Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Enantioselective Insertion of Vinyl Diazoacetates into O-H Bonds of Carboxylic Acids

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1. General information

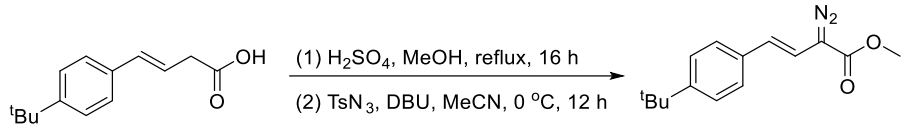
Unless otherwise stated, all reactions were carried out in dry reaction tubes under an argon atmosphere. Solvents were dried prior to use. Commercially obtained reagents were used as received. Reactions were monitored by analytical thin-layer chromatography (TLC) using pre-coated (0.20 mm thickness) silica gel plates with F_{254} indicator. Visualization of spots after TLC was accomplished by exposure to UV light (254 nm) and/or staining agents (iodine vapor, $KMnO_4$ in water). For column chromatography, 200-300 mesh silica gel was used. NMR spectra were recorded on Bruker AVANCE III 400 MHz (400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR, 376 MHz for ^{19}F NMR) spectrometer using residual solvent peaks as the internal standard ($CDCl_3$: 7.26 ppm for ^1H NMR, 77.16 ppm for ^{13}C NMR; DMSO-d_6: 2.50 ppm for ^1H NMR, 39.52 ppm for ^{13}C NMR). Data for ^1H NMR spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, m = multiplet), coupling constants *J* in Hertz (Hz), and integration. Data for ^{13}C NMR spectra were reported in terms of chemical shift (δ ppm). High resolution mass spectra (HRMS) were performed on Agilent 6540 Q-TOF or Agilent 6230A TOF mass spectrometer (ESI). Melting points were uncorrected and determined on a SGW X-4B melting point apparatus. Enantiomeric excesses (ee) values were determined by chiral HPLC analysis using an Agilent 1260 LC instrument on Daicel Chiralpak IA, IB,IC, ID, IE or OD-H column. Optical rotations were determined on a Rudolph Autopol I automatic polarimeter and reported as follows: $[\alpha]_D^T$: (c: g/100 mL, solvent).

All chiral phosphoric acids are commercial products and are produced by the company DAICEL.

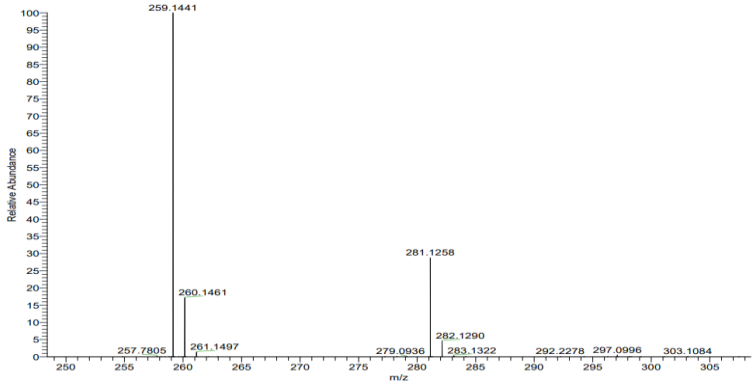
2. Preparation of substrates

The Carboxylic acid compounds 1 were purchased from Energy Chemical and Bide Pharmatech Ltd.

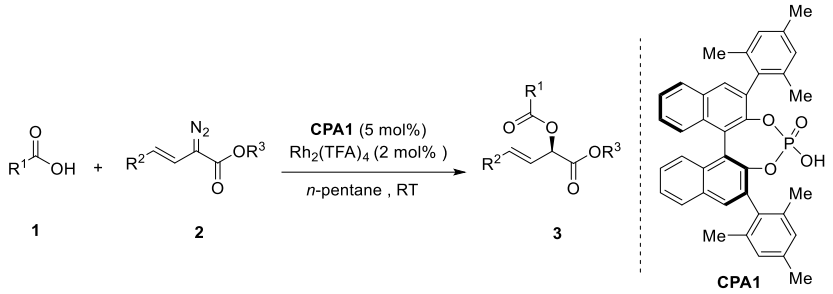
The diazo compounds 2 were prepared according to literature procedures[1].
methyl (*E*)-4-(4-(tert-butyl)phenyl)-2-diazobut-3-enoate was new compound.



Step 1: A solution of (*E*)-4-(4-(tert-butyl)phenyl)but-3-enoic acid (2.0 g, 9.17 mmol, 1.0 equiv), in MeOH (20.0 mL), then added a drop H_2SO_4 .The reaction was stirred at 100 °C for 16 hours. The reaction mixture was concentrated under vacuum to give crude methyl (*E*)-4-(4-(tert-butyl)phenyl)but-3-enoate as a yellow oil (1.5 g, 70%), which was used without further purification.
Step 2: DBU (1.1 g, 6.9 mmol, 1.6 equiv) and methyl (*E*)-4-(4-(tert-butyl)phenyl)but-3-enoate (1.0 g, 4.3 mmol, 1.0 equiv) were added to a solution of TsN_3 (1.3 g, 6.5 mmol, 1.5 equiv) in CH_3CN (20 mL) at 0 °C and the resulting mixture was stirred for 1 hours. The reaction mixture was then diluted with distilled water (20 mL) and extracted with EtOAc (20 mL*3). The combined organic layers were washed with brine (20 mL*2), then dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Petroleum ether/ EtOAc = 100:1) to give **2f** as a red solid (0.8 g, 73%), mp: 66-67 °C.
R_f (Petroleum ether/ EtOAc = 20:1) = 0.6.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.26 (m, 4H), 6.42 (d, *J* = 16.4 Hz, 1H), 6.16 (d, *J* = 16.4 Hz, 1H), 3.81 (s, 3H), 1.30 (s, 9H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.8, 150.3, 134.1, 125.9, 125.7, 125.5, 123.1, 110.2, 52.3, 34.6, 31.3.
HRMS(ESI) m/z**:** $[M+H]^+$ Calculated for $C_{15}H_{19}N_2O_2$ 259.1441; Found 259.1441.

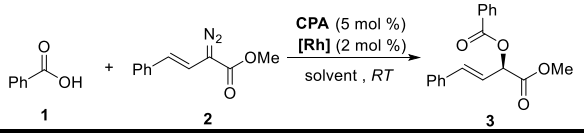


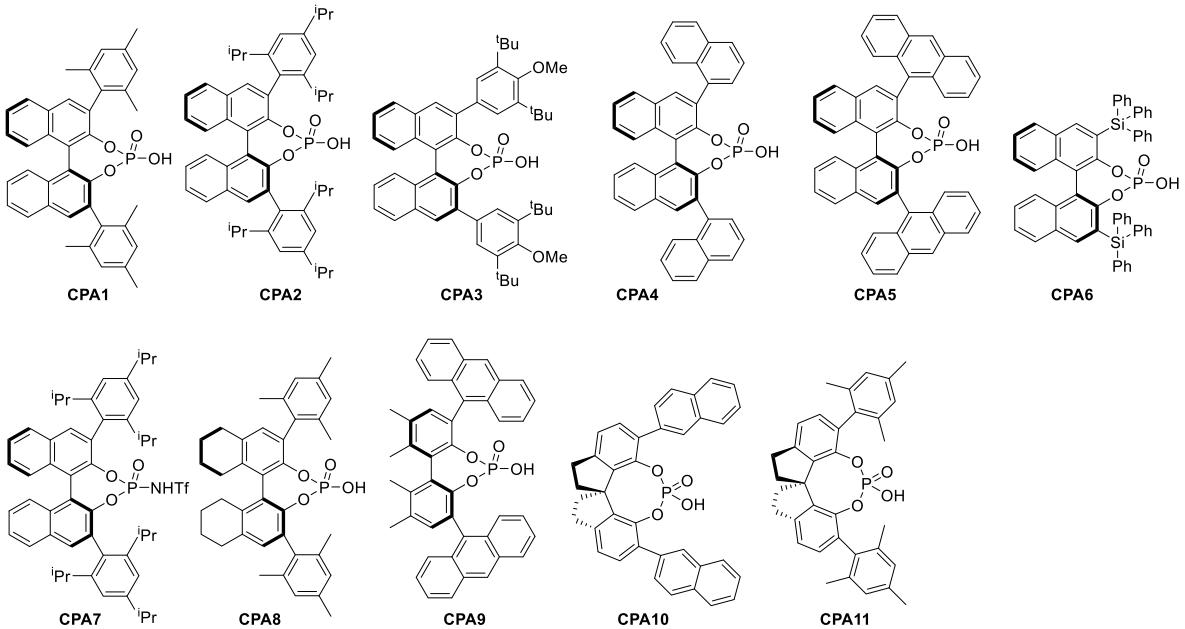
3. Experimental Procedures



To a dry reaction tube were added $Rh_2(TFA)_4$ (2.6 mg, 0.004 mmol, 2 mol%), CPA1 (5.8 mg, 0.01 mmol, 5 mol%), **1** (0.2 mmol) and *n*-pentane (2 mL) under argon atmosphere. Then, a solution of **2** (0.4 mmol) in *n*-pentane (2 mL) was added via syringe, the resulting reaction was stirred at rt for 5 min. The reaction solution was concentrated under vacuum; the crude residue was purified by silica gel column chromatography to give **3**. [Note: The racemic sample was prepared via general procedure without adding CPA1.]

4. Table S1 Optimization of the reaction conditions[a]





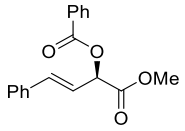
entry	[Rh]	CPA	solvent	T (°C)	yield (%)[b]	ee (%)[c]
1	$Rh_2(TFA)_4$	**CPA1**	*n*-pentane	25	88	94
2	$Rh_2(TFA)_4$	**CPA2**	*n*-pentane	25	59	86
3	$Rh_2(TFA)_4$	**CPA3**	*n*-pentane	25	50	9
4	$Rh_2(TFA)_4$	**CPA4**	*n*-pentane	25	35	45
5	$Rh_2(TFA)_4$	**CPA5**	*n*-pentane	25	32	34
6	$Rh_2(TFA)_4$	**CPA6**	*n*-pentane	25	32	0
7	$Rh_2(TFA)_4$	**CPA7**	*n*-pentane	25	35	0
8	$Rh_2(TFA)_4$	**CPA8**	*n*-pentane	25	78	87

9	$Rh_2(TFA)_4$	**CPA9**	*n*-pentane	25	48	27
10	$Rh_2(TFA)_4$	**CPA10**	*n*-pentane	25	41	19
11	$Rh_2(TFA)_4$	**CPA11**	*n*-pentane	25	61	85
12	$Rh_2(esp)_4$	**CPA1**	*n*-pentane	25	35	86
13	$Rh_2(PTTL)_4$	**CPA1**	*n*-pentane	25	47	78
14	$Rh_2(Oct)_4$	**CPA1**	*n*-pentane	25	70	91
15	$Rh_2(TFA)_4$	**CPA1**	DCM	25	70	23
16	$Rh_2(TFA)_4$	**CPA1**	DCE	25	73	44
17	$Rh_2(TFA)_4$	**CPA1**	toluene	25	80	45
18	$Rh_2(TFA)_4$	**CPA1**	$CHCl_3$	25	72	58
19	$Rh_2(TFA)_4$	**CPA1**	*n*-pentane	0	52	95
20	$Rh_2(TFA)_4$	**CPA1**	*n*-pentane	15	86	94
21	$Rh_2(TFA)_4$	**CPA1**	*n*-pentane	35	90	92
22[e]	$Rh_2(TFA)_4$	**CPA1**	*n*-pentane	25	80	94

[a] Reaction conditions: **[Rh]** (2 mol %), **CPA** (5 mol %), **1** (0.2 mmol, 1 equiv), **2** (0.4 mmol, 2 equiv) in solvent (4 mL) for 5 min. [b] Isolated yield. [c] ee value was determined by chiral HPLC. [e] **1** (0.2 mmol, 1 equiv), **2** (0.3 mmol, 1.5 equiv).

5. Analytic Data for Synthesized Compounds

(*R*,*E*)-1-methoxy-1-oxo-4-phenylbut-3-en-2-yl benzoate[2] (3aa)



Prepared according to general procedure from $Rh_2(TFA)_4$ (2.6 mg, 0.004 mmol, 2 mol%), CPA1(5.8 mg, 0.01 mmol, 5 mol%), benzoic acid (24.4 mg, 0.2 mmol, 1.0 equiv) and methyl (*E*)-2-diazo-4-phenylbut-3-enoate (80.8 mg, 0.4 mmol, 2.0 equiv) in *n*-pentane (4 mL) at rt for 5 min. The desired product was purified by silica gel column chromatography (Petroleum ether: ethyl acetate = 20:1-5:1) and obtained as colorless oil (52.1 mg, 88%).

R_f (Petroleum ether/ EtOAc = 20:1) = 0.3.

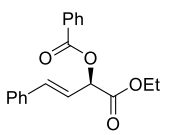
HPLC (IA, *i*-PrOH/*n*-hexane = 10/90, flow rate = 1 mL/min, λ = 215 nm) t_R = 7.931 min (major), 8.568 min (minor), 94% ee.

$[\alpha]_D^{25}$: -85.500 (c = 0.2, CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16-8.13 (m, 2H), 7.62-7.57 (m, 1H), 7.49-7.43 (m, 4H), 7.37-7.29 (m, 3H), 6.91 (d, *J* =17.2 Hz, 1H), 6.40 (dd, *J* = 16.0, 7.2 Hz, 1H), 5.88 (dd, *J* = 7.2, 1.2 Hz, 1H), 3.81 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.2, 165.7, 135.6, 135.5, 133.5, 130.0, 129.3, 128.7, 128.7, 128.5, 126.9, 120.9, 73.6, 52.8.

(*R*,*E*)-1-ethoxy-1-oxo-4-phenylbut-3-en-2-yl benzoate[4] (3ab)



Prepared according to general procedure from $Rh_2(TFA)_4$ (2.6 mg, 0.004 mmol, 2 mol%), CPA1(5.8 mg, 0.01 mmol, 5 mol%), benzoic acid (24.4 mg, 0.2 mmol, 1.0 equiv) and ethyl (*E*)-2-diazo-4-phenylbut-3-enoate (86.4 mg, 0.4 mmol, 2.0 equiv) in *n*-pentane (4 mL) at rt for 5 min. The desired product was purified by silica gel column chromatography (Petroleum ether: ethyl acetate = 20:1-

5:1) and obtained as yellow oil (49.0 mg, 79%).

R_f (Petroleum ether/ EtOAc = 20:1) = 0.3.

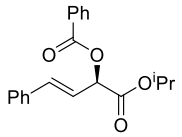
HPLC (IA, *i*-PrOH/*n*-hexane = 10/90, flow rate = 1 mL/min, λ = 215 nm) t_R = 7.310 min (major), 8.043 min (minor), 94% ee.

$[\alpha]_D^{25}$: -59.900 (c = 0.2, CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16-8.13 (m, 2H), 7.62-7.58 (m, 1H), 7.50-7.43 (m, 4H), 7.38-7.30 (m, 3H), 6.92 (dd, *J* = 16.0, 1.2 Hz, 1H), 6.41 (dd, *J* = 16.0, 7. Hz, 1H), 5.85 (dd, *J* = 7.2, 1.2 Hz, 1H), 4.27 (m, 2H), 1.30 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.7, 165.8, 135.7, 135.3, 133.5, 130.0, 129.4, 128.7, 128.6, 128.5, 126.9, 121.1, 73.7, 61.9, 14.2.

(*R*,*E*)-1-isopropoxy-1-oxo-4-phenylbut-3-en-2-yl benzoate (3ac)



Prepared according to general procedure from $Rh_2(TFA)_4$ (2.6 mg, 0.004 mmol, 2 mol%), CPA1(5.8 mg, 0.01 mmol, 5 mol%), benzoic acid (24.4 mg, 0.2 mmol, 1.0 equiv) and isopropyl (E)-2-diazo-4-phenylbut-3-enoate (92.0 mg, 0.4 mmol, 2.0 equiv) in *n*-pentane (4 mL) at rt for 5 min. The desired product was purified by silica gel column chromatography (Petroleum ether: ethyl acetate = 20:1-5:1) and obtained as colorless oil (47.4 mg, 73%).

R_f (Petroleum ether/ EtOAc = 20:1) = 0.3.

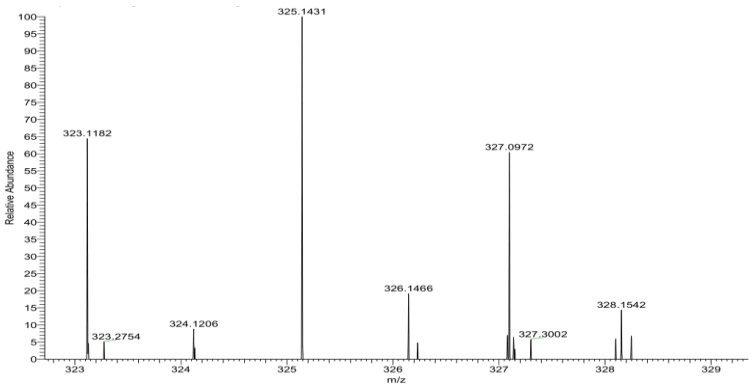
HPLC (IA, *i*-PrOH/*n*-hexane = 1/99, flow rate = 1 mL/min, λ = 215 nm) t_R = 11.114 min (major), 12.474 min (minor), 96% ee.

$[\alpha]_D^{25}$: -53.400 (c = 0.2, CH_2Cl_2).

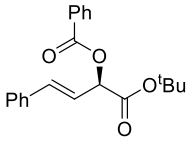
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16-8.13 (m, 2H), 7.61-7.57 (m, 1H), 7.50-7.41 (m, 4H), 7.38-7.27 (m, 3H), 6.91 (d, *J* = 16.0 Hz, 1H), 6.40 (dd, *J* = 16.0, 6.8 Hz, 1H), 5.81 (dd, *J* = 6.8, 1.2 Hz, 1H), 5.12 (m, 1H), 1.31 (d, *J* = 6.4 Hz, 3H), 1.25 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.3, 165.8, 135.8, 135.2, 133.5, 130.0, 129.5, 128.8, 128.6, 128.6, 127.0, 121.3, 73.9, 69.7, 21.8, 21.7.

HRMS(ESI) m/z**:** $[M+H]^+$ Calculated for $C_{20}H_{20}O_4$ 325.1434; Found 325.1431.



(*R*,*E*)-1-(tert-butoxy)-1-oxo-4-phenylbut-3-en-2-yl benzoate (3ad)



Prepared according to general procedure from $Rh_2(TFA)_4$ (2.6 mg, 0.004 mmol, 2 mol%), CPA1(5.8 mg, 0.01 mmol, 5 mol%), benzoic acid (24.4 mg, 0.2 mmol, 1.0 equiv) and tert-butyl (*E*)-2-diazo-4-phenylbut-3-enoate (97.6 mg, 0.4 mmol, 2.0 equiv) in *n*-pentane (4 mL) at rt for 5 min. The desired product was purified by silica gel column chromatography (Petroleum ether: ethyl acetate = 20:1-5:1) and obtained as white solid (53.5 mg, 79%), mp: 93-94 ℃.

R_f (Petroleum ether/ EtOAc = 20:1) = 0.3.

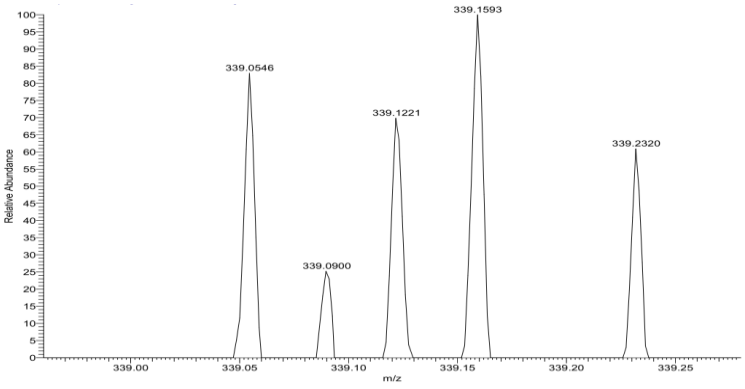
HPLC (IE, *i*-PrOH/*n*-hexane = 1/99, flow rate = 1 mL/min, λ = 215 nm) t_R = 14.008 min (major), 11.925 min (minor), 97% ee.

$[\alpha]_D^{25}$: -43.100 (c = 0.2, CH_2Cl_2).

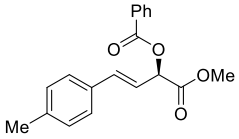
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09-8.06 (m, 2H), 7.53-7.48 (m, 1H), 7.41-7.36 (m, 4H), 7.29-7.21 (m, 3H), 6.82 (dd, *J* = 16.0, 1.2 Hz, 1H), 6.32 (dd, *J* = 16.0, 6.8 Hz, 1H), 5.67 (dd, *J* = 6.8, 1.6 Hz, 1H), 1.41 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.7, 165.8, 135.9, 134.8, 133.4, 129.9, 129.6, 128.7, 128.5, 126.9, 121.6, 82.8, 74.0, 28.0.

HRMS(ESI) m/z**:** $[M+H]^+$ Calculated for $C_{21}H_{22}O_4$ 335.1591; Found 335.1593.



(*R*,*E*)-1-methoxy-1-oxo-4-(p-tolyl)but-3-en-2-yl benzoate (3ae)



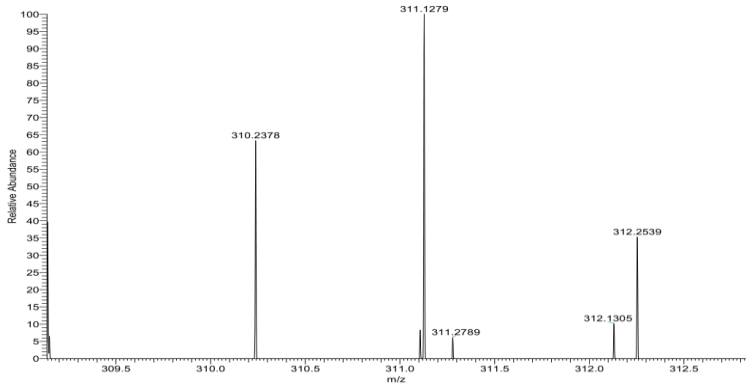
Prepared according to general procedure from $Rh_2(TFA)_4$ (2.6 mg, 0.004 mmol, 2 mol%), CPA1(5.8 mg, 0.01 mmol, 5 mol%), benzoic acid (24.4 mg, 0.2 mmol, 1.0 equiv) and methyl (*E*)-2-diazo-4-(p-tolyl)but-3-enoate (86.4 mg, 0.4 mmol, 2.0 equiv) in *n*-pentane (4 mL) at rt for 5 min. The desired product was purified by silica gel column chromatography (Petroleum ether: ethyl acetate = 20:1-5:1) and obtained as yellow oil (42.2 mg, 68%).

R_f (Petroleum ether/ EtOAc = 20:1) = 0.3.

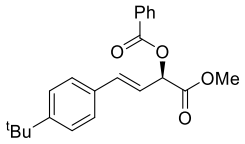
HPLC (IA, *i*-PrOH/*n*-hexane = 1/99, flow rate = 1 mL/min, λ = 215 nm) t_R = 13.317 min (major), 14.225 min (minor), 94% ee.

$[\alpha]_D^{25}$: -81.200 (c = 0.2, CH_2Cl_2).

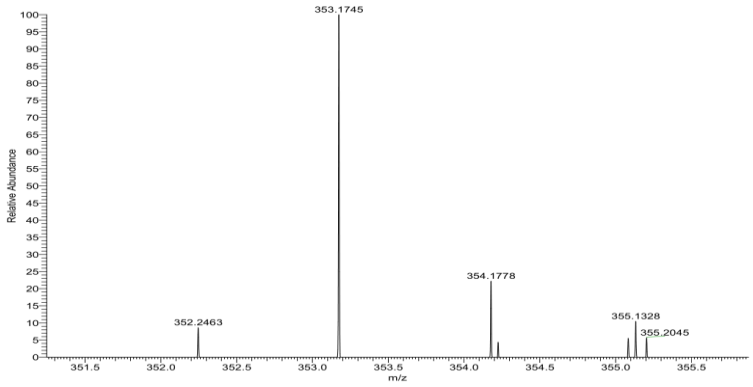
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15-8.13 (m, 2H), 7.60-7.56 (m, 1H), 7.48-7.44 (m, 2H), 7.34-7.32 (m, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 6.87 (d, *J* = 15.6 Hz, 1H), 6.35 (dd, *J* = 16.0, 7.2 Hz, 1H), 5.85 (dd, *J* = 7.2, 1.2 Hz, 1H), 3.79 (s, 3H), 2.34 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.3, 165.8, 138.7, 135.6, 133.5, 132.8, 130.0, 129.5, 129.3, 128.5, 126.9, 119.8, 73.8, 52.8, 21.3.
HRMS(ESI) m/z**:** $[M+H]^+$ Calculated for $C_{19}H_{18}O_4$ 311.1278; Found 311.1279.



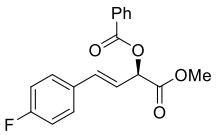
(*R*,*E*)-4-(4-(tert-butyl)phenyl)-1-methoxy-1-oxobut-3-en-2-yl benzoate (3af)



Prepared according to general procedure from $Rh_2(TFA)_4$ (2.6 mg, 0.004 mmol, 2 mol%), CPA1(5.8 mg, 0.01 mmol, 5 mol%), benzoic acid (24.4 mg, 0.2 mmol, 1.0 equiv) and methyl methyl (*E*)-4-(4-(tert-butyl)phenyl)-2-diazobut-3-enoate (104 mg, 0.4 mmol, 2.0 equiv) in *n*-pentane (4 mL) at rt for 5 min. The desired product was purified by silica gel column chromatography (Petroleum ether: ethyl acetate = 20:1-5:1) and obtained as yellow oil (49.3 mg, 70%).
R_f (Petroleum ether/ EtOAc = 20:1) = 0.3.
HPLC (IA, *i*-PrOH/*n*-hexane = 10/90, flow rate = 1 mL/min, λ = 215 nm) t_R = 6.985 min (major), 6.337 min (minor), 92% ee.
$[\alpha]_D^{25}$: -81.200 (c = 0.2, CH_2Cl_2).
^{1}H NMR (400 MHz, Chloroform-d) δ 8.07-8.05 (m, 2H), 7.53-7.49 (m, 1H), 7.39 (t, J = 8.0 Hz, 2H), 7.30 (s, 4H), 6.81 (d, J = 16.0 Hz, 1H), 6.28 (dd, J = 16.0, 7.2 Hz, 1H), 5.77 (d, J = 6.0 Hz, 1H), 3.72 (s, 3H), 1.24 (s, 9H).
^{13}C NMR (101 MHz, Chloroform-d) δ 169.4, 165.9, 152.0, 135.6, 133.6, 132.9, 130.1, 129.4, 128.6, 126.7, 125.8, 120.13, 73.9, 52.8, 34.8, 31.4.
HRMS(ESI) m/z**:** $[M+H]^+$ Calculated for $C_{22}H_{24}O_4$ 353.1747; Found 353.1745.



(*R*,*E*)-4-(4-fluorophenyl)-1-methoxy-1-oxobut-3-en-2-yl benzoate (3ag)



Prepared according to general procedure from $Rh_2(TFA)_4$ (2.6 mg, 0.004 mmol, 2 mol%), CPA1(5.8 mg, 0.01 mmol, 5 mol%), benzoic acid (24.4 mg, 0.2 mmol, 1.0 equiv) and methyl methyl (*E*)-2-diazo-4-(4-fluorophenyl)but-3-enoate (88.0 mg, 0.4 mmol, 2.0 equiv) in *n*-pentane (4 mL) at rt for 5 min. The desired product was purified by silica gel column chromatography (Petroleum ether: ethyl acetate = 20:1-5:1) and obtained as yellow oil (52.8 mg, 84%).

R_f (Petroleum ether/ EtOAc = 20:1) = 0.3.

HPLC (IA, *i*-PrOH/*n*-hexane = 10/90, flow rate = 1 mL/min, λ = 215 nm) t_R = 9.381 min (major), 10.153 min (minor), 92% ee.

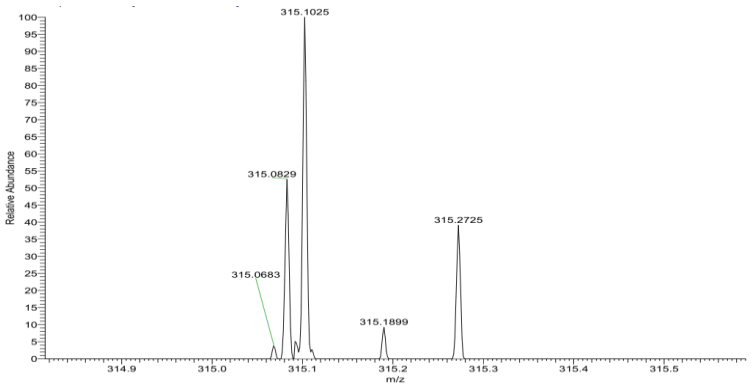
$[\alpha]_D^{25}$: -63.400 (c = 0.2, CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15-8.13 (m, 2H), 7.62-7.58 (m, 1H), 7.49-7.40 (m, 4H), 7.07-7.01 (m, 2H), 6.87 (d, *J* = 17.2 Hz, 1H), 6.32 (dd, *J* = 16.0, 7.2 Hz, 1H), 5.86 (dd, *J* = 7.2, 1.2 Hz, 1H), 3.81 (s, 3H).

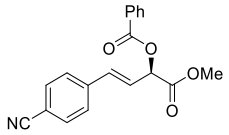
^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.2, 165.7, 162.9(d, $^1J_{C-F}$ = 249.2 Hz), 134.3, 133.6, 131.8(d, $^3J_{C-F}$ = 3.4 Hz), 130.0, 129.2, 128.6, 128.5, 120.7(d, $^4J_{C-F}$ = 2.3 Hz), 115.7(d, $^2J_{C-F}$ = 21.6 Hz), 73.53, 52.84.

^{19}F NMR (282 MHz, Chloroform-*d*) δ -112.70.

HRMS(ESI) m/z**:** $[M+H]^+$ Calculated for $C_{18}H_{15}FO_4$ 315.1027; Found 315.1025.



(*R*,*E*)-4-(4-cyanophenyl)-1-methoxy-1-oxobut-3-en-2-yl benzoate (3ah)



Prepared according to general procedure from $Rh_2(TFA)_4$ (2.6 mg, 0.004 mmol, 2 mol%), CPA1(5.8 mg, 0.01 mmol, 5 mol%), benzoic acid (24.4 mg, 0.2 mmol, 1.0 equiv) and methyl (*E*)-4-(4-cyanophenyl)-2-diazobut-3-enoate (90.8 mg, 0.4 mmol, 2.0 equiv) in *n*-pentane (2 mL) and DCM (2 ml) at rt for 5 min. The desired product was purified by silica gel column chromatography (Petroleum ether: ethyl acetate = 20:1-5:1) and obtained as yellow oil (50.2 mg, 79%).

R_f (Petroleum ether/ EtOAc = 20:1) = 0.3.

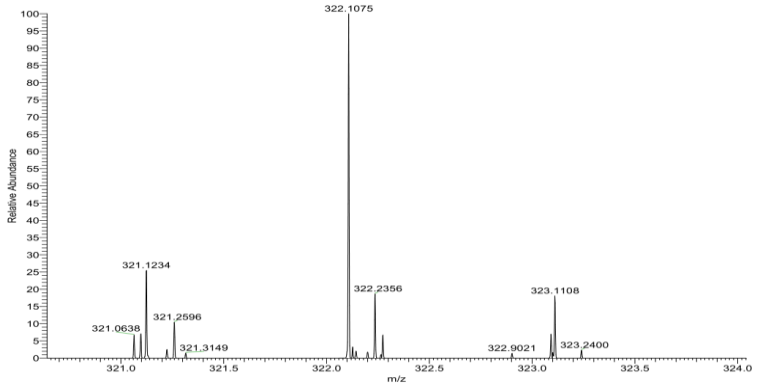
HPLC (IA, *i*-PrOH/*n*-hexane = 20/80, flow rate = 1 mL/min, λ = 215 nm) t_R = 14.236 min (major), 15.533 min (minor), 77% ee.

$[\alpha]_D^{25}$: -51.100 (c = 0.2, CH_2Cl_2).

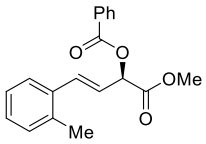
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 7.2 Hz, 2H), 7.65-7.61 (m, 3H), 7.57-7.47 (m, 4H), 6.92 (d, *J* = 15.6 Hz, 1H), 6.55 (dd, *J* = 16.0, 6.4 Hz, 1H), 5.94 (d, *J* = 7.6 Hz, 1H), 3.83 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.6, 165.5, 140.0, 133.8, 133.0, 132.6, 130.0, 129.0, 128.6, 127.4, 125.0, 118.7, 111.8, 72.9, 53.0.

HRMS(ESI) m/z**:** $[M+H]^+$ Calculated for $C_{19}H_{15}NO_4$ 322.1074; Found 322.1075.



(*R*,*E*)-1-methoxy-1-oxo-4-(o-tolyl)but-3-en-2-yl benzoate (3ai)



Prepared according to general procedure from $Rh_2(TFA)_4$ (2.6 mg, 0.004 mmol, 2 mol%), CPA1(5.8 mg, 0.01 mmol, 5 mol%), benzoic acid (24.4 mg, 0.2 mmol, 1.0 equiv) and methyl (*E*)-2-diazo-4-(o-tolyl)but-3-enoate (86.4 mg, 0.4 mmol, 2.0 equiv) in *n*-pentane (4 mL) at rt for 5 min. The desired product was purified by silica gel column chromatography (Petroleum ether: ethyl acetate = 20:1-5:1) and obtained as yellow oil (49.0 mg, 79%).

R_f (Petroleum ether/ EtOAc = 20:1) = 0.3.

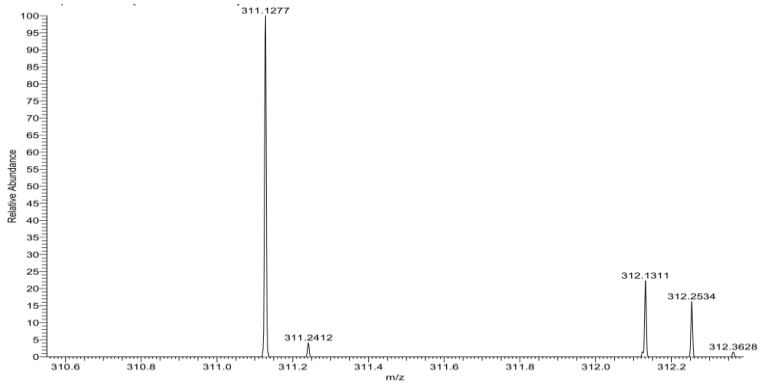
HPLC (IA, *i*-PrOH/*n*-hexane = 1/99, flow rate = 1 mL/min, λ = 215 nm) t_R = 9.660 min (major), 10.536 min (minor), 90% ee.

$[\alpha]_D^{25}$: -54.800 (c = 0.2, CH_2Cl_2).

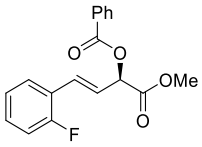
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15-8.13 (m, 2H), 7.61-7.57 (m, 1H), 7.52-7.44 (m, 3H), 7.21-7.18 (m, 2H), 7.17-7.13 (m, 2H), 6.29 (dd, *J* = 15.6, 7.2 Hz, 1H), 5.89 (dd, *J* = 7.2, 1.2 Hz, 1H), 3.81 (s, 3H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.3, 165.7, 136.0, 134.7, 133.5, 133.5, 130.5, 130.0, 129.9, 129.3, 128.5, 126.3, 125.9, 122.2, 73.9, 52.8, 19.8.

HRMS(ESI) m/z**:** $[M+H]^+$ Calculated for $C_{19}H_{18}O_4$ 311.1278; Found 311.1277.



(*R*,*E*)-4-(2-fluorophenyl)-1-methoxy-1-oxobut-3-en-2-yl benzoate (3aj)



Prepared according to general procedure from $Rh_2(TFA)_4$ (2.6 mg, 0.004 mmol, 2 mol%), CPA1(5.8 mg, 0.01 mmol, 5 mol%), benzoic acid (24.4 mg, 0.2 mmol, 1.0 equiv) and methyl (*E*)-2-diazo-4-(2-fluorophenyl)but-3-enoate (88.0 mg, 0.4 mmol, 2.0 equiv) in *n*-pentane (4 mL) at rt for 5 min. The desired product was purified by silica gel column chromatography (Petroleum ether: ethyl acetate = 20:1-5:1) and obtained as yellow oil (59.7 mg, 95%).

R_f (Petroleum ether/ EtOAc = 20:1) = 0.3.

HPLC (IA, *i*-PrOH/*n*-hexane = 5/95, flow rate = 1 mL/min, λ = 215 nm) t_R = 9.179 min (major), 9.857 min (minor), 92% ee.

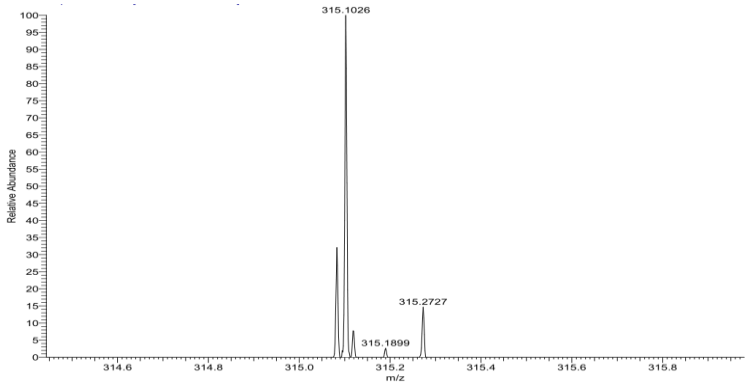
$[\alpha]_D^{25}$: -73.400 (c = 0.2, CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17-8.13 (m, 2H), 7.62-7.58 (m, 1H), 7.51-7.45 (m, 3H), 7.29-7.24 (m, 1H), 7.14-7.03 (m, 3H), 6.52 (dd, *J* = 16.0, 7.2 Hz, 1H), 5.90 (dd, *J* = 6.8, 1.6 Hz, 1H), 3.81 (s, 3H).

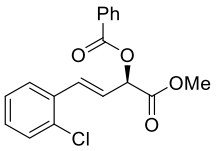
^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.0, 165.7, 160.5 (d, *J* = 250.8 Hz), 133.6, 130.1, 130.0 (d, *J* = 8.4 Hz), 129.2, 128.5, 128.0 (d, *J* = 3.4 Hz), 124.3 (d, *J* = 3.6 Hz), 123.6 (d, *J* = 5.7 Hz), 123.4 (d, *J* = 11.9 Hz), 115.95 (d, *J* = 22.1 Hz), 73.6, 52.8.

^{19}F NMR (282 MHz, Chloroform-*d*) δ -116.89.

HRMS(ESI) m/z**:** $[M+H]^+$ Calculated for $C_{18}H_{15}FO_4$ 315.1027; Found 315.1026.



(*R*,*E*)-4-(2-chlorophenyl)-1-methoxy-1-oxobut-3-en-2-yl benzoate (3ak)



Prepared according to general procedure from $Rh_2(TFA)_4$ (2.6 mg, 0.004 mmol, 2 mol%), CPA1(5.8 mg, 0.01 mmol, 5 mol%), benzoic acid (24.4 mg, 0.2 mmol, 1.0 equiv) and methyl (*E*)-4-(2-chlorophenyl)-2-diazobut-3-enoate (94.4 mg, 0.4 mmol, 2.0 equiv) in *n*-pentane (4 mL) at rt for 5 min. The desired product was purified by silica gel column chromatography (Petroleum ether: ethyl acetate = 20:1-5:1) and obtained as yellow oil (62.7 mg, 95%).

R_f (Petroleum ether/ EtOAc = 20:1) = 0.3.

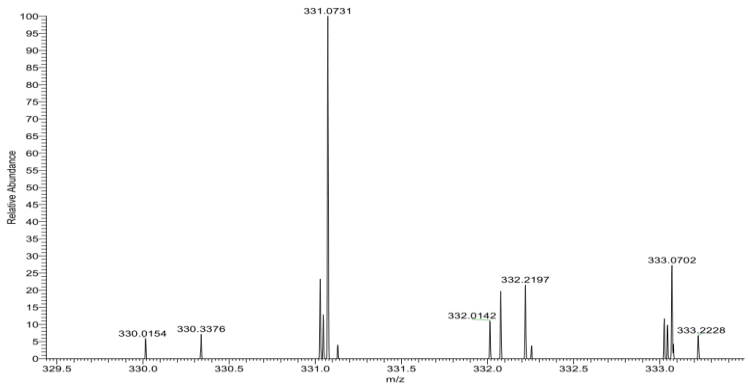
HPLC (IA, *i*-PrOH/*n*-hexane = 10/90, flow rate = 1 mL/min, λ = 215 nm) t_R = 17.560 min (major), 19.113 min (minor), 92% ee.

$[\alpha]_D^{25}$: -36.600 (c = 0.2, CH_2Cl_2).

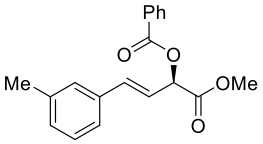
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17-8.14 (m, 2H), 7.62-7.55 (m, 2H), 7.50-7.46 (m, 2H), 7.39-7.32 (m, 2H), 7.25-7.22 (m, 2H), 6.41 (dd, *J* = 15.6, 6.4 Hz, 1H), 5.93 (dd, *J* = 6.8, 1.6 Hz, 1H), 3.82 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.0, 165.7, 133.7, 133.6, 131.3, 130.0, 129.9, 129.6, 129.2, 128.6, 127.1, 127.0, 123.6, 73.4, 52.9.

HRMS(ESI) m/z**:** $[M+H]^+$ Calculated for $C_{18}H_{15}ClO_4$ 331.0732; Found 331.0731.



(*R*,*E*)-1-methoxy-1-oxo-4-(m-tolyl)but-3-en-2-yl benzoate (3al)



Prepared according to general procedure from $Rh_2(TFA)_4$ (2.6 mg, 0.004 mmol, 2 mol%), CPA1(5.8 mg, 0.01 mmol, 5 mol%), benzoic acid (24.4 mg, 0.2 mmol, 1.0 equiv) and methyl (*E*)-2-diazo-4-(m-tolyl)but-3-enoate (86.4 mg, 0.4 mmol, 2.0 equiv) in *n*-pentane (4 mL) at rt for 5 min. The desired product was purified by silica gel column chromatography (Petroleum ether: ethyl acetate = 20:1-5:1) and obtained as yellow oil (50.2 mg, 81%).

R_f (Petroleum ether/ EtOAc = 20:1) = 0.3.

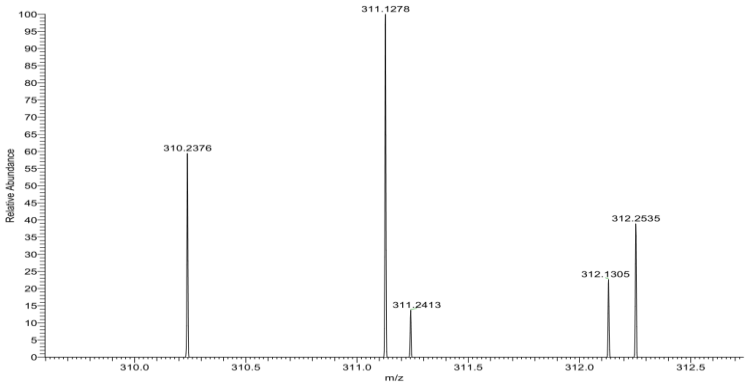
HPLC (IA, *i*-PrOH/*n*-hexane = 10/90, flow rate = 1 mL/min, λ = 215 nm) t_R = 6.849 min (major), 7.480 min (minor), 94% ee.

$[\alpha]_D^{25}$: -77.300 (c = 0.2, CH_2Cl_2).

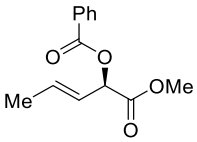
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 8.0 Hz, 2H), 7.61-7.56 (m, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.26-7.21 (m, 3H), 7.11-7.10 (m, 1H), 6.88 (d, *J* = 15.6 Hz, 1H), 6.39 (dd, *J* = 16.0, 7.2 Hz, 1H), 5.86 (d, *J* = 7.2 Hz, 1H), 3.80 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.3, 165.77, 138.4, 135.7, 135.5, 133.6, 130.0, 129.5, 129.3, 128.7, 128.5, 127.6, 124.1, 120.7, 73.7, 52.8, 21.4.

HRMS(ESI) m/z**:** $[M+H]^+$ Calculated for $C_{19}H_{18}O_4$ 311.1278; Found 311.1278.



(*R*,*E*)-1-methoxy-1-oxopent-3-en-2-yl benzoate (3am)



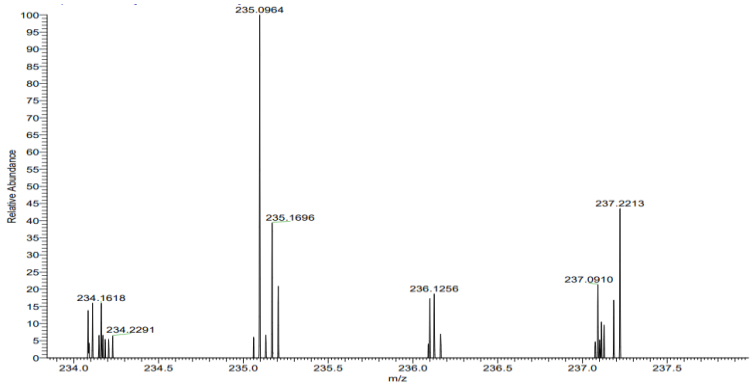
Prepared according to general procedure from $Rh_2(TFA)_4$ (2.6 mg, 0.004 mmol, 2 mol%), CPA1(5.8 mg, 0.01 mmol, 5 mol%), benzoic acid (24.4 mg, 0.2 mmol, 1.0 equiv) and methyl (*E*)-2-diazopent-3-enoate (56.0 mg, 0.4 mmol, 2.0 equiv) in *n*-pentane (4 mL) at rt for 5 min. The desired product was purified by silica gel column chromatography (Petroleum ether: ethyl acetate = 20:1-5:1) and obtained as colorless oil (30.4 mg, 65%).

R_f (Petroleum ether/ EtOAc = 20:1) = 0.3.

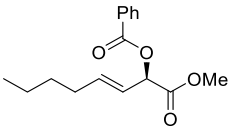
HPLC (IC, *i*-PrOH/*n*-hexane = 1/99, flow rate = 1 mL/min, λ = 215 nm) t_R = 15.857 min (major), 14.823 min (minor), 92% ee.

$[\alpha]_D^{25}$: -12.800 (c = 0.2, CH_2Cl_2).

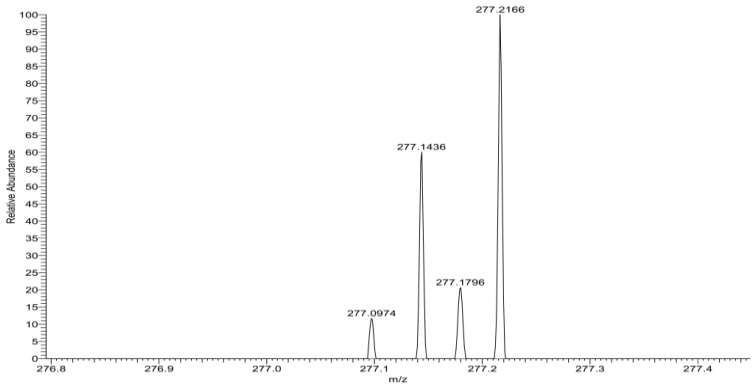
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11-8.09 (m, 2H), 7.60-7.56 (m, 1H), 7.48-7.43 (m, 2H), 6.09-6.03 (m, 1H), 5.75-5.73 (m, 1H), 5.65-5.63 (m, 1H), 3.78 (s, 3H), 1.81-1,79 (m, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.6, 165.8, 133.4, 133.1, 129.9, 129.4, 128.4, 123.2, 73.7, 52.6, 18.0.
HRMS(ESI) m/z**:** $[M+H]^+$ Calculated for $C_{13}H_{14}O_4$ 235.0965; Found 235.0964.



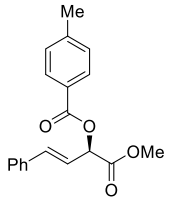
(*R*,*E*)-1-methoxy-1-oxooct-3-en-2-yl benzoate (3an)



Prepared according to general procedure from $Rh_2(TFA)_4$ (2.6 mg, 0.004 mmol, 2 mol%), CPA1(5.8 mg, 0.01 mmol, 5 mol%), benzoic acid (24.4 mg, 0.2 mmol, 1.0 equiv) and methyl (*E*)-2-diazooct-3-enoate (72.8 mg, 0.4 mmol, 2.0 equiv) in *n*-pentane (4 mL) at rt for 5 min. The desired product was purified by silica gel column chromatography (Petroleum ether: ethyl acetate = 20:1-5:1) and obtained as colorless oil (38.6 mg, 70%).
R_f (Petroleum ether/ EtOAc = 20:1) = 0.3.
HPLC (IC, *i*-PrOH/*n*-hexane = 1/99, flow rate = 1 mL/min, λ = 215 nm) t_R = 12.620 min (major), 11.859 min (minor), 92% ee.
$[\alpha]_D^{25}$: -40.500(c = 0.2, CH_2Cl_2).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12-8.09 (m, 2H), 7.61-7.56 (m, 1H), 7.48-7.44 (m, 2H), 6.08-6.01 (m, 1H), 5.72-5.63 (m, 2H), 3.78 (s, 3H), 2.13 (q, *J* = 6.8 Hz, 2H), 1.37 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.7, 165.81, 138.3, 133.4, 130.0, 129.4, 128.5, 121.8, 73.8, 52.6, 32.1, 30.8, 22.2, 13.9.
HRMS(ESI) m/z**:** $[M+H]^+$ Calculated for $C_{16}H_{20}O_4$ 277.1434; Found 277.1436.



(*R*,*E*)-1-methoxy-1-oxo-4-phenylbut-3-en-2-yl 4-methylbenzoate[2] (3ba)



Prepared according to general procedure from $Rh_2(TFA)_4$ (2.6 mg, 0.004 mmol, 2 mol%), CPA1(5.8 mg, 0.01 mmol, 5 mol%), 4-methylbenzoic acid (27.3 mg, 0.2 mmol, 1.0 equiv) and methyl (*E*)-2-diazo-4-phenylbut-3-enoate (80.8 mg, 0.4 mmol, 2.0 equiv) in *n*-pentane (4 mL) at rt for 5 min. The desired product was purified by silica gel column chromatography (Petroleum ether: ethyl acetate = 20:1-5:1) and obtained as yellow oil (50.8 mg, 82%).

R_f (Petroleum ether/ EtOAc = 20:1) = 0.3.

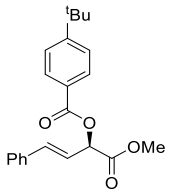
HPLC (IA, *i*-PrOH/*n*-hexane = 10/90, flow rate = 1 mL/min, λ = 215 nm) t_R = 9.310 min (major), 9.941 min (minor), 94% ee.

$[\alpha]_D^{25}$: -63.000 (c = 0.2, CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04-8.01 (m, 2H), 7.45-7.43 (m, 2H), 7.37-7.25 (m, 5H), 6.90 (d, *J* = 16.0 Hz, 1H), 6.40 (dd, *J* = 16.0, 6.8 Hz, 1H), 5.86 (dd, *J* = 7.2, 1.6 Hz, 1H), 3.80 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.3, 165.8, 144.3, 135.6, 135.4, 130.0, 129.2, 128.7, 128.6, 126.9, 126.6, 121.1, 73.5, 52.7, 21.8.

(*R*,*E*)-1-methoxy-1-oxo-4-phenylbut-3-en-2-yl 4-(tert-butyl)benzoate (3ca)



Prepared according to general procedure from $Rh_2(TFA)_4$ (2.6 mg, 0.004 mmol, 2 mol%), CPA1(5.8 mg, 0.01 mmol, 5mol%), 4-(tert-butyl)benzoic acid (35.6 mg, 0.2 mmol) and methyl (*E*)-2-diazo-4-phenylbut-3-enoate (80.8 mg, 0.4 mmol, 2.0 equiv) in *n*-pentane (4 mL) at rt for 5 min. The desired product was purified by silica gel column chromatography (Petroleum ether: ethyl acetate = 20:1-5:1) and obtained as yellow oil (56.3 mg, 80%).

R_f (Petroleum ether/ EtOAc = 20:1) = 0.3.

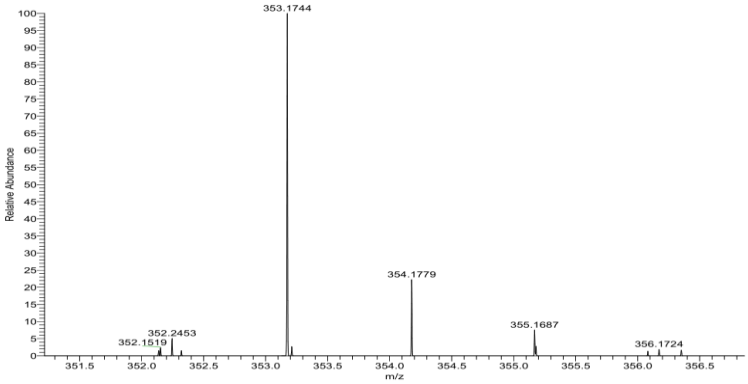
HPLC (IA, *i*-PrOH/*n*-hexane = 1/99, flow rate = 1 mL/min, λ = 215 nm) t_R = 15.450 min (major), 14.251 min (minor), 90% ee.

[α]$_D^{25}$: -49.500 (c = 0.2, CH_2Cl_2).

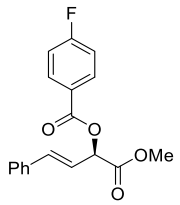
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08-7.06 (m, 2H), 7.50-7.29 (m, 7H), 6.90 (d, *J* = 16 Hz, 1H), 6.40 (dd, *J* = 16, 6.8 Hz, 1H), 5.87 (dd, *J* = 7.2, 1.6 Hz, 1H), 3.80 (s, 3H), 1.34 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.3, 165.7, 157.3, 135.7, 135.2, 129.9, 128.7, 128.6, 126.9, 126.5, 125.5, 121.1, 73.4, 52.7, 35.2, 31.1.

HRMS(ESI) m/z**:** $[M+H]^+$ Calculated for $C_{22}H_{24}O_4$ 353.1744; Found 353.1747.



(*R*,*E*)-1-methoxy-1-oxo-4-phenylbut-3-en-2-yl 4-fluorobenzoate (3da)



Prepared according to general procedure from $Rh_2(TFA)_4$ (2.6 mg, 0.004 mmol, 2 mol%), CPA1(5.8 mg, 0.01 mmol, 5 mol%), 4-fluorobenzoic acid (28.0 mg, 0.2 mmol, 1.0 equiv) and methyl (*E*)-2-diazo-4-phenylbut-3-enoate (80.8 mg, 0.4 mmol, 2.0 equiv) in *n*-pentane (4 mL) at rt for 5 min. The desired product was purified by silica gel column chromatography (Petroleum ether: ethyl acetate = 20:1-5:1) and obtained as colorless oil (46.5 mg, 74%).

R_f (Petroleum ether/ EtOAc = 20:1) = 0.3.

HPLC (IA, *i*-PrOH/*n*-hexane = 10/90, flow rate = 1 mL/min, λ = 215 nm) t_R = 8.287 min (major), 9.167 min (minor), 90% ee.

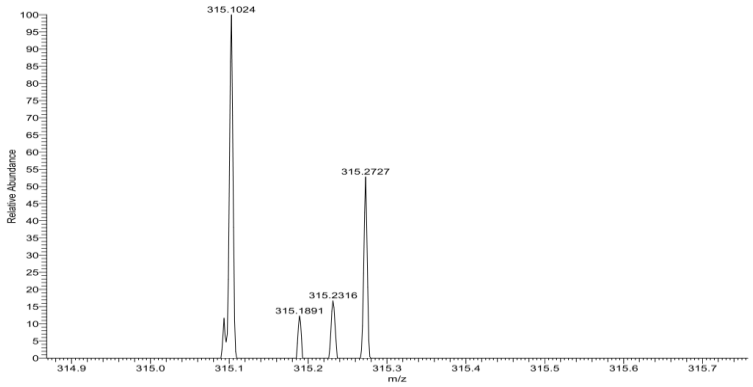
[α]$_D^{25}$: -71.800 (c = 0.2, CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18-8.13 (m, 2H), 7.46-7.43 (m, 2H), 7.38-7.30 (m, 3H), 7.17-7.13 (m, 2H), 6.90 (d, *J* = 16.0 Hz, 1H), 6.39 (dd, *J* = 15.6, 7.2 Hz, 1H), 5.85 (dd, *J* = 7.2, 1.2 Hz, 1H), 3.81 (s, 3H).

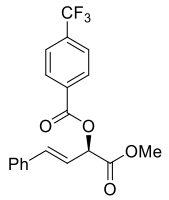
^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.1, 166.1 (d, $^1J_{C\text{-}F}$= 255.9 Hz), 164.7, 135.7, 135.5, 132.6 (d, $^3J_{C\text{-}F}$= 9.5 Hz), 128.8, 128.7, 126.9, 125.5 (d, $^4J_{C\text{-}F}$= 2.9 Hz), 120.8, 115.7 (d, $^2J_{C\text{-}F}$ = 22.2 Hz), 73.72, 52.79.

^{19}F NMR (282 MHz, Chloroform-*d*) δ -104.61.

HRMS(ESI) m/z**:** $[M+H]^+$ Calculated for $C_{18}H_{15}FO_4$ 315.1027; Found 315.1024.



(*R*,*E*)-1-methoxy-1-oxo-4-phenylbut-3-en-2-yl 4-(trifluoromethyl)benzoate (3ea)



Prepared according to general procedure from $Rh_2(TFA)_4$ (2.6 mg, 0.004 mmol, 2 mol%), CPA1(5.8 mg, 0.01 mmol, 5 mol%), 4-(trifluoromethyl)benzoic acid (38.0 mg, 0.2 mmol, 1.0 equiv) and methyl (*E*)-2-diazo-4-phenylbut-3-enoate (80.8 mg, 0.4 mmol, 2.0 equiv) in *n*-pentane (4 mL) at rt for 5 min. The desired product was purified by silica gel column chromatography (Petroleum ether: ethyl acetate = 20:1-5:1) and obtained as yellow oil (37.9 mg, 52%).

R_f (Petroleum ether/ EtOAc = 20:1) = 0.3.

HPLC (IA, *i*-PrOH/*n*-hexane = 1/99, flow rate = 1 mL/min, λ = 215 nm) t_R = 11.194 min (major), 13.421 min (minor), 92% ee.

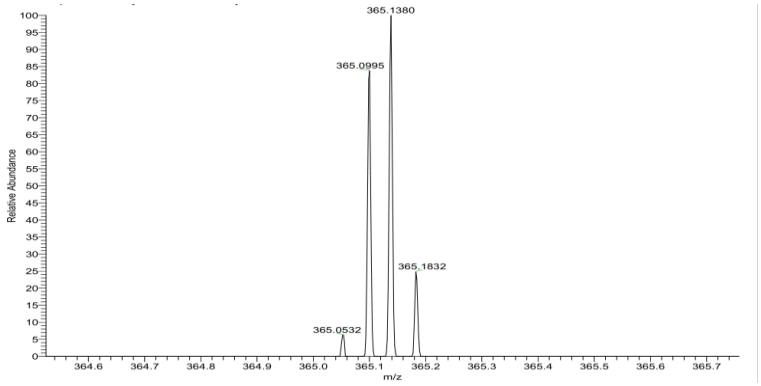
$[\alpha]_D^{25}$: -61.700 (c = 0.2, CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26-8.24 (m, 2H), 7.75-7.73 (m, 2H), 7.46-7.43 (m, 2H), 7.38-7.31 (m, 3H), 6.91 (d, *J* = 15.2 Hz, 1H), 6.40 (dd, *J* = 15.6, 7.2 Hz, 1H), 5.89 (dd, *J* = 7.2, 1.2 Hz, 1H), 3.82 (s, 3H).

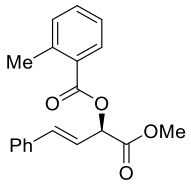
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 164.6, 136.1, 135.5, 135.4, 134.9 (q, $^2J_{C-F}$ = 32.8 Hz), 132.5, 130.4, 128.8, 128.7, 126.9, 125.6(q, $^3J_{C-F}$ = 3.7 Hz), 123.6 (q, $^1J_{C-F}$ = 273.7 Hz), 120.4, 74.1, 52.9.

^{19}F NMR (282 MHz, Chloroform-*d*) δ -63.16.

HRMS(ESI) m/z**:** $[M+H]^+$ Calculated for $C_{19}H_{15}F_3O_4$ 365.0995; Found 365.0995.



(*R*,*E*)-1-methoxy-1-oxo-4-phenylbut-3-en-2-yl 2-methylbenzoate[2] (3fa)



Prepared according to general procedure from $Rh_2(TFA)_4$ (2.6 mg, 0.004 mmol, 2 mol%), CPA1(5.8 mg, 0.01 mmol, 5 mol%), 2-methylbenzoic acid (27.2 mg, 0.2 mmol, 1.0 equiv) and methyl (*E*)-2-diazo-4-phenylbut-3-enoate (80.8 mg, 0.4 mmol, 2.0 equiv) in *n*-pentane (4 mL) at rt for 5 min. The desired product was purified by silica gel column chromatography (Petroleum ether: ethyl acetate = 20:1-5:1) and obtained as colorless oil (57.0 mg, 92%).

R_f (Petroleum ether/ EtOAc = 20:1) = 0.3.

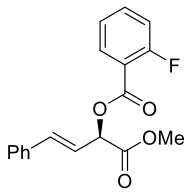
HPLC (IA, *i*-PrOH/*n*-hexane = 10/90, flow rate = 1 mL/min, λ = 215 nm) t_R = 7.047 min (major), 8.547 min (minor), 93% ee.

$[\alpha]_D^{25}$: -106.700 (c = 0.2, CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.45-7.41 (m, 3H), 7.36-7.24 (m, 5H), 6.90 (d, *J* = 17.6 Hz, 1H), 6.39 (dd, *J* = 16.0, 7.2 Hz, 1H), 5.85 (d, *J* = 6.8 Hz, 1H), 3.81 (s, 3H), 2.64 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.4, 166.7, 140.8, 135.6, 135.5, 132.6, 131.8, 131.1, 128.8, 128.7, 128.7, 127.0, 125.9, 121.0, 73.6, 52.8, 21.9.

(*R*,*E*)-1-methoxy-1-oxo-4-phenylbut-3-en-2-yl 2-fluorobenzoate (3ga)



Prepared according to general procedure from $Rh_2(TFA)_4$ (2.6 mg, 0.004 mmol, 2 mol%), **C1**(5.8 mg, 0.01 mmol, 5 mol%), 2-fluorobenzoic acid (28.0 mg, 0.2 mmol, 1.0 equiv) and methyl (*E*)-2-diazo-4-phenylbut-3-enoate (80.8 mg, 0.4 mmol, 2.0 equiv) in *n*-pentane (4 mL) at rt for 5-15 min. The desired product was purified by silica gel column chromatography (Petroleum ether: ethyl acetate = 20:1-5:1) and obtained as yellow oil (48.4mg, 77%).

R_f (Petroleum ether/ EtOAc = 20:1) = 0.3.

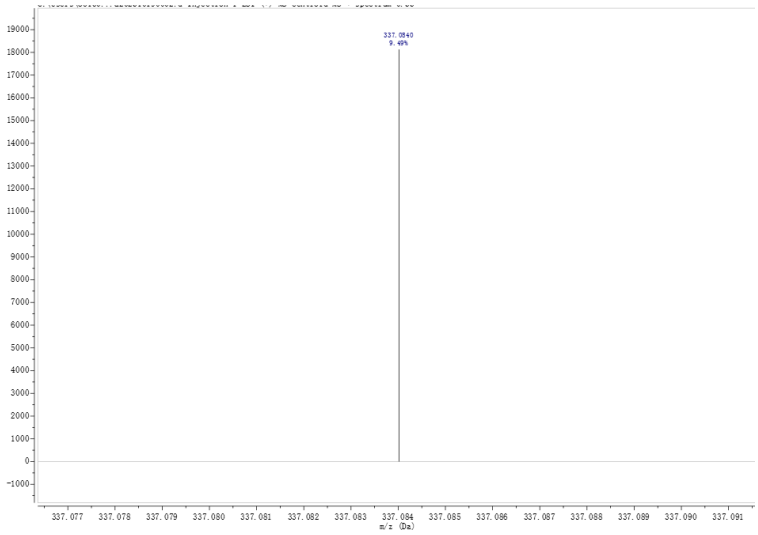
HPLC (IA, *i*-PrOH/*n*-hexane = 1/99, flow rate = 1 mL/min, λ = 215 nm) t_R = 13.930 min (major), 15.930 min (minor), 82% ee.

$[\alpha]_D^{25}$: -69.600 (c = 0.2, CH_2Cl_2).

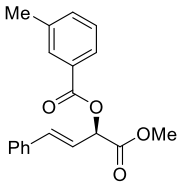
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (td, *J* = 7.6, 2.0 Hz, 1H), 7.59-7.53(m, 1H), 7.45-7.42 (m, 2H), 7.37-7.14 (m, 5H), 6.94 (d, *J* = 16.0 Hz, 1H), 6.38 (dd, *J* = 16.0, 6.8 Hz, 1H), 5.89 (d, *J* = 7.2 Hz, 1H), 3.81 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.9, 163.4 (d, *J* = 3.6 Hz), 162.3 (d, *J* = 261.4 Hz), 135.6, 135.4, 135.2 (d, *J* = 9.1 Hz), 132.5, 128.7, 128.6, 126.9, 124.1 (d, *J* = 4.0 Hz), 120.5, 117.8 (d, *J* = 9.4 Hz), 117.2 (d, *J* = 22.1 Hz), 73.8, 52.8.

HRMS (ESI) m/z: $[M+Na]^+$ Calculated for $C_{18}H_{15}FO_4$ 337.0847; Found 337.0840.



(*R,E*)-1-methoxy-1-oxo-4-phenylbut-3-en-2-yl 3-methylbenzoate[2] (3ha)



Prepared according to general procedure from $Rh_2(TFA)_4$ (2.6 mg, 0.004 mmol, 2 mol%), CPA1(5.8 mg, 0.01 mmol, 5 mol%), 3-methylbenzoic acid (27.2 mg, 0.2 mmol, 1.0 equiv) and methyl (*E*)-2-diazo-4-phenylbut-3-enoate (80.8 mg, 0.4 mmol, 2.0 equiv) in *n*-pentane (4 mL) at rt for 5 min. The desired product was purified by silica gel column chromatography (Petroleum ether: ethyl acetate = 20:1-5:1) and obtained as colorless oil (50.8 mg, 82%).

R_f (Petroleum ether/ EtOAc = 20:1) = 0.3.

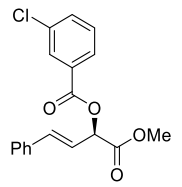
HPLC (IC, *i*-PrOH/*n*-hexane = 5/95, flow rate = 1 mL/min, λ = 215 nm) t_R = 18.806 min (major), 16.260 min (minor), 94% ee.

$[\alpha]_D^{25}$: -86.800 (c = 0.2, CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95-7.94 (m, 2H), 7.46-7.29 (m, 7H), 6.90 (d, *J* = 15.6 Hz, 1H), 6.41 (dd, *J* = 16.0, 7.2 Hz, 1H), 5.86 (d, *J* = 8.4 Hz, 1H), 3.80 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.3, 166.0, 138.4, 135.6, 135.6, 134.4, 130.5, 129.2, 128.8, 128.7, 128.5, 127.2, 127.0, 121.0, 73.7, 52.8, 21.4.

(*R,E)*-1-methoxy-1-oxo-4-phenylbut-3-en-2-yl 3-chlorobenzoate (3ia)



Prepared according to general procedure from $Rh_2(TFA)_4$ (2.6 mg, 0.004 mmol, 2 mol%), CPA1(5.8 mg, 0.01 mmol, 5 mol%), 3-chlorobenzoic acid (31.4 mg, 0.2 mmol, 1.0 equiv) and methyl (*E*)-2-diazo-4-phenylbut-3-enoate (80.8 mg, 0.4 mmol, 2.0 equiv) in *n*-pentane (4 mL) at rt for 5 min. The desired product was purified by silica gel column chromatography (Petroleum ether: ethyl acetate

= 20:1-5:1) and obtained as yellow oil (48.0 mg, 73%).

R_f (Petroleum ether/ EtOAc = 20:1) = 0.3.

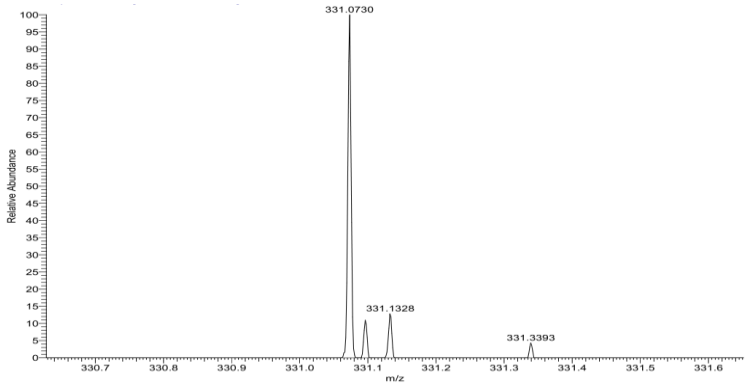
HPLC (IA, *i*-PrOH/*n*-hexane = 10/90, flow rate = 1 mL/min, λ = 215 nm) t_R = 7.830 min (major), 8.535 min (minor), 92% ee.

$[\alpha]_D^{25}$: -73.500 (c = 0.2, CH_2Cl_2).

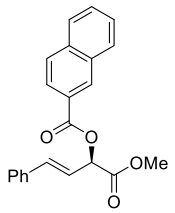
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11-8.00 (m, 2H), 7.58-7.55 (m, 1H), 7.46-7.30 (m, 6H), 6.90 (d, *J* = 14.8 Hz, 1H), 6.39 (dd, *J* = 16.0, 7.2 Hz, 1H), 5.86 (dd, *J* = 7.2, 1.2 Hz, 1H), 3.81 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.0, 164.6, 136.0, 135.4, 134.7, 133.6, 131.0, 130.0, 129.9, 128.9, 128.8, 128.1, 126.9, 120.5, 74.0, 52.9.

HRMS(ESI) m/z**:** $[M+H]^+$ Calculated for $C_{18}H_{15}ClO_4$ 331.0732; Found 331.0730.



(*R*,*E*)-1-methoxy-1-oxo-4-phenylbut-3-en-2-yl 2-naphthoate (3ja)



Prepared according to general procedure from $Rh_2(TFA)_4$ (2.6 mg, 0.004 mmol, 2 mol%), CPA1(5.8 mg, 0.01 mmol, 5 mol%), 2-naphthoic acid (34.4 mg, 0.2 mmol, 1.0 equiv) and methyl (*E*)-2-diazo-4-phenylbut-3-enoate (80.8 mg, 0.4 mmol, 2.0 equiv) in *n*-pentane (4 mL) at rt for 5 min. The desired product was purified by silica gel column chromatography (Petroleum ether: ethyl acetate = 20:1-5:1) and obtained as yellow oil (20.8 mg, 30%).

R_f (Petroleum ether/ EtOAc = 20:1) = 0.3.

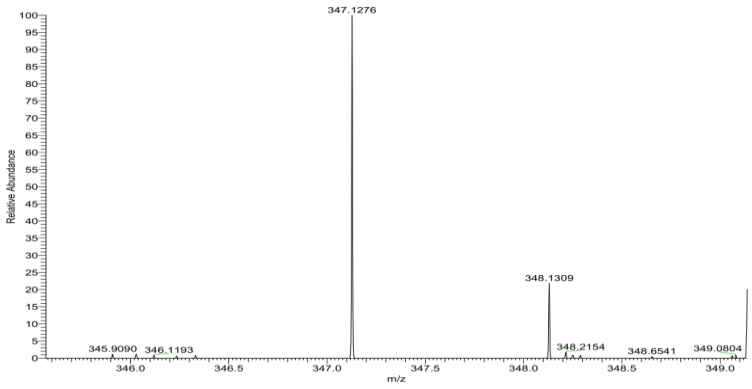
HPLC (IC, *i*-PrOH/*n*-hexane = 10/90, flow rate = 1 mL/min, λ = 215 nm) t_R = 22.623 min (major), 13.509 min (minor), 92% ee.

$[\alpha]_D^{25}$: -32.800 (c = 0.2, CH_2Cl_2).

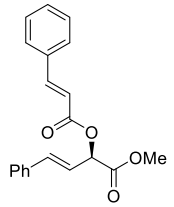
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.72 (t, *J* = 1.2 Hz, 1H), 8.14 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.98 (d, *J* =8.0 1H), 7.90 (t, *J* = 8.8 Hz, 2H), 7.63-7.53 (m, 2H), 7.48-7.45 (m, 2H), 7.40-7.30 (m, 3H), 6.95 (d, *J* = 17.2 Hz, 1H), 6.46 (dd, *J* = 16.0, 7.2 Hz, 1H), 5.94 (dd, *J* = 7.2, 1.2 Hz, 1H), 3.83 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.3, 165.9, 135.8, 135.7, 135.6, 132.5, 131.7, 129.5, 128.8, 128.7, 128.6, 128.4, 127.9, 127.0, 126.8, 126.5, 125.4, 121.0, 73.8, 52.8.

HRMS(ESI) m/z**:** $[M+H]^+$ Calculated for $C_{22}H_{18}O_4$ 347.1278; Found 347.1276.



methyl (*R*,*E*)-2-(cinnamoyloxy)-4-phenylbut-3-enoate[2] (3ka)



Prepared according to general procedure from $Rh_2(TFA)_4$ (2.6 mg, 0.004 mmol, 2 mol%), CPA1(5.8 mg, 0.01 mmol, 5 mol%), cinnamic acid (29.6 mg, 0.2 mmol, 1.0 equiv) and methyl (*E*)-2-diazo-4-phenylbut-3-enoate (80.8 mg, 0.4 mmol, 2.0 equiv) in *n*-pentane (4 mL) at rt for 5 min. The desired product was purified by silica gel column chromatography (Petroleum ether: ethyl acetate = 20:1-5:1) and obtained as yellow oil (37.4 mg, 58%).

R_f (Petroleum ether/ EtOAc = 20:1) = 0.3.

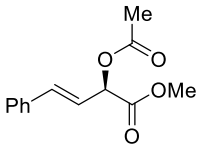
HPLC (IA, *i*-PrOH/*n*-hexane = 10/90, flow rate = 1 mL/min, λ = 215 nm) t_R = 14.299 min (major), 16.249 min (minor), 82% ee.

$[\alpha]_D^{25}$: -45.800 (c = 0.2, CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 16.0 Hz, 1H), 7.57-7.54 (m, 2H), 7.45-7.42 (m, 2H), 7.41-7.39 (m, 3H), 7.37-7.33 (m, 3H), 6.87 (dd, *J* = 16.0, 1.6 Hz, 1H), 6.58 (d, *J* = 16.0 Hz, 1H), 6.34 (dd, *J* = 16.0, 7.2 Hz, 1H), 5.78 (dd, *J* = 7.2, 1.6 Hz, 1H), 3.81 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.3, 166.0, 146.4, 135.6, 135.5, 134.2, 130.7, 129.0, 128.7, 128.6, 128.3, 126.9, 120.9, 116.9, 73.3, 52.8.

methyl (*R*,*E*)-2-acetoxy-4-phenylbut-3-enoate[2] (3la)



Prepared according to general procedure from $Rh_2(TFA)_4$ (2.6 mg, 0.004 mmol, 2 mol%), **C1**(5.8 mg, 0.01 mmol, 5 mol%), acetic acid (12 mg, 0.2 mmol, 1.0 equiv) and methyl (*E*)-2-diazo-4-phenylbut-3-enoate (80.8 mg, 0.4 mmol, 2.0 equiv) in *n*-pentane (4 mL) at rt for 5-15 min. The desired product was purified by silica gel column chromatography (Petroleum ether: ethyl acetate = 20:1-5:1) and obtained as yellow oil (43.1 mg, 92%).

R_f (Petroleum ether/ EtOAc = 20:1) = 0.3.

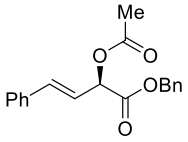
HPLC (IA, *i*-PrOH/*n*-hexane = 10/90, flow rate = 1 mL/min, λ = 215 nm) t_R = 11.581 min (major), 9.075 min (minor), 73% ee.

$[\alpha]_D^{25}$: -53.400 (c = 0.2, CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42-7.40 (m, 2H), 7.36 – 7.29 (m, 3H), 6.81 (d, *J* = 14.8 Hz, 1H), 6.26 (dd, *J* = 16.0, 7.2 Hz, 1H), 5.63 (dd, *J* = 7.2, 1.2 Hz, 1H), 3.78 (s, 3H), 2.20 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.2, 169.2, 135.5, 135.4, 128.7, 128.65, 126.9, 120.7, 73.2, 52.8, 20.8.

benzyl (*R*,*E*)-2-acetoxy-4-phenylbut-3-enoate (3lc)



Prepared according to general procedure from $Rh_2(TFA)_4$ (2.6 mg, 0.004 mmol, 2 mol%), **C1**(5.8 mg, 0.01 mmol, 5 mol%), acetic acid (12 mg, 0.2 mmol, 1.0 equiv) and benzyl (*E*)-2-diazo-4-phenylbut-3-enoate (111.2 mg, 0.4 mmol, 2.0 equiv) in *n*-pentane (4 mL) at rt for 5-15 min. The desired product was purified by silica gel column chromatography (Petroleum ether: ethyl acetate = 20:1-5:1) and obtained as colorless oil (52.1. mg, 84%).

R_f (Petroleum ether/ EtOAc = 20:1) = 0.3.

HPLC (IA, *i*-PrOH/*n*-hexane = 1/99, flow rate = 1 mL/min, λ = 215 nm) t_R =12.414 min (major), 13.794 min (minor), 82% ee.

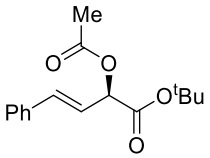
$[\alpha]_D^{25}$: -57.500 (c = 0.2, CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.27 (m, 10H), 6.80 (dd, *J* = 16.0, 1.2 Hz, 1H), 6.25 (dd, *J* = 16.0, 7.2 Hz, 1H), 5.66 (dd, *J* = 7.2, 1.6 Hz, 1H), 5.22 (d, *J* = 2.8 Hz, 2H), 2.19 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.2, 168.61, 135.6, 135.4, 135.2, 128.7, 128.6, 128.6, 128.5, 128.2, 126.9, 120.7, 73.2, 67.4, 20.8.

HRMS (ESI) m/z: $[M+Na]^+$ Calculated for $C_{19}H_{18}O_4$ 333.1097; Found 333.1096.

tert-butyl (*R*,*E*)-2-acetoxy-4-phenylbut-3-enoate[3] (3ld)



Prepared according to general procedure from $Rh_2(TFA)_4$ (2.6 mg, 0.004 mmol, 2 mol%), CPA1(5.8 mg, 0.01 mmol, 5 mol%), acetic acid (12 mg, 0.2 mmol, 1.0 equiv) and tert-butyl (*E*)-2-diazo-4-phenylbut-3-enoate (97.6 mg, 0.4 mmol, 2.0 equiv) in *n*-pentane (4 mL) at rt for 5 min. The desired product was purified by silica gel column chromatography (Petroleum ether: ethyl acetate = 20:1-5:1) and obtained as colorless oil (34.0 mg, 62%).

R_f (Petroleum ether/ EtOAc = 20:1) = 0.3.

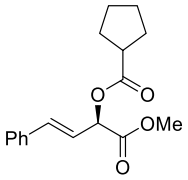
HPLC (IA, *i*-PrOH/*n*-hexane = 1/99, flow rate = 1 mL/min, λ = 215 nm) t_R = 5.833 min (major), 6.275 min (minor), 86% ee.

$[\alpha]_D^{25}$: -17.600 (c = 0.2, CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43-7.39 (m, 2H), 7.36-7.28 (m, 3H), 6.80 (d, *J* = 16.0 Hz, 1H), 6.25 (dd, *J* = 16.0, 6.8 Hz, 1H), 5.49 (dd, *J* = 6.8, 1.2 Hz, 1H), 2.20 (s, 3H), 1.48 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.2, 167.8, 135.8, 134.7, 128.7, 128.5, 126.8, 121.3, 82.8, 73.7, 28.0, 20.8.

(*R*,*E*)-1-methoxy-1-oxo-4-phenylbut-3-en-2-yl cyclopentanecarboxylate[2] (3ma)



Prepared according to general procedure from $Rh_2(TFA)_4$ (2.6 mg, 0.004 mmol, 2 mol%), **C1**(5.8 mg, 0.01 mmol, 5 mol%), cyclopentanecarboxylic acid (22.8 mg, 0.2 mmol, 1.0 equiv) and methyl (*E*)-2-diazo-4-phenylbut-3-enoate (80.8 mg, 0.4 mmol, 2.0 equiv) in *n*-pentane (4 mL) at rt for 5-15 min. The desired product was purified by silica gel column chromatography (Petroleum ether: ethyl acetate = 20:1-5:1) and obtained as yellow oil (35.7 mg, 62%).

R_f (Petroleum ether/ EtOAc = 20:1) = 0.3.

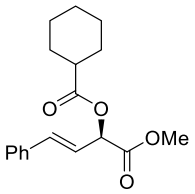
HPLC (IA, *i*-PrOH/*n*-hexane = 10/90, flow rate = 1 mL/min, λ = 215 nm) t_R = 5.678 min (major), 6.462 min (minor), 80% ee.

$[\alpha]_D^{25}$: -43.100 (c = 0.2, CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.39 (m, 2H), 7.36 – 7.26 (m, 3H), 6.80 (d, *J* = 16.0 Hz, 1H), 6.28 (dd, *J* = 16.0, 7.2 Hz, 1H), 5.62 (dd, *J* = 7.2, 1.6 Hz, 1H), 3.77 (s, 3H), 2.94 – 2.86 (m, 1H), 2.00 – 1.85 (m, 4H), 1.77-1.69 (m, 2H), 1.65-1.57 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.0, 169.4, 135.6, 135.1, 128.7, 128.6, 126.9, 121.0, 72.9, 52.7, 43.5, 30.1, 29.8, 25.9, 25.9.

(*R*,*E*)-1-methoxy-1-oxo-4-phenylbut-3-en-2-yl cyclohexanecarboxylate[2] (3na)



Prepared according to general procedure from $Rh_2(TFA)_4$ (2.6 mg, 0.004 mmol, 2 mol%), CPA1(5.8 mg, 0.01 mmol, 5 mol%), cyclohexanecarboxylic acid (25.6 mg, 0.2 mmol, 1.0 equiv) and methyl (*E*)-2-diazo-4-phenylbut-3-enoate (80.8 mg, 0.4 mmol, 2.0 equiv) in *n*-pentane (4 mL) at rt for 5 min. The desired product was purified by silica gel column chromatography (Petroleum ether: ethyl acetate = 20:1-5:1) and obtained as yellow oil (47.1 mg, 78%).

R_f (Petroleum ether/ EtOAc = 20:1) = 0.3.

HPLC (IA, *i*-PrOH/*n*-hexane = 10/90, flow rate = 1 mL/min, λ = 215 nm) t_R = 5.585 min (major), 6.321 min (minor), 90% ee.

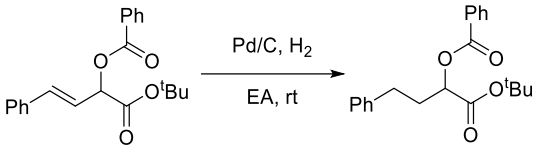
$[\alpha]_D^{25}$: -147.760 (c = 0.2, CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 1.6 Hz, 2H), 7.35-7.28 (m, 3H), 6.80 (d, *J* = 14.8 Hz, 1H), 6.27 (dd, *J* = 16.0, 6.8 Hz, 1H), 5.62 (dd, *J* = 6.8, 1.2 Hz, 1H), 3.77 (s, 3H), 2.51-2.44 (m, 1H), 2.05-1.94 (m, 2H), 1.80-1.76 (m, 2H), 1.69-1.63 (m, 1H), 1.57-1.48 (m, 2H), 1.38-1.26 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.2, 169.3, 135.6, 135.1, 128.7, 128.6, 126.9, 121.0, 72.8, 52.7, 42.9, 29.0, 28.8, 25.7, 25.4, 25.3.

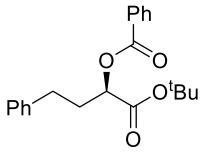
6. Further Transformation

Hydrogenation of 3ad to ester 4ad



3ad (64.3 mg, 0.19 mmol) was dissolved in EA (4.0 mL), then10% Pd/C (20 wt%) was added. The resulting solution was stirred at rt under atmosphere of H_2 (balloon) for overnight. After completion, purification by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) gave the product 4ad in 91% yield with 97% ee as white solid. mp: 61-62 °C.

1-(tert-butoxy)-1-oxo-4-phenylbutan-2-yl benzoate (4ad)



R_f (Petroleum ether/ EtOAc = 20:1) = 0.4.

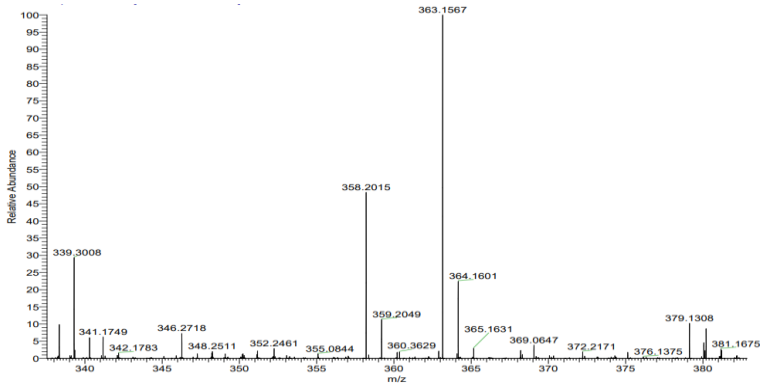
HPLC (IE, *i*-PrOH/*n*-hexane = 0.5/99.5, flow rate = 1 mL/min, λ = 215 nm) t_R = 15.180 min (major), 14.249 min (minor), 97% ee.

$[\alpha]_D^{25}$: 27.200(c = 0.2, CH_2Cl_2).

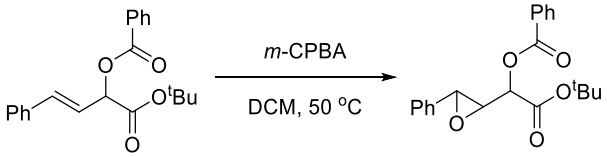
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09-8.06 (m, 2H), 7.60-7.55 (m, 1H), 7.47-7.43 (m, 2H), 7.32-7.28 (m, 2H), 7.24-7.20 (m, 3H), 5.14 (dd, *J* = 8.0, 4.0 Hz, 1H), 2.84 (dd, *J* = 12.0, 8.0 Hz, 2H), 2.32-2.25 (m, 2H), 1.47 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.2, 166.1, 140.8, 133.3, 129.9, 129.7, 128.6, 128.5, 128.4, 126.3, 82.3, 72.7, 33.0, 31.6, 28.0.

HRMS(ESI) m/z**:** $[M+H]^+$ Calculated for $C_{21}H_{25}O_4$ 341.1747; Found 341.1749.

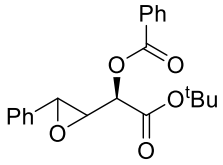


Epoxidation of 3ad

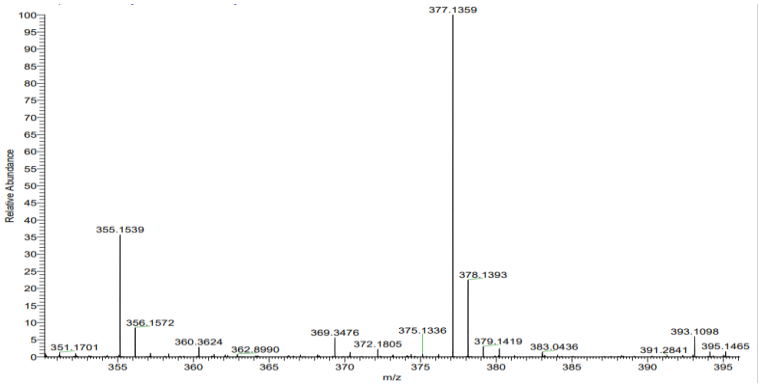


To an ice-bath cold solution of 3ad (40.0 mg, 0.1 mmol) in chloroform (2 mL) was added *m*-CPBA (30.6 mg, 0.15 mmol). The resulting mixture was stirred at room temperature for 12 h and then washed with a saturated sodium bicarbonate aqueous solution, brine, dried Na_2SO_4 and concentrated. The crude oil was purified through chromatography (silica-gel, petroleum ether/ethyl acetate = 20:1) to give product 5ad in 74% yield as white solid. mp: 80-81°C.

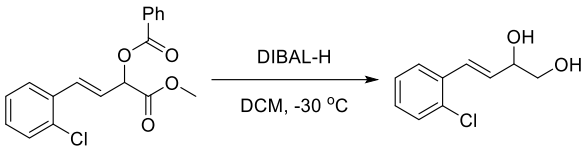
2-(tert-butoxy)-2-oxo-1-(3-phenyloxiran-2-yl)ethyl benzoate (5ad)



R_f (Petroleum ether/ EtOAc = 20:1) = 0.2.
HPLC (IC, *i*-PrOH/*n*-hexane = 5/95, flow rate = 1 mL/min, λ = 215 nm) t_R = 18.070 min (major), 9.820 min (minor), t_R' = 13.994 min (major), 11.020 min (minor), 1.8/1 dr (96%/96% ee).
$[\alpha]_D^{25}$: -26.600(c = 0.2, CH_2Cl_2).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16-8.13 (m, 2H), 7.50-7.44 (m, 3H), 7.40-7.34 (m, 5H), 5.18 (d, *J* = 6.0 Hz, 1H), 4.09 (d, *J* = 2.0 Hz, 1H), 3.54-3.52 (m, 1H), 1.49 (s, 9H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.9, 165.7, 135.7, 133.6, 130.0, 129.1, 128.7, 128.6, 128.5, 125.7, 83.4, 73.6, 60.3, 56.3, 28.1.
HRMS(ESI) m/z**:** $[M+H]^+$ Calculated for $C_{21}H_{23}O_4$ 355.1540; Found 355.1539.

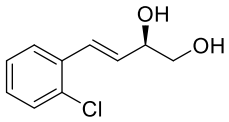


Reduction of 3ak to diol 6ak



3ak (50 mg, 0.15 mmol, 1.0 equiv) was dissolved in anhydrous DCM (2 mL) under Ar in a 10 mL Schlenk tube. Then DIBAL-H (3.0 M in DCM, 0.2 mL, 0.6 mmol, 5 equiv) was added under Ar at -30 °C and stirred for 3 h. The resulting solution was quenched by the addition of sat. potassium sodium tartrate (aq.) and the biphasic mixture was stirred for 1 h at -30 °C. Then the reaction mixture was diluted with water and extracted with DCM. The combined organic layers were dried over Na_2SO_4 and the solvent removed in vacuo. The crude product was purified by column chromatography (DCM/MeOH = 20:1) and gave allylic alcohol 6ak (19.0 mg, 64%) as yellow oil.

(*E*)-4-(2-chlorophenyl)but-3-ene-1,2-diol (6ak)



R_f (DCM/MeOH = 20:1) = 0.2.

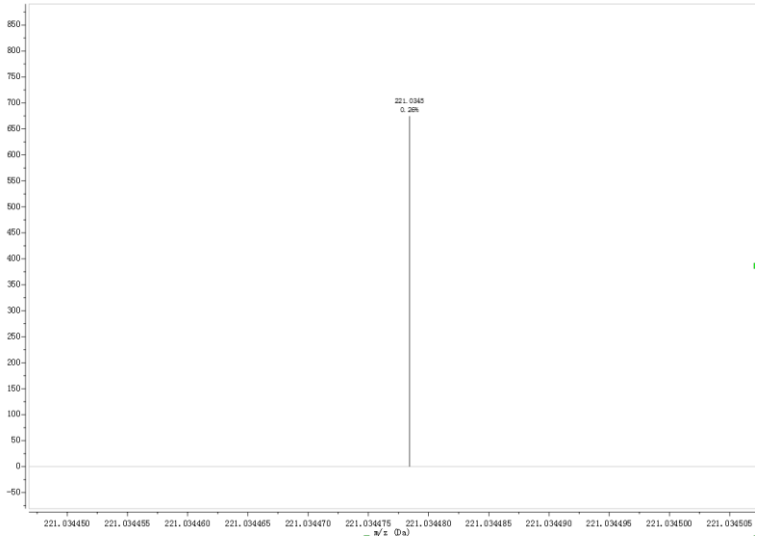
HPLC (IC, *i*-PrOH/*n*-hexane = 10/90, flow rate = 1 mL/min, λ = 215 nm) t_R = 11.208 min (major), 12.486 min (minor), 90% ee.

$[\alpha]_D^{25}$: -9.500(c = 0.2, CH_2Cl_2).

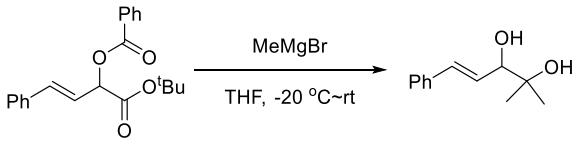
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54-7.49 (m, 1H), 7.37 – 7.32 (m, 1H), 7.24 – 7.16 (m, 2H), 7.08 (dd, J = 16.0, 1.6 Hz, 1H), 6.20 (dd, J = 16.0, 6.4 Hz, 1H), 4.50-4046 (m, 1H), 3.78 (dd, J = 11.2, 3.2 Hz, 1H), 3.62 (dd, J = 11.2, 7.2 Hz, 1H), 2.83 (s, 1H), 2.57 (s, 1H).

^{13}C NMR (101 MHz, Chloroform-d) δ 134.5, 133.2, 130.7, 129.8, 128.9, 128.3, 126.93, 126.9, 73.2, 66.4.

HRMS(ESI) m/z**:** $[M+Na]^+$ Calculated for $C_{10}H_{11}ClO_2$ 221.0340; Found 221.0345.

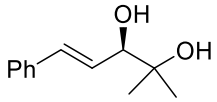


Synthesis of diol 7ad



A solution of 3ad (50 mg, 0.15 mmol) in THF (2 mL) was injected into a 10 mL Schlenk tube filled with Ar. The solution was cooled down to -20 °C and allowed to stir for 15- 30 minutes. Thereafter, methyl magnesium bromide (0.3 mL, 3.0 mol/L in THF, 0.75 mmol, 5.0 equiv) was added dropwise. The formed mixture was stirred at -20 °C for 2 h. After heating to room temperature, the reaction continued to stir overnight and monitored by TLC analysis. After completion, the resulting mixture was quenched with saturated NH_4Cl in H_2O. The resulting solution was extracted with ethyl acetate to give a combined organic layer that was dried over anhydrous Na_2SO_4. Further purification by column chromatography on silica gel (DCM/MeOH = 20:1) afforded 7ad as colorless oil. (17.3 mg, 60% yield).

(*E*)-2-methyl-5-phenylpent-4-ene-2,3-diol[2] (7ad)



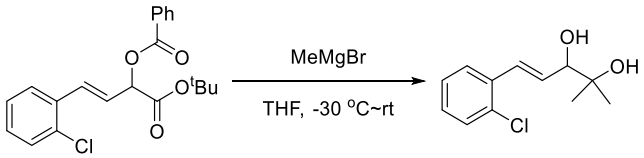
R_f (DCM/MeOH = 20:1) = 0.2.

HPLC (IC, *i*-PrOH/*n*-hexane = 5/95, flow rate = 1 mL/min, λ = 215 nm) t_R = 14.769 min (major), 12.831 min (minor), 98% ee.

$[\alpha]_D^{25}$: 14.100(c = 0.2, CH_2Cl_2).

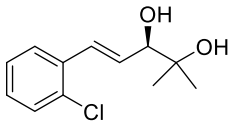
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41-7.38 (m, 2H), 7.35-7.30 (m, 2H), 7.28-7.26 (m, 1H), 6.66 (d, *J* = 14.8 Hz, 1H), 6.25 (dd, *J* = 16.0, 7.2 Hz, 1H), 4.09 (dd, *J* = 7.2, 1.6 Hz, 1H), 2.28 (s, 1H), 2.14 (s, 1H), 1.28 (s, 3H), 1.22 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.5, 133.0, 128.6, 127.9, 127.8, 126.6, 79.8, 73.1, 26.5, 23.9.



A solution of 3ak (50 mg, 0.15 mmol) in THF (2 mL) was injected into a 10 mL Schlenk tube filled with Ar. The solution was cooled down to -30 °C and allowed to stir for 15- 30 minutes. Thereafter, methyl magnesium bromide (0.3 mL, 3.0 mol/L in THF, 0.75 mmol, 5.0 equiv) was added dropwise. The formed mixture was stirred at -30 °C for 2 h. After heating to room temperature, the reaction continued to stir overnight and monitored by TLC analysis. After completion, the resulting mixture was quenched with saturated NH_4Cl in H_2O. The resulting solution was extracted with ethyl acetate to give a combined organic layer that was dried over anhydrous Na_2SO_4. Further purification by column chromatography on silica gel (DCM/MeOH = 20:1) afforded 7ak as colorless oil. (21.0 mg, 62% yield).

(*E*)-5-(2-chlorophenyl)-2-methylpent-4-ene-2,3-diol (7ak)



R_f (DCM/MeOH = 20:1) = 0.2.

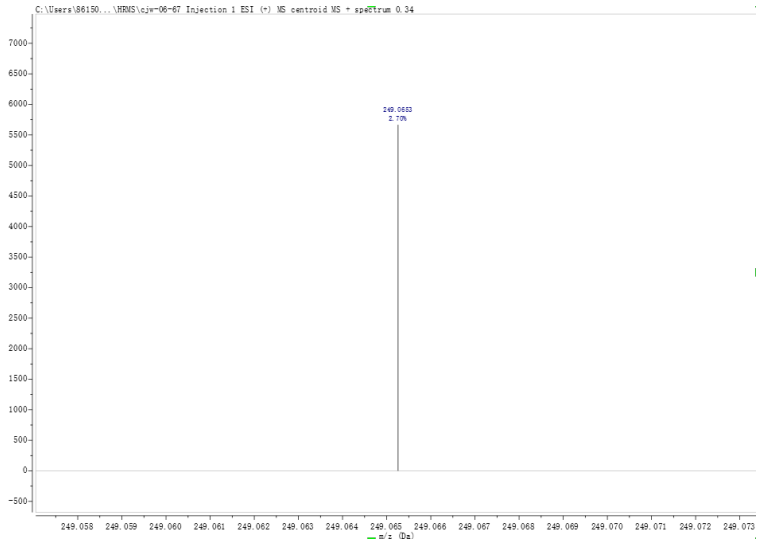
HPLC (IC, *i*-PrOH/*n*-hexane = 10/90, flow rate = 1 mL/min, λ = 215 nm) t_R = 7.864 min (major), 6.701 min (minor), 91% ee.

$[\alpha]_D^{25}$: 6.000(c = 0.2, CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.51 (m, 1H), 7.37-7.34 (m, 1H), 7.25-7.16 (m, 2H), 7.03 (dd, *J* = 16.0, 1.2 Hz, 1H), 6.23 (dd, *J* = 16.0, 7.2 Hz, 1H), 4.12 (dd, *J* = 7.2, 1.2 Hz, 1H), 2.66 (s, 1H), 2.39 (d, *J* = 15.2 Hz, 1H), 1.29 (s, 3H), 1.22 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.8, 133.2, 131.0, 129.7, 129.1, 128.9, 127.0, 126.9, 79.6, 73.1, 26.5, 24.0.

HRMS(ESI) m/z**:** $[M+Na]^+$ Calculated for $C_{12}H_{15}ClO_2$ 249.0653; Found 249.0653.


C:\Users\86150...\HRMS\cjw-06-67 Injection 1 ESI (+) MS centroid MS + spectrum 0.34
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2.70%
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6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
249.058
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249.061
249.062
249.063
249.064
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249.069
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249.071
249.072
249.073
m/z (Da)

7. X-ray crystallographic data

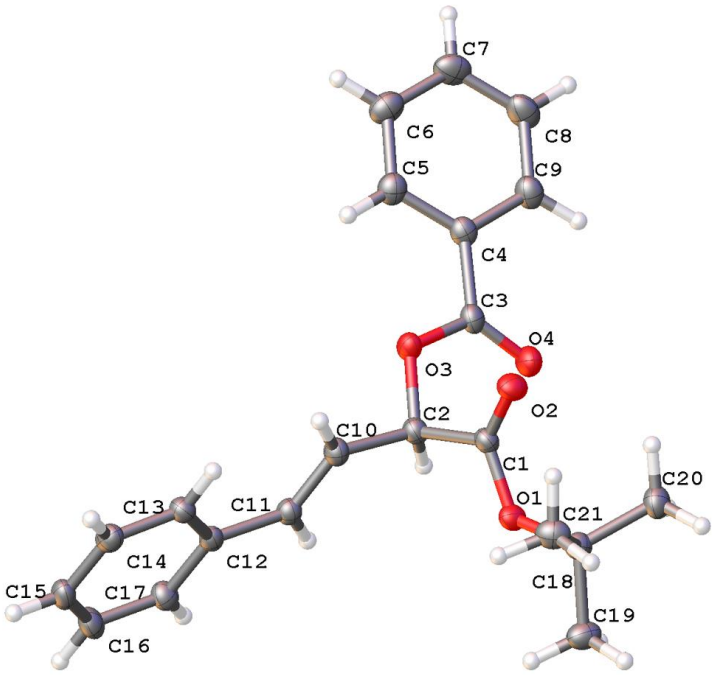


Figure S1. X-ray crystal structure of 3ad

Table S2 Crystal data and structure refinement for 3ad.

Empirical formula	C21 H22 O4	
Formula weight	338.38	
Temperature	213.00 K	
Wavelength	1.34139 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 5.95320(10) Å	a= 90.0640(10)°.
	b = 10.2293(2) Å	b= 93.1930(10)°.
	c = 22.7669(4) Å	g= 92.5580(10)°.
Volume	1382.90(4) $Å^3$	
Z	3	
Density (calculated)	1.219 Mg/m^3	
Absorption coefficient	0.431 mm^{-1}	
F(000)	540	
Crystal size	0.07 x 0.07 x 0.05 mm^3	
Theta range for data collection	3.383 to 54.990°.	
Index ranges	-7<=h<=7, -12<=k<=12, -27<=l<=27	
Reflections collected	43148	
Independent reflections	10370 [R(int) = 0.0562]	

Completeness to theta = 53.594°	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7508 and 0.4930
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10370 / 3 / 685
Goodness-of-fit on F^2	1.029
Final R indices [I>2sigma(I)]	R1 = 0.0322, wR2 = 0.0817
R indices (all data)	R1 = 0.0339, wR2 = 0.0831
Absolute structure parameter	0.17(7)
Extinction coefficient	n/a
Largest diff. peak and hole	0.108 and -0.138 e.$Å^{-3}$

8. References

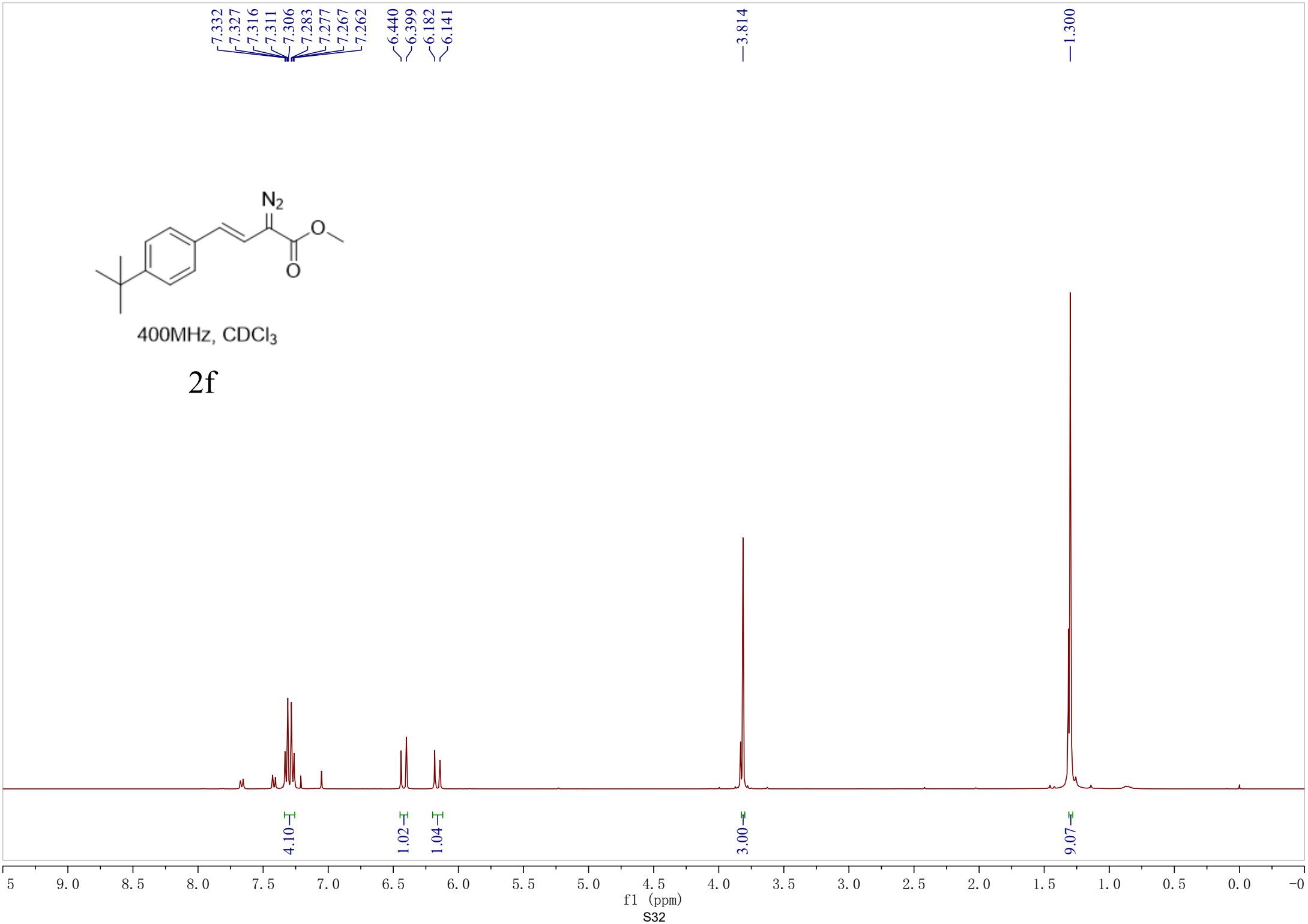
[1] (a) Shim, S. Y.; Cho, S. M.; Venkateswarlu, A.; Ryu, D. H. *Angew. Chem. Int. Ed*. **2017**, *56*, 8585. (b) Zha, G.-F.; Han, J.-B.; Hu, X.-Q.; Qin, H.-L.; Fang, W.-Y.; Zhang, C.-P. *Chem. Commun*. **2016**, *52*, 7458.

[2] Xu, Y.-Y.; Gao, Z.-H.; Li, C.-B.; Ye, S. *Angew. Chem. Int. Ed.* **2023**, *62*, e202218362.

[3] Xia, C.; Shen, J.-F.; Liu, D.-L.; Zhang, W.-B. *Org. Lett.* **2017**, *19*, 4251.

[4] Pisella. G.; Gagnebin, A.; Waser, J. *Org. Lett.* **2020**, *22*, 3884.

[5]Kimberly M. S.; Michael T. C.; C. Guy. G.; Jeffrey S. J. *J. Am. Chem. Soc.* **2012**, *134*, 20197.


7.332
7.327
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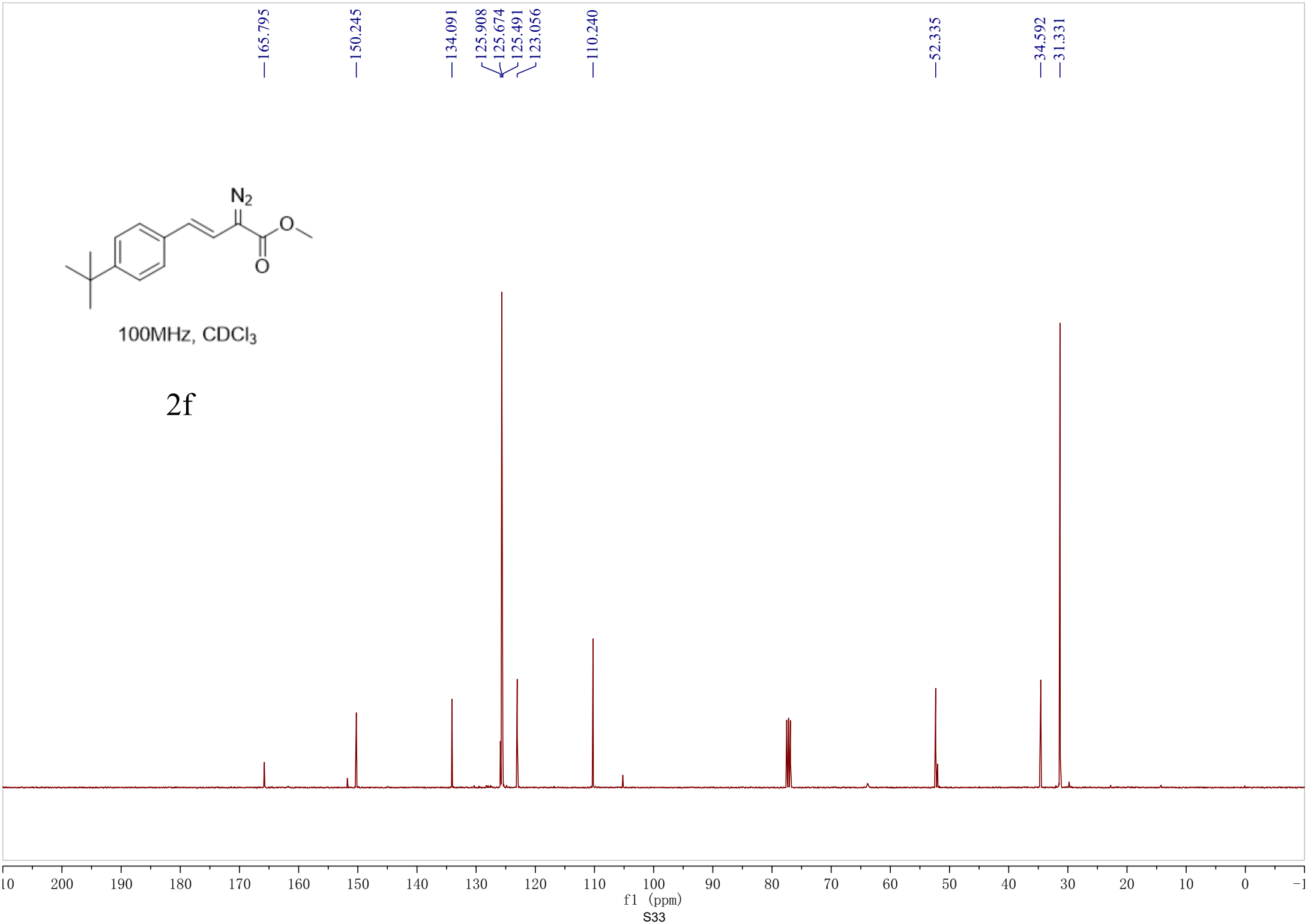
7.311
7.306
7.283
7.277
7.267
7.262
6.440
6.399
6.182
6.141
3.814
1.300
N2
O
O
400MHz, CDCl3
2f
4.10
1.02
1.04
3.00
9.07
f1 (ppm)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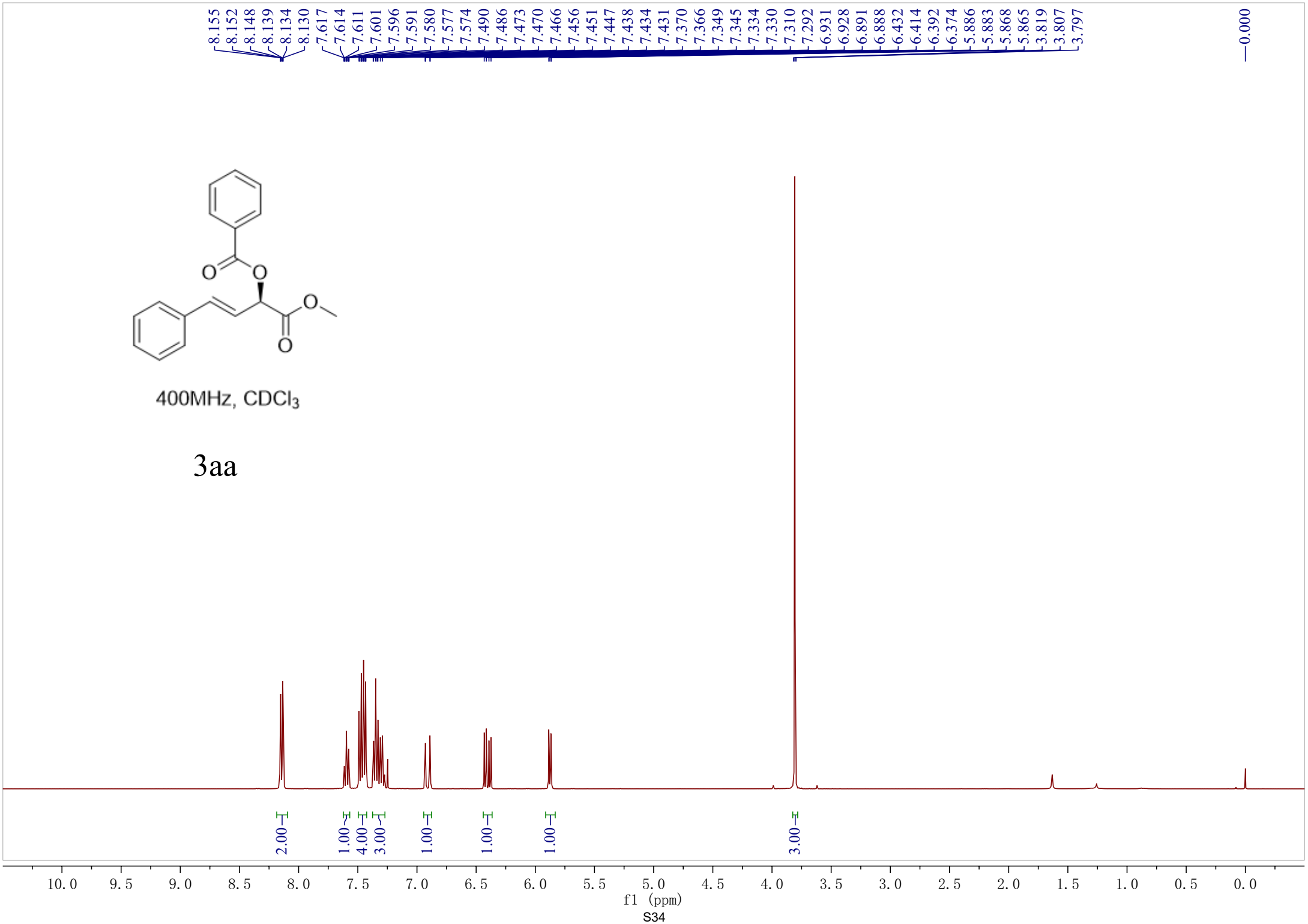
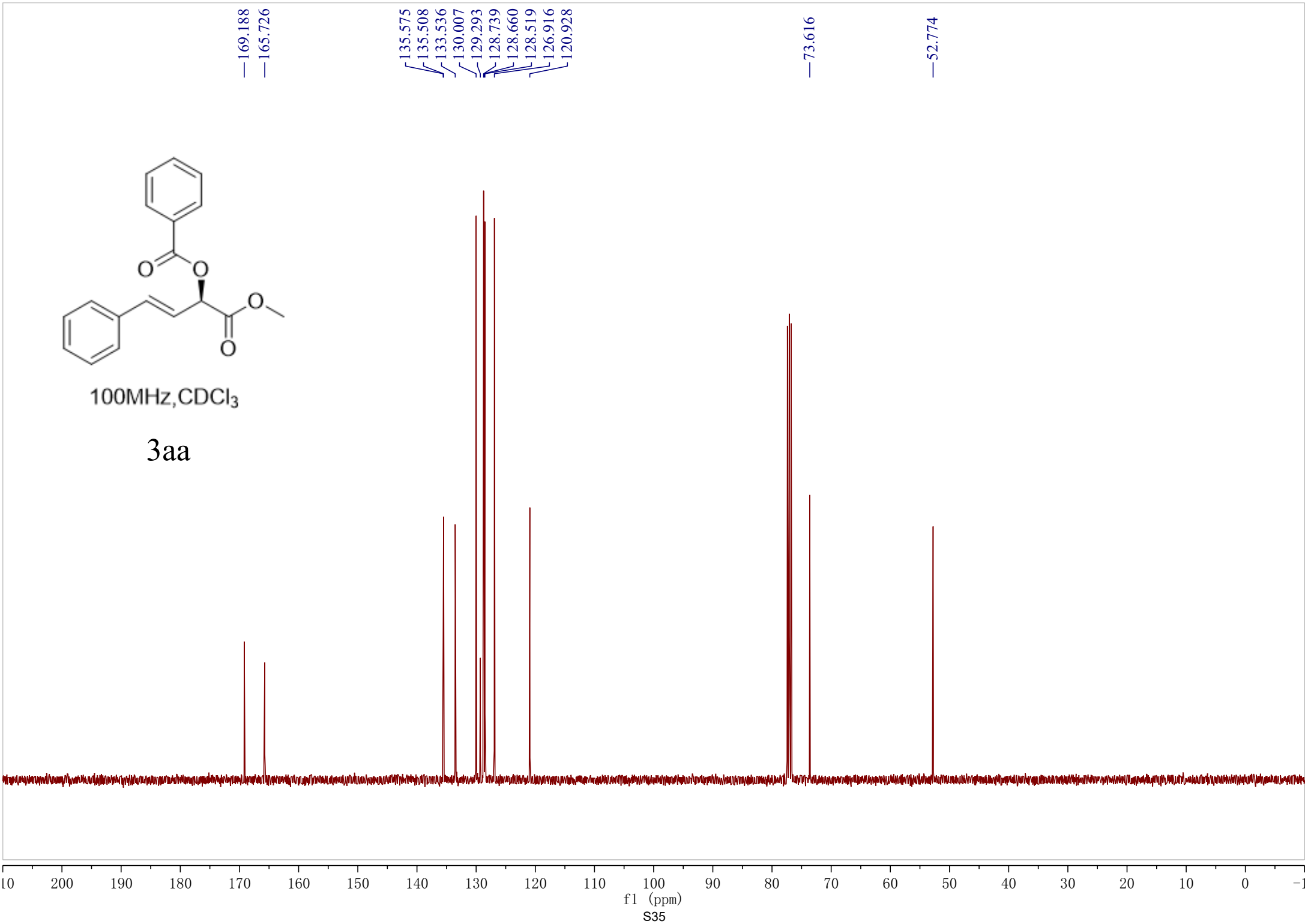
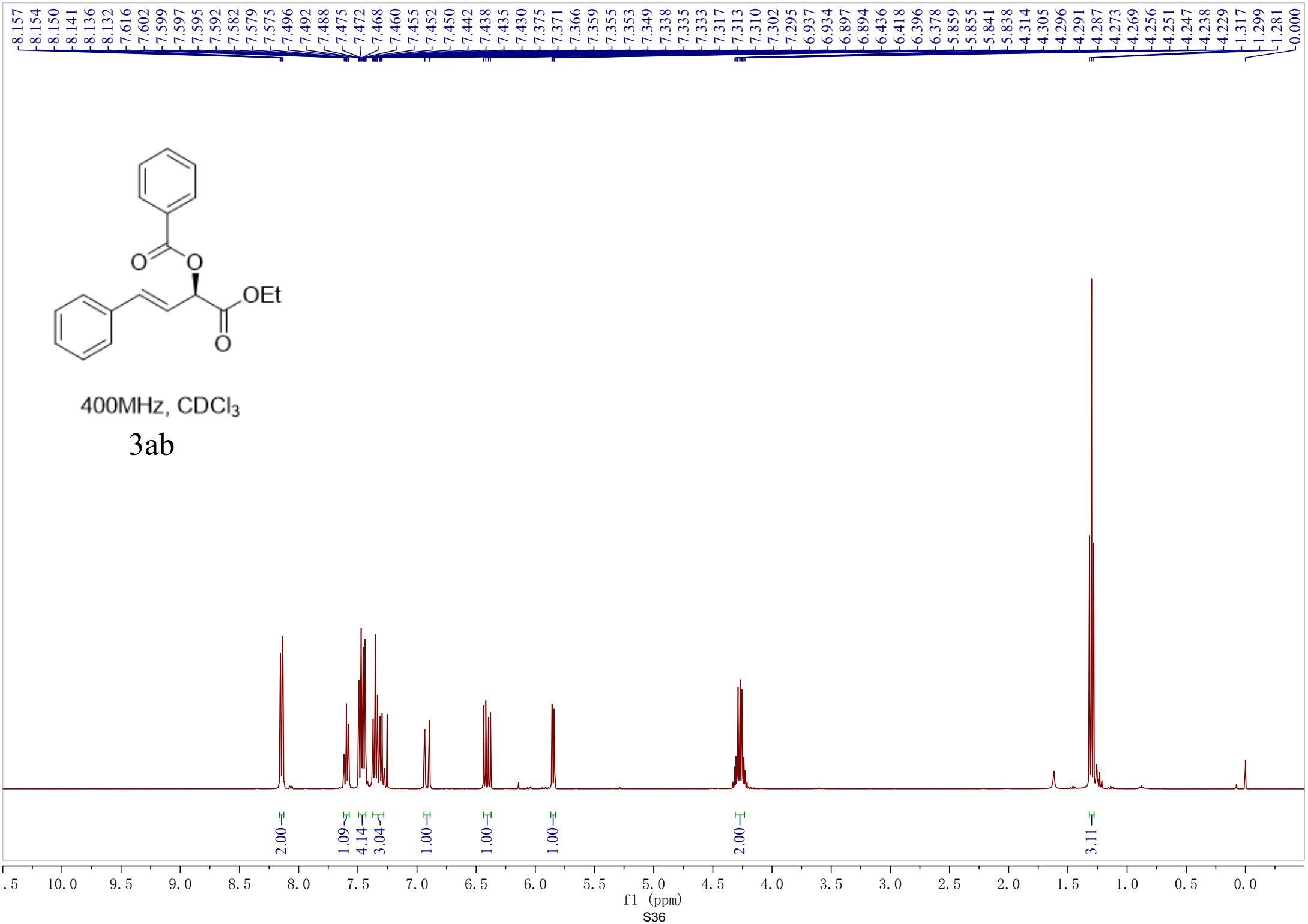
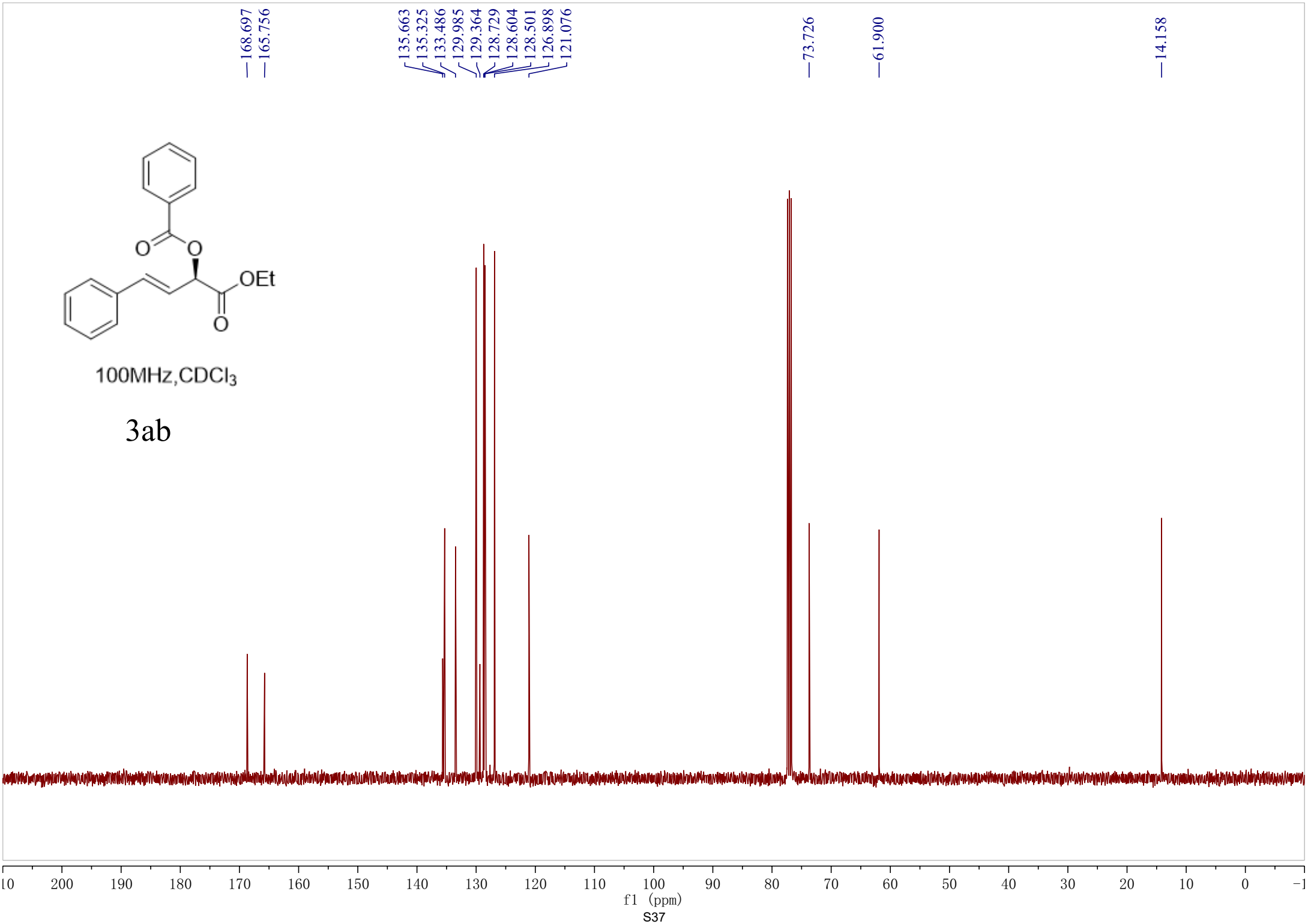
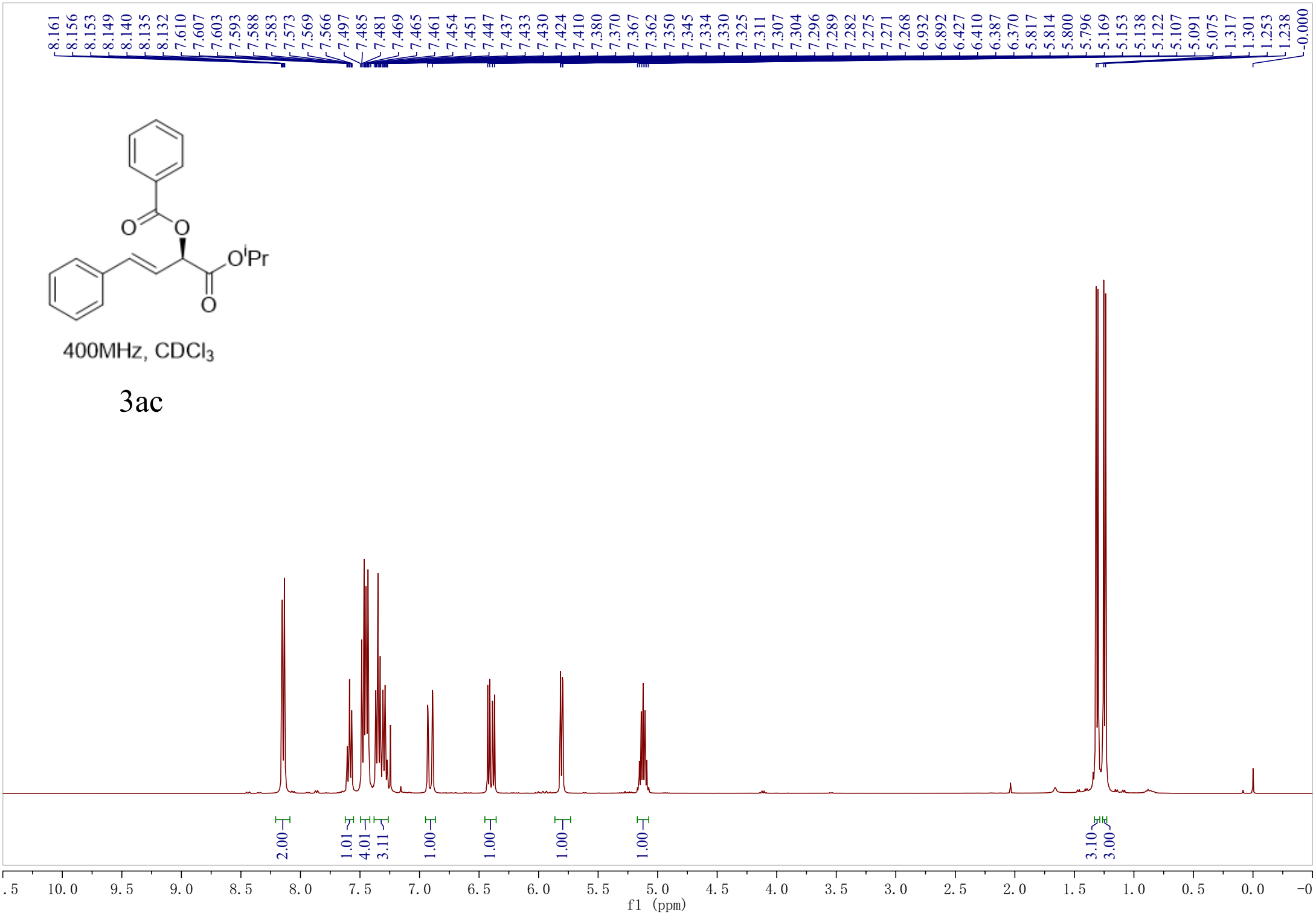
125.674
125.491
123.056
110.240
52.335
34.592
31.331
N2
O
O
100MHz, CDCl3
2f
f1 (ppm)

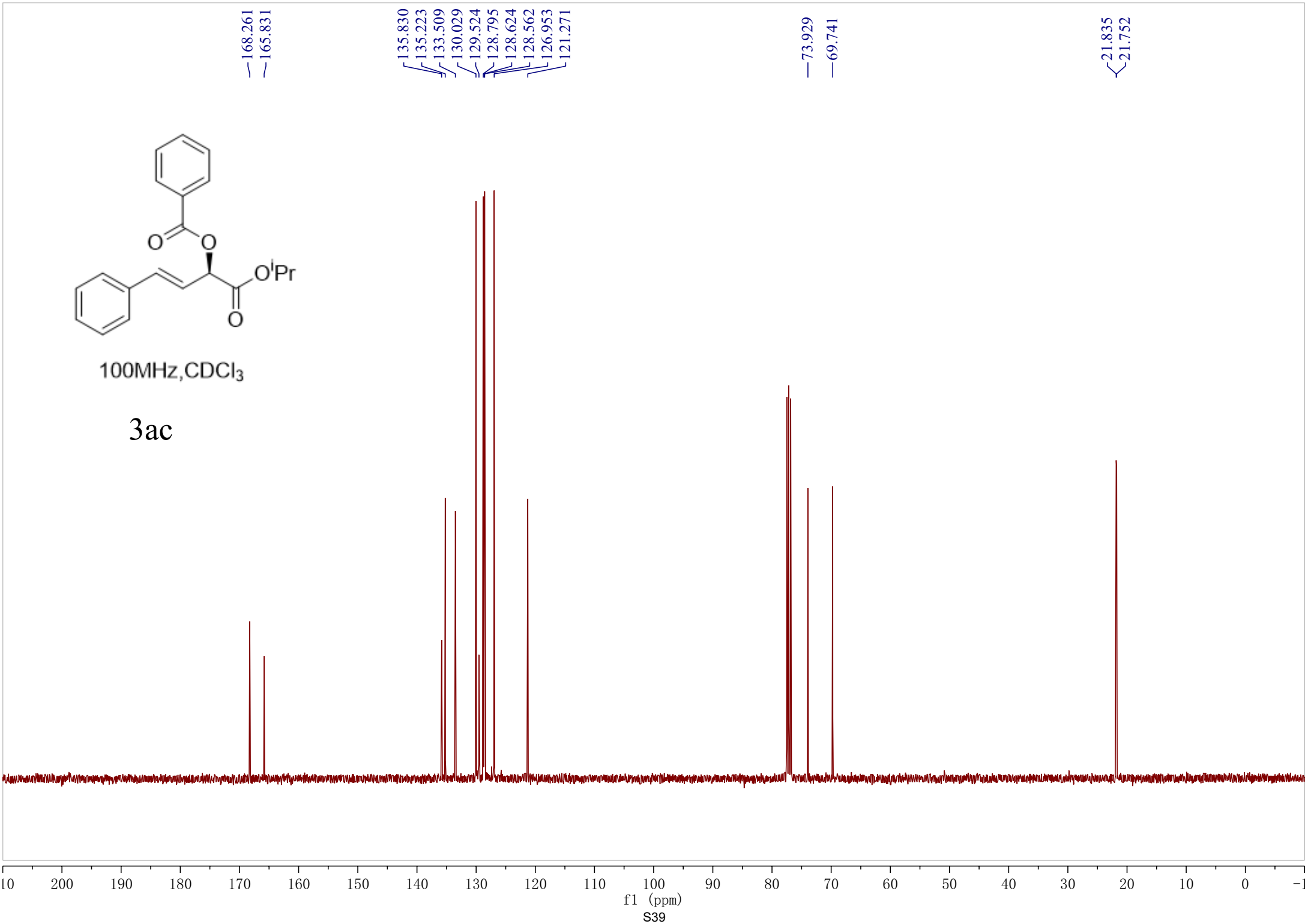

8.155
8.152
8.148
8.139
8.134
8.130
7.617
7.614
7.611
7.601
7.596
7.591
7.580
7.577
7.574
7.490
7.486
7.473
7.470
7.466
7.456
7.451
7.447
7.438
7.434
7.431
7.370
7.366
7.349
7.345
7.334
7.330
7.310
7.292
6.931
6.928
6.891
6.888
6.432
6.414
6.392
6.374
5.886
5.883
5.868
5.865
3.819
3.807
3.797
0.000
O
O
O
O
400MHz, CDCl3
3aa
2.00
1.00
4.00
3.00
1.00
1.00
1.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

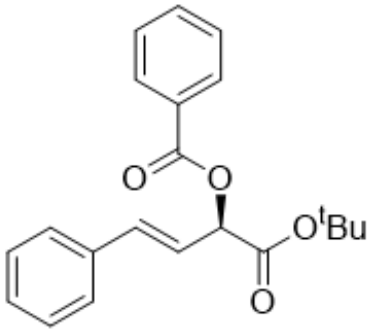

169.188
165.726
135.575
135.508
133.536
130.007
129.293
128.739
128.660
128.519
126.916
120.928
73.616
52.774
O
O
O
O
100MHz,CDCl3
3aa
f1 (ppm)


8.157
8.154
8.150
8.141
8.136
8.132
7.616
7.602
7.599
7.597
7.595
7.592
7.582
7.579
7.575
7.496
7.492
7.488
7.475
7.472
7.468
7.460
7.455
7.452
7.450
7.442
7.438
7.435
7.430
7.375
7.371
7.366
7.359
7.355
7.353
7.349
7.338
7.335
7.333
7.317
7.313
7.310
7.302
7.295
6.937
6.934
6.897
6.894
6.436
6.418
6.396
6.378
5.859
5.855
5.841
5.838
4.314
4.305
4.296
4.291
4.287
4.273
4.269
4.256
4.251
4.247
4.238
4.229
1.317
1.299
1.281
0.000
O
O
OEt
O
400MHz, CDCl3
3ab
2.00
1.09
4.14
3.04
1.00
1.00
1.00
2.00
3.11
f1 (ppm)


168.697
165.756
135.663
135.325
133.486
129.985
129.364
128.729
128.604
128.501
126.898
121.076
73.726
61.900
14.158
OEt
O
O
O
100MHz,CDCl3
3ab
f1 (ppm)

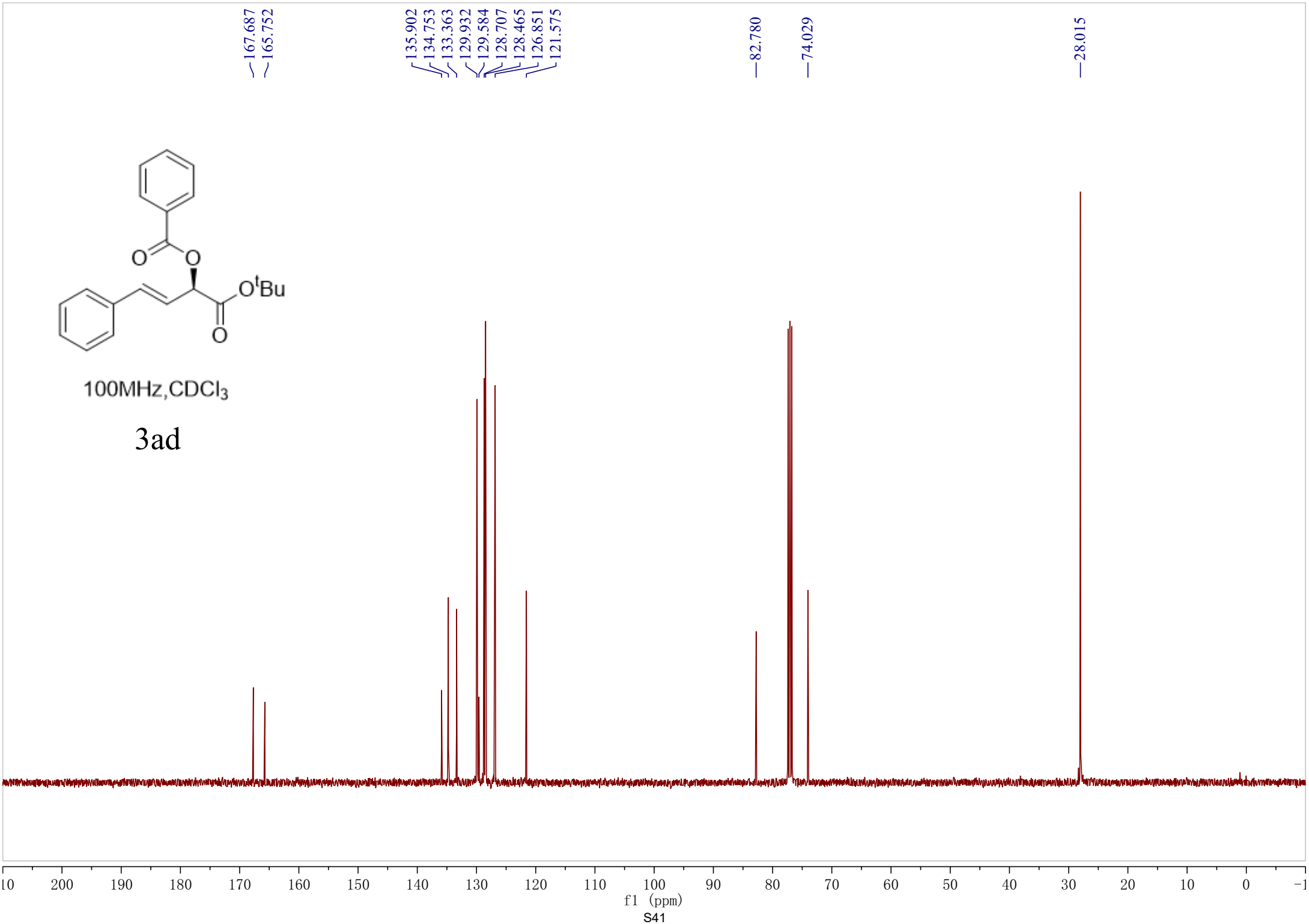

8.161
8.156
8.153
8.149
8.140
8.135
8.132
7.610
7.607
7.603
7.593
7.588
7.583
7.573
7.569
7.566
7.497
7.485
7.481
7.469
7.465
7.461
7.454
7.451
7.447
7.437
7.433
7.430
7.424
7.410
7.380
7.370
7.367
7.362
7.350
7.345
7.334
7.330
7.325
7.311
7.307
7.304
7.296
7.289
7.282
7.275
7.271
7.268
6.932
6.892
6.427
6.410
6.387
6.370
5.817
5.814
5.800
5.796
5.169
5.153
5.138
5.122
5.107
5.091
5.075
1.317
1.301
1.253
1.238
0.000
O
O
O
O
iPr
400MHz, CDCl3
3ac
2.00
1.01
4.01
3.11
1.00
1.00
1.00
1.00
3.10
3.00
f1 (ppm)

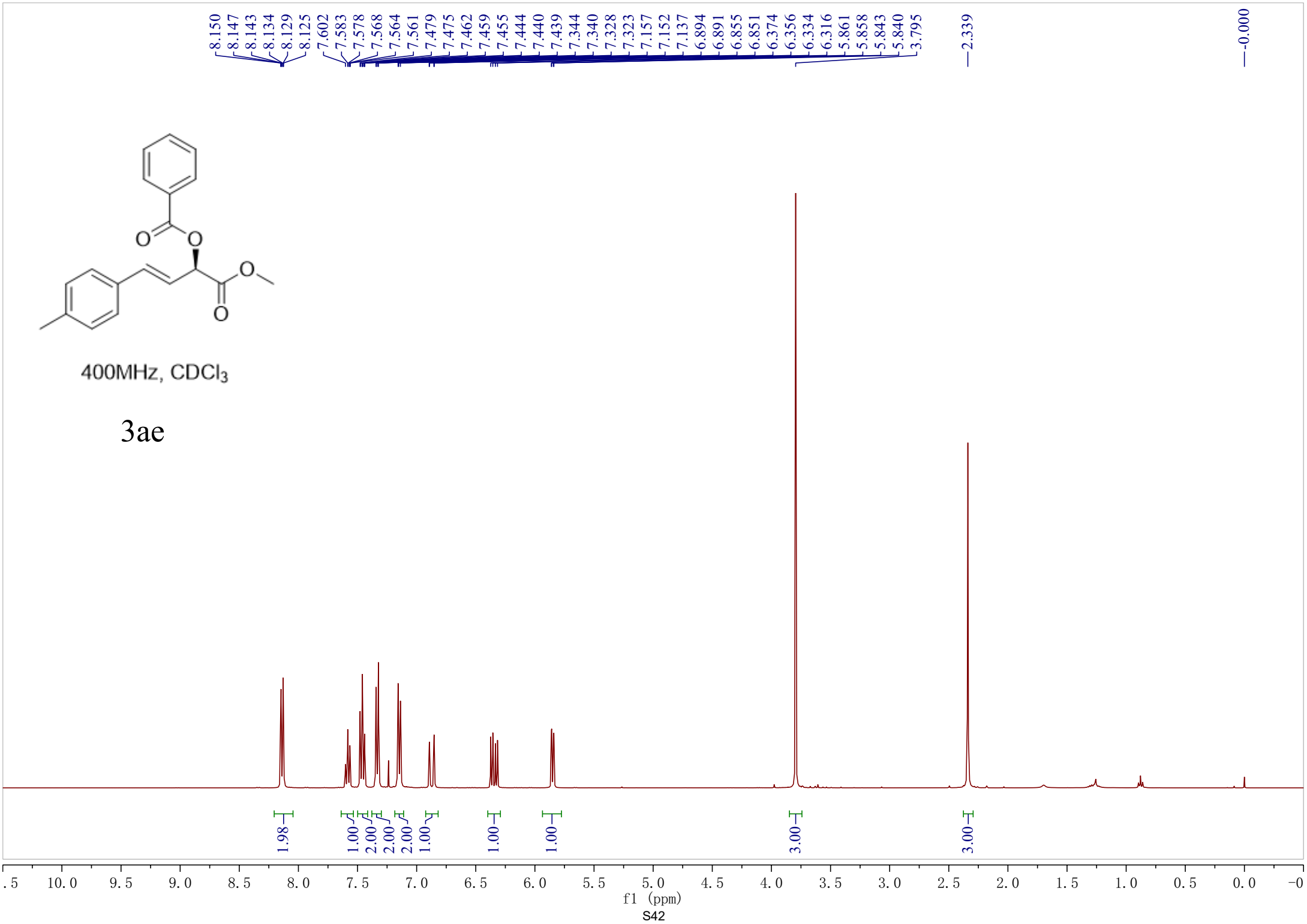

168.261
165.831
135.830
135.223
133.509
130.029
129.524
128.795
128.624
128.562
126.953
121.271
73.929
69.741
21.835
21.752
O
O
O
O
iPr
100MHz,CDCl3
3ac
f1 (ppm)

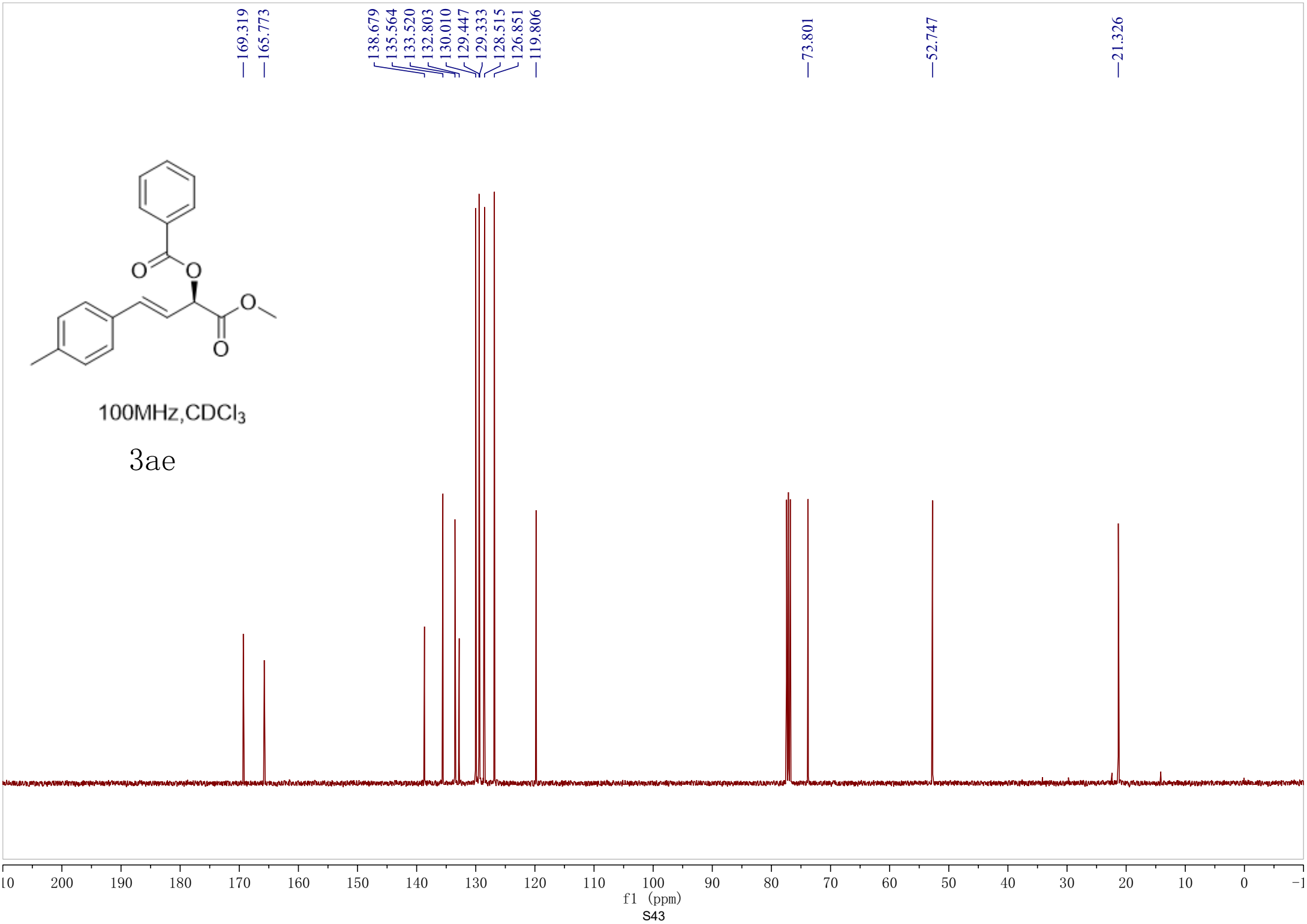


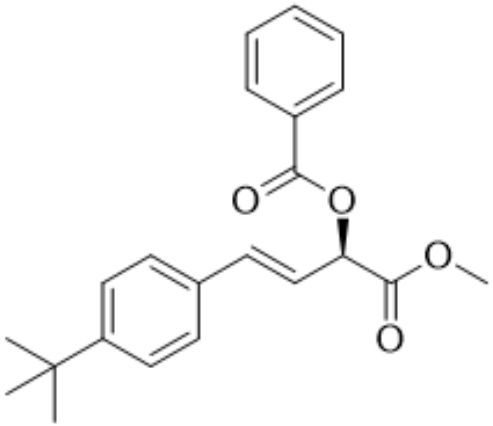
400MHz, $CDCl_3$

3ad


167.687
165.752
135.902
134.753
133.363
129.932
129.584
128.707
128.465
126.851
121.575
82.780
74.029
28.015
O
O
O
O
tBu
100MHz,CDCl3
3ad
f1 (ppm)

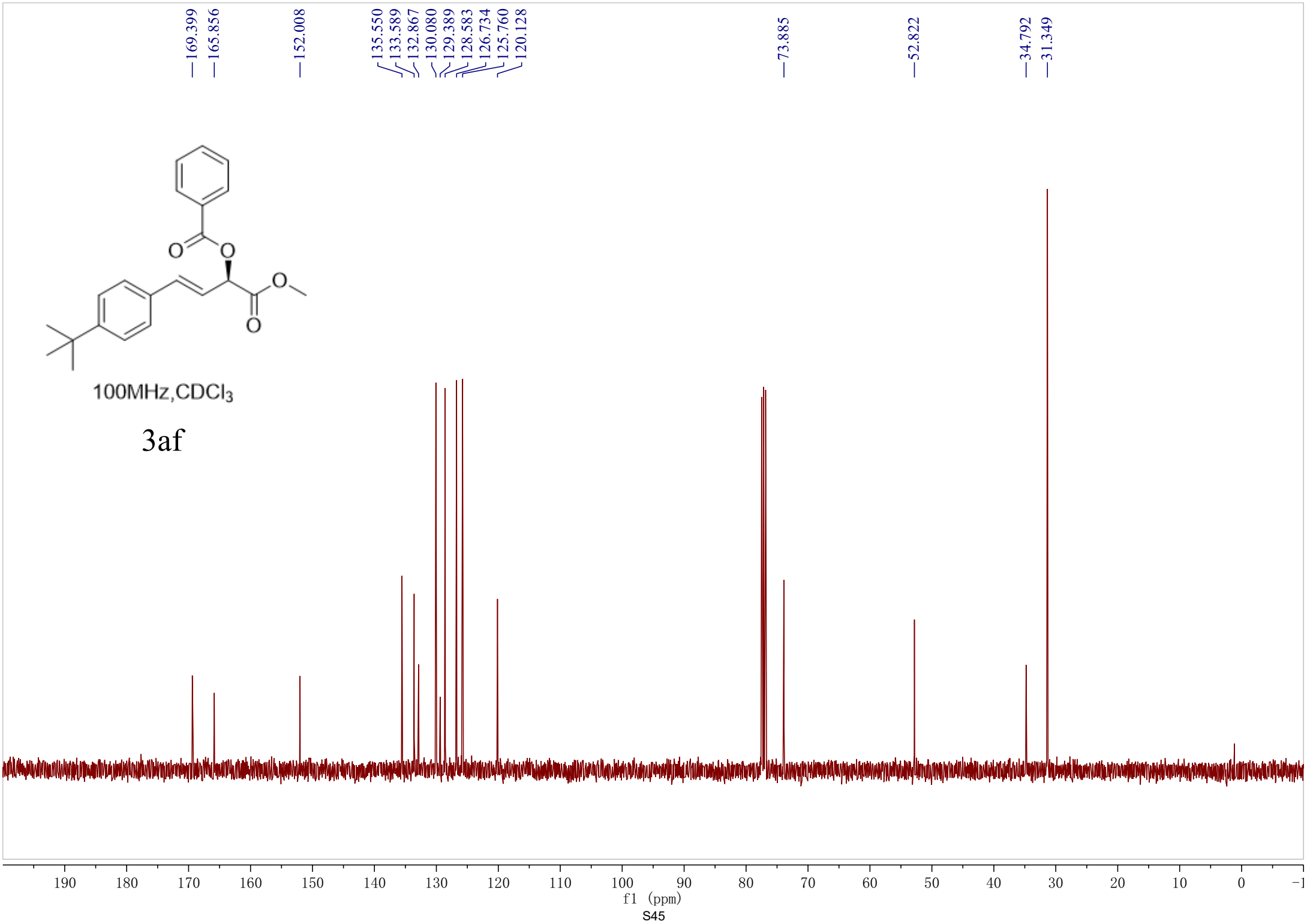

8.150
8.147
8.143
8.134
8.129
8.125
7.602
7.583
7.578
7.568
7.564
7.561
7.479
7.475
7.462
7.459
7.455
7.444
7.440
7.439
7.344
7.340
7.328
7.323
7.157
7.152
7.137
6.894
6.891
6.855
6.851
6.374
6.356
6.334
6.316
5.861
5.858
5.843
5.840
3.795
2.339
-0.000
O
O
O
O
400MHz, CDCl3
3ae
1.98
1.00
2.00
2.00
2.00
1.00
1.00
1.00
3.00
3.00
f1 (ppm)

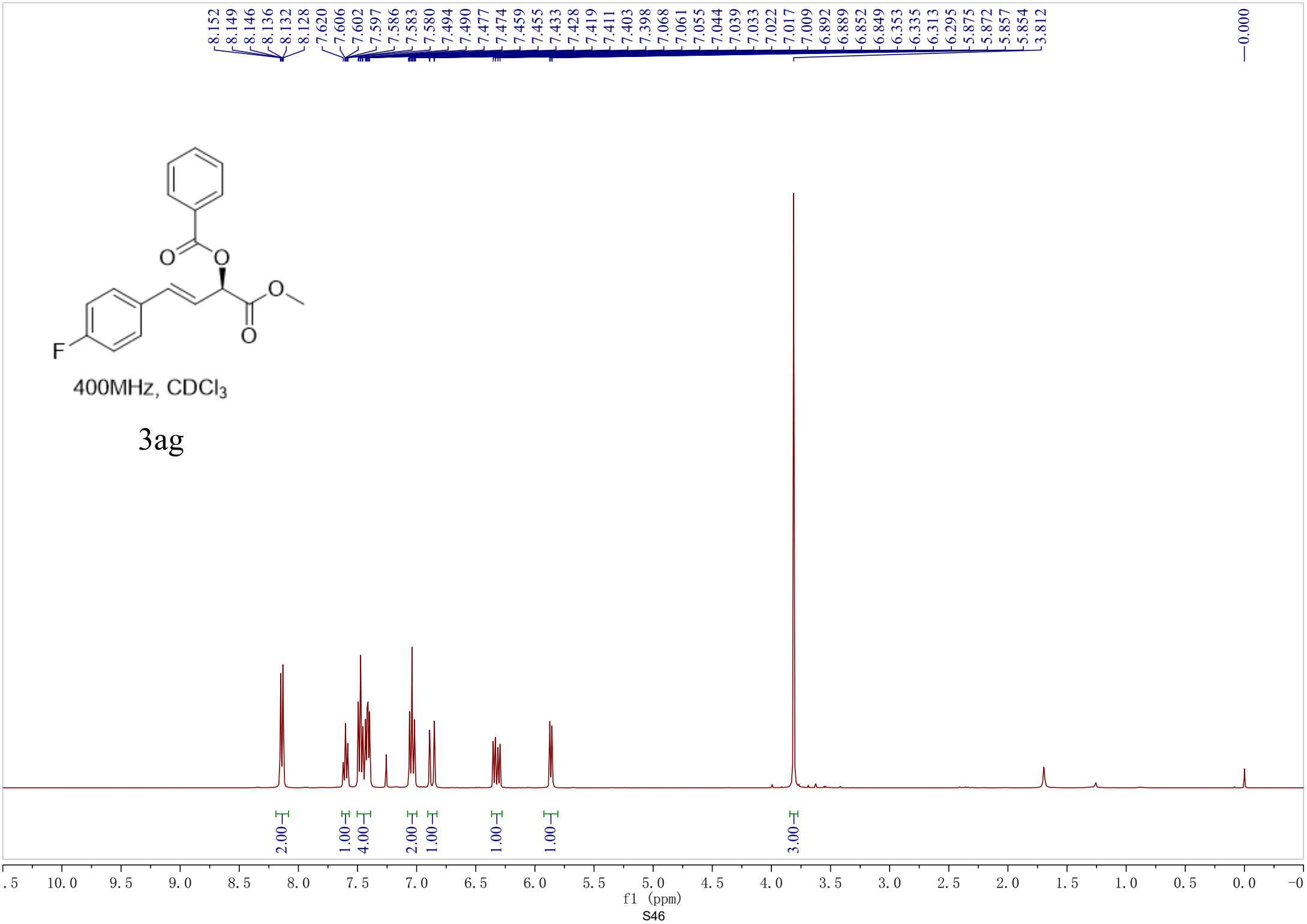

169.319
165.773
138.679
135.564
133.520
132.803
130.010
129.447
129.333
128.515
126.851
119.806
73.801
52.747
21.326
O
O
O
O
100MHz,CDCl3
3ae
f1 (ppm)



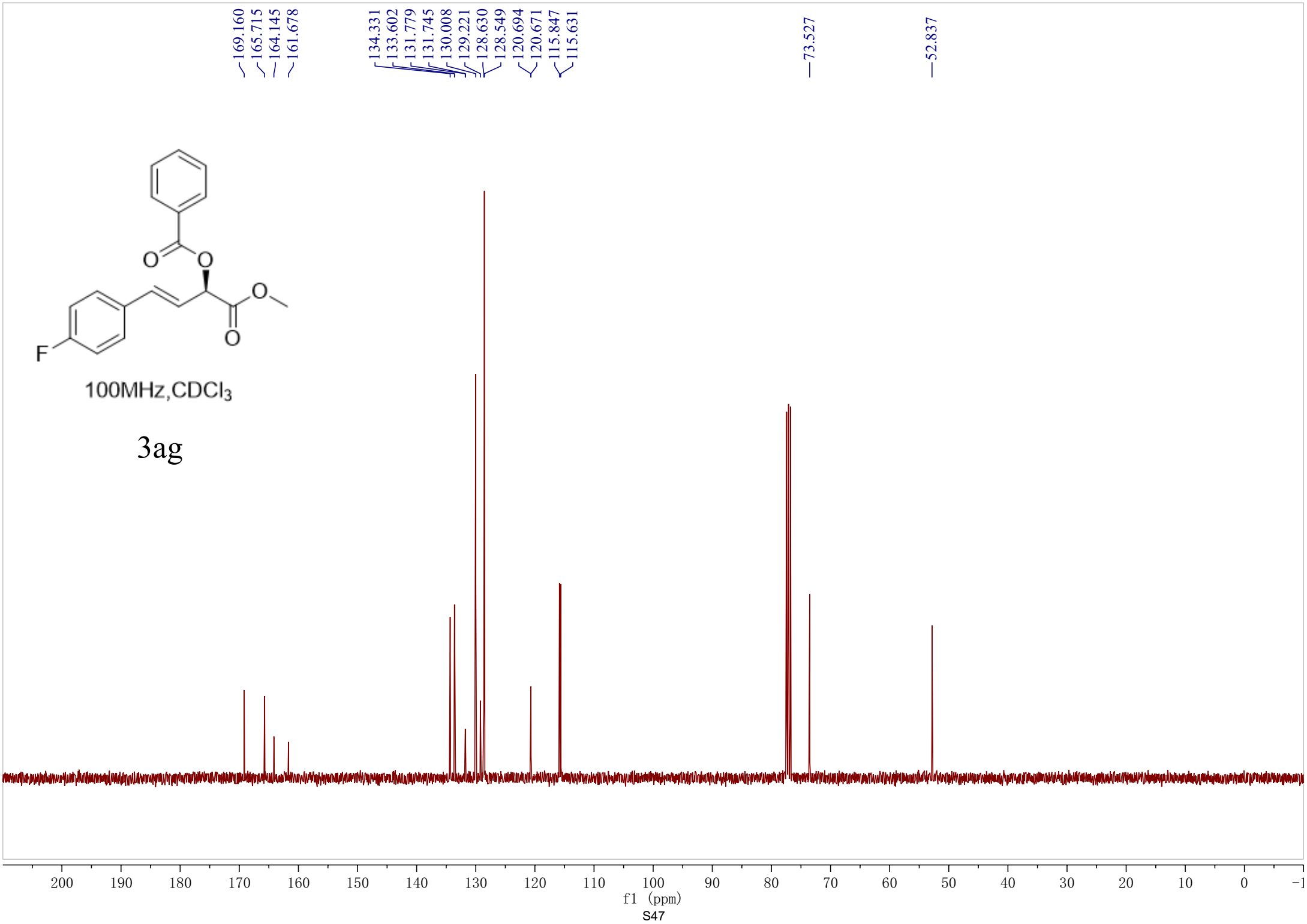
400MHz, $CDCl_3$

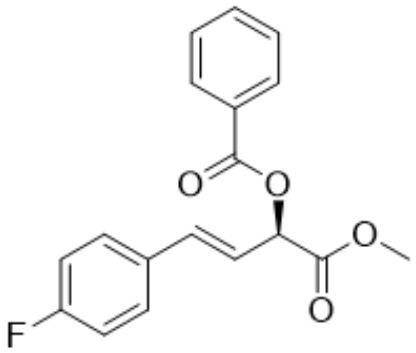
3af


169.399
165.856
152.008
135.550
133.589
132.867
130.080
129.389
128.583
126.734
125.760
120.128
73.885
52.822
34.792
31.349
O
O
O
O
100MHz,CDCl3
3af
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)


8.152
8.149
8.146
8.136
8.132
8.128
7.620
7.606
7.602
7.597
7.586
7.583
7.580
7.494
7.490
7.477
7.474
7.459
7.455
7.433
7.428
7.419
7.411
7.403
7.398
7.068
7.061
7.055
7.044
7.039
7.033
7.022
7.017
7.009
6.892
6.889
6.852
6.849
6.353
6.335
6.313
6.295
5.875
5.872
5.857
5.854
3.812
0.000
O
O
O
O
F
400MHz, CDCl3
2.00
1.00
4.00
2.00
1.00
1.00
1.00
3.00
f1 (ppm)

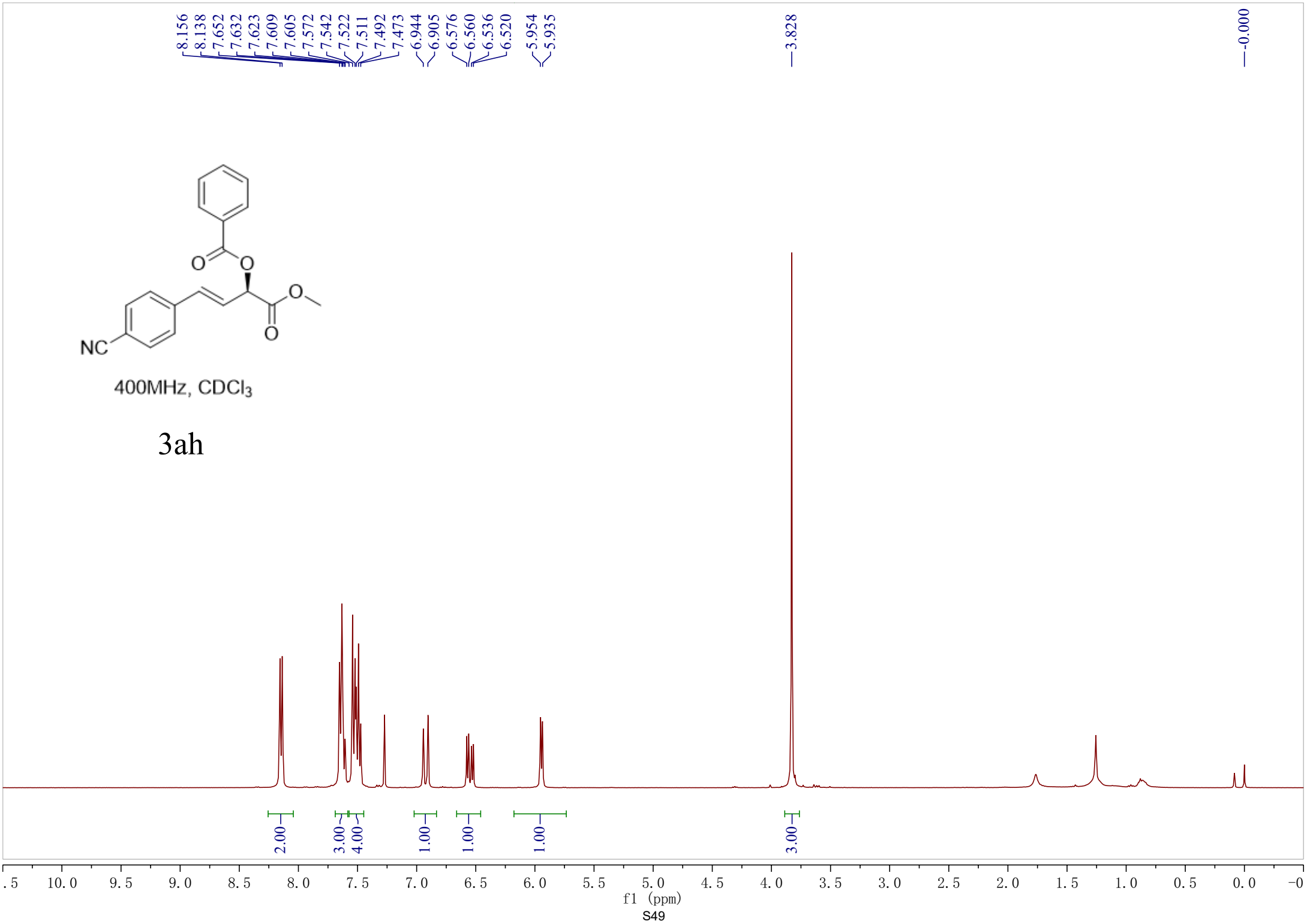
3ag

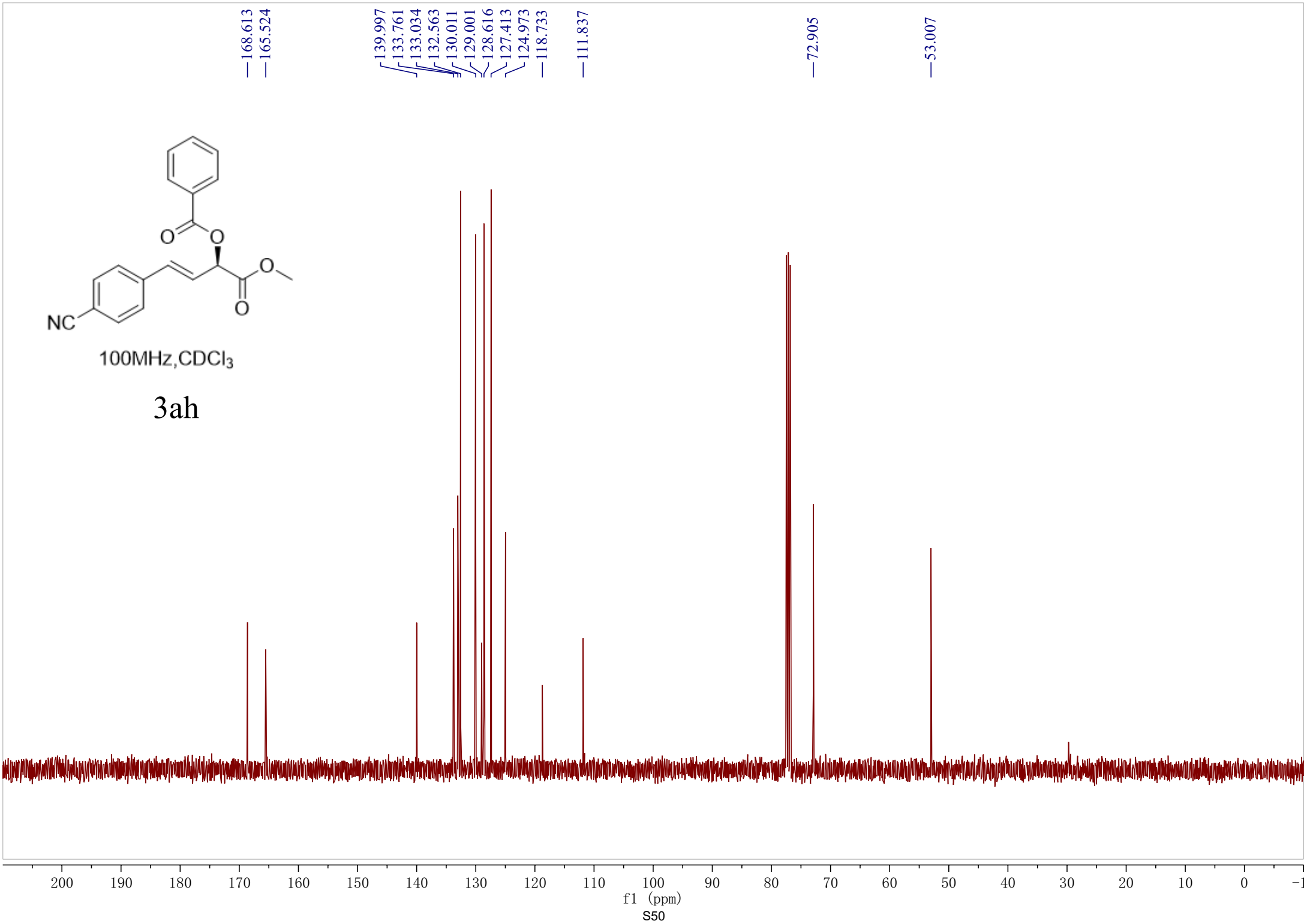

169.160
165.715
164.145
161.678
134.331
133.602
131.779
131.745
130.008
129.221
128.630
128.549
120.694
120.671
115.847
115.631
73.527
52.837
O
O
O
O
F
100MHz,CDCl3
3ag
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)

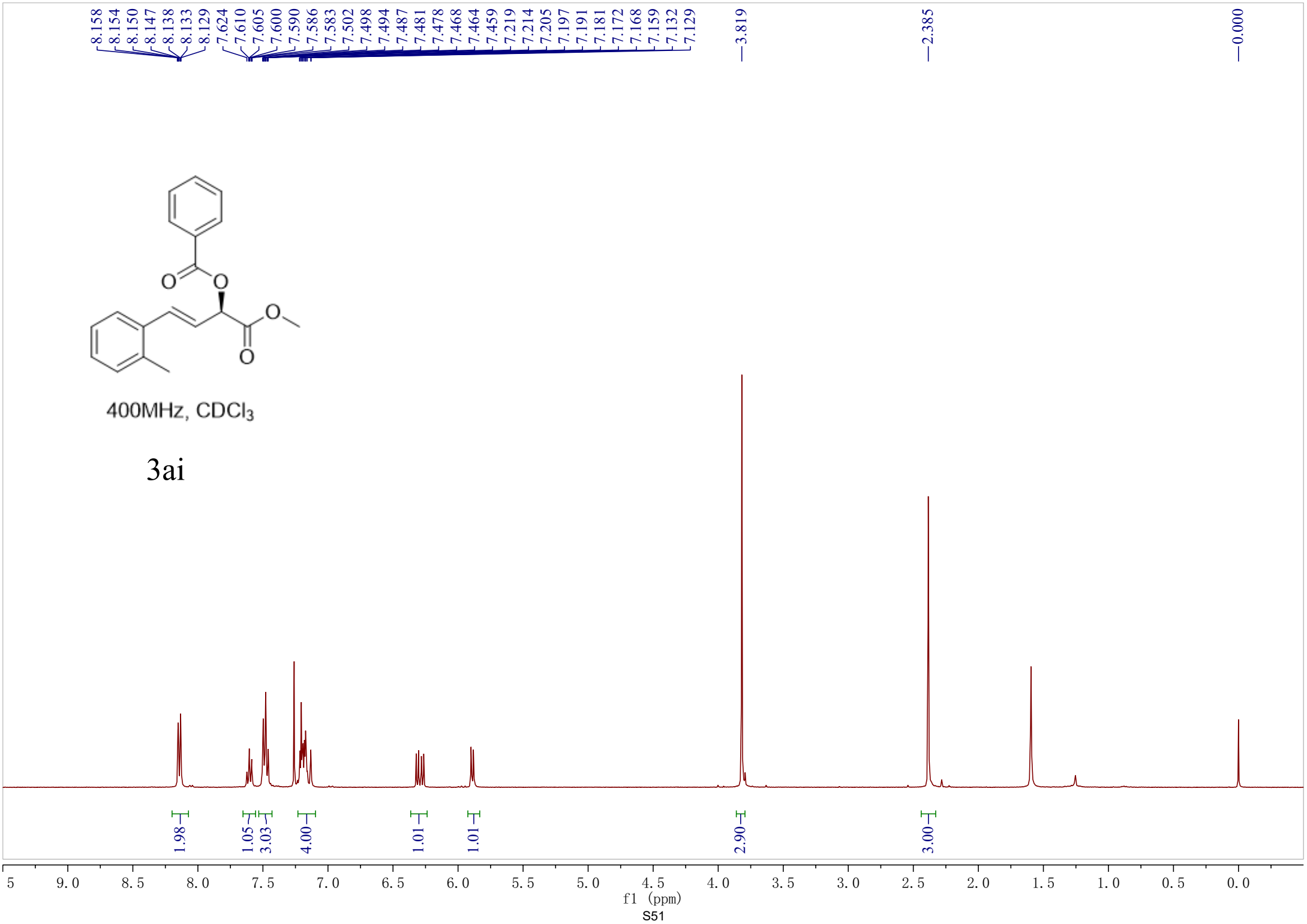


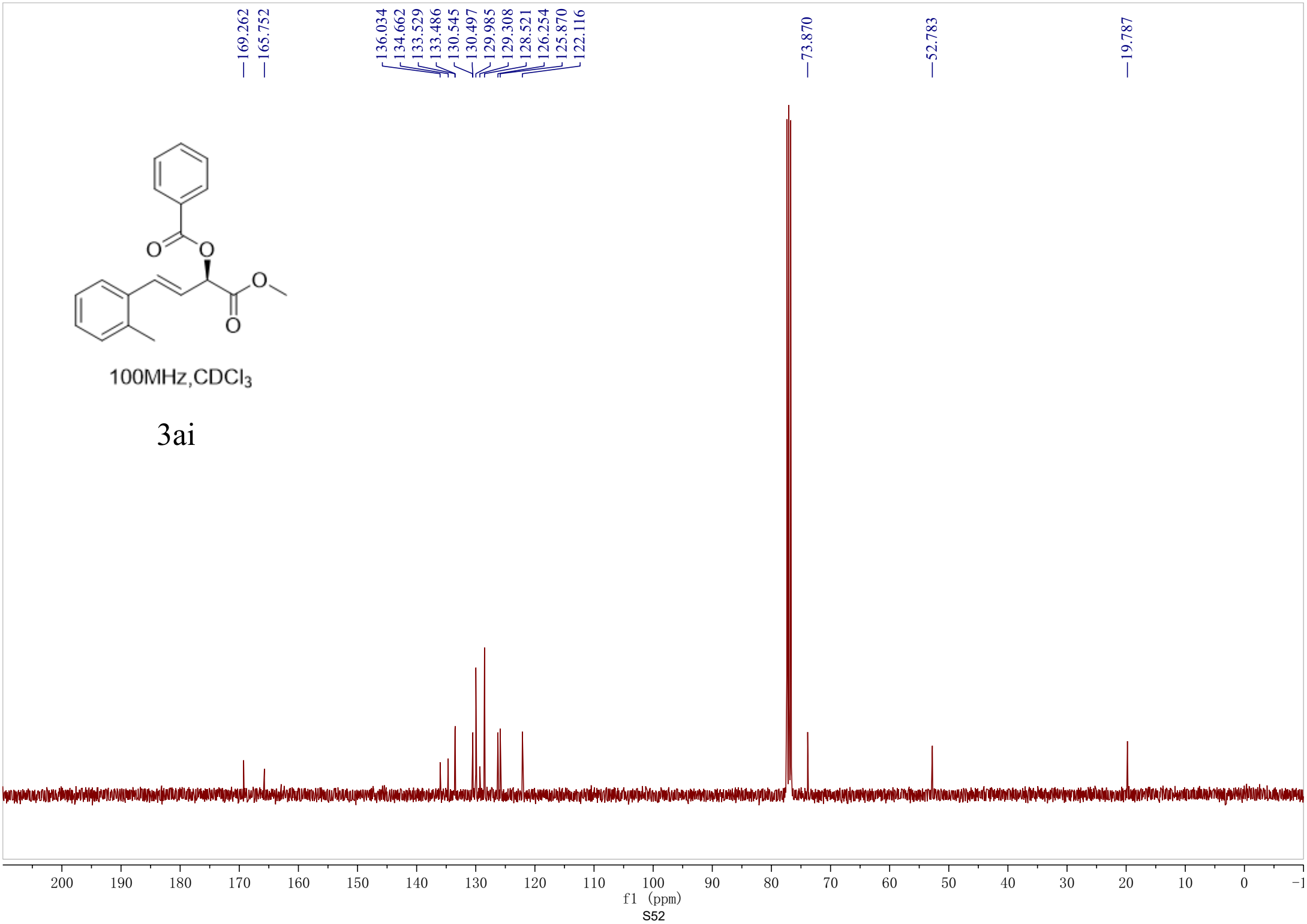
282MHz, $CDCl_3$

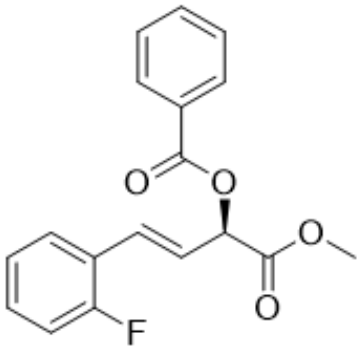
3ag


8.156
8.138
7.652
7.632
7.623
7.609
7.605
7.572
7.542
7.522
7.511
7.492
7.473
6.944
6.905
6.576
6.560
6.536
6.520
5.954
5.935
3.828
-0.000
O
O
O
O
NC
400MHz, CDCl3
3ah
2.00
3.00
4.00
1.00
1.00
1.00
3.00
f1 (ppm)


168.613
165.524
139.997
133.761
133.034
132.563
130.011
129.001
128.616
127.413
124.973
118.733
111.837
72.905
53.007
O
O
O
O
NC
100MHz,CDCl3
3ah
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

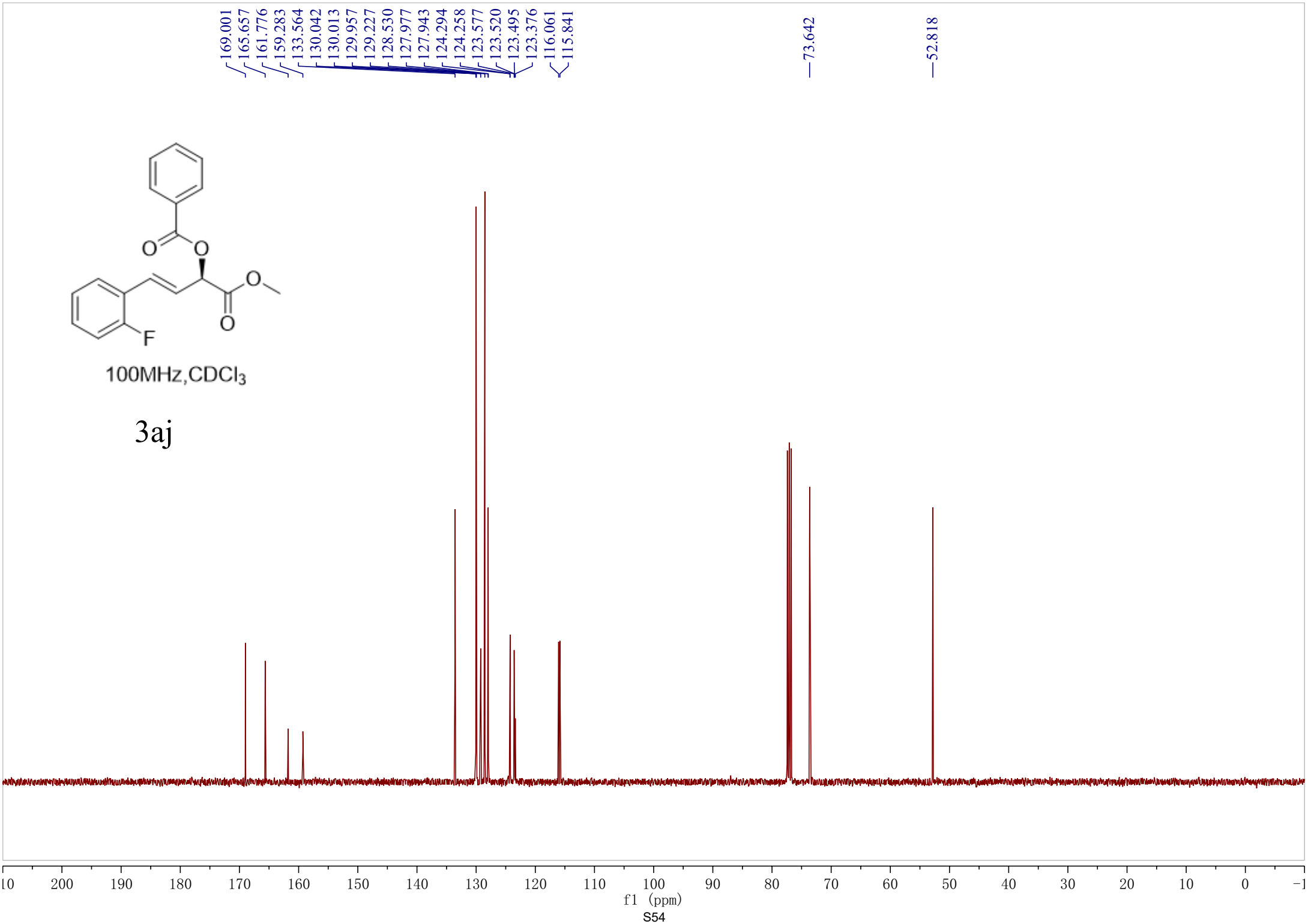

8.158
8.154
8.150
8.147
8.138
8.133
8.129
7.624
7.610
7.605
7.600
7.590
7.586
7.583
7.502
7.498
7.494
7.487
7.481
7.478
7.468
7.464
7.459
7.219
7.214
7.205
7.197
7.191
7.181
7.172
7.168
7.159
7.132
7.129
3.819
2.385
0.000
O
O
O
O
400MHz, CDCl3
3ai
1.98
1.05
3.03
4.00
1.01
1.01
2.90
3.00
f1 (ppm)

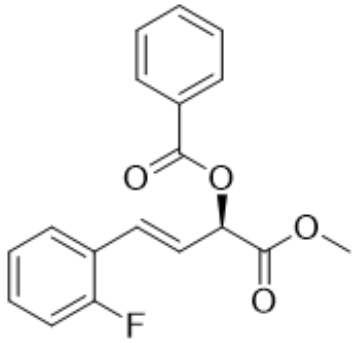

169.262
165.752
136.034
134.662
133.529
133.486
130.545
130.497
129.985
129.308
128.521
126.254
125.870
122.116
73.870
52.783
19.787
O
O
O
O
100MHz,CDCl3
3ai
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)



400MHz, $CDCl_3$

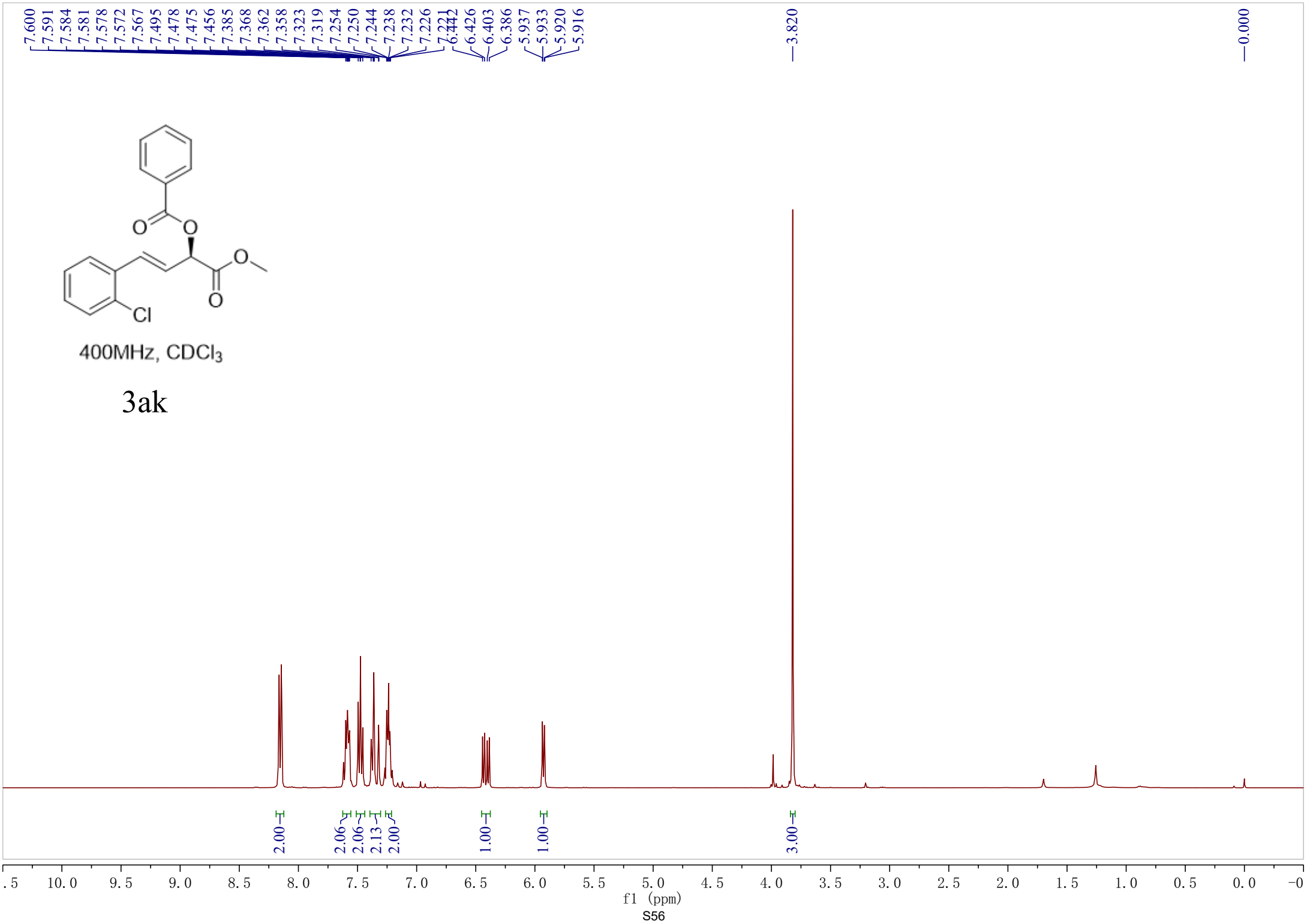
3aj

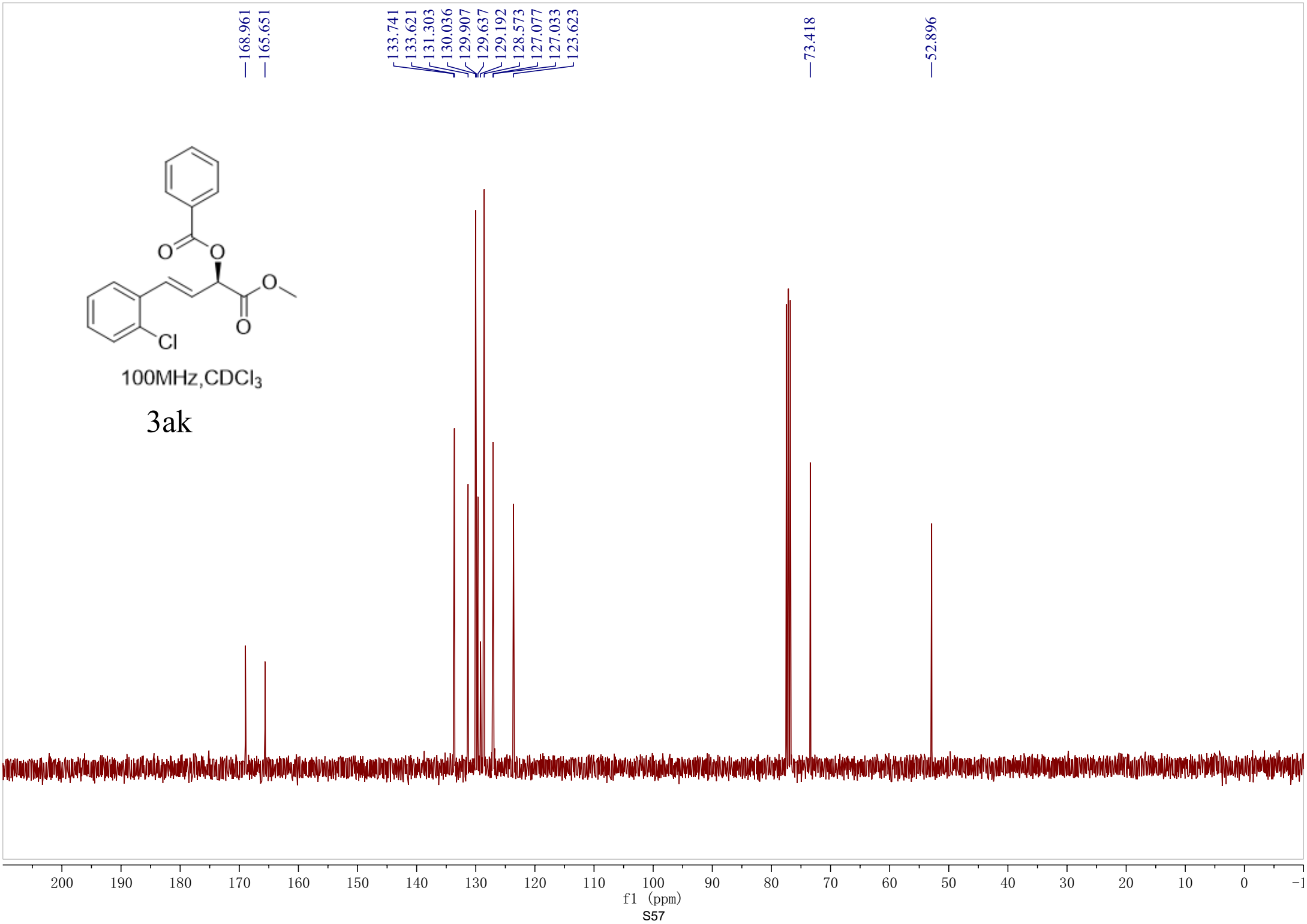

169.001
165.657
161.776
159.283
133.564
130.042
130.013
129.957
129.227
128.530
127.977
127.943
124.294
124.258
123.577
123.520
123.495
123.376
116.061
115.841
73.642
52.818
O
O
O
O
F
100MHz,CDCl3
3aj
f1 (ppm)

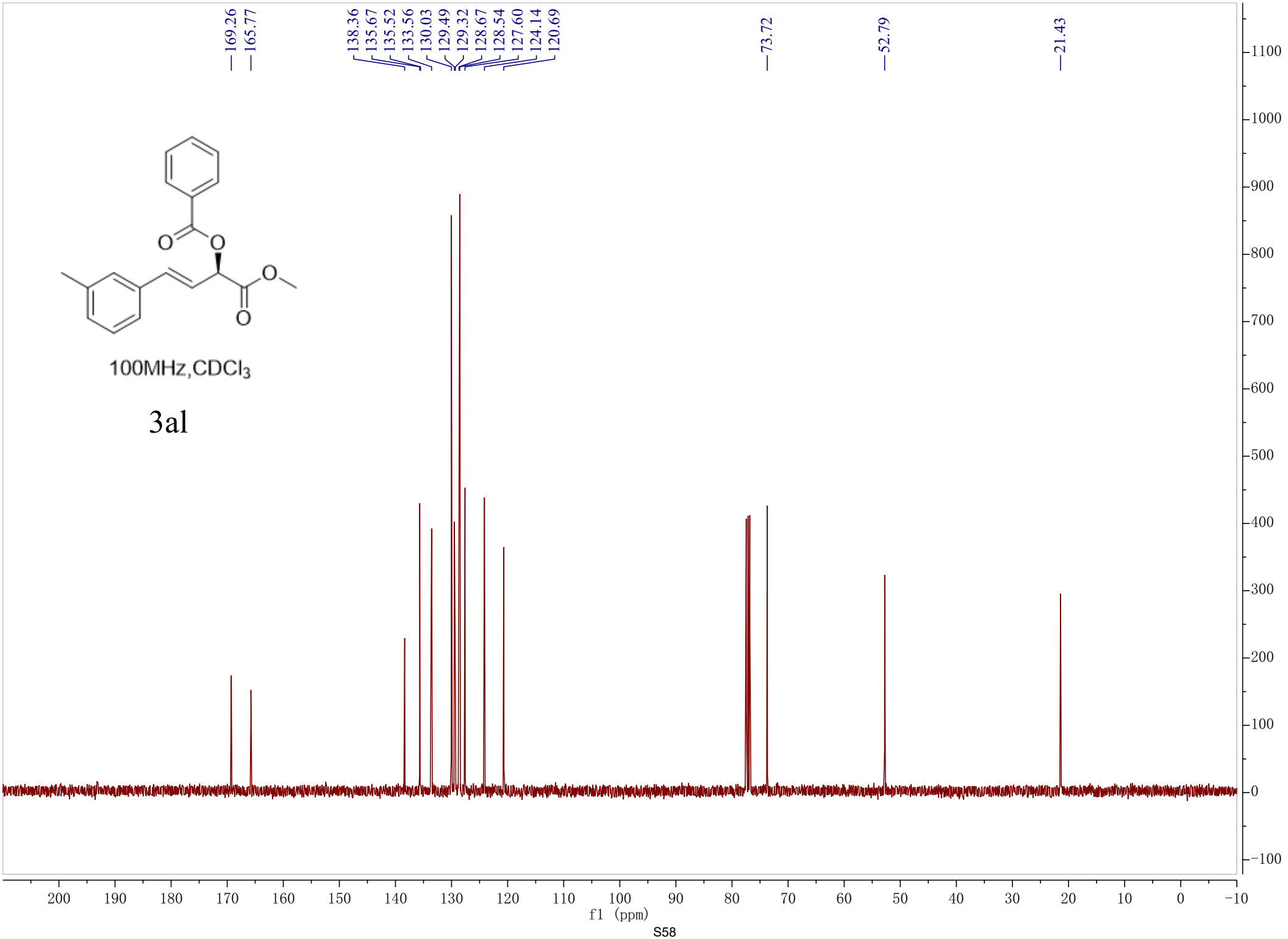


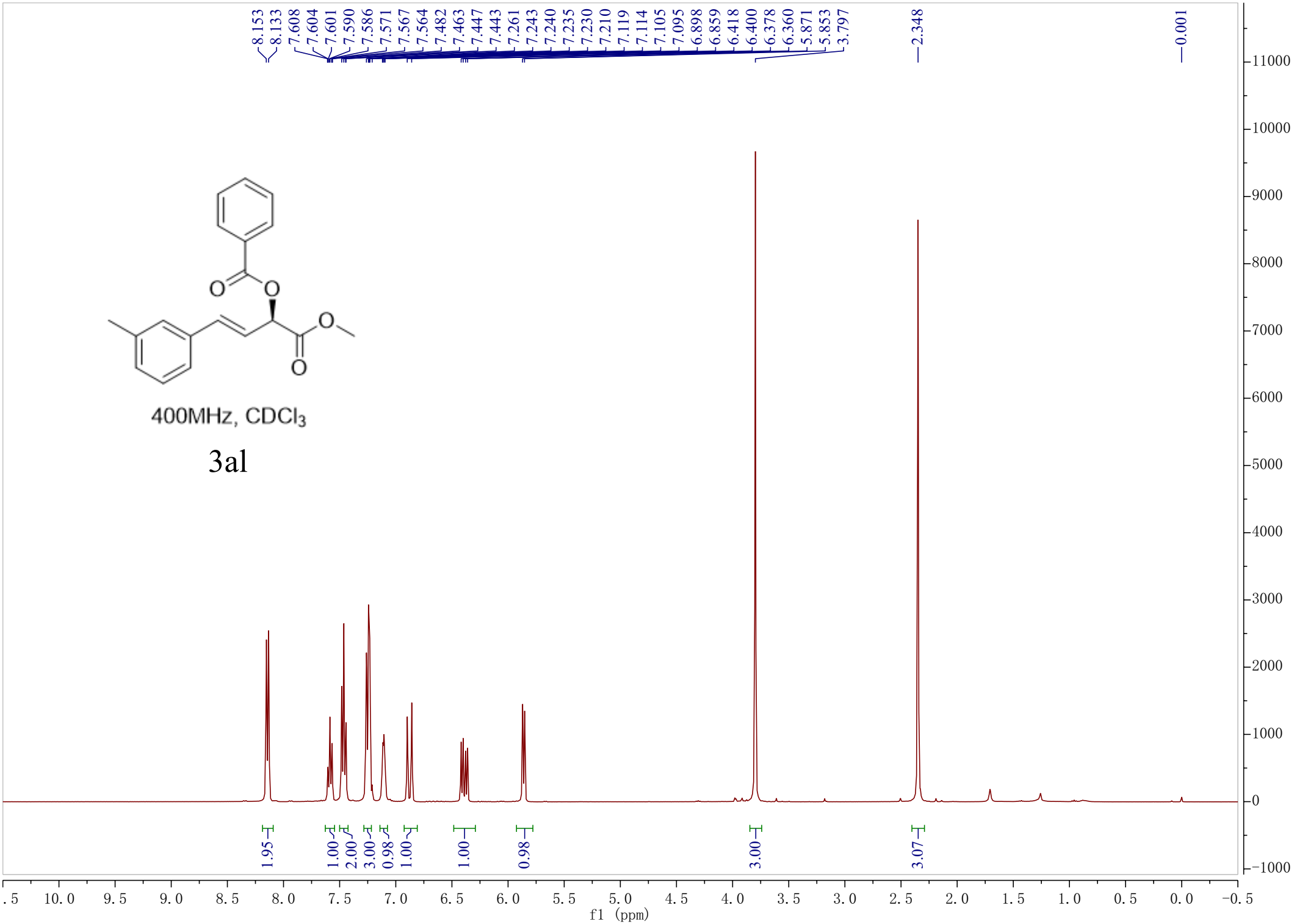
282MHz, $CDCl_3$

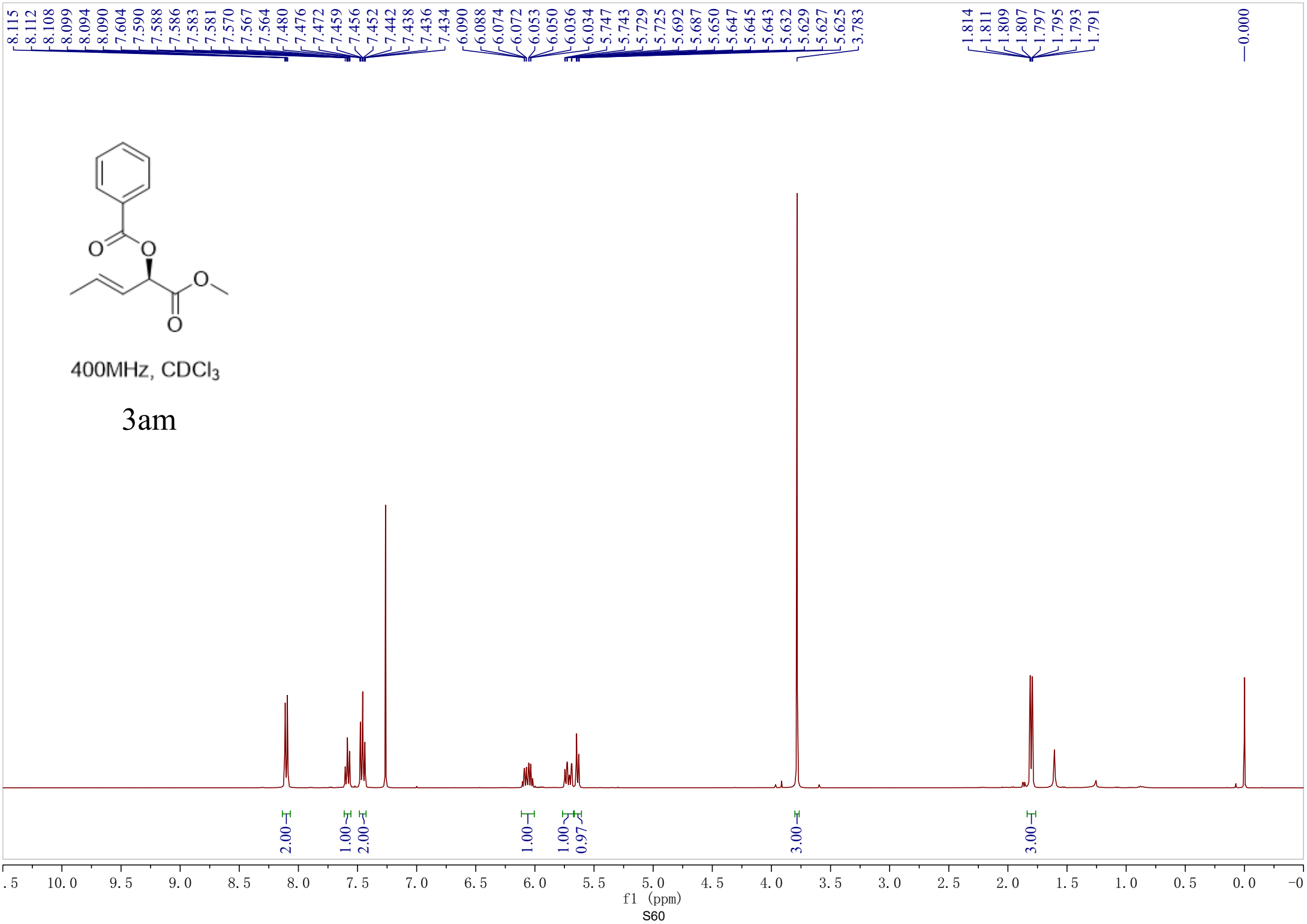
3aj

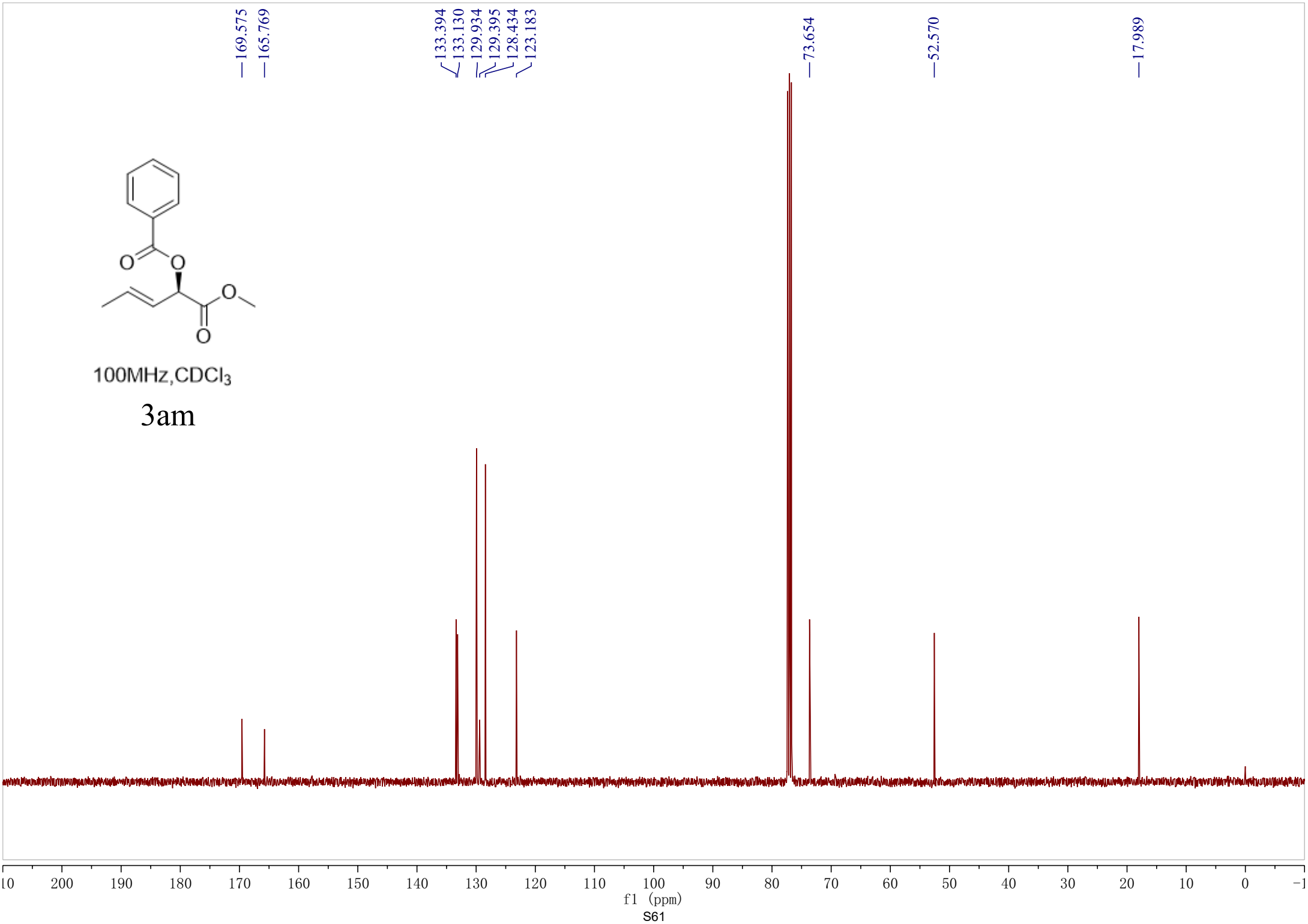

7.600
7.591
7.584
7.581
7.578
7.572
7.567
7.495
7.478
7.475
7.456
7.385
7.368
7.362
7.358
7.323
7.319
7.254
7.250
7.244
7.238
7.232
7.226
7.221
6.426
6.403
6.386
5.937
5.933
5.920
5.916
3.820
0.000
O
O
O
O
Cl
400MHz, CDCl3
3ak
2.00
2.06
2.06
2.13
2.00
1.00
1.00
3.00
f1 (ppm)

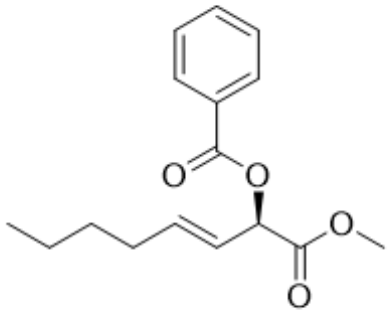

168.961
165.651
133.741
133.621
131.303
130.036
129.907
129.637
129.192
128.573
127.077
127.033
123.623
73.418
52.896
O
O
O
O
Cl
100MHz,CDCl3
3ak
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


169.26
165.77
138.36
135.67
135.52
133.56
130.03
129.49
129.32
128.67
128.54
127.60
124.14
120.69
73.72
52.79
21.43
100MHz,CDCl3
3al
f1 (ppm)


8.153
8.133
7.608
7.604
7.601
7.590
7.586
7.571
7.567
7.564
7.482
7.463
7.447
7.443
7.261
7.243
7.240
7.235
7.230
7.210
7.119
7.114
7.105
7.095
6.898
6.859
6.418
6.400
6.378
6.360
5.871
5.853
3.797
2.348
0.001
O
O
O
O
400MHz, CDCl3
3al
1.95
1.00
2.00
3.00
0.98
1.00
1.00
0.98
3.00
3.07
f1 (ppm)

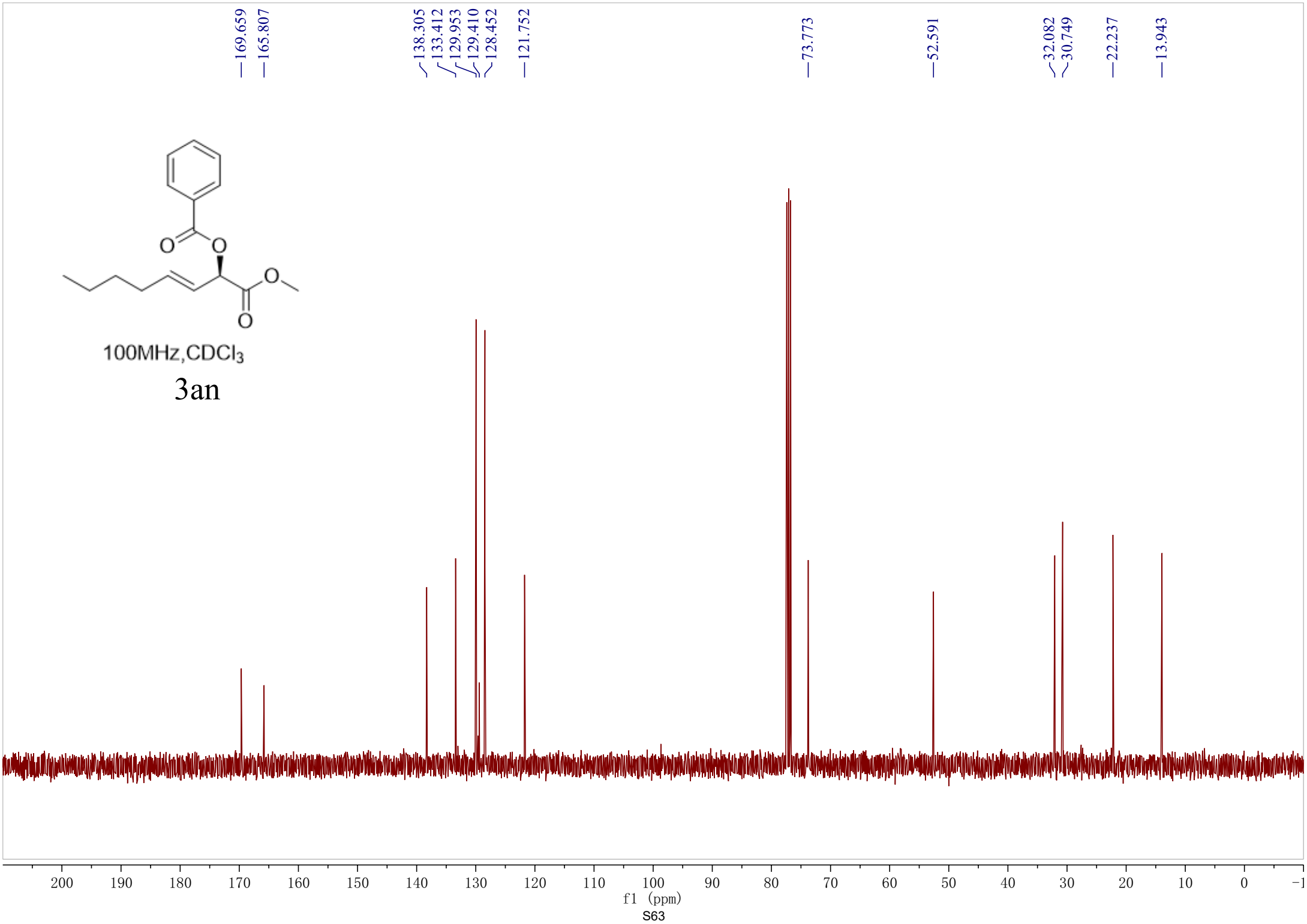

8.115
8.112
8.108
8.099
8.094
8.090
7.604
7.590
7.588
7.586
7.583
7.581
7.570
7.567
7.564
7.480
7.476
7.472
7.459
7.456
7.452
7.442
7.438
7.436
7.434
6.090
6.088
6.074
6.072
6.053
6.050
6.036
6.034
5.747
5.743
5.729
5.725
5.692
5.687
5.650
5.647
5.645
5.643
5.632
5.629
5.627
5.625
3.783
1.814
1.811
1.809
1.807
1.797
1.795
1.793
1.791
0.000
O
O
O
O
400MHz, CDCl3
3am
2.00
1.00
2.00
1.00
1.00
0.97
3.00
3.00
f1 (ppm)

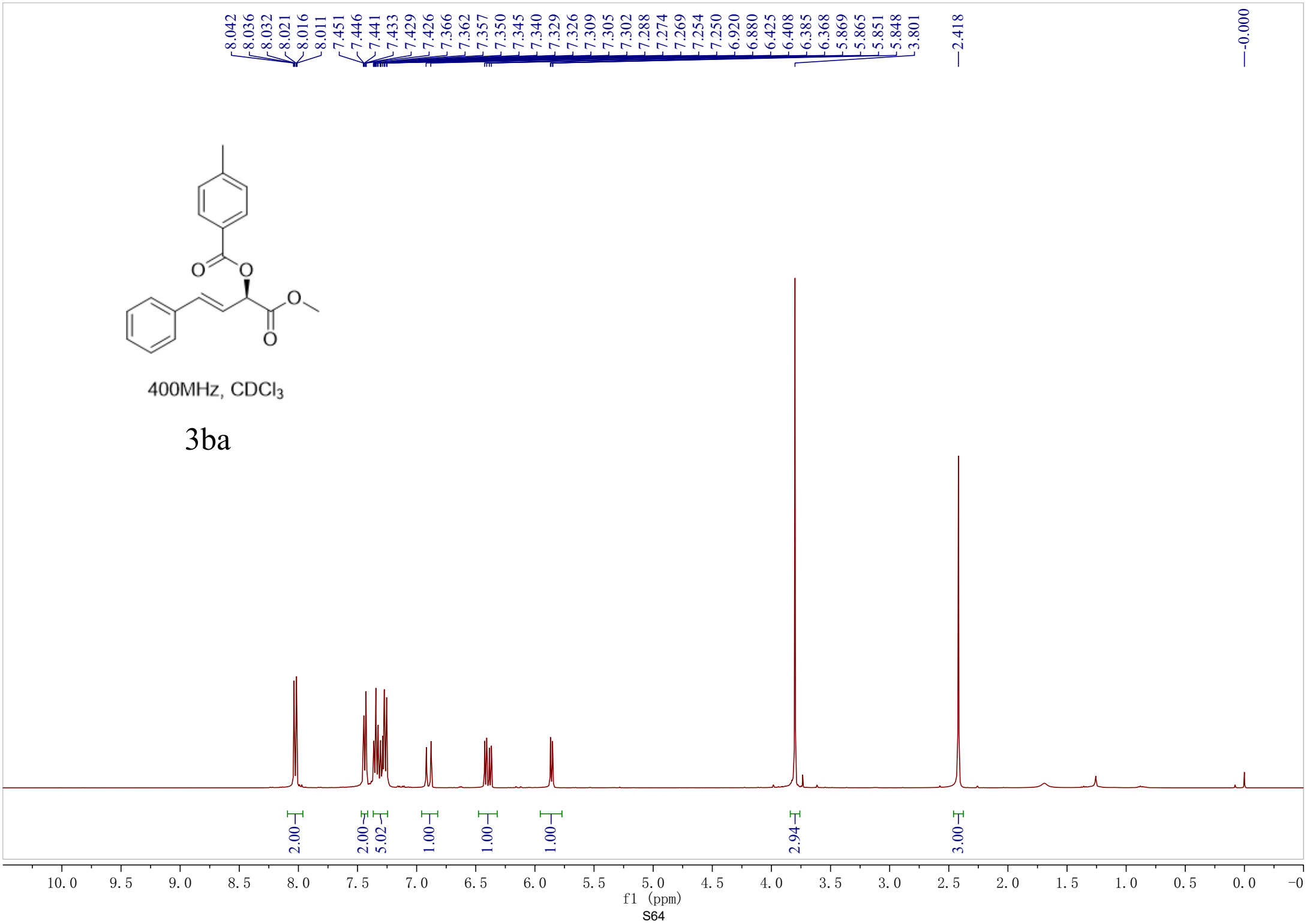

169.575
165.769
133.394
133.130
129.934
129.395
128.434
123.183
73.654
52.570
17.989
O
O
O
O
100MHz,CDCl3
3am
f1 (ppm)

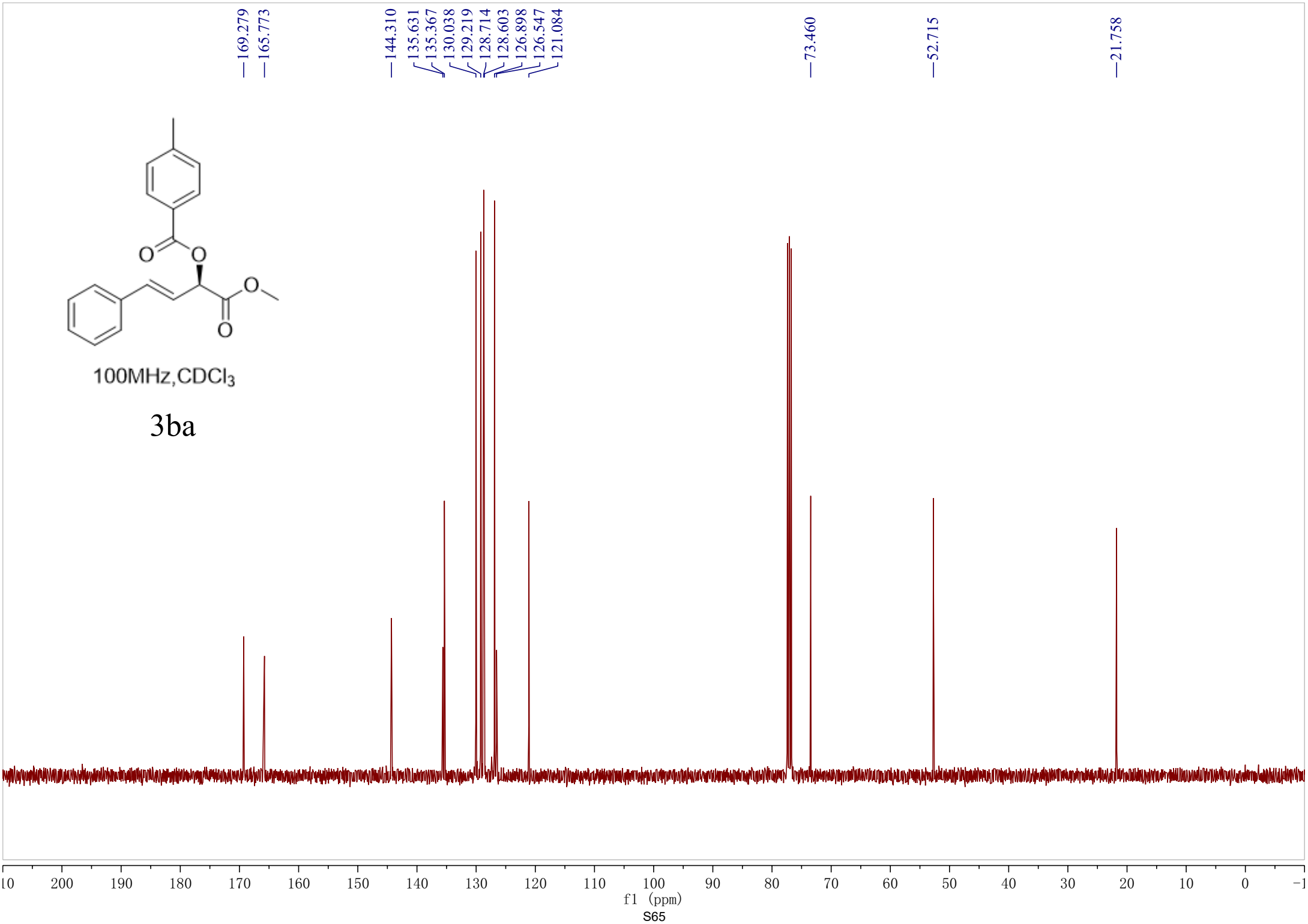


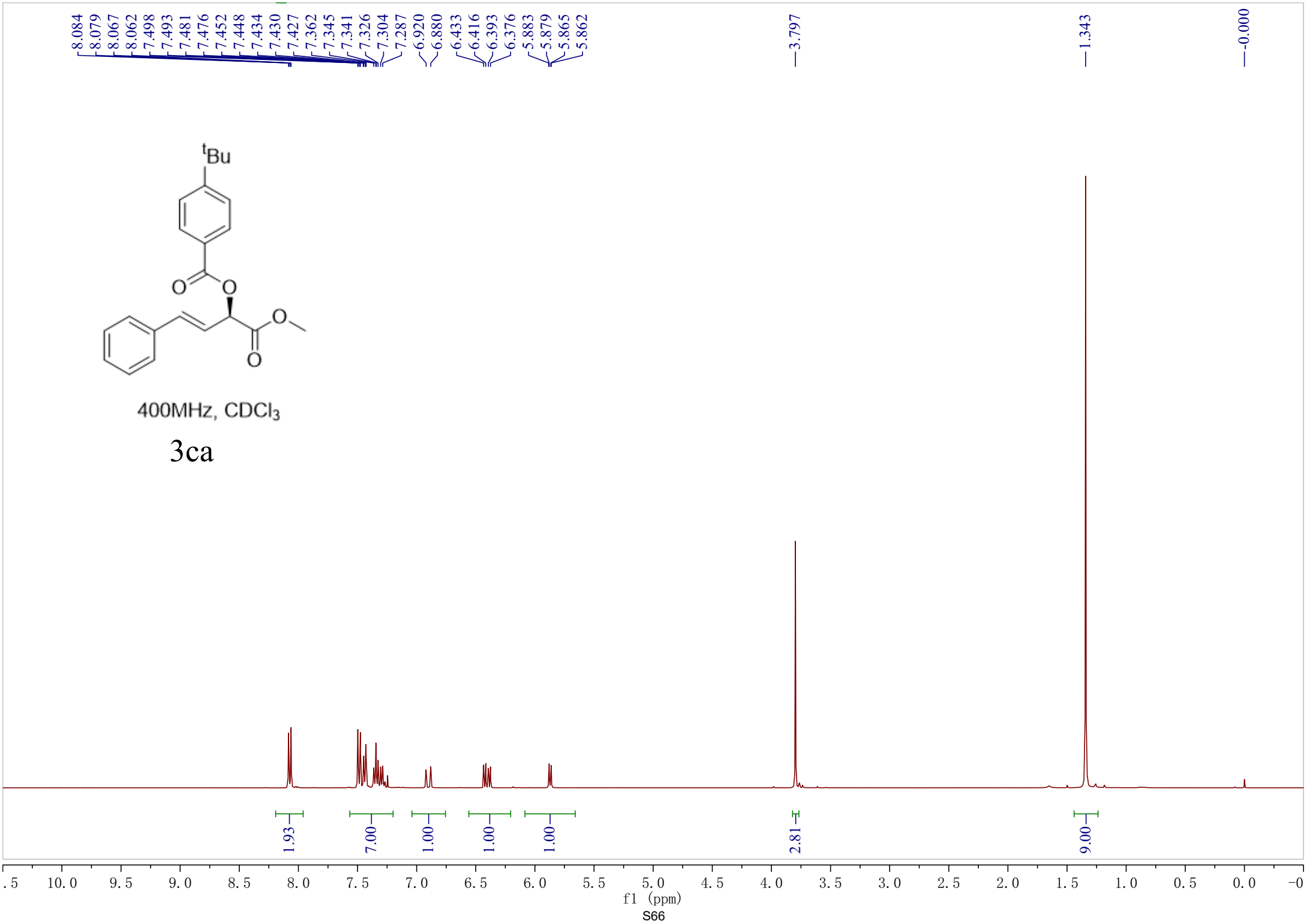
400MHz, $CDCl_3$

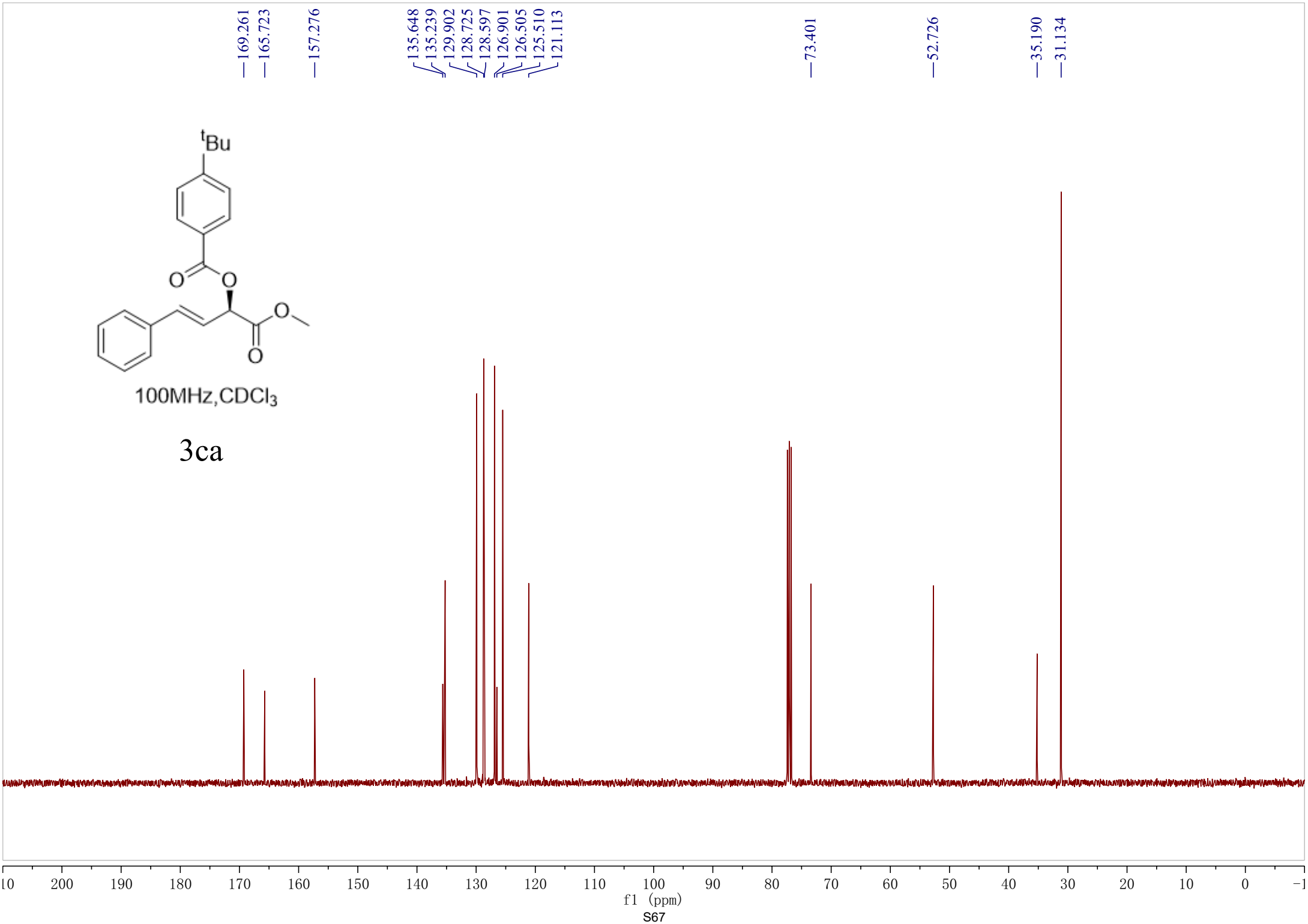
3an

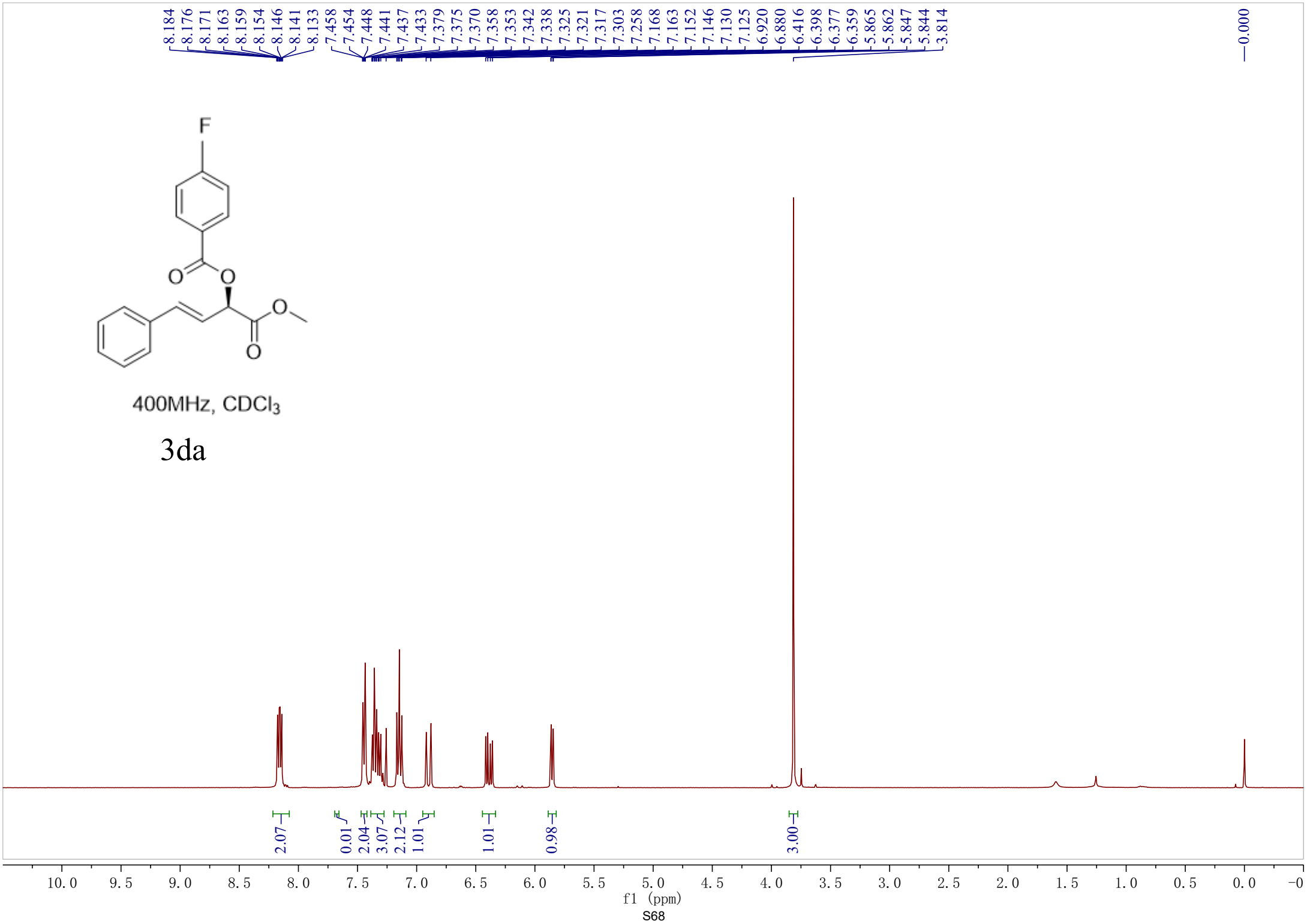

169.659
165.807
138.305
133.412
129.953
129.410
128.452
121.752
73.773
52.591
32.082
30.749
22.237
13.943
100MHz,CDCl3
3an
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)

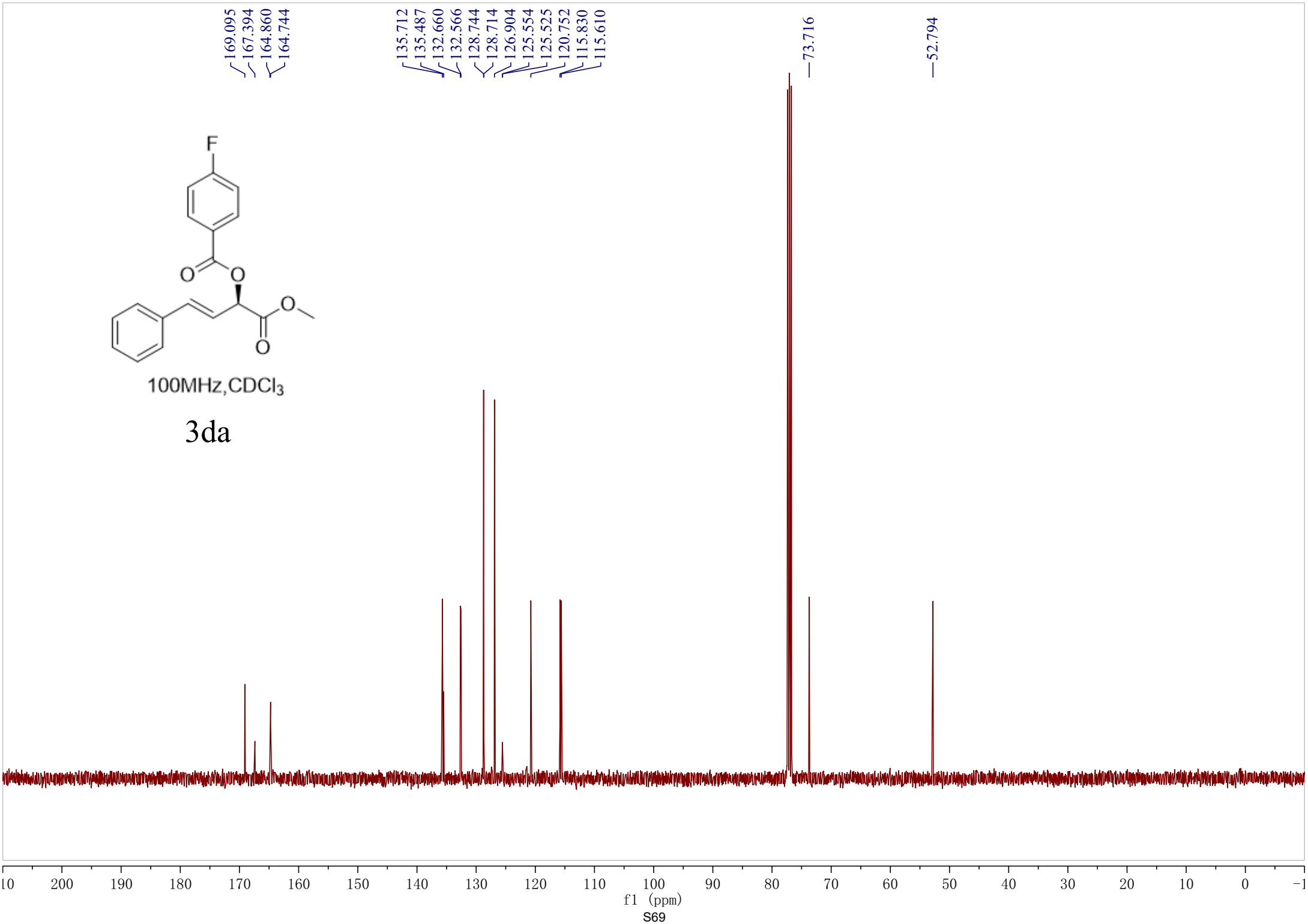

8.042
8.036
8.032
8.021
8.016
8.011
7.451
7.446
7.441
7.433
7.429
7.426
7.366
7.362
7.357
7.350
7.345
7.340
7.329
7.326
7.309
7.305
7.302
7.288
7.274
7.269
7.254
7.250
6.920
6.880
6.425
6.408
6.385
6.368
5.869
5.865
5.851
5.848
3.801
2.418
-0.000
O
O
O
O
400MHz, CDCl3
3ba
2.00
2.00
5.02
1.00
1.00
1.00
2.94
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

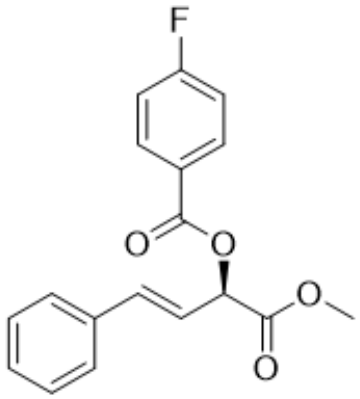

169.279
165.773
144.310
135.631
135.367
130.038
129.219
128.714
128.603
126.898
126.547
121.084
73.460
52.715
21.758
O
O
O
O
100MHz,CDCl3
3ba
f1 (ppm)


8.084
8.079
8.067
8.062
7.498
7.493
7.481
7.476
7.452
7.448
7.434
7.430
7.427
7.362
7.345
7.341
7.326
7.304
7.287
6.920
6.880
6.433
6.416
6.393
6.376
5.883
5.879
5.865
5.862
3.797
1.343
-0.000
tBu
O
O
O
O
400MHz, CDCl3
3ca
1.93
7.00
1.00
1.00
1.00
2.81
9.00
f1 (ppm)


169.261
165.723
157.276
135.648
135.239
129.902
128.725
128.597
126.901
126.505
125.510
121.113
73.401
52.726
35.190
31.134
tBu
O
O
O
O
100MHz,CDCl3
3ca
f1 (ppm)

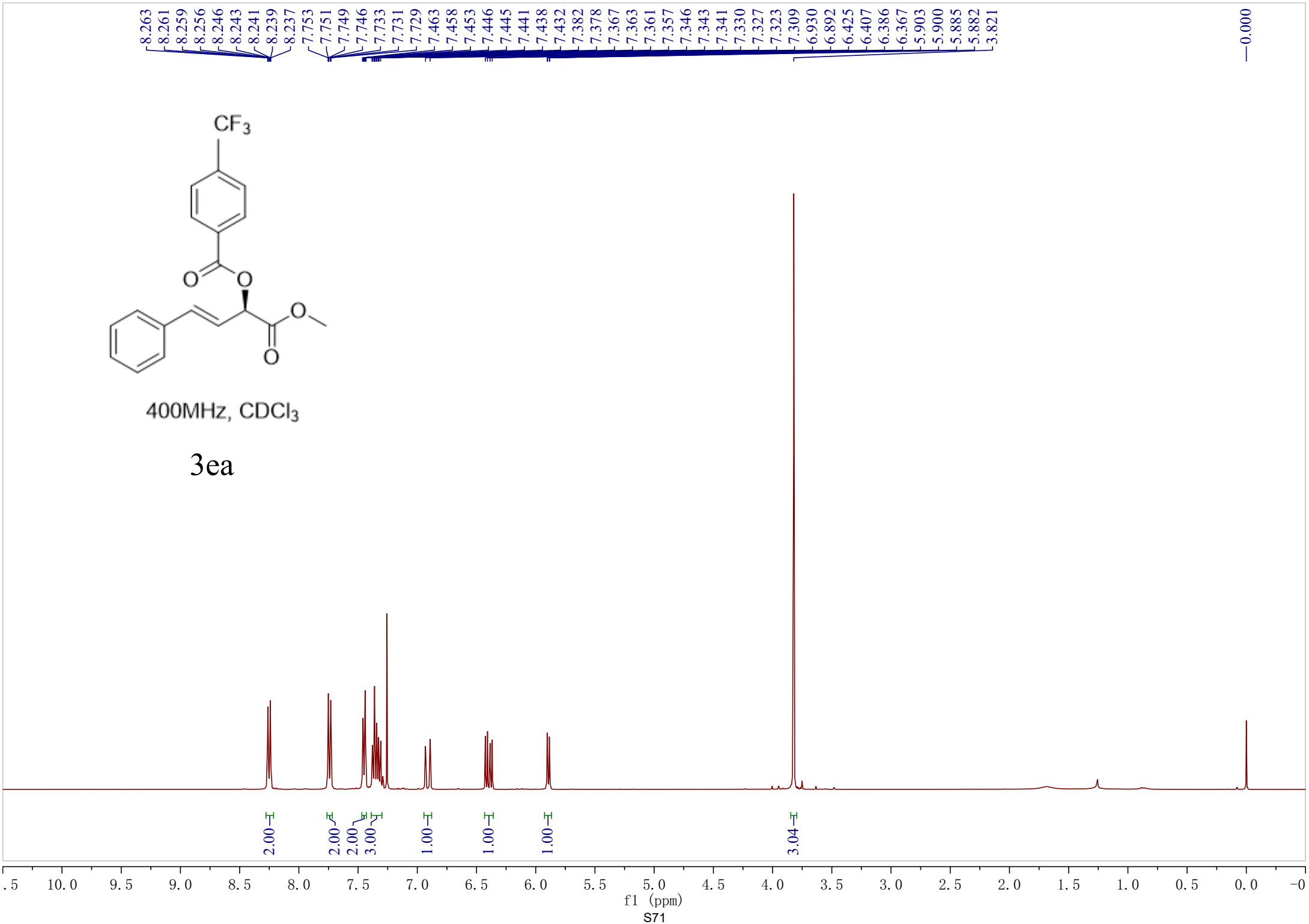

8.184
8.176
8.171
8.163
8.159
8.154
8.146
8.141
8.133
7.458
7.454
7.448
7.441
7.437
7.433
7.379
7.375
7.370
7.358
7.353
7.342
7.338
7.325
7.321
7.317
7.303
7.258
7.168
7.163
7.152
7.146
7.130
7.125
6.920
6.880
6.416
6.398
6.377
6.359
5.865
5.862
5.847
5.844
3.814
0.000
F
O
O
O
O
400MHz, CDCl3
3da
2.07
0.01
2.04
3.07
2.12
1.01
1.01
0.98
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

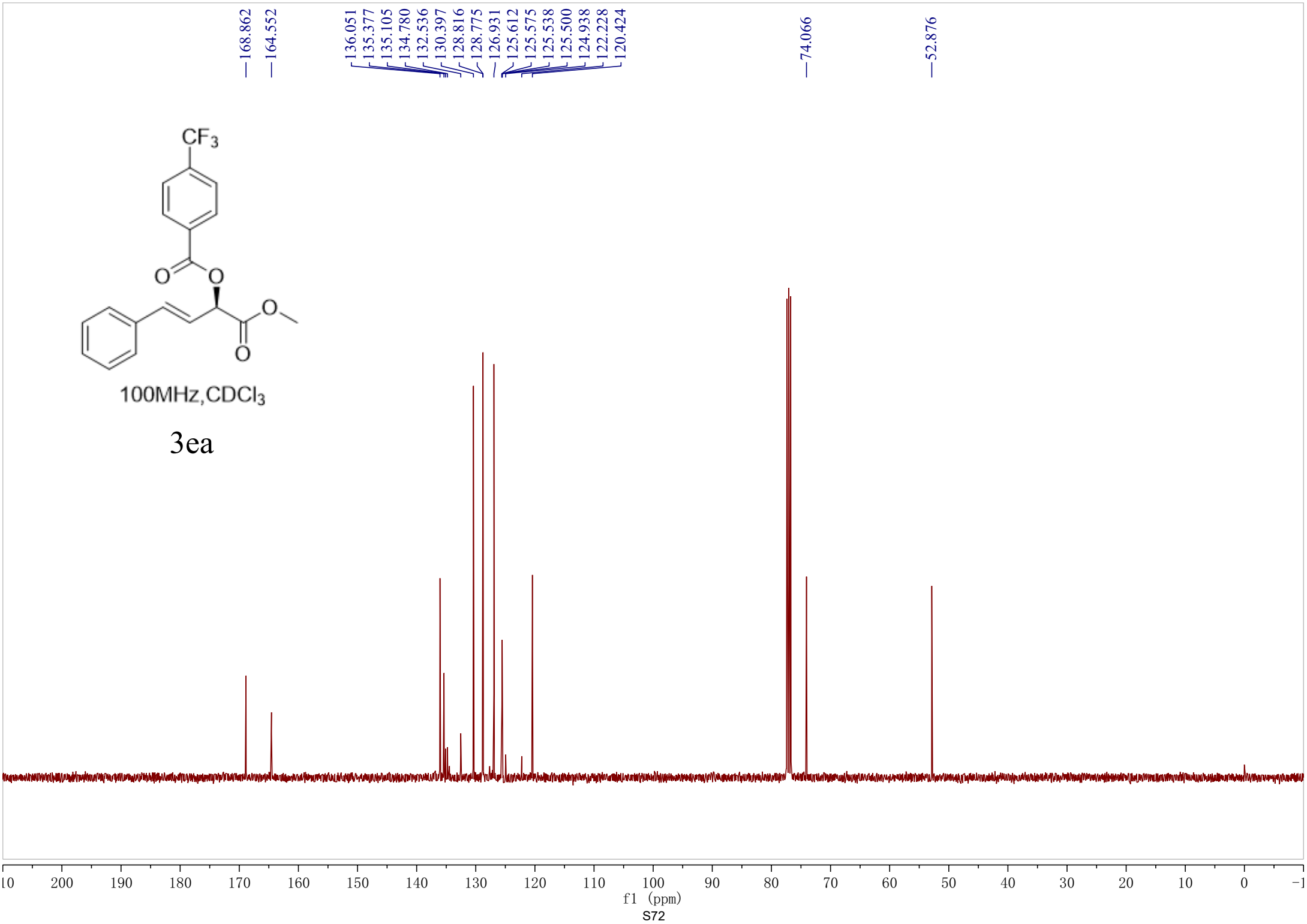

169.095
167.394
164.860
164.744
135.712
135.487
132.660
132.566
128.744
128.714
126.904
125.554
125.525
120.752
115.830
115.610
73.716
52.794
F
O
O
O
O
100MHz,CDCl3
3da
f1 (ppm)

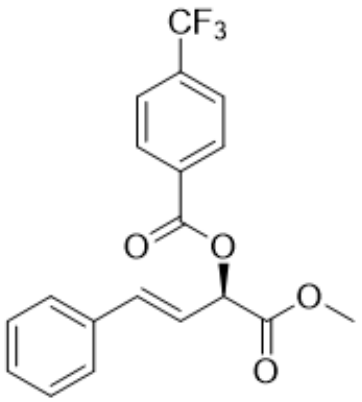


282MHz, $CDCl_3$

3da

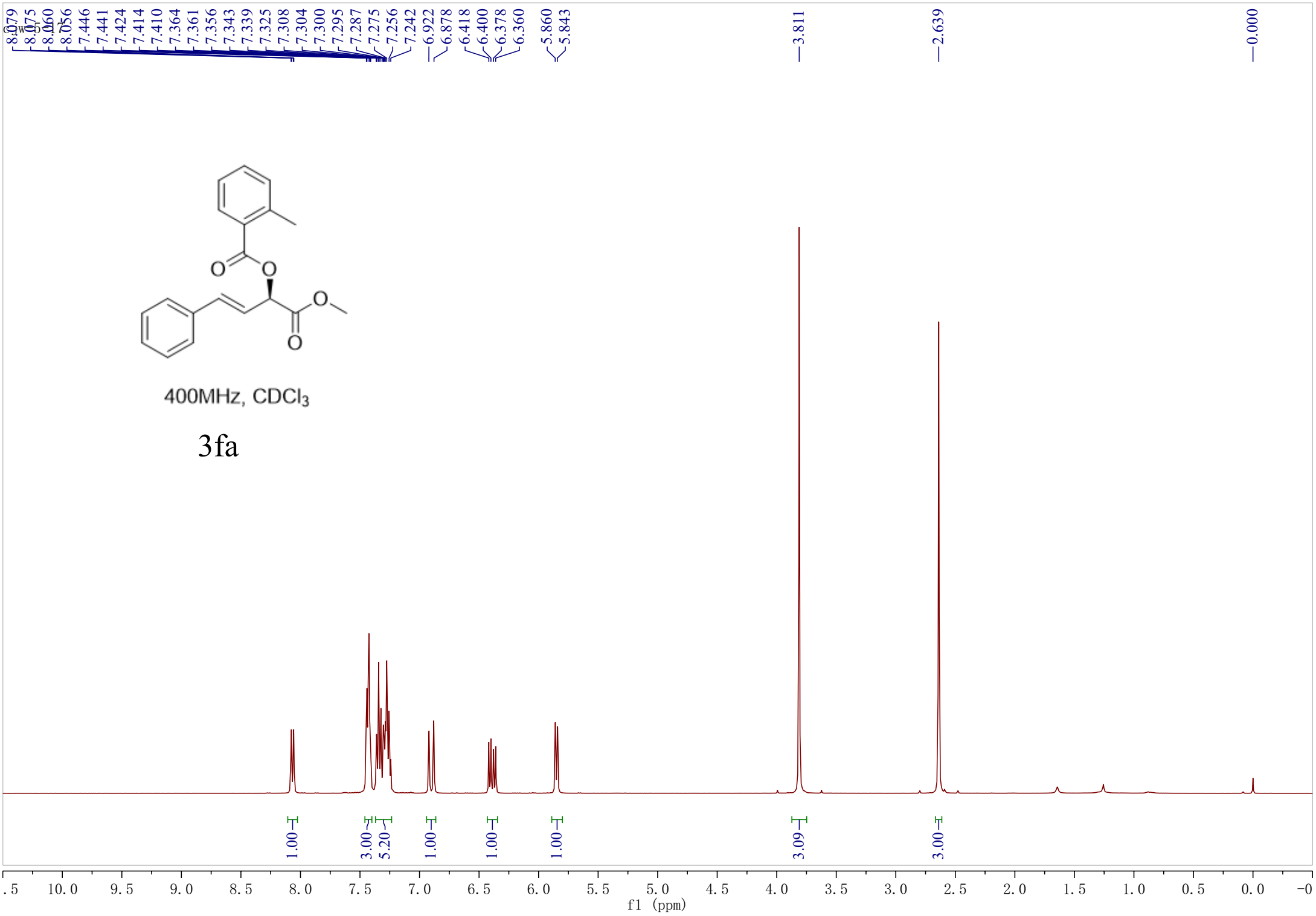

8.263
8.261
8.259
8.256
8.246
8.243
8.241
8.239
8.237
7.753
7.751
7.749
7.746
7.733
7.731
7.729
7.463
7.458
7.453
7.446
7.445
7.441
7.438
7.432
7.382
7.378
7.367
7.363
7.361
7.357
7.346
7.343
7.341
7.330
7.327
7.323
7.309
6.930
6.892
6.425
6.407
6.386
6.367
5.903
5.900
5.885
5.882
3.821
0.000
CF3
O
O
O
O
400MHz, CDCl3
3ea
2.00
2.00
2.00
3.00
1.00
1.00
1.00
3.04
f1 (ppm)

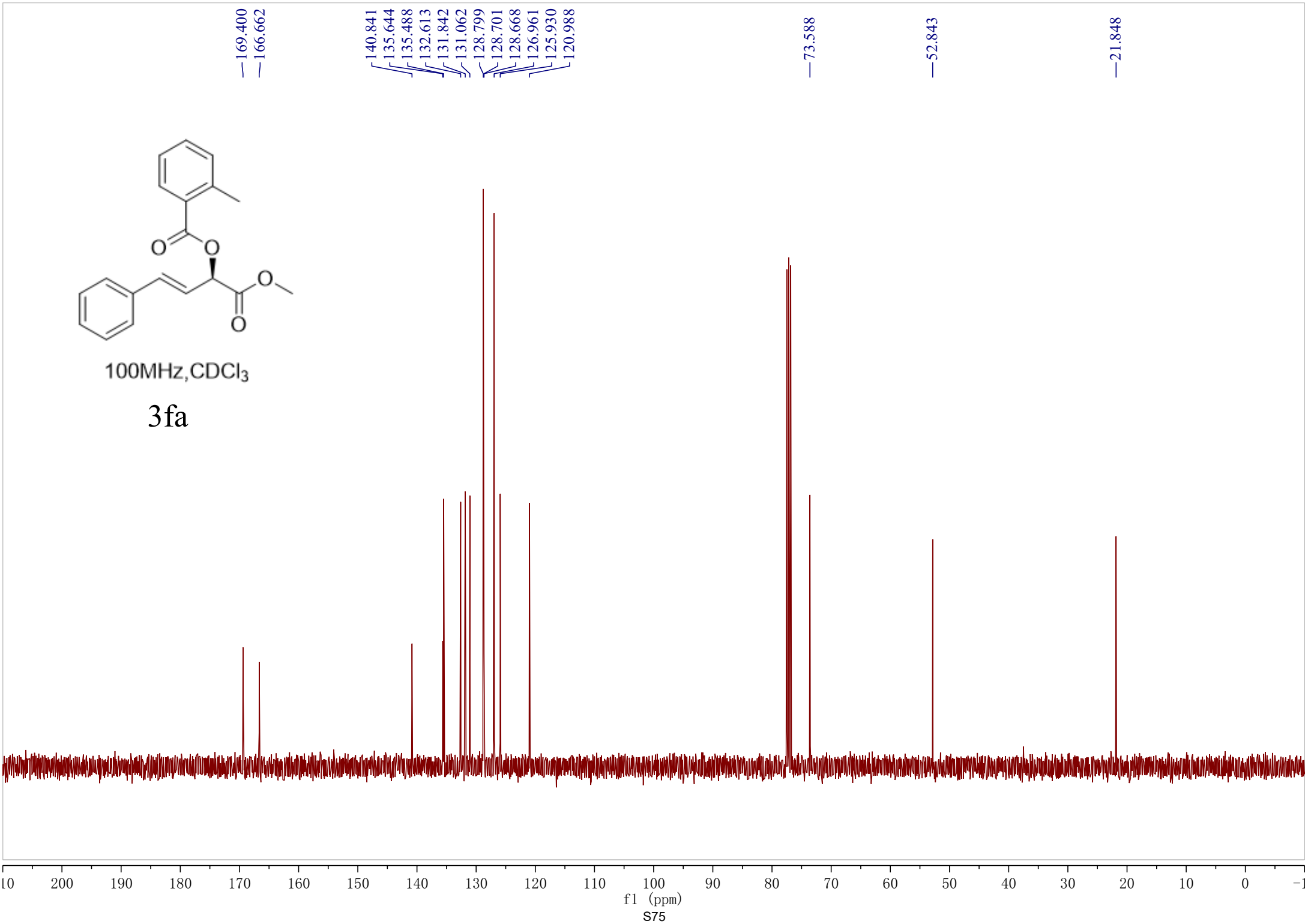

168.862
164.552
136.051
135.377
135.105
134.780
132.536
130.397
128.816
128.775
126.931
125.612
125.575
125.538
125.500
124.938
122.228
120.424
74.066
52.876
CF3
O
O
O
O
100MHz,CDCl3
3ea
f1 (ppm)

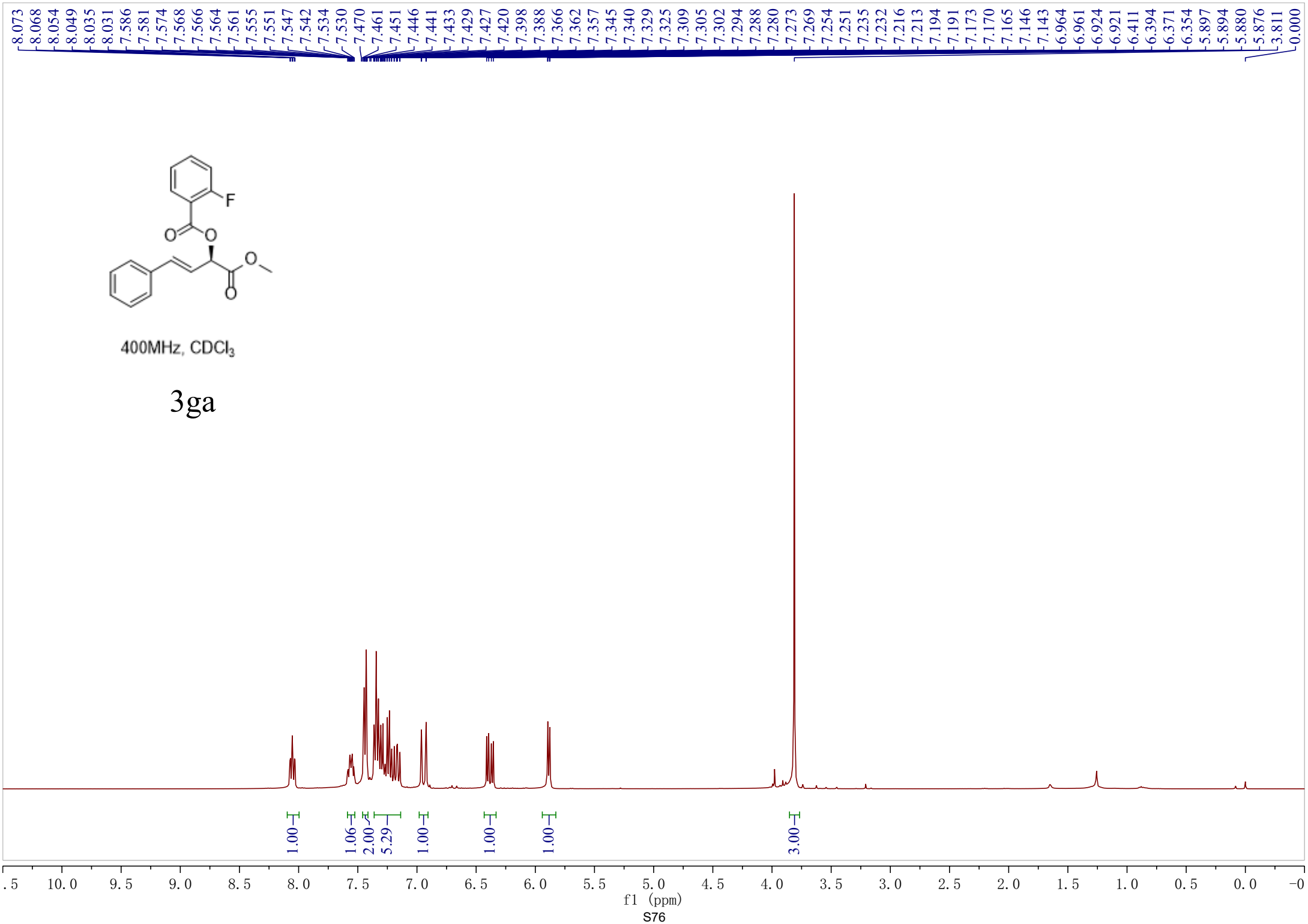


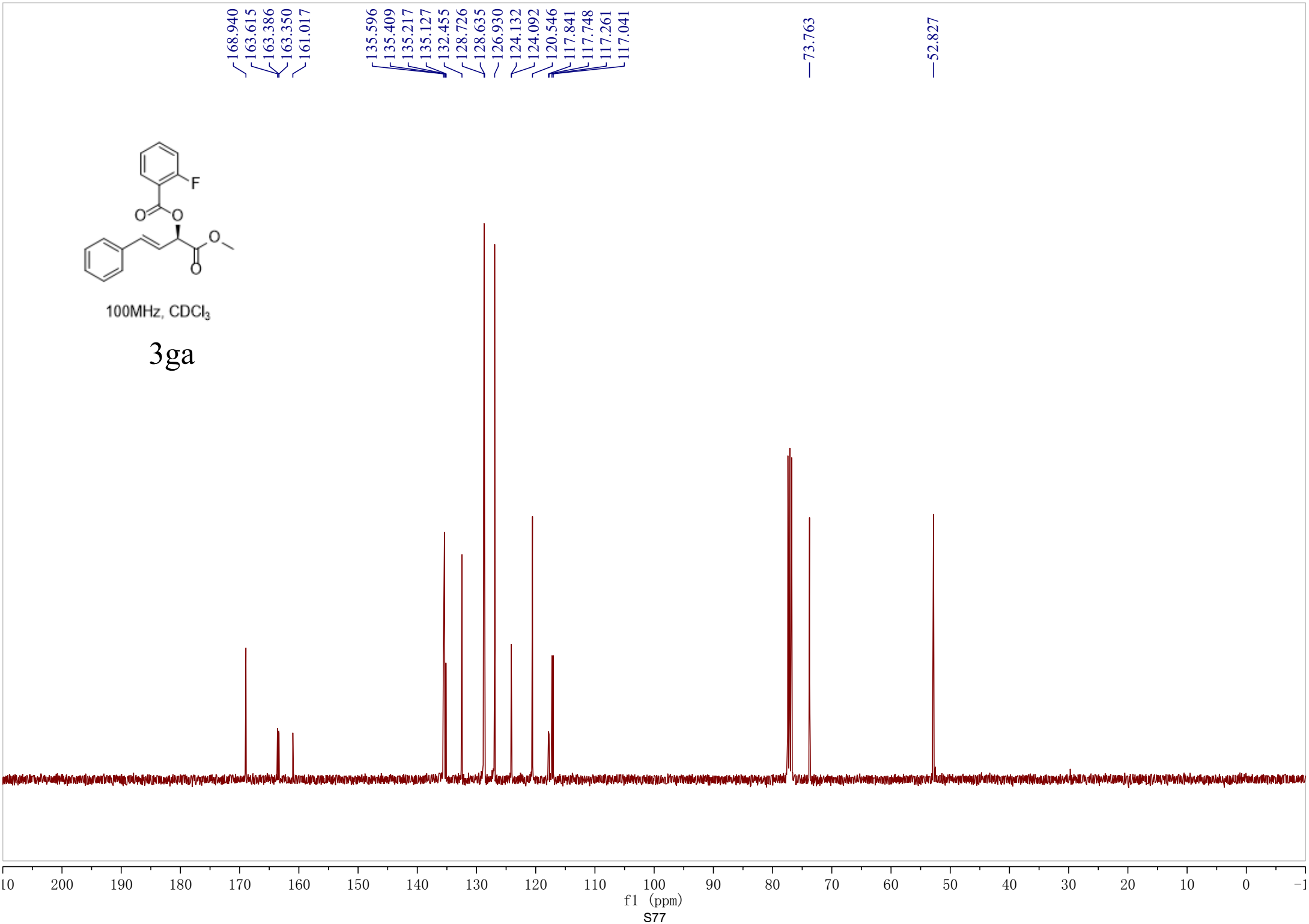
282MHz, $CDCl_3$

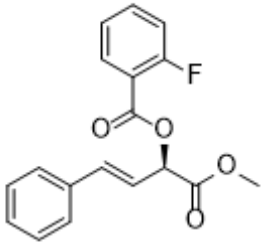
3ea


8.079
8.175
8.060
8.056
7.446
7.441
7.424
7.414
7.410
7.364
7.361
7.356
7.343
7.339
7.325
7.308
7.304
7.300
7.295
7.287
7.275
7.256
7.242
6.922
6.878
6.418
6.400
6.378
6.360
5.860
5.843
3.811
2.639
0.000
400MHz, CDCl3
3fa
1.00
3.00
5.20
1.00
1.00
1.00
3.09
3.00
f1 (ppm)


169.400
166.662
140.841
135.644
135.488
132.613
131.842
131.062
128.799
128.701
128.668
126.961
125.930
120.988
73.588
52.843
21.848
O
O
O
O
100MHz,CDCl3
3fa
f1 (ppm)

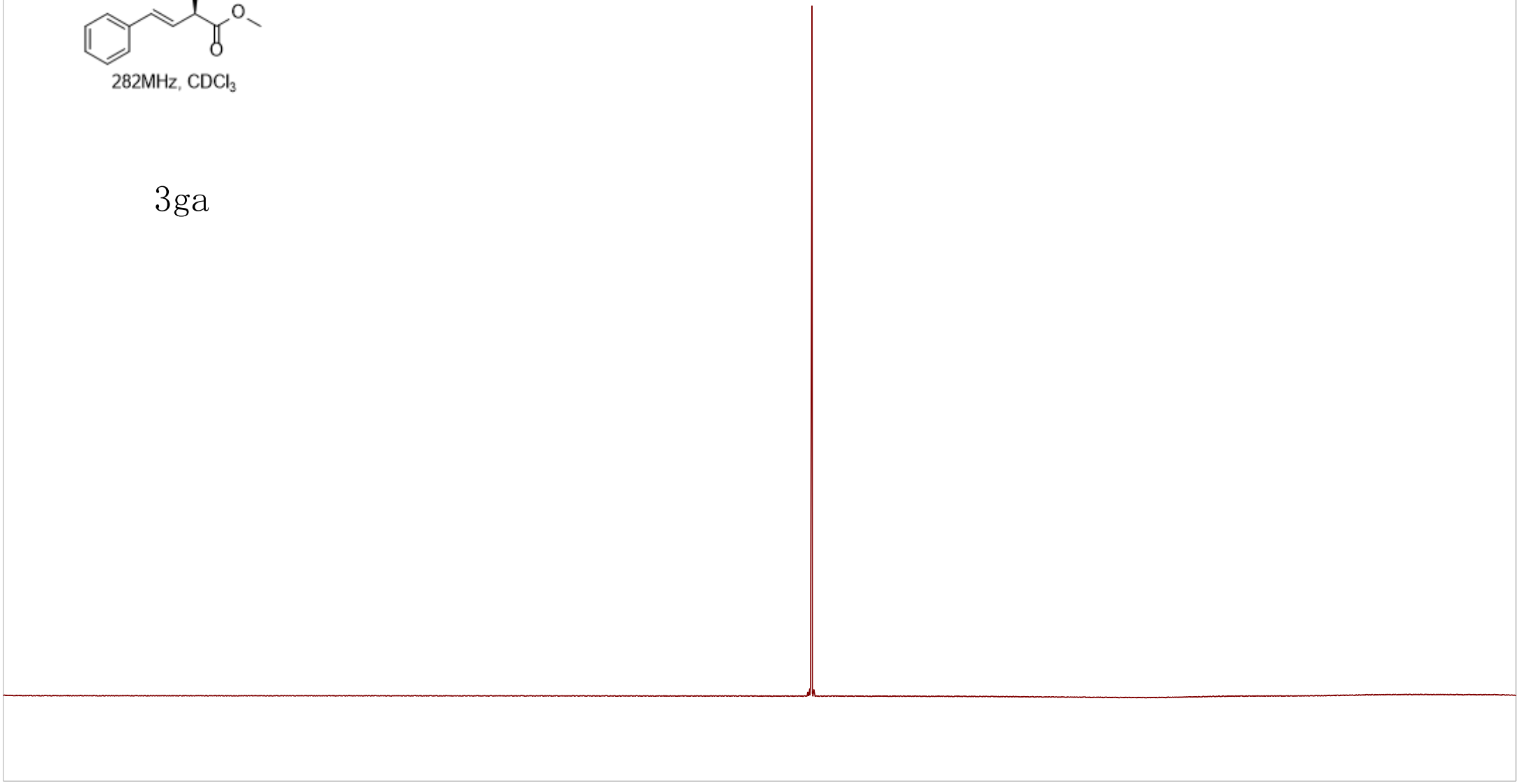

8.073
8.068
8.054
8.049
8.035
8.031
7.586
7.581
7.574
7.568
7.566
7.564
7.561
7.555
7.551
7.547
7.542
7.534
7.530
7.470
7.461
7.451
7.446
7.441
7.433
7.429
7.427
7.420
7.398
7.388
7.366
7.362
7.357
7.345
7.340
7.329
7.325
7.309
7.305
7.302
7.294
7.288
7.280
7.273
7.269
7.254
7.251
7.235
7.232
7.216
7.213
7.194
7.191
7.173
7.170
7.165
7.146
7.143
6.964
6.961
6.924
6.921
6.411
6.394
6.371
6.354
5.897
5.894
5.880
5.876
3.811
0.000
F
O
O
O
O
400MHz, CDCl3
3ga
1.00
1.06
2.00
5.29
1.00
1.00
1.00
3.00
f1 (ppm)

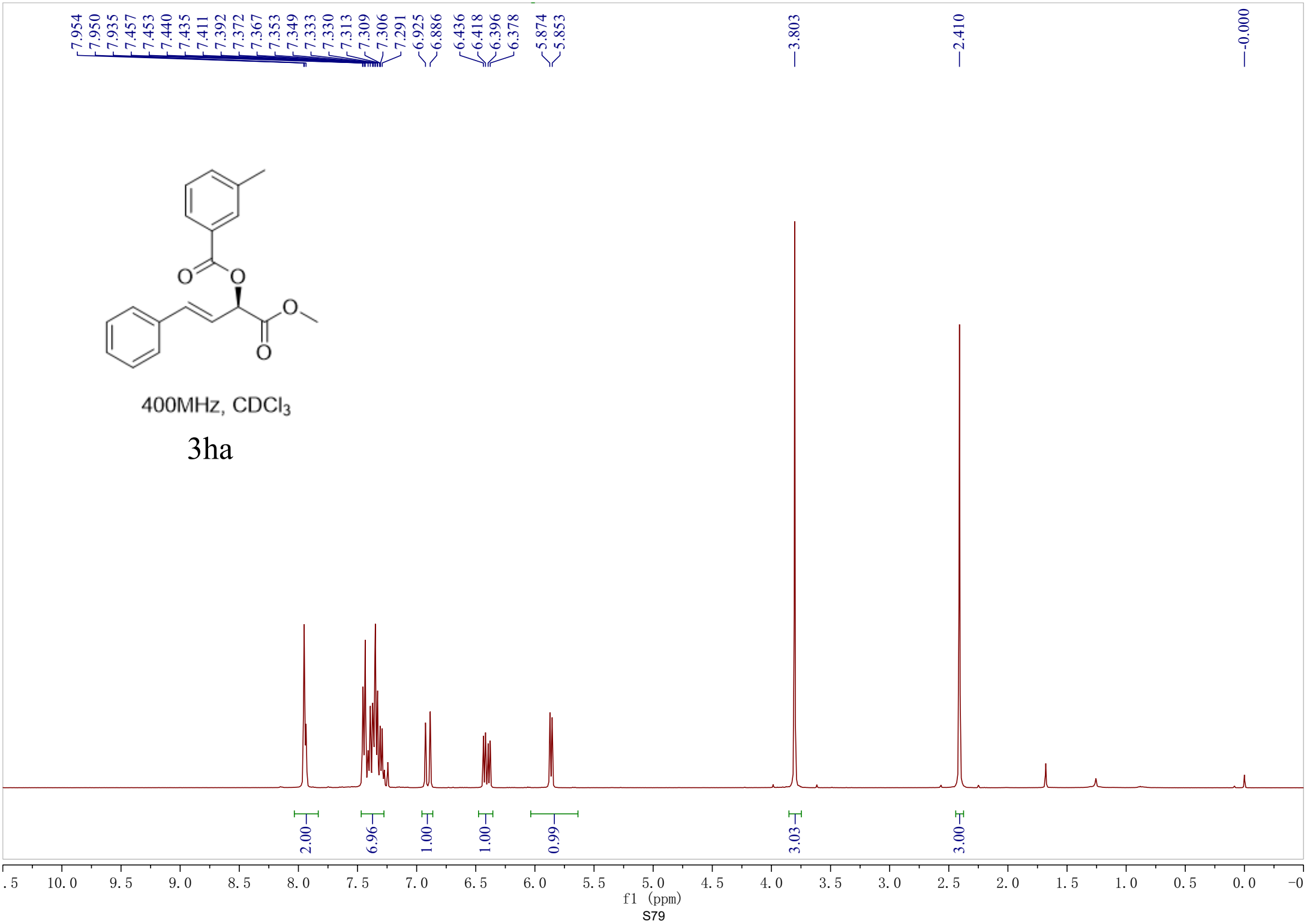

168.940
163.615
163.386
163.350
161.017
135.596
135.409
135.217
135.127
132.455
128.726
128.635
126.930
124.132
124.092
120.546
117.841
117.748
117.261
117.041
73.763
52.827
F
O
O
O
O
100MHz, CDCl3
3ga
f1 (ppm)

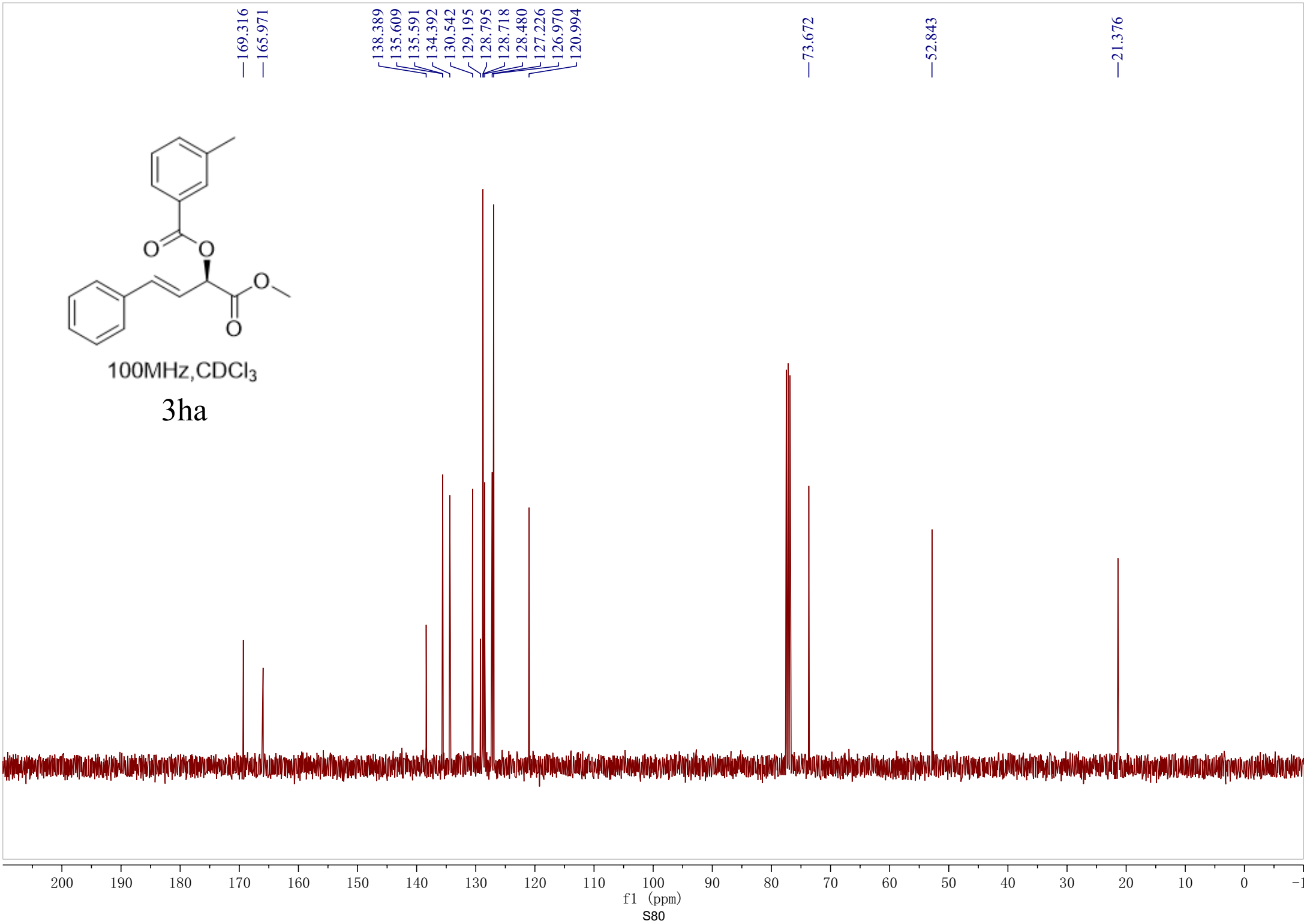


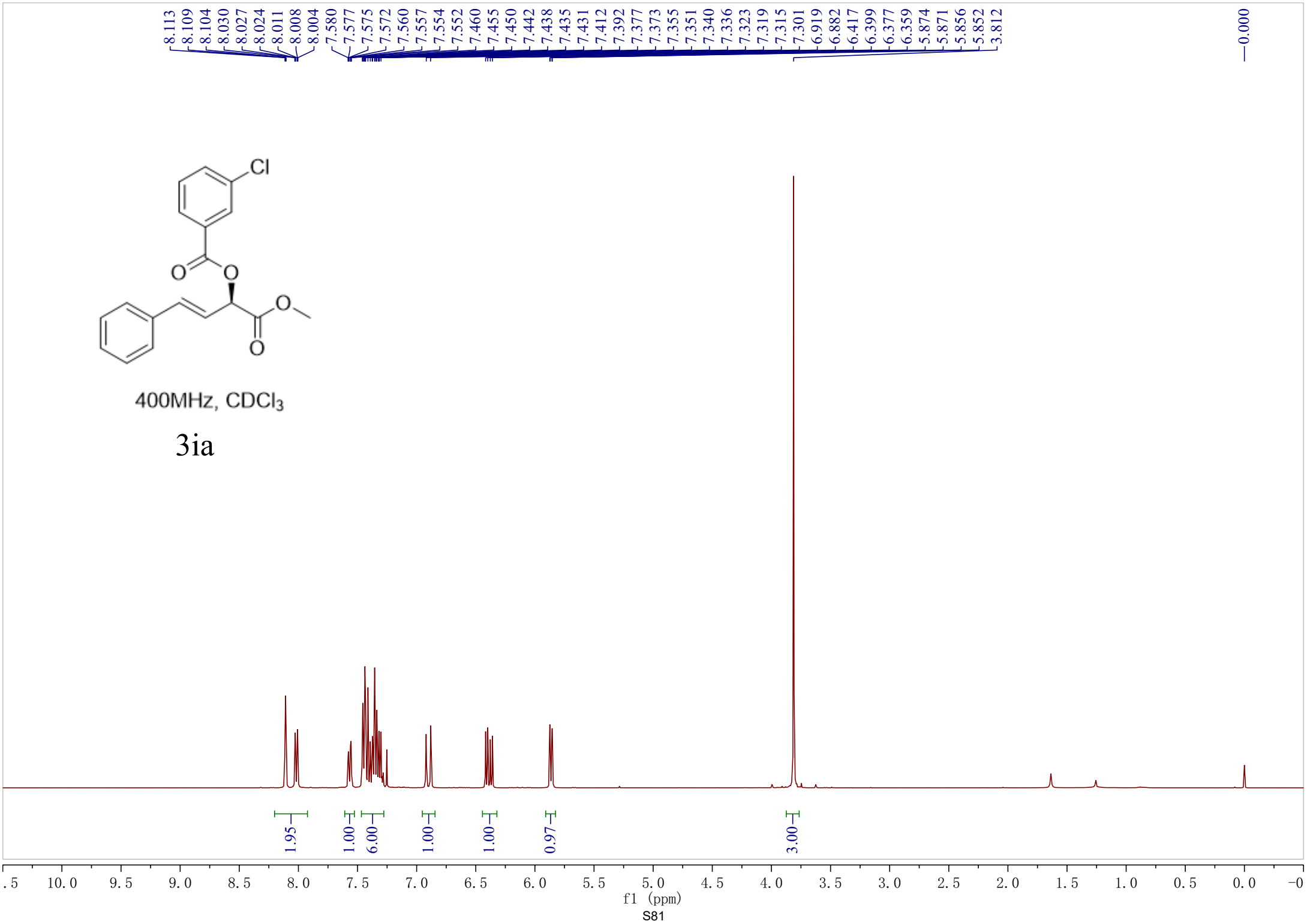
282MHz, $CDCl_3$

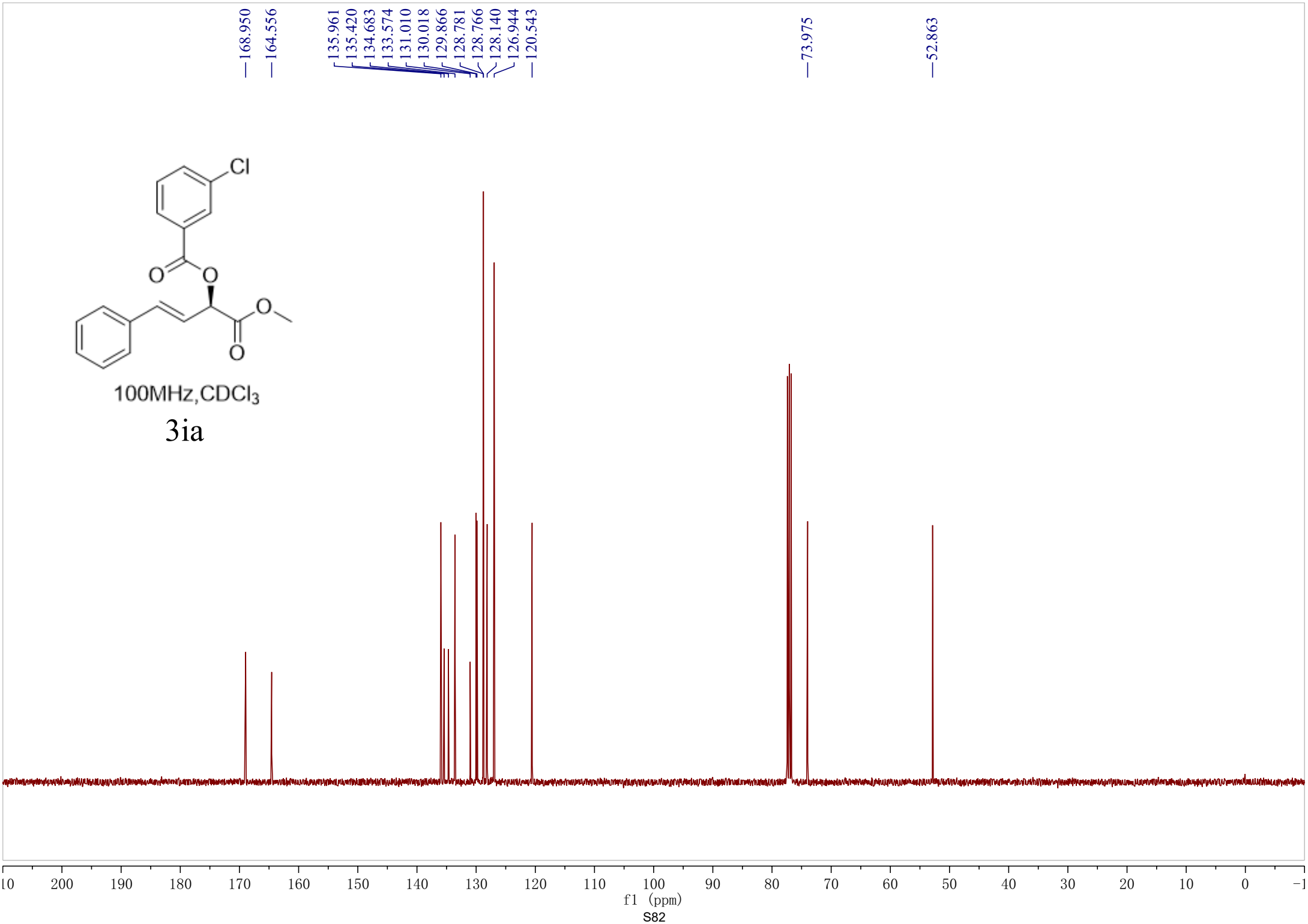
3ga

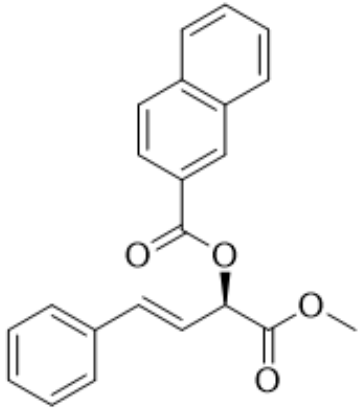



7.954
7.950
7.935
7.457
7.453
7.440
7.435
7.411
7.392
7.372
7.367
7.353
7.349
7.333
7.330
7.313
7.309
7.306
7.291
6.925
6.886
6.436
6.418
6.396
6.378
5.874
5.853
3.803
2.410
-0.000
O
O
O
O
400MHz, CDCl3
3ha
2.00
6.96
1.00
1.00
0.99
3.03
3.00
f1 (ppm)


169.316
165.971
138.389
135.609
135.591
134.392
130.542
129.195
128.795
128.718
128.480
127.226
126.970
120.994
73.672
52.843
21.376
100MHz,CDCl3
3ha
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

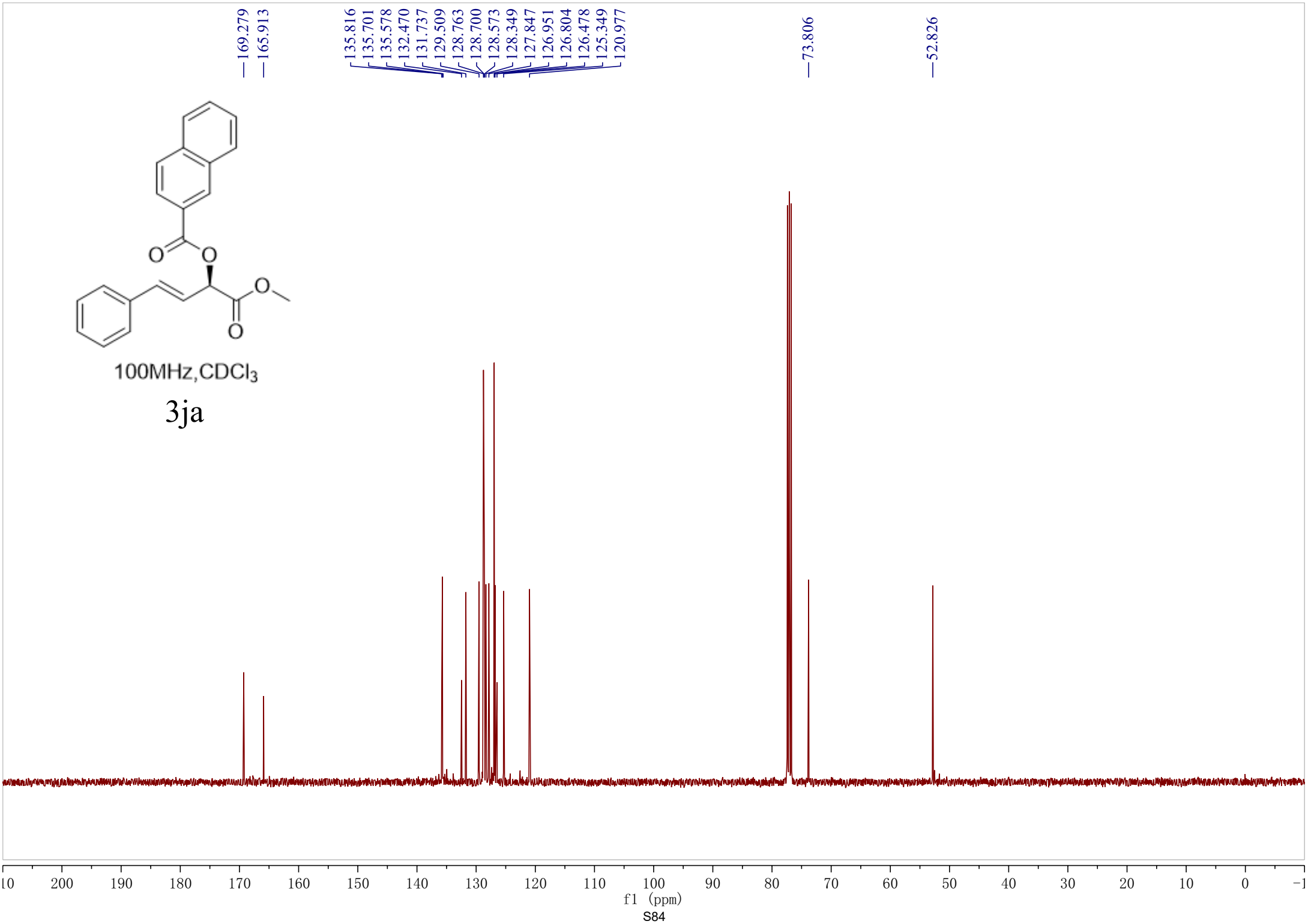

8.113
8.109
8.104
8.030
8.027
8.024
8.011
8.008
8.004
7.580
7.577
7.575
7.572
7.560
7.557
7.554
7.552
7.460
7.455
7.450
7.442
7.438
7.435
7.431
7.412
7.392
7.377
7.373
7.355
7.351
7.340
7.336
7.323
7.319
7.315
7.301
6.919
6.882
6.417
6.399
6.377
6.359
5.874
5.871
5.856
5.852
3.812
0.000
Cl
O
O
O
O
400MHz, CDCl3
3ia
1.95
1.00
6.00
1.00
1.00
0.97
3.00
f1 (ppm)

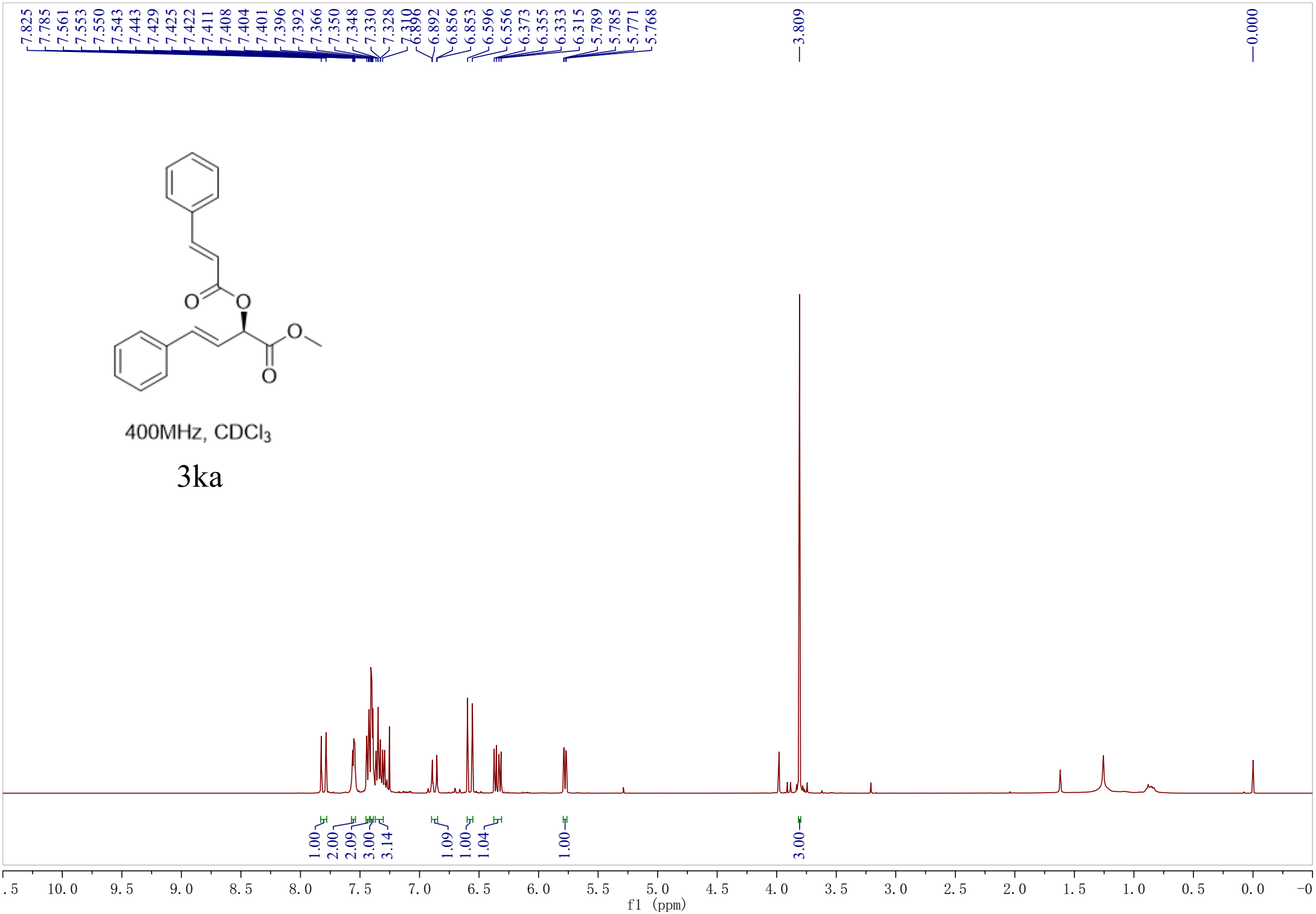

168.950
164.556
135.961
135.420
134.683
133.574
131.010
130.018
129.866
128.781
128.766
128.140
126.944
120.543
73.975
52.863
Cl
O
O
O
O
100MHz,CDCl3
3ia
f1 (ppm)

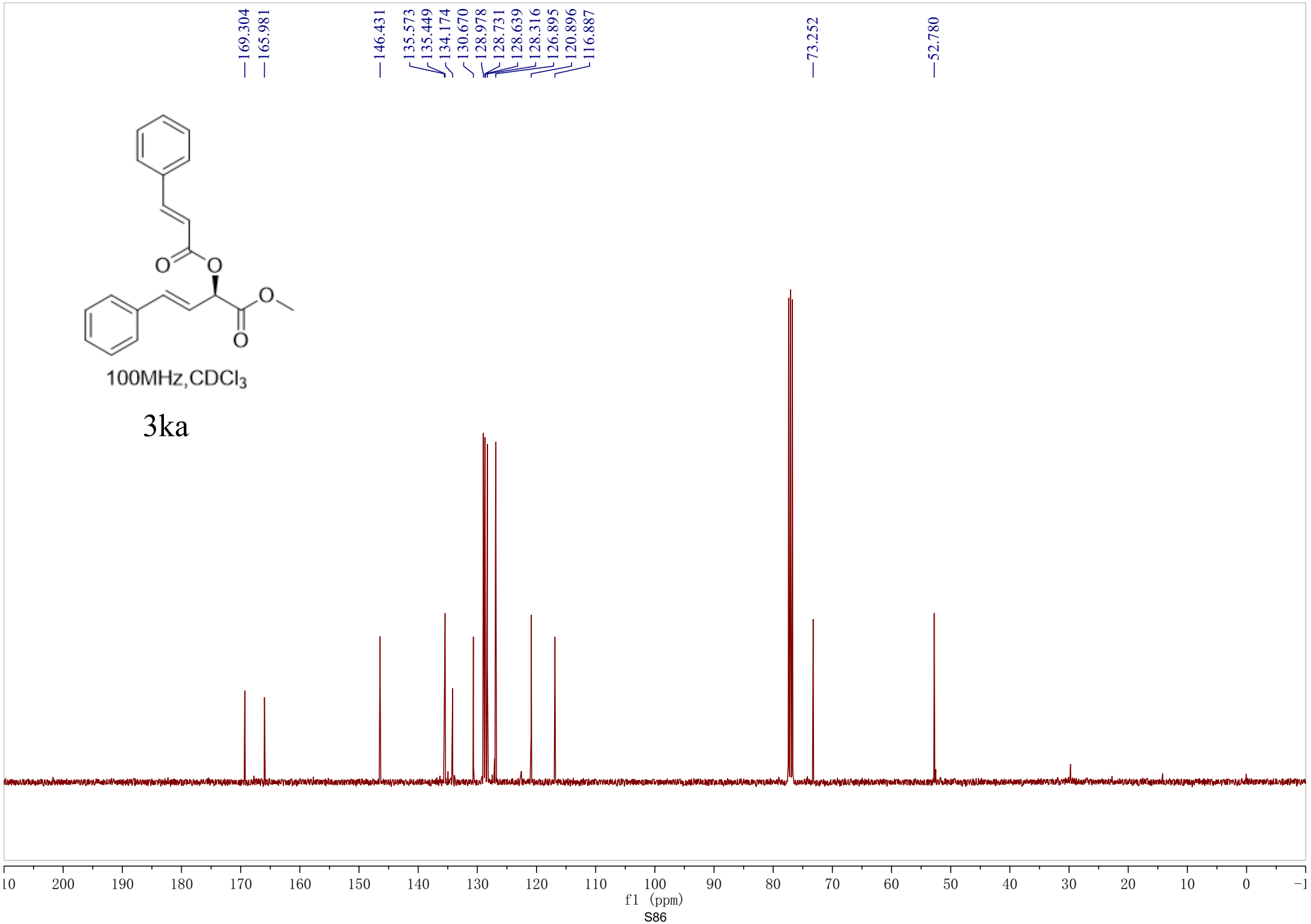


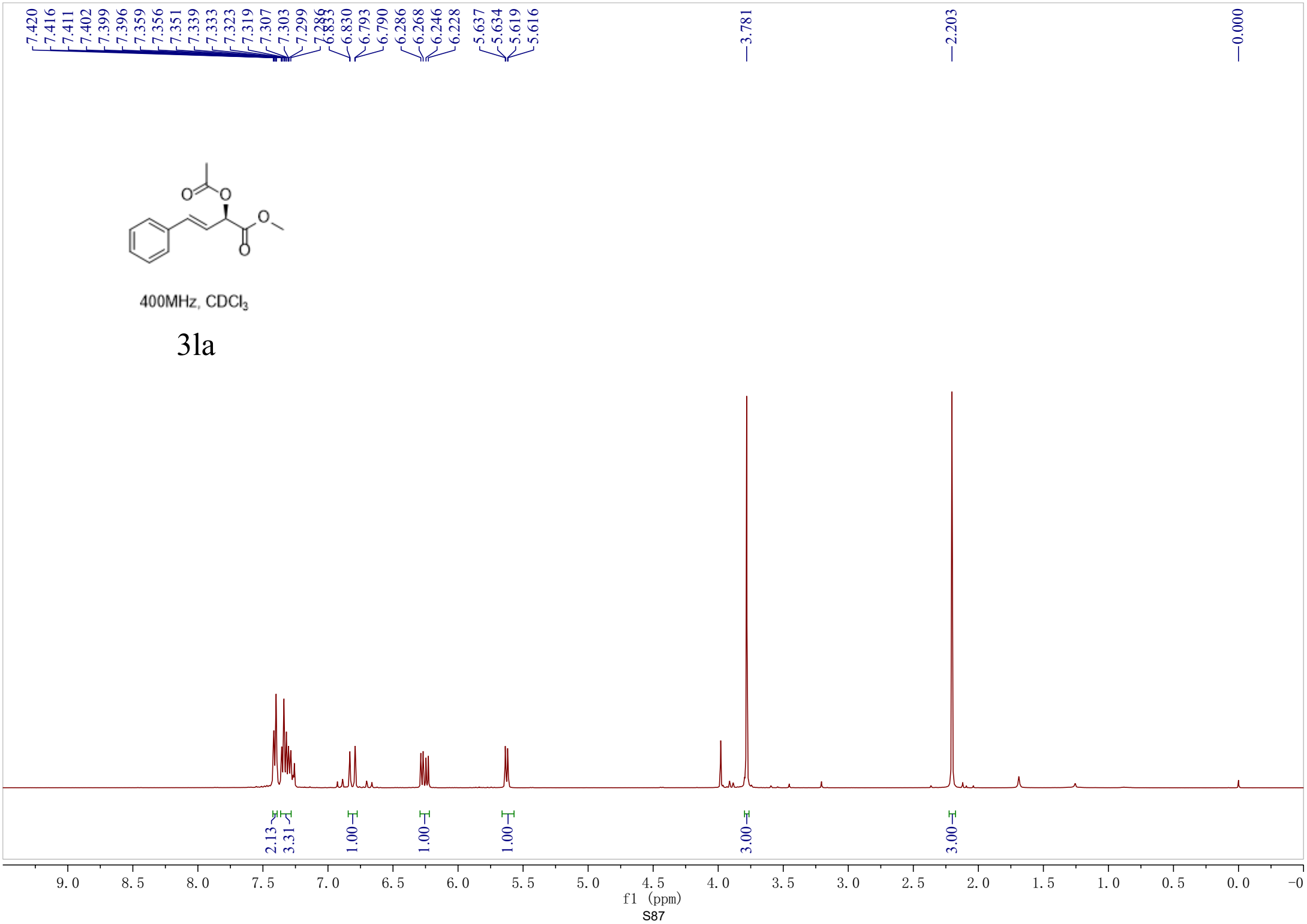
400MHz, $CDCl_3$

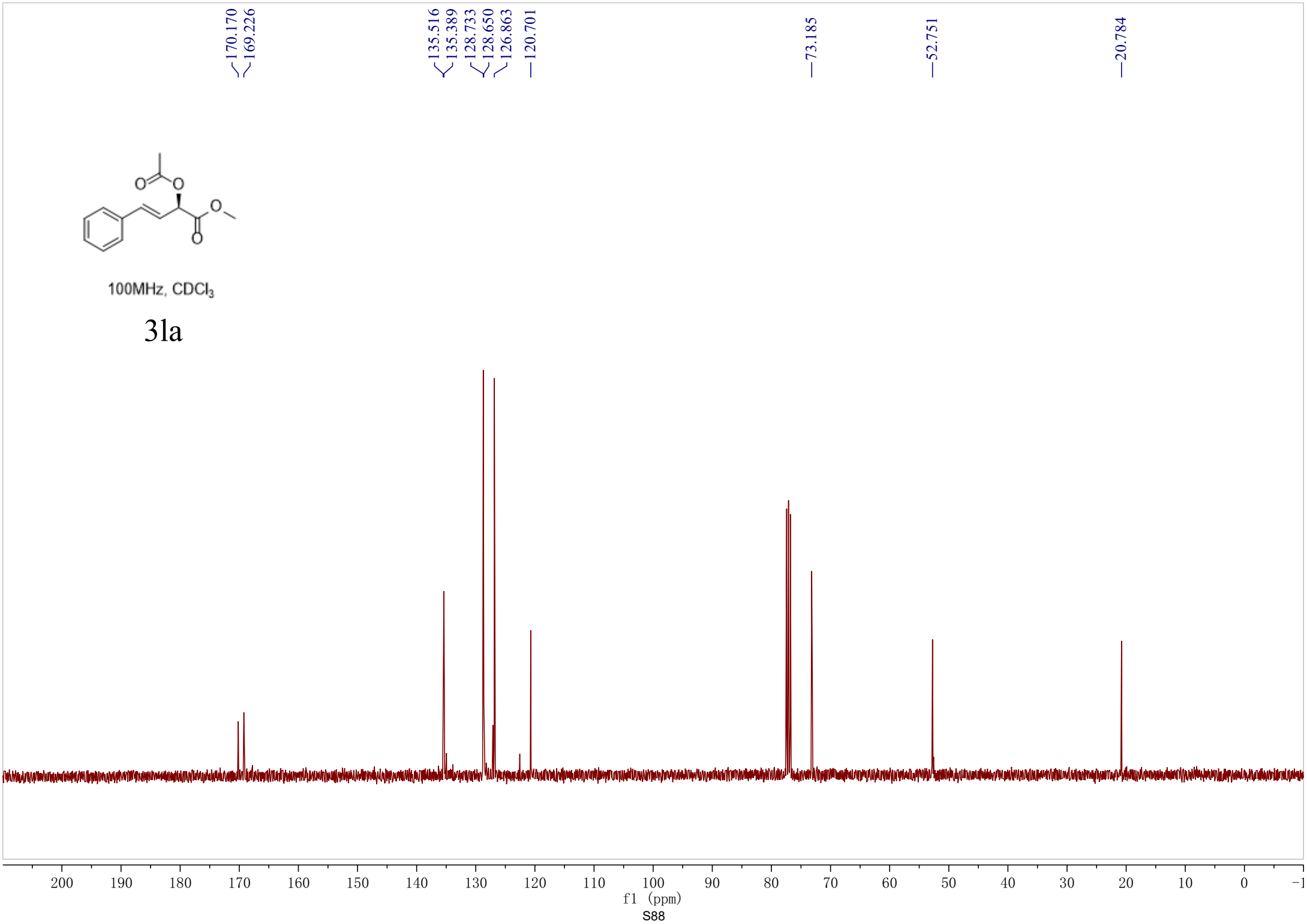
3ja

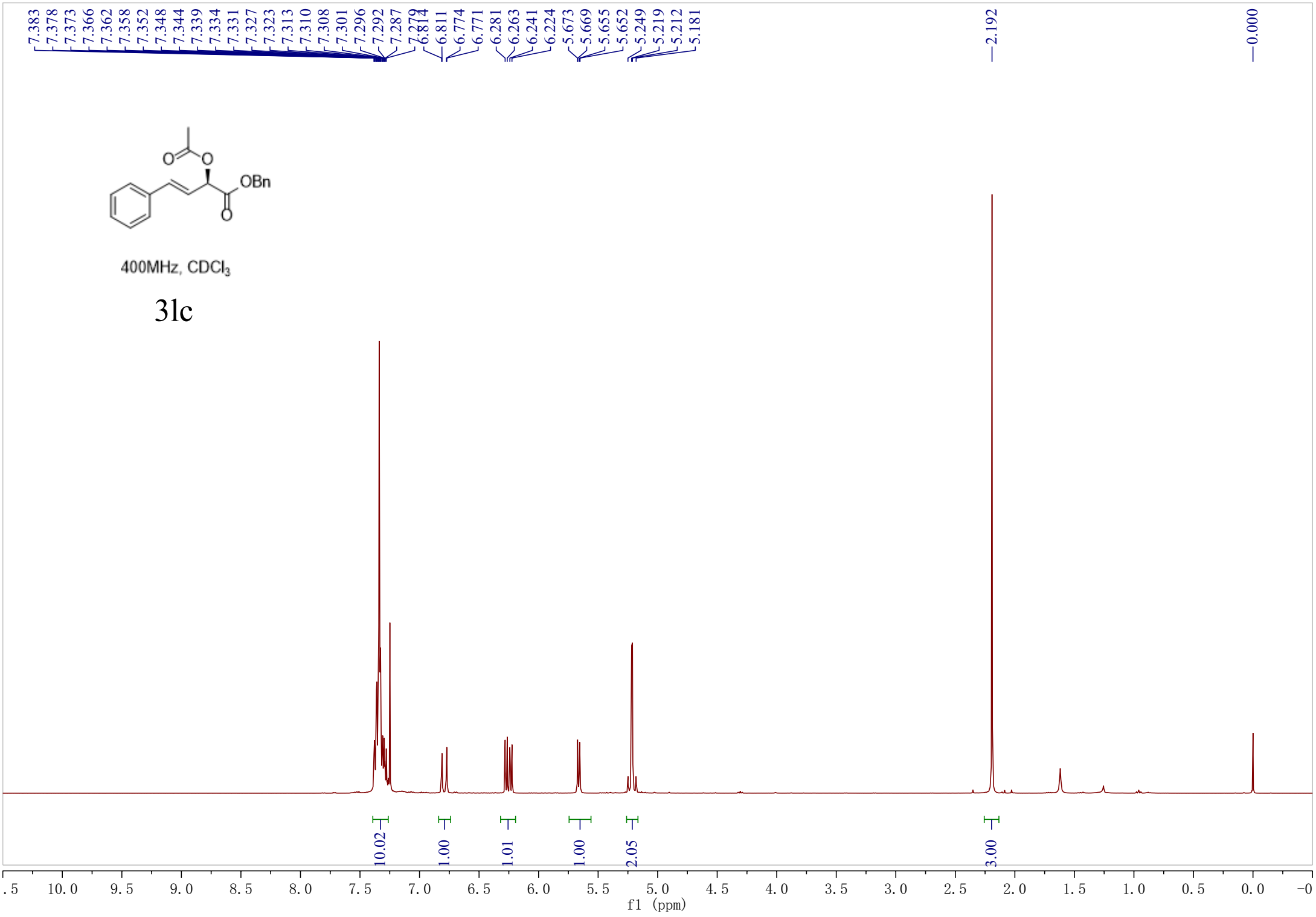

169.279
165.913
135.816
135.701
135.578
132.470
131.737
129.509
128.763
128.700
128.573
128.349
127.847
126.951
126.804
126.478
125.349
120.977
73.806
52.826
O
O
O
O
100MHz,CDCl3
3ja
f1 (ppm)

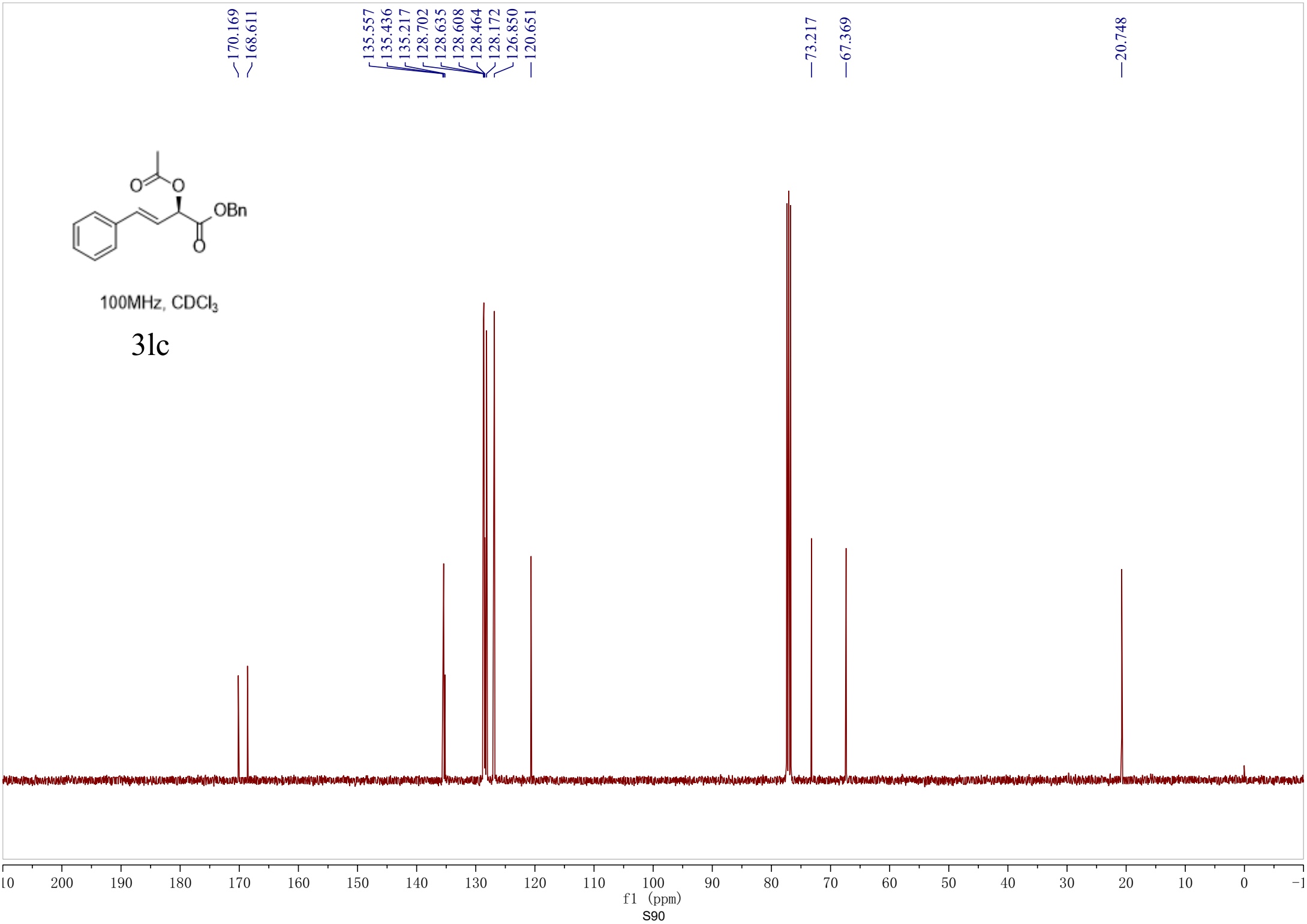

7.825
7.785
7.561
7.553
7.550
7.543
7.443
7.429
7.425
7.422
7.411
7.408
7.404
7.401
7.396
7.392
7.366
7.350
7.348
7.330
7.328
7.310
6.892
6.856
6.853
6.596
6.556
6.373
6.355
6.333
6.315
5.789
5.785
5.771
5.768
3.809
0.000
O
O
O
O
400MHz, CDCl3
3ka
1.00
2.00
2.09
3.00
3.14
1.09
1.00
1.04
1.00
3.00
f1 (ppm)

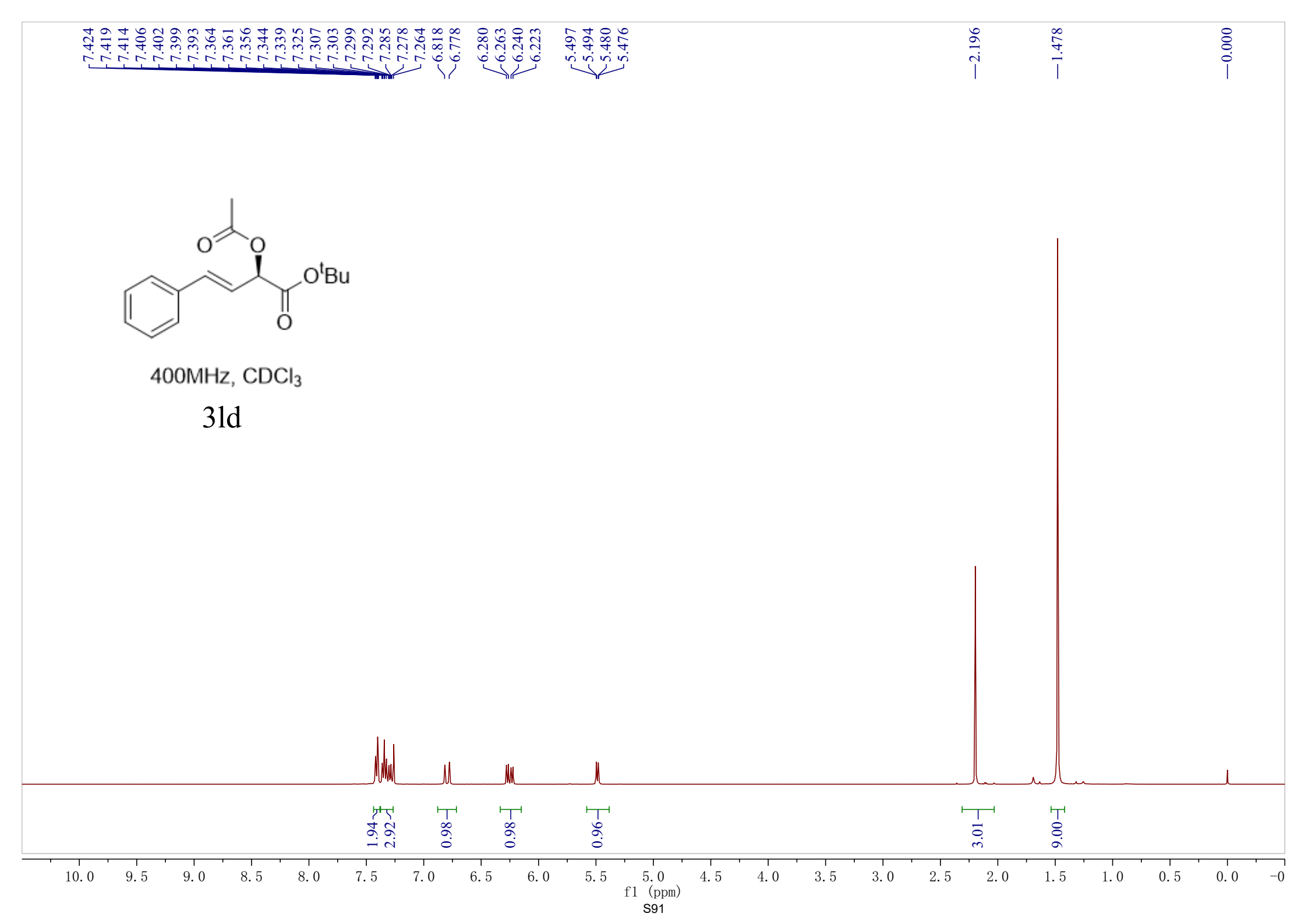

169.304
165.981
146.431
135.573
135.449
134.174
130.670
128.978
128.731
128.639
128.316
126.895
120.896
116.887
73.252
52.780
O
O
O
O
100MHz,CDCl3
3ka
f1 (ppm)

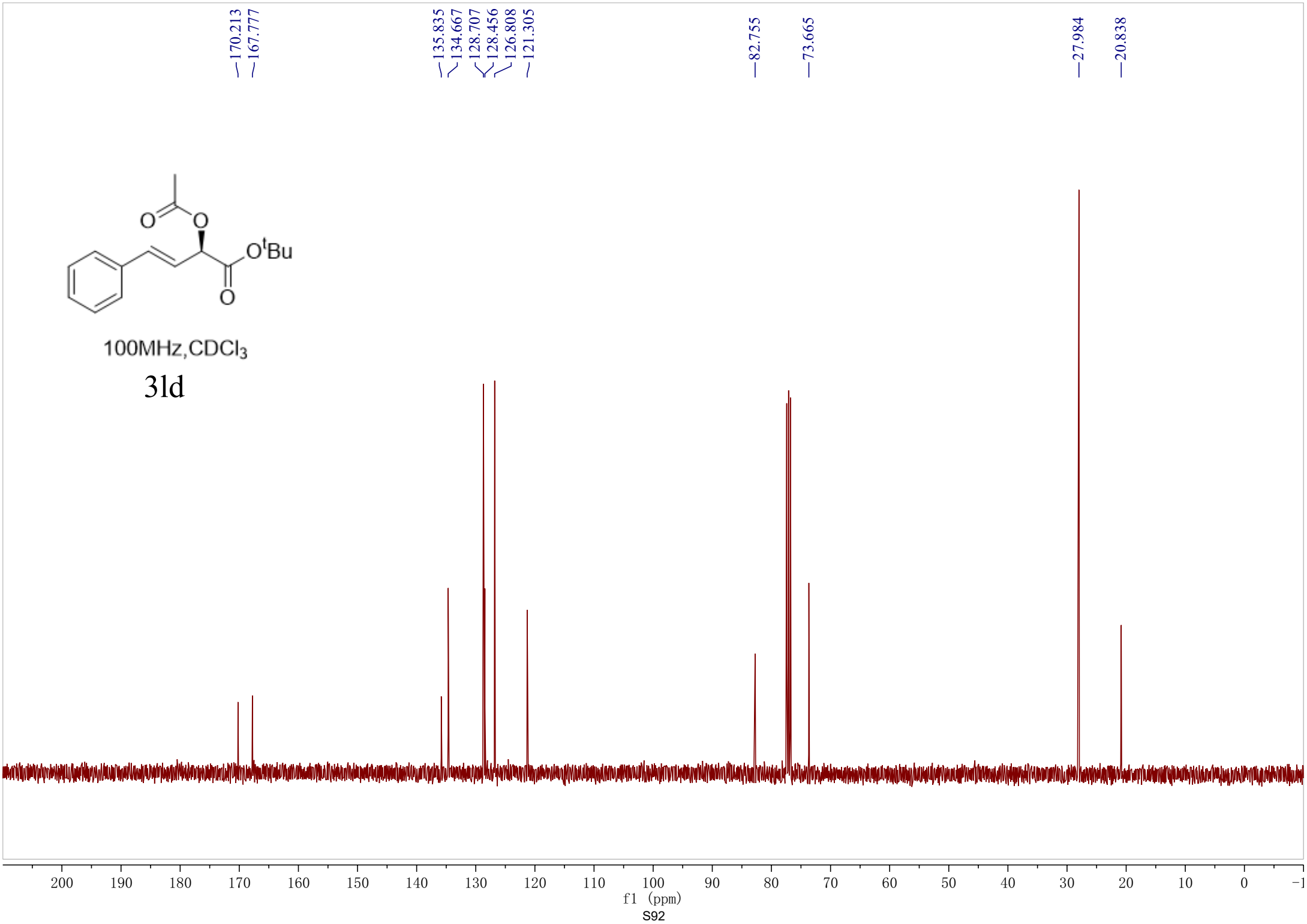

7.420
7.416
7.411
7.402
7.399
7.396
7.359
7.356
7.351
7.339
7.333
7.323
7.319
7.307
7.303
7.299
7.286
6.833
6.830
6.793
6.790
6.286
6.268
6.246
6.228
5.637
5.634
5.619
5.616
3.781
2.203
0.000
400MHz, CDCl3
3la
2.13
3.31
1.00
1.00
1.00
3.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

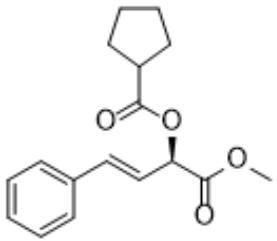

170.170
169.226
135.516
135.389
128.733
128.650
126.863
120.701
73.185
52.751
20.784
100MHz, CDCl3
3la
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)


7.383
7.378
7.373
7.366
7.362
7.358
7.352
7.348
7.344
7.339
7.334
7.331
7.327
7.323
7.313
7.310
7.308
7.301
7.296
7.292
7.287
7.279
6.814
6.811
6.774
6.771
6.281
6.263
6.241
6.224
5.673
5.669
5.655
5.652
5.249
5.219
5.212
5.181
2.192
0.000
OBn
400MHz, CDCl3
31c
10.02
1.00
1.01
1.00
2.05
3.00
f1 (ppm)


170.169
168.611
135.557
135.436
135.217
128.702
128.635
128.608
128.464
128.172
126.850
120.651
73.217
67.369
20.748
OBn
100MHz, CDCl3
3lc
f1 (ppm)

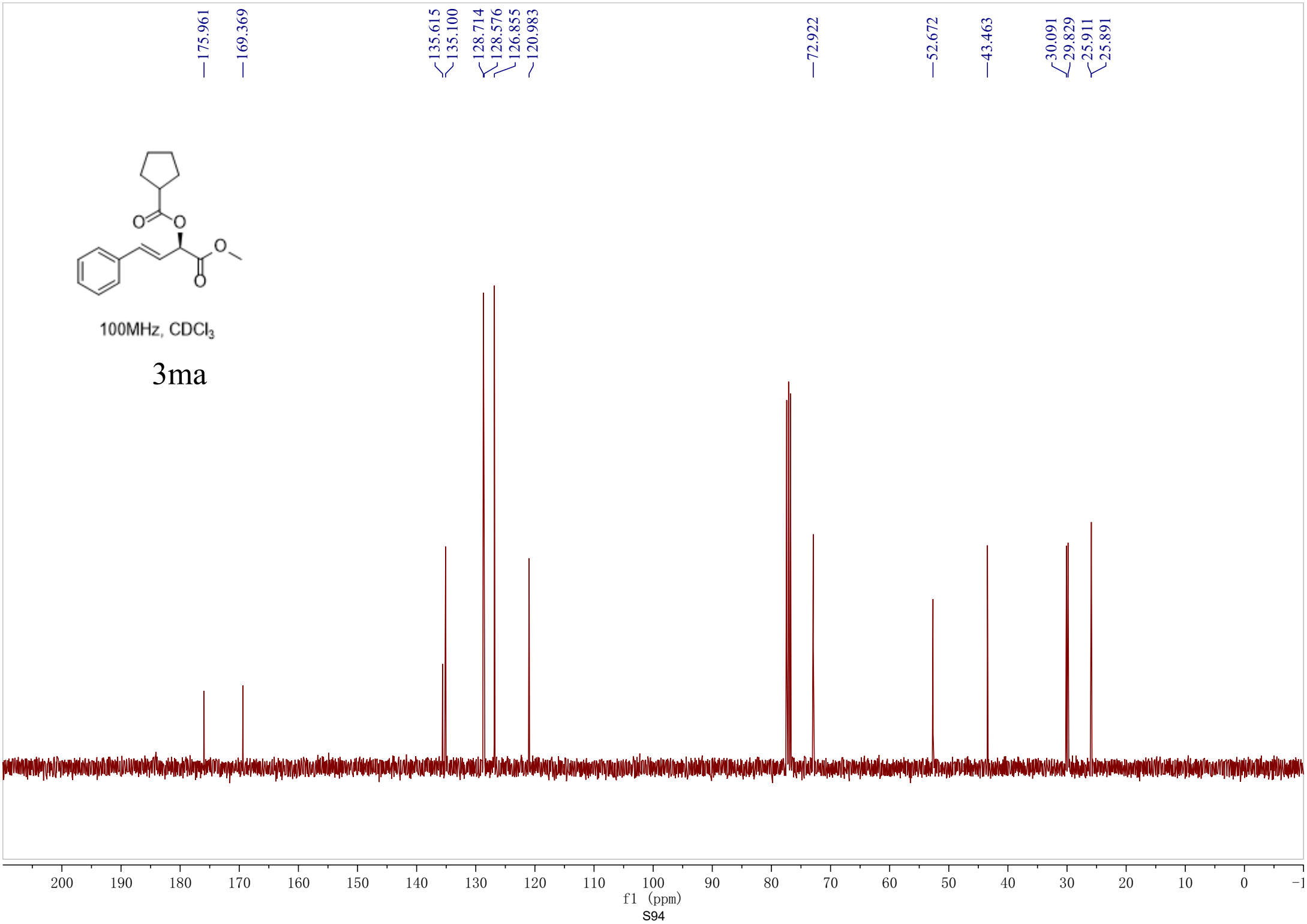

7.424
7.419
7.414
7.406
7.402
7.399
7.393
7.364
7.361
7.356
7.344
7.339
7.325
7.307
7.303
7.299
7.292
7.285
7.278
7.264
6.818
6.778
6.280
6.263
6.240
6.223
5.497
5.494
5.480
5.476
2.196
1.478
0.000
O
O
O
O
tBu
400MHz, CDCl3
3ld
1.94
2.92
0.98
0.98
0.96
3.01
9.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

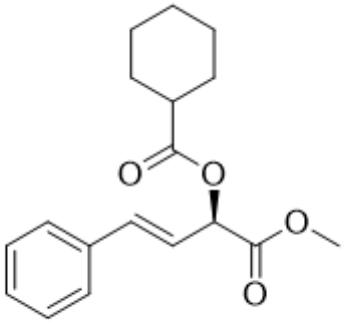

170.213
167.777
135.835
134.667
128.707
128.456
126.808
121.305
82.755
73.665
27.984
20.838
O
O
O
O
tBu
100MHz,CDCl3
3ld
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)



400MHz, $CDCl_3$

3ma

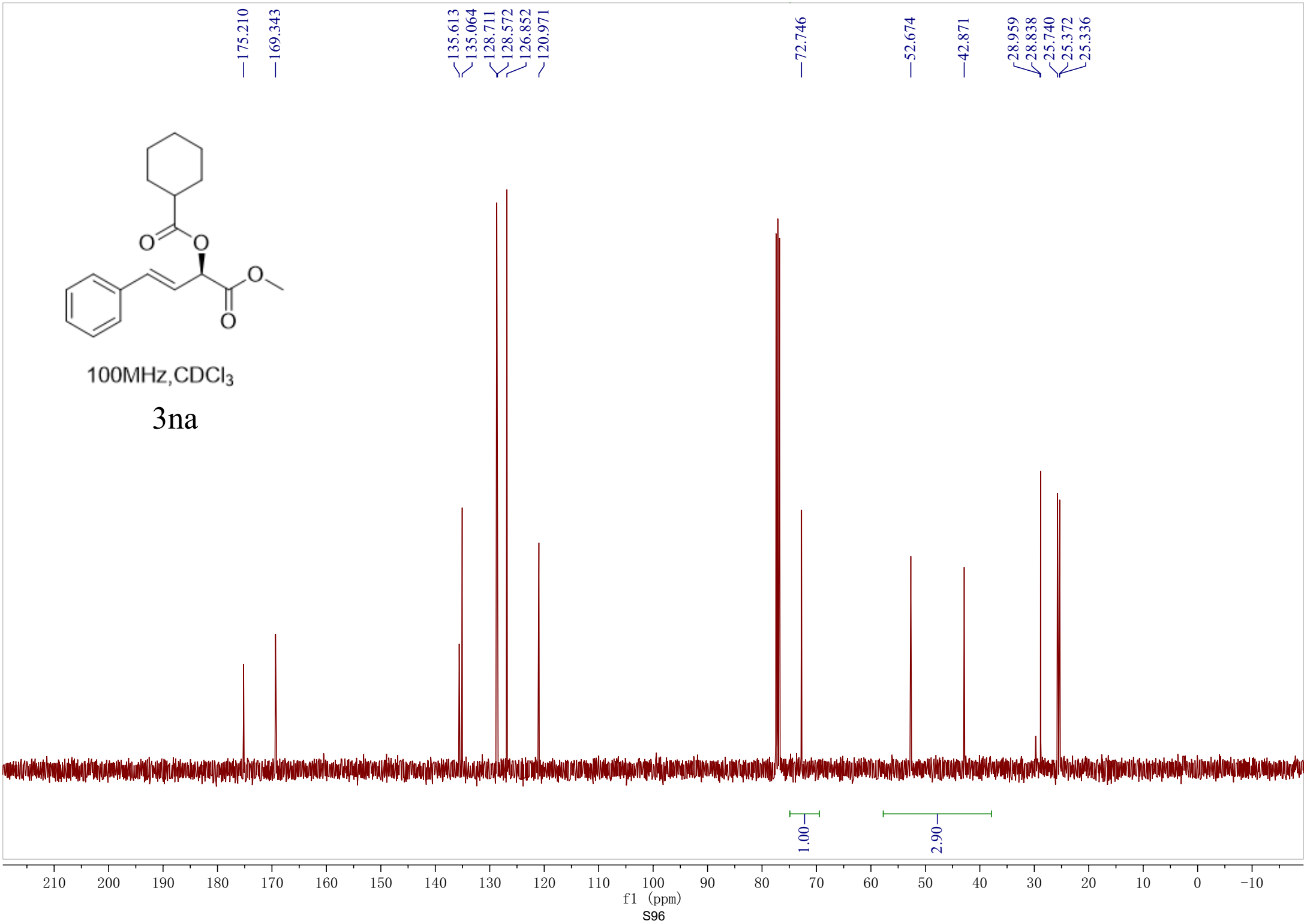

175.961
169.369
135.615
135.100
128.714
128.576
126.855
120.983
72.922
52.672
43.463
30.091
29.829
25.911
25.891
100MHz, CDCl3
3ma
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

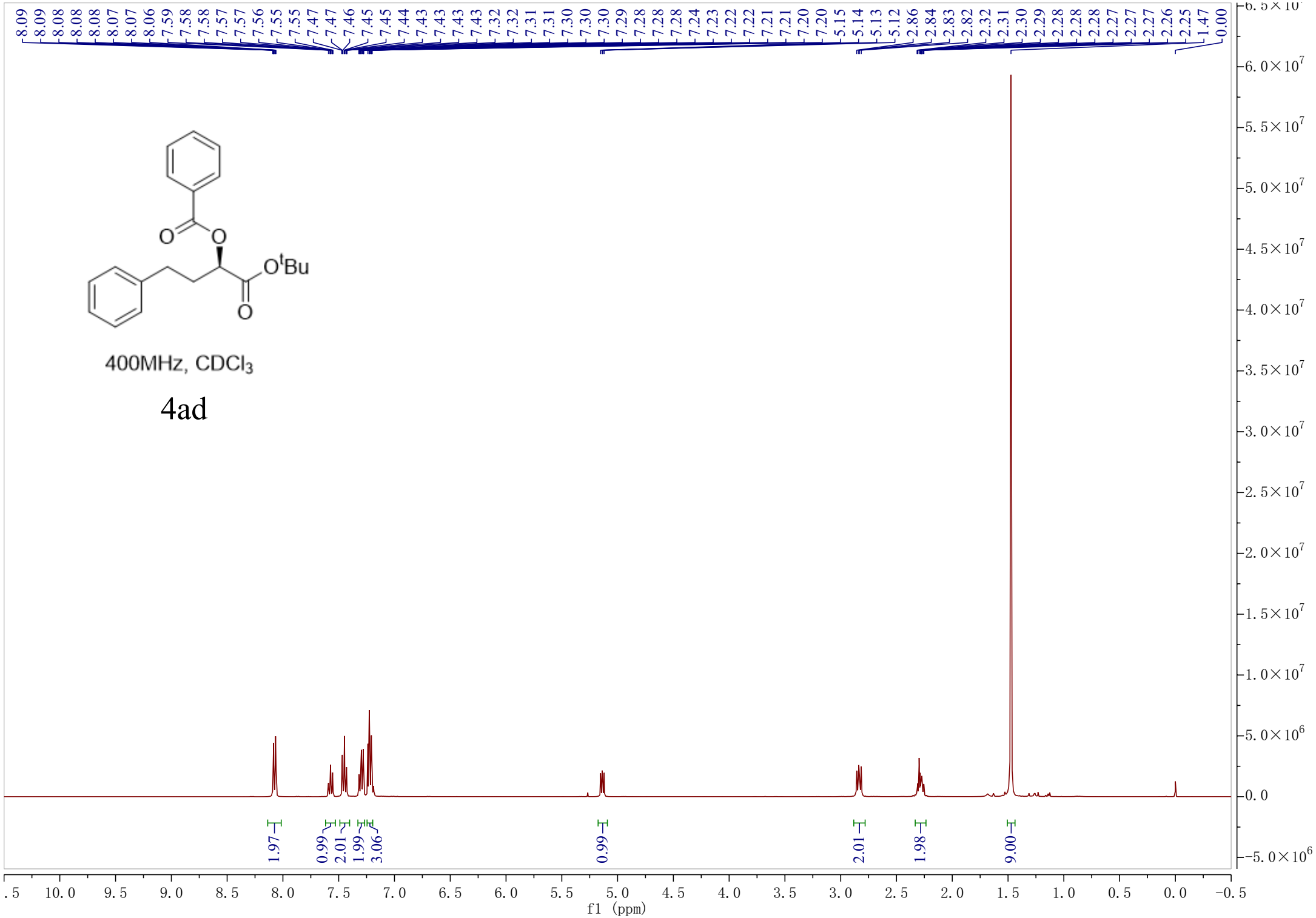


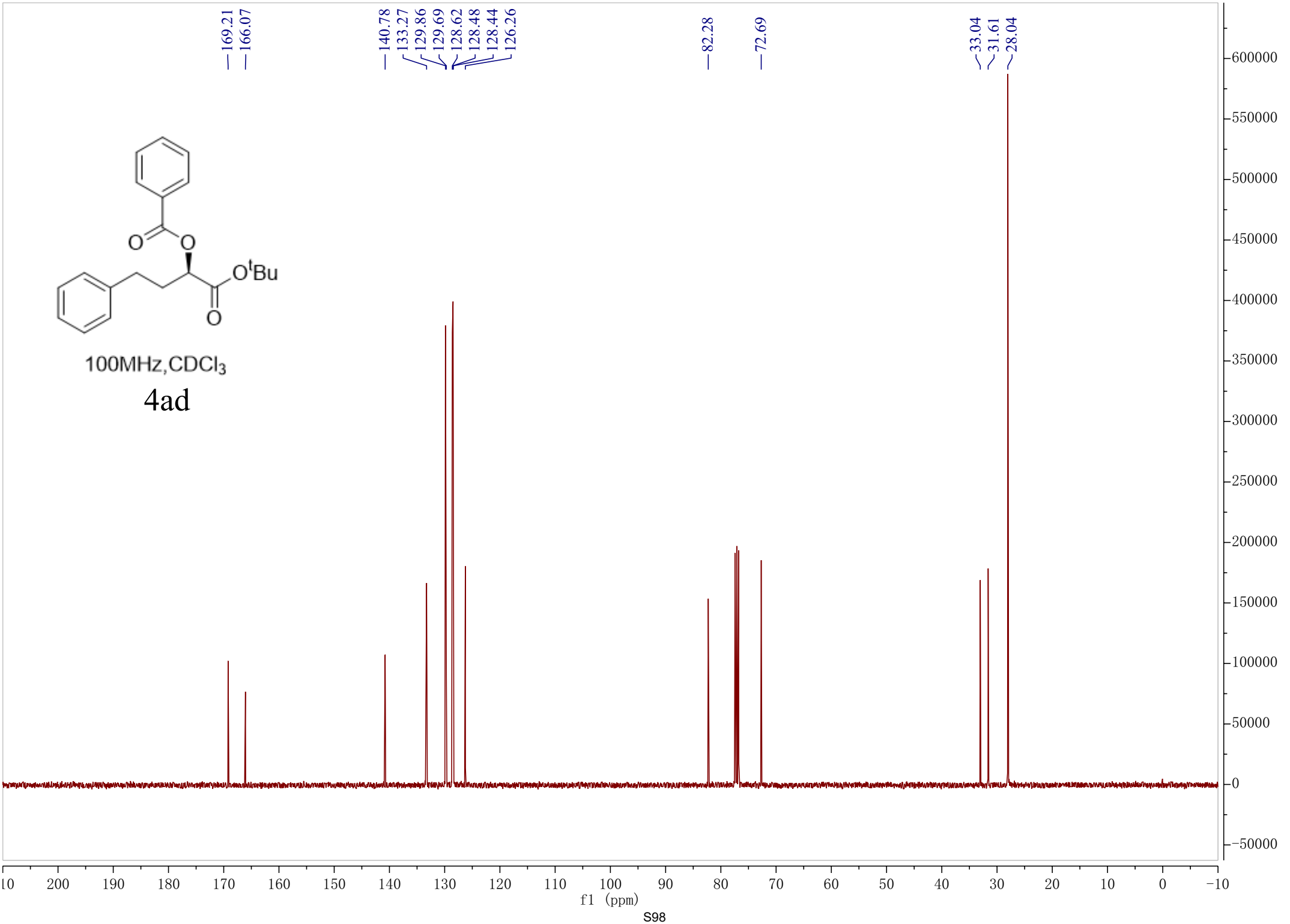
400MHz, $CDCl_3$

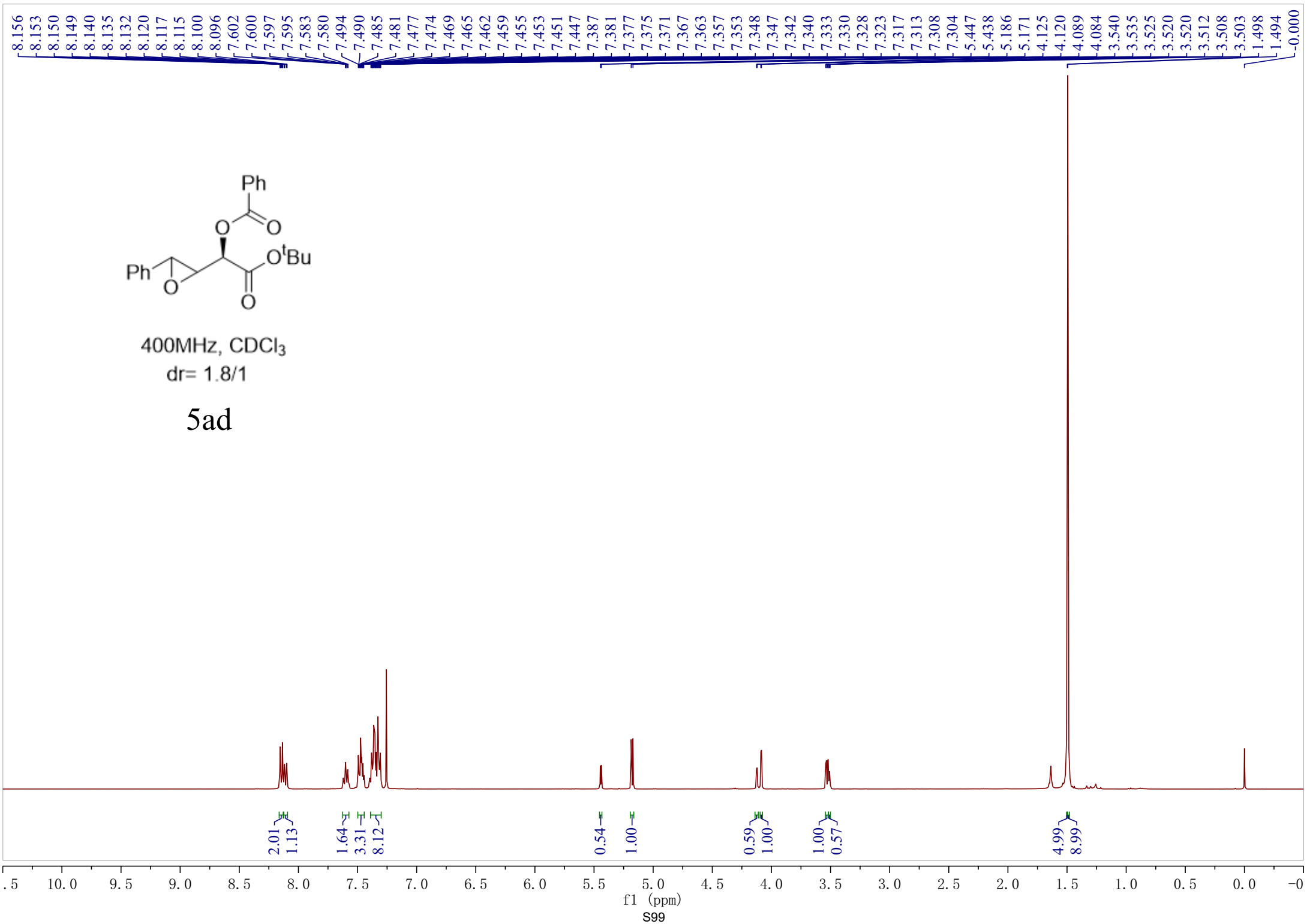
3na

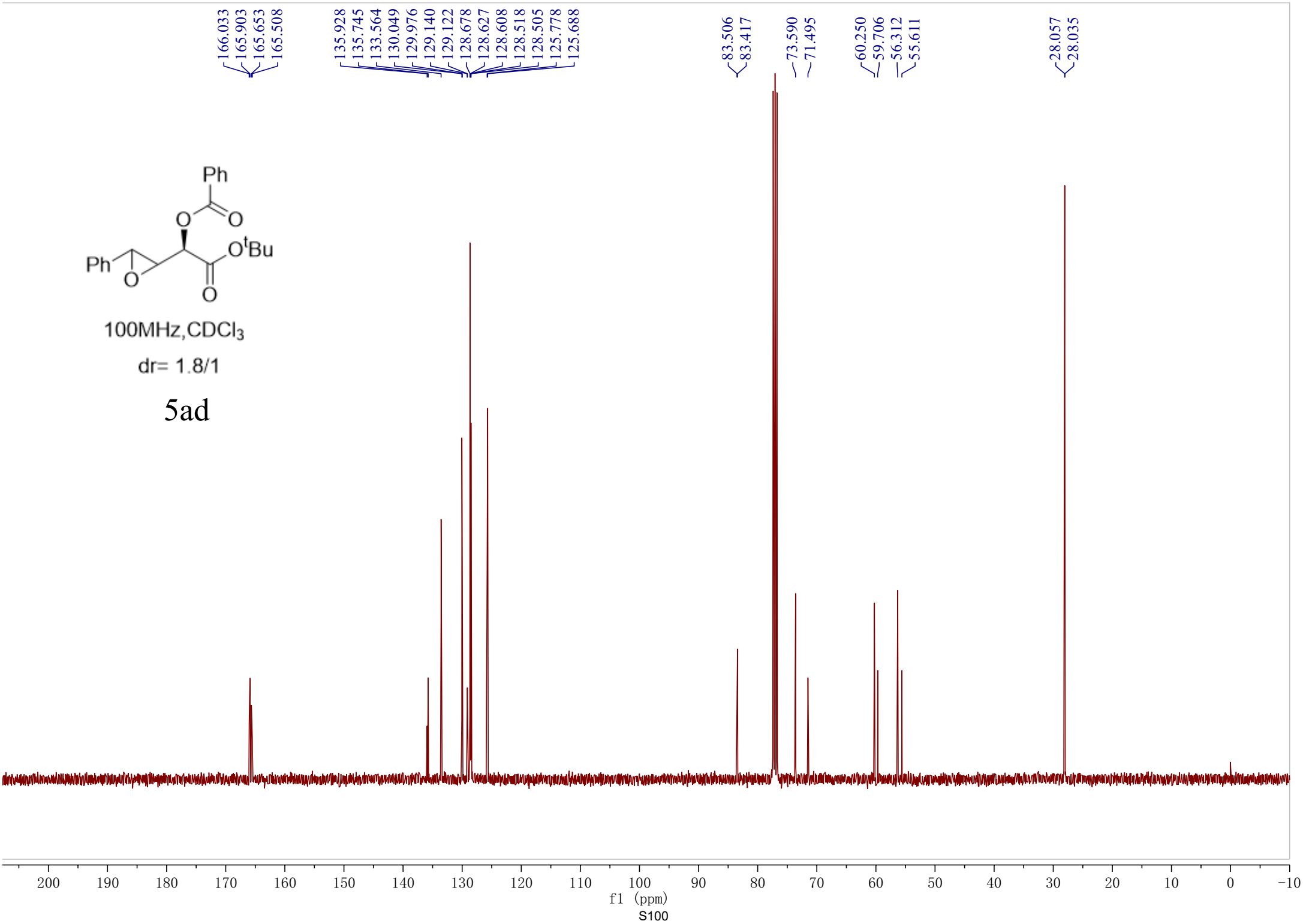
f1 (ppm)

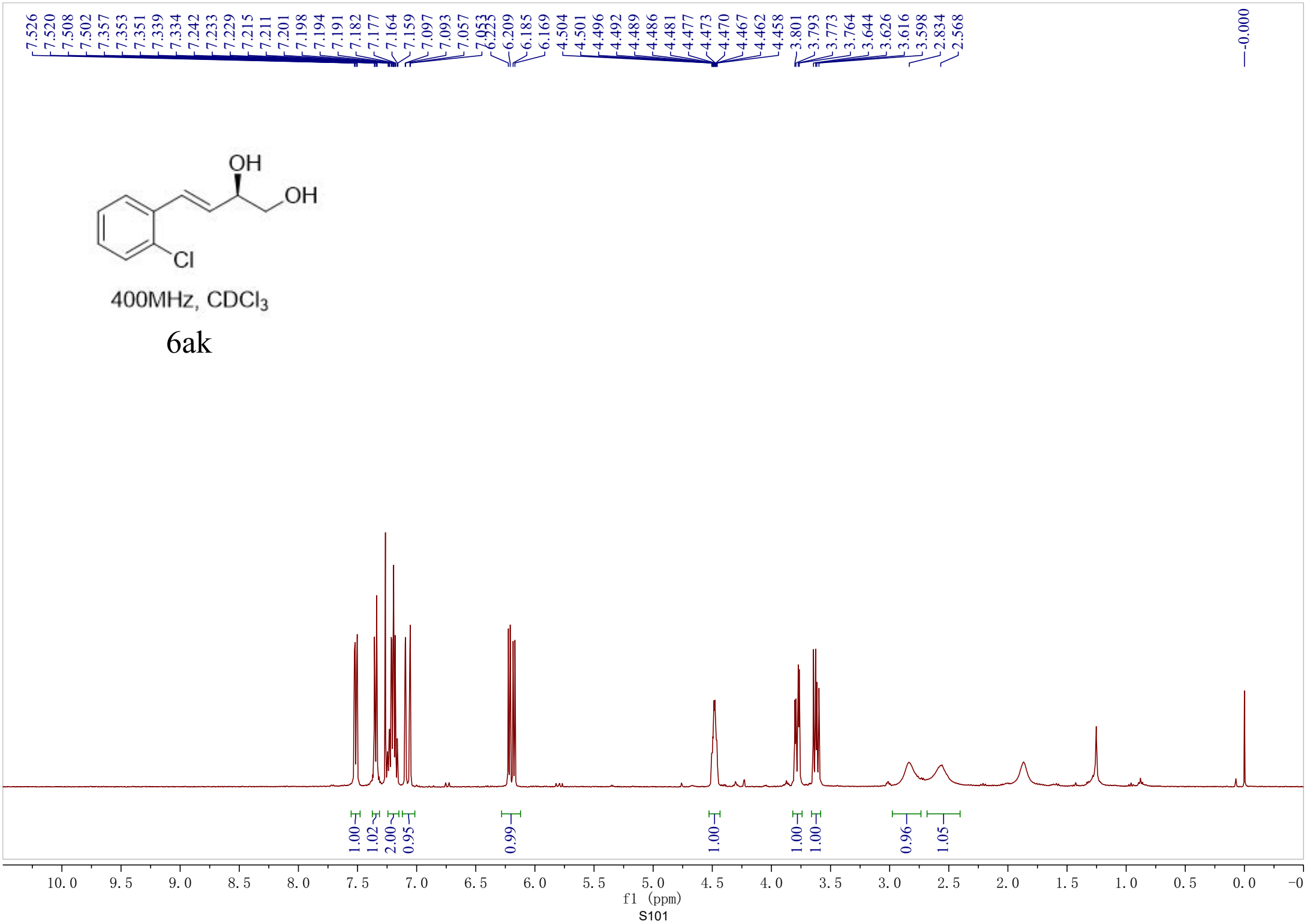

175.210
169.343
135.613
135.064
128.711
128.572
126.852
120.971
72.746
52.674
42.871
28.959
28.838
25.740
25.372
25.336
100MHz,CDCl3
3na
1.00
2.90
f1 (ppm)

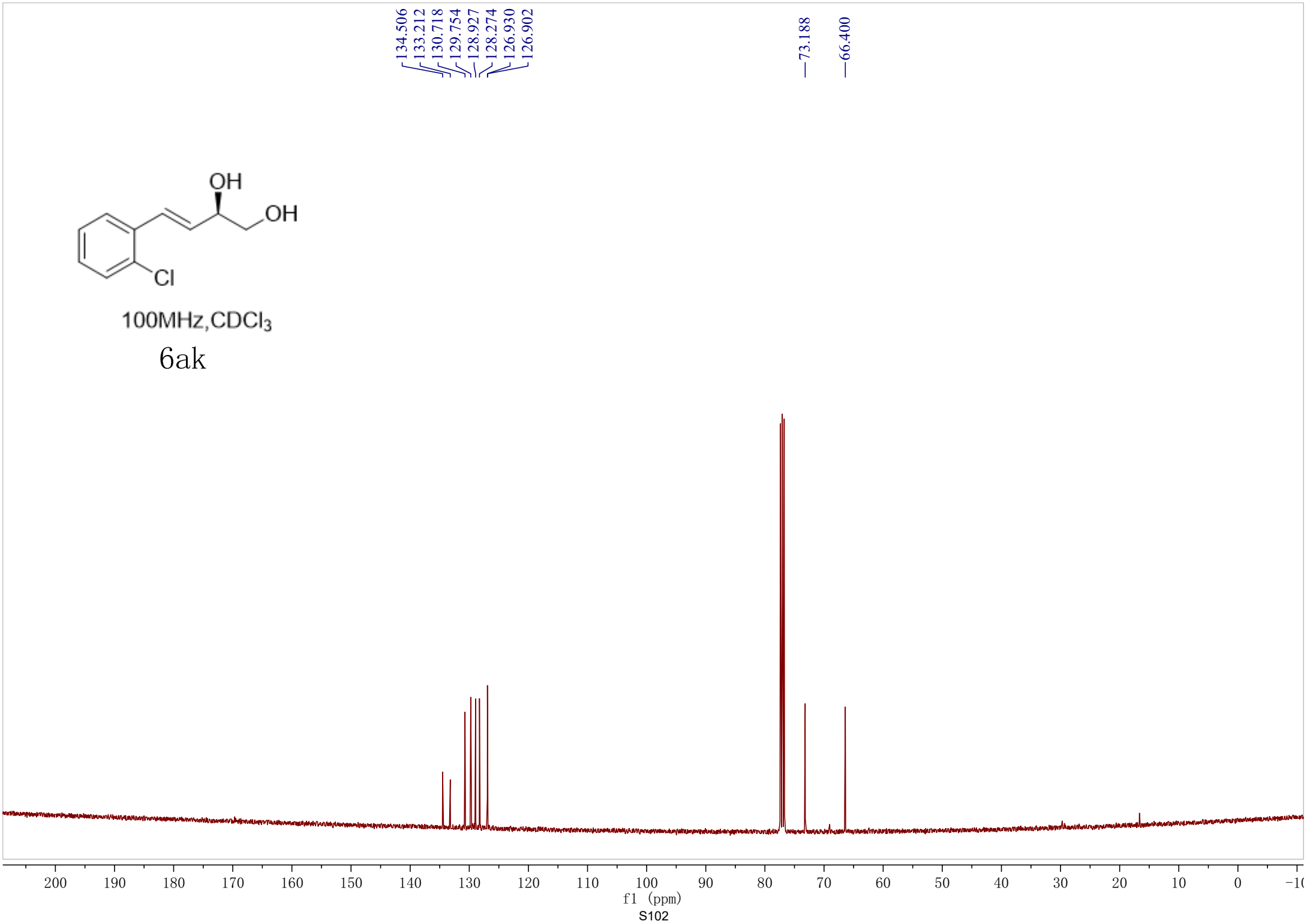

8.09 8.09 8.08 8.08 8.08 8.07 8.07 8.06 7.59 7.58 7.58 7.57 7.57 7.56 7.55 7.55 7.47 7.47 7.46 7.45 7.45 7.44 7.43 7.43 7.43 7.32 7.32 7.31 7.31 7.30 7.30 7.30 7.29 7.28 7.28 7.28 7.24 7.23 7.22 7.22 7.21 7.21 7.20 7.20 5.15 5.14 5.13 5.12 2.86 2.84 2.83 2.82 2.32 2.31 2.30 2.29 2.28 2.28 2.28 2.27 2.27 2.27 2.26 2.25 1.47 0.00
O
O
O
O
tBu
400MHz, CDCl3
4ad
1.97
0.99
2.01
1.99
3.06
0.99
2.01
1.98
9.00
f1 (ppm)

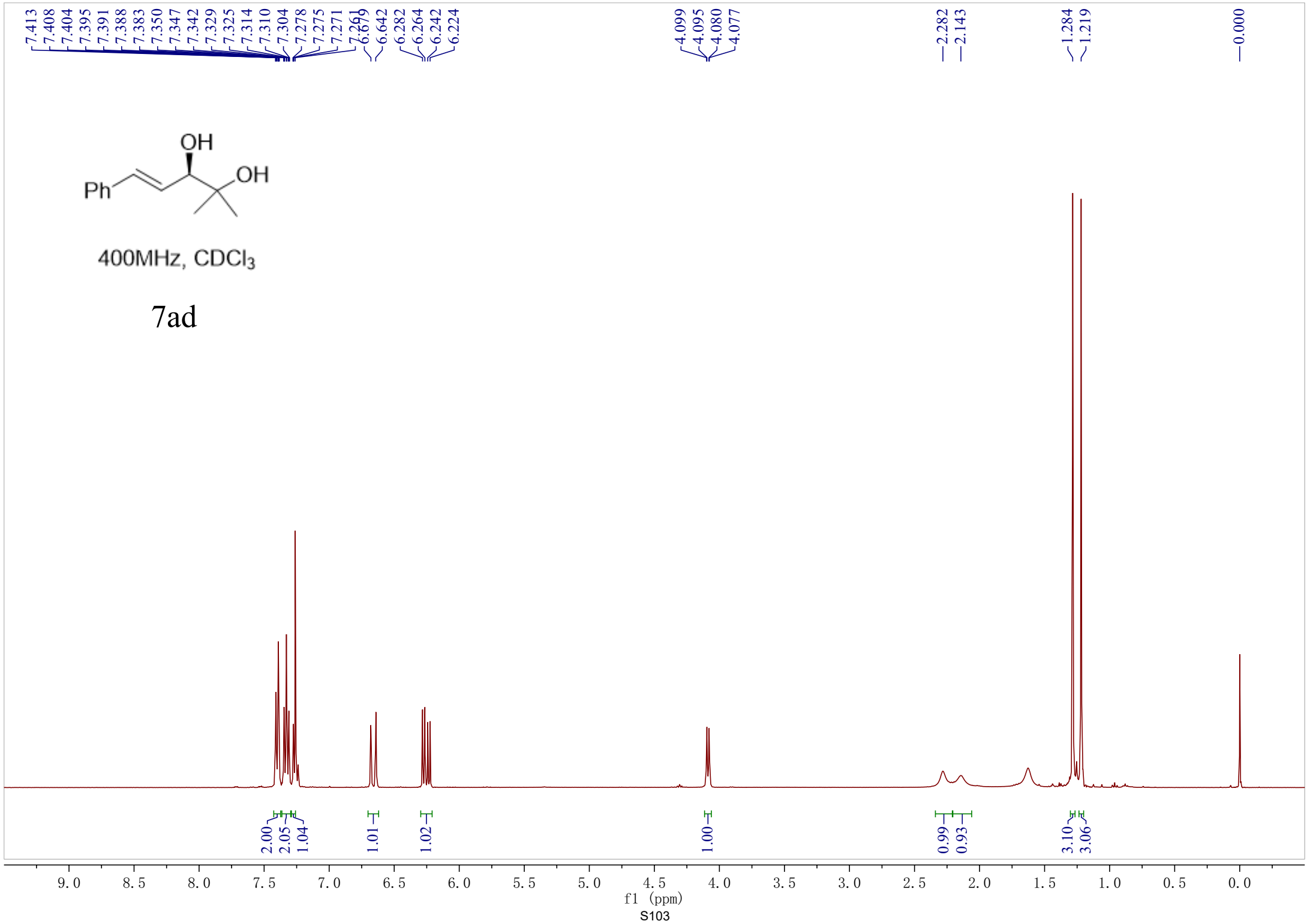

169.21
166.07
140.78
133.27
129.86
129.69
128.62
128.48
128.44
126.26
82.28
72.69
33.04
31.61
28.04
O
O
O
O
tBu
100MHz,CDCl3
4ad
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
f1 (ppm)

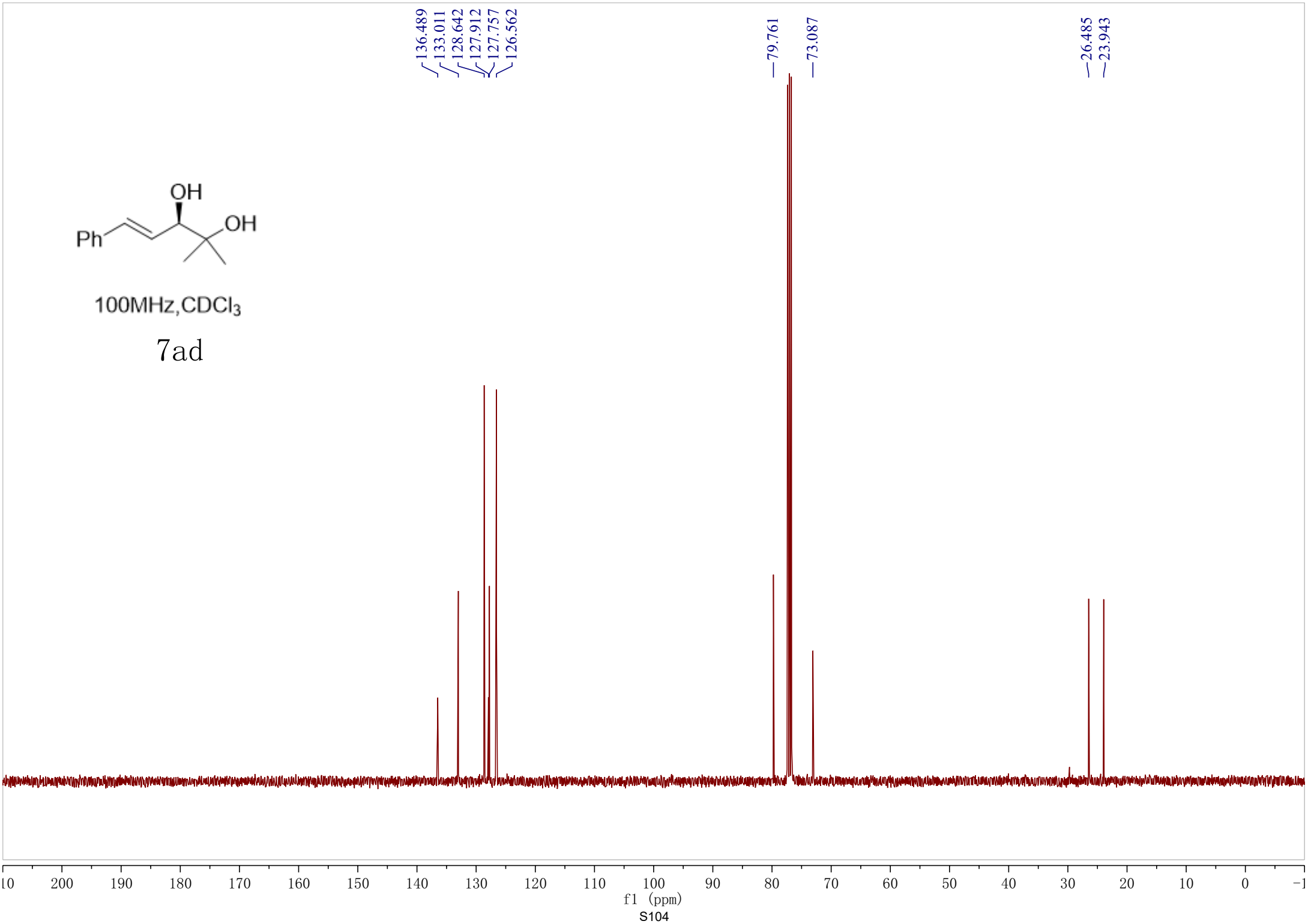

Ph
O
O
O
O
tBu
Ph
O
O
400MHz, CDCl3
dr= 1.8/1
5ad
f1 (ppm)

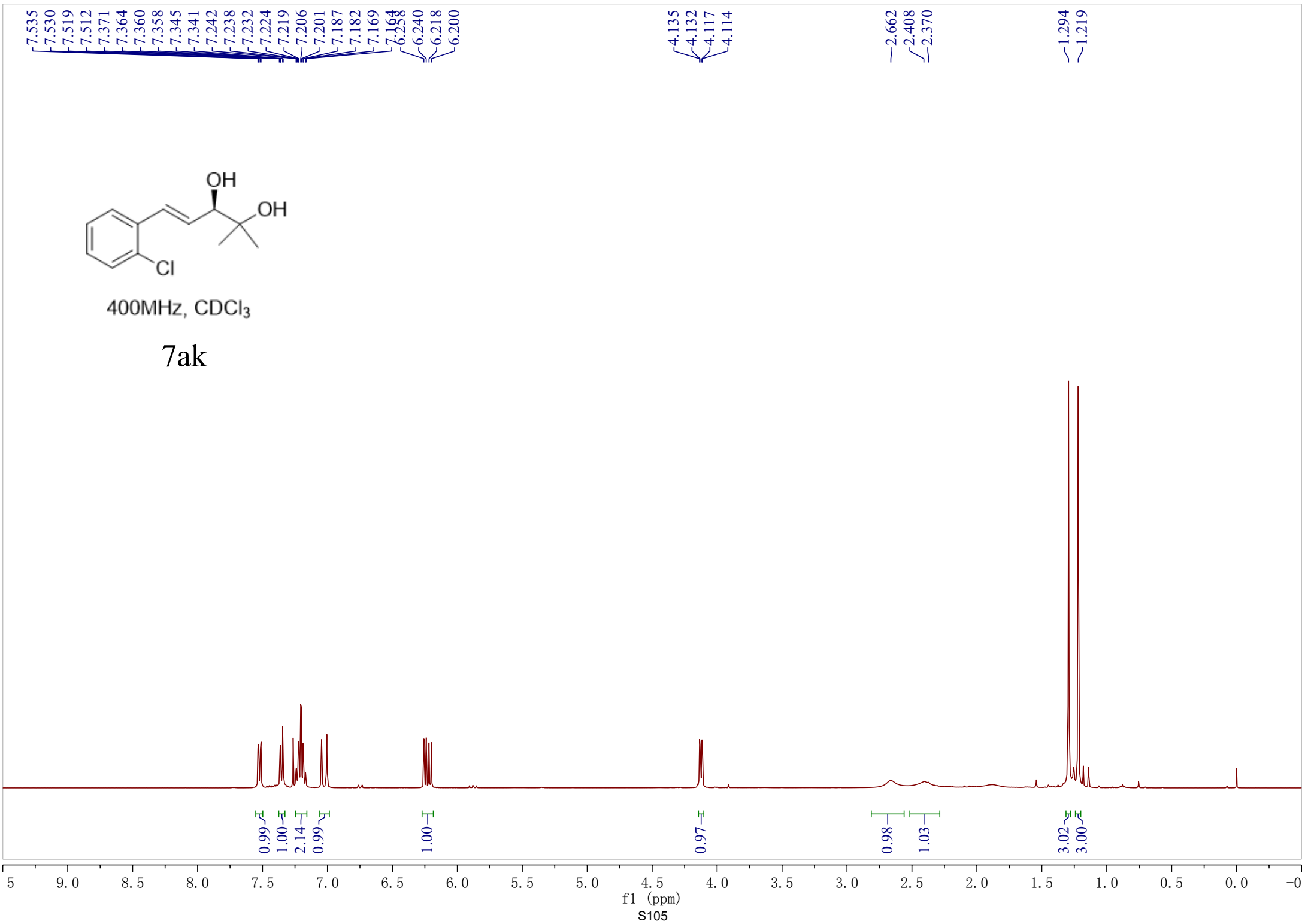

166.033
165.903
165.653
165.508
135.928
135.745
133.564
130.049
129.976
129.140
129.122
128.678
128.627
128.608
128.518
128.505
125.778
125.688
83.506
83.417
73.590
71.495
60.250
59.706
56.312
55.611
28.057
28.035
Ph
O
O
O
Ph
O
O
tBu
100MHz,CDCl3
dr= 1.8/1
5ad
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

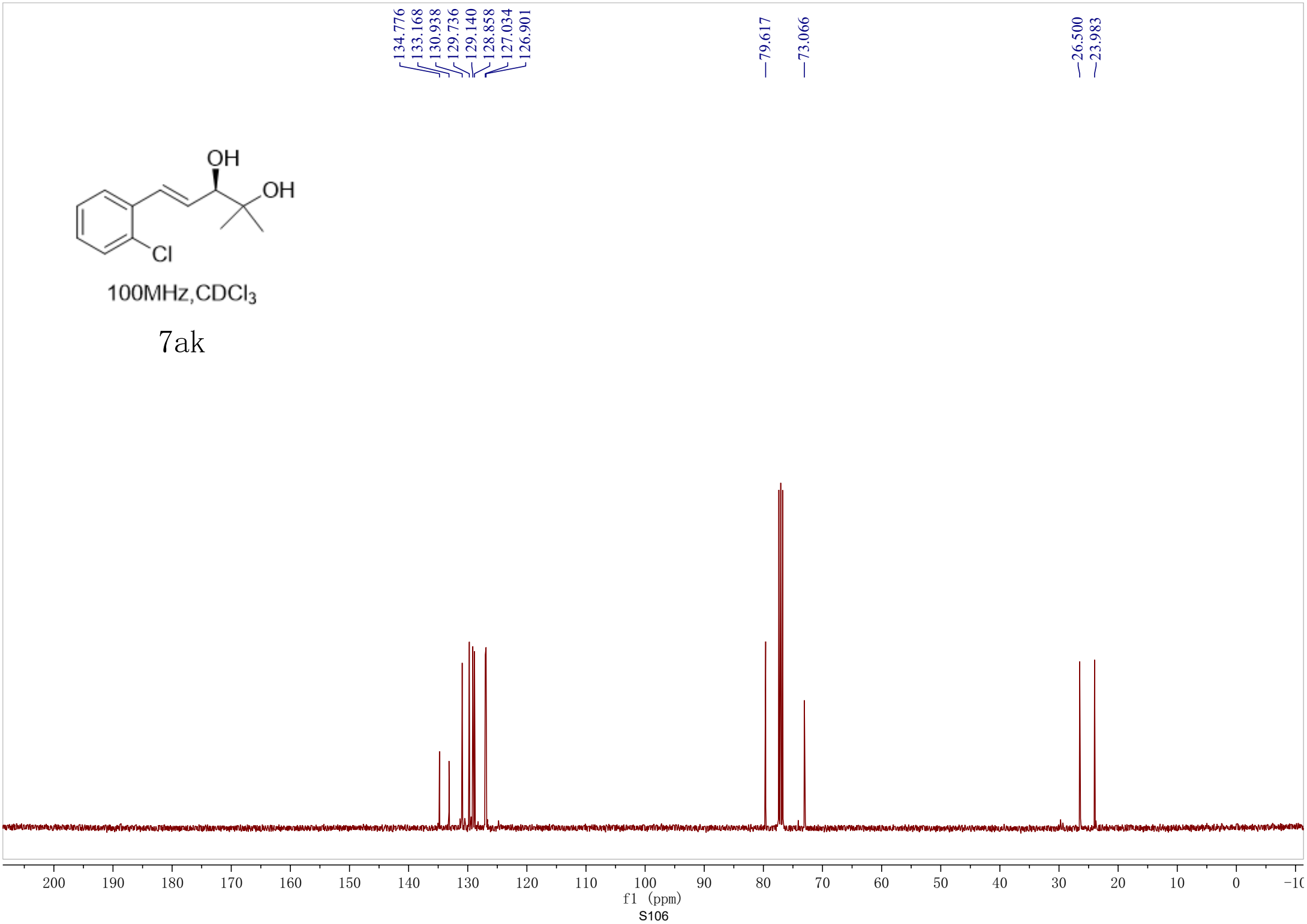

7.526
7.520
7.508
7.502
7.357
7.353
7.351
7.339
7.334
7.242
7.233
7.229
7.215
7.211
7.201
7.198
7.194
7.191
7.182
7.177
7.164
7.159
7.097
7.093
7.057
6.225
6.209
6.185
6.169
4.504
4.501
4.496
4.492
4.489
4.486
4.481
4.477
4.473
4.470
4.467
4.462
4.458
3.801
3.793
3.773
3.764
3.644
3.626
3.616
3.598
2.834
2.568
-0.000
OH
OH
Cl
400MHz, CDCl3
6ak
1.00
1.02
2.00
0.95
0.99
1.00
1.00
1.00
0.96
1.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


134.506
133.212
130.718
129.754
128.927
128.274
126.930
126.902
73.188
66.400
OH
OH
Cl
100MHz,CDCl3
6ak
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

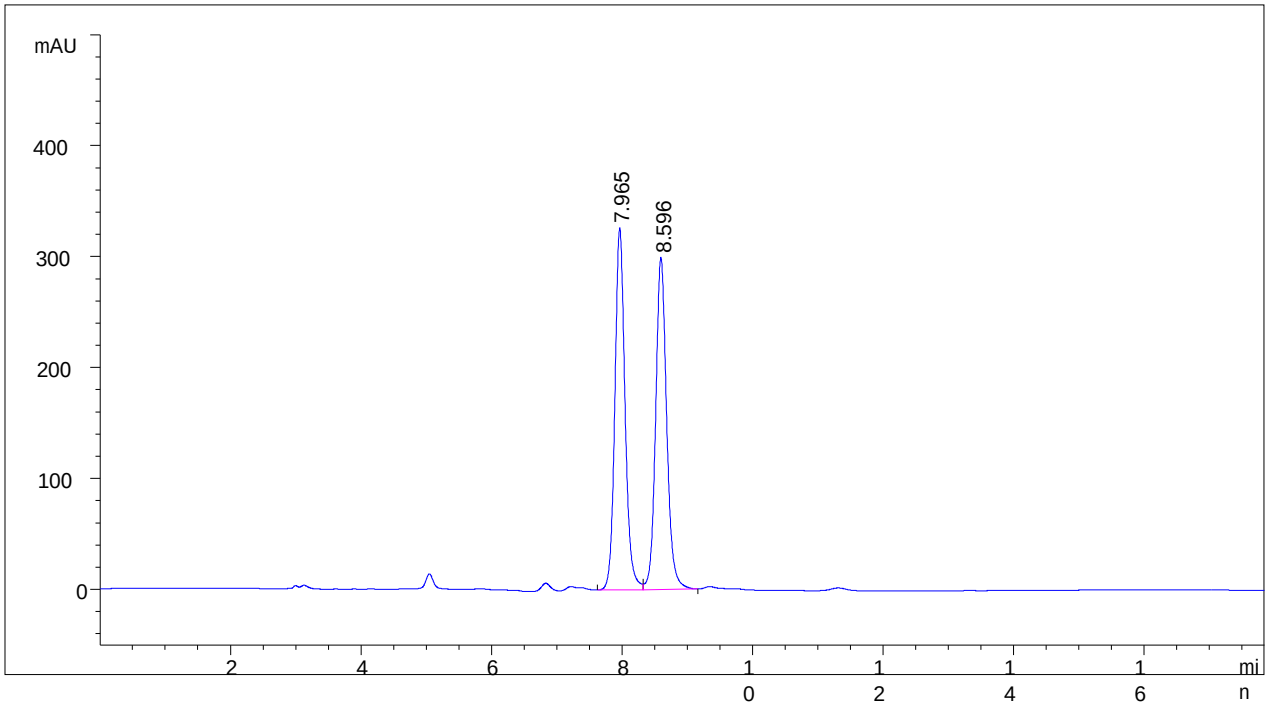

7.413
7.408
7.404
7.395
7.391
7.388
7.383
7.350
7.347
7.342
7.329
7.325
7.314
7.310
7.304
7.278
7.275
7.271
7.261
6.679
6.642
6.282
6.264
6.242
6.224
4.099
4.095
4.080
4.077
2.282
2.143
1.284
1.219
0.000
OH
OH
Ph
400MHz, CDCl3
7ad
2.00
2.05
1.04
1.01
1.02
1.00
0.99
0.93
3.10
3.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


136.489
133.011
128.642
127.912
127.757
126.562
79.761
73.087
26.485
23.943
OH
OH
Ph
100MHz,CDCl3
7ad
f1 (ppm)

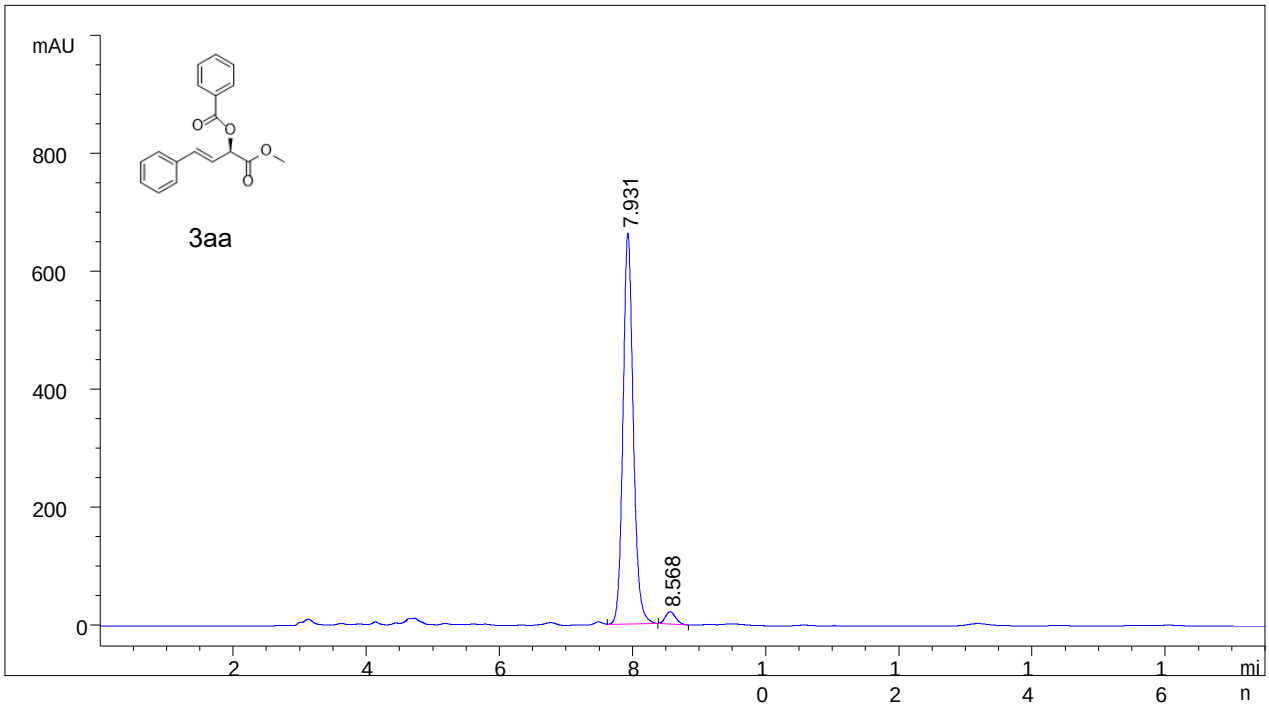

7.535
7.530
7.519
7.512
7.371
7.364
7.360
7.358
7.345
7.341
7.242
7.238
7.232
7.224
7.219
7.206
7.201
7.187
7.182
7.169
7.164
6.258
6.240
6.218
6.200
4.135
4.132
4.117
4.114
2.662
2.408
2.370
1.294
1.219
OH
OH
Cl
400MHz, CDCl3
7ak
0.99
1.00
2.14
0.99
1.00
0.97
0.98
1.03
3.02
3.00
f1 (ppm)


134.776
133.168
130.938
129.736
129.140
128.858
127.034
126.901
79.617
73.066
26.500
23.983
OH
OH
Cl
100MHz,CDCl3
7ak
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Daicel Chiralpak IA column, n-hexane/i-PrOH= 90/10, flow rate= 1ml/min, l= 225 nm

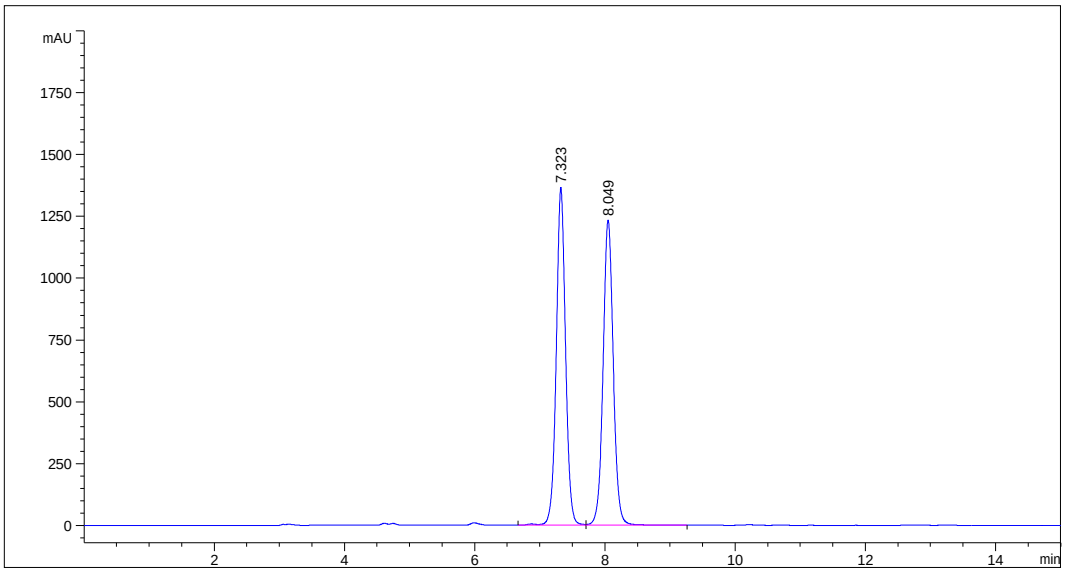


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.965	BV	0.1646	3543.10278	326.47565	50.2250
2	8.596	VB	0.1789	3511.35767	299.19202	49.7750

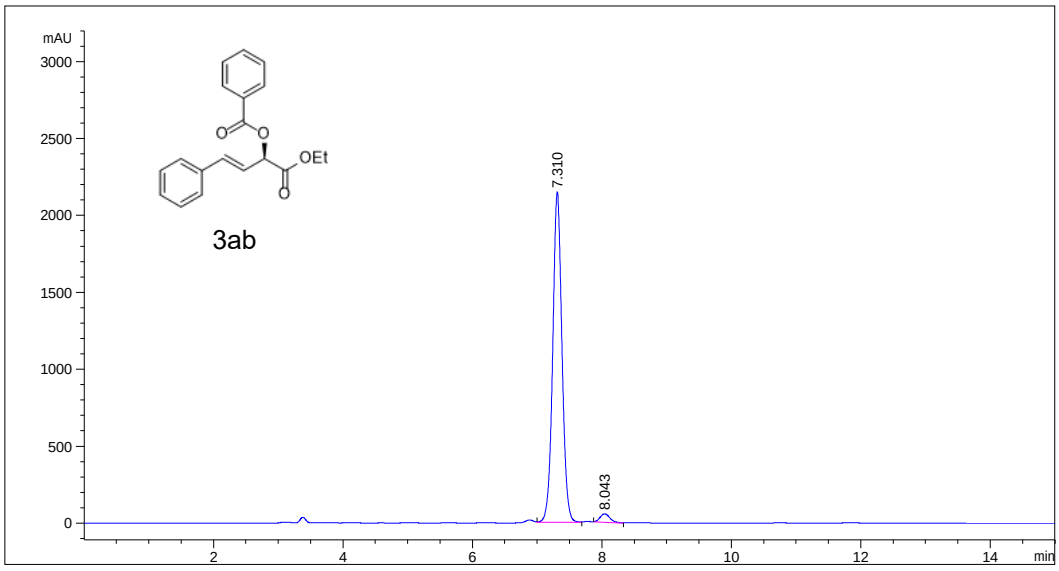


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.931	MM	0.1787	7103.59473	662.44354	96.9323
2	8.568	MM	0.1799	224.81451	20.83109	3.0677

Daicel Chiralpak IA column, n-hexane/i-PrOH= 99/1, flow rate= 1ml/min, l= 225 nm

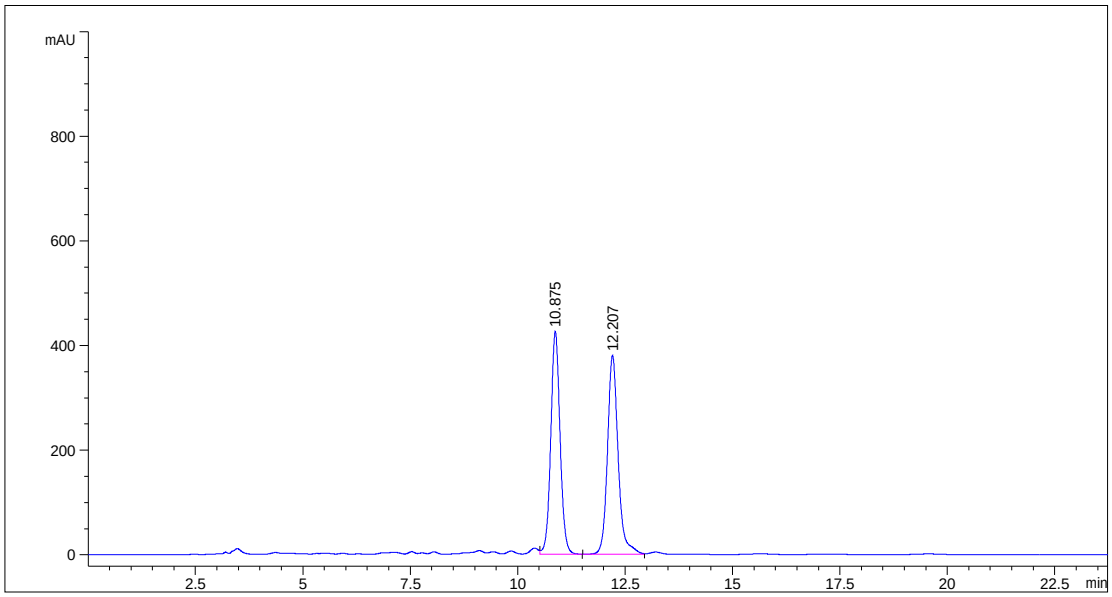


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.323	VV R	0.1505	1.35878e4	1366.67114	50.3647
2	8.049	VV R	0.1656	1.33910e4	1233.83960	49.6353

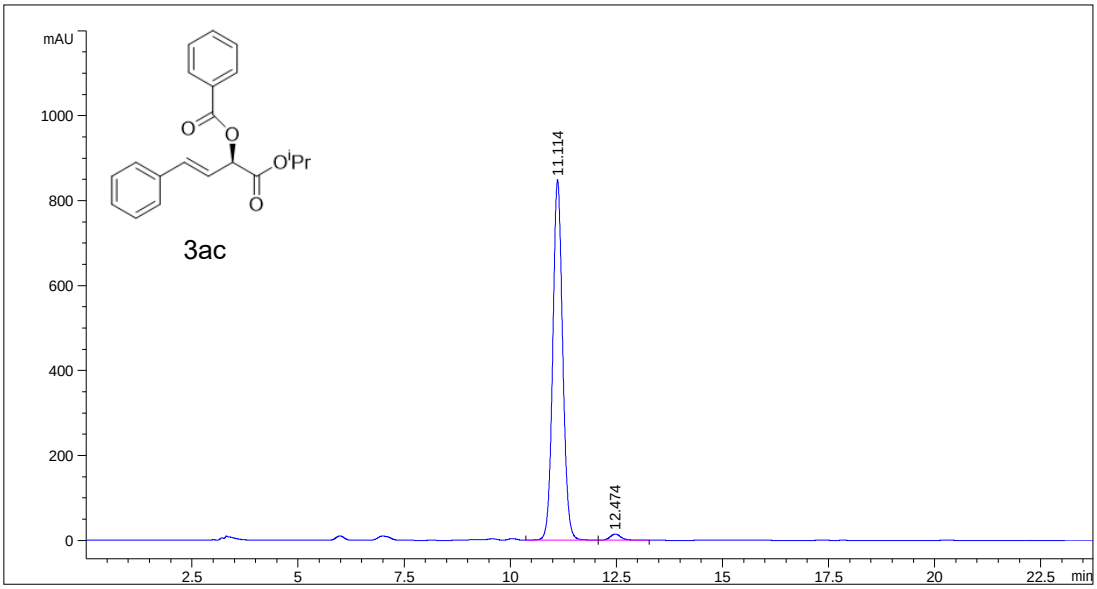


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.310	MM	0.1656	2.13320e4	2147.56055	97.2864
2	8.043	MM	0.1773	595.00867	55.94276	2.7136

Daicel Chiralpak IA column, n-hexane/i-PrOH= 90/10, flow rate= 1ml/min, l= 225 nm

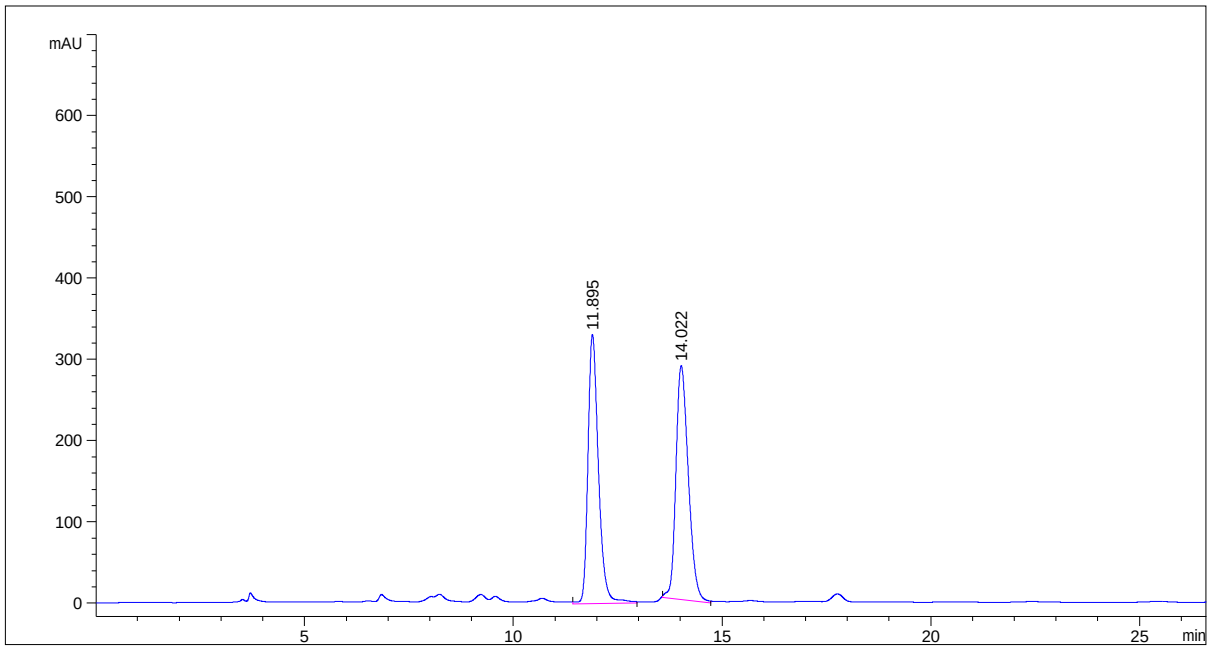


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.875	FM	0.2499	6379.17139	425.47589	49.2960
2	12.207	MF	0.2878	6561.36865	379.94095	50.7040

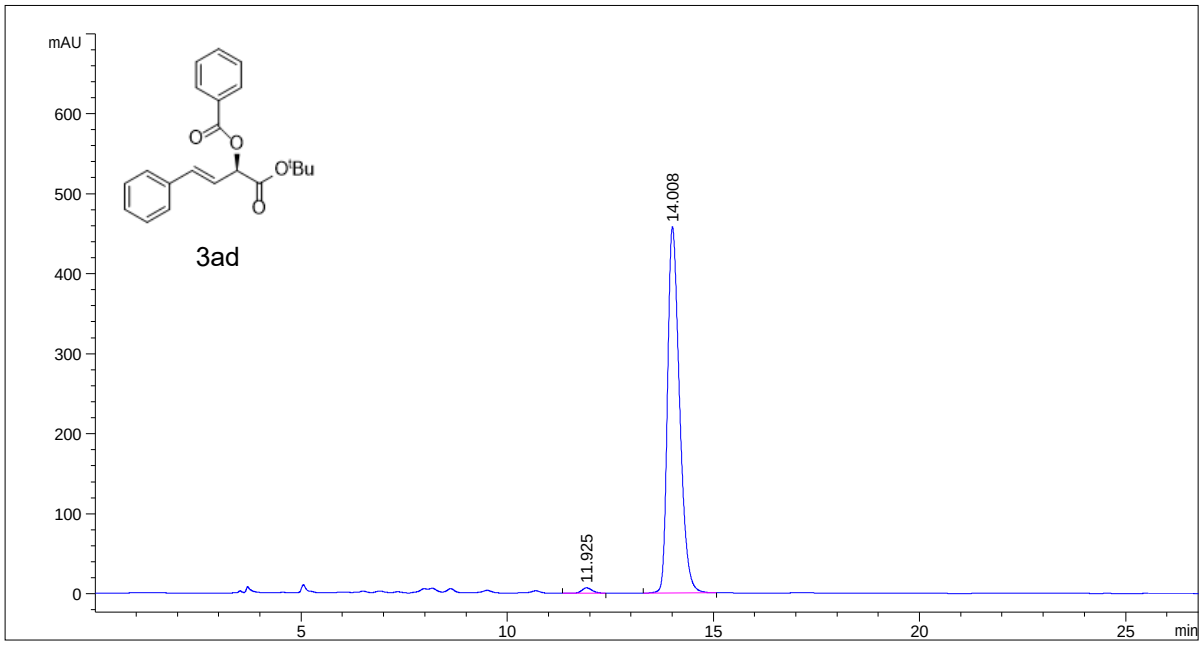


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.114	BB	0.2501	1.38259e4	848.55725	98.0982
2	12.474	BB	0.2754	268.03305	14.72089	1.9018

Daicel Chiralpak IA column, n-hexane/i-PrOH= 90/10, flow rate= 1ml/min, l= 225 nm

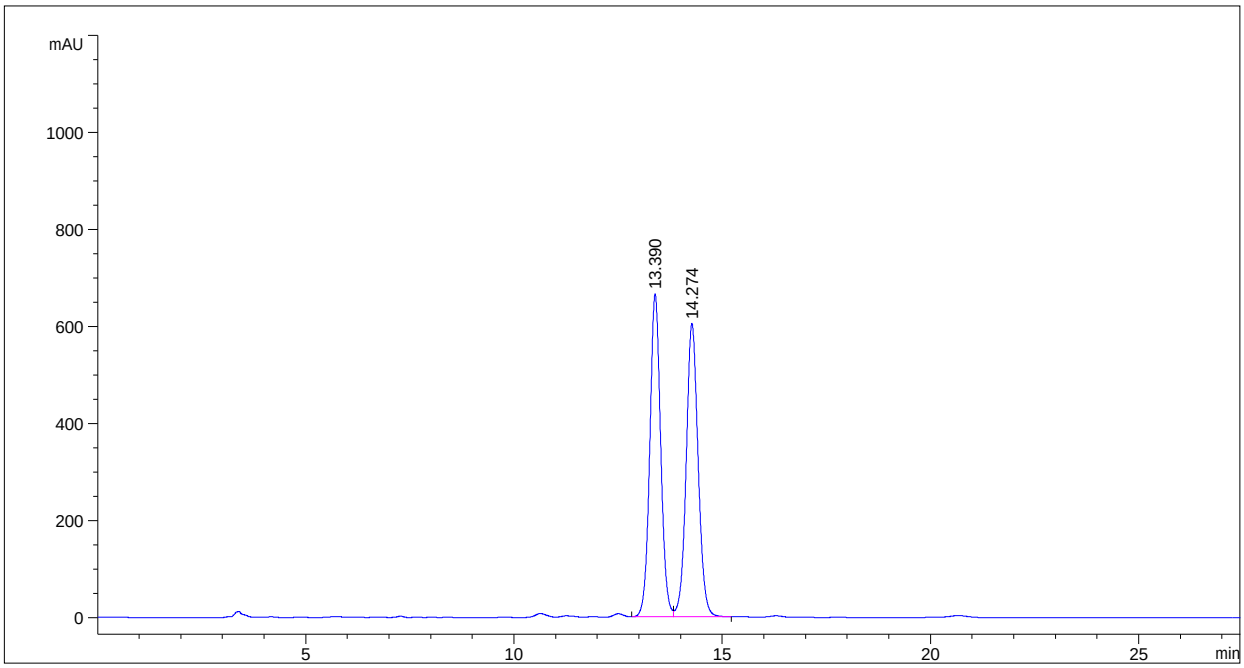


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.895	MM	0.2910	5782.97168	331.26053	49.2854
2	14.022	MM	0.3442	5950.67627	288.10541	50.7146

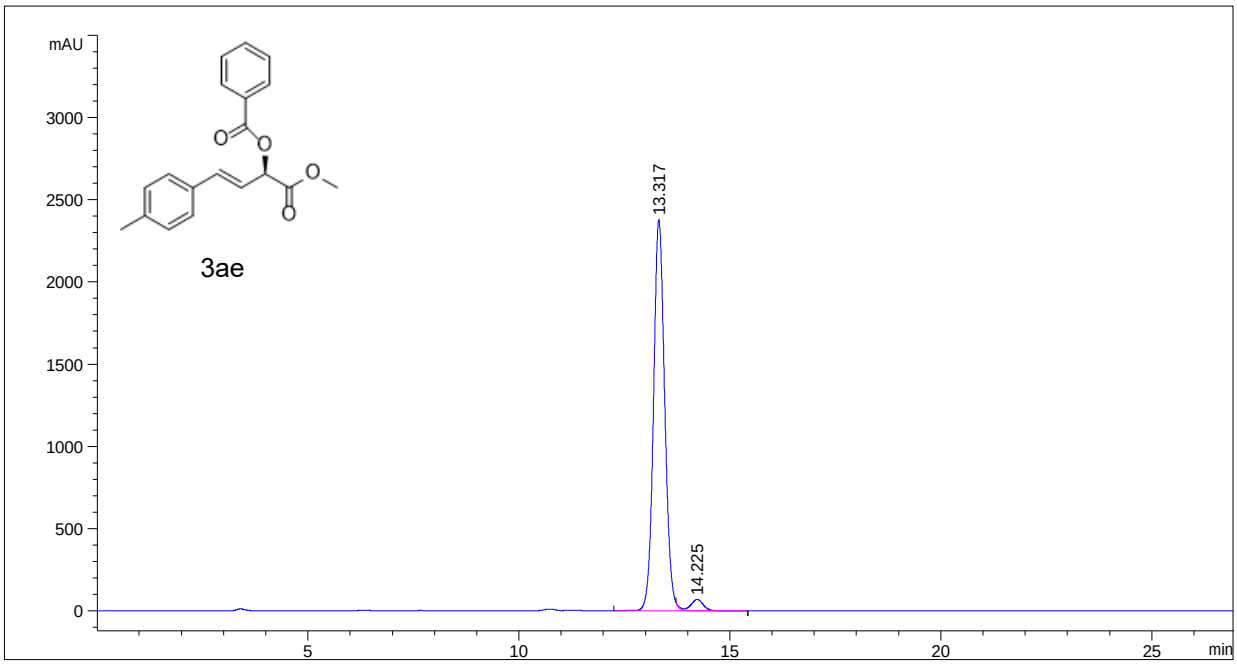


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.925	BB	0.2670	118.98124	6.77290	1.2694
2	14.008	BB	0.3121	9254.13965	457.32693	98.7306

Daicel Chiralpak IA column, n-hexane/i-PrOH= 99/1, flow rate= 1ml/min, l= 225 nm

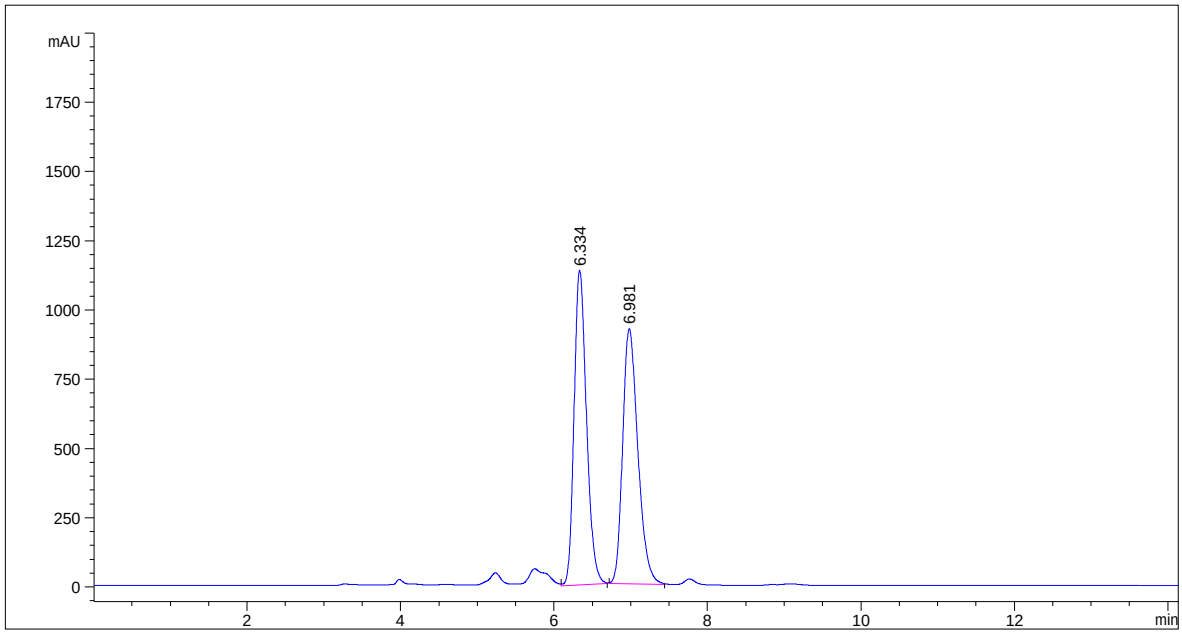


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.390	BV	0.2794	1.20995e4	664.67523	50.1028
2	14.274	VB	0.3048	1.20499e4	603.93945	49.8972

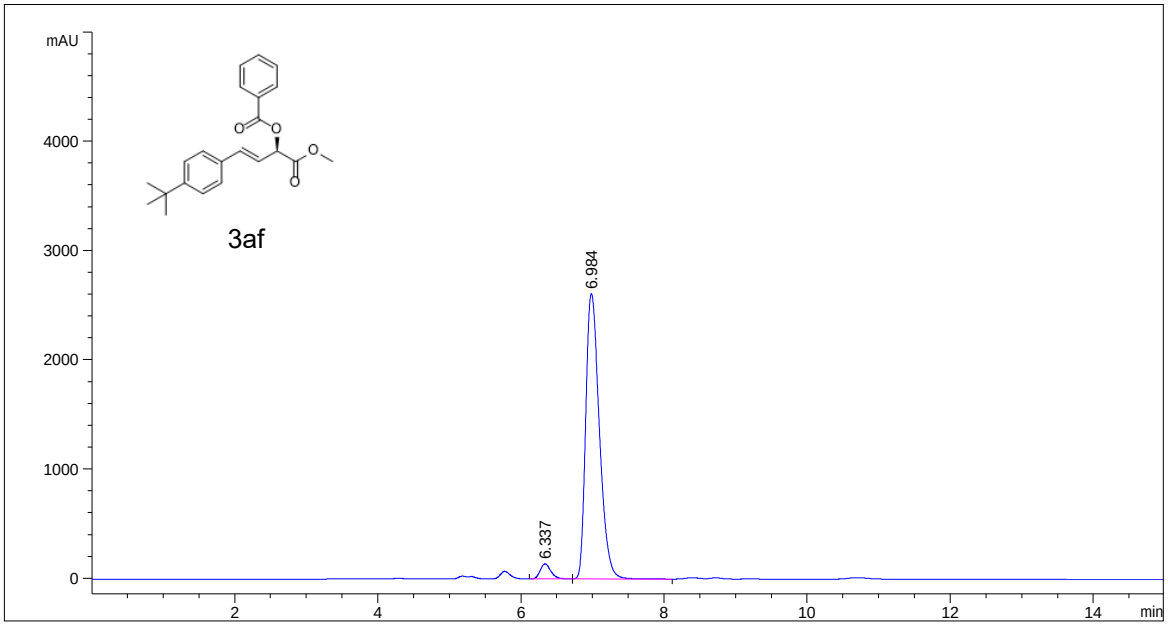


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.317	VV R	0.2842	4.40992e4	2376.69922	96.7728
2	14.225	VB E	0.3136	1470.61548	70.14804	3.2272

Daicel Chiralpak IA column, n-hexane/i-PrOH= 90/10, flow rate= 1ml/min, I= 225 nm

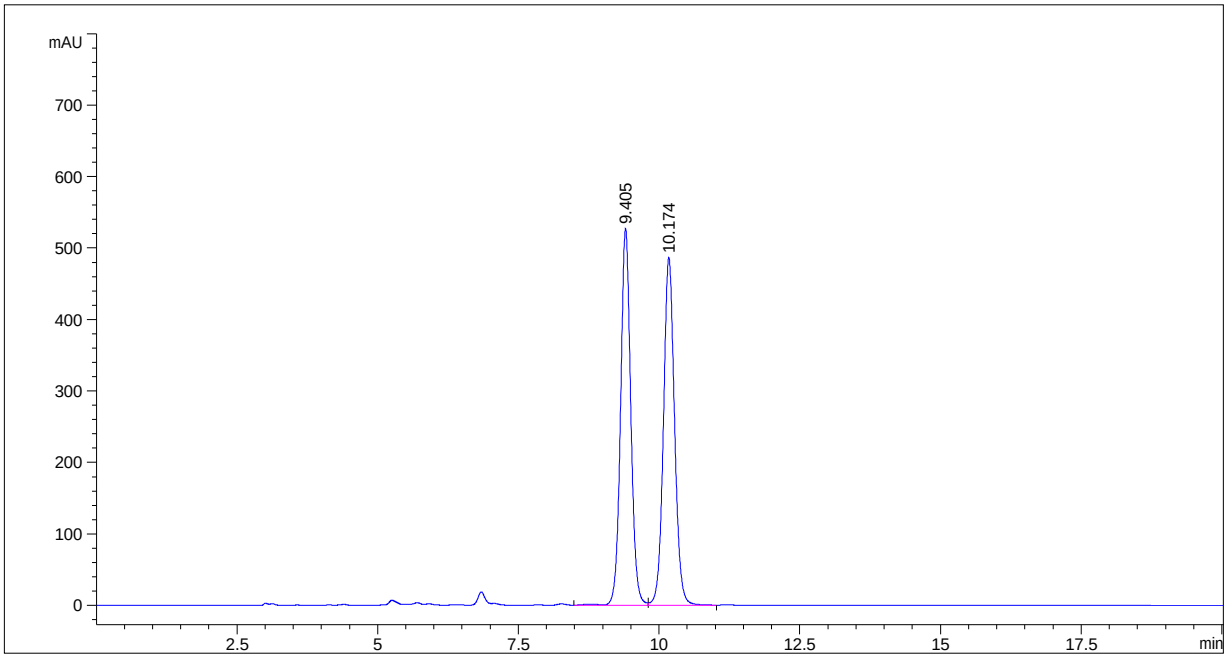


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.334	MM	0.1875	1.27712e4	1135.26404	50.1998
2	6.981	MM	0.2292	1.26695e4	921.13525	49.8002

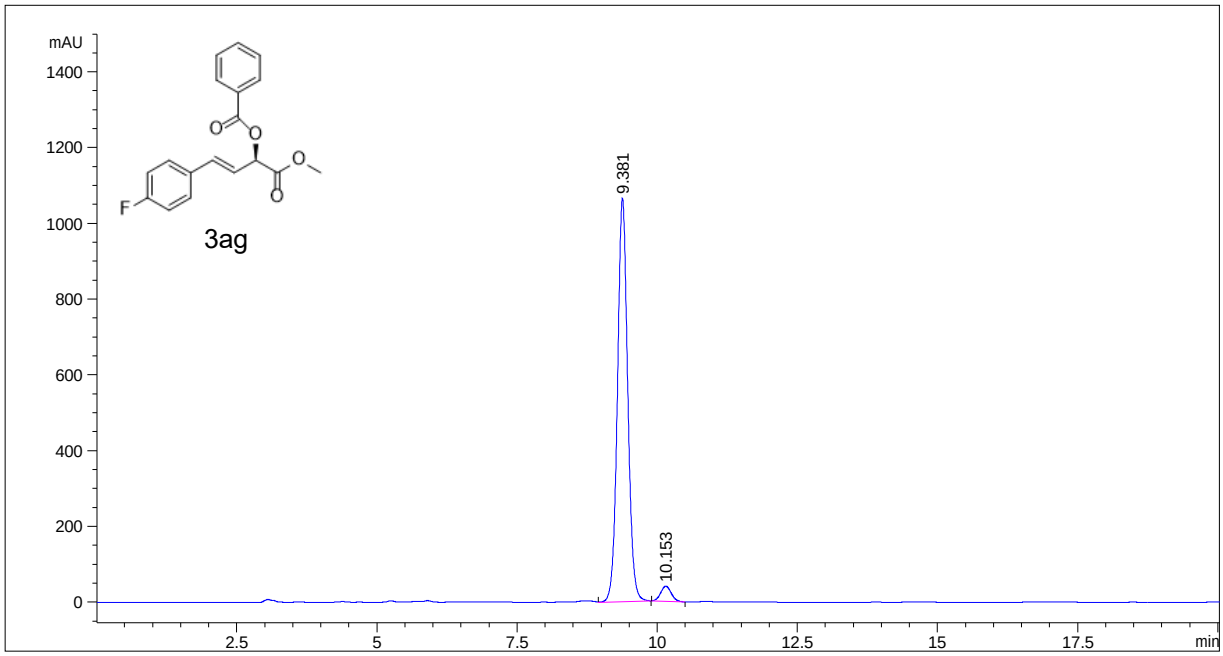


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.337	BV	0.1628	1478.91553	139.36082	4.1059
2	6.984	VB	0.2042	3.45407e4	2612.80713	95.8941

Daicel Chiralpak IA column, n-hexane/i-PrOH= 90/10, flow rate= 1ml/min, l= 225 nm

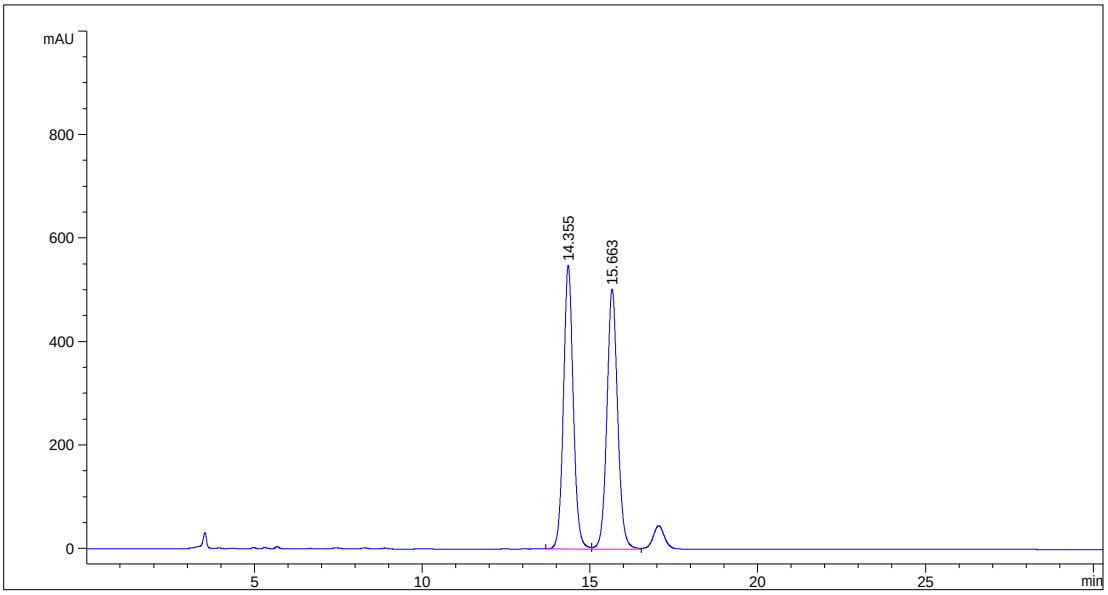


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.405	VV R	0.1918	6629.52539	526.79810	49.8685
2	10.174	VB	0.2088	6664.49463	486.43228	50.1315

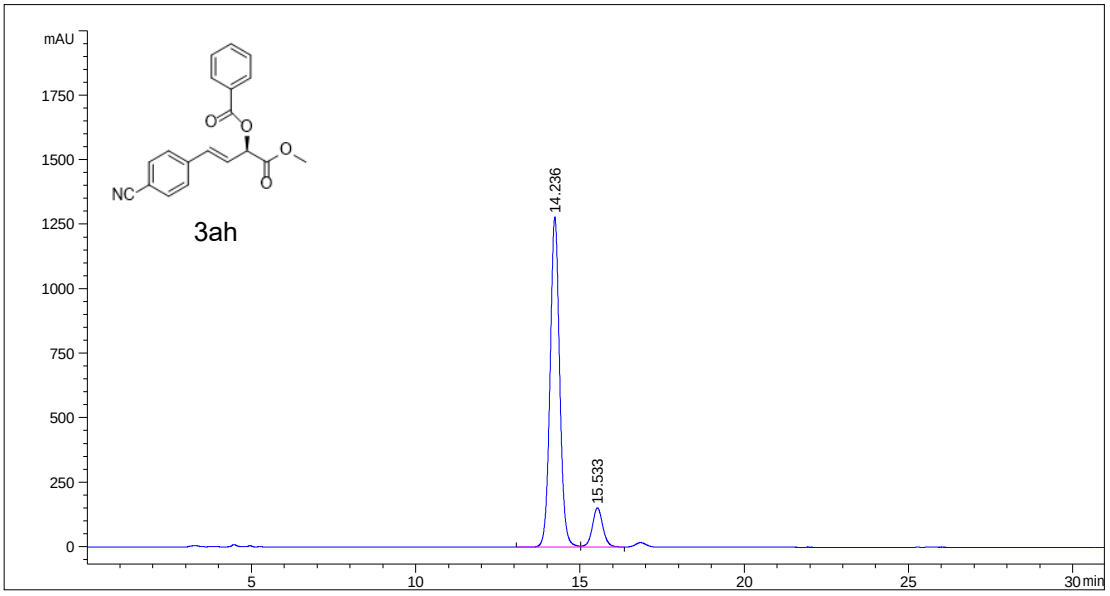


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.381	MM	0.2119	1.35429e4	1065.27844	96.2430
2	10.153	MM	0.2193	528.67023	40.18607	3.7570

Daicel Chiralpak IA column, n-hexane/i-PrOH= 80/20, flow rate= 1ml/min, l= 225 nm

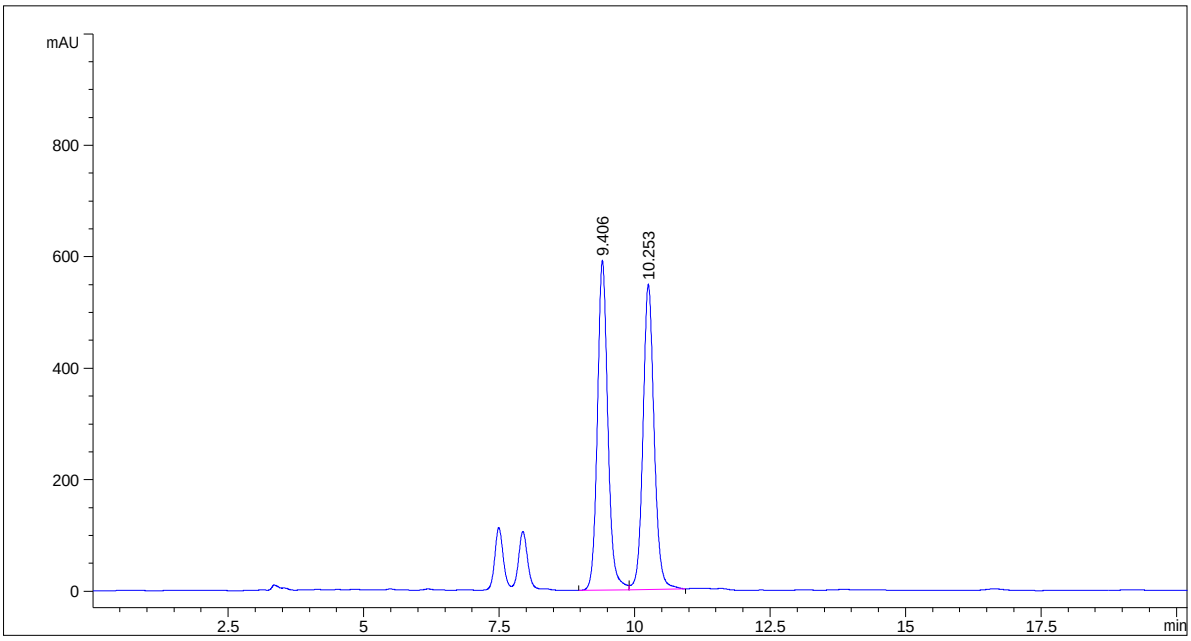


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.355	BV	0.3102	1.11456e4	548.20746	49.8994
2	15.663	VV	0.3399	1.11906e4	502.26080	50.1006

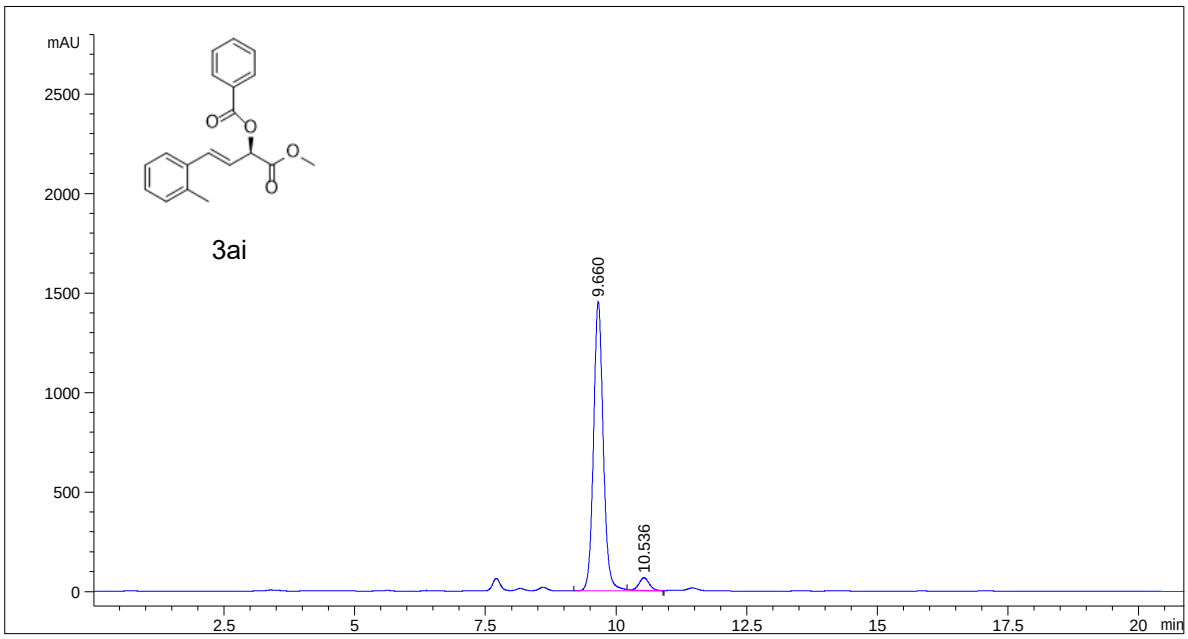


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.236	BV	0.3106	2.59528e4	1279.96545	88.5136
2	15.533	VB	0.3373	3367.88672	152.11409	11.4864

Daicel Chiralpak IA column, n-hexane/i-PrOH= 99/1, flow rate= 1ml/min, l= 225 nm

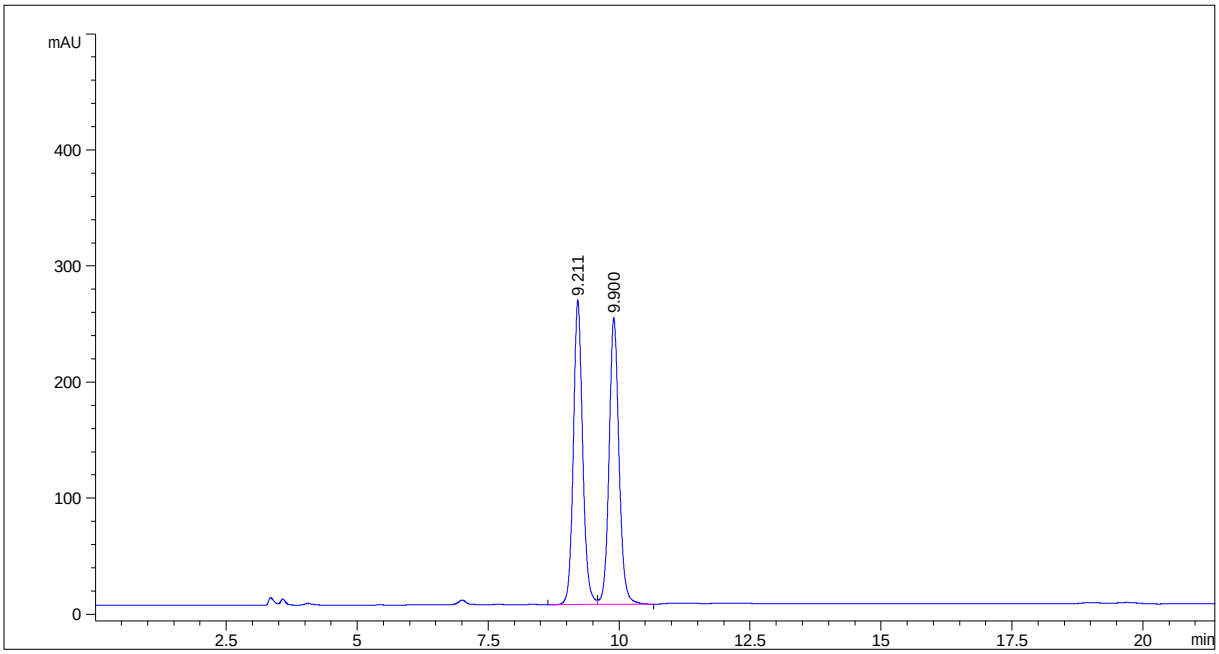


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.406	BV	0.2034	7918.80811	590.81531	50.2653
2	10.253	VB	0.2170	7835.20947	547.48535	49.7347

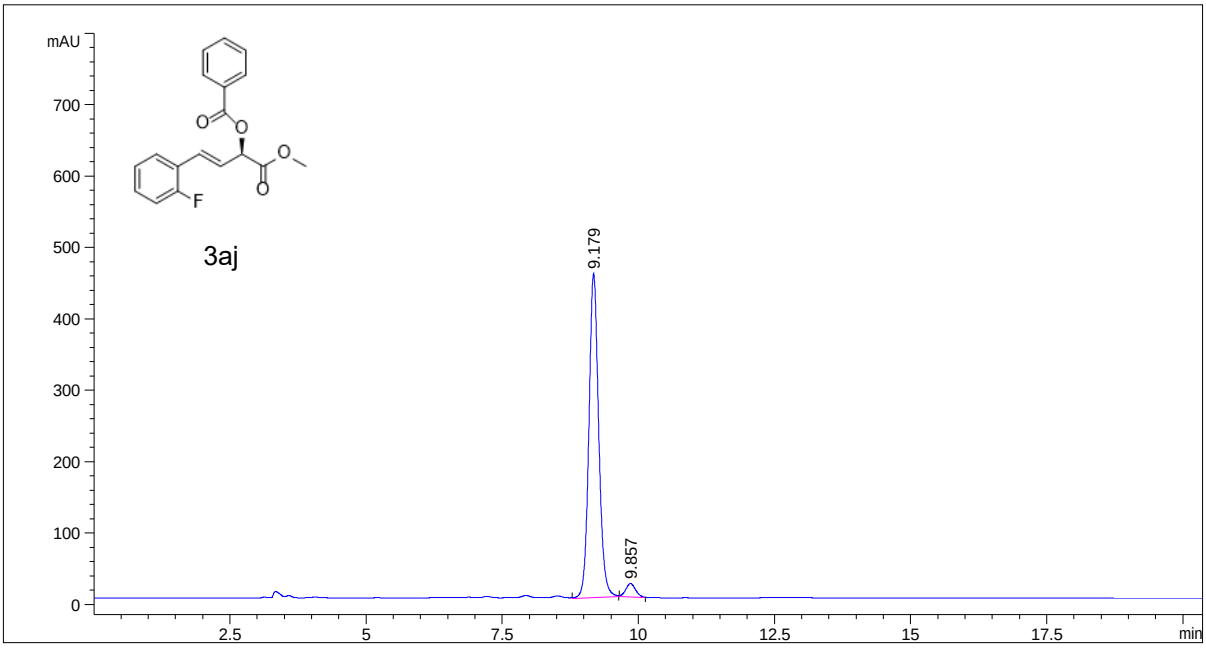


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.660	BV R	0.1987	1.88809e4	1452.40186	95.5777
2	10.536	VB E	0.2080	873.60095	64.49343	4.4223

Daicel Chiralpak IA column, n-hexane/i-PrOH= 95/5, flow rate= 1ml/min, l= 225 nm

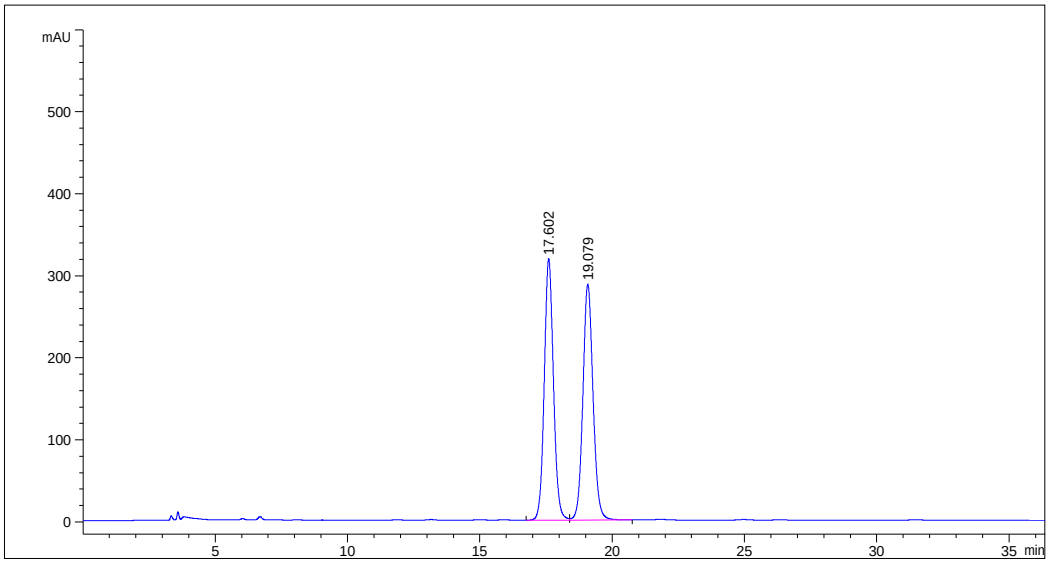


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.211	BV	0.1871	3237.52734	262.17526	49.8969
2	9.900	VB	0.2007	3250.90942	246.79601	50.1031

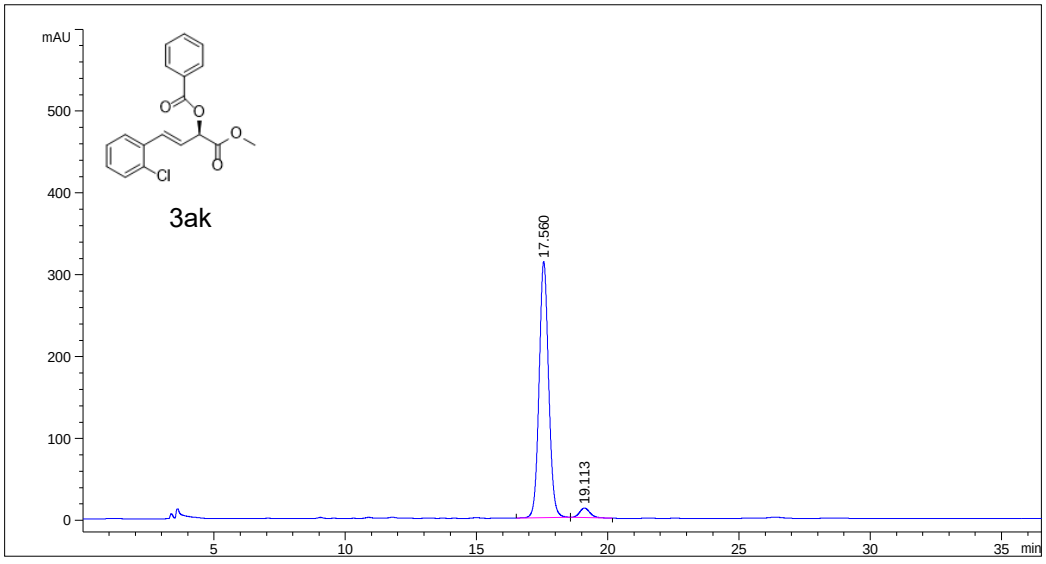


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.179	MM	0.2083	5674.10986	453.95990	95.9659
2	9.857	MM	0.2102	238.52286	18.90963	4.0341

Daicel Chiralpak IA column, n-hexane/i-PrOH= 90/10, flow rate= 1ml/min, I= 225 nm



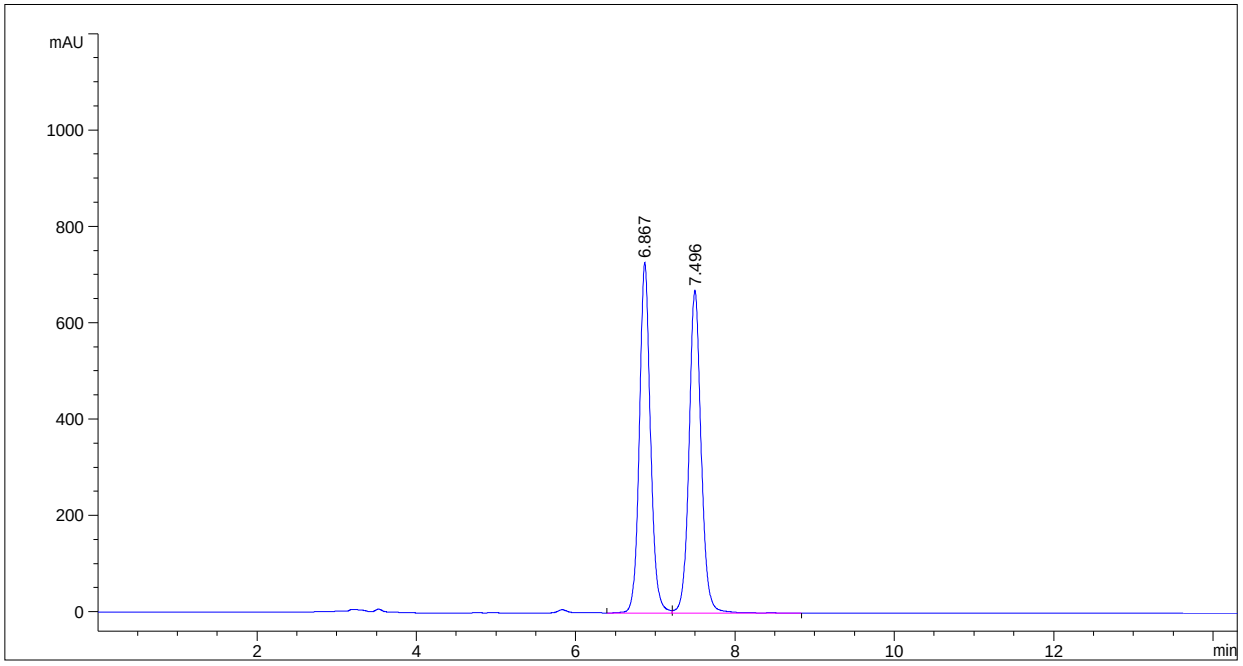
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.602	BV	0.3694	7685.94385	318.66260	50.0037
2	19.079	VB	0.4101	7684.81689	287.27124	49.9963



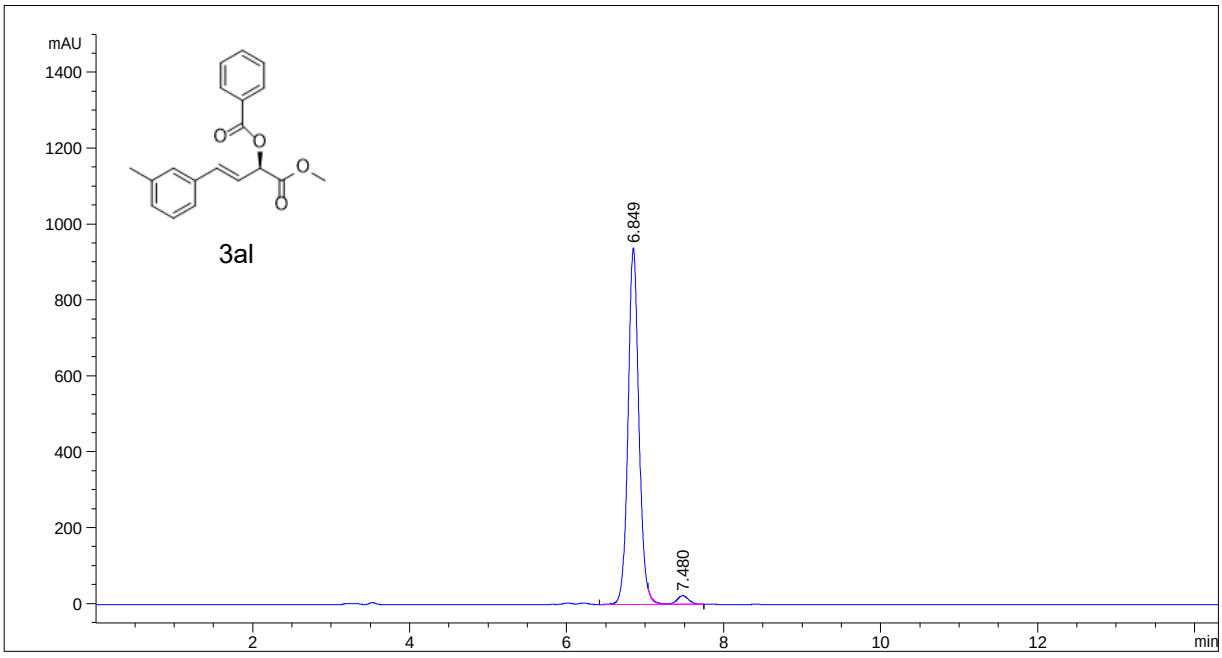
3ak

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.560	BB	0.3865	7873.25342	312.92920	96.0693
2	19.113	BB	0.4229	322.13931	11.71307	3.9307

Daicel Chiralpak IA column, n-hexane/i-PrOH=90/10, flow rate= 1ml/min, l= 225 nm

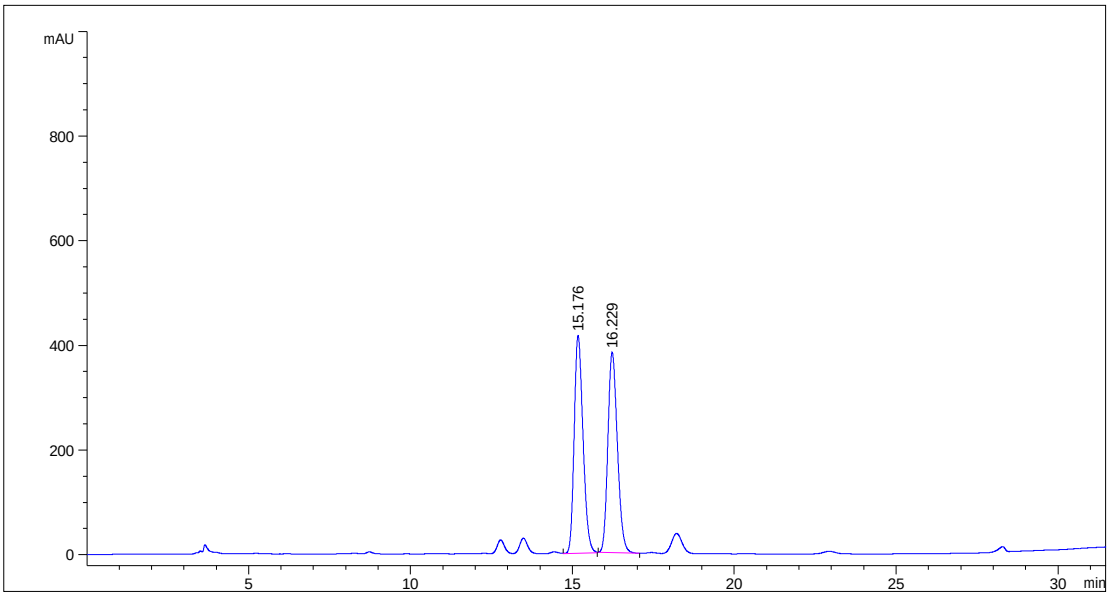


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.867	BV	0.1470	7040.90918	727.20612	49.8035
2	7.496	VV R	0.1606	7096.48096	669.72040	50.1965

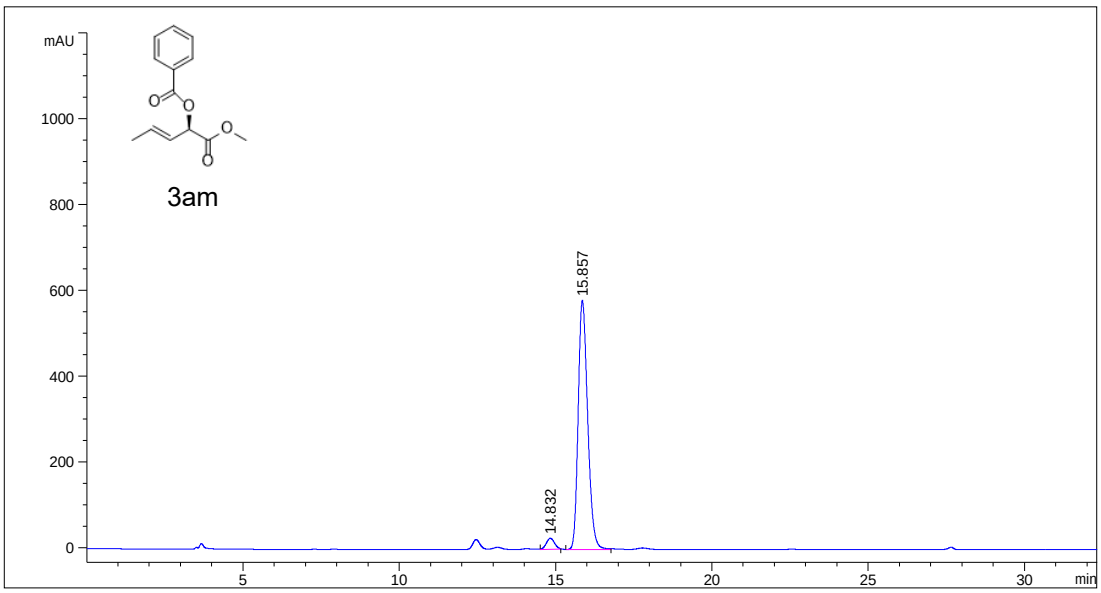


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.849	BV R	0.1463	9043.94824	939.79712	97.2482
2	7.480	VB E	0.1678	255.90981	22.82184	2.7518

Daicel Chiralpak IC column, n-hexane/i-PrOH= 99/1, flow rate= 1ml/min, l= 225 nm

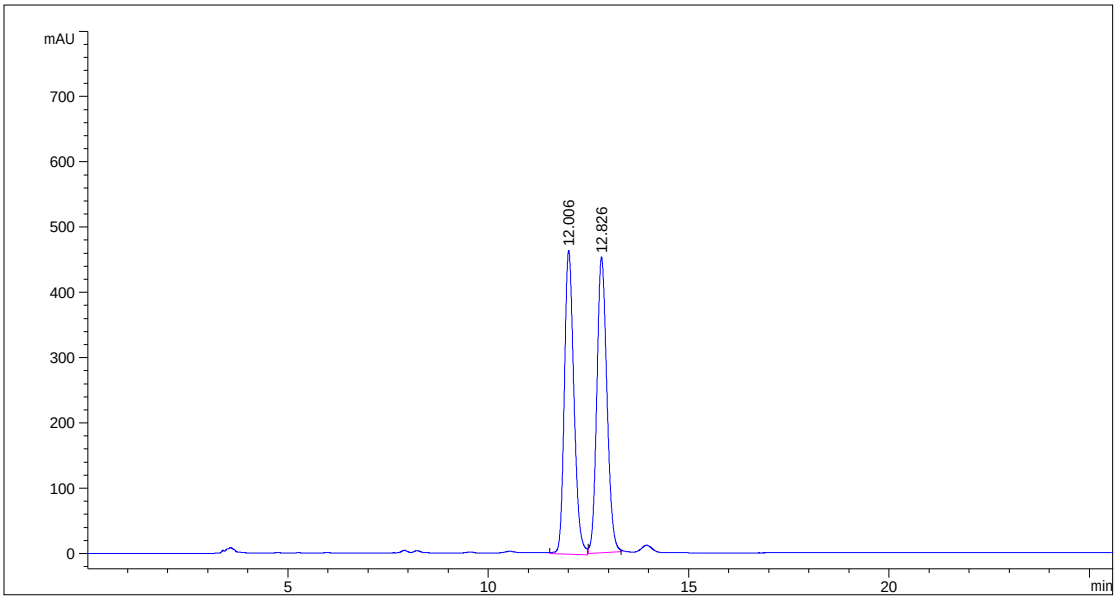


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.176	MM	0.3158	7889.67188	416.38354	50.1132
2	16.229	MM	0.3417	7854.03857	383.06940	49.8868

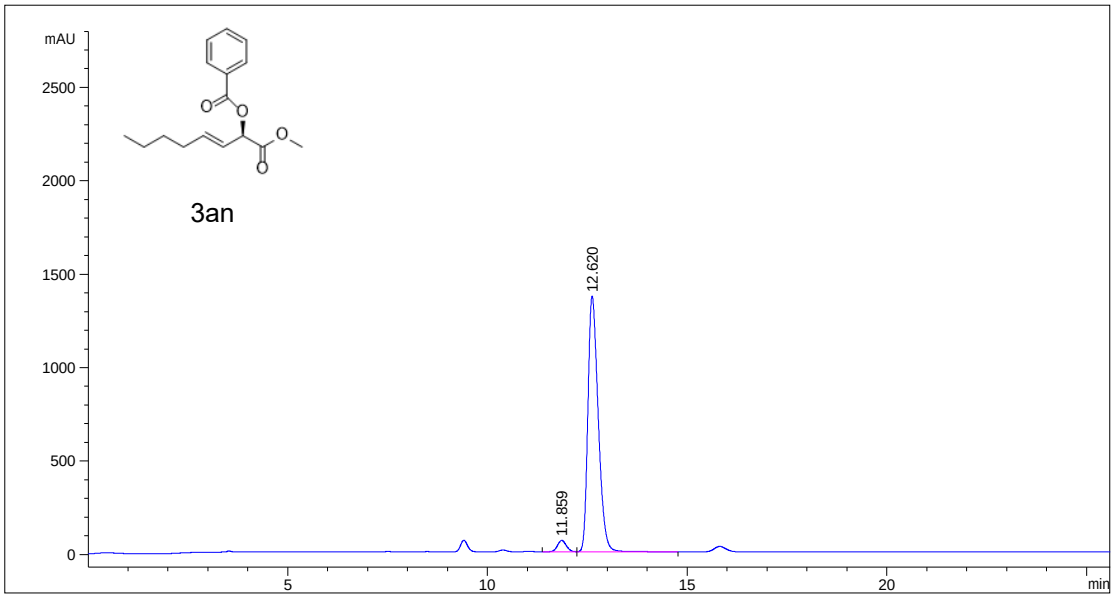


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.832	MM	0.3075	480.66867	26.05021	3.7653
2	15.857	MM	0.3525	1.22849e4	580.78302	96.2347

Daicel Chiralpak IC column, n-hexane/i-PrOH= 99/1, flow rate= 1ml/min, l= 225 nm

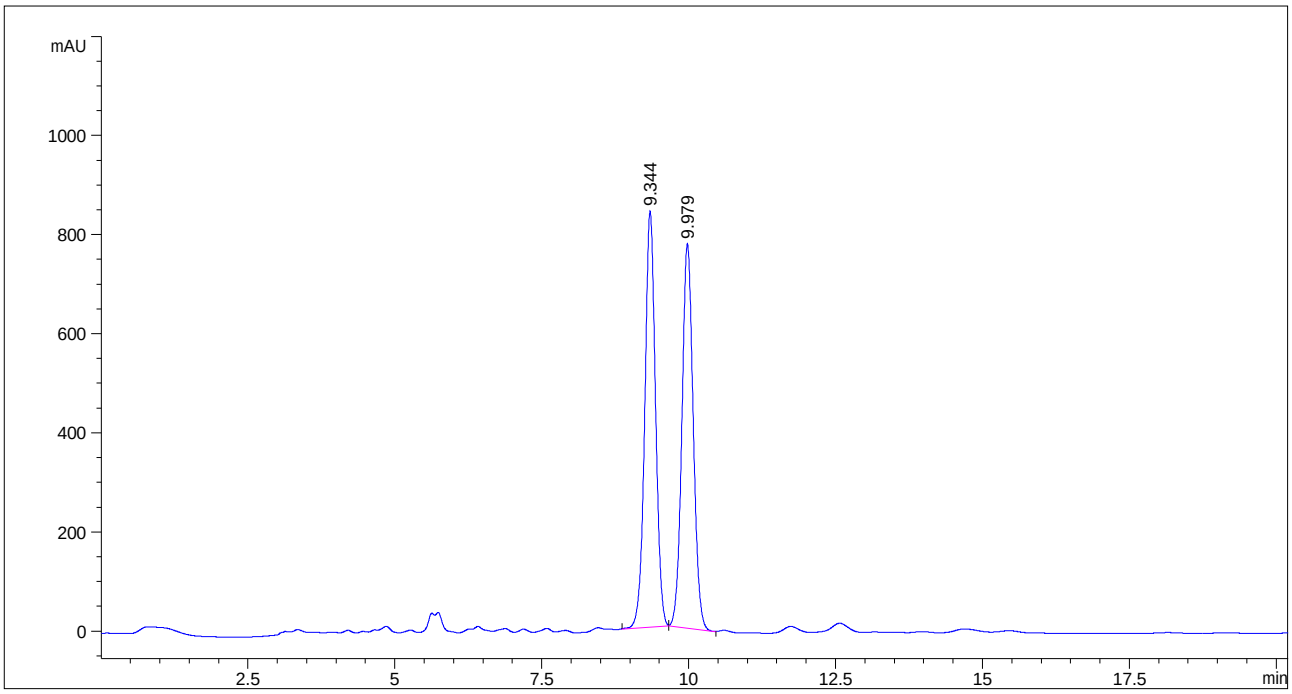


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.006	MM	0.2766	7728.74854	465.72897	49.4401
2	12.826	MM	0.2909	7903.79980	452.78943	50.5599

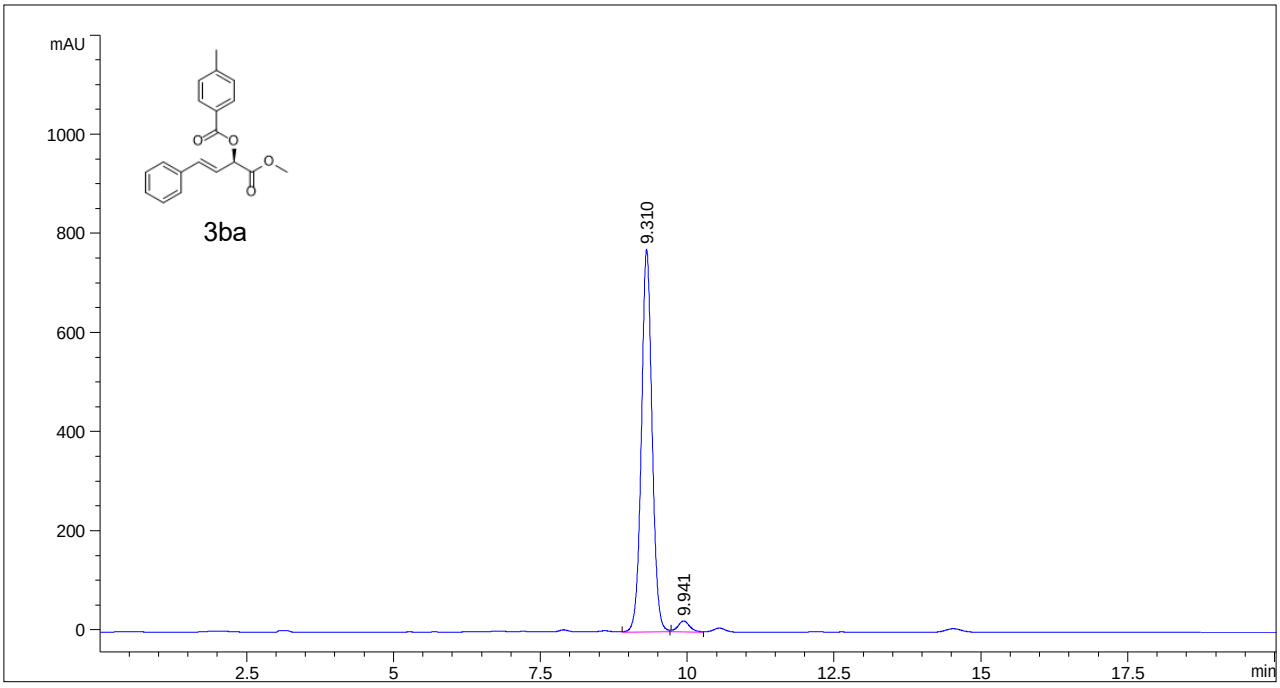


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.859	BV	0.2405	962.83429	61.54699	3.7577
2	12.620	VV R	0.2765	2.46604e4	1369.83203	96.2423

Daicel Chiralpak IA column, n-hexane/i-PrOH= 90/10, flow rate= 1ml/min, l= 225 nm

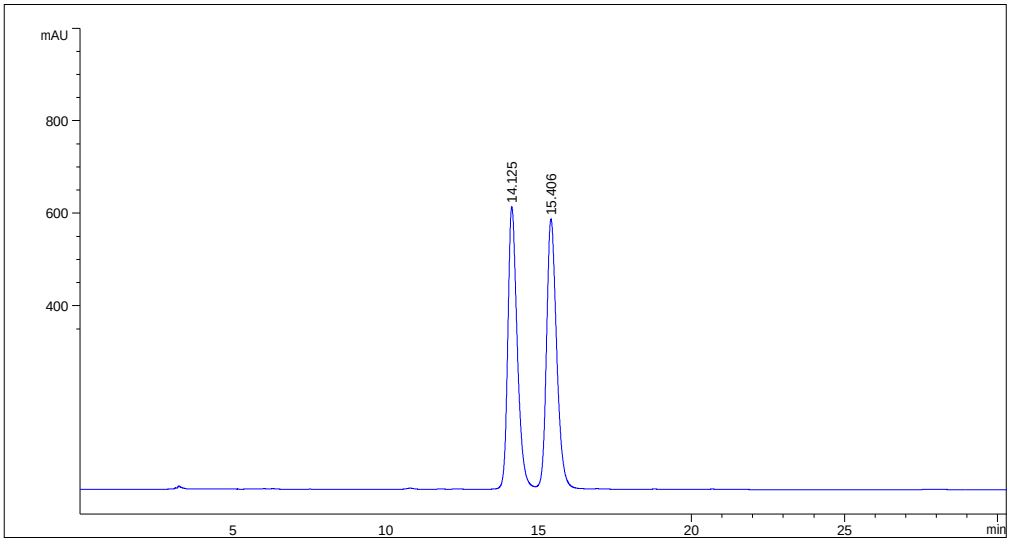


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.344	MM	0.2120	1.06867e4	840.12842	50.6959
2	9.979	MM	0.2231	1.03933e4	776.31976	49.3041

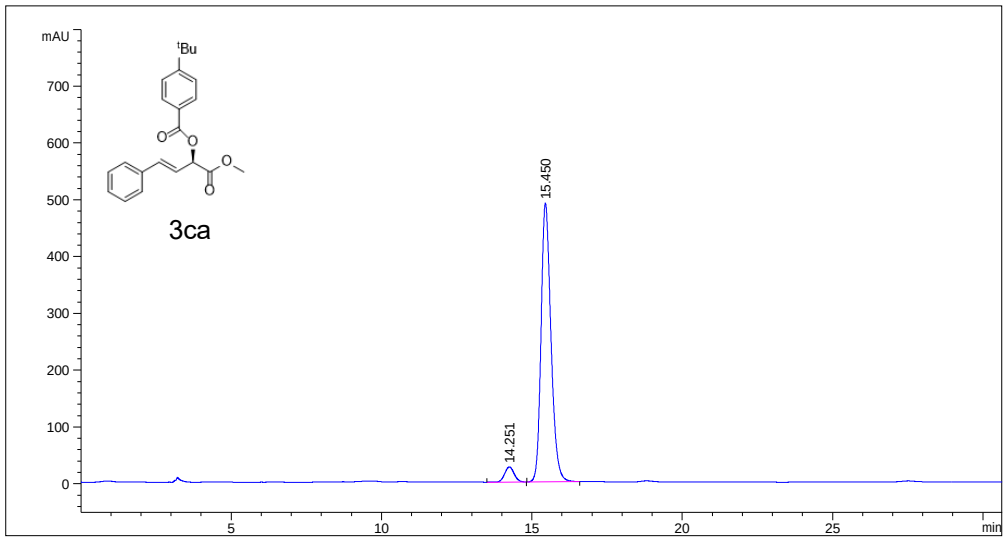


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.310	MM	0.2108	9765.87695	772.13281	96.8915
2	9.941	MM	0.2364	313.31094	22.08788	3.1085

Daicel Chiralpak IA column, n-hexane/i-PrOH= 99/1, flow rate= 1ml/min, l= 225 nm

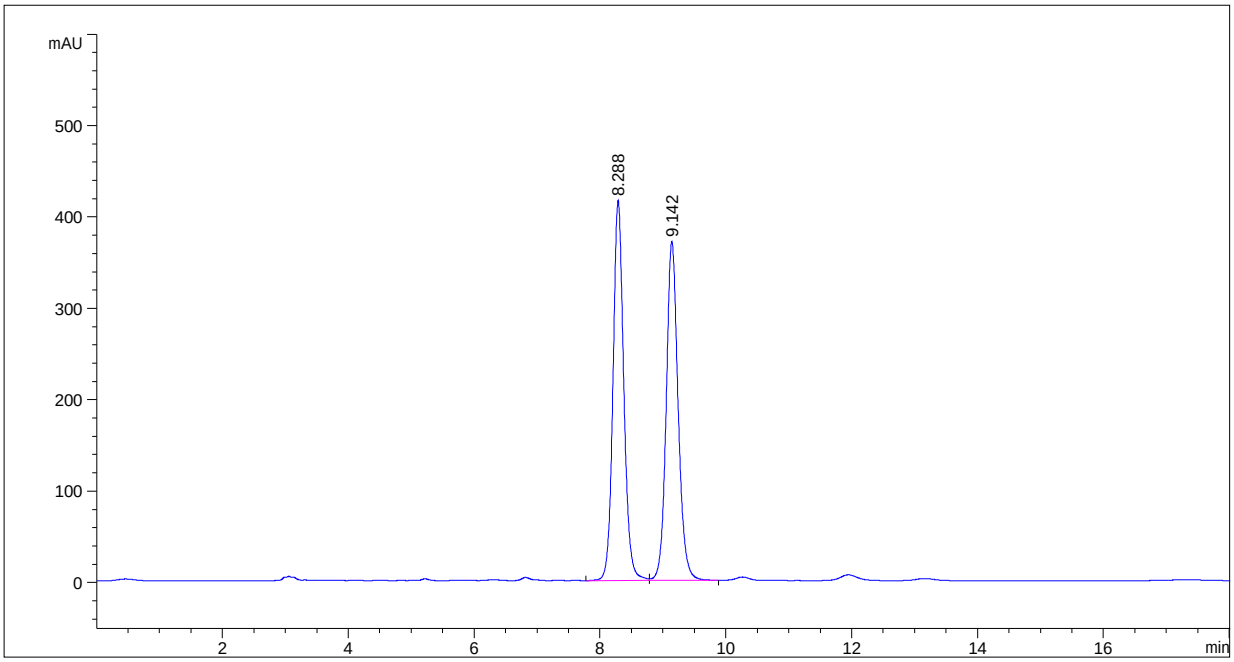


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.125	BV	0.3244	1.30535e4	610.53583	49.3461
2	15.406	VB	0.3508	1.33994e4	583.71381	50.6539

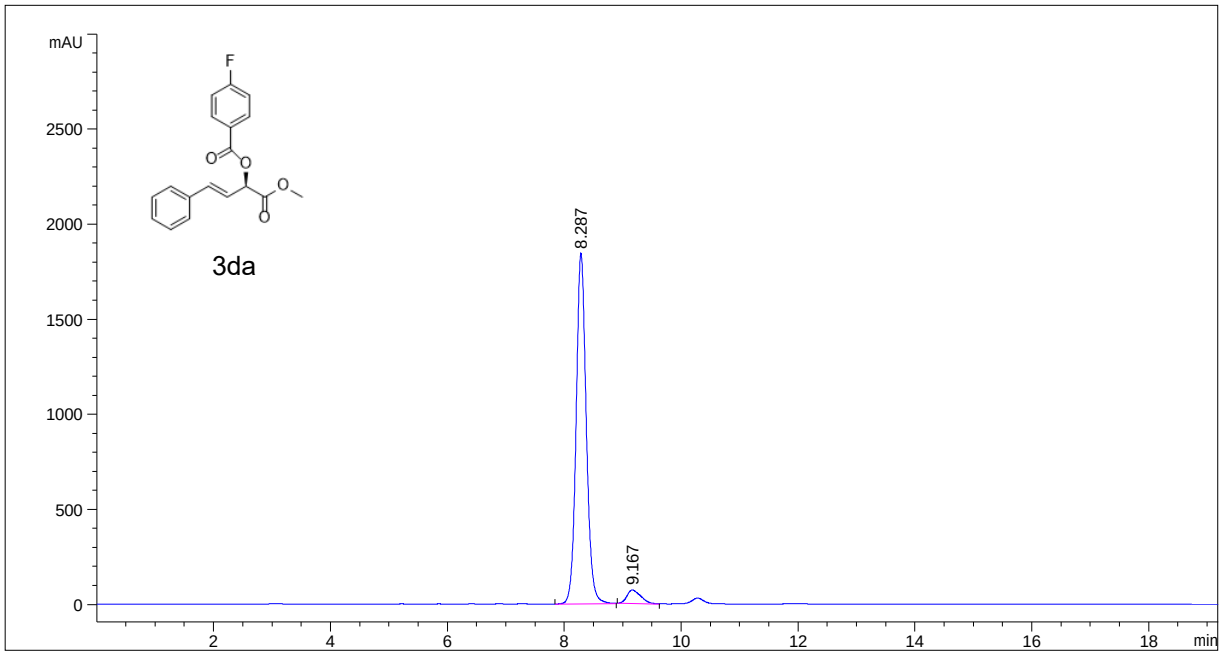


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.251	BB	0.3417	589.16113	26.87877	4.9921
2	15.450	BB	0.3506	1.12128e4	490.67963	95.0079

Daicel Chiralpak IA column, n-hexane/i-PrOH= 90/10, flow rate= 1ml/min, l= 225 nm

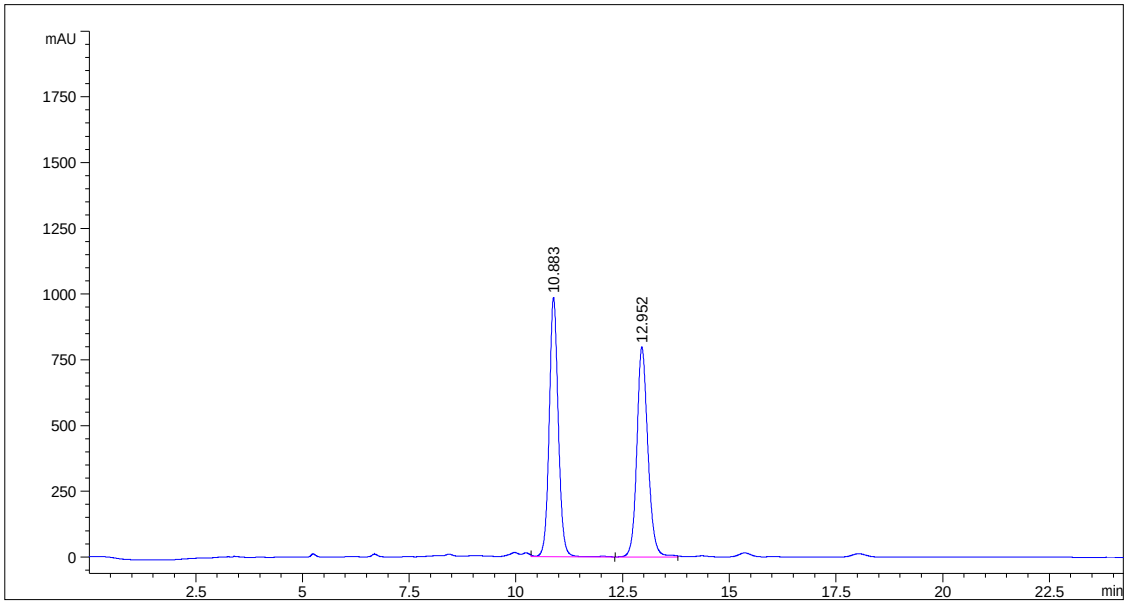


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.288	BV	0.1812	4960.36670	415.87848	50.4609
2	9.142	VB	0.1991	4869.75146	371.12924	49.5391

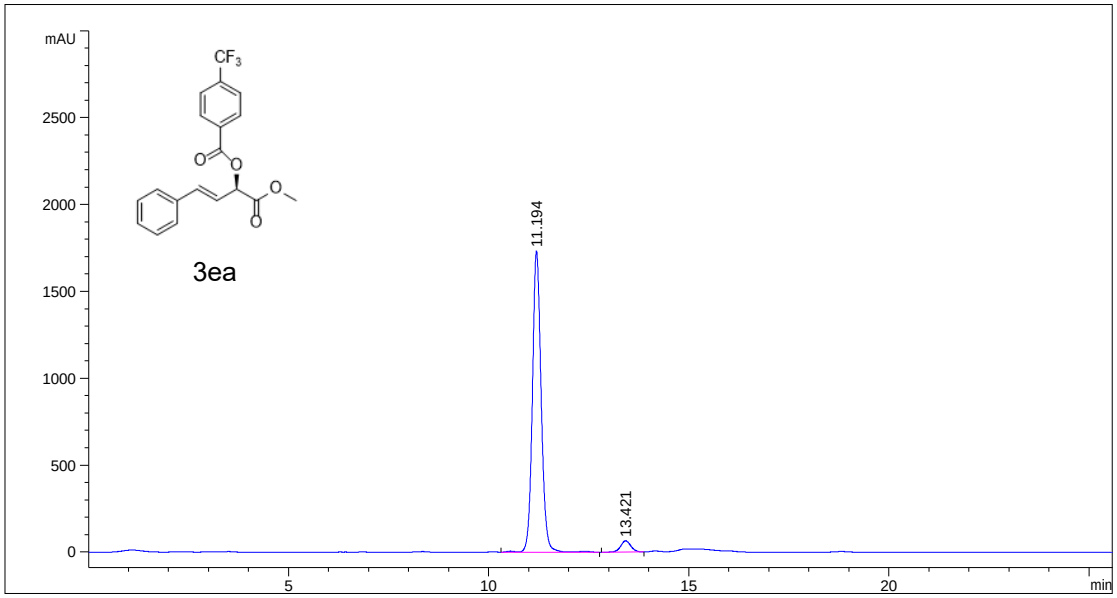


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.287	MM	0.2006	2.22019e4	1844.85913	94.9465
2	9.167	MM	0.2745	1181.68298	71.75167	5.0535

Daicel Chiralpak IA column, n-hexane/i-PrOH= 99/1, flow rate= 1ml/min, l= 225 nm

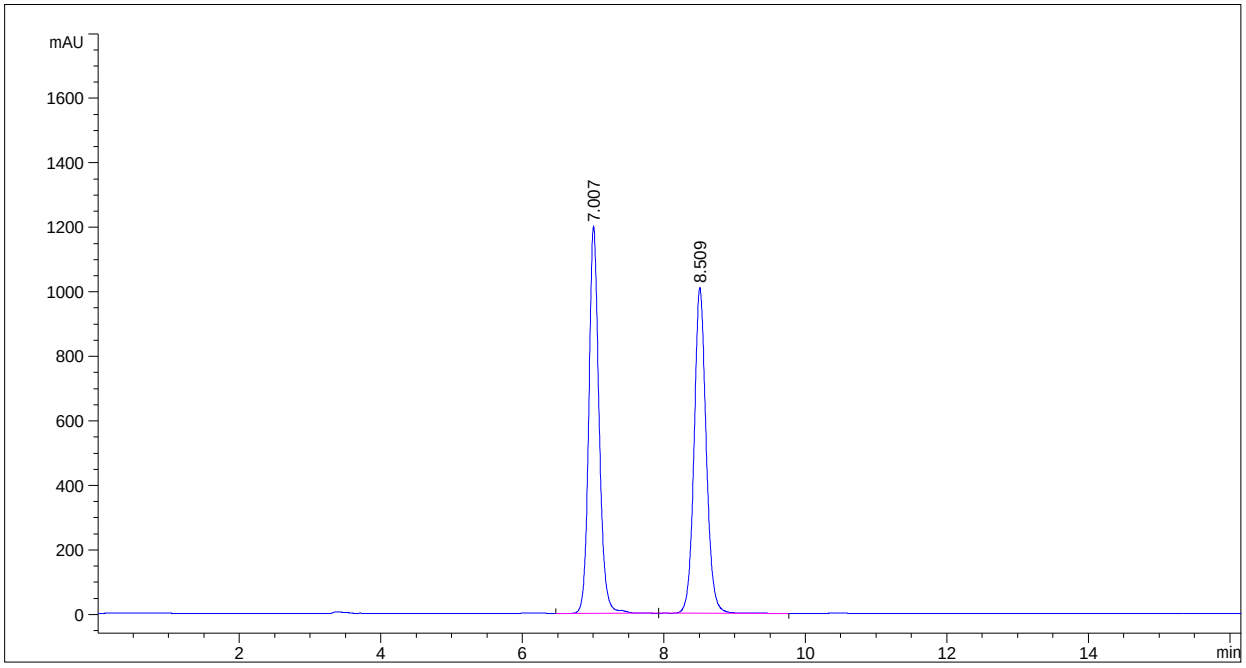


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.883	FM	0.2456	1.45302e4	985.86926	50.2693
2	12.952	MF	0.2999	1.43746e4	798.76099	49.7307

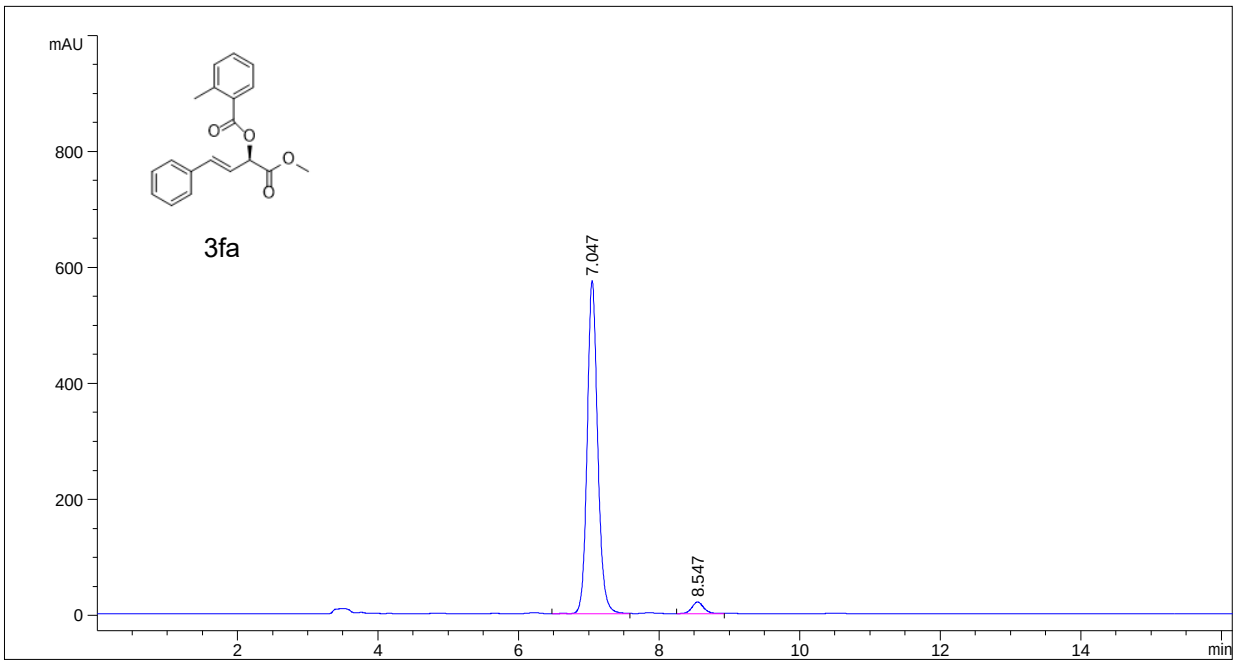


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.194	VV R	0.2306	2.64092e4	1733.35840	95.8629
2	13.421	BB	0.2719	1139.73499	64.27171	4.1371

Daicel Chiralpak IA column, n-hexane/i-PrOH= 90/10, flow rate= 1ml/min, l= 225 nm

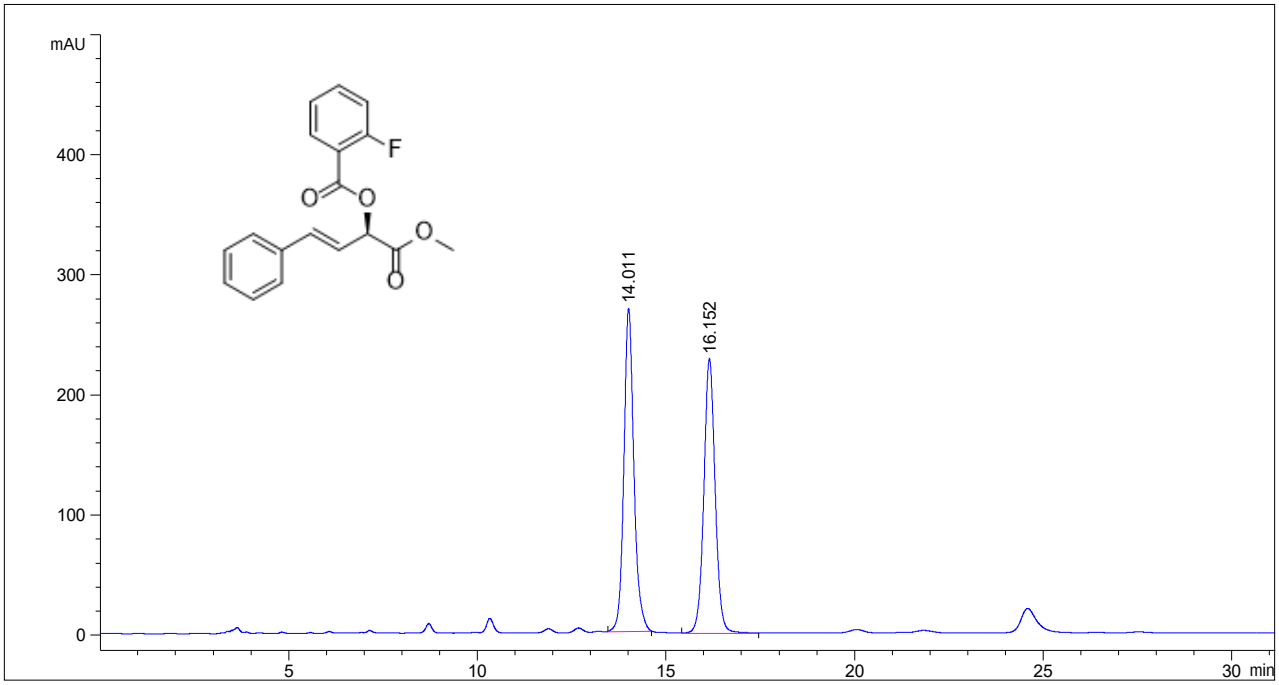


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.007	VB R	0.1538	1.20977e4	1198.19812	50.1825
2	8.509	VV R	0.1808	1.20097e4	1009.10419	49.8175

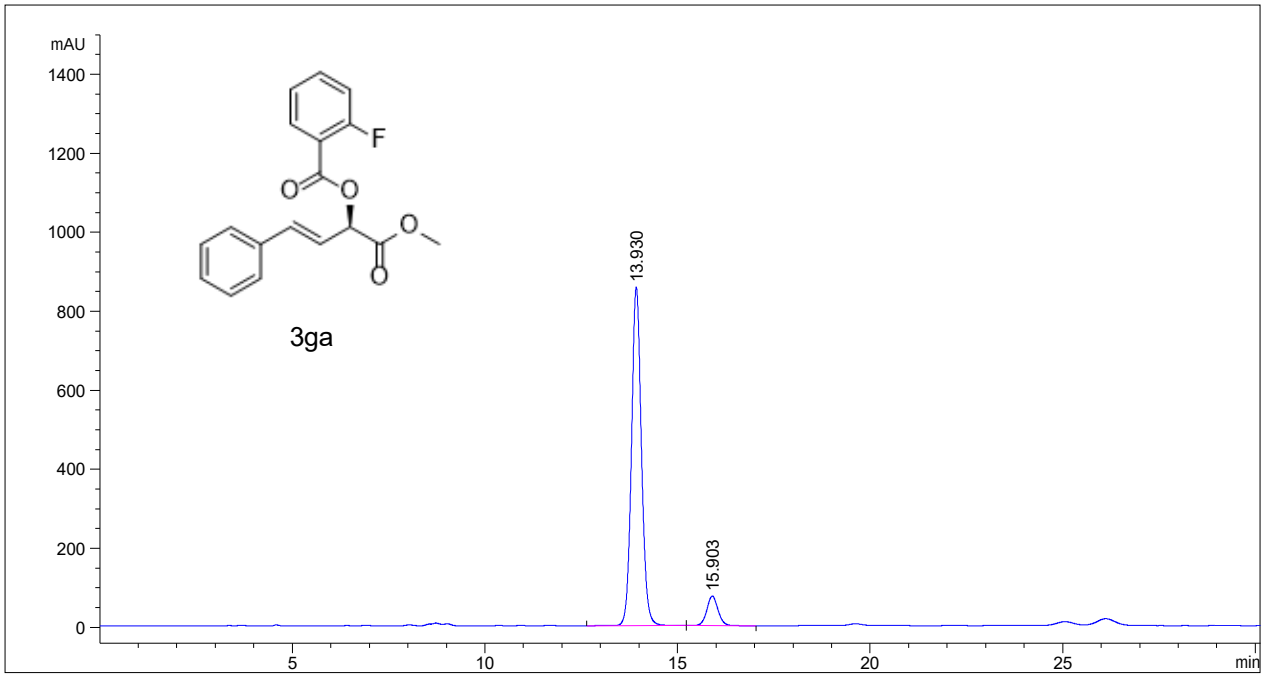


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.047	MF	0.1727	5946.88379	573.77856	96.1410
2	8.547	FM	0.1988	238.70164	20.01125	3.8590

Daicel Chiralpak IA column, n-hexane/i-PrOH= 99/1, flow rate= 1ml/min, l= 225 nm

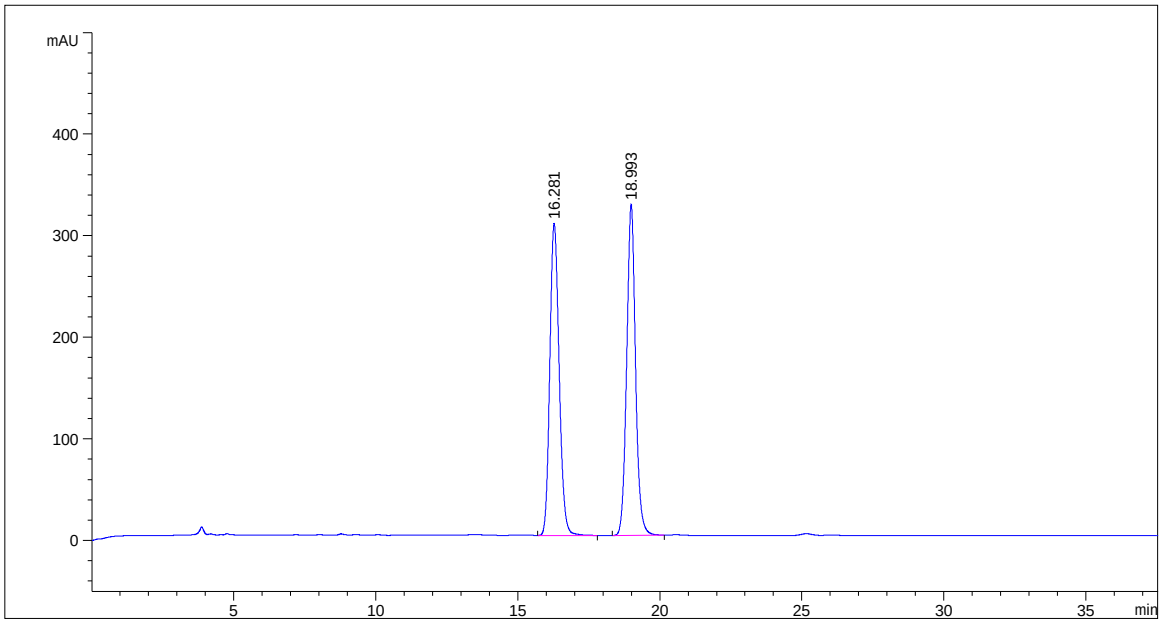


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.011	MM	0.3079	4972.43066	269.12485	50.9101
2	16.152	MM	0.3494	4794.65332	228.73445	49.0899

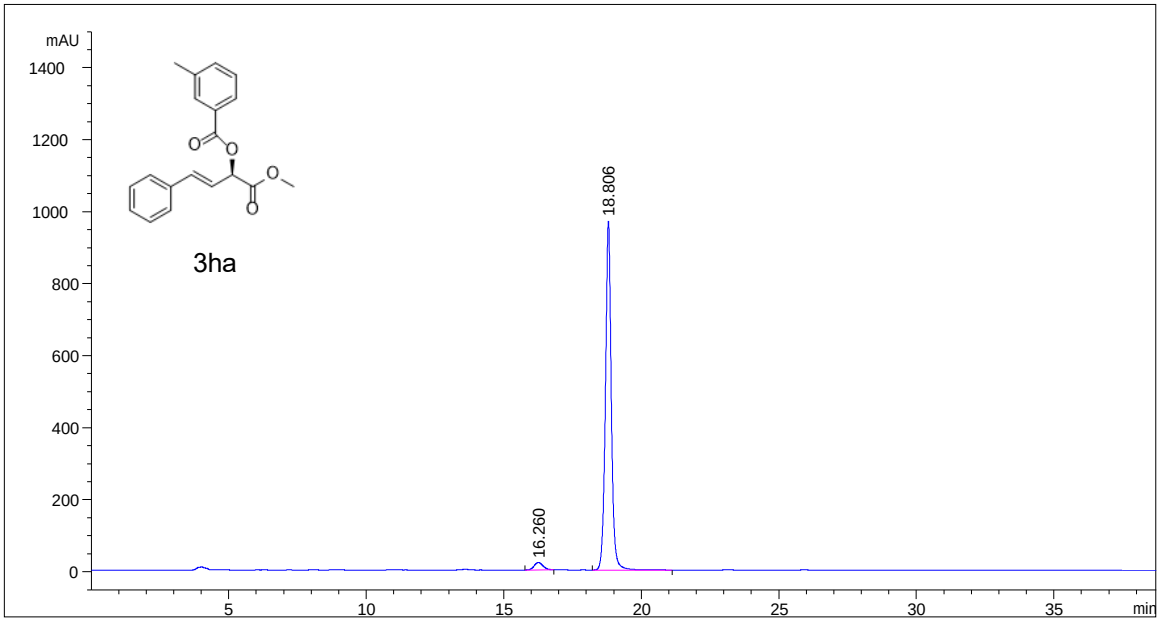


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.930	VB R	0.2750	1.54345e4	857.63745	91.0444
2	15.903	BB	0.3103	1518.21667	74.95245	8.9556

Daicel Chiralpak IC column, n-hexane/i-PrOH= 95/5, flow rate= 1ml/min, l= 225 nm

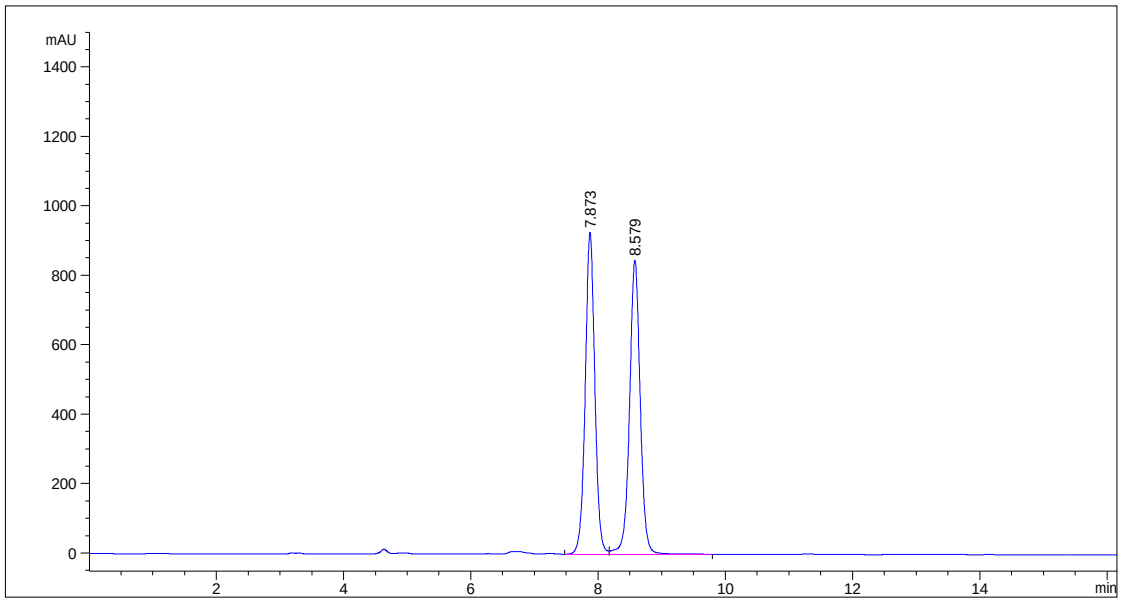


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.281	BB	0.3531	7009.52490	307.31076	49.8348
2	18.993	BB	0.3266	7055.99414	325.94910	50.1652

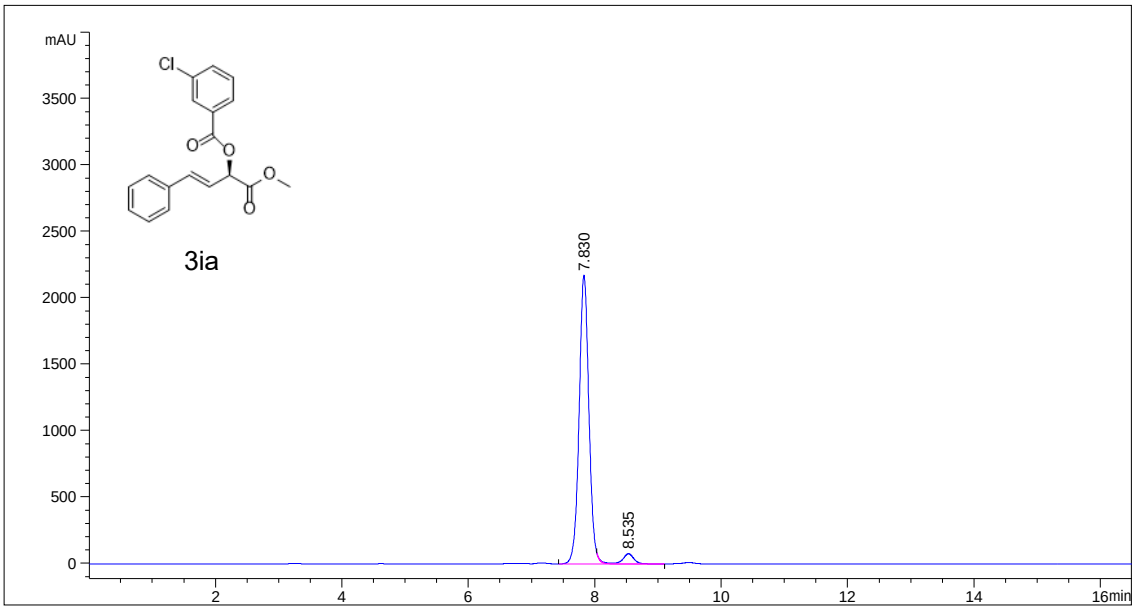


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.260	BB	0.3460	449.80698	20.26518	3.0360
2	18.806	BB	0.2200	1.43660e4	968.91638	96.9640

Daicel Chiralpak IA column, n-hexane/i-PrOH= 90/10, flow rate= 1ml/min, l= 225 nm

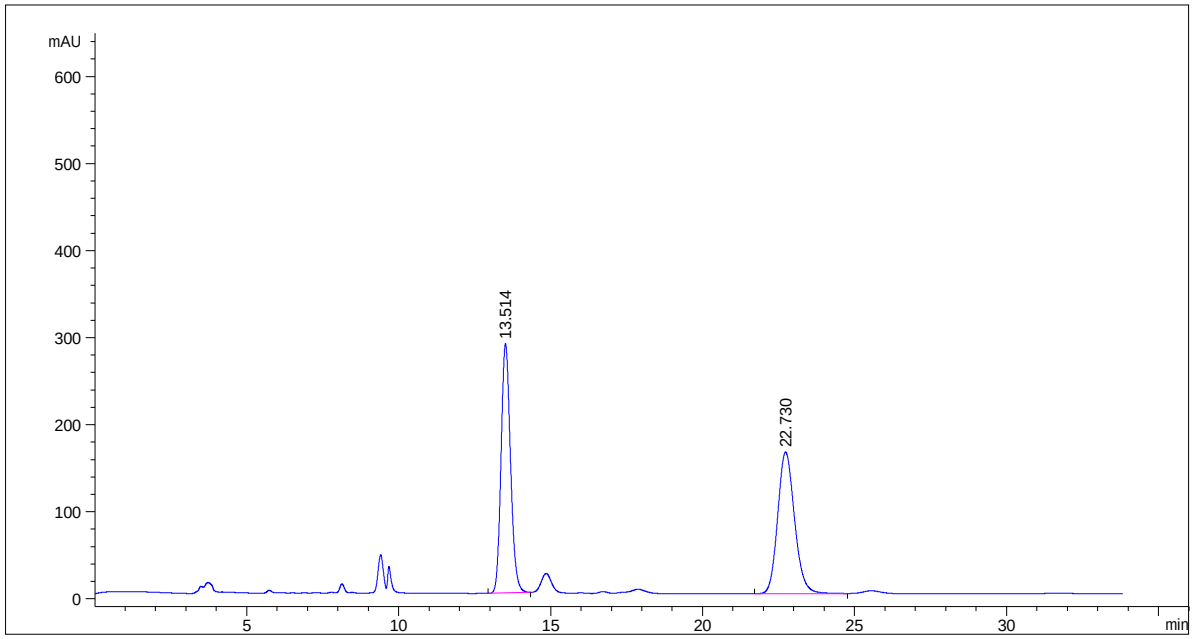


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.873	BV	0.1602	9705.61133	926.81873	49.5687
2	8.579	VB	0.1771	9874.50684	846.54553	50.4313

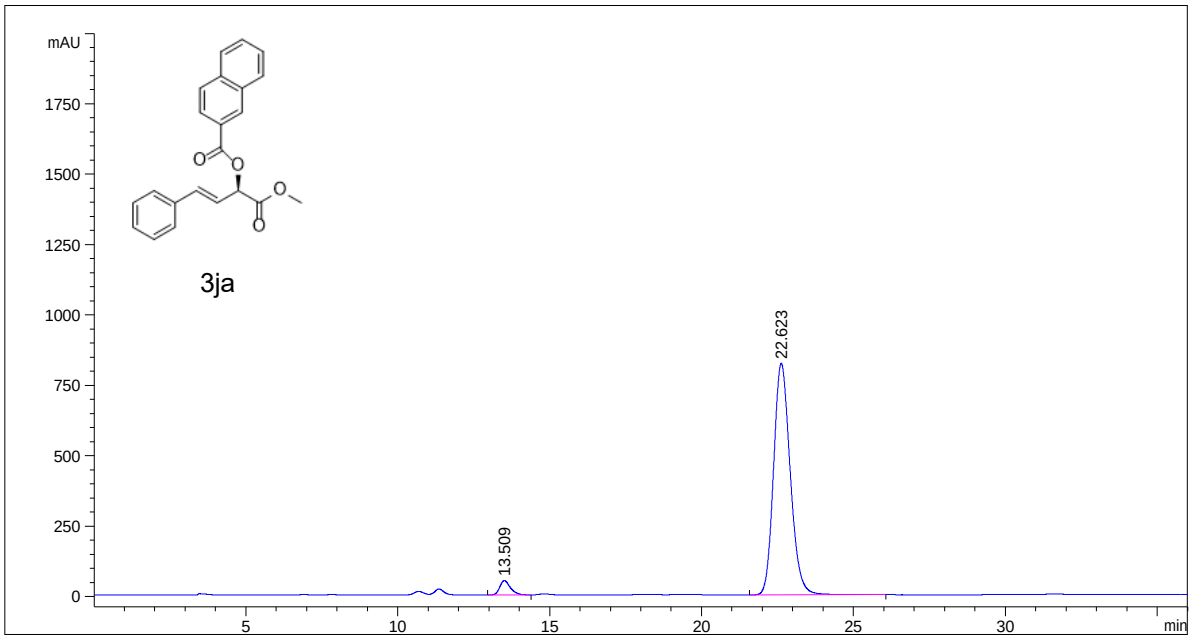


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.830	BV R	0.1643	2.33315e4	2173.08276	96.0707
2	8.535	VB E	0.1858	954.25330	76.37509	3.9293

Daicel Chiralpak IC column, n-hexane/i-PrOH= 90/10, flow rate= 1ml/min, l= 225 nm

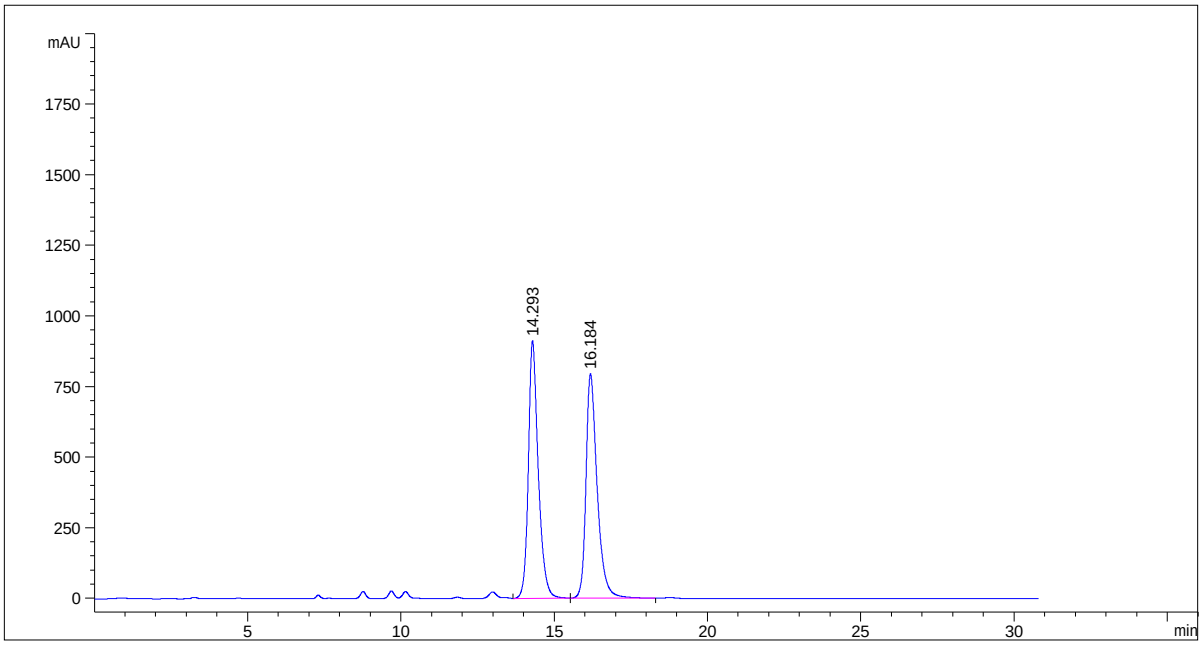


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.514	BB	0.3326	6173.01855	286.22501	49.6608
2	22.730	BB	0.5929	6257.34424	162.63890	50.3392

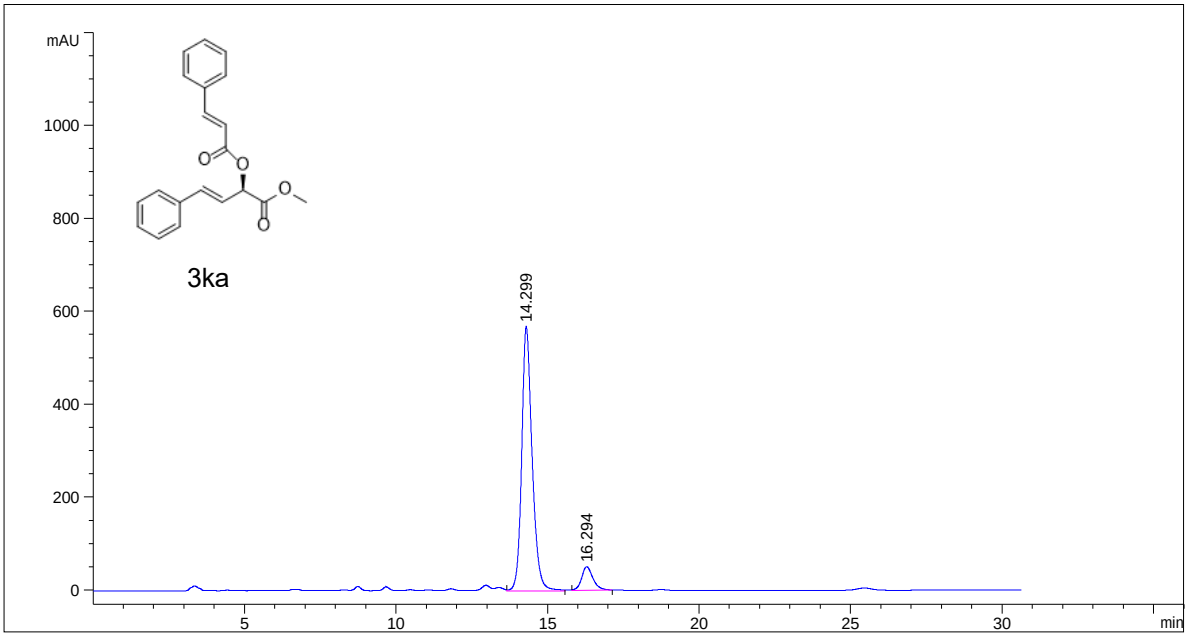


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.509	BB	0.3636	1230.80688	51.18144	3.7847
2	22.623	BB	0.5870	3.12897e4	822.13940	96.2153

Daicel Chiralpak IA column, n-hexane/i-PrOH= 90/10, flow rate= 1ml/min, l= 225 nm

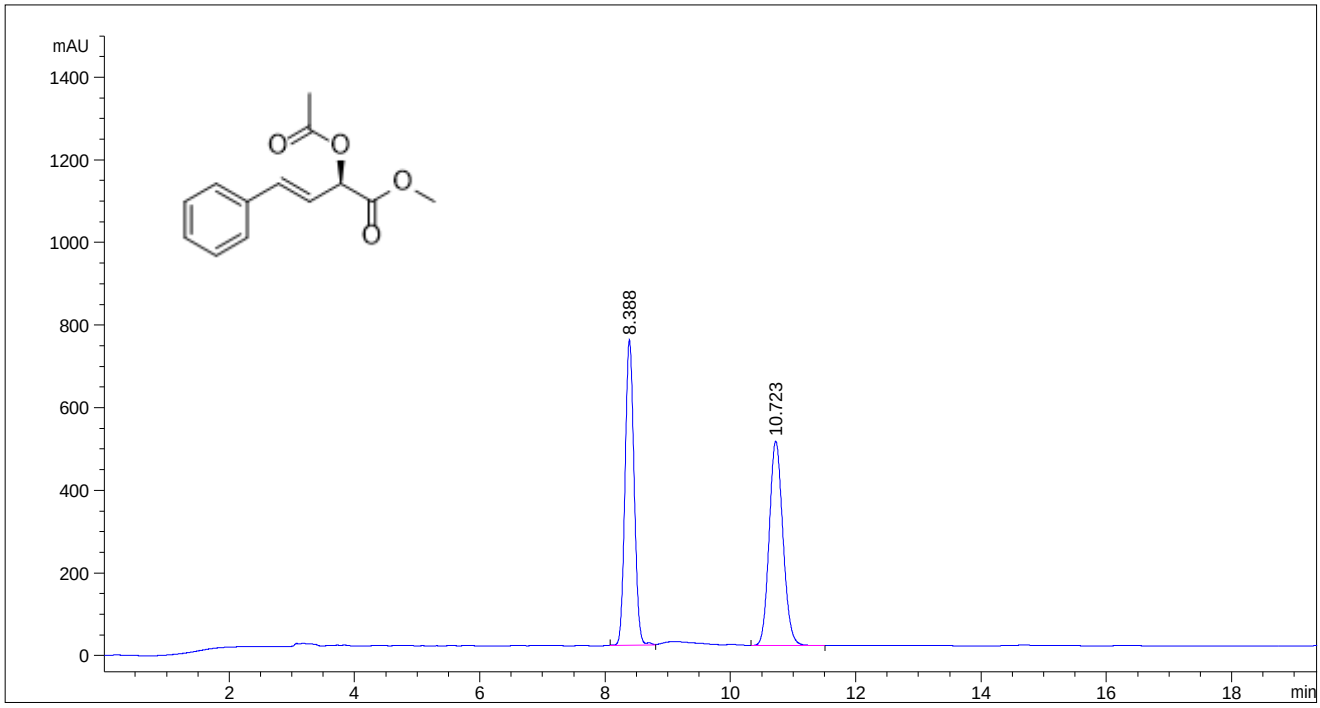


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.293	BB	0.3296	2.04626e4	912.52448	50.3887
2	16.184	BB	0.3789	2.01469e4	794.22131	49.6113

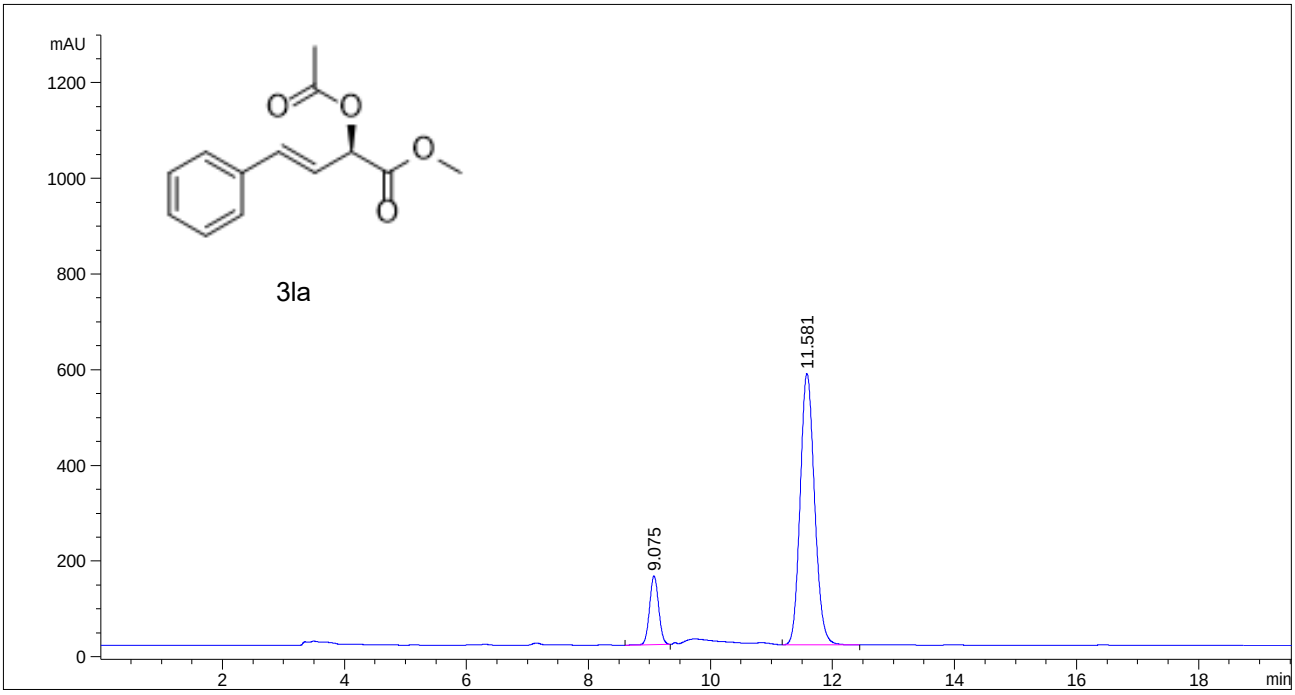


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.299	MM	0.3998	1.36575e4	569.30121	91.0963
2	16.294	MM	0.4352	1334.88074	51.11976	8.9037

Daicel Chiralpak IC column, n-hexane/i-PrOH= 90/10, flow rate= 2ml/min, l= 225 nm

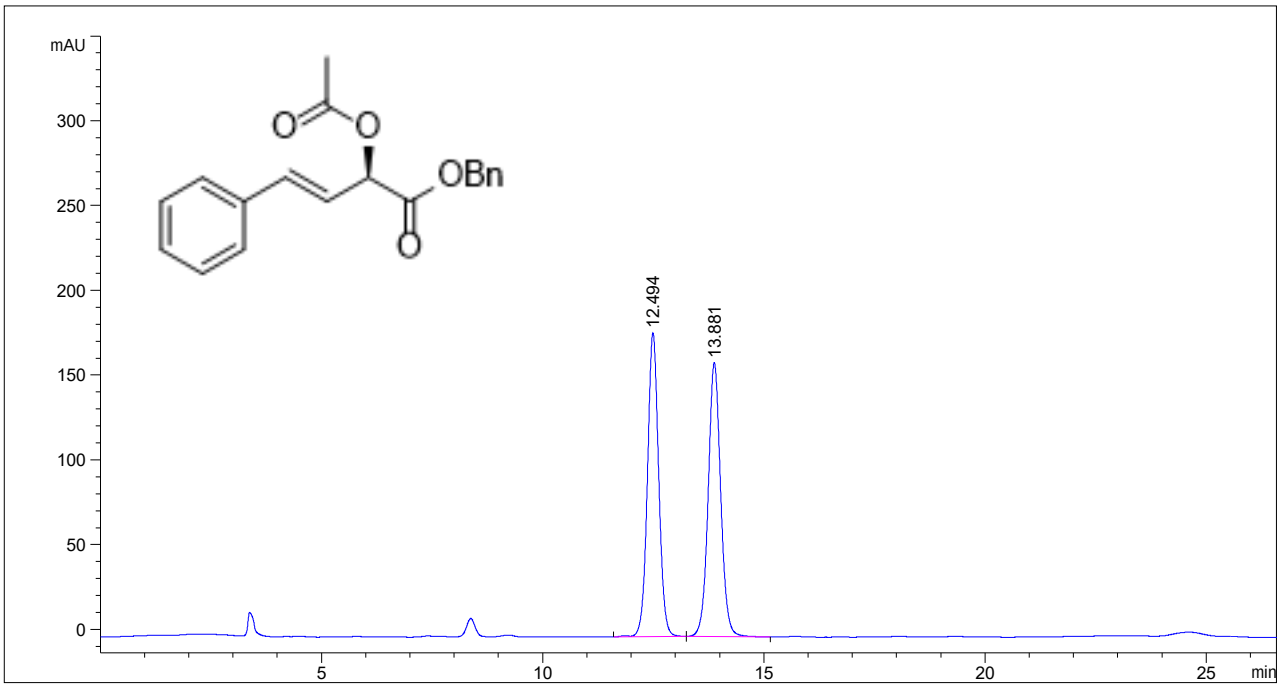


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.388	MM	0.1670	7412.86475	739.65570	49.5541
2	10.723	BB	0.2369	7546.28271	494.93903	50.4459

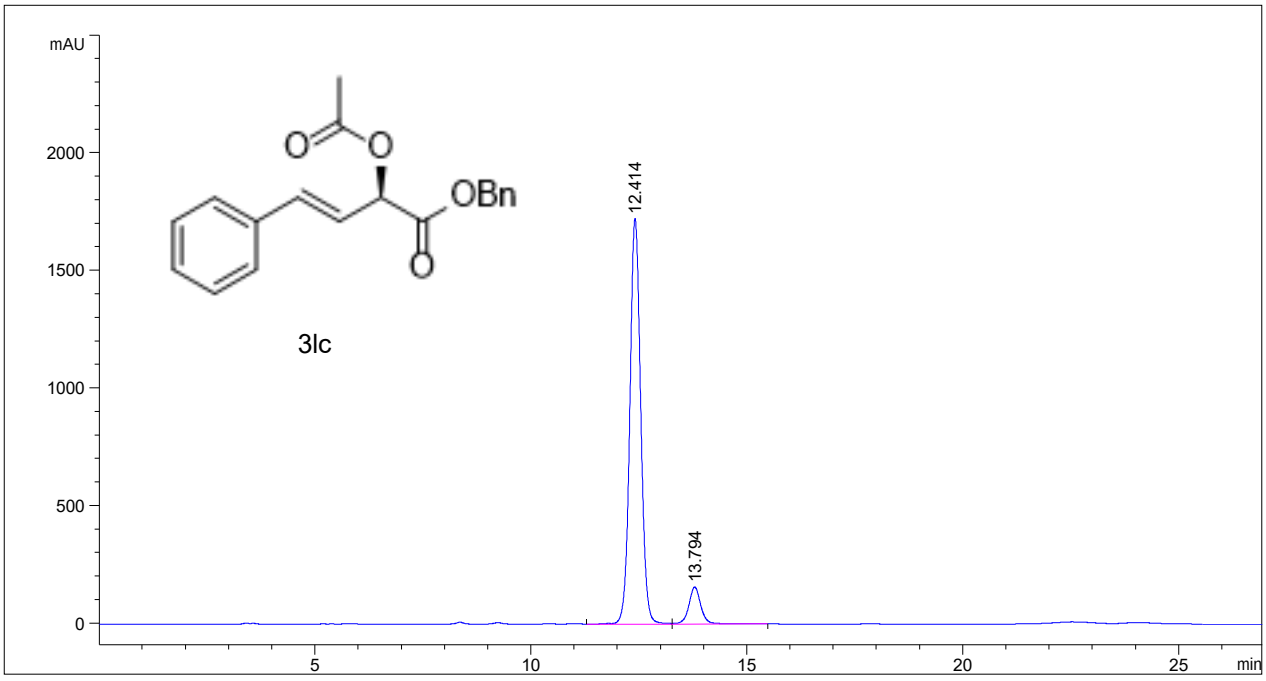


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.075	VB R	0.1606	1485.57422	143.66560	13.7737
2	11.581	BB	0.2542	9299.98145	567.40314	86.2263

Daicel Chiralpak IA column, n-hexane/i-PrOH= 99/1, flow rate= 2ml/min, l= 225 nm

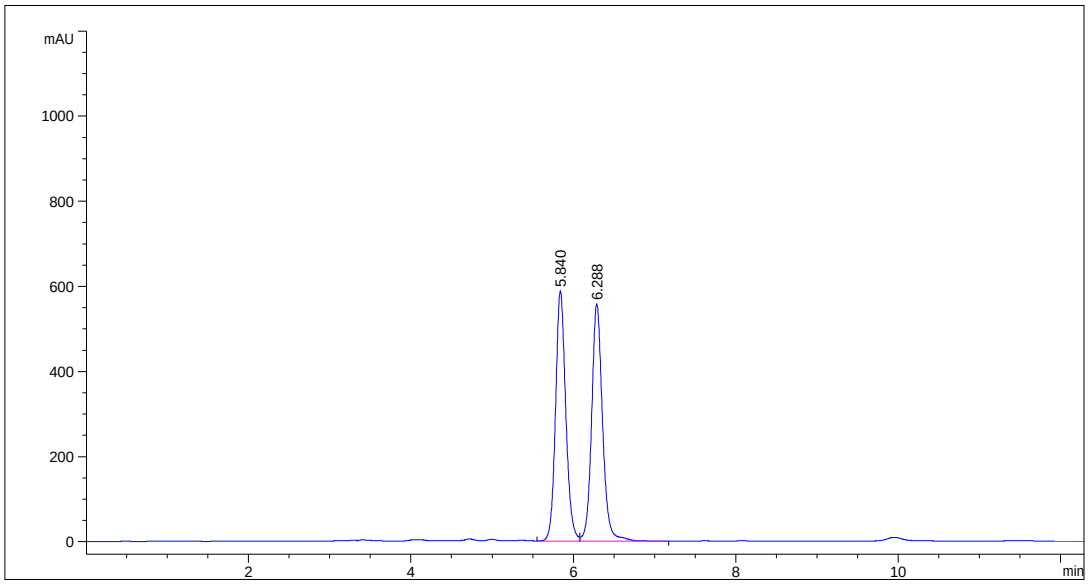


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.494	VB R	0.2696	3157.61230	179.17632	49.8742
2	13.881	BB	0.2990	3173.54077	161.66350	50.1258

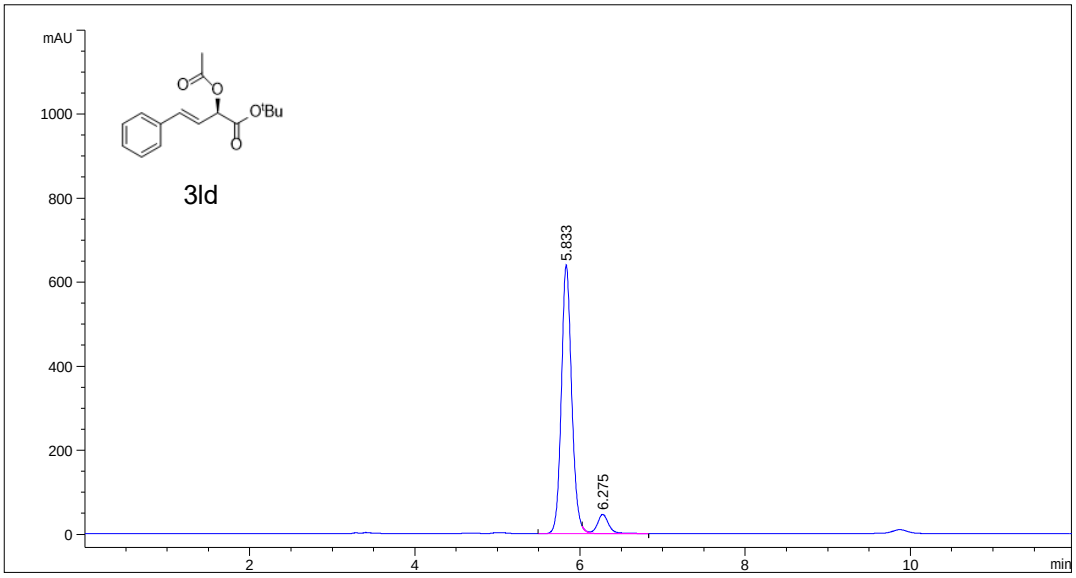


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.414	VV R	0.2700	3.01761e4	1724.10620	90.8638
2	13.794	VB	0.2908	3034.16895	157.48047	9.1362

Daicel Chiralpak IA column, n-hexane/i-PrOH= 99/1, flow rate= 1ml/min, l= 225 nm

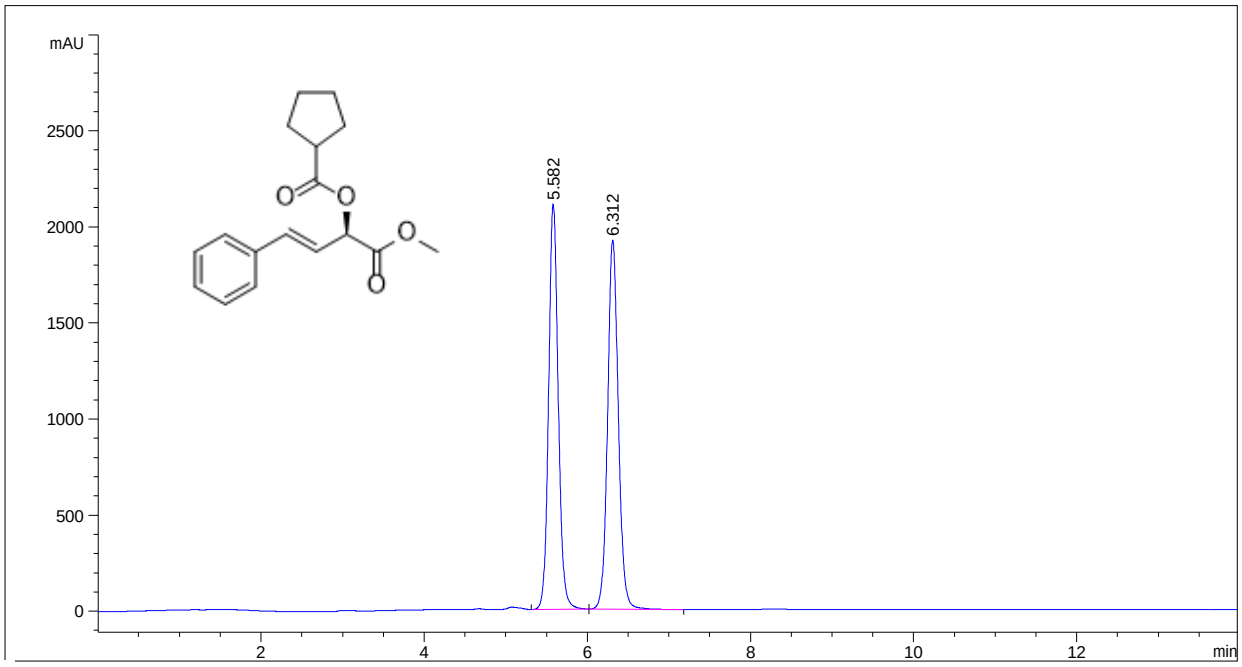


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.840	BV	0.1328	5124.74316	587.54614	49.7523
2	6.288	VB	0.1404	5175.78223	557.17218	50.2477

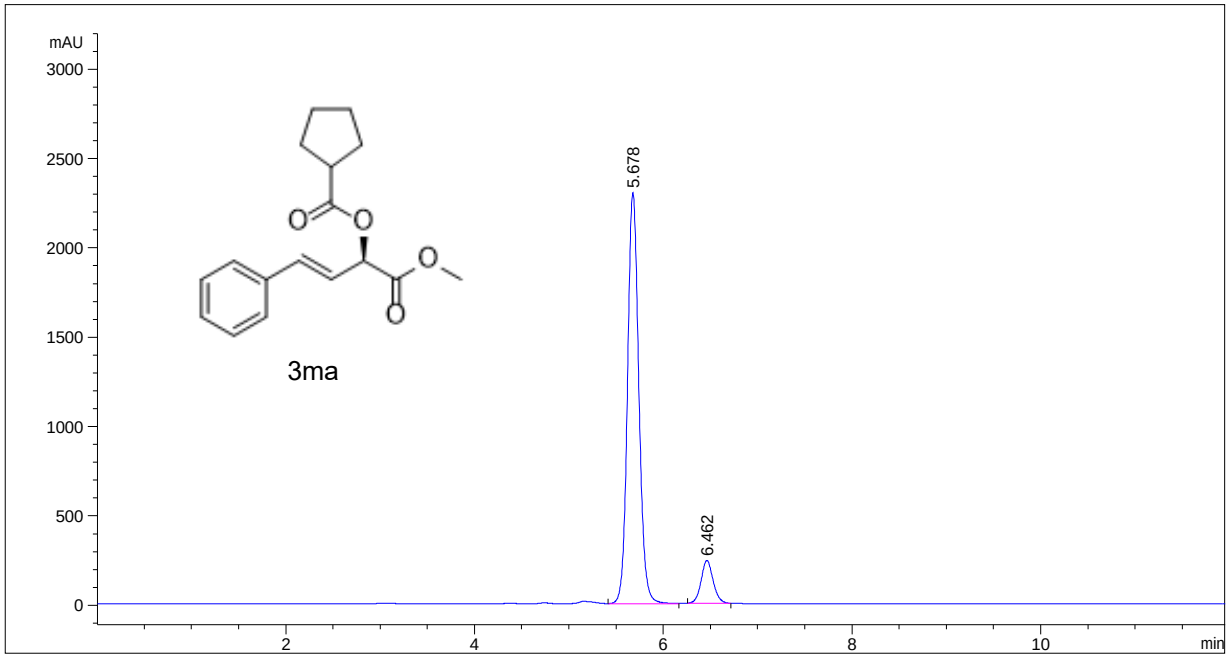


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.833	BV R	0.1327	5576.90283	639.57050	92.7884
2	6.275	VB E	0.1421	433.44193	45.91528	7.2116

Daicel Chiralpak IA column, n-hexane/i-PrOH= 90/10, flow rate= 2ml/min, l= 225 nm

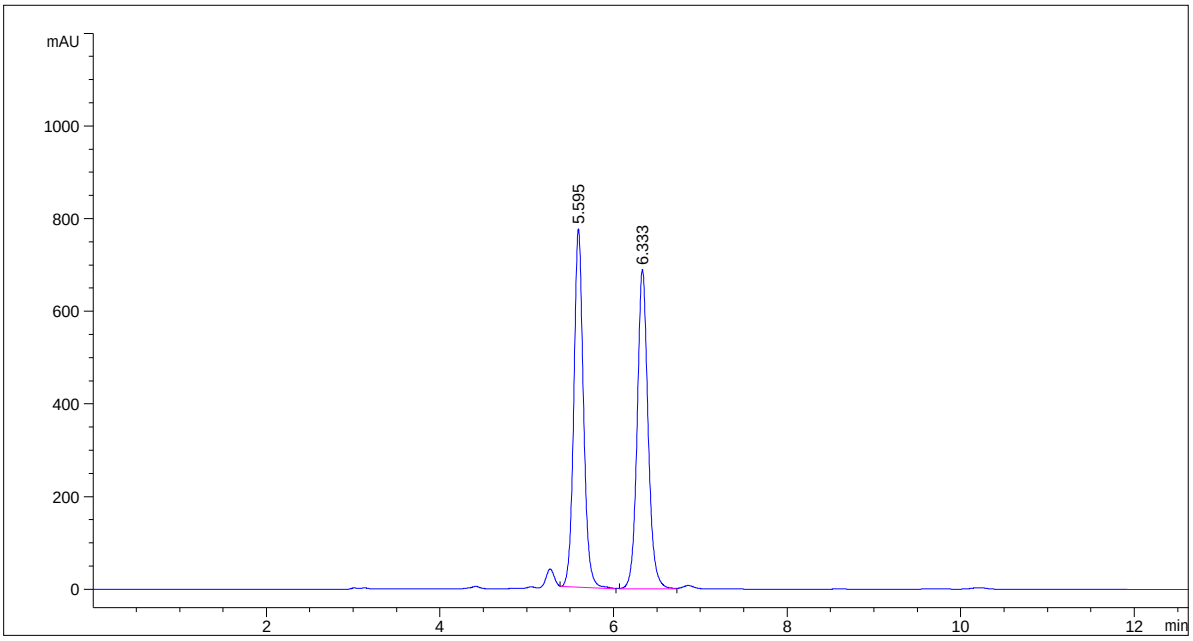


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.582	BB	0.1259	1.73125e4	2107.05591	49.6231
2	6.312	BB	0.1409	1.75755e4	1918.53528	50.3769

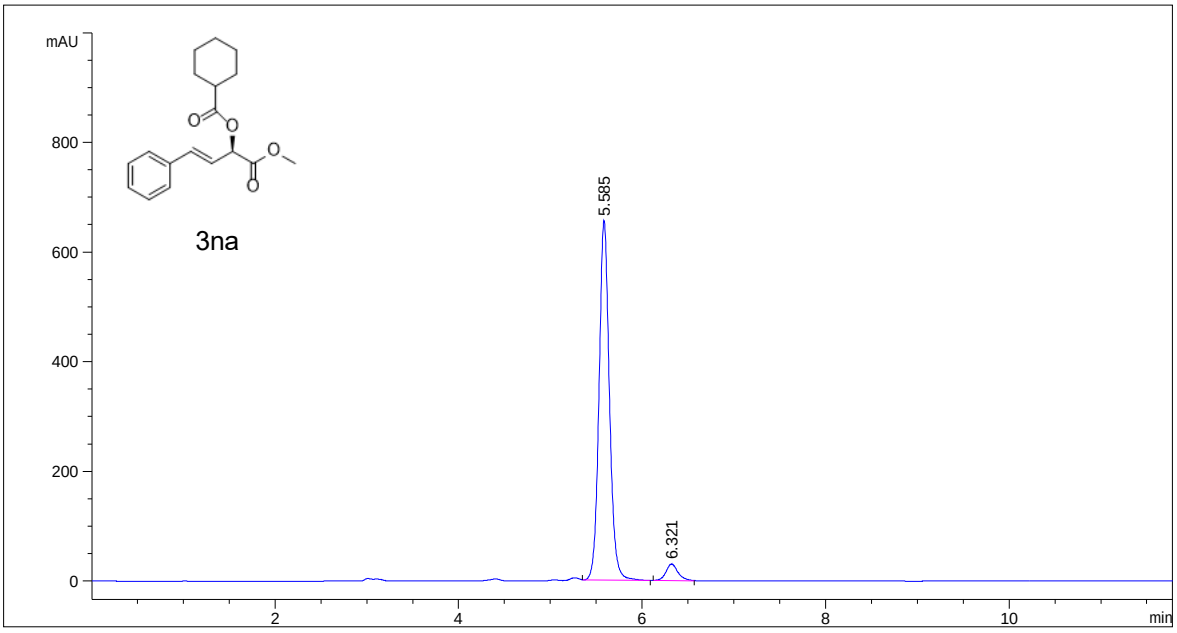


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.678	MM	0.1392	1.92211e4	2301.38574	89.9934
2	6.462	MM	0.1481	2137.24634	240.56883	10.0066

Daicel Chiralpak IA column, n-hexane/i-PrOH= 90/10, flow rate= 1ml/min, l= 225 nm

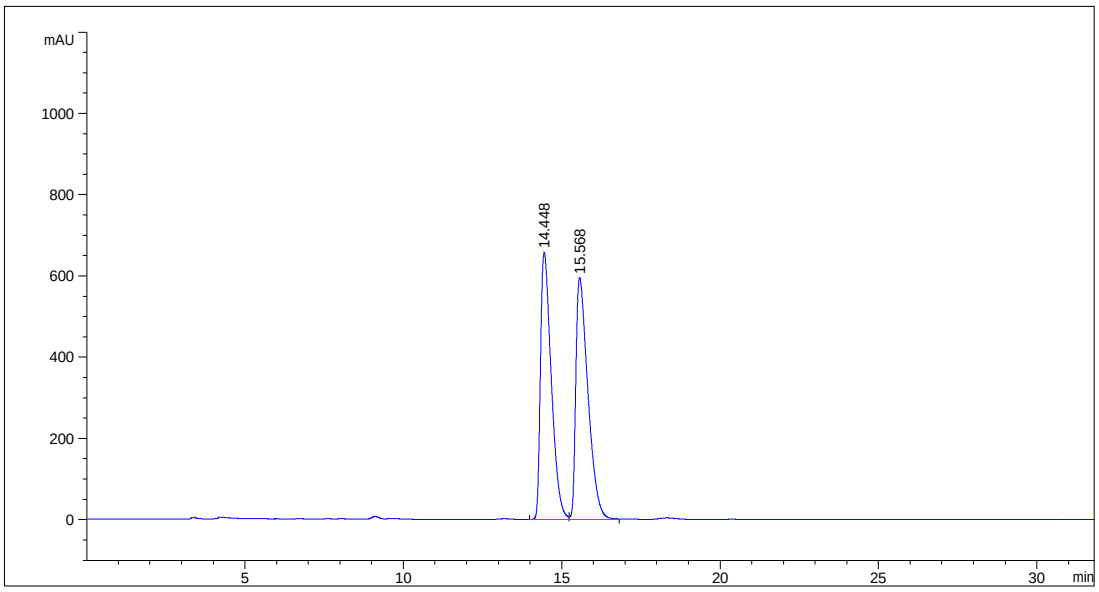


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.595	MM	0.1288	5979.01563	773.52271	49.8768
2	6.333	MM	0.1454	6008.55371	688.88965	50.1232

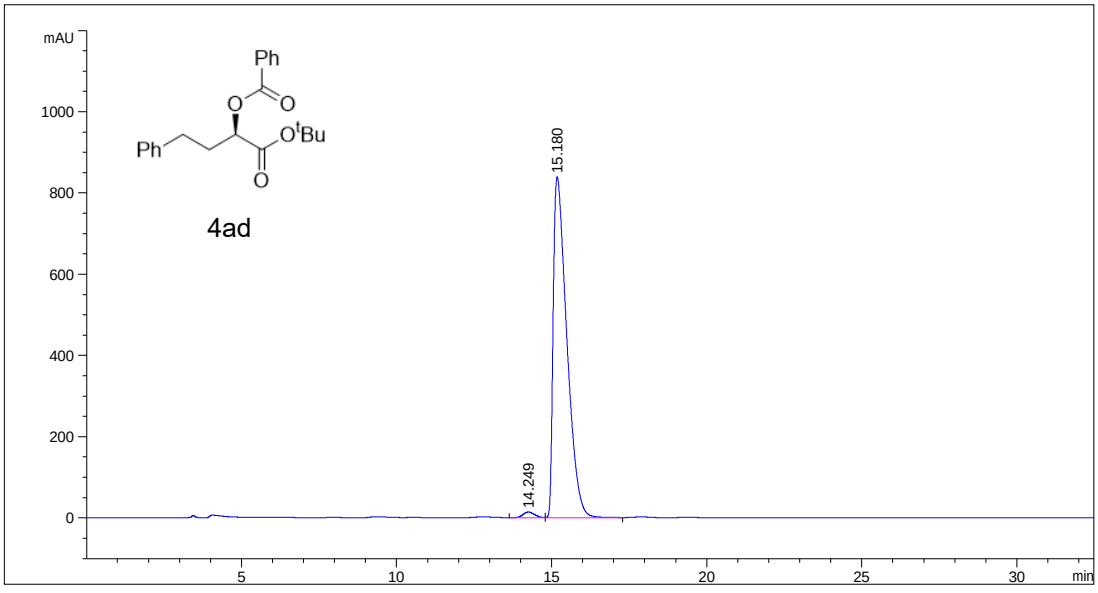


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.585	MM	0.1310	5160.92969	656.56628	94.8532
2	6.321	MM	0.1539	280.03644	30.32376	5.1468

Daicel Chiralpak IA column, n-hexane/i-PrOH= 90/10, flow rate= 1ml/min, l= 225 nm

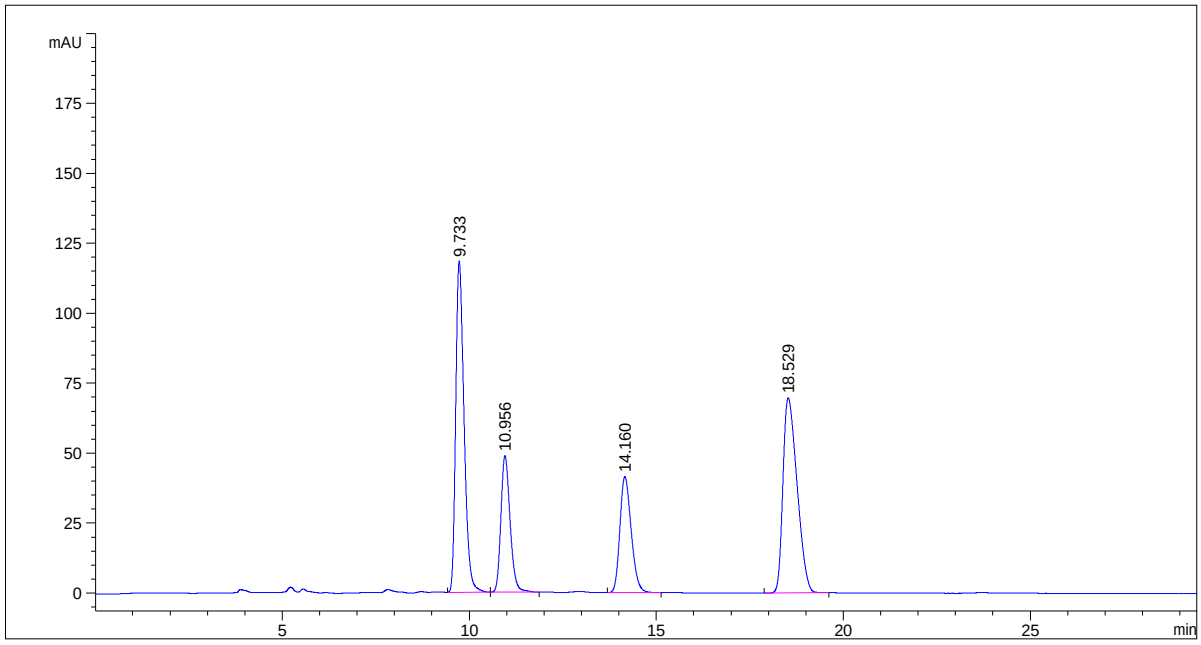


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.448	BV	0.3606	1.55231e4	657.09741	49.4890
2	15.568	MF	0.4440	1.58437e4	594.68665	50.5110

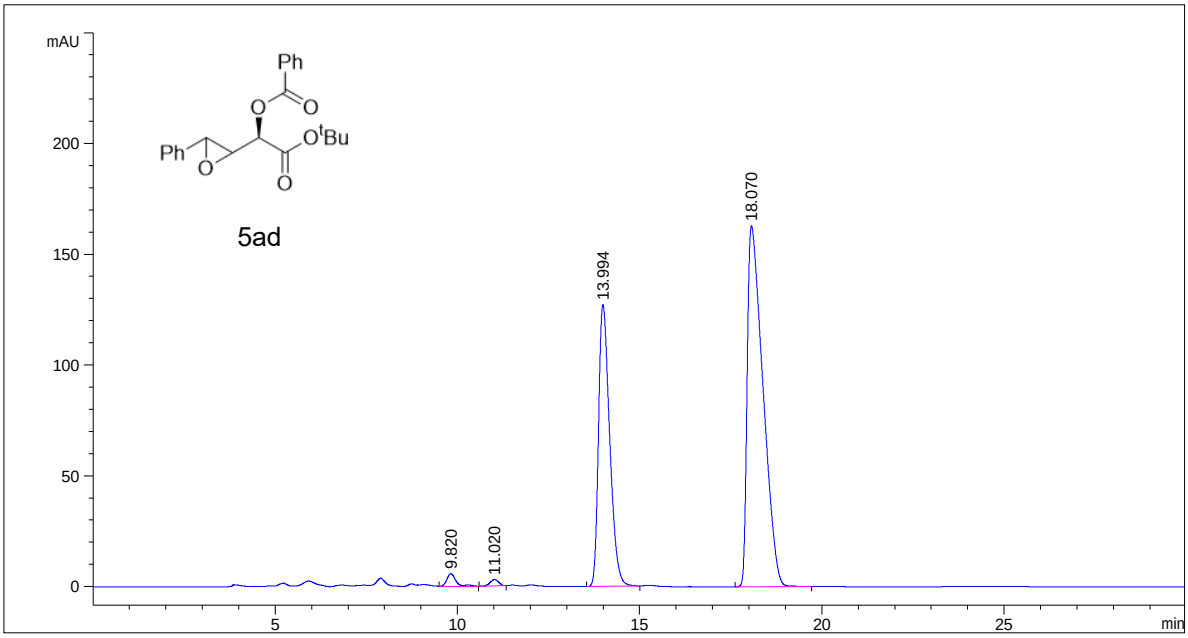


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.249	BV	0.4079	360.85562	13.89896	1.3919
2	15.180	VB	0.4613	2.55650e4	839.39697	98.6081

Daicel Chiralpak IA column, n-hexane/i-PrOH= 90/10, flow rate= 1ml/min, l= 225 nm

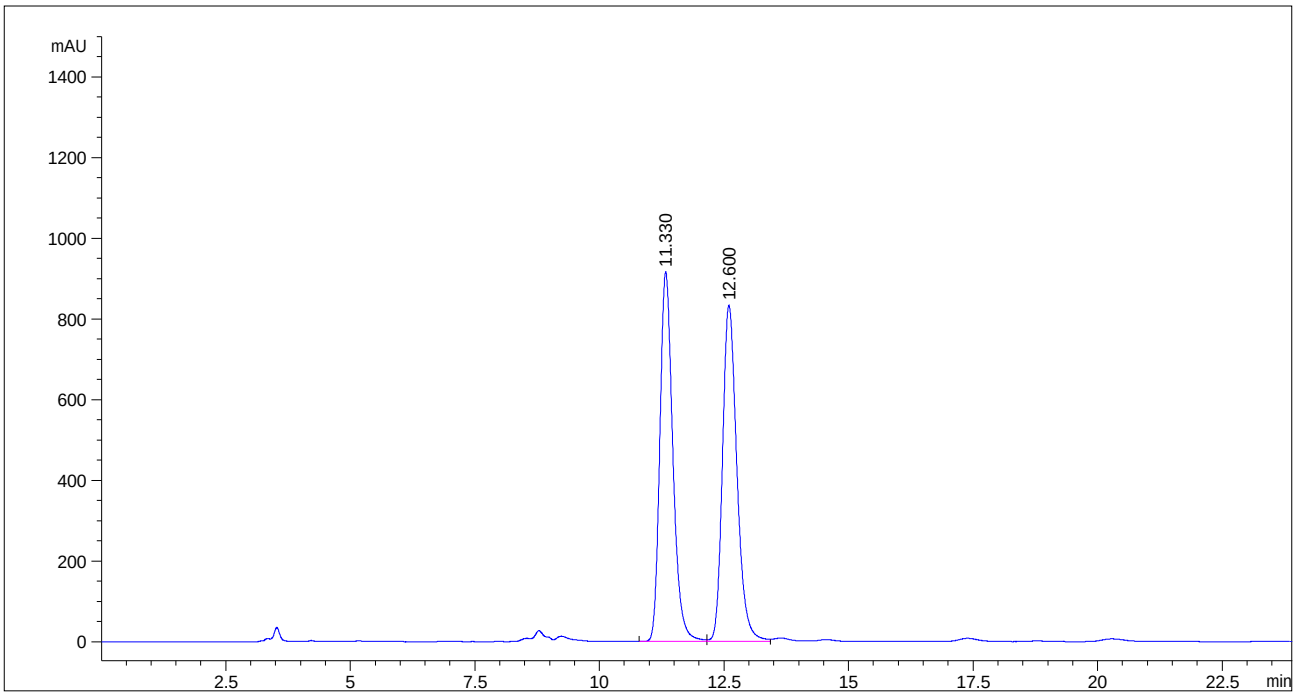


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.733	BB	0.2362	1819.68066	118.48602	33.9186
2	10.956	BB	0.2645	838.72797	48.81547	15.6338
3	14.160	BB	0.3267	876.62695	41.46204	16.3402
4	18.529	BB	0.4094	1829.80676	69.67362	34.1074

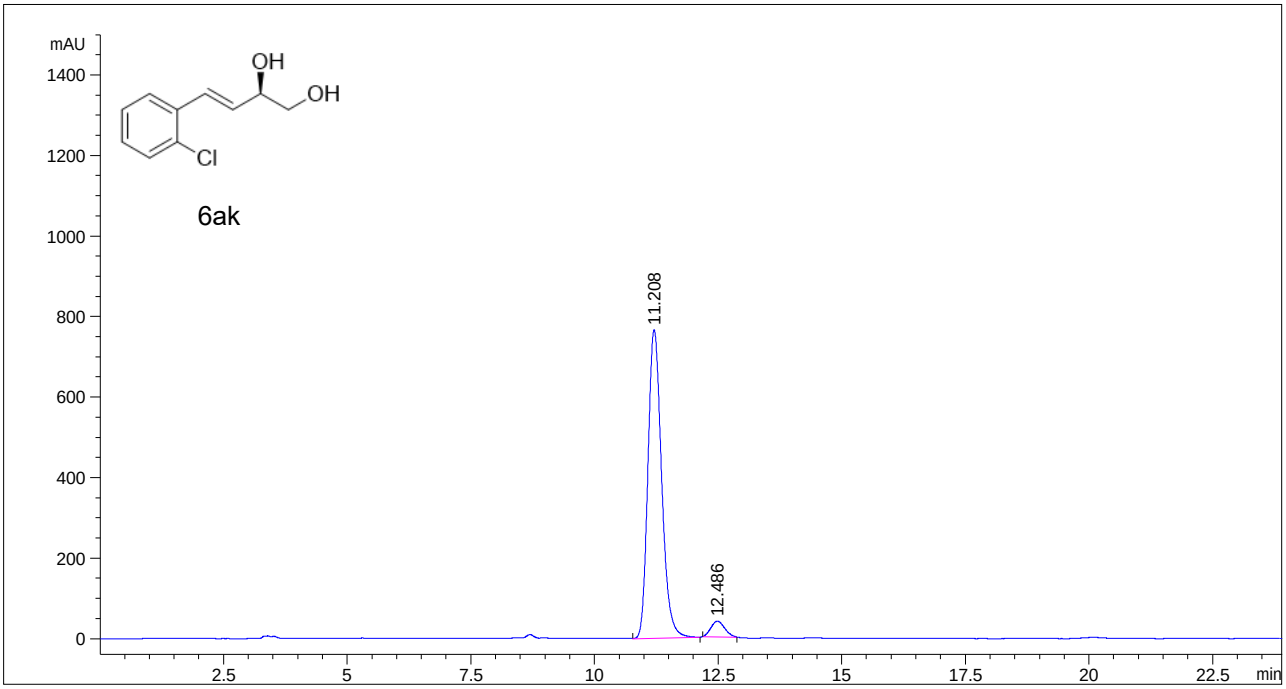


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.820	BV R	0.2603	97.76487	5.69523	1.2643
2	11.020	BB	0.2495	46.38356	2.88594	0.5998
3	13.994	BB	0.3259	2701.73730	127.16734	34.9395
4	18.070	BB	0.4658	4886.73535	162.97511	63.1964

Daicel Chiralpak IC column, n-hexane/i-PrOH= 90/10, flow rate= 1ml/min, l= 225 nm

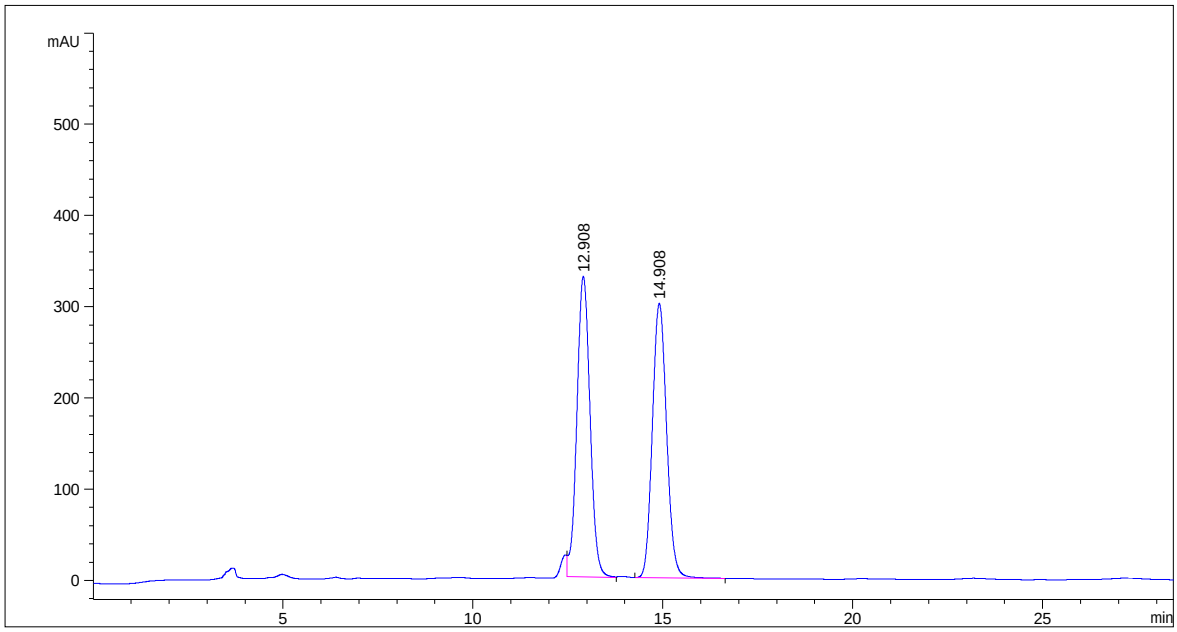


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.330	BV	0.2788	1.66289e4	915.96826	49.7630
2	12.600	MF	0.3355	1.67873e4	833.96619	50.2370

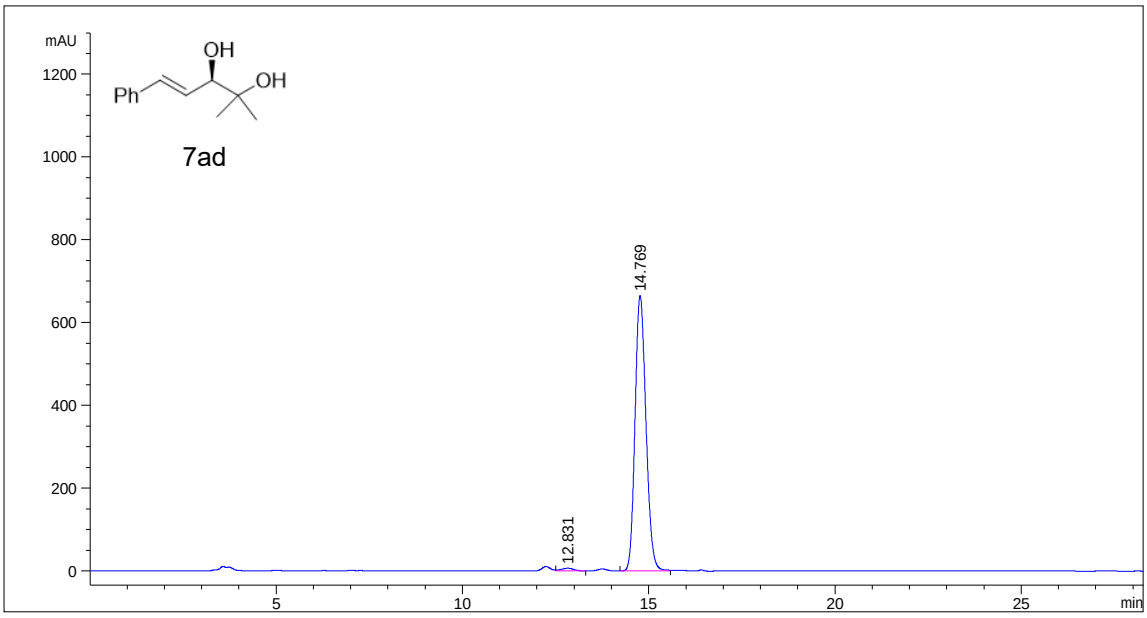


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.208	MM	0.3209	1.47702e4	767.03333	94.9998
2	12.486	MM	0.3276	777.40930	39.55107	5.0002

Daicel Chiralpak IA column, n-hexane/i-PrOH= 90/10, flow rate= 1ml/min, l= 225 nm

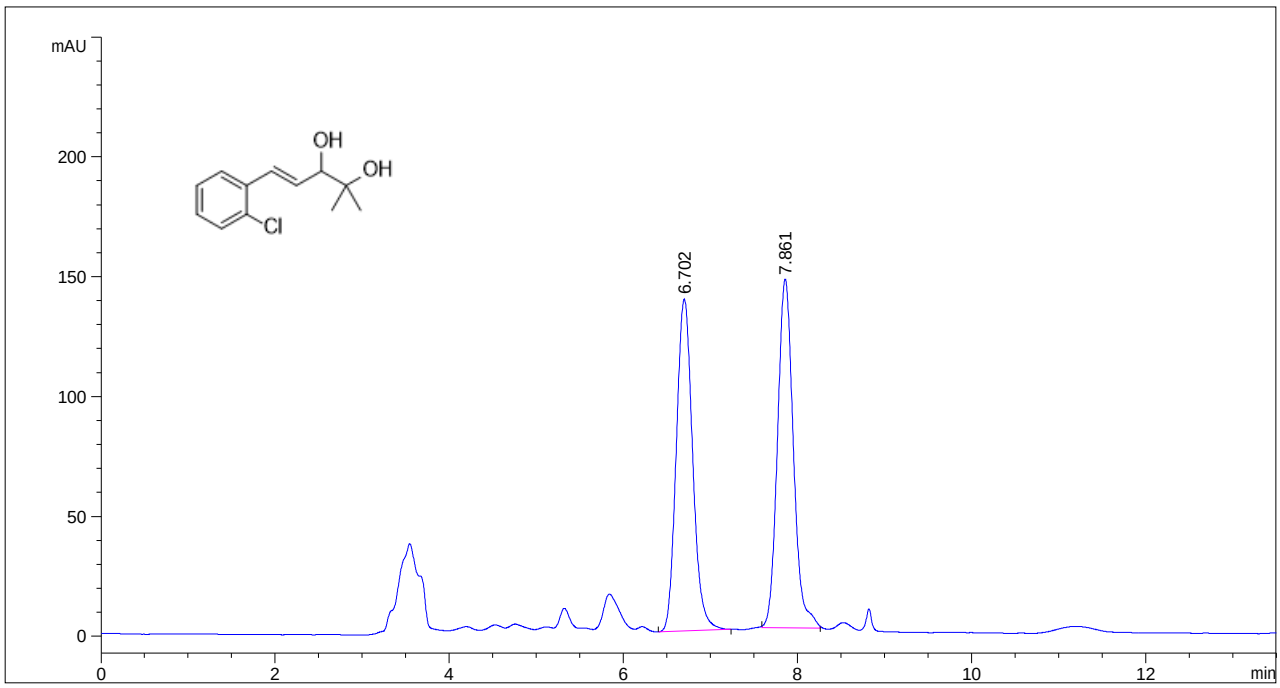


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.908	MM	0.4021	7944.22461	329.31006	50.3473
2	14.908	BB	0.4077	7834.63916	301.00024	49.6527

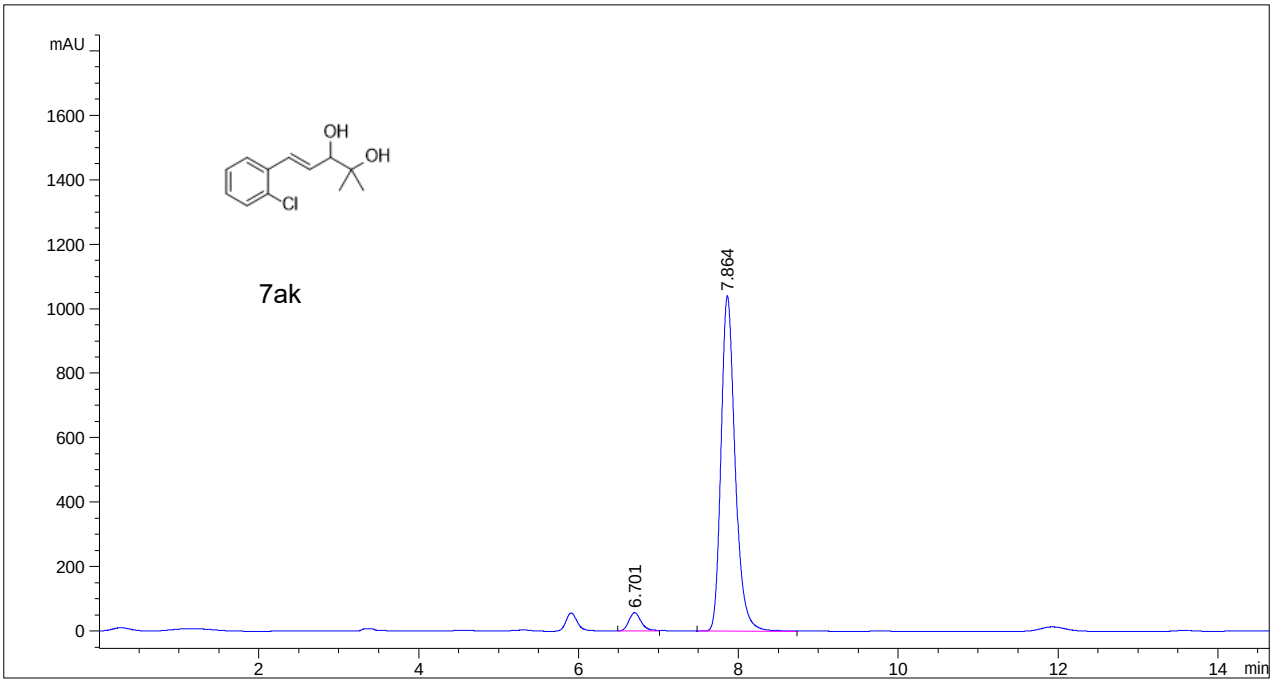


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.831	VB	0.3362	142.37741	6.38394	1.0393
2	14.769	MF	0.3399	1.35573e4	664.86224	98.9607

Daicel Chiralpak IC column, n-hexane/i-PrOH= 90/10, flow rate= 1ml/min, l= 225 nm



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.702	BB	0.2031	1805.69214	138.47121	49.5248
2	7.861	MM	0.2109	1840.34326	145.42366	50.4752



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.701	MF	0.1781	609.90961	57.09093	4.5461
2	7.864	MF	0.2051	1.28061e4	1040.84814	95.4539