Electronic Supplementary Information

Highly Regioselective and Ligand-Controlled Diastereodivergent Aminomethylative Annulation of Dienyl Alcohols Enabled by Hydrogen-Bonding Assisting Effect

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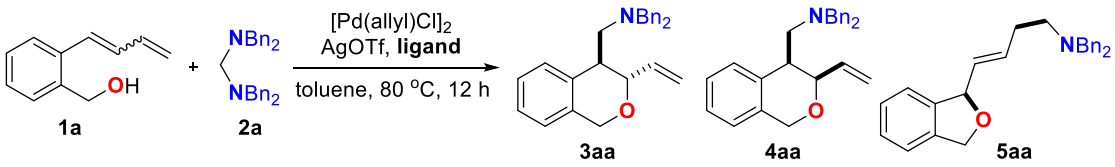
General Information

All non-aqueous reactions and manipulations were using standard Schlenk techniques. All solvents before use were dried and degassed by standard methods and stored under nitrogen atmosphere. All reactions were monitored by TLC with silica gel-coated plates. NMR spectra were recorded on Bruker 400 spectromete and Bruker AV500M spectromete. Chemical shifts were reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. Coupling constants (*J*) were reported in Hz and refered to apparent peak multiplications. High resolution mass spectra (HRMS) were recorded on Bruker MicroTOF-QII mass (ESI). High performance liquid chromatography (HPLC) was recorded on Agilent 1260 instument. GC analysis were performed on Agilent 7890B instrument with Hp-5 column. GC-MS analysis were performed with Agilent 7890B/5975B GC-MS system. All commercially available compounds were purchased from Adamas or Energy Chemical. Aminals used here were known compounds and synthesized according to the reported methods[1,2]. Dienols used here were synthesized according to the reported methods[3-5]. Flash column chromatography was performed using 200-300 mesh silica gels.

1. Optimization of the Reaction Conditions

N,*N*,*N*',*N*'-tetrabenzylmethanediamine **2a** (146 mg, 0.36 mmol), $[Pd(allyl)Cl]_2$ (2.8 mg, 2.5 mol%), AgOTf (4.6 mg, 6 mol%), bidentate phosphine ligand (0.015 mmol, 5 mol%) or monodentate phosphine ligand (0.03 mmol, 10 mol%), (2-(buta-1,3-dien-1-yl)phenyl)methanol **1a** (48 mg, 0.30 mmol) and toluene (1.0 mL) were added to a 25 mL flame-dried Young-type tube under N_2 atmosphere. The reaction mixture was stirred at 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 (eluted with petroleum ether/ethyl acetate = 200/1 to 50/1) on a silica gel to give the desired products **3aa**, **4aa** and **5aa**. The dr value of the crude reaction mixture was determined by ^{1}HNMR analysis.

Table S1. Screening of ligands[a]



1a **2a** **3aa** **4aa** **5aa**

entry	ligand	yield (%) **3aa** + **4aa**	**3aa/4aa**[b]	yield (%) **5aa**
1	**L1**	40	5:1	45
2	**L2**	59	>20:1	trace
3	**L3**	43	>20:1	trace
4	**L4**	50	1:5	trace
5	**L5**	28	>20:1	trace
6	**L6**	14	>20:1	trace
7	**L7**	18	>20:1	trace
8	**L8**	14	>20:1	trace
9	**L9**	17	>20:1	trace
10	**L10**	63	18:1	5
11	**L11**	trace	-	-
12	**L12**	trace	-	-
13	**L13**	trace	-	-
14	**L14**	49	>20:1	3
15	**L15**	51	>20:1	10
16	**L16**	51	14:1	trace
17	**L17**	65	>20:1	14
18	**L18**	72	8:1	10

[a]Reaction comditions: **1a** (0.3 mmol), **2a** (0.36 mmol), $[Pd(allyl)Cl]_2$ (2.5 mol%), AgOTf (6 mol%), bidentate phosphine ligand (5 mol%) or monodentate phosphine ligand (10 mol%) , toluene (1.0 mL), 80 °C,12 h, isolated yield. [b]The ratio of **3aa** and **4aa** was determined by ^{1}H NMR.

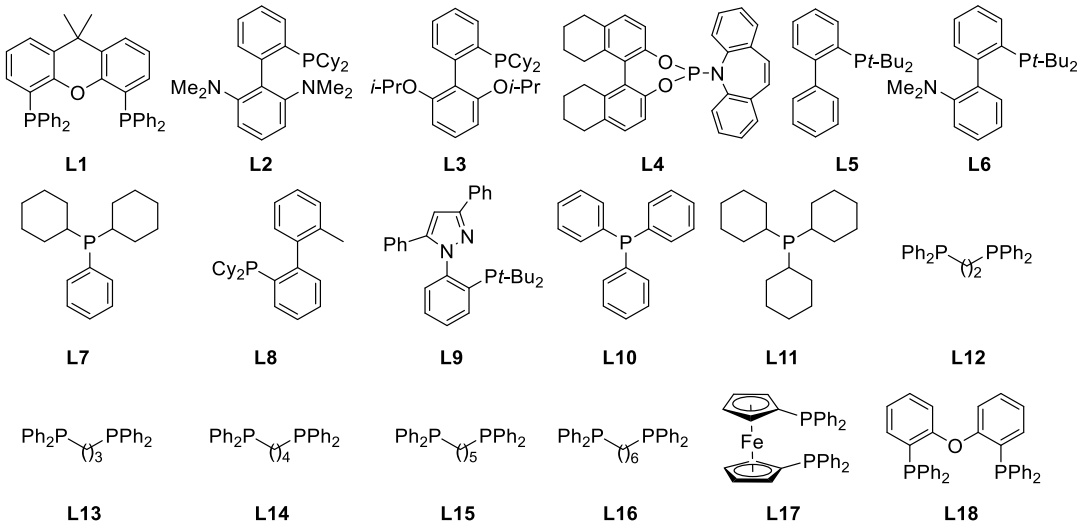
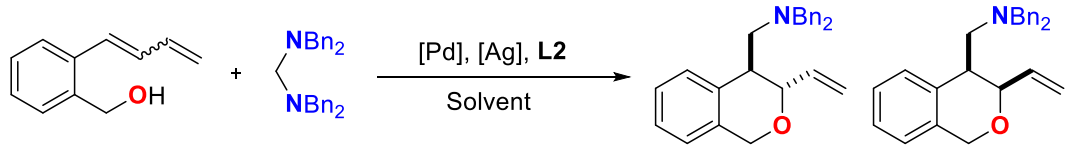


Figure S1. The structure of ligands

2.1 Optimization of the reaction conditions for the synthesis of 3aa

N,*N*,*N'*,*N'*-tetrabenzylmethanediamine **2a** (146 mg, 0.36 mmol), palladium salt (0.015 mmol, 5 mol%), silver salt (6 mol% or 12 mol%), **L2** (0.03 mmol, 10 mol%), (2-(buta-1,3-dien-1-yl)phenyl)methanol **1a** (48 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 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 (eluted with petroleum ether/ethyl acetate = 200/1 to 50/1) on a silica gel to give the desired product **3aa**. The dr value of the crude reaction mixture was determined by ^{1}HNMR analysis.

Table S2. Optimization of the reaction conditions for the synthesis of **3aa**[a]



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

entry	[Pd]	[Ag] (x mol%)	Solvent	yield (%) **3aa + 4aa**	**3aa/4aa**[d]
1	$[Pd(allyl)Cl]_2$	AgOTf (6)	toluene	59	>20:1
2	$PdCl_2$	AgOTf (12)	toluene	48	>20:1
3	$PdBr_2$	AgOTf (12)	toluene	50	>20:1
4	$Pd(COD)Cl_2$	AgOTf (12)	toluene	52	>20:1
5	$[Pd(allyl)Cl]_2$	AgOTf (6)	CH_3CN	47	20:1
6	$[Pd(allyl)Cl]_2$	AgOTf (6)	DME	60	>20:1
7	$[Pd(allyl)Cl]_2$	AgOTf (6)	anisole	60	>20:1
8	$[Pd(allyl)Cl]_2$	AgOTf (6)	THF	22	>20:1
9	$[Pd(allyl)Cl]_2$	AgOTf (6)	CH_2Cl_2	65	18:1
10	$[Pd(allyl)Cl]_2$	AgOTf (6)	DMF	29	20:1
11	$[Pd(allyl)Cl]_2$	AgOTf (6)	DMSO	5	-
12	$[Pd(allyl)Cl]_2$	AgOTf (6)	CH_2Cl_2 : toluene = 3: 2	67	>20:1
13[b]	**$[Pd(allyl)Cl]_2$**	**AgOTf (6)**	**CH_2Cl_2 : toluene = 3 : 2**	**86**	**>20:1**
14[b]	$[Pd(allyl)Cl]_2$	$AgBF_4$ (6)	CH_2Cl_2 : toluene = 3 : 2	85	>20:1
15[b]	$[Pd(allyl)Cl]_2$	$AgSbF_6$ (6)	CH_2Cl_2 : toluene = 3 : 2	71	15:1
16[b]	$[Pd(allyl)Cl]_2$	$AgClO_4$ (6)	CH_2Cl_2 : toluene = 3 : 2	85	>20:1
17[b]	-	AgOTf (6)	CH_2Cl_2 : toluene = 3 : 2	ND	-
18[b]	$[Pd(allyl)Cl]_2$	-	CH_2Cl_2 : toluene = 3 : 2	53	11:1
19[b,c]	$[Pd(allyl)Cl]_2$	AgOTf (6)	CH_2Cl_2 : toluene = 3 : 2	65	>20:1
20[b]	$[Pd(allyl)Cl]_2$	AgOTf (6)	CH_2Cl_2 : toluene = 2 : 3	73	>20:1
21[b]	$[Pd(allyl)Cl]_2$	AgOTf (6)	CH_2Cl_2 : toluene = 1 : 1	80	>20:1
22[b]	$[Pd(allyl)Cl]_2$	AgOTf (6)	CH_2Cl_2 : toluene = 4 : 1	84	>20:1

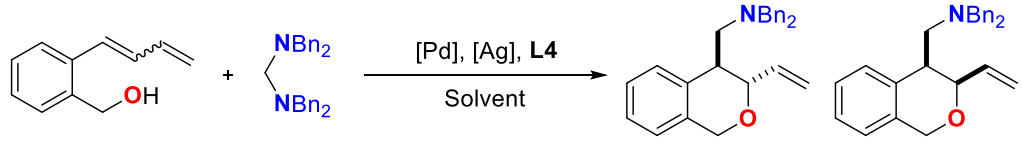
[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.36 mmol), [Pd] (5 mol%), [Ag] (6 mol% or 12 mol%), **L2** (10 mol%), solvent (1.0 mL), 80 °C, 12 h, isolated yield. [b]**1a** (0.36 mmol), **2a** (0.3 mmol). [c]**L2** (5 mol%). [d]The ratio of **3aa** and **4aa** was determined by ^{1}H NMR.

2.2 Optimization of the reaction conditions for the synthesis of 4aa

N,*N*,*N'*,*N'*-tetrabenzylmethanediamine **2a** (122 mg, 0.30 mmol), palladium salt (0.015 mmol, 5 mol%), silver salt (6 mol% or 12 mol%), **L4** (0.03 mmol, 10 mol%), (2-(buta-1,3-dien-1-yl)phenyl)methanol **1a** (58 mg, 0.36 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 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 (eluted with petroleum ether/ethyl acetate = 200/1 to

50/1) on a silica gel to give the desired product **4aa**. The dr value of the crude reaction mixture was determined by ^{1}HNMR analysis.

Table S3. Optimization of the reaction conditions for the synthesis of **4aa**[a]



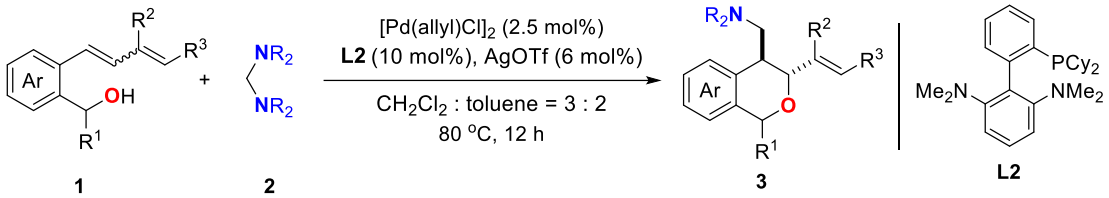
1a **2a** **3aa** **4aa**

entry	[Pd]	[Ag] (x mol%)	solvent	T/ °C	yield (%) 3aa + 4aa	3aa/4aa[c]
1	$PdBr_2$	AgOTf (12)	CH_2Cl_2	80	90	1:7
2	PdI_2	AgOTf (12)	CH_2Cl_2	80	88	1:7
3	$Pd(CH_3CN)_2Cl_2$	AgOTf (12)	CH_2Cl_2	80	88	1:7
4	$Pd(COD)Cl_2$	AgOTf (12)	CH_2Cl_2	80	75	1:7
5	$Pd(COD)Br_2$	AgOTf (12)	CH_2Cl_2	80	80	1:5
6	$Pd(OAc)_2$	-	CH_2Cl_2	80	trace	-
7	$[Pd(allyl)Cl]_2$	AgOTf (6)	CH_2Cl_2	80	79	1:5
8	$PdBr_2$	AgOTf (12)	CH_2Cl_2	60	84	1:9
9	$PdBr_2$	AgOTf (12)	CH_2Cl_2	40	81	1:10
10	$PdBr_2$	AgOTf (12)	CH_2Cl_2	rt	62	1:14
11[b]	**$PdBr_2$**	**AgOTf** (12)	**CH_2Cl_2**	**rt**	**89**	**1:14**
12[b]	$PdBr_2$	$AgClO_4$ (12)	CH_2Cl_2	rt	84	1:4
13[b]	$PdBr_2$	$AgBF_4$ (12)	CH_2Cl_2	rt	87	1:8
14[b]	$PdBr_2$	$AgPF_6$ (12)	CH_2Cl_2	rt	87	1:6
15[b]	$PdBr_2$	$AgSbF_6$ (12)	CH_2Cl_2	rt	87	1:6
16[b]	$PdBr_2$	AgOTf (12)	toluene	rt	38	1:8
17[b]	$PdBr_2$	AgOTf (12)	anisole	rt	67	1:8
18[b]	$PdBr_2$	AgOTf (12)	DME	rt	29	1:13
19[b]	$PdBr_2$	AgOTf (12)	THF	rt	35	1:19
20[b]	$PdBr_2$	AgOTf (12)	1,4-dioxane	rt	60	1:14

[a]Reaction conditions: **1a** (0.36 mmol), **2a** (0.30 mmol), [Pd] (5 mol%), [Ag] (6 mol% or 12 mol%), **L4** (10 mol%), solvent (1.0 mL), 12 h, isolated yield. [b]24 h. [c]The ratio of **3aa** and **4aa** was determined by ^{1}H NMR.

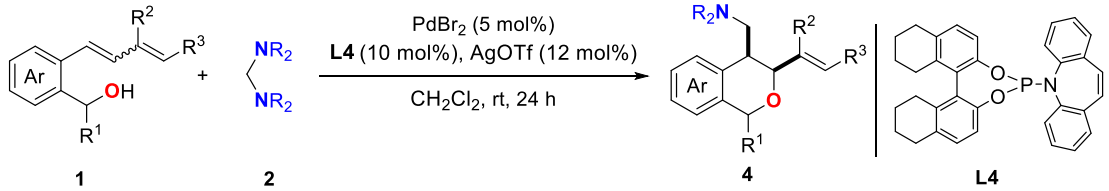
2. General Procedure for the Catalytic Reaction

Method A:



Aminal **2** (0.30 mmol), $[Pd(allyl)Cl]_2$ (2.8 mg, 2.5 mol%), **L2** (13.0 mg, 10 mol%), AgOTf (4.6 mg, 6 mol%), dienol **1** (0.36 mmol) and solvent (CH_2Cl_2 : toluene = 3 : 2, 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 °C for 12 hours, and then cooled to room temperature. The solvent was removed under reduced pressure, the residue was purified by flash chromatography (deluted with petroleum ether/ethyl acetate = 200/1 to 50/1) on a silica gel to give the desired product **3** as colorless oil. The dr value of the crude reaction mixture was determined by ^{1}HNMR analysis.

Method B:

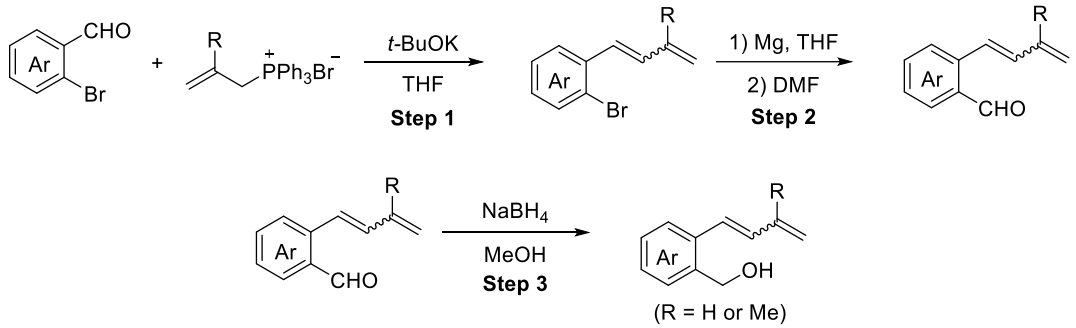


Aminal **2** (0.30 mmol), $PdBr_2$ (4.0 mg, 5 mol%), **L4** (16.0 mg, 10 mol%), AgOTf (9.3 mg, 12 mol%), dienol **1** (0.36 mmol) and CH_2Cl_2 (1.0 mL) were added to a 25 mL flame-dried Young-type tube under N_2 atmosphere. The reaction mixture was stirred at room temperature for 24 hours. The solvent was removed under reduced pressure, the residue was purified by flash chromatography (deluted with petroleum ether/ethyl acetate = 200/1 to 50/1) on a silica gel to give the desired product **4** as colorless oil. The dr value of the crude reaction mixture was determined by ^{1}HNMR analysis.

3. Preparation and Characterization Data of Dienols

3.1. Preparation of Dienol Derivatives

General Procedure A. Synthesis of dienol substrates **1a-1l** and **1p**.

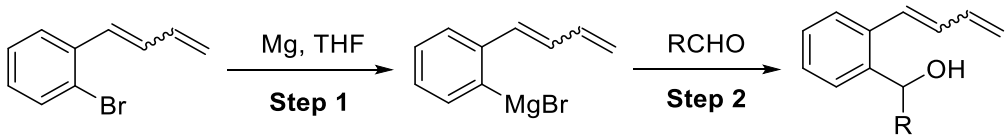


Step 1. *t*-BuOK (14.6 g, 130 mmol) was added to a stirred suspension of allyltriphenylphosphonium bromide (38.2 g, 100 mmol) in dry THF under N_2 at 0 ℃, the mixture was then stirred at room temperature for 30 minutes. After the mixture was cooled again to 0 ℃, 2-Bromobenzaldehyde (18.4 g, 84 mmol) in THF was added dropwise and the reaction was kept stirring for 3 hours with TLC detection. The mixture was poured into saturated aq. NH_4Cl and extracted with EtOAc for 3 times. The combined organic extracts were dried over anhydrous Na_2SO_4, concentrated, and purified by flash column chromatography (deluted with petroleum ether) on a silica gel to afford conjugated dienes (14.9 g, 85% yield).

Step 2. A grain of I_2 and a small quantity of 1-bromo-2-(buta-1,3-dien-1-yl)benzene were added to the mixture of Mg (1.6 g, 66 mmol) and THF (50 mL) in a 200 mL three-neck flask under N_2 atmosphere. The reaction mixture was stirred under heating until the solution become colorless. Then a solution of 1-bromo-2-(buta-1,3-dien-1-yl)benzene (12.4 g, 60 mmol) in THF (50 mL) was added slowly to the reaction mixture and stirred at 90 °C for 12 hours. The reaction mixture was cooled to room temperature and *N*,*N*-dimethylformamide (6.9 mL, 90 mmol) was added dropwise to the solution. The reaction mixture was stirred at room temperature for 5 hours and quenched by saturated aq. NH_4Cl (100 mL). The solvent was evaporated under reduced pressure and the residue was extracted by CH_2Cl_2 (50 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by flash column chromatography (deluted with petroleum ether/ethyl acetate = 30/1) on a silica gel to afford 2-(buta-1,3-dien-1-yl)benzaldehyde (6.4 g, 67% yield).

Step 3. 2-(buta-1,3-dien-1-yl)benzaldehyde (4.5 g, 28.5 mmol) was dissolved in MeOH (50 mL). the reaction mixture was added $NaBH_4$ (1.6 g, 42.8 mmol) in portions at 0 °C and stirred at room temperature for 2 hours. The resulting mixture was quenched by saturated aq. NH_4Cl (20 mL). The solvent was evaporated under reduced pressure and the residue was extracted by CH_2Cl_2 (50 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) on a silica gel to afford (2-(buta-1,3-dien-1-yl)phenyl)methanol **1a** (4.0 g, 88% yield).

General Procedure B. Synthesis of dienol substrates **1m** and **1n**.

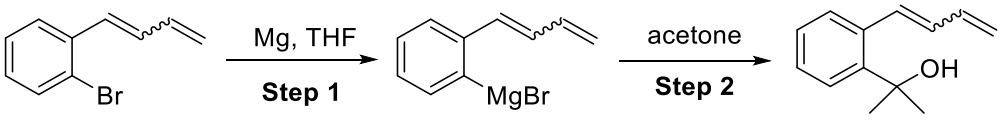


(R = C_6H_5- , 4-$MeOC_6H_4$-)

Step 1. A grain of I_2 and a small quantity of 1-bromo-2-(buta-1,3-dien-1-yl)benzene were added to the mixture of Mg (0.5 g, 22 mmol) and THF (50 mL) in a 200 mL three-neck flask under N_2 atmosphere. The reaction mixture was stirred with heating until the solution become colorless. Then a solution of 1-bromo-2-(buta-1,3-dien-1-yl)benzene (4.2 g, 20 mmol) in THF (50 mL) was added slowly to the reaction mixture and stirred at 90 °C for 12 hours. The reaction mixture was cooled to room temperature and used for next step.

Step 2. Benzaldehyde (2.1 g, 20 mmol) was dissolved in THF (50 mL) under N_2 atomosphere. Then (2-(buta-1,3-dien-1-yl)phenyl)magnesium bromide was added to the reaction mixture and stirred at 0 °C for 30 minutes and stirred at room temperature for 1 hour. After that, the reaction mixture was quenched by saturated aq. NH_4Cl (100 mL). The reaction mixture was extracted with EtOAc (20 mL × 3) and dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by flash chromatography (deluted with petroleum ether/ethyl acetate = 5:1) on a cilica gel to give (2-(buta-1,3-dien-1-yl)phenyl)(phenyl)methanol **1m** (3.4 g, 71% yield).

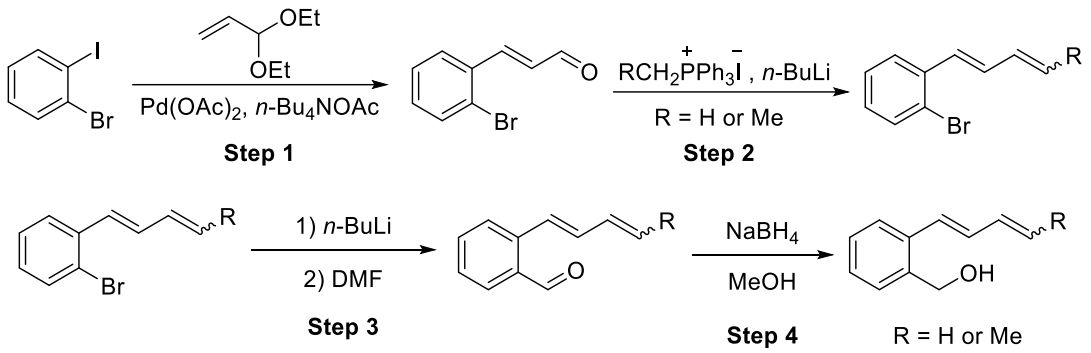
General Procedure C. Synthesis of dienol substrate **1o**.



Step 1. A grain of I_2 and a small quantity of 1-bromo-2-(buta-1,3-dien-1-yl)benzene were added to the mixture of Mg (0.5 g, 22 mmol) and THF (50 mL) in a 200 mL three-neck flask under N_2 atmosphere. The reaction mixture was stirred with heating until the solution become colorless. Then a solution of 1-bromo-2-(buta-1,3-dien-1-yl)benzene (4.2 g, 20 mmol) in THF (50 mL) was added slowly to the reaction mixture and stirred at 90 °C for 12 hours. The reaction mixture was cooled to room temperature and used for next step.

Step 2. Acetone (1.2 g, 20 mmol) was dissolved in THF (50 mL) under N_2 atomosphere. Then the reaction mixture was added (2-(buta-1,3-dien-1-yl)phenyl)magnesium bromide and stirred at room temperature for 1 hour. After that, the reaction mixture was quenched by saturated aq. NH_4Cl (100 mL). The reaction mixture was extracted with EtOAc (20 mL ×3) and dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by flash chromatography (deluted with petroleum ether/ethyl acetate = 5:1) on a silica gel to give 2-(2-(buta-1,3-dien-1-yl)phenyl)propan-2-ol **1o** (2.0 g, 52% yield).

General Procedure D. Synthesis of dienol substrates **1q** and *E*-**1a**.



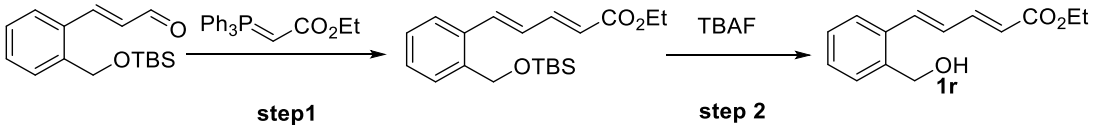
Step 1. The acrolein diethyl acetal (7.8 g, 60 mmol), $Pd(OAc)_2$ (200 mg, 2 mol%), K_2CO_3 (9.0 g, 75 mmol), KCl (3.5 g, 50 mmol) and *n*-Bu_4NOAc (30.2 g, 100 mmol) were added to a solution of 1-bromo-2-iodobenzene (14.1 g, 50 mmol) in DMF (100 mL). The mixture was stirred at 90 °C for 12 hours. After cooling to room temperature, 2 M HCl was slowly added to the reaction mixture and the mixture was stirred at room temperature for another 10 minutes. Then the mixture was extracted with Et_2O (20 mL ×3) and dried with anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by flash column chromatography (deluted with petroleum ether/ethyl acetate = 50/1 to 20/1) on a silica gel to give the desired product (*E*)-3-(2-bromophenyl)acrylaldehyde (4.3 g, 41% yield).

Step 2. The *n*-butyllithium (2.5 M in Hexane, 9.6 mL, 24 mmol) was added dropwise to a suspension of methyl triphenylphosphonium iodide (9.2 g, 24 mmol) in THF (100 mL) at 0 °C. The mixture was stirred at 0 °C for 2 hours. A solution of (*E*)-3-(2-bromophenyl)acrylaldehyde (4.2 g, 20 mmol) in THF (30 mL) was added to the mixture and stirred at room temperature for 12 hours. Then the mixture was quenched with saturated aq. NH_4Cl (50 mL) and extracted with CH_2Cl_2 (50 mL × 3). The combined organic layer was dried over Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by flash column chromatography (diluted with petroleum ether) on a silica gel to give the desired product (*E*)-1-bromo-2-(buta-1,3-dien-1-yl)benzene (2.8 g, 67% yield).

Step 3. The *n*-butyllithium (2.5 M in Hexane, 9.2 mL, 24 mmol) was added dropwise to a solution of (*E*)-1-bromo-2-(buta-1,3-dien-1-yl)benzene (2.8 g, 13.5 mmol) in THF (80 mL) at -78 °C. The mixture was stirred at 0 °C for 2 hours. After that, the *N*,*N*-dimethylformamide (3.1 mL, 40 mmol) was added dropwise to the solution and stirred at -78 °C for additional 30 minutes. The reaction mixture was quenched by saturated aq. NH_4Cl (50 mL). The mixture was extracted with CH_2Cl_2 and dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by flash column chromatography (deluted with petroleum ether/ethyl acetate = 50/1 to 30/1) on a silica gel to afford (*E*)-2-(buta-1,3-dien-1-yl)benzaldehyde (1.3 g, 62% yield).

Step 4. (*E*)-2-(buta-1,3-dien-1-yl)benzaldehyde (1.3 g, 8.2 mmol) was dissolved in MeOH (50 mL). The reaction mixture was added $NaBH_4$ (0.5 g, 12.3 mmol) in portions at 0 °C and stirred at room temperature for 2 hours. The resulting mixture was quenched by saturated aq. NH_4Cl (20 mL). The solvent was evaporated under reduced pressure and the residue was extracted by CH_2Cl_2 (50 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 (deluted with petroleum ether/ethyl acetate = 5/1) on a silica gel to afford (*E*)-(2-(buta-1,3-dien-1-yl)phenyl)methanol *E*-**1a** (1.1 g, 83% yield).

General Procedure E. Synthesis of dienol substrate **1r**.

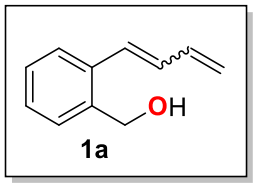


Step 1. A solution of (*E*)-3-(2-(((tert-butyldimethylsilyl)oxy)methyl)phenyl)acrylaldehyde (2.7 g, 10 mmol) in CH_2Cl_2 (50 mL) was treated with ethyl 2-(triphenyl-l5-phosphaneylidene)acetate (4.2 g, 12 mmol). The reaction mixture was stirred at room temperature for 16 hours. After evaporation of the solvent under reduced pressure, the residue was treated with Hexanes / Et_2O (9:1, 100 mL) and stirred for 15 minutes. The solvent was removed under reduced pressure, the residue was purified by flash chromatography (deluted with petroleum ether/ethyl acetate = 100/1 to 20/1) on a silica gel to afford ethyl (*2E,4E*)-5-(2-(((tert-butyldimethylsilyl)oxy)methyl)phenyl)penta-2,4-dienoate (2.3 g, 66% yield).

Step 2. Ethyl (*2E,4E*)-5-(2-(((tert-butyldimethylsilyl)oxy)methyl)phenyl)penta-2,4-dienoate was dissolved in THF (30 mL), the above solution was added TBAF (1.0 mol/L in THF, 8.0 mL) at room temperature and stirred for 2 hours. The reaction mixture was extracted with EtOAc (20 mL × 3) and dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by flash chromatography (deluted with petroleum ether/ethyl acetate = 20/1 to 5/1) on a silica gel to afford ethyl (2*E*,4*E*)-5-(2-(hydroxymethyl)phenyl)penta-2,4-dienoate **1r** (1.2 g, 79% yield).

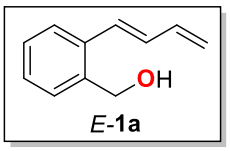
3.2. Characterization Data of Substrates

(2-(buta-1,3-dien-1-yl)phenyl)methanol (1a)



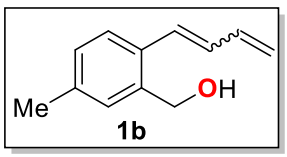
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 4.3 g, 88% yield, (*E* / *Z* = 1 : 3.5). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55-7.57 (m, 0.22H), 7.40-7.43 (m, 0.78H), 7.22-7.35 (m, 3H), 6.33-6.91 (m, 3H), 5.33-5.38 (m, 1H), 5.17-5.21 (m, 1H), 4.74 (s, 0.47H), 4.65 (s, 1.53H), 1.80 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.8, 137.8, 137.4, 136.0, 135.7, 133.2, 132.3, 132.0, 130.1, 129.4, 128.7, 128.34, 128.33, 127.9, 127.8, 127.7, 127.5, 125.9, 119.8, 118.3, 63.6, 63.5; **HRMS** (ESI) calcd for $C_{11}H_{13}O$ $[M+H]^+$: 161.0966, found: 161.0963.

(*E*)-(2-(buta-1,3-dien-1-yl)phenyl)methanol (*E*-1a)



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 1.1 g, 83% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48-7.49 (m, 1H), 7.13-7.47 (m, 3H), 6.77 (d, *J* = 15.6 Hz, 1H), 6.66 (dd, *J* = 15.2 Hz, 10.0 Hz, 1H), 6.44-6.53 (m, 1H), 5.30 (d, *J* = 16.8 Hz, 1H), 5.15-5.17 (m, 1H), 4.55 (d, *J* = 2.4 Hz, 2H), 2.98 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.7, 137.4, 135.6, 131.6, 129.3, 128.4, 127.9, 127.6, 125.5, 118.0, 62.8; **HRMS** (ESI) calcd for $C_{11}H_{13}O$ $[M+H]^+$: 161.0966, found: 161.0957.

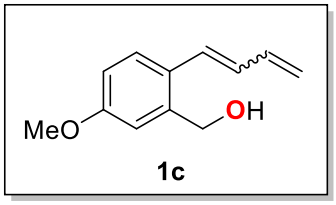
(2-(buta-1,3-dien-1-yl)-5-methylphenyl)methanol (1b)



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 1.8 g, 87% yield, (*E* / *Z* > 20 : 1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.5 Hz, 1H), 7.09-7.16 (m, 2H), 6.87 (d, *J* = 15.5 Hz, 1H), 6.68-6.74 (m, 1H), 6.50-6.57 (m, 1H), 5.31-5.34 (m, 1H), 5.16-5.18 (m, 1H), 4.71 (s, 2H), 2.34 (s, 3H), 1.67 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 137.8, 137.63, 137.55,

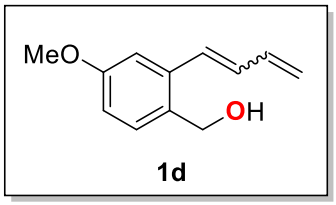
133.1, 131.2, 129.5, 129.3, 129.1, 125.8, 117.8, 63.6, 21.3; **HRMS** (ESI) calcd for $C_{12}H_{15}O$ $[M+H]^+$: 175.1117, found: 175.1117.

(2-(buta-1,3-dien-1-yl)-5-methoxyphenyl)methanol (1c)



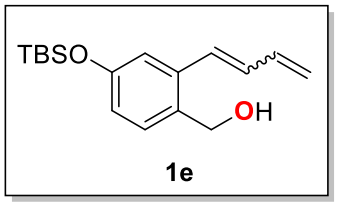
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 1.5 g, 82% yield, (*E* / *Z* = 1 : 2). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.17-7.47 (m, 1H), 6.99 (d, *J* = 3.0 Hz, 0.67H), 6.91 (d, *J* = 2.5 Hz, 0.33H), 6.60-6.81 (m, 2H), 6.25-6.59 (m, 2H), 5.27-5.34 (m, 1H), 5.12-5.16 (m, 1H), 5.36-5.41 (m, 1H), 4.68 (s, 0.65H), 4.60 (s, 1.35H), 3.78-3.79 (m, 3H), 2.16 (br, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 159.4, 159.2, 140.4, 139.4, 137.6, 133.4, 131.4, 131.2, 130.1, 128.9, 128.2, 127.84, 127.80, 127.1, 119.2, 117.1, 113.7, 113.5, 113.0, 112.6, 63.2, 55.4; **HRMS** (ESI) calcd for $C_{12}H_{15}O_2$ $[M+H]^+$: 191.1067, found: 191.1068.

(2-(buta-1,3-dien-1-yl)-4-methoxyphenyl)methanol (1d)



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 1.3 g, 72% yield, (*E* / *Z* = 1 : 2.2). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.21-7.30 (m, 1H), 6.78-7.08 (m, 2H), 6.62-6.77 (m, 1H), 6.32-6.61 (m, 2H), 5.34-5.38 (m, 1H), 5.17-5.22 (m, 1H), 4.65 (s, 0.69H), 4.56 (s, 1.31H), 3.80-3.82 (m, 3H), 1.81-1.86 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 159.6, 158.9, 137.5, 137.33, 137.27, 133.1, 132.3, 132.0, 131.3, 130.6, 130.6, 129.7, 129.4, 128.3, 120.0, 118.5, 115.8, 113.3, 112.7, 111.0, 63.09, 63.06, 55.43, 55.41; **HRMS** (ESI) calcd for $C_{12}H_{15}O_2$ $[M+H]^+$: 191.1067, found: 191.1066.

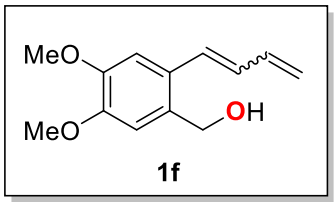
(2-(buta-1,3-dien-1-yl)-4-((tert-butyldimethylsilyl)oxy)phenyl)methanol (1e)



1e

The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 2.4 g, 82% yield, (*E* / *Z* = 1 : 1.9). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.95-7.05 (m, 1H), 6.54-6.83 (m, 2H), 6.10-6.52 (m, 3H), 5.14-5.18 (m, 1H), 4.98-5.01 (m, 1H), 4.42 (s, 0.70H), 4.33 (s, 1.30H), 1.94 (br, 1H), 0.80-0.81 (m, 9H), 0.01-0.02 (m, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.6, 154.9, 137.4, 137.3, 137.1, 133.1, 132.0, 131.8, 131.7, 131.1, 130.3, 129.5, 129.4, 128.3, 121.6, 119.6, 119.3, 119.1, 118.2, 117.1, 62.91, 62.89, 25.7, 18.3, -4.3, -4.4; **HRMS** (ESI) calcd for $C_{17}H_{27}O_2Si$ $[M+H]^+$: 291.1775, found: 291.1773.

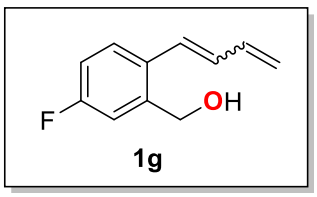
(2-(buta-1,3-dien-1-yl)-4,5-dimethoxyphenyl)methanol (1f)



1f

The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 1.6 g, 85% yield, (*E* / *Z* = 1 : 19). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.01 (s, 1H), 6.87 (S, 1H), 6.54-6.66 (m, 2H), 6.34 (t, *J* = 11.2 Hz, 1H), 5.34-5.38 (m, 1H), 5.18-5.21 (m, 1H), 4.71 (s, 0.10H), 4.60 (s, 1.90H), 3.90 (s, 3H), 3.87 (m, 3H), 1.77 (br, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.4, 147.9, 133.2, 131.7, 131.5, 128.2, 128.1, 119.6, 113.2, 111.4, 63.1, 56.2, 56.0; **HRMS** (ESI) calcd for $C_{13}H_{17}O_3$ $[M+H]^+$: 221.1172, found: 221.1173.

(2-(buta-1,3-dien-1-yl)-5-fluorophenyl)methanol (1g)

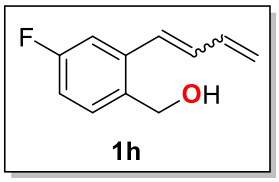


1g

The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 2.5 g, 82% yield, (*E* / *Z* = 1 : 2.6). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.09-7.50 (m, 2H), 6.92-6.98 (m, 1H), 6.30-6.79 (m, 3H), 5.32-5.39 (m, 1H), 5.18-5.21 (m, 1H), 4.71 (s, 0.55H), 4.62 (s, 1.45H), 2.04 (br, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.7 (d, $J_{C\text{-}F}$ = 246 Hz), 163.6 (d, $J_{C\text{-}F}$ = 245 Hz), 141.3 (d, $J_{C\text{-}F}$ = 7 Hz), 140.1 (d, $J_{C\text{-}F}$ = 7 Hz), 137.2, 132.9, 132.5, 131.8 (d, $J_{C\text{-}F}$ = 2 Hz), 131.6 (d, $J_{C\text{-}F}$ = 8 Hz), 131.1 (d, $J_{C\text{-}F}$ = 3 Hz), 128.1, 127.6 (d, $J_{C\text{-}}$

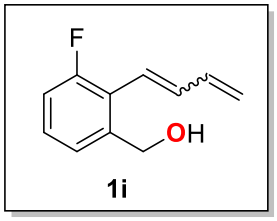
$_F$ = 8 Hz), 127.1, 120.1, 118.4, 115.0 (d, J_{C-F} = 13 Hz), 114.7 (d, J_{C-F} = 14 Hz), 114.3, 114.0, 113.8, 62.73, 62.72; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.0, -114.2; **HRMS** (ESI) calcd for $C_{11}H_{12}FO$ $[M+H]^+$: 179.0867, found: 179.0863.

(2-(buta-1,3-dien-1-yl)-4-fluorophenyl)methanol (1h)



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 2.3 g, 78% yield, (*E* / *Z* = 1 : 1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 9.0 Hz, 6.0 Hz, 0.49H), 7.11-7.22 (m, 1.51H), 6.94-6.98 (m, 1H), 6.62-6.76 (m, 1H), 6.32-6.56 (m, 2H), 5.33-5.39 (m, 1H), 5.18-5.21 (m, 1H), 4.74 (s, 1H), 4.64 (s, 1H), 1.86 (br, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.5 (d, J_{C-F} = 246 Hz), 163.4 (d, J_{C-F} = 245 Hz), 141.4 (d, J_{C-F} = 7 Hz), 140.1 (d, J_{C-F} = 7 Hz), 137.2, 132.9, 132.5, 131.9, 131.6 (d, J_{C-F} = 4 Hz), 131.6 (d, J_{C-F} = 8 Hz), 131.1 (d, J_{C-F} = 3 Hz), 128.1, 127.6 (d, J_{C-F} = 8 Hz), 127.2, 120.1, 118.4, 115.0 (d, J_{C-F} = 16 Hz), 114.8 (d, J_{C-F} = 17 Hz), 114.3 (d, J_{C-F} = 22 Hz), 114.1 (d, J_{C-F} = 21 Hz), 62.8; **^{19}F NMR** (470 MHz, $CDCl_3$) δ -114.0, -114.3; **HRMS** (ESI) calcd for $C_{11}H_{12}FO$ $[M+H]^+$: 179.0867, found: 179.0865.

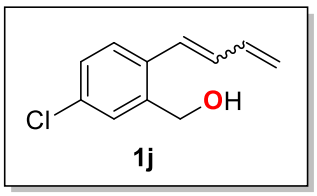
(2-(buta-1,3-dien-1-yl)-3-fluorophenyl)methanol (1i)



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 1.3 g, 80% yield, (*E* / *Z* = 1.6 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14-7.30 (m, 2H), 6.98-7.05 (m, 1H), 6.63-6.92 (m, 1H), 6.16-6.59 (m, 2H), 5.34-5.39 (m, 1H), 5.18-5.25 (m, 1H), 4.72 (s, 1.23H), 4.60 (s, 0.77H), 2.00 (br, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.3 (d, J_{C-F} = 248 Hz), 160.8 (d, J_{C-F} = 244 Hz), 141.4 (d, J_{C-F} = 3 Hz), 140.4 (d, J_{C-F} = 3 Hz), 138.0, 136.9 (d, J_{C-F} = 10 Hz), 134.7 (d, J_{C-F} = 1 Hz), 133.3 (d, J_{C-F} = 2 Hz), 129.0 (d, J_{C-F} = 9 Hz), 128.3 (d, J_{C-F} = 9 Hz), 124.1 (d, J_{C-F} = 3 Hz), 123.8 (d, J_{C-F} = 12 Hz), 123.3, 123.2 (d, J_{C-F} = 17 Hz), 123.0 (d, J_{C-F} = 3 Hz), 121.2, 120.3, 119.0, 115.7 (d, J_{C-F} = 23 Hz), 114.9 (d,

$J_{C\text{-}F}$ = 23 Hz), 63.3 (d, $J_{C\text{-}F}$ = 3 Hz), 62.9 (d, $J_{C\text{-}F}$ = 3 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.5, -113.8; **HRMS** (ESI) calcd for $C_{11}H_{12}FO$ $[M+H]^+$: 179.0867, found: 179.0867.

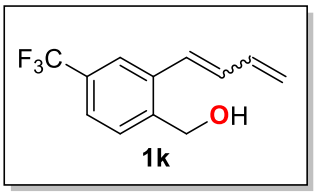
(2-(buta-1,3-dien-1-yl)-5-chlorophenyl)methanol (1j)



1j

The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 2.2 g, 83% yield, (*E* / *Z* = 1 : 2.8). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41-7.44 (m, 1H), 7.15-7.33 (m, 2H), 6.51-6.73 (m, 1H), 6.30-6.50 (m, 2H), 5.33-5.38 (m, 1H), 5.18-5.22 (m, 1H), 4.65 (s, 0.52H), 4.56 (s, 1.48H), 2.49-2.54 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 140.6, 139.4, 137.1, 134.0, 133.6, 133.4, 132.8, 132.7, 132.3, 131.2, 128.02, 127.99, 127.3, 127.2, 127.0, 126.9, 120.4, 118.8, 62.6, 62.5; **HRMS** (ESI) calcd for $C_{11}H_{12}ClO$ $[M+H]^+$: 195.0571, found: 195.0572.

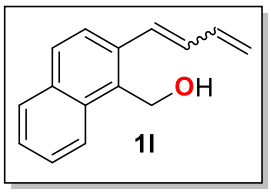
(2-(buta-1,3-dien-1-yl)-4-(trifluoromethyl)phenyl)methanol (1k)



1k

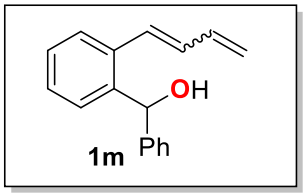
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 1.8 g, 81% yield, (*E* / *Z* = 1 : 4.7). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46-7.76 (m, 3H), 6.38-6.79 (m, 3H), 5.40-5.44 (m, 1H), 5.24-5.28 (m, 1H), 4.78 (s, 0.34H), 4.69 (s, 1.66H), 2.13 (br, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 142.6, 141.2, 136.8, 136.4, 135.9, 133.6, 133.5, 132.4, 130.0 (q, $J_{C\text{-}F}$ = 32 Hz), 128.4, 127.7, 127.5, 126.6 (d, $J_{C\text{-}F}$ = 4 Hz), 125.3 (q, $J_{C\text{-}F}$ = 270 Hz), 124.4 (q, $J_{C\text{-}F}$ = 4 Hz), 124.2 (q, $J_{C\text{-}F}$ = 4 Hz), 122.6 (d, $J_{C\text{-}F}$ = 4 Hz), 121.3, 121.0, 119.8, 62.8, 62.7; **^{19}F NMR** (470 MHz, $CDCl_3$) δ -62.5, -62.6; **HRMS** (ESI) calcd for $C_{12}H_{12}F_3O$ $[M+H]^+$: 229.0835, found: 229.0833.

(2-(buta-1,3-dien-1-yl)naphthalen-1-yl)methanol (1l)



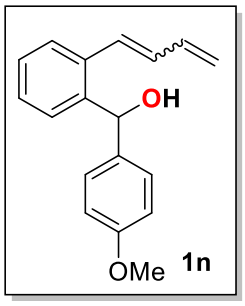
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 1.0 g, 80% yield, (*E* / *Z* = 1 : 1.9). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.16-8.17 (d, *J* = 8.5 Hz, 0.65H), 8.11-8.12 (d, *J* = 8.5 Hz, 0.35H), 7.70-7.80 (m, 2H), 7.31-7.62 (m, 3H), 6.51-7.20 (m, 2H), 6.36-6.49 (m, 1H), 5.33-5.39 (m, 1H), 5.14-5.23 (m, 1H), 5.07 (s, 0.70H), 5.01 (d, *J* = 3.5 Hz, 1.30H), 2.03-2.10 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 137.5, 134.5, 134.1, 133.3, 133.25, 133.16. 133.1, 132.7, 132.5, 132.4, 132.2, 130.0, 129.5, 128.9, 128.5, 128.3, 128.0, 127.0, 126.8, 125.8, 124.3, 124.2, 123.9, 120.0, 118.6, 59.1, 57.6; **HRMS** (ESI) calcd for $C_{15}H_{15}O$ $[M+H]^+$: 211.1117, found: 211.1117.

(2-(buta-1,3-dien-1-yl)phenyl)(phenyl)methanol (1m)



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 3.4 g, 71% yield, (*E* / *Z* = 10.1 : 1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45-7.47 (m, 1H), 7.34-7.36 (m, 1H), 7.22-7.27 (m, 4H), 7.15-7.21 (m, 3H), 6.79 (d, *J* = 15.5 Hz, 1H), 6.37-6.61 (m, 2H), 5.96 (d, *J* = 2.0 Hz, 0.91H), 5.87 (d, *J* = 1.5 Hz, 0.09H), 5.25-5.30 (m, 1H), 5.09-5.14 (m, 1H), 2.58-2.67 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.0, 140.6, 137.3, 135.4, 132.0, 129.8, 128.5, 127.8, 127.8, 127.5, 127.1, 126.9, 126.1, 118.1, 72.8; **HRMS** (ESI) calcd for $C_{17}H_{17}O$ $[M+H]^+$: 237.1274, found: 237.1274.

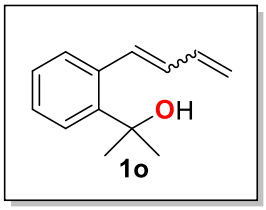
(2-(buta-1,3-dien-1-yl)phenyl)(4-methoxyphenyl)methanol (1n)



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 2.3 g, 76% yield, (*E* / *Z* = 9.0 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43-7.55 (m, 2H), 7.11-7.32 (m, 4H), 6.72-6.84 (m, 3H), 6.21-6.65 (m, 2H), 6.01 (s, 0.90H), 5.89 (s, 0.10H), 5.26-5.32 (m, 1H), 5.11-5.16 (m, 1H), 3,74-3.75 (m, 3H), 2.37 (s, 1H); **^{13}C NMR**

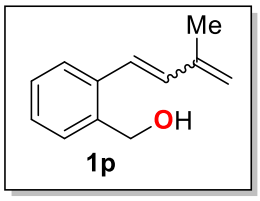
(100 MHz, $CDCl_3$) δ 159.0, 140.8, 137.4, 135.3, 132.0, 129.8, 128.3, 127.9, 127.8, 126.8, 126.1, 118.1, 113.9, 72.6, 55.3; **HRMS** (ESI) calcd for $C_{18}H_{18}O_2Na$ $[M+Na]^+$: 289.1204, found: 289.1205.

2-(2-(buta-1,3-dien-1-yl)phenyl)propan-2-ol (1o)



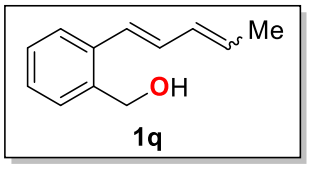
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 2.0 g, 52% yield, (*E*/ *Z* = 1 : 2.3). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26-7.58 (m, 2H), 7.01-7.25 (m, 3H), 6.27-6.62 (m, 2H), 5.29-5.35 (m, 1H), 5.11-5.17 (m, 1H), 1.84-2.03 (m, 1H), 1.66 (s, 1.80H), 1.61 (s, 4.20H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.3, 144.9, 137.8, 136.5, 135.2, 133.9, 133.6, 132.6, 132.3, 131.1, 130.6, 128.3, 127.52, 127.46, 126.7, 125.3, 125.2, 119.0, 117.4, 73.8, 31.5, 31.0; **HRMS** (ESI) calcd for $C_{13}H_{17}O$ $[M+H]^+$: 189.1279, found: 189.1260.

(2-(3-methylbuta-1,3-dien-1-yl)phenyl)methanol (1p)



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 1.2 g, 78% yield, (*E*/ *Z* = 1 : 2.0). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11-7.59 (m, 4H), 6.26-6.86 (m, 2H), 4.93-5.13 (m, 2H), 4.73 (s, 0.66H), 4.62 (s, 1.34H), 2.08 (br, 1H), 1.98-1.99 (m, 1H), 1.50-1.51 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.3, 141.9, 138.4, 137.8, 137.0, 136.3, 134.2, 129.6, 128.5, 128.2, 127.6, 127.5, 127.4, 127.24, 127.17, 125.9, 125.3, 118.7, 117.9, 63.50, 63.46, 22.0, 18.7; **HRMS** (ESI) calcd for $C_{12}H_{15}O$ $[M+H]^+$: 175.1117, found: 175.1118.

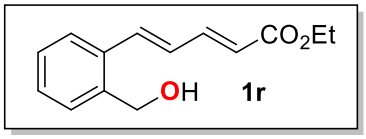
(2-((1*E*)-penta-1,3-dien-1-yl)phenyl)methanol (1q)



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 0.8 g, 73% yield, (*EE* / *EZ* = 1 : 6.1). **^{1}H NMR**

(400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.2 Hz, 0.14H), 7.51 (dd, *J* = 8.0 Hz, 1.2 Hz, 0.86H), 7.15-7.31 (m, 3H), 6.63-7.06 (m, 2H), 6.18-6.28 (m, 1H), 5.57-5.87 (m, 1H), 4.66-4.67 (m, 2H), 2.12 (br, 1H), 1.80-1.86 (m, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 137.6, 137.5, 136.52, 136.46, 132.2, 131.7, 131.0, 129.9, 128.59, 128.57, 128.3, 128.2, 127.8, 127.6, 127.3, 126.6, 126.2, 125.8, 125.6, 63.53, 63.49, 18.5, 13.8; **HRMS** (ESI) calcd for $C_{12}H_{14}ONa$ $[M+Na]^+$: 197.0942, found: 197.0953.

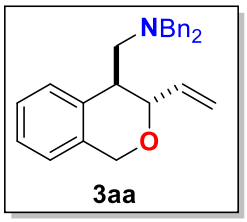
ethyl (*2E*,*4E*)-5-(2-(hydroxymethyl)phenyl)penta-2,4-dienoate (1r)



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 1.2 g, 79% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57-7.59 (m, 1H), 7.42-7.48 (M, 0.86H), 7.15-7.31 (m, 1H), 7.35-7.38 (m, 1H), 7.22-7.30 (m, 3H), 6.77-6.84 (m, 1H), 5.98 (dd, *J* = 15.6 Hz, 0.8 Hz, 1H), 4.73 (s, 2H), 4.17-4.23 (m, 2H), 2.50 (s, 1H), 1.32 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.2, 144.8, 138.6, 137.1, 134.8, 129.0, 128.8, 128.2, 128.1, 126.1, 121.6, 63.1, 60.5, 14.4; **HRMS** (ESI) calcd for $C_{14}H_{16}O_3Na$ $[M+Na]^+$: 255.0997, found: 255.1000.

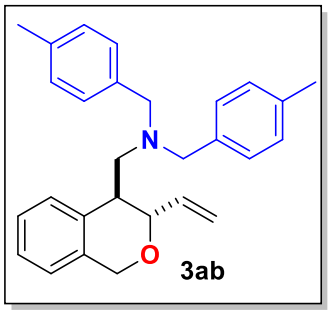
4. Experimental Characterization Data for Products

***Trans*-*N*,*N*-dibenzyl-1-(3-vinylisochroman-4-yl)methanamine (3aa)**



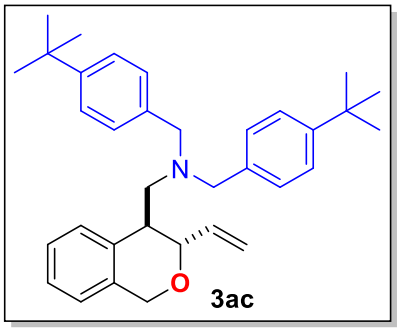
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 95 mg, 86% yield, > 20:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.12-7.33 (m, 13H), 6.88-6.90 (m, 1H), 5.89-5.97 (m, 1H), 5.14-5.23 (m, 2H), 4.74 (d, *J* = 15.2 Hz, 1H), 4.65-4.66 (m, 1H), 4.57 (d, *J* = 15.2 Hz, 1H), 3.71 (d, *J* = 13.6 Hz, 2H), 3.61 (d, *J* = 13.6 Hz, 2H), 2.79-2.92 (m, 2H), 2.60 (dd, *J* = 12.4 Hz, 4.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.4, 137.0, 134.9, 134.6, 129.4, 129.1, 128.3, 127.0, 126.4, 126.2, 124.0, 117.8, 74.4, 63.4, 59.8, 59.2, 39.8; **HRMS** (ESI) calcd for $C_{26}H_{28}NO$ $[M+H]^+$: 370.2165, found: 370.2161.

***Trans*-*N*,*N*-bis(4-methylbenzyl)-1-(3-vinylisochroman-4-yl)methanamine (3ab)**



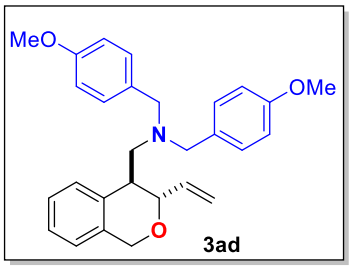
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 107 mg, 90% yield, > 20:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.09-7.23 (m, 11H), 6.91 (d, *J* = 6.8 Hz, 1H), 5.90-5.99 (m, 1H), 5.14-5.24 (m, 2H), 4.76 (d, *J* = 15.2 Hz, 1H), 4.66-4.67 (m, 1H), 4.59 (d, *J* = 15.2 Hz, 1H), 3.66 (d, *J* = 13.6 Hz, 2H), 3.56 (d, *J* = 13.6 Hz, 2H), 2.80-2.90 (m, 2H), 2.58 (dd, *J* = 11.6 Hz, 3.6 Hz, 1H), 2.32 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.1, 136.5, 136.3, 135.1, 134.6, 129.5, 129.0, 126.5, 126.1, 124.0, 117.7, 74.5, 63.5, 59.7, 58.7, 39.7, 21.2; **HRMS** (ESI) calcd for $C_{28}H_{32}NO$ $[M+H]^+$: 398.2478, found: 398.2472.

***Trans*-*N*,*N*-bis(4-(tert-butyl)benzyl)-1-(3-vinylisochroman-4-yl)methanamine (3ac)**



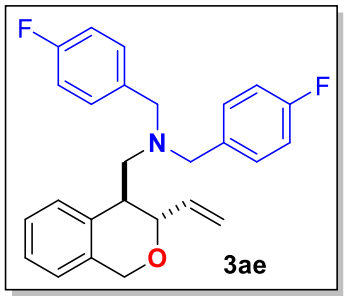
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 136 mg, 94% yield, > 20:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24-7.32 (m, 8H), 7.09-7.20 (m, 3H), 6.88-6.90 (m, 1H), 5.87-5.96 (m, 1H), 5.11-5.20 (m, 2H), 4.75 (d, *J* = 15.2 Hz, 1H), 4.69-4.70 (m, 1H), 4.58 (d, *J* = 15.2 Hz, 1H), 3.65 (d, *J* = 14.0 Hz, 2H), 3.61 (d, *J* = 14.0 Hz, 2H), 2.80-2.91 (m, 2H), 2.61 (dd, *J* = 12.0 Hz, 4.4 Hz, 1H), 1.30 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.8, 137.1, 136.4, 135.2, 134.6, 129.5, 128.7, 126.4, 126.1, 125.2, 124.0, 117.7, 74.6, 63.6, 59.9, 58.8, 39.8, 34.6, 31.6; **HRMS** (ESI) calcd for $C_{34}H_{44}NO$ $[M+H]^+$: 482.3417, found: 482.3408.

***Trans*-*N*,*N*-bis(4-methoxybenzyl)-1-(3-vinylisochroman-4-yl)methanamine (3ad)**



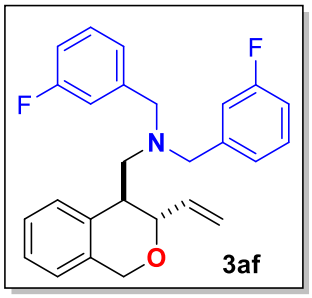
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 82 mg, 64% yield, > 20:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21-7.23 (m, 4H), 7.10-7.18 (m, 3H), 6.82-6.91 (m, 5H), 5.90-5.99 (m, 1H), 5.15-5.24 (m, 2H), 4.75 (d, *J* = 15.2 Hz, 1H), 4.63-4.65 (m, 1H), 4.59 (d, *J* = 15.2 Hz, 1H), 3.78 (s, 6H), 3.62 (d, *J* = 13.6 Hz, 2H), 3.53 (d, *J* = 13.6 Hz, 2H), 2.78-2.88 (m, 2H), 2.57 (dd, *J* = 11.6 Hz, 4.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.7, 137.1, 135.1, 134.6, 131.4, 130.1, 129.4, 126.4, 126.1, 124.0, 117.7, 113.7, 74.5, 63.5, 59.6, 58.3, 55.3, 39.7; **HRMS** (ESI) calcd for $C_{28}H_{32}NO_3$ $[M+H]^+$: 430.2382, found: 430.2385.

***Trans*-*N*,*N*-bis(4-fluorobenzyl)-1-(3-vinylisochroman-4-yl)methanamine (3ae)**



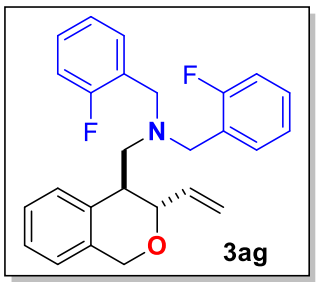
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 92 mg, 76% yield, > 20:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23-7.26 (m, 4H), 7.11-7.14 (m, 3H), 6.90-6.99 (m, 5H), 5.88-5.96 (m, 1H), 5.15-5.24 (m, 2H), 4.75 (d, *J* = 15.2 Hz, 1H), 4.61-4.62 (m, 1H), 4.57 (d, *J* = 15.2 Hz, 1H), 3.64 (d, *J* = 13.6 Hz, 2H), 3.55 (d, *J* = 13.6 Hz, 2H), 2.78-2.88 (m, 2H), 2.57 (dd, *J* = 12.0 Hz, 4.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.3 (d, $J_{C\text{-}F}$ = 243 Hz), 136.8, 134.92, 134.88, 134.7 (d, $J_{C\text{-}F}$ = 15 Hz), 130.4 (d, $J_{C\text{-}F}$ = 8 Hz), 129.4, 126.5, 126.3, 124.1, 118.0, 115.3 (d, $J_{C\text{-}F}$ = 21 Hz), 74.2, 63.3, 59.6, 58.4, 39.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.7; **HRMS** (ESI) calcd for $C_{26}H_{26}F_2NO$ $[M+H]^+$: 406.1977, found: 406.1968.

***Trans*-*N*,*N*-bis(3-fluorobenzyl)-1-(3-vinylisochroman-4-yl)methanamine (3af)**



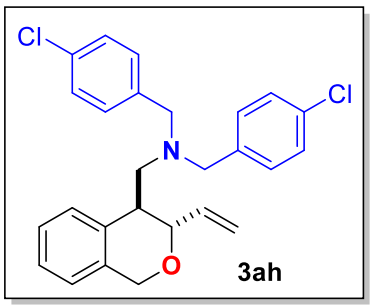
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 89 mg, 73% yield, > 20:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22-7.27 (m, 2H), 7.15-7.18 (m, 3H), 7.01-7.08 (m, 4H), 6.91 (s, 3H), 5.88-6.00 (m, 1H), 5.16-5.25 (m, 2H), 4.75 (d, *J* = 15.2 Hz, 1H), 4.62-4.63 (m, 1H), 4.58 (d, *J* = 15.2 Hz, 1H), 3.68 (d, *J* = 14.0 Hz, 2H), 3.61 (d, *J* = 14.0 Hz, 2H), 2.79-2. 91 (m, 2H), 2.61 (dd, *J* = 12.4 Hz, 4.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.3 (d, $J_{C\text{-}F}$ = 244 Hz), 141.9 (d, $J_{C\text{-}F}$ = 7 Hz), 136.7, 134.6, 134.5, 129.9 (d, $J_{C\text{-}F}$ = 8 Hz), 129.4, 126.5, 126.4, 124.5 (d, $J_{C\text{-}F}$ = 3 Hz), 124.1, 118.2, 115.8 (d, $J_{C\text{-}F}$ = 21 Hz), 114.2 (d, $J_{C\text{-}F}$ = 21 Hz), 74.3, 63.3, 59.9, 58.8, 39.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.8; **HRMS** (ESI) calcd for $C_{26}H_{26}F_2NO$ $[M+H]^+$: 406.1977, found: 406.1976.

***Trans*-*N*,*N*-bis(2-fluorobenzyl)-1-(3-vinylisochroman-4-yl)methanamine (3ag)**



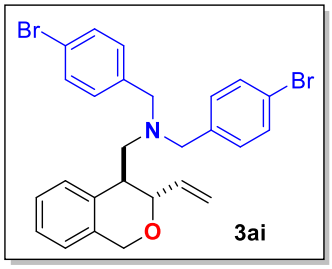
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 92 mg, 76% yield, > 20:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (t, *J* = 7.6 Hz, 2H), 6.97-7.20 (m, 9H), 6.90-6.91 (m, 1H), 5.87-5.96 (m, 1H), 5.13-5.23 (m, 2H), 4.75 (d, *J* = 15.6 Hz, 1H), 4.64-4.65 (m, 1H), 4.57 (d, *J* = 15.6 Hz, 1H), 3.80 (d, *J* = 14.0 Hz, 2H), 3.72 (d, *J* = 14.0 Hz, 2H), 2.80-2. 92 (m, 2H), 2.63 (dd, *J* = 12.0 Hz, 4.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.7 (d, J_{C-F} = 245 Hz), 136.9, 134.8 (d, J_{C-F} = 21 Hz), 131.4 (d, J_{C-F} = 5 Hz), 129.5, 128.76, 128.68, 126.5, 126.2, 126.0 (d, J_{C-F} = 14 Hz), 124.0, 123.98, 117.9, 115.4 (d, J_{C-F} = 22 Hz), 74.2, 63.3, 59.6, 52.0 (d, J_{C-F} = 1 Hz), 39.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.8; **HRMS** (ESI) calcd for $C_{26}H_{26}F_2NO$ $[M+H]^+$: 406.1977, found: 406.1968.

***Trans*-*N*,*N*-bis(4-chlorobenzyl)-1-(3-vinylisochroman-4-yl)methanamine (3ah)**



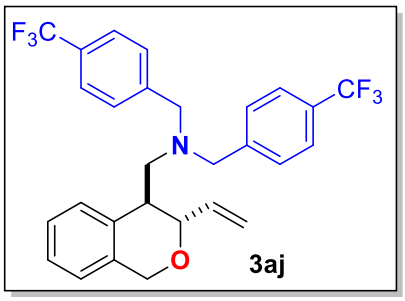
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 108 mg, 82% yield, > 20:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11-7.26 (m, 11H), 6.90-6.92 (m, 1H), 5.88-5.96 (m, 1H), 5.16-5.24 (m, 2H), 4.75 (d, *J* = 15.6 Hz, 1H), 4.61-4.63 (m, 1H), 4.58 (d, *J* = 15.2 Hz, 1H), 3.64 (d, *J* = 14.0 Hz, 2H), 3.55 (d, *J* = 14.0 Hz, 2H), 2.79-2.88 (m, 2H), 2.57 (dd, *J* = 11.2 Hz, 3.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.6, 136.7, 134.54, 134.52, 132.8, 130.2, 129.4, 128.5, 126.44, 126.35, 124.1, 118.2, 74.2, 63.2, 59.7, 58.4, 39.6; **HRMS** (ESI) calcd for $C_{26}H_{26}Cl_2NO$ $[M+H]^+$: 438.1386, found: 438.1379.

***Trans*-*N*,*N*-bis(4-bromobenzyl)-1-(3-vinylisochroman-4-yl)methanamine (3ai)**



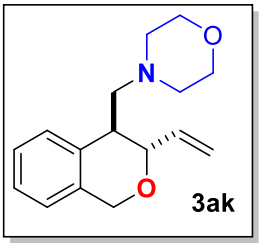
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 95 mg, 60% yield, > 20:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39-7.42 (m, 4H), 7.14-7.16 (m, 7H), 6.90-6.93 (m, 1H), 5.88-5.97 (m, 1H), 5.16-5.25 (m, 2H), 4.76 (d, *J* = 15.2 Hz, 1H), 4.61-4.63 (m, 1H), 4.59 (d, *J* = 15.6 Hz, 1H), 3.63 (d, *J* = 14.0 Hz, 2H), 3.54 (d, *J* = 14.0 Hz, 2H), 2.79-2.87 (m, 2H), 2.58 (dd, *J* = 10.4 Hz, 3.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.1, 136.7, 134.5, 131.5, 130.6, 129.4, 126.5, 126.4, 124.1, 120.9, 118.2, 74.2, 63.2, 59.7, 58.4, 39.6; **HRMS** (ESI) calcd for $C_{26}H_{26}Br_2NO$ $[M+H]^+$: 526.0376, found: 526.0373.

***Trans*-*N*,*N*-bis(4-(trifluoromethyl)benzyl)-1-(3-vinylisochroman-4-yl)methanamine (3aj)**



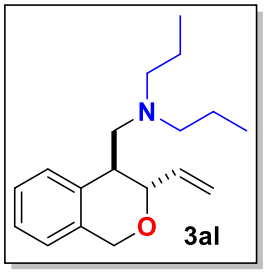
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 106 mg, 70% yield, > 20:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53-7.55 (m, 4H), 7.39-7.41 (m, 4H), 7.16-7.17 (m, 3H), 6.92-6.93, (m, 1H), 5.88-5.96 (m, 1H), 5.16-5.24 (m, 2H), 4.76 (d, *J* = 15.6 Hz, 1H), 4.66-4.67 (m, 1H), 4.57 (d, *J* = 15.6 Hz, 1H), 3.75 (d, *J* = 14.0 Hz, 2H), 3.69 (d, *J* = 14.4 Hz, 2H), 2.83-2.92 (m, 2H), 2.65 (dd, *J* = 12.0 Hz, 4.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.2, 136.5, 134.6, 134.4, 130.0, 129.7 (d, $J_{C\text{-}F}$ = 32 Hz), 129.5, 129.0, 128.4 (q, $J_{C\text{-}F}$ = 270 Hz), 126.5 (d, $J_{C\text{-}F}$ = 4 Hz), 125.5 (q, $J_{C\text{-}F}$ = 4 Hz), 124.2, 118.4, 74.2, 63.2, 60.0, 58.9, 39.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.4; **HRMS** (ESI) calcd for $C_{28}H_{26}F_6NO$ $[M+H]^+$: 506.1913, found: 506.1895.

***Trans*-4-((3-vinylisochroman-4-yl)methyl)morpholine (3ak)**



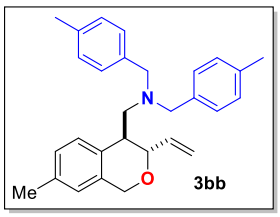
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 49 mg, 63% yield, > 20:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26-7.30 (m, 1H), 7.14-7.21 (m, 2H), 6.96-6.98 (m, 1H), 5.95-6.03 (m, 1H), 5.33 (dt, *J* = 18.8 Hz, 1.2 Hz, 1H), 5.25 (dt, *J* = 10.8 Hz, 1.6 Hz, 1H), 4.83 (d, *J* = 15.2 Hz, 1H), 4.73 (d, *J* = 15.6 Hz, 1H), 4.59-4.61 (m, 1H), 3.67-3.76 (m, 4H), 2.84-2.89 (m, 1H), 2.75 (dd, *J* = 12.4 Hz, 9.2 Hz, 1H), 2.38-2.55 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.9, 135.0, 134.6, 129.2, 126.7, 126.3, 124.1, 118.3, 74.6, 67.2, 63.9, 63.6, 54.1, 38.2; **HRMS** (ESI) calcd for $C_{16}H_{22}NO_2$ $[M+H]^+$: 260.1645, found: 260.1639.

***Trans*-*N*-propyl-*N*-((3-vinylisochroman-4-yl)methyl)propan-1-amine (3al)**



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 59 mg, 72% yield, > 20:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23-7.25 (m, 1H), 7.12-7.19 (m, 2H), 6.94-6.96 (m, 1H), 5.95-6.04 (m, 1H), 5.30 (dt, *J* = 17.6 Hz, 1.6 Hz, 1H), 5.21 (dt, *J* = 10.8 Hz, 1.6 Hz, 1H), 4.83 (d, *J* = 15.2 Hz, 1H), 4.67-4.71 (m, 2H), 2.73-2.81 (m, 2H), 2.34-2.50 (m, 5H), 1.42-1.51 (m, 4H), 0.86 (t, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.0, 135.2, 134.6, 129.5, 126.5, 126.1, 124.0, 118.0, 73.9, 63.2, 60.4, 56.9, 40.0, 20.6, 12.1; **HRMS** (ESI) calcd for $C_{18}H_{28}NO$ $[M+H]^+$: 274.2165, found: 274.2159.

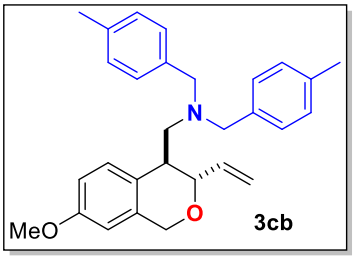
***Trans*-1-(7-methyl-3-vinylisochroman-4-yl)-*N*,*N*-bis(4-methylbenzyl)methanamine (3bb)**



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 106 mg, 86% yield, > 20:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17-7.21 (m, 4H), 7.04-7.10 (m, 5H), 6.94-6.96 (m,

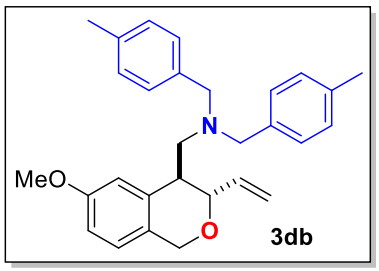
1H), 6.71 (s, 1H), 5.90-5.98 (m, 1H), 5.13-5.23 (m, 2H), 4.68-4.71 (m, 2H), 4.55 (d, *J* = 15.2 Hz, 1H), 3.66 (d, *J* = 13.6 Hz, 2H), 3.53 (d, *J* = 13.6 Hz, 2H), 2.76-2.89 (m, 2H), 2.54 (dd, *J* = 12.4 Hz, 4.4 Hz, 1H), 2.30 (s, 6H), 2.26 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.2, 136.4, 136.3, 135.6, 134.4, 132.0, 129.3, 129.01, 128.97, 127.3, 124.5, 117.6, 74.5, 63.5, 59.7, 58.6, 39.3, 21.22, 21.19; **HRMS** (ESI) calcd for $C_{29}H_{34}NO$ $[M+H]^+$: 412.2635, found: 412.2621.

***Trans*-1-(7-methoxy-3-vinylisochroman-4-yl)-*N*,*N*-bis(4-methylbenzyl)methanamine (3cb)**



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 105 mg, 82% yield, > 20:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19-7.21 (m, 4H), 7.09-7.10 (m, 5H), 6.73 (dd, *J* = 8.4 Hz, 2.8 Hz, 1H), 6.44 (d, *J* = 2.4 Hz, 1H), 5.89-5.98 (m, 1H), 5.14-5.24 (m, 2H), 4.72 (d, *J* = 15.2 Hz, 1H), 4.63-4.65 (m, 1H), 4.56 (d, *J* = 15.2 Hz, 1H), 3.73 (s, 3H), 3.65 (d, *J* = 13.6 Hz, 2H), 3.55 (d, *J* = 14.0 Hz, 2H), 2.86 (dd, *J* = 12.4 Hz, 9.2 Hz, 1H), 2.74-2.78 (m, 1H), 2.54 (dd, *J* = 12.0 Hz, 4.4 Hz, 1H), 2.31 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.9, 137.1, 136.4, 136.3, 135.7, 130.4, 128.99, 128.98, 127.2, 117.7, 113.0, 108.5, 74.7, 63.6, 59.7, 58.6, 55.3, 38.9, 21.2; **HRMS** (ESI) calcd for $C_{29}H_{34}NO_2$ $[M+H]^+$: 428.2584, found: 428.2575.

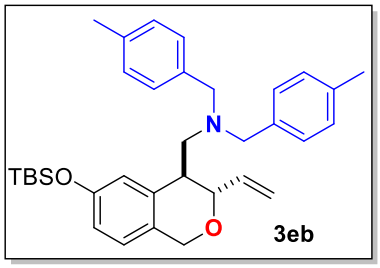
***Trans*-1-(6-methoxy-3-vinylisochroman-4-yl)-*N*,*N*-bis(4-methylbenzyl)methanamine (3db)**



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 94 mg, 73% yield, > 20:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20-7.22 (m, 4H), 7.09-7.10 (m, 4H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.67-6.72 (m, 2H), 5.90-5.98 (m, 1H), 5.13-5.24 (m, 2H), 4.70 (d, *J* = 14.4 Hz,

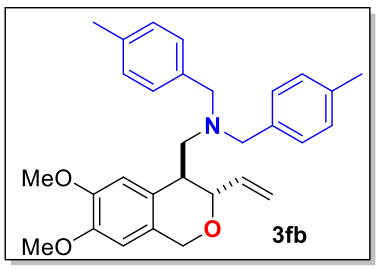
1H), 4.61-4.63 (m, 1H), 4.53 (d, *J* = 14.8 Hz, 1H), 3.75 (s, 3H), 3.65 (d, *J* = 13.6 Hz, 2H), 3.57 (d, *J* = 14.0 Hz, 2H), 2.90 (dd, *J* = 12.8 Hz, 9.2 Hz, 1H), 2.75-2.79 (m, 1H), 2.60 (dd, *J* = 12.4 Hz, 4.8 Hz, 1H), 2.31 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.1, 137.2, 136.5, 136.4, 136.2, 129.01, 128.99, 126.7, 125.0, 117.7, 114.2, 112.4, 74.4, 63.3, 59.6, 58.7, 55.3, 40.1, 21.2; **HRMS** (ESI) calcd for $C_{29}H_{34}NO_2$ $[M+H]^+$: 428.2590, found: 428.2590.

Trans-1-(6-((_tert_-butyldimethylsilyl)oxy)-3-vinylisochroman-4-yl)-_N_,_N_-bis(4-methylbenzyl)methanamine (3eb)



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 114 mg, 72% yield, > 20:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21-7.23 (m, 4H), 7.09-7.11 (m, 4H), 6.77 (d, *J* = 8.4 Hz, 1H), 6.68 (d, *J* = 2.4 Hz, 1H), 6.63 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 5.90-5.99 (m, 1H), 5.14-5.23 (m, 2H), 4.69 (d, *J* = 14.8 Hz, 1H), 4.60-4.62 (m, 1H), 4.54 (d, *J* = 14.8 Hz, 1H), 3.65 (d, *J* = 13.6 Hz, 2H), 3.57 (d, *J* = 12.4 Hz, 2H), 2.87 (dd, *J* = 12.4 Hz, 9.2 Hz, 1H), 2.71-2.75 (m, 1H), 2.56 (dd, *J* = 12.8 Hz, 4.8 Hz, 1H), 2.32 (m, 6H), 0.99 (s, 9H), 0.18 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.1, 137.3, 136.5, 136.4, 136.2, 129.1, 129.0, 127.4, 125.0, 120.6, 118.2, 117.6, 74.5, 63.6, 59.5, 58.7, 39.9, 25.9, 21.2, 18.4, -4.2, -4.3; **HRMS** (ESI) calcd for $C_{34}H_{46}NO_2Si$ $[M+H]^+$: 528.3298, found: 528.3299.

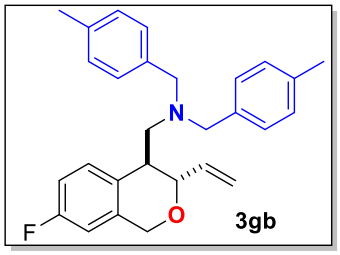
Trans-1-(6,7-dimethoxy-3-vinylisochroman-4-yl)-_N_,_N_-bis(4-methylbenzyl)methanamine (3fb)



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 107 mg, 78% yield, > 20:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21-7.23 (m, 4H), 7.09-7.11 (m, 4H), 6.67 (s, 1H), 6.39 (s,

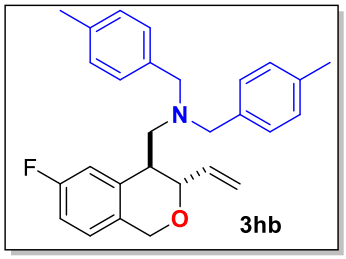
1H), 5.90-5.98 (m, 1H), 5.16-5.27 (m, 2H), 4.69 (d, *J* = 14.8 Hz, 1H), 4.59-4.61 (m, 1H), 4.54 (d, *J* = 14.4 Hz, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 3.57-3.65 (m, 4H), 2.87 (dd, *J* = 12.8 Hz, 8.8 Hz, 1H), 2.70-2.74 (m, 1H), 2.61 (dd, *J* = 12.8 Hz, 5.2 Hz, 1H), 2.31 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.7, 147.6, 137.1, 136.5, 136.2, 128.99, 128.95, 127.0, 126.4, 117.7, 112.1, 106.7, 74.7, 63.3, 59.5, 58.7, 56.0, 55.9, 39.4, 21.2; **HRMS** (ESI) calcd for $C_{30}H_{36}NO_3$ $[M+H]^+$: 458.2690, found: 458.2670.

***Trans*-1-(7-fluoro-3-vinylisochroman-4-yl)-*N*,*N*-bis(4-methylbenzyl)methanamine (3gb)**



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 112 mg, 90% yield, > 20:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14-7.20 (m, 5H), 7.09-7.12 (m, 4H), 6.85 (t, *J* = 8.0 Hz, 1H), 6.61 (d, *J* = 8.8 Hz, 1H), 5.86-5.94 (m, 1H), 5.15-5.22 (m, 2H), 4.70 (d, *J* = 15.6 Hz, 1H), 4.61-4.62 (m, 1H), 4.54 (d, *J* = 15.6 Hz, 1H), 3.54-3.62 (m, 4H), 2.75-2.84 (m, 2H), 2.47-2.56 (m, 1H), 2.31 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.4 (d, J_{C-F} = 243 Hz), 136.7, 136.55, 136.47, 136.4 136.2, 131.1 (d, J_{C-F} = 8 Hz), 130.7 (d, J_{C-F} = 3 Hz), 129.0 (d, J_{C-F} = 5 Hz), 118.0, 113.7 (d, J_{C-F} = 21 Hz), 110.6 (d, J_{C-F} = 21 Hz), 74.5, 63.3 (d, J_{C-F} = 2 Hz), 59.6, 58.8, 39.0, 21.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.4; **HRMS** (ESI) calcd for $C_{28}H_{31}FNO$ $[M+H]^+$: 416.2384, found: 416.2373.

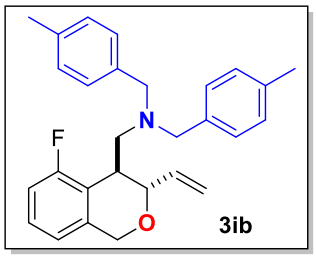
***Trans*-1-((6-fluoro-3-vinylisochroman-4-yl)-*N*,*N*-bis(4-methylbenzyl)methanamine (3hb)**



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 85 mg, 68% yield, > 20:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.10-7.21 (m, 8H), 6.99 (dd, *J* = 9.6 Hz, 1.6 Hz, 1H), 6.79-6.87 (m, 2H), 5.87-5.96 (m, 1H),

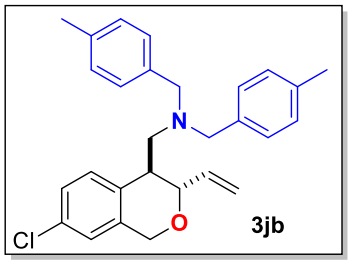
5.17-5.23 (m, 2H), 4.70 (d, J = 9.6 Hz, 1H), 4.52-4.56 (m, 2H), 3.54-3.62 (m, 4H), 2.76-2.83 (m, 2H), 2.53-2.60 (m, 1H), 2.32 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.6 (d, $J_{C\text{-}F}$ = 242 Hz), 137.6 (d, $J_{C\text{-}F}$ = 7 Hz), 136.8, 136.6, 136.1, 130.1 (d, $J_{C\text{-}F}$ = 3 Hz), 129.1, 129.0, 125.5 (d, $J_{C\text{-}F}$ = 8 Hz), 118.1, 115.9 (d, $J_{C\text{-}F}$ = 21 Hz), 113.4 (d, $J_{C\text{-}F}$ = 22 Hz), 74.6, 63.6, 59.2, 58.8, 39.7, 21.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.3; **HRMS** (ESI) calcd for $C_{28}H_{31}FNO$ $[M+H]^+$: 416.2384, found: 416.2377.

Trans-1-(5-fluoro-3-vinylisochroman-4-yl)-_N,N_-bis(4-methylbenzyl)methanamine (3ib)



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 100 mg, 80% yield, > 20:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20-7.23 (m, 4H), 7.06-7.11 (m, 5H), 6.88 (t, J = 9.2 Hz, 1H), 6.71 (d, J = 7.6 Hz, 1H), 5.86-5.95 (m, 1H), 5.14-5.20 (m, 2H), 4.88-4.90 (m, 1H), 4.72 (d, J = 15.6 Hz, 1H), 4.55 (d, J = 15.6 Hz, 1H), 3.81 (d, J = 14.0 Hz, 2H), 3.47 (d, J = 14.0 Hz, 2H), 3.12 (dd, J = 10.8 Hz, 2.8 Hz, 1H), 2.86-2.92 (m, 1H), 2.56 (dd, J = 12.4 Hz, 2.4 Hz, 1H), 2.32 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.3 (d, $J_{C\text{-}F}$ = 244 Hz), 137.2 (d, $J_{C\text{-}F}$ = 6 Hz), 136.5, 136.4 (d, $J_{C\text{-}F}$ = 1 Hz), 128.99, 128.95, 127.3 (d, $J_{C\text{-}F}$ = 9 Hz), 122.4 (d, $J_{C\text{-}F}$ = 18 Hz), 119.7 (d, $J_{C\text{-}F}$ = 3 Hz), 118.0, 113.1, 112.9, 72.8, 61.9 (d, $J_{C\text{-}F}$ = 2 Hz), 58.5, 57.6, 33.8, 21.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -120.7; **HRMS** (ESI) calcd for $C_{28}H_{31}FNO$ $[M+H]^+$: 416.2384, found: 416.2381.

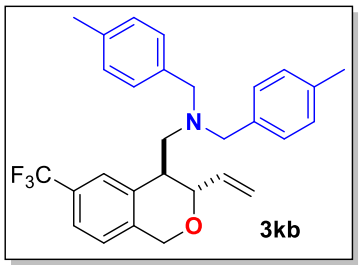
Trans-1-(7-chloro-3-vinylisochroman-4-yl)-_N,N_-bis(4-methylbenzyl)methanamine (3jb)



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 106 mg, 82% yield, > 20:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.09-7.12 (m, 4H), 7.00-7.05 (m, 6H),

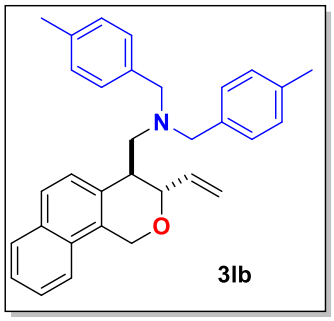
6.80 (s, 1H), 5.76-5.85 (m, 1H), 5.07-5.13 (m, 2H), 4.60 (d, *J* = 15.6 Hz, 1H), 4.51-4.53 (m, 1H), 4.44 (d, *J* = 15.6 Hz, 1H), 3.46-3.53 (m, 4H), 2.65-2.75 (m, 2H), 2.46 (dd, *J* = 11.6 Hz, 4.4 Hz, 1H), 2.23 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.63, 136.56, 136.3, 136.1, 133.7, 131.8, 130.9, 129.02, 128.98, 126.6, 124.0, 118.1, 74.4, 63.1, 59.4, 58.8, 39.1, 21.2; **HRMS** (ESI) calcd for $C_{28}H_{31}ClNO$ $[M+H]^+$: 432.2089, found: 432.2084.

***Trans*-*N*,*N*-bis(4-methylbenzyl)-1-(6-(trifluoromethyl)-3-vinylisochroman-4-yl)methanamine (3kb)**



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 77 mg, 55% yield , > 20:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 4H), 7.10 (d, *J* = 8.0 Hz, 4H), 7.00 (d, *J* = 8.0 Hz, 1H), 5.85-5.93 (m, 1H), 5.18-5.24 (m, 2H), 4.76 (d, *J* = 15.6 Hz, 1H), 4.54-4.56 (m, 2H), 3.68 (d, *J* = 13.6 Hz, 2H), 3.55 (d, *J* = 13.6 Hz, 2H), 2.76-2.87 (m, 2H), 2.57-2.61 (m, 1H), 2.31 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.4, 136.6, 136.5, 136.1, 136.0, 129.1, 129.0, 128.9 (d, $J_{C\text{-}F}$ = 32 Hz), 128.5 (q, $J_{C\text{-}F}$ = 270 Hz), 126.8 (q, $J_{C\text{-}F}$ = 4 Hz), 124.5, 122.9 (q, $J_{C\text{-}F}$ = 4 Hz), 118.4, 74.8, 63.5, 59.3, 59.0, 39.4, 21.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.2; **HRMS** (ESI) calcd for $C_{29}H_{31}F_3NO$ $[M+H]^+$: 466.2352, found: 466.2345.

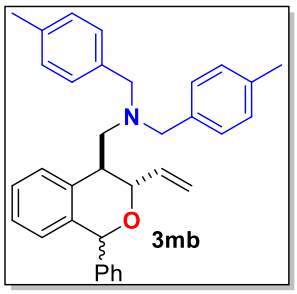
***Trans*-*N*,*N*-bis(4-methylbenzyl)-1-(3-vinyl-3,4-dihydro-1H-benzo[h]isochromen-4-yl)methanamine (3lb)**



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 70 mg, 52% yield, > 20:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77-7.79 (m, 1H), 7.59-7.65 (m, 2H), 7.40-7.46 (m, 2H), 7.21-7.24 (m, 5H), 7.09 (d, *J* = 7.6 Hz,

4H), 5.92-6.00 (m, 1H), 5.02-5.27 (m, 4H), 4.79-4.81 (m, 1H), 3.71 (d, *J* = 13.6 Hz, 2H), 3.59 (d, *J* = 13.6 Hz, 2H), 2.93-2.99 (m, 1H), 2.87-2.89 (m, 1H), 2.67 (dd, *J* = 12.4 Hz, 4.4 Hz, 1H), 2.30 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.8, 136.5, 136.3, 132.2, 132.1, 129.2, 129.1, 129.0, 128.7, 127.9, 126.6, 126.2, 125.4, 121.7, 118.0, 73.7, 61.3, 59.4, 58.8, 40.4, 21.2; **HRMS** (ESI) calcd for $C_{32}H_{34}NO$ $[M+H]^+$: 448.2635, found: 448.2625.

***Trans*-*N*,*N*-bis(4-methylbenzyl)-1-(1-phenyl-3-vinylisochroman-4-yl)methanamine (3mb)**

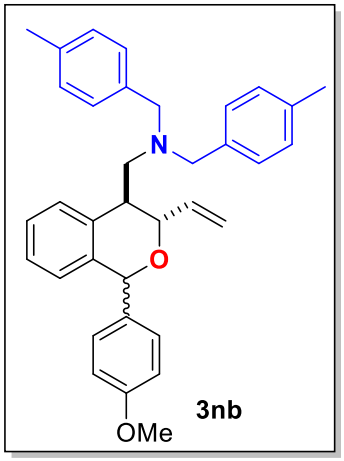


The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 116 mg, 85% yield, 3:1 dr.

3mb-1: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26-7.37 (m, 3H), 7.22-7.25 (m, 2H), 7.15-7.20 (m, 3H), 7.12 (d, *J* = 7.6 Hz, 4H), 7.05 (d, *J* = 7.6 Hz, 4H), 6.84 (d, *J* = 7.6 Hz, 1H), 5.84-5.92 (m, 1H), 5.76 (s, 1H), 5.28 (d, *J* = 17.2 Hz, 1H), 5.11 (d, *J* = 10.8 Hz, 1H), 4.49 (s, 1H), 3.71 (d, *J* = 13.6 Hz, 2H), 3.46 (d, *J* = 14.0 Hz, 2H), 3.01-3.03 (m, 1H), 2.82 (dd, *J* = 12.8 Hz, 5.6 Hz, 1H), 2.73 (dd, *J* = 12.8 Hz, 8.0 Hz, 1H), 2.31 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.8, 138.3, 136.7, 136.30, 136.27, 135.1, 129.6, 128.9, 128.6, 128.3, 127.9, 127.0, 126.3, 126.0, 115.9, 77.1, 72.5, 58.5, 55.3, 40.5, 21.2; **HRMS** (ESI) calcd for $C_{34}H_{36}NO$ $[M+H]^+$: 474.2797, found: 474.2796;

3mb-2: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15-7.30 (m, 9H), 7.07-7.09 (m, 4H), 7.01-7.05 (m, 1H), 6.94-6.95 (m, 2H), 6.66 (d, *J* = 7.6 Hz, 1H), 6.03-6.12 (m, 1H), 5.62 (s, 1H), 5.20-5.28 (m, 2H), 4.98 (d, *J* = 5.6 Hz, 1H), 3.76 (d, *J* = 13.6 Hz, 2H), 3.58 (d, *J* = 13.6 Hz, 2H), 3.05 (dd, *J* = 12.0 Hz, 9.6 Hz, 1H), 2.95 (dd, *J* = 9.2 Hz, 5.2 Hz, 1H), 2.63 (dd, *J* = 12.4 Hz, 5.6 Hz, 1H), 2.30 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.2, 137.1, 136.8, 136.5, 136.4, 134.8, 129.8, 129.1, 128.9, 128.8, 128.4, 127.9, 126.4, 126.4, 126.3, 118.6, 74.5, 73.8, 60.2, 59.0, 39.2, 21.3; **HRMS** (ESI) calcd for $C_{34}H_{36}NO$ $[M+H]^+$: 474.2797, found: 474.2798.

***Trans*-1-(1-(4-methoxyphenyl)-3-vinylisochroman-4-yl)-*N*,*N*-bis(4-methylbenzyl)methanamine (3nb)**

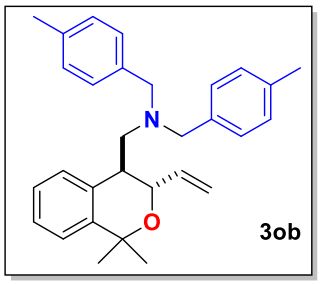


The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 121 mg, 80% yield, 2.8:1 dr.

3nb-1: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.6 Hz, 1H), 7.14-7.25 (m, 3H), 7.09-7.11 (m, 6H), 7.03-7.05 (m, 3H), 6.79-6.84 (m, 3H), 5.84-5.92 (m, 1H), 5.74 (s, 1H), 5.22-5.27 (m, 1H), 5.08-5.11 (m, 1H), 4.46-4.48 (m, 1H), 3.76 (s, 3H), 3.71 (d, *J* = 13.6 Hz, 2H), 3.45 (d, *J* = 14.0 Hz, 2H), 2.99-3.03 (m, 1H), 2.82 (dd, *J* = 13.2 Hz, 5.6 Hz, 1H), 2.71 (dd, *J* = 12.8 Hz, 8.0 Hz, 1H), 2.30 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.2, 138.3, 136.8, 136.3, 135.4, 135.1, 130.5, 130.2, 129.7, 128.9, 128.6, 127.0, 126.2, 126.0, 115.8, 113.6, 76.7, 72.1, 58.5, 55.4, 55.3, 40.5, 21.2; **HRMS** (ESI) calcd for $C_{35}H_{38}NO_2$ $[M+H]^+$: 504.2897, found: 504.2903.

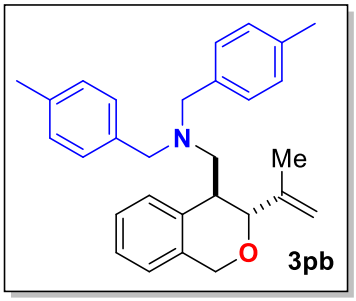
3nb-2: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.0 Hz, 4H), 7.16 (d, *J* = 4.0 Hz, 2H), 7.02-7.08 (m, 5H), 6.83-6.86 (m, 2H), 6.64-6.72 (m, 3H), 6.02-6.11 (m, 1H), 5.58 (s, 1H), 5.19-5.27 (m, 2H), 4.94 (d, *J* = 5.2 Hz, 1H), 3.78 (s, 3H), 3.73 (d, *J* = 13.6 Hz, 2H), 3.60 (d, *J* = 13.6 Hz, 2H), 2.90-3.02 (m, 2H), 2.64 (dd, *J* = 12.0 Hz, 5.2 Hz, 1H), 2.30 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.3, 137.4, 136.8, 136.4, 136.4, 134.9, 134.6, 130.0, 129.8, 129.1, 128.9, 126.4, 126.3, 126.3, 118.5, 113.8, 74.0, 73.9, 60.3, 58.9, 55.3, 39.2, 21.3; **HRMS** (ESI) calcd for $C_{35}H_{38}NO_2$ $[M+H]^+$: 504.2897, found: 504.2893.

***Trans*-1-(1,1-dimethyl-3-vinylisochroman-4-yl)-*N*,*N*-bis(4-methylbenzyl)methanamine (3ob)**



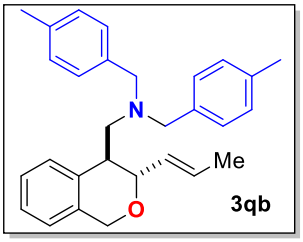
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 41 mg, 32% yield, > 20:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.2 Hz, 1H), 7.16-7.21 (m, 4H), 7.08-7.15 (m, 6H), 7.02-7.04 (m, 1H), 5.95-6.04 (m, 1H), 5.27 (d, *J* = 17.2 Hz, 1H), 5.15 (d, *J* = 10.4 Hz, 1H), 4.39 (t, *J* = 6.4 Hz, 1H), 3.64 (d, *J* = 13.2 Hz, 2H), 3.48 (d, *J* = 13.6 Hz, 2H), 2.91-2.95 (m, 1H), 2.61-2.71 (m, 2H), 2.31 (s, 6H), 1.51 (s, 3H), 1.28 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.7, 139.3, 136.5, 136.2, 135.4, 129.2, 129.0, 126.2, 126.1, 124.8, 117.2, 74.3, 73.5, 58.6, 58.3, 40.3, 31.6, 30.8, 21.2; **HRMS** (ESI) calcd for $C_{30}H_{36}NO$ $[M+H]^+$: 426.2797, found: 426.2805.

***Trans*-*N*,*N*-bis(4-methylbenzyl)-1-(3-(prop-1-en-2-yl)isochroman-4-yl)methanamine (3pb)**



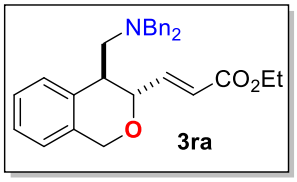
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 37 mg, 30% yield, > 20:1 dr. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.18-7.24 (m, 5H), 7.09-7.15 (m, 6H), 6.87-6.89 (m, 1H), 4.88 (s, 1H), 4.66 (s, 1H), 4.51-4.54 (m, 3H), 3.56-3.62 (m, 4H), 2.98-2.98 (m, 1H), 2.89 (dd, *J* = 12.0 Hz, 9.0Hz, 1H), 2.91-2.95 (m, 1H), 2.59 (dd, *J* = 13.0 Hz, 5.5Hz, 1H), 2.32 (s, 6H), 1.81 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.1, 136.5, 136.3, 135.7, 134.9, 129.2, 129.05, 129.00, 126.4, 125.9, 123.9, 114.2, 63.5, 60.3, 58.6, 37.5, 21.2, 20.3;**HRMS** (ESI) calcd for $C_{29}H_{34}NO$ $[M+H]^+$: 412.2640, found: 412.2639.

***Trans*-*N*,*N*-bis(4-methylbenzyl)-1-(3-((*E*)-prop-1-en-1-yl)isochroman-4-yl)methanamine (3qb)**



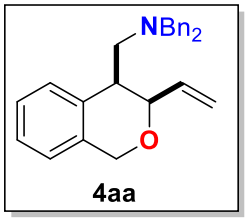
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 43 mg, 35% yield, > 20:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20-7.23 (m, 5H), 7.09-7.14 (m, 6H), 6.90-6.92 (m, 1H), 5.65-5.75, (m, 1H), 5.41-5.46 (m, 1H), 4.96 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 4.75 (d, *J* = 15.6 Hz, 1H), 4.58 (d, *J* = 15.6 Hz, 1H), 3.67(d, *J* = 13.6 Hz, 2H), 3.57 (d, *J* = 13.7 Hz, 2H), 2.88 (dd, *J* = 12.4 Hz, 8.8 Hz, 1H), 2.67-2.71 (m, 1H), 2.56 (dd, *J* = 12.8 Hz, 5.2 Hz, 1H), 2.31 (s, 6H), 1.84 (dd, *J* = 6.8 Hz, 1.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.4, 136.2, 135.2, 134.9, 130.0, 129.9, 129.0, 129.02, 128.7, 126.3, 126.1, 123.9, 69.2, 63.2, 59.5, 58.4, 41.1, 21.2, 13.9; **HRMS** (ESI) calcd for $C_{29}H_{34}NO$ $[M+H]^+$: 412.2640, found: 412.2644.

***Trans*-*N*,*N*-dibenzyl-1-(3-((*E*)-prop-1-en-1-yl)isochroman-4-yl)methanamine (3ra)**



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 43 mg, 35% yield, > 20:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23-7.32 (m, 10H), 7.10-7.18 (m, 3H), 7.03 (dd, *J* = 16.0 Hz, 5.2 Hz, 1H), 6.90-6.92 (m, 1H), 5.95 (dd, *J* = 16.0 Hz, 1.6 Hz, 2H), 4.79-4.80 (m, 1H), 4.75 (d, *J* = 15.2 Hz, 1H), 4.58 (d, *J* = 15.2 Hz, 1H), 4.13-4.18 (m, 2H), 3.75 (d, *J* = 13.6 Hz, 2H), 3.58 (d, *J* = 13.6 Hz, 2H), 2.92 (dd, *J* = 12.8 Hz, 10.0 Hz, 1H), 2.77-2.80 (m, 1H), 2.61 (dd, *J* = 12.8 Hz, 4.4 Hz, 1H), 1.28 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.4, 147.0, 139.2, 134.2, 134.0, 129.3, 129.1, 128.4, 127.2, 126.7, 126.5, 124.3, 122.6, 73.1, 63.9, 60.5, 59.9, 59.5, 40.2, 14.4; **HRMS** (ESI) calcd for $C_{29}H_{32}NO_3$ $[M+H]^+$: 442.2382, found: 442.2377.

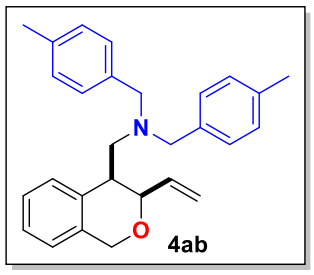
***Cis*-*N*,*N*-dibenzyl-1-(3-vinylisochroman-4-yl)methanamine (4aa)**



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 98 mg, 89% yield (combination yield of *cis*- and *trans*-product), 14:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27-7.30 (m, 1H), 7.15-7.23 (m, 12H), 6.92-6.94 (m, 1H), 5.93-6.01 (m, 1H), 5.33 (dt, *J* = 17.6 Hz, 2.0 Hz, 1H), 5.20 (dt, *J* = 10.8 Hz, 1.6 Hz, 1H), 4.73-4.82 (m, 2H), 4.29-4.32 (m, 1H), 3.76 (d, *J* = 14.0 Hz, 2H), 3.45 (d, *J* = 14.0 Hz, 2H), 2.80-2.89 (m, 2H), 2.62 (dd, *J* = 12.8 Hz, 8.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.2, 137.4, 137.0 133.8, 130.1, 128.7, 128.1, 126.7, 126.3, 125.6, 123.8, 115.1, 76.7, 67.8, 58.8, 55.6, 40.4; **HRMS** (ESI) calcd for $C_{26}H_{27}NONa$ $[M+Na]^+$: 392.1990, found: 392.1982.

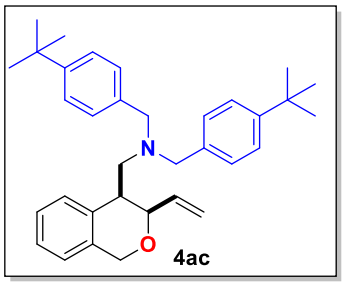
***Cis*-*N*,*N*-bis(4-methylbenzyl)-1-(3-vinylisochroman-4-yl)methanamine (4ab)**

The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 93 mg, 78% yield (combination yield of *cis*- and *trans*-product), 15:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26-7.29 (m, 1H), 7.18-7.22 (m, 2H), 7.06-7.09 (m, 4H), 7.02-7.04 (m, 4H), 6.94-6.96 (m, 1H), 5.96-6.02 (m, 1H), 5.32 (dt, *J* = 14.0 Hz, 1.2 Hz, 1H), 5.20 (dt, *J* = 8.4 Hz, 1.2 Hz, 1H), 4.77-4.83 (m, 2H), 4.30-4.32 (m, 1H), 3.68 (d, *J* = 11.2 Hz, 2H), 3.43 (d, *J* = 10.8 Hz, 2H), 2.81-2.89 (m, 2H), 2.59 (dd, *J* = 8.0 Hz, 4.0Hz, 1H), 2.30 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.7, 137.2, 136.3, 136.2, 134.0, 130.3, 128.9, 128.8, 126.4, 125.8, 123.9, 115.2, 68.0, 58.5, 55.7, 40.6, 21.2; **HRMS** (ESI) calcd for $C_{28}H_{32}NO$ $[M+H]^+$: 398.2484, found: 398.2483.



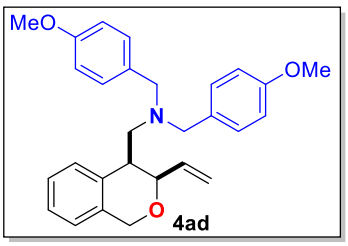
***Cis*-*N*,*N*-bis(4-(tert-butyl)benzyl)-1-(3-vinylisochroman-4-yl)methanamine (4ac)**

The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 100 mg, 69% yield (combination yield of *cis*- and *trans*-product), 14:1 dr. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28-7.29 (m, 1H), 7.19-7.24 (m, 6H), 7.12-7.14 (m, 4H), 6.92-6.93 (m, 1H), 5.95-6.01 (m, 1H), 5.31 (dt, *J* = 17.5 Hz, 1.2 Hz, 1H), 5.19 (dt, *J* = 11.0 Hz, 1.5 Hz, 1H), 4.70-4.82 (m, 2H), 4.30-4.32 (m, 1H), 3.75 (d, *J* = 14.0 Hz, 2H), 3.40 (d, *J* = 13.5 Hz, 2H), 2.86-2.89 (m, 1H), 2.81 (dd, *J* = 13.5 Hz, 5.5 Hz, 1H), 2.61 (dd, *J* = 13.5 Hz, 8.5 Hz, 1H), 1.29 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.5, 137.7, 137.1, 136.4, 133.9, 130.4, 128.6, 126.4, 125.7, 125.0, 123.9, 115.3, 77.4, 67.9, 58.5, 55.4, 40.7, 34.5, 31.5; **HRMS** (ESI) calcd for $C_{34}H_{44}NO$ $[M+H]^+$: 482.3423, found: 482.3418.

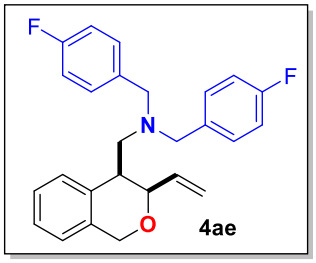


***Cis*-*N*,*N*-bis(4-methoxybenzyl)-1-(3-vinylisochroman-4-yl)methanamine (4ad)**

The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 96 mg, 75% yield (combination yield of *cis*- and *trans*-product), 8:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26-7.30 (m, 1H), 7.17-7.22 (m, 2H), 7.09-7.12 (m, 4H), 6.92-6.96 (m, 1H), 6.74-6.78 (m, 4H), 5.94-6.02 (m, 1H), 5.33 (dt, *J* = 17.2 Hz, 1.6 Hz, 1H), 5.20 (dt, *J* = 10.8 Hz, 1.6 Hz, 1H), 4.75-4.83 (m, 2H), 4.29-4.31 (m, 1H), 3.76 (s, 6H), 3.65 (d, *J* = 13.6 Hz, 2H), 3.39 (d, *J* = 13.6 Hz, 2H), 2.79-2.87 (m, 2H), 2.58 (dd, *J* = 12.0 Hz, 7.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.5, 137.7, 137.2, 134.0 131.4, 130.2, 130.0, 126.4, 125.7, 123.9, 115.2, 113.6, 68.0, 58.1, 55.5, 55.3, 40.6; **HRMS** (ESI) calcd for $C_{28}H_{32}NO_3$ $[M+H]^+$: 430.2382, found: 430.2399.

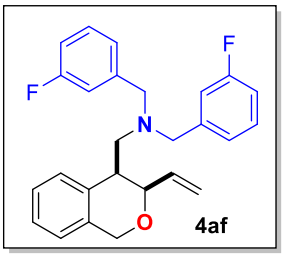


***Cis*-*N*,*N*-bis(4-fluorobenzyl)-1-(3-vinylisochroman-4-yl)methanamine (4ae)**



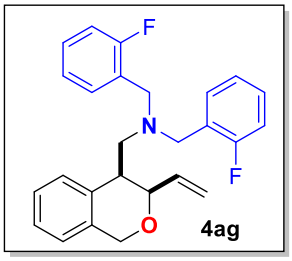
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 75 mg, 62% yield (combination yield of *cis*- and *trans*-product), 8:1 dr. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.20-7.25 (m, 3H), 7.10-7.13 (m, 4H), 6.87-6.96 (m, 5H), 5.91-5.99 (m, 1H), 5.33 (dt, *J* = 17.5 Hz, 1.5 Hz, 1H), 5.29(dt, *J* = 11.0 Hz, 2.0 Hz, 1H), 4.73-4.83 (m, 2H), 4.30-4.32 (m, 1H), 3.70 (d, *J* = 14.0 Hz, 2H), 3.38 (d, *J* = 14.0 Hz, 2H), 2.84-2.88 (m, 1H), 2.80 (dd, *J* = 13.0 Hz, 5.0 Hz, 1H), 2.59 (dd, *J* = 13.0 Hz, 8.5 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.7 (d, $J_{C\text{-}F}$ = 243 Hz), 137.3, 136.9, 134.7 (d, $J_{C\text{-}F}$ = 3 Hz), 133.8, 130.1 (d, $J_{C\text{-}F}$ = 8 Hz), 126.5, 125.6, 124.0, 115.3, 115.0, 114.8, 77.1, 67.9, 58.0, 55.2, 40.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.3; **HRMS** (ESI) calcd for $C_{26}H_{26}F_2NO$ $[M+H]^+$: 406.1982, found: 406.1977.

***Cis*-*N*,*N*-bis(3-fluorobenzyl)-1-(3-vinylisochroman-4-yl)methanamine (4af)**



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 60 mg, 49% yield (combination yield of *cis*- and *trans*-product), 7:1 dr. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.23-7.26 (m, 3H), 7.15-7.19 (m, 2H), 6.97-6.98 (m, 3H), 6.85-6.89 (m, 4H), 5.92-5.98 (m, 1H), 5.33 (dt, *J* = 17.5 Hz, 1.5 Hz, 1H), 5.23 (dt, *J* = 11 Hz, 1.5 Hz, 1H), 4.85 (abq, *J* = 15.2 Hz, 2 H), 4.34 (m, 1H), 3.76(d, *J* = 14.5 Hz, 2H), 3.42 (s, *J* = 14 Hz, 2H), 2.89 (m, 1H), 2.82 (dd, *J* = 13.0 Hz, 5.0 Hz, 1H), 2.62 (dd, *J* = 13.0 Hz, 8.5 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.0 (d, $J_{C\text{-}F}$ = 244 Hz), 141.9 (d, $J_{C\text{-}F}$ = 7 Hz), 137.2, 137.0, 133.9, 130.2, 129.7 (d, $J_{C\text{-}F}$ = 8 Hz), 126.8, 125.8, 124.3 (d, $J_{C\text{-}F}$ = 3 Hz), 124.2, 115.6 (d, $J_{C\text{-}F}$ = 8 Hz), 115.4, 113.9 (d, $J_{C\text{-}F}$ = 21 Hz), 77.2, 68.1, 58.6, 55.6, 40.6; **^{19}F NMR** (470 MHz, $CDCl_3$) δ -113.5; **HRMS** (ESI) calcd for $C_{26}H_{26}F_2NO$ $[M+H]^+$: 406.1982, found: 406.1983.

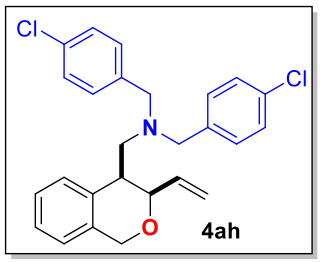
***Cis*-*N*,*N*-bis(2-fluorobenzyl)-1-(3-vinylisochroman-4-yl)methanamine (4ag)**



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 89 mg, 73% yield (combination yield of *cis*- and *trans*-product), 6:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25-7.28 (m, 1H), 7.12-7.22 (m, 6H), 6.93-6.98 (m, 5H), 5.93-6.02 (m, 1H), 5.33 (dt, *J* = 19.2 Hz, 1.6 Hz, 1H), 5.20 (dt, *J* = 10.4 Hz, 1.6 Hz, 1H), 4.76-4.85 (m, 2 H), 4.32-4.33 (m, 1H), 3.77 (d, *J* = 14.4 Hz, 2H), 3.64 (d, *J* = 14.4 Hz, 2H), 2.84-2.91 (m, 2H), 2.57-2.63(m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.4 (d, $J_{C\text{-}F}$ = 244 Hz), 137.4, 136.9, 133.9, 131.0 (d, $J_{C\text{-}F}$ = 4 Hz), 130.3, 128.4 (d, $J_{C\text{-}F}$ = 8 Hz), 126.5, 126.0 (d, $J_{C\text{-}F}$ = 14 Hz), 125.8, 123.94, 123.88 (d, $J_{C\text{-}F}$ = 3 Hz), 115.3, 115.2 (d, $J_{C\text{-}F}$ = 22 Hz), 77.2, 68.1, 55.6, 51.7 (d, $J_{C\text{-}F}$ = 2 Hz), 40.5; **^{19}F NMR** (470 MHz, $CDCl_3$) δ -117.8; **HRMS** (ESI) calcd for $C_{26}H_{26}F_2NO$ $[M+H]^+$: 406.1982, found: 406.1989.

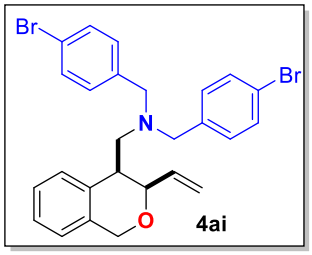
***Cis*-*N*,*N*-bis(4-chlorobenzyl)-1-(3-vinylisochroman-4-yl)methanamine (4ah)**

The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 69 mg, 53% yield (combination yield of *cis*- and *trans*-product), 6:1 dr.



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16-7.26 (m, 7H), 7.06-7.08 (m, 4H), 6.97-6.98 (m, 1H), 6.74-6.78 (m, 1H), 5.94-6.02 (m, 1H), 5.33 (dt, *J* = 17.0 Hz, 1.5 Hz, 1H), 5.22 (dt, *J* = 10.5 Hz, 1.5 Hz, 1H), 4.84 (abq, *J* = 15.3 Hz, 2H), 4.31-4.33 (m, 1H), 3.71 (d, *J* = 14.0 Hz, 2H), 3.37 (d, *J* = 14.0 Hz, 2H), 2.85-2.88 (m, 1H), 2.76-2.80(m, 1H), 2.55-2.60 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 137.6, 137.3, 137.0, 134.0, 132.5, 130.2, 130.0, 128.4, 126.7, 125.7, 124.1, 115.5, 68.0, 58.2, 55.4, 40.5; **HRMS** (ESI) calcd for $C_{26}H_{26}Cl_2NO$ $[M+H]^+$: 438.1391, found: 438.1390.

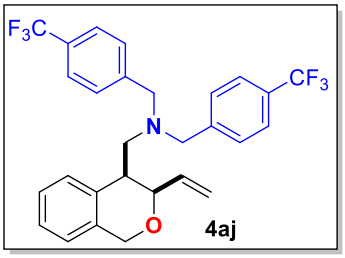
***Cis*-*N*,*N*-bis(4-bromobenzyl)-1-(3-vinylisochroman-4-yl)methanamine (4ai)**



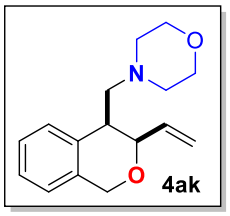
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 68 mg, 43% yield (combination yield of *cis*- and *trans*-product), 7:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31-7.33 (m, 4H), 7.21-7.24 (m, 3H), 6.97-7.02 (m, 5H), 5.91-5.99 (m, 1H), 5.34 (d, *J* = 17.6 Hz, 1H), 5.22 (d, *J* = 10.8 Hz, 1H), 4.74-4.84 (m, 2H), 4.32-4.32 (m, 1H), 3.70 (d, *J* = 14.4 Hz, 2H), 3.36 (d, *J* = 14.0 Hz, 2H), 2.75-2.86 (m, 2H), 2.54-2.60 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.1, 137.3, 136.9, 134.0, 131.4, 130.4, 130.2, 126.7, 125.7, 124.1, 120.6, 115.5, 77.1, 68.0, 58.3, 55.4, 40.5; **HRMS** (ESI) calcd for $C_{26}H_{26}Br_2NO$ $[M+H]^+$: 526.0381, found: 526.0395.

Cis-_N_,_N_-bis(4-(trifluoromethyl)benzyl)-1-(3-vinylisochroman-4-yl)methanamine (4aj)

The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 48 mg, 32% yield (combination yield of *cis*- and *trans*-product), 3:1 dr. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.0 Hz, 4H), 7.24-7.29 (m, 7H), 6.98 (d, *J* = 7.0 Hz, 1H), 5.92-5.99 (m, 1H), 5.34 (d, *J* = 17.5 Hz, 1H), 5.23 (d, *J* = 11.0 Hz, 1H), 4.84 (d, *J* = 15.5 Hz, 1H), 4.72 (d, *J* = 15.0 Hz, 1H), 4.34-4.35 (m, 1H), 3.84 (d, *J* = 14.0 Hz, 2H), 3.47 (d, *J* = 14.5 Hz, 2H), 2.87-2.90 (m, 1H), 2.79-2.82 (m, 1H), 2.60-2.64 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.2, 137.1, 136.8, 134.0, 130.3, 129.6 (q, $J_{C\text{-}F}$ = 32 Hz), 128.8, 127.6 (q, $J_{C\text{-}F}$ = 270 Hz), 126.9, 125.7, 125.3 (d, $J_{C\text{-}F}$ = 4 Hz), 124.2, 115.6, 77.0, 68.0, 58.6, 55.4, 40.5; **^{19}F NMR** (470 MHz, $CDCl_3$) δ -62.4,; **HRMS** (ESI) calcd for $C_{28}H_{26}F_6NO$ $[M+H]^+$: 506.1919, found: 506.1922.

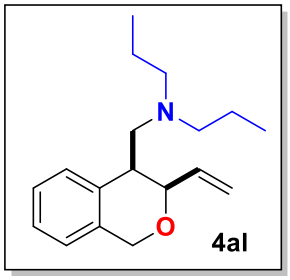


Cis-4-((3-vinylisochroman-4-yl)methyl)morpholine (4ak)



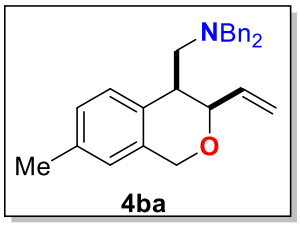
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 53 mg, 68% yield (combination yield of *cis*- and *trans*-product), 6:1 dr. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.17-7.23 (m, 3H), 6.99-7.00 (m, 1H), 6.09-6.16 (m, 1H), 5.36 (dt, *J* = 17.5 Hz, 1.5 Hz, 1H), 5.20 (dt, *J* = 11.0 Hz, 2.0 Hz, 1H), 4.87-4.96 (m, 2H), 4.33-4.35 (m, 1H), 3.68 (t, *J* = 4.5 Hz, 4H), 2.86-2.89 (m, 1H), 2.78 (dd, *J* = 13.0 Hz, 7.0 Hz, 1H), 2.30-2.50 (m, 5H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 137.5, 137.2, 134.2, 129.8, 126.5, 126.1, 124.0, 114.8, 77.6, 68.3, 67.3, 60.6, 54.1, 39.4; **HRMS** (ESI) calcd for $C_{16}H_{22}NO_2$ $[M+H]^+$: 260.1651, found: 260.1650.

***Cis*-*N*-propyl-*N*-((3-vinylisochroman-4-yl)methyl)propan-1-amine (4al)**



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 72 mg, 88% yield (combination yield of *cis*- and *trans*-product), 2:1 dr. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28-7.30 (m, 1H), 7.13-7.18 (m, 2H), 6.97-7.00 (m, 1H), 6.06-6.13 (m, 1H), 5.37 (dt *J* = 17.5 Hz, 1.5 Hz, 1H), 5.21 (dt, *J* = 10.5 Hz, 2.0 Hz, 1H), 4.87-4.96 (m, 2H), 4.33-4.34 (m, 1H), 2.76-2.80 (m, 2H), 2.28-2.43 (m, 5H), 1.30-1.38 (m, 4H), 0.83 (t, *J* = 7.5 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.1, 137.3, 133.8, 130.2, 126.2, 125.8, 123.8, 115.0, 76.9, 68.3, 56.9, 56.6, 40.7, 20.2, 12.1; **HRMS** (ESI) calcd for $C_{18}H_{28}NO$ $[M+H]^+$: 274.2171, found: 274.2171.

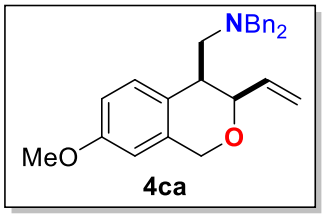
***Cis*-*N*,*N*-dibenzyl-1-(7-methyl-3-vinylisochroman-4-yl)methanamine (4ba)**



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 90 mg, 78% yield (combination yield of *cis*- and *trans*-product), 7:1 dr. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.17-7.25 (m, 11H), 7.02-7.03 (m, 1H), 6.77 (s, 1H), 5.94-6.01 (m, 1H), 5.31 (dt, *J* = 17.0 Hz, 1.5 Hz, 1H), 5.19 (dt, *J* = 11.0 Hz, 1.5 Hz, 1H), 4.79 (q, *J* =

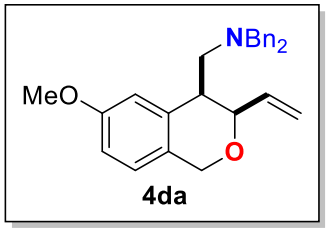
15.0 Hz, 2H), 4.28-4.30 (m, 1H), 3.73 (d, *J* = 13.5 Hz, 2H), 3.47 (d, *J* = 13.5 Hz, 2H), 2.81-2.85 (m, 2H), 2.54-2.59 (m, 1H), 2.34 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 139.4, 137.2, 136.0, 134.6, 133.8, 130.1, 128.9, 128.2, 126.8, 126.7, 124.4, 115.2, 77.5, 68.0, 58.9, 55.9, 40.3, 21.3; **HRMS** (ESI) calcd for $C_{27}H_{30}NO$ $[M+H]^+$: 384.2327, found: 384.2330.

***Cis*-*N*,*N*-dibenzyl-1-(7-methoxy-3-vinylisochroman-4-yl)methanamine (4ca)**



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 81 mg, 68% yield (combination yield of *cis*- and *trans*-product), 7:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16-7.24 (m, 11H), 6.77-6.80 (m, 1H), 6.47-6.48 (m, 1H), 5.93-6.10 (m, 1H), 5.32 (dt, *J* = 17.2 Hz, 1.6 Hz, 1H), 5.19 (dt, *J* = 10.8 Hz, 1.6 Hz, 1H), 4.79 (abq, *J* = 15.2 Hz, 2H), 4.27-4.29 (m, 1H), 3.80 (s, 3H), 3.74 (d, *J* = 13.6 Hz, 2H), 3.45 (d, *J* = 13.6 Hz, 2H), 2.78-2.84 (m, 2H), 2.53-2.59 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.3, 139.4, 137.2, 135.1, 131.3, 129.8, 128.9, 128.2, 126.8, 115.2, 112.2, 108.4, 77.7, 68.1, 59.0, 55.9, 55.4, 39.9; **HRMS** (ESI) calcd for $C_{27}H_{30}NO_2$ $[M+H]^+$: 400.2277, found: 400.2274.

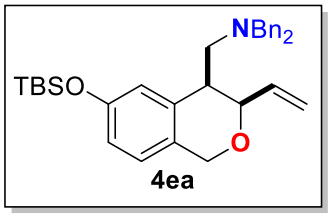
***Cis*-*N*,*N*-dibenzyl-1-(6-methoxy-3-vinylisochroman-4-yl)methanamine (4da)**



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 109 mg, 91% yield (combination yield of *cis*- and *trans*-product), 7:1 dr. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.16-7.25 (m, 10H), 6.76-6.86 (m, 3H), 5.94-6.00 (m, 1H), 5.32 (dt, *J* = 17.5 Hz, 2.0 Hz, 1H), 5.19 (dt, *J* = 10.5 Hz, 1.5 Hz, 1H), 4.70-4.77 (m, 2H), 4.26-4.28 (m, 1H), 3.79 (s, 3H), 3.72 (d, *J* = 14.0 Hz, 2H), 3.47 (d, *J* = 14.0 Hz, 2H), 2.79-2.87 (m, 2H), 2.87 (dd, *J* = 12.5 Hz, 5.0 Hz, 1H), 2.80-2.81 (m, 1H), 2.63 (dd, *J* = 13.0 Hz, 7.5 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 157.6, 139.4, 138.9, 137.1, 128.9, 128.2, 126.8, 126.1,

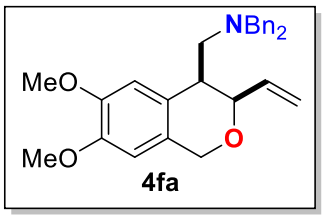
125.0, 115.3, 114.7, 113.1, 77.2, 67.7, 59.1, 55.9, 55.5, 41.0; **HRMS** (ESI) calcd for $C_{27}H_{30}NO_2$ $[M+H]^+$: 400.2277, found: 400.2275.

***Cis*-*N*,*N*-dibenzyl-1-(6-((tert-butyldimethylsilyl)oxy)-3-vinylisochroman-4-yl)methanamine (4ea)**



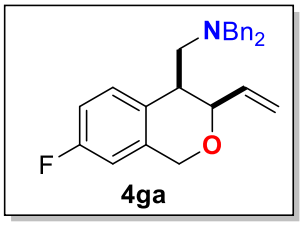
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 118 mg, 79% yield (combination yield of *cis*- and *trans*-product), 8:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15-7.25 (m, 10H), 6.78-6.83 (m, 2H), 6.68-6.71 (m, 1H), 5.92-6.01 (m, 1H), 5.32 (dt, *J* = 17.2 Hz, 2.0 Hz, 1H), 5.19 (dt, *J* = 10.8 Hz, 1.6 Hz, 1H), 4.69-4.77 (m, 2H), 4.26-4.28 (m, 1H), 3.73 (d, *J* = 13.6 Hz, 2H), 3.46 (d, *J* = 13.6 Hz, 2H), 2.75-2.85 (m, 2H), 2.56-2.61 (m, 1H), 1.02 (t, *J* = 2.8 Hz, 9H), 0.22 (d, *J* = 3.6 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.6, 139.3, 139.0, 137.2, 129.0, 128.2, 126.8, 126.7, 124.8, 121.4, 118.4, 115.2, 77.4, 67.8, 59.1, 55.9, 40.7, 25.9, 18.3, -4.19, -4.20; **HRMS** (ESI) calcd for $C_{32}H_{42}NO_2Si$ $[M+H]^+$:500.2985, found: 500.2980.

***Cis*-*N*,*N*-dibenzyl-1-(6,7-dimethoxy-3-vinylisochroman-4-yl)methanamine (4fa)**



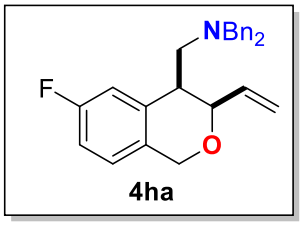
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 122 mg, 95% yield (combination yield of *cis*- and *trans*-product), 6:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17-7.25 (m, 10H), 6.76 (s, 1H), 6.43 (s, 1H), 5.95-6.03 (m, 1H), 5.33 (d, *J* = 17.2 Hz, 1H), 5.21 (dd, *J* = 10.8 Hz, 0.8 Hz, 1H), 4.67-4.77 (m, 2H), 4.26 (s, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.79 (d, *J* = 14.0 Hz, 2H), 3.46 (d, *J* = 14.0 Hz, 2H), 2.86 (dd, *J* = 12.8 Hz, 4.4 Hz, 1H), 2.75-2.77 (m, 1H), 2.65 (dd, *J* = 12.4 Hz, 8.0 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 148.0, 147.1, 139.4, 137.2, 129.8, 128.8, 128.2, 126.8, 125.7, 115.1, 113.1, 106.7, 77.43, 77.36, 67.8, 59.2, 56.0, 40.3; **HRMS** (ESI) calcd for $C_{28}H_{32}NO_3$ $[M+H]^+$: 430.2382, found: 430.2383.

***Cis*-*N*,*N*-dibenzyl-1-(7-fluoro-3-vinylisochroman-4-yl)methanamine (4ga)**



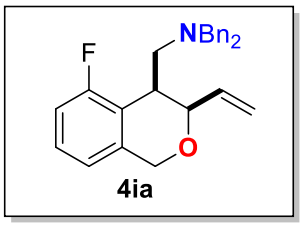
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 98 mg, 84% yield (combination yield of *cis*- and *trans*-product), 10:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16-7.27 (m, 11H), 6.89-6.94 (m, 1H), 6.62-6.65 (m, 1H), 5.91-5.99 (m, 1H), 5.19-5.33 (m, 2H), 4.68-4.78 (m, 2H), 4.26-4.27 (m, 1H), 3.79 (d, *J* = 14.0 Hz, 2H), 3.41 (d, *J* = 14.0 Hz, 2H), 2.75-2.83 (m, 2H), 2.59 (dd, *J* = 12.8 Hz, 8.8 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.6 (d, $J_{C\text{-}F}$ = 243 Hz), 139.3, 136.8, 135.8 (d, $J_{C\text{-}F}$ = 7 Hz), 133.3, 132.0 (d, $J_{C\text{-}F}$ = 7 Hz), 128.8, 128.2, 126.9, 115.5, 112.9 (d, $J_{C\text{-}F}$ = 21 Hz), 110.5 (d, $J_{C\text{-}F}$ = 22 Hz), 77.4, 67.8, 59.1, 55.4, 40.0; **^{19}F NMR** (470 MHz, $CDCl_3$) δ -116.3; **HRMS** (ESI) calcd for $C_{26}H_{27}FNO$ $[M+H]^+$: 388.2077, found: 388.2072.

***Cis*-*N*,*N*-dibenzyl-1-(6-fluoro-3-vinylisochroman-4-yl)methanamine (4ha)**



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 82 mg, 71% yield (combination yield of *cis*- and *trans*-product), 7:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16-7.26 (m, 10H), 7.01-7.04 (m, 1H), 6.84-6.92 (m, 2H), 5.89-5.97 (m, 1H), 5.19-5.33 (m, 2H), 4.69-4.77 (m, 2H), 4.25-4.27 (m, 1H), 3.77 (d, *J* = 13.6 Hz, 2H), 3.41 (d, *J* = 13.6 Hz, 2H), 2.76-2.82 (m, 2H), 2.55-2.62 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.9 (d, $J_{C\text{-}F}$ = 242.0 Hz), 139.8 (d, $J_{C\text{-}F}$ = 8 Hz), 139.2, 136.6, 129.4 (d, $J_{C\text{-}F}$ = 3 Hz), 129.0, 128.3, 126.9, 125.4 (d, $J_{C\text{-}F}$ = 8 Hz), 116.8 (d, $J_{C\text{-}F}$ = 21 Hz), 115.6, 113.7 (d, $J_{C\text{-}F}$ = 22 Hz), 67.6, 59.2, 55.4, 40.6; **^{19}F NMR** (470 MHz, $CDCl_3$) δ -117.5; **HRMS** (ESI) calcd for $C_{26}H_{27}FNO$ $[M+H]^+$: 388.2077, found: 388.2072.

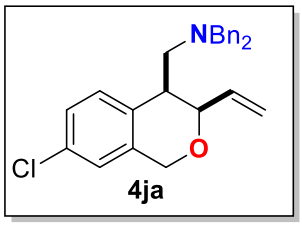
***Cis*-*N*,*N*-dibenzyl-1-(5-fluoro-3-vinylisochroman-4-yl)methanamine (4ia)**



4ia

The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 104 mg, 90% yield (combination yield of *cis*- and *trans*-product), 2:1 dr. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.15-7.24 (m, 11H), 6.96 (t, *J* = 8.5 Hz, 1H), 6.73 (d, *J* = 7.5 Hz, 1H), 6.06-6.12 (m, 1H), 5.34 (dt, *J* = 17.5 Hz, 1.5 Hz, 1H), 5.22 (dt, *J* = 11.0 Hz, 1.5 Hz, 1H), 4.70-4.78 (m, 2H), 4.21-4.22 (m, 1H), 3.68 (d, *J* = 14.0 Hz, 2H), 3.53 (d, *J* = 14.0 Hz, 2H), 3.25-3.27 (m, 1H), 2.94 (dd, *J* = 13.5 Hz, 6.5 Hz, 1H), 2.52 (dd, *J* = 13.0 Hz, 6.5 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.7 (d, $J_{C\text{-}F}$ = 244 Hz), 139.4, 137.3, 136.6 (d, $J_{C\text{-}F}$ = 5.5 Hz), 129.0, 128.1, 127.6 (d, $J_{C\text{-}F}$ = 8.5 Hz), 126.7, 125.8 (d, $J_{C\text{-}F}$ = 19 Hz), 119.7 (d, $J_{C\text{-}F}$ = 3 Hz), 115.0, 112.8 (d, $J_{C\text{-}F}$ = 22 Hz), 77.4, 67.6, 58.5, 55.1, 35.2; **^{19}F NMR** (470 MHz, $CDCl_3$) δ -118.0; **HRMS** (ESI) calcd for $C_{26}H_{27}FNO$ $[M+H]^+$: 388.2077, found: 388.2076.

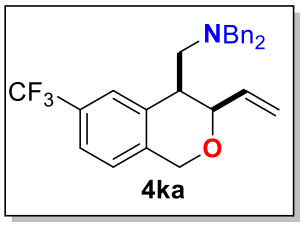
***Cis*- *N*,*N*-dibenzyl-1-(7-chloro-3-vinylisochroman-4-yl)methanamine (4ja)**



4ja

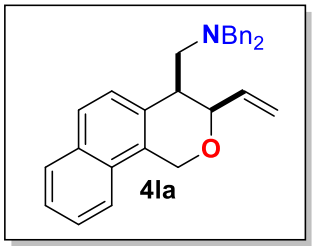
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 86 mg, 71% yield (combination yield of *cis*- and *trans*-product), 9:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17-7.25 (m, 12H), 6.920-6.922 (m, 1H), 5.89-5.97 (m, 1H), 5.19-5.33 (m, 2H), 4.66-4.76 (m, 2H), 4.25-4.26 (m, 1H), 3.78 (d, *J* = 13.6 Hz, 2H), 3.40 (d, *J* = 14.0 Hz, 2H), 2.75-2.82 (m, 2H), 2.54-2.60 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 139.2, 136.6, 136.1, 135.6, 132.1, 131.8, 128.8, 128.3, 126.9, 125.8, 123.9, 115.6, 67.5, 59.2, 55.3, 40.1; **HRMS** (ESI) calcd for $C_{26}H_{27}ClNO$ $[M+H]^+$: 404.1781, found: 404.1780.

***Cis*-*N*,*N*-dibenzyl-1-(6-(trifluoromethyl)-3-vinylisochroman-4-yl)methanamine (4ka)**



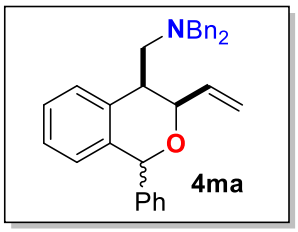
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 104 mg, 79% yield (combination yield of *cis*- and *trans*-product), > 20:1 dr. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.63 (s, 1H),7.45 (d, *J* = 8.0 Hz, 1H), 7.14-7.23 (m, 10H), 7.00 (d, *J* = 8.0 Hz, 1H), 5.91-5.98 (m, 1H), 5.23-5.35 (m, 2H), 4.71-4.81 (m, 2H), 4.27-4.28 (m, 1H), 3.85 (d, *J* = 14.0 Hz, 2H), 3.33 (d, *J* = 13.5 Hz, 2H), 2.81-2.83 (m, 1H), 2.78 (dd, *J* = 13.5 Hz, 4.5 Hz, 1H), 2.64 (dd, *J* = 13.0 Hz, 10.0 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 139.1, 138.4, 137.7, 136.4, 128.8, 128.3, 127.7 (d, $J_{C\text{-}F}$ = 4 Hz), 127.5 (q, $J_{C\text{-}F}$ = 270 Hz), 126.9, 124.4, 123.1 (d, $J_{C\text{-}F}$ = 4 Hz), 115.8, 76.9, 67.8, 59.5, 55.0, 40.3 ; **^{19}F NMR** (470 MHz, $CDCl_3$) δ -62.1; **HRMS** (ESI) calcd for $C_{27}H_{27}F_3NO$ $[M+H]^+$: 438.2045, found: 438.2037.

Cis-_N_,_N_-dibenzyl-1-(3-vinyl-3,4-dihydro-1_H_-benzo[_h_]isochromen-4-yl)methanamine (4la)



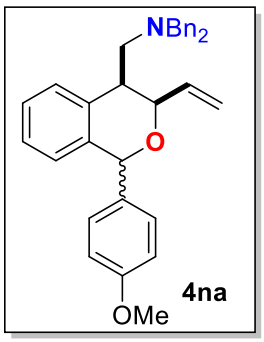
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 84 mg, 67% yield (combination yield of *cis*- and *trans*-product), 11:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76-7.79 (m, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.50-7.52 (m, 1H), 7.30-7.40 (m, 3H), 7.04-7.14 (m, 10H), 5.93-6.02 (m, 1H), 5.30 (d, *J* = 17.2 Hz, 1H), 5.07-5.17 (m, 3H), 4.29-4.30 (m, 1H), 3.69 (d, *J* = 14.0 Hz, 2H), 3.41 (d, *J* = 14.0 Hz, 2H), 2.83-2.89 (m, 2H), 2.58-2.63 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 139.3, 137.2, 135.5, 132.4, 129.3, 128.9, 128.7, 128.5, 128.1, 126.8, 126.2, 125.9, 125.4, 121.7, 115.3, 77.1, 66.6, 59.1, 55.9, 41.1; **HRMS** (ESI) calcd for $C_{30}H_{30}NO$ $[M+H]^+$: 420.2327, found: 420.2331.

Cis-_N_,_N_-dibenzyl-1-(1-phenyl-3-vinylisochroman-4-yl)methanamine (4ma)



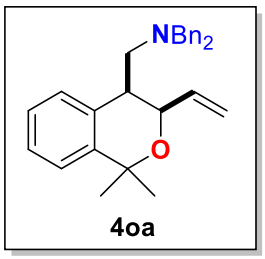
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 77 mg, 58% yield (combination yield of *cis*- and *trans*-product), 3:1 dr. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36-7.40 (m, 1H), 7.25-7.31 (m, 4H), 7.17-7.23 (m, 12H), 7.12-7.14 (m, 0.50H), 7.61-7.84 (m, 1.50H), 5.99-6.08 (m, 0.25H), 5.83-5.91 (m, 0.75H), 5.73 (s, 0.73H), 5.67 (s, 0.27H), 5.09-5.32 (m, 2H), 5.49-5.55 (m, 1H), 3.74-3.99 (m, 2H), 3.48 (d, *J* = 14.0 Hz, 1.45H), 3.36 (d, *J* = 14.0 Hz, 0.55H), 3.96-3.03 (m, 1H), 2.69-2.84 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 142.8, 142.1, 139.5, 139.4, 138.2, 138.0, 137.3, 137.0, 136.6, 135.0, 130.8, 129.7, 129.2, 128.9, 128.7, 128.5, 128.3, 128.2, 128.0, 127.9, 127.1, 126.8, 126.6, 126.5, 126.3, 126.1, 125.6, 116.0, 115.5, 81.7, 78.2, 77.1, 72.4, 59.3, 59.0, 56.2, 55.3, 40.6, 40.5; **HRMS** (ESI) calcd for $C_{32}H_{32}NO$ $[M+H]^+$: 446.2484, found: 446.2490.

***Cis*-*N*,*N*-dibenzyl-1-(1-(4-methoxyphenyl)-3-vinylisochroman-4-yl)methanamine (4na)**



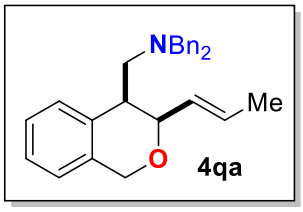
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 78 mg, 55% yield (combination yield of *cis*- and *trans*-product), 2:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36-7.41 (m, 1H), 7.08-7.28 (m, 13.50H), 6.78-6.84 (m, 2H), 6.61-6.68 (m, 1.50H), 5.98-6.07 (m, 0.32H), 5.83-5.91 (m, 0.68H), 5.71 (s, 0.68H), 5.65 (s, 0.32H), 5.08-5.32 (m, 2H), 4.47-4.54 (m, 1H), 3.94-4.00 (m, 5H), 3.48 (d, *J* = 14.0 Hz, 1.39H), 3.34 (d, *J* = 14.5 Hz, 0.61H), 2.95-3.03 (m, 1H), 2.68-2.84 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.3, 159.2, 139.5, 139.4, 138.3, 138.1, 137.4, 137.3, 136.8, 135.3, 135.1, 134.6, 130.8, 130.4, 130.2, 129.7, 128.9, 128.7, 128.3, 128.2, 127.1, 126.8, 126.7, 126.5, 126.2, 126.0, 125.6, 115.8, 115.5, 113.8, 113.6, 81.1, 78.2, 76.7, 71.9, 59.3, 59.0, 56.1, 55.4, 55.32, 55.30, 40.6, 40.5; **HRMS** (ESI) calcd for $C_{33}H_{34}NO_2$ $[M+H]^+$: 476.2590, found: 476.2604.

***Cis*-*N*,*N*-dibenzyl-1-(1,1-dimethyl-3-vinylisochroman-4-yl)methanamine (4oa)**



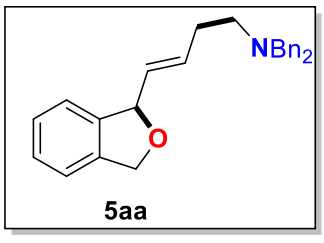
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 48 mg, 40% yield (combination yield of *cis*- and *trans*-product), 6:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21-7.27 (m, 3H), 7.11-7.19 (m, 10H), 7.00-7.02 (m, 1H), 5.97-6.05 (m, 1H), 5.29-5.33 (m, 1H), 5.18-5.20 (m, 1H), 4.42-4.44 (m, 1H), 3.89 (d, *J* = 14.0 Hz, 2H), 3.33 (d, *J* = 14.0 Hz, 2H), 2.81-2.85 (m, 1H), 2.74 (dd, *J* = 13.2 Hz, 4.4 Hz, 1H), 2.65 (dd, *J* = 12.8 Hz, 10.0 Hz, 1H), 1.42 (s, 3H), 1.09 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 142.3, 139.6, 137.9, 137.3, 130.7, 128.7, 128.2, 126.7, 126.6, 125.5, 125.2, 115.2, 76.1, 72.5, 59.2, 55.0, 41.7, 31.3, 28.9; **HRMS** (ESI) calcd for $C_{28}H_{32}NO$ $[M+H]^+$: 398.2484, found: 398.2490.

Cis-*N*,*N*-dibenzyl-1-(3-((*E*)-prop-1-en-1-yl)isochroman-4-yl)methanamine (4qa)



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 46 mg, 40% yield (combination yield of *cis*- and *trans*-product), > 20:1 dr. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15-7.29 (m, 13H), 6.93-6.95 (m, 1H), 5.60-5.75 (m, 2H), 4.72-4.82 (m, 2H), 4.26-4.27 (m, 1H), 3.73 (d, *J* = 14.0 Hz, 2H), 3.50 (d, *J* = 14.0 Hz, 2H), 2.85-2.90 (m, 2H), 2.63 (dd, *J* = 14.8 Hz, 9.6 Hz, 1H), 1.76 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.4, 137.9, 134.1, 130.1, 129.9, 128.9, 128.2, 127.3, 126.8, 126.4, 125.7, 124.0, 67.9, 58.9, 55.6, 40.8, 18.1; **HRMS** (ESI) calcd for $C_{27}H_{30}NO$ $[M+H]^+$: 384.2327, found: 384.2328.

(*E*)-*N*,*N*-dibenzyl-4-(1,3-dihydroisobenzofuran-1-yl)but-3-en-1-amine (5aa)

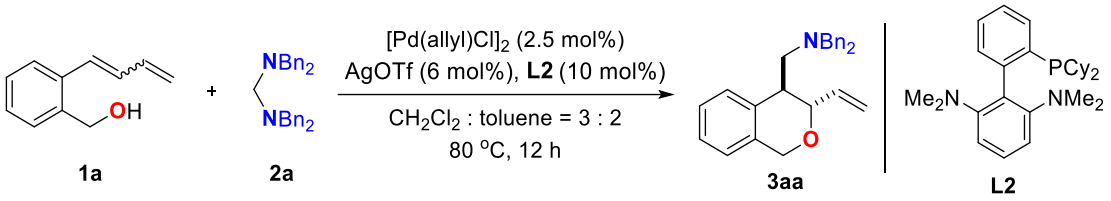


The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 50 mg, 45% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.36 (m, 4H), 7.19-7.30 (m, 9H), 7.06-7.08 (m, 1H), 5.77-5.84 (m, 1H), 5.51-5.57 (m, 2H), 5.03-5.14 (m, 2H), 3.53-3.61 (m, 4H), 2.57 (t, *J*

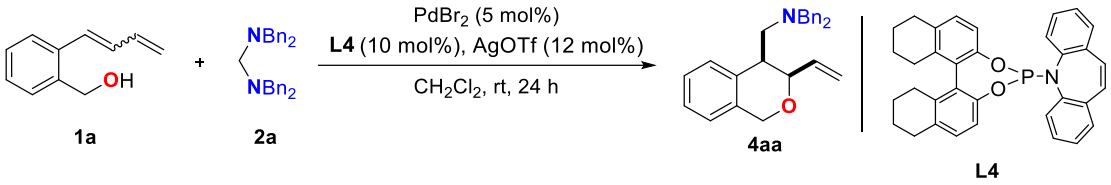
= 7.2 Hz, 2H), 2.28-2.34 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 141.4, 139.9, 139.3, 132.5, 130.7, 128.9, 128.3, 127.6, 127.4, 126.9, 122.10, 121.06, 85.4, 72.6, 58.3, 53.1, 30.1; **HRMS** (ESI) calcd for $C_{26}H_{28}NO$ $[M+H]^+$: 370.2171, found: 370.2169.

5. Synthetic Transformation of Products

Gram-scale synthesis of 3aa and 4aa

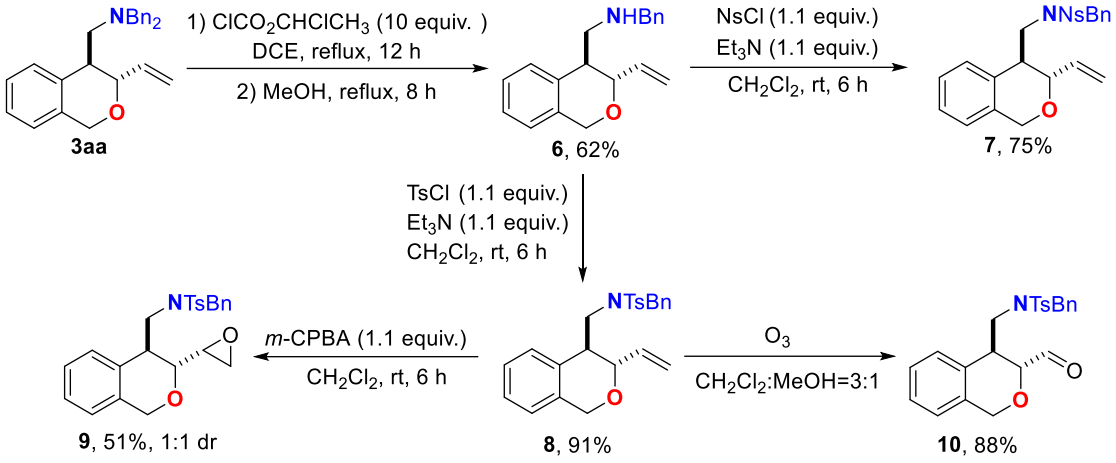


N,*N*,*N*′,*N*′-tetrabenzylmethanediamine **2a** (1.22 g, 3 mmol), $[Pd(allyl)Cl]_2$ (28 mg, 0.075 mmol), (2-(buta-1,3-dien-1-yl)phenyl)methanol **1a** (0.578 g, 3.6 mmol), AgOTf (46.1 mg, 0.18 mmol), **L2** (131 mg, 0.3 mmol) and solvent (CH_2Cl_2 : toluene = 3 : 2, 10 mL) were added to a 100 mL flame-dried Young-type tube under N_2 atmosphere. The reaction mixture was stirred at 80 °C for 12 hours, and then cooled to room temperature. The solvent was removed under reduced pressure, the residue was purified by flash chromatography (deluted with petroleum ether/ethyl acetate = 100/1 to 20/1) on a silica gel to afford the desired product **3aa** (1.00 g, 90% yield, > 20:1 dr).



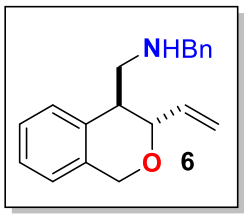
N,*N*,*N*′,*N*′-tetrabenzylmethanediamine **2a** (2.03 g, 5 mmol), $PdBr_2$ (67 mg, 0.25 mmol), (2-(buta-1,3-dien-1-yl)phenyl)methanol **1a** (0.96 g, 6 mmol), AgOTf (154 mg, 0.6 mmol), **L4** (258 mg, 0.5 mmol) and CH_2Cl_2 (10 mL) were added to a 100 mL flame-dried Young-type tube under N_2 atmosphere. The reaction mixture was stirred at room temperature for 24 hours. The solvent was removed under reduced pressure, the residue was purified by flash chromatography (deluted with petroleum ether/ethyl acetate = 100/1 to 20/1) on a silica gel to afford the desired product **4aa** (1.50 g, 82% yield, 14:1 dr).

Synthetic utility of the product



Trans-*N*,*N*-dibenzyl-1-(3-vinylisochroman-4-yl)methanamine **3aa** (738 mg, 2 mmol) was dissolved in DCE (20 mL) and 1-chloroethyl carbonochloridate (2.86 g, 20 mmol) was added dropwise at 0 °C with vigorous stirring[6]. After that, the reaction was refluxed for 24 hours. After evaporation of the solvent under reduced pressure, the mixture was added methanol and refluxed for 12 hours. After evaporation of the solvent under reduced pressure, the residue was dissolved in a mixture of ethyl acetate (10 mL) and quenched with saturated $NaHCO_3$ (10 mL). The resulting mixture was separated and the aqueous layer was extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with saturated $NaHCO_3$ (50 mL) and dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by flash column chromatography (deluted with petroleum ether/ethyl acetate = 20/1 to 5/1) on a silica gel to give the desired product **6** (350 mg, 62%).

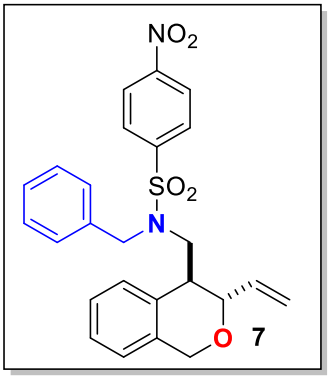
***Trans*-*N*-benzyl-1-(3-vinylisochroman-4-yl)methanamine (6)**



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27-7.33 (m, 4H), 7.21-7.24 (m, 2H), 7.13-7.20 (m, 2H), 6.98 (d, *J* = 7.5 Hz, 1H), 5.89-5.96 (m, 1H), 5.27-5.31 (m, 1H), 5.20-5.22 (d, *J* = 10.5 Hz, 1H), 4.74-4.81 (m, 2H), 4.53 (t, *J* = 6.0 Hz, 1H), 3.73-3.79 (m, 2H), 3.07-3.11 (m, 1H), 2.82-2.87 (m, 2H), 1.50 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 140.5, 137.1, 135.3, 134.6, 128.4, 128.2, 128.0, 127.0, 126.9, 126.2, 124.4, 118.3, 76.5, 65.5, 54.1, 51.4, 41.6; **HRMS** (ESI) calcd for $C_{19}H_{22}NO$ $[M+H]^+$: 280.1701, found: 280.1702.

The mixture of Et_3N (60.6 mg, 0.6 mmol) and *trans*-*N*-benzyl-1-(3-vinylisochroman-4-yl)methanamine **6** (140 mg, 0.5 mmol) was dissolved in CH_2Cl_2 (5.0 mL) and NsCl (122 mg, 0.55 mmol) was added under N_2 atmosphere at 0 °C with constantly stirring. After that, the mixture was stirred at room temperature for 4 hours. Water (5 mL) and ethyl acetate (5 mL) were added to this mixture and stirring for 5 minutes, the resulting mixture was separated and the aqueous layer was extracted with ethyl acetate (5 mL × 3). The combined organic layers were washed with brine for 3 times and dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by flash column chromatography (deluted with petroleum ether/ethyl acetate = 20/1 to 5/1) on a silica gel to give the desired product **7** (180 mg, 75%).

***Trans*-*N*-benzyl-4-nitro-*N*-((3-vinylisochroman-4-yl)methyl)benzenesulfonamide (7)**



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27-8.30 (m, 2H), 7.94-7.96 (m, 2H), 7.28-7.30 (m, 3H), 7.21-7.26 (m, 2H), 7.10-7.18 (m, 2H), 6.91-6.96 (m, 2H), 5.69-5.77 (m, 1H), 5.11 (d, *J* = 10.8 Hz, 1H), 5.03 (d, *J* = 17.6 Hz, 1H), 4.74 (d, *J* = 16.0 Hz, 1H), 4.65 (d, *J* = 15.6 Hz, 1H), 4.58 (d, *J* = 14.8 Hz, 1H), 4.45 (dd, *J* = 5.6 Hz, 1.2 Hz, 1H), 4.29 (d, *J* = 15.2 Hz, 1H), 3.79 (dd, *J* = 14.4 Hz, 10.0 Hz, 1H), 3.16 (dd, *J* = 14.0 Hz, 4.8 Hz, 1H), 2.85 (dd, *J* = 10.0 Hz, 4.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.0, 145.6, 135.5, 135.1, 134.6, 132.3, 129.6, 129.0, 128.6, 128.5, 128.4, 127.1, 126.8, 124.4, 124.3, 119.1, 72.0, 62.3, 54.1, 53.8, 40.0; **HRMS** (ESI) calcd for $C_{25}H_{25}N_2O_5S$ $[M+H]^+$: 465.1484, found: 465.1483.

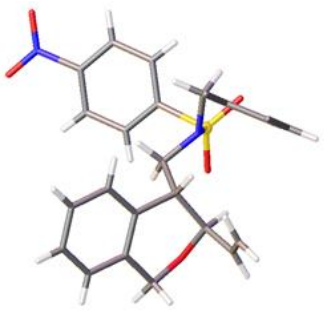
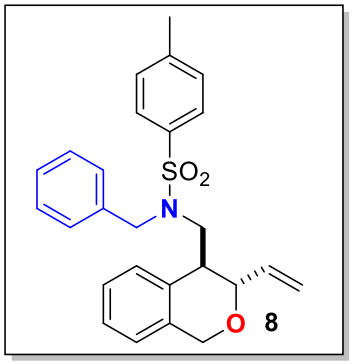


Figure S2. The X-ray structure of **7**

The mixture of Et_3N (35.1 mg, 0.32 mmol) and *Trans*-*N*-benzyl-1-(3-vinylisochroman-4-yl)methanamine **6** (81 mg, 0.29 mmol) was dissolved in CH_2Cl_2 (5.0 mL) and TsCl (61.0 mg, 0.32 mmol) was added under N_2 atmosphere at 0 °C with constantly stirring. After that, the mixture was stirred at room temperature for 4 hours. Water (5 mL) and ethyl acetate (5 mL) were added to this mixture and stirring for 5 minutes, the resulting mixture was separated and the aqueous layer was extracted with ethyl acetate (5 mL × 3). The combined organic layers were washed with brine for 3 times and dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by flash column chromatography (deluted with petroleum ether/ethyl acetate = 20/1 to 5/1) on a silica gel to give the desired product **8** (115.0 mg, 91%).

***Trans*-*N*-benzyl-4-methyl-*N*-((3-vinylisochroman-4-yl)methyl)benzenesulfonamide (8)**

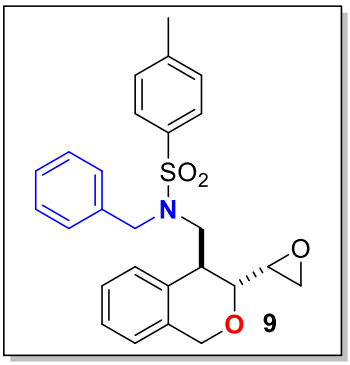


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72-7.73 (m, 2H), 7.23-7.30 (m, 7H), 7.09-7.15 (m, 2H), 6.93-6.95 (m, 1H), 6.88-6.90 (m, 1H), 5.67-5.74 (m, 1H), 5.04-5.06 (m, 1H), 4.98 (d, *J* = 17.0 Hz, 1H), 4.71 (d, *J* = 15.5 Hz, 1H), 4.61 (d, *J* = 15.5 Hz, 1H), 4.55 (d, *J* = 15.0 Hz, 1H), 4.48 (dd, *J* = 5.5 Hz, 1.5 Hz, 1H), 4.14 (d, *J* = 15.0 Hz, 1H), 3.71 (dd, *J* = 14.0 Hz, 10.0 Hz, 1H), 3.01 (dd, *J* = 14.0 Hz, 4.5 Hz, 1H), 2.78 (dd, *J* = 10.0 Hz, 4.5 Hz, 1H), 2.42 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.5, 136.5, 136.5, 135.4, 134.6, 132.9, 129.9, 129.7, 128.8, 128.7, 128.0, 127.5, 126.8, 126.6, 124.1, 118.6, 72.1, 62.3, 54.5, 53.9, 40.1, 21.6; **HRMS** (ESI) calcd for $C_{26}H_{28}NO_3S$ $[M+H]^+$: 434.1790, found: 434.1795.

Trans-*N*-benzyl-4-methyl-*N*-((3-vinylisochroman-4-yl)methyl)benzenesulfonamid **8** (347 mg, 0.80 mmol) was dissolved in CH_2Cl_2 (5.0 mL) and *m*-CPBA (152 mg, 0.88 mmol) was added under N_2 atmosphere at 0 °C with constantly stirring[7]. After that, the mixture was stirred at room temperature for 4 hours. Water (5 mL) and ethyl acetate (5 mL) were added to this mixture and stirring for 5 minutes, the resulting mixture was separated and the aqueous layer was extracted with ethyl acetate (5 mL × 3). The combined organic layers were washed with brine for 3 times and dried over anhydrous

Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by flash column chromatography (deluted with petroleum ether/ethyl acetate = 20/1 to 5/1) on a silica gel to give the desired product **9** (183 mg, 51%, 1:1 dr).

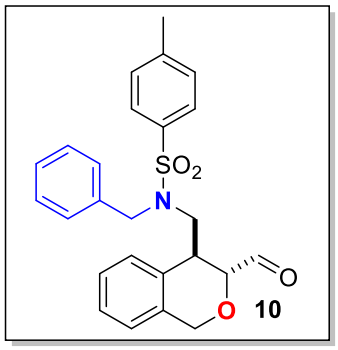
***Trans*-*N*-benzyl-4-methyl-*N*-((3-(oxiran-2-yl)isochroman-4-yl)methyl)benzenesulfonamide (9)**



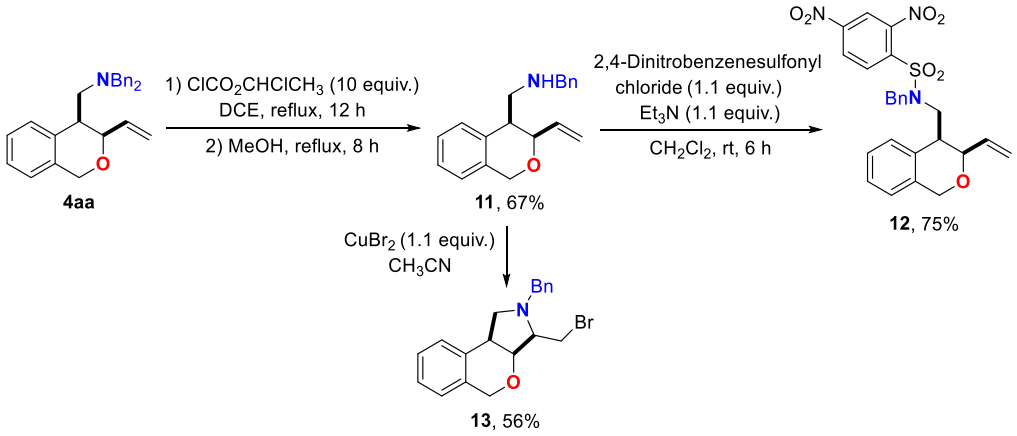
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71-7.73 (m, 2H), 7.22-7.34 (m, 7H), 7.10-7.18 (m, 2H), 6.88-6.98 (m, 2H), 4.84-4.90 (m, 1H), 4.70 (d, *J* = 15.5 Hz, 1H), 4.45-4.52 (m, 1H), 4.15 (dd, *J* = 14.5 Hz, 7.5 Hz, 1H), 3.59-3.91 (m, 2H), 2.96-3.02 (m 1H), 2.87-2.93 (m, 1H), 2.78 (dd, *J* = 10.0 Hz, 4.0 Hz, 0.50H), 2.64 (dd, *J* = 10.5 Hz, 4.5 Hz, 0.50H), 2.55-2.58 (m, 1H), 2.42 (s, 3H), 2.32 (dd, *J* = 5.0 Hz, 2.5 Hz, 0.50H), 2.16 (dd, *J* = 5.0 Hz, 2.5 Hz, 0.50H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.65, 143.56, 136.3, 136.13, 136.11, 134.3, 134.0, 132.6, 132.3, 130.0, 129.9, 129.8, 129.4, 129.3, 129.0, 128.82, 128.76, 128.1, 127.4, 127.0, 126.89, 126.87, 126.7, 124.4, 124.2, 73.4, 72.5, 63.8, 63.3, 54.5, 54.3, 53.8, 53.6, 51.6, 50.8, 45.2, 44.3, 38.4, 37.3, 21.6; **HRMS** (ESI) calcd for $C_{26}H_{28}NO_4S$ $[M+H]^+$: 450.1739, found: 450.1739.

Trans-*N*-benzyl-4-methyl-*N*-((3-vinylisochroman-4-yl)methyl)benzenesulfonamid **8** (87 mg, 0.2 mmol) was dissolved in solvent (CH_2Cl_2 / MeOH = 3 : 1, 2.0 mL) and O_3 was bubbled at -78 °C with constantly stirring for 6 minutes[8]. After that, the mixture of Me_2S / H_2O = 1 : 1 (1 mL) was added at -78 °C and then stirred at room temperature for 1 hour. Water (5 mL) and CH_2Cl_2 (5 mL) were added to this mixture and stirring for 5 minutes, the resulting mixture was separated and the aqueous layer was extracted with CH_2Cl_2 (5 mL × 3). The combined organic layers were washed with brine for 3 times and dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by flash column chromatography (deluted with petroleum ether/ethyl acetate = 30/1 to 10/1) on a silica gel to give the desired product **10** (77 mg, 88%).

***Trans*-*N*-benzyl-*N*-((3-formylisochroman-4-yl)methyl)-4-methylbenzenesulfonamide (10)**



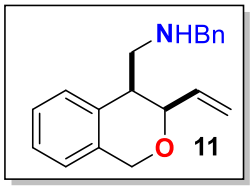
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (s, 1H), 7.72-7.74 (m, 2H), 7.25-7.34 (m, 7H), 7.08-7.15 (m, 2H), 6.87-6.90 (m, 2H), 5.04 (d, *J* = 16.0 Hz, 1H), 4.77 (d, *J* = 15.6 Hz, 1H), 4.62 (d, *J* = 14.4 Hz, 1H), 4.51 (d, *J* = 1.2 Hz, 1H), 4.12 (d, *J* = 14.4 Hz, 1H), 3.71 (dd, *J* = 14.0 Hz, 10.8 Hz, 1H), 3.16 (dd, *J* = 10.4 Hz, 4.0 Hz, 1H), 3.01 (dd, *J* = 14.0 Hz, 4.4 Hz, 1H), 2.42 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.4, 143.7, 136.0, 135.8, 133.4, 130.8, 129.8, 129.0, 128.8, 128.7, 128.6, 128.2, 127.3, 126.8, 124.3, 76.7, 64.5, 54.3, 53.0, 35.9, 21.5; **HRMS** (ESI) calcd for $C_{25}H_{26}NO_4S$ $[M+H]^+$: 436.1583, found: 436.1574.



Cis-*N*,*N*-dibenzyl-1-(3-vinylisochroman-4-yl)methanamine **4aa** (738 mg, 2 mmol) was dissolved in DCE (20 mL) and 1-chloroethyl carbonochloridate (2.86 g, 20 mmol) was added dropwise at 0 °C with vigorous stirring[6]. After that, the reaction was refluxed for 24 hours. After evaporation of the solvent under reduced pressure, the mixture was added methanol and refluxed for 12 hours. The solvent was removed under reduced pressure, the residue was dissolved in a mixture of ethyl acetate (10 mL) and quenched with saturated $NaHCO_3$ (10 mL). The resulting mixture was separated and the aqueous layer was extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with saturated $NaHCO_3$ (50 mL) and dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by flash

column chromatography (deluted with petroleum ether/ethyl acetate = 20/1 to 5/1) on a silica gel to give the desired product **11** (374 mg, 67%).

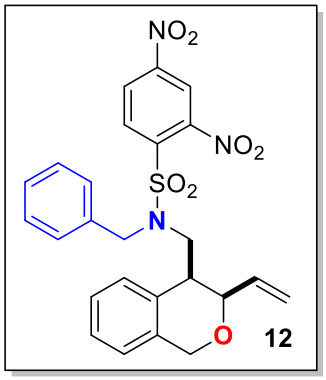
***Cis*-*N*-benzyl-1-(3-vinylisochroman-4-yl)methanamine (11)**



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19-7.31 (m, 8H), 7.02-7.04 (m, 1H), 5.97-6.05 (m, 1H), 5.40-5.44 (m, 1H), 5.23-5.26 (m, 1H), 4.99 (d, *J* = 15.6 Hz, 1H), 4.90 (d, *J* = 15.2 Hz, 1H), 4.34-4.36 (m, 1H), 3.77 (d, *J* = 13.6 Hz, 1H), 3.70 (d, *J* = 13.2 Hz, 1H), 3.05 (dd, *J* = 11.6 Hz, 5.2 Hz, 1H), 2.90-2.93 (m, 1H), 2.83 (dd, *J* = 11.6 Hz, 6.4 Hz, 1H), 1.73 (br, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 140.5, 136.9, 136.7, 134.6, 129.3, 128.4, 128.1, 126.9, 126.7, 126.5, 124.3, 115.6, 77.3, 68.4, 54.2, 50.8, 41.9; **HRMS** (ESI) calcd for $C_{19}H_{22}NO$ $[M+H]^+$: 280.1701, found: 280.1703.

The mixture of Et_3N (44 mg, 0.43 mmol) and *cis*-*N*-benzyl-1-(3-vinylisochroman-4-yl)methanamine **11** (100 mg, 0.36 mmol) was dissolved in CH_2Cl_2 (5.0 mL) and 2,4-Dinitrobenzenesulfonyl chloride (115 mg, 0.43 mmol) was added under N_2 atmosphere at 0 ^{o}C with constantly stirring. After that, the mixture was stirred at room temperature for 4 hours. Water (5 mL) and ethyl acetate (5 mL) were added to this mixture and stirring for 5 minutes, the resulting mixture was separated and the aqueous layer was extracted with ethyl acetate (5 mL ×3). The combined organic layers were washed with brine for 3 times and dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by flash column chromatography (deluted with petroleum ether/ethyl acetate = 20/1 to 5/1) on a silica gel to give the desired product **12** (138 mg, 75%).

***Cis*-*N*-benzyl-2,4-dinitro-*N*-((3-vinylisochroman-4-yl)methyl)benzenesulfonamide (12)**



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 2.0 Hz, 1H), 8.05 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.26-7.28 (m, 3H), 7.13-7.17 (m, 3H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.83-6.89 (m, 2H), 5.69-5.75 (m, 1H), 5.29-5.33 (m, 1H), 5.14-5.16 (m, 1H), 4.82-4.92 (m, 2H), 4.62 (d, *J* = 16.0 Hz, 1H), 4.45 (d, *J* = 15.5 Hz, 1H), 4.26-4.28 (m, 1H), 3.56-3.68 (m, 2H), 3.03-3.05 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 149.2, 147.4, 139.4, 135.2, 134.9, 134.6, 134.1, 132.1, 130.0, 129.0, 128.7, 128.4, 127.3, 126.2, 125.8, 124.3, 119.5, 116.3, 76.2, 68.3, 52.5, 49.0, 39.4; **HRMS** (ESI) calcd for $C_{25}H_{24}N_3O_7S$ $[M+H]^+$: 510.1335, found: 510.1324.

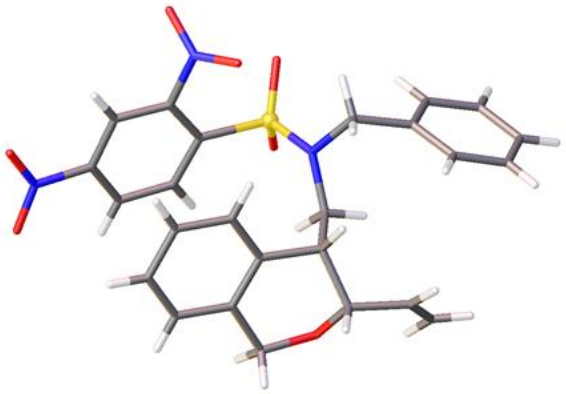
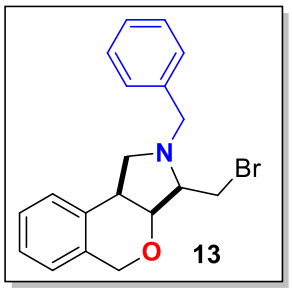


Figure S3. The X-ray structure of **12.**

Cis-N-benzyl-1-(3-vinylisochroman-4-yl)methanamine **10** (56 mg, 0.20 mmol) was dissolved in CH_3CN (5.0 mL), the mixture was added $CuBr_2$ (45 mg, 0.20 mmol) at room temperature with constantly stirring. After that, the mixture was stirred at room temperature for 6 hours. Water (5 mL) and ethyl acetate (5 mL) were added to this mixture and stirring for 5 minutes, the resulting mixture was separated and the aqueous layer was extracted with ethyl acetate (5 mL × 3). The combined organic layers were washed with brine for 3 times and dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by flash column chromatography (deluted with petroleum ether/ethyl acetate = 100/1 to 20/1) on a silica gel to give the desired product **13** (40 mg, 56%)[9].

2-benzyl-3-(bromomethyl)-1,2,3,3a,5,9b-hexahydroisochromeno[3,4-c]pyrrole (13)

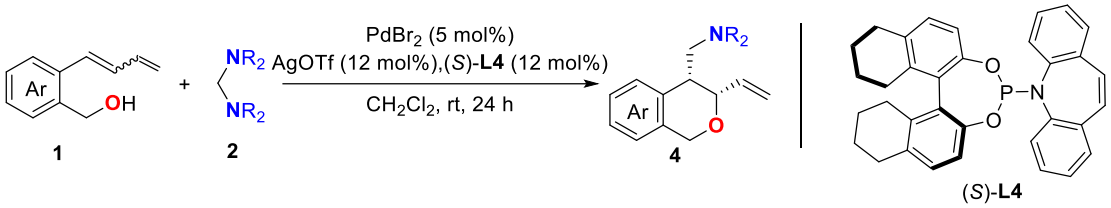


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.34 (m, 5H), 7.13-7.21 (m, 2H), 7.00-7.05 (m, 2H), 5.03 (d, *J* = 15.2 Hz, 1H), 4.88 (d, *J* = 15.2 Hz, 1H), 4.33-4.38 (m, 1H), 3.93 (s, 1H), 3.51-3.59 (m, 2H), 2.97-3.02 (m, 2H), 2.82 (dd, *J* = 11.2 Hz, 4.0 Hz, 1H), 2.69 (t, *J* = 11.2 Hz, 1H), 2.43 (t, *J* = 11.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.8, 134.9, 134.4, 129.1, 128.7, 128.5, 127.4, 127.0, 126.7, 124.3, 74.0, 68.7, 62.1, 55.4, 55.0, 49.4, 40.2; **HRMS** (ESI) calcd for $C_{19}H_{21}BrNO$ $[M+H]^+$: 358.0807, found: 358.0815.

6. Catalytic Asymmetric Reactions with Chiral L4

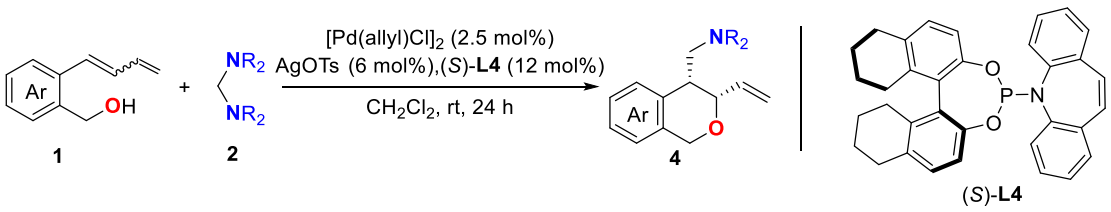
7.1 The general procedure for the asymmetic reactions

Method C:



In a glove box, the mixture of $PdBr_2$ (4.0 mg, 0.015 mmol), (*S*)-**L4** (18.5 mg, 0.036 mmol), AgOTf (9.3 mg, 0.036 mmol) and CH_2Cl_2 (1 mL) was added to a Young-type tube and stirred at 45 ^oC for 30 minutes. After the mixture was cooled to room temperature, *N*,*N*,*N*′,*N*′-tetrabenzylmethanediamine **2** (0.3 mmol) and **1** (0.36 mmol) were added under nitrogen atmosphere. The reaction mixture was degassed via the freeze-thaw method and stirred at room temperature for 24 hours. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (eluted with petroleum ether/diethyl ether = 200/1 to 50/1) on a silica gel to give the desired chiral product **4**. The dr value of the crude reaction mixture was determined by ^{1}HNMR analysis. The ee value was determined by HPLC with chiral column.

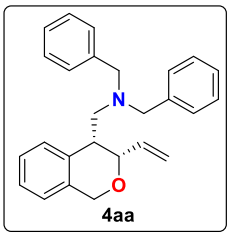
Method D:



In a glove box, the mixture of $[Pd(allyl)Cl]_2$ (2.8 mg, 0.0075 mmol), (*S*)-**L4** (18.5 mg, 0.036 mmol), AgOTs (5.0 mg, 0.018 mmol) and CH_2Cl_2 (1 mL) was added to a Young-type tube and stirred at 45 ^oC for 30 minutes. After the mixture was cooled to room temperature, *N*,*N*,*N*′,*N*′-tetrabenzylmethanediamine **2** (0.3 mmol) and **1** (0.36 mmol) were added under nitrogen atmosphere. The reaction mixture was degassed via the freeze-thaw method and stirred at room temperature for 24 hours. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (eluted with petroleum ether/diethyl ether = 200/1 to 50/1) on a silica gel to give the desired chiral product **4**. The dr value of the crude reaction mixture was

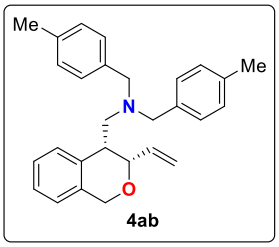
determined by ^{1}HNMR analysis. The ee value was determined by HPLC with chiral column.

***Cis*-*N*,*N*-dibenzyl-1-((3*S*,4*R*)-3-vinylisochroman-4-yl)methanamine (4aa)**



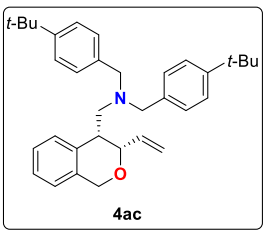
The title compound was prepared according to the general procedure by using (*S*)-**L4** as ligand and purified by column chromatography to give colorless oil. (**Method C**: 96 mg, 87% yield, 14:1 dr; **Method D**: 43 mg, 39% yield, dr = 12 : 1). The spectral data of **4aa** was consistent with spectral data from the general method preparation. The ee was determined to be (**Method C**: 74% ee, **Method D**: 92% ee) [Determined by HPLC with a Chiralpak AD-H column (90 : 10 = Hexane : isopropanol, 0.5 mL / min, 220 nm, 25 ^{o}C); t (major) = 7.8 min, t (minor) = 8.4 min. $[\alpha]_D^{20}$= 45.4 ($CHCl_3$, c 0.88)].

***Cis*-*N*,*N*-bis(4-methylbenzyl)-1-((3*S*,4*R*)-3-vinylisochroman-4-yl)methanamine (4ab)**



The title compound was prepared according to the general procedure by using (*S*)-**L4** as ligand and purified by column chromatography to give colorless oil. (**Method C**: 91 mg, 76% yield, 15:1 dr; **Method D**: 43 mg, 36% yield, 13:1 dr). The spectral data of **4ab** was consistent with spectral data from the general method preparation. The ee was determined to be (**Method C**: 67% ee, **Method D**: 85% ee) [Determined by HPLC with a Chiralpak AD-H column (98 : 2 = Hexane : isopropanol, 0.7 mL / min, 254 nm, 25 ^{o}C); t (major) = 7.0 min, t (minor) = 8.2 min. $[\alpha]_D^{20}$= 55.6 ($CHCl_3$, c 0.51)].

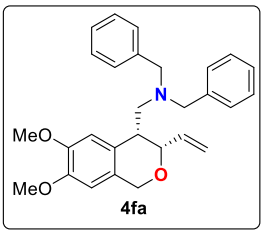
***Cis*-*N*,*N*-bis(4-(tert-butyl)benzyl)-1-((3*S*,4*R*)-3-vinylisochroman-4-yl)methanamine (4ac)**



The title compound was prepared according to the general procedure by using (*S*)-**L4** as ligand and purified by column chromatography to give colorless oil. (**Method C**: 96 mg, 64% yield, 14:1 dr; **Method D**: 46 mg, 32% yield, 13:1 dr). The spectral data of **4ac** was consistent with spectral data from the general method preparation. The ee was determined to be (**Method C**: 73% ee, **Method**

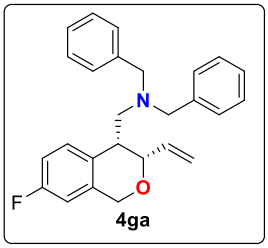
D: 89% ee) [Determined by HPLC with a Chiralcel OD-H column (99.5 : 0.5 = Hexane : isopropanol, 1.0 mL / min, 254 nm, 25 °C); t (major) = 12.1 min, t (minor) = 13.9 min. $[\alpha]_D^{20}$= 49.6 ($CHCl_3$, c 0.38)].

***Cis*-*N*,*N*-dibenzyl-1-((3*S*,4*R*)-6,7-dimethoxy-3-vinylisochroman-4-yl)methanamine (4fa)**



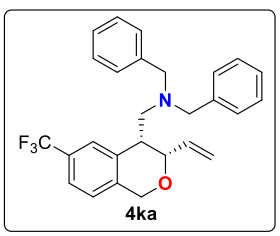
The title compound was prepared according to the general procedure by using (*S*)-**L4** as ligand and purified by column chromatography to give colorless oil. (**Method C**: 117 mg, 91% yield, 6:1 dr; **Method D**: 48 mg, 37% yield, 10:1 dr). The spectral data of **4ad** was consistent with spectral data from the general method preparation. The ee was determined to be (**Method C**: 79% ee, **Method D**: 92% ee) [Determined by HPLC with a Chiralpak AD-H column (90 : 10 = Hexane : isopropanol, 1.0 mL / min, 254 nm, 25 °C); t (minor) = 9.3 min, t (major) = 17.1 min. $[\alpha]_D^{20}$= 21.4 ($CHCl_3$, c 0.44)].

***Cis*-*N*,*N*-dibenzyl-1-((3*S*,4*R*)-7-fluoro-3-vinylisochroman-4-yl)methanamine (4ga)**



The title compound was prepared according to the general procedure by using (*S*)-**L4** as ligand and purified by column chromatography to give colorless oil. (**Method C**: 89 mg, 77% yield, 10:1 dr; **Method D**: 36 mg, 31% yield, 6:1 dr). The spectral data of **4ga** was consistent with spectral data from the general method preparation. The ee was determined to be (**Method C**: 84% ee, **Method D**: 94% ee) [Determined by HPLC with a Chiralpak AD-H column (98 : 2 = Hexane : isopropanol, 0.7 mL / min, 220 nm, 25 °C); t (major) = 8.2 min, t (minor) = 9.9 min. $[\alpha]_D^{20}$= 63.8 ($CHCl_3$, c 0.34)].

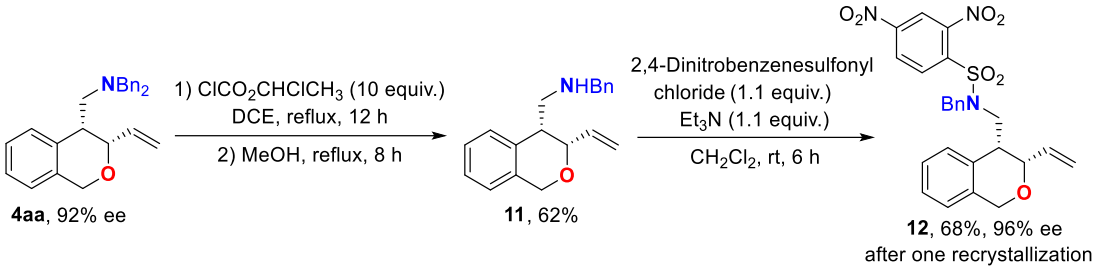
***Cis*-*N*-benzyl-2,4-dinitro-*N*-(((3*S*,4*R*)-3-vinylisochroman-4-yl)methyl)benzenesulfonamide (4ka)**



The title compound was prepared according to the general procedure by using (*S*)-**L4** as ligand and purified by column chromatography to give colorless oil. (**Method C**: 101 mg, 77% yield, > 20:1 dr; **Method D**: 88 mg, 67% yield, > 20:1 dr). The spectral data of **4aa** was consistent with spectral data from the

general method preparation. The ee was determined to be (**Method C**: 93% ee, **Method D**: 94% ee) [Determined by HPLC with a Chiralcel OD-H column (98 : 2 = Hexane : isopropanol, 1.0 mL / min, 254 nm, 25 °C); t (minor) = 5.1 min, t (major) = 6.0 min. $[\alpha]_D^{20}$= 75.8 ($CHCl_3$, c 0.81].

7.2 Determination of the Absolute Stereochemistry:



N,*N*-dibenzyl-1-((*3S*,*4R*)-3-vinylisochroman-4-yl)methanamine **4aa** (256 mg, 0.69 mmol) was dissolved in DCE (10 mL) and 1-chloroethyl carbonochloridate (0.99 g, 6.9 mmol) was added dropwise at 0 °C with vigorous stirring[6]. After that, the reaction was refluxed for 24 hours. After evaporation of the solvent under reduced pressure, the residue was dissolved in a mixture of ethyl acetate (5 mL) and quenched with saturated $NaHCO_3$ (5 mL). The resulting mixture was separated and the aqueous layer was extracted with ethyl acetate (5 mL ×3). The combined organic layers were washed with saturated $NaHCO_3$ (50 mL) and 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 5/1) to give the desired chiral product **11** (119 mg, 62%).

The mixture of Et_3N (44 mg, 0.43 mmol) and *N*-benzyl-1-((*3S*,*4R*)-3-vinylisochroman-4-yl)methanamine **11** (100 mg, 0.36 mmol) was dissolved in CH_2Cl_2 (5.0 mL) and 2,4-dinitrobenzenesulfonyl chloride (115 mg, 0.43 mmol) was added under N_2 atmosphere at 0 °C with constantly stirring. After that, the mixture was stirred at room temperature for 4 hours. Water (5 mL) and ethyl acetate (5 mL) were added to this mixture and stirring for 5 minutes, the resulting mixture was separated and the aqueous layer was extracted with ethyl acetate (5 mL ×3). The combined organic layers were washed with brine for 3 times and dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by flash column chromatography (deluted with petroleum ether/ethyl acetate = 20/1 to 5/1) on

a silica gel to give the desired chiral product **12** (125 mg, 68%). The ee was determined to be 96% ee (after one recrystallization) [Determined by HPLC with a Chiralpak AD-H column (90 : 10 = Hexane : isopropanol, 1.0 mL / min, 254 nm, 25 ^{o}C); t (minor) = 32.9 min, t (major) = 34.5 min. $[\alpha]_D^{20}$= -11.6 ($CHCl_3$, c 0.90).

As shown below, we have determined the absolute stereochemistry of chiral product **4aa** by X-ray diffraction of the derivative chiral compound **12**. By analogy, the other cyclization products were assigned as (*3S,4R*) tentatively as well.

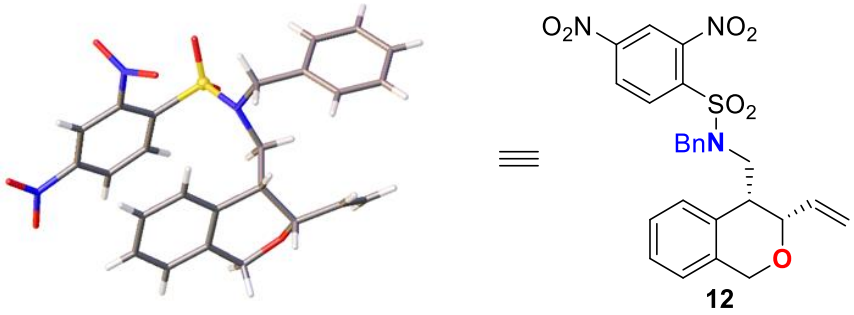
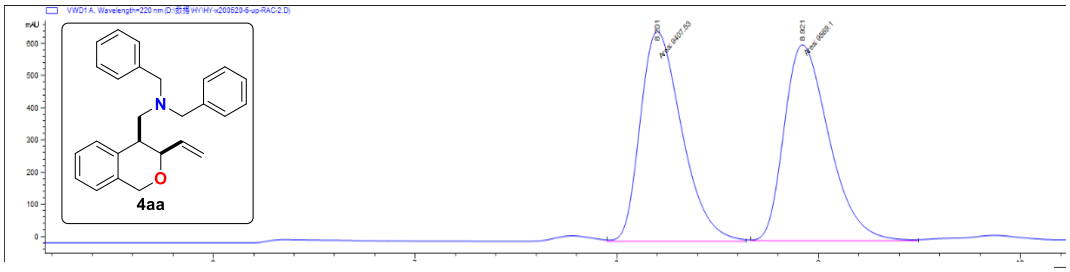
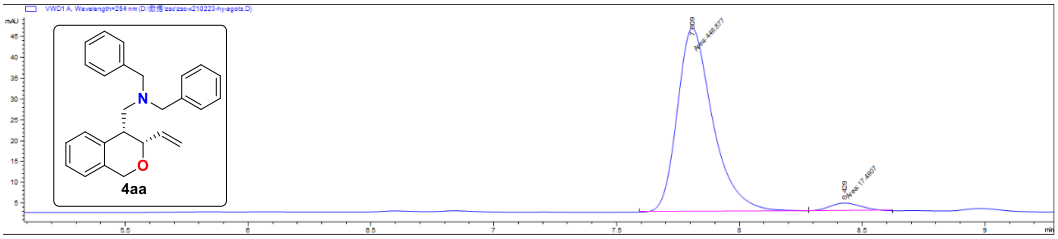


Figure S4. X-ray structure of **(*3S,4R*-12)**

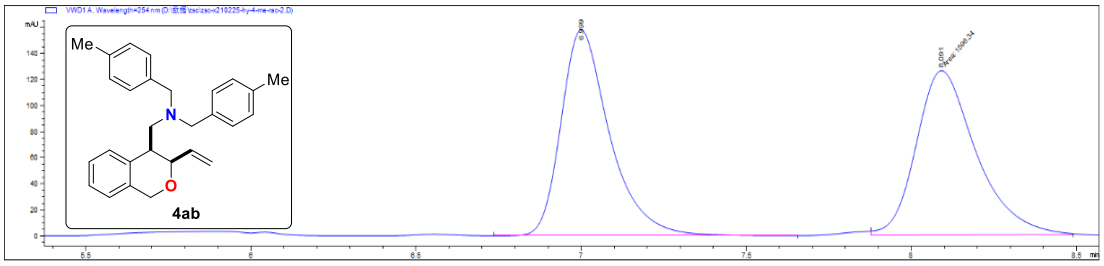
7. Copies of HPLC of products



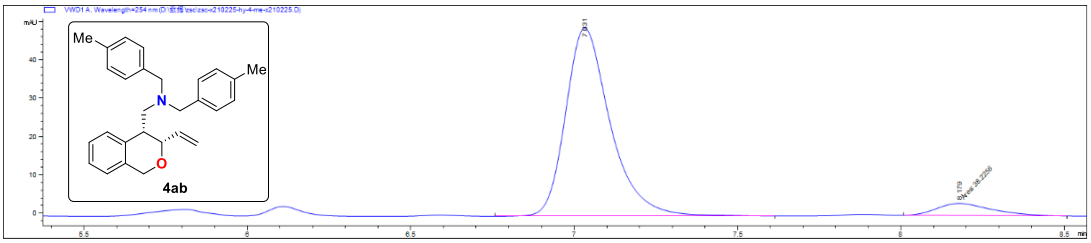
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.201	FM	0.2396	9407.53223	654.49213	49.5743
2	8.921	MF	0.2604	9569.09766	612.49451	50.4257
Totals :				1.89766e4	1266.98663	



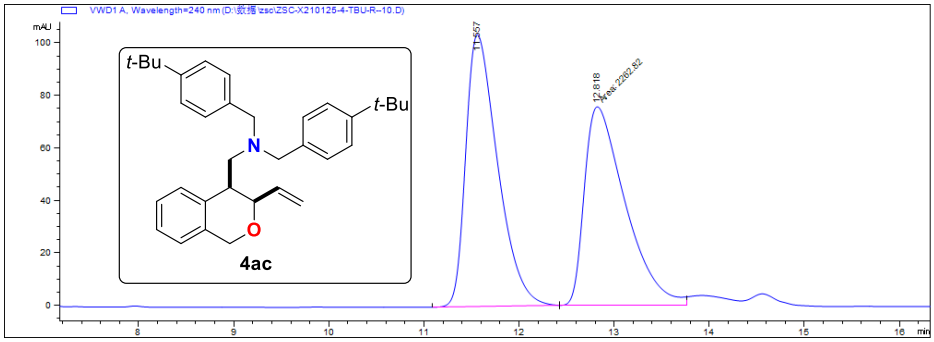
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.809	MF	0.1680	446.87747	44.34336	96.2334
2	8.429	FM	0.1537	17.49071	1.89647	3.7666
Totals :				464.36818	46.23982	



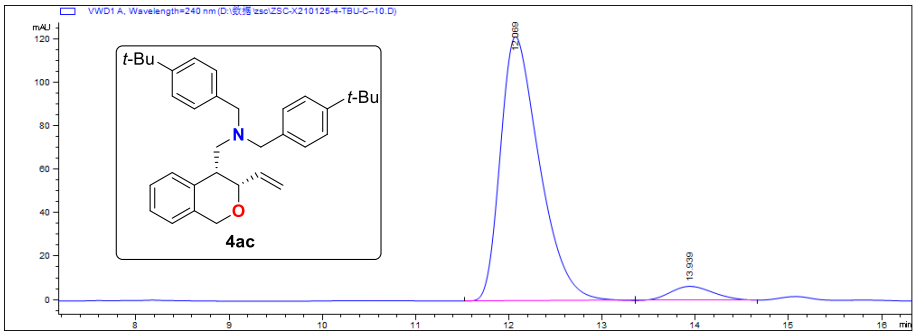
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.999	BB	0.1537	1615.41113	157.40831	50.2968
2	8.091	MM	0.2114	1596.34375	125.83637	49.7032
Totals :				3211.75488	283.24468	



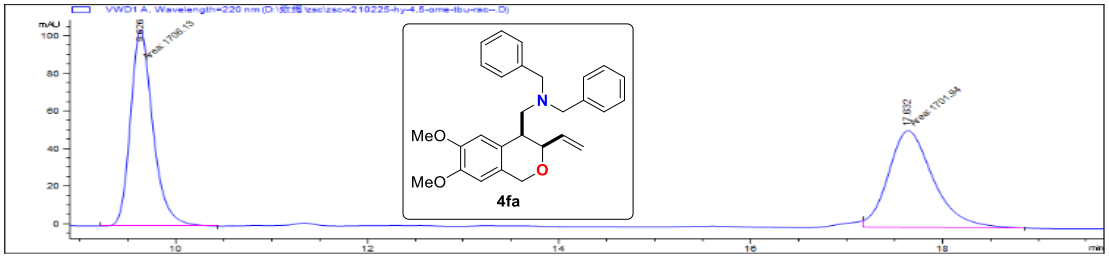
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.031	BB	0.1431	466.52808	49.00911	92.4269
2	8.179	MM	0.1991	38.22557	3.19962	7.5731
Totals :				504.75365	52.20873	



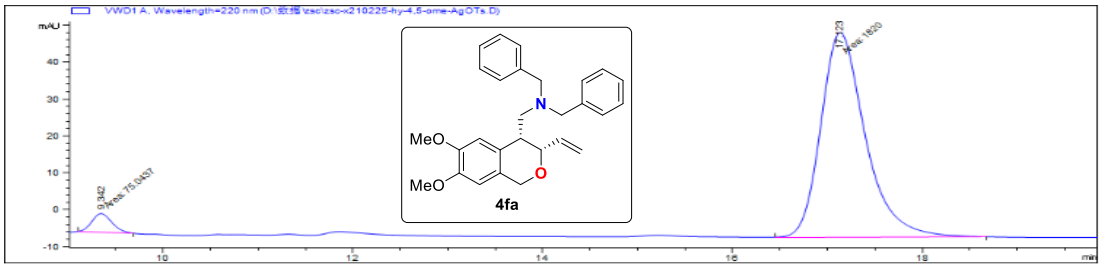
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.557	BB	0.3544	2401.69873	103.23074	51.4886
2	12.818	MF	0.5002	2262.82471	75.40160	48.5114
Totals :				4664.52344	178.63233	



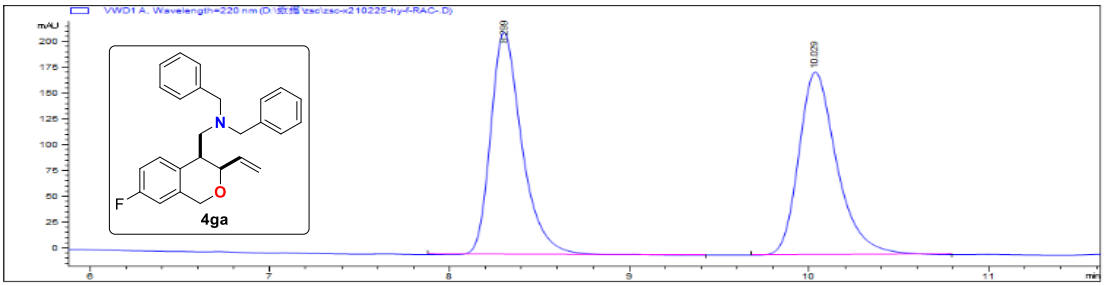
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.069	BB	0.4423	3543.88965	121.85902	94.5114
2	13.939	BB	0.4977	205.80540	6.42545	5.4886
Totals :				3749.69505	128.28447	



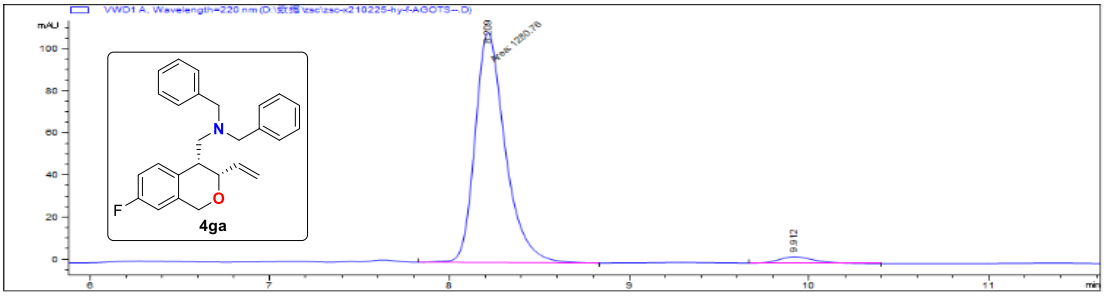
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.626	MM	0.2724	1706.13293	104.39068	50.0615
2	17.632	FM	0.5470	1701.94202	51.86120	49.9385
Totals :				3408.07495	156.25188	



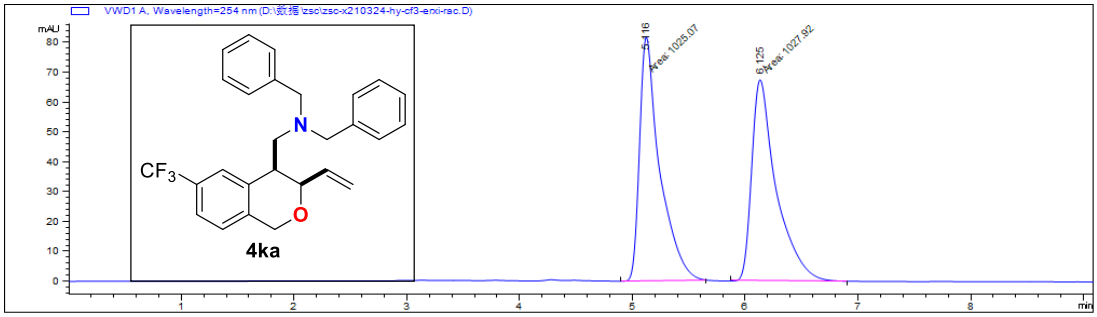
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.342	MM	0.2463	75.04367	5.07762	3.9600
2	17.123	MM	0.5452	1820.00220	55.63900	96.0400
Totals :				1895.04587	60.71662	



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.299	BV R	0.1835	2610.06250	215.21078	49.9977
2	10.029	BB	0.2241	2610.30225	176.90424	50.0023
Totals :				5220.36475	392.11502	

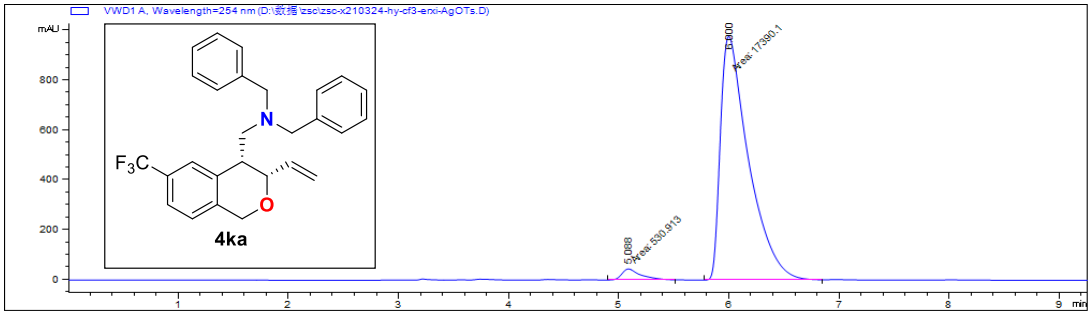


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.209	FM	0.1951	1280.76013	109.40417	96.8627
2	9.912	BB	0.2062	41.48204	3.05896	3.1373
Totals :				1322.24218	112.46314	



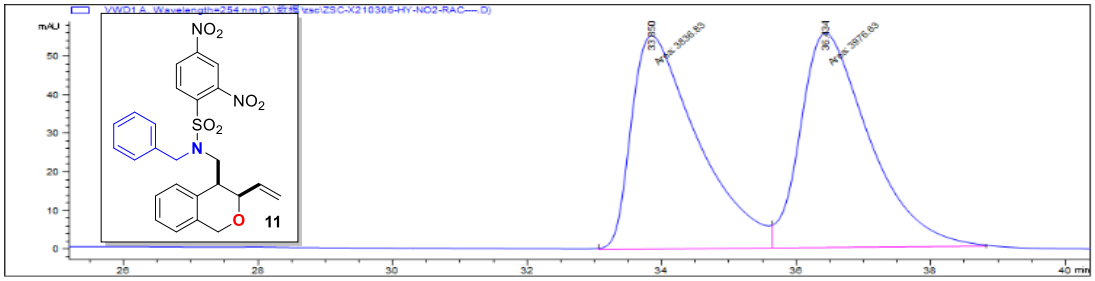
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.116	MF	0.2080	1025.06555	82.12666	49.9304
2	6.125	MF	0.2527	1027.92224	67.78989	50.0696

Totals : 2052.98779 149.91656

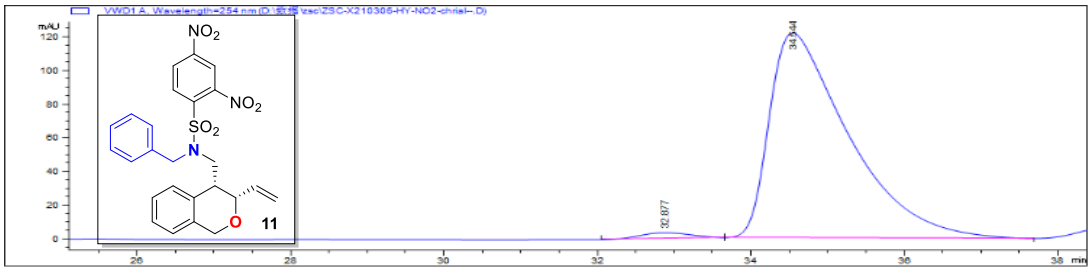


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.088	MM	0.1997	530.91290	44.30978	2.9625
2	6.000	MM	0.2960	1.73901e4	979.20825	97.0375

Totals : 1.79210e4 1023.51803



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.850	MF	1.1524	3836.83496	55.49157	49.1054
2	36.434	FM	1.1889	3976.62866	55.74629	50.8946
Totals :				7813.46362	111.23786	

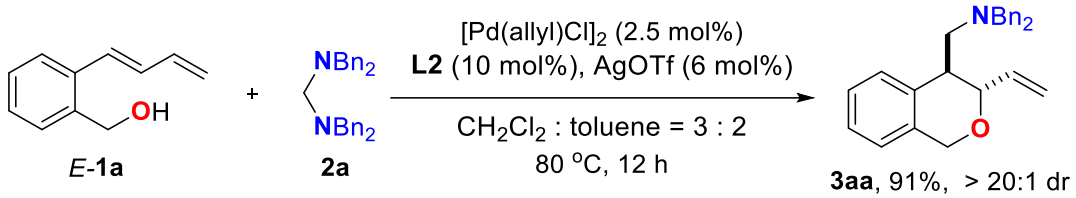


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.877	BB	0.6748	158.78146	3.50986	1.7809
2	34.544	BB	1.0559	8757.04492	121.92727	98.2191
Totals :				8915.82639	125.43713	

9 Mechanistic Studies

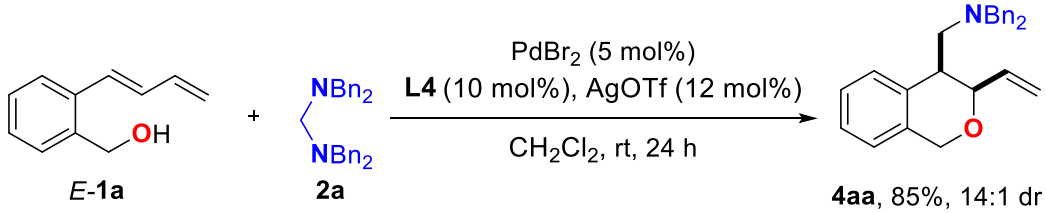
9.1 Control experiment

9.1.1 Control experiment by using *E*-1a as starting material



E-**1a** **2a** **3aa**, 91%, > 20:1 dr

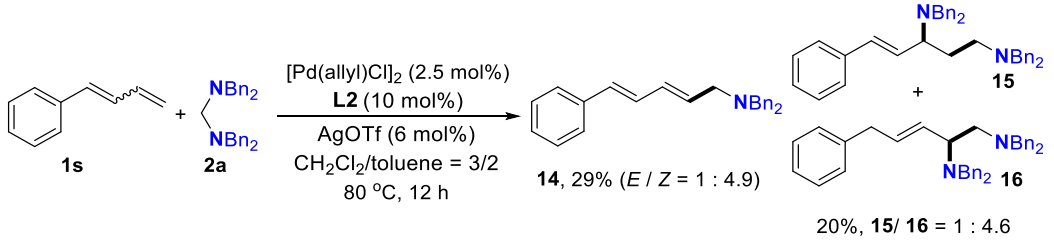
Aminal **2a** (122 mg, 0.30 mmol), [Pd(allyl)Cl]$_2$ (2.8 mg, 2.5 mol%), **L2** (13.0 mg, 10 mol%), AgOTf (4.6 mg, 6 mol%), dienol *E*-**1a** (58 mg, 0.36 mmol) and solvent (CH_2Cl_2 : toluene = 3 : 2, 1.0 mL) were added to a 25 mL flame-dried Young-type tube under N_2 atmosphere. The reaction mixture was stirred at 80 °C for 12 hours, and then cooled to room temperature. The solvent was removed under reduced pressure, the residue was purified by flash chromatography (deluted with petroleum ether/ethyl acetate = 200/1 to 50/1) on a silica gel to give product **3aa** as colorless oil (101 mg, 91%, > 20:1 dr).



E-**1a** **2a** **4aa**, 85%, 14:1 dr

Aminal **2a** (122 mg, 0.30 mmol), $PdBr_2$ (4.0 mg, 5 mol%), **L4** (15.5 mg, 10 mol%), AgOTf (9.3 mg, 12 mol%), dienol *E*-**1a** (58 mg, 0.36 mmol) and CH_2Cl_2 (1.0 mL) were added to a 25 mL flame-dried Young-type tube under N_2 atmosphere. The reaction mixture was stirred at room temperature for 12 hours, and then cooled to room temperature. The solvent was removed under reduced pressure, the residue was purified by flash chromatography (deluted with petroleum ether/ethyl acetate = 200/1 to 50/1) on a silica gel to give product **4aa** as colorless oil (94 mg, 85%, 14:1 dr).

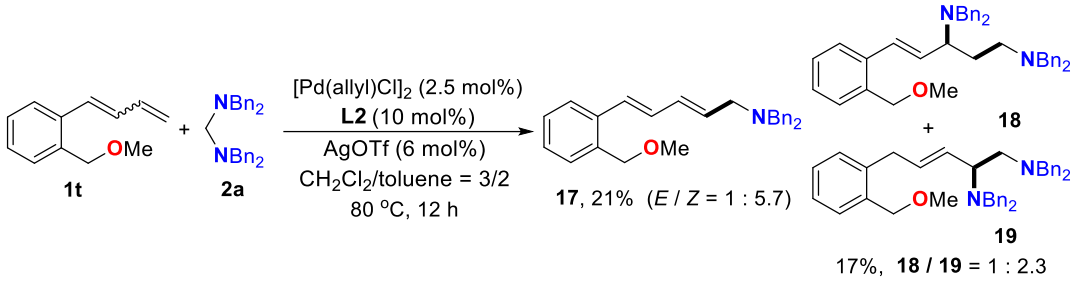
9.1.2 Control experiment



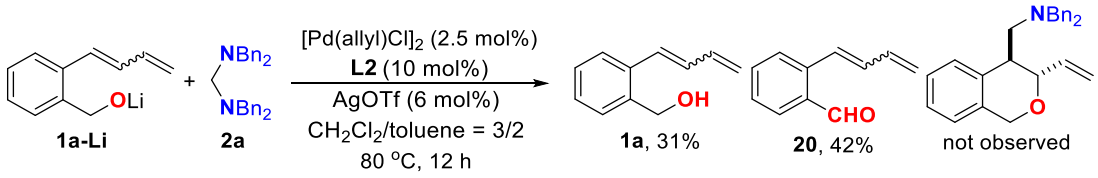
1s **2a** **14**, 29% (*E* / *Z* = 1 : 4.9) 20%, **15**/ **16** = 1 : 4.6

Aminal **2a** (122 mg, 0.30 mmol), [Pd(allyl)Cl]$_2$ (2.8 mg, 2.5 mol%), **L2** (13.0 mg, 10 mol%), AgOTf (4.6 mg, 6 mol%), diene **1s** (49 mg, 0.36 mmol) and solvent (CH_2Cl_2 :

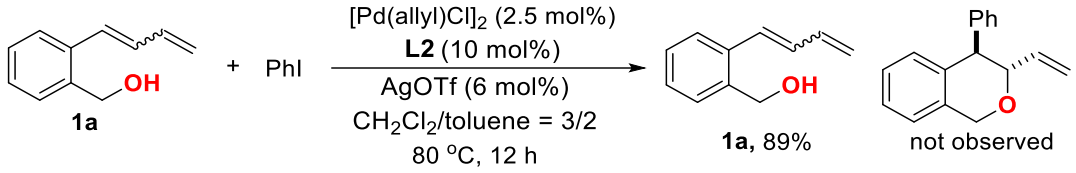
toluene = 3 : 2, 1.0 mL) were added to a 25 mL flame-dried Young-type tube under N_2 atmosphere. The reaction mixture was stirred at 80 °C for 12 hours, and then cooled to room temperature. The solvent was removed under reduced pressure, the residue was purified by flash chromatography (deluted with petroleum ether/ethyl acetate = 200/1 to 50/1) on a silica gel to give products **14** (29 mg, 29%, *E*/ *Z* = 1:4.9, determined by ^{1}HNMR), **15** and **16** (32 mg, 20%, **15**:**16** = 1:4.6, determined by ^{1}HNMR) as colorless oil. The spectral data of **14**, **15** and **16** were consistent with spectral data from the reported methods[10,11].



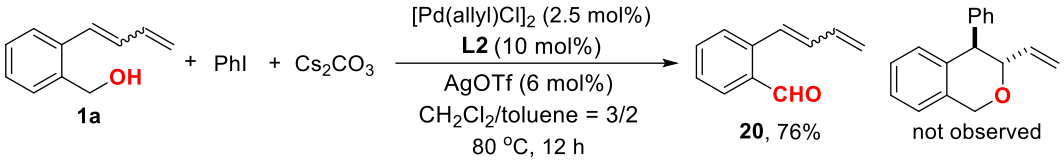
Aminal **2a** (122 mg, 0.30 mmol), $[Pd(allyl)Cl]_2$ (2.8 mg, 2.5 mol%), **L2** (13.0 mg, 10 mol%), AgOTf (4.6 mg, 6 mol%), diene **1t** (63 mg, 0.36 mmol) and solvent (CH_2Cl_2 : toluene = 3 : 2, 1.0 mL) were added to a 25 mL flame-dried Young-type tube under N_2 atmosphere. The reaction mixture was stirred at 80 °C for 12 hours, and then cooled to room temperature. The solvent was removed under reduced pressure, the residue was purified by flash chromatography (deluted with petroleum ether/ethyl acetate = 200/1 to 50/1) on a silica gel to give products **17** (24 mg, 21%, *E*/ *Z* = 1: 5.7, determined by ^{1}HNMR), **18** and **19** (29 mg, 17%, **18**: **19** = 1:2.3) as colorless oil.



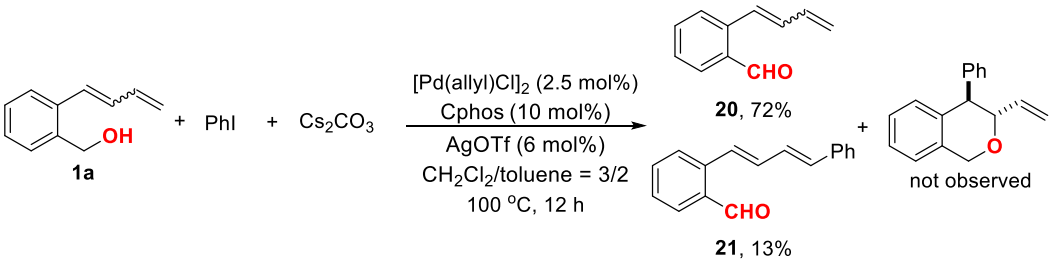
LDA (0.36 mmol) was added to the THF solution of **1a** (58 mg, 0.36 mmol) at 0°C and stired for 10 minutes, then drain the solvent. Aminal **2a** (122 mg, 0.30 mmol), $[Pd(allyl)Cl]_2$ (2.8 mg, 2.5 mol%), **L2** (13.0 mg, 10 mol%), AgOTf (4.6 mg, 6 mol%), and solvent (CH_2Cl_2 : toluene = 3 : 2, 1.0 mL) were added to Young-type tube under N_2 atmosphere. The reaction mixture was stirred at 80 °C for 12 hours, and then cooled to room temperature. The solvent was removed under reduced pressure, the residue was purified by flash chromatography (deluted with petroleum ether/ethyl acetate = 200/1 to 50/1) on a silica gel to give the byproduct **20** (24 mg, 42%) and recycle **1a** (18 mg, 31%).



PhI (120.6 mg, 0.60 mmol), $[Pd(allyl)Cl]_2$ (2.8 mg, 2.5 mol%), **L2** (13.0 mg, 10 mol%), AgOTf (4.6 mg, 6 mol%), dienol **1a** (48 mg, 0.30 mmol) and solvent (CH_2Cl_2 : toluene = 3 : 2, 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 °C for 12 hours, and then cooled to room temperature. The solvent was removed under reduced pressure, the residue was purified by flash chromatography (deluted with petroleum ether/ethyl acetate = 20/1 to 5/1) on a silica gel to recycle **1a** (52 mg, 89%).

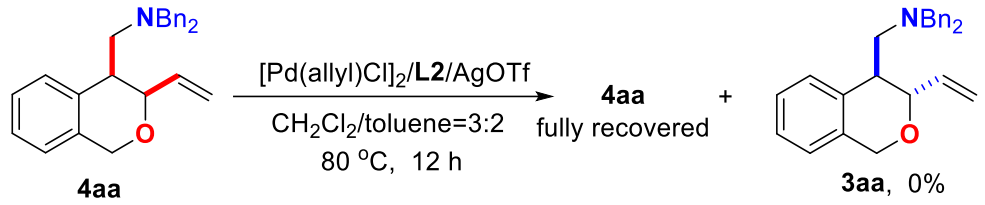


PhI (120.6 mg, 0.60 mmol), $[Pd(allyl)Cl]_2$ (2.8 mg, 2.5 mol%), **L2** (13.0 mg, 10 mol%), AgOTf (4.6 mg, 6 mol%), dienol **1a** (48 mg, 0.30 mmol), Cs_2CO_3 (195.6 mg, 0.60 mmol), and solvent (CH_2Cl_2 : toluene = 3 : 2, 1.0 mL) were added to a 25 mL flame-dried Young-type tube under N_2 atmosphere. The reaction mixture was stirred at 80 °C for 12 hours, and then cooled to room temperature. The solvent was removed under reduced pressure, the residue was purified by flash chromatography (deluted with petroleum ether/ethyl acetate = 20/1 to 5/1) on a silica gel to give the byproduct **20** (43 mg, 76%).

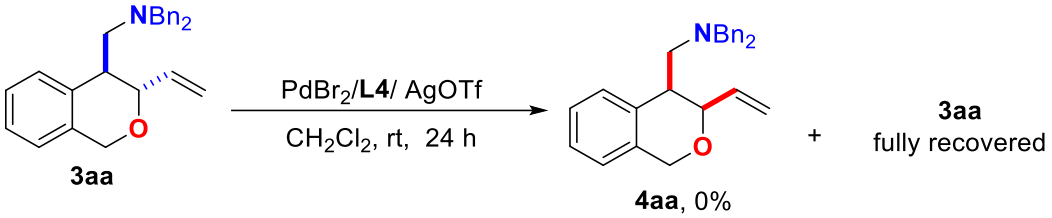


PhI (120.6 mg, 0.60 mmol), $[Pd(allyl)Cl]_2$ (2.8 mg, 2.5 mol%), **L2** (13.0 mg, 10 mol%), AgOTf (4.6 mg, 6 mol%), dienol **1a** (48 mg, 0.30 mmol), Cs_2CO_3 (195.6 mg, 0.60 mmol), and solvent (CH_2Cl_2 : toluene = 3 : 2, 1.0 mL) were added to a 25 mL flame-dried Young-type tube under N_2 atmosphere. The reaction mixture was stirred at 100 °C for 12 hours, and then cooled to room temperature. The solvent was removed under reduced pressure, the residue was purified by flash chromatography (deluted with

petroleum ether/ethyl acetate = 20/1 to 5/1) on a silica gel to give the byproduct **20** (34.1 mg, 72%) and **21** (9.1 mg, 13%).

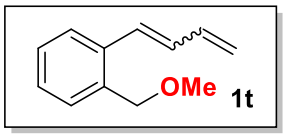


4aa (110.7 mg, 0.30 mmol), $[Pd(allyl)Cl]_2$ (2.8 mg, 2.5 mol%), **L2** (13.0 mg, 10 mol%), AgOTf (4.6 mg, 6 mol%), and solvent (CH_2Cl_2 : toluene = 3 : 2, 1.0 mL) were added to a 25 mL flame-dried Young-type tube under N_2 atmosphere. The reaction mixture was stirred at 80 °C for 12 hours, and then cooled to room temperature. The solvent was removed under reduced pressure, the residue was purified by flash chromatography (deluted with petroleum ether/ethyl acetate = 200/1 to 50/1) on a silica gel to give product **4aa** as colorless oil (fully recovered).



3aa (110.7 mg, 0.30 mmol), $PdBr_2$ (4.0 mg, 5 mol%), **L4** (15.5 mg, 10 mol%), AgOTf (9.3 mg, 12 mol%), and CH_2Cl_2 (1.0 mL) were added to a 25 mL flame-dried Young-type tube under N_2 atmosphere. The reaction mixture was stirred at room temperature for 12 hours, and then cooled to room temperature. The solvent was removed under reduced pressure, the residue was purified by flash chromatography (deluted with petroleum ether/ethyl acetate = 200/1 to 50/1) on a silica gel to give product **3aa** as colorless oil (fully recovered).

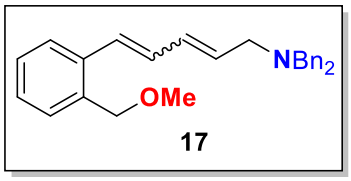
1-(buta-1,3-dien-1-yl)-2-(methoxymethyl)benzene (1t)



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 0.6 g, 55% yield (*E*/ *Z* = 1 : 6.7). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.5 Hz, 0.13H), 7.39-7.41 (m, 0.87H), 7.18-7.23 (m, 3H), 6.57-6.88 (m, 2H), 6.51-6.55 (m, 0.13H), 6.36 (t, *J* = 11.0 Hz, 0.87H), 5.33-5.36 (m, 1H), 5.16-5.20 (m, 1H), 4.43-4.52 (m, 2H), 3.38-3.40 (m, 3H); **^{13}C NMR** (125 MHz,

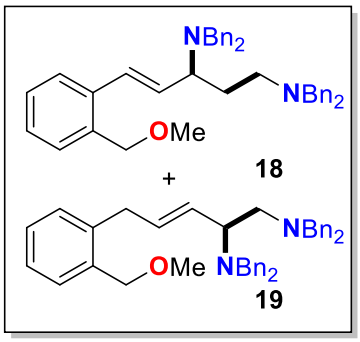
$CDCl_3$) δ 137.6, 136.23, 136.20, 133.4, 131.8, 130.0, 128.7, 128.5, 127.5, 119.5, 72.7, 58.4; **HRMS** (ESI) calcd for $C_{12}H_{14}ONa$ $[M+Na]^+$: 197.0942, found: 197.0948.

***N,N*-dibenzyl-1-(2-vinyl-2,3-dihydrobenzofuran-3-yl)methanamine (17)**



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 24 mg, 21% yield (*E*/ *Z* = 5.7 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.6 Hz, 1H), 7.20-7.40 (m, 13H), 6.69-6.92 (m, 2H), 6.33-6.43 (m, 1H), 5.88-5.95 (m, 0.85H), 5.68-5.73 (m, 0.15H), 4.50 (s, 2H), 3.60-3.61 (m, 4H), 3.39 (s, 3H), 3.29 (d, *J* = 7.2 Hz, 0.30H), 3.16 (d, *J* = 6.8 Hz, 1.70H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 139.7, 136.7, 135.0, 133.5, 132.6, 130.8, 129.5, 129.0, 128.9, 128.3, 128.2, 127.3, 127.0, 125.6, 73.0, 58.2, 58.0, 55.6; **HRMS** (ESI) calcd for $C_{27}H_{30}NO$ $[M+H]^+$: 384.2327, found: 384.2325.

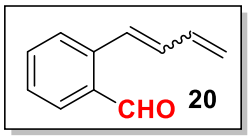
***(E)*-N^1,N^1,N^3,N^3-tetrabenzyl-5-(2-(methoxymethyl)phenyl)pent-4-ene-1,3-diamine and (*E*)-N^1,N^1,N^2,N^2-tetrabenzyl-5-(2-(methoxymethyl)phenyl)pent-3-ene-1,2-diamine (18 + 19)**



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 29 mg, 17% yield (**18** / **19** = 1 : 2.6). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.11-7.47 (m, 23H), 6.90-7.09 (m, 1H), 6.49 (d, *J* = 16.0 Hz, 0.28H), 6.02 (dd, *J* = 16.0 Hz, 9.0 Hz, 0.28H), 5.70 (dd, *J* = 15.0 Hz, 7.0 Hz, 0.72H), 5.45-5.51 (m, 0.72H), 4.34-4.47 (m, 2H), 3.55-4.02 (m, 5H), 3.23-3.50 (m, 7H), 2.98-3.00 (m, 1.72H), 2.62-2.82 (m, 1.72H), 2.33-2.38 (m, 0.28H), 1.73-1.78 (m, 0.28H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 142.3, 140.5, 139.9, 139.8, 136.8, 136.4, 135.4, 134.9, 130.6, 130.4, 129.5, 129.2, 129.1, 129.0, 128.9, 128.8, 128.31, 128.29, 128.26, 128.2, 128.0, 127.9, 127.4, 126.90, 126.88, 126.8, 126.4, 126.0,

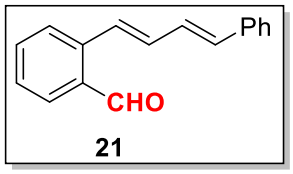
73.1, 59.3, 58.9, 58.8, 58.5, 58.4, 58.0, 57.9, 55.9, 53.9, 51.2, 41.6; **HRMS** (ESI) calcd for $C_{41}H_{45}N_2O$ $[M+H]^+$: 581.3532, found: 581.3540.

2-(buta-1,3-dien-1-yl)benzaldehyde (20)



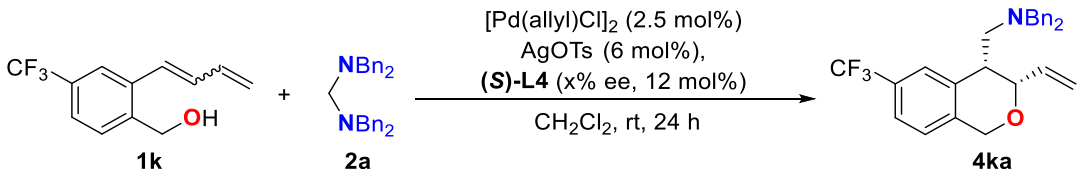
The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil, 24 mg, 42% yield (*E*/ *Z* = 1 : 2.6). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.26 (s, 0.28H), 10.20 (s, 0.72H), 7.90 (d, *J* = 7.6 Hz, 0.72H), 7.81 (d, *J* = 7.6 Hz, 0.28H), 7.32-7.62 (m, 3H), 6.43-6.91 (m, 3H), 5.21-5.45 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.5, 192.2, 140.0, 139.6, 137.0, 134.7, 133.81, 133.78, 133.7, 133.5, 132.7, 132.5, 132.1, 131.0, 129.6, 128.5, 127.73, 127.67, 127.0, 121.0, 119.6; **HRMS** (ESI) calcd for $C_{11}H_{10}ONa$ $[M+Na]^+$: 181.0624, found: 181.0635.

2-((*1E*,*3E*)-4-phenylbuta-1,3-dien-1-yl)benzaldehyde (21)



The title compound was prepared according to the general procedure and purified by column chromatography to give colorless oil. 9.1 mg, 13% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.28 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.61-7.68 (m, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.45-7.46 (m, 2H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.32-7.35 (m, 2H), 7.24-7.27 (m, 1H), 7.07 (dd, *J* = 15.5 Hz, 10.5 Hz, 1H), 6.96 (dd, *J* = 15.5 Hz, 10.5 Hz, 1H), 6.74 (d, *J* = 15.5 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.8, 139.8, 137.1, 134.9, 134.4, 133.7, 132.65, 132.61, 129.2, 128.8, 128.4, 128.1, 127.6, 126.8, 126.7.

9.2 Non-Linear Effect Studies



entry	x	yield (%)	ee (%)
1	15.6%	61%	22%
2	29.9%	65%	37%
3	44.2%	62%	56%
4	60%	61%	64%
5	75.4%	66%	77%
6	90.5%	59%	92%
7	100%	67%	94%

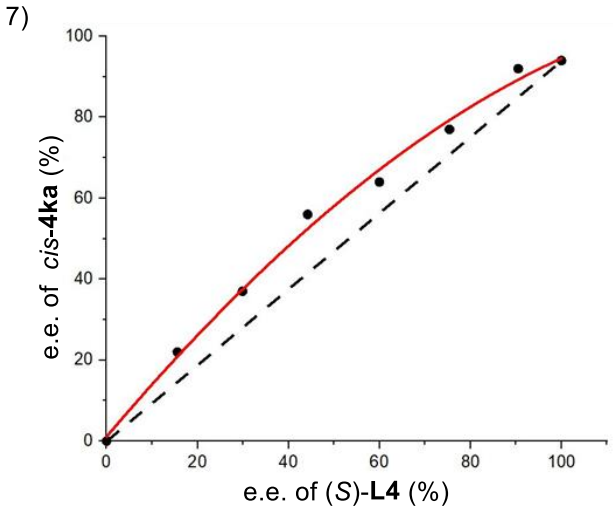
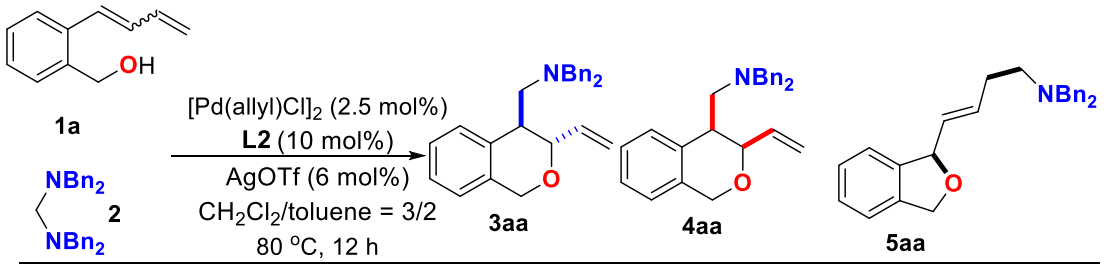


Figure S5. Non-Linear relationship between optically ligand L4 and product *cis*-4ka

In a glove box, the mixture of $[Pd(allyl)Cl]_2$ (2.8 mg, 0.0075 mmol), (*S*)-**L4** with different ee values (18.5 mg, 0.036 mmol), AgOTs (5.0 mg, 0.018 mmol) and CH_2Cl_2 (1 mL) was added to a Young-type tube and stirred at 45 ^oC for 30 minutes. After the mixture cooled to room temperature, *N*,*N*,*N'*,*N'*-tetrabenzylmethanediamine **2a** (0.3 mmol) and **1k** (0.36 mmol) were added under nitrogen. The reaction mixture was degassed via the freeze-thaw method and stirred at rt for 24 hours. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (eluted with petroleum ether/diethyl ether = 100/1 to 50/1) on a silica gel to give the desired product. [The ee value of the product was determined by HPLC with a Chiralpak AD-H column (90 : 10 = Hexane : isopropanol, 0.5 mL / min, 220 nm, 25 ^oC); t (major) = 7.8 min, t (minor) = 8.4 min. As shown in **Figure S5**, the non-linear relationship between the ee value of enantioenriched ligand **L4** and the ee value of the ***cis*-4ka**.

9.3 Investigation the effect of additive.

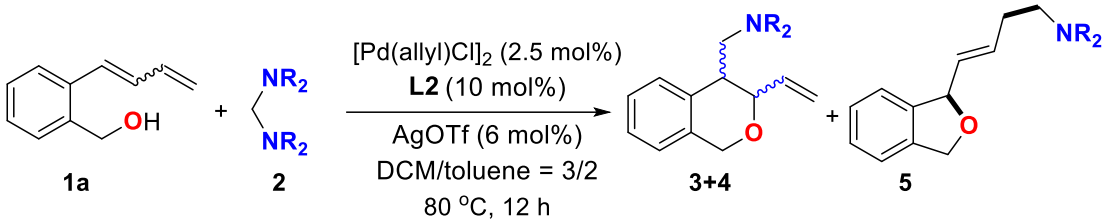
Aminal **2a** (122 mg, 0.30 mmol), $[Pd(allyl)Cl]_2$ (2.8 mg, 2.5 mol%), **L2** (13.0 mg, 10 mol%), AgOTf (4.6 mg, 6 mol%), addtive (3.0 mmol, 10 eq.), dienol **1a** (58 mg, 0.36 mmol) and solvent (CH_2Cl_2 : toluene = 3 : 2, 1.0 mL) were added to a 25 mL flame-dried Young-type tube under N_2 atmosphere. The reaction mixture was stirred at 80 °C for 12 hours, and then cooled to room temperature. The solvent was removed under reduced pressure, the residue was purified by flash chromatography (deluted with petroleum ether/ethyl acetate = 200/1 to 50/1) on a silica gel to give product **3aa** as colorless oil. The dr value of the crude reaction mixture was determined by **^{1}HNMR** analysis. The rr value of the crude reaction mixture was determined by GC and GCMS.



entry	additive	*d.r.*	**3aa**	*r.r.*
1	no	> 20:1	86%	68:1
2	10 eq. MeOH	> 20:1	42%	151:1
3	10 eq. *t*-BuOH	> 20:1	56%	76:1
4	10 eq. Bn_2NMe	> 20:1	58%	153:1

Figure S6. Additive effect for the Pd-catalyzed aminomethylative annulation with L2.

9.4 Hammett studies



Aminal **2** (0.30 mmol), $[Pd(allyl)Cl]_2$ (2.8 mg, 2.5 mol%), **L2** (13.0 mg, 10 mol%), AgOTf (4.6 mg, 6 mol%), addtive (3.0 mmol, 10 eq.), dienol **1a** (58 mg, 0.36 mmol) and solvent (CH_2Cl_2 : toluene = 3 : 2, 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 °C for

12 hours, and then cooled to room temperature. The rr value of the crude reaction mixture was determined by GC and GCMS.

r.r.:	18/1	51/1	89/1	68/1	174/1	213/1
R:	4-CF_3PhCH_2-	4-$ClPhCH_2$-	4-$FPhCH_2$-	$PhCH_2$-	4-$MePhCH_2$-	4-$OMePhCH_2$-

electron-withdrawing ⟹ electron-donating

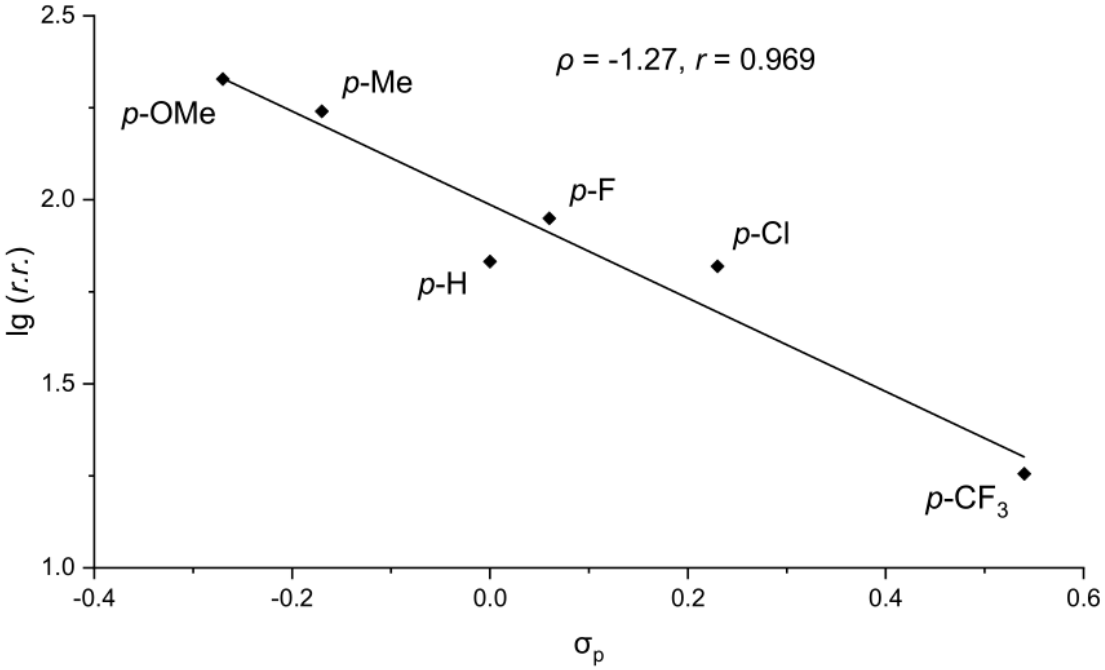


Figure S7. Hammett plot for the Pd-catalyzed Aminomethylative Annulation with L2.

9.5 Computational study

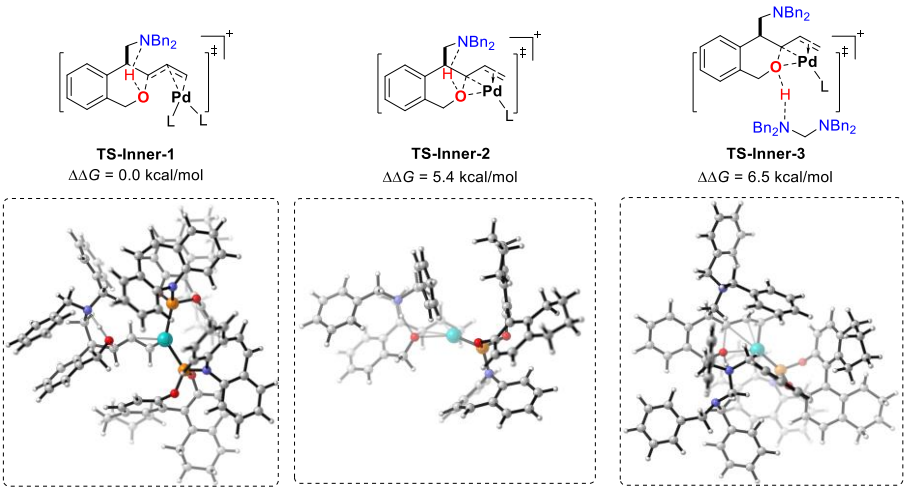


Figure S8. The relative free energies of the calculated possible transition states for the inner-sphere reductive elimination when electron-deficient **L4** was utilized as ligand.

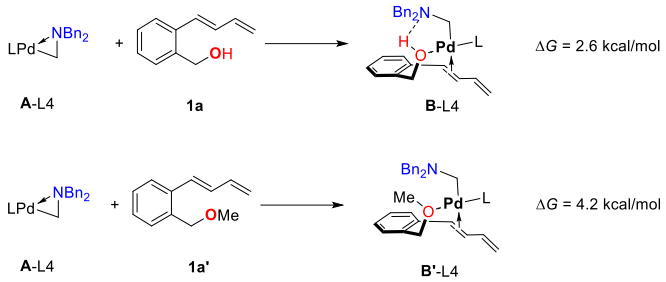


Figure S9. Calculated Gibbs energy for the coordination of **1a** and **1a'** substrates to Pd(II) center in cyclopalladated complex A using P-alkene ligand.

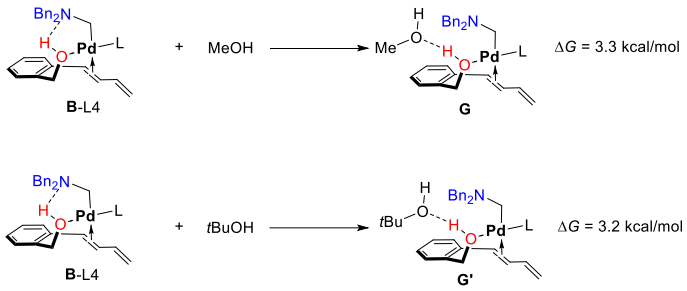
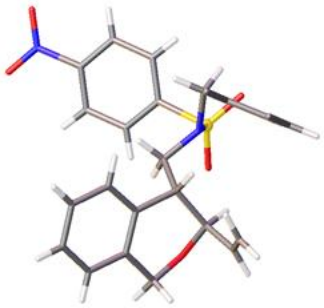


Figure S10. Calculated Gibbs energy for disruption of the intramolecular H-bond in intermediate **B** by methanol and *t*-butanol.

10 X-ray Crystallographic Data

Sample preparation: Racemic Compound **7** (30 mg) was dissolved in anhydrous *n*-Hexane (1.0 mL) in a 5 mL sample vial. The resulting mixture was left at -20 ℃ under airtight conditions until the white crystals precipitated.



(**7**)

The ellipsoid contour percent probability lever is 50%

Crystal data and structure refinement for HY-X20927-1

Identification code	HY-X20927-1
Empirical formula	$C_{25}H_{24}N_2O_5S$
Formula weight	464.52
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.60983(19)
b/Å	31.1413(5)
c/Å	10.11618(15)
α/°	90
β/°	91.5530(12)
γ/°	90
Volume/Å^3	4600.85(12)
Z	8
ρ_{calc}g/cm^3	1.341
μ/mm^{-1}	1.582
F(000)	1952.0
Crystal size/mm^3	0.2 ×0.2 ×0.15
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/ °	8.3 to 140.096
Index ranges	-10 ≤ h ≤ 17, -37 ≤ k ≤ 34, -12 ≤ l ≤ 11
Reflections collected	18304
Independent reflections	8507 [R_{int} = 0.0215, R_{sigma} = 0.0264]
Data/restraints/parameters	8507/2/595
Goodness-of-fit on F^2	0.954
Final R indexes [I>=2σ (I)]	R_1 = 0.0591, wR_2 = 0.2117

Final R indexes [all data]	R_1 = 0.0792, wR_2 = 0.2480
Largest diff. peak/hole / e Å^{-3}	0.56/-0.38

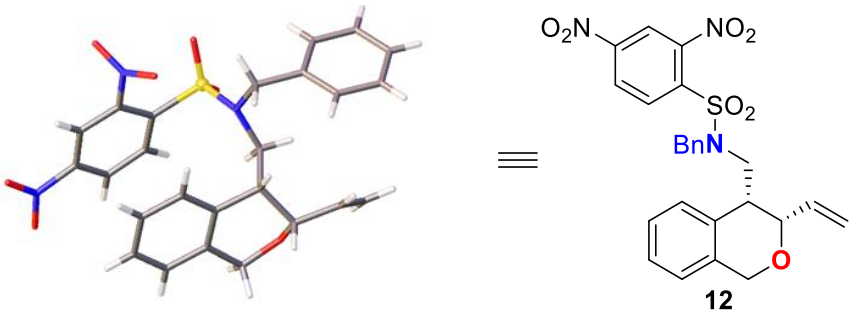
Sample preparation: Racemic compound **12** (30 mg) was dissolved in anhydrous *n*-Hexane (1.0 mL) in a 5 mL sample vial. The resulting mixture was left at room temperature under airtight conditions until the white crystals precipitated.

(**12**)

The ellipsoid contour percent probability lever is 50%

Identification code	hy-x2020921
Empirical formula	$C_{25}H_{21}N_3O_7S$
Formula weight	507.51
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	7.2994(2)
b/Å	8.0887(3)
c/Å	21.2887(8)
α/°	91.614(3)
β/°	94.807(2)
γ/°	100.145(2)
Volume/Å^3	1231.76(7)
Z	2
ρ_{calc}g/cm^3	1.368
μ/mm^{-1}	1.604
F(000)	528.0
Crystal size/mm^3	0.25 × 0.2 × 0.15
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.344 to 139.74
Index ranges	-8 ≤ h ≤ 6, -9 ≤ k ≤ 9, -25 ≤ l ≤ 24
Reflections collected	7263
Independent reflections	4455 [R_{int} = 0.0146, R_{sigma} = 0.0219]
Data/restraints/parameters	4455/2/325
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0584, wR_2 = 0.1702
Final R indexes [all data]	R_1 = 0.0629, wR_2 = 0.1764
Largest diff. peak/hole / e Å^{-3}	0.65/-0.46

Sample preparation: chiral compound **12** (30 mg) was dissolved in anhydrous *n*-Hexane (1.0 mL) in a 5 mL sample vial. The resulting mixture was left at room temperature under airtight conditions until the white crystals precipitated.



(*3S,4R*-**12**)

The ellipsoid contour percent probability lever is 50%

Crystal data and structure refinement for hy-*cis*.

Identification code	hy-*cis*
Empirical formula	$C_{25}H_{23}N_3O_7S$
Formula weight	509.52
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	7.58320(10)
b/Å	15.88330(10)
c/Å	10.58560(10)
α/°	90
β/°	104.4290(10)
γ/°	90
Volume/Å^3	1234.78(2)
Z	2
ρ_{calc}g/cm^3	1.370
μ/mm^{-1}	1.600
F(000)	532.0
Crystal size/mm^3	0.3 × 0.21 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.626 to 139.888
Index ranges	$-5 \le h \le 8$, $-19 \le k \le 19$, $-12 \le l \le 12$
Reflections collected	8204
Independent reflections	4459 [R_{int} = 0.0201, R_{sigma} = 0.0212]
Data/restraints/parameters	4459/1/325
Goodness-of-fit on F^2	0.822
Final R indexes [I>=2σ (I)]	R_1 = 0.0379, wR_2 = 0.0962

Final R indexes [all data]	R_1 = 0.0383, wR_2 = 0.0976
Largest diff. peak/hole / e Å^{-3}	0.19/-0.47
Flack parameter	0.032(7)

11. References

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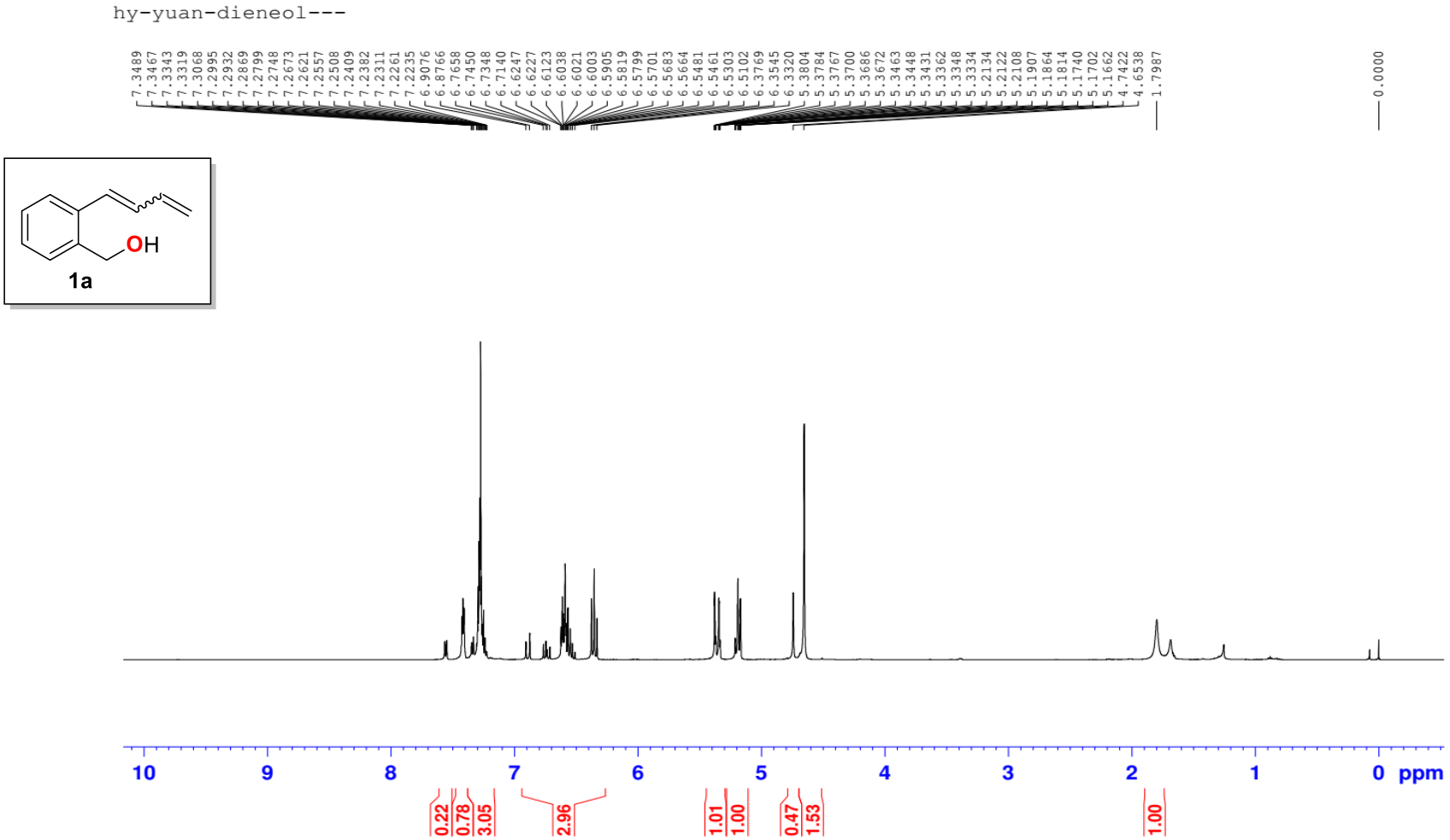
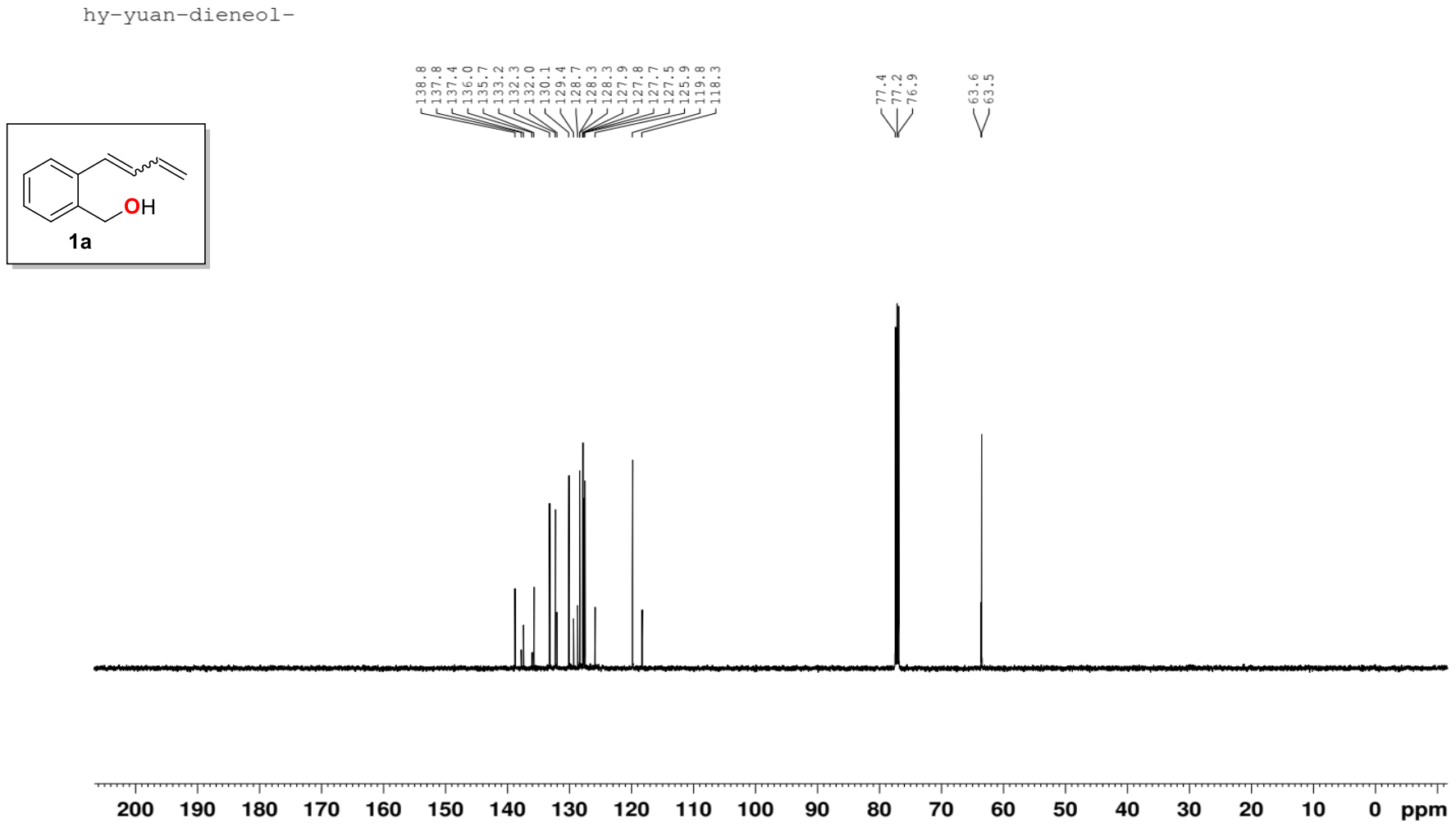
12. Copies of NMR of Materials and Products

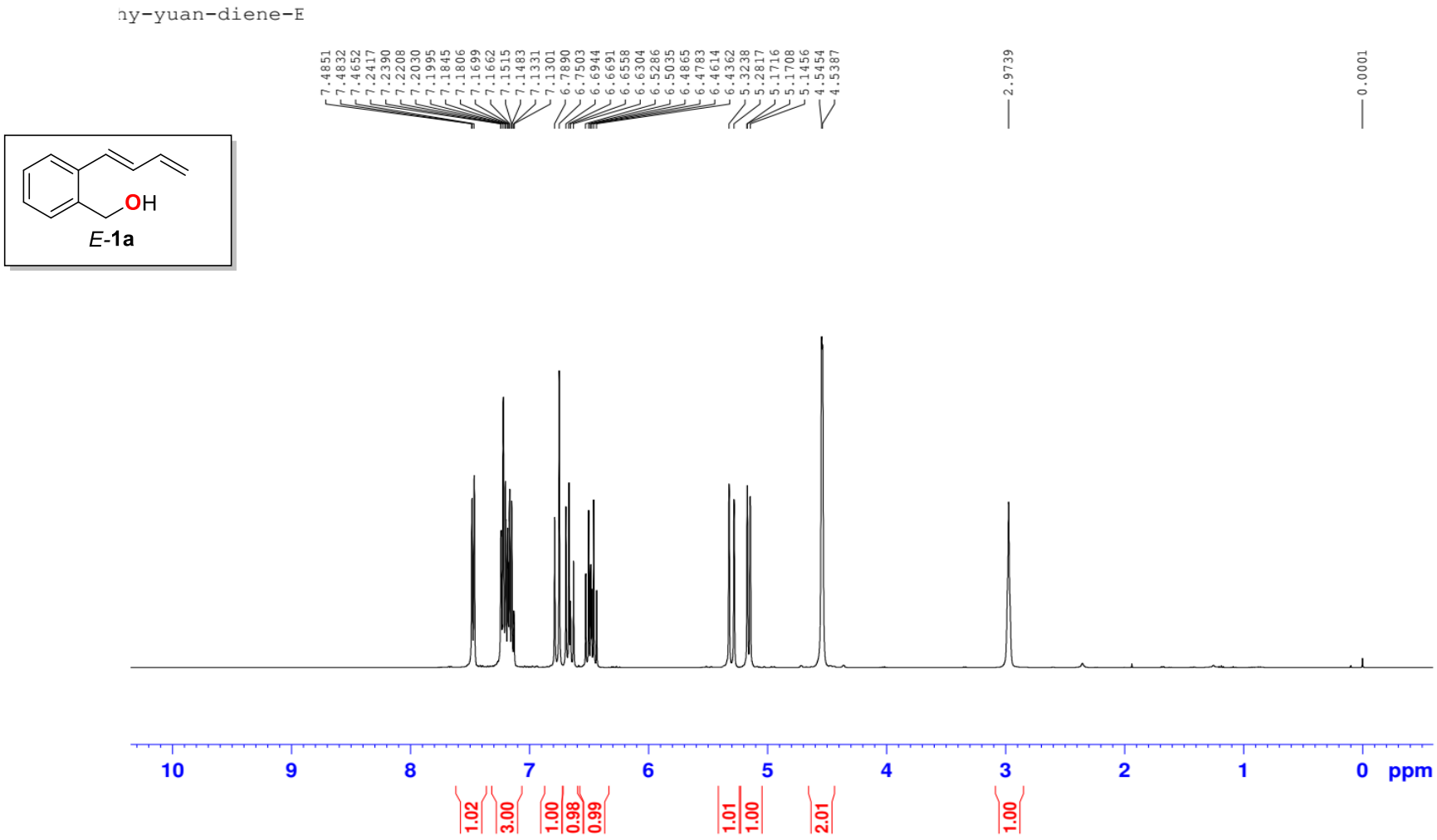
hy-S-**1a** ^{1}**H NMR** (500MHz $CDCl_3$)



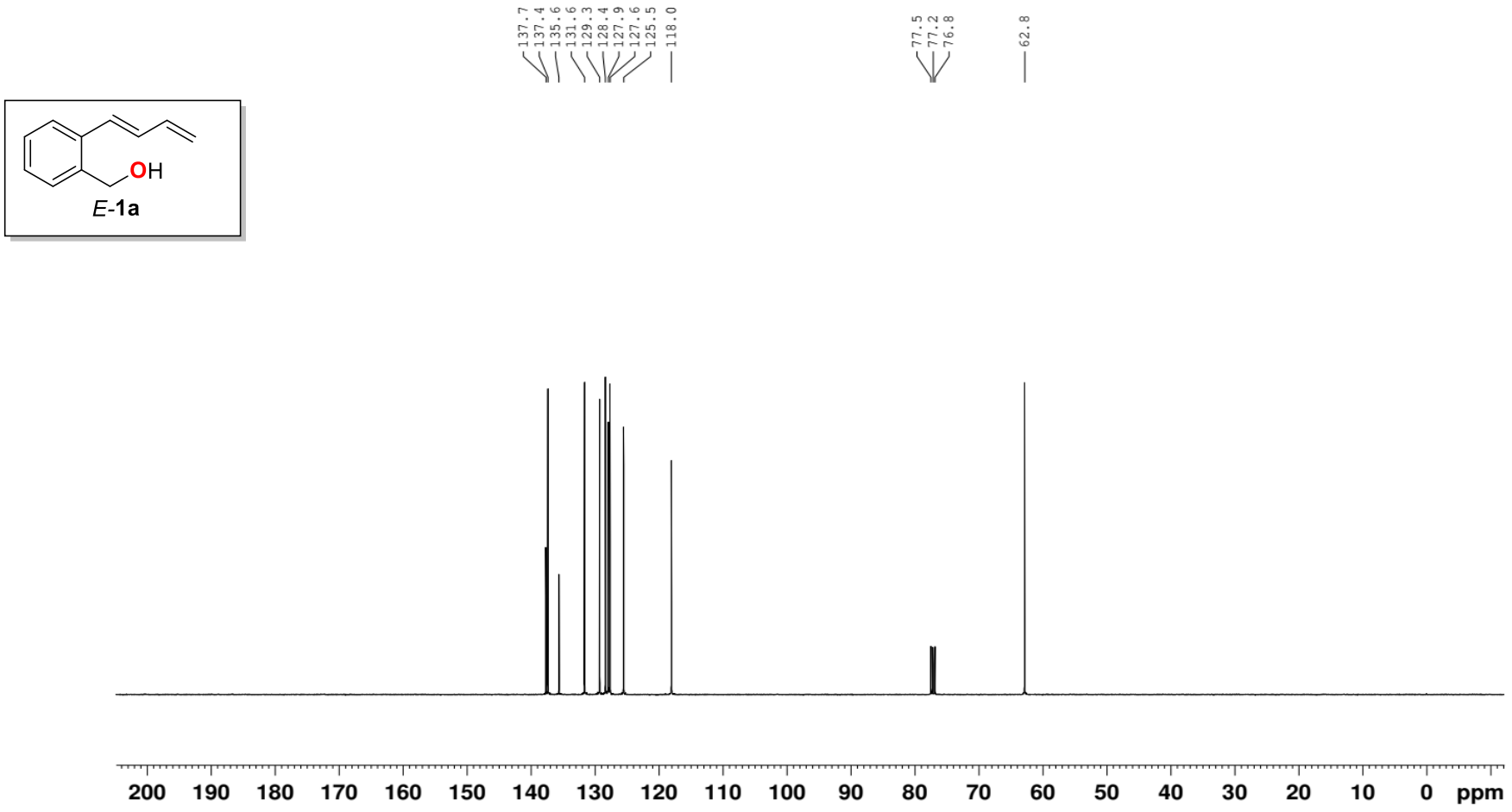
hy-S-**1a** ^{13}C NMR (125MHz $CDCl_3$)



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



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



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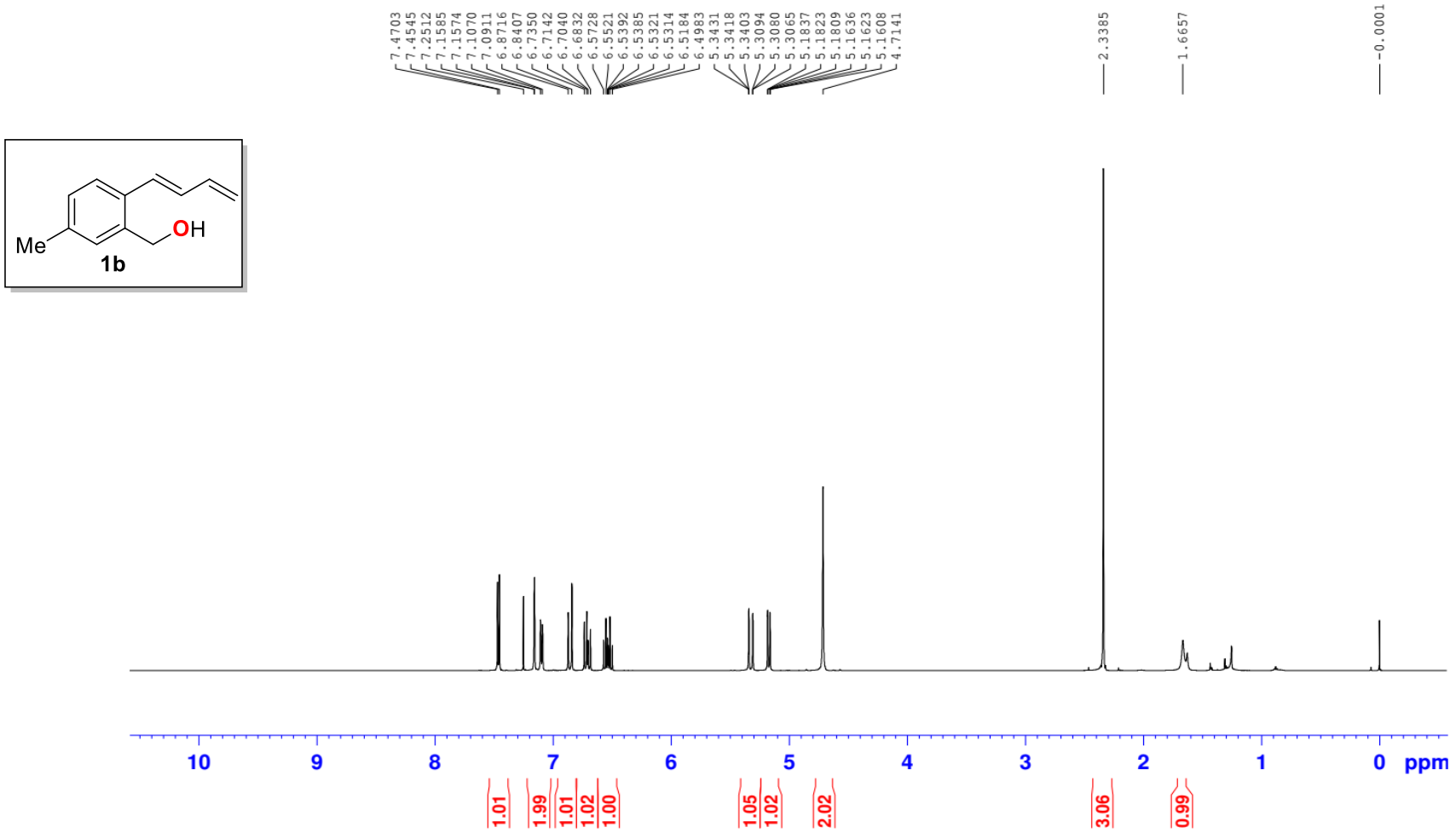

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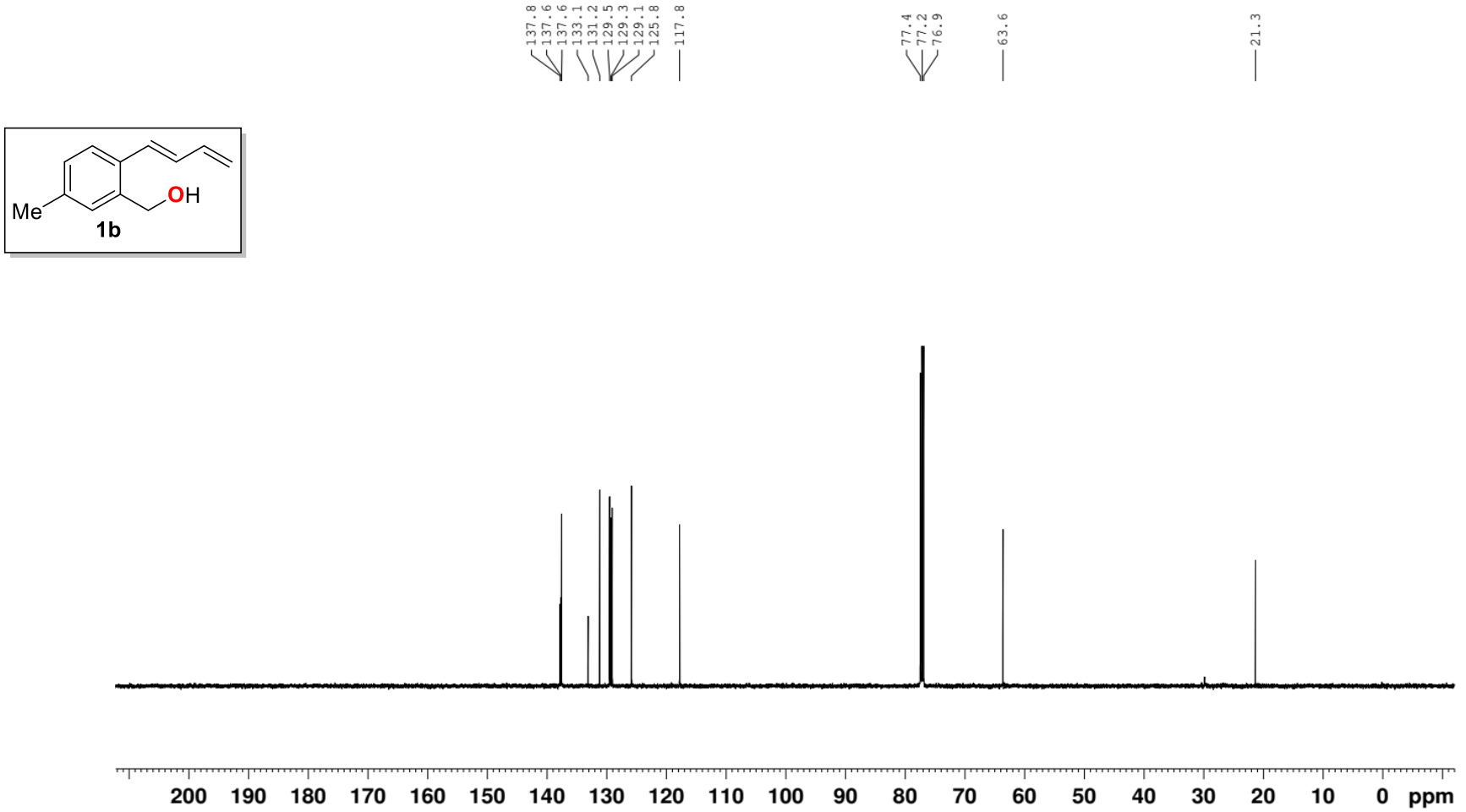

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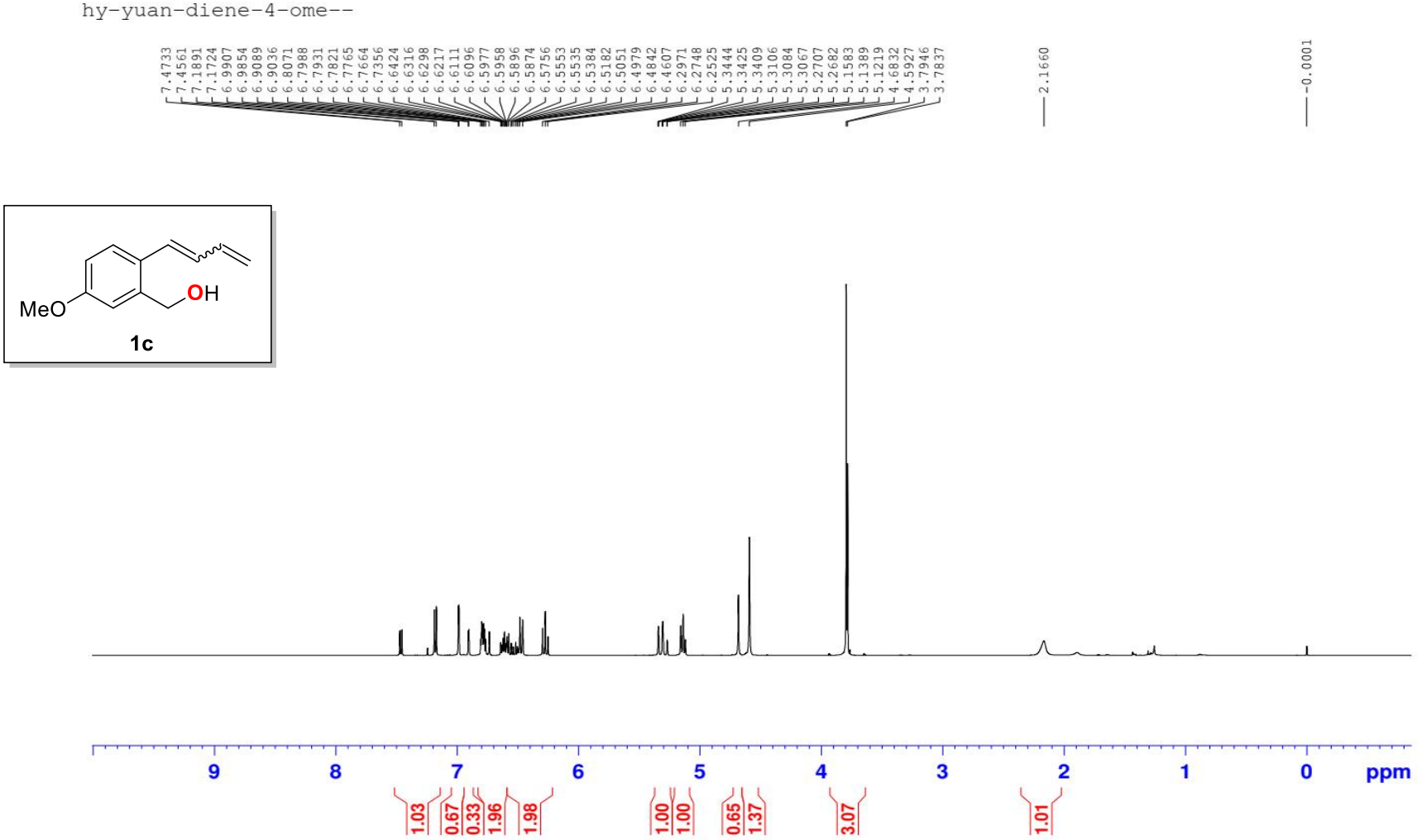

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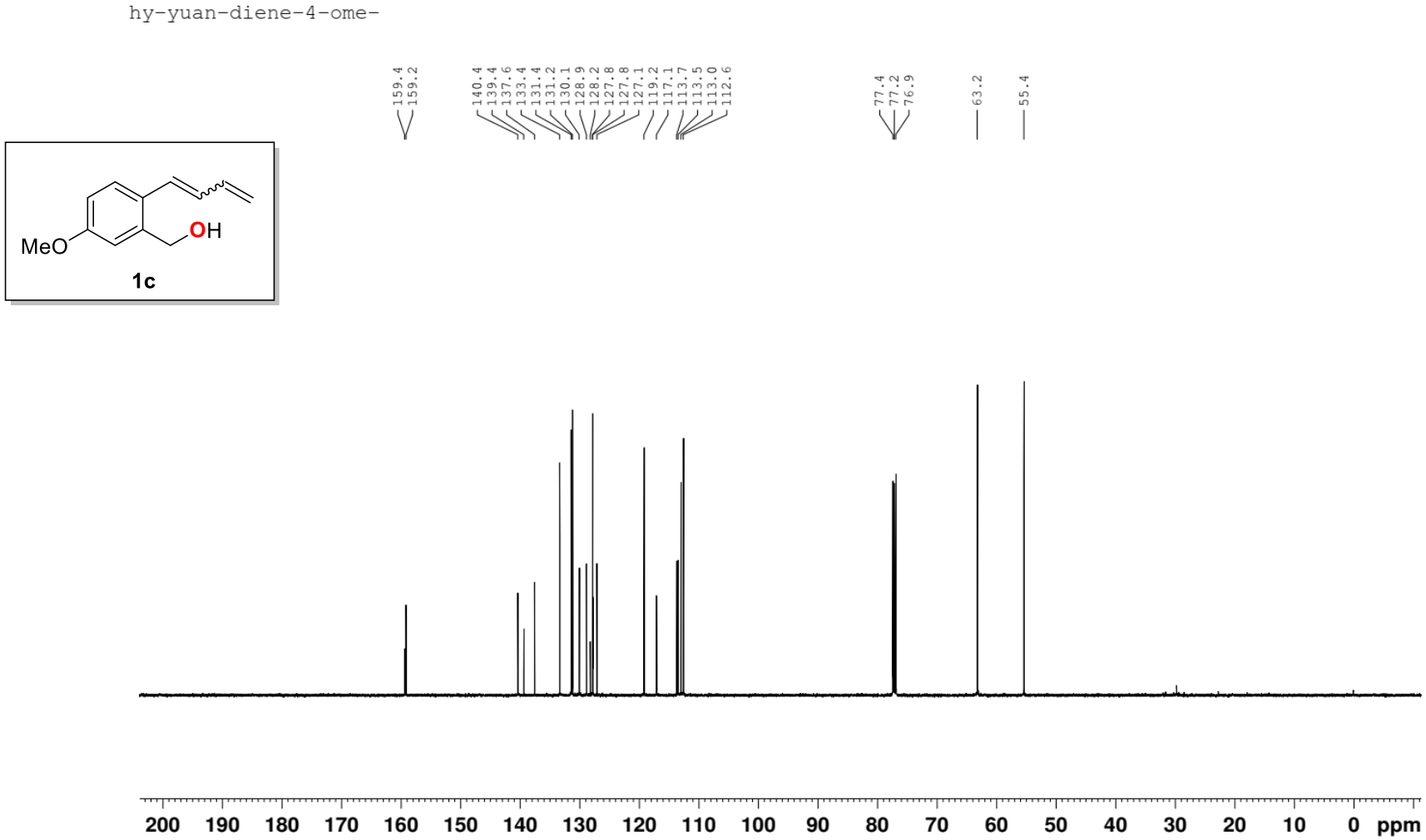

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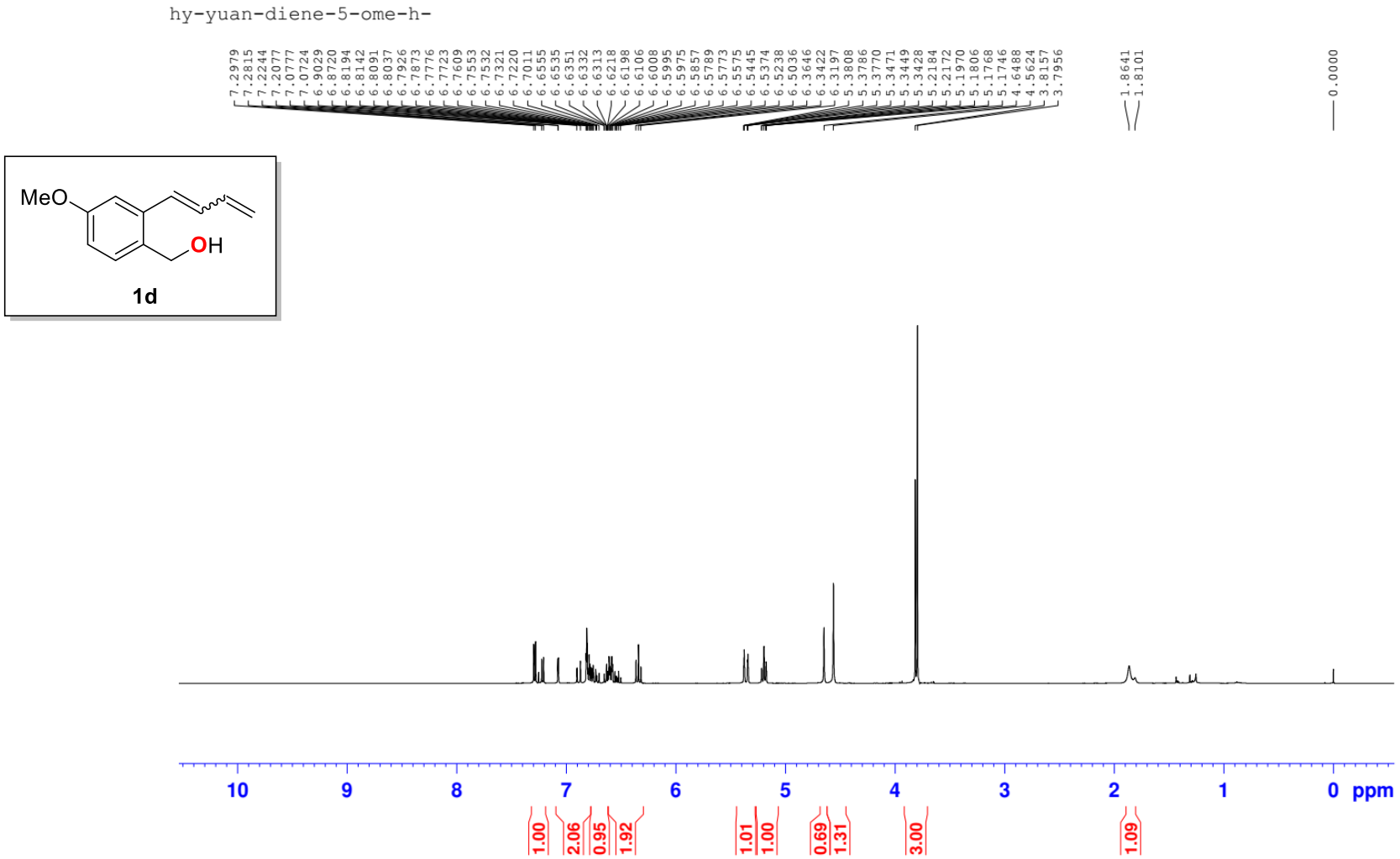

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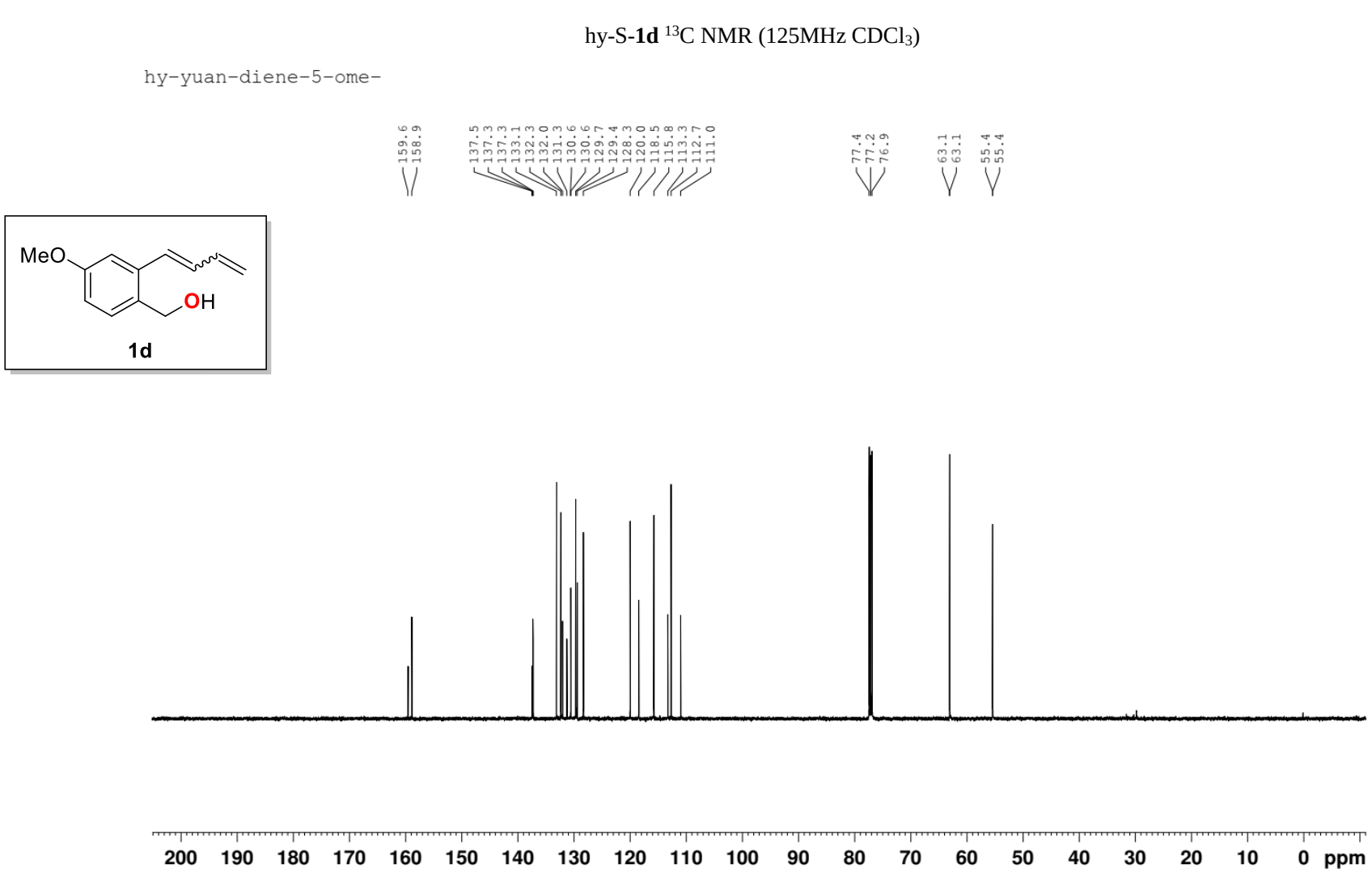

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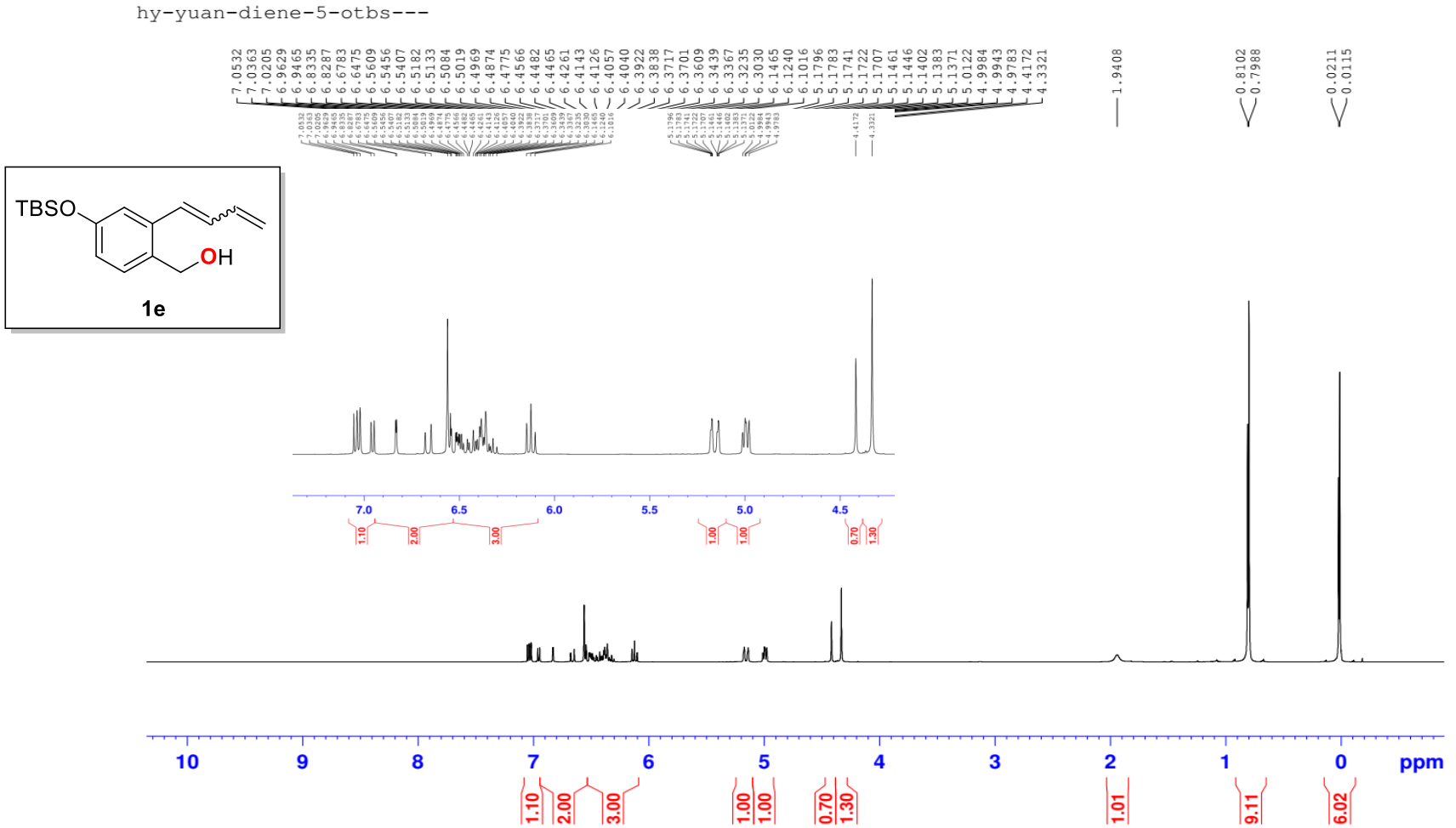

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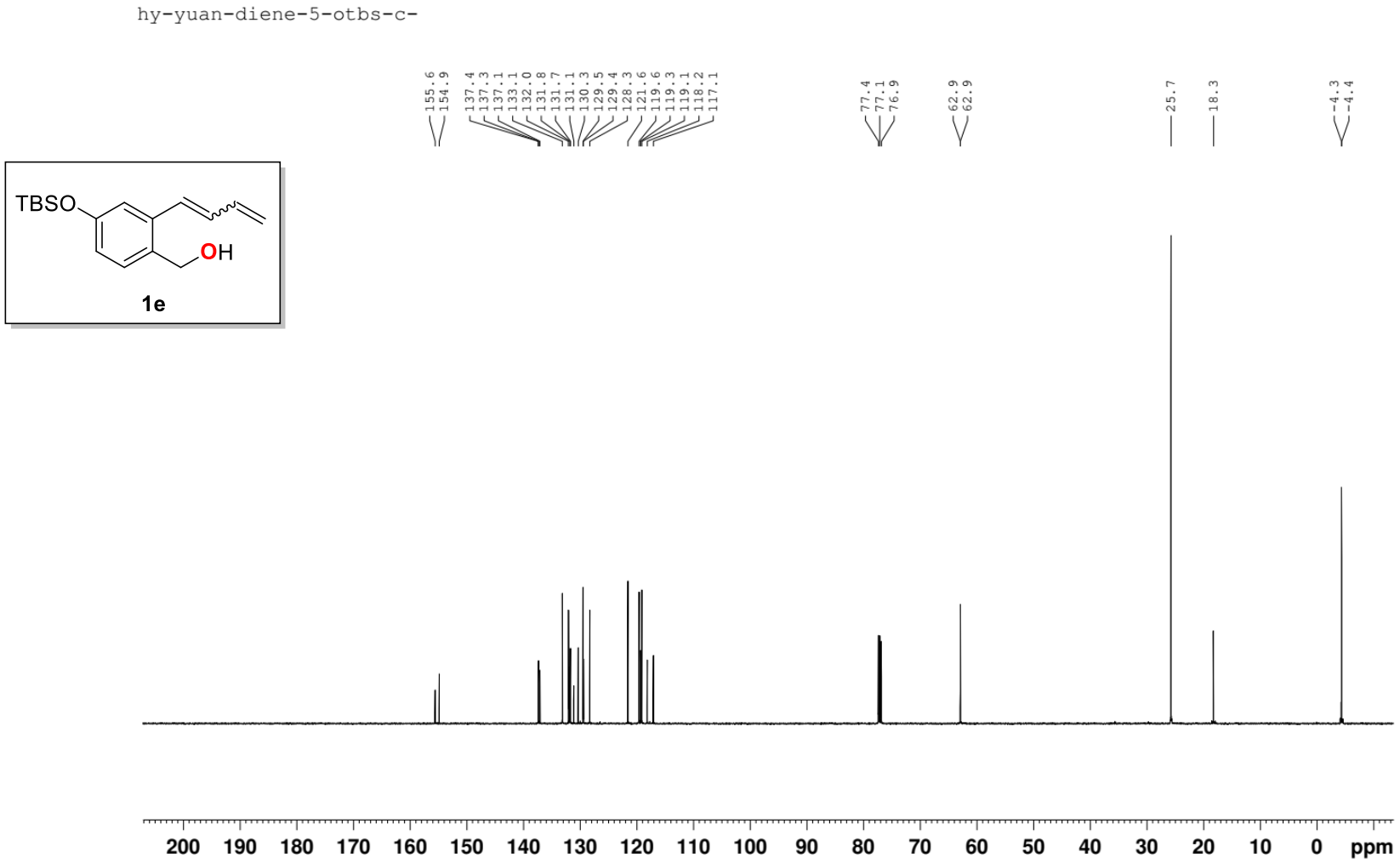

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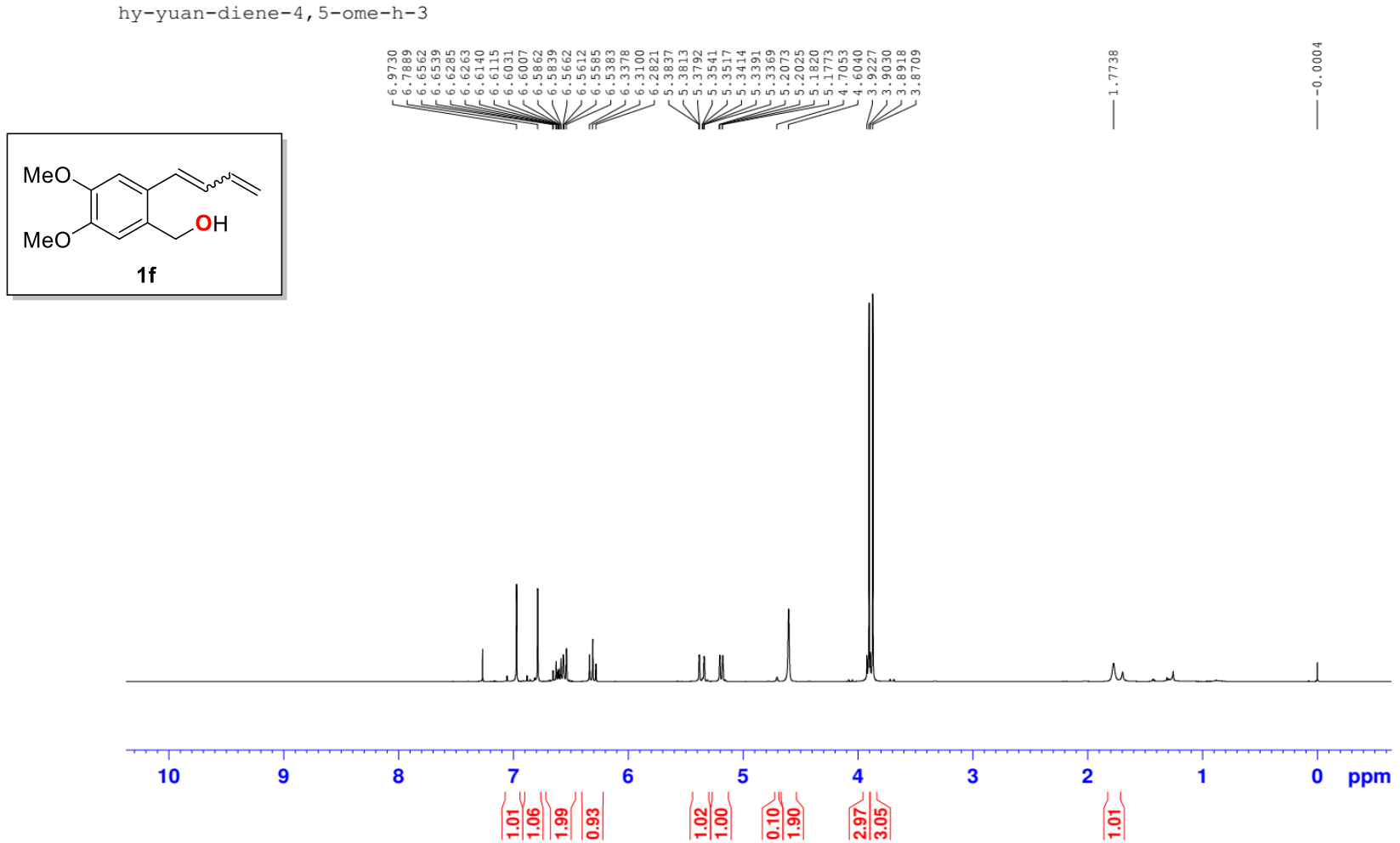

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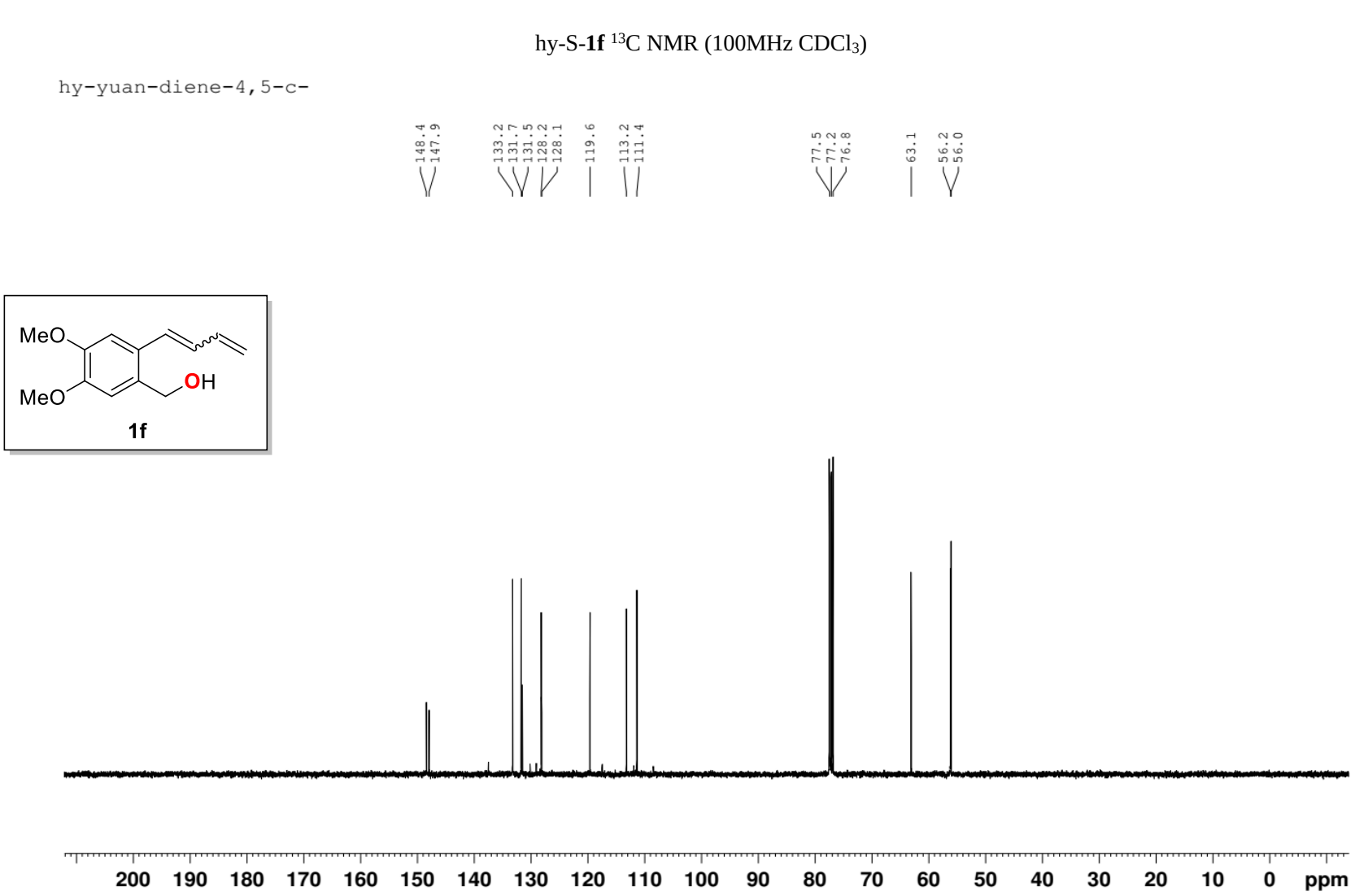

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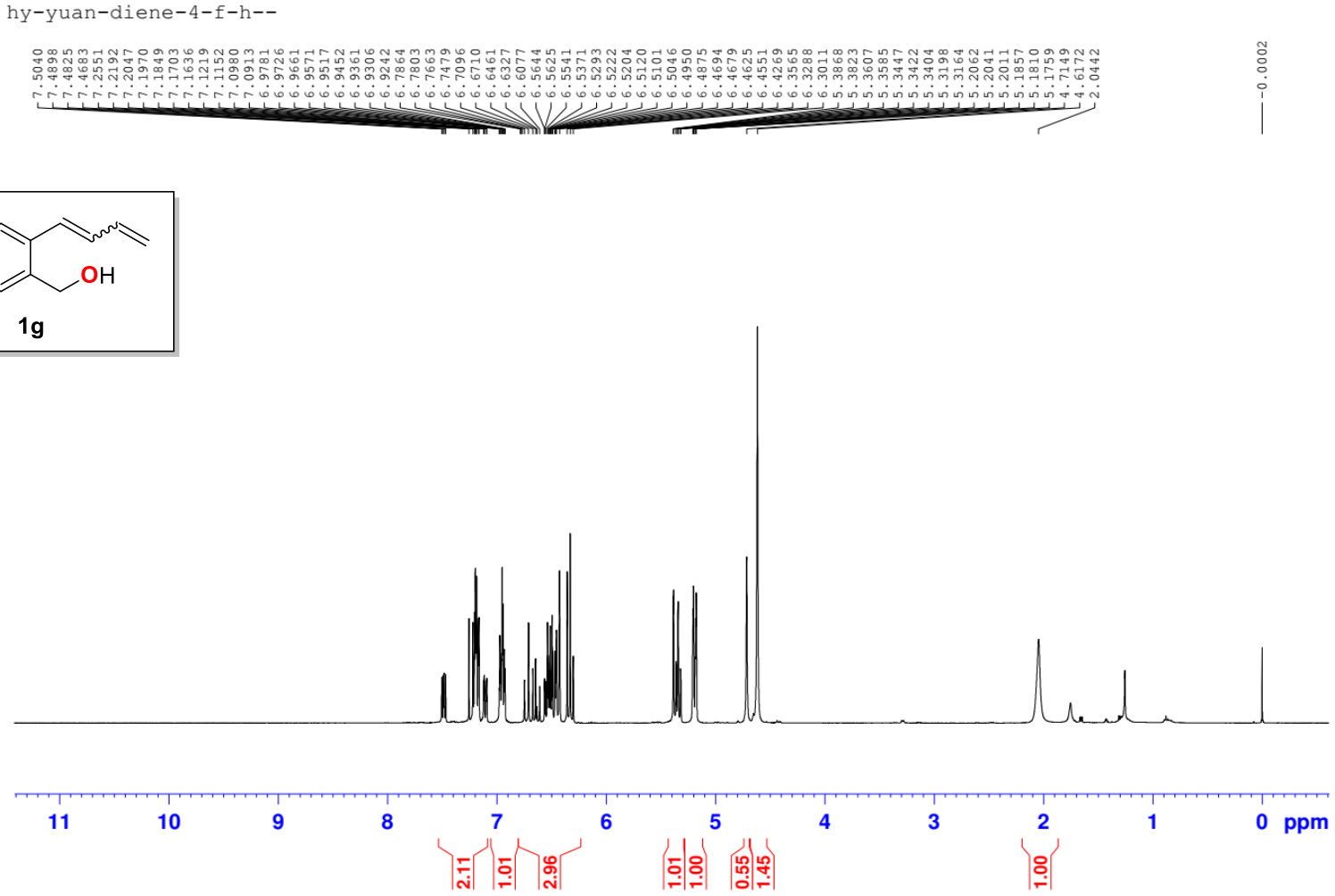
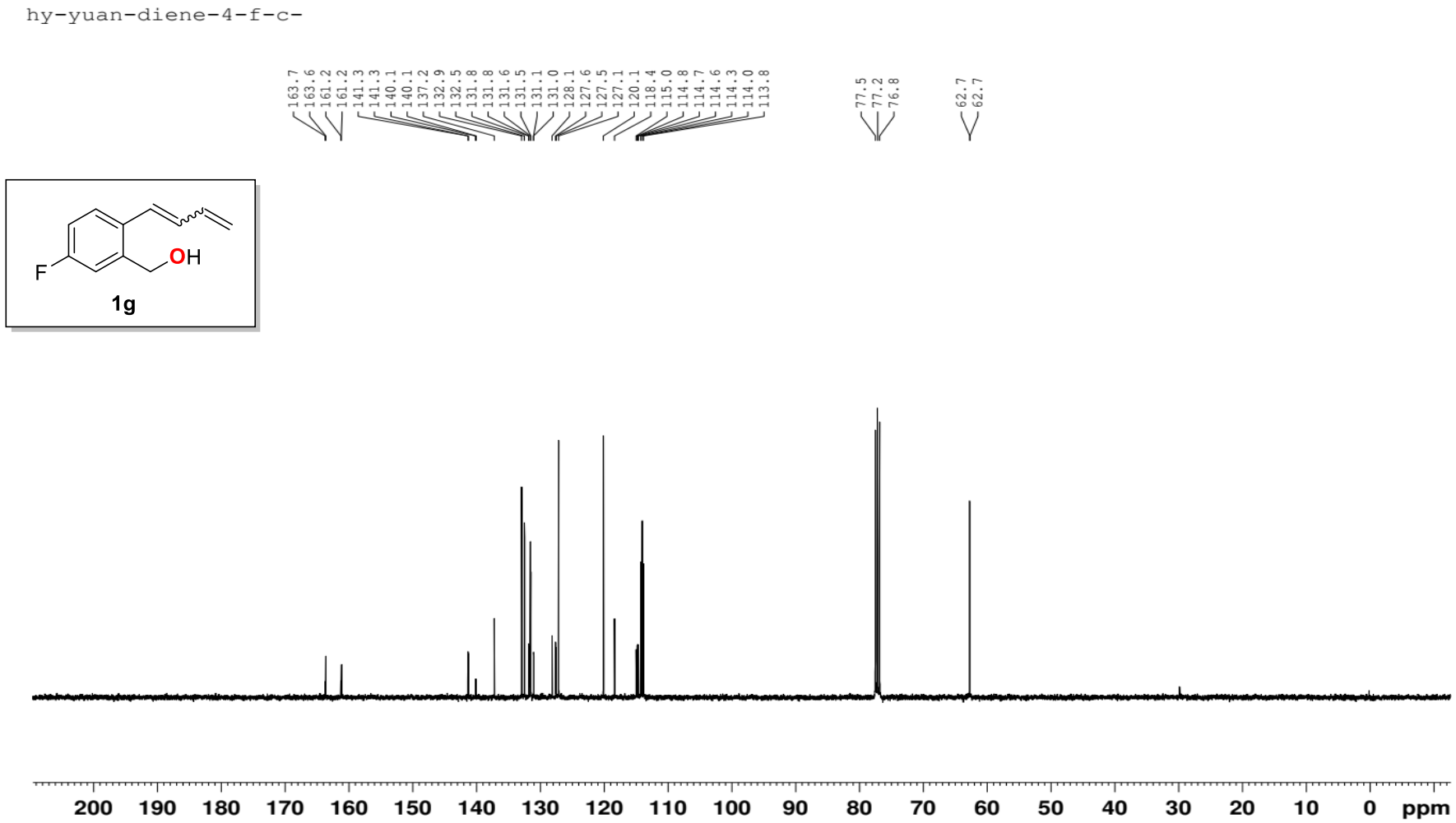
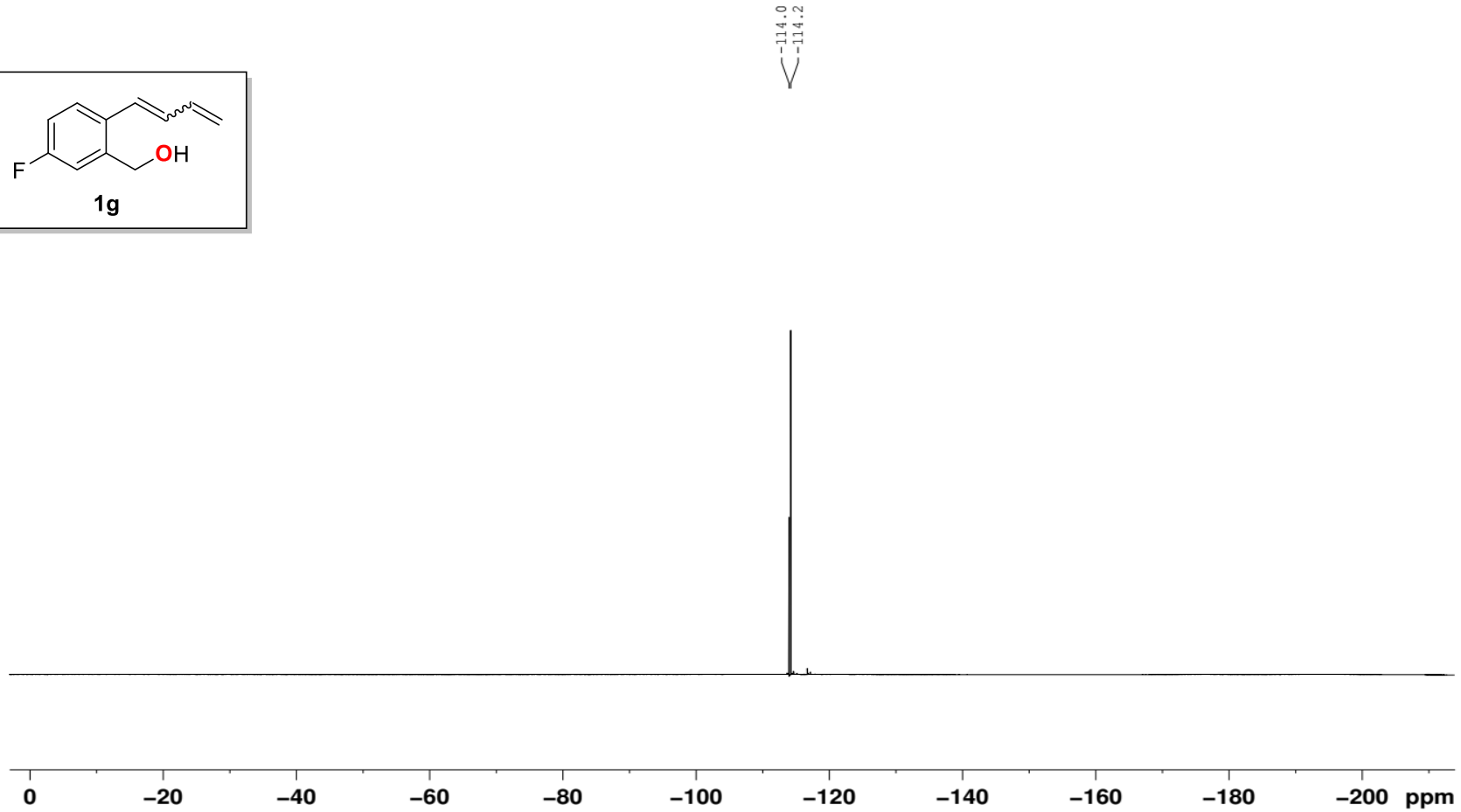


hy-S-**1g** ^{13}C NMR (100MHz $CDCl_3$)

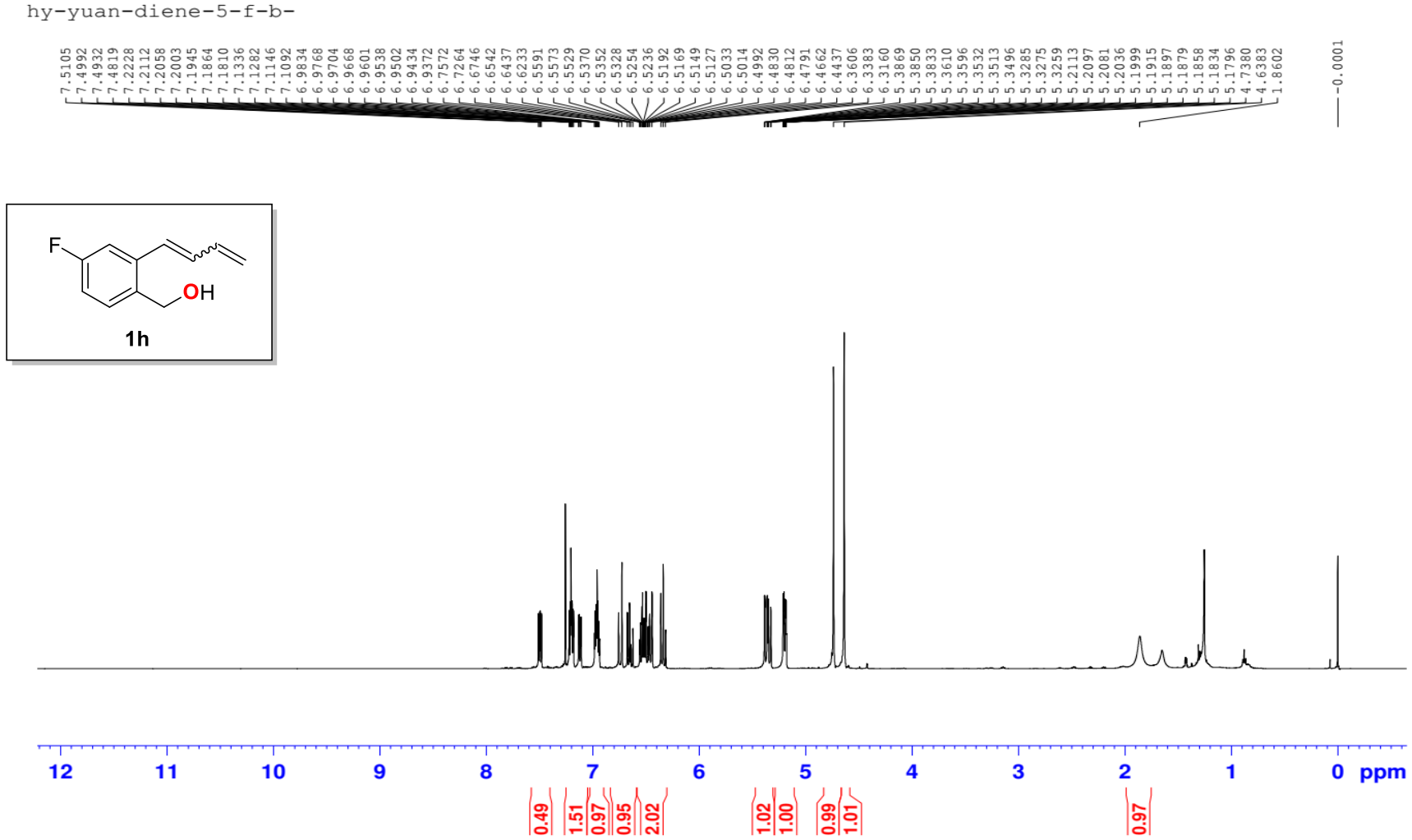


hy-S-**1g** ^{19}F NMR (376MHz $CDCl_3$)

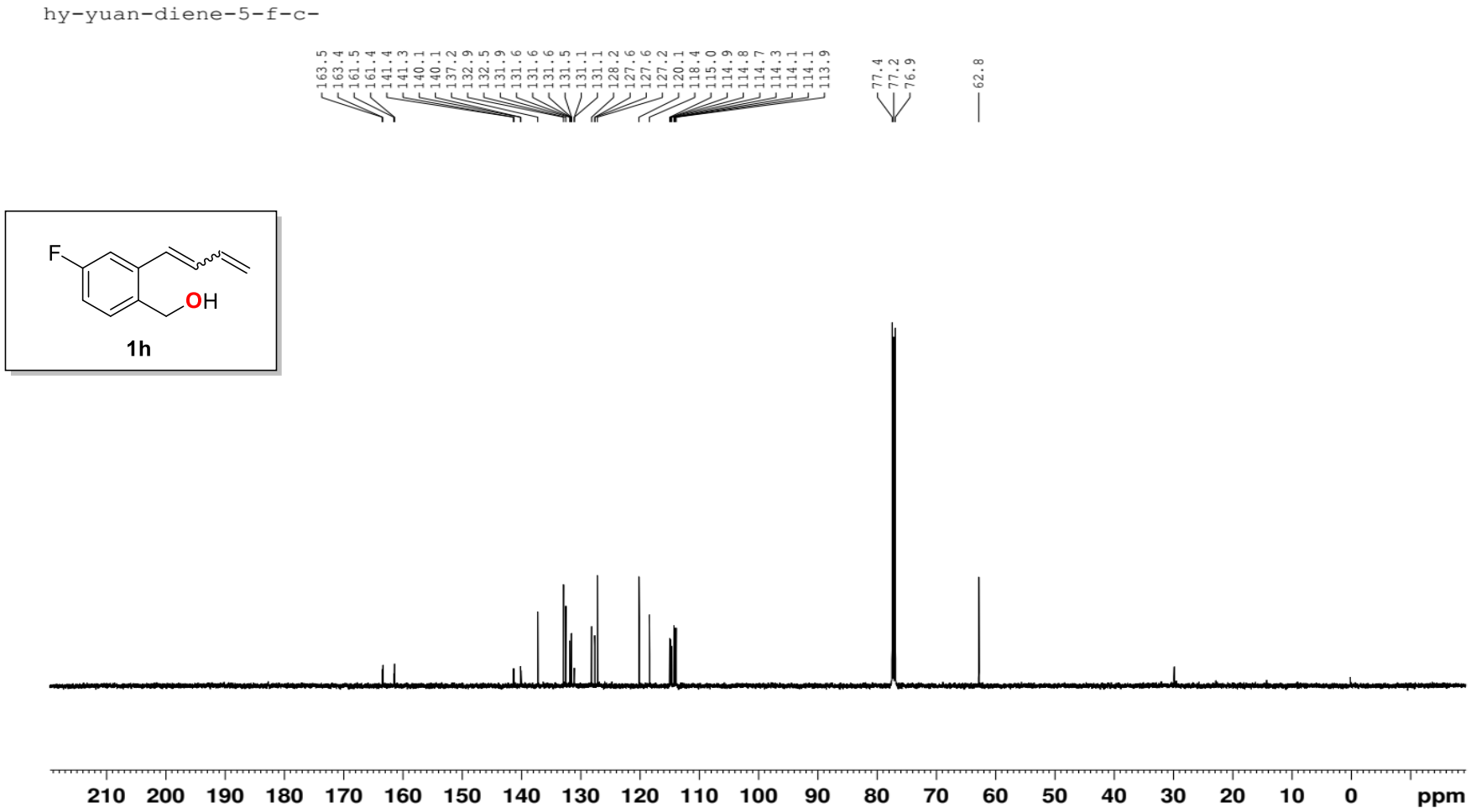
hy-yuan-diene-4-f-f



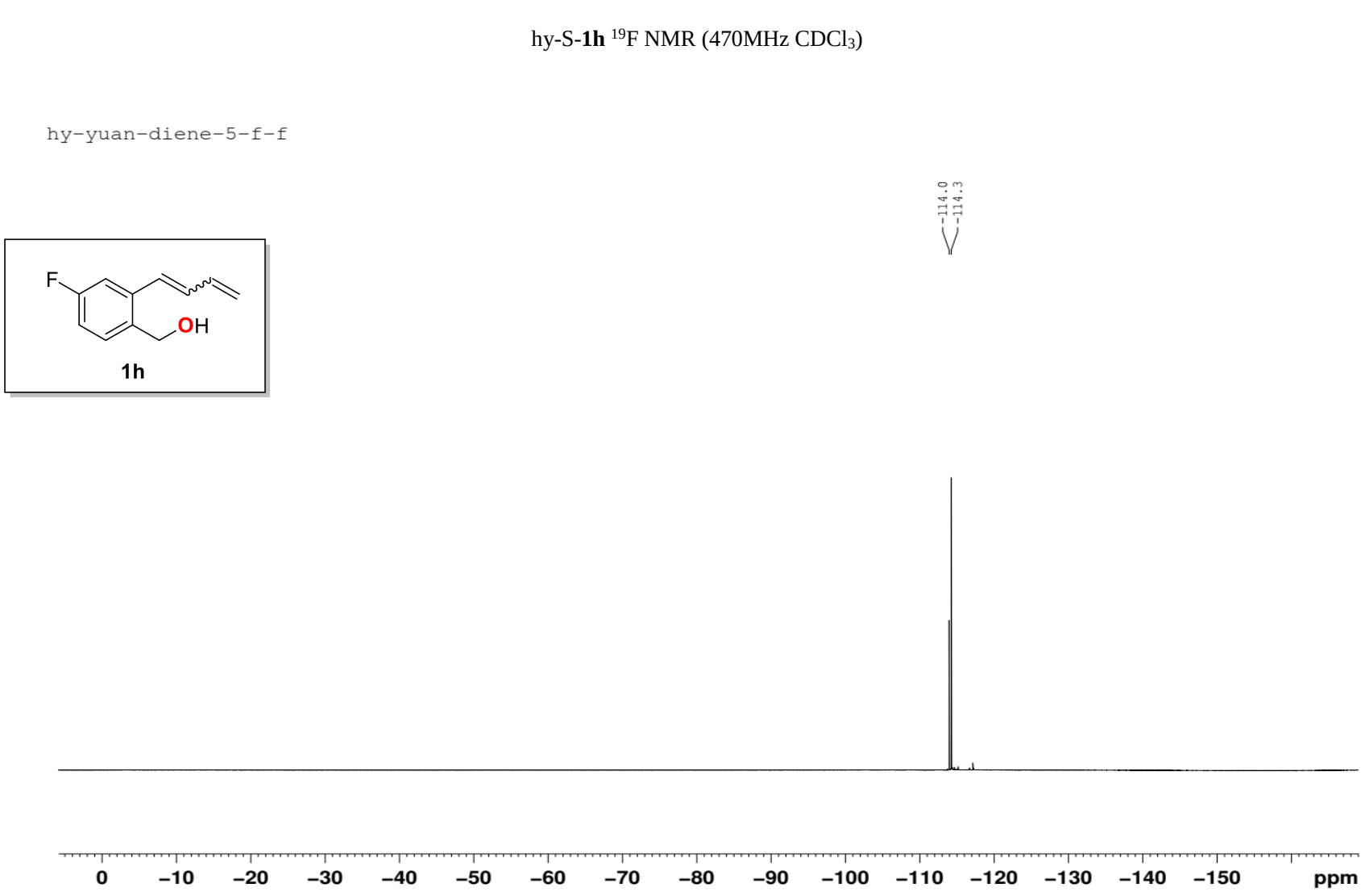
hy-S-**1h** ^{1}H NMR (500MHz $CDCl_3$)



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



hy-S-**1h** ^{19}F NMR (470MHz $CDCl_3$)



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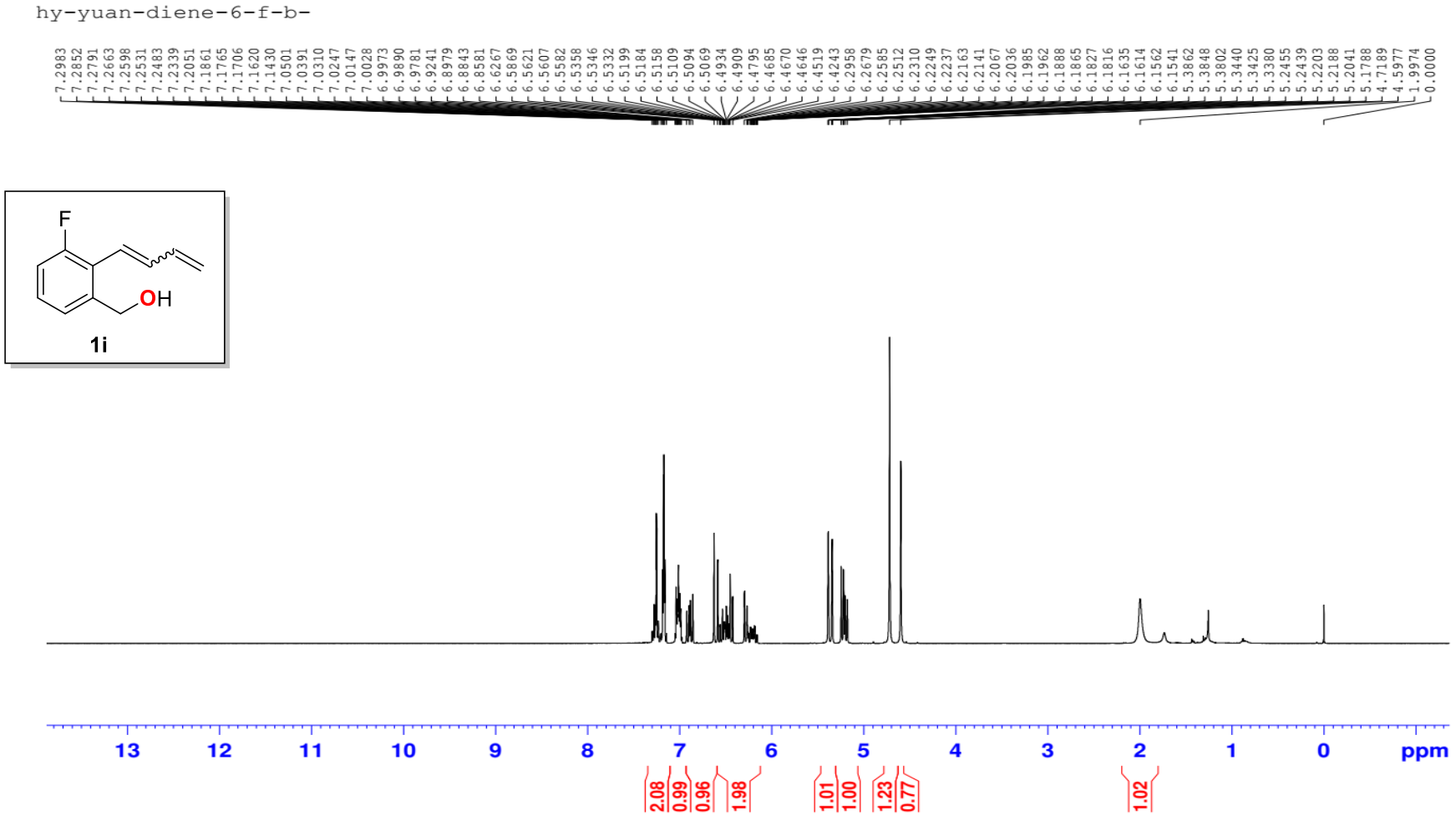

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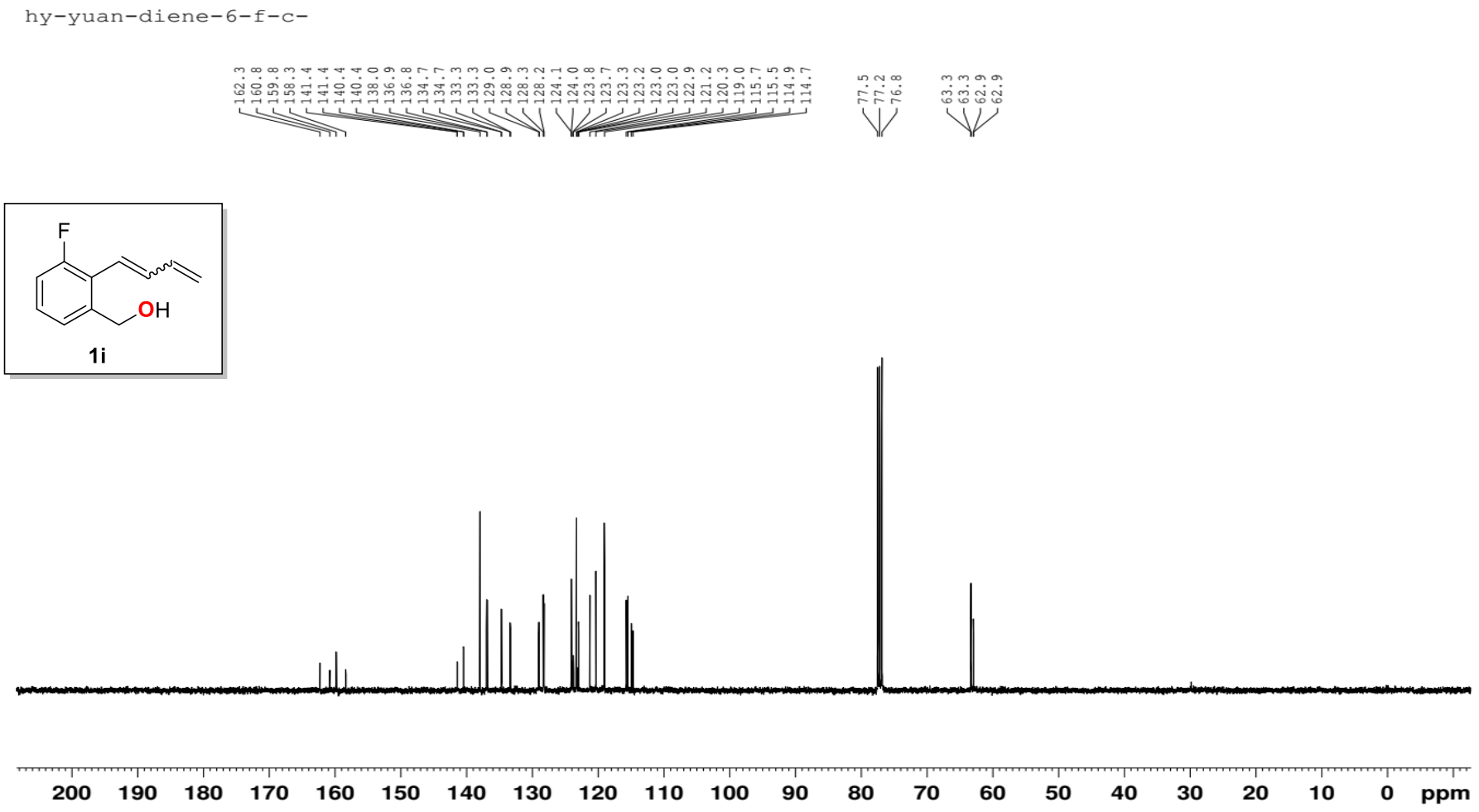
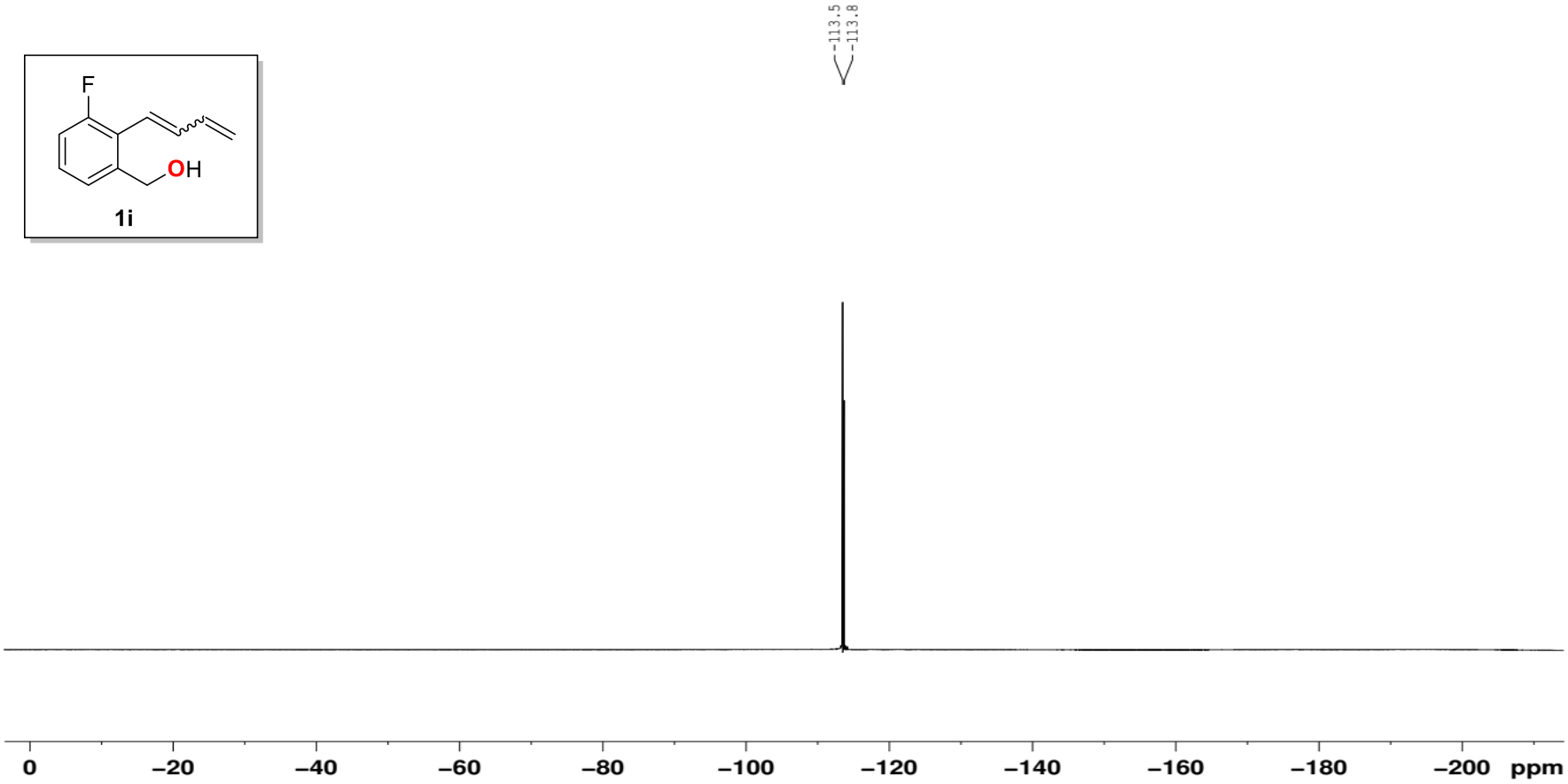


hy-S-**1i** ^{19}F NMR (376MHz $CDCl_3$)

hy-yuan-diene-6-f--f

1i



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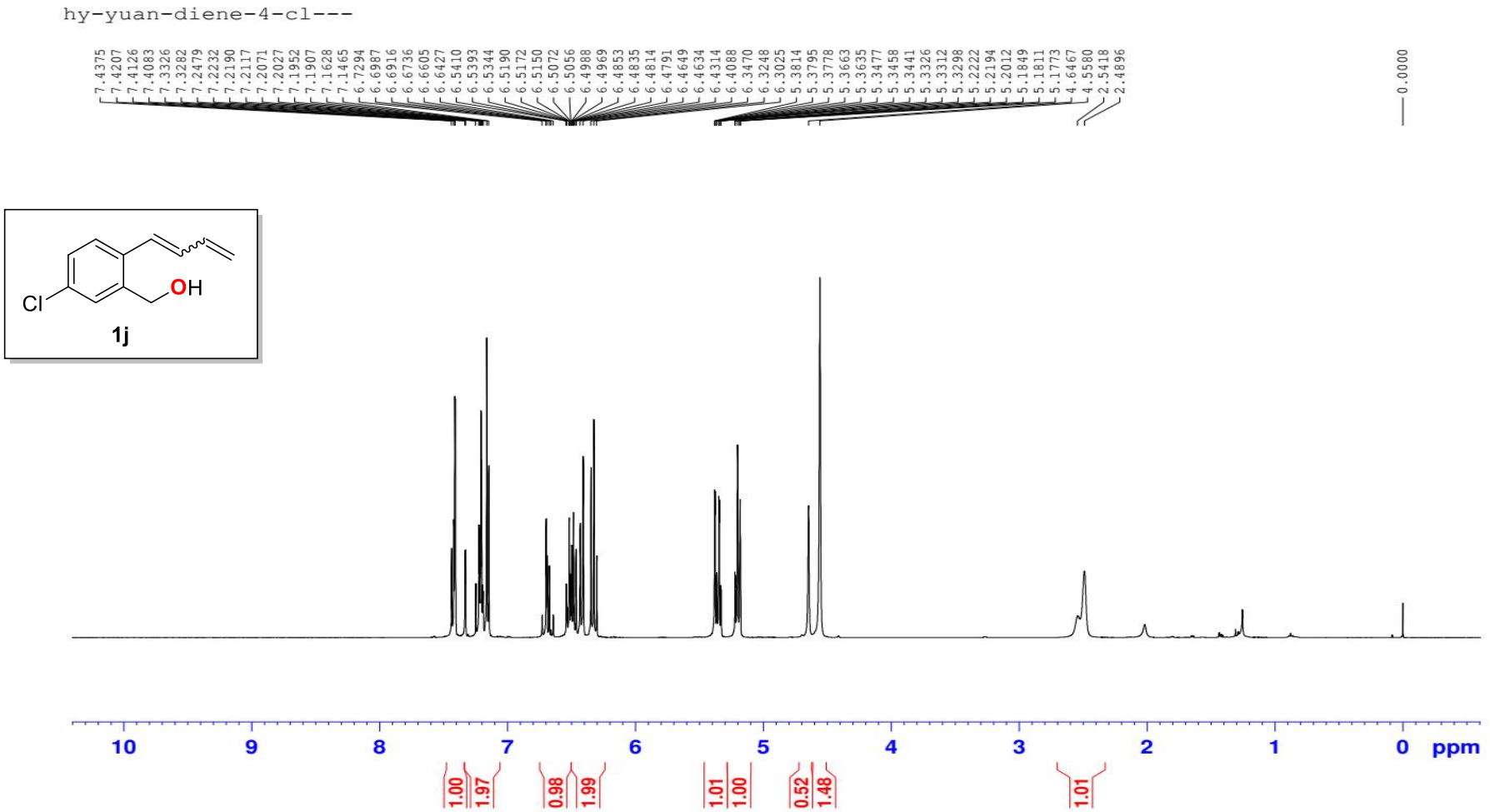
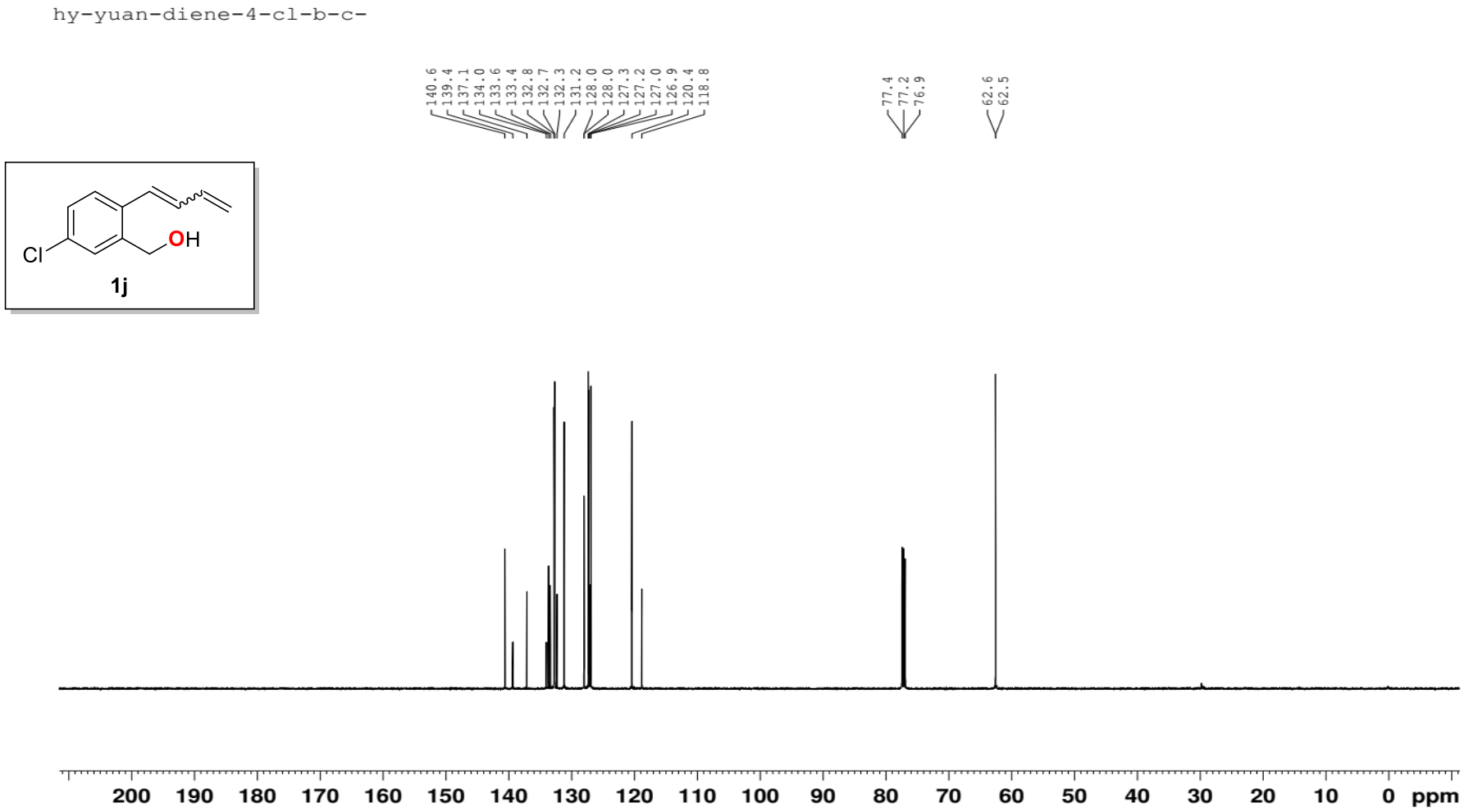
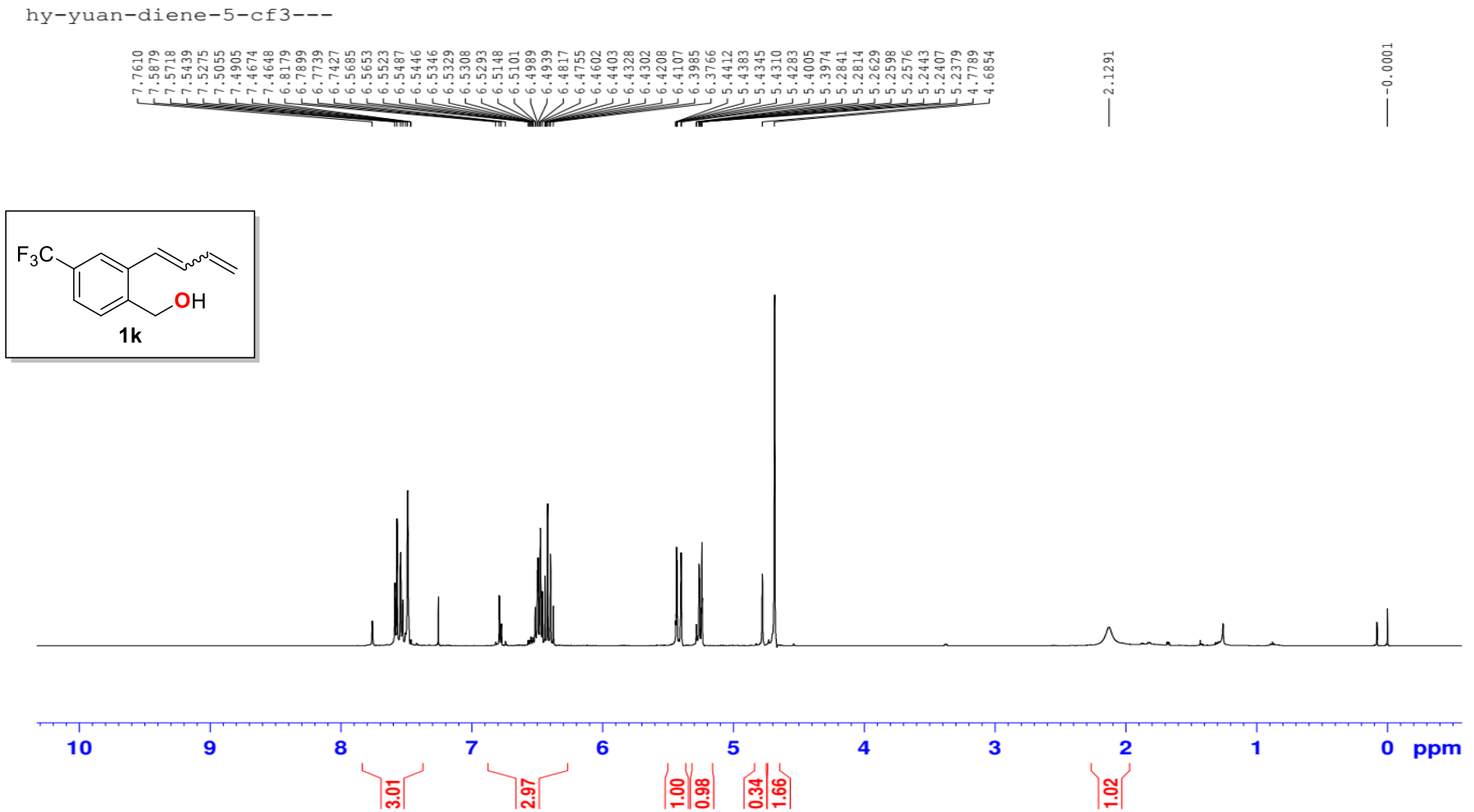


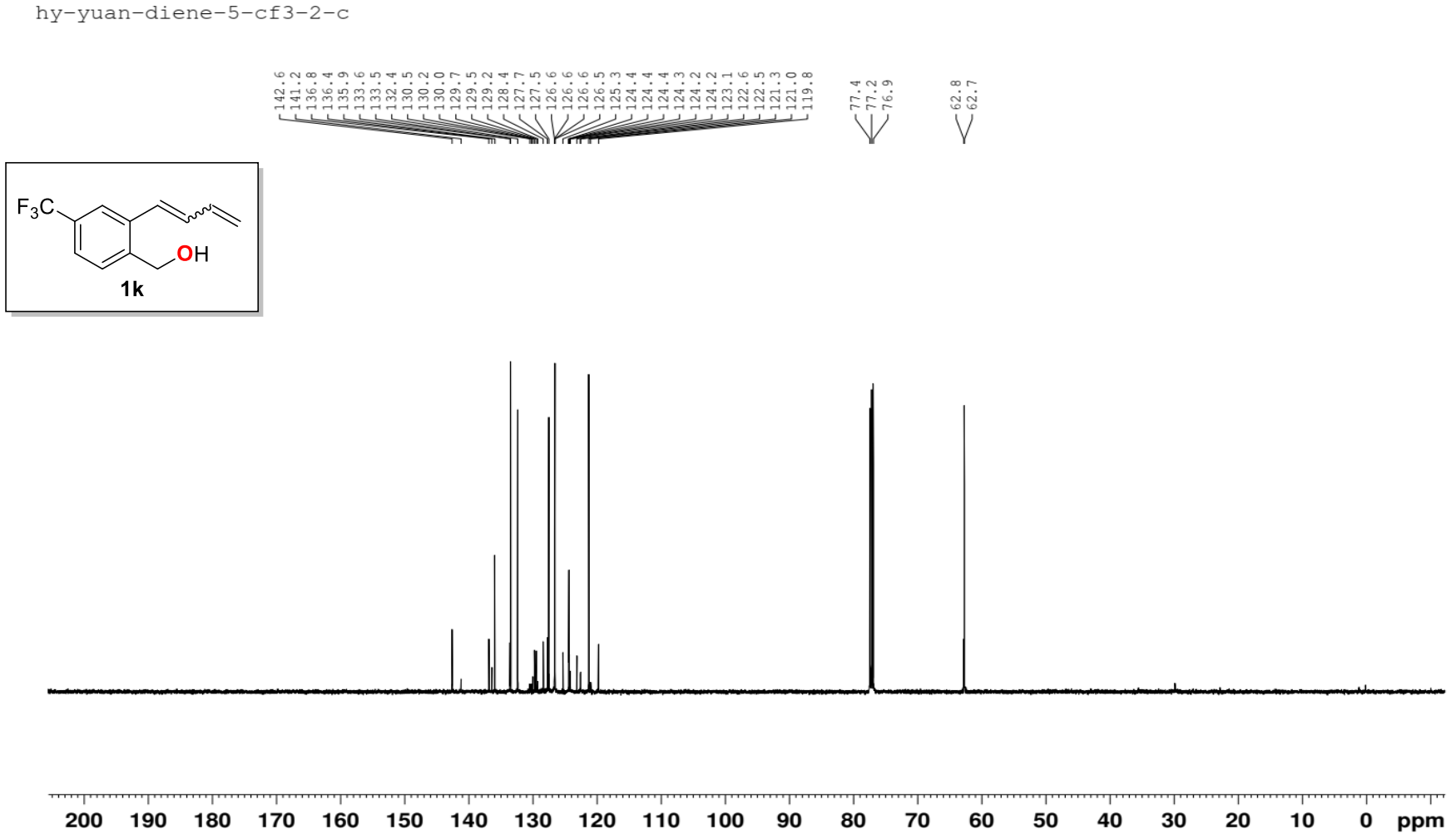
hy-S-**1j** ^{13}C NMR (125MHz $CDCl_3$)



hy-S-**1k** ^{1}H NMR (500MHz $CDCl_3$)

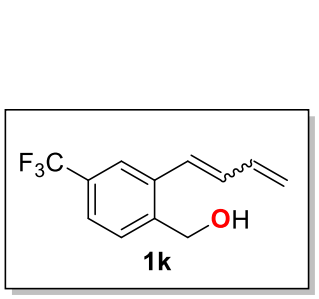


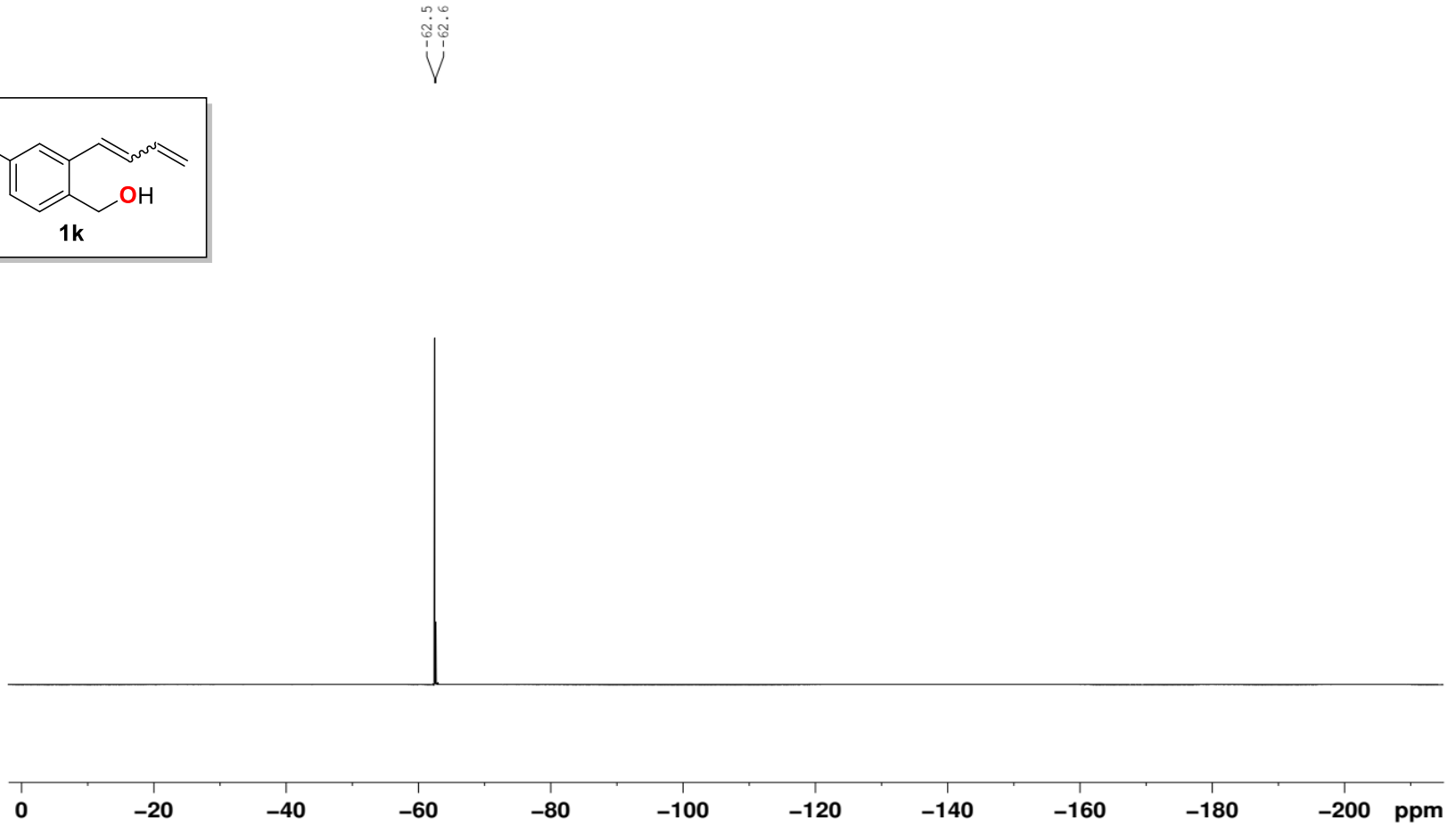
hy-S-**1k** ^{13}C NMR (125MHz $CDCl_3$)



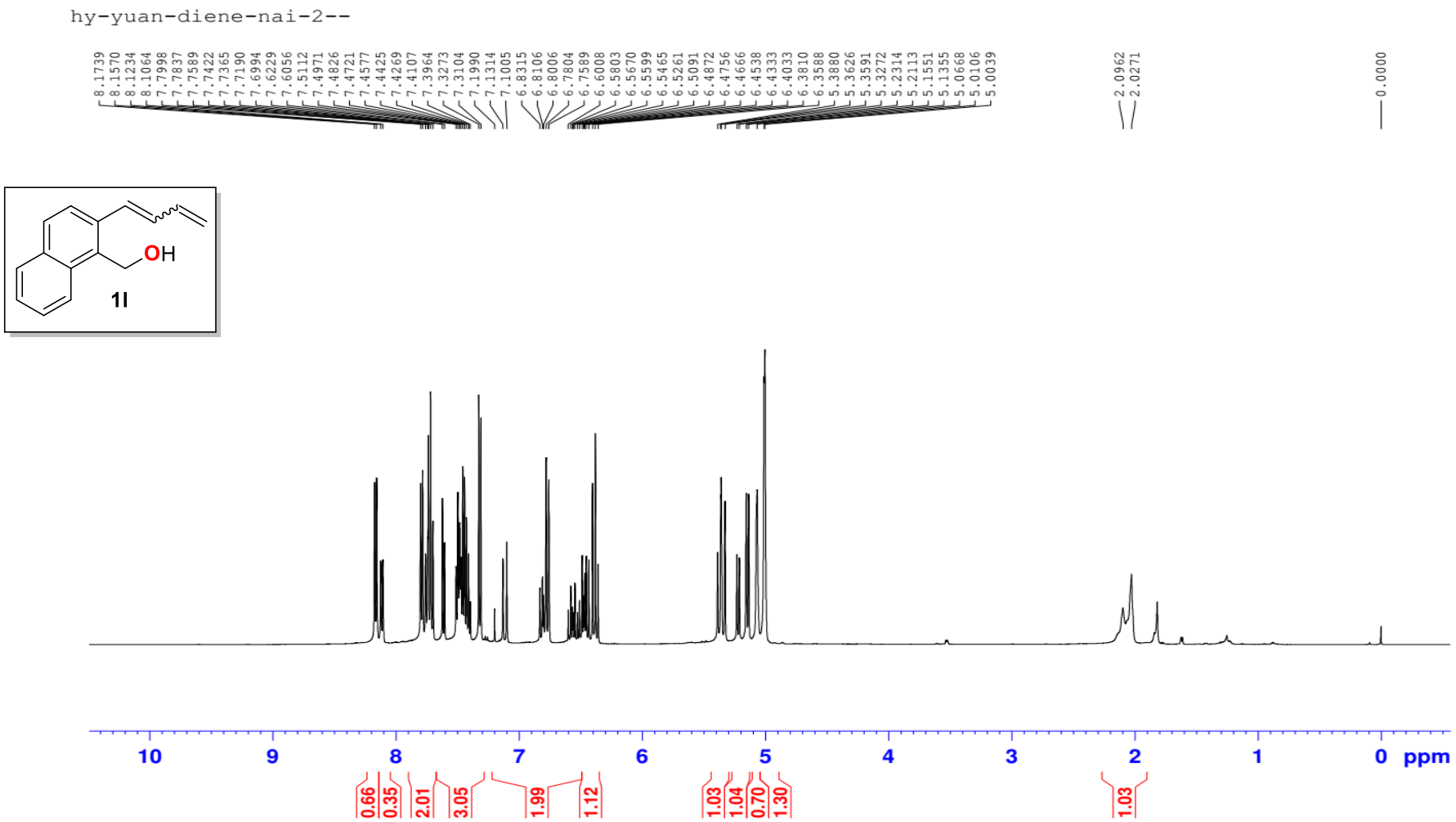
hy-S-**1k** ^{19}F NMR (470MHz $CDCl_3$)

hy-yuan-diene-5-cf3-f

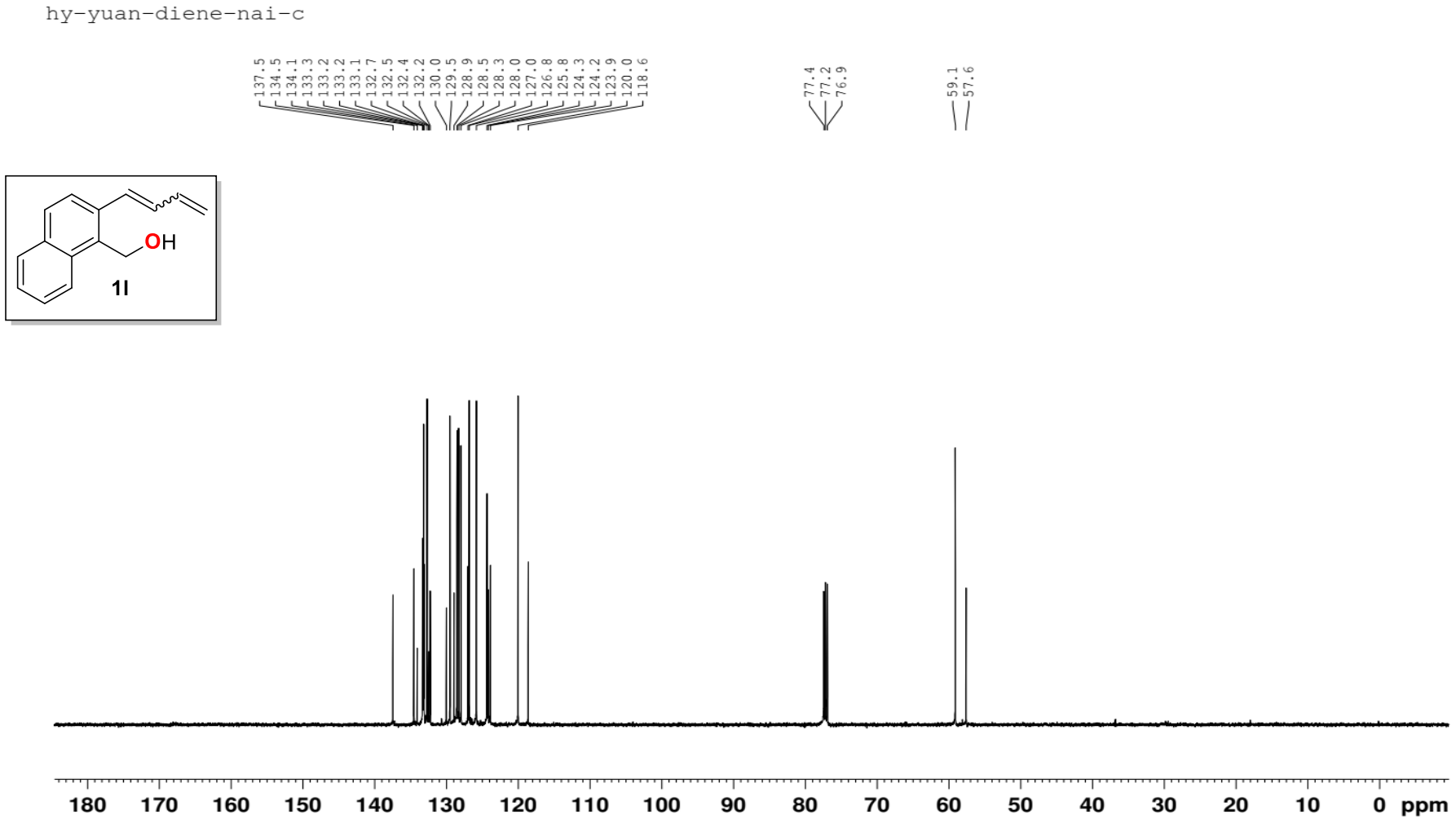




hy-S-**1l** ^{1}H NMR (500MHz $CDCl_3$)



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



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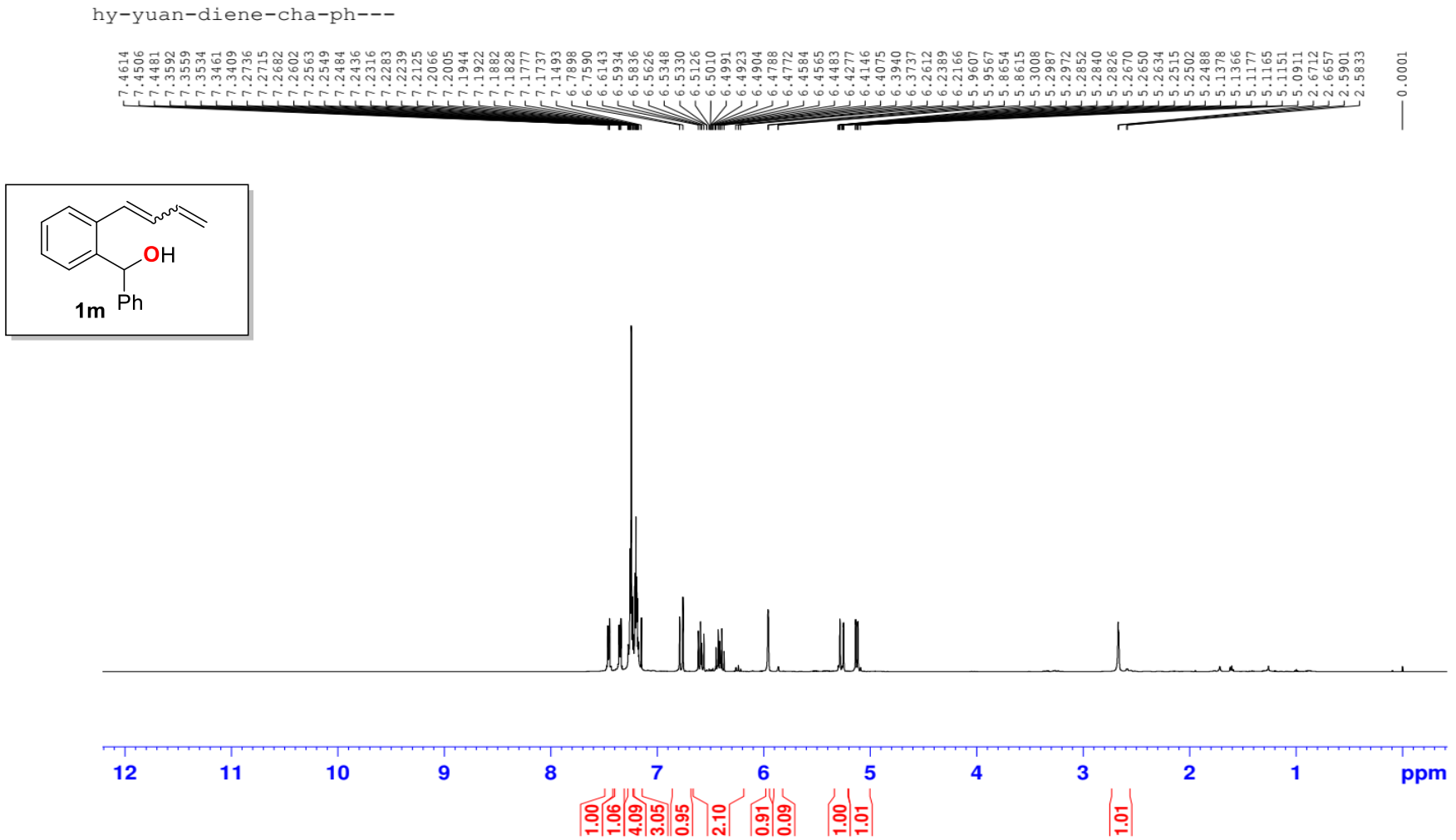

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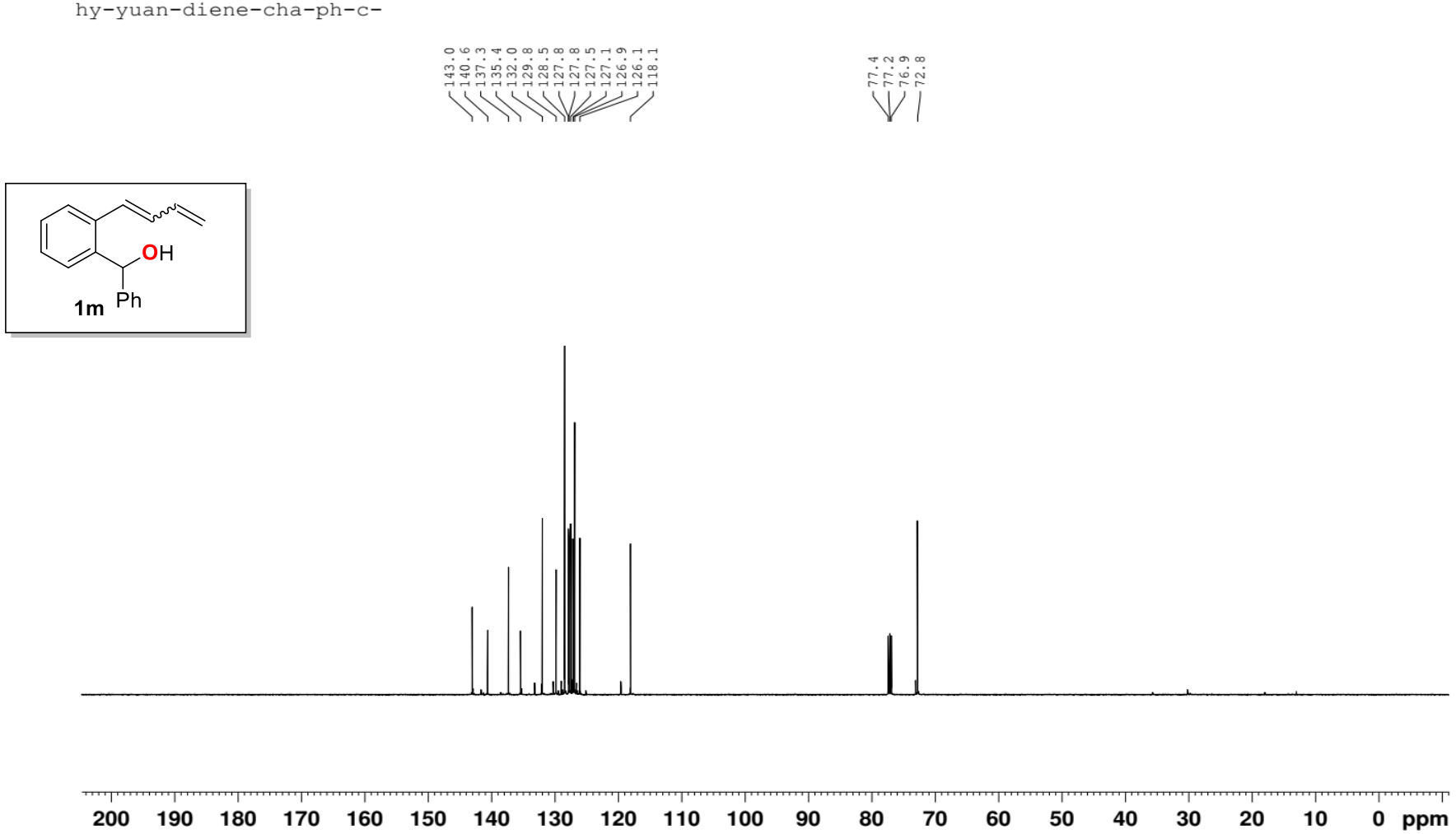

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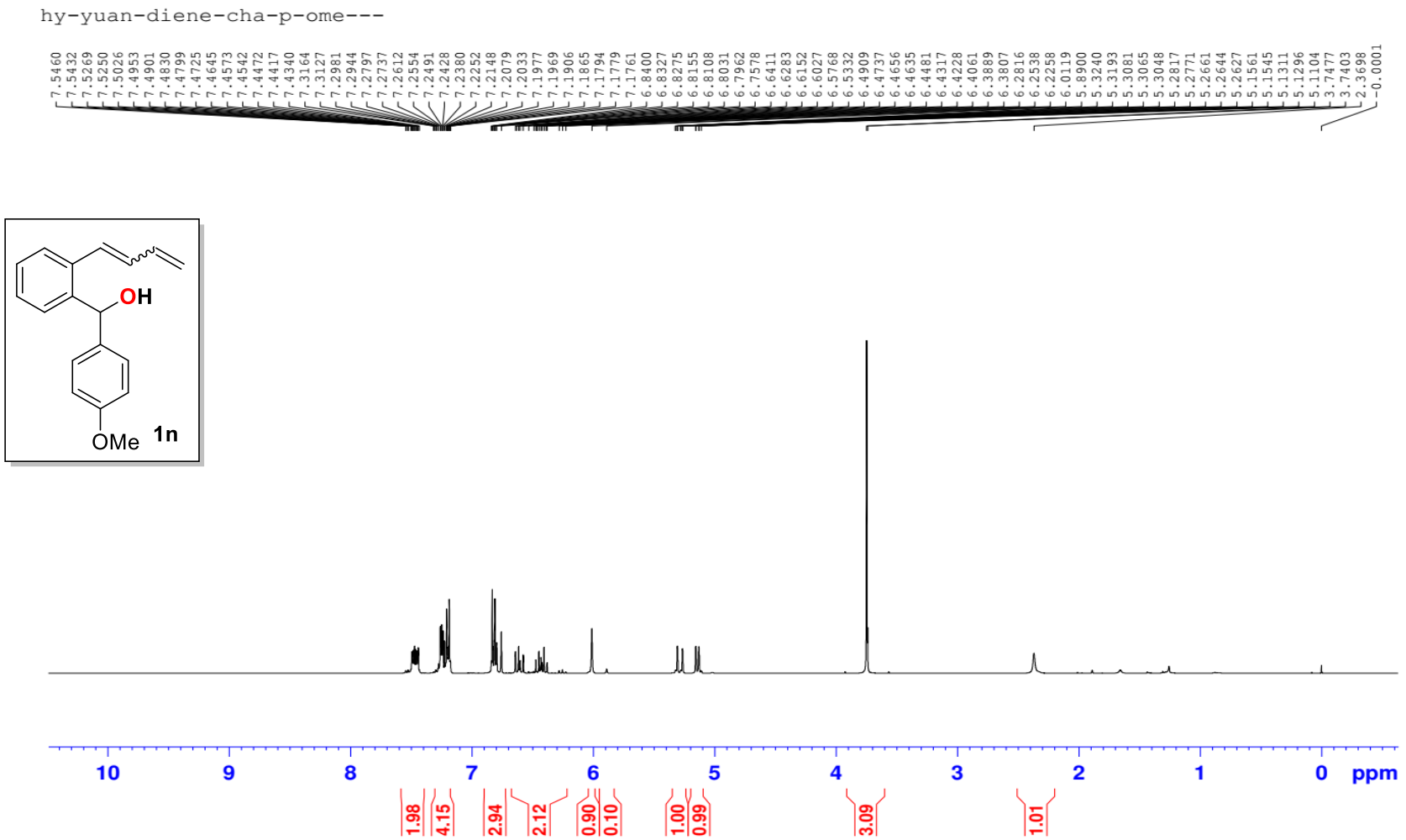

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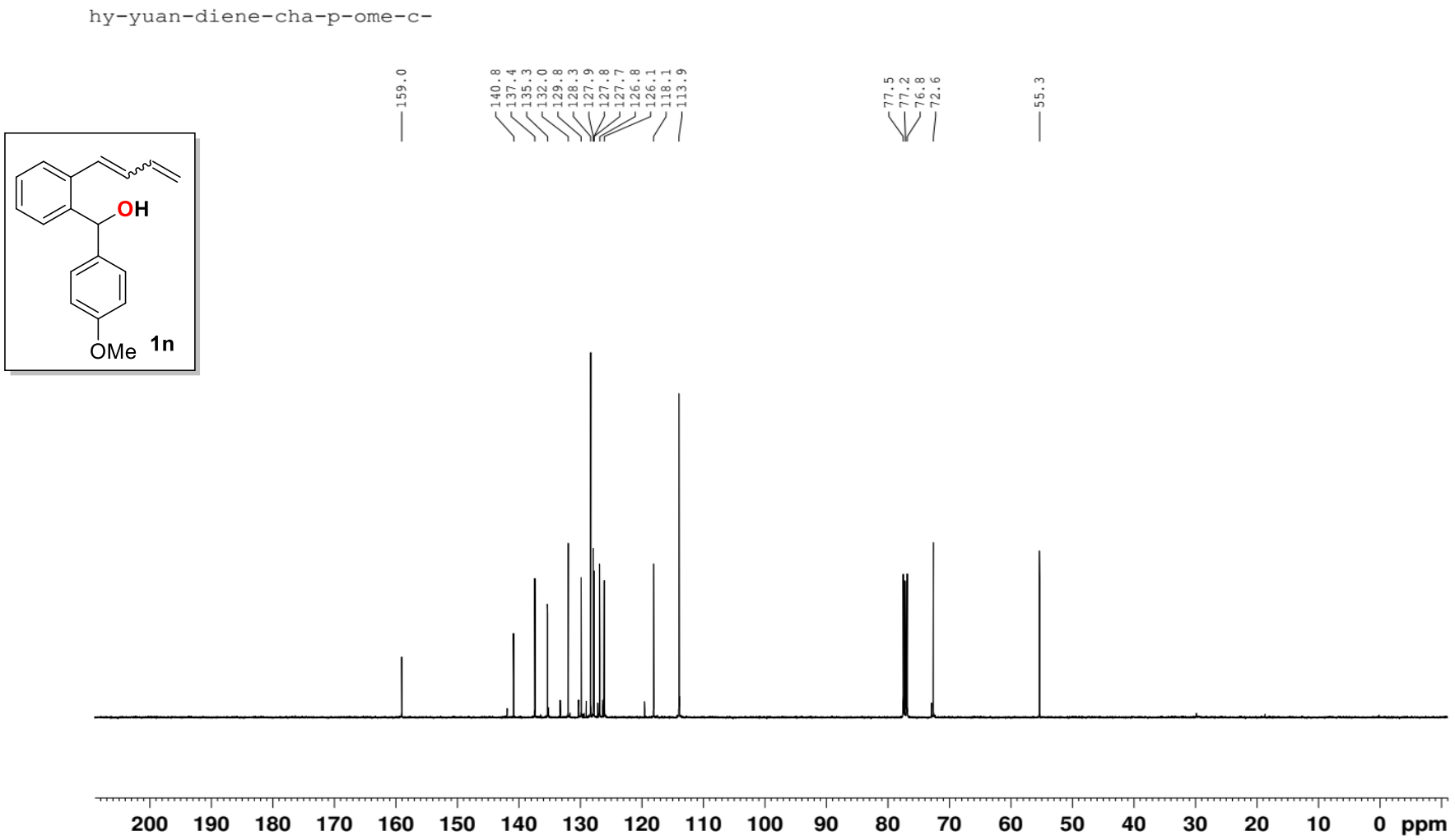

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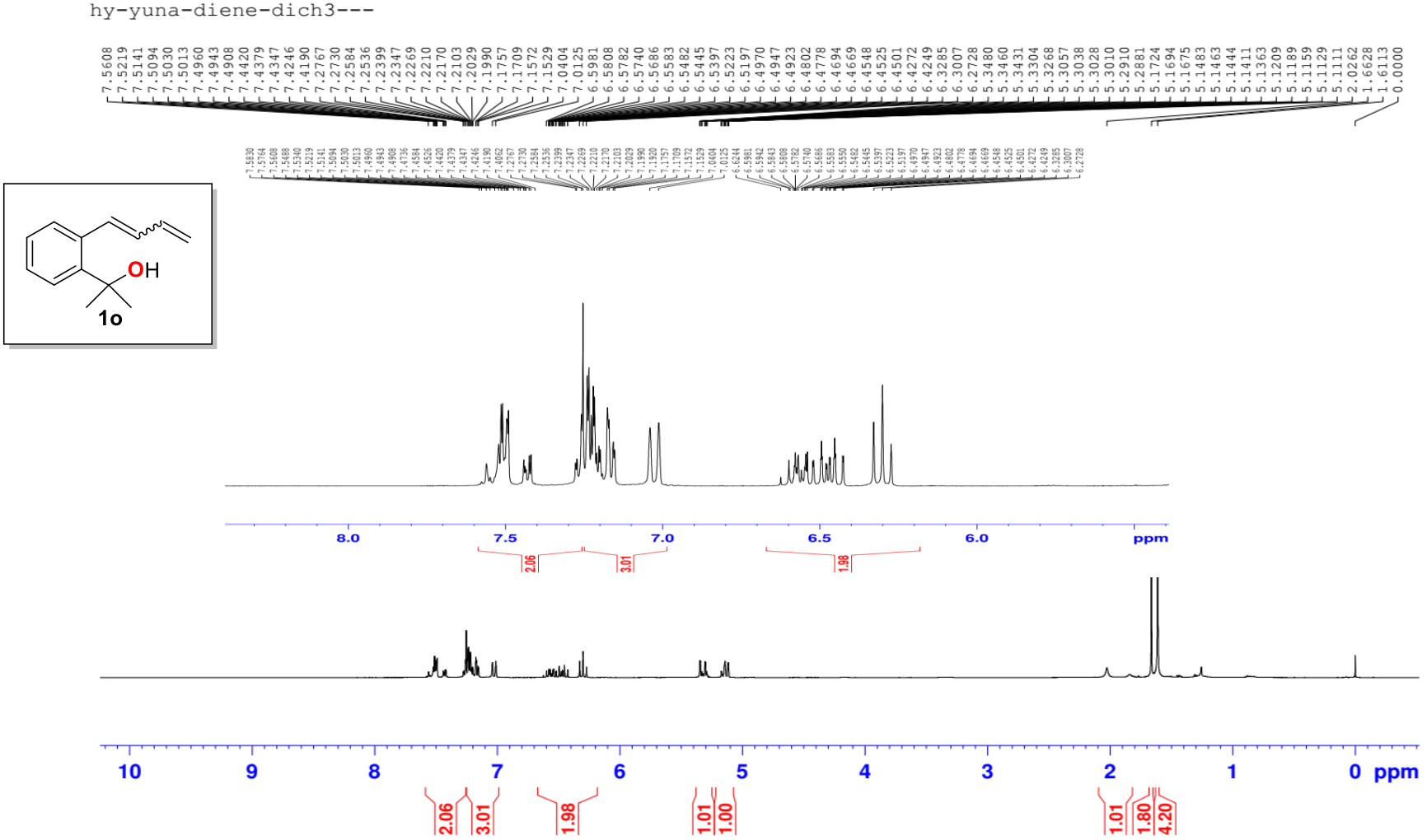
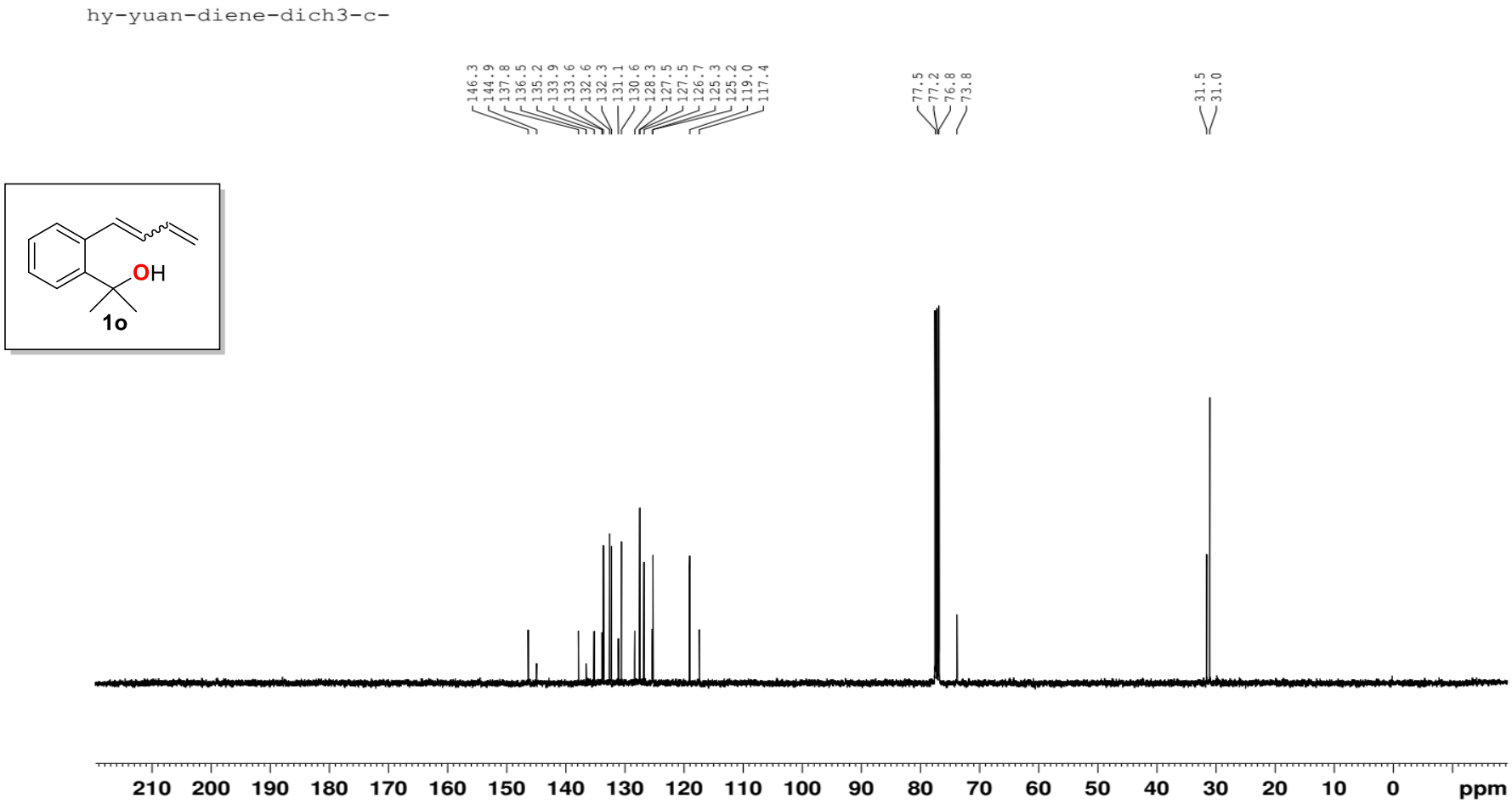
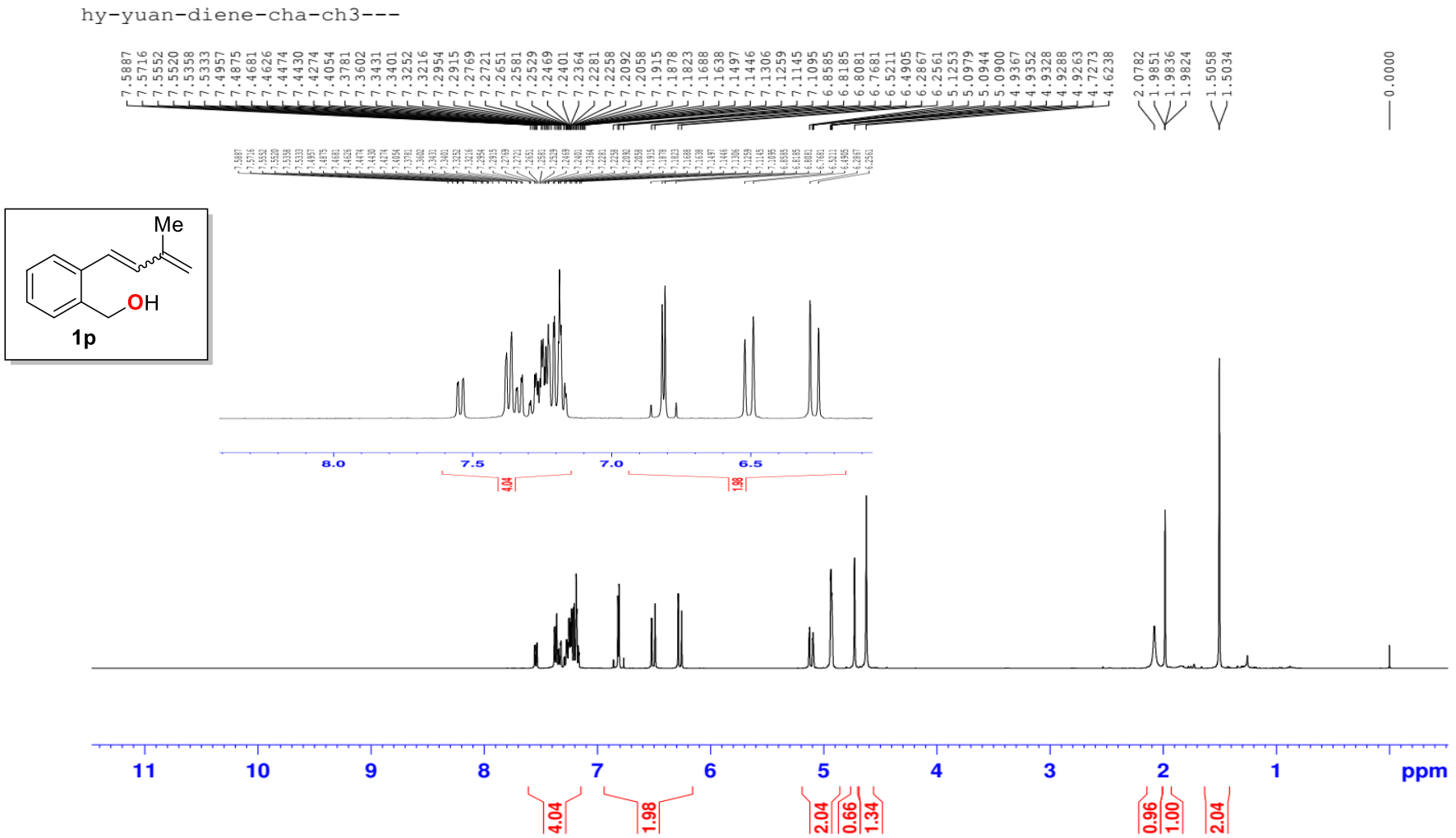


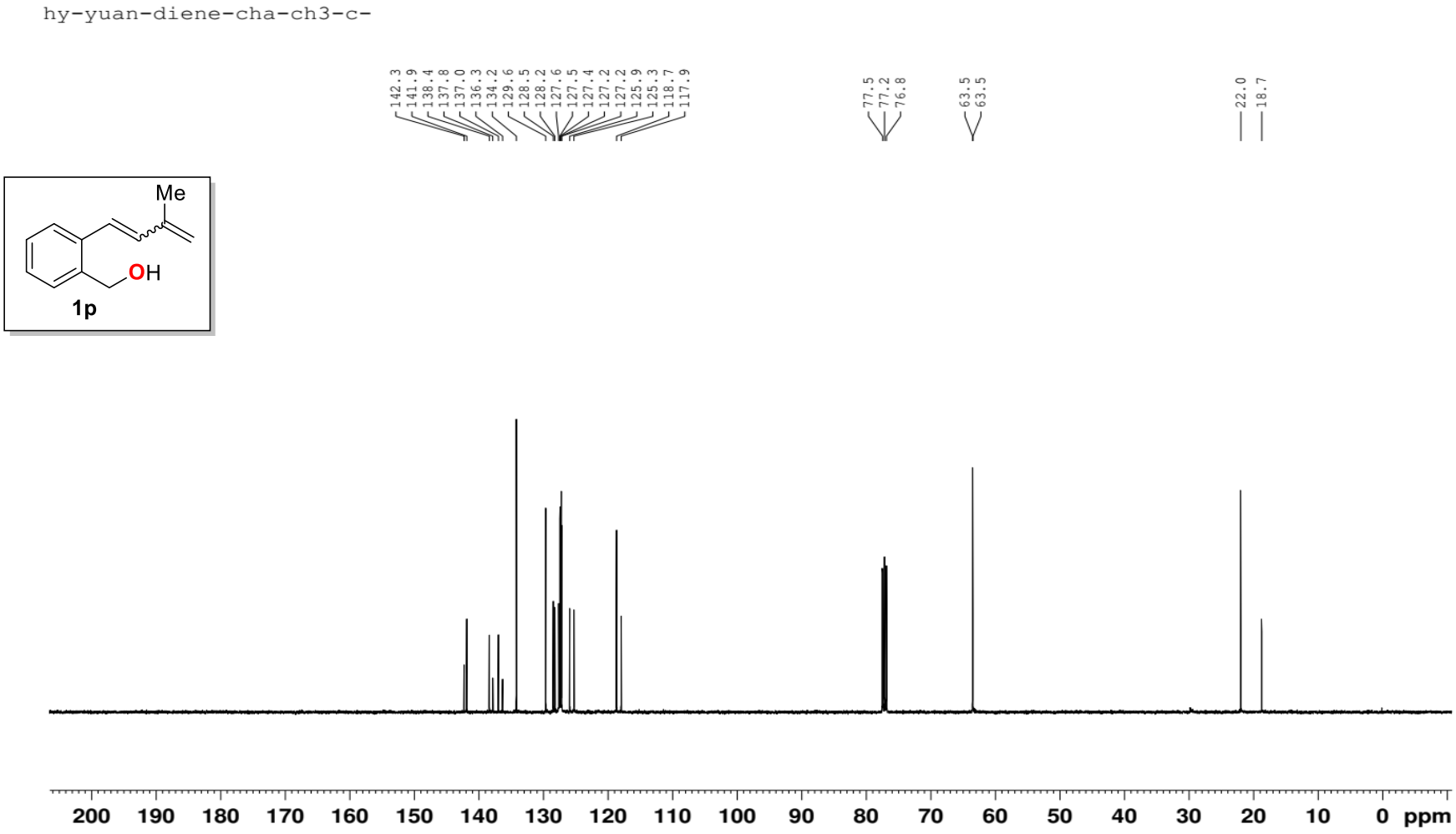
hy-S-**1o** ^{13}C NMR (100MHz $CDCl_3$)



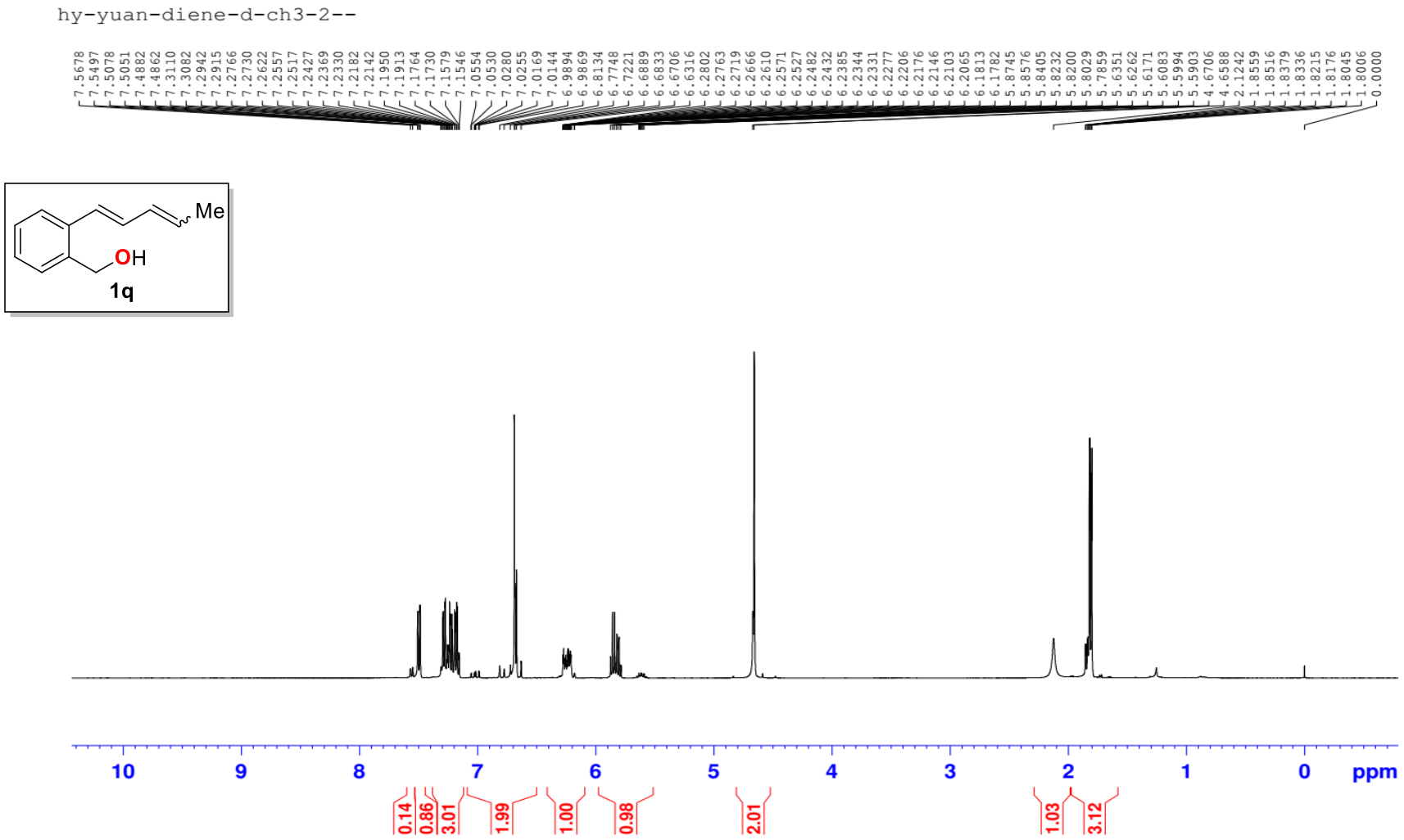
hy-S-**1p** ^{1}H NMR (400MHz $CDCl_3$)



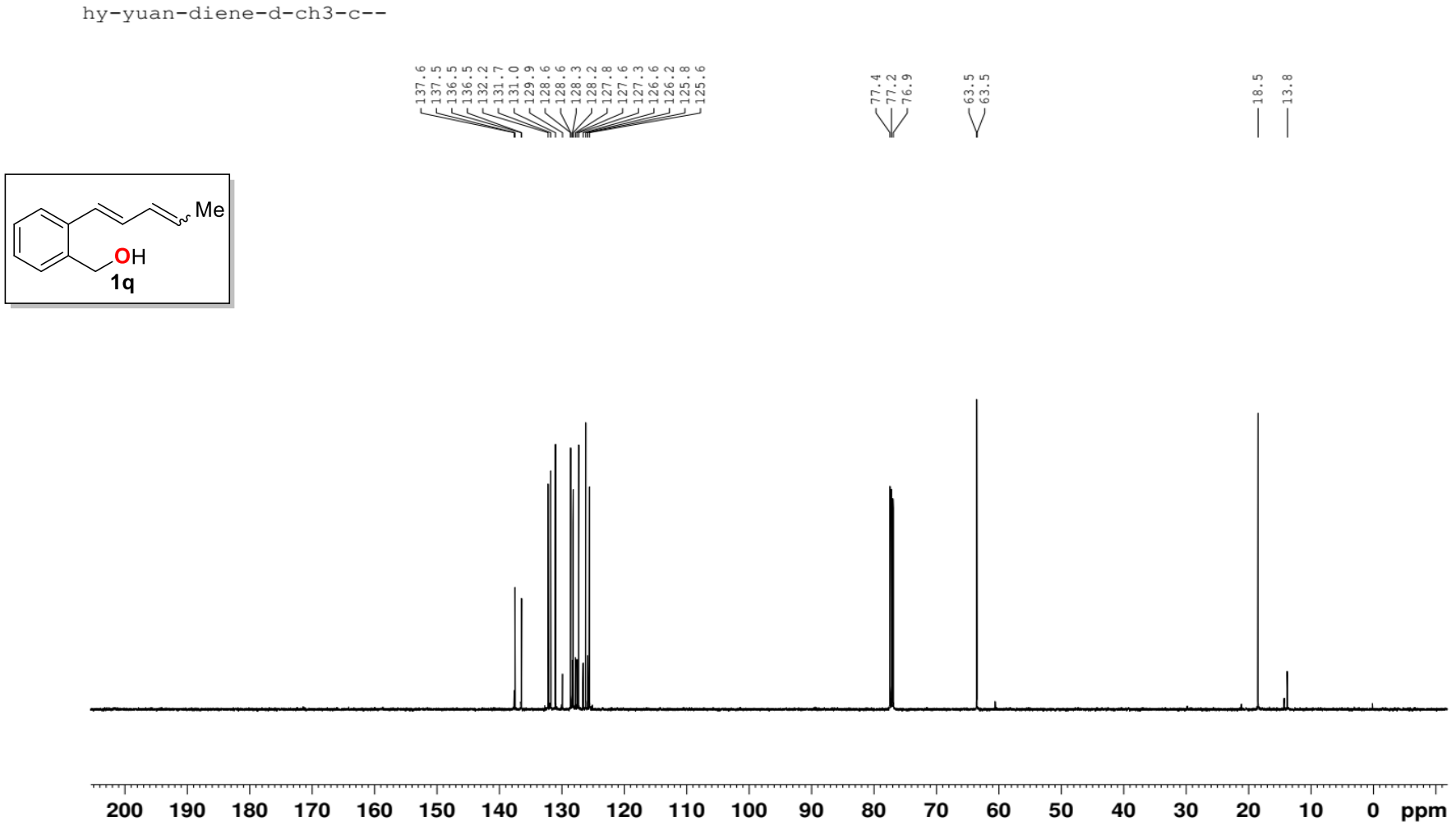
hy-S-**1p** ^{13}C NMR (100MHz $CDCl_3$)



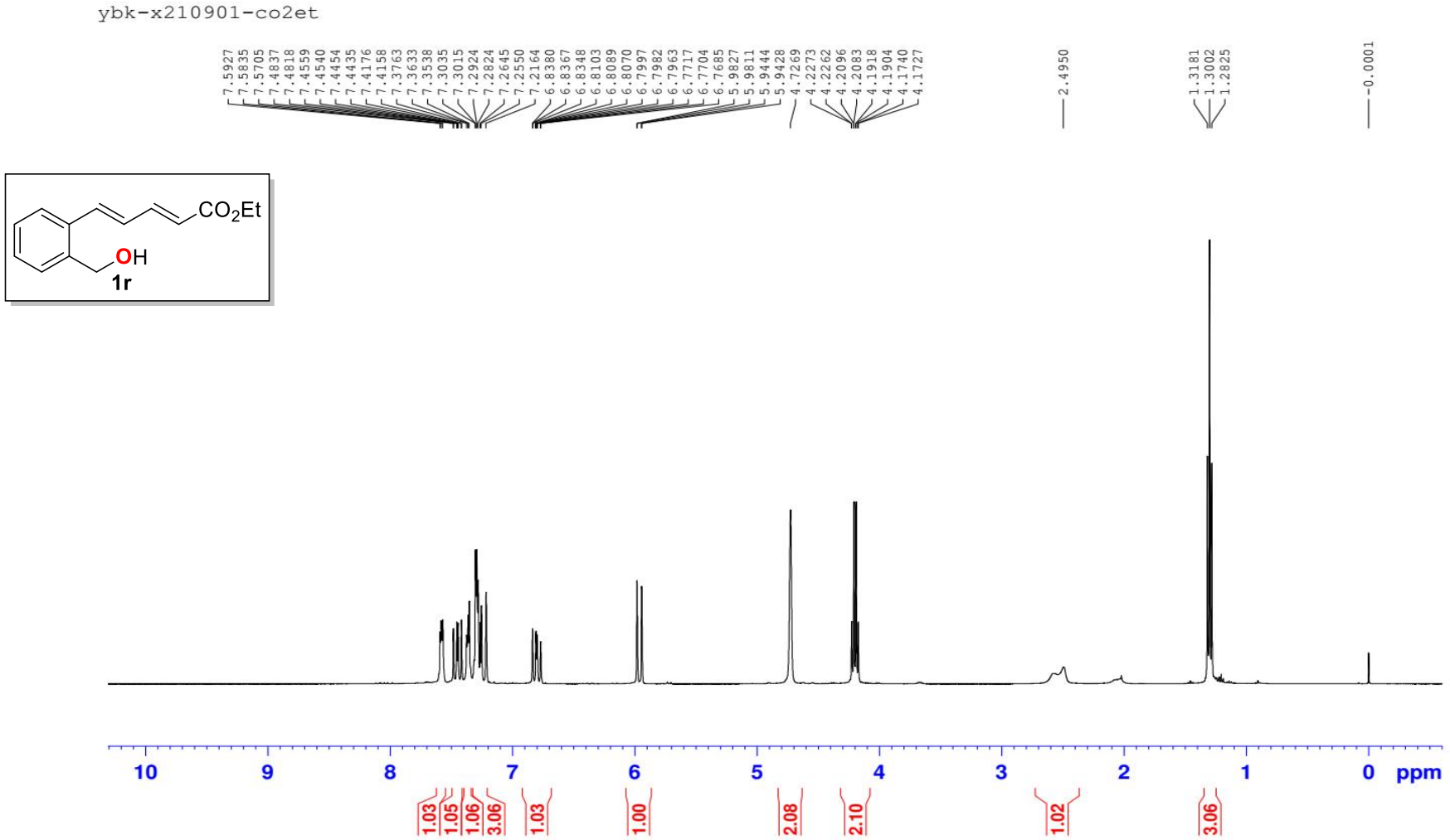
hy-S-**1q** ^{1}H NMR (400MHz $CDCl_3$)



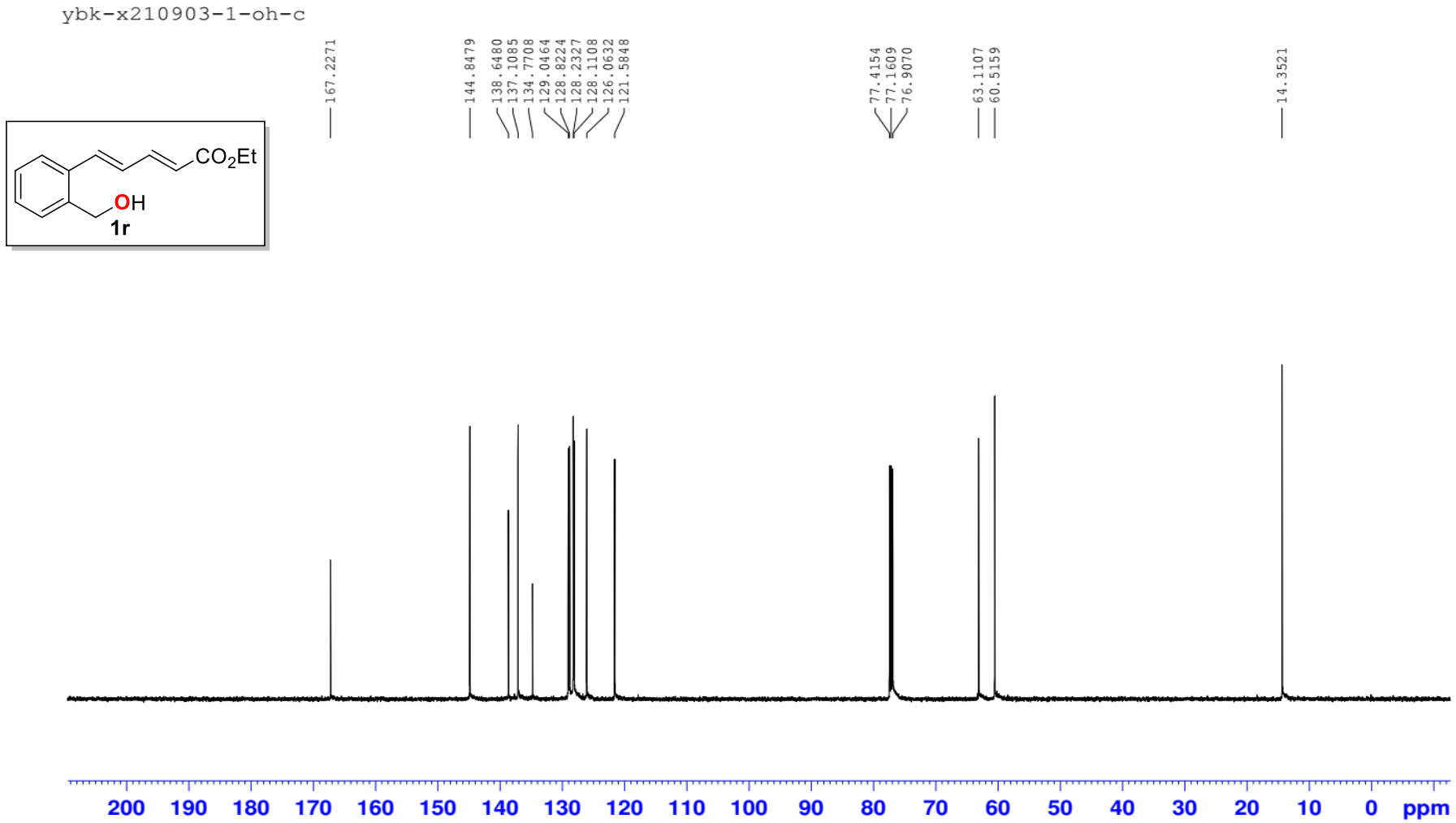
hy-S-**1q** ^{13}C NMR (125MHz $CDCl_3$)



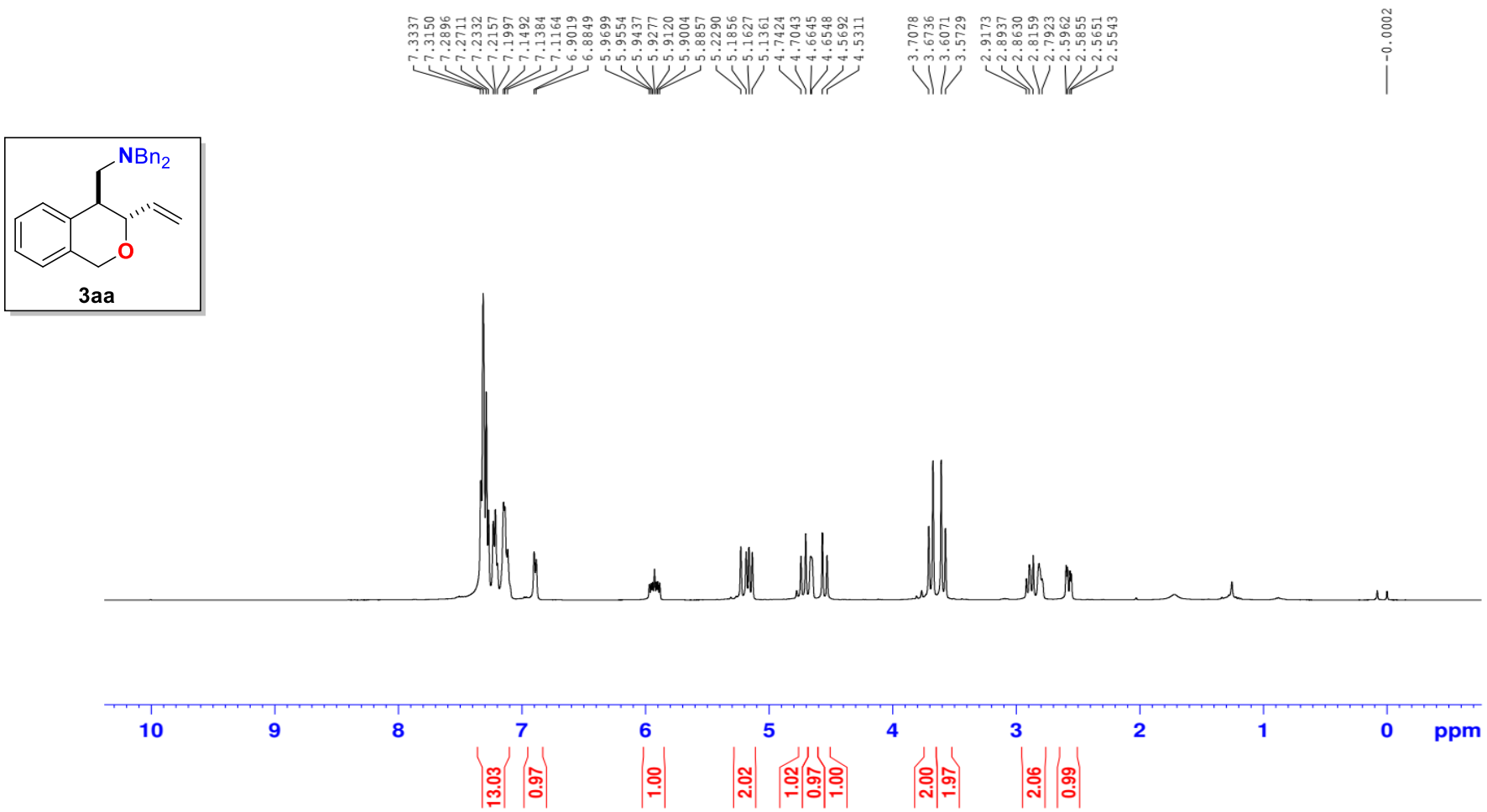
hy-S-**1r** ^{1}H NMR (400MHz $CDCl_3$)



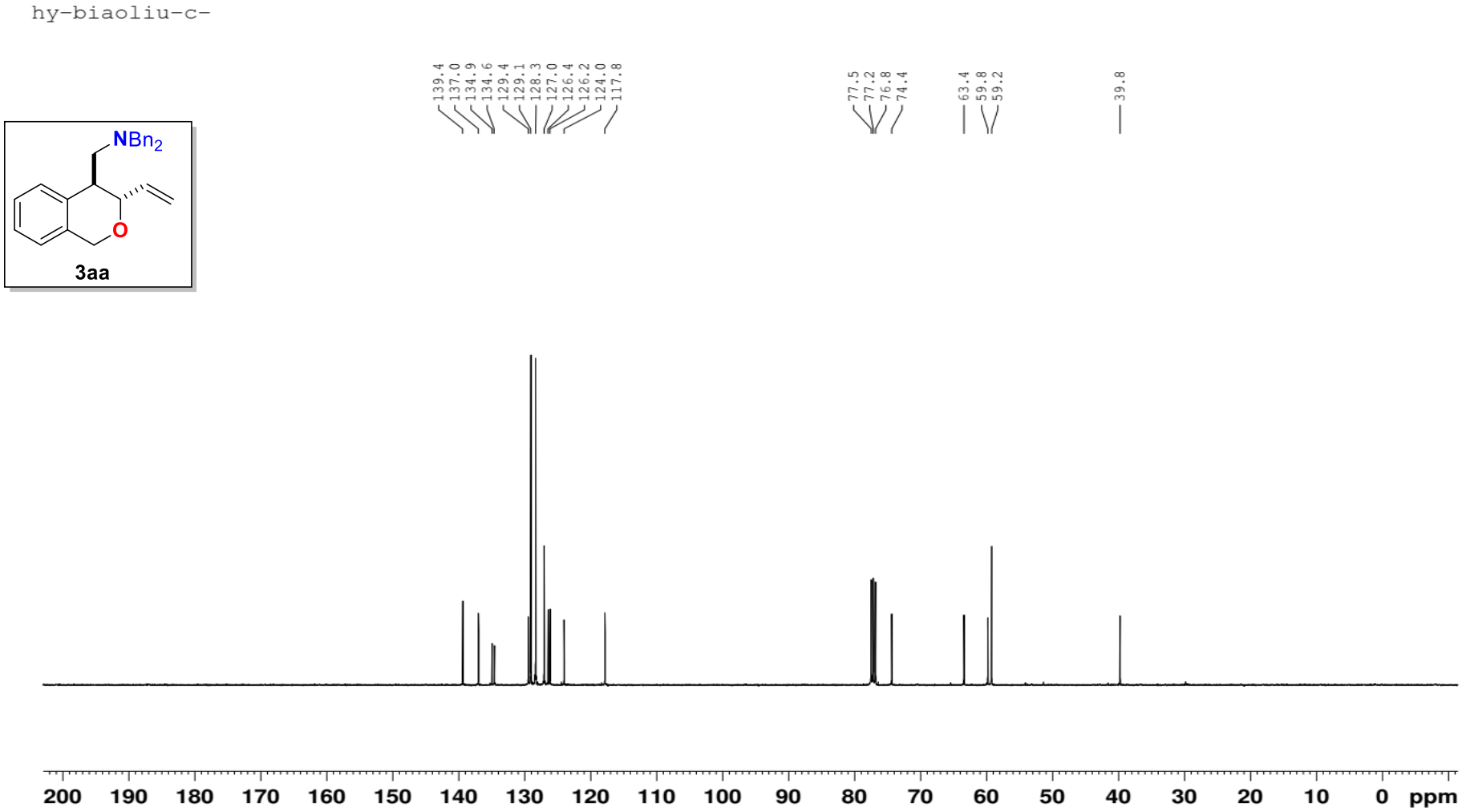
hy-S-**1r** ^{13}C NMR (125MHz $CDCl_3$)



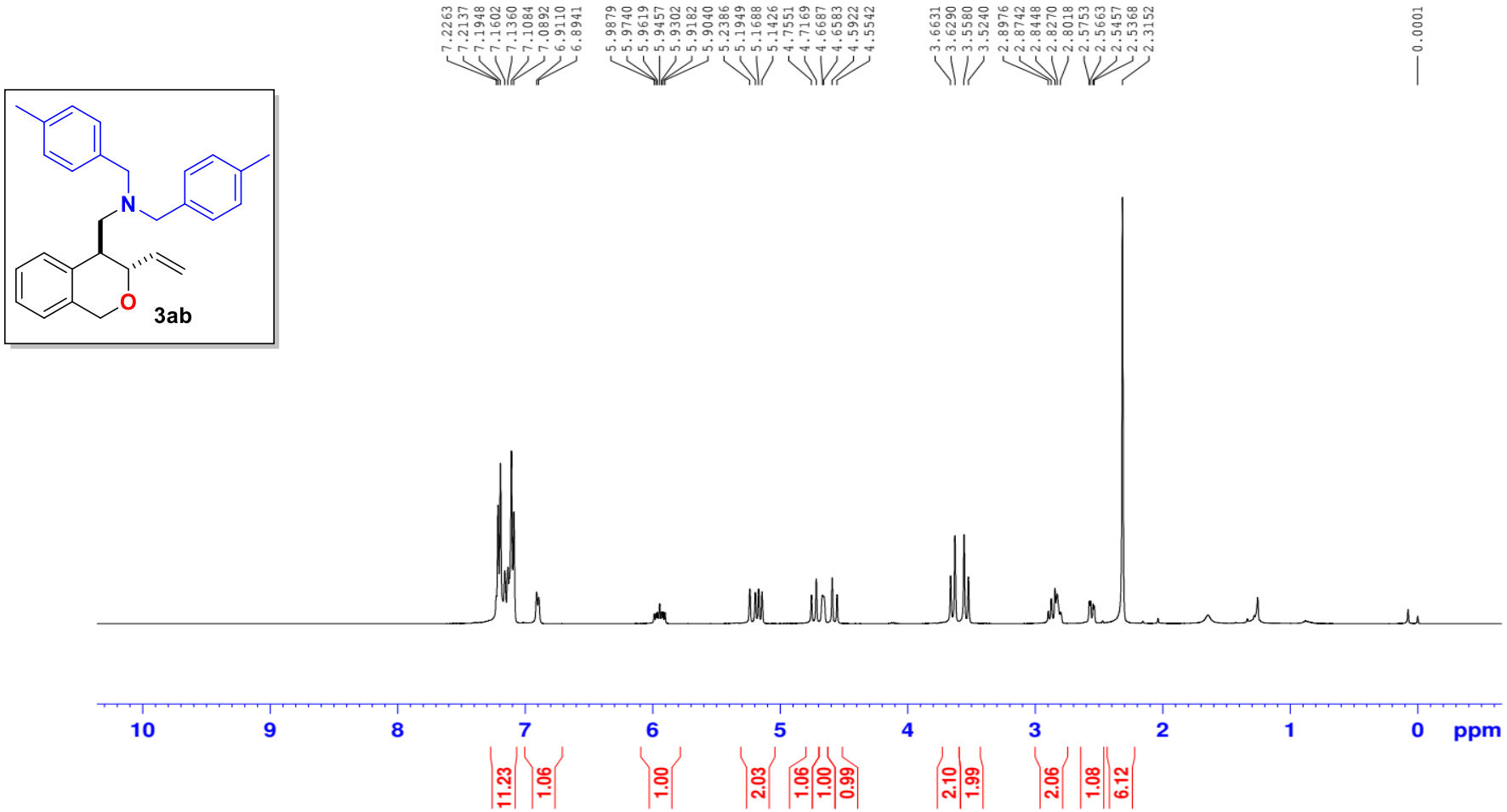
hy-P-**3aa** ^{1}H NMR (400MHz $CDCl_3$)



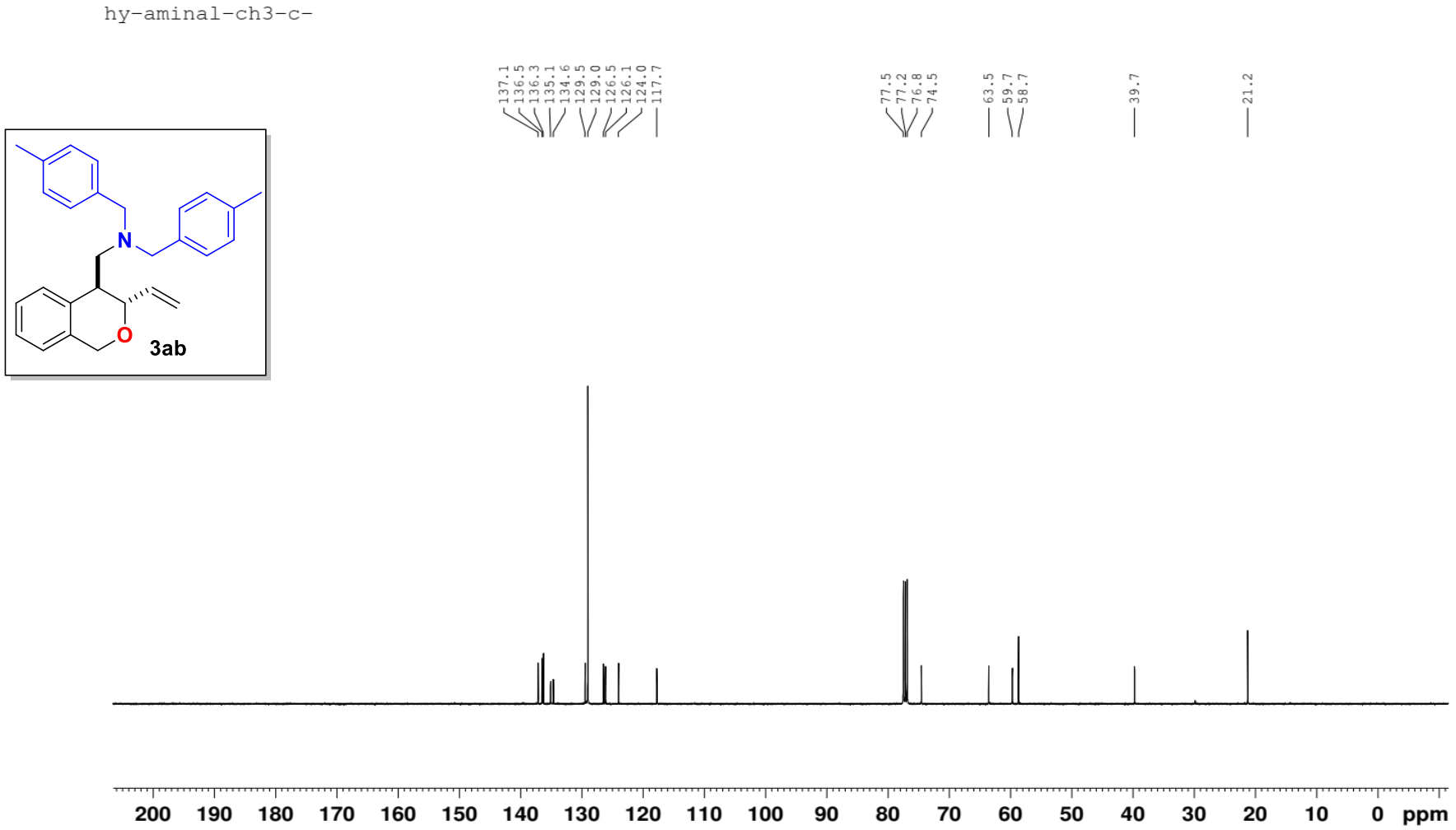
hy-P-**3aa** ^{13}C NMR (100MHz $CDCl_3$)



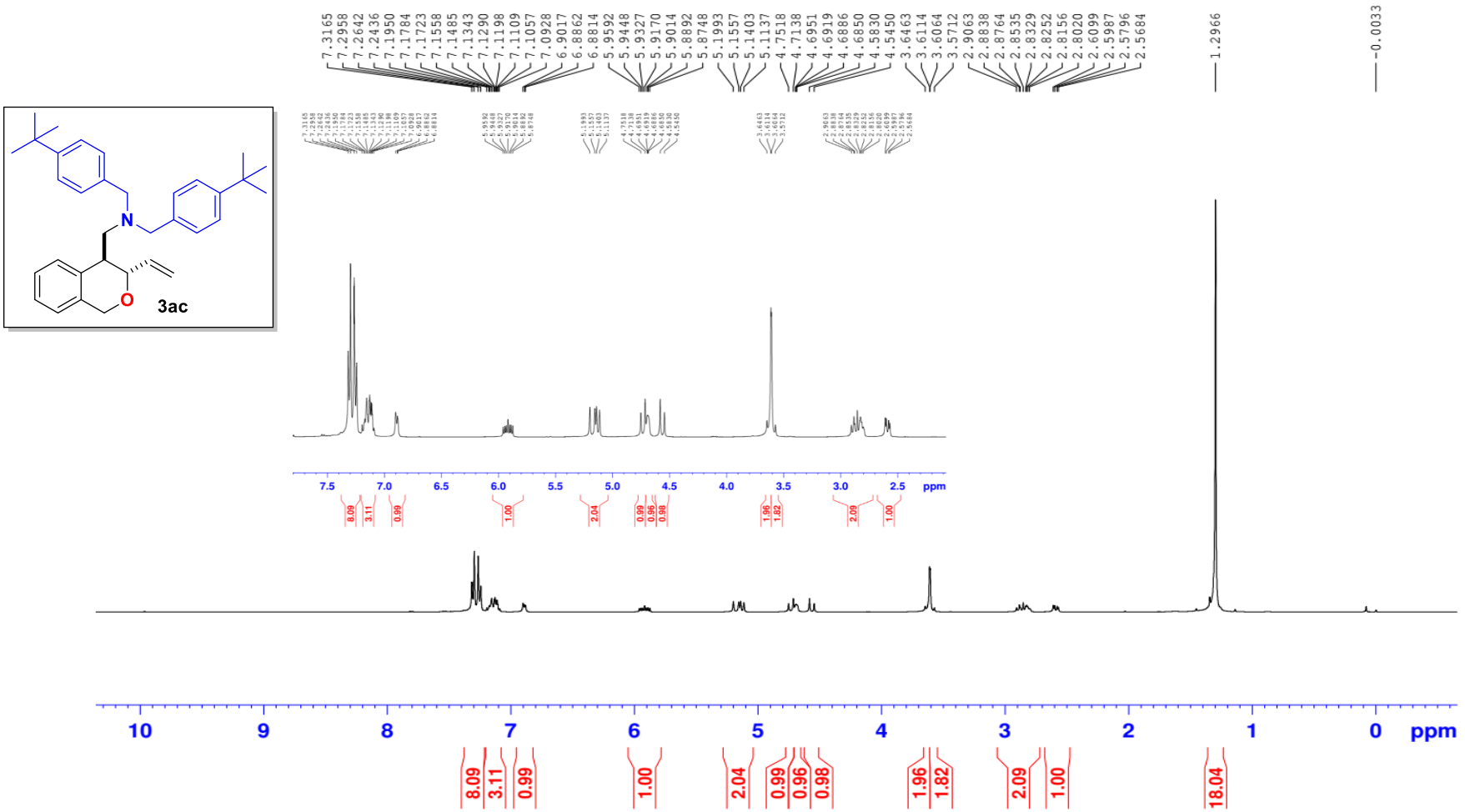
hy-P-**3ab** ^{1}H NMR (400MHz $CDCl_3$)



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

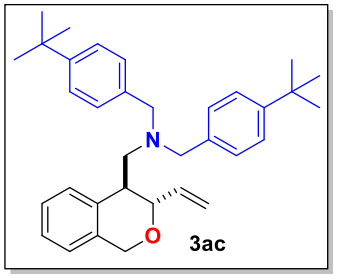


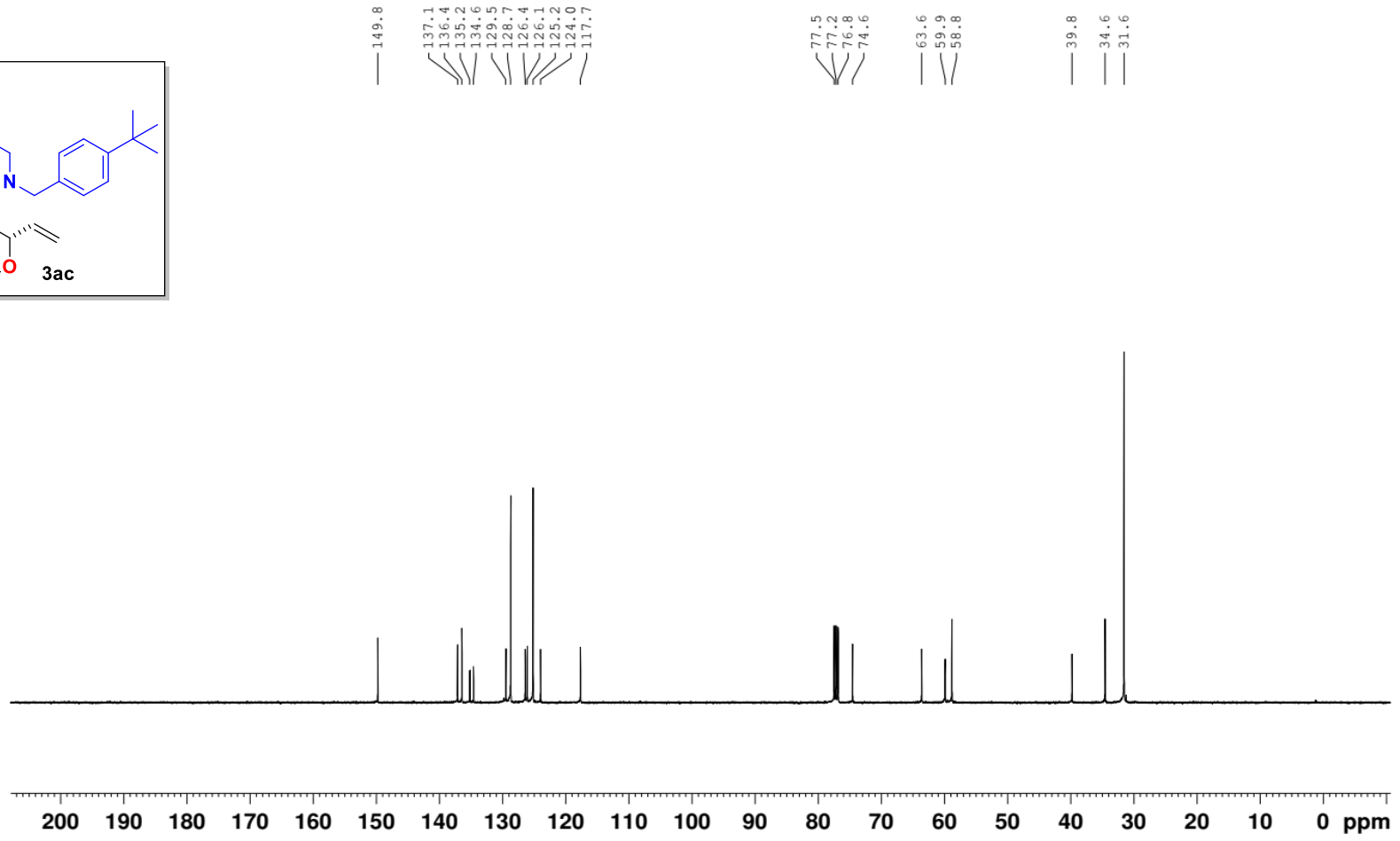
hy-P-**3ac** ^{1}H NMR (400MHz $CDCl_3$)



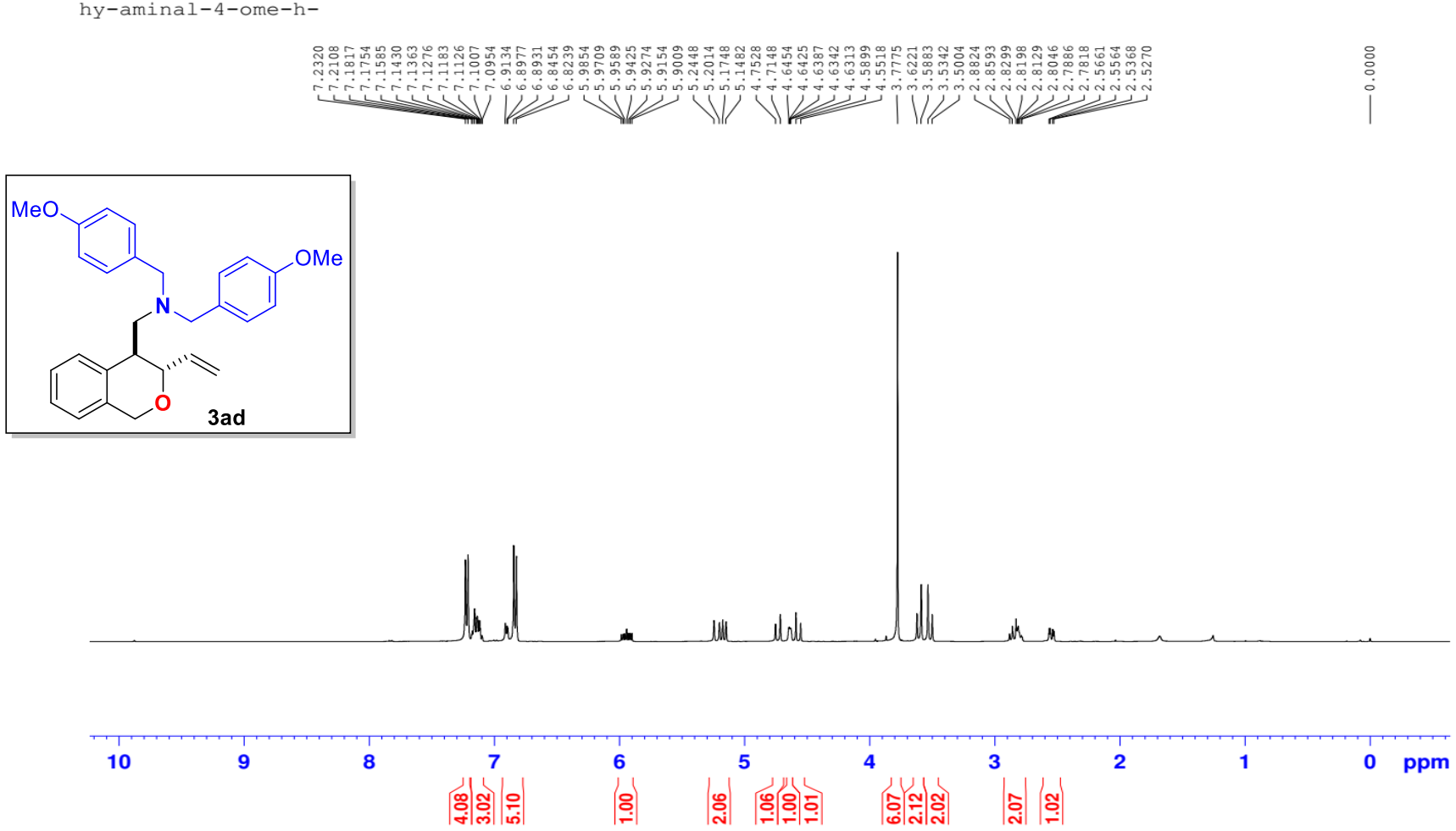
hy-P-**3ac** ^{13}C NMR (100MHz $CDCl_3$)

hy-aminal-p-tbu-c-

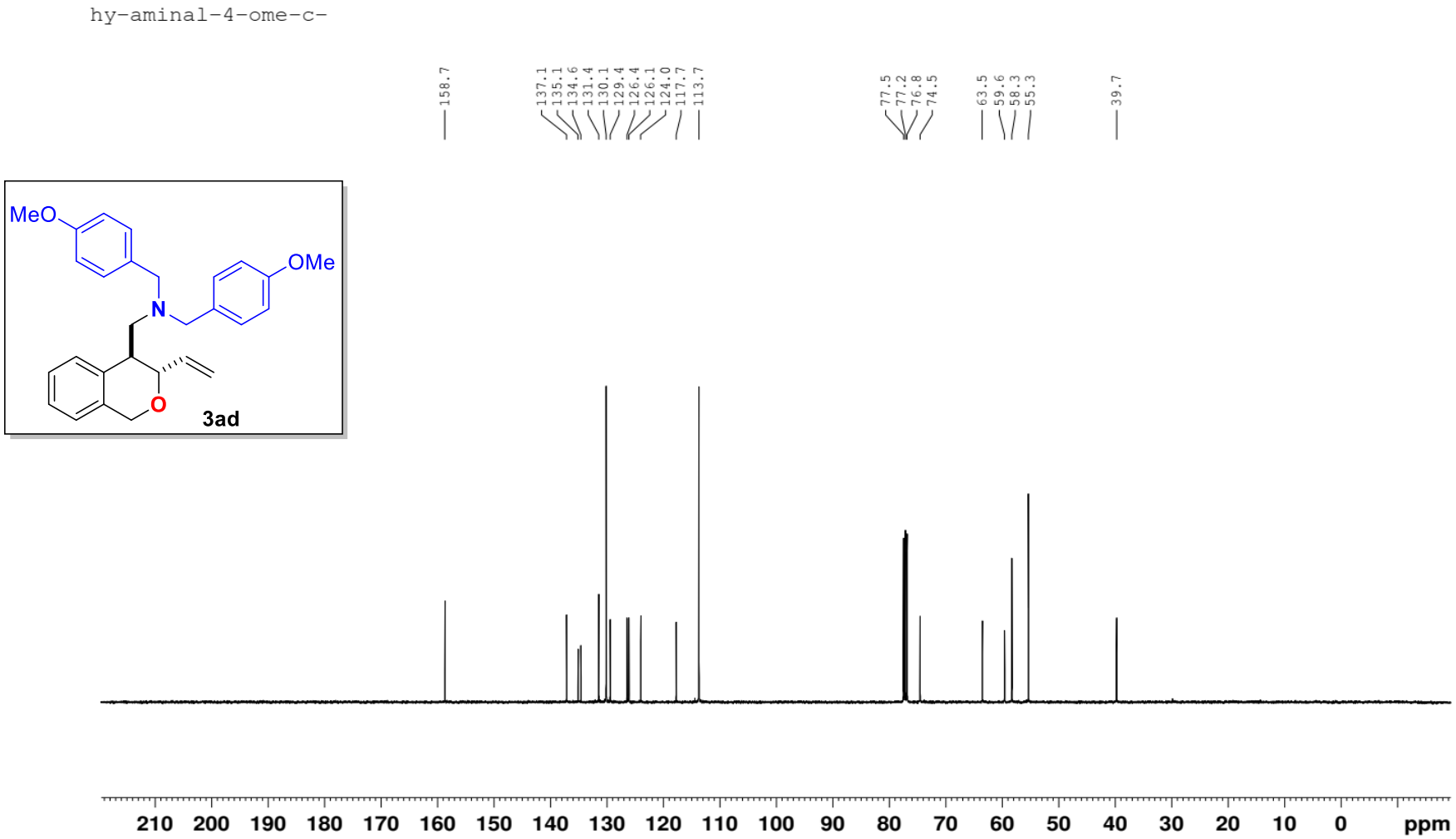




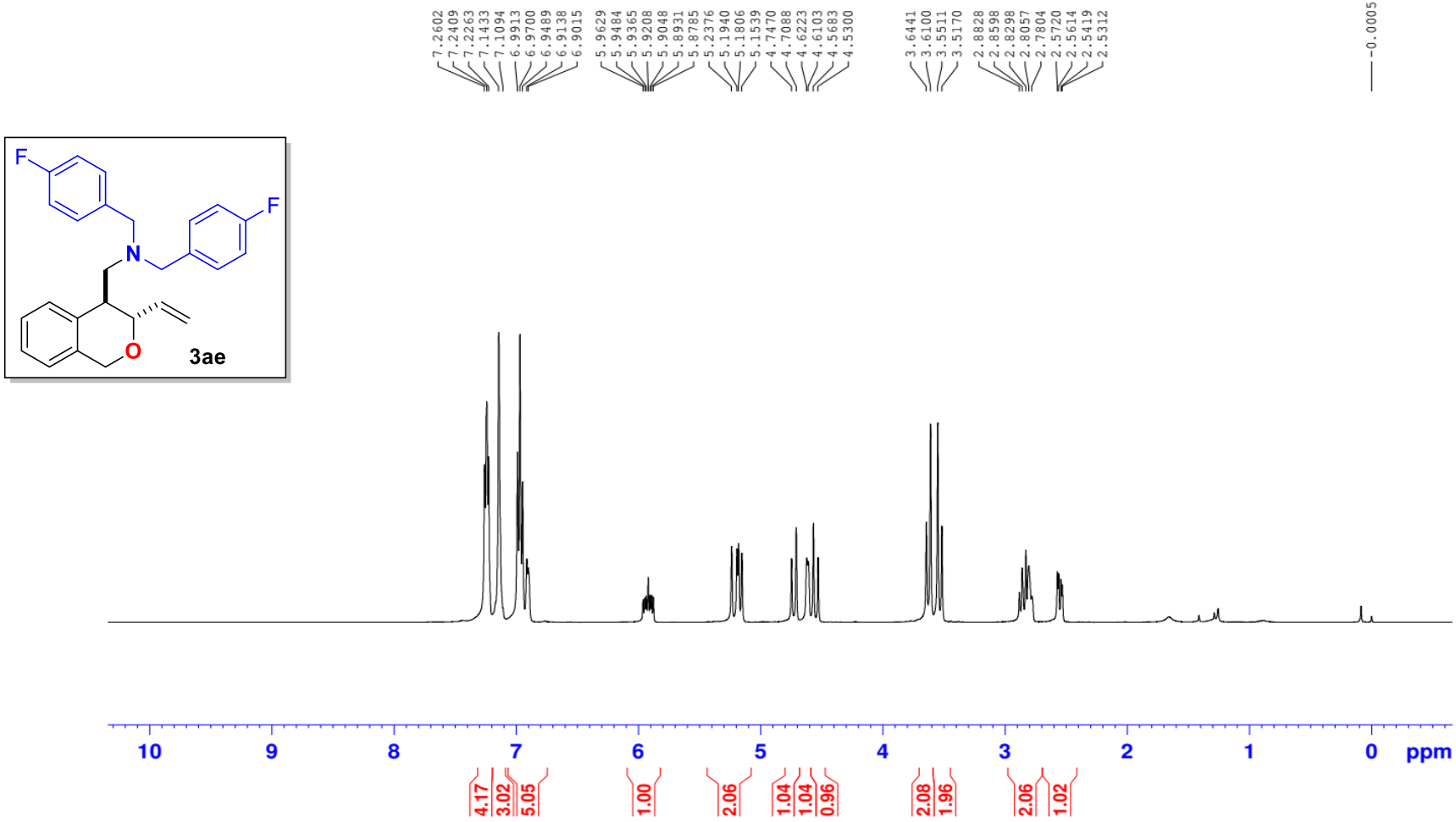
hy-P-**3ad** ^{1}H NMR (400MHz $CDCl_3$)



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

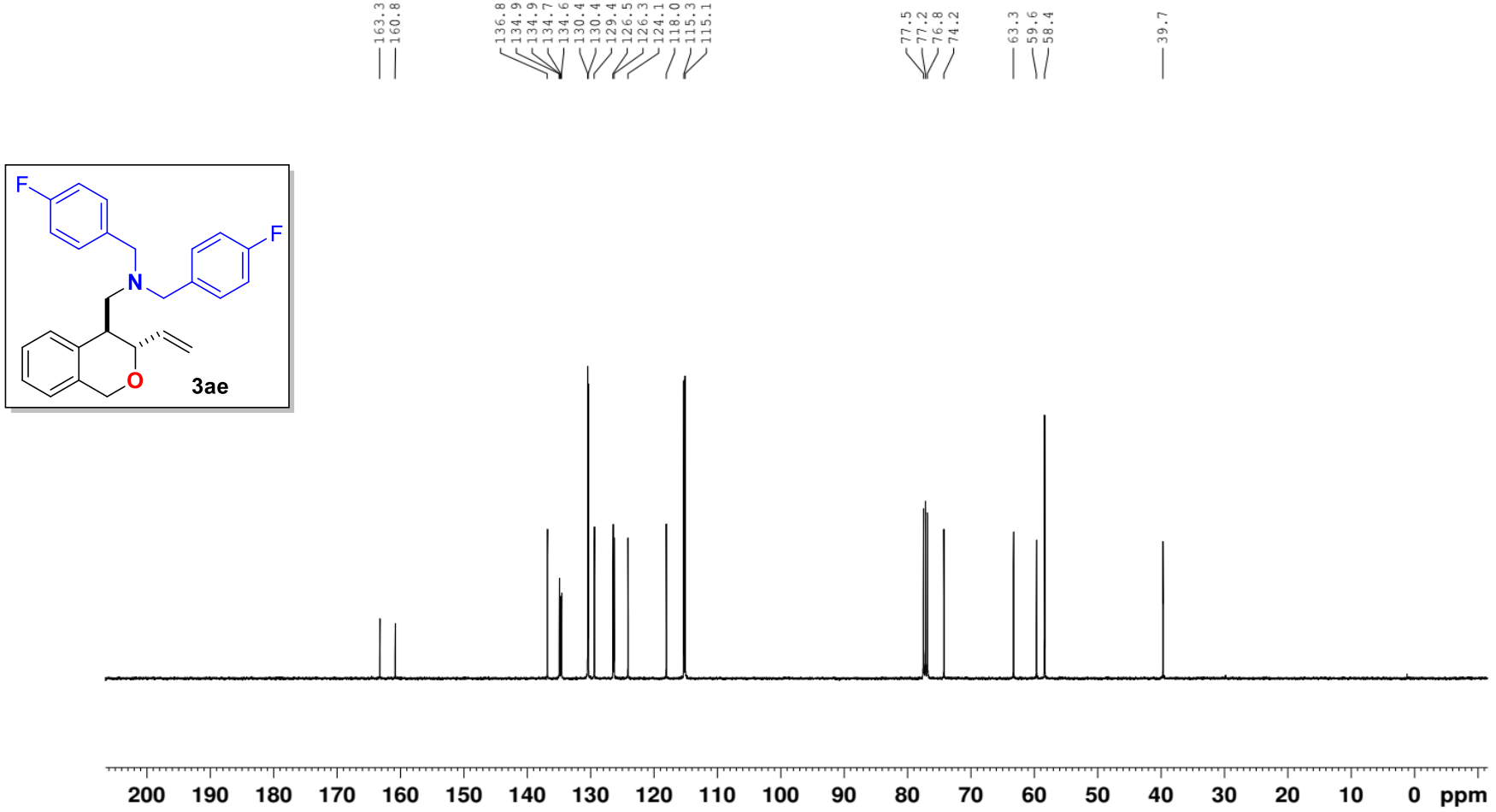


hy-P-**3ae** ^{1}H NMR (400MHz $CDCl_3$)



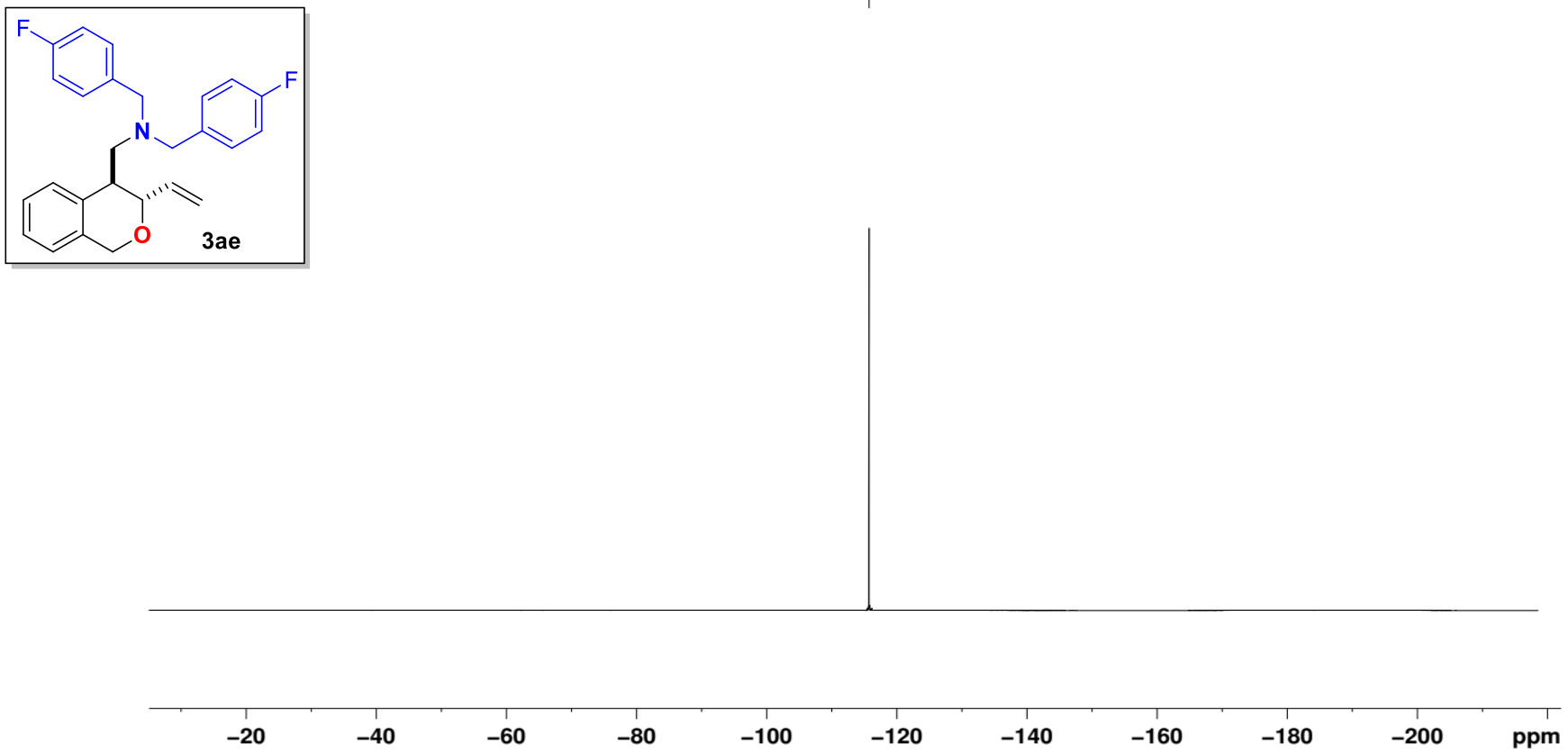
hy-P-**3ae** ^{13}C NMR (100MHz $CDCl_3$)

hy-aminal-p-f-c-

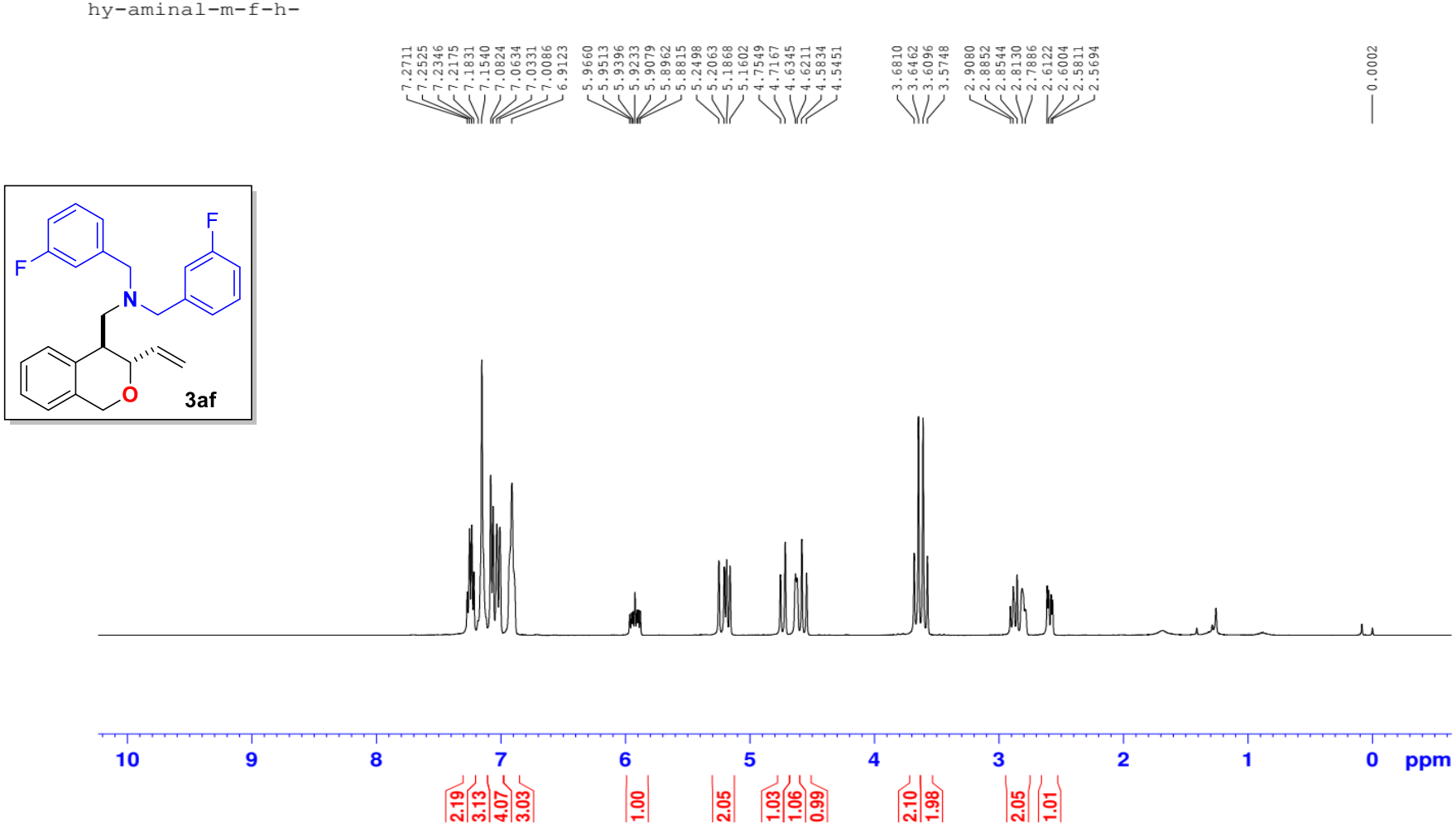


hy-P-**3ae** ^{19}F NMR (376MHz $CDCl_3$)

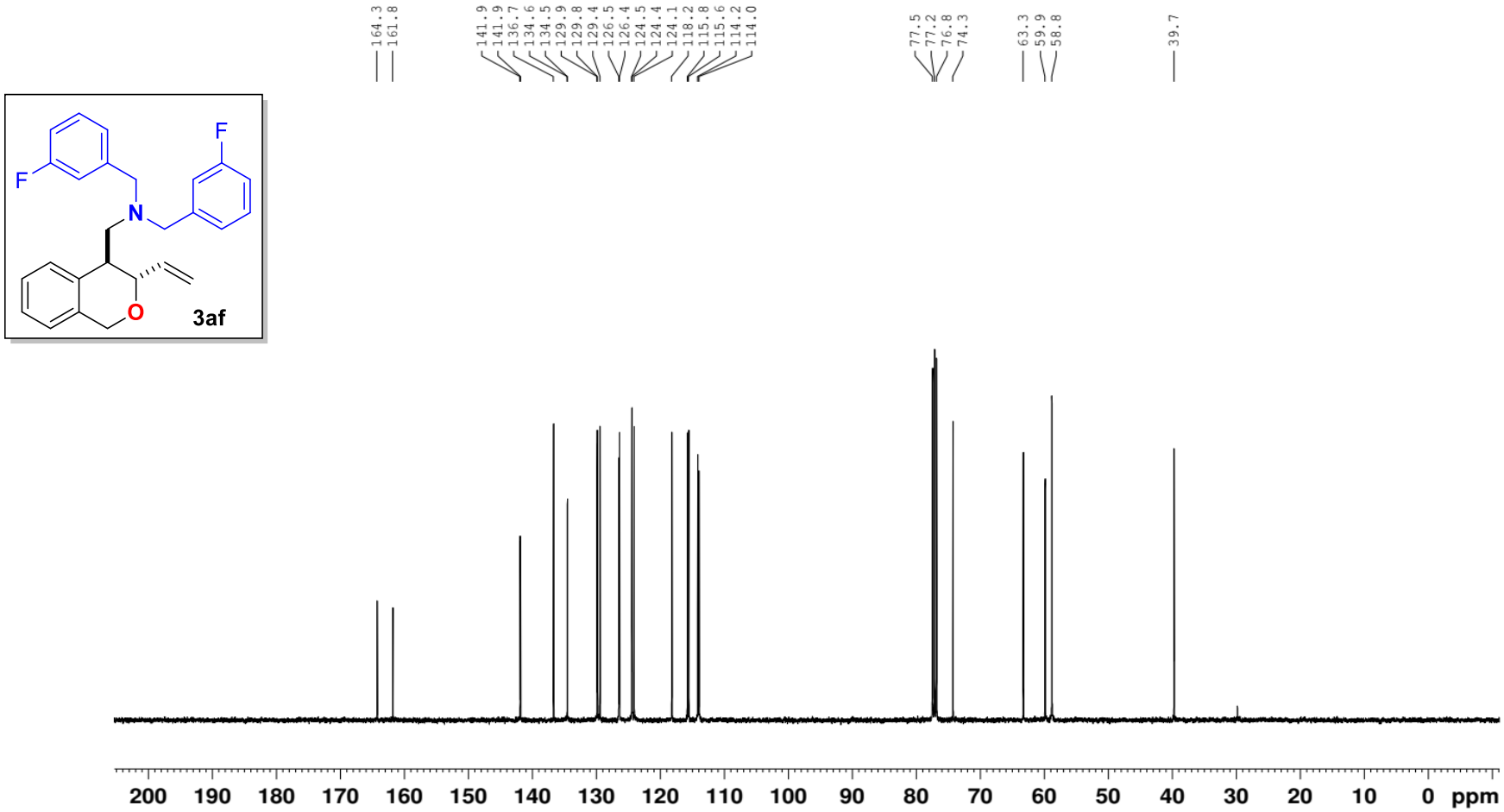
hy-aminal-p-f-f



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

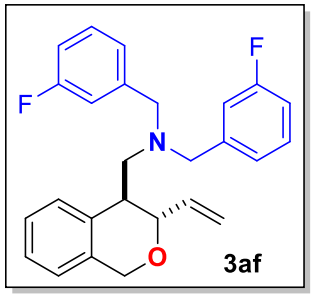


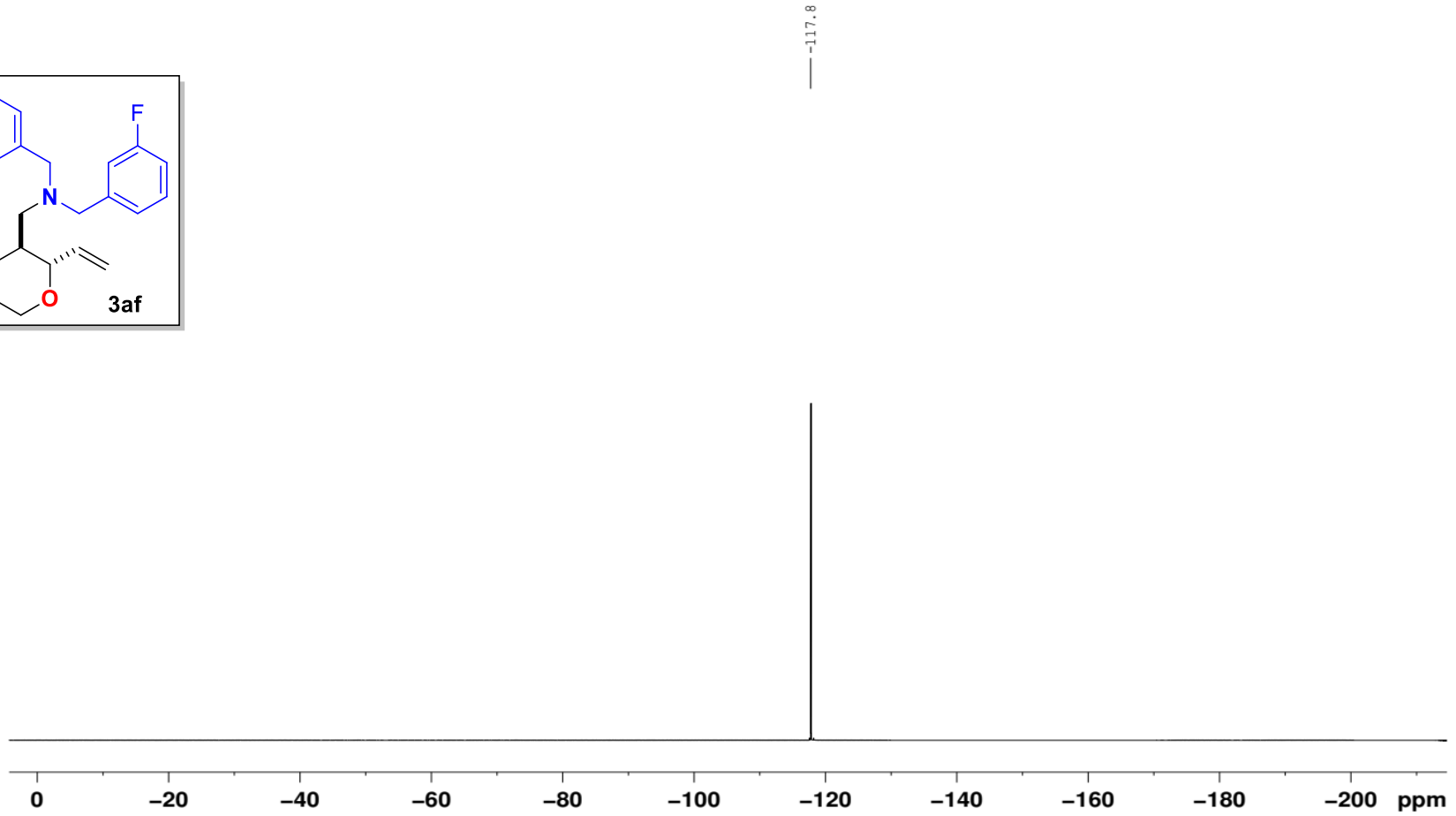
hy-P-**3af** ^{13}C NMR (100MHz $CDCl_3$)



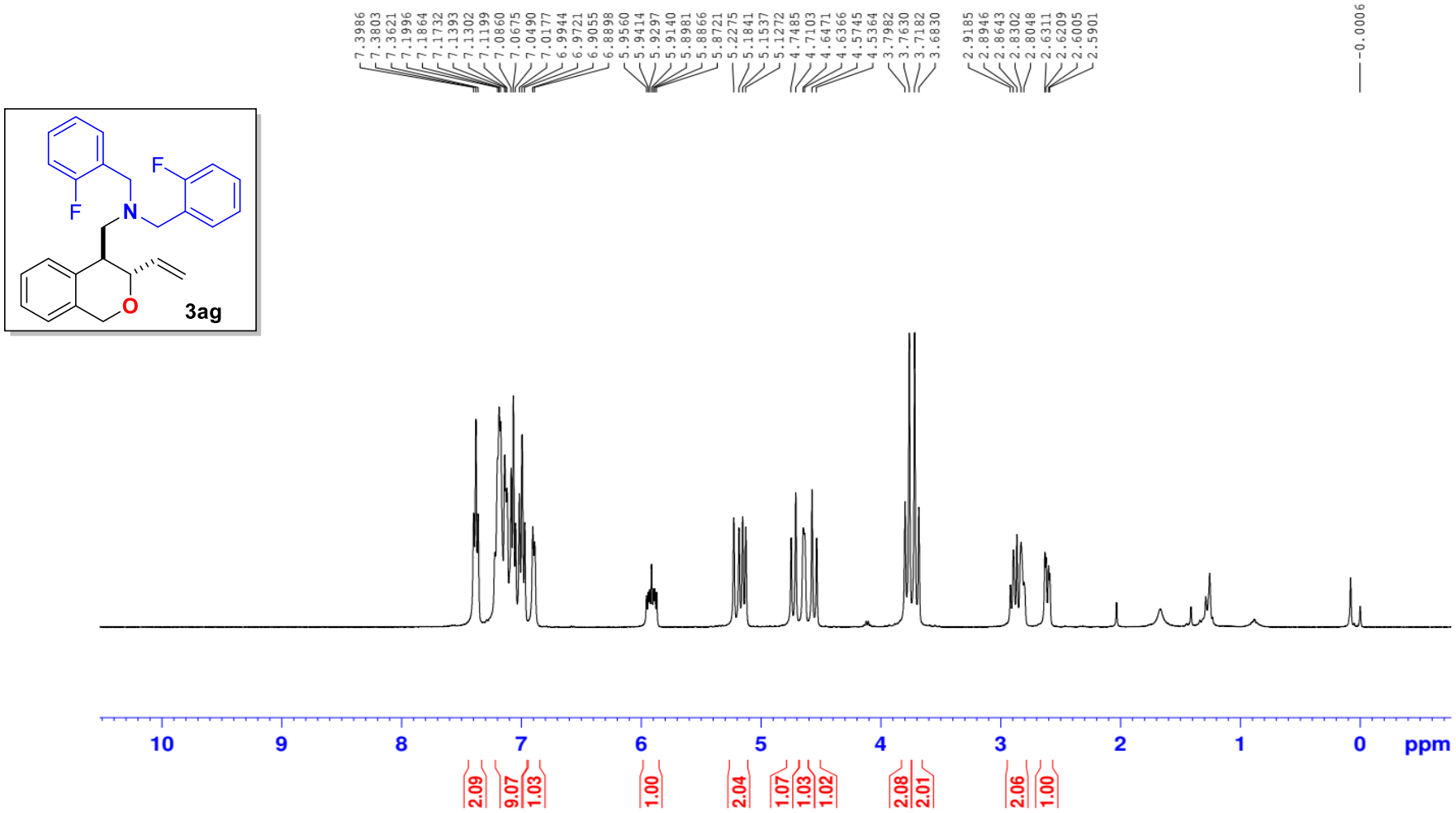
hy-P-**3af** ^{19}F NMR (376MHz $CDCl_3$)

hy-aminal-m-f-f

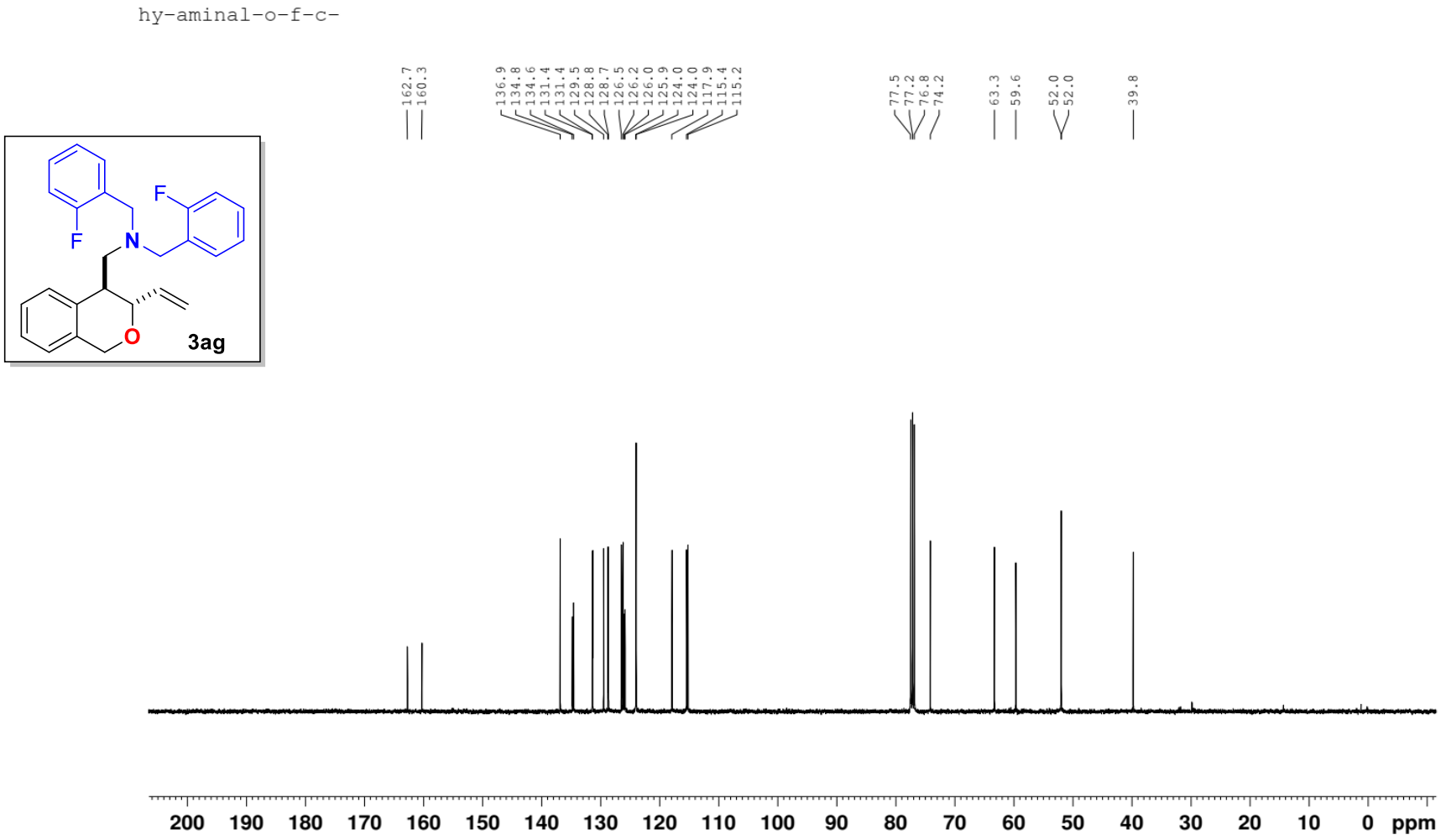




hy-P-**3ag** ^{1}H NMR (400MHz $CDCl_3$)

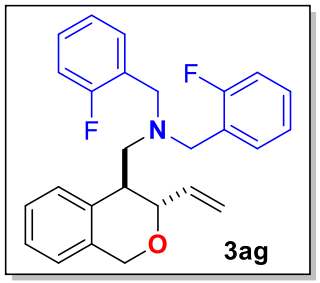


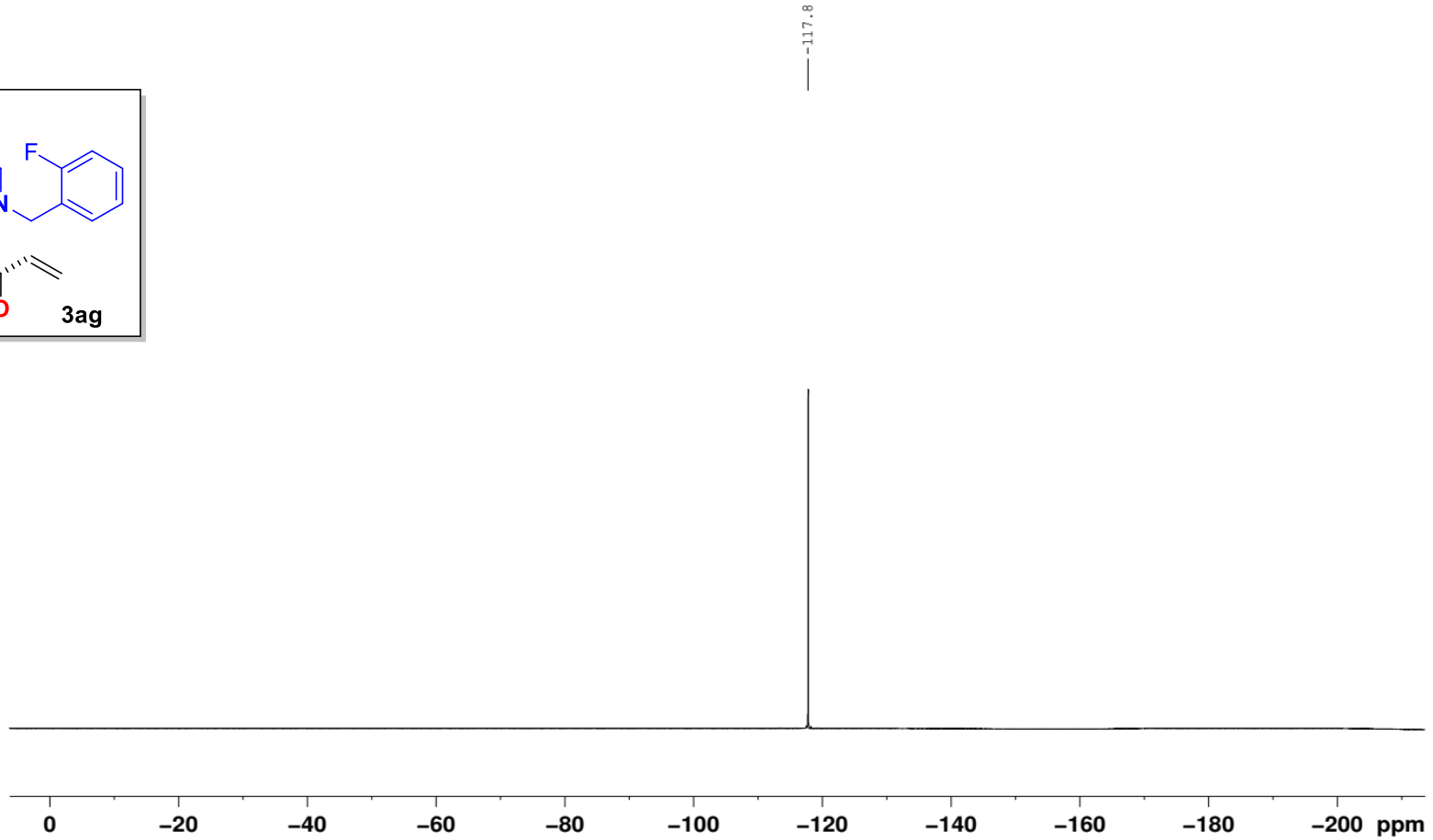
hy-P-**3ag** ^{13}C NMR (100MHz $CDCl_3$)



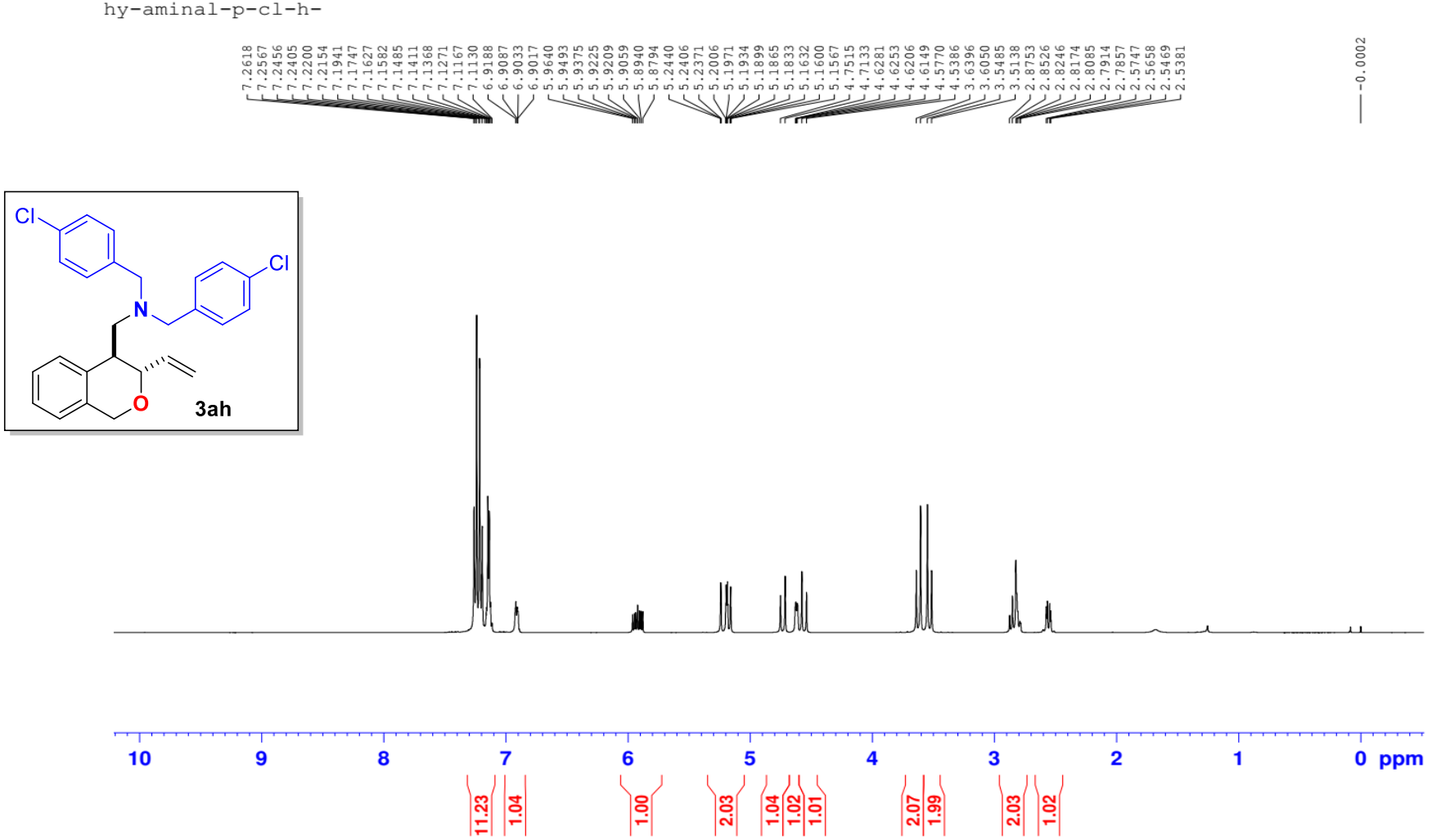
hy-P-**3ag** ^{19}F NMR (376MHz $CDCl_3$)

hy-aminal-o-f-f



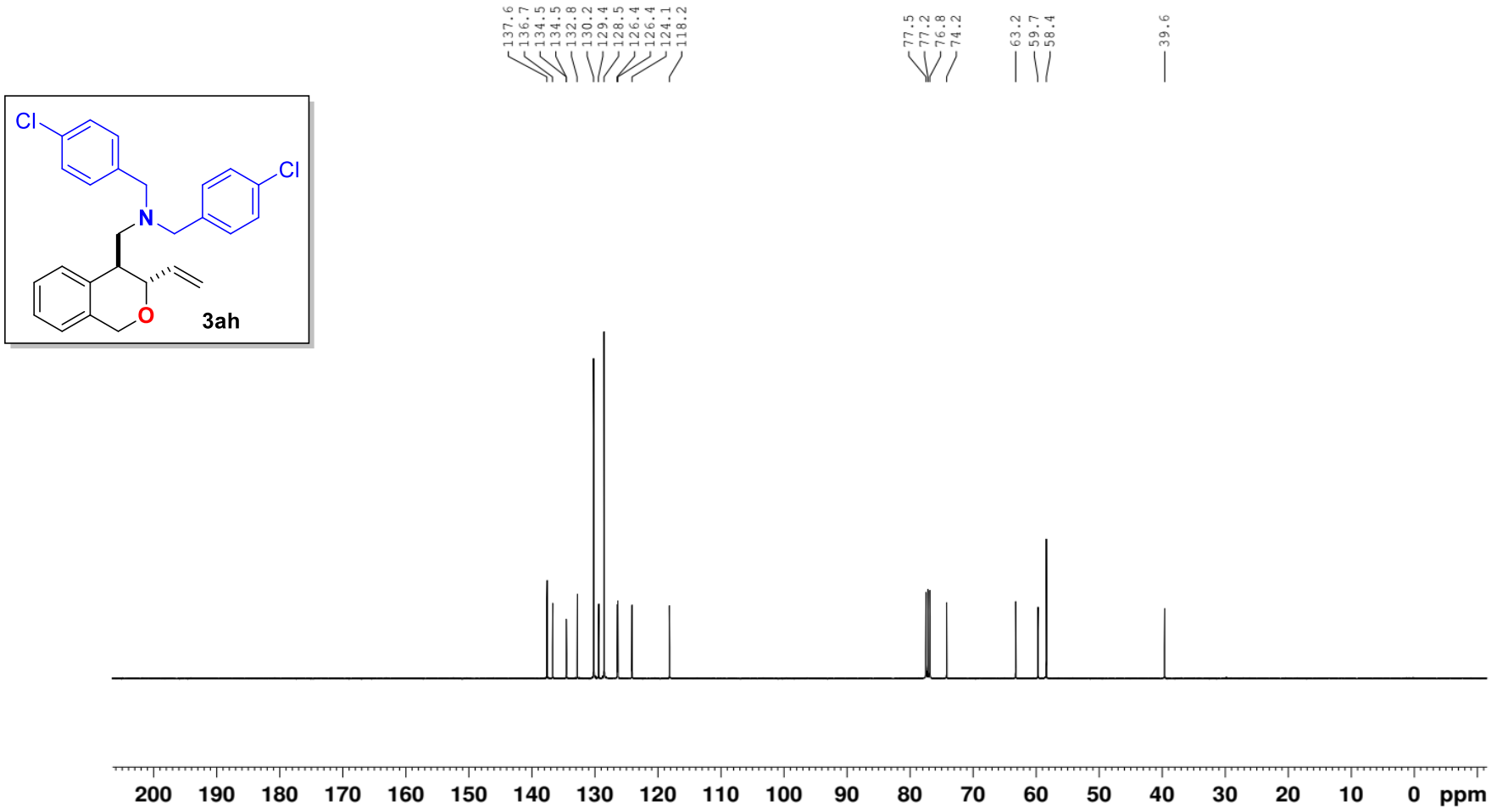


hy-P-**3ah** ^{1}H NMR (400MHz $CDCl_3$)

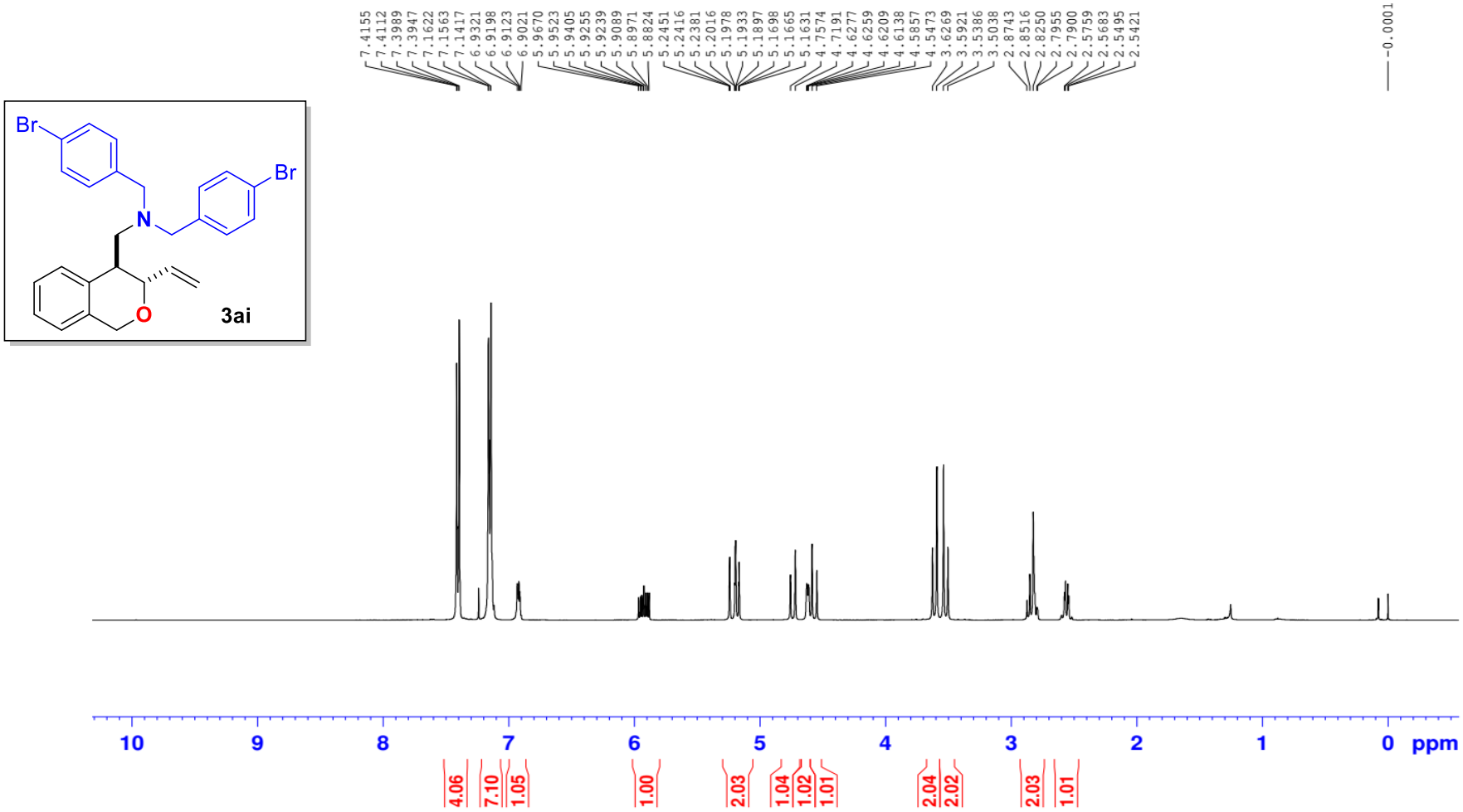


hy-P-**3ah** ^{13}C NMR (100MHz $CDCl_3$)

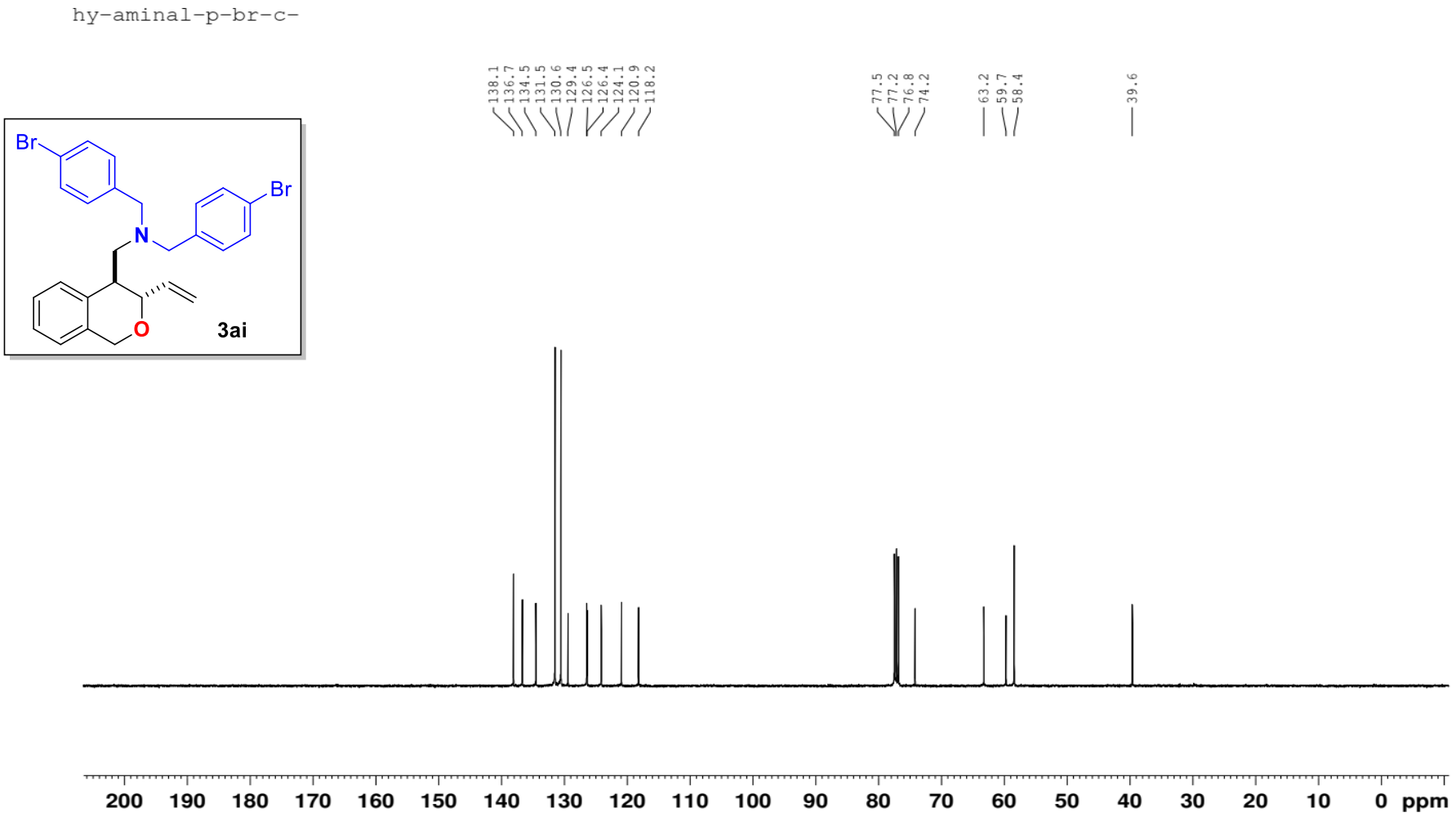
hy-aminal-p-cl-c-



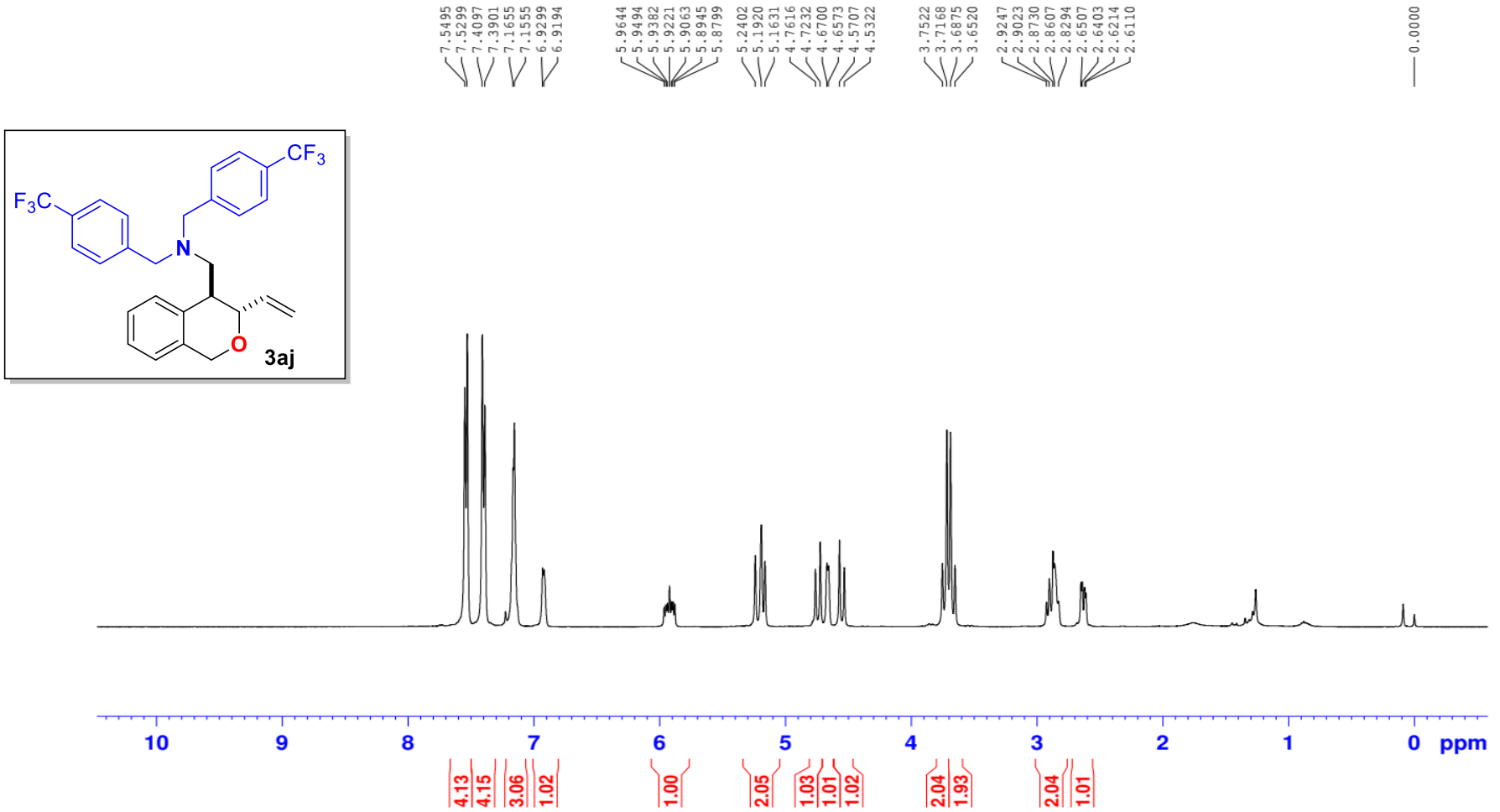
hy-P-**3ai** ^{1}H NMR (400MHz $CDCl_3$)



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

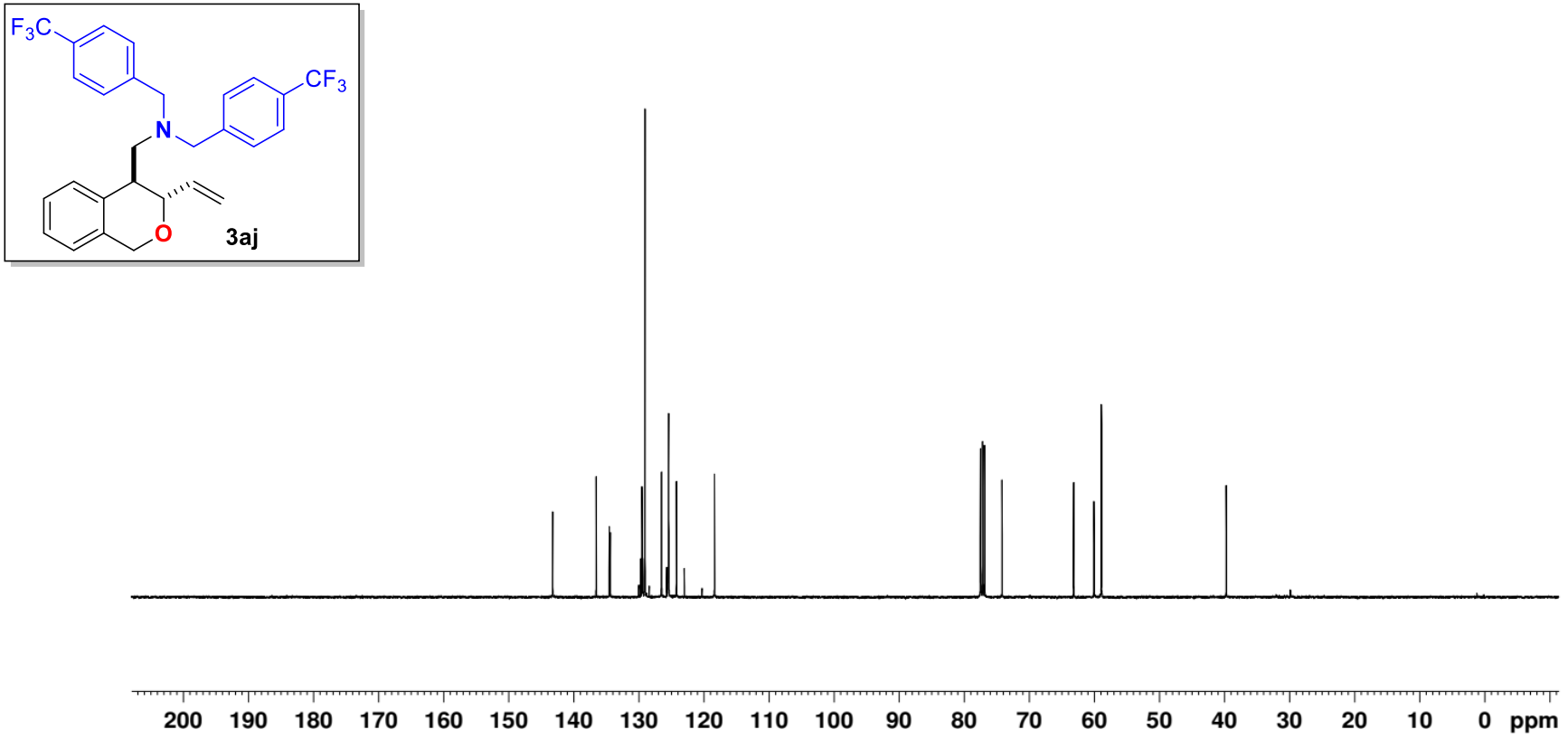


hy-P-**3aj** ^{1}H NMR (400MHz $CDCl_3$)

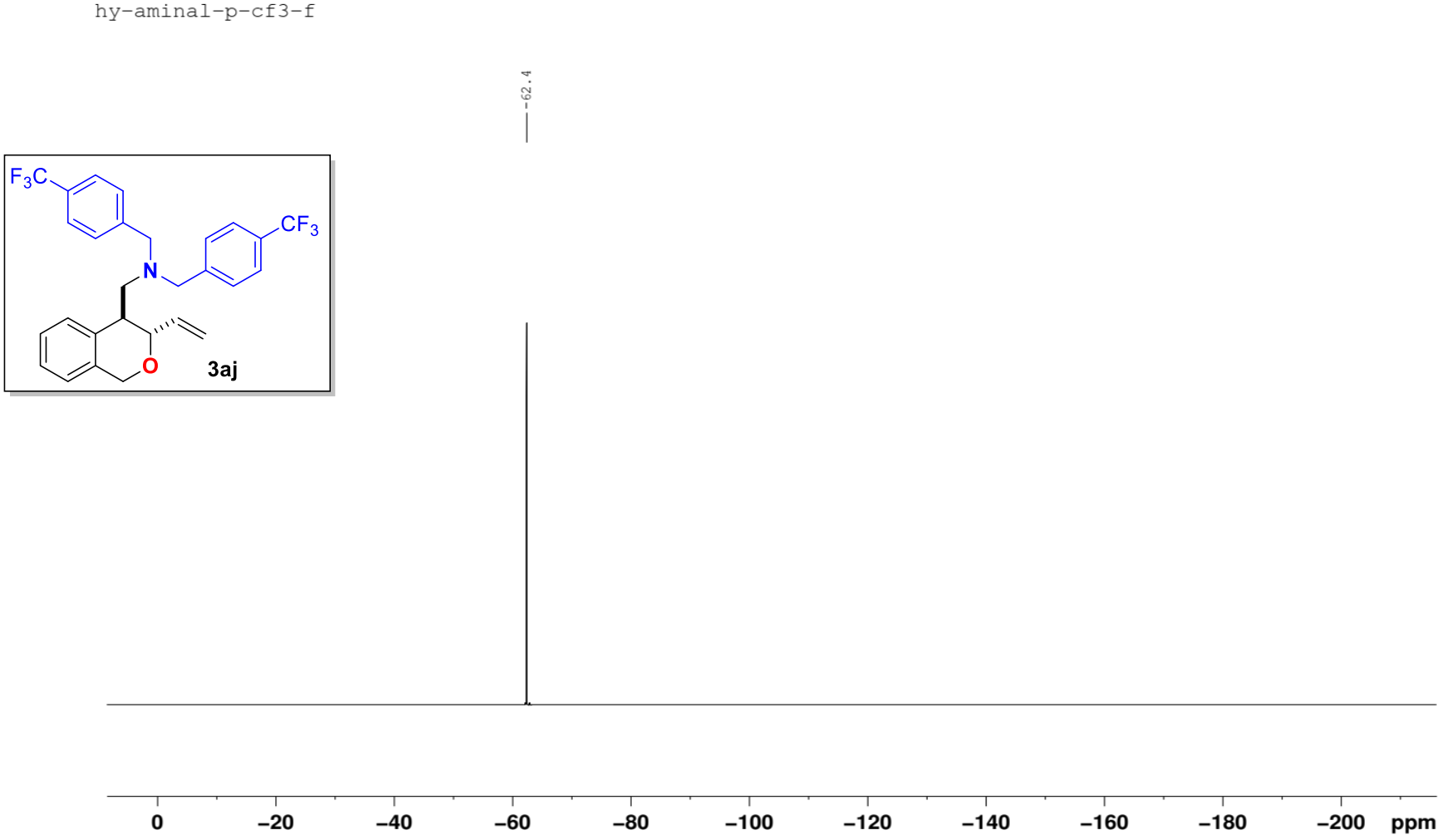


hy-P-**3aj** ^{13}C NMR (100MHz $CDCl_3$)

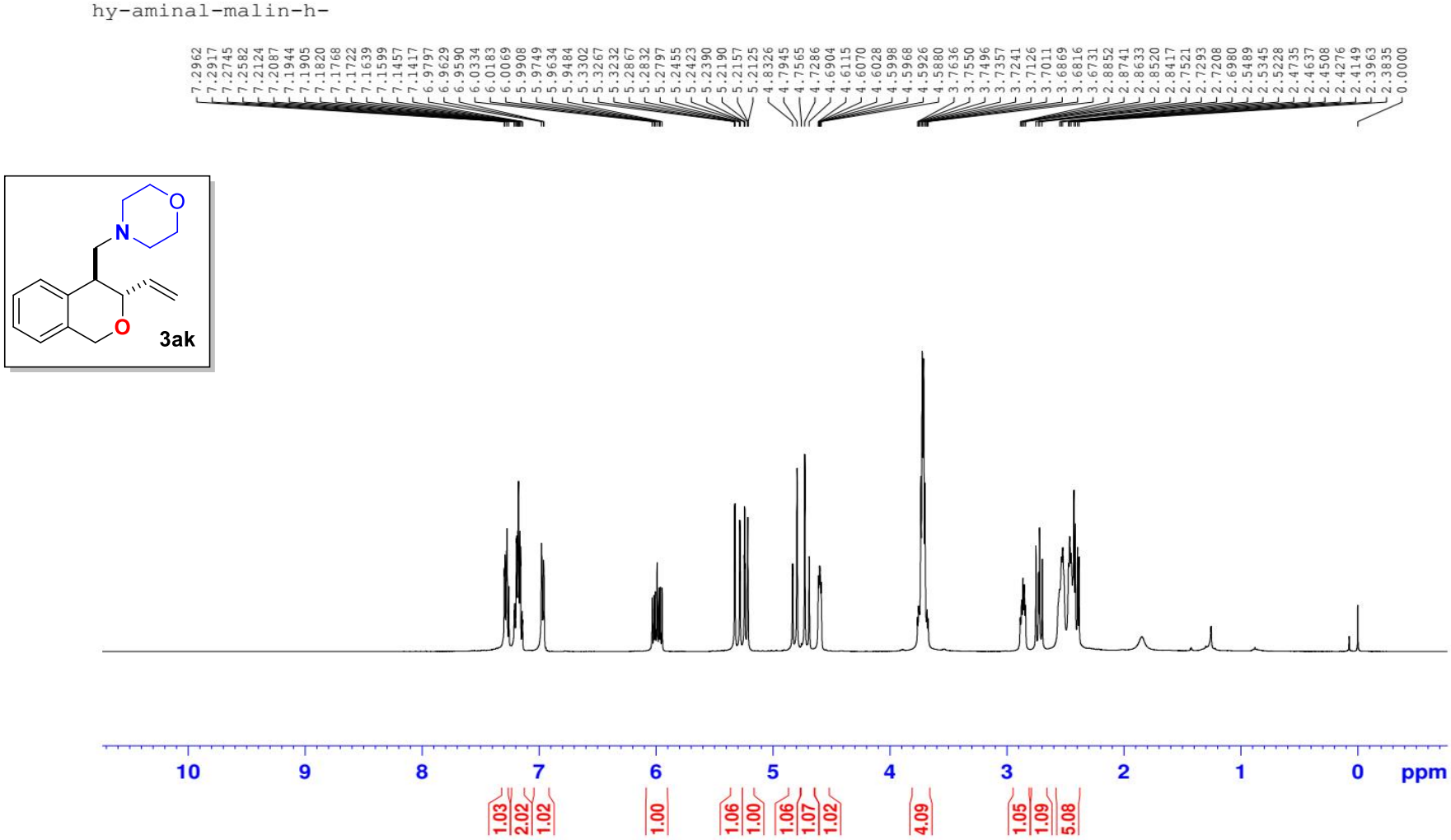
hy-aminal-p-cf3-c--



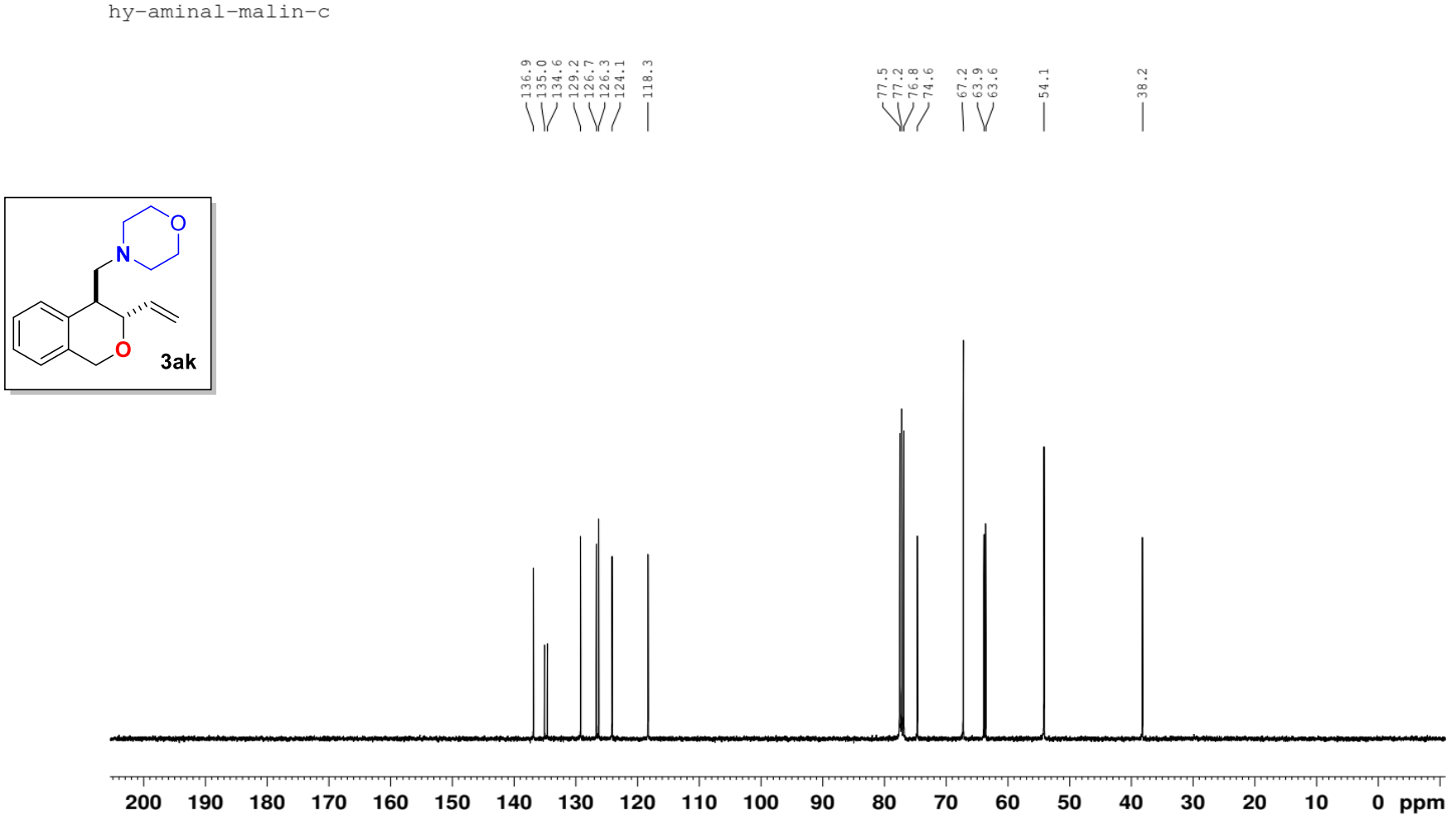
hy-P-**3aj** ^{19}F NMR (376MHz $CDCl_3$)



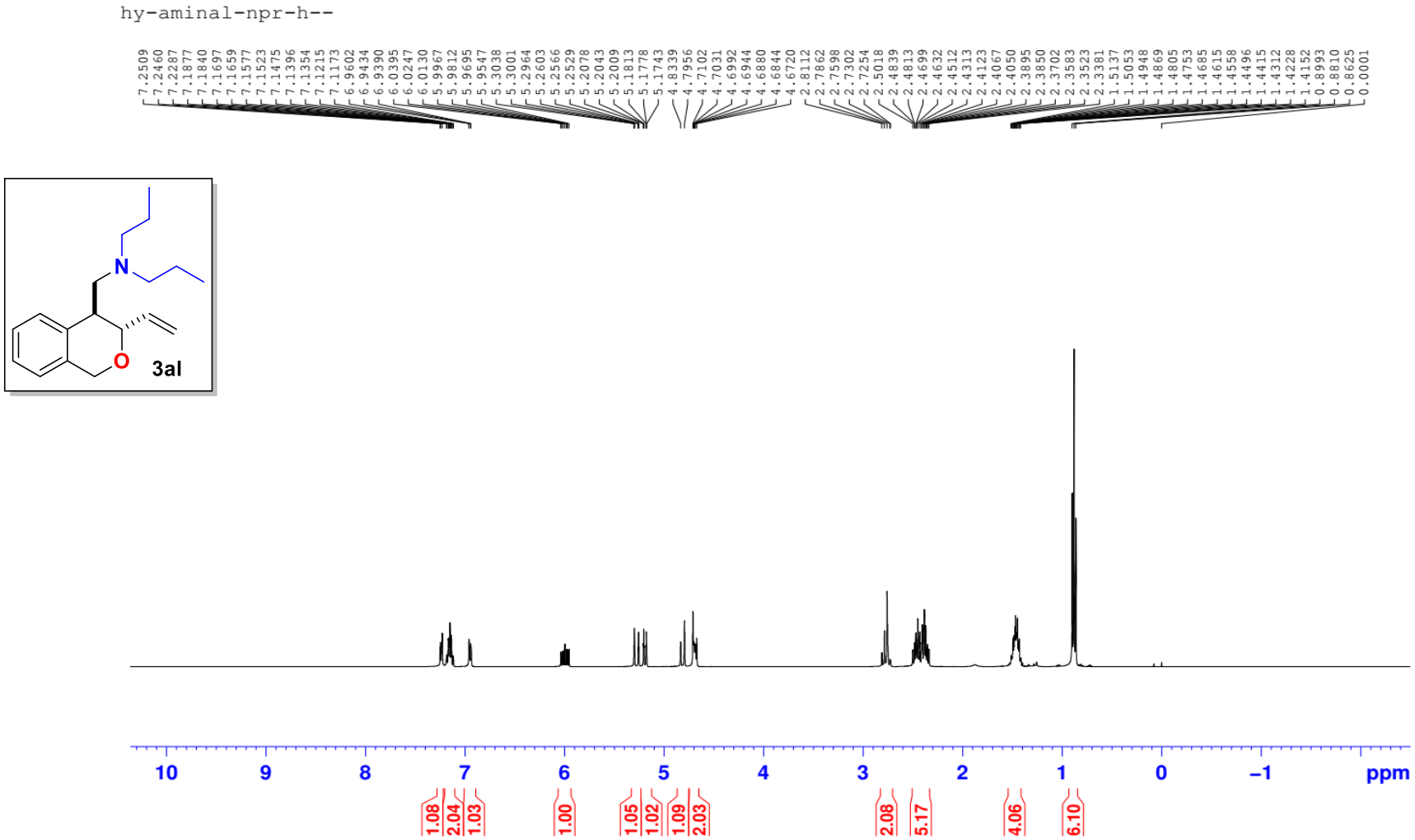
hy-P-**3ak** ^{1}H NMR (400MHz $CDCl_3$)



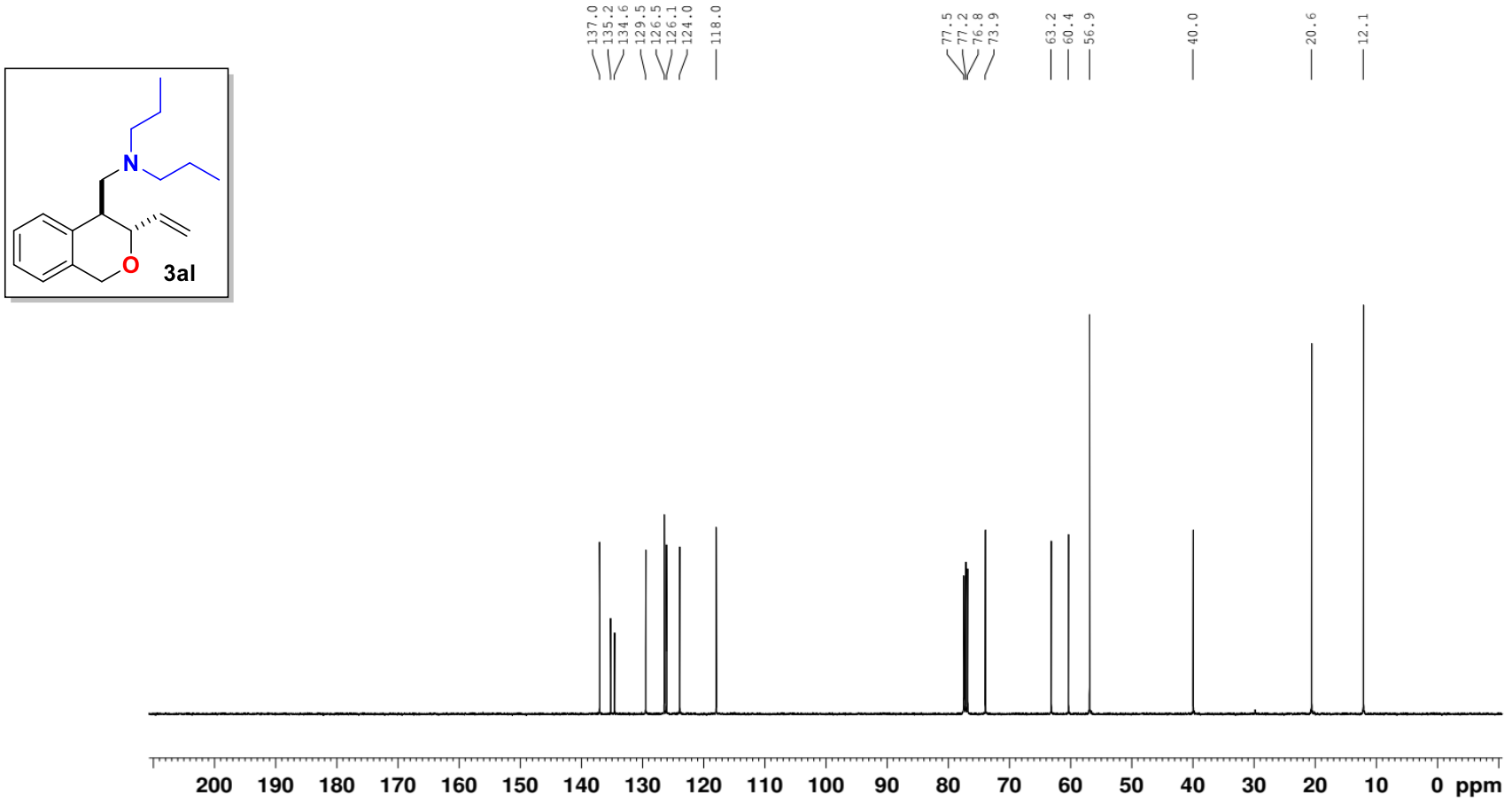
hy-P-**3ak** ^{13}C NMR (100MHz $CDCl_3$)



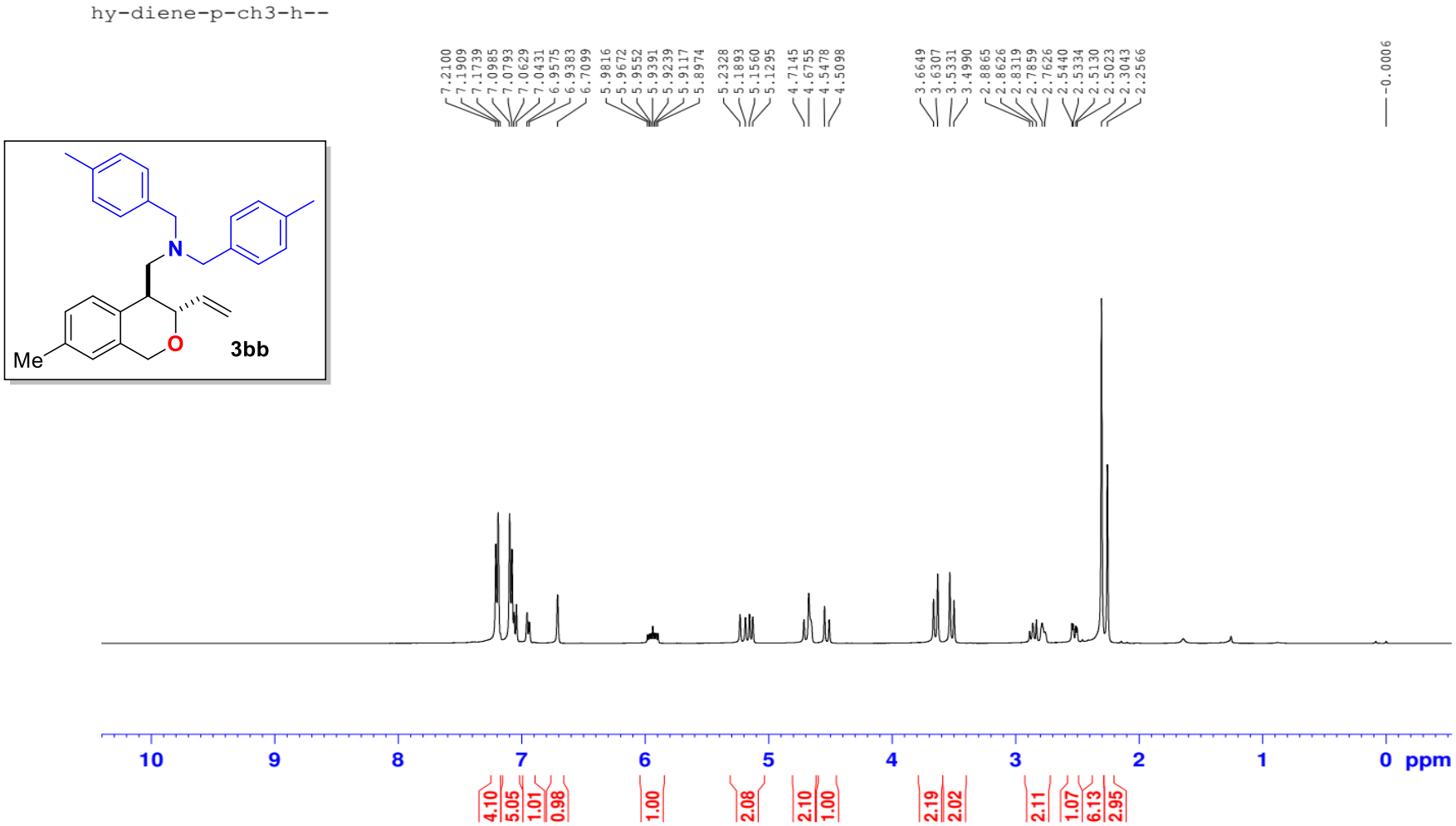
hy-P-**3al** ^{1}H NMR (400MHz $CDCl_3$)



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

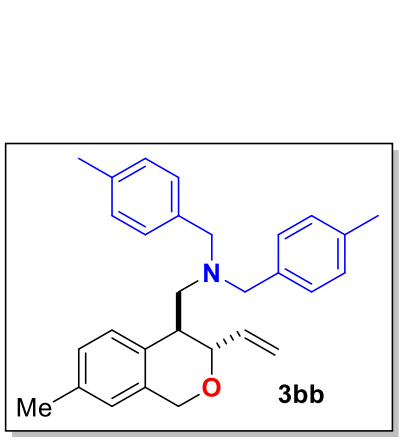


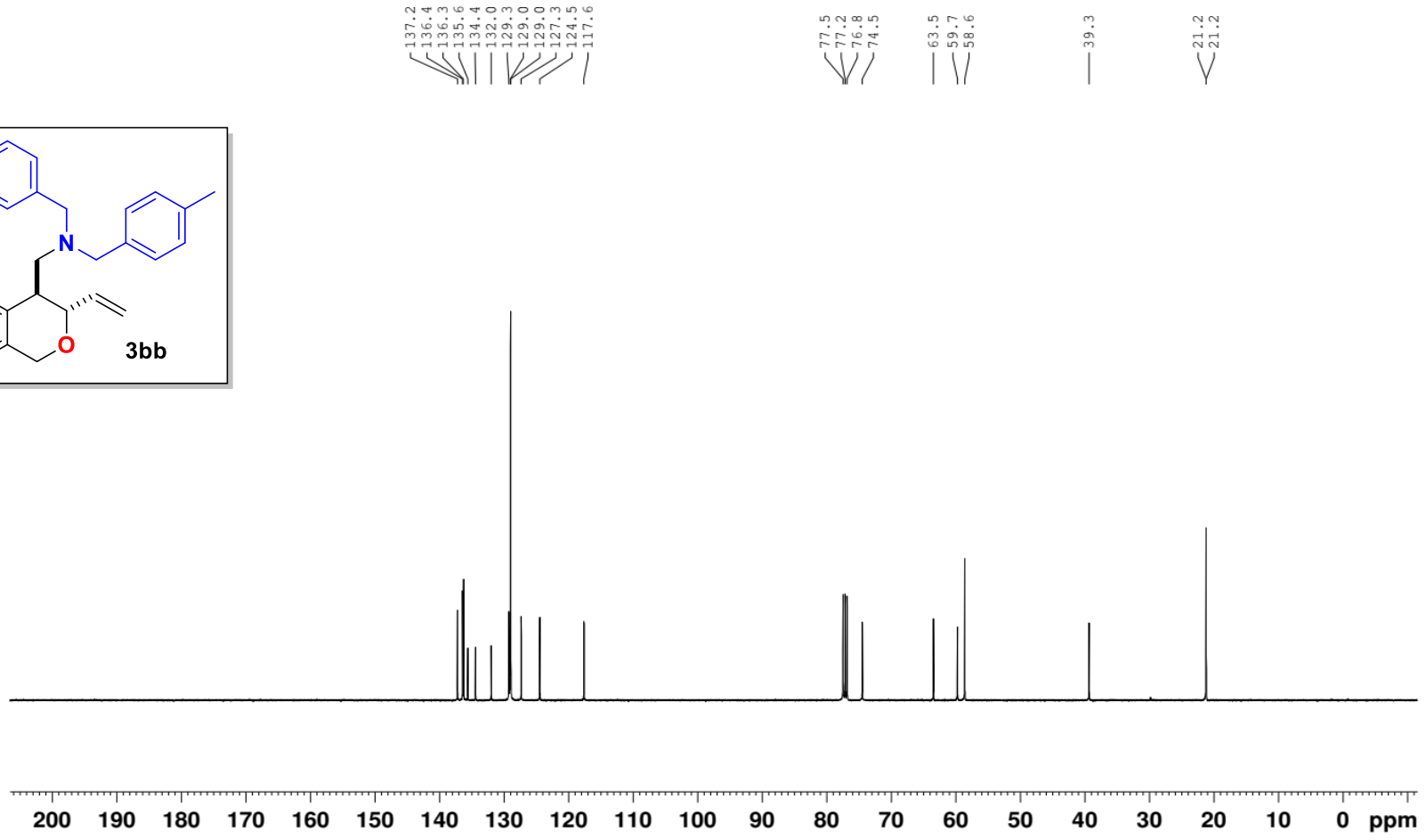
hy-P-**3bb** ^{1}H NMR (400MHz $CDCl_3$)



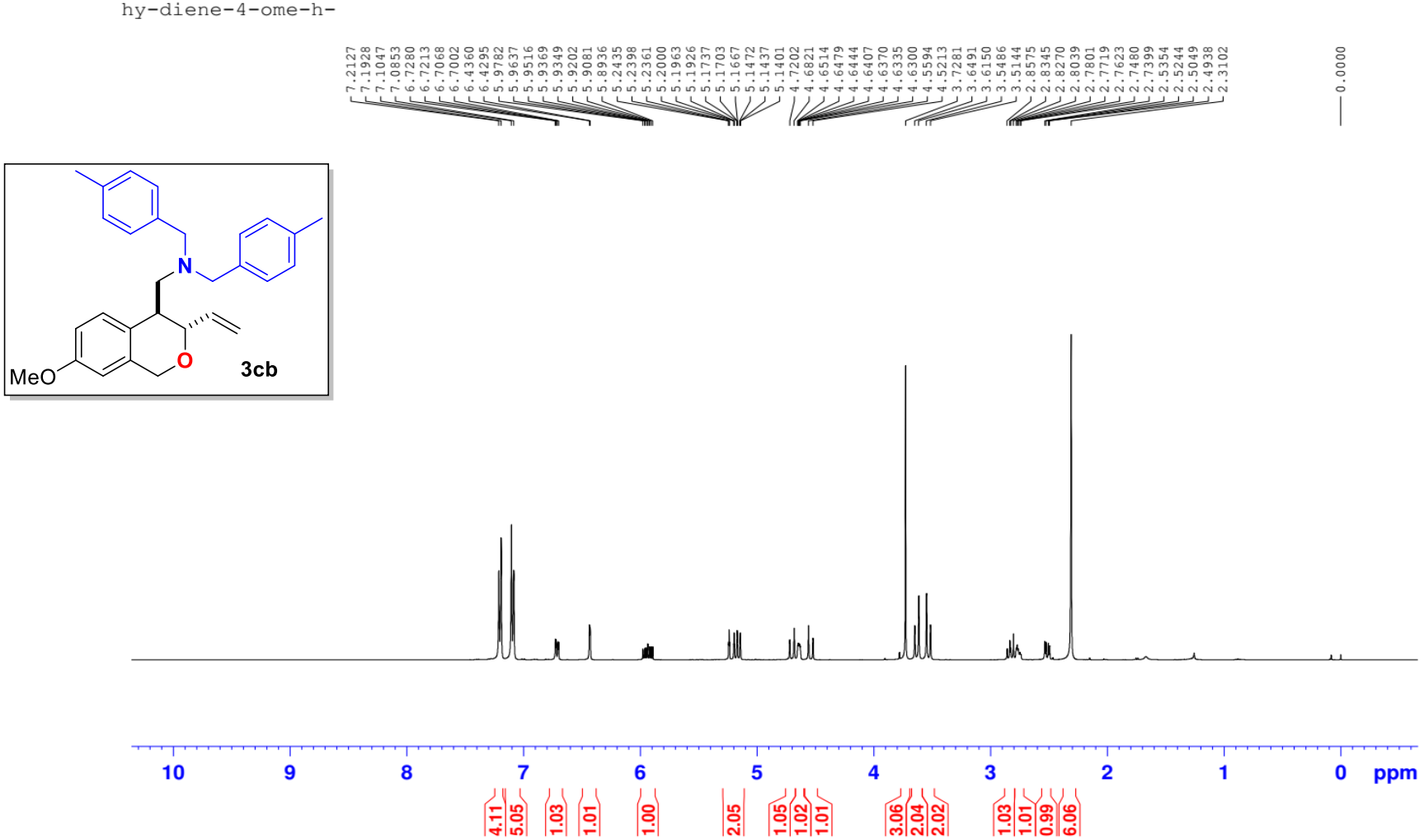
hy-P-**3bb** ^{13}C NMR (100MHz $CDCl_3$)

hy-diene-p-ch3-c-



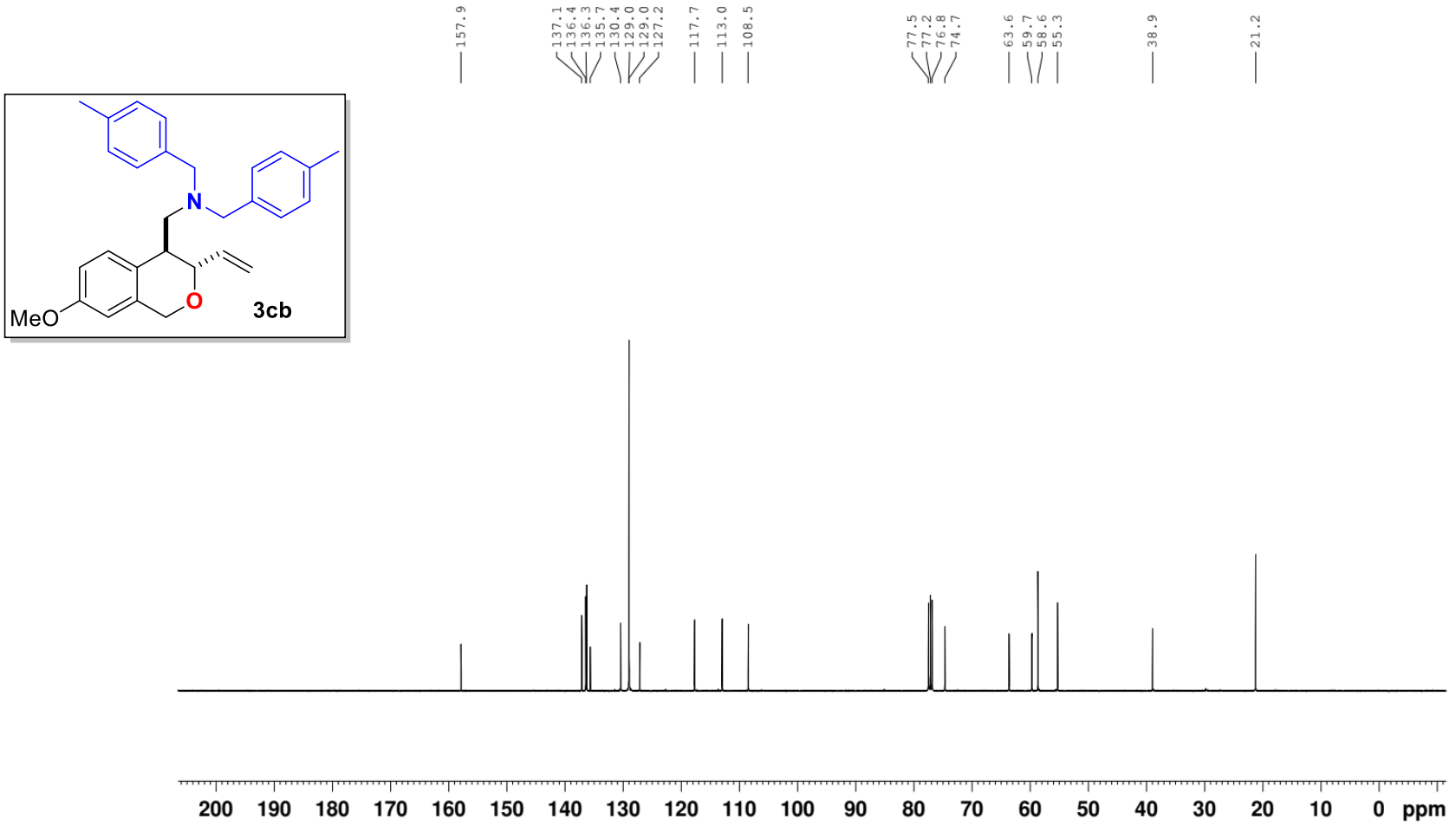


hy-P-**3cb** ^{1}H NMR (400MHz $CDCl_3$)

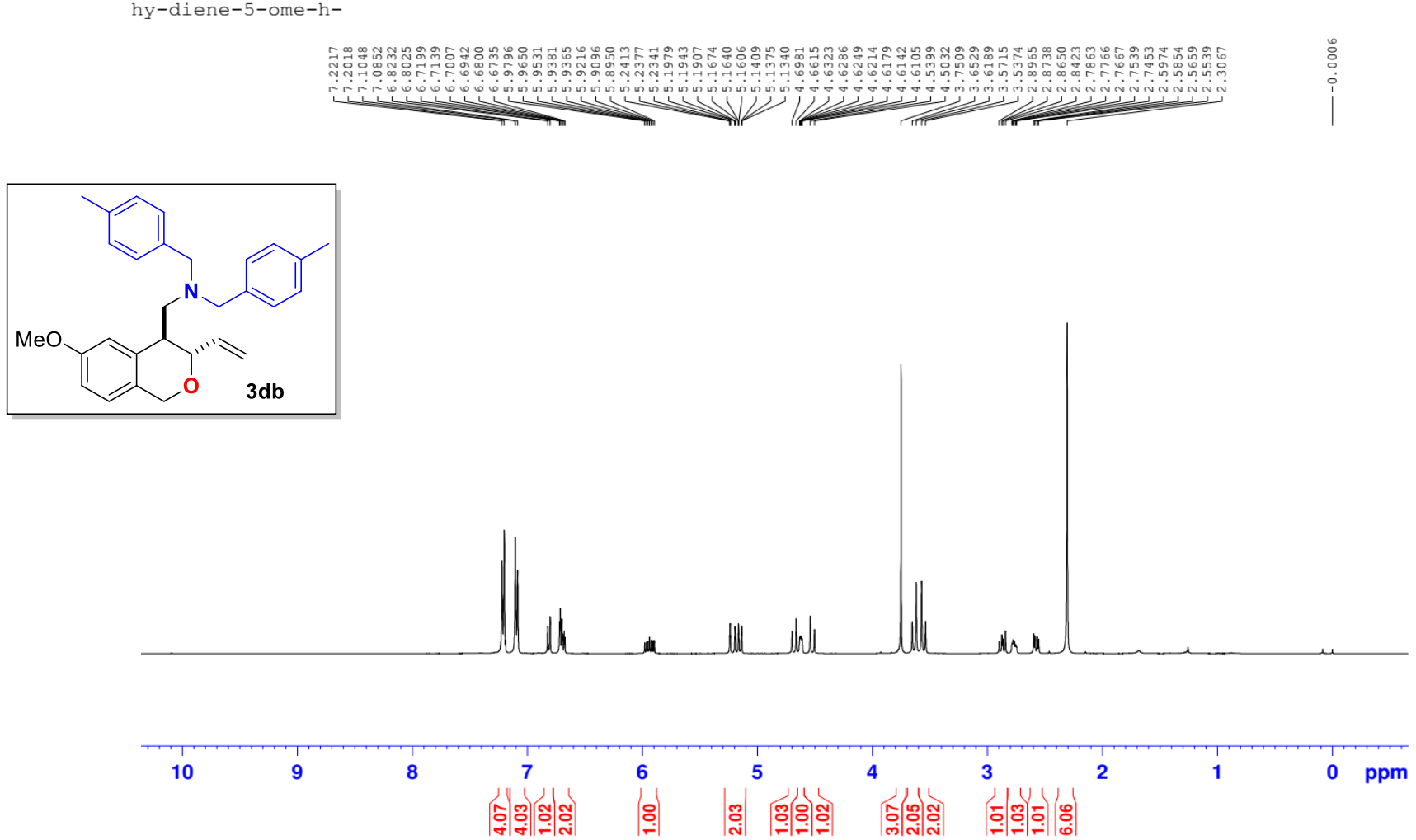


hy-P-**3cb** ^{13}C NMR (100MHz $CDCl_3$)

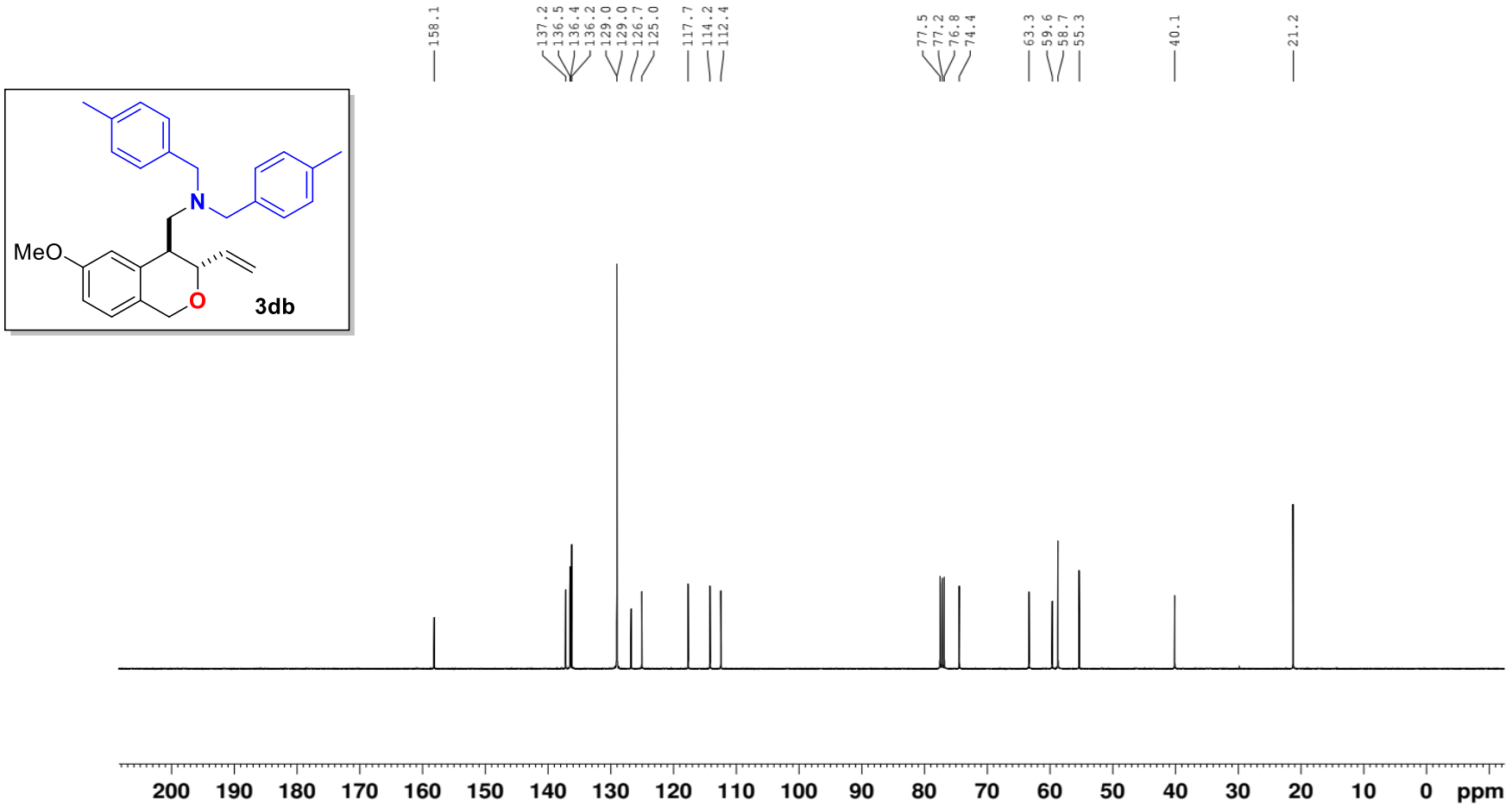
hy-diene-4-ome-c-



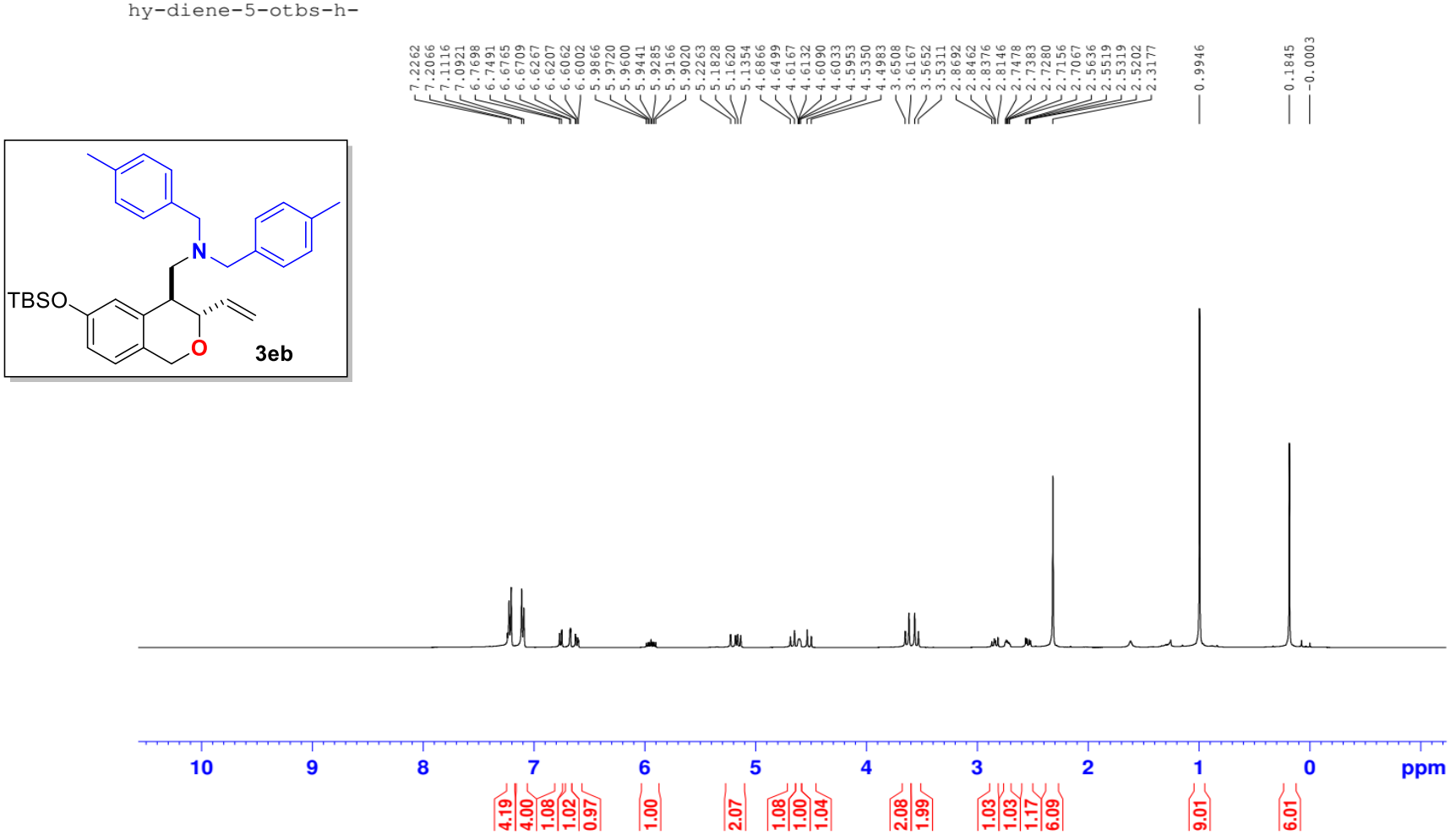
hy-P-**3db** ^{1}H NMR (400MHz $CDCl_3$)



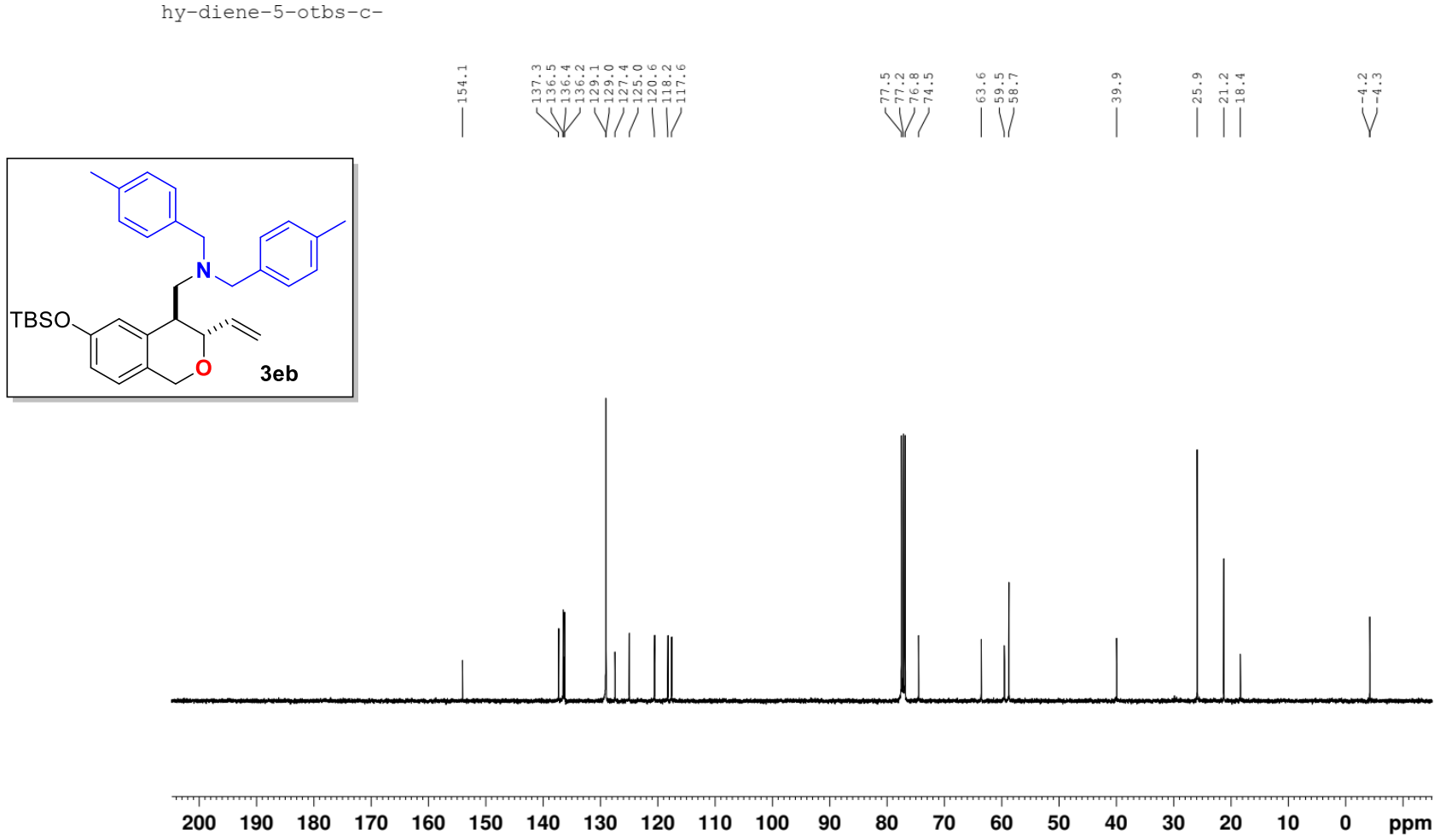
hy-P-**3db** ^{13}C NMR (100MHz $CDCl_3$)



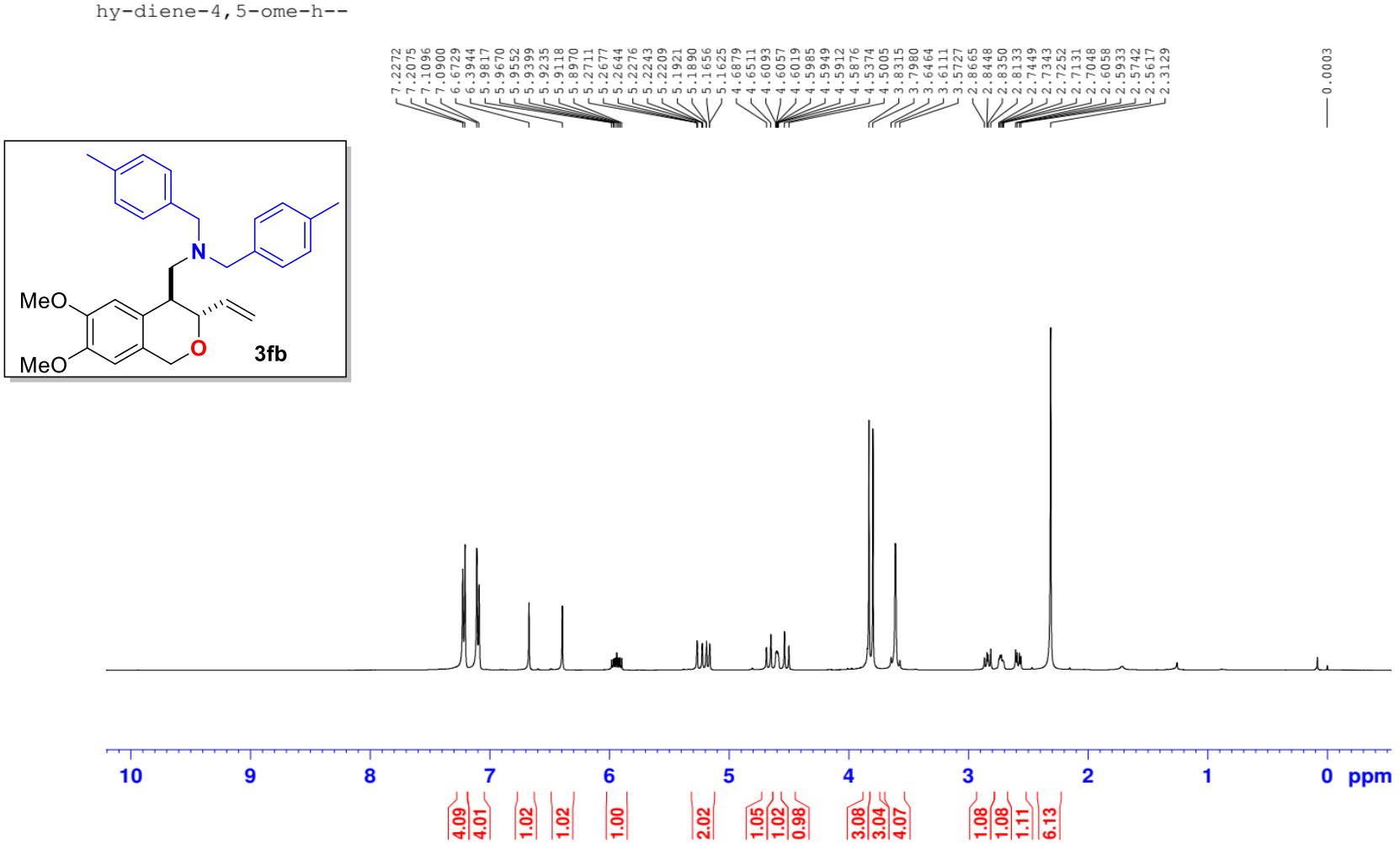
hy-P-**3eb** ^{1}H NMR (400MHz $CDCl_3$)



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

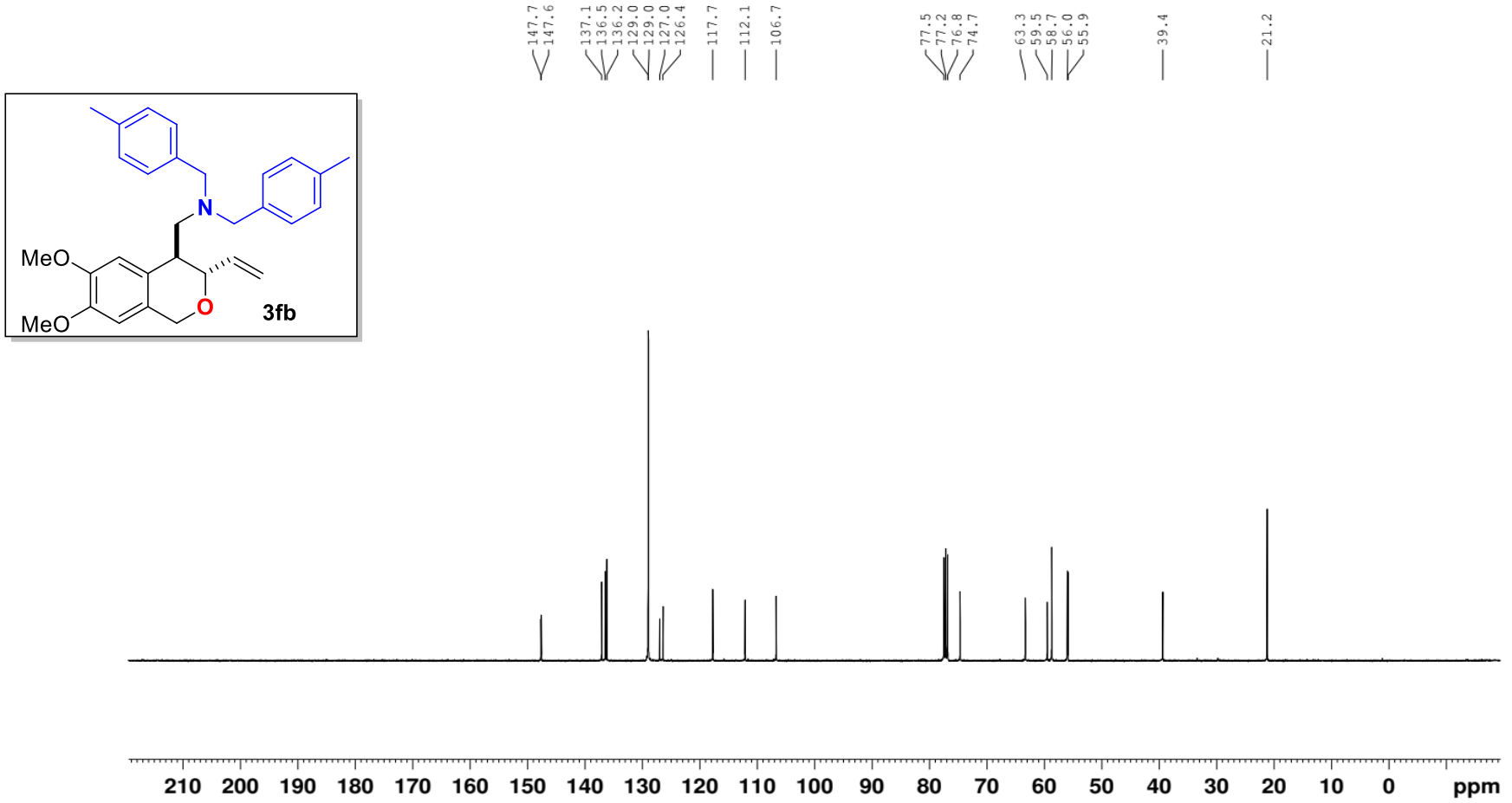


hy-P-**3fb** ^{1}H NMR (400MHz $CDCl_3$)

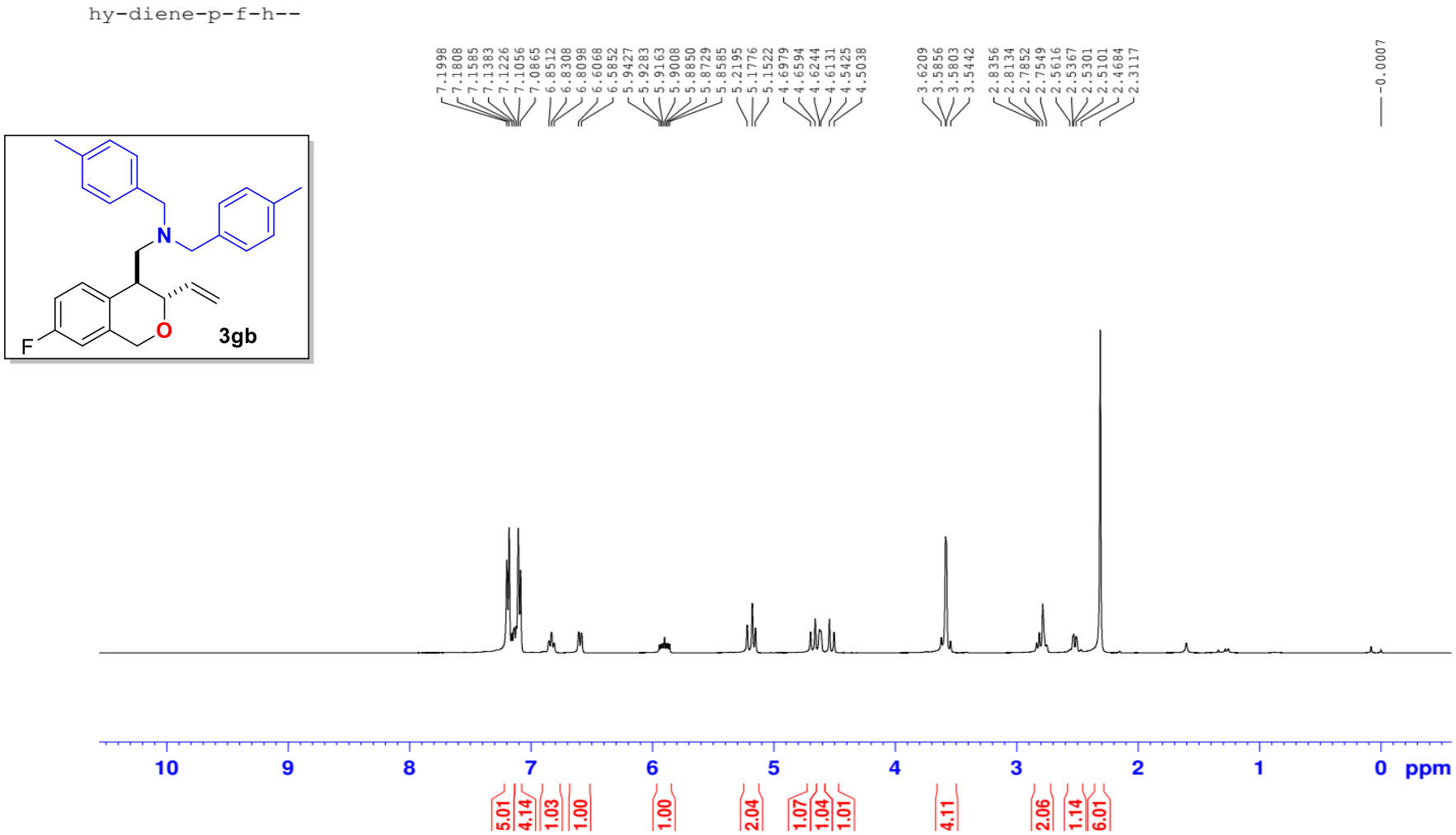


hy-P-**3fb** ^{13}C NMR (100MHz $CDCl_3$)

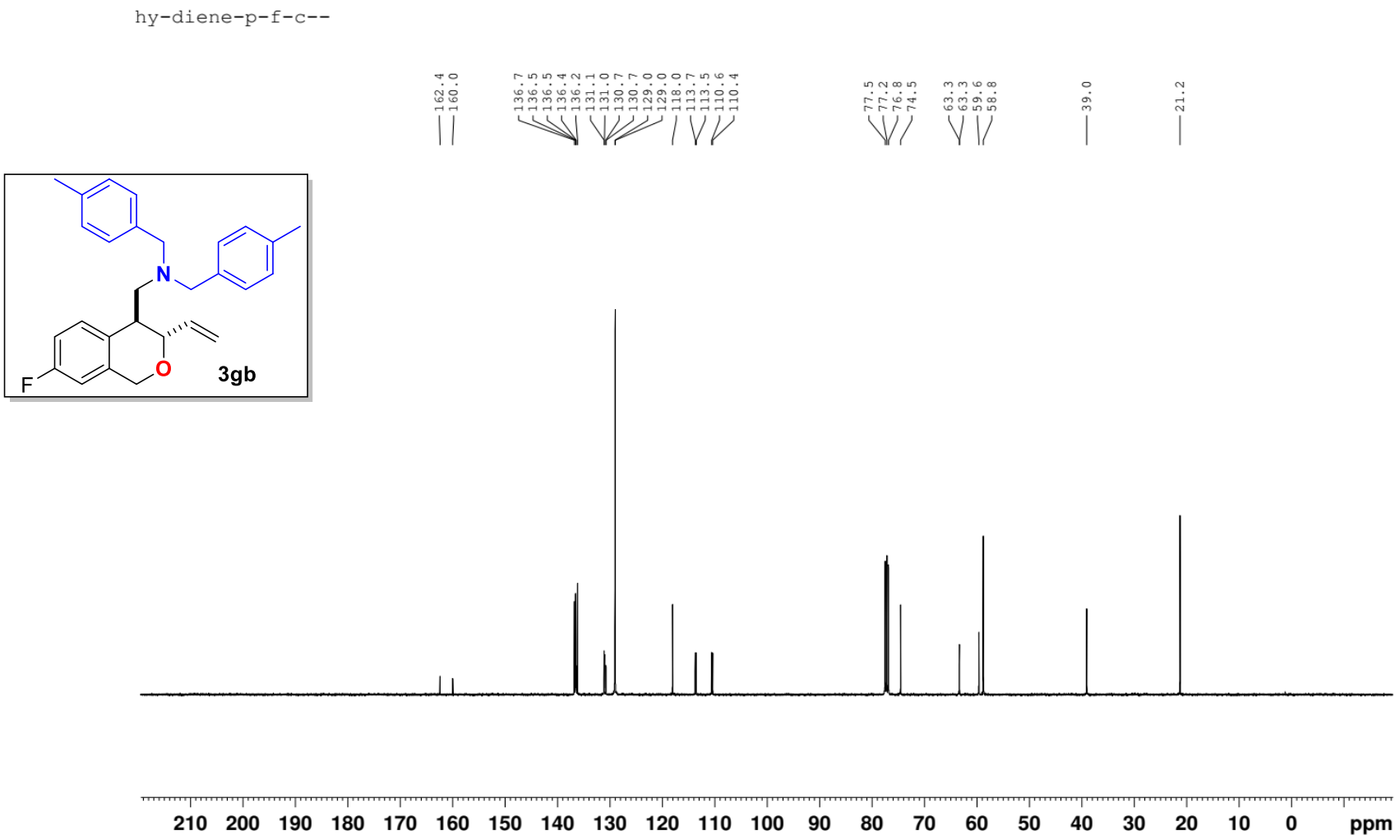
hy-diene-4,5-ome-c-



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

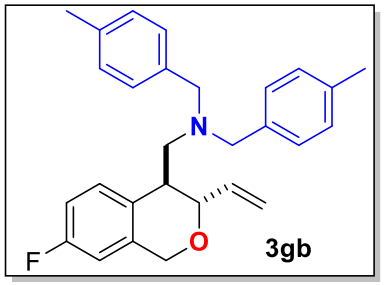


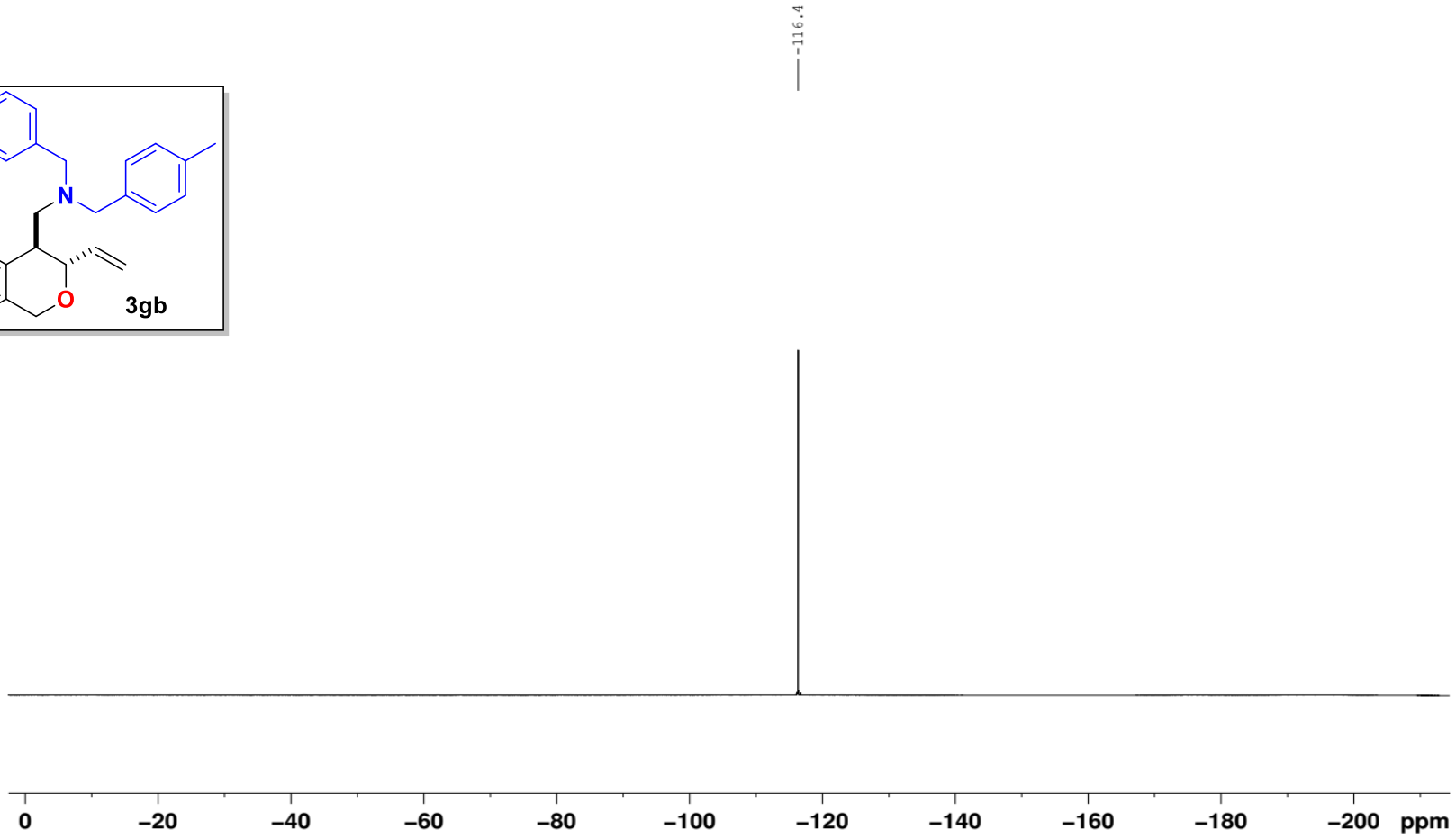
hy-P-**3gb** ^{13}C NMR (100MHz $CDCl_3$)



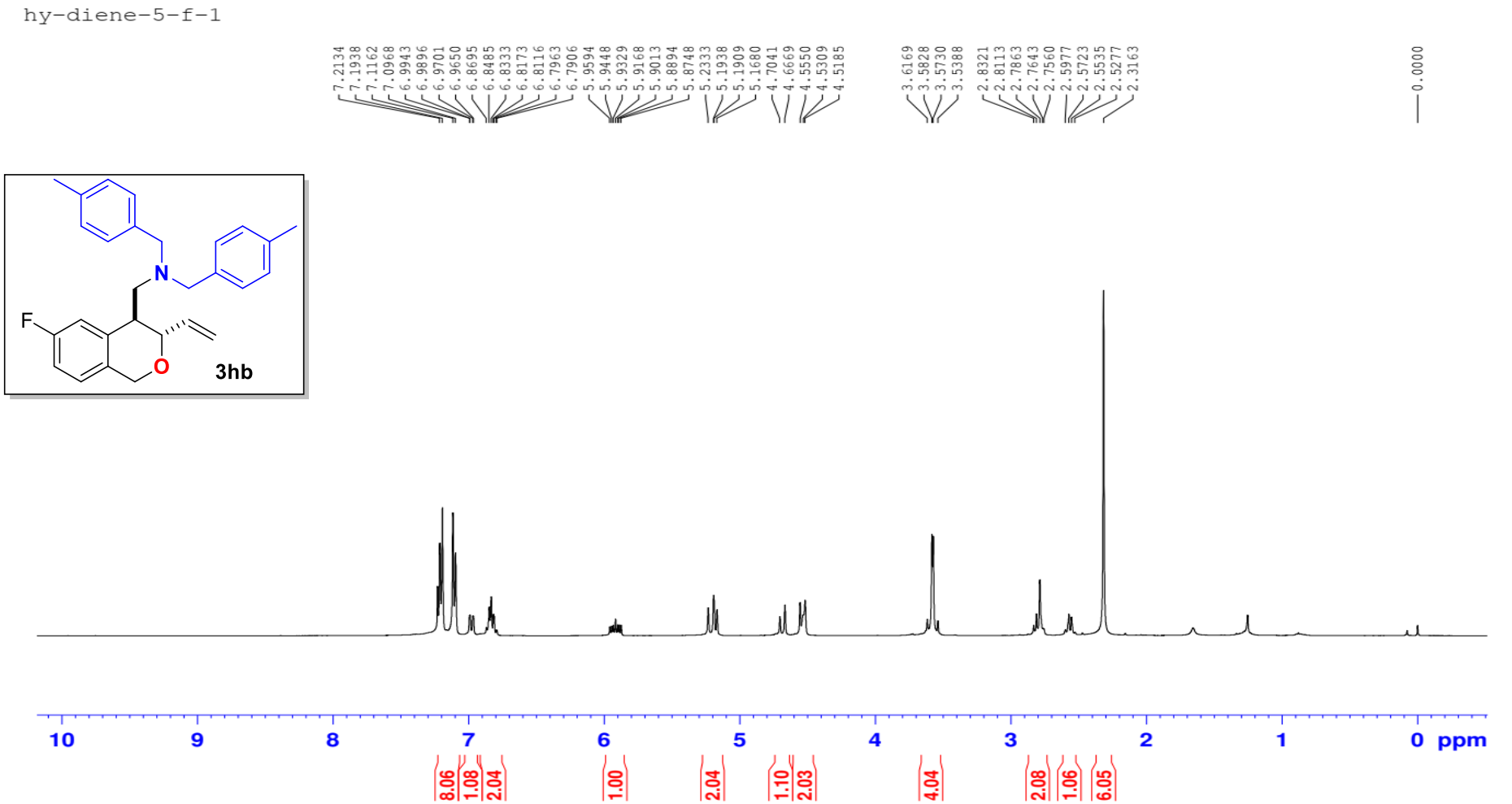
hy-P-**3gb** ^{19}F NMR (376MHz $CDCl_3$)

hy-diene-p-f-f

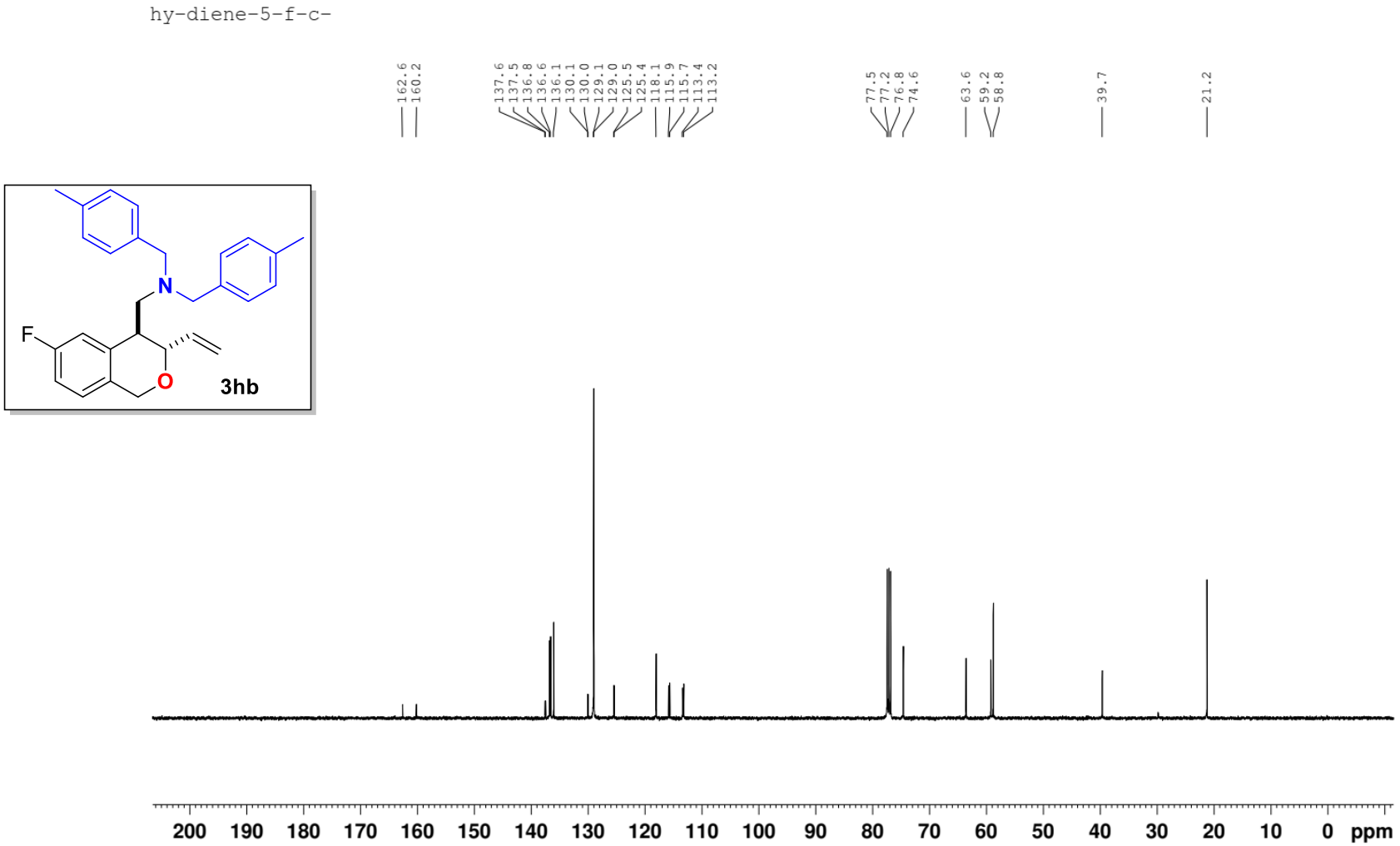




hy-P-**3hb** ^{1}H NMR (400MHz $CDCl_3$)

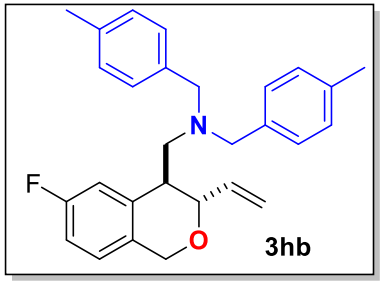


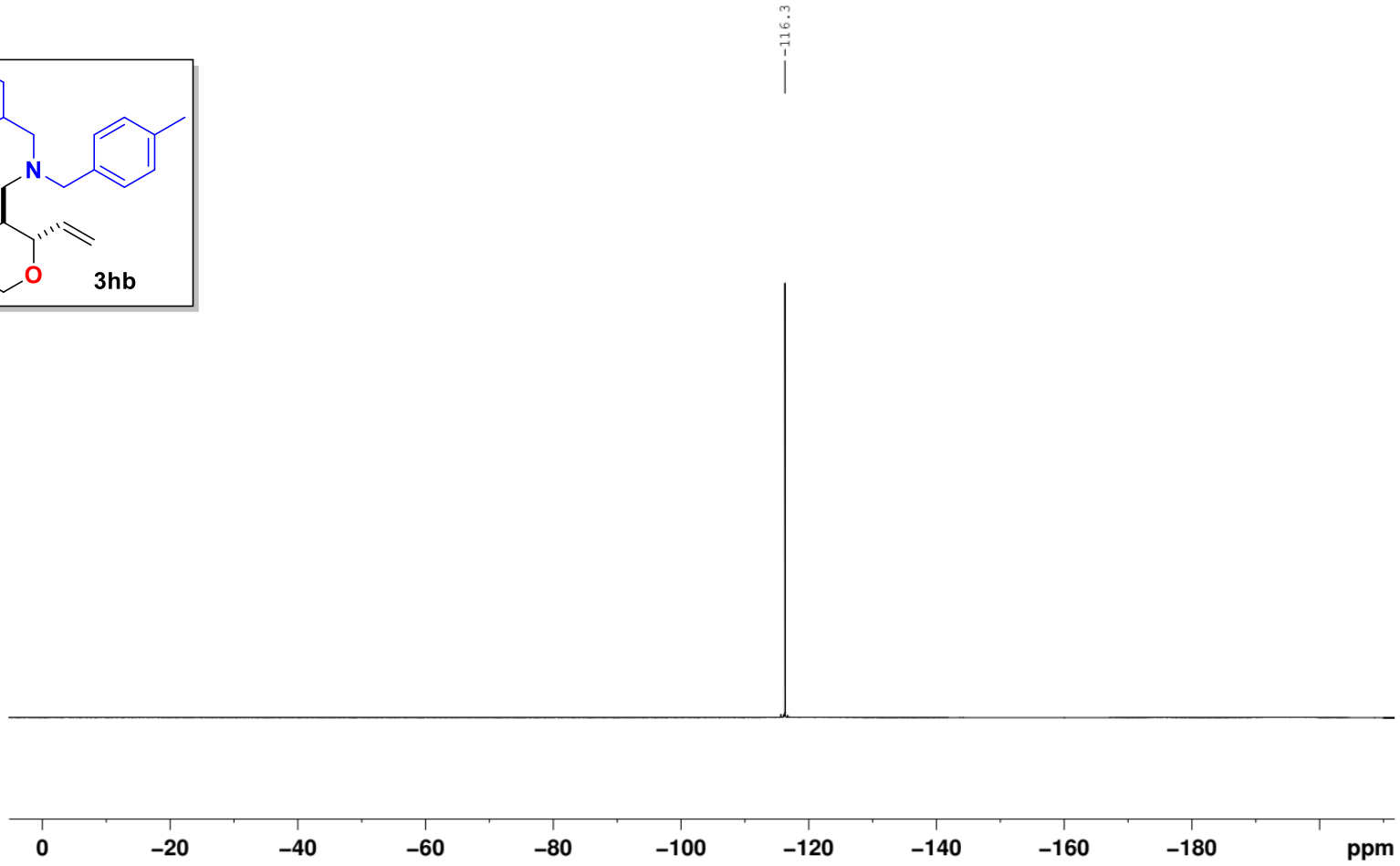
hy-P-**3hb** ^{13}C NMR (100MHz $CDCl_3$)



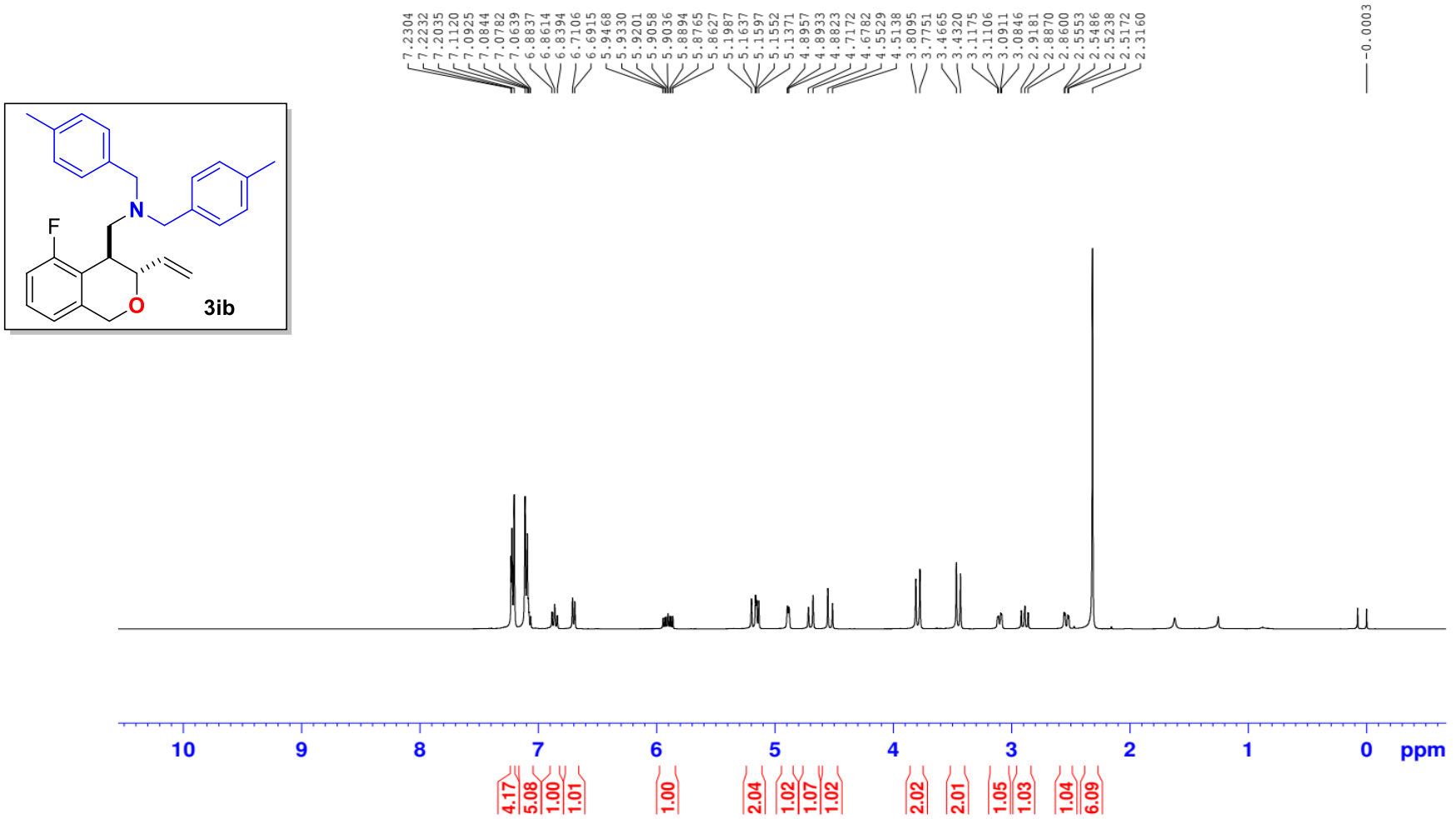
hy-P-**3hb** ^{19}F NMR (376MHz $CDCl_3$)

hy-diene-5-f-f



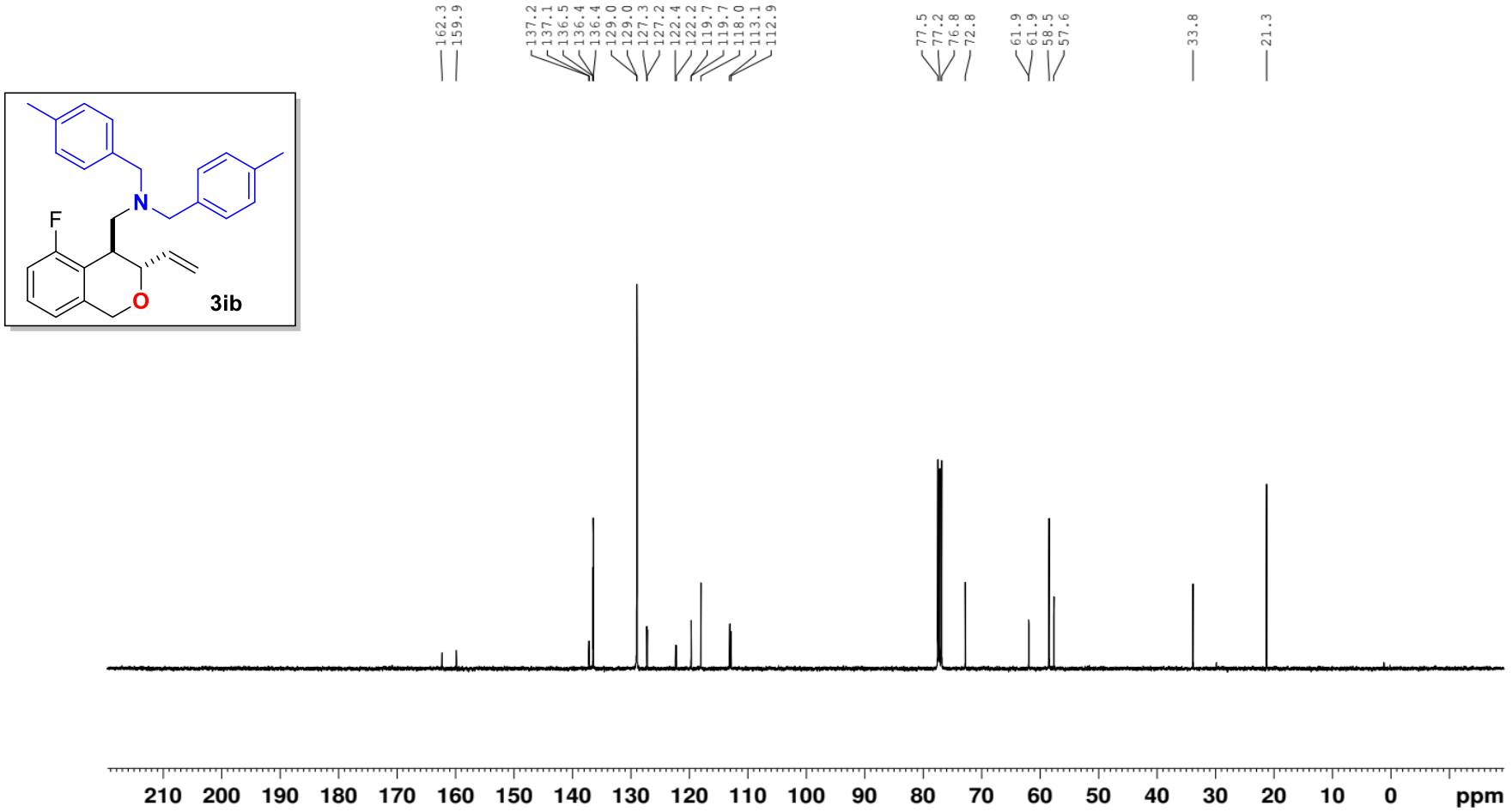


hy-P-**3ib** ^{1}H NMR (400MHz $CDCl_3$)

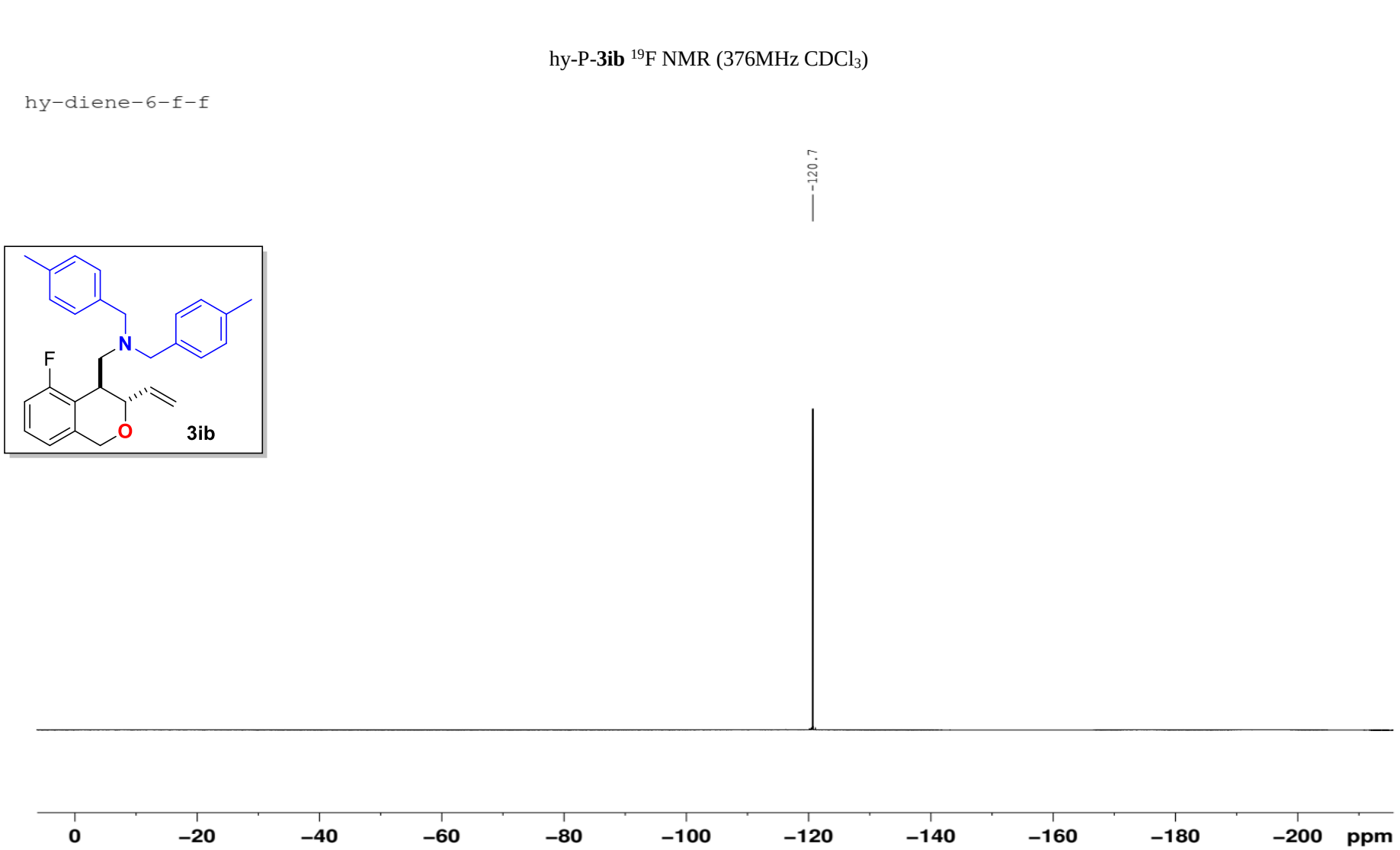


hy-P-**3ib** ^{13}C NMR (100MHz $CDCl_3$)

hy-diene-6-f-c-

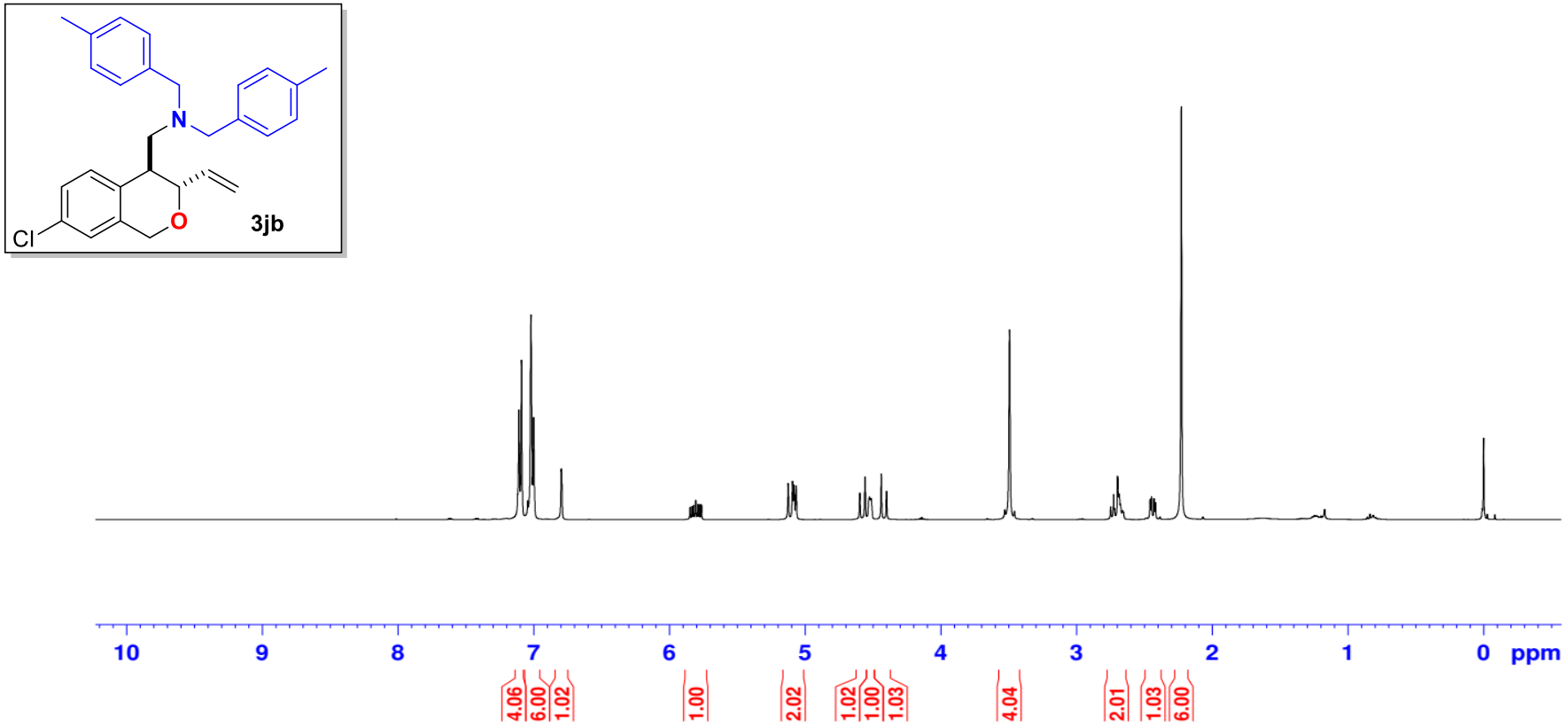


hy-P-**3ib** ^{19}F NMR (376MHz $CDCl_3$)

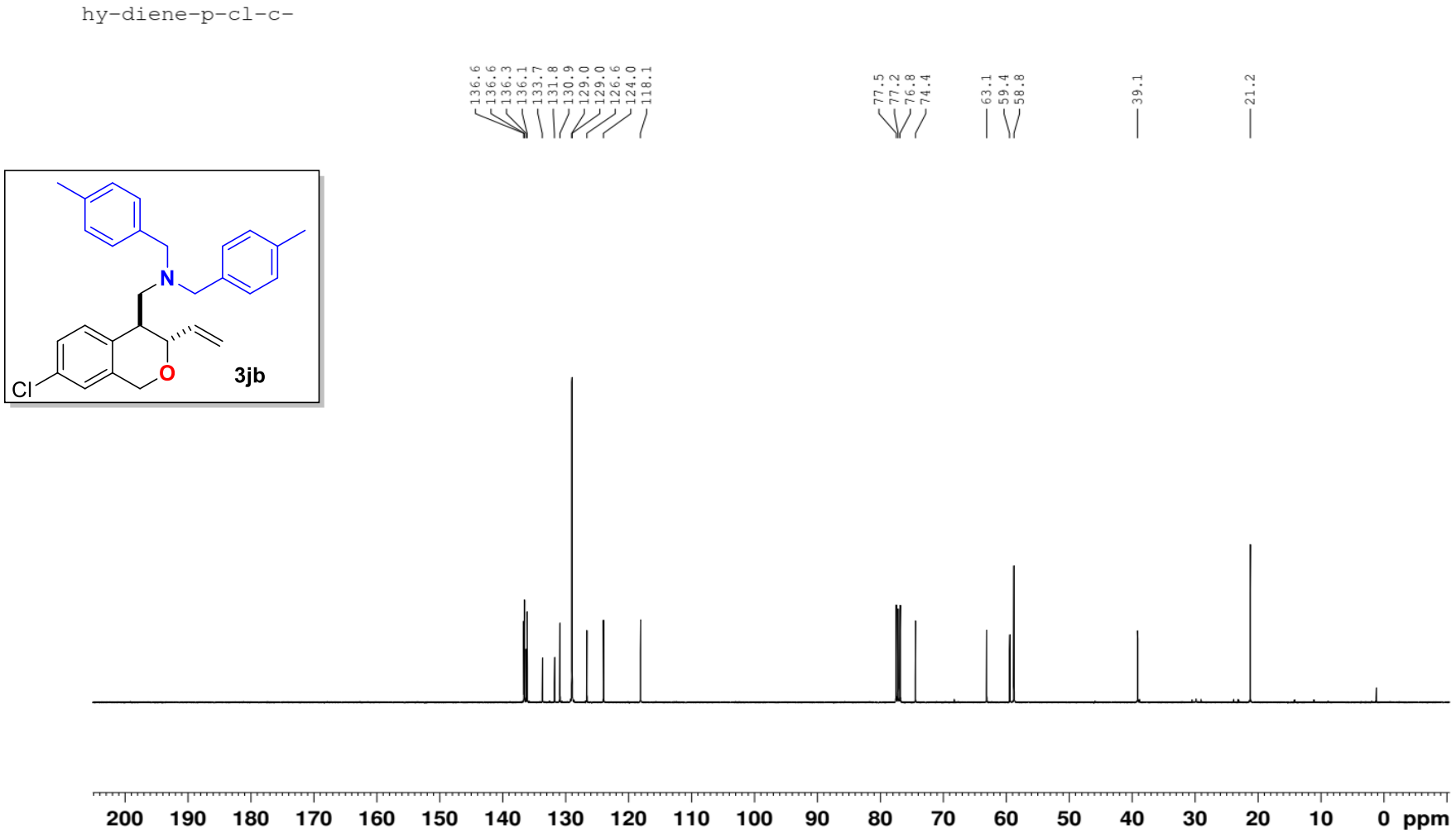


hy-P-**3jb** ^{1}H NMR (400MHz $CDCl_3$)

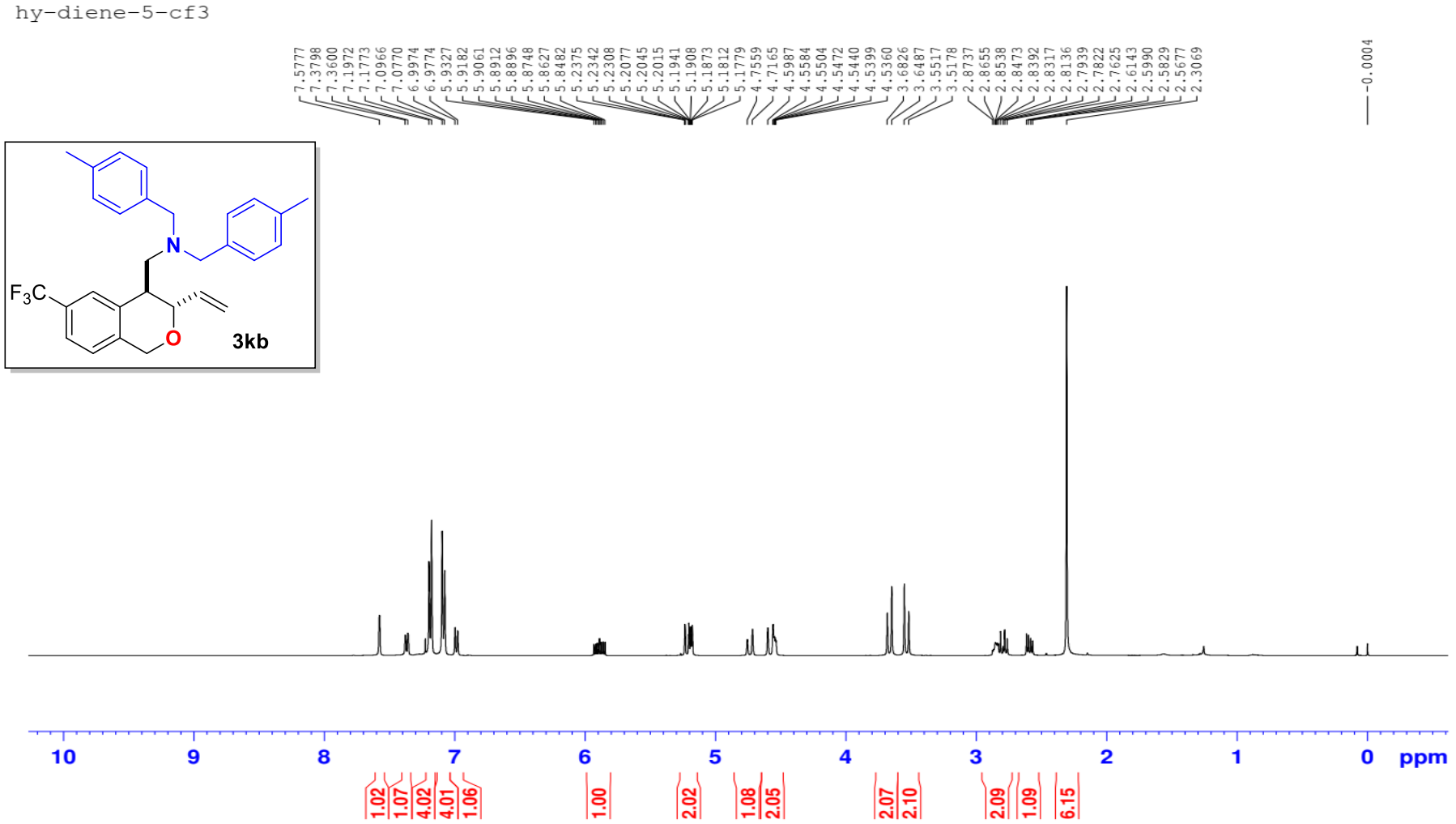
hy-diene-p-cl-h-



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

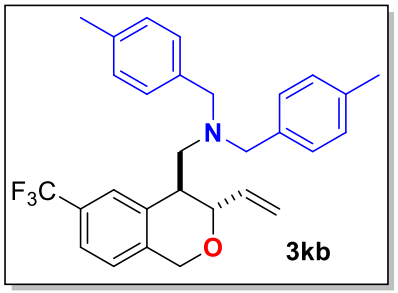


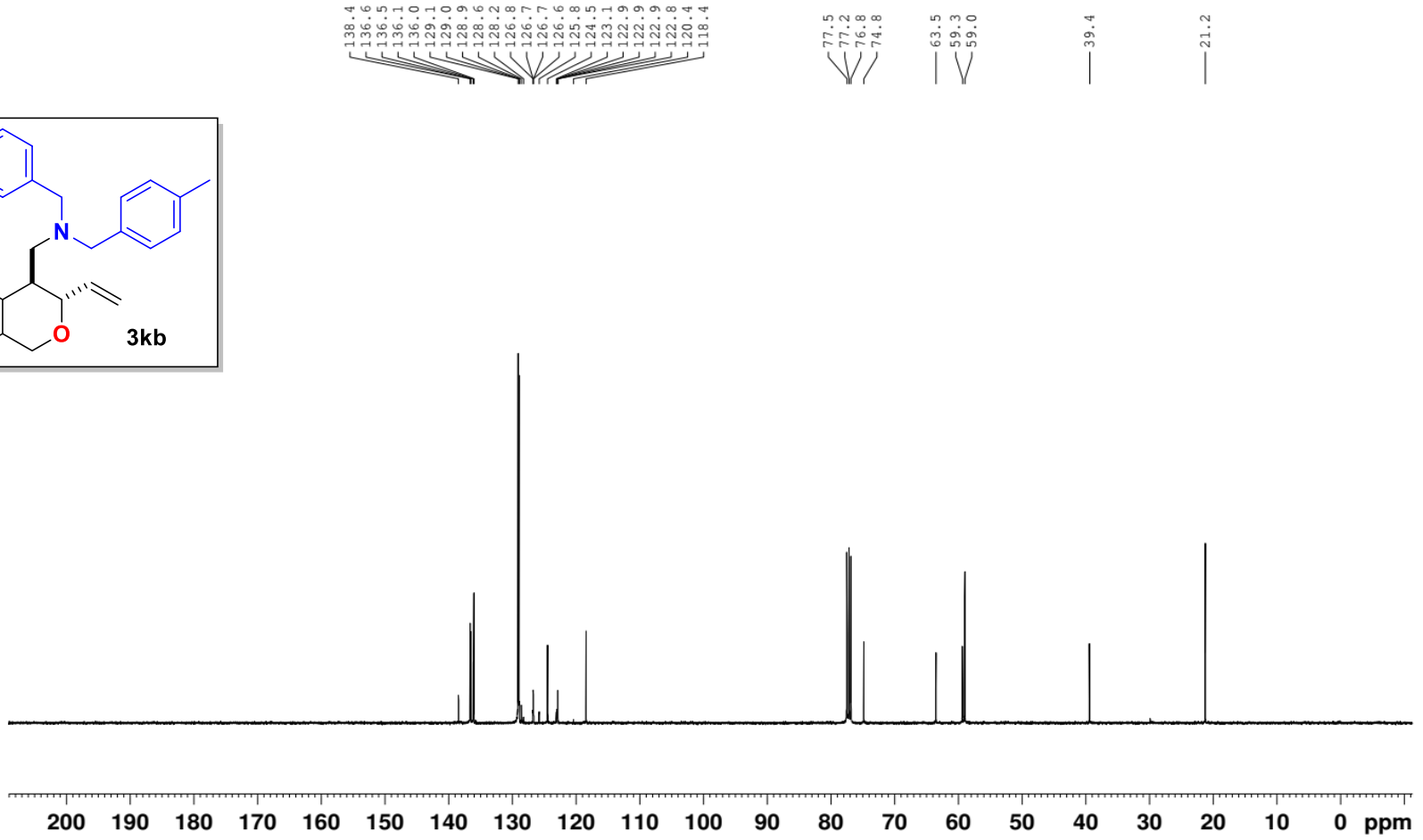
hy-P-**3kb** ^{1}H NMR (400MHz $CDCl_3$)



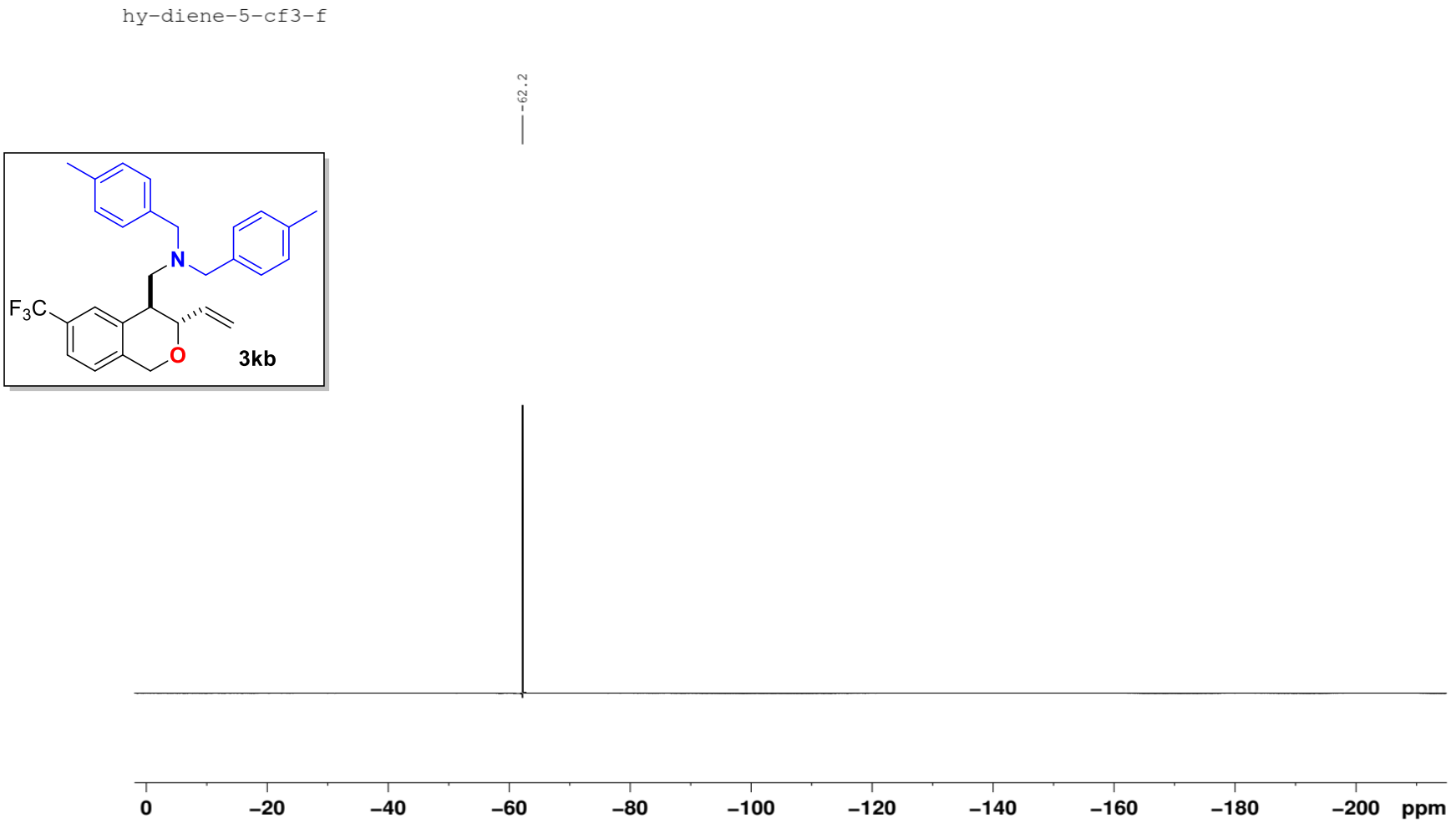
hy-P-**3kb** ^{13}C NMR (100MHz $CDCl_3$)

hy-diene-5-cf3-c--

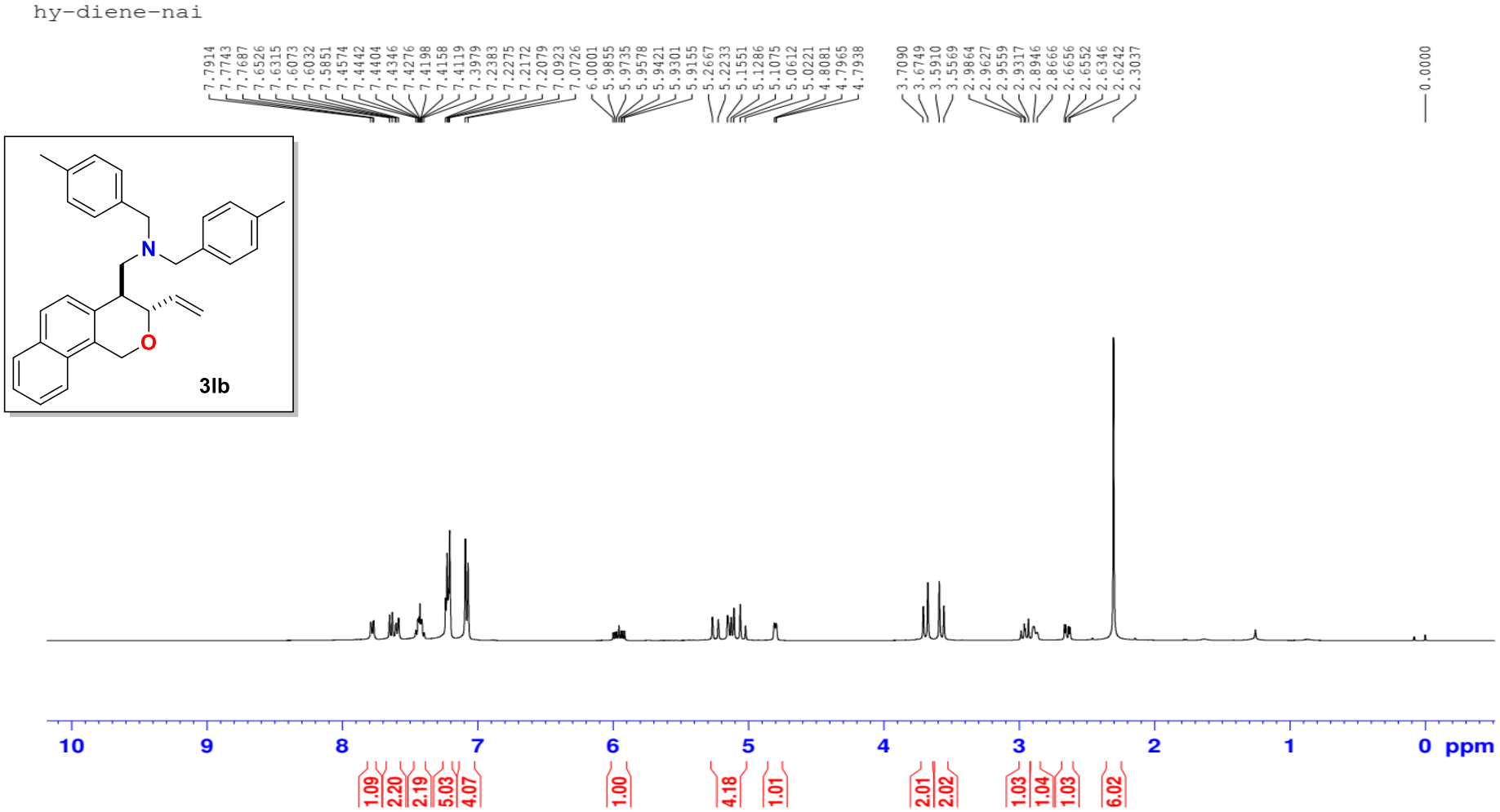




hy-P-**3kb** ^{19}F NMR (376MHz $CDCl_3$)

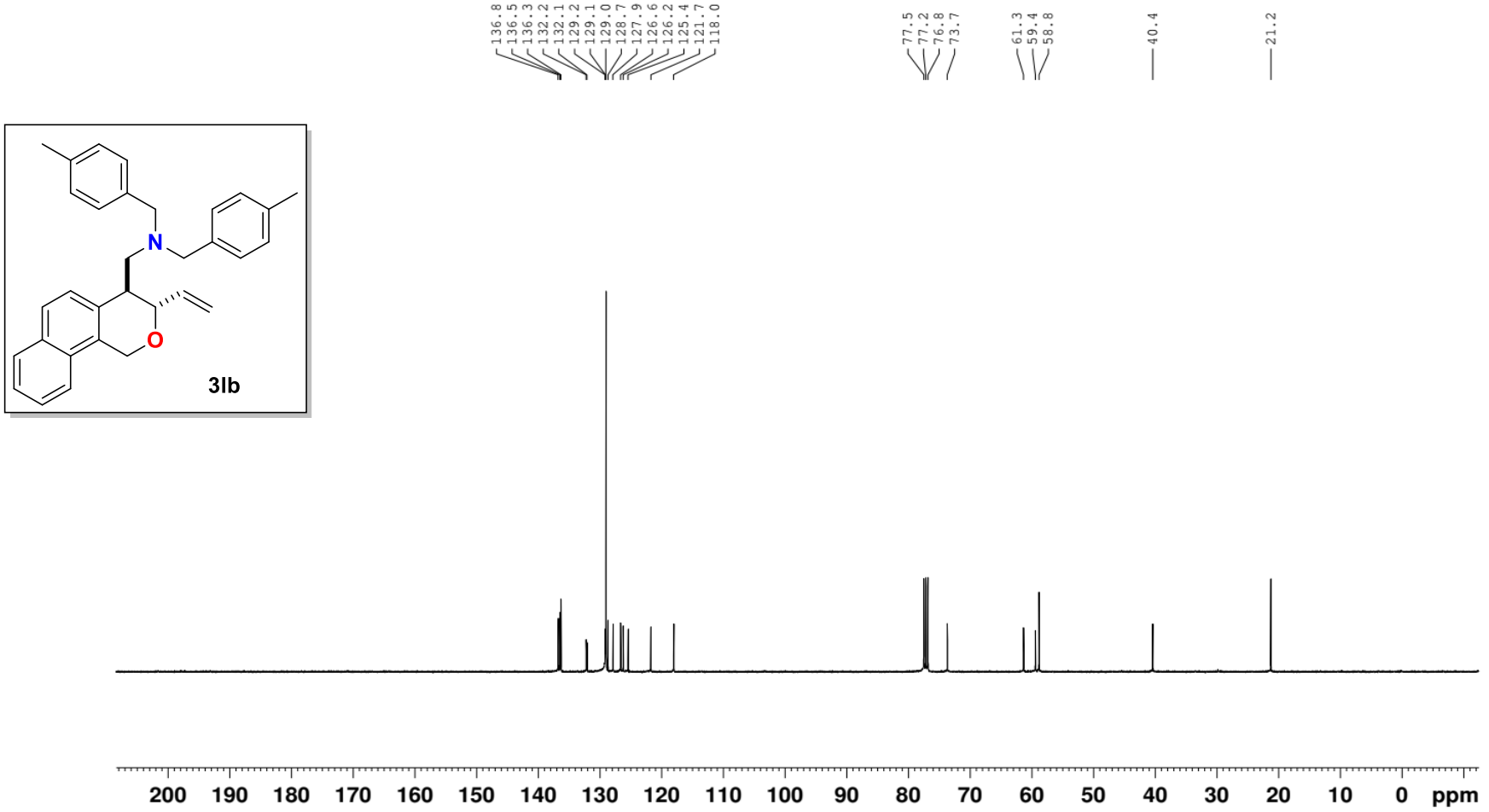


hy-P-**3lb** ^{1}H NMR (400MHz $CDCl_3$)

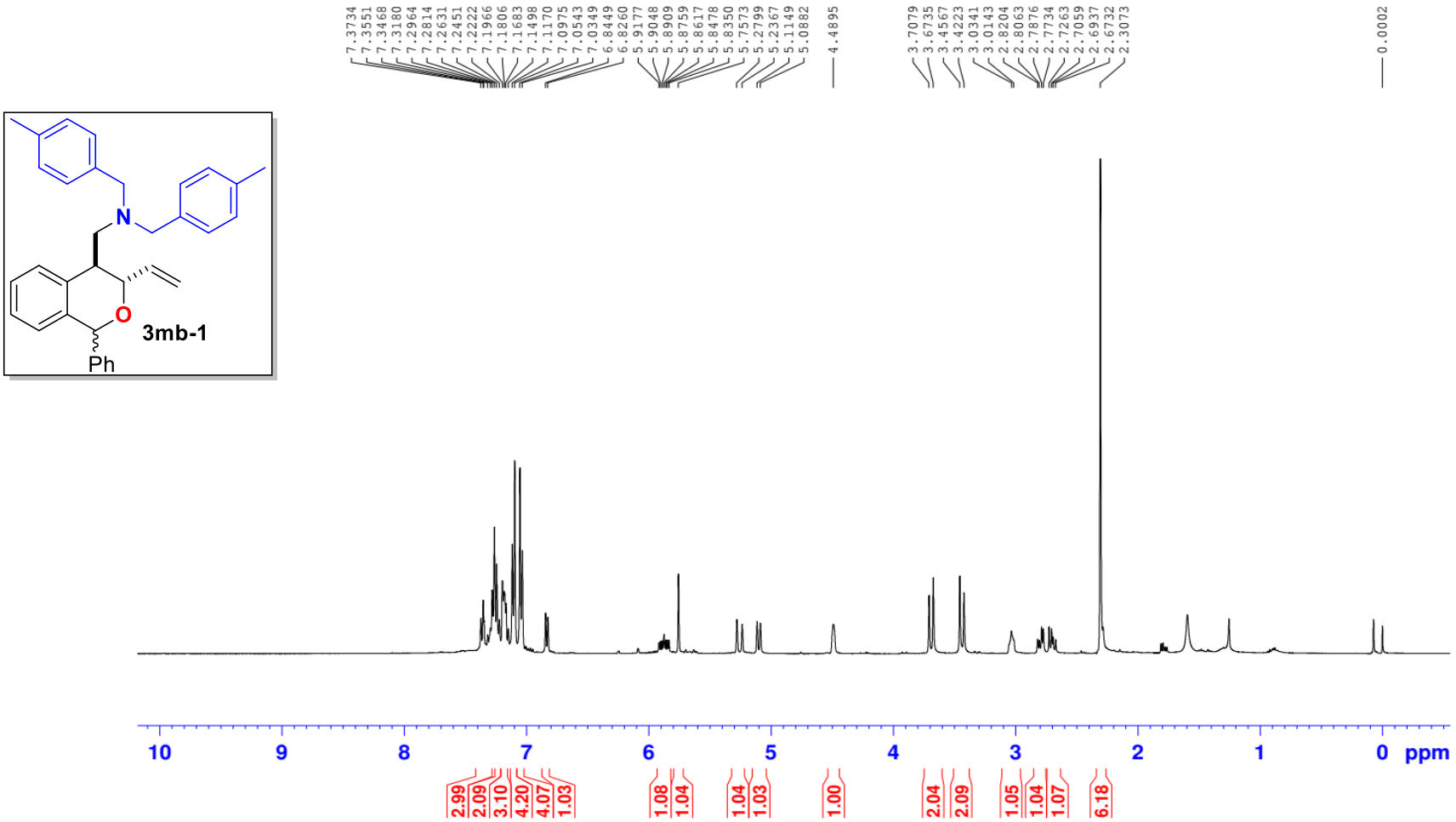


hy-P-**3lb** ^{13}C NMR (100MHz $CDCl_3$)

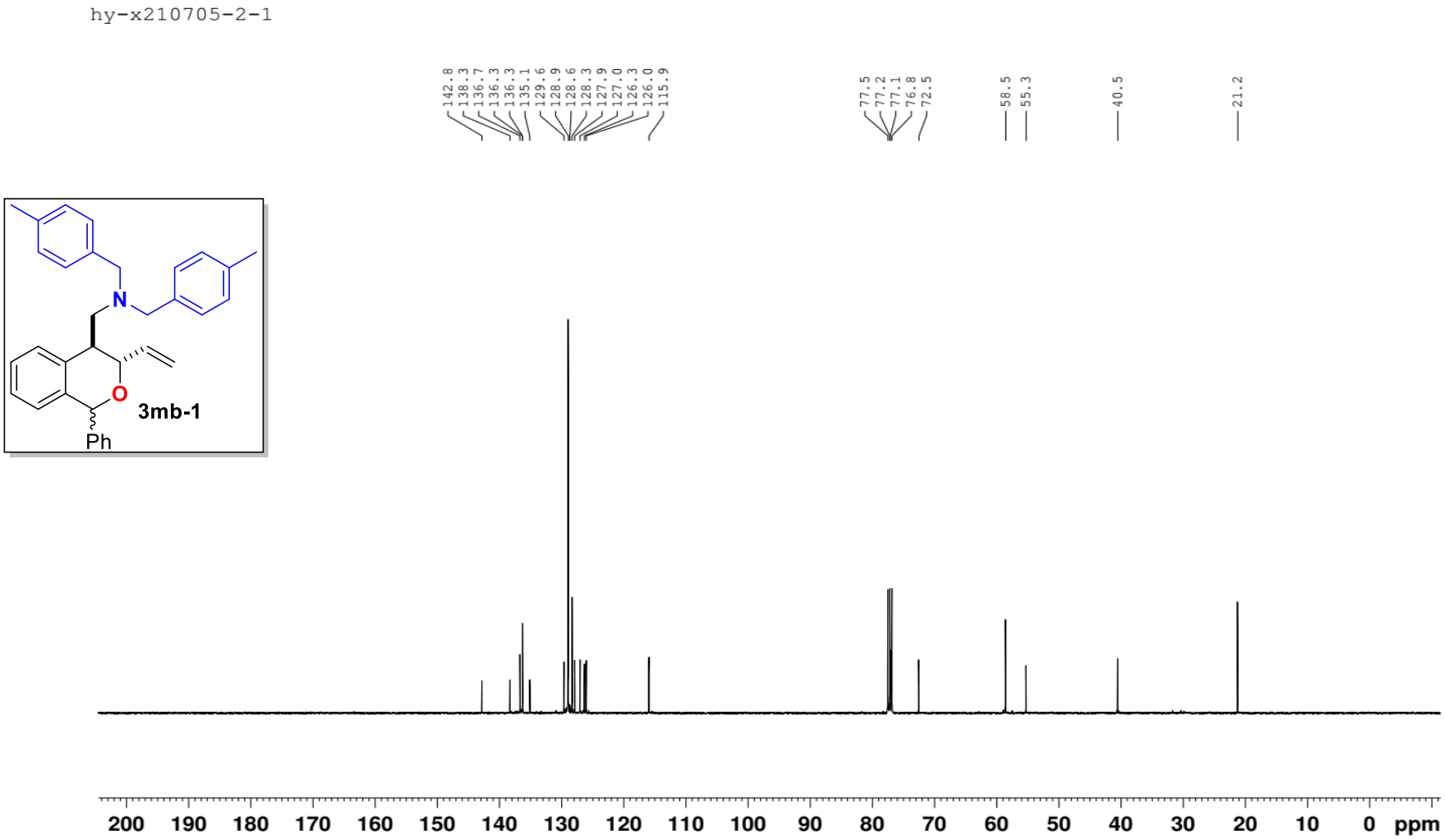
hy-diene-nai-c-



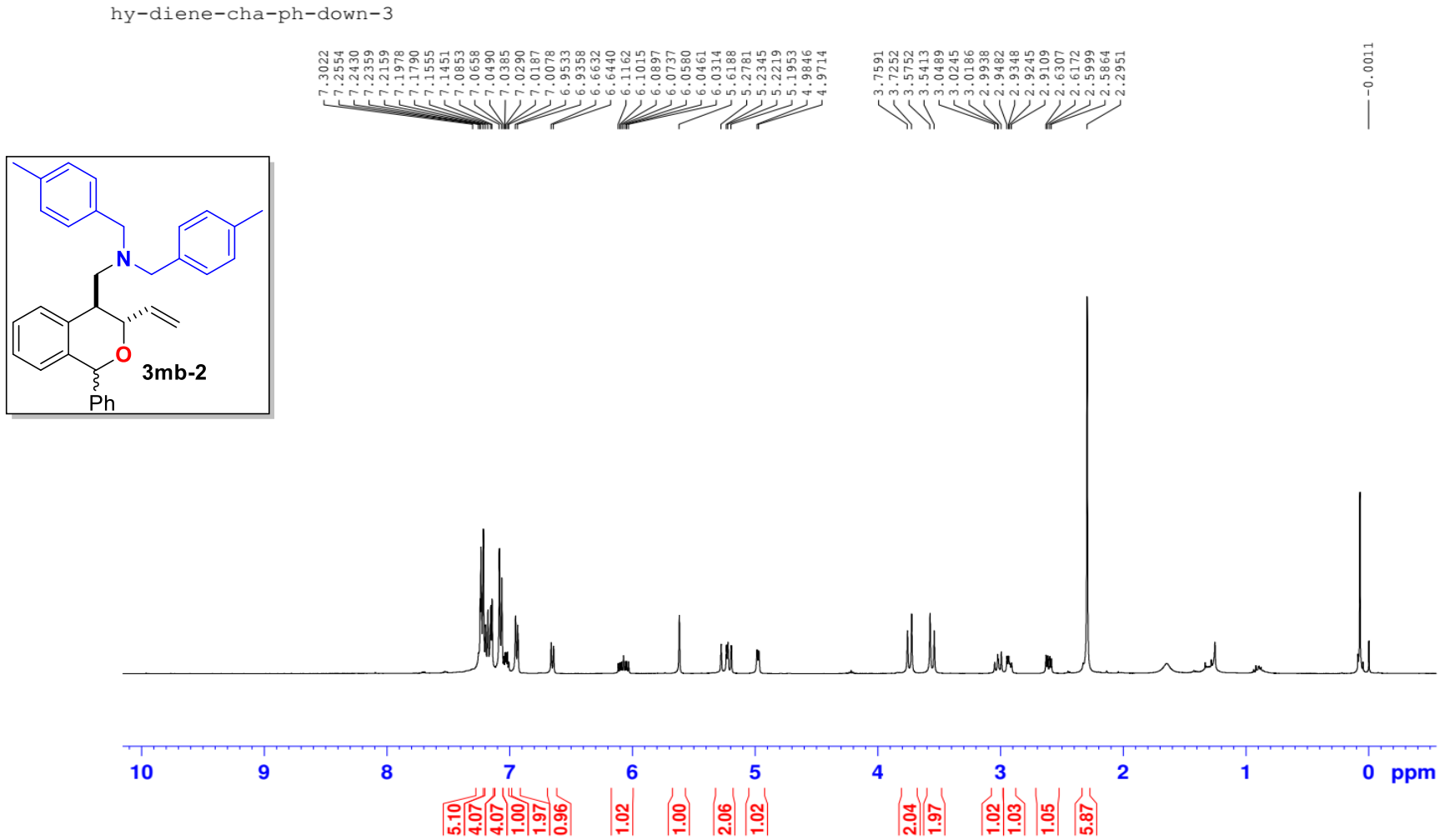
hy-P-**3mb-1** ^{1}H NMR (400MHz $CDCl_3$)



hy-P-**3mb-1** ^{13}C NMR (100MHz $CDCl_3$)

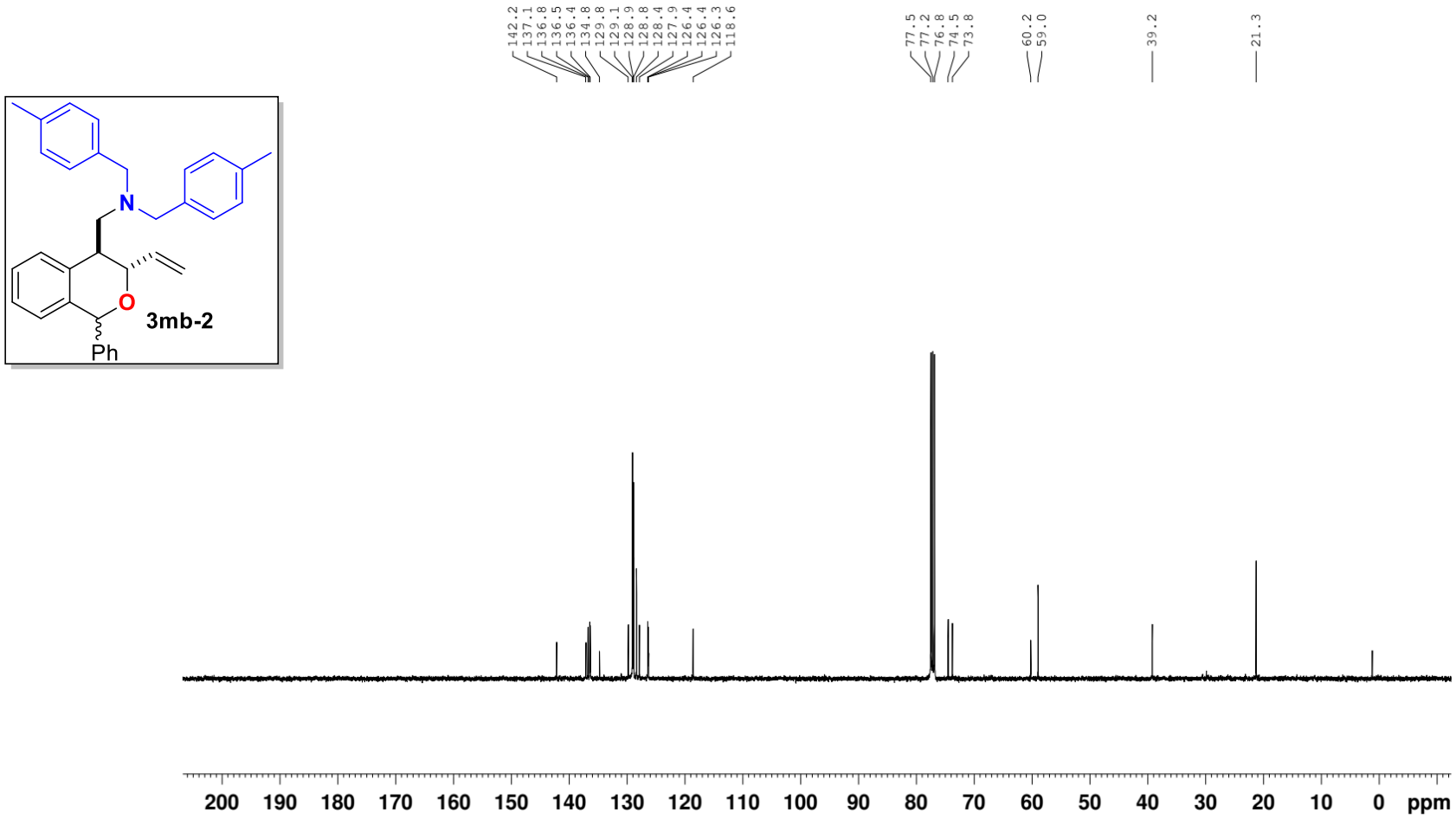


hy-P-**3mb-2** ^{1}H NMR (400MHz $CDCl_3$)

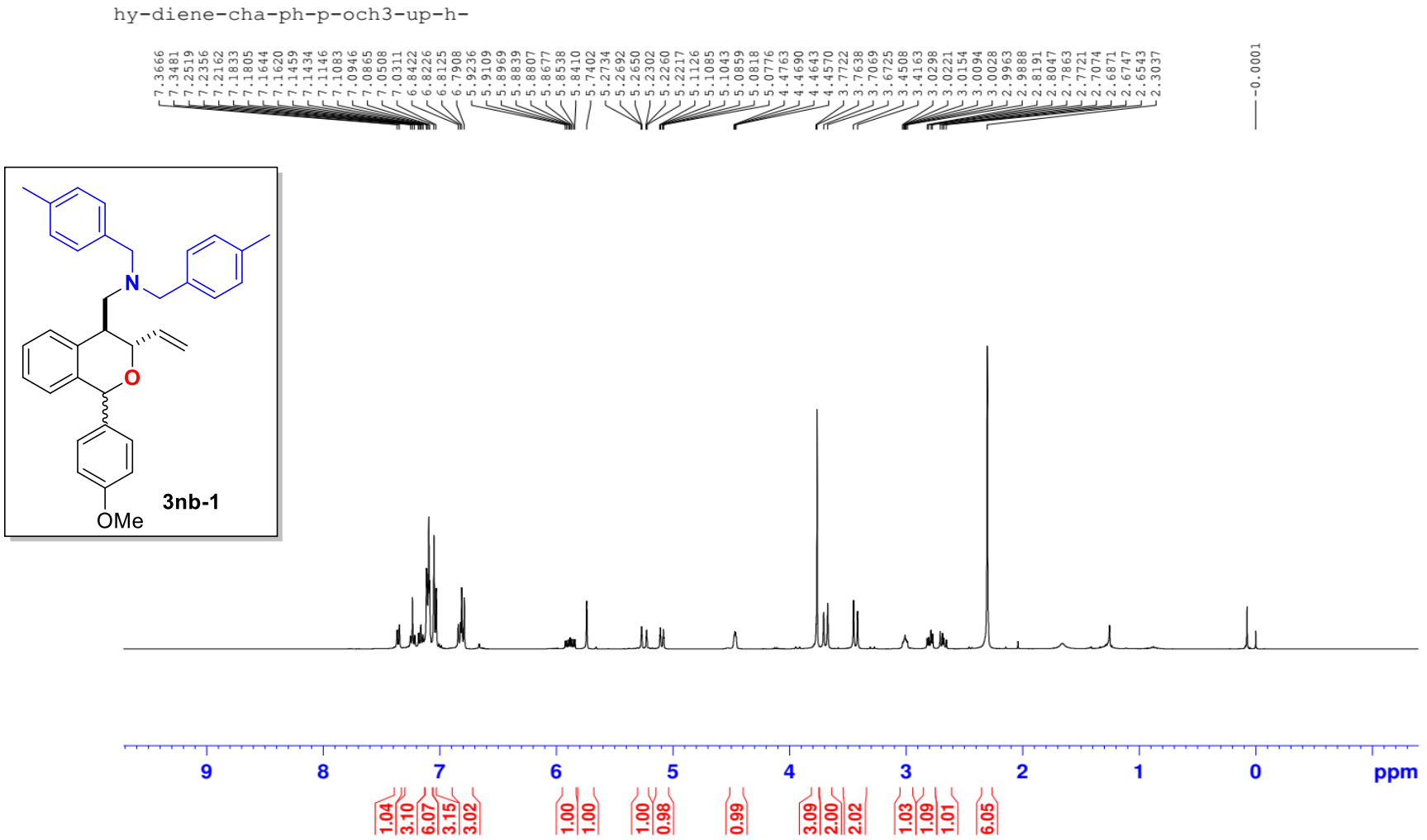


hy-P-**3mb-2** ^{13}C NMR (100MHz $CDCl_3$)

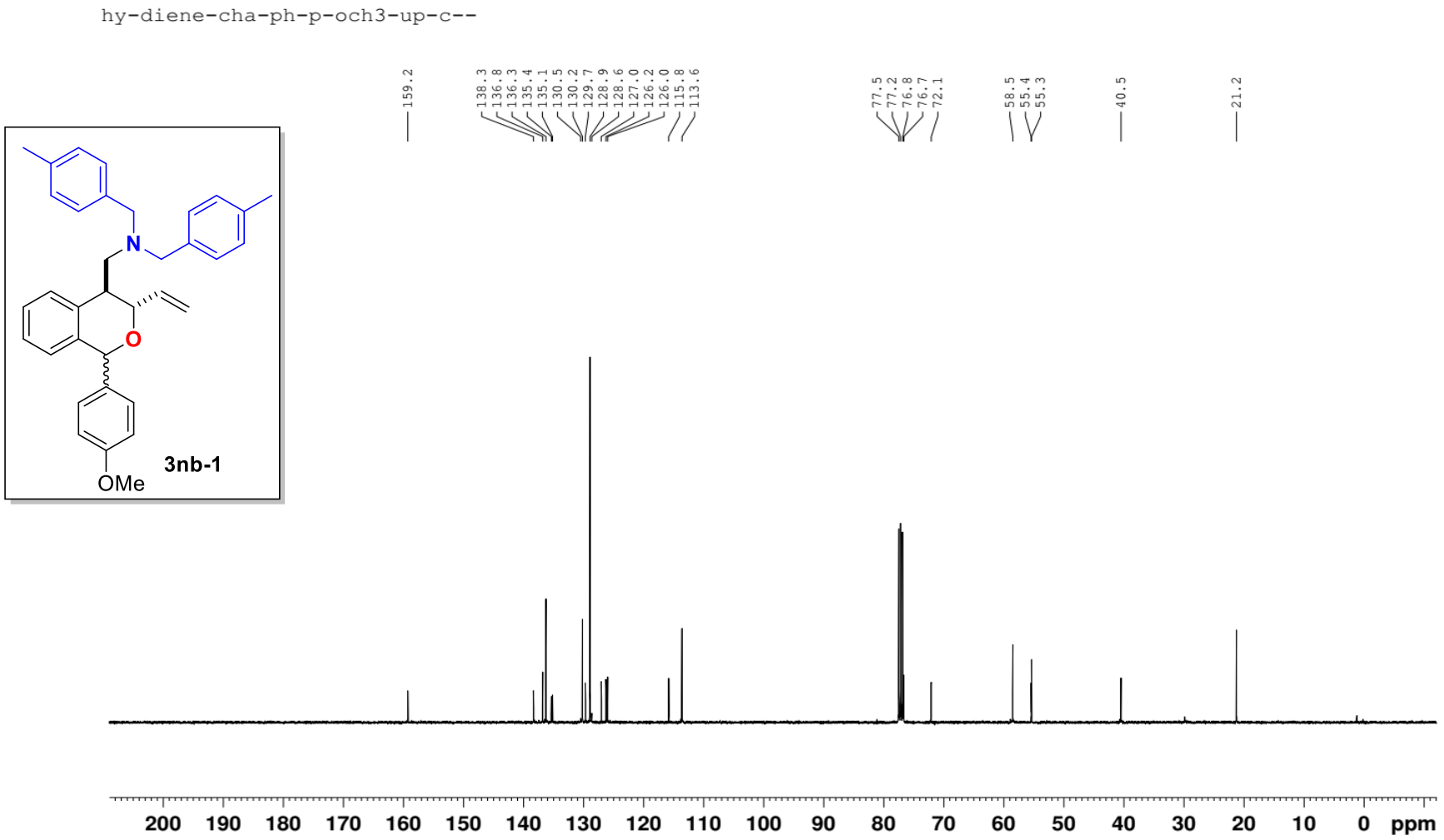
hy-diene-cha-ph-down-c-



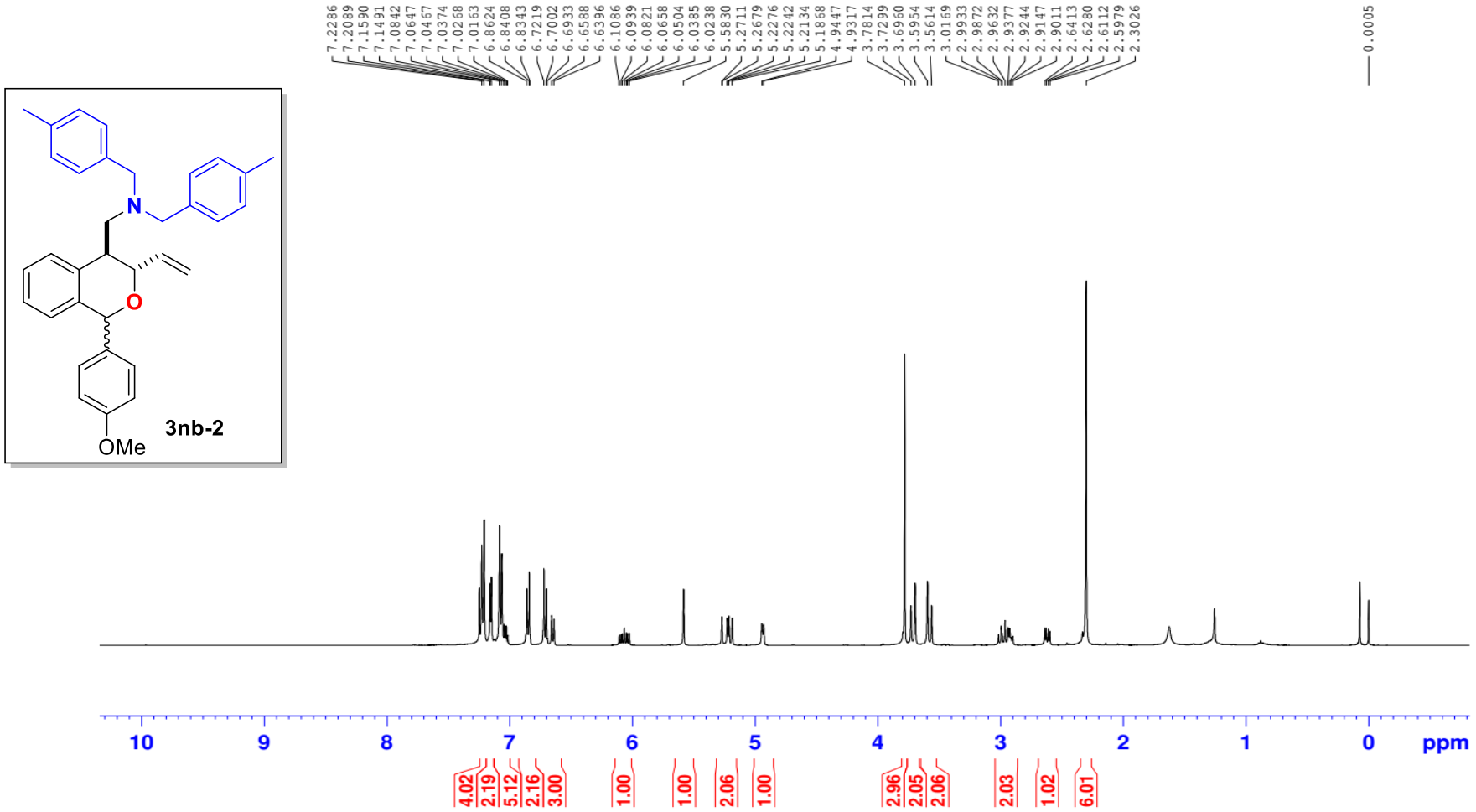
hy-P-**3nb-1** ^{1}H NMR (400MHz $CDCl_3$)



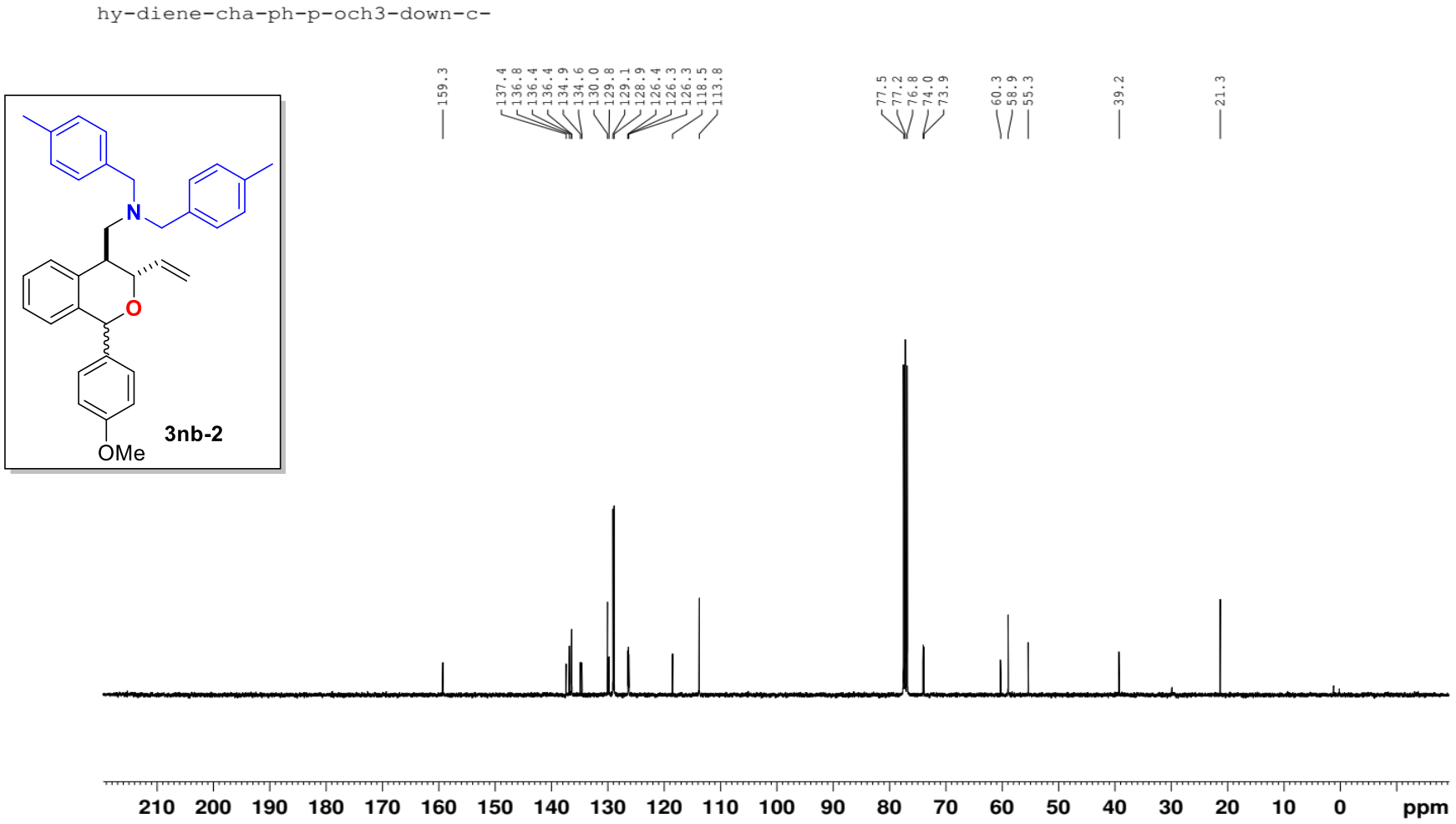
hy-P-**3nb-1** ^{13}C NMR (100MHz $CDCl_3$)



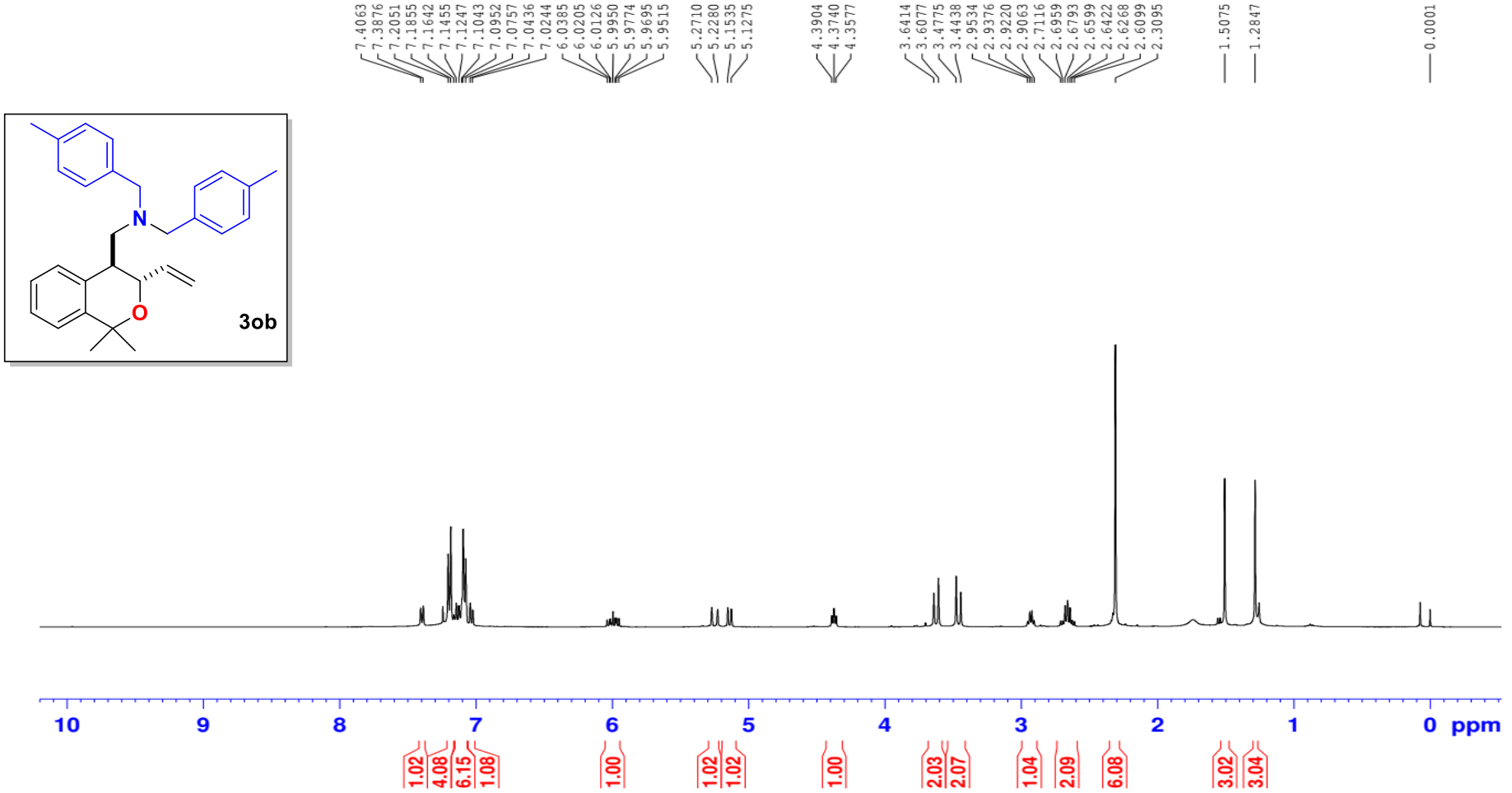
hy-P-**3nb-2** ^{1}H NMR (400MHz $CDCl_3$)



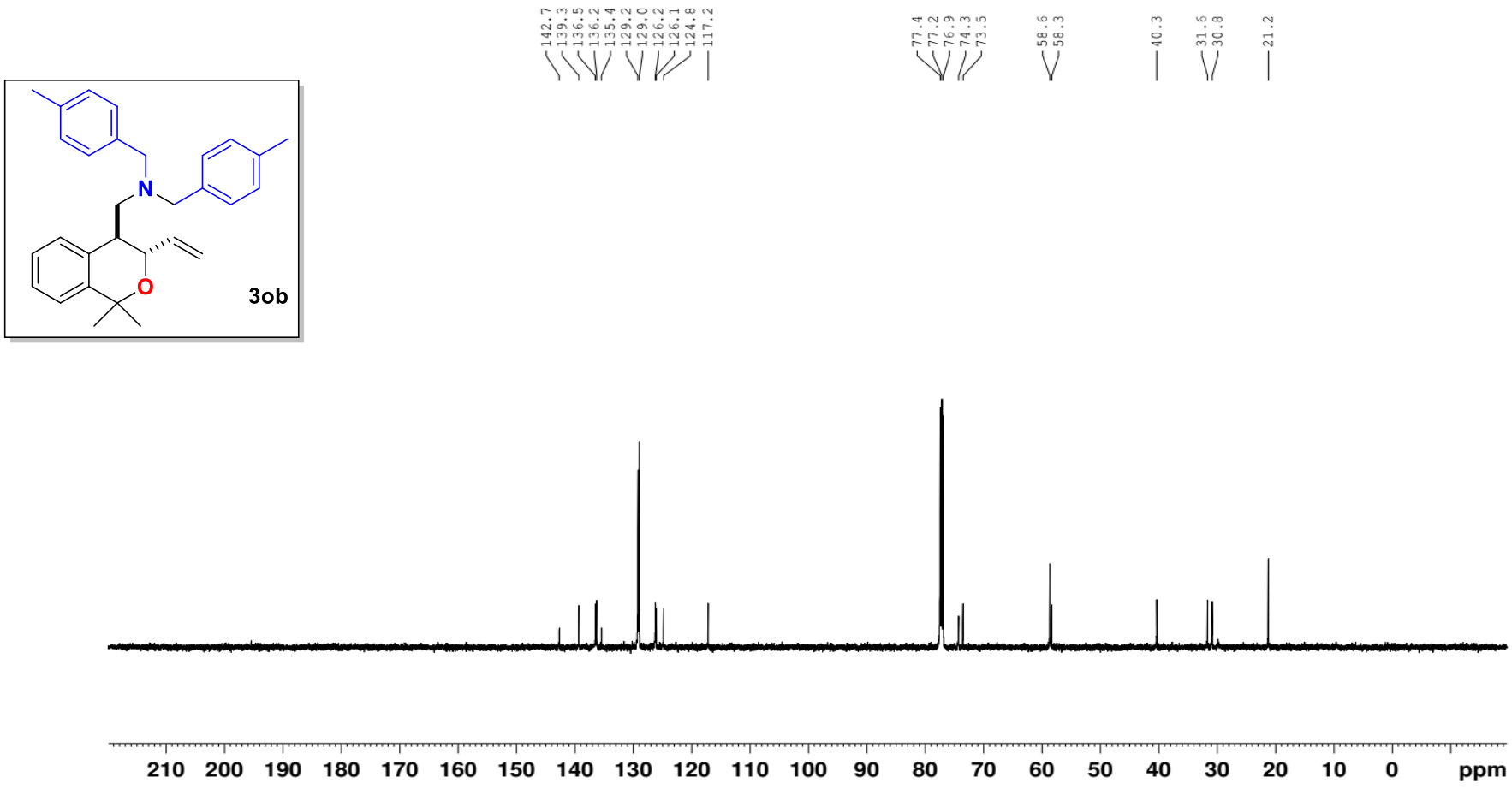
hy-P-**3nb-2** ^{13}C NMR (100MHz $CDCl_3$)



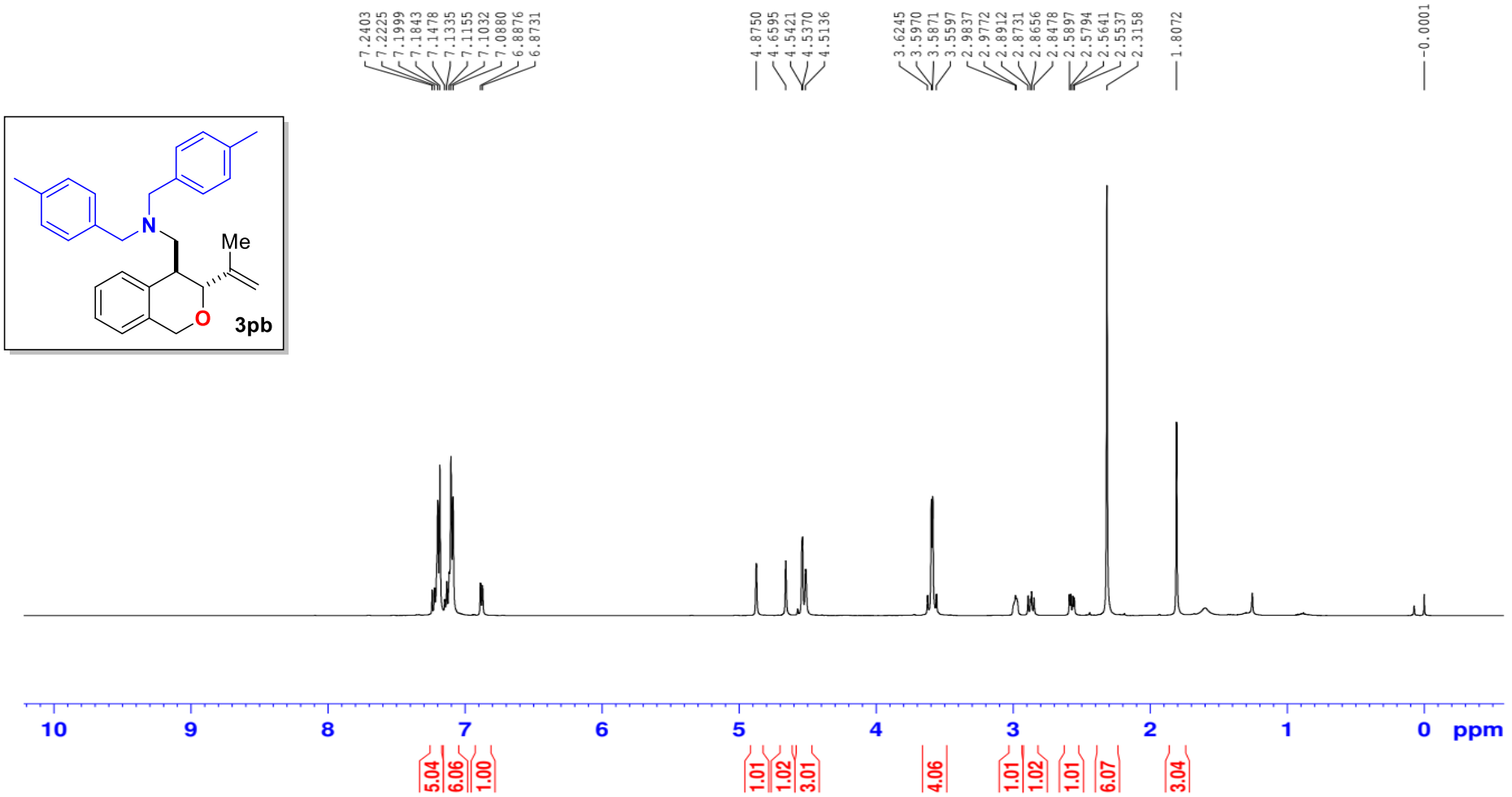
hy-P-**3ob** ^{1}H NMR (400MHz $CDCl_3$)



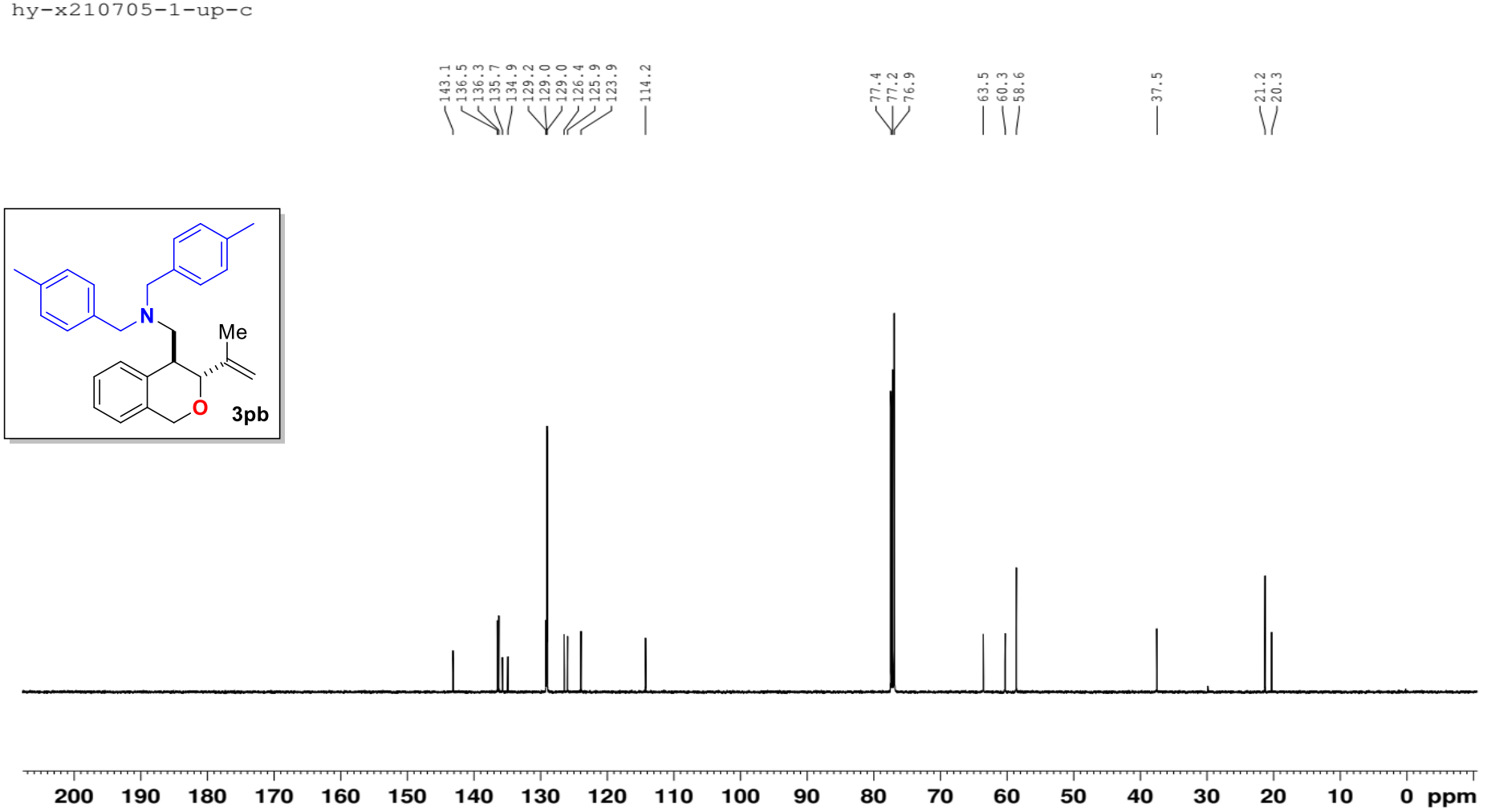
hy-P-**3ob** ^{13}C NMR (100MHz $CDCl_3$)



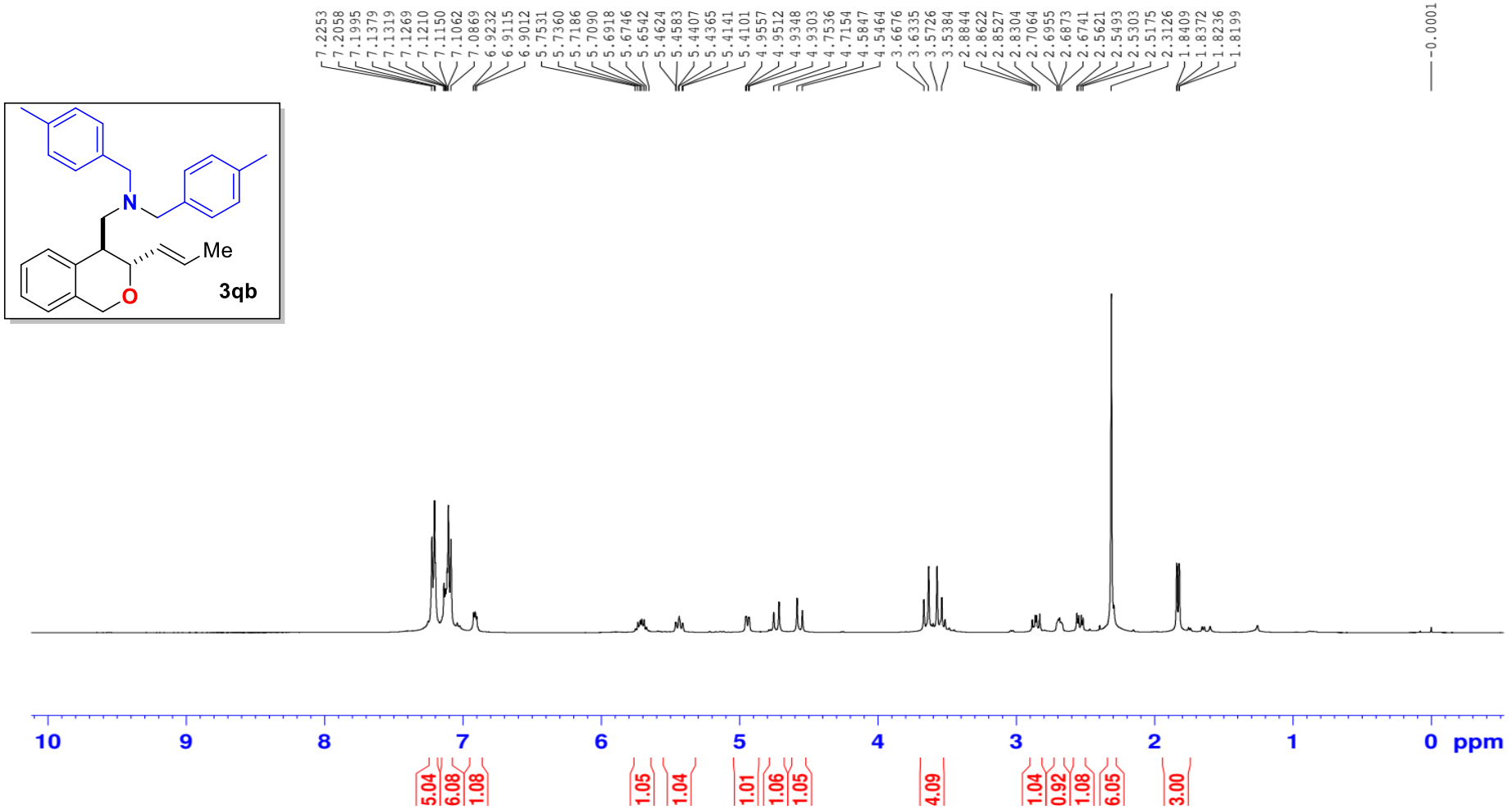
hy-P-**3pb** ^{1}H NMR (500MHz $CDCl_3$)



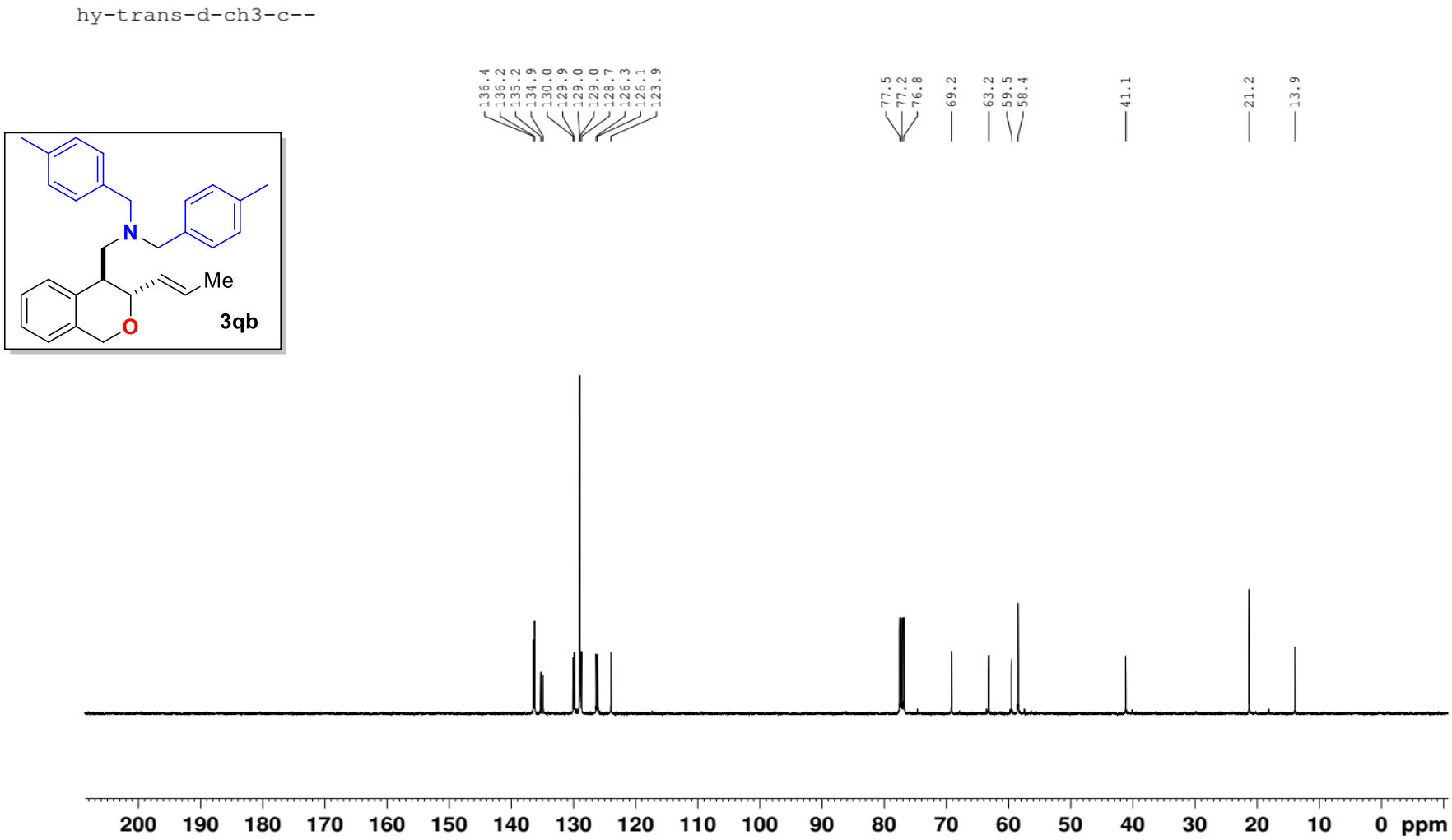
hy-P-**3pb** ^{13}C NMR (125MHz $CDCl_3$)



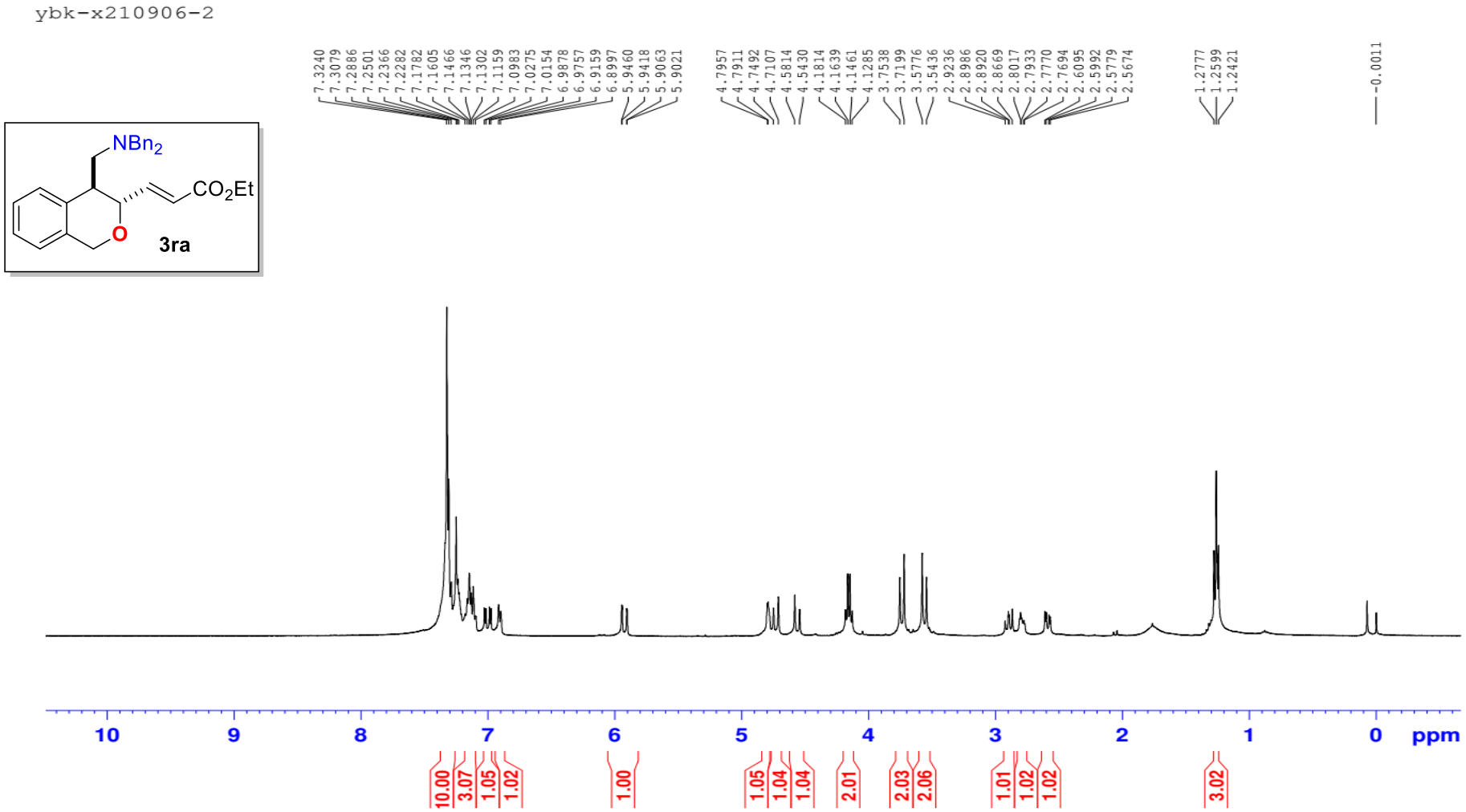
hy-P-**3qb** ^{1}H NMR (400MHz $CDCl_3$)



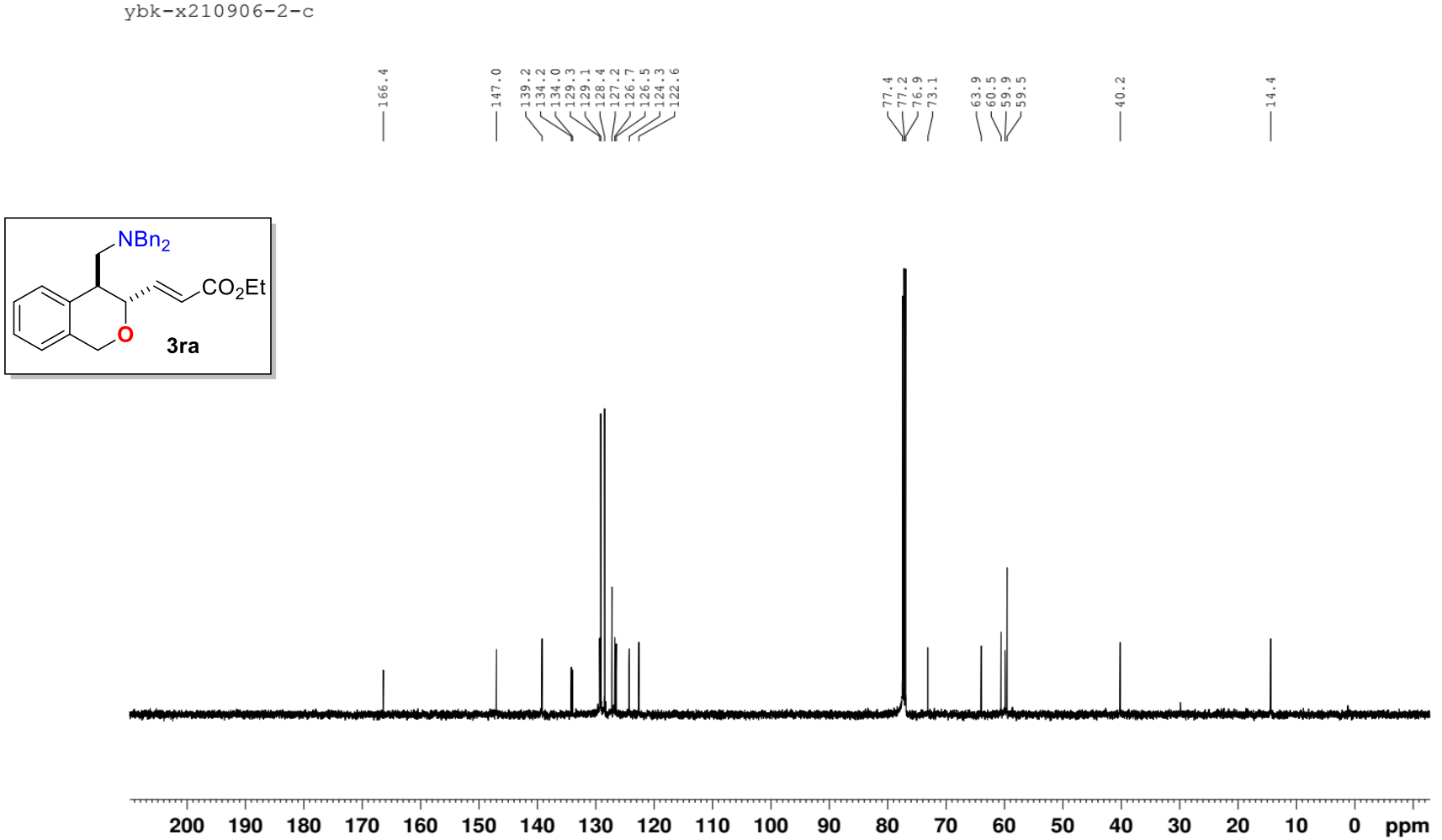
hy-P-**3qb** ^{13}C NMR (100MHz $CDCl_3$)



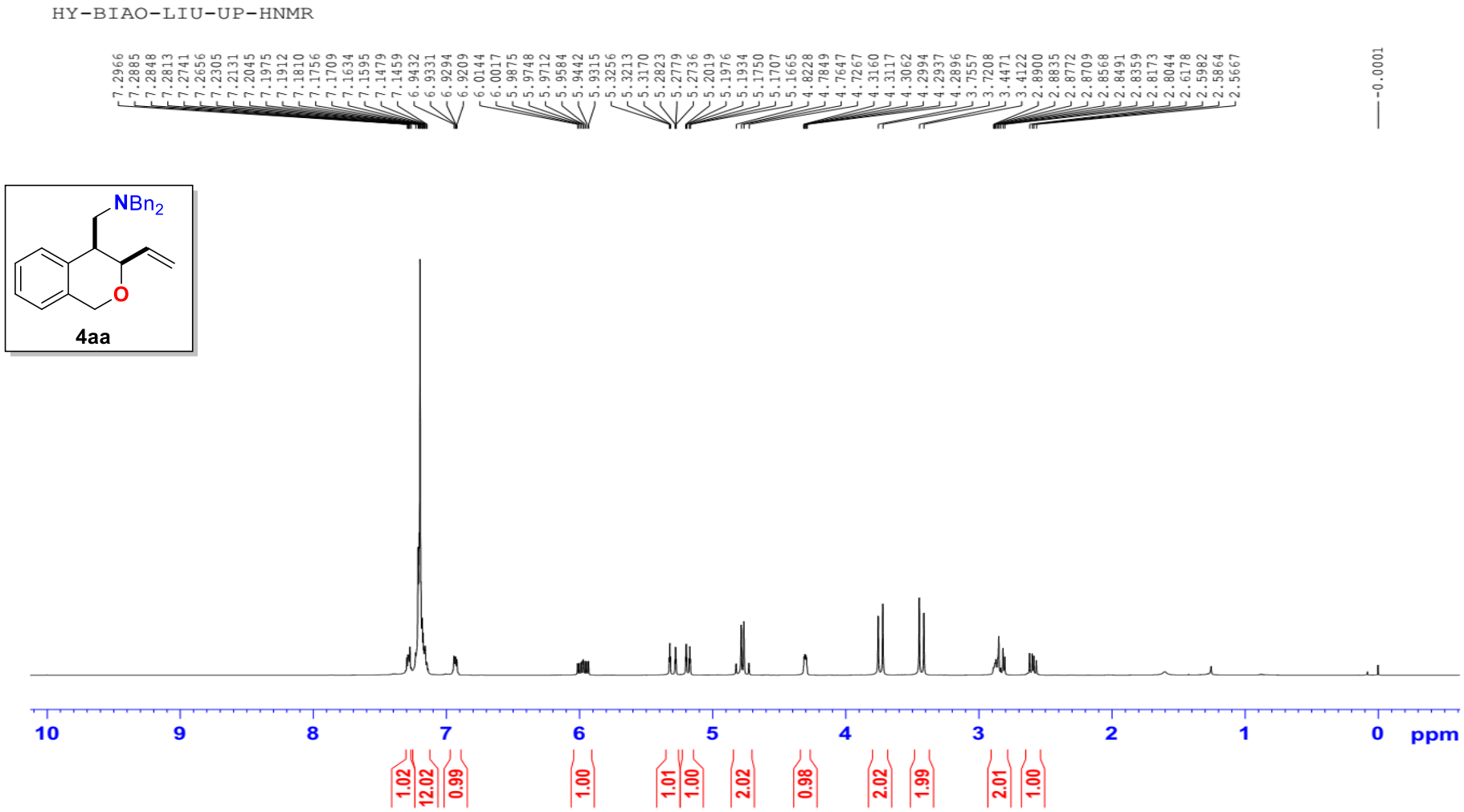
hy-P-**3ra** ^{1}H NMR (400MHz $CDCl_3$)



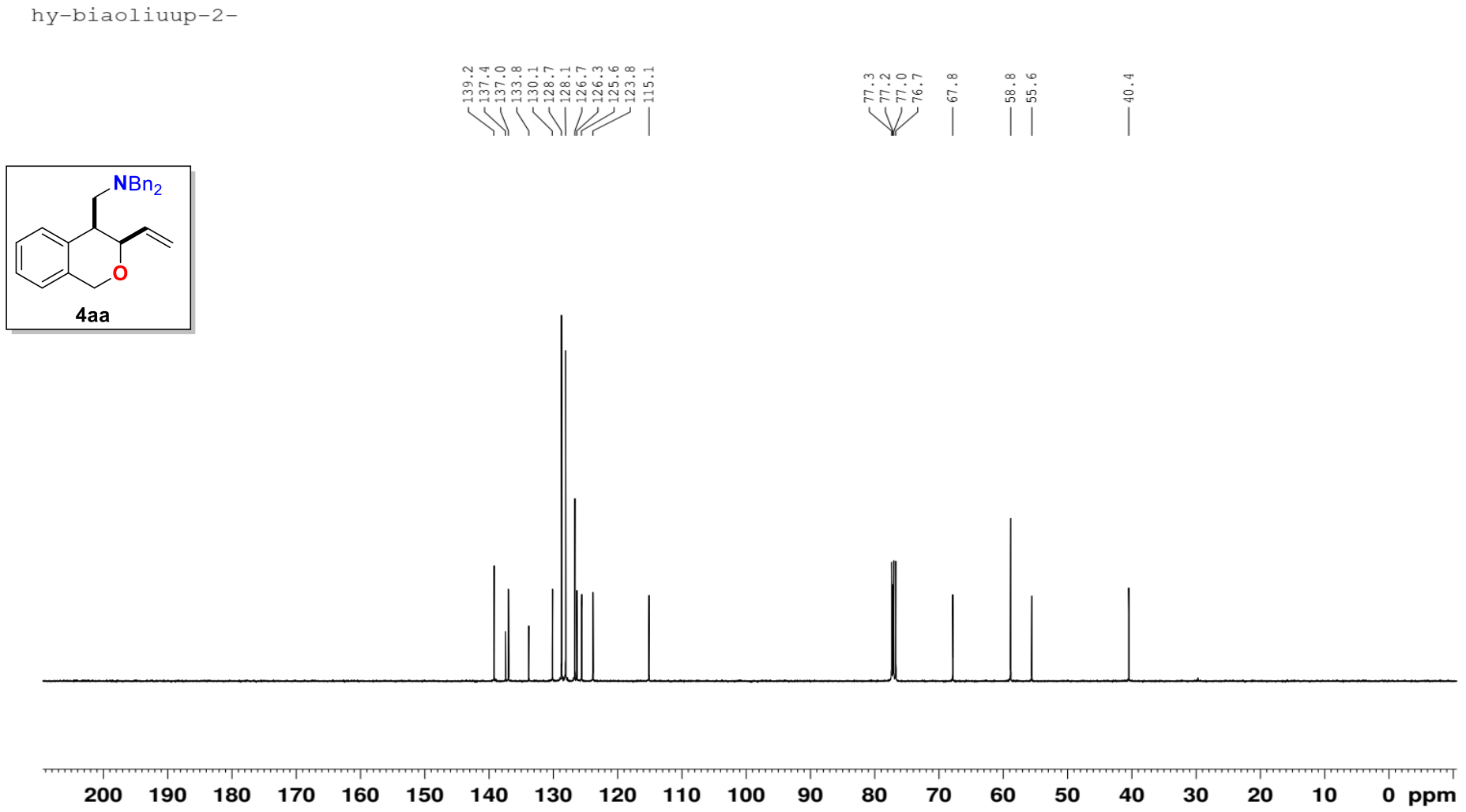
hy-P-**3ra** ^{13}C NMR (125MHz $CDCl_3$)



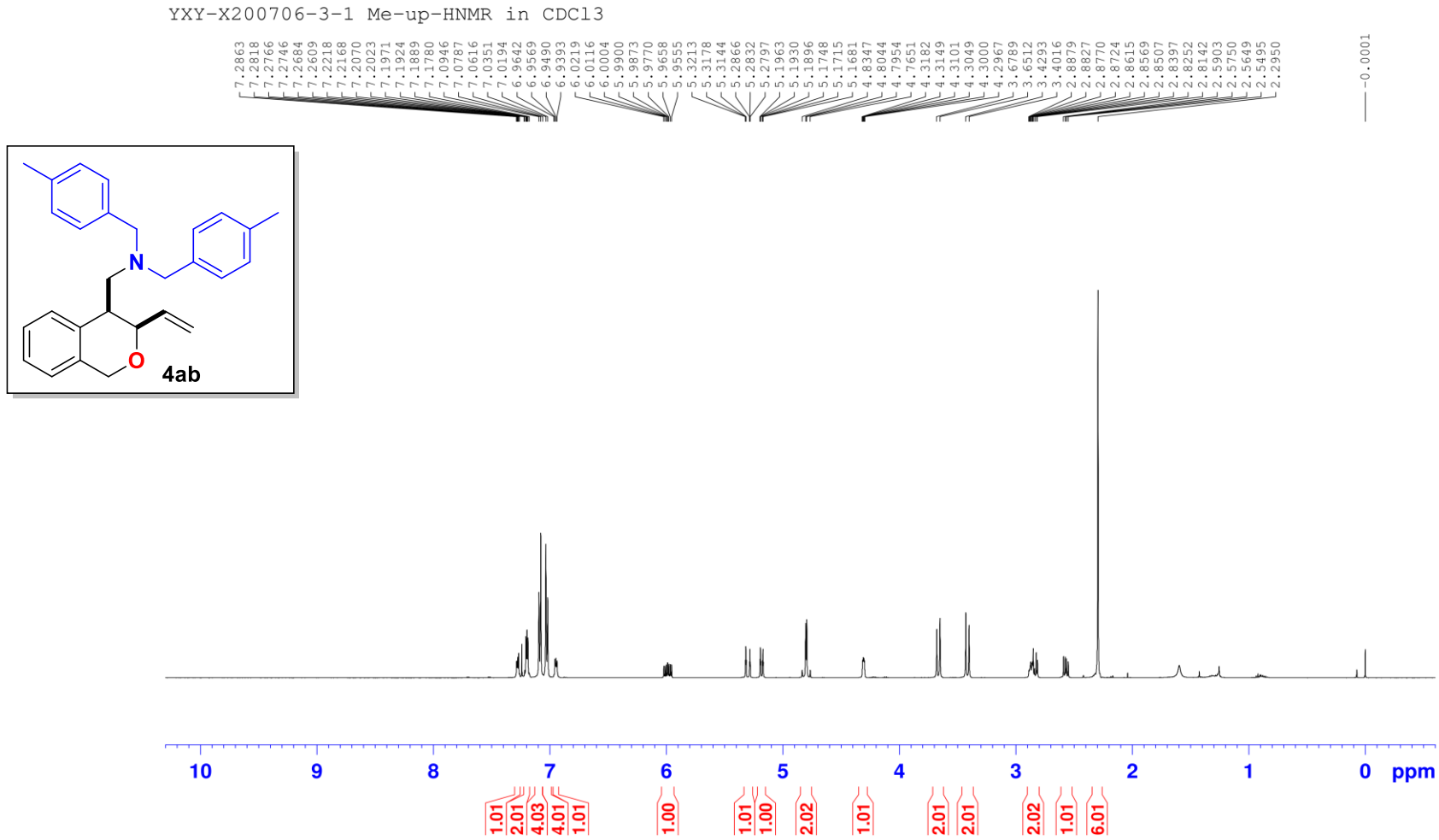
hy-P-**4aa** ^{1}H NMR (400MHz $CDCl_3$)



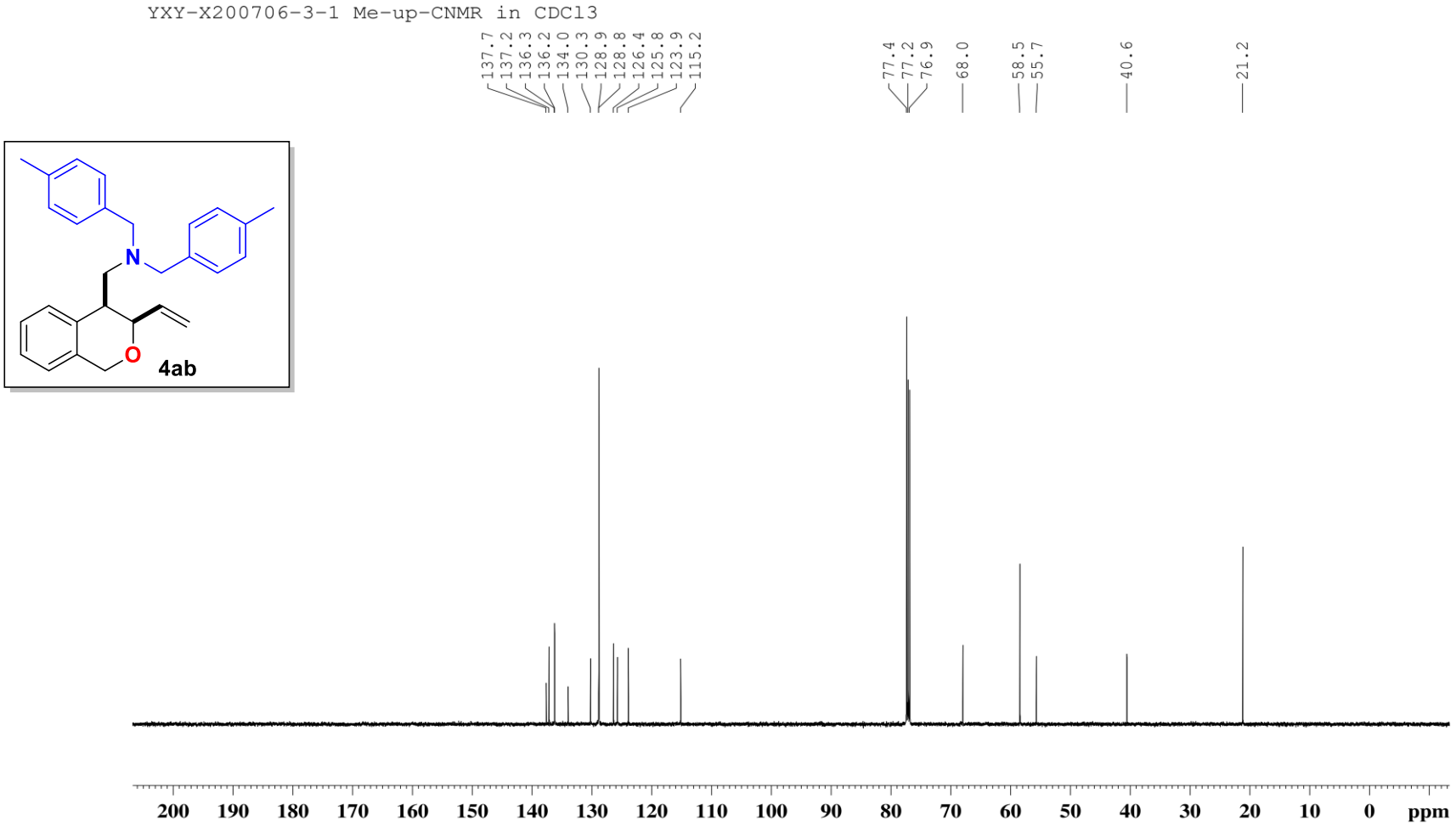
hy-P-**4aa** ^{13}C NMR (100MHz $CDCl_3$)



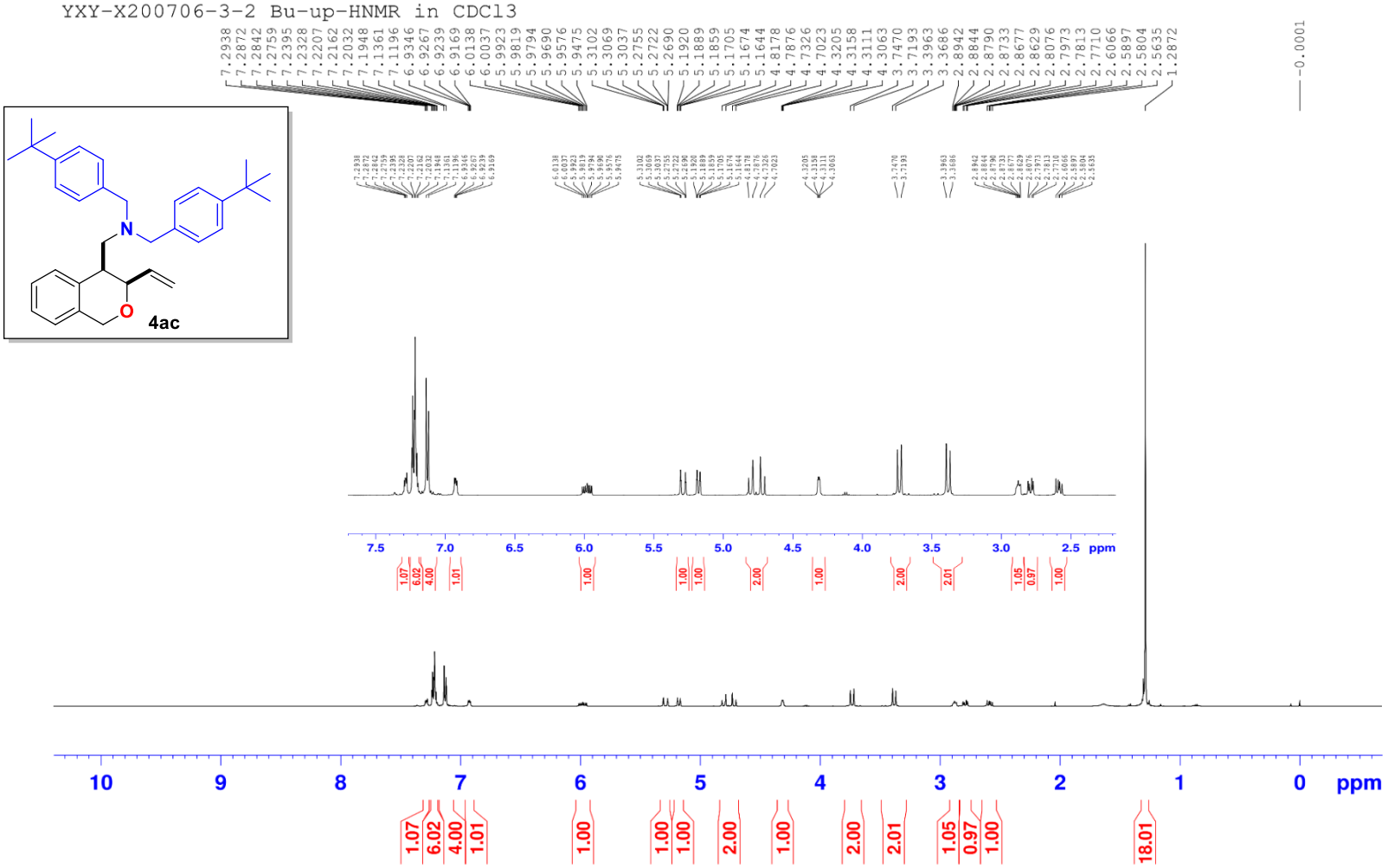
hy-P-**4ab** ^{1}H NMR (400MHz $CDCl_3$)



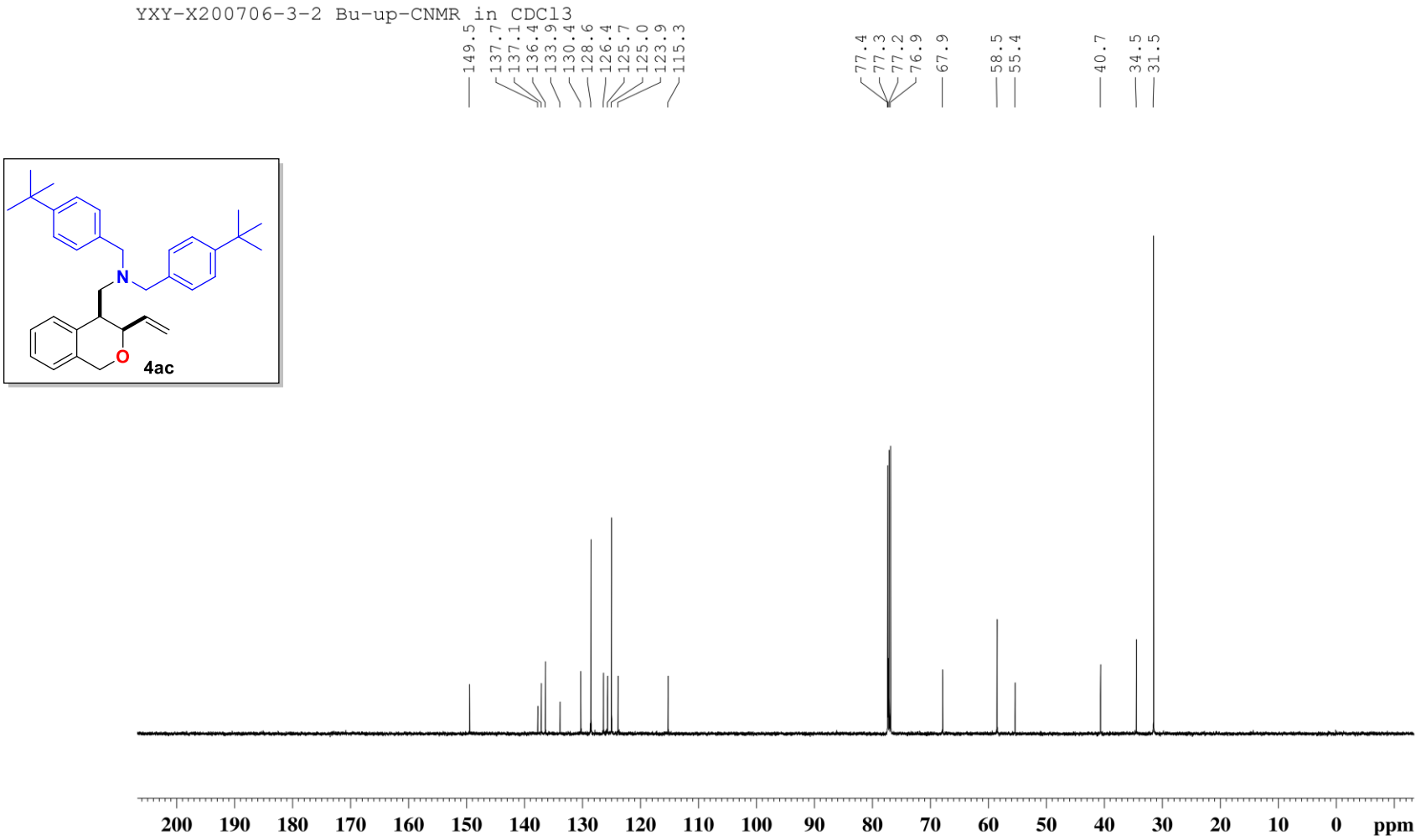
hy-P-**4ab** ^{13}C NMR (100MHz $CDCl_3$)



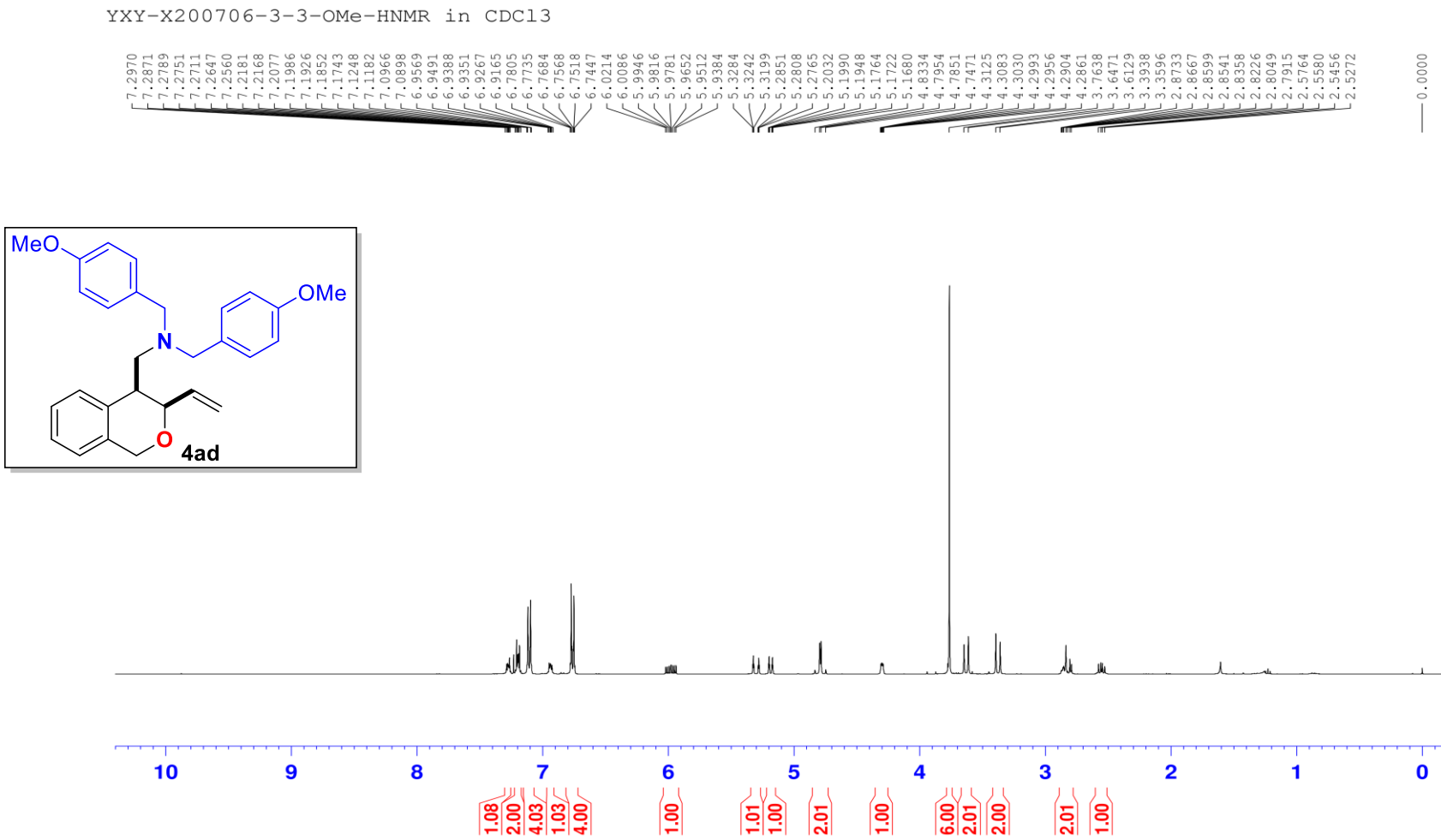
hy-P-**4ac** ^{1}H NMR (500MHz $CDCl_3$)



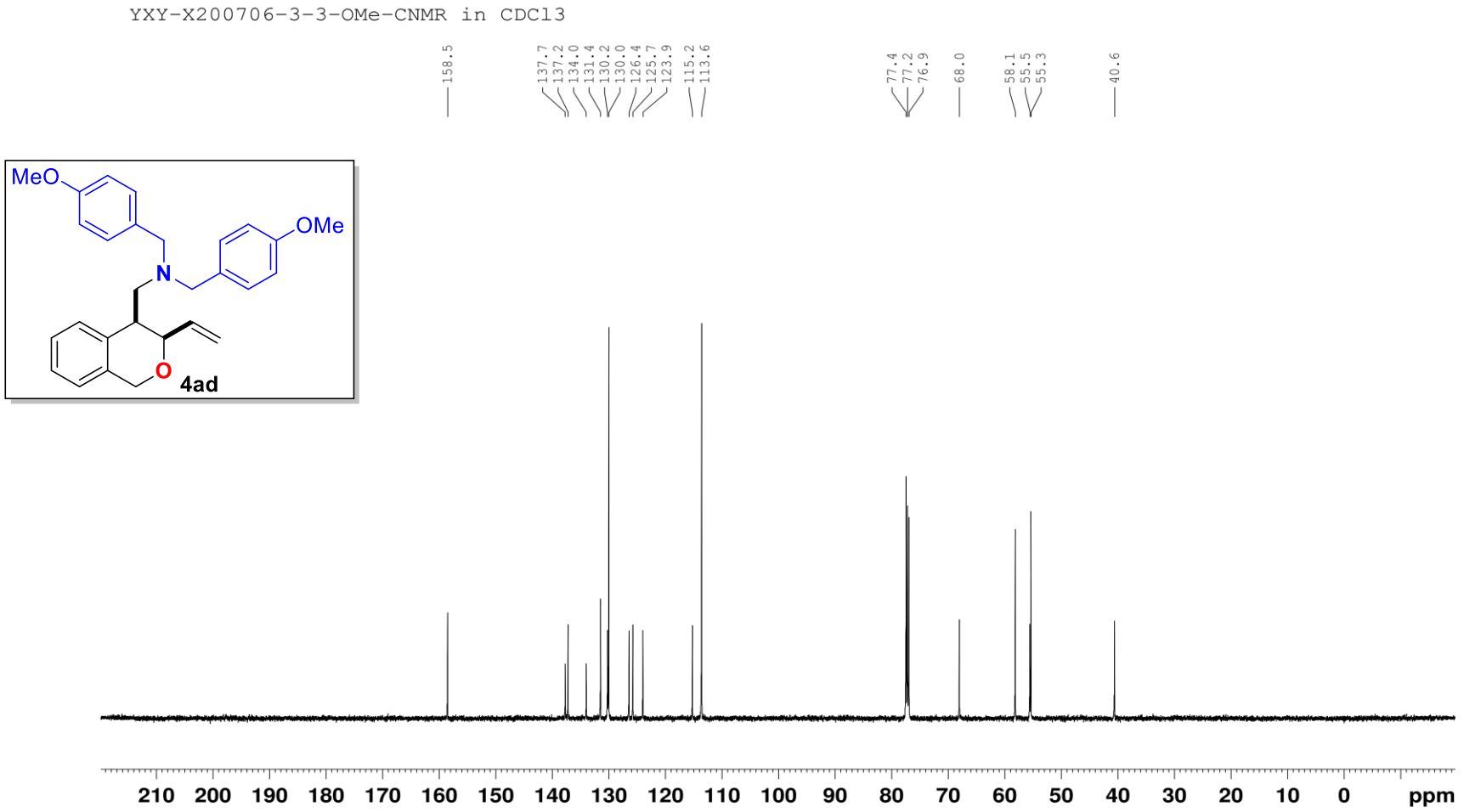
hy-P-**4ac** ^{13}C NMR (125MHz $CDCl_3$)



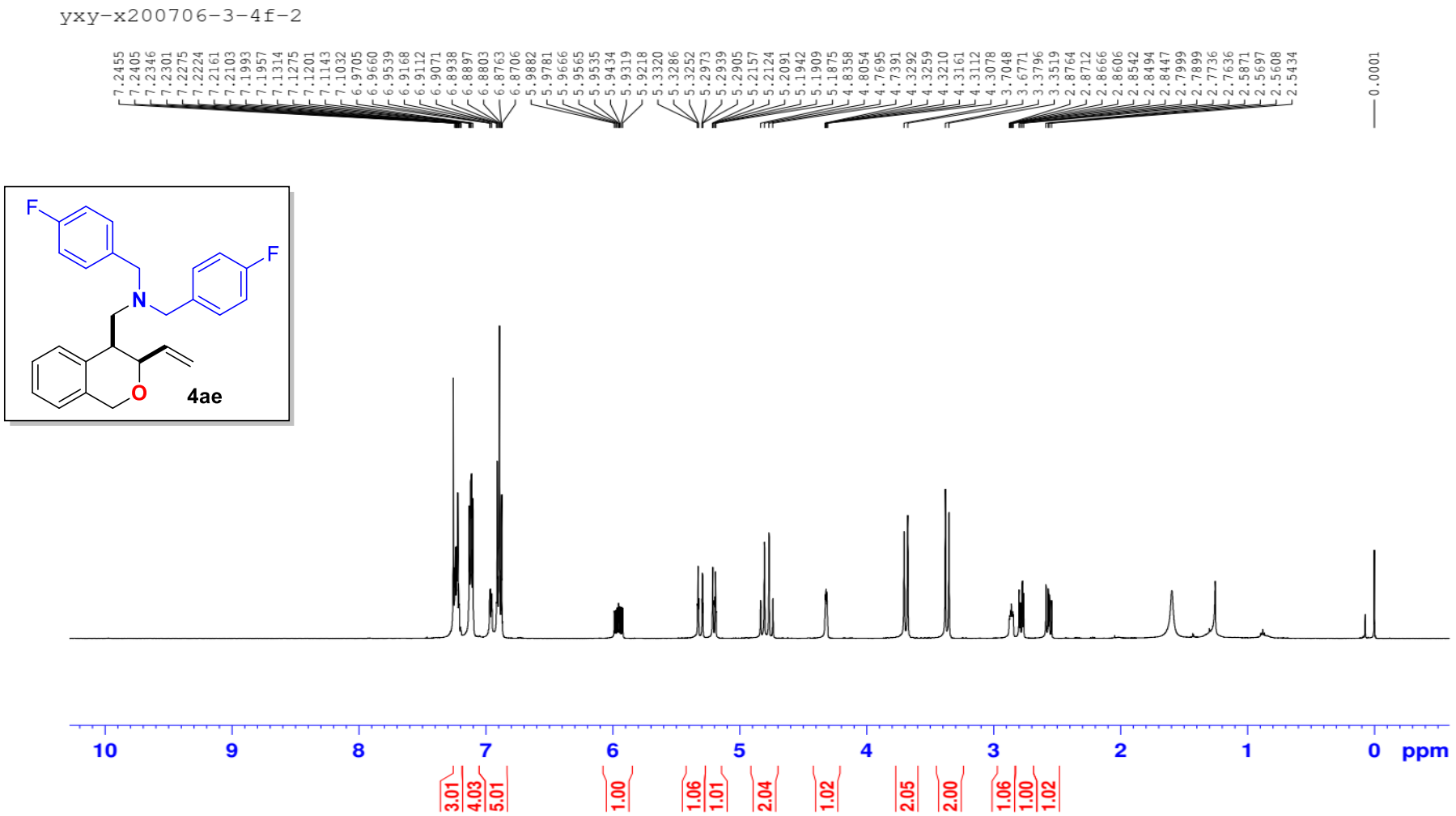
hy-P-**4ad** ^{1}H NMR (400MHz $CDCl_3$)



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

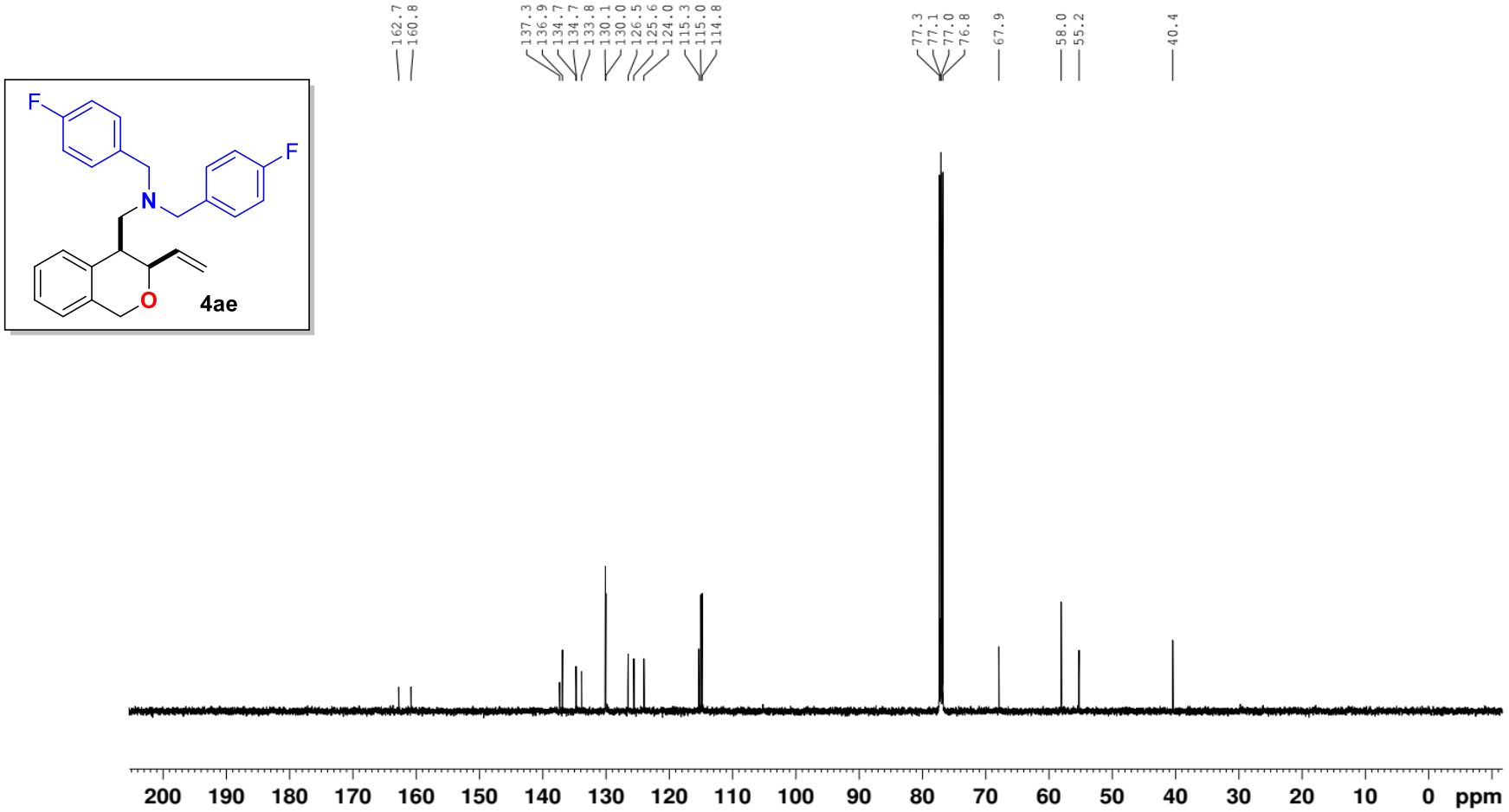


hy-P-**4ae** ^{1}H NMR (500MHz $CDCl_3$)

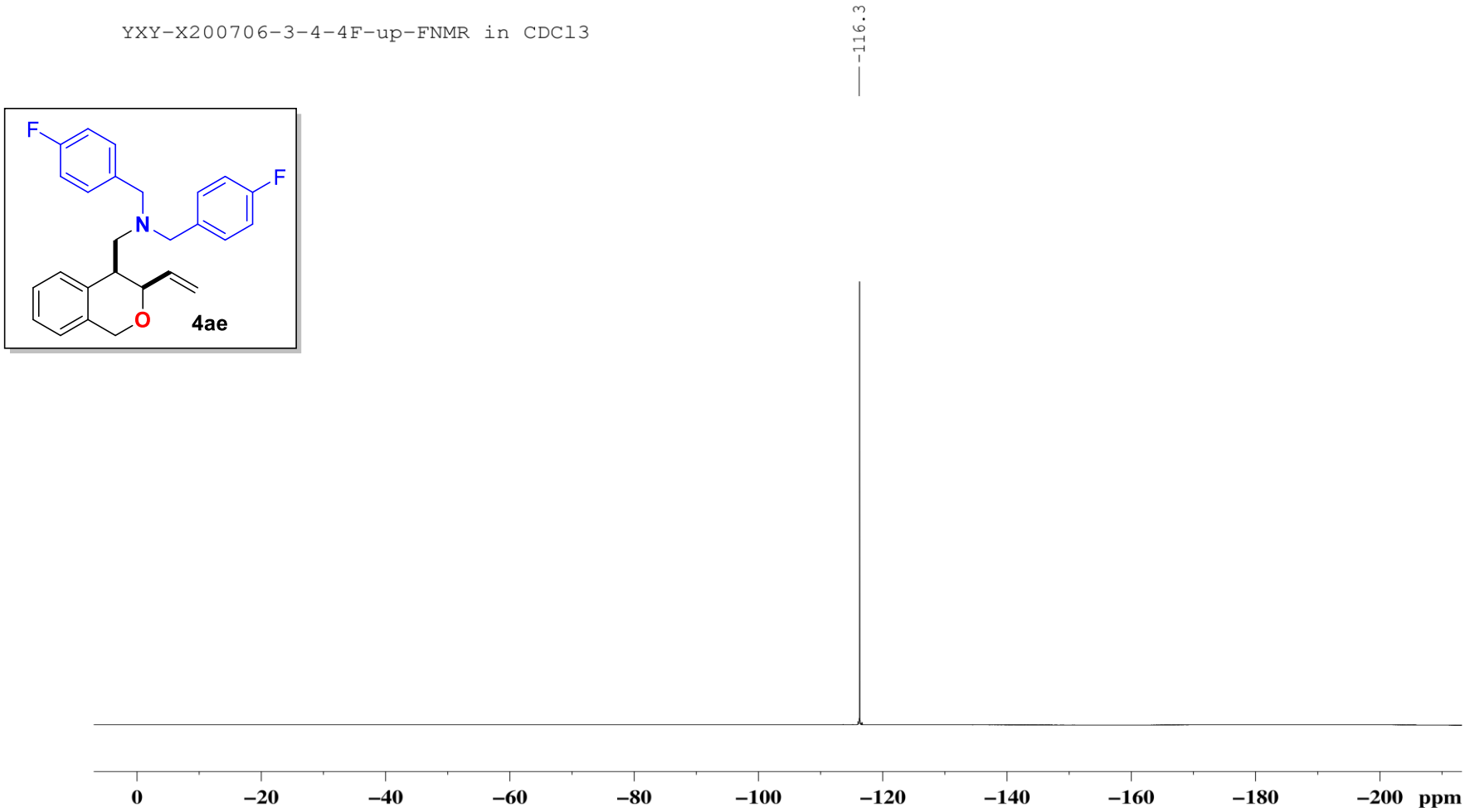


hy-P-**4ae** ^{13}C NMR (125MHz $CDCl_3$)

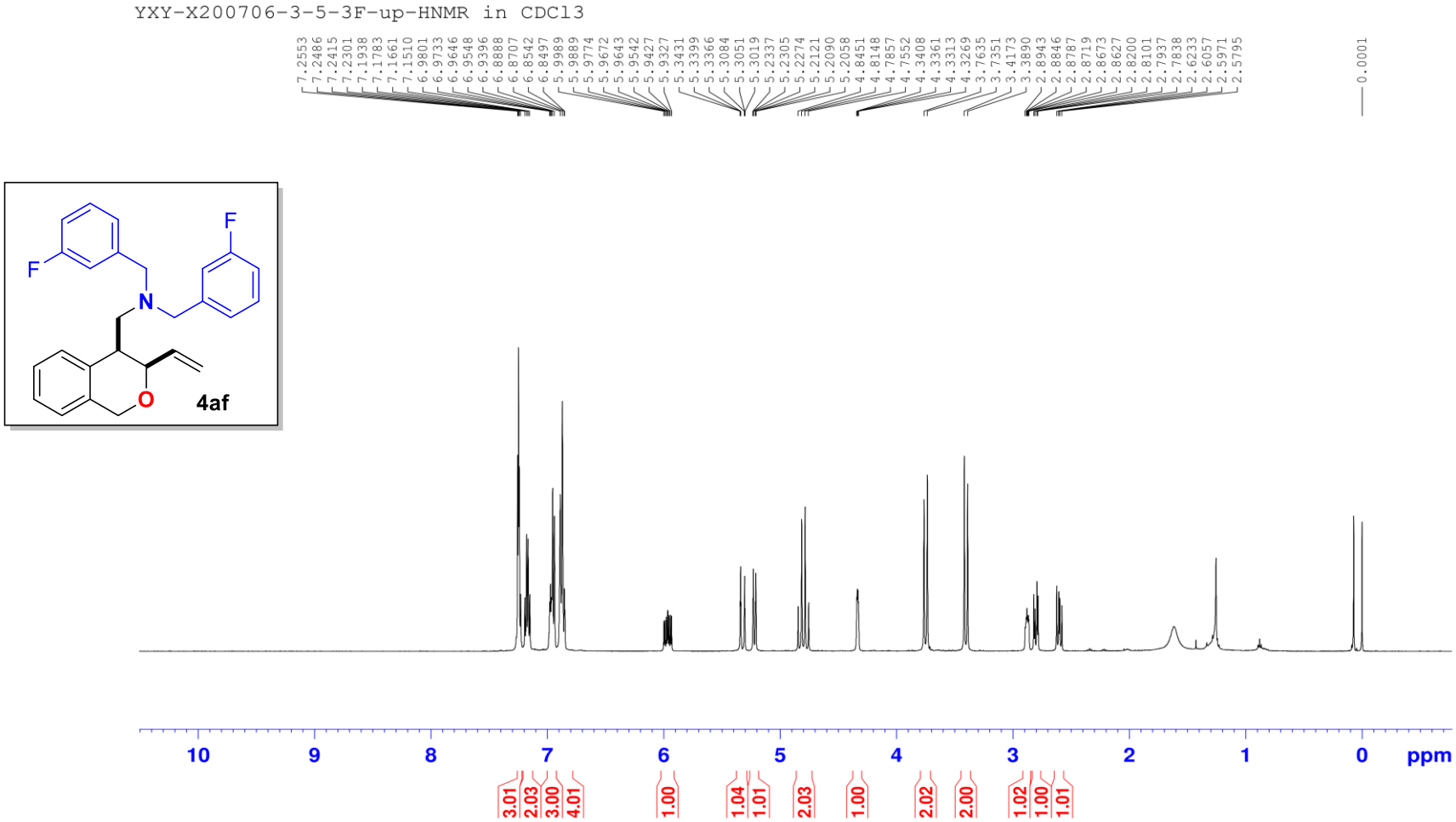
yxy-x200706-3-4f-2-c



hy-P-**4ae** ^{19}F NMR (376MHz $CDCl_3$)

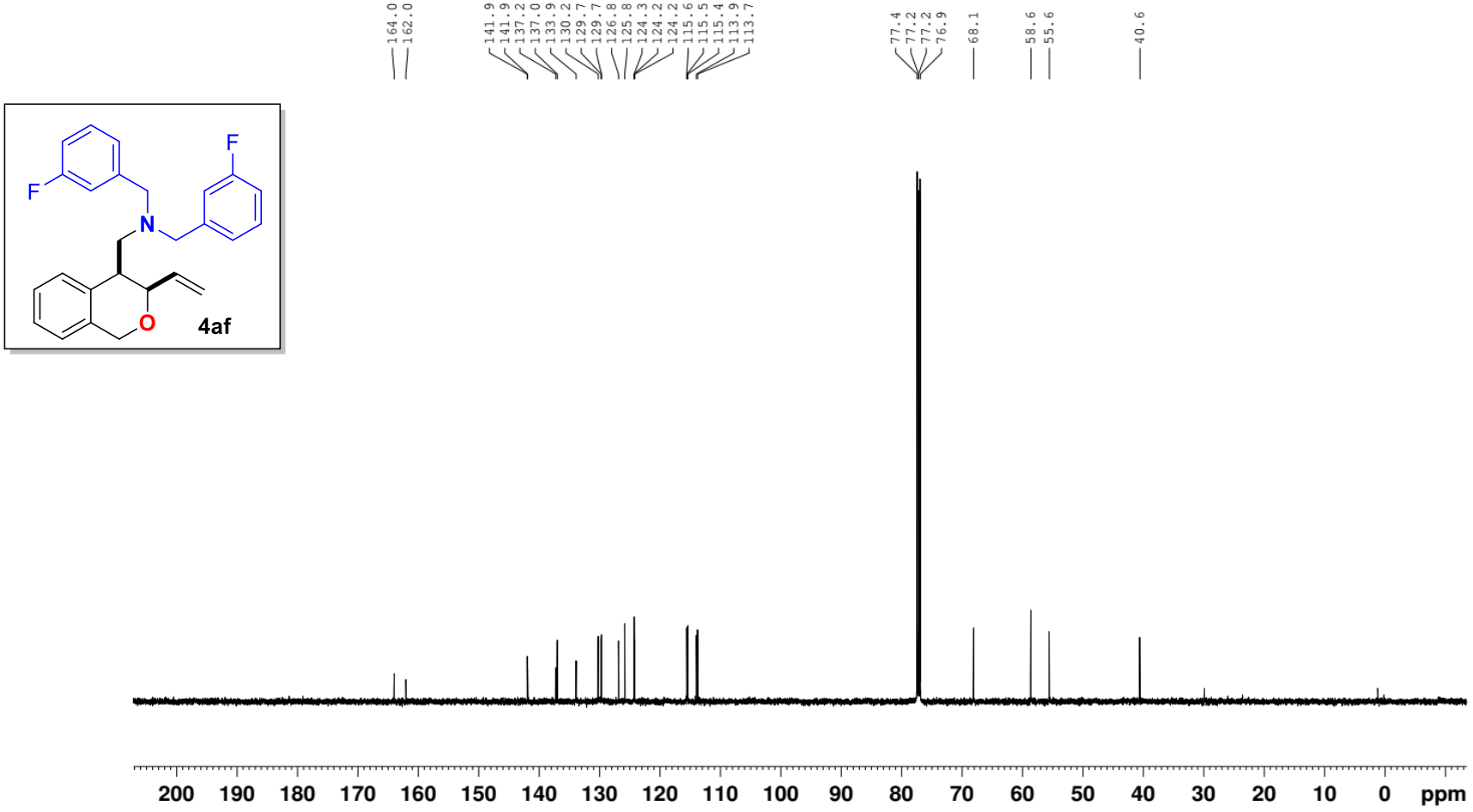


hy-P-**4af** ^{1}H NMR (500MHz $CDCl_3$)

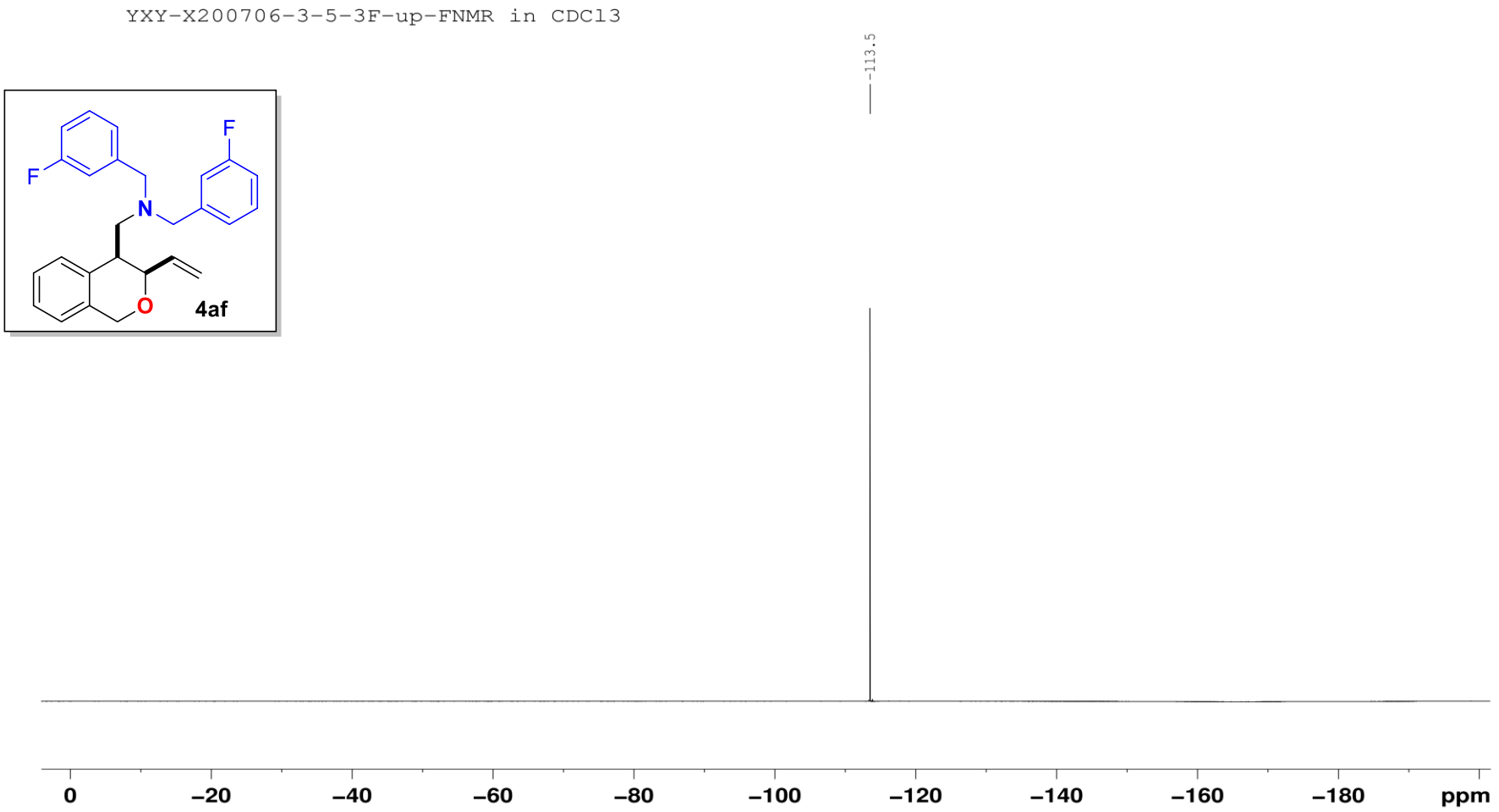


hy-P-**4af** ^{13}C NMR (125MHz $CDCl_3$)

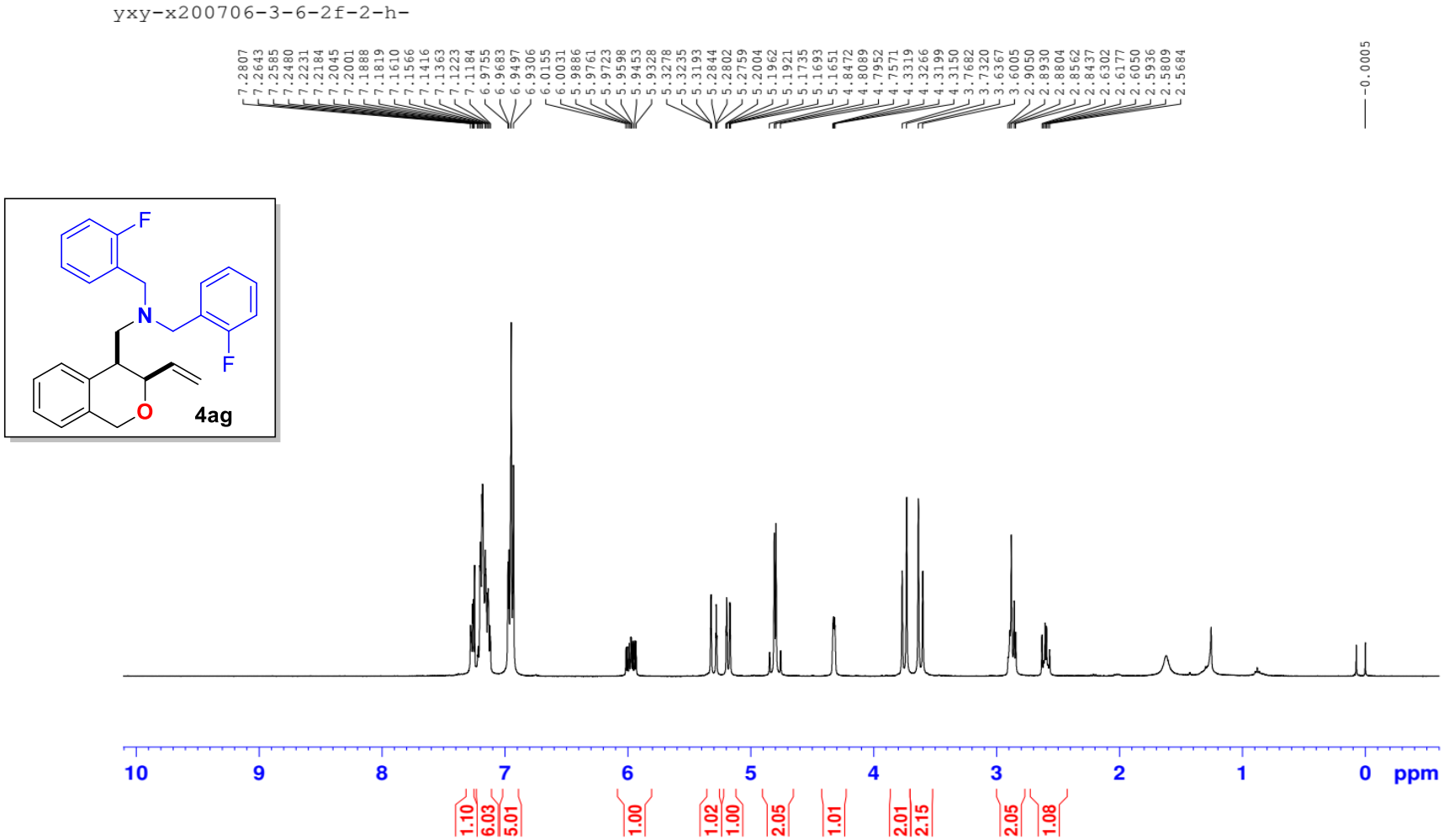
yxy-x200706-3-5-3f-up-c-



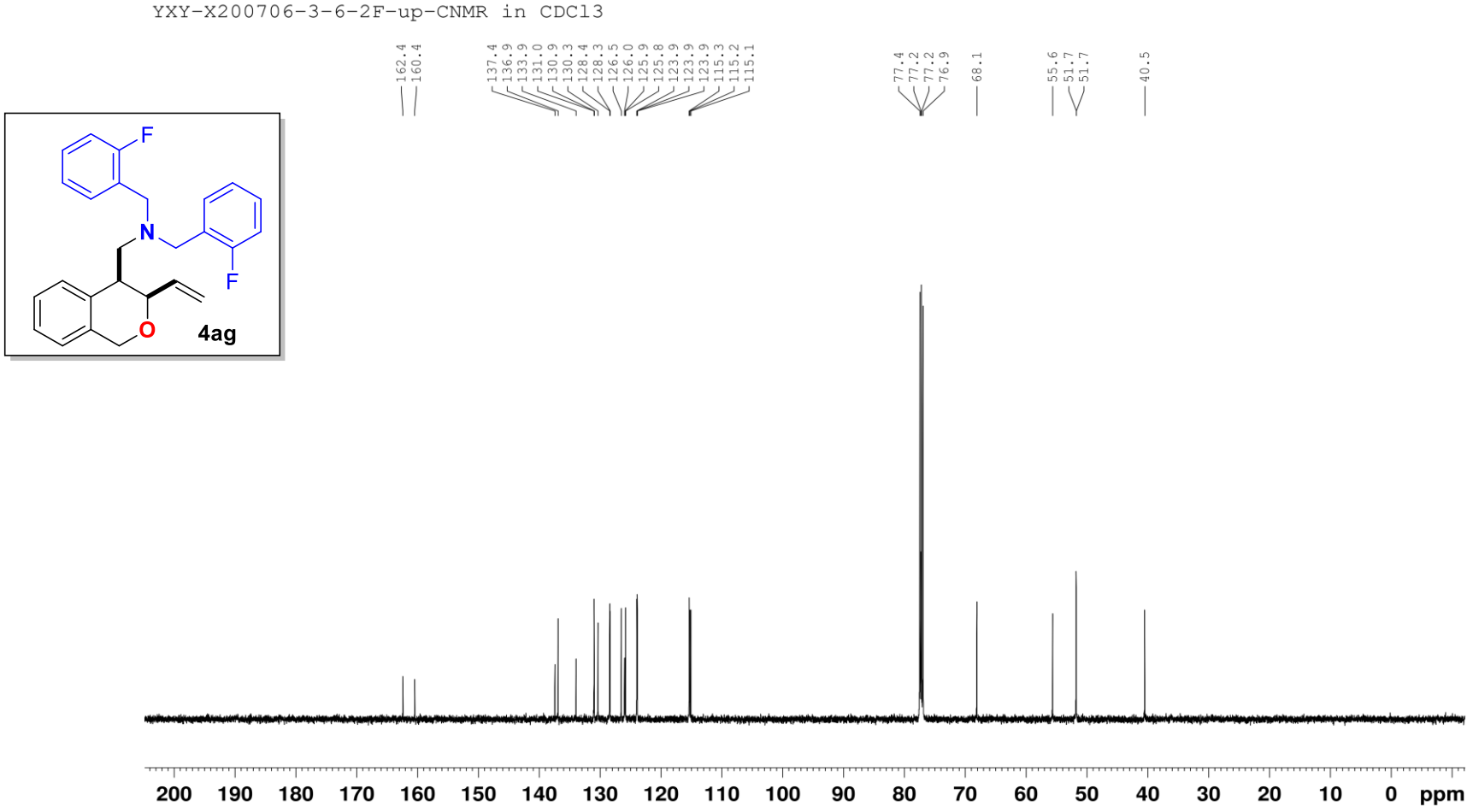
hy-P-**4af** ^{19}F NMR (470MHz $CDCl_3$)



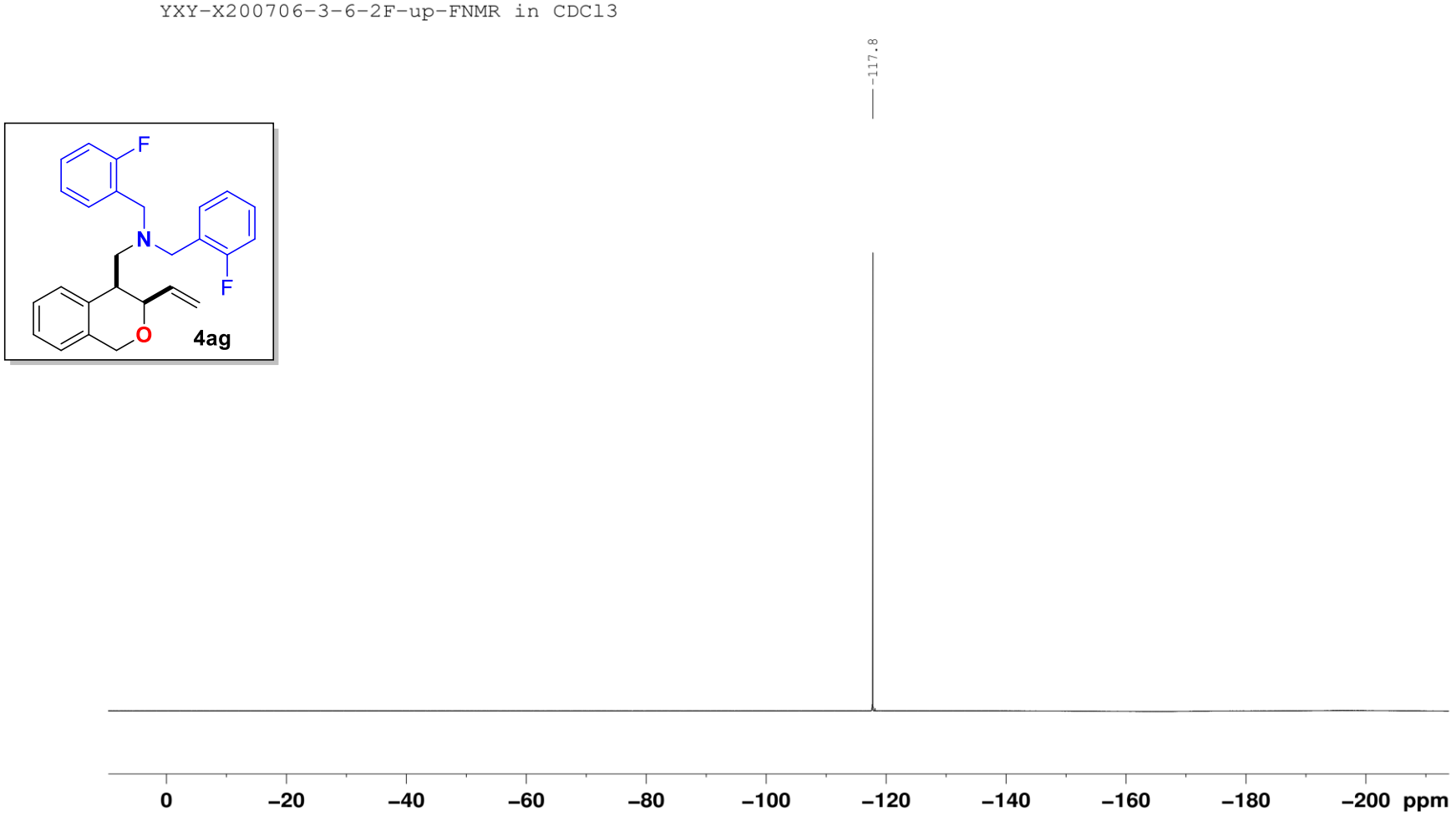
hy-P-**4ag** ^{1}H NMR (400MHz $CDCl_3$)



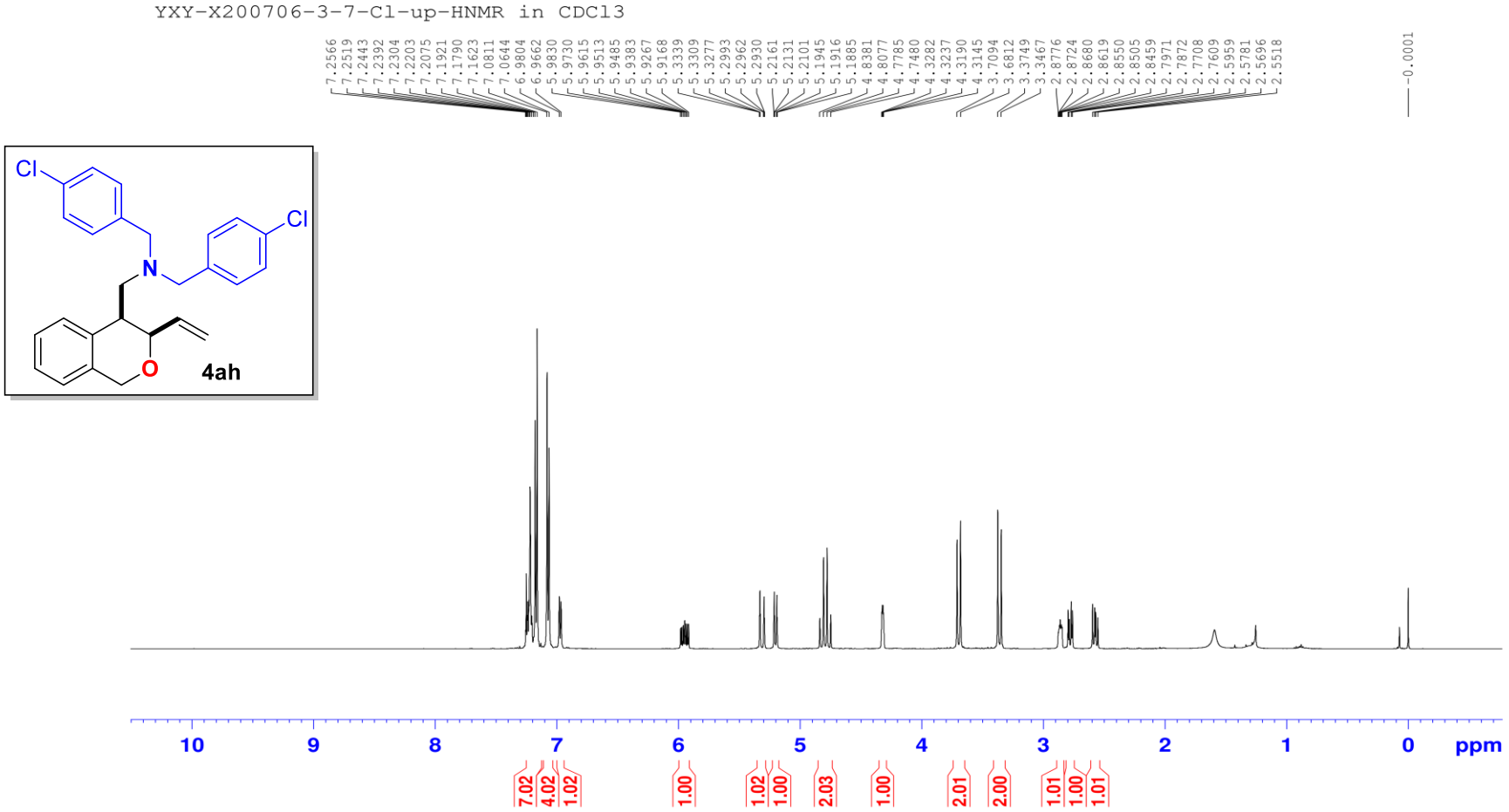
hy-P-**4ag** ^{13}C NMR (125MHz $CDCl_3$)



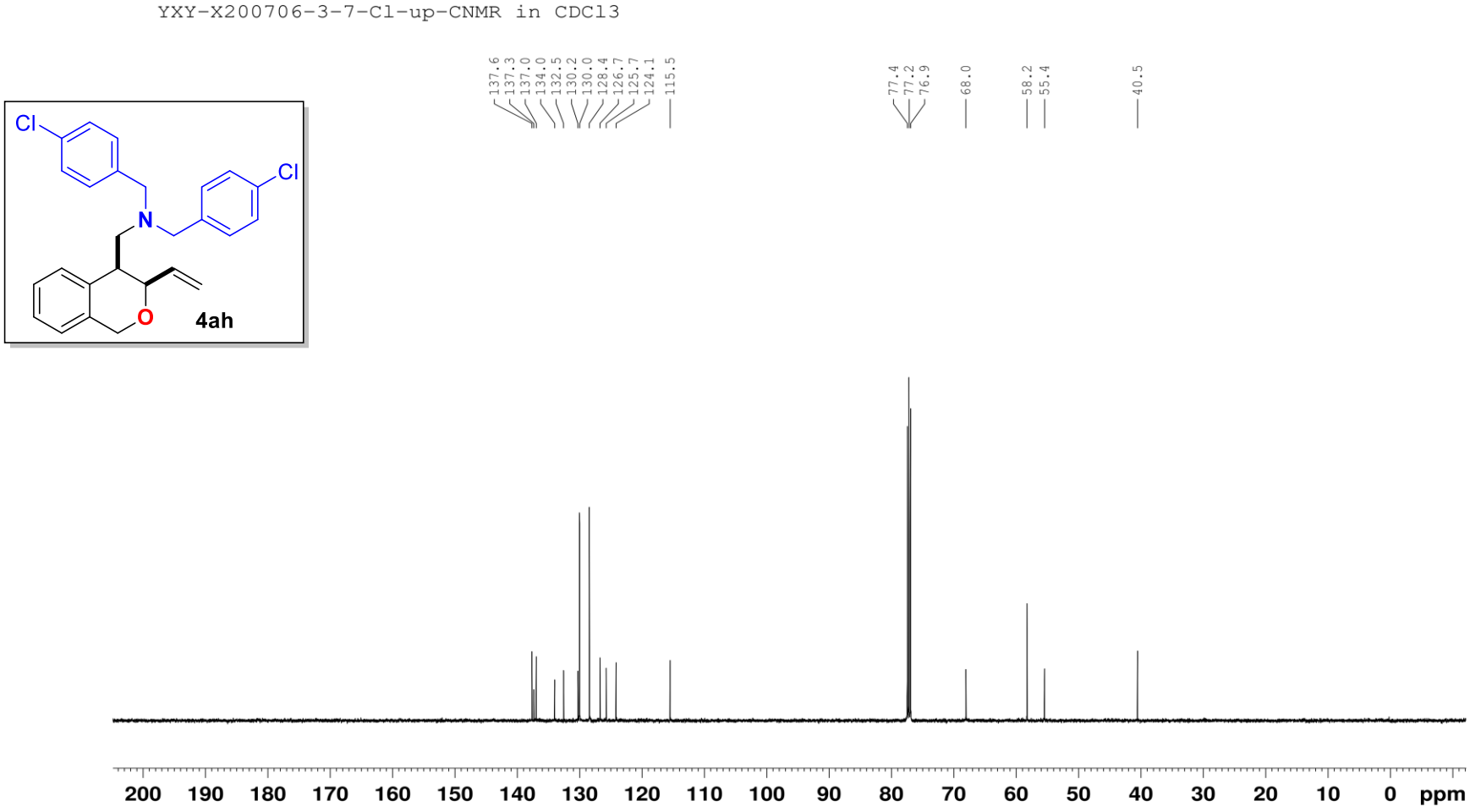
hy-P-**4ag** ^{19}F NMR (470MHz $CDCl_3$)



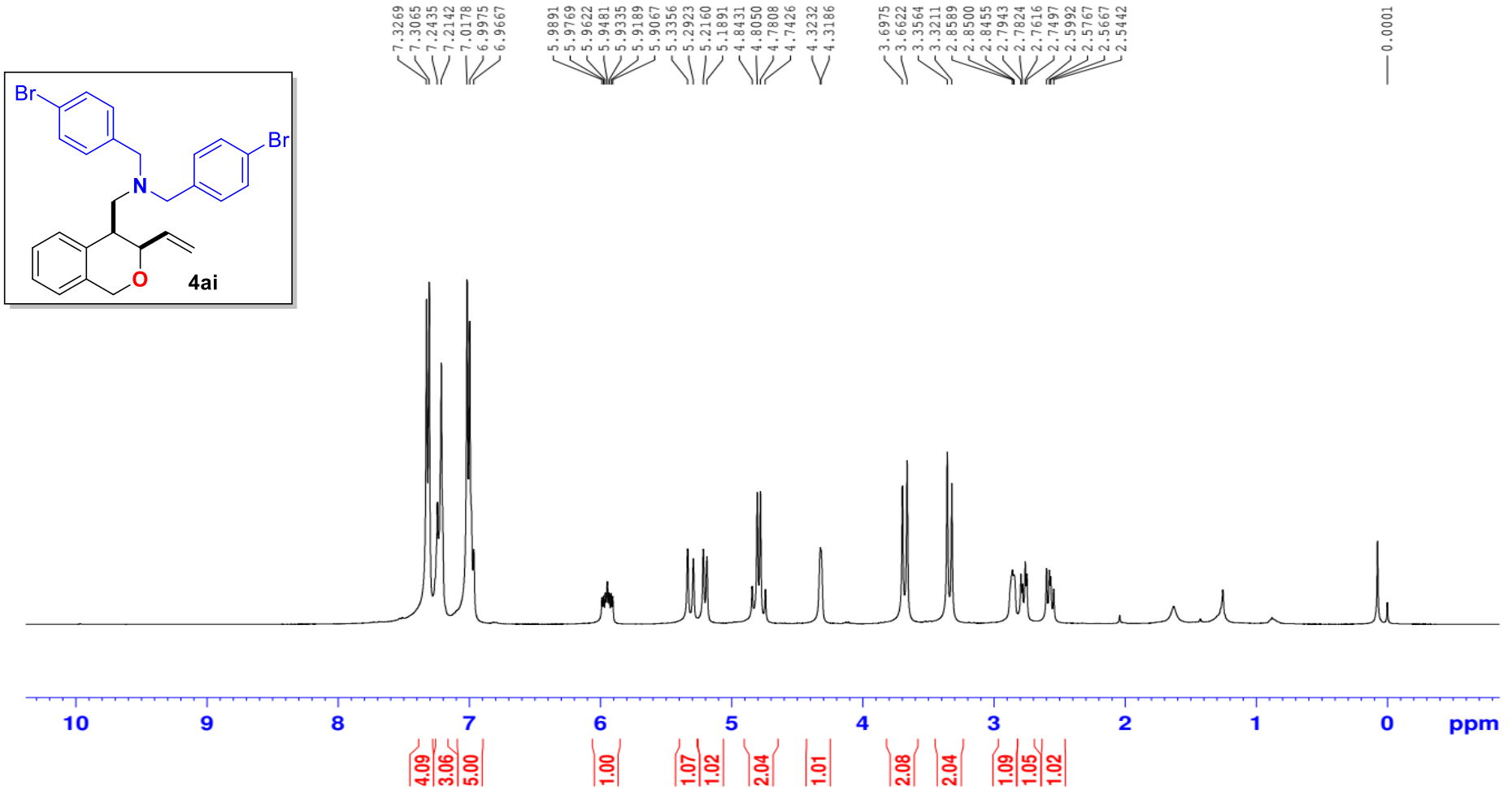
hy-P-**4ah** ^{1}H NMR (500MHz $CDCl_3$)



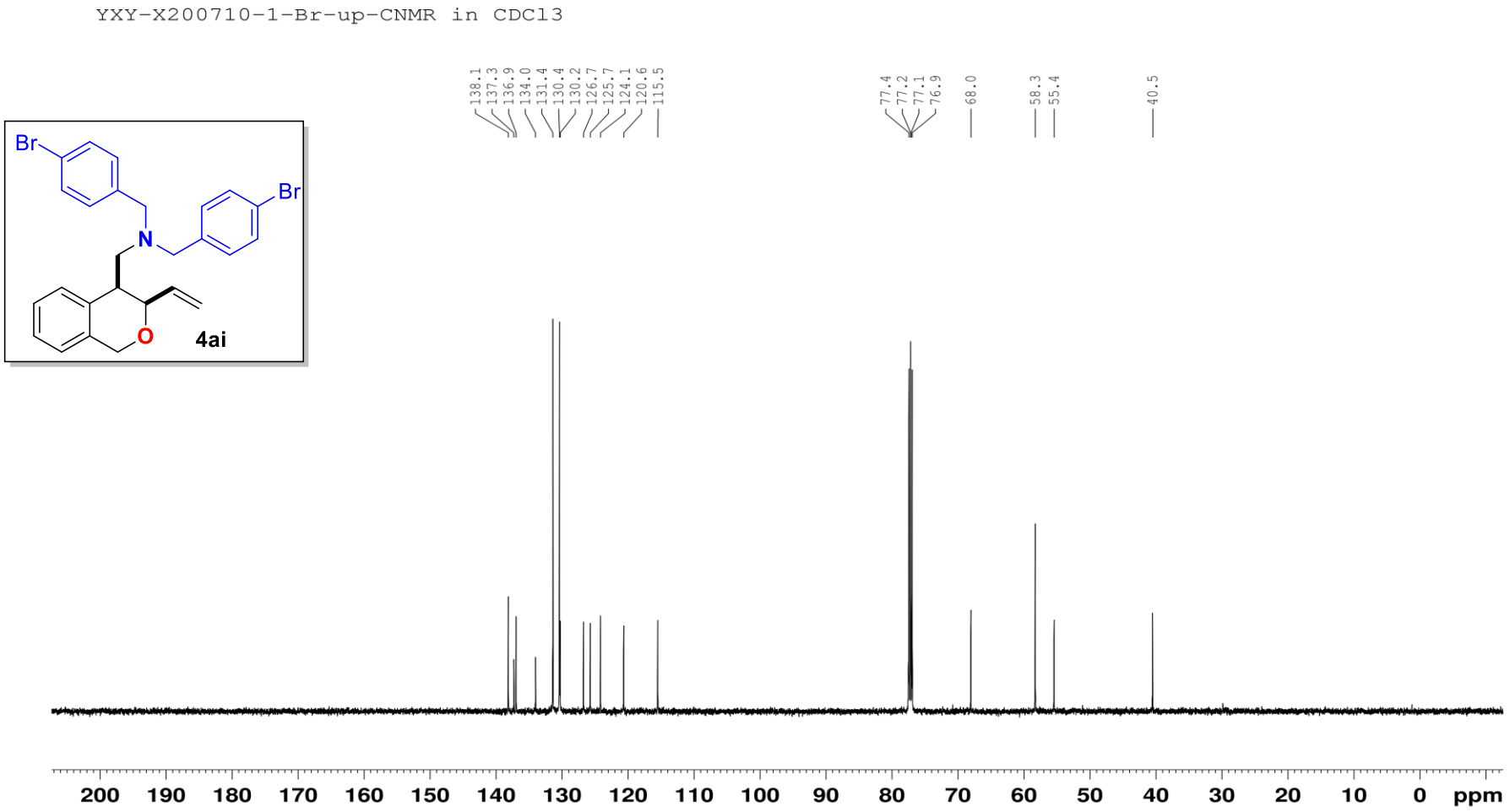
hy-P-**4ah** ^{13}C NMR (125MHz $CDCl_3$)



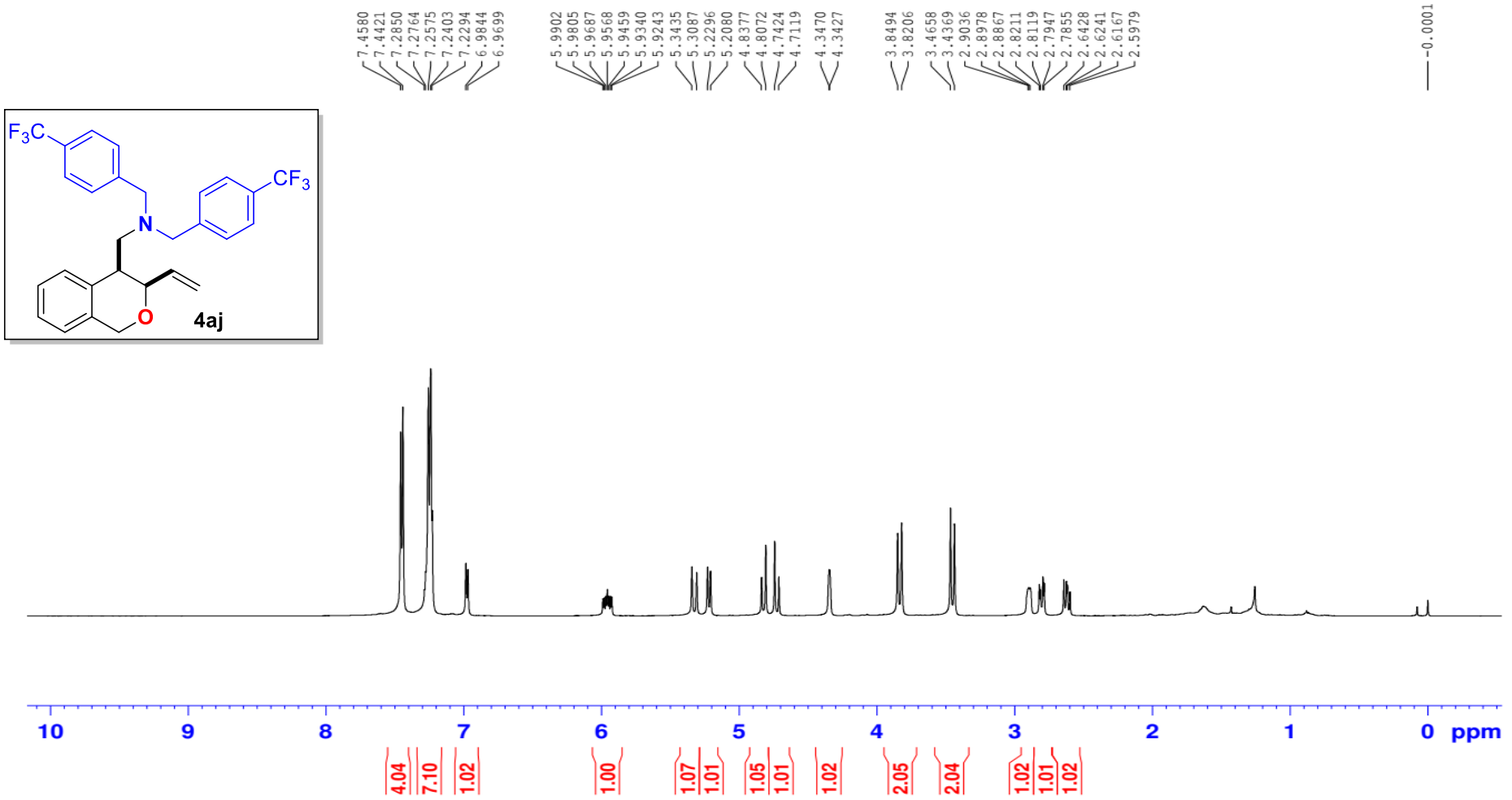
hy-P-**4ai** ^{1}H NMR (400MHz $CDCl_3$)



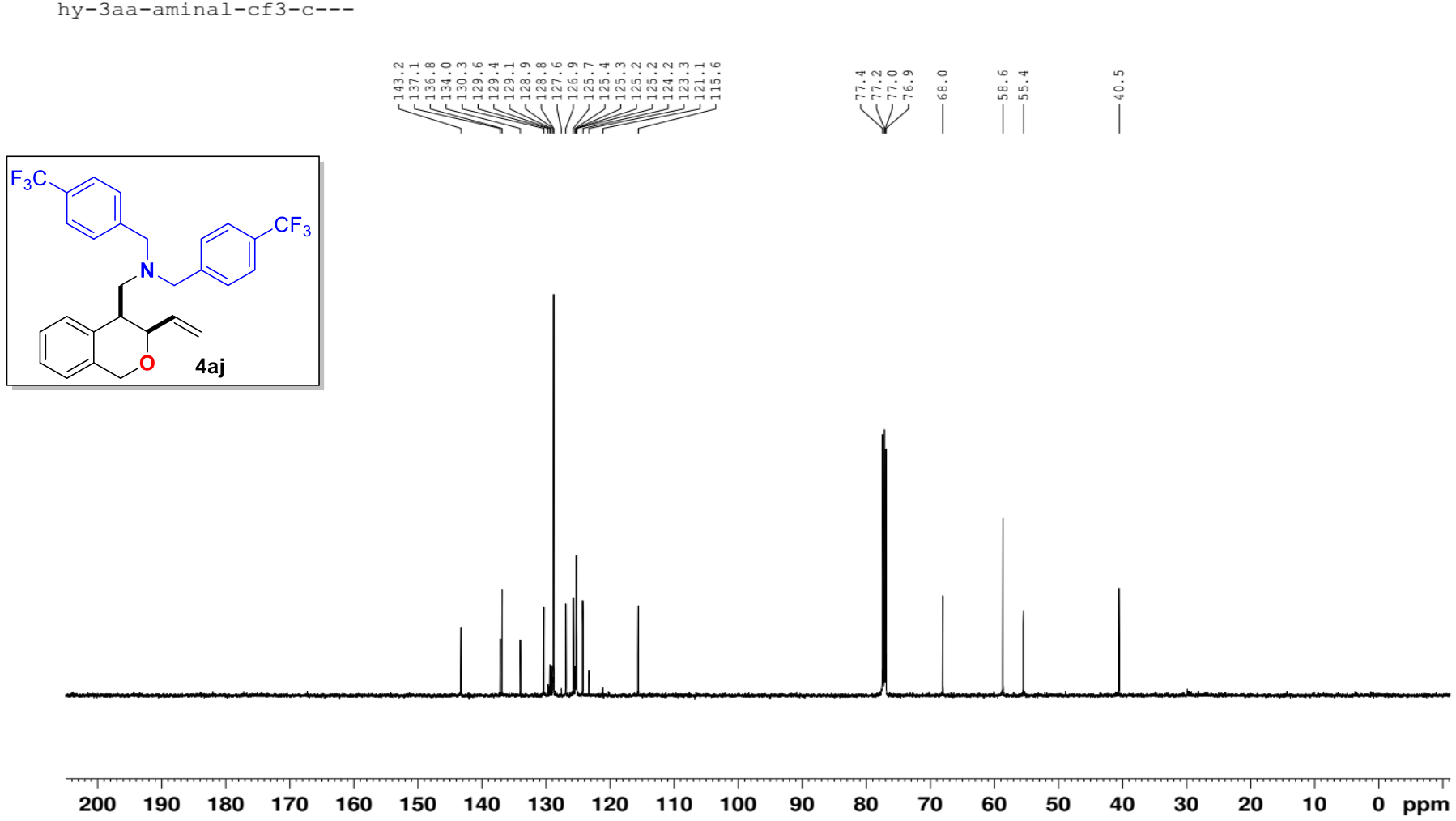
hy-P-**4ai** ^{13}C NMR (100MHz $CDCl_3$)



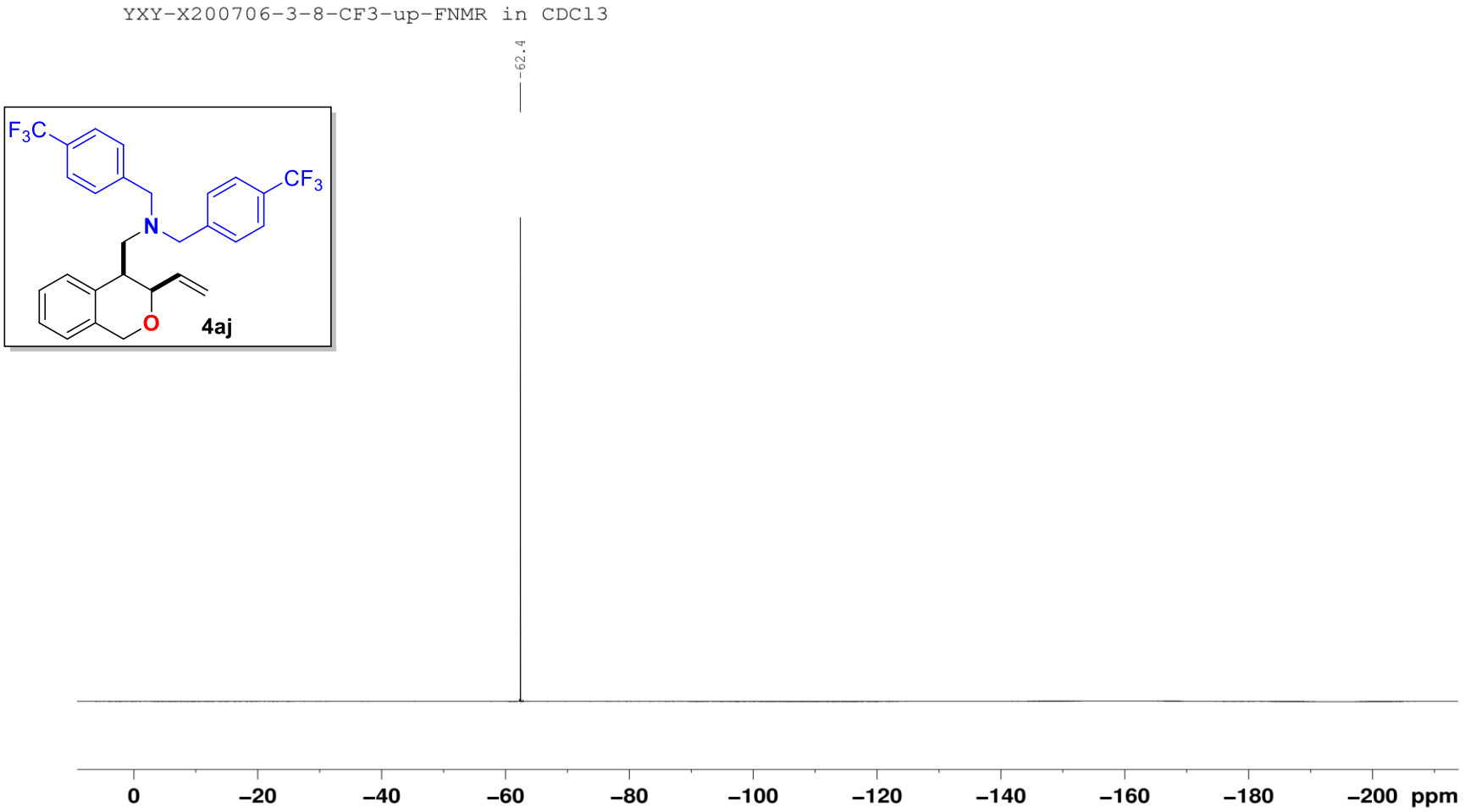
hy-P-**4aj** ^{1}H NMR (500MHz $CDCl_3$)



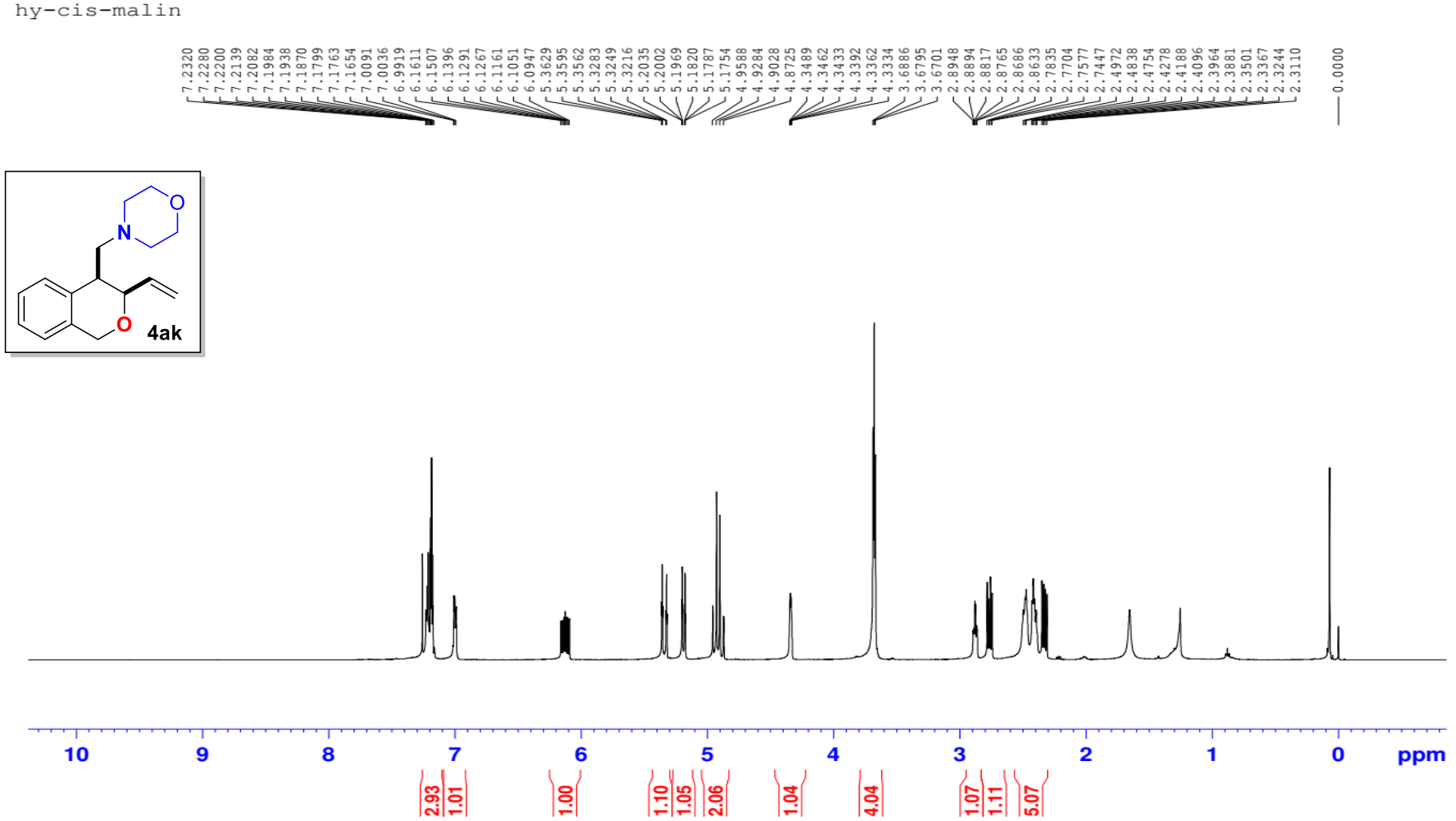
hy-P-**4aj** ^{13}C NMR (125MHz $CDCl_3$)



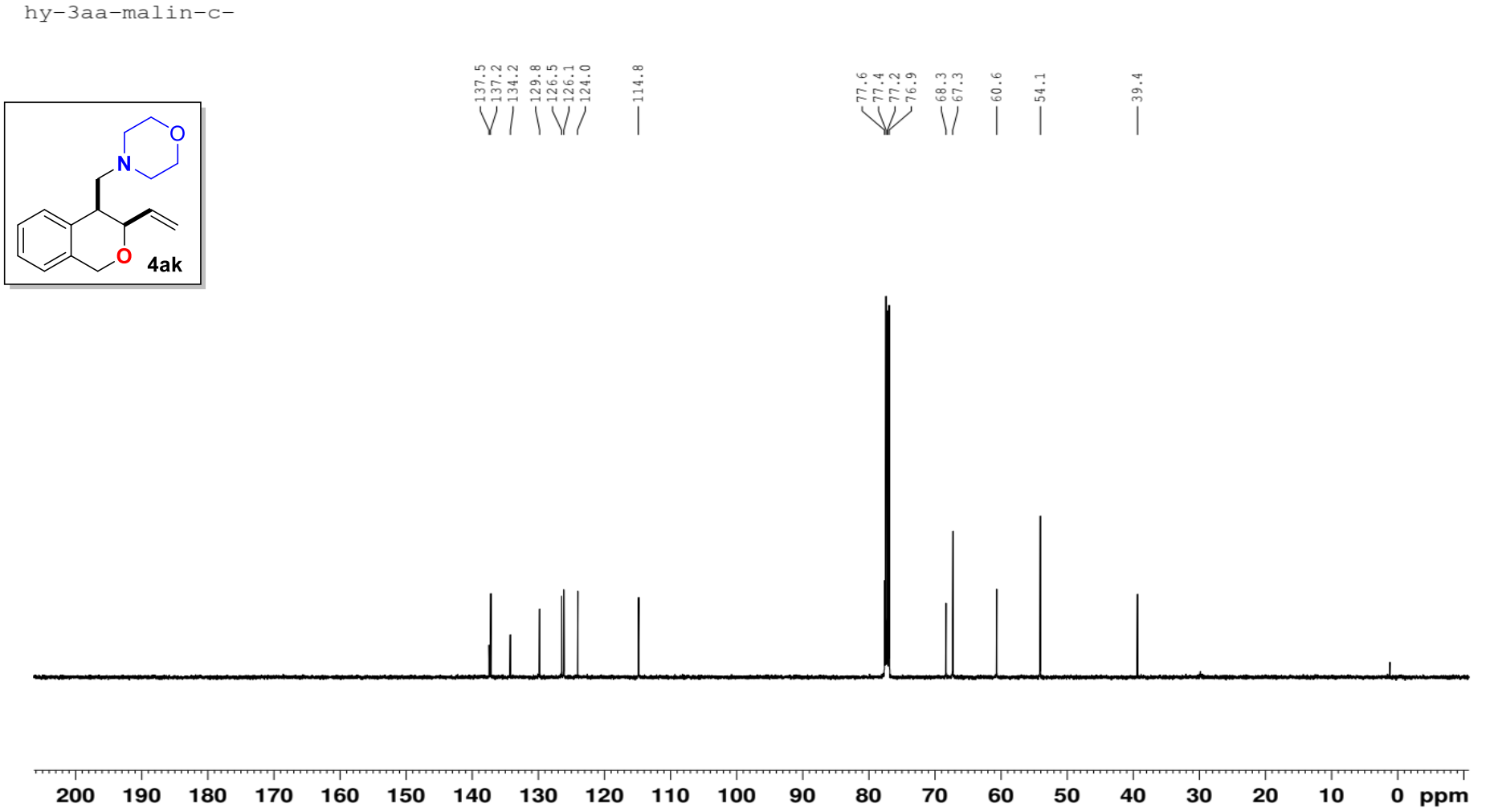
hy-P-**4aj** ^{19}F NMR (470MHz $CDCl_3$)



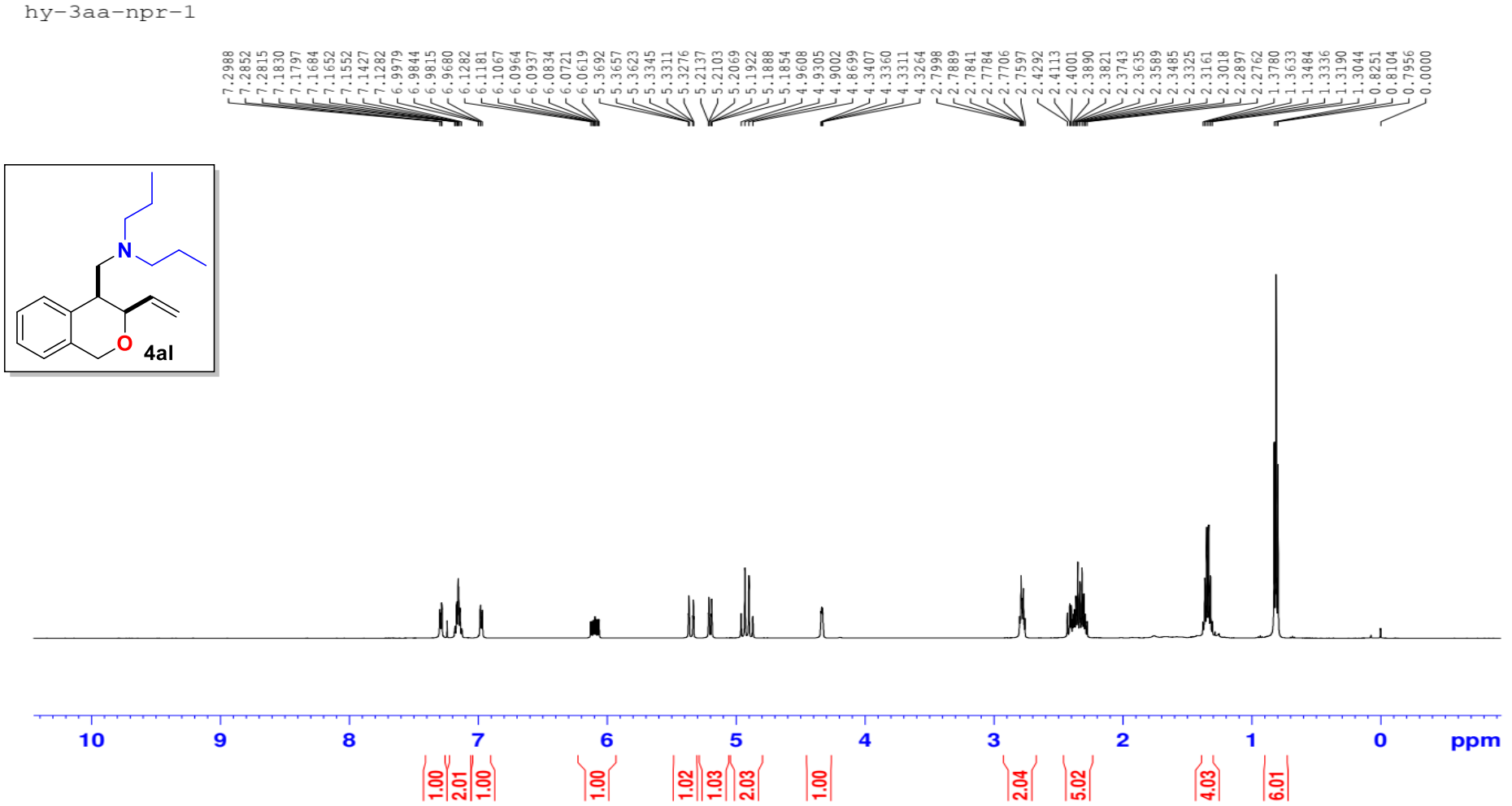
hy-P-**4ak** ^{1}H NMR (500MHz $CDCl_3$)



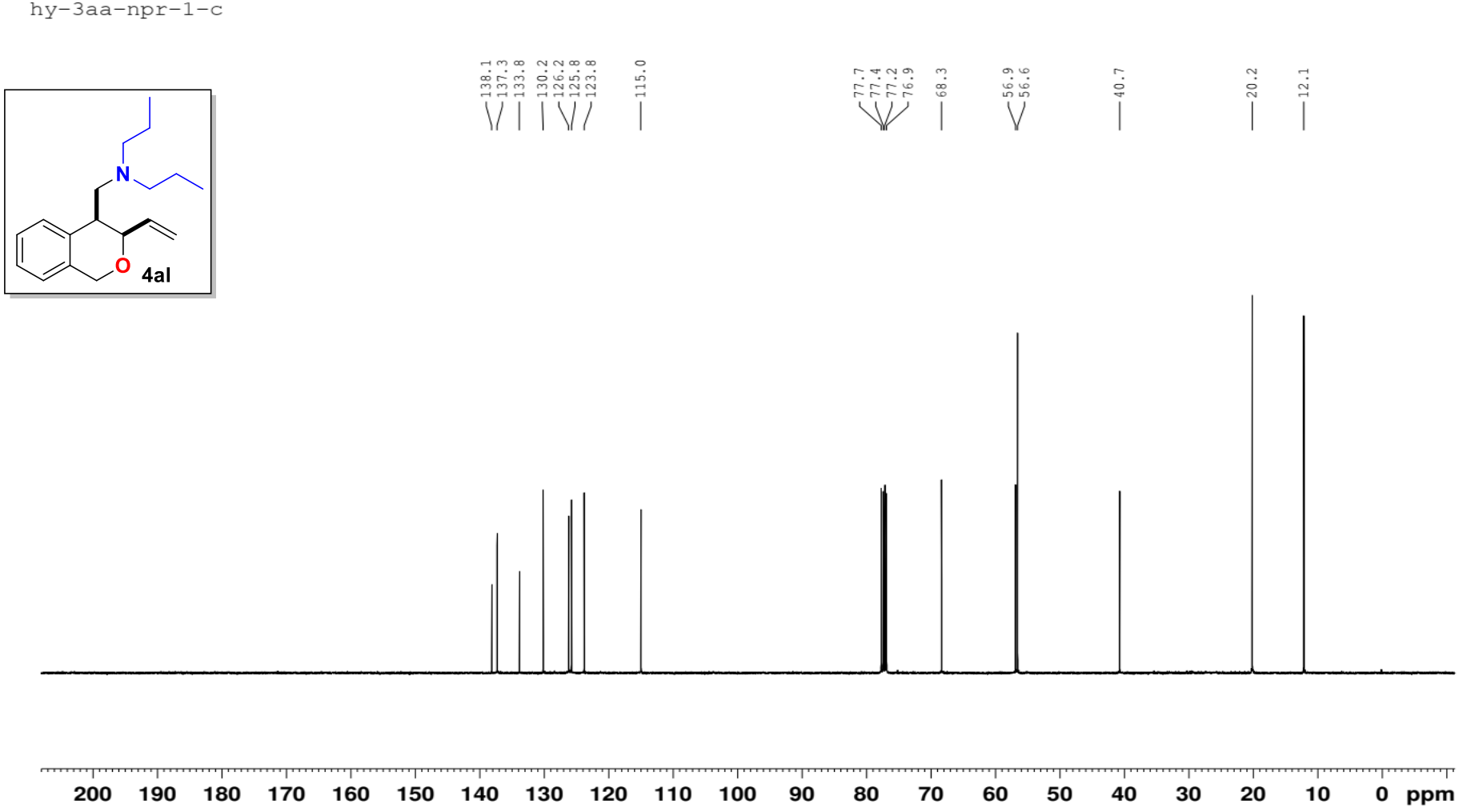
hy-P-**4ak** ^{13}C NMR (125MHz $CDCl_3$)



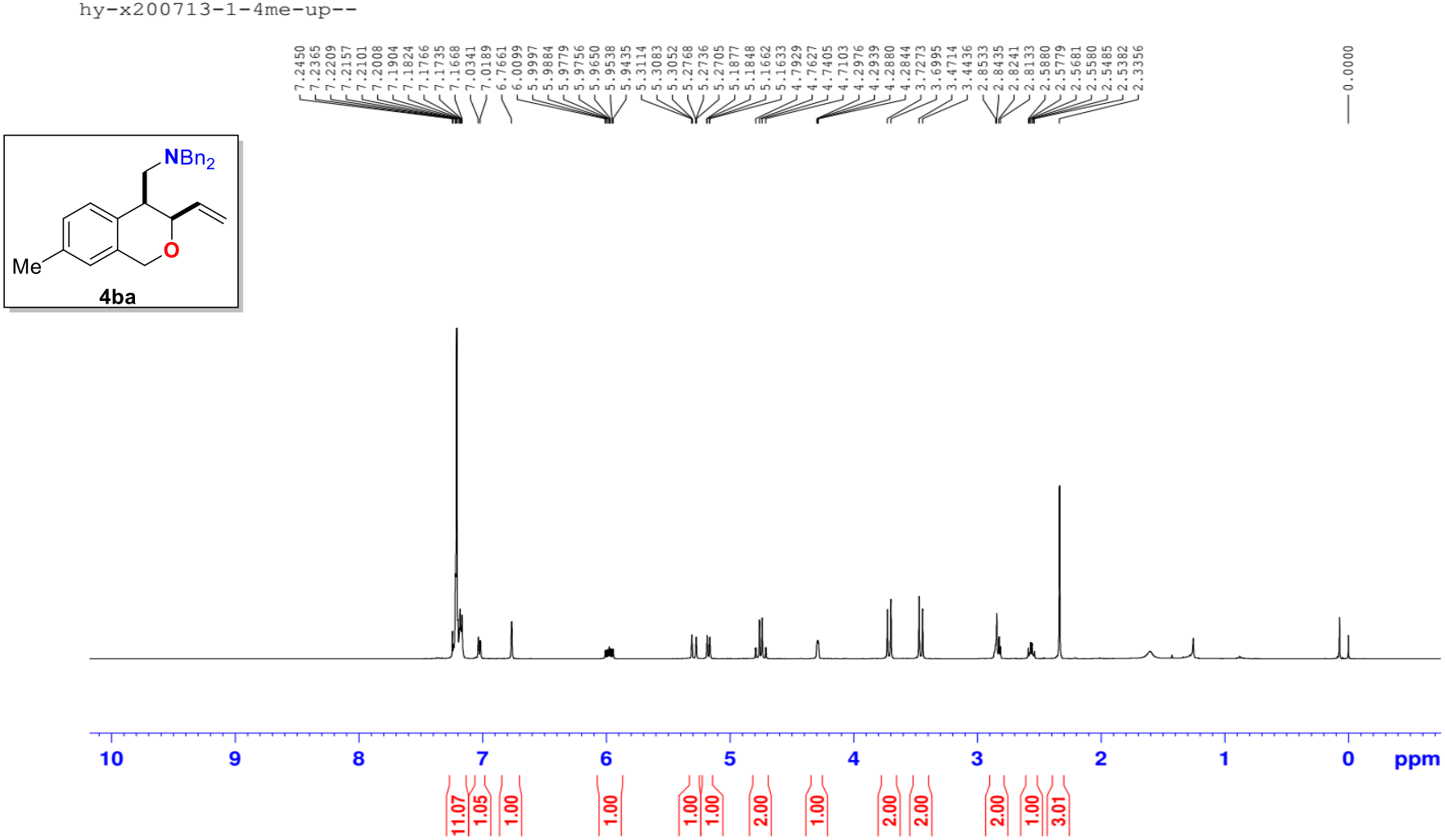
hy-P-**4al** ^{1}H NMR (500MHz $CDCl_3$)



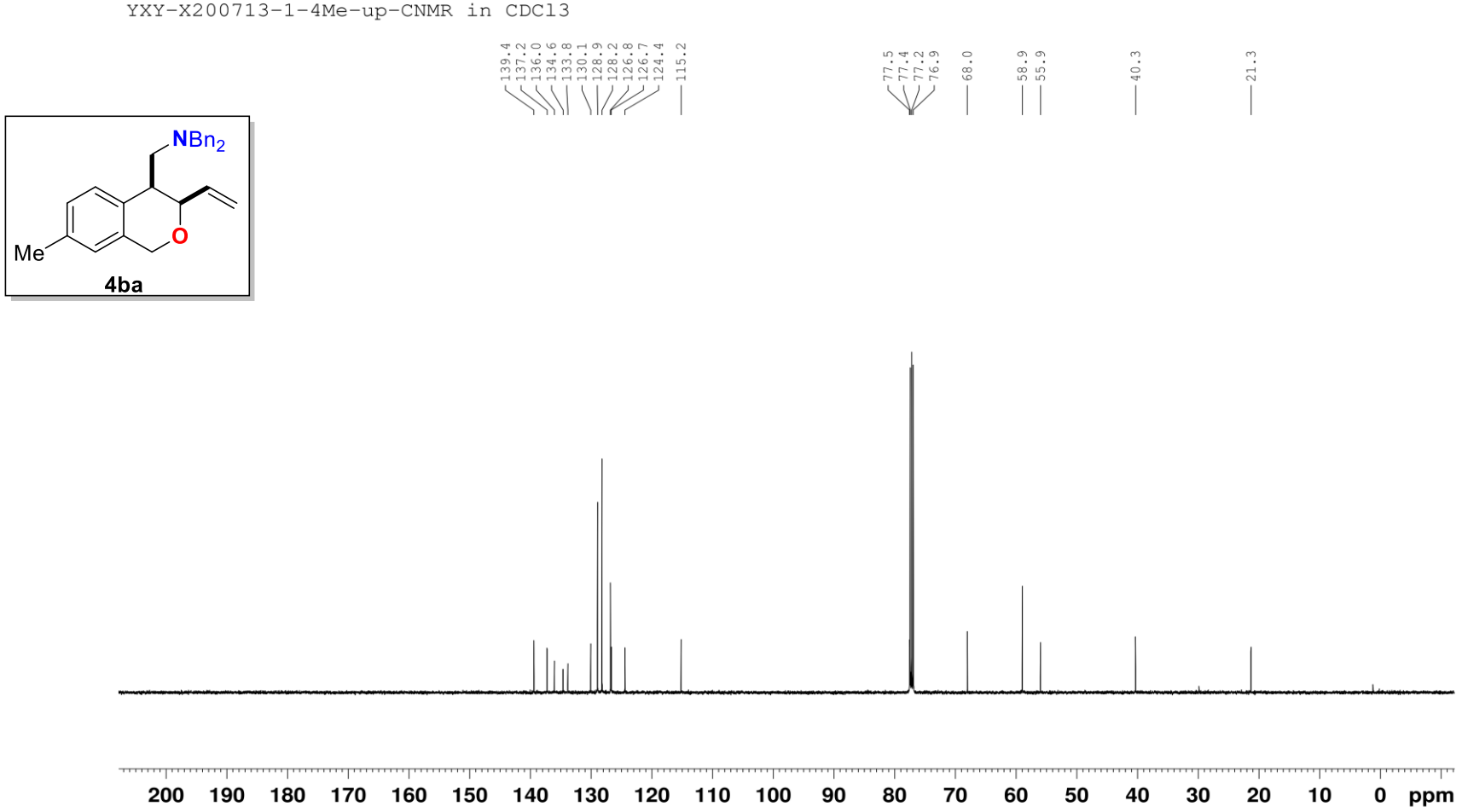
hy-P-**4al** ^{13}C NMR (125MHz $CDCl_3$)



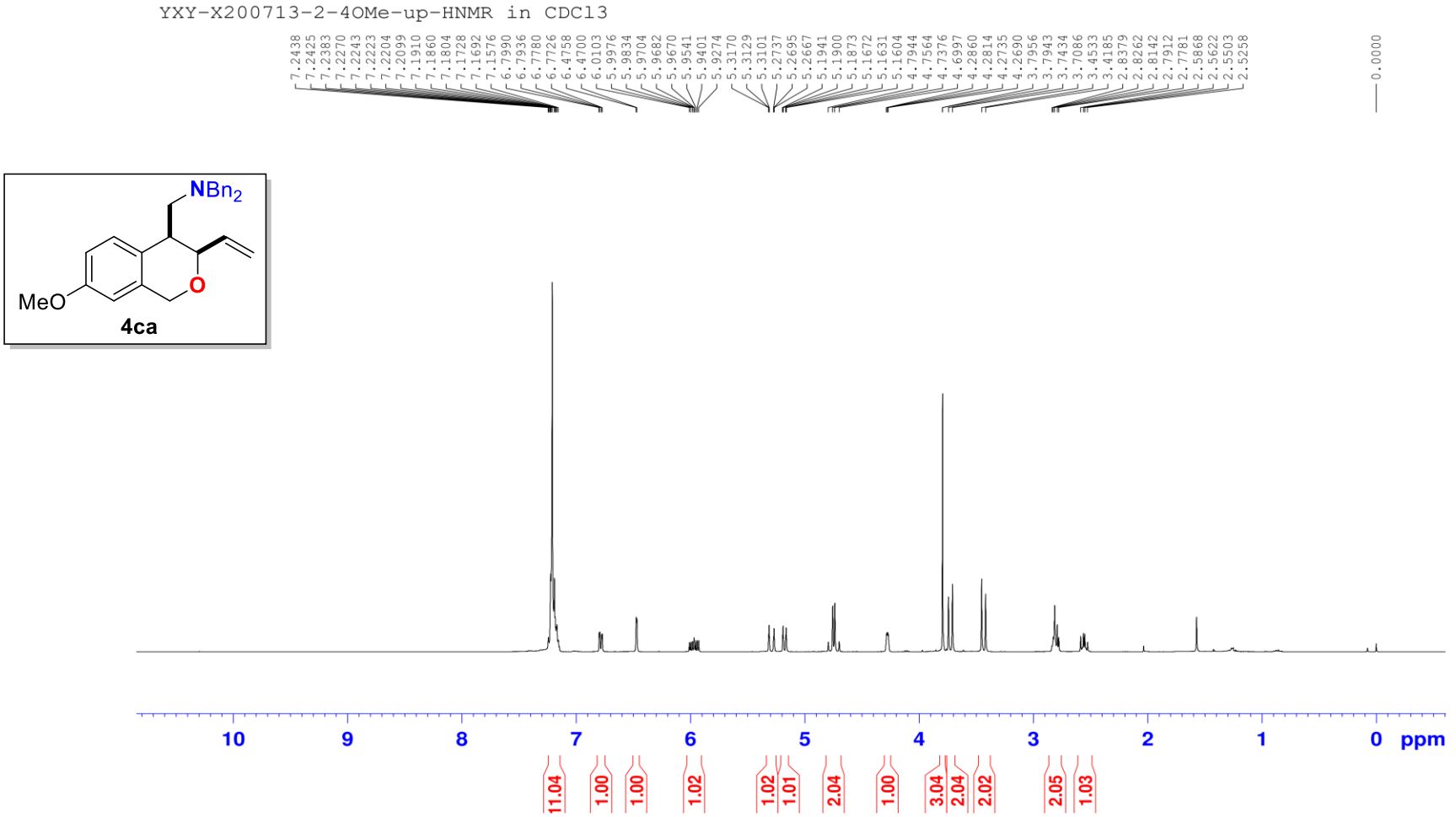
hy-P-**4ba** ^{1}H NMR (500MHz $CDCl_3$)



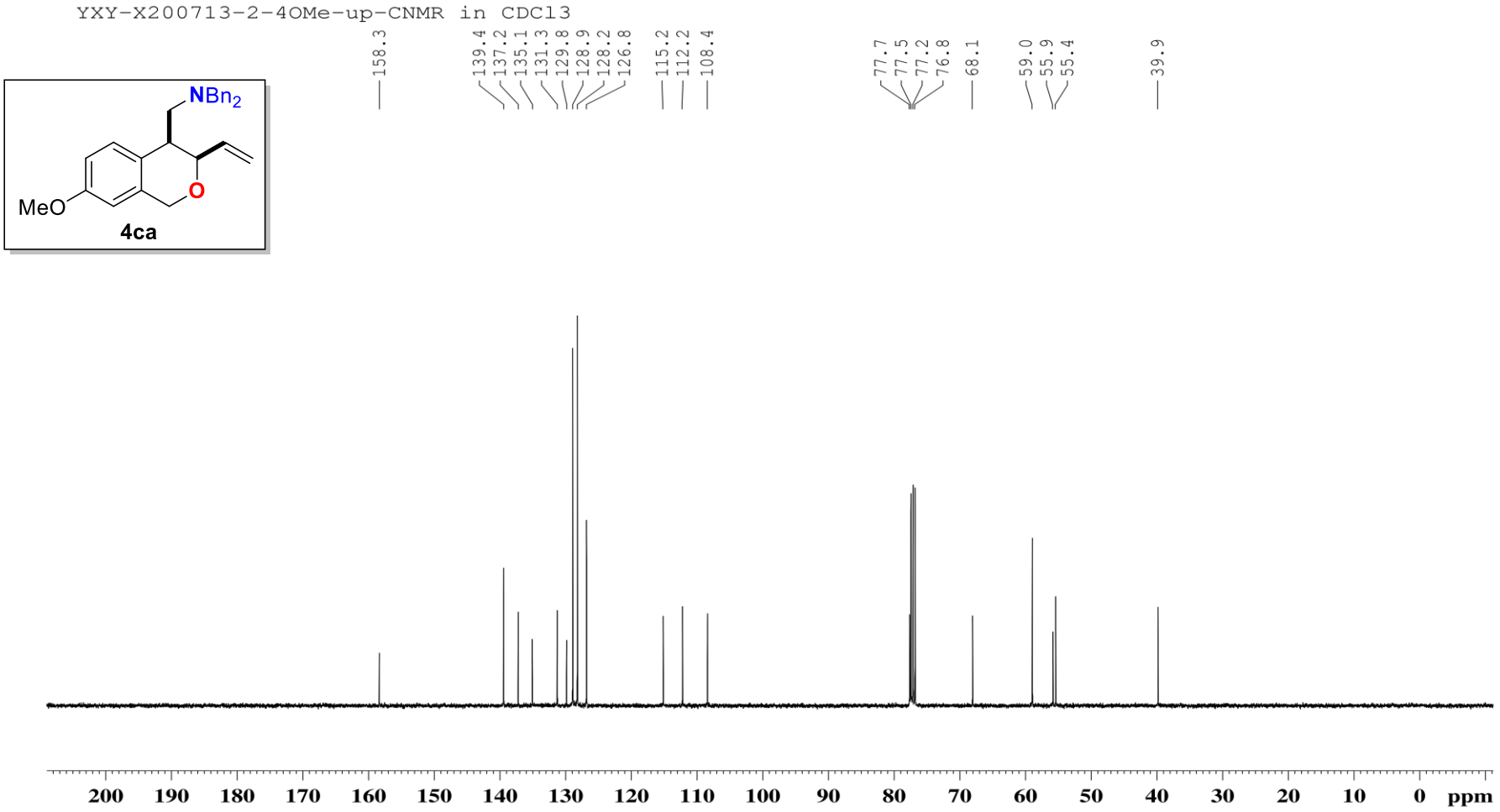
hy-P-**4ba** ^{13}C NMR (125MHz $CDCl_3$)



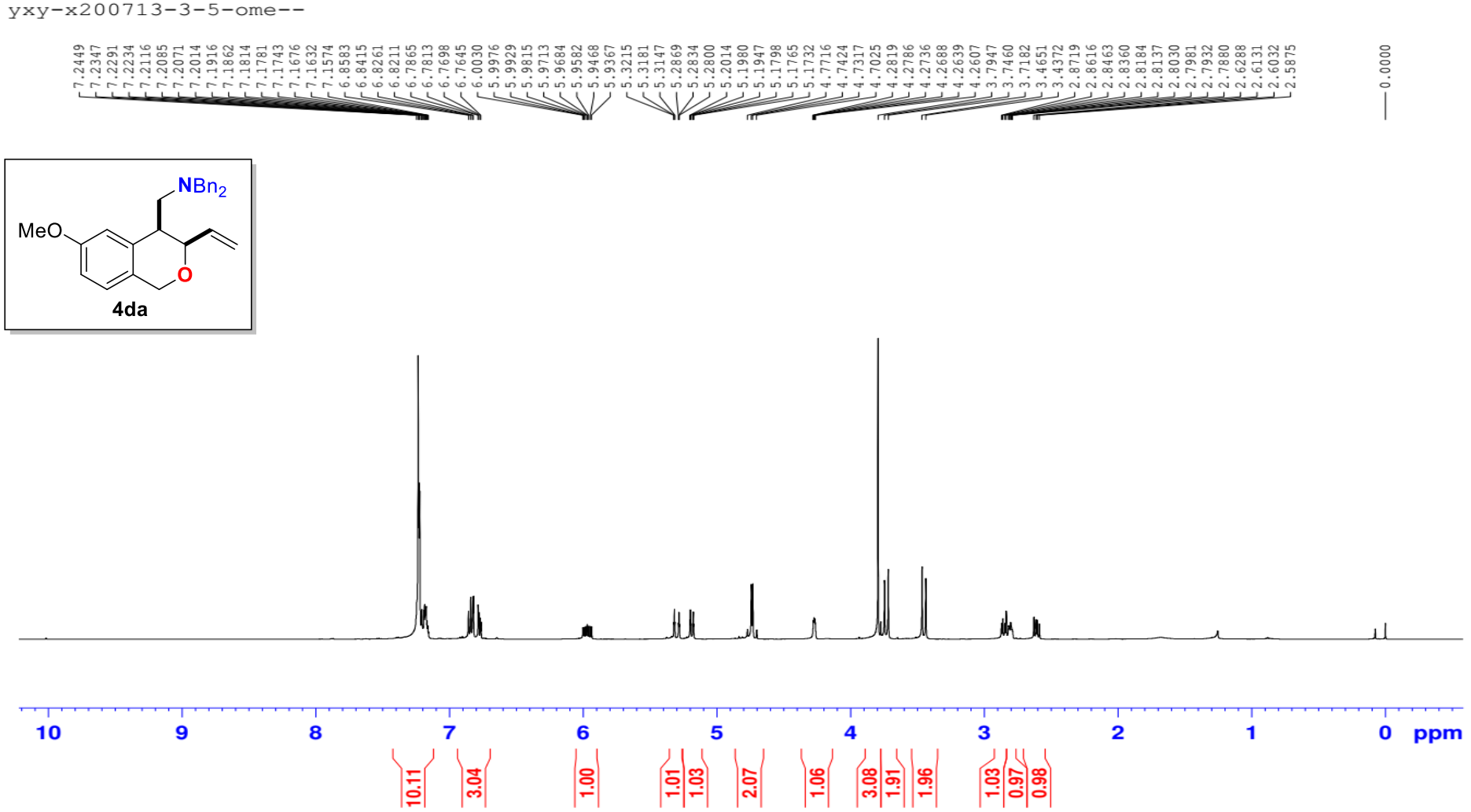
hy-P-**4ca** ^{1}H NMR (400MHz $CDCl_3$)



hy-P-**4ca** ^{13}C NMR (100MHz $CDCl_3$)

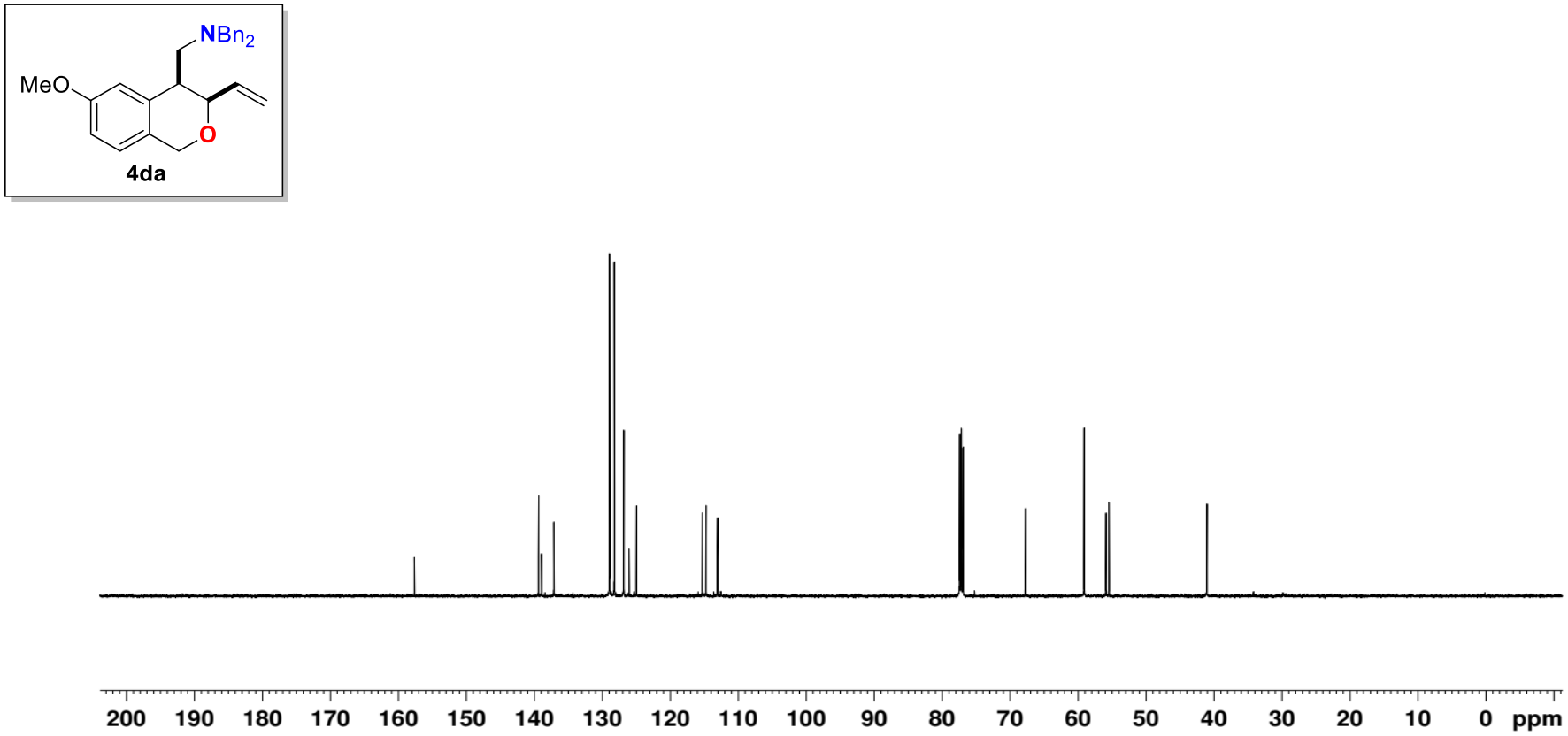


hy-P-**4da** ^{1}H NMR (500MHz $CDCl_3$)

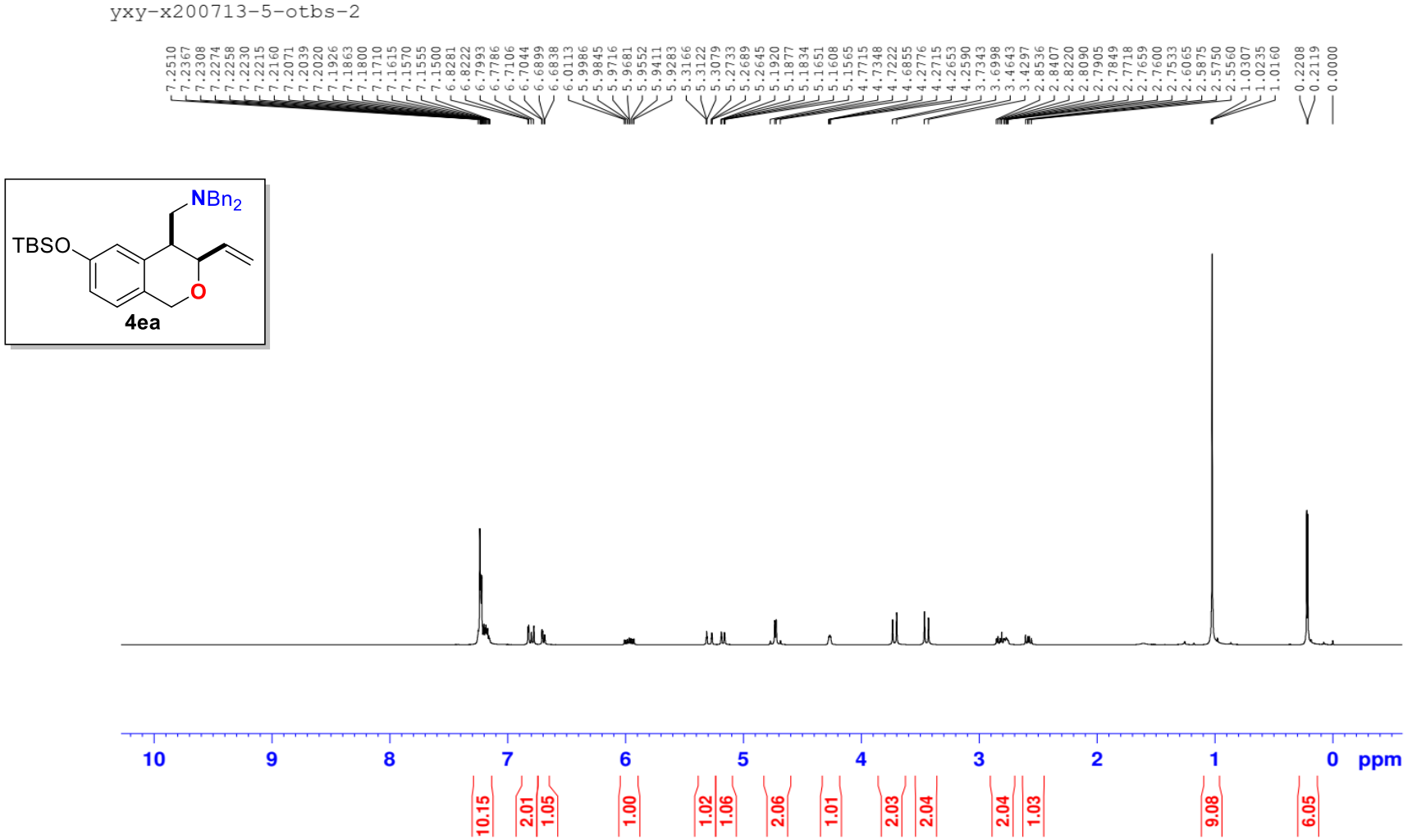


hy-P-**4da** ^{13}C NMR (125MHz $CDCl_3$)

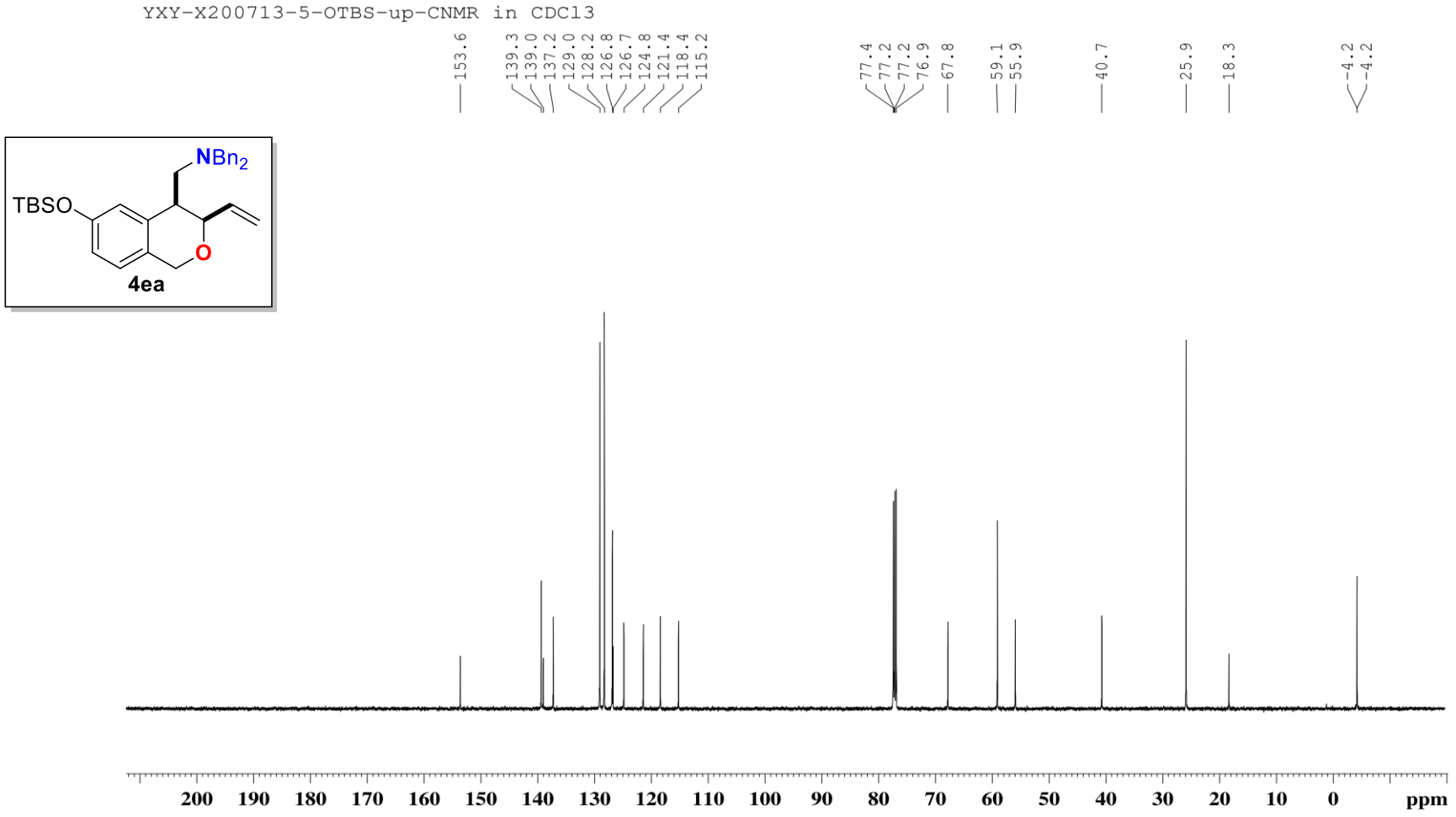
yxy-x200713-3-5-ome-2-c



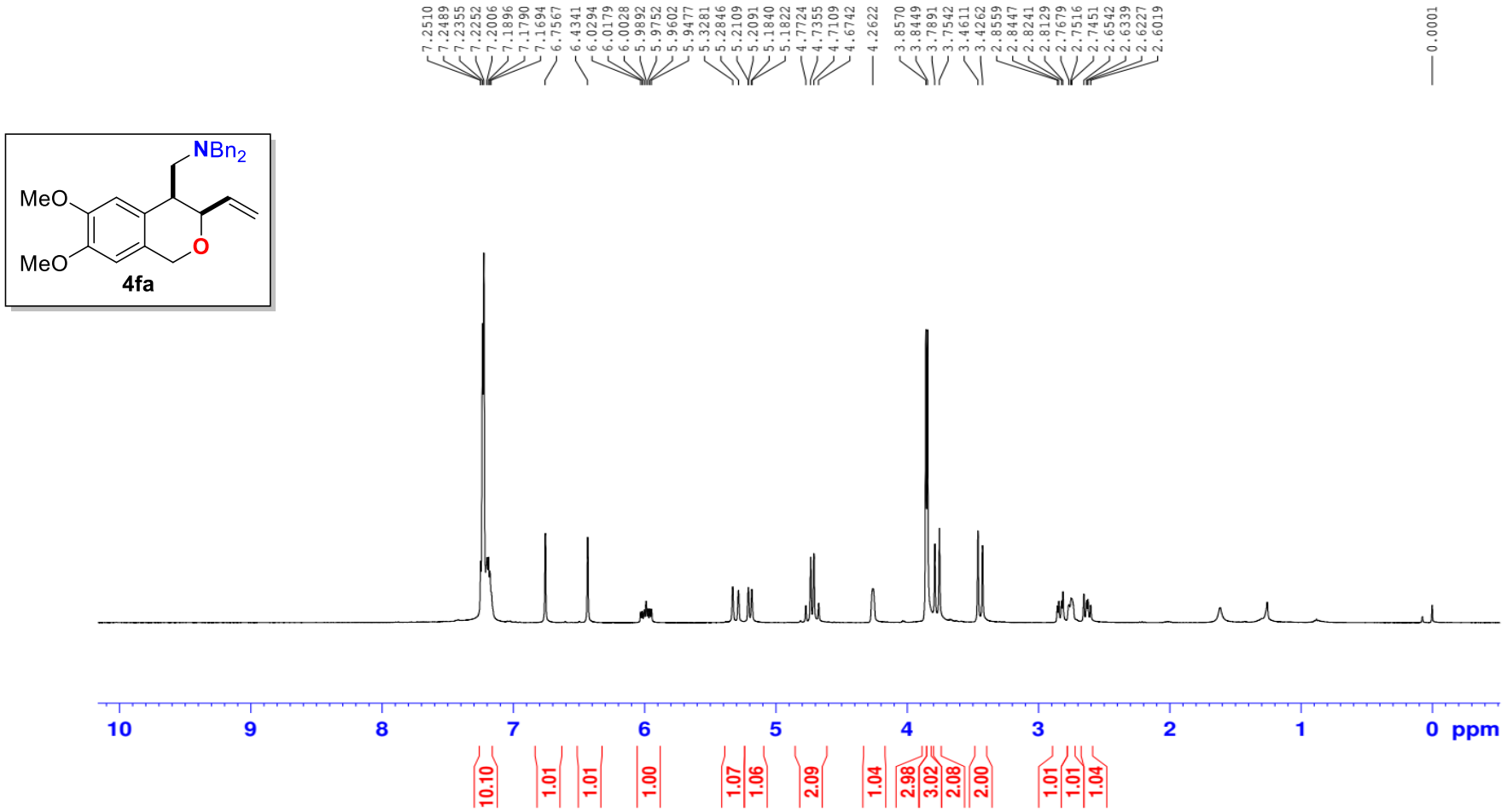
hy-P-**4ea** ^{1}H NMR (400MHz $CDCl_3$)



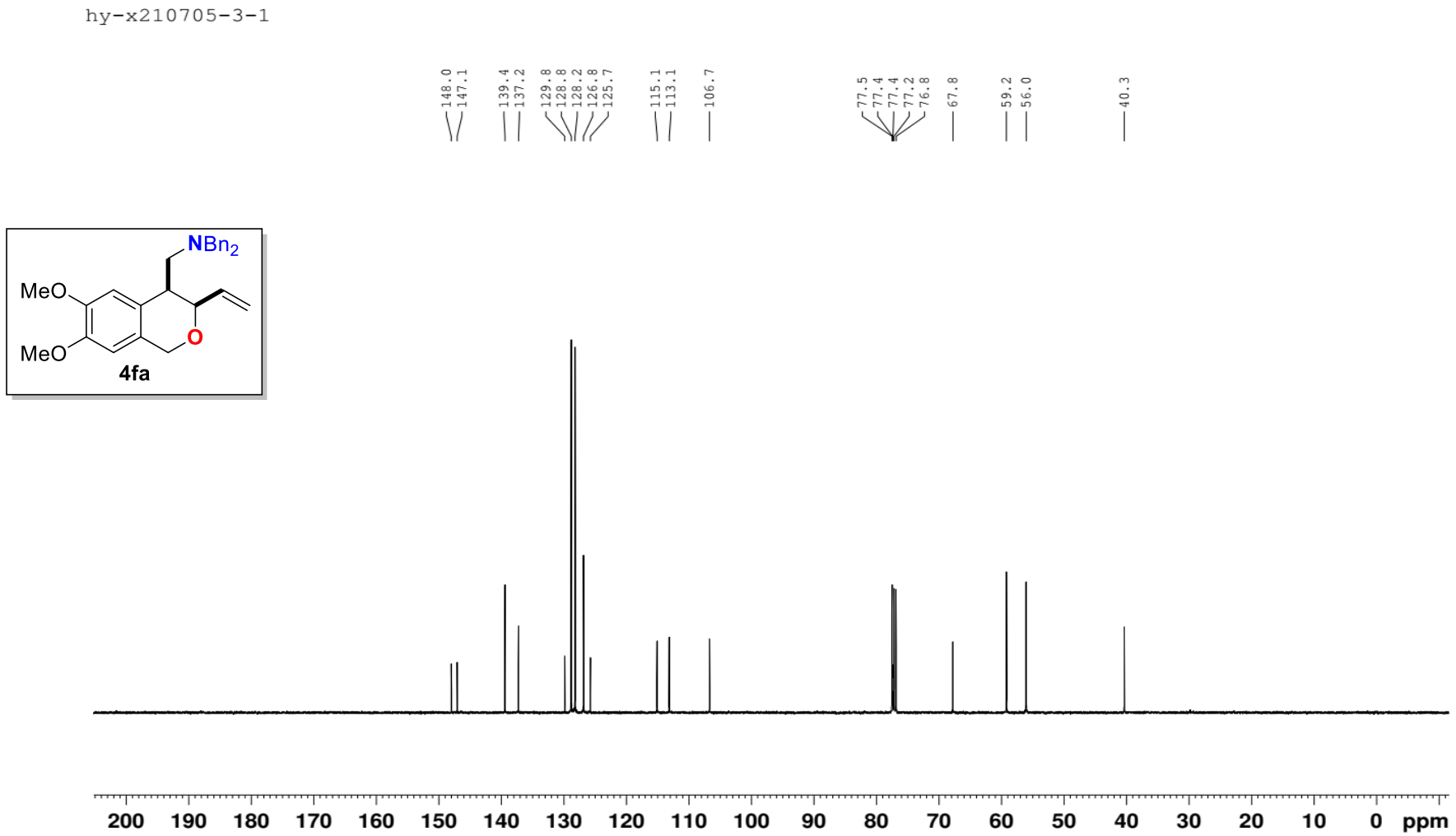
hy-P-**4ea** ^{13}C NMR (125MHz $CDCl_3$)



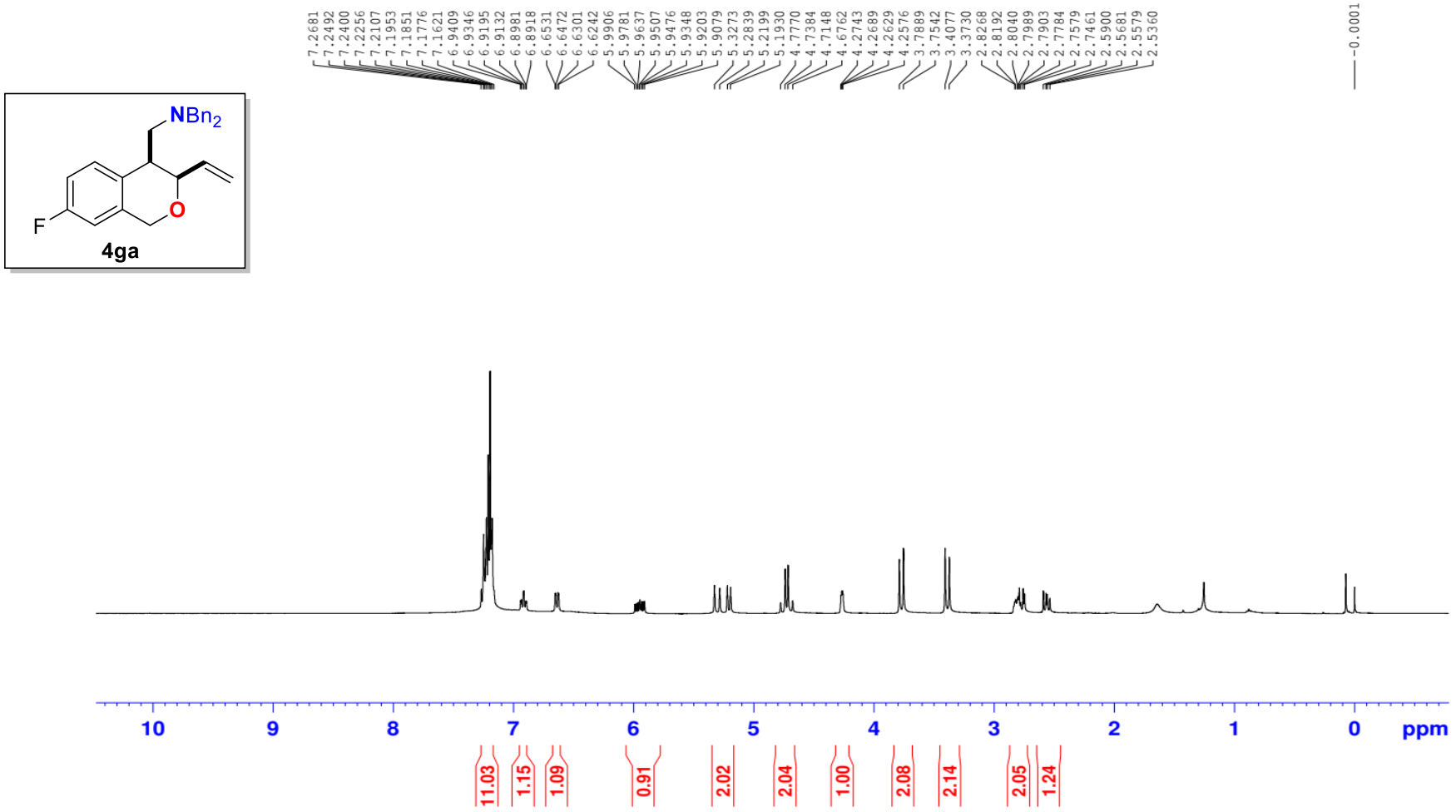
hy-P-**4fa** ^{1}H NMR (400MHz $CDCl_3$)



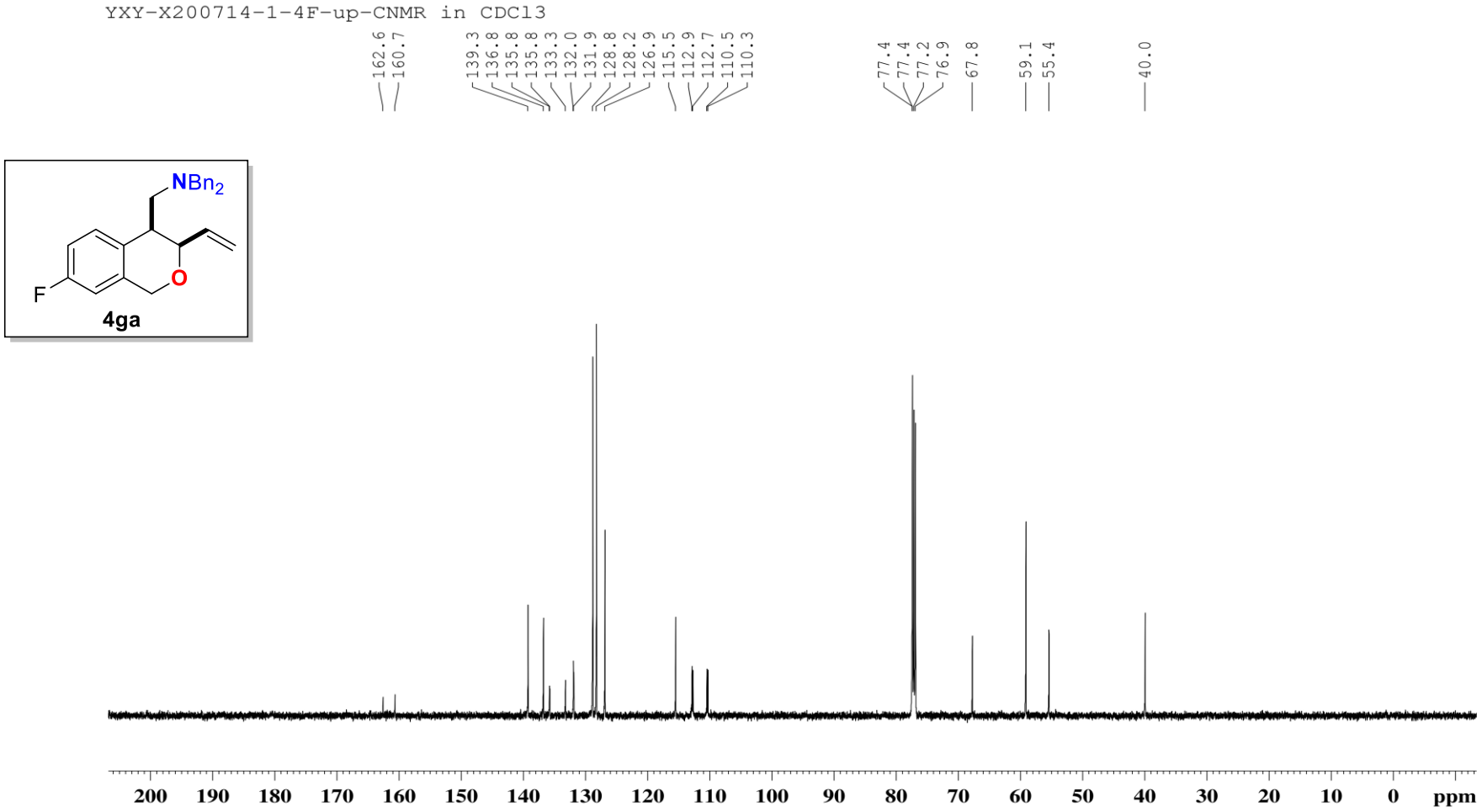
hy-P-**4fa** ^{13}C NMR (100MHz $CDCl_3$)



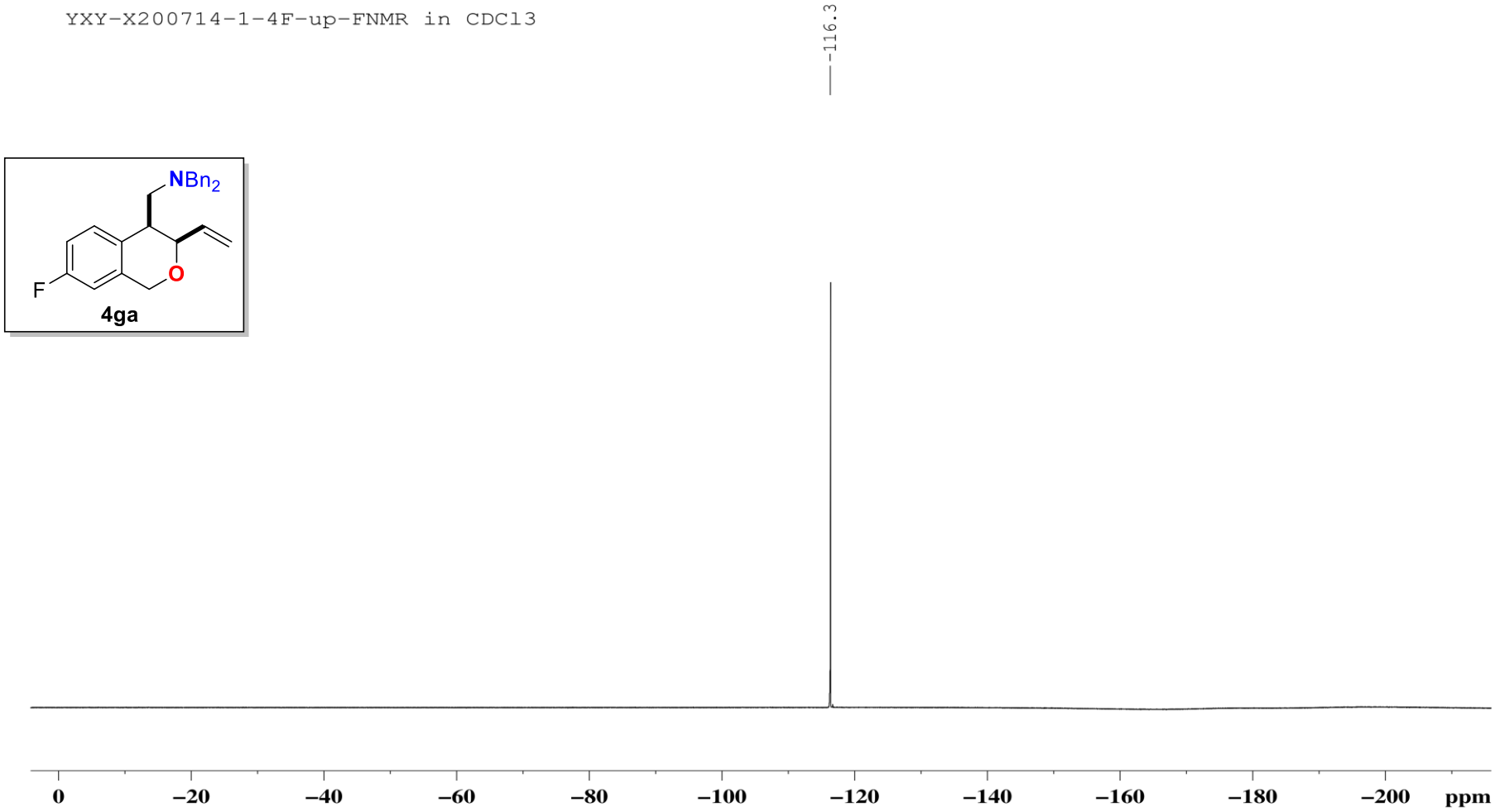
hy-P-**4ga** ^{1}H NMR (400MHz $CDCl_3$)



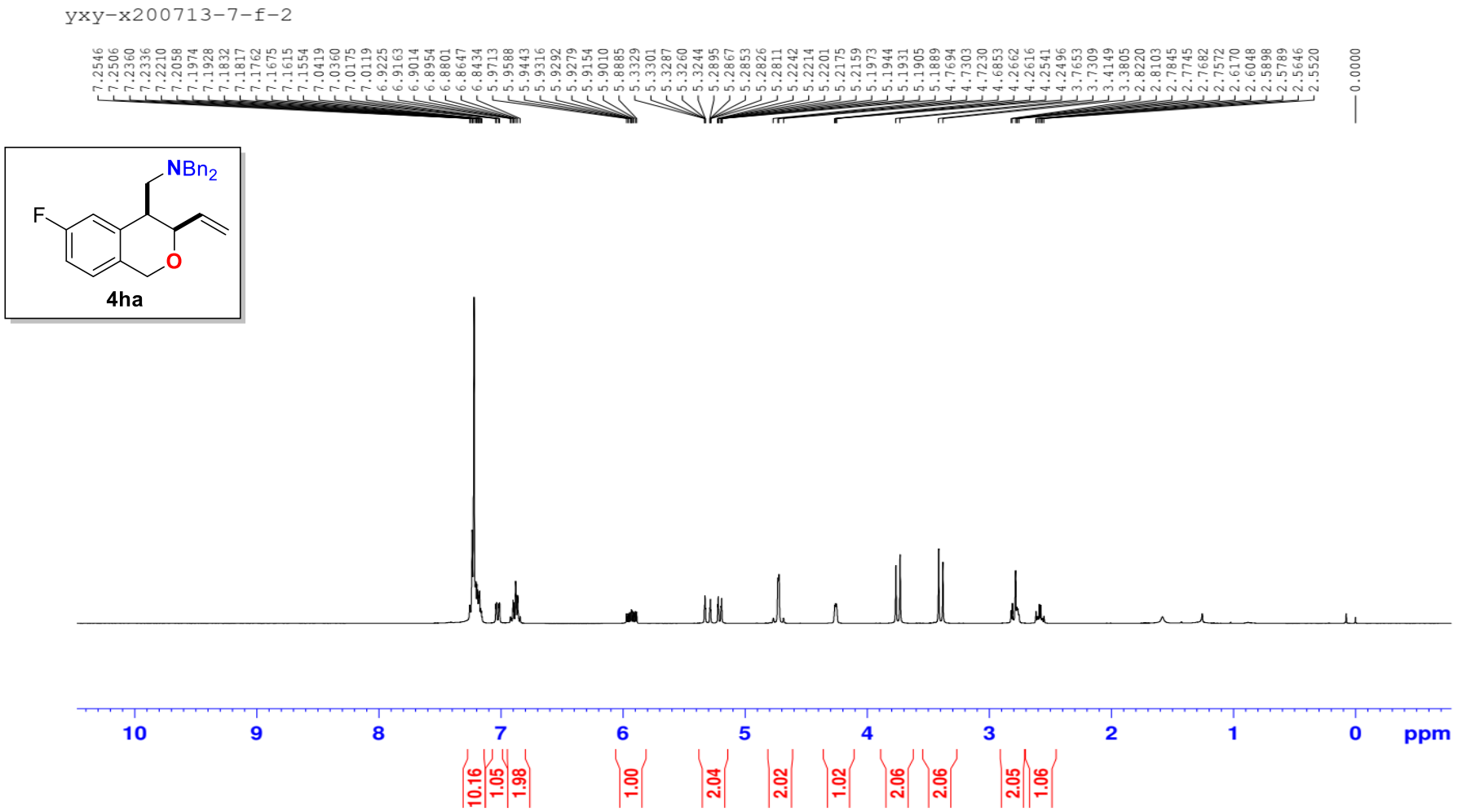
hy-P-**4ga** ^{13}C NMR (125MHz $CDCl_3$)



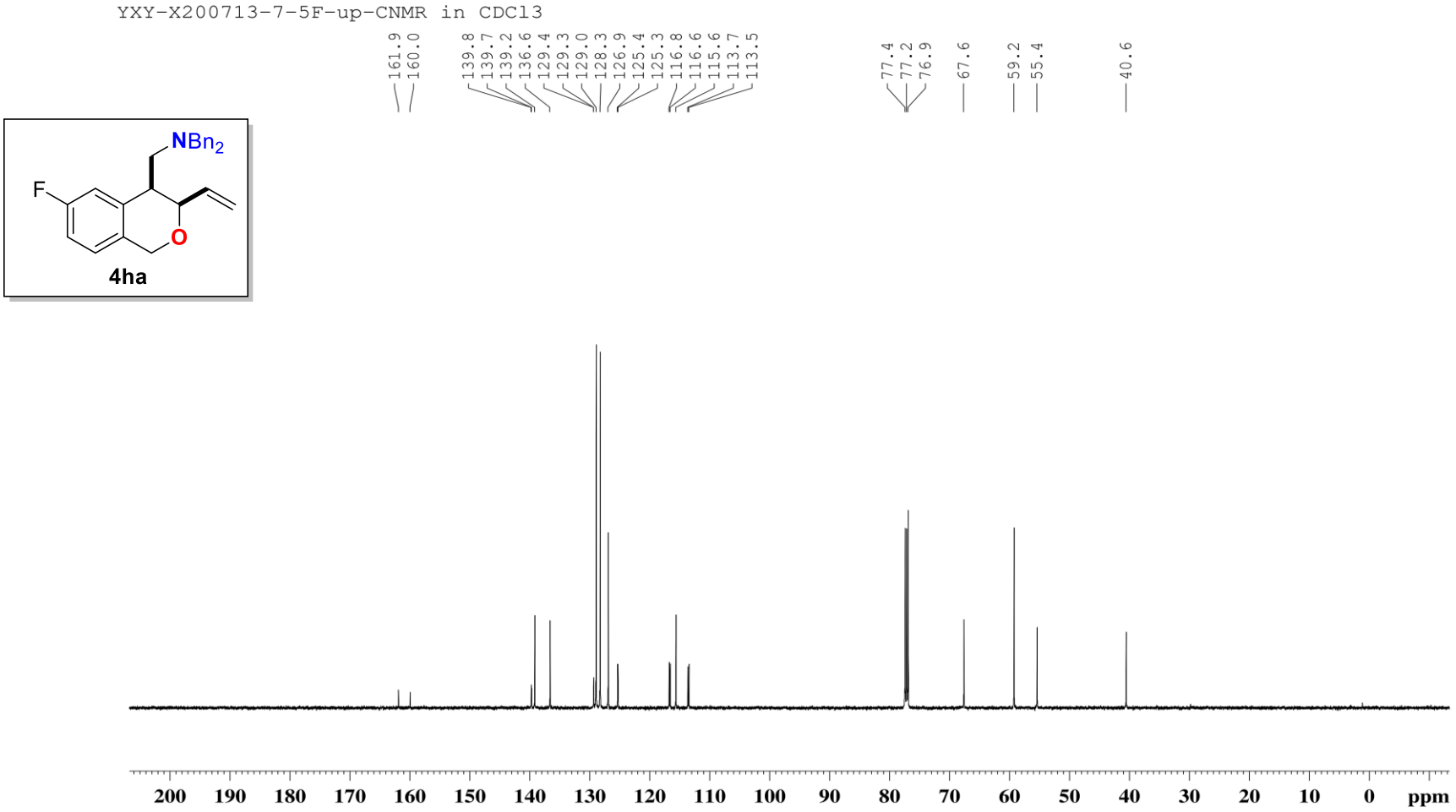
hy-P-**4ga** ^{19}F NMR (470MHz $CDCl_3$)



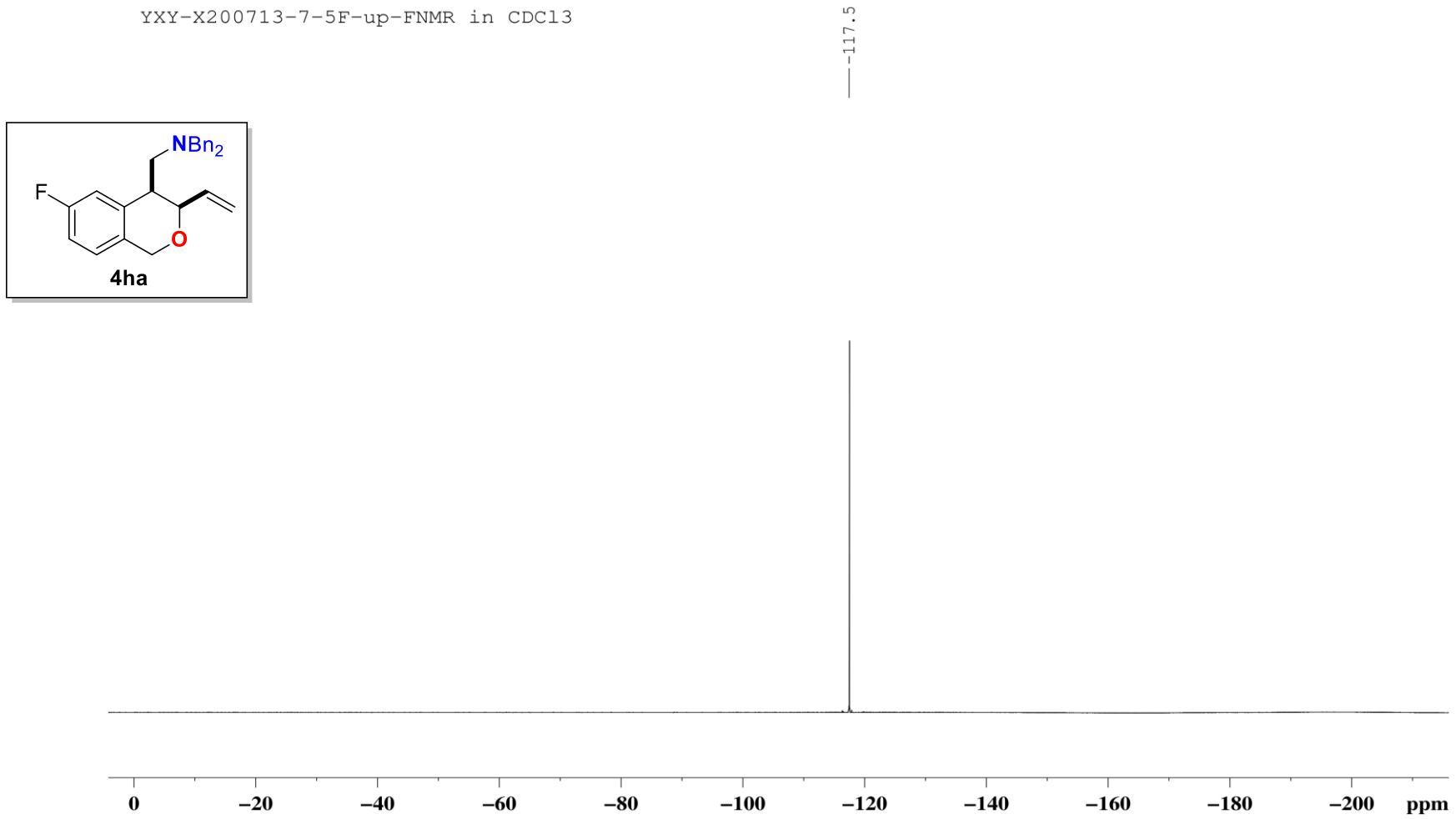
hy-P-**4ha** ^{1}H NMR (400MHz $CDCl_3$)



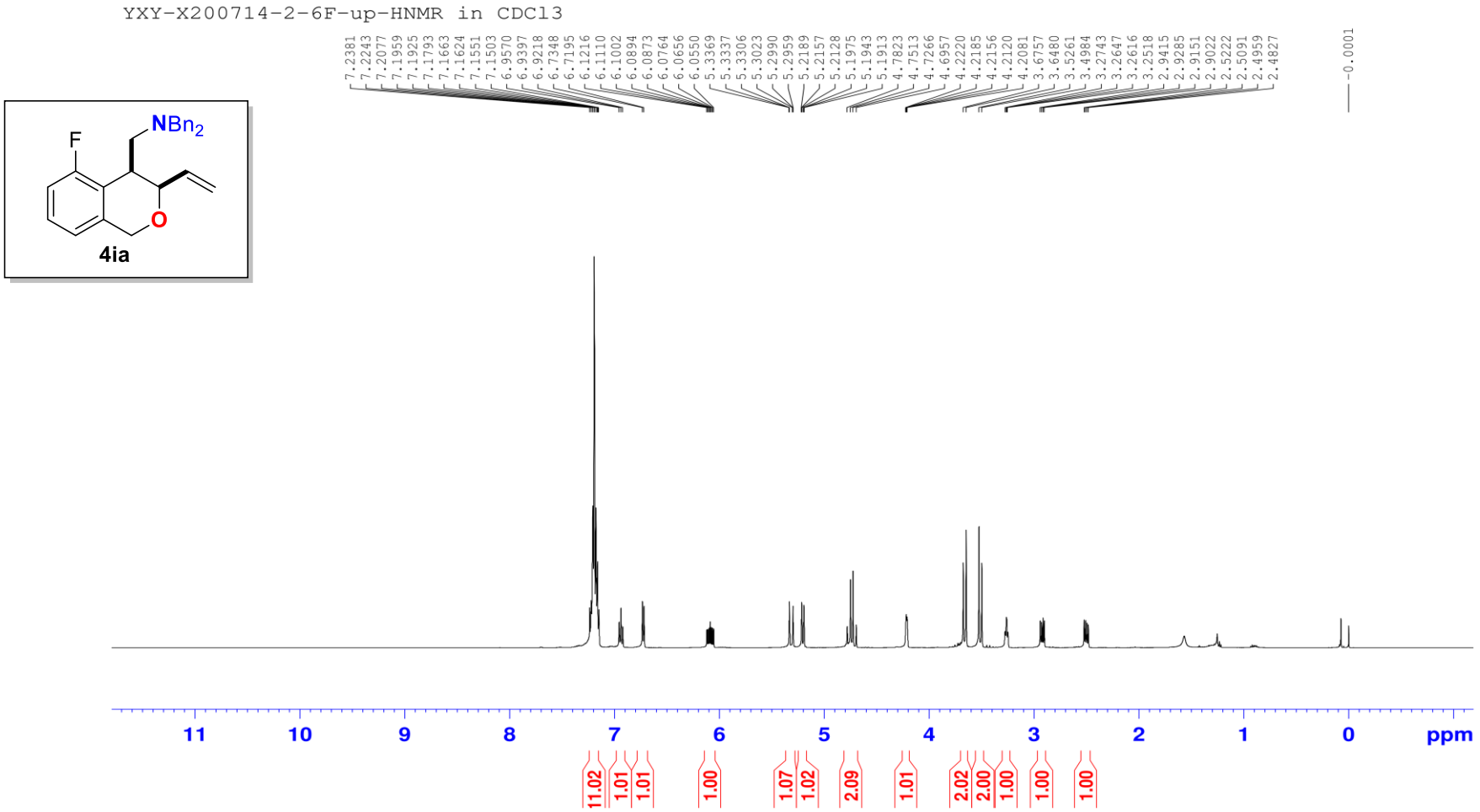
hy-P-**4ha** ^{13}C NMR (125MHz $CDCl_3$)



hy-P-**4ha** ^{19}F NMR (470MHz $CDCl_3$)

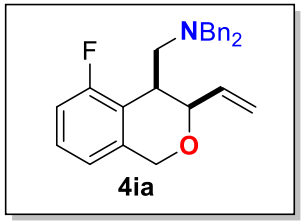


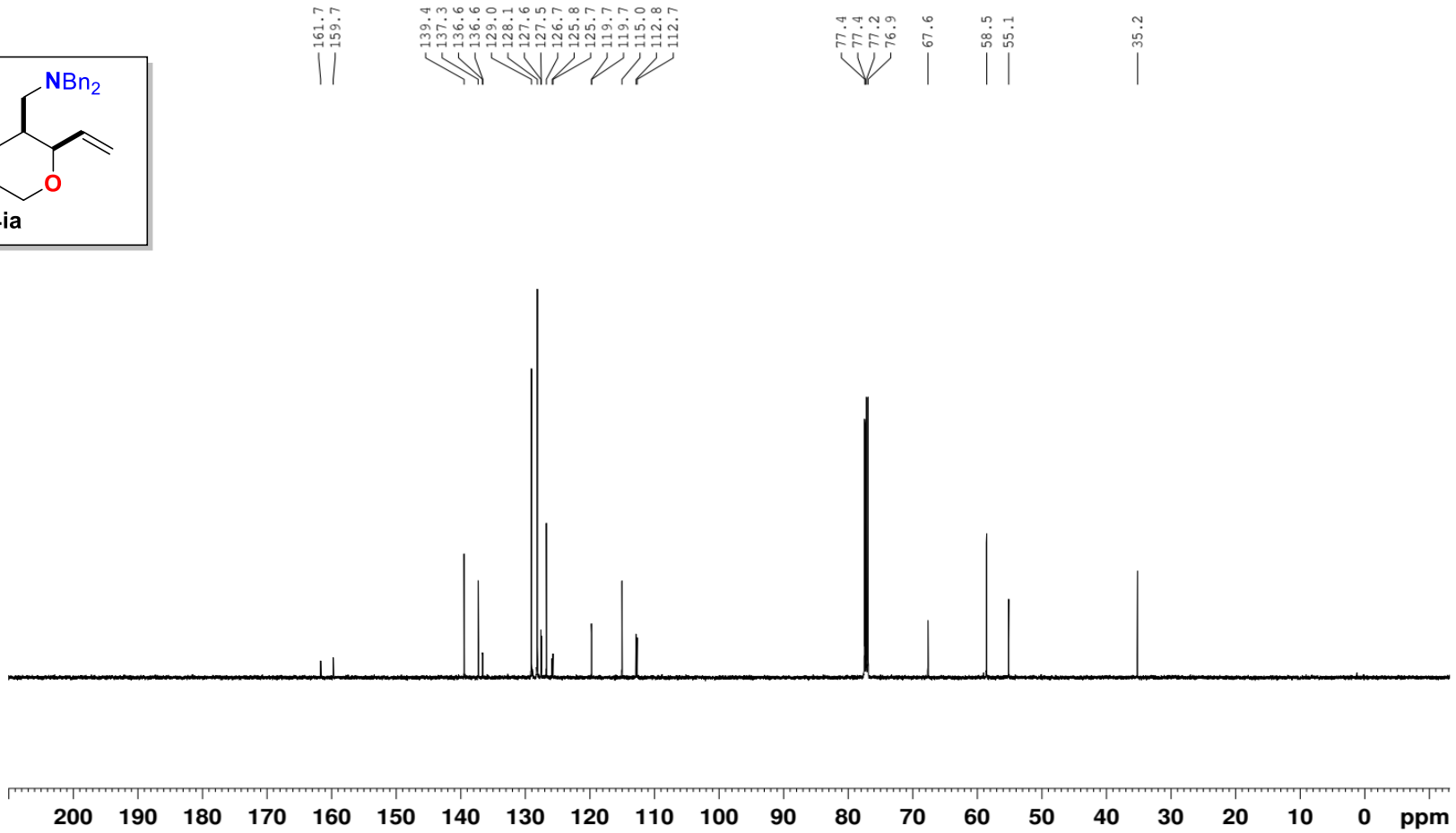
hy-P-**4ia** ^{1}H NMR (500MHz $CDCl_3$)



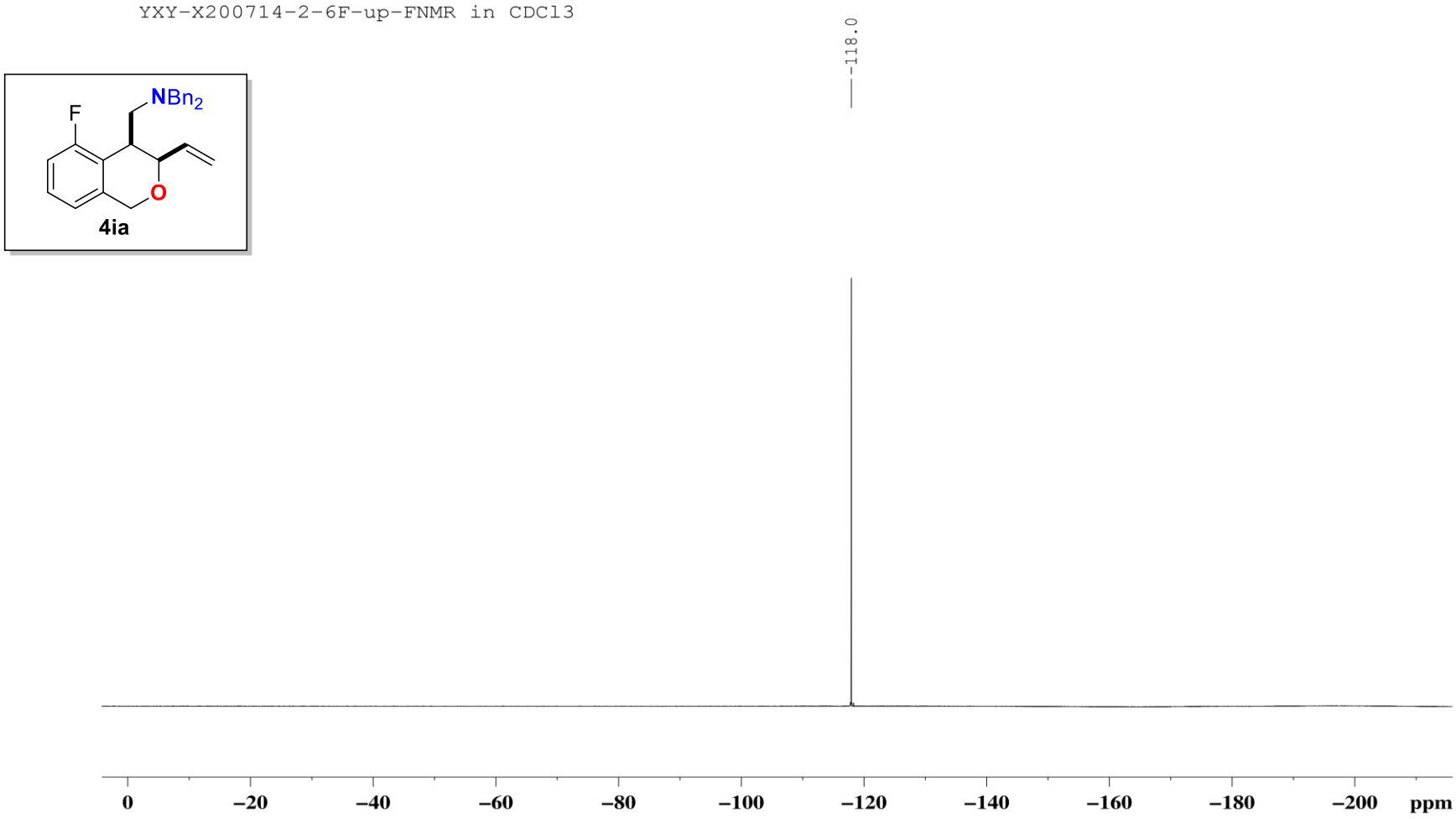
hy-P-**4ia** ^{13}C NMR (125MHz $CDCl_3$)

yxy-x200714-2-6-f-c

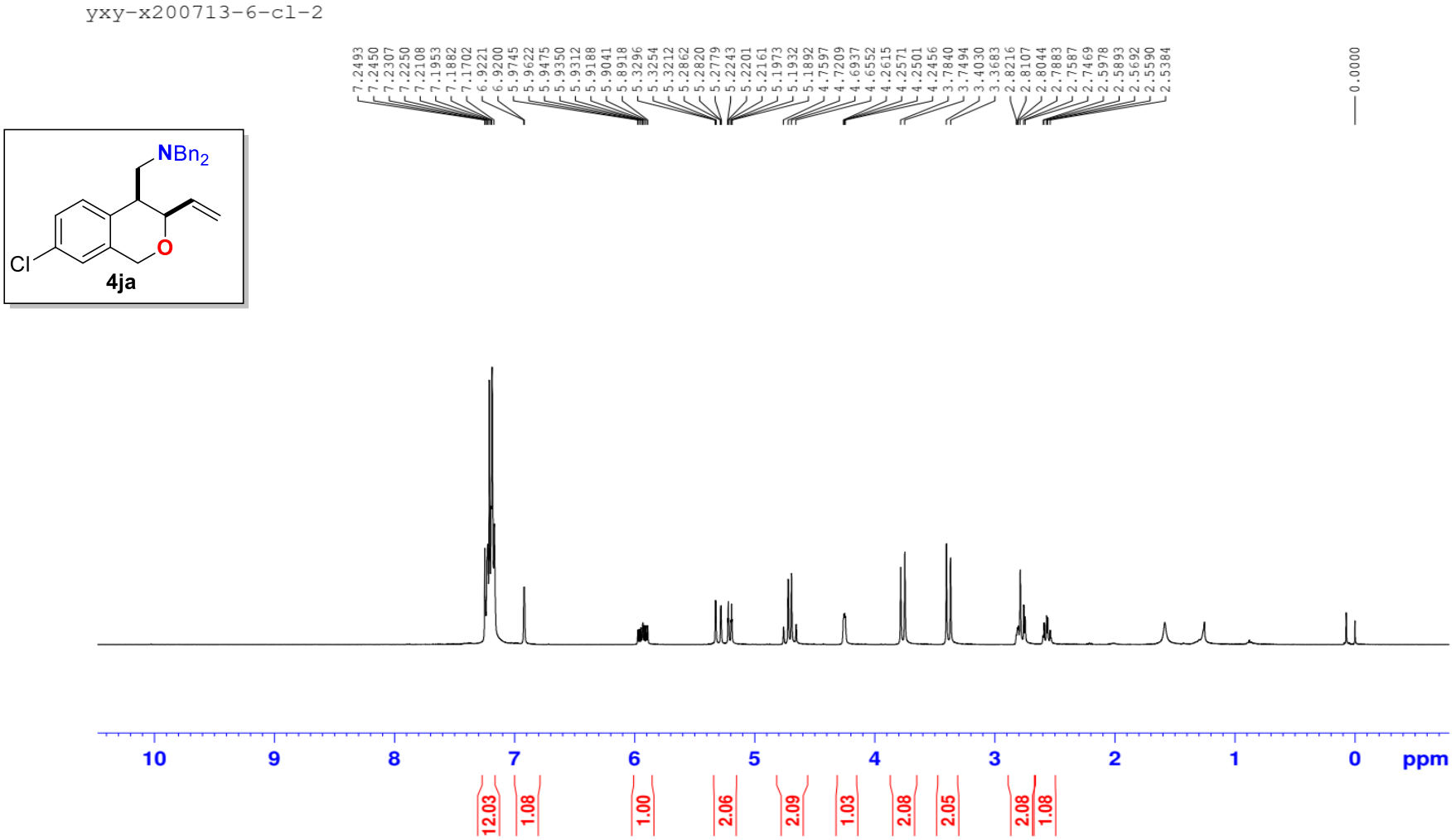




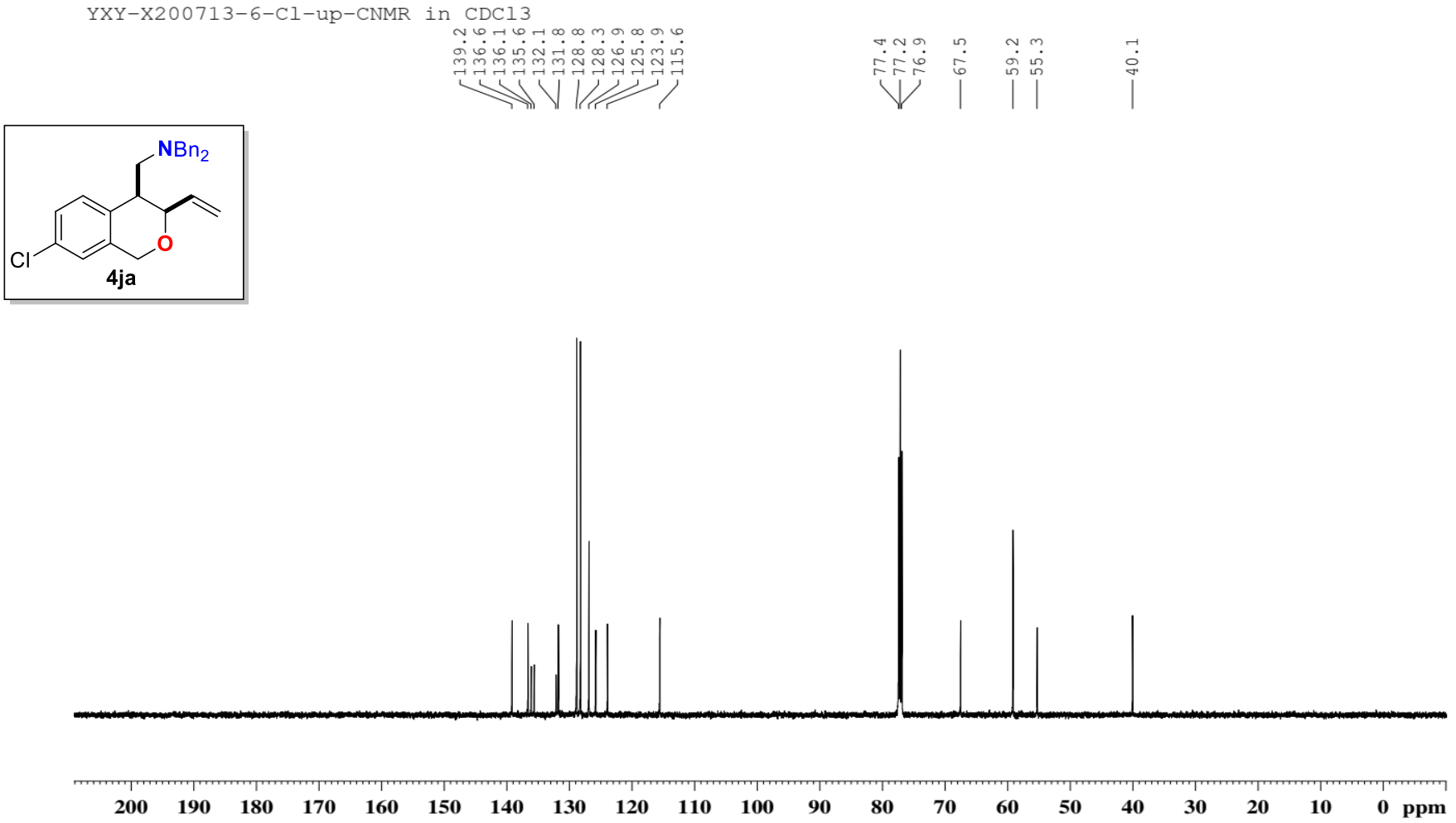
hy-P-**4ia** ^{19}F NMR (470MHz $CDCl_3$)



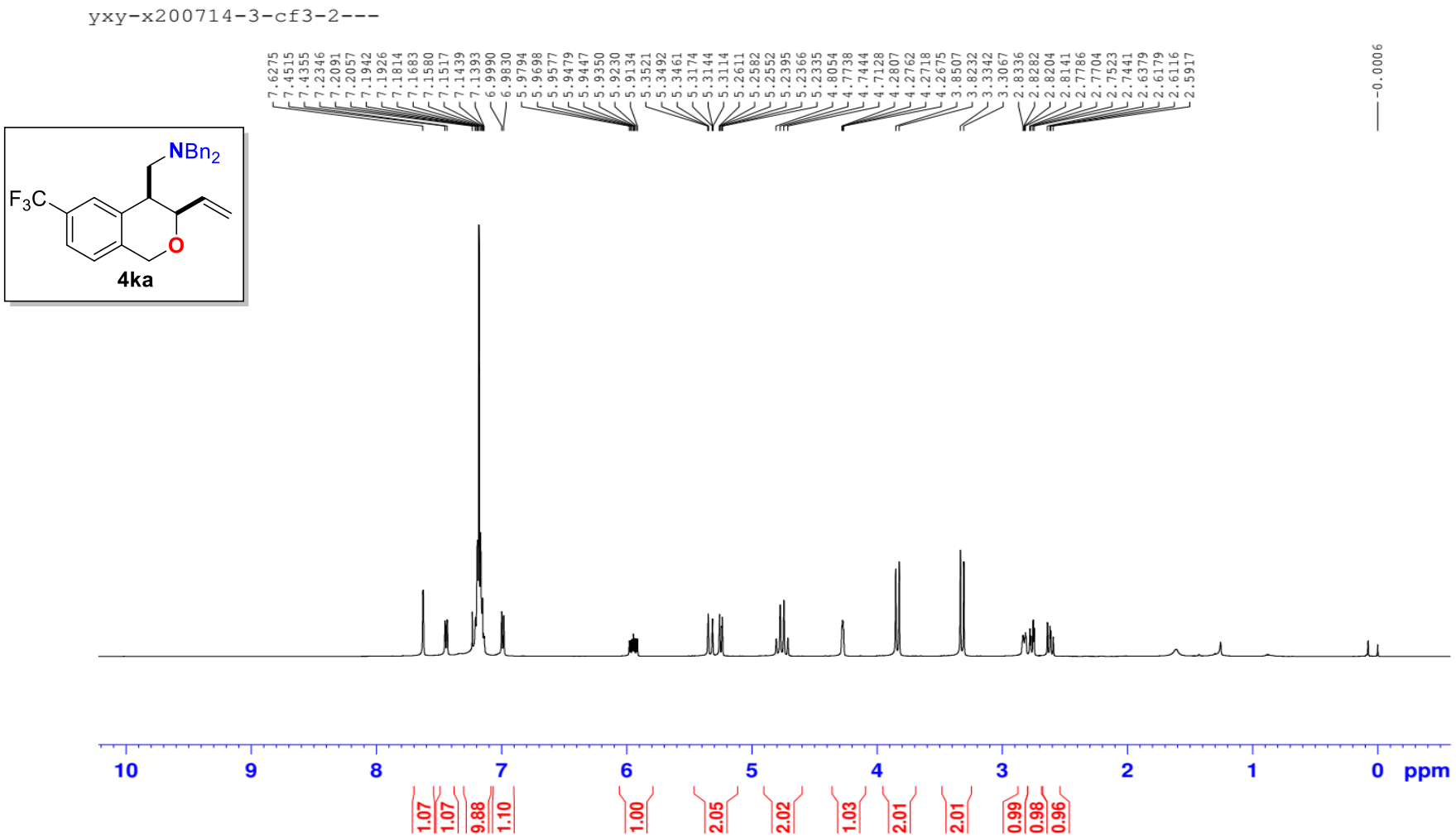
hy-P-**4ja** ^{1}H NMR (400MHz $CDCl_3$)



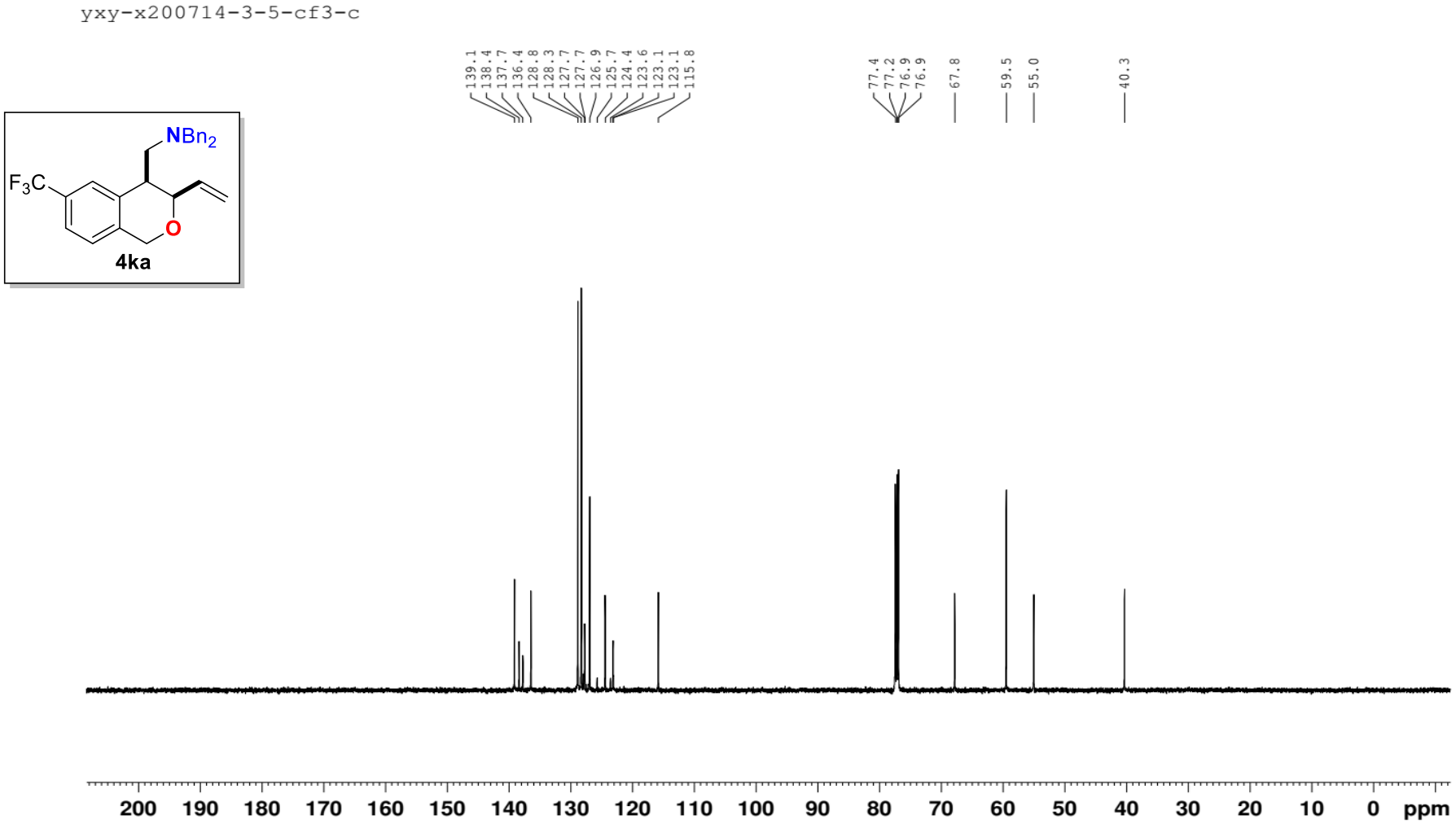
hy-P-**4ja** ^{13}C NMR (125MHz $CDCl_3$)



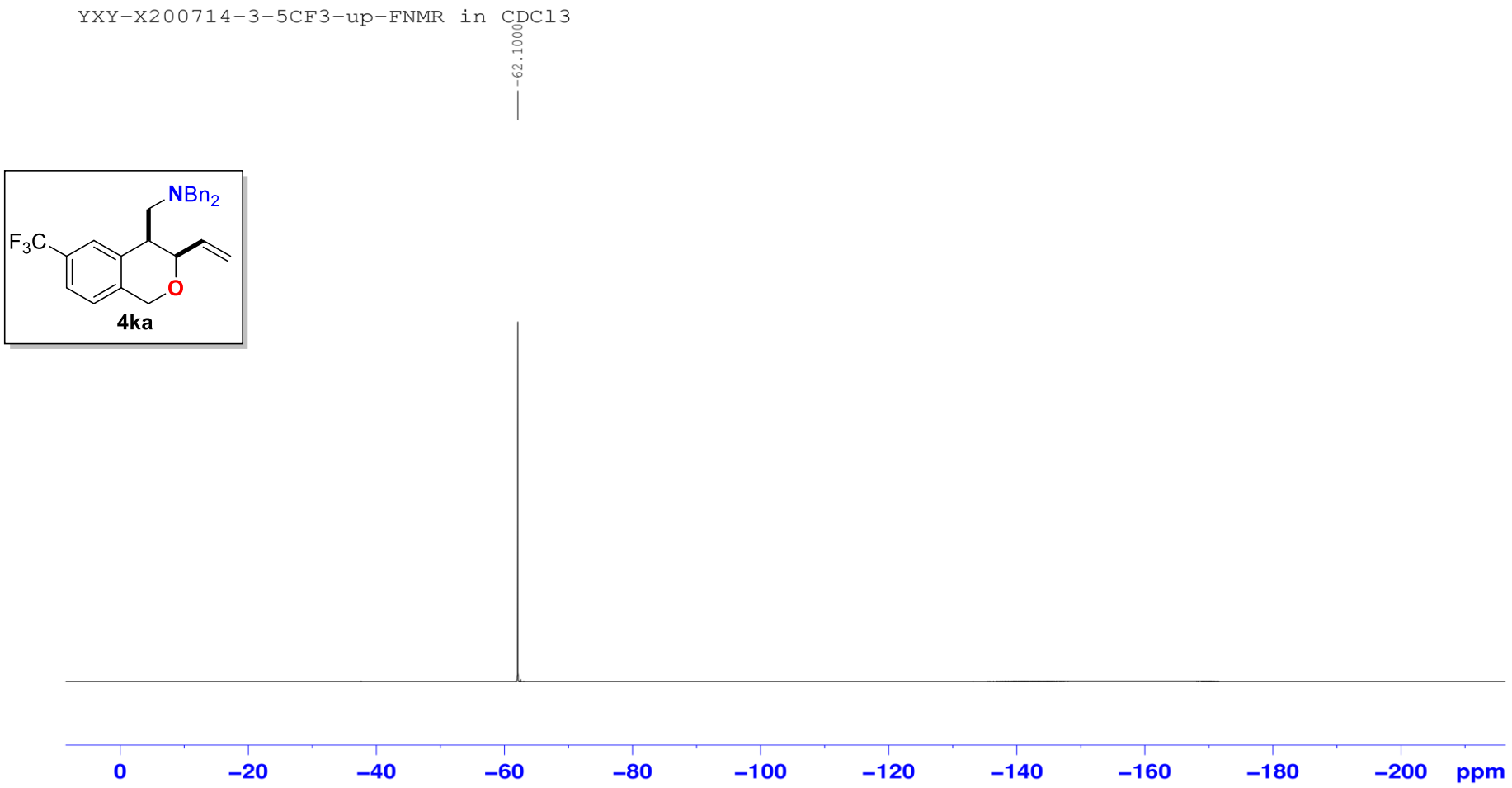
hy-P-**4ka** ^{1}H NMR (500MHz $CDCl_3$)



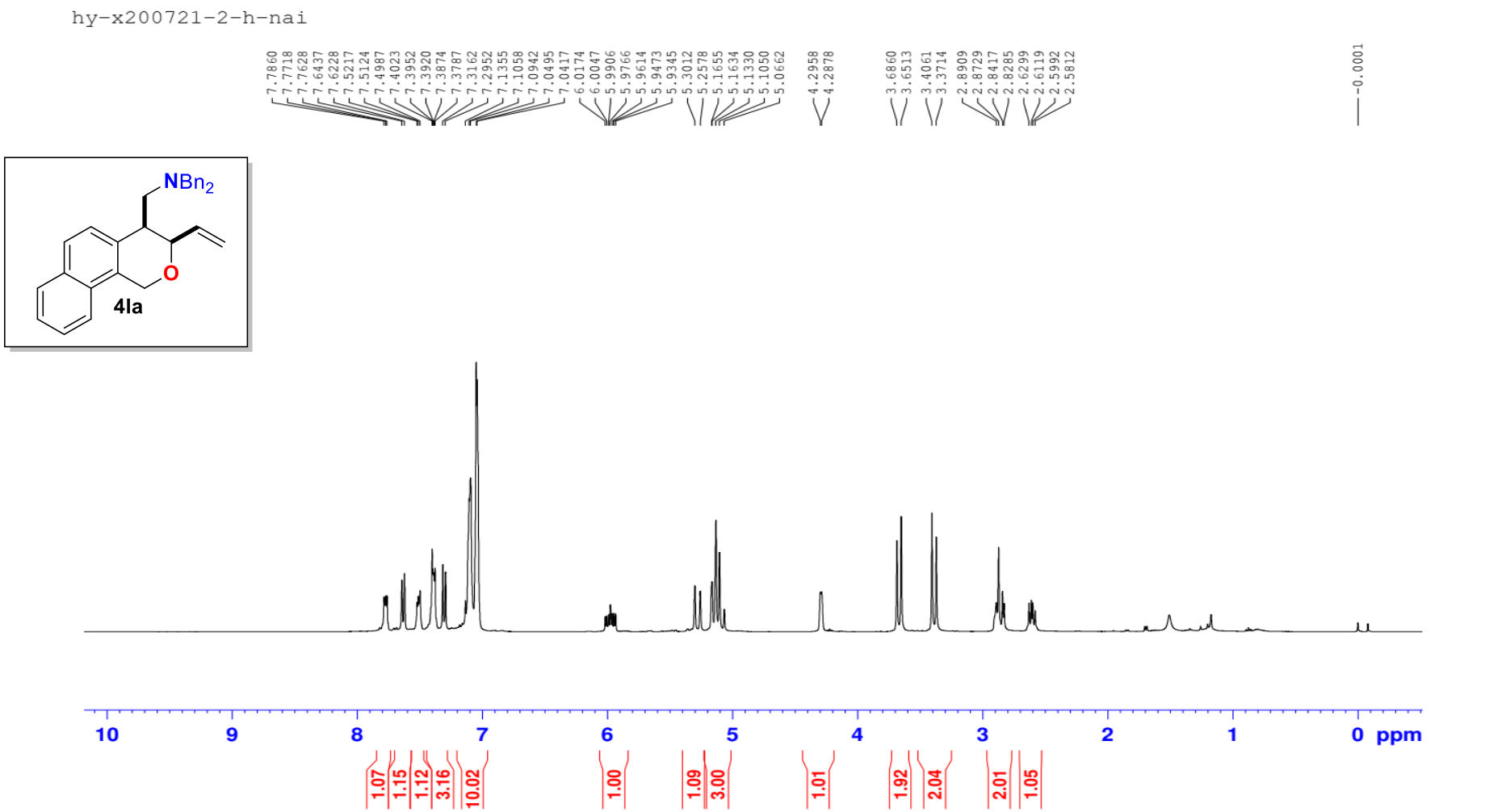
hy-P-**4ka** ^{13}C NMR (125MHz $CDCl_3$)



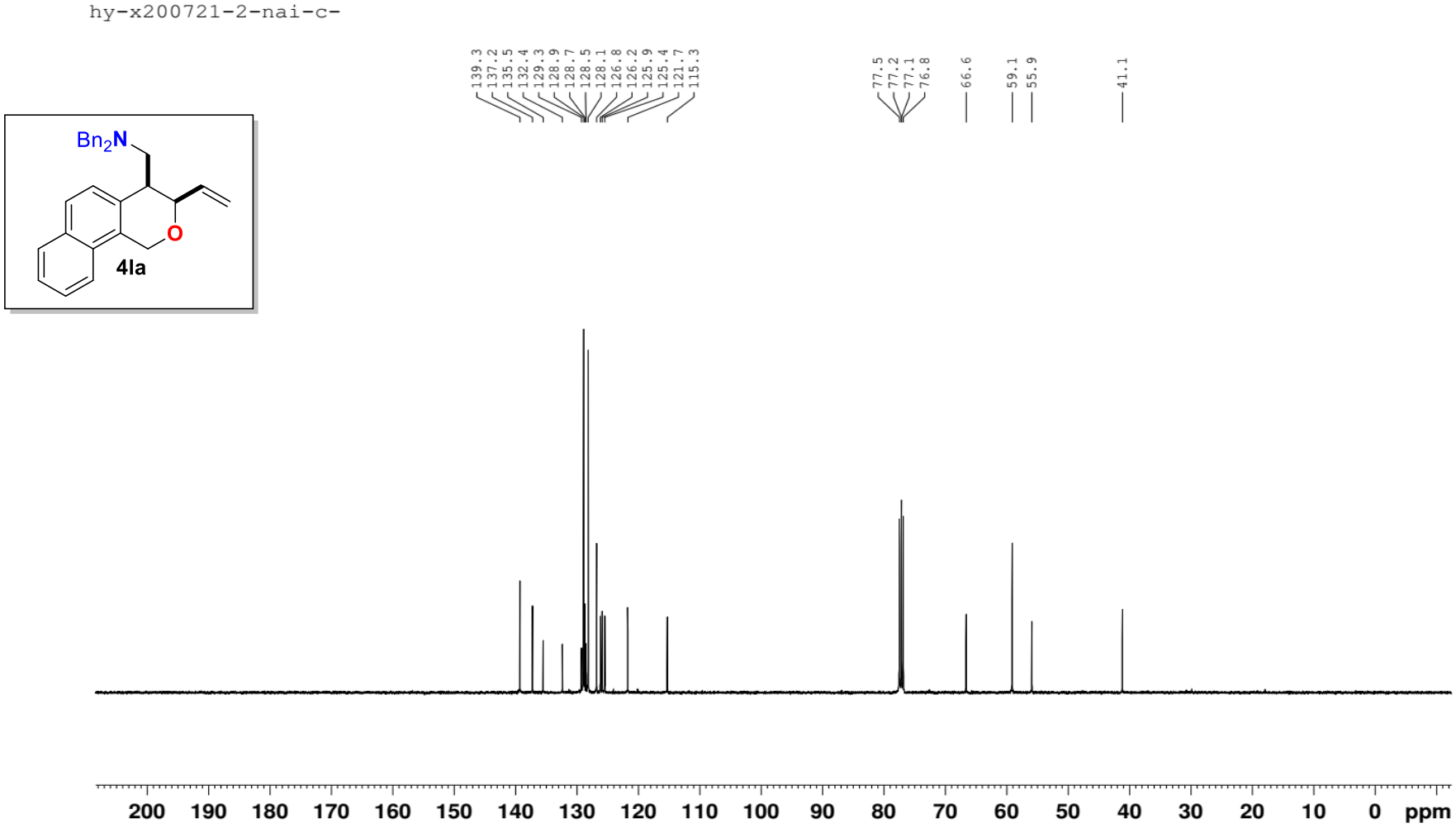
hy-P-**4ka** ^{19}F NMR (470MHz $CDCl_3$)



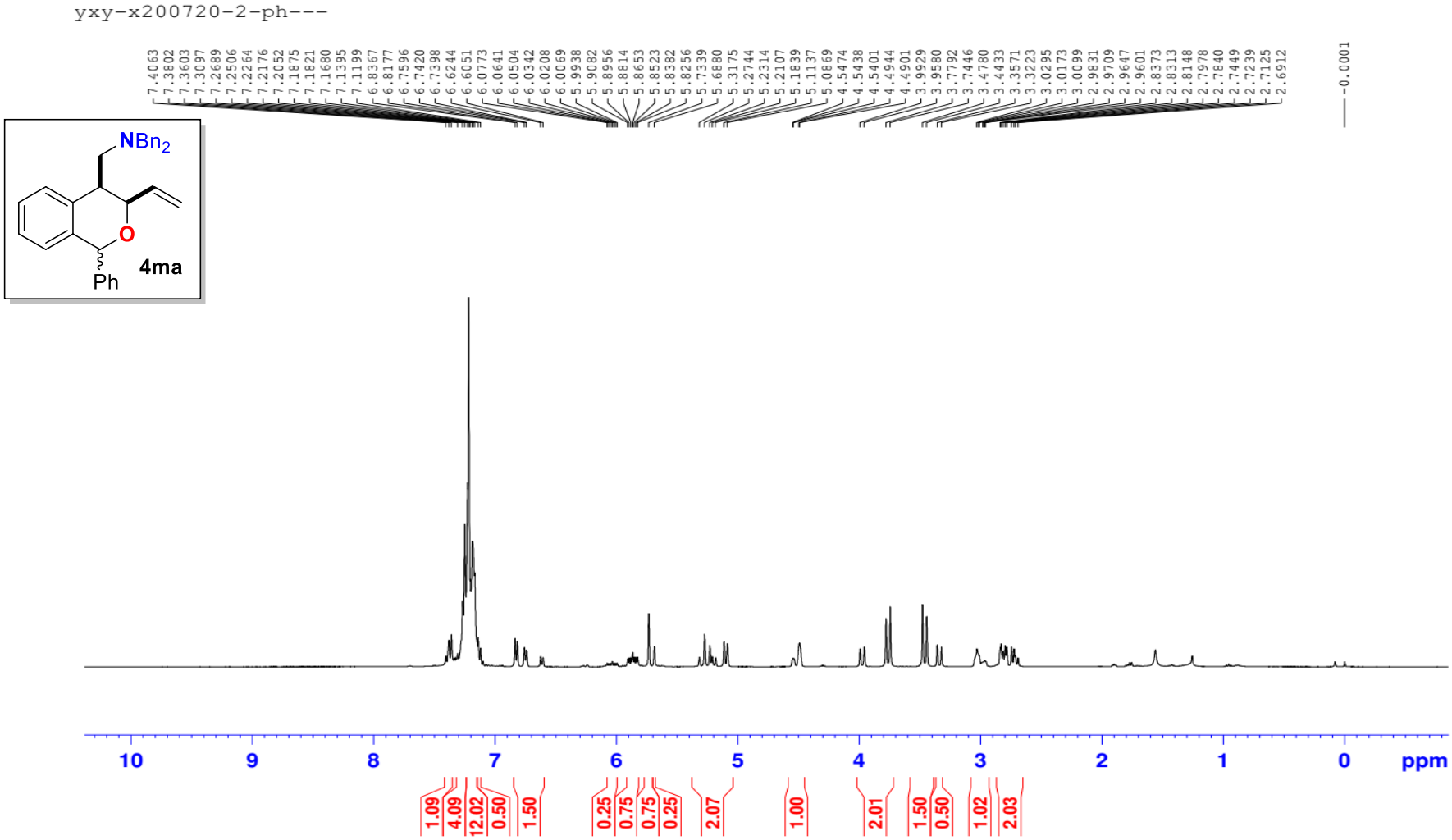
hy-P-**4la** ^{1}H NMR (400MHz $CDCl_3$)



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

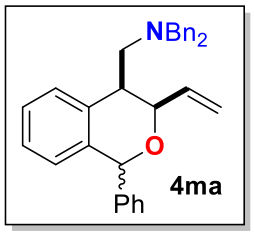


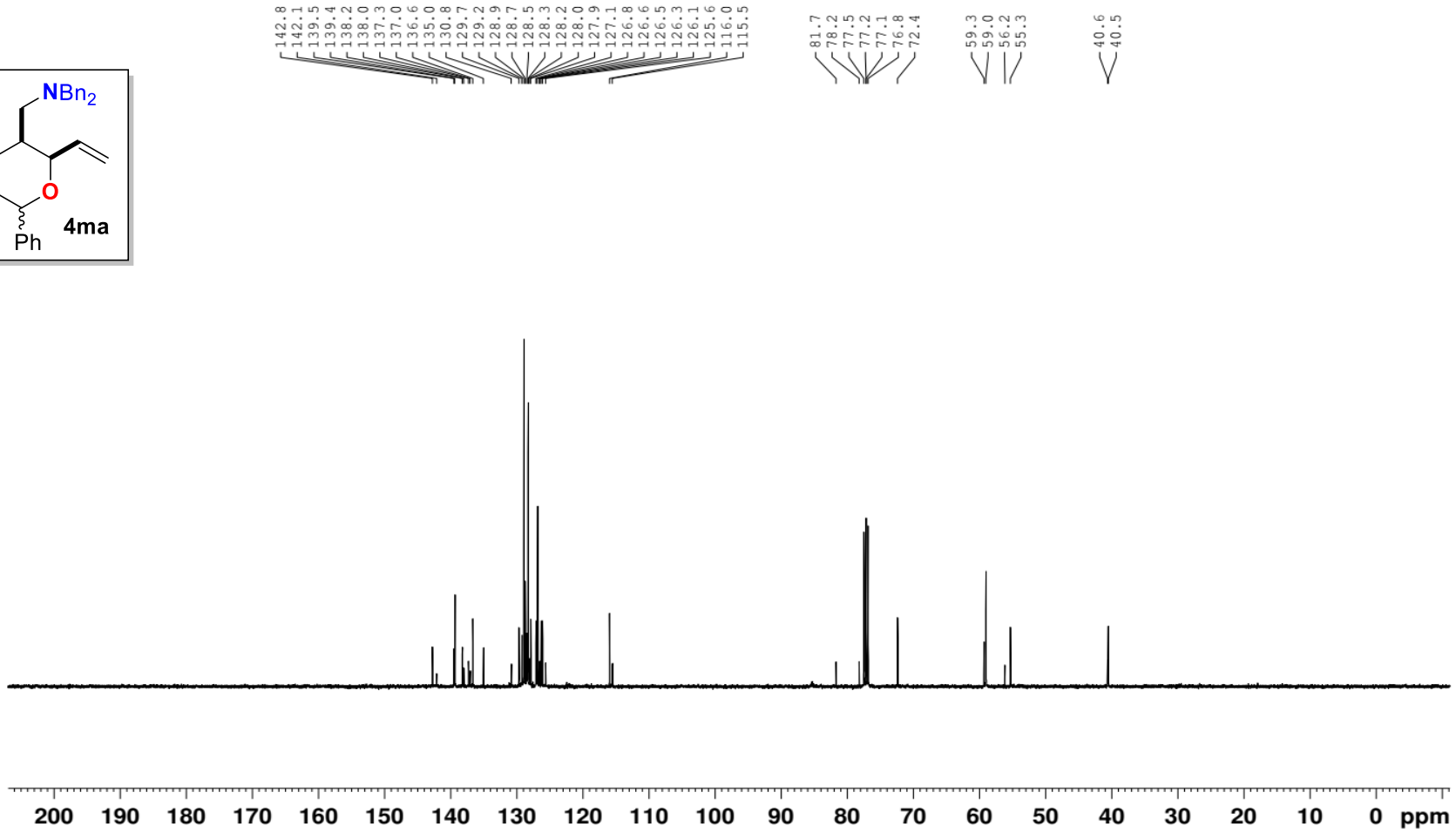
hy-P-**4ma** ^{1}H NMR (500MHz $CDCl_3$)



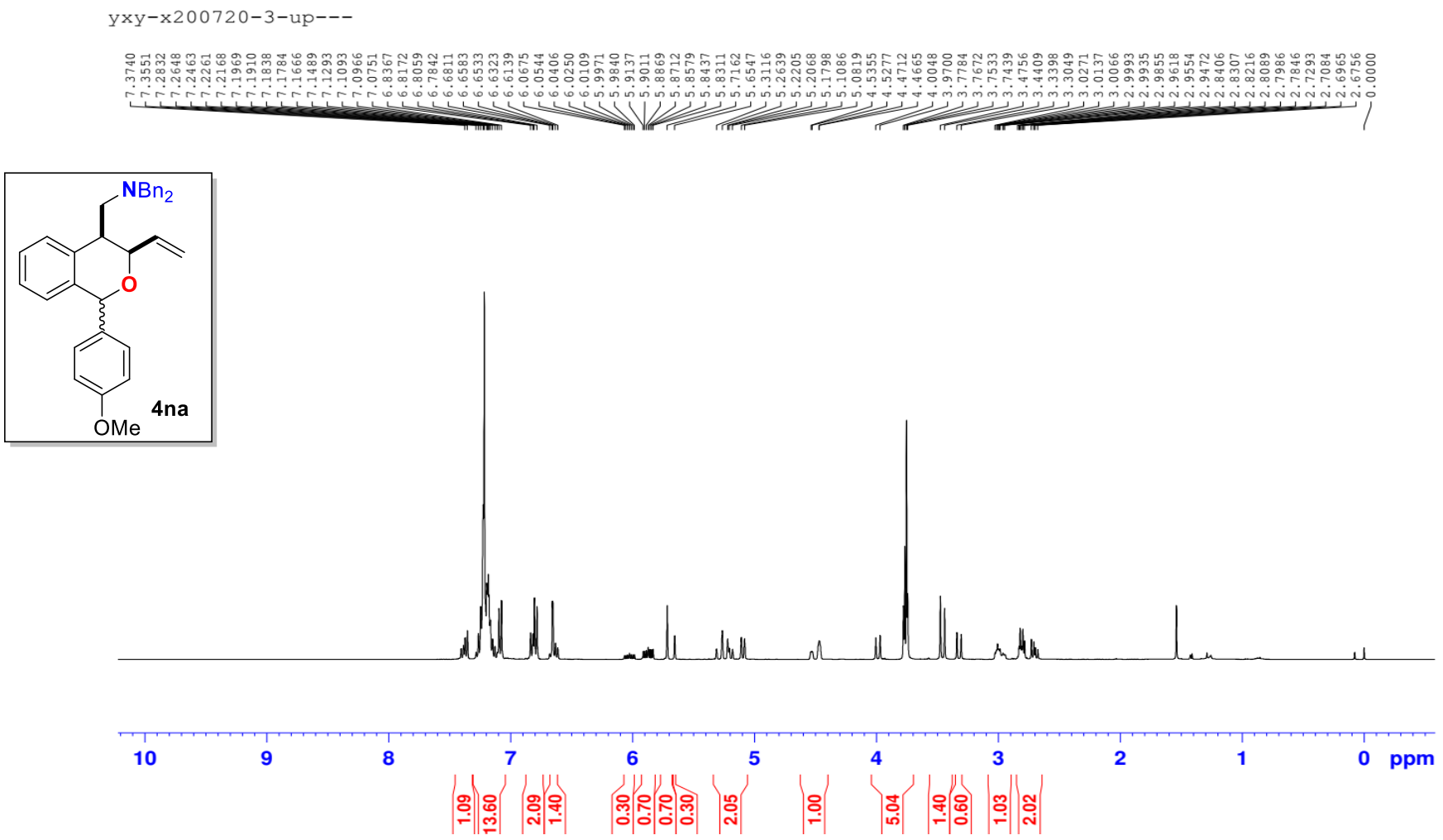
hy-P-**4ma** ^{13}C NMR (125MHz $CDCl_3$)

yxy-x200720-2-ph-c-

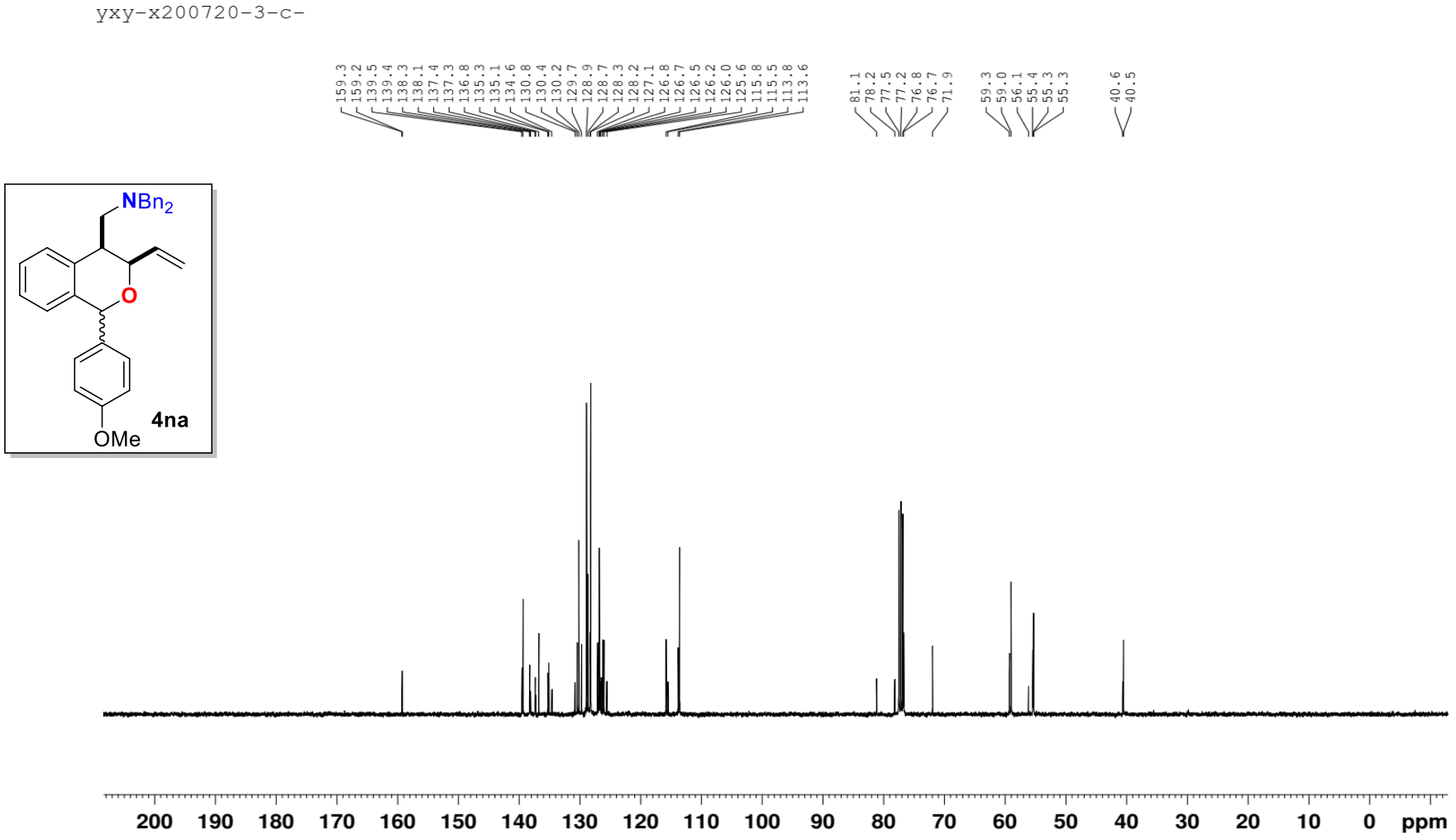




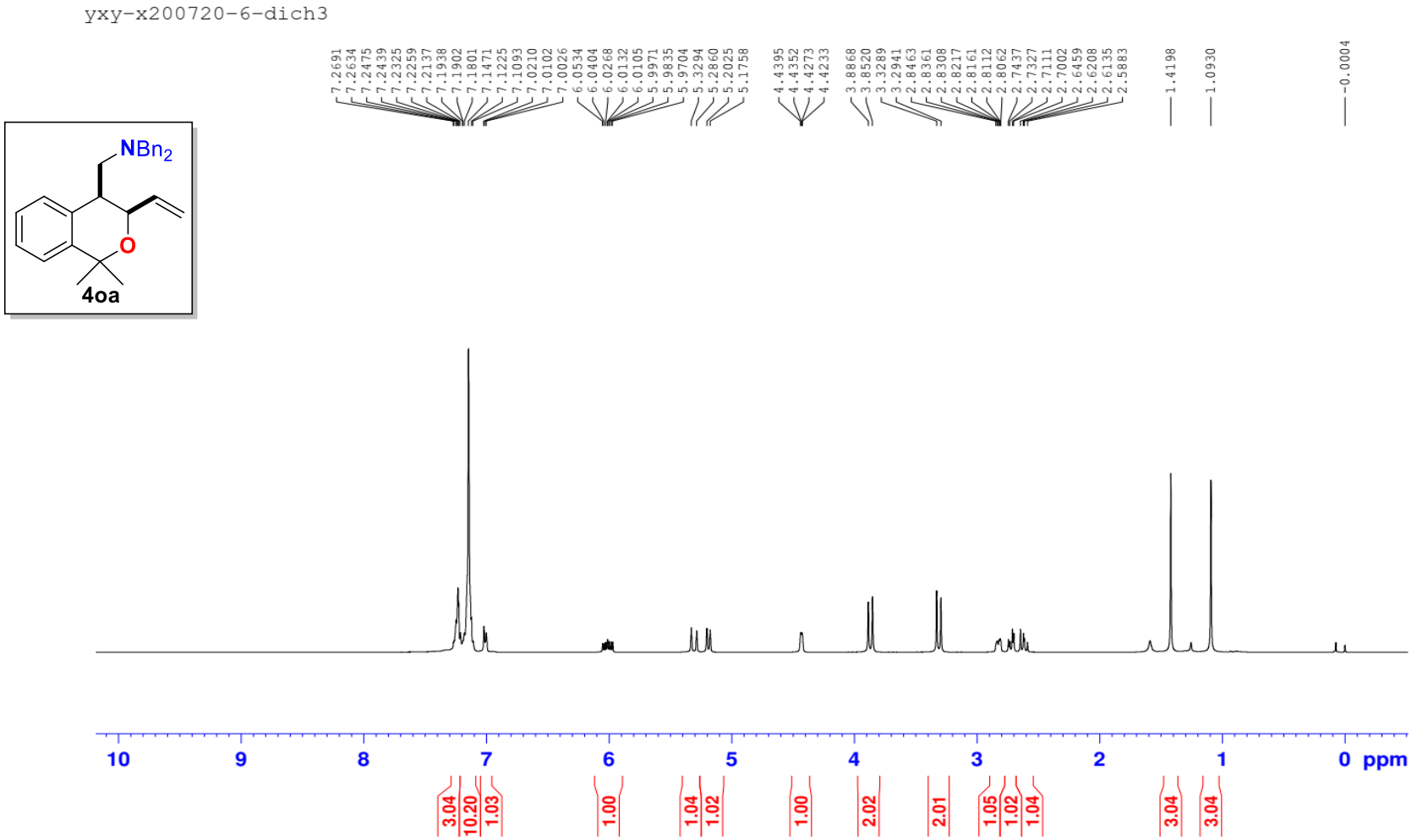
hy-P-**4na** ^{1}H NMR (400MHz $CDCl_3$)



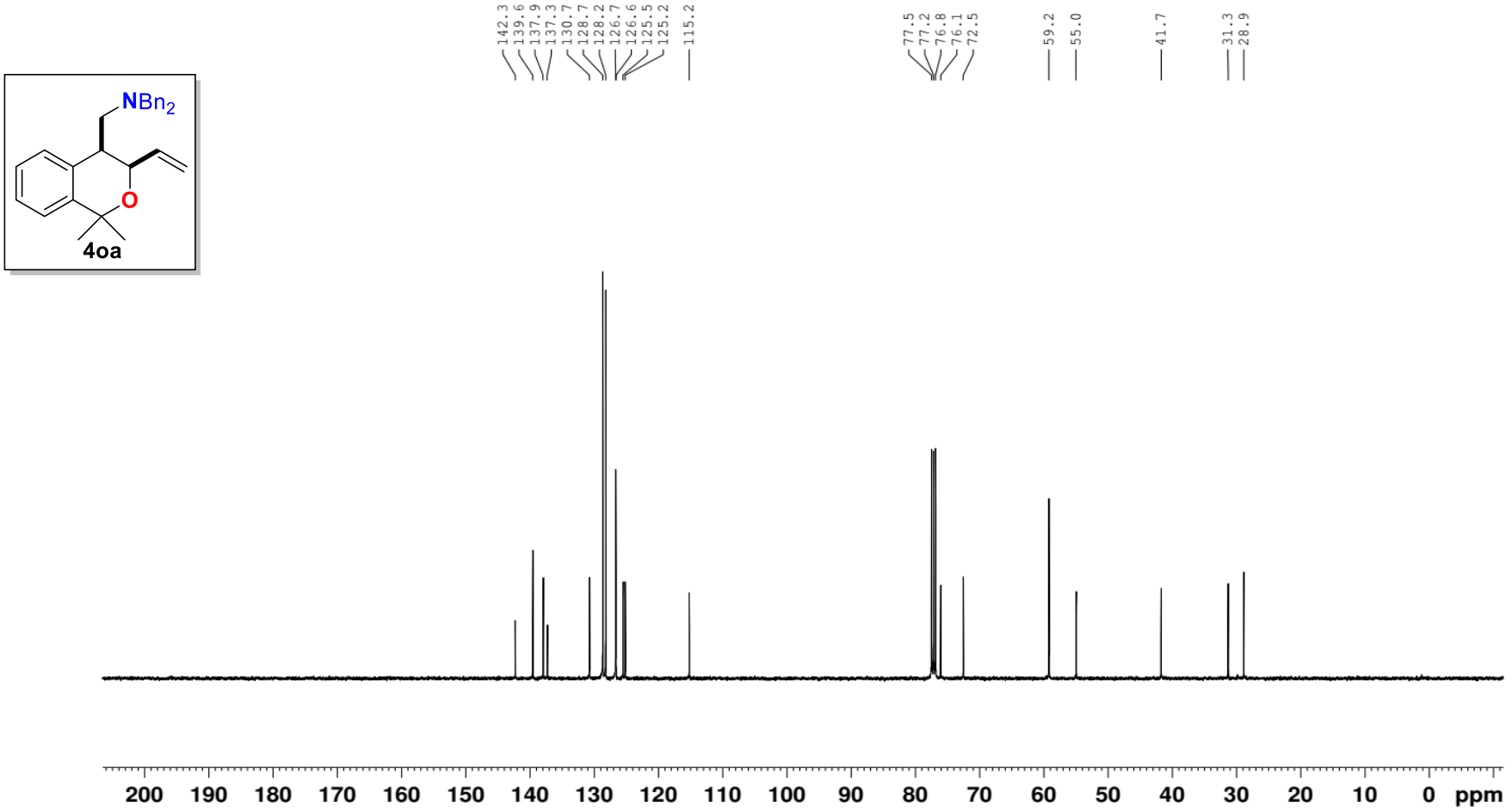
hy-P-**4na** ^{13}C NMR (100MHz $CDCl_3$)



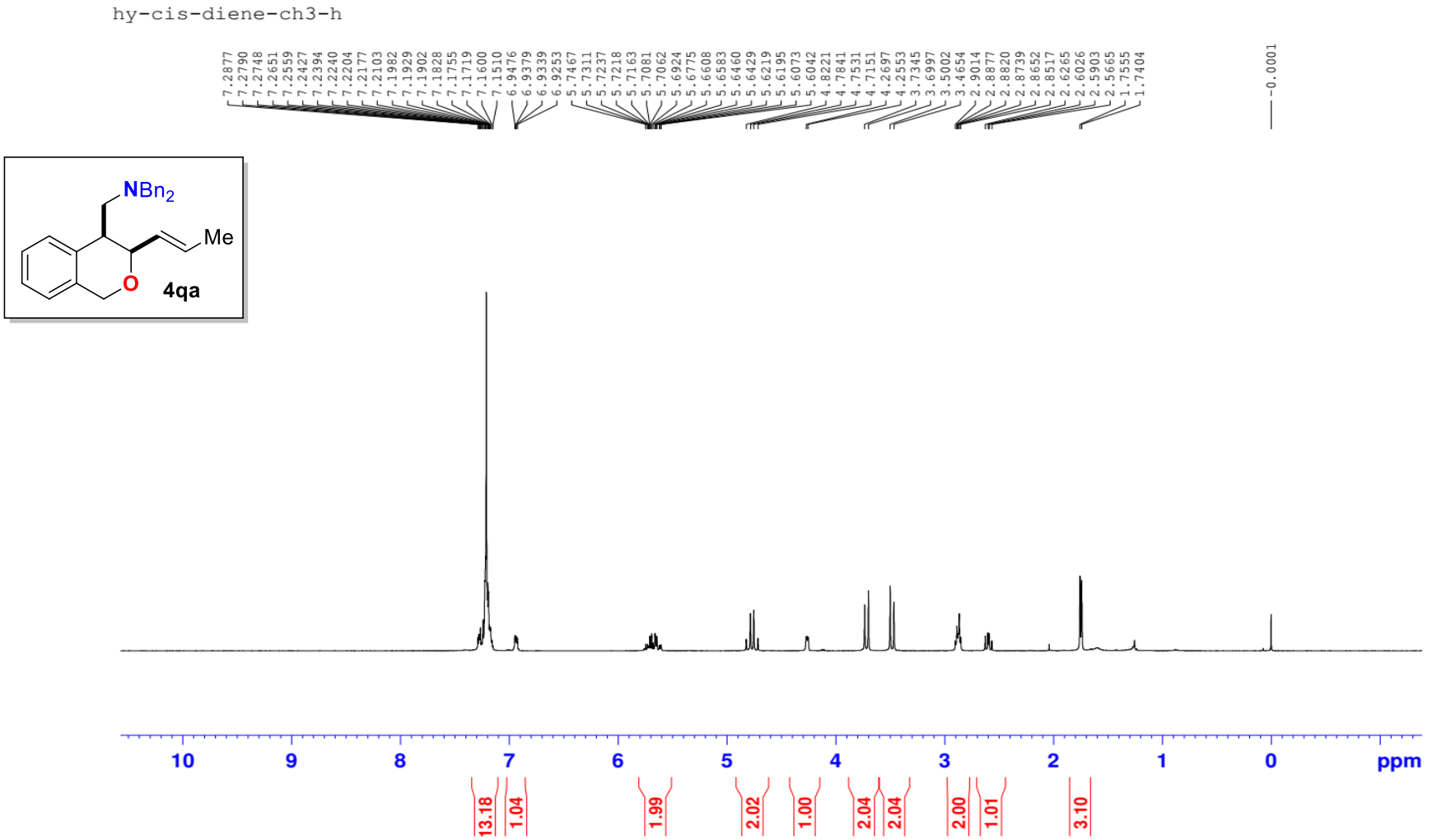
hy-P-**4oa** ^{1}H NMR (400MHz $CDCl_3$)



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

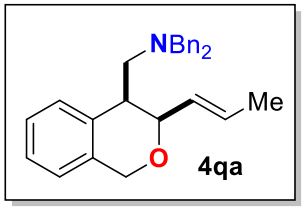


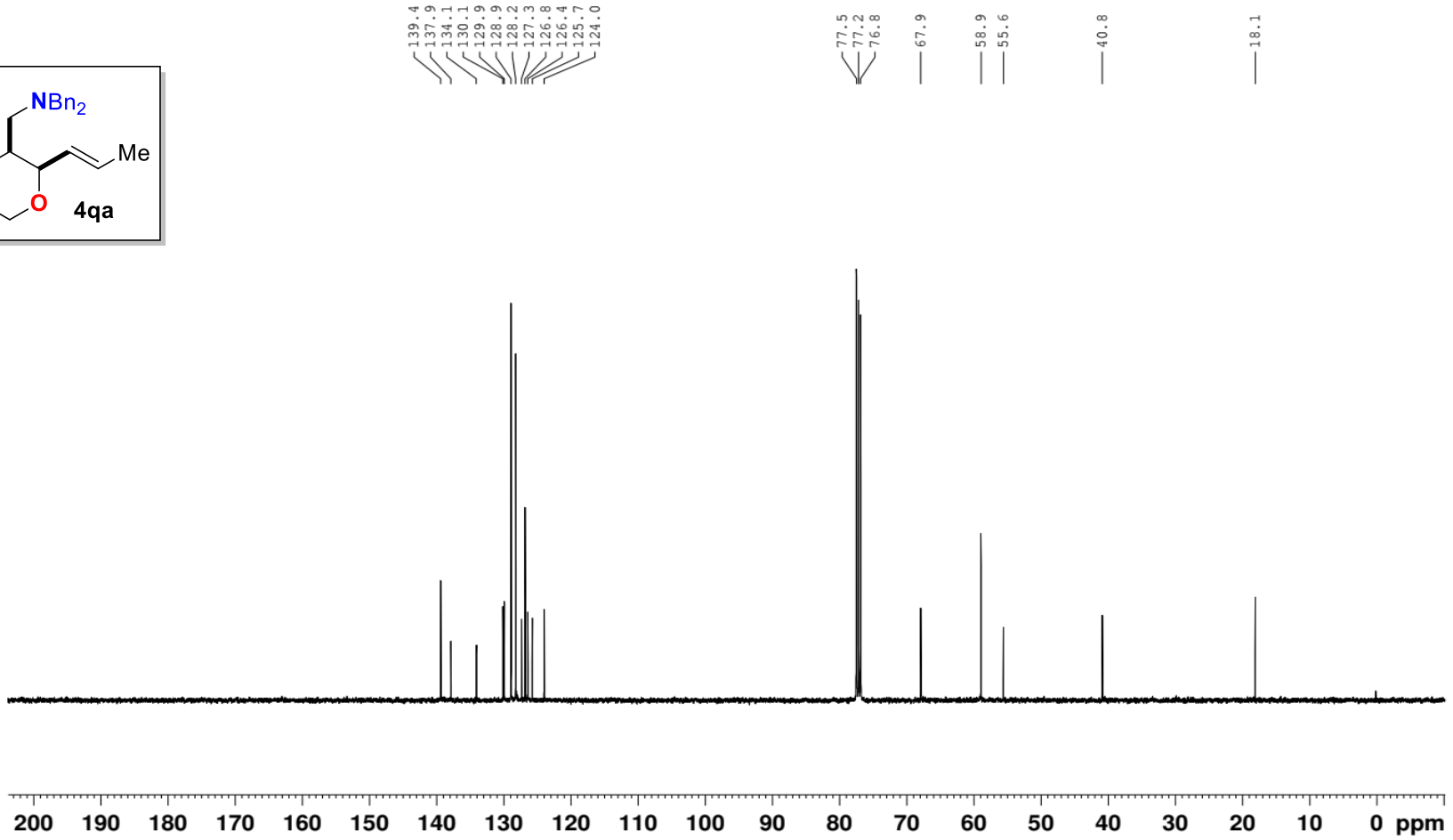
hy-P-**4qa** ^{1}H NMR (400MHz $CDCl_3$)



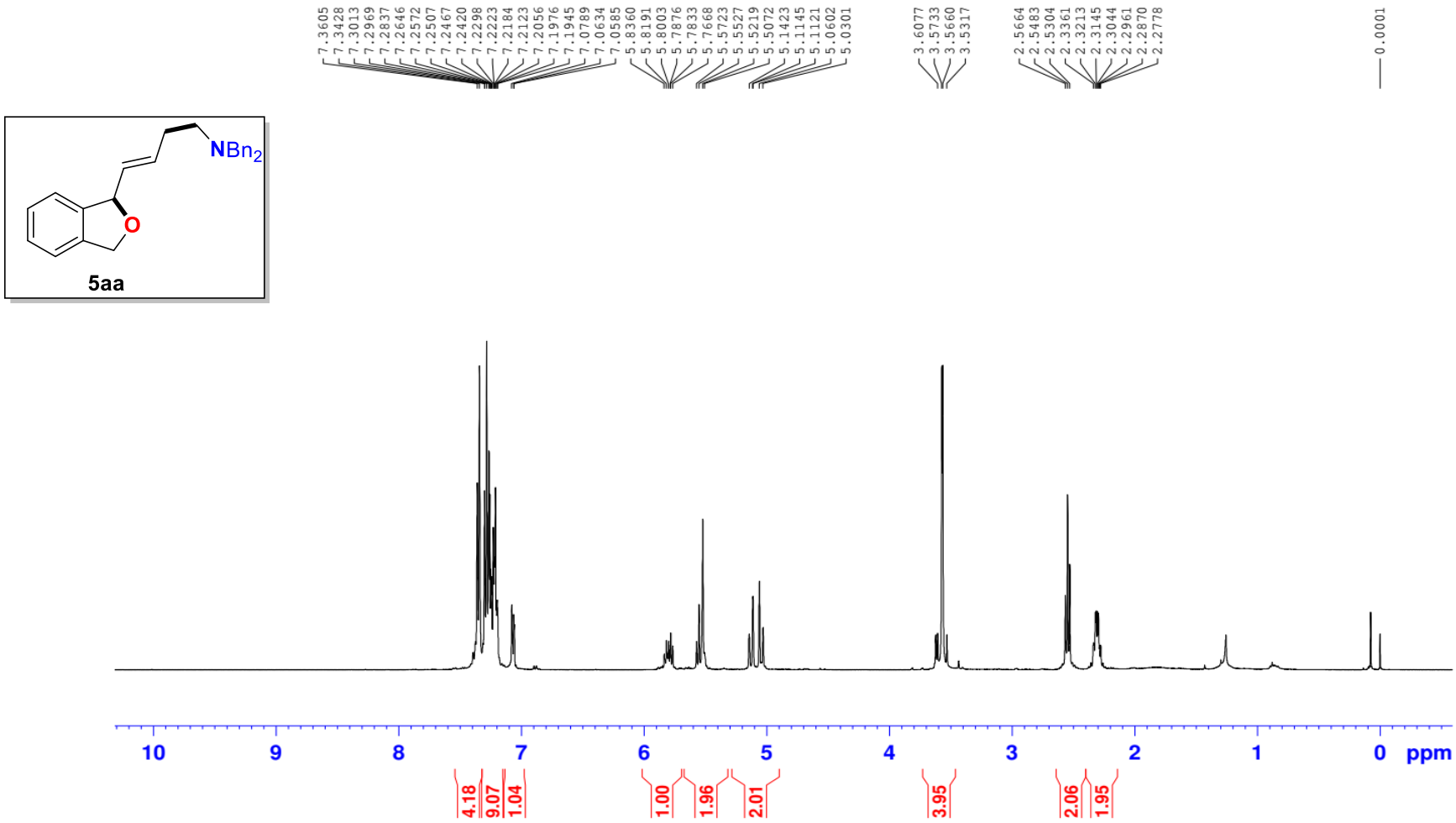
hy-P-**4qa** ^{13}C NMR (100MHz $CDCl_3$)

hy-cis-diene-ch3-c

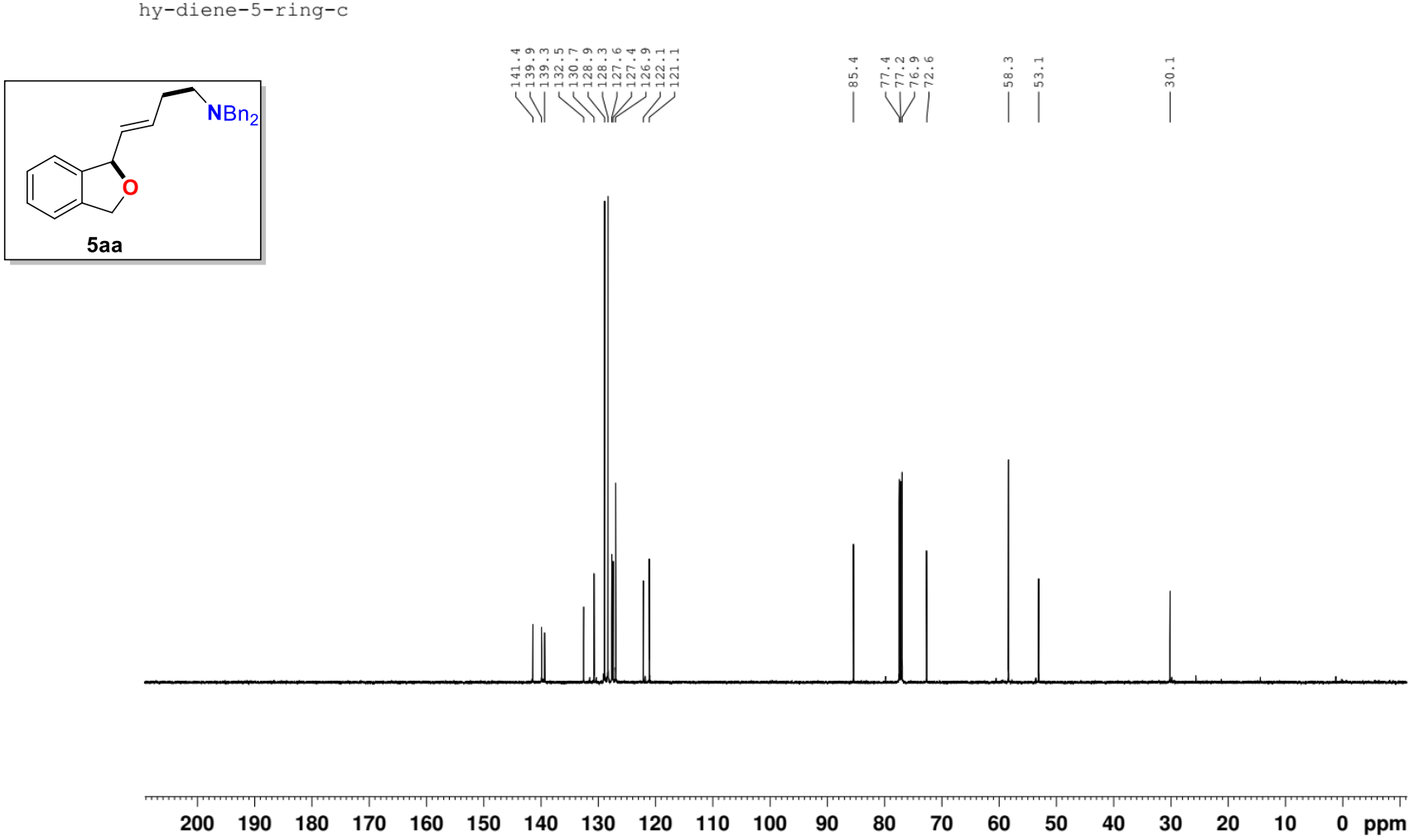




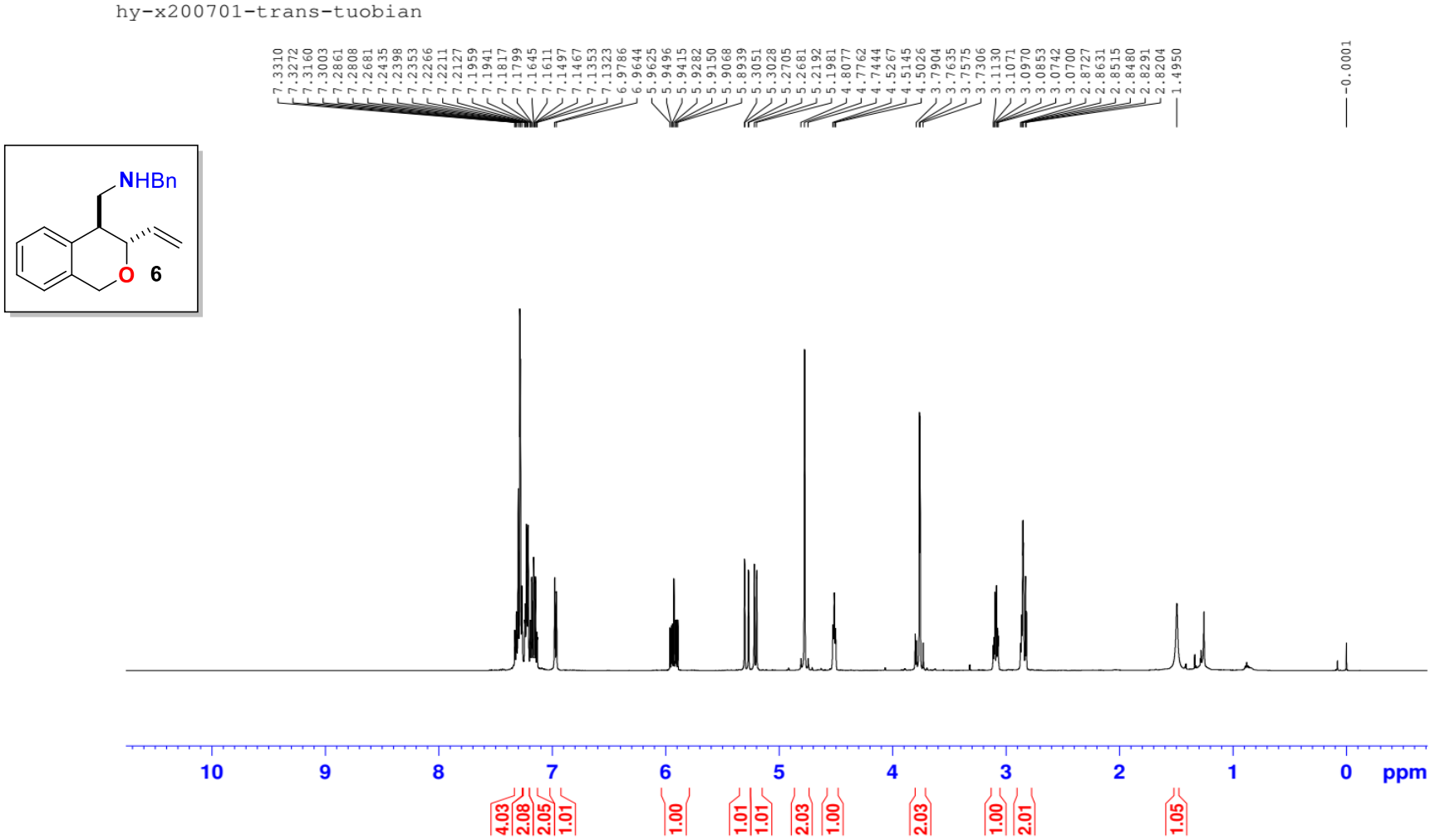
hy-P-**5aa** ^{1}H NMR (400MHz $CDCl_3$)



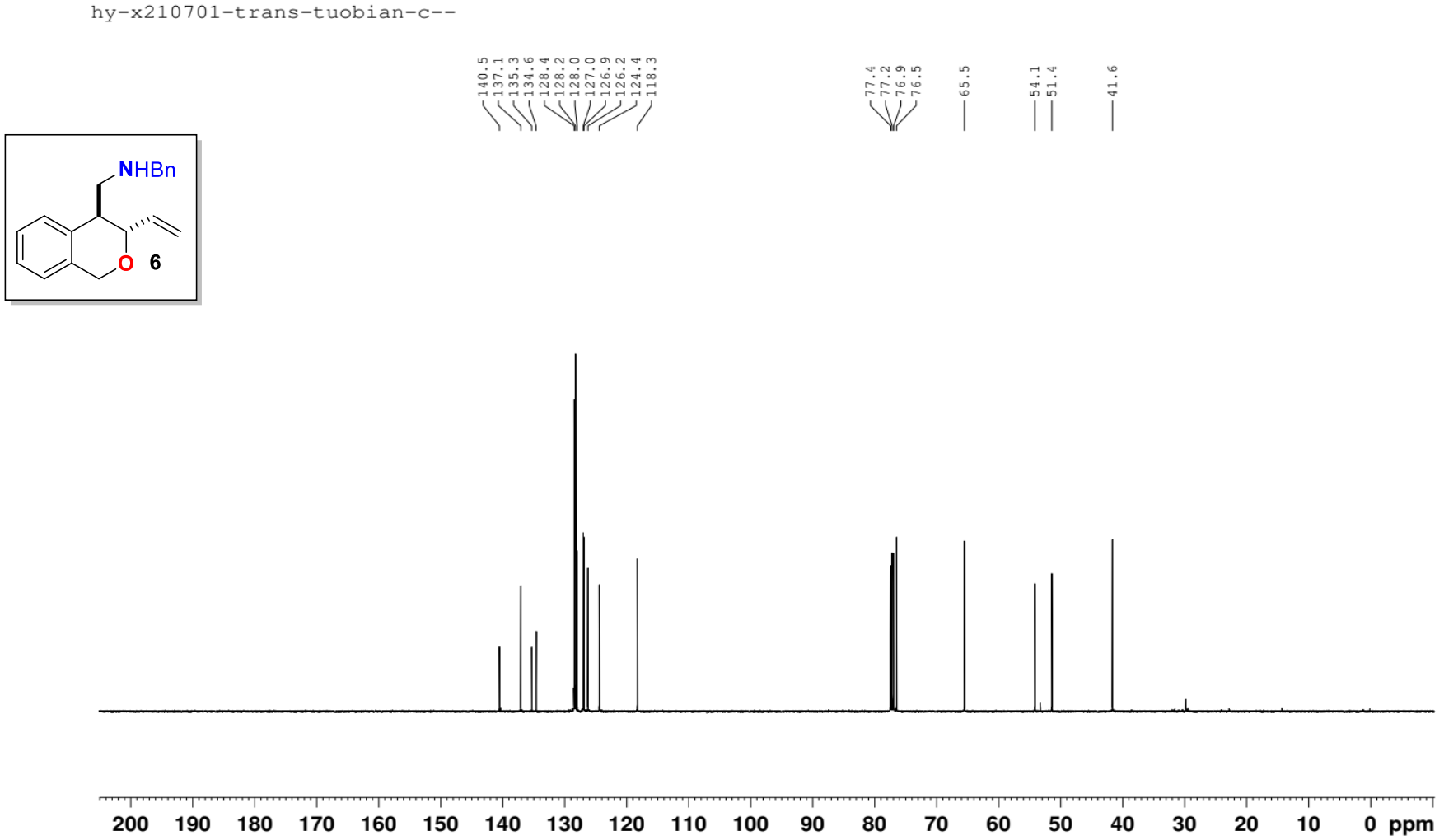
hy-P-**5aa** ^{13}C NMR (125MHz $CDCl_3$)



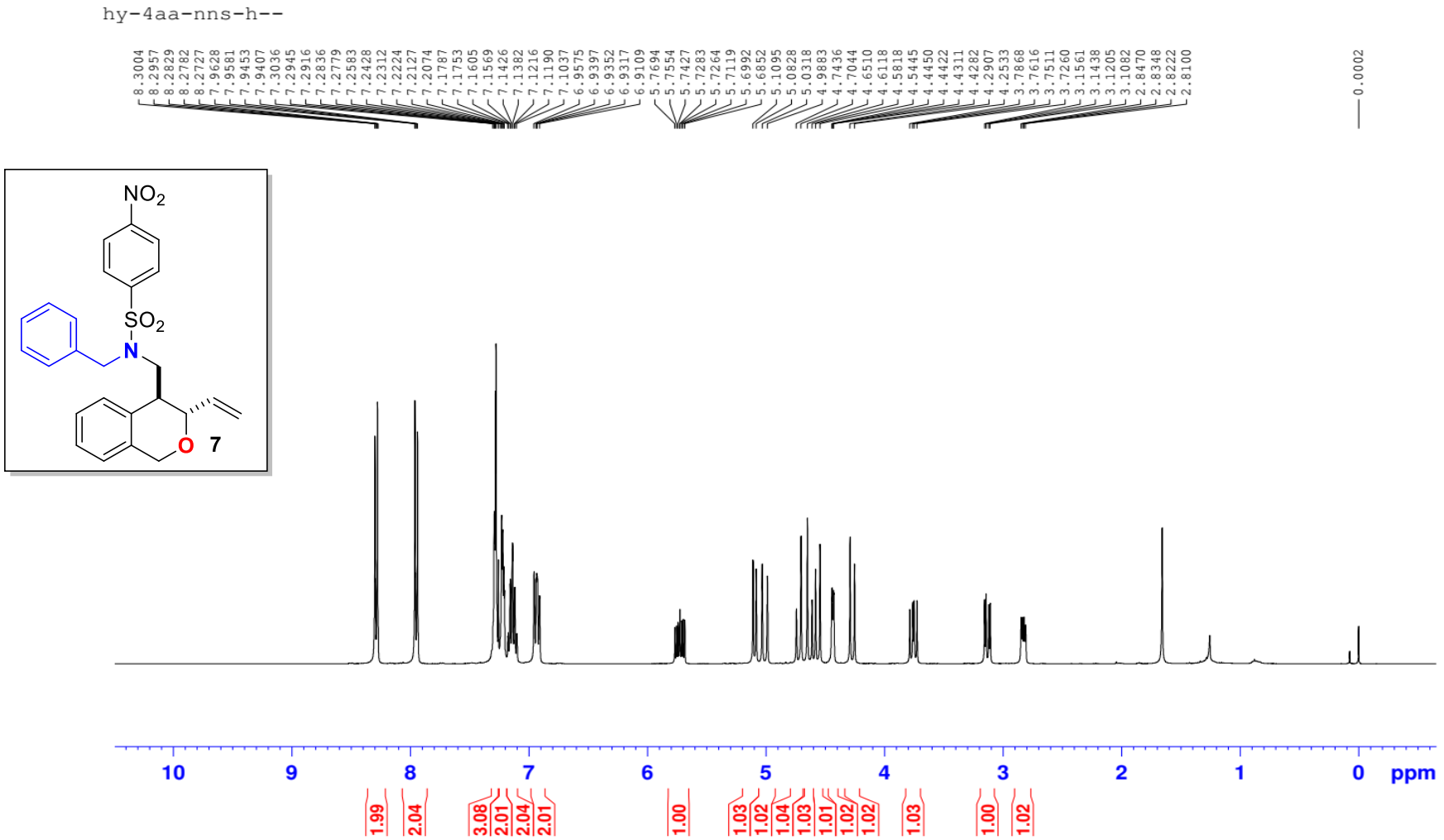
hy-P-**6** ^{1}H NMR (500MHz $CDCl_3$)



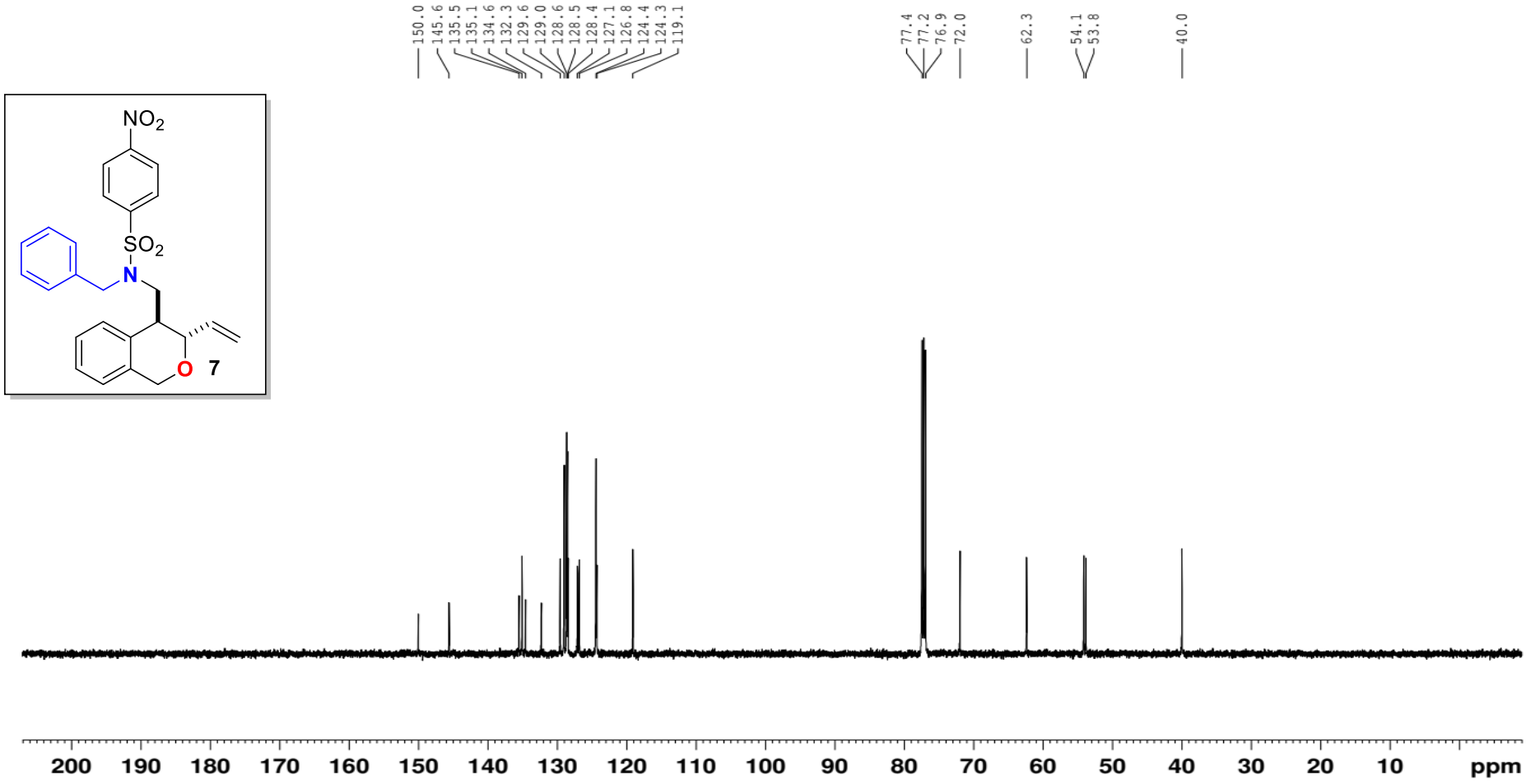
hy-P-**6** ^{13}C NMR (125MHz $CDCl_3$)



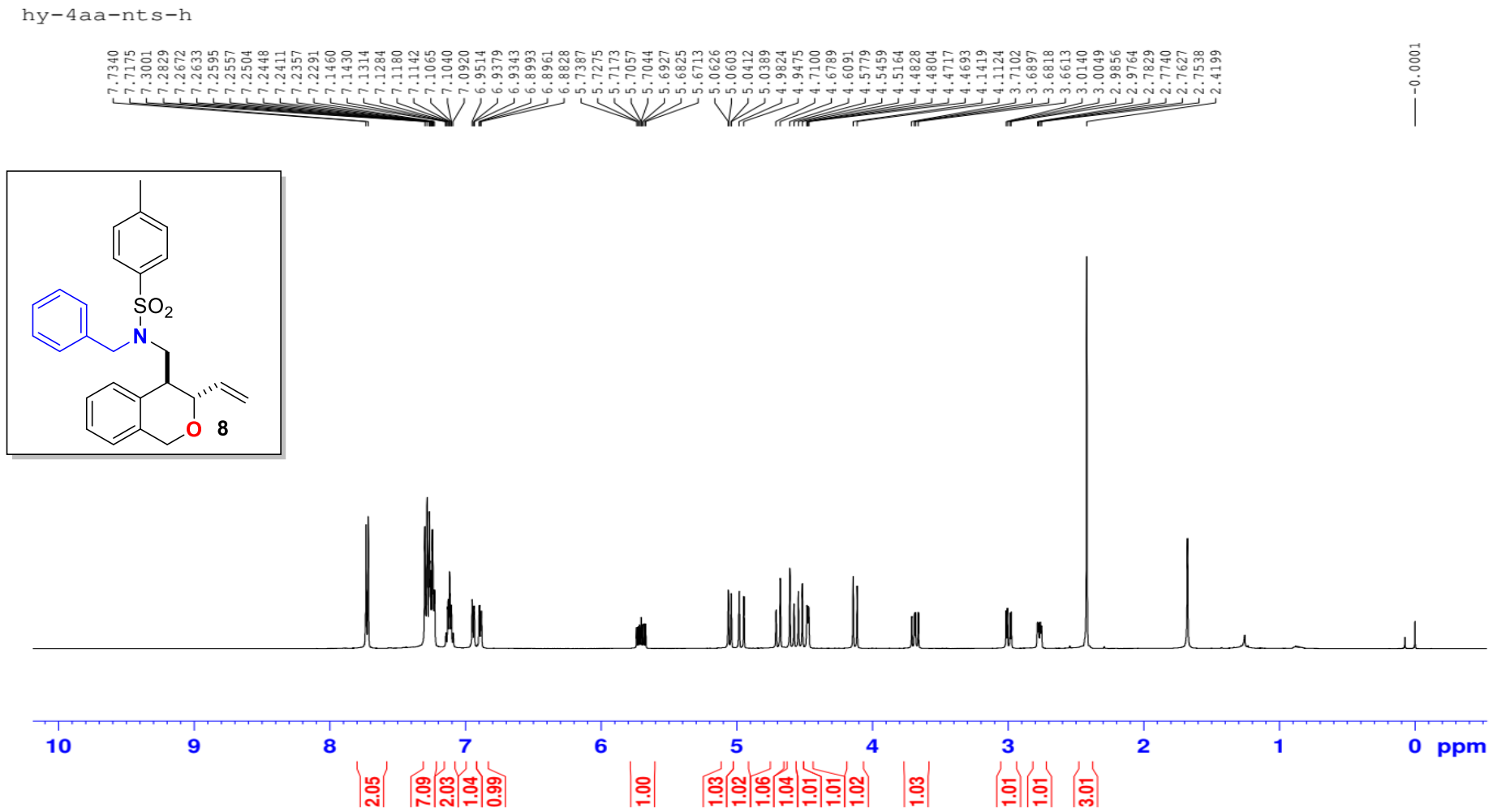
hy-P-**7** ^{1}H NMR (400MHz $CDCl_3$)



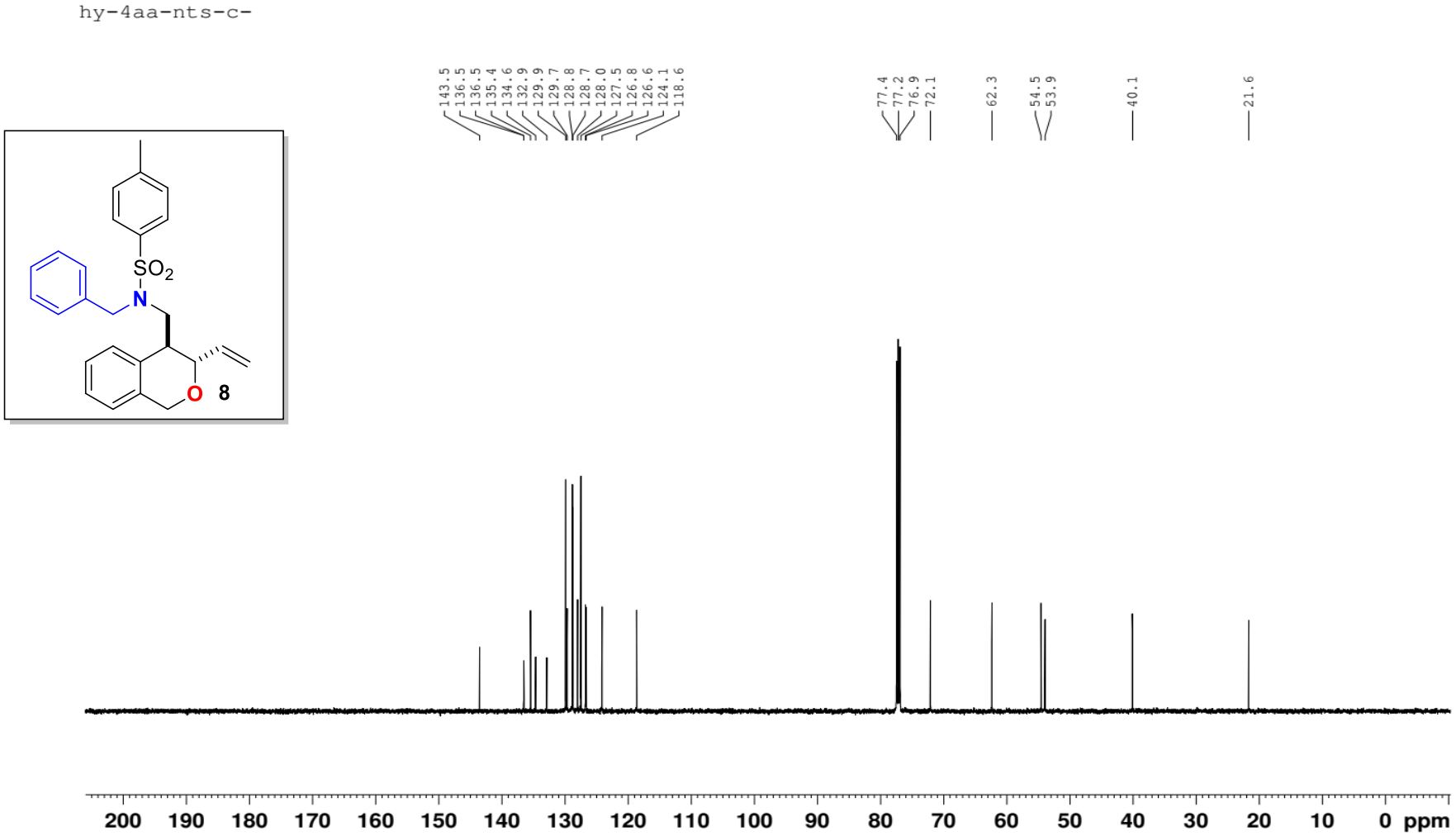
hy-P-**7** ^{13}C NMR (100MHz $CDCl_3$)



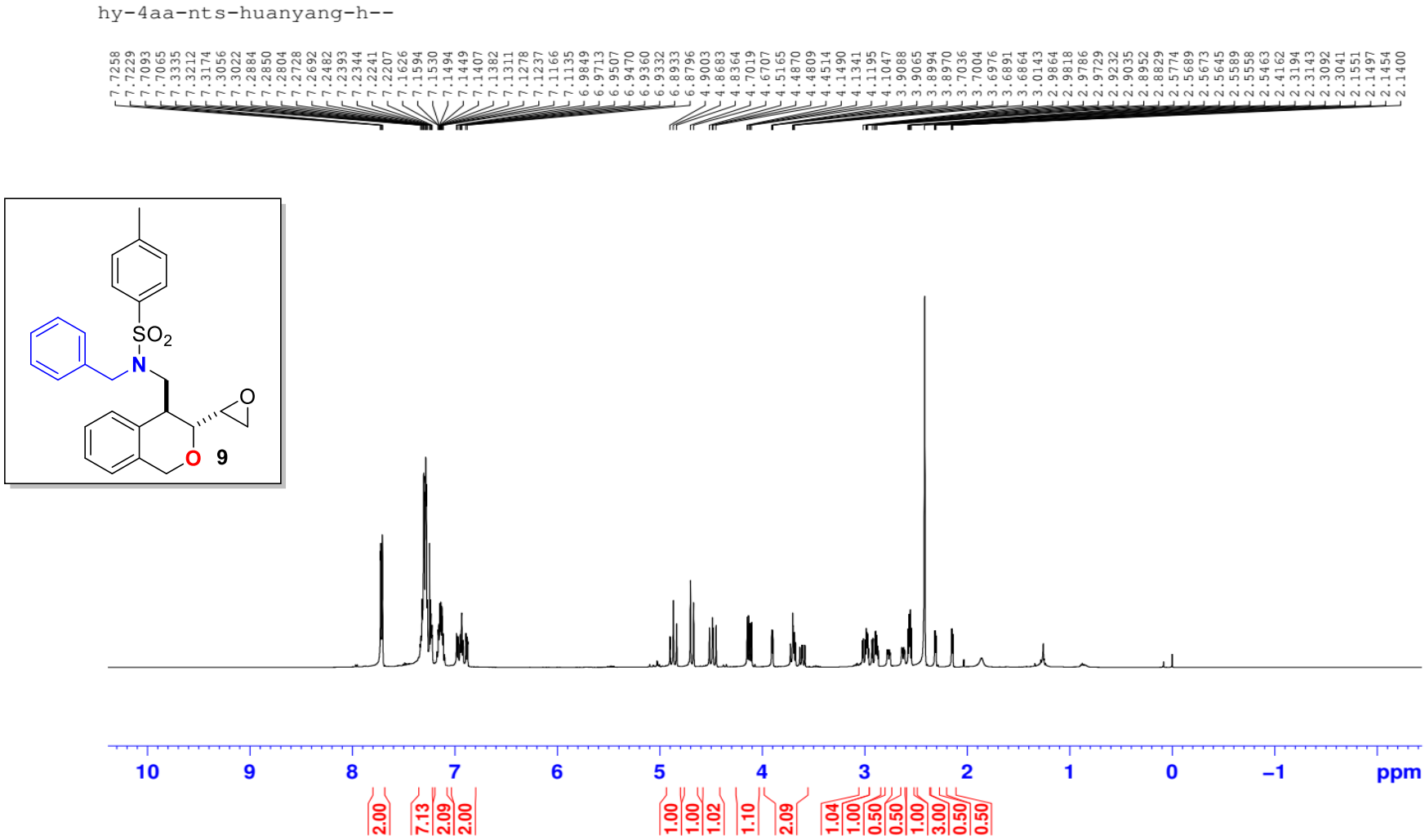
hy-P-**8** ^{1}H NMR (500MHz $CDCl_3$)



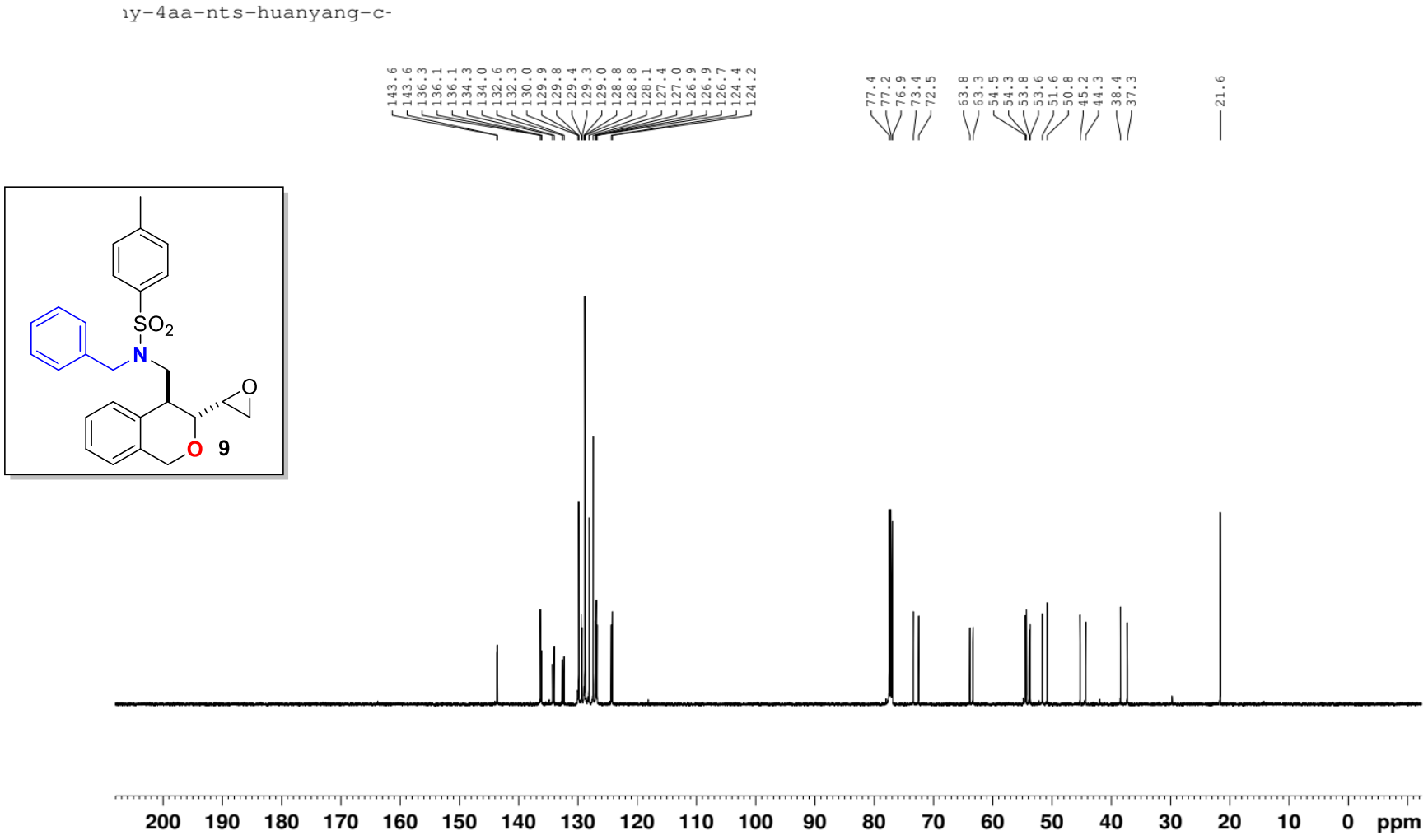
hy-P-**8** ^{13}C NMR (125MHz $CDCl_3$)



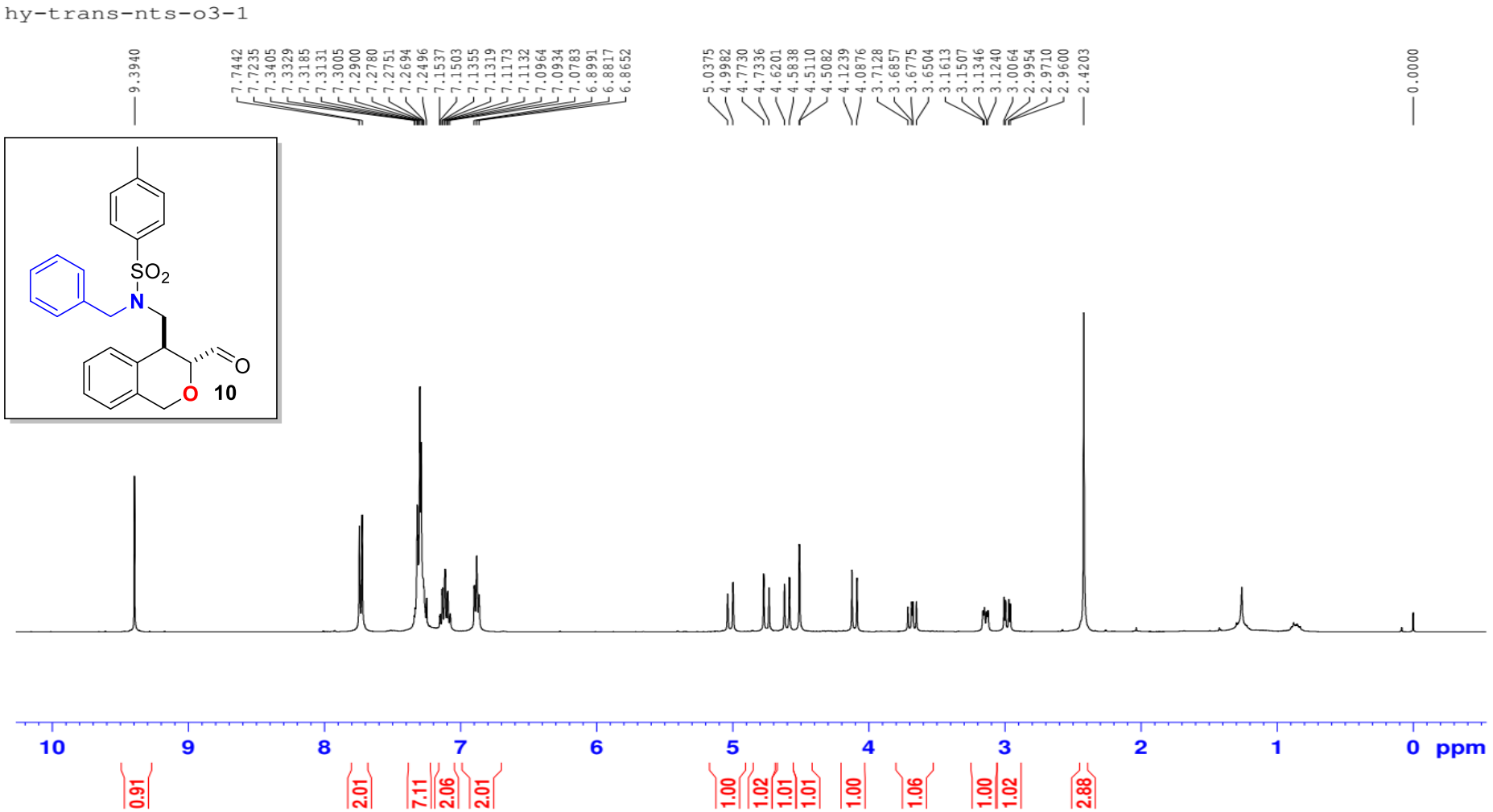
hy-P-**9** ^{1}H NMR (500MHz $CDCl_3$)



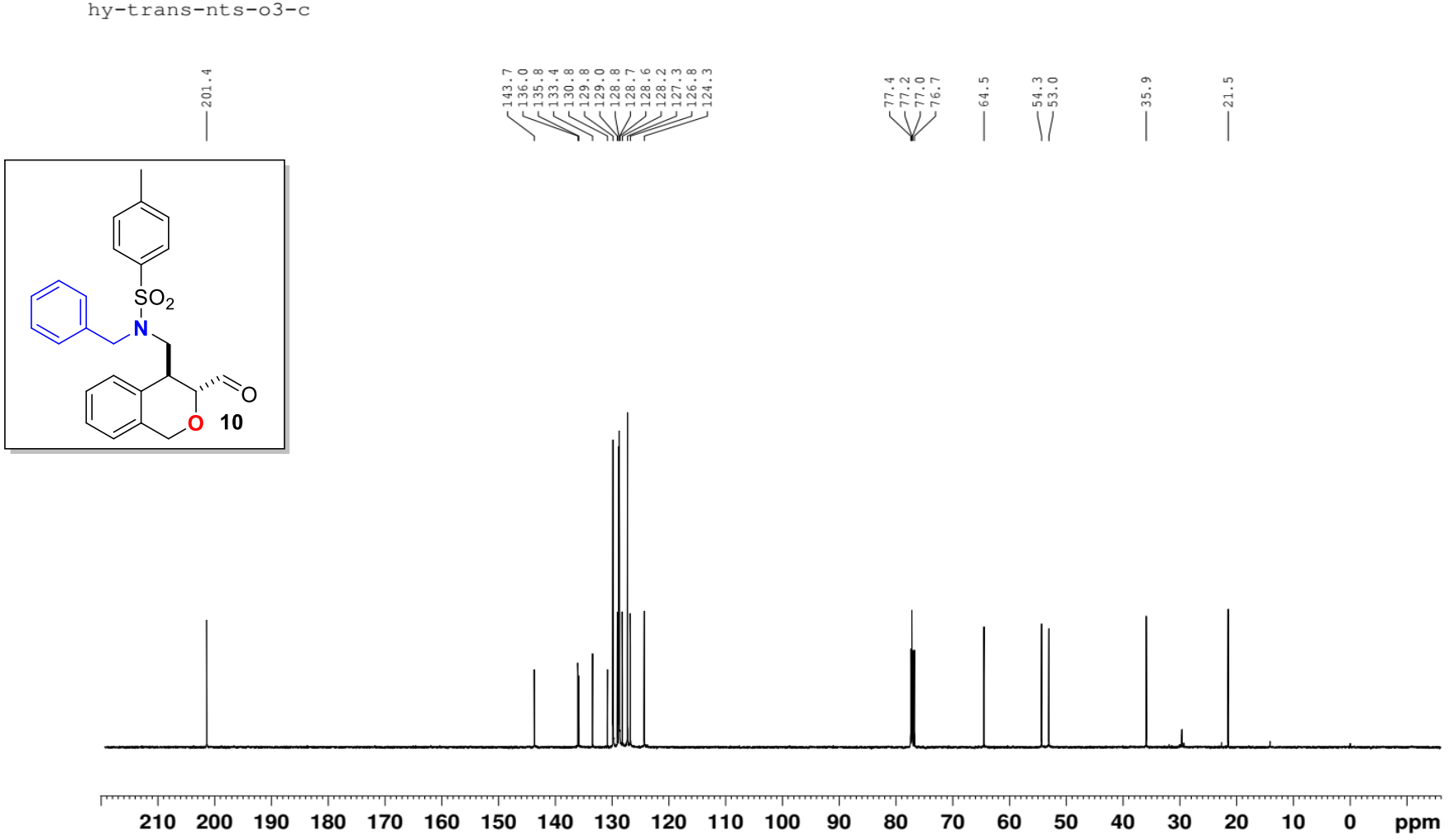
hy-P-**9** ^{13}C NMR (125MHz $CDCl_3$)



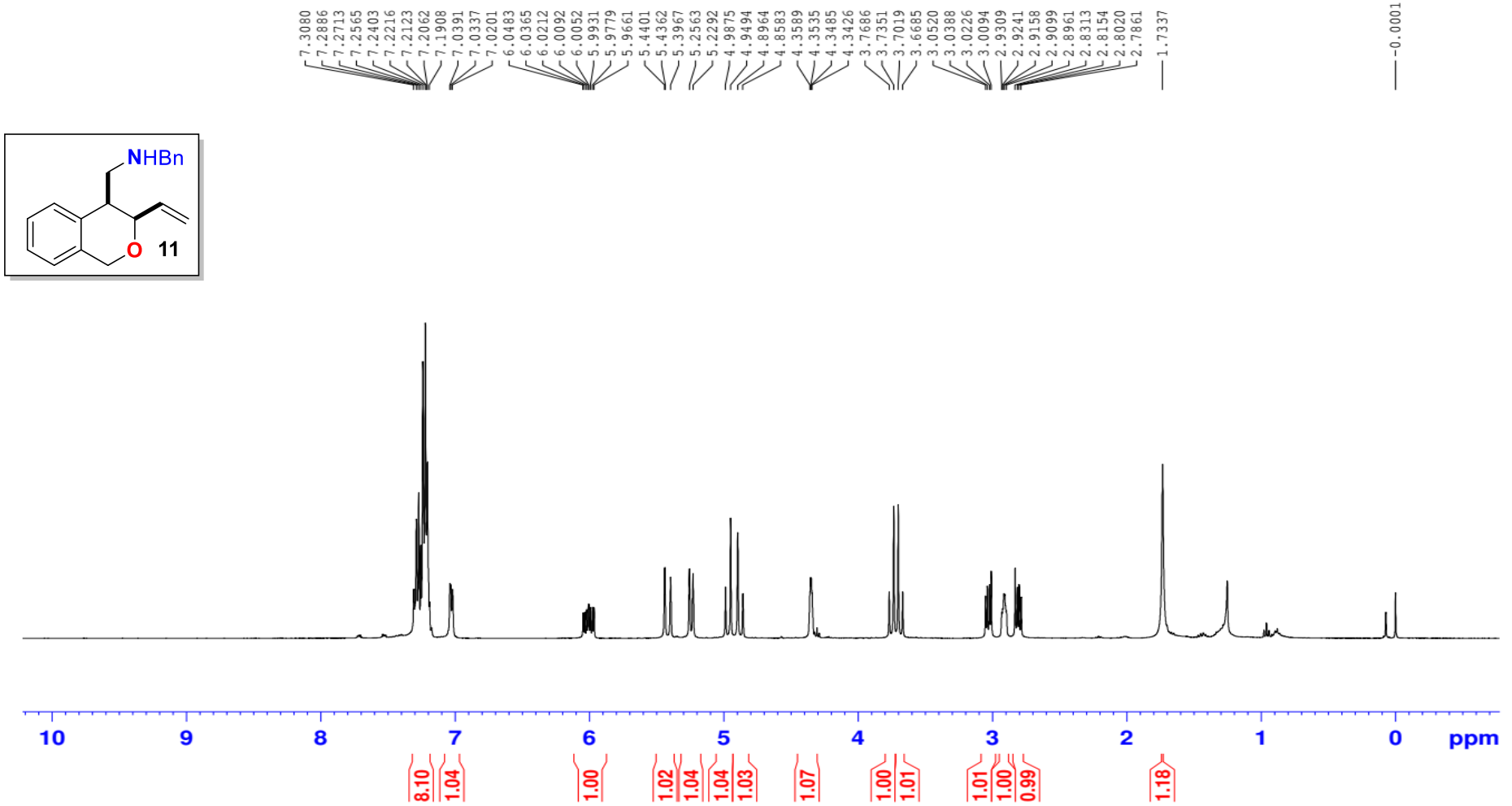
hy-P-**10** ^{1}H NMR (400MHz $CDCl_3$)



hy-P-**10** ^{13}C NMR (100MHz $CDCl_3$)

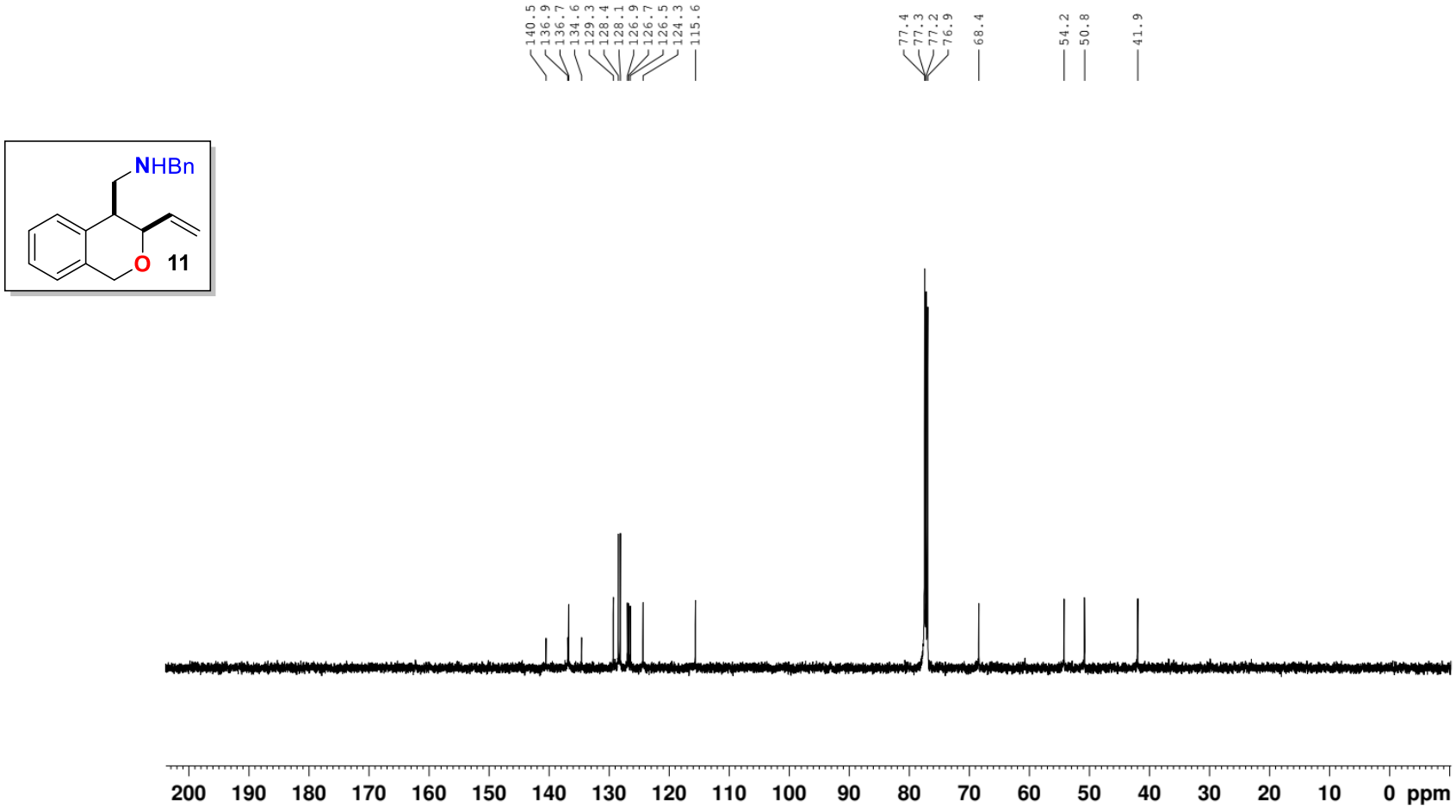


hy-P-**11** ^{1}H NMR (400MHz $CDCl_3$)

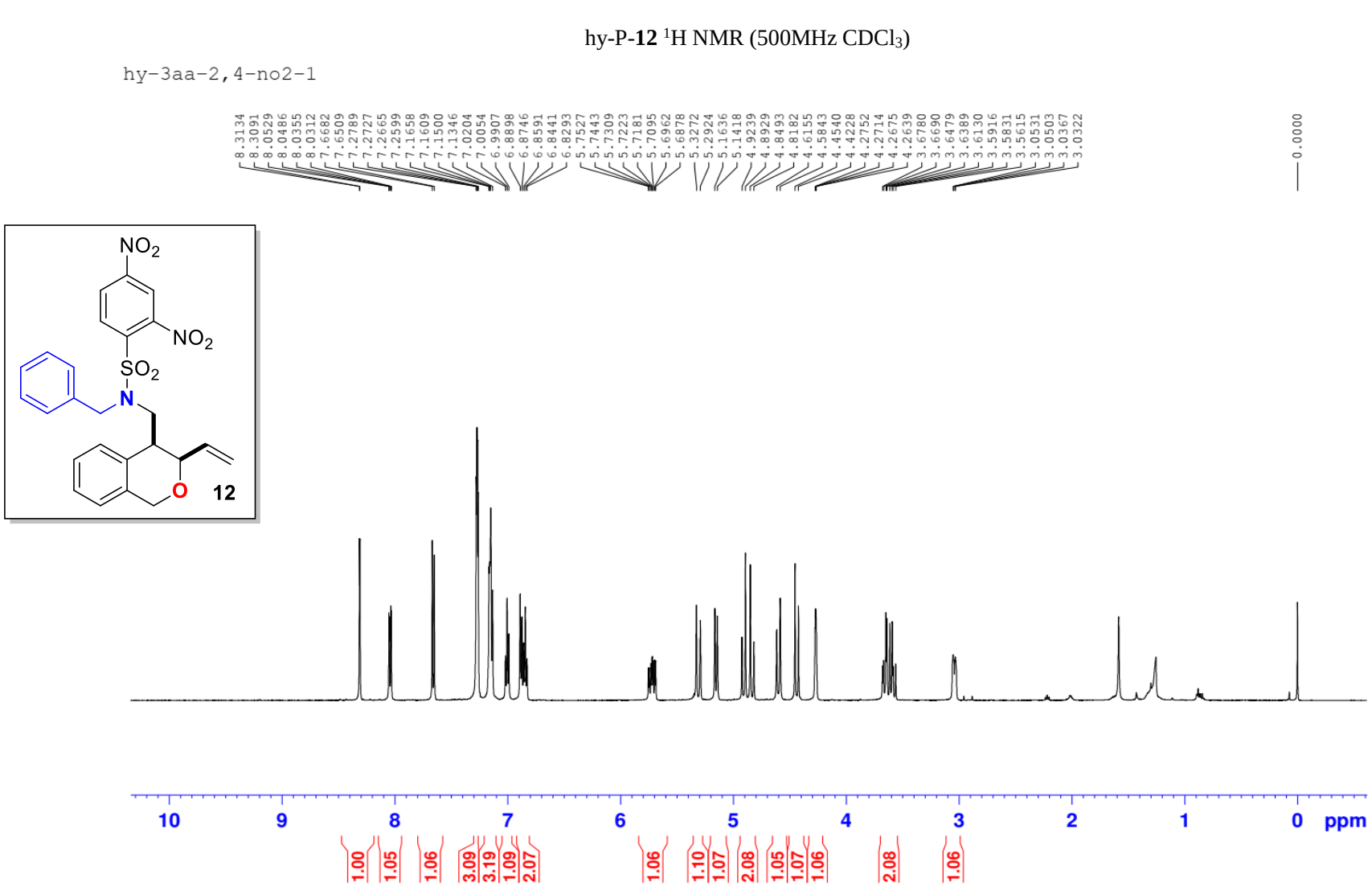


hy-P-**11** ^{13}C NMR (125MHz $CDCl_3$)

hy-3aa-tuobian-c--

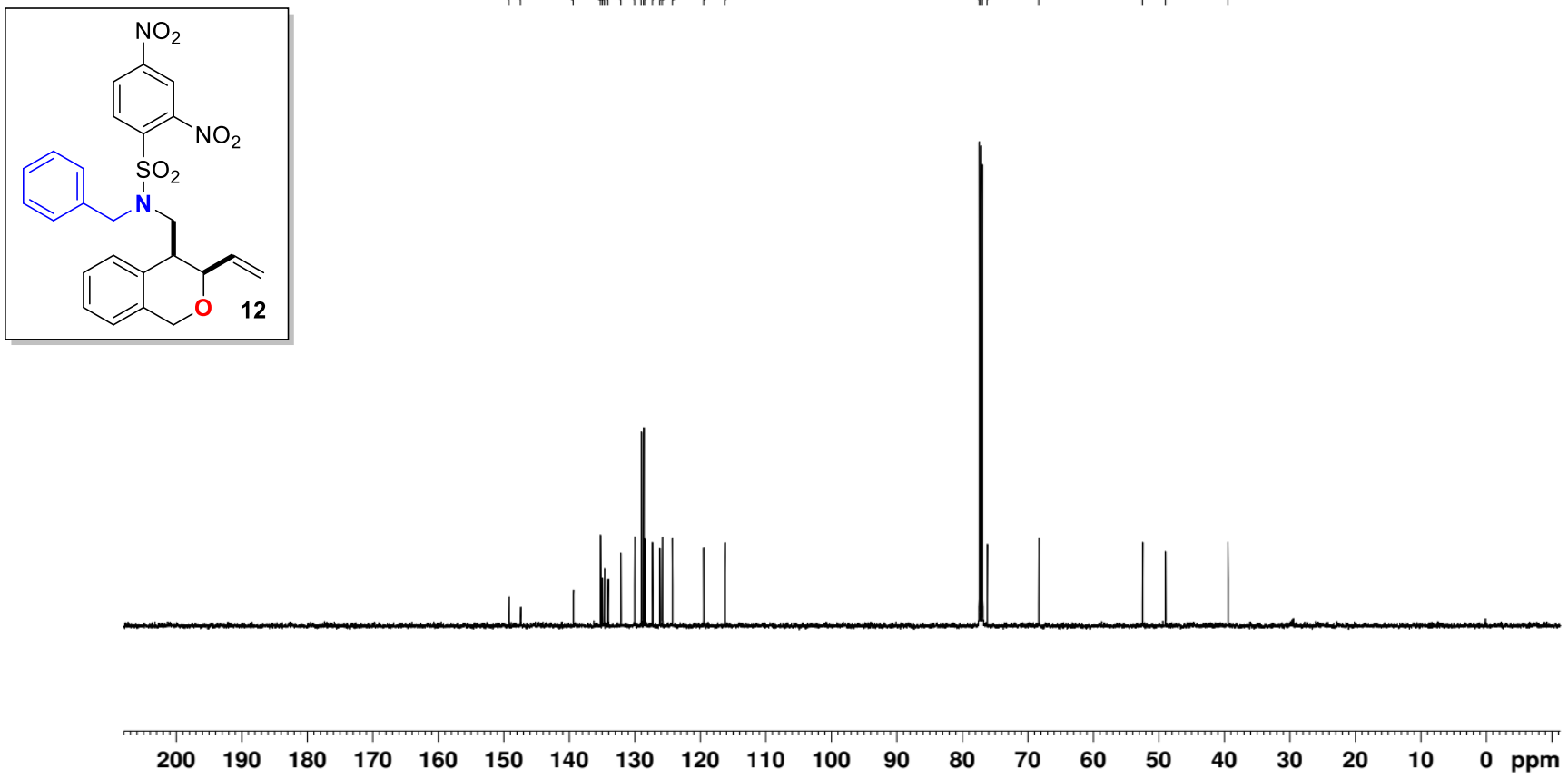


hy-P-**12** ^{1}H NMR (500MHz $CDCl_3$)

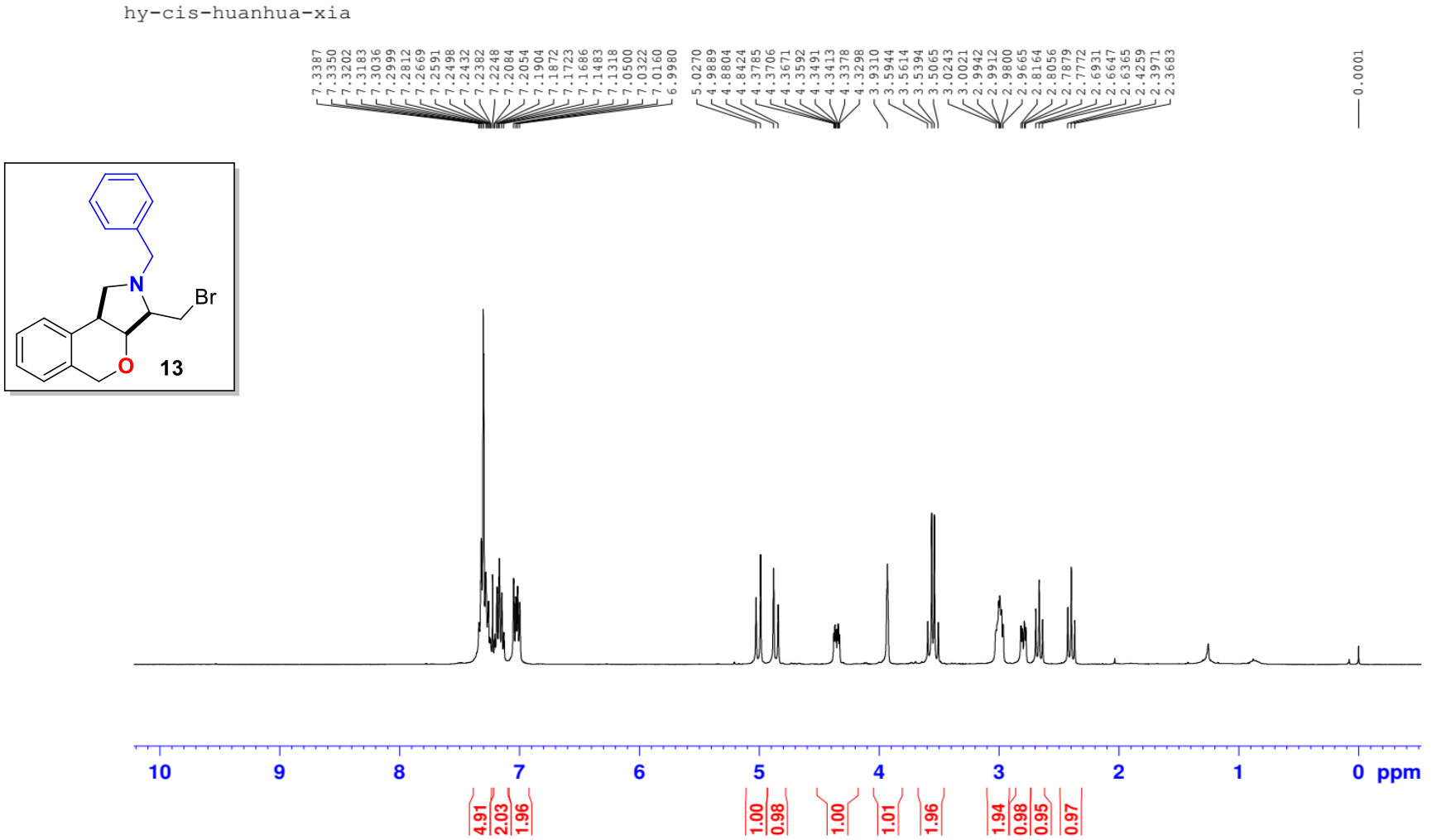


hy-P-**12** ^{13}C NMR (125MHz $CDCl_3$)

hy-3aa-2,4-no2-1-c

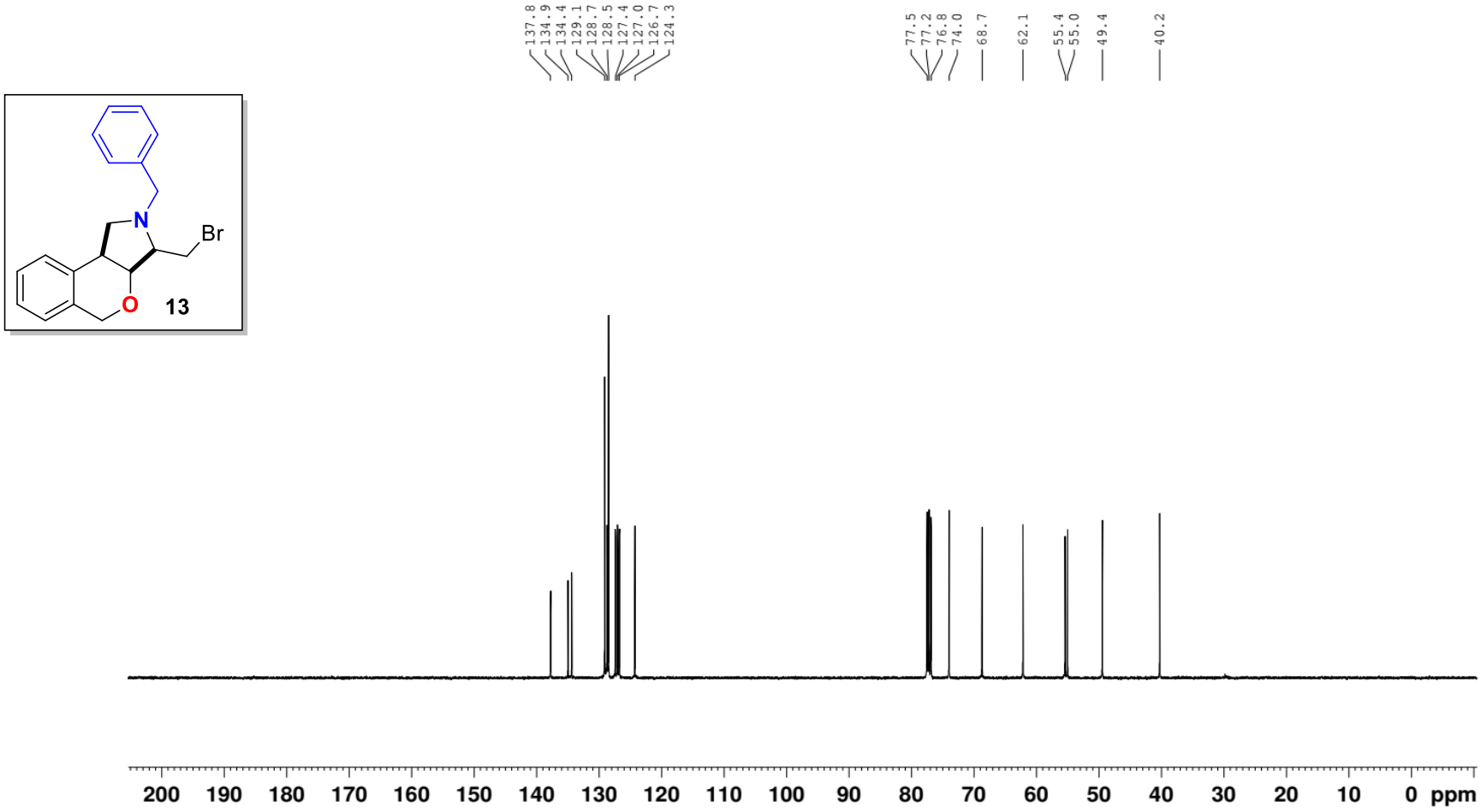


hy-P-**13** ^{1}H NMR (400MHz $CDCl_3$)

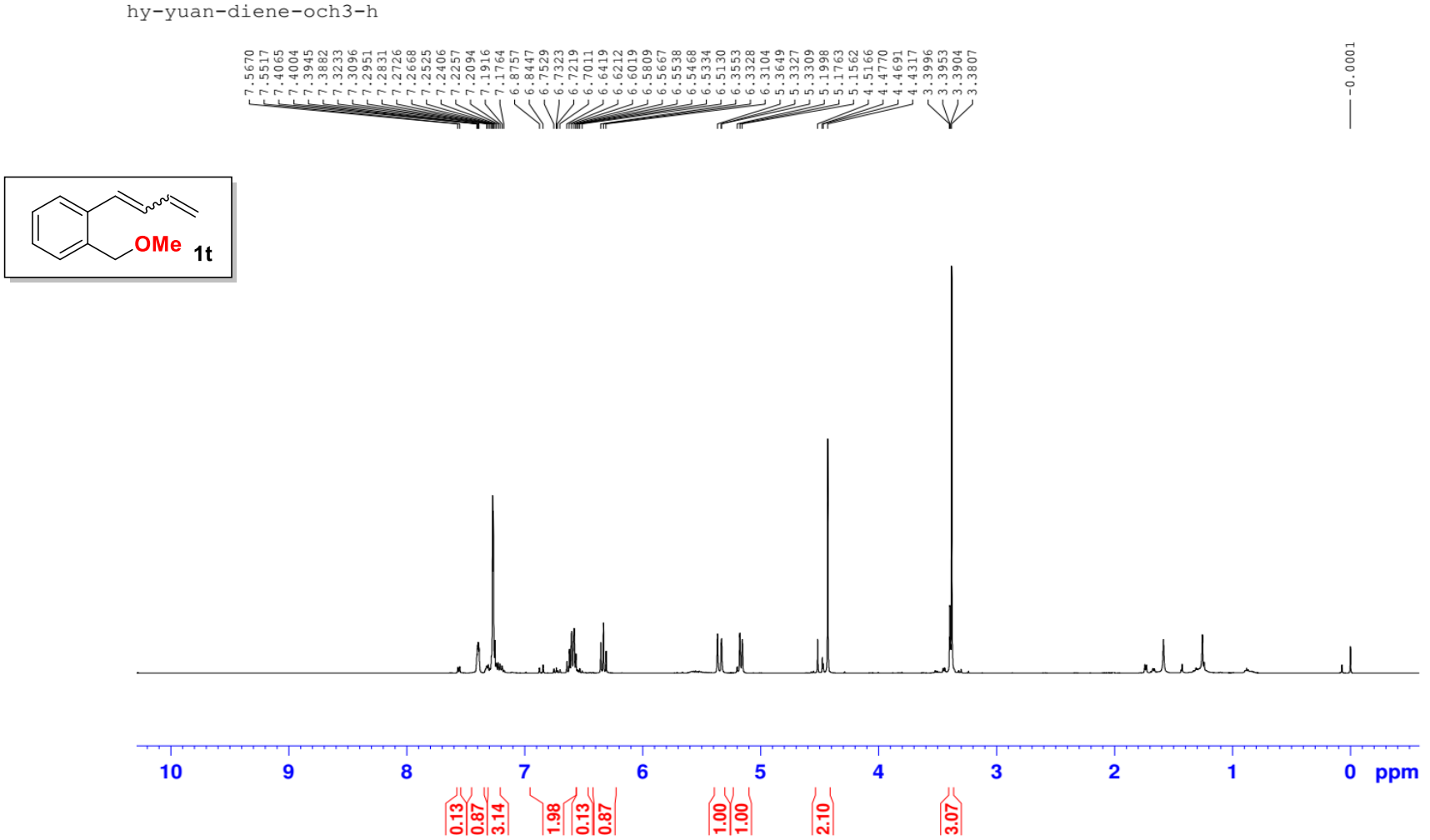


hy-P-**13** ^{13}C NMR (100MHz $CDCl_3$)

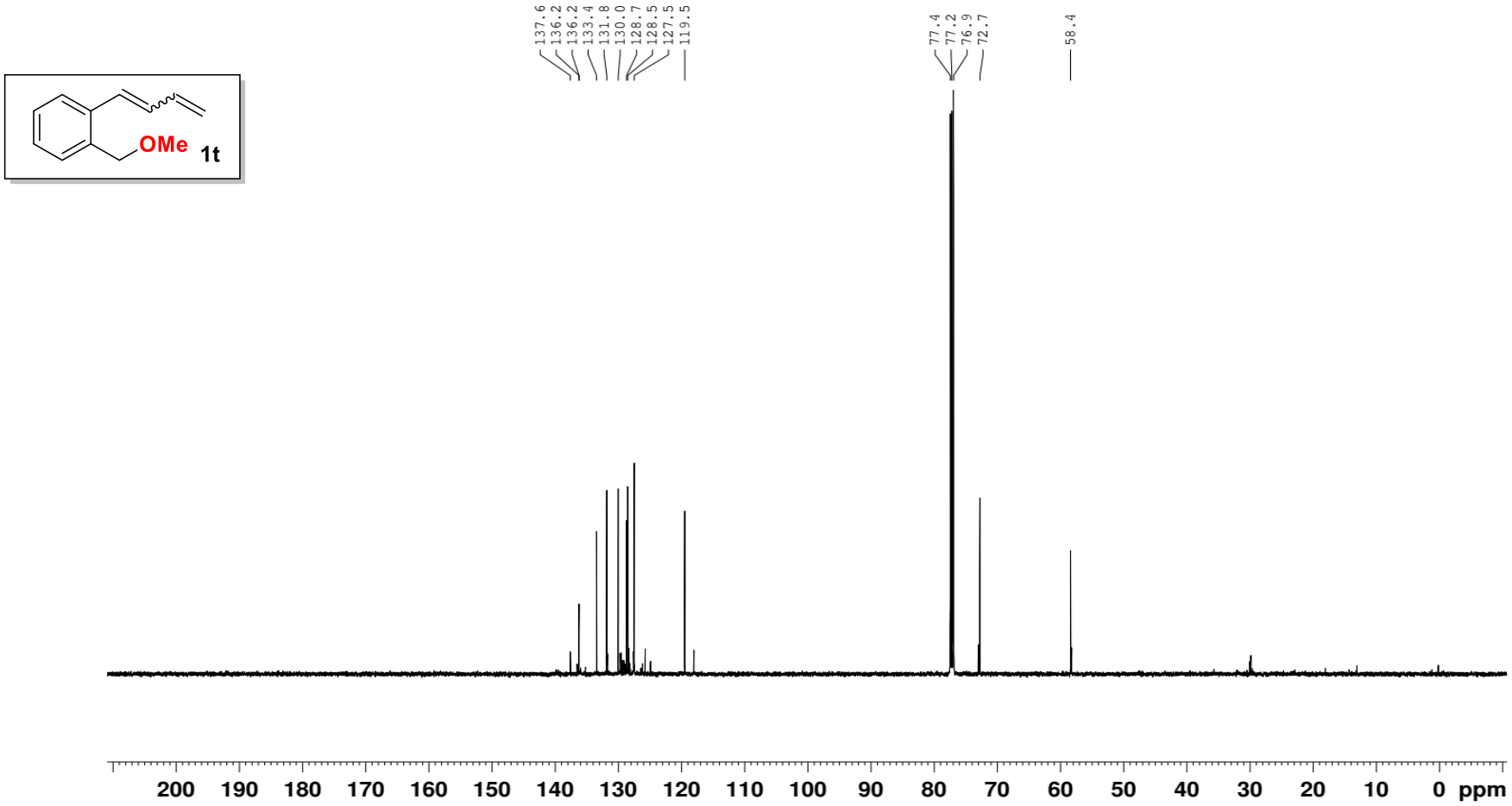
hy-cis-huanhua-xia-c-



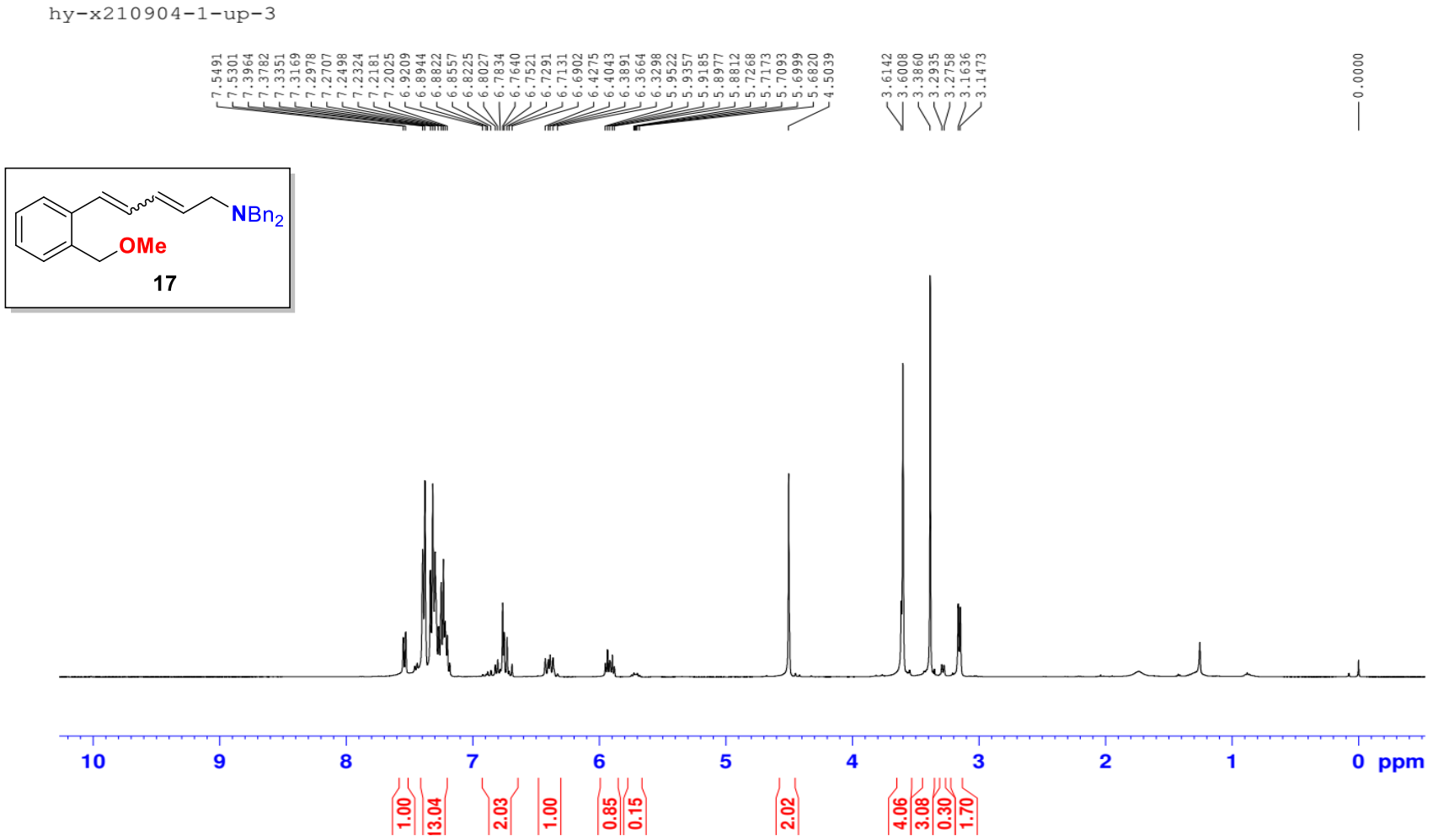
hy-**S-1t** ^{1}H NMR (500MHz $CDCl_3$)



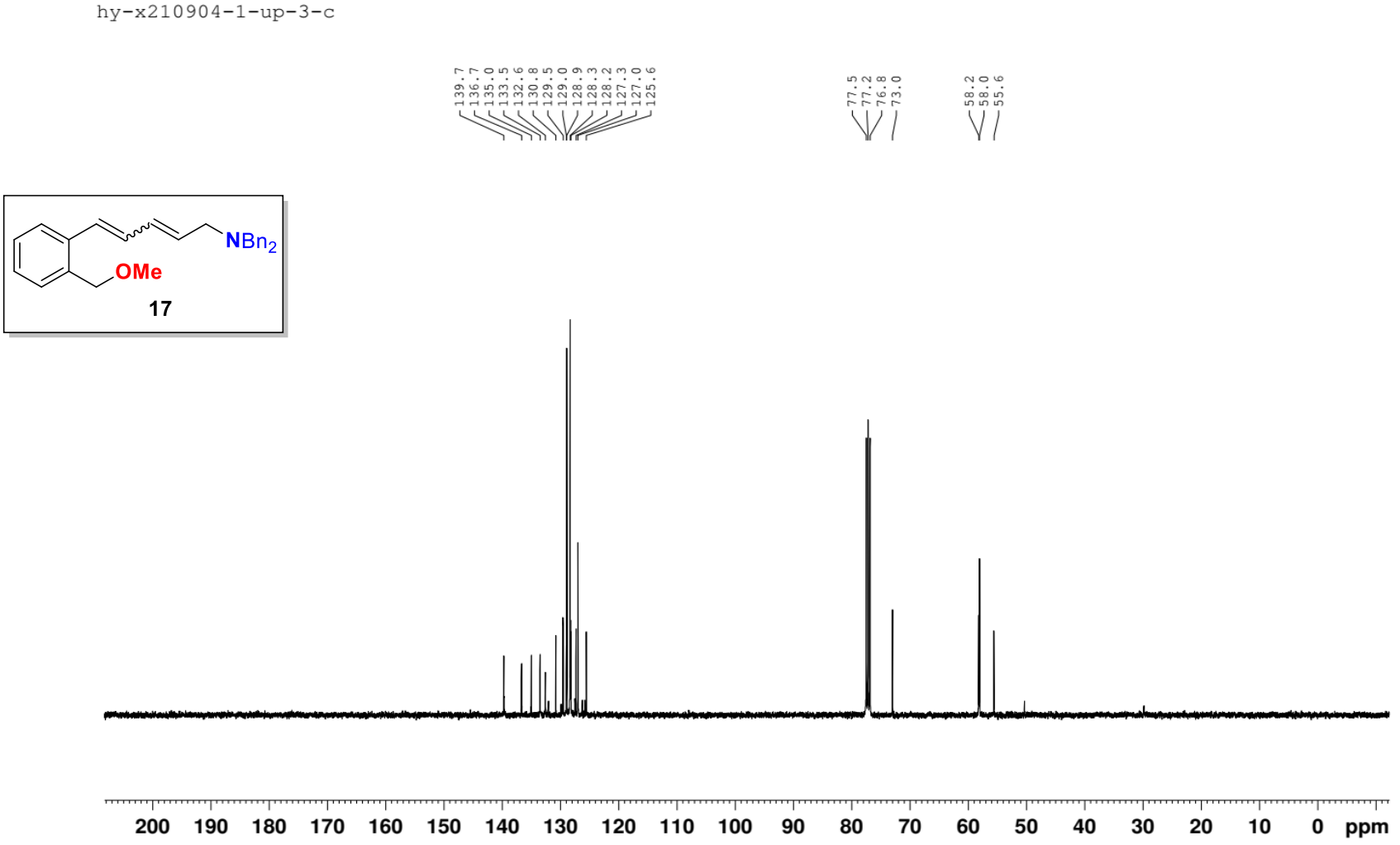
hy-**S-1t** ^{13}C NMR (125MHz $CDCl_3$)



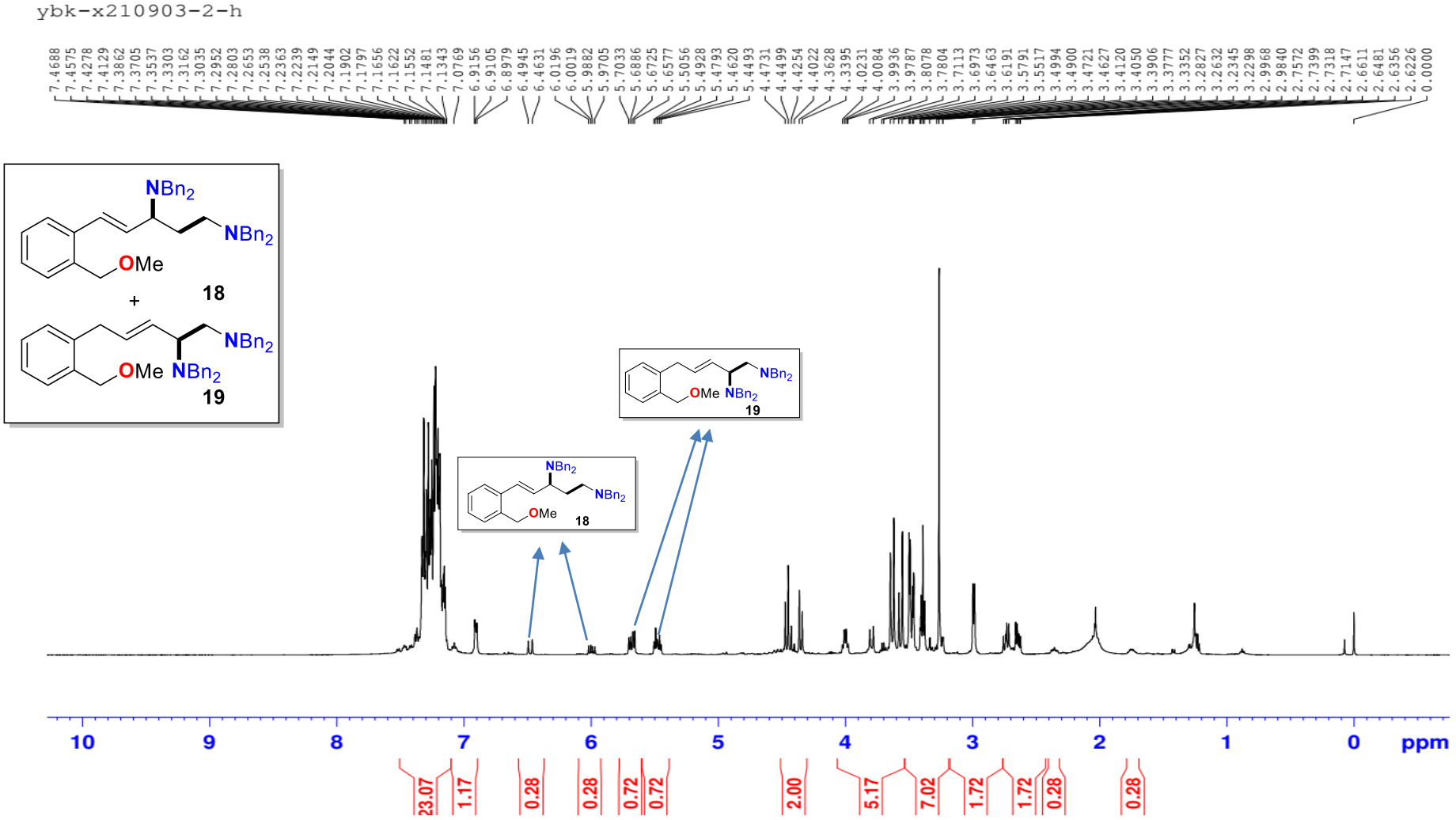
hy-P-**17** ^{1}H NMR (400MHz $CDCl_3$)



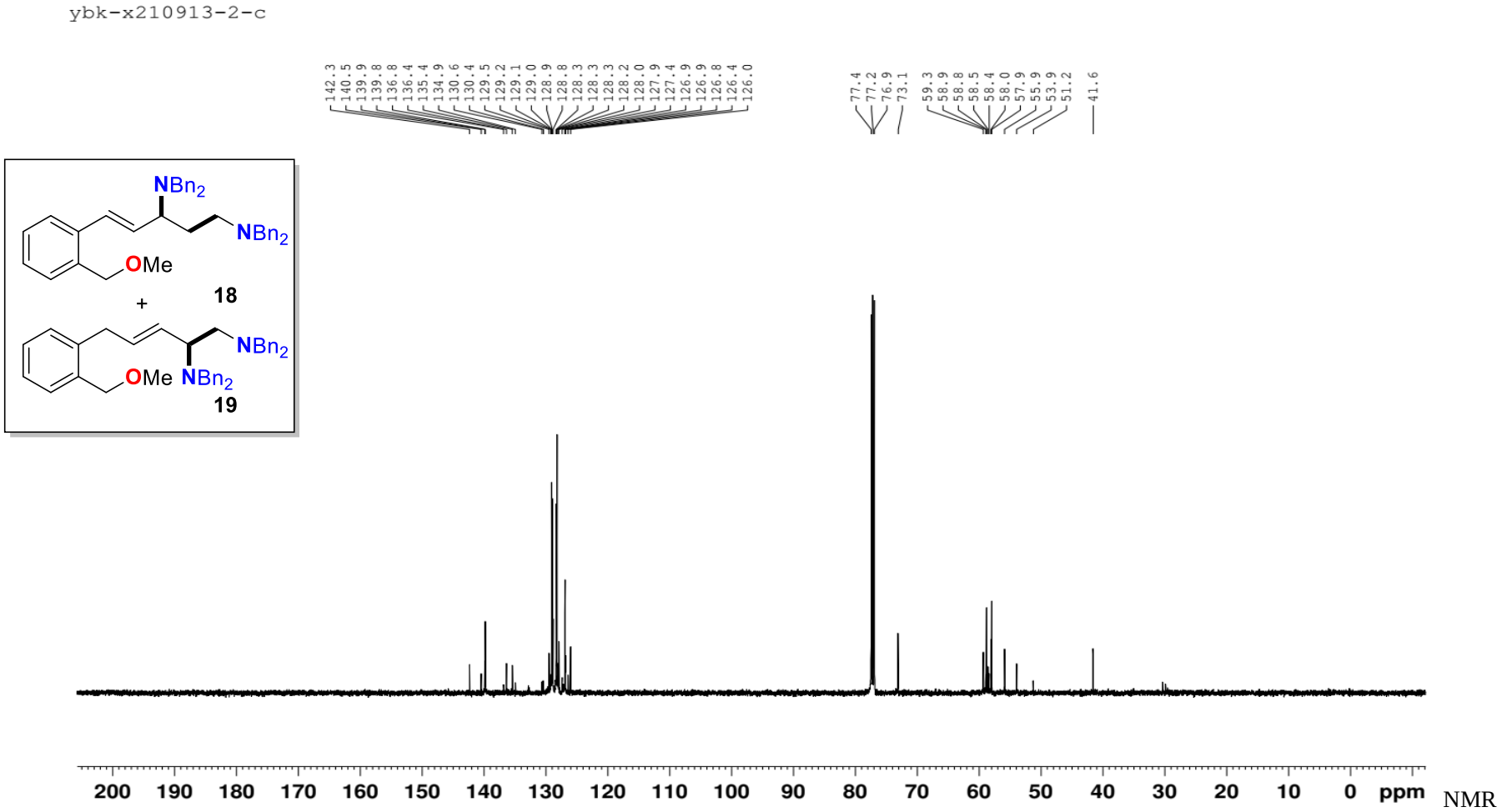
hy-P-**17** ^{13}C NMR (125MHz $CDCl_3$)



hy-P-**18** + **19** ^{1}H NMR (500MHz $CDCl_3$)

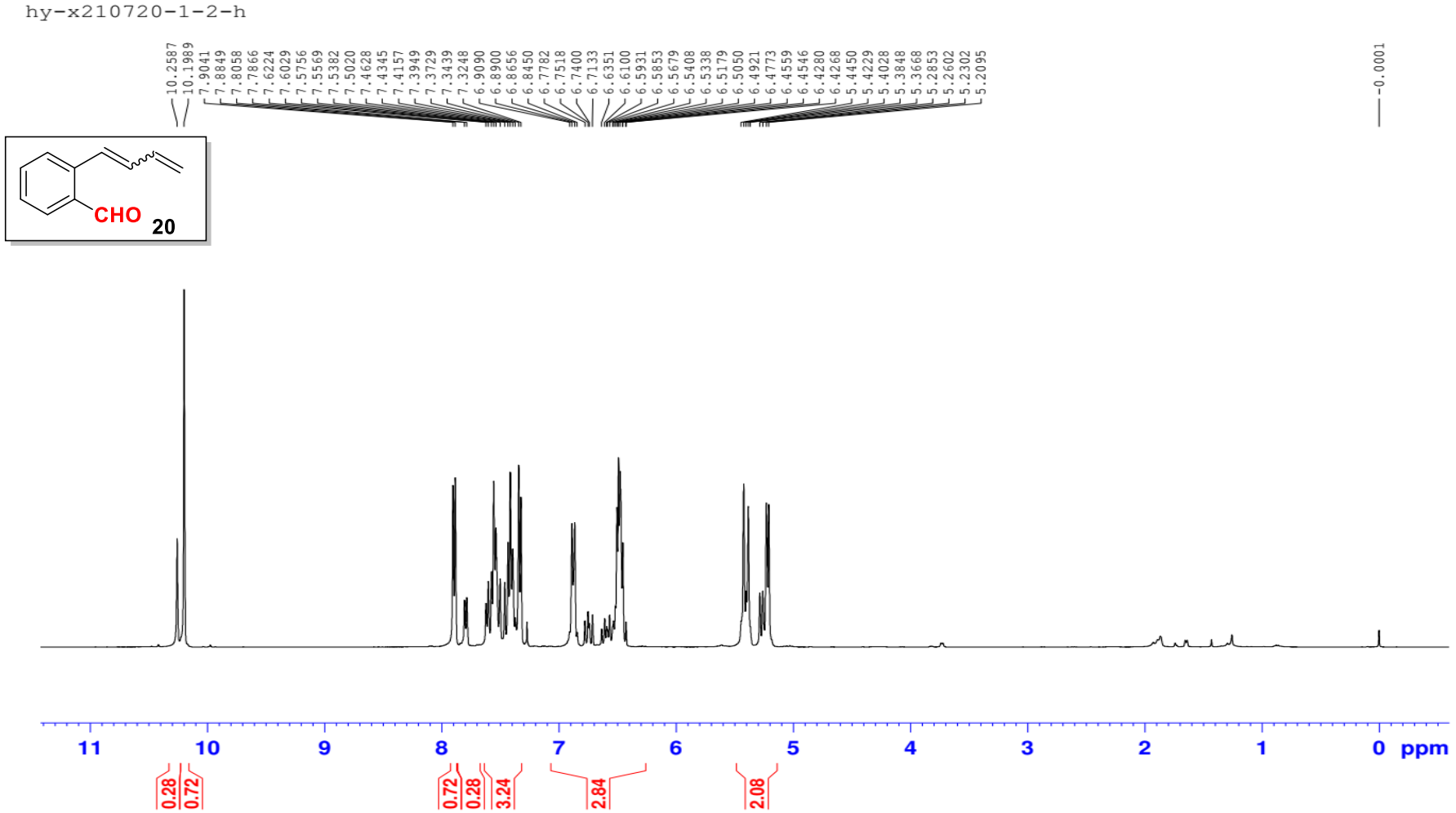


hy-P-**18** + **19** ^{13}C (125MHz $CDCl_3$)

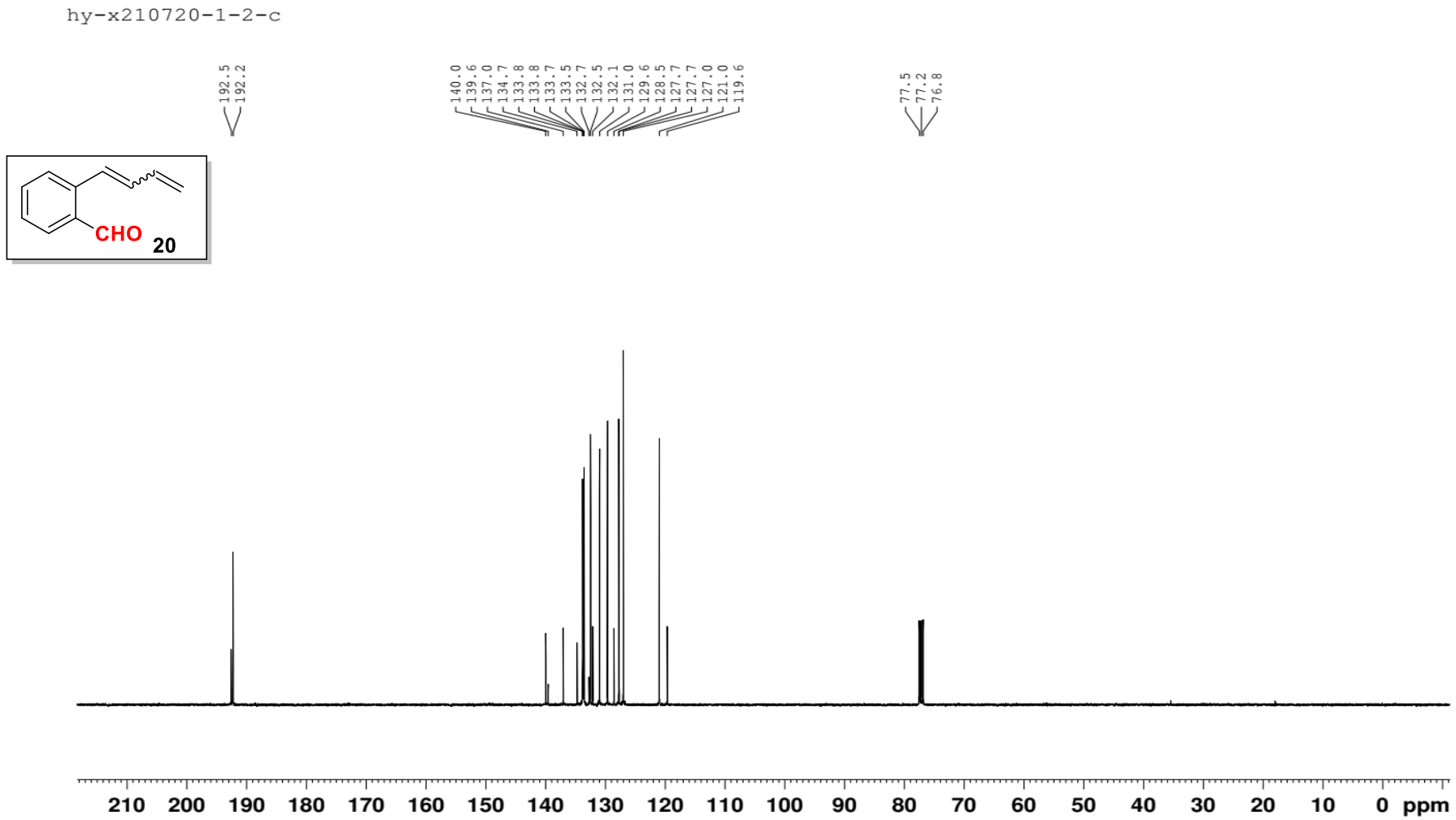


NMR

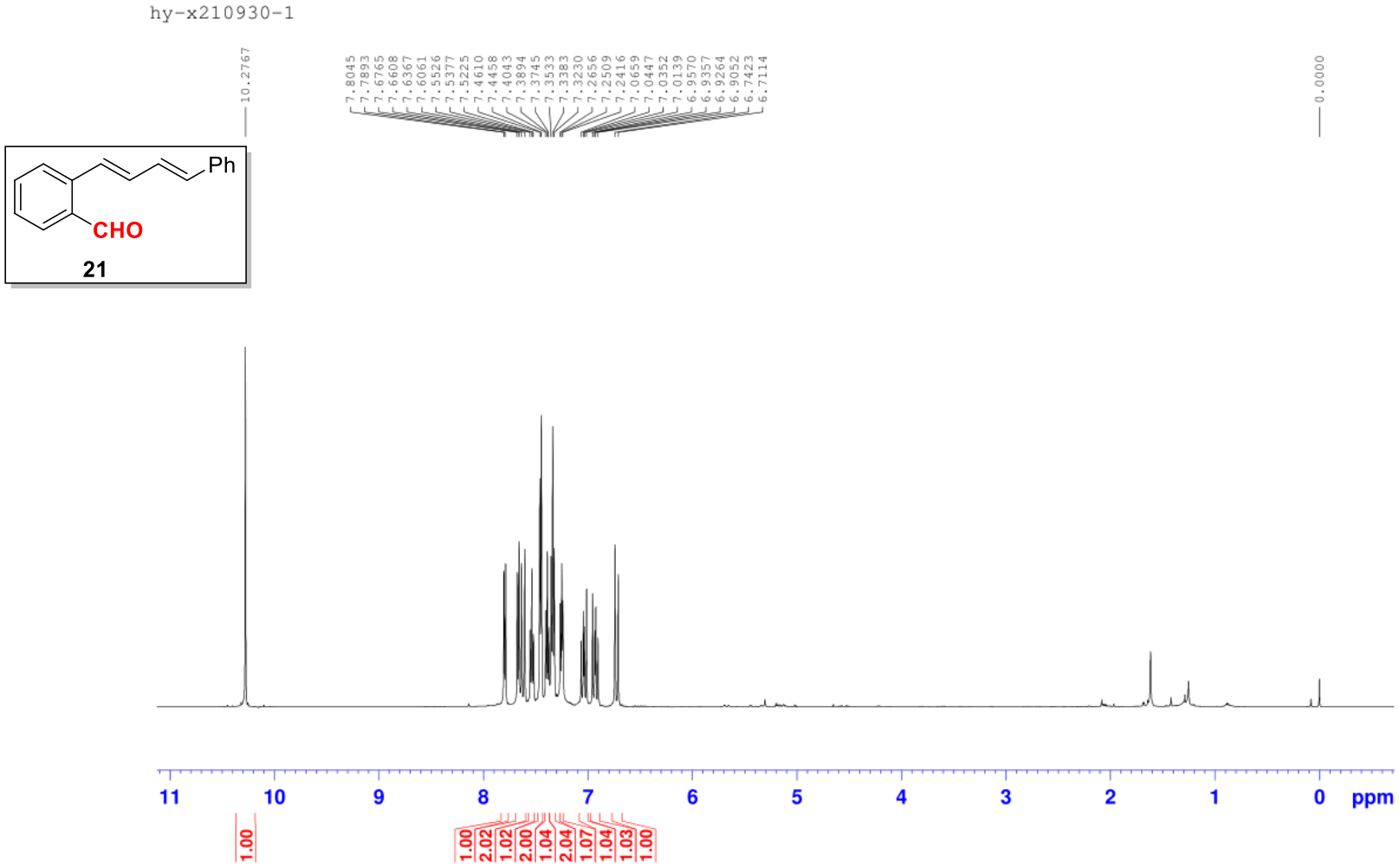
hy-P-**20** ^{1}H NMR (400MHz $CDCl_3$)



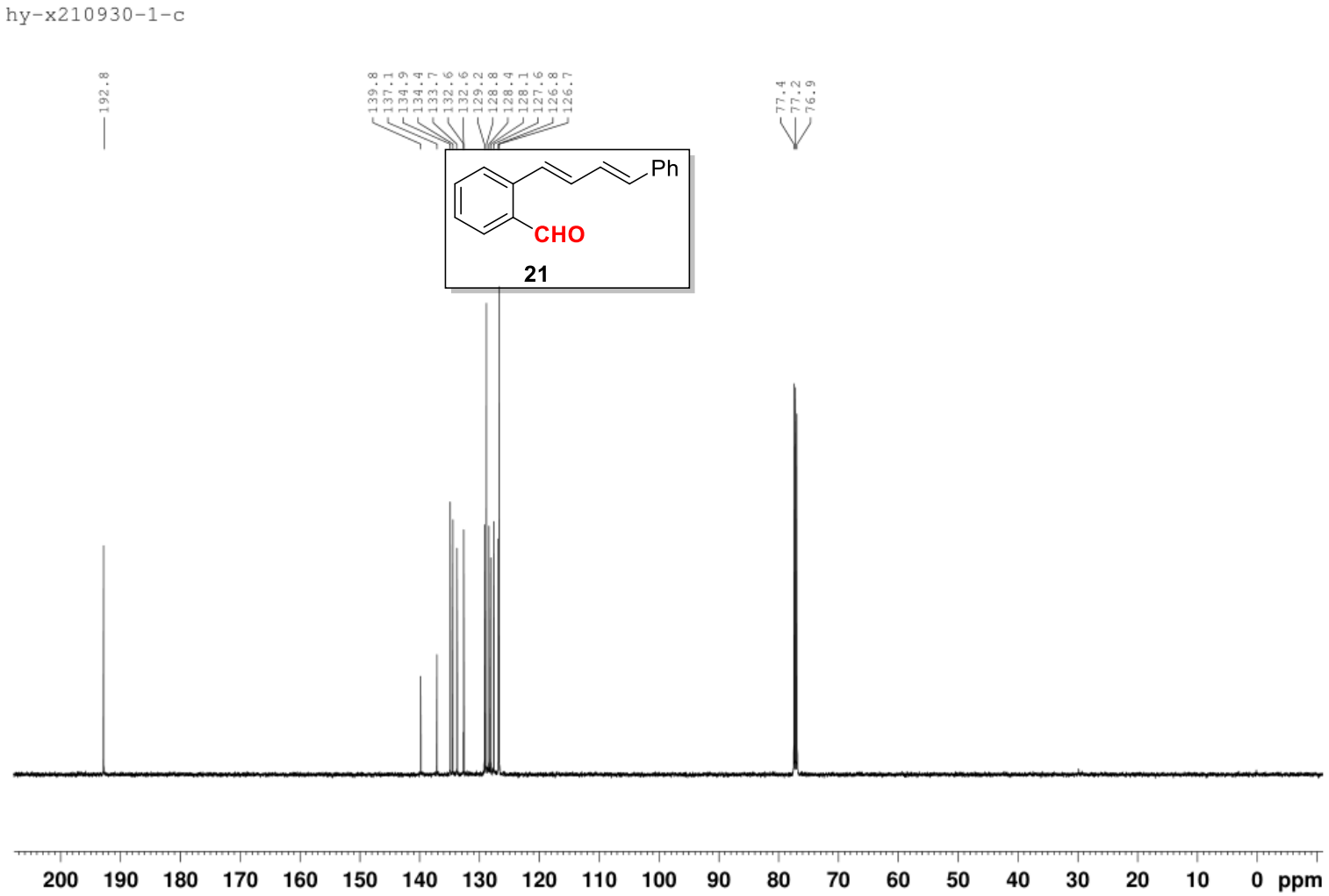
hy-P-**20** ^{13}C NMR (100MHz $CDCl_3$)



hy-P-**21** ^{1}H NMR (500MHz $CDCl_3$)



hy-P-**21** ^{13}C NMR (125MHz $CDCl_3$)



13. Computational data

Computational Methods

All density functional theory (DFT) calculations were conducted using the GAUSSIAN 16 series of programs. Density functional B3-LYP[13] with a standard 6-31G(d) basis set (SDD basis set for Pd) was used for geometry optimizations. Harmonic frequency calculations were performed for all stationary points to confirm them as local minima or transition structures, and to derive thermochemical corrections for the enthalpies and free energies. All minima had zero imaginary frequency and all transition states had only one imaginary frequency. The DFT method M06 functional[14] with larger basis set 6-311+G(d) (SDD basis set for Pd) was used to calculate single point energies with dichloromethane as solvent with a continuum solvation model (SMD[15]). The energies reported in this study are M06-calculated Gibbs free energies in methanol solvent. The optimized structures were displayed using CYLview.[16]

B3-LYP and M06 absolute calculation energies, enthalpies, and free energies.

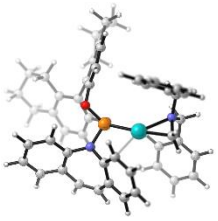
Geometry	$E_{(elec\text{-}B3\text{-}LYP)}$[1]	$H_{(corr\text{-}B3\text{-}LYP)}$[2]	$G_{(corr\text{-}B3\text{-}LYP)}$[3]	$E_{(solv\text{-}M06)}$[4]	IF[5]
A-L4	-2624.010202	0.883609	0.751689	-2622.965038	-
1a	-501.560102	0.213002	0.163615	-501.3208005	-
B-L4	-3125.589938	1.098962	0.940800	-3124.307206	-
C	-3125.603981	1.100529	0.946547	-3124.334721	-
L4	-1860.261462	0.589732	0.497893	-1859.535566	-
TS-Inner-1	-4985.848779	1.690731	1.465468	-4983.863877	-321.2
TS-Inner-2	-3125.566871	1.099170	0.944140	-3124.296357	-235.5
TS-Inner-3	-4358.186435	1.651486	1.427764	-4356.288961	-269.8
2a	-1232.605335	0.549166	0.459005	-1231.969734	-
A-L2	-2306.261405	0.969578	0.836011	-2305.322676	-
E	-2807.830132	1.185929	1.025236	-2806.669612	-
TS-Outer	-4040.43357	1.734228	1.507835	-4038.629369	-627.3

1a'	-540.869653	0.242857	0.189825	-540.599164	-
B'-L4	-3164.883582	1.129190	0.966522	-3163.582533	-
MeOH	-115.712205	0.055706	0.028755	-115.683225	-
G	-3241.315546	1.157528	0.985854	-3240.001482	-
*t*BuOH	-233.666735	0.143864	0.107237	-233.5689236	-
G'	-3359.269285	1.245695	1.066792	-3357.889705	-

[1]The electronic energy calculated by B3-LYP in gas phase. [2]The thermal correction to enthalpy calculated by B3-LYP in gas phase. [3]The thermal correction to Gibbs free energy calculated by B3-LYP in gas phase. [4]The electronic energy calculated by M06 in dichloromethane solvent. [5]The B3-LYP calculated imaginary frequencies for the transition states.

B3-LYP geometries for all the optimized compounds and transition states.

A-L4



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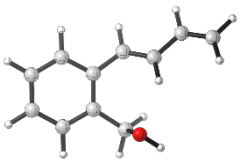
N	-3.42183400	1.43570400	1.09008200
C	-4.26453900	0.51745900	0.48173300
C	-3.43239000	2.88013300	0.64791000
C	-3.76704900	3.10967900	-0.80243300
C	-2.76232000	3.06648900	-1.77933100
C	-3.07510800	3.27411700	-3.12375600
C	-4.39463700	3.53178600	-3.50455100
C	-5.39936700	3.59268400	-2.53614900
C	-5.08524000	3.38577100	-1.19163600
C	-3.12407700	1.34668100	2.56931800
C	-3.13522700	-0.03882100	3.15926000
C	-1.97622300	-0.82863400	3.15079200
C	-1.99218100	-2.10521900	3.71556200
C	-3.16110000	-2.60261100	4.29671500
C	-4.31647200	-1.81787900	4.31888200
C	-4.30093900	-0.54100900	3.75556400
H	-4.90229300	0.89223700	-0.31226300
H	-4.65433600	-0.27742500	1.11039400
H	-4.15974700	3.39212600	1.29061500
H	-2.43939600	3.26846600	0.89008100
H	-1.73252600	2.89025900	-1.48109500
H	-2.28851800	3.24945800	-3.87288500
H	-4.63623700	3.70087500	-4.54986700
H	-6.42309000	3.81219800	-2.82461600
H	-5.86817900	3.45138000	-0.43898200
H	-2.14781700	1.82144300	2.69882500
H	-3.87258000	1.97543400	3.06826900

H	-1.05829500	-0.44423100	2.71457500
H	-1.08635700	-2.70463000	3.71267900
H	-3.16813500	-3.59161300	4.74609400
H	-5.22281800	-2.19217400	4.78576600
H	-5.19657100	0.07566500	3.79435700
C	3.08413400	0.28000000	0.45522600
C	2.19448800	-0.67022500	0.96847900
C	2.62273400	-1.86349400	1.53856200
C	3.98399000	-2.13576300	1.55347700
C	4.90927700	-1.26467800	0.96160300
C	4.46162800	-0.05892200	0.38651200
C	2.54923100	1.58725200	-0.04024100
C	1.58210000	1.58405400	-1.05256800
C	1.13041700	2.75437000	-1.65477900
C	1.61890000	3.97020800	-1.19202500
C	2.50329900	4.03230800	-0.10600200
C	2.95987800	2.83907100	0.49007600
H	1.89395200	-2.55848100	1.94162000
H	4.33975200	-3.06018900	2.00206500
H	0.42413100	2.69616200	-2.47689400
H	1.28960000	4.89400900	-1.66171400
O	0.81127700	-0.41674800	0.93406700
O	1.04359700	0.36262700	-1.49089700
P	-0.04321900	-0.37105900	-0.48116600
C	-0.77718500	-4.39231700	0.23772400
C	0.53496600	-4.52967400	-0.05753600
H	-1.17328500	-5.01505900	1.03722200
H	1.09327900	-5.25580100	0.53078200
N	-0.12746000	-1.90219400	-1.21679600
C	1.28158200	-3.93432700	-1.16422300
C	2.37884200	-4.64207500	-1.68914100
C	3.08702300	-4.17192600	-2.79047500
C	2.70830100	-2.97214000	-3.39577700
C	1.63314700	-2.24377800	-2.88649100

C	0.93683100	-2.70478700	-1.76619000
H	2.66089500	-5.58424600	-1.22638600
H	3.92627800	-4.74125000	-3.17862300
H	3.25011900	-2.59772500	-4.25919700
H	1.34326900	-1.30205400	-3.33664300
C	-4.14001200	-3.27047200	-1.05759100
C	-3.13021200	-3.98820400	-0.41984800
C	-1.77716600	-3.59573500	-0.47061300
C	-1.46033800	-2.43396200	-1.20591200
C	-2.47692400	-1.70884900	-1.87628400
C	-3.81906500	-2.13027900	-1.79374900
H	-5.16930200	-3.60949700	-0.99262800
H	-3.38623400	-4.87986400	0.14654000
H	-2.19044200	-0.94572100	-2.59753700
H	-4.58477700	-1.58258500	-2.33479500
C	6.38152000	-1.64851500	0.98198400
H	6.78780100	-1.40927700	1.97667200
H	6.47475300	-2.73626400	0.87611100
C	7.22122300	-0.93181900	-0.08012700
H	8.28638900	-1.11104500	0.10531300
H	6.99762000	-1.34420700	-1.07395200
C	6.90699900	0.56572800	-0.07004800
H	7.13510700	0.98037000	0.92235500
H	7.53728200	1.10286400	-0.78823800
C	5.43139300	0.80780700	-0.40932100
H	5.19107500	1.86807500	-0.30651500
H	5.27179900	0.57849000	-1.47459900
C	3.79372500	2.89823100	1.76520500
H	3.11079600	2.71217900	2.60915700
H	4.51782500	2.08190100	1.79992100
C	4.49723700	4.24205000	1.98881000
H	4.93777600	4.25866200	2.99230200
H	5.32819300	4.35126100	1.27738200
C	3.51443300	5.40037800	1.80411000

H	3.99523900	6.36173700	2.01752100
H	2.68669900	5.29377300	2.51951100
C	2.96982000	5.39958400	0.37215700
H	2.14885100	6.12016900	0.27170700
H	3.76027100	5.75147300	-0.30812300

1a



C	-2.85436400	-1.45916100	-0.26030500
C	-1.49757000	-1.71404500	-0.09153600
C	-0.56497400	-0.68109400	0.13534500
C	-1.05402700	0.64650200	0.24755200
C	-2.42348500	0.88316500	0.07854200
C	-3.32455800	-0.14736100	-0.18323200
H	-3.54133400	-2.28041100	-0.44668700
H	-1.13350400	-2.73700500	-0.15194600
H	-2.78817300	1.90402300	0.16646900
H	-4.38157600	0.06966700	-0.30983900
C	0.84282500	-1.08168500	0.26729000
H	0.98525600	-2.10536000	0.61868200
C	1.95141800	-0.37769100	-0.05425400
H	1.85480300	0.61751400	-0.48322500
C	-0.17200400	1.82075200	0.59323500
H	0.60422000	1.50808400	1.30592800
H	-0.78472700	2.59421200	1.07918200
O	0.42160200	2.34852300	-0.60162500
H	0.98260500	3.09582700	-0.33765000
C	3.29467800	-0.90953100	0.10137900
H	3.37553200	-1.91425000	0.51867400
C	4.41474200	-0.24793800	-0.23272600
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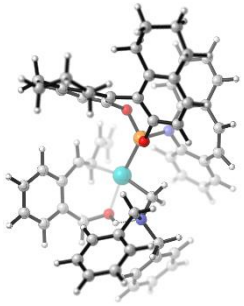
B-L4



Pd	-1.42875800	-0.24167300	-0.96670400
N	-2.84236100	-0.15500100	1.58321500
C	-1.94734200	-1.06438500	0.89332800
C	-3.87888500	-0.88039200	2.38897700
C	-5.03668600	-1.39734800	1.56546500
C	-6.06539100	-0.52026300	1.18737600
C	-7.14571800	-0.97245100	0.43023900
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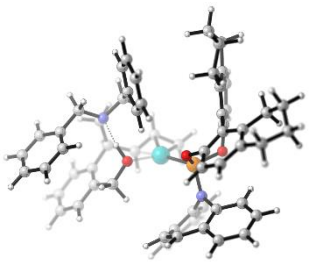

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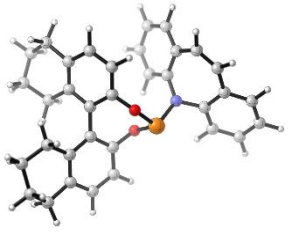
L4



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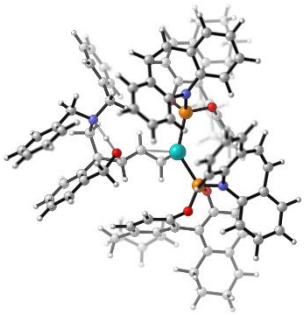
TS-Inner-1



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H	2.76780800	4.95694300	-2.13692300
H	4.14427600	2.23548400	0.59412800
H	3.05457700	1.62135600	-0.62691400
H	6.45820700	3.03706000	-0.06677000
H	8.31856800	2.81313400	-1.66675400
H	7.91793900	1.85770900	-3.92851300
H	5.63391900	1.09417000	-4.55414600
H	3.77536500	1.29791000	-2.94715500
H	4.72638200	4.33082100	0.70308500

H	4.65615300	5.09923900	-0.87512600
H	3.30069800	5.06412400	2.58175000
H	2.49368400	7.09568200	3.74984200
H	2.22066100	9.22614200	2.49585600
H	2.75668900	9.30806100	0.06985900
H	3.56777200	7.28178000	-1.09214800
C	-0.43373300	7.67332000	-1.56104100
C	0.10360900	6.46821300	-2.00725200
C	0.30969300	5.39387800	-1.12940300
C	-0.03344400	5.54746700	0.22299000
C	-0.57481900	6.76103700	0.66716400
C	-0.77837100	7.81911500	-0.21494300
H	-0.59249500	8.48944800	-2.25988800
H	0.35651400	6.34874200	-3.05890500
H	-0.83552500	6.87697400	1.71686700
H	-1.20254900	8.75194100	0.14484700
C	0.85351100	4.07765200	-1.67921200
H	0.54023200	4.02502500	-2.73232800
C	0.16005700	2.90758600	-0.99659300
H	-0.88413500	3.12218800	-0.77303900
C	0.12676300	4.42074000	1.22326100
H	-0.84571600	4.05986500	1.57080200
H	0.69798000	4.75144100	2.09662000
O	0.79606700	3.26505500	0.68166500
H	1.80582200	3.49598500	0.43642600
C	0.38045300	1.53449000	-1.32156300
H	1.35609700	1.18990900	-1.64524500
C	-0.67574800	0.62553600	-1.29928700
H	-1.69433700	1.00057800	-1.24580800
H	-0.56571500	-0.32879900	-1.80917100
Pd	-0.39017600	-0.13066600	0.78355000
C	2.99109200	-3.24362800	-1.80550400
C	3.44180800	-2.03440500	-1.25750800
C	4.79251100	-1.69788500	-1.24031600

C	5.71563700	-2.61330000	-1.72856800
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C	3.95209300	-4.20995000	-2.20173600
C	1.51955900	-3.48314300	-1.91498200
C	0.74512900	-3.42669000	-0.75004300
C	-0.61510000	-3.71854300	-0.74709700
C	-1.22340700	-4.04029900	-1.95418500
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H	5.10172500	-0.74211500	-0.83636900
H	6.77281800	-2.35685300	-1.72798600
H	-1.17147400	-3.68056300	0.18268000
H	-2.28496800	-4.27591500	-1.97104300
O	2.52246700	-1.11495200	-0.73651300
O	1.35970800	-3.05729700	0.45272600
P	1.61897600	-1.42955800	0.65455700
C	5.24329100	-0.14650000	2.26386500
C	5.60058500	-1.42657400	2.01850100
H	5.99430400	0.61920500	2.07512800
H	6.60871200	-1.59432000	1.64430600
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C	4.85001600	-2.63919400	2.33330400
C	5.56913900	-3.80932000	2.64430600
C	4.92401000	-4.97175000	3.05126400
C	3.53136400	-4.98611100	3.16105800
C	2.79720600	-3.84574400	2.84045200
C	3.44115100	-2.68566600	2.39998700
H	6.65407300	-3.78595400	2.58030300
H	5.50292600	-5.85910800	3.29027400
H	3.01646800	-5.88598100	3.48540800
H	1.71552000	-3.84874300	2.90230600
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C	4.05519600	1.53637000	3.62447800
C	4.01283000	0.33392700	2.88960500

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H	3.00593000	2.94644800	4.86576900
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H	0.85823600	1.66942900	4.77454800
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C	5.94206400	-6.31494000	-2.64562000
H	6.68405900	-6.93636700	-3.16055700
H	5.88498000	-6.67915100	-1.61028200
C	4.56645700	-6.44314300	-3.30399900
H	4.62352300	-6.08065500	-4.34069100
H	4.25302200	-7.49262300	-3.35442100
C	3.52021700	-5.63600100	-2.52627800
H	2.56483000	-5.64964300	-3.05532000
H	3.32509700	-6.14187900	-1.56773200
C	1.61292700	-3.53684600	-4.46853800
H	1.68520400	-2.45382900	-4.65729800
H	2.64598300	-3.88093700	-4.38644600
C	0.92946900	-4.19917200	-5.67067200
H	1.43381600	-3.88900300	-6.59360600
H	1.03637800	-5.29147500	-5.60476500
C	-0.55692500	-3.83733200	-5.71115600
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C	-1.25329600	-4.35305300	-4.44782500
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H	-1.35162900	-5.44718900	-4.52093200
C	-5.28844200	-0.00520600	-0.82862000
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C	-7.25735200	-1.36223700	-1.34996800
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C	-4.60273200	1.31806100	-0.68581000
C	-3.95552600	1.62282700	0.52159400
C	-3.45749900	2.89775700	0.78510900
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C	-4.06215400	3.57247700	-1.47246100
C	-4.57850600	2.28569700	-1.72697700
H	-4.52827000	-3.33196600	-0.74040800
H	-6.91064700	-3.48451700	-1.45529800
H	-3.02179900	3.10131900	1.75862800
H	-3.18044300	4.87721800	-0.00411200
O	-3.22863300	-1.16021600	-0.24282900
O	-3.80538900	0.63584000	1.48828200
P	-2.63640600	-0.55356100	1.18034300
C	-1.82914400	-4.21356500	2.99779200
C	-2.98879500	-4.54996600	2.38710900
H	-1.03139400	-4.95421400	2.99573000
H	-3.04170400	-5.53988300	1.93659200
N	-3.06587700	-1.65028200	2.40278500
C	-4.24523300	-3.80079700	2.39773500
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C	-5.52773600	-1.73399800	2.60618900
C	-4.30054400	-2.39054000	2.47241000
H	-5.43177000	-5.59522700	2.31621400
H	-7.60666300	-4.42643800	2.48856400
H	-7.66524400	-1.94348700	2.70277300
H	-5.53971500	-0.65321100	2.68011500
C	-0.52960500	-2.02185100	5.77228200
C	-0.71486500	-3.10210300	4.91371700
C	-1.57806600	-3.01954900	3.80420100

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C	-2.04199000	-0.70458000	4.42628100
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H	0.12952100	-2.11950800	6.62982400
H	-0.20857700	-4.04305900	5.11365100
H	-2.58054700	0.21784800	4.22937300
H	-1.07822900	0.02093000	6.21102600
C	-8.72423800	-1.52349800	-1.72149200
H	-8.79557400	-1.65653000	-2.81206400
H	-9.10982400	-2.45210000	-1.28293600
C	-9.59808700	-0.33419600	-1.31202200
H	-10.59296000	-0.42959700	-1.76224300
H	-9.74119700	-0.33302300	-0.22223600
C	-8.92646700	0.97339300	-1.73594500
H	-8.78600800	0.97384700	-2.82658700
H	-9.56201900	1.83507000	-1.49986900
C	-7.57154900	1.13498800	-1.03642400
H	-7.05894400	2.02051400	-1.41729200
H	-7.74868800	1.34345300	0.03050000
C	-5.00593800	1.90645500	-3.14131300
H	-4.17726800	1.33686500	-3.59108400
H	-5.84948900	1.21397100	-3.12401100
C	-5.32228100	3.10674500	-4.04109700
H	-5.46136800	2.76187400	-5.07232500
H	-6.27199400	3.56572300	-3.73115000
C	-4.20535600	4.14973200	-3.95951200
H	-4.39537000	4.98416300	-4.64459900
H	-3.25657500	3.69078700	-4.27339600
C	-4.08333000	4.67245700	-2.52450200
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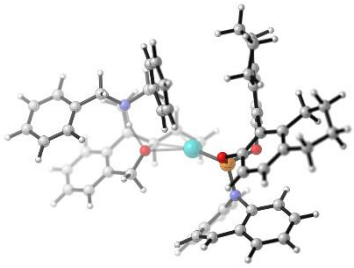

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C	2.48587500	-2.64944600	-0.64521600
C	1.62859400	-3.12978400	0.50088200
C	0.90895200	-2.21886200	1.28992100
C	0.08801700	-2.67676500	2.32066500
C	-0.02539900	-4.04701200	2.57307200
C	0.68207500	-4.96032000	1.78846400
C	1.50491000	-4.50257400	0.75765900
C	4.57618000	-2.83837300	0.69160400
C	5.87072700	-2.28401800	1.22375000
C	5.87625800	-1.39615000	2.30864400
C	7.08110400	-0.95022500	2.84877000
C	8.29488500	-1.39398600	2.31733400
C	8.30092500	-2.28503000	1.24371200
C	7.09371900	-2.72845500	0.70166500
H	4.11777100	-1.92520400	-2.31494200
H	5.57009000	-1.76164300	-1.32473600
H	1.93780500	-1.93182600	-1.25751500
H	2.79690300	-3.48704100	-1.27732200
H	0.99041900	-1.15232200	1.09638100
H	-0.47279500	-1.96237800	2.91589000
H	-0.66577300	-4.40125100	3.37579400
H	0.59517600	-6.02638600	1.97696000
H	2.04808700	-5.21863300	0.14482800
H	3.89982600	-3.09444200	1.50832000
H	4.76016500	-3.74985200	0.11336500
H	4.93529400	-1.06494300	2.74196800

H	7.07381000	-0.26507200	3.69101000
H	9.23254200	-1.05378200	2.74711200
H	9.24119000	-2.64469400	0.83623100
H	7.10319400	-3.44611400	-0.11623300
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C	-4.93159300	0.14584000	2.76974200
C	-5.76919800	-0.61708200	1.94400400
C	-5.27863000	-1.10066700	0.71627100
C	-3.31995100	-1.43187700	-0.88796100
C	-2.81270400	-0.56756100	-1.86613300
C	-2.34828800	-1.02759300	-3.09534300
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C	-3.21336400	-2.83118100	-1.10580500
H	-3.01706300	1.13439300	2.97609200
H	-5.31306700	0.51023300	3.72060000
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H	-2.00465500	-2.77235300	-4.29633000
O	-1.87820100	0.39495800	0.77890900
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P	-1.49028300	1.24491800	-0.58674900
C	-0.31786600	4.41497700	1.62589800
C	-1.48170300	4.15963800	2.26714600
H	0.54153200	4.67347600	2.24213100
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N	-1.85263000	2.87254400	-0.32174700
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C	-5.22363100	4.17767600	1.87777100
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C	-2.99680100	3.35073200	0.40826400

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C	0.86881400	5.43317900	-0.29773700
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H	0.30238800	5.21997900	-3.64647700
C	-7.18369100	-0.91240200	2.42143500
H	-7.14055900	-1.73857800	3.14786600
H	-7.56739200	-0.04790600	2.97708300
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C	-7.49857600	-2.34485500	0.38898300
H	-7.24939900	-3.23612800	0.98294300
H	-8.19412800	-2.67175900	-0.39284900
C	-6.23004000	-1.78171900	-0.26263600
H	-5.72227500	-2.56330500	-0.83133300
H	-6.52271500	-1.02756400	-1.01003200
C	-3.49019300	-3.80954200	0.03050600
H	-2.61503700	-3.78569500	0.69831000
H	-4.32824900	-3.47262400	0.64395700
C	-3.71968900	-5.25385900	-0.42999000
H	-3.74329400	-5.91517900	0.44427100
H	-4.70190200	-5.34013800	-0.91627300
C	-2.62859700	-5.68497200	-1.41268200
H	-2.75110600	-6.73563700	-1.70074100

H	-1.64649800	-5.59845400	-0.92582200
C	-2.67263200	-4.79546900	-2.65915100
H	-1.80755900	-4.99277600	-3.30462800
H	-3.55711800	-5.06673000	-3.25564400
C	7.61320300	1.73666500	-0.04570700
C	6.77665900	0.99326900	-0.87329700
C	5.40225400	0.87802500	-0.61315500
C	4.86579900	1.52486400	0.51523100
C	5.71501600	2.27940400	1.33612400
C	7.07540900	2.39228000	1.06436800
H	8.67214200	1.81576700	-0.27299000
H	7.19371800	0.50604500	-1.75301700
H	5.29537900	2.78313200	2.20496200
H	7.71343100	2.98591500	1.71300900
C	4.54598000	0.10838000	-1.62563000
H	5.06160400	0.21820500	-2.59587700
C	3.20052000	0.76449200	-1.84332100
H	3.21551200	1.84143600	-1.68778000
C	3.38353900	1.44882100	0.85278100
H	2.90633100	2.41622000	0.61746500
H	3.26406300	1.31461500	1.94132700
O	2.73909700	0.40691500	0.16841700
H	3.42364000	-1.01651600	0.24793300
C	2.20394500	0.29367000	-2.72309700
H	2.23171500	-0.73730300	-3.06772100
C	1.11340900	1.11831100	-3.14626100
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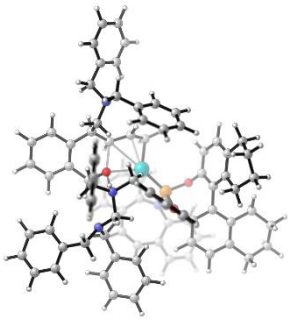

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C	5.94944000	-4.39356800	-2.56416500
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C	8.44042200	-5.48893600	-1.95153900
C	8.09497300	-4.22081600	-1.47656200
C	5.32021700	-2.87244700	0.71163700
C	4.00666000	-3.33141500	1.31150200
C	3.17106000	-4.20444200	0.59821200
C	1.98352000	-4.67174300	1.16081200
C	1.61633300	-4.28379400	2.45337800
C	2.44883300	-3.43280800	3.18035500
C	3.63437800	-2.95954000	2.60847300
H	5.47827600	-0.17536700	-0.01395400
H	3.86726700	-0.84954800	0.25705300
H	6.43119300	-1.60558400	-2.17715600
H	7.30835600	-1.86186200	-0.67460200
H	4.97862300	-3.96481500	-2.79915900
H	5.58440800	-6.21773900	-3.64704600
H	7.80398900	-7.19807900	-3.10194000
H	9.41169000	-5.91053500	-1.70787100
H	8.80208800	-3.66190000	-0.86732500
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H	2.17747900	-3.13571000	4.18955600
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C	-4.91887100	0.45497700	0.44517600
C	-6.23315200	0.18360800	0.79539500
C	-6.71967800	-1.13028600	0.83765900
C	-5.84430900	-2.20199400	0.57899400
C	-3.47792100	-3.05250300	0.14438600
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C	-1.95771100	-4.21926500	-1.37213700
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C	-2.41641400	-5.14717500	0.82859800
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P	-2.06014100	-0.67714100	-1.65420200
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H	-7.19954700	-0.66145300	-3.48474500
H	-4.79400000	-1.28949700	-3.40298300
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H	-6.50445400	-3.81583100	-0.64083000
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H	2.51113700	-2.34917300	-1.10781800
C	1.04468300	-2.17607000	-2.69577500
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H	0.68039200	-3.18582200	-2.52874100
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N	1.58905700	1.49153400	1.72916600
C	2.96813700	2.02583600	2.09173200
H	2.93472100	3.08311700	1.82201300

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H	2.26918100	-0.41232500	2.37994600
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H	0.29961500	-0.36067400	6.75311100
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C	3.45240600	1.81861200	3.50683400
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C	4.88976500	0.60476400	5.05551800
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C	4.45795500	1.41583000	6.10658200
H	3.21392600	3.08685600	6.66647000
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H	4.84678000	1.26351700	7.10919100
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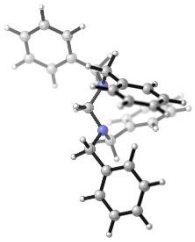
2a



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C	-2.70019300	0.57002200	0.45558300
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H	-2.95778600	0.68104800	1.51589500
H	-1.39321300	0.39768600	-1.61451400
N	0.60862400	0.20981600	-0.94676800
C	1.36876800	-0.50023800	-1.98714800
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H	3.17327200	0.32919500	-3.86982500
C	5.66497200	-0.13814000	-1.60044000
H	5.36771500	-0.80907500	0.42914600
H	5.63600600	0.51047600	-3.65739900
H	6.74465300	-0.05833200	-1.50350500
C	0.43199400	2.48011800	0.15183900
C	-0.47222800	3.54544500	0.08831400
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H	-1.42430400	5.17220800	1.13623300
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H	-1.92865000	-2.22414400	0.52807100
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C	-0.06254000	-1.93305900	1.54487100
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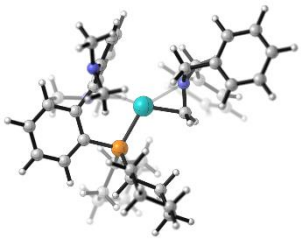

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C	-7.21106600	-0.54288400	1.74695300
C	-7.06443700	-0.72537300	0.37103300
C	-5.79117200	-0.87943000	-0.18042200
C	-3.17668900	1.17455300	-1.15629500
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C	-1.61423300	5.18321000	-1.51693800
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H	-1.90680700	0.23574900	1.85470700
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H	-8.20073800	-0.42645300	2.17886200
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H	-5.68481100	-1.03303500	-1.25225300
H	-3.13189900	0.66341500	-2.12318100
H	-4.22977600	1.23417400	-0.86056400
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C	2.19285700	-2.10690100	-0.92291900
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H	4.24722300	-1.32475800	1.69540400
H	5.45587700	-3.29784300	0.87188400
H	4.57652600	-4.55693700	-1.09654500
H	2.51151600	-3.79664900	-2.21560700
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H	-1.02593400	-3.79737000	0.80108900
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H	3.56062000	-1.35604800	-2.92175300
P	1.74284400	0.04310200	0.85790800
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C	1.96724400	2.86598700	0.44702200

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H	3.80745100	1.87982600	2.36553500
H	4.68259100	0.81152600	1.26745500
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H	4.70113400	5.04463800	0.43180200
H	3.81909800	4.48326400	1.84732500
C	1.78010800	-0.18903200	2.72499800
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H	2.84035700	-0.20603000	3.01387700
C	1.15560500	0.77716400	5.00081200
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C	1.19871000	-1.72835300	4.67402000
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C	0.53447200	-0.56213700	5.41719700
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H	2.20208900	0.81270300	5.33634400
H	0.71547500	-2.67752100	4.93607000
H	2.24708000	-1.81435000	4.99403900
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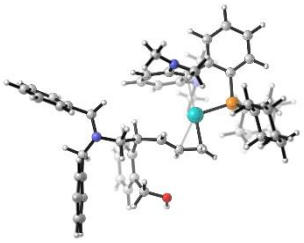
E



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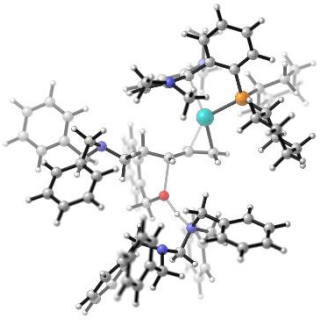
TS-Outer



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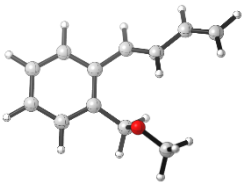

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H	-0.57418400	2.35405900	1.16817300
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C	4.17966000	-1.15010400	-0.22574300
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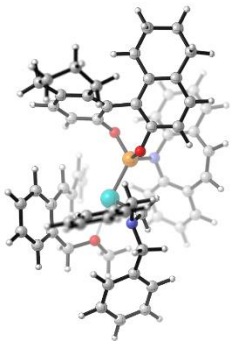
B'-L4



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C	6.51627400	-2.19868700	-1.96094300
C	5.26537800	-1.78230400	-2.42748600
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C	1.80000900	3.11680400	-4.00739700
C	2.26465300	4.40866100	-4.26686300
C	2.85910200	5.15331600	-3.24805000
C	2.98232900	4.60097100	-1.96987000
C	2.51237100	3.31362000	-1.71103800
H	2.54199600	-1.72728600	-1.23302000
H	0.87762900	-1.23630100	-1.74083800
H	3.20682100	-0.68829500	-3.60901900
H	3.70261300	0.97344300	-3.29359000
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H	8.31442900	-1.61867500	-0.92030000
H	6.85770100	-3.21114100	-2.15813900
H	4.64821300	-2.47172500	-2.99987100
H	0.94288000	0.75095300	-3.37401100
H	0.55963300	1.22753200	-1.72109200
H	1.34075500	2.53901200	-4.80654900
H	2.16605500	4.82803600	-5.26421400
H	3.22454200	6.15687600	-3.44713800
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H	-2.21637100	3.31999500	3.95433700
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H	-4.25244000	5.04152700	2.73343900
C	2.77829500	4.24969000	2.07209500

C	1.98232000	3.15422200	2.39387300
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C	1.54991100	0.80662900	2.88428200
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C	1.78588900	-0.42644100	3.43347600
H	2.79266800	-0.82496900	3.49553600
C	4.51423900	0.29334100	2.00115400
H	4.62136200	-0.12867900	3.01282700
H	5.52122100	0.38731100	1.58038000
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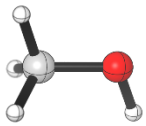

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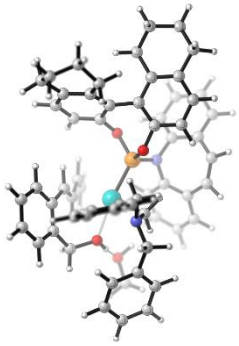

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H	-0.85215700	-1.11707500	1.78506000
H	-3.02311200	-0.31237500	3.75289900
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H	1.66720800	0.70951900	-3.76604600
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C	7.50499300	0.70283600	0.40363600
H	7.55526800	1.61978100	1.00820300
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H	5.85976700	1.47844700	-0.77344200
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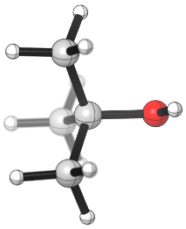

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G’

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H	0.15881500	3.17836500	4.78175100
H	-0.00510300	5.63346400	5.06087100
H	-0.81400700	7.04925500	3.18238100
H	-1.45081500	5.98542200	1.02404400
H	-1.28304800	3.53198000	0.74839500
C	3.96297400	0.04062500	0.25143600
C	2.98913800	-0.35640100	1.17070200
C	3.30871500	-0.87198100	2.42204000
C	4.64622600	-1.07512700	2.72937900
C	5.65559300	-0.82796400	1.78767000
C	5.31870500	-0.28431500	0.53327300
C	3.55910500	0.77821700	-0.98610600
C	2.63803400	0.21225300	-1.87727600
C	2.40764300	0.75935900	-3.13799400
C	3.02649600	1.95507000	-3.47680500
C	3.82807700	2.64226600	-2.55469000
C	4.08885600	2.06248300	-1.29792600
H	2.51510600	-1.12120600	3.11759600
H	4.91766600	-1.47211800	3.70469300
H	1.76682300	0.23801400	-3.84044300
H	2.86541000	2.38081300	-4.46448600
O	1.63116700	-0.19061800	0.86106500
O	1.95489700	-0.96812500	-1.55135500
P	0.83887000	-1.01965300	-0.32571600
C	0.20212300	-3.76325700	2.59133500
C	1.55292100	-3.82865800	2.55597700
H	-0.27588900	-3.76693400	3.56915400
H	2.07185700	-3.87600700	3.51174200
N	0.86845300	-2.68627100	-0.03994800
C	2.40302100	-3.99490400	1.37779500
C	3.59937800	-4.72634600	1.50159000
C	4.40865900	-4.98186100	0.40017100
C	4.03866800	-4.50324100	-0.85976900
C	2.86905400	-3.75924200	-1.00613600

C	2.06625700	-3.48535300	0.10484000
H	3.87671300	-5.11219500	2.47912400
H	5.32092600	-5.55872200	0.52030800
H	4.66036000	-4.70486200	-1.72714700
H	2.57955600	-3.36987600	-1.97468100
C	-2.74885700	-4.82977700	0.51673100
C	-1.92387500	-4.55935400	1.60434600
C	-0.69833600	-3.88314900	1.44488100
C	-0.35953700	-3.41762900	0.15521900
C	-1.18414200	-3.69647900	-0.93852400
C	-2.37221000	-4.40912800	-0.76426900
H	-3.66575600	-5.39401700	0.66245400
H	-2.20016300	-4.91416000	2.59379900
H	-0.88695700	-3.35781200	-1.92495500
H	-2.97955800	-4.66068400	-1.63025700
C	7.09544500	-1.13421100	2.17283300
H	7.46913300	-0.31181700	2.80188700
H	7.11891600	-2.02864200	2.80733100
C	8.03159500	-1.30348300	0.97234600
H	9.07199800	-1.34258400	1.31463800
H	7.82532900	-2.25913100	0.47033700
C	7.82188000	-0.15517400	-0.01689000
H	8.03158600	0.80091000	0.48386100
H	8.52104100	-0.22993000	-0.85785700
C	6.38440300	-0.15979100	-0.55034000
H	6.21332300	0.71853900	-1.17599800
H	6.26014500	-1.02243000	-1.22377500
C	4.84383300	2.86116600	-0.23977500
H	4.09047300	3.28087800	0.44519800
H	5.46216700	2.20995500	0.38034100
C	5.68832400	4.00937700	-0.80485700
H	6.05915400	4.62631100	0.02173000
H	6.57252100	3.60548300	-1.31854400
C	4.86874300	4.84787900	-1.78765000

H	5.44753700	5.70385700	-2.15278800
H	3.98763400	5.25567100	-1.27258000
C	4.42702500	3.97847600	-2.96862700
H	3.70968600	4.51901300	-3.59840300
H	5.29884700	3.78221200	-3.61122200
C	-1.37478800	4.73614100	-2.24653000
C	-0.93834700	3.44417300	-2.52545500
C	-1.76680800	2.31895400	-2.33364100
C	-3.05722800	2.52431400	-1.77798200
C	-3.47424600	3.82804400	-1.49366100
C	-2.65815800	4.93393000	-1.73875700
H	-0.71649700	5.58075600	-2.42705400
H	0.06108300	3.29272100	-2.92462600
H	-4.46325300	3.97822400	-1.06896500
H	-3.01925500	5.93484100	-1.52140600
C	-1.19546800	1.03420600	-2.77614500
H	-0.13959300	1.11068300	-3.02338800
C	-1.80346600	-0.14451900	-3.12241100
H	-2.87004100	-0.29153000	-2.99547200
C	-4.01537400	1.40061800	-1.48491400
H	-4.34858700	0.91695900	-2.41279600
H	-4.90262700	1.79783500	-0.98389100
O	-3.42752500	0.40847000	-0.61612100
H	-3.94726000	-0.43019300	-0.72499100
C	-1.11751700	-1.21311900	-3.83417000
H	-0.04241200	-1.11003100	-3.97031700
C	-1.75050300	-2.27555100	-4.36040600
H	-2.82454000	-2.40783600	-4.25033400
H	-1.21868800	-3.03073800	-4.93085800
C	-6.01327400	-2.38536400	-1.34394600
O	-4.62986200	-1.91498700	-1.29173400
H	-4.05624400	-2.64886200	-1.00655800
C	-6.39621400	-2.97175300	0.01886800
H	-7.43898200	-3.30722800	0.01812300

H	-5.76955100	-3.83798500	0.26413400
H	-6.27344500	-2.22185000	0.80640000
C	-6.84961800	-1.14731600	-1.66693500
H	-6.52907200	-0.70038900	-2.61437400
H	-7.90614500	-1.41760500	-1.76067900
H	-6.75922300	-0.39856100	-0.87260000
C	-6.12387700	-3.43259400	-2.45822800
H	-7.15601000	-3.78412300	-2.56159300
H	-5.80723000	-3.00963900	-3.41735500
H	-5.49796200	-4.30731200	-2.24220200