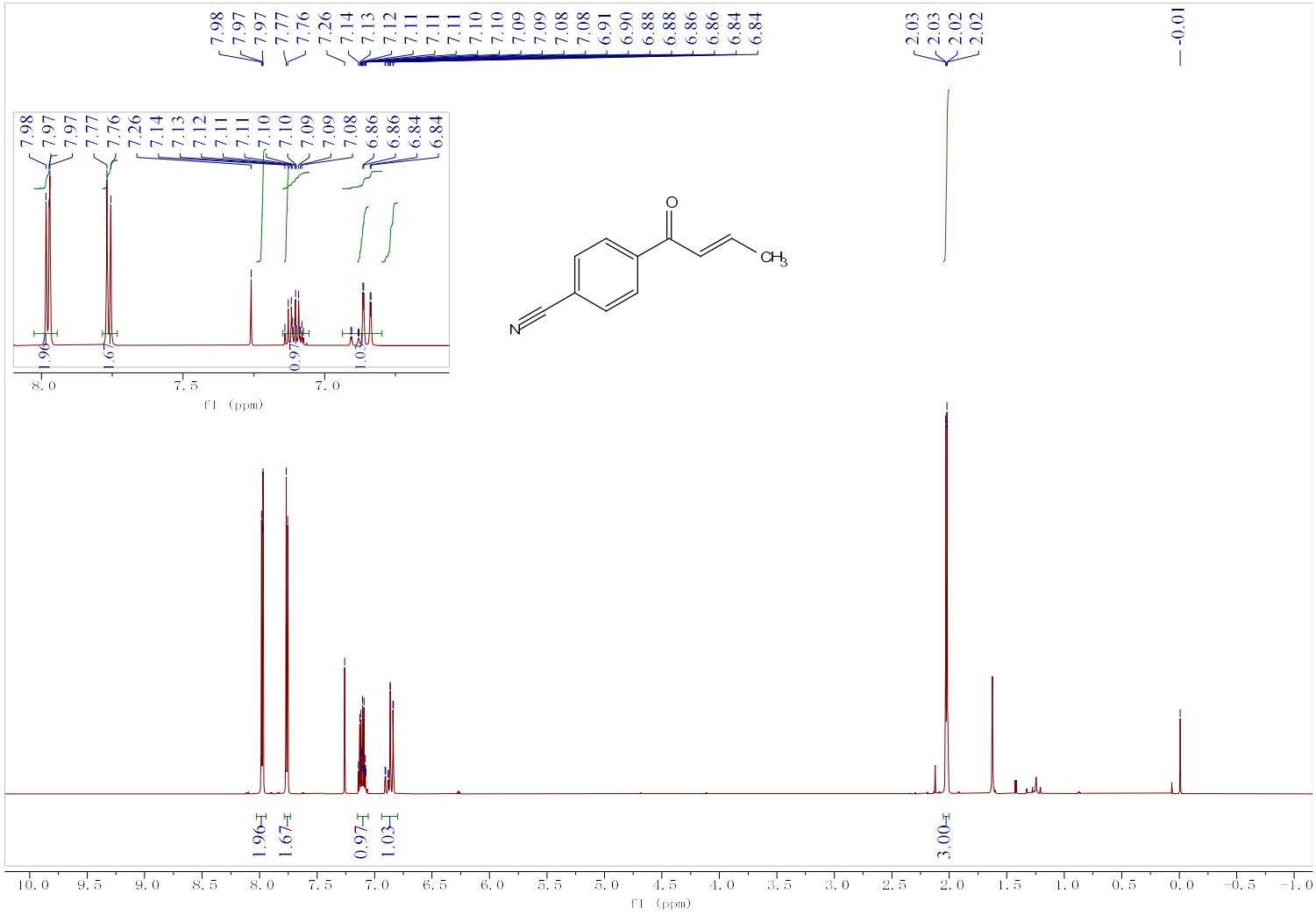
^{1}H NMR Spectrum of 2k (600 MHz, Chloroform-*d*)



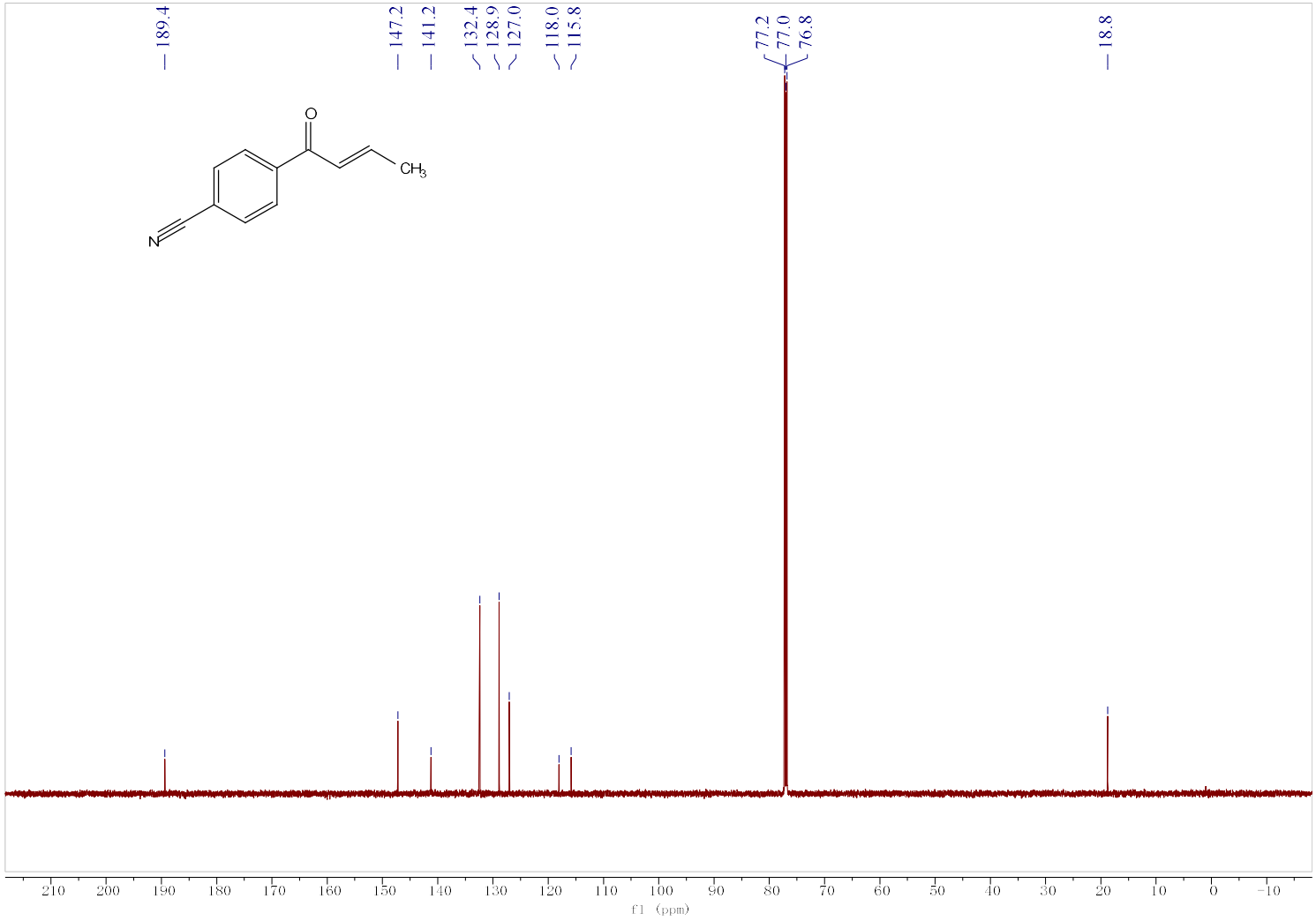
^{13}C NMR Spectrum of 2k (150 MHz, Chloroform-*d*)



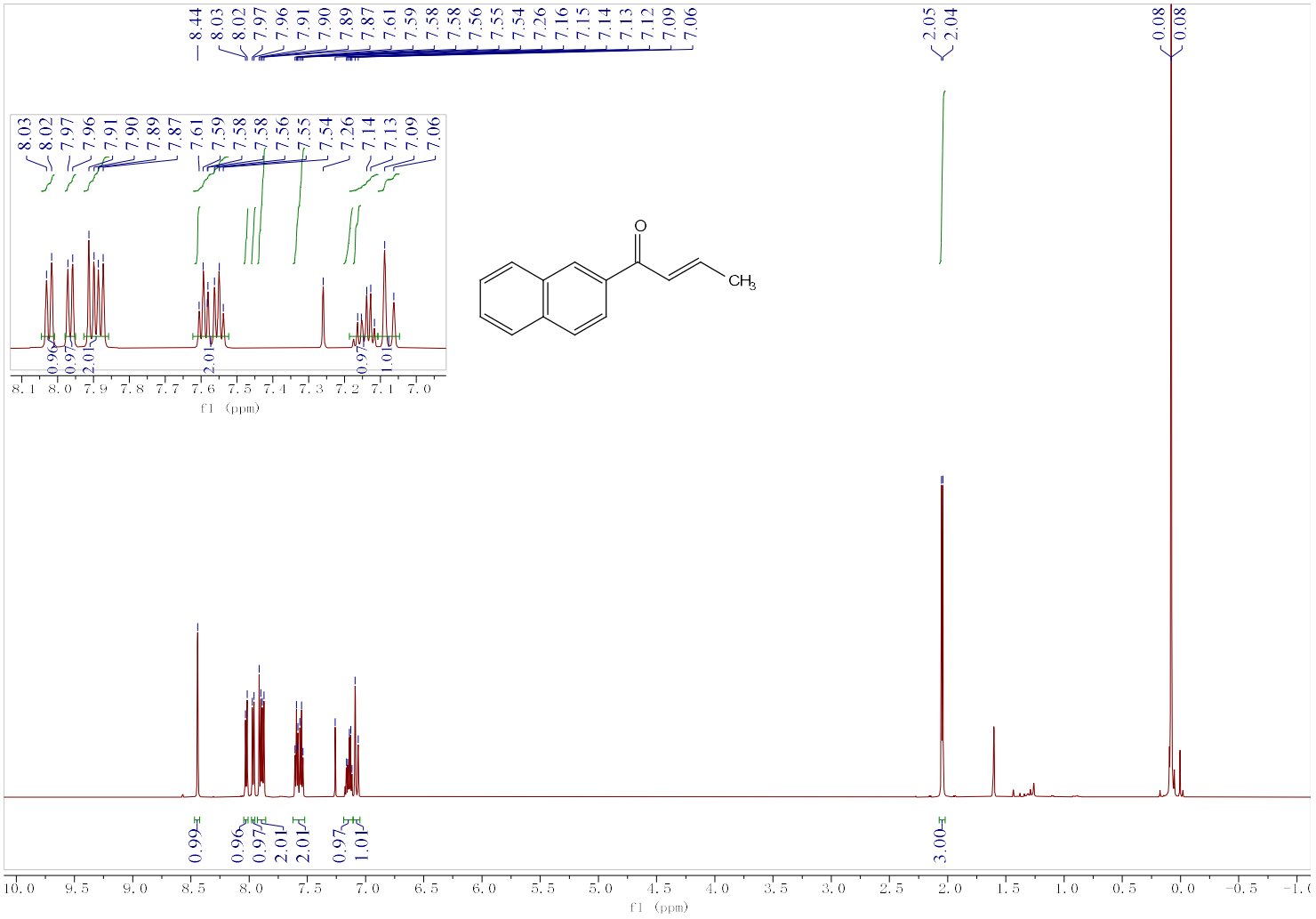
^{1}H NMR Spectrum of 2l (600 MHz, Chloroform-*d*)



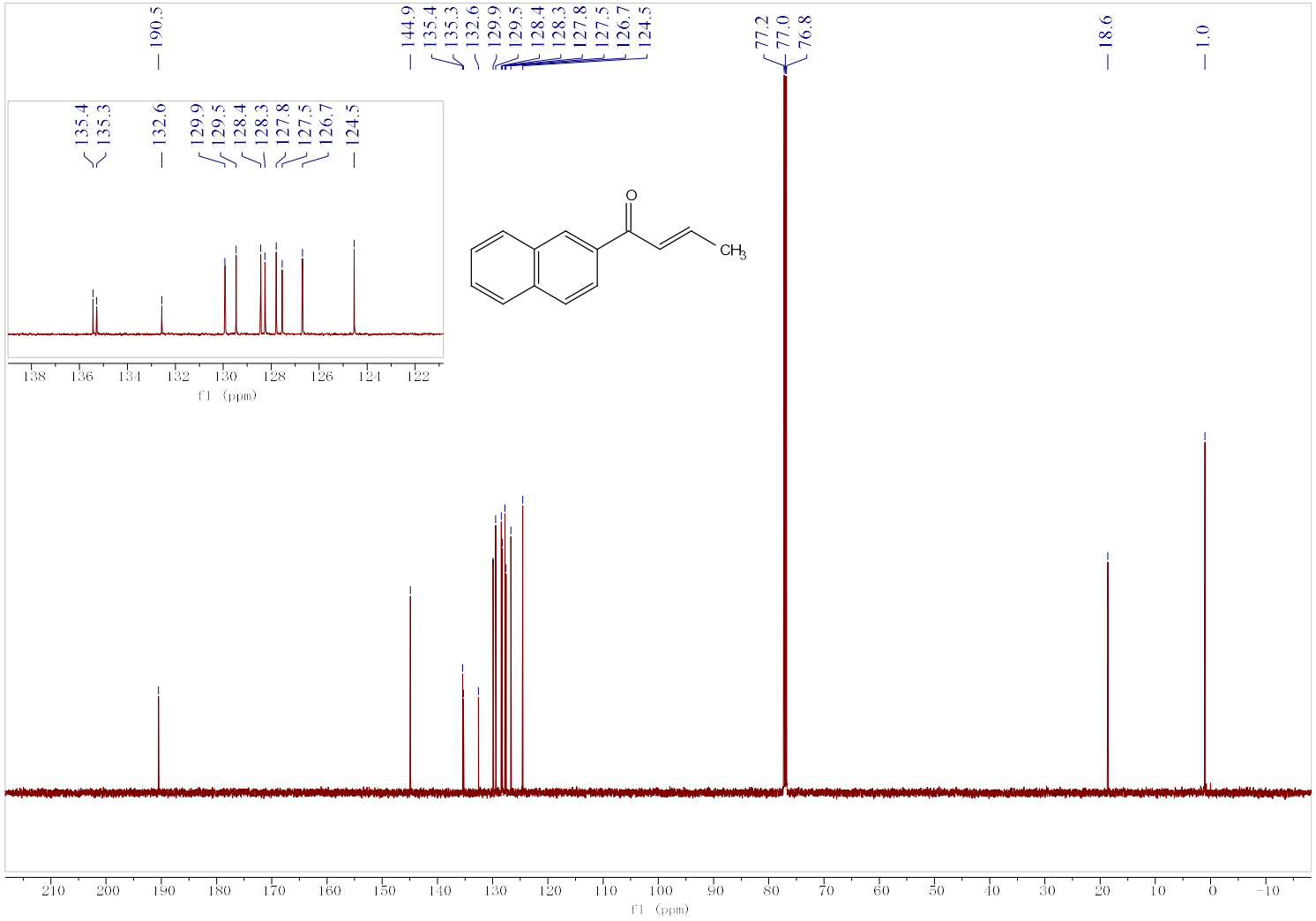
^{13}C NMR Spectrum of 2l (150 MHz, Chloroform-*d*)



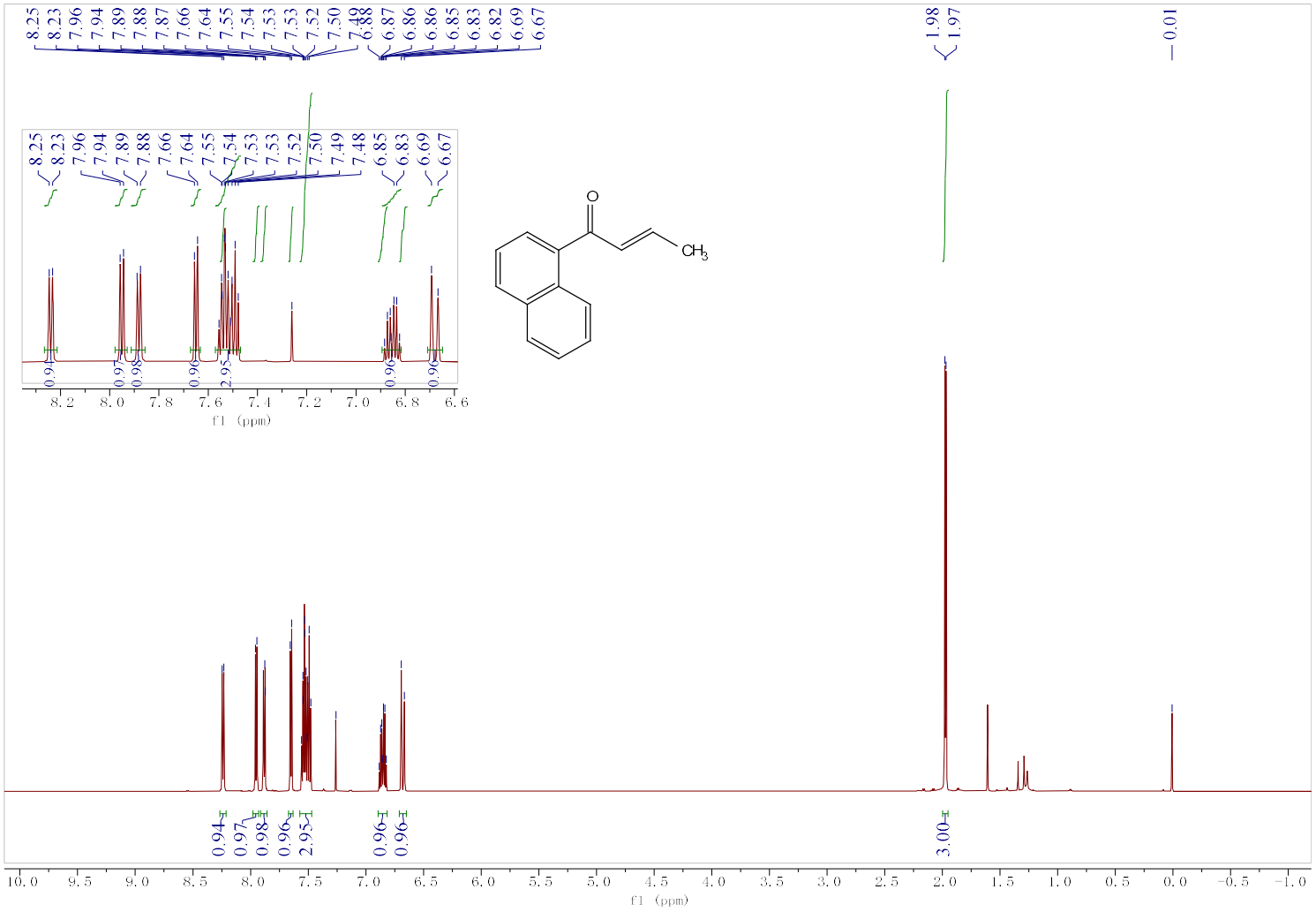
^{1}H NMR Spectrum of 2m (600 MHz, Chloroform-*d*)



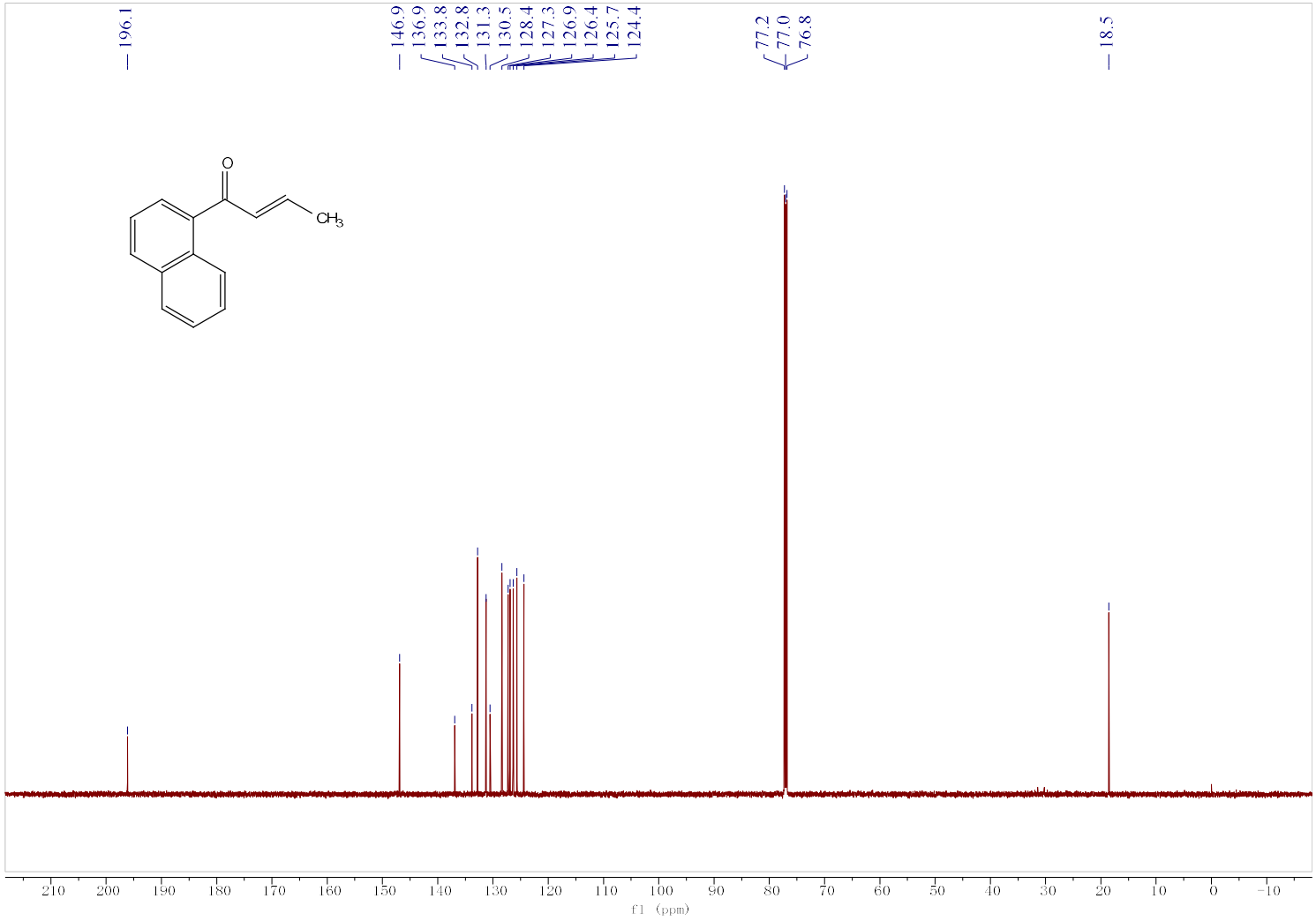
^{13}C NMR Spectrum of 2m (150 MHz, Chloroform-*d*)



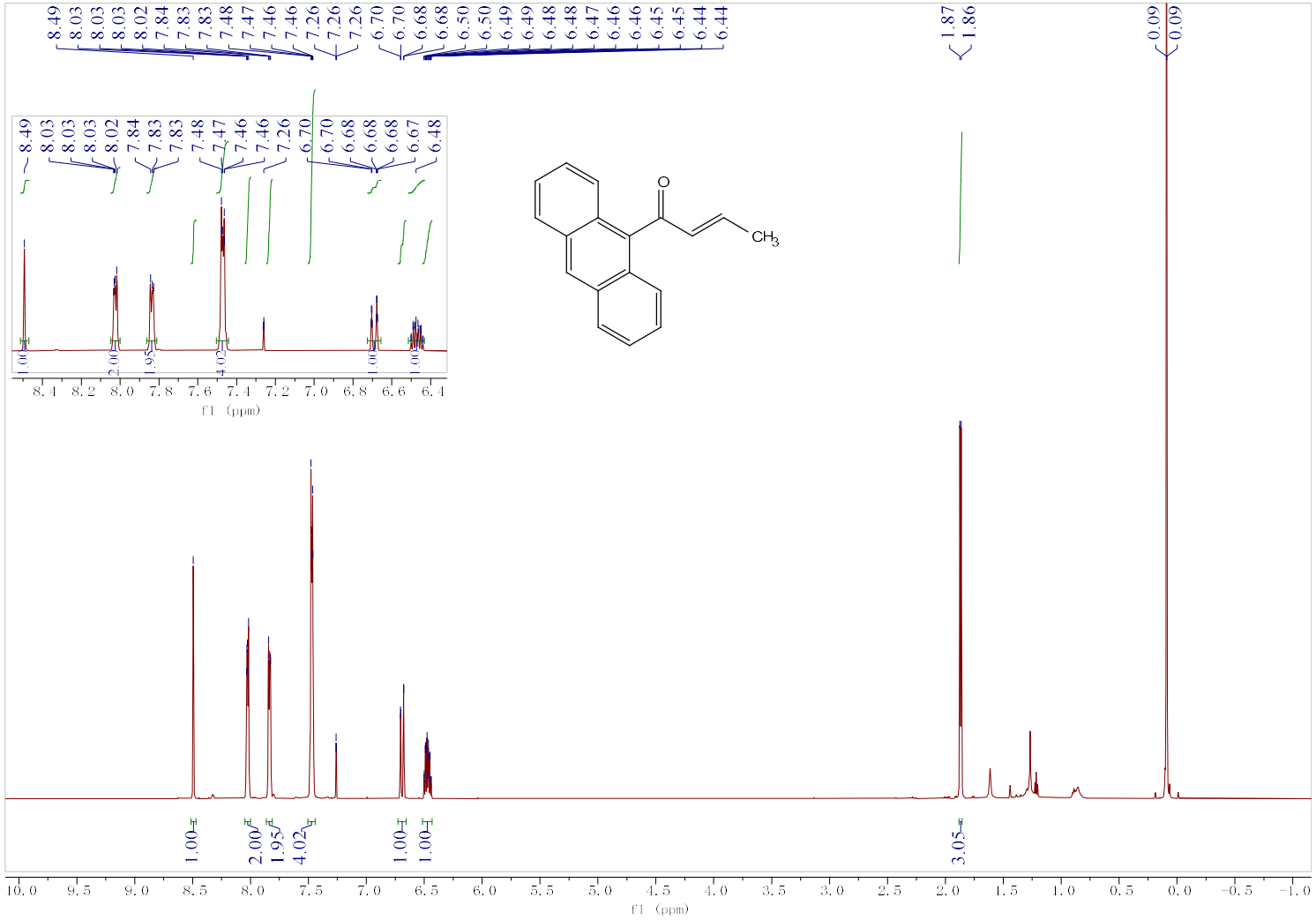
^{1}H NMR Spectrum of 2n (600 MHz, Chloroform-*d*)



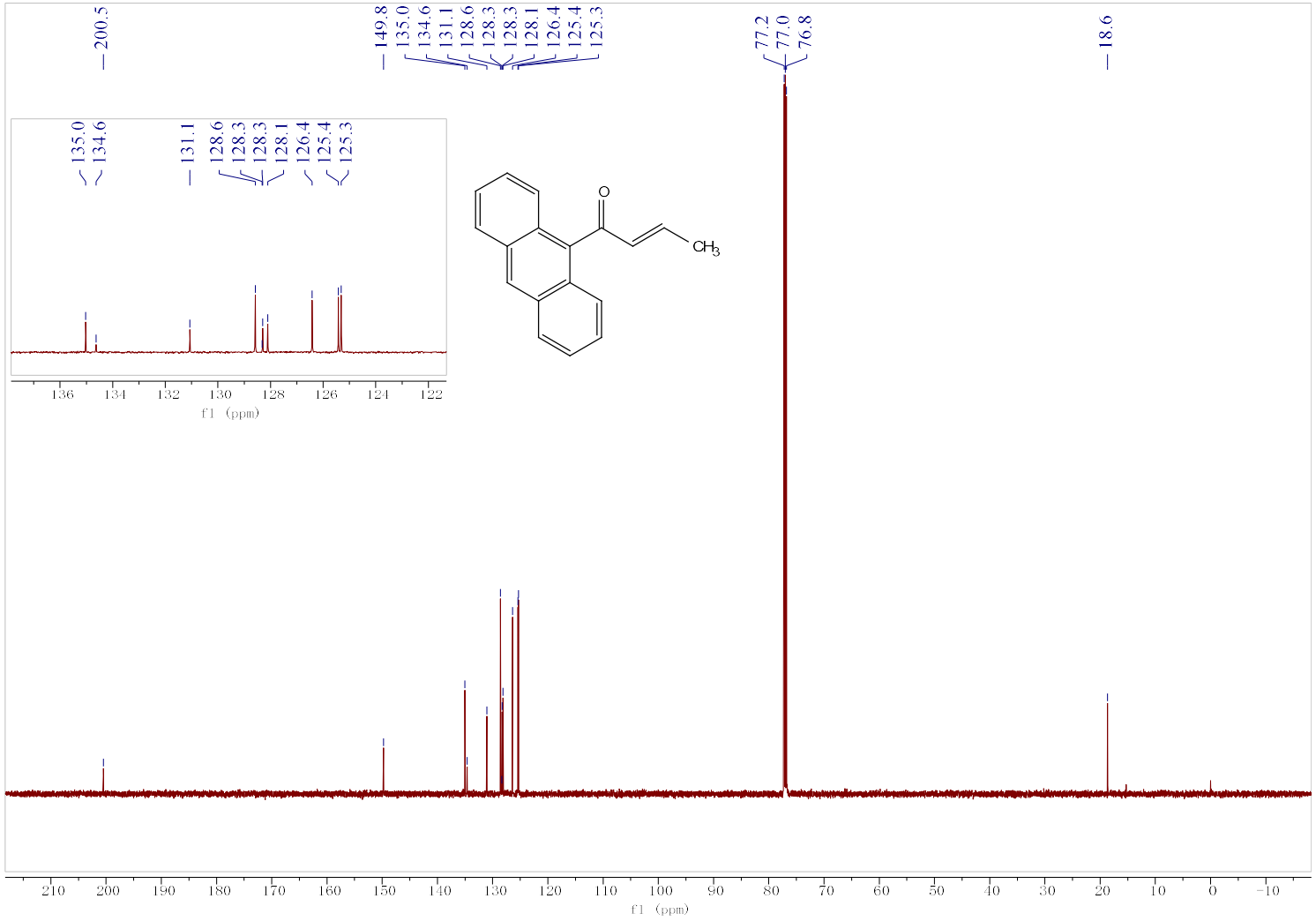
^{13}C NMR Spectrum of 2n (150 MHz, Chloroform-*d*)



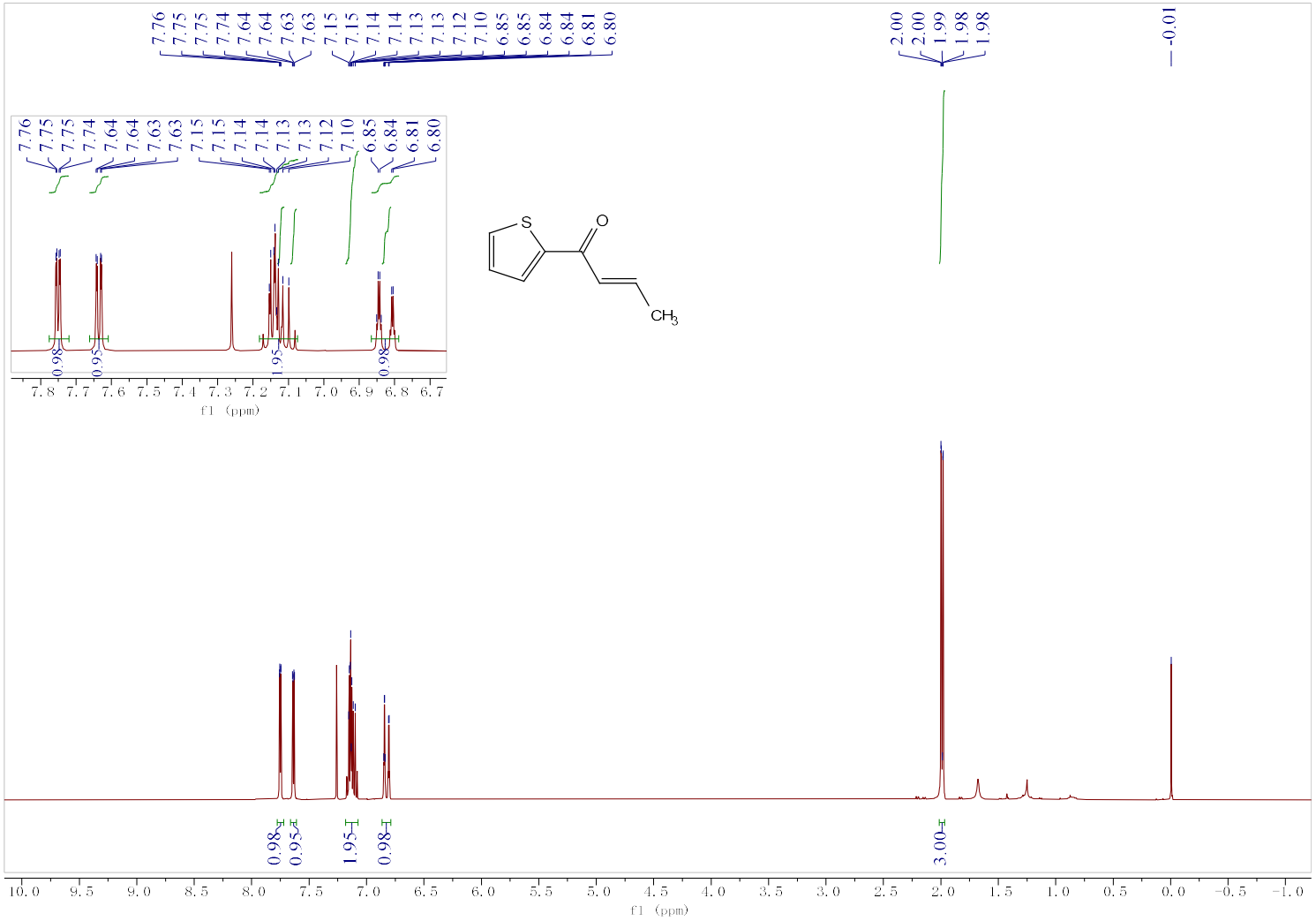
^{1}H NMR Spectrum of 2o (600 MHz, Chloroform-*d*)



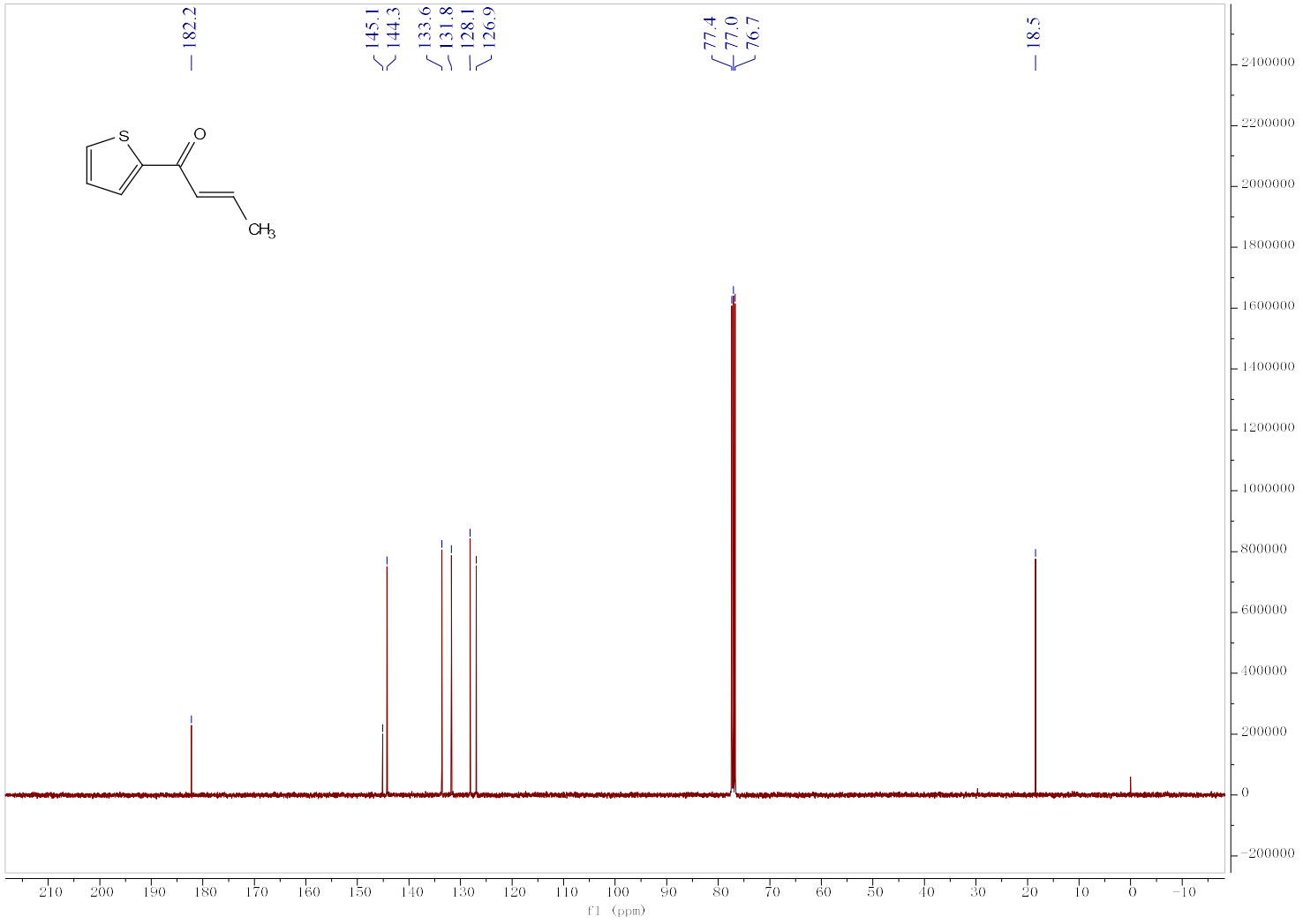
^{13}C NMR Spectrum of 2o (150 MHz, Chloroform-*d*)



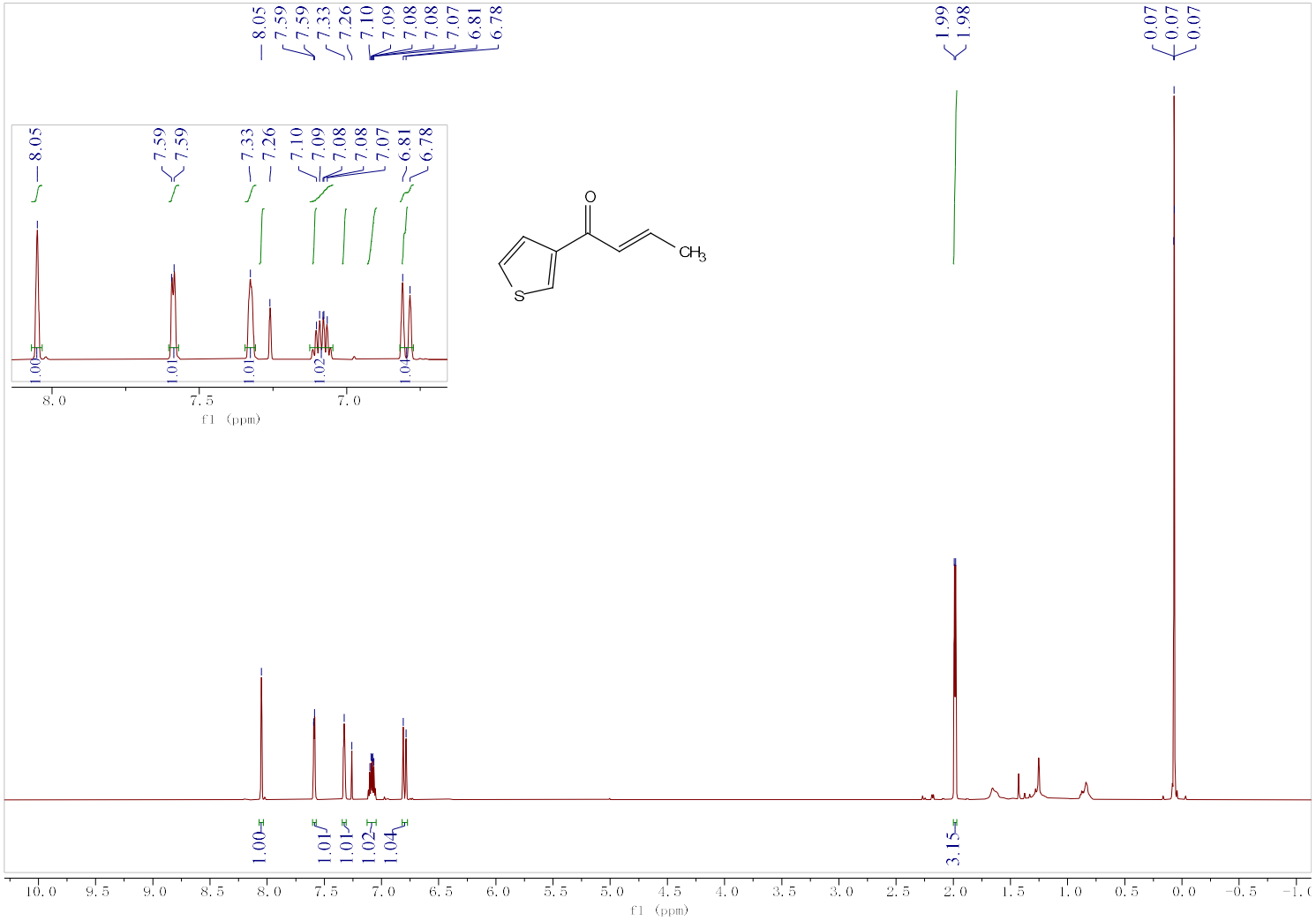
^{1}H NMR Spectrum of 2p (600 MHz, Chloroform-*d*)



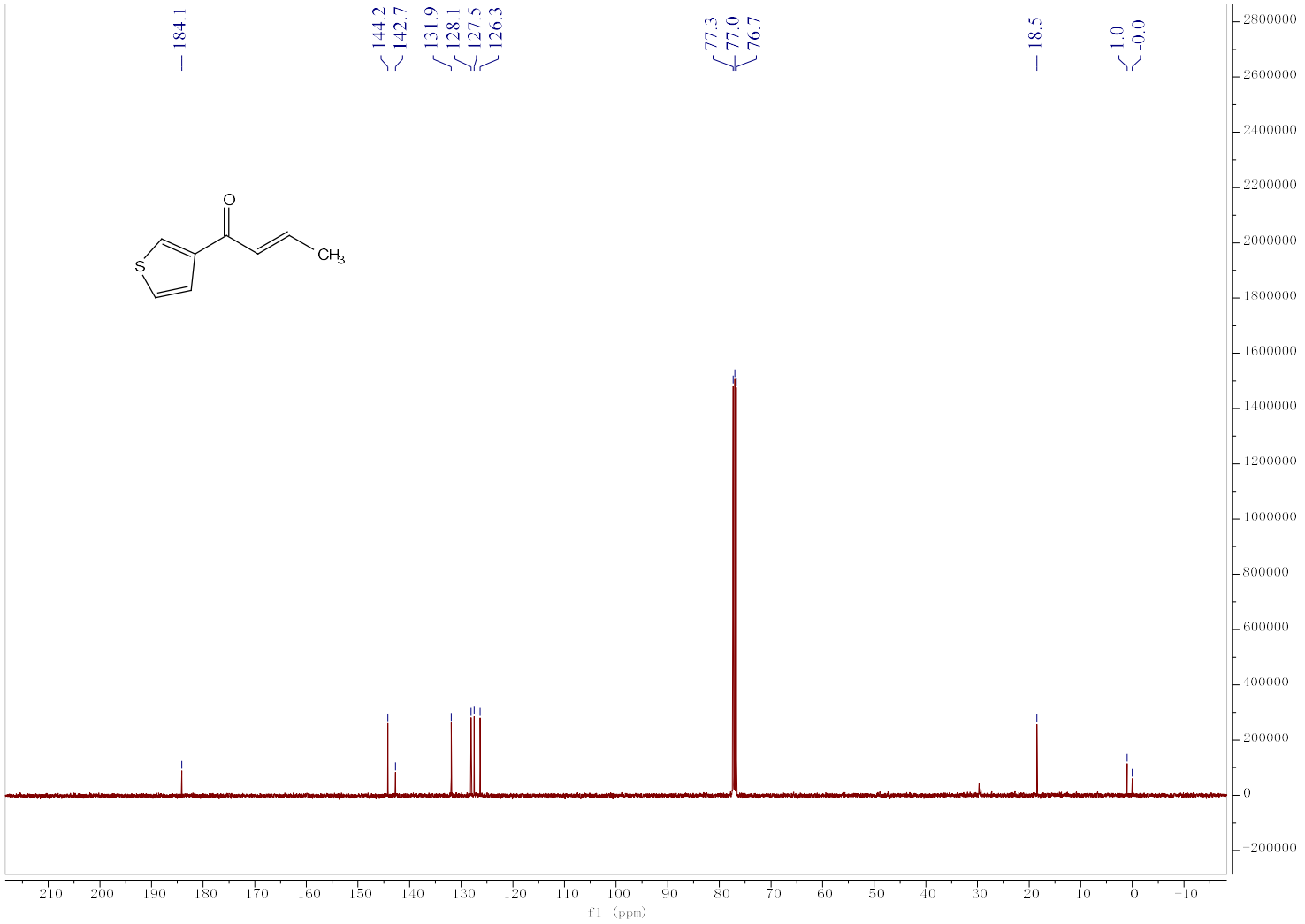
^{13}C NMR Spectrum of 2p (150 MHz, Chloroform-*d*)



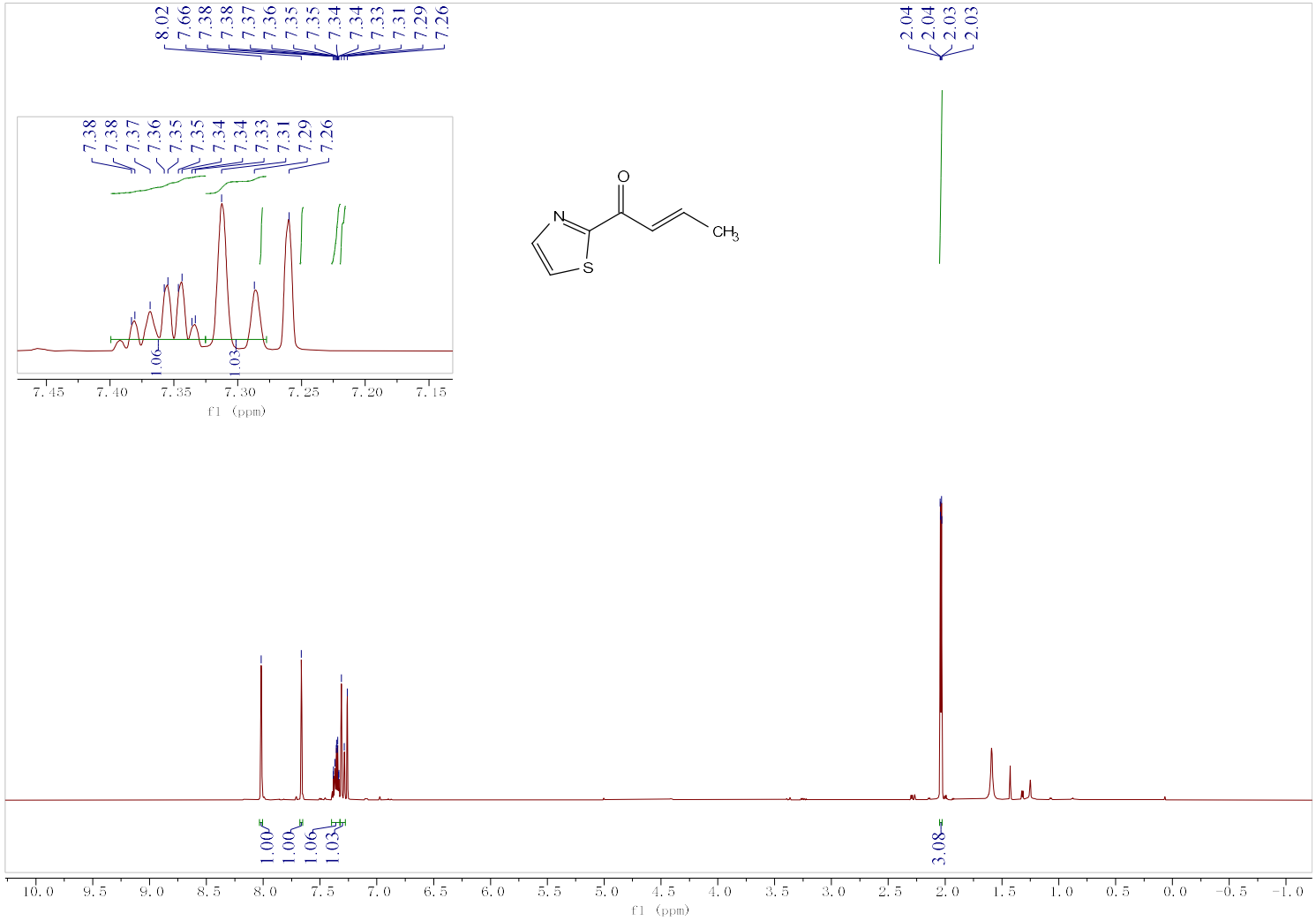
^{1}H NMR Spectrum of 2q (600 MHz, Chloroform-*d*)



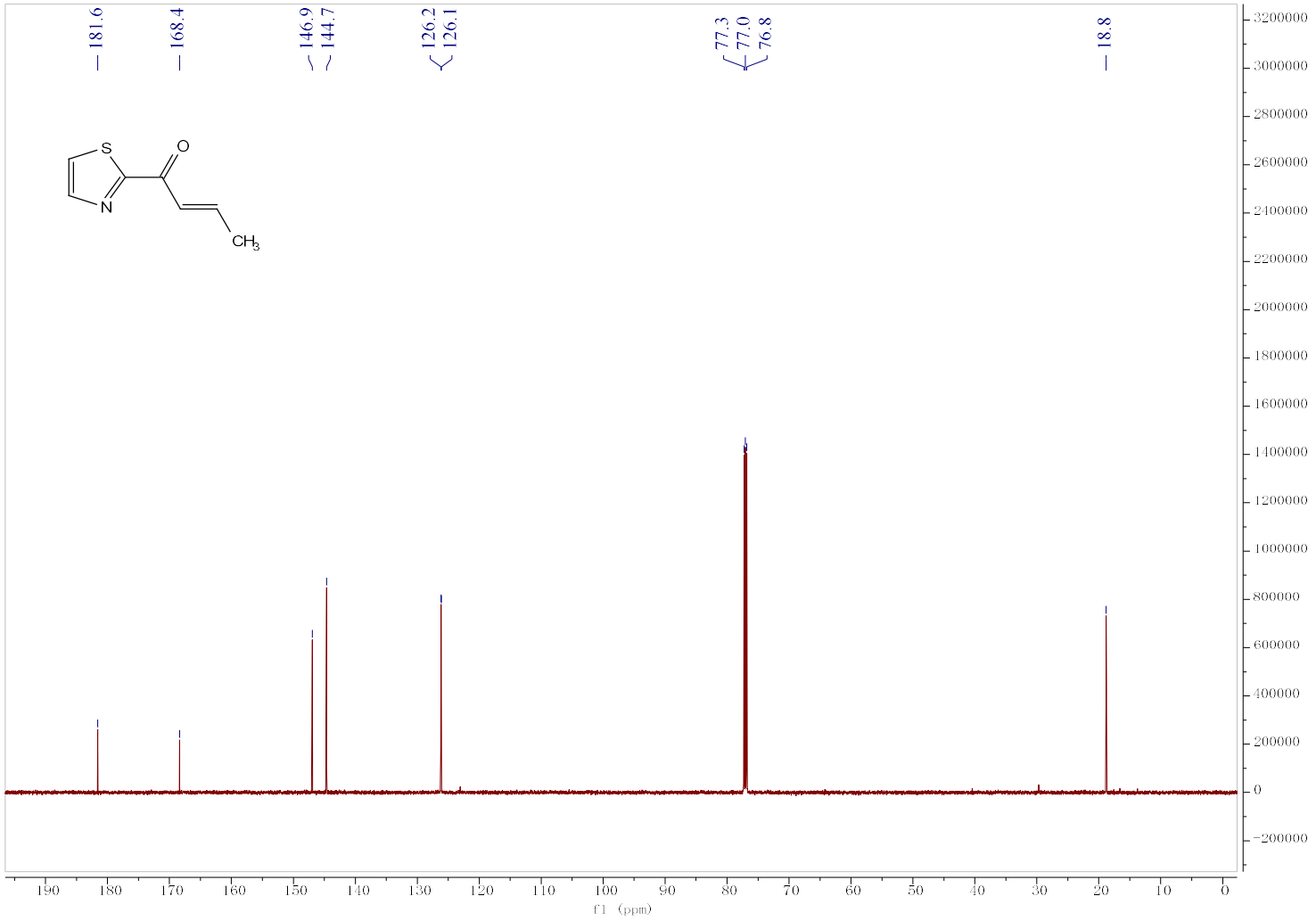
^{13}C NMR Spectrum of 2q (150 MHz, Chloroform-*d*)



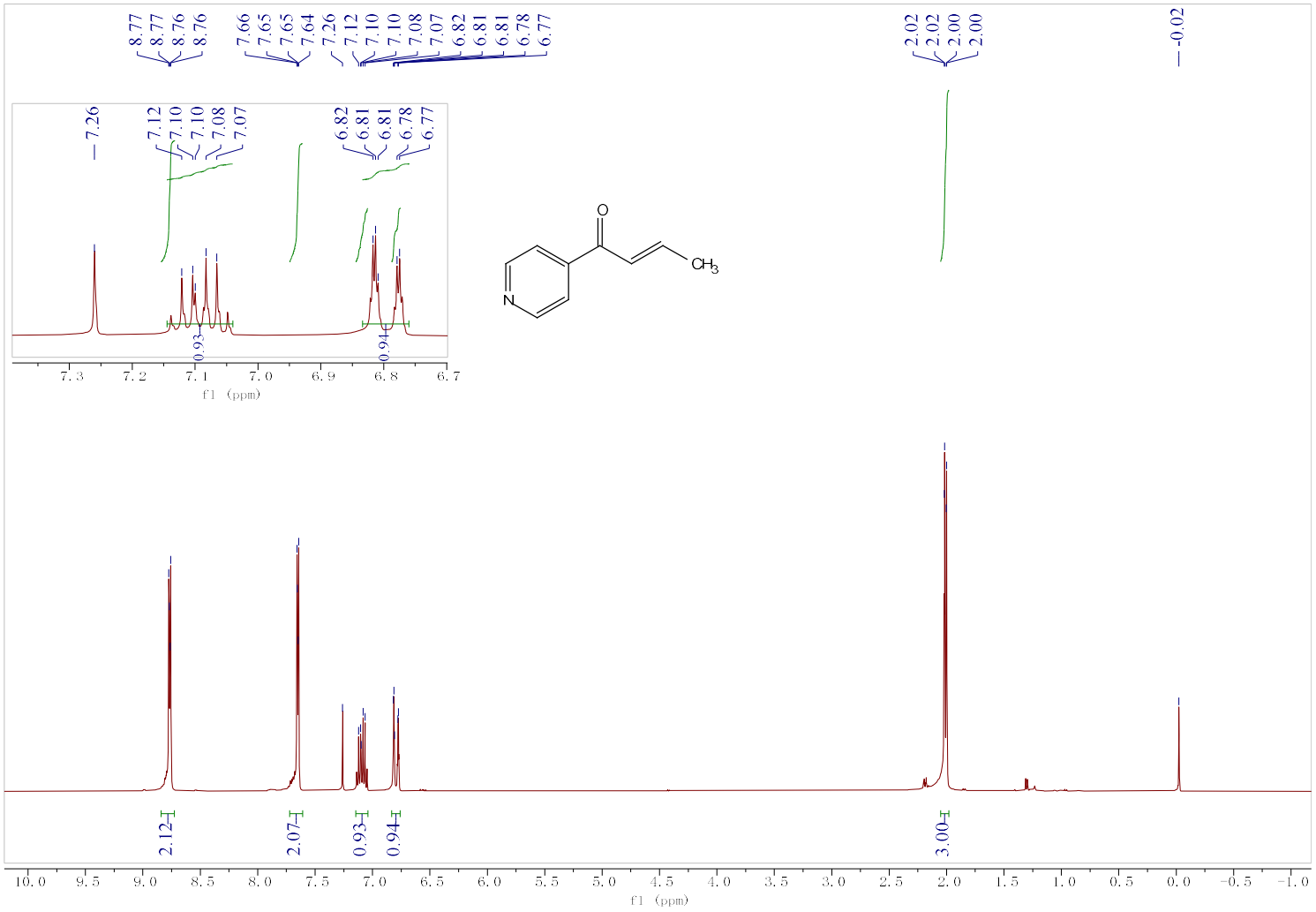
^{1}H NMR Spectrum of 2r (600 MHz, Chloroform-*d*)



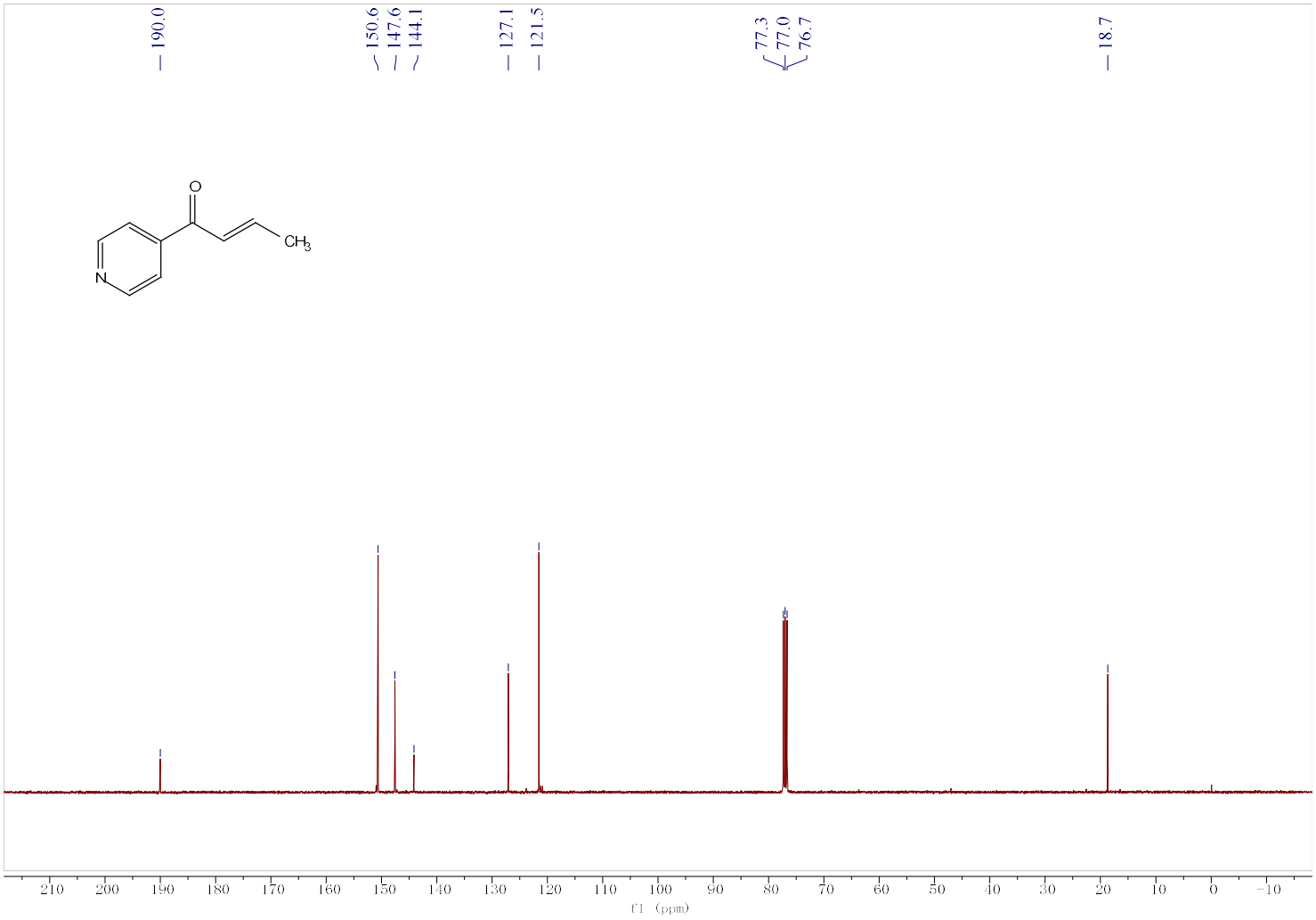
^{13}C NMR Spectrum of 2r (150 MHz, Chloroform-*d*)



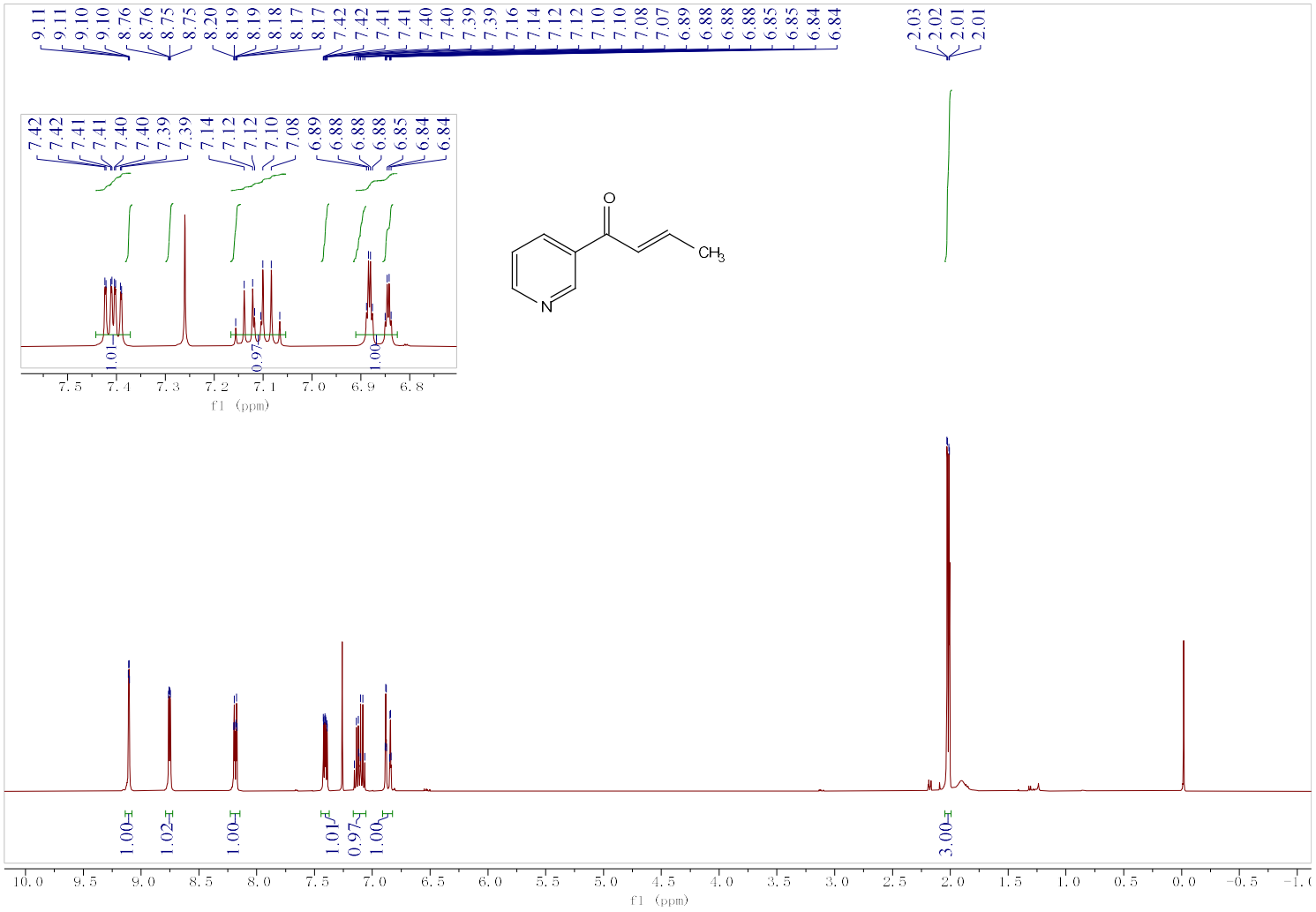
^{1}H NMR Spectrum of 2s (600 MHz, Chloroform-*d*)



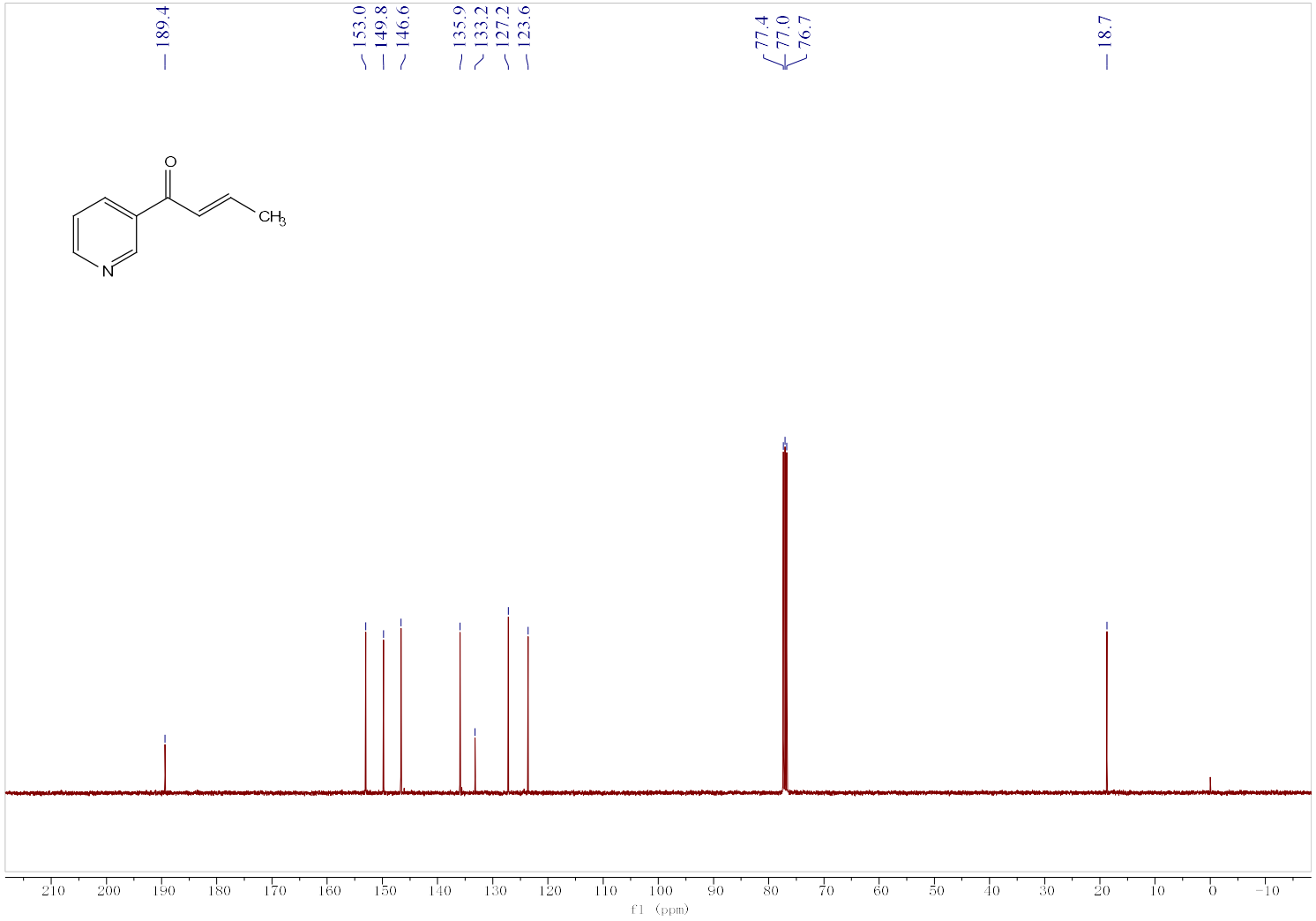
^{13}C NMR Spectrum of 2s (150 MHz, Chloroform-*d*)



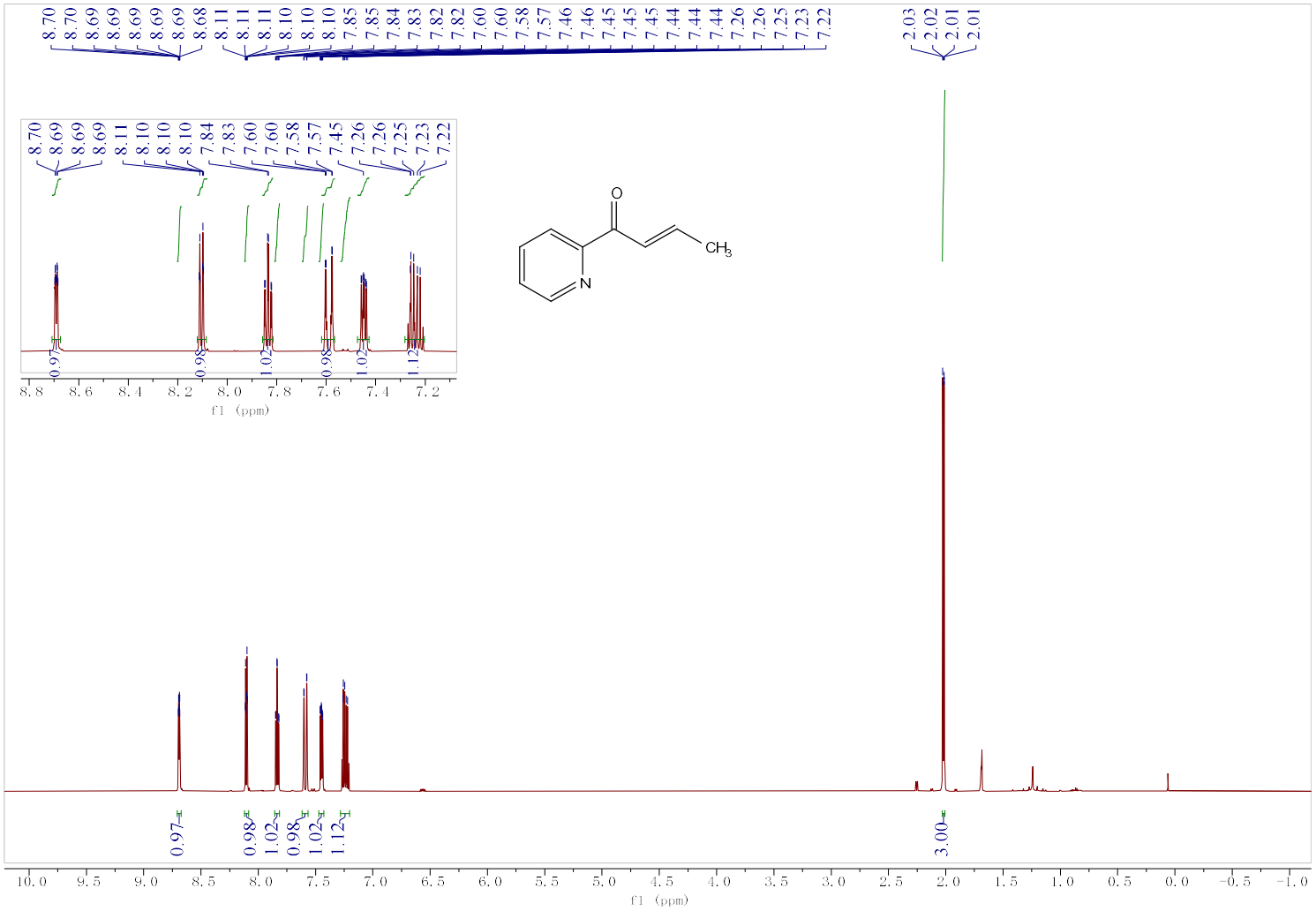
^{1}H NMR Spectrum of 2t (600 MHz, Chloroform-*d*)



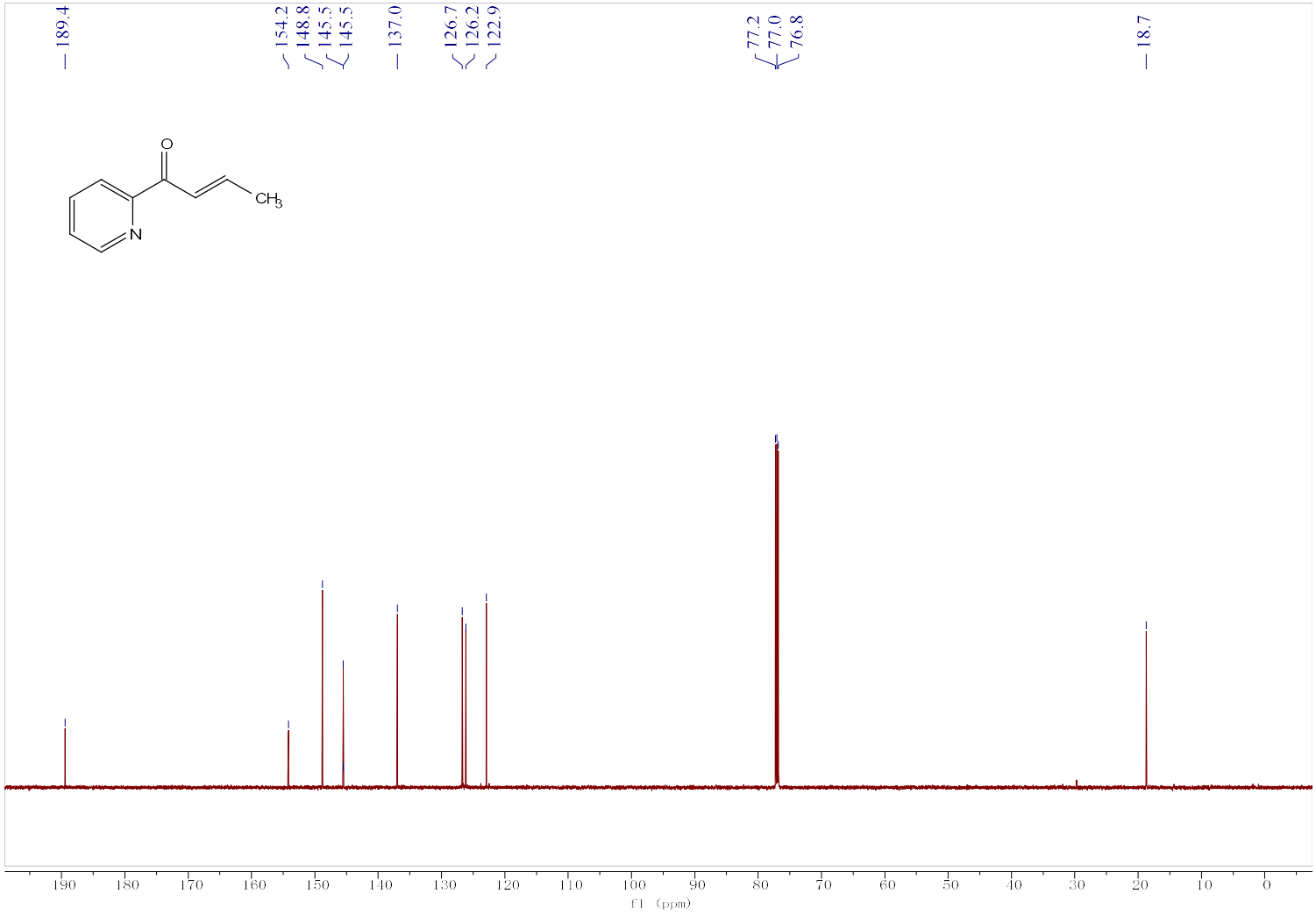
^{13}C NMR Spectrum of 2t (150 MHz, Chloroform-*d*)



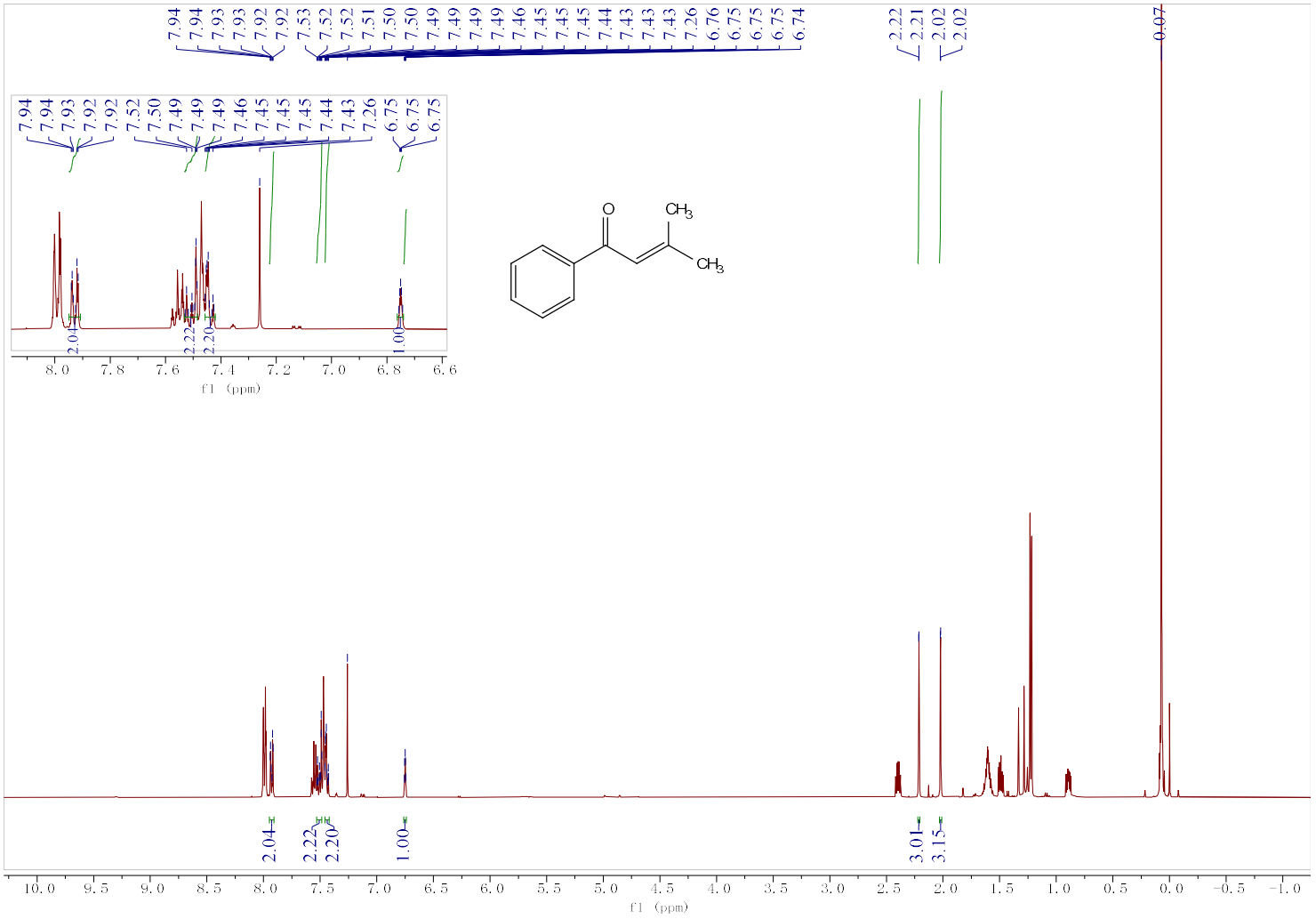
^{1}H NMR Spectrum of 2u (600 MHz, Chloroform-*d*)



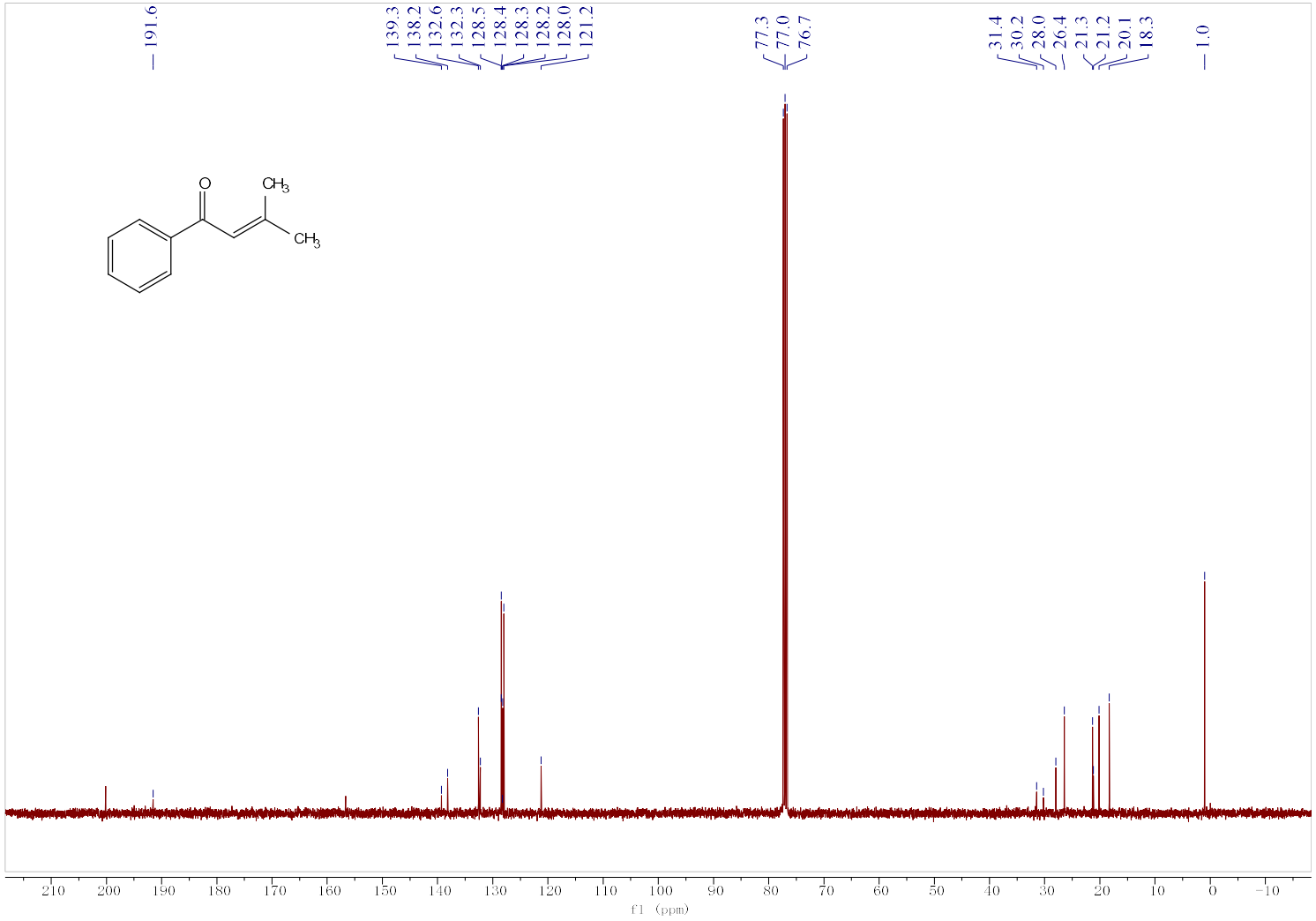
^{13}C NMR Spectrum of 2u (150 MHz, Chloroform-*d*)



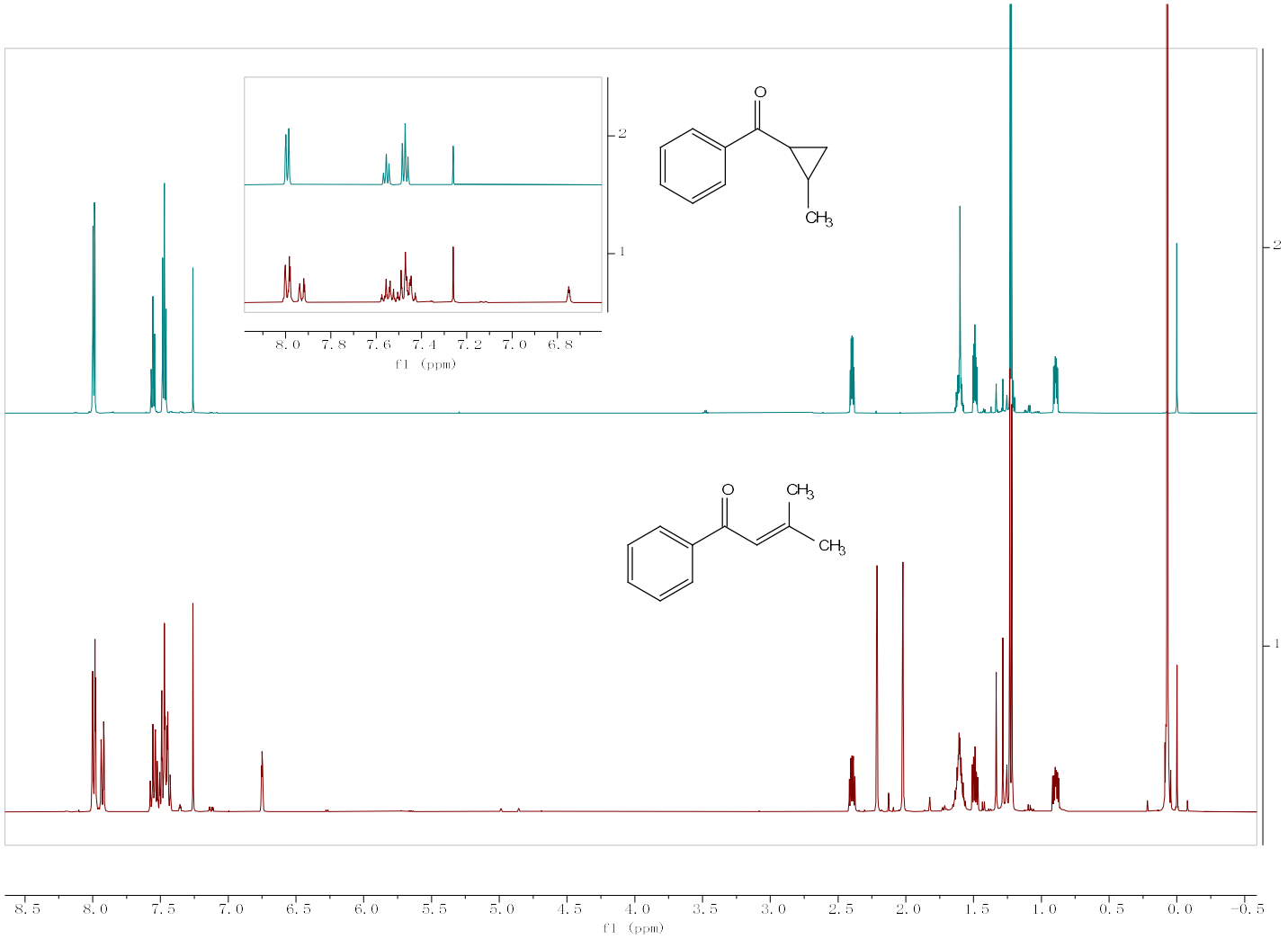
^{1}H NMR Spectrum of 4a (400 MHz, Chloroform-*d*)



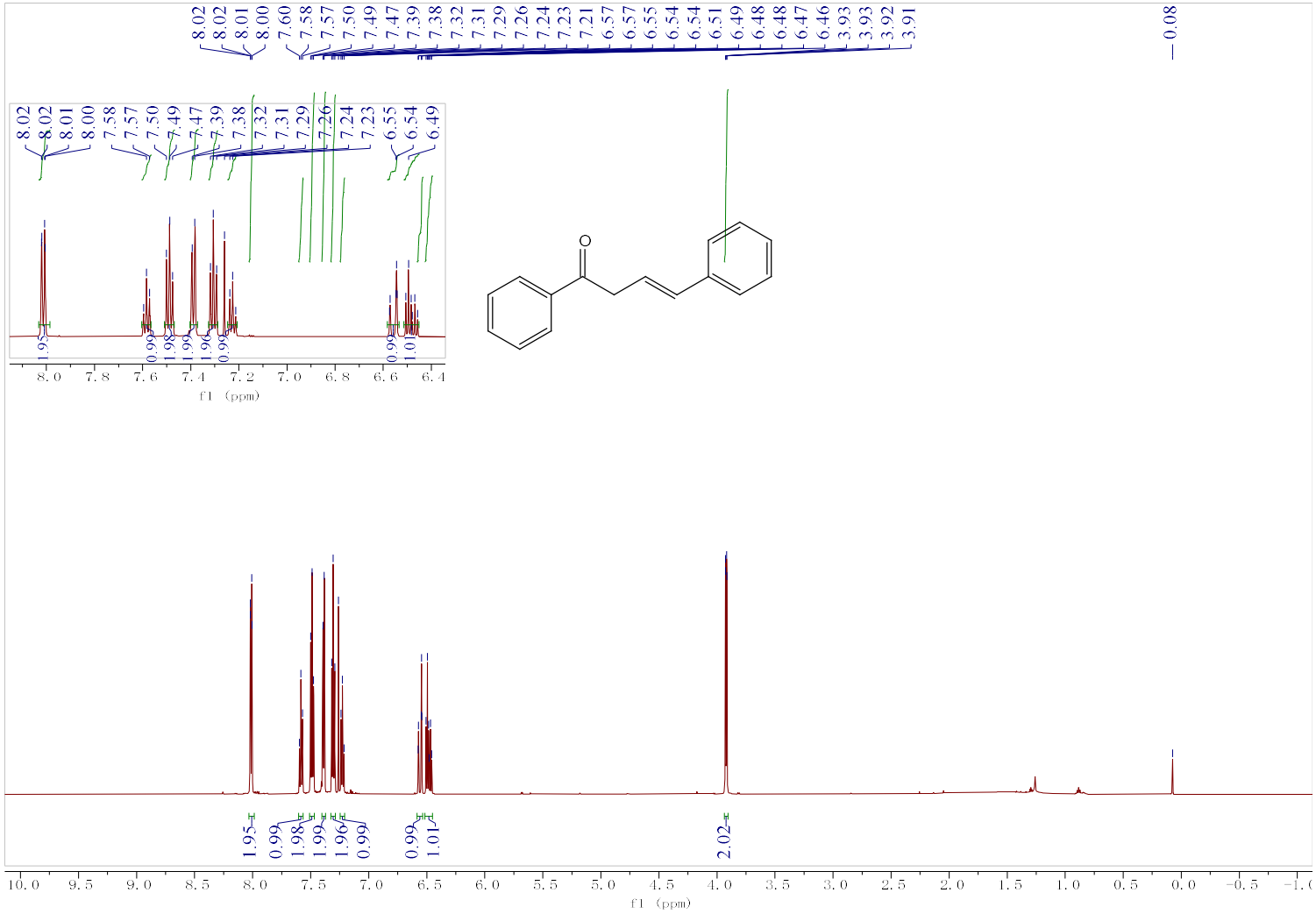
^{13}C NMR Spectrum of 4a (100 MHz, Chloroform-*d*)



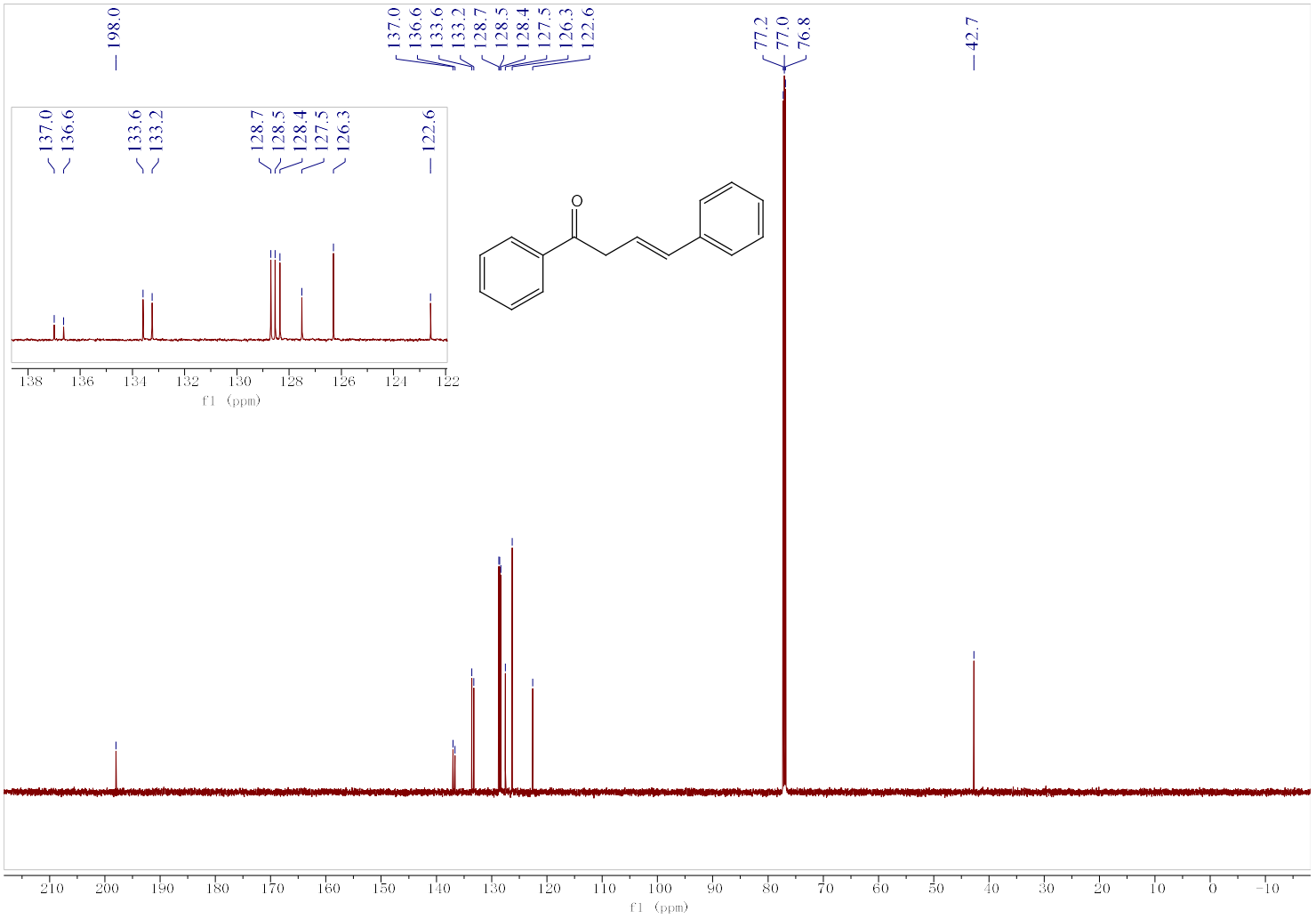
^{1}H NMR Spectrum between 3a and 4a (400 MHz, Chloroform-*d*)



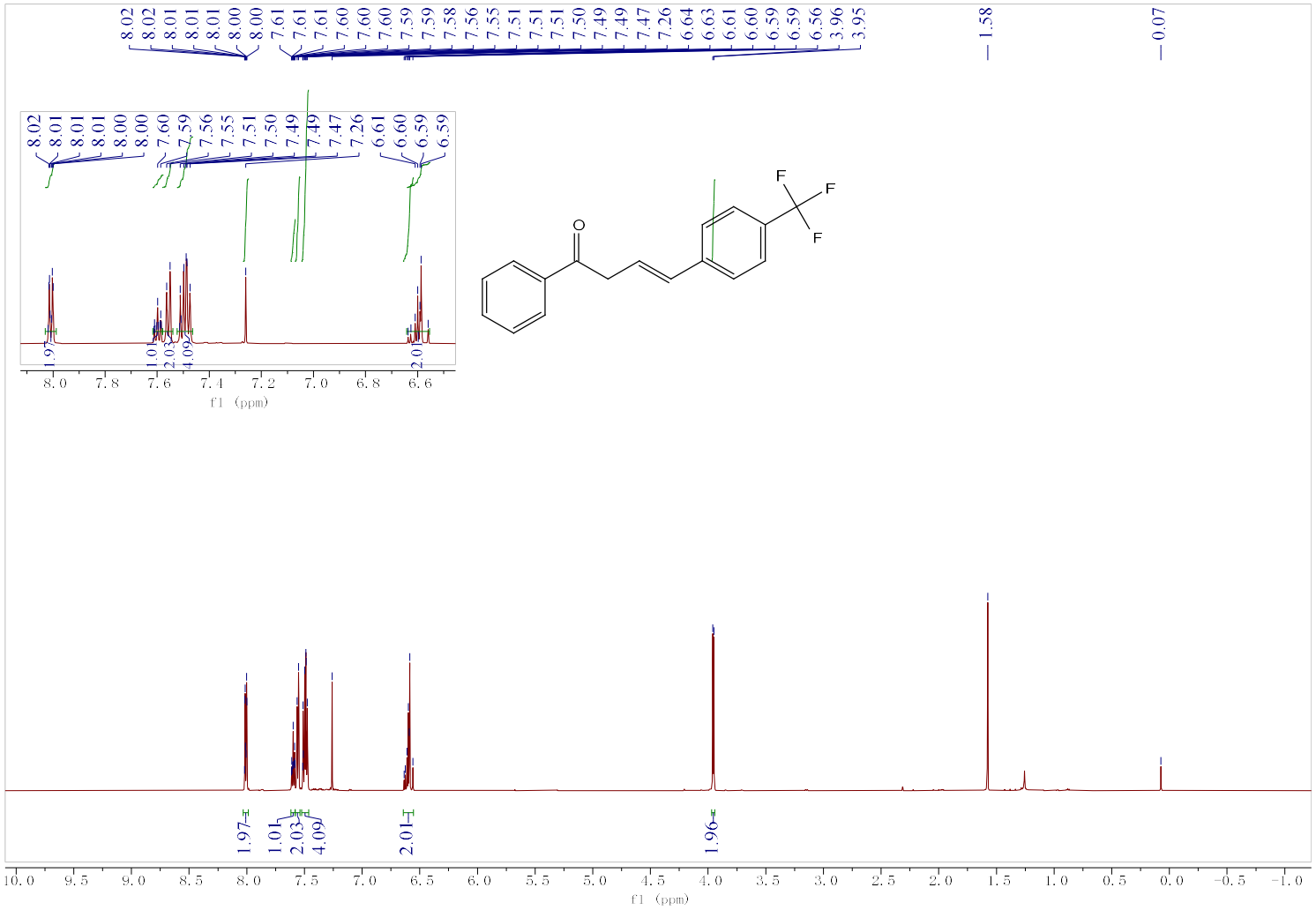
^{1}H NMR Spectrum of 4b (600 MHz, Chloroform-*d*)



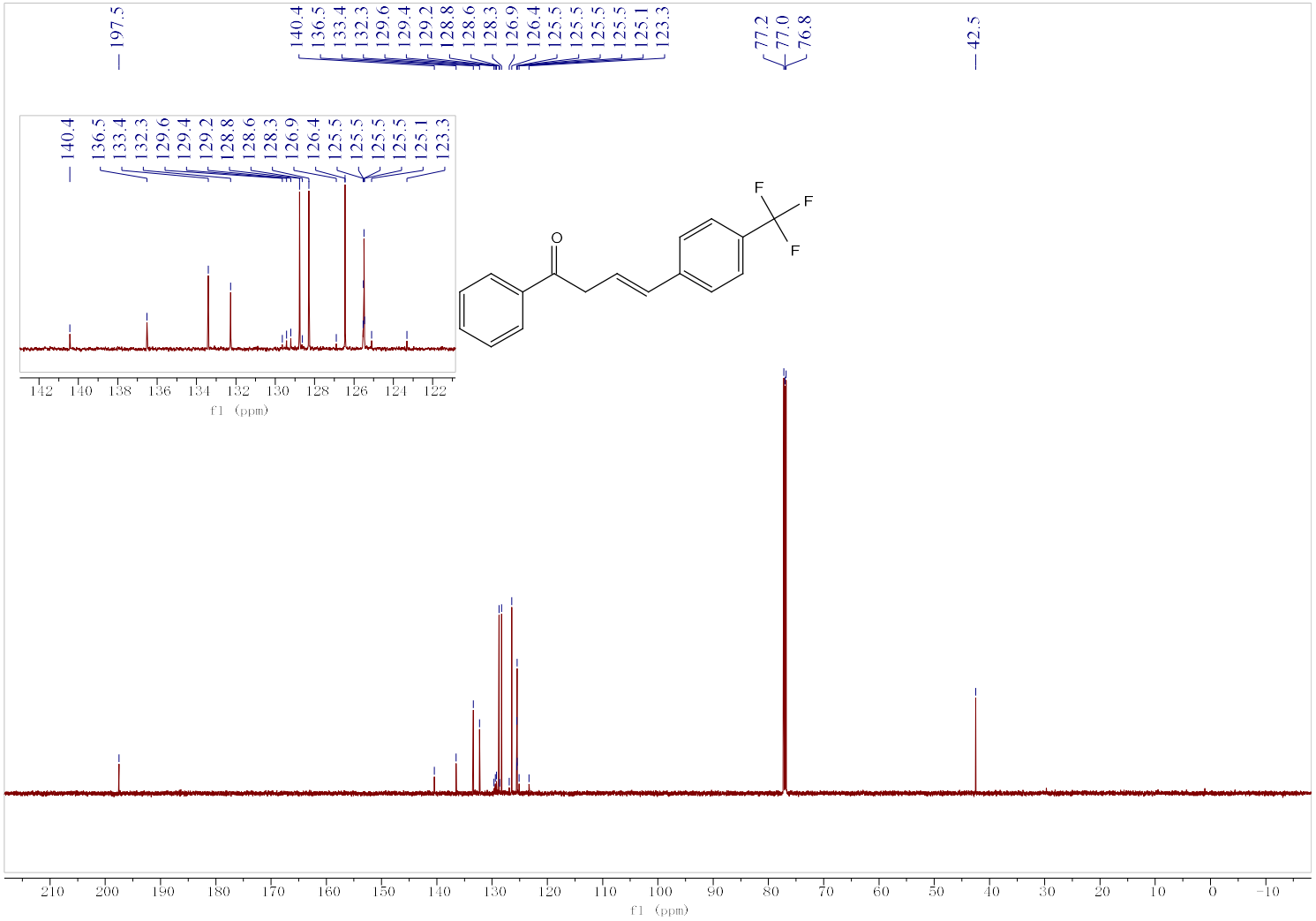
^{13}C NMR Spectrum of 4b (150 MHz, Chloroform-*d*)



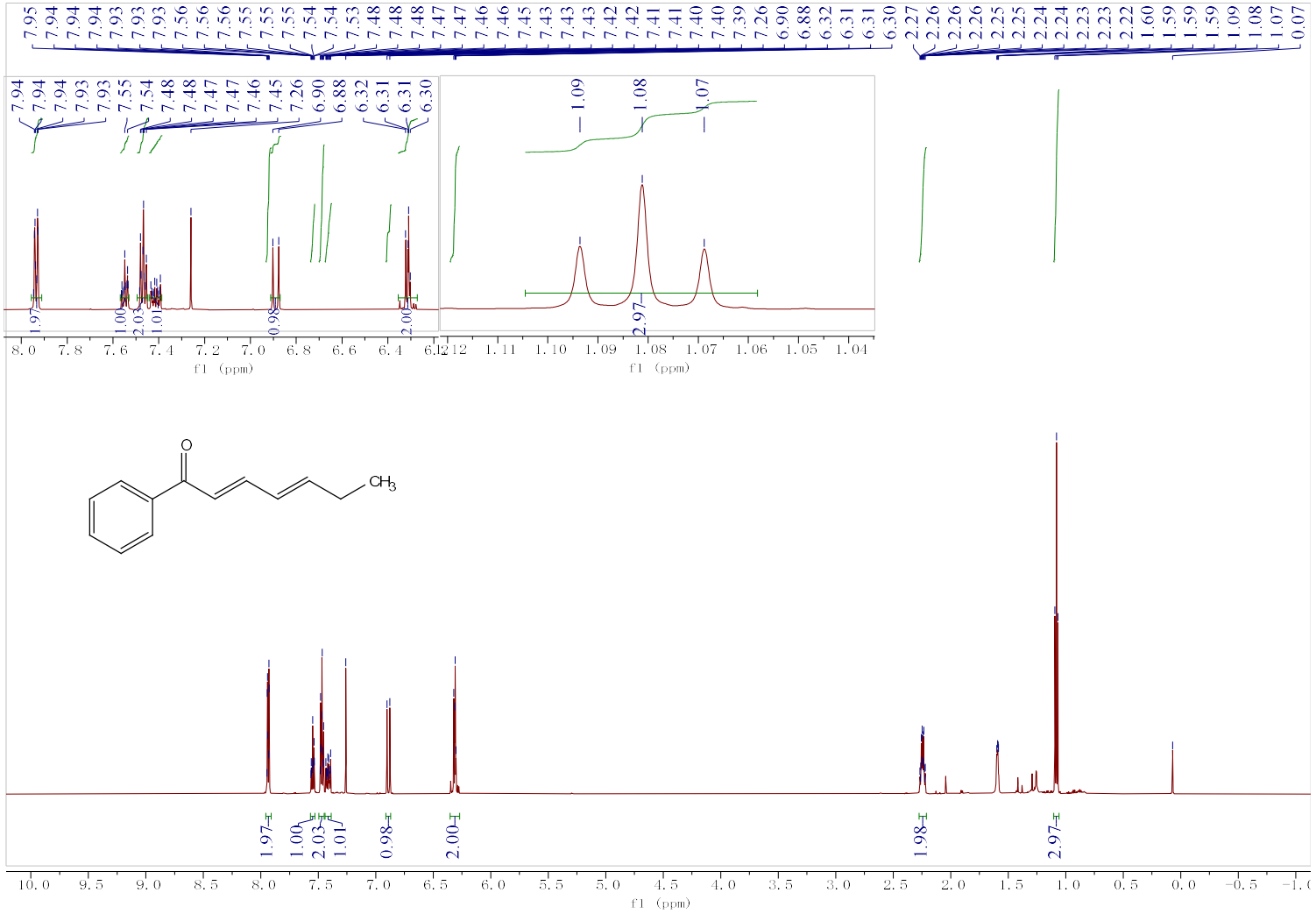
^{1}H NMR Spectrum of 4c (600 MHz, Chloroform-*d*)



^{13}C NMR Spectrum of 4c (150 MHz, Chloroform-*d*)

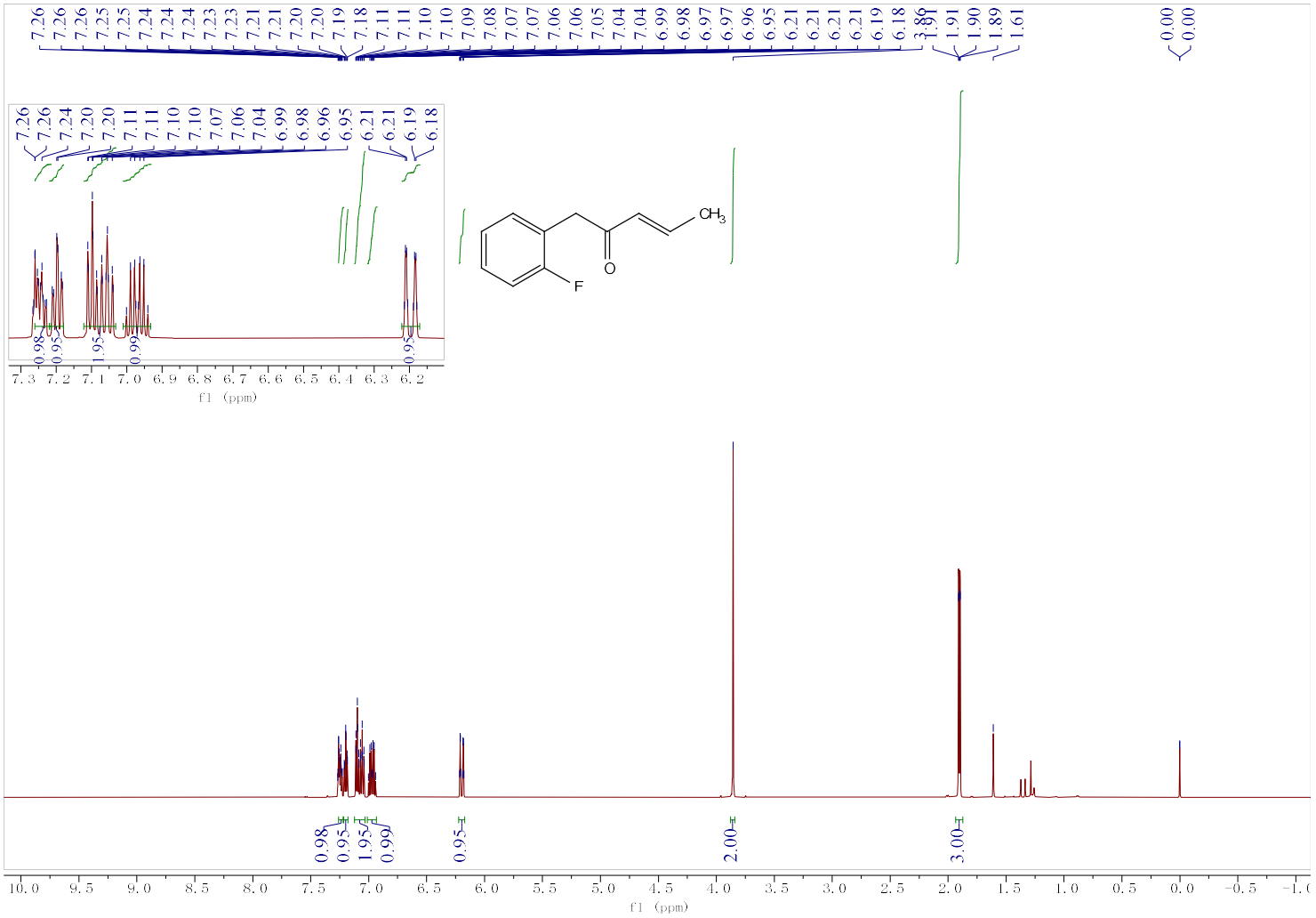


^{1}H NMR Spectrum of 4d (600 MHz, Chloroform-*d*)



^{13}C NMR Spectrum of 4d (150 MHz, Chloroform-*d*)

^{1}H NMR Spectrum of 4e (600 MHz, Chloroform-*d*)



^{13}C NMR Spectrum of 4e (150 MHz, Chloroform-*d*)