Supplementary Information for

Palladium-Catalyzed Aminomethylation and Cyclization of Enynol to *O*-Heterocycle Confined 1,3-Dienes

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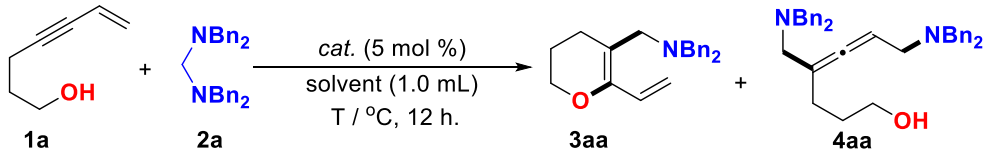
1. General Information

All non-aqueous reactions and manipulations were using standard Schlenk techniques. All solvents before using were dried by standard methods and stored under N_2 atmosphere. All reactions were monitored by TLC with silica gel-coated plates. NMR spectra were recorded on BRUKER Avence III 400 MHz or 500 MHz NMR spectrometers. Chemical shifts were reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. NMR data are reported as follows: chemical shift, multiplicity, coupling constants (Hz) and integration. Coupling constants (*J*) were reported in Hz and referred to apparent peak multiplications. High resolution mass spectra (HRMS) were recorded on Bruker MicroTOF-QII mass instrument (ESI). Single crystal X-ray diffraction analyses were recorded on Bruker SMART APEX II. All commercially available compounds were purchased from Adamas or Energy Chemical. Aminals used here were known compounds and synthesized according to the reported methods.[1] Enynols used here were synthesized according to the reported methods.[2] Flash column chromatography was performed using 200-300 mesh silica gels.

2. Optimization of the Reaction Conditions

Table S1. Evaluation of catalysts.[a]

N,*N*,*N*′,*N*′-tetrabenzylmethanediamine **2a** (146 mg, 0.36 mmol), palladium salt (0.015 mmol, 5 mol %), silver salt (0.03 mmol, 10 mol %), ligand (6 mol %), enynol **1a** (33 mg, 0.30 mmol) and solvent (1.0 mL) were added to a 25 mL flame-dried Young-type tube under N_2 atmosphere. The reaction mixture was stirred at the designed temperature for 12 hours and then cooled to room temperature. The solvent was removed under reduced pressure, the crude product was purified by flash chromatography on silica gels (petroleum ether/ethyl acetate = 200/1 to 50/1) directly to give the desired product **3aa**.



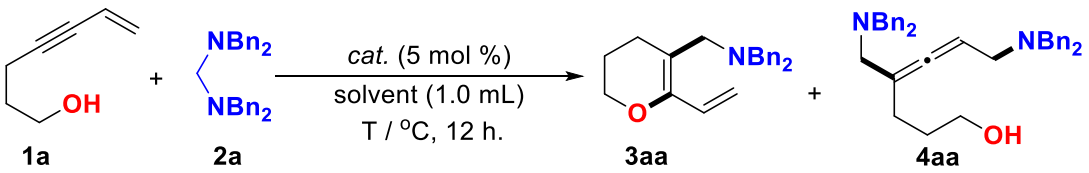
1a **2a** **3aa** **4aa**

entry	[Pd]	Ligand/[Ag]	solvent	T/°C	Yield/% **3aa**	Yield/% **4aa**
1	$PdBr_2$	Xantphos/AgOTf	DME	100	52	33
2	$Pd(CH_3CN)_2Cl_2$	Xantphos/AgOTf	DME	100	52	31
3[b]	$[Pd(allyl)Cl]_2$	Xantphos/AgOTf	DME	100	72	trace
4	$[Pd(allyl)Cl]_2$	Xantphos	DME	100	N.D	N.D
5[c]	$Pd_2(dba)_3$	Xantphos	DME	100	50	7
6	$Pd_2(dba)_3$	Xantphos	DME	100	N.D	N.D

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.36 mmol), [Pd] (5 mol %), [Ag] (12 mol %), Ligand (6 mol %), solvent (1.0 mL), 12 h, isolated yield. [b][Ag] (6 mol %), [c]HOTf (5 mol %).

Table S2. Evaluation of ligands.[a]

N,*N*,*N*′,*N*′-tetrabenzylmethanediamine **2a** (146 mg, 0.36 mmol), palladium salt (0.015 mmol, 5 mol %), silver salt (0.03 mmol, 10 mol %), ligand (6 mol % or 12 mol %), enynol **1a** (33 mg, 0.30 mmol) and solvent (1.0 mL) were added to a 25 mL flame-dried Young-type tube under N_2 atmosphere. The reaction mixture was stirred at the designed temperature for 12 hours and then cooled to room temperature. The solvent was removed under reduced pressure, the crude product was purified by flash chromatography on silica gels (petroleum ether/ethyl acetate = 200/1 to 50/1) directly to give the desired product **3aa**.



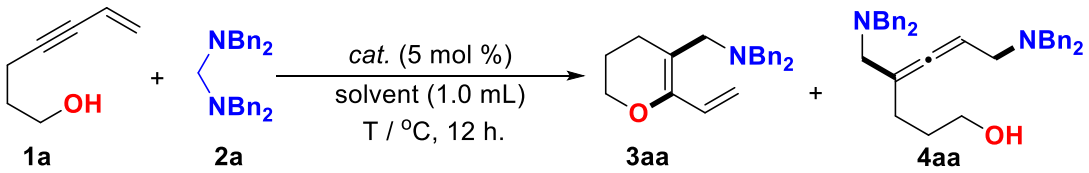
1a **2a** **3aa** **4aa**

entry	[Pd]	Ligand/[Ag]	solvent	T/°C	Yield/% **3aa**	Yield/% **4aa**
1	$[Pd(allyl)Cl]_2$	Xantphos/AgOTf	DME	100	81	trace
2	$[Pd(allyl)Cl]_2$	dppb/AgOTf	DME	100	N.D	N.D
3[b]	$[Pd(allyl)Cl]_2$	Trixiephos/AgOTf	DME	100	38	trace
4[c]	$[Pd(allyl)Cl]_2$	**L1**/AgOTf	DME	100	34	N.D

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.36 mmol), [Pd] (5 mol %), [Ag] (6 mol %), ligand (6 mol %), solvent (1.0 mL), 12 h, isolated yield. [b]ligand (12 mol %), [c]**L1**=1,2-Bis((di-*tert*-butylphosphino)methyl)benzene

Table S3. Evaluation of temperature.[a]

N,*N*,*N*′,*N*′-tetrabenzylmethanediamine **2a** (146 mg, 0.36 mmol), $Pd(Xantphos)(CH_3CN)_2(OTf)_2$ (16 mg, 5 mol %), enynol **1a** (33 mg, 0.30 mmol) and solvent (1.0 mL) were added to a 25 mL flame-dried Young-type tube under N_2 atmosphere. The reaction mixture was stirred at the designed temperature for 12 hours and then cooled to room temperature. The solvent was removed under reduced pressure, the crude product was purified by flash chromatography on silica gels (petroleum ether/ethyl acetate = 200/1 to 50/1) directly to give the desired product **3aa**.



1a **2a** **3aa** **4aa**

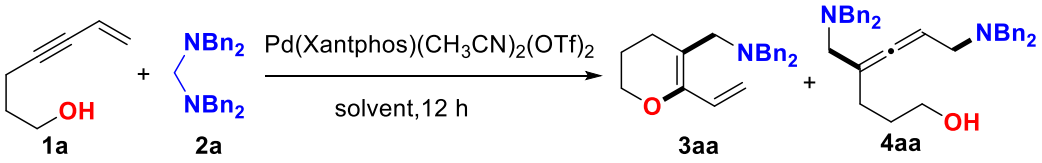
entry	[Pd]	solvent	T/°C	Yield/% **3aa**	Yield/% **4aa**
1	$Pd(Xantphos)(CH_3CN)_2(OTf)_2$	DME	100	81	trace
2	$Pd(Xantphos)(CH_3CN)_2(OTf)_2$	DME	120	76	trace
3	$Pd(Xantphos)(CH_3CN)_2(OTf)_2$	DME	80	38	53
4	$Pd(Xantphos)(CH_3CN)_2(OTf)_2$	DME	60	28	57

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.36 mmol), [Pd] (5 mol %), solvent (1.0 mL), 12 h, isolated yield.

Table S4. Evaluation of solvents.[a]

N,*N*,*N*′,*N*′-tetrabenzylmethanediamine **2a** (146 mg, 0.36 mmol), $Pd(Xantphos)(CH_3CN)_2(OTf)_2$ (16 mg, 5 mol %), enynol **1a** (33 mg, 0.30 mmol) and solvent (1.0 mL) were added to a 25 mL flame-dried Young-type tube under N_2 atmosphere. The reaction mixture was stirred at the designed temperature for 12 hours and then cooled to room temperature. The solvent was removed under reduced pressure, the crude product was purified by flash chromatography on silica gels

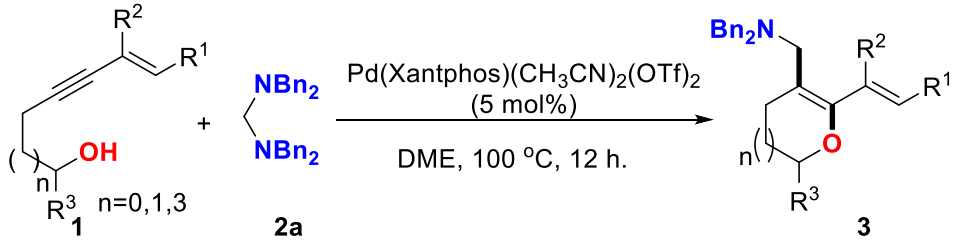
(petroleum ether/ethyl acetate = 200/1 to 50/1) directly to give the desired product **3aa**.



entry	[Pd]	solvent	T/°C	Yield/% **3aa**	Yield/% **4aa**
1	$Pd(Xantphos)(CH_3CN)_2(OTf)_2$	DME	100	81	trace
2	$Pd(Xantphos)(CH_3CN)_2(OTf)_2$	THF	100	70	13
3	$Pd(Xantphos)(CH_3CN)_2(OTf)_2$	DCM	100	40	26
4	$Pd(Xantphos)(CH_3CN)_2(OTf)_2$	CH_3CN	100	trace	61
5	$Pd(Xantphos)(CH_3CN)_2(OTf)_2$	*p*-xylene	100	63	trace
6	$Pd(Xantphos)(CH_3CN)_2(OTf)_2$	mesitylene	100	67	trace
7	$Pd(Xantphos)(CH_3CN)_2(OTf)_2$	DMF	100	23	trace
8	$Pd(Xantphos)(CH_3CN)_2(OTf)_2$	DMSO	100	31	trace

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.36 mmol), [Pd] (5 mol %), solvent (1.0 mL), 12 h, isolated yield.

3. General Procedure for the Catalytic Reaction

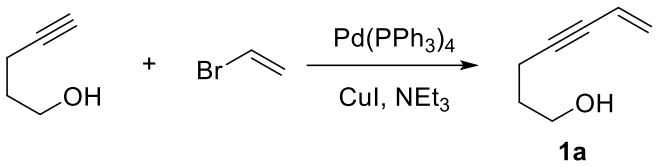


Aminal **2a** (0.36 mmol), Pd(Xantphos)$(CH_3CN)_2(OTf)_2$ (16.0 mg, 5 mol %), enynol **1** (0.30 mmol) and DME (1.0 mL) were added to a 25 mL flame-dried Young-type tube under N_2 atmosphere. The reaction mixture was stirred at 100 ℃ in an oil bath for 12 hours and then cooled to room temperature. The solvent was removed under reduced pressure, the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 200/1 to 50/1) to give the desired product as a colorless oil.

4. Preparation and Spectral Data of Substrates

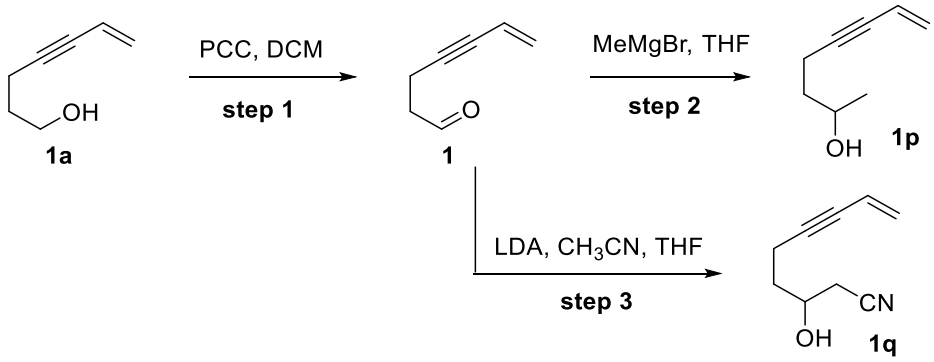
a) Preparation of Enynol Derivatives

General Procedure A. Synthesis of substrate **1a.**



Step 1. The mixture of copper (I) iodide (190 mg, 2 mol %) and tetrakis(triphenylphosphine)palladium (578 mg, 1 mol %) were dissolved in triethylamine (14 mL) under N_2 atmosphere at 0 ℃. The 4-Pentyn-1-ol (4.2 g, 50 mmol) and vinyl bromide (1.0 M in THF, 70 mL, 70 mmol) were added and the resulting mixture was stirred at 45 ℃ in an oil bath until the complete conversion of the starting material. The reaction mixture was cooled to room temperature and filtered. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (petroleum ether/ethyl acetate = 10/1 to 5/1) to afford **1a** (4.68 g, 85% yield).

General Procedure B. Synthesis of substrates **1p** and **1q**.



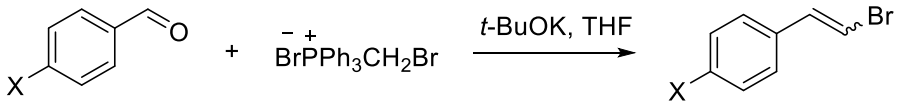
Step 1. The mixture of pyridinium chlorochromate (15.0 g, 70 mmol) and silica gel (15.0 g) was dissolved in CH_2Cl_2 (80 mL) under N_2 atmosphere at 0 ℃. hept-6-en-4-yn-1-ol (5.5 g, 50 mmol) was added and stirred at room temperature for 2 hours until the complete conversion of the starting material. The reaction mixture was filtered and washed with Et_2O (10 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 20/1 to 10/1) to afford **1** (3.90 g, 72% yield).

Step 2. A solution of Methylmagnesium bromide (3.0 M in THF, 4.0 mL, 12 mmol) was added dropwise to a solution of crude 6-hepten-4-ynal (1.1 g, 10 mmol) in THF

(20 mL) at 0 ℃ under N_2 atmosphere. The reaction mixture was stirred at room temperature for 1 hour. The reaction was quenched by saturated NH_4Cl solution and extracted with Et_2O (20 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 10/1 to 5/1) to afford substrate **1p** (930 mg, 75% yield).

Step 3. To a stirred solution of dry CH_3CN (0.25 g, 6 mmol) and dry tetrahydrofuran (10 mL) was added dropwise lithium diisopropylamide (3 mL, 6 mmol, 2M solution, in THF/heptane/ethylbenzene) at -78 ℃, and the solution was stirred at the same temperature for 1 hour under nitrogen atmosphere. A solution of 6-hepten-4-ynal (0.54 g, 5.0 mmol) in dried THF (5 mL) was then introduced via a syringe. The temperature was maintained at -78 ˚C, and the reaction mixture was stirred for an additional 1 hour. Next, the reaction mixture was allowed to warm to room temperature. After being stirred for an additional 3 hours, the reaction was quenched by saturated NH_4Cl solution and extracted with DCM (20 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 5/1 to 2/1) to afford substrate **1q** (325 mg, 44% yield).

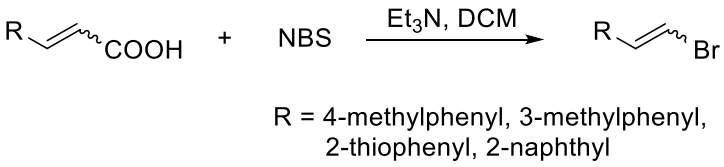
General Procedure C. Synthesis of alkenyl bromides.



X = F, Cl, CF_3

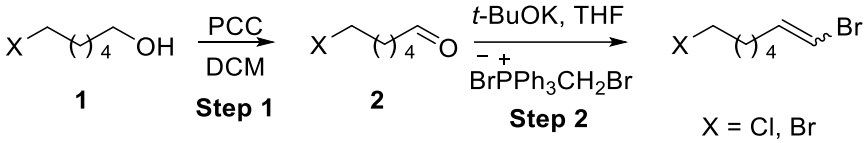
To a cooled (-78 ˚C) suspension of bromomethyltriphenylphosphonium bromide (21.0 g, 48.0 mmol) in dried THF (150 mL) under nitrogen atmosphere, was added potassium *tert*-butoxide (6.3 g, 56.0 mmol). The resulting yellow mixture was stirred at the indicated temperature for 1 hour. A solution of benzaldehyde derivative (40 mmol) in dried THF (5 mL) was then introduced via a syringe. The temperature was maintained at -78 ℃, and the mixture was stirred for additional 5 hours. The mixture was diluted with petroleum ether (80 mL), and filtered under reduced pressure. The residue obtained was purified by column chromatography (silica gel, petroleum ether) to afford (2-bromovinyl)benzene derivative (yield: 75%-80%) as a yellow oil.

General Procedure D. Synthesis of alkenyl bromides.



Triethylamine (112 mg, 1.1 mmol) was added to a solution of the *α, β*-unsaturated aromatic carboxylic acid (22 mmol, 1.0 eq.) in dichloromethane (120 mL, technical grade). After the mixture was stirred for 5 minutes at room temperature, NBS (9.54 g, 26.4 mmol, 1.2 eq.) was added. After 20 minutes no more gas evolution was observed. Then dichloromethane was evaporated under reduced pressure and the residue was purified by flash chromatography (silica gel, petroleum ether) to afford the product (yield: 60%-90%) as a yellow oil.

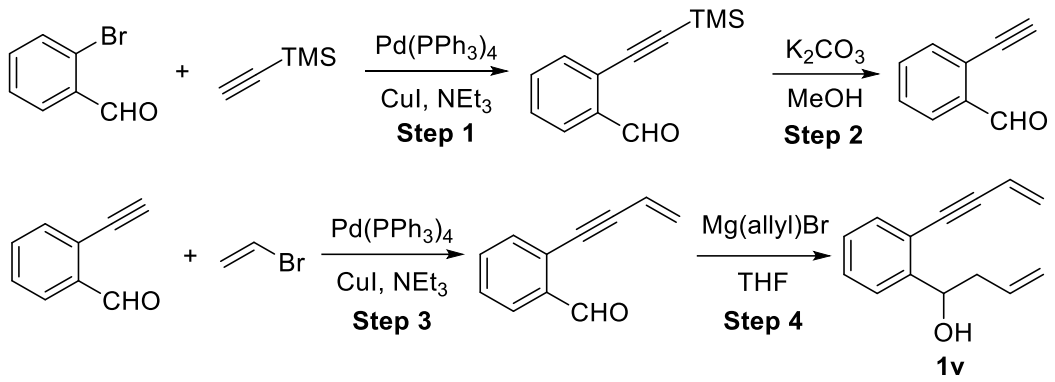
General Procedure E. Synthesis of alkenyl bromides.



Step 1. The mixture of pyridinium chlorochromate (9.0 g, 42 mmol) and silica gel (10.0 g) was dissolved in CH_2Cl_2 (80 mL) under an N_2 atmosphere at 0 ℃. Substrate **1** (30 mmol, 1.0 eq) was added and stirred at room temperature for 2 hours until the complete conversion of the starting material. The reaction mixture was filtered and washed with Et_2O (10 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 10/1 to 5/1) to afford aliphatic aldehyde **2** (yield: 80%-85%) as a colorless oil.

Step 2. To a cooled (-78 ℃) suspension of bromomethyltriphenylphosphonium bromide (21.0 g, 48.0 mmol) in dried THF (150 mL) under nitrogen atmosphere, was added potassium *tert*-butoxide (6.3 g, 56.0 mmol). The resulting yellow mixture was stirred at the indicated temperature for 1 hour. A solution of aliphatic aldehyde **2** (24 mmol, 1.0 eq) in dried THF (5 mL) was then introduced via a syringe. The temperature was maintained at –78 ˚C, and the mixture was stirred for additional 5 hours. The mixture was diluted with petroleum ether (80 mL), and filtered under reduced pressure. The residue obtained was purified by column chromatography (silica gel, petroleum ether) to afford Alkenyl bromide derivative (yield: 70%-90%) as a yellow oil.

General Procedure F. Synthesis of substrate **1v**.



Step 1. The mixture of copper (I) iodide (190 mg, 2 mol %) and tetrakis(triphenylphosphine)palladium (578 mg, 1 mol %) were dissolved in triethylamine (13.8 mL) under N_2 atmosphere at 0 ℃. 2-Bromobenzaldehyde (9.25 g, 50 mmol) and ethynyltrimethylsilane (9.2 mL, 65 mmol) were added and the resulting mixture was stirred at 45 ℃ in an oil bath until the complete conversion of the starting material. The reaction mixture was cooled to room temperature and filtered. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (petroleum ether/ethyl acetate = 50/1 to 20/1) to afford 2-((trimethylsilyl)ethynyl)benzaldehyde (9.3 g, 92% yield).

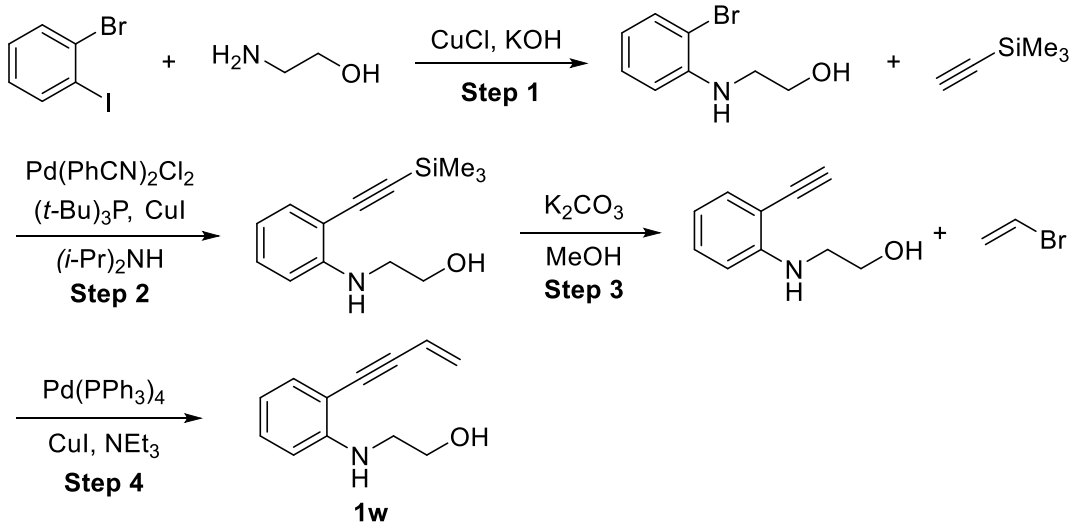
Step 2. 2-((Trimethylsilyl)ethynyl)benzaldehyde (9.3 g, 46 mmol) was dissolved in anhydrous MeOH (60 mL) under N_2 atmosphere at room temperature. K_2CO_3 (635 mg, 4.6 mmol) was added and stirred for 10 minutes until the complete conversion of the starting material. The reaction was quenched by H_2O and extracted with CH_2Cl_2 (40 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the crude product was used for the next step directly without further purification.

Step 3. The mixture of copper (I) iodide (175 mg, 2 mol %) and tetrakis(triphenylphosphine)palladium (532 mg, 1 mol %) were dissolved in triethylamine (12.8 mL) under N_2 atmosphere at 0 ℃. The crude 2-ethynylbenzaldehyde and vinyl bromide (1.0 M in THF, 60 mL, 60 mmol) were added and the resulting mixture was stirred at 45 ℃ in an oil bath until the complete conversion of the starting material. The reaction mixture was cooled to room temperature and filtered. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (petroleum ether/ethyl acetate = 50/1 to 20/1) to afford 2-(but-3-en-1-yn-1-yl)benzaldehyde (6.3 g, 87% yield).

Step 4. A solution of allylmagnesium bromide (1.0 M in THF, 24 mL, 24 mmol) was added dropwise to a solution of 2-(but-3-en-1-yn-1-yl)benzaldehyde (3.1 g, 20

mmol in THF (30 mL) at 0 ℃ under N_2 atmosphere. The reaction mixture was stirred at room temperature for 1 hour. The reaction was quenched by saturated NH_4Cl solution and extracted with EtOAc (20 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 10/1) to afford substrate **1v** (3.4 g, 85% yield).

General Procedure G. Synthesis of substrate **1w**.



Step 1. CuCl (495 mg, 10 mol %), KOH (5.6 g, 100 mmol), 1-bromo-2-iodobenzene (6.5 mL, 50 mmol) and amino alcohol (9.15 g, 150 mmol) were added to a 100 mL round-bottomed flask under N_2 atmosphere. The reaction mixture was stirred at room temperature for 8-12 hours. The resulting mixture was diluted with water (80 mL) before extraction with ethyl acetate, and dried over Na_2SO_4. The filtrate was concentrated under reduced pressure, and the mixture was purified by column chromatography on silica gel (petroleum ether/ ethyl acetate = 5/1) to afford the desired product 2-((2-bromophenyl)amino)ethan-1-ol (yield: 7.8 g, 72%).

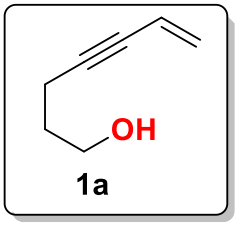
Step 2. The mixture of copper (I) iodide (78 mg, 2 mol %) and Bis(benzonitrile) palladium chloride (234 mg, 3 mol %) were dissolved in 1,4-dioxane (40 mL) under N_2 atmosphere. 2-((2-bromophenyl)amino)ethan-1-ol (4.3 g, 20 mmol), ethynyltrimethysilane (4.0 mL, 30 mmol), *Tri-tert*-butylphosphine (290 uL, 1.2 mmol), and Diisopropylamine (8.0 mL, 58 mmol) were added and the mixture was stirred at 45 ℃ in an oil bath until the complete conversion of the starting material. The reaction mixture was cooled to room temperature and filtered. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (petroleum ether/ethyl acetate = 5/1) to afford 2-((2-((trimethylsilyl)ethynyl)phenyl)amino)ethan-1-ol (3.6 g, 75% yield).

Step 3. 2-((2-((trimethylsilyl)ethynyl)phenyl)amino)ethan-1-ol (3.6 g, 15 mmol) was dissolved in anhydrous MeOH (50 mL) under N_2 atmosphere at room temperature. K_2CO_3 (552 mg, 4 mmol) was added into the reaction system and stirred for 30 minutes until the complete conversion of starting material. The reaction was quenched by H_2O and extracted with CH_2Cl_2 (30 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure, the crude product was used for the next step directly without further purification.

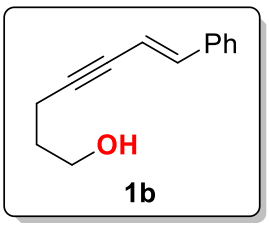
Step 4. The mixture of copper (I) iodide (57 mg, 2 mol %) and tetrakis(triphenylphosphine)palladium (174 mg, 1 mol %) were dissolved in triethylamine (4 mL) under N_2 atmosphere at 0 ℃. the crude product 2-((2-ethynylphenyl)amino)ethan-1-ol and vinyl bromide (1.0 M in THF, 21 mL, 21 mmol) were added and the resulting mixture was stirred at 45 ℃ in an oil bath until the complete conversion of the starting material. The reaction mixture was cooled to room temperature and filtered. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (petroleum ether/ethyl acetate = 5/1 ~ 3/1) to afford **1w** (2.3 g, 80% yield).

b) Substrates Characterization

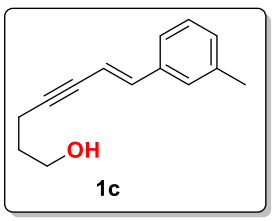
Hept-6-en-4-yn-1-ol (1a): The title compound was prepared according to the **general procedure A** and purified by flash column chromatography (petroleum ether/ethyl acetate = 10/1 ~ 5/1) to give yellow oil, 4.68 g, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81-5.73 (m, 1H), 5.58-5.53 (m, 1H), 5.41-5.38 (m, 1H), 3.77 (t, *J* = 6.4 Hz, 2H), 2.46-2.42 (m, 2H), 1.83-1.76 (m, 2H), 1.50 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.0, 117.5, 90.2, 80.0, 61.9, 31.4, 16.1; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_7H_{11}O$: 111.0804, found: 111.0802.



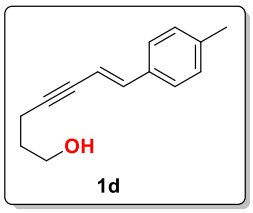
(*E*)-7-phenylhept-6-en-4-yn-1-ol (1b): The title compound was prepared according to the **general procedure A** and purified by flash column chromatography (petroleum ether/ethyl acetate = 10/1 ~ 5/1) to give red oil, 1.6 g, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.24 (m, 5H), 6.85 (d, *J* = 16.4 Hz, 1H), 6.12 (d, *J* = 16.4 Hz, 1H), 3.79 (t, *J* = 6.0 Hz, 2H), 2.50 (t, *J* = 6.8 Hz, 2H), 1.86-1.79 (m, 2H), 1.65 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 136.6, 128.8, 128.5, 126.2, 108.7, 91.9, 80.4, 61.9, 31.5, 16.4; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{15}O$: 187.1117, found: 187.1118.



(*E*)-7-(*m*-tolyl)hept-6-en-4-yn-1-ol (1c): The title compound was prepared according to the **general procedure A** and purified by flash column chromatography (petroleum ether/ethyl acetate = 10/1 ~ 5/1) to give yellow oil, 1.58 g, 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.13 (m, 3H), 7.06-7.05 (m, 1H), 6.81 (d, *J* = 16.4 Hz, 1H), 6.09 (dt, *J* = 16.4 Hz, 2.4 Hz, 1H), 3.78-3.74 (m, 2H), 2.50-2.46 (m, 2H), 2.32 (s, 3H), 2.22 (s, 1H), 1.84-1.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 138.4, 136.5, 129.3, 128.7, 126.9, 123.4, 108.4, 91.8, 80.5, 62.0, 31.5, 21.5, 16.4; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{17}O$: 201.1274, found: 201.1275.



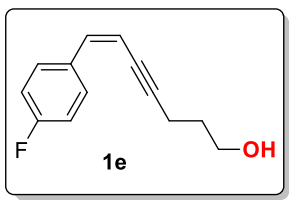
(*E*)-7-(*p*-tolyl)hept-6-en-4-yn-1-ol (1d): The title compound was prepared according to the **general procedure A** and purified by flash column chromatography (petroleum ether/ethyl acetate = 10/1 ~ 5/1) to give yellow oil, 1.64 g, 82% yield. ^{1}H NMR (500



1d

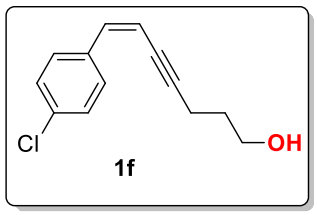
MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 16.5 Hz, 1H), 6.06 (dt, *J* = 16.0 Hz, 2.0 Hz, 1H), 3.80 (t, *J* = 6.5 Hz, 2H), 2.52-2.49 (m, 2H), 2.33 (s, 3H), 1.85-1.80 (m, 2H), 1.58 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.5, 138.5, 133.9, 129.5, 126.2, 107.6, 91.5, 80.6, 62.0, 31.6, 21.4, 16.4; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{17}O$: 201.1274, found: 201.1278.

(*Z*)-7-(4-fluorophenyl)hept-6-en-4-yn-1-ol (1e): The title compound was prepared according to the **general procedure A** and purified by flash column chromatography (petroleum ether/ethyl acetate = 10/1 ~ 5/1) to give red oil, 1.90 g, 93% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.85-7.81 (m, 2H), 7.05-7.00 (m, 2H), 6.50 (d, *J* = 11.6 Hz, 1H), 5.63 (dt, *J* = 11.6 Hz, 2.8 Hz, 1H), 3.77-3.76 (m, 2H), 2.57-2.53 (m, 2H), 1.98 (s, 1H), 1.87-1.80 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.4 (d, J_{C-F} = 246.8 Hz), 136.4, 132.9 (d, J_{C-F} = 3.5 Hz), 130.3 (d, J_{C-F} = 7.8 Hz), 115.3 (d, J_{C-F} = 21.3 Hz), 107.6 (d, J_{C-F} = 2.4 Hz), 96.7, 79.5, 61.7, 31.3, 16.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.5; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{14}FO$: 205.1023, found: 205.1023.



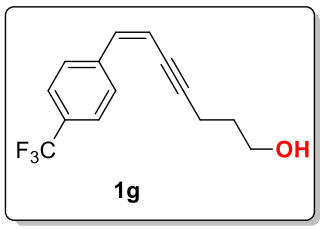
1e

(*Z*)-7-(4-chlorophenyl)hept-6-en-4-yn-1-ol (1f): The title compound was prepared according to the **general procedure A** and purified by flash column chromatography (petroleum ether/ethyl acetate = 10/1 ~ 5/1) to give yellow oil, 1.70 g, 81% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.78-7.76 (m, 2H), 7.32-7.26 (m, 2H), 6.49 (d, *J* = 12.0 Hz, 1H), 5.67 (dt, *J* = 12.0 Hz, 2.4 Hz, 1H), 3.78-3.74 (m, 2H), 2.57-2.53 (m, 2H), 1.97 (t, *J* = 4.4 Hz, 1H), 1.87-1.80 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.3, 135.1, 133.7, 129.7, 128.4, 108.7, 97.5, 79.4, 61.6, 31.3, 16.5; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{14}ClO$: 221.0728, found: 221.0733.



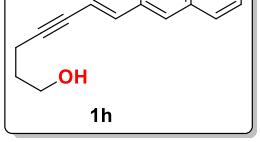
1f

(*Z*)-7-(4-(trifluoromethyl)phenyl)hept-6-en-4-yn-1-ol (1g): The title compound was prepared according to the **general procedure A** and purified by flash column chromatography (petroleum ether/ethyl acetate = 10/1 ~ 5/1) to give red oil, 1.1 g, 87%

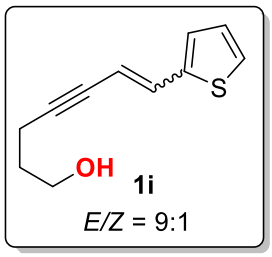


yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 6.58 (d, *J* = 12.0 Hz, 1H), 5.79 (dt, *J* = 12.0 Hz, 2.4 Hz, 1H), 3.82-3.78 (m, 2H), 2.60-2.56 (m, 2H), 1.90-1.83 (m, 2H), 1.46 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0 (d, J_{C-F} = 4.0 Hz), 136.1, 129.4 (q, J_{C-F} = 32.1 Hz), 128.6, 125.2 (q, J_{C-F} = 3.8 Hz), 120.2 (q, J_{C-F} = 270.4 Hz), 110.8, 98.2, 79.3, 61.7, 31.1, 16.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{14}F_3O$: 255.0991, found: 255.0999.

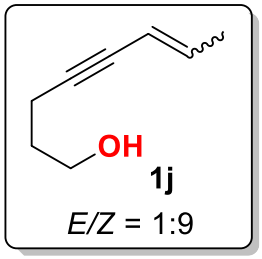
(*E*)-7-(naphthalen-2-yl)hept-6-en-4-yn-1-ol (1h): The title compound was prepared according to the **general procedure A** and purified by flash column chromatography (petroleum ether/ethyl acetate = 10/1 ~ 5/1) to give yellow solid, 1.30 g, 56% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11-8.09 (m, 1H), 7.83-7.76 (m, 2H), 7.68-7.64 (m, 1H), 7.59-7.57 (m, 1H), 7.52-7.45 (m, 2H), 7.43-7.39 (m, 1H), 6.17 (dt, *J* = 16.0 Hz, 2.0 Hz, 1H), 3.81 (t, *J* = 6.0 Hz, 2H), 2.55-2.51 (m, 2H), 1.88-1.81 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 134.0, 133.7, 130.9, 128.8, 128.6, 126.4, 126.0, 125.6, 123.7, 123.3, 111.4, 91.8, 80.7, 61.8, 31.5, 16.3; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{17}O$: 237.1274, found: 237.1279.



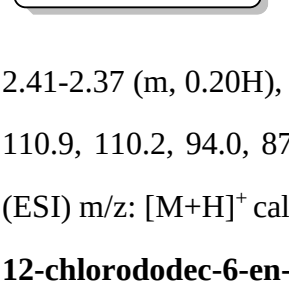
7-(thiophen-2-yl)hept-6-en-4-yn-1-ol (1i): The title compound was prepared according to the **general procedure A** and purified by flash column chromatography (petroleum ether/ethyl acetate = 10/1 ~ 5/1) to give red oil, 2.70 g, 88% yield (*E*/*Z* = 9:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.13 (m, 1H), 7.01-6.81 (m, 3H), 5.92 (dt, *J* = 16.0 Hz, 2.4 Hz, 0.90H), 5.50 (dt, *J* = 11.2 Hz, 2.4 Hz, 0.10H), 3.79 (t, *J* = 6.0 Hz, 0.20H), 3.74 (t, *J* = 6.0 Hz, 1.80H), 2.63-2.59 (m, 0.20H), 2.49-2.45 (m, 1.80H), 2.38 (s, 1H), 1.92-1.86 (m, 0.20H), 1.82-1.75 (m, 1.80H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 140.8, 133.2, 131.5, 129.1, 127.6, 126.5, 126.3, 126.3, 125.0, 107.9, 105.3, 100.0, 92.4, 80.0, 79.9, 61.6, 61.6, 31.4, 31.1, 16.7, 16.2; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{11}H_{13}OS$: 193.0682, found: 193.0681.



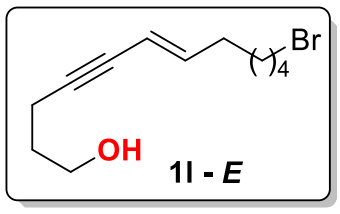
Oct-6-en-4-yn-1-ol (1j): The title compound was prepared according to the **general procedure A** and purified by flash column chromatography (petroleum ether/ethyl acetate = 10/1 ~ 5/1) to give yellow oil, 3.14 g, 84% yield (*E/Z* = 1:9). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.10-6.01 (m, 0.10H), 5.93-5.86 (m, 0.90H), 5.48-5.43 (m, 1H), 3.76-3.70 (m, 2H), 2.66 (s, 1H), 2.49-2.45 (m, 1.80H), 2.41-2.37 (m, 0.20H), 1.86-1.74 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 137.2, 110.9, 110.2, 94.0, 87.5, 79.7, 77.7, 61.5, 31.5, 31.4, 18.4, 16.1, 15.9, 15.7; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_8H_{13}O$: 125.0961, found: 125.0968.



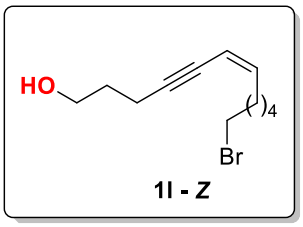
12-chlorododec-6-en-4-yn-1-ol (1k): The title compound was prepared according to the **general procedure A** and purified by flash column chromatography (petroleum ether/ethyl acetate = 10/1 ~ 5/1) to give colorless oil, 1.40 g, 65% yield (*E/Z* = 2:3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 (dt, *J* = 15.6 Hz, 7.2 Hz, 0.40H), 5.78 (dt, *J* = 10.8 Hz, 7.2 Hz, 0.60H), 5.47-5.43 (m, 1H), 3.78-3.74 (m, 2H), 3.56-3.51 (m, 2H), 2.49-2.45 (m, 1.20H), 2.43-2.39 (m, 0.80H), 2.32-2.27 (m, 1.20H), 2.12-2.08 (m, 0.80H), 1.89 (s, 1H), 1.83-1.73 (m, 4H), 1.49-1.42 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 142.4, 110.1, 109.7, 93.7, 87.9, 79.8, 77.9, 61.9, 61.8, 45.1, 45.0, 32.8, 32.5, 31.6, 31.5, 29.8, 28.2, 28.1, 26.4, 26.4, 16.2, 16.0; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{20}ClO$: 215.1197, found: 215.1196



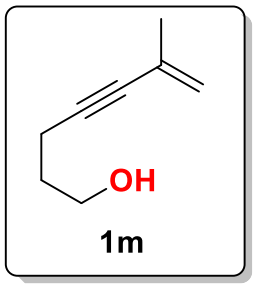
(*E*)-12-bromododec-6-en-4-yn-1-ol (1l): The title compound was prepared according to the **general procedure A** and purified by flash column chromatography (petroleum ether/ethyl acetate = 10/1 ~ 5/1) to give colorless oil, 875 mg, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 (dt, *J* = 16.0 Hz, 7.2 Hz, 1H), 5.48-5.43 (m, 1H), 3.76 (t, *J* = 6.0 Hz, 2H), 3.40 (t, *J* = 6.8 Hz, 2H), 2.44-2.40 (m, 2H), 2.13-2.08 (m, 2H), 1.89-1.82 (m, 2H), 1.81-1.75 (m, 2H), 1.66 (s, 1H), 1.49-1.39 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 110.1, 88.0, 79.8, 62.0, 33.8, 32.8, 32.7, 31.5, 28.1, 27.7, 16.1; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{20}BrO$: 259.0692, found: 259.0695.



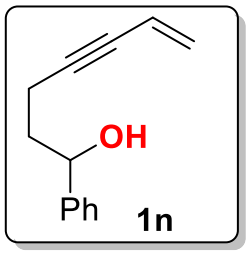
(*Z*)-12-bromododec-6-en-4-yn-1-ol (1l): The title compound was prepared according to the **general procedure A** and purified by flash column chromatography (petroleum ether/ethyl acetate = 10/1 ~ 5/1) to give colorless oil, 875 mg, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85-5.78 (m, 1H), 5.47-5.43 (m, 1H), 3.77 (t, *J* = 6.4 Hz, 2H), 3.42 (t, *J* = 7.2 Hz, 2H), 2.50-2.46 (m, 2H), 2.32-2.27 (m, 2H), 1.92-1.87 (m, 2H), 1.85-1.77 (m, 3H), 1.51-1.42 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 109.7, 93.7, 77.9, 61.9, 34.0, 32.7, 31.6, 29.8, 28.0, 27.7, 16.2; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{20}BrO$: 259.0692, found: 259.0695.



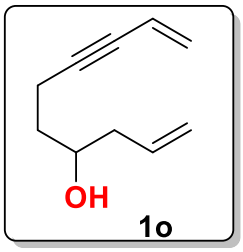
6-methylhept-6-en-4-yn-1-ol (1m): The title compound was prepared according to the **general procedure A** and purified by flash column chromatography (petroleum ether/ethyl acetate = 10/1 ~ 5/1) to give yellow oil, 1.80 g, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.21-5.15 (m, 2H), 3.76 (t, *J* = 6.4 Hz, 2H), 2.43 (t, *J* = 7.2 Hz, 2H), 1.89 (s, 1H), 1.87 (d, *J* = 1.2 Hz, 3H), 1.82-1.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.2, 120.8, 88.5, 82.5, 61.9, 31.4, 23.9, 15.9; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_8H_{13}O$: 125.0961, found: 125.0958.



1-phenylhept-6-en-4-yn-1-ol (1n): The title compound was prepared according to the **general procedure B** and purified by flash column chromatography (petroleum ether/ethyl acetate = 10/1 ~ 5/1) to give yellow oil, 1.50 g, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.33 (m, 4H), 7.30-7.26 (m, 1H), 5.83-5.74 (m, 1H), 5.54 (dd, *J* = 17.6 Hz, 2.4 Hz, 1H), 5.38 (dd, *J* = 10.8 Hz, 2.0 Hz, 1H), 4.86-4.82 (m, 1H), 2.49-2.43 (m, 1H), 2.40-2.36 (m, 1H), 2.07-2.06 (m, 1H), 2.04-1.97 (m, 1H), 1.96-1.89 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 128.7, 127.8, 126.0, 126.0, 117.6, 90.2, 80.2, 73.5, 37.8, 16.2; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{15}O$: 187.1117, found: 187.1119.

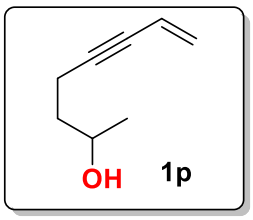


Deca-1,9-dien-7-yn-4-ol (1o): The title compound was prepared according to the **general procedure B** and purified by flash column chromatography (petroleum ether/ethyl acetate = 10/1 ~ 5/1) to give yellow oil, 1.80 g, 80% yield. ^{1}H NMR (400

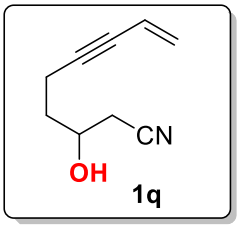


MHz, $CDCl_3$) δ 5.87-5.73 (m, 2H), 5.58-5.53 (m, 1H), 5.40-5.37 (m, 1H), 5.17-5.13 (m, 2H), 3.81-3.79 (m, 1H), 2.46 (t, *J* = 6.8 Hz, 2H), 2.34-2.29 (m, 1H), 2.23-2.17 (m, 1H), 1.85-1.84 (m, 1H), 1.73-1.70 (m, 1H), 1.68-1.65 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.6, 126.0, 118.5, 117.6, 90.4, 79.9, 69.8, 42.0, 35.4, 16.0; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{10}H_{15}O$: 151.1117, found: 151.1117.

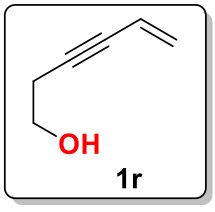
Oct-7-en-5-yn-2-ol (1p): The title compound was prepared according to the **general procedure B** and purified by flash column chromatography (petroleum ether/ethyl acetate = 10/1 ~ 5/1) to give yellow oil, 930 mg, 75% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 5.81-5.73 (m, 1H), 5.53 (dd, *J* = 17.2 Hz, 2.0 Hz, 1H), 5.37 (dd, *J* = 11.2 Hz, 2.4 Hz, 1H), 3.98-3.90 (m, 1H), 2.45-2.41 (m, 2H), 2.13 (s, 1H), 1.69-1.64 (m, 2H), 1.21 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.9, 117.5, 90.4, 79.9, 67.1, 37.6, 23.4, 16.0; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_8H_{13}O$: 125.0961, found: 125.0957.



3-hydroxynon-8-en-6-ynenitrile (1q): The title compound was prepared according to the **general procedure B** and purified by flash column chromatography (petroleum ether/ethyl acetate = 5/1 ~ 2/1) to give yellow oil, 325 mg, 44% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 5.80-5.72 (m, 1H), 5.60-5.55 (m, 1H), 5.45-5.41 (m, 1H), 4.18-4.13 (m, 1H), 2.65-2.56 (m, 3H), 2.53-2.48 (m, 2H), 1.83-1.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.6, 117.6, 117.2, 88.9, 80.8, 66.9, 34.9, 26.2, 15.8; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_9H_{12}NO$: 150.0913, found: 150.0910.

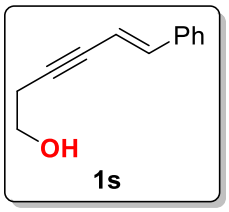


Hex-5-en-3-yn-1-ol (1r): The title compound was preared according to the **general procedure A** and purified by flash column chromatography (petroleum ether/ethyl acetate = 10/1 ~ 5/1) to give yellow oil, 1.60 g, 85% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 5.83-5.75 (m, 1H), 5.57 (dd, *J* = 17.6 Hz, 2.0 Hz, 1H), 5.42 (dd, *J* = 11.2 Hz, 2.0

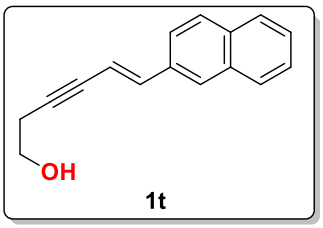


Hz, 1H), 3.75-3.73 (m, 2H), 2.61-2.57 (m, 2H), 2.08 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.6, 117.3, 87.3, 81.2, 61.2, 23.8; HRMS (ESI) m/z: $[M+H]^+$ calcd for C_6H_9O: 97.0648, found: 97.0647.

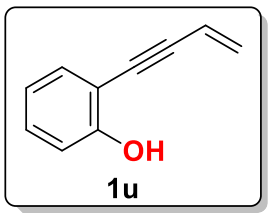
(*E*)-6-phenylhex-5-en-3-yn-1-ol (1s): The title compound was preared according to the **general procedure A** and purified by flash column chromatography (petroleum ether/ethyl acetate = 10/1 ~ 5/1) to give red oil, 1.30 g, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.35 (m, *2*H), 7.34-7.29 (m, 2H), 7.28-7.24 (m, 1H), 6.89 (d, *J* = 16.0 Hz, 1H), 6.12 (dt, *J* = 16.4 Hz, 2.0 Hz, 1H), 3.80-3.75 (m, 2H), 2.67-2.63 (m, 2H), 1.92 (t, *J* = 6.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.1, 136.4, 128.8, 128.6, 126.3, 108.3, 88.9, 81.8, 61.3, 24.2; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{13}O$: 173.0961, found: 173.0960.



(*E*)-6-(naphthalen-2-yl)hex-5-en-3-yn-1-ol (1t): The title compound was preared according to the **general procedure A** and purified by flash column chromatography (petroleum ether/ethyl acetate = 10/1 ~ 5/1) to give yellow solid, 1.50 g, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11-8.09 (m, 1H), 7.84-7.78 (m, 2H), 7.72-7.68 (m, 1H), 7.60-7.58 (m, 1H), 7.53-7.40 (m, 3H), 6.18 (dt, *J* = 16.0 Hz, 2.0 Hz, 1H), 3.83-3.79 (m, 2H), 2.71-2.67 (m, 2H), 2.03 (t, *J* = 6.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.2, 133.9, 133.7, 130.9, 128.9, 128.7, 126.5, 126.1, 125.7, 123.7, 123.4, 111.0, 88.8, 82.0, 61.3, 24.1; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{15}O$: 223.1117, found: 223.1118.

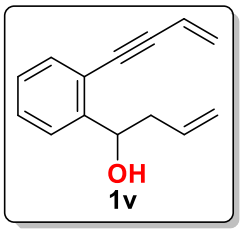


2-(but-3-en-1-yn-1-yl)phenol (1u): The title compound was preared according to the **general procedure F** and purified by flash column chromatography (petroleum ether/ethyl acetate = 20/1 ~ 10/1) to give yellow oil, 187 mg, 26% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.33 (m, 1H), 7.27-7.22 (m, 1H), 6.96-6.94 (m, 1H), 6.90-6.86 (m, 1H), 6.02 (dd, *J* = 17.2 Hz, 11.2 Hz, 1H), 5.80-5.76 (m, 2H), 5.59 (dd, *J* = 11.2 Hz, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 131.8, 130.7,

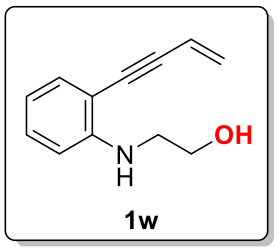


127.9, 120.5, 116.7, 114.8, 109.6, 95.2, 83.8; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{10}H_9O$: 145.0653, found: 145.0664.

1-(2-(but-3-en-1-yn-1-yl)phenyl)but-3-en-1-ol (1v): The title compound was preared according to the **general procedure F** and purified by flash column chromatography (petroleum ether/ethyl acetate = 10/1 ~ 5/1) to give yellow oil, 3.40 g, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.50 (m, 1H), 7.43-7.41 (m, 1H), 7.36-7.31 (m, 1H), 7.23-7.19 (m, 1H), 6.07-6.00 (m, 1H), 5.90-5.82 (m, 1H), 5.70 (dd, *J* = 17.6 Hz, 2.0 Hz, 1H), 5.54 (dd, *J* = 11.2 Hz, 2.0 Hz, 1H), 5.19-5.12 (m, 3H), 2.66-2.61 (m, 1H), 2.47-2.42 (m, 1H), 2.28 (d, *J* = 3.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.8, 134.8, 132.3, 128.9, 127.2, 127.2, 125.4, 120.5, 118.3, 117.1, 93.3, 87.6, 71.4, 42.9; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{15}O$: 199.1123, found: 199.1121.

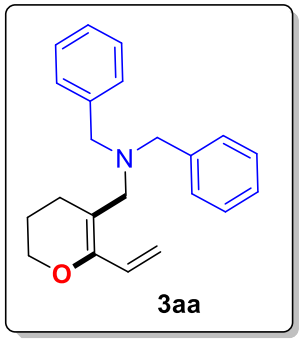


2-((2-(but-3-en-1-yn-1-yl)phenyl)amino)ethan-1-ol (1w): The title compound was preared according to the **general procedure G** and purified by flash column chromatography (petroleum ether/ethyl acetate = 5/1 ~ 3/1) to give yellow oil, 2.30 g, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.28 (m, 1H), 7.21-7.17 (m, 1H), 6.67-6.63 (m, 2H), 6.03 (dd, *J* = 17.2 Hz, 11.2 Hz, 1H), 5.69 (dd, *J* = 17.6 Hz, 2.0 Hz, 1H), 5.52 (dd, *J* = 11.2 Hz, 2.0 Hz, 1H), 4.86 (s, 1H), 3.86-3.83 (m, 2H), 3.39-3.38 (m, 2H), 1.82 (t, *J* = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 132.5, 130.1, 126.6, 117.2, 117.0, 109.9, 108.1, 94.2, 86.6, 61.4, 45.8; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{14}NO$: 188.1075, found: 188.1075.



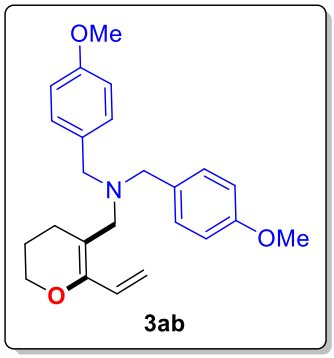
5. Products Characterization

***N,N*-dibenzyl-1-(6-vinyl-3,4-dihydro-2*H*-pyran-5-yl)methanamine (3aa):** The title compound was prepared according to the general procedure and purified by flash column chromatography (petroleum ether/ethyl acetate = 100/1 ~ 50/1) to give yellow oil, 77 mg, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.27 (m, 8H), 7.22-7.19 (m, 2H), 6.60 (dd, *J* = 16.8 Hz, 10.8 Hz, 1H), 5.48 (dd, *J* = 16.4 Hz, 2.4 Hz, 1H), 5.03 (dd, *J* = 10.8 Hz, 2.0 Hz, 1H), 3.94 (t, *J* = 5.2 Hz, 2H), 3.49 (s, 4H), 3.03 (s, 2H), 2.20 (t, *J* = 6.8 Hz, 2H), 1.84-1.79 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 140.2, 128.9, 128.3, 128.3, 126.9, 113.1, 111.0, 65.7, 58.2, 54.8, 24.7, 22.8; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{26}NO$: 320.2009, found: 320.2014.



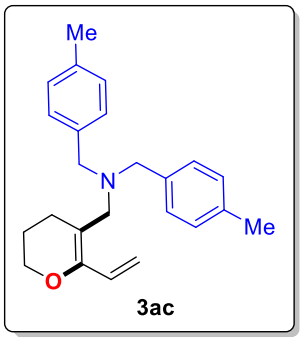
3aa

***N,N*-bis(4-methoxybenzyl)-1-(6-vinyl-3,4-dihydro-2*H*-pyran-5-yl)methanamine (3ab):** The title compound was prepared according to the general procedure and purified by flash column chromatography (petroleum ether/ethyl acetate = 100/1 ~ 50/1) to give yellow oil, 77 mg, 68% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24-7.23 (m, 4H), 6.85-6.82 (m, 4H), 6.60 (dd, *J* = 17.0 Hz, 11.0 Hz, 1H), 5.47 (dd, *J* = 16.5 Hz, 2.0 Hz, 1H), 5.03 (dd, *J* = 11.0 Hz, 2.0 Hz, 1H), 3.95 (t, *J* = 5.0 Hz, 2H), 3.79 (s, 6H), 3.41 (s, 4H), 3.00 (s, 2H), 2.17 (t, *J* = 6.5 Hz, 2H), 1.85-1.80 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.6, 147.8, 132.2, 130.0, 128.4, 113.6, 112.9, 111.3, 65.7, 57.3, 55.4, 54.5, 24.8, 22.8; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{30}NO_3$: 380.2220, found: 380.2229.



3ab

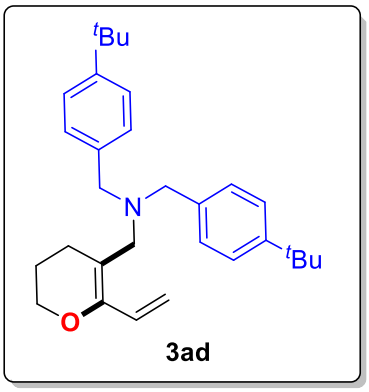
***N,N*-bis(4-methylbenzyl)-1-(6-vinyl-3,4-dihydro-2*H*-pyran-5-yl)methanamine (3ac):** The title compound was prepared according to the general procedure and purified by flash column chromatography (petroleum ether/ethyl acetate = 100/1 ~ 50/1) to give yellow oil, 68 mg, 65% yield. ^{1}H NMR (400



3ac

MHz, $CDCl_3$) δ 7.24-7.21 (m, 4H), 7.09 (d, *J* = 7.6 Hz, 4H), 6.60 (dd, *J* = 16.8 Hz, 10.8 Hz, 1H), 5.46 (dd, *J* = 16.8 Hz, 2.0 Hz, 1H), 5.02 (dd, *J* = 11.2 Hz, 2.0 Hz, 1H), 3.94 (t, *J* = 5.2 Hz, 2H), 3.44 (s, 4H), 3.01 (s, 2H), 2.32 (s, 6H), 2.20 (t, *J* = 6.8 Hz, 2H), 1.85-1.79 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 137.1, 136.3, 128.9, 128.8, 128.4, 112.9, 111.3, 65.7, 57.7, 54.6, 24.7, 22.8, 21.2; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{30}NO$: 348.2322, found: 348.2332.

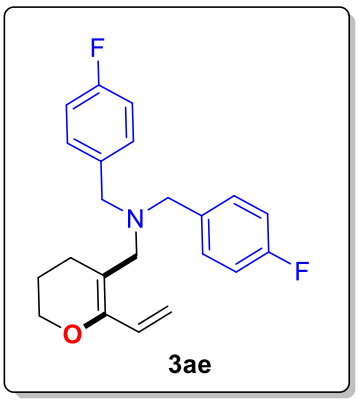
***N,N*-bis(4-(*tert*-butyl)benzyl)-1-(6-vinyl-3,4-dihydro-2*H*-pyran-5-yl)methanamine**



3ad

(3ad): The title compound was prepared according to the general procedure and purified by flash column chromatography (petroleum ether/ethyl acetate = 100/1 ~ 50/1) to give yellow oil, 103 mg, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.28 (m, 8H), 6.60 (dd, *J* = 16.8 Hz, 10.8 Hz, 1H), 5.46 (dd, *J* = 17.2 Hz, 2.0 Hz, 1H), 5.02 (dd, *J* = 10.8 Hz, 1.6 Hz, 1H), 3.94 (t, *J* = 5.2 Hz, 2H), 3.47 (s, 4H), 3.05 (s, 2H), 2.25 (t, *J* = 6.4 Hz, 2H), 1.86-1.80 (m, 2H), 1.30 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 147.8, 137.2, 128.4, 125.1, 112.9, 111.4, 65.7, 57.7, 54.9, 34.6, 31.6, 24.7, 22.9; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{30}H_{42}NO$: 432.3266, found: 432.3263.

***N,N*-bis(4-fluorobenzyl)-1-(6-vinyl-3,4-dihydro-2*H*-pyran-5-yl)methanamine**

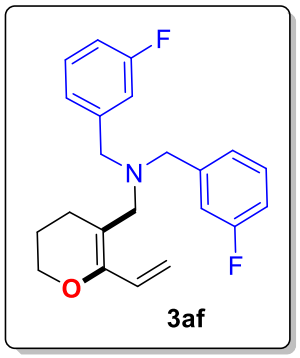


3ae

(3ae): The title compound was prepared according to the general procedure and purified by flash column chromatography (petroleum ether/ethyl acetate = 100/1 ~ 50/1) to give yellow oil, 78 mg, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.26 (m, 4H), 7.01-6.96 (m, 4H), 6.57 (dd, *J* = 17.2 Hz, 11.2 Hz, 1H), 5.49 (d, *J* = 16.4 Hz, 1H), 5.05 (d, *J* = 10.8 Hz, 1H), 3.96 (t, *J* = 4.8 Hz, 2H), 3.43 (s, 4H), 3.00 (s, 2H), 2.15 (t, *J* = 6.4 Hz, 2H), 1.86-1.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2 (d, J_{C-F} = 242.9 Hz), 148.0, 135.6 (d, J_{C-F} = 2.7 Hz), 130.3 (d, J_{C-F} = 7.8 Hz), 128.1, 115.2 (d, J_{C-F} = 21.1 Hz), 113.4, 110.6, 65.7, 57.3,

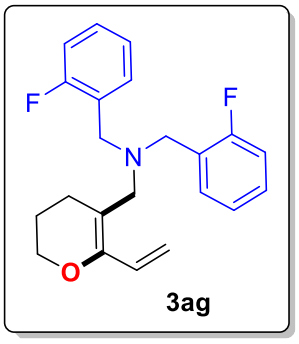
54.6, 24.8, 22.7; ^{19}F NMR (376 MHz, $CDCl_3$) -116.2; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{24}NOF_2$: 356.1821, found: 356.1823.

***N*,*N*-bis(3-fluorobenzyl)-1-(6-vinyl-3,4-dihydro-2*H*-pyran-5-yl)methanamine**



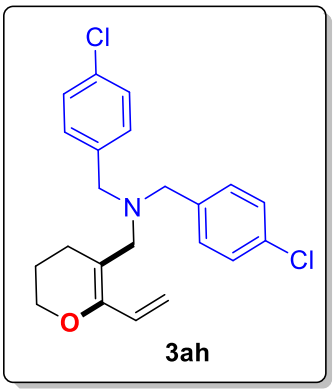
(3af): The title compound was prepared according to the general procedure and purified by flash column chromatography (petroleum ether/ethyl acetate = 100/1 ~ 50/1) to give yellow oil, 81 mg, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.23 (m, 2H), 7.10-7.06 (m, 4H), 6.94-6.90 (m, 2H), 6.57 (dd, *J* = 16.8 Hz, 10.8 Hz, 1H), 5.50 (d, *J* = 16.8 Hz, 1H), 5.06 (d, *J* = 10.8 Hz, 1H), 3.96 (t, *J* = 4.8 Hz, 2H), 3.49 (s, 4H), 3.04 (s, 2H), 2.20 (t, *J* = 6.0 Hz, 2H), 1.86-1.83 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.1 (d, $J_{C\text{-}F}$ = 243.8 Hz), 148.2, 142.7 (d, $J_{C\text{-}F}$ = 6.8 Hz), 129.8 (d, $J_{C\text{-}F}$ = 8.1 Hz), 128.1, 124.3 (d, $J_{C\text{-}F}$ = 2.5 Hz), 115.5 (d, $J_{C\text{-}F}$ = 21.1 Hz), 114.0 (d, $J_{C\text{-}F}$ = 21.2 Hz), 113.6, 110.4, 65.7, 57.8, 54.9, 24.7, 22.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.7; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{24}NOF_2$: 356.1821, found: 356.1827.

***N*,*N*-bis(2-fluorobenzyl)-1-(6-vinyl-3,4-dihydro-2*H*-pyran-5-yl)methanamine**



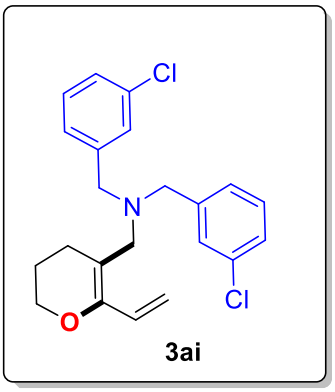
(3ag): The title compound was prepared according to the general procedure and purified by flash column chromatography (petroleum ether/ethyl acetate = 100/1 ~ 50/1) to give yellow oil, 84 mg, 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.42 (m, 2H), 7.22-7.16 (m, 2H), 7.11-7.07 (m, 2H), 7.01-6.97 (m, 2H), 6.60 (dd, *J* = 16.8 Hz, 10.8 Hz, 1H), 5.49 (dd, *J* = 16.8 Hz, 2.0 Hz, 1H), 5.05 (dd, *J* = 11.2 Hz, 2.4 Hz, 1H), 3.96 (t, *J* = 5.2 Hz, 2H), 3.58 (s, 4H), 3.09 (s, 2H), 2.17 (t, *J* = 6.8 Hz, 2H), 1.85-1.79 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (d, $J_{C\text{-}F}$ = 244.3 Hz), 148.0, 131.2 (d, $J_{C\text{-}F}$ = 4.5 Hz), 128.5 (d, $J_{C\text{-}F}$ = 8.0 Hz), 128.2, 126.7 (d, $J_{C\text{-}F}$ = 13.8 Hz), 124.0 (d, $J_{C\text{-}F}$ = 3.6 Hz), 115.4 (d, $J_{C\text{-}F}$ = 22 Hz), 113.4, 110.9, 65.7, 55.0, 50.7 (d, $J_{C\text{-}F}$ = 2.2 Hz), 24.5, 22.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.4; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{24}NOF_2$: 356.1821, found: 356.1828.

***N*,*N*-bis(4-chlorobenzyl)-1-(6-vinyl-3,4-dihydro-2*H*-pyran-5-yl)methanamine**



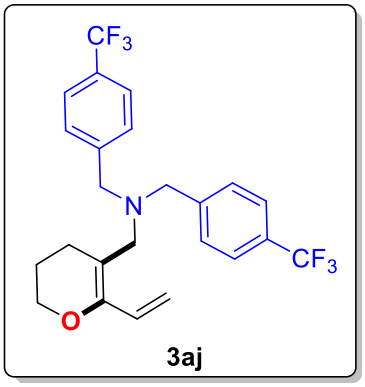
(3ah): The title compound was prepared according to the general procedure and purified by flash column chromatography (petroleum ether/ethyl acetate = 100/1 ~ 50/1) to give yellow oil, 97 mg, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.23 (m, 8H), 6.56 (dd, *J* = 16.8 Hz, 10.8 Hz, 1H), 5.49 (dd, *J* = 17.2 Hz, 2.0 Hz, 1H), 5.05 (dd, *J* = 10.8 Hz, 2.0 Hz, 1H), 3.95 (t, *J* = 4.8 Hz, 2H), 3.43 (s, 4H), 3.00 (s, 2H), 2.15 (t, *J* = 6.4 Hz, 2H), 1.85-1.81 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 138.4, 132.7, 130.1, 128.5, 128.1, 113.6, 110.4, 65.7, 57.5, 54.8, 24.8, 22.7; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{24}NOCl_2$: 388.1230, found: 388.1238.

***N*,*N*-bis(3-chlorobenzyl)-1-(6-vinyl-3,4-dihydro-2*H*-pyran-5-yl)methanamine**



(3ai): The title compound was prepared according to the general procedure and purified by flash column chromatography (petroleum ether/ethyl acetate = 100/1 ~ 50/1) to give yellow oil, 96 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (s, 2H), 7.17-7.13 (m, 6H), 6.48 (dd, *J* = 16.8 Hz, 10.8 Hz, 1H), 5.43 (d, *J* = 17.2 Hz, 1H), 4.99 (d, *J* = 10.8 Hz, 1H), 3.88 (t, *J* = 4.8 Hz, 2H), 3.38 (s, 4H), 2.95 (s, 2H), 2.10 (t, *J* = 6.0 Hz, 2H), 1.79-1.74 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.3, 142.0, 134.3, 129.6, 128.8, 128.0, 127.2, 126.9, 113.7, 110.2, 65.7, 57.8, 54.9, 24.8, 22.7; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{24}NOCl_2$: 388.1230, found: 388.1234.

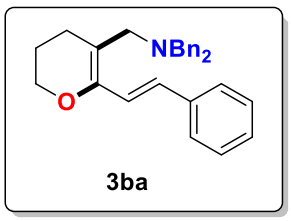
***N*,*N*-bis(4-(trifluoromethyl)benzyl)-1-(6-vinyl-3,4-dihydro-2*H*-pyran-5-yl)methan**



amine (3aj): The title compound was prepared according to the general procedure and purified by flash column chromatography (petroleum ether/ethyl acetate = 100/1 ~ 50/1) to give yellow oil, 87 mg, 64%

yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 4H), 7.45 (d, *J* = 8.0 Hz, 4H), 6.58 (dd, *J* = 16.8 Hz, 11.2 Hz, 1H), 5.52 (dd, *J* = 16.8 Hz, 2.0 Hz, 1H), 5.08 (dd, *J* = 11.2 Hz, 2.0 Hz, 1H), 3.95 (t, *J* = 4.8 Hz, 2H), 3.56 (s, 4H), 3.06 (s, 2H), 2.19 (t, *J* = 6.4 Hz, 2H), 1.87-1.81 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 144.0, 129.2 (q, J_{C-F} = 32.1 Hz), 128.9, 127.9, 125.3 (q, J_{C-F} = 3.7 Hz), 123.0, 113.9, 110.0, 65.7, 57.9, 55.1, 24.8, 22.7; ^{19}F NMR (376 MHz, $CDCl_3$) -62.4; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{24}NOF_6$: 456.1757, found: 456.1764.

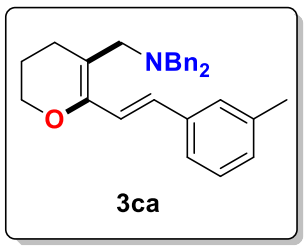
(*E*)-*N*,*N*-dibenzyl-1-(6-styryl-3,4-dihydro-2*H*-pyran-5-yl)methanamine (3ba): The



3ba

title compound was prepared according to the general procedure and purified by flash column chromatography (petroleum ether/ethyl acetate = 100/1 ~ 50/1) to give yellow oil, 114 mg, 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.40 (m, 2H), 7.38-7.36 (m, 4H), 7.34-7.31 (m, 3H), 7.30-7.28 (m, 3H), 7.24-7.20 (m, 3H), 6.99 (d, *J* = 16.0 Hz, 1H), 6.85 (d, *J* = 15.6 Hz, 1H), 4.00 (t, *J* = 5.2 Hz, 2H), 3.54 (s, 4H), 3.14 (s, 2H), 2.25 (t, *J* = 6.4 Hz, 2H), 1.89-1.83 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 140.1, 137.8, 128.9, 128.7, 128.3, 127.6, 127.5, 126.9, 126.8, 120.2, 111.9, 65.8, 58.4, 55.1, 25.4, 22.9; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{30}NO$: 396.2322, found: 396.2327.

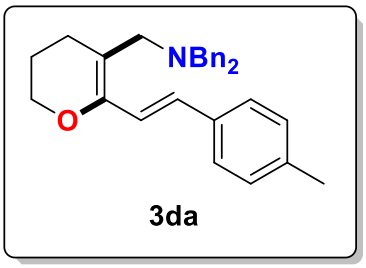
(*E*)-*N*,*N*-dibenzyl-1-(6-(3-methylstyryl)-3,4-dihydro-2*H*-pyran-5-yl)methanamine



3ca

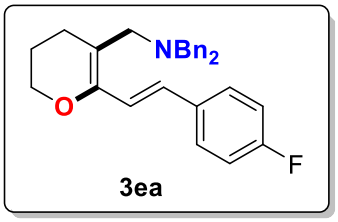
(3ca): The title compound was prepared according to the general procedure and purified by flash column chromatography (petroleum ether/ethyl acetate = 100/1 ~ 50/1) to give yellow oil, 113 mg, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.36 (m, 4H), 7.31-7.27 (m, 4H), 7.23-7.21 (m, 5H), 7.06-7.03 (m, 1H), 6.97 (d, *J* = 16.0 Hz, 1H), 6.82 (d, *J* = 15.6 Hz, 1H), 3.99 (t, *J* = 5.2 Hz, 2H), 3.55 (s, 4H), 3.14 (s, 2H), 2.37 (s, 3H), 2.25 (t, *J* = 6.8 Hz, 2H), 1.88-1.83 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.3, 140.1, 138.2, 137.7, 128.9, 128.6, 128.3, 127.7, 127.5, 126.9, 124.0, 119.9, 111.7, 65.8, 58.3, 55.1, 25.3, 22.9, 21.6; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{29}H_{32}NO$: 410.2478, found: 410.2479.

(*E*)-*N*,*N*-dibenzyl-1-(6-(4-methylstyryl)-3,4-dihydro-2*H*-pyran-5-yl)methanamine



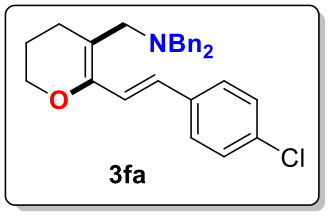
(3da): The title compound was prepared according to the general procedure and purified by flash column chromatography (petroleum ether/ethyl acetate = 100/1 ~ 50/1) to give yellow oil, 110 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.28 (m, 4H), 7.25-7.20 (m, 6H), 7.17-7.13 (m, 2H), 7.07-7.05 (m, 2H), 6.87 (d, *J* = 15.6 Hz, 1H), 6.75 (d, *J* = 15.6 Hz, 1H), 3.92 (t, *J* = 4.8 Hz, 2H), 3.47 (s, 4H), 3.06 (s, 2H), 2.28 (s, 3H), 2.17 (t, *J* = 6.8 Hz, 2H), 1.81-1.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 140.2, 137.3, 135.0, 129.4, 128.9, 128.3, 127.5, 126.9, 126.7, 119.3, 111.4, 65.8, 58.4, 55.2, 25.4, 22.9, 21.4; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{29}H_{32}NO$: 410.2478, found: 410.2483.

(*E*)-*N*,*N*-dibenzyl-1-(6-(4-fluorostyryl)-3,4-dihydro-2*H*-pyran-5-yl)methanamine



(3ea): The title compound was prepared according to the general procedure and purified by flash column chromatography (petroleum ether/ethyl acetate = 100/1 ~ 50/1) to give yellow oil, 116 mg, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.34 (m, 6H), 7.31-7.28 (m, 4H), 7.25-7.20 (m, 2H), 7.04-6.98 (m, 2H), 6.89 (d, *J* = 15.6 Hz, 1H), 6.80 (d, *J* = 15.6 Hz, 1H), 3.99 (t, *J* = 4.8 Hz, 2H), 3.54 (s, 4H), 3.13 (s, 2H), 2.25 (t, *J* = 6.4 Hz, 2H), 1.89-1.83 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6 (d, $J_{C\text{-}F}$ = 245.1 Hz), 148.1, 140.1, 134.0 (d, $J_{C\text{-}F}$ = 3.3 Hz), 128.9, 128.3, 128.2 (d, $J_{C\text{-}F}$ = 8.0 Hz), 126.9, 126.4, 120.0 (d, $J_{C\text{-}F}$ = 2.3 Hz), 115.7 (d, $J_{C\text{-}F}$ = 21.7 Hz), 111.9, 65.8, 58.4, 55.1, 25.5, 22.9; ^{19}F NMR (376 MHz, $CDCl_3$) -114.7; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{29}NOF$: 414.2228, found: 414.2235.

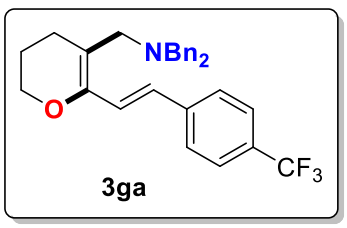
(*E*)-*N*,*N*-dibenzyl-1-(6-(4-chlorostyryl)-3,4-dihydro-2*H*-pyran-5-yl)methanamine



(3fa): The title compound was prepared according to the general procedure and purified by flash column chromatography (petroleum ether/ethyl acetate = 100/1 ~

50/1) to give yellow oil, 120 mg, 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.35 (m, 4H), 7.33-7.27 (m, 8H), 7.24-7.20 (m, 2H), 6.94 (d, *J* = 16.0 Hz, 1H), 6.78 (d, *J* = 15.6 Hz, 1H), 3.99 (t, *J* = 4.4 Hz, 2H), 3.54 (s, 4H), 3.13 (s, 2H), 2.25 (t, *J* = 6.4 Hz, 2H), 1.88-1.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 140.0, 136.3 133.0, 128.9, 128.8, 128.3, 127.9, 127.0, 126.2, 120.7, 112.4, 65.8, 58.4, 55.1, 25.5, 22.8; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{29}NOCl$: 430.1932, found: 430.1937.

(*E*)-*N*,*N*-dibenzyl-1-(6-(4-(trifluoromethyl)styryl)-3,4-dihydro-2*H*-pyran-5-yl)methanamine (3ga): The title compound was prepared according to the general procedure and purified by flash column chromatography (petroleum ether/ethyl acetate = 100/1 ~ 50/1) to give yellow oil, 129 mg, 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.55 (m, 2H), 7.48-7.46 (m, 2H), 7.37-7.35 (m, 4H), 7.31-7.28 (m, 4H), 7.25-7.20 (m, 2H), 7.05 (d, *J* = 15.6 Hz, 1H), 6.85 (d, *J* = 15.6 Hz, 1H), 4.00 (t, *J* = 4.8 Hz, 2H), 3.55 (s, 4H), 3.14 (s, 2H), 2.26 (t, *J* = 6.4 Hz, 2H), 1.89-1.83 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 141.3, 139.9, 129.0, 128.6 (q, J_{C-F} = 31.9 Hz), 128.4, 127.0, 126.8, 126.0, 125.6 (q, J_{C-F} = 3.8 Hz), 123.1, 122.5, 113.6, 65.8, 58.4, 55.1, 25.6, 22.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.3; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{29}H_{29}NOF_3$: 464.2196, found: 464.2201.



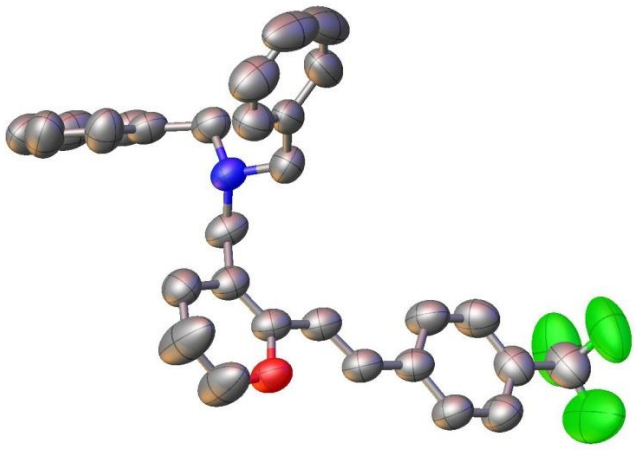
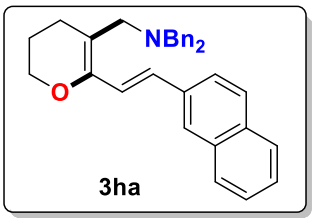


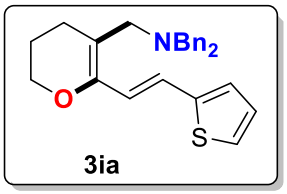
Figure S1. The ORTEP drawing of product **3ga.**

(*E*)-*N*,*N*-dibenzyl-1-(6-(2-(naphthalen-2-yl)vinyl)-3,4-dihydro-2*H*-pyran-5-yl)methanamine (3ha): The title compound was prepared according to the general procedure and purified by flash column chromatography (petroleum ether/ethyl



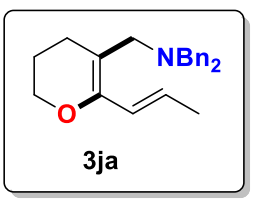
acetate = 100/1 ~ 50/1) to give yellow oil, 127 mg, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.59-7.54 (m, 2H), 7.45-7.39 (m, 3H), 7.28 (d, *J* = 8.0 Hz, 4H), 7.23-7.17 (m, 4H), 7.15-7.12 (m, 2H), 6.96 (d, *J* = 15.2 Hz, 1H), 3.99 (t, *J* = 4.8 Hz, 2H), 3.47 (s, 4H), 3.08 (s, 2H), 2.21 (t, *J* = 6.8 Hz, 2H), 1.86-1.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 140.2, 135.6, 133.9, 131.6, 128.9, 128.6, 128.3, 127.9, 126.9, 126.1, 125.9, 125.7, 124.6, 124.3, 123.6, 123.1, 112.1, 65.9, 58.4, 55.2, 25.4, 22.9; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{32}H_{32}NO$: 446.2478, found: 446.2485.

(*E*)-*N*,*N*-dibenzyl-1-(6-(2-(thiophen-2-yl)vinyl)-3,4-dihydro-2*H*-pyran-5-yl)metha



namine (3ia): The title compound was prepared according to the general procedure and purified by flash column chromatography (petroleum ether/ethyl acetate = 100/1 ~ 50/1) to give yellow oil, 115 mg, 96% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.5 Hz, 4H), 7.31-7.28 (m, 4H), 7.23-7.20 (m, 2H), 7.16 (d, *J* = 4.5 Hz, 1H), 7.00-6.96 (m, 3H), 6.85 (d, *J* = 15.5 Hz, 1H), 3.96 (t, *J* = 5.0 Hz, 2H), 3.53 (s, 4H), 3.09 (s, 2H), 2.22 (t, *J* = 6.5 Hz, 2H), 1.86-1.81 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.8, 143.3, 140.1, 128.9, 128.3, 127.7, 126.9, 126.1, 124.2, 120.8, 119.8, 111.9, 65.8, 58.3, 55.1, 25.3, 22.8; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{28}NOS$: 402.1886, found: 402.1891.

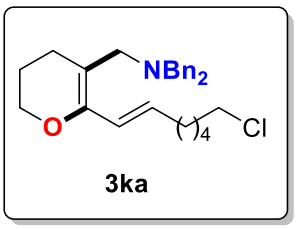
(*E*)-*N*,*N*-dibenzyl-1-(6-(prop-1-en-1-yl)-3,4-dihydro-2*H*-pyran-5-yl)methanamine



(3ja): The title compound was prepared according to the general procedure and purified by flash column chromatography (petroleum ether/ethyl acetate = 100/1 ~ 50/1) to give yellow oil, 83 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.33 (m, 4H), 7.31-7.27 (m, 4H), 7.25-7.19 (m, 2H), 6.27 (dd, *J* = 15.2 Hz, 1.6 Hz, 1H), 6.04-5.95 (m, 1H), 3.92 (t, *J* = 4.8 Hz, 2H), 3.50 (s, 4H), 3.02 (s, 2H), 2.18 (t, *J* = 6.8 Hz, 2H), 1.84-1.78 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8,

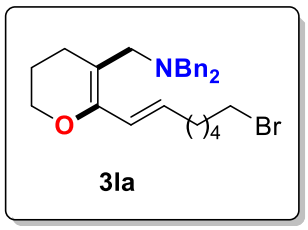
140.3, 128.9, 128.2, 126.8, 125.1, 123.0, 108.3, 65.7, 58.2, 54.8, 24.7, 22.9, 18.4; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{28}NO$: 334.2165, found: 334.2166.

(*E*)-*N*,*N*-dibenzyl-1-(6-(7-chlorohept-1-en-1-yl)-3,4-dihydro-2*H*-pyran-5-yl)methanamine (3ka): The title compound was prepared according to the general procedure and purified by flash column chromatography (petroleum ether/ethyl acetate = 100/1 ~ 50/1) to give yellow oil, 90 mg, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.34 (m, 4H), 7.31-7.27 (m, 4H), 7.25-7.19 (m, 2H), 6.26 (d, *J* = 15.2 Hz, 1H), 5.99-5.92 (m, 1H), 3.93 (t, *J* = 4.8 Hz, 2H), 3.55-3.51 (m, 2H), 3.50-3.47 (m, 4H), 3.02 (s, 2H), 2.19-2.11 (m, 4H), 1.84-1.75 (m, 4H), 1.51-1.39 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 140.3, 129.8, 128.9, 128.3, 126.8, 122.0, 108.7, 65.7, 58.2, 54.9, 45.2, 32.7, 32.7, 28.8, 26.6, 24.8, 22.9; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{35}NOCl$: 424.2402, found: 424.2405.



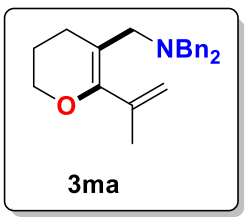
3ka

(*E*)-*N*,*N*-dibenzyl-1-(6-(7-bromohept-1-en-1-yl)-3,4-dihydro-2*H*-pyran-5-yl)methanamine (3la): The title compound was prepared according to the general procedure and purified by flash column chromatography (petroleum ether/ethyl acetate = 100/1 ~ 50/1) to give yellow oil, 84 mg, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.35 (m, 4H), 7.31-7.28 (m, 4H), 7.23-7.20 (m, 2H), 6.26 (d, *J* = 15.2 Hz, 1H), 5.99-5.92 (m, 1H), 3.93 (t, *J* = 5.2 Hz, 2H), 3.50 (s, 4H), 3.41 (t, *J* = 7.2 Hz, 2H), 3.02 (s, 2H), 2.20-2.11 (m, 4H), 1.91-1.79 (m, 4H), 1.50-1.40 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.8, 140.3, 129.8, 128.9, 128.3, 126.9, 122.1, 108.8, 65.8, 58.2, 54.9, 34.0, 32.9, 32.7, 28.7, 27.9, 24.8, 22.9; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{35}NOBr$: 468.1897, found: 468.1904.



3la

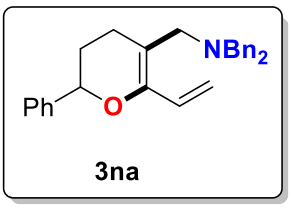
***N*,*N*-dibenzyl-1-(6-(prop-1-en-2-yl)-3,4-dihydro-2*H*-pyran-5-yl)methanamine (3ma):** The title compound was prepared according to the general procedure and purified by flash column chromatography (petroleum ether/ethyl acetate = 100/1 ~ 50/1) to give yellow oil, 66 mg, 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.2 Hz, 4H), 7.31-7.28 (m, 4H), 7.23-7.19 (m, 2H), 5.11-5.10 (m, 1H), 4.86 (d, *J* = 1.2



3ma

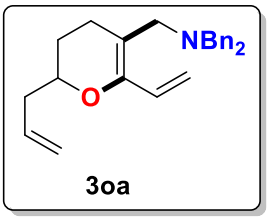
Hz 1H), 3.92 (t, *J* = 4.8 Hz, 2H), 3.46 (s, 4H), 3.02 (s, 2H), 2.19 (t, *J* = 6.4 Hz, 2H), 1.85-1.80 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 140.5, 139.7, 128.7, 128.3, 126.8, 117.3, 106.1, 66.1, 58.0, 55.9, 23.4, 22.9, 21.7; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{28}NO$: 334.2165, found: 334.2173.

***N,N*-dibenzyl-1-(2-phenyl-6-vinyl-3,4-dihydro-2*H*-pyran-5-yl)methanamine (3na):**



The title compound was prepared according to the general procedure and purified by flash column chromatography (petroleum ether/ethyl acetate = 100/1 ~ 50/1) to give yellow oil, 70 mg, 59% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.29 (m, 11H), 7.27-7.19 (m, 4H), 6.66 (dd, *J* = 16.8 Hz, 10.8 Hz, 1H), 5.60 (dd, *J* = 17.2 Hz, 2.4 Hz, 1H), 5.08 (dd, *J* = 10.8 Hz, 2.0 Hz, 1H), 4.78 (dd, *J* = 9.6 Hz, 2.4 Hz, 1H), 3.51 (s, 4H), 3.08 (s, 2H), 2.38-2.20 (m, 2H), 2.12-2.04 (m, 1H), 1.91-1.81 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 142.4, 140.1, 128.9, 128.4, 128.3, 128.1, 127.5, 126.9, 125.8, 113.6, 110.9, 76.4, 58.3, 54.7, 30.1, 25.0; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{30}NO$: 396.2322, found: 396.2327.

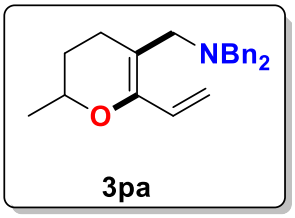
1-(2-allyl-6-vinyl-3,4-dihydro-2*H*-pyran-5-yl)-*N,N*-dibenzylmethanamine (3oa):



The title compound was prepared according to the general procedure and purified by flash column chromatography (petroleum ether/ethyl acetate = 100/1 ~ 50/1) to give yellow oil, 60 mg, 56% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 6.8 Hz, 4H), 7.31-7.27 (m, 4H), 7.24-7.19 (m, 2H), 6.59 (dd, *J* = 16.8 Hz, 10.8 Hz, 1H), 5.93-5.83 (m, 1H), 5.52 (dd, *J* = 16.8 Hz, 2.0 Hz, 1H), 5.12-5.04 (m, 3H), 3.77-3.71 (m, 1H), 3.49 (s, 4H), 3.04 (s, 2H), 2.47-2.40 (m, 1H), 2.31-2.21 (m, 3H), 1.89-1.83 (m, 1H), 1.57-1.47 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 140.2, 134.7, 128.9, 128.3, 128.2, 126.9, 117.1, 113.3, 110.7, 74.4, 58.2, 54.6, 39.8, 27.4, 24.9; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{30}NO$: 360.2322, found: 360.2327.

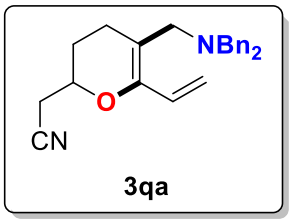
***N,N*-dibenzyl-1-(2-methyl-6-vinyl-3,4-dihydro-2*H*-pyran-5-yl)methanamine (3pa):**

The title compound was prepared according to the general procedure and purified by flash column chromatography (petroleum ether/ethyl acetate = 100/1 ~ 50/1) to give yellow oil, 68 mg, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.34 (m, 4H),



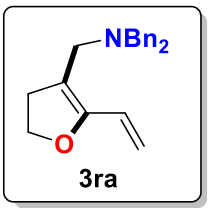
7.31-7.27 (m, 4H), 7.23-7.19 (m, 2H), 6.69-6.60 (m, 1H), 5.52 (dd, *J* = 16.8 Hz, 2.0 Hz, 1H), 5.07-5.01 (m, 1H), 3.88-3.80 (m, 1H), 3.49 (s, 4H), 3.04 (s, 2H), 2.24-2.19 (m, 2H), 1.87-1.81 (m, 1H), 1.63-1.46 (m, 1H), 1.31-1.28 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 140.2, 128.9, 128.3, 128.3, 126.9, 113.1, 110.5, 71.2, 58.1, 54.6, 29.6, 25.1, 21.1; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{28}NO$: 334.2165, found: 334.2172.

2-(5-((dibenzylamino)methyl)-6-vinyl-3,4-dihydro-2*H*-pyran-2-yl)acetonitrile



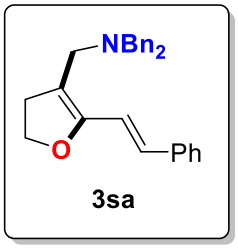
(3qa): The title compound was prepared according to the general procedure and purified by flash column chromatography (petroleum ether/ethyl acetate = 20/1 ~ 10/1) to give yellow oil, 32 mg, 30% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.28 (m, 8H), 7.24-7.20 (m, 2H), 6.56 (dd, *J* = 16.8 Hz, 10.8 Hz, 1H), 5.55 (dd, *J* = 16.8 Hz, 1.6 Hz, 1H), 5.09 (dd, *J* = 11.2 Hz, 1.6 Hz, 1H), 4.00-3.93 (m, 1H), 3.50 (s, 4H), 3.05 (s, 2H), 2.68-2.56 (m, 2H), 2.28-2.25 (m, 2H), 2.04-1.94 (m, 1H), 1.69-1.61 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 139.9, 128.8, 128.3, 127.3, 127.0, 117.0, 114.2, 110.8, 70.1, 58.4, 54.4, 27.1, 24.1, 23.9; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{27}N_2O$: 359.2118, found: 359.2123.

***N*,*N*-dibenzyl-1-(2-vinyl-4,5-dihydrofuran-3-yl)methanamine (3ra):** The title



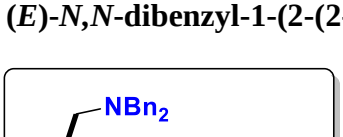
compound was prepared according to the general procedure and purified by flash column chromatography (petroleum ether/ethyl acetate = 100/1 ~ 50/1) to give yellow oil, 67 mg, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (m, 4H), 7.32-7.28 (m, 4H), 7.24-7.20 (m, 2H), 6.32 (dd, *J* = 17.2 Hz, 11.2 Hz, 1H), 5.45 (d, *J* = 17.2 Hz, 1H), 5.15 (d, *J* = 11.2 Hz, 1H), 4.28 (t, *J* = 9.2 Hz, 2H), 3.53 (s, 4H), 3.13 (s, 2H), 2.80 (t, *J* = 9.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 139.9, 128.7, 128.3, 126.9, 123.6, 114.9, 112.0, 68.3, 58.2, 50.0, 33.9; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{24}NO$: 306.1852, found: 306.1857.

(*E*)-*N*,*N*-dibenzyl-1-(2-styryl-4,5-dihydrofuran-3-yl)methanamine (3sa): The title compound was prepared according to the general procedure and purified by flash column chromatography (petroleum ether/ethyl acetate = 100/1 ~ 50/1) to give yellow oil, 99 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.37 (m, 6H), 7.34-7.28 (m, 6H), 7.25-7.21 (m, 3H), 6.81 (d, *J* = 16.0 Hz, 1H), 6.67 (d, *J* = 16.0 Hz, 1H), 4.33 (t, *J* = 9.2 Hz, 2H), 3.58 (s, 4H), 3.24 (s, 2H), 2.85 (t, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 139.9, 137.2, 129.3, 128.8, 128.7, 128.4, 127.8, 127.0, 126.8, 115.0, 112.8, 68.4, 58.3, 50.1, 34.3; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{28}NO$: 382.2165, found: 382.2174.



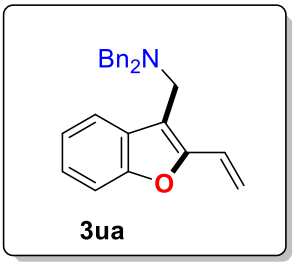
3sa

(*E*)-*N*,*N*-dibenzyl-1-(2-(2-(naphthalen-2-yl)vinyl)-4,5-dihydrofuran-3-yl)methanamine (3ta): The title compound was prepared according to the general procedure and purified by flash column chromatography (petroleum ether/ethyl acetate = 100/1 ~ 50/1) to give yellow oil, 119 mg, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20-8.18 (m, 1H), 7.85-7.83 (m, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.64-7.59 (m, 2H), 7.52-7.45 (m, 3H), 7.39-7.37 (m, 4H), 7.32-7.28 (m, 4H), 7.25-7.20 (m, 2H), 6.76 (d, *J* = 15.6 Hz, 1H), 4.39 (t, *J* = 9.2 Hz, 2H), 3.59 (s, 4H), 3.26 (s, 2H), 2.89 (t, *J* = 9.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.6, 139.9, 134.8, 133.9, 131.4, 128.8, 128.6, 128.4, 128.2, 127.0, 126.2, 126.0, 125.7, 124.0, 123.5, 117.8, 113.1, 68.5, 58.4, 50.2, 34.3; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{31}H_{30}NO$: 432.2322, found: 432.2322.



3ta

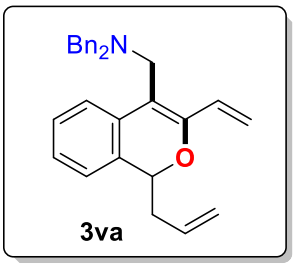
***N*,*N*-dibenzyl-1-(2-vinylbenzofuran-3-yl)methanamine (3ua):** The title compound was prepared according to the general procedure and purified by flash column chromatography (petroleum ether/ethyl acetate = 100/1 ~ 50/1) to give yellow oil, 77 mg, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.62 (m, 1H), 7.40-7.28 (m, 9H), 7.26-7.18 (m, 4H), 6.72 (dd, *J* = 17.2 Hz, 11.2 Hz, 1H), 5.93 (dd, *J* = 17.2 Hz, 1.6 Hz, 1H), 5.36 (dd, *J* = 11.2 Hz, 1.2 Hz, 1H), 3.64 (s, 2H), 3.54 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 152.2, 139.5, 129.8, 129.2,



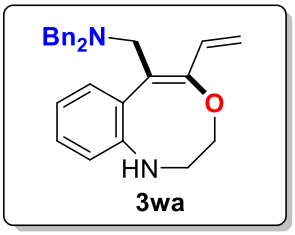
3ua

128.3, 127.1, 124.9, 123.5, 122.6, 120.9, 115.4, 115.1, 110.9, 58.6, 47.6; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{24}NO$: 354.1858, found: 354.1862.

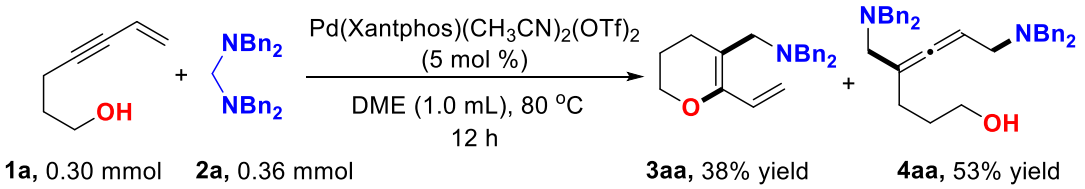
1-(1-allyl-3-vinyl-1*H*-isochromen-4-yl)-*N*,*N*-dibenzylmethanamine (3va): The title compound was prepared according to the general procedure and purified by flash column chromatography (petroleum ether/ethyl acetate = 100/1 ~ 50/1) to give yellow oil, 58 mg, 48% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.19 (m, 8H), 7.15-7.11 (m, 3H), 7.07-7.05 (m, 2H), 6.90-6.88 (m, 1H), 6.71-6.64 (m, 1H), 5.83-5.73 (m, 2H), 5.21-5.18 (m, 1H), 4.96-4.90 (m, 3H), 3.50-3.38 (m, 6H), 2.60-2.52 (m, 1H), 2.35-2.28 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 139.6, 134.0, 132.8, 131.6, 129.5, 128.3, 128.2, 127.5, 127.1, 126.5, 123.7, 123.6, 117.7, 117.2, 111.4, 76.6, 58.3, 49.6, 38.5; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{29}H_{30}NO$: 408.2327, found: 408.2330.



(*E*)-*N*,*N*-dibenzyl-1-(5-vinyl-2,3-dihydro-1*H*-benzo[e][1,4]oxazocin-6-yl)methanamine (3wa): The title compound was prepared according to the general procedure and purified by flash column chromatography (petroleum ether/ethyl acetate = 10/1 ~ 5/1) to give yellow oil, 81 mg, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.77 (m, 1H), 7.33-7.31 (m, 5H), 7.29-7.24 (m, 5H), 7.20-7.16 (m, 3H), 7.15-7.10 (m, 1H), 6.72 (dd, *J* = 17.6 Hz, 11.6 Hz, 1H), 5.78 (dd, *J* = 17.6 Hz, 1.6 Hz, 1H), 5.47 (dd, *J* = 11.6 Hz, 1.6 Hz, 1H), 4.26 (t, *J* = 5.6 Hz, 2H), 3.87 (t, *J* = 5.6 Hz, 2H), 3.76 (s, 2H), 3.55 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.0, 136.9, 136.7, 129.3, 129.1, 128.1, 126.8, 125.9, 122.3, 120.7, 120.1, 119.7, 111.7, 109.3, 62.1, 58.8, 49.4, 46.0; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{29}N_2O$: 397.2280, found: 397.2280.



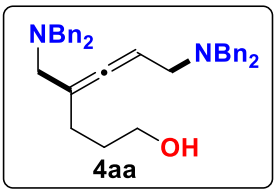
Procedure for the synthesis of 3aa and 4aa



1a, 0.30 mmol **2a**, 0.36 mmol **3aa**, 38% yield **4aa**, 53% yield

Aminal **2a** (0.36 mmol), Pd(Xantphos)$(CH_3CN)_2(OTf)_2$ (16.0 mg, 5 mol %), enynol **1a** (0.30 mmol) and DME (1.0 mL) were added to a 25 mL flame-dried Young-type tube under N_2 atmosphere. The reaction mixture was stirred at 80 ℃ in an oil bath for 12 hours and then cooled to room temperature. The solvent was removed under reduced pressure, the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 10/1 to 5/1) to give the **3aa** (36 mg, 38% yield) and **4aa** as colorless oil (82 mg, 53% yield).

7-(dibenzylamino)-4-((dibenzylamino)methyl)hepta-4,5-dien-1-ol (4aa): ^{1}H NMR

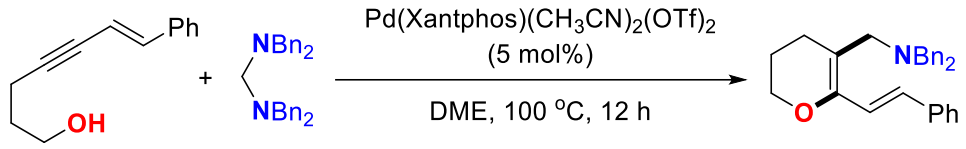


4aa

(400 MHz, $CDCl_3$) δ 7.36-7.33 (m, 8H), 7.31-7.26 (m, 8H), 7.24-7.20 (m, 4H), 5.23-5.19 (m, 1H), 3.66-3.49 (m, 10H), 3.12-2.97 (m, 2H), 2.96-2.92 (m, 2H), 2.13-2.09 (m, 2H), 1.57-1.50 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.0, 139.6, 139.6, 129.0, 128.9, 128.3, 127.0, 127.0, 101.6, 88.5, 62.5, 58.1, 57.7, 56.7, 52.9, 30.6, 26.5; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{36}H_{41}N_2O$: 517.3219, found: 517.3222.

6. Synthetic Transformation of Products

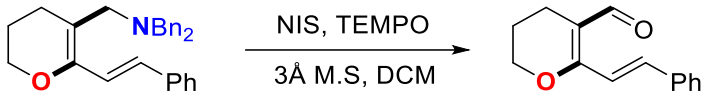
Gram-scale synthesis of 3aa



1b **2a** **3ba**, 86%

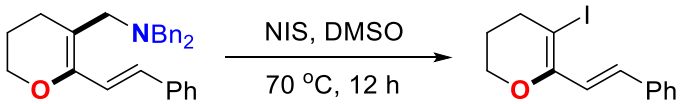
N,*N*,*N*′,*N*′-tetrabenzylmethanediamine **2a** (4.87 g, 12 mmol), Pd(Xantphos)(CH_3CN)$_2$(OTf)$_2$ (525 mg, 0.5 mmol), (*E*)-7-phenylhept-6-en-4-yn-1-ol **1b** (1.86 g, 10 mmol) and DME (30 mL) were added to a 100 mL flame-dried Young-type tube under N_2 atmosphere. The reaction mixture was stirred at 100 ℃ for 12 hours in an oil bath and then cooled to room temperature. The solvent was removed under reduced pressure, the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 500/1 to 100/1) to afford the desired product **3ba** (3.44 g, 86% yield).

Synthetic transformation of product[3]



3ba **5**, 60%

The (*E*)-7-phenylhept-6-en-4-yn-1-ol **3ba** (118 mg, 0.30 mmol), NIS (202 mg, 0.90 mmol), TEMPO (94 mg, 0.60 mmol) and activated powdered 3 Å molecular sieves (0.45 g) were stirred with dry dichloromethane (6.0 mL) under N_2 atmosphere at room temperature for 4 hours. The reaction mixture was diluted with dichloromethane (15 mL), washed with saturated sodium thiosulfate solution (15 mL), and dried (Na_2SO_4). The solvent was removed under reduced pressure, the crude product was purified by flash chromatography on silica gels (petroleum ether/ethyl acetate = 10/1) directly to give **5** (38 mg, 60%).

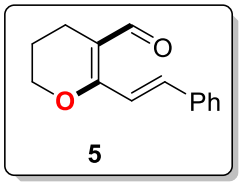


3ba **6**, 67%

The (*E*)-7-phenylhept-6-en-4-yn-1-ol **3ba** (118 mg, 0.30 mmol) and NIS (67 mg, 0.30 mmol), were stirred with dry DMSO (2.0 mL) under N_2 atmosphere at 70 ℃ for 12 hours in an oil bath. The reaction was quenched by H_2O and extracted with Et_2O (20 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4. After

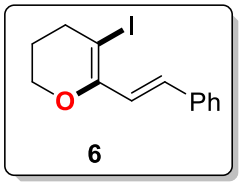
evaporation of the solvent under reduced pressure, the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100/1) to afford substrate **6** (63 mg, 67% yield).

(*E*)-6-styryl-3,4-dihydro-2*H*-pyran-5-carbaldehyde (5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.16 (s, 1H), 7.51-7.49 (m, 2H), 7.40-7.31 (m, 4H), 7.29-7.26 (m, 1H), 4.23 (t, *J* = 4.8 Hz, 2H), 2.39 (t, *J* = 6.4 Hz, 2H), 1.95-1.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.4, 165.7, 135.9, 135.7, 129.4, 129.0, 127.5, 116.8, 115.8, 67.5, 21.1, 18.8; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{15}O_2$: 215.1072, found: 215.1071.



5

(*E*)-5-iodo-6-styryl-3,4-dihydro-2*H*-pyran (6): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 1.2 Hz, 2H), 7.44-7.31 (m, 2H), 7.27-7.22 (m, 1H), 7.02 (d, *J* = 16.0 Hz, 1H), 6.89 (d, *J* = 15.6 Hz, 1H), 4.20 (t, *J* = 5.2 Hz, 2H), 2.70 (t, *J* = 6.4 Hz, 2H), 2.00-1.94 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.8, 136.8, 131.6, 128.7, 128.1, 127.1, 125.1, 75.1, 66.3, 36.4, 25.8; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{14}IO$: 313.0089, found: 313.0082.

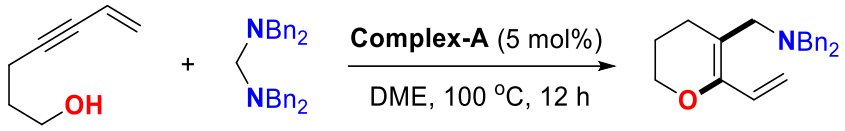


6

7. Mechanistic Experiments

To gain insights into the possible mechanism of this reaction, some mechanism experiments were conducted. The Xantphos-ligated palladium-complex-A was synthesized according to our previous report procedure in gram scale. With the Xantphos-ligated palladium-complex-**A** in hand, a series of control experiments were conducted.

The catalytic reaction of enynol 1a and aminal 2a by complex A

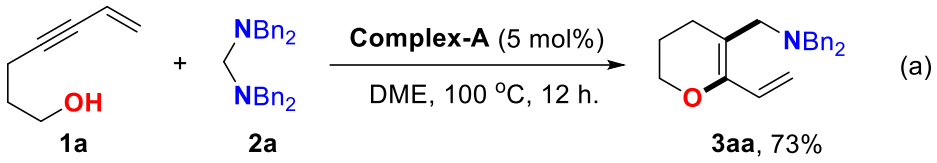


1a **2a** **3aa**

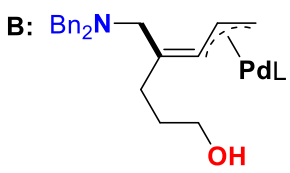
N,*N*,*N*',*N*'-tetrabenzylmethanediamine **2a** (146 mg, 0.36 mmol), hept-6-en-4-yn-1-ol **1a** (33.0 mg, 0.30 mmol), [Pd(Xantphos)(CH_2NBn_2)]OTf (15.6 mg, 0.015 mmol) and DME (1.0 mL) were added to a 25 mL flame-dried Young-type tube under N_2 atmosphere. The reaction mixture was stirred at 100 ℃ for 12 hours in an oil bath and then cooled to room temperature. The solvent was removed under reduced pressure, the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 200/1 to 50/1) to give the desired product **3aa** as a colorless oil (73 mg, 76%).

HRMS-analysis of the catalytic reaction system

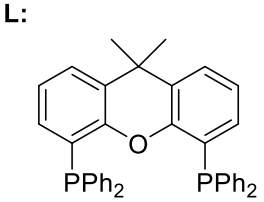
In order to provide a proof-of-concept for the proposed reaction mechanism, the mother liquid of the catalytic reaction was characterized by HRMS. Palladium complex **B** (Figure S2) was detected in the mother liquid. The result indicated that the catalytic reaction does occur according to the reaction mechanism proposed above.



1a **2a** **3aa**, 73%



Calcd. m/z for [**B**-OTf]: 1004.2978
Found: 1004.2994



A mixture of *N*,*N*,*N*',*N*'-tetrabenzylmethanediamine **2a** (146 mg, 0.36 mmol), hept-6-en-4-yn-1-ol **1a** (33.0 mg, 0.30 mmol), [Pd(Xantphos)(CH_2NBn_2)]OTf (15.6

mg, 0.015 mmol) and DME (1.0 mL) were added to a 25 mL flame-dried Young-type tube in the glove box. The reaction mixture was stirred at 100 ℃ for 30 minutes. After cooled to room temperature, some reaction mixture was taken and injected into HRMS (ESI). The HRMS (ESI) analysis of the reaction mixture showed a peck at m/z 1004.2994, which corresponds to the mass of [**B**-OTf]$^+$.

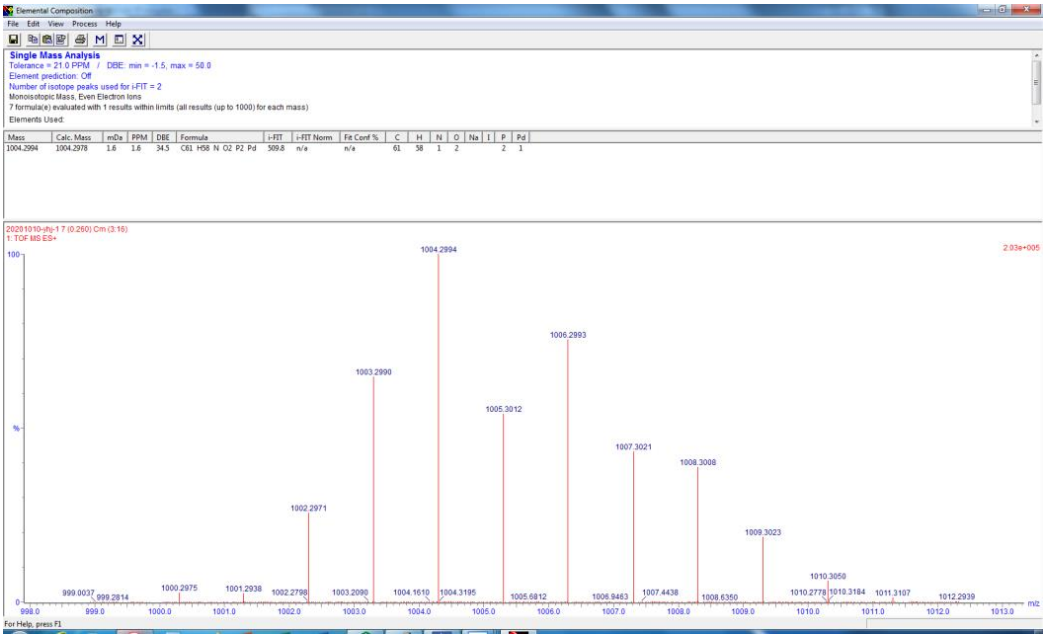
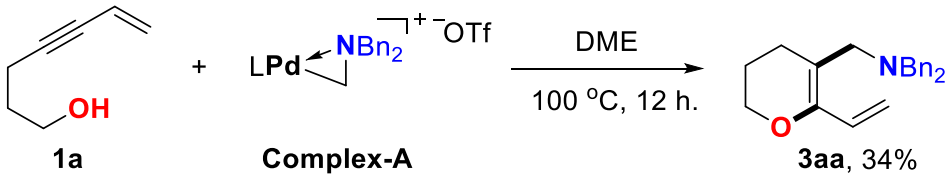


Figure S2. Observed HRMS date for palladium complex **B**

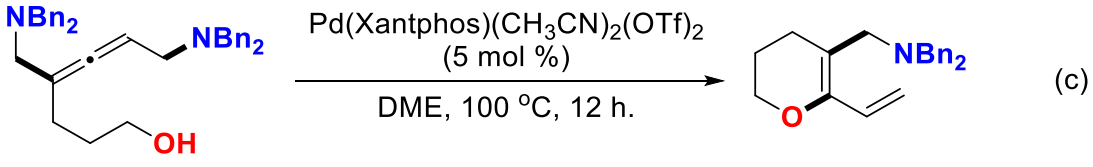
Stoichiometric reaction of enynol 1a and complex A



1a **Complex-A** **3aa**, 34%

The hept-6-en-4-yn-1-ol **1a** (22 mg, 0.20 mmol), [Pd(Xantphos)(CH_2NBn_2)]OTf (208 mg, 0.20 mmol) and DME (1.0 mL) were added to a 25 mL flame-dried Young-type tube under N_2 atmosphere. The mixture was stirred at 100 ℃ for 12 hours, then cooled to room temperature. The solvent was removed under reduced pressure, the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 200/1 to 50/1) to give the desired product **3aa** as a colorless oil (21 mg, 34%).

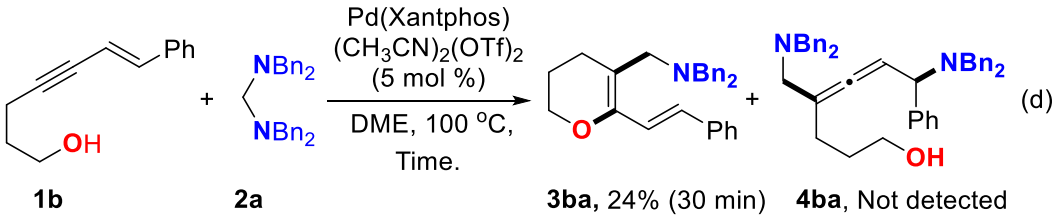
Intermediate 4aa was demonstrated



4aa **3aa**, 68%

The **4aa** (155 mg, 0.3 mmol), Pd(Xantphos)$(CH_3CN)_2(OTf)_2$ (16 mg, 0.015 mmol) and DME (1.0 mL) were added to a 25 mL flame-dried Young-type tube under N_2 atmosphere. The mixture was stirred at 100 ℃ for 12 hours, then cooled to room temperature. The solvent was removed under reduced pressure, the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 200/1 to 50/1) to give the desired product **3aa** as a colorless oil (65 mg, 68%).

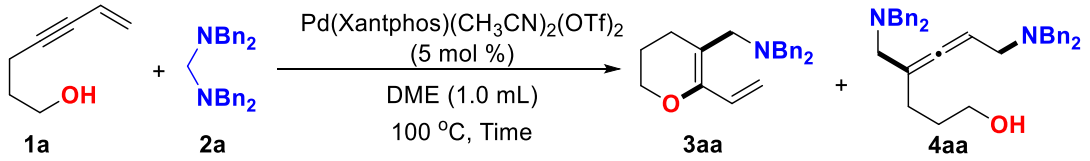
Intermediate 4ba was ruled out



A mixture of *N*,*N*,*N*′,*N*′-tetrabenzylmethanediamine **2a** (146 mg, 0.36 mmol), **1b** (54 mg, 0.30 mmol), , Pd(Xantphos)$(CH_3CN)_2(OTf)_2$ (16.0 mg, 5 mol %), and DME (1.0 mL) were added to a 25 mL flame-dried Young-type tube under N_2 atmosphere. The mixture was stirred at 100 ℃. The **4ba** was monitored at different moments by TLC. The result show that **4ba** was not detected, which ruled out the possibility of **4ba** as an intermediate.

Experiments for monitoring

Parallel experiments: *N*,*N*,*N*′,*N*′-tetrabenzylmethanediamine **2a** (146 mg, 0.36 mmol), hept-6-en-4-yn-1-ol **1a** (33.0 mg, 0.30 mmol), Pd(Xantphos)$(CH_3CN)_2(OTf)_2$ (16.0 mg, 5 mol %), and DME (1.0 mL) were added to a 25 mL flame-dried Young-type tube under N_2 atmosphere. The reaction mixture was stirred at 100 ℃. The yields of **3aa** and **4aa** were determined at different moments using $Cl_2CHCHCl_2$ as internal standard by ^{1}H NMR analysis. As shown in **Figure S3**



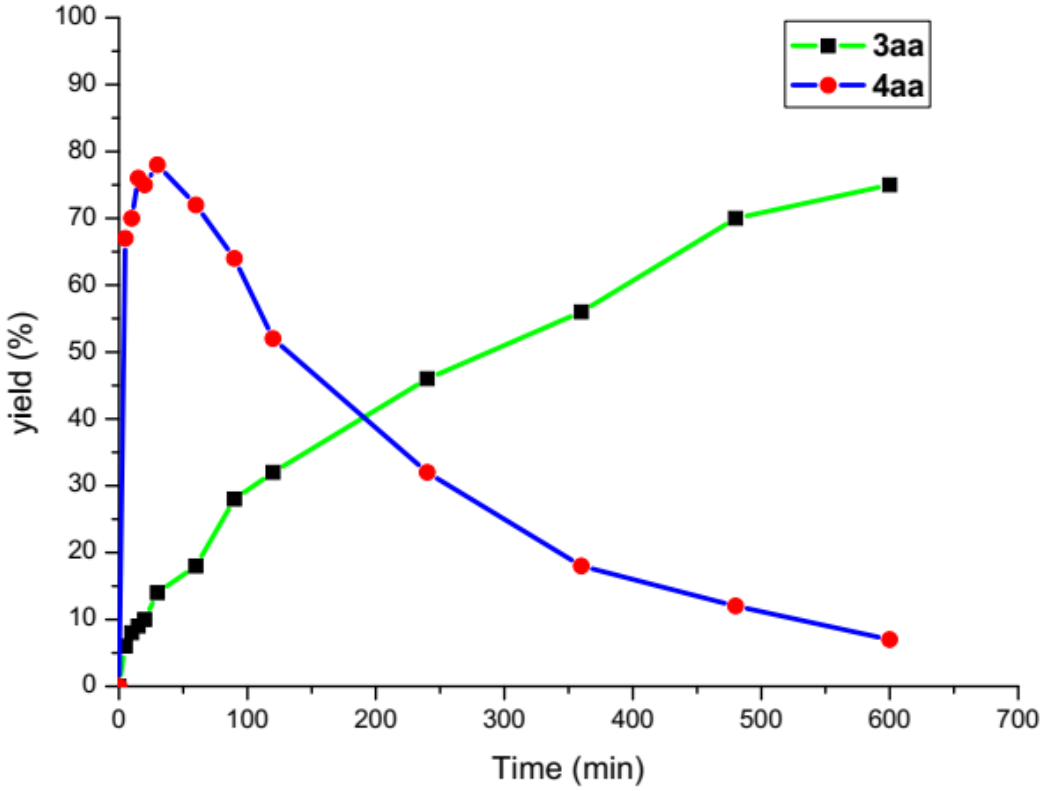
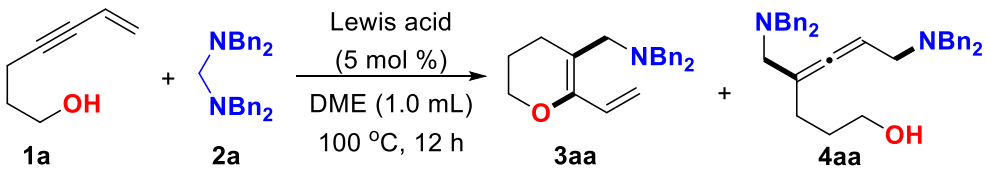


Figure S3. Reaction profile for the standard reaction

Control Experiments with Lewis acids and Bronsted acids

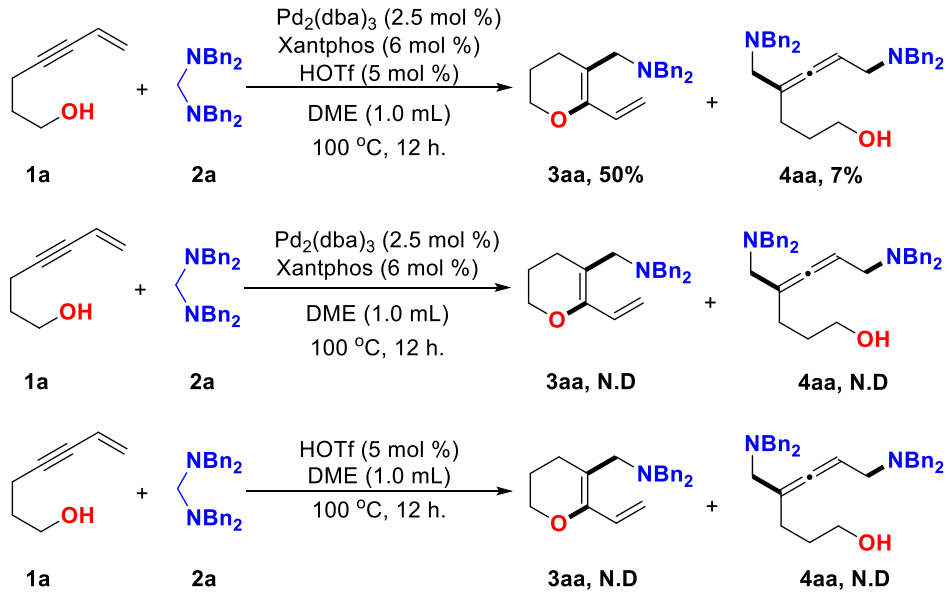
N,*N*,*N*',*N*'-tetrabenzylmethanediamine **2a** (146 mg, 0.36 mmol), Lewis acid (0.015 mmol, 5 mol %), or Bronsted acid (5 mol%) enynol **1a** (33 mg, 0.30 mmol) and DME (1.0 mL) were added to a 25 mL flame-dried Young-type tube under N_2 atmosphere. The reaction mixture was stirred at the designed temperature for 12 hours and then cooled to room temperature. The desired product **3aa** cannot be obtained by using Lewis acids, which ruled out the possibility that palladium functioned as a Lewis acid. Moreover, the HOTf alone can not catalyze the desired reaction at all.



1a 2a 3aa 4aa

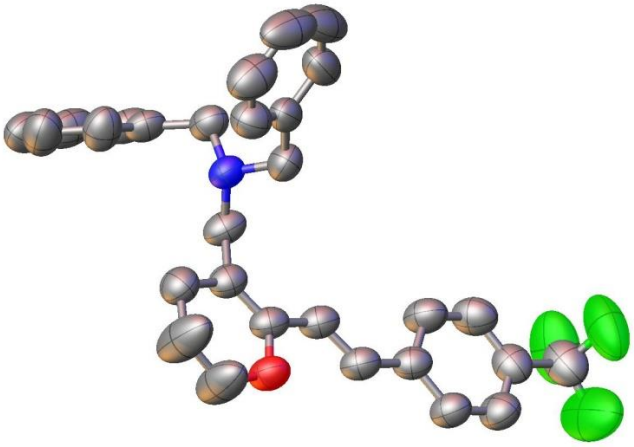
entry	Lewis acid	Yield/% 3aa	Yield/% 4aa
1	AgOTf	N.D	N.D
2	$Zn(OTf)_2$	N.D	N.D
3	$Cu(OTf)_2$	N.D	N.D
4	$Fe(OTf)_3$	N.D	N.D
5	$Sc(OTf)_3$	N.D	N.D
6	$Al(OTf)_3$	N.D	N.D

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.36 mmol), Lewis acid (5 mol %), DME (1.0 mL), 12 h, isolated yield.



8. X-ray Single Crystal Data for Compound 3ga

Sample preparation: Compound **3ga** (30 mg) was dissolved in anhydrous CH_2Cl_2 (1.0 mL) in a 5 mL sample vial, and CH_3OH (3.0 mL) was added carefully to form a two-phase interface. The resulting mixture was left at -20 ℃ under airtight conditions until the white crystals precipitated.



CCDC 2048261 (**3ga**)

The ellipsoid contour percent probability lever is 50%

Crystal data and structure refinement for 3ga

Identification code	YHJ-X200901-CF_3
Empirical formula	$C_{29}H_{26}F_3NO$
Formula weight	461.51
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.5127(3)
b/Å	12.4644(5)
c/Å	12.5617(7)
α/°	108.394(4)
β/°	111.688(4)
γ/°	96.626(3)
Volume/$Å^3$	1267.02(11)
Z	2
$\rho_{calc}g/cm^3$	1.210
μ/mm^{-1}	0.725
F(000)	484.0
Crystal size/mm^3	0.3 × 0.2 × 0.15
Radiation	CuKα (λ = 1.54184)

2Θ range for data collection/ °	7.748 to 140.158
Index ranges	$-11 \leq h \leq 8$, $-14 \leq k \leq 15$, $-15 \leq l \leq 14$
Reflections collected	8460
Independent reflections	4672 [R_{int} = 0.0159, R_{sigma} = 0.0208]
Data/restraints/parameters	4672/1/307
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0688, wR_2 = 0.2117
Final R indexes [all data]	R_1 = 0.0826, wR_2 = 0.2311
Largest diff. peak/hole / e $Å^{-3}$	0.30/-0.27

9. References

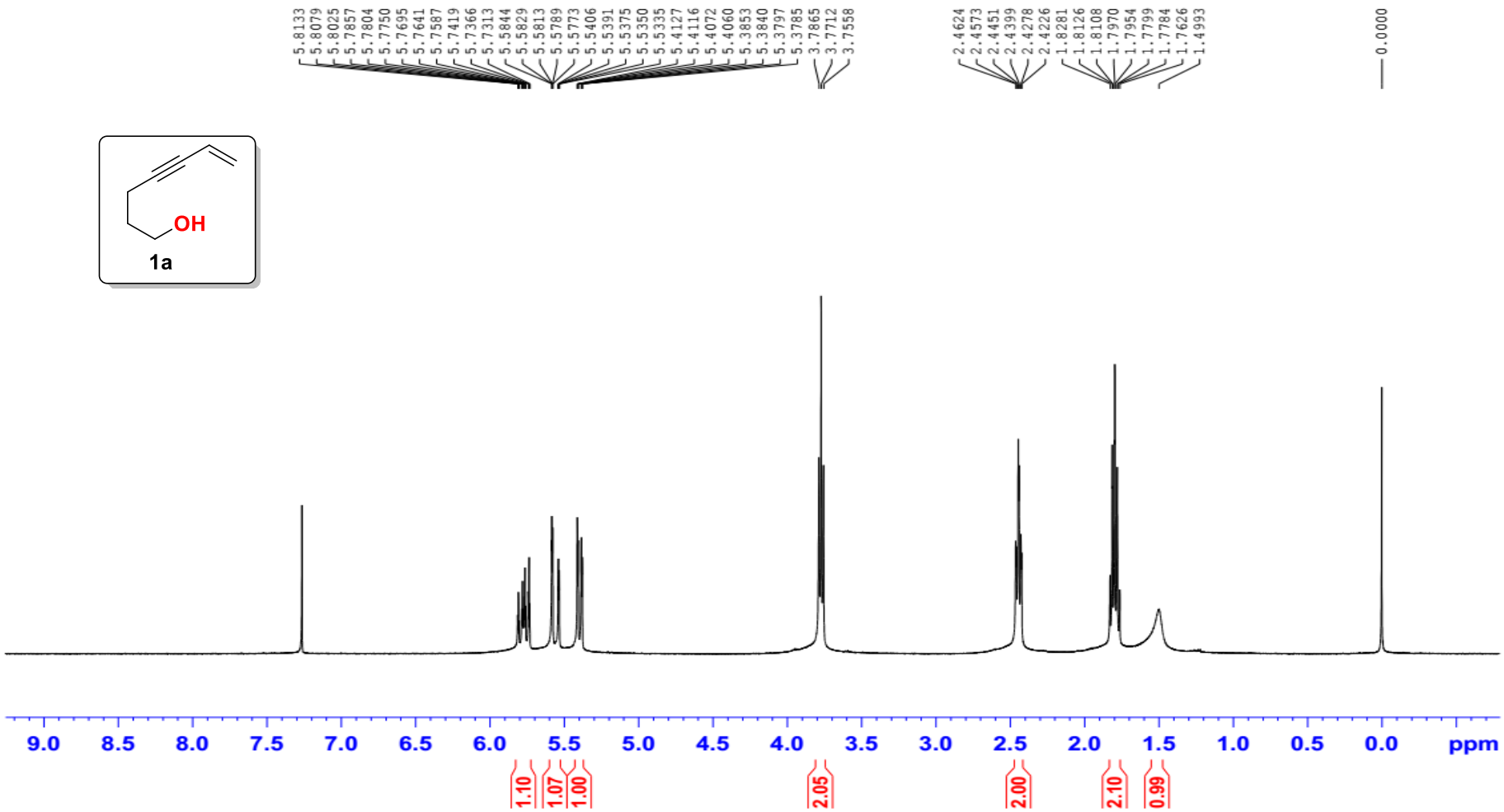
1. (a) Heaney, H.; Papageorgiou, G.; Wilkins, R. F. *Tetrahedron* **1997**, *53*, 2941-2958; (b) Rosenau, T.; Potthast, A.; Kosma, P. *Tetrahedron* **2004**, *60*, 301-306.

2. (a) Yoshida, K.; Shida, H.; Takahashi, H.; Yanagisawa, A. *Chem. Eur. J.* **2011**, *17*, 344-349; (b) Zhang, Y.; Yu, B.; Gao, B.; Zhang, T.; Huang, H. *Org. Lett.* **2019**, *21*, 535-539; (c) Yin, H.; Jin, M.; Chen, W.; Chen, C.; Zheng, L.; Wei, P.; Han, S. *Tetrahedron Lett*. **2012**, *53*, 12651270; (d) Feng, X.; Zhang, H.; Lu, W.; Yamamoto, Y.; Almansour, A. I.; Arumugam, N.; Kumar, R. S.; Bao, M. *Synthesis* **2017**, *49*, 2727-2732.

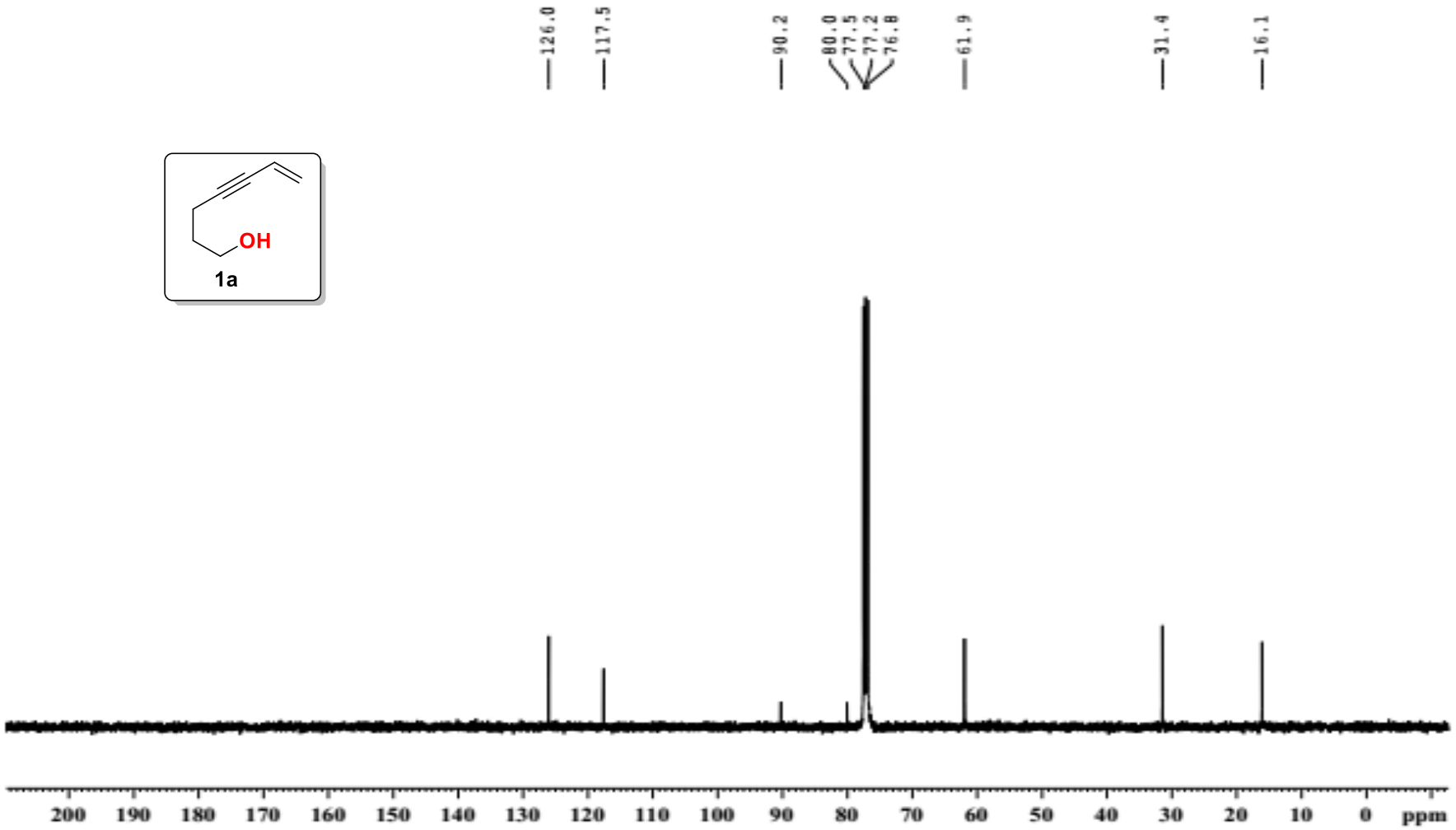
3. Grayson, E. J.; Davis, B. G. *Org. Lett*. **2005**, *7*, 2361-2364.

10. NMR Spectra of Materials and Products

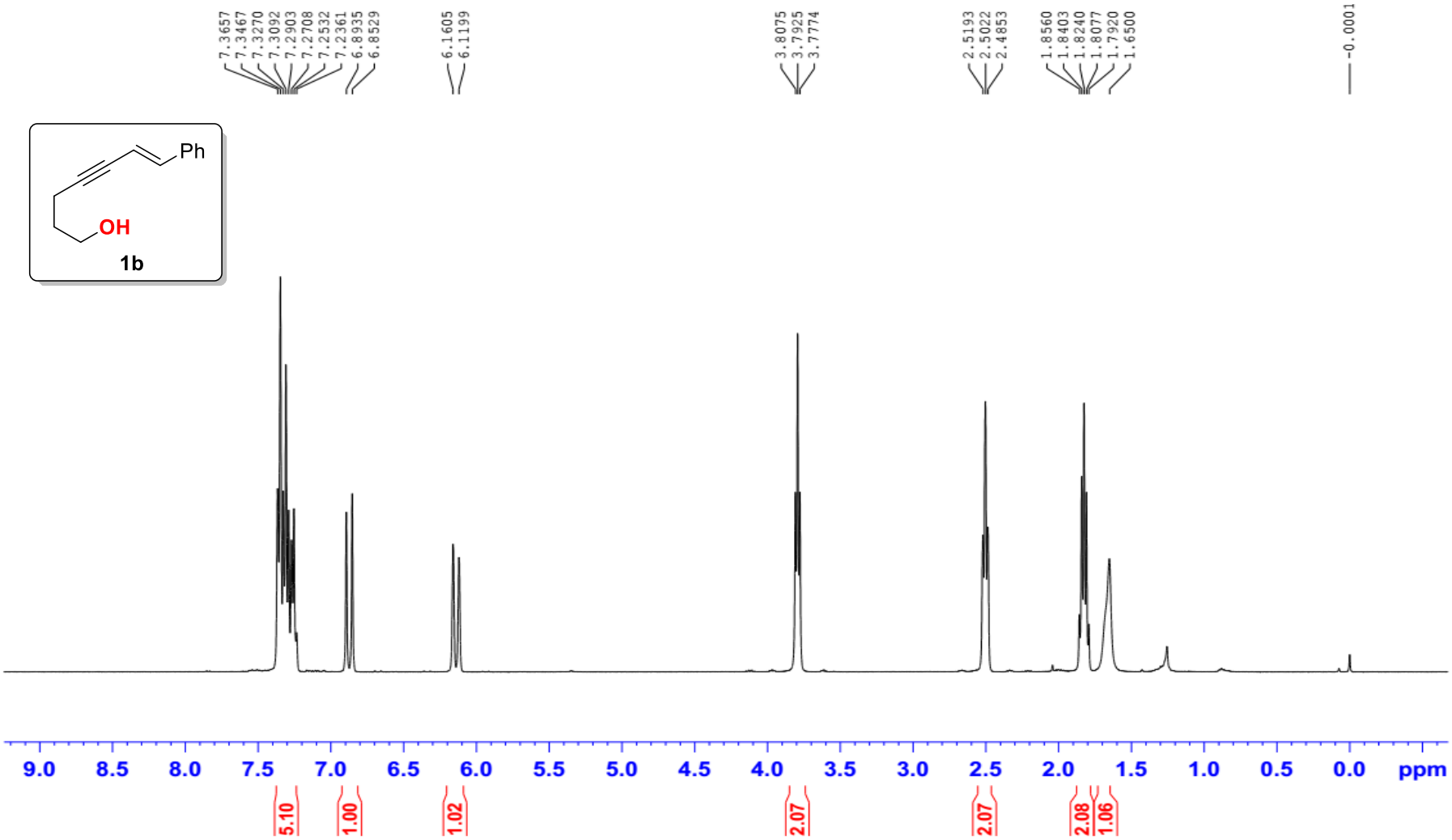
YHJ-S-**1a** ^{1}H NMR (400MHz $CDCl_3$)



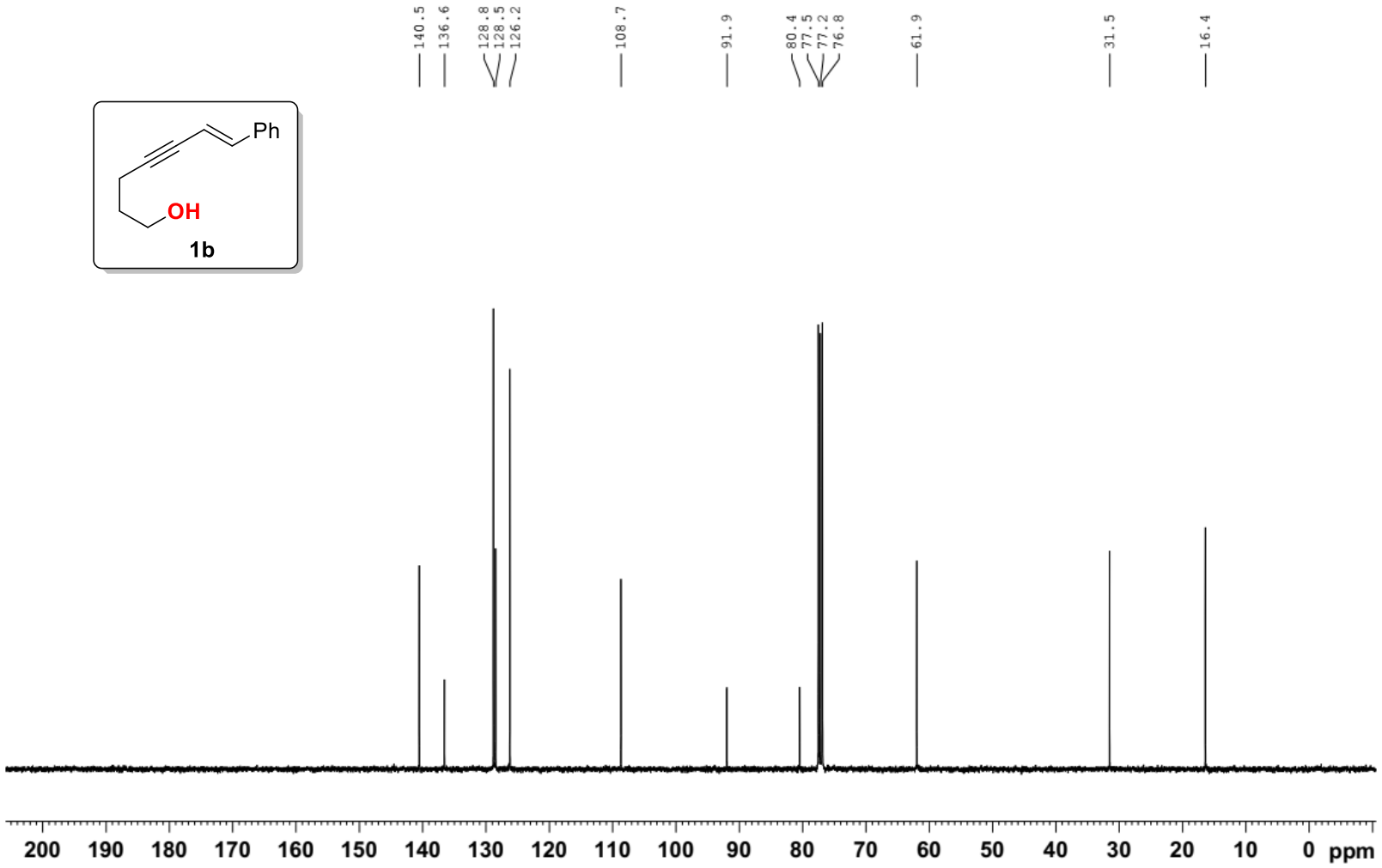
YHJ-S-**1a** ^{13}C NMR (100MHz $CDCl_3$)



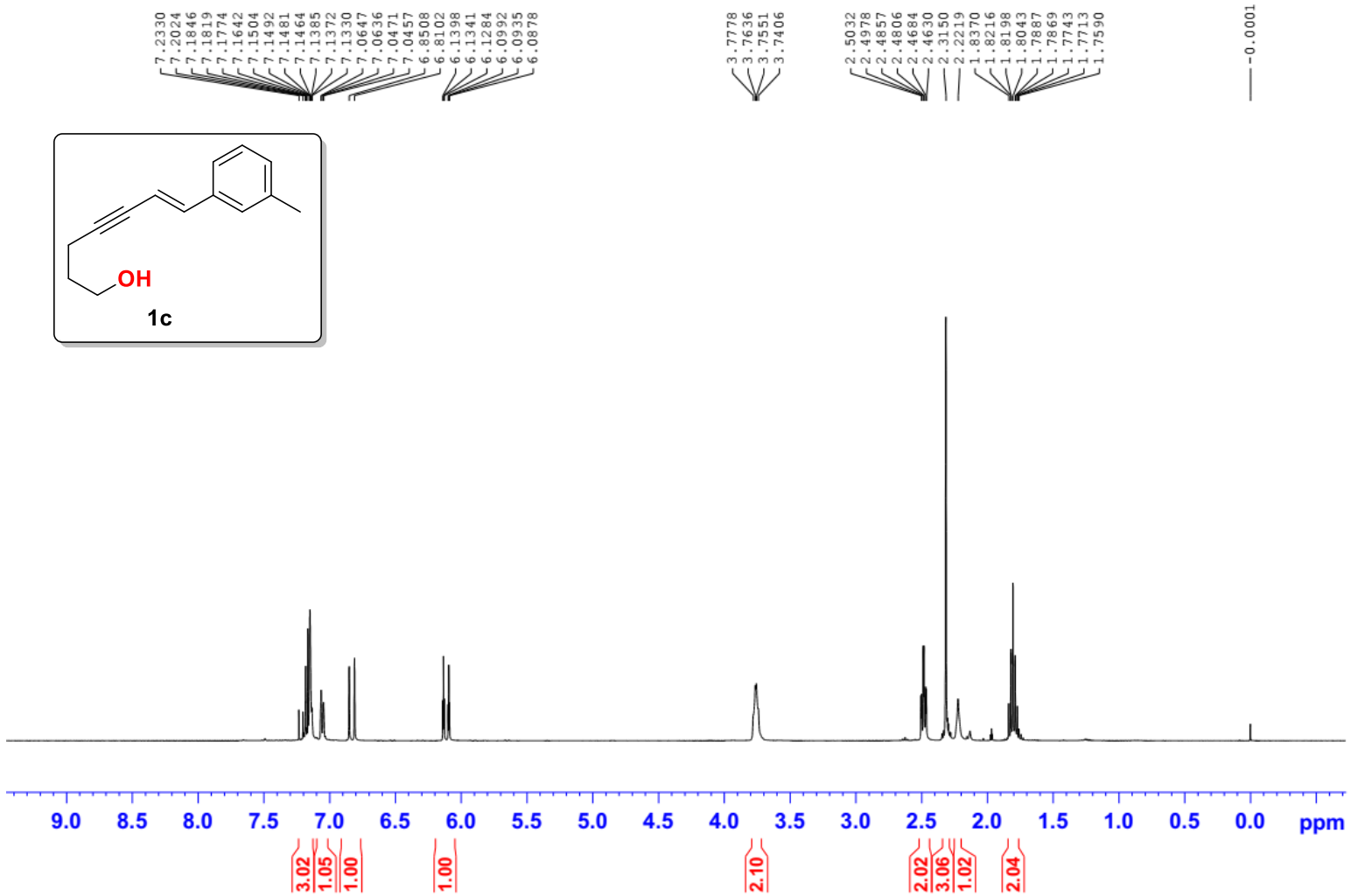
YHJ-S-**1b** ^{1}H NMR (400MHz $CDCl_3$)



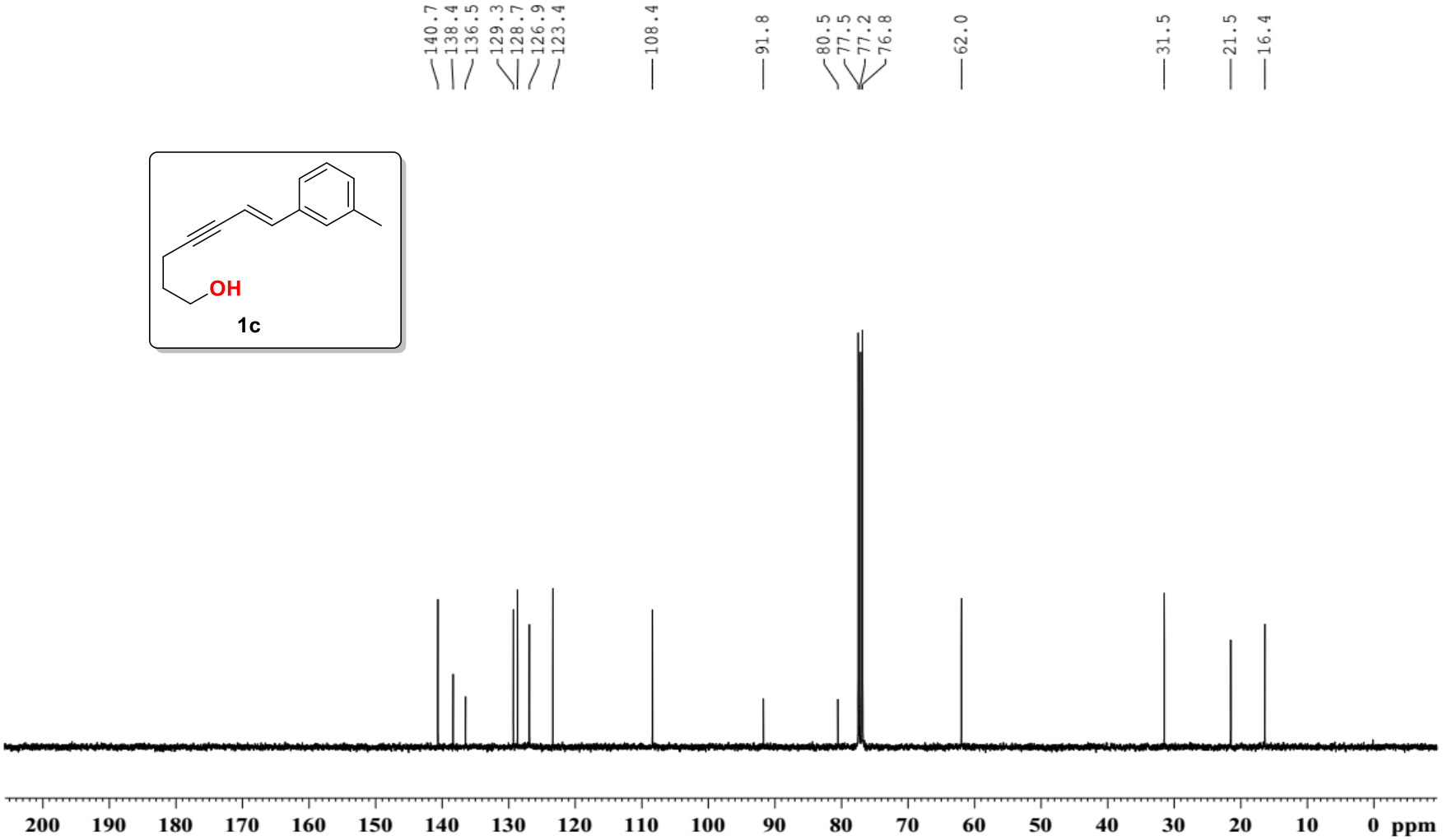
YHJ-S-**1b** ^{13}C NMR (100MHz $CDCl_3$)



YHJ-S-**1c** ^{1}H NMR (400MHz $CDCl_3$)



YHJ-S-**1c** ^{13}C NMR (100MHz $CDCl_3$)



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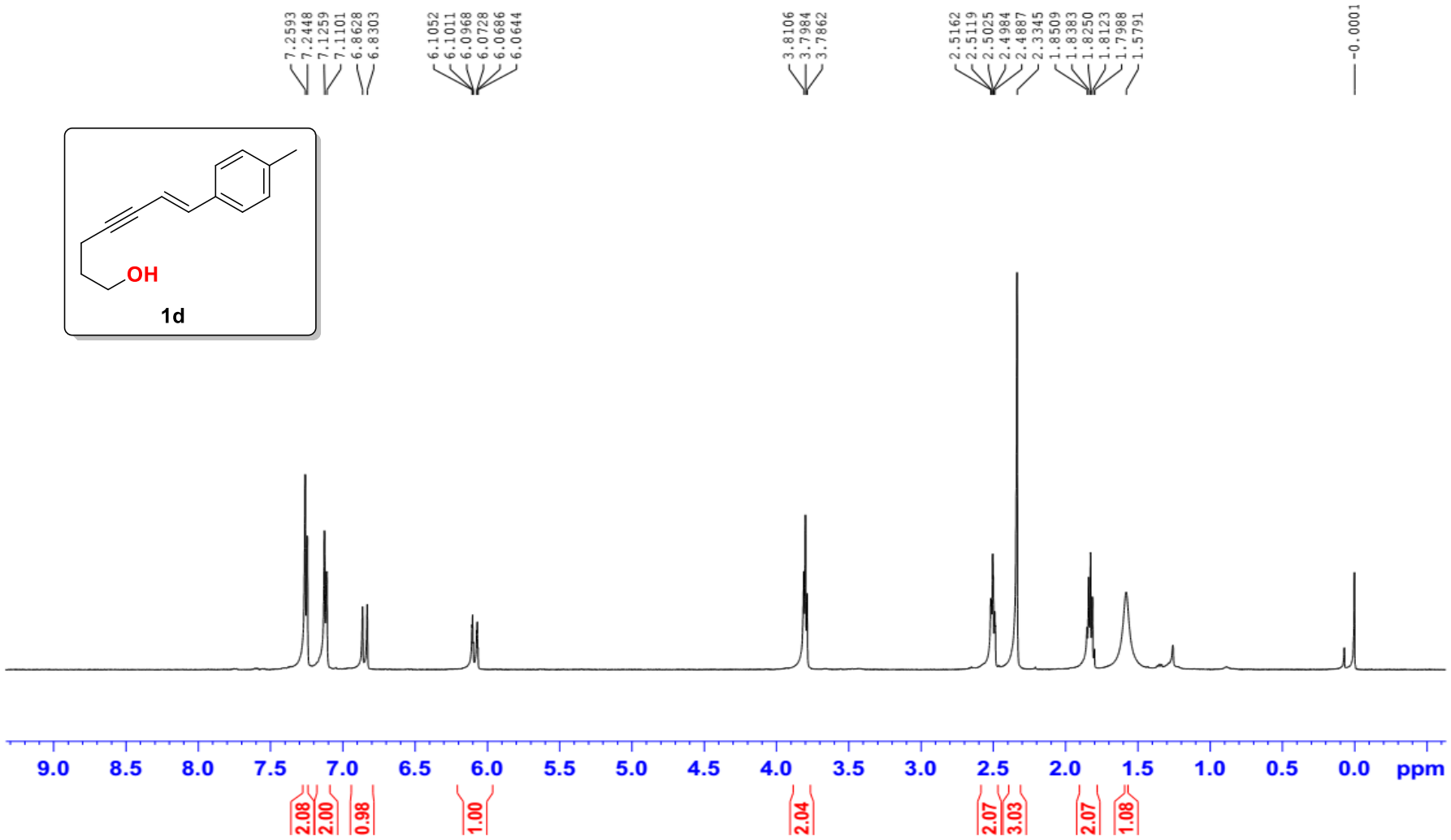
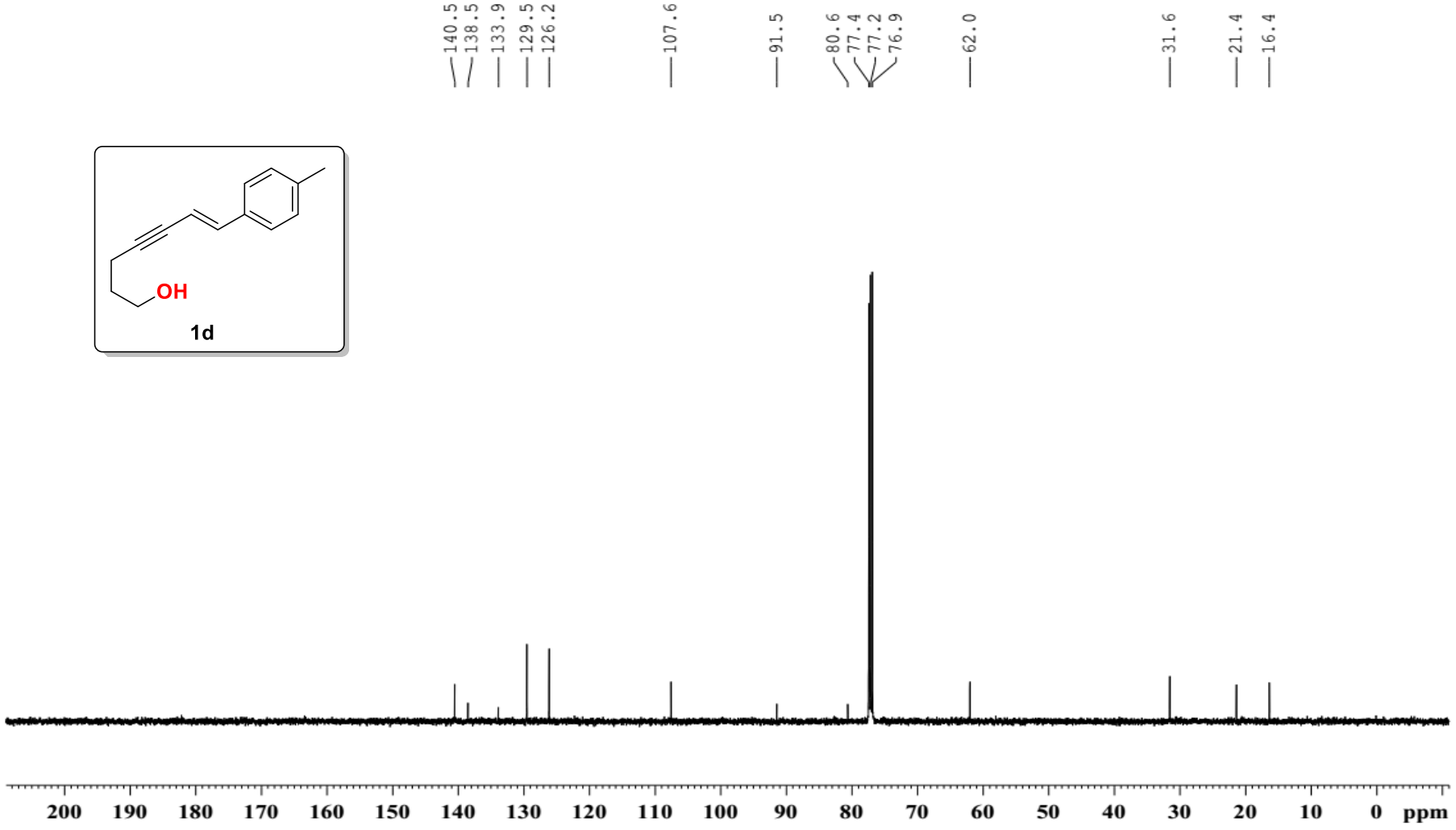
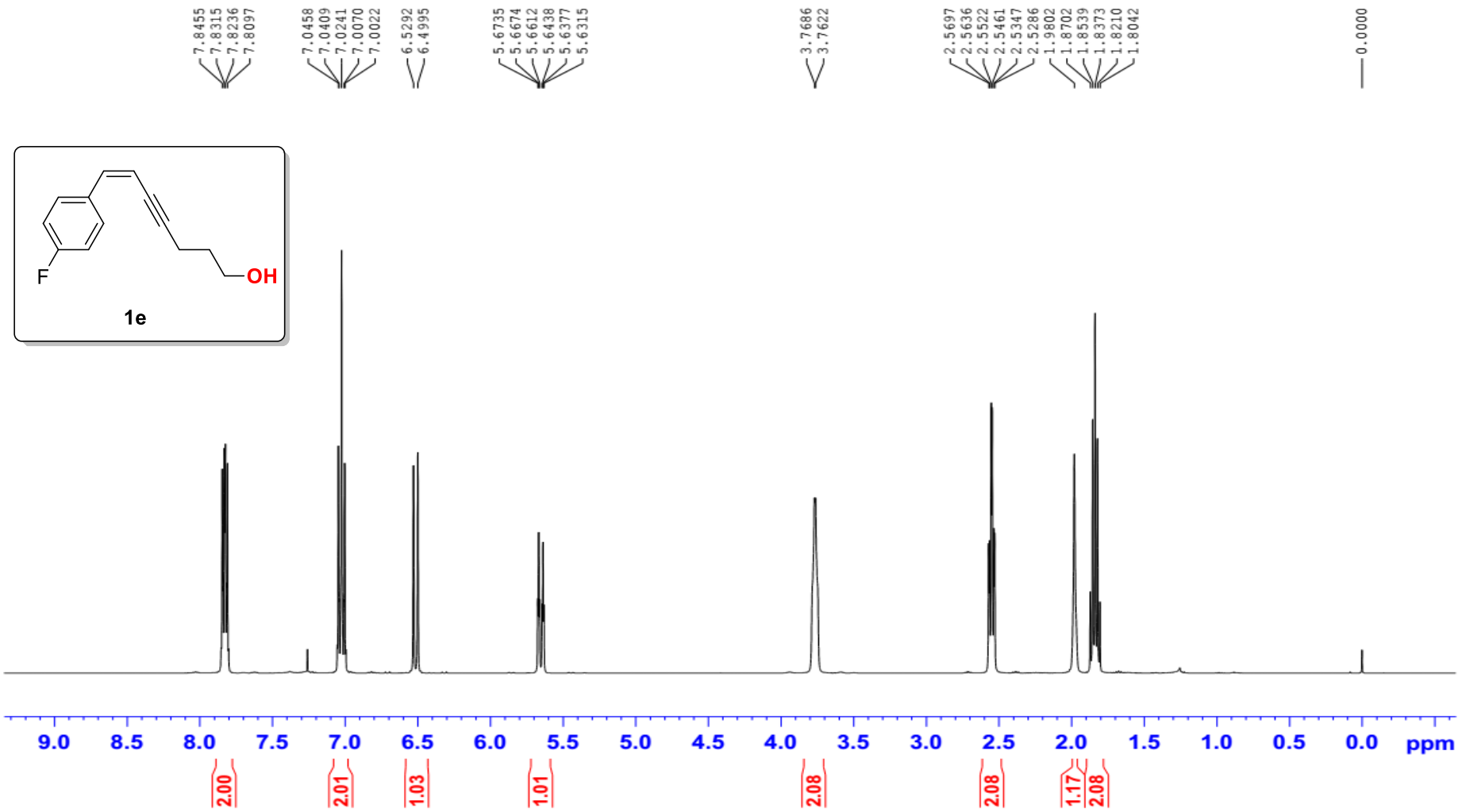


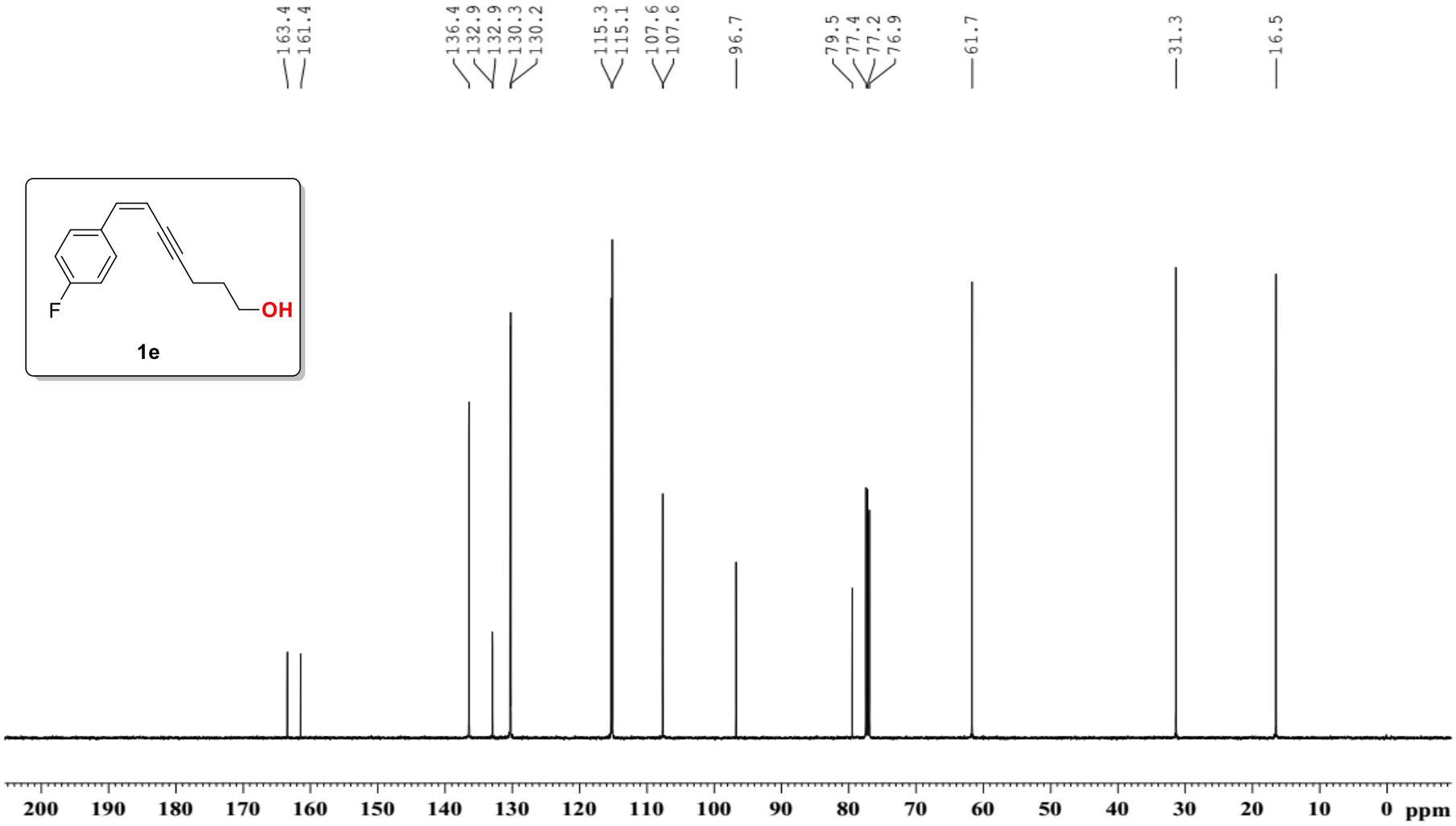
YHJ-S-**1d** ^{13}C NMR (125MHz $CDCl_3$)



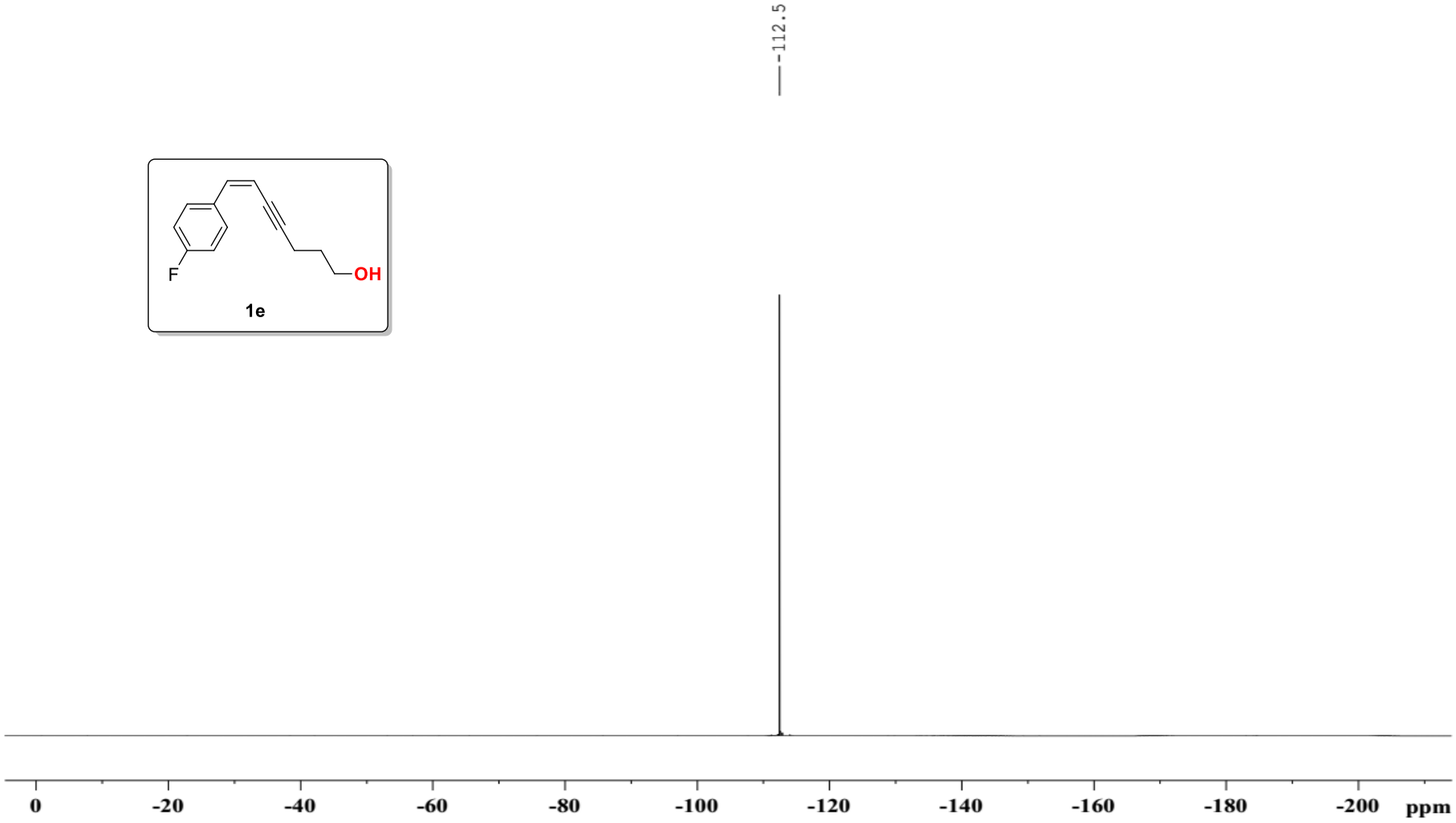
YHJ-S-**1e** ^{1}H NMR (400MHz $CDCl_3$)



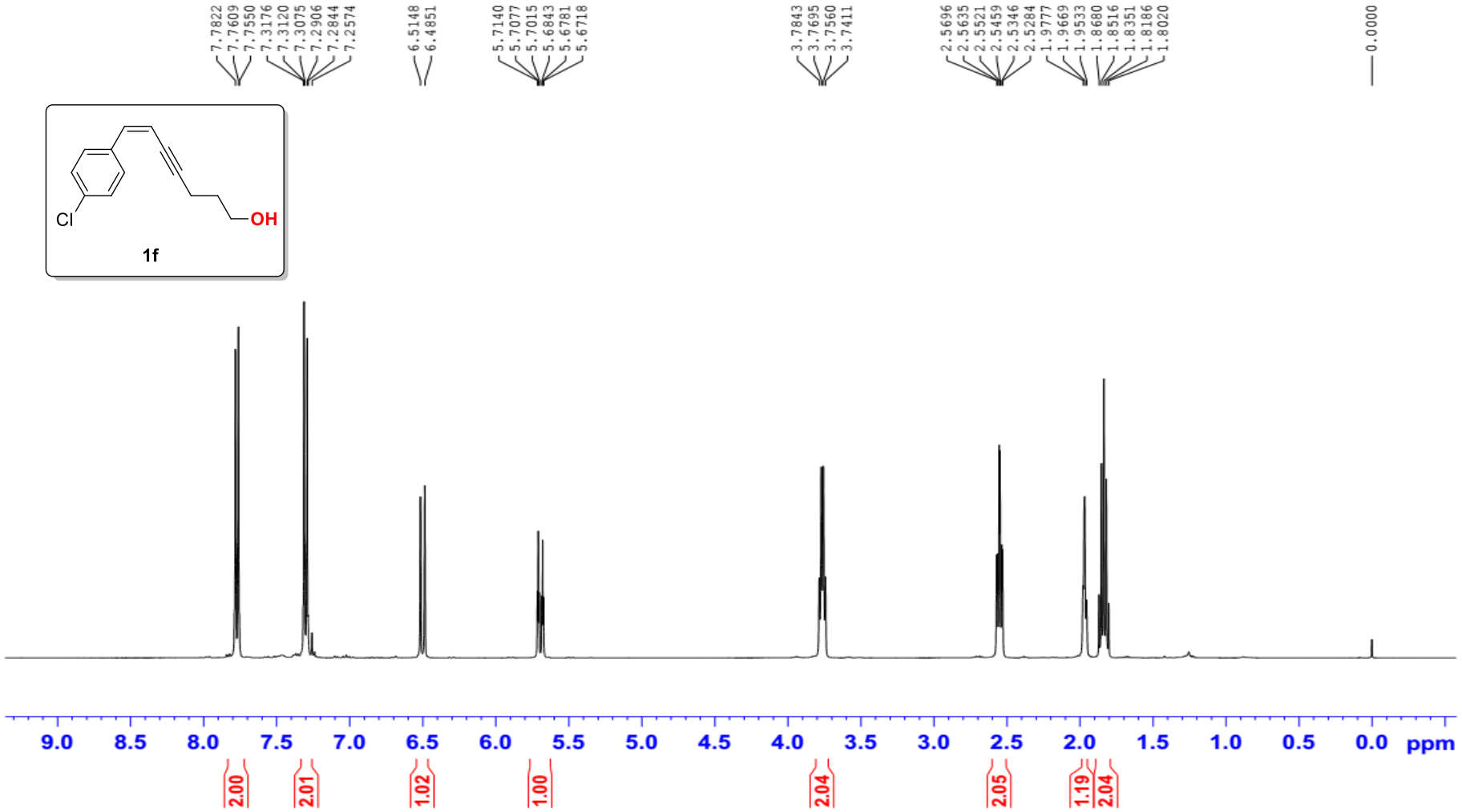
YHJ-S-**1e** ^{13}C NMR (125MHz $CDCl_3$)



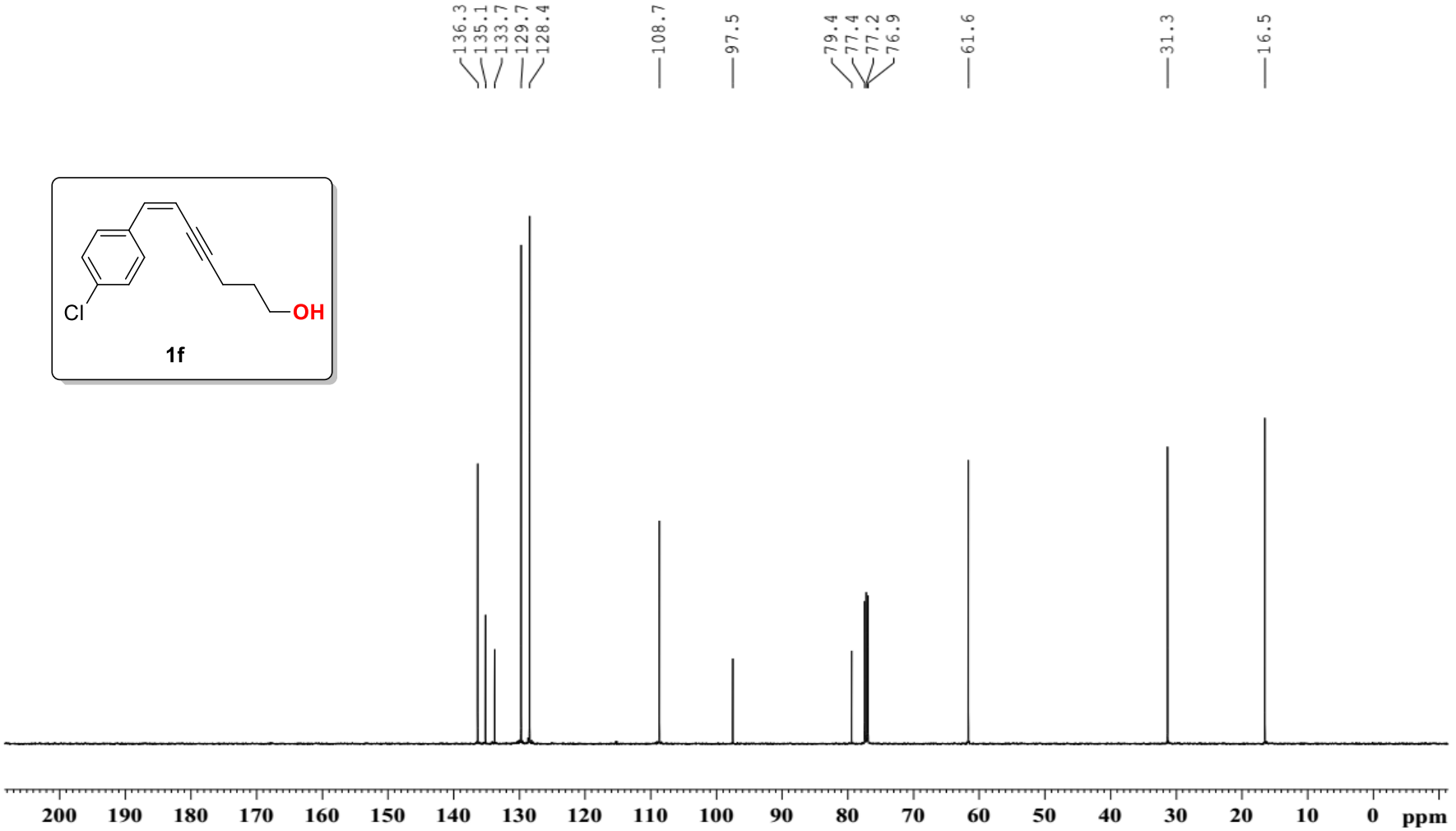
YHJ-S-**1e** ^{19}F NMR (376MHz $CDCl_3$)



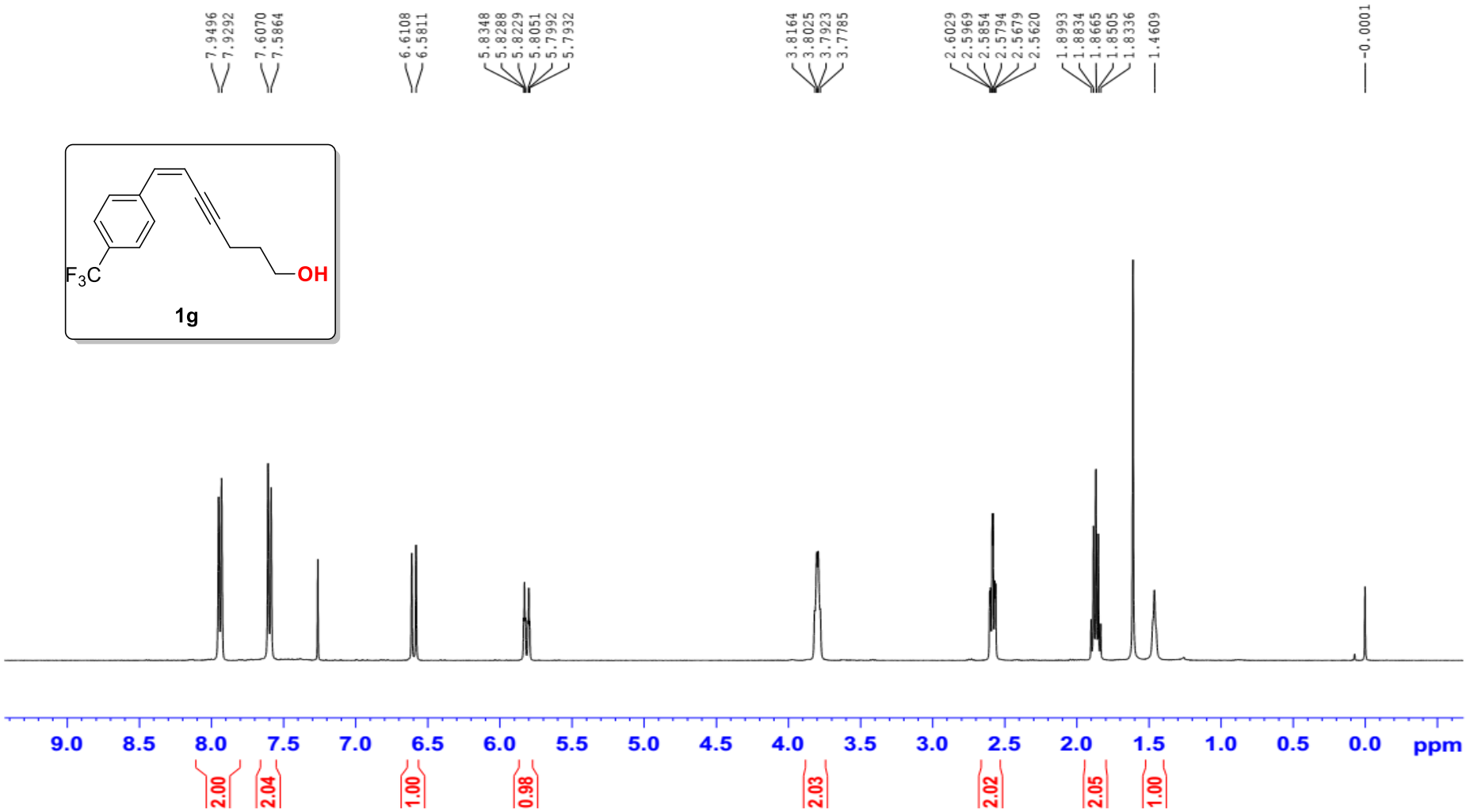
YHJ-S-**1f** ^{1}H NMR (400MHz $CDCl_3$)



YHJ-S-**1f** ^{13}C NMR (125MHz $CDCl_3$)



YHJ-S-**1g** ^{1}H NMR (400MHz $CDCl_3$)



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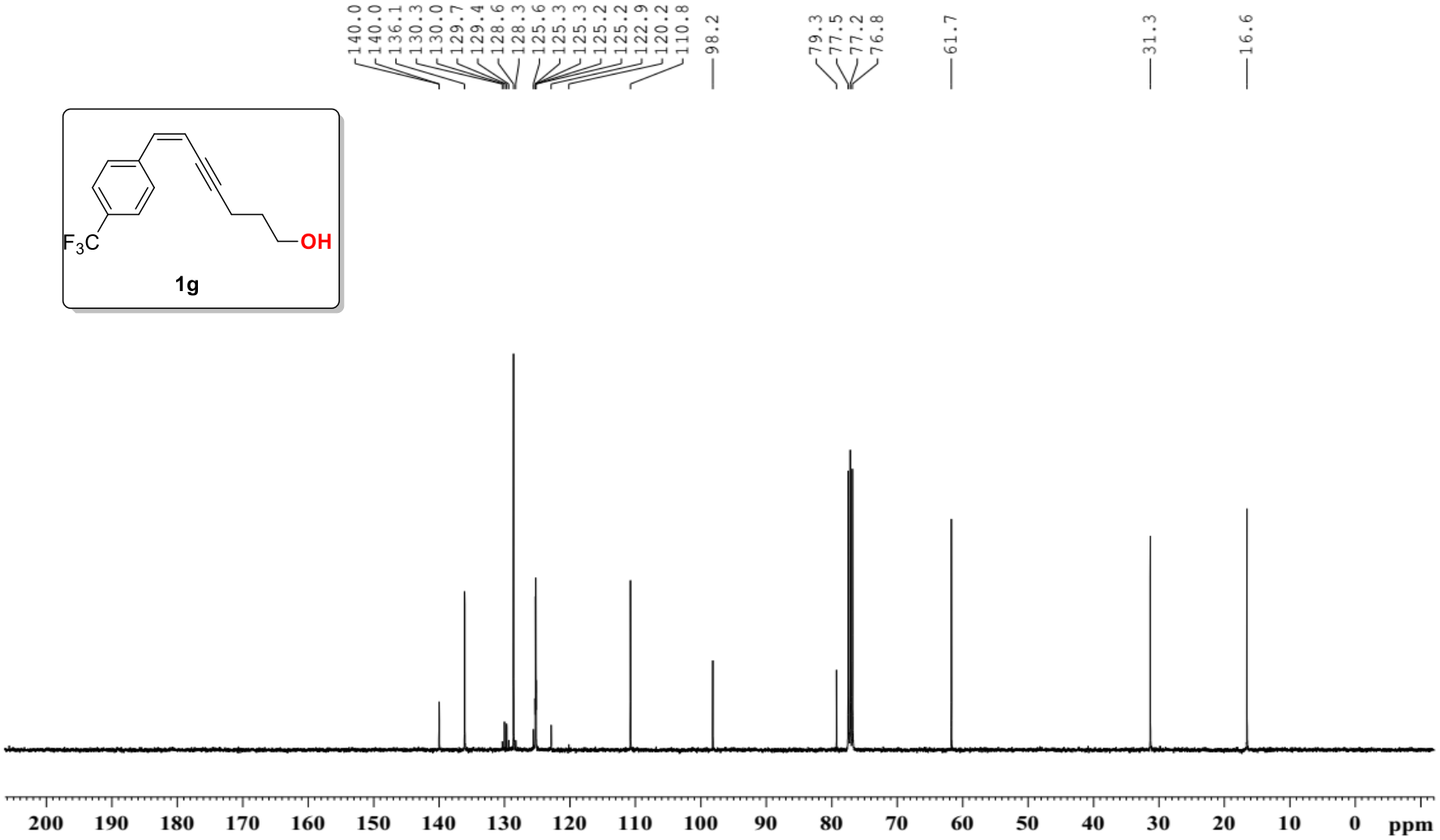
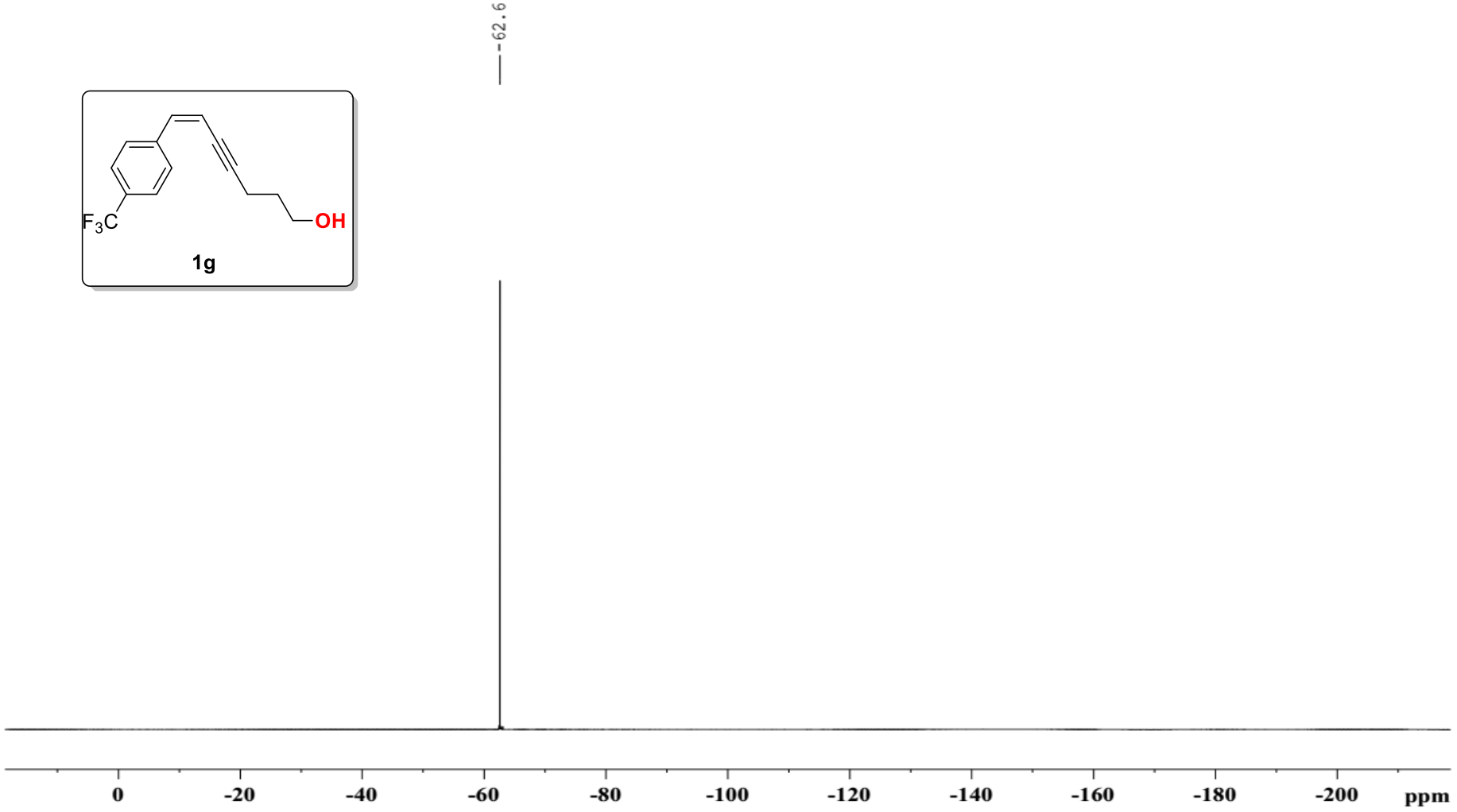
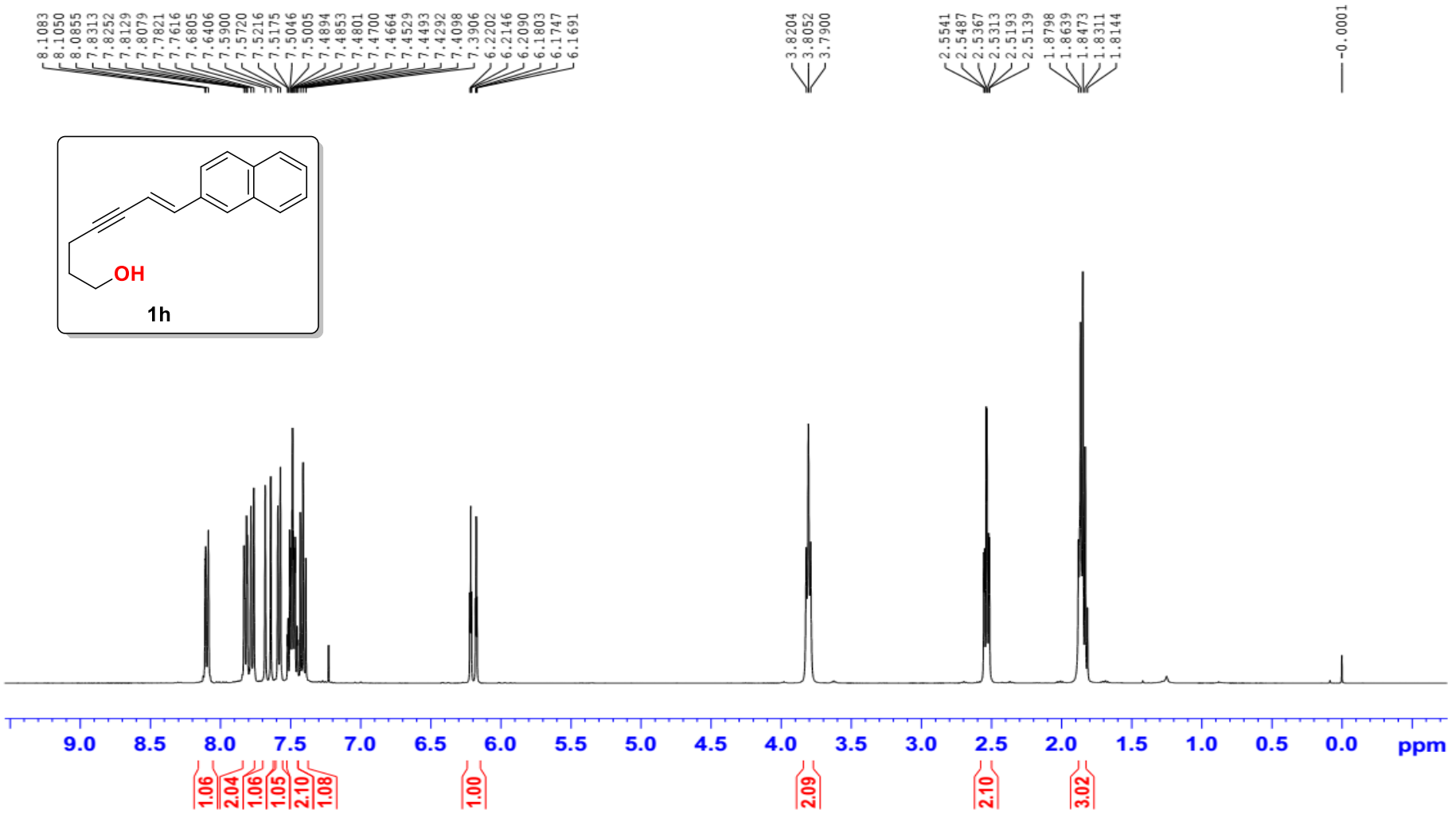


YHJ-S-**1g** ^{19}F NMR (376MHz $CDCl_3$)



YHJ-S-**1h** ^{1}H NMR (400MHz $CDCl_3$)



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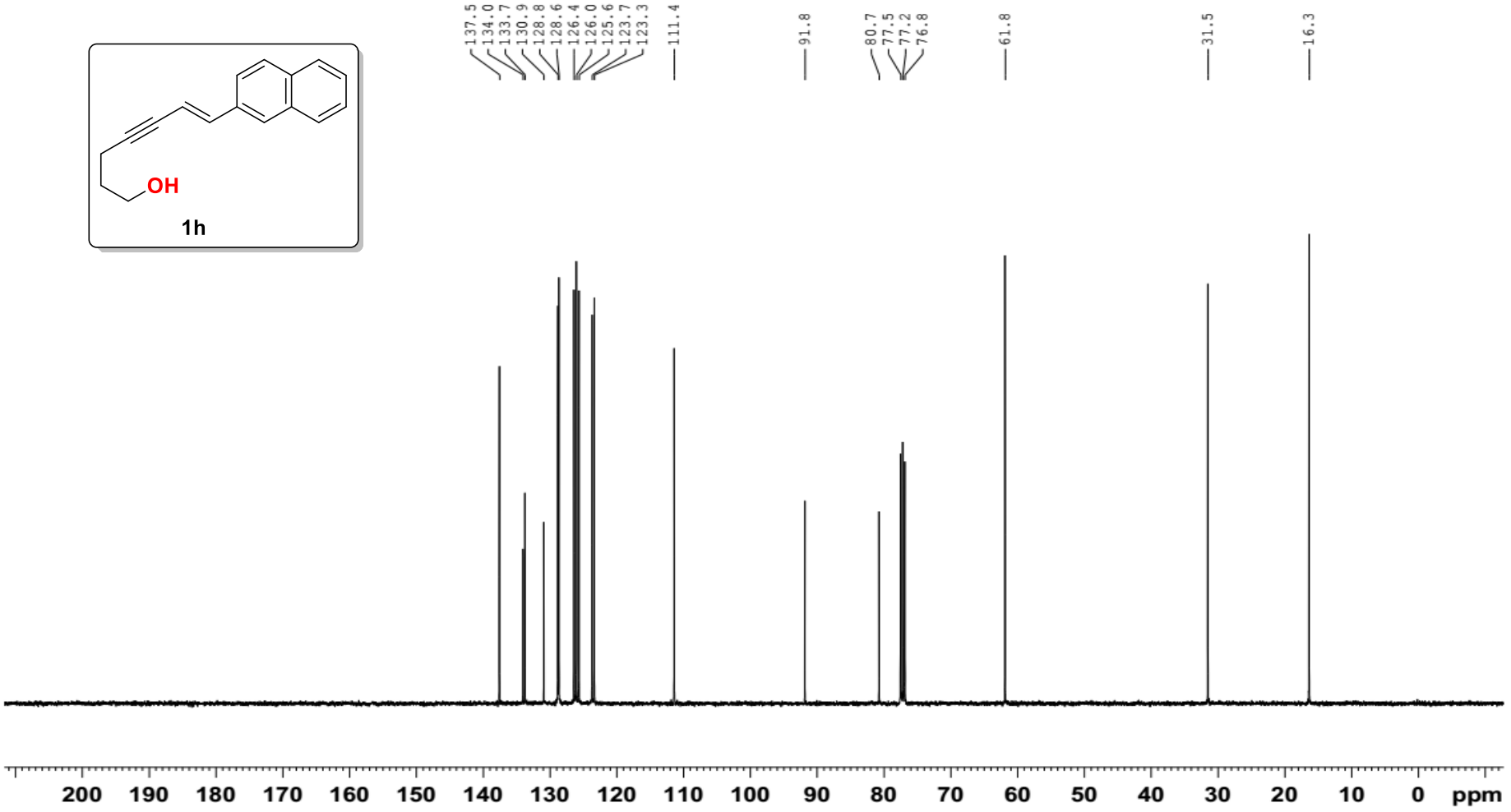

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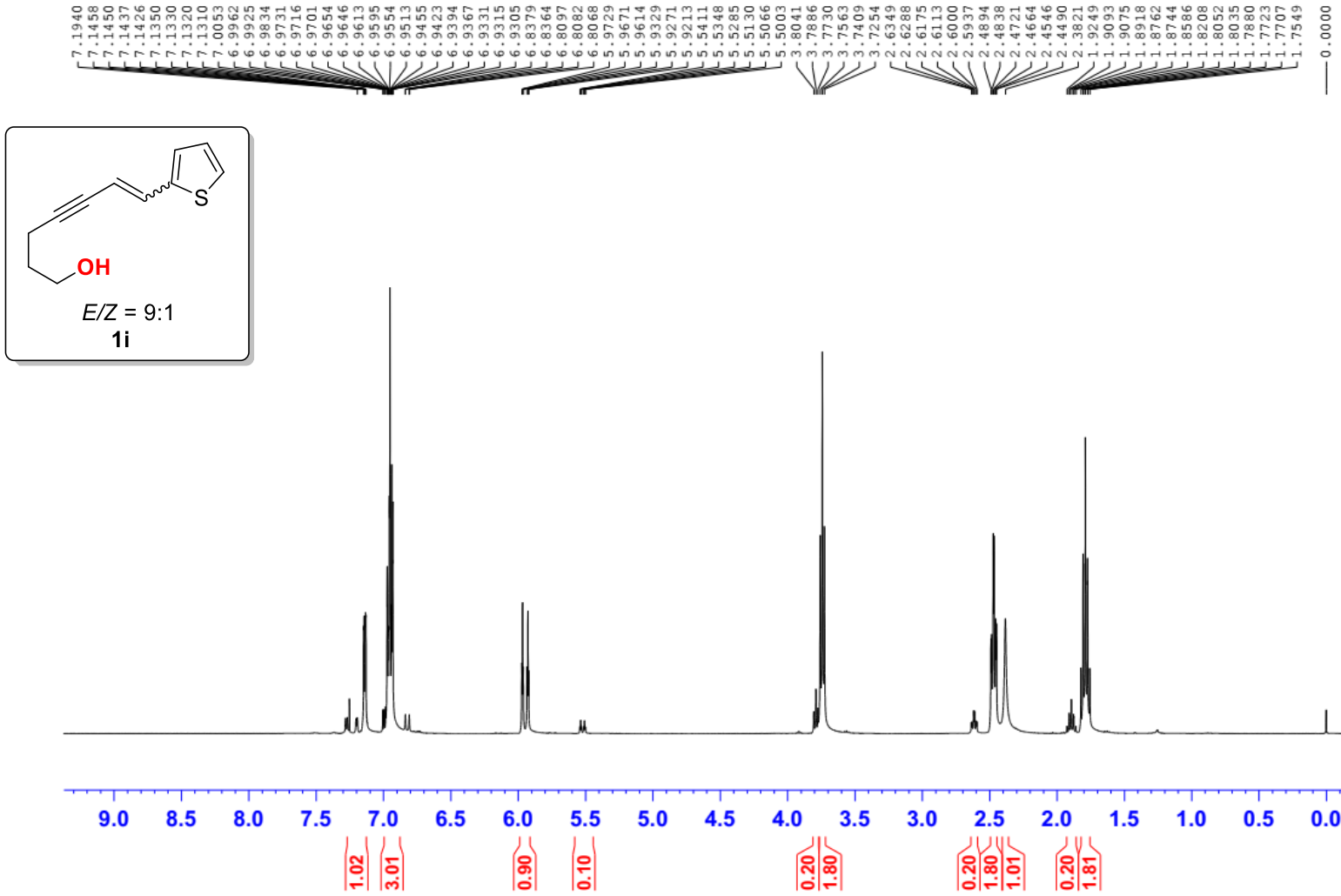
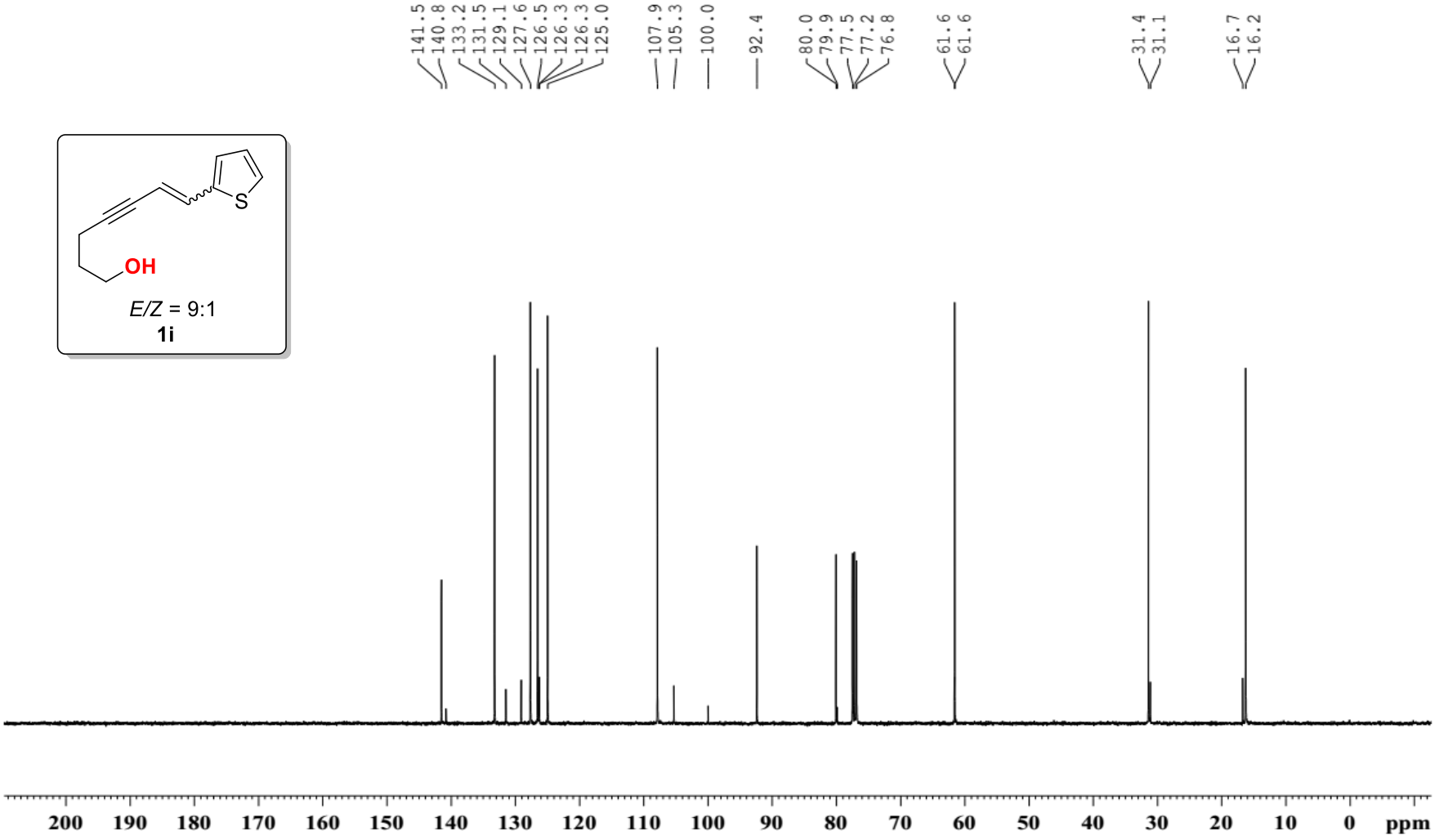
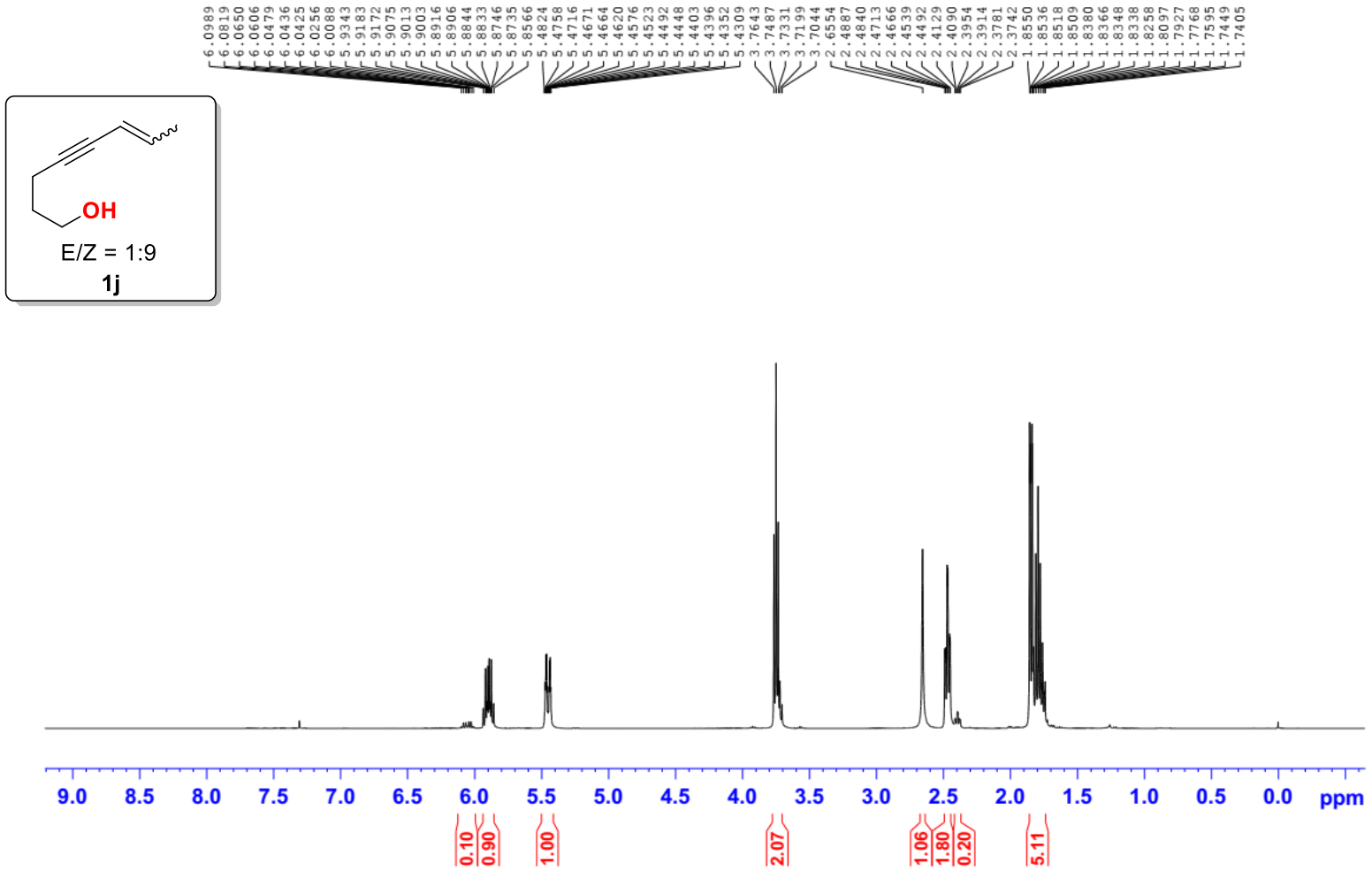


YHJ-S-**1i** ^{13}C NMR (100MHz $CDCl_3$)



YHJ-S-**1j** ^{1}H NMR (400MHz $CDCl_3$)



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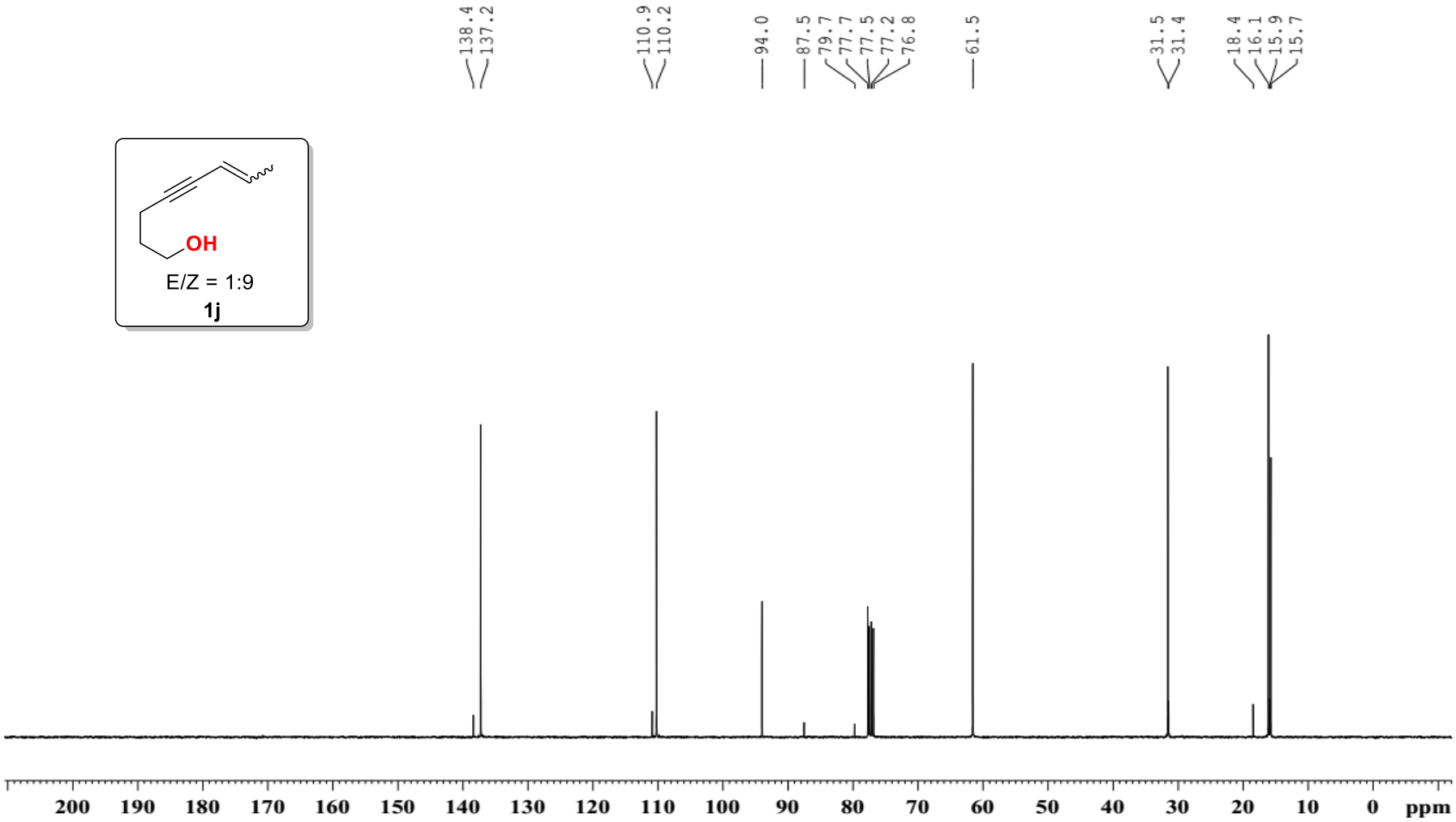
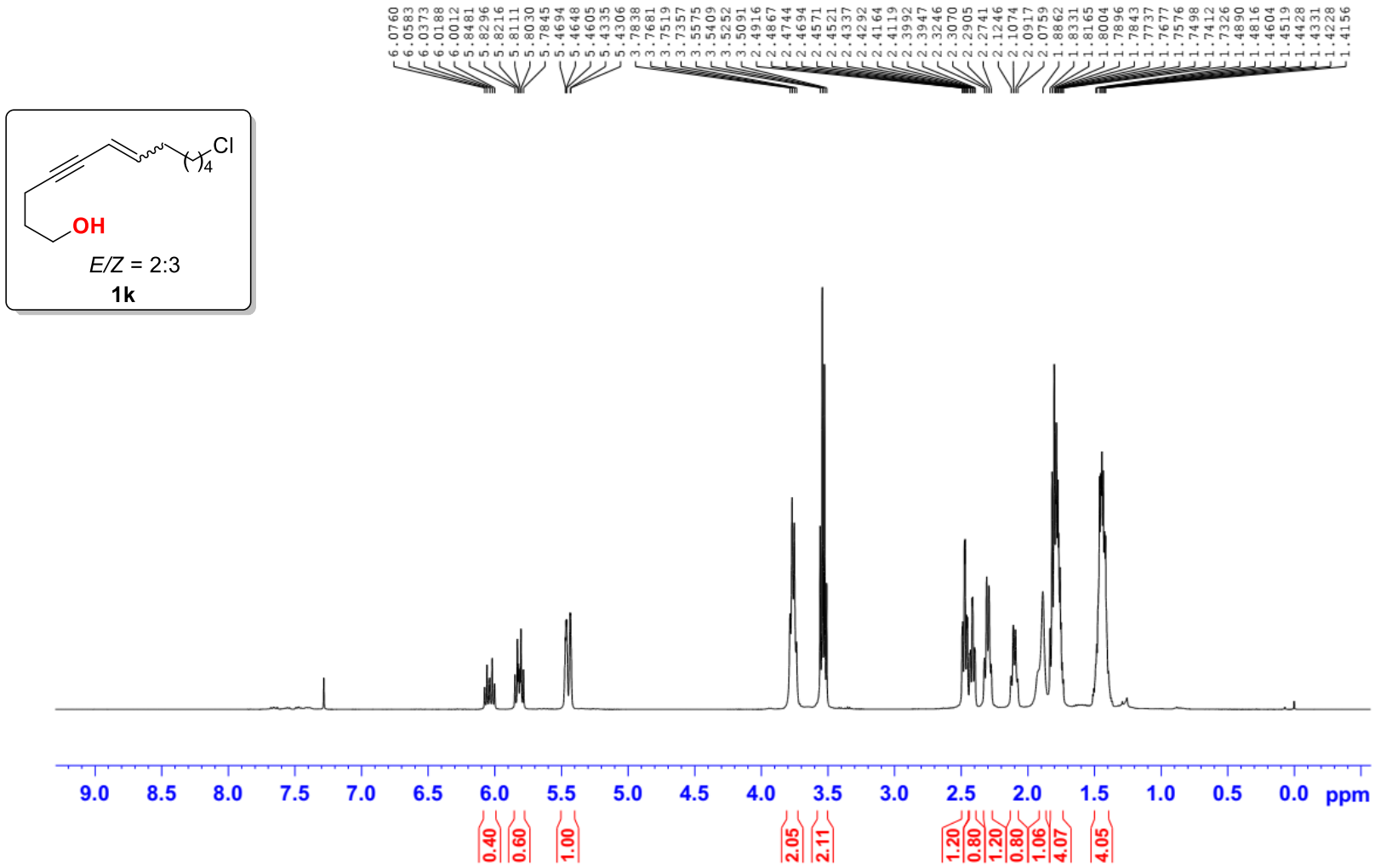
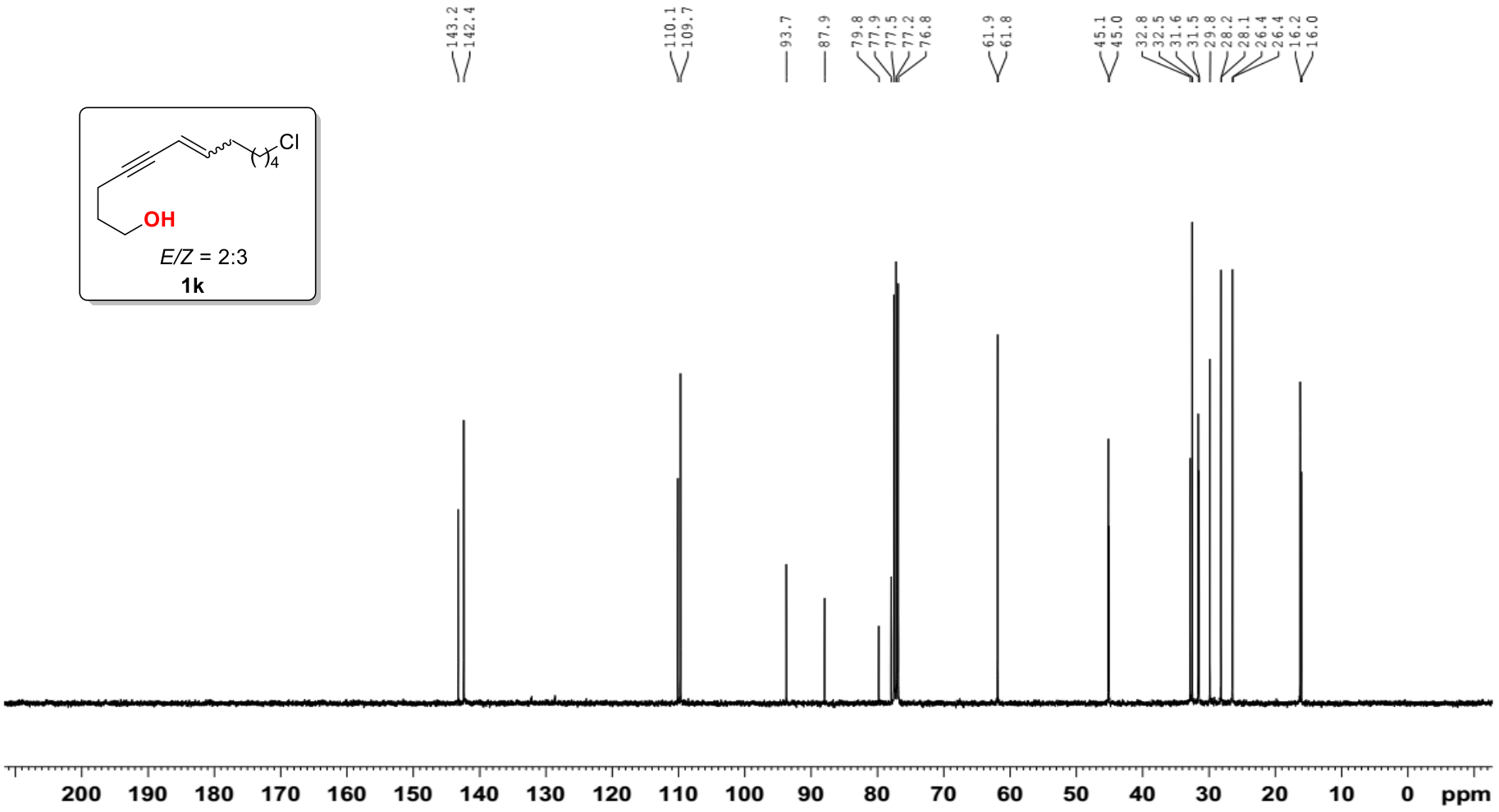


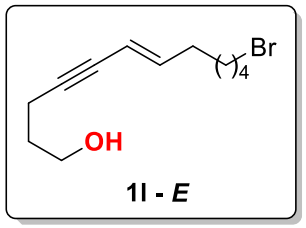
YHJ-S-**1k** ^{1}H NMR (400MHz $CDCl_3$)



YHJ-S-**1k** ^{13}C NMR (100MHz $CDCl_3$)

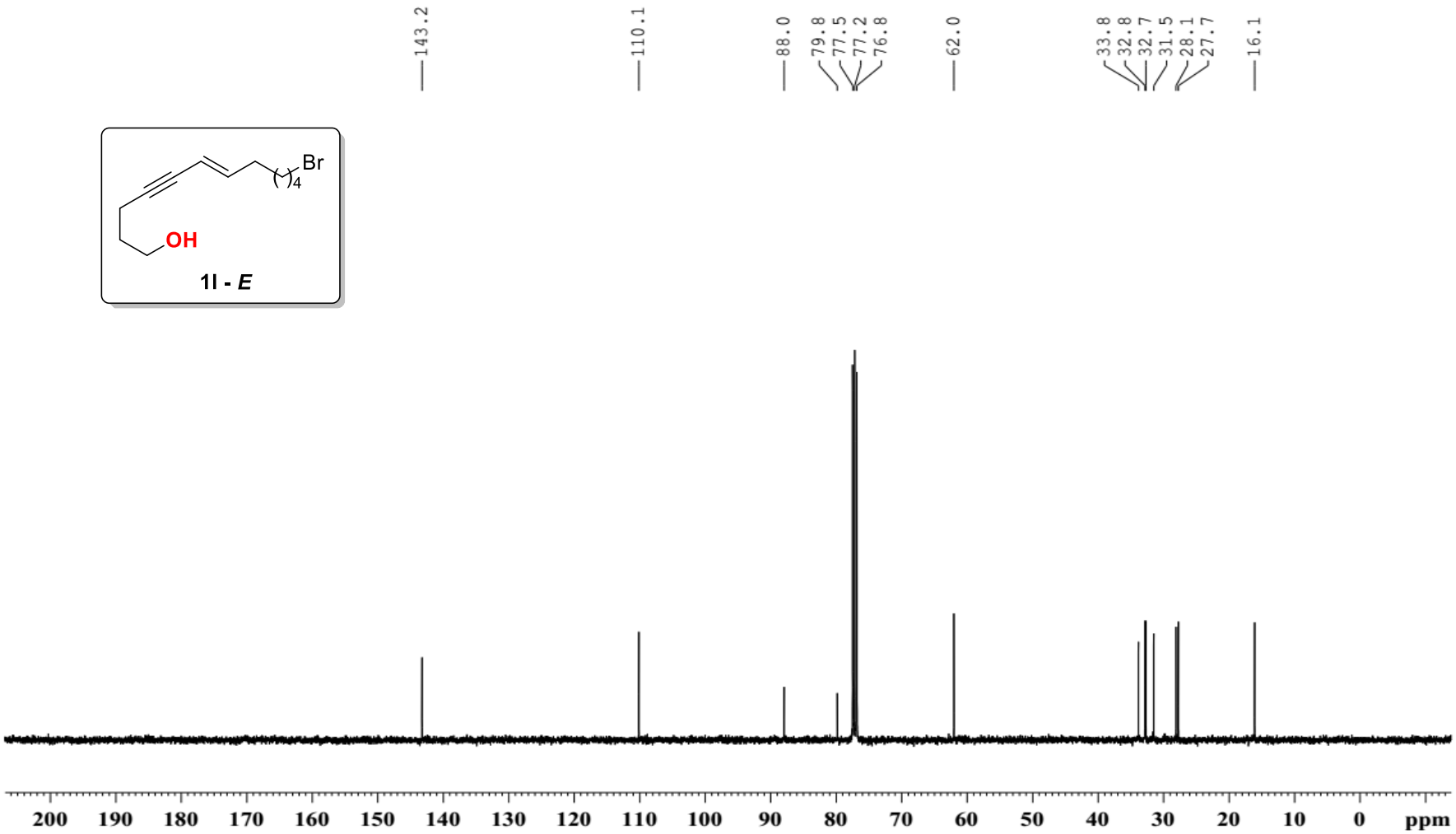


YHJ-S-**1l-*E*** ^{1}H NMR (400MHz $CDCl_3$)

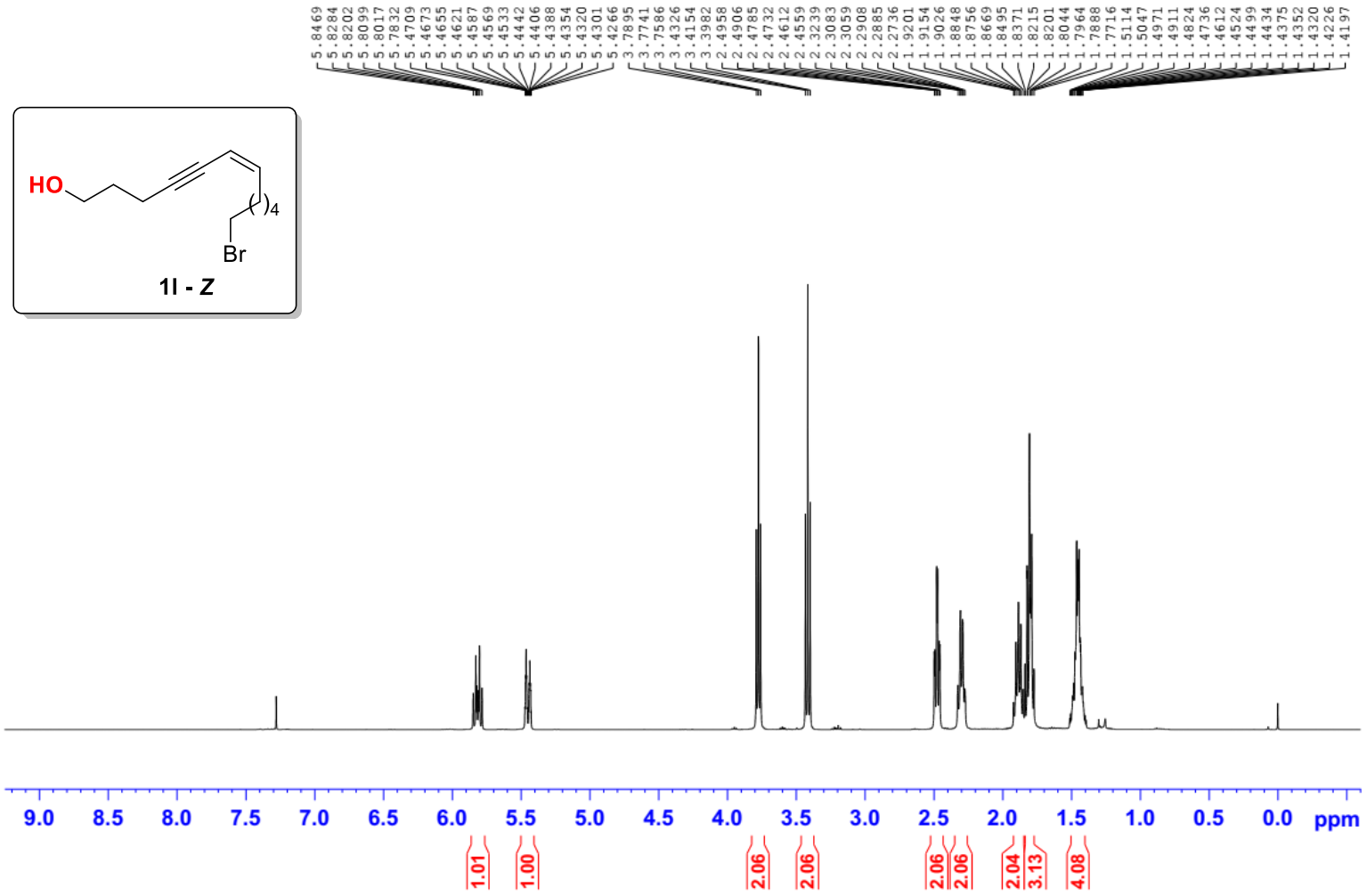


1l - *E*

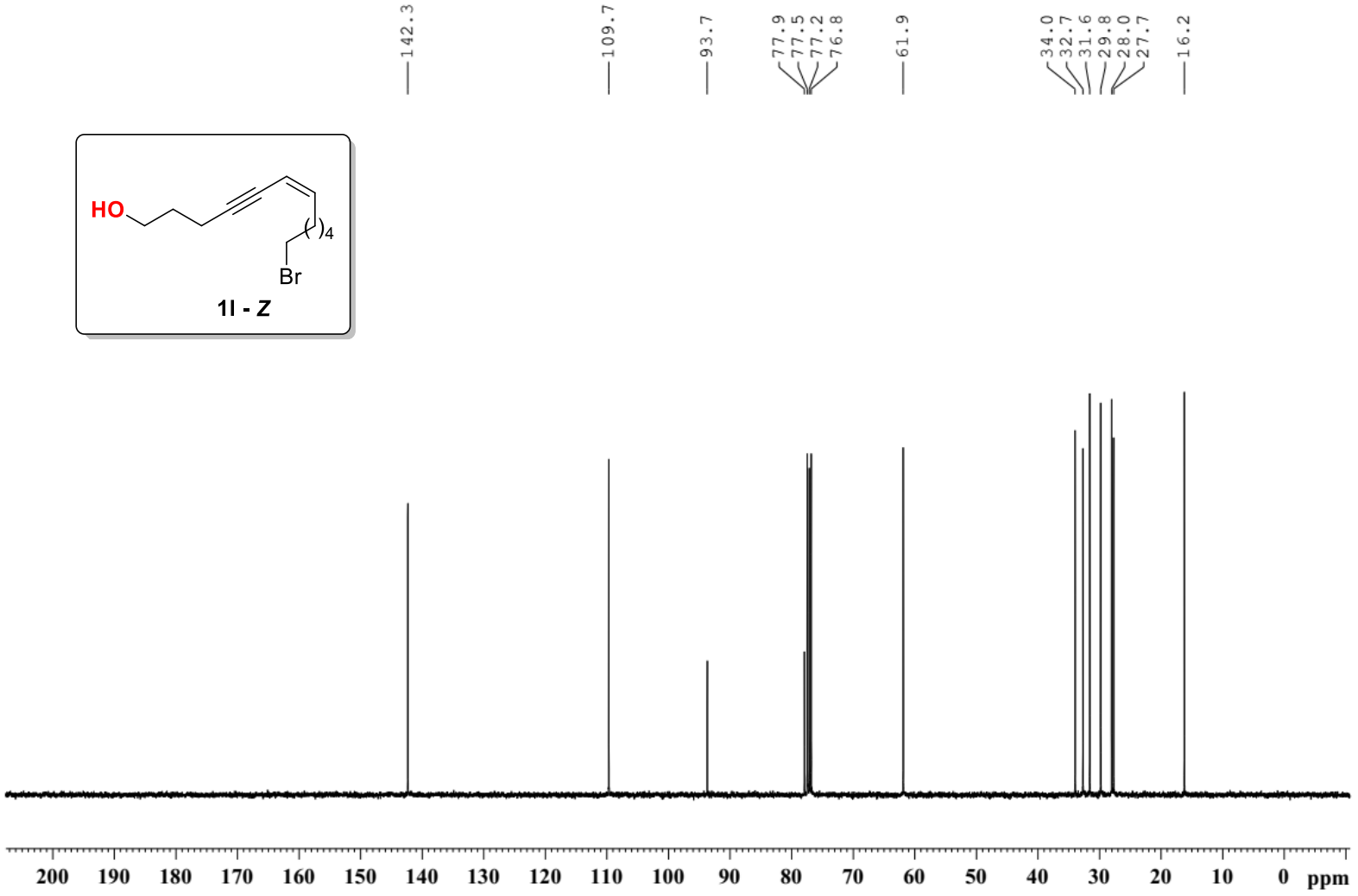
YHJ-S-**1l-*E*** ^{13}C NMR (100MHz $CDCl_3$)



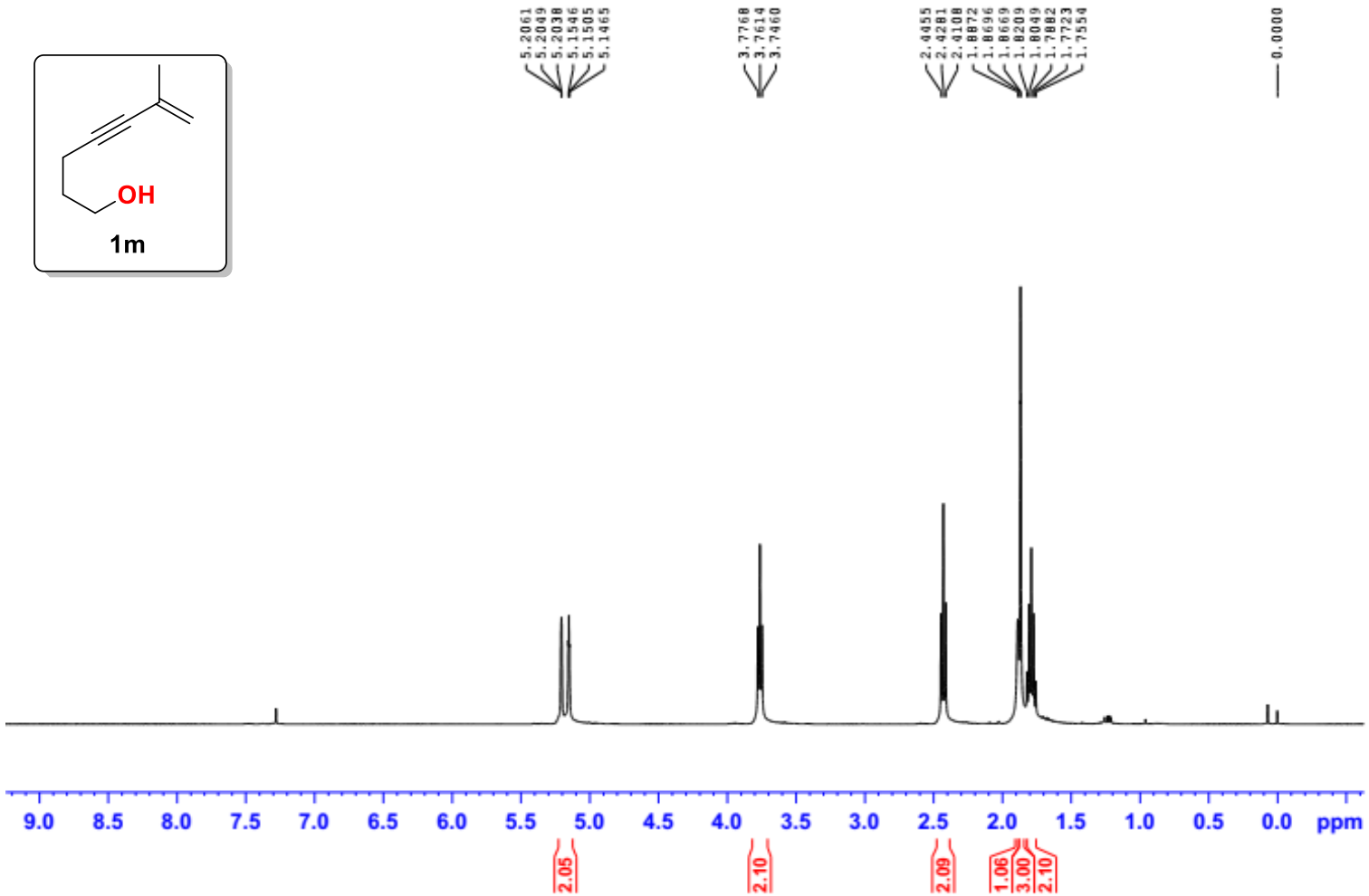
YHJ-S-**1l-*Z*** ^{1}H NMR (400MHz $CDCl_3$)



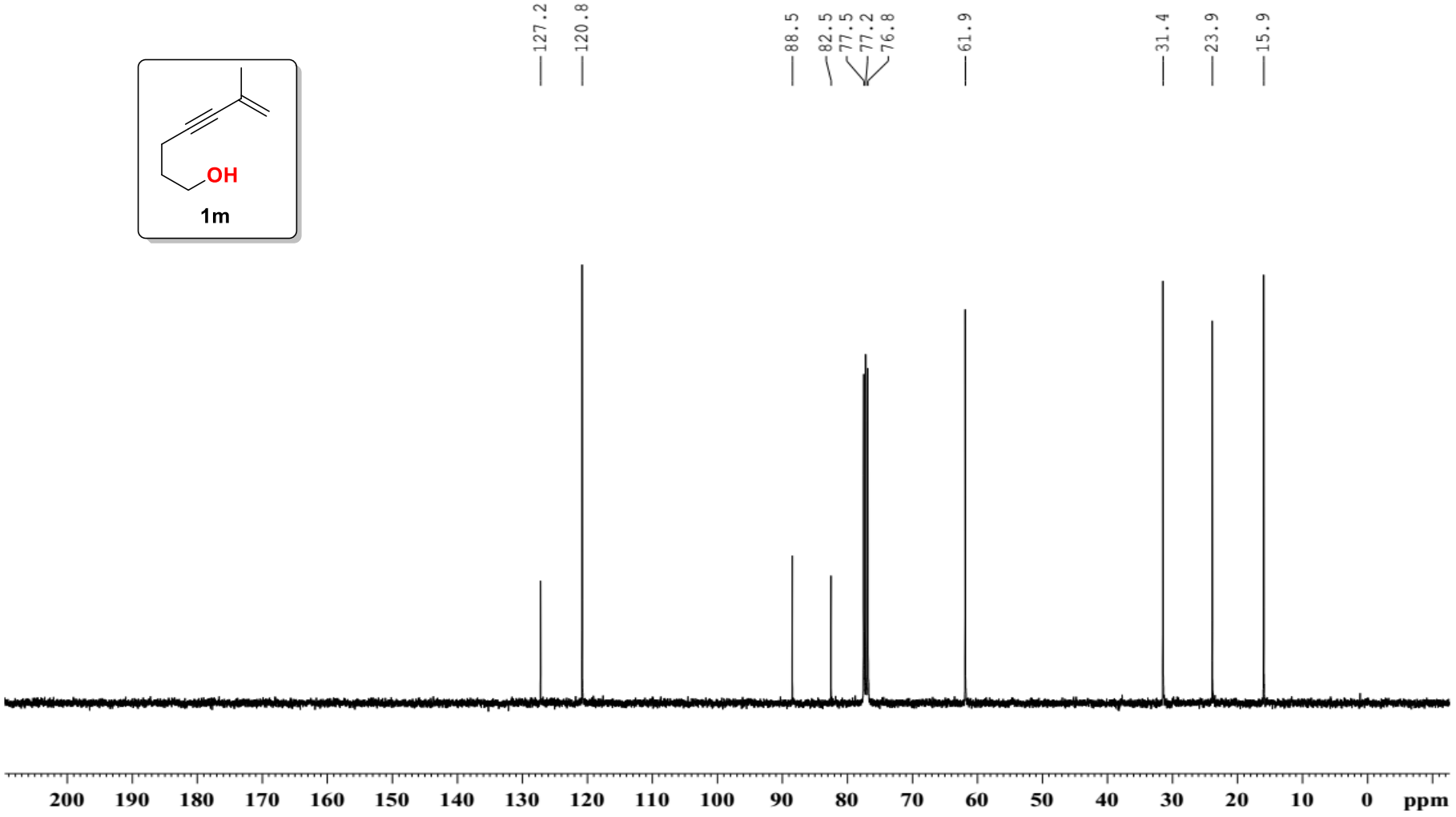
YHJ-S-**1l-*Z*** ^{13}C NMR (100MHz $CDCl_3$)



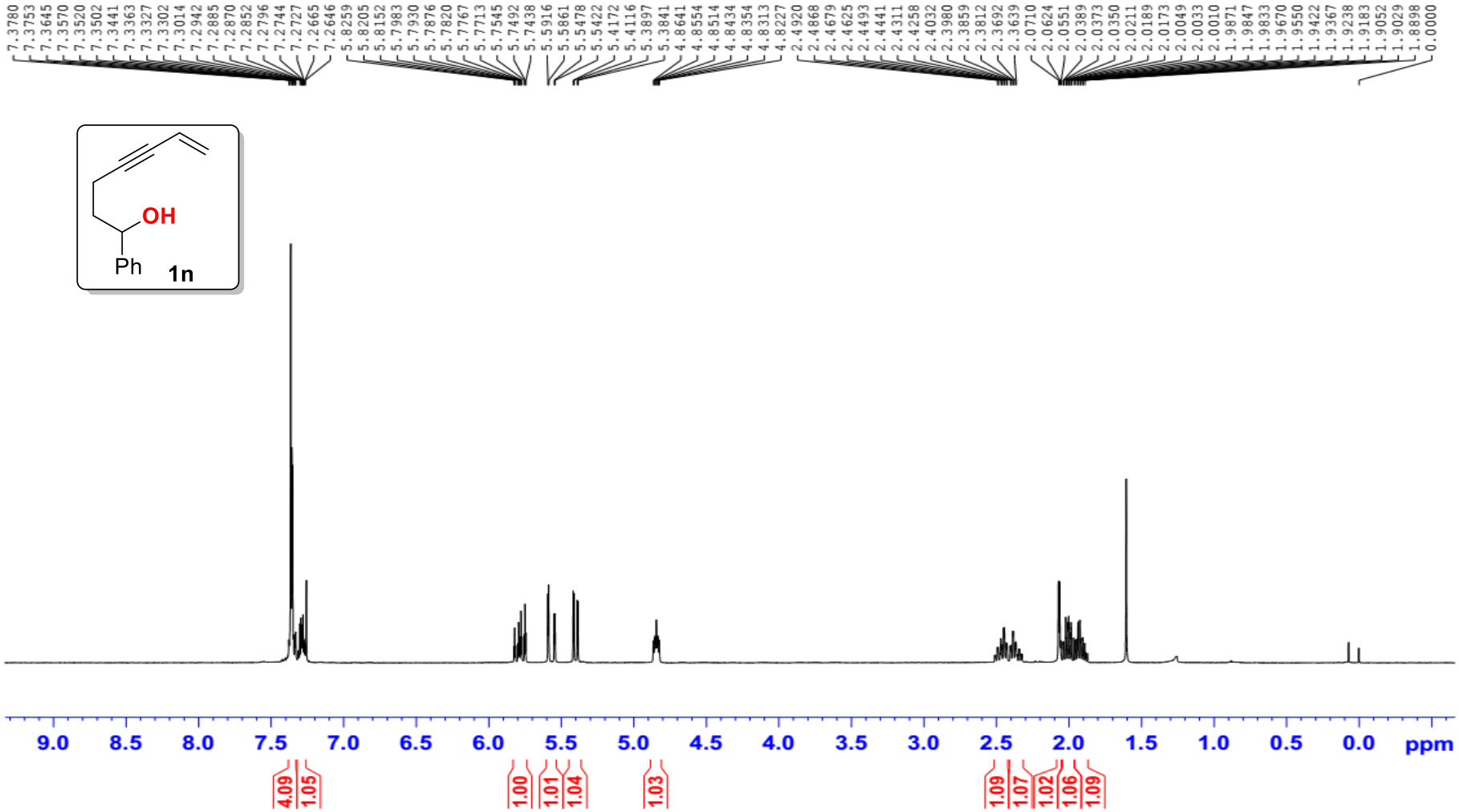
YHJ-S-**1m** ^{1}H NMR (400MHz $CDCl_3$)



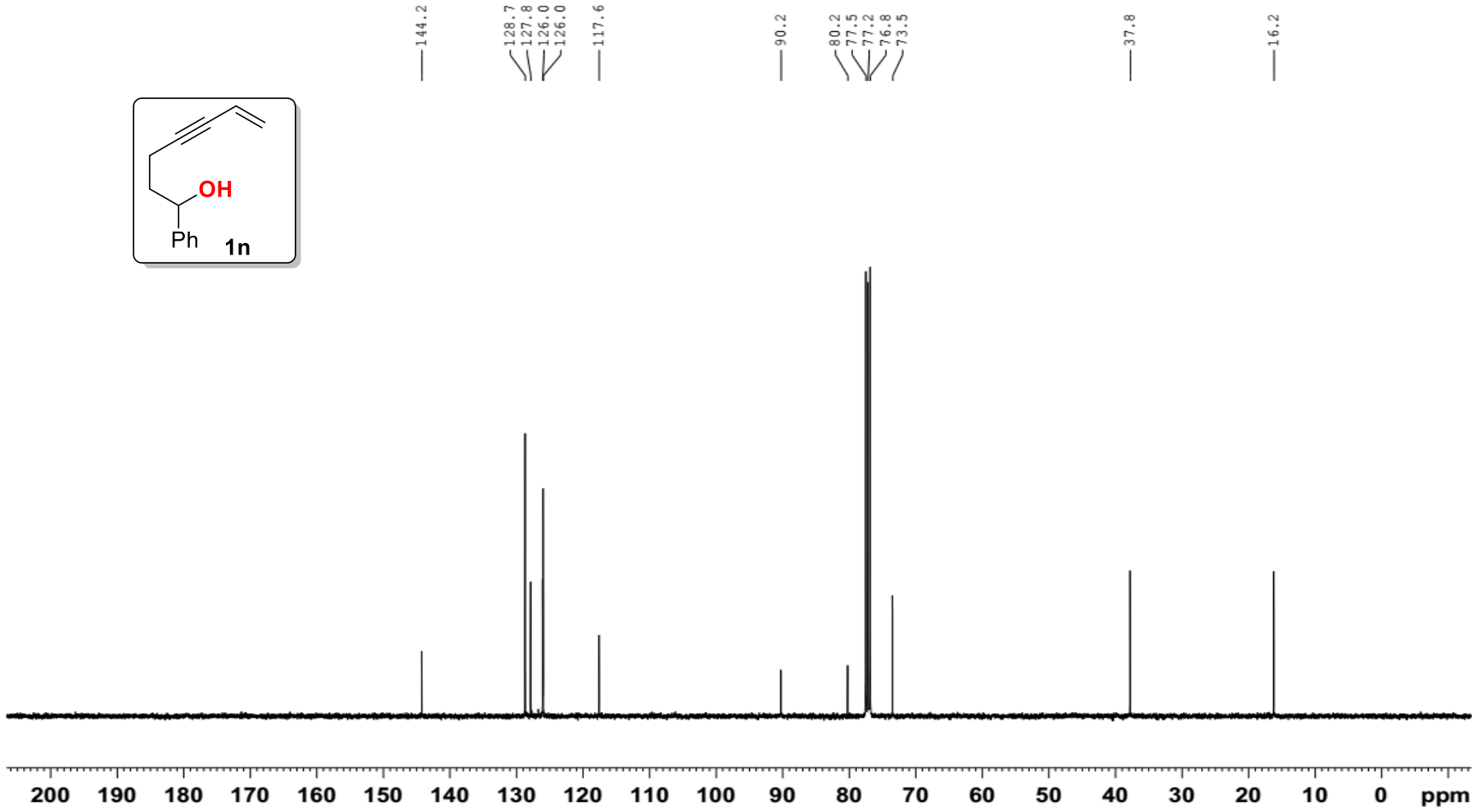
YHJ-S-**1m** ^{13}C NMR (100MHz $CDCl_3$)



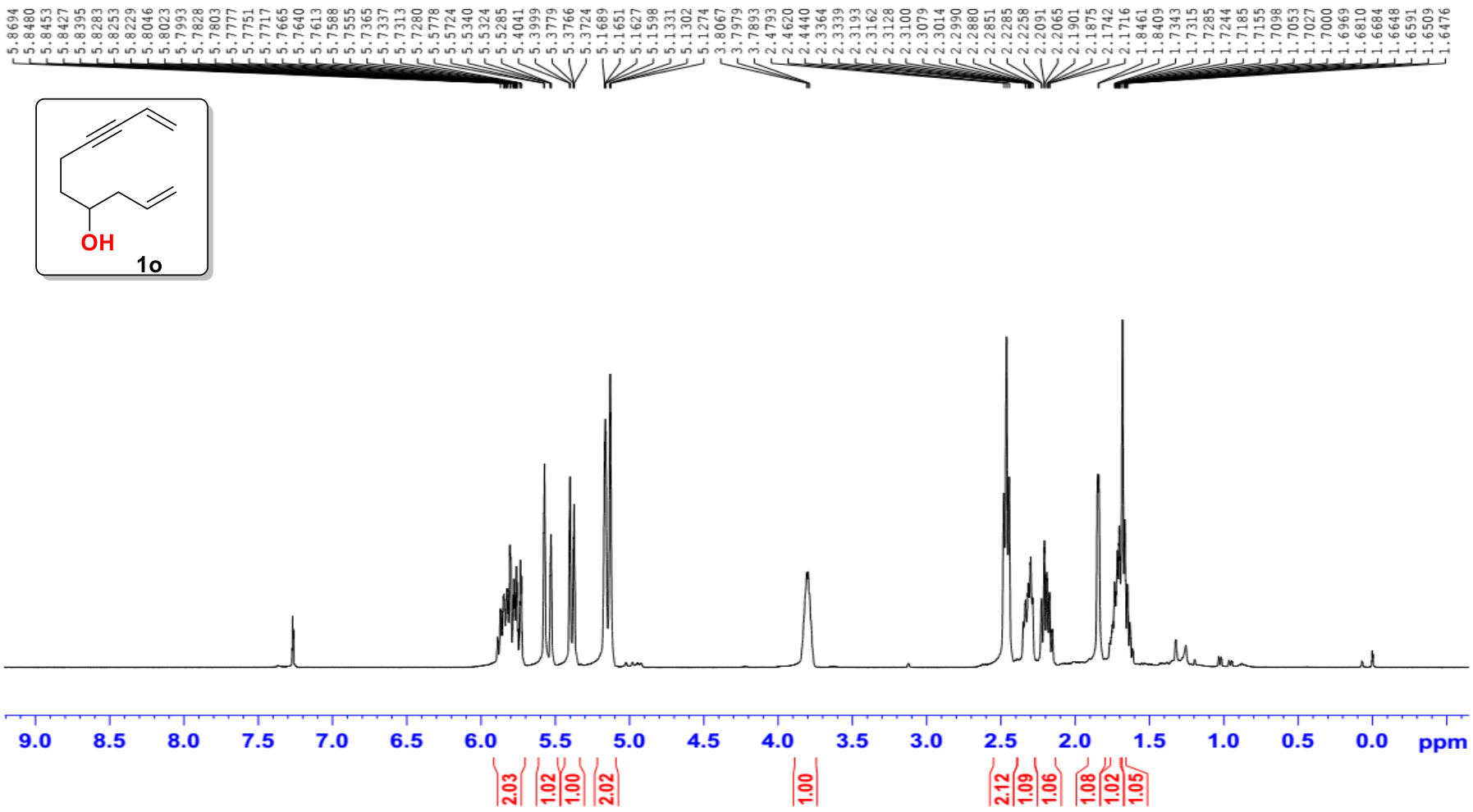
YHJ-S-**1n** ^{1}H NMR (400MHz $CDCl_3$)



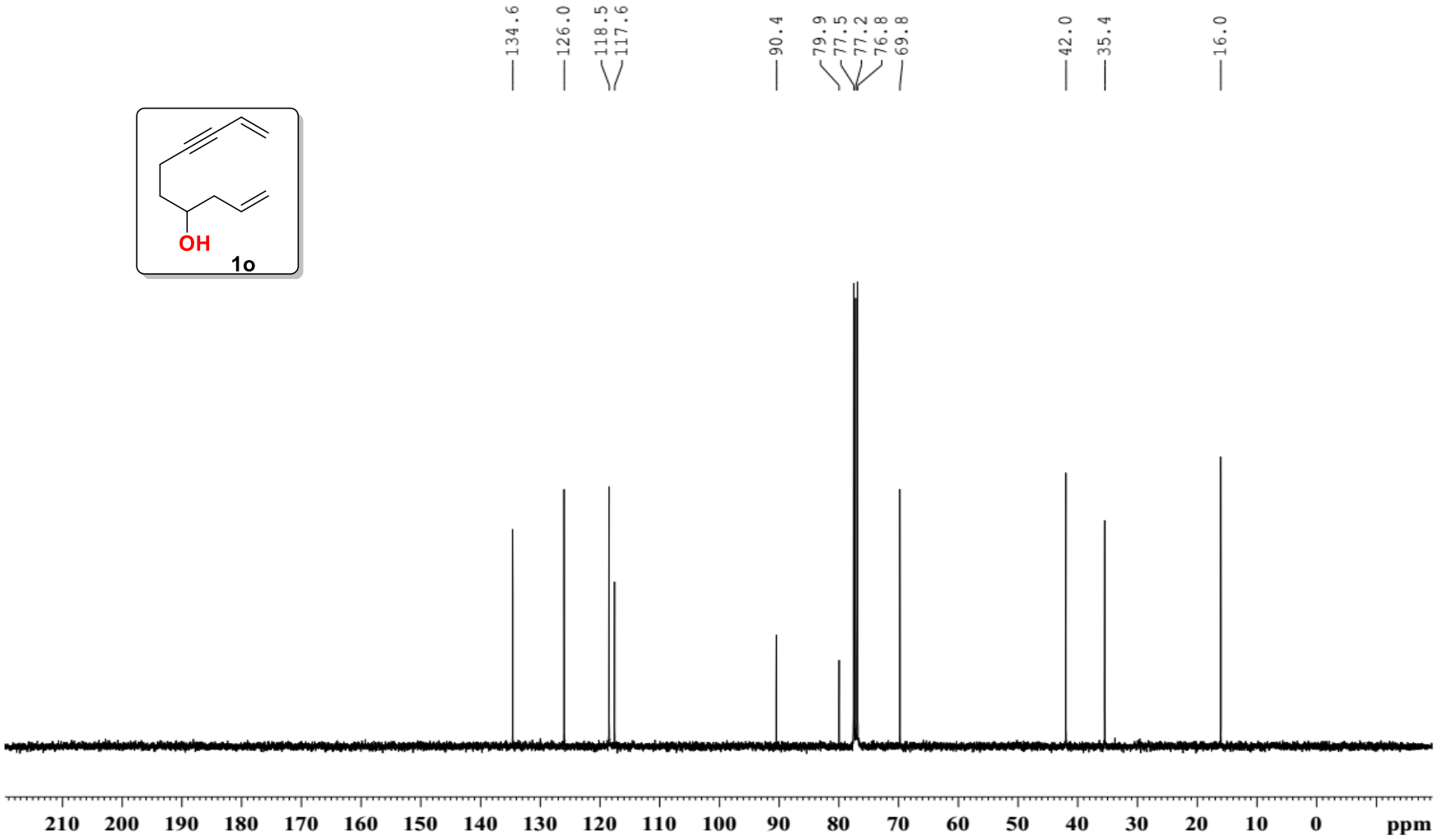
YHJ-S-**1n** ^{13}C NMR (100MHz $CDCl_3$)



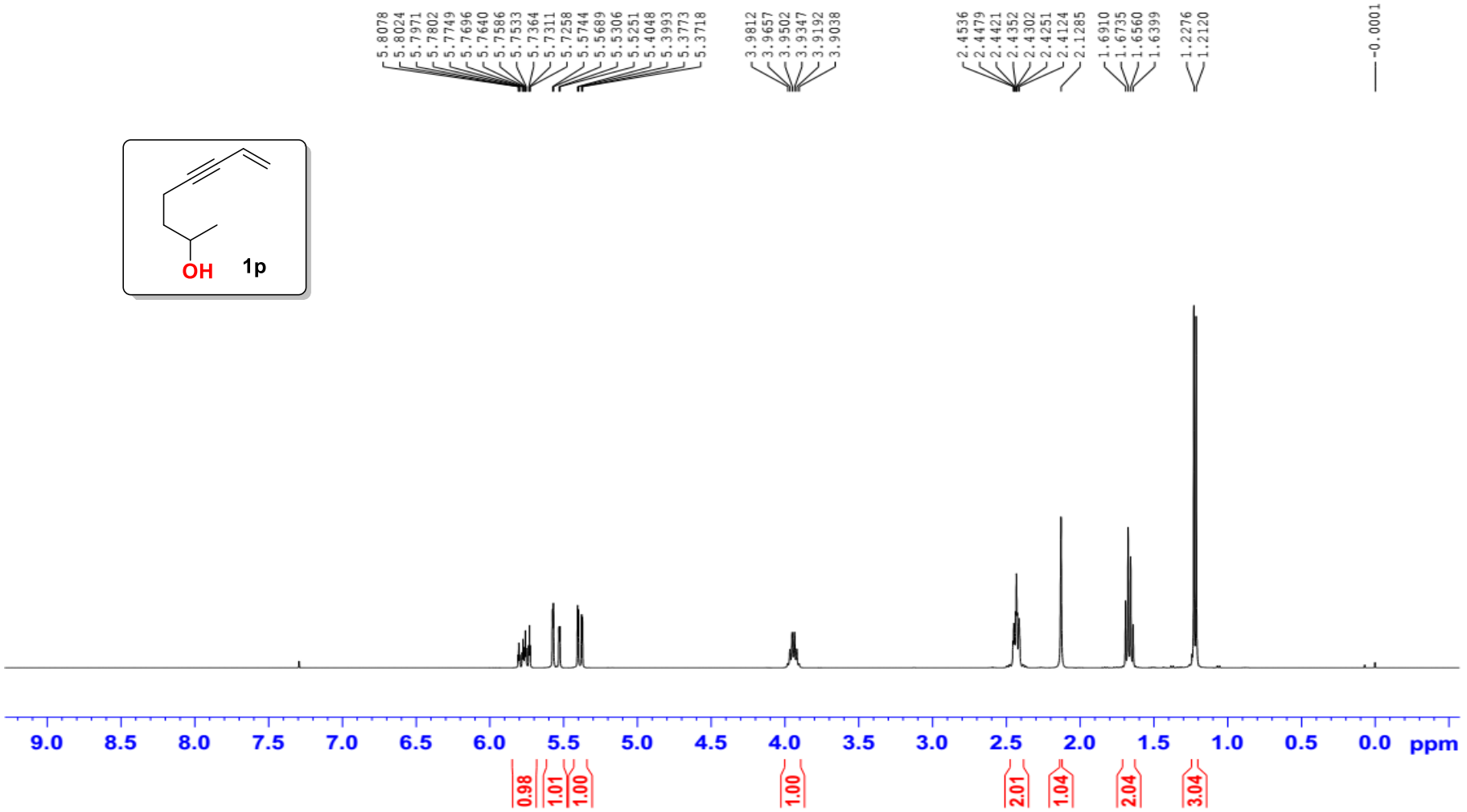
YHJ-S-**1o** ^{1}H NMR (400MHz $CDCl_3$)



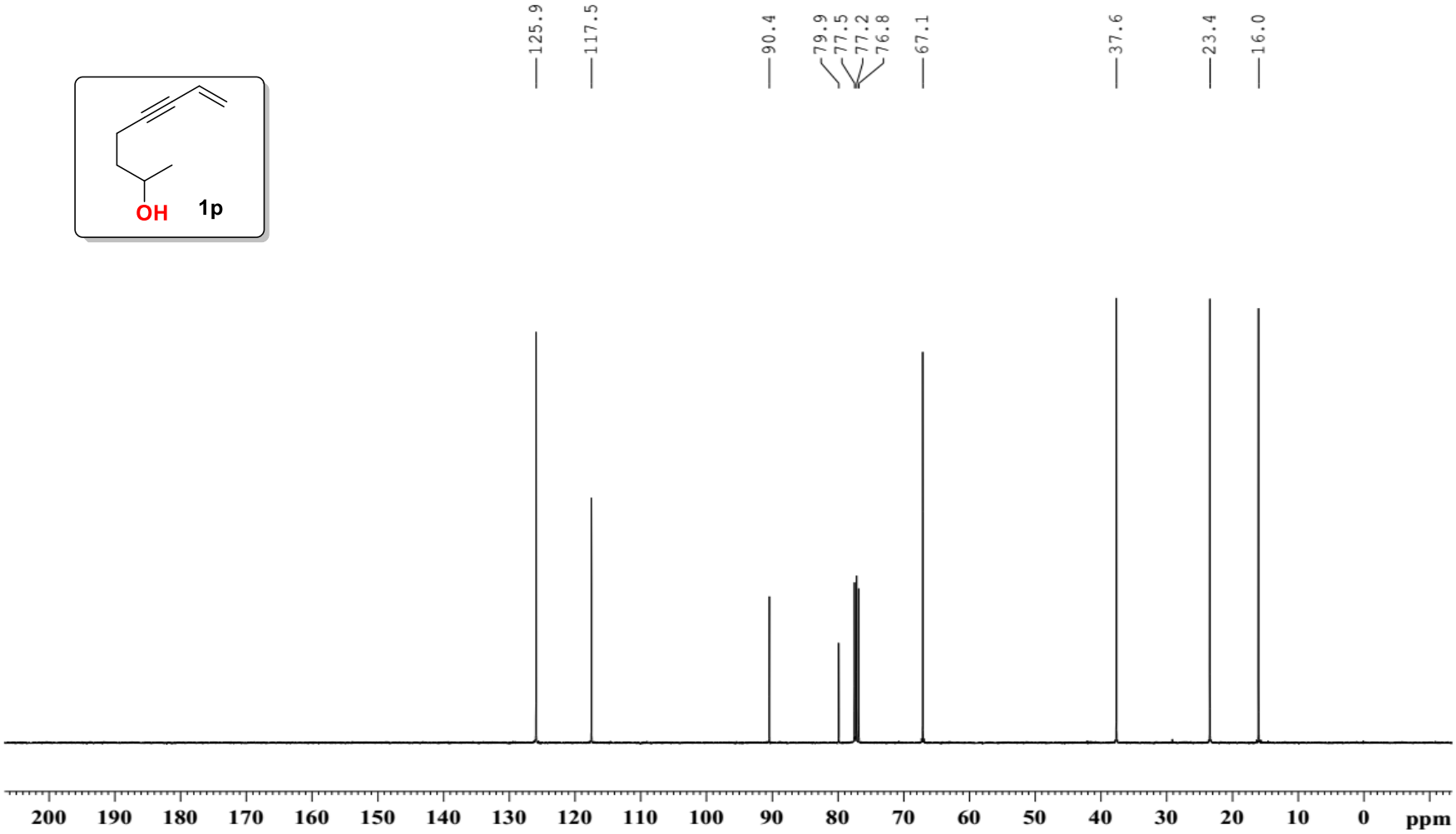
YHJ-S-**1o** ^{13}C NMR (100MHz $CDCl_3$)



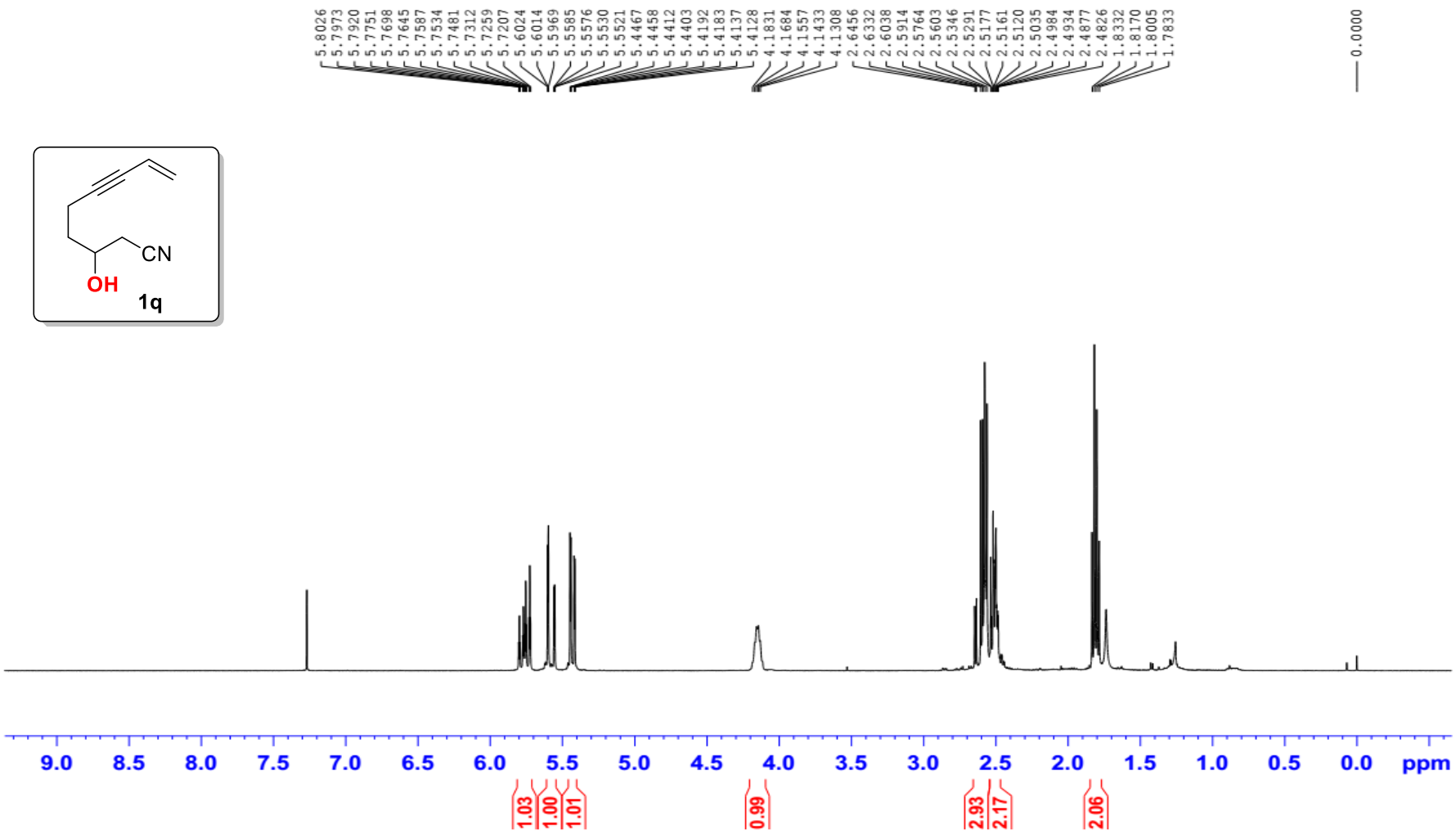
YHJ-S-**1p** ^{1}H NMR (400MHz $CDCl_3$)



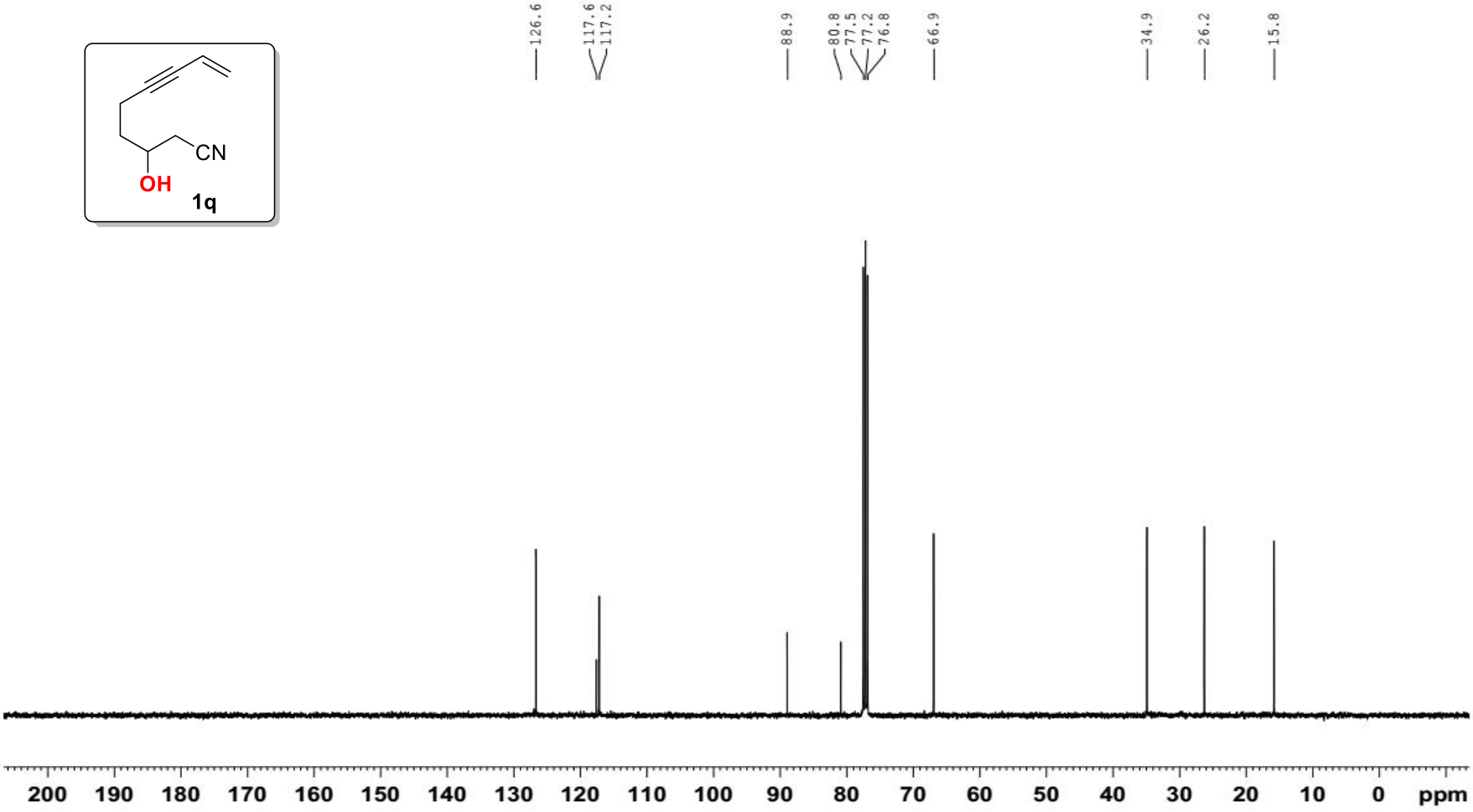
YHJ-S-**1p** ^{13}C NMR (100MHz $CDCl_3$)



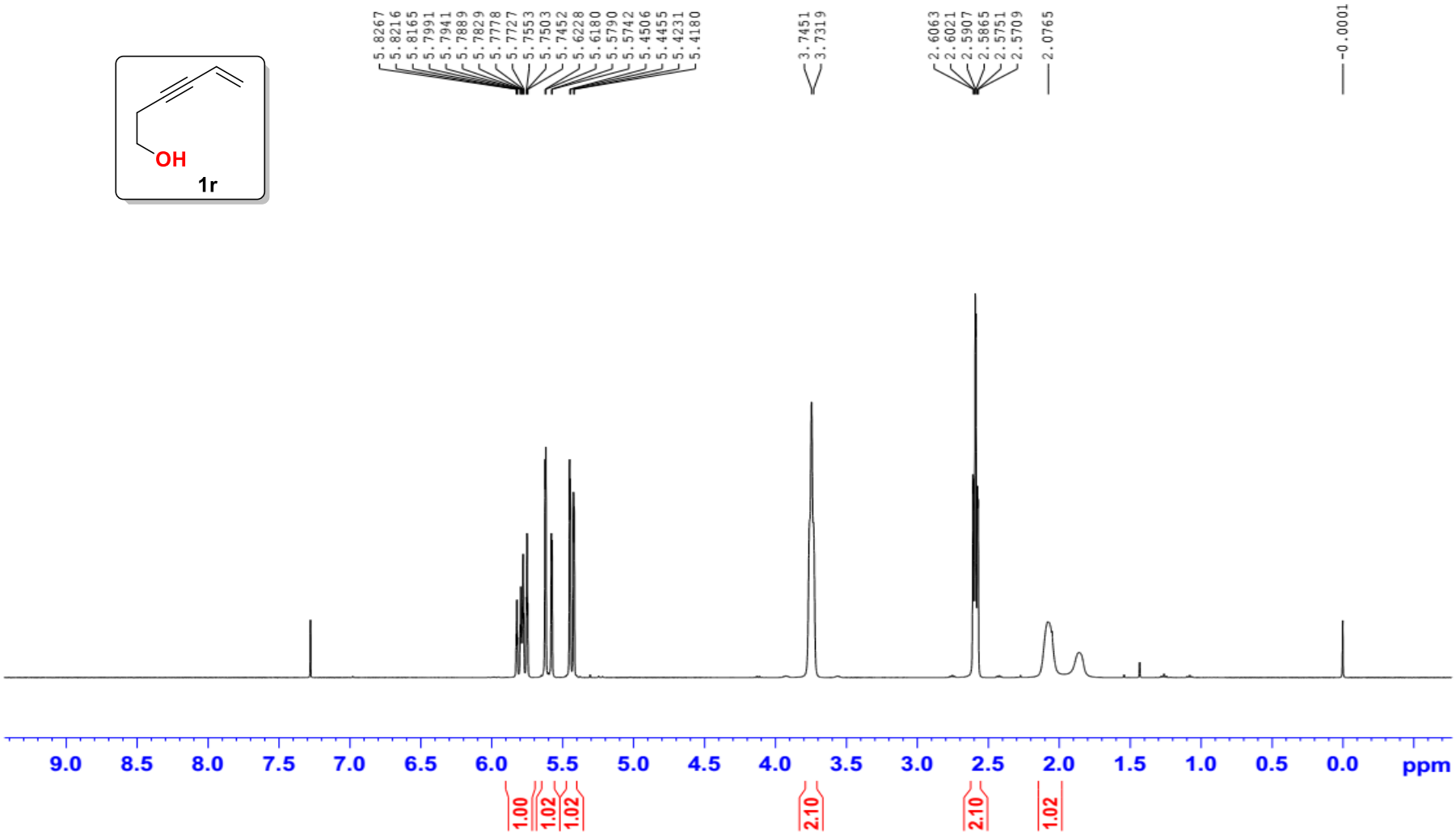
YHJ-S-**1q** ^{1}H NMR (400MHz $CDCl_3$)



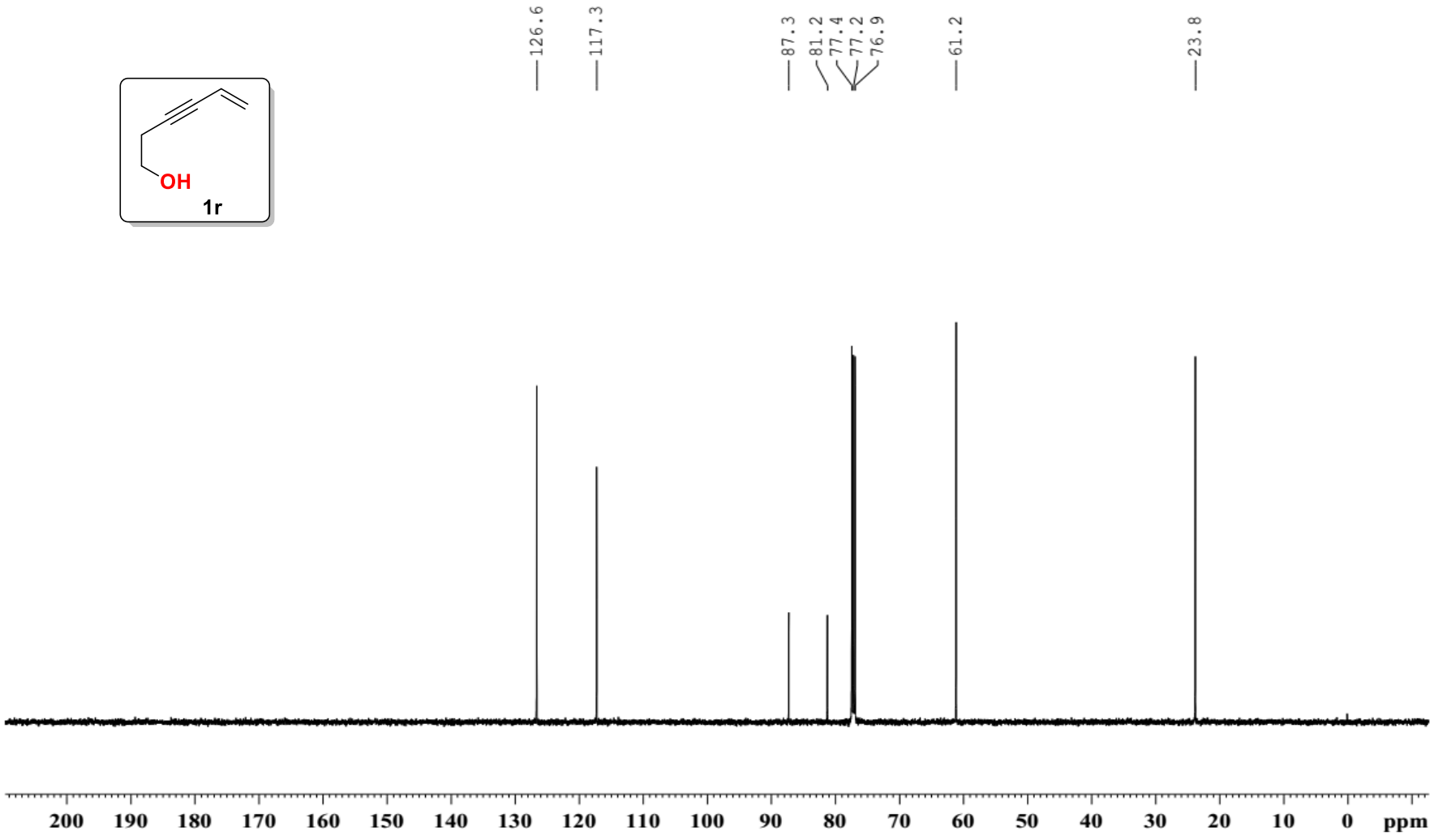
YHJ-S-**1q** ^{13}C NMR (100MHz $CDCl_3$)



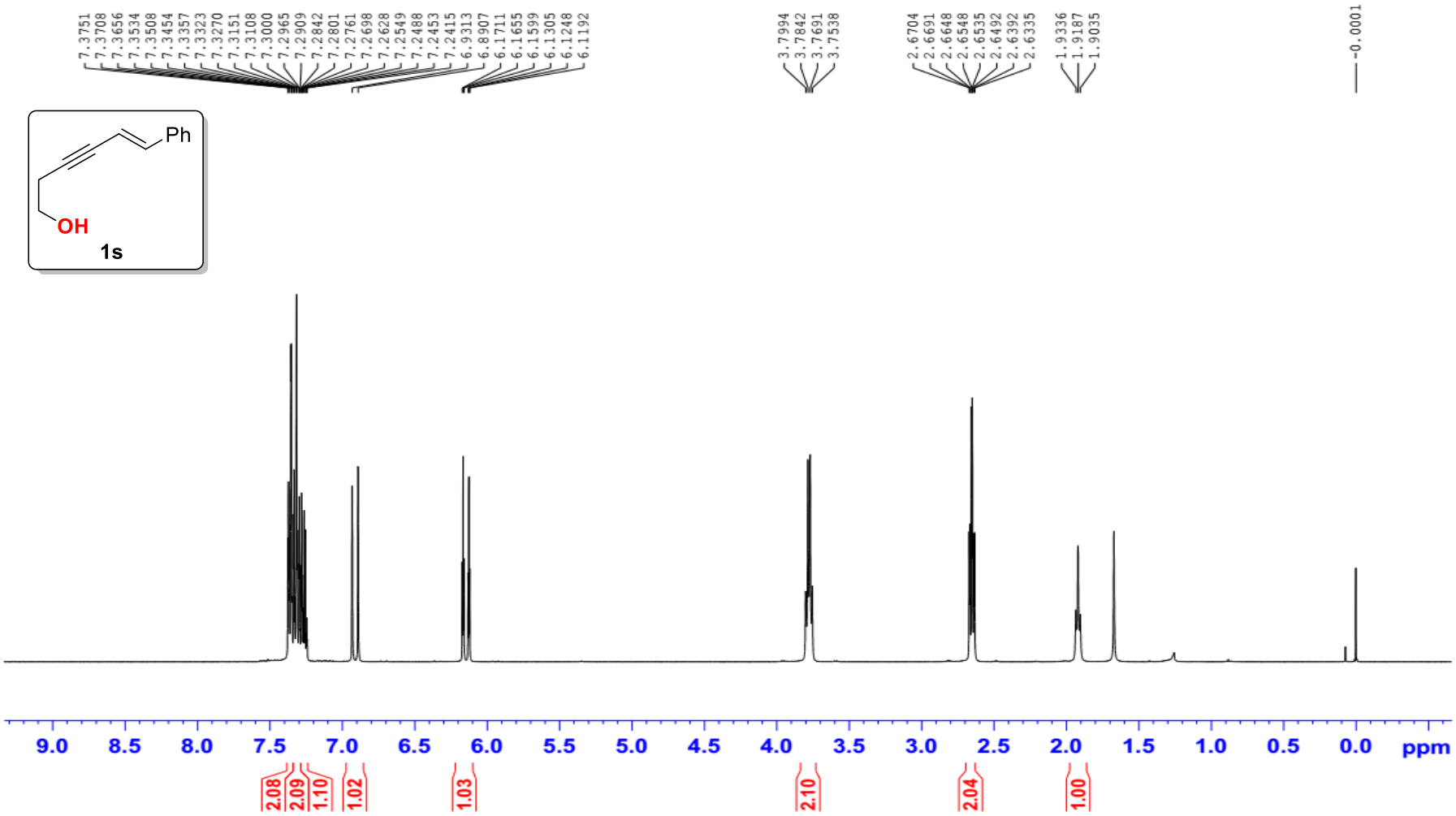
YHJ-S-**1r** ^{1}H NMR (400MHz $CDCl_3$)



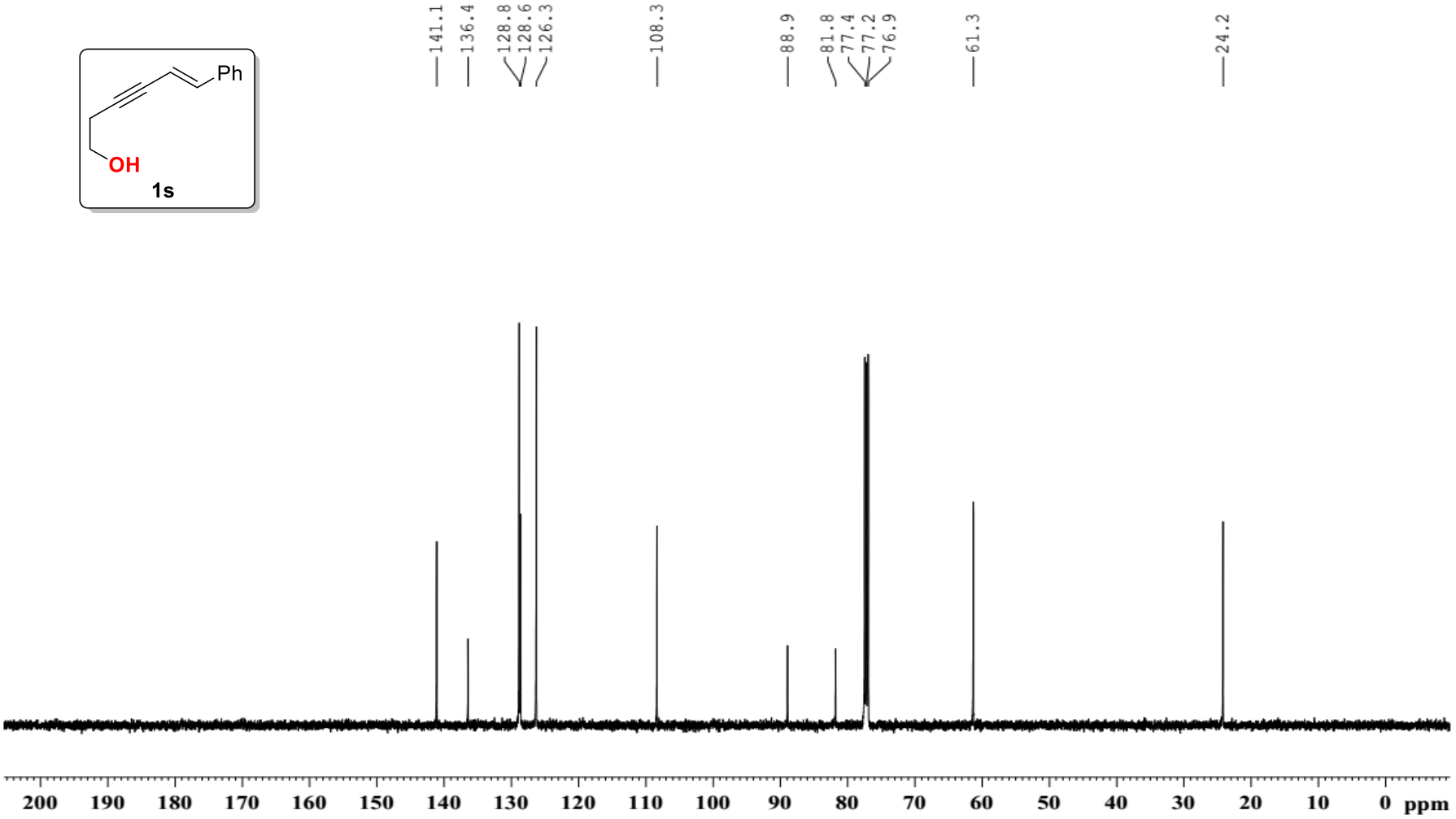
YHJ-S-**1r** ^{13}C NMR (100MHz $CDCl_3$)



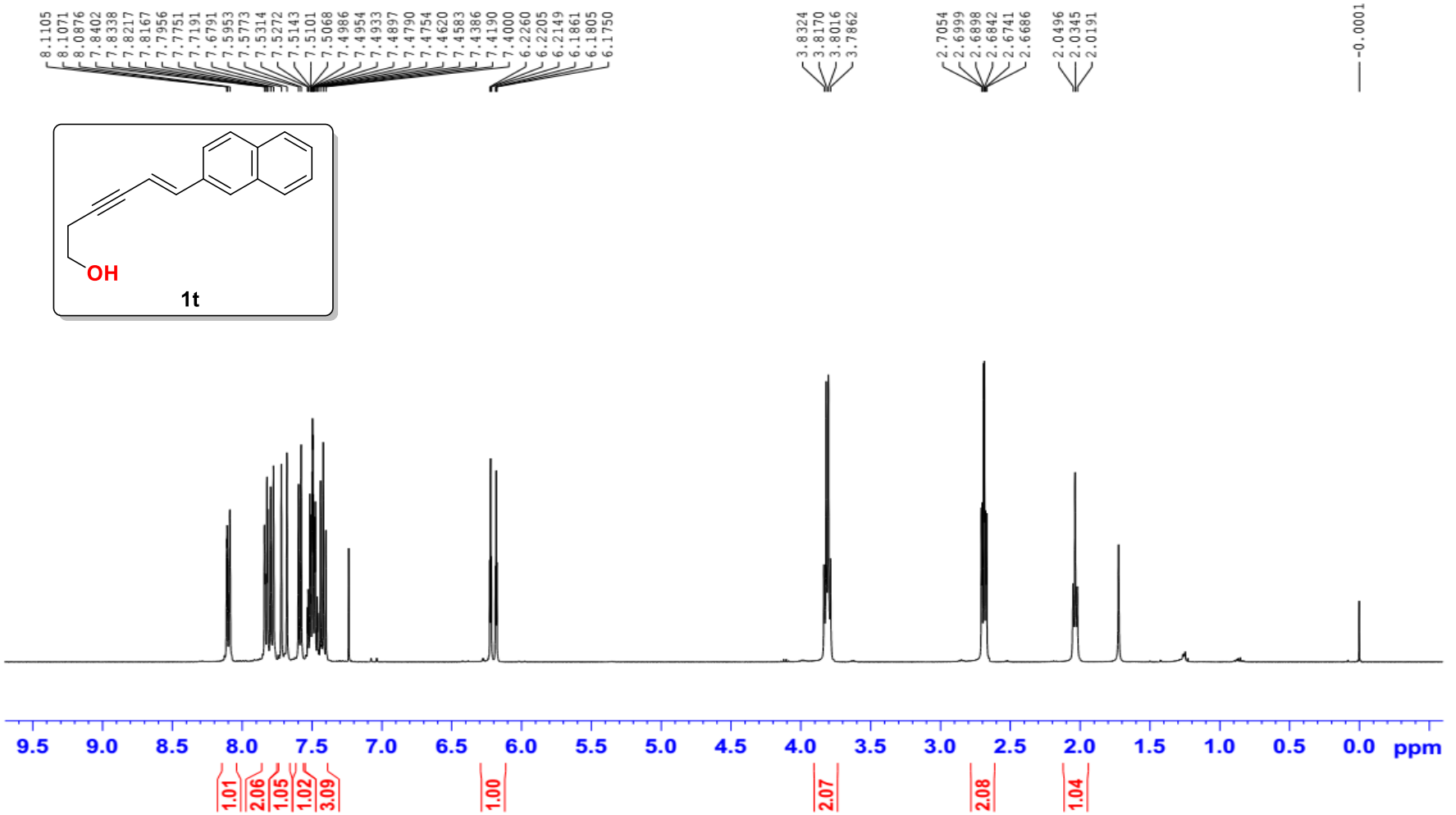
YHJ-S-**1s** ^{1}H NMR (400MHz $CDCl_3$)



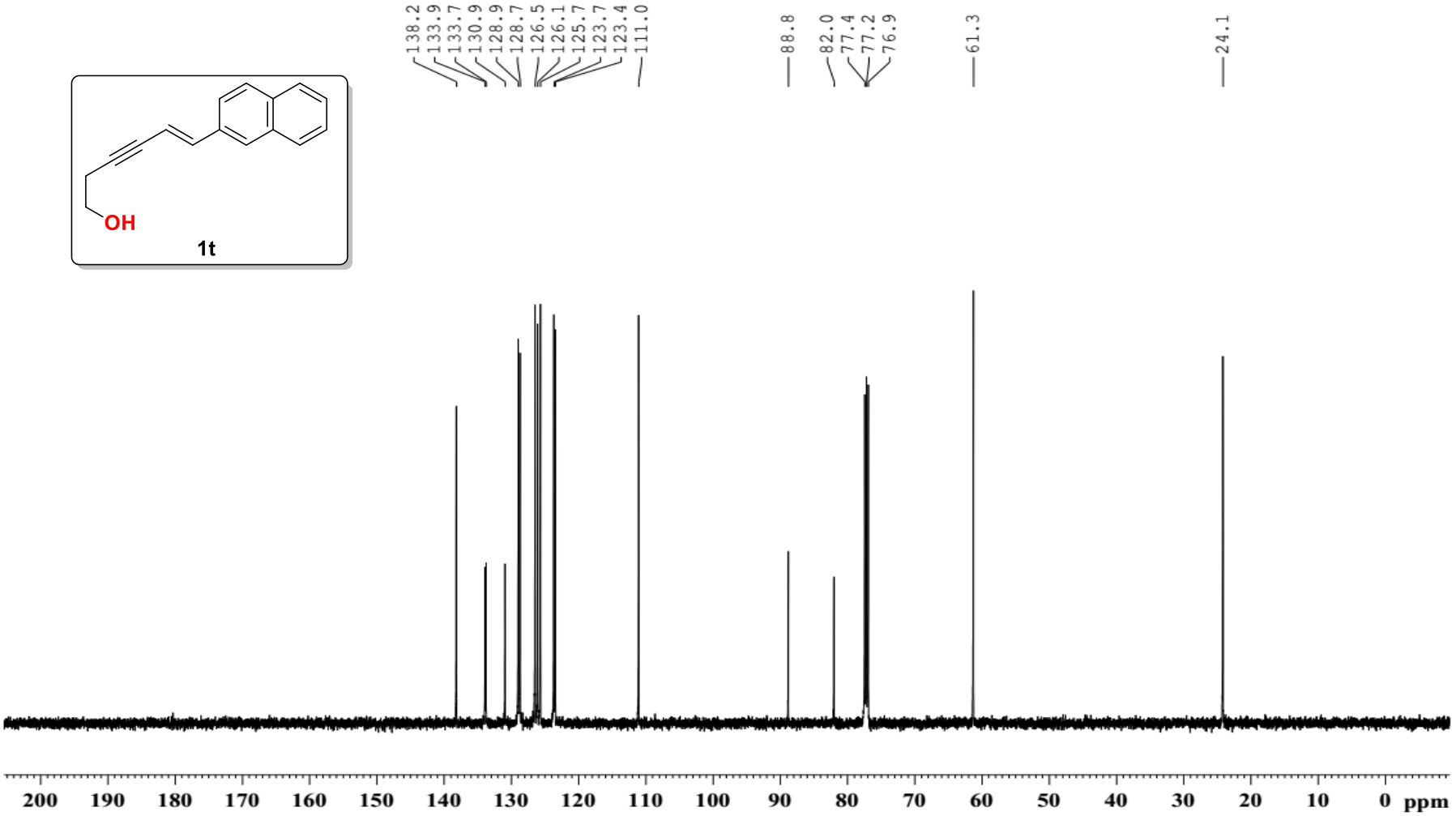
YHJ-S-**1s** ^{13}C NMR (125MHz $CDCl_3$)



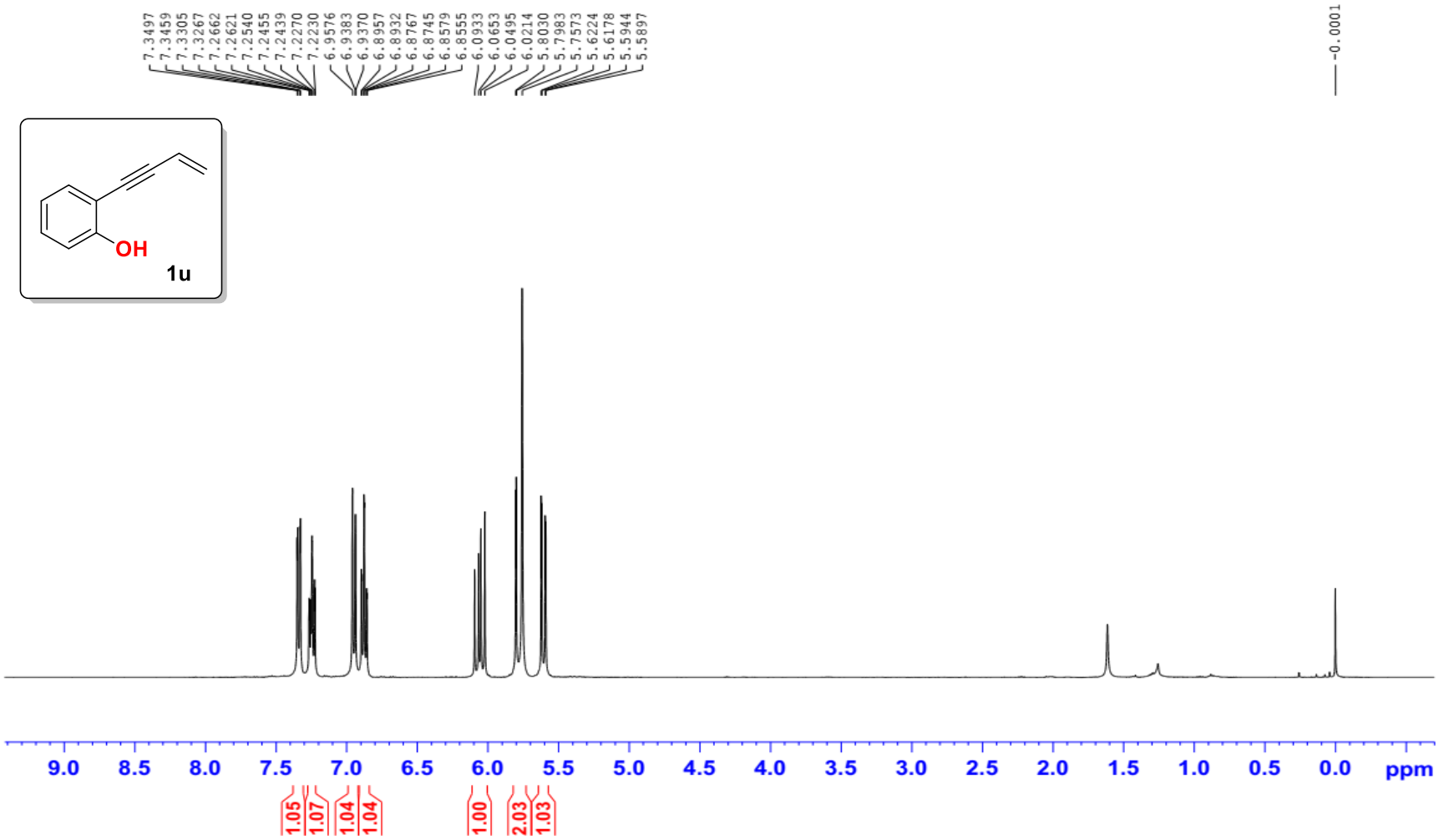
YHJ-S-**1t** ^{1}H NMR (400MHz $CDCl_3$)



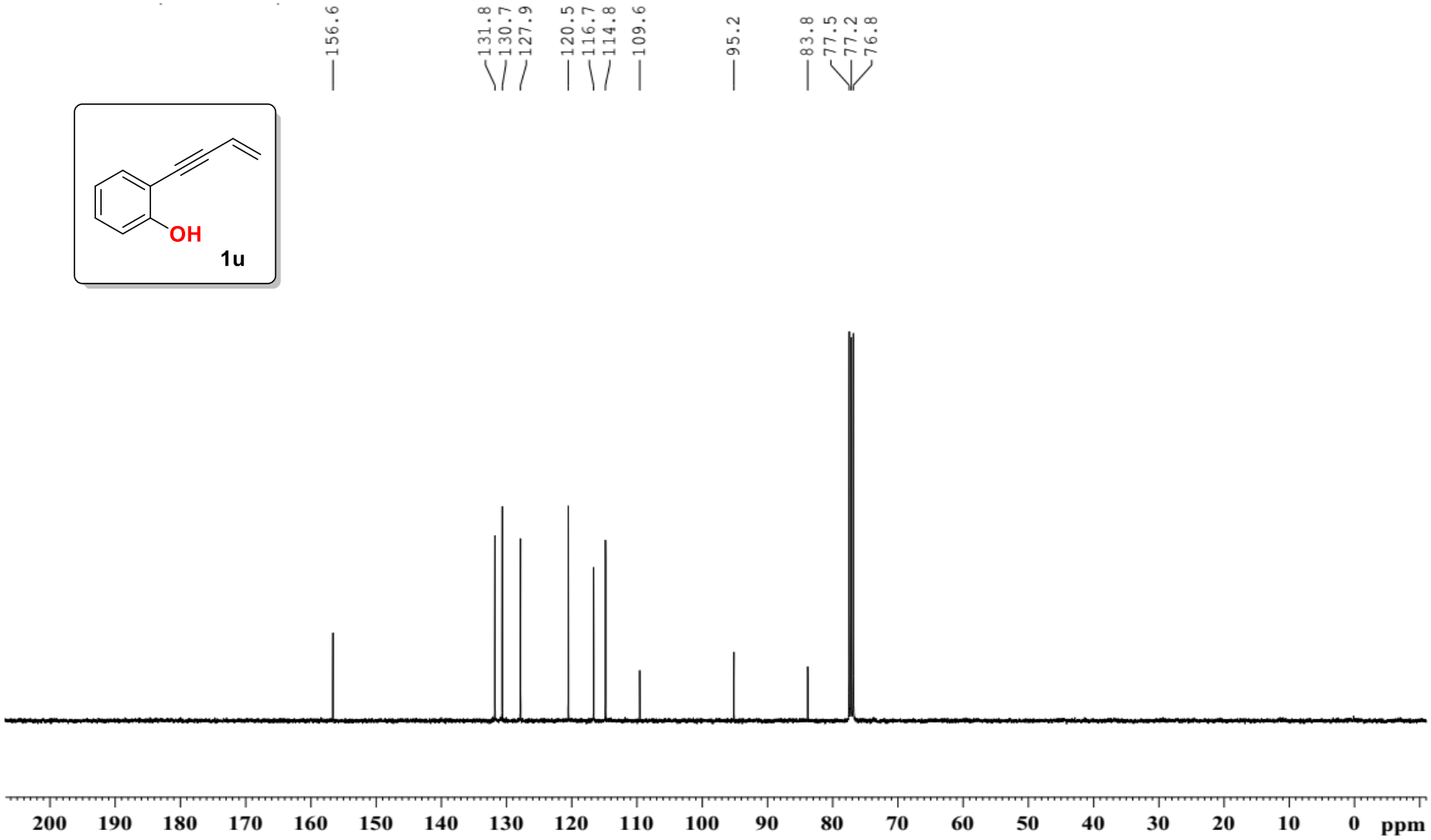
YHJ-S-**1t** ^{13}C NMR (125MHz $CDCl_3$)



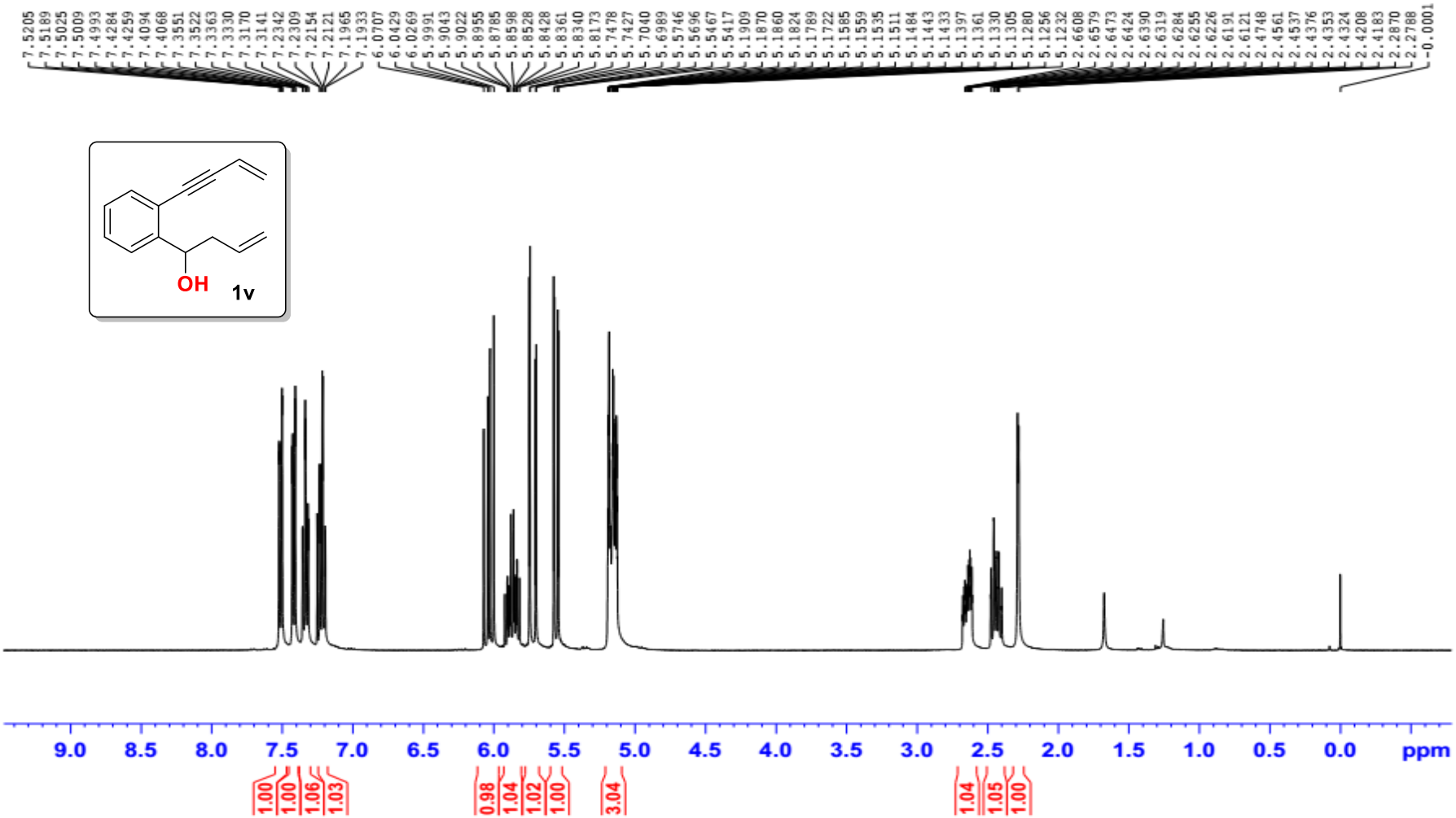
YHJ-S-**1u** ^{1}H NMR (400MHz $CDCl_3$)



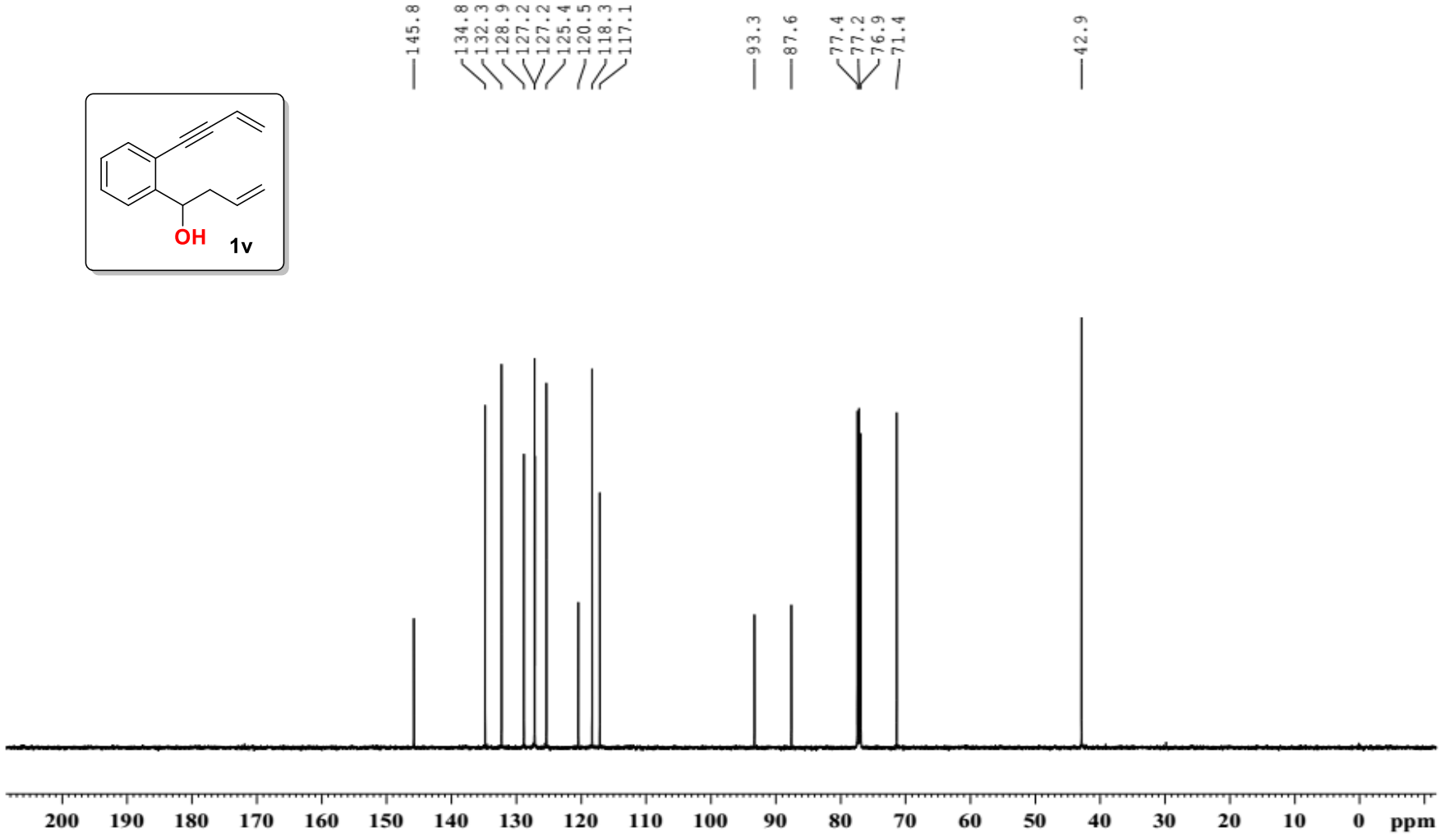
YHJ-S-**1u** ^{13}C NMR (100MHz $CDCl_3$)



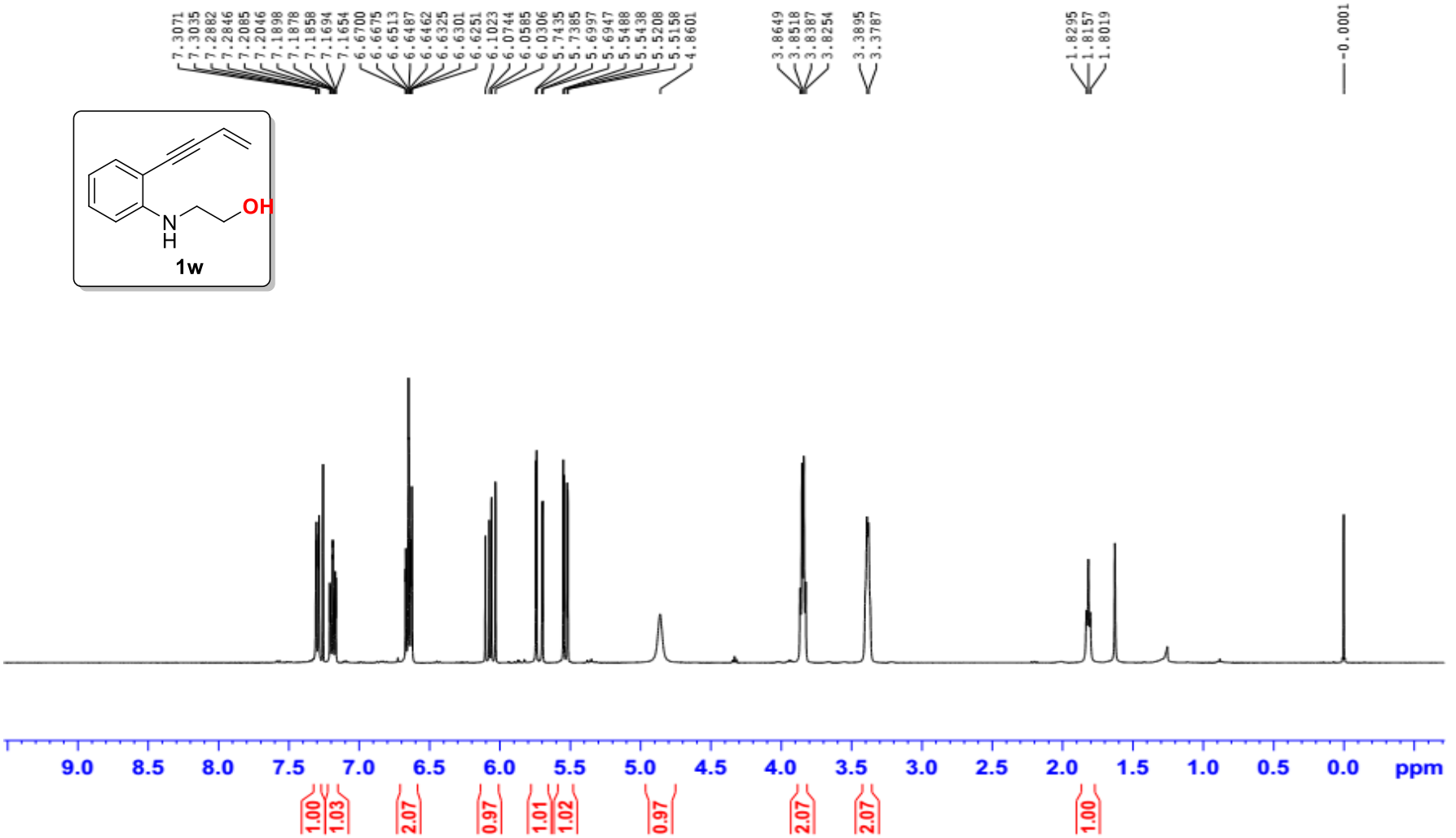
YHJ-S-**1v** ^{1}H NMR (400MHz $CDCl_3$)



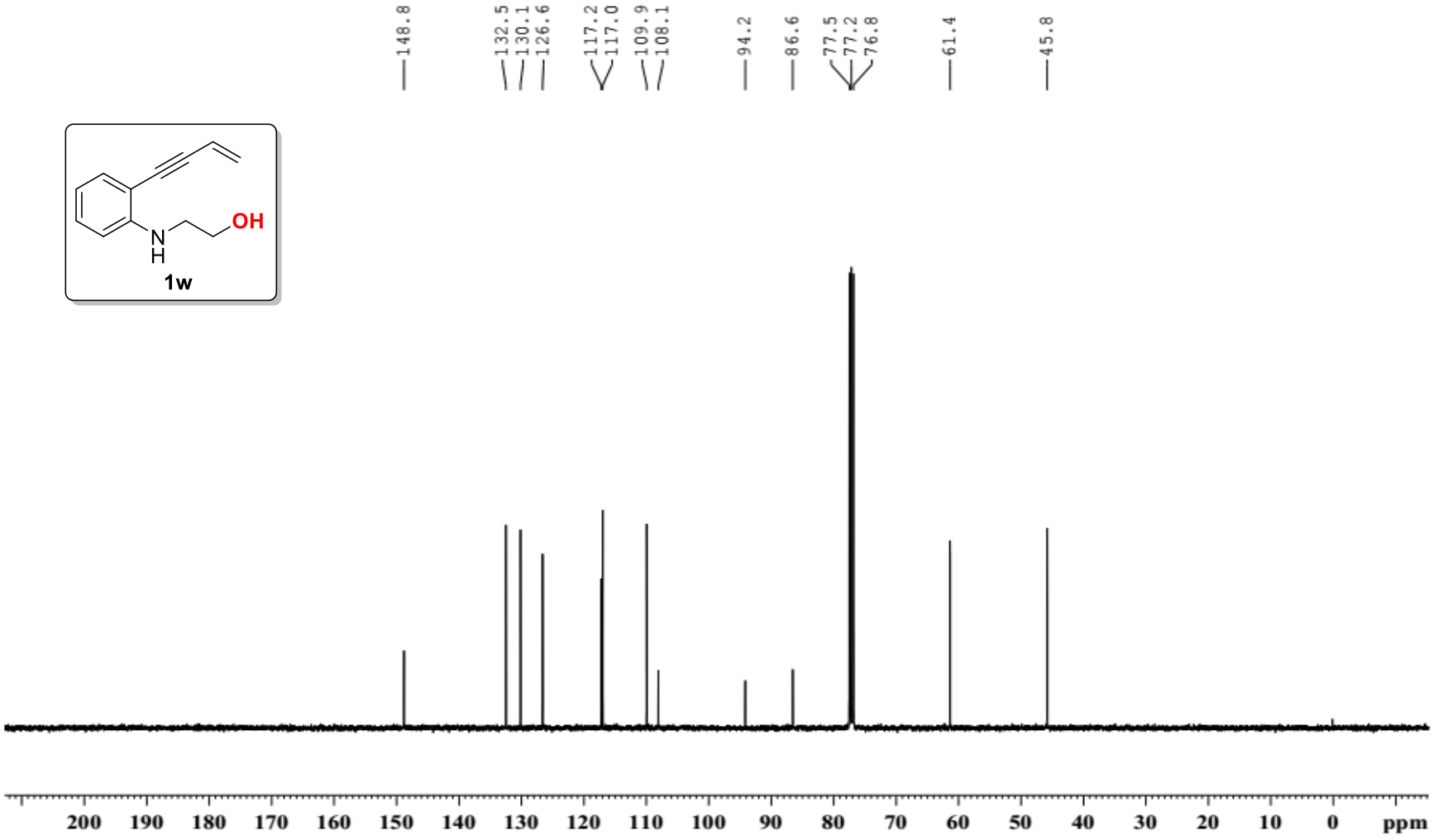
YHJ-S-**1v** ^{13}C NMR (125MHz $CDCl_3$)



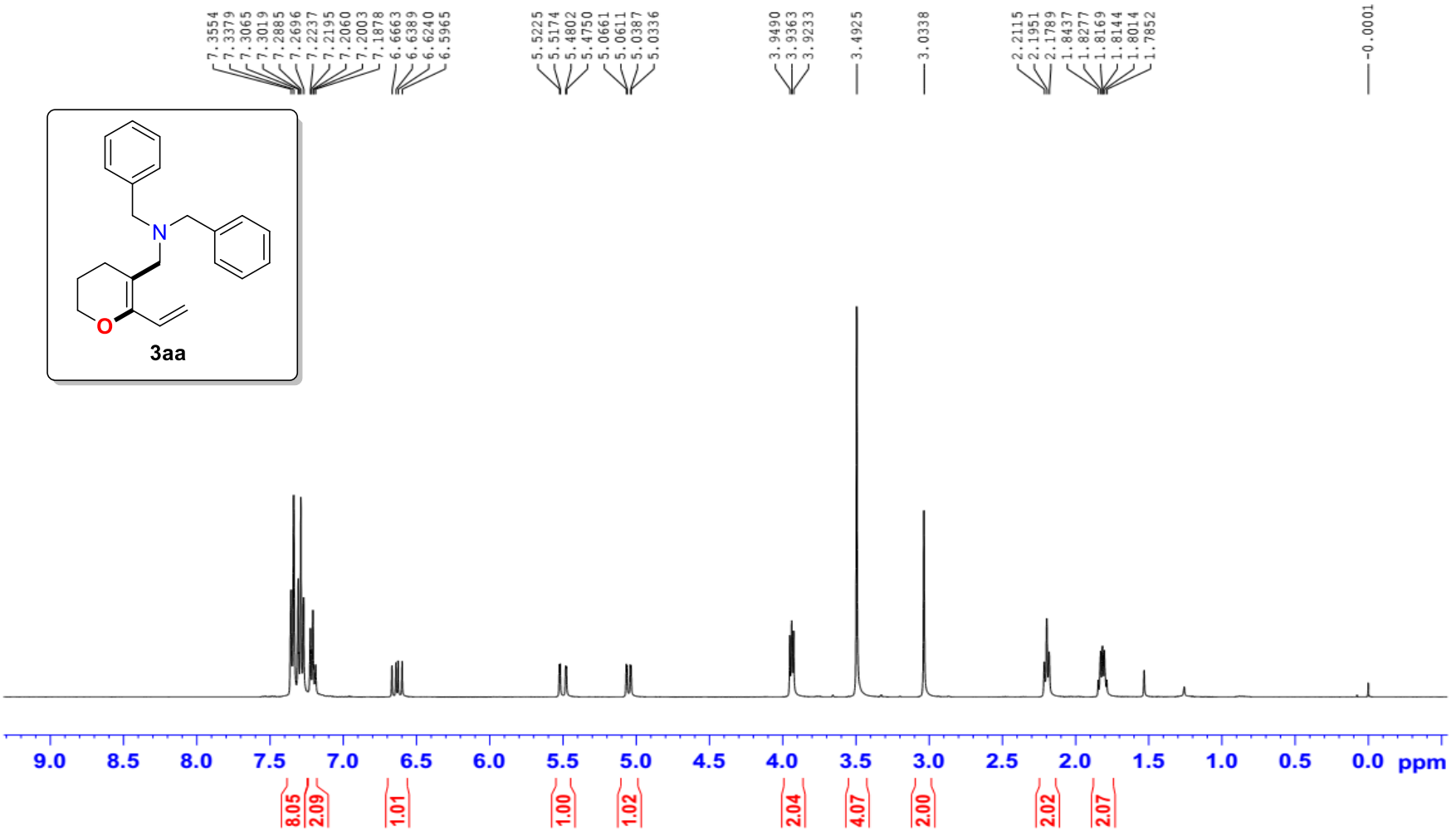
YHJ-S-**1w** ^{1}H NMR (400MHz $CDCl_3$)



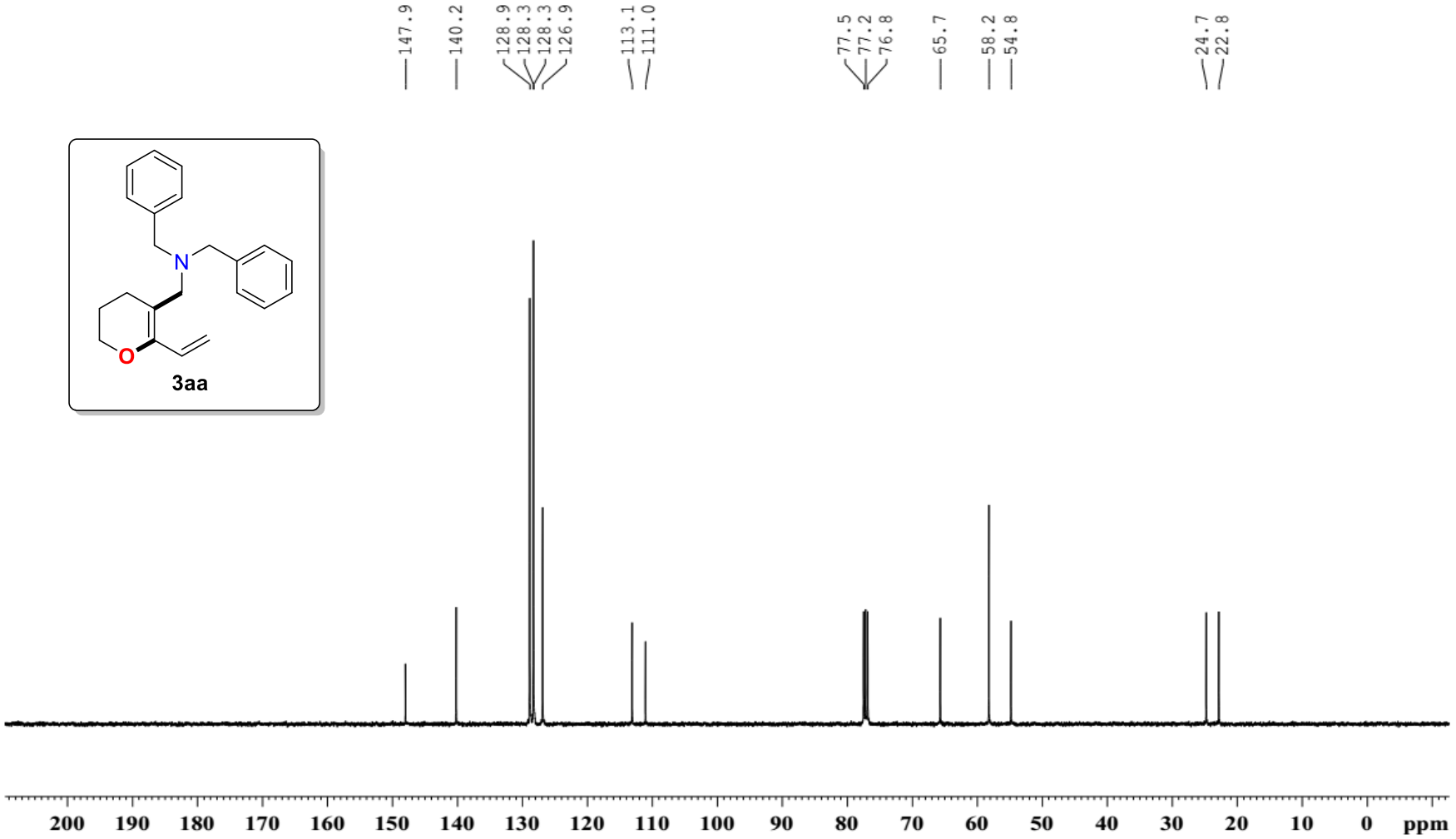
YHJ-S-**1w** ^{13}C NMR (100MHz $CDCl_3$)



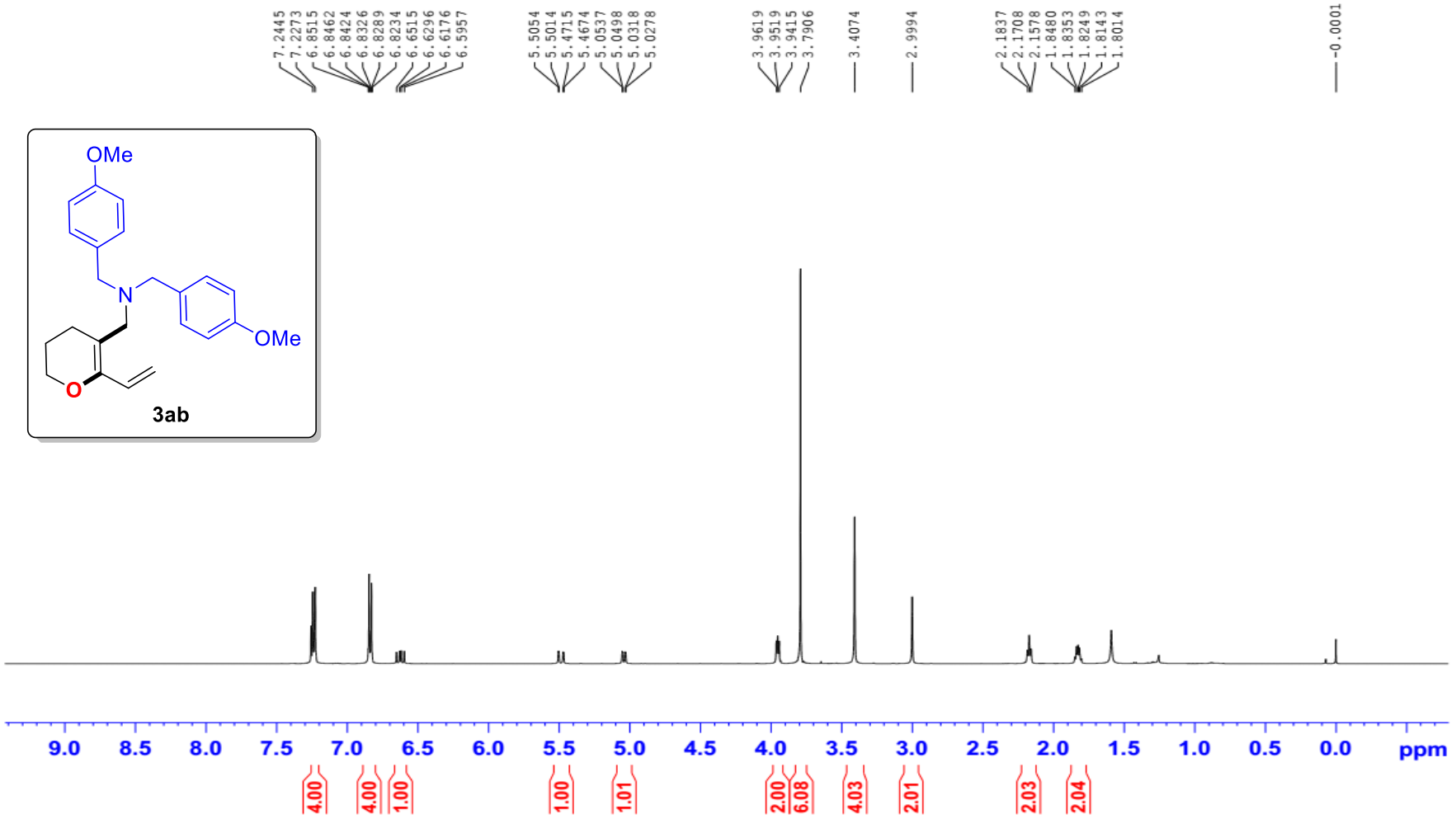
YHJ-P-**3aa** ^{1}H NMR (400MHz $CDCl_3$)



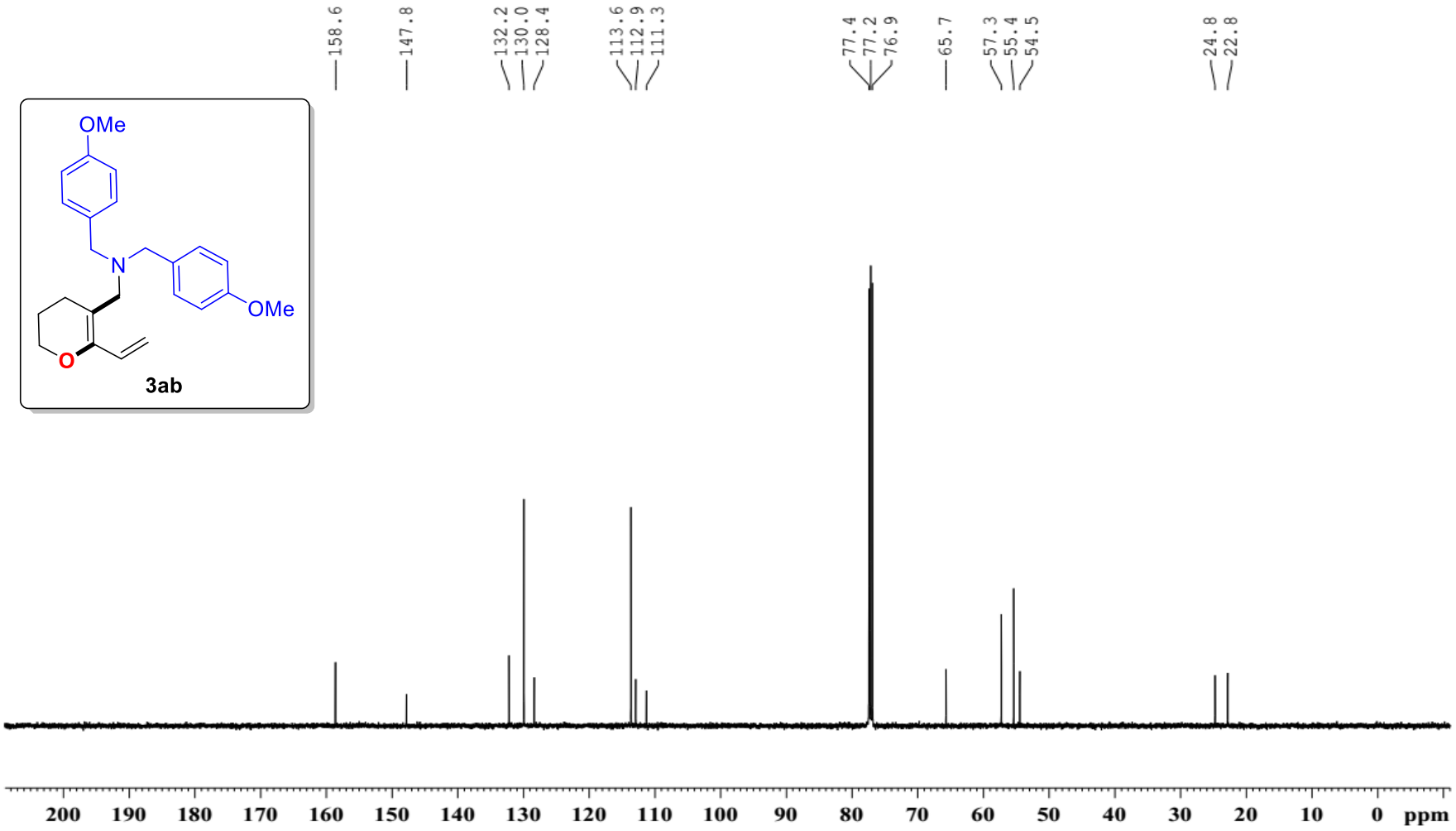
YHJ-P-**3aa** ^{13}C NMR (100MHz $CDCl_3$)



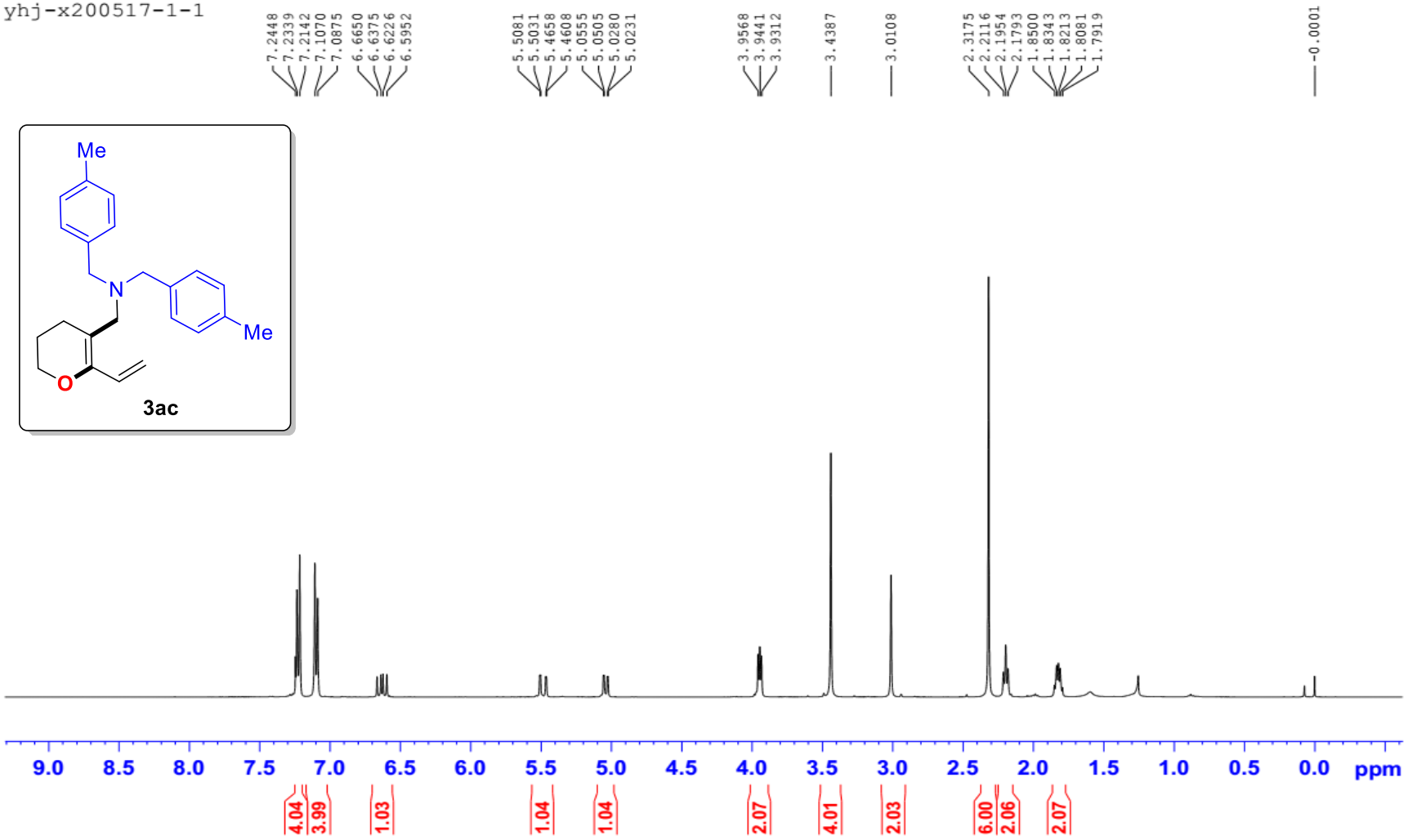
YHJ-P-**3ab** ^{1}H NMR (500MHz $CDCl_3$)



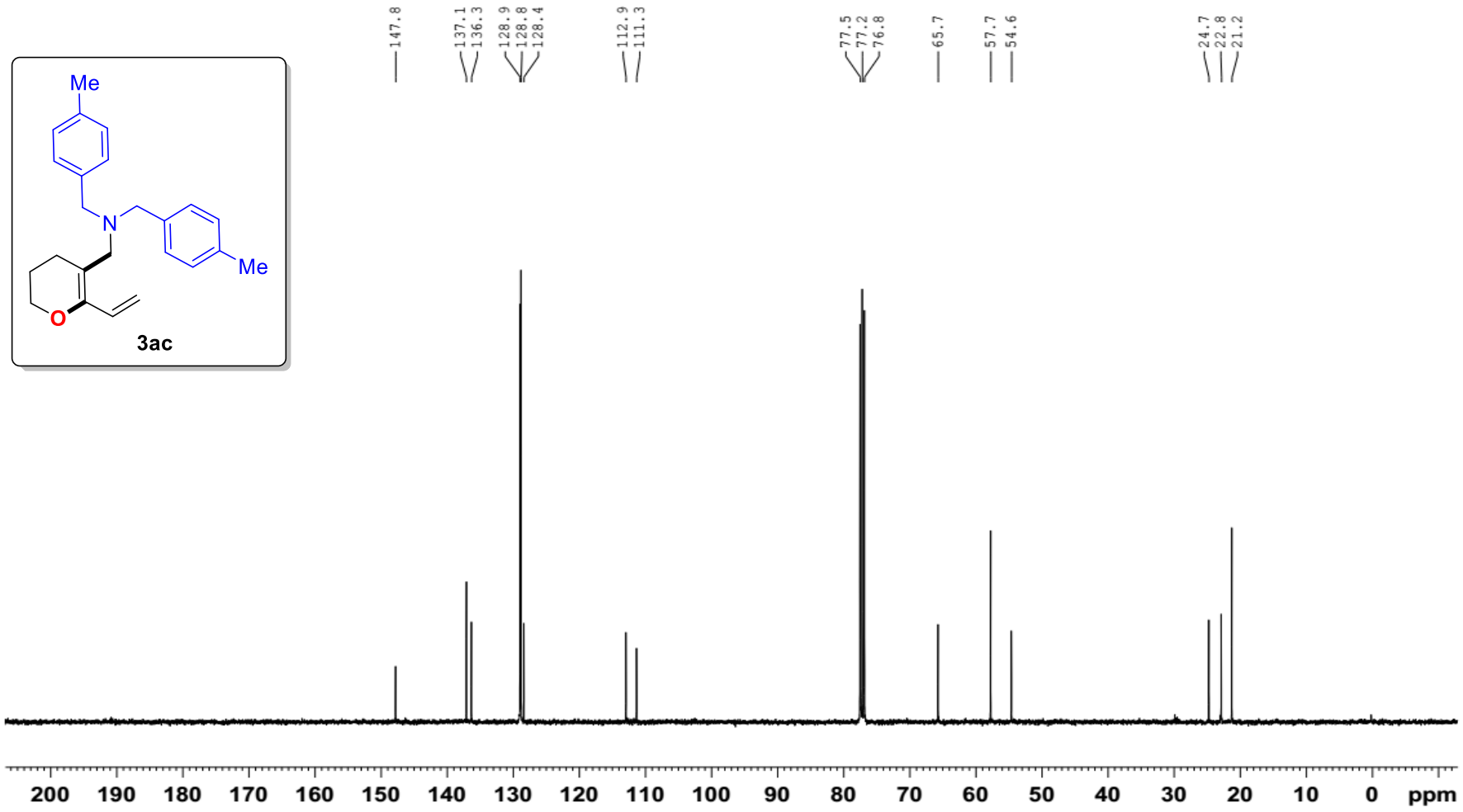
YHJ-P-**3ab** ^{13}C NMR (125MHz $CDCl_3$)



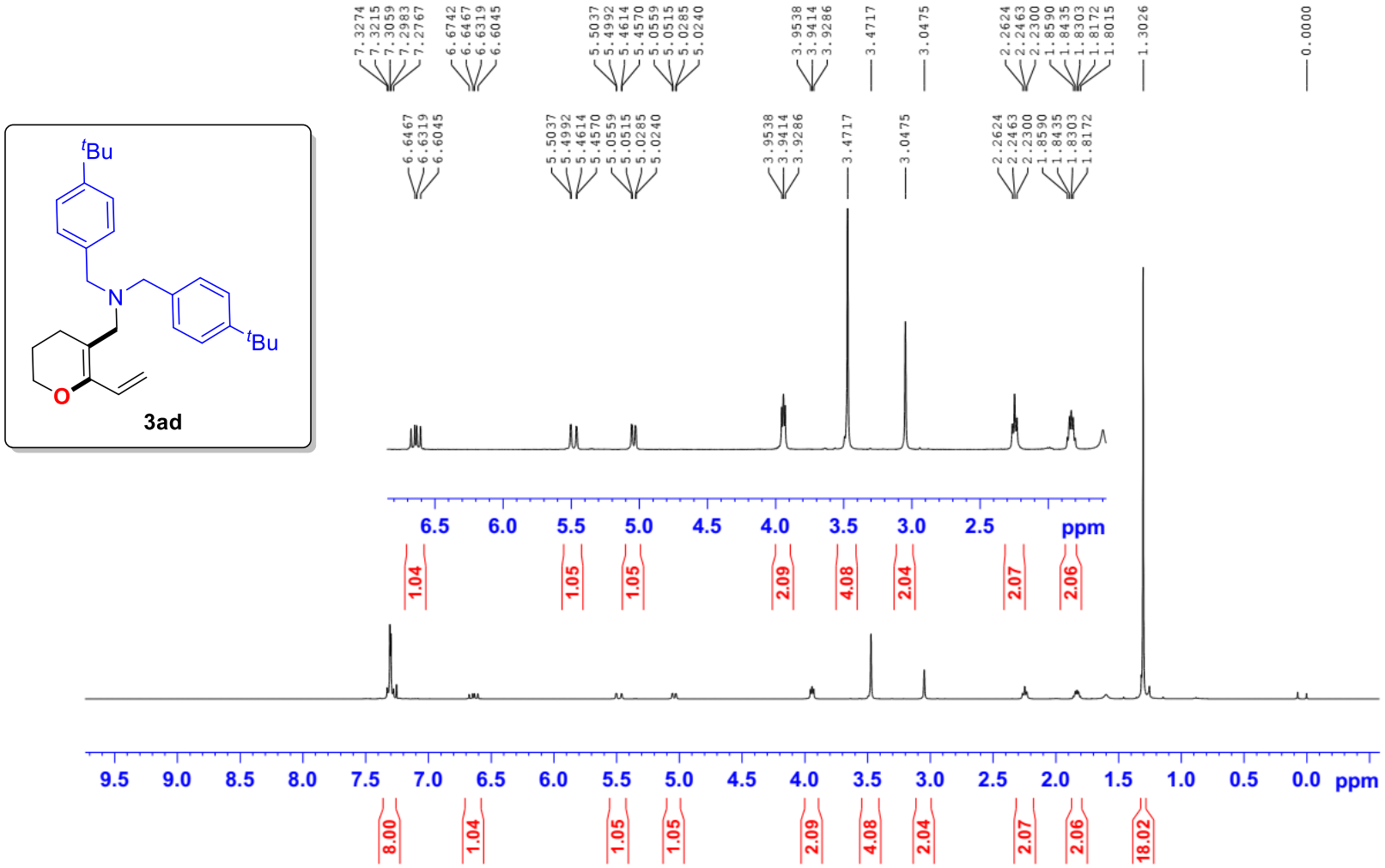
YHJ-P-**3ac** ^{1}H NMR (400MHz $CDCl_3$)



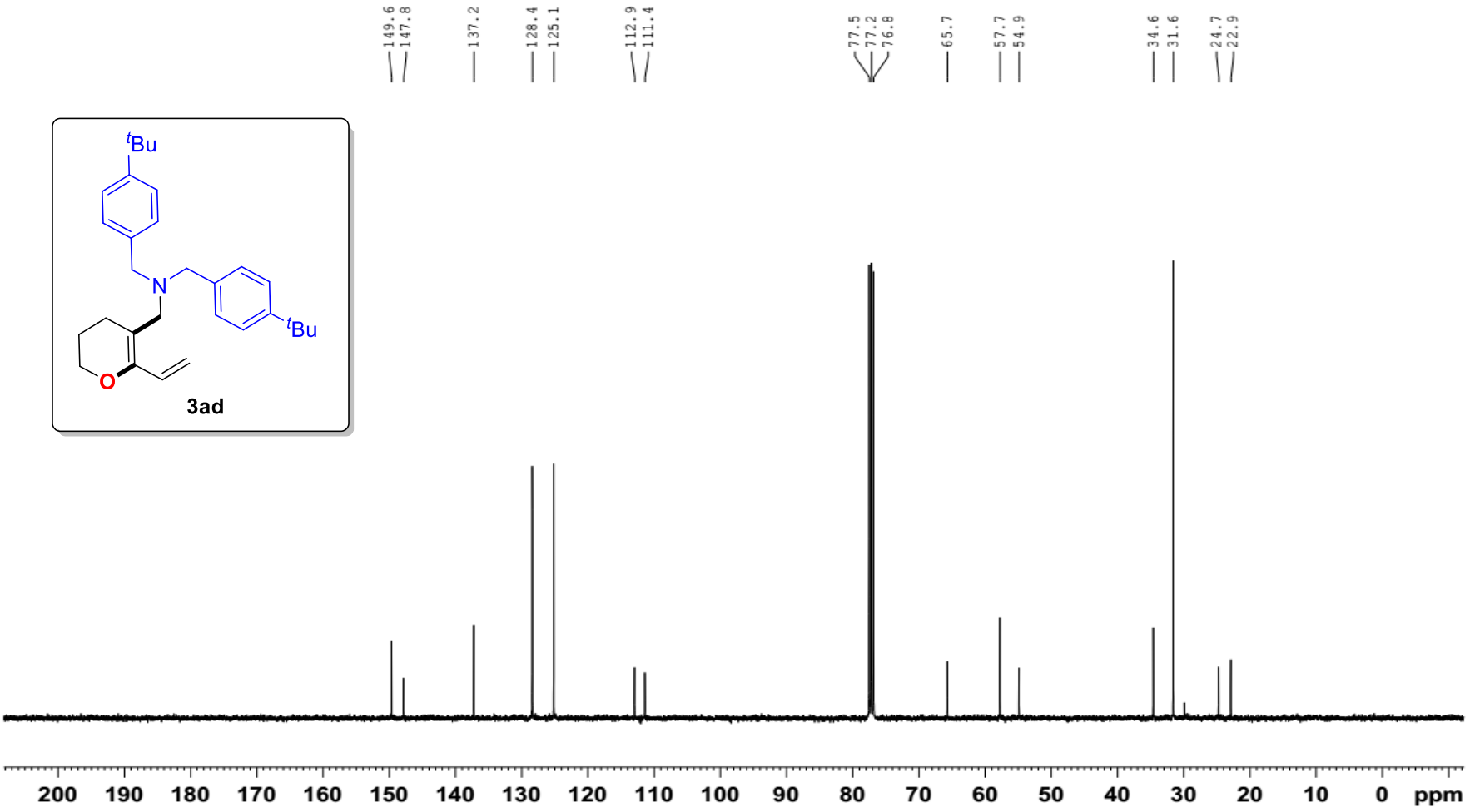
YHJ-P-**3ac** ^{13}C NMR (100MHz $CDCl_3$)



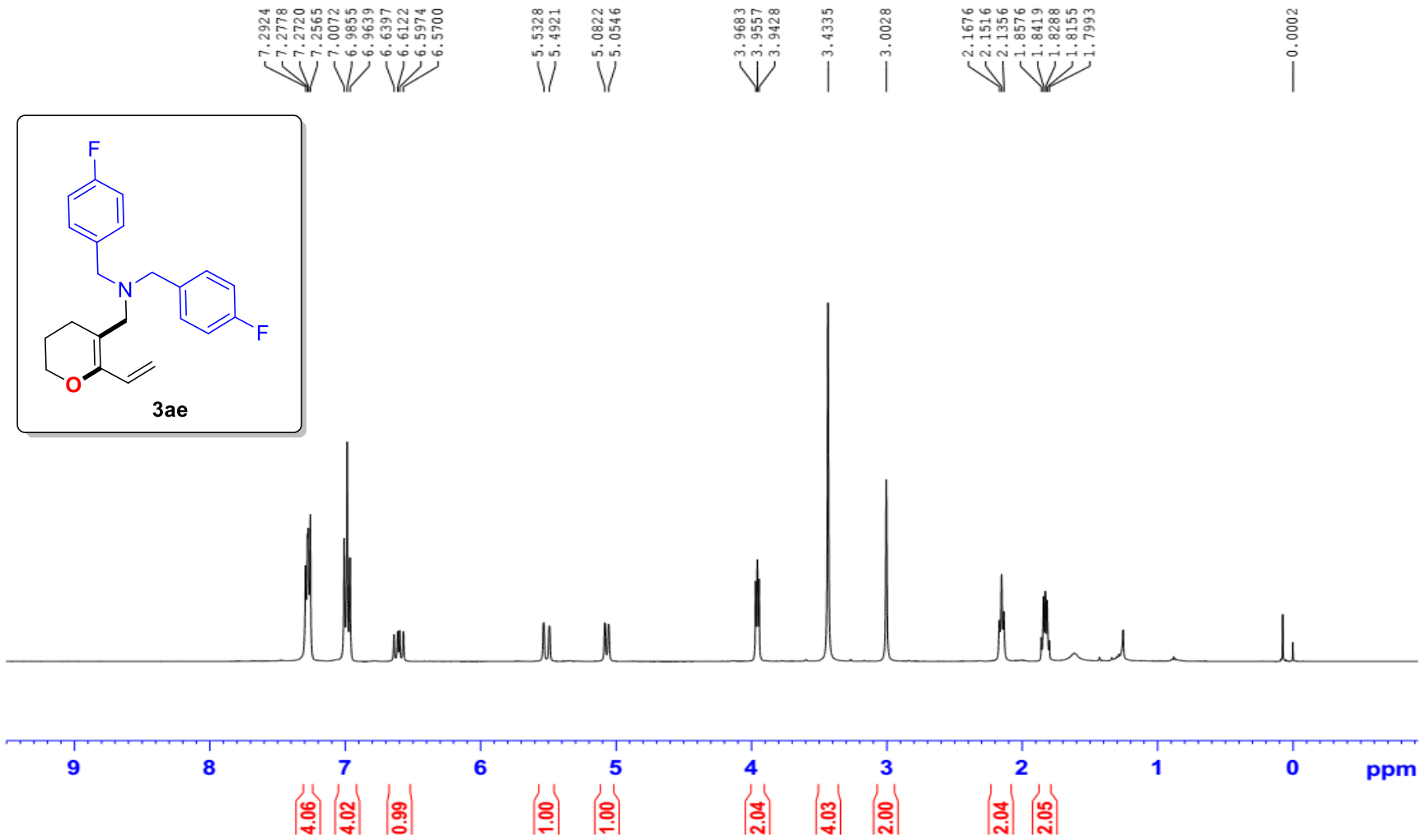
YHJ-P-**3ad** ^{1}H NMR (400MHz $CDCl_3$)



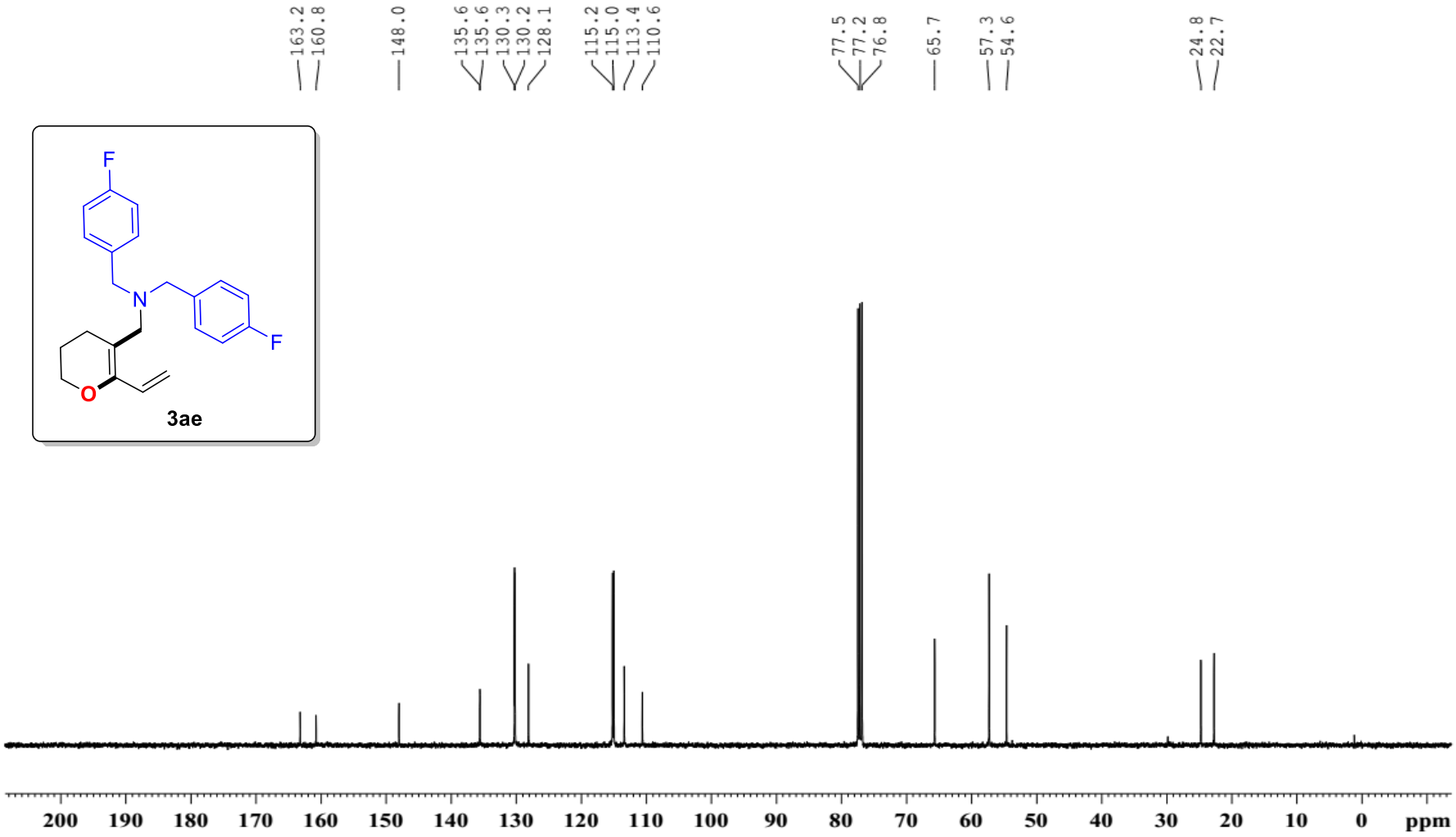
YHJ-P-**3ad** ^{13}C NMR (100MHz $CDCl_3$)



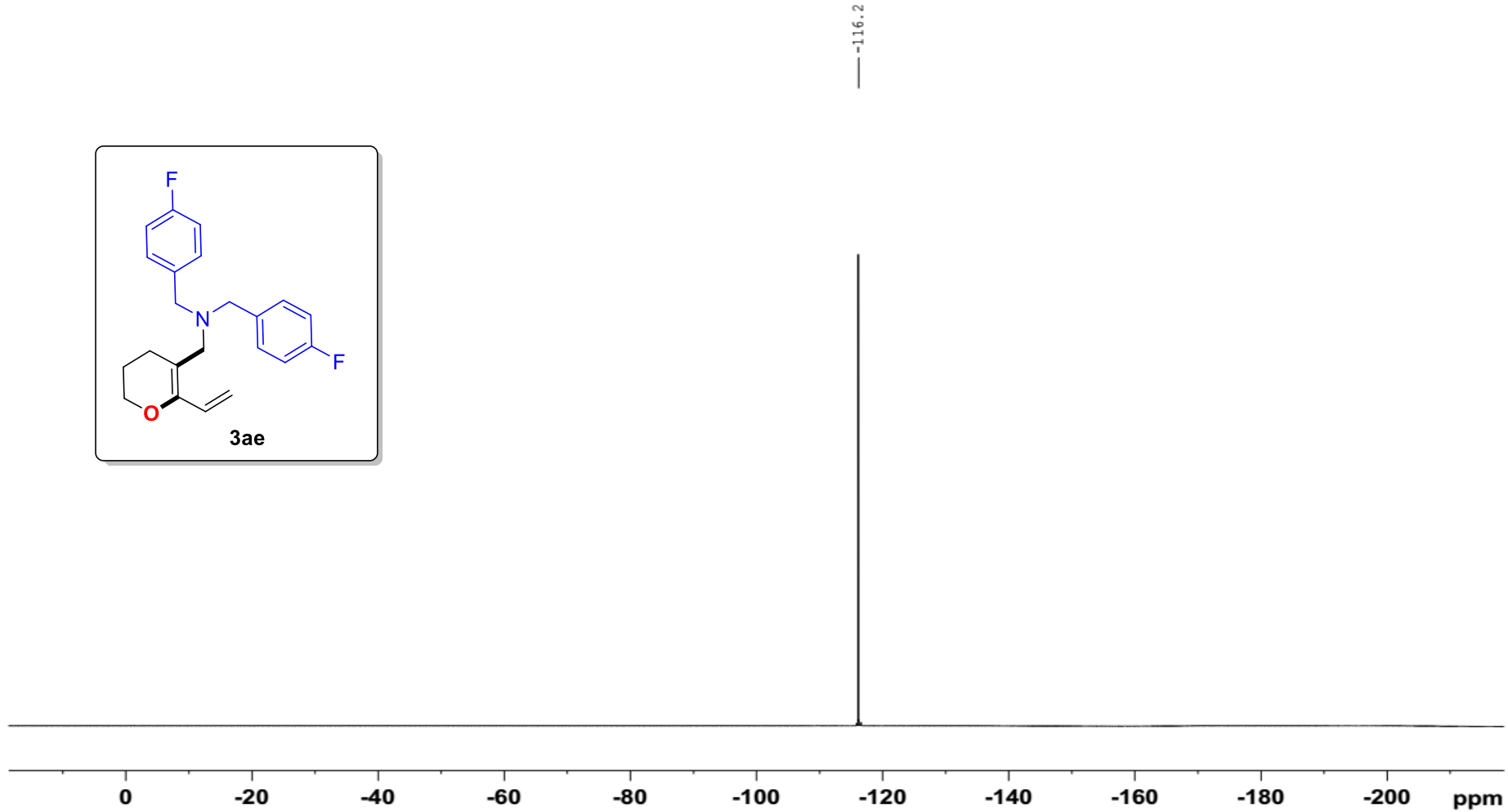
YHJ-P-**3ae** ^{1}H NMR (400MHz $CDCl_3$)



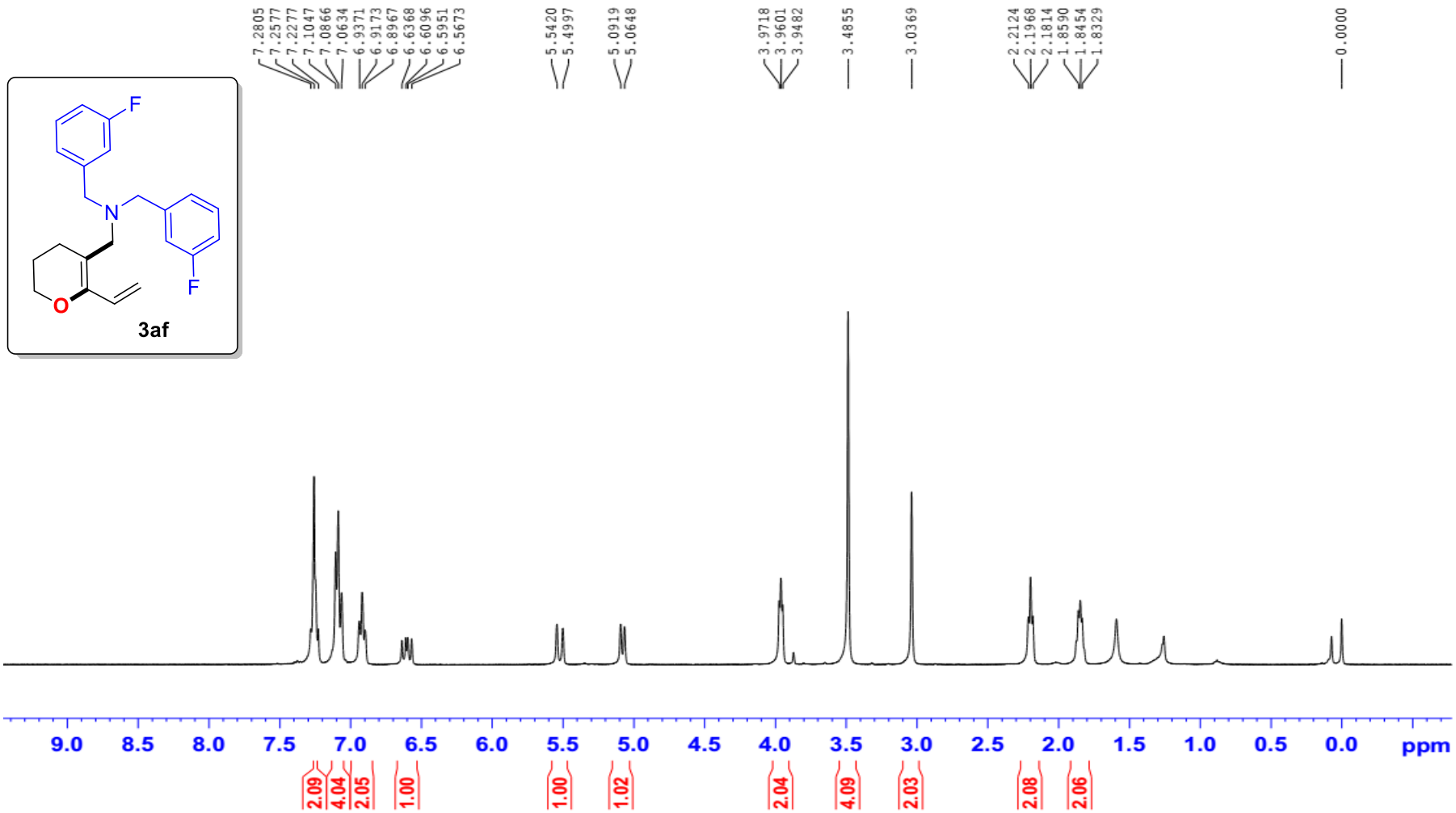
YHJ-P-**3ae** ^{13}C NMR (100MHz $CDCl_3$)



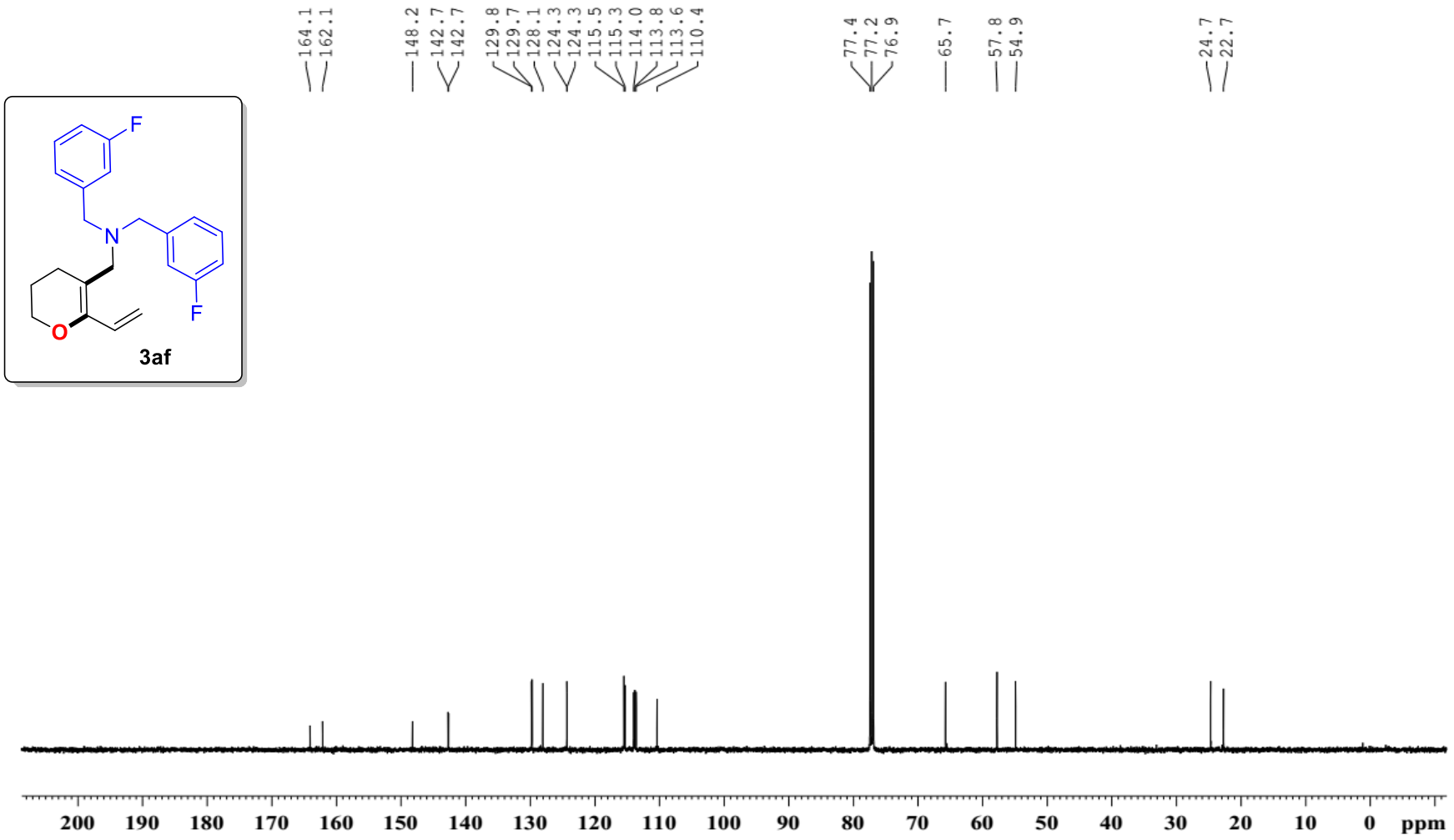
YHJ-P-**3ae** ^{19}F NMR (376MHz $CDCl_3$)



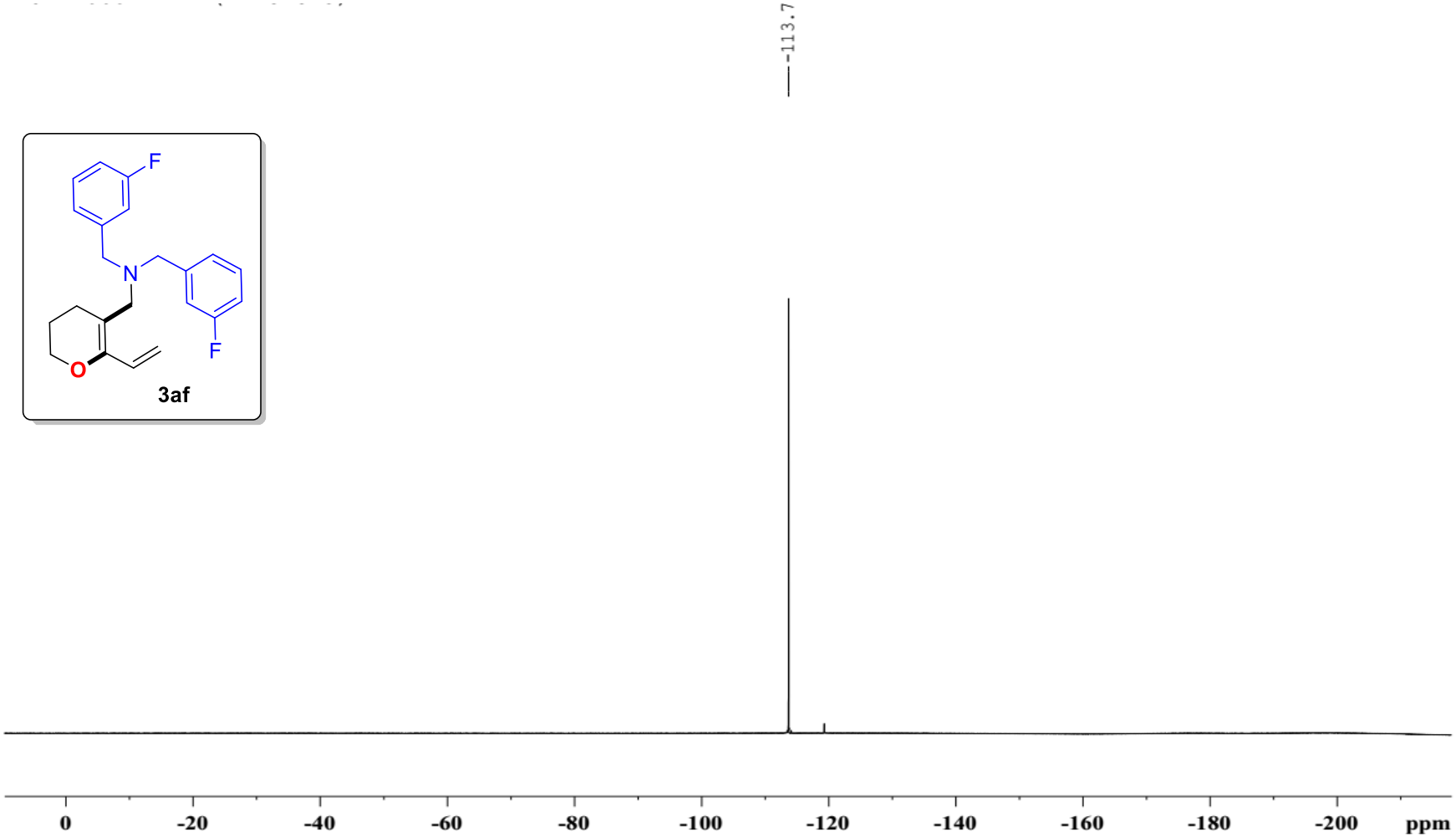
YHJ-P-**3af** ^{1}H NMR (400MHz $CDCl_3$)



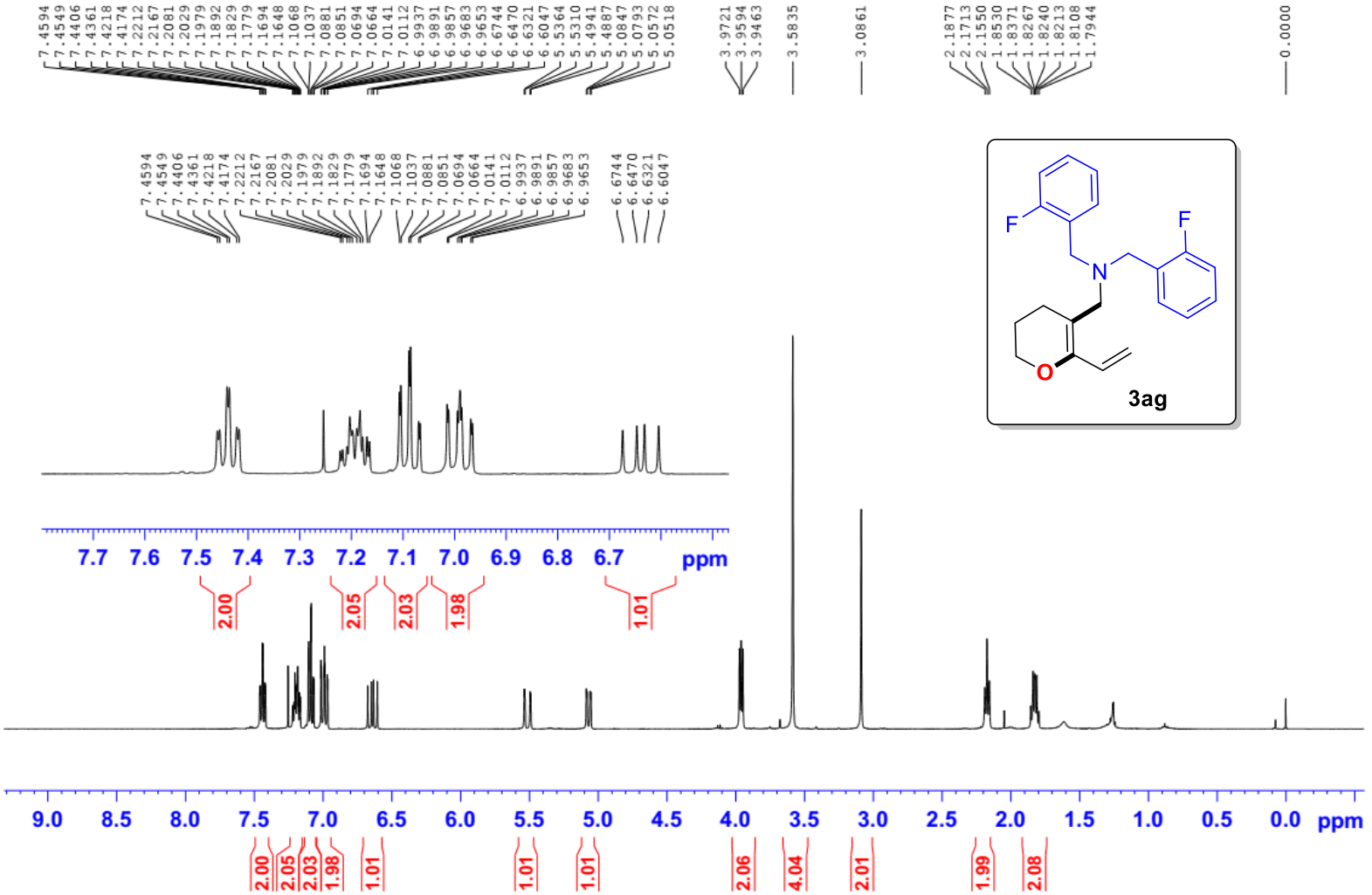
YHJ-P-**3af** ^{13}C NMR (125MHz $CDCl_3$)



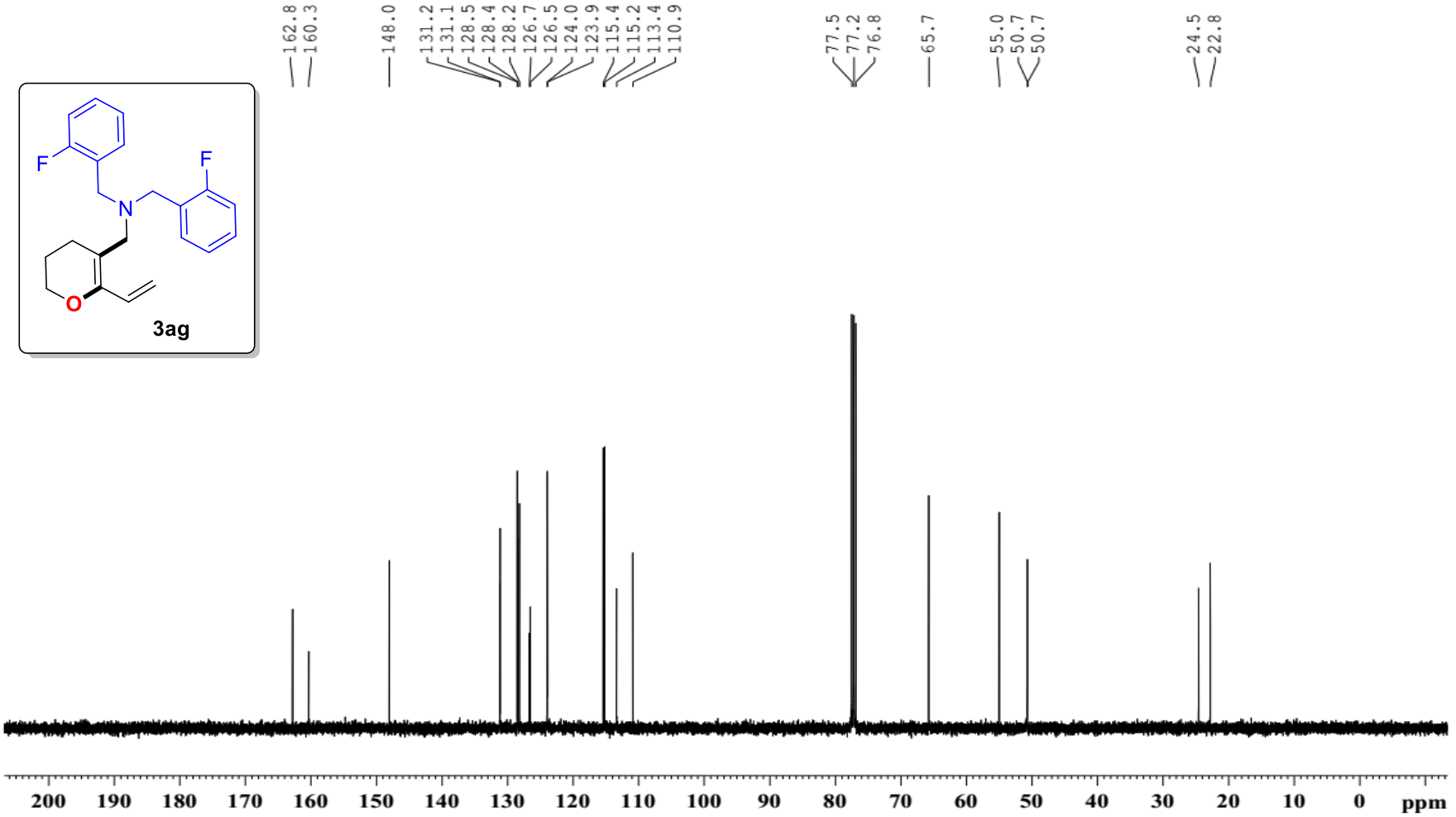
YHJ-P-**3af** ^{19}F NMR (376MHz $CDCl_3$)



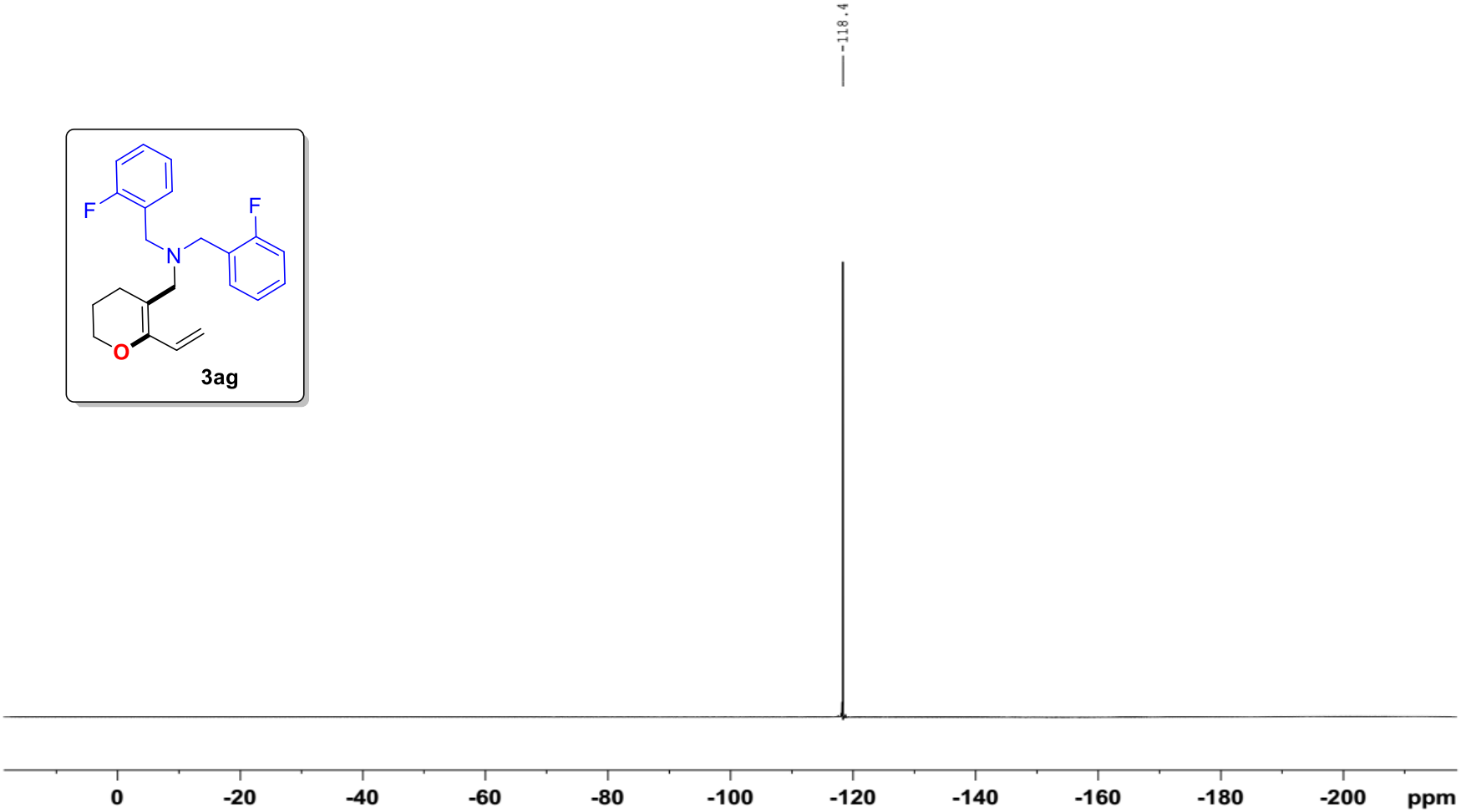
YHJ-P-**3ag** ^{1}H NMR (400MHz $CDCl_3$)



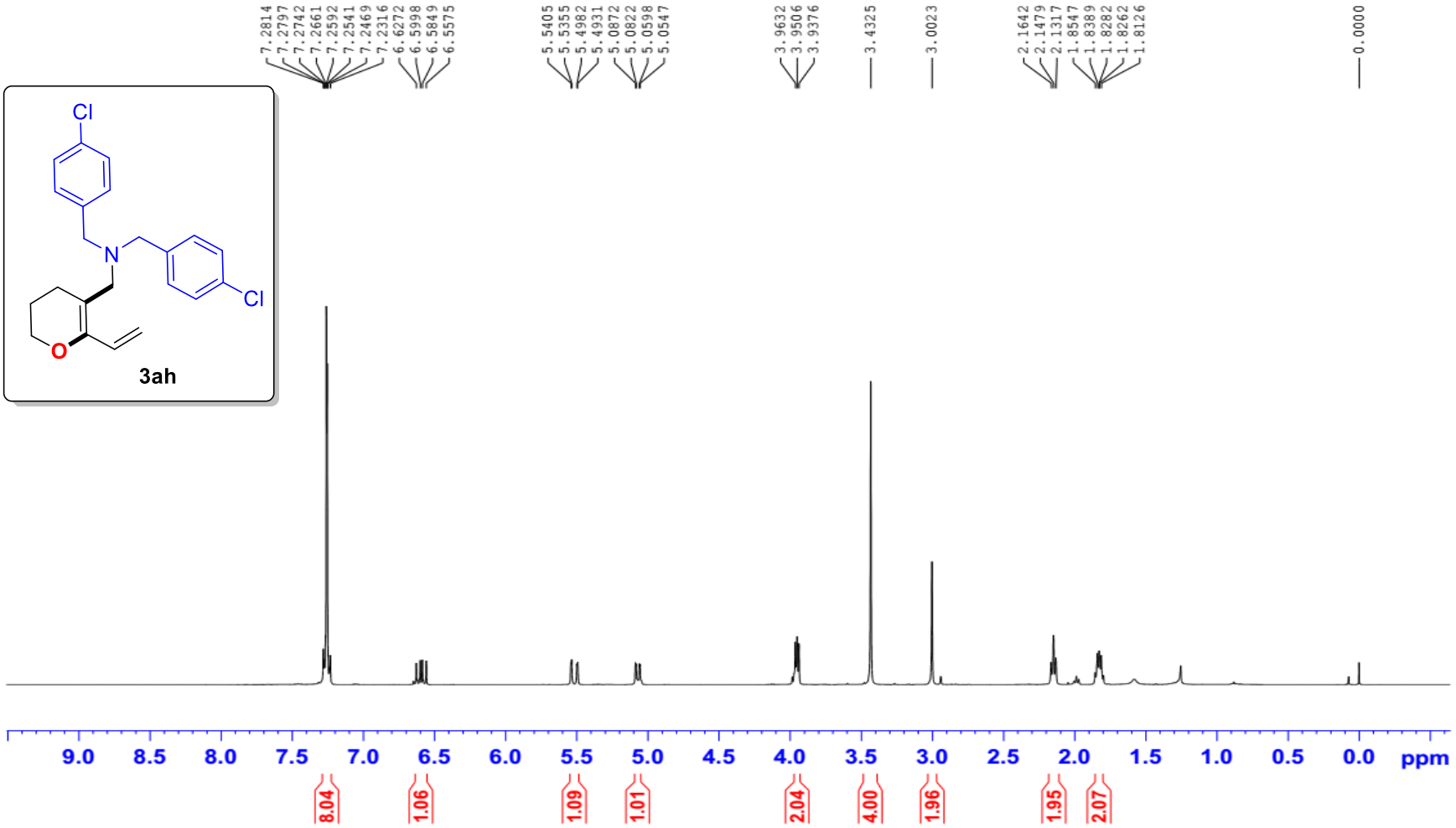
YHJ-P-**3ag** ^{13}C NMR (100MHz $CDCl_3$)



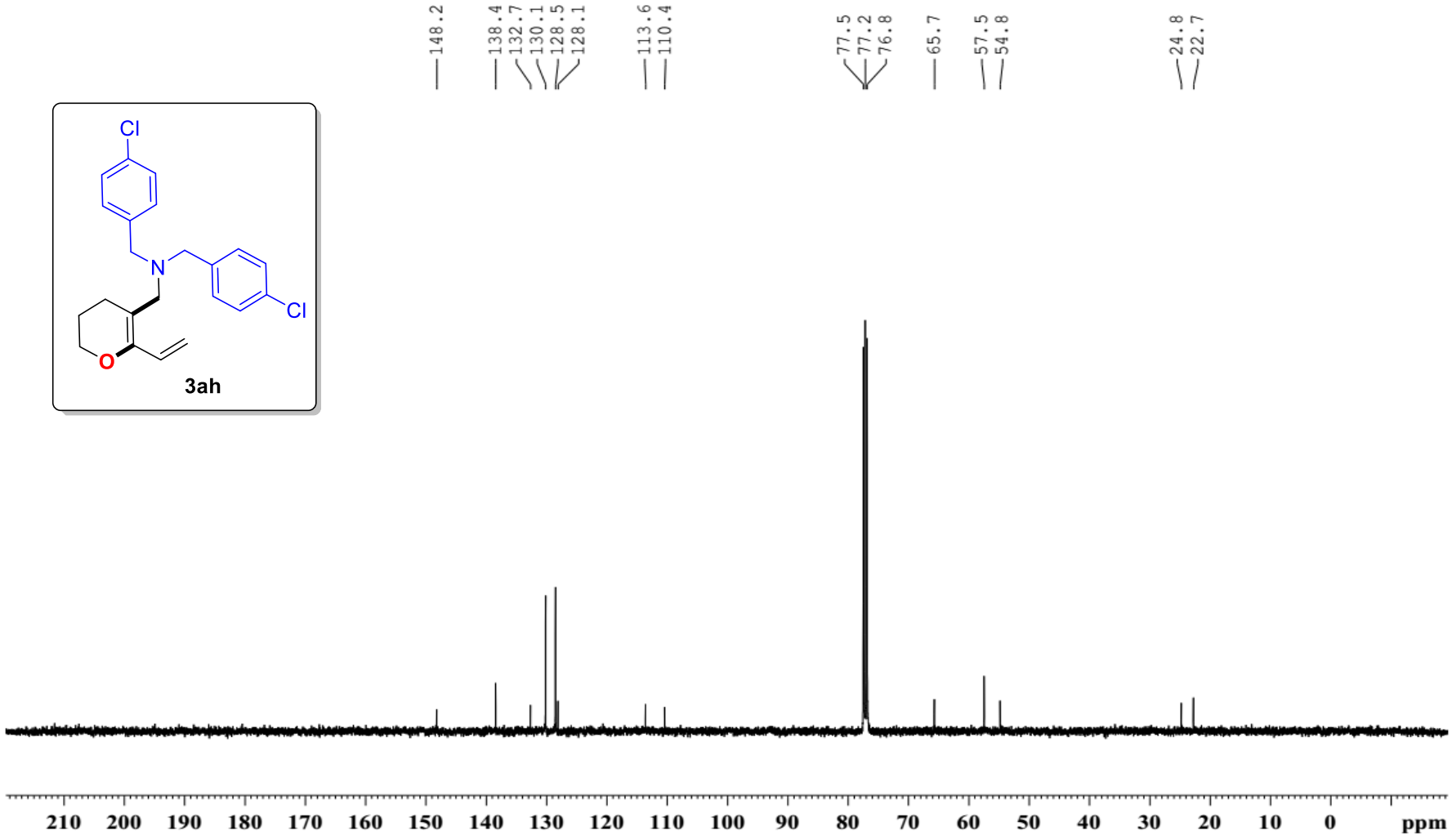
YHJ-P-**3ag** ^{19}F NMR (376MHz $CDCl_3$)



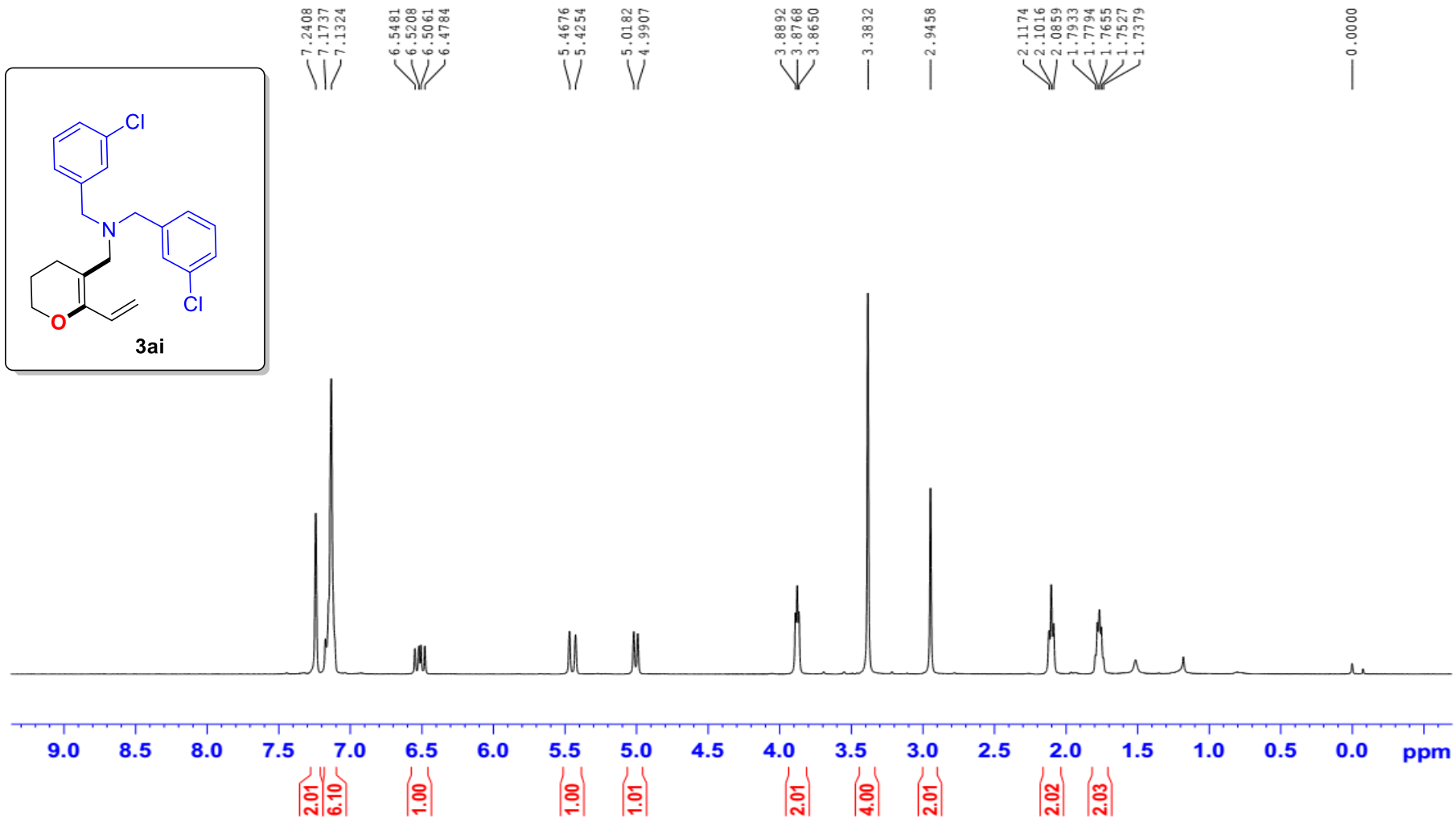
YHJ-P-**3ah** ^{1}H NMR (400MHz $CDCl_3$)



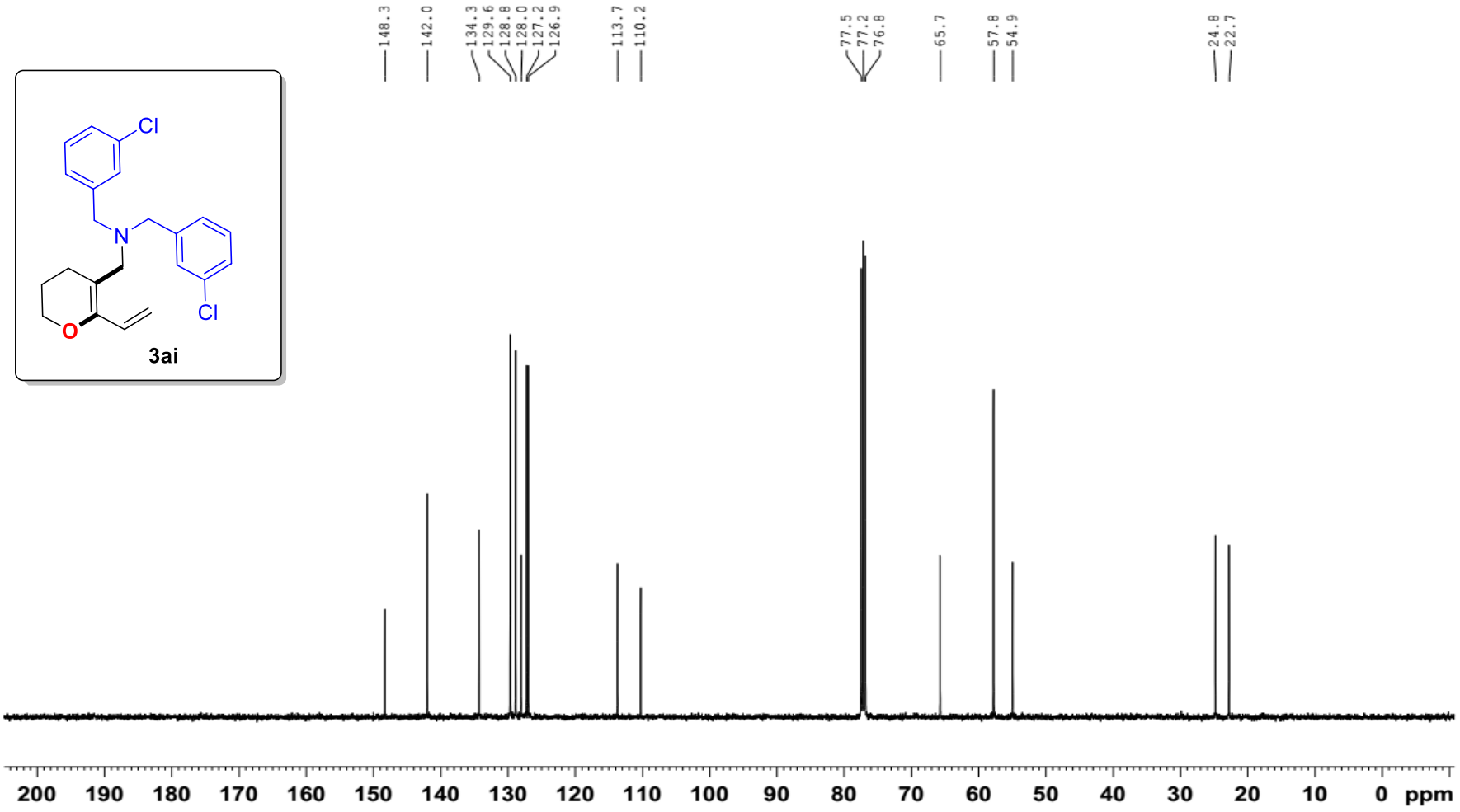
YHJ-P-**3ah** ^{13}C NMR (100MHz $CDCl_3$)



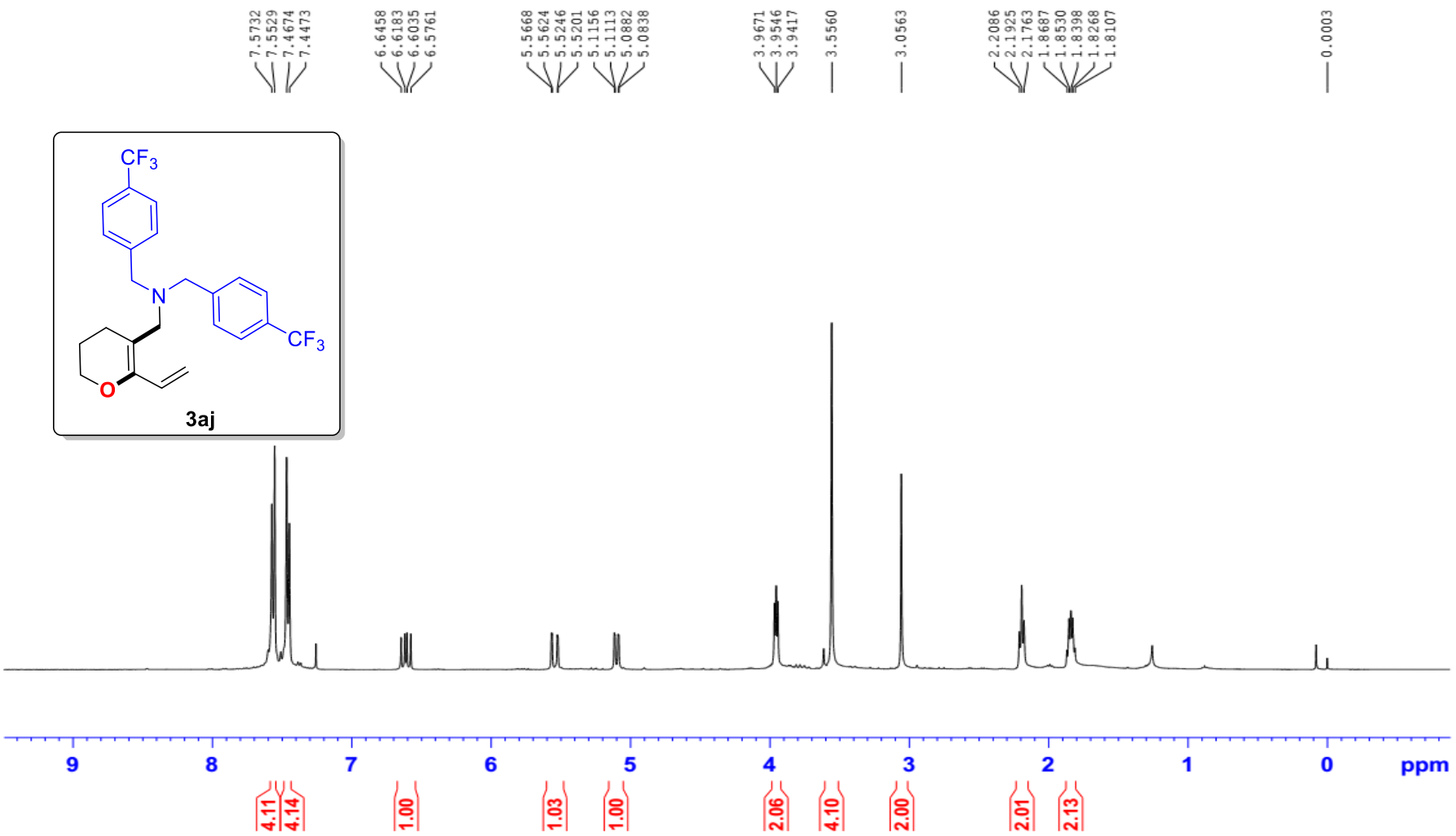
YHJ-P-**3ai** ^{1}H NMR (400MHz $CDCl_3$)



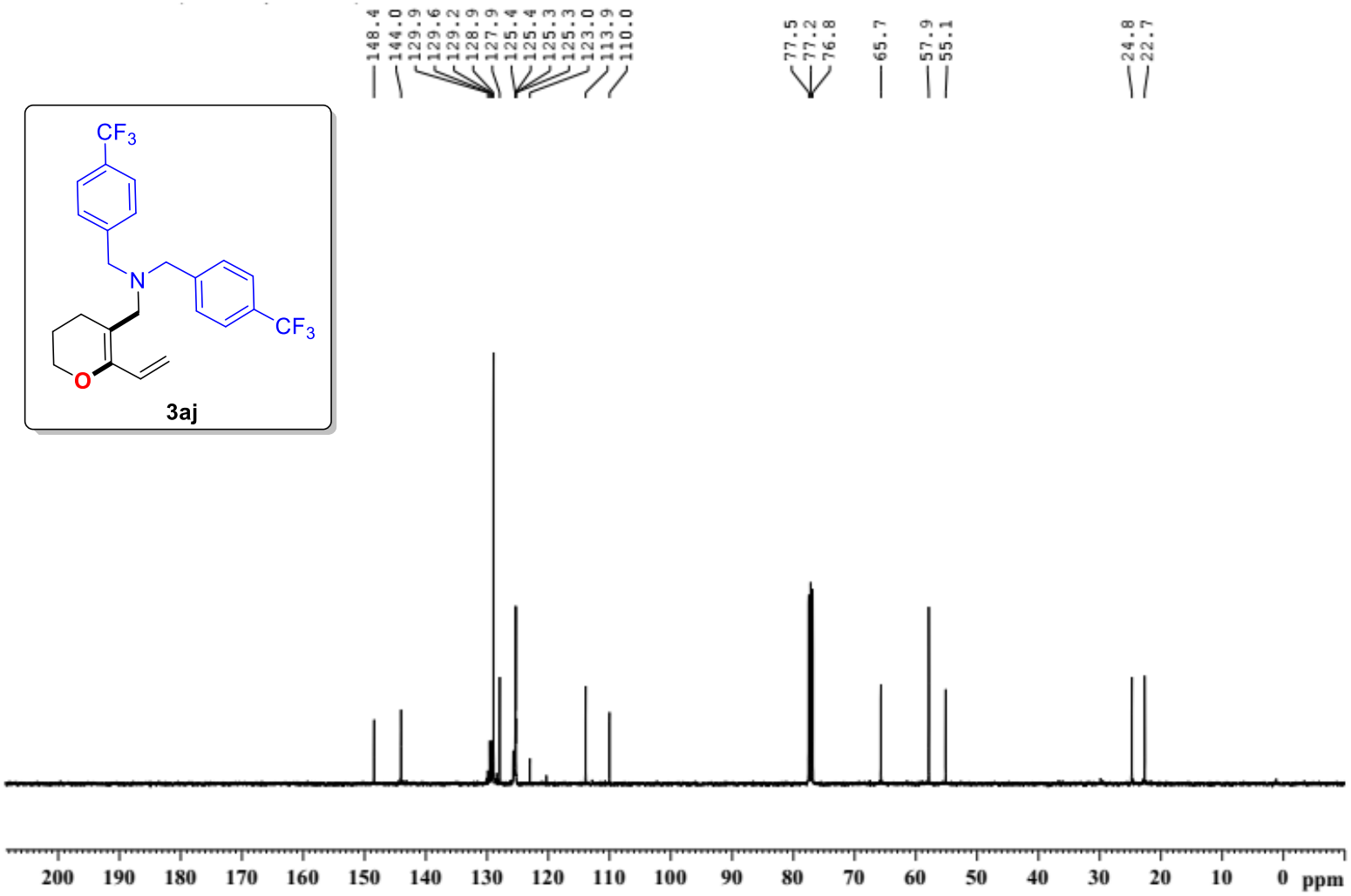
YHJ-P-**3ai** ^{13}C NMR (125MHz $CDCl_3$)



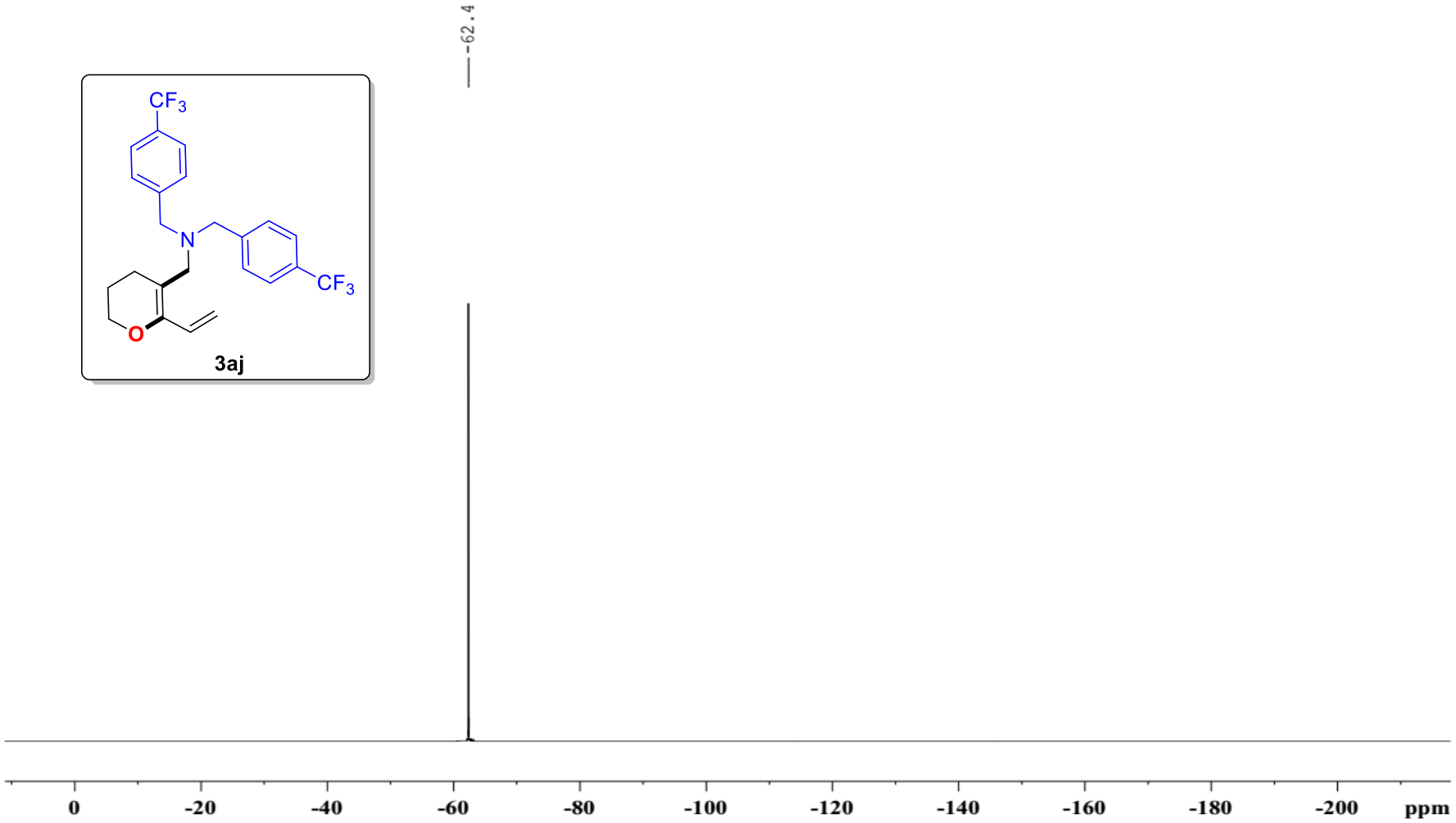
YHJ-P-**3aj** ^{1}H NMR (400MHz $CDCl_3$)



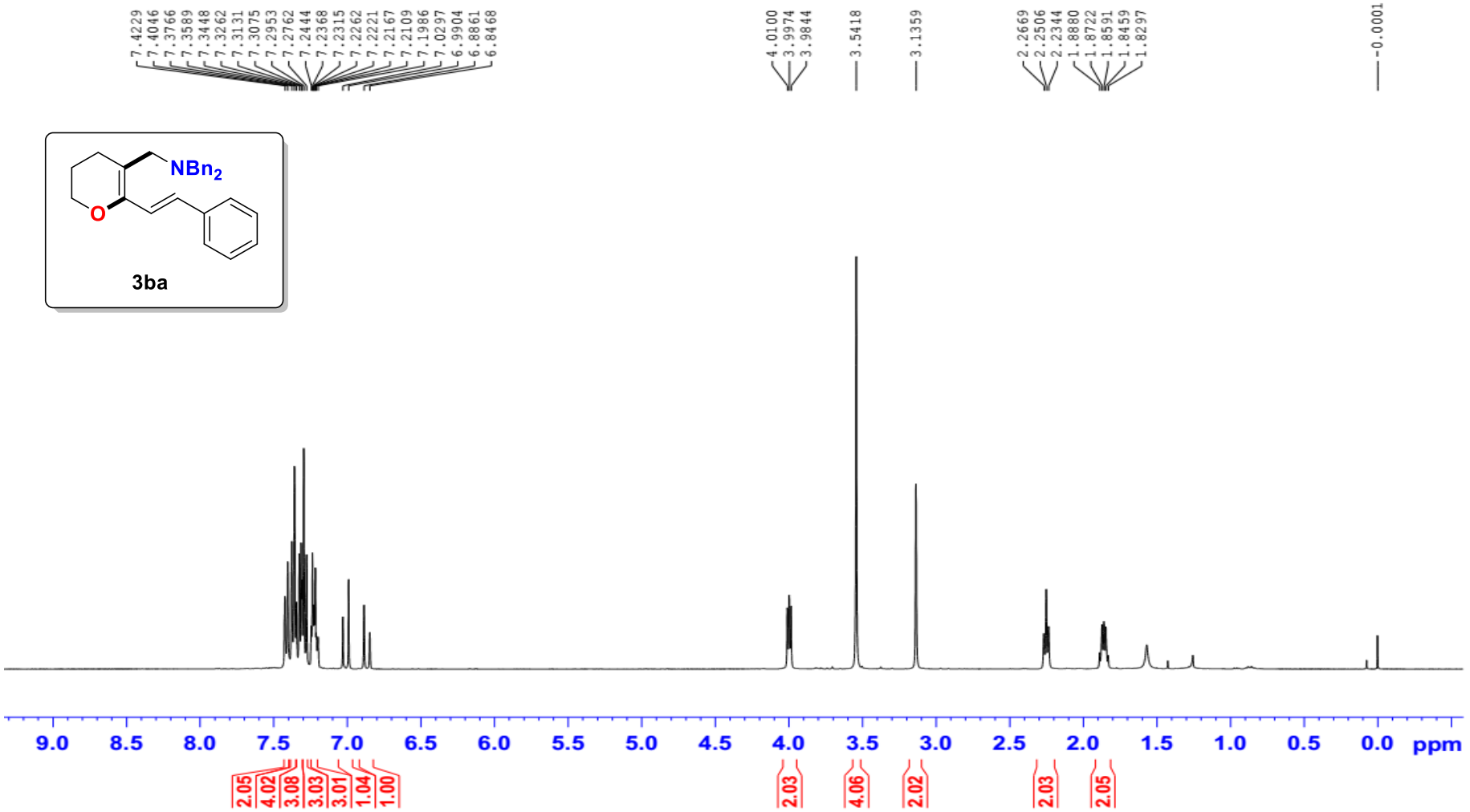
YHJ-P-**3aj** ^{13}C NMR (100MHz $CDCl_3$)



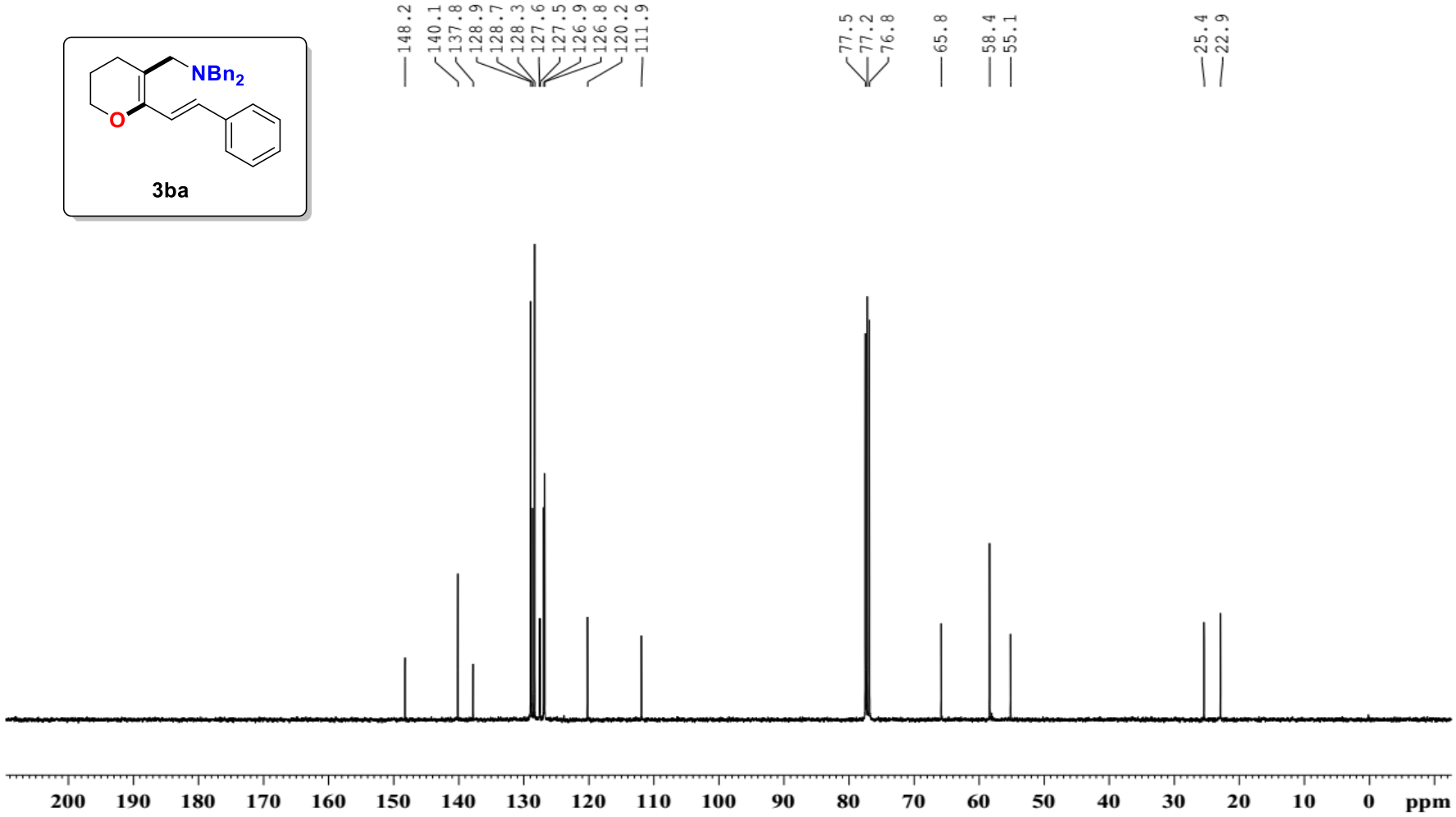
YHJ-P-**3aj** ^{19}F NMR (376MHz $CDCl_3$)



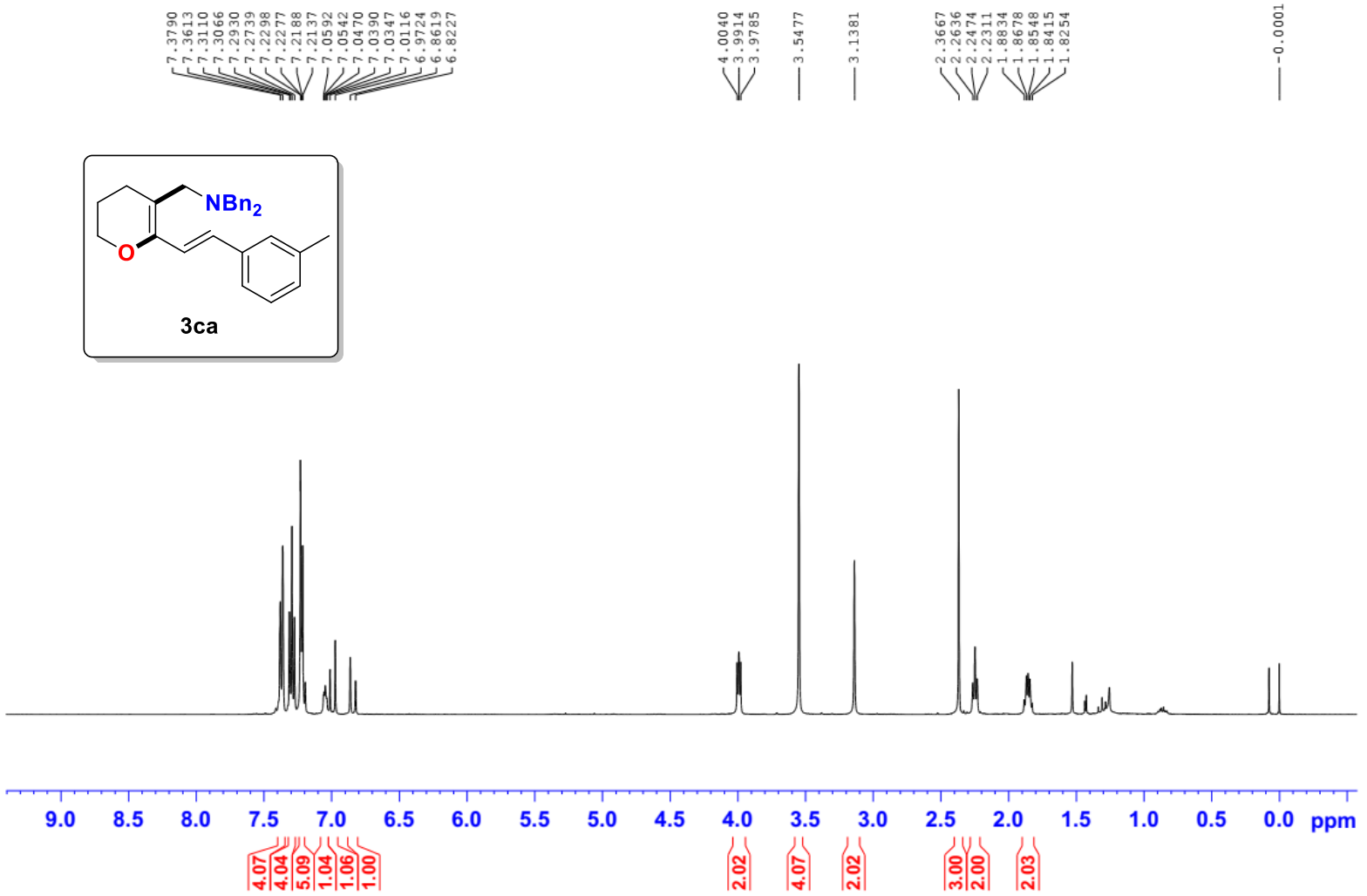
YHJ-P-**3ba** ^{1}H NMR (400MHz $CDCl_3$)



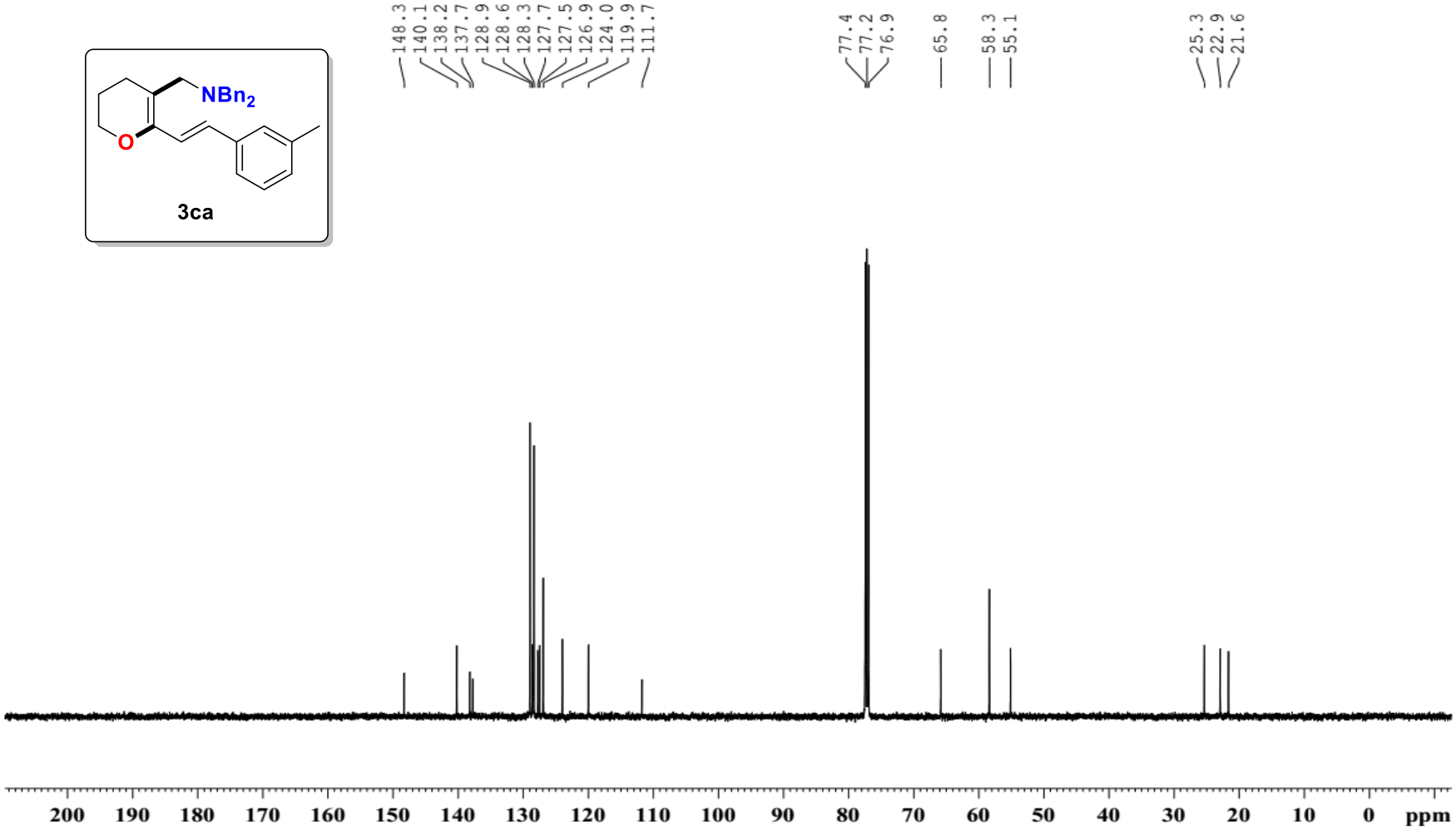
YHJ-P-**3ba** ^{13}C NMR (100MHz $CDCl_3$)



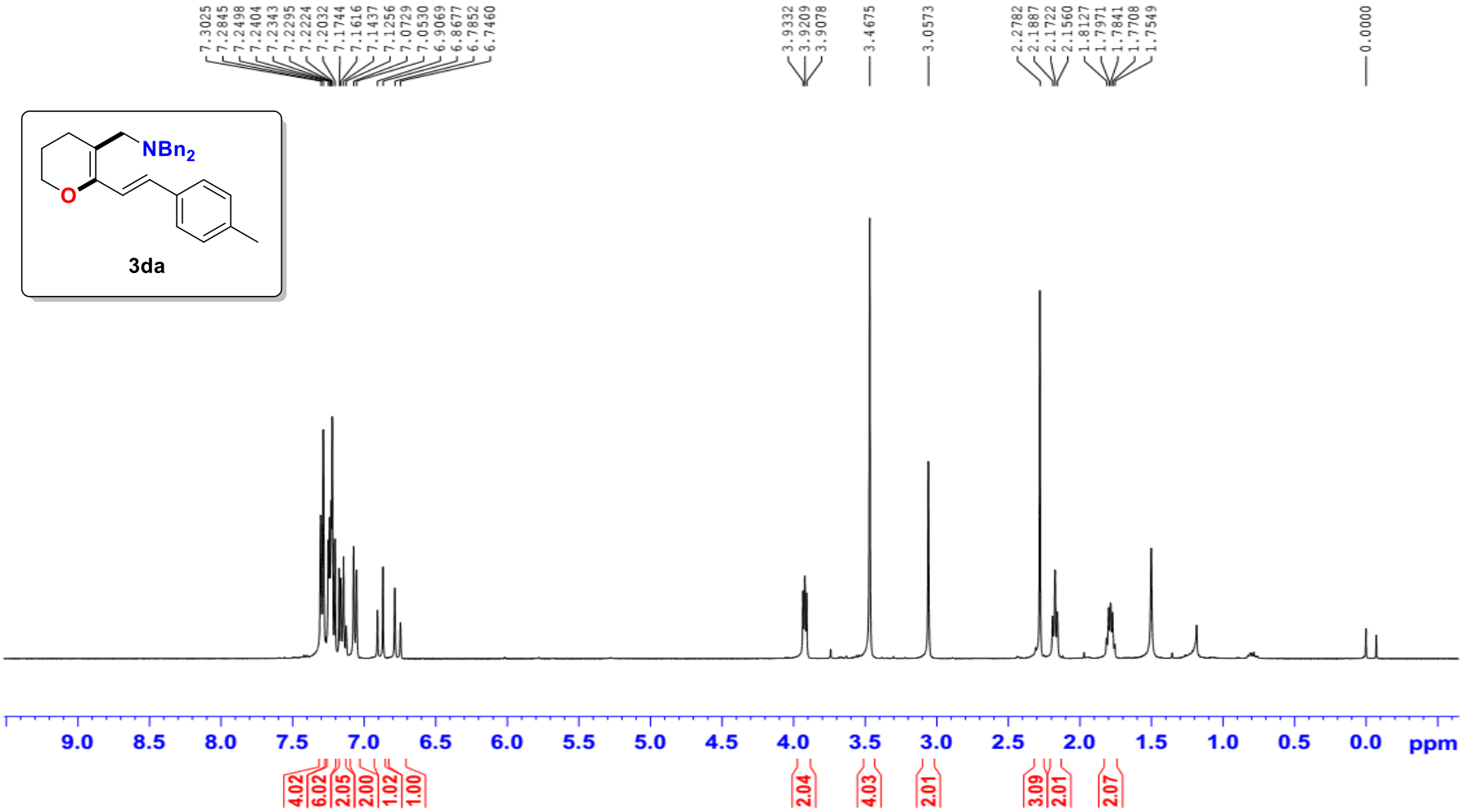
YHJ-P-**3ca** ^{1}H NMR (400MHz $CDCl_3$)



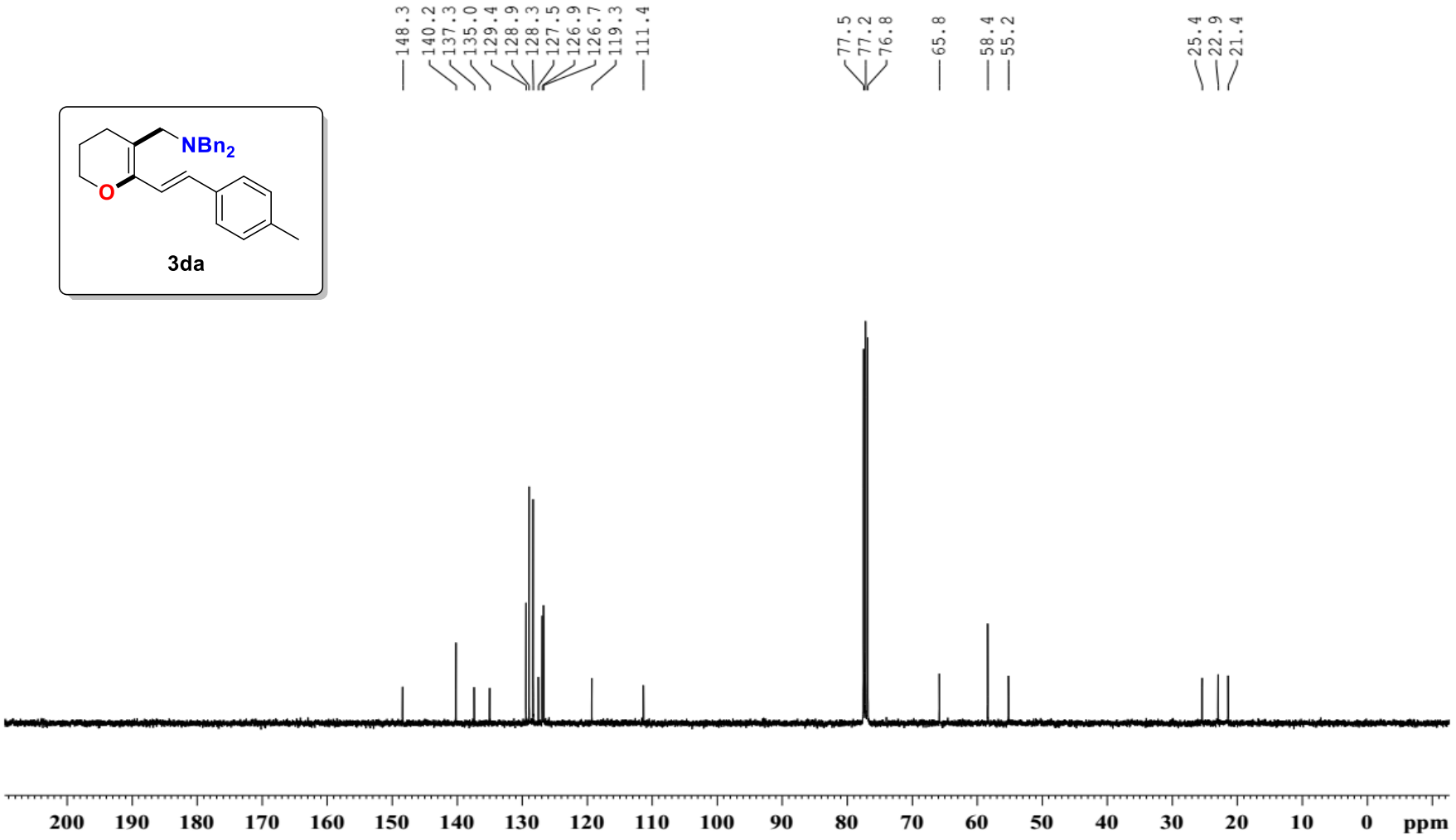
YHJ-P-**3ca** ^{13}C NMR (125MHz $CDCl_3$)



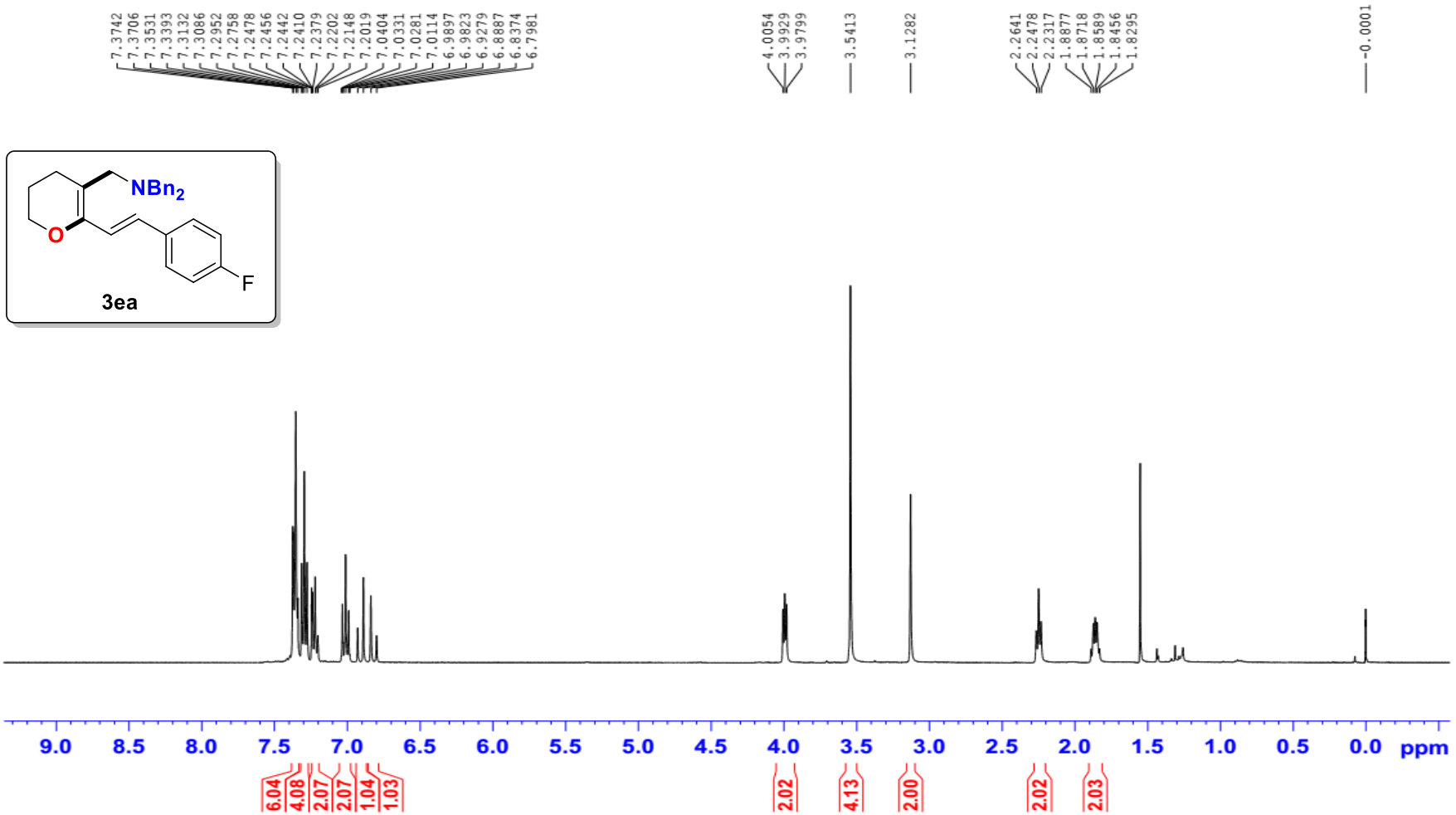
YHJ-P-**3da** ^{1}H NMR (400MHz $CDCl_3$)



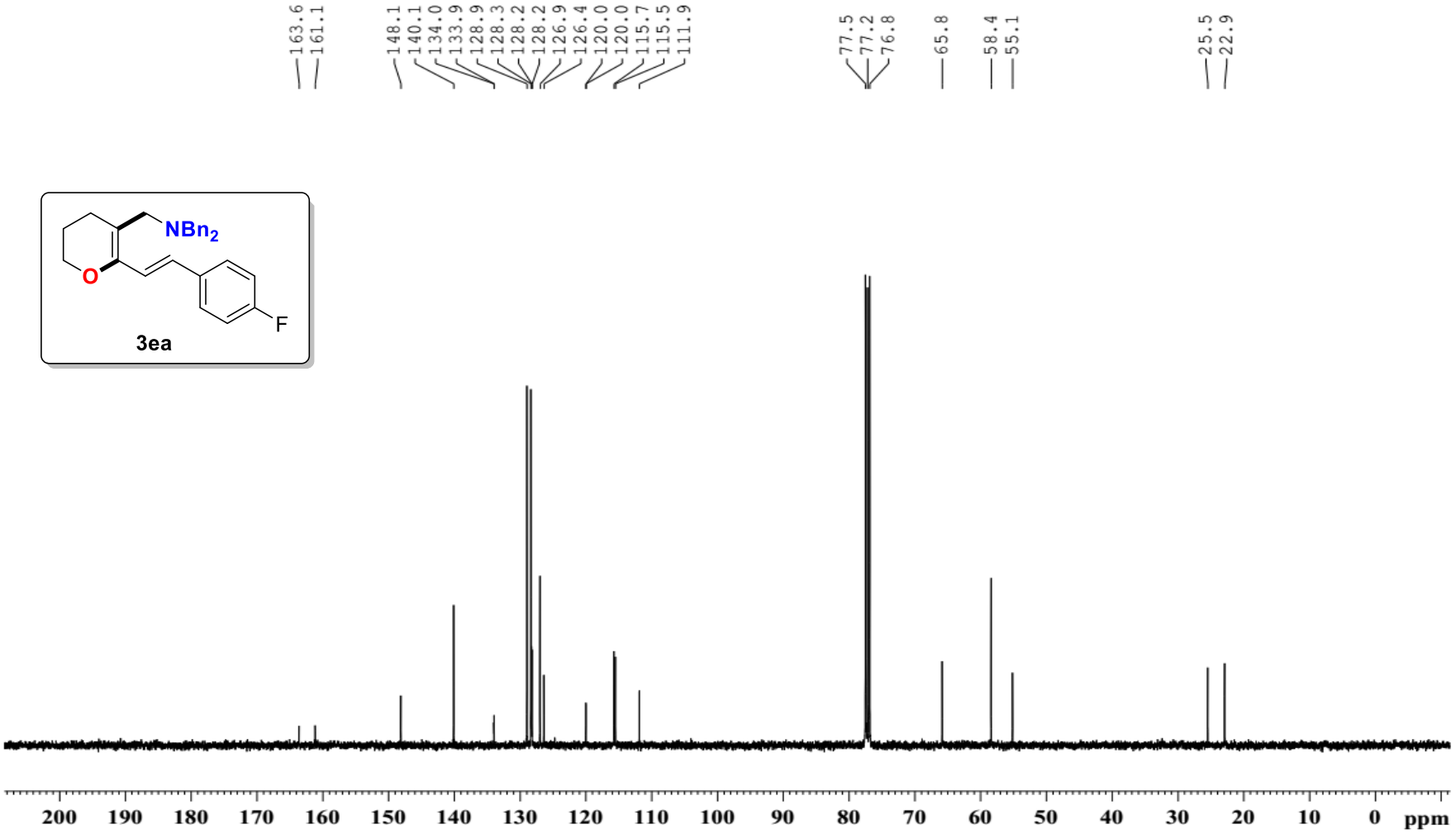
YHJ-P-**3da** ^{13}C NMR (100MHz $CDCl_3$)



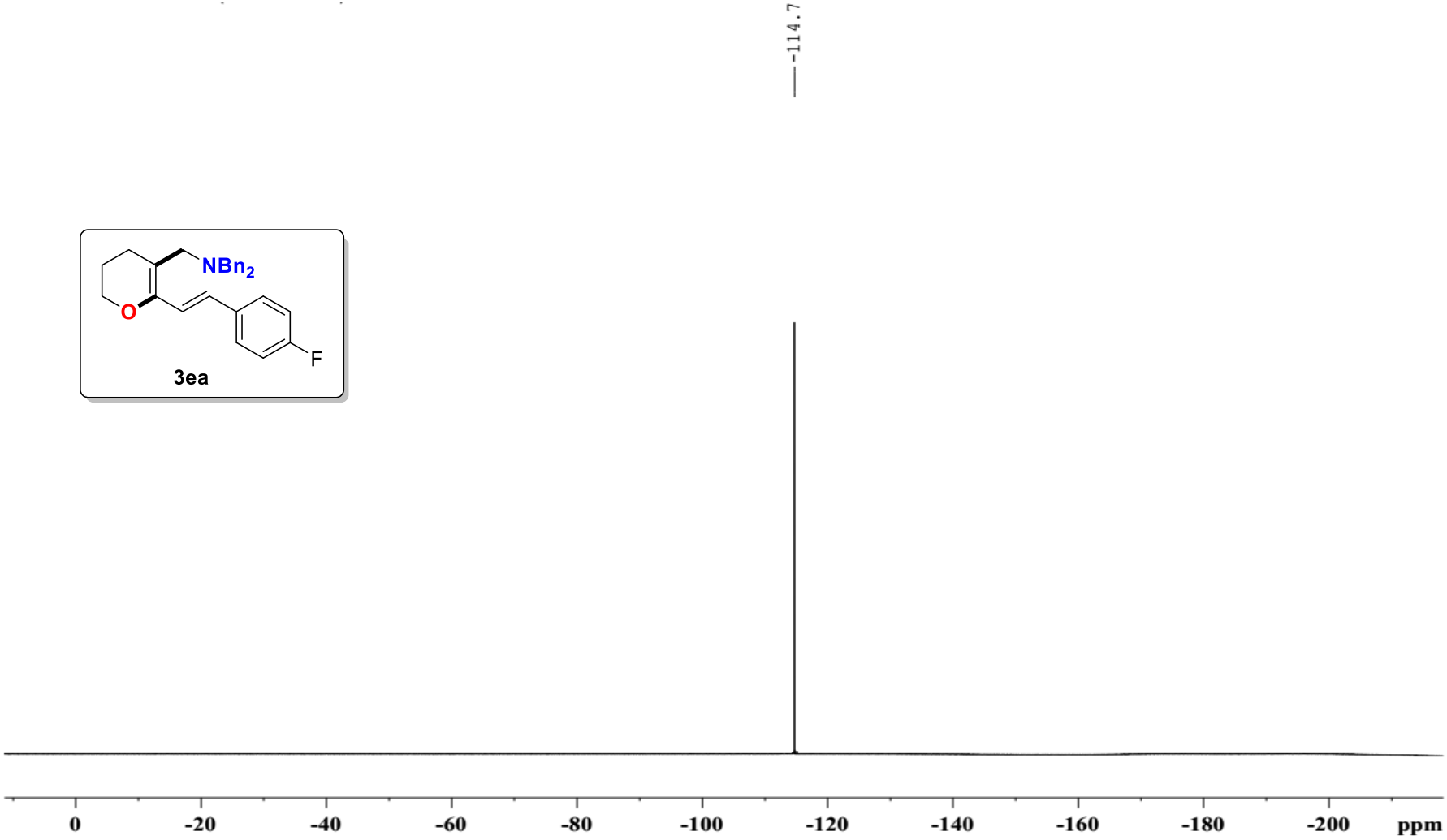
YHJ-P-**3ea** ^{1}H NMR (400MHz $CDCl_3$)



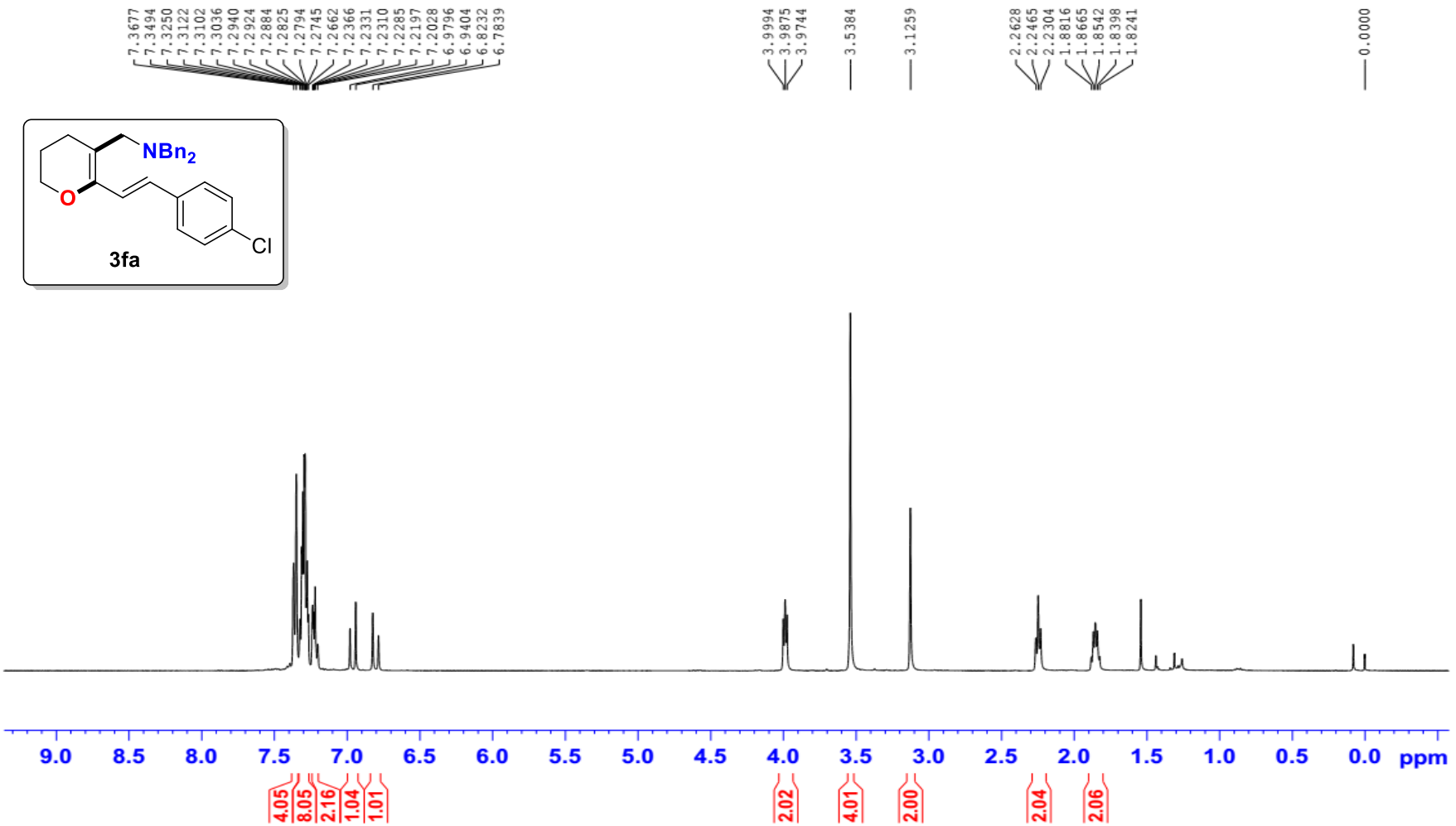
YHJ-P-**3ea** ^{13}C NMR (100MHz $CDCl_3$)



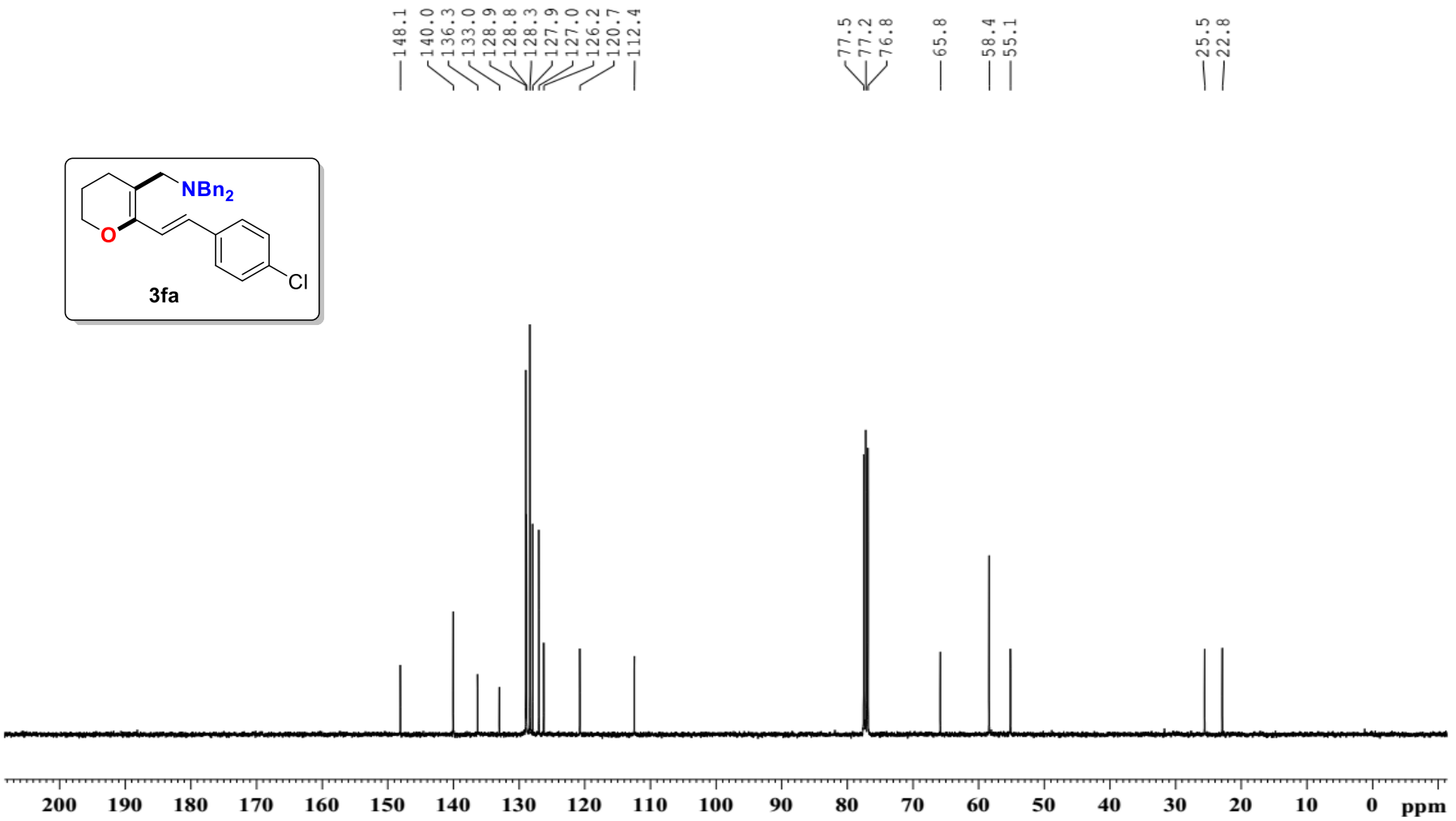
YHJ-P-**3ea** ^{19}F NMR (376MHz $CDCl_3$)



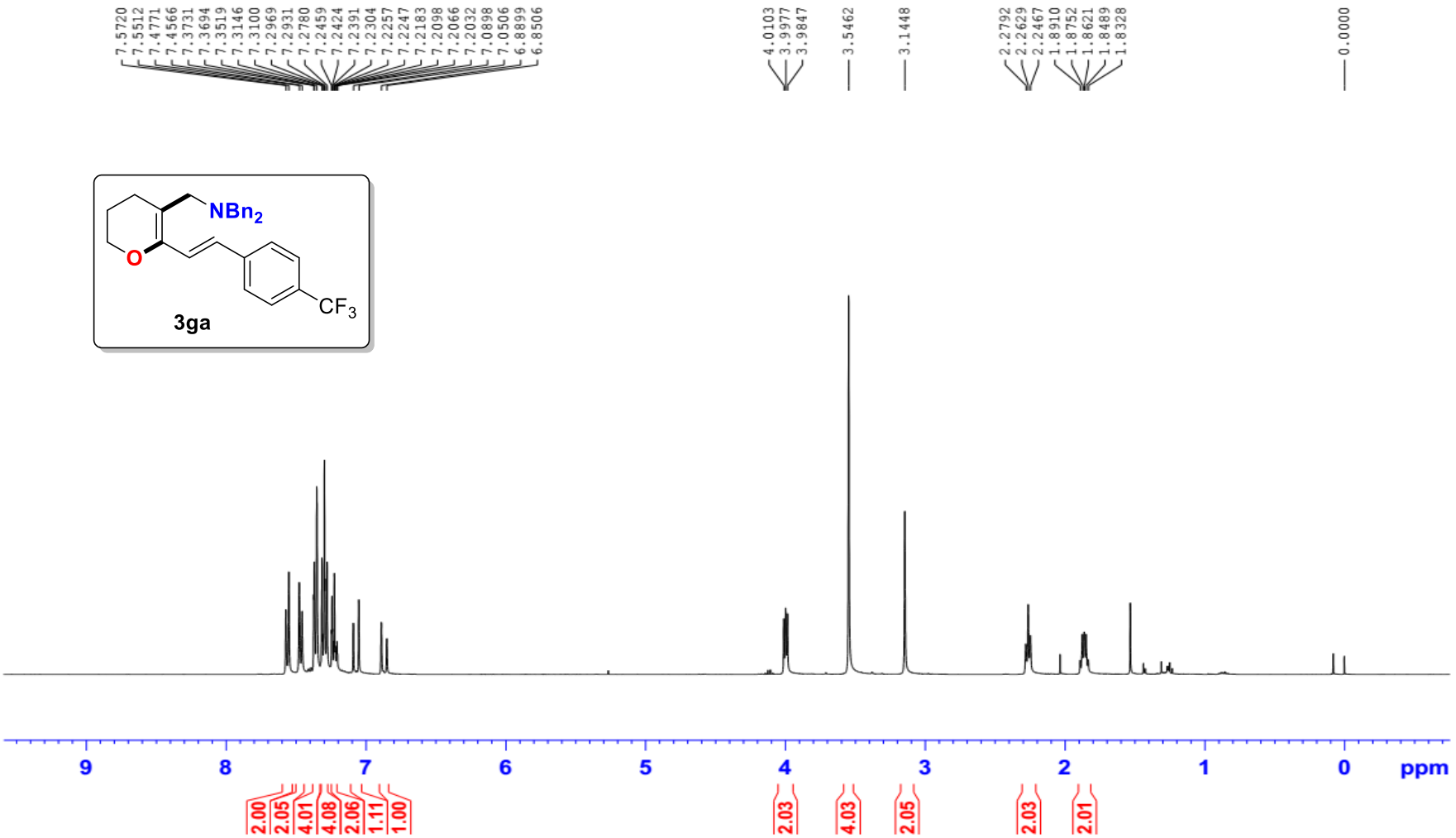
YHJ-P-**3fa** ^{1}H NMR (400MHz $CDCl_3$)



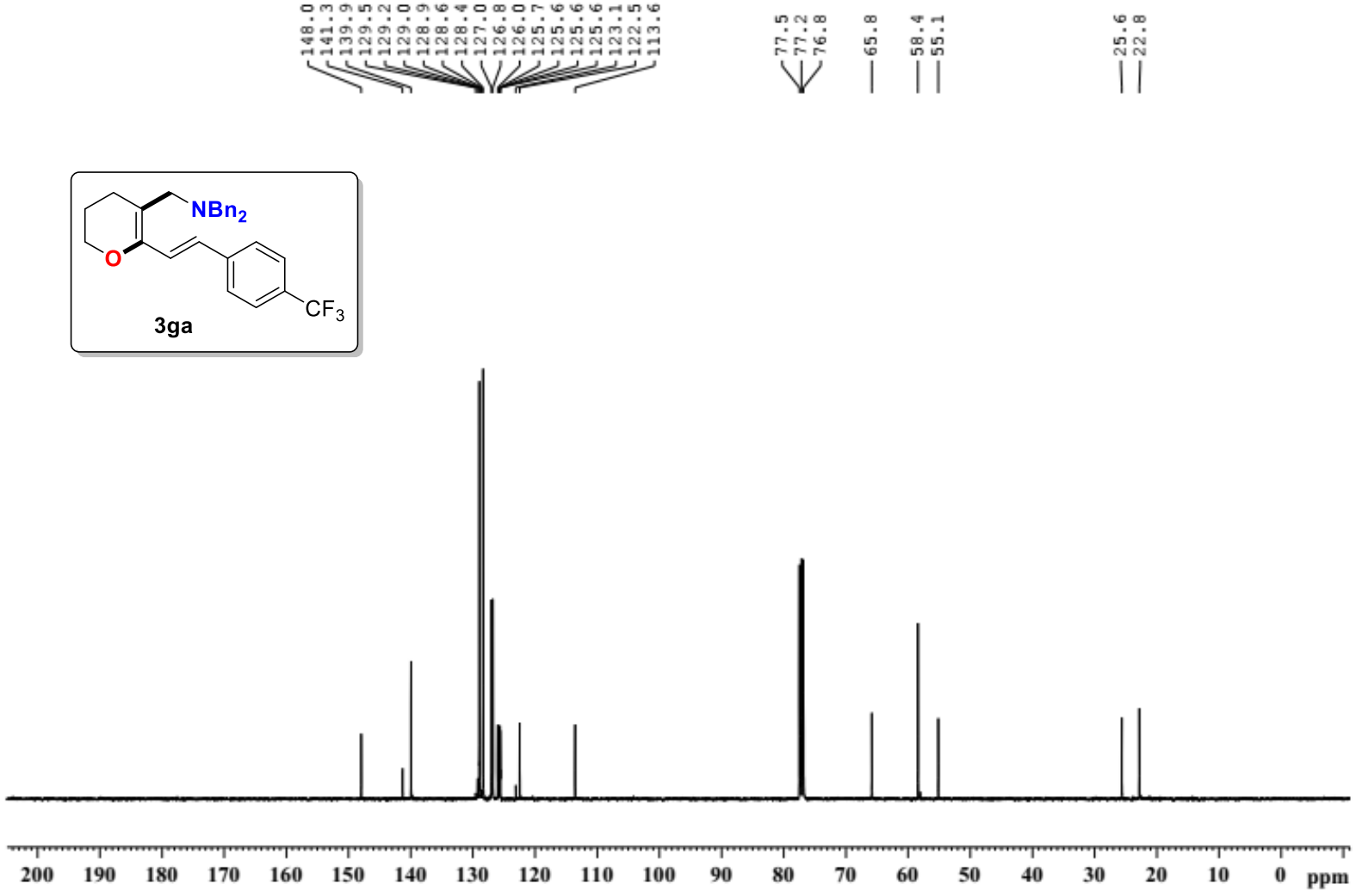
YHJ-P-**3fa** ^{13}C NMR (100MHz $CDCl_3$)



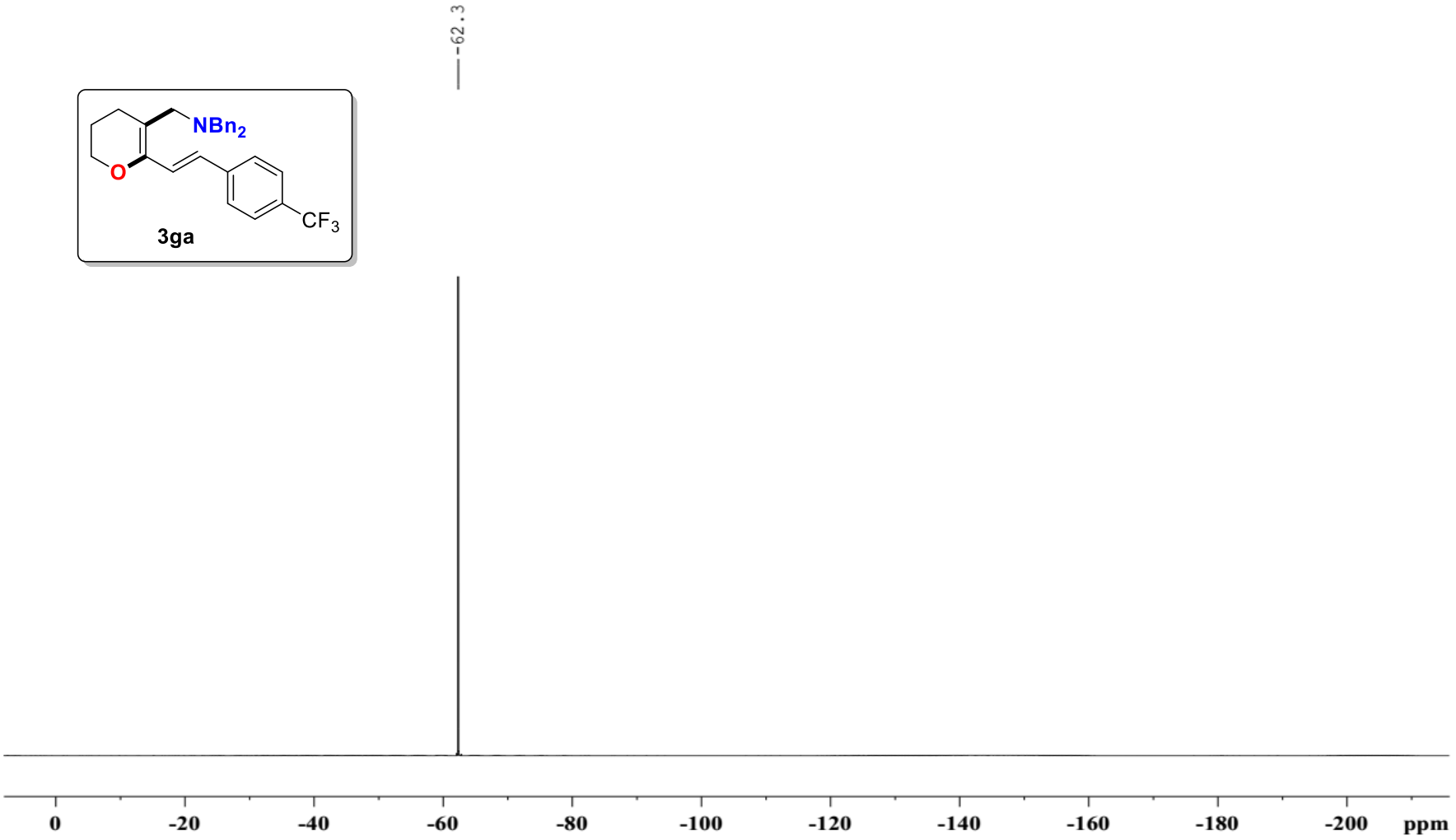
YHJ-P-**3ga** ^{1}H NMR (400MHz $CDCl_3$)



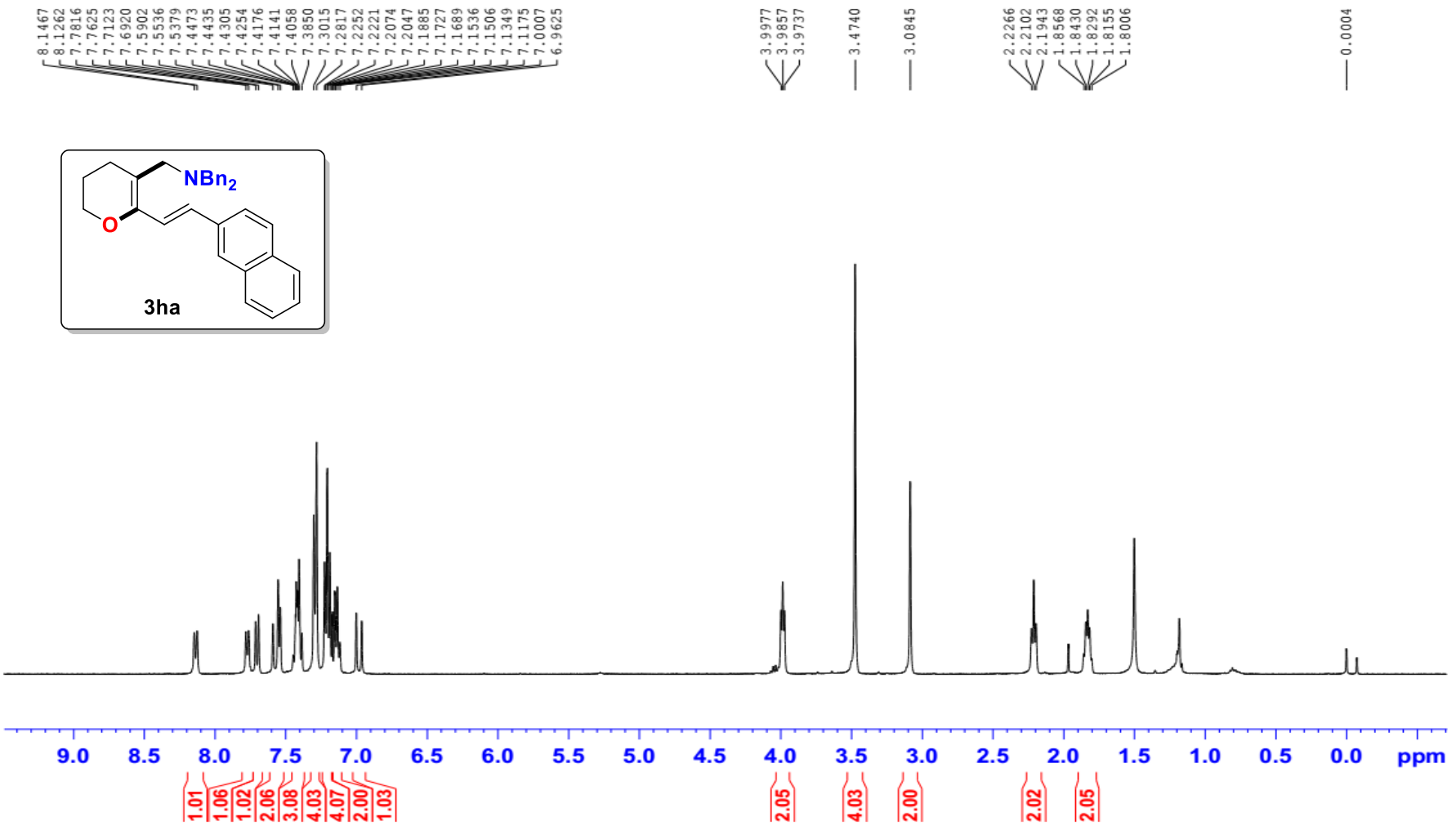
YHJ-P-**3ga** ^{13}C NMR (100MHz $CDCl_3$)



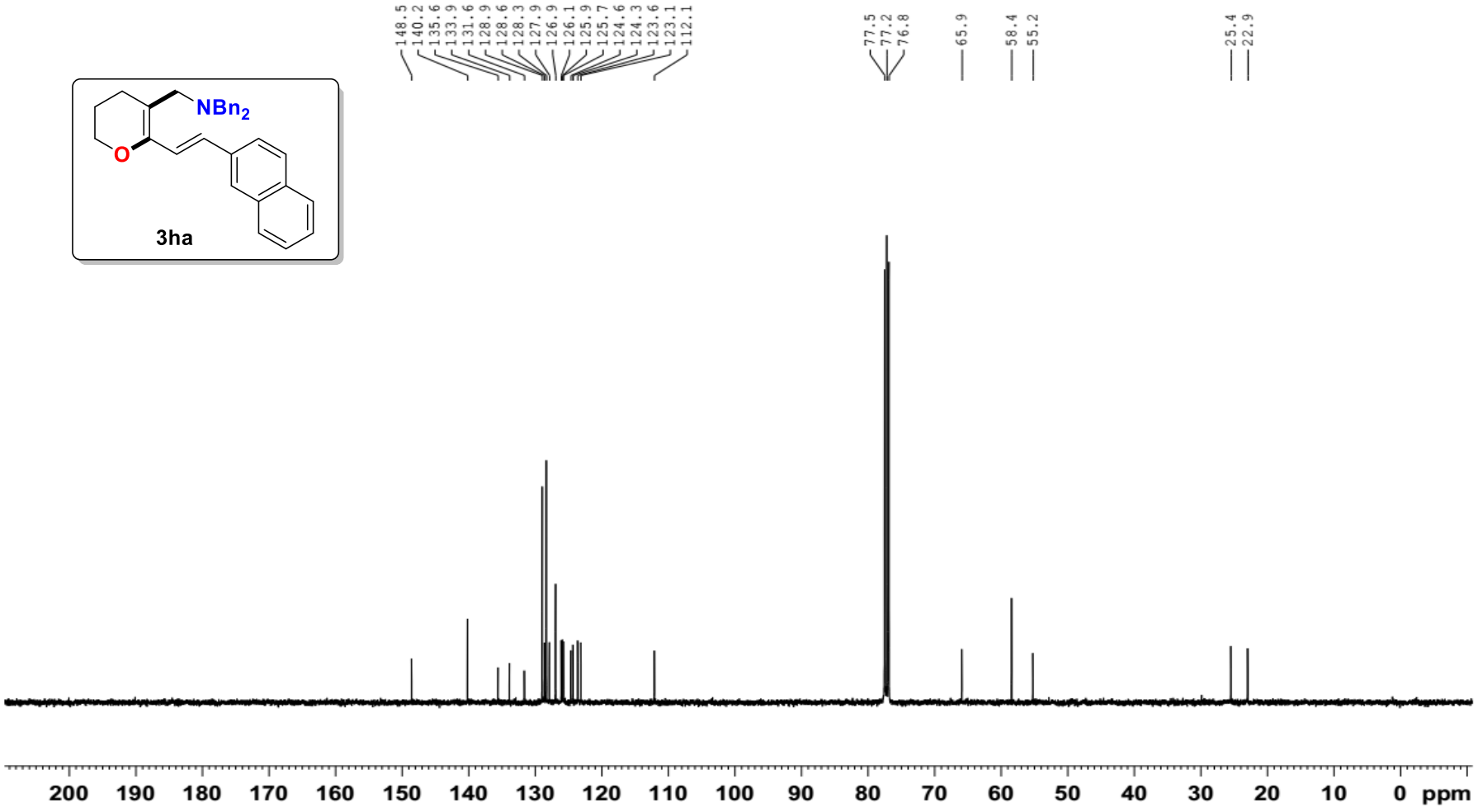
YHJ-P-**3ga** ^{19}F NMR (376MHz $CDCl_3$)



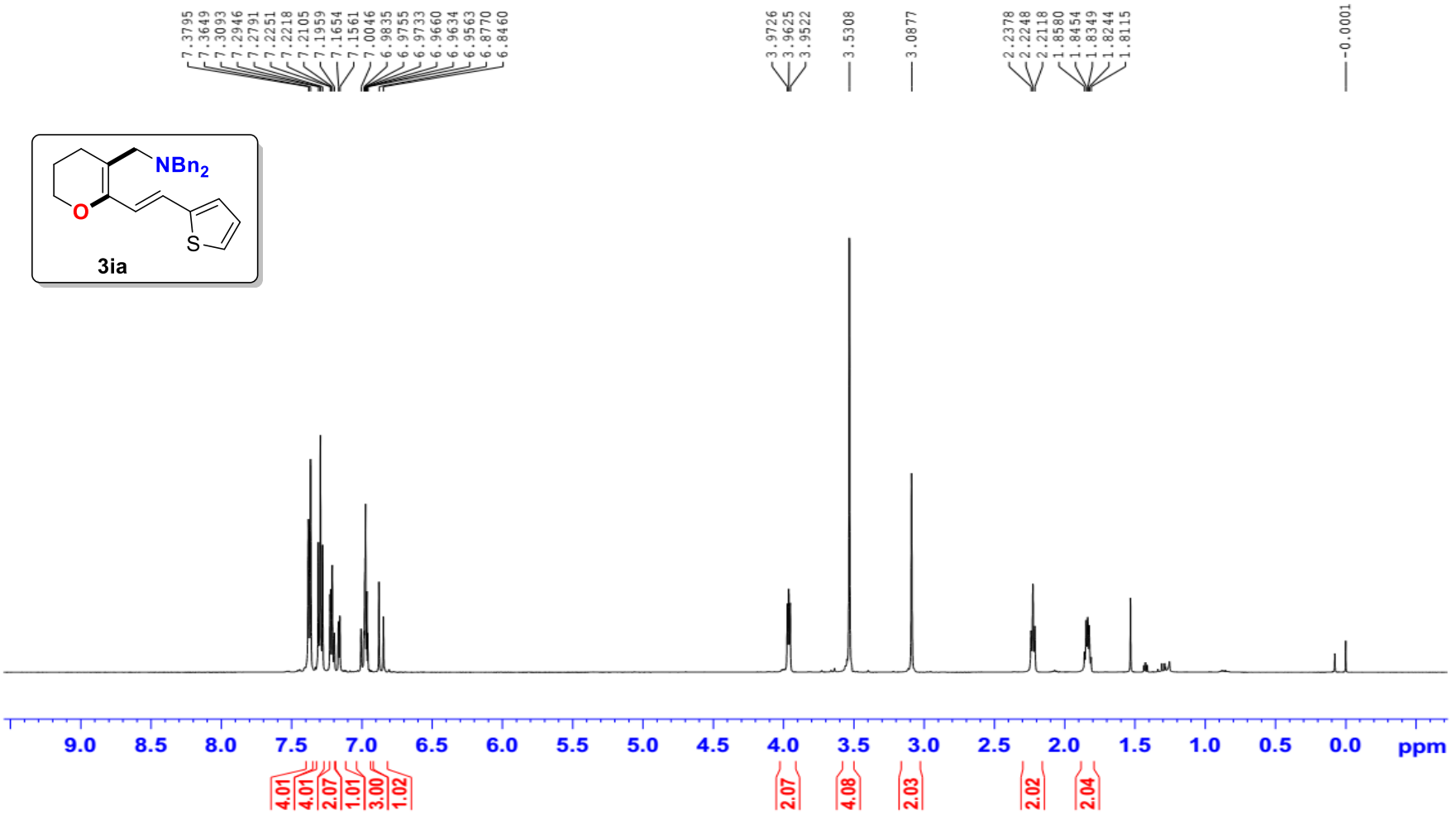
YHJ-P-**3ha** ^{1}H NMR (400MHz $CDCl_3$)



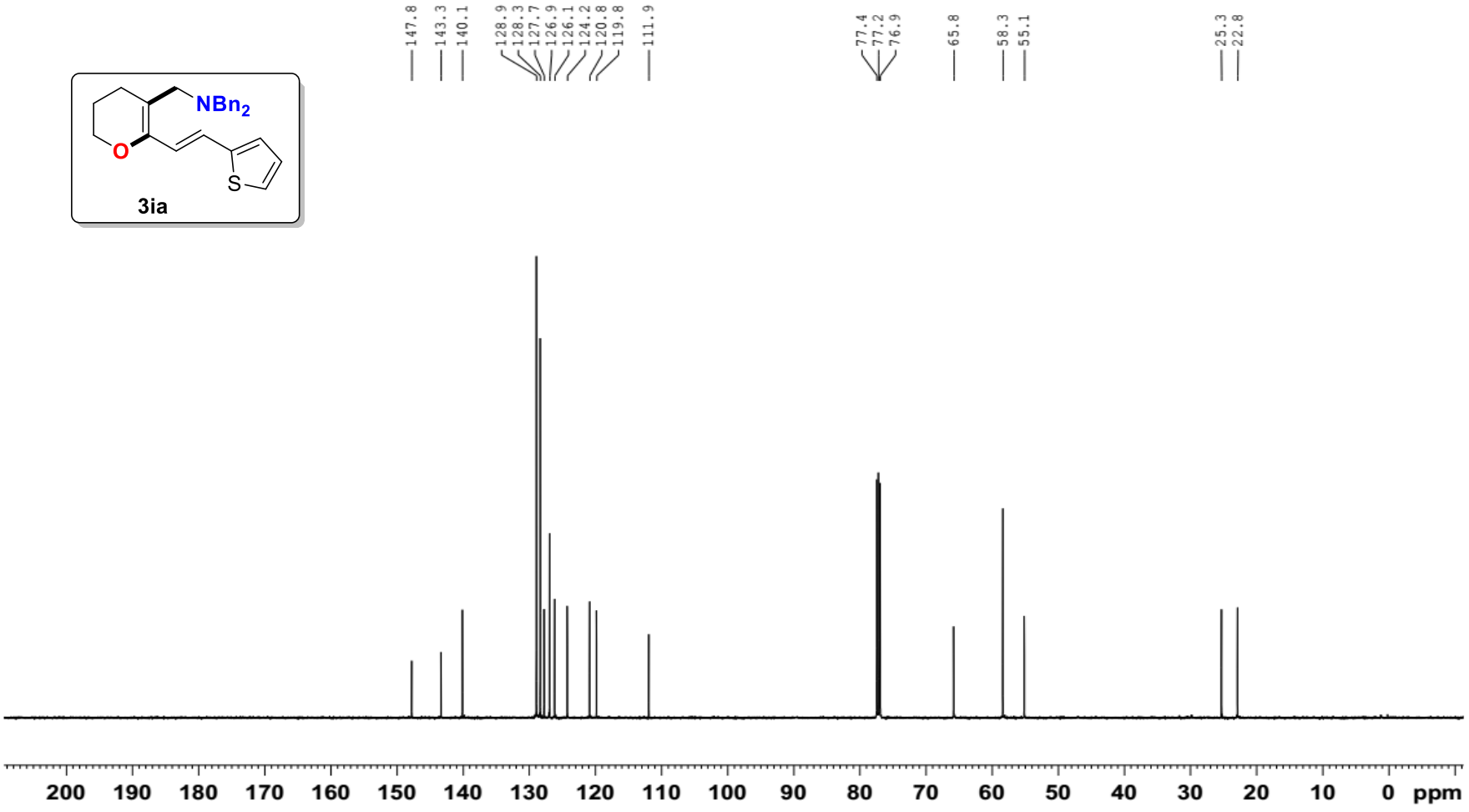
YHJ-P-**3ha** ^{13}C NMR (100MHz $CDCl_3$)



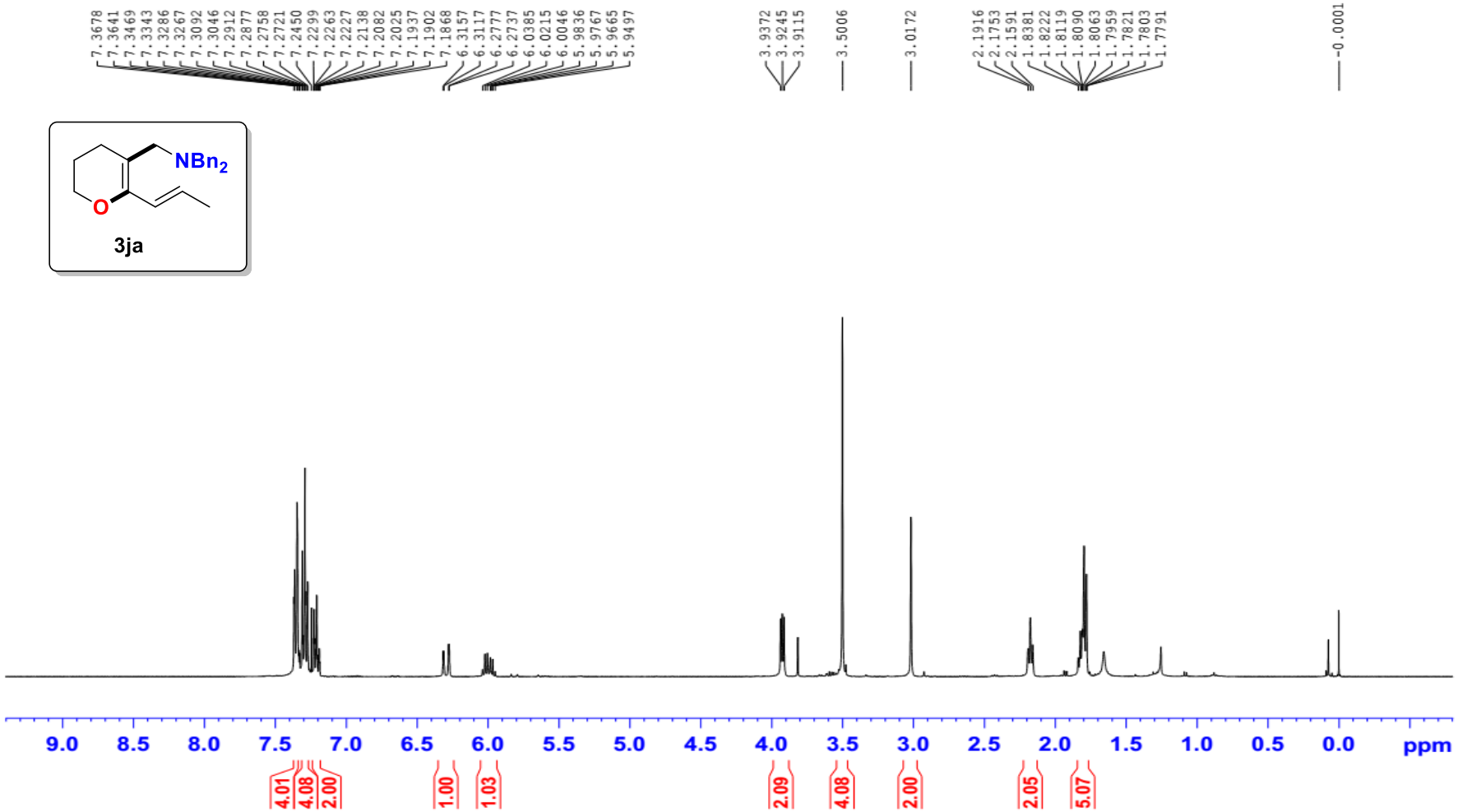
YHJ-P-**3ia** ^{1}H NMR (500MHz $CDCl_3$)



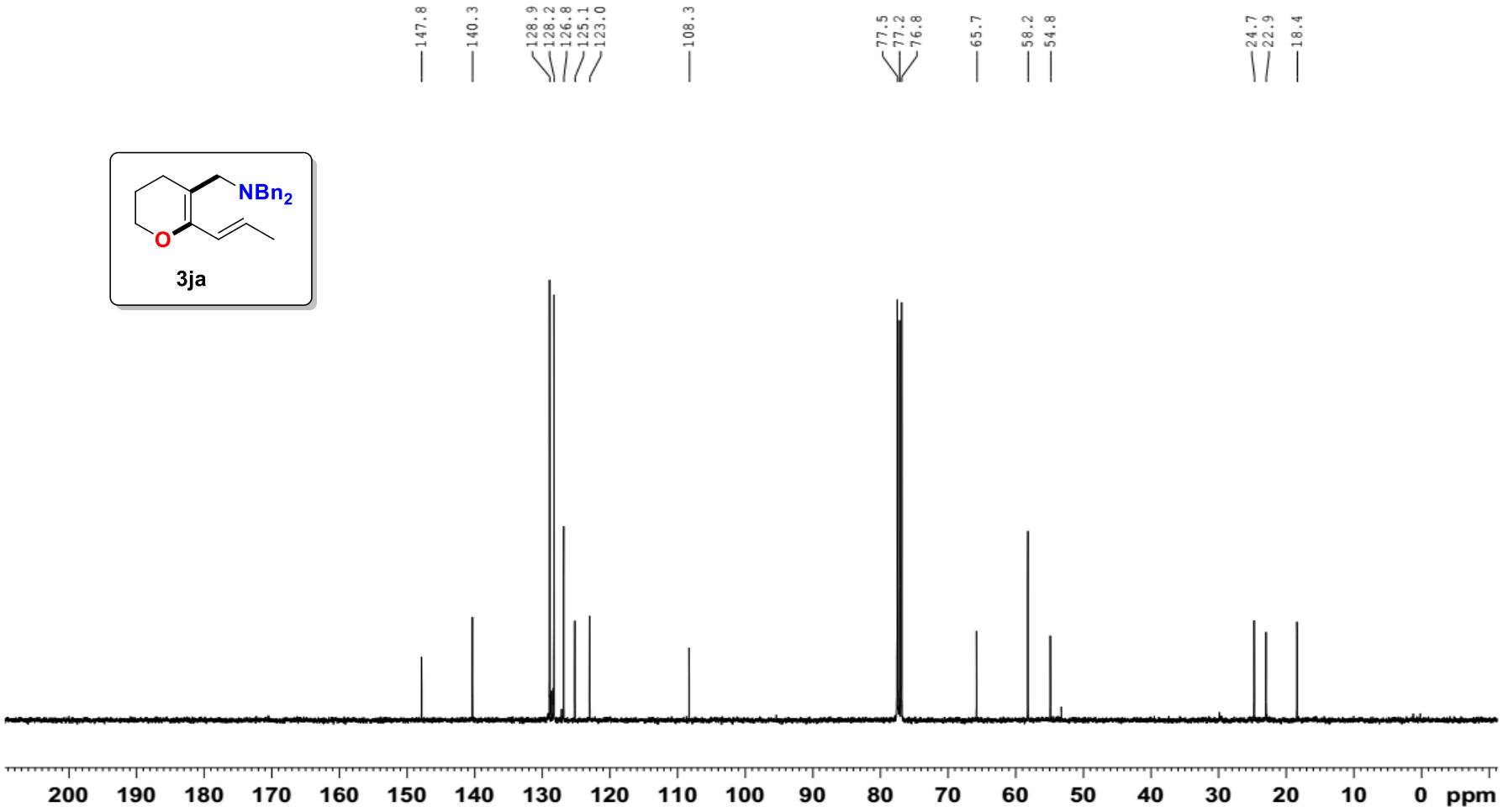
YHJ-P-**3ia** ^{13}C NMR (125MHz $CDCl_3$)



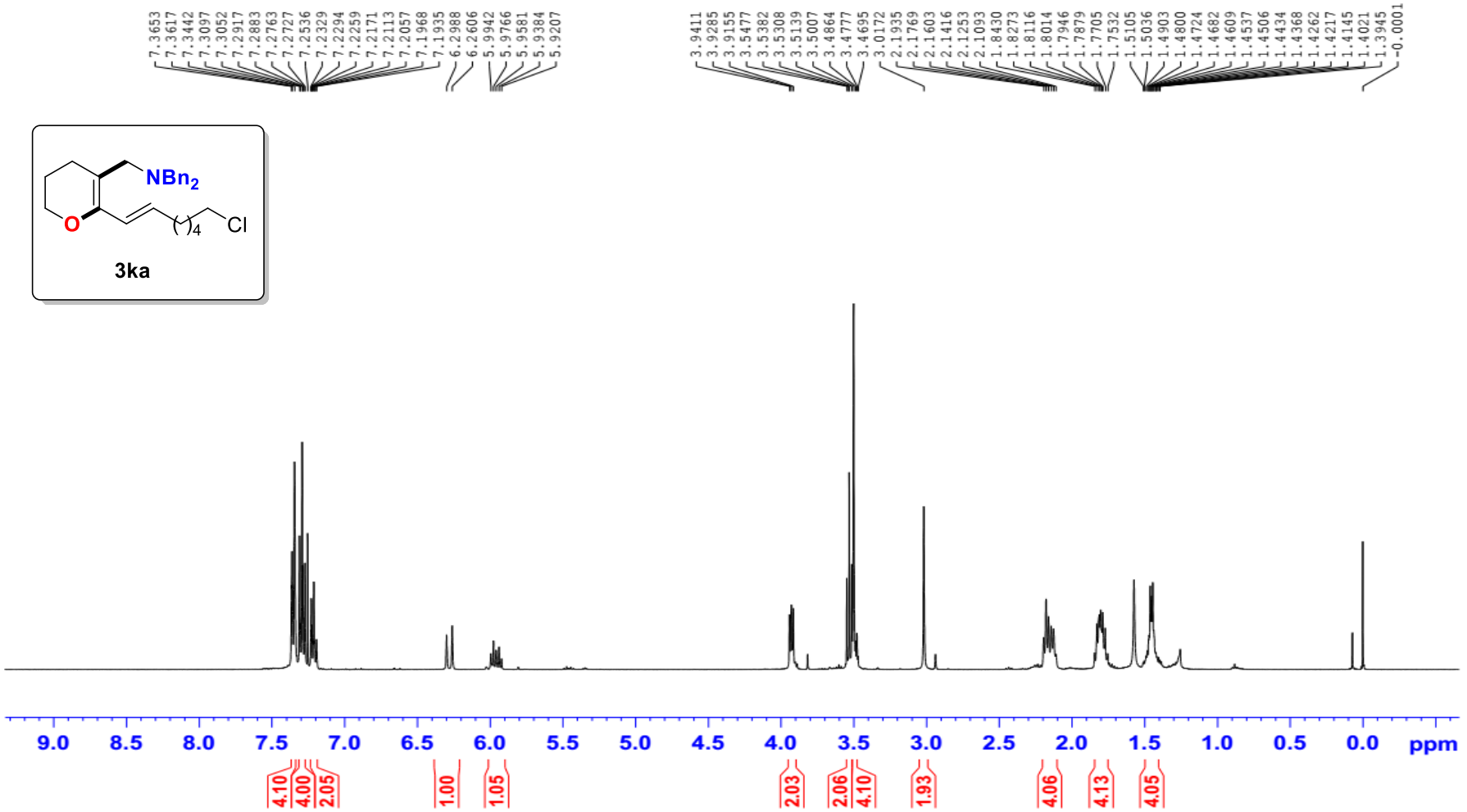
YHJ-P-**3ja** ^{1}H NMR (400MHz $CDCl_3$)



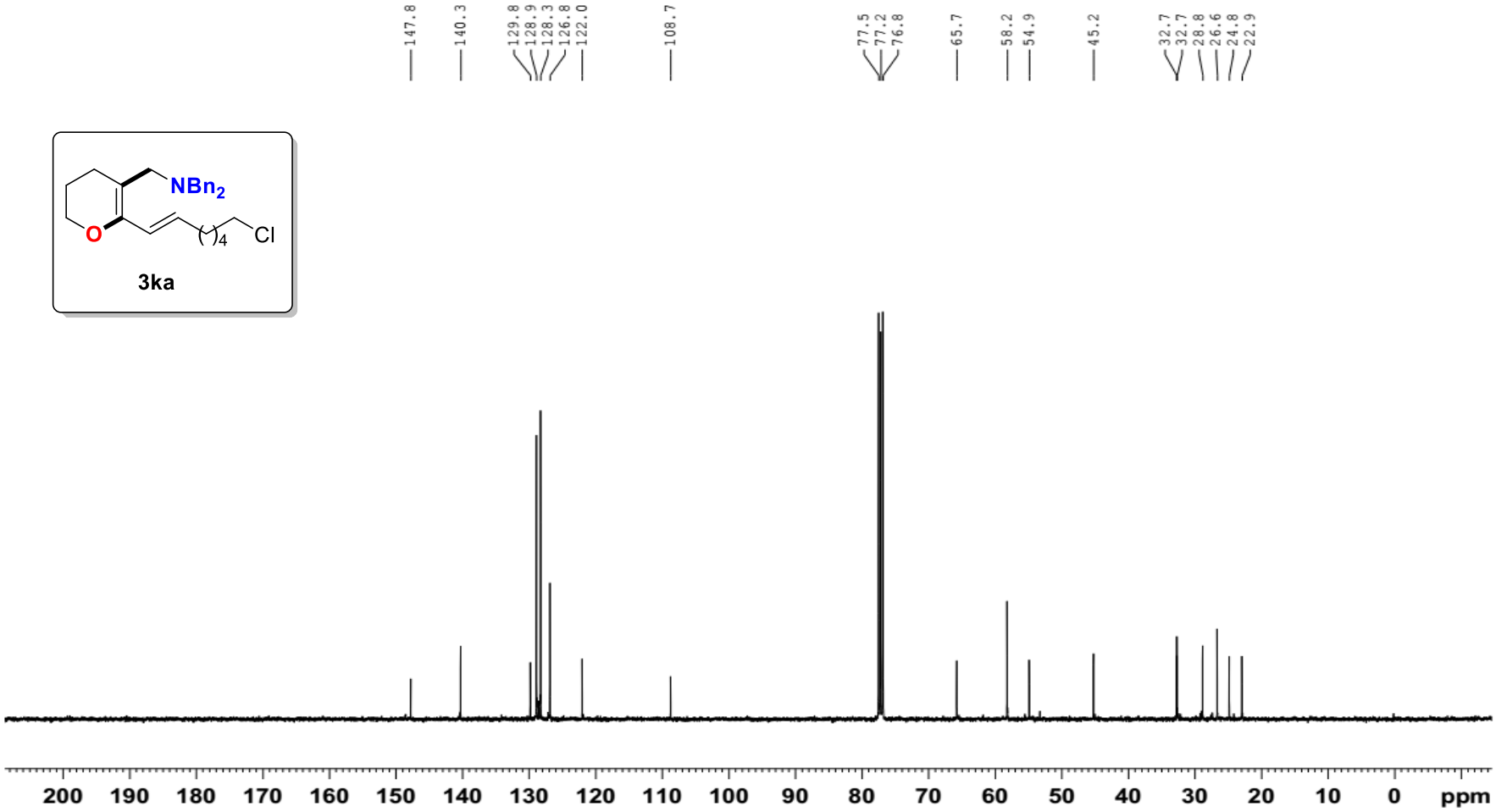
YHJ-P-**3ja** ^{13}C NMR (100MHz $CDCl_3$)



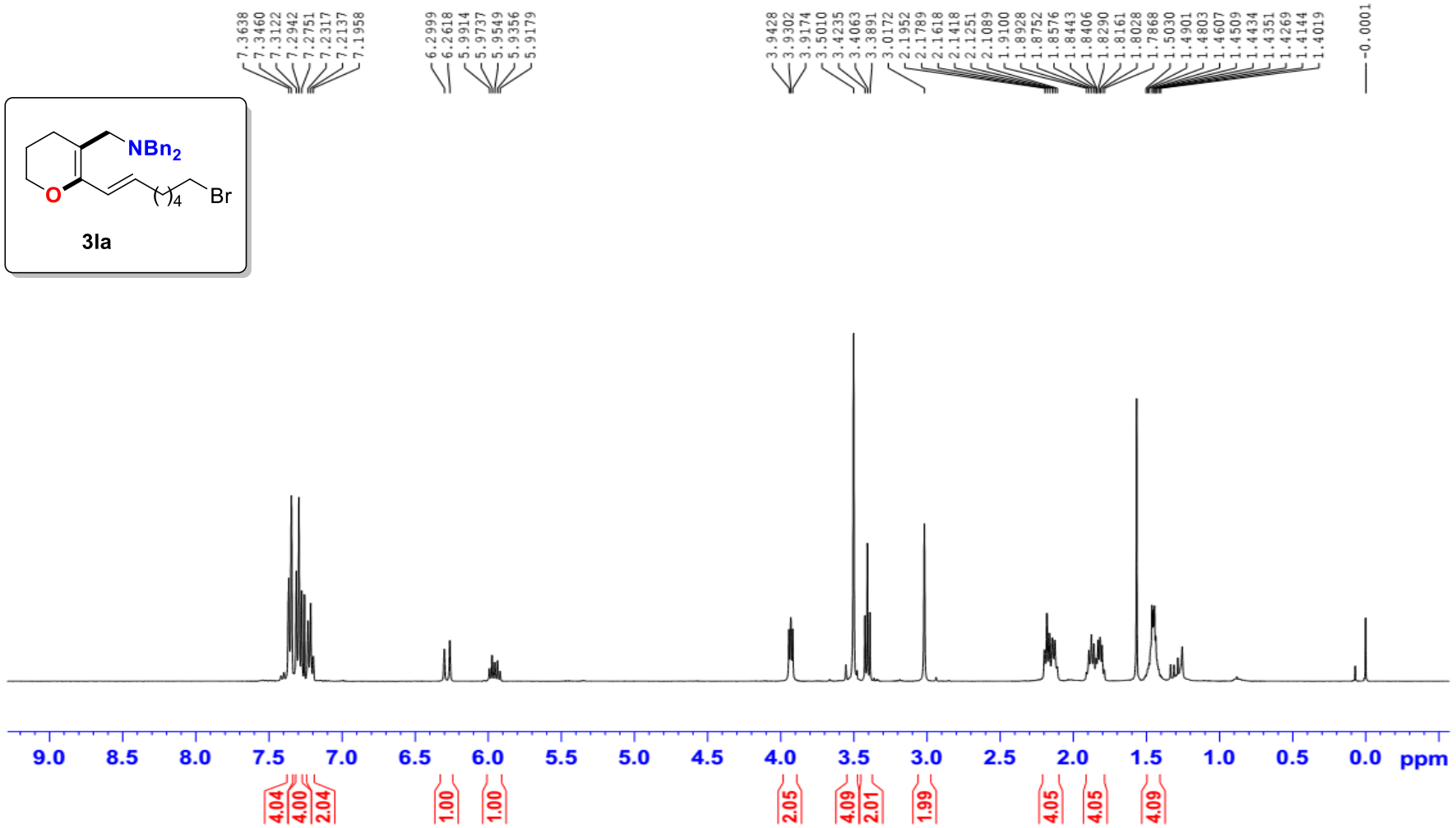
YHJ-P-**3ka** ^{1}H NMR (400MHz $CDCl_3$)



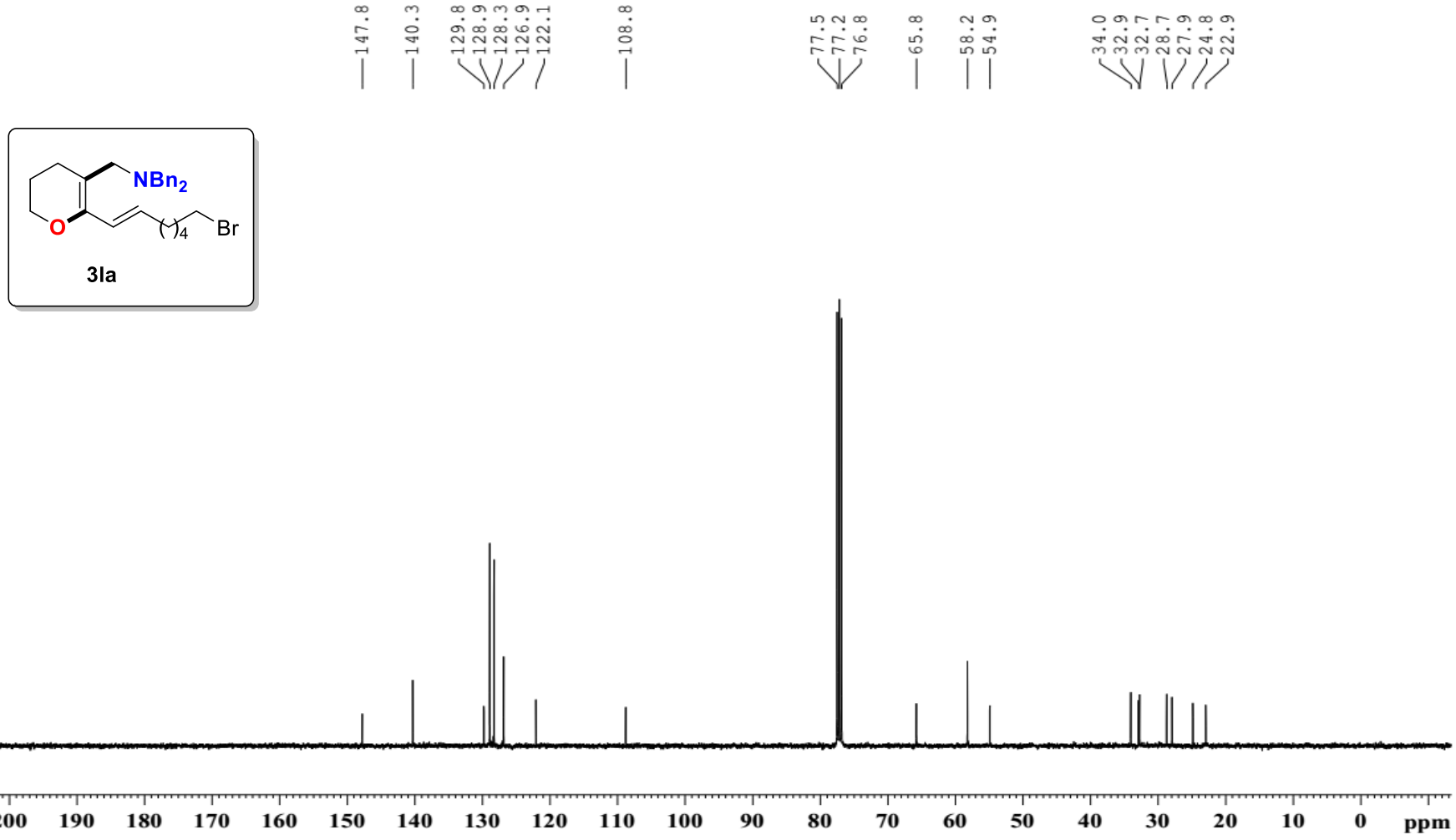
YHJ-P-**3ka** ^{13}C NMR (100MHz $CDCl_3$)



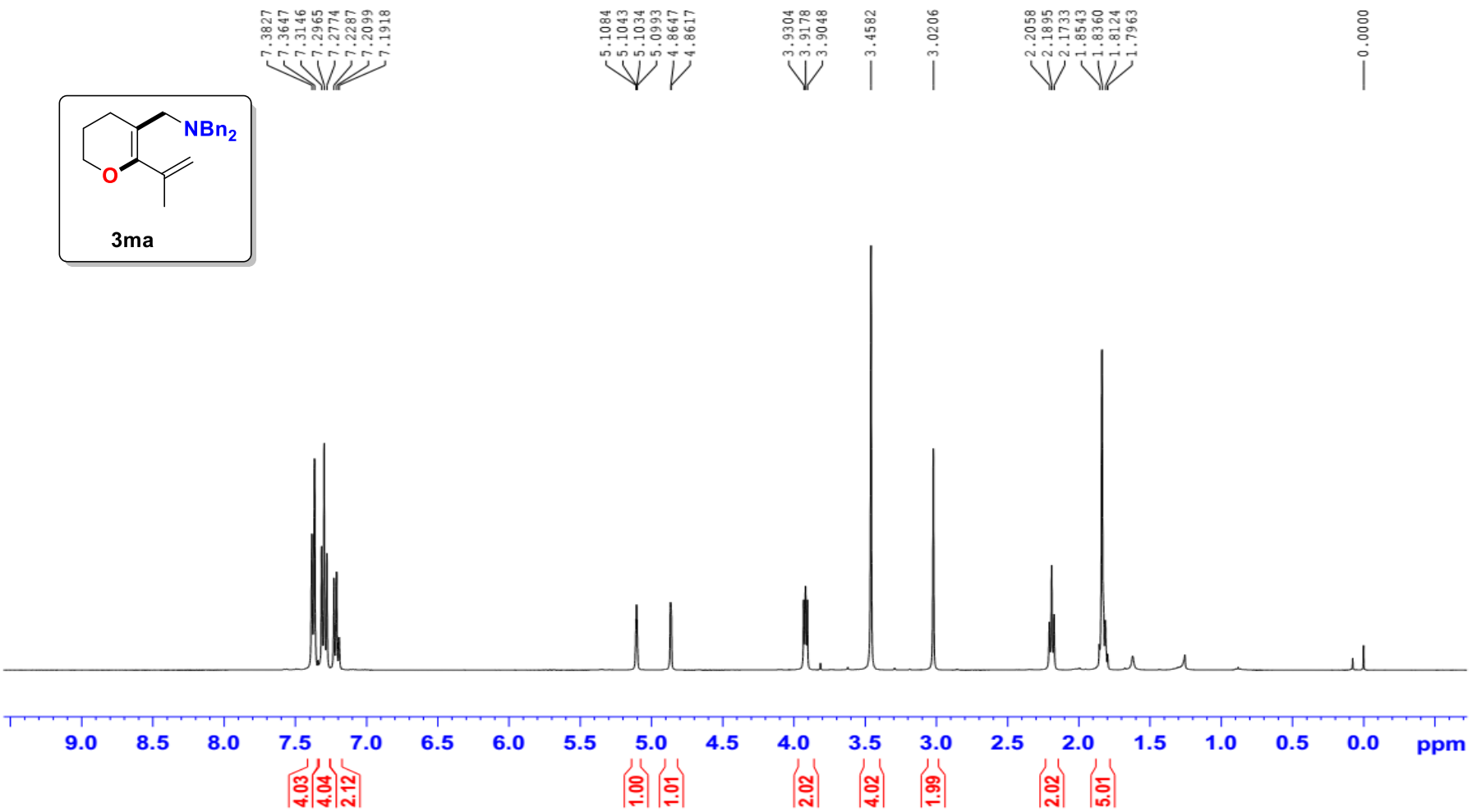
YHJ-P-**3la** ^{1}H NMR (400MHz $CDCl_3$)



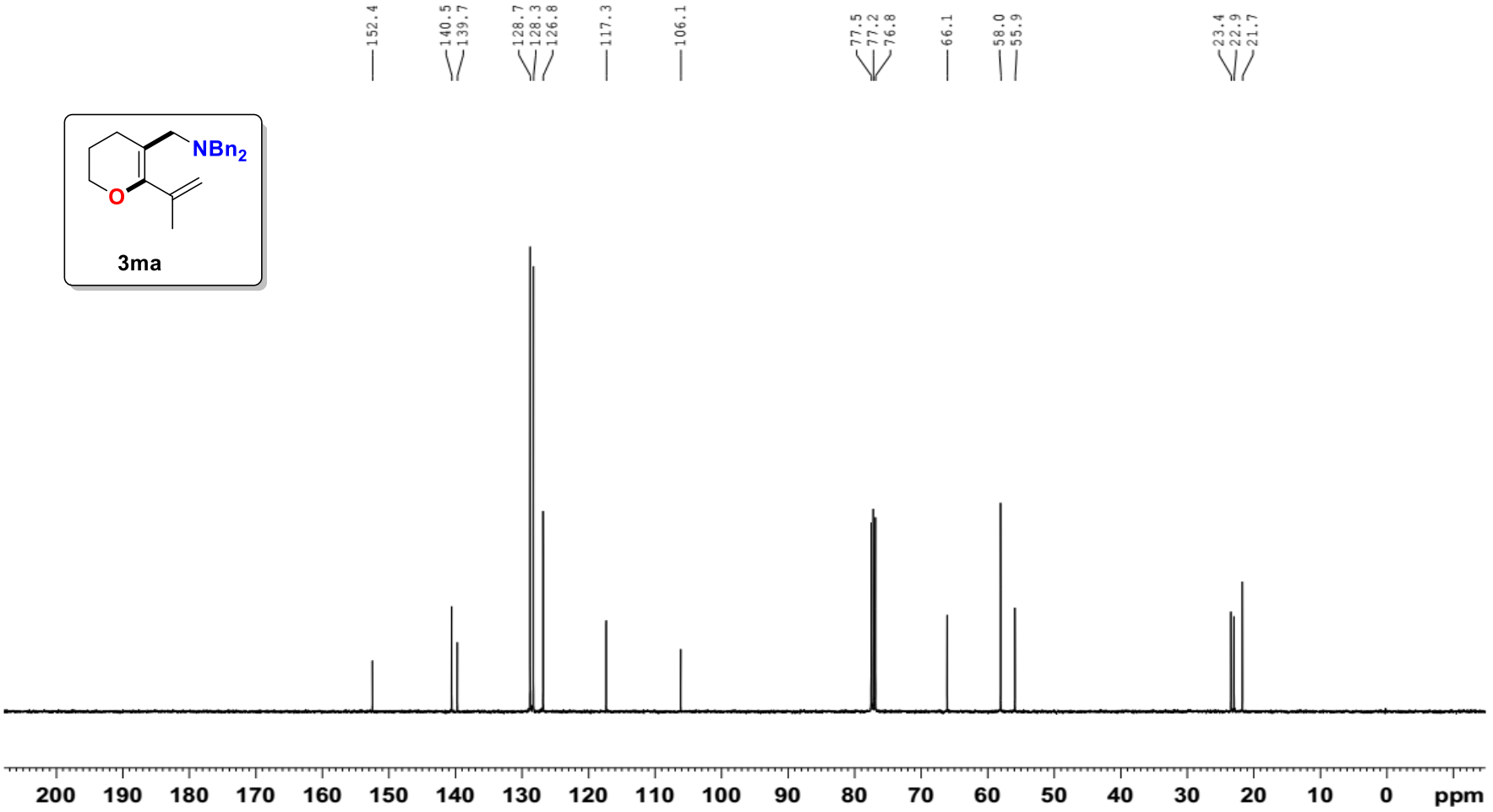
YHJ-P-**3la** ^{13}C NMR (125MHz $CDCl_3$)



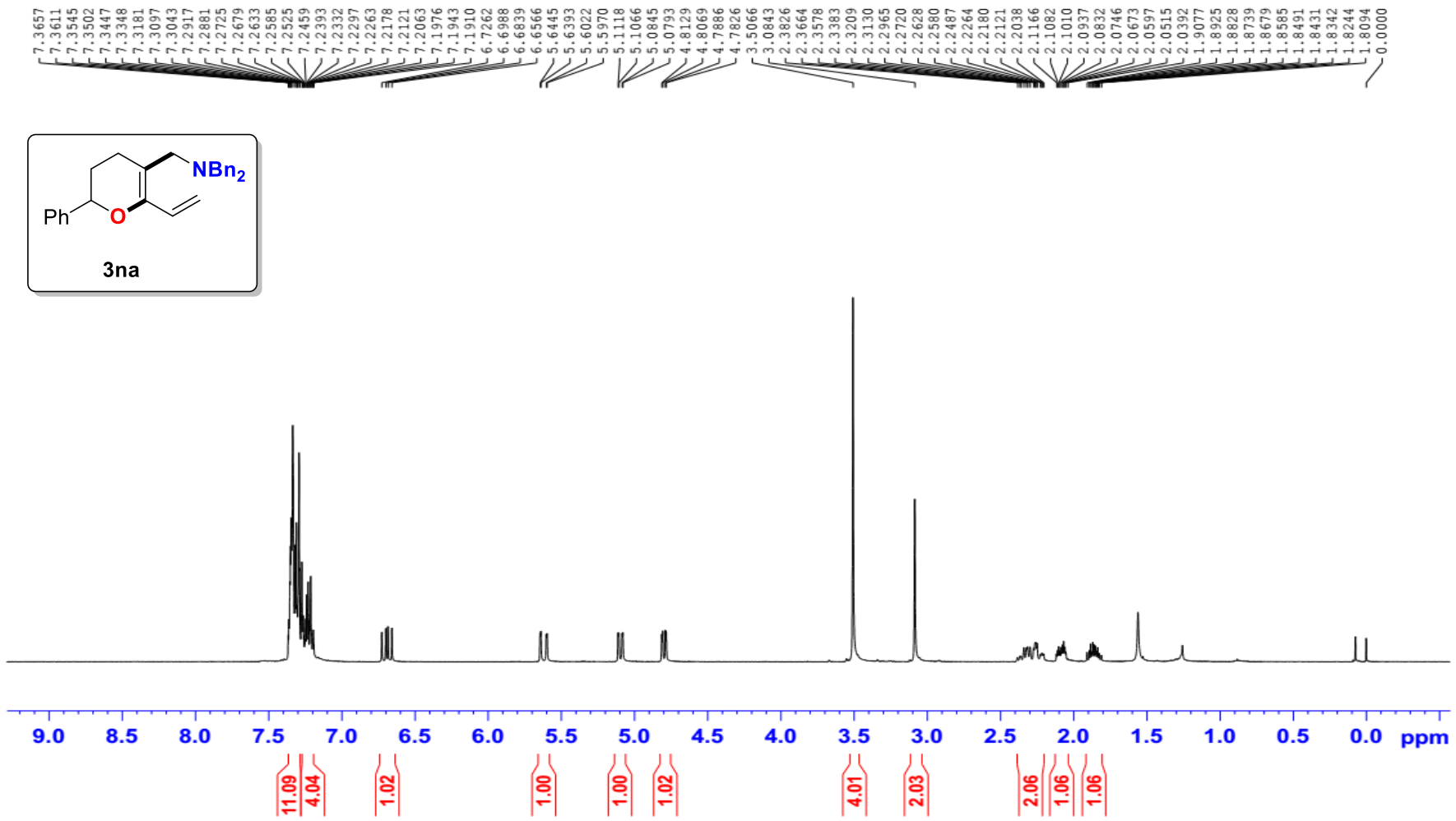
YHJ-P-**3ma** ^{1}H NMR (400MHz $CDCl_3$)



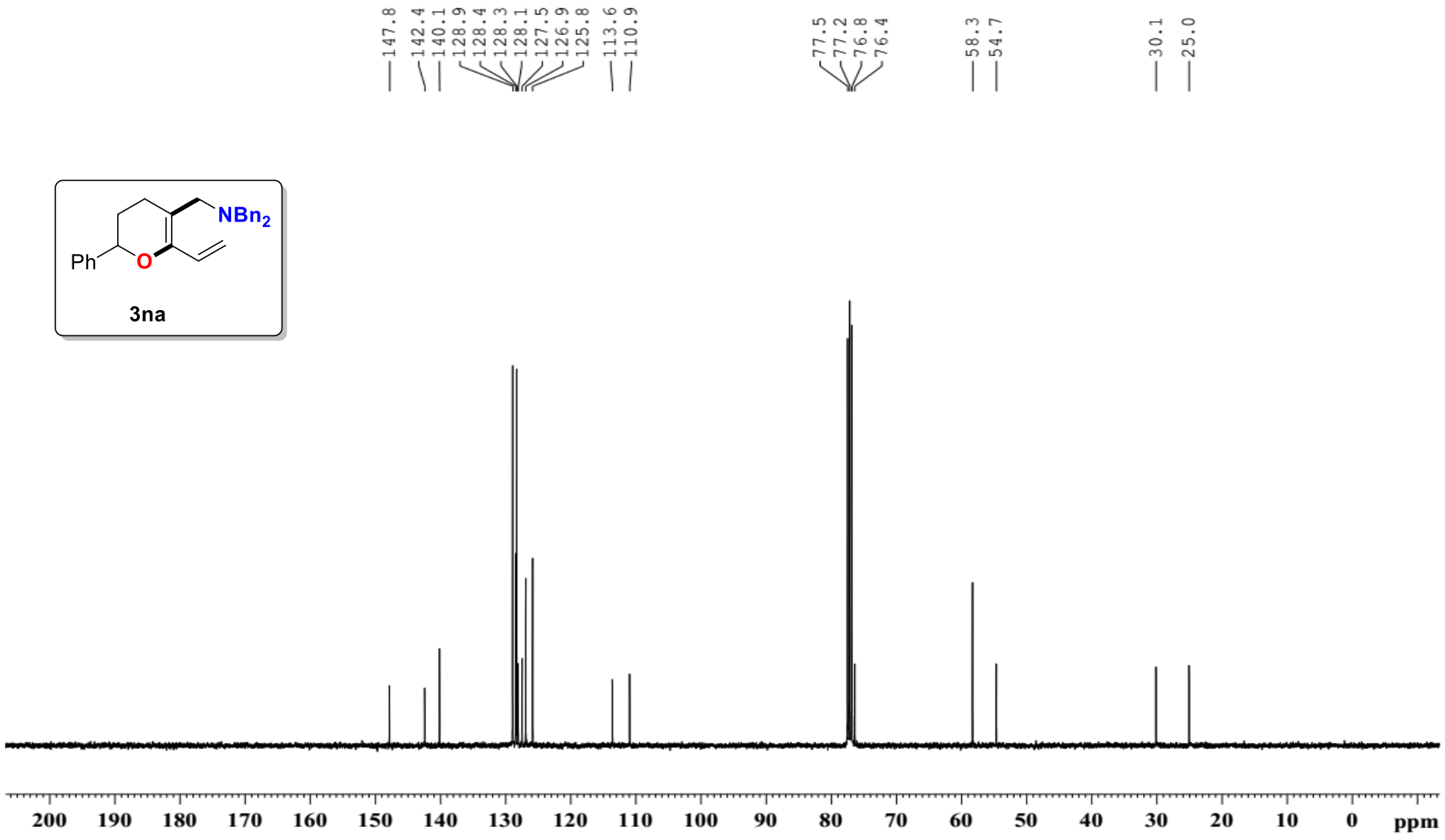
YHJ-P-**3ma** ^{13}C NMR (100MHz $CDCl_3$)



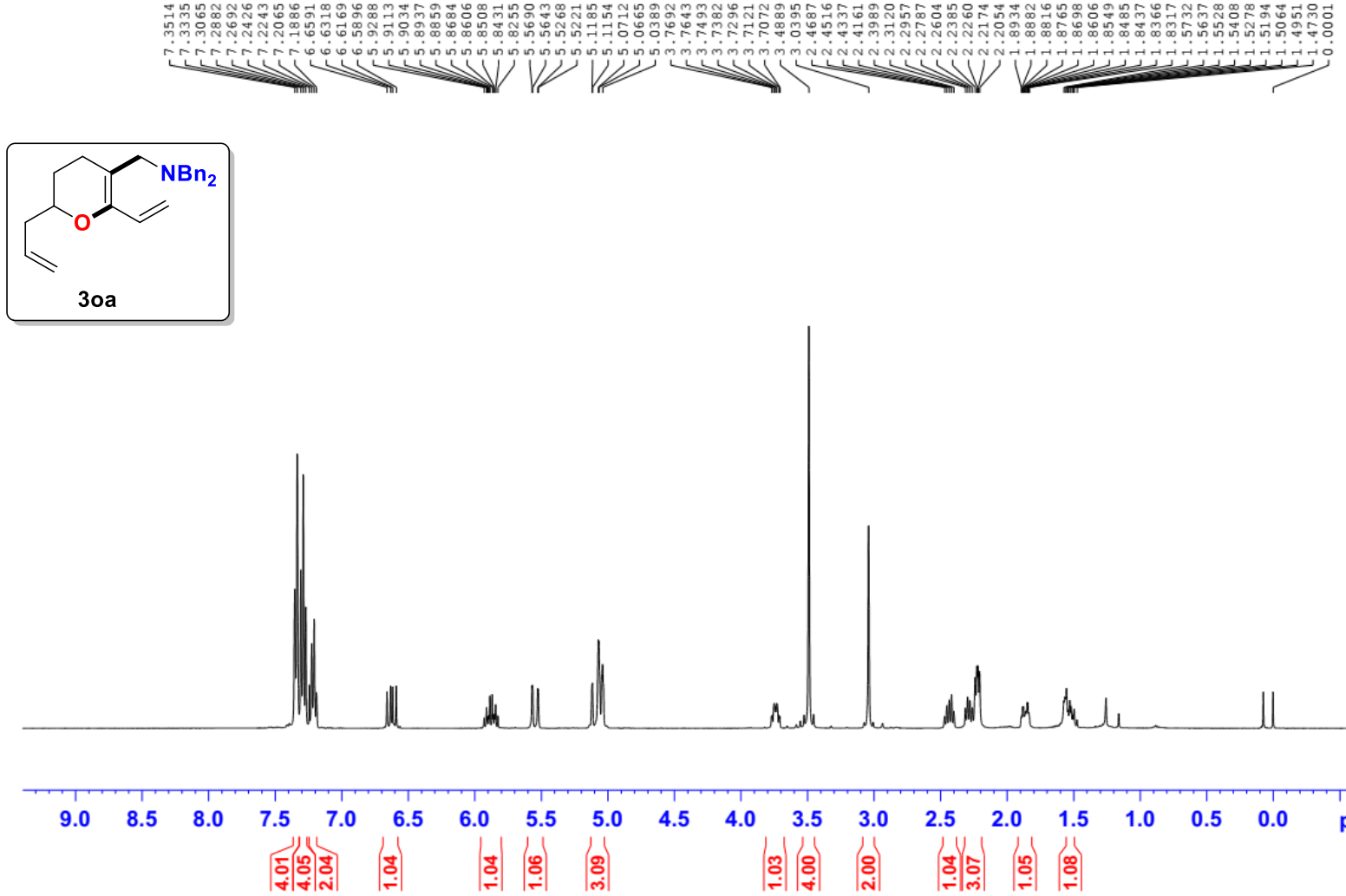
YHJ-P-**3na** ^{1}H NMR (400MHz $CDCl_3$)



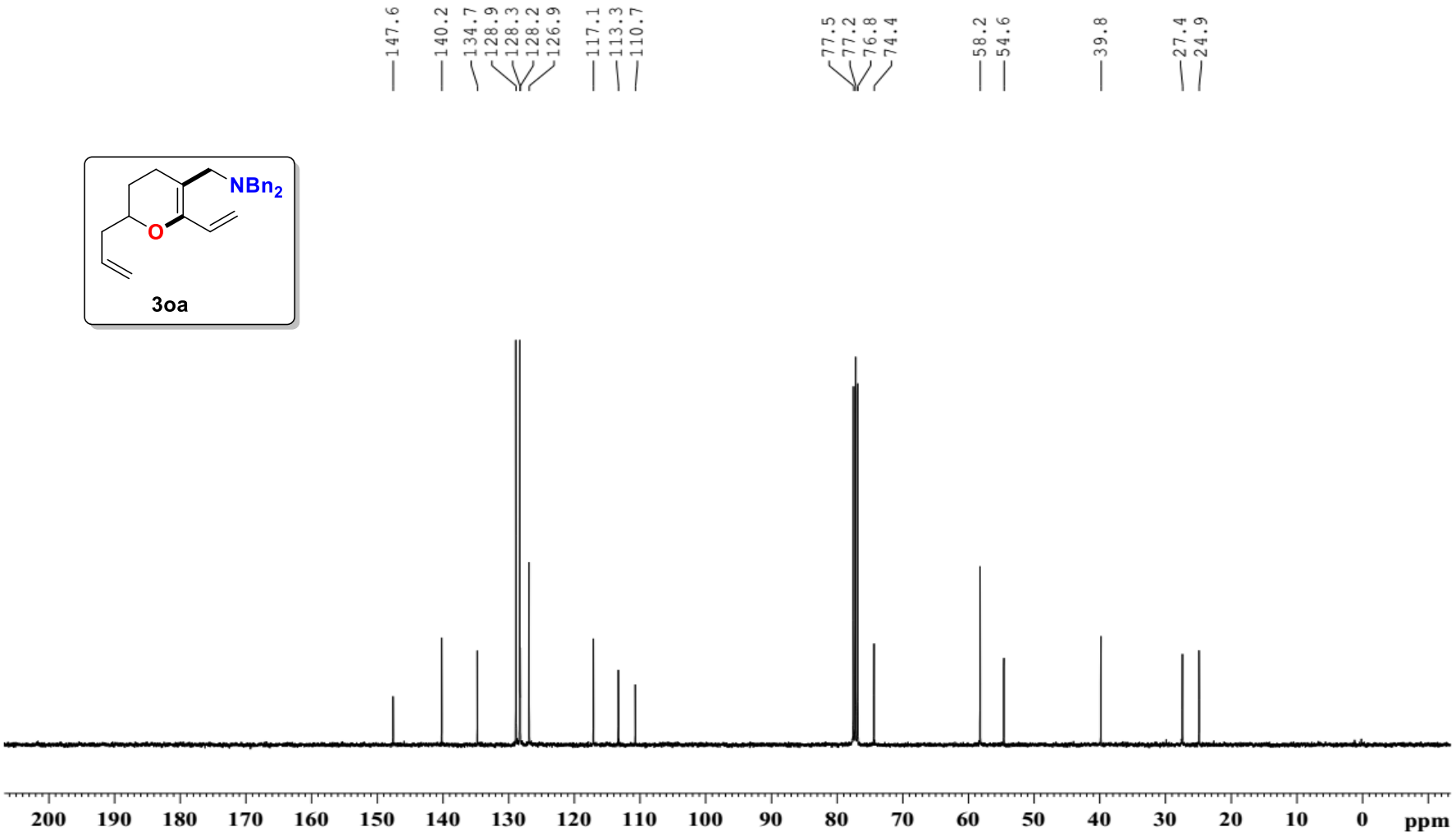
YHJ-P-**3na** ^{13}C NMR (100MHz $CDCl_3$)



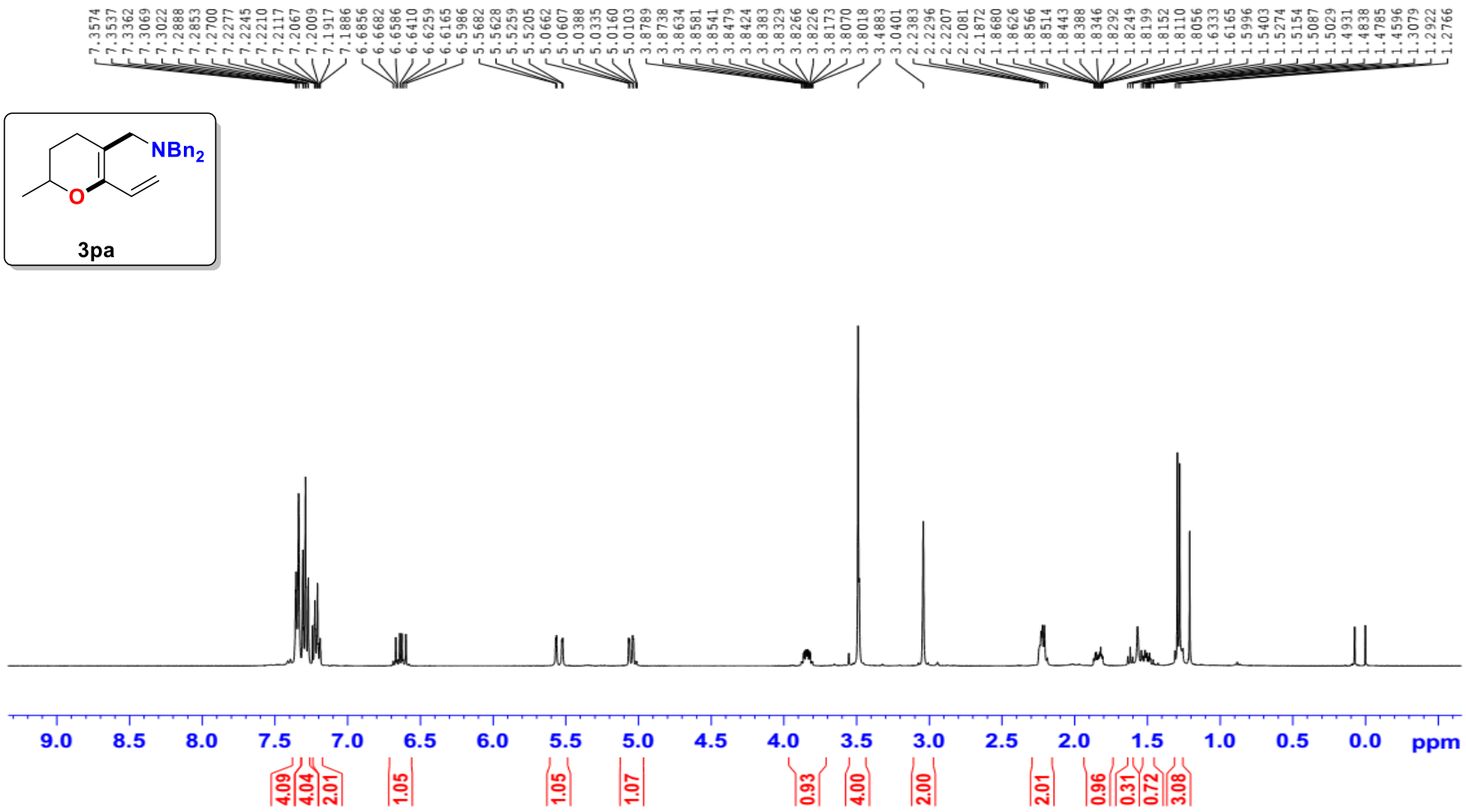
YHJ-P-**3oa** ^{1}H NMR (400MHz $CDCl_3$)



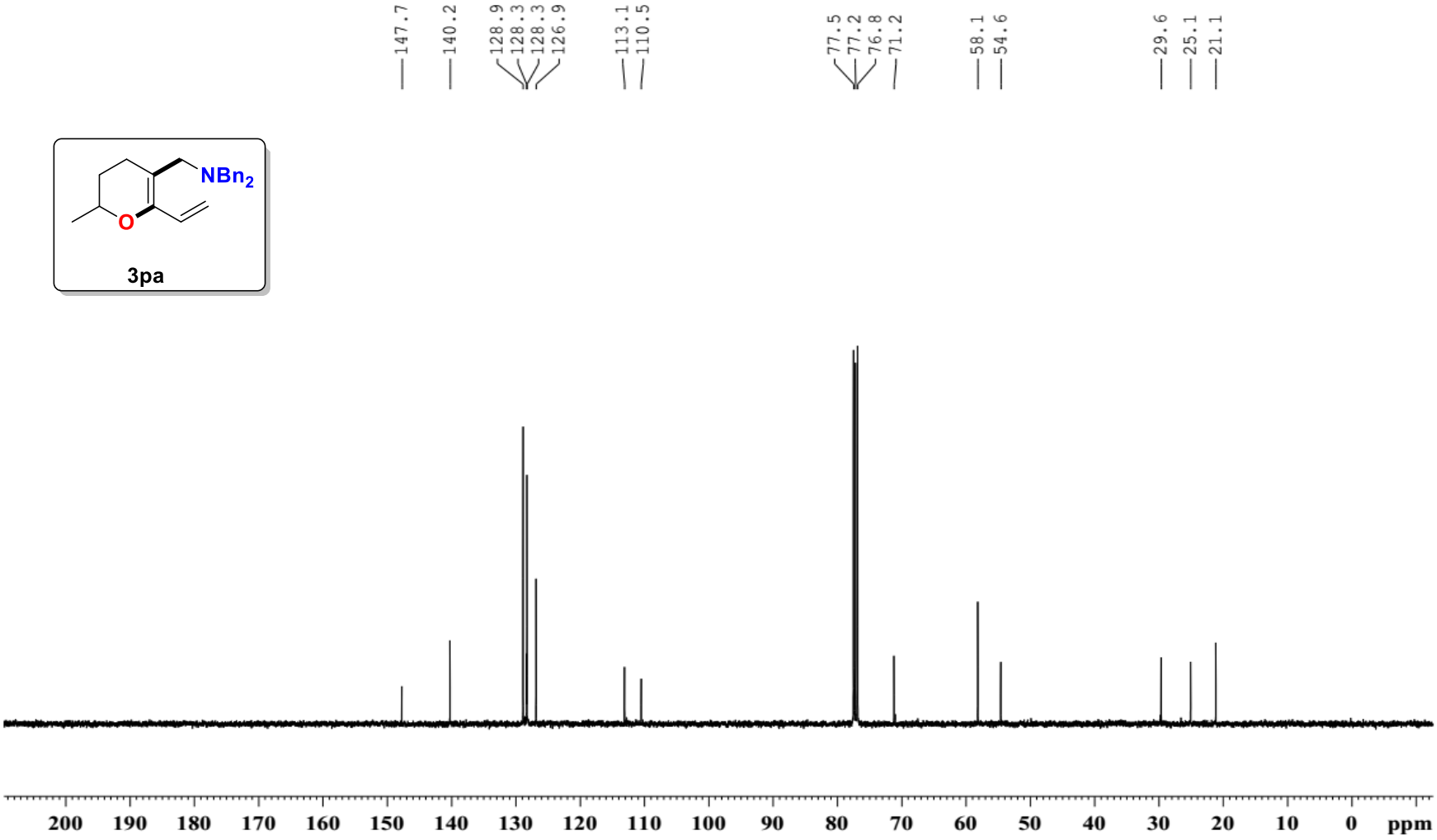
YHJ-P-**3oa** ^{13}C NMR (100MHz $CDCl_3$)



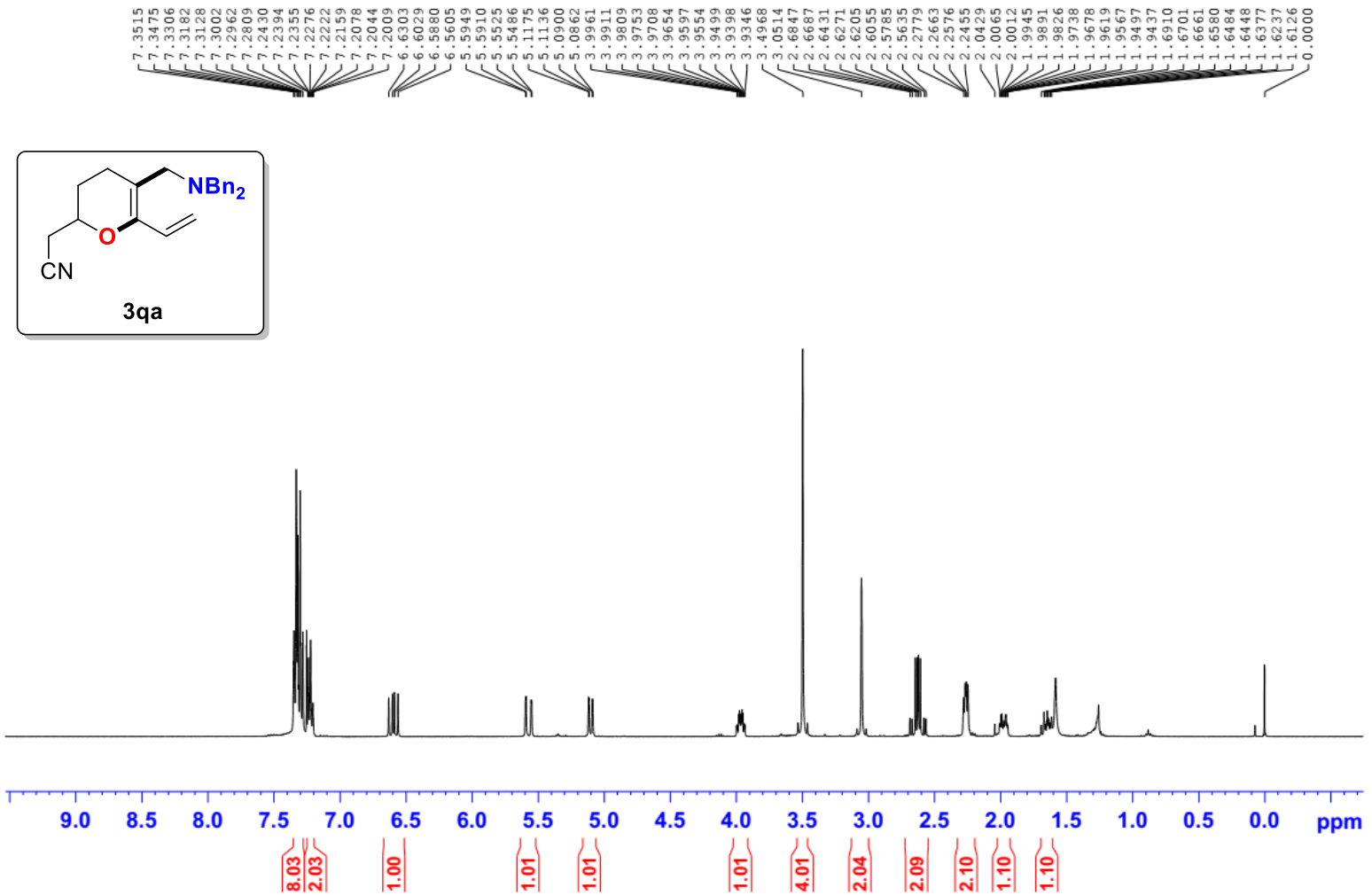
YHJ-P-**3pa** ^{1}H NMR (400MHz $CDCl_3$)



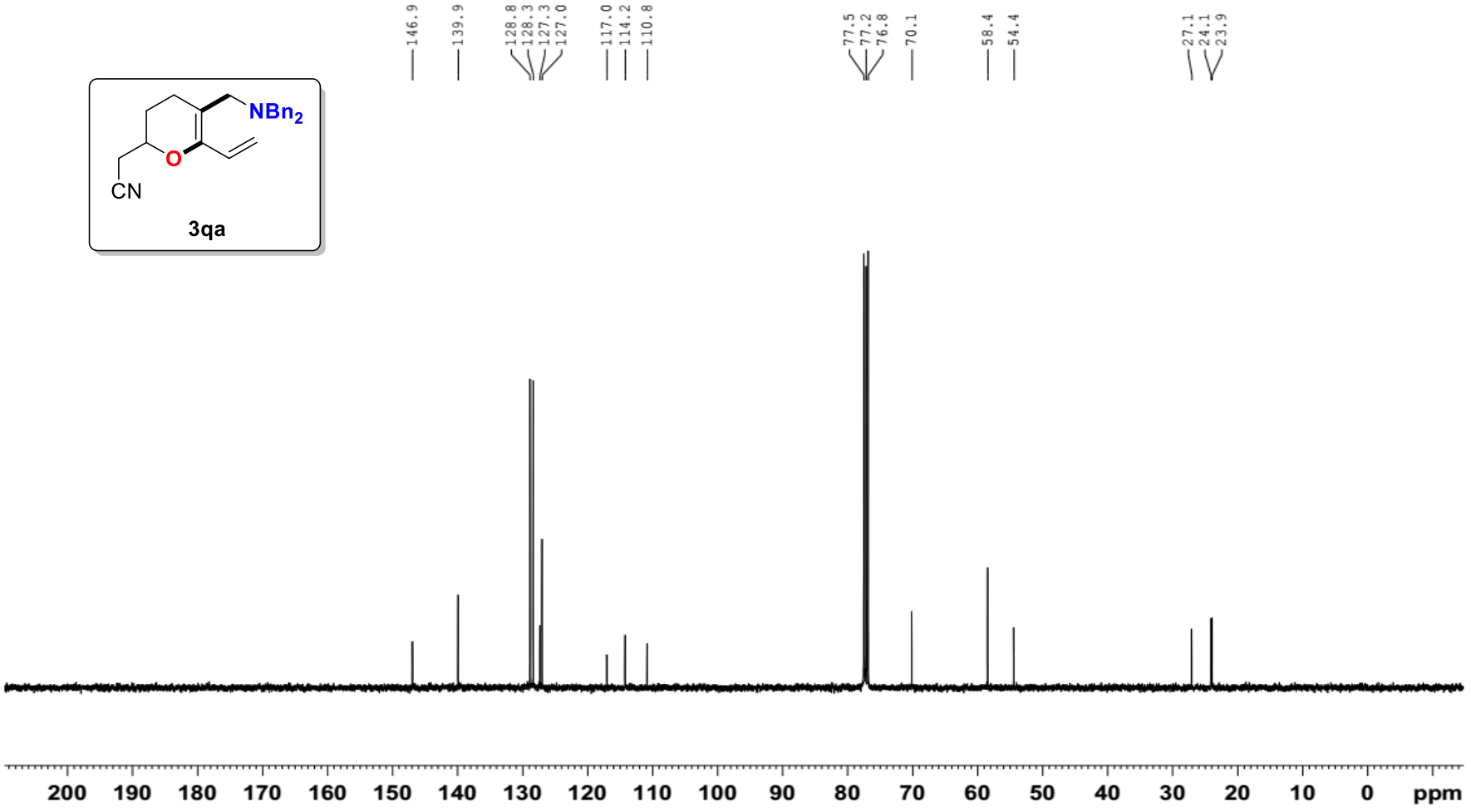
YHJ-P-**3pa** ^{13}C NMR (100MHz $CDCl_3$)



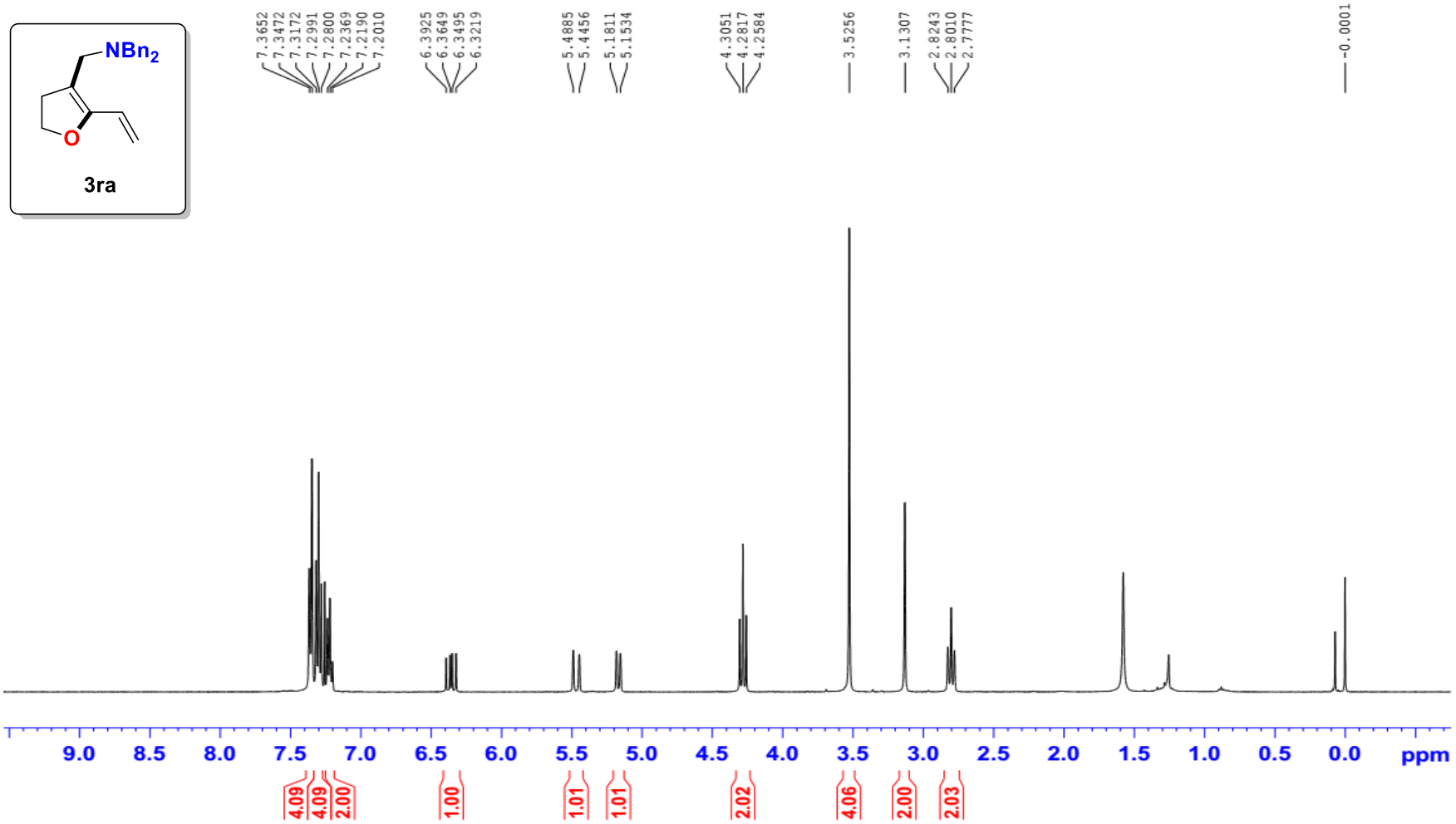
YHJ-P-**3qa** ^{1}H NMR (400MHz $CDCl_3$)



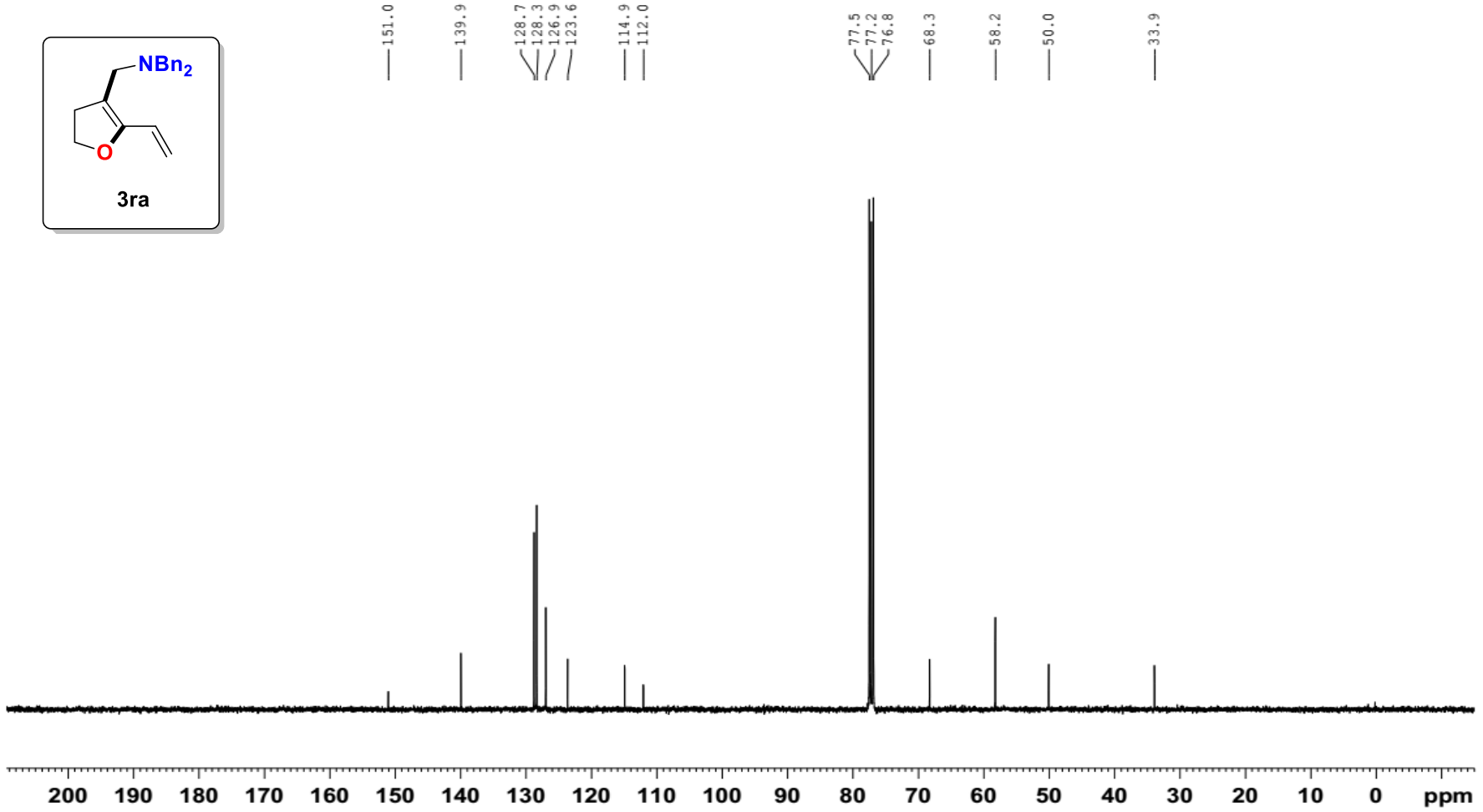
YHJ-P-**3qa** ^{13}C NMR (100MHz $CDCl_3$)



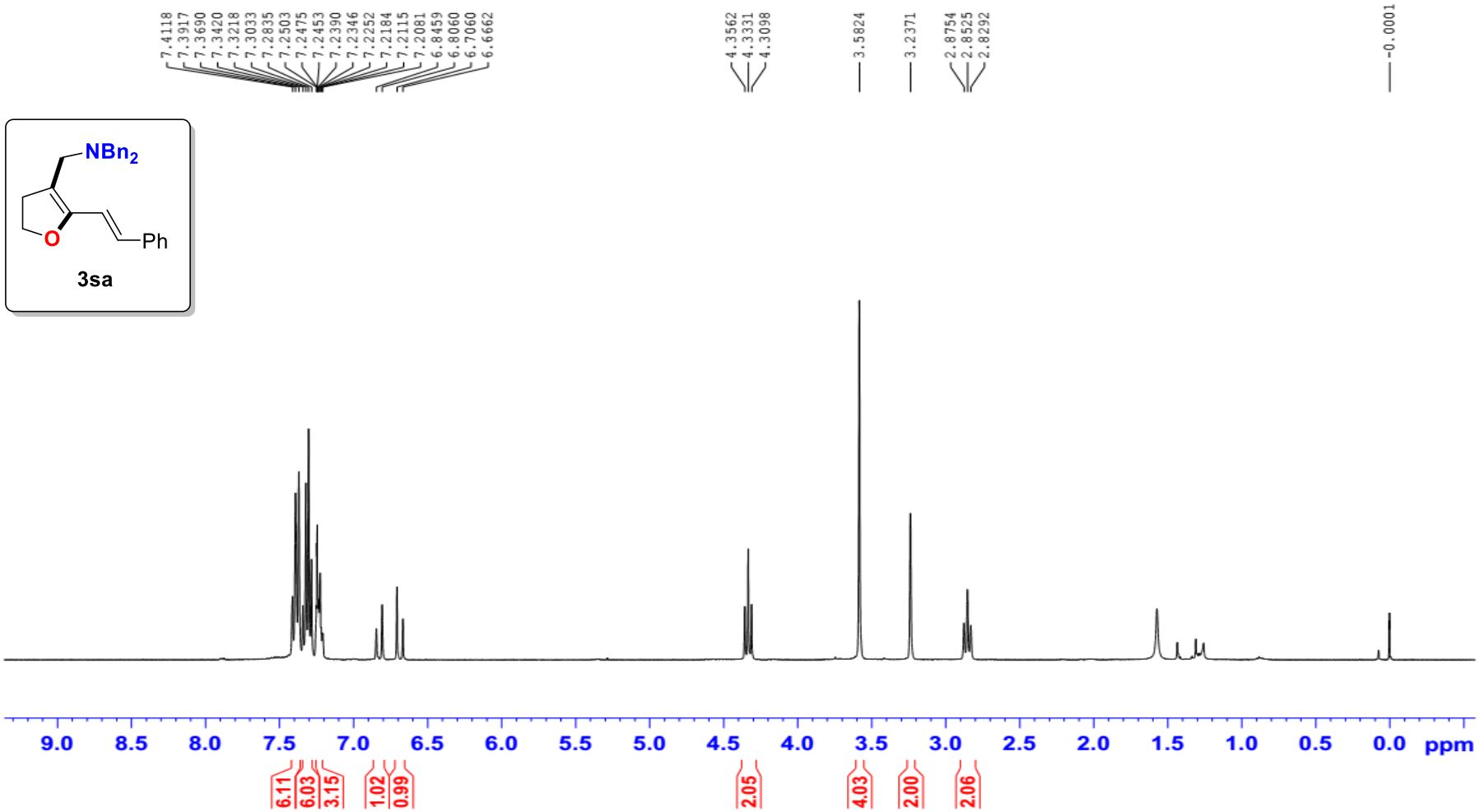
YHJ-P-**3ra** ^{1}H NMR (400MHz $CDCl_3$)



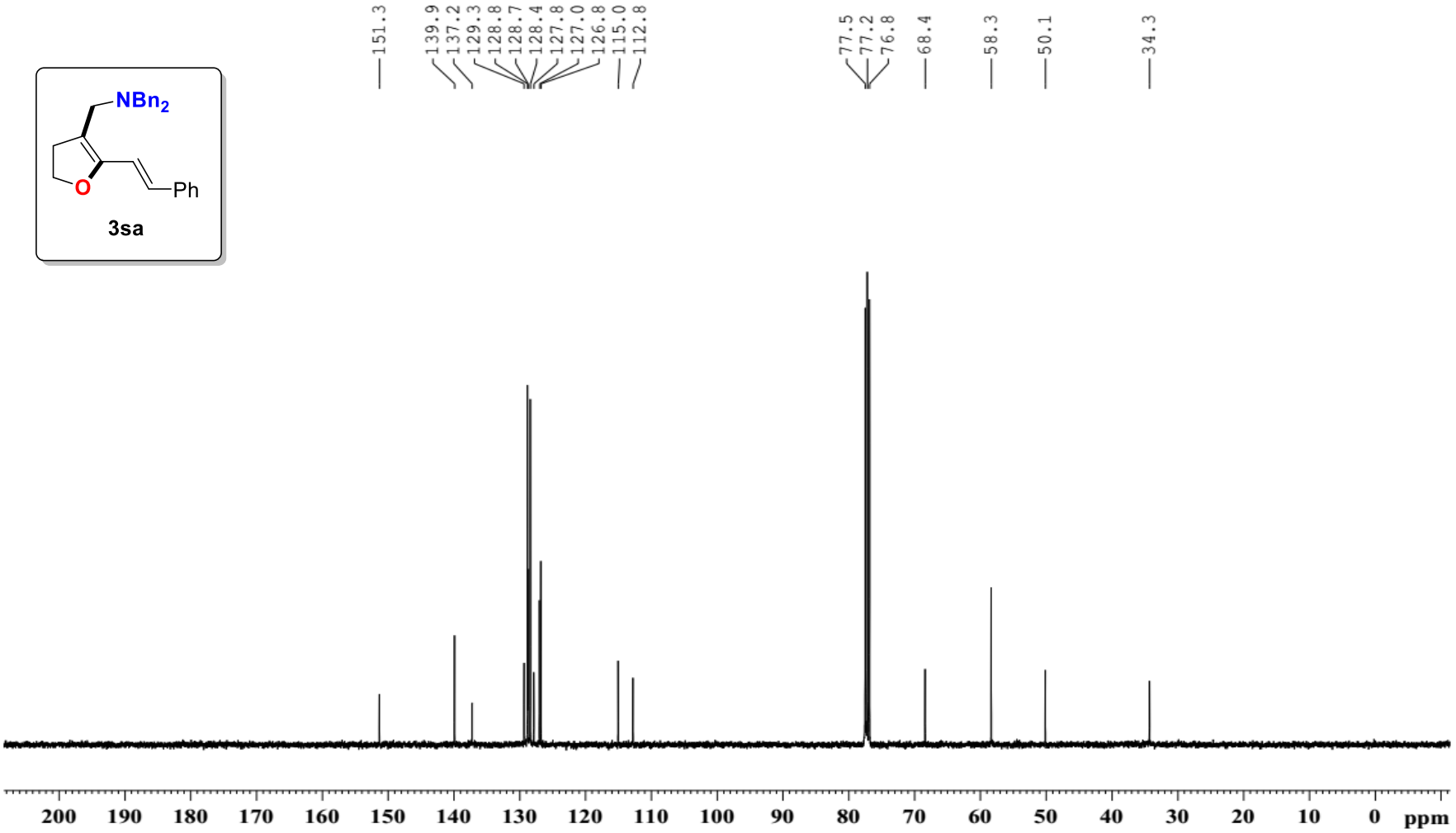
YHJ-P-**3ra** ^{13}C NMR (100MHz $CDCl_3$)



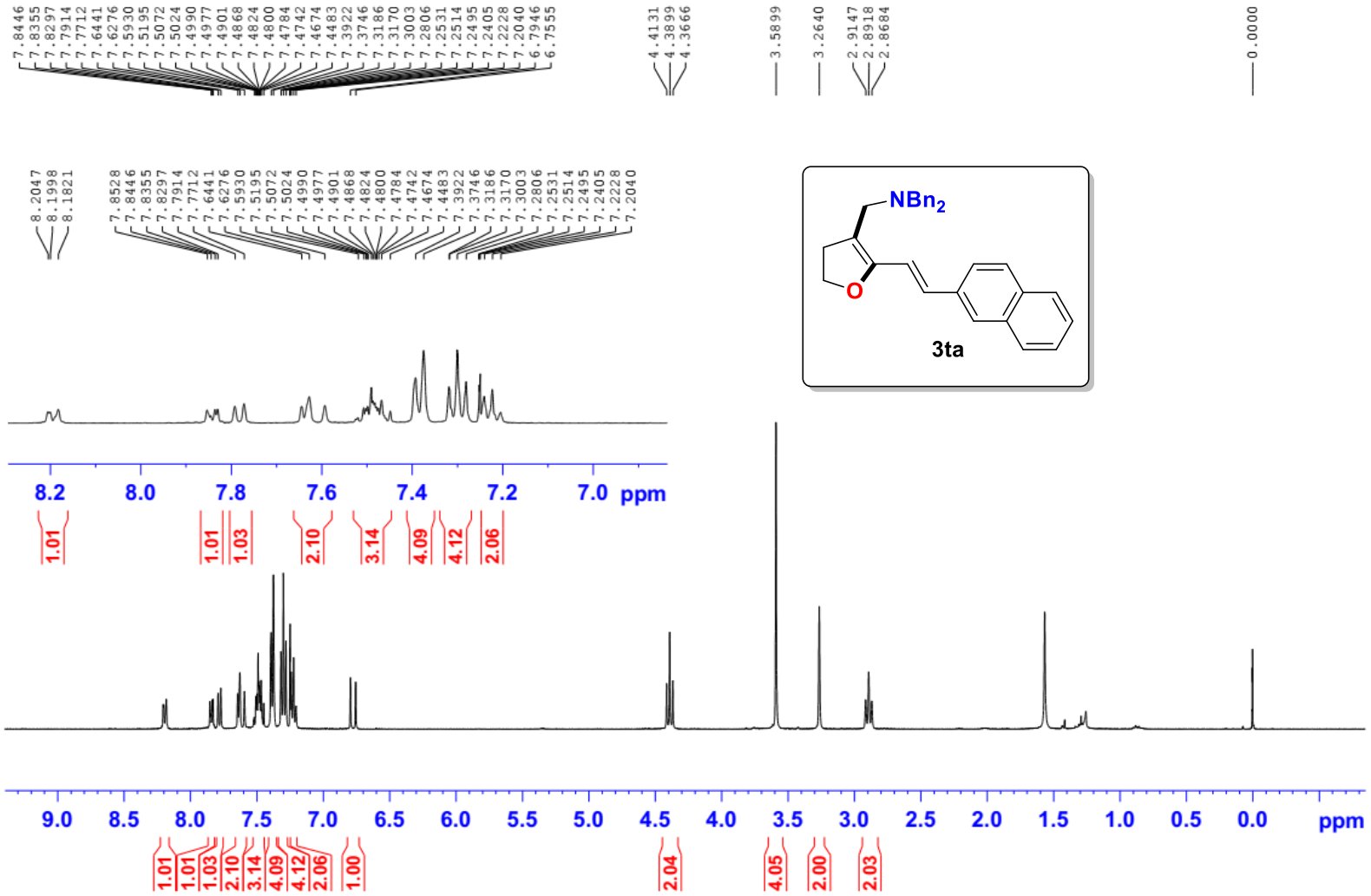
YHJ-P-**3sa** ^{1}H NMR (400MHz $CDCl_3$)



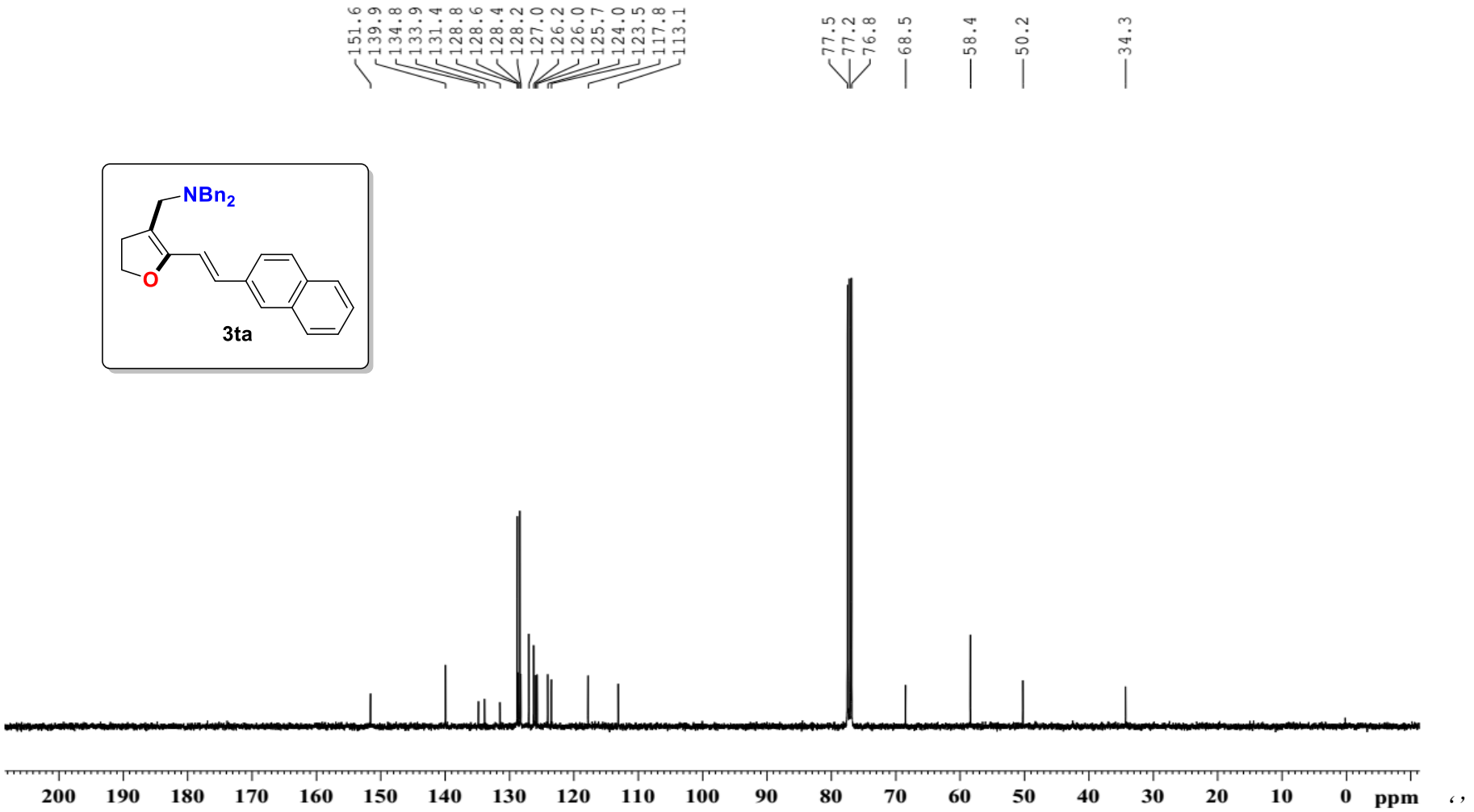
YHJ-P-**3sa** ^{13}C NMR (100MHz $CDCl_3$)



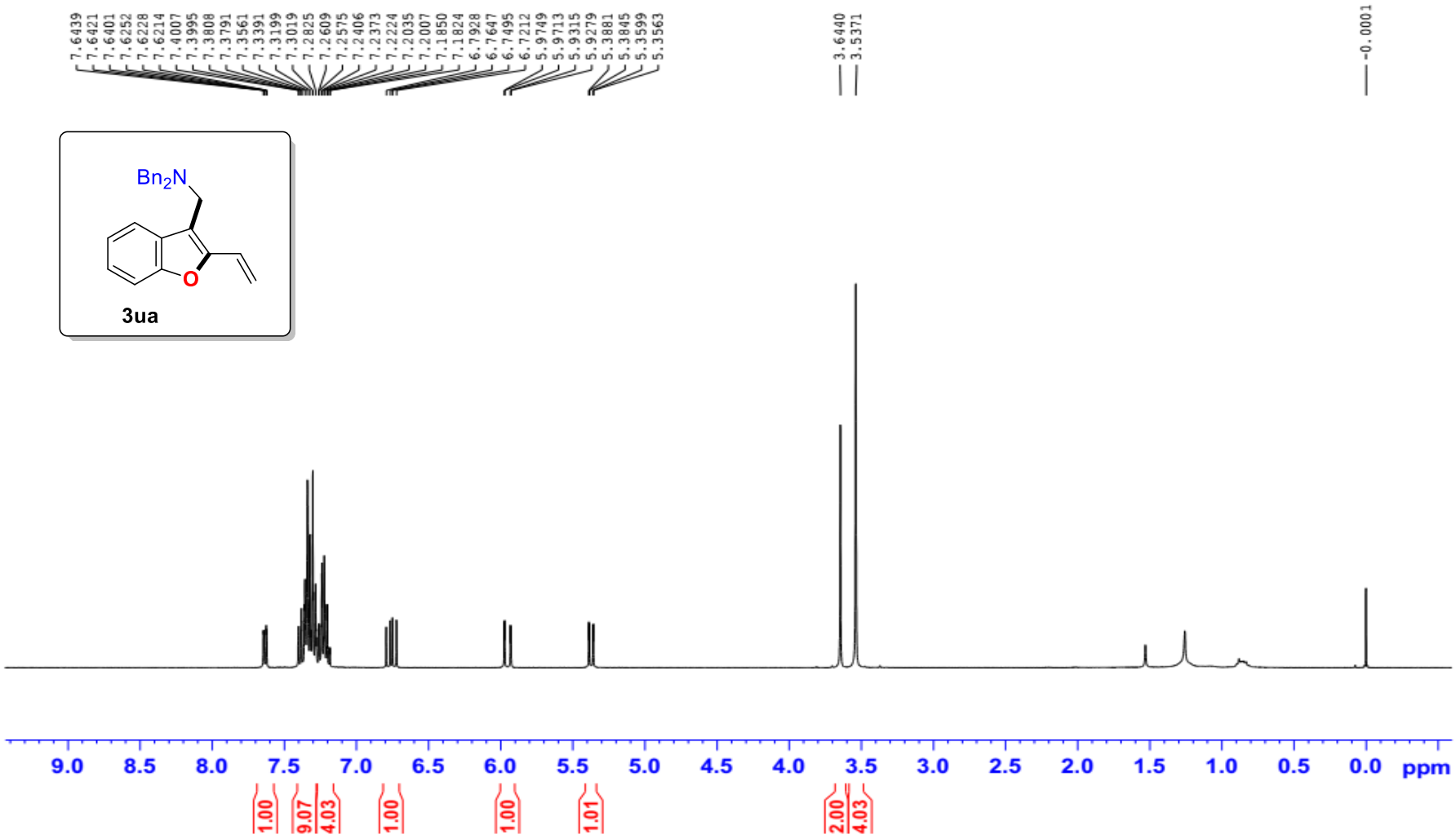
YHJ-P-**3ta** ^{1}H NMR (400MHz $CDCl_3$)



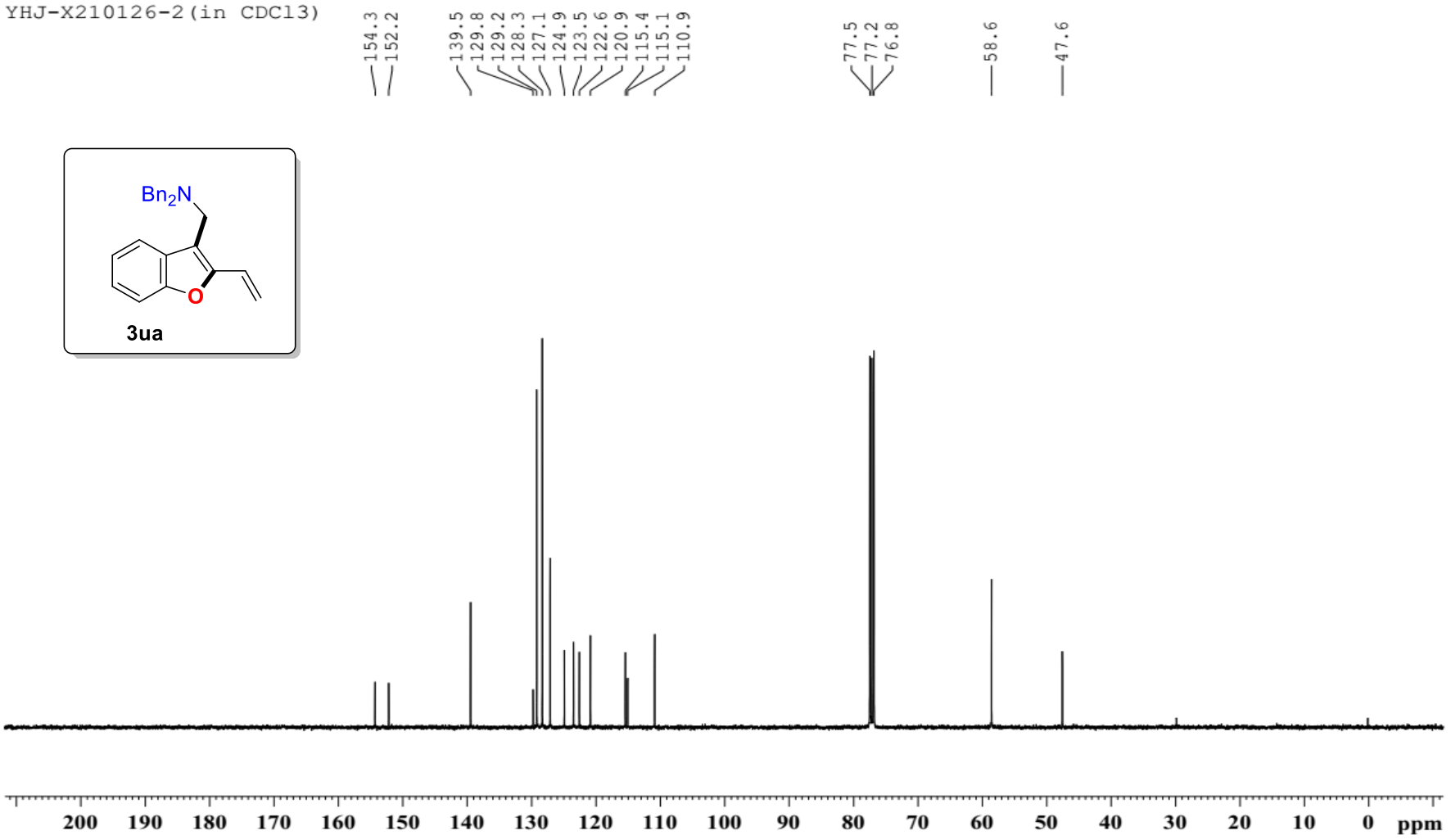
YHJ-P-**3ta** ^{13}C NMR (125MHz $CDCl_3$)



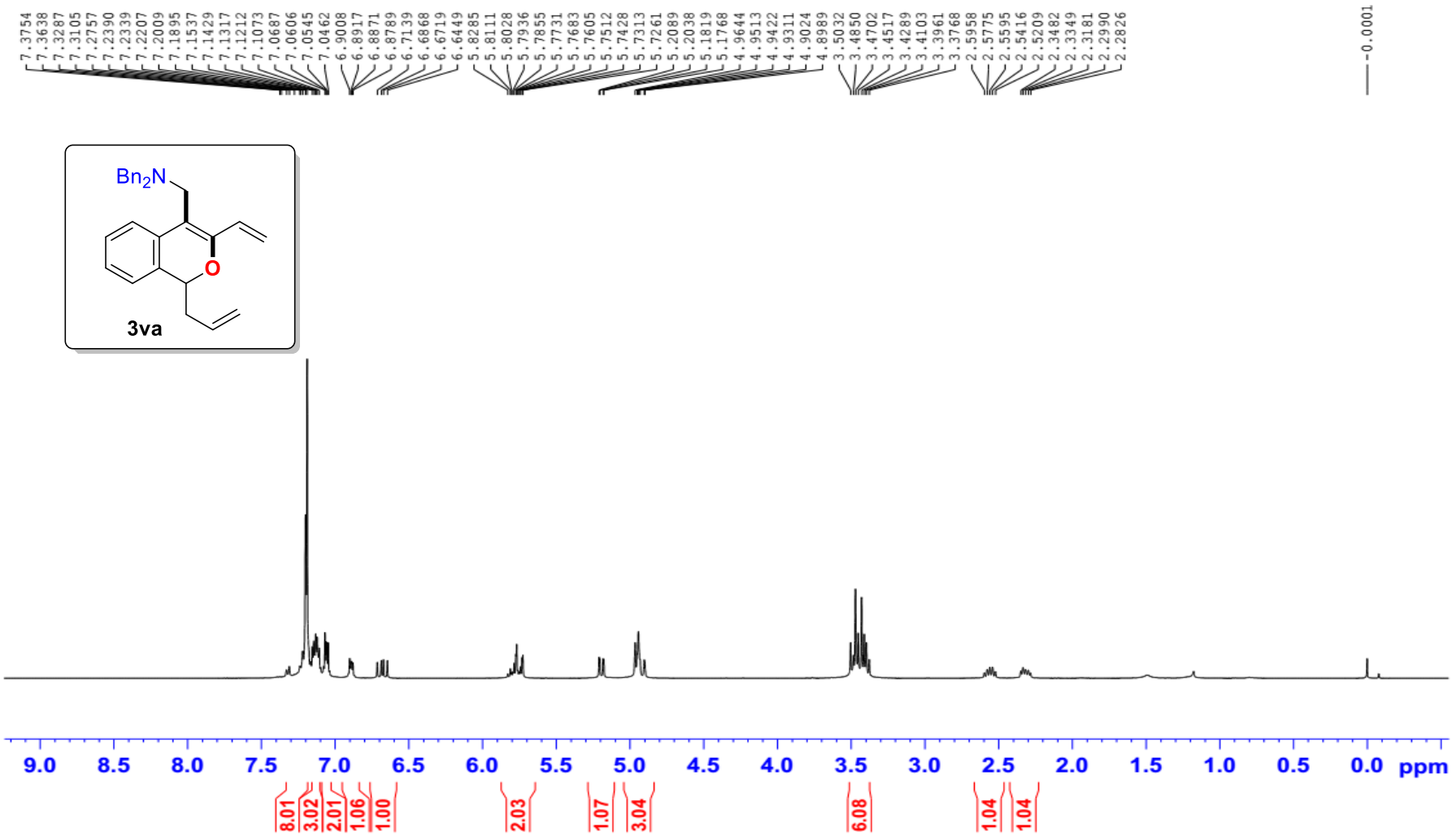
YHJ-P-**3ua** ^{1}H NMR (400MHz $CDCl_3$)



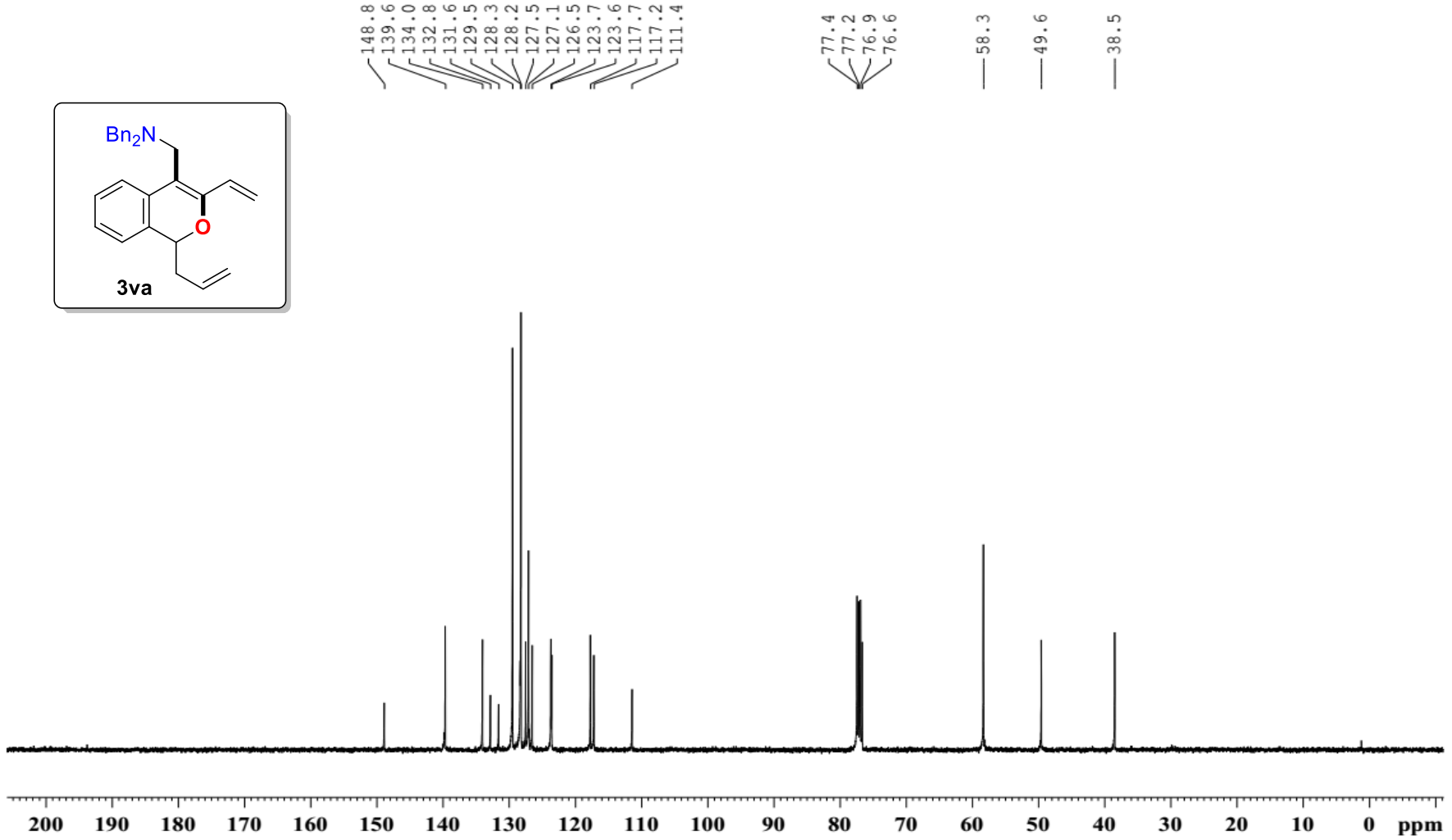
YHJ-P-**3ua** ^{13}C NMR (100MHz $CDCl_3$)



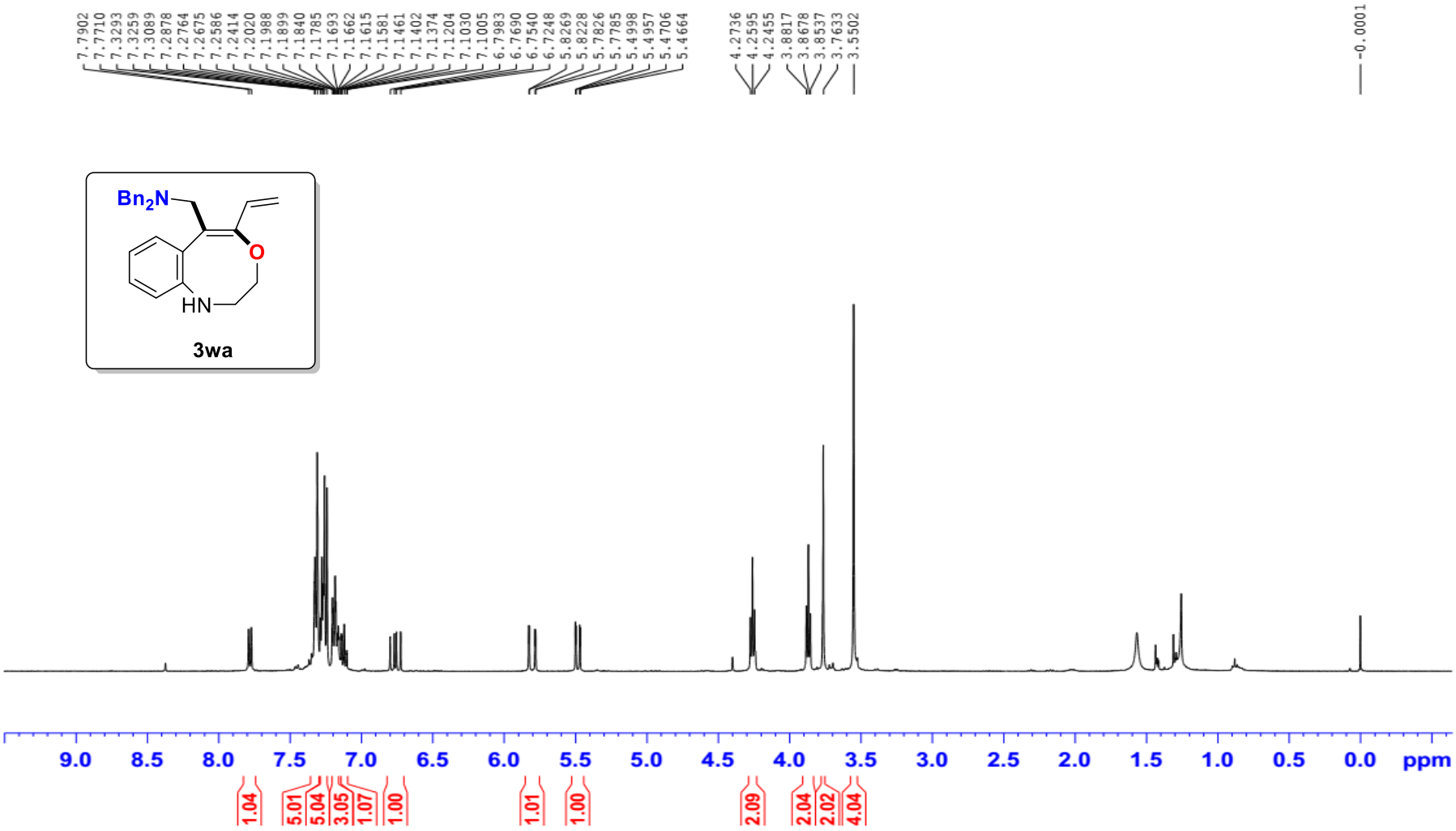
YHJ-P-**3va** ^{1}H NMR (400MHz $CDCl_3$)



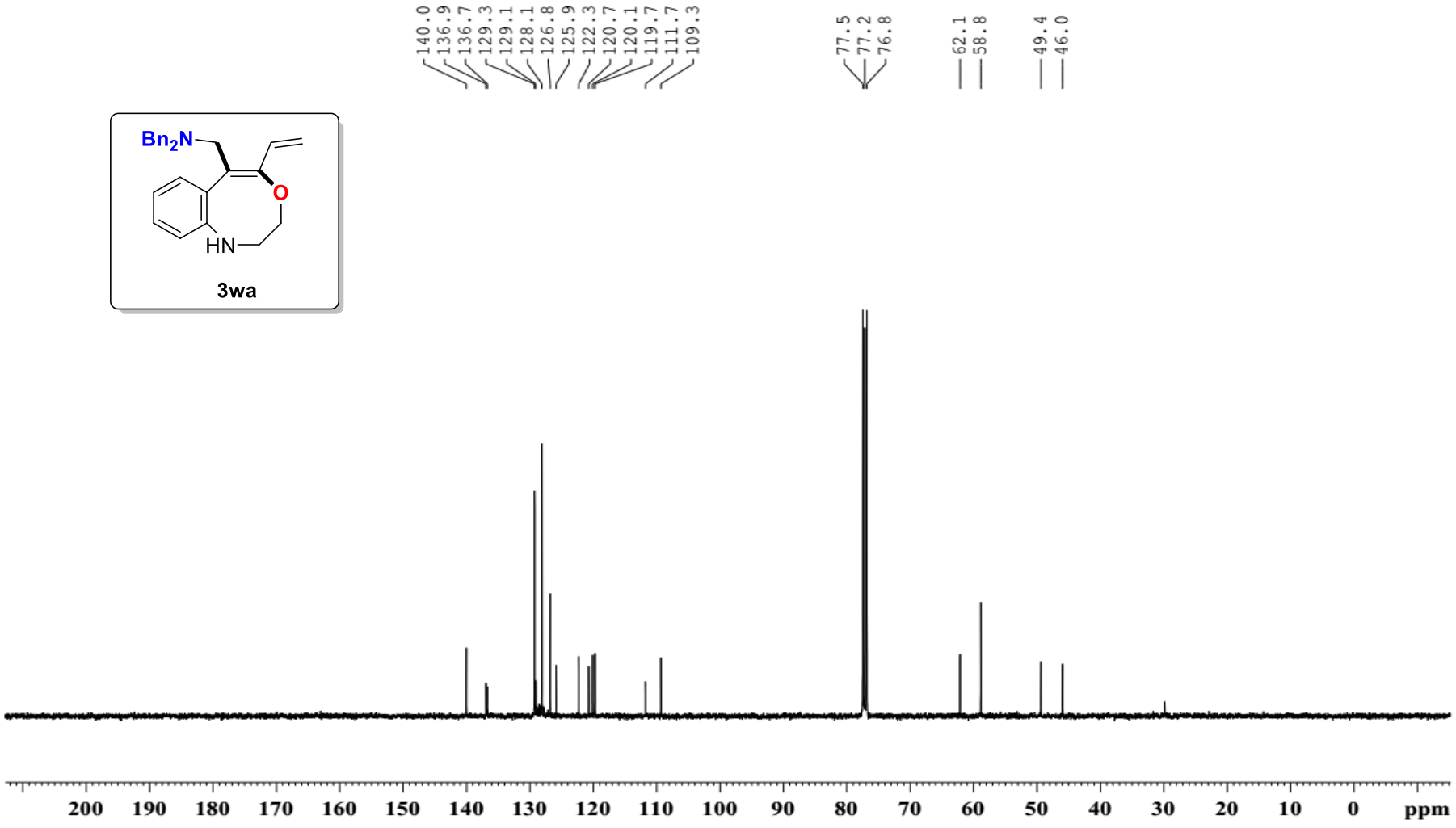
YHJ-P-**3va** ^{13}C NMR (100MHz $CDCl_3$)



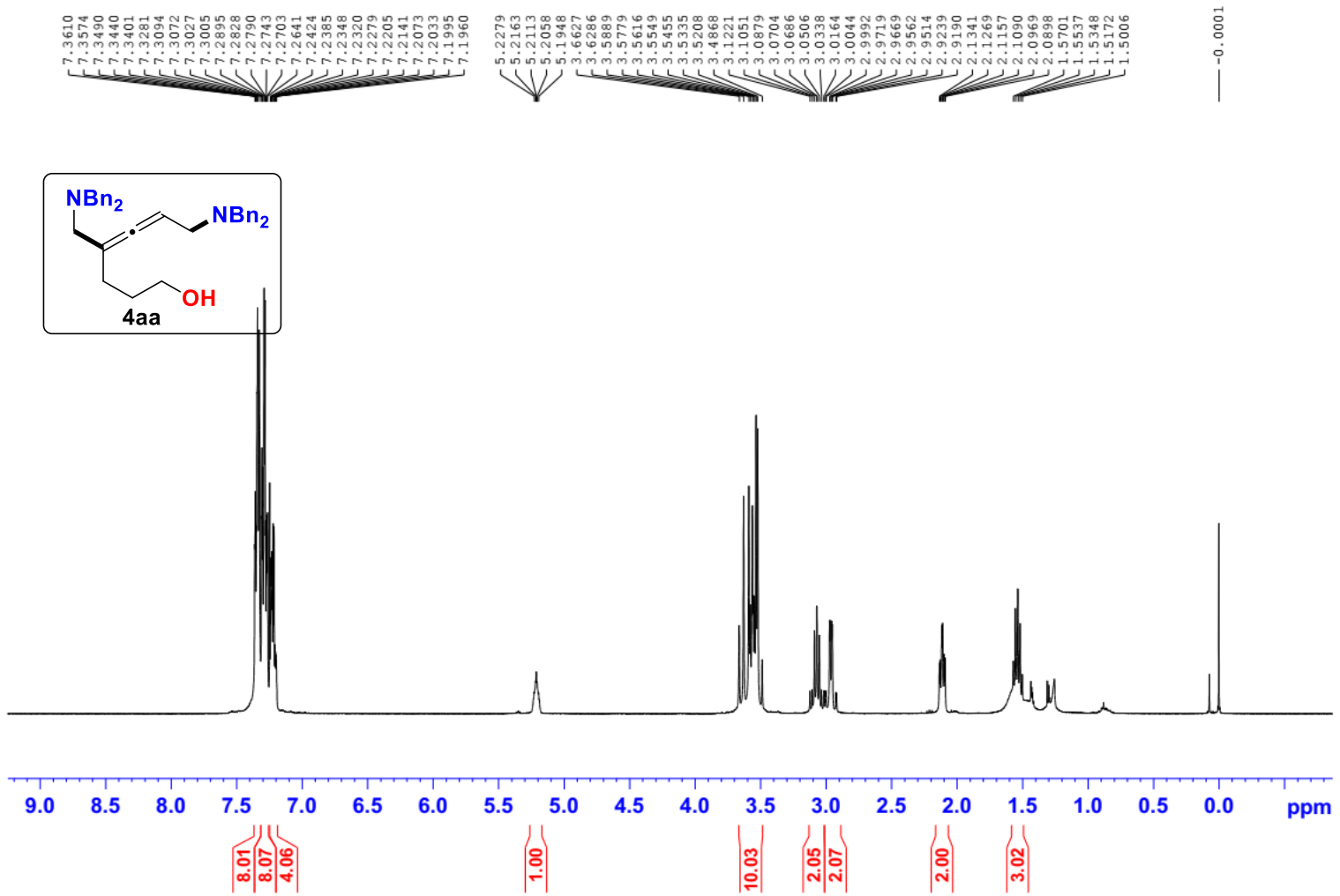
YHJ-P-**3wa** ^{1}H NMR (400MHz $CDCl_3$)



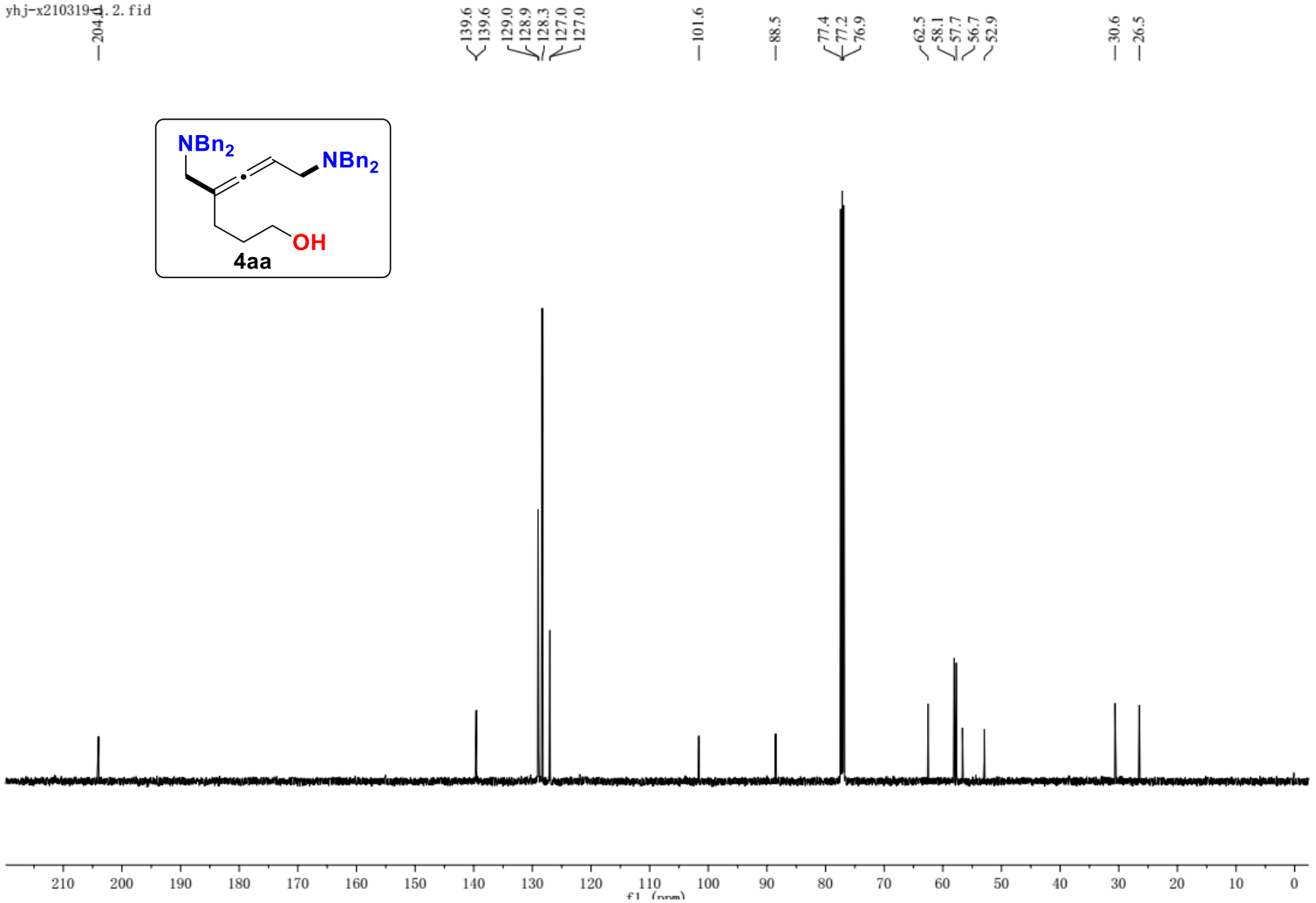
YHJ-P-**3wa** ^{13}C NMR (125MHz $CDCl_3$)



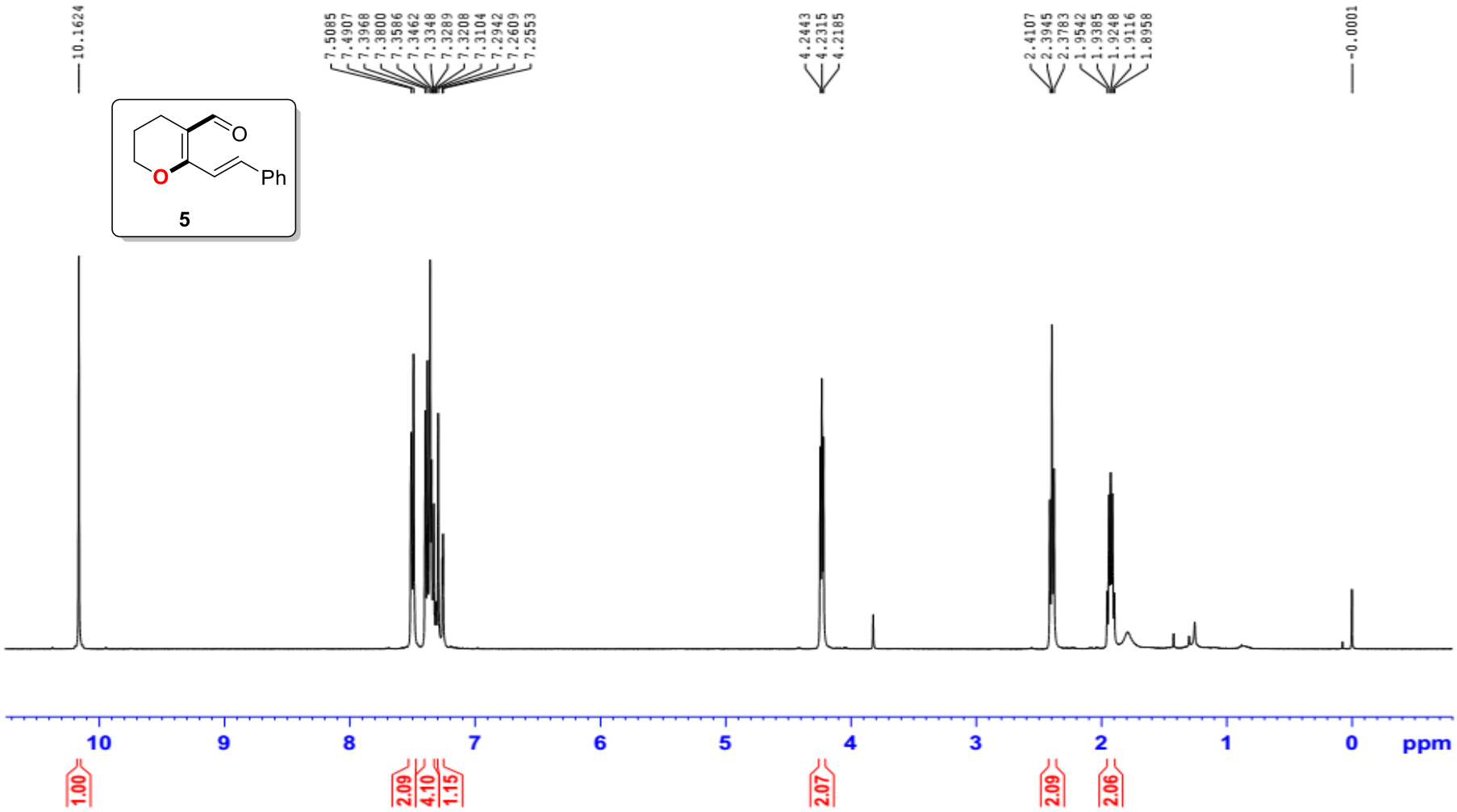
YHJ-P-**4aa** ^{1}H NMR (400MHz $CDCl_3$)



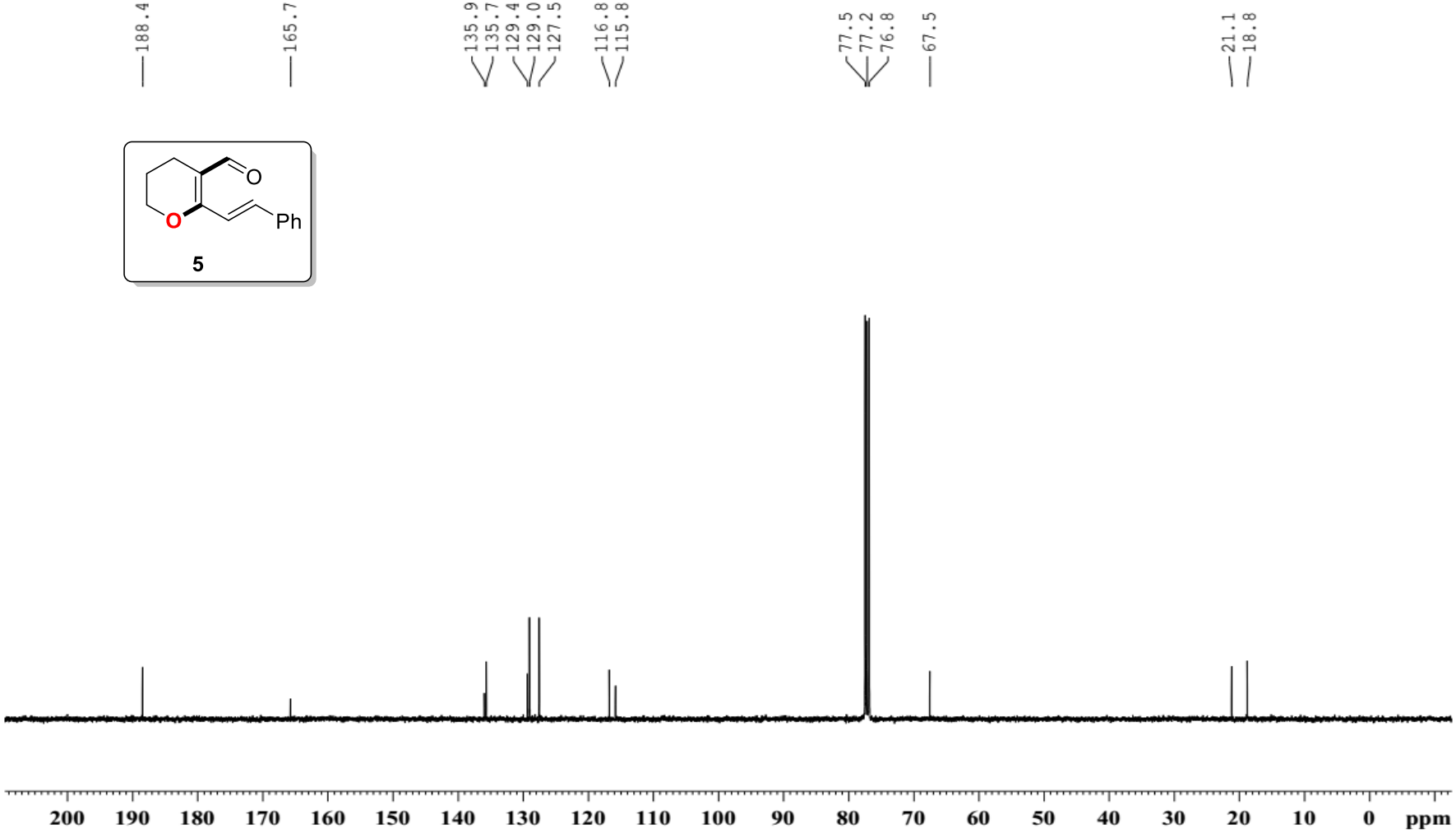
YHJ-P-**4aa** ^{13}C NMR (125MHz $CDCl_3$)



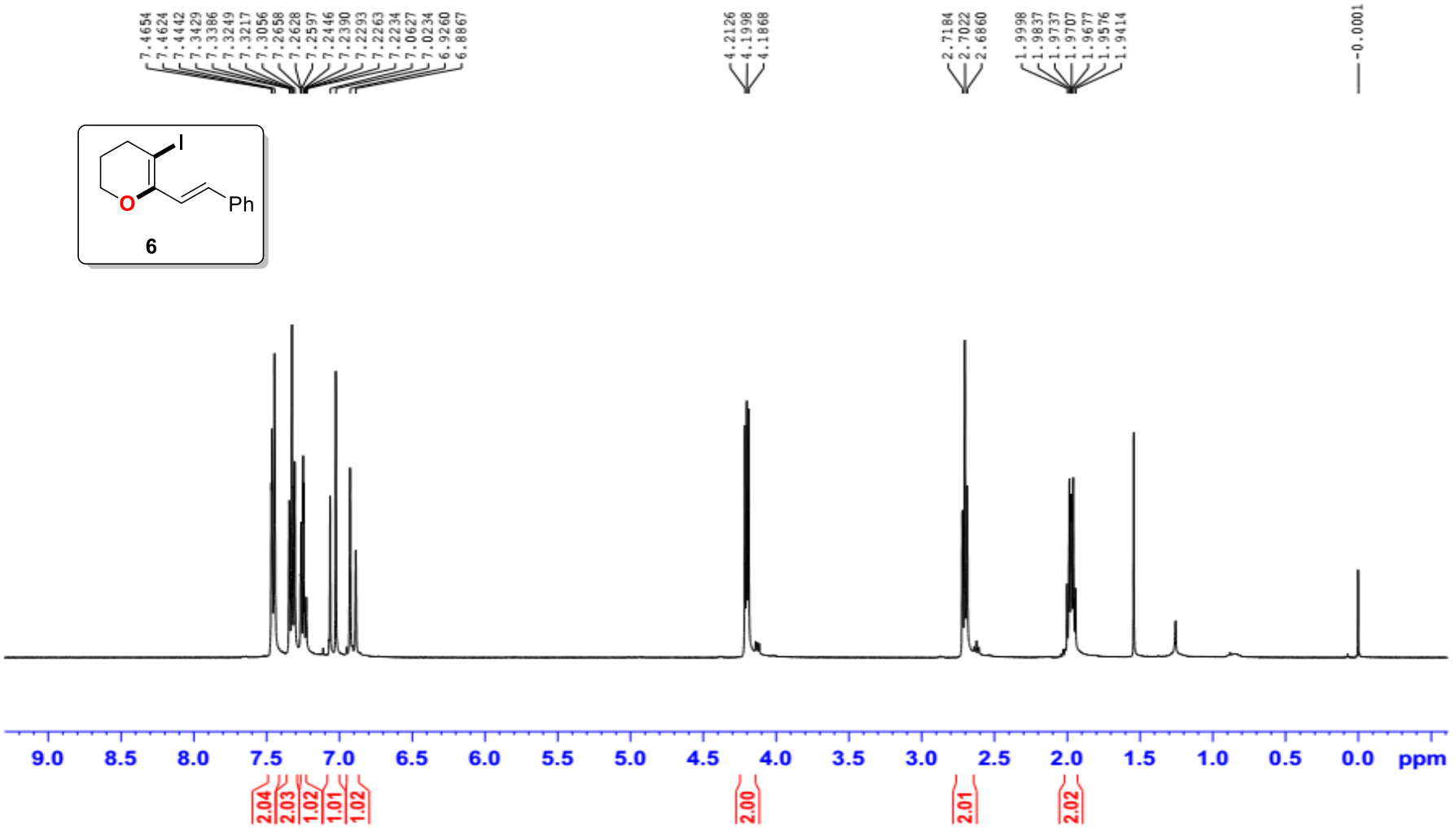
YHJ-P-**5** ^{1}H NMR (400MHz $CDCl_3$)



YHJ-P-**5** ^{13}C NMR (100MHz $CDCl_3$)



YHJ-P-**6** ^{1}H NMR (400MHz $CDCl_3$)



YHJ-P-**6** ^{13}C NMR (125MHz $CDCl_3$)