

Cu-catalyzed highly selective reductive functionalization of 1,3-diene using H₂O as stoichiometric hydrogen atom donor

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Supporting Information

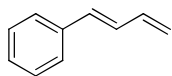
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1. General Considerations

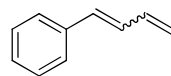
All manipulations were conducted with Schlenk tube. ^1H -NMR spectra were recorded on Bruker AVIII-400 spectrometers. Chemical shifts (in ppm) were referenced to tetramethylsilane ($\delta = 0$ ppm) in CDCl_3 as an internal standard. ^{13}C -NMR spectra were obtained by using the same NMR spectrometers and were calibrated with CDCl_3 ($\delta = 77.00$ ppm). ^{19}F -NMR spectra were obtained by the same NMR and CF_3COOH was employed as external standard for the ^{19}F -NMR measurement. IR spectra were recorded using a Bruker ALPHA. High resolution mass spectrometry (HRMS) data were obtained on a QTOF mass analyzer with electrospray ionization (ESI) through a Bruker Daltonicsmior OTOF-QII. Dry 1,2-dichloroethane was purchased from Energy Chemical. Substrates were purchased from Aldrich, TCI, Acros, Energy, Aladdin, or synthesized according to the procedures outlined below. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

2. Synthesis of Diene Substrates

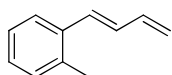
These substrates were prepared according to the corresponding literature reports. Analytical data (^1H NMR, ^{13}C NMR) matches with the corresponding literature.



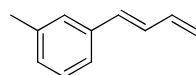
1a: (*E*)-buta-1,3-dien-1-ylbenzene¹



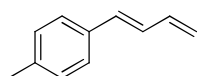
1a-mix: buta-1,3-dien-1-ylbenzene²



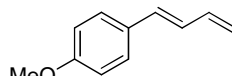
1b: (*E*)-1-(buta-1,3-dien-1-yl)-2-methylbenzene¹



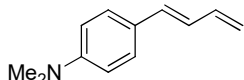
1c: (*E*)-1-(buta-1,3-dien-1-yl)-3-methylbenzene¹



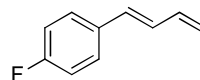
1d: (*E*)-1-(buta-1,3-dien-1-yl)-4-methylbenzene¹



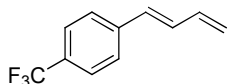
1e: (*E*)-1-(buta-1,3-dien-1-yl)-4-methoxybenzene¹



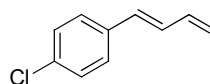
1f: (*E*)-4-(buta-1,3-dien-1-yl)-*N,N*-dimethylaniline³



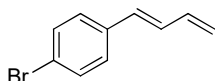
1g: (*E*)-1-(buta-1,3-dien-1-yl)-4-fluorobenzene³



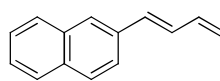
1h: (*E*)-1-(buta-1,3-dien-1-yl)-4-(trifluoromethyl)benzene⁴



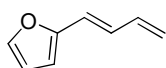
1i: (*E*)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene¹



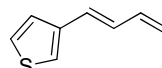
1j: (*E*)-1-bromo-4-(buta-1,3-dien-1-yl)benzene³



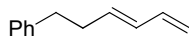
1l: (*E*)-2-(buta-1,3-dien-1-yl)naphthalene¹



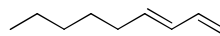
1m: (*E*)-2-(buta-1,3-dien-1-yl)furan¹



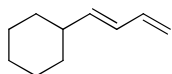
1n: (*E*)-3-(buta-1,3-dien-1-yl)thiophene⁵



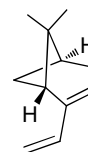
1o: (*E*)-hexa-3,5-dien-1-ylbenzene¹



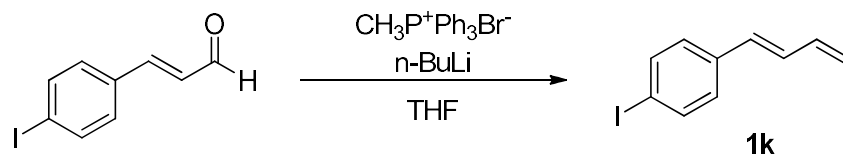
1p: (*E*)-nona-1,3-diene⁶



1q: (*E*)-buta-1,3-dien-1-ylcyclohexane¹



1r: (1*R*,5*S*)-6,6-dimethyl-2-vinylbicyclo[3.1.1]hept-2-ene⁷

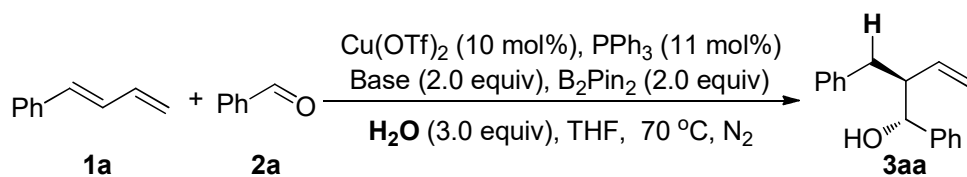


Preparation of (*E*)-1-(buta-1,3-dien-1-yl)-4-iodobenzene (**1k**):

A suspension of methyltriphenylphosphonium bromide (2.9 g, 8.1 mmol) in dry THF (30 ml) was cooled at 0°C with an ice bath under inert atmosphere. Then *n*-BuLi (3.2 ml, 2.5 M in *n*-hexane, 8.1 mmol) was added dropwise. After stirring for 30 min, the solution of (*E*)-3-(4-iodophenyl)acrylaldehyde (1.4g, 5.4 mmol) in THF (20 ml) was added dropwise. Then the reaction mixture was warmed to room temperature for one hour. Then the reaction mixture was quenched with sat. NH_4Cl aq. (20 mL), and extracted by EtOAc (20 mL $\times$ 3). The combined organic layers were dried over MgSO_4 and concentrated in vacuo. The residue was purified by silica-gel column chromatography to give the yellow solid **1k** (0.89g, 64%).

3. The effect of different reaction conditions

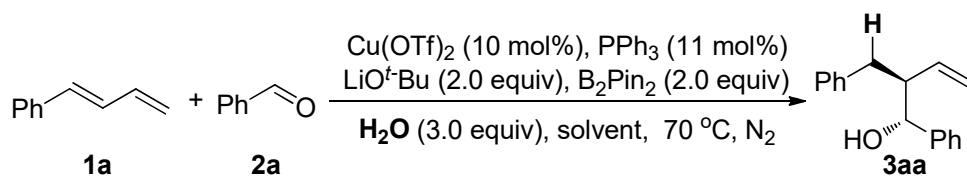
Table S1. The effect of different base ^a



entry	base	yield (%) ^b	dr
1	LiO ^t -Bu	76	5:1
2	NaO ^t -Bu	52	4:1
3	KO ^t -Bu	69	5:1
4	LiOH	63	1:1
5	LiOMe	66	2:1
6	Li ₂ CO ₃	70	4:1
7	Na ₂ CO ₃	64	3:1
8	KOEt	89	1:1
9	KOAc	30	5:1

^a **1a** (0.25 mmol), **2a** (0.5 mmol), B₂Pin₂ (0.5 mmol), base (0.5 mmol), Cu(OTf)₂ (10 mol %), PPh₃ (11 mol%), H₂O (3.0 equiv), THF (1.5 ml). ^b Isolated yield of both diastereomers, dr was determined by ¹H-NMR.

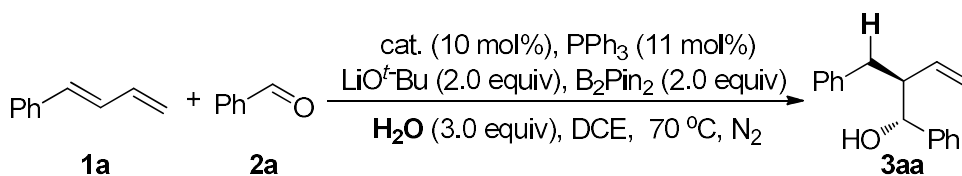
Table S2. The effect of different solvent ^a



entry	solvent	yield (%) ^b	dr
1	1,4-dioxane	64	4:1
2	toluene	80	9:1
3	DMA	64	1:1
4	DCE	93	>20:1
5	CHCl ₃	58	10:1
6	DMSO	58	3:1
7	Ph-Cl	89	15:1
8	isopropanol	81	2:1

^a **1a** (0.25 mmol), **2a** (0.5 mmol), B₂Pin₂ (0.5 mmol), LiO^tBu (0.5 mmol), Cu(OTf)₂ (10 mol%), PPh₃ (11 mol%), H₂O (3.0 equiv), solvent (1.5 ml). ^b Isolated yield of both diastereomers, dr was determined by ¹H-NMR.

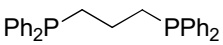
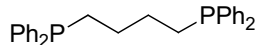
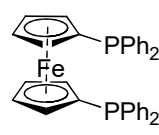
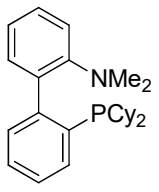
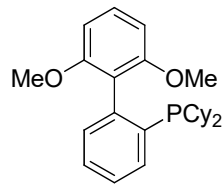
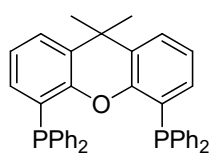
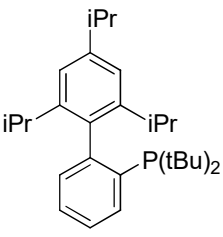
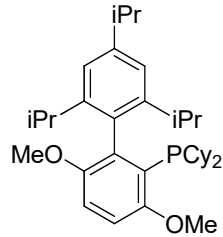
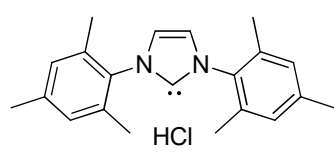
Table S3. The effect of different catalyst ^a



entry	solvent	yield (%) ^b	dr
1	Cu(acac) ₂	76	>20:1
2	CuCl	78	>20:1
3	CuBr	88	>20:1
4	CuOAc	23	13:1
5	Cu(OH) ₂	14	11:1
6	CuI	74	>20:1

^a **1a** (0.25 mmol), **2a** (0.5 mmol), B₂Pin₂ (0.5 mmol), LiO^tBu (0.5 mmol), cat. (10 mol%), PPh₃ (11 mol%), H₂O (3.0 equiv), DCE (1.5 ml). ^b Isolated yield of both diastereomers, dr was determined by ¹H-NMR.

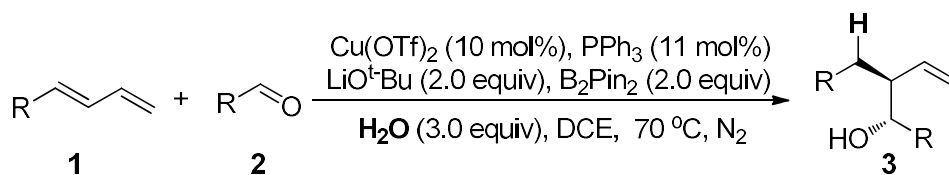
Table S4. The effect of different ligand ^{a,b}

$ \begin{array}{c} \text{Ph} \text{---} \text{CH} \text{=CH} \text{CH}_2 \\ \mathbf{1a} \end{array} + \begin{array}{c} \text{Ph} \text{---} \text{CHO} \\ \mathbf{2a} \end{array} \xrightarrow[\text{H}_2\text{O (3.0 equiv), DCE, 70 }^\circ\text{C, N}_2]{\text{Cu(OTf)}_2 \text{ (10 mol\%), ligand (11 mol\%)}, \text{LiO}^t\text{Bu (2.0 equiv), B}_2\text{Pin}_2 \text{ (2.0 equiv)}} \begin{array}{c} \text{H} \\ \\ \text{Ph} \text{---} \text{CH} \text{---} \text{CH} \text{---} \text{CH}_2 \\ \quad \\ \text{HO} \quad \text{Ph} \\ \mathbf{3aa} \end{array} $		
 85% (10:1)	 85% (10:1)	 83% (12:1)
 79% (>20:1)	 91% (>20:1)	 84% (2:1)
 70% (9:1)	 35% (7:1)	 85% (>20:1)

^a **1a** (0.25 mmol), **2a** (0.5 mmol), B₂Pin₂ (0.5 mmol), LiO^tBu (0.5 mmol), Cu(OTf)₂ (10 mol%), ligand (11 mol%), H₂O (3.0 equiv), DCE (1.5 ml). ^b Isolated yield of both diastereomers, dr were determined by ¹H-NMR.

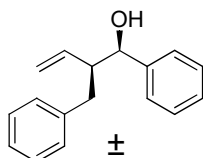
4. General procedure for the reaction

General procedure for Cu-catalyzed highly selective reductive functionalization of 1,3-diene:

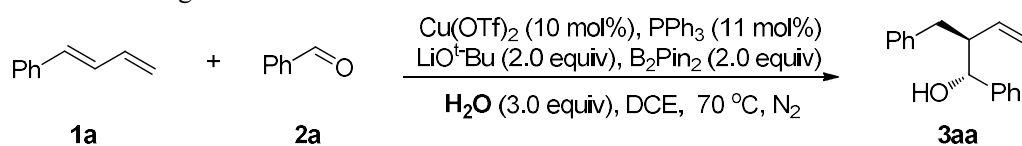


A stirring bar containing oven dried 25-ml Schlenk tube was charged with Cu(OTf)₂ (9.1mg, 0.025 mmol, 10 mol%), PPh₃ (7.2mg, 0.0275 mmol, 11 mol%), B₂Pin₂ (127 mg, 0.50 mmol, 2.0 equiv) and LiO^tBu (40mg, 0.50 mmol, 2.0 equiv). The tube was then evacuated and back-filled under a N₂ flow (this sequence was repeated three times). Diene **1** (0.25 mmol, 1.0 equiv), water (13.5μL, 3.0 equiv), anhydrous DCE (1.0 ml) were added subsequently under N₂. The reaction mixture was stirred for 1.5 h at r.t. Then the solution of **2** (0.50 mmol, 2.0 equiv) in anhydrous DCE (0.5 ml) were added into the reaction system. The reaction was stirred at 70 °C for 24h. After cooling to r.t, the reaction mixture diluted with EtOAc(10 ml) and H₂O (10 ml). Then it was extracted with EtOAc (10 ml × 3). The organic layer was combined and dried over Na₂SO₄. Then filtered and concentrated by rotary evaporation. The residue was purified by silica gelcolumn chromatography to afford the product **3**.

Based on the literature *J. Am. Chem. Soc.* **2013**, *135*, 6026, the configuration of the product **3aa** (racemic) is shown as bellow:



Procedure for large scale reaction



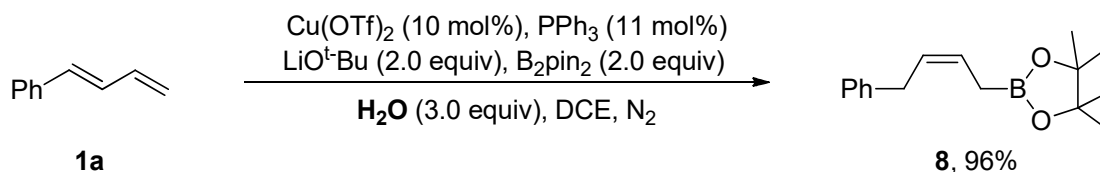
1.5 g, 11.5 mmol 2.4 g, 23 mmol

75 % yield, >20:1 dr, 2g

The general procedure was followed using **1a** (1.5 g, 11.5 mmol, 1.0 equiv), **2a** (2.44 g, 23 mmol, 2.0 equiv), Cu(OTf)₂ (416 mg, 1.15 mmol, 10 mol%), PPh₃ (332 mg, 1.27 mmol, 11 mol%), B₂Pin₂ (5.84 g, 23 mmol, 2.0 equiv), LiO^{*t*}Bu (1.84 g, 23 mmol, 2.0 equiv), water (0.62 mL, 3.0 equiv), anhydrous DCE (69 mL) to afford **3aa** (2 g, 75%, >20:1 dr).

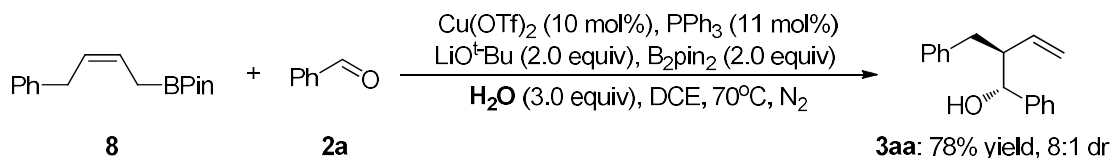
5. Control experiments

5-1. The reaction without aldehyde.



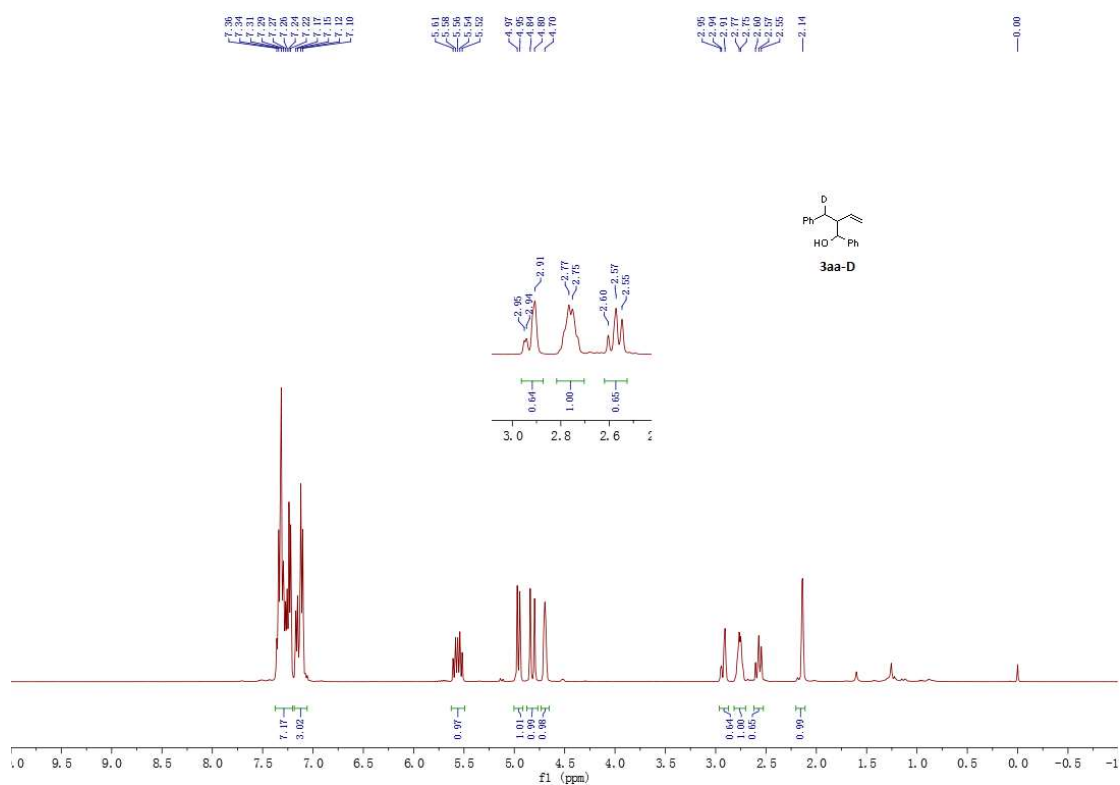
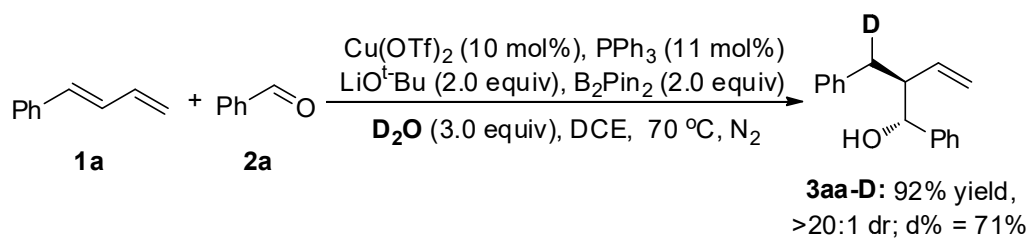
A stirring bar containing oven dried 25-ml Schlenk tube was charged with Cu(OTf)_2 (9.1mg, 0.025 mmol, 10 mol%), PPh_3 (7.2mg, 0.0275 mmol, 11 mol%), B_2Pin_2 (127 mg, 0.50 mmol, 2.0 equiv) and LiO^tBu (40mg, 0.50 mmol, 2.0 equiv). The tube was then evacuated and back-filled under a N_2 flow (this sequence was repeated three times). Diene **1a** (33 mg, 0.25 mmol), water (13.5 μL , 3.0 equiv), anhydrous DCE (1.0 ml) were added subsequently under N_2 condition. The reaction mixture was stirred for 1.5 h at room temperature and diluted with EtOAc (10 ml) and H_2O (10 ml). Then it was extracted with EtOAc (10 ml $\times$ 3). The organic layer was combined and dried over Na_2SO_4 , filtered and concentrated by rotary evaporation. The residue was purified by silica gel column chromatography to afford the product **8** (62mg, 96%). Spectral data matches the cited literature.^[8,9] **$^1\text{H-NMR}$** (CDCl_3 , 400 MHz) δ : 7.28-7.24 (m, 2H), 7.22-7.15 (m, 3H), 5.68-5.62 (m, 1H), 5.60-5.54 (m, 1H), 3.39 (d, J = 8.0 Hz, 2H), 1.80 (d, J = 8.0 Hz, 2H), 1.25 (s, 12H); **$^{13}\text{C NMR}$** (CDCl_3 , 100 MHz) δ : 141.2, 128.4, 128.2, 128.0, 125.7, 125.2, 83.2, 33.3, 24.7 ppm; **IR** (neat): 3022, 2980, 2928, 1328, 1145, 968, 739 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{16}\text{H}_{23}\text{BO}_2\text{Na}$ ($M + \text{Na}$) $^+$: 281.1689, found 281.1693.

5-2. The reaction of **8** with **2a**.

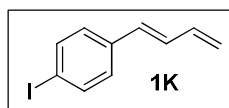


A stirring bar containing oven dried 25-ml Schlenk tube was charged with Cu(OTf)_2 (9.1mg, 0.025 mmol, 10 mol%), PPh_3 (7.2mg, 0.0275 mmol, 11 mol%), B_2Pin_2 (127 mg, 0.50 mmol, 2.0 equiv) and LiO^tBu (40mg, 0.50 mmol, 2.0 equiv). The tube was then evacuated and back-filled under a N_2 flow (this sequence was repeated three times). The intermediate **8** (65 mg, 0.25 mmol, 1.0 equiv), water (13.5 μL , 3.0 equiv), anhydrous DCE (1.0 ml) were added subsequently under N_2 condition. The reaction mixture was stirred for 1.5 h at r.t. and then **2a** (53 mg, 0.50 mmol, 2.0 equiv) dissolved in anhydrous DCE (0.5 ml) were added, the tube was stirred at 70 °C for 24h. After cooling to r.t, the reaction mixture diluted with EtOAc (10 ml) and H_2O (10 ml). Then it was extracted with EtOAc (10 ml $\times$ 3). The organic layer was combined and dried over Na_2SO_4 , filtered and concentrated by rotary evaporation. The residue was purified by silica gel column chromatography to afford the product **3aa** (46mg, 78%, 8:1 dr).

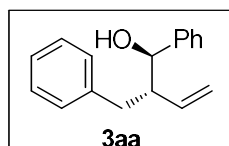
5-3. Deuterium labeling experiment



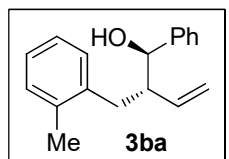
6. Analytical data for compounds



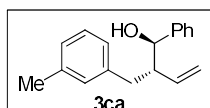
(*E*)-1-(buta-1,3-dien-1-yl)-4-iodobenzene **(1k)**: ¹H-NMR (CDCl₃, 400 MHz) δ : 7.63 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 6.78 (dd, J_1 = 16 Hz, J_2 = 12 Hz, 1H), 6.53-6.44 (m, 2H), 5.36 (d, J = 20 Hz, 1H), 5.21 (d, J = 12 Hz, 1H); ¹³C-NMR (CDCl₃, 100 MHz) δ : 137.6, 136.8, 136.6, 131.6, 130.4, 128.1, 118.4, 92.8 ppm; IR (neat): 3033, 3006, 2962, 1481, 1416, 1003, 811 cm⁻¹; HRMS (ESI-TOF) m/z calcd for C₁₀H₉INa (M + Na)⁺: 278.9647, found 278.9651.



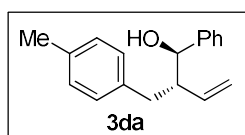
2-benzyl-1-phenylbut-3-en-1-ol (**3aa**):^[10] The general procedure was followed using (*E*)-buta-1,3-dien-1-ylbenzene (**1a**, 33 mg, 0.25 mmol) and benzaldehyde (**2a**, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1:10) afforded product **3aa** as a colorless oil (56 mg, 93% yield, >20:1 dr): R_f = 0.5 (EtOAc : petroleum ether = 1 : 5); ¹H-NMR (CDCl₃, 400 MHz) δ : 7.33-7.21 (m, 7H), 7.16-7.10 (m, 3H), 5.60-5.51 (m, 1H), 4.95 (d, J = 8.0 Hz, 1H), 4.81 (d, J = 16 Hz, 1H), 4.70-4.67 (m, 1H), 2.93 (dd, J_1 = 16 Hz, J_2 = 4.0 Hz, 1H), 2.80-2.73 (m, 1H), 2.60-2.54 (m, 1H), 2.19-2.11 (m, 1H); ¹³C-NMR (CDCl₃, 100 MHz) δ : 142.3, 140.0, 137.5, 129.2, 128.1, 128.0, 127.5, 126.7, 125.8, 117.7, 76.3, 52.7, 36.1 ppm; IR (neat): 3417, 3081, 3029, 2924, 1494, 1452, 916 cm⁻¹; HRMS (ESI-TOF) m/z calcd for C₁₇H₁₈ONa (M + Na)⁺: 261.1255, found 261.1242.



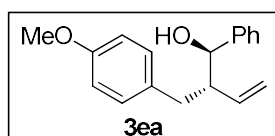
2-(2-methylbenzyl)-1-phenylbut-3-en-1-ol (**3ba**): The general procedure was followed using (*E*)-1-(buta-1,3-dien-1-yl)-2-methylbenzene (**1b**, 36 mg, 0.25 mmol) and benzaldehyde (**2a**, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product **3ba** as a colorless oil (56 mg, 88% yield, >20:1 dr): R_f = 0.5 (EtOAc : petroleum ether = 1 : 5); ¹H-NMR (CDCl₃, 400 MHz) δ : 7.35-7.27 (m, 5H), 7.06-7.02 (m, 4H), 5.66-5.57 (m, 1H), 4.93 (d, J = 8.0 Hz 1H), 4.77-4.73 (m, 2H), 2.97-2.93 (m, 1H), 2.69-2.66 (m, 1H), 2.52-2.46 (m, 1H), 2.21 (brs, 1H), 2.15 (s, 3H); ¹³C-NMR (CDCl₃, 100 MHz) δ : 142.4, 138.3, 137.7, 136.2, 130.0, 129.9, 128.1, 127.5, 126.6, 125.8, 125.4, 117.6, 76.7, 51.8, 33.0, 19.4 ppm; IR (neat): 3427, 3065, 3025, 2925, 1491, 1454, 746 cm⁻¹; HRMS (ESI-TOF) m/z calcd for C₁₈H₂₀ONa (M + Na)⁺: 275.1412, found 275.1413.



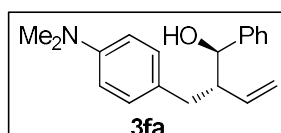
2-(3-methylbenzyl)-1-phenylbut-3-en-1-ol (**3ca**): The general procedure was followed using (*E*)-1-(buta-1,3-dien-1-yl)- 3-methyl-benzene (**1c**, 36 mg, 0.25 mmol) and benzaldehyde (**2a**, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product **3ca** as a colorless oil (50 mg, 78% yield, >20:1 dr): R_f = 0.5 (EtOAc : petroleum ether = 1:5); ¹H-NMR (CDCl₃, 400 MHz) δ : 7.35-7.25 (m, 5H), 7.14-7.11 (m, 1H), 6.97-6.95 (m, 1H), 6.92-6.90 (m, 2H), 5.60-5.51 (m, 1H), 4.96 (d, J = 8.0 Hz, 1H), 4.84 (d, J = 16 Hz, 1H), 4.73-4.63 (m, 1H), 2.90-2.86 (m, 1H), 2.80-2.73 (m, 1H), 2.57-2.51 (m, 1H), 2.29 (s, 3H), 2.14(brs, 1H); ¹³C-NMR (CDCl₃, 100 MHz) δ : 142.3, 139.9, 137.7, 137.6, 130.0, 128.1, 127.9, 127.5, 126.8, 126.5, 126.3, 117.6, 76.4, 52.6, 36.1, 21.4 ppm; IR (neat): 3415, 3062, 3028, 2920, 1490, 1452, 701 cm⁻¹; HRMS (ESI-TOF) m/z calcd for C₁₈H₂₀ONa (M + Na)⁺: 275.1412, found 275.1413.



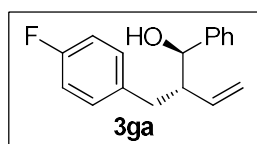
2-(4-methylbenzyl)-1-phenylbut-3-en-1-ol (**3da**): The general procedure was followed using (*E*)-1-(buta-1,3-dien-1-yl)-4-methyl-benzene (**1d**, 36 mg, 0.25 mmol) and benzaldehyde (**2a**, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product **3da** as a colorless oil (32 mg, 51% yield, >20:1 dr): R_f = 0.5 (EtOAc : petroleum ether = 1 : 5); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 7.36-7.25 (m, 5H), 7.05 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 8.0 Hz, 2H), 5.60-5.51 (m, 1H), 4.97 (d, J = 12 Hz, 1H), 4.84 (d, J = 16 Hz, 1H), 4.69 (d, J = 4.0 Hz, 1H), 2.90-2.85 (m, 1H), 2.79-2.72 (m, 1H), 2.57-2.51 (m, 1H), 2.29 (s, 3H), 2.15 (brs, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 142.3, 137.6, 136.8, 135.2, 129.1, 128.8, 128.1, 127.5, 126.8, 117.7, 76.3, 52.7, 35.7, 21.0 ppm; **IR** (neat): 3407, 3026, 2978, 2921, 1514, 1451, 702 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{18}\text{H}_{20}\text{ONa}$ ($\text{M} + \text{Na}$) $^+$: 275.1412, found 275.1400.



2-(4-methoxybenzyl)-1-phenylbut-3-en-1-ol (**3ea**): The general procedure was followed using (*E*)-1-(buta-1,3-dien-1-yl)-4-methoxybenzene (**1e**, 41 mg, 0.25 mmol) and benzaldehyde (**2a**, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product **3ea** as a colorless solid (52 mg, 78% yield, >20:1 dr): R_f = 0.4 (EtOAc : petroleum ether = 1 : 5); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 7.35-7.25 (m, 5H), 7.02 (d, J = 8.0 Hz, 2H), 6.78 (d, J = 8.0 Hz, 2H), 5.59-5.50 (m, 1H), 4.96 (d, J = 12 Hz, 1H), 4.82 (d, J = 16 Hz, 1H), 4.67 (d, J = 4.0 Hz, 1H), 3.74 (s, 3H), 2.86 (dd, J_1 = 12 Hz, J_2 = 4.0 Hz, 1H), 2.73-2.69 (m, 1H), 2.55-2.50 (m, 1H), 2.21 (brs, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 157.6, 142.3, 137.7, 132.0, 130.1, 128.1, 127.5, 126.7, 117.7, 113.4, 76.3, 55.1, 52.8, 35.3 ppm; **IR** (neat): 3383, 3031, 2919, 2835, 1512, 1245, 702 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{18}\text{H}_{20}\text{O}_2\text{Na}$ ($\text{M} + \text{Na}$) $^+$: 291.1361, found 291.1359.

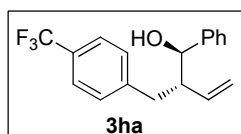


2-(4-(dimethylamino)benzyl)-1-phenylbut-3-en-1-ol (**3fa**): The general procedure was followed using (*E*)-4-(buta-1,3-dien-1-yl)-*N,N*-dimethylaniline (**1f**, 43 mg, 0.25 mmol) and benzaldehyde (**2a**, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 5) afforded product **3fa** as a yellow oil (48.5 mg, 69% yield, >20:1 dr): R_f = 0.3 (EtOAc : petroleum ether = 1 : 5); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 7.35-7.24 (m, 5H), 7.00 (d, J = 8.0 Hz, 2H), 6.65 (d, J = 8.0 Hz, 2H), 5.60-5.51 (m, 1H), 4.97 (d, J = 8.0 Hz, 1H), 4.86 (d, J = 16 Hz, 1H), 4.67 (d, J = 4.0 Hz, 1H), 2.88 (s, 6H), 2.82-2.70 (m, 2H), 2.54-2.49 (m, 1H), 2.23 (brs, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 148.9, 142.3, 137.9, 129.8, 128.0, 127.9, 127.4, 126.8, 117.5, 112.7, 76.2, 52.7, 40.8, 35.3 ppm; **IR** (neat): 3419, 3069, 3028, 2799, 1952, 1614, 702 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{18}\text{H}_{21}\text{O}_2(\text{M} + \text{H})^+$: 282.1858, found 282.1855.

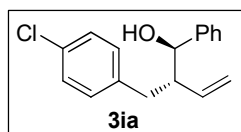


2-(4-fluorobenzyl)-1-phenylbut-3-en-1-ol (**3ga**): The general procedure was followed using (*E*)-1-(buta-1,3-dien-1-yl)-4-fluorobenzene (**1g**, 37 mg, 0.25 mmol) and benzaldehyde (**2a**, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product **3ga** as a colorless oil (53 mg, 83% yield, >20:1 dr): R_f = 0.5

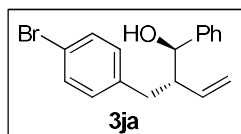
(EtOAc : petroleum ether = 1 : 5); **¹H-NMR** (CDCl₃, 400 MHz) δ : 7.36-7.25 (m, 5H), 7.05 (t, J = 6.0 Hz, 2H), 6.91 (t, J = 8.0 Hz, 2H), 5.58-5.49 (m, 1H), 4.95 (d, J = 12 Hz, 1H), 4.79 (d, J = 20 Hz, 1H), 4.68 (d, J = 4.0 Hz, 1H), 2.91 (dd, J_1 = 12 Hz, J_2 = 4.0 Hz, 1H), 2.73-2.66 (m, 1H), 2.58-2.52 (m, 1H), 2.15 (brs, 1H); **¹³C-NMR** (CDCl₃, 100 MHz) δ : 161.2 (d, J = 242 Hz), 142.3, 137.4, 135.6 (d, J = 3 Hz), 130.6 (d, J = 8 Hz), 128.2, 127.6, 126.7, 117.9, 114.8 (d, J = 21 Hz), 76.4, 52.9, 35.3 ppm; **¹⁹F-NMR** (CDCl₃, 376 MHz) δ : -117.6; **IR** (neat): 3412, 3068, 3033, 2924, 1603, 1222, 703 cm⁻¹; **HRMS** (ESI-TOF) m/z calcd for C₁₇H₁₇FONa(M + Na)⁺: 279.1161, found 279.1159.



1-phenyl-2-(4-(trifluoromethyl)benzyl)but-3-en-1-ol (**3ha**): The general procedure was followed using (*E*)-1-(buta-1,3-dien-1-yl)-4-(trifluoromethyl)benzene (**1h**, 50 mg, 0.25 mmol) and benzaldehyde (**2a**, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product **3ha** as a colorless oil (59 mg, 77% yield, 16:1 dr): R_f = 0.5 (1:5EtOAc: petroleum ether); **¹H-NMR** (CDCl₃, 400 MHz) δ : 7.48 (d, J = 8.0 Hz, 2H), 7.36-7.26 (m, 5H), 7.20 (d, J = 8.0 Hz, 2H), 5.59-5.50 (m, 1H), 4.95 (d, J = 12 Hz, 1H), 4.77 (d, J = 16 Hz, 1H), 4.68 (d, J = 8.0 Hz, 1H), 3.03-3.00 (m, 1H), 2.74-2.72 (m, 1H), 2.65-2.62 (m, 1H), 2.23 (brs, 1H); **¹³C-NMR** (CDCl₃, 100 MHz) δ : 144.4, 142.2, 137.0, 129.6, 128.2, 127.7, 126.6, 124.9 (q, J = 4 Hz), 118.13, 76.4, 52.6, 35.9 ppm; **¹⁹F-NMR** (CDCl₃, 376 MHz) δ : -62.2 ppm; **IR** (neat): 3408, 3068, 3032, 2927, 1640, 1326, 703 cm⁻¹; **HRMS** (ESI-TOF) m/z calcd for C₁₈H₁₆F₃O (M - H)⁻: 305.1153, found 305.1152.

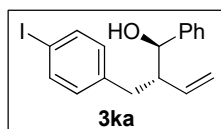


2-(4-chlorobenzyl)-1-phenylbut-3-en-1-ol (**3ia**): The general procedure was followed using (*E*)-1-(buta-1,3-dien-1-yl)-4-chlorobenzene (**1i**, 41 mg, 0.25 mmol) and benzaldehyde (**2a**, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product **3ia** as a yellow liquid (56 mg, 82% yield, >20:1 dr): R_f = 0.5 (EtOAc : petroleum ether = 1 : 5); **¹H-NMR** (CDCl₃, 400 MHz) δ : 7.35-7.25 (m, 5H), 7.19 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 8.0 Hz, 2H), 5.57-5.48 (m, 1H), 4.95 (d, J = 12 Hz, 1H), 4.78 (d, J = 16 Hz, 1H), 4.67 (d, J = 4.0 Hz, 1H), 2.91 (dd, J_1 = 12 Hz, J_2 = 4.0 Hz, 1H), 2.73-2.64 (m, 1H), 2.57-2.51 (m, 1H), 2.14 (brs, 1H); **¹³C-NMR** (CDCl₃, 100 MHz) δ : 142.3, 138.6, 137.3, 131.5, 130.6, 128.2, 128.1, 127.6, 126.6, 118.0, 76.4, 52.8, 35.5 ppm; **IR** (neat): 3411, 3066, 3030, 2924, 1491, 918, 703 cm⁻¹; **HRMS** (ESI-TOF) m/z calcd for C₁₇H₁₇ClONa (M + Na)⁺: 295.0866, found 295.0858.

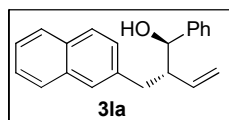


2-(4-bromobenzyl)-1-phenylbut-3-en-1-ol (**3ja**): The general procedure was followed using (*E*)-1-bromo-4-(buta-1,3-dien-1-yl)benzene (**1j**, 52 mg, 0.25 mmol) and benzaldehyde (**2a**, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product **3ja** as a colorless liquid (75 mg, 95% yield, >20:1 dr): R_f = 0.5 (EtOAc : petroleum ether = 1 : 5); **¹H-NMR** (CDCl₃, 400 MHz) δ : 7.35-7.33 (m, 4H), 7.30-7.24 (m, 3H), 6.98-6.91 (m, 2H), 5.57-5.48 (m, 1H), 4.95 (d, J = 8.0 Hz, 1H), 4.78 (d, J = 16 Hz, 1H), 4.72-4.62 (m, 1H), 2.92-2.88 (m, 1H), 2.73-2.66 (m, 1H), 2.56-2.50 (m, 1H), 2.18-2.08 (m, 1H); **¹³C-NMR** (CDCl₃, 100 MHz) δ : 142.2, 139.1, 137.2, 131.1, 131.0, 128.2, 127.6, 126.6, 119.5, 118.0, 76.4, 52.7, 35.5 ppm; **IR** (neat): 3411, 3066, 3029, 2924, 1488, 1010, 704 cm⁻¹; **HRMS** (ESI-TOF) m/z

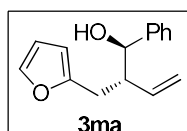
calcd for $C_{17}H_{17}BrONa$ ($M + Na$)⁺: 339.0360, found 339.0360.



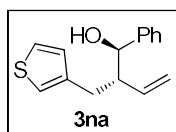
2-(4-iodobenzyl)-1-phenylbut-3-en-1-ol (**3ka**): The general procedure was followed using (*E*)-1-(buta-1,3-dien-1-yl)-4-iodobenzene (**1k**, 64 mg, 0.25 mmol) and benzaldehyde (**2a**, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product **3ka** as a yellow liquid (72 mg, 78% yield, 18:1 dr): R_f = 0.5 (EtOAc : petroleum ether = 1 : 5); ¹H-NMR (CDCl₃, 400 MHz) δ : 7.54 (d, J = 8.0 Hz, 2H), 7.36-7.24 (m, 5H), 6.85 (d, J = 8.0 Hz, 2H), 5.57-5.48 (m, 1H), 4.96 (d, J = 12 Hz, 1H), 4.79 (d, J = 16 Hz, 1H), 4.70-4.63 (m, 1H), 2.91-2.87 (m, 1H), 2.73-2.66 (m, 1H), 2.52-2.44 (m, 1H), 2.14-2.06 (m, 1H); ¹³C-NMR (CDCl₃, 100 MHz) δ : 142.2, 139.7, 137.2, 137.0, 131.4, 128.2, 127.6, 126.6, 118.0, 91.0, 76.3, 52.6, 35.6 ppm; IR (neat): 3433, 3067, 3029, 2925, 1725, 1485, 704 cm⁻¹; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{16}IO$ ($M - H$)⁻: 363.0246, found 363.0248.



2-(naphthalen-2-ylmethyl)-1-phenylbut-3-en-1-ol (**3la**): The general procedure was followed using (*E*)-2-(buta-1,3-dien-1-yl)naphthalene (**1l**, 45 mg, 0.25 mmol) and benzaldehyde (**2a**, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 5) afforded product **3la** as a yellow solid (63 mg, 88% yield, >20:1 dr): R_f = 0.4 (EtOAc : petroleum ether = 1 : 5); ¹H-NMR (CDCl₃, 400 MHz) δ : 7.77-7.70 (m, 3H), 7.54 (s, 1H), 7.43-7.38 (m, 2H), 7.36-7.24 (m, 6H), 5.63-5.54 (m, 1H), 4.92 (d, J = 8.0 Hz, 1H), 4.80 (d, J = 16 Hz, 1H), 4.72 (d, J = 4.0 Hz, 1H), 3.08 (dd, J_1 = 12 Hz, J_2 = 4.0 Hz, 1H), 2.89-2.82 (m, 1H), 2.76-2.67 (m, 1H), 2.21 (brs, 1H); ¹³C-NMR (CDCl₃, 100 MHz) δ : 142.3, 137.6, 137.5, 133.4, 131.9, 128.1, 127.9, 127.54, 127.50, 127.4, 126.7, 125.7, 125.1, 117.8, 76.4, 52.6, 36.4 ppm; IR (neat): 3383, 3007, 2916, 2852, 1452, 1007, 700 cm⁻¹; HRMS (ESI-TOF) m/z calcd for $C_{21}H_{20}ONa$ ($M + Na$)⁺: 311.1412, found 311.1405.

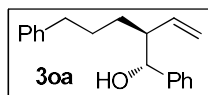


2-(furan-2-ylmethyl)-1-phenylbut-3-en-1-ol (**3ma**): The general procedure was followed using (*E*)-2-(buta-1,3-dien-1-yl)furan (**1m**, 30 mg, 0.25 mmol) and benzaldehyde (**2a**, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1:10) afforded product **3ma** as a colorless oil (35 mg, 61% yield, 14:1 dr): R_f = 0.5 (EtOAc : petroleum ether = 1 : 5); ¹H-NMR (CDCl₃, 400 MHz) δ : 7.35-7.25 (m, 6H), 6.29-6.21 (m, 1H), 6.03-5.95 (m, 1H), 5.65-5.56 (m, 1H), 5.03-4.93 (m, 2H), 4.69 (d, J = 4.0 Hz, 1H), 2.89-2.85 (m, 2H), 2.76-2.69 (m, 1H), 2.15 (brs, 1H); ¹³C-NMR (CDCl₃, 100 MHz) δ : 154.0, 142.0, 140.9, 137.5, 128.1, 127.6, 126.7, 117.5, 110.1, 106.3, 76.0, 49.9, 28.6 ppm; IR (neat): 3432, 3114, 3030, 2924, 1452, 1009, 733 cm⁻¹; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{16}O_2Na$ ($M + Na$)⁺: 251.1048, found 251.1045.

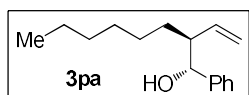


1-phenyl-2-(thiophen-3-ylmethyl)but-3-en-1-ol (**3na**): The general procedure was followed using (*E*)-3-(buta-1,3-dien-1-yl)thiophene (**1n**, 34 mg, 0.25 mmol) and benzaldehyde (**2a**, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product **3na** as a yellow liquid (49 mg, 80% yield, 13:1 dr): R_f = 0.5 (EtOAc : petroleum ether = 1 : 5); ¹H-NMR (CDCl₃, 400 MHz) δ : 7.28-7.16 (m, 5H), 7.13 (m, 1H), 6.83-6.81 (m, 2H), 5.55-5.46

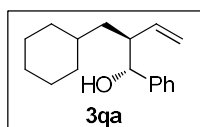
(m, 1H), 4.93 (d, $J = 8$ Hz, 1H), 4.83 (d, $J = 16$ Hz, 1H), 4.59-4.58 (m, 1H), 2.82 (dd, $J_1 = 12$ Hz, $J_2 = 4.0$ Hz, 1H), 2.73-2.66 (m, 1H), 2.63-2.57 (m, 1H), 2.08 (brs, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 142.2, 140.2, 137.8, 128.7, 128.1, 127.5, 126.7, 124.9, 121.2, 117.7, 76.2, 51.8, 30.7 ppm; **IR** (neat): 3429, 3079, 3030, 2923, 1451, 917, 763 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{15}\text{H}_{16}\text{OSNa}$ ($\text{M} + \text{Na}$) $^+$: 267.0820, found 267.0806.



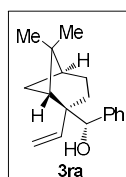
1,5-diphenyl-2-vinylpentan-1-ol (3oa): The general procedure was followed using (*E*)-hexa-3,5-dien-1-ylbenzene (**1o**, 40 mg, 0.25 mmol) and benzaldehyde (**2a**, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 9) afforded product **3oa** as a colorless oil (29 mg, 43% yield, 6:1 dr): $R_f = 0.5$ (EtOAc : petroleum ether = 1 : 4); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 7.26-7.16 (m, 7H), 7.10-6.98 (m, 3H), 5.46-5.37 (m, 1H), 4.99-4.89 (m, 2H), 4.53-4.51 (m, 1H), 2.56-2.21 (m, 3H), 2.00 (m, 1H), 1.64-1.53 (m, 2H), 1.45-1.35 (m, 1H), 1.21-1.15 (m, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 142.5, 142.4, 138.3, 128.3, 128.2, 128.0, 127.4, 126.7, 125.6, 117.5, 76.9, 51.3, 35.9, 29.3, 29.2 ppm; **IR** (neat): 3433, 3064, 3028, 2927, 1454, 1024, 701 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{19}\text{H}_{22}\text{ONa}$ ($\text{M} + \text{Na}$) $^+$: 289.1568, found 289.1571.



1-phenyl-2-vinyloctan-1-ol (3pa): The general procedure was followed using (*E*)-nona-1,3-diene (**1p**, 31 mg, 0.25 mmol) and benzaldehyde (**2a**, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 15) afforded product **3pa** as a yellow liquid (24 mg, 41% yield, 7:1 dr): $R_f = 0.6$ (EtOAc : petroleum ether = 1 : 5); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 7.27-7.18 (m, 5H), 5.47-5.38 (m, 1H), 5.01-4.91 (m, 2H), 4.58-4.51 (m, 1H), 2.34-2.32 (m, 1H), 2.06-1.95 (m, 1H), 1.57-1.47 (m, 1H), 1.18-1.09 (m, 9H), 0.79 (t, $J = 6.0$ Hz, 3H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 142.5, 138.5, 128.0, 127.3, 126.7, 117.3, 76.9, 51.4, 31.8, 29.6, 29.3, 27.2, 22.6, 14.1 ppm; **IR** (neat): 3411, 3067, 3029, 2855, 1455, 1024, 702 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{16}\text{H}_{24}\text{ONa}$ ($\text{M} + \text{Na}$) $^+$: 255.1725, found 255.1719.

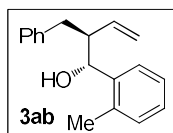


2-(cyclohexylmethyl)-1-phenylbut-3-en-1-ol (3qa): The general procedure was followed using (*E*)-buta-1,3-dien-1-ylcyclohexane (**1q**, 34 mg, 0.25 mmol) and benzaldehyde (**2a**, 53 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product **3qa** as a colorless oil (28 mg, 45% yield, 7:1 dr): $R_f = 0.6$ (EtOAc : petroleum ether = 1 : 5); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 7.34-7.25 (m, 5H), 5.54-5.45 (m, 1H), 5.09-5.00 (m, 2H), 4.61-4.58 (m, 1H), 2.60-2.54 (m, 1H), 2.07-2.06 (m, 1H), 1.74-1.55 (m, 5H), 1.32-1.11 (m, 6H), 0.95-0.67 (m, 2H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 142.4, 138.7, 127.9, 127.3, 126.7, 117.2, 77.1, 48.3, 37.3, 34.63, 34.58, 32.1, 26.6, 26.4, 26.1 ppm; **IR** (neat): 3431, 3067, 3029, 2923, 1449, 913, 703 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{17}\text{H}_{24}\text{ONa}$ ($\text{M} + \text{Na}$) $^+$: 267.1725, found 267.1719.

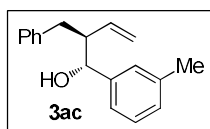


A containing stirring bar oven dried 25-ml Schlenk tube was charged with $\text{Cu}(\text{OTf})_2$ (9.1mg, 0.025 mmol, 10 mol%), PPh_3 (7.2mg, 0.0275 mmol, 11 mol%), B_2Pin_2 (127 mg, 0.50 mmol, 2.0 equiv) and LiO^tBu (40mg, 0.50 mmol, 2.0 equiv). The tube was then evacuated and back-filled under a N_2 flow (this sequence was repeated

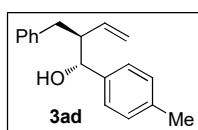
three times). Diene **1r** (37 mg, 0.25 mmol, 1.0 equiv), water (13.5 μ L, 3.0 equiv), anhydrous DCE (1.0 ml) were added subsequently under N₂ condition. The reaction mixture was stirred for 1.5 h at r.t and then **2a** (53 mg, 0.50 mmol, 2.0 equiv) dissolved in anhydrous DCE (0.5 ml) were added, the tube was stirred at 70 °C for 48 h. After cooling to r.t, the reaction mixture diluted with EtOAc (10 ml) and H₂O (10 ml). Then it was extracted with EtOAc (10 ml $\times$ 3). The organic layer was combined and dried over Na₂SO₄, filtered and concentrated by rotary evaporation. The residue was purified by silica gel column chromatography to afford the product **3ra** as a yellow liquid (31 mg, 49% yield, >20:1 dr): R_f = 0.6 (EtOAc : petroleum ether = 1 : 5); ¹H-NMR (CDCl₃, 400 MHz) δ : 7.23-7.11 (m, 5H), 5.81-5.74 (m, 1H), 5.22 (d, J = 12 Hz, 1H), 4.92 (d, J = 20 Hz, 1H), 4.38 (d, J = 8.0 Hz, 1H), 2.48 (t, J = 6.0 Hz, 1H), 2.19-2.13 (m, 2H), 1.76-1.69 (m, 4H), 1.26-1.24 (m, 1H), 1.18 (s, 3H), 1.16-1.13 (m, 1H), 0.72 (s, 3H); ¹³C-NMR (CDCl₃, 100 MHz) δ : 145.3, 141.5, 128.4, 127.4, 127.3, 115.0, 78.1, 48.8, 46.9, 40.1, 38.9, 28.1, 26.4, 25.7, 24.5, 23.7 ppm; IR (neat): 3458, 3078, 3028, 2917, 1409, 1042, 729 cm⁻¹; HRMS (ESI-TOF) m/z calcd for C₁₈H₂₄ONa (M + Na)⁺: 279.1725, found 279.1723.



2-benzyl-1-(o-tolyl)but-3-en-1-ol (**3ab**): The general procedure was followed using (*E*)-buta-1,3-dien-1-ylbenzene (**1a**, 33 mg, 0.25 mmol) and 2-methylbenzaldehyde (**2b**, 60 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product **3ab** as a yellow oil (57 mg, 91% yield, >20:1 dr): R_f = 0.5 (EtOAc : petroleum ether = 1 : 5); ¹H-NMR (CDCl₃, 400 MHz) δ : 7.48 (d, J = 8.0 Hz, 1H), 7.23-7.20 (m, 3H), 7.18-7.07 (m, 5H), 5.69-5.60 (m, 1H), 4.96 (d, J = 4.0 Hz, 1H), 4.89 (d, J = 12 Hz, 1H), 4.75 (d, J = 16 Hz, 1H), 3.09 (d, J = 12 Hz, 1H), 2.75-2.63 (m, 2H), 2.31 (s, 3H), 1.98 (brs, 1H); ¹³C-NMR (CDCl₃, 100 MHz) δ : 141.0, 140.4, 138.1, 134.7, 130.4, 129.3, 128.0, 127.2, 126.4, 126.0, 125.7, 117.1, 73.1, 51.8, 35.4, 19.4 ppm; IR (neat): 3386, 3065, 3026, 2925, 1602, 1492, 700 cm⁻¹; HRMS (ESI-TOF) m/z calcd for C₁₈H₂₀ONa (M + Na)⁺: 275.1412, found 275.1406.

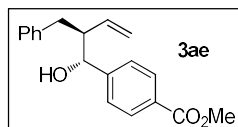


2-benzyl-1-(m-tolyl)but-3-en-1-ol (**3ac**): The general procedure was followed using (*E*)-buta-1,3-dien-1-ylbenzene (**1a**, 33 mg, 0.25 mmol) and 3-methylbenzaldehyde (**2c**, 60 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product **3ac** as a colorless oil (59 mg, 93% yield, >20:1 dr): R_f = 0.5 (EtOAc : petroleum ether = 1 : 5); ¹H-NMR (CDCl₃, 400 MHz) δ : 7.25-7.20 (m, 3H), 7.15-7.14 (m, 1H), 7.12-7.07 (m, 5H), 5.61-5.52 (m, 1H), 4.95 (d, J = 8.0 Hz, 1H), 4.82 (d, J = 16 Hz, 1H), 4.65 (d, J = 8.0 Hz, 1H), 2.95-2.91 (m, 1H), 2.79-2.72 (m, 1H), 2.60-2.54 (m, 1H), 2.35 (s, 3H), 2.14 (brs, 1H); ¹³C-NMR (CDCl₃, 100 MHz) δ : 142.3, 140.1, 137.7, 129.3, 128.2, 128.02, 127.97, 127.4, 125.7, 123.8, 117.6, 76.4, 52.6, 36.1, 21.5 ppm; IR (neat): 3415, 3063, 3027, 2922, 1605, 1452, 702 cm⁻¹; HRMS (ESI-TOF) m/z calcd for C₁₈H₂₀ONa (M + Na)⁺: 275.1412, found 275.1407.

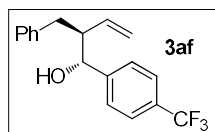


2-benzyl-1-(p-tolyl)but-3-en-1-ol (**3ad**): The general procedure was followed using (*E*)-buta-1,3-dien-1-ylbenzene (**1a**, 33 mg, 0.25 mmol) and 4-methylbenzaldehyde (**2d**, 60 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product **3ad** as a colorless oil (60mg, 94% yield, >20:1 dr): R_f = 0.5 (EtOAc : petroleum ether = 1 :

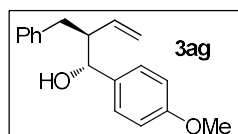
5); **¹H-NMR** (CDCl₃, 400 MHz) δ : 7.25-7.20 (m, 4H), 7.18-7.10 (m, 5H), 5.59-5.50 (m, 1H), 4.95 (d, J = 12 Hz, 1H), 4.81 (d, J = 16 Hz, 1H), 4.64 (d, J = 8.0 Hz, 1H), 2.93 (dd, J_1 = 16 Hz, J_2 = 4.0 Hz, 1H), 2.78-2.71 (m, 1H), 2.59-2.53 (m, 1H), 2.33 (s, 3H), 2.13 (brs, 1H); **¹³C-NMR** (CDCl₃, 100 MHz) δ : 140.1, 139.3, 137.6, 137.1, 129.3, 128.8, 128.0, 126.7, 125.7, 117.6, 76.2, 52.6, 36.3, 21.1 ppm; **IR** (neat): 3417, 3063, 3027, 2922, 1640, 1451, 915 cm⁻¹; **HRMS** (ESI-TOF) m/z calcd for C₁₈H₂₀ONa (M + Na)⁺: 275.1412, found 275.1413.



Methyl 4-(2-benzyl-1-hydroxybut-3-en-1-yl) benzoate (**3ae**): The general procedure was followed using (*E*)-buta-1,3-dien-1-ylbenzene (**1a**, 33 mg, 0.25 mmol) and methyl 4-formylbenzoate (**2e**, 82 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 5) afforded product **3ae** as a colorless solid (68mg, 91% yield, >20:1 dr): R_f = 0.3 (EtOAc : petroleum ether = 1 : 5); **¹H-NMR** (CDCl₃, 400 MHz) δ : 7.99 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.25-7.21 (m, 2H), 7.17-7.13 (m, 1H), 7.09 (d, J = 8.0 Hz, 2H), 5.60-5.51 (m, 1H), 4.96 (d, J = 12 Hz, 1H), 4.83-4.75 (m, 2H), 3.89 (s, 3H), 2.89 (d, J = 12 Hz, 1H), 2.81-2.68 (m, 1H), 2.62-2.56 (m, 1H), 2.47 (brs, 1H); **¹³C-NMR** (CDCl₃, 100 MHz) δ : 167.0, 147.7, 139.7, 137.2, 129.3, 129.2, 129.1, 128.1, 126.7, 125.8, 118.0, 75.9, 52.7, 52.0, 35.9 ppm; **IR** (neat): 3503, 3068, 3029, 2854, 1707, 1288, 862 cm⁻¹; **HRMS** (ESI-TOF) m/z calcd for C₁₉H₂₀O₃Na (M + Na)⁺: 319.1310, found 319.1305.

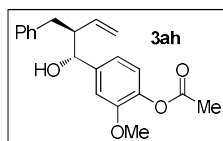


2-benzyl-1-(4-(trifluoromethyl)phenyl)but-3-en-1-ol (**3af**): The general procedure was followed using (*E*)-buta-1,3-dien-1-ylbenzene (**1a**, 33 mg, 0.25 mmol) and methyl 4-(trifluoromethyl)benzaldehyde (**2f**, 87 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product **3af** as a yellow solid (73mg, 95% yield, >20:1 dr): R_f = 0.5 (EtOAc : petroleum ether = 1 : 5); **¹H-NMR** (CDCl₃, 400 MHz) δ : 7.59 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.26-7.23 (m, 2H), 7.18-7.15 (m, 1H), 7.11-7.09 (m, 2H), 5.60-5.51 (m, 1H), 4.99 (d, J = 12 Hz, 1H), 4.85 (d, J = 16 Hz, 1H), 4.77-4.75 (m, 1H), 2.89-2.85 (m, 1H), 2.80-2.74 (m, 1H), 2.63-2.57 (m, 1H), 2.24-2.23 (m, 1H); **¹³C-NMR** (CDCl₃, 100 MHz) δ : 146.3, 139.6, 137.0, 129.5, 129.2, 128.2, 127.0, 126.0, 125.0 (q, J = 4.0 Hz), 118.3, 75.7, 52.6, 35.9 ppm; **¹⁹F-NMR** (CDCl₃, 376 MHz) δ : -62.36 ppm; **IR** (neat): 3417, 3082, 3029, 2926, 1715, 1328, 841 cm⁻¹; **HRMS** (ESI-TOF) m/z calcd for C₁₈H₁₆F₃O (M - H)⁻: 305.1153, found 305.1152.

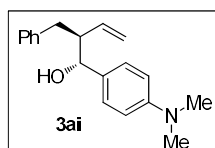


2-benzyl-1-(4-methoxyphenyl)but-3-en-1-ol (**3ag**): The general procedure was followed using (*E*)-buta-1,3-dien-1-yl benzene (**1a**, 33 mg, 0.25 mmol) and methyl 4-methoxybenzaldehyde (**2g**, 68 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product **3ag** as a colorless oil (60mg, 89% yield, >20:1 dr): R_f = 0.4 (EtOAc : petroleum ether = 1 : 5); **¹H-NMR** (CDCl₃, 400 MHz) δ : 7.26-7.21 (m, 4H), 7.17-7.11 (m, 3H), 6.86 (d, J = 8.0 Hz, 2H), 5.59-5.50 (m, 1H), 4.95 (d, J = 12 Hz, 1H), 4.81 (d, J = 20 Hz, 1H), 4.63 (d, J = 8.0 Hz, 1H), 3.79 (s, 3H), 2.93 (d, J = 16 Hz, 1H), 2.75-2.74 (m, 1H), 2.59-2.54 (m, 1H), 2.12 (brs, 1H); **¹³C-NMR** (CDCl₃, 100 MHz) δ : 158.9, 140.1, 137.6, 134.5, 129.3, 128.0, 127.9, 125.8, 117.6, 113.4, 76.0, 55.2, 52.7, 36.4 ppm; **IR** (neat): 3429, 3066, 3028, 2930, 1610, 1248,

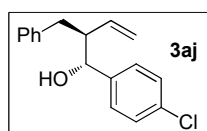
832 cm⁻¹; **HRMS** (ESI-TOF) m/z calcd for C₁₈H₂₀O₂Na (M + Na)⁺: 291.1361, found 291.1358.



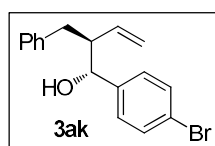
4-(2-benzyl-1-hydroxybut-3-en-1-yl)-2-methoxyphenyl acetate (**3ah**): The general procedure was followed using (*E*)-buta-1,3-dien-1-yl benzene (**1a**, 33 mg, 0.25 mmol) and methyl 4-formyl-2-methoxyphenyl acetate (**2h**, 97 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 6) afforded product **3ah** as a yellow oil (70mg, 86% yield, >20:1 dr): R_f = 0.4 (EtOAc : petroleum ether = 1 : 3); ¹H-NMR (CDCl₃, 400 MHz) δ : 7.26-7.22 (m, 2H), 7.17-7.11 (m, 3H), 6.99-6.94 (m, 2H), 6.86 (d, J = 8.0 Hz, 2H), 5.63-5.54 (m, 1H), 4.97 (d, J = 12 Hz, 1H), 4.83 (d, J = 16 Hz, 1H), 4.66 (d, J = 4.0 Hz, 1H), 3.80 (s, 3H), 2.93 (d, J = 12 Hz, 1H), 2.81-2.68 (m, 1H), 2.64-2.58 (m, 1H), 2.30-2.27 (m, 4H); ¹³C-NMR (CDCl₃, 100 MHz) δ : 169.1, 150.7, 141.4, 139.9, 138.8, 137.4, 129.2, 128.1, 125.8, 122.2, 118.9, 117.7, 110.8, 76.0, 55.8, 52.5, 36.1, 20.6 ppm; **IR** (neat): 3462, 3066, 3027, 2936, 1764, 1456, 912 cm⁻¹; **HRMS** (ESI-TOF) m/z calcd for C₂₀H₂₂O₄Na (M + Na)⁺: 349.1416, found 349.1404.



2-benzyl-1-(4-(dimethylamino)phenyl)but-3-en-1-ol (**3ai**): The general procedure was followed using (*E*)-buta-1,3-dien-1-ylbenzene (**1a**, 33 mg, 0.25 mmol) and methyl 4-(dimethylamino)benzaldehyde (**2i**, 75 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 6) afforded product **3ai** as a yellow oil (57mg, 81% yield, >20:1 dr): R_f = 0.3 (EtOAc : petroleum ether = 1:5); ¹H-NMR (CDCl₃, 400 MHz) δ : 7.24-7.22 (m, 2H), 7.18-7.13 (m, 5H), 6.70 (d, J = 8.0 Hz, 2H), 5.60-5.51 (m, 1H), 4.94 (d, J = 8 Hz, 1H), 4.81 (d, J = 16 Hz, 1H), 4.59 (d, J = 4.0 Hz, 1H), 2.97-2.93 (m, 7H), 2.83-2.70 (m, 1H), 2.59-2.54 (m, 1H), 2.02 (brs, 1H); ¹³C-NMR (CDCl₃, 100 MHz) δ : 150.0, 140.3, 137.9, 130.1, 129.3, 128.0, 127.7, 125.7, 117.3, 112.1, 76.2, 52.6, 40.6, 36.6 ppm; **IR** (neat): 3405, 3076, 3027, 2921, 1614, 1349, 818 cm⁻¹; **HRMS** (ESI-TOF) m/z calcd for C₁₉H₂₄NO (M + H)⁺: 282.1858, found 282.1854.

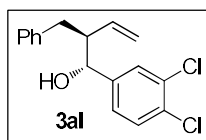


2-benzyl-1-(4-chlorophenyl)but-3-en-1-ol (**3aj**): The general procedure was followed using (*E*)-buta-1,3-dien-1-ylbenzene (**1a**, 33 mg, 0.25 mmol) and 4-chlorobenzaldehyde (**2j**, 70 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product **3aj** as a yellow oil (67mg, 97% yield, >20:1 dr): R_f = 0.5 (EtOAc : petroleum ether = 1 : 5); ¹H-NMR (CDCl₃, 400 MHz) δ : 7.32-7.30 (m, 2H), 7.26-7.23 (m, 4H), 7.18-7.09 (m, 3H), 5.58-5.49 (m, 1H), 4.98 (d, J = 12 Hz, 1H), 4.83 (d, J = 20 Hz, 1H), 4.68-4.66 (m, 1H), 2.88 (dd, J_1 = 12 Hz, J_2 = 4.0 Hz, 1H), 2.74-2.71 (m, 1H), 2.60-2.55 (m, 1H), 2.14-2.13 (m, 1H); ¹³C-NMR (CDCl₃, 100 MHz) δ : 140.8, 139.7, 137.2, 133.2, 129.2, 128.2, 128.12, 128.09, 125.9, 118.1, 75.7, 52.6, 36.1 ppm; **IR** (neat): 3431, 3081, 3028, 2925, 1600, 1491, 701 cm⁻¹; **HRMS** (ESI-TOF) m/z calcd for C₁₇H₁₇ClNaO (M + Na)⁺: 295.0866, found 295.0870.

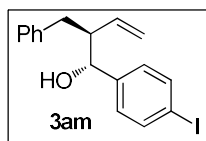


2-benzyl-1-(4-bromophenyl)but-3-en-1-ol(**3ak**): The general procedure was followed using (*E*)-buta-1,3-dien-1-ylbenzene (**1a**, 33 mg, 0.25 mmol) and 4-bromobenzaldehyde (**2k**, 93 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded

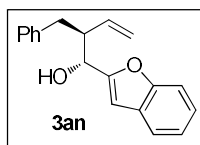
product **3ak** as a colorless oil (69mg, 87% yield, >20:1 dr): R_f = 0.4 (EtOAc : petroleum ether = 1 : 5); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 7.45 (d, J = 8.0 Hz, 2H), 7.26-7.22 (m, 2H), 7.17 (m, 3H), 7.10 (d, J = 8.0 Hz, 2H), 5.57-5.48 (m, 1H), 4.97 (d, J = 8.0 Hz, 1H), 4.82 (d, J = 16 Hz, 1H), 4.65 (d, J = 4.0 Hz, 1H), 2.87 (d, J = 16 Hz, 1H), 2.73-2.72 (m, 1H), 2.60-2.54 (m, 1H), 2.19 (brs, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 141.3, 139.7, 137.1, 131.2, 129.2, 128.4, 128.1, 125.9, 121.3, 118.1, 75.7, 52.5, 36.1 ppm; **IR** (neat): 3413, 3080, 3027, 2977, 1640, 1490, 825 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{17}\text{H}_{17}\text{BrONa}$ ($\text{M} + \text{Na}$) $^+$: 339.0360, found 339.0356.



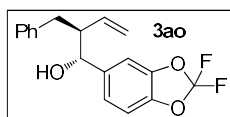
2-benzyl-1-(3,4-dichlorophenyl)but-3-en-1-ol (**3al**): The general procedure was followed using (*E*)-buta-1,3-dien-1-ylbenzene (**1a**, 33 mg, 0.25 mmol) and 3,4-dichlorobenzaldehyde (**2l**, 88 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product **3al** as a colorless oil (70mg, 91% yield, >20:1 dr): R_f = 0.4 (EtOAc : petroleum ether = 1 : 5); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 7.32-7.30 (m, 2H), 7.18-7.15 (m, 2H), 7.10-7.07 (m, 1H), 7.05-7.01 (m, 3H), 5.50-5.41 (m, 1H), 4.92 (d, J = 12 Hz, 1H), 4.76 (d, J = 16 Hz, 1H), 4.60-4.50 (m, 1H), 2.79-2.76 (m, 1H), 2.64-2.63 (m, 1H), 2.54-2.48 (m, 1H), 2.17 (brs, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 142.6, 139.4, 136.9, 132.2, 131.3, 130.0, 129.2, 128.7, 128.2, 126.1, 126.0, 118.4, 75.1, 52.5, 36.0 ppm; **IR** (neat): 3430, 3065, 3028, 2924, 1712, 1469, 884 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{17}\text{H}_{15}\text{Cl}_2\text{O}$ ($\text{M} - \text{H}$) $^-$: 305.0500, found 305.0502.



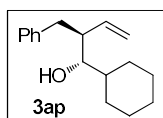
2-benzyl-1-(4-iodophenyl)but-3-en-1-ol (**3am**): The general procedure was followed using (*E*)-buta-1,3-dien-1-ylbenzene (**1a**, 33 mg, 0.25 mmol) and 4-iodobenzaldehyde (**2m**, 116 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1:10) afforded product **3am** as a colorless oil (86mg, 94% yield, >20:1 dr): R_f = 0.5 (EtOAc : petroleum ether = 1 : 5); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 7.65 (d, J = 8.0 Hz, 2H), 7.26-7.22 (m, 2H), 7.18-7.14 (m, 1H), 7.11-7.03 (m, 4H), 5.57-5.48 (m, 1H), 4.98 (d, J = 12 Hz, 1H), 4.83 (d, J = 20 Hz, 1H), 4.64-4.62 (m, 1H), 2.89-2.84 (m, 1H), 2.75-2.70 (m, 1H), 2.59-2.54 (m, 1H), 2.16-2.15 (m, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 141.9, 139.7, 137.1, 129.2, 128.7, 128.1, 125.9, 118.1, 93.0, 75.8, 52.5, 36.1 ppm; **IR** (neat): 3402, 3079, 3027, 2923, 1588, 1488, 821 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{17}\text{H}_{17}\text{IONa}$ ($\text{M} + \text{Na}$) $^+$: 387.0222, found 387.0222.



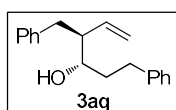
1-(benzofuran-2-yl)-2-benzylbut-3-en-1-ol (**3an**): The general procedure was followed using (*E*)-buta-1,3-dien-1-ylbenzene (**1a**, 33 mg, 0.25 mmol) and benzofuran-2-carbaldehyde (**2n**, 73 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 8) afforded product **3an** as a colorless solid (47 mg, 68% yield, >20:1 dr): R_f = 0.4 (EtOAc : petroleum ether = 1 : 5); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 7.54 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.26-7.16 (m, 7H), 6.62 (s, 1H), 5.75-5.66 (m, 1H), 5.07-4.98 (m, 2H), 4.81-4.78 (m, 1H), 3.01-2.93 (m, 2H), 2.72-2.66 (m, 1H), 2.34 (d, J = 8.0 Hz, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 157.6, 154.7, 139.5, 136.9, 129.3, 128.2, 127.9, 126.0, 124.1, 122.8, 121.0, 118.5, 111.2, 104.1, 70.2, 51.0, 36.6 ppm; **IR** (neat): 3350, 3029, 2925, 2856, 1420, 1253, 919 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{19}\text{H}_{18}\text{O}_2\text{Na}$ ($\text{M} + \text{Na}$) $^+$: 301.1204, found 301.1196.



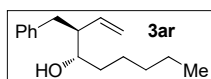
2-benzyl-1-(2,2-difluorobenzo[d][1,3]dioxol-5-yl)but-3-en-1-ol (**3ao**): The general procedure was followed using (*E*)-buta-1,3-dien-1-ylbenzene (**1a**, 33 mg, 0.25 mmol) and 2,2-difluorobenzo[d][1,3]dioxole-5-carbaldehyde (**2o**, 93 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product **3ao** as a yellow oil (64mg, 81% yield, >20:1 dr): R_f = 0.4 (EtOAc : petroleum ether = 1 : 5); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 7.27-7.23 (m, 2H), 7.19-7.11 (m, 3H), 7.07(s, 1H), 7.01-6.97(m, 2H), 5.58-5.49 (m, 1H), 4.99 (d, J = 12 Hz, 1H), 4.83 (d, J = 16 Hz, 1H), 4.68-4.67 (m, 1H), 2.92-2.87 (m, 1H), 2.76-2.69 (m, 1H), 2.63-2.57 (m, 1H), 2.15 (m, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 143.7, 142.9, 139.5, 138.7, 137.0, 134.1, 131.6, 129.2, 128.2, 126.0, 121.9, 118.2, 108.8, 108.0, 75.8, 52.7, 36.2 ppm; $^{19}\text{F-NMR}$ (CDCl_3 , 376 MHz) δ : -49.73, -49.71, -49.74, -50.00 ppm; **IR** (neat): 3414, 3083, 3029, 2925, 1642, 1448, 816 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{18}\text{H}_{15}\text{F}_2\text{O}_3$ ($\text{M} - \text{H}$) $^-$: 317.0989, found 317.0972.



2-benzyl-1-cyclohexylbut-3-en-1-ol (**3ap**): The general procedure was followed using (*E*)-buta-1,3-dien-1-ylbenzene (**1a**, 33 mg, 0.25 mmol) and cyclohexanecarbaldehyde (**2p**, 56 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 25) afforded product **3ap** as a colorless oil (48mg, 79% yield, 8:1 dr): R_f = 0.7 (EtOAc : petroleum ether = 1 : 5); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 7.27-7.23 (m, 2H), 7.16-7.14 (m, 3H), 5.67-5.58 (m, 1H), 4.98 (d, J = 12 Hz, 1H), 4.84 (d, J = 16 Hz, 1H), 3.33-3.14 (m, 1H), 3.05 (d, J = 12 Hz, 1H), 2.72-2.51 (m, 2H), 1.77-1.53 (m, 7H), 1.25-1.02 (m, 5H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 140.5, 139.0, 129.4, 128.0, 125.7, 116.4, 78.3, 48.7, 40.3, 36.0, 30.2, 26.5, 26.4, 26.0 ppm; **IR** (neat): 3412, 3067, 3028, 2851, 1639, 1449, 741 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{17}\text{H}_{24}\text{ONa}$ ($\text{M} + \text{Na}$) $^+$: 267.1725, found 267.1724.

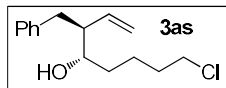


4-benzyl-1-phenylhex-5-en-3-ol (**3aq**): The general procedure was followed using (*E*)-buta-1,3-dien-1-ylbenzene (**1a**, 33 mg, 0.25 mmol) and 3-phenylpropanal (**2q**, 67 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product **3aq** as a colorless solid (53mg, 80% yield, 7:1 dr): R_f = 0.4 (EtOAc : petroleum ether = 1 : 5); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 7.22-7.01 (m, 10H), 5.59-5.50 (m, 1H), 4.98-4.83 (m, 2H), 3.51-3.47 (m, 1H), 2.82-2.77 (m, 2H), 2.59-2.50 (m, 2H), 2.43-2.36 (m, 1H), 1.87-1.55 (m, 3H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 142.1, 140.0, 137.9, 129.1, 128.43, 128.39, 128.1, 125.83, 125.81, 117.7, 73.0, 52.3, 36.9, 35.7, 32.3 ppm; **IR** (neat): 3385, 3318, 3082, 2937, 1452, 1085, 699 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{19}\text{H}_{22}\text{ONa}$ ($\text{M} + \text{Na}$) $^+$: 289.1568, found 289.1563.



3-benzyl-1-nonen-4-ol (**3ar**): The general procedure was followed using (*E*)-buta-1,3-dien-1-ylbenzene (**1a**, 33 mg, 0.25 mmol) and hexanal (**2r**, 50 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 20) afforded product **3ar** as a colorless oil (46mg, 79% yield, 9:1 dr): R_f = 0.7 (EtOAc : petroleum ether = 1 : 5); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 7.27-7.24 (m, 2H), 7.18-7.14 (m, 3H), 5.69-5.60 (m, 1H), 5.04 (d, J = 12 Hz, 1H), 4.92 (d, J = 16 Hz, 1H), 3.61-3.46 (m, 1H), 2.91 (dd, J_1 = 12 Hz, J_2 = 4.0 Hz, 1H), 2.65-2.59 (m, 1H), 2.48-2.41 (m, 1H),

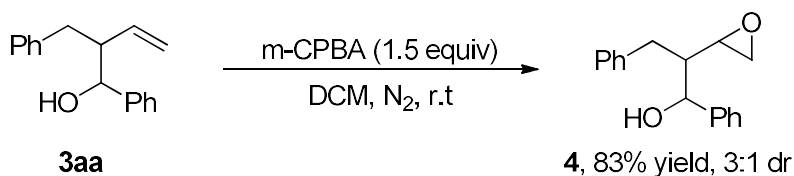
1.62-1.45 (m, 3H), 1.31-1.23 (m, 6H), 0.89 (t, $J = 6$ Hz, 3H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 140.2, 138.3, 129.2, 128.1, 125.8, 117.4, 73.7, 52.2, 36.7, 33.8, 31.8, 25.6, 22.6, 14.0 ppm; **IR** (neat): 3348, 3083, 2921, 2857, 1494, 918, 698 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{16}\text{H}_{24}\text{ONa}$ ($\text{M} + \text{Na}$) $^{+}$: 255.1725, found 255.1724.



3-benzyl-8-chlorooct-1-en-4-ol (**3as**): The general procedure was followed using (*E*)-buta-1,3-dien-1-ylbenzene (**1a**, 33 mg, 0.25 mmol) and 4-chlorobutanol (**2s**, 60 mg, 0.50 mmol). Purification of this material by chromatography on silica gel (EtOAc : petroleum ether = 1 : 10) afforded product **3as** as a colorless oil (50mg, 78% yield, 8:1 dr): $R_f = 0.4$ (EtOAc : petroleum ether = 1 : 5); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 7.28-7.24 (m, 2H), 7.19-7.14 (m, 3H), 5.68-5.59 (m, 1H), 5.05 (d, $J = 8.0$ Hz, 1H), 4.94 (d, $J = 16$ Hz, 1H), 3.55-3.52 (m, 3H), 2.93-2.88 (m, 1H), 2.66-2.60 (m, 1H), 2.49-2.45 (m, 1H), 1.83-1.74 (m, 2H), 1.64-1.58 (m, 2H), 1.47-1.46 (m, 1H), 1.40-1.26 (m, 2H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 140.0, 138.0, 129.2, 128.1, 125.9, 117.6, 73.4, 52.2, 44.9, 36.8, 33.0, 32.5, 23.3 ppm; **IR** (neat): 3391, 3079, 3027, 2928, 1495, 916, 702 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{15}\text{H}_{21}\text{ClONa}$ ($\text{M} + \text{Na}$) $^{+}$: 275.1179, found 275.1184.

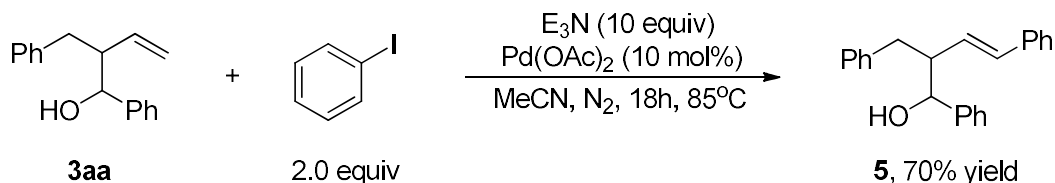
7. Further transformations for the product

7-1 Procedure for synthesis of **4**¹¹



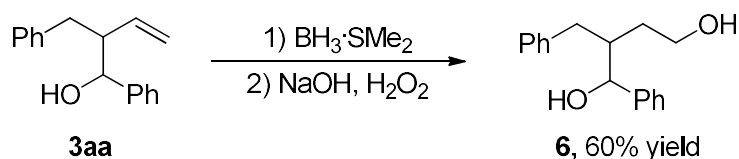
A containing stirring bar oven dried 10 ml Schlenk tube was charged with 3-chlorobenzoperoxoic acid (76mg, 0.375 mmol). The tube was then evacuated and back-filled under a N₂ flow (this sequence was repeated three times). A solution of **3aa** (60 mg, 0.25 mmol) in dry DCM (1.3 ml) was added by syringe. The reaction mixture was stirred overnight at room temp under N₂ was diluted with DCM (3 ml). After having been washed with saturated solution of K₂CO₃ (2 × 10 ml), the organic layer was separated and dried with Na₂SO₄, and solvent was removed under reduced pressure. The product was purified by silica gel column chromatography (EtOAc : petroleum ether = 1 : 8) to afford the product **4** (53 mg, 83% yield, 3:1 dr): R_f = 0.3 (EtOAc : petroleum ether = 1 : 5); ¹H-NMR (CDCl₃, 400 MHz) δ: 7.40-7.02 (m, 10H), 5.03-4.64 (m, 1H), 2.99-2.10 (m, 6H), 1.79-1.74 (m, 1H); ¹³C-NMR (CDCl₃, 100 MHz) δ: 142.7, 142.1, 139.7, 139.1, 129.6, 128.9, 128.4, 128.30, 128.26, 127.9, 127.4, 126.3, 126.14, 126.08, 74.8, 74.0, 53.1, 52.9, 50.7, 49.9, 47.6, 47.4, 33.7, 32.4 ppm; IR (neat): 3442, 3060, 3028, 2925, 1602, 1451, 887 cm⁻¹; HRMS (ESI-TOF) *m/z* calcd for C₁₇H₁₈O₂Na (M + Na)⁺: 277.1204, found 277.1204.

7-2 Procedure for synthesis of **5**¹²



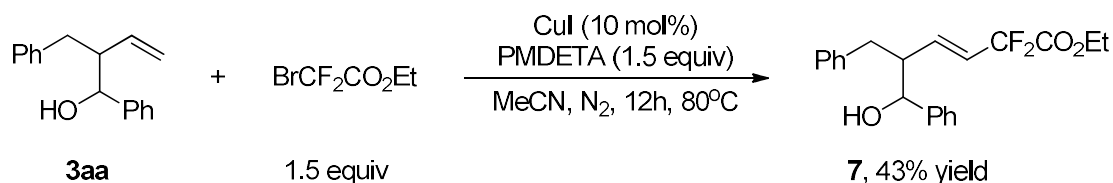
A containing stirring bar oven dried 10 ml Schlenk tube was charged with Pd(OAc)₂ (0.0185 mmol, 4.1 mg). The tube was then evacuated and back-filled under a N₂ flow (this sequence was repeated three times). Et₃N (1.85 mmol, 187 mg), iodobenzene (0.37 mmol, 75.5 mg) and a solution of **3aa** (0.185 mmol, 44.1 mg) in dry MeCN (1.8 ml) was added by syringe. The reaction mixture was stirred at 85°C for 18 h under N₂ and then cooled to room temperature. The mixture was concentrated in vacuo and residue was purified by silica gelcolumn chromatography (EtOAc : petroleum ether = 1 : 10) to afford the product **5** (41 mg, 70% yield): R_f = 0.4 (EtOAc : petroleum ether = 1 : 5); ¹H-NMR (CDCl₃, 400 MHz) δ: 7.36-7.33 (m, 4H), 7.28-7.12 (m, 11H), 6.16 (d, *J* = 16 Hz, 1H), 5.98-5.92 (m, 1H), 4.83-4.74 (m, 1H), 2.98-2.88 (m, 2H), 2.71-2.66 (m, 1H), 2.15-2.14 (m, 1H); ¹³C-NMR (CDCl₃, 100 MHz) δ: 142.2, 139.9, 137.3, 132.5, 129.4, 129.3, 128.4, 128.1, 127.5, 127.1, 126.7, 126.1, 125.8, 76.6, 51.9, 36.7 ppm; IR (neat): 3391, 3025, 2914, 1451, 1005, 743, 696 cm⁻¹; HRMS (ESI-TOF) *m/z* calcd for C₂₃H₂₂ONa (M + Na)⁺: 337.1568, found 337.1562.

7-3 Procedure for synthesis of **6**¹³



In an oven dried 10 ml Schlenk tube, $\text{BH}_3\cdot\text{SMe}_2$ (0.3 ml, 2.0 M, 0.6 mmol, 3.0 equiv) was added to a solution of **3aa** (0.20mmol, 48 mg, 1.0 equiv) in dry THF (2.0 ml) at 0°C. The reaction mixture was stirred at room temperature under N_2 for 3 h, then an aqueous solution of 10% NaOH (0.36 ml, 4.5 equiv) and 30% H_2O_2 (0.12 ml, 6.0 equiv) were added. After stirring for 3 h, the mixture was extracted with EtOAc (3 $\times$ 10 ml). The organic layer was separated and dried with Na_2SO_4 , and solvent was removed under reduced pressure. The product was purified by silica gel column chromatography (EtOAc : petroleum ether = 1 : 2) to afford the product **6** (32mg, 60% yield): R_f = 0.5 (EtOAc : petroleum ether = 1 : 1); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 7.37-7.34 (m, 4H), 7.29-7.21 (m, 3H), 7.16-7.13 (m, 1H), 7.07-7.06 (m, 2H), 4.89-4.81 (m, 1H), 3.67-3.50 (m, 4H), 2.73-2.70 (m, 1H), 2.47-2.41 (m, 1H), 2.31-2.18 (m, 1H), 1.67-1.62 (m, 1H), 1.49-1.45 (m, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 142.7, 140.6, 129.1, 128.3, 128.2, 127.2, 126.5, 125.8, 75.7, 60.8, 45.1, 34.8, 32.2 ppm; **IR** (neat): 3350, 3061, 3027, 2930, 1493, 1451, 702 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{17}\text{H}_{20}\text{O}_2\text{Na}$ ($\text{M} + \text{Na}$) $^+$: 279.1361, found 279.1357.

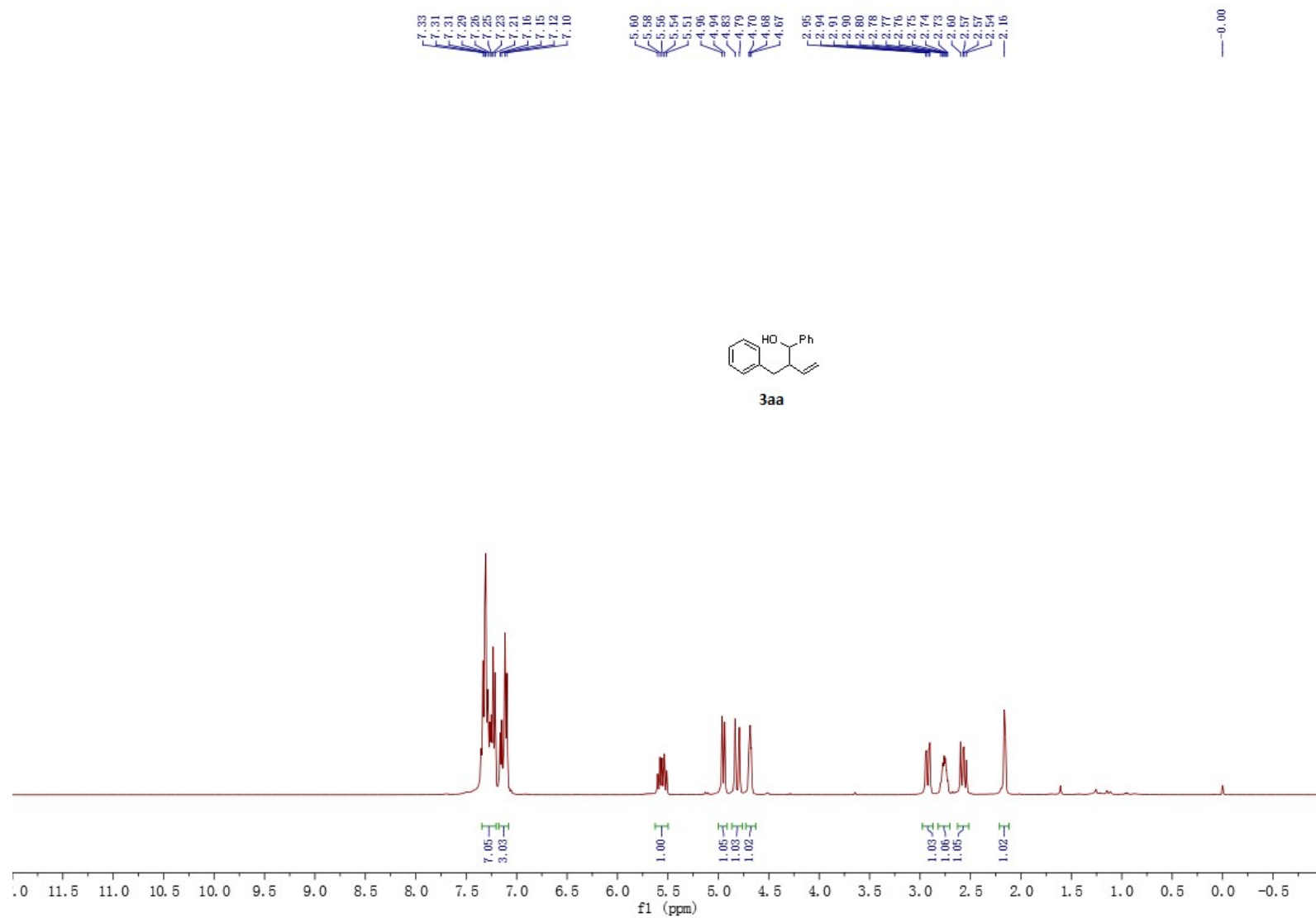
7-4 Procedure for synthesis of **7**¹⁴

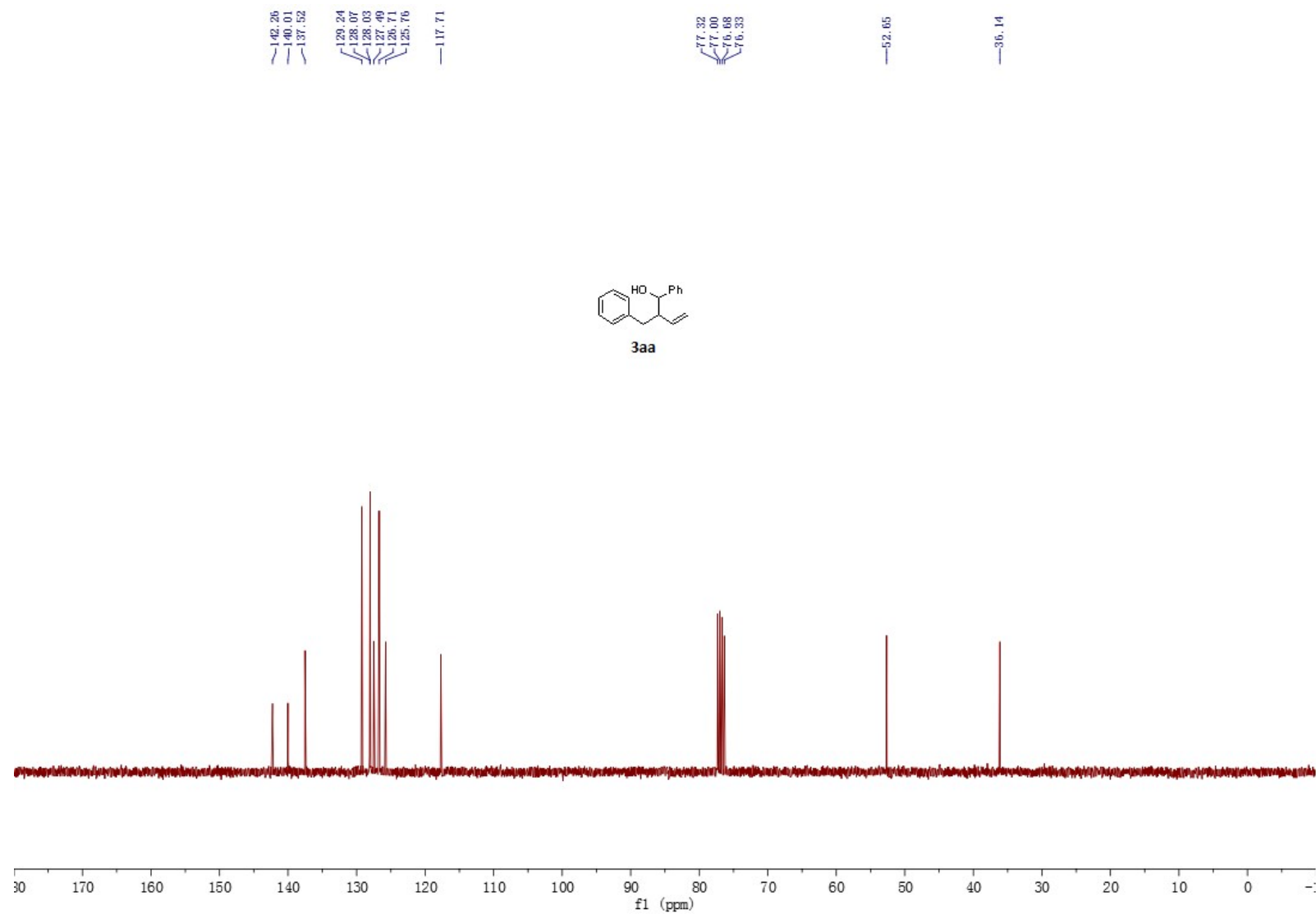


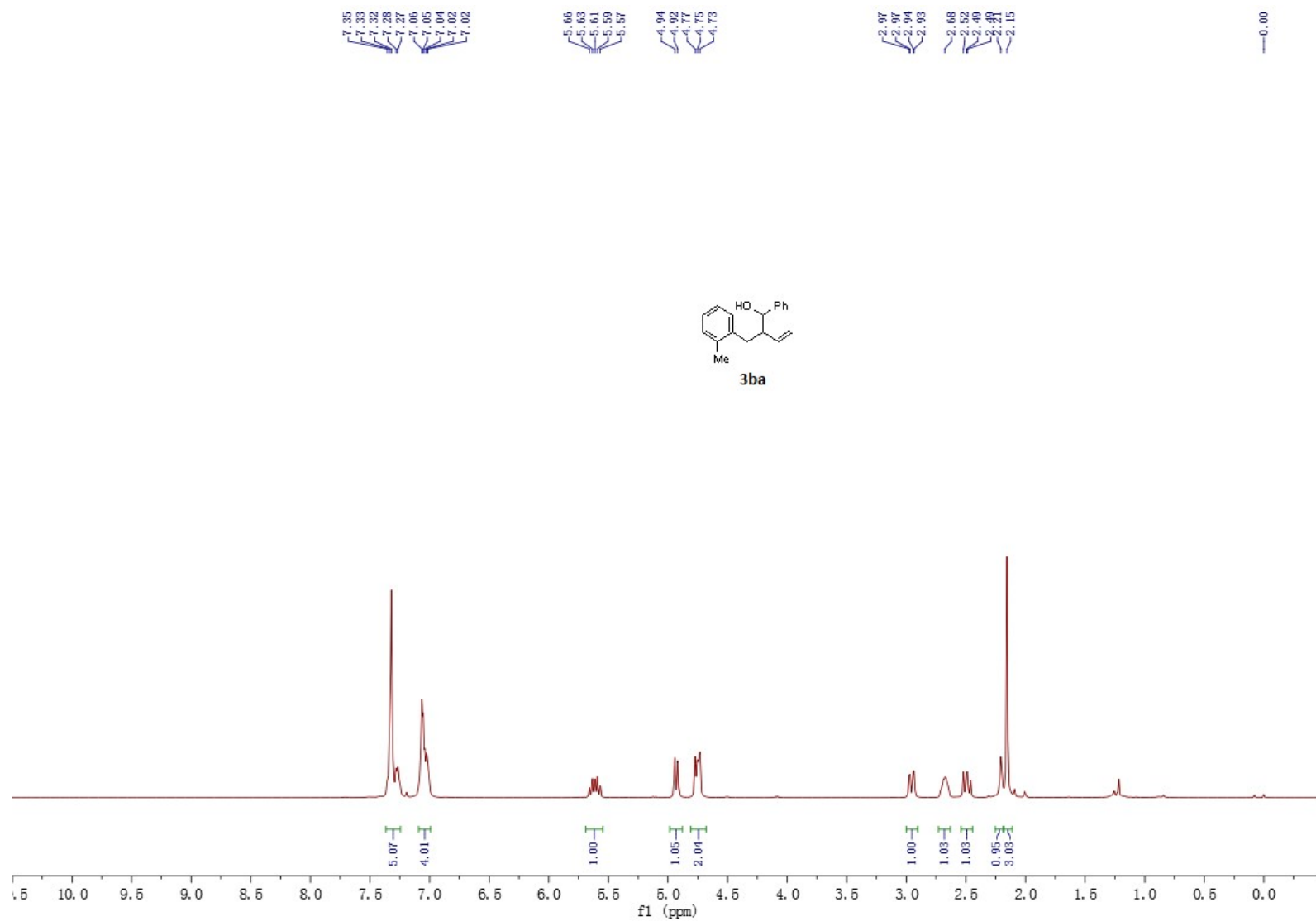
A containing stirring bar oven dried 10 ml Schlenk tube was charged with CuI (0.02mmol, 3.8 mg). The tube was then evacuated and back-filled under a N_2 flow (this sequence was repeated three times). Pentamethyldiethylenetriamine (0.3mmol, 52mg), a solution of **3aa** (0.20 mmol, 48 mg) in dry MeCN (0.8 ml) and ethylbromodifluoroacetate (0.30mmol, 61mg) was added subsequently. The reaction mixture was heated to 80°C. After stirring for 12h, the reaction was cooled to room temperature. The reaction mixture was diluted with EtOAc and filtered with a pad of Celite. The filtrate was concentrated, and the residue was purified with silica gel chromatography (EtOAc : petroleum ether = 1 : 8) to give the product **7** (31 mg, 43% yield): R_f = 0.5 (EtOAc : petroleum ether = 1 : 5); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 7.35-7.33 (m, 2H), 7.29-7.22 (m, 5H), 7.18-7.14 (m, 1H), 7.08-7.06 (m, 2H), 6.09-6.03 (m, 1H), 5.29 (dd, J_1 = 28 Hz, J_2 = 12 Hz, 1H), 4.72 (d, J = 4.0 Hz, 1H), 4.15 (q, J = 8.0 Hz, 2H), 3.03-2.99 (m, 1H), 2.86-2.73 (m, 1H), 2.66-2.61 (m, 1H), 2.08 (s, 1H), 1.23 (t, J = 6 Hz, 3H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 163.7 (t, J = 35 Hz), 141.8, 139.0, 138.5 (t, J = 9.0 Hz), 129.3, 128.3, 128.2, 127.9, 126.5, 126.1, 123.5 (t, J = 25.5 Hz), 111.8 (t, J = 247 Hz), 76.0, 62.7, 51.4, 36.0, 13.8 ppm; $^{19}\text{F-NMR}$ (CDCl_3 , 376 MHz) δ : -103.35, -104.02, -104.23, -104.91 ppm; **IR** (neat): 3441, 3063, 3030, 2924, 1764, 1670, 702 cm^{-1} ; **HRMS** (ESI-TOF) m/z calcd for $\text{C}_{21}\text{H}_{22}\text{F}_2\text{O}_3\text{Na}$ ($\text{M} + \text{Na}$) $^+$: 383.1435, found 383.1427.

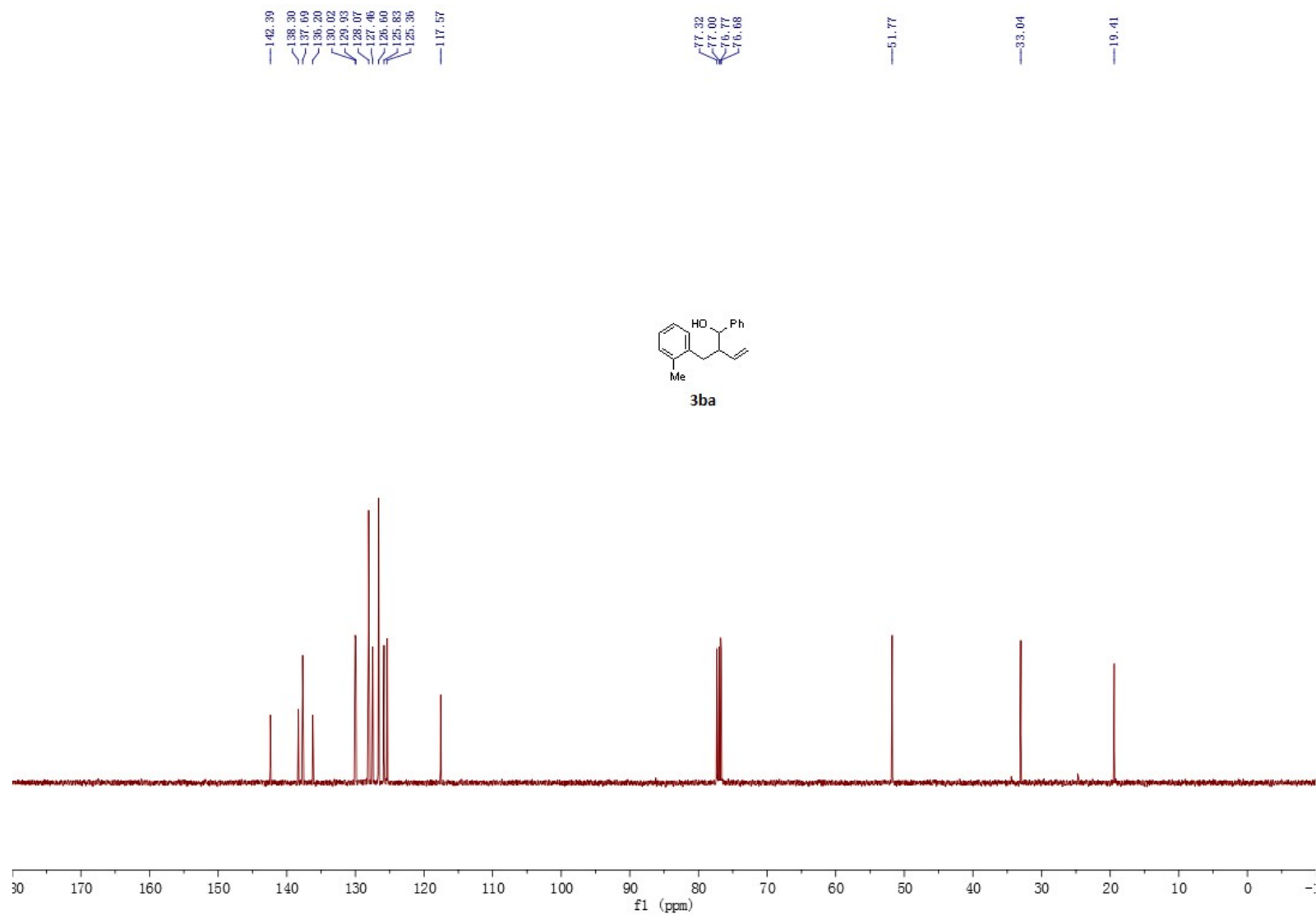
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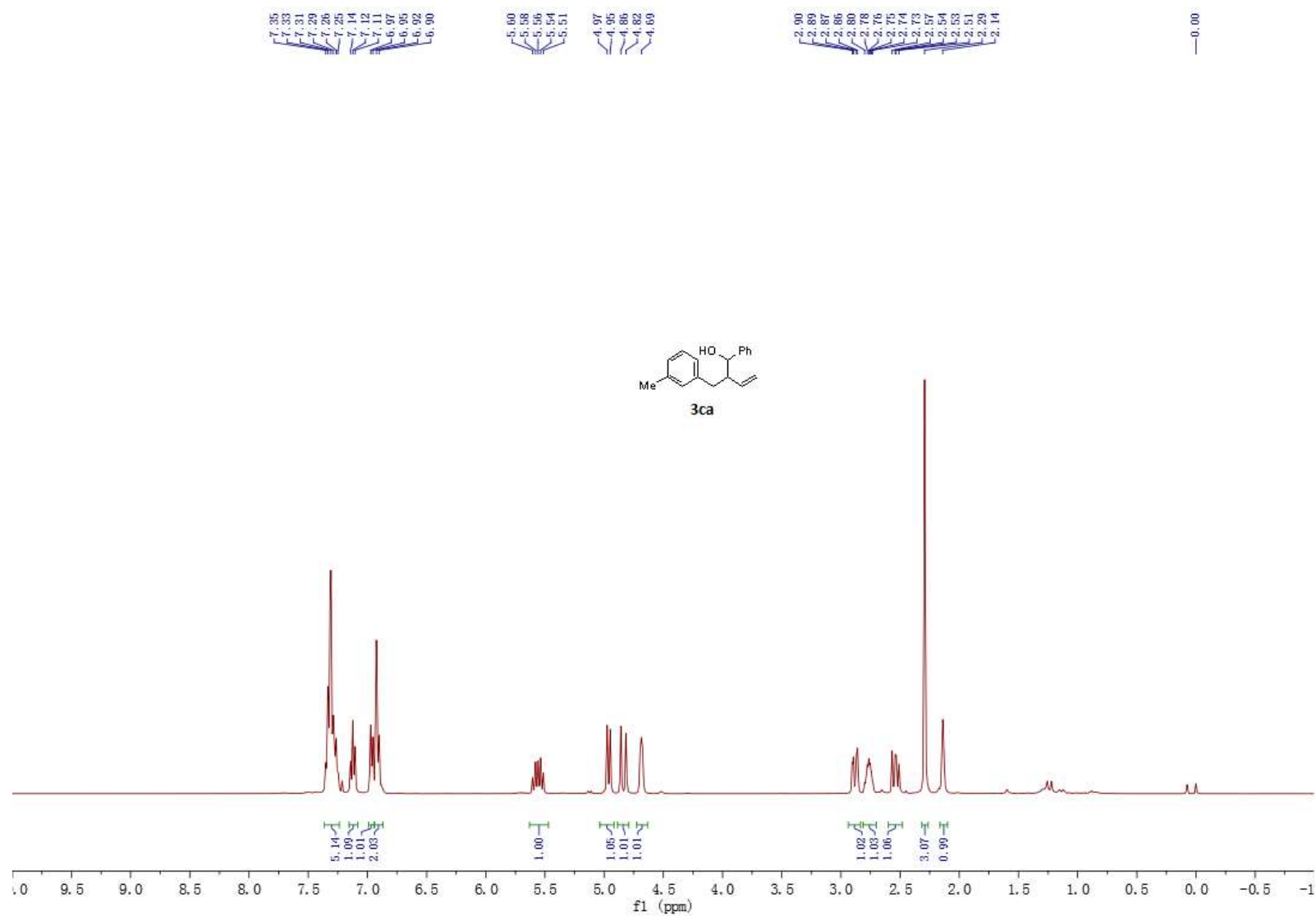
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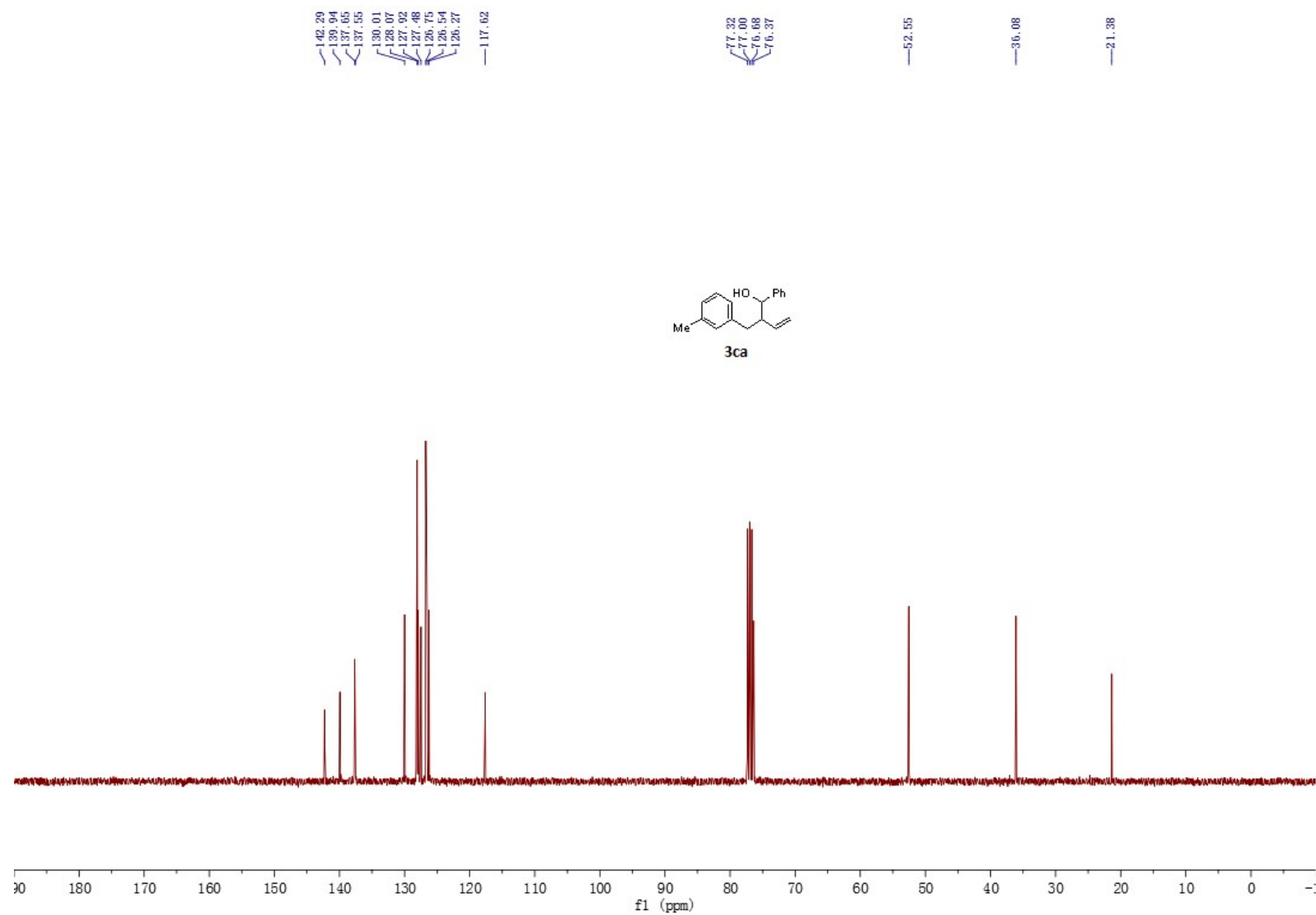


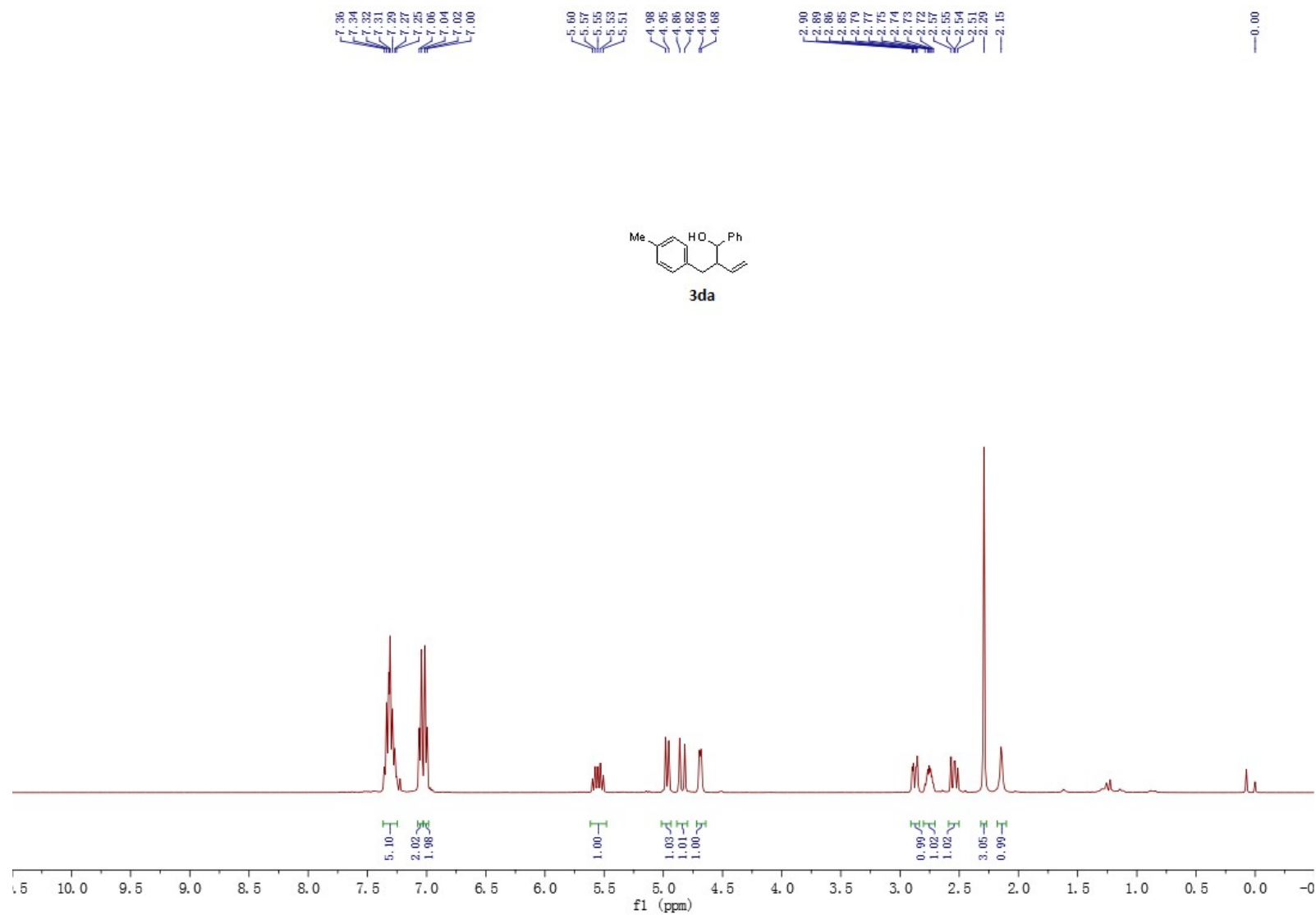


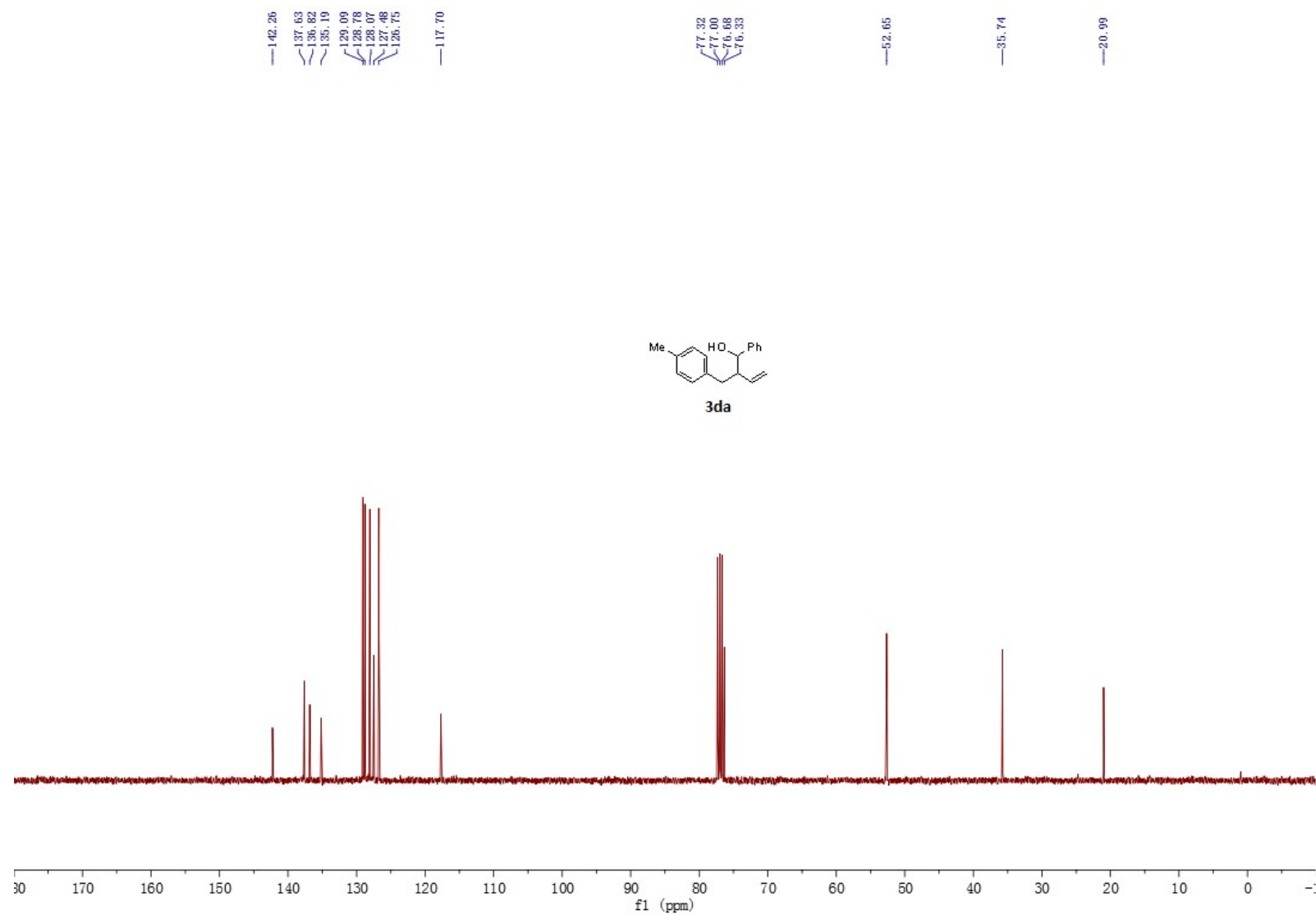


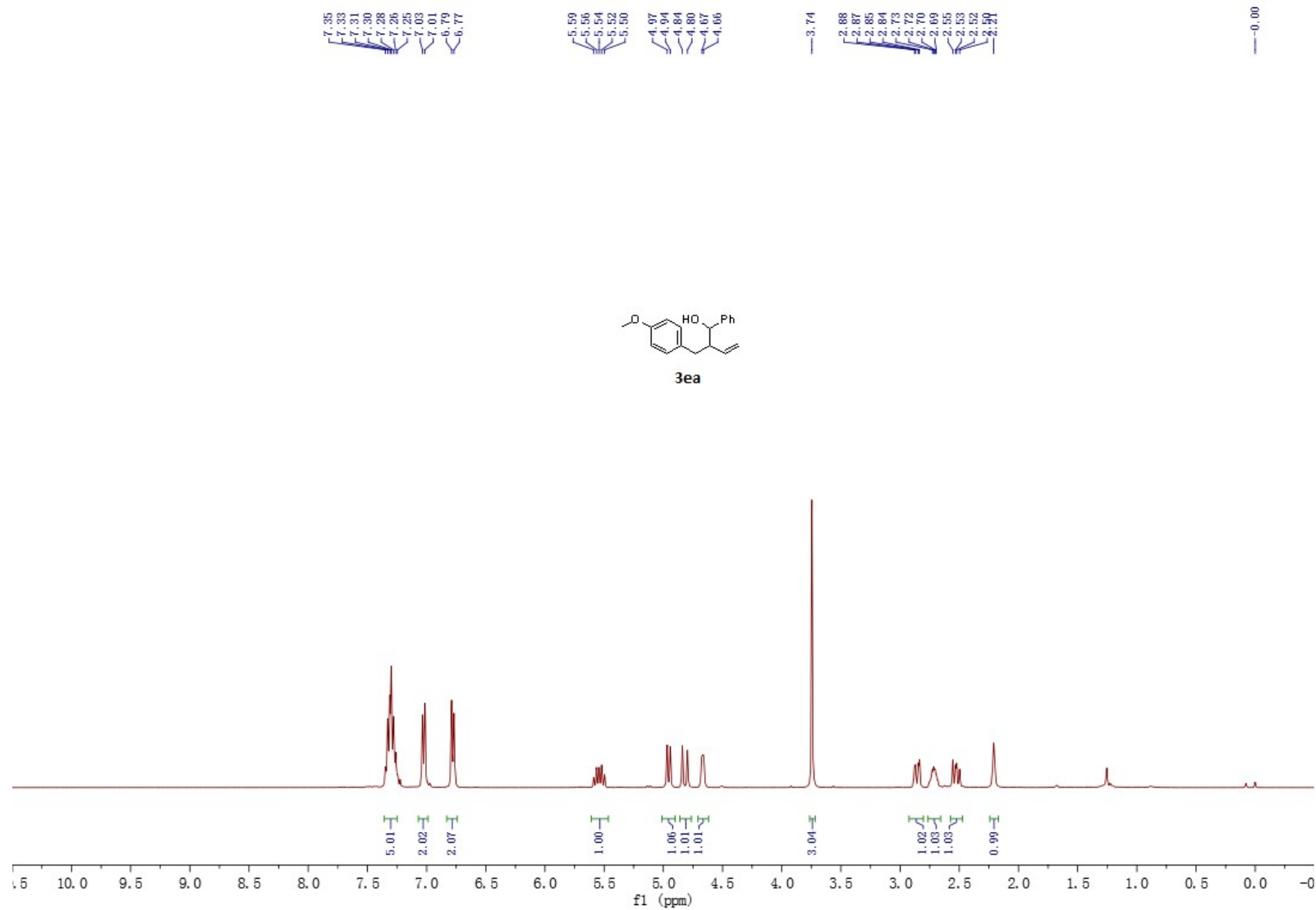


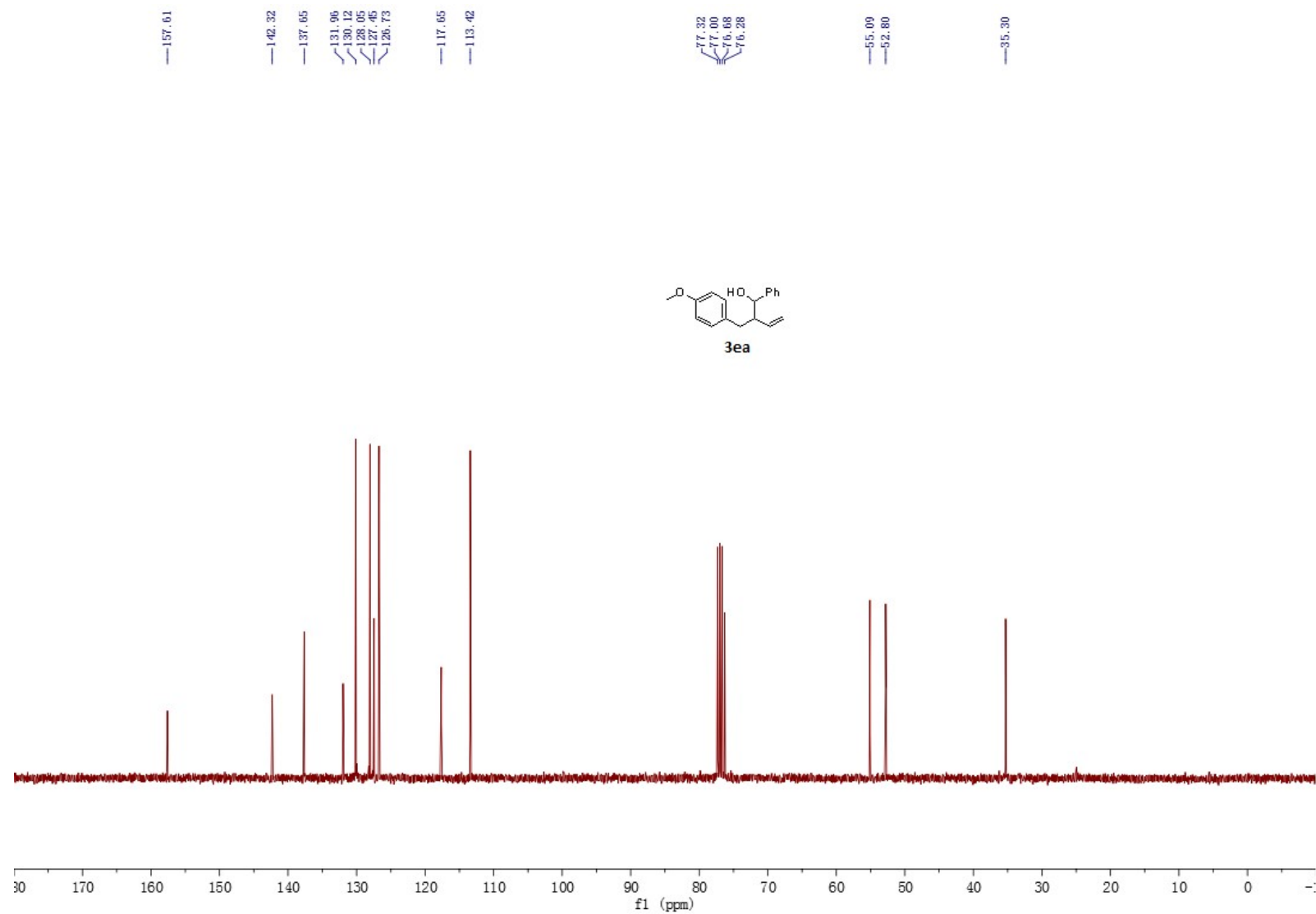


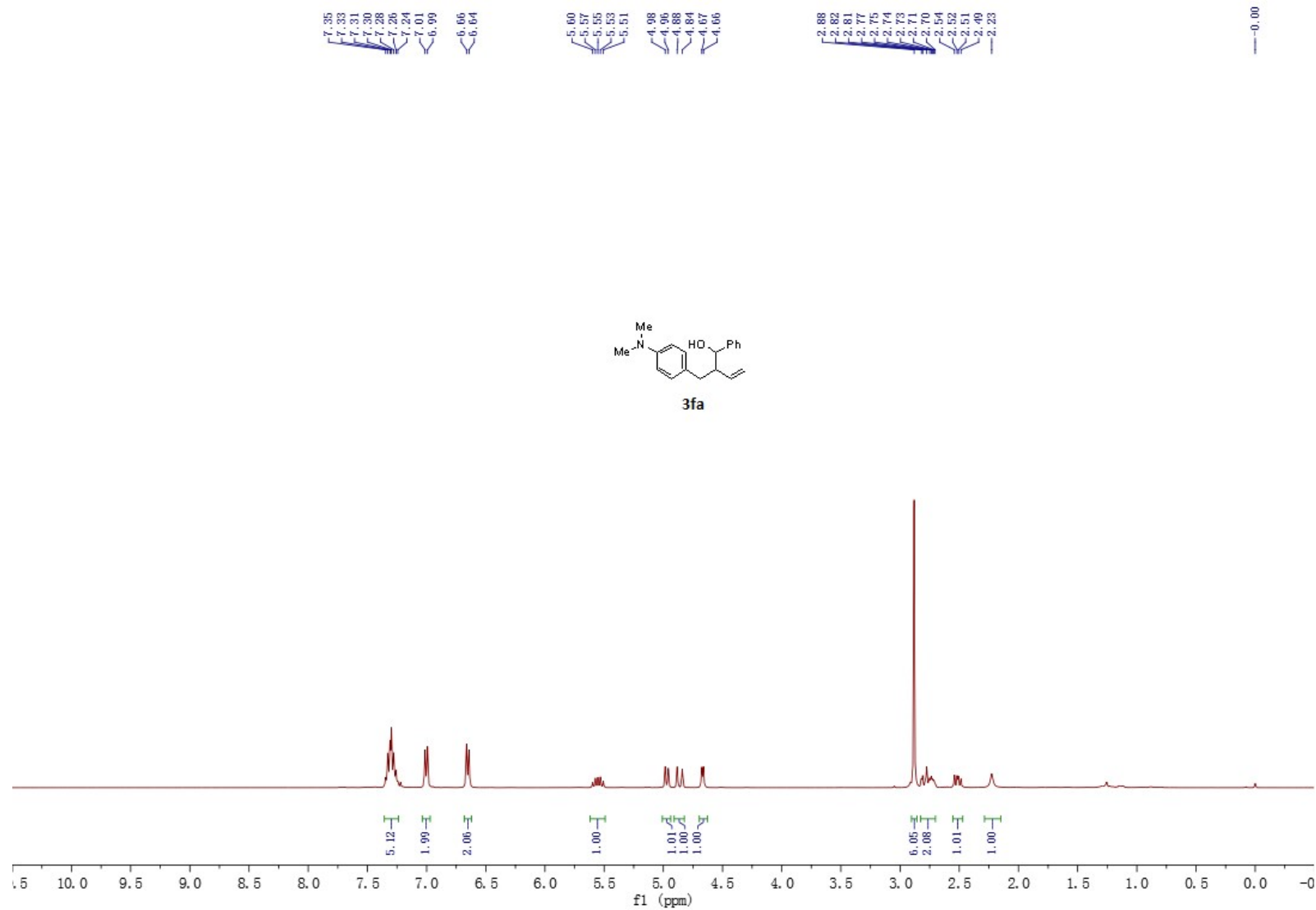


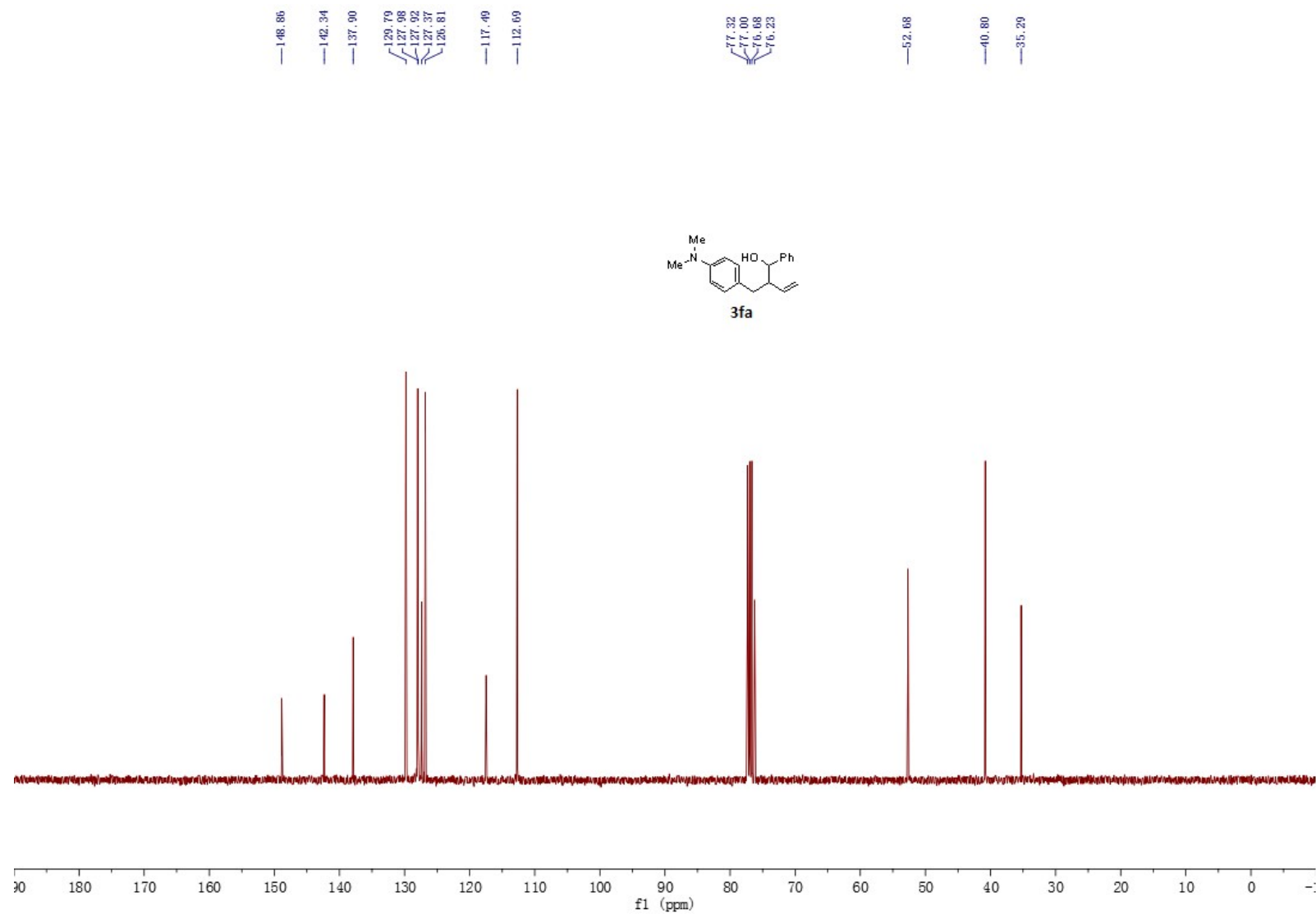


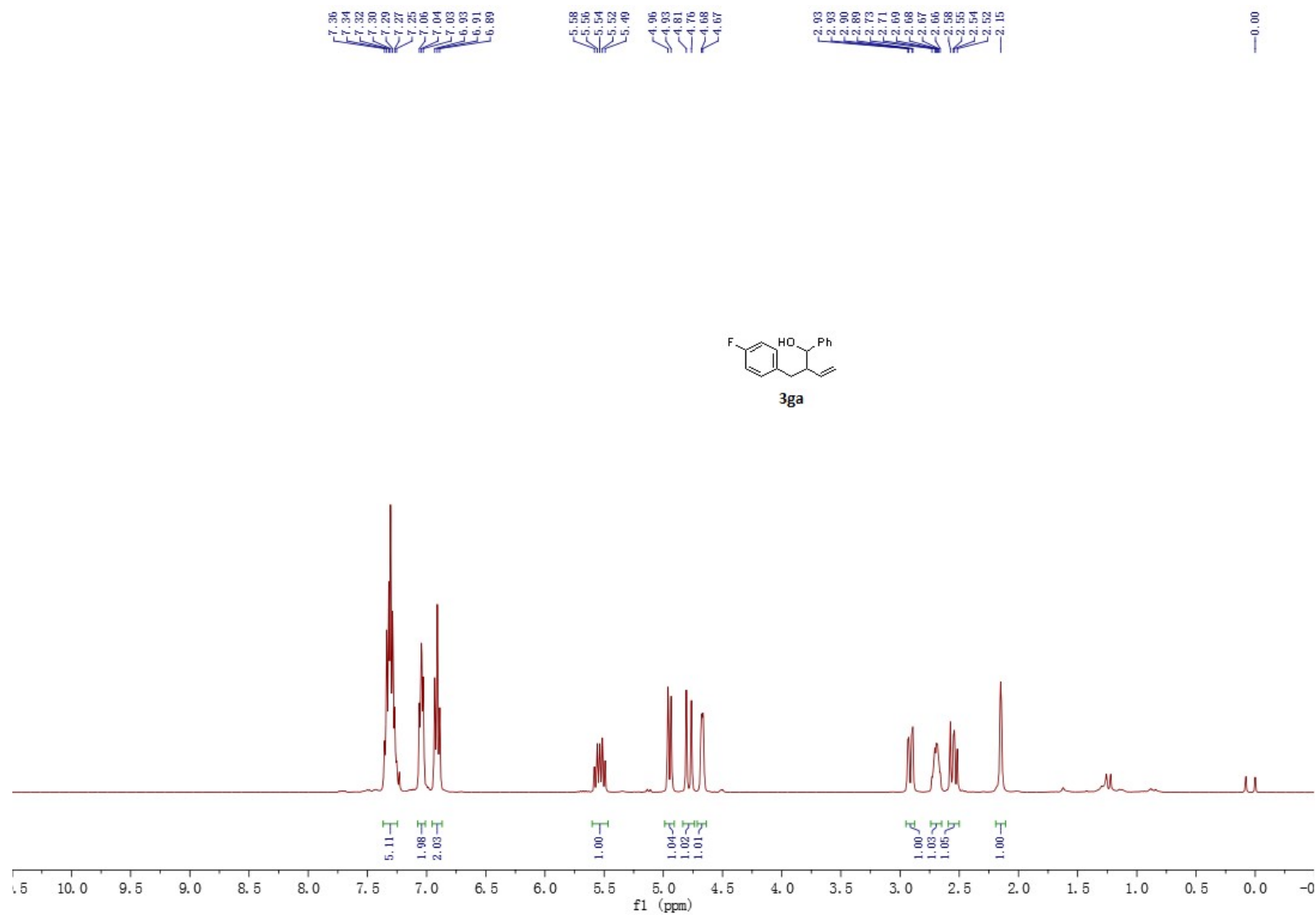


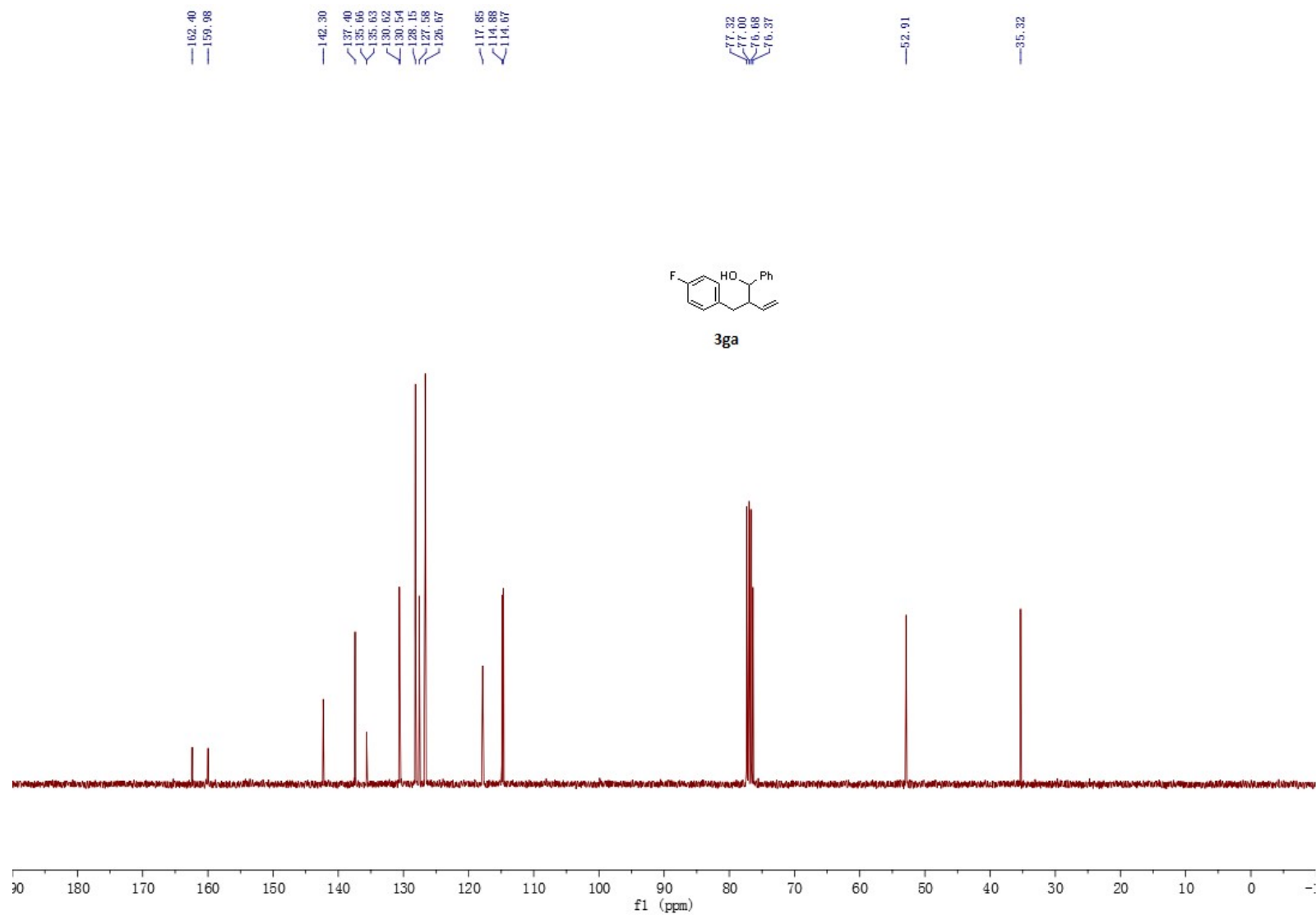


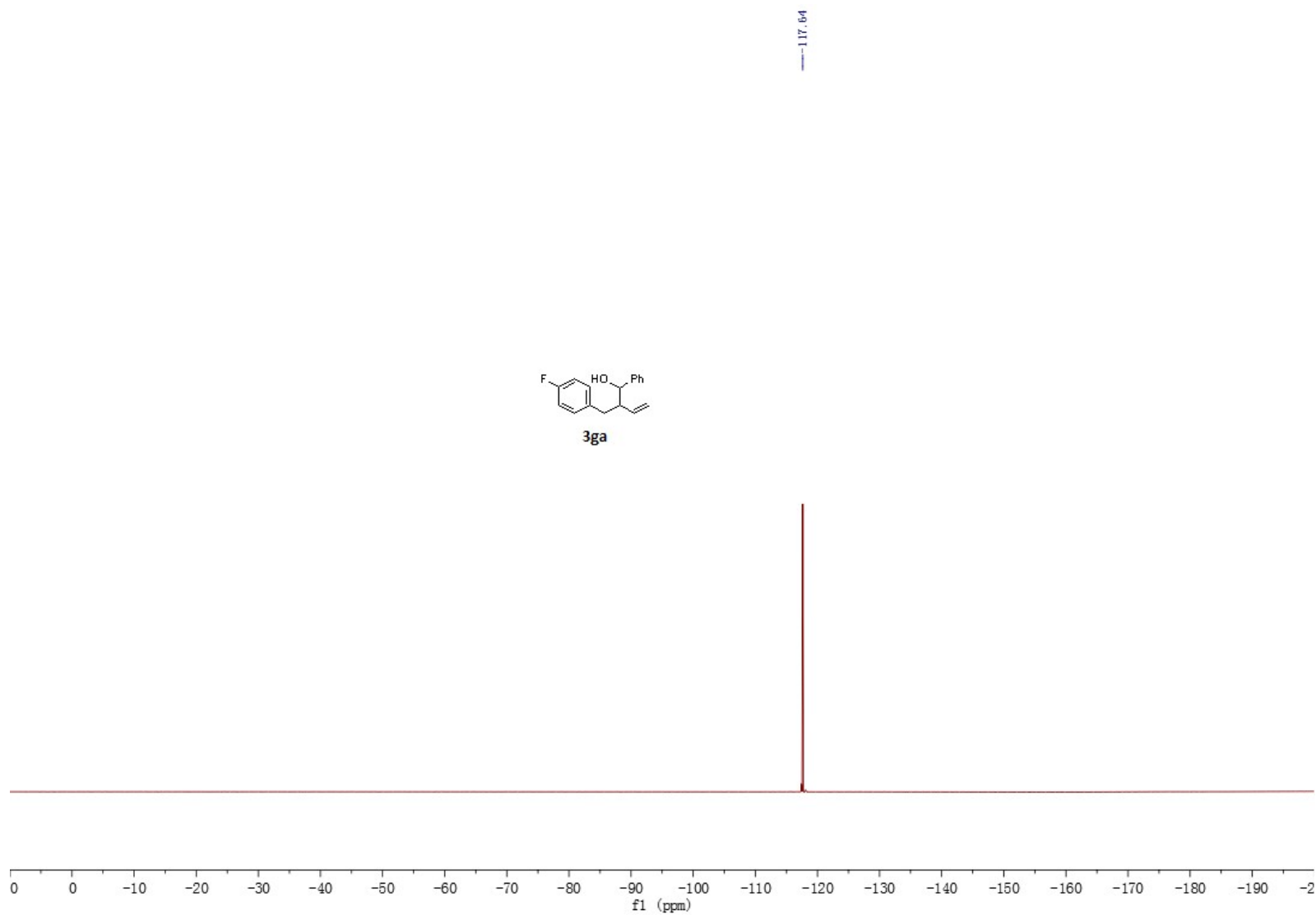
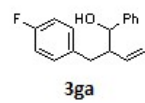


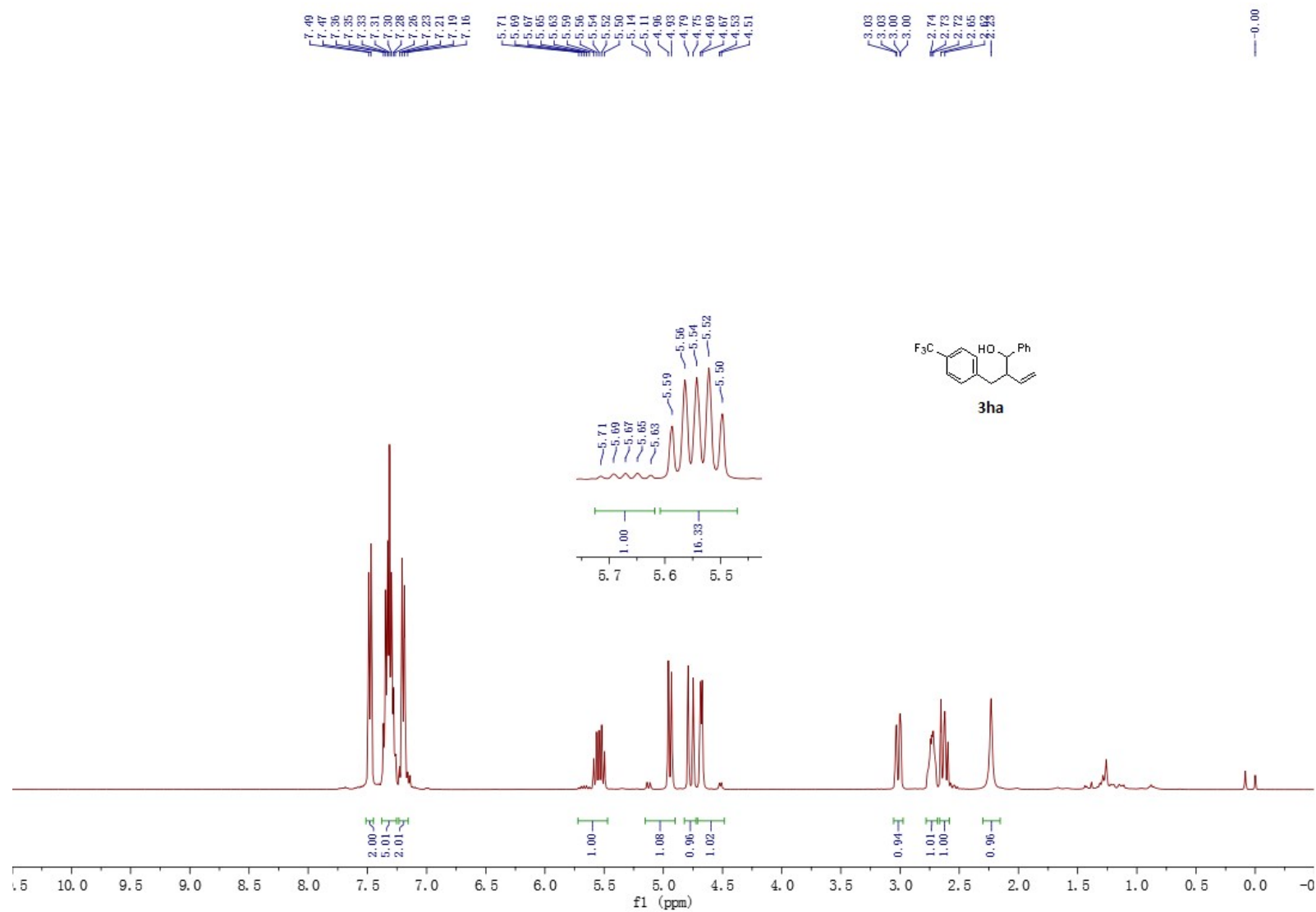


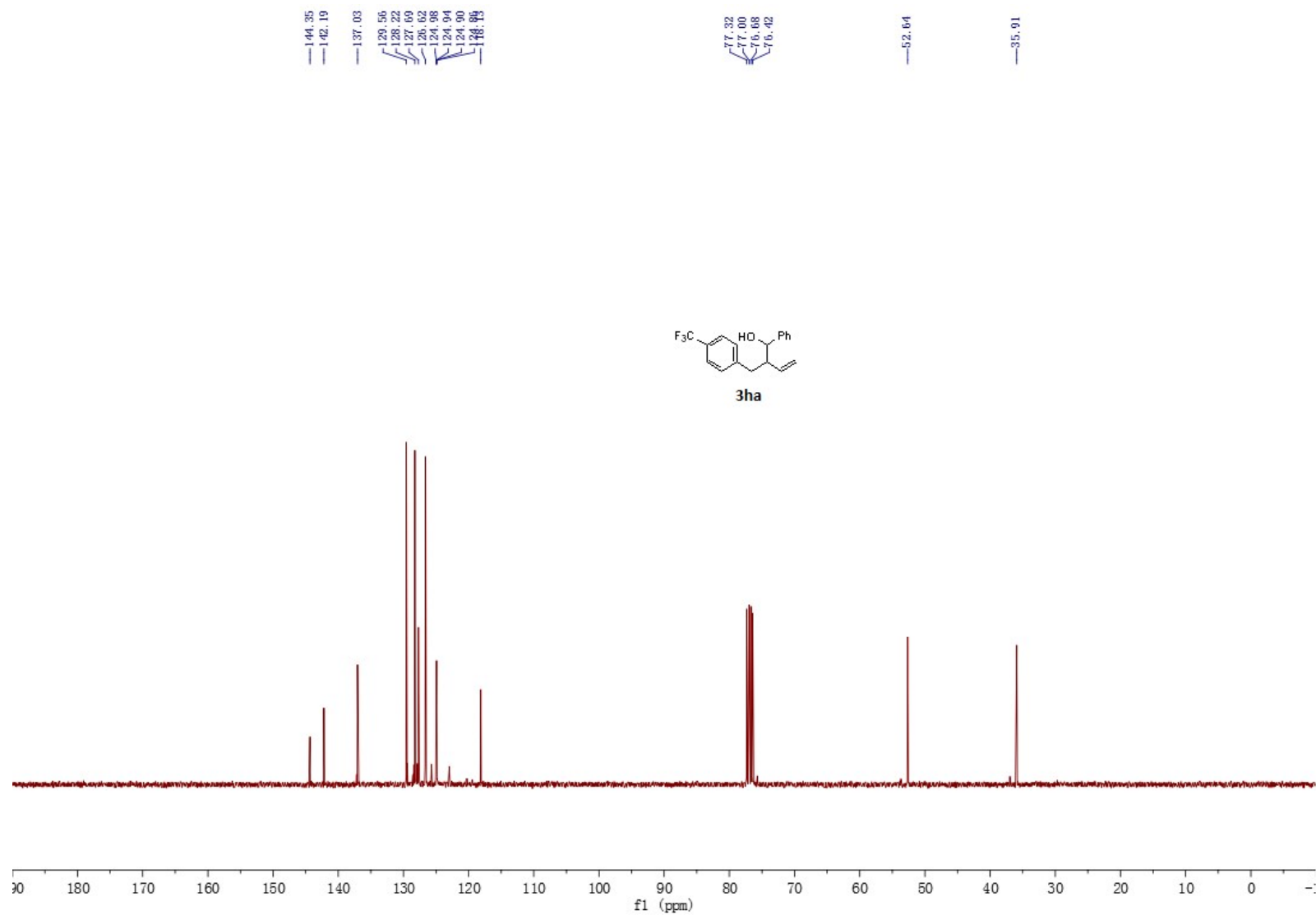


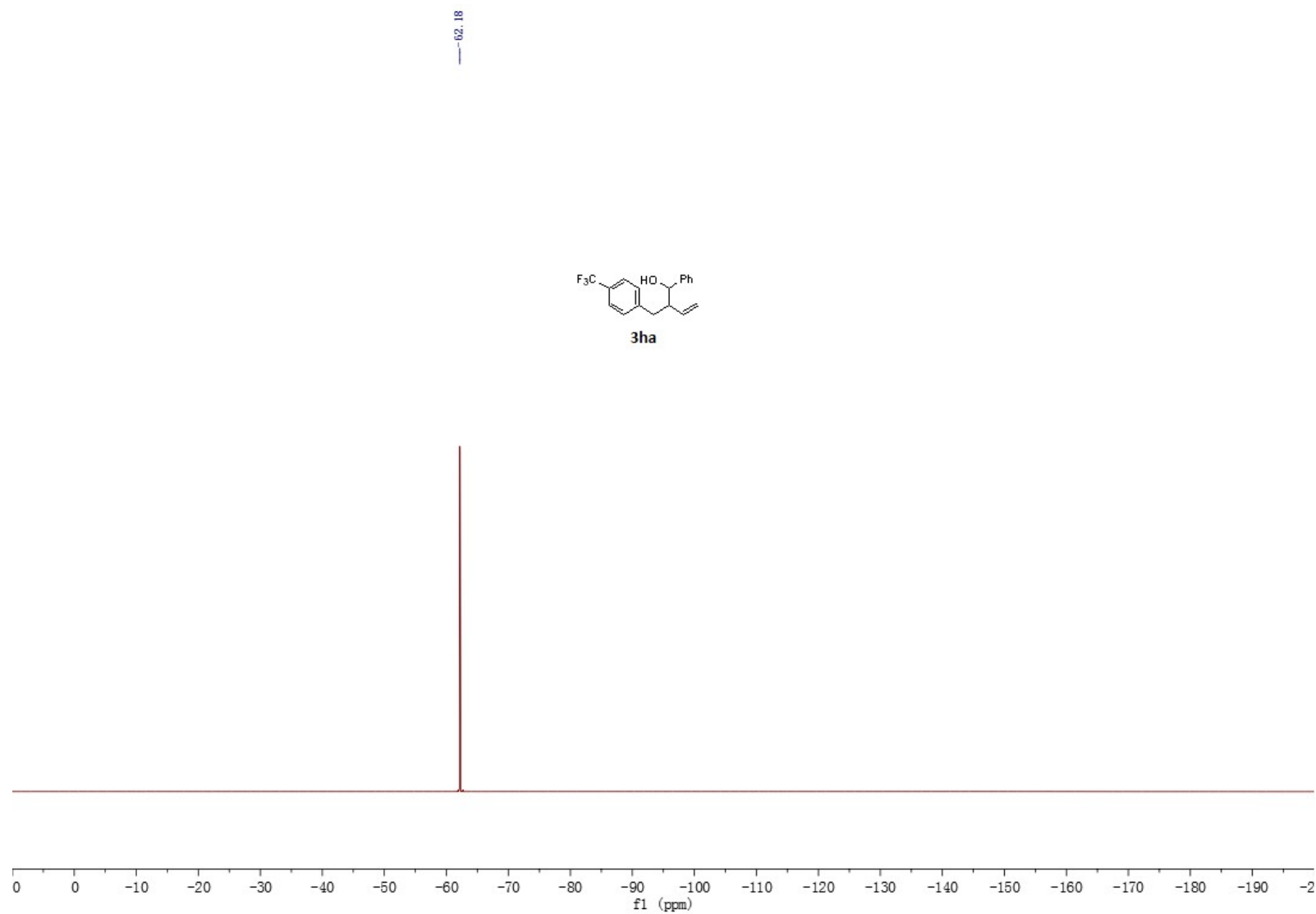


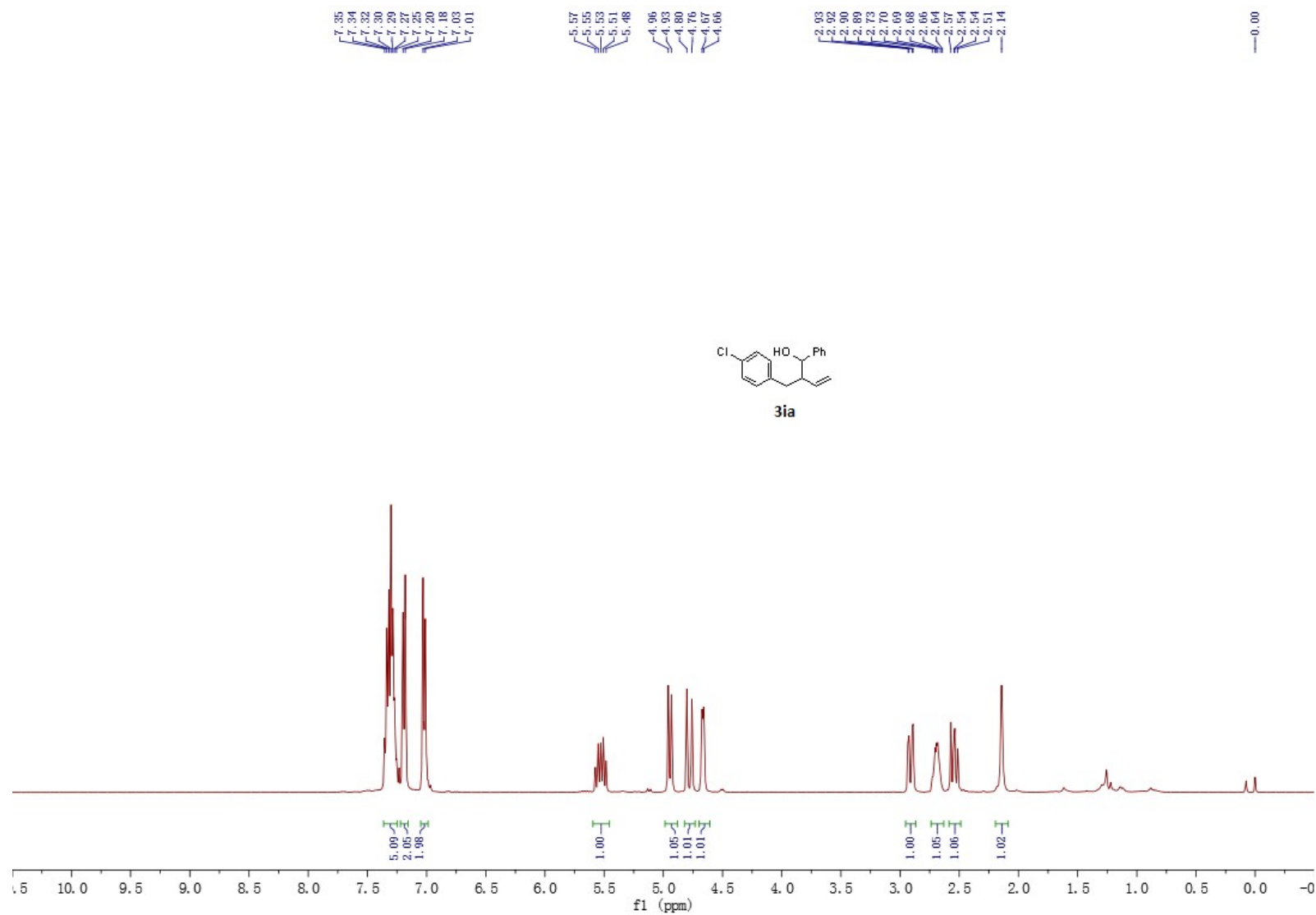


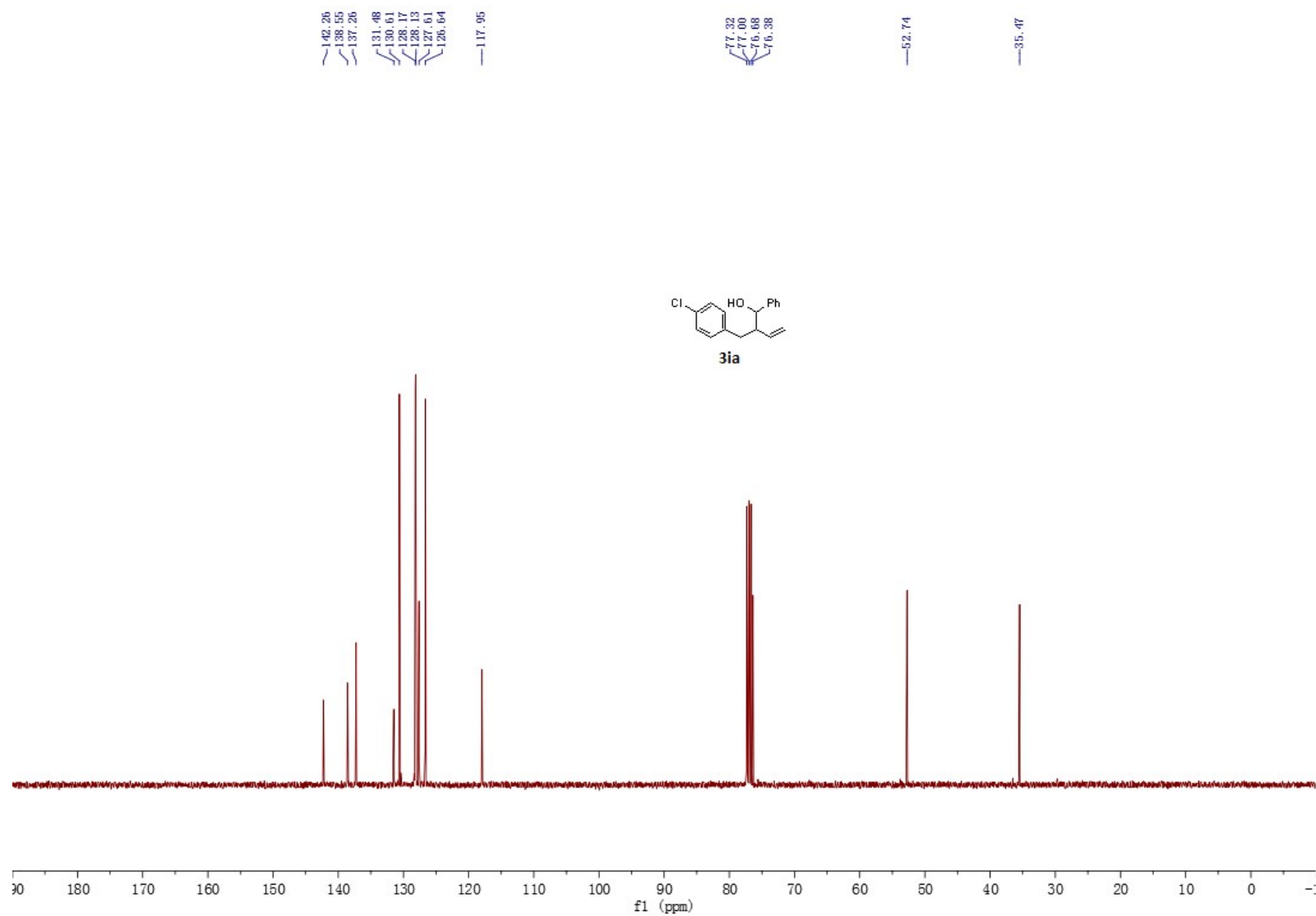


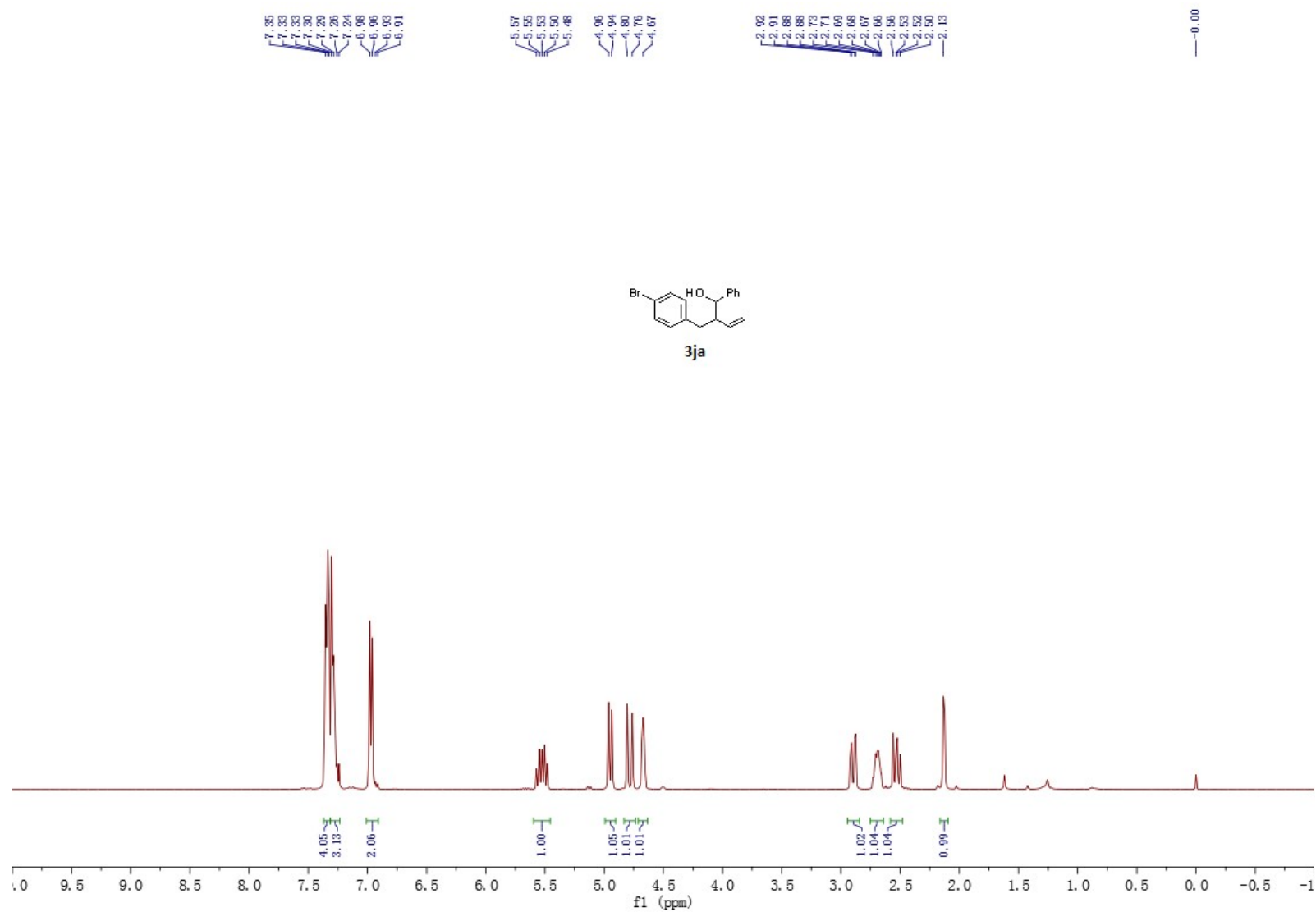


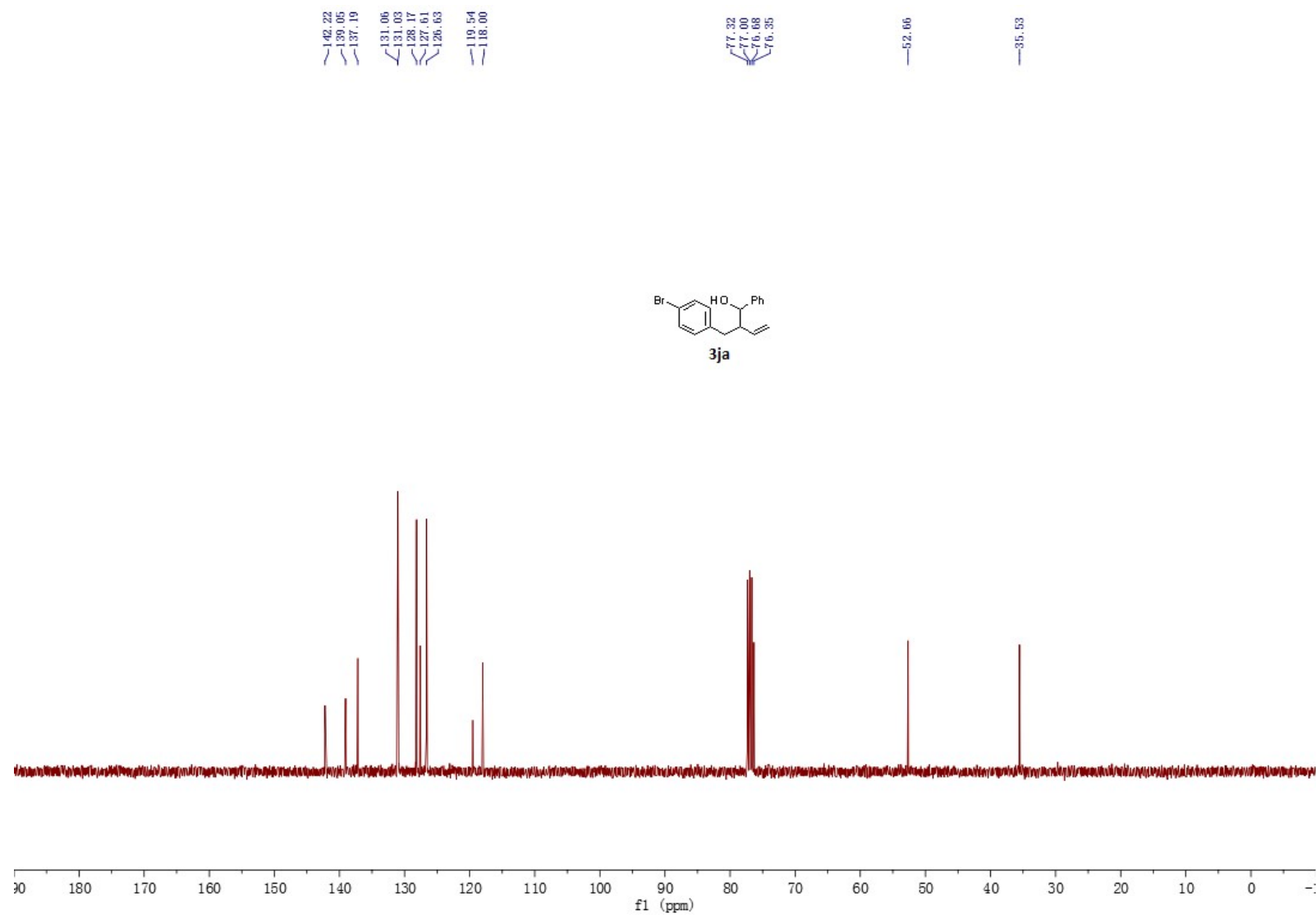


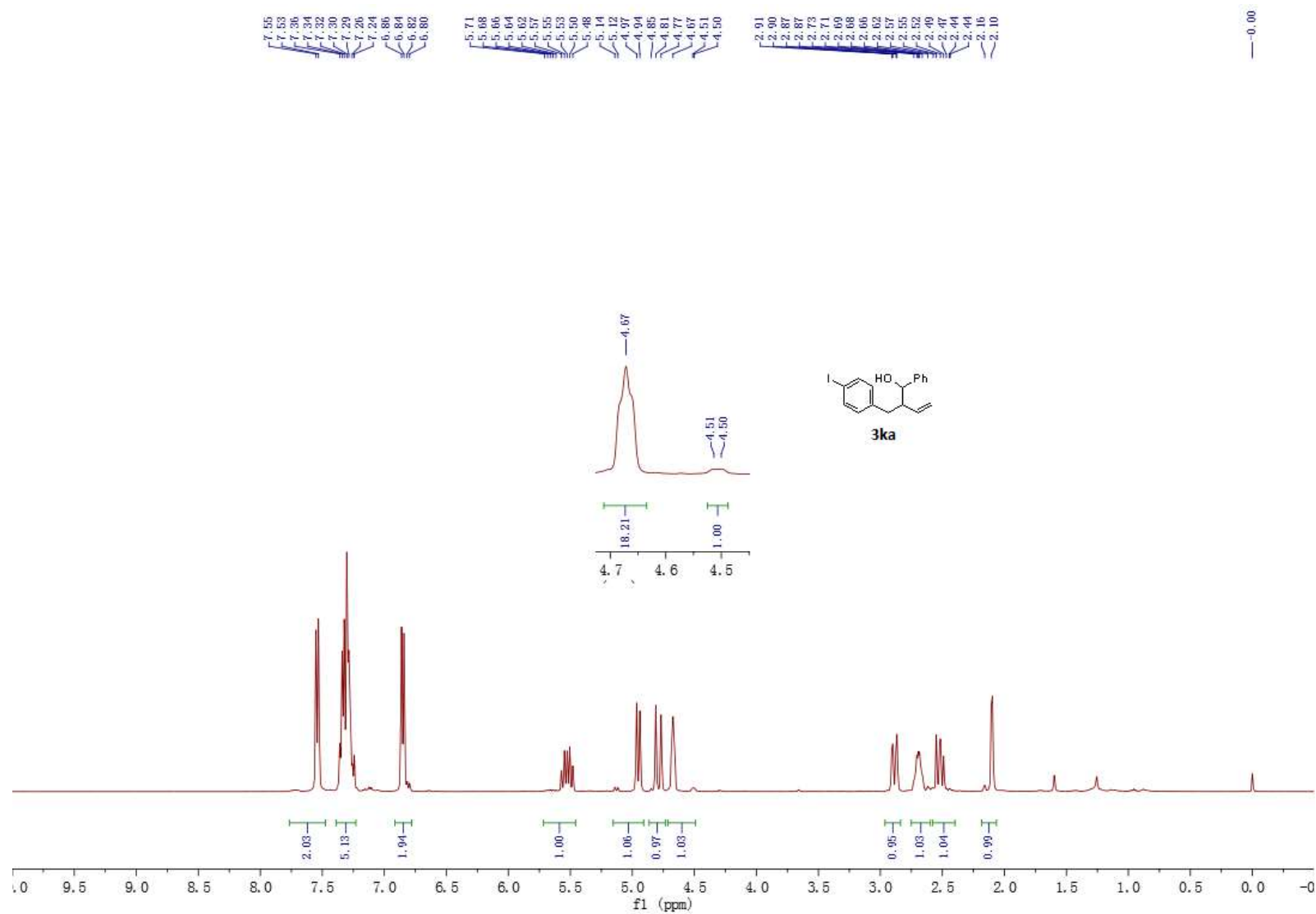


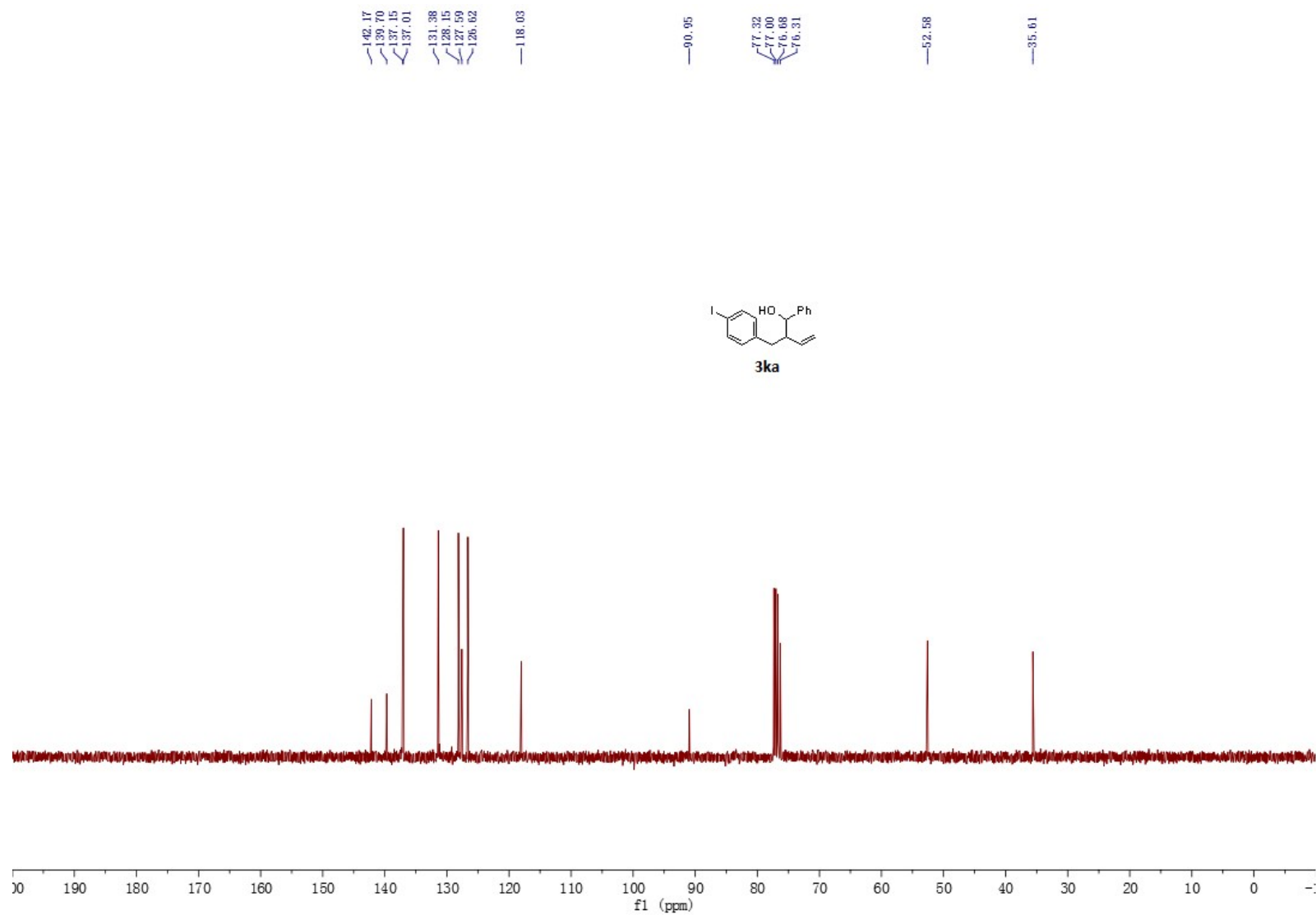


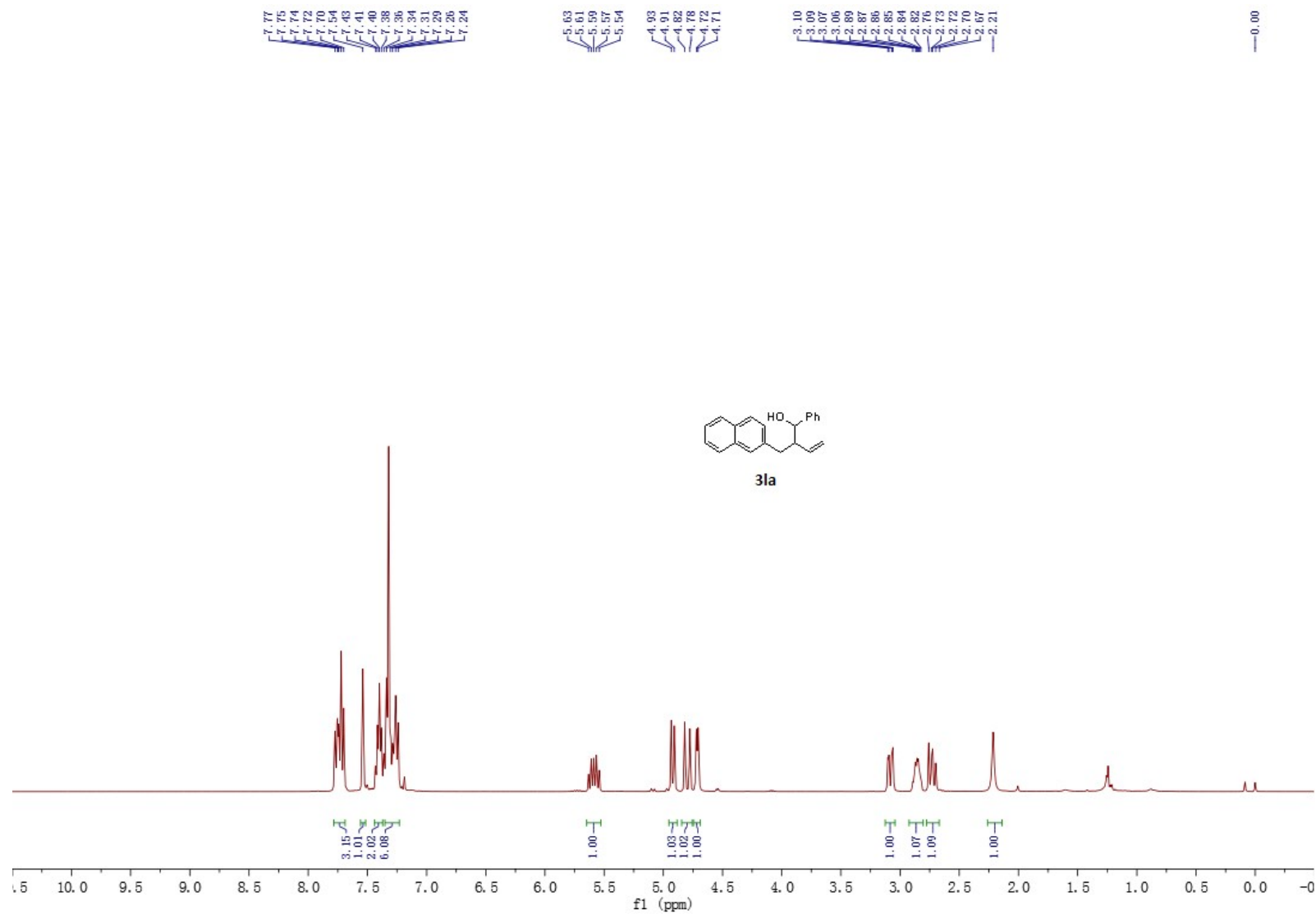


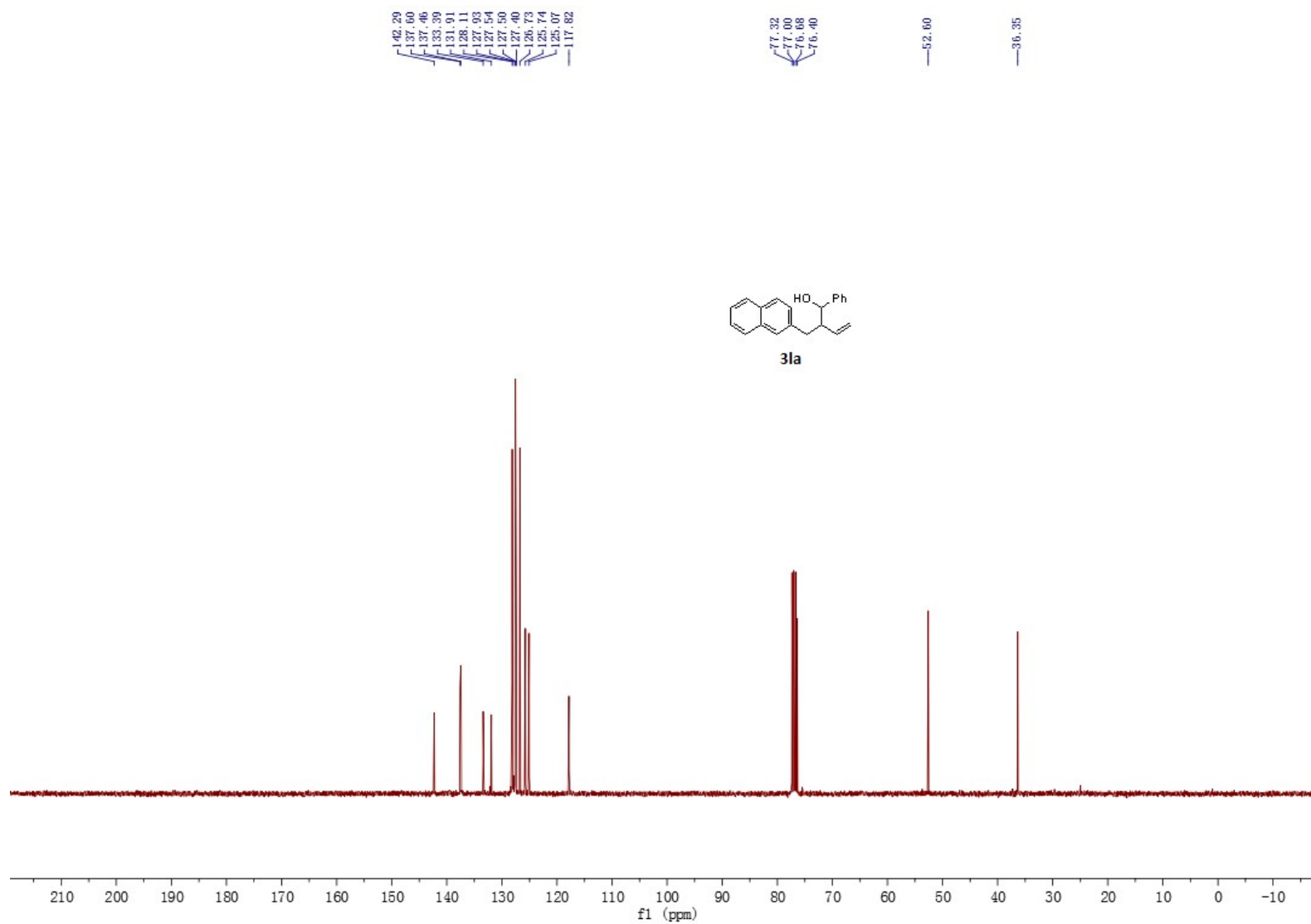


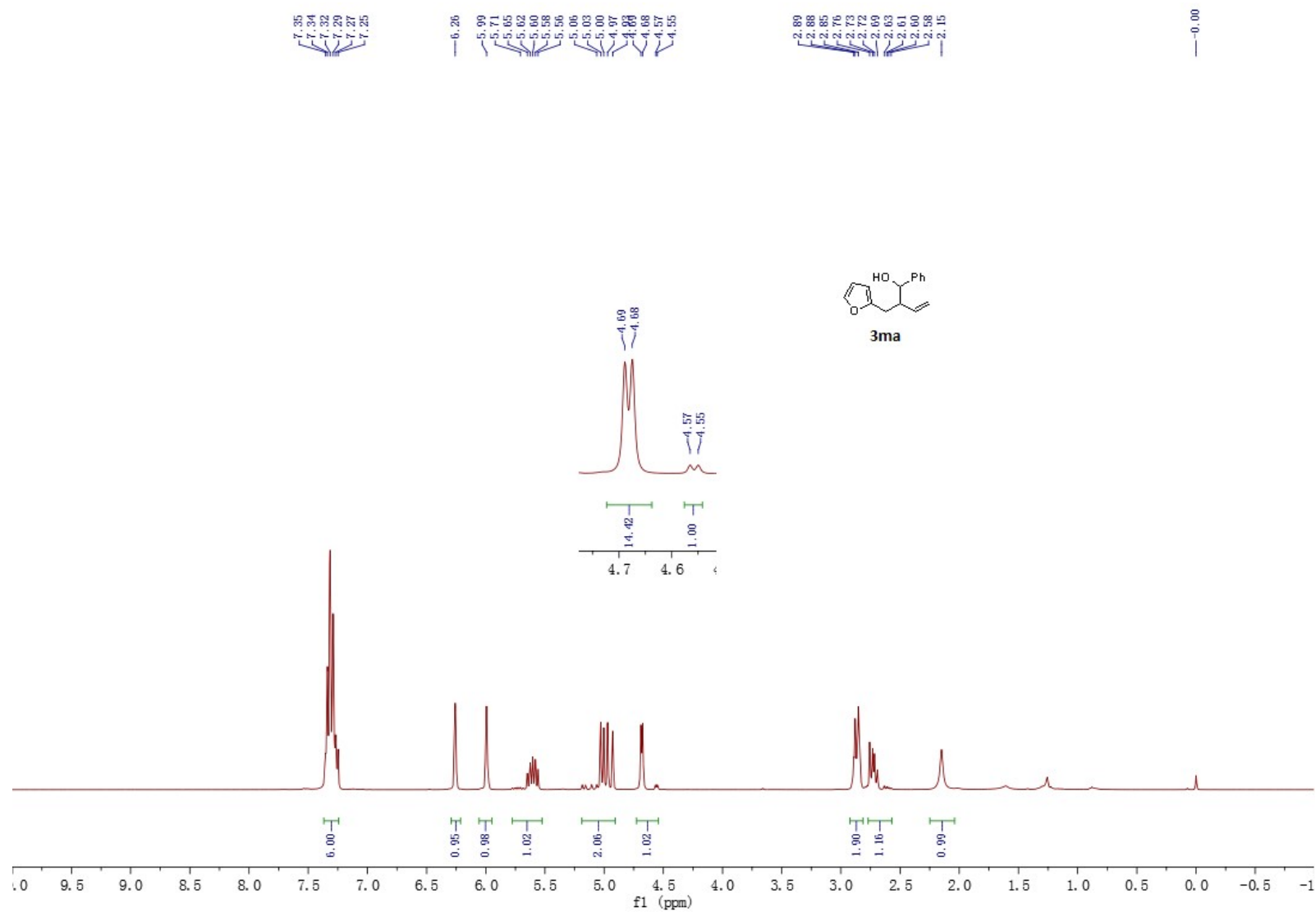


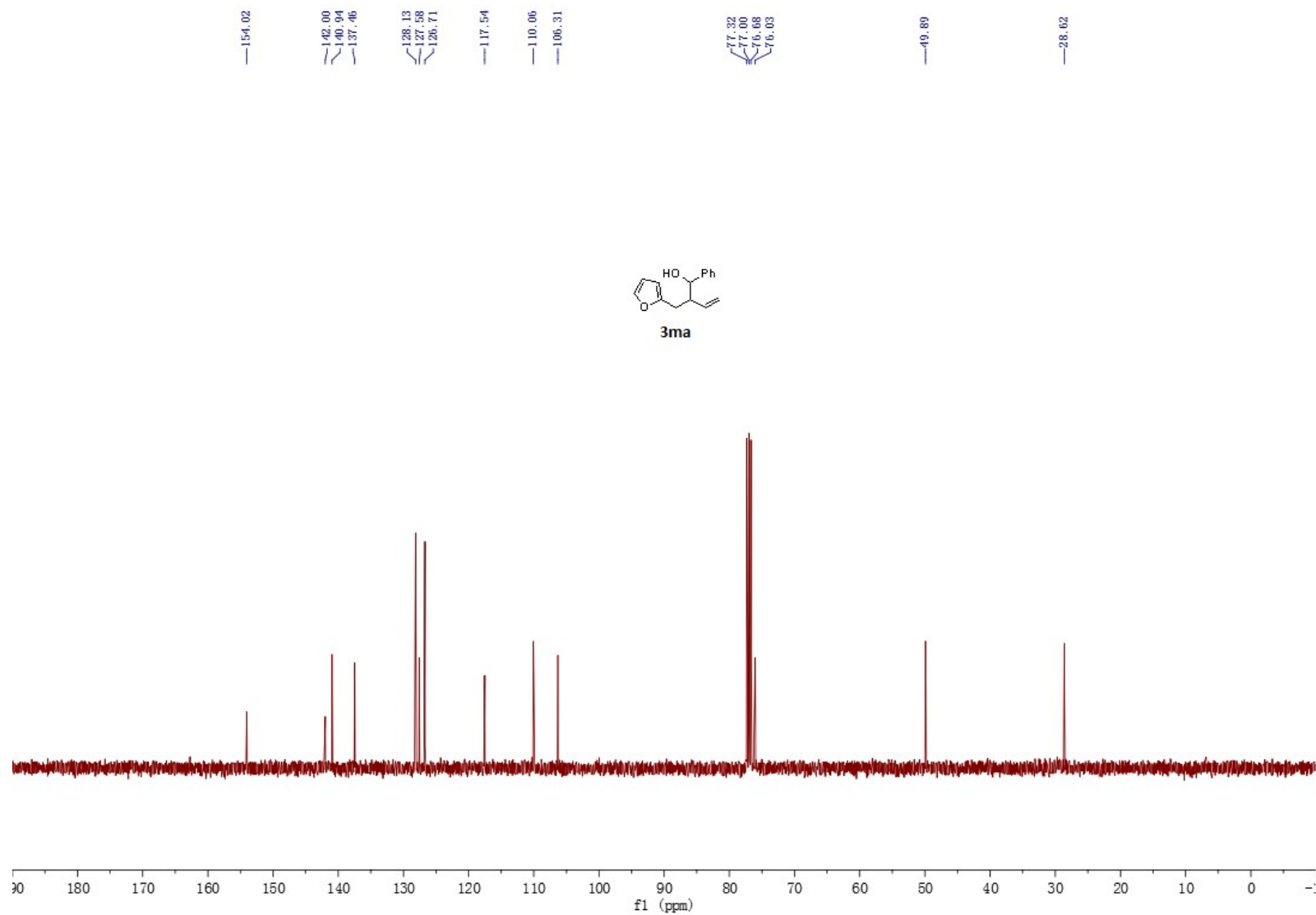


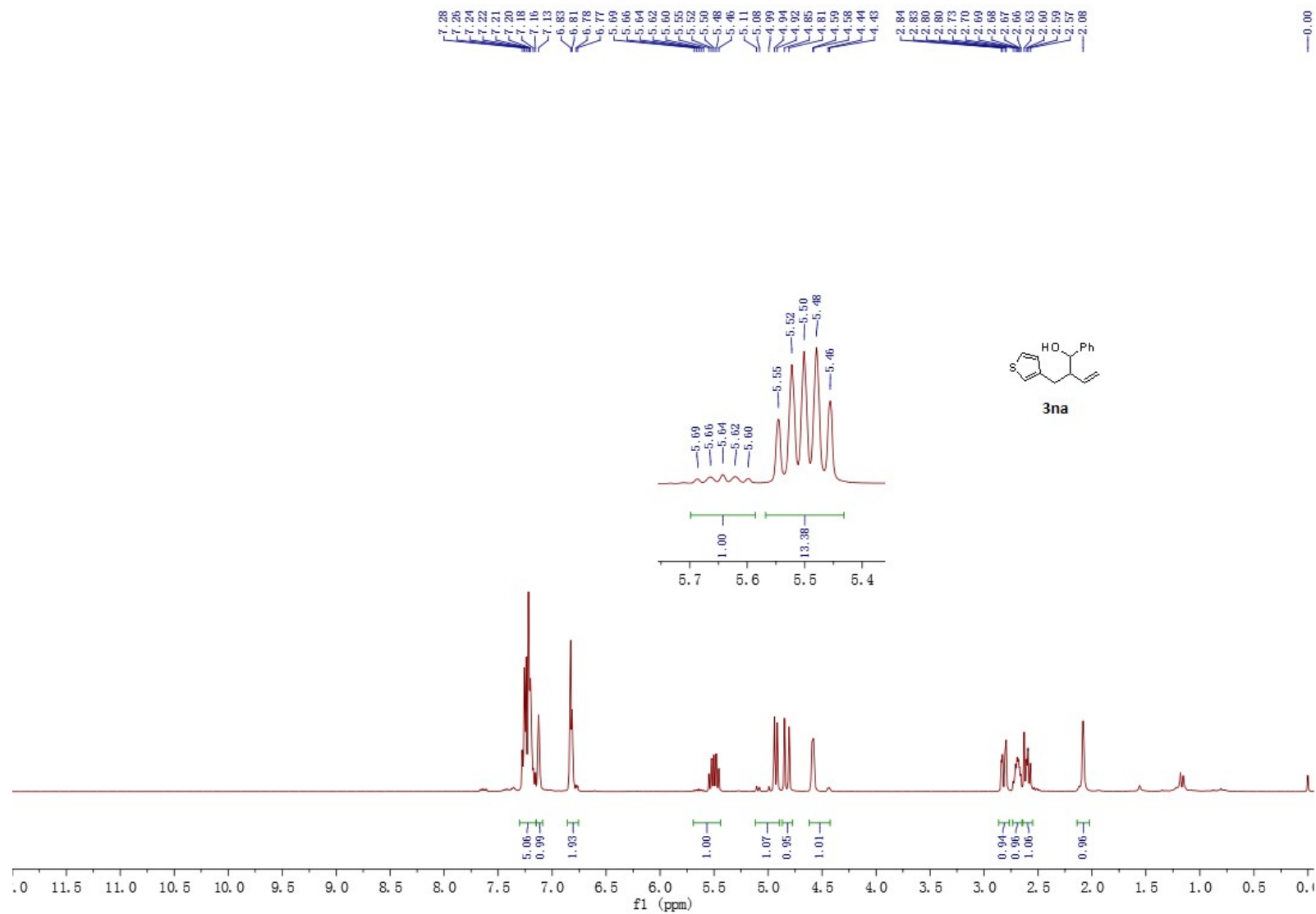


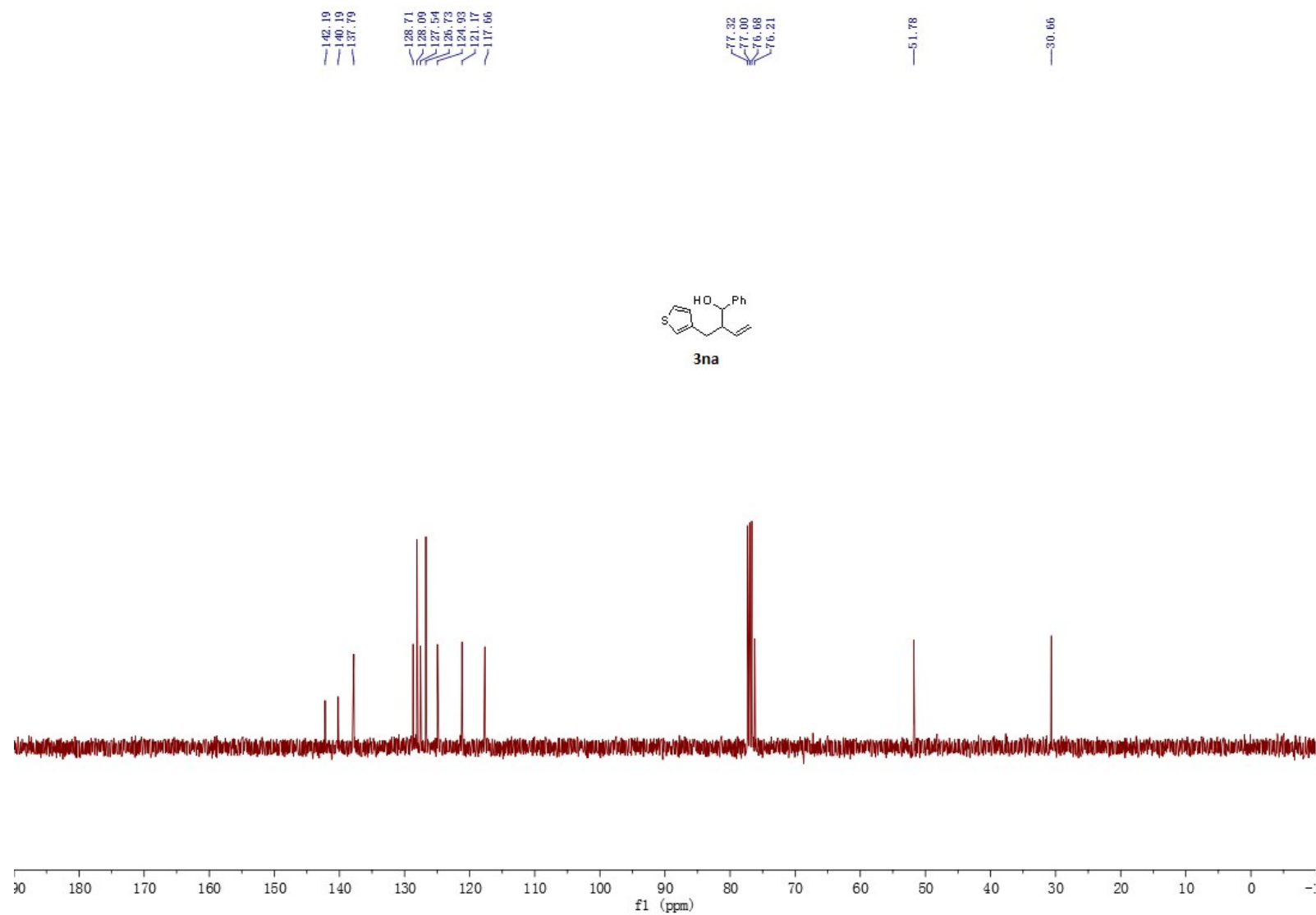


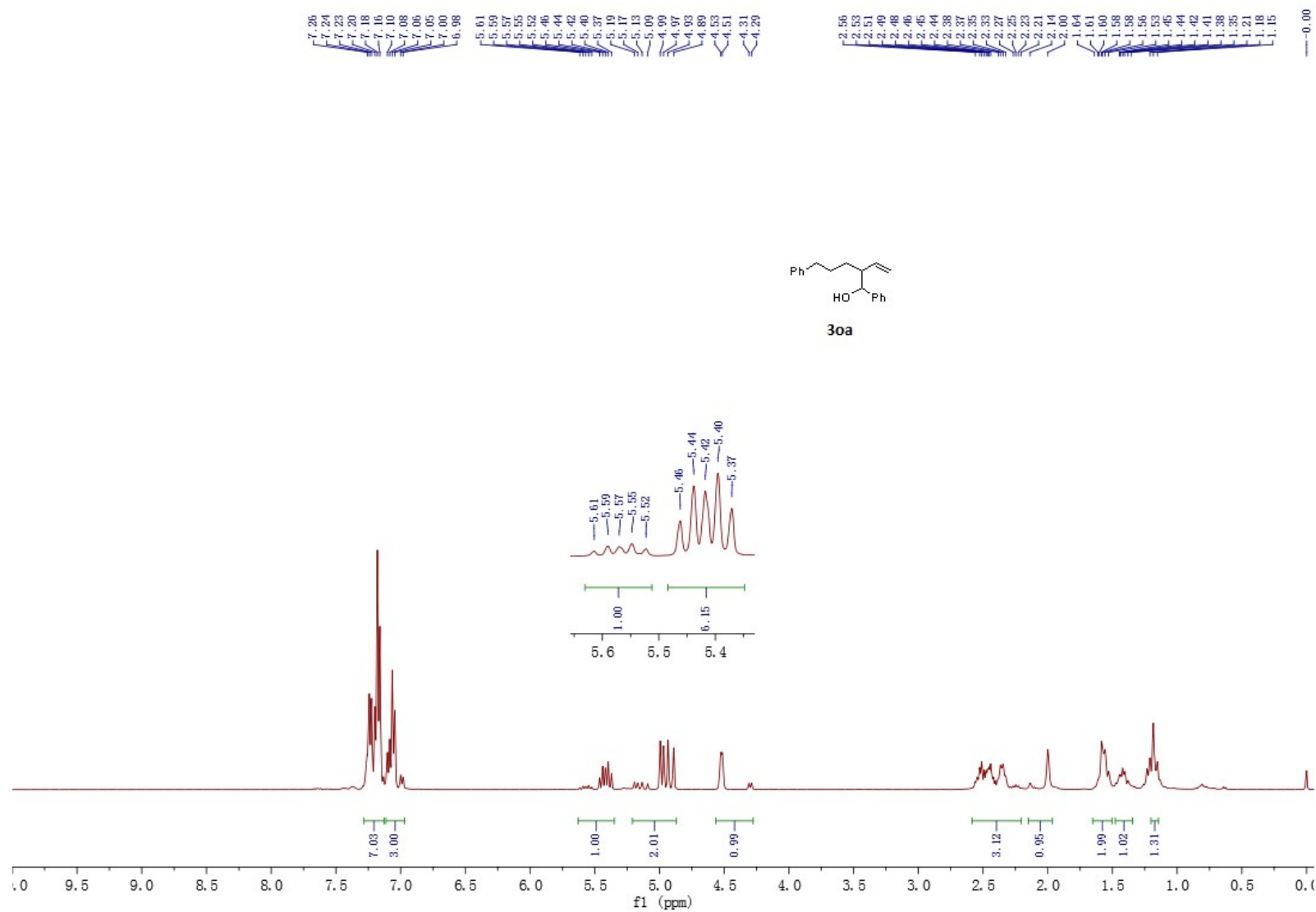


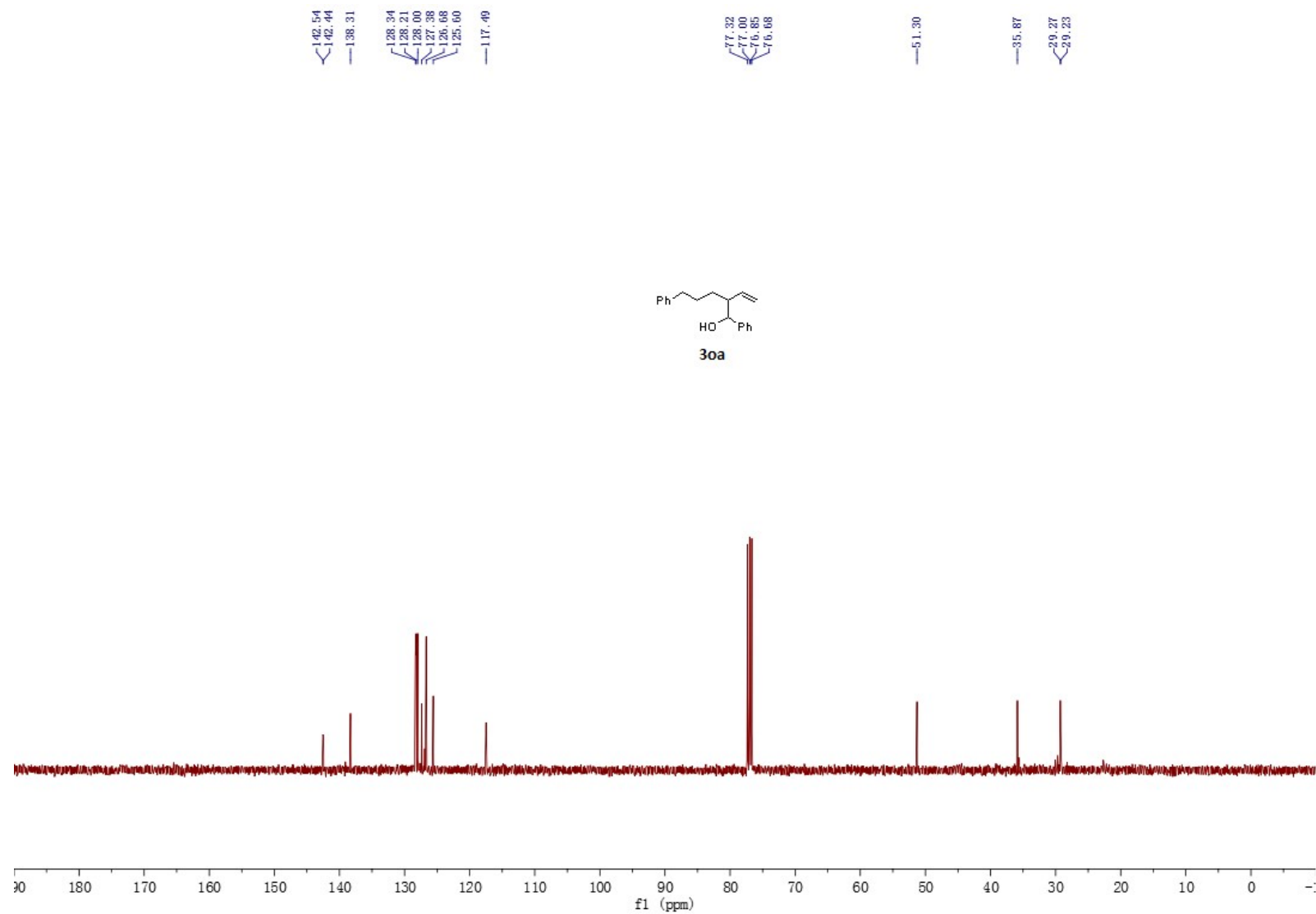


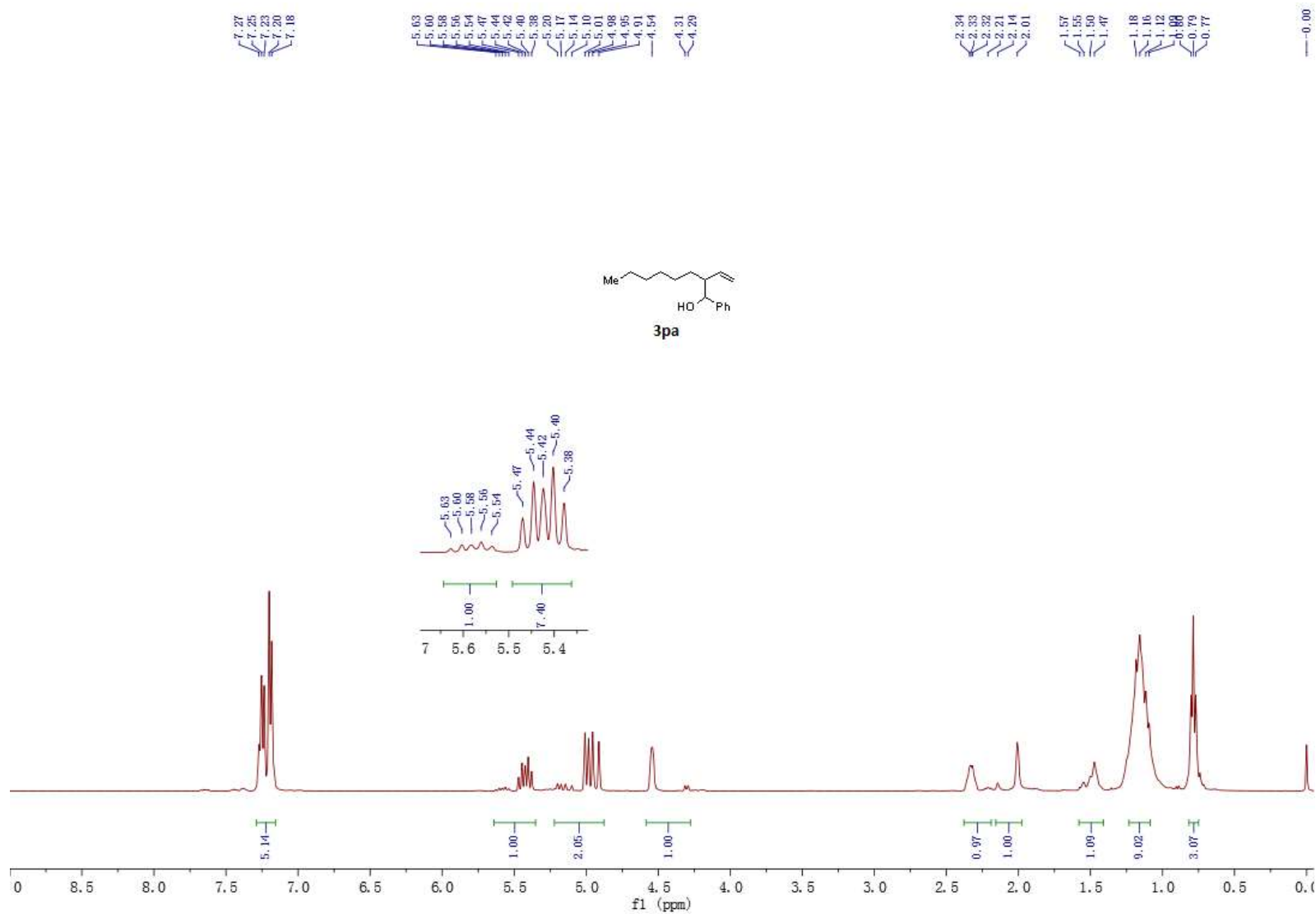


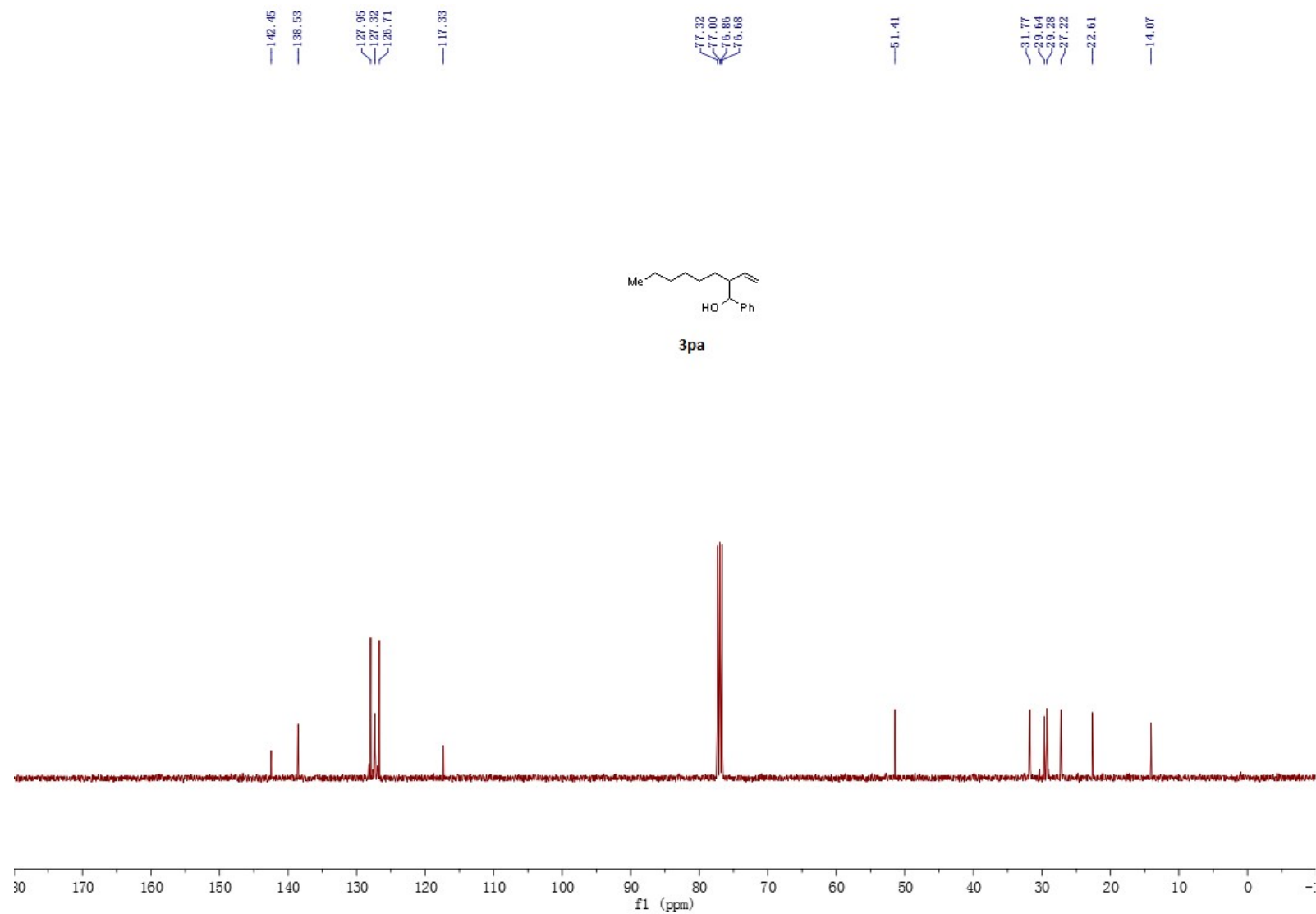


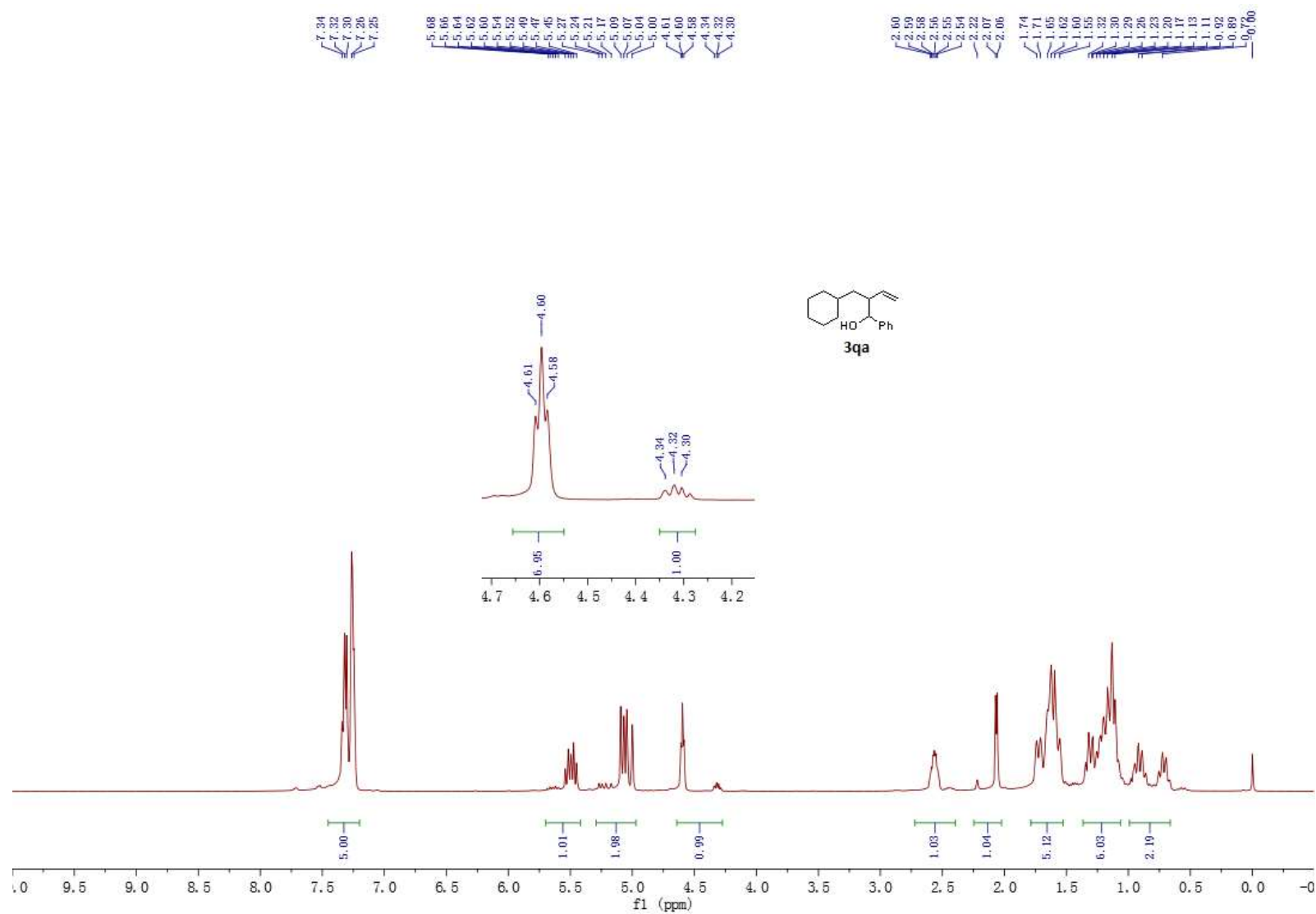


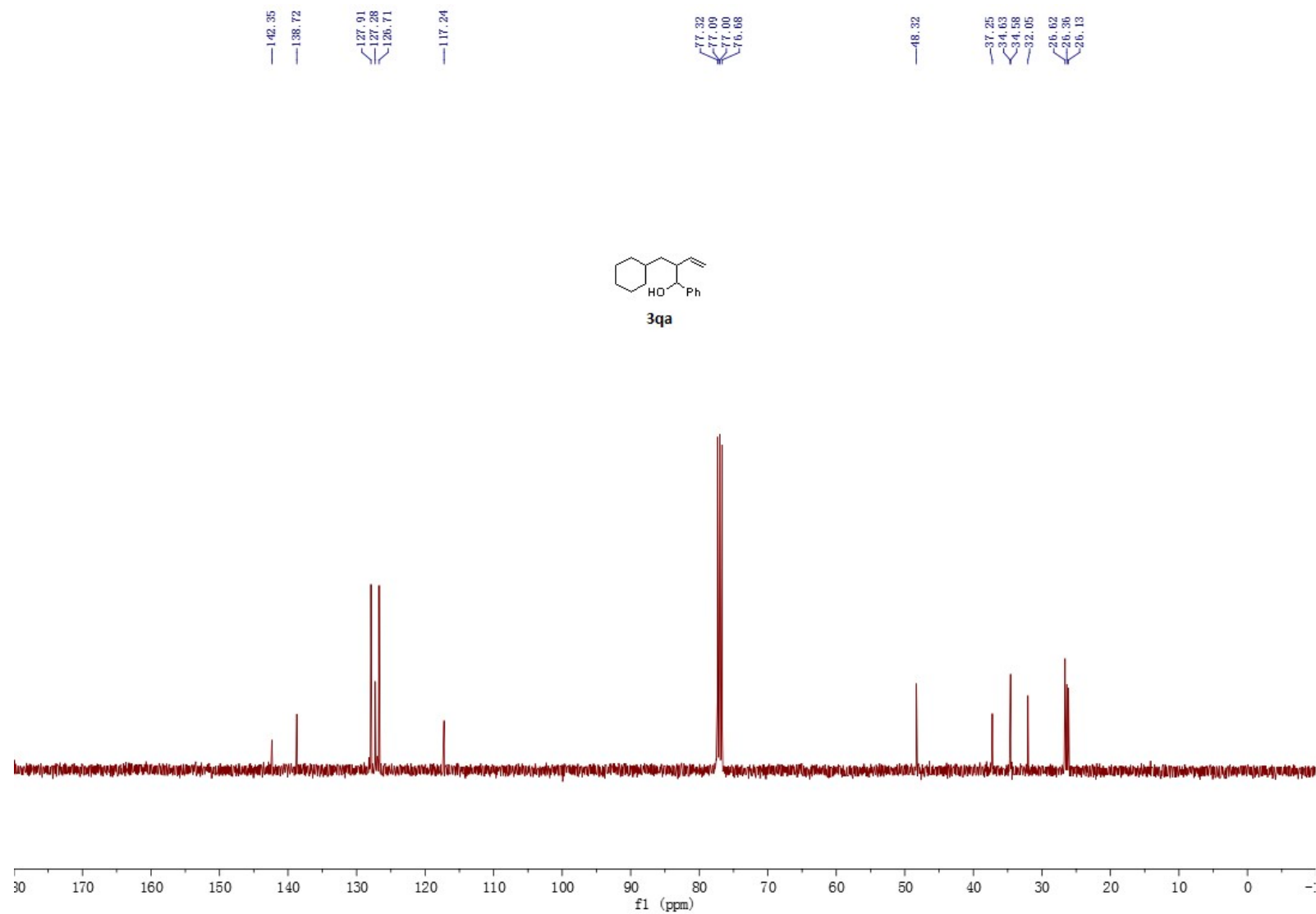


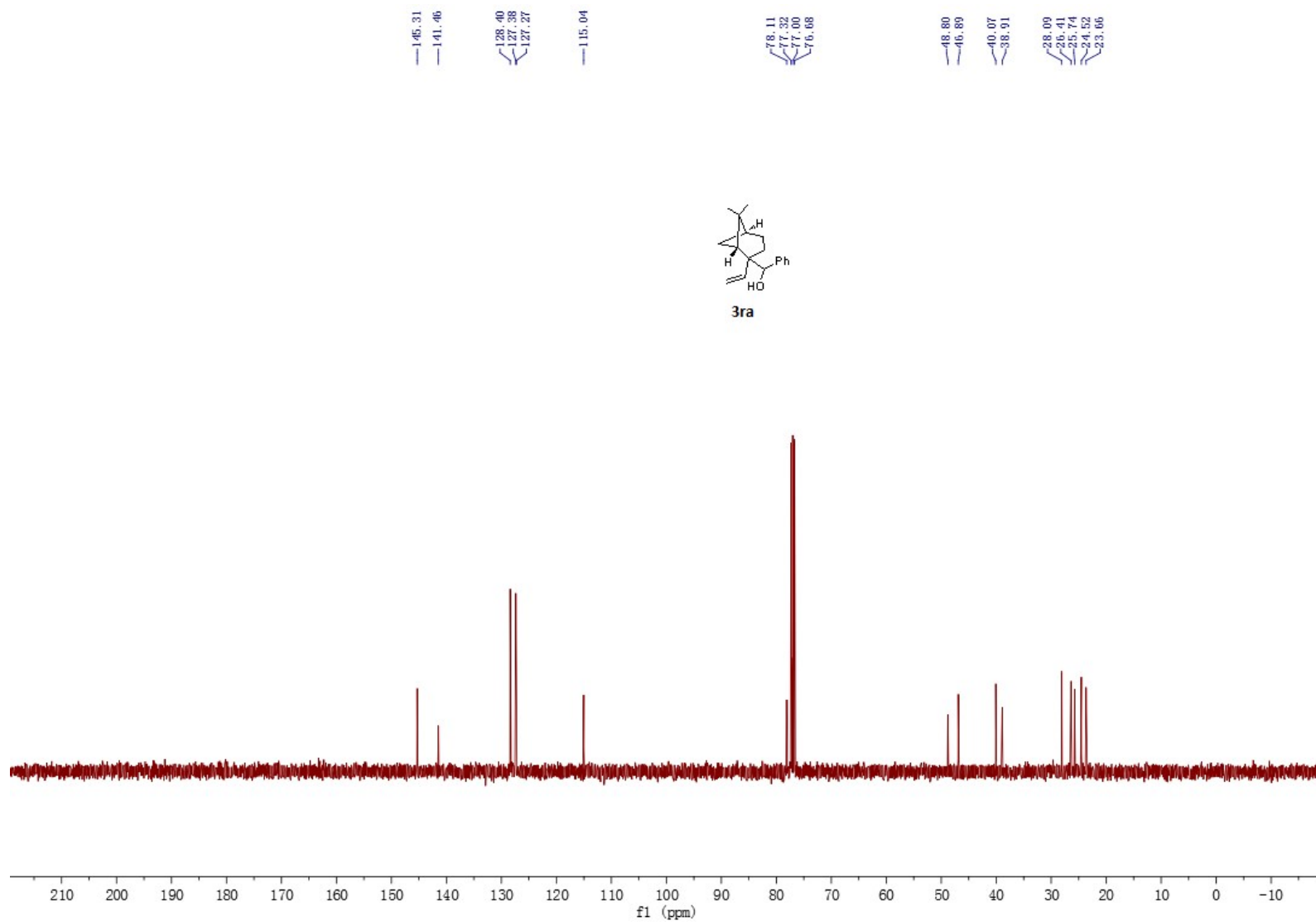


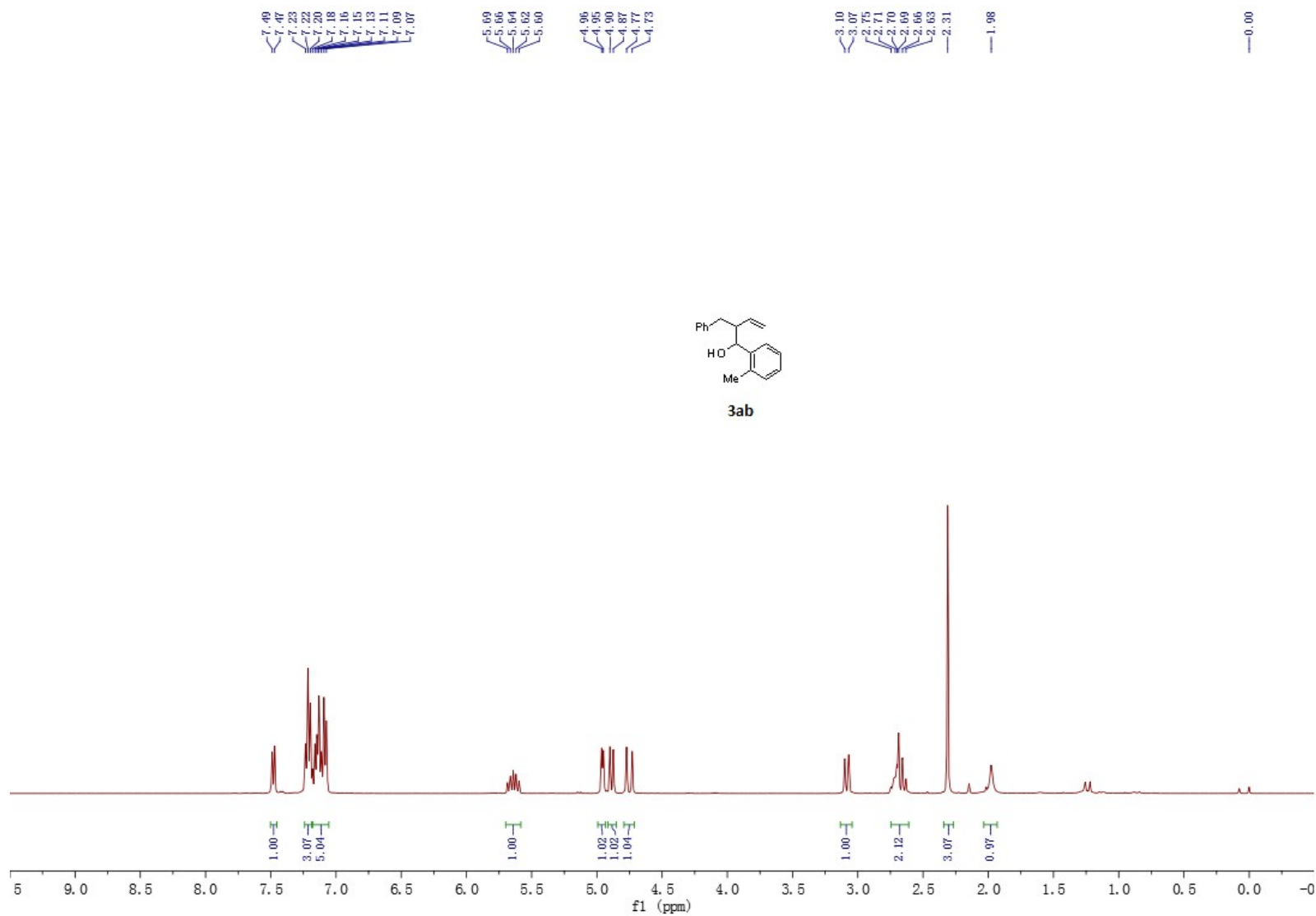


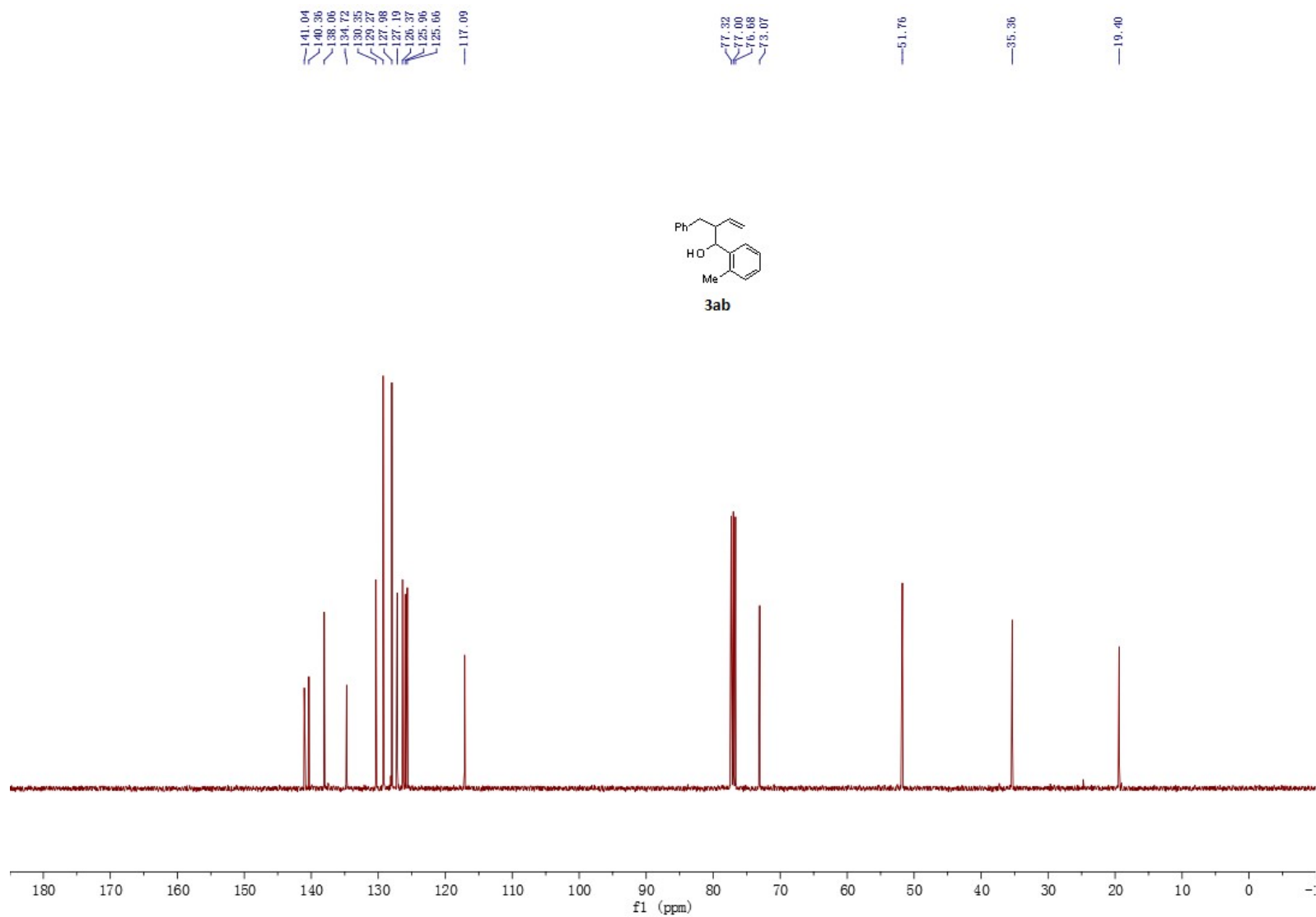


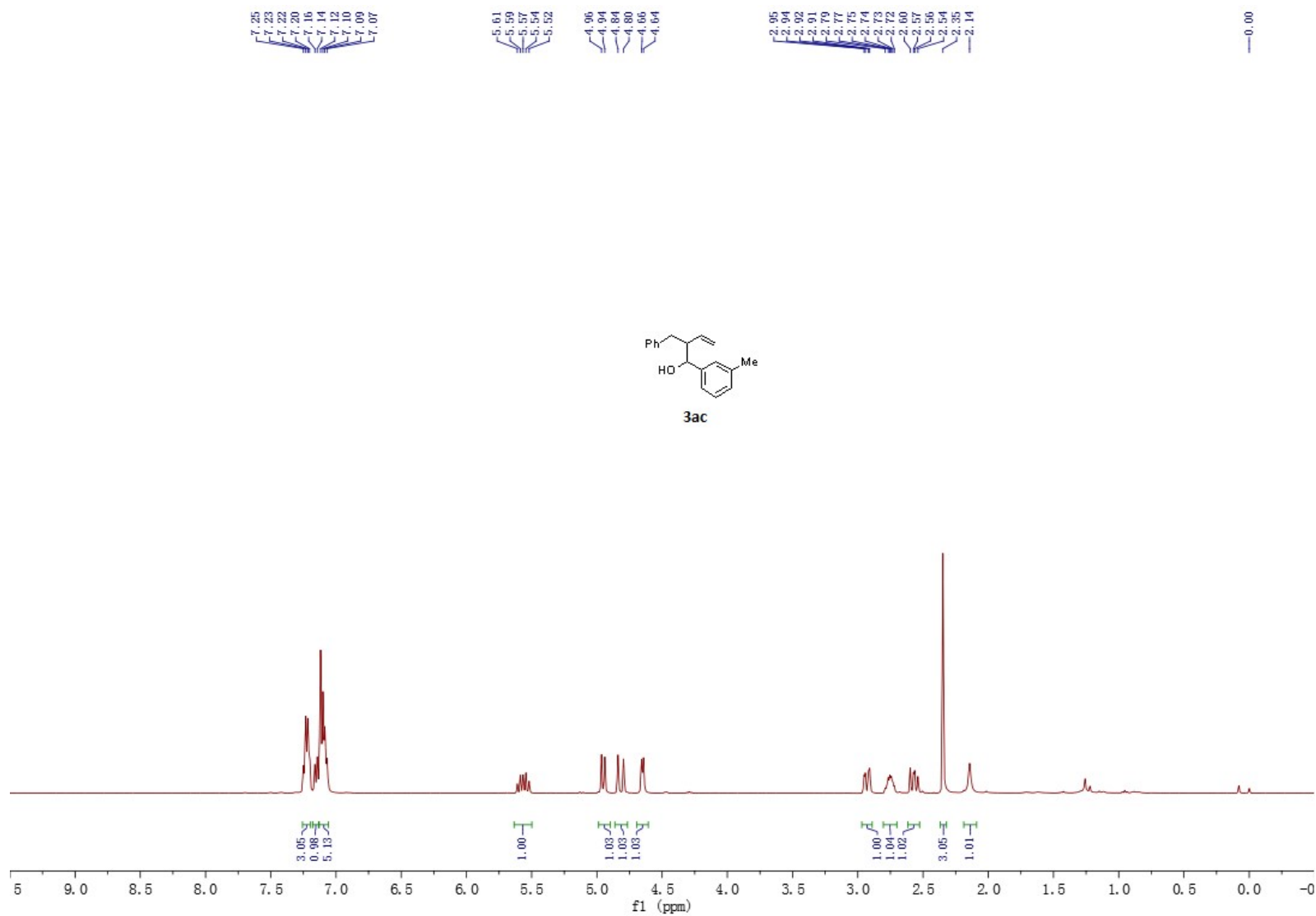


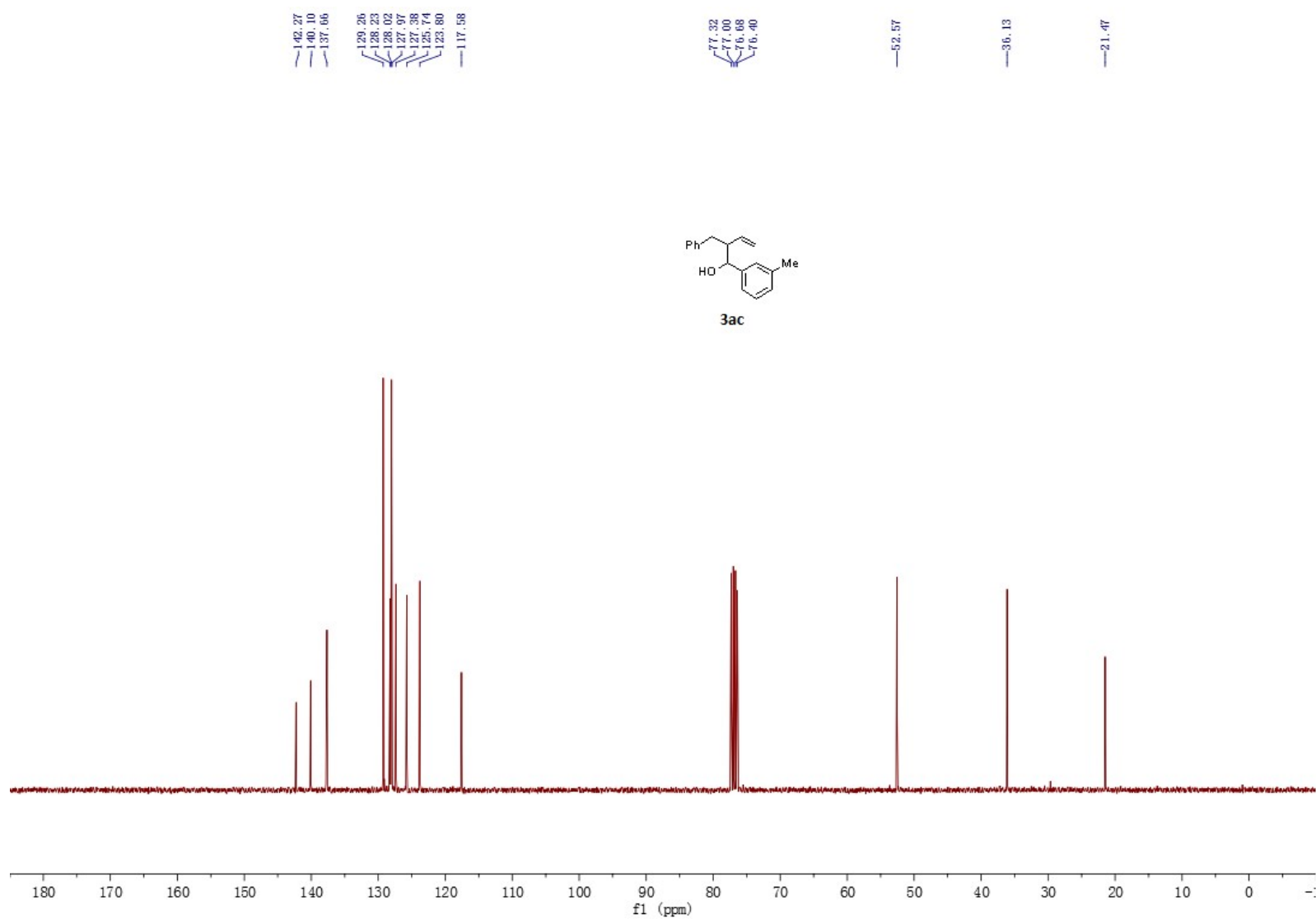


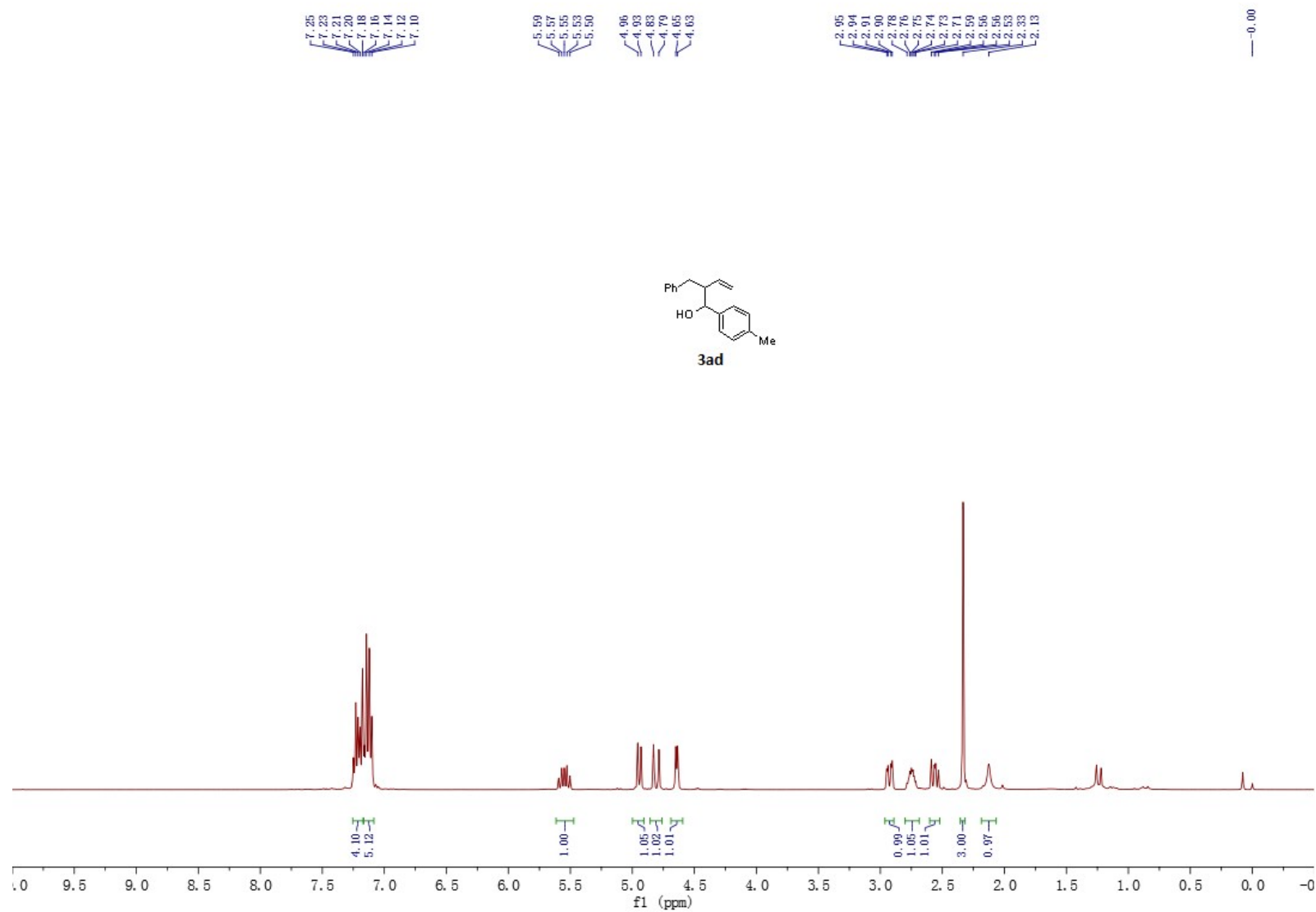


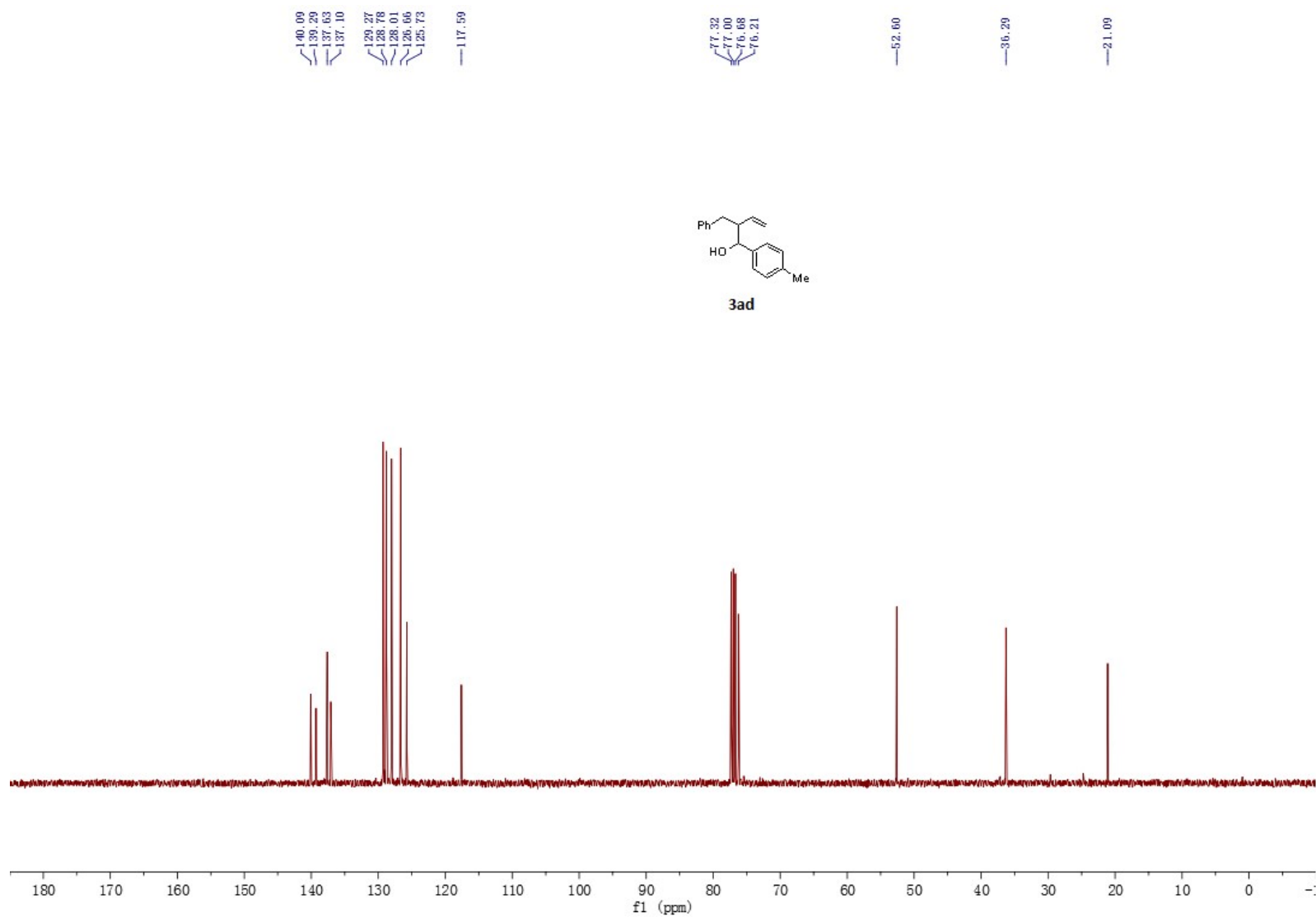


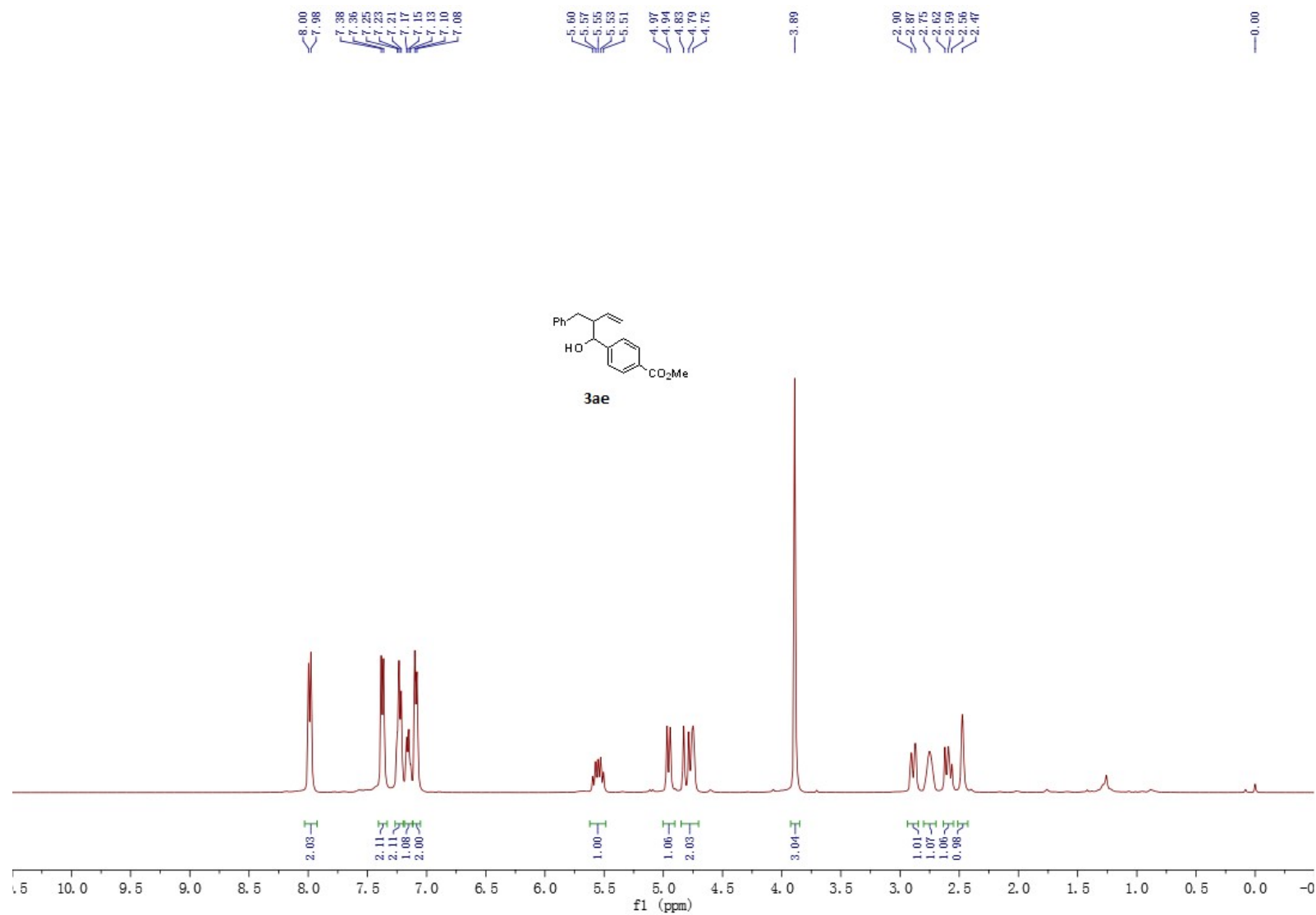


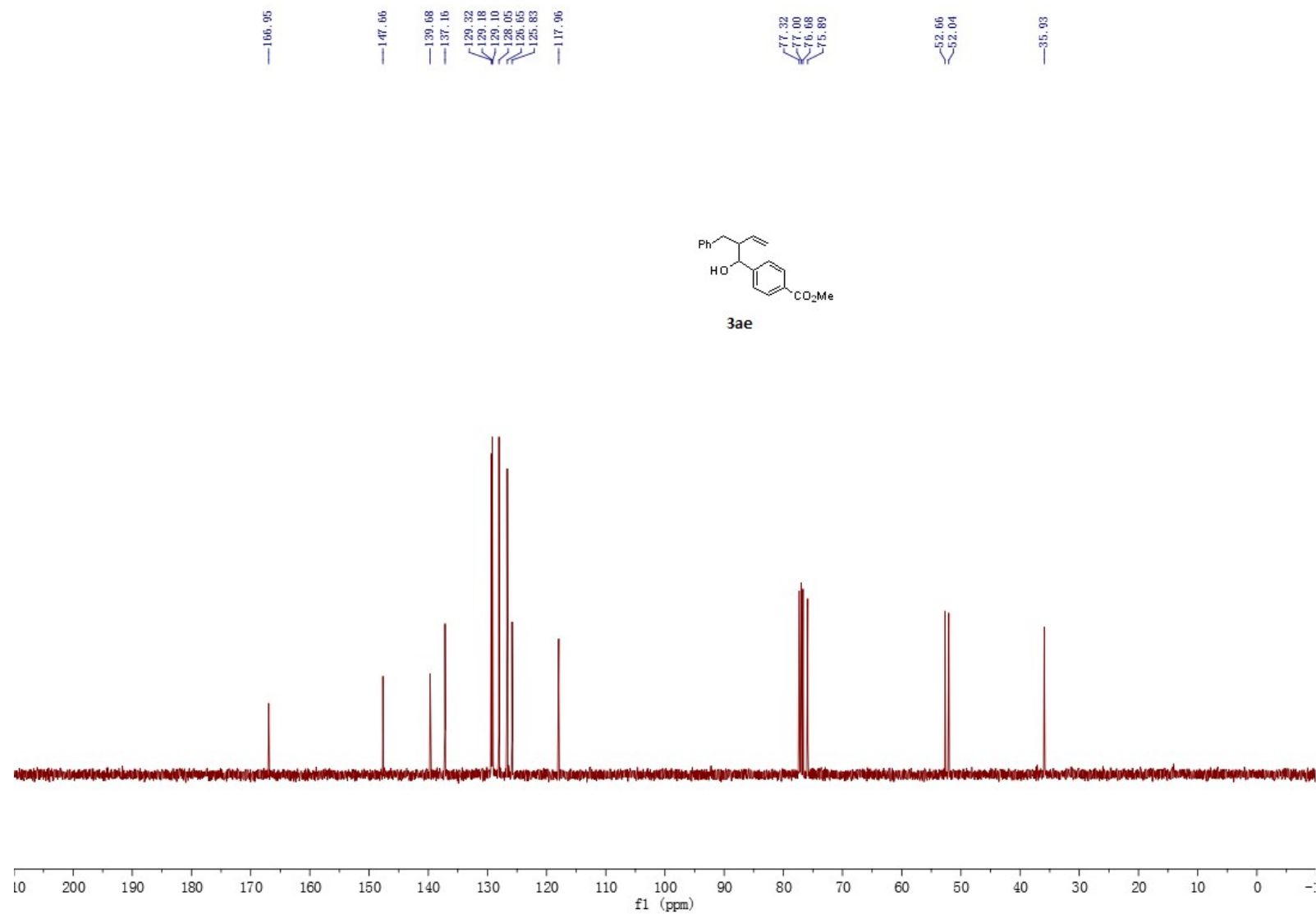


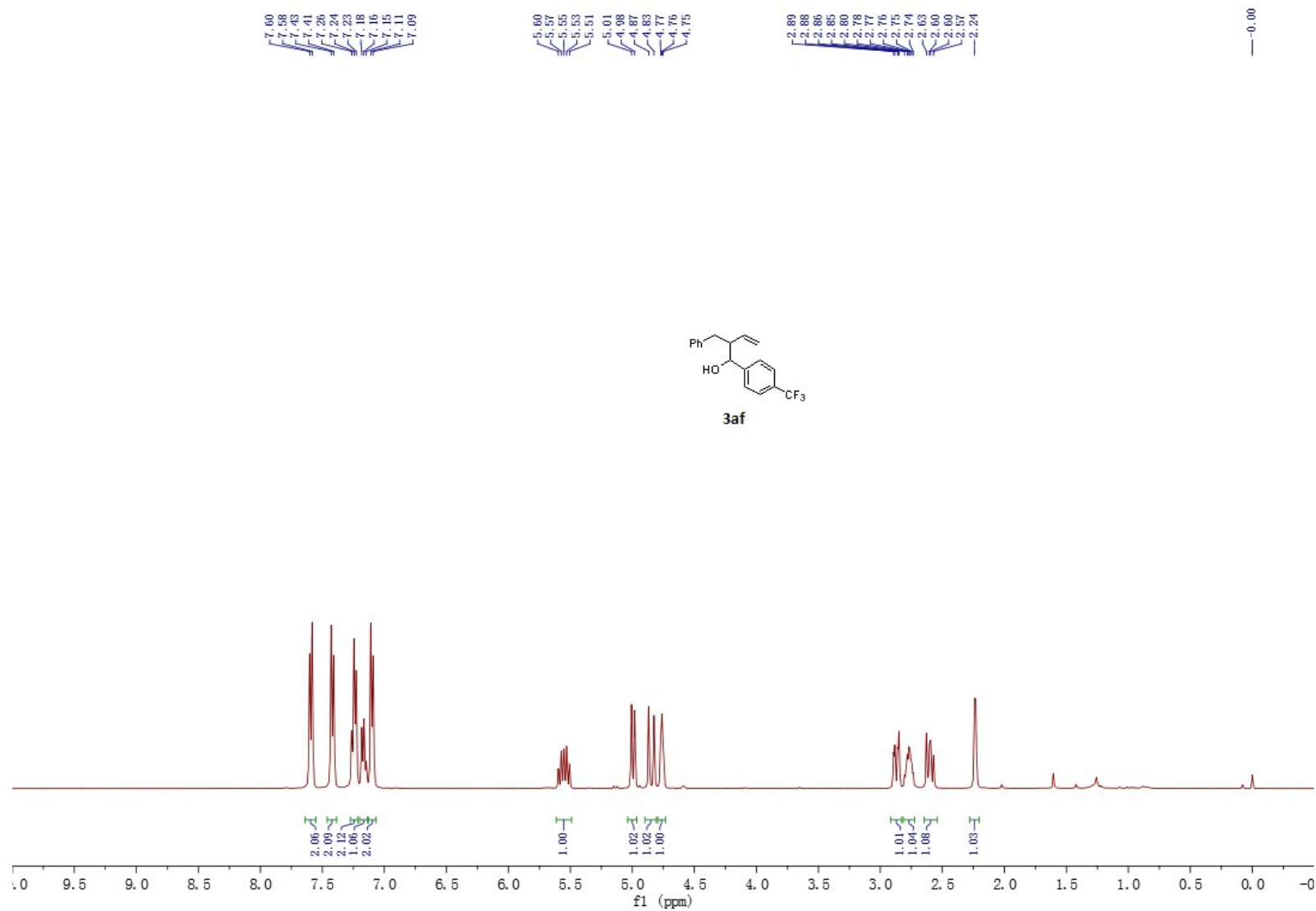


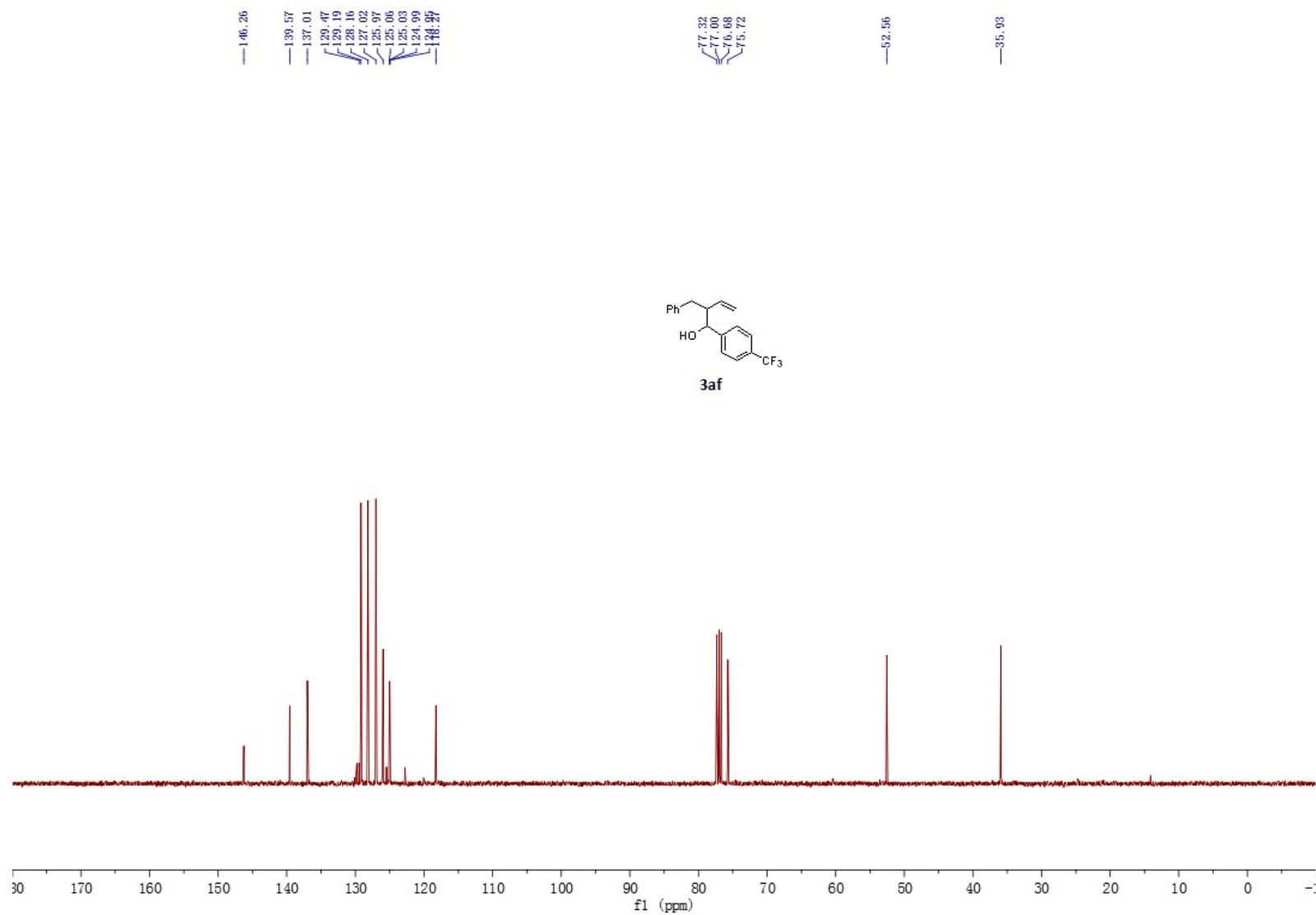


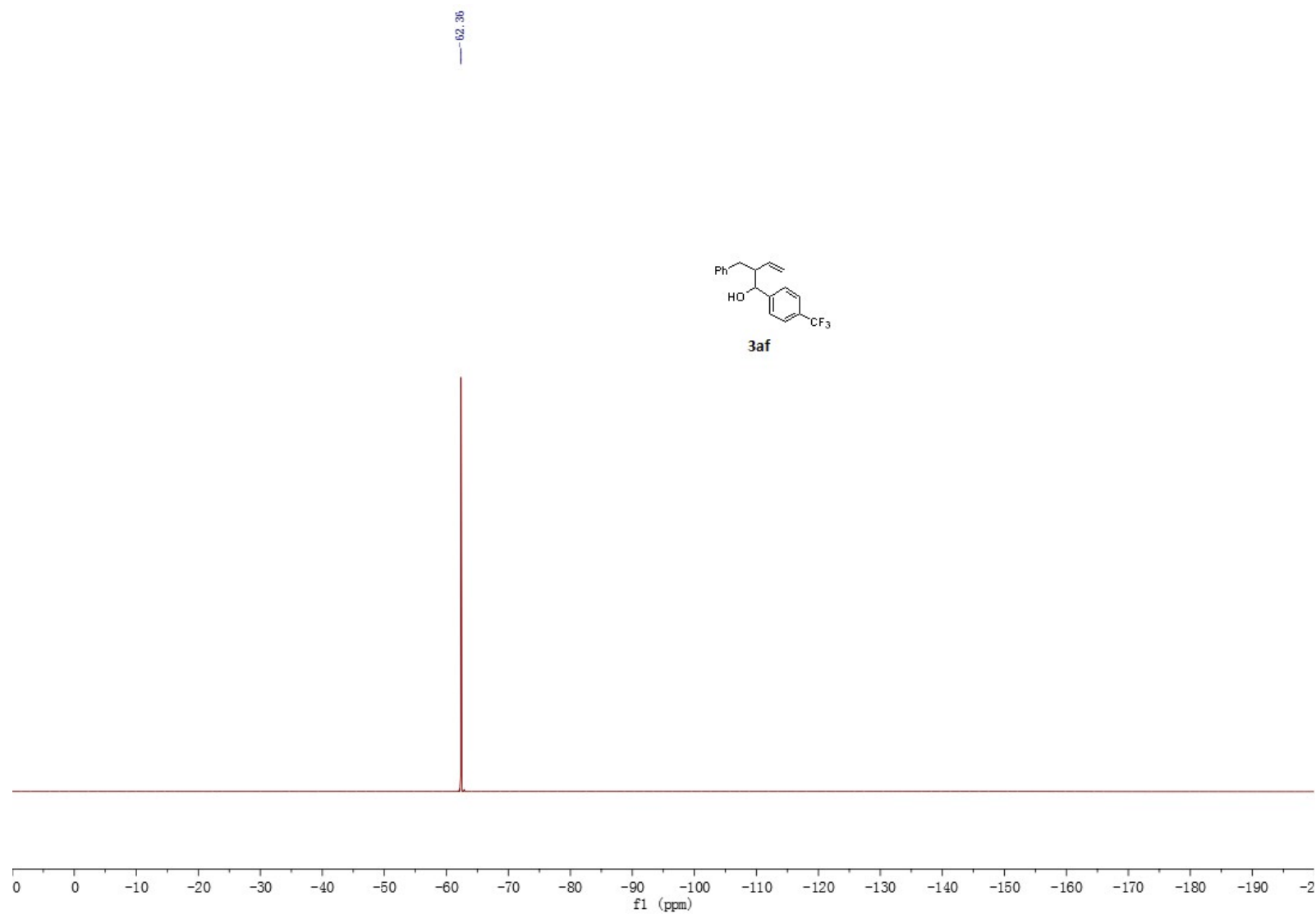


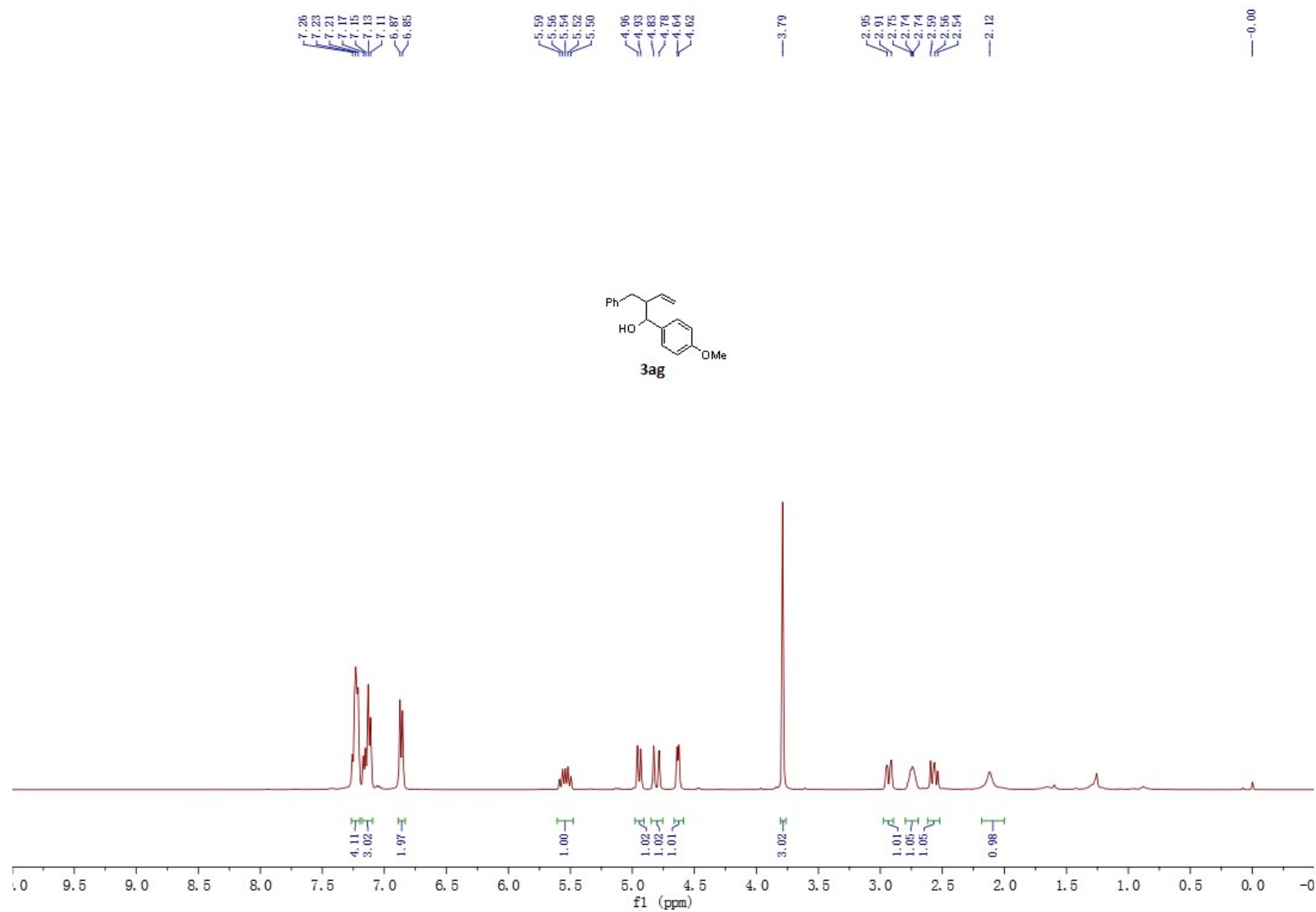


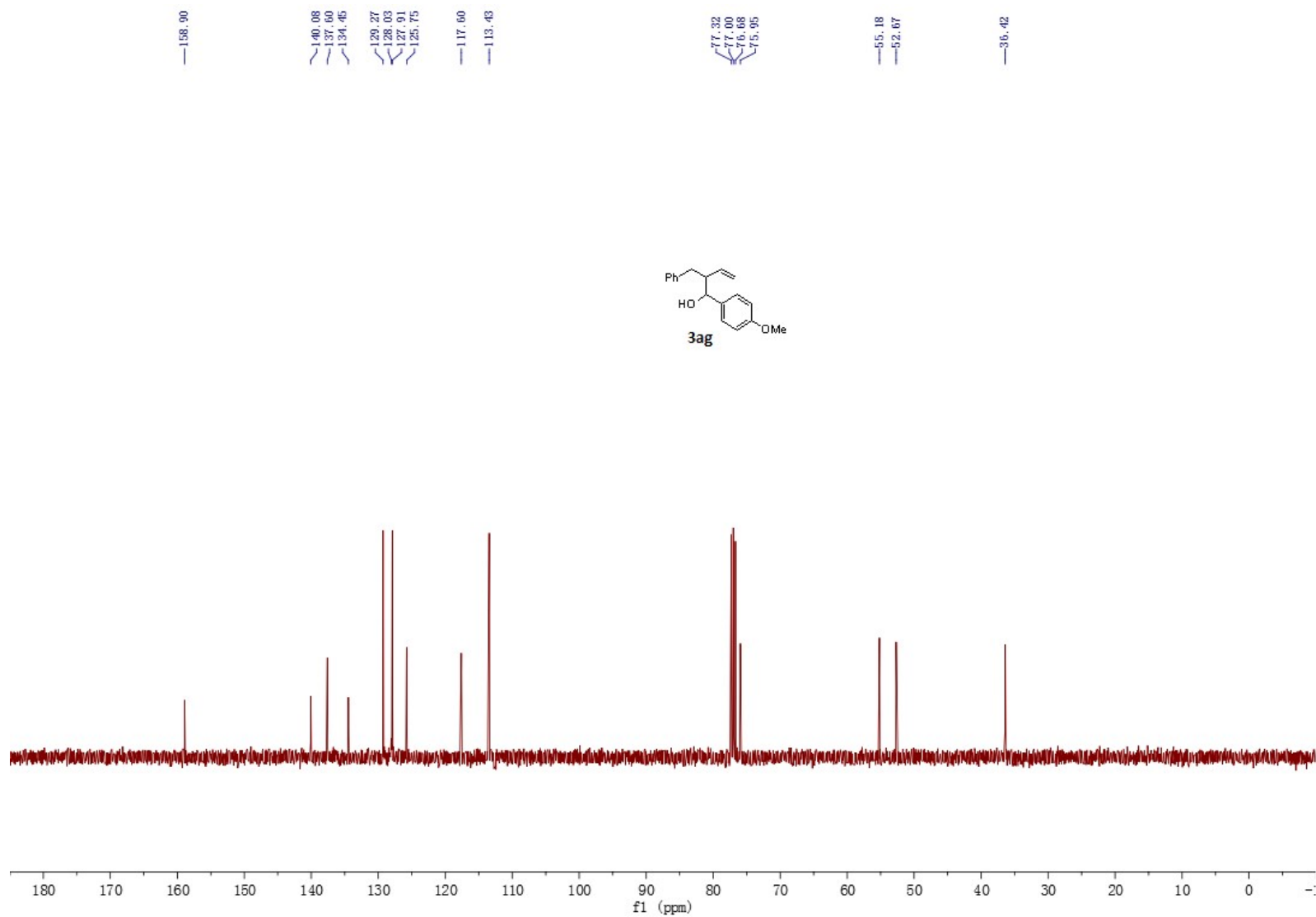


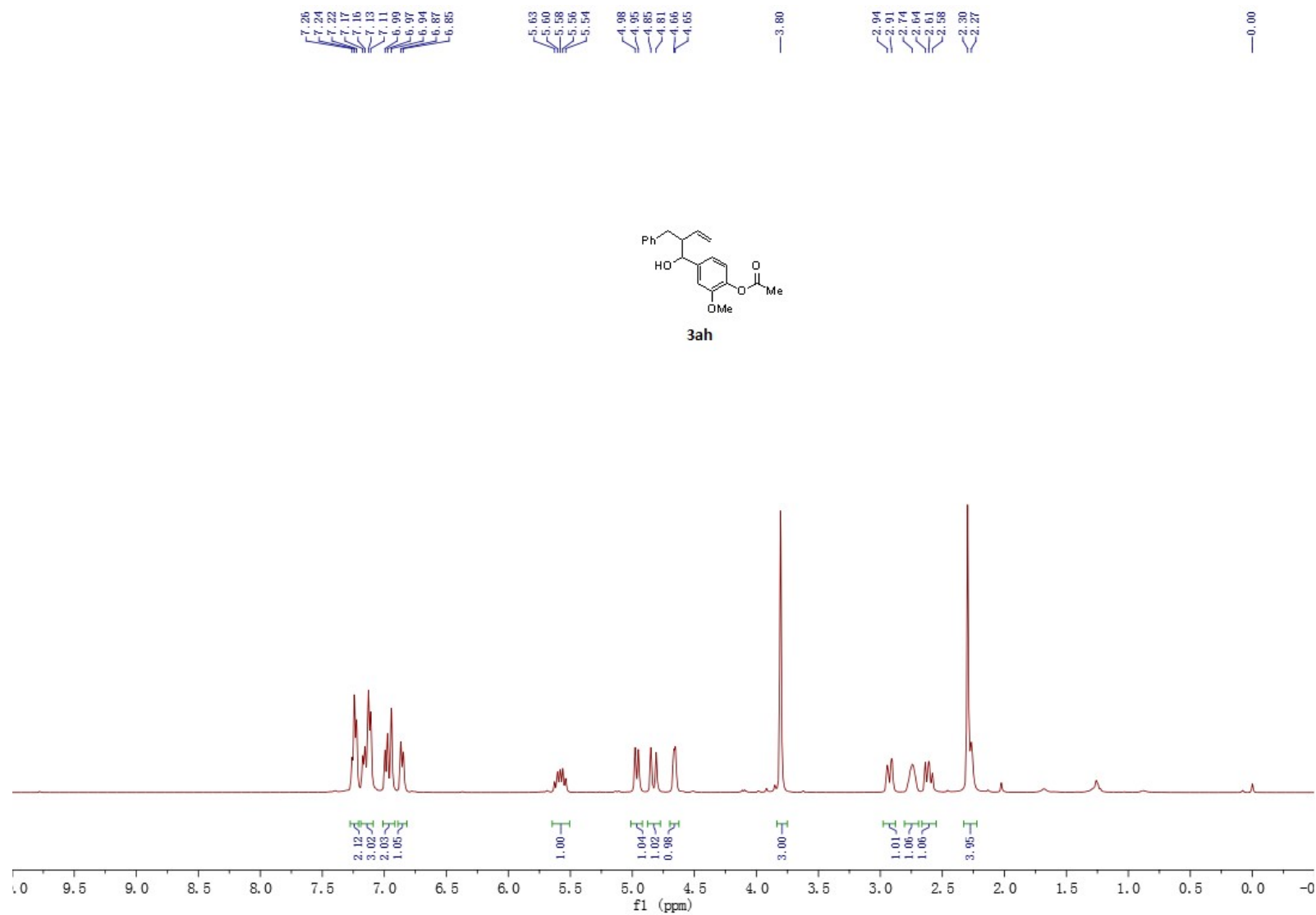


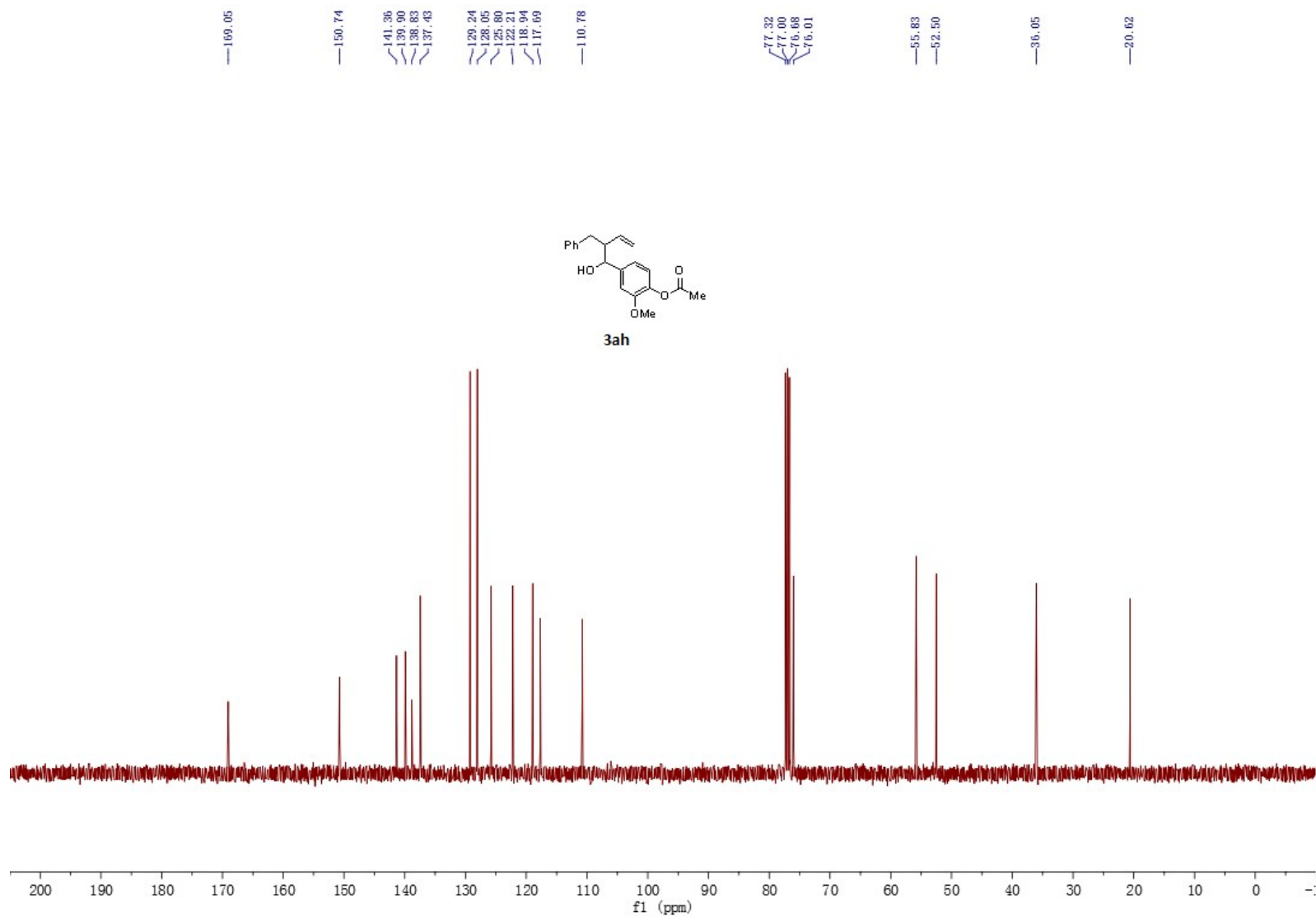


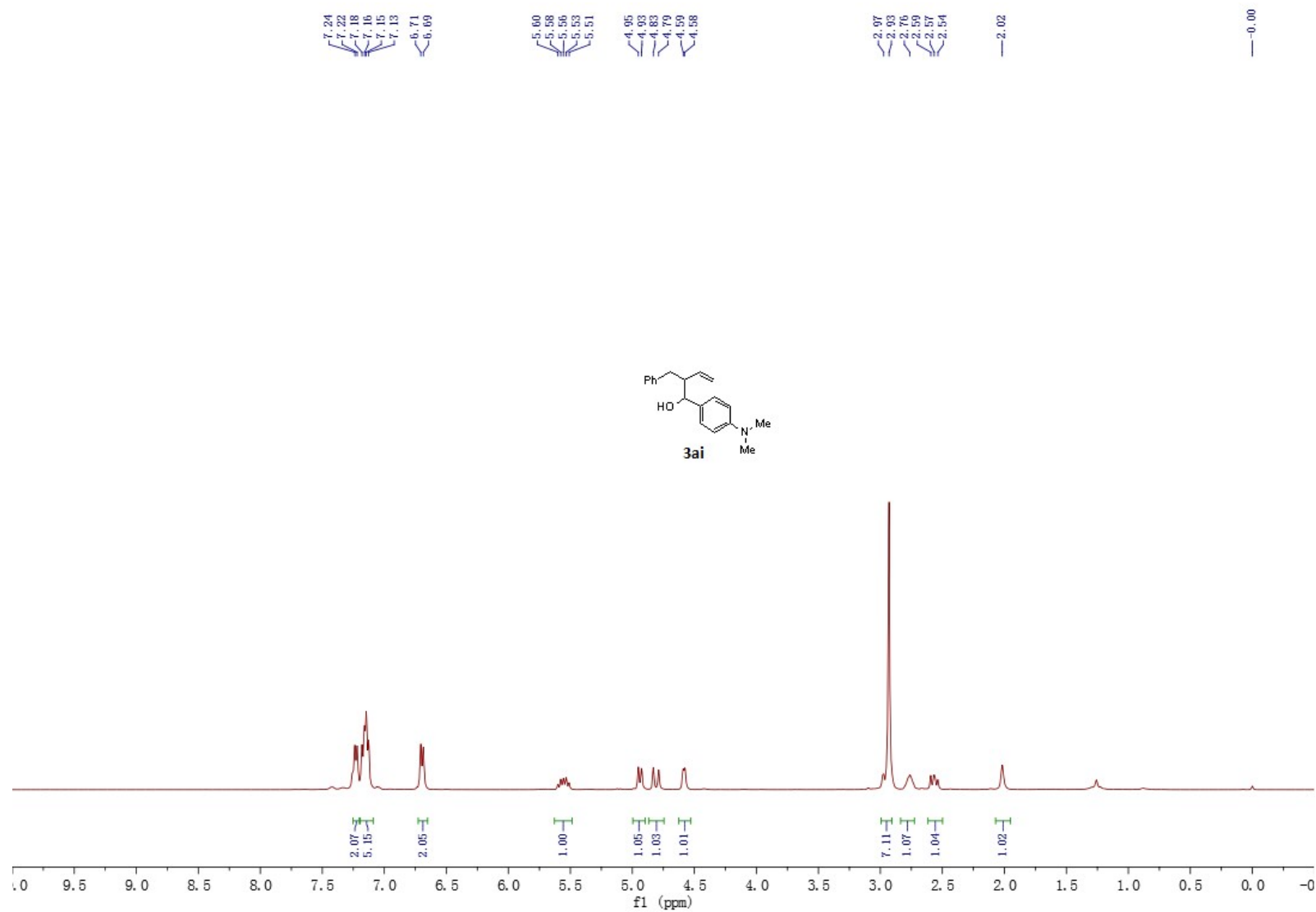


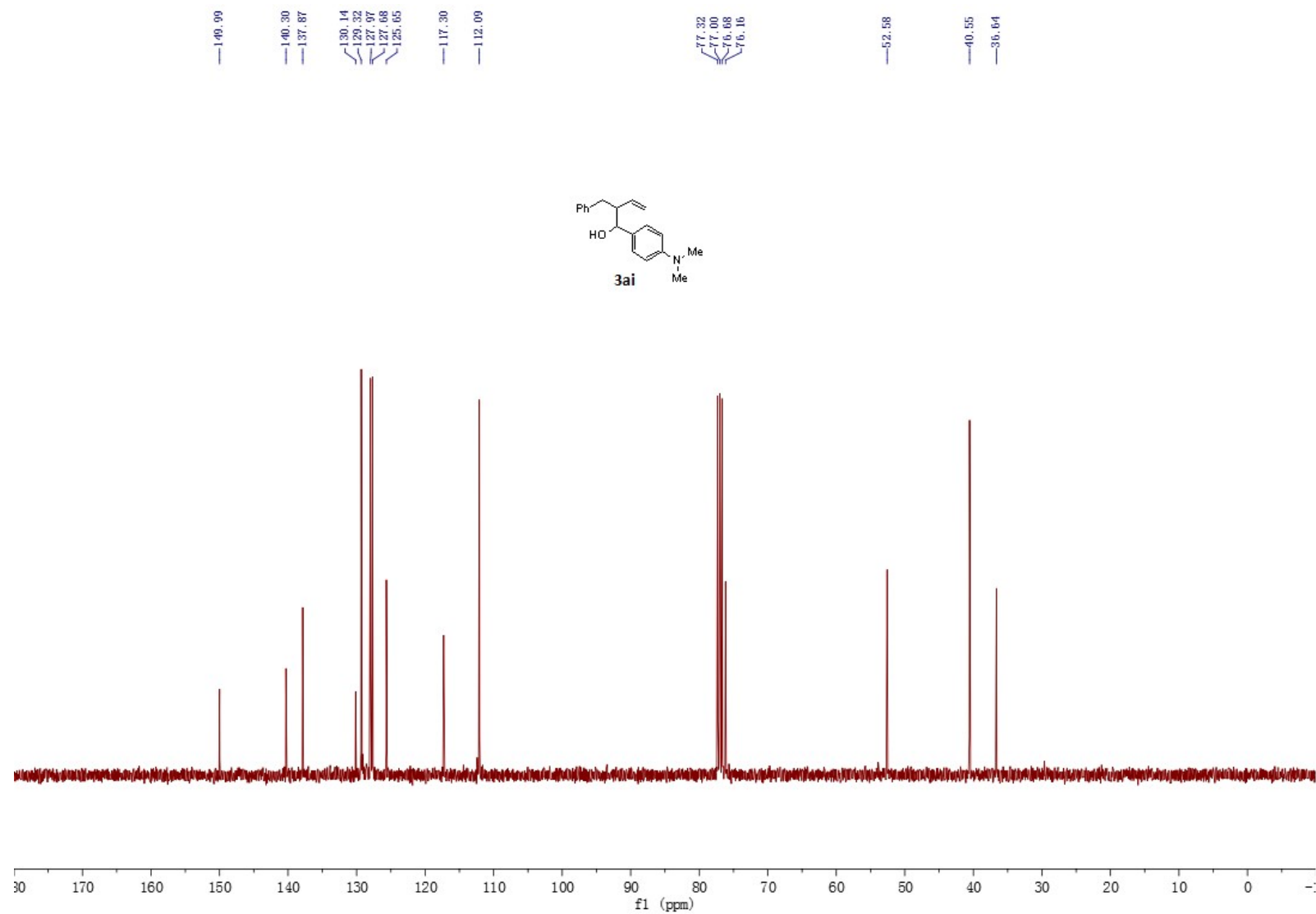


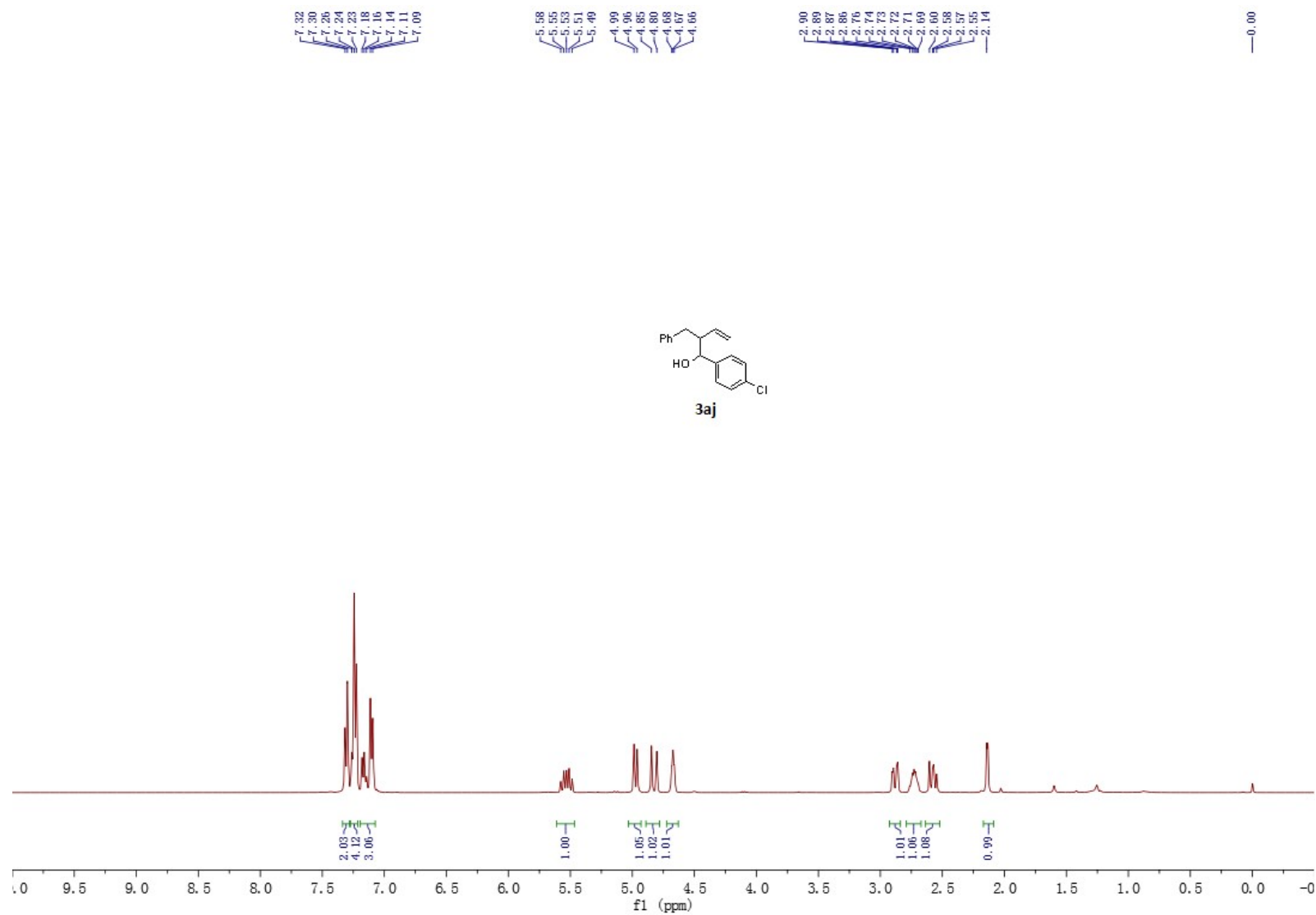


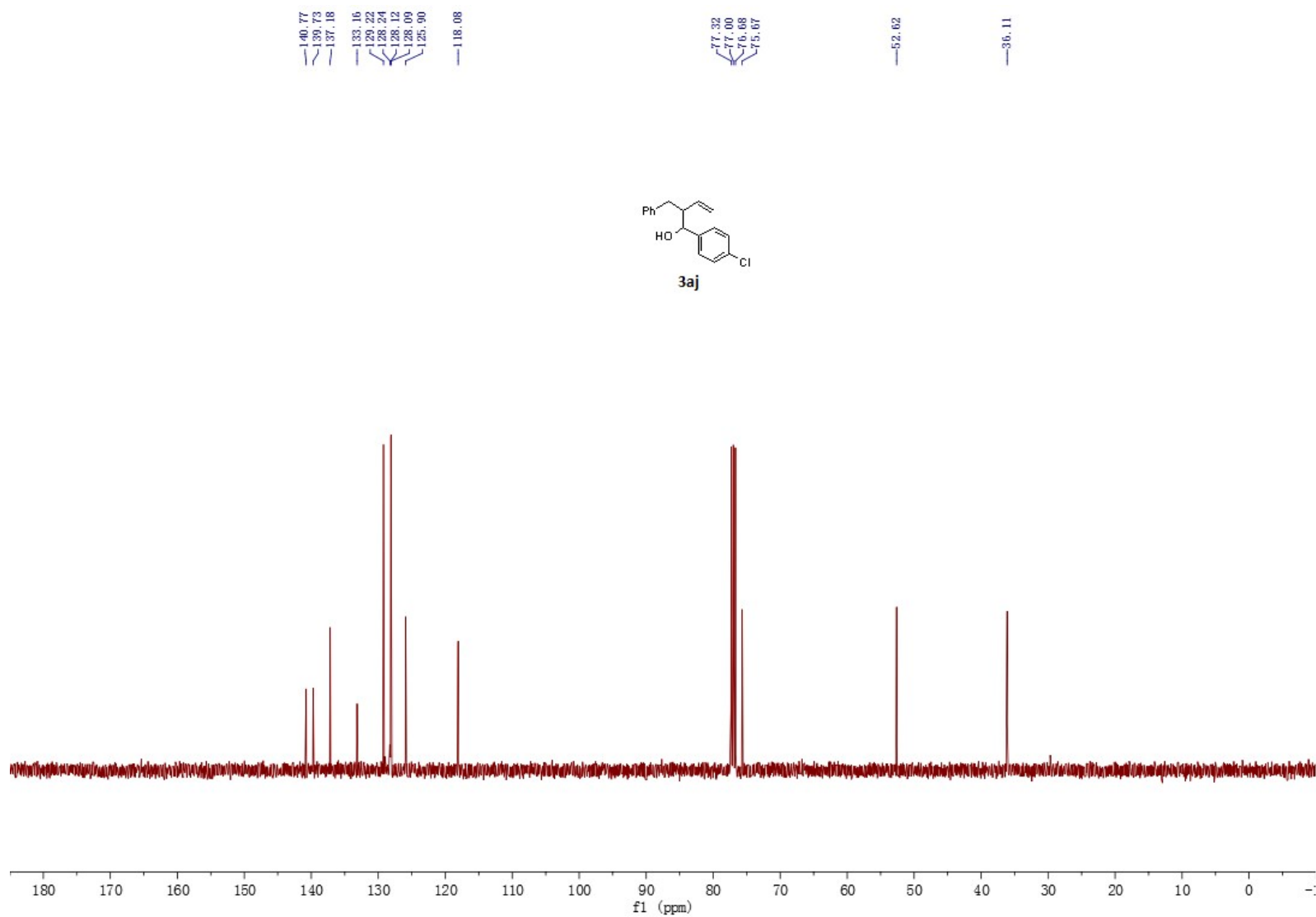


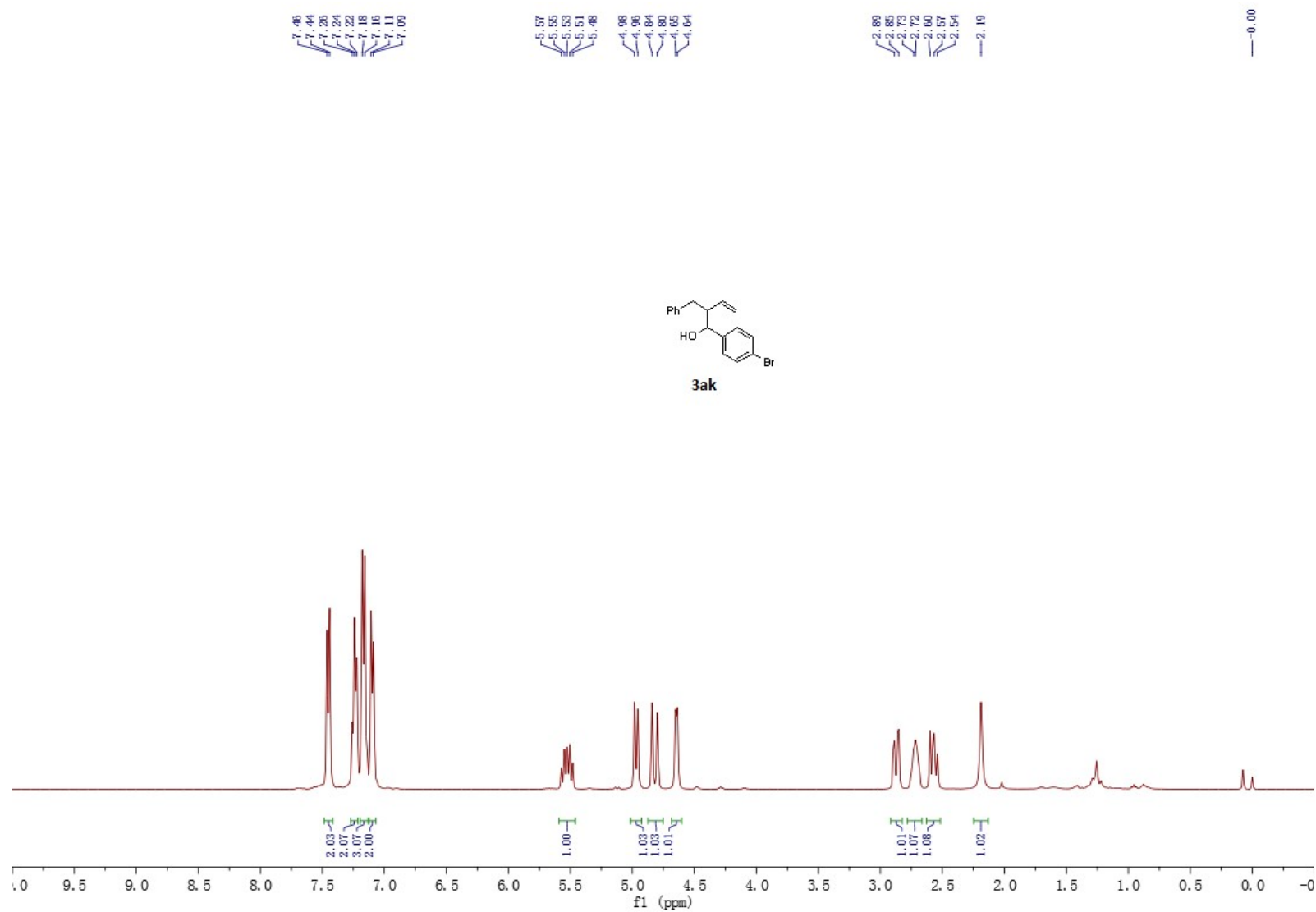


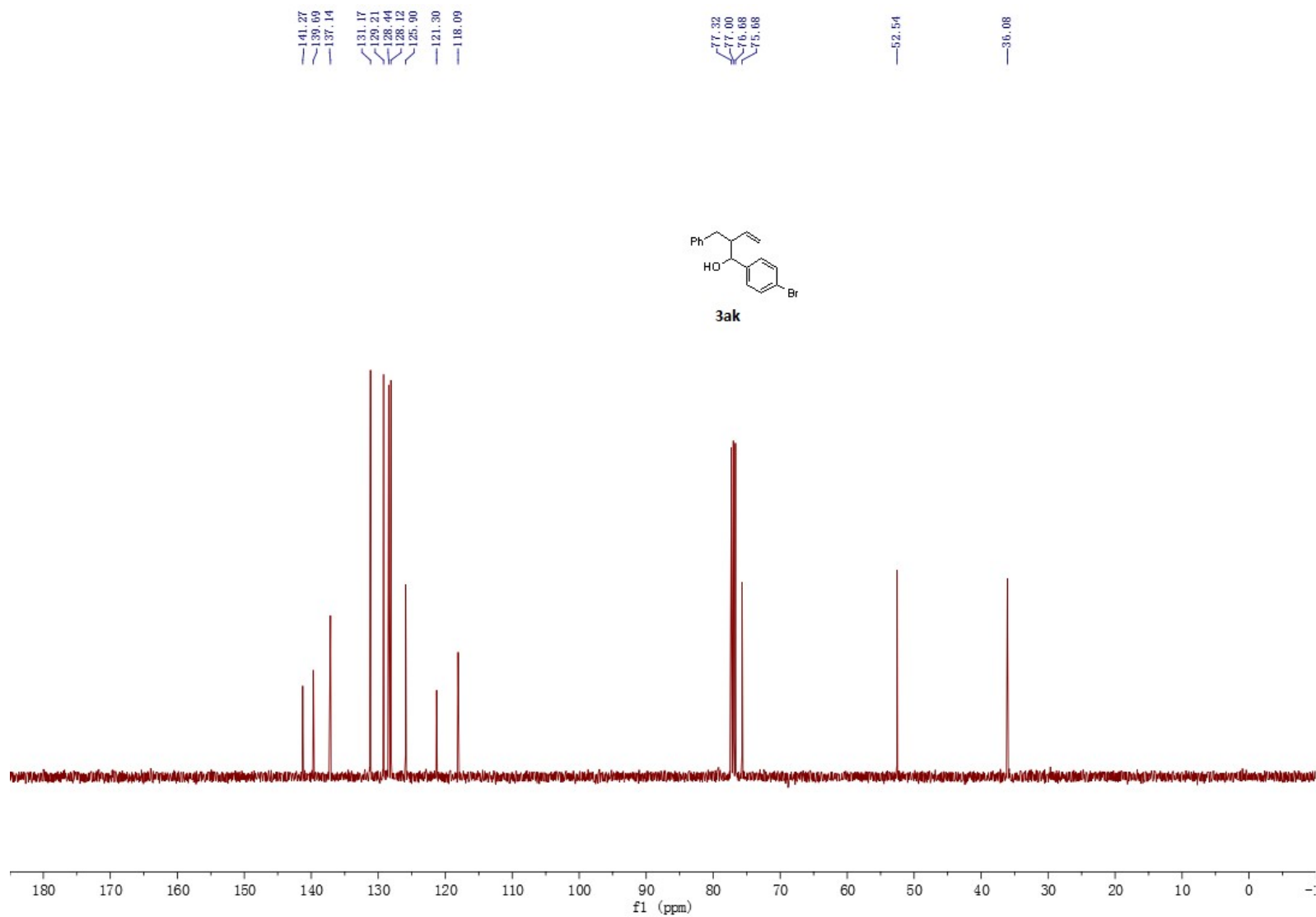


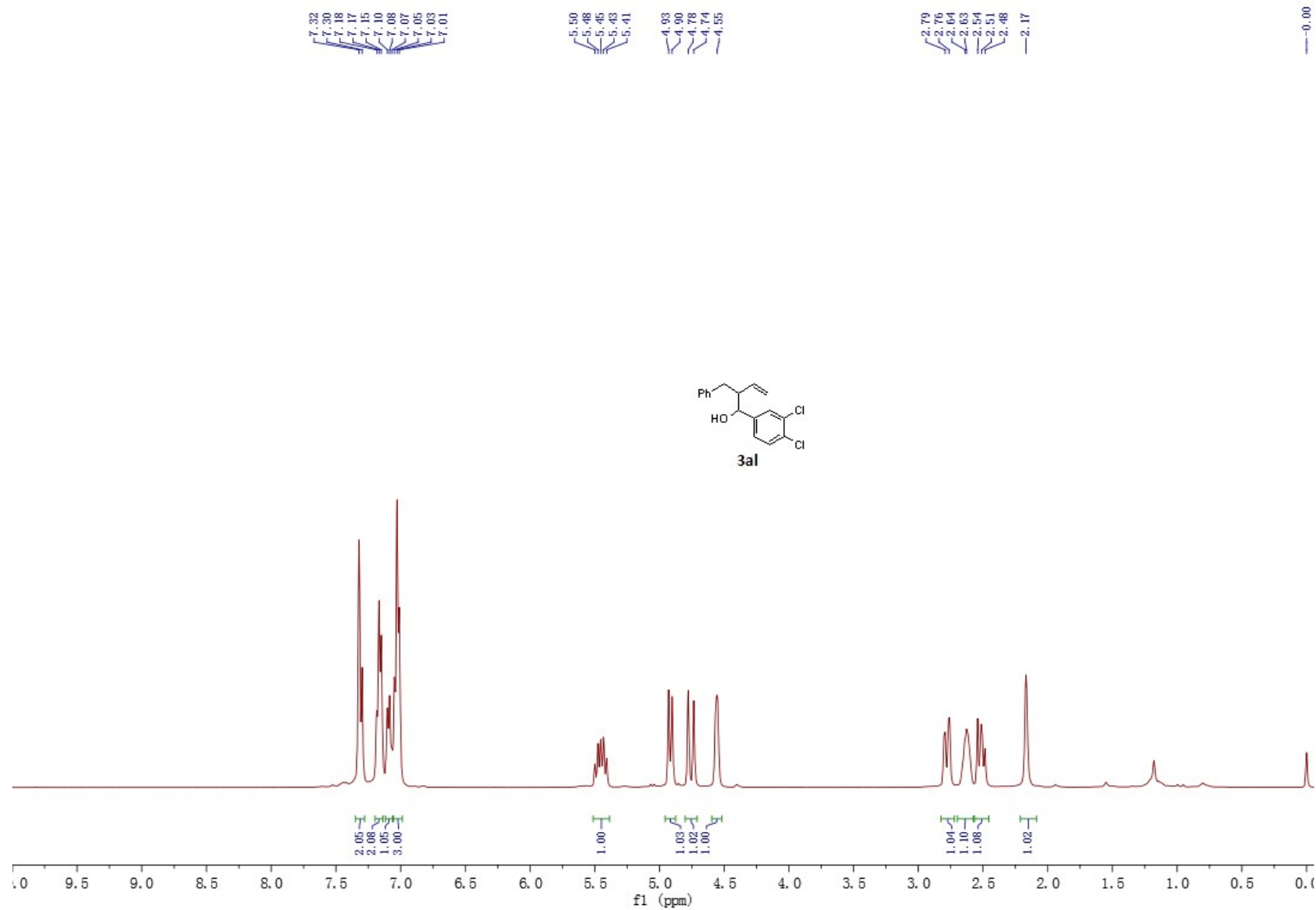


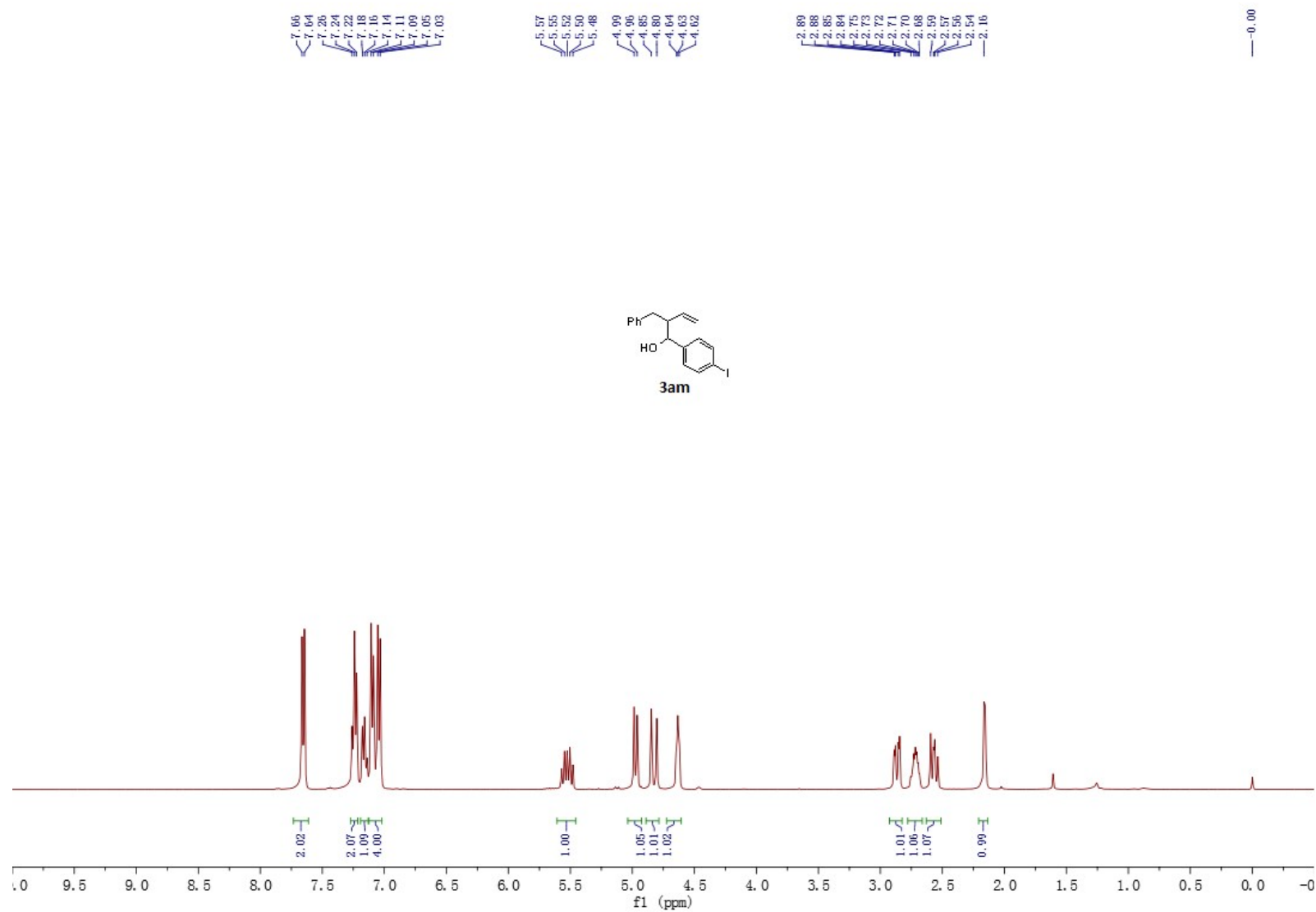


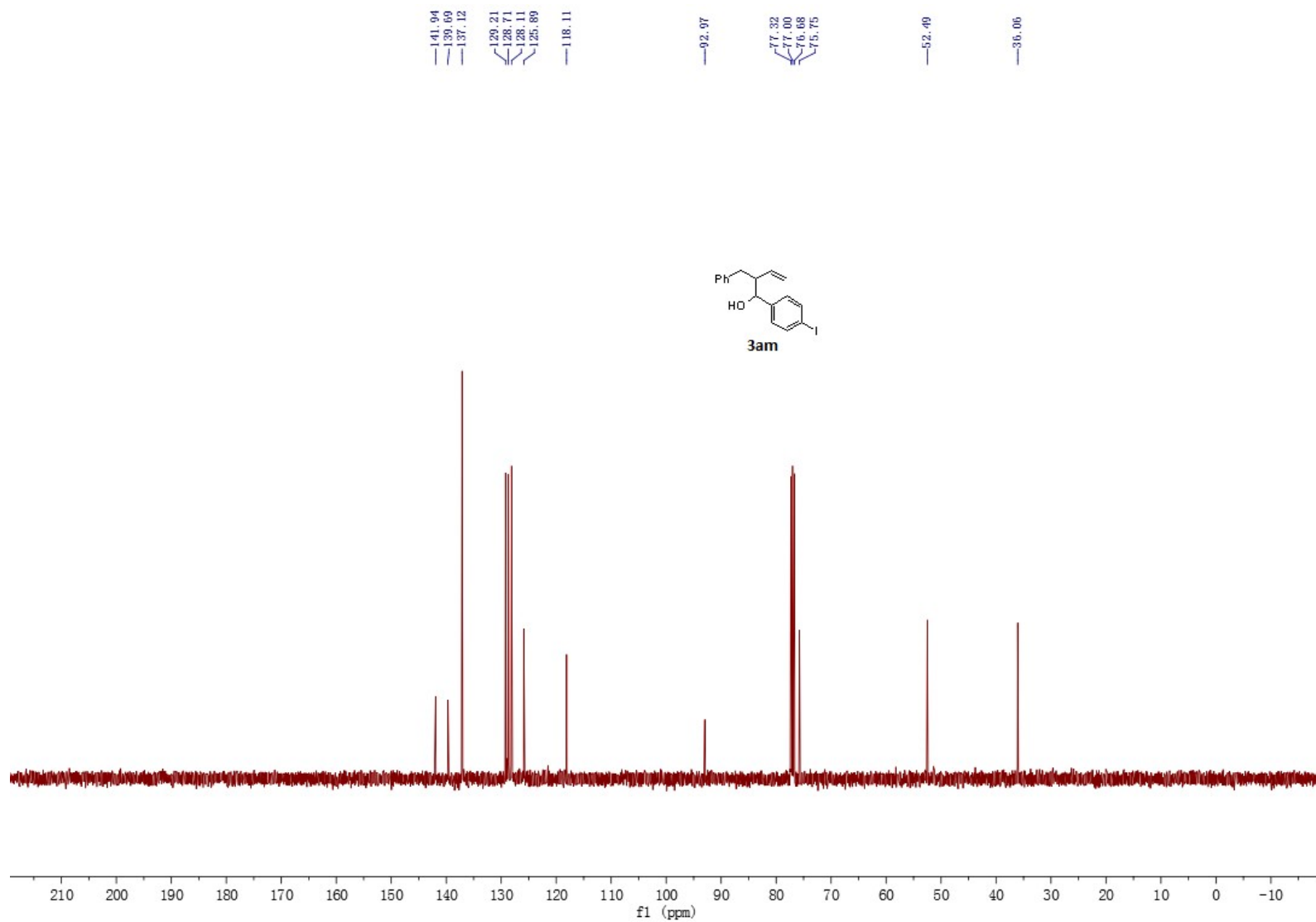


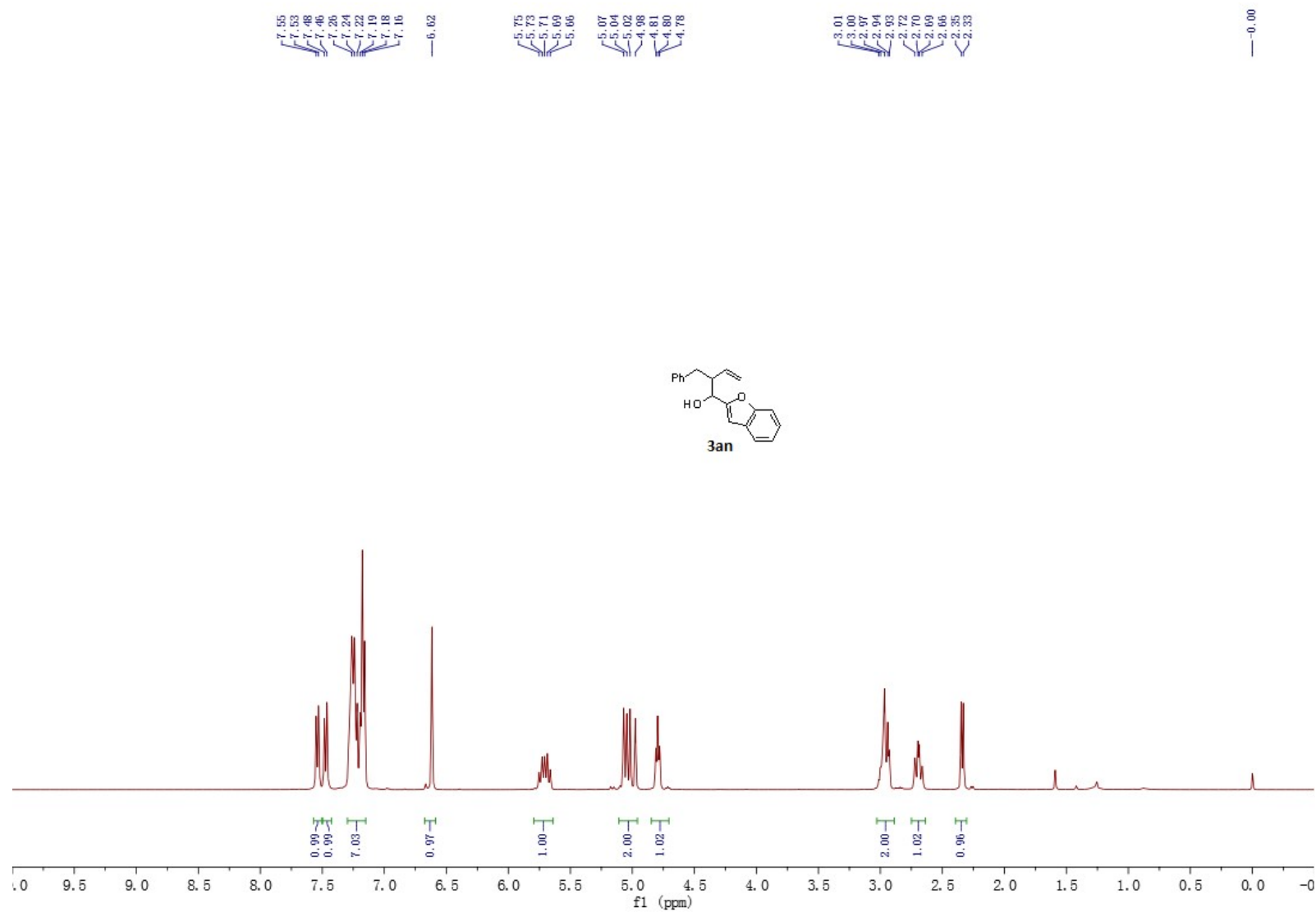


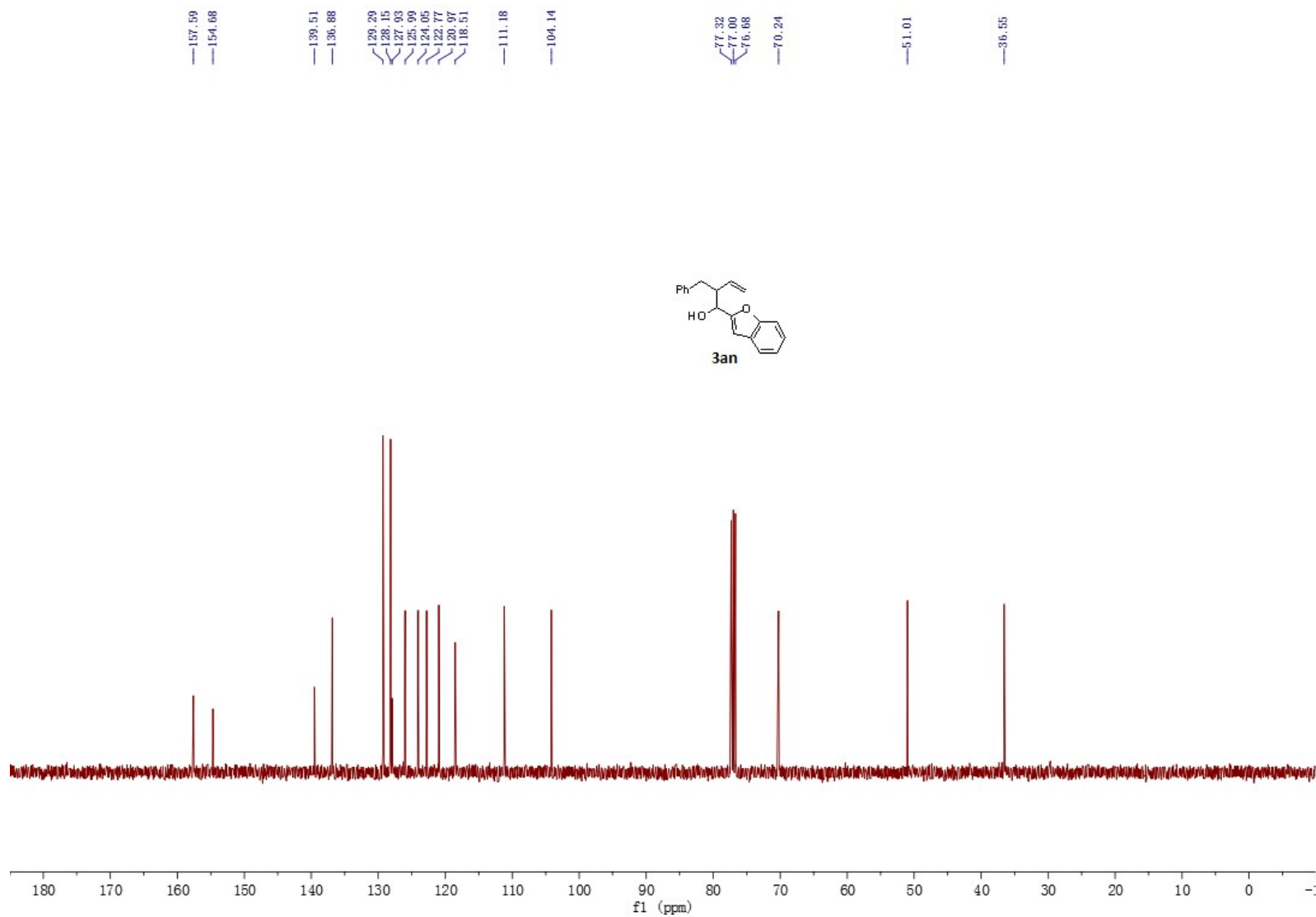


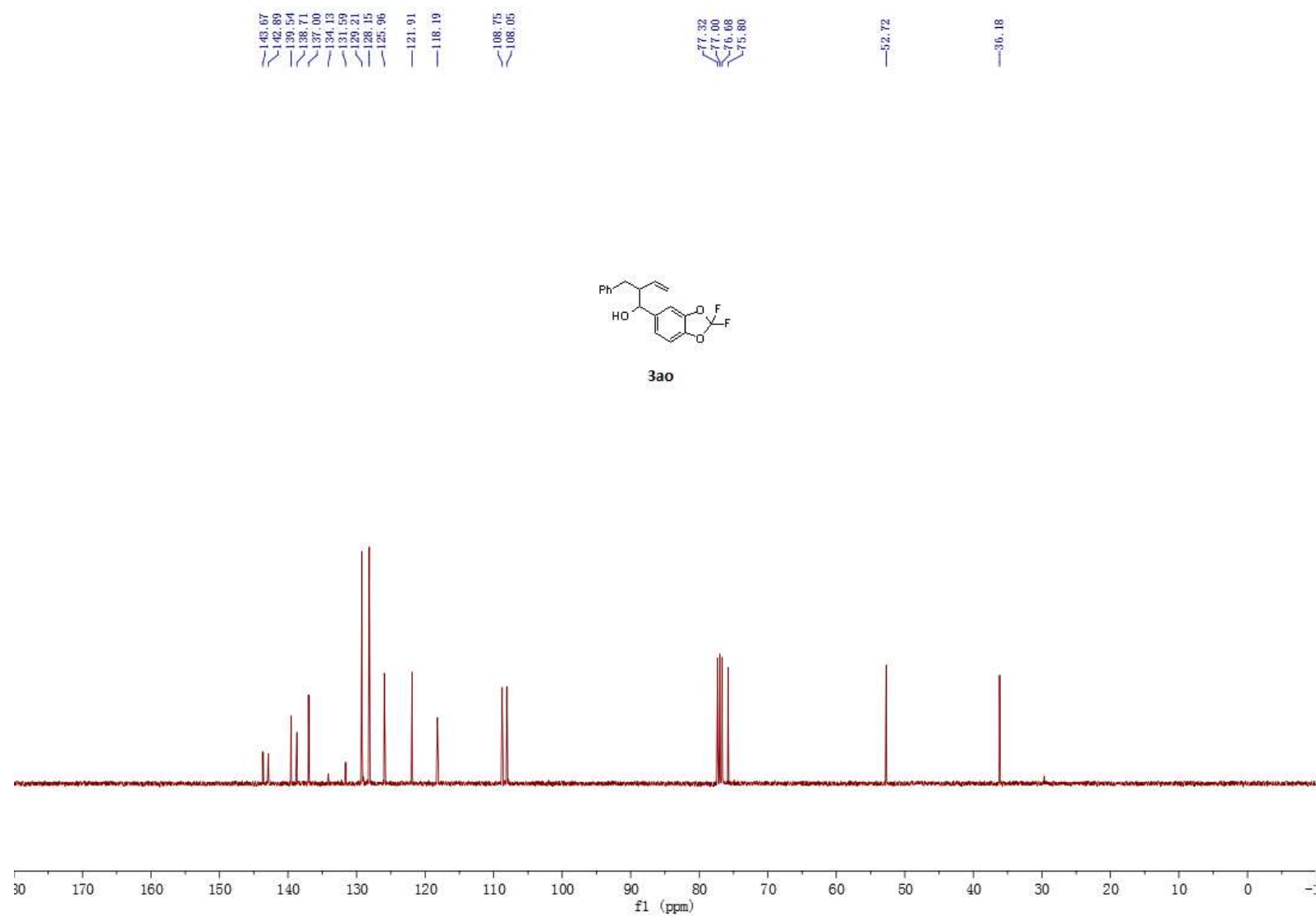




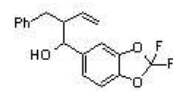




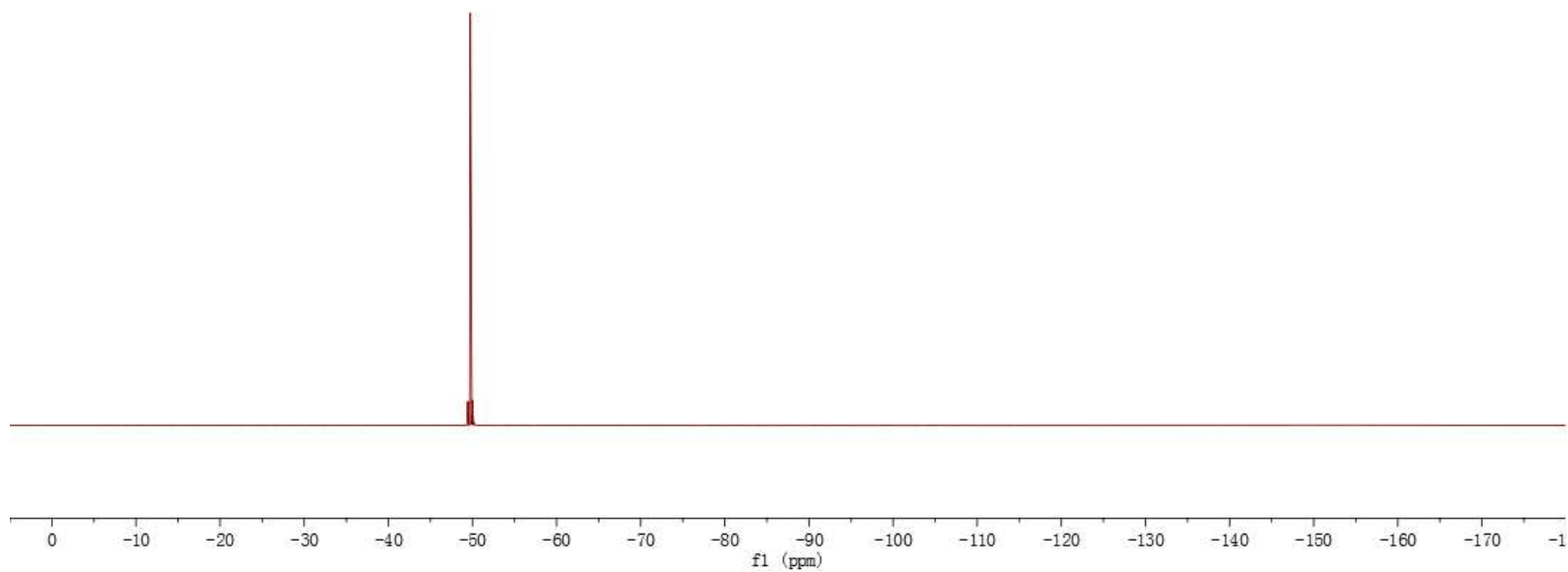


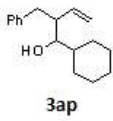


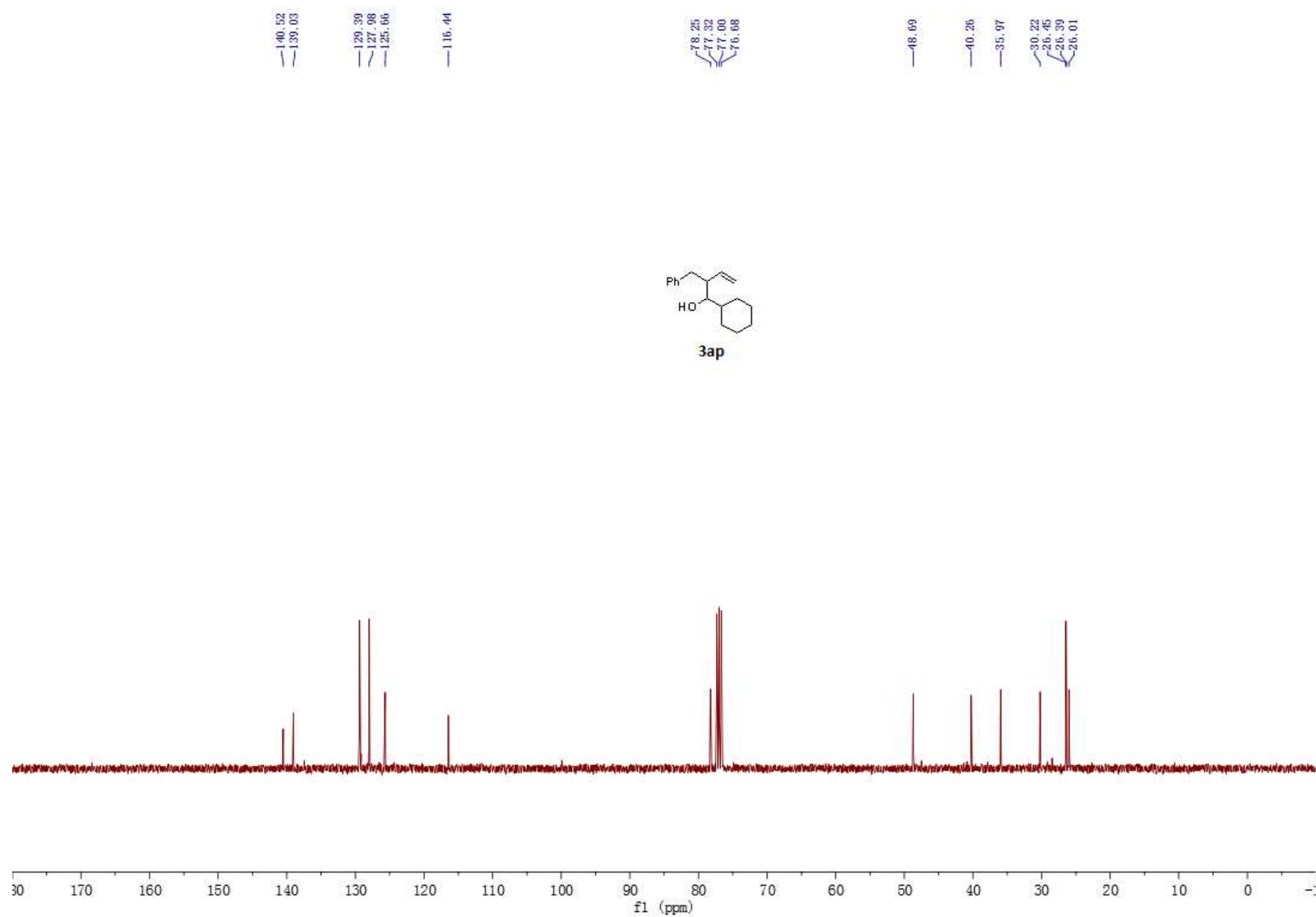
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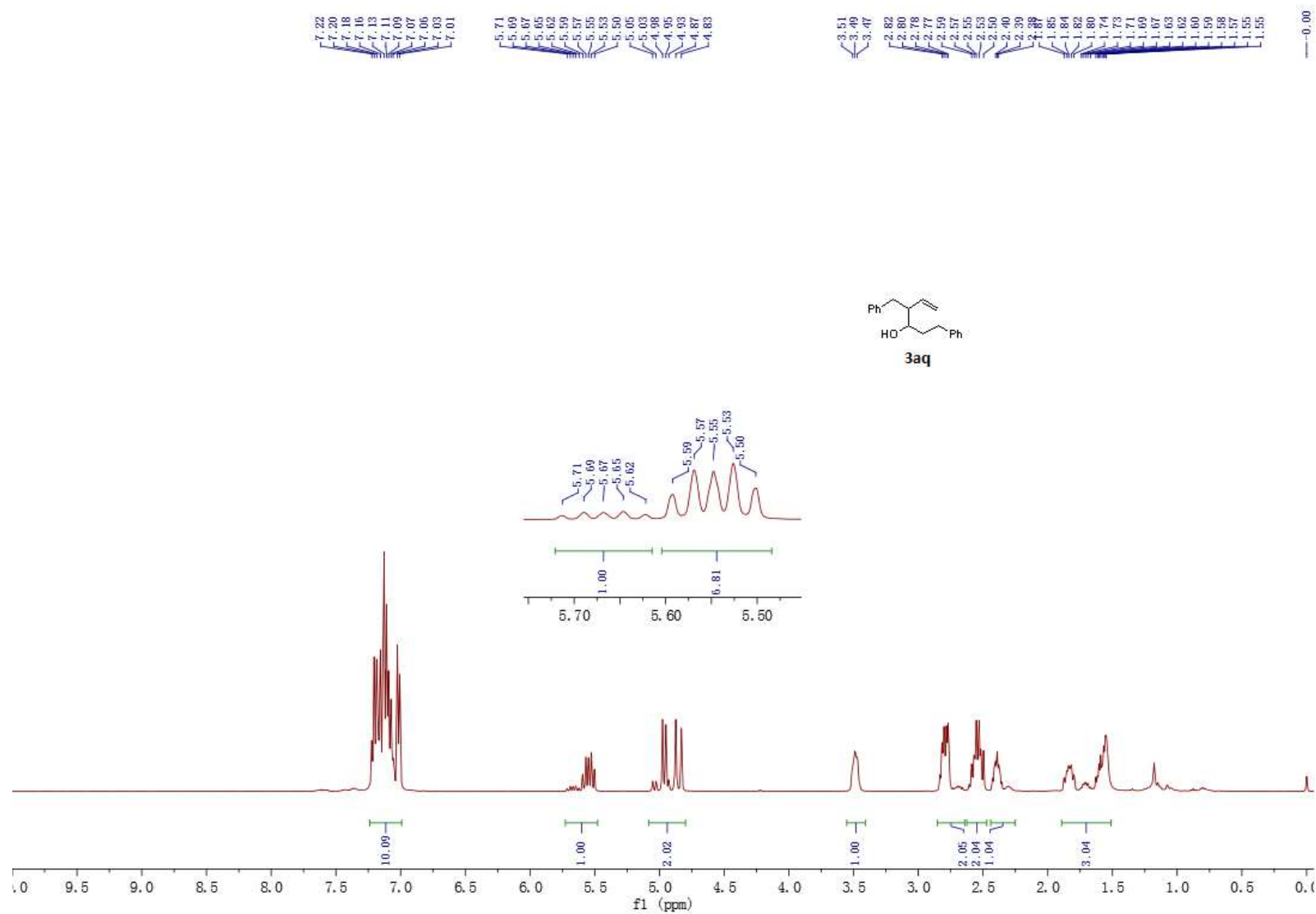


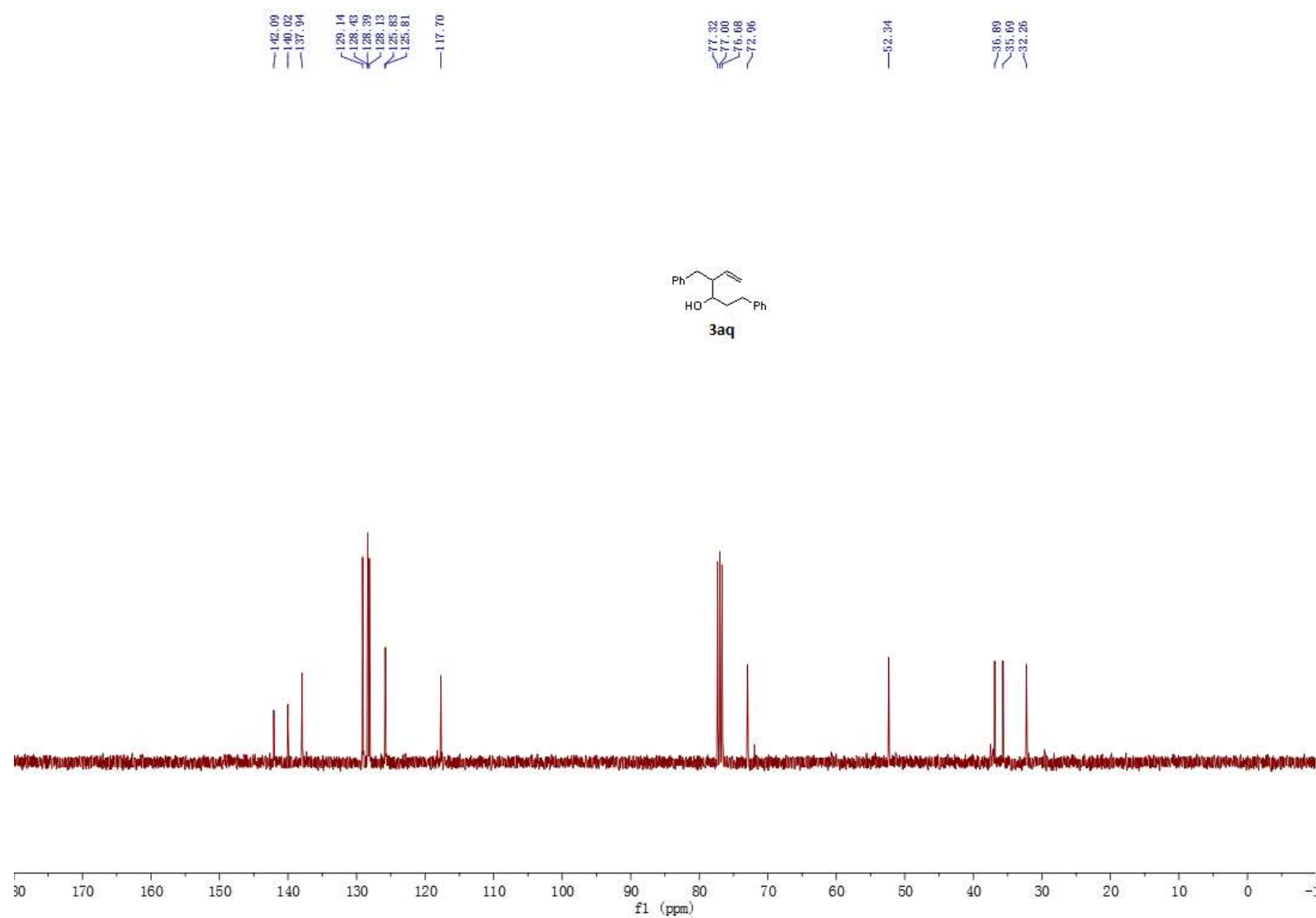
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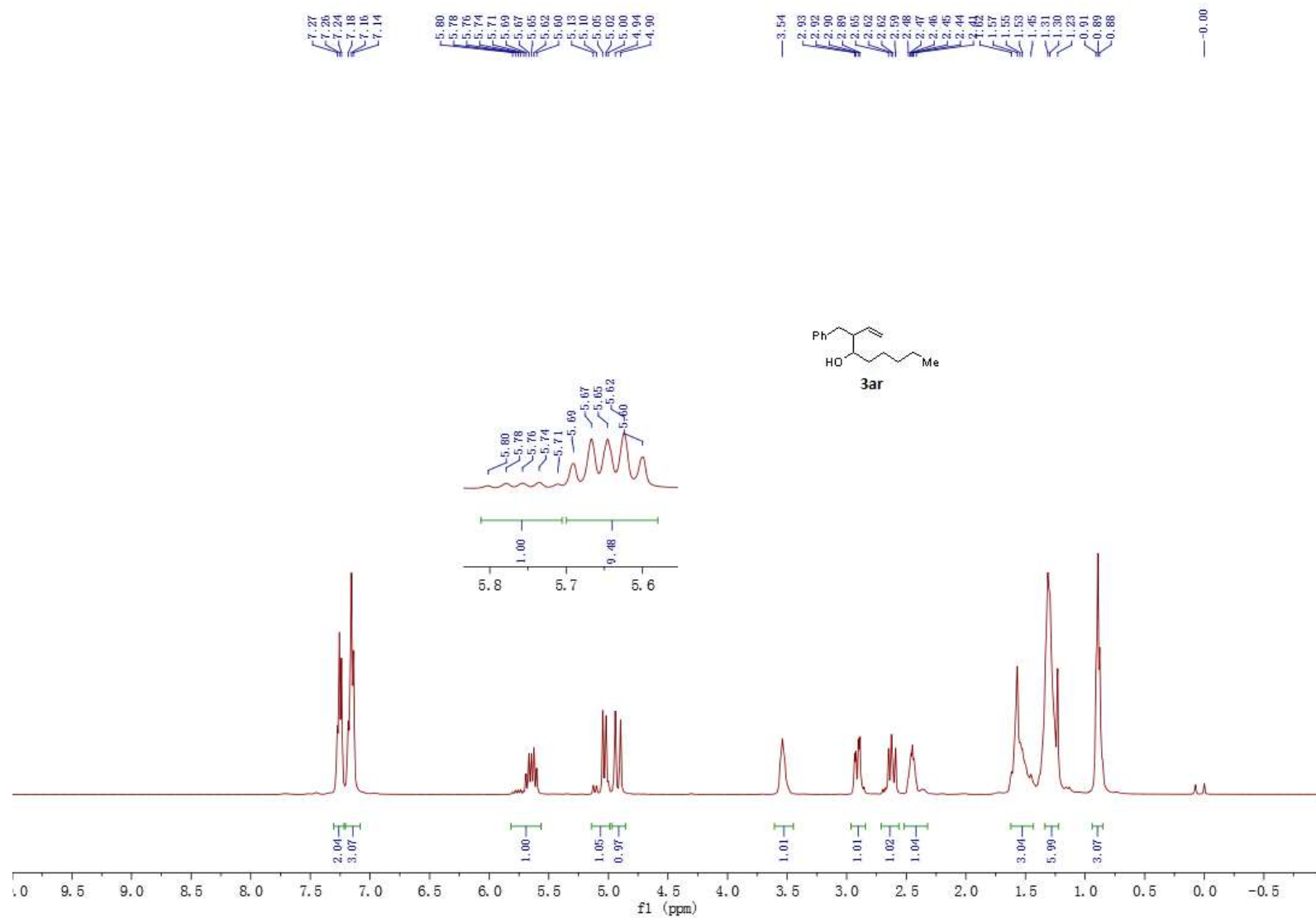


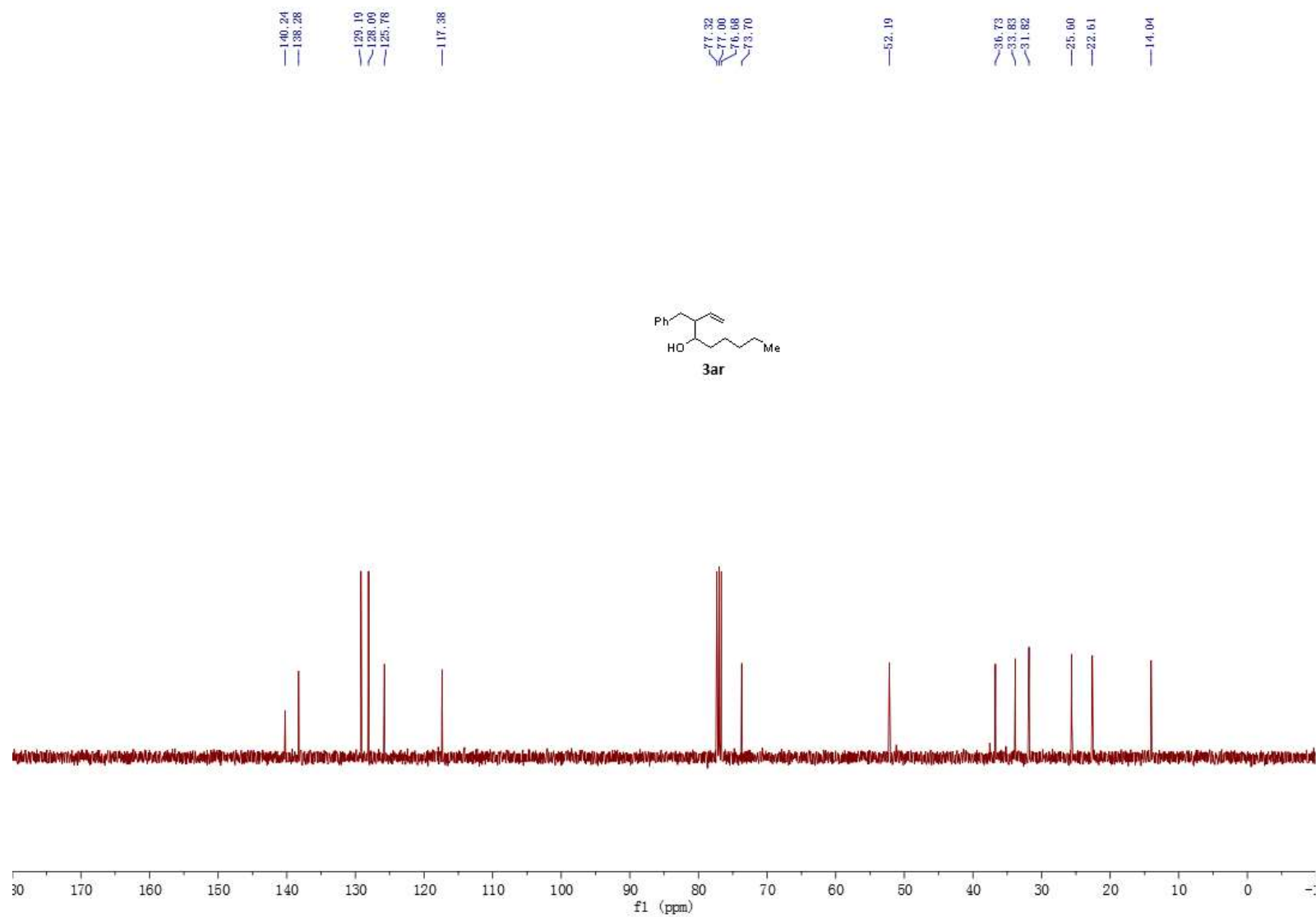


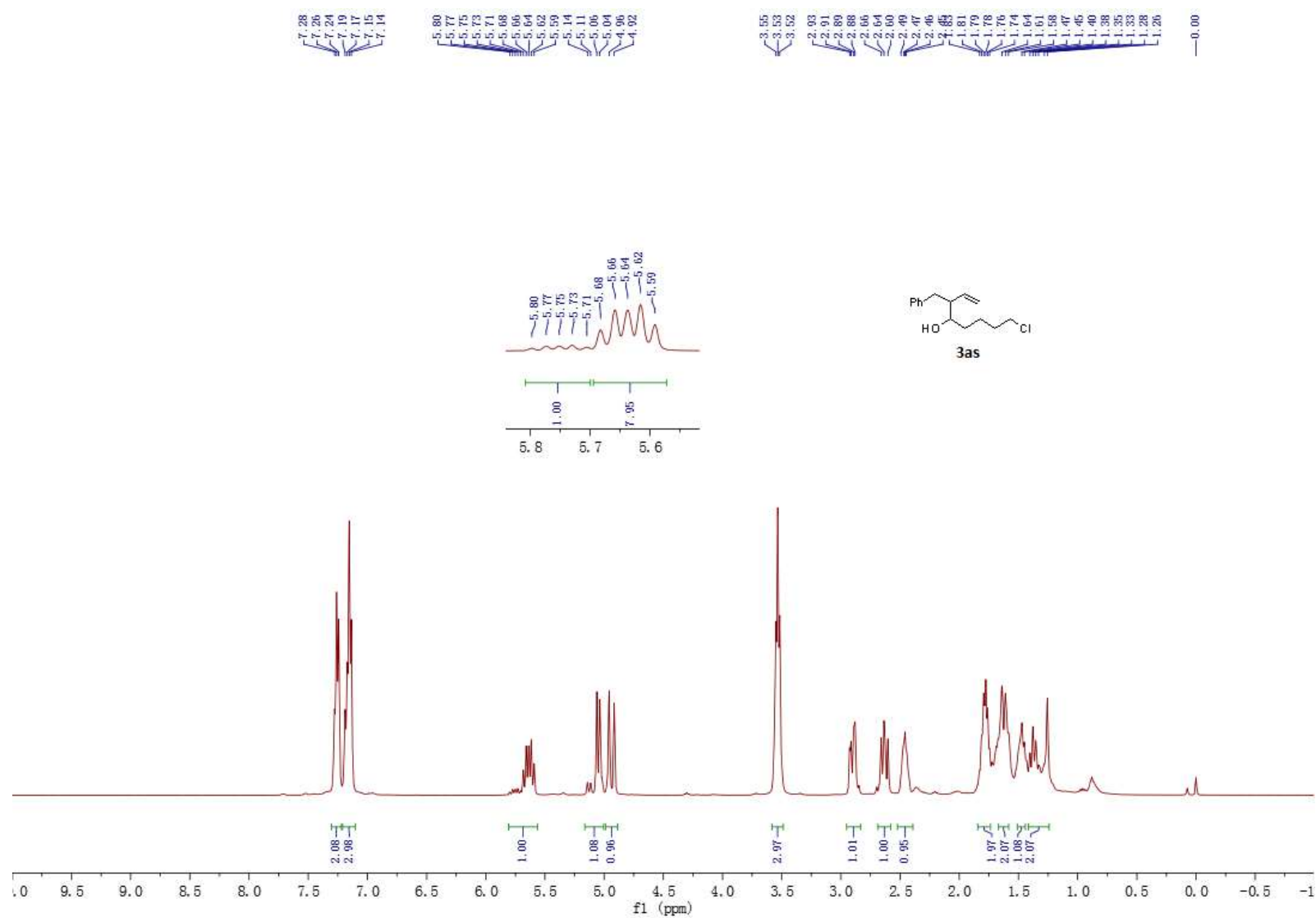


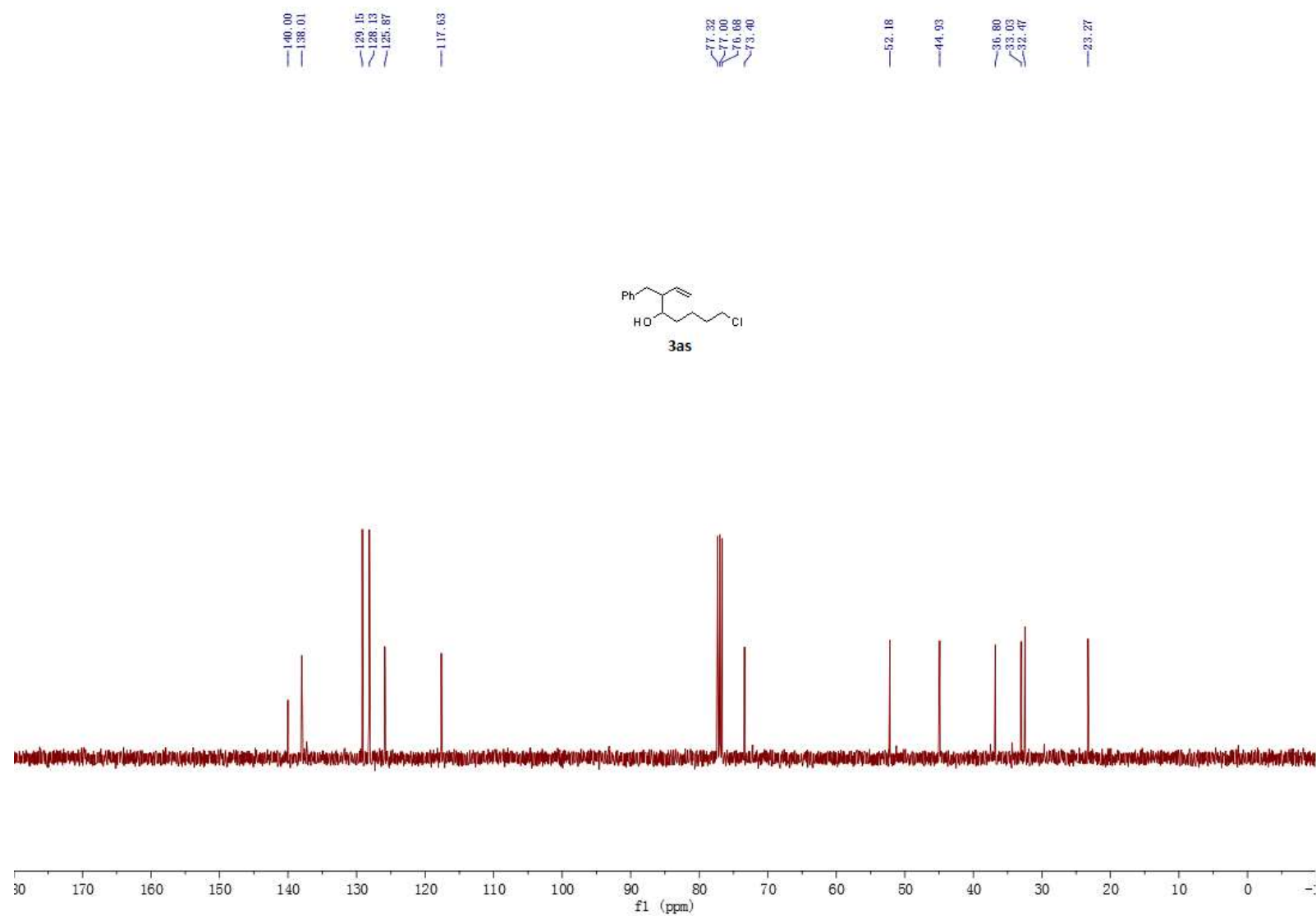


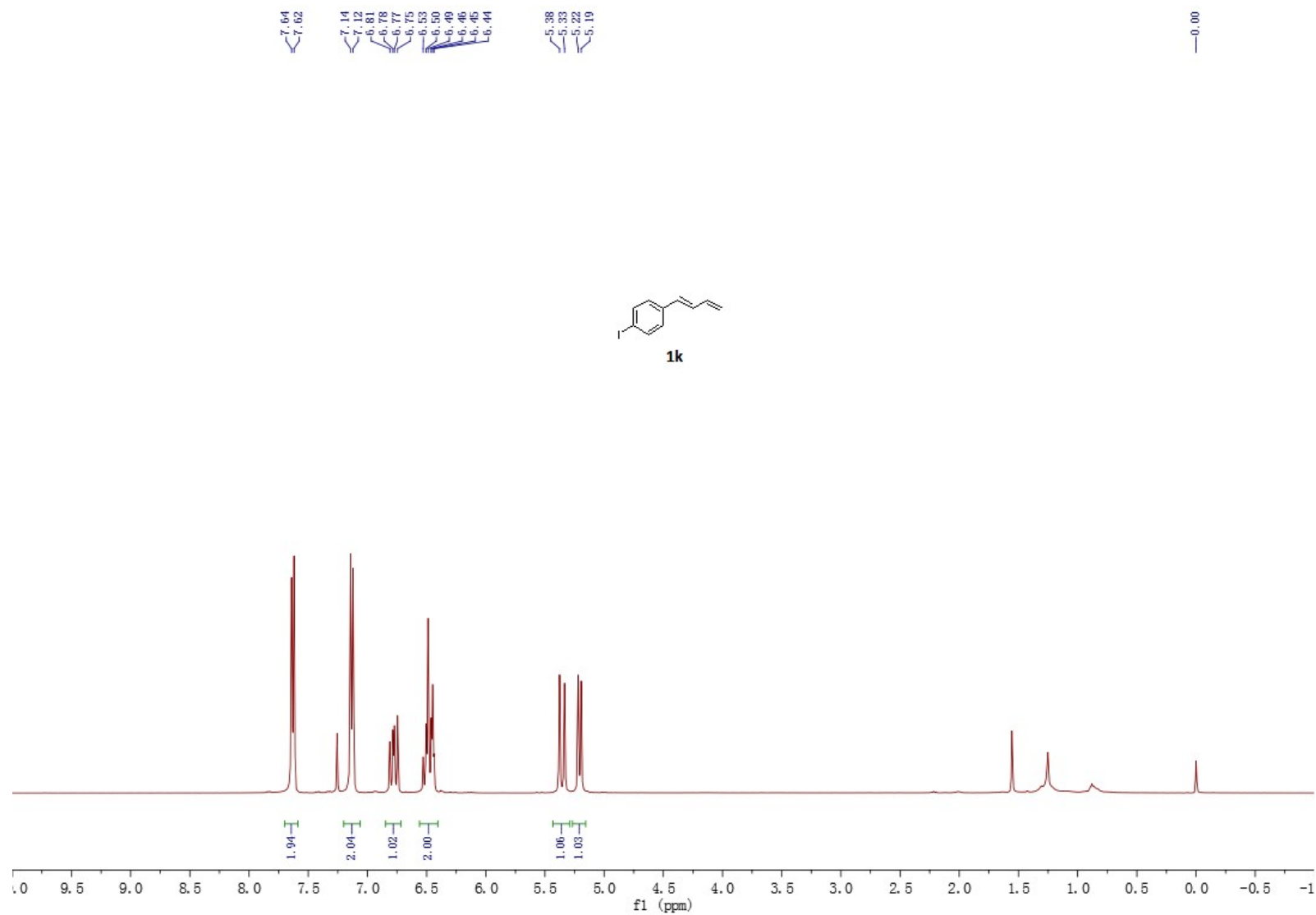


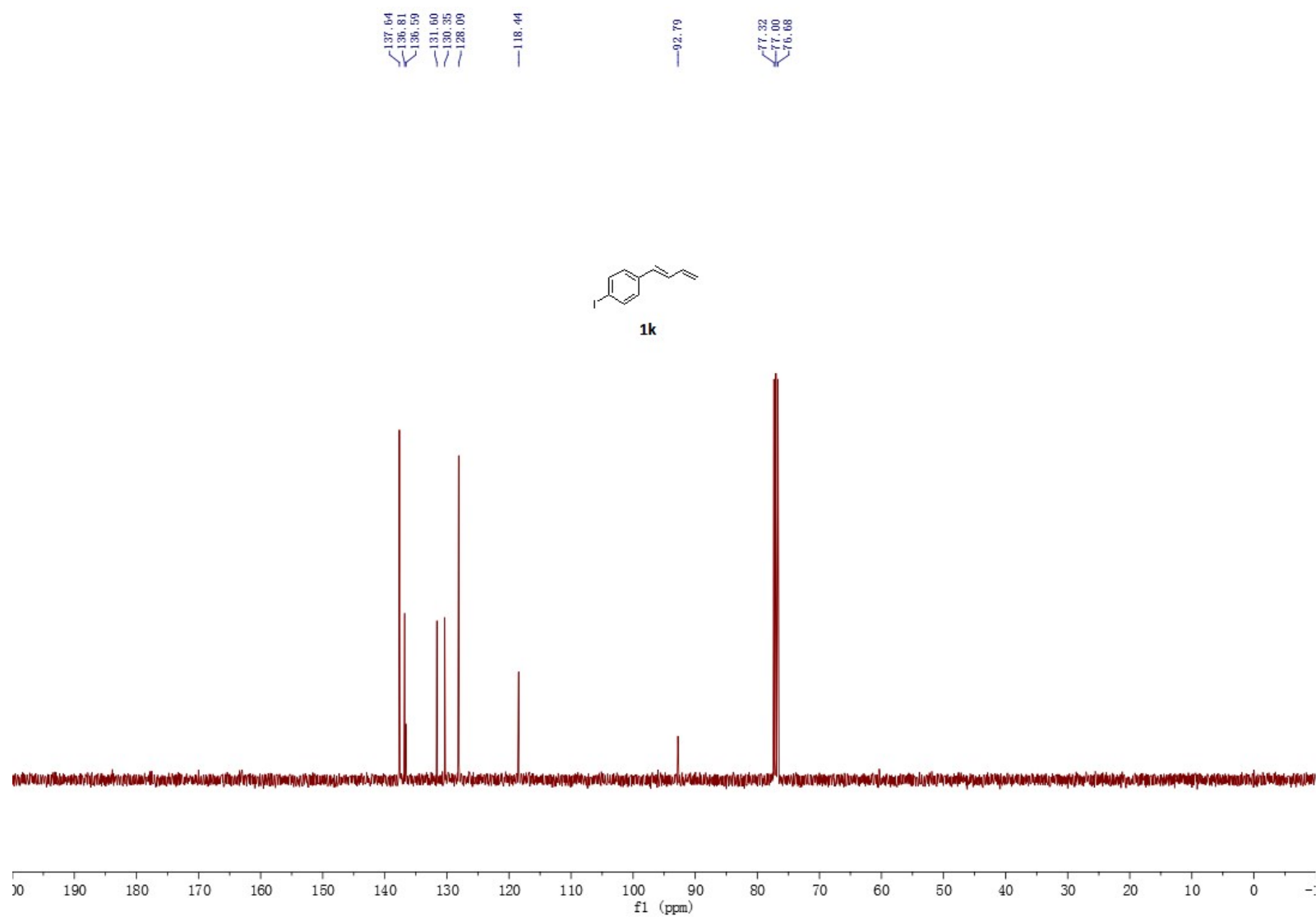


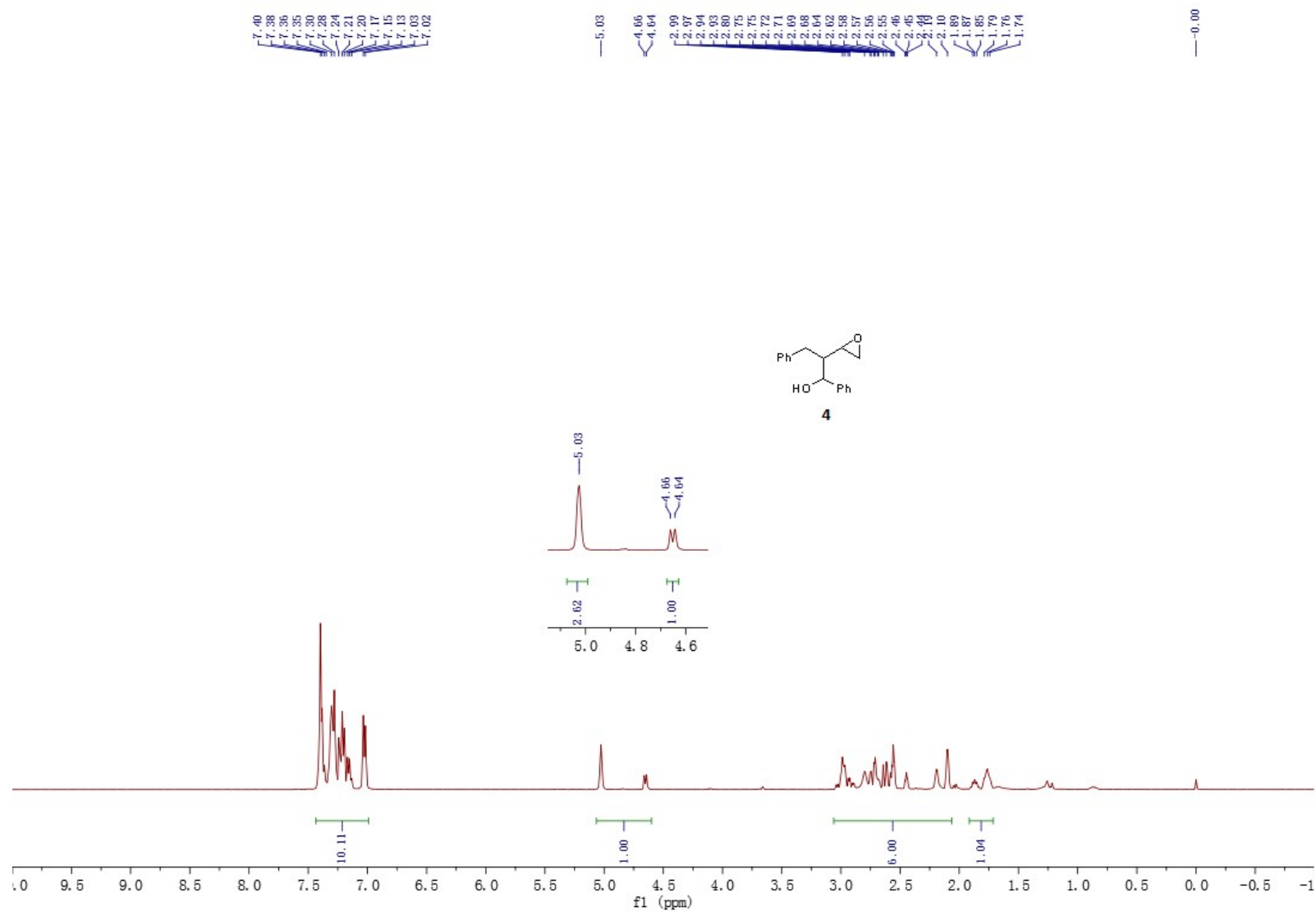


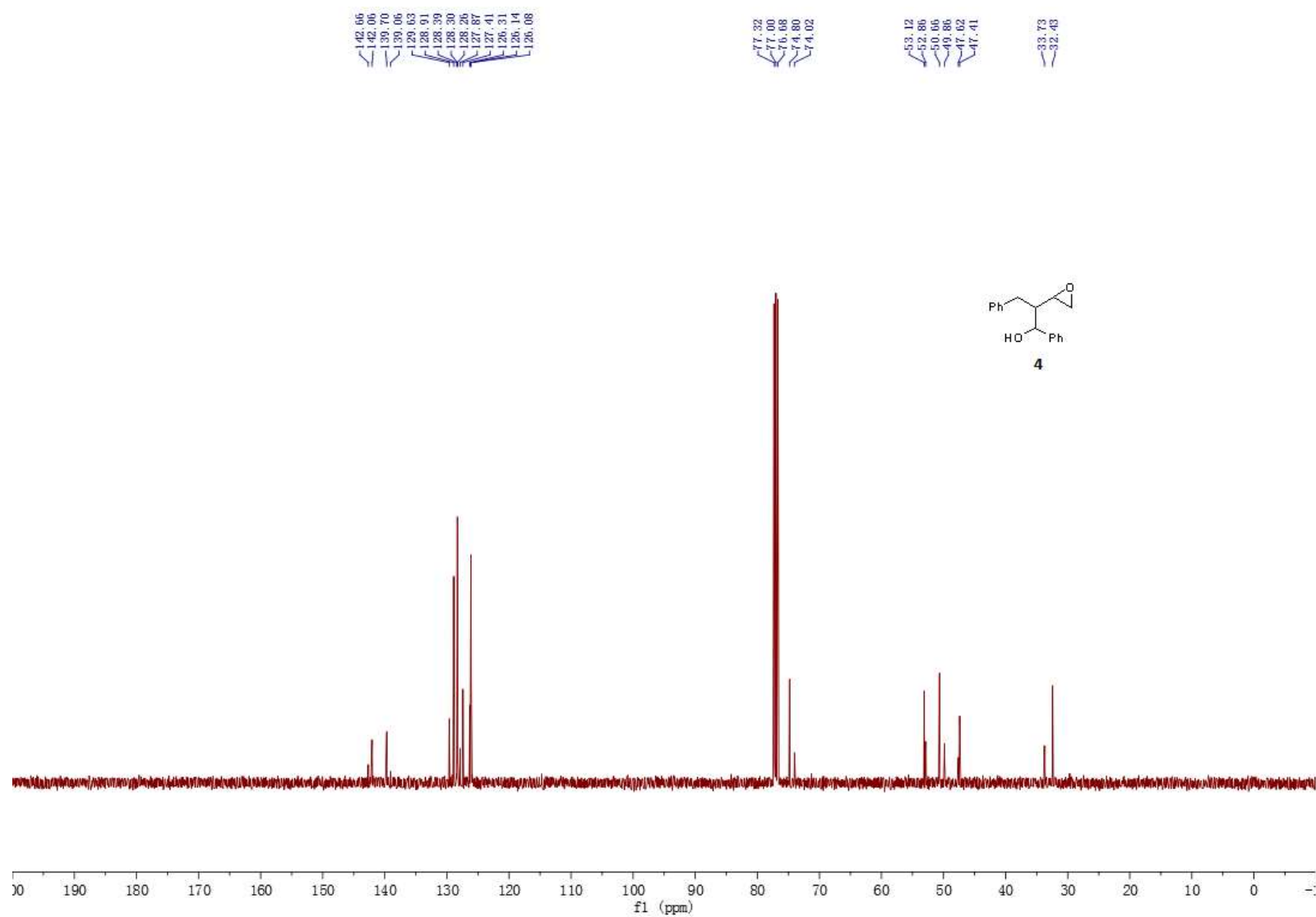


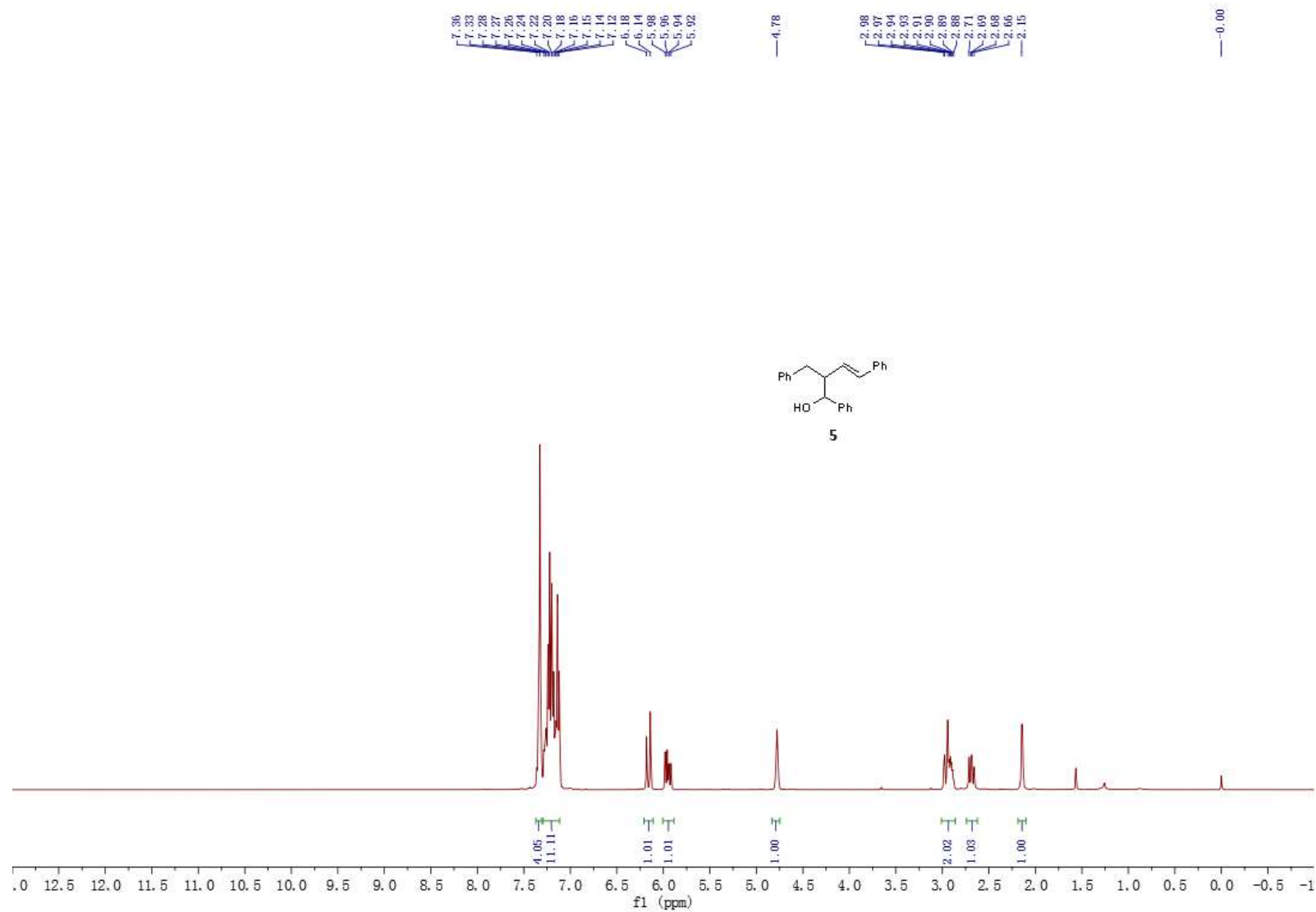


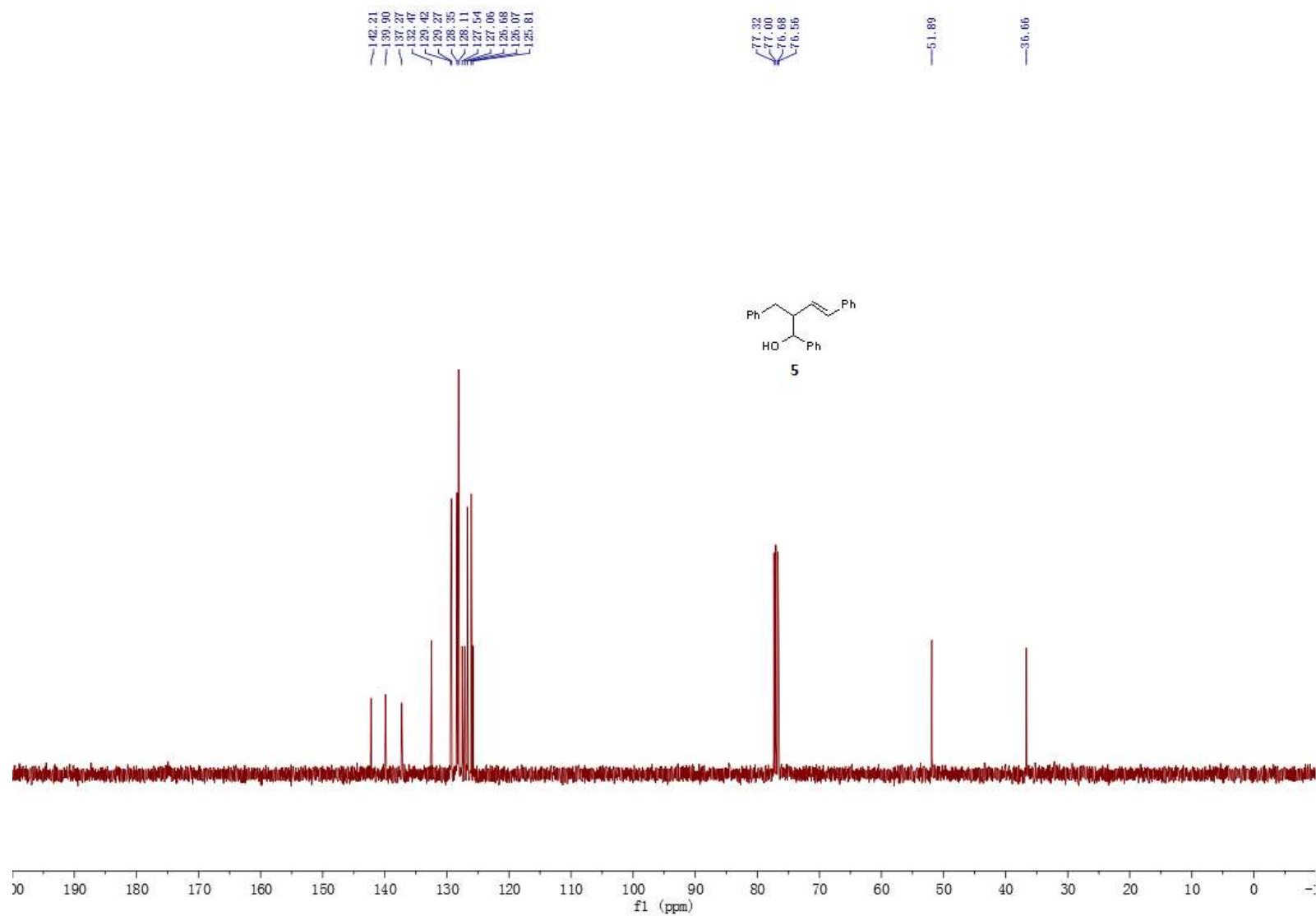


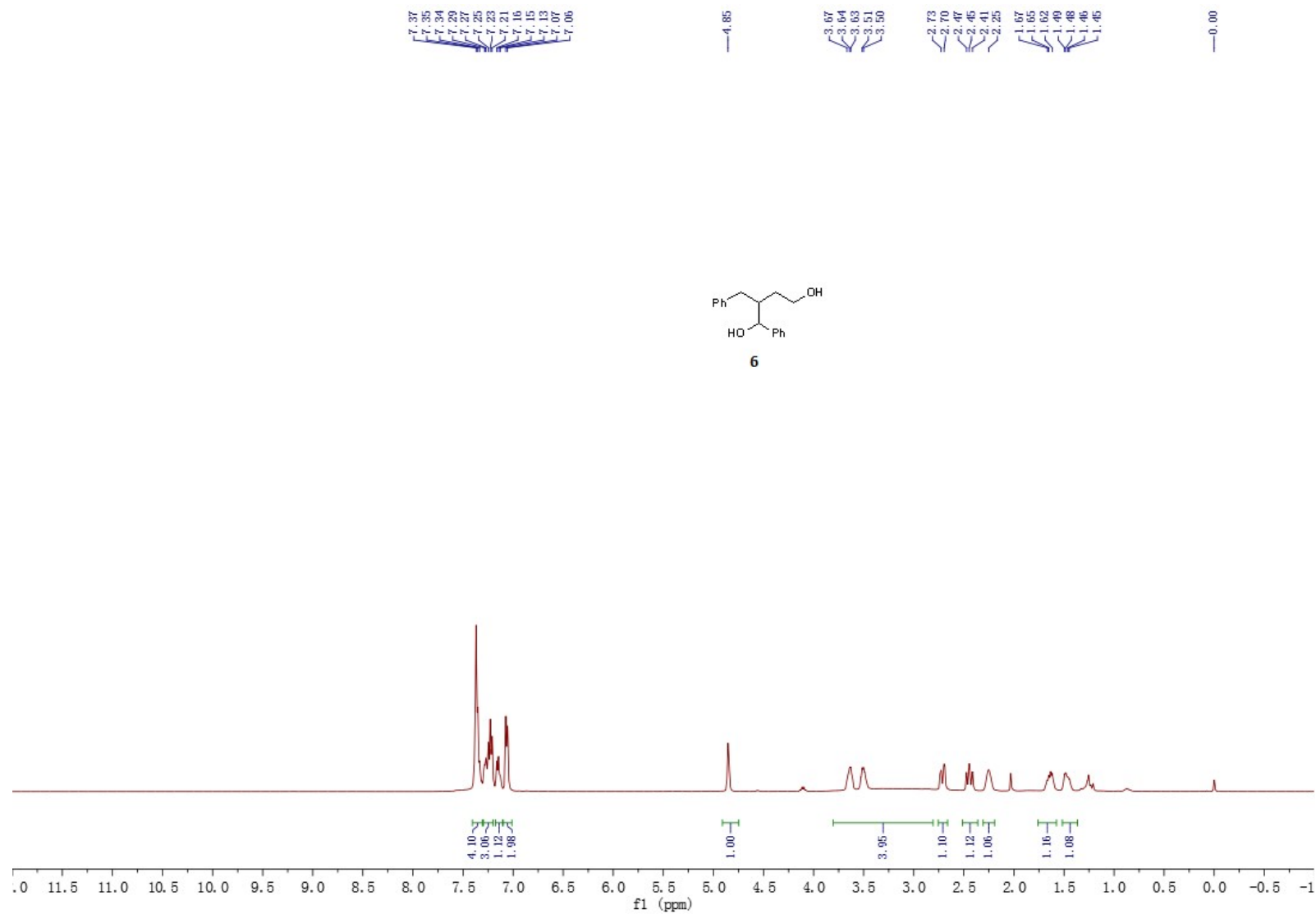


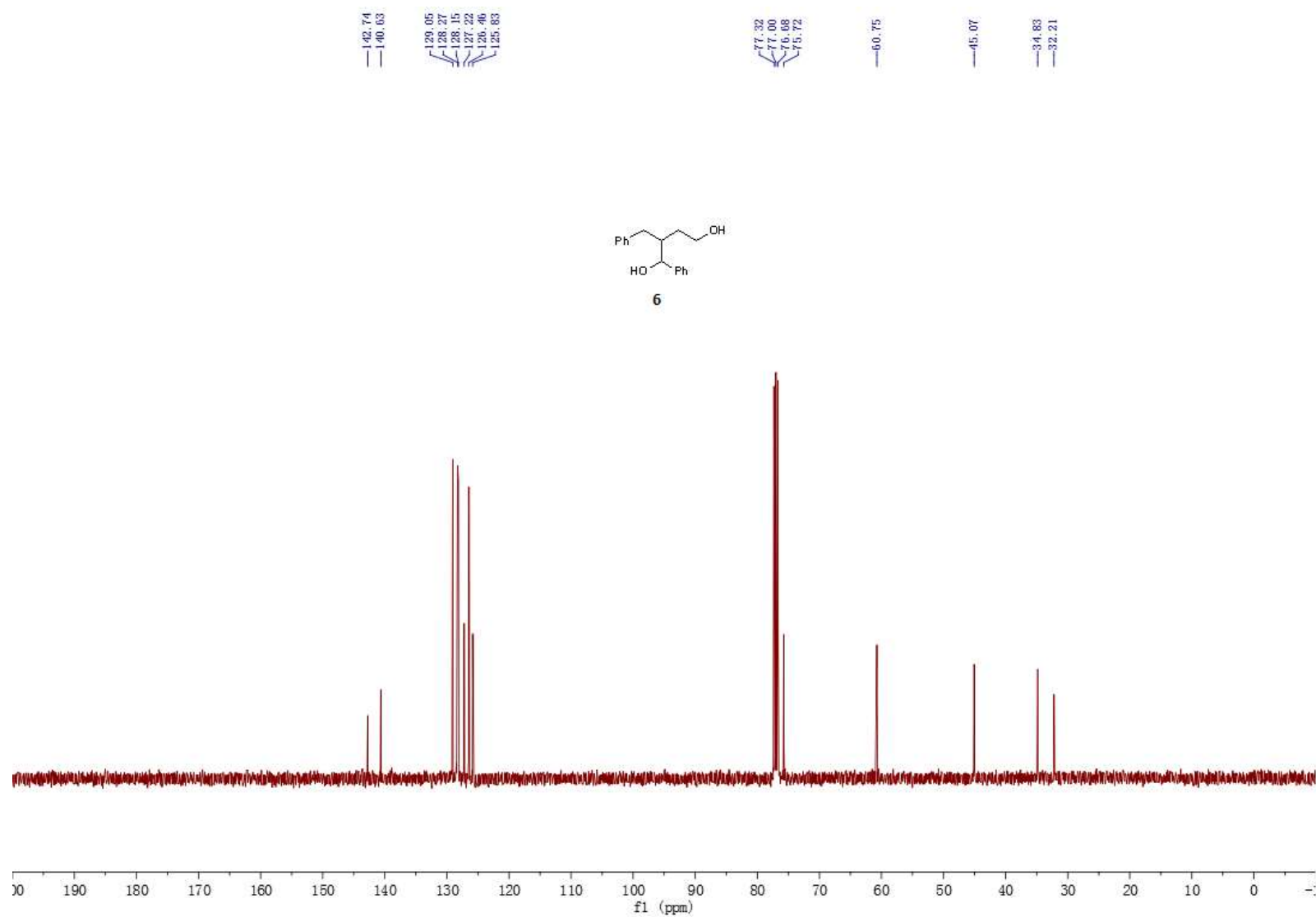


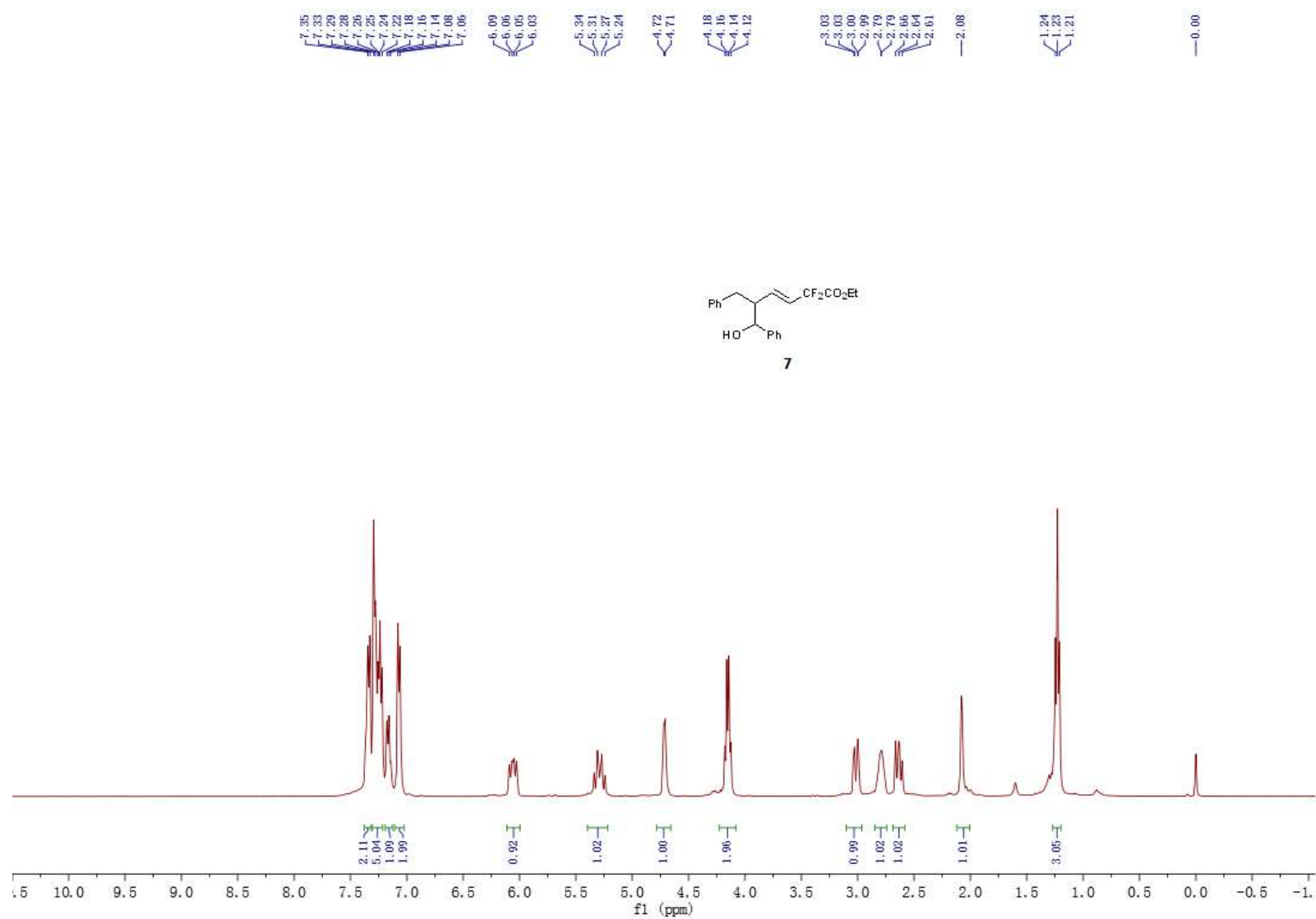


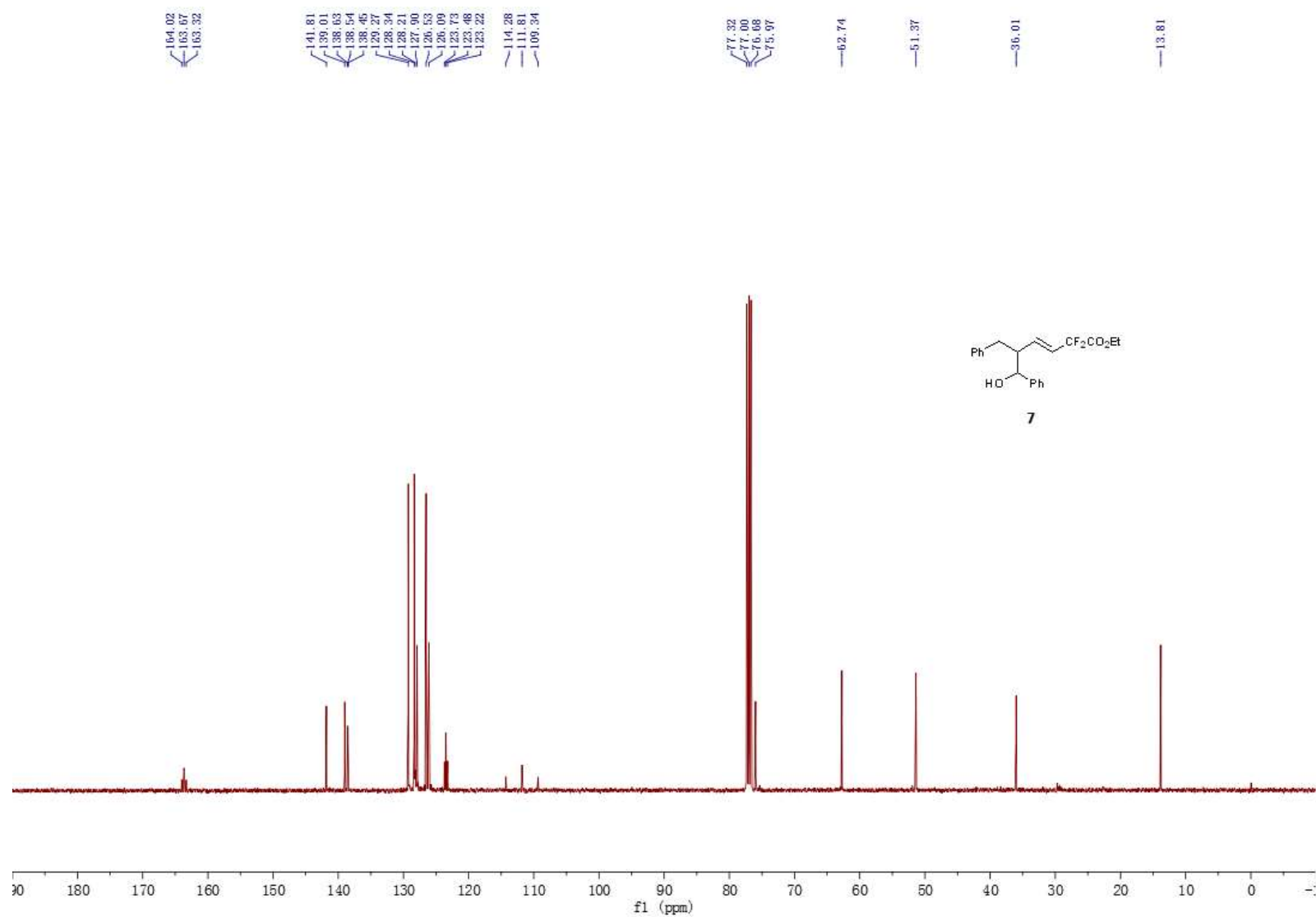




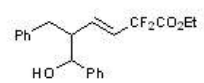




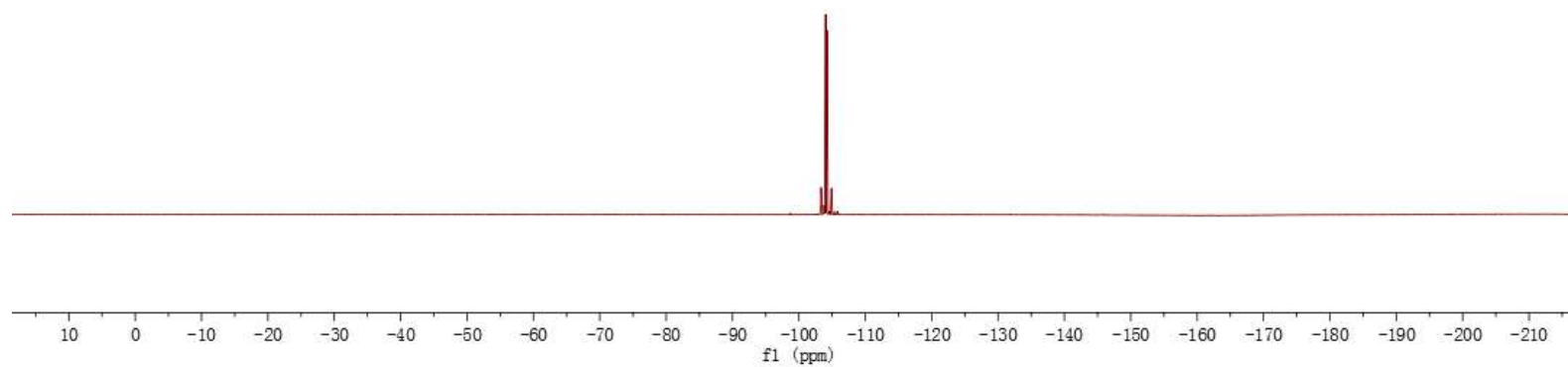




103.35
104.02
104.23
104.91



7



S112