

Supporting Information

For

Ni-Catalyzed Deaminative Hydroalkylation of Internal Alkynes

Ze-Fan Zhu, Jia-Lin Tu and Feng Liu*

Jiangsu Key Laboratory of Neuropsychiatric Diseases and Department of Medicinal Chemistry,
College of Pharmaceutical Sciences, Soochow University, 199 Ren-Ai Road, Suzhou, Jiangsu
215123, People's Republic of China

E-mail: fliu2@suda.edu.cn

Table of contents

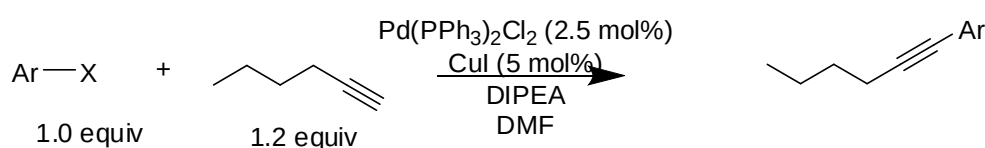
1. General remarks	S1
2. Synthesis of alkynes	S1
3. Synthesis of pyridinium salts	S3
4. Optimization of the Reaction Conditions	S4
5. General experimental procedure.....	S6
6. Gram-scale reaction.....	S7
7. Mechanistic studies	S8
a) Radical trapping experiment	S8
b) Isotopic labelling experiment.....	S8
8. Characterization of the substrates and products.....	S9
9. NMR Spectra for the substrates and products	S40

1. General remarks

^1H NMR spectra were recorded on 400 or 600 MHz (100 or 150 MHz for ^{13}C NMR, 376 or 564 MHz for ^{19}F NMR) agilent NMR spectrometer with CDCl_3 as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts were reported in parts per million (ppm, δ scale) downfield from TMS at 0.00 ppm and referenced to the CDCl_3 at 7.26 ppm (for ^1H NMR) or 77.16 ppm (for ^{13}C NMR). ^{19}F NMR chemical shifts were determined relative to CFCl_3 at δ 0.00 ppm. Mass spectroscopy data of the products were collected on a GCT PremierTM (CI) and Agilent Technologies 1290 Infinity (ESI). Mass Spectrometer Infrared (FT-IR) spectra were recorded on a Varian 1000FT-IR, ν_{max} in cm^{-1} . Melting points were measured using SGW, X-4B and values are uncorrected. All commercially available reagents and solvents were used as received unless otherwise specified.

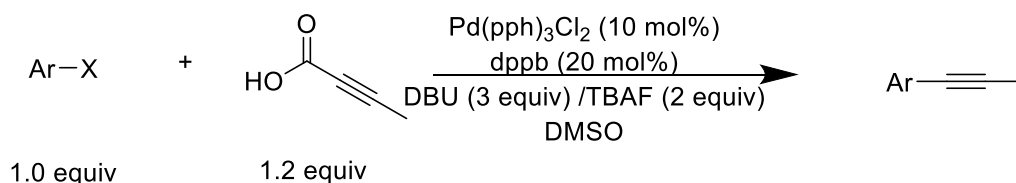
2. Synthesis of alkynes

Procedure A:



To a 25 mL two-neck bottle, $\text{Ar}-\text{X}$ (5 mmol, 1.0 equiv), $\text{PdCl}_2(\text{PPh}_3)_2$ (87.7 mg, 0.125 mmol, 2.5 mol%), CuI (47.5 mg, 0.25 mmol, 5 mol%), NEt_3 (1.5 mL), and DMF (2.5 mL) were added. The tube was degassed under reduced pressure and refilled with Ar for three times. The mixture was stirred at 80 °C for 5 minutes. Then 1-Hexyne (0.69 mL, 6 mmol, 1.2 equiv) was added into the mixture to stir for 12h. After cooling to room temperature, saturated NH_4Cl solution was poured into the reaction mixture and extracted with CH_2Cl_2 . The organic layer was washed with water, dried over Na_2SO_4 , and filtered. The filtrate was concentrated *in vacuo*. The residue was purified by silica gel column chromatography to afford alkyne. (*Angew. Chem. Int. Ed.* **2015**, 54, 12923–12927.)

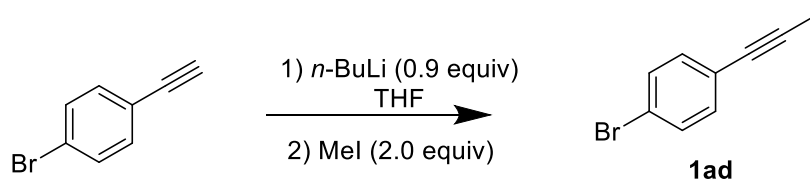
Procedure B:



To a 50 mL two-neck bottle, $\text{PdCl}_2(\text{PPh}_3)_2$ (35 mg, 0.05 mmol, 1 mol%), 1,4-bis(diphenylphosphino)butane (dppb) (42 mg, 0.10 mmol, 2 mol%), 2-butynoic acid (0.50 g, 6.0 mmol, 1.2 equiv), ArX (5.0 mmol, 1.0 equiv), DMSO (15 mL), and

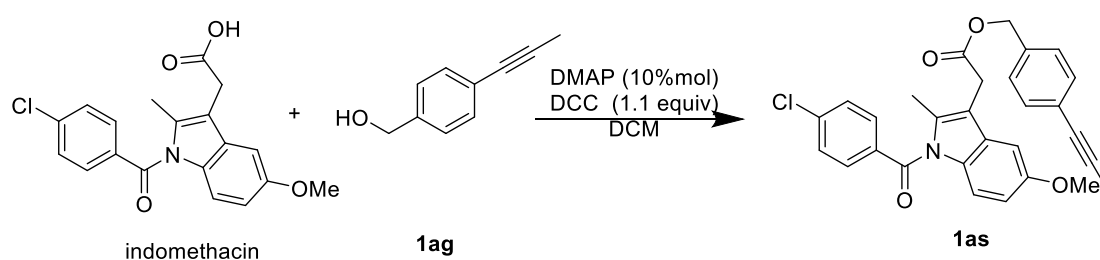
DBU (2.2 mL, 15mmol, 3.0 equiv) or TBAF (1 M in THF, 10 mL, 10 mmol) were added. The tube was degassed under reduced pressure and refilled with Ar for three times. The solution was stirred at 110 °C for 12 h. After cooling to room temperature, sat. NH₄Cl aq. was poured into the reaction mixture and extracted with CH₂Cl₂. The organic layer was washed with water, dried over Na₂SO₄, and filtered. The filtrate was concentrated *in vacuo*. The residue was purified by silica gel column chromatography to afford alkyne. (*Angew. Chem. Int. Ed.* **2015**, 54, 12923–12927.)

Procedure C:



To a dried 50 mL two-neck bottle, 4-bromophenylacetylene (900 mg, 5.0 mmol) and anhydrous THF (25 mL) were added. The bottle was allowed to be cooled around -78 °C; *n*-BuLi (2.5 M in THF, 1.8 mL, 4.5 mmol) was added dropwise and the reaction mixture was stirred for 1 h. To the reaction mixture, MeI (0.62 mL, 10 mmol) was added dropwise, and the reaction mixture was stirred at room temperature for 2 h. After quenching with sat. NH₄Cl aq., the mixture was extracted with CH₂Cl₂. The organic layer was dried over Na₂SO₄, and filtered. The filtrate was concentrated *in vacuo*. The residue was purified by silica gel column chromatography and further purification by silica gel chromatography provided pure product **1ad** (72%) as a pale yellow oil. (*Angew. Chem. Int. Ed.* **2015**, 54, 12923–12927.)

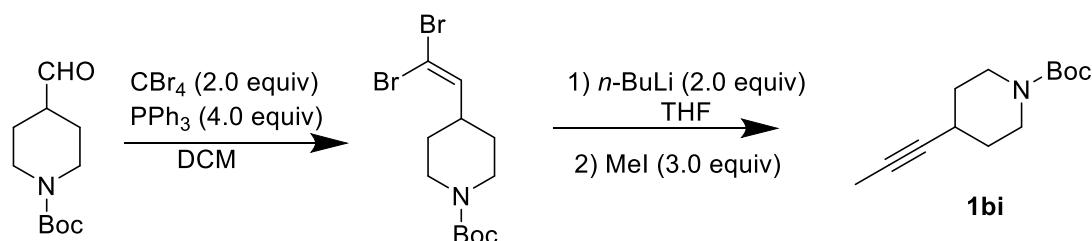
Procedure D:



To a 100 ml oven-dried round-bottomed flask equipped with magnetic stir bar added indomethacin (1.0g, 3.0 mmol), (4-(prop-1-yn-1-yl)phenyl)methanol (**1ag**) (481.8 mg, 3.3 mmol), DMAP (36.6 mg, 0.3 mmol) and DCM (50 ml). Then DCC (681 mg, 3.3 mmol) dissolved in DCM (10 ml) was added dropwise. The mixture was stirred at room temperature for overnight. The mixture was quenched by sat. NH₄Cl aq, extracted by EtOAc, washed by sat NaHCO₃, sat NaCl. The organic layer was dried over Na₂SO₄, and filtered. The filtrate was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (DCM : EtOAc = 10:1 to DCM : EtOAc = 2:1) and further purification by silica gel chromatography provided pure

product as yellow solid.

Procedure E:

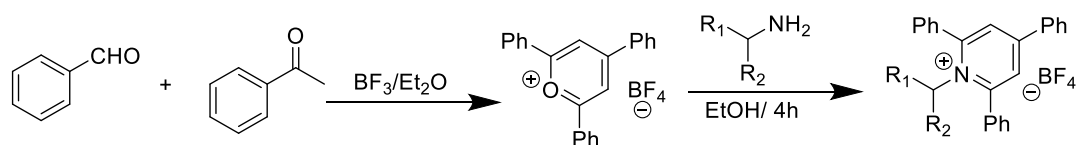


Step 1: To a solution of carbon tetrabromide (3.31 g, 10.0 mmol) and tri-phenylphosphine (5.24 g, 20.0 mmol) in dichloromethane (CH_2Cl_2 , 20 ml) was added dropwise a solution of *tert*-butyl 4-formylpiperidine-1-carboxylate (1.0 g, 5 mmol) in CH_2Cl_2 (30 ml) at 0 °C, and the mixture was stirred at 0 °C for 1 h. This solution was diluted with diethyl ether (Et_2O , 50 ml), and the precipitate was filtered off. The filtrate was concentrated *in vacuo*. The residue was chromatographed on silica gel (10% EtOAc –hexane) to give 1.4755 g (80%) of *tert*-butyl 4-(2,2-dibromovinyl)piperidine-1-carboxylate as a white solid.

Step 2: To a solution of *tert*-butyl 4-(2,2-dibromovinyl)piperidine-1-carboxylate (738 mg, 2.0 mmol) in tetrahydrofuran (THF, 4.0 ml) was added *n*-butyllithium (*n*-BuLi, 2.5 M solution in hexane, 1.6 ml, 4.0 mmol) at -78 °C under a nitrogen atmosphere, and the mixture was stirred at -78 °C for 1 h and at 0 °C for 1 h. Ethyl chloroformate (0.4 ml, 6.0 mmol) was added at -78 °C, and the reaction mixture was allowed to warm to rt to stir for overnight. The resulting mixture was poured into water, and extracted with EtOAc . The extract was washed with brine, dried and evaporated. The residue was chromatographed on silica gel (10% EtOAc –hexane) to give 413 mg (93%) of **1bi** as a colorless oil. (*Chem. Pharm. Bull.* **2004**, 52, 6, 675–687.)

3. Synthesis of pyridinium salts

Procedure F:



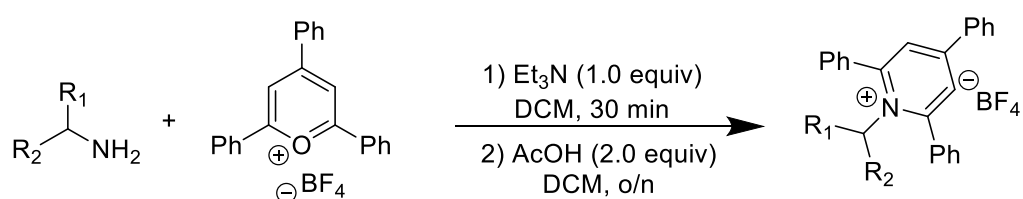
Synthesis of triphenylpyrylium tetrafluoroborate: Benzaldehyde (1 equiv) and acetophenone (2 equiv) were placed in a closed two-necked flask equipped with a magnetic stirrer, then boron trifluoride etherate (2.5 equiv) was added dropwise under argon treatment. The mixture was reacted at 100 °C for two hours and cooled to ambient temperature. Methyl *tert*-butyl ether was added to the reaction mixture and the resulting suspension stirred at ambient temperature. The solid was collected by filtration and washed with methyl *tert*-butyl ether. Recrystallization by acetone and

methyl *tert*-butyl ether to get pure light yellow solid.

A closed flask equipped with a magnetic stir bar was charged with triphenylpyrylium tetrafluoroborate (1.0 equiv) and the corresponding primary amine (1.2 equiv). Ethanol (1.0 M) was added to the reaction vessel and the tube sealed. No precautions to protect the reaction mixture from air and moisture were taken. The reaction mixture was heated to 90 °C for 4 h and then cooled to ambient temperature. Methyl *tert*-butyl ether was added to the reaction mixture and the resulting suspension stirred at room temperature. The solid was collected by filtration and washed with methyl *tert*-butyl ether. After the operations required the solids were dried under reduced pressure to obtain the analytically pure pyridinium salts.

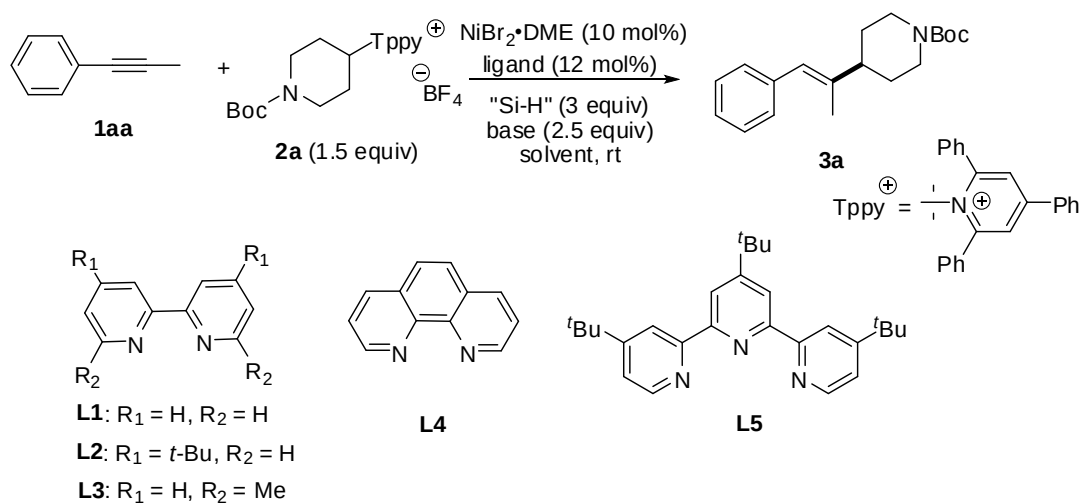
Amine hydrochlorides as starting materials: In case amine hydrochlorides were used as feedstocks for the pyridinium salts, the amine hydrochloride (1.2 equiv) was added to a clean and closed flask. Ethanol (1.0 M) and triethyl amine (1.2 equiv) were added. The resulting suspension was stirred for 30 min at ambient temperature. Triphenylpyrylium tetrafluoroborate (1.0 equiv) was added, the tube sealed and stirred for 4 h at 90 °C. Methyl *tert*-butyl ether was added to the reaction mixture and the resulting suspension stirred at room temperature for at least 1 h to complete the precipitation process. The solid was collected by filtration and washed with methyl *tert*-butyl ether. After the operations required the solids were dried under reduced pressure to obtain the analytically pure pyridinium salts. To remove water-soluble impurities, the collected solids were washed with water before washing with methyl *tert*-butyl ether. (*Org. Biomol. Chem.*, **2019**,17, 1531–1534.)

Procedure G:



This reaction was set-up under air. The alkyl amine (1.1 equiv) was added to a suspension of 2,4,6-triphenylpyrylium tetrafluoroborate (1.0 equiv) and CH_2Cl_2 (0.5 M) in a round-bottomed flask equipped with a stir bar. The mixture was stirred as Et_3N (1.0 equiv for free base amines; 2.0 equiv for amine hydrochloride salts) was added by syringe. And the mixture was stirred at rt for 30 min. Then acetic acid (2.0 equiv) was added to the mixture by needle and the mixture was stirred at rt overnight. The filtrate was then washed successively with aq. HCl (1.0 M), aq. $NaHCO_3$ (sat.), and sat. $NaCl$, dried with Na_2SO_4 , filtered, and purified by silica gel chromatography with acetone/ CH_2Cl_2 as the eluent. (*J. Am. Chem. Soc.* **2019**, 141, 6, 2257–2262.)

4. Optimization of the Reaction Conditions^{a,b}



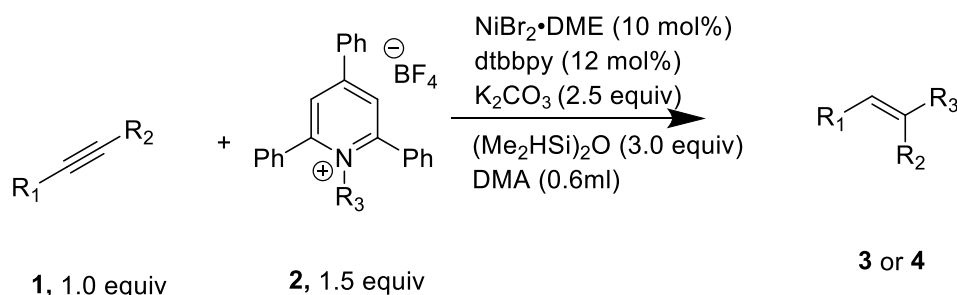
Entry	Ligand	"Si-H"	Base	Solvent	Yield [%]
1	-	(EtO) ₂ MeSiH	K ₂ CO ₃	DMA	23
2	L1	(EtO) ₂ MeSiH	K ₂ CO ₃	DMA	63
3	L2	(EtO) ₂ MeSiH	K ₂ CO ₃	DMA	59
4	L3	(EtO) ₂ MeSiH	K ₂ CO ₃	DMA	< 5
5	L4	(EtO) ₂ MeSiH	K ₂ CO ₃	DMA	40
6	L5	(EtO) ₂ MeSiH	K ₂ CO ₃	DMA	46
7 ^c	L2	PMHS	K ₂ CO ₃	DMA	56
8	L2	(EtO) ₃ SiH	K ₂ CO ₃	DMA	10
9	L2	(Me₂HSi)₂O	K₂CO₃	DMA	73
10	L2	Et ₃ SiH	K ₂ CO ₃	DMA	< 5
11	L1	(Me ₂ HSi) ₂ O	K ₂ CO ₃	DMA	62
12	L2	(Me ₂ HSi) ₂ O	Na ₂ CO ₃	DMA	45
13	L2	(Me ₂ HSi) ₂ O	Cs ₂ CO ₃	DMA	24
14	L2	(Me ₂ HSi) ₂ O	K ₃ PO ₄	DMA	54
15	L2	(Me ₂ HSi) ₂ O	K ₂ CO ₃	DMF	62
16	L2	(Me ₂ HSi) ₂ O	K ₂ CO ₃	DMSO	5
17	L2	(Me ₂ HSi) ₂ O	K ₂ CO ₃	THF	40
18	L2	(Me ₂ HSi) ₂ O	K ₂ CO ₃	CH ₃ CN	28
19 ^d	L2	(Me ₂ HSi) ₂ O	K ₂ CO ₃	DMA	< 10
20 ^e	L2	(Me ₂ HSi) ₂ O	K ₂ CO ₃	DMA	0

^a Reaction conditions: A mixture of **1a** (0.2 mmol), **2a** (0.3 mmol), NiBr₂•DME (nickel(II) bromide dimethoxyethane, 10 mol%), ligand (12 mol%), "Si-H" (0.6 mmol) and base (0.5 mmol) in solvent (0.6 mL, used without dehydration) was stirred at rt for 6 h. ^b Isolated yields. ^c PMHS =

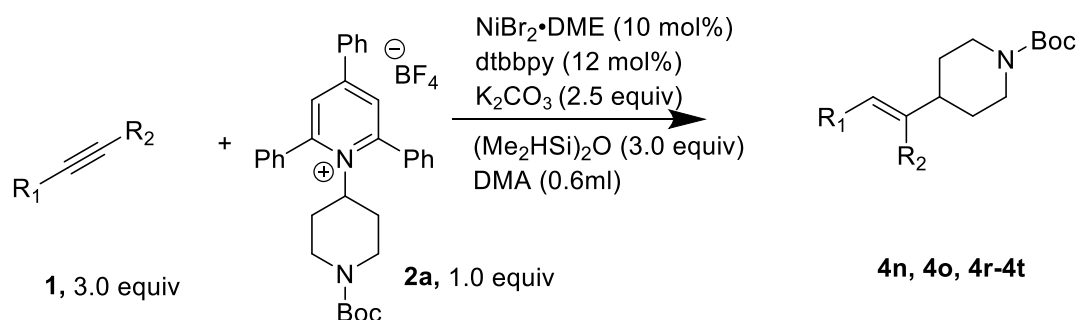
polymethylhydrosiloxane. ^d NiCl₂ or Ni(acac)₂ as catalyst. ^e No Ni catalysis.

Our investigation commenced with 1-Phenylpropyne **1a** and Katritzky salt **2a** as the model substrates to screen the reaction conditions (Table 1). An initial evaluation of the parameters revealed very good regio- and stereo-selectivity to afford the desired product **3a** with various commercially available bi-/tri-dentate nitrogen ligands (entries 2, 3, 5 and 6). Next, we briefly screened a series of “Si-H” species, inorganic bases, solvents (used without dehydration), and nickel catalysts (entries 7–19). In the presence of catalyst NiBr₂•DME, the combination of ligand **L2**, (Me₂HSi)₂O, K₂CO₃, and DMA was determined to be the optimal reaction conditions (entry 9), offering the desired product **3a** in 73% yield with excellent regiocontrol (> 20:1 r.r.) and stereoselectivity (> 20:1 *E:Z*). Without nickel catalysis, most of the starting material was recovered and no desired product was detected (entry 20).

5. General experimental procedure

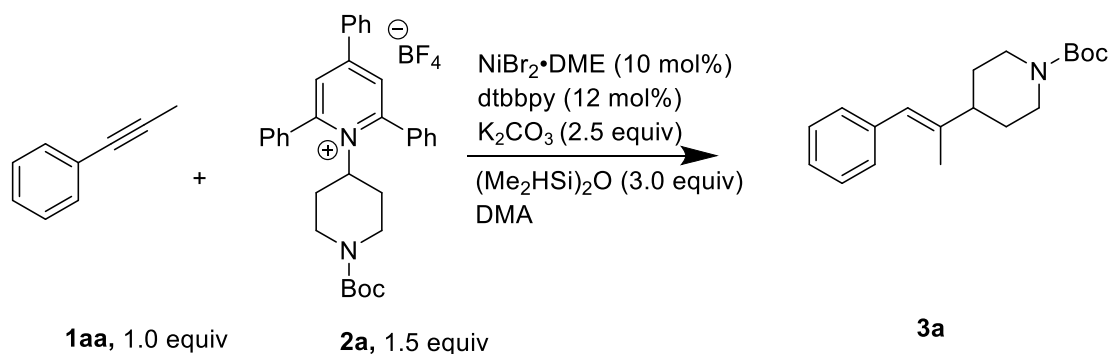


To a 10 mL Schlenk tube equipped with a magnetic stir bar was added NiBr₂•DME (6.3 mg, 0.02 mmol, 10 mol%), 4,4'-Di-*tert*-butyl-2,2'-dipyridyl (6.6 mg, 0.024 mmol, 12 mol%), K₂CO₃ (69.1 mg, 0.5 mmol, 2.5 equiv) and the Katritzky salt (0.3 mmol, 1.5 equiv). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then the alkyne (0.2 mmol, 1.0 equiv) and silane (80 mg, 0.6 mmol, 3.0 equiv) was added. At last, degassed DMA (0.6 mL) was added. The mixture was stirred at room temperature for 4-24 hours. The solvent was removed on a rotary evaporator under reduced pressure and the residue was subjected to column chromatography isolation on silica gel by elution with hexane / ethyl acetate to give the corresponding product.



Procedure for low-boiling point alkynes: To a 10 mL Schlenk tube equipped with a magnetic stir bar was added $\text{NiBr}_2 \cdot \text{DME}$ (6.3 mg, 0.02 mmol, 10 mol%), 4,4'-Di-*tert*-butyl-2,2'-dipyridyl (6.6 mg, 0.024 mmol, 12 mol%), K_2CO_3 (69.1 mg, 0.5 mmol, 2.5 equiv) and the Katritzky salt (0.2 mmol, 1.0 equiv). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then the alkyne (0.6 mmol, 3.0 equiv) and silane (80 mg, 0.6 mmol, 3.0 equiv) was added. At last, degassed DMA (0.6 mL) was added. The mixture was stirred at room temperature for 6-8 hours. The solvent was removed on a rotary evaporator under reduced pressure and the residue was subjected to column chromatography isolation on silica gel by elution with hexane/ ethyl acetate to give the corresponding product.

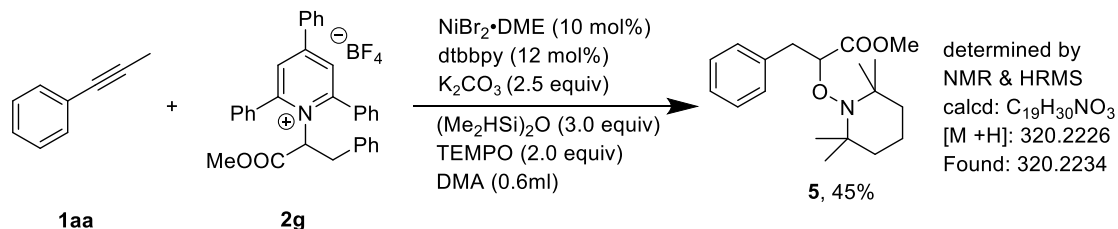
6. Gram-scale reaction



To a 100 mL Schlenk tube equipped with a magnetic stir bar was added $\text{NiBr}_2 \cdot \text{DME}$ (154 mg, 0.5 mmol, 10 mol%), 4,4'-Di-*tert*-butyl-2,2'-dipyridyl (161 mg, 0.6 mmol, 12 mol%), K_2CO_3 (1.7 g, 0.5 mmol, 2.5 equiv) and the Katritzky salts (4.3 g, 7.5 mmol, 1.5 equiv). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then the alkyne (0.625 mL, 5.0 mmol, 1.0 equiv) and silane (2.4 mL, 15.0 mmol, 3.0 equiv) was added. At last, degassed DMA (15.0 mL) was added. The mixture was stirred at room temperature for about 8 hours. The solvent was removed on a rotary evaporator under reduced pressure and the residue was subjected to column chromatography isolation on silica gel by elution with hexane / ethyl acetate (100:1) to hexane / ethyl acetate (20:1) to give the corresponding product **3a** (1.05 g, 70%).

7. Mechanistic studies

a) Radical trapping experiment



When 2.0 equiv of TEMPO was added to the reaction of **1aa** with **2g** under the standard conditions, no desired product (**3g**) was detected by TLC. A TEMPO-trapped product was determined by HRMS and NMR.

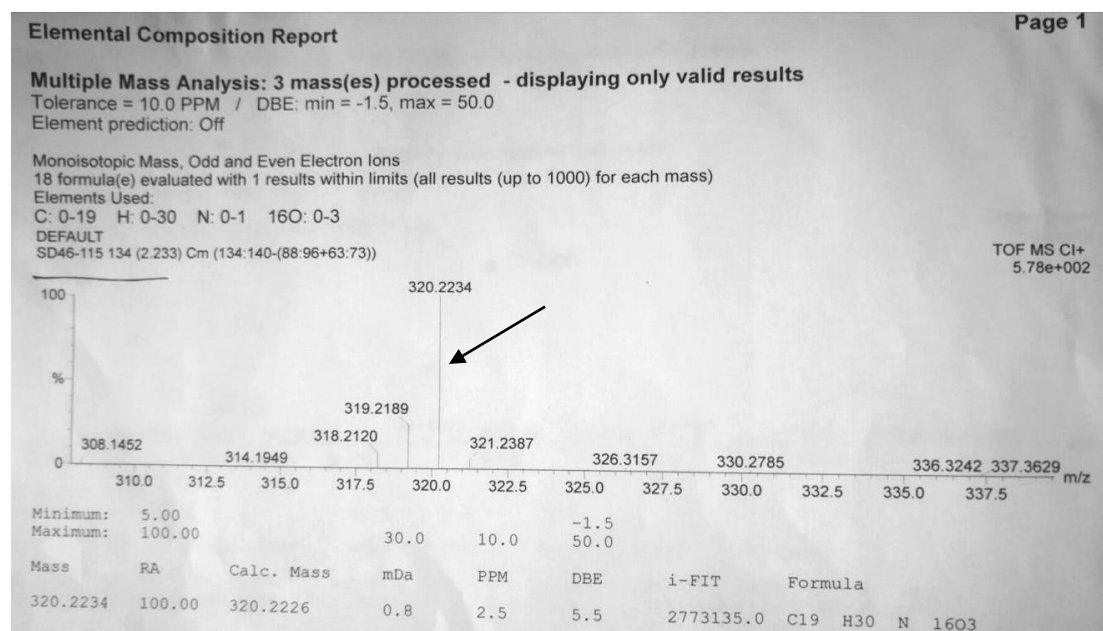
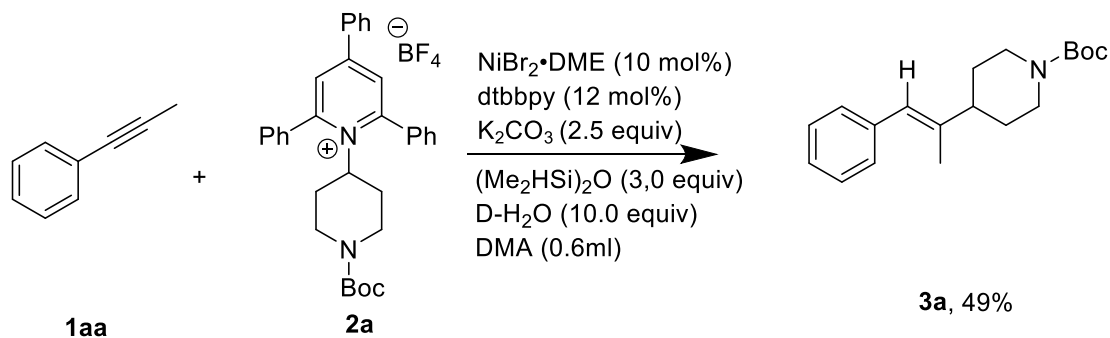


Figure S1. HRMS trace of the TEMPO trapping experiment.

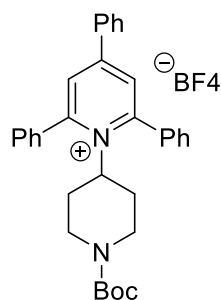
b) Isotopic labelling experiment



To a 10 mL Schlenk tube equipped with a magnetic stir bar was added NiBr₂·DME

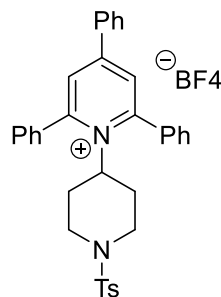
(6.3 mg, 0.02 mmol, 10 mol%), 4,4'-Di-*tert*-butyl-2,2'-dipyridyl (6.6 mg, 0.024 mmol, 12 mol%), K₂CO₃ (69.1 mg, 0.5 mmol, 2.5 equiv) and Katritzky salt **2a** (0.3 mmol, 1.5 equiv). The resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then the alkyne **1aa** (0.2 mmol, 1.0 equiv) and silane (80 mg, 0.6 mmol, 3.0 equiv) was added. At last, degassed dry DMA (0.6 mL) and D₂O (40 μ L, 2 mmol) was added. The resulting mixture was stirred at r.t for 6 hours. After the reaction was finished, the solvent was removed on a rotary evaporator under reduced pressure and the residue was subjected to column chromatography isolation on silica gel by elution with hexane / ethyl acetate to give the corresponding product **3a** as white solid (29.6 mg, 49% yield).

8. Characterization of the substrates and products



1-(1-(*tert*-Butoxycarbonyl)piperidin-4-yl)-2,4,6-triphenylpyridin-1-ium

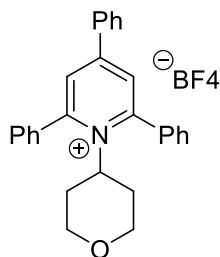
tetrafluoroborate (2a): Prepared via general procedure F; white solid; ¹H NMR (600 MHz, CDCl₃) δ 7.80 – 7.65 (m, 8H), 7.63 – 7.53 (m, 6H), 7.53 – 7.48 (m, 1H), 7.47 – 7.39 (m, 2H), 4.76 (t, *J* = 12.0 Hz, 1H), 4.02 – 3.79 (m, 2H), 2.27 – 2.00 (m, 4H), 1.72 – 1.55 (m, 2H), 1.30 (s, 9H); ¹³C NMR (150 MHz, CDCl₃) δ 157.2, 155.5, 154.3, 134.1, 133.9, 132.1, 131.2, 129.7, 129.4, 129.1, 128.4, 80.2, 70.0, 44.7, 43.8, 32.8, 28.4; ¹⁹F NMR (564 MHz, CDCl₃) δ -152.96 (s), -153.01 (s).



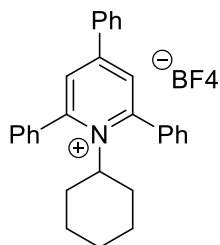
2,4,6-Triphenyl-1-(1-tosylpiperidin-4-yl)pyridin-1-ium tetrafluoroborate (2b) :

Prepared via general procedure F; white solid; ¹H NMR (400 MHz, CDCl₃) δ 7.73 (s,

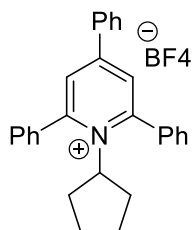
2H), 7.71 – 7.64 (m, 6H), 7.61 – 7.48 (m, 7H), 7.45 – 7.36 (m, 4H), 7.22 (d, J = 8.0 Hz, 2H), 4.58 – 4.47 (m, 1H), 3.63 – 3.54 (m, 2H), 2.40 (s, 3H), 2.25 – 2.16 (m, 2H), 1.85 – 1.70 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 157.3, 155.5, 143.9, 133.9, 133.7, 133.2, 132.2, 131.2, 129.8, 129.7, 129.3, 129.2, 128.4, 128.3, 127.5, 69.1, 46.4, 32.3, 21.7; ^{19}F NMR (564 MHz, CDCl_3) δ -152.88 (s), -152.93 (s).



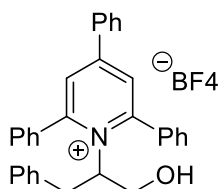
2,4,6-Triphenyl-1-(tetrahydro-2H-pyran-4-yl)pyridin-1-ium tetrafluoroborate (2c): Prepared via general procedure F; yellowish solid; ^1H NMR (400 MHz, CDCl_3) δ 7.79 – 7.70 (m, 6H), 7.69 – 7.64 (m, 2H), 7.63 – 7.53 (m, 6H), 7.50 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.5 Hz, 2H), 4.94 – 4.80 (m, 1H), 3.76 – 3.65 (m, 2H), 2.78 (t, J = 11.2 Hz, 2H), 2.05 (d, J = 11.9 Hz, 2H), 1.92 – 1.78 (m, 2H); ^{13}C NMR (600 MHz, CDCl_3) δ 157.3, 155.3, 134.1, 133.9, 132.1, 131.2, 129.7, 129.4, 129.1, 128.4, 128.3, 69.2, 67.9, 33.9; ^{19}F NMR (376 MHz, CDCl_3) δ -152.86 (s), -152.92 (s);



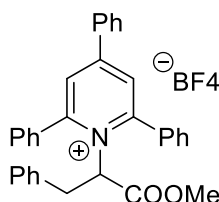
1-Cyclohexyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2d): Prepared via general procedure F; white solid; ^1H NMR (600 MHz, CDCl_3) δ 7.76 (s, 2H), 7.71 (t, J = 6.8 Hz, 6H), 7.63 – 7.52 (m, 6H), 7.49 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 4.64 – 4.55 (m, 1H), 2.15 – 2.05 (m, 2H), 1.61 – 1.52 (m, 2H), 1.52 – 1.40 (m, 2H), 1.37 – 1.30 (m, 1H), 0.78 – 0.67 (m, 2H), 0.65 – 0.54 (m, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 157.2, 155.1, 134.12, 134.09, 131.9, 130.9, 129.6, 129.4, 128.9, 128.4, 128.2, 72.0, 33.7, 26.6, 24.7; ^{19}F NMR (564 MHz, CDCl_3) δ -153.30 (s), -153.36 (s).



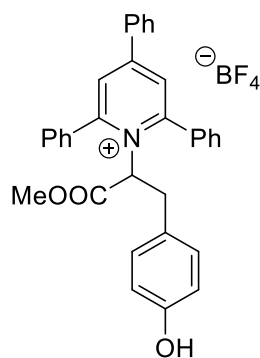
1-Cyclopentyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2e): Prepared via general procedure F; white solid; ^1H NMR (600 MHz, CDCl_3) δ 7.78 – 7.74 (m, 6H), 7.69 (d, J = 7.4 Hz, 2H), 7.60 – 7.53 (m, 6H), 7.49 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 5.02 (p, J = 9.0 Hz, 1H), 2.25 – 2.16 (m, 2H), 2.03 – 1.96 (m, 2H), 1.18 – 1.10 (m, 2H), 0.96 – 0.87 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 157.8, 154.9, 134.2, 134.1, 132.0, 130.9, 129.7, 129.6, 129.0, 128.3, 128.2, 70.8, 33.8, 24.7; ^{19}F NMR (564 MHz, CDCl_3) δ -153.38 (s), -153.43 (s).



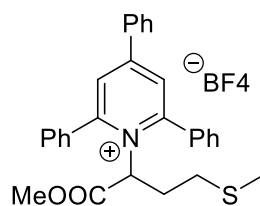
1-(1-Hydroxy-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2f): Prepared via general procedure F; white solid; ^1H NMR (400 MHz, CDCl_3) δ 7.85 – 7.71 (m, 7H), 7.68 – 7.29 (m, 10H), 7.19 – 7.13 (m, 1H), 7.12 – 7.07 (m, 2H), 6.60 – 6.55 (m, 2H), 5.45 – 5.32 (m, 1H), 3.79 – 3.69 (m, 1H), 3.54 (dd, J = 11.9, 5.6 Hz, 1H), 3.26 – 3.17 (m, 1H), 2.53 (dd, J = 14.1, 7.9 Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 155.1, 135.8, 133.7, 133.5, 132.3, 131.1, 130.2, 129.8, 129.1, 129.0, 128.6, 128.3, 127.5, 73.3, 62.4, 38.5; ^{19}F NMR (564 MHz, CDCl_3) δ -152.59 (s), -152.64 (s).



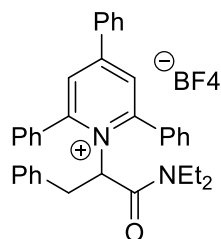
(1-Methoxy-1-oxo-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2g): Prepared via general procedure F; white solid; ^1H NMR (600 MHz, CDCl_3) δ 7.93 (s, 2H), 7.86 – 7.69 (m, 4H), 7.60 (t, J = 7.2 Hz, 2H), 7.57 – 7.40 (m, 9H), 7.14 – 7.05 (m, 3H), 6.77 (d, J = 7.3 Hz, 2H), 5.64 (dd, J = 7.5, 3.7 Hz, 1H), 3.69 (s, 3H), 3.49 – 3.42 (m, 1H), 2.93 (dd, J = 14.4, 8.0 Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 168.0, 157.1, 157.0, 136.4, 133.8, 132.5, 132.4, 131.7, 129.8, 129.6, 129.2, 129.1, 128.72, 128.66, 128.0, 127.3, 70.3, 53.9, 37.8; ^{19}F NMR (564 MHz, CDCl_3) δ -152.80 (d, J = 4.5 Hz), -152.86 (d, J = 3.5 Hz).



1-(3-(4-Hydroxyphenyl)-1-methoxy-1-oxopropan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2h): Prepared via general procedure F; yellowish solid; ^1H NMR (600 MHz, CDCl_3) δ 7.92 (s, 2H), 7.86 – 7.83 (m, 2H), 7.79 – 7.46 (m, 13H), 6.62 (d, J = 8.5 Hz, 2H), 6.44 (d, J = 8.4 Hz, 2H), 5.60 (t, J = 6.7 Hz, 1H), 3.70 (s, 3H), 3.15 (dd, J = 14.8, 7.1 Hz, 1H), 2.89 (dd, J = 14.8, 6.4 Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 168.2, 157.1, 156.3, 133.4, 132.9, 132.2, 131.9, 130.0, 129.8, 129.4, 128.7, 127.8, 116.3, 70.9, 53.9, 36.7; ^{19}F NMR (564 MHz, CDCl_3) δ -151.85 (s), -151.90 (s); HRMS (ESI) calcd $\text{C}_{33}\text{H}_{28}\text{NO}_3$ $[\text{M}-\text{BF}_4]^+$: 486.2064, found: 486.2062.

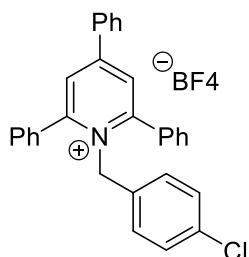


(1-Methoxy-4-(methylthio)-1-oxobutan-2-yl)-2,4,6-triphenylpyridin-1-ium tetra-fluoroborate (2i): Prepared via general procedure F; white solid; ^1H NMR (400 MHz, CDCl_3) δ 7.87 (s, 2H), 7.81 – 7.64 (m, 5H), 7.63 – 7.50 (m, 8H), 7.46 (t, J = 7.3 Hz, 2H), 5.92 (d, J = 7.7 Hz, 1H), 3.73 (s, 3H), 2.37 – 2.16 (m, 3H), 1.95 – 1.85 (m, 1H), 1.84 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 168.4, 156.9, 133.8, 132.5, 132.2, 131.5, 129.6, 129.2, 129.1, 128.5, 127.9, 66.7, 53.9, 31.4, 30.8, 14.7; ^{19}F NMR (564 MHz, CDCl_3) δ -152.74 (s), -152.79 (s).

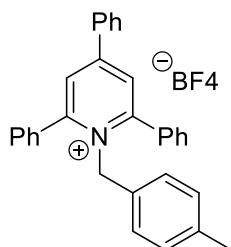


1-(1-(Diethylamino)-1-oxo-3-phenylpropan-2-yl)-2,4,6-triphenylpyridin-1-ium-tetrafluoroborate (2j): Prepared via general procedure F; Green solid; ^1H NMR (600 MHz, CDCl_3) δ 8.04 (br, 2H), 7.85 (s, 2H), 7.76 (d, J = 7.7 Hz, 2H), 7.74 – 7.49 (m, 9H), 7.46 (t, J = 7.6 Hz, 2H), 7.16 – 7.07 (m, 3H), 6.87 (d, J = 7.5 Hz, 2H), 5.96 (dd,

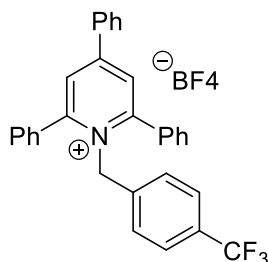
$J = 9.5, 3.4$ Hz, 1H), 3.53 (dd, $J = 14.3, 3.2$ Hz, 1H), 3.23 – 3.04 (m, 2H), 2.96 – 2.85 (m, 1H), 2.26 – 2.10 (m, 2H), 0.98 (t, $J = 6.2$ Hz, 3H), 0.37 (t, $J = 6.3$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 165.2, 157.7, 155.8, 145.8, 135.8, 133.9, 133.6, 132.4, 131.2, 129.9, 129.7, 129.0, 128.93, 128.87, 128.5, 128.4, 127.4, 70.9, 41.3, 40.6, 39.1, 12.8, 12.2; ^{19}F NMR (564 MHz, CDCl_3) δ -152.75 (s), -152.80 (s); HRMS (ESI) calcd $\text{C}_{36}\text{H}_{35}\text{N}_2\text{O} [\text{M}-\text{BF}_4]^+$: 511.2744, found: 511.2743.



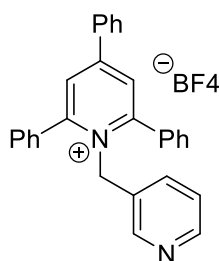
1-(4-Chlorobenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2k): Prepared via general procedure F; white solid; ^1H NMR (400 MHz, CDCl_3) δ 7.89 (s, 2H), 7.75 (d, $J = 7.4$ Hz, 2H), 7.65 (d, $J = 6.9$ Hz, 4H), 7.59 – 7.41 (m, 9H), 7.05 (d, $J = 8.1$ Hz, 2H), 6.41 (d, $J = 8.1$ Hz, 2H), 5.73 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 157.5, 156.6, 134.4, 133.8, 132.8, 132.5, 131.2, 129.9, 129.4, 129.2, 129.1, 128.3, 127.9, 126.8, 57.7; ^{19}F NMR (564 MHz, CDCl_3) δ -152.64 (s), -152.69 (s).



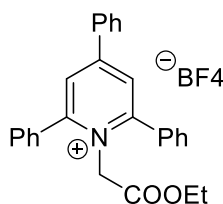
1-(4-Methylbenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2l): Prepared via general procedure F; white solid; ^1H NMR (400 MHz, CDCl_3) δ 7.89 (s, 2H), 7.77 (d, $J = 7.2$ Hz, 2H), 7.64 (d, $J = 6.6$ Hz, 4H), 7.59 – 7.38 (m, 9H), 6.88 (d, $J = 7.7$ Hz, 2H), 6.32 (d, $J = 7.7$ Hz, 2H), 5.71 (s, 2H), 2.22 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 157.6, 156.3, 138.3, 133.9, 132.9, 132.4, 131.1, 131.0, 129.9, 129.5, 129.2, 128.3, 126.6, 126.2, 58.2, 21.1; ^{19}F NMR (564 MHz, CDCl_3) δ -153.00 (s), -153.05 (s).



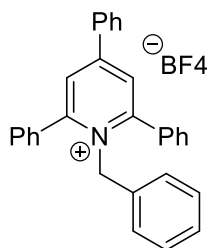
2,4,6-Triphenyl-1-(4-(trifluoromethyl)benzyl)pyridin-1-ium tetrafluoroborate (2m) : Prepared via general procedure F; yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 7.99 (s, 2H), 7.83 (d, $J = 7.3$ Hz, 2H), 7.65 (d, $J = 6.7$ Hz, 4H), 7.59 – 7.45 (m, 9H), 7.37 (d, $J = 7.9$ Hz, 2H), 6.63 (d, $J = 7.7$ Hz, 2H), 5.86 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.5, 156.7, 138.0, 133.7, 132.7, 132.6, 131.2, 130.4 (q, $J = 32.7$ Hz), 129.9, 129.4, 129.2, 128.3, 126.9, 126.8, 125.8 (q, $J = 3.6$ Hz), 123.6 (q, $J = 272.2$ Hz), 58.0; ^{19}F NMR (377 MHz, CDCl_3) δ -62.77 (s), -152.48 (s), -152.53 (d, $J = 2.0$ Hz).



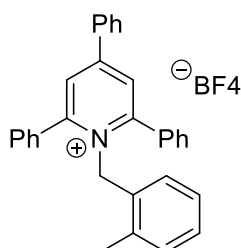
2,4,6-Triphenyl-1-(pyridin-3-ylmethyl)pyridin-1-ium tetrafluoroborate (2n) : Prepared via general procedure F; white solid; ^1H NMR (600 MHz, CDCl_3) δ 8.38 (dd, $J = 4.8, 1.2$ Hz, 1H), 7.96 (s, 2H), 7.82 – 7.78 (m, 2H), 7.71 (d, $J = 1.9$ Hz, 1H), 7.68 (d, $J = 7.2$ Hz, 4H), 7.59 (t, $J = 7.4$ Hz, 1H), 7.54 (t, $J = 7.4$ Hz, 4H), 7.50 (t, $J = 7.3$ Hz, 4H), 7.04 (dd, $J = 7.9, 4.8$ Hz, 1H), 6.86 (d, $J = 8.0$ Hz, 1H), 5.83 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 157.6, 157.0, 149.7, 147.5, 134.6, 133.8, 132.70, 132.66, 131.5, 130.1, 130.0, 129.6, 129.2, 128.3, 126.9, 123.8, 56.1; ^{19}F NMR (564 MHz, CDCl_3) δ -152.76 (s), -152.81 (s).



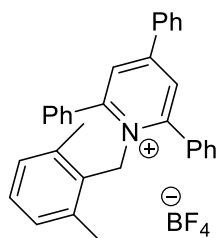
1-(2-Ethoxy-2-oxoethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2o): Prepared via general procedure F; white solid; ^1H NMR (400 MHz, CDCl_3) δ 7.97 (s, 2H), 7.95 – 7.67 (m, 5H), 7.68 – 7.47 (m, 10H), 5.12 (s, 2H), 4.00 (q, $J = 7.0$ Hz, 2H), 1.04 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 167.2, 157.5, 157.1, 134.0, 132.6, 132.3, 131.4, 129.9, 129.2, 128.4, 126.3, 62.9, 56.7, 14.0; ^{19}F NMR (564 MHz, CDCl_3) δ -153.40 (s), -153.46 (d, $J = 0.9$ Hz).



1-Benzyl-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2p): Prepared via general procedure F; white solid; ^1H NMR (400 MHz, CDCl_3) δ 7.94 (s, 2H), 7.81 (d, $J = 7.0$ Hz, 2H), 7.71 – 7.43 (m, 13H), 7.22 – 7.06 (m, 3H), 6.46 (d, $J = 7.1$ Hz, 2H), 5.77 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 157.7, 156.4, 134.3, 133.9, 132.9, 132.5, 131.1, 129.9, 129.3, 129.2, 128.9, 128.4, 128.3, 126.7, 126.4, 58.4; ^{19}F NMR (564 MHz, CDCl_3) δ -153.13 (s), -153.19 (s).

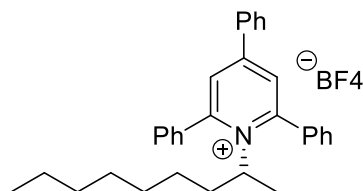


1-(2-Methylbenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2q): Prepared via general procedure F; yellowish solid; ^1H NMR (600 MHz, CDCl_3) δ 7.96 (s, 2H), 7.83 (d, $J = 7.3$ Hz, 2H), 7.69 – 7.51 (m, 7H), 7.51 – 7.45 (m, 2H), 7.45 – 7.37 (m, 4H), 7.14 – 7.08 (m, 2H), 6.93 – 6.87 (m, 1H), 6.47 – 6.40 (m, 1H), 5.66 (s, 2H), 1.63 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 157.8, 156.4, 135.5, 134.0, 133.2, 132.6, 132.5, 131.1, 130.7, 129.9, 129.1, 129.0, 128.3, 128.2, 126.8, 126.4, 124.9, 56.1, 18.7; ^{19}F NMR (564 MHz, CDCl_3) δ -153.17 (s), -153.23 (s); FT-IR (thin film, KBr): ν (cm^{-1}) 1619, 1559, 1051, 767, 704; HRMS (ESI) calcd $\text{C}_{31}\text{H}_{26}\text{N} [\text{M}-\text{BF}_4]^+$: 412.2060, found: 412.2065.

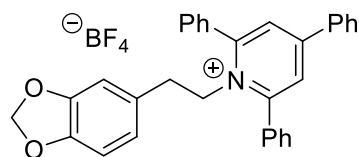


1-(2,6-Dimethylbenzyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2r) : Prepared via general procedure G; yellow solid; ^1H NMR (400 MHz, CDCl_3) δ 7.89 (s, 2H), 7.80 (d, $J = 7.1$ Hz, 2H), 7.73 – 7.65 (m, 4H), 7.62 – 7.51 (m, 3H), 7.51 – 7.40 (m, 6H), 6.86 (t, $J = 7.3$ Hz, 1H), 6.63 (d, $J = 7.3$ Hz, 2H), 5.95 (s, 2H), 1.72 (s, 6H); ^{13}C NMR (150 MHz, CDCl_3) δ 158.8, 155.7, 136.4, 133.5, 132.6, 131.5, 131.1, 130.0,

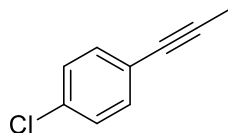
129.4, 129.1, 129.0, 128.9, 128.6, 128.2, 127.3, 126.6, 57.3, 20.3; ^{19}F NMR (564 MHz, CDCl_3) δ -152.78 (s), -152.84 (s); FT-IR (thin film, KBr): ν (cm^{-1}) 2921, 2851, 1616, 1055, 701; HRMS (ESI) calcd $\text{C}_{32}\text{H}_{28}\text{N}[\text{M}-\text{BF}_4]^+$: 426.2216, found: 426.2218.



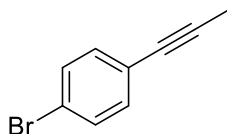
(R)-1-(Nonan-2-yl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2s): Prepared via general procedure F; green solid; ^1H NMR (600 MHz, CDCl_3) δ 7.87 – 7.65 (m, 7H), 7.64 – 7.55 (m, 6H), 7.54 – 7.44 (m, 4H), 4.92 – 4.87 (m, 1H), 1.81 – 1.73 (m, 1H), 1.42 (d, J = 5.7 Hz, 3H), 1.27 – 1.24 (m, 2H), 1.24 – 1.20 (m, 2H), 1.15 – 1.07 (m, 4H), 1.05 – 0.95 (m, 3H), 0.84 (t, J = 7.3 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 157.3, 155.3, 134.1, 134.0, 132.1, 131.0, 129.7, 129.5, 128.9, 128.5, 67.2, 37.0, 31.7, 29.0, 28.8, 26.8, 22.6, 21.9, 14.1; ^{19}F NMR (564 MHz, CDCl_3) δ -153.30 (s), -153.35 (s).



1-(2-(Benzo[d][1,3]dioxol-5-yl)ethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (2t): Prepared via general procedure F; white solid; ^1H NMR (600 MHz, CDCl_3) δ 7.83 (s, 2H), 7.79 (d, J = 7.2 Hz, 4H), 7.72 (d, J = 7.7 Hz, 2H), 7.65 – 7.57 (m, 6H), 7.53 (t, J = 7.3 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 6.45 (d, J = 7.9 Hz, 1H), 5.82 (s, 2H), 5.74 (d, J = 7.9 Hz, 1H), 5.65 (s, 1H), 4.58 – 4.50 (m, 2H), 2.64 – 2.54 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 156.6, 156.1, 147.9, 146.8, 134.2, 132.9, 132.2, 131.2, 129.8, 129.5, 129.2, 128.9, 128.3, 126.8, 121.4, 108.6, 108.5, 101.1, 56.1, 35.5, 29.8; ^{19}F NMR (564 MHz, CDCl_3) δ -153.18 (s), -153.24 (s).

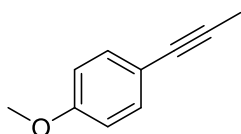


1-Chloro-4-(prop-1-yn-1-yl)benzene (1ac): Prepared via general procedure B; colorless oil; 68%; ^1H NMR (400 MHz, CDCl_3) δ 7.33 (d, J = 7.8 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 133.5, 132.8, 128.6, 122.7, 87.0, 78.8, 4.4.

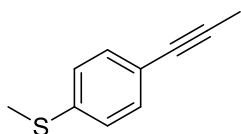


1-Bromo-4-(prop-1-yn-1-yl)benzene (1ad):

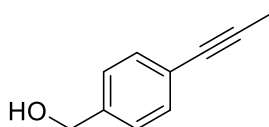
Prepared via general procedure C; ^1H NMR (400 MHz, CDCl_3) δ 7.41 (d, J = 7.9 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 2.04 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 133.1, 131.5, 123.1, 121.7, 87.3, 78.9, 4.5.



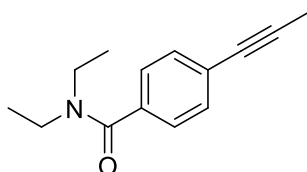
1-Methoxy-4-(prop-1-yn-1-yl)benzene (1ae): Prepared via general procedure B; white solid; 85%; ^1H NMR (600 MHz, CDCl_3) δ 7.34 (d, J = 8.6 Hz, 2H), 6.82 (d, J = 8.7 Hz, 2H), 3.78 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 159.1, 132.9, 116.3, 113.9, 84.2, 79.5, 55.2, 4.3.



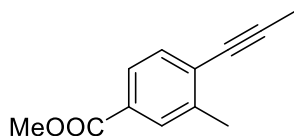
Methyl(4-(prop-1-yn-1-yl)phenyl)sulfane (1af): Prepared via general procedure B; ^1H NMR (400 MHz, CDCl_3) δ 7.30 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 8.2 Hz, 2H), 2.46 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.3, 131.9, 126.1, 120.6, 85.9, 79.5, 15.6, 4.5.



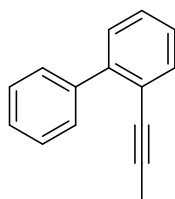
(4-(Prop-1-yn-1-yl)phenyl)methanol (1ag): Prepared via general procedure B; white solid; ^1H NMR (400 MHz, CDCl_3) δ 7.36 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 4.59 (s, 2H), 2.40 (br, 1H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.3, 131.7, 126.8, 123.2, 86.0, 79.7, 64.8, 4.4.



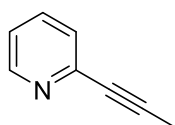
***N,N*-Diethyl-4-(prop-1-yn-1-yl)benzamide (1ah):** Prepared via general procedure B; ^1H NMR (400 MHz, CDCl_3) δ 7.36 (d, $J = 7.9$ Hz, 2H), 7.25 (d, $J = 7.8$ Hz, 2H), 3.60 – 3.41 (m, 2H), 3.31 – 3.12 (m, 2H), 2.02 (s, 3H), 1.27 – 1.14 (m, 3H), 1.12 – 0.97 (m, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 170.9, 136.3, 131.6, 126.4, 125.1, 87.3, 79.3, 43.4, 39.4, 14.3, 13.0, 4.4.



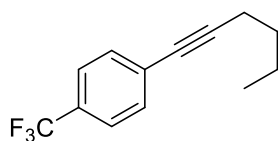
Methyl 3-methyl-4-(prop-1-yn-1-yl)benzoate (1ai): Prepared via general procedure B; yellow oil; 65%; ^1H NMR (400 MHz, CDCl_3) δ 7.84 (s, 1H), 7.76 (d, $J = 8.0$ Hz, 1H), 7.39 (d, $J = 8.0$ Hz, 1H), 3.89 (s, 3H), 2.43 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.0, 140.2, 131.9, 130.4, 128.8, 128.7, 126.7, 93.2, 78.3, 52.2, 20.7, 4.7.



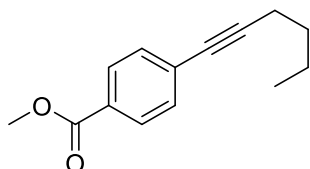
2-(Prop-1-yn-1-yl)-1,1'-biphenyl (1aj): Prepared via general procedure B; yellow oil; 65%; ^1H NMR (400 MHz, CDCl_3) δ 7.58 (d, $J = 7.4$ Hz, 2H), 7.49 (d, $J = 7.5$ Hz, 1H), 7.40 (t, $J = 7.3$ Hz, 2H), 7.37 – 7.29 (m, 3H), 7.26 – 7.21 (m, 1H), 1.91 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 143.7, 140.9, 133.3, 129.6, 129.4, 128.0, 127.9, 127.3, 127.1, 122.4, 89.0, 79.3, 4.6.



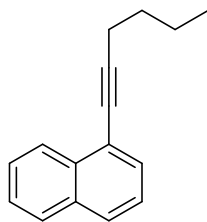
2-(Prop-1-yn-1-yl)pyridine (1ak): Prepared via general procedure B; yellow oil; 49%; ^1H NMR (400 MHz, CDCl_3) δ 8.52 (d, $J = 3.8$ Hz, 1H), 7.59 (t, $J = 7.4$ Hz, 1H), 7.34 (d, $J = 7.8$ Hz, 1H), 7.19 – 7.13 (m, 1H), 2.06 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 149.9, 144.0, 136.1, 126.7, 122.4, 86.7, 79.7, 4.4.



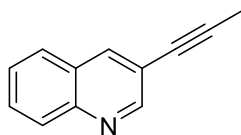
1-(Hex-1-yn-1-yl)-4-(trifluoromethyl)benzene (1al): Prepared via general procedure A; Yellow oil; 97%; ^1H NMR (400 MHz, CDCl_3) δ 7.53 (d, $J = 8.4$ Hz, 2H), 7.48 (d, $J = 8.3$ Hz, 2H), 2.43 (t, $J = 7.0$ Hz, 2H), 1.66 – 1.56 (m, 2H), 1.53 – 1.43 (m, 2H), 0.96 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 131.9, 129.2 (q, $J_{\text{C-F}} = 32.5$ Hz), 128.1 (q, $J_{\text{C-F}} = 1.0$ Hz), 125.2 (q, $J_{\text{C-F}} = 3.8$ Hz), 124.2 (q, $J = 272.1$ Hz), 93.5, 79.6, 30.8, 22.2, 19.3, 13.8.



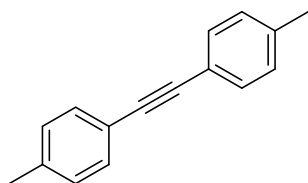
Methyl 4-(hex-1-yn-1-yl)benzoate (1am): Prepared via general procedure A; ^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, $J = 8.0$ Hz, 2H), 7.44 (d, $J = 8.0$ Hz, 2H), 3.90 (s, 3H), 2.43 (t, $J = 6.9$ Hz, 2H), 1.62 – 1.55 (m, 2H), 1.55 – 1.41 (m, 2H), 0.95 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.8, 131.6, 129.5, 129.1, 128.9, 94.1, 80.2, 52.3, 30.8, 22.2, 19.3, 13.7.



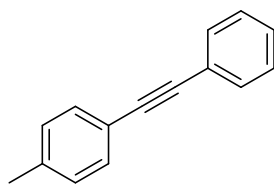
1-(Hex-1-yn-1-yl)naphthalene (1an) : Prepared via general procedure A; yellow oil; ~100%; ^1H NMR (600 MHz, CDCl_3) δ 8.35 (d, $J = 8.3$ Hz, 1H), 7.84 (d, $J = 8.0$ Hz, 1H), 7.78 (d, $J = 8.3$ Hz, 1H), 7.63 (d, $J = 7.1$ Hz, 1H), 7.58 – 7.54 (m, 1H), 7.52 – 7.49 (m, 1H), 7.41 – 7.39 (m, 1H), 2.59 (t, $J = 7.1$ Hz, 2H), 1.75 – 1.68 (m, 2H), 1.61 – 1.53 (m, 2H), 1.01 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 133.7, 133.3, 130.1, 128.3, 128.0, 126.6, 126.4, 126.3, 125.4, 122.0, 95.7, 78.7, 31.2, 22.3, 19.6, 13.8.



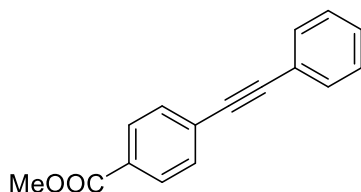
3-(Prop-1-yn-1-yl)quinoline (1ao): Prepared via general procedure B; ^1H NMR (400 MHz, CDCl_3) δ 8.85 (d, $J = 1.9$ Hz, 1H), 8.08 (d, $J = 1.2$ Hz, 1H), 8.03 (d, $J = 8.5$ Hz, 1H), 7.70 – 7.58 (m, 2H), 7.46 (t, $J = 7.5$ Hz, 1H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.5, 146.6, 137.9, 129.6, 129.3, 127.4, 127.3, 127.1, 118.2, 89.5, 77.2, 4.5.



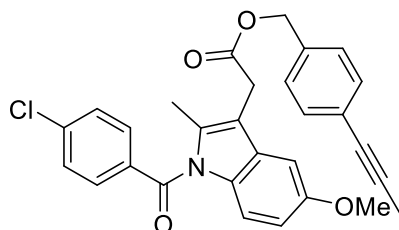
1,2-Di-*p*-tolylethyne (1ap): Prepared via general procedure A; white solid; 93%; ^1H NMR (400 MHz, CDCl_3) δ 7.43 (d, J = 7.8 Hz, 4H), 7.16 (d, J = 7.7 Hz, 4H), 2.37 (s, 6H); ^{13}C NMR (150 MHz, CDCl_3) δ 138.3, 131.6, 129.2, 120.5, 89.0, 21.6.



1-Methyl-4-(phenylethynyl)benzene (1aq): Prepared via general procedure A; yellowish solid; 57%; ^1H NMR (600 MHz, CDCl_3) δ 7.54 – 7.52 (m, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.37 – 7.31 (m, 3H), 7.18 – 7.15 (m, 2H), 2.38 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 138.5, 131.7, 131.6, 129.3, 128.5, 128.2, 123.6, 120.3, 89.7, 88.9, 21.7.

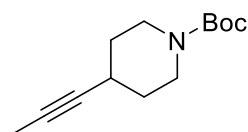


Methyl 4-(phenylethynyl)benzoate (1ar): Prepared via general procedure A; yellow solid; 84%; ^1H NMR (600 MHz, CDCl_3) δ 8.02 (d, J = 8.2 Hz, 2H), 7.59 (d, J = 8.2 Hz, 2H), 7.58 – 7.53 (m, 2H), 7.38 – 7.35 (m, 3H), 3.92 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 166.6, 131.8, 131.6, 129.6, 129.5, 128.8, 128.5, 128.1, 122.8, 92.5, 88.7, 52.3.

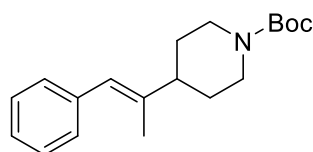


4-(Prop-1-yn-1-yl)benzyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (1as): Prepared

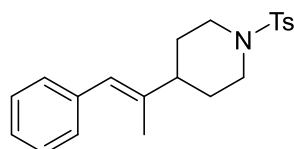
via general procedure D; yellow solid; m.p. 113-116 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 7.8 Hz, 2H), 7.20 (d, J = 7.8 Hz, 2H), 6.94 – 6.86 (m, 2H), 6.67 (d, J = 7.8 Hz, 1H), 5.10 (s, 2H), 3.77 (s, 3H), 3.71 (s, 2H), 2.35 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.7, 168.4, 156.2, 139.4, 136.1, 135.1, 134.0, 131.8, 131.3, 130.9, 130.7, 129.3, 128.2, 124.3, 115.1, 112.5, 112.0, 101.3, 86.7, 79.4, 66.5, 55.8, 30.6, 13.5, 4.5; FT-IR (thin film, KBr): ν (cm^{-1}) 2931, 1729, 1645, 1362, 1148; HRMS (ESI) calcd $\text{C}_{29}\text{H}_{25}^{35}\text{ClNO}_4$ $[\text{M} + \text{H}]^+$: 486.1472, found: 486.1470.



tert-Butyl 4-(prop-1-yn-1-yl)piperidine-1-carboxylate (1bi): Prepared via general procedure E; colorless oil; 93%; ^1H NMR (400 MHz, CDCl_3) δ 3.74 – 3.61 (m, 2H), 3.17 – 3.05 (m, 2H), 2.53 – 2.43 (m, 1H), 1.78 (d, J = 2.3 Hz, 3H), 1.75 – 1.66 (m, 2H), 1.54 – 1.48 (m, 2H), 1.44 (s, 9H); ^{13}C NMR (150 MHz, CDCl_3) δ 154.9, 81.4, 79.5, 42.8, 42.0, 31.9, 28.6, 27.2, 3.6; FT-IR (thin film, KBr): ν (cm^{-1}) 2921, 1689, 1425, 1228, 1168;

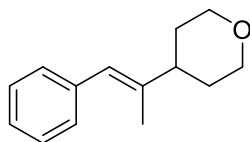


tert-Butyl (E)-4-(1-phenylprop-1-en-2-yl)piperidine-1-carboxylate (3a): 44 mg (73%, major : minor >20:1 r.r.); white solid; m.p. 63-65 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.32 (t, J = 7.4 Hz, 2H), 7.27 – 7.16 (m, 3H), 6.30 (s, 1H), 4.32 – 4.13 (m, 2H), 2.82 – 2.67 (m, 2H), 2.16 (t, J = 11.8 Hz, 1H), 1.84 (s, 3H), 1.80 – 1.69 (m, 2H), 1.56 – 1.45 (m, 11H); ^{13}C NMR (100 MHz, CDCl_3) δ 154.9, 142.0, 138.4, 129.0, 128.1, 126.1, 124.1, 79.4, 46.3, 44.3, 30.8, 28.6, 16.1; FT-IR (thin film, KBr): ν (cm^{-1}) 2944, 1686, 1425, 1228, 1161; HRMS (ESI) calcd $\text{C}_{19}\text{H}_{28}\text{NO}_2$ $[\text{M} + \text{H}]^+$: 302.2120, found: 302.2123.



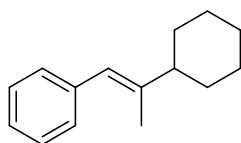
(E)-4-(1-Phenylprop-1-en-2-yl)-1-tosylpiperidine (3b): 31 mg (44%, major : minor >20:1 r.r.); colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.69 – 7.65 (m, 2H), 7.36 – 7.28 (m, 4H), 7.21 – 7.17 (m, 3H), 6.24 (s, 1H), 3.93 – 3.87 (m, 2H), 2.44 (s, 3H), 2.28 (td, J = 11.8, 2.7 Hz, 2H), 1.98 – 1.88 (m, 1H), 1.83 –

1.77 (m, 5H), 1.73 (td, $J = 12.1, 3.8$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 143.6, 141.3, 138.2, 133.4, 129.7, 129.0, 128.2, 127.9, 126.3, 124.6, 46.8, 45.5, 30.3, 21.7, 16.0; FT-IR (thin film, KBr): ν (cm^{-1}) 2925, 1726, 1338, 1165, 721; HRMS (ESI) calcd $\text{C}_{21}\text{H}_{26}\text{NO}_2\text{S}$ $[\text{M} + \text{H}]^+$: 356.1684, found: 356.1678.



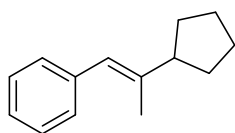
(E)-4-(1-Phenylprop-1-en-2-yl)tetrahydro-2H-pyran (3c):

26.5 mg (66%, major : minor >20:1 r.r.); yellowish oil; ^1H NMR (600 MHz, CDCl_3) δ 7.32 (t, $J = 7.6$ Hz, 2H), 7.24 (d, $J = 7.4$ Hz, 2H), 7.19 (t, $J = 7.3$ Hz, 1H), 6.30 (s, 1H), 4.07 (t, $J = 3.0$ Hz, 1H), 4.06 – 4.04 (m, 1H), 3.52 – 3.43 (m, 2H), 2.29 – 2.23 (m, 1H), 1.85 (d, $J = 0.9$ Hz, 3H), 1.72 – 1.67 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 142.1, 138.6, 129.1, 128.1, 126.1, 124.0, 68.4, 45.2, 31.7, 16.2; FT-IR (thin film, KBr): ν (cm^{-1}) 2934, 2838, 1439, 1128, 701; HRMS (CI) calcd $\text{C}_{14}\text{H}_{19}\text{O}$ $[\text{M} + \text{H}]^+$: 203.1436, found: 203.1433.



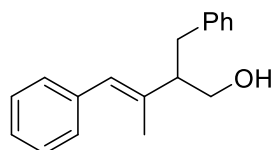
(E)-(2-Cyclohexylprop-1-en-1-yl)benzene (3d):

35 mg (88%, major : minor >20:1 r.r.); yellowish oil; ^1H NMR (400 MHz, CDCl_3) δ 7.33 – 7.28 (m, 2H), 7.25 – 7.22 (m, 2H), 7.20 – 7.14 (m, 1H), 6.27 (s, 1H), 2.05 – 1.98 (m, 1H), 1.83 (d, $J = 1.3$ Hz, 3H), 1.82 – 1.76 (m, 4H), 1.76 – 1.68 (m, 1H), 1.37 – 1.24 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.5, 139.1, 129.1, 128.1, 125.8, 123.1, 48.4, 32.1, 26.9, 26.5, 16.3; FT-IR (thin film, KBr): ν (cm^{-1}) 2921, 2848, 1642, 1442, 694; HRMS (CI) calcd $\text{C}_{15}\text{H}_{21}$ $[\text{M} + \text{H}]^+$: 201.1643, found: 201.1644.



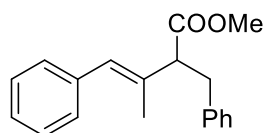
(E)-(2-Cyclopentylprop-1-en-1-yl)benzene (3e):

23 mg (62%, major : minor >20:1 r.r.); yellowish oil; ^1H NMR (600 MHz, CDCl_3) δ 7.33 – 7.29 (m, 2H), 7.26 – 7.23 (m, 2H), 7.19 – 7.16 (m, 1H), 6.32 (s, 1H), 2.61 – 2.53 (m, 1H), 1.87 – 1.81 (m, 5H), 1.75 – 1.68 (m, 2H), 1.66 – 1.58 (m, 2H), 1.53 – 1.46 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 142.2, 139.0, 129.1, 128.1, 125.8, 123.3, 50.0, 31.3, 25.6, 16.2; FT-IR (thin film, KBr): ν (cm^{-1}) 2948, 1692, 1422, 1171, 701; HRMS (ESI) calcd $\text{C}_{14}\text{H}_{19}$ $[\text{M} + \text{H}]^+$: 187.1487, found: 187.1484.



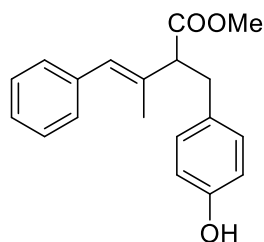
(E)-2-Benzyl-3-methyl-4-phenylbut-3-en-1-ol (3f):

23 mg (47%, major : minor >20:1 r.r.); yellowish oil; ^1H NMR (400 MHz, CDCl_3) δ 7.34 – 7.26 (m, 4H), 7.23 – 7.16 (m, 6H), 6.31 (s, 1H), 3.70 – 3.66 (m, 2H), 2.86 – 2.77 (m, 2H), 2.76 – 2.66 (m, 1H), 1.85 (d, $J = 1.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.1, 137.9, 137.6, 129.1, 129.0, 128.8, 128.6, 128.5, 128.4, 128.2, 126.4, 126.2, 63.8, 53.8, 36.5, 15.2; FT-IR (thin film, KBr): ν (cm^{-1}) 3349, 2921, 1492, 1028, 701; HRMS (ESI) calcd $\text{C}_{18}\text{H}_{20}\text{ONa}$ $[\text{M} + \text{Na}]^+$: 275.1412, found: 275.1423.



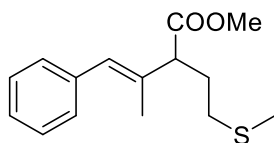
Methyl (E)-2-benzyl-3-methyl-4-phenylbut-3-enoate (3g) (major product):

30 mg (53%, major : minor = 7:1 r.r.); colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.25 (m, 4H), 7.23 – 7.14 (m, 6H), 6.34 (s, 1H), 3.67 (s, 3H), 3.44 (t, $J = 7.6$ Hz, 1H), 3.26 (dd, $J = 13.6, 8.0$ Hz, 1H), 2.95 (dd, $J = 13.7, 7.3$ Hz, 1H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.8, 139.4, 137.7, 135.0, 129.1, 129.0, 128.5, 128.2, 126.6, 126.5, 57.1, 52.1, 36.9, 16.0; FT-IR (thin film, KBr): ν (cm^{-1}) 2948, 1732, 1439, 1151, 697; HRMS (ESI) calcd $\text{C}_{19}\text{H}_{20}\text{O}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 303.1361, found: 303.1361.



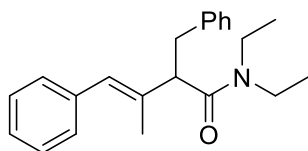
Methyl (E)-2-(4-hydroxybenzyl)-3-methyl-4-phenylbut-3-enoate (3h) (major product):

69 mg (93%, major : minor = 16:1 r.r.); yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.31 (t, $J = 7.4$ Hz, 2H), 7.24 – 7.15 (m, 3H), 7.06 (d, $J = 8.0$ Hz, 2H), 6.74 (d, $J = 8.0$ Hz, 2H), 6.37 (s, 1H), 5.51 (s, 1H), 3.68 (s, 3H), 3.41 (t, $J = 7.6$ Hz, 1H), 3.19 (dd, $J = 13.7, 8.3$ Hz, 1H), 2.89 (dd, $J = 13.2, 7.1$ Hz, 1H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.2, 154.3, 137.6, 135.0, 131.3, 130.2, 129.5, 129.0, 128.2, 126.6, 115.4, 57.4, 52.1, 36.0, 16.0; FT-IR (thin film, KBr): ν (cm^{-1}) 3392, 2955, 1709, 1215, 697; HRMS (CI) calcd $\text{C}_{19}\text{H}_{20}\text{O}_3$ $[\text{M}]^+$: 296.1412, found: 296.1412.



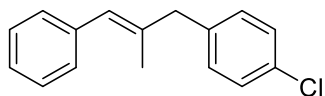
Methyl (*E*)-3-methyl-2-(2-(methylthio)ethyl)-4-phenylbut-3-enoate (3i) (major product):

30 mg (58%, major : minor = 6:1 r.r.); yellowish oil; ^1H NMR (400 MHz, CDCl_3) δ 7.36 – 7.30 (m, 3H), 7.27 – 7.20 (m, 2H), 6.46 (s, 1H), 3.71 (s, 3H), 3.36 (t, J = 7.5 Hz, 1H), 2.55 – 2.45 (m, 2H), 2.26 – 2.15 (m, 1H), 2.11 (s, 3H), 2.00 – 1.91 (m, 1H), 1.86 (d, J = 1.3 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.9, 137.6, 134.8, 129.3, 129.1, 128.2, 126.7, 53.8, 52.1, 32.0, 29.3, 15.5; FT-IR (thin film, KBr): ν (cm^{-1}) 2911, 1729, 1435, 1141, 697; HRMS (ESI) calcd $\text{C}_{15}\text{H}_{21}\text{O}_2\text{S}$ $[\text{M} + \text{H}]^+$: 265.1262, found: 265.1258.



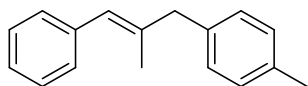
(*E*)-2-Benzyl-*N,N*-diethyl-3-methyl-4-phenylbut-3-enamide (3j) (major product):

52 mg (81%, major : minor = 9:1 r.r.); yellow oil; ^1H NMR (600 MHz, CDCl_3) δ 7.29 (t, J = 7.6 Hz, 2H), 7.25 – 7.22 (m, 2H), 7.21 – 7.17 (m, 3H), 7.17 – 7.12 (m, 3H), 6.22 (s, 1H), 3.49 – 3.42 (m, 2H), 3.40 – 3.31 (m, 2H), 3.27 – 3.20 (m, 1H), 3.19 – 3.12 (m, 1H), 2.90 (dd, J = 13.4, 6.6 Hz, 1H), 1.88 (d, J = 1.0 Hz, 3H), 1.08 (t, J = 7.1 Hz, 3H), 1.01 (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 171.2, 140.6, 137.8, 136.5, 129.4, 128.9, 128.4, 128.2, 128.1, 126.4, 126.1, 55.0, 41.8, 40.6, 38.0, 15.7, 14.5, 13.0; FT-IR (thin film, KBr): ν (cm^{-1}) 2971, 1629, 1425, 1131, 701; HRMS (ESI) calcd $\text{C}_{22}\text{H}_{28}\text{NO}$ $[\text{M} + \text{H}]^+$: 322.2171, found: 322.2165.



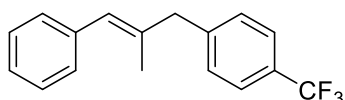
(*E*)-1-Chloro-4-(2-methyl-3-phenylallyl)benzene (3k) (major product):

41 mg (84%, major : minor = 8:1 r.r.); yellowish oil; ^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.28 (m, 3H), 7.27 – 7.21 (m, 4H), 7.21 – 7.15 (m, 2H), 6.35 (s, 1H), 3.44 (s, 2H), 1.78 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 138.4, 138.2, 137.7, 132.1, 130.5, 129.0, 128.6, 128.2, 127.2, 126.4, 46.5, 17.8; FT-IR (thin film, KBr): ν (cm^{-1}) 2918, 1489, 1088, 1015, 694; HRMS (CI) calcd $\text{C}_{16}\text{H}_{16}^{35}\text{Cl}$ $[\text{M} + \text{H}]^+$: 243.0941, found: 243.0937.



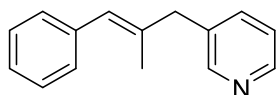
(E)-1-Methyl-4-(2-methyl-3-phenylallyl)benzene (3l) (major product):

41 mg (93%, major : minor = 6:1 r.r.); colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.29 (m, 2H), 7.28 – 7.24 (m, 3H), 7.22 – 7.17 (m, 1H), 7.15 – 7.12 (m, 3H), 6.37 (s, 1H), 3.44 (s, 2H), 2.34 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 145.8, 138.5, 138.4, 136.9, 135.8, 129.2, 129.0, 128.2, 126.7, 126.1, 46.8, 21.2, 17.8; FT-IR (thin film, KBr): ν (cm^{-1}) 2918, 1515, 1018, 801, 694; HRMS (ESI) calcd $\text{C}_{17}\text{H}_{19}$ $[\text{M} + \text{H}]^+$: 223.1487, found: 223.1494.



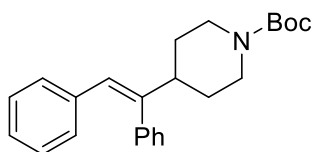
(E)-1-(2-Methyl-3-phenylallyl)-4-(trifluoromethyl)benzene (3m) (major product):

43.5 mg (79%, major : minor = 7:1 r.r.); yellowish oil; ^1H NMR (600 MHz, CDCl_3) δ 7.56 (d, $J = 7.9$ Hz, 2H), 7.36 (d, $J = 7.8$ Hz, 2H), 7.32 (t, $J = 7.5$ Hz, 2H), 7.25 (d, $J = 7.4$ Hz, 2H), 7.21 (t, $J = 7.3$ Hz, 1H), 6.38 (s, 1H), 3.53 (s, 2H), 1.79 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 144.1, 138.1, 137.1, 129.4, 129.0, 128.7 (q, $J_{\text{C-F}} = 32.3$ Hz), 128.3, 127.7, 126.5, 125.4 (q, $J_{\text{C-F}} = 7.2, 3.5$ Hz), 122.7 (q, $J_{\text{C-F}} = 272.0$ Hz), 47.0, 17.8; FT-IR (thin film, KBr): ν (cm^{-1}) 2908, 1616, 1318, 1065, 694; HRMS (ESI) calcd $\text{C}_{17}\text{H}_{16}\text{F}_3$ $[\text{M} + \text{H}]^+$: 277.1204, found: 277.1216.



(E)-3-(2-Methyl-3-phenylallyl)pyridine (3n) (major product):

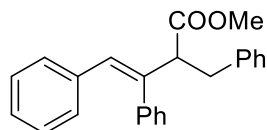
40.5 mg (97%, major : minor = 5:1 r.r.); yellowish oil; ^1H NMR (400 MHz, CDCl_3) δ 8.55 (s, 1H), 8.51 (s, 1H), 7.60 (d, $J = 7.1$ Hz, 1H), 7.37 – 7.30 (m, 2H), 7.29 – 7.16 (m, 4H), 6.38 (s, 1H), 3.48 (s, 2H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.4, 147.8, 138.0, 136.9, 136.7, 135.5, 129.0, 128.3, 127.7, 126.5, 123.6, 44.2, 17.8; FT-IR (thin film, KBr): ν (cm^{-1}) 2918, 1572, 1422, 1024, 697; HRMS (ESI) calcd $\text{C}_{15}\text{H}_{16}\text{N}$ $[\text{M} + \text{H}]^+$: 210.1283, found: 210.1286.



tert-Butyl (Z)-4-(1,2-diphenylvinyl)piperidine-1-carboxylate (3o):

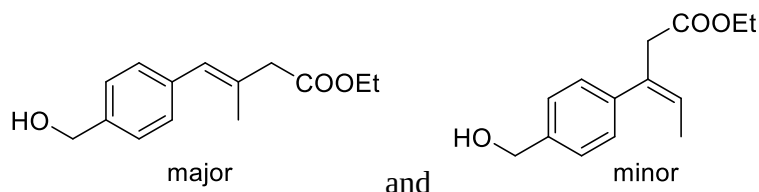
53 mg (73%); yellowish solid; m.p. 99–103 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.27 (m, 3H), 7.11 (d, $J = 7.1$ Hz, 2H), 7.08 – 6.99 (m, 3H), 6.86 (d, $J = 6.4$ Hz, 2H),

6.40 (s, 1H), 4.32 – 4.09 (m, 2H), 2.79 – 2.63 (m, 2H), 2.46 (t, $J = 11.8$ Hz, 1H), 1.86 – 1.73 (m, 2H), 1.53 – 1.36 (m, 11H); ^{13}C NMR (150 MHz, CDCl_3) δ 154.9, 146.8, 140.9, 137.3, 129.2, 129.0, 128.7, 127.9, 127.1, 126.4, 125.5, 79.5, 45.8, 44.3, 31.3, 28.6; FT-IR (thin film, KBr): ν (cm^{-1}) 2921, 1666, 1425, 1121, 694; HRMS (ESI) calcd $\text{C}_{24}\text{H}_{29}\text{NO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 386.2096, found: 386.2093.



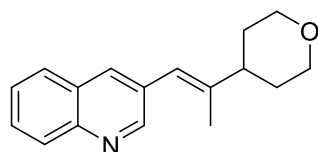
Methyl (Z)-2-benzyl-3,4-diphenylbut-3-enoate (3p):

40 mg (58%); yellowish oil; ^1H NMR (400 MHz, CDCl_3) δ 7.31 – 7.27 (m, 3H), 7.26 – 7.22 (m, 2H), 7.22 – 7.16 (m, 3H), 7.11 – 7.05 (m, 5H), 6.92 – 6.87 (m, 2H), 6.65 (s, 1H), 3.74 (dd, $J = 9.0, 6.2$ Hz, 1H), 3.64 (s, 3H), 3.24 (dd, $J = 13.8, 9.1$ Hz, 1H), 3.00 (dd, $J = 13.9, 6.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.6, 140.2, 139.7, 139.4, 136.6, 129.4, 129.3, 129.2, 129.0, 128.8, 128.5, 128.0, 127.5, 126.9, 126.5, 56.5, 52.1, 37.7; FT-IR (thin film, KBr): ν (cm^{-1}) 3028, 1732, 1492, 1155, 694; HRMS (ESI) calcd $\text{C}_{24}\text{H}_{23}\text{O}_2$ $[\text{M} + \text{H}]^+$: 343.1698, found: 343.1701.



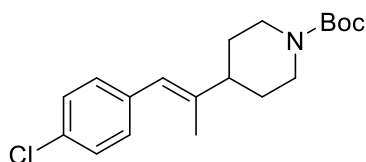
(E)-ethyl 4-(4-(hydroxymethyl)phenyl)-3-methylbut-3-enoate and (Z)-ethyl 3-(4-(hydroxymethyl)phenyl)pent-3-enoate (3q):

18.5 mg (40%, major : minor = 5:1 r.r.); colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.31 (m, 2H), 7.28 – 7.24 (m, 2H), 6.38 (s, 1H)/5.72 (q, $J = 6.9$ Hz, 0.2H), 4.68 (d, $J = 5.2$ Hz, 2H), 4.22 – 4.14 (m, 2H)/4.05 (q, $J = 7.1$ Hz, 0.4H), 3.34 – 3.33 (m, 0.4H)/3.17 (d, $J = 1.0$ Hz, 2H), 1.94 (d, $J = 1.3$ Hz, 3H)/1.63 (dt, $J = 6.9, 1.0$ Hz, 0.6H), 1.67 (t, $J = 5.5$ Hz, 1H), 1.28 (t, $J = 7.1$ Hz, 3H)/1.15 (t, $J = 7.1$ Hz, 0.6H); ^{13}C NMR (150 MHz, CDCl_3) δ 171.7, 139.8, 139.5, 139.1, 137.3, 132.0, 129.2, 128.9, 128.8, 127.0, 126.5, 65.3, 60.8, 60.7, 46.1, 18.2, 14.4, 14.3; FT-IR (thin film, KBr): ν (cm^{-1}) 3406, 2925, 1732, 1155, 1038; HRMS (ESI) calcd $\text{C}_{14}\text{H}_{18}\text{O}_3\text{Na}$ $[\text{M} + \text{Na}]^+$: 257.1154, found: 257.1149.

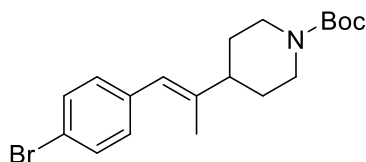


(E)-3-(2-(Tetrahydro-2H-pyran-4-yl)prop-1-en-1-yl)quinoline (3r):

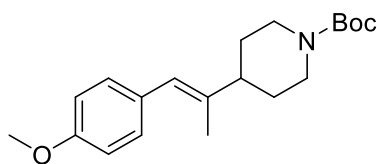
37 mg (73%, major : minor >20:1 r.r.); yellowish oil; ^1H NMR (400 MHz, CDCl_3) δ 8.80 (s, 1H), 8.07 (d, $J = 8.4$ Hz, 1H), 7.98 (s, 1H), 7.79 (d, $J = 8.0$ Hz, 1H), 7.67 (t, $J = 7.5$ Hz, 1H), 7.53 (t, $J = 7.4$ Hz, 1H), 6.41 (s, 1H), 4.13 – 4.05 (m, 2H), 3.55 – 3.45 (m, 2H), 2.44 – 2.30 (m, 1H), 1.94 (s, 3H), 1.80 – 1.68 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.2, 146.6, 145.5, 134.6, 131.6, 129.3, 129.1, 128.0, 127.8, 126.8, 120.6, 68.4, 45.3, 31.7, 16.4; FT-IR (thin film, KBr): ν (cm^{-1}) 2945, 1489, 1235, 1128, 751; HRMS (ESI) calcd $\text{C}_{17}\text{H}_{20}\text{NO}$ $[\text{M} + \text{H}]^+$: 254.1545, found: 254.1543.



tert-Butyl (E)-4-(1-(4-chlorophenyl)prop-1-en-2-yl)piperidine-1-carboxylate (4a): 36 mg (53%, major : minor >20:1 r.r.); white solid; m.p. 53-56 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.27 (d, $J = 8.1$ Hz, 2H), 7.14 (d, $J = 8.2$ Hz, 2H), 6.22 (s, 1H), 4.32 – 4.10 (m, 2H), 2.81 – 2.63 (m, 2H), 2.22 – 2.07 (m, 1H), 1.80 (s, 3H), 1.77 – 1.68 (m, 2H), 1.50 – 1.44 (m, 11H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.0, 143.0, 136.9, 131.8, 130.3, 128.3, 123.1, 79.5, 46.3, 44.3, 30.8, 28.6, 16.2; FT-IR (thin film, KBr): ν (cm^{-1}) 2928, 1679, 1422, 1161, 1068; HRMS (ESI) calcd $\text{C}_{19}\text{H}_{27}^{35}\text{ClNO}_2$ $[\text{M} + \text{H}]^+$: 336.1730, found: 336.1731.

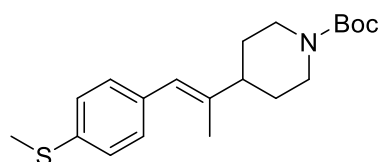


tert-Butyl (E)-4-(1-(4-bromophenyl)prop-1-en-2-yl)piperidine-1-carboxylate (4b): 51 mg (67%, major : minor >20:1 r.r.); yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.42 (d, $J = 8.4$ Hz, 2H), 7.08 (d, $J = 8.4$ Hz, 2H), 6.20 (s, 1H), 4.28 – 4.15 (m, 2H), 2.79 – 2.66 (m, 2H), 2.17 – 2.10 (m, 1H), 1.80 (d, $J = 1.1$ Hz, 3H), 1.76 – 1.69 (m, 2H), 1.50 – 1.45 (m, 11H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.0, 143.1, 137.4, 131.2, 130.7, 123.1, 119.9, 79.5, 46.4, 44.2, 30.8, 28.6, 16.2; FT-IR (thin film, KBr): ν (cm^{-1}) 2931, 1686, 1422, 1161, 761; HRMS (ESI) calcd $\text{C}_{19}\text{H}_{26}^{79}\text{BrNO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 402.1045, found: 402.1040.



tert-Butyl (E)-4-(1-(4-methoxyphenyl)prop-1-en-2-yl)piperidine-1-carboxylate (4c): 52 mg (79%, major : minor >20:1 r.r.); yellowish oil; ^1H NMR (400 MHz, CDCl_3) δ

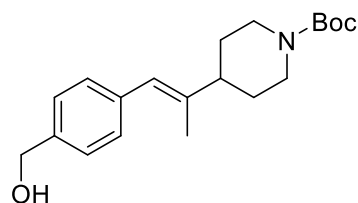
7.16 (d, $J = 8.6$ Hz, 2H), 6.86 (d, $J = 8.7$ Hz, 2H), 6.23 (s, 1H), 4.28 – 4.12 (m, 2H), 3.81 (s, 3H), 2.80 – 2.67 (m, 2H), 2.17 – 2.09 (m, 1H), 1.82 (d, $J = 1.0$ Hz, 3H), 1.77 – 1.68 (m, 2H), 1.52 – 1.45 (m, 11H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.9, 155.0, 140.7, 131.1, 130.2, 123.6, 113.6, 79.5, 55.4, 46.4, 44.2, 30.9, 28.6, 16.2; FT-IR (thin film, KBr): ν (cm^{-1}) 2938, 1689, 1422, 1248, 1168; HRMS (ESI) calcd $\text{C}_{20}\text{H}_{30}\text{NO}_3$ $[\text{M} + \text{H}]^+$: 332.2226, found: 332.2227.



tert-Butyl

(E)-4-(1-(4-(methylthio)phenyl)prop-1-en-2-yl)piperidine-1-carboxylate (4d):

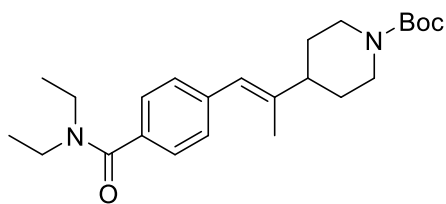
43 mg (63%, major : minor >20:1 r.r.); yellowish oil; ^1H NMR (400 MHz, CDCl_3) δ 7.21 (d, $J = 7.8$ Hz, 2H), 7.15 (d, $J = 7.7$ Hz, 2H), 6.23 (s, 1H), 4.29 – 4.11 (m, 2H), 2.78 – 2.66 (m, 2H), 2.48 (s, 3H), 2.20 – 2.06 (m, 1H), 1.82 (s, 3H), 1.77 – 1.67 (m, 2H), 1.52 – 1.42 (m, 11H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.0, 142.1, 135.9, 135.5, 129.5, 126.6, 123.6, 79.5, 46.4, 44.3, 30.9, 28.6, 16.3, 16.2; FT-IR (thin film, KBr): ν (cm^{-1}) 2935, 1689, 1419, 1228, 1168; HRMS (ESI) calcd $\text{C}_{20}\text{H}_{29}\text{NO}_2\text{SNa}$ $[\text{M} + \text{Na}]^+$: 370.1817, found: 370.1813.



tert-Butyl

(E)-4-(1-(4-(hydroxymethyl)phenyl)prop-1-en-2-yl)piperidine-1-carboxylate (4e):

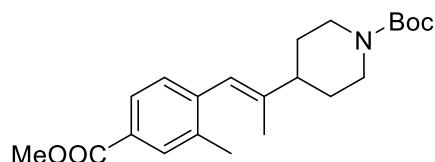
24 mg (43%, major : minor >20:1 r.r.); yellowish solid; m.p. 72-76 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.31 (d, $J = 7.8$ Hz, 2H), 7.21 (d, $J = 7.7$ Hz, 2H), 6.27 (s, 1H), 4.67 (s, 2H), 4.25 – 4.16 (m, 2H), 2.78 – 2.67 (m, 2H), 2.16 – 2.09 (m, 1H), 1.82 (s, 3H), 1.76 – 1.69 (m, 2H), 1.50 – 1.44 (m, 11H); ^{13}C NMR (150 MHz, CDCl_3) δ 155.0, 142.3, 138.8, 137.9, 129.2, 126.9, 123.8, 79.5, 65.3, 46.4, 44.2, 30.9, 28.6, 16.2; FT-IR (thin film, KBr): ν (cm^{-1}) 3429, 2921, 1662, 1431, 1168; HRMS (ESI) calcd $\text{C}_{20}\text{H}_{29}\text{NO}_3\text{Na}$ $[\text{M} + \text{Na}]^+$: 354.2045, found: 354.2048.



tert-Butyl

(E)-4-(1-(4-(diethylcarbamoyl)phenyl)prop-1-en-2-yl)piperidine-1-carboxylate (4f):

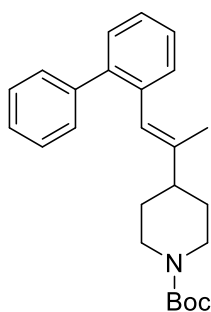
54 mg (68%, major : minor >20:1 r.r.); yellowish oil; ^1H NMR (400 MHz, CDCl_3) δ 7.31 (d, $J = 7.5$ Hz, 2H), 7.23 (d, $J = 7.6$ Hz, 2H), 6.27 (s, 1H), 4.29 – 4.12 (m, 2H), 3.60 – 3.47 (m, 2H), 3.35 – 3.18 (m, 2H), 2.81 – 2.63 (m, 2H), 2.20 – 2.08 (m, 1H), 1.83 (s, 3H), 1.77 – 1.70 (m, 2H), 1.53 – 1.43 (m, 11H), 1.32 – 1.17 (m, 3H), 1.17 – 1.04 (m, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 171.4, 154.9, 143.2, 139.4, 134.9, 128.9, 126.3, 123.6, 79.5, 46.4, 44.1, 43.4, 39.4, 30.8, 28.6, 16.3, 14.4, 13.1; FT-IR (thin film, KBr): ν (cm^{-1}) 2925, 1689, 1482, 1245, 697; HRMS (ESI) calcd $\text{C}_{24}\text{H}_{37}\text{N}_2\text{O}_3$ $[\text{M} + \text{H}]^+$: 401.2804, found: 401.2802.



tert-Butyl

(E)-4-(1-(4-(methoxycarbonyl)-2-methylphenyl)prop-1-en-2-yl)piperidine-1-carboxylate (4g):

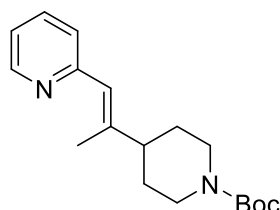
62 mg (78%, major : minor >20:1 r.r.); white solid; m.p. 64-66 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.84 (s, 1H), 7.80 (d, $J = 8.0$ Hz, 1H), 7.16 (d, $J = 7.9$ Hz, 1H), 6.24 (s, 1H), 4.30 – 4.16 (m, 2H), 3.89 (s, 3H), 2.80 – 2.69 (m, 2H), 2.24 (s, 3H), 2.22 – 2.14 (m, 1H), 1.80 – 1.73 (m, 2H), 1.66 (d, $J = 0.8$ Hz, 3H), 1.57 – 1.48 (m, 2H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.4, 154.9, 143.6, 142.7, 136.7, 130.9, 129.5, 128.1, 126.7, 122.5, 79.5, 52.1, 45.7, 44.4, 31.0, 28.6, 19.9, 16.1; FT-IR (thin film, KBr): ν (cm^{-1}) 2938, 1719, 1686, 1158, 764; HRMS (ESI) calcd $\text{C}_{22}\text{H}_{31}\text{NO}_4\text{Na}$ $[\text{M} + \text{Na}]^+$: 396.2151, found: 396.2156.



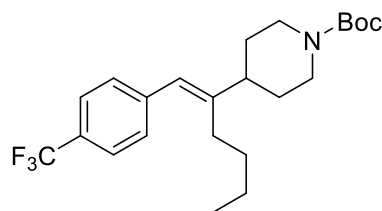
tert-Butyl (E)-4-(1-([1,1'-biphenyl]-2-yl)prop-1-en-2-yl)piperidine-1-carboxylate

(4h):

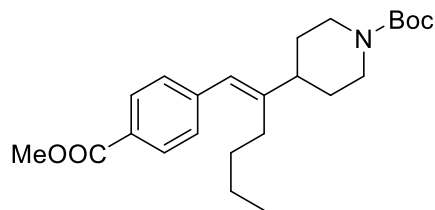
48 mg (64%, major : minor >20:1 r.r.); yellow oil; ^1H NMR (600 MHz, CDCl_3) δ 7.36 – 7.24 (m, 9H), 6.08 (s, 1H), 4.22 – 4.03 (m, 2H), 2.71 – 2.60 (m, 2H), 2.09 – 2.02 (m, 1H), 1.66 (s, 3H), 1.62 – 1.58 (m, 2H), 1.45 (s, 9H), 1.41 – 1.31 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 155.0, 141.6, 141.3, 141.1, 136.6, 130.2, 129.8, 127.9, 126.91, 126.87, 126.7, 124.4, 79.4, 45.7, 44.3, 30.6, 28.6, 16.1; FT-IR (thin film, KBr): ν (cm^{-1}) 2935, 1689, 1425, 1168, 740; HRMS (ESI) calcd $\text{C}_{25}\text{H}_{31}\text{NO}_2$ $[\text{M}]^+$: 377.2355, found: 377.2347.

***tert*-Butyl (*E*)-4-(1-(pyridin-2-yl)prop-1-en-2-yl)piperidine-1-carboxylate (4i):**

33 mg (55%, major : minor >20:1 r.r.); yellow solid; m.p. 42-45 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.56 (d, J = 3.2 Hz, 1H), 7.60 (t, J = 7.5 Hz, 1H), 7.18 (d, J = 7.8 Hz, 1H), 7.09 – 7.02 (m, 1H), 6.34 (s, 1H), 4.31 – 4.08 (m, 2H), 2.80 – 2.65 (m, 2H), 2.24 – 2.10 (m, 1H), 2.02 (s, 3H), 1.80 – 1.69 (m, 2H), 1.52 – 1.41 (m, 11H); ^{13}C NMR (150 MHz, CDCl_3) δ 157.4, 154.9, 149.1, 146.8, 136.0, 124.1, 124.0, 120.8, 79.5, 46.7, 44.3, 30.7, 28.6, 16.5; FT-IR (thin film, KBr): ν (cm^{-1}) 2934, 1682, 1419, 1161, 767; HRMS (CI) calcd $\text{C}_{18}\text{H}_{27}\text{N}_2\text{O}_2$ $[\text{M} + \text{H}]^+$: 303.2073, found: 303.2081.

***tert*-Butyl****(*E*)-4-(1-(4-(trifluoromethyl)phenyl)hex-1-en-2-yl)piperidine-1-carboxylate (4j):**

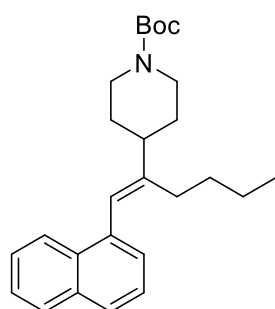
47 mg (58%, major : minor >20:1 r.r.); yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.55 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 6.25 (s, 1H), 4.31 – 4.15 (m, 2H), 2.80 – 2.66 (m, 2H), 2.24 – 2.18 (m, 2H), 2.18 – 2.09 (m, 1H), 1.81 – 1.74 (m, 2H), 1.48 (s, 9H), 1.45 – 1.38 (m, 3H), 1.35 – 1.24 (m, 3H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 155.0, 149.4, 142.4, 128.9, 128.2 (q, $J_{\text{C-F}}$ = 32.3 Hz), 125.1 (q, $J_{\text{C-F}}$ = 3.6 Hz), 124.5 (q, $J_{\text{C-F}}$ = 271.7 Hz), 123.0, 79.6, 44.5, 43.2, 31.9, 31.2, 30.5, 28.6, 23.1, 14.0; FT-IR (thin film, KBr): ν (cm^{-1}) 2931, 1692, 1325, 1121, 804; HRMS (CI) calcd $\text{C}_{23}\text{H}_{32}\text{NO}_2\text{F}_3$ $[\text{M}]^+$: 411.2385, found: 411.2386.



tert-Butyl

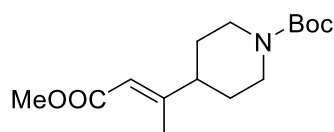
(E)-4-(1-(4-(methoxycarbonyl)phenyl)hex-1-en-2-yl)piperidine-1-carboxylate (4k):

42 mg (53%, major : minor >20:1 r.r.); yellowish oil; ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 8.0$ Hz, 2H), 7.25 (d, $J = 8.3$ Hz, 2H), 6.26 (s, 1H), 4.31 – 4.15 (m, 2H), 3.91 (s, 3H), 2.79 – 2.65 (m, 2H), 2.26 – 2.21 (m, 2H), 2.21 – 2.10 (m, 1H), 1.82 – 1.71 (m, 2H), 1.52 – 1.45 (m, 11H), 1.33 – 1.27 (m, 4H), 0.87 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.2, 155.0, 149.5, 143.6, 129.6, 128.7, 127.8, 123.4, 79.6, 52.2, 44.5, 43.4, 31.9, 31.2, 30.7, 28.6, 23.1, 14.0; FT-IR (thin film, KBr): ν (cm^{-1}) 2935, 1719, 1682, 1278, 1171; HRMS (ESI) calcd $\text{C}_{24}\text{H}_{35}\text{NO}_4\text{Na}$ $[\text{M} + \text{Na}]^+$: 424.2464, found: 424.2460.



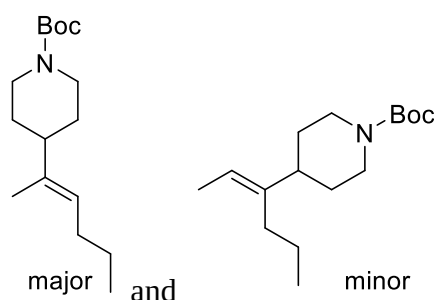
tert-Butyl (E)-4-(1-(naphthalen-1-yl)hex-1-en-2-yl)piperidine-1-carboxylate (4l):

52 mg (67%, major : minor =11:1 r.r.); yellowish oil; ^1H NMR (600 MHz, CDCl_3) δ 7.91 – 7.89 (m, 1H), 7.85 – 7.82 (m, 1H), 7.73 (d, $J = 8.2$ Hz, 1H), 7.48 – 7.44 (m, 2H), 7.43 – 7.40 (m, 1H), 7.27 – 7.24 (m, 1H), 6.60 (s, 1H), 4.38 – 4.17 (m, 2H), 2.86 – 2.73 (m, 2H), 2.29 – 2.22 (m, 1H), 2.11 – 2.04 (m, 2H), 1.96 – 1.88 (m, 2H), 1.62 – 1.55 (m, 2H), 1.49 (s, 9H), 1.35 – 1.28 (m, 2H), 1.16 – 1.09 (m, 2H), 0.71 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 155.0, 148.4, 136.1, 133.6, 132.3, 128.4, 126.9, 126.3, 125.8, 125.7, 125.4, 125.3, 122.0, 79.5, 44.5, 42.2, 32.2, 31.2, 30.7, 28.7, 22.9, 13.9; FT-IR (thin film, KBr): ν (cm^{-1}) 2935, 1692, 1422, 1225, 1165; HRMS (CI) calcd $\text{C}_{26}\text{H}_{35}\text{NO}_2$ $[\text{M}]^+$: 393.2668, found: 393.2677.



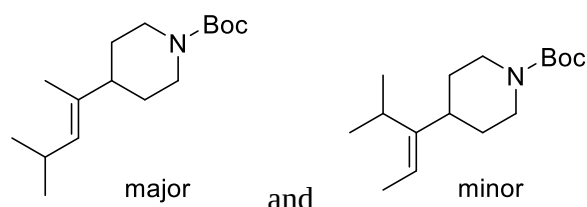
tert-Butyl (E)-4-(4-methoxy-4-oxobut-2-en-2-yl)piperidine-1-carboxylate (4m):

39 mg (69%, major : minor >20:1 r.r.); white solid; m.p. 59-62 °C; ^1H NMR (400 MHz, CDCl_3) δ 5.66 (s, 1H), 4.26 – 4.11 (m, 2H), 3.67 (s, 3H), 2.76 – 2.62 (m, 2H), 2.19 – 2.05 (m, 4H), 1.74 – 1.60 (m, 2H), 1.50 – 1.36 (m, 11H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.5, 162.6, 154.8, 114.6, 79.7, 51.0, 46.8, 44.1, 30.3, 28.6, 17.3; FT-IR (thin film, KBr): ν (cm^{-1}) 2925, 1716, 1682, 1228, 1161; HRMS (ESI) calcd $\text{C}_{15}\text{H}_{25}\text{NO}_4\text{Na}$ $[\text{M} + \text{Na}]^+$: 306.1681, found: 306.1680.



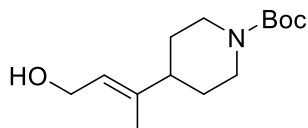
***tert*-Butyl (*E*)-4-(hex-2-en-2-yl)piperidine-1-carboxylate (4n):**

32 mg (60%, major : minor = 1.5:1 r.r.); yellowish oil; ^1H NMR (400 MHz, CDCl_3) δ 5.21 (q, J = 13.0, 6.4 Hz, 0.4H)/5.14 (t, J = 6.6 Hz, 0.6H), 4.24 – 4.03 (m, 2H), 2.75 – 2.57 (m, 2H), 2.04 – 1.87 (m, 3H), 1.66 – 1.54 (m, 5H), 1.45 (s, 9H), 1.38 – 1.21 (m, 4H), 0.94 – 0.81 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.0, 143.9, 138.5, 123.8, 117.9, 79.4, 45.5, 44.6, 43.3, 31.7, 31.0, 30.0, 28.6, 23.1, 22.3, 14.5, 13.9, 13.4; FT-IR (thin film, KBr): ν (cm^{-1}) 2925, 1692, 1489, 1242, 697; HRMS (ESI) calcd $\text{C}_{16}\text{H}_{29}\text{NO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 290.2096, found: 290.2092.



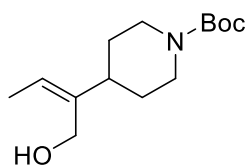
***tert*-Butyl (*E*)-4-(4-methylpent-2-en-2-yl)piperidine-1-carboxylate (4o):**

25 mg (47%, major : minor = 2.6:1 r.r.); yellowish oil; ^1H NMR (400 MHz, CDCl_3) δ 5.16 (q, J = 6.7 Hz, 0.27H)/ 4.96 (d, J = 8.8 Hz, 0.68H), 4.24 – 4.03 (m, 2H), 2.88 – 2.78 (m, 0.27H)/2.56 – 2.43 (m, 0.67H), 2.74 – 2.59 (m, 2H), 2.01 – 1.85 (m, 1H), 1.63 – 1.49 (m, 5H), 1.45 (s, 9H), 1.40 – 1.27 (m, 2H), 0.98 (d, J = 7.0 Hz, 1.67H)/ 0.91 (d, J = 6.6 Hz, 4.55H); ^{13}C NMR (150 MHz, CDCl_3) δ 155.0, 149.2, 136.0, 131.7, 116.9, 79.3, 45.4, 44.6, 37.9, 33.9, 31.0, 29.0, 28.6, 27.0, 23.3, 21.0, 14.4, 13.0; FT-IR (thin film, KBr): ν (cm^{-1}) 2931, 1692, 1419, 1228, 1175; HRMS (ESI) calcd $\text{C}_{16}\text{H}_{29}\text{NO}_2$ $[\text{M}]^+$: 267.2198, found: 267.2204.



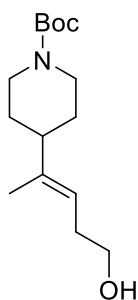
***tert*-Butyl (*E*)-4-(4-hydroxybut-2-en-2-yl)piperidine-1-carboxylate (4p):**

21.4 mg (47%, major : minor = 1:1 r.r.); yellowish oil; ^1H NMR (600 MHz, CDCl_3) δ 5.41 (t, J = 6.7 Hz, 1H), 4.23 – 4.08 (m, 4H), 2.73 – 2.63 (m, 2H), 2.02 – 1.97 (m, 1H), 1.67 – 1.62 (m, 5H), 1.46 (s, 9H), 1.42 – 1.33 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 155.0, 142.7, 122.8, 79.5, 59.5, 45.3, 44.4, 30.7, 28.6, 14.8; FT-IR (thin film, KBr): ν (cm^{-1}) 3406, 2935, 1696, 1425, 1165; HRMS (CI) calcd $\text{C}_{14}\text{H}_{25}\text{NO}_3$ $[\text{M}]^+$: 255.1834, found: 255.1843.



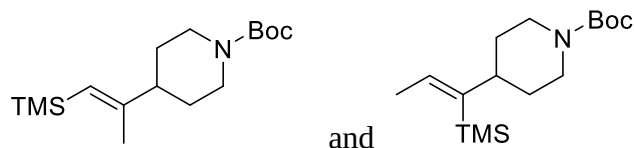
***tert*-Butyl (*Z*)-4-(1-hydroxybut-2-en-2-yl)piperidine-1-carboxylate (4p'):**

Yellowish oil; ^1H NMR (600 MHz, CDCl_3) δ 5.42 (q, J = 6.8 Hz, 1H), 4.26 – 4.08 (m, 4H), 2.75 – 2.61 (m, 2H), 2.24 – 2.13 (m, 1H), 1.70 (d, J = 6.6 Hz, 3H), 1.68 – 1.61 (m, 2H), 1.45 (s, 9H), 1.39 – 1.30 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 155.0, 142.9, 122.5, 79.4, 59.4, 44.5, 41.4, 31.6, 28.6, 13.4; FT-IR (thin film, KBr): ν (cm^{-1}) 3402, 2928, 1672, 1429, 1171; HRMS (CI) calcd $\text{C}_{14}\text{H}_{25}\text{NO}_3$ $[\text{M}]^+$: 255.1834, found: 255.1843.

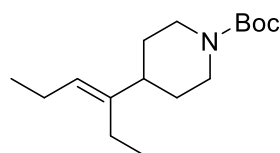


***tert*-Butyl (*E*)-4-(5-hydroxypent-2-en-2-yl)piperidine-1-carboxylate (4q) (major product):**

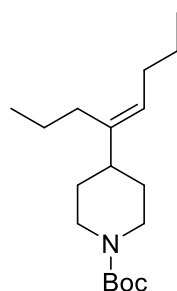
21 mg (41%, major : minor = 2:1 r.r.); yellowish oil; ^1H NMR (400 MHz, CDCl_3) δ 5.17 (t, J = 6.6 Hz, 1H), 4.24 – 4.06 (m, 2H), 3.68 – 3.55 (m, 2H), 2.74 – 2.58 (m, 2H), 2.34 – 2.22 (m, 2H), 1.99 (t, J = 11.4 Hz, 1H), 1.67 – 1.53 (m, 5H), 1.45 (s, 9H), 1.41 – 1.31 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 155.0, 142.2, 119.1, 79.5, 62.6, 45.6, 44.6, 31.5, 31.0, 28.6, 14.7; FT-IR (thin film, KBr): ν (cm^{-1}) 2928, 1696, 1425, 1235, 1168; HRMS (ESI) calcd $\text{C}_{15}\text{H}_{27}\text{NO}_3\text{Na}$ $[\text{M} + \text{Na}]^+$: 292.1889, found: 292.1885.



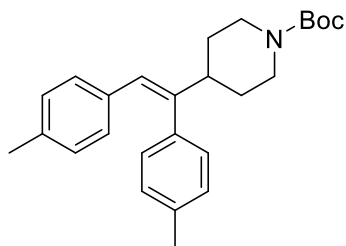
tert-Butyl (E)-4-(1-(trimethylsilyl)prop-1-en-2-yl)piperidine-1-carboxylate (4r): 26 mg (44%, major : minor = 1:1 r.r.); yellowish oil; ^1H NMR (400 MHz, CDCl_3) δ 6.03 (q, J = 6.9 Hz, 0.5H)/5.19 (s, 0.5H), 4.24 – 4.04 (m, 2H), 2.73 – 2.59 (m, 2H), 2.09 – 1.93 (m, 1H), 1.75 (s, 1.5)/1.74 (d, J = 5.5 Hz, 1.5H), 1.69 – 1.61 (m, 1H)/1.58 – 1.50 (m, 1H), 1.45 (s, 9H), 1.39 – 1.28 (m, 2H), 0.15 (s, 4.5H)/0.08 (s, 4.5H); ^{13}C NMR (150 MHz, CDCl_3) δ 158.0, 155.0, 154.9, 143.8, 134.4, 121.9, 79.4, 79.3, 47.7, 44.7, 41.8, 32.9, 31.0, 28.6, 20.2, 18.0, 0.6, 0.2; FT-IR (thin film, KBr): ν (cm^{-1}) 2934, 1692, 1235, 1168, 837; HRMS (CI) calcd $\text{C}_{16}\text{H}_{31}\text{NO}_2\text{Si}$ $[\text{M}]^+$: 297.2124, found: 297.2128.



tert-Butyl (E)-4-(hex-3-en-3-yl)piperidine-1-carboxylate (4s): 29 mg (54%); yellowish oil; ^1H NMR (400 MHz, CDCl_3) δ 5.07 (t, J = 6.9 Hz, 1H), 4.22 – 4.05 (m, 2H), 2.72 – 2.61 (m, 2H), 2.07 – 1.97 (m, 4H), 1.96 – 1.90 (m, 1H), 1.69 – 1.59 (m, 2H), 1.46 (s, 9H), 1.40 – 1.22 (m, 2H), 0.99 – 0.91 (m, 6H); ^{13}C NMR (150 MHz, CDCl_3) δ 155.0, 144.1, 125.5, 79.3, 44.6, 43.2, 31.8, 28.6, 22.6, 21.0, 14.8, 14.3; FT-IR (thin film, KBr): ν (cm^{-1}) 2961, 1689, 1419, 1225, 1168; HRMS (CI) calcd $\text{C}_{16}\text{H}_{30}\text{NO}_2$ $[\text{M}]^+$: 268.2277, found: 268.2272.

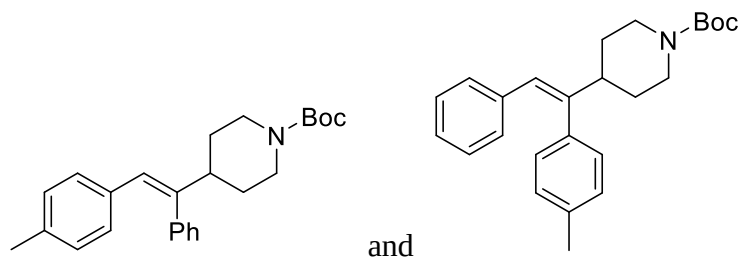


tert-Butyl (E)-4-(oct-4-en-4-yl)piperidine-1-carboxylate (4t): 25 mg (42%); yellowish oil; ^1H NMR (400 MHz, CDCl_3) δ 5.10 (t, J = 6.9 Hz, 1H), 4.25 – 4.03 (m, 2H), 2.75 – 2.57 (m, 2H), 2.02 – 1.93 (m, 4H), 1.93 – 1.86 (m, 1H), 1.70 – 1.57 (m, 2H), 1.45 (s, 9H), 1.39 – 1.22 (m, 6H), 0.95 – 0.82 (m, 6H); ^{13}C NMR (150 MHz, CDCl_3) δ 155.0, 143.0, 124.2, 79.3, 44.6, 43.2, 32.1, 31.9, 29.9, 28.6, 23.3, 22.7, 14.5, 14.0; FT-IR (thin film, KBr): ν (cm^{-1}) 2925, 1489, 1248, 1041, 697; HRMS (ESI) calcd $\text{C}_{18}\text{H}_{33}\text{NO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 318.2409, found: 318.2406.



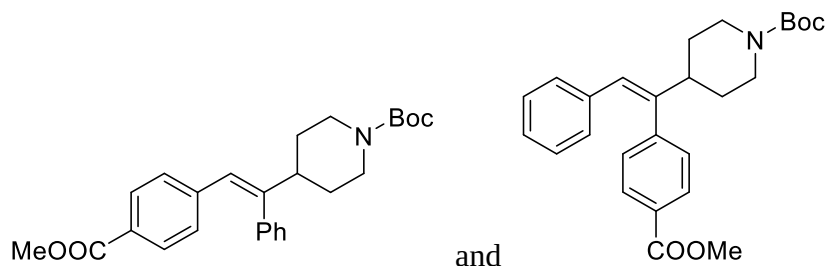
***tert*-Butyl (Z)-4-(1,2-di-*p*-tolylvinyl)piperidine-1-carboxylate (4u):**

41 mg (53%); yellowish solid; m.p. 94-97 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.13 (d, $J = 7.8$ Hz, 2H), 6.99 (d, $J = 7.9$ Hz, 2H), 6.89 (d, $J = 8.0$ Hz, 2H), 6.77 (d, $J = 8.1$ Hz, 2H), 6.34 (s, 1H), 4.26 – 4.07 (m, 2H), 2.75 – 2.65 (m, 2H), 2.45 – 2.38 (m, 1H), 2.36 (s, 3H), 2.23 (s, 3H), 1.80 – 1.73 (m, 2H), 1.47 – 1.43 (m, 11H); ^{13}C NMR (150 MHz, CDCl_3) δ 154.9, 145.8, 138.1, 136.6, 136.0, 134.5, 129.4, 129.0, 128.8, 128.7, 125.1, 79.4, 45.9, 44.5, 31.3, 28.6, 21.4, 21.2; FT-IR (thin film, KBr): ν (cm^{-1}) 2921, 1686, 1425, 1161, 731; HRMS (ESI) calcd $\text{C}_{26}\text{H}_{33}\text{NO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 414.2409, found: 414.2414.



***tert*-Butyl (Z)-4-(1-phenyl-2-(*p*-tolyl)vinyl)piperidine-1-carboxylate (4v):**

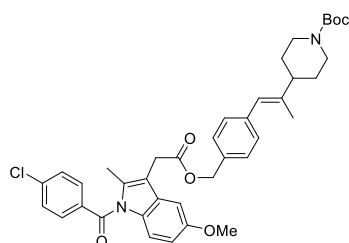
39 mg (52%, major : minor = 1:1 r.r.); yellowish oil; ^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.27 (m, 2H), 7.15 – 7.01 (m, 3H), 6.99 (d, $J = 8.0$ Hz, 1H), 6.90 – 6.85 (m, 2H), 6.74 (d, $J = 8.2$ Hz, 1H), 6.37 (s, 0.5H)/6.36 (s, 0.5H), 4.26 – 4.11 (m, 2H), 2.77 – 2.65 (m, 2H), 2.48 – 2.40 (m, 1H), 2.36 (s, 1.5H)/2.22 (s, 1.5H), 1.84 – 1.74 (m, 2H), 1.50 – 1.42 (m, 11H); ^{13}C NMR (150 MHz, CDCl_3) δ 154.9, 146.8, 145.8, 141.2, 137.9, 137.4, 136.7, 136.1, 134.4, 129.4, 129.2, 129.1, 129.0, 128.8, 128.7, 127.9, 127.0, 126.3, 125.31, 125.26, 79.5, 45.9, 45.8, 44.4, 31.3, 28.6, 21.4, 21.2; FT-IR (thin film, KBr): ν (cm^{-1}) 2931, 1692, 1422, 1161, 701; HRMS (ESI) calcd $\text{C}_{25}\text{H}_{32}\text{NO}_2$ $[\text{M} + \text{H}]^+$: 378.2433, found: 378.2425.



tert-Butyl

(Z)-4-(2-(4-(methoxycarbonyl)phenyl)-1-phenylvinyl)piperidine-1-carboxylate (4w):

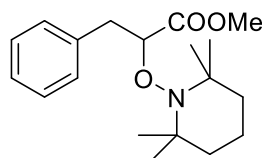
40 mg (48%, major : minor = 2.3:1 r.r.); yellowish oil; ^1H NMR (400 MHz, CDCl_3) δ 8.00 – 7.97 (m, 0.6H)/7.74 – 7.71 (m, 1.5H), 7.32 – 7.28 (m, 2H), 7.20 – 7.17 (m, 0.6H)/6.92 – 6.87 (m, 1.5H), 7.09 – 7.05 (m, 2.3H)/6.86 – 6.82 (m, 0.7H), 6.45 (s, 0.3H)/6.42 (s, 0.7H), 4.27 – 4.12 (m, 2H), 3.92 (s, 1H)/ 3.84 (s, 2H), 2.77 – 2.64 (m, 2H), 2.51 – 2.42 (m, 1H), 1.84 – 1.74 (m, 2H), 1.49 – 1.41 (m, 11H); ^{13}C NMR (150 MHz, CDCl_3) δ 167.1, 167.0, 154.9, 149.5, 146.2, 145.8, 142.2, 140.4, 136.8, 130.0, 129.24, 129.19, 129.1, 128.82, 128.76, 128.1, 127.8, 127.5, 126.7, 126.2, 124.7, 79.57, 79.55, 52.2, 52.1, 45.9, 45.5, 44.3, 31.3, 31.2, 28.6; FT-IR (thin film, KBr): ν (cm^{-1}) 2945, 1719, 1689, 1275, 1168; HRMS (ESI) calcd $\text{C}_{26}\text{H}_{31}\text{NO}_4\text{Na}$ $[\text{M} + \text{Na}]^+$: 444.2151, found: 444.2149.



tert-Butyl

(E)-4-(1-(4-((2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetoxy)methyl)phenyl)prop-1-en-2-yl)piperidine-1-carboxylate (4x):

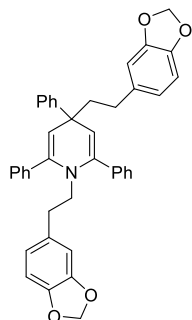
107 mg (80%, major : minor >20:1 r.r.); yellowish oil; ^1H NMR (400 MHz, CDCl_3) δ 7.66 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 7.5 Hz, 2H), 6.96 – 6.87 (m, 2H), 6.68 (d, J = 8.8 Hz, 1H), 6.29 (s, 1H), 5.14 (s, 2H), 4.32 – 4.17 (m, 2H), 3.78 (s, 3H), 3.73 (s, 2H), 2.81 – 2.69 (m, 2H), 2.38 (s, 3H), 2.23 – 2.13 (m, 1H), 1.84 (s, 3H), 1.81 – 1.72 (m, 2H), 1.54 – 1.46 (m, 11H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.8, 168.4, 156.2, 155.0, 142.8, 139.4, 138.7, 136.0, 134.0, 133.5, 131.3, 130.9, 130.7, 129.24, 129.20, 128.2, 123.6, 115.1, 112.7, 112.0, 101.3, 79.5, 66.9, 55.8, 46.4, 44.4, 30.9, 30.6, 28.6, 16.3, 13.5; FT-IR (thin film, KBr): ν (cm^{-1}) 2925, 1689, 1362, 1161, 701; HRMS (ESI) calcd $\text{C}_{39}\text{H}_{43}^{35}\text{ClN}_2\text{O}_6\text{Na}$ $[\text{M} + \text{Na}]^+$: 693.2707, found: 693.2702.



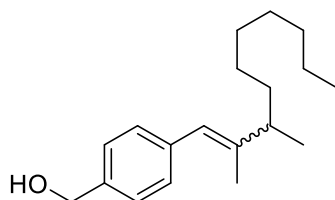
Methyl 3-phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propanoate (5):

colorless oil; 45%; ^1H NMR (400 MHz, CDCl_3) δ 7.32 (t, J = 7.0 Hz, 2H), 7.27 (d, J = 6.8 Hz, 1H), 7.25 – 7.19 (m, 2H), 4.52 (dd, J = 10.0, 5.4 Hz, 1H), 3.57 (s, 3H), 3.32 (dd, J = 13.1, 5.2 Hz, 1H), 3.11 – 3.01 (m, 1H), 1.57 – 1.45 (m, 4H), 1.42 – 1.32 (m,

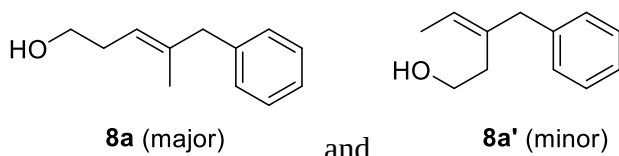
2H), 1.30 (s, 3H), 1.19 (s, 6H), 1.09 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 172.9, 135.8, 129.2, 128.2, 126.5, 86.4, 60.4, 59.3, 50.9, 40.1, 40.0, 38.4, 33.4, 32.7, 20.1, 19.9, 16.9; HRMS (CI) calcd $\text{C}_{19}\text{H}_{30}\text{NO}_3$ $[\text{M} + \text{H}]^+$: 320.2226, found: 320.2234.



1,4-Bis(2-(benzo[d][1,3]dioxol-5-yl)ethyl)-2,4,6-triphenyl-1,4-dihydropyridine (6): 71 mg (78%); yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.58 – 7.50 (m, 6H), 7.44 – 7.33 (m, 8H), 7.18 (t, $J = 7.3$ Hz, 1H), 6.67 (d, $J = 7.9$ Hz, 1H), 6.64 (d, $J = 1.5$ Hz, 1H), 6.58 (dd, $J = 7.9, 1.6$ Hz, 1H), 6.42 (d, $J = 7.8$ Hz, 1H), 5.92 (dd, $J = 7.9, 1.6$ Hz, 1H), 5.90 (d, $J = 1.4$ Hz, 1H), 5.87 (s, 2H), 5.77 (s, 2H), 5.12 (s, 2H), 3.21 – 3.14 (m, 2H), 2.62 – 2.54 (m, 2H), 2.24 – 2.18 (m, 2H), 2.13 – 2.05 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 151.5, 147.6, 147.3, 145.6, 145.5, 143.2, 138.1, 137.0, 133.0, 128.5, 128.2, 128.1, 126.5, 125.7, 121.3, 121.1, 113.3, 109.1, 108.9, 108.2, 108.0, 100.8, 100.7, 50.3, 47.1, 43.9, 34.6, 32.5; FT-IR (thin film, KBr): ν (cm^{-1}) 2921, 1489, 1242, 1038, 701; HRMS (ESI) calcd $\text{C}_{41}\text{H}_{36}\text{NO}_4$ $[\text{M} + \text{H}]^+$: 606.2644, found: 606.2640.

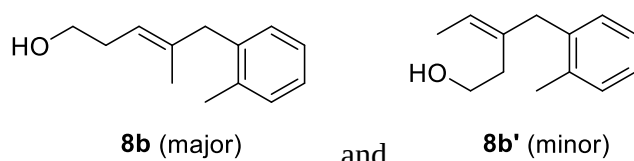


(4-(2,3-Dimethyldec-1-en-1-yl)phenyl)methanol (7): 27 mg (52%, major : minor >20:1 r.r.); colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.31 (d, $J = 8.2$ Hz, 2H), 7.24 (d, $J = 8.1$ Hz, 2H), 6.26 (s, 1H), 4.67 (s, 2H), 2.32 – 2.20 (m, 1H), 1.76 (d, $J = 1.3$ Hz, 3H), 1.72 – 1.63 (m, 1H), 1.50 – 1.39 (m, 1H), 1.38 – 1.18 (m, 10H), 1.07 (d, $J = 6.9$ Hz, 3H), 0.88 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.8, 138.5, 138.3, 129.3, 126.9, 124.0, 65.5, 43.8, 35.3, 32.1, 29.9, 29.5, 27.8, 22.8, 19.9, 14.3, 14.2; FT-IR (thin film, KBr): ν (cm^{-1}) 3332, 2921, 1459, 1014, 868; HRMS (CI) calcd $\text{C}_{19}\text{H}_{30}\text{O}$ $[\text{M}]^+$: 274.2297, found: 274.2291.



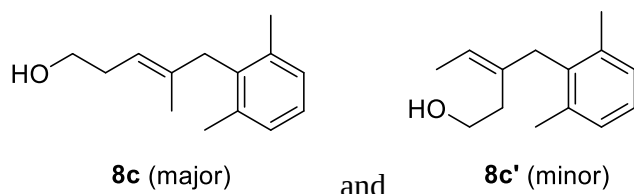
(E)-4-Methyl-5-phenylpent-3-en-1-ol (8a):

24 mg (68% yield, major : minor = 1.3:1 r.r.); yellowish oil; ^1H NMR (600 MHz, CDCl_3) δ 7.31 – 7.27 (m, 2H), 7.22 – 7.16 (m, 3H), 5.50 (q, J = 6.8 Hz, 0.43H)/ 5.27 (t, J = 7.3 Hz, 0.55H), 3.66 (t, J = 6.6 Hz, 1.1H)/3.60 (t, J = 6.8 Hz, 0.9H), 3.34 (s, 0.9H)/ 3.33 (s, 1.1H), 2.34 (q, J = 6.8 Hz, 1.1H)/2.30 (t, J = 6.8 Hz, 0.9H), 1.69 (d, J = 6.8 Hz, 1.4H)/1.60 (s, 1.6H); ^{13}C NMR (150 MHz, CDCl_3) δ 140.20, 140.15, 138.2, 135.6, 129.0, 128.9, 128.44, 128.39, 126.23, 126.15, 124.3, 122.0, 62.6, 60.9, 46.4, 44.0, 32.9, 31.7, 16.2, 13.7; FT-IR (thin film, KBr): ν (cm^{-1}) 3342, 2908, 1492, 1041, 694; HRMS (CI) calcd $\text{C}_{12}\text{H}_{16}\text{O}$ $[\text{M}]^+$: 176.1201, found: 176.1204.



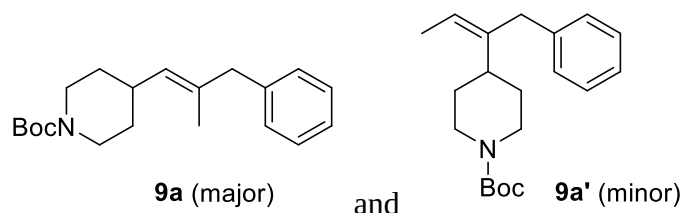
(E)-4-Methyl-5-(o-tolyl)pent-3-en-1-ol (8b):

19 mg (51% yield, major : minor = 1.5:1 r.r.); yellowish oil; ^1H NMR (400 MHz, CDCl_3) δ 7.17 – 7.08 (m, 4H), 5.24 (q, J = 6.6 Hz, 0.4H)/5.06 (t, J = 6.8 Hz, 0.6H), 3.70 – 3.58 (m, 2H), 3.32 (s, 2H), 2.40 – 2.29 (m, 2H), 2.26 (d, J = 3.5 Hz, 3H), 1.65 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.0, 137.2, 136.96, 136.93, 134.5, 130.34, 130.28, 130.0, 129.8, 126.43, 126.35, 125.99, 125.95, 123.7, 121.6, 62.6, 61.1, 43.4, 41.0, 33.7, 31.7, 19.57, 19.55, 16.8, 13.7; FT-IR (thin film, KBr): ν (cm^{-1}) 3335, 2921, 1462, 1048, 734; HRMS (CI) calcd $\text{C}_{13}\text{H}_{18}\text{O}$ $[\text{M}]^+$: 190.1358, found: 190.1363.

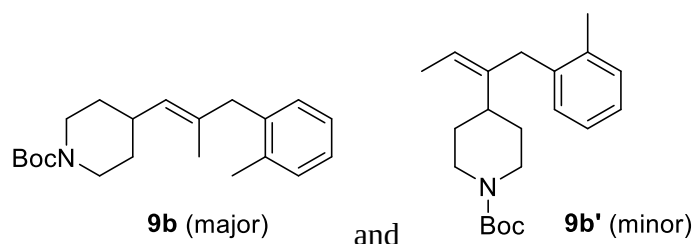


(E)-5-(2,6-Dimethylphenyl)-4-methylpent-3-en-1-ol (8c):

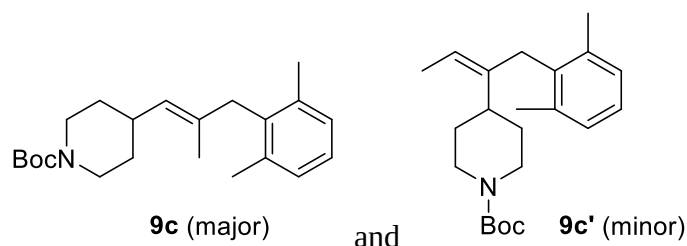
18 mg (45% yield, major : minor = 3.5:1 r.r.); yellowish oil; ^1H NMR (600 MHz, CDCl_3) δ 7.07 – 6.99 (m, 3H), 4.82 (q, J = 13.6, 6.7 Hz, 0.25H)/ 4.67 (t, J = 7.5 Hz, 0.75H), 3.80 – 3.76 (m, 0.5H)/ 3.52 (t, J = 6.6 Hz, 1.5H), 3.31 (s, 2H), 2.48 – 2.43 (m, 1H), 2.29 – 2.21 (m, 7H), 1.75 (s, 2.25H)/1.57 (d, J = 6.8 Hz, 0.75H); ^{13}C NMR (150 MHz, CDCl_3) δ 137.3, 136.4, 136.1, 128.0, 126.1, 120.9, 119.1, 62.5, 61.3, 38.8, 36.6, 35.0, 31.6, 20.04, 19.96, 19.6, 17.6; FT-IR (thin film, KBr): ν (cm^{-1}) 3352, 2918, 1469, 1041, 767; HRMS (CI) calcd $\text{C}_{14}\text{H}_{20}\text{O}$ $[\text{M}]^+$: 204.1514, found: 204.1517.



***tert*-Butyl (*E*)-4-(2-methyl-3-phenylprop-1-en-1-yl)piperidine-1-carboxylate (**9a**):** 49 mg (78% yield, major : minor = 1.5:1 r.r.); yellowish oil; ^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.29 (m, 2H), 7.27 – 7.19 (m, 3H), 5.18 – 5.11 (m, 1H), 4.24 – 4.05 (m, 2H), 3.32 (s, 1.2H)/3.31 (s, 0.8H), 2.87 – 2.76 (m, 1H), 2.74 – 2.63 (m, 1H), 2.44 – 2.33 (m, 0.6H)/1.82–1.75 (m, 0.4H), 1.75–1.26 (m, 4H), 1.72 – 1.68 (m, 1.2H)/1.61 (d, J = 1.2 Hz, 1.8H), 1.52 (s, 5.4H)/1.50 (s, 3.6H); ^{13}C NMR (150 MHz, CDCl_3) δ 155.02, 155.00, 142.1, 140.8, 140.3, 134.2, 131.0, 129.3, 128.9, 128.34, 128.26, 126.1, 125.9, 122.1, 79.40, 79.35, 46.3, 44.2, 39.9, 38.3, 35.4, 32.2, 30.2, 28.61, 28.59, 16.1, 13.1; FT-IR (thin film, KBr): ν (cm^{-1}) 2931, 1696, 1425, 1158, 694; HRMS (ESI) calcd $\text{C}_{20}\text{H}_{29}\text{NO}_2\text{Na}$ [$\text{M} + \text{Na}$] $^+$: 338.2096, found: 338.2092.



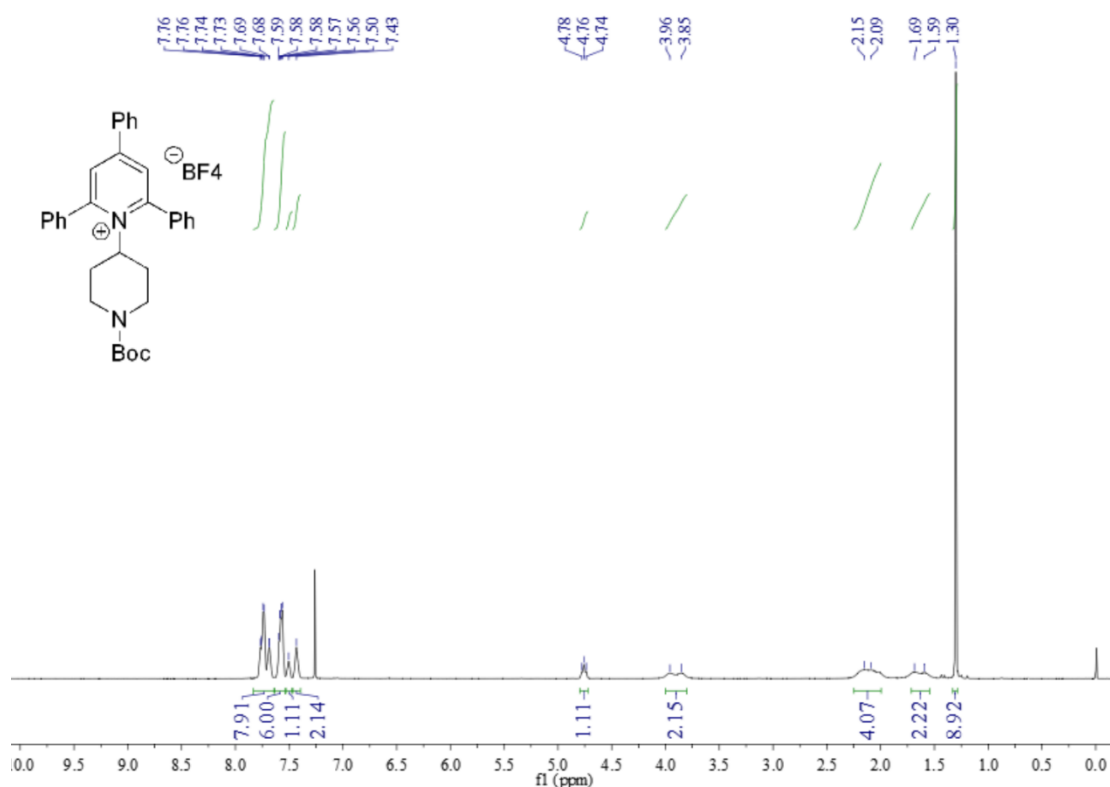
***tert*-Butyl (*E*)-4-(2-methyl-3-(*o*-tolyl)prop-1-en-1-yl)piperidine-1-carboxylate (**9b**):** 32 mg (67% yield, major : minor = 1.7:1 r.r.); yellowish oil; ^1H NMR (600 MHz, CDCl_3) δ 7.14 – 7.10 (m, 3H), 7.10 – 7.04 (m, 1H), 4.92 – 4.89 (m, 0.63H)/4.70 – 4.66 (m, 0.37H), 4.28 – 4.15 (m, 0.74H)/4.10 – 3.95 (m, 1.26H), 3.27 (s, 1.31H)/3.20 (s, 0.73H), 2.82 – 2.66 (m, 2H), 2.40 – 2.31 (m, 1H), 2.25 (s, 1.9H)/2.19 (s, 1.1H), 1.76 – 1.17 (m, 4H), 1.61 (d, J = 0.7 Hz, 1.9H)/1.59 – 1.56 (m, 1.1H), 1.48 (s, 3.3H)/1.45 (s, 5.7H); ^{13}C NMR (150 MHz, CDCl_3) δ 155.02, 154.99, 141.0, 138.4, 138.1, 137.0, 136.9, 133.1, 130.7, 130.6, 130.24, 130.21, 129.7, 126.28, 126.27, 125.9, 120.0, 79.5, 79.4, 44.2, 43.4, 38.3, 36.3, 35.3, 32.2, 30.0, 28.6, 19.6, 19.4, 16.6, 13.0; FT-IR (thin film, KBr): ν (cm^{-1}) 2925, 1692, 1425, 1235, 1161; HRMS (ESI) calcd $\text{C}_{21}\text{H}_{31}\text{NO}_2\text{Na}$ [$\text{M} + \text{Na}$] $^+$: 352.2252, found: 352.2250.



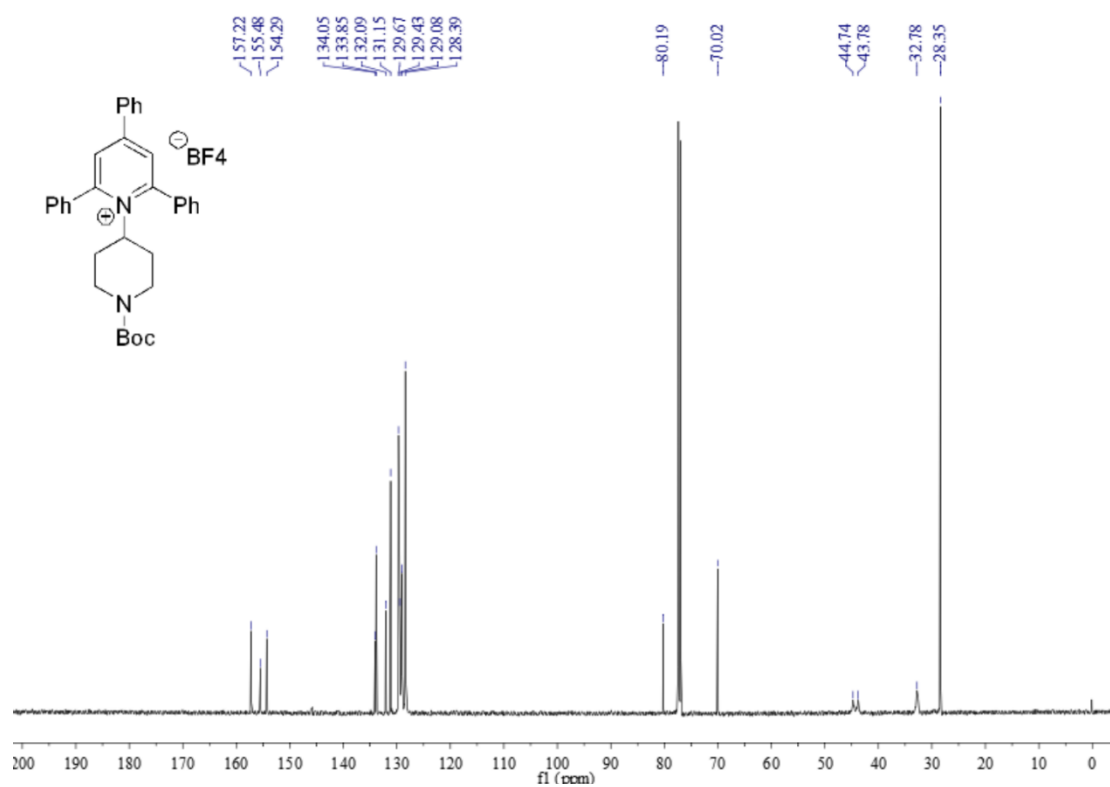
***tert*-Butyl (*E*)-4-(3-(2,6-dimethylphenyl)-2-methylprop-1-en-1-yl)piperidine-1-**

carboxylate (9c):

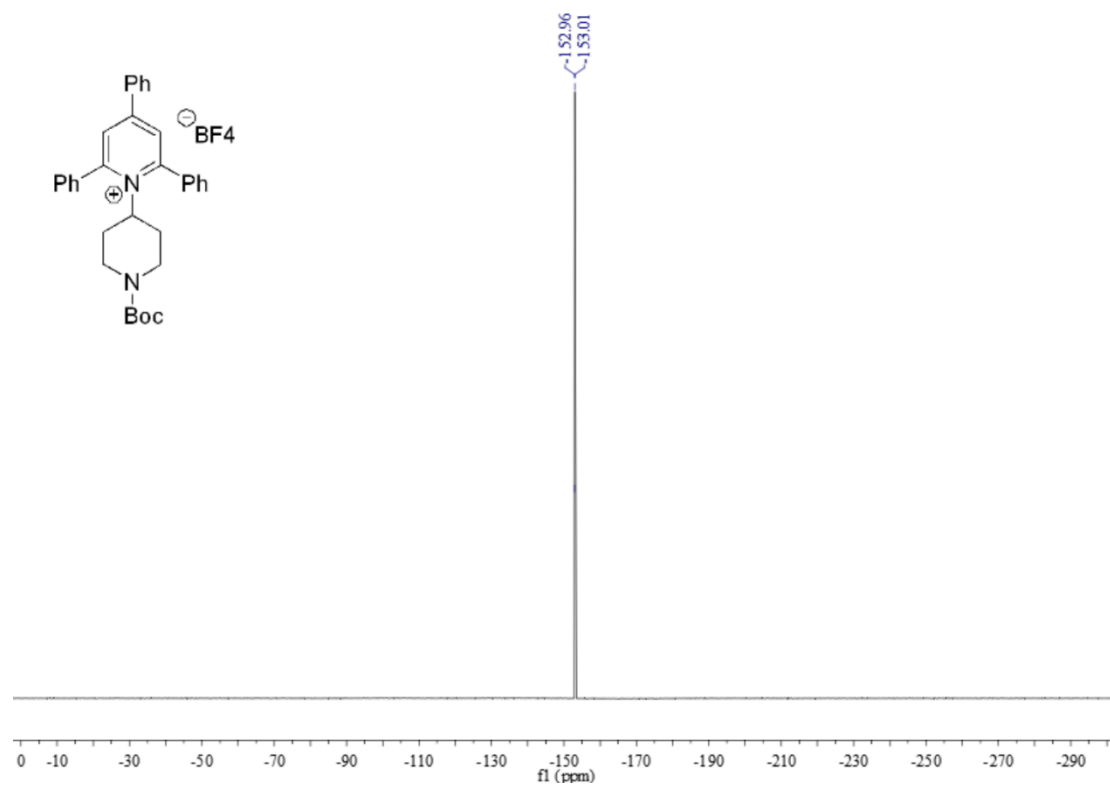
49 mg (71% yield, major : minor = 2.4:1 r.r.); yellowish oil; ^1H NMR (600 MHz, CDCl_3) δ 7.05 – 6.97 (m, 3H), 4.54 – 4.51 (m, 0.78H)/4.50 – 4.47 (m, 0.3H), 4.31 – 4.18 (m, 0.6H)/ 4.07 – 3.89 (m, 1.51H), 3.27 (s, 1.5H)/3.20 – 3.18 (m, 0.6H), 2.81 – 2.67 (m, 2H), 2.36 – 2.29 (m, 1H), 2.22 (s, 4.24H)/ 2.17 (s, 1.61H), 1.78 – 1.05 (m, 4H), 1.70 (s, 2.2H)/1.52 – 1.50 (m, 0.9H), 1.49 (s, 2.75H)/1.43 (s, 6.57H); ^{13}C NMR (150 MHz, CDCl_3) δ 155.0, 154.9, 139.1, 137.32, 137.28, 136.8, 136.5, 131.8, 128.3, 128.0, 127.9, 126.02, 125.97, 117.3, 79.6, 79.3, 44.1, 38.7, 38.4, 35.2, 32.1, 29.9, 28.7, 28.6, 20.0, 19.8, 17.4, 12.9; FT-IR (thin film, KBr): ν (cm^{-1}) 2925, 1692, 1419, 1161, 767; HRMS (CI) calcd $\text{C}_{22}\text{H}_{33}\text{NO}_2$ $[\text{M}]^+$: 343.2511, found: 343.2503.

9. NMR Spectra for the substrates and products ^1H NMR of **2a**

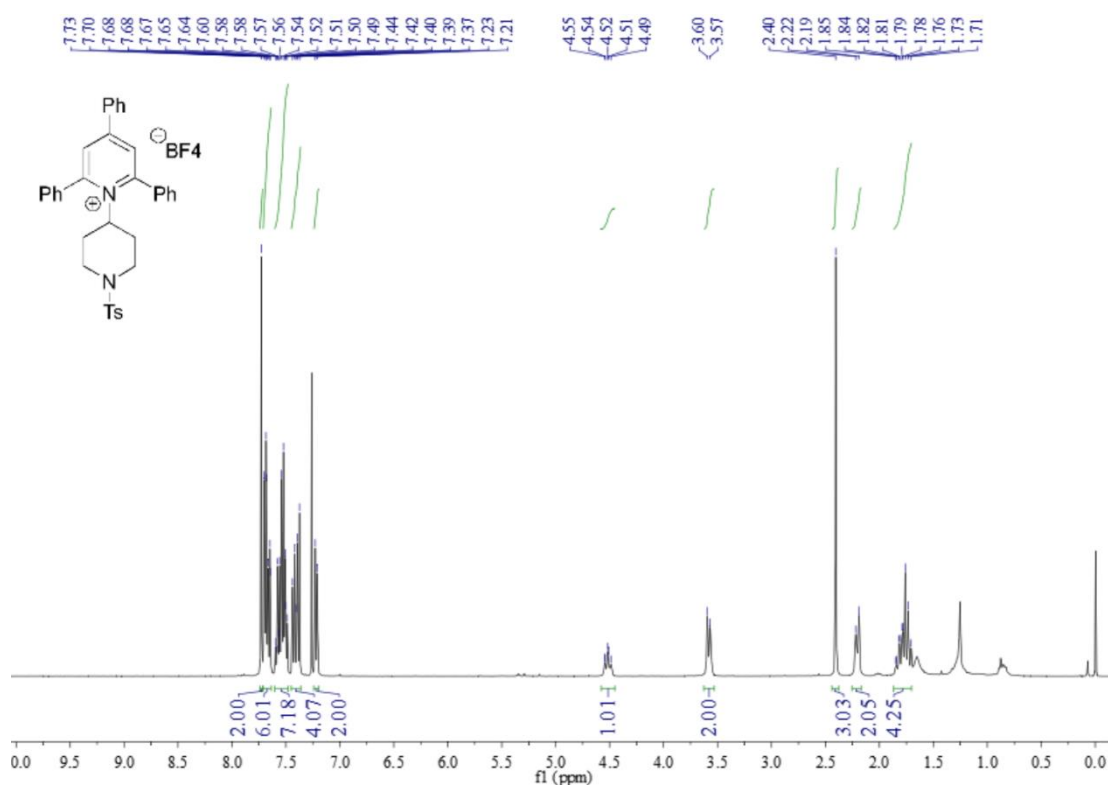
¹³C NMR of **2a**



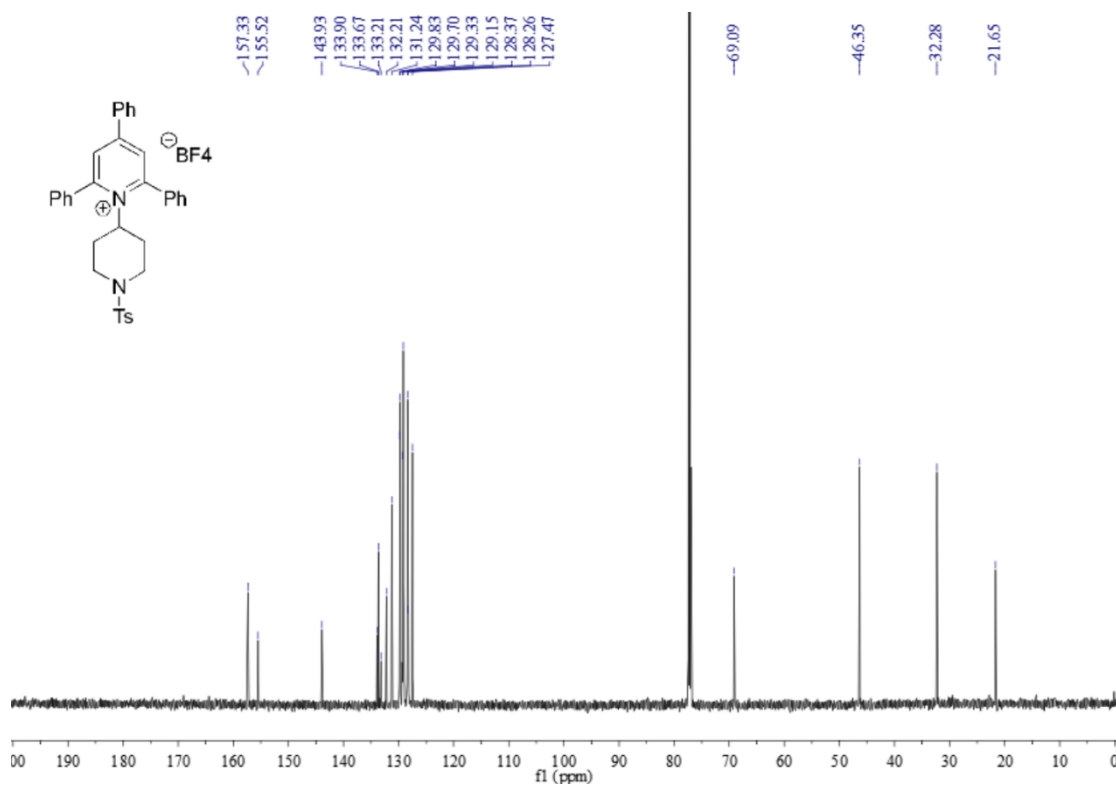
¹⁹F NMR of **2a**



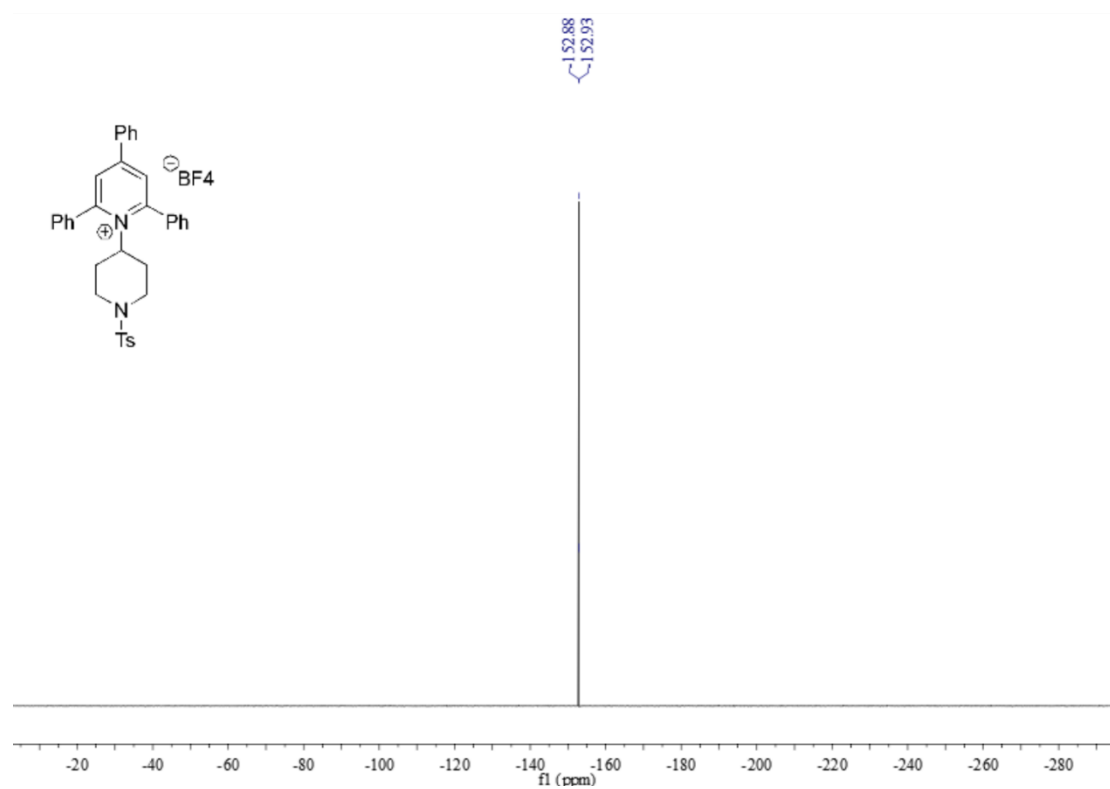
¹H NMR of **2b**



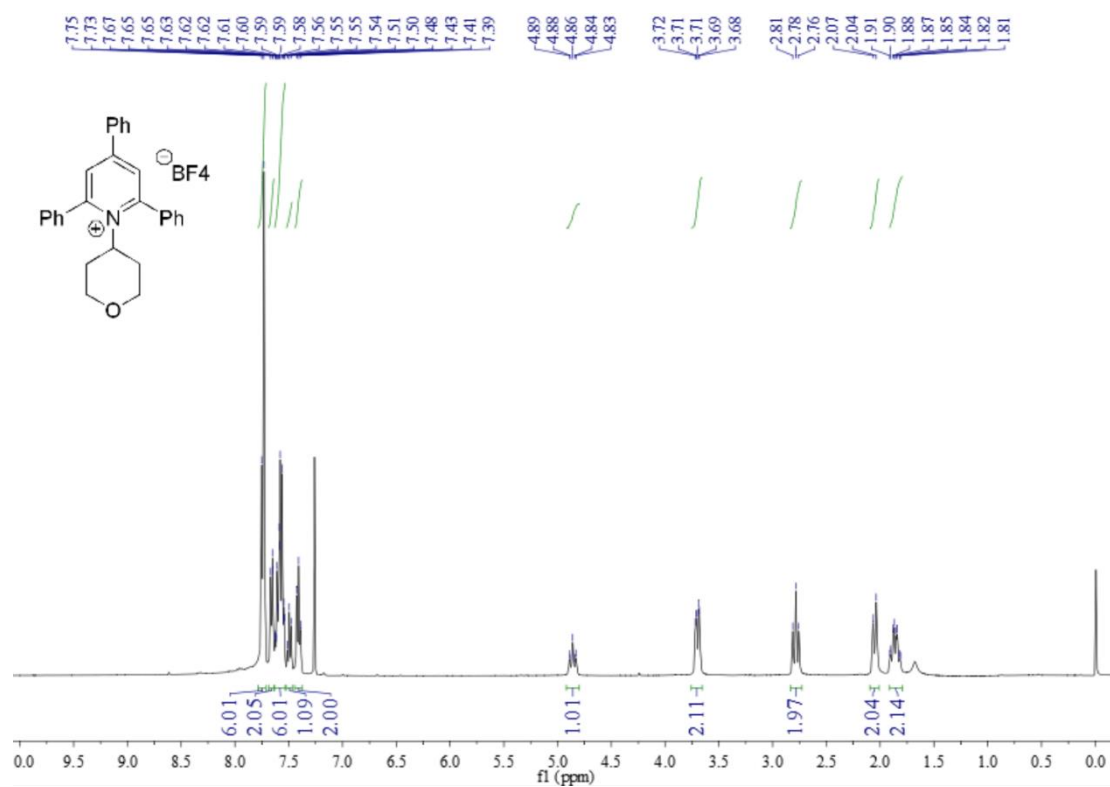
¹³C NMR of **2b**



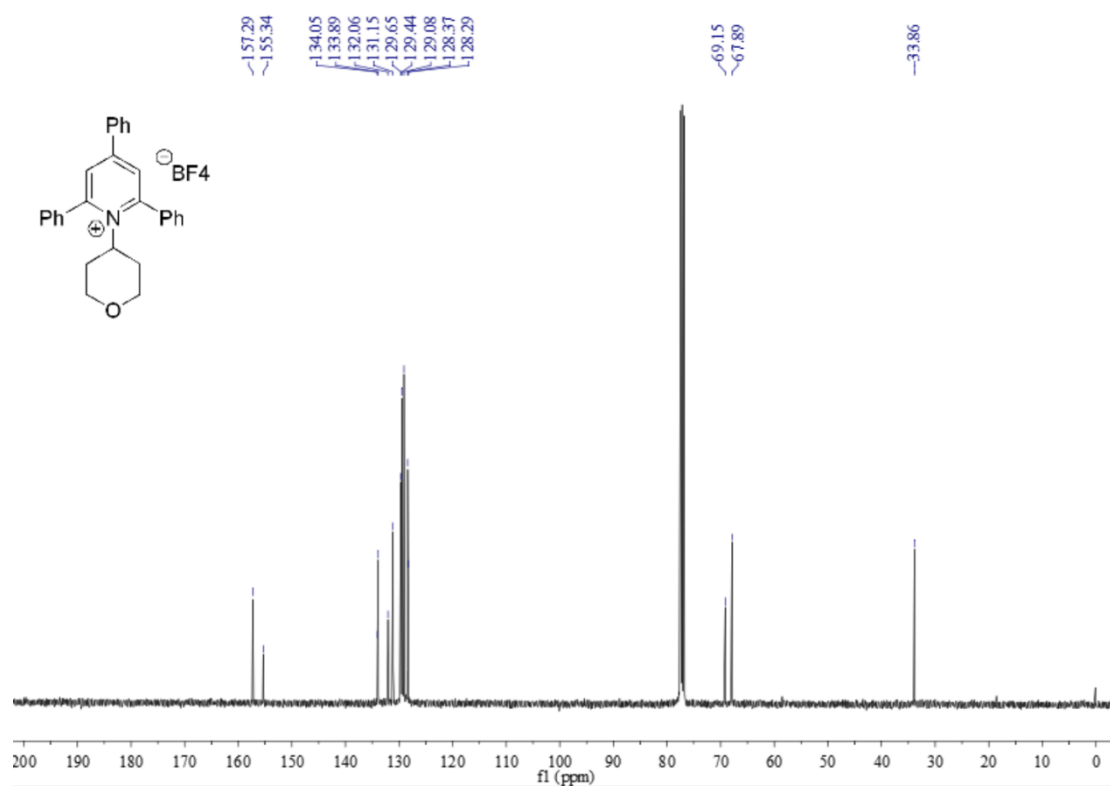
¹⁹F NMR of **2b**



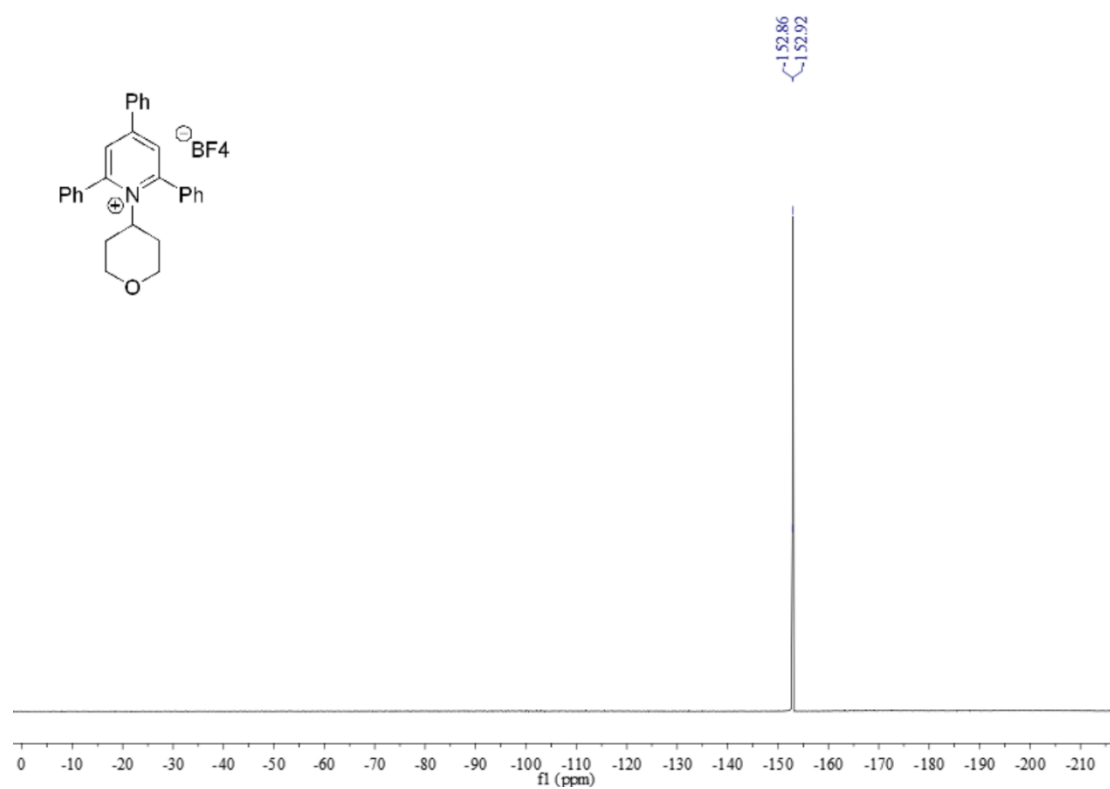
¹H NMR of **2c**



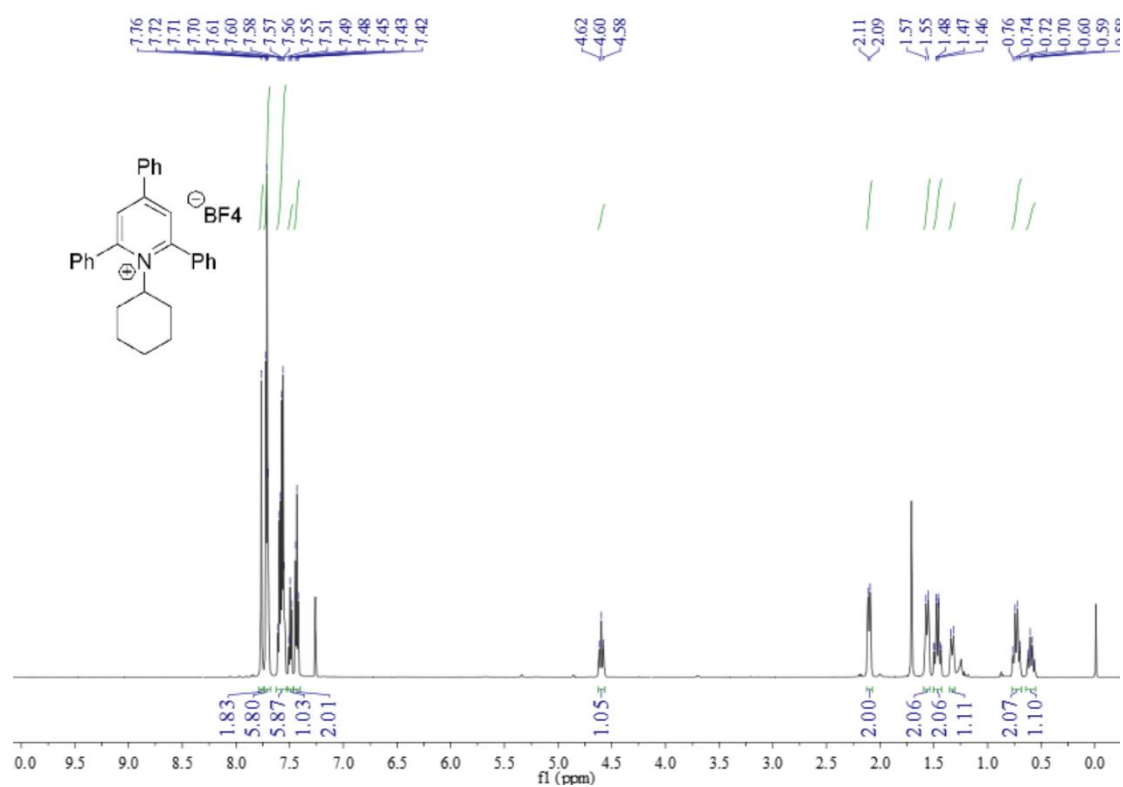
¹³C NMR of **2c**



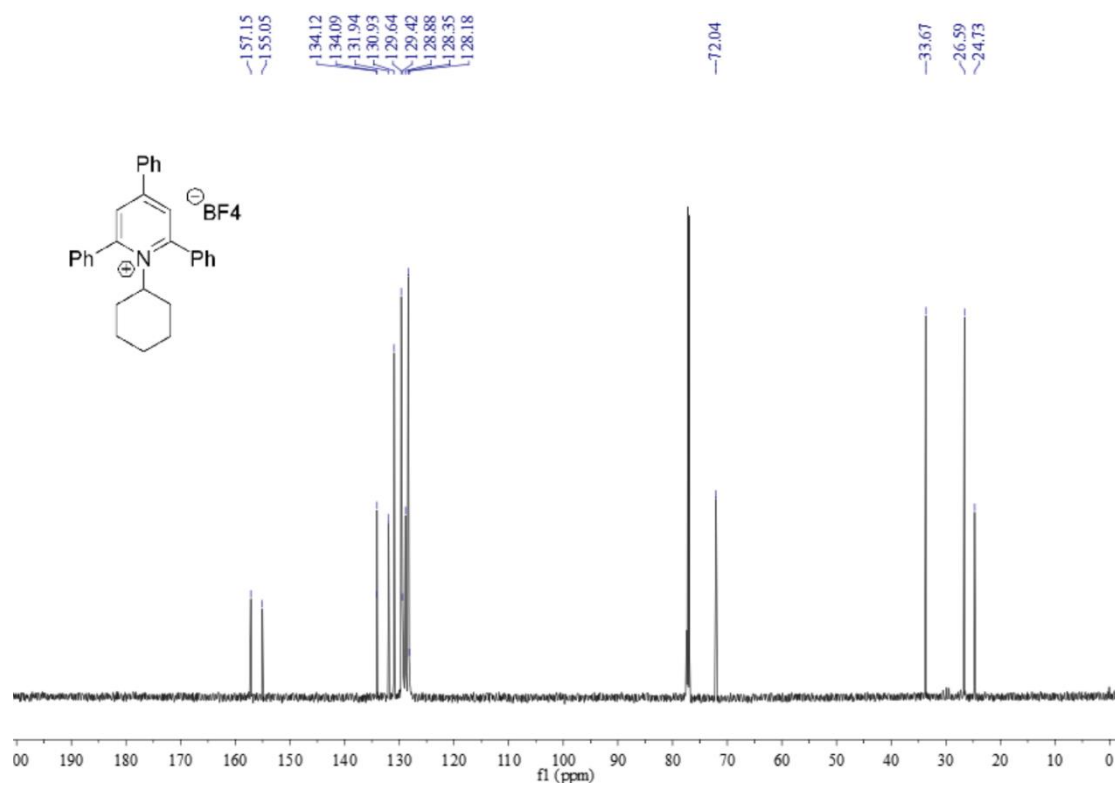
¹⁹F NMR of **2c**



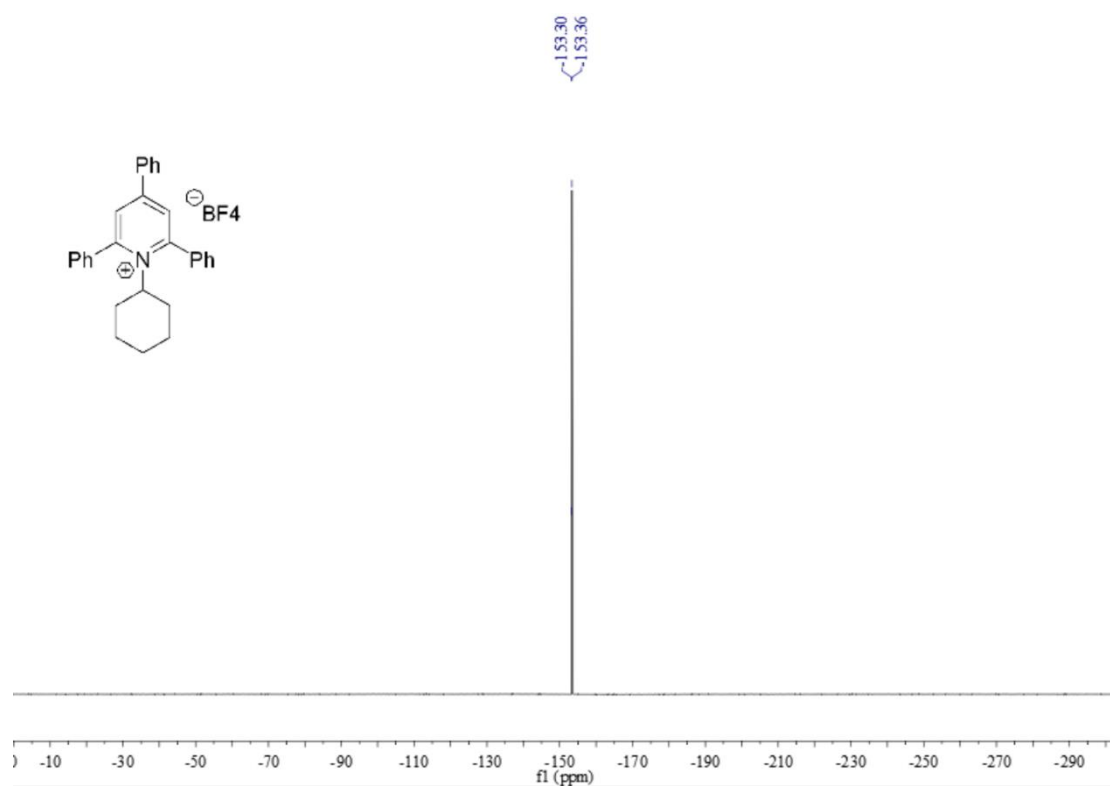
¹H NMR of **2d**



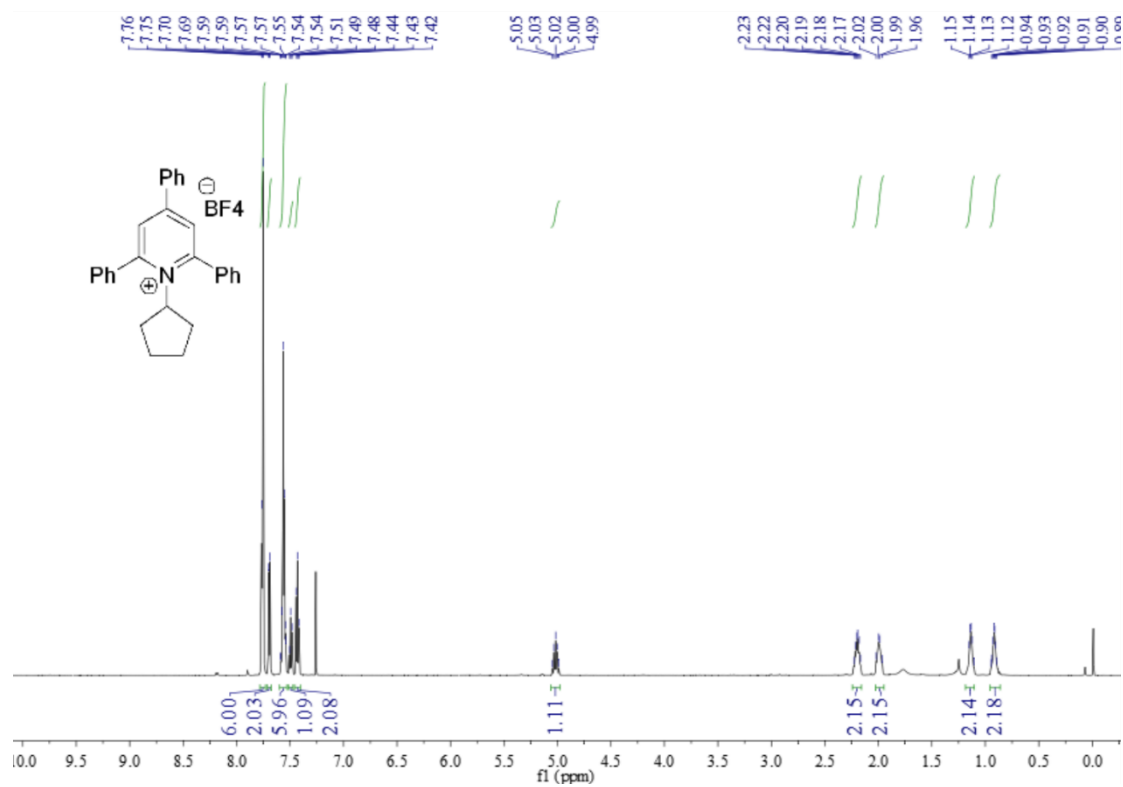
¹³C NMR of **2d**



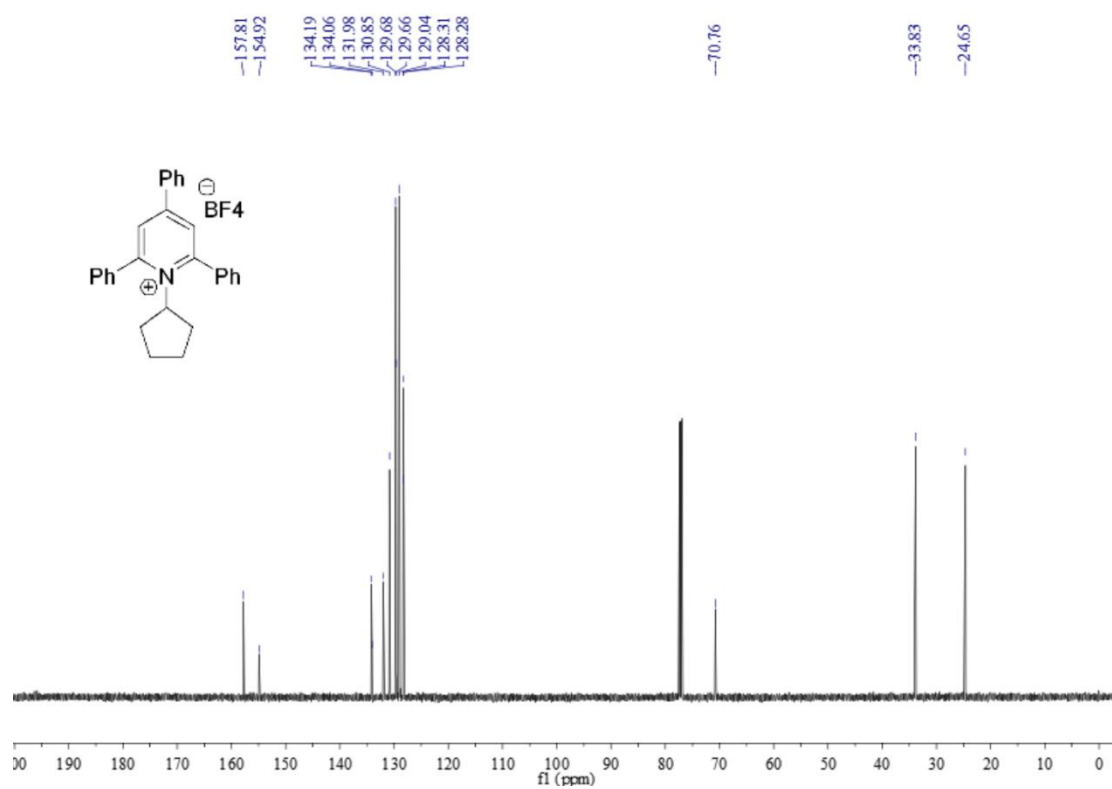
¹⁹F NMR of **2d**



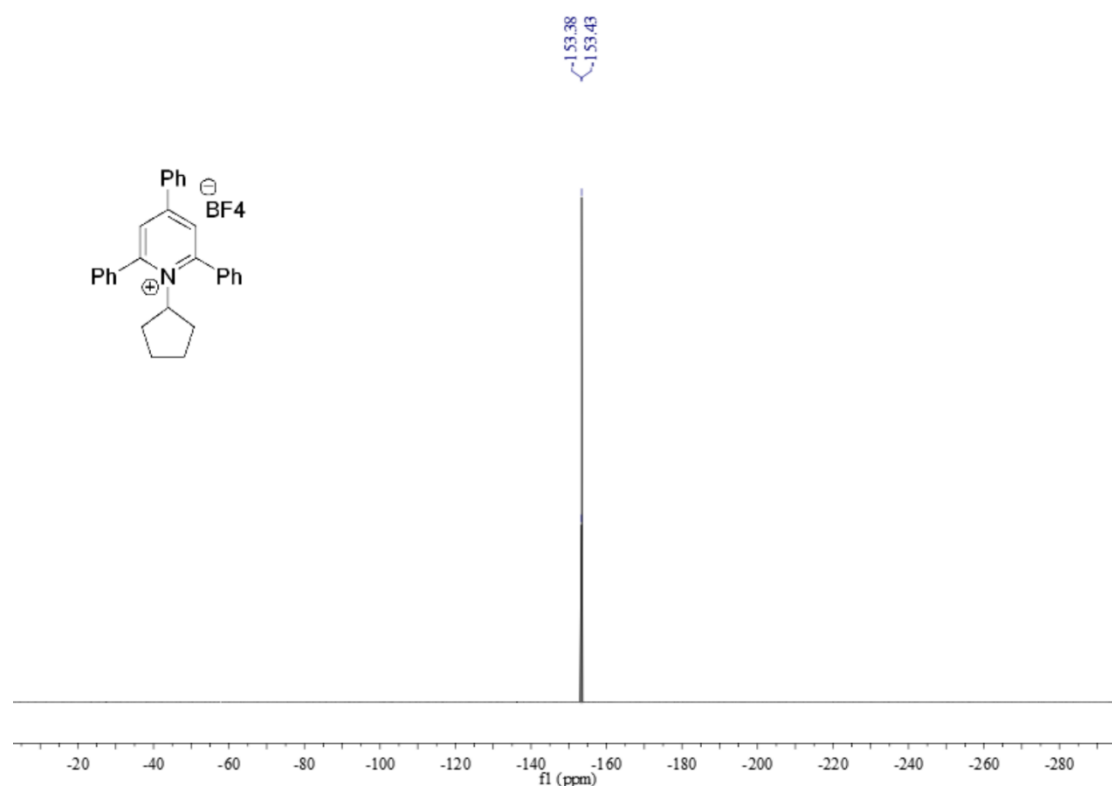
¹H NMR of **2e**



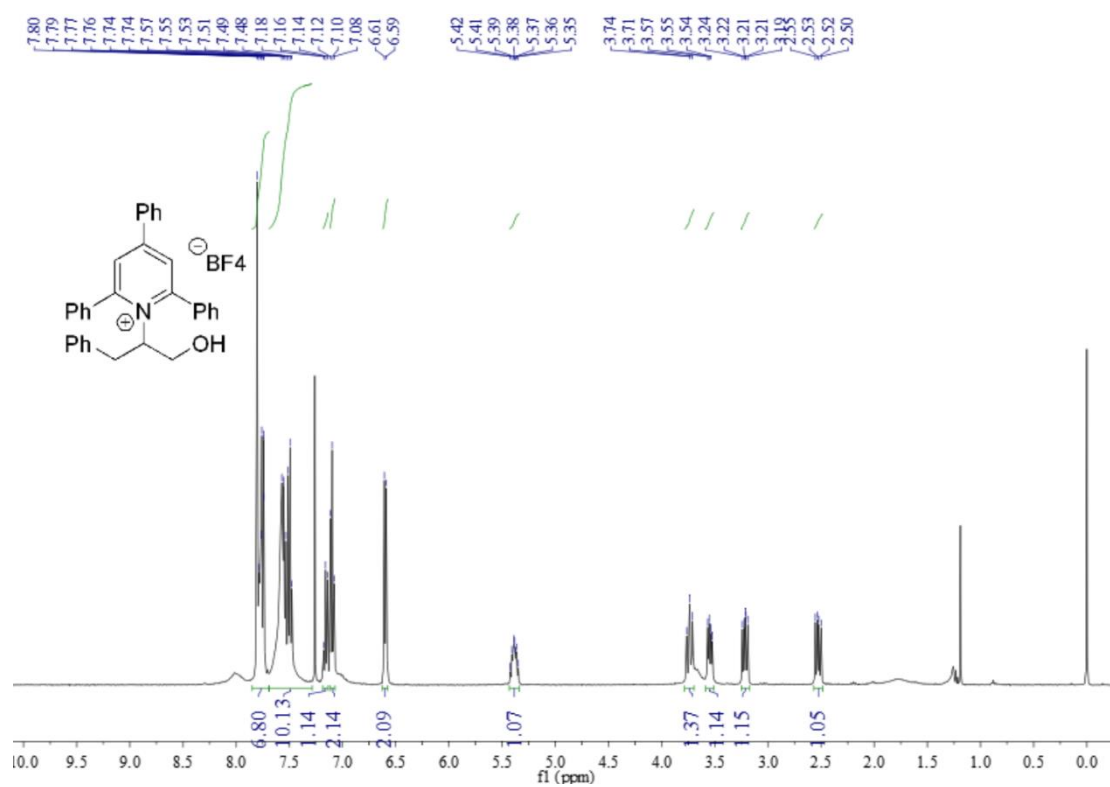
¹³C NMR of **2e**



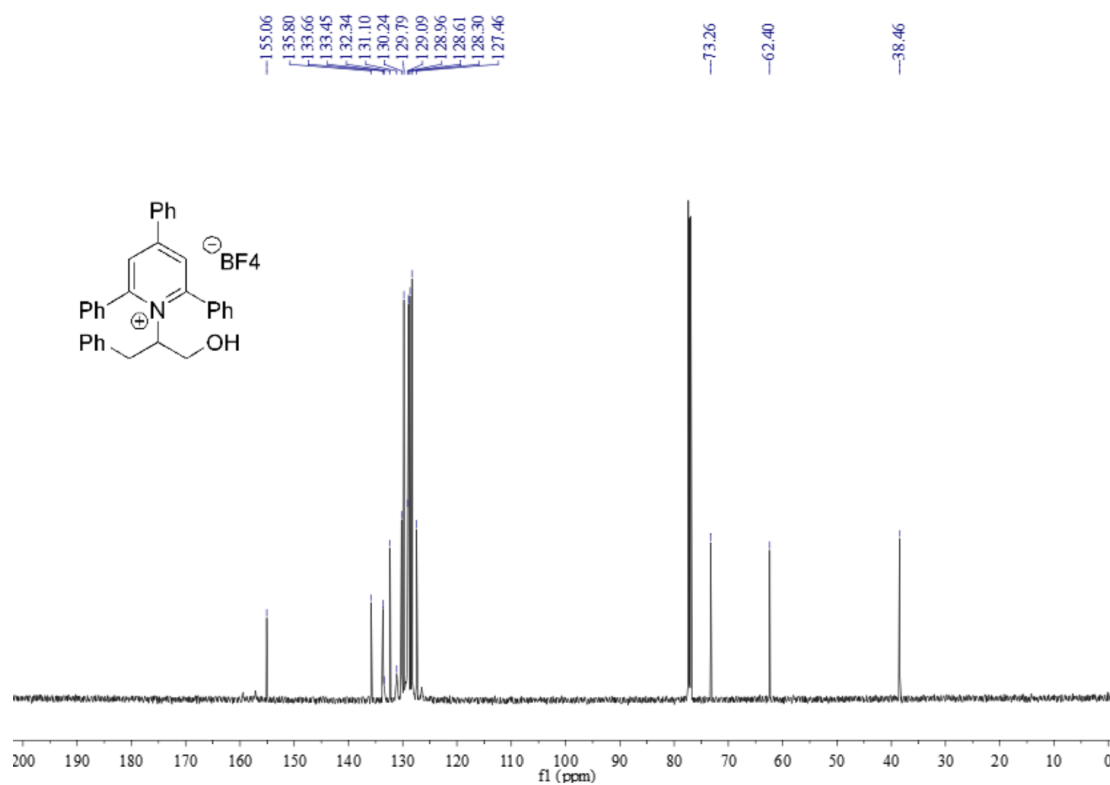
¹⁹F NMR of **2e**



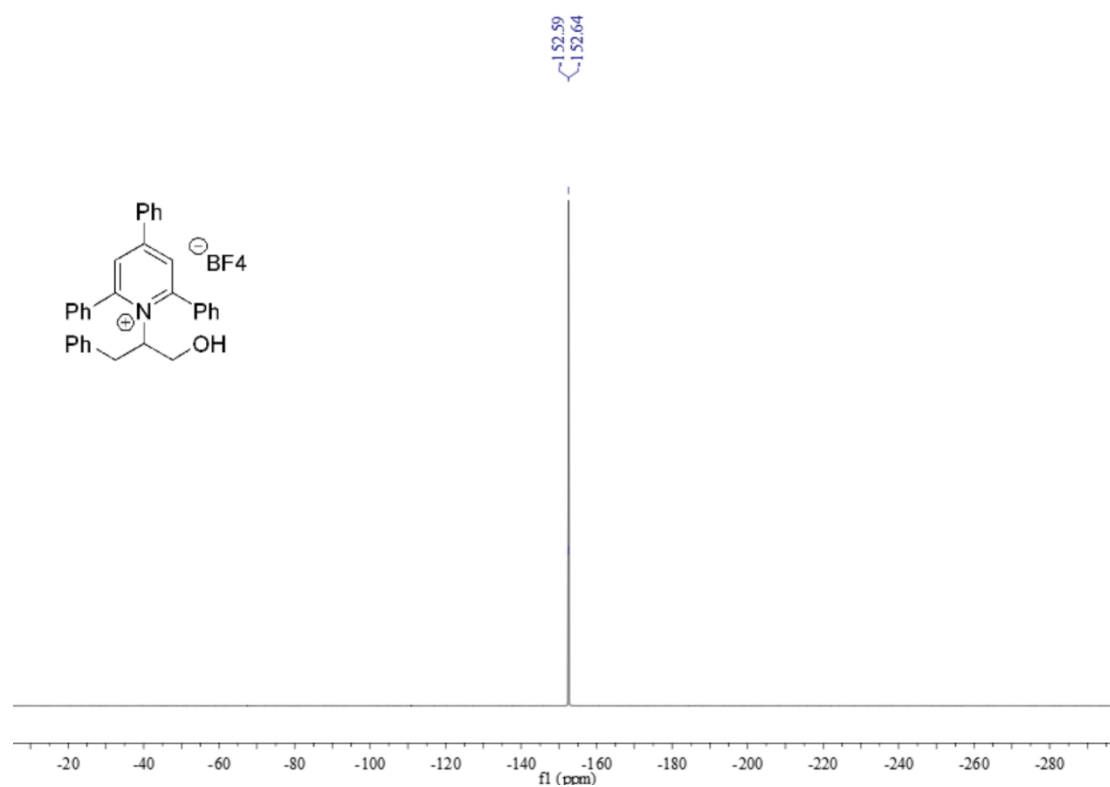
¹H NMR of **2f**



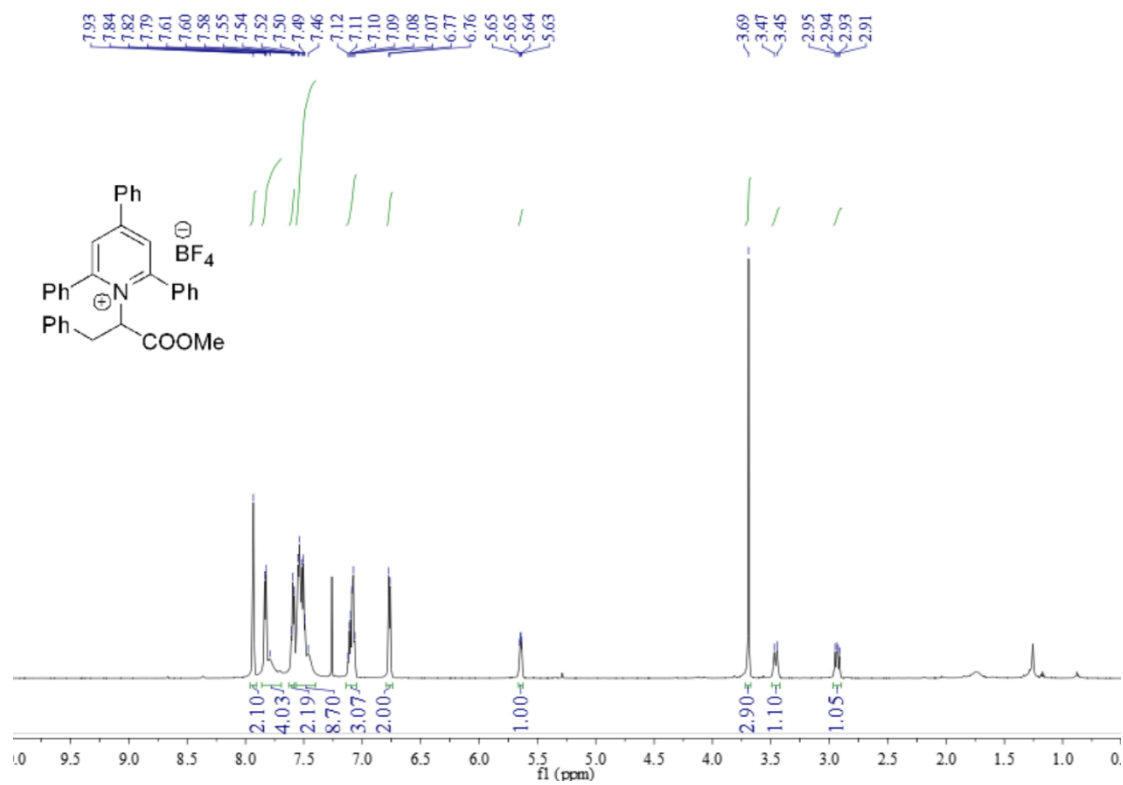
¹³C NMR of **2f**



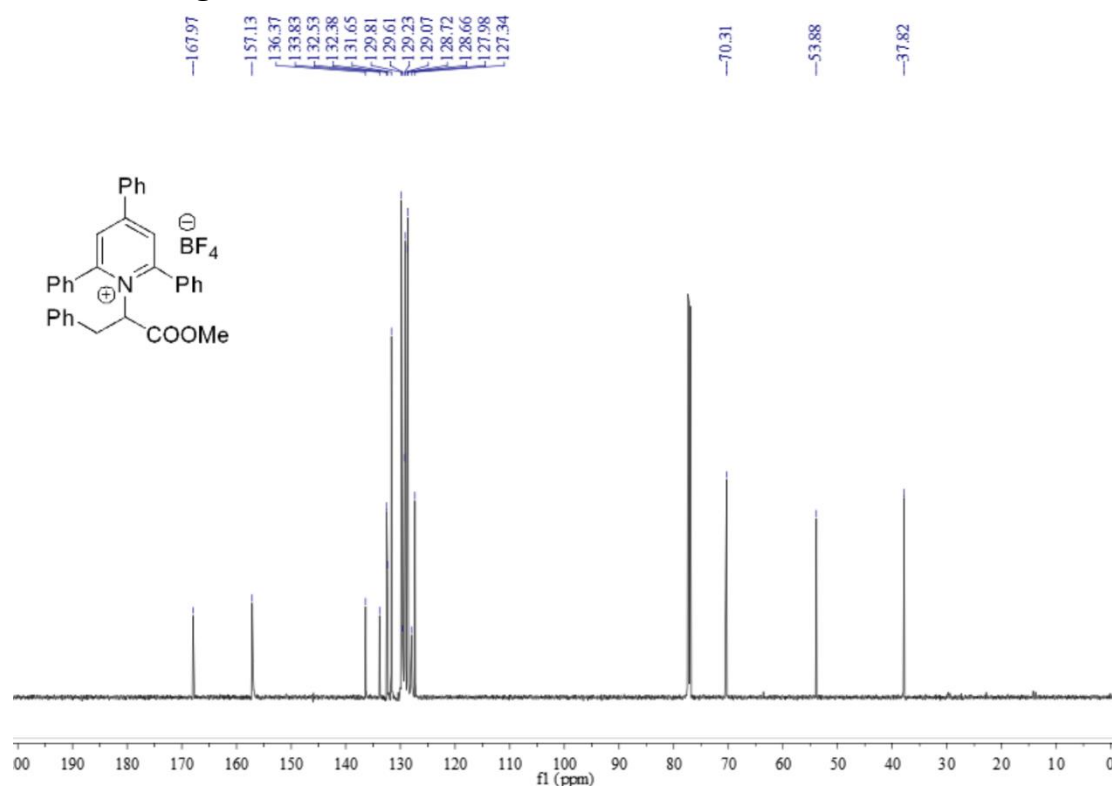
¹⁹F NMR of **2f**



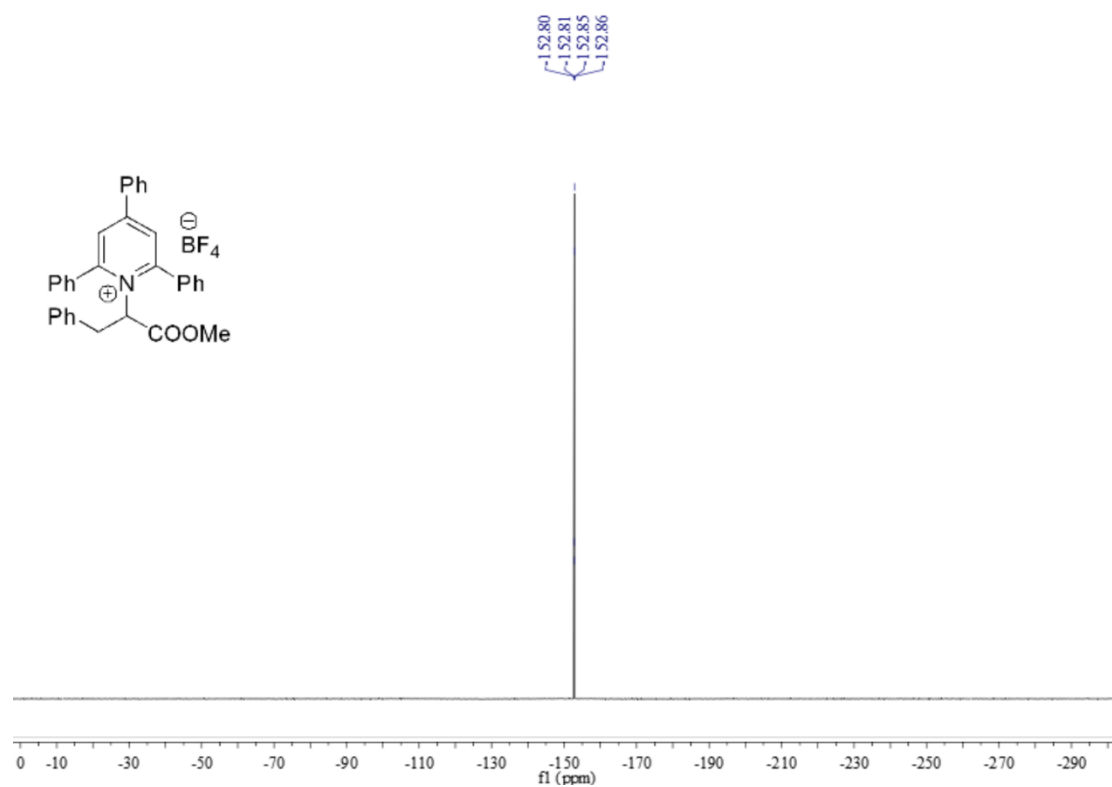
¹H NMR of **2g**



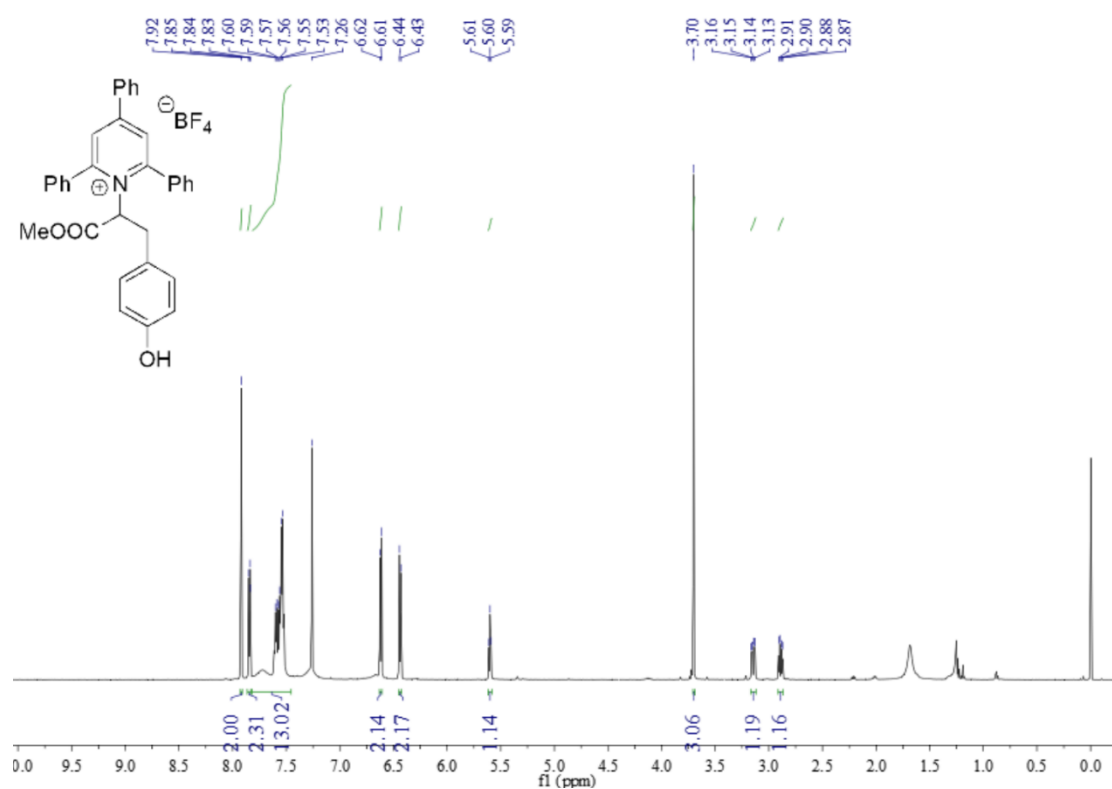
¹³C NMR of **2g**



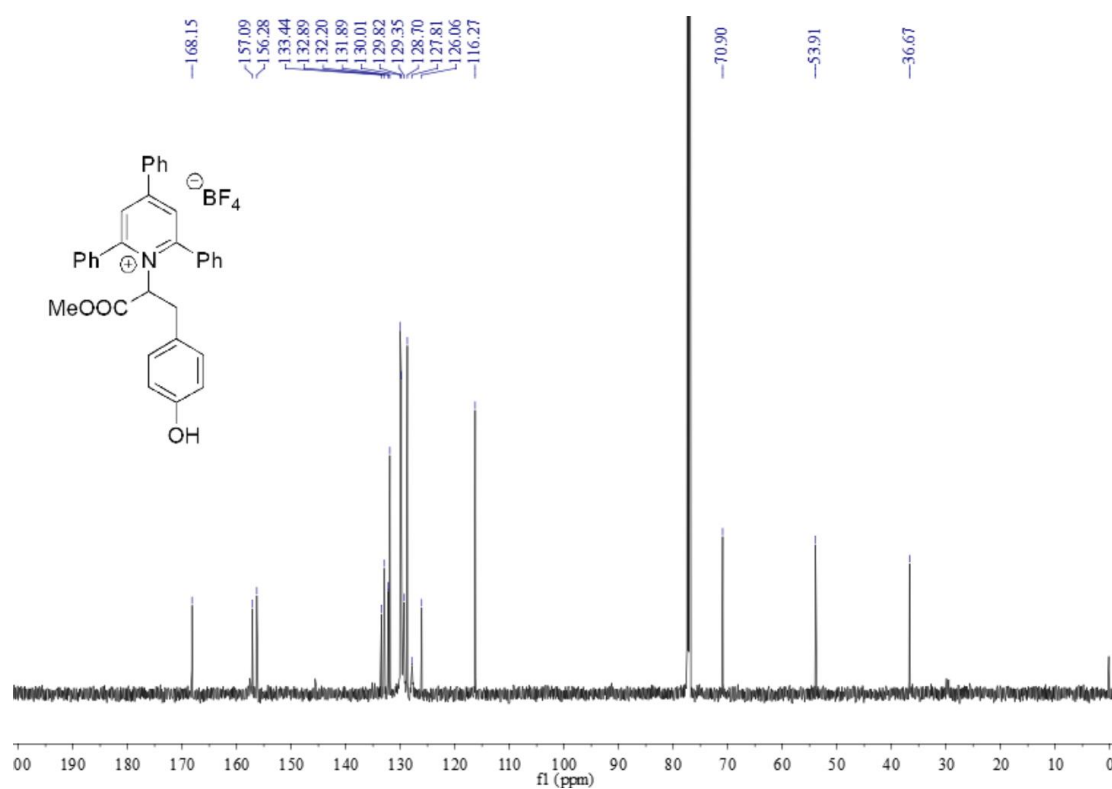
¹⁹F NMR of **2g**



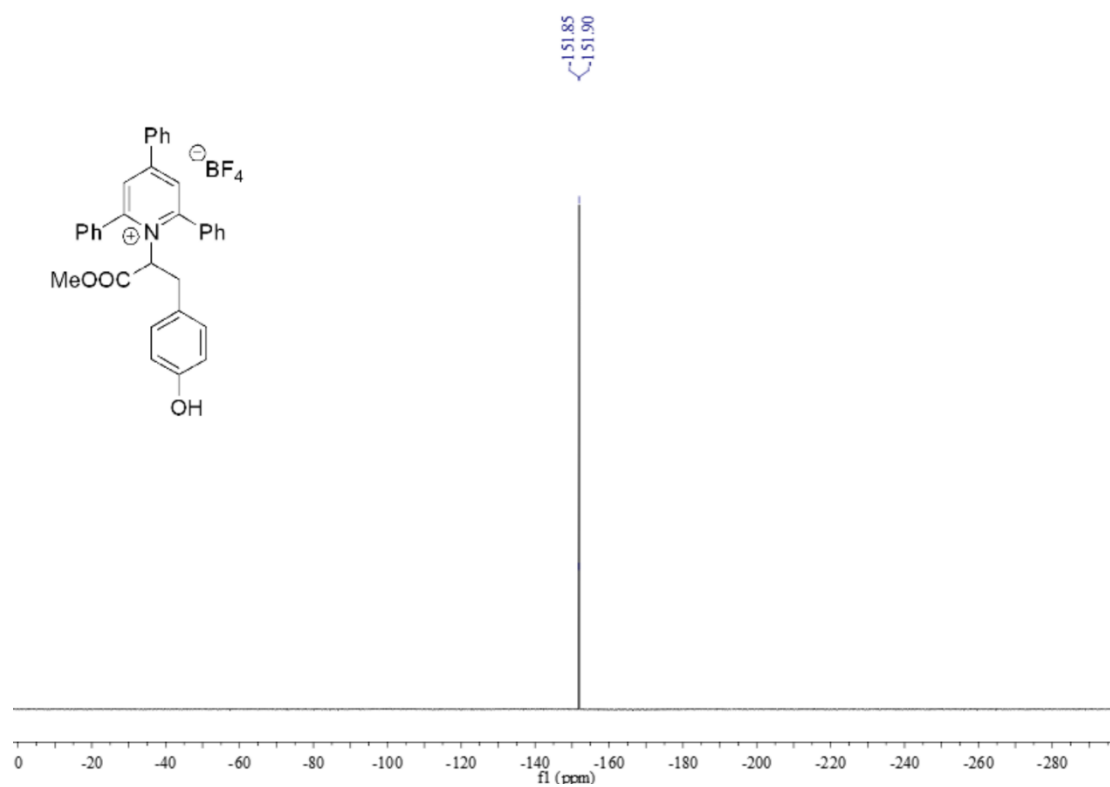
¹H NMR of **2h**



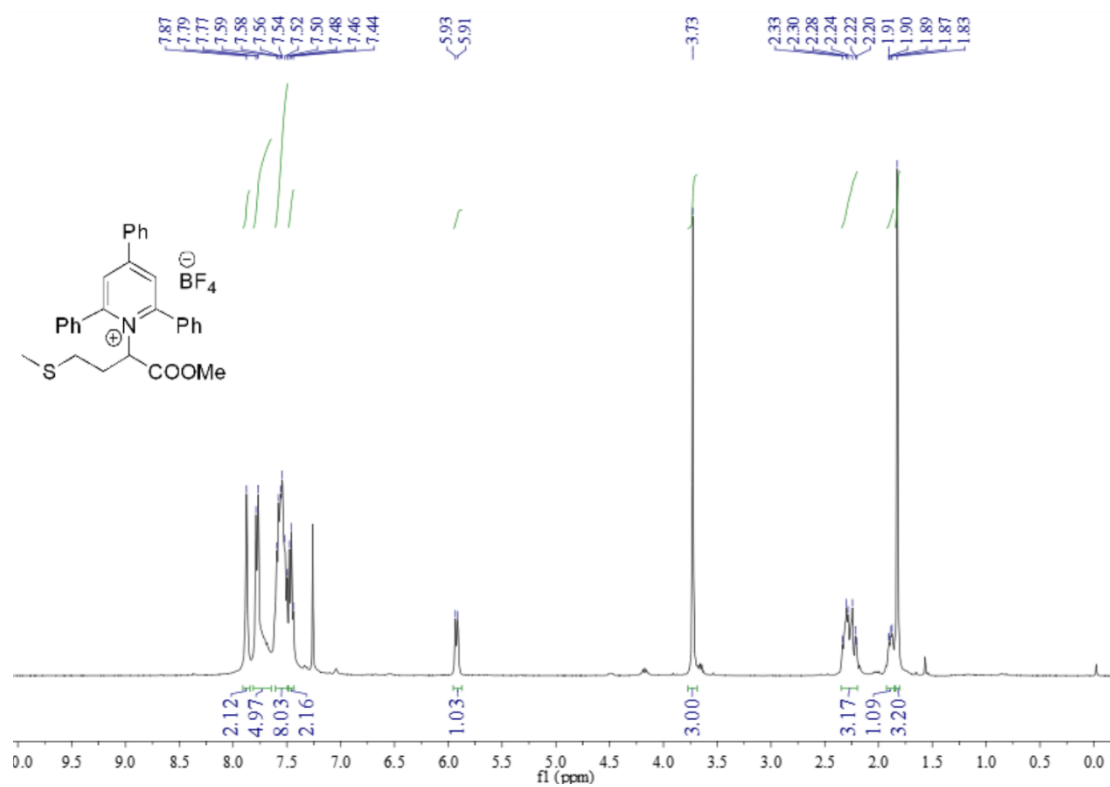
¹³C NMR of **2h**



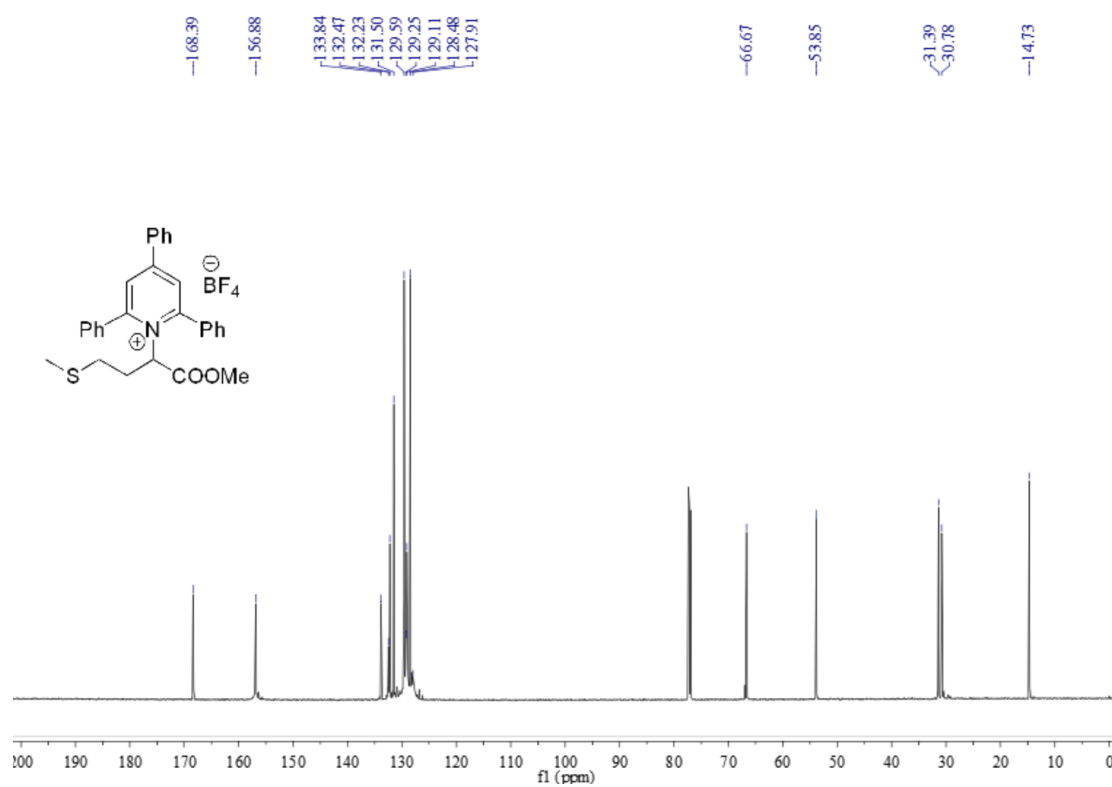
¹⁹F NMR of **2h**



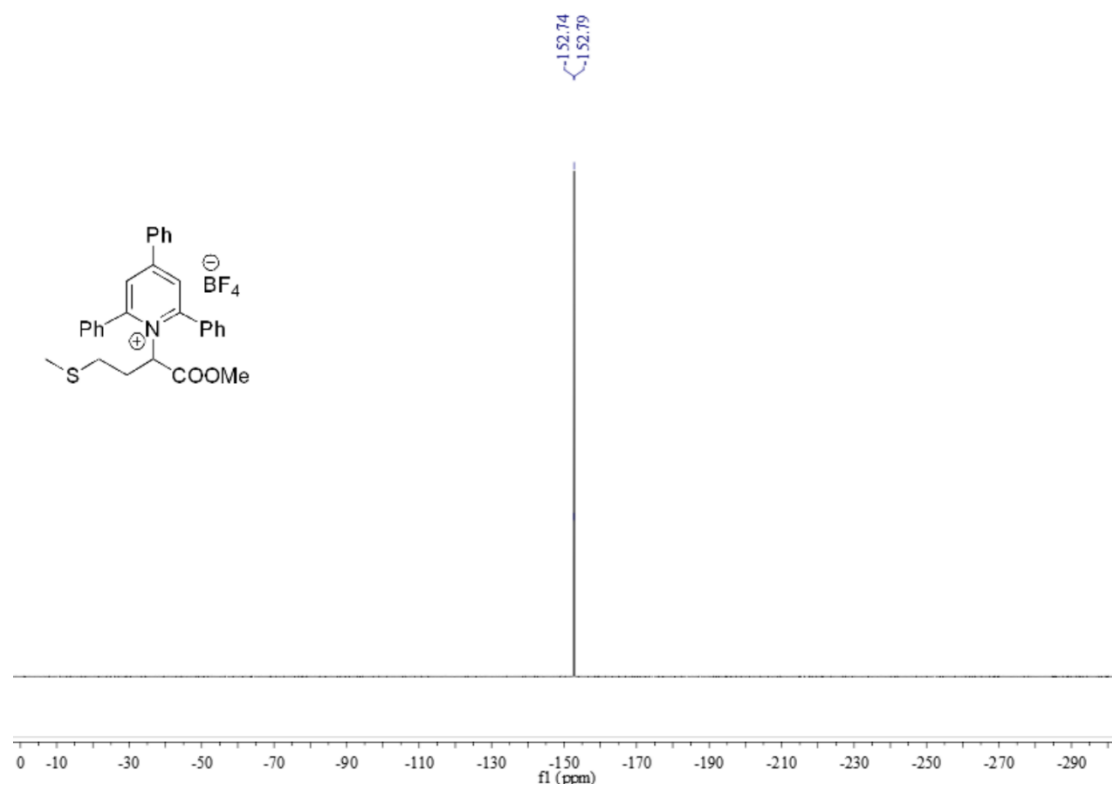
¹H NMR of **2i**



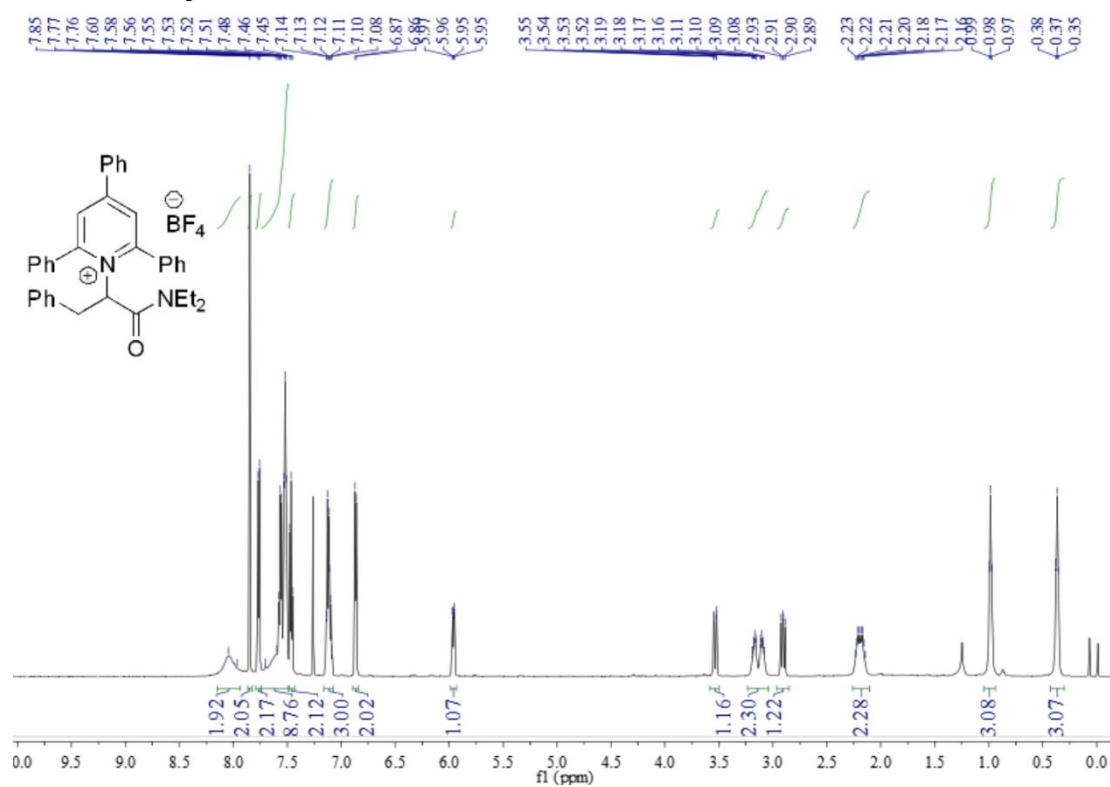
¹³C NMR of **2i**



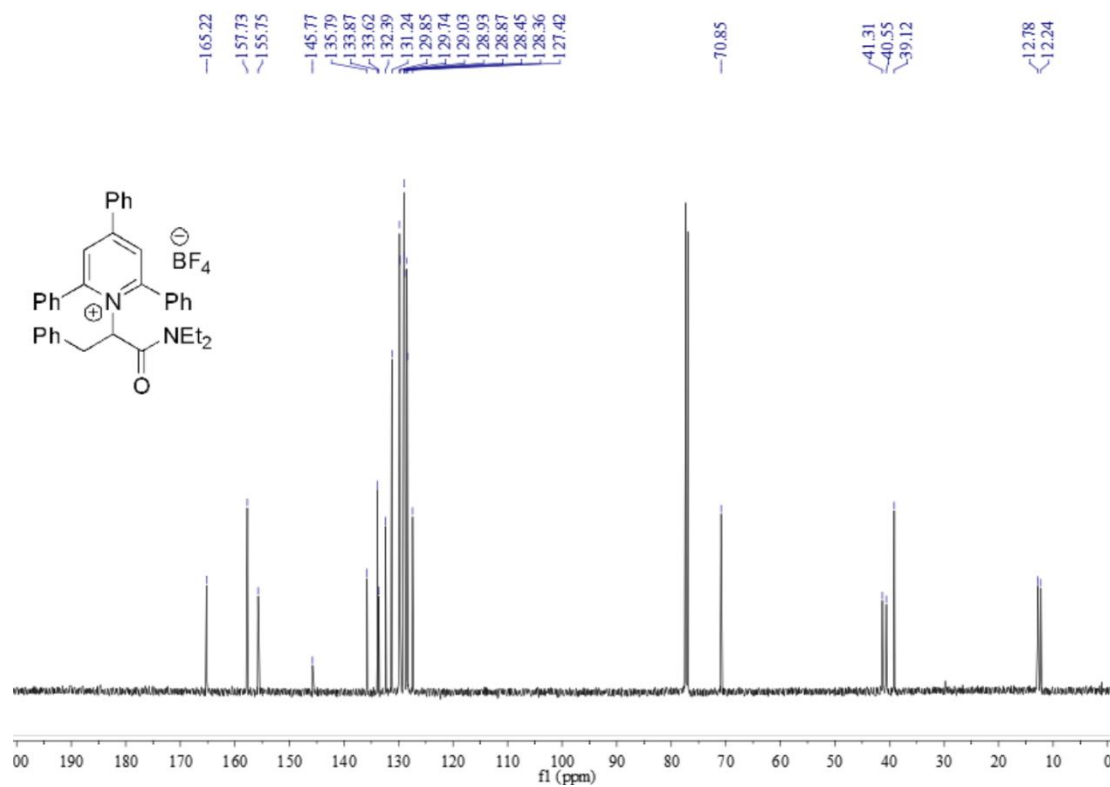
¹⁹F NMR of **2i**



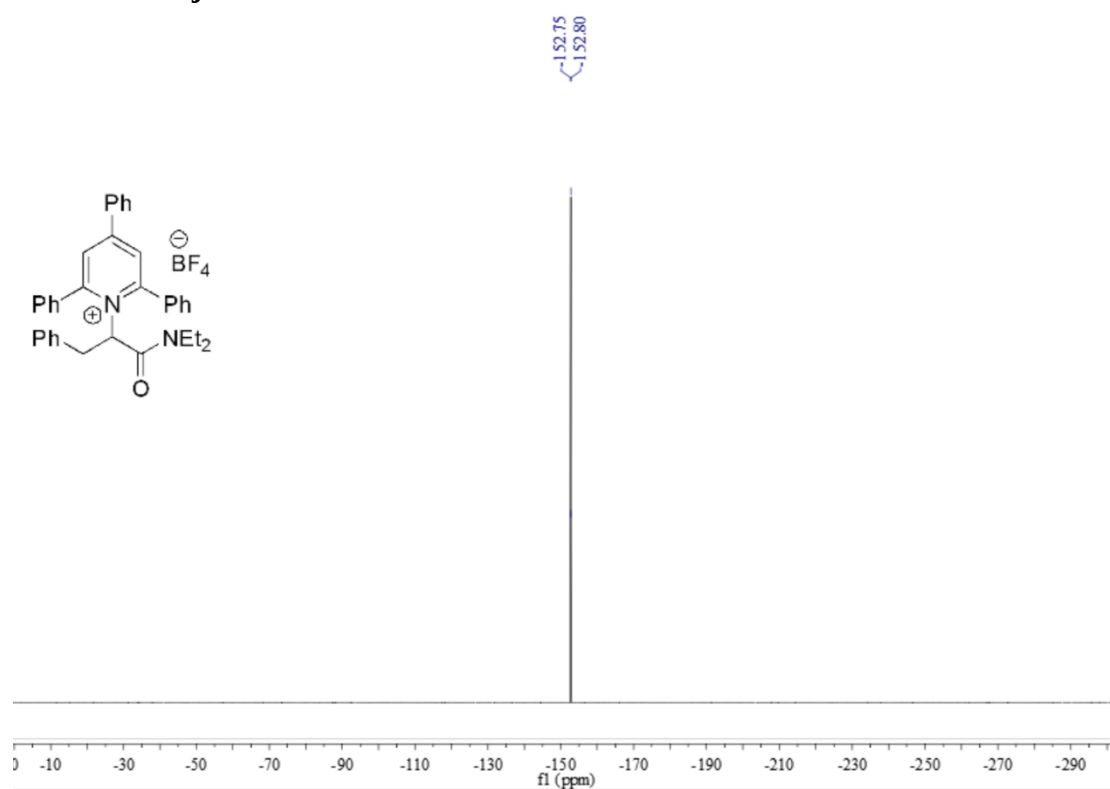
¹H NMR of **2j**



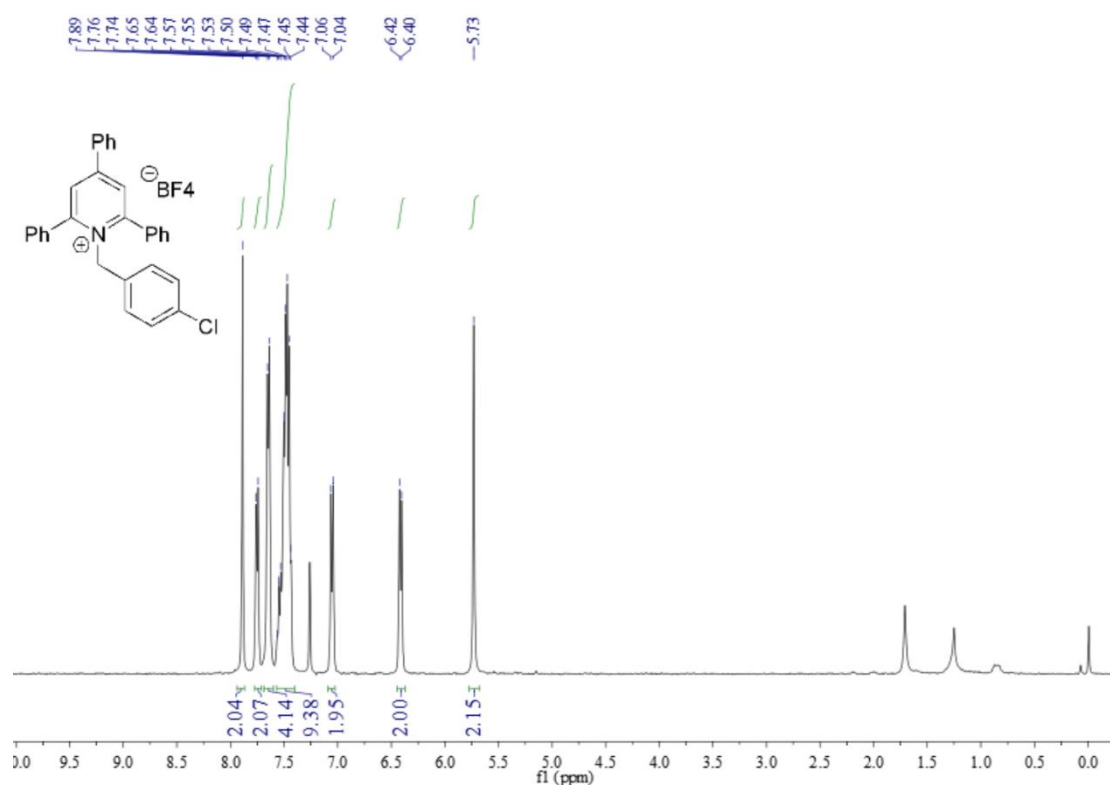
¹³C NMR of **2j**



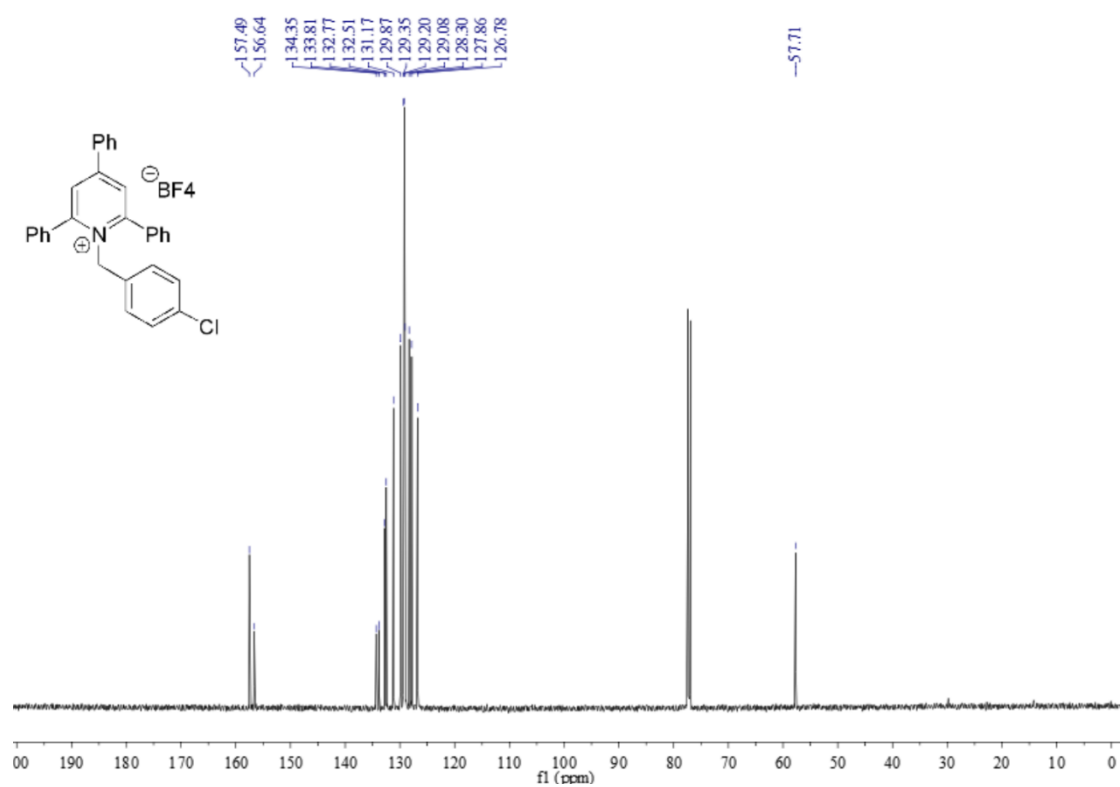
¹⁹F NMR of **2j**



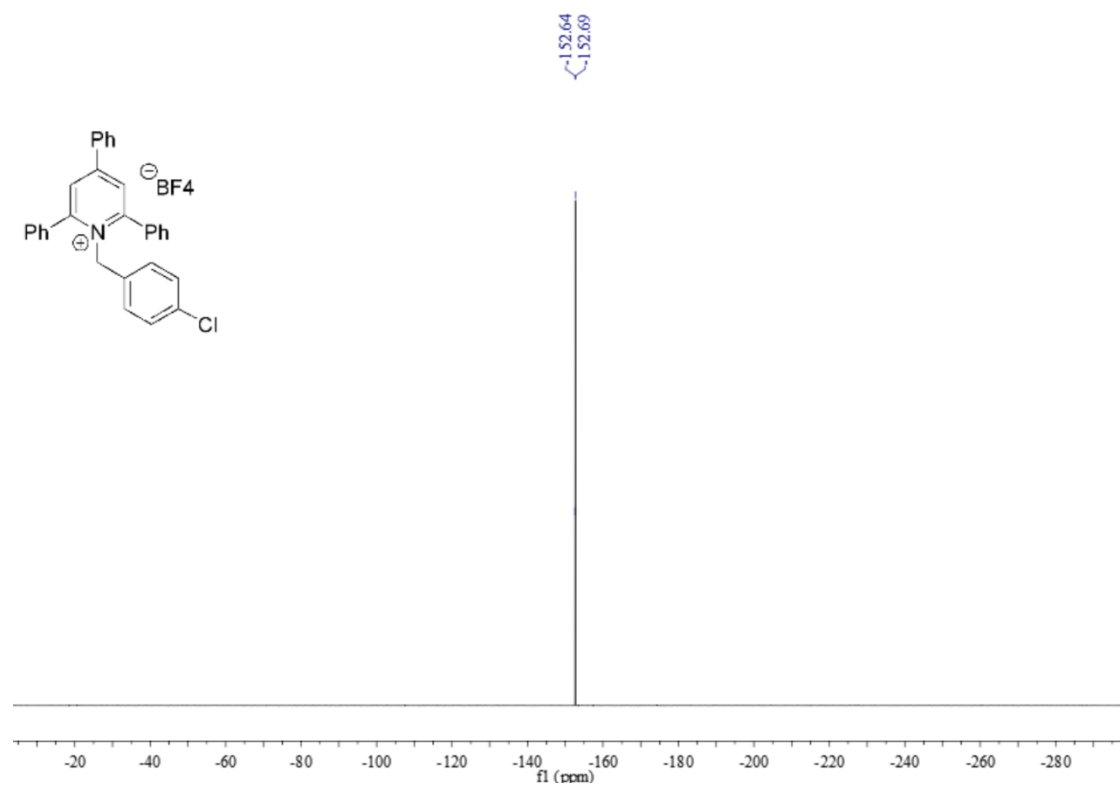
¹H NMR of **2k**



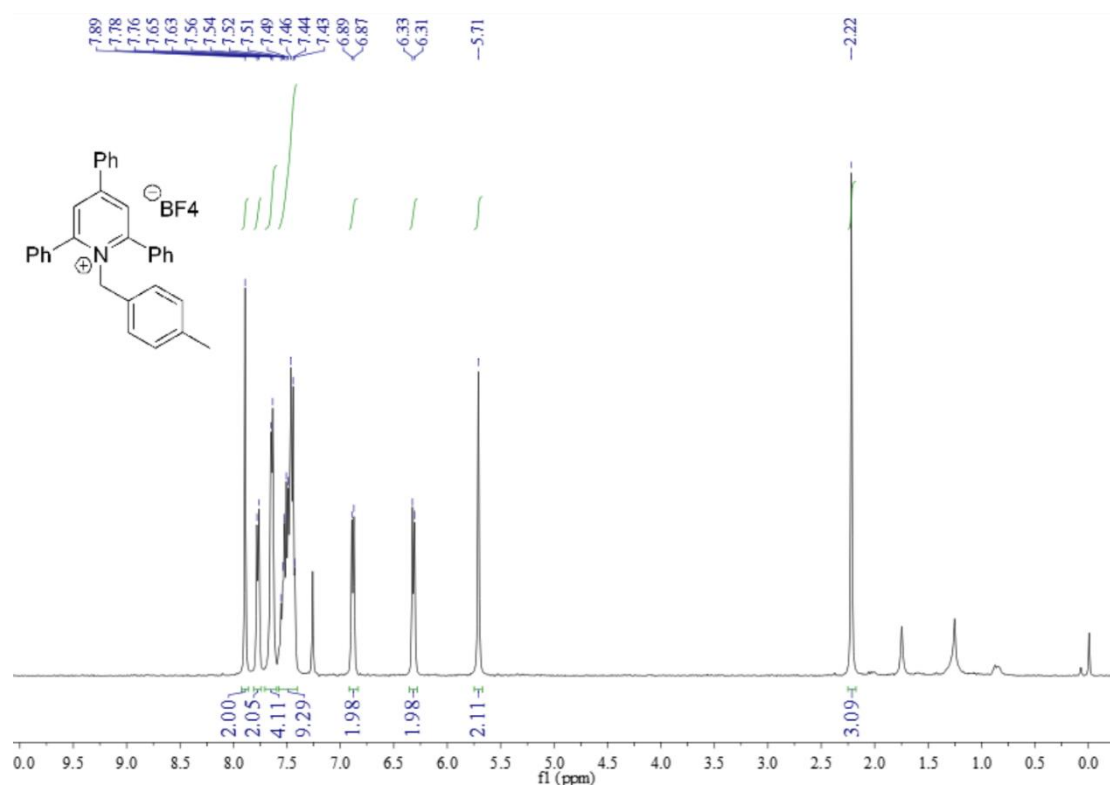
¹³C NMR of **2k**



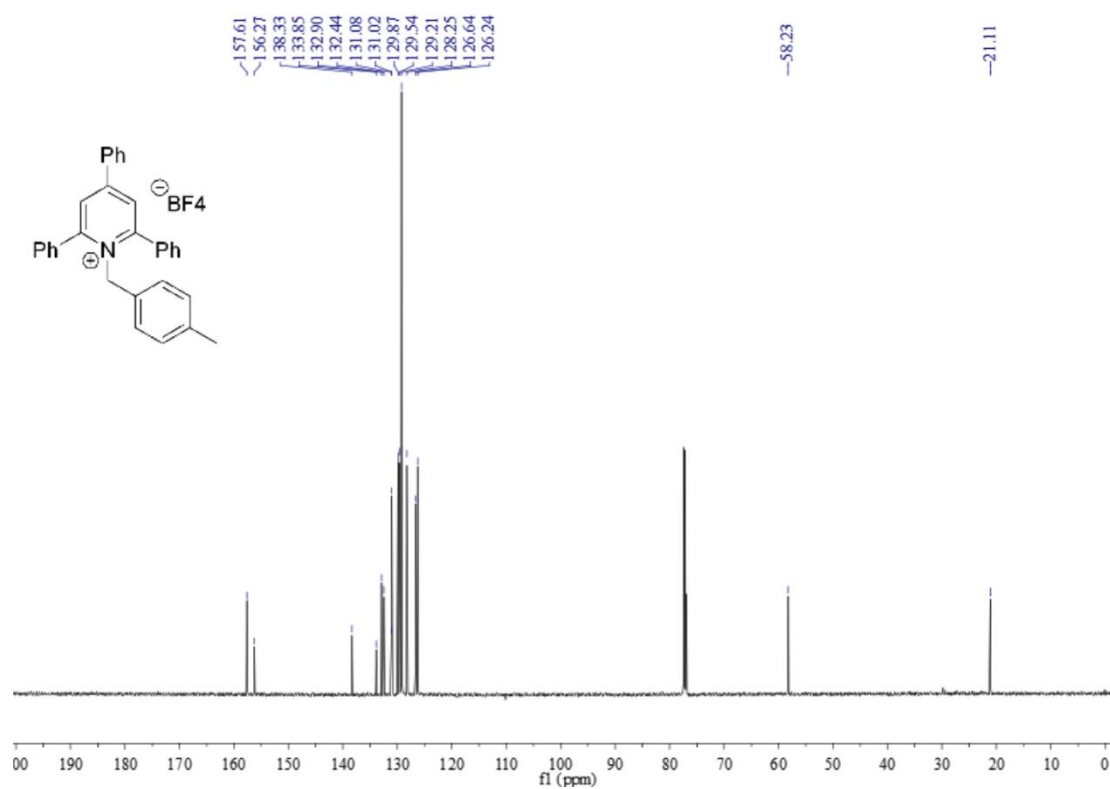
¹⁹F NMR of **2k**



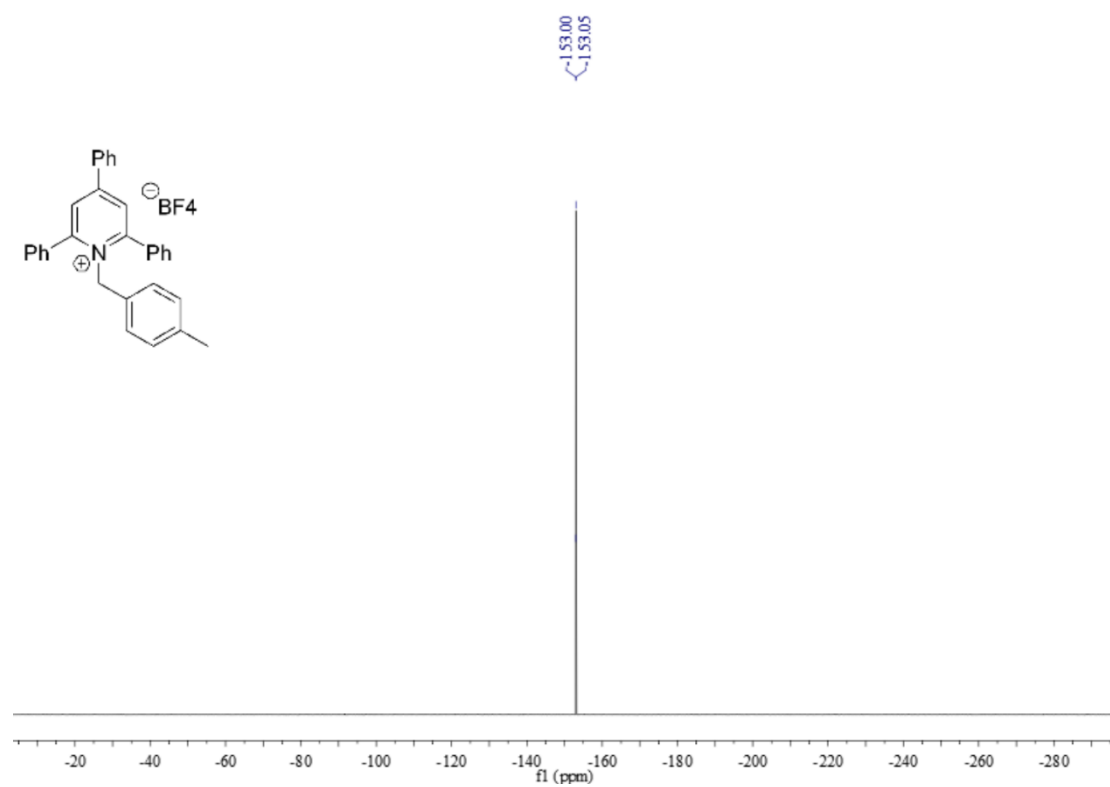
¹H NMR of **2l**



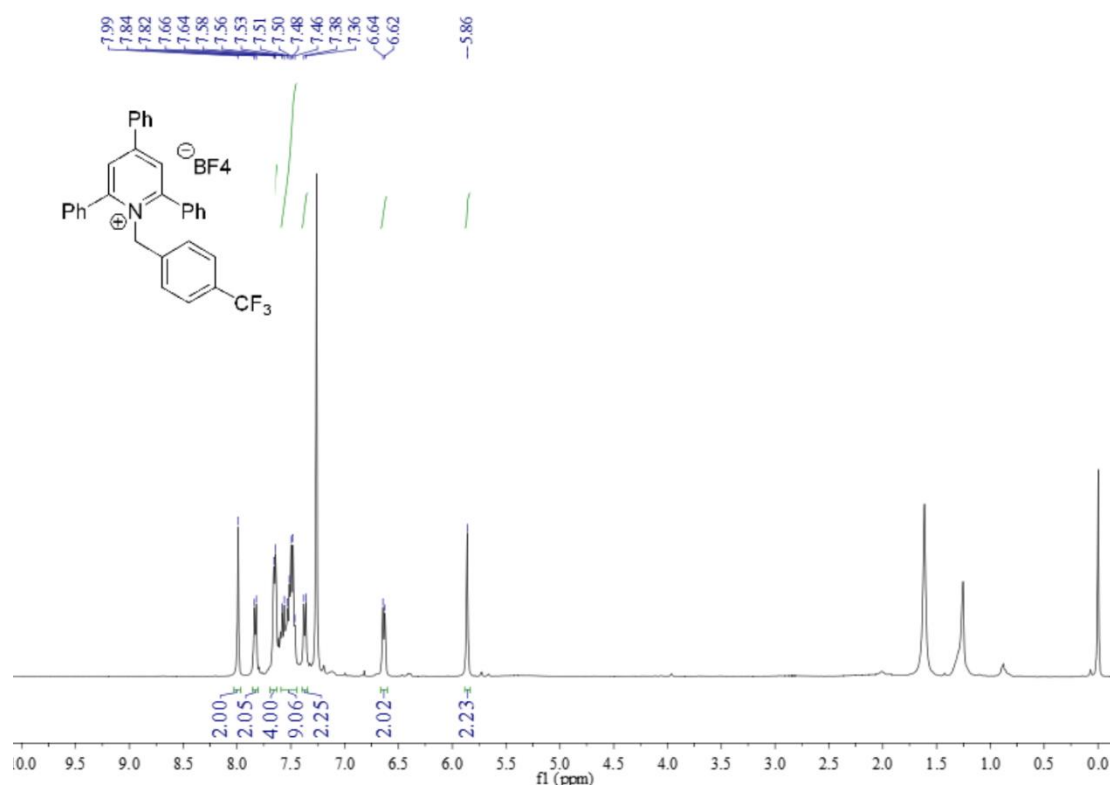
¹³C NMR of **2l**



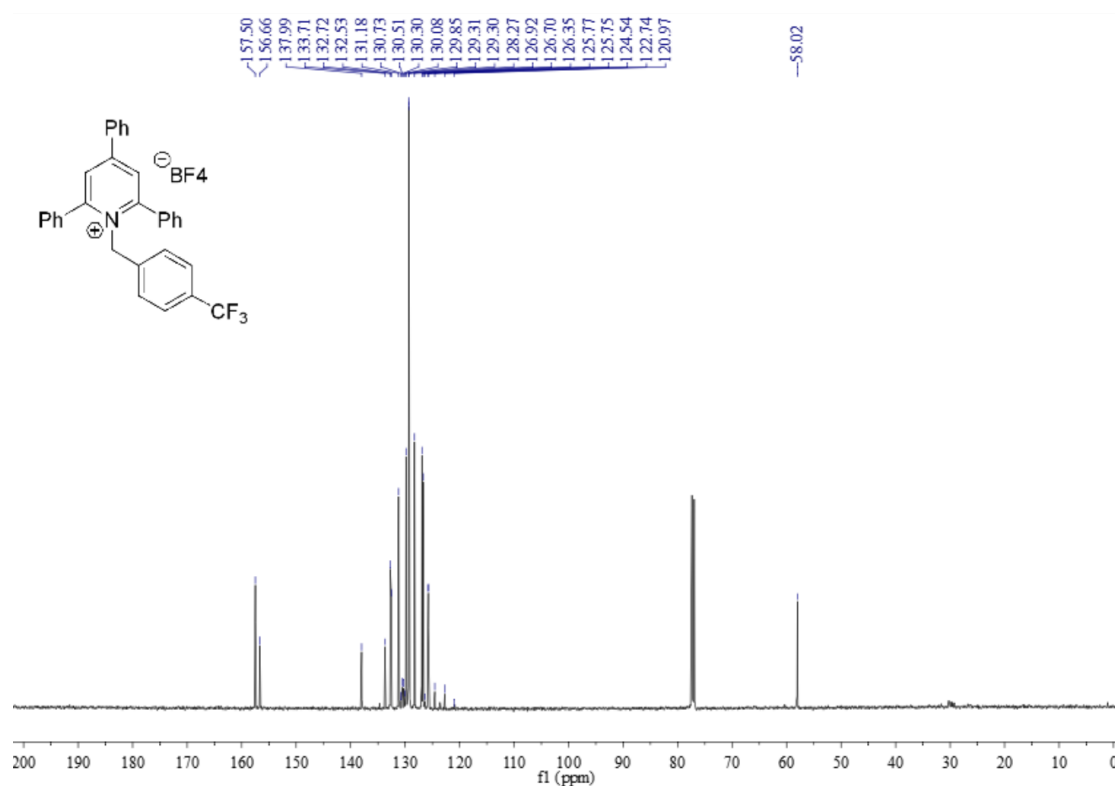
¹⁹F NMR of **2l**



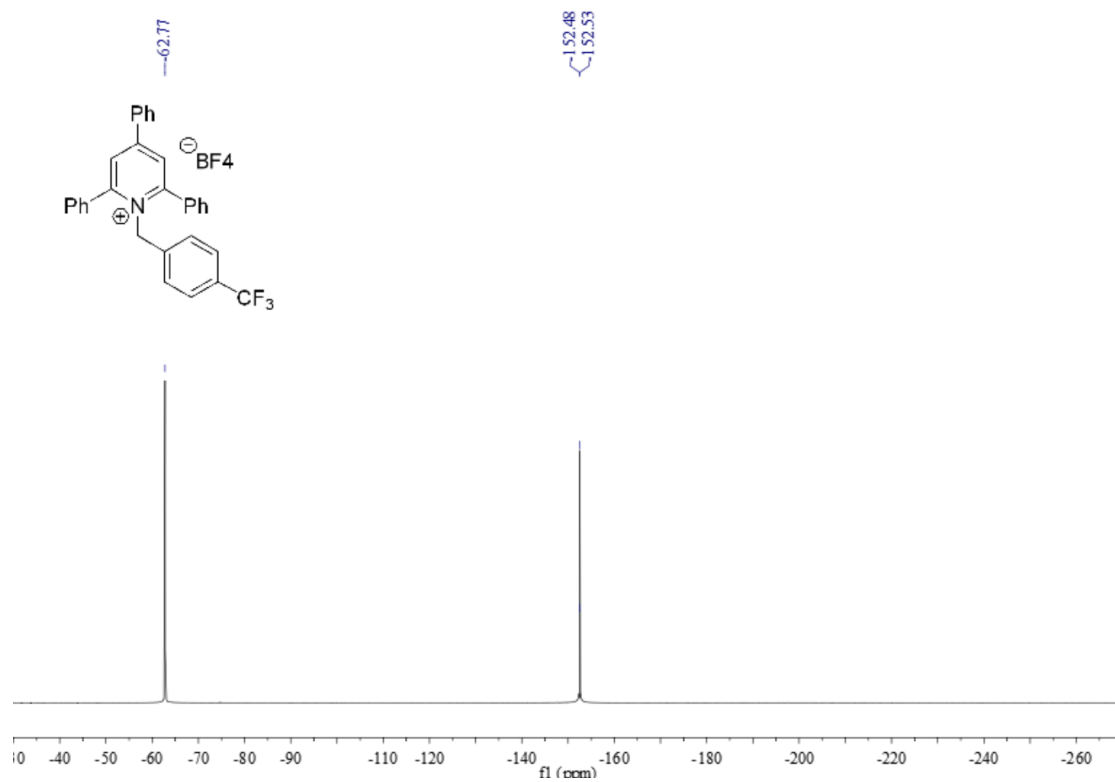
¹H NMR of **2m**



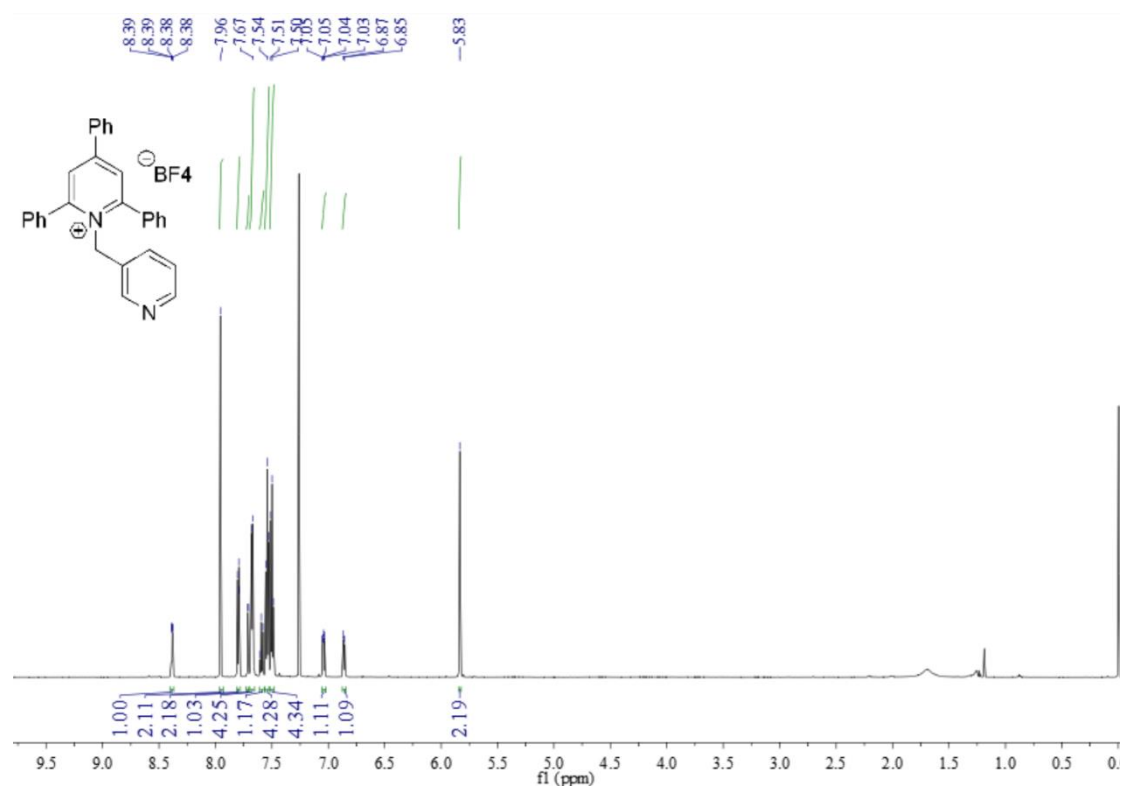
¹³C NMR of **2m**



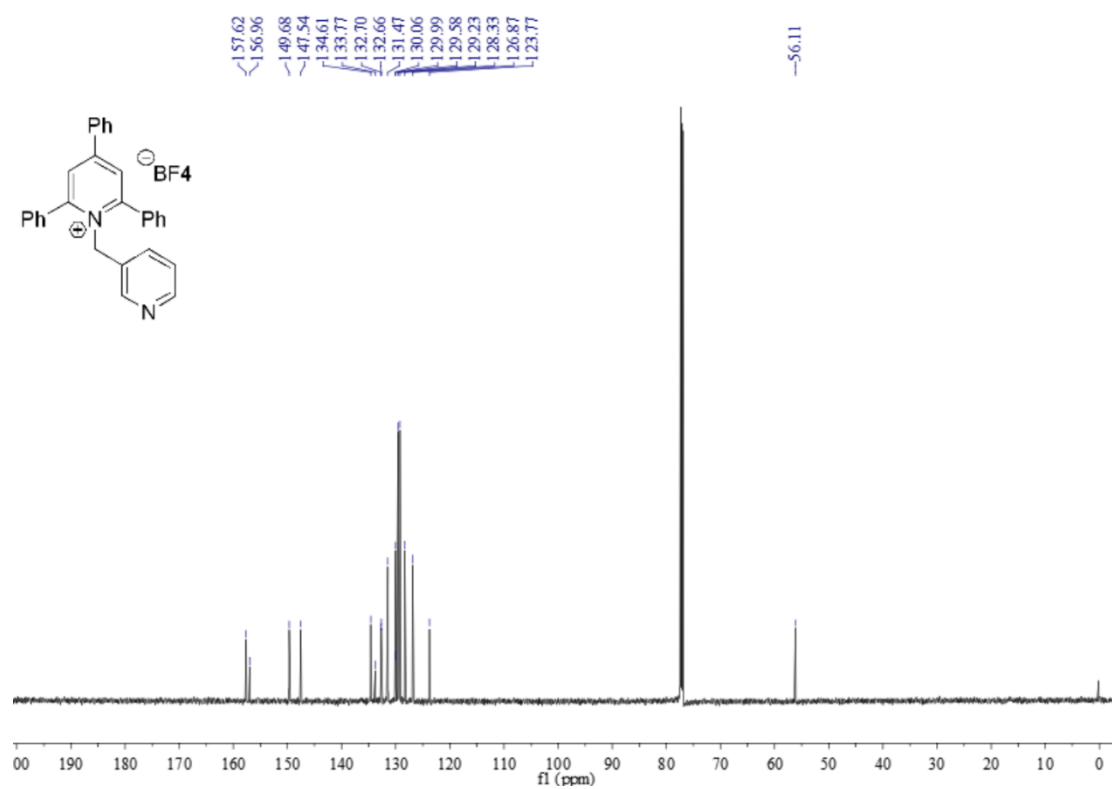
¹⁹F NMR of **2m**



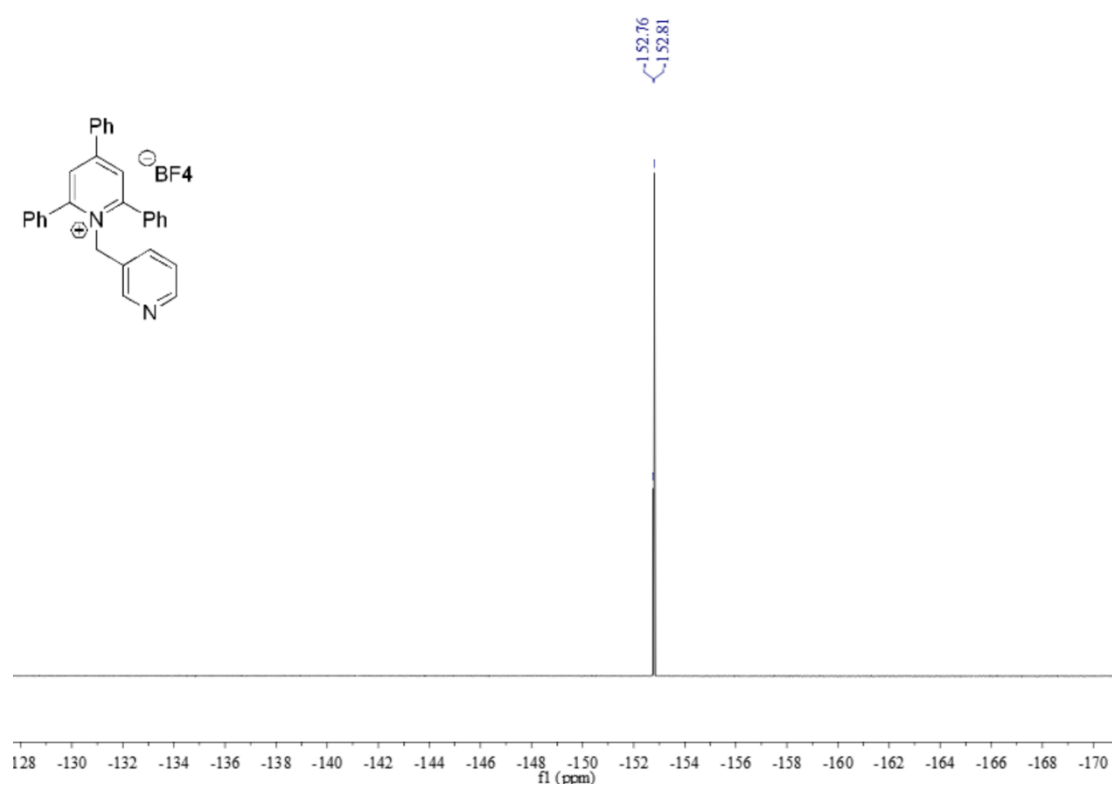
¹H NMR of **2n**



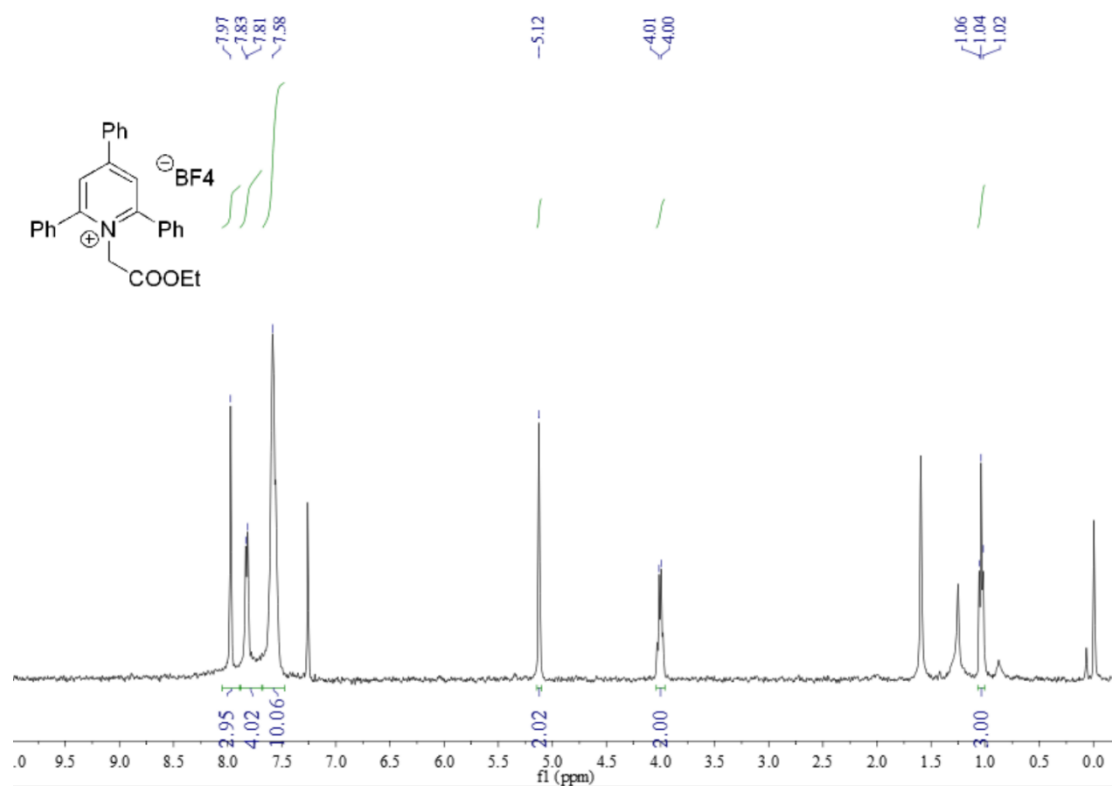
¹³C NMR of **2n**



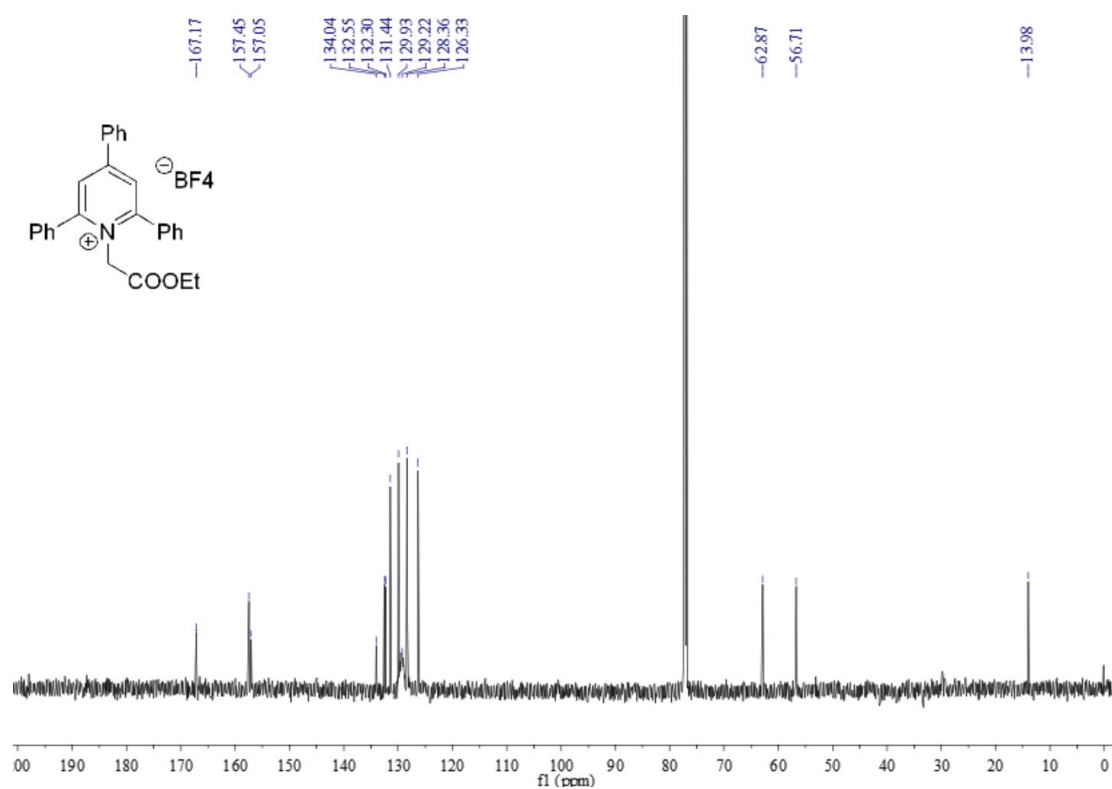
¹⁹F NMR of **2n**



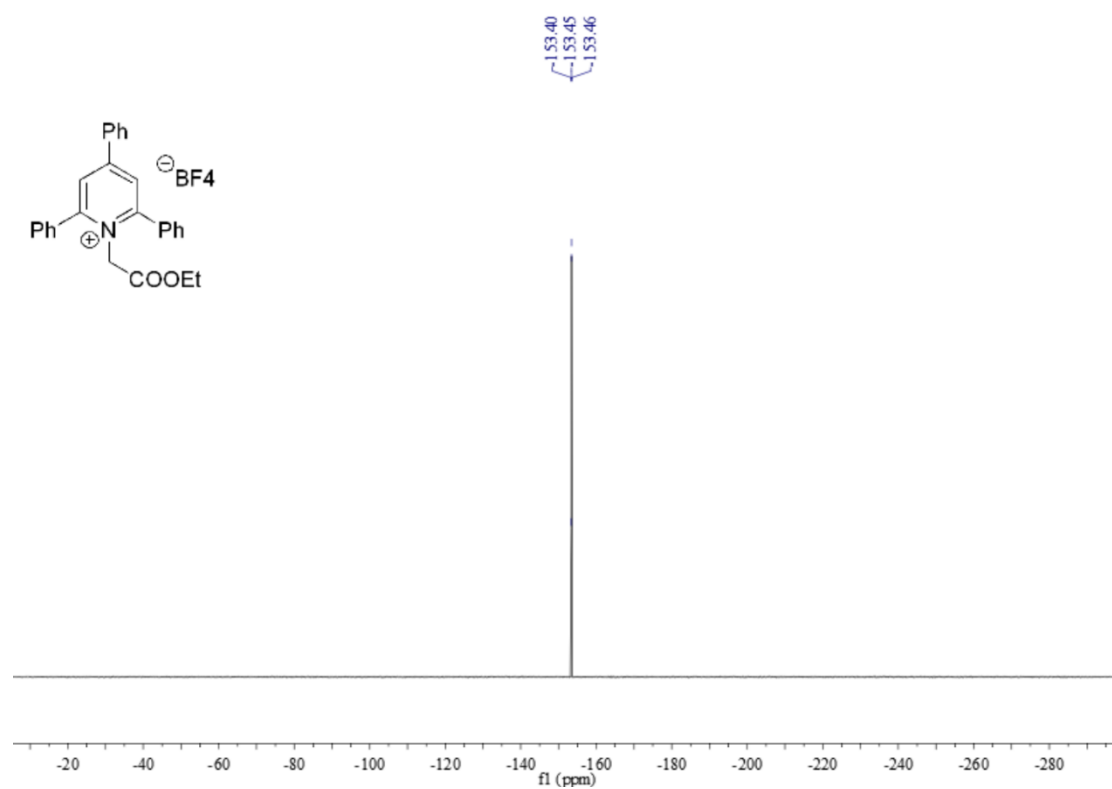
¹H NMR of **2o**



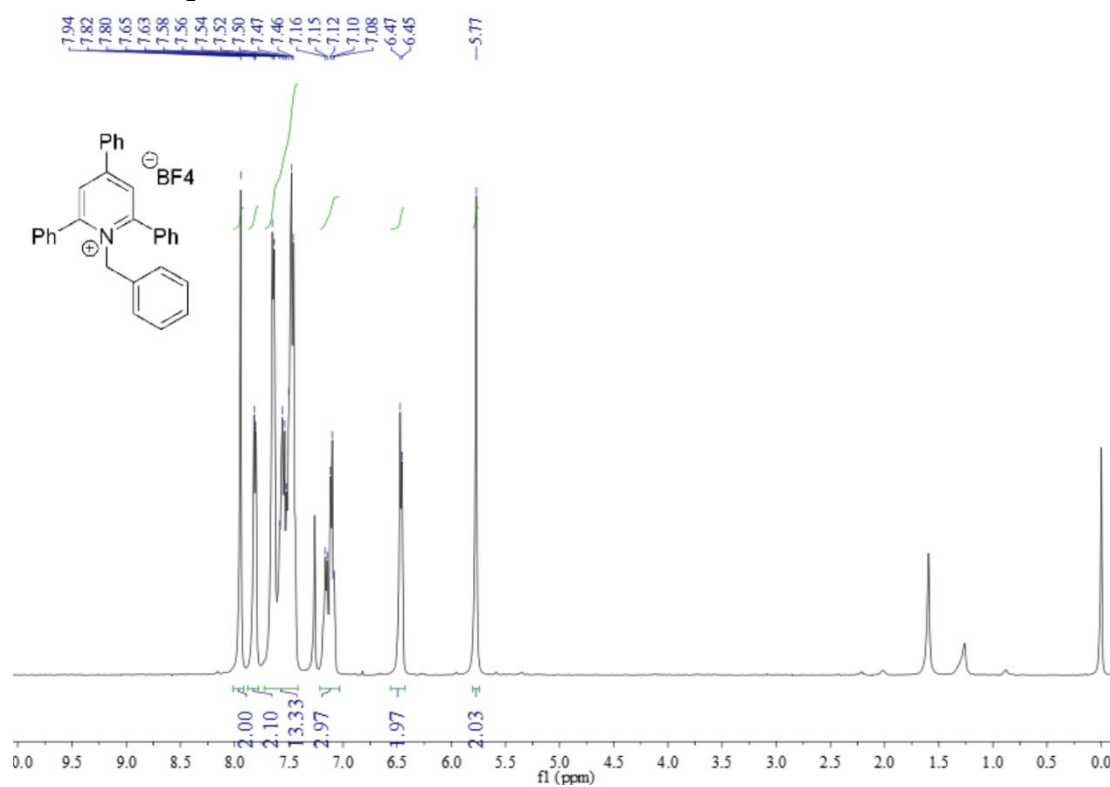
¹³C NMR of **2o**



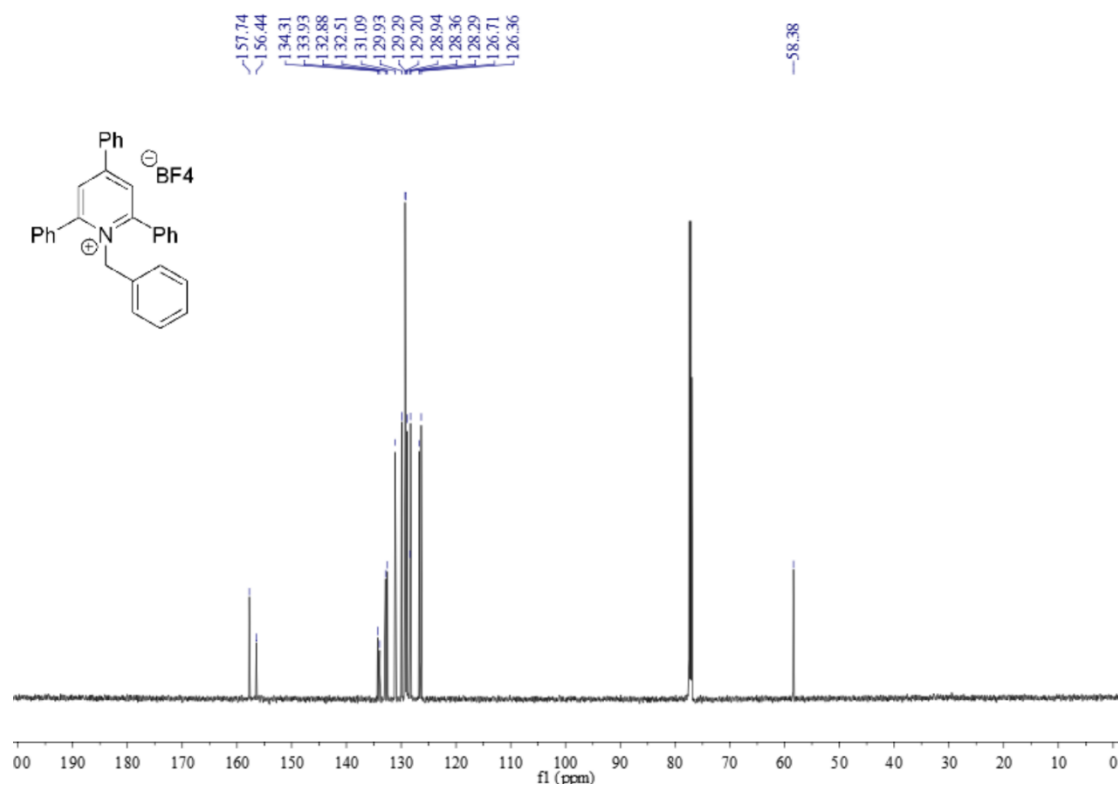
¹⁹F NMR of **2o**



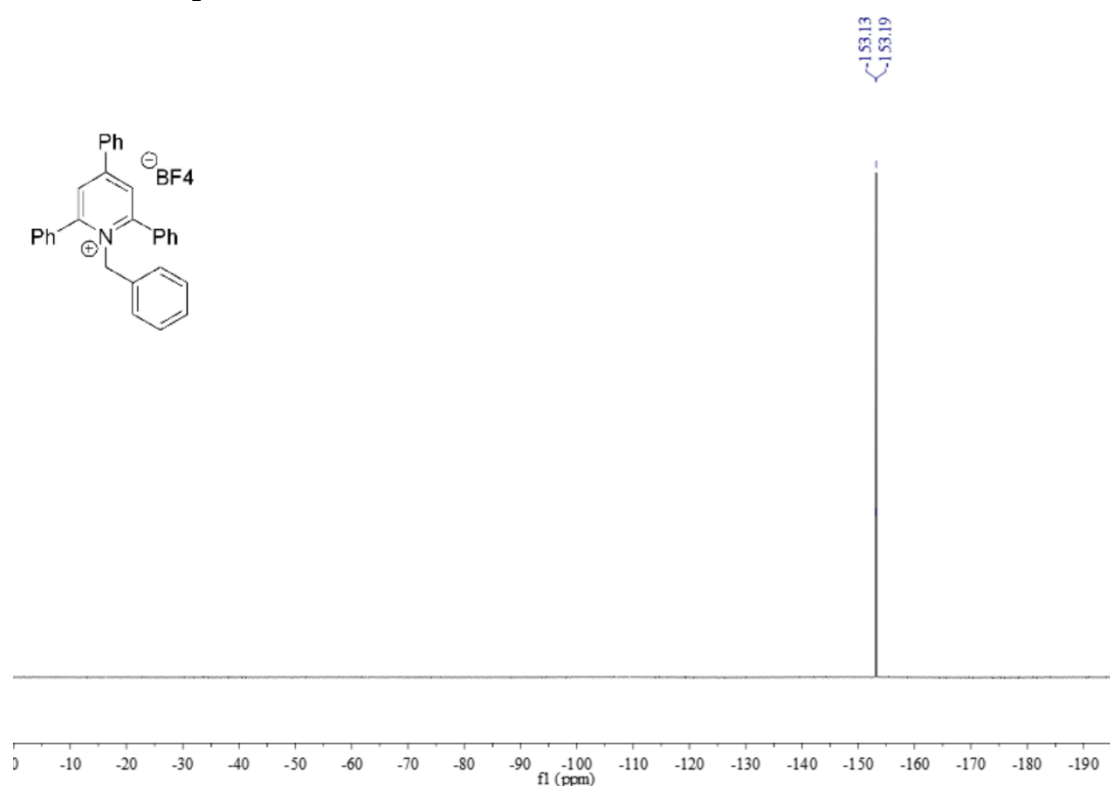
¹H NMR of **2p**



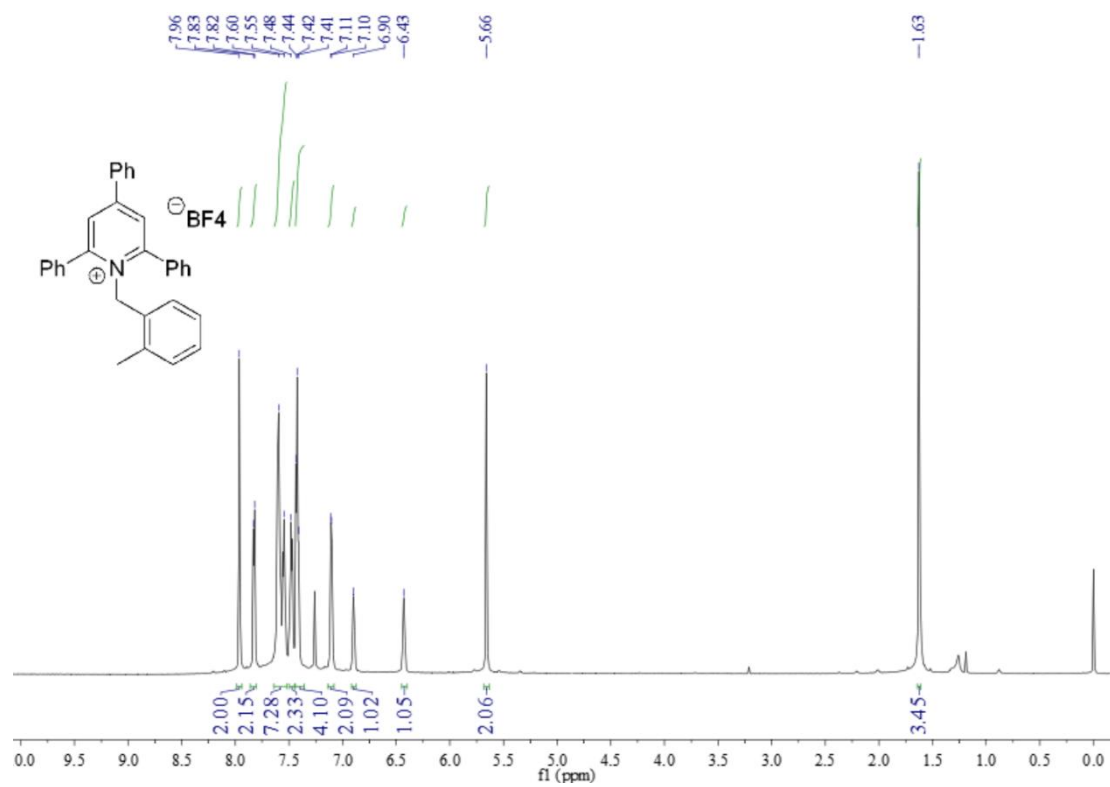
¹³C NMR of **2p**



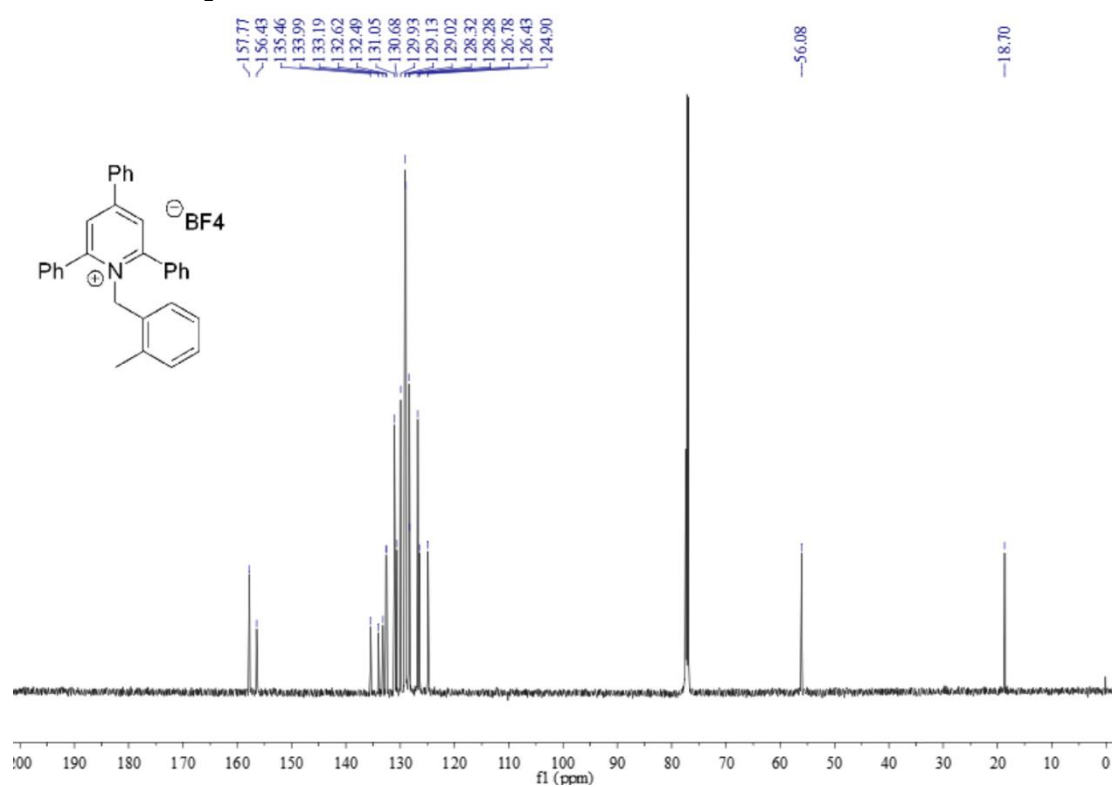
¹⁹F NMR of **2p**



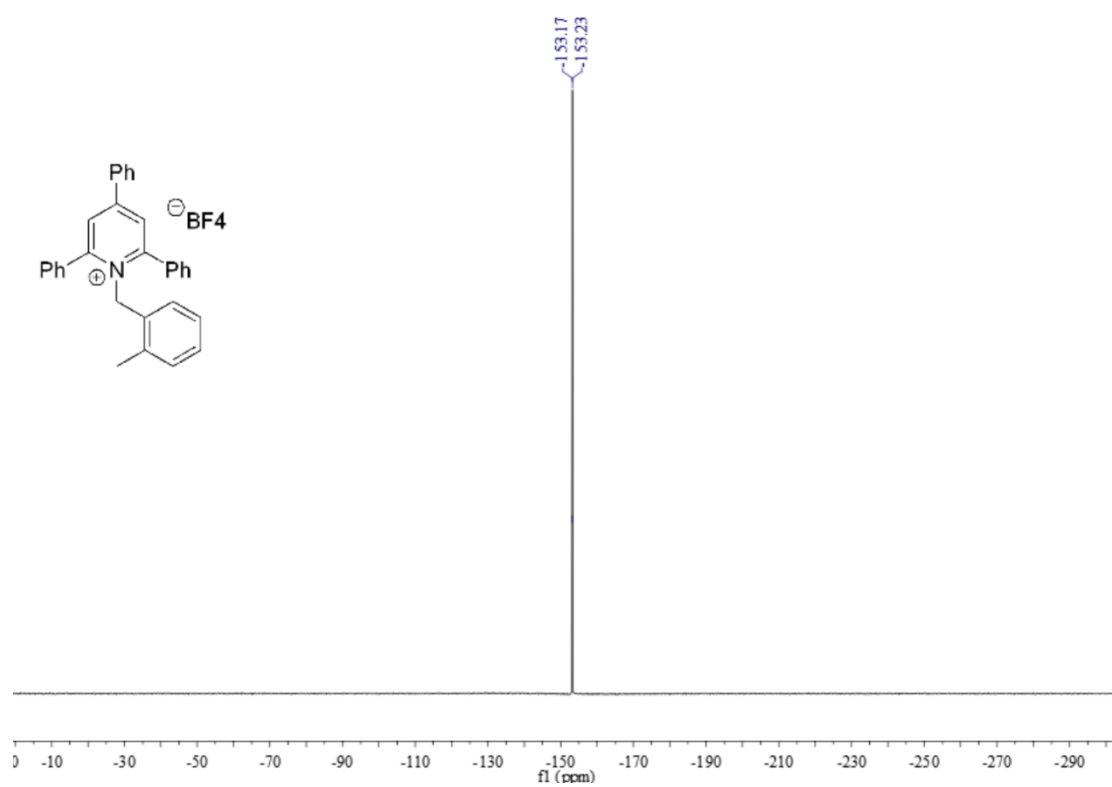
¹H NMR of **2q**



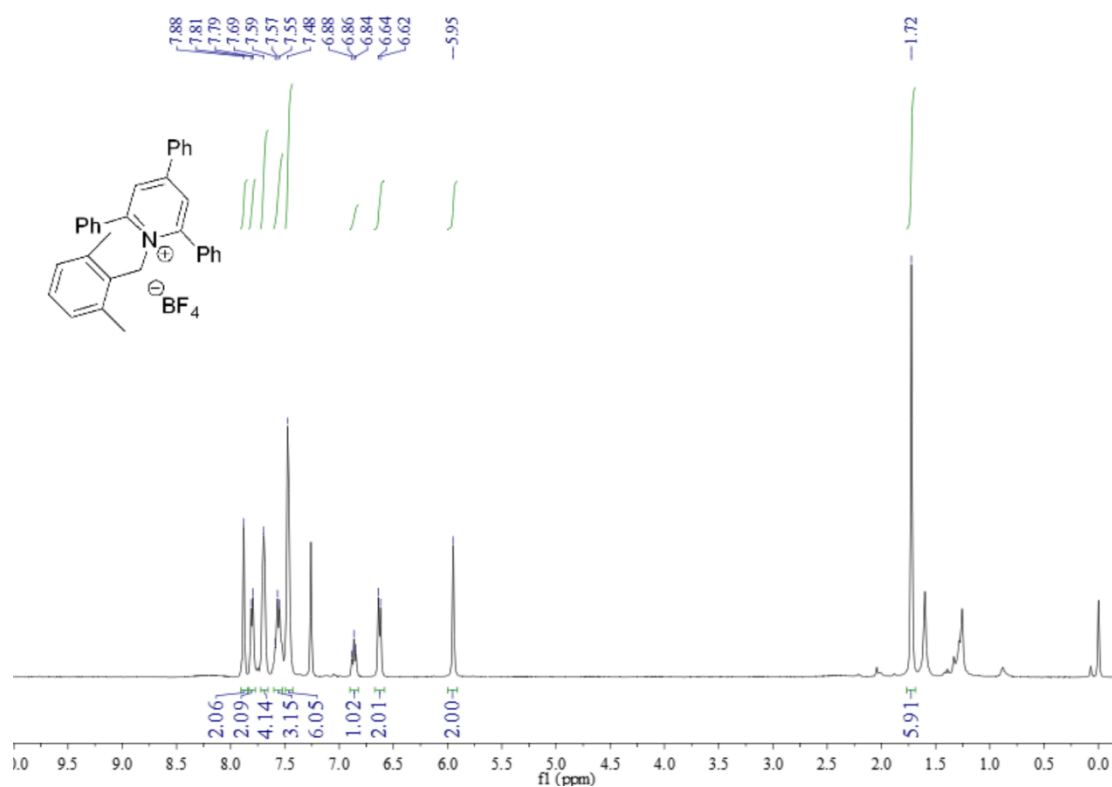
¹³C NMR of **2q**



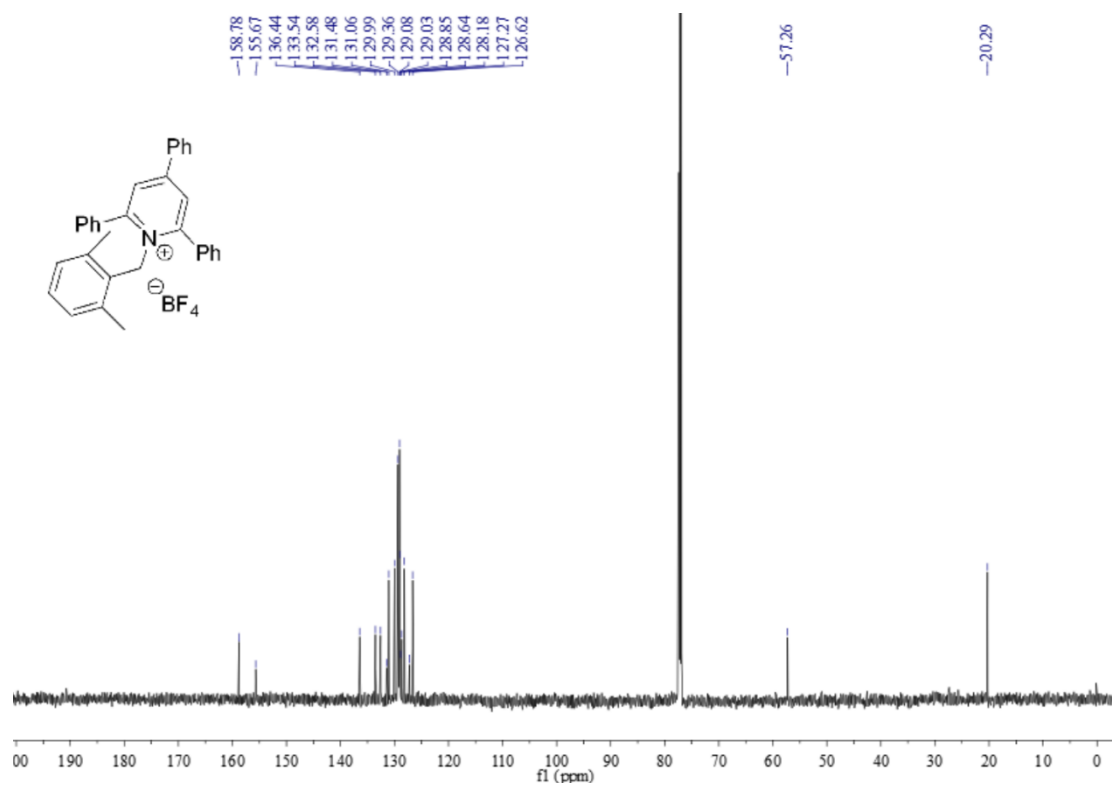
¹⁹F NMR of **2q**



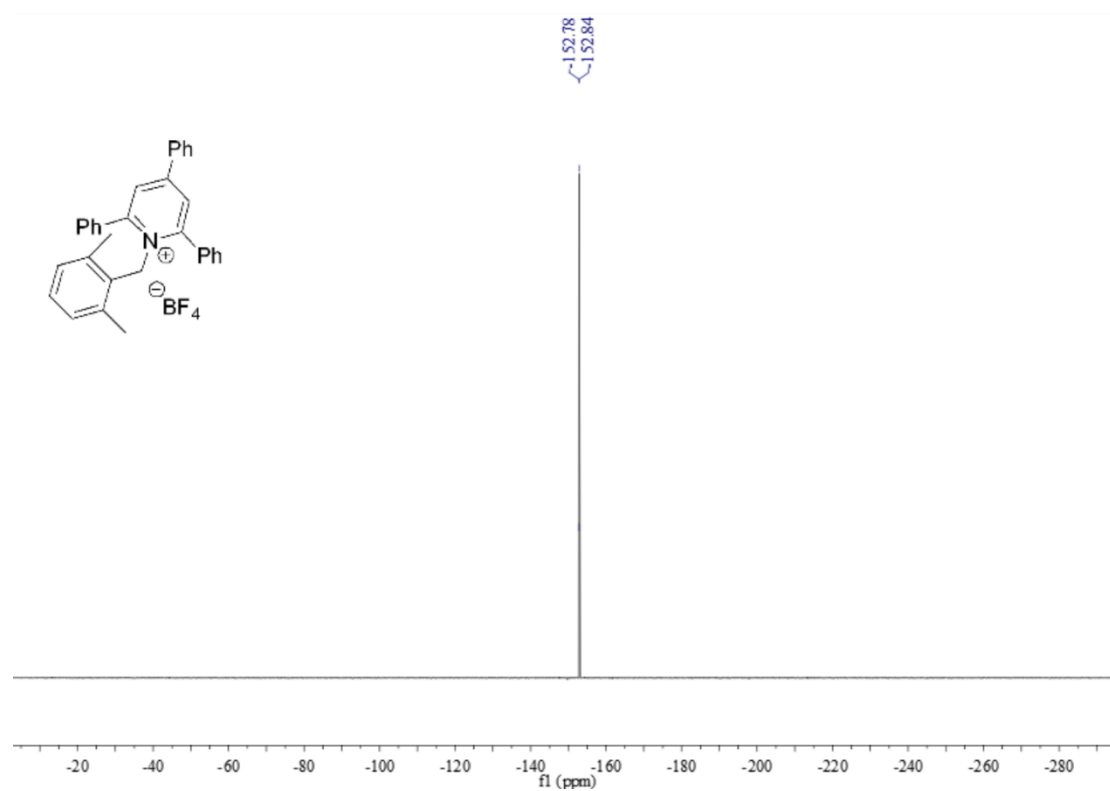
¹H NMR of **2r**



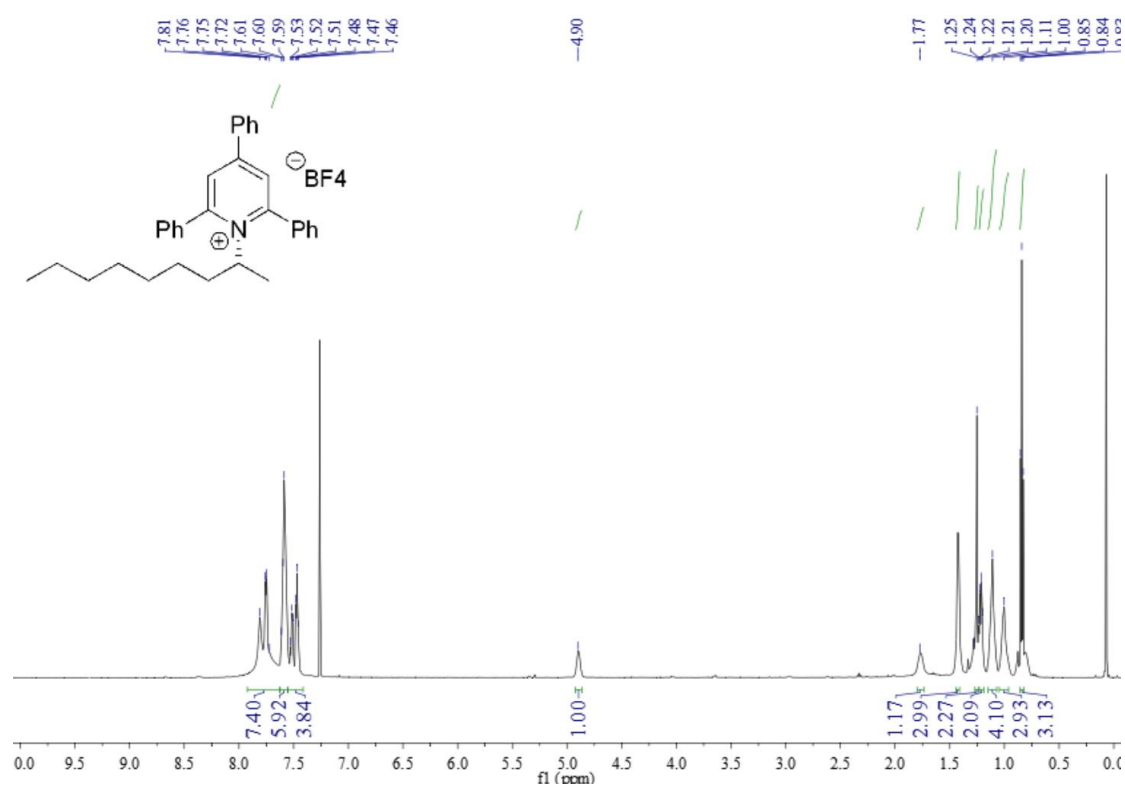
¹³C NMR of **2r**



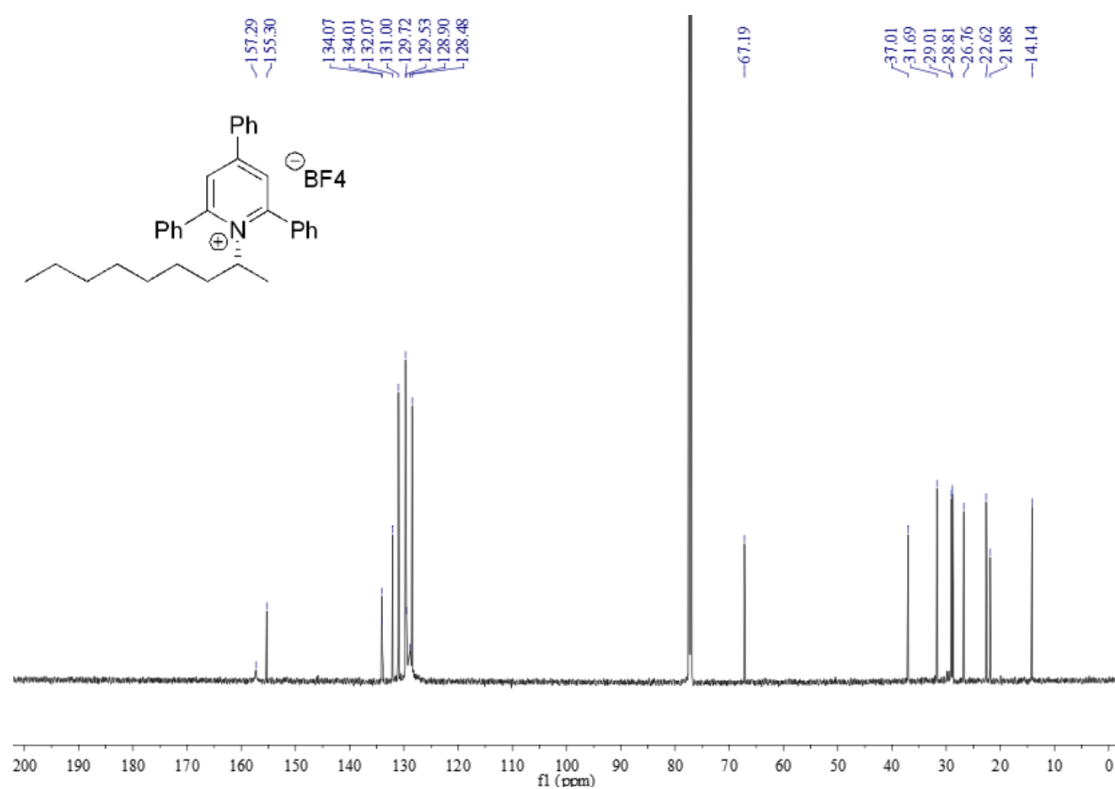
¹⁹F NMR of **2r**



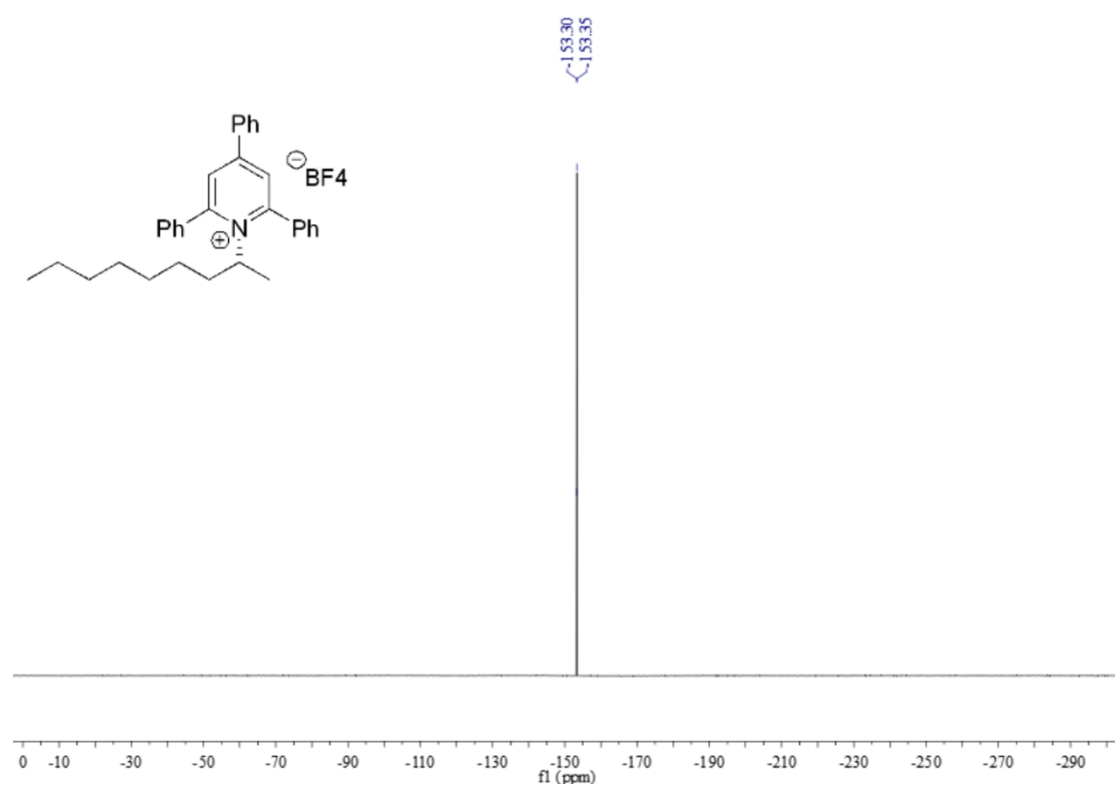
¹H NMR of **2s**



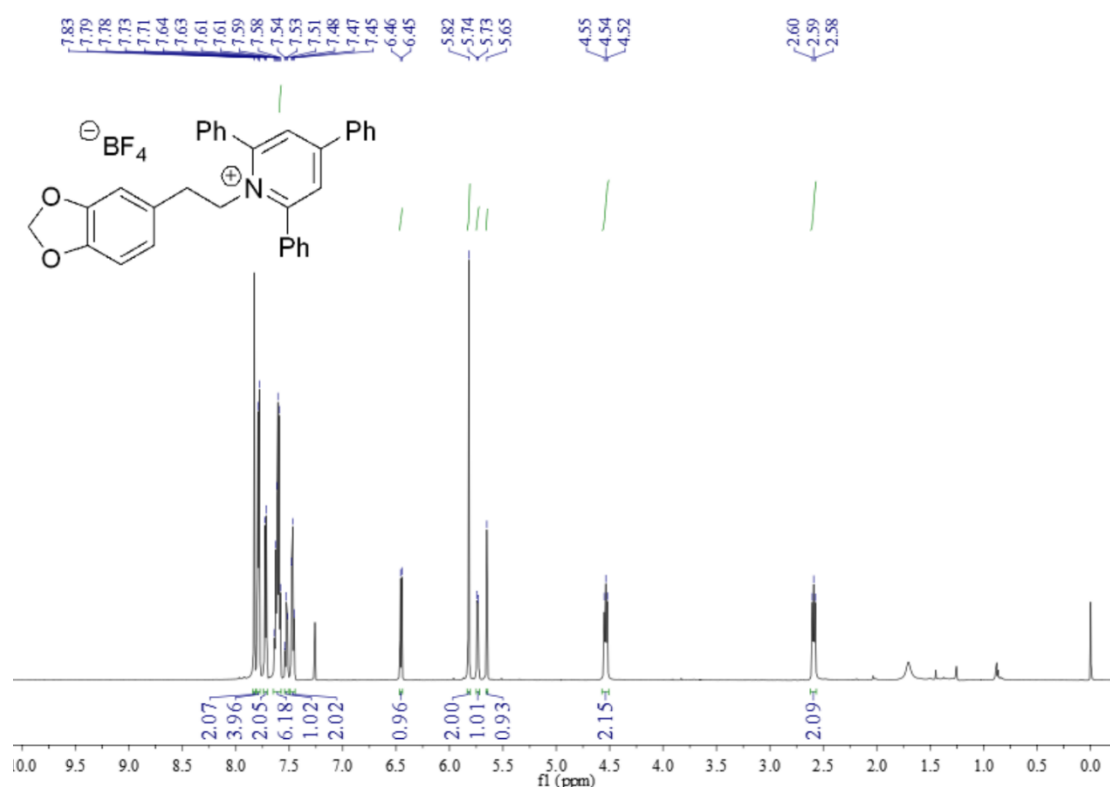
¹³C NMR of **2s**



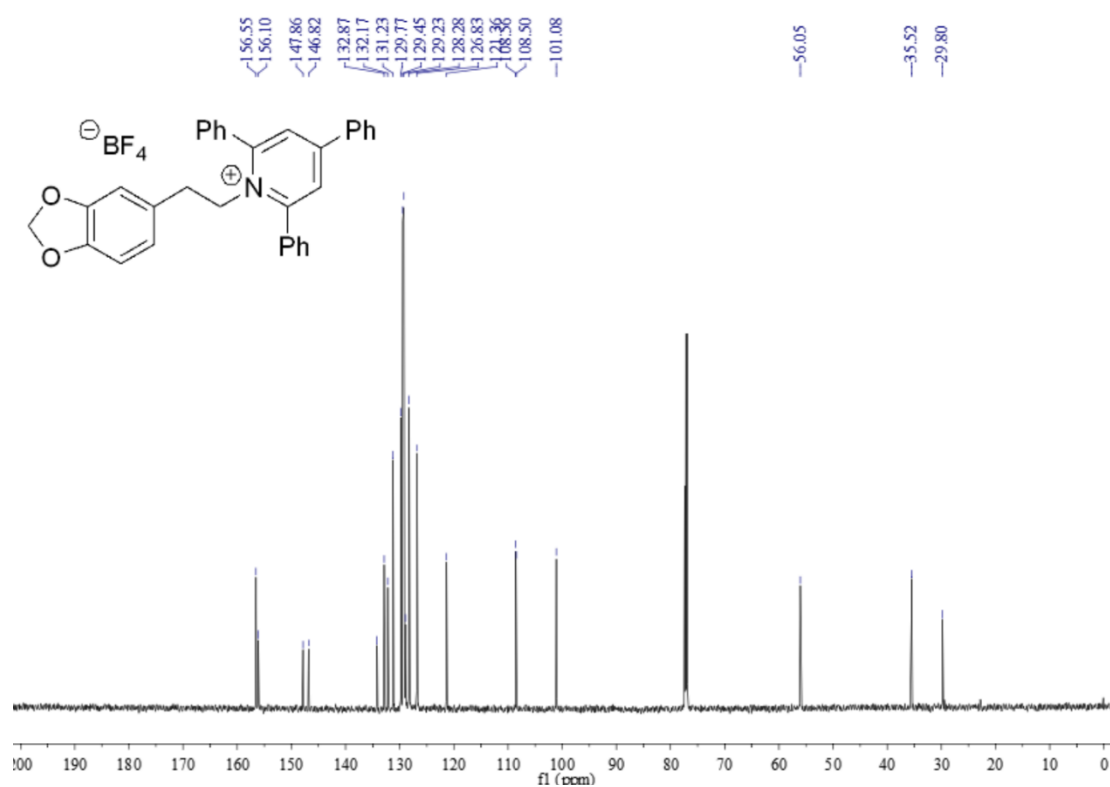
¹⁹F NMR of **2s**



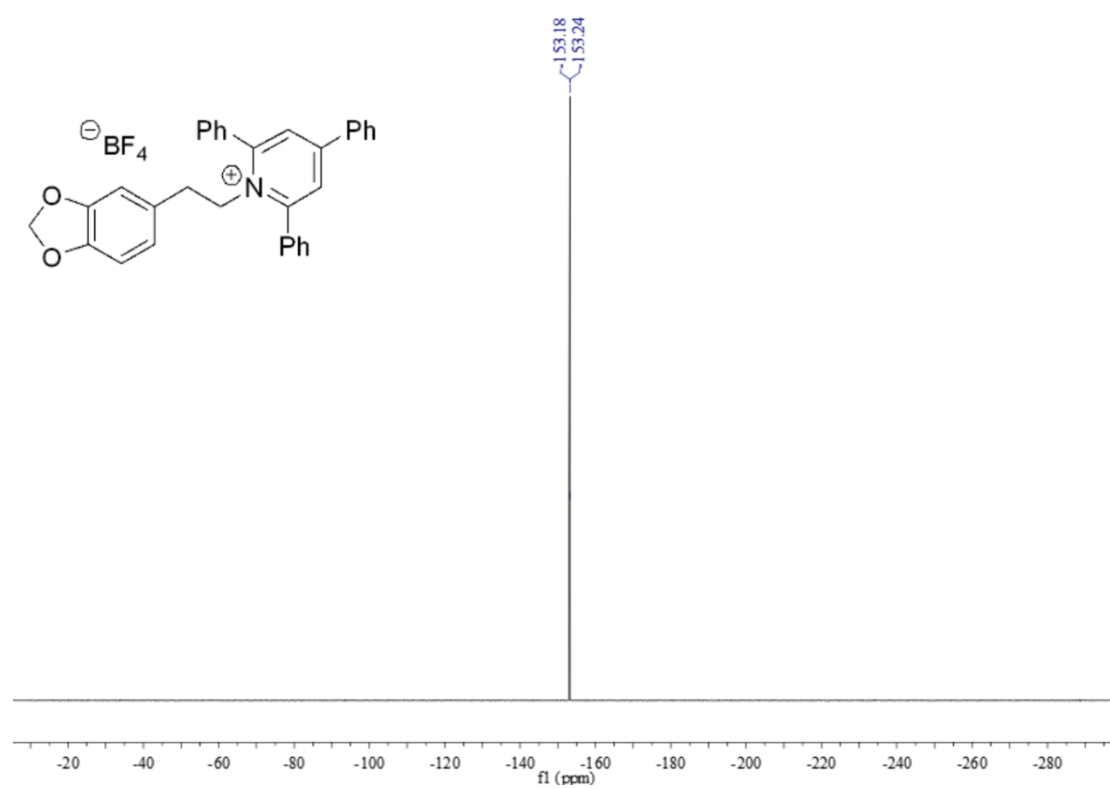
¹H NMR of **2t**



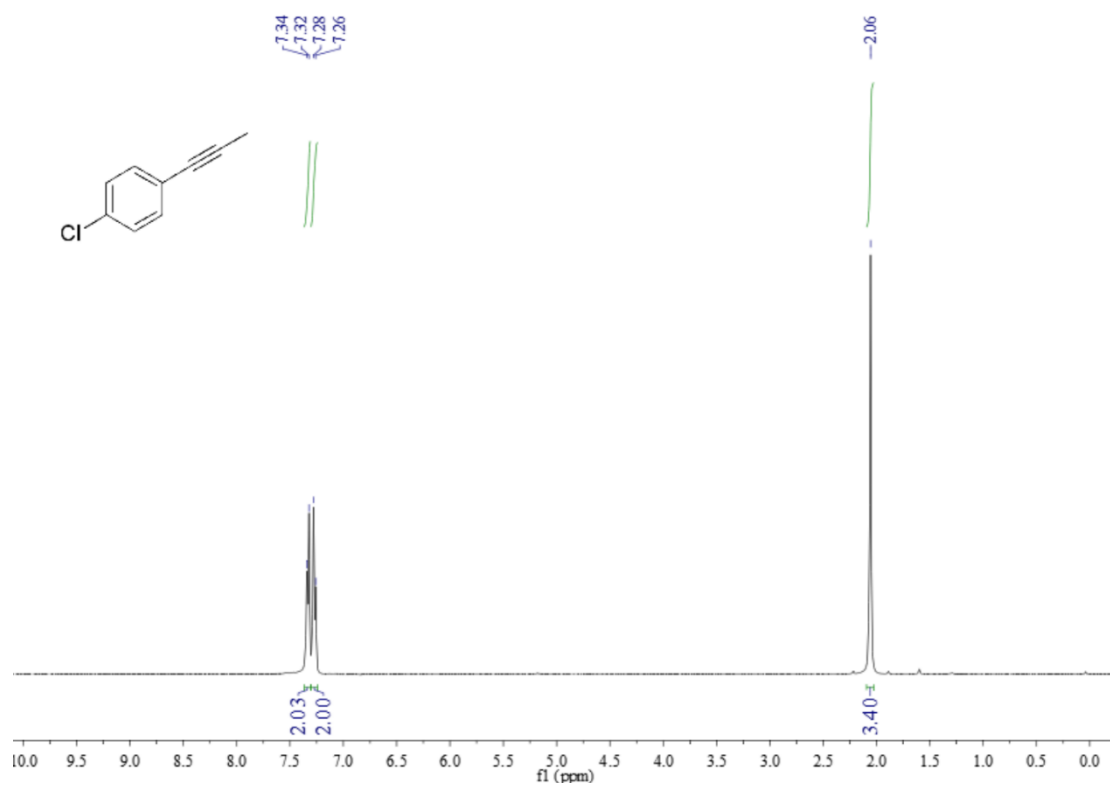
¹³C NMR of **2t**



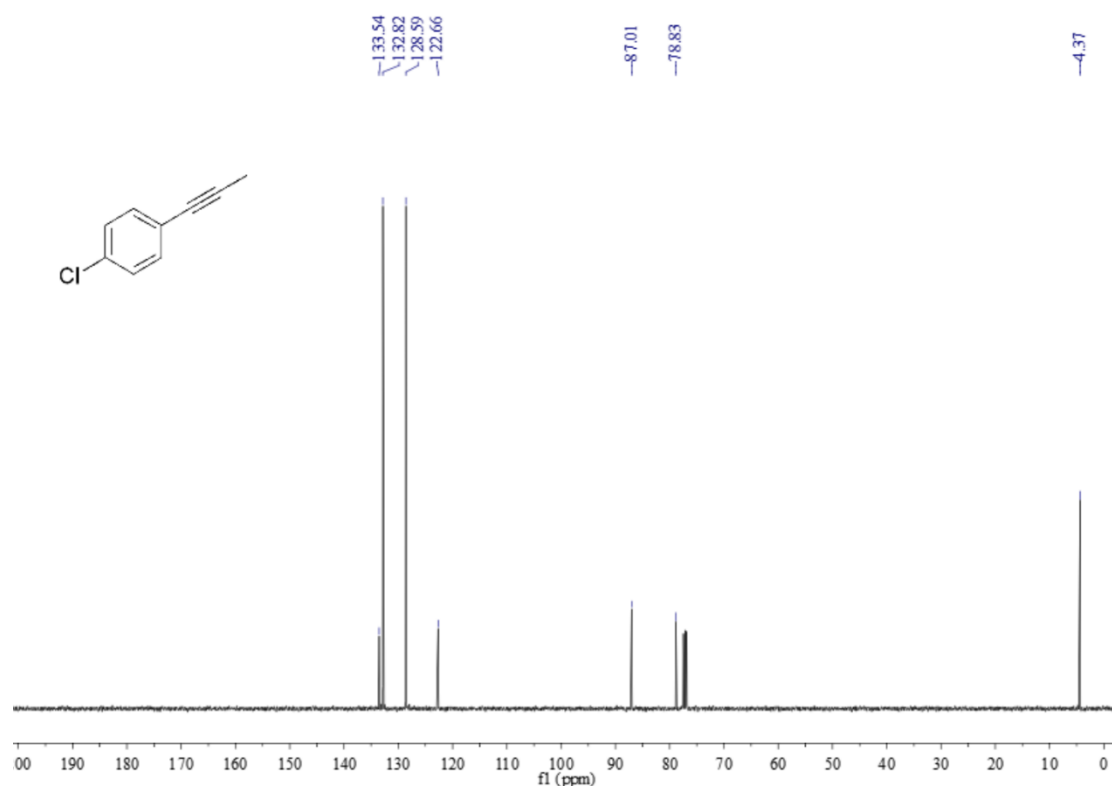
¹⁹F NMR of **2t**



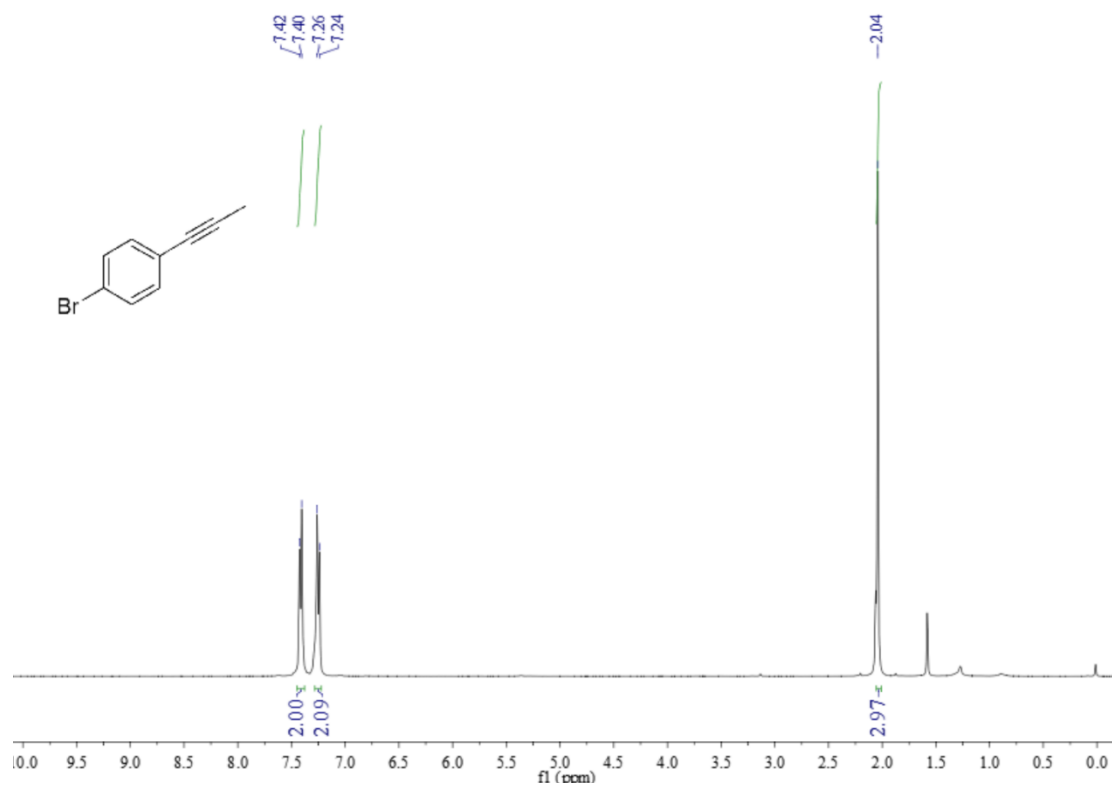
¹H NMR of **1ac**



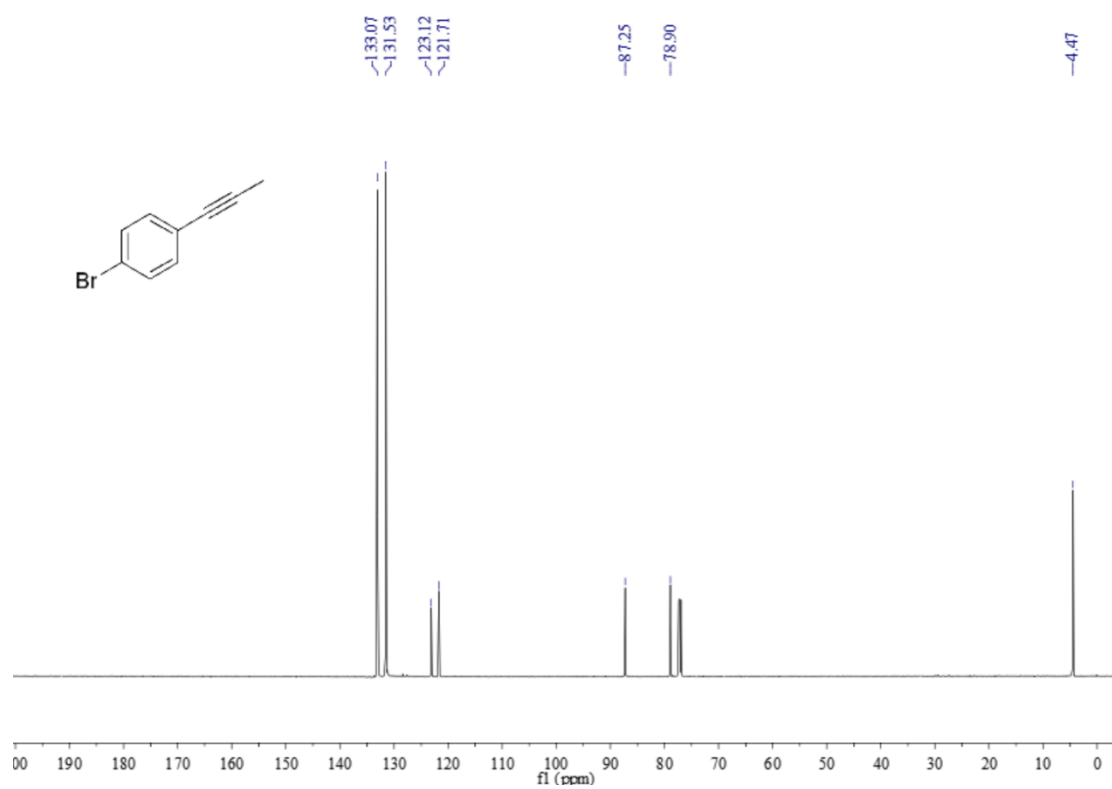
¹³C NMR of **1ac**



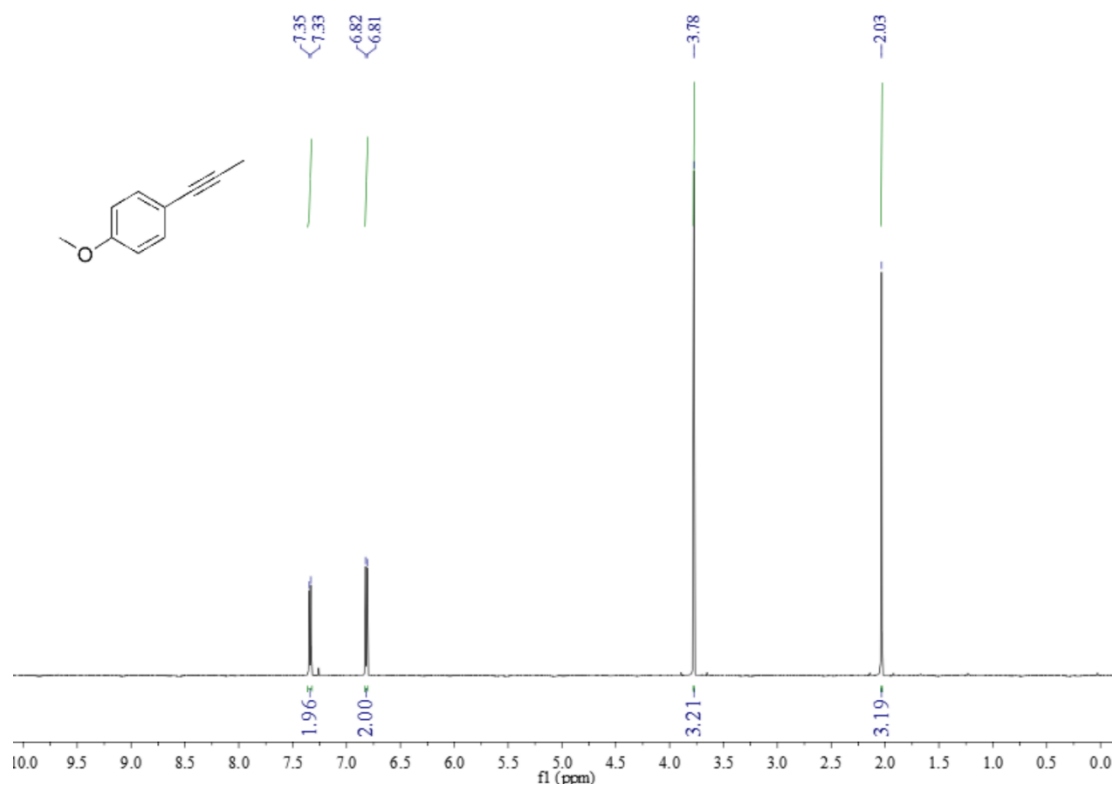
¹H NMR of **1ad**



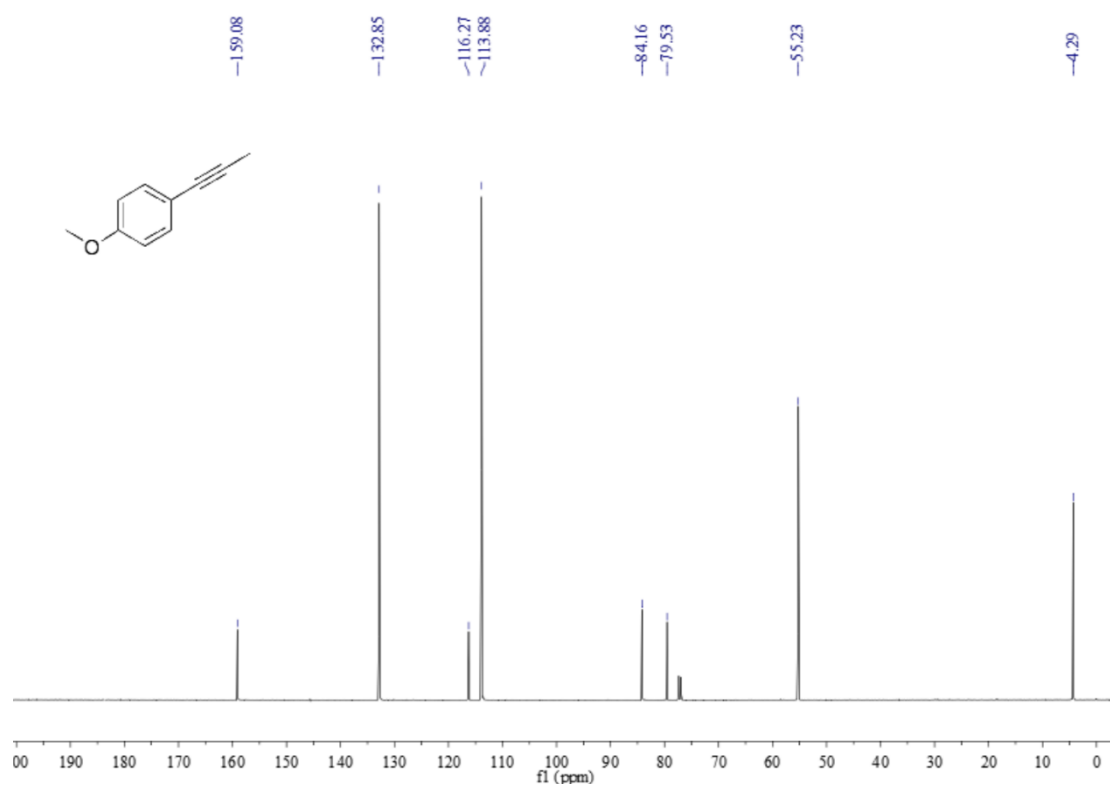
^{13}C NMR of **1ad**



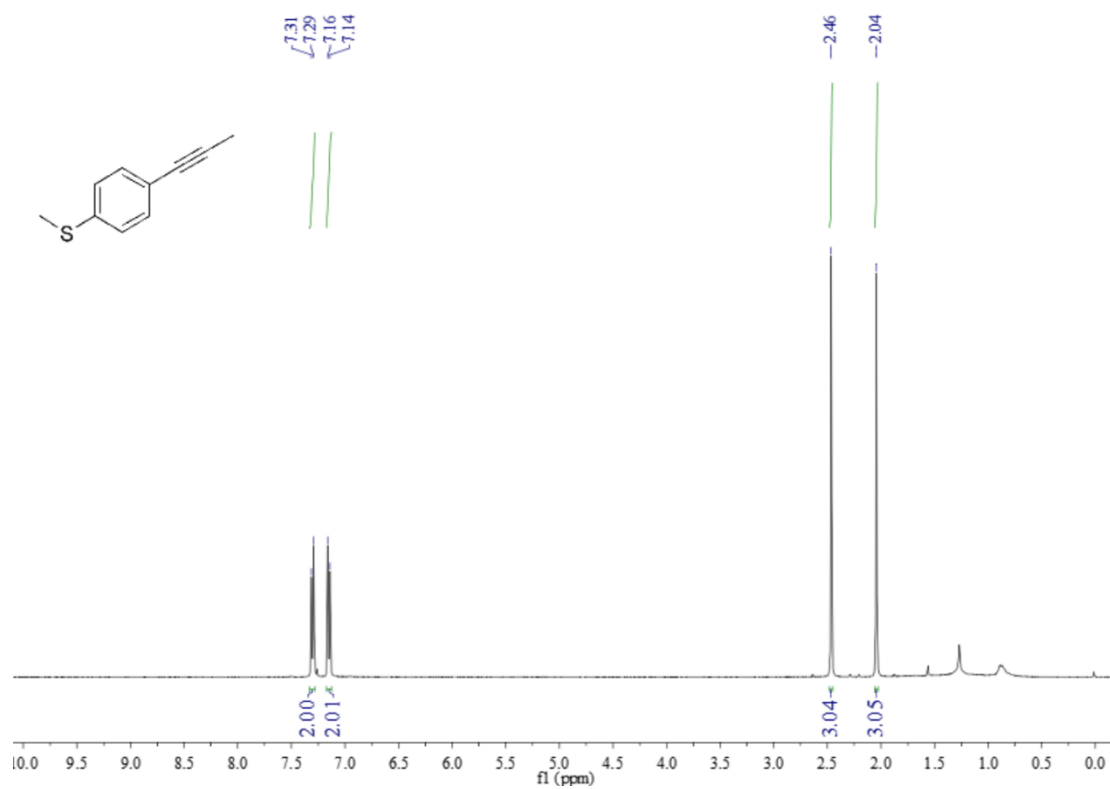
^1H NMR of **1ae**



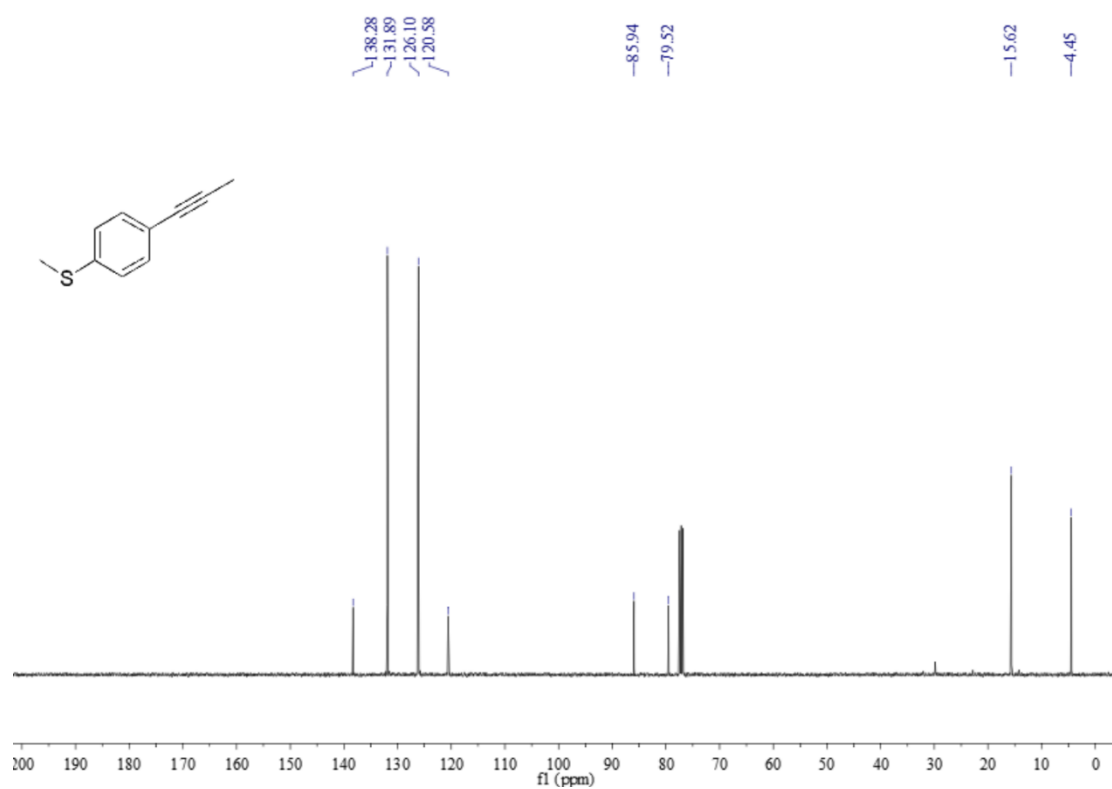
¹³C NMR of **1ae**



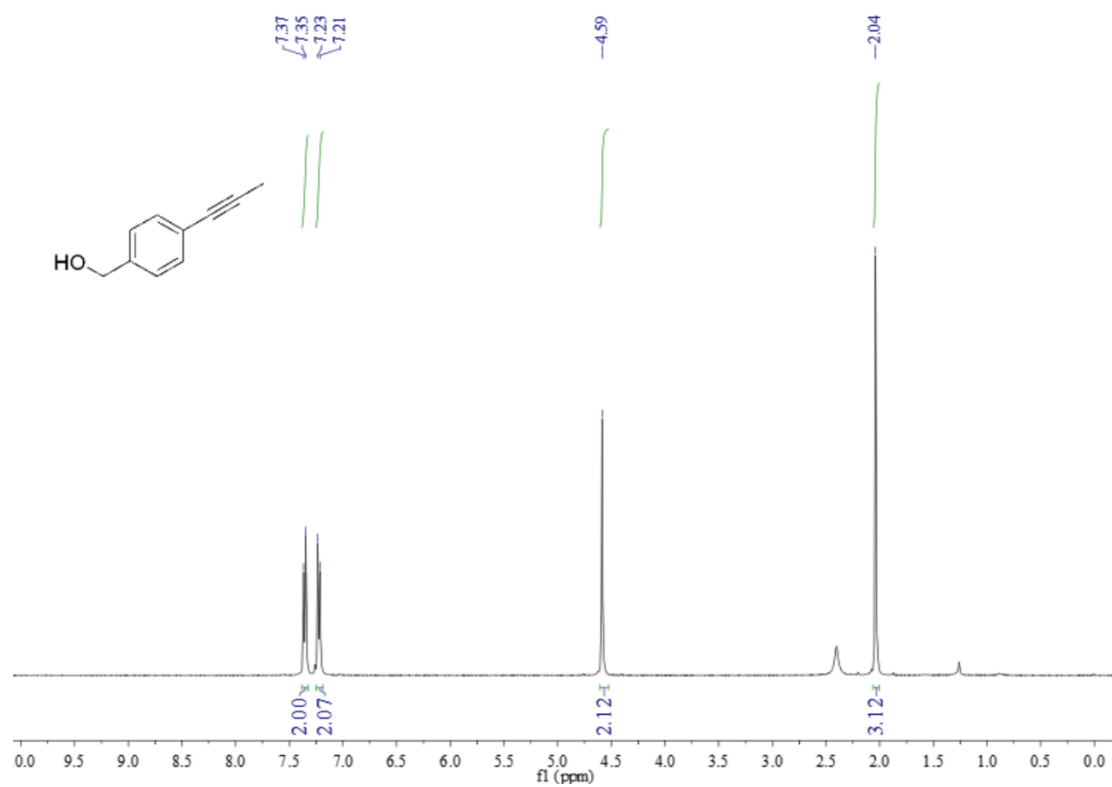
¹H NMR of **1af**



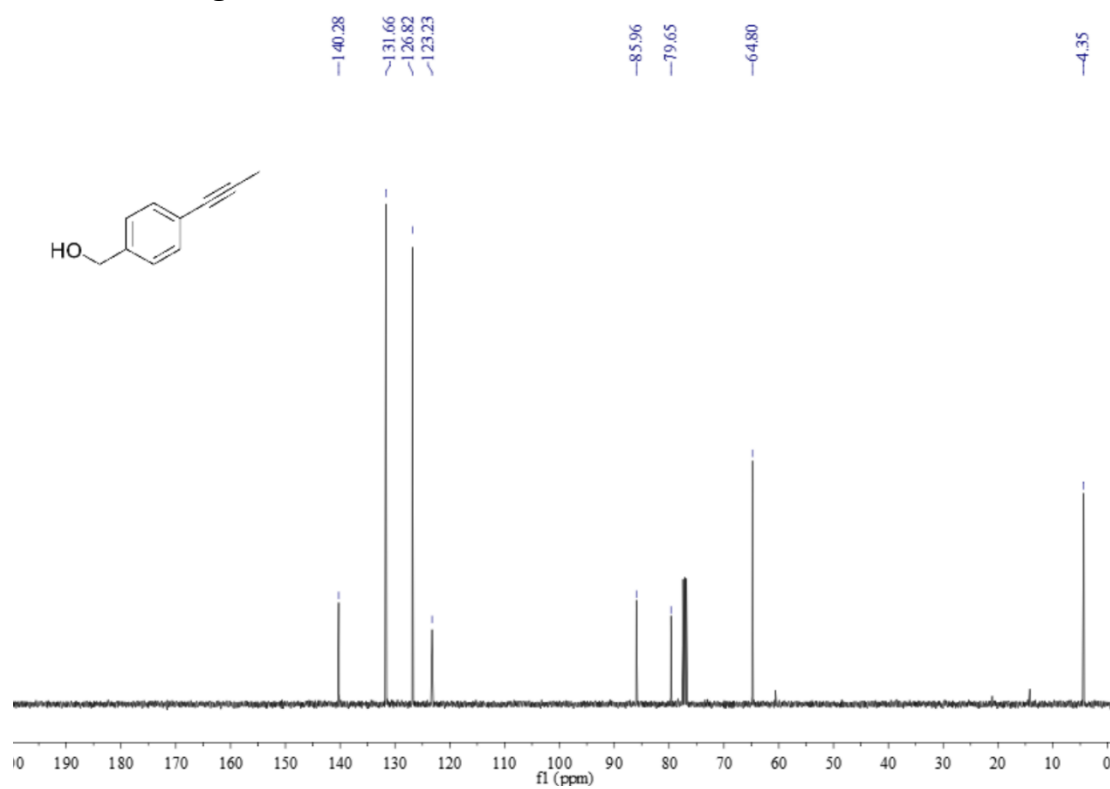
¹³C NMR of **1af**



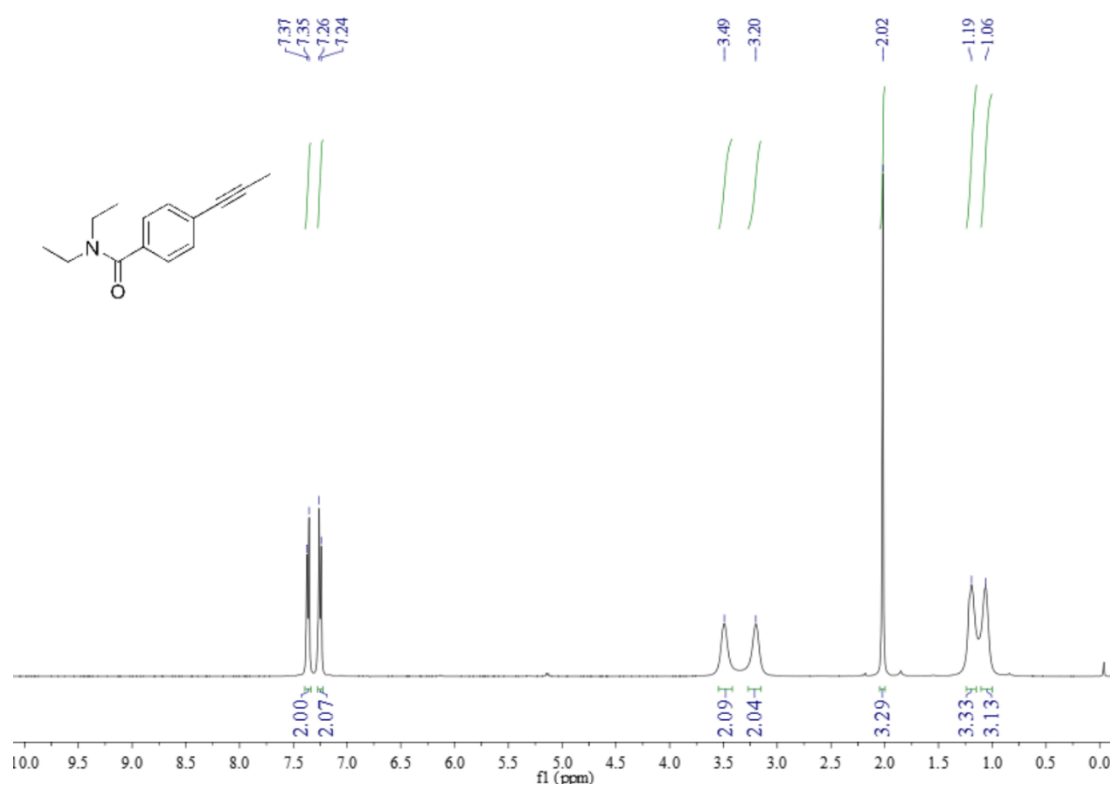
¹H NMR of **1ag**



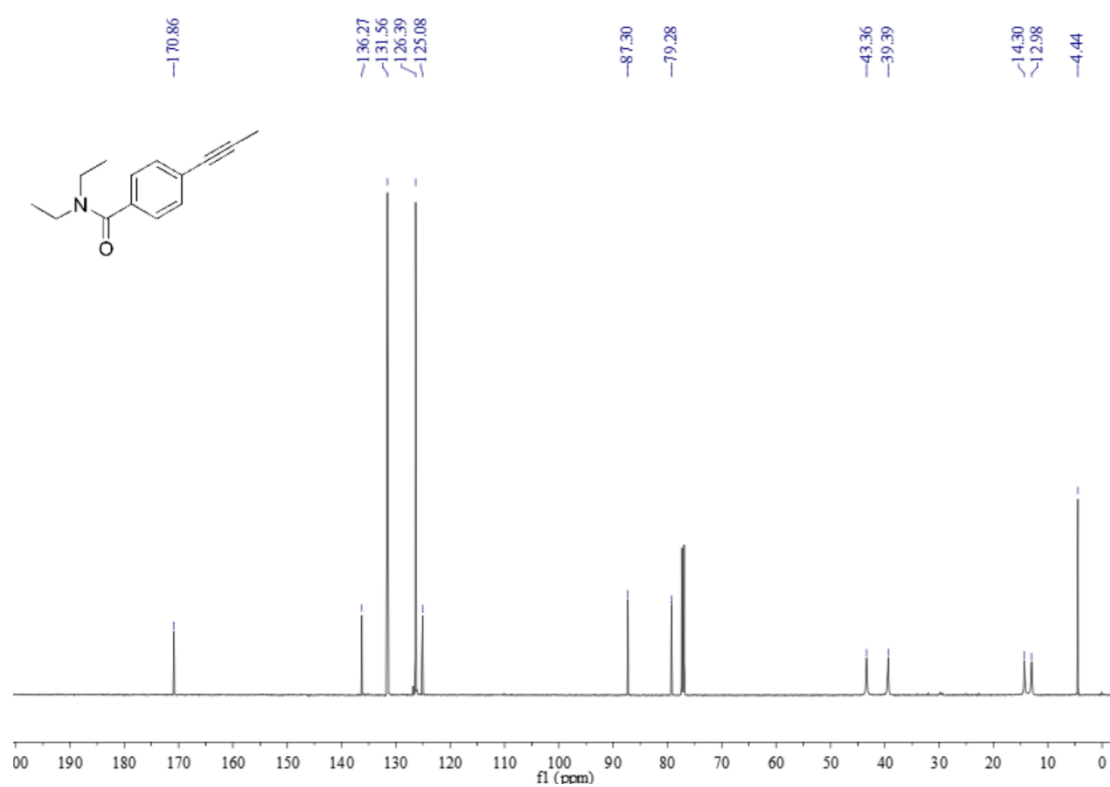
^{13}C NMR of **1ag**



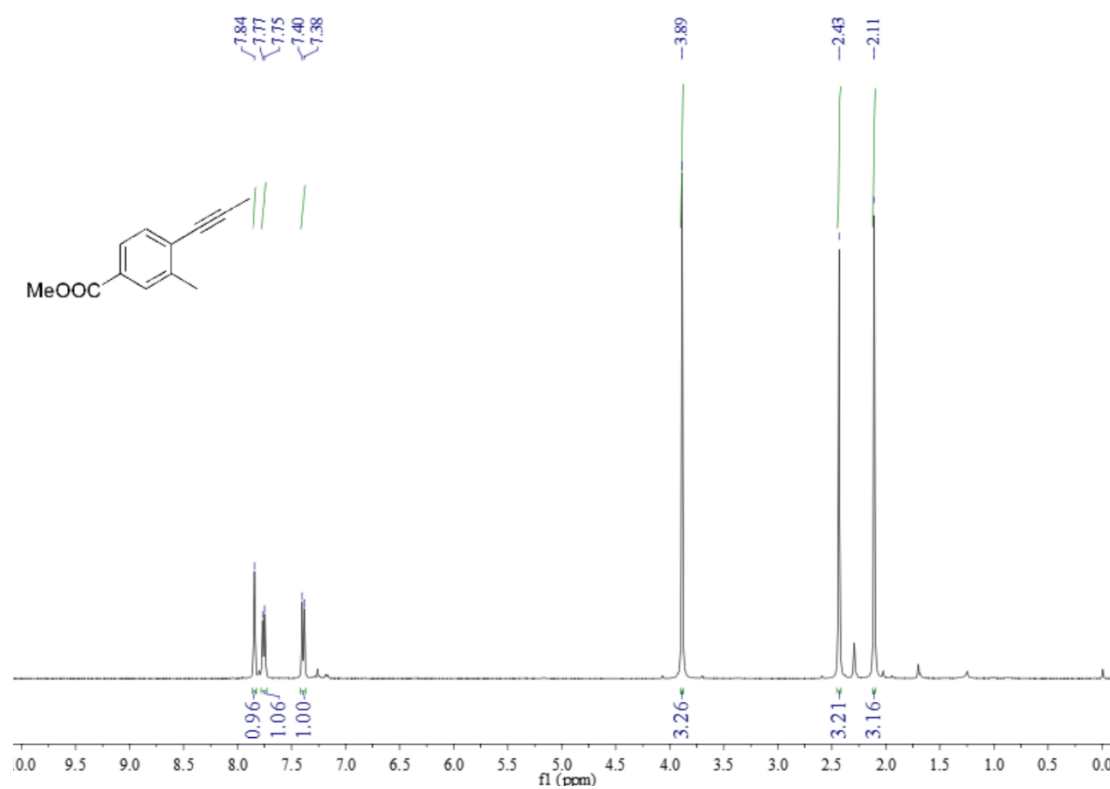
^1H NMR of **1ah**



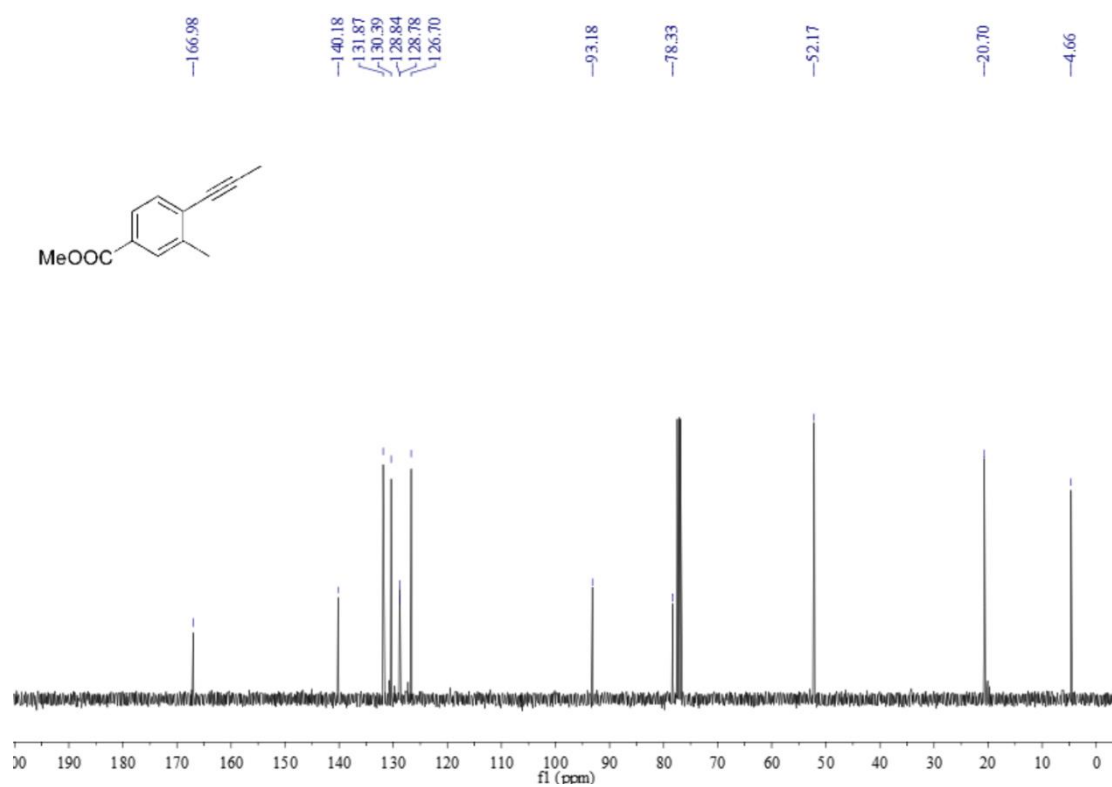
¹³C NMR of **1ah**



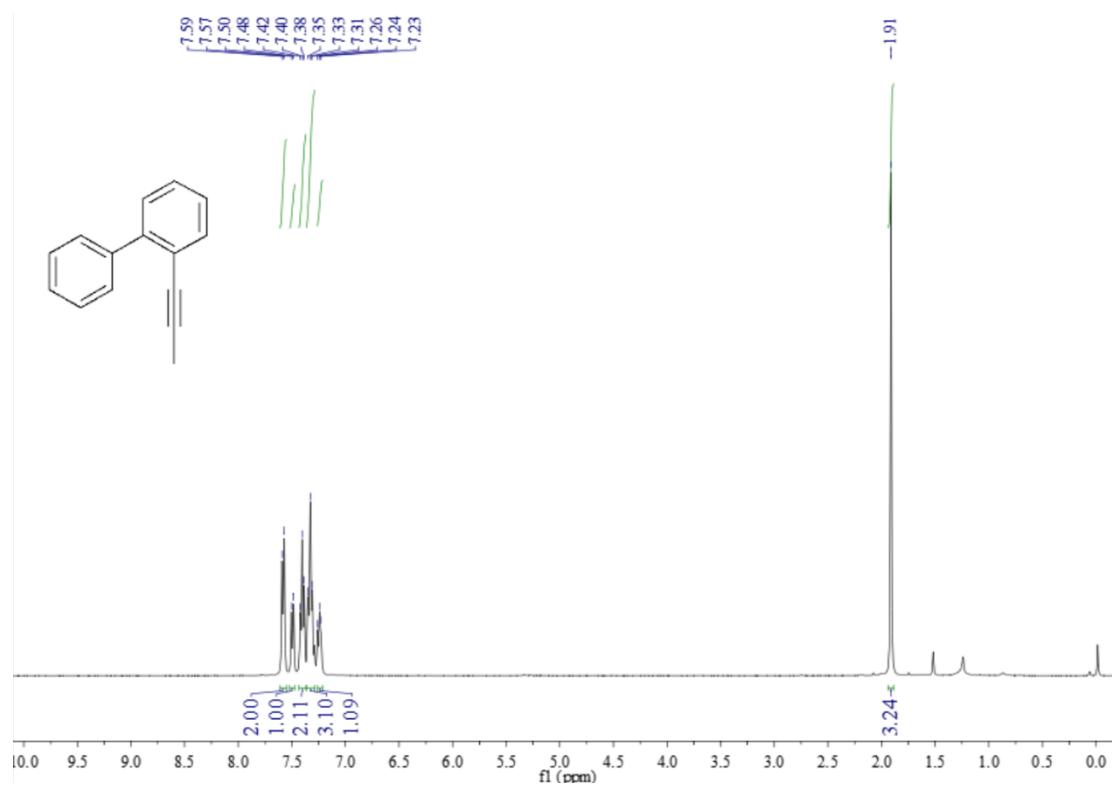
¹H NMR of **1ai**



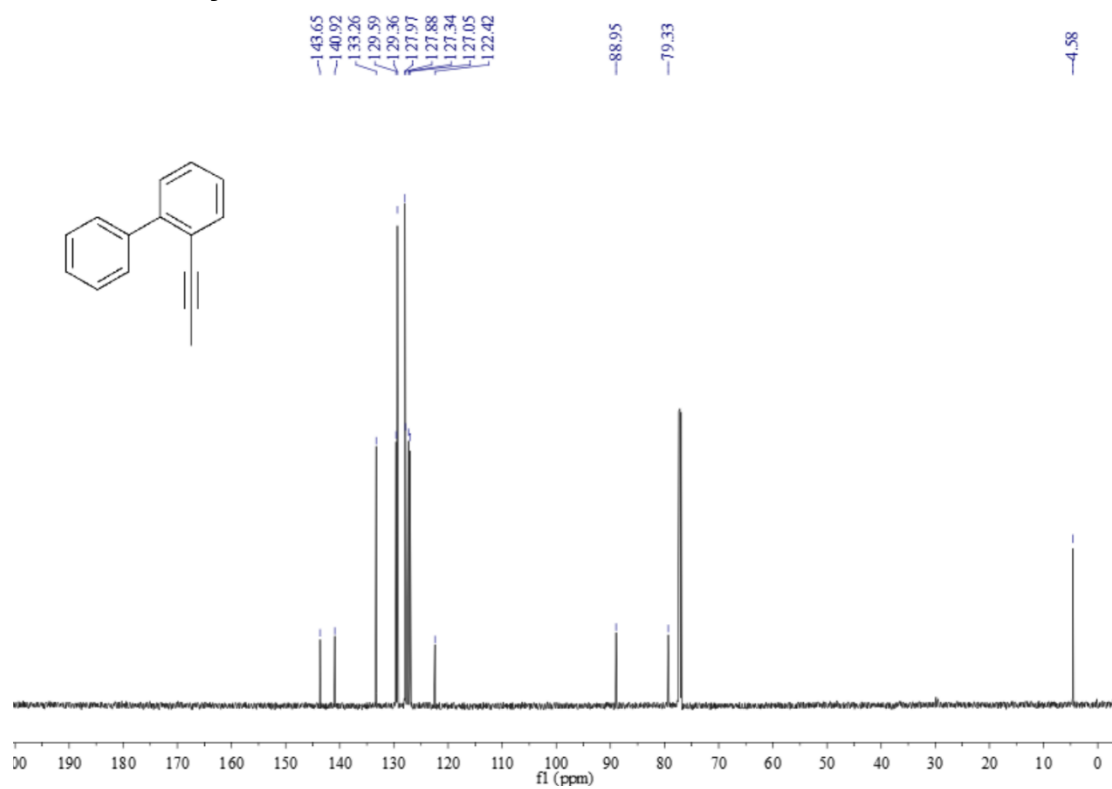
¹³C NMR of **1ai**



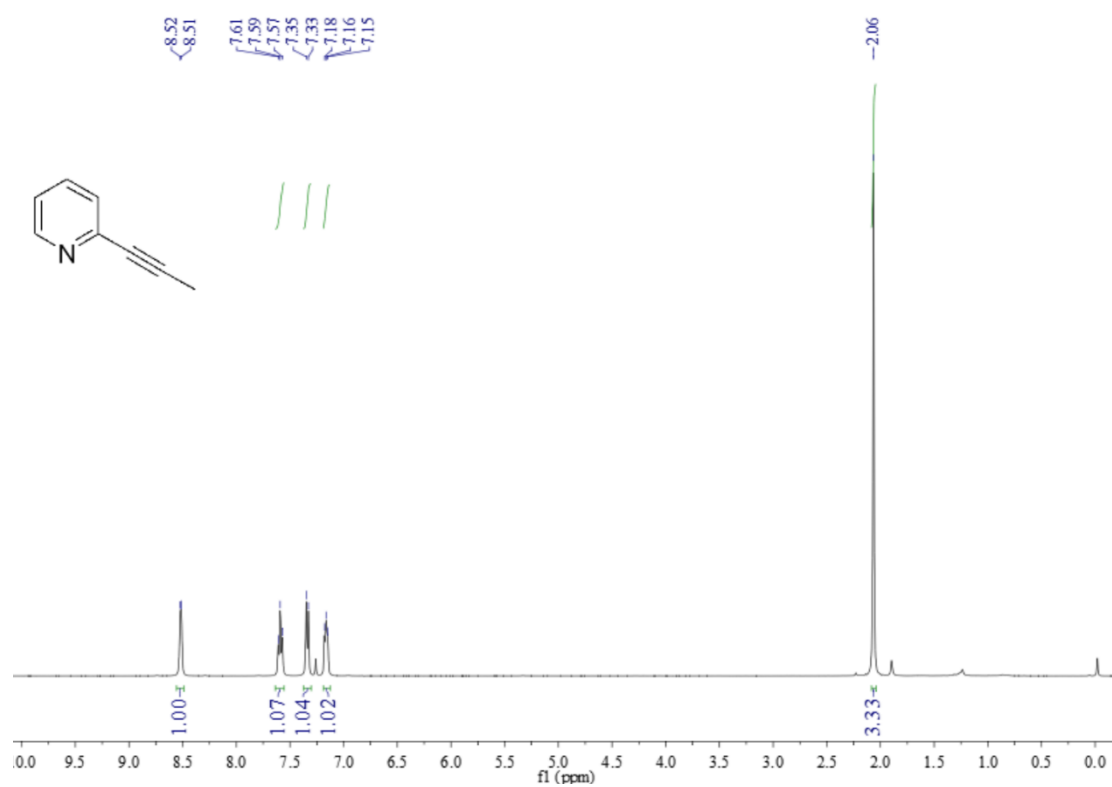
¹H NMR of **1aj**



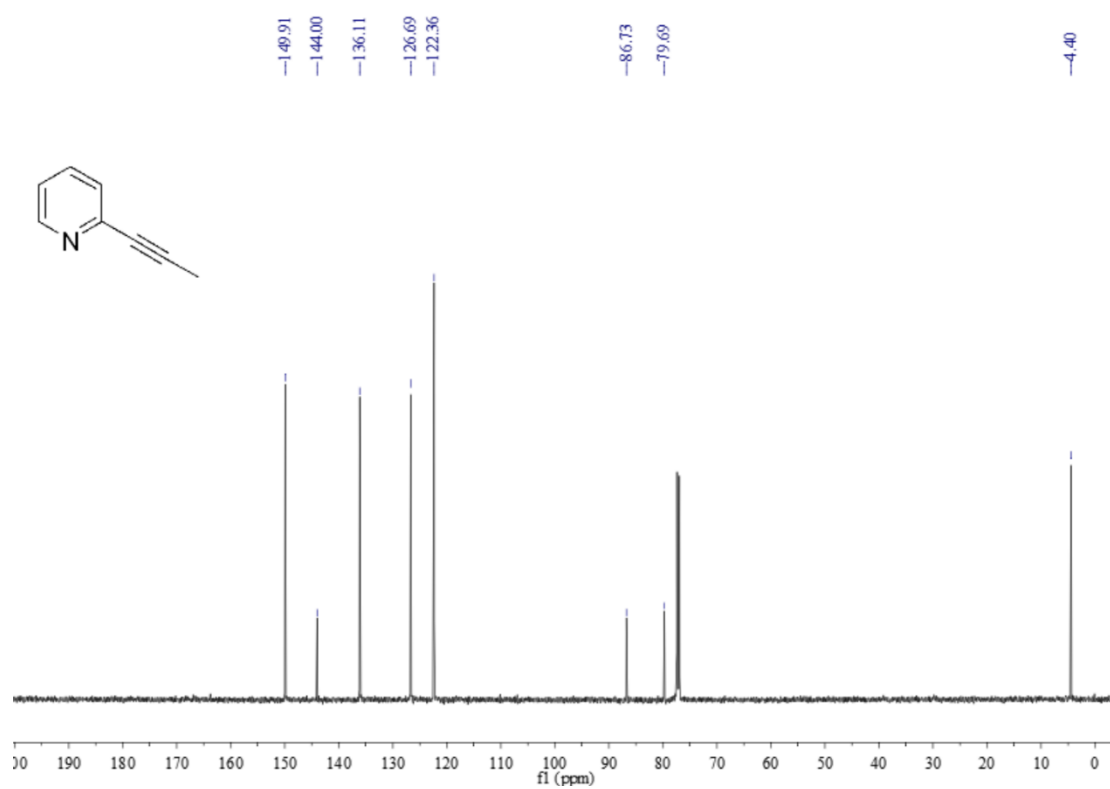
¹³C NMR of **1aj**



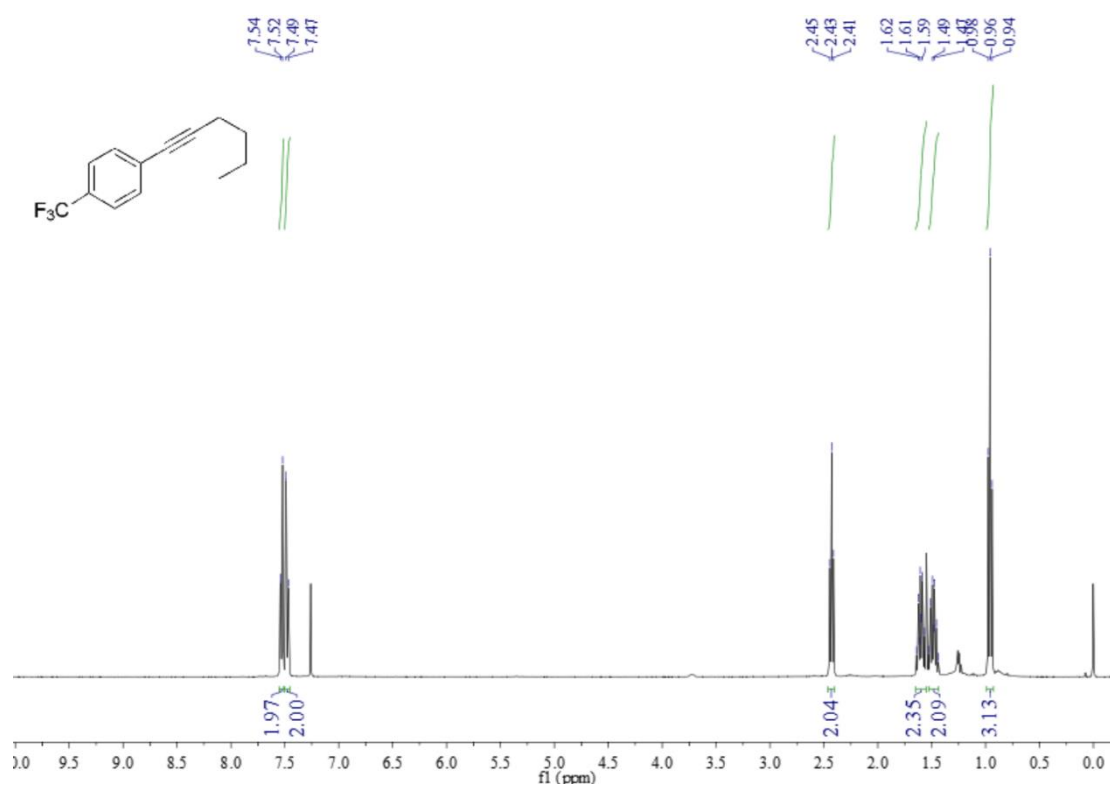
¹H NMR of **1ak**



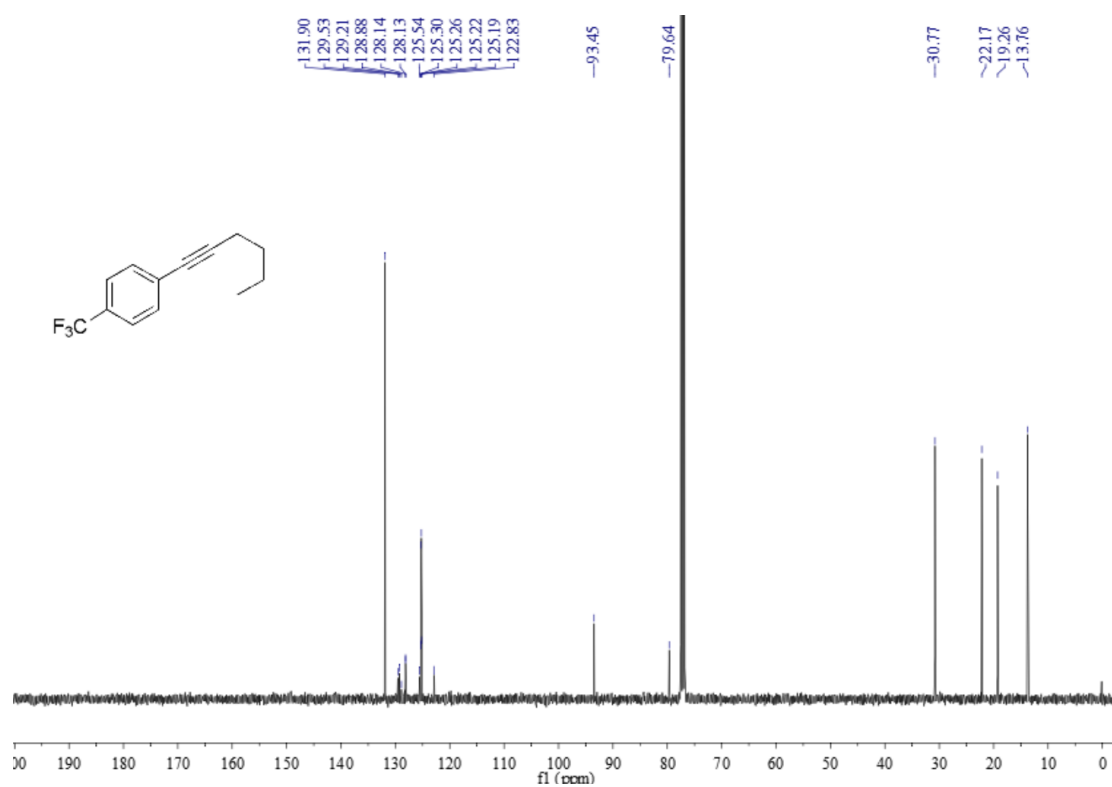
^{13}C NMR of **1ak**



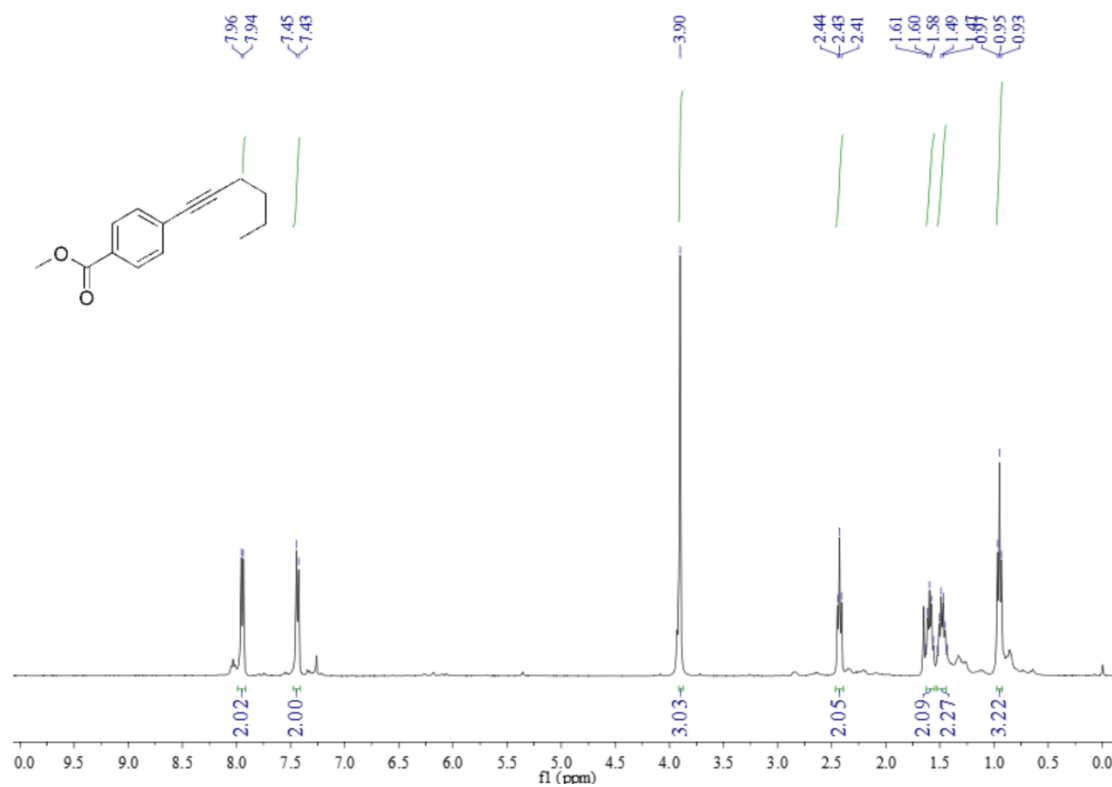
^1H NMR of **1al**



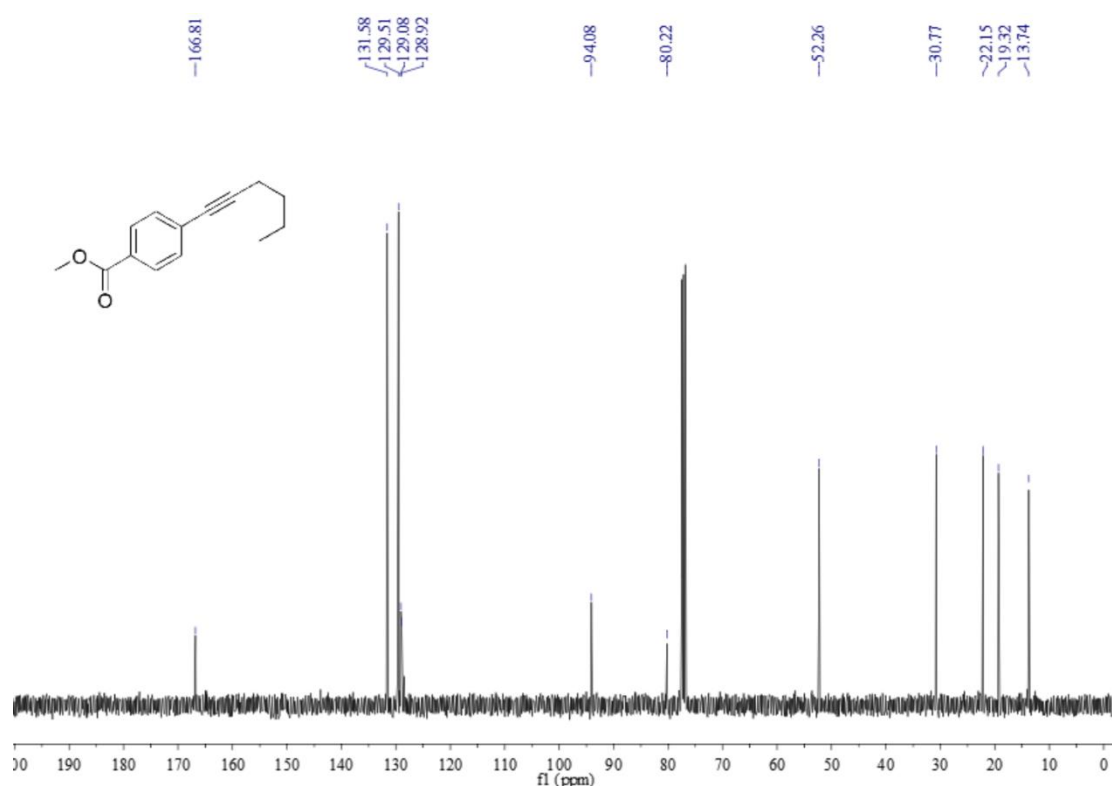
¹³C NMR of **1al**



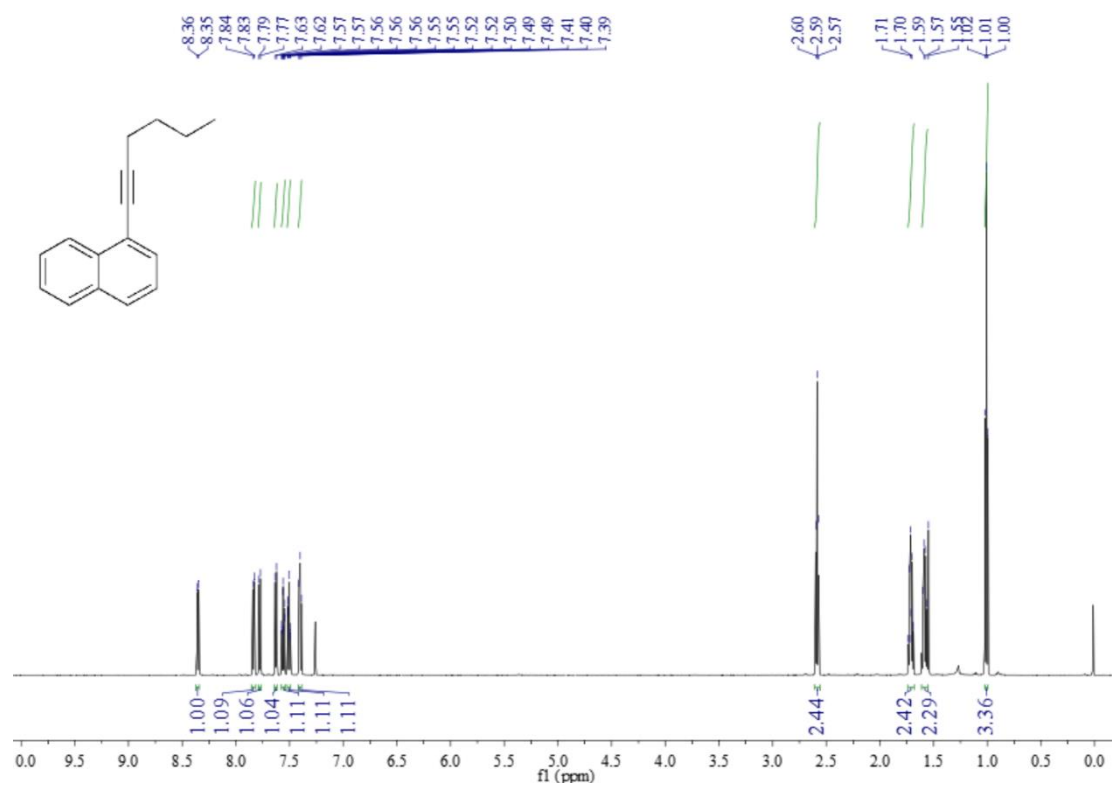
¹H NMR of **1am**



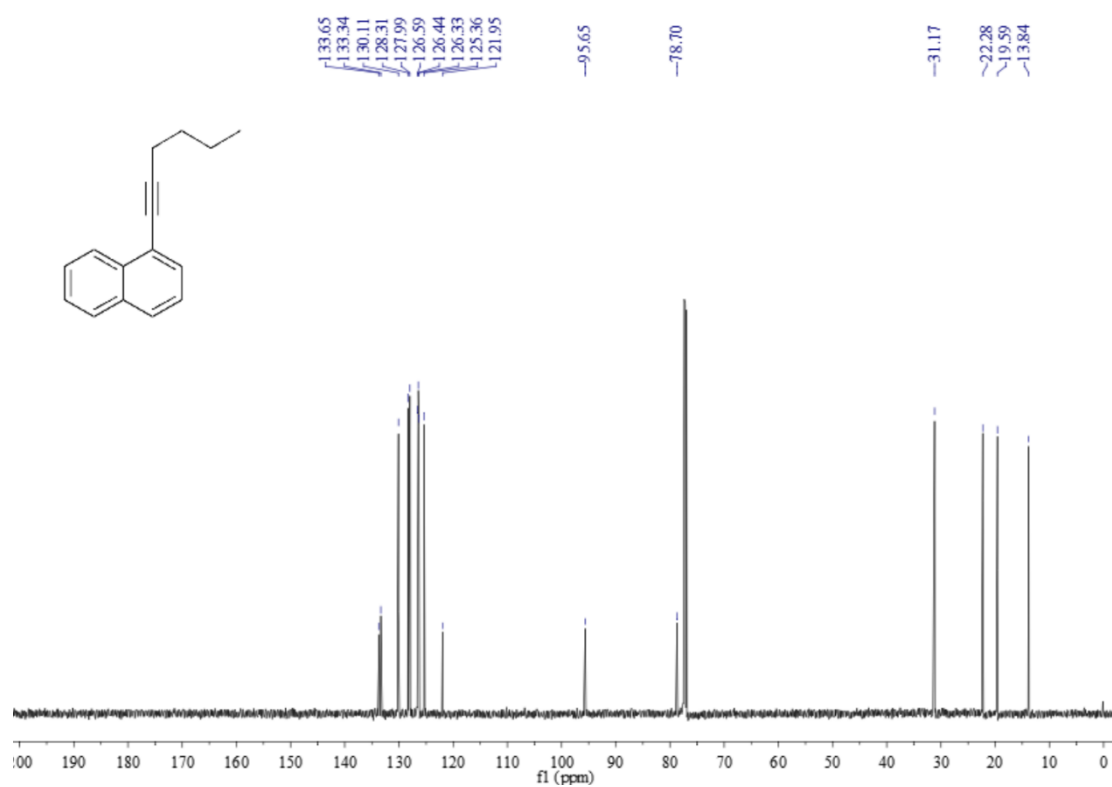
^{13}C NMR of **1am**



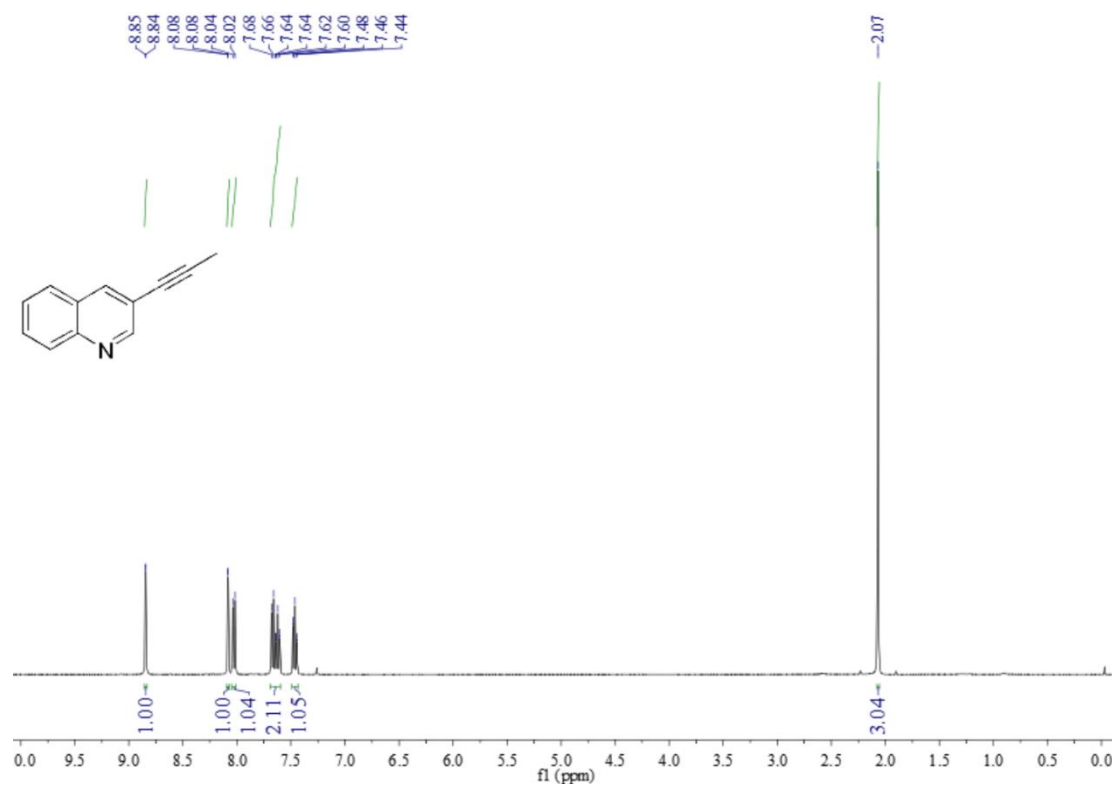
^1H NMR of **1an**



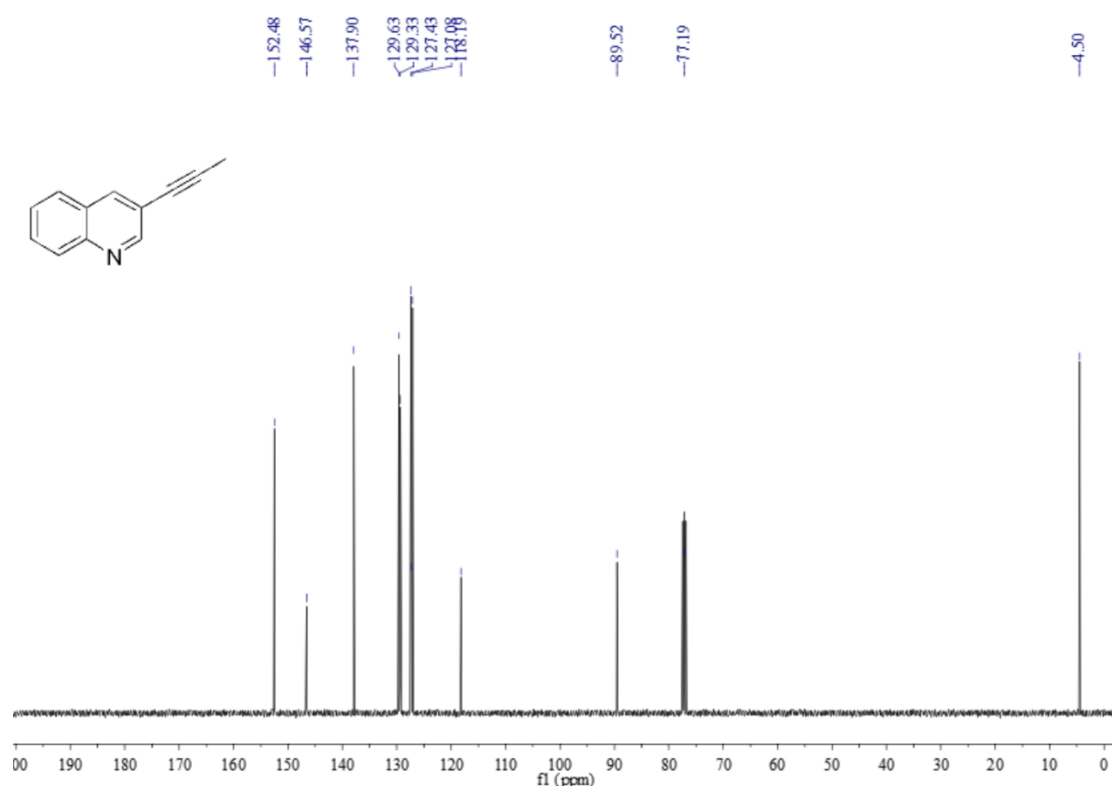
¹³C NMR of **1an**



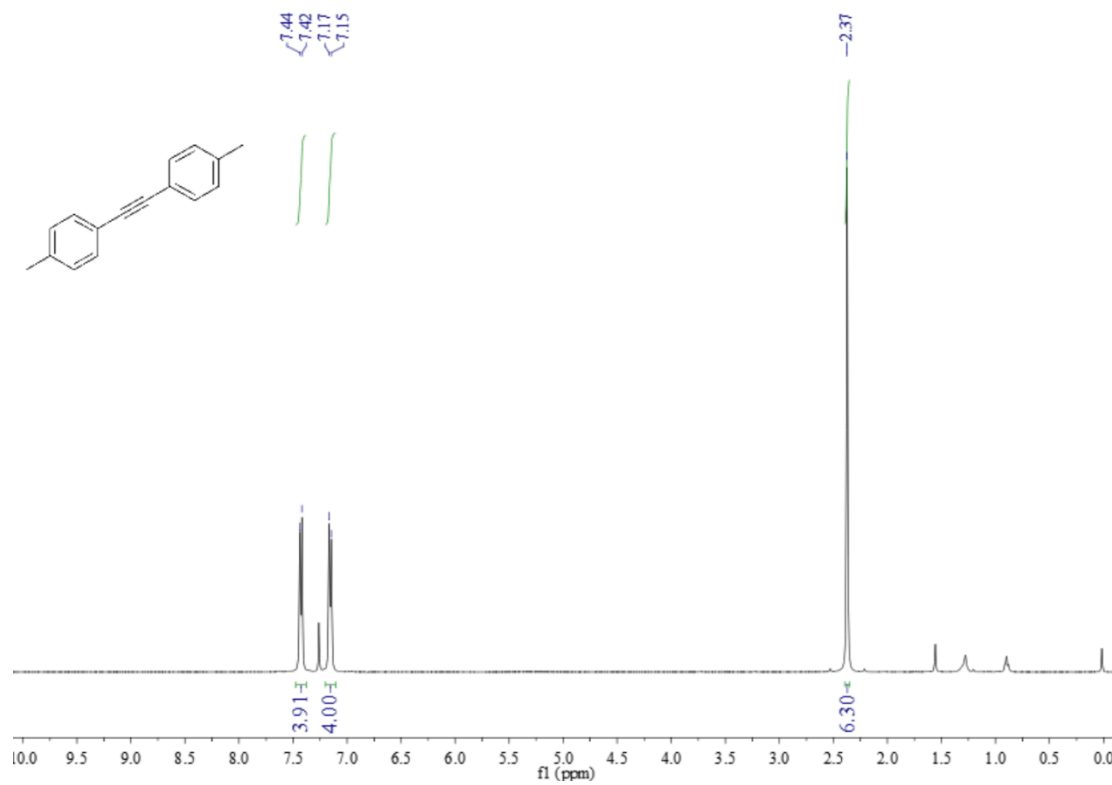
¹H NMR of **1ao**



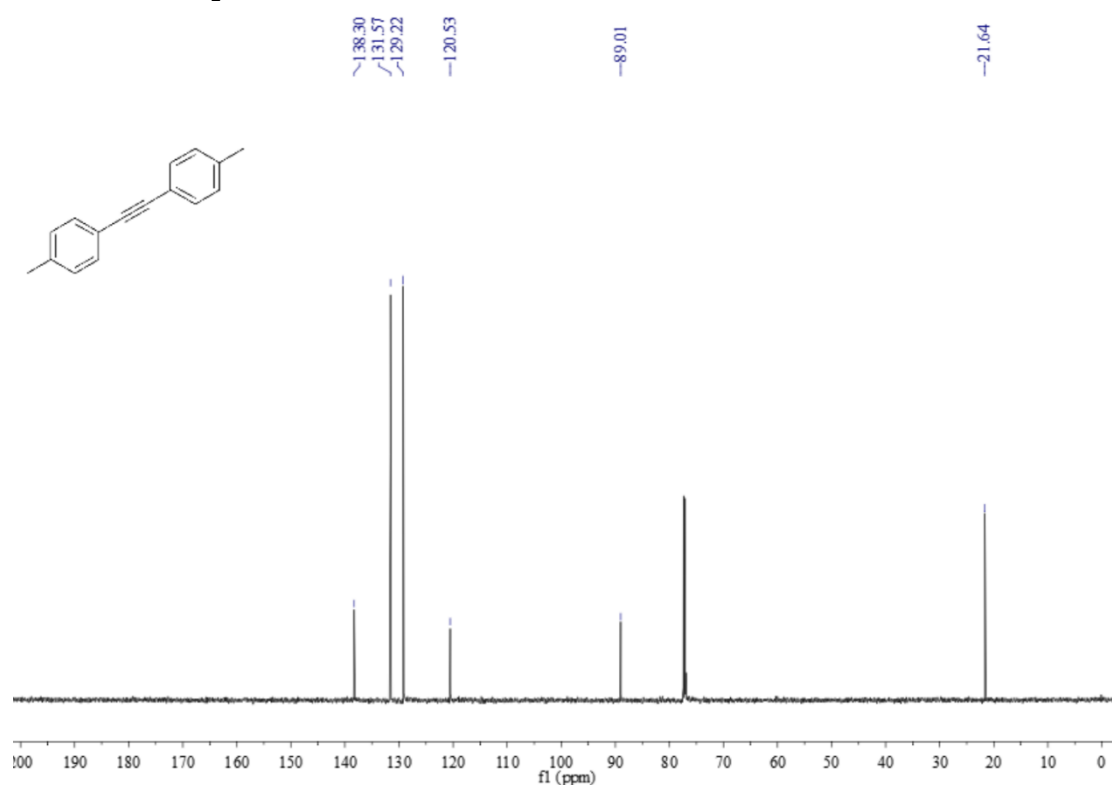
¹³C NMR of **1ao**



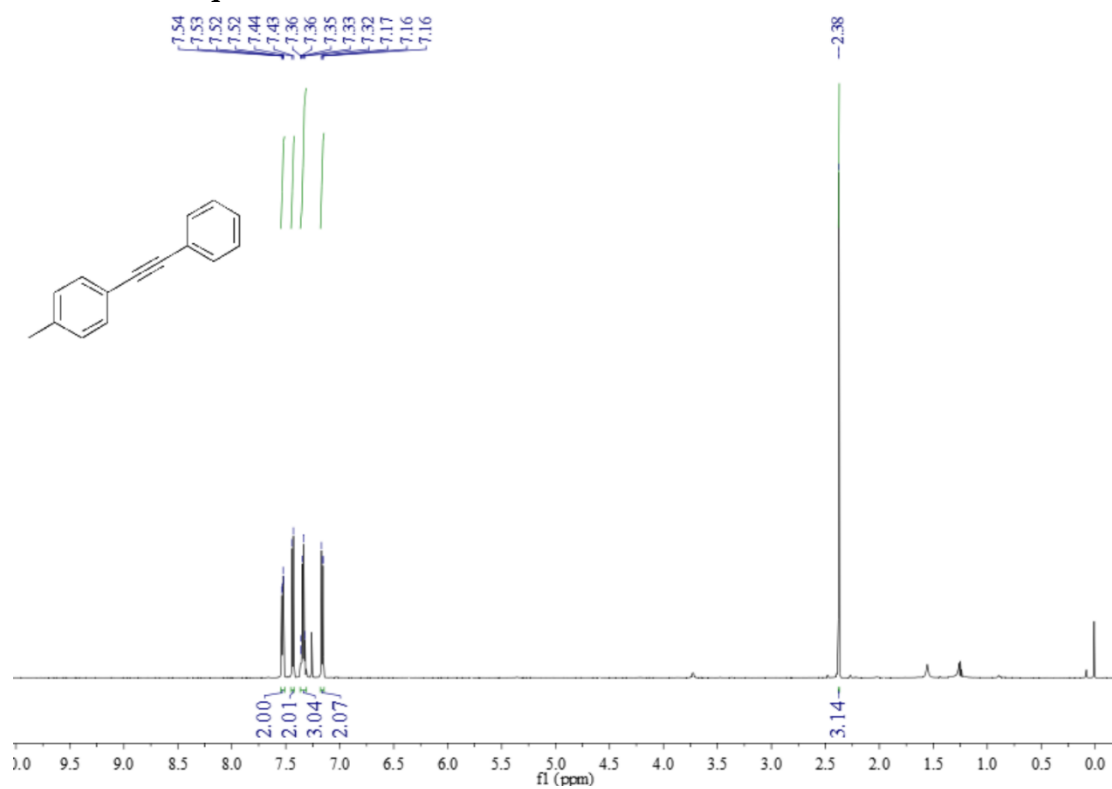
¹H NMR of **1ap**



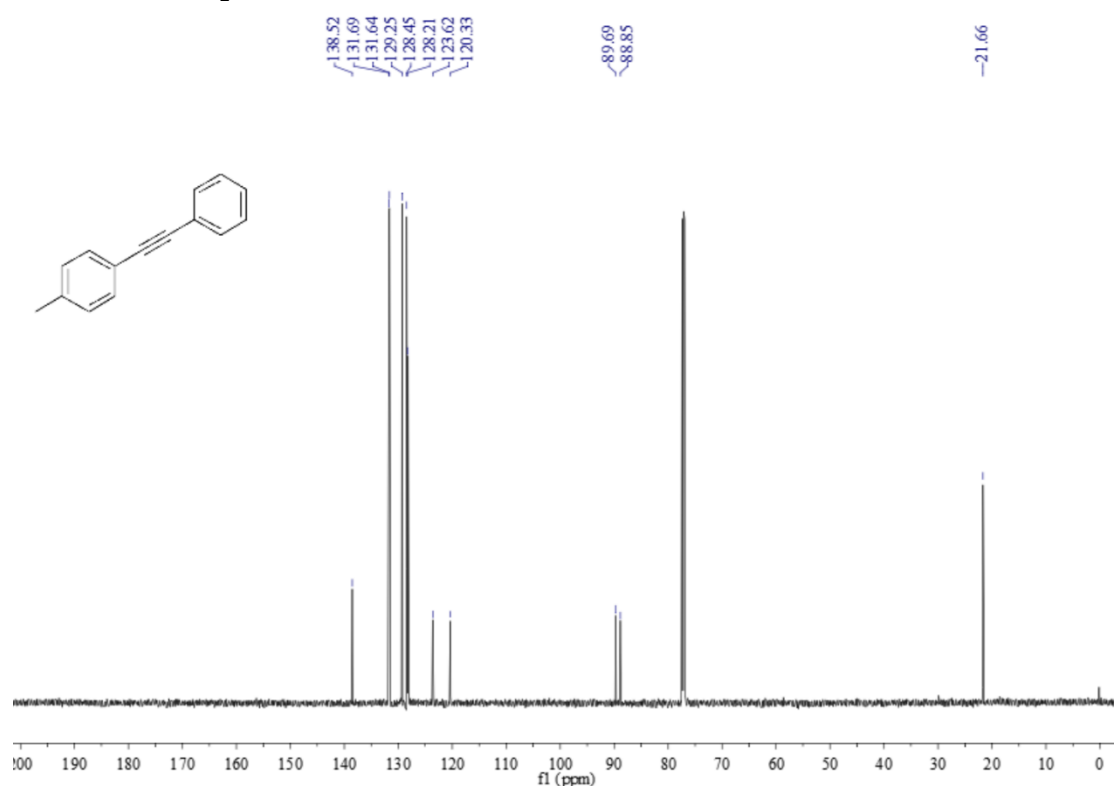
^{13}C NMR of **1ap**



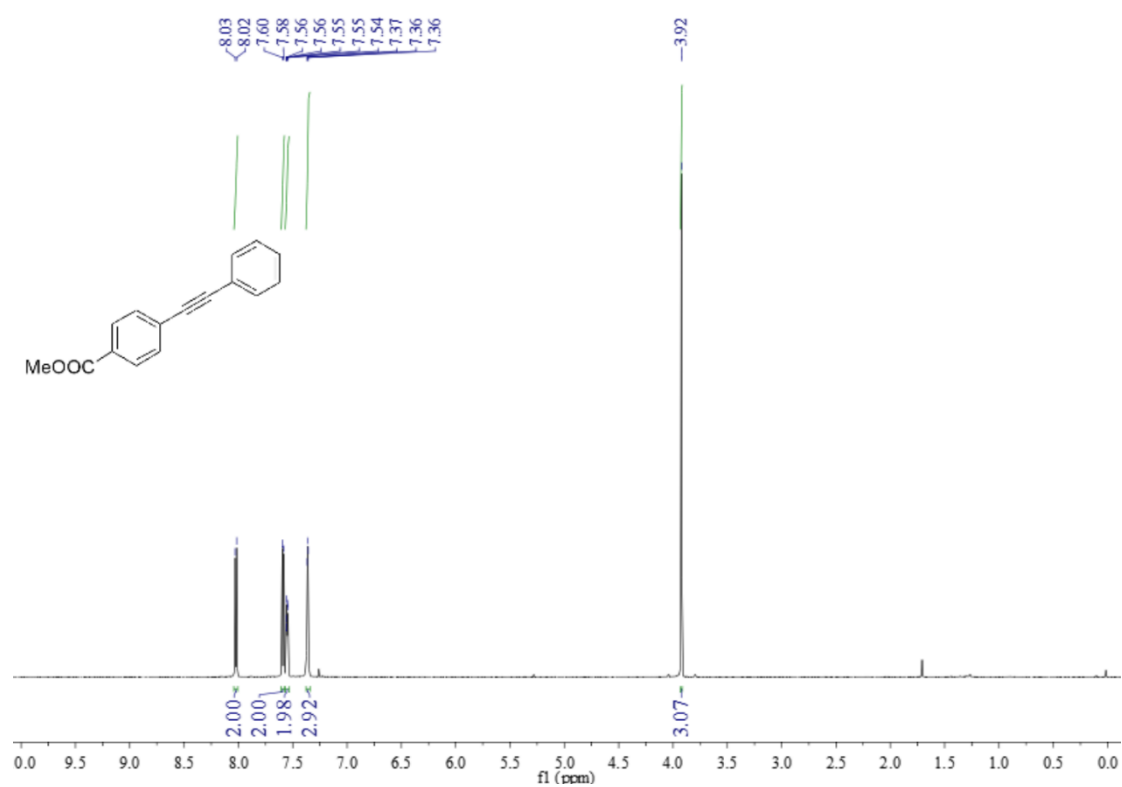
^1H NMR of **1aq**



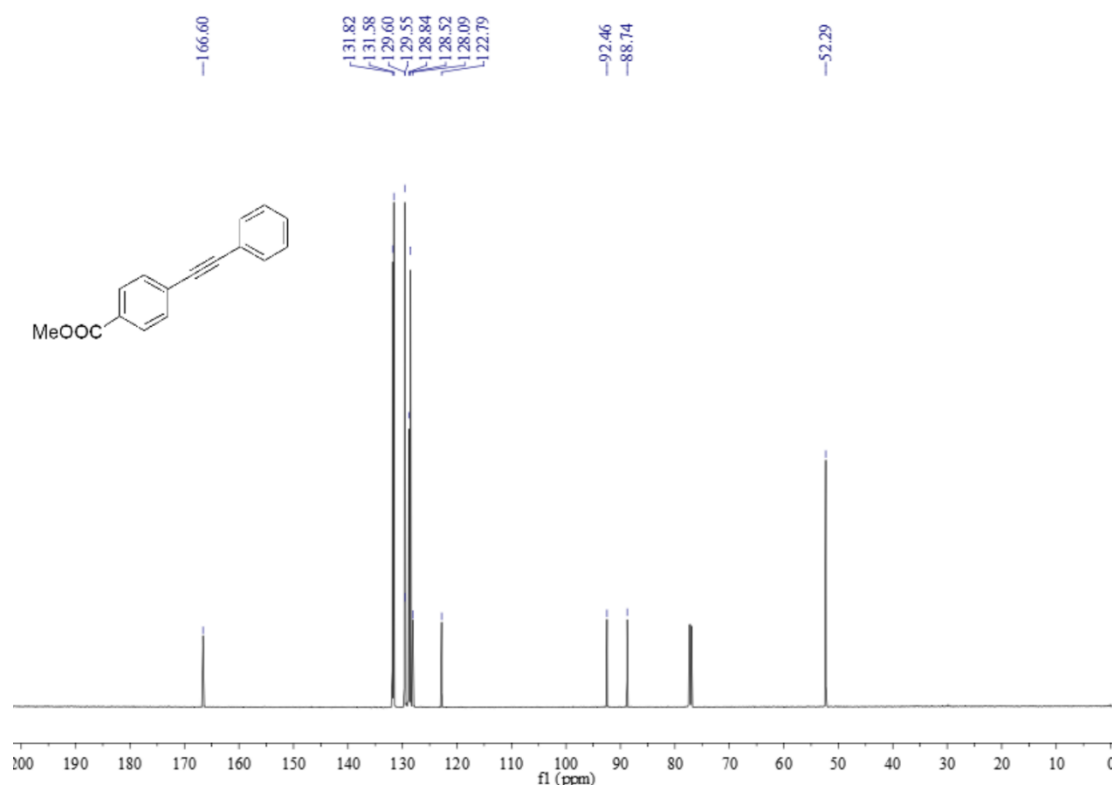
^{13}C NMR of **1aq**



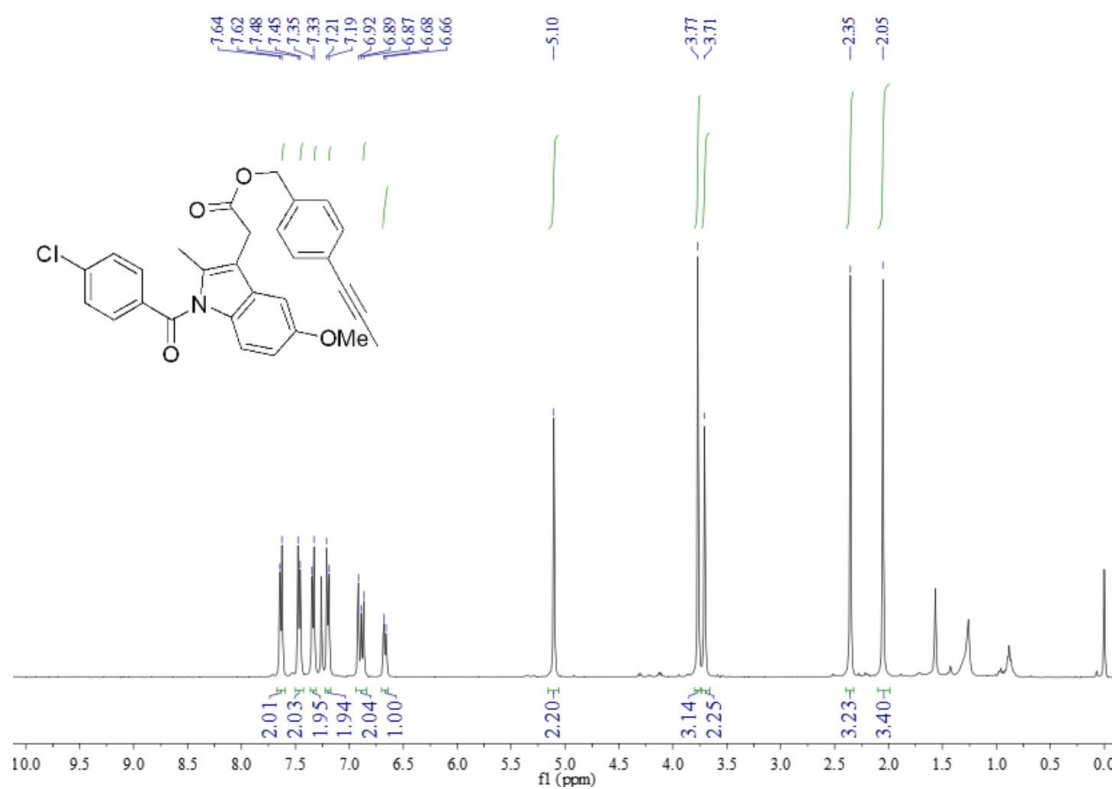
^1H NMR of **1ar**



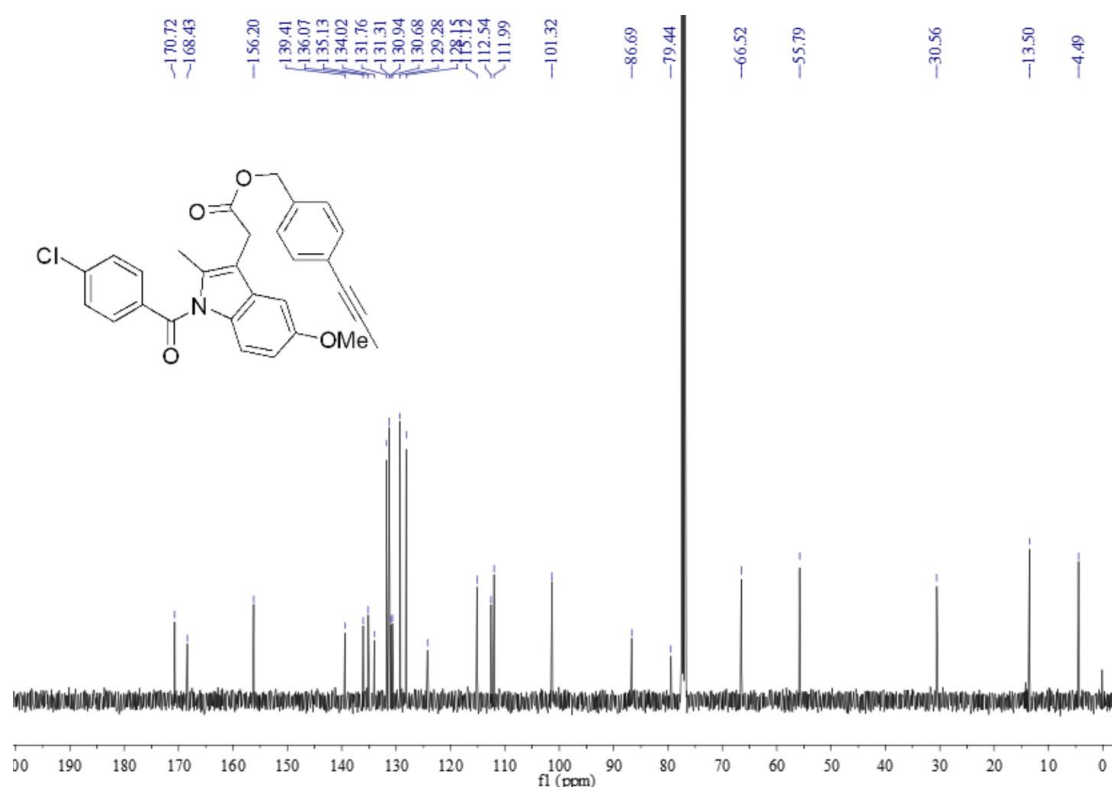
^{13}C NMR of **1ar**



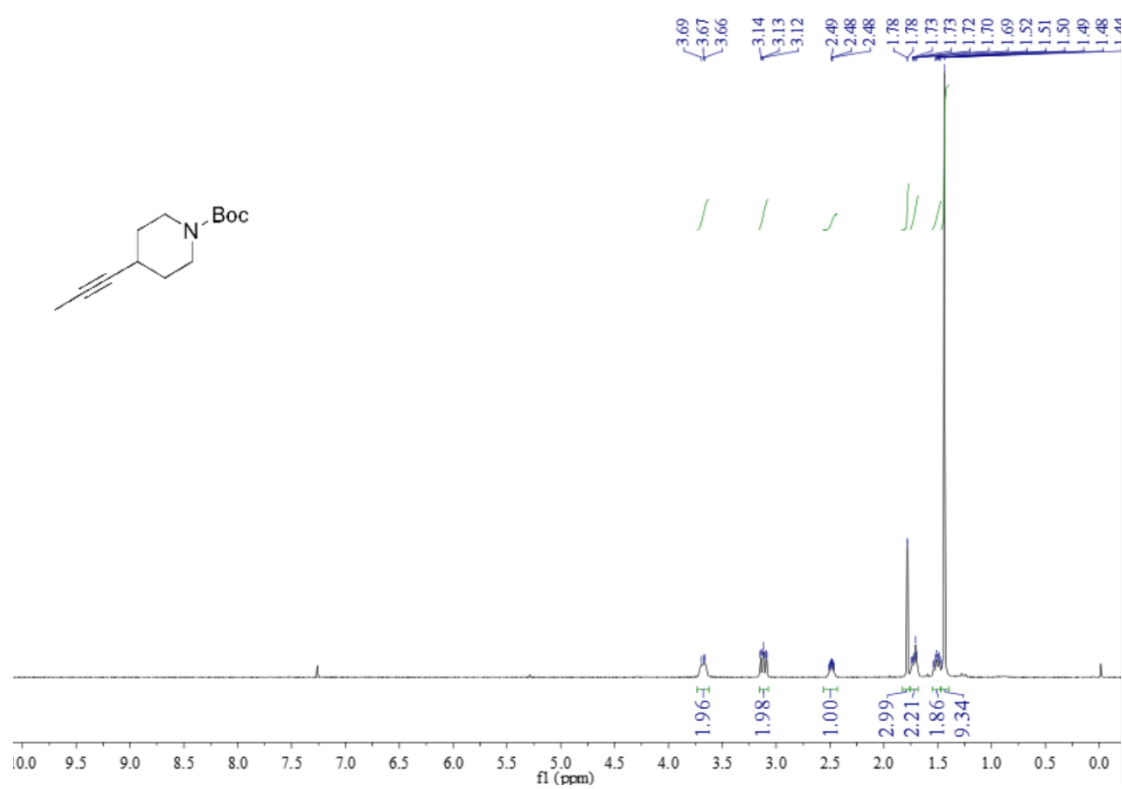
^1H NMR of **1as**



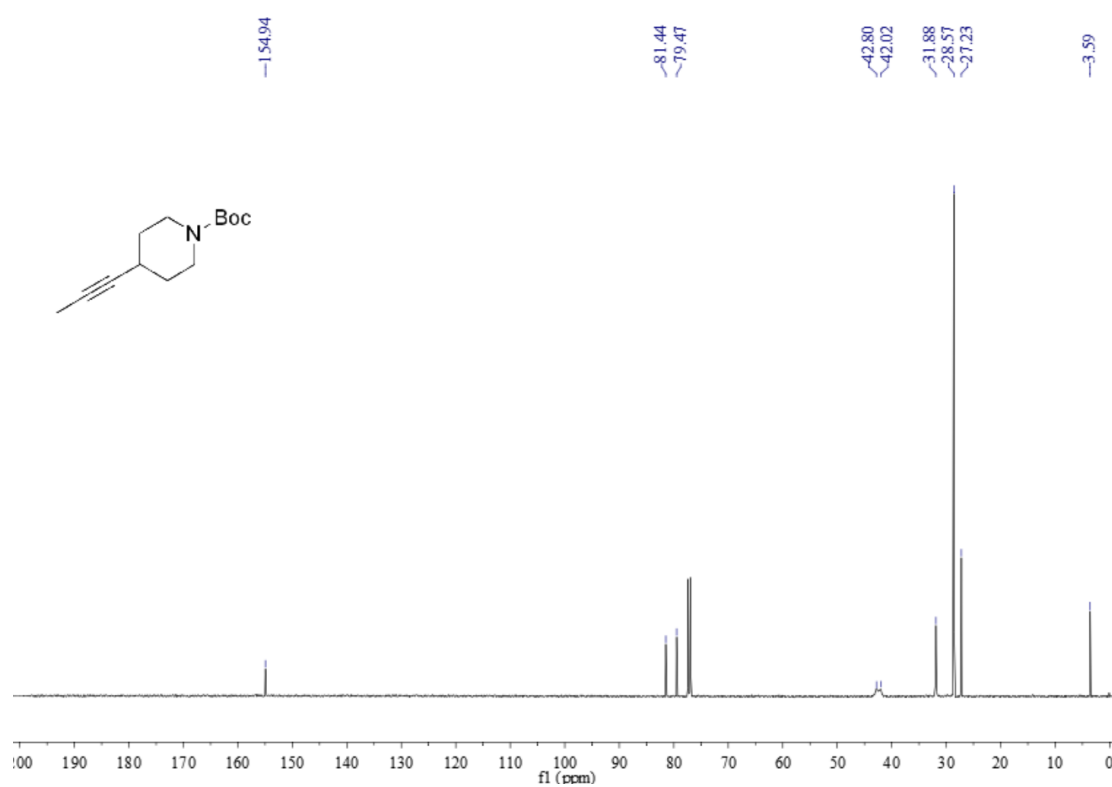
¹³C NMR of **1as**



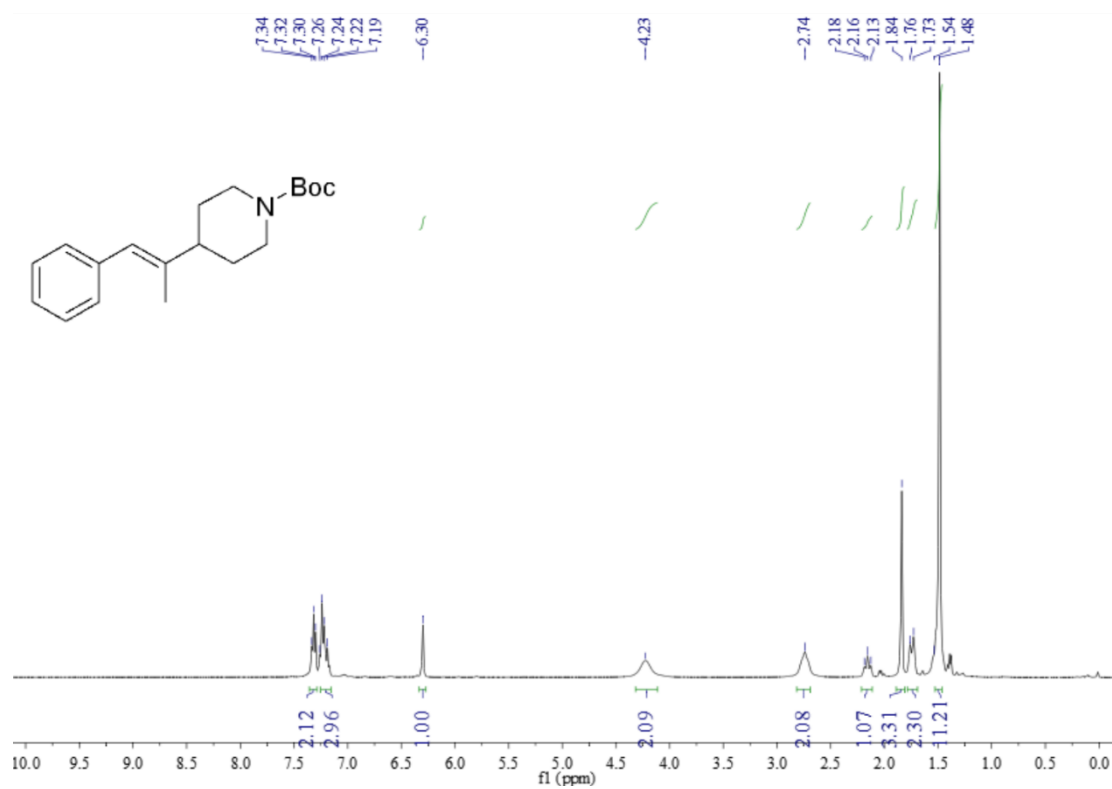
¹H NMR of **1bi**



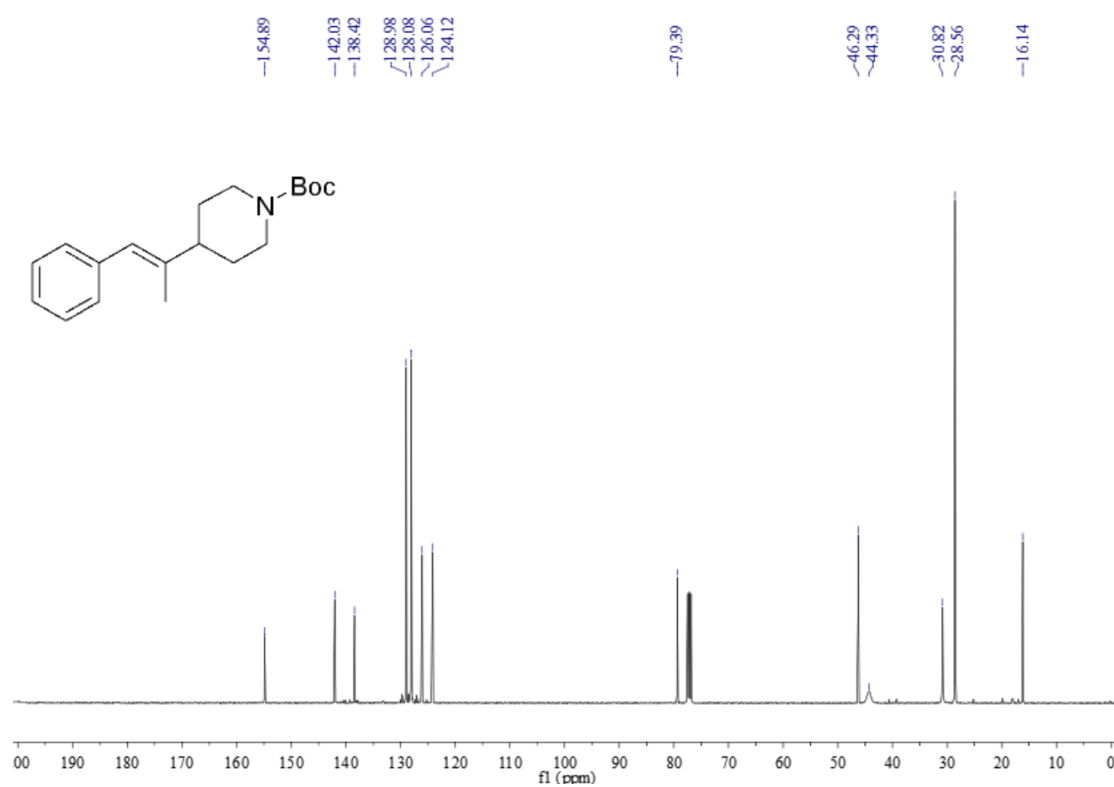
¹³C NMR of **1bi**



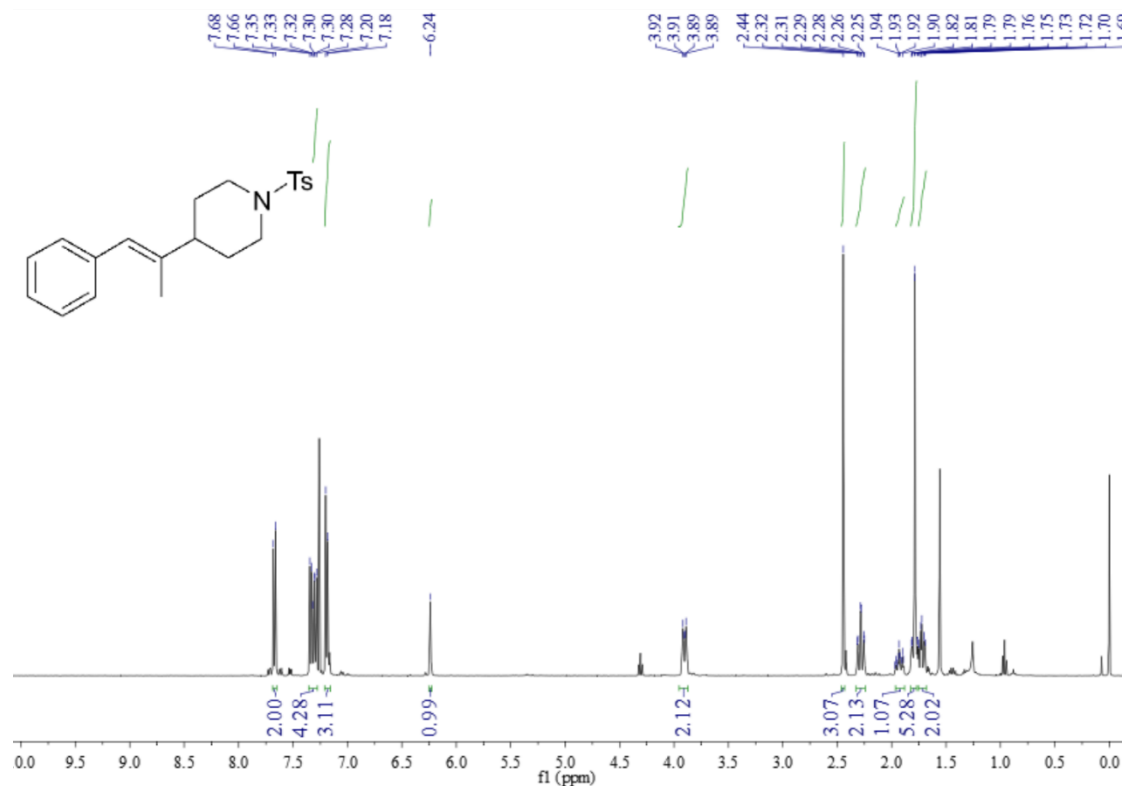
¹H NMR of **3a**



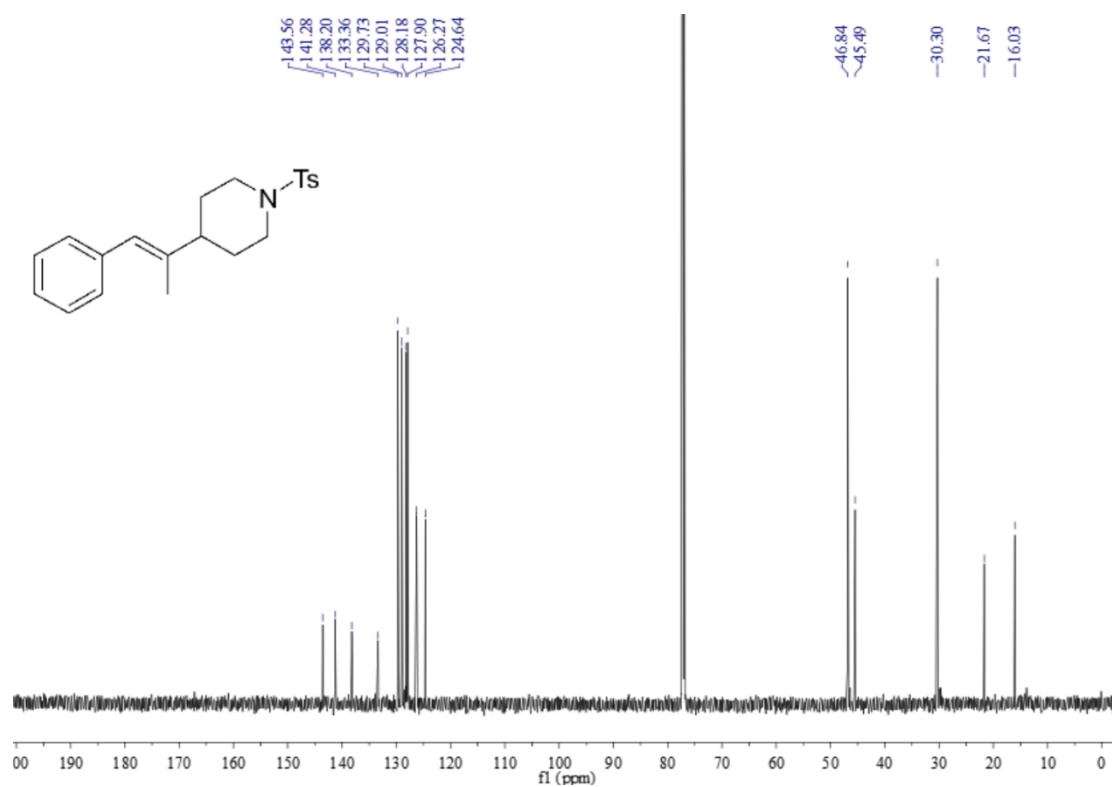
¹³C NMR of **3a**



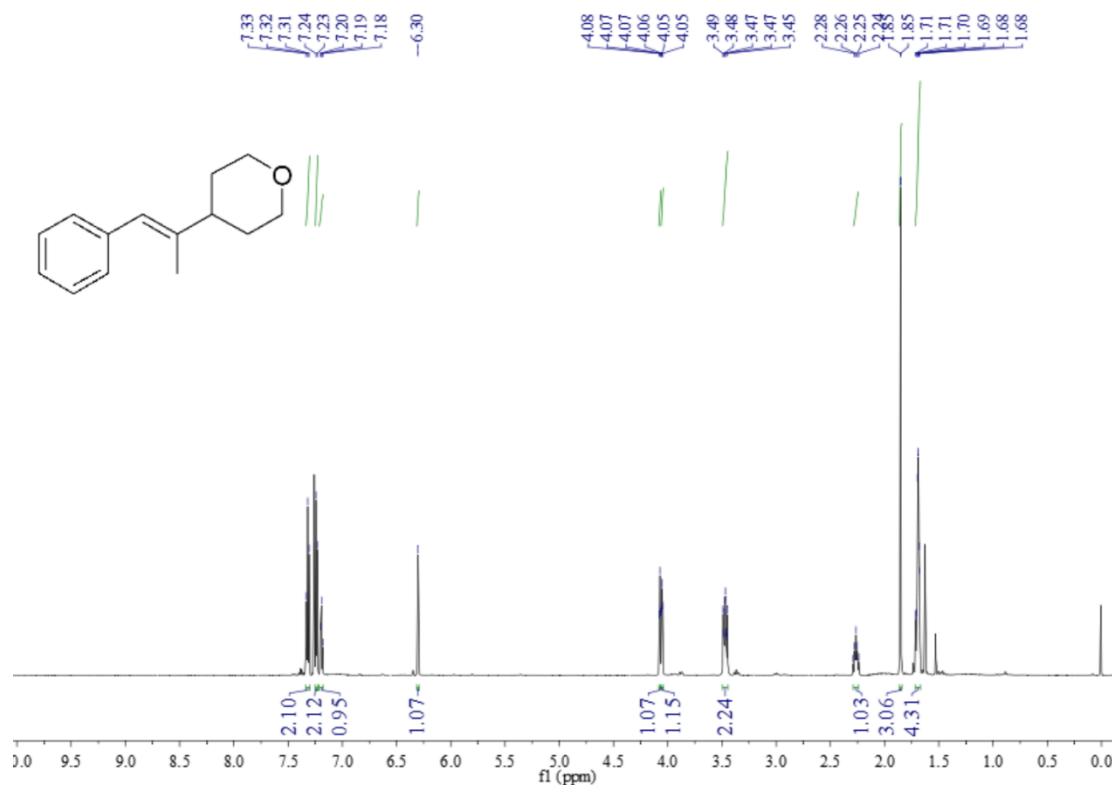
¹H NMR of **3b**



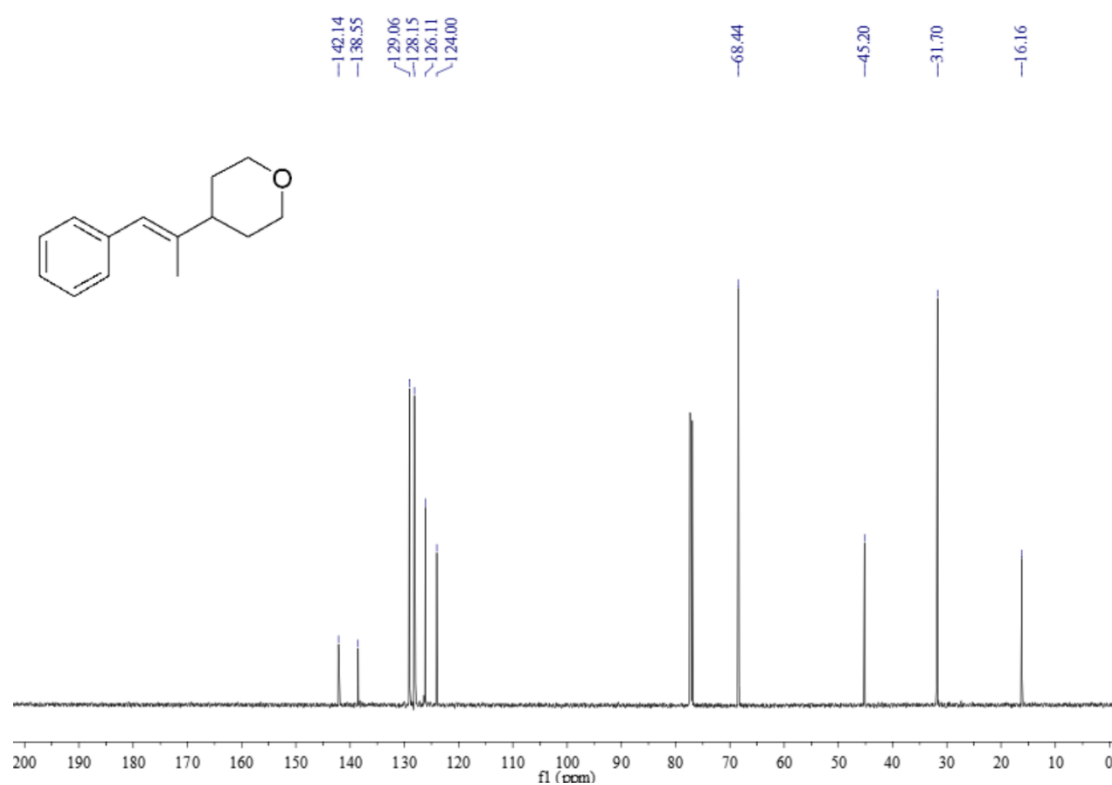
^{13}C NMR of **3b**



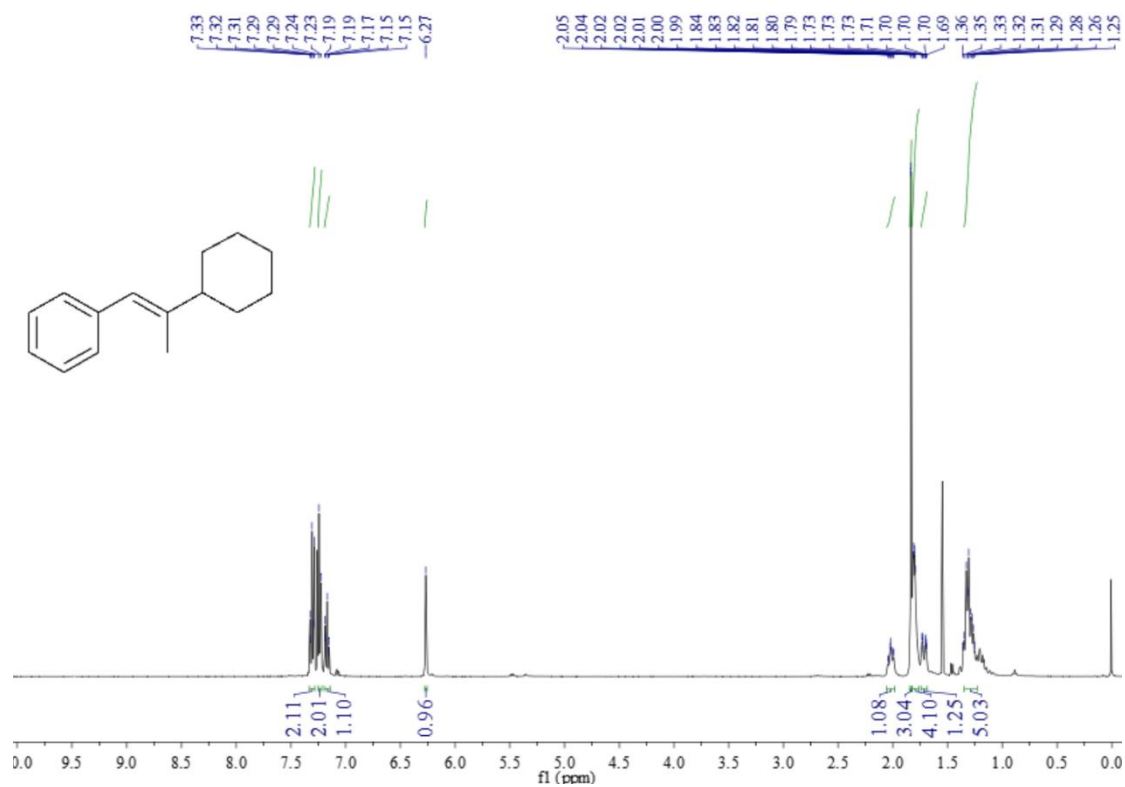
^1H NMR of **3c**



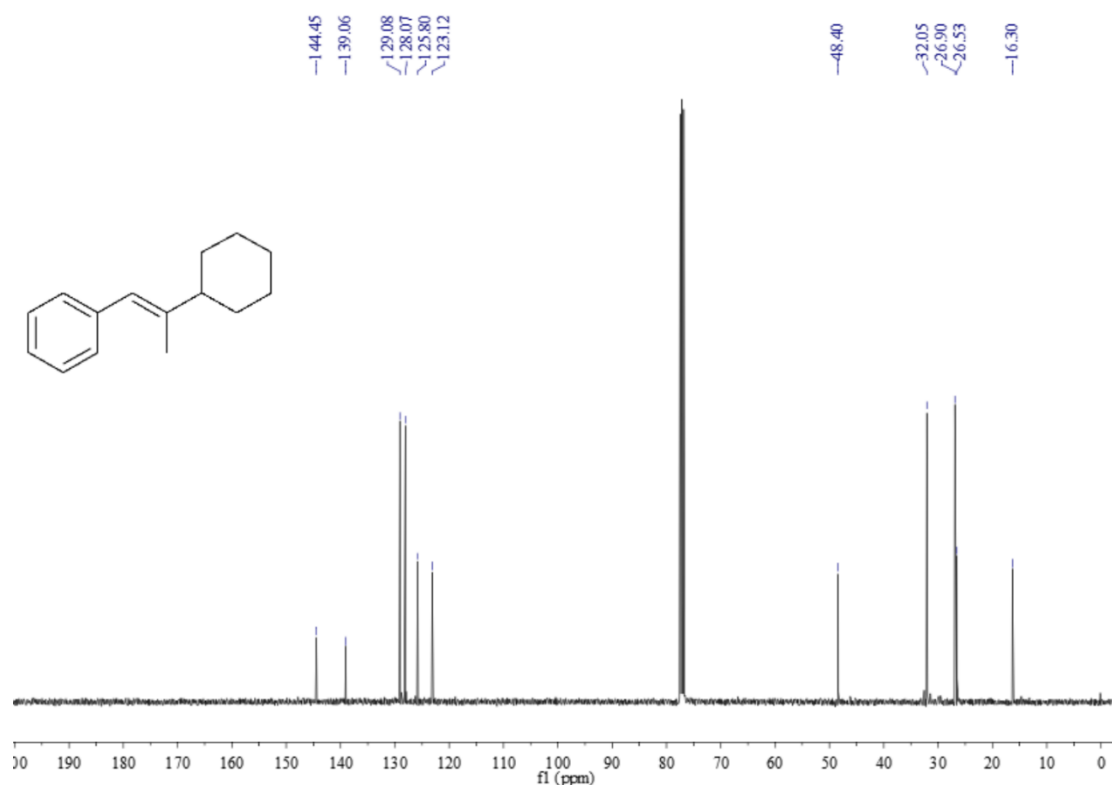
^{13}C NMR of **3c**



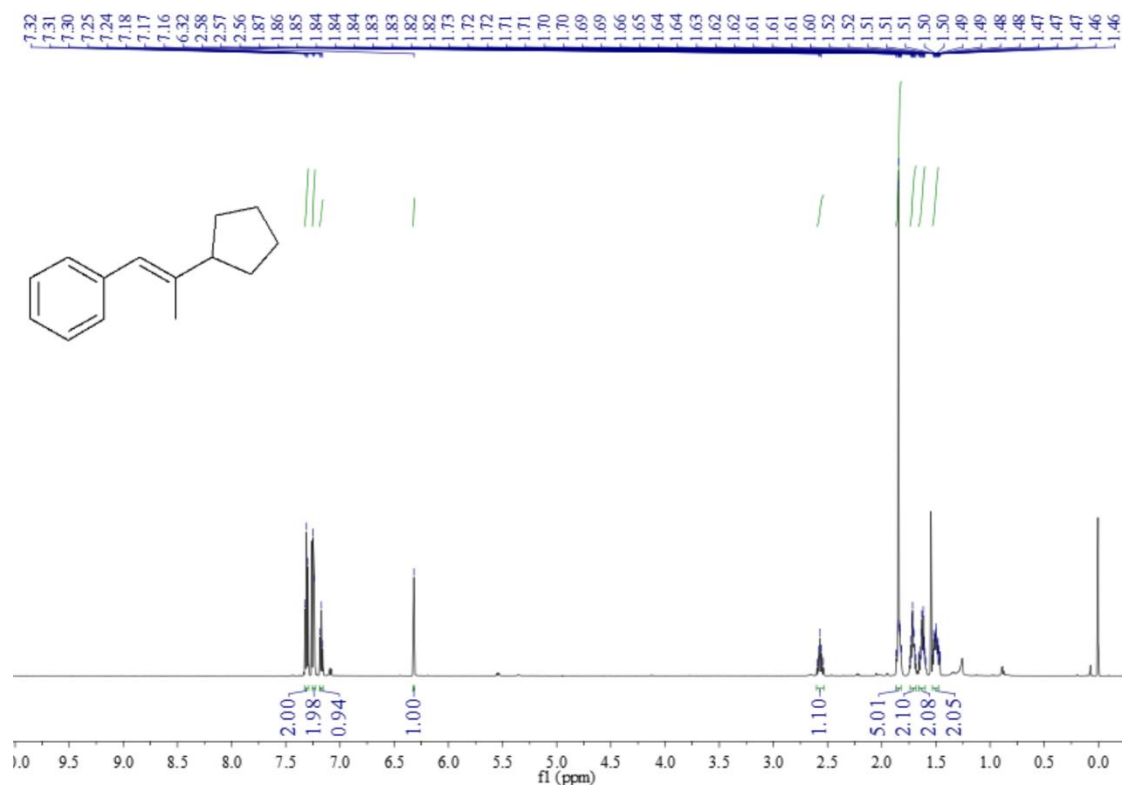
^1H NMR of **3d**



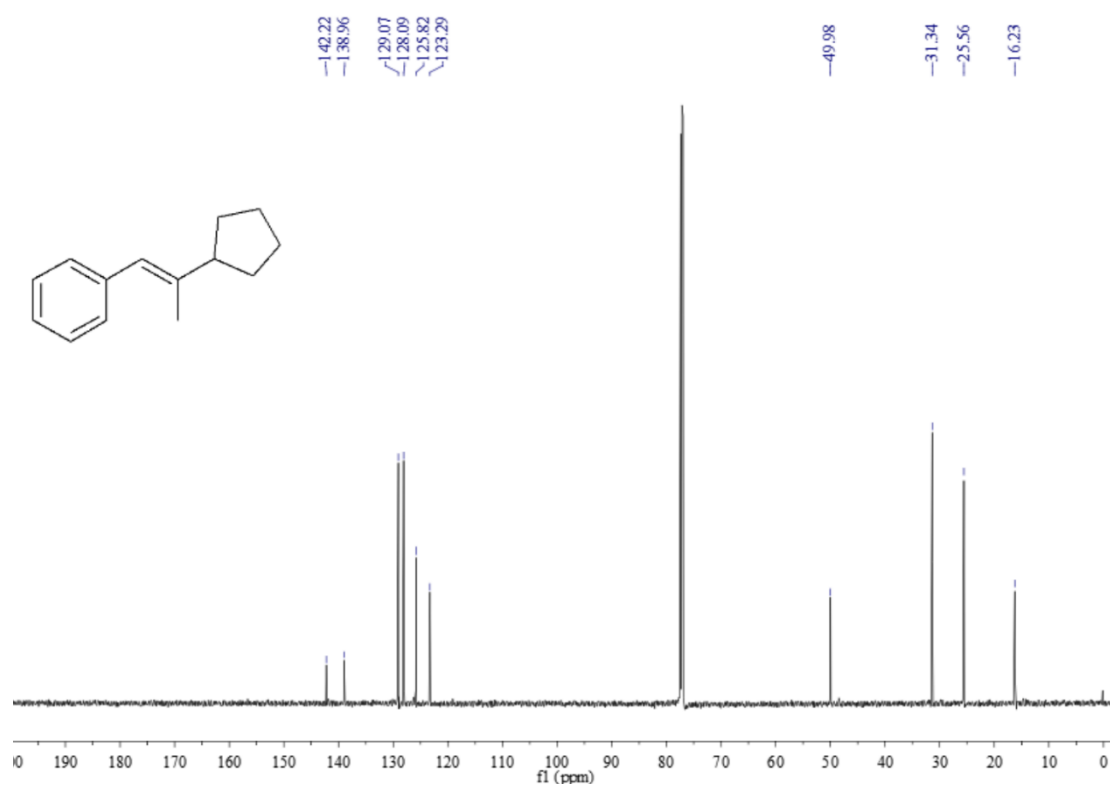
¹³C NMR of **3d**



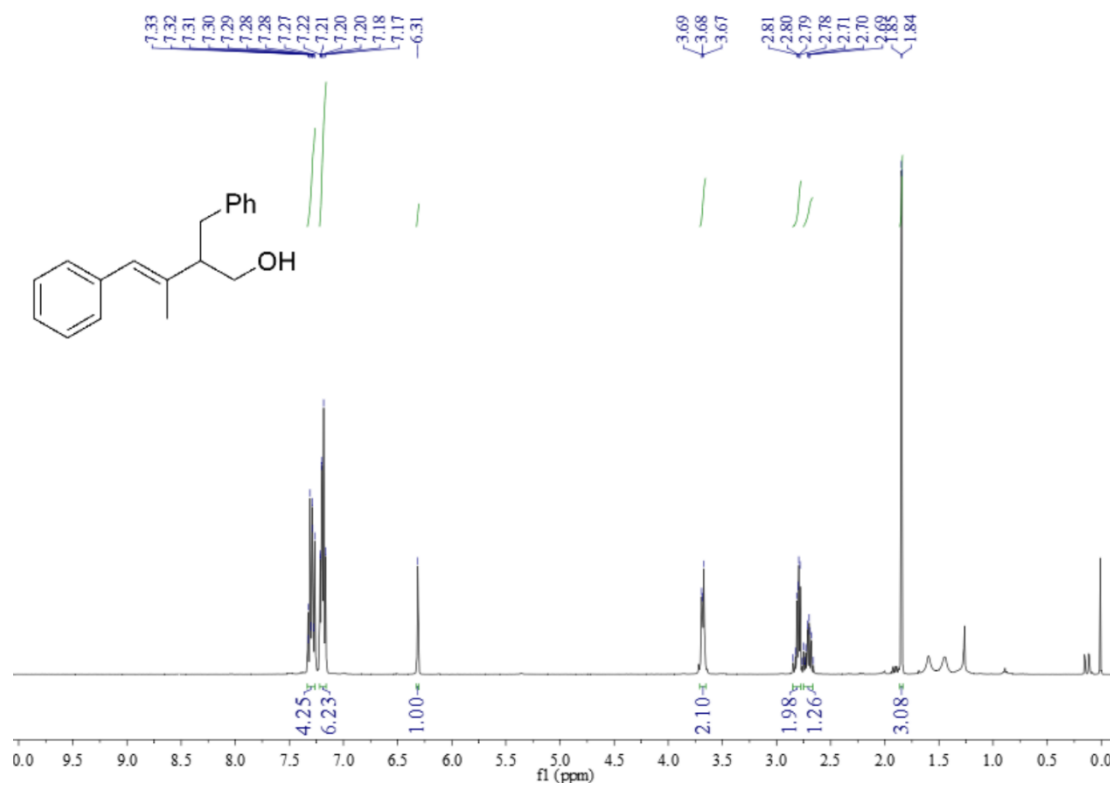
¹H NMR of **3e**



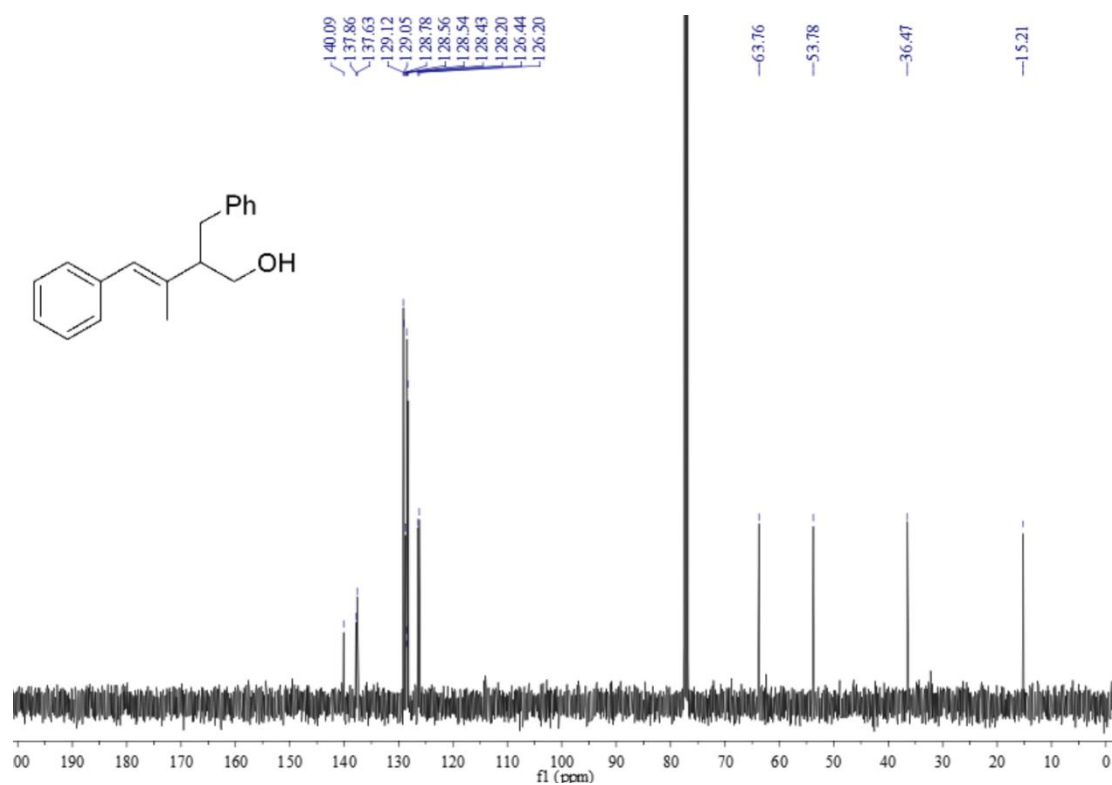
^{13}C NMR of **3e**



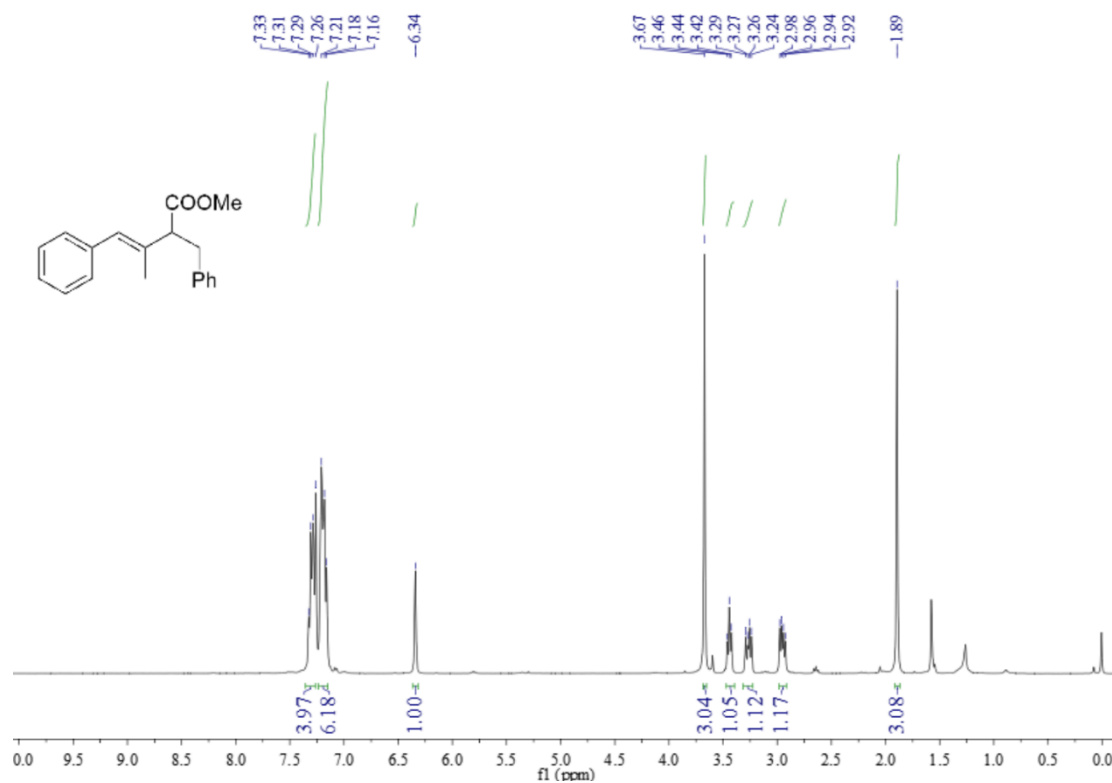
^1H NMR of **3f**



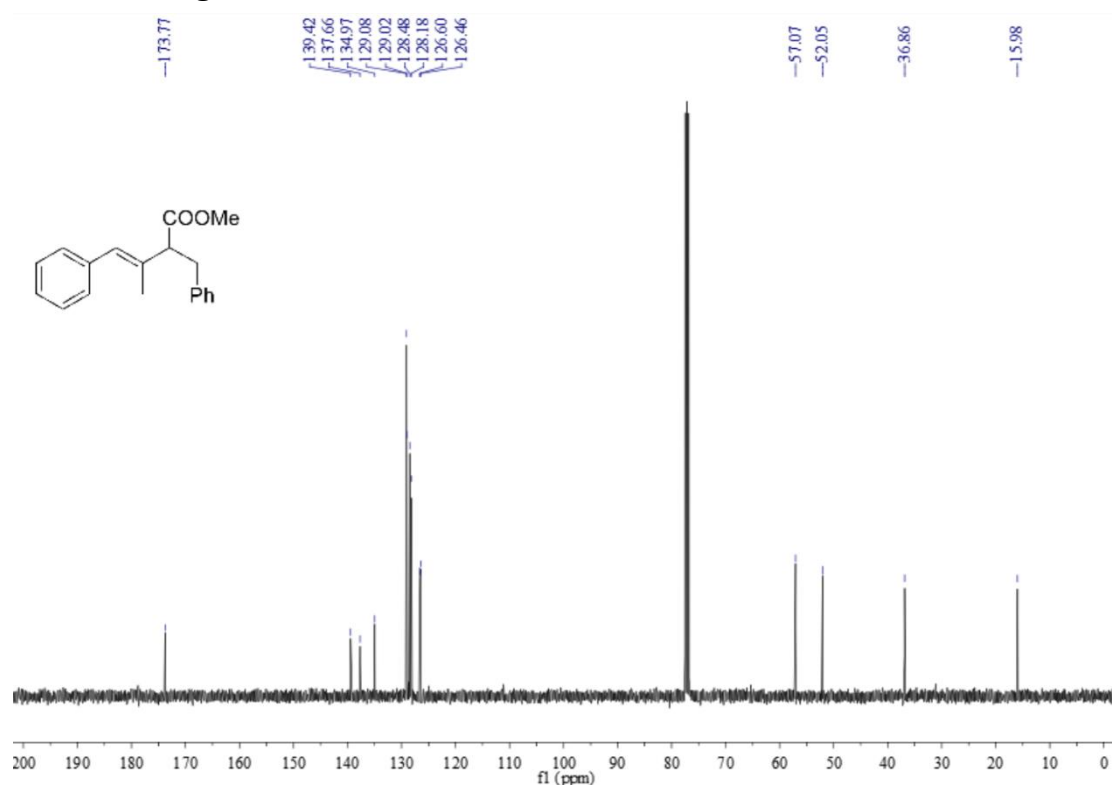
¹³C NMR of **3f**



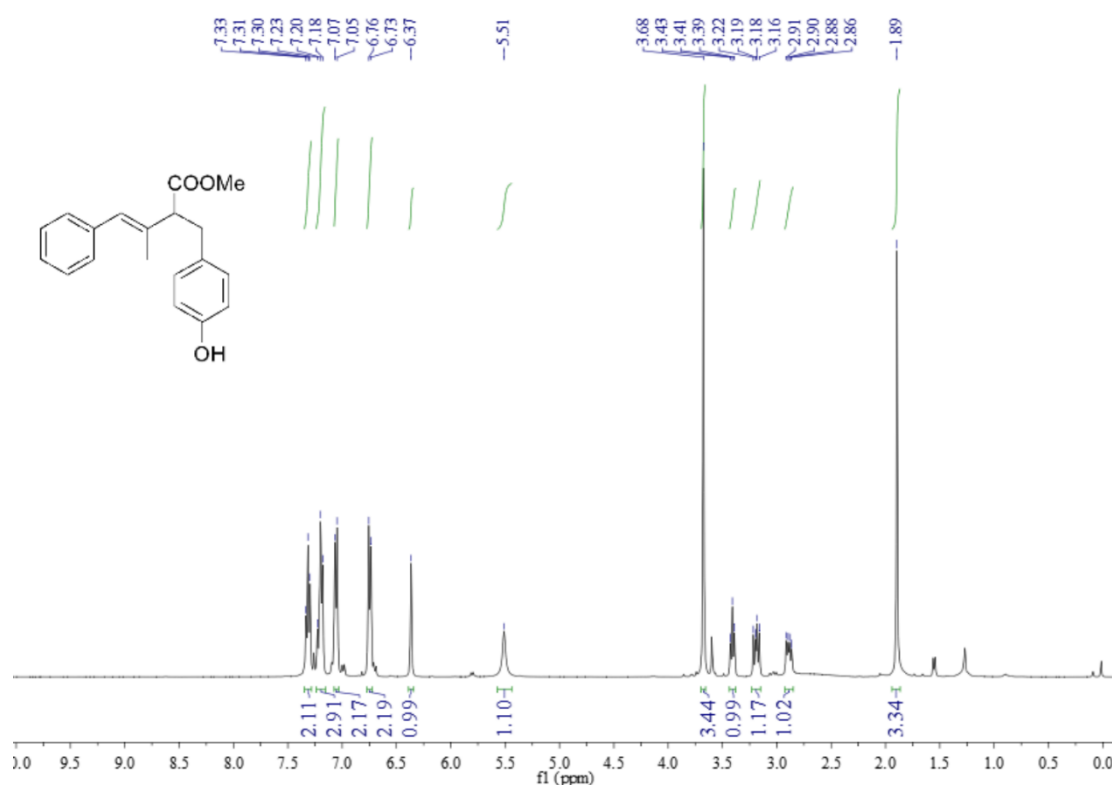
¹H NMR of **3g**



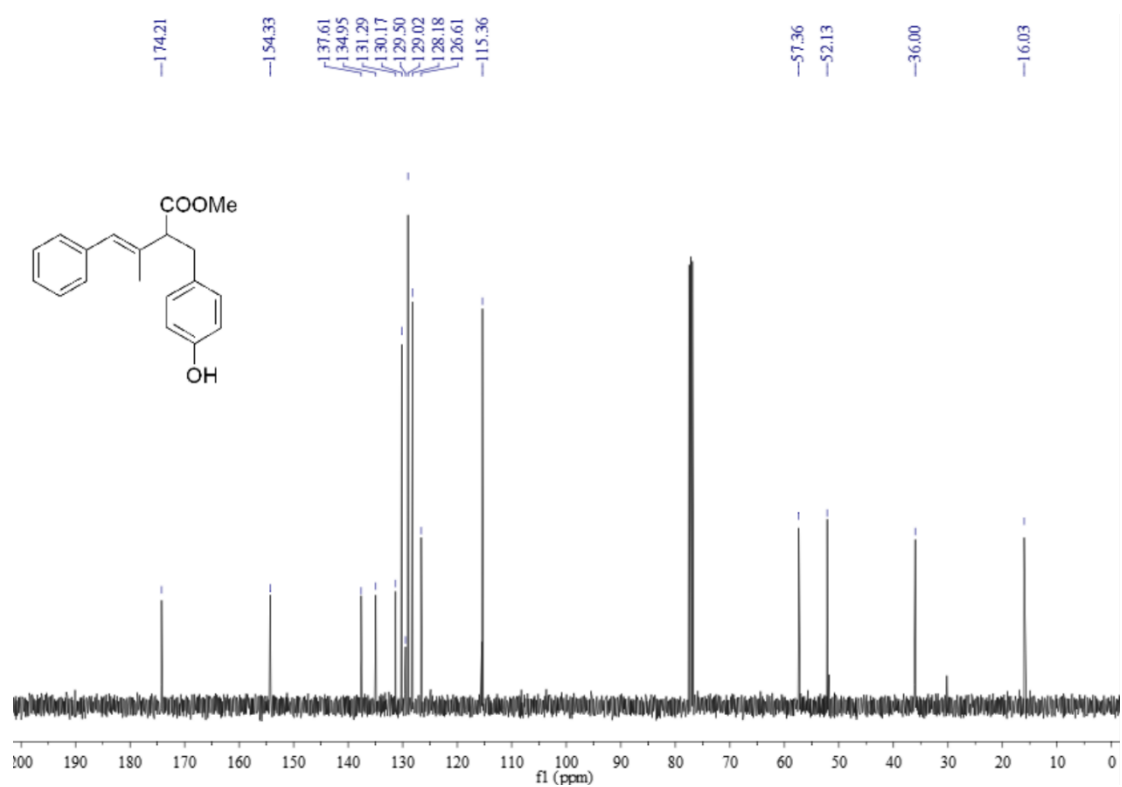
^{13}C NMR of **3g**



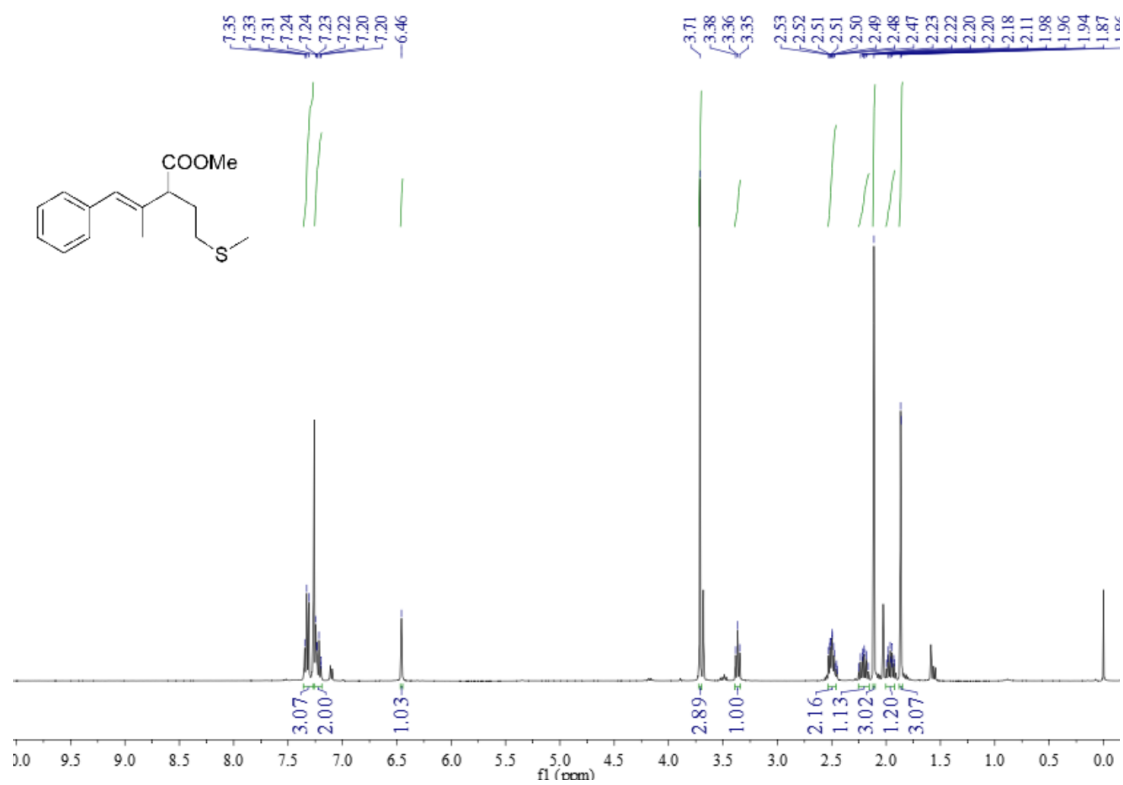
^1H NMR of **3h**



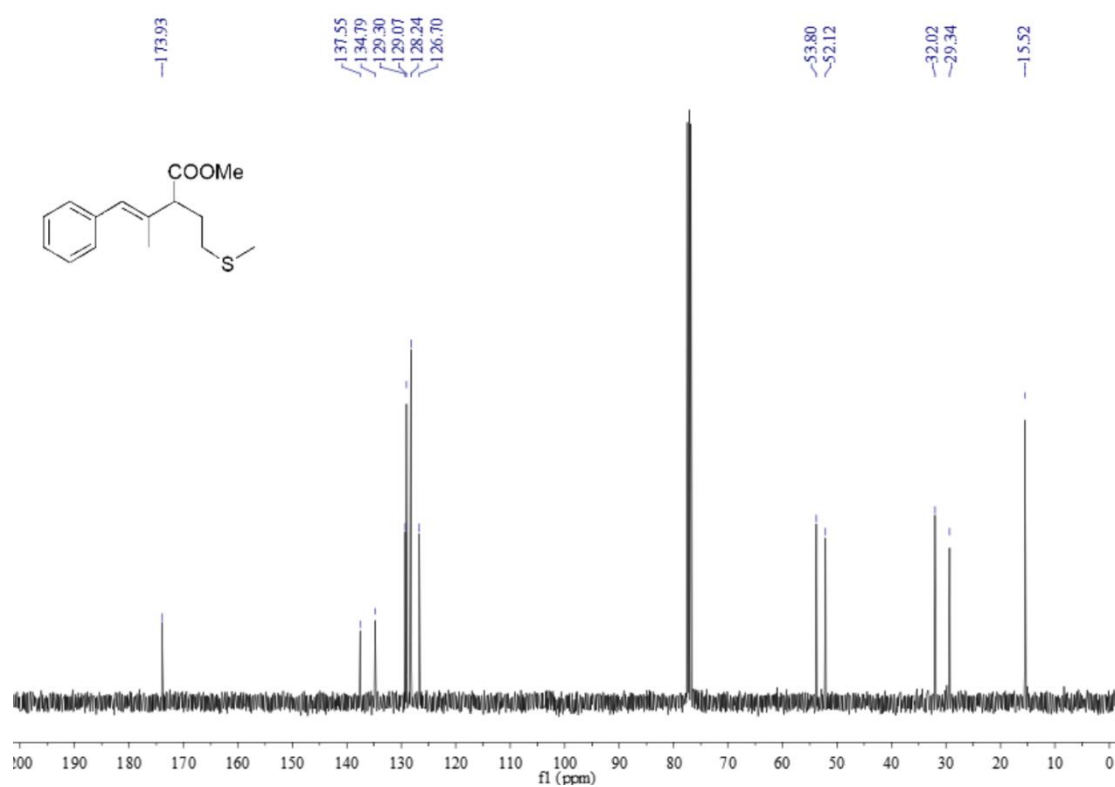
¹³C NMR of **3h**



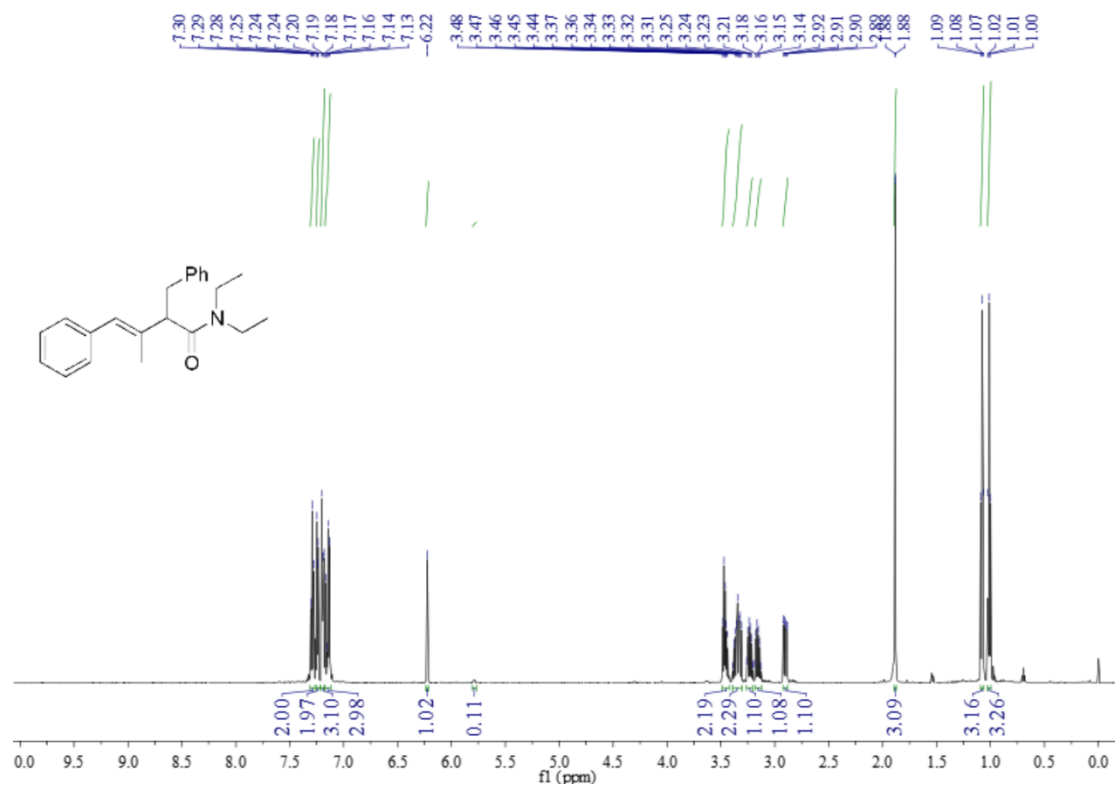
¹H NMR of **3i**



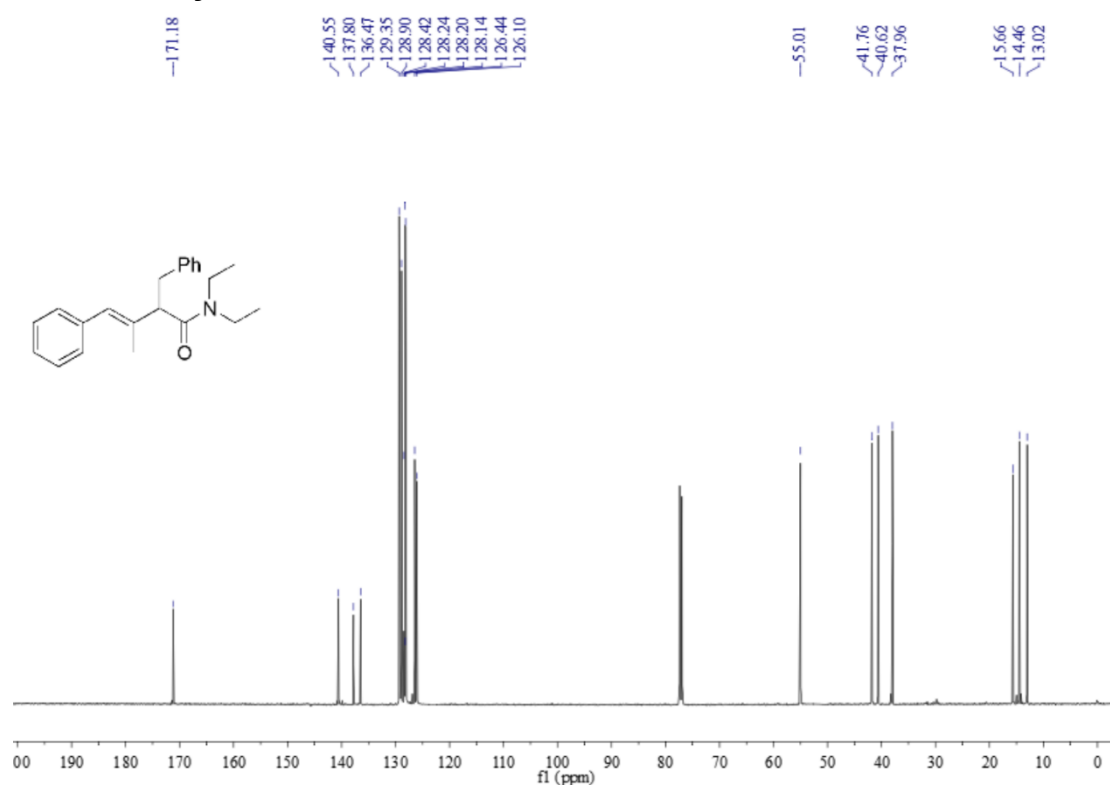
¹³C NMR of **3i**



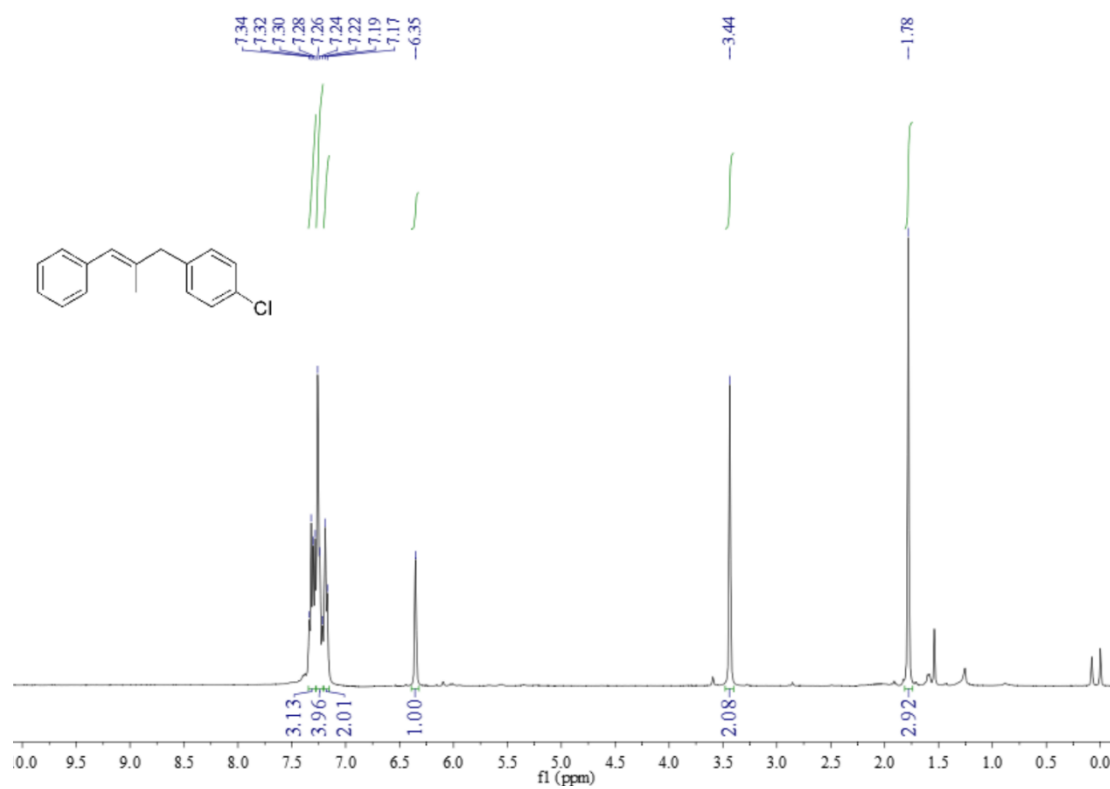
¹H NMR of **3j**



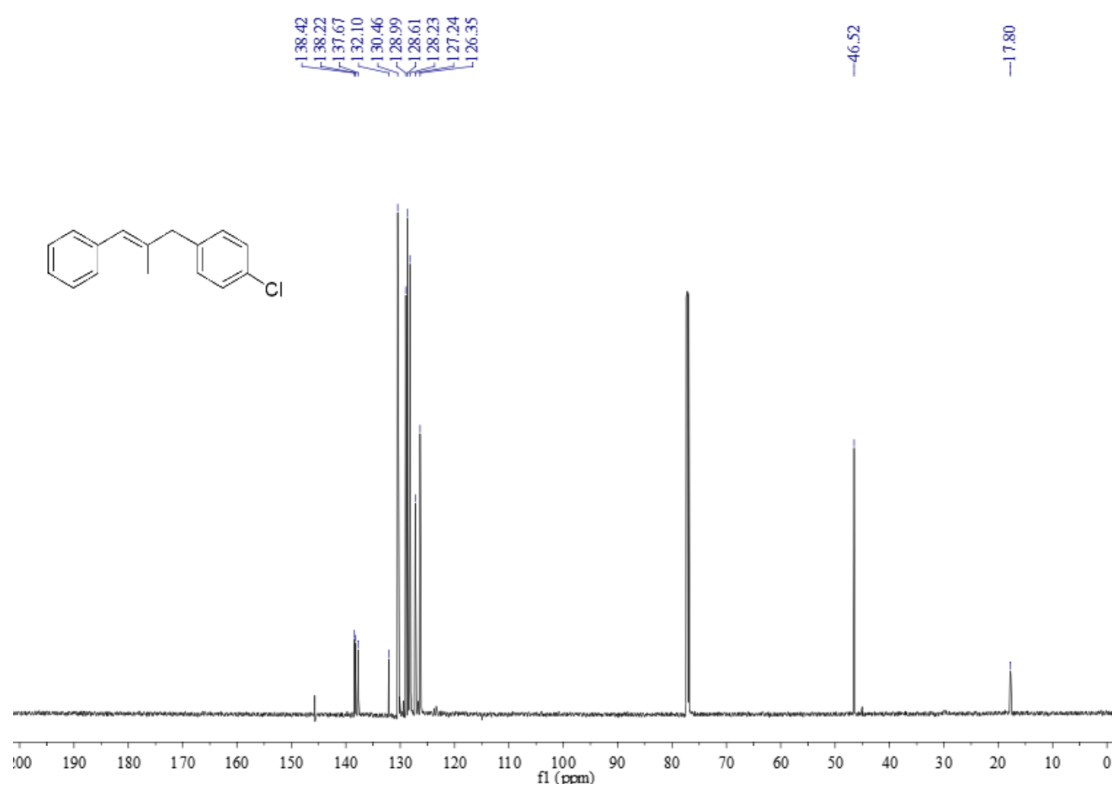
¹³C NMR of **3j**



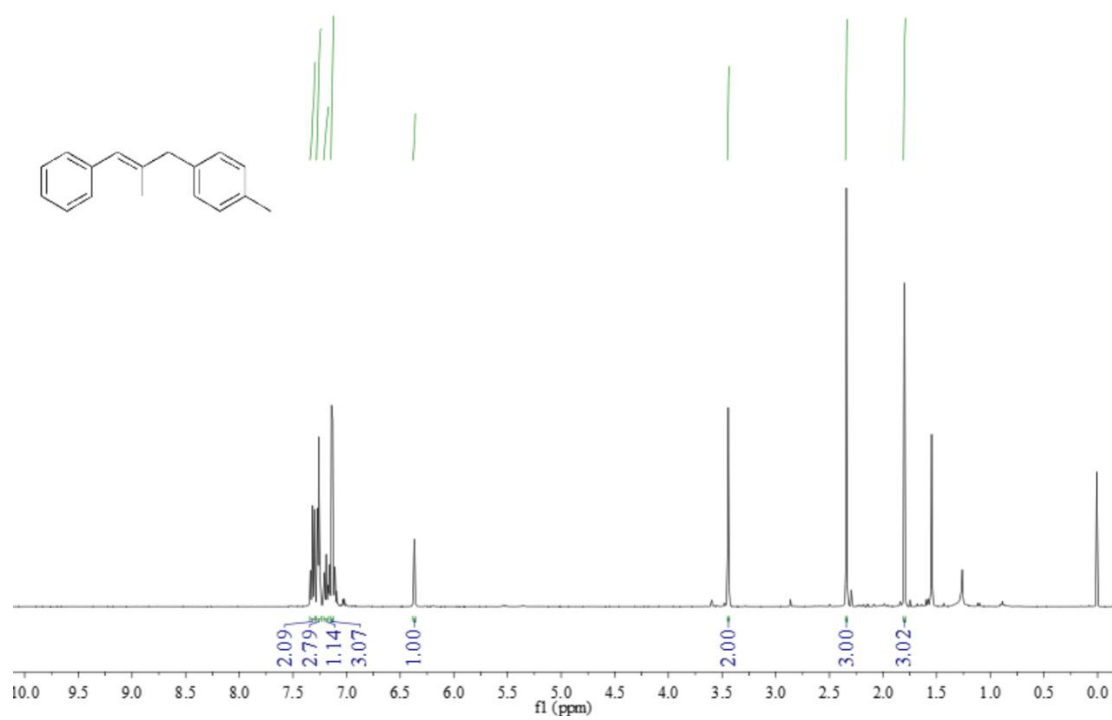
¹H NMR of **3k**



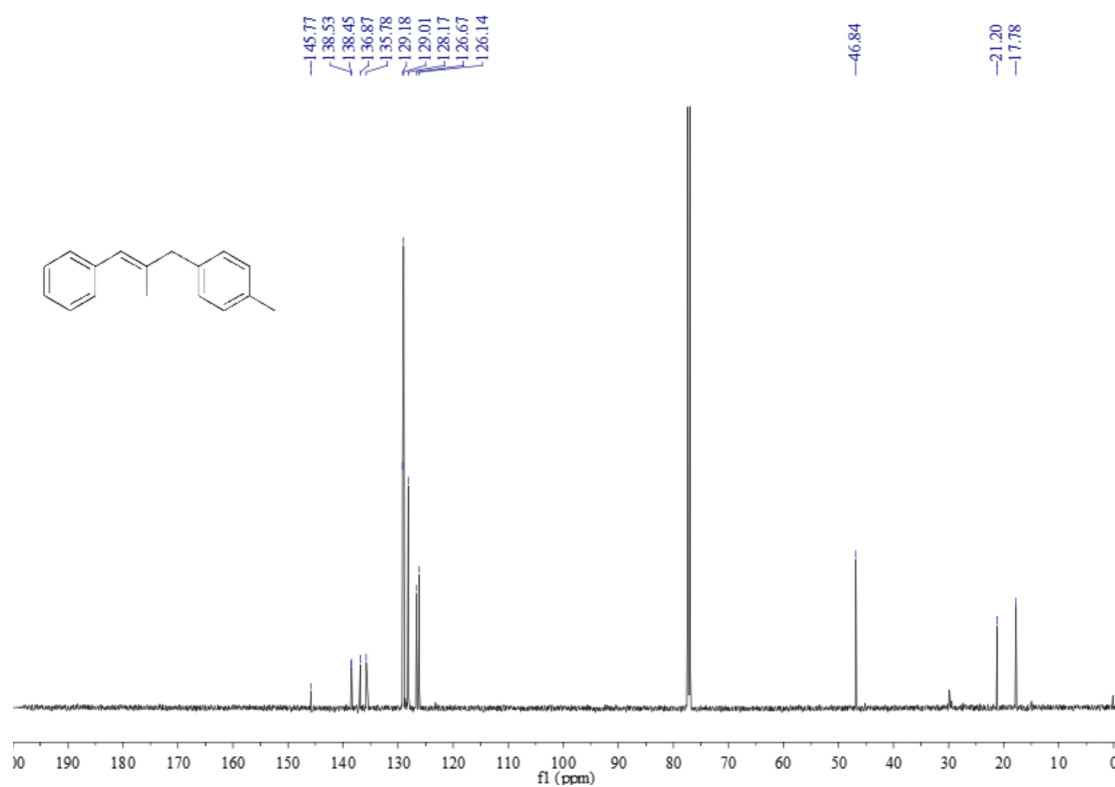
¹³C NMR of **3k**



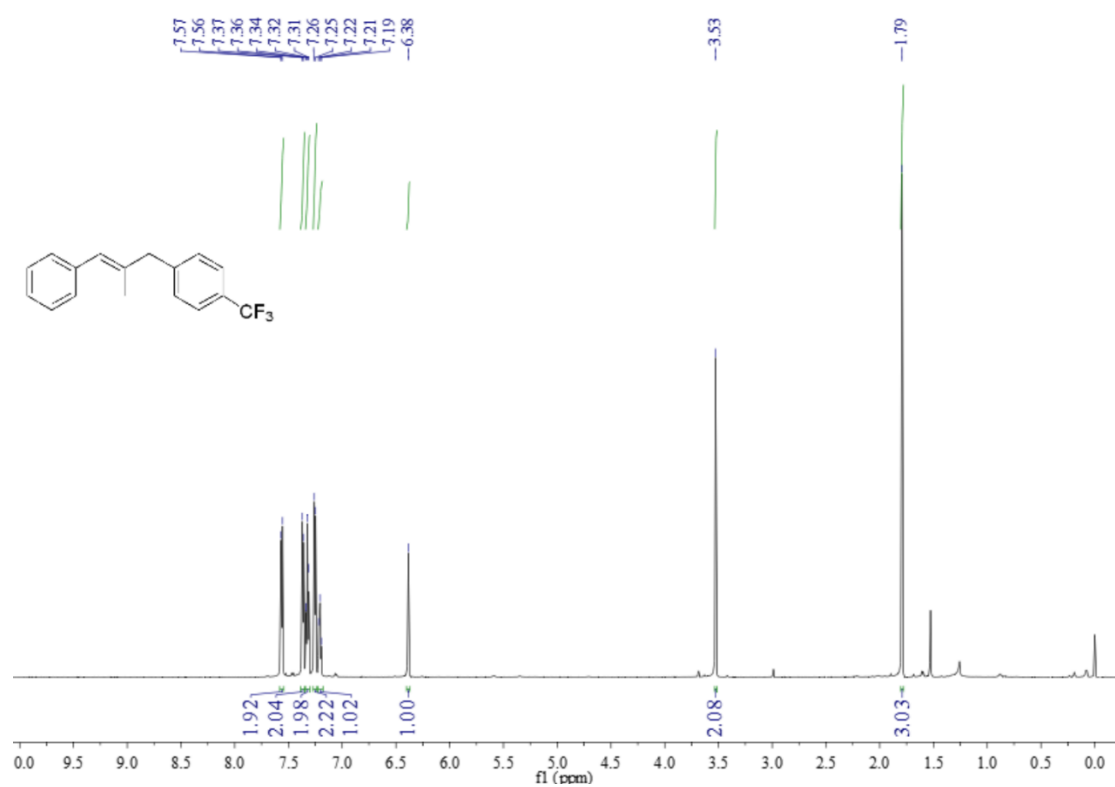
¹H NMR of **3l**



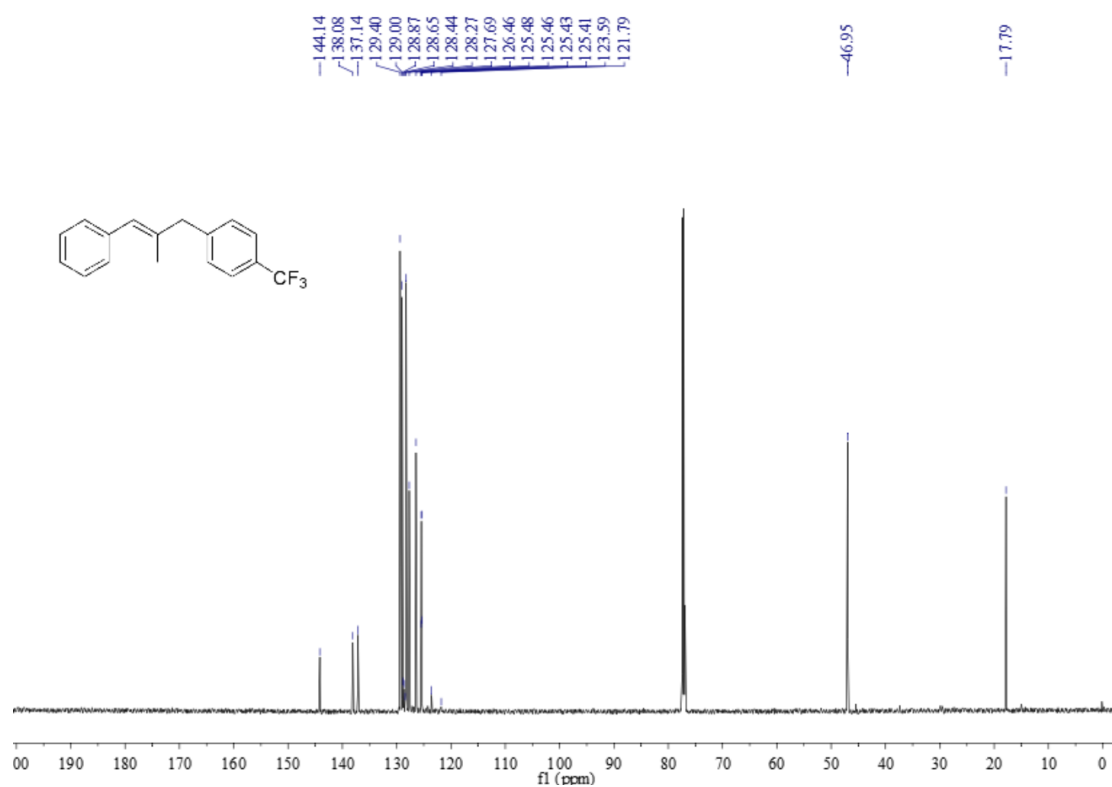
¹³C NMR of **3l**



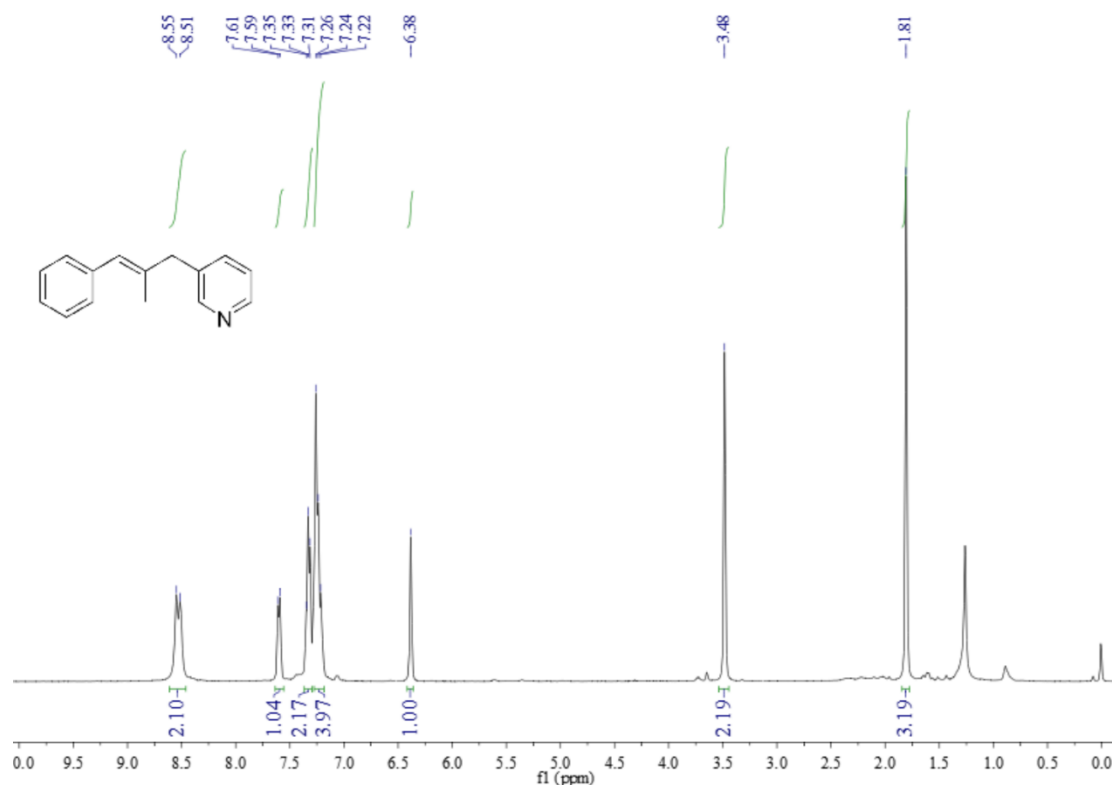
¹H NMR of **3m**



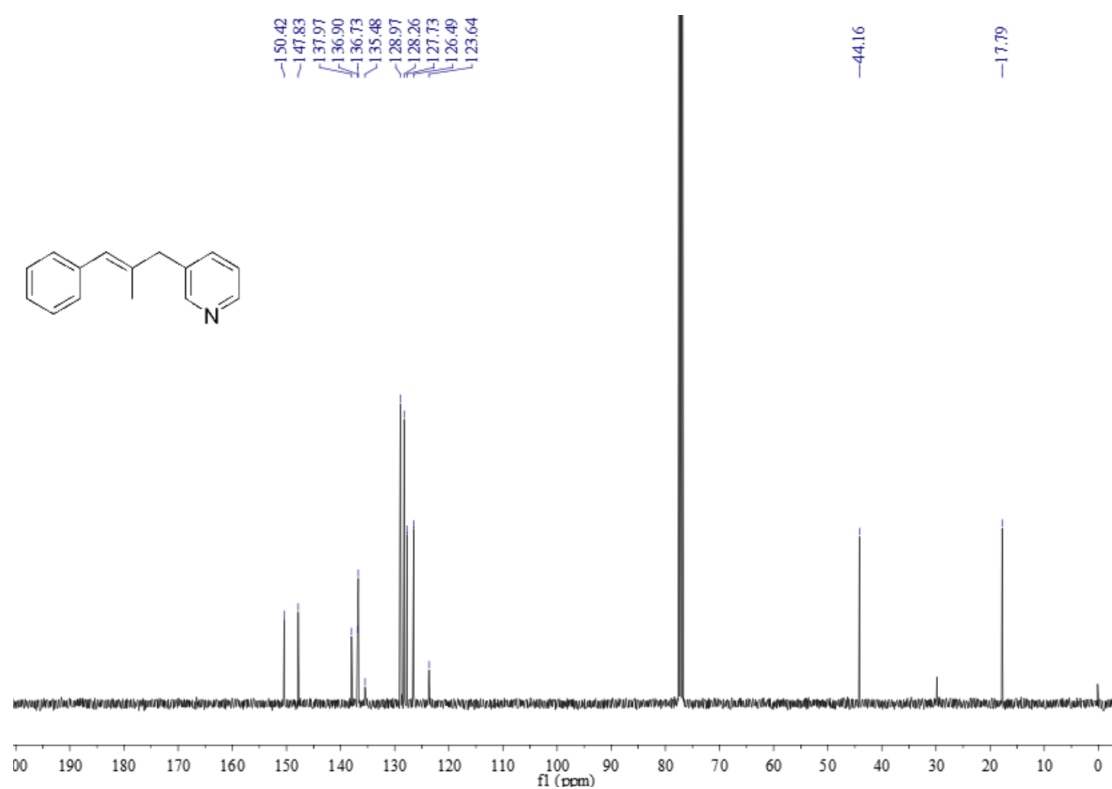
¹³C NMR of **3m**



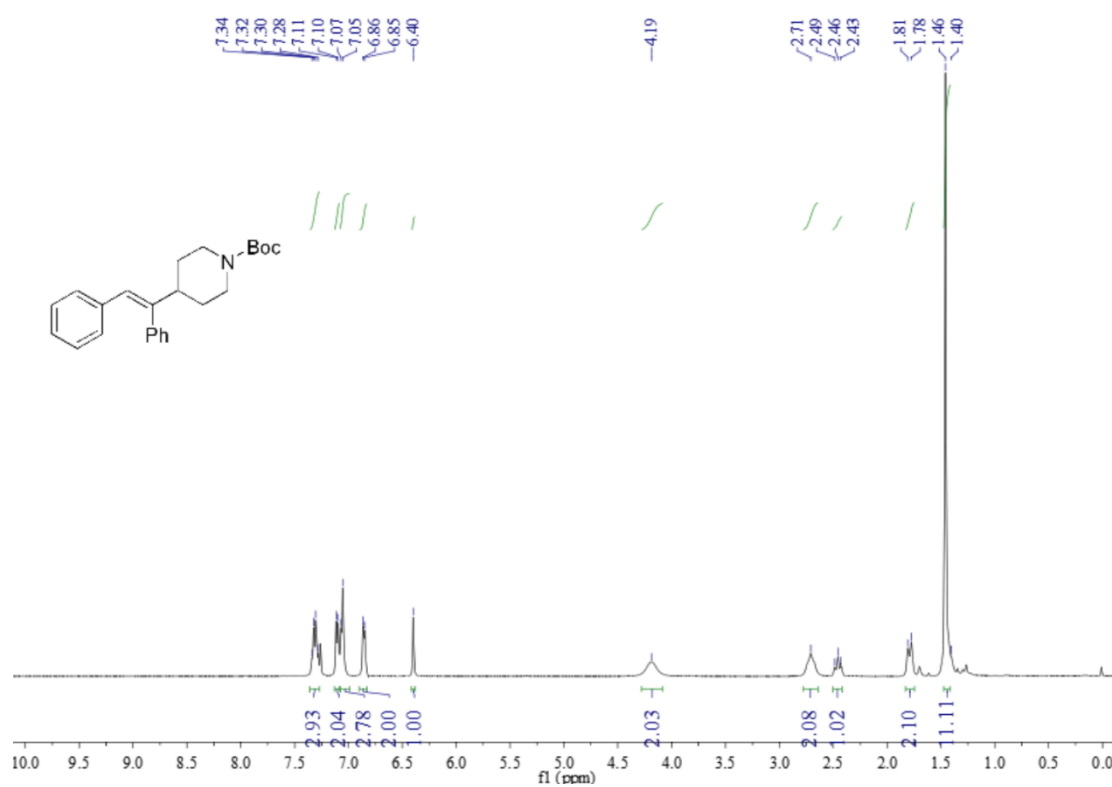
¹H NMR of **3n**



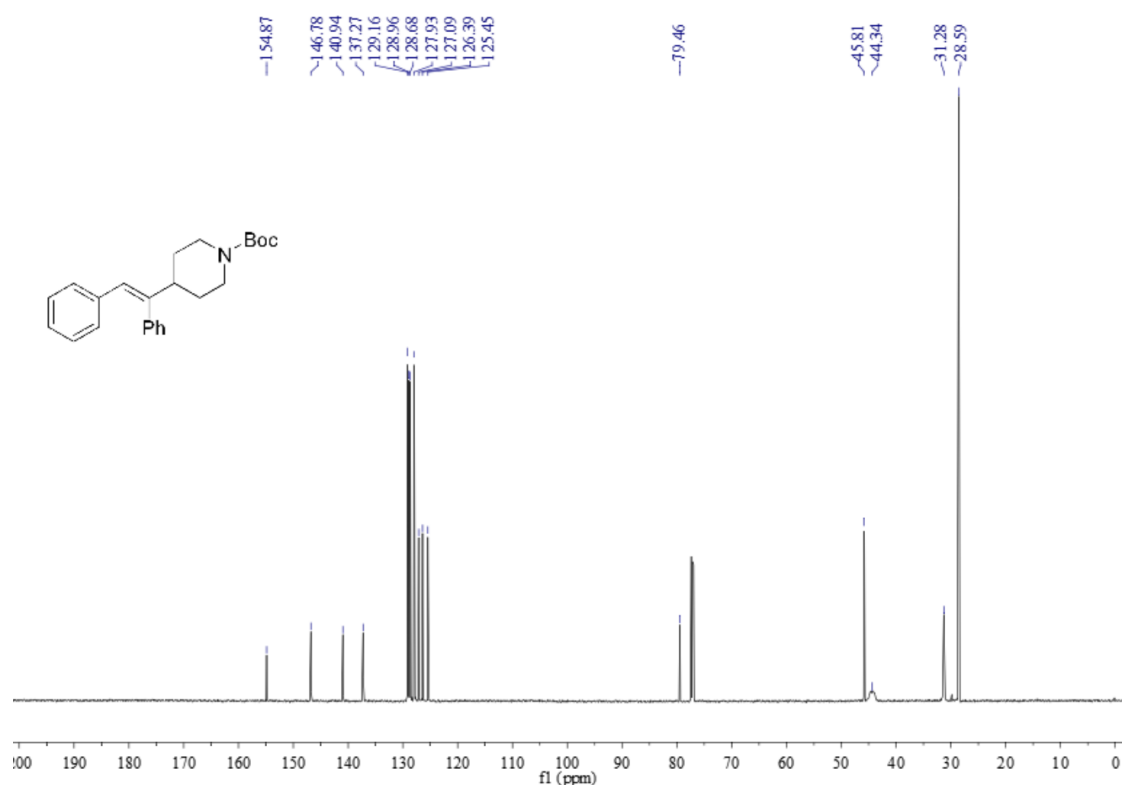
^{13}C NMR of **3n**



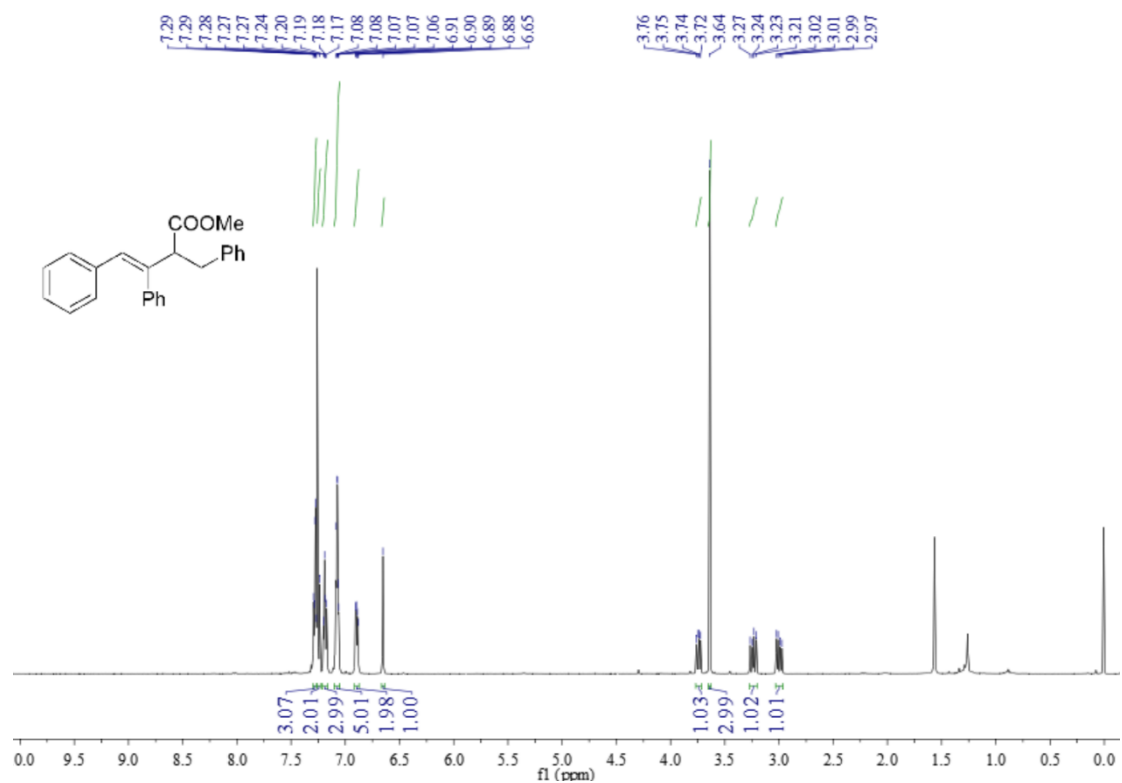
^1H NMR of **3o**



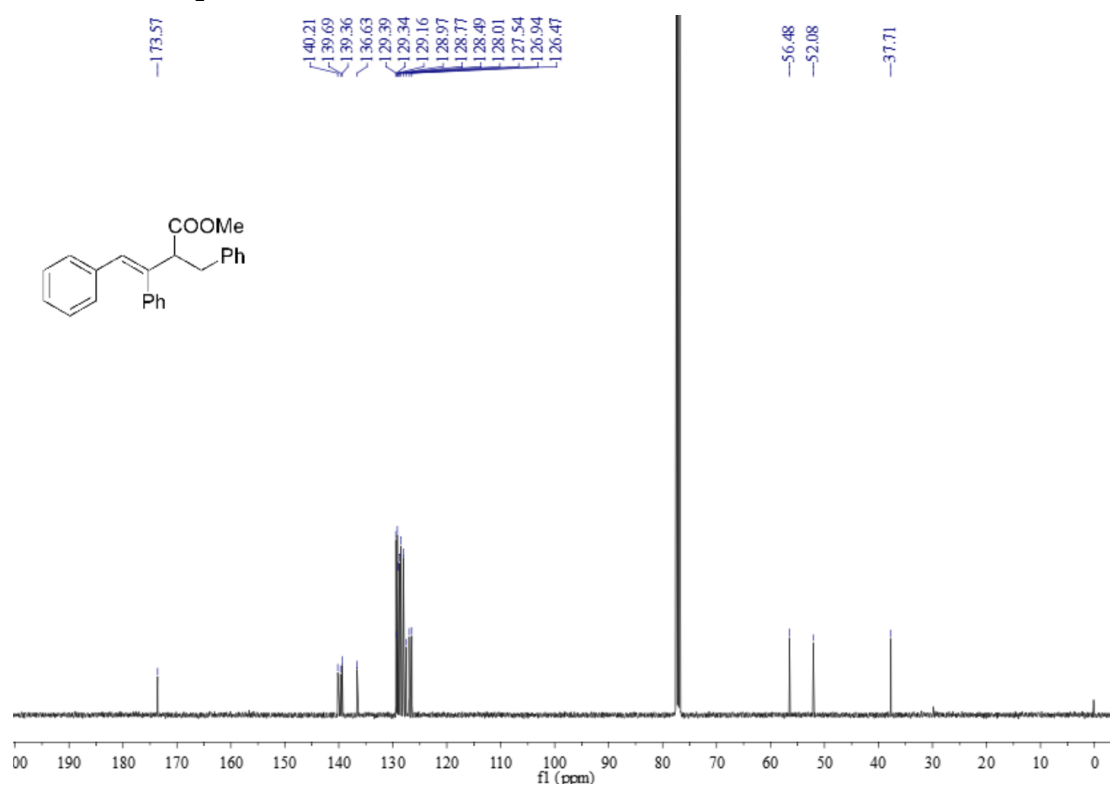
¹³C NMR of **3o**



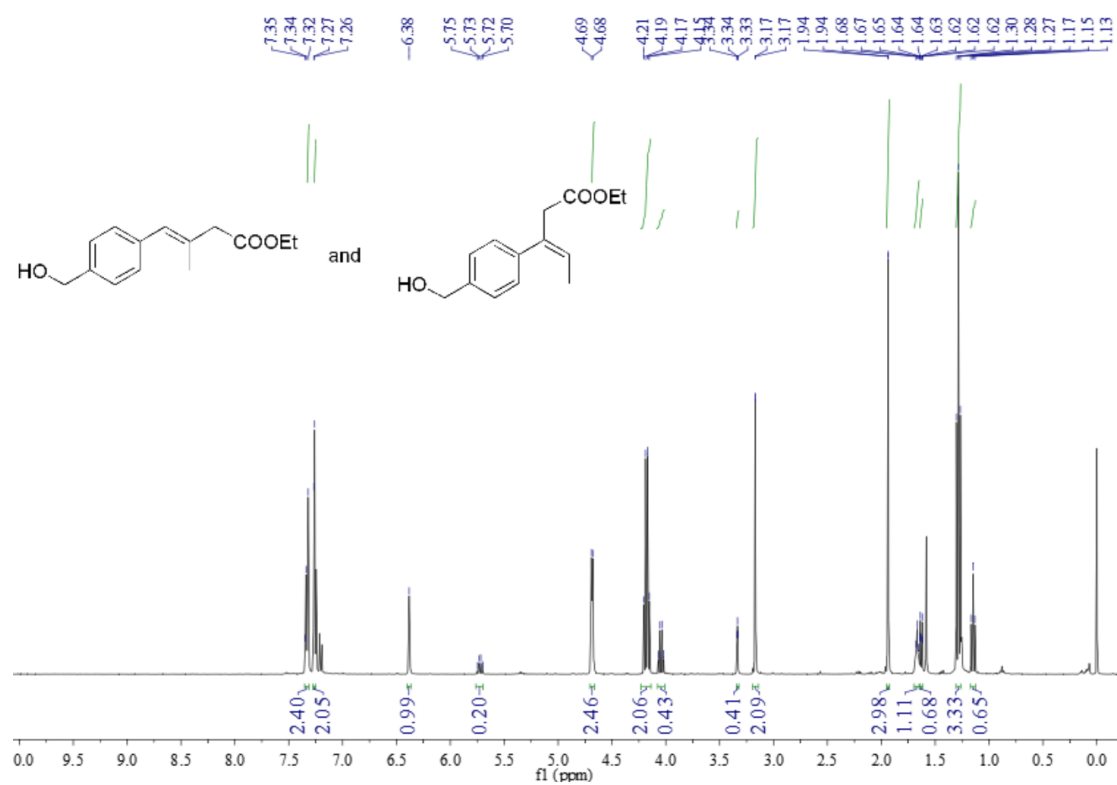
¹H NMR of **3p**



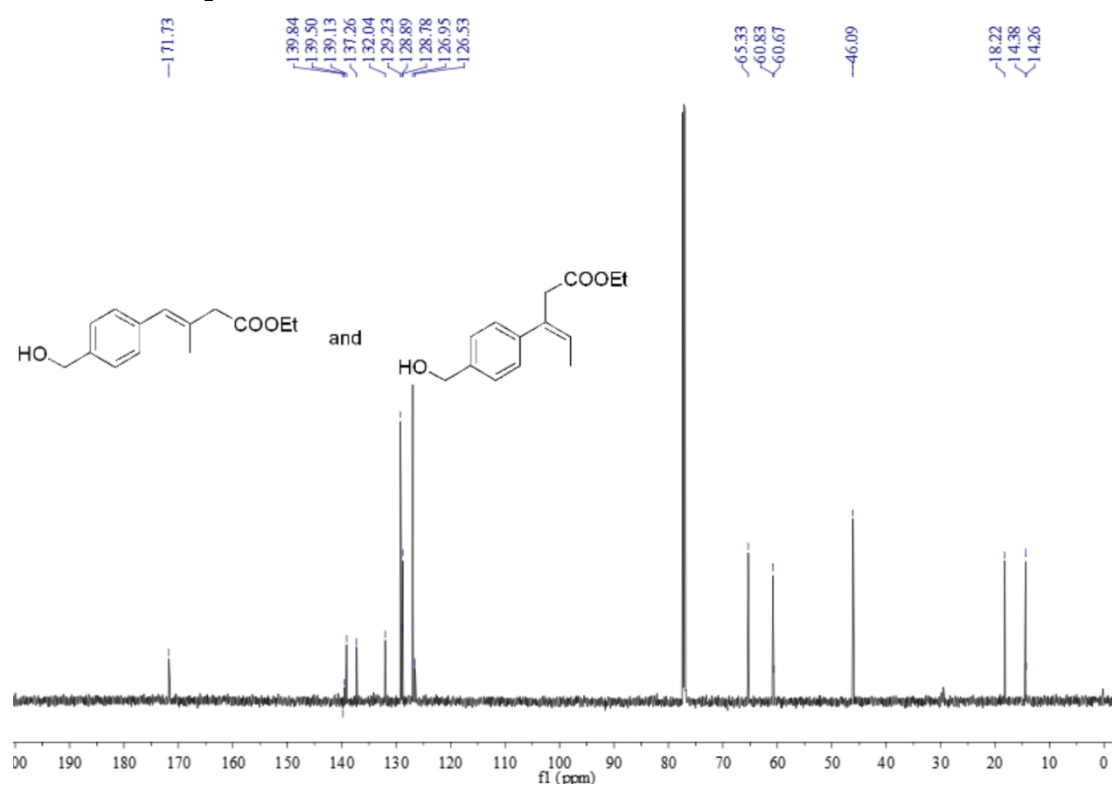
¹³C NMR of **3p**



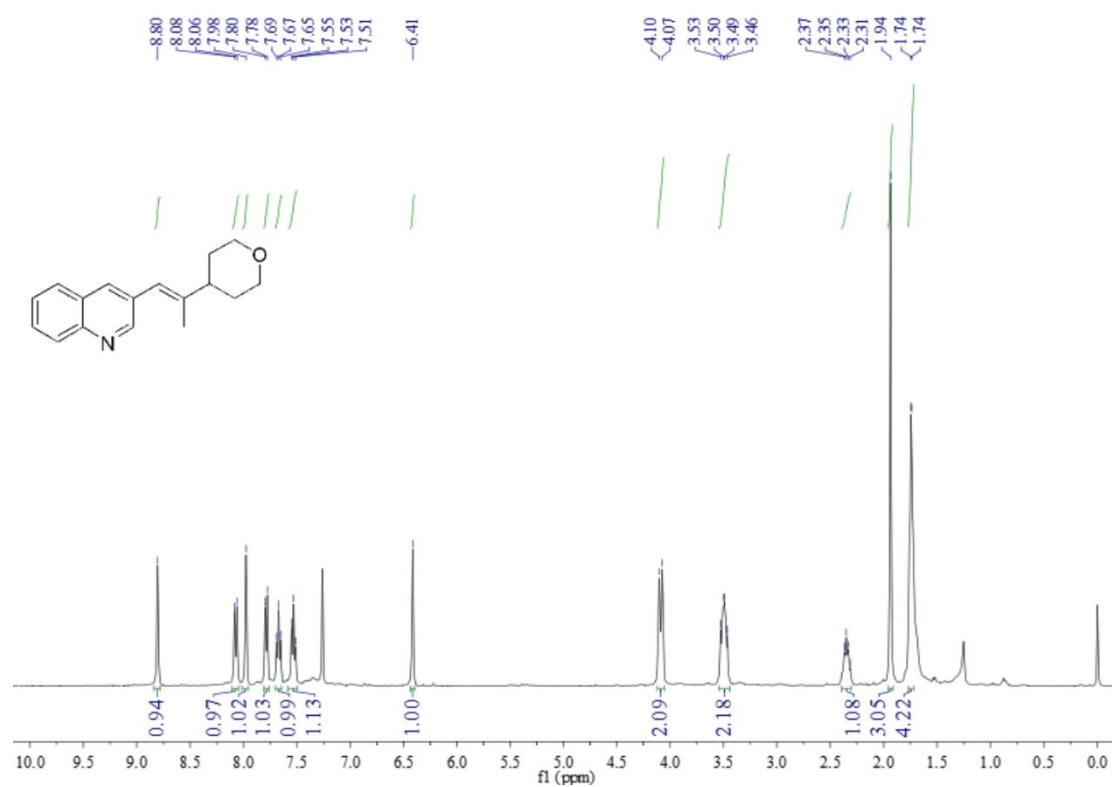
¹H NMR of **3q**



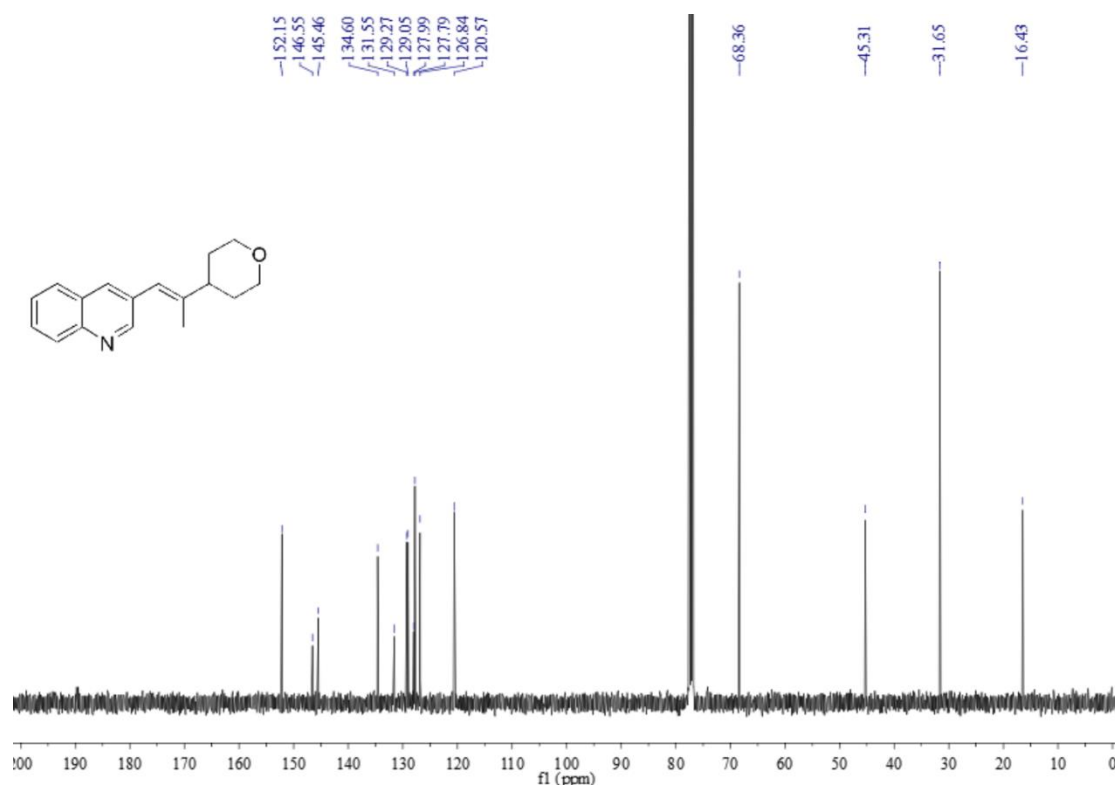
¹³C NMR of **3q**



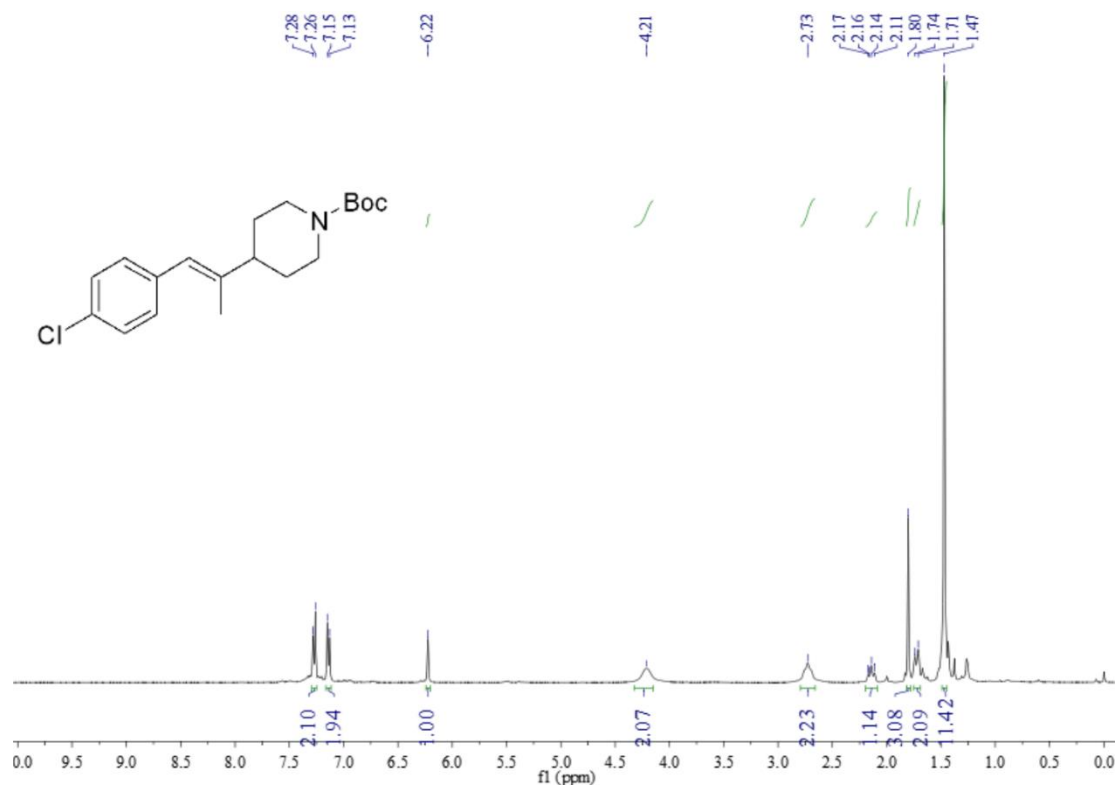
¹H NMR of **3r**



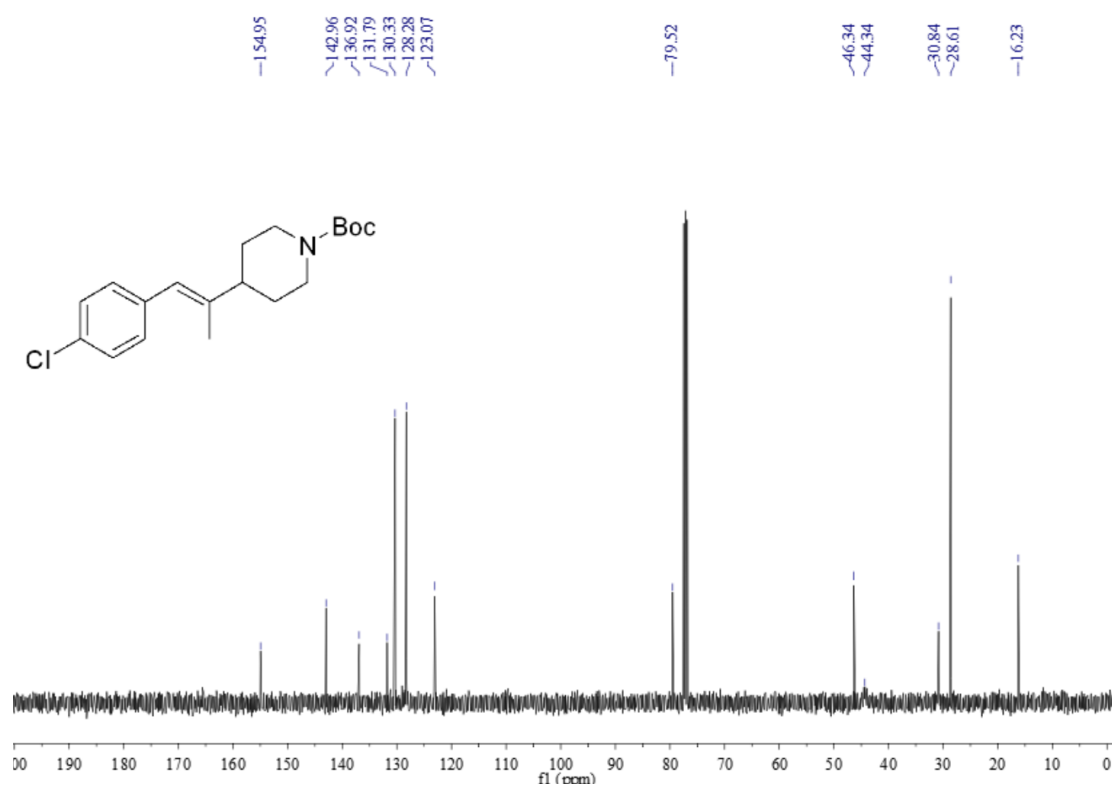
¹³C NMR of **3r**



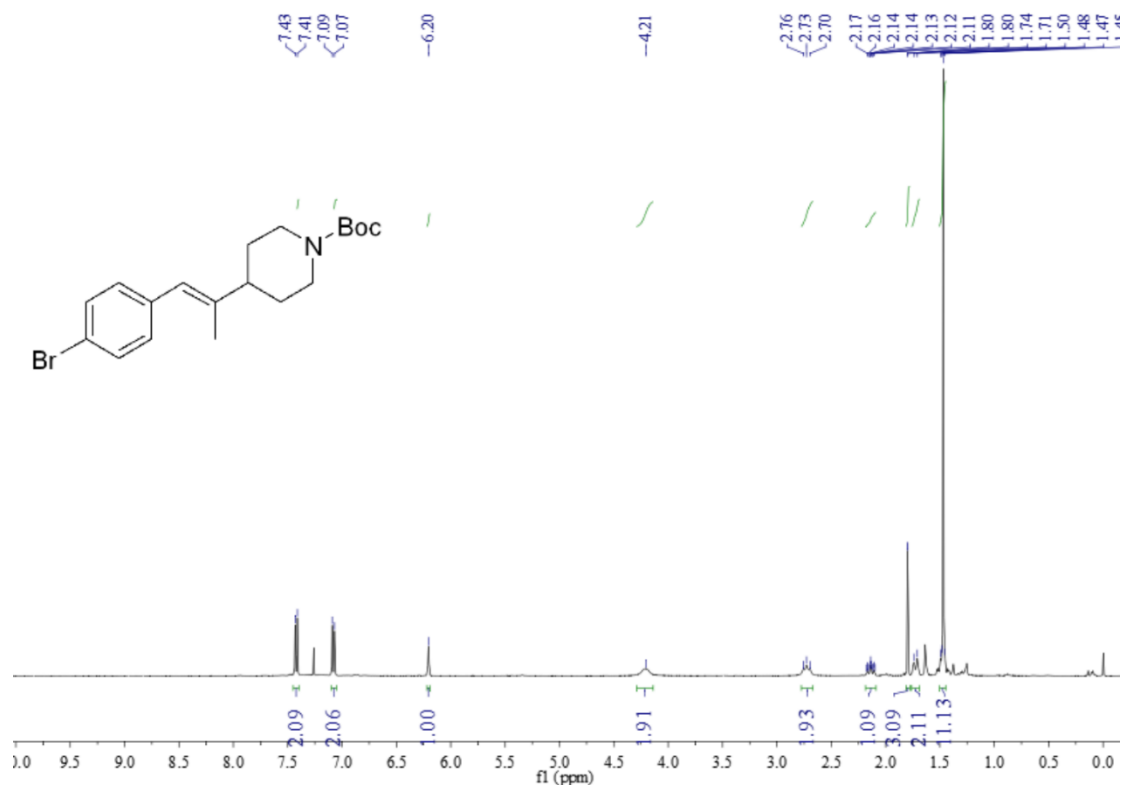
¹H NMR of **4a**



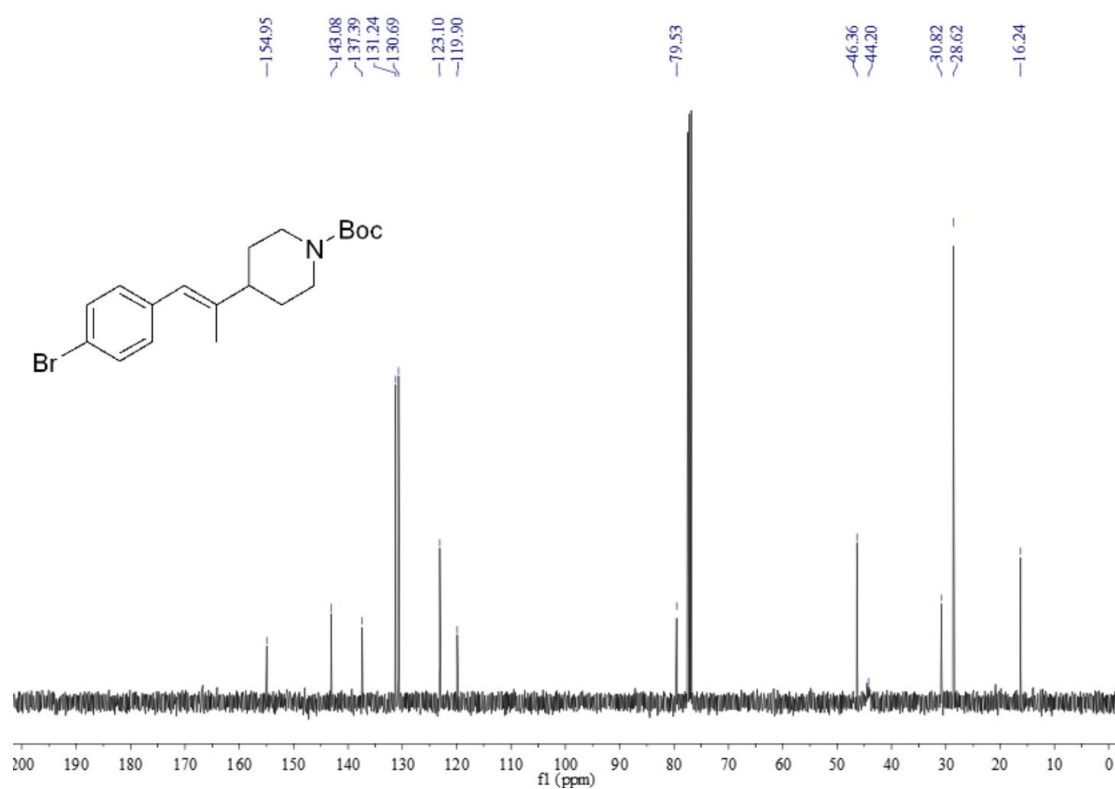
^{13}C NMR of **4a**



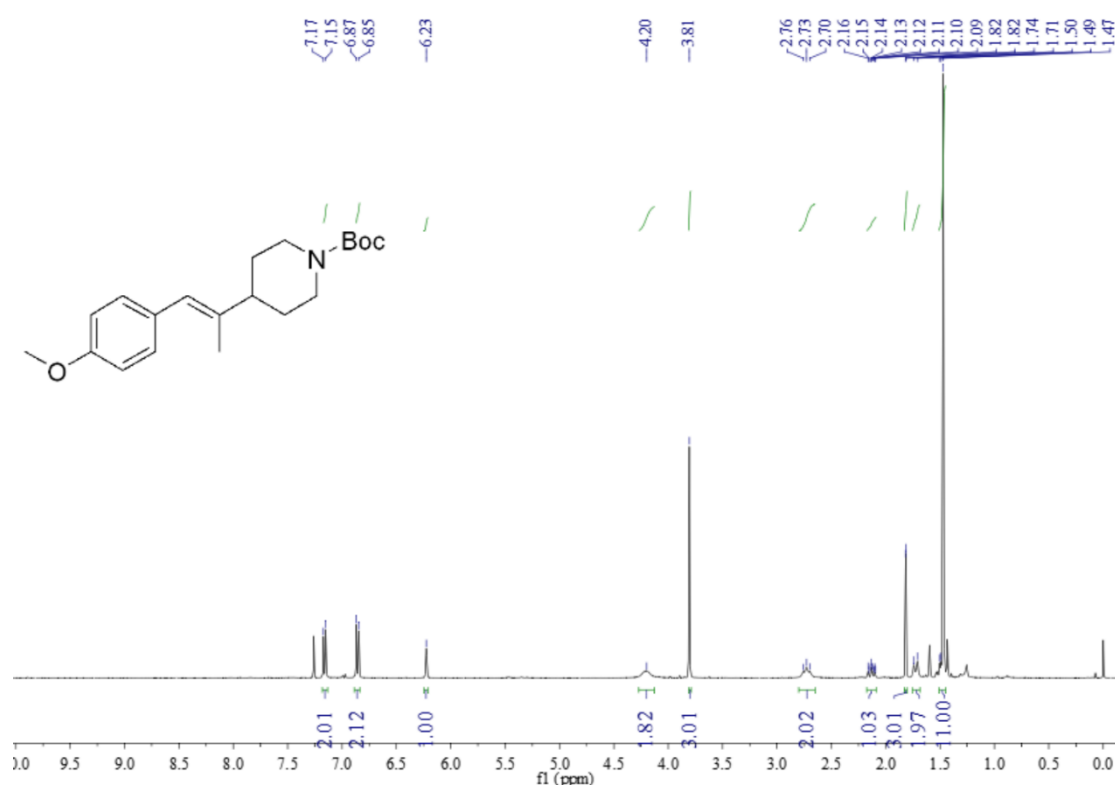
^1H NMR of **4b**



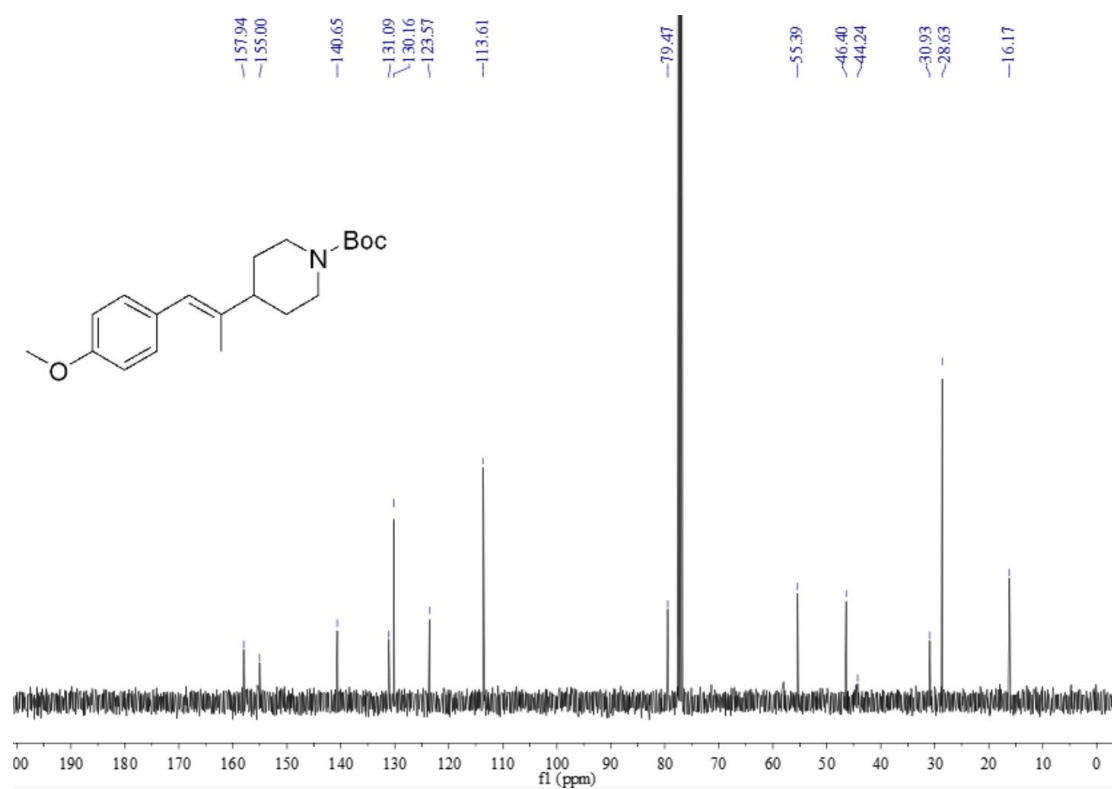
¹³C NMR of **4b**



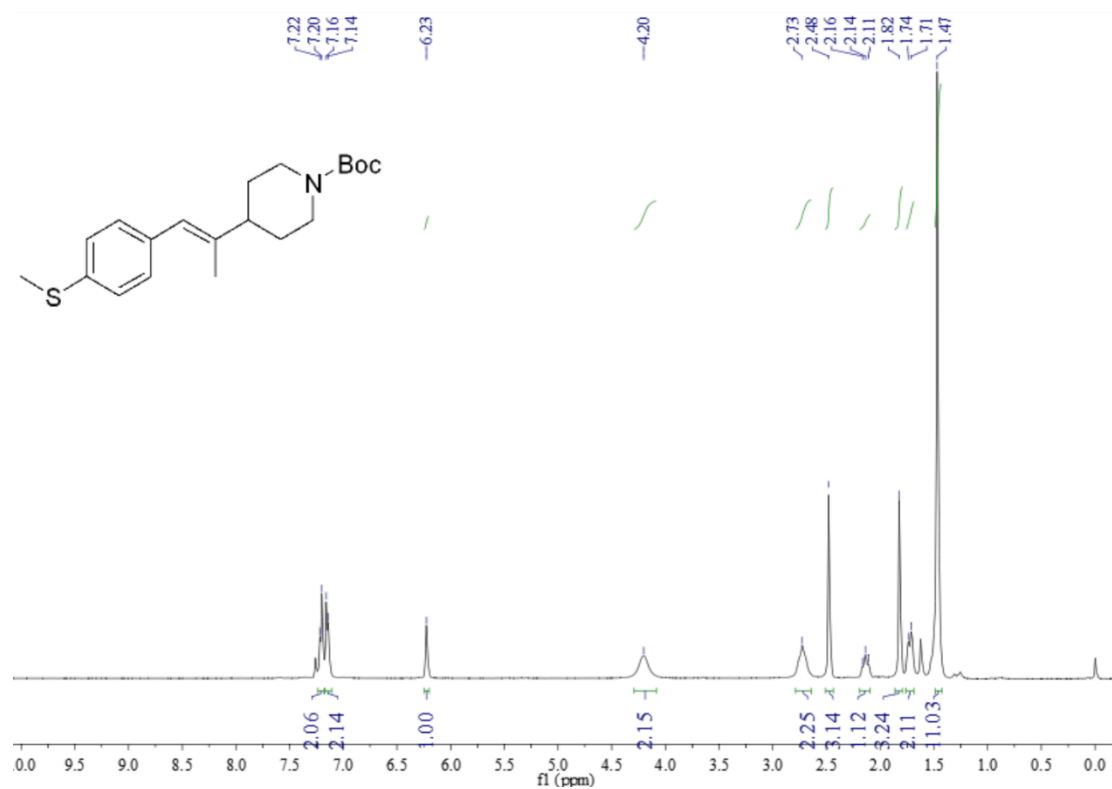
¹H NMR of **4c**



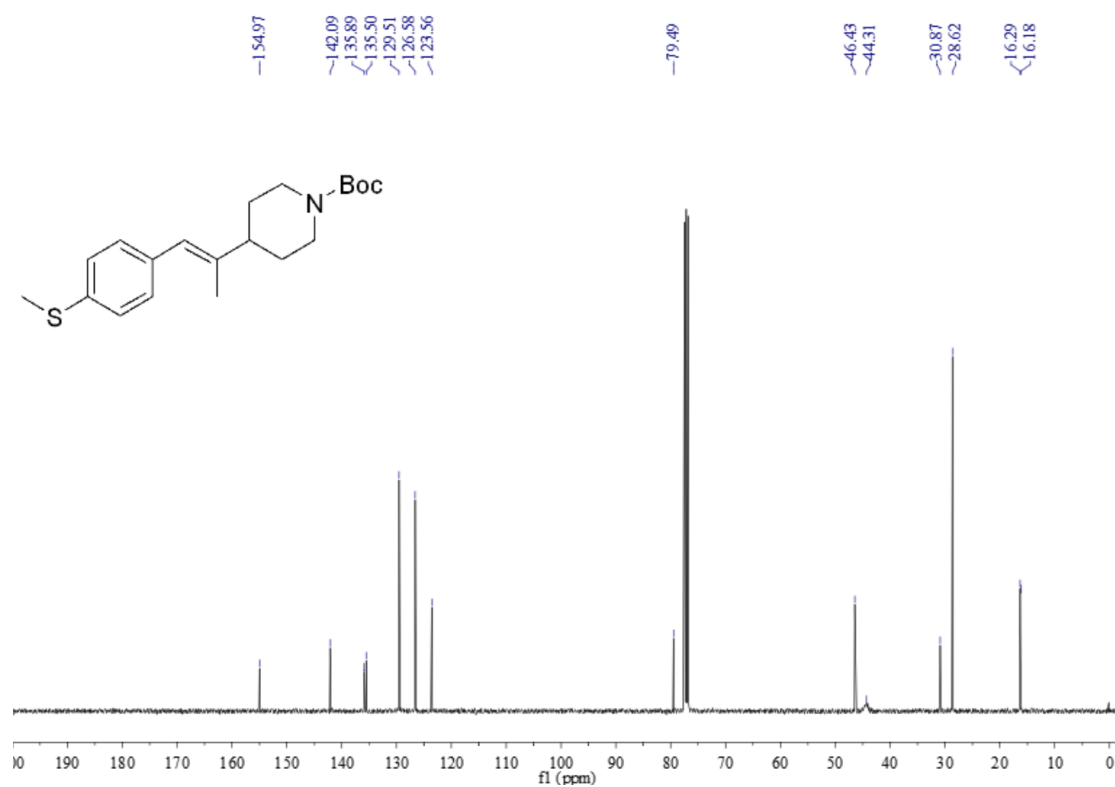
¹³C NMR of **4c**



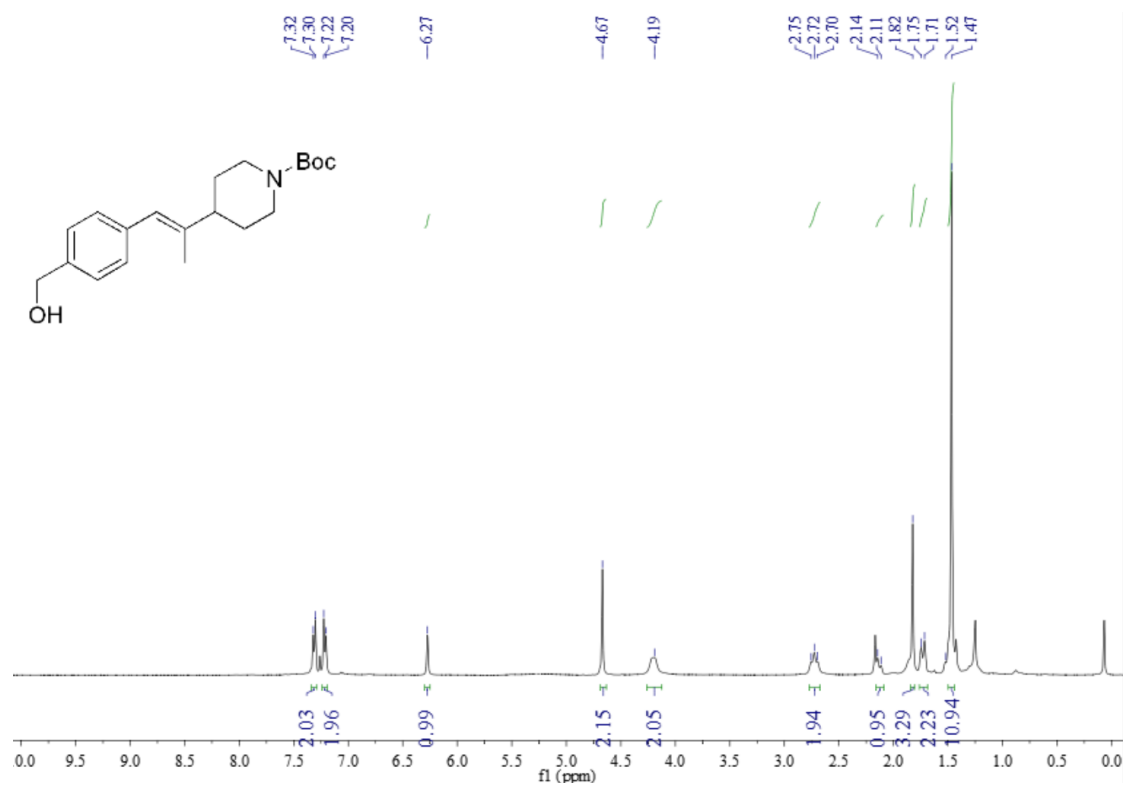
¹H NMR of **4d**



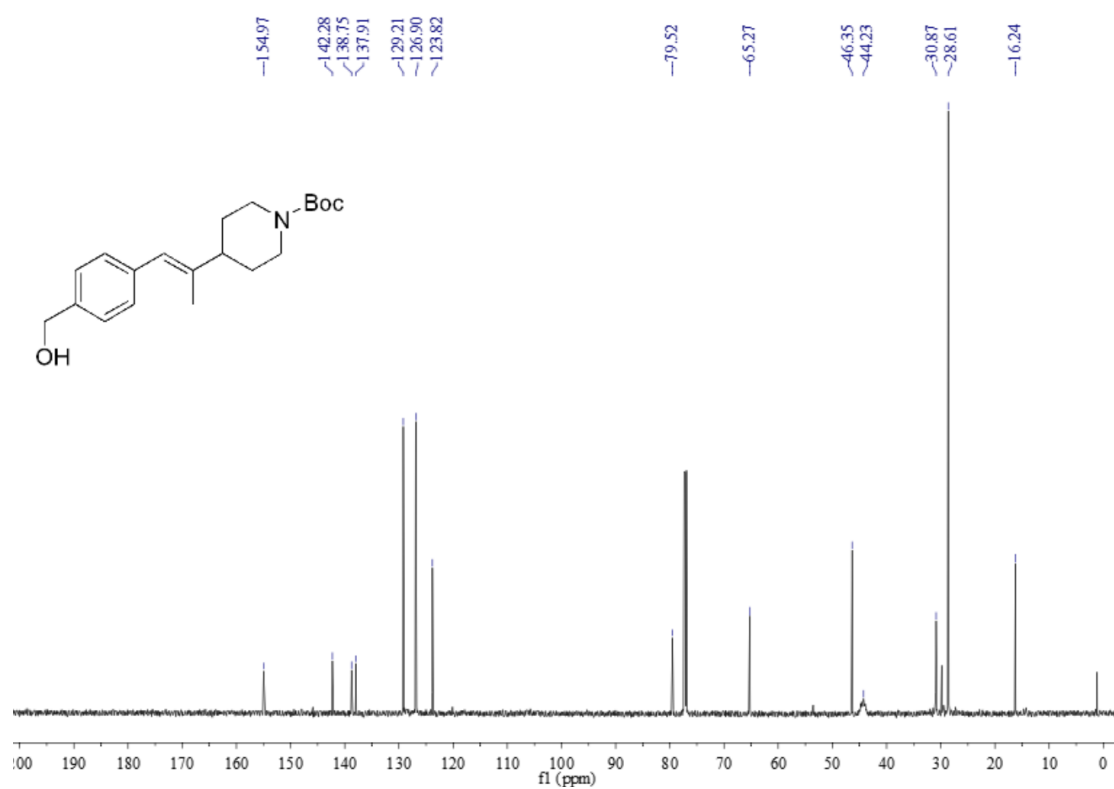
¹³C NMR of **4d**



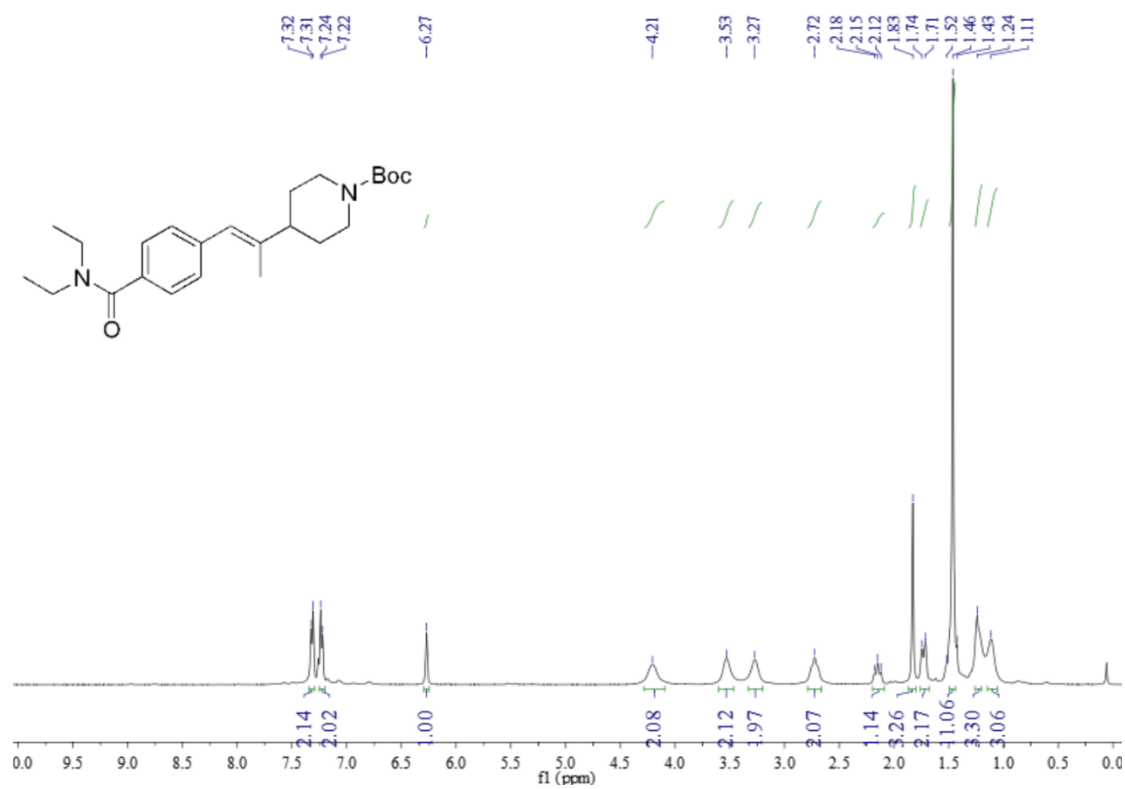
¹H NMR of **4e**



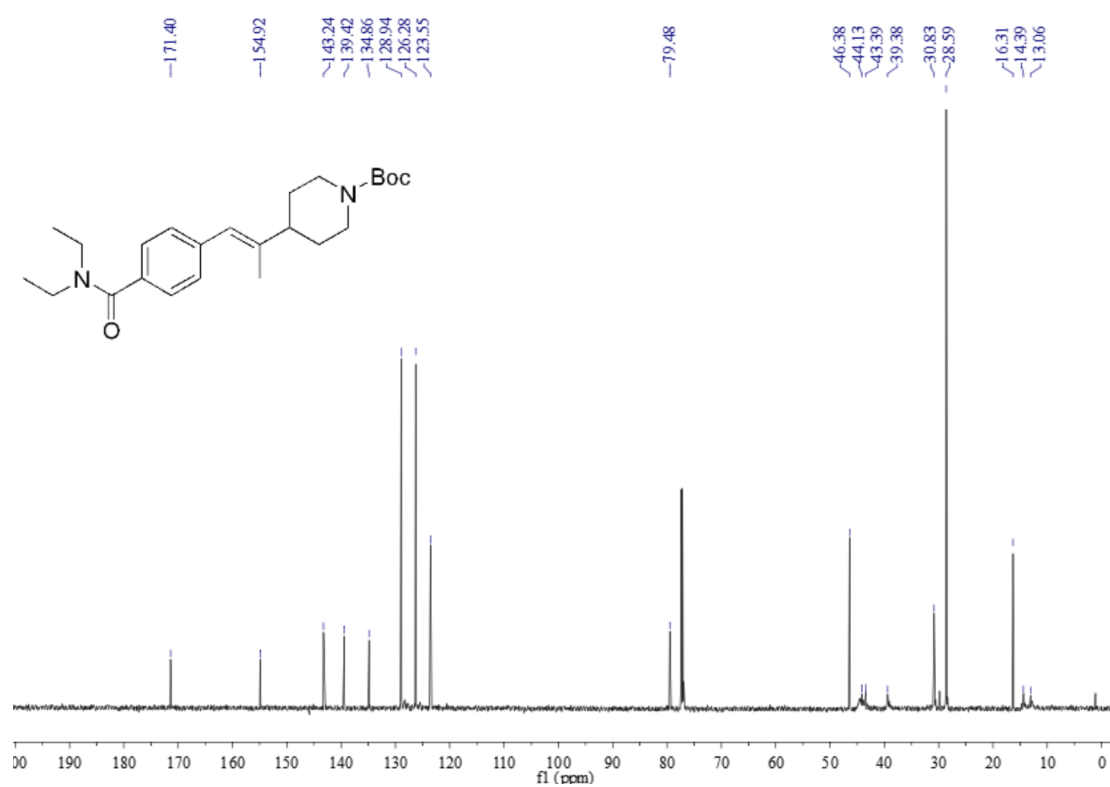
¹³C NMR of **4e**



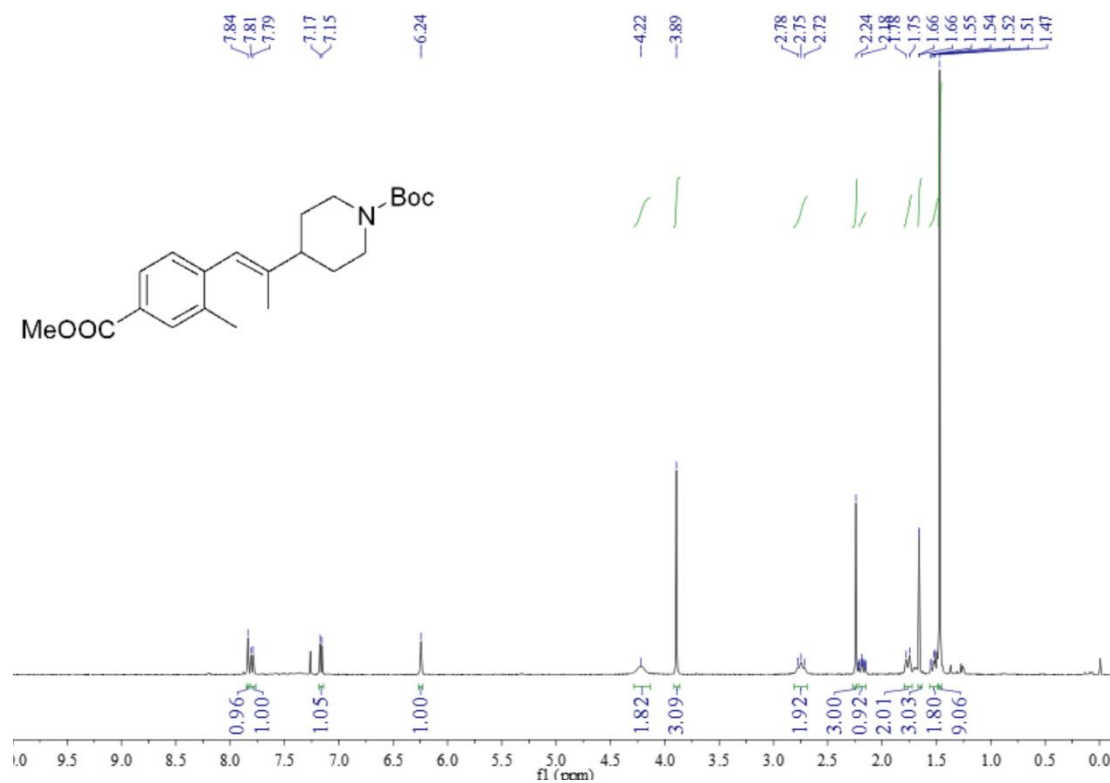
¹H NMR of **4f**



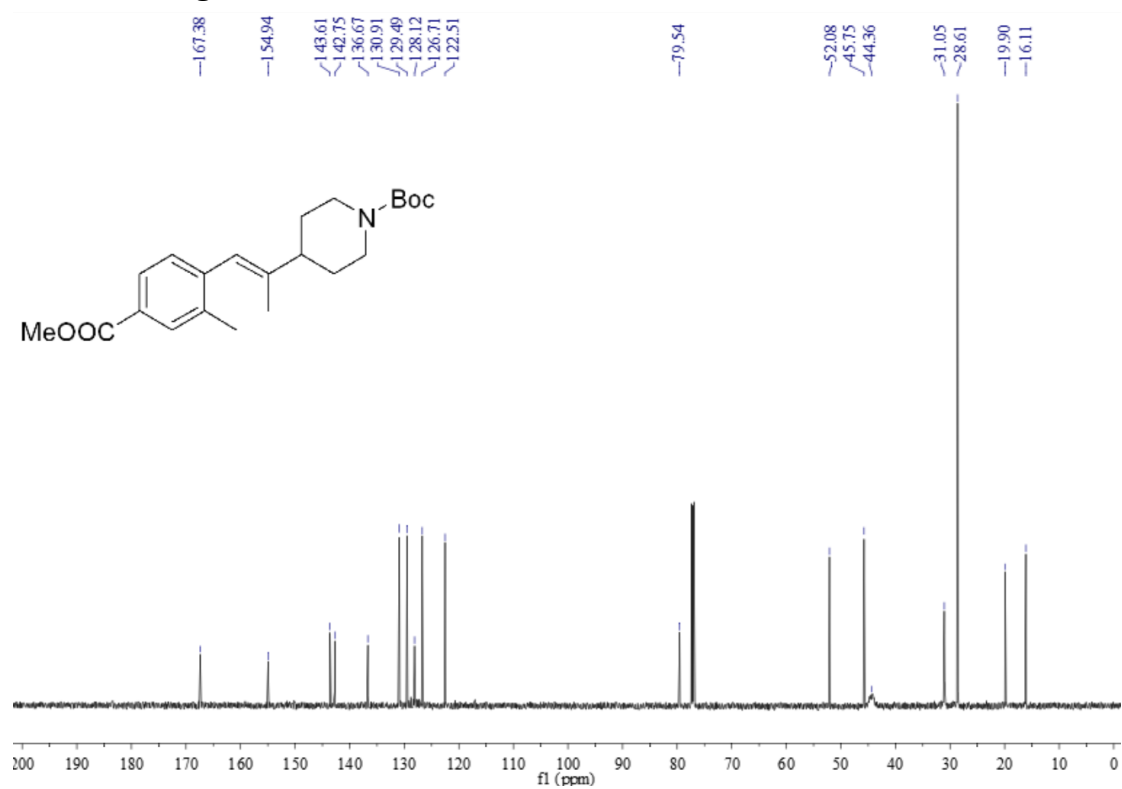
¹³C NMR of **4f**



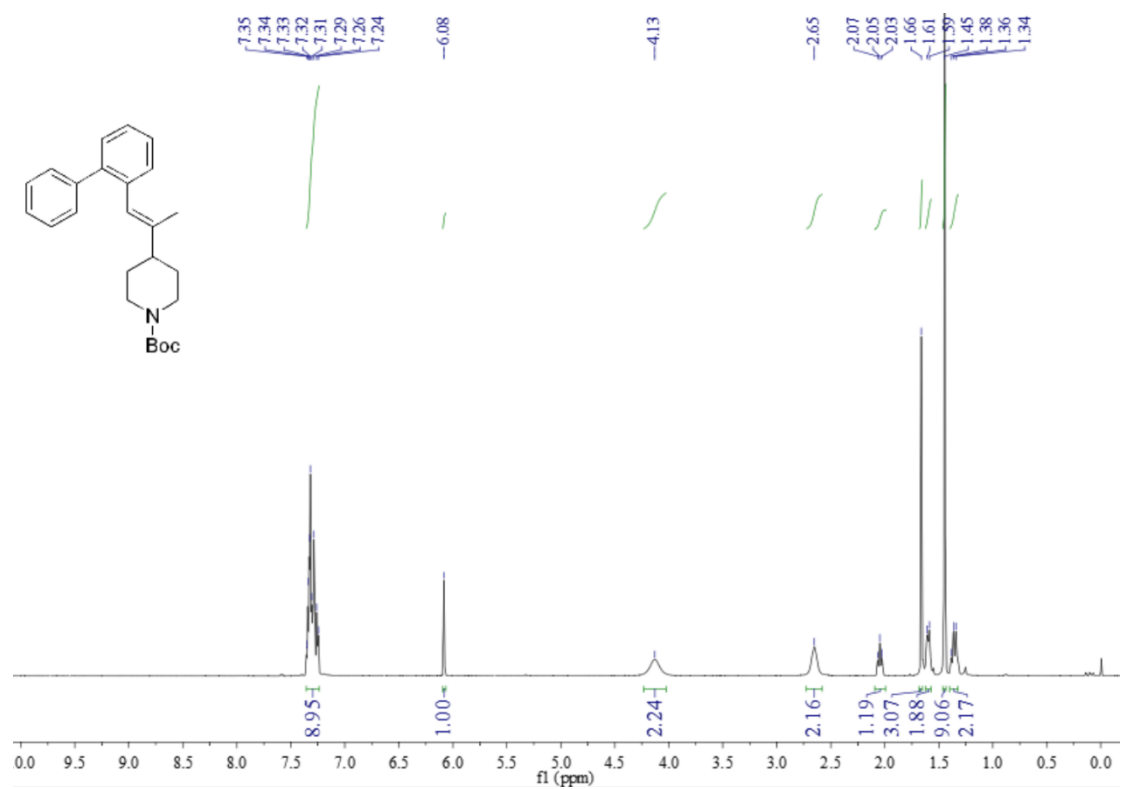
¹H NMR of **4g**



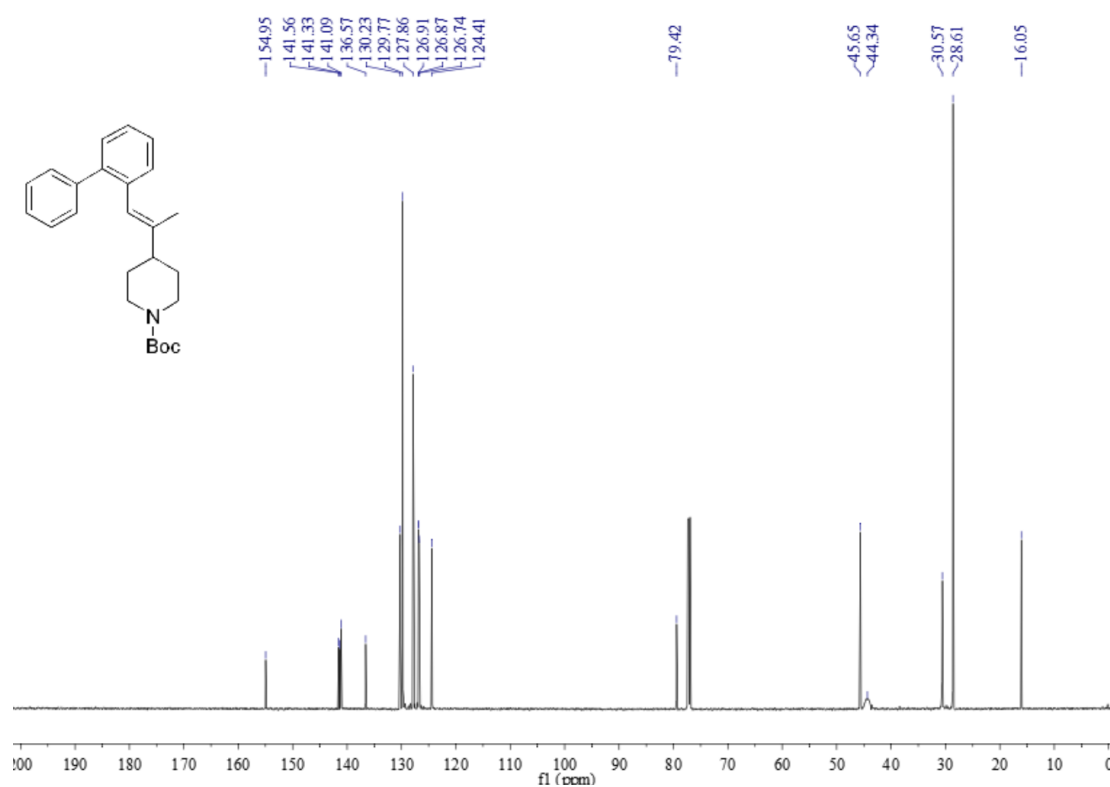
¹³C NMR of **4g**



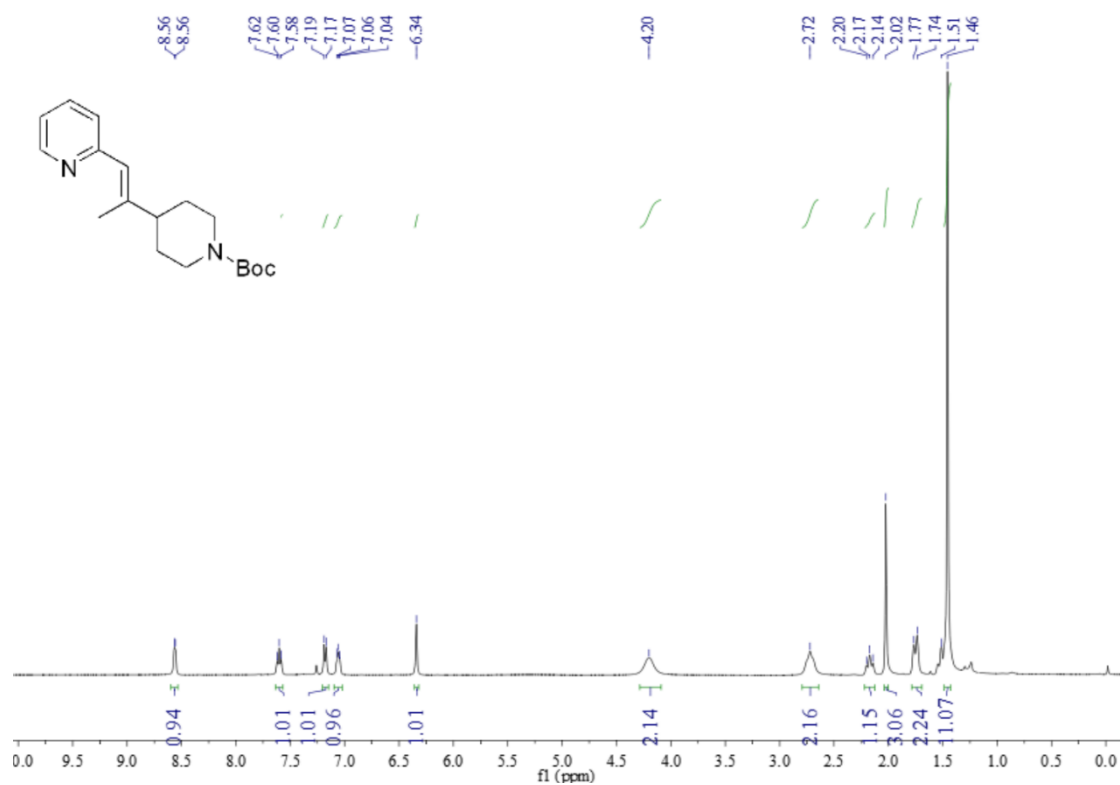
¹H NMR of **4h**



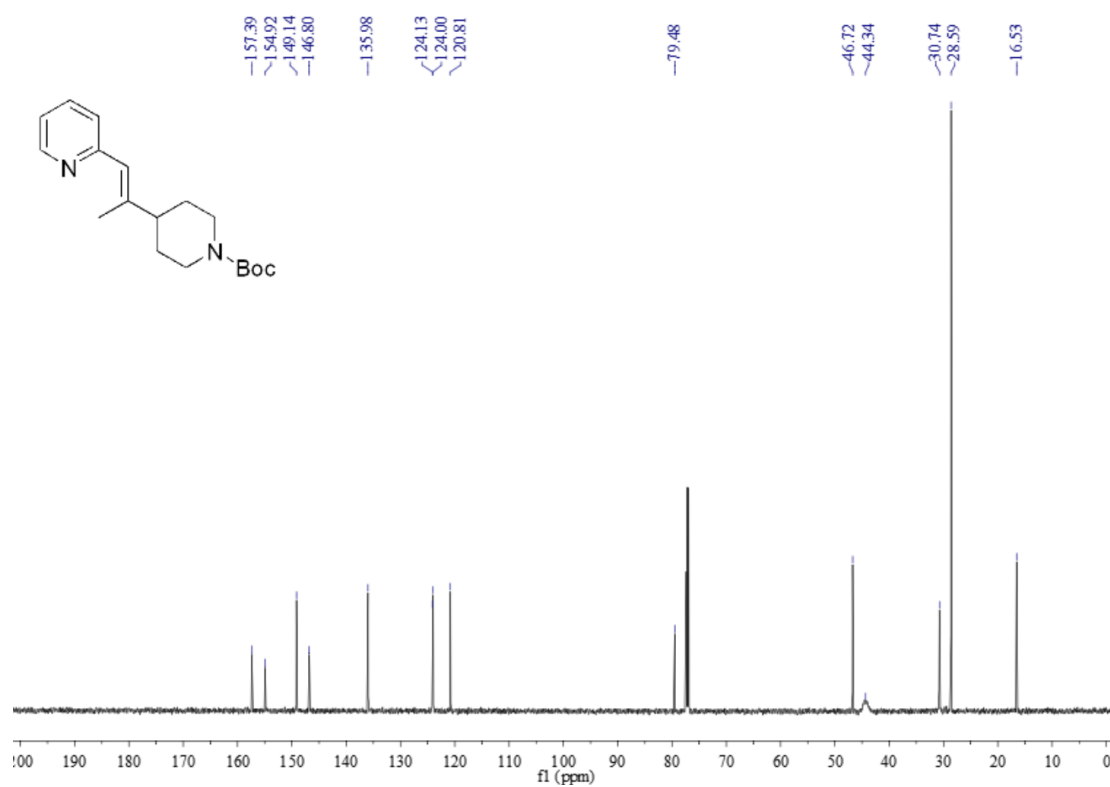
¹³C NMR of **4h**



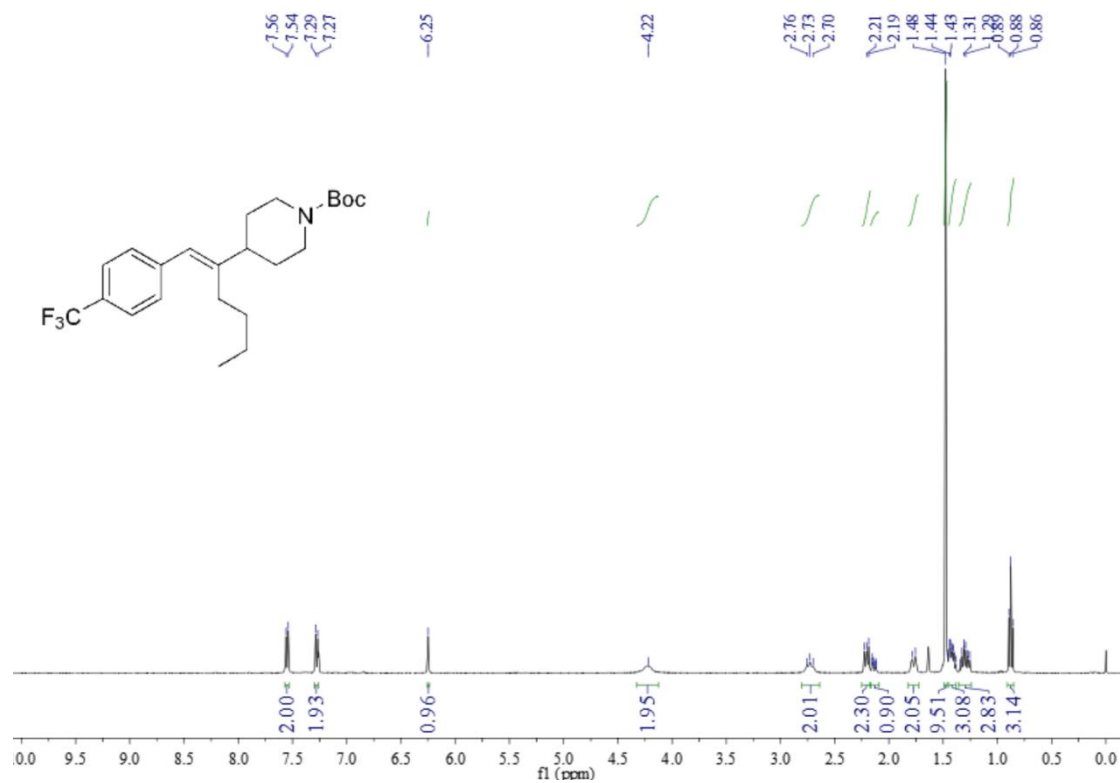
¹H NMR of **4i**



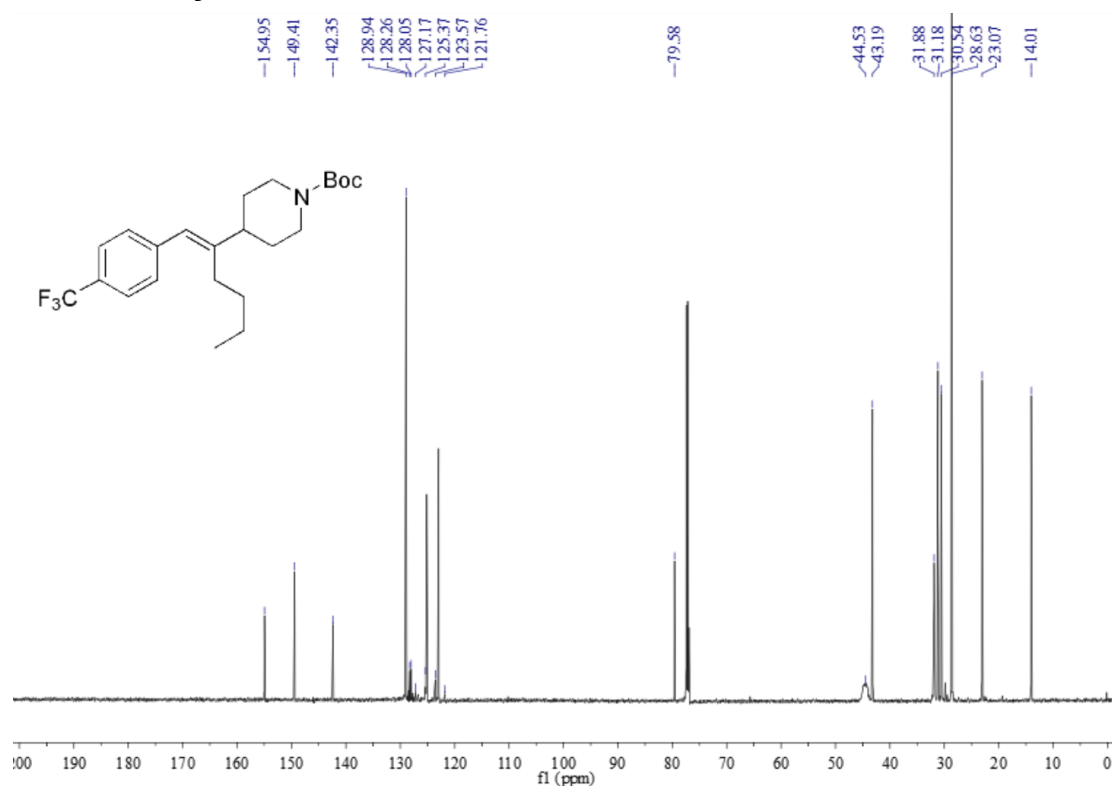
¹³C NMR of **4i**



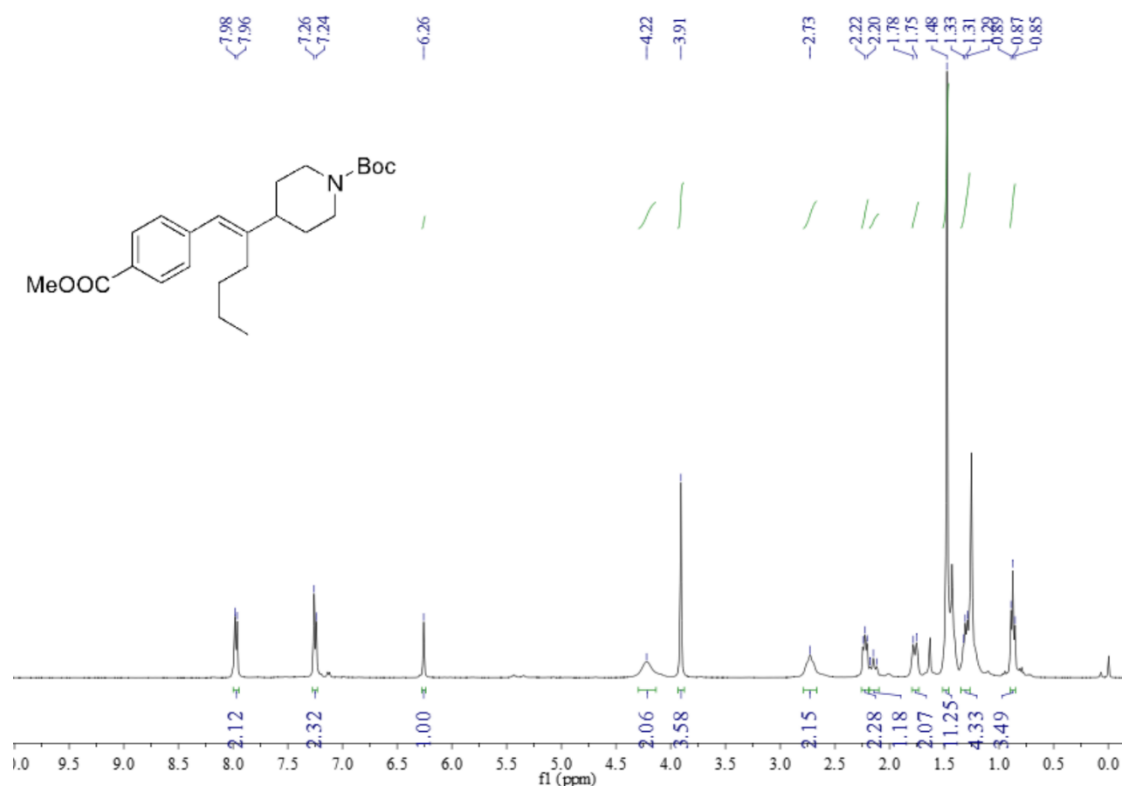
¹H NMR of **4j**



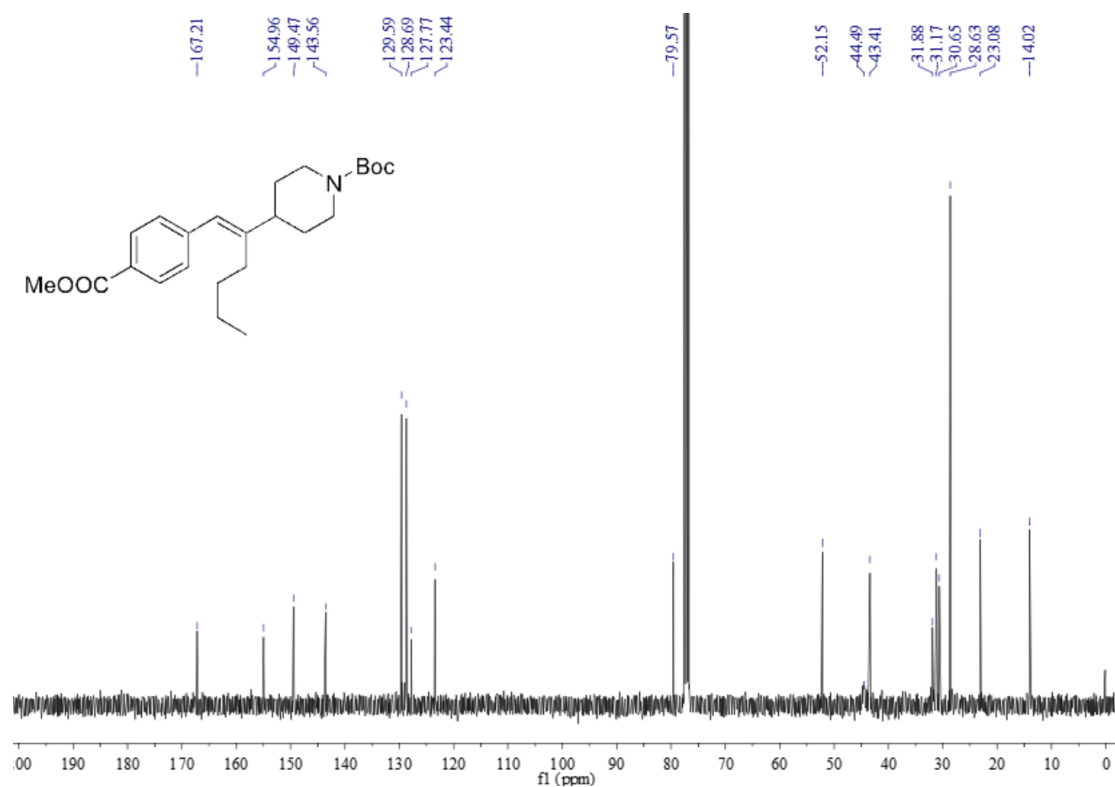
¹³C NMR of **4j**



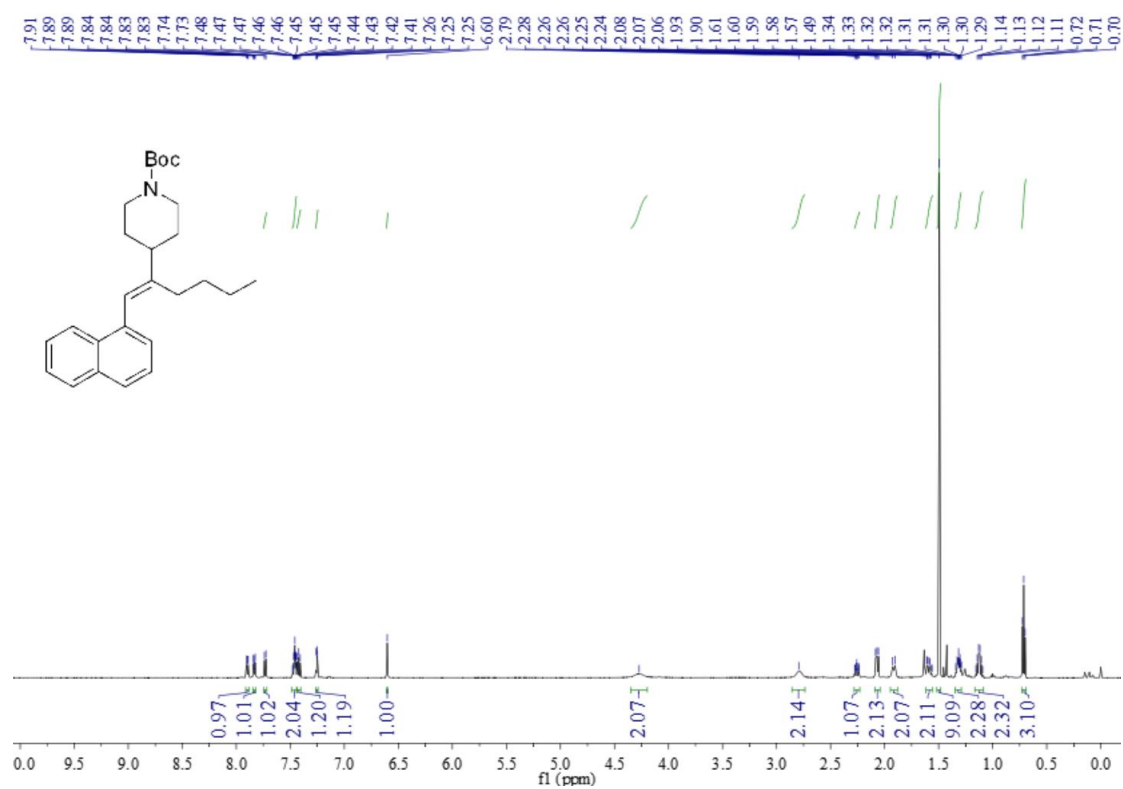
¹H NMR of **4k**



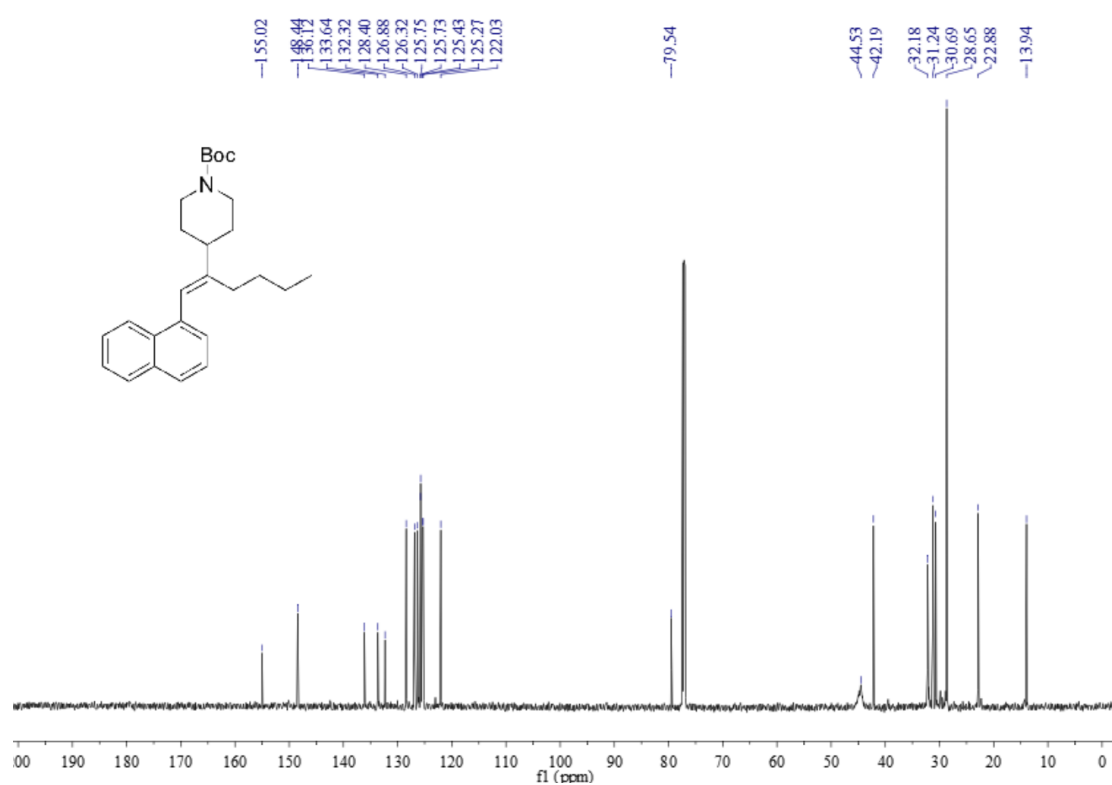
¹³C NMR of **4k**



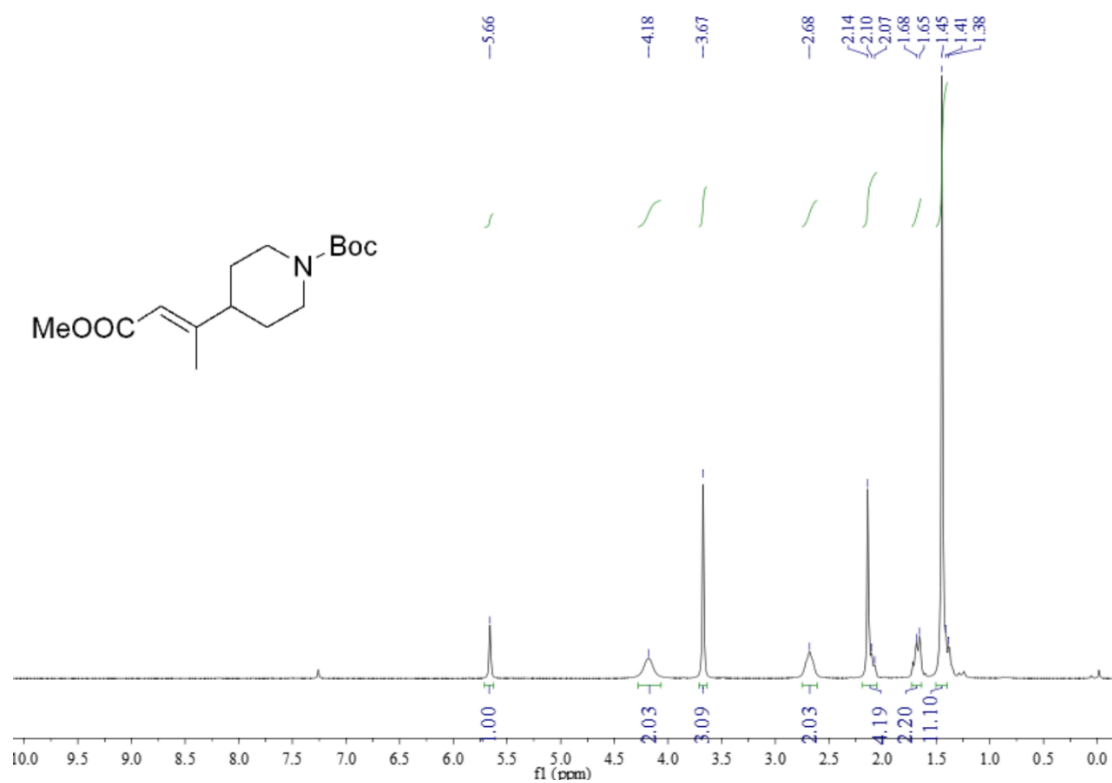
¹H NMR of **4l**



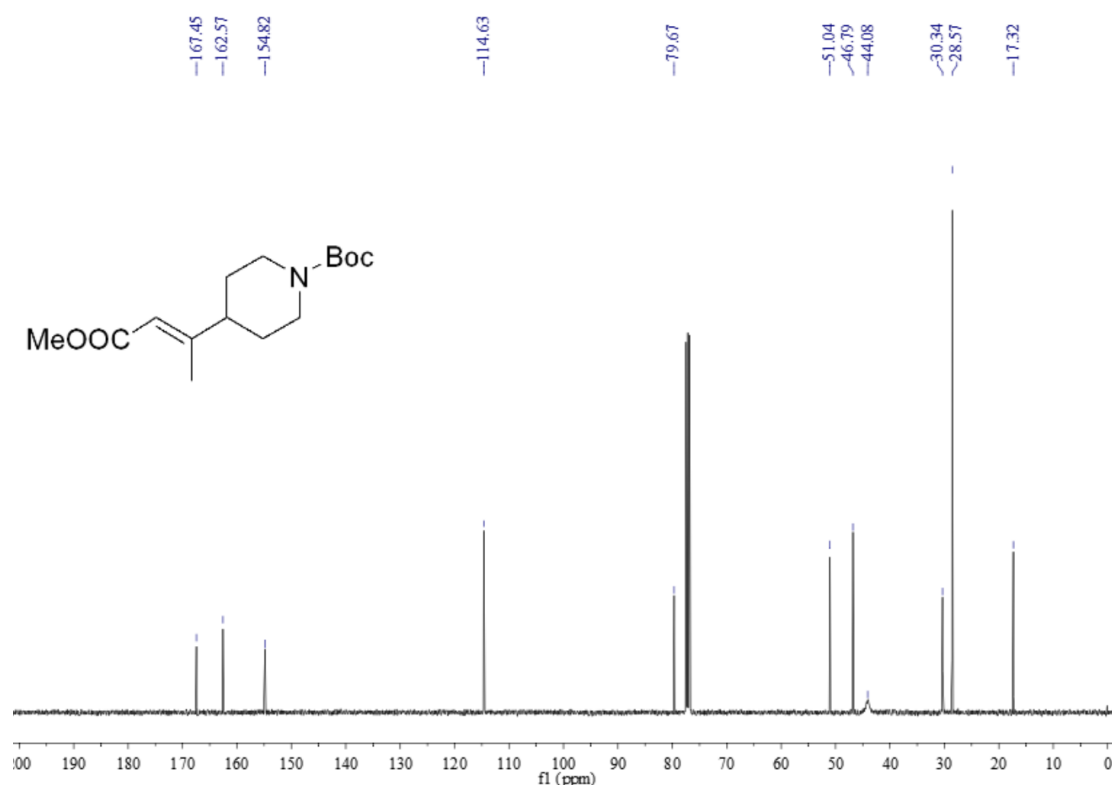
¹³C NMR of **4l**



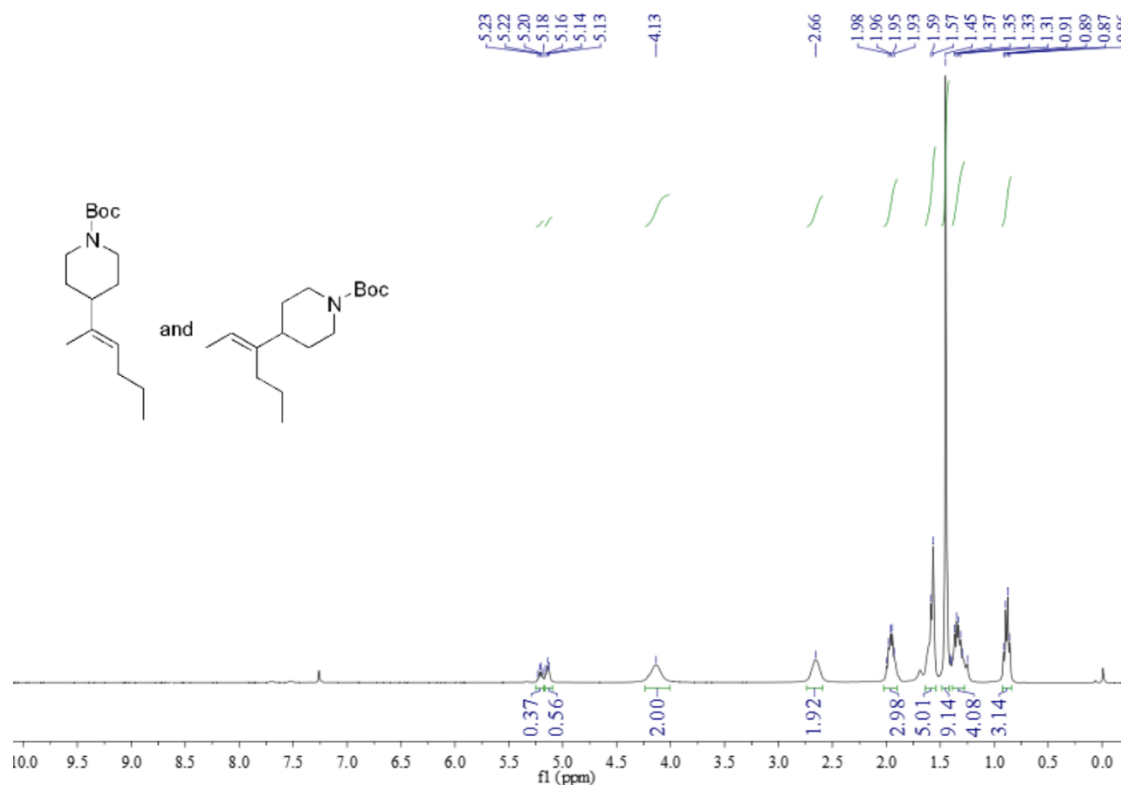
¹H NMR of **4m**



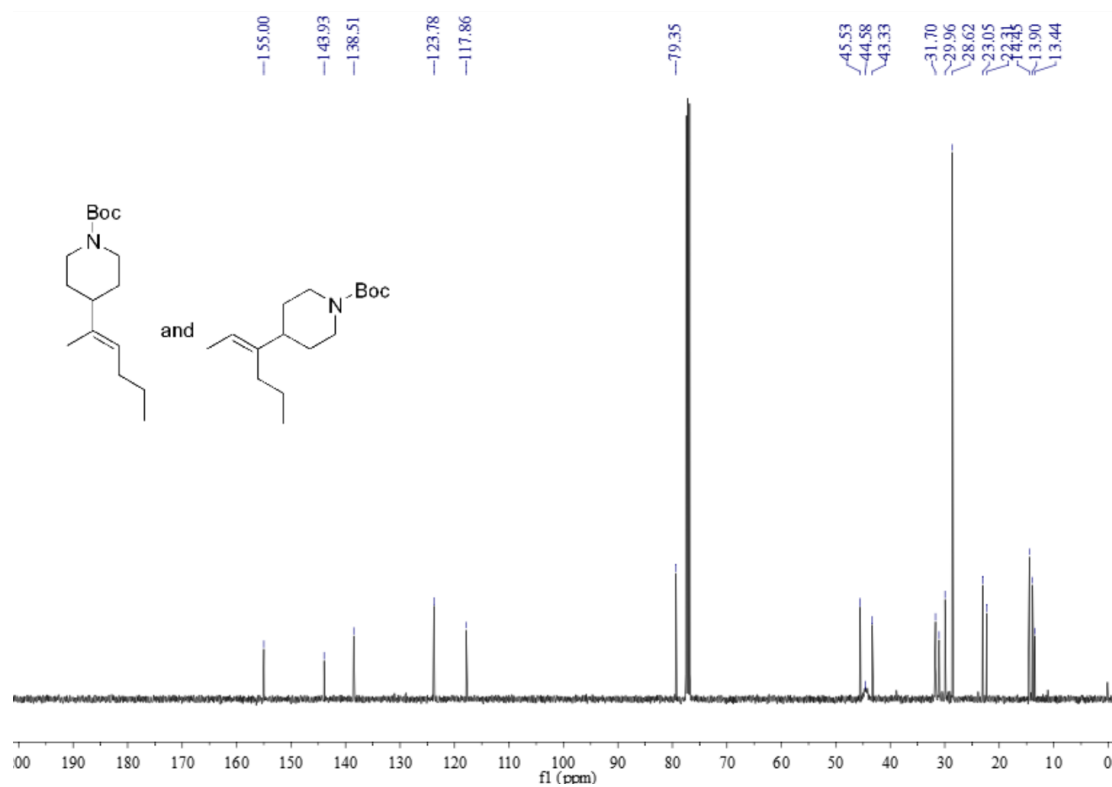
¹³C NMR of **4m**



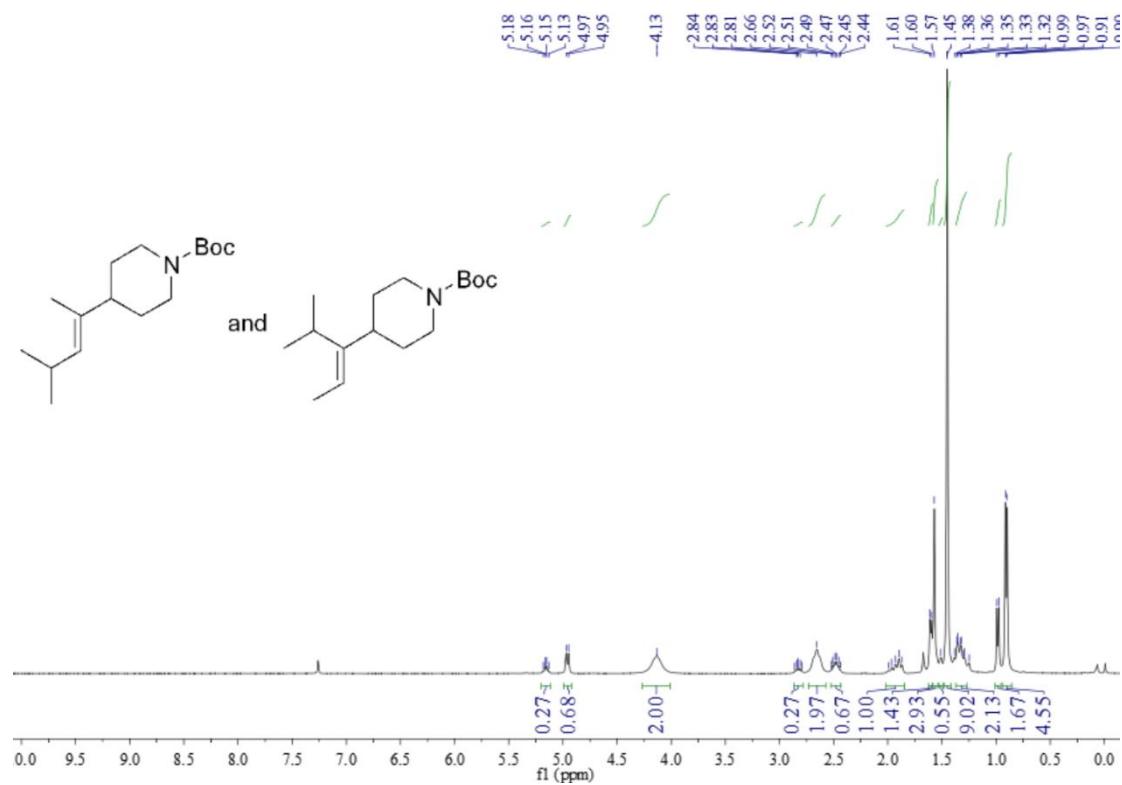
¹H NMR of **4n**



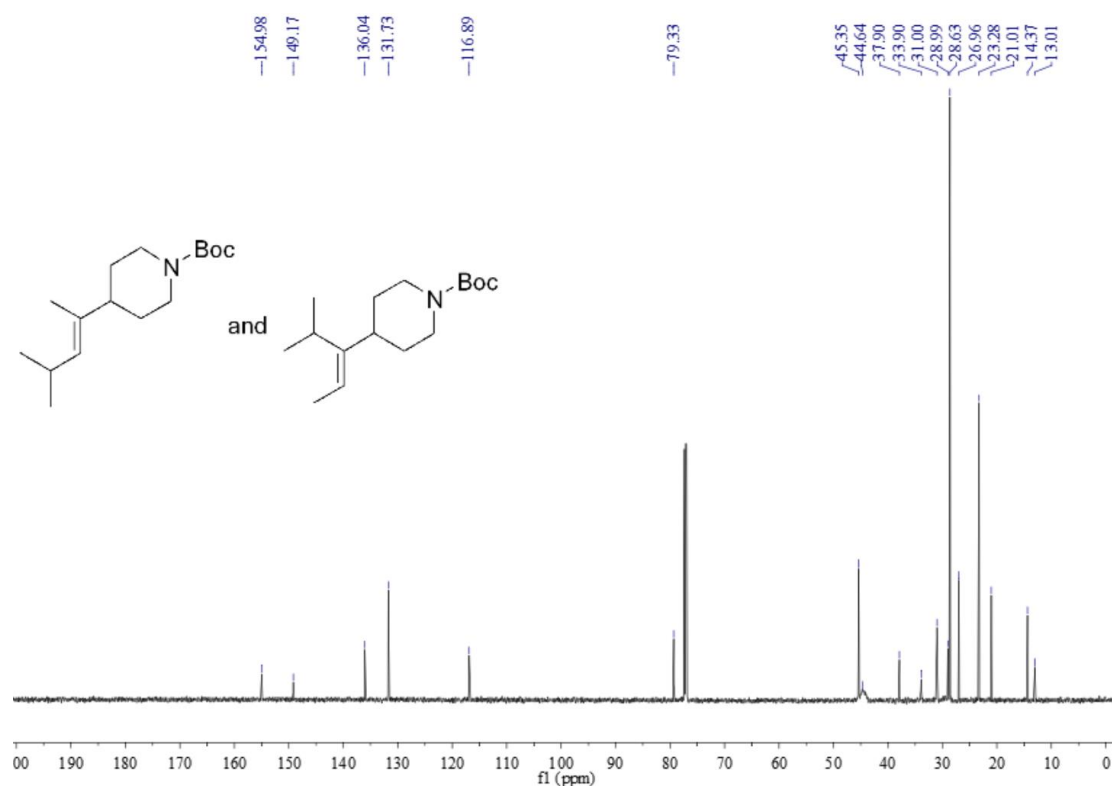
¹³C NMR of **4n**



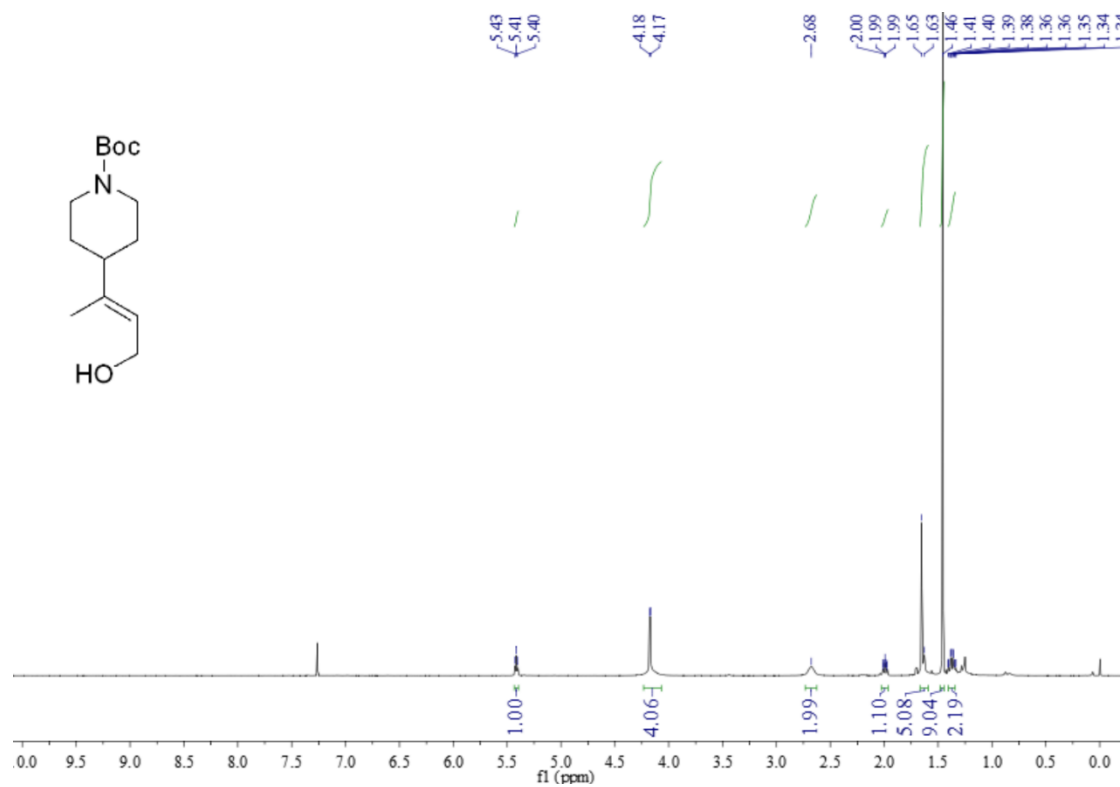
¹H NMR of **4o**



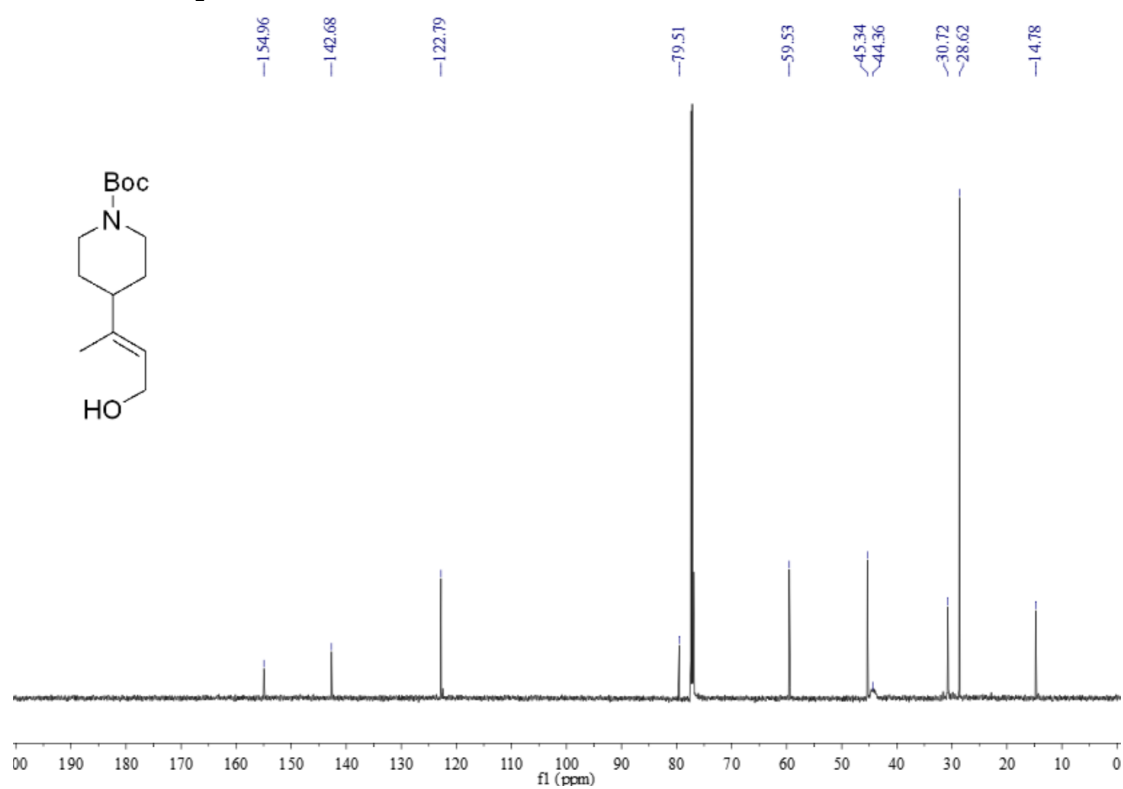
¹³C NMR of **4o**



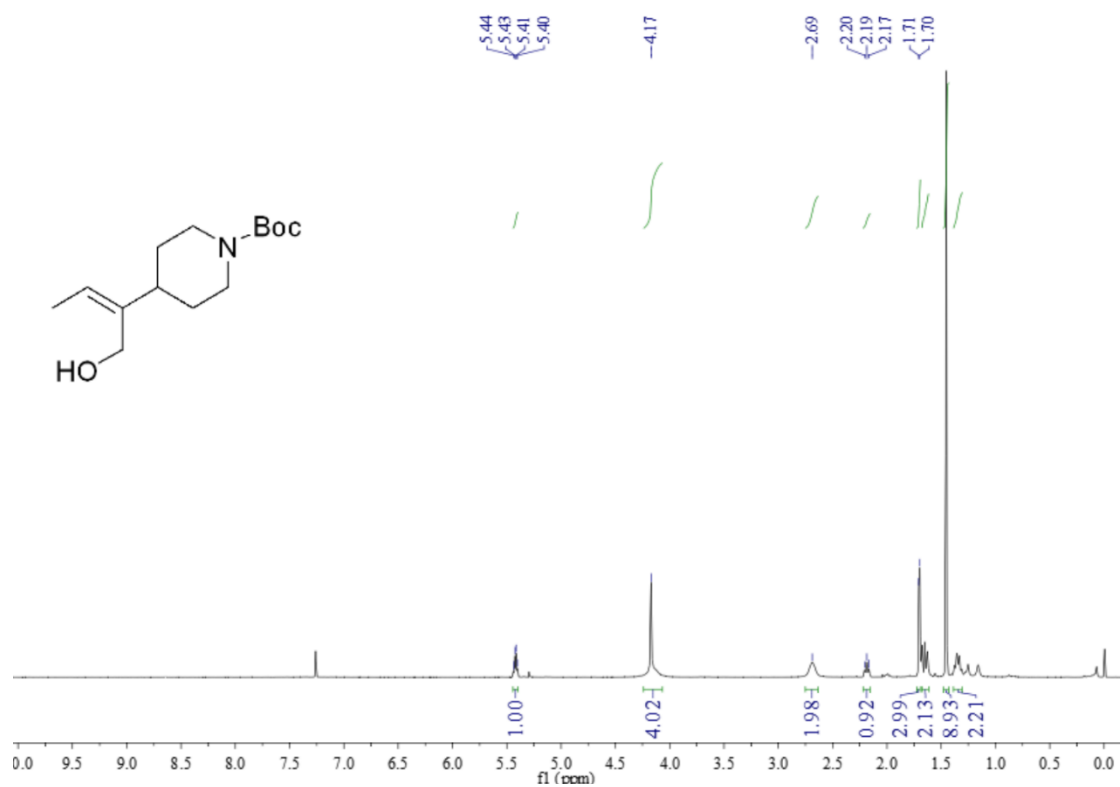
¹H NMR of **4p**



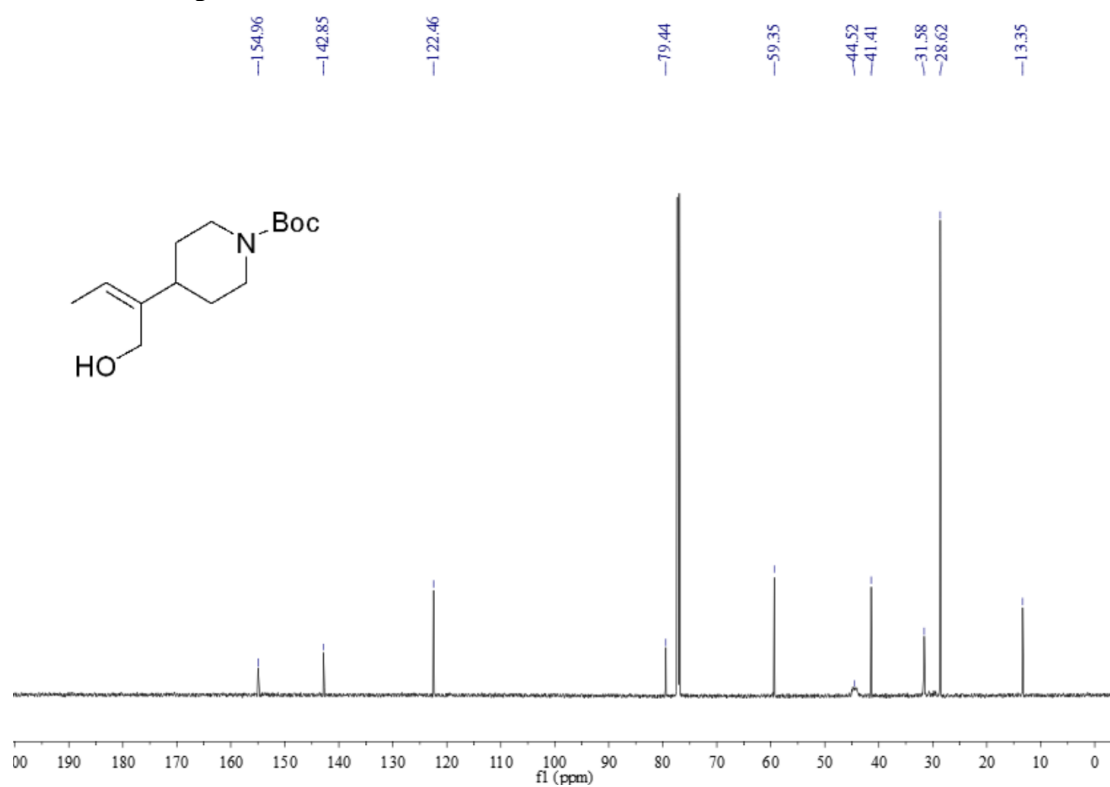
^{13}C NMR of **4p**



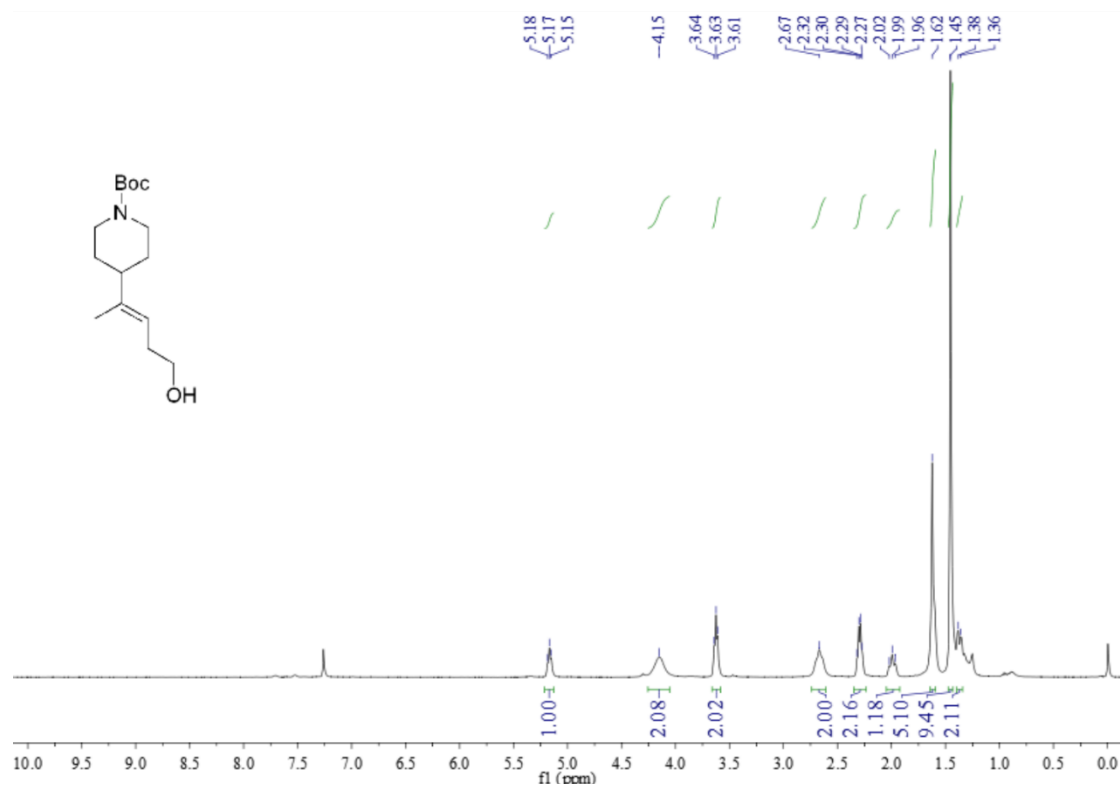
^1H NMR of **4p'**



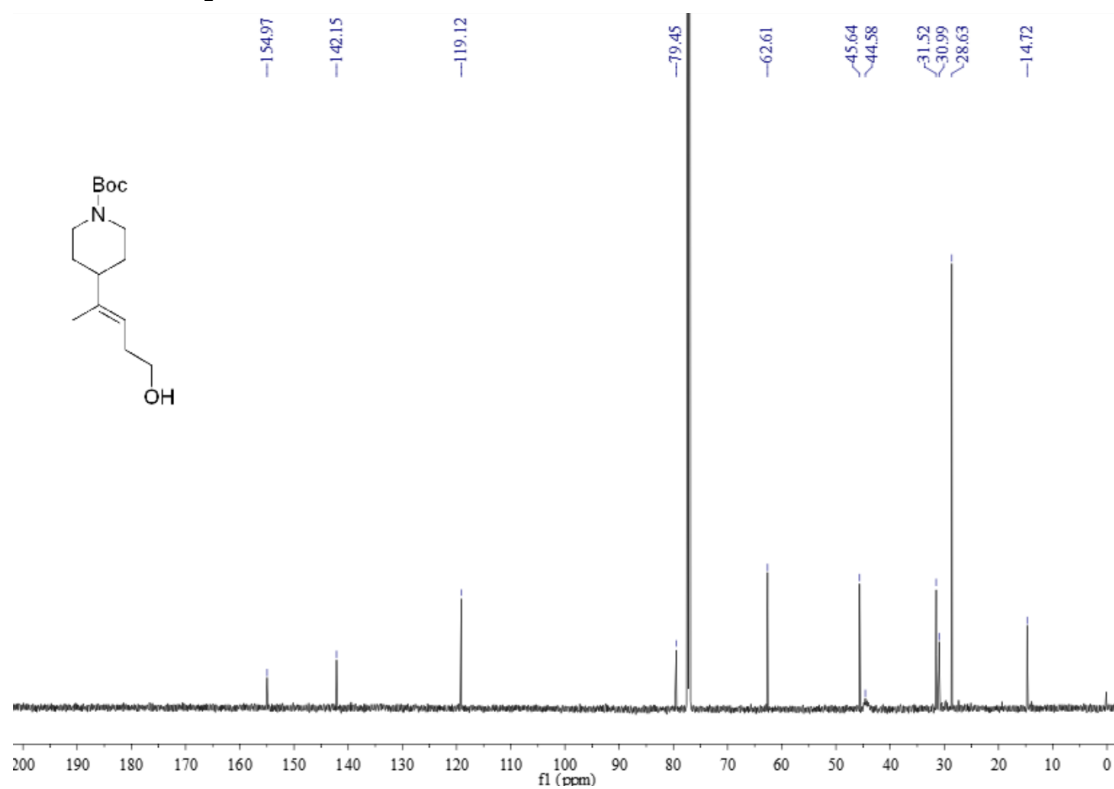
^{13}C NMR of **4p'**



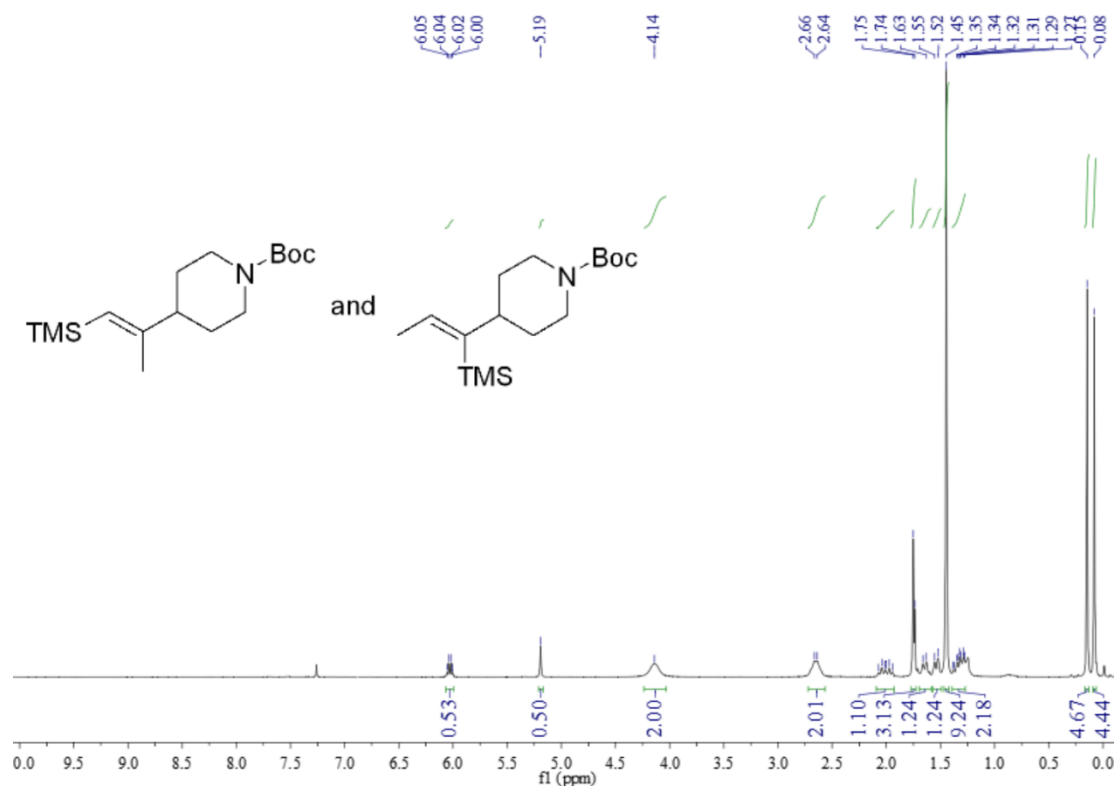
^1H NMR of **4q**



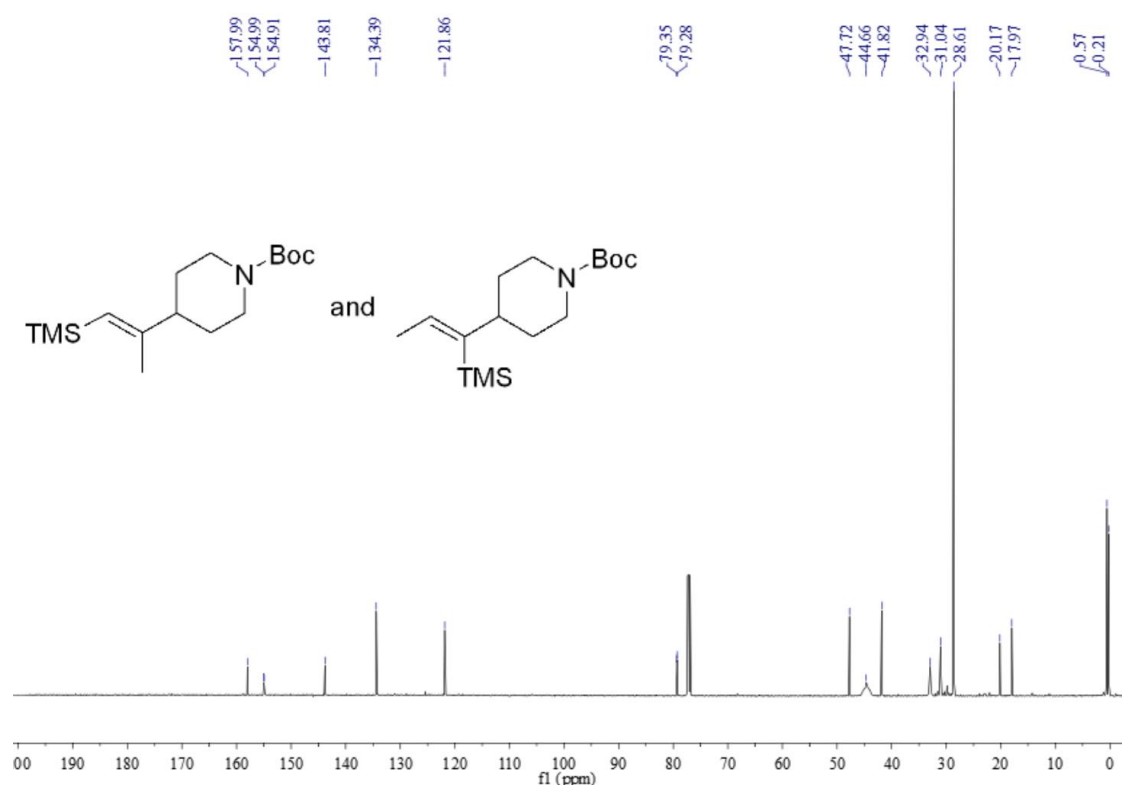
¹³C NMR of **4q**



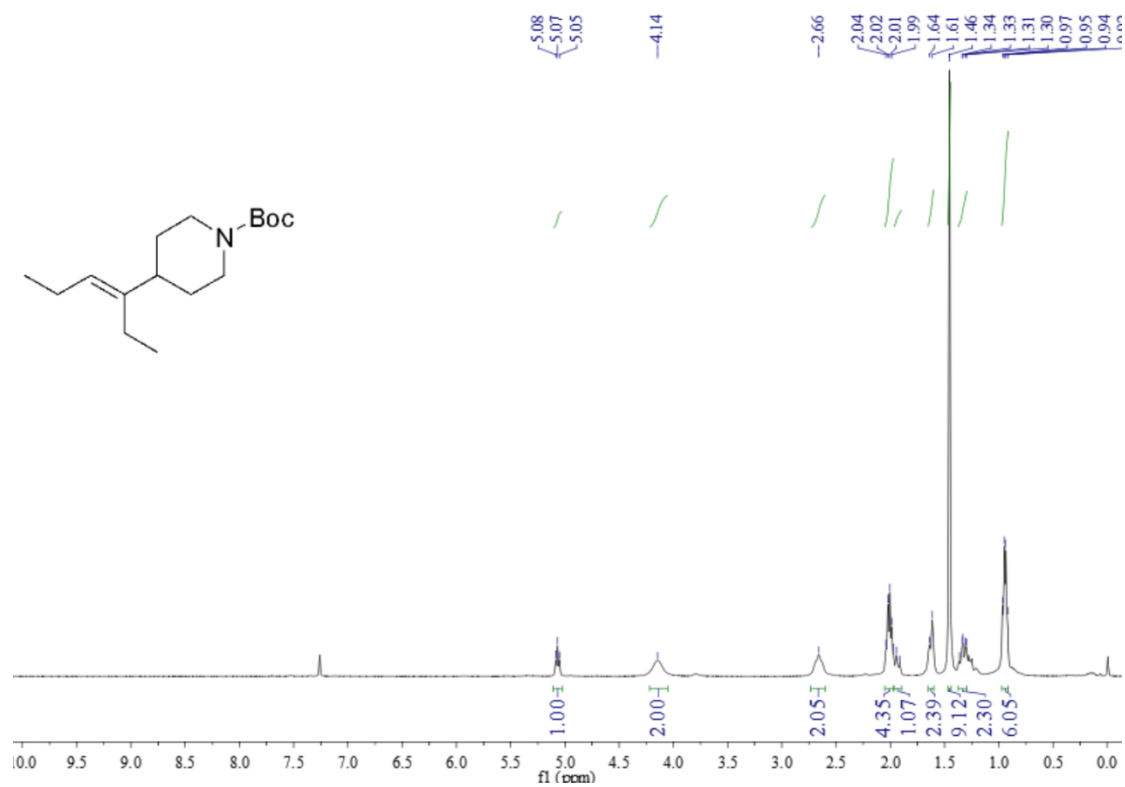
¹H NMR of **4r**



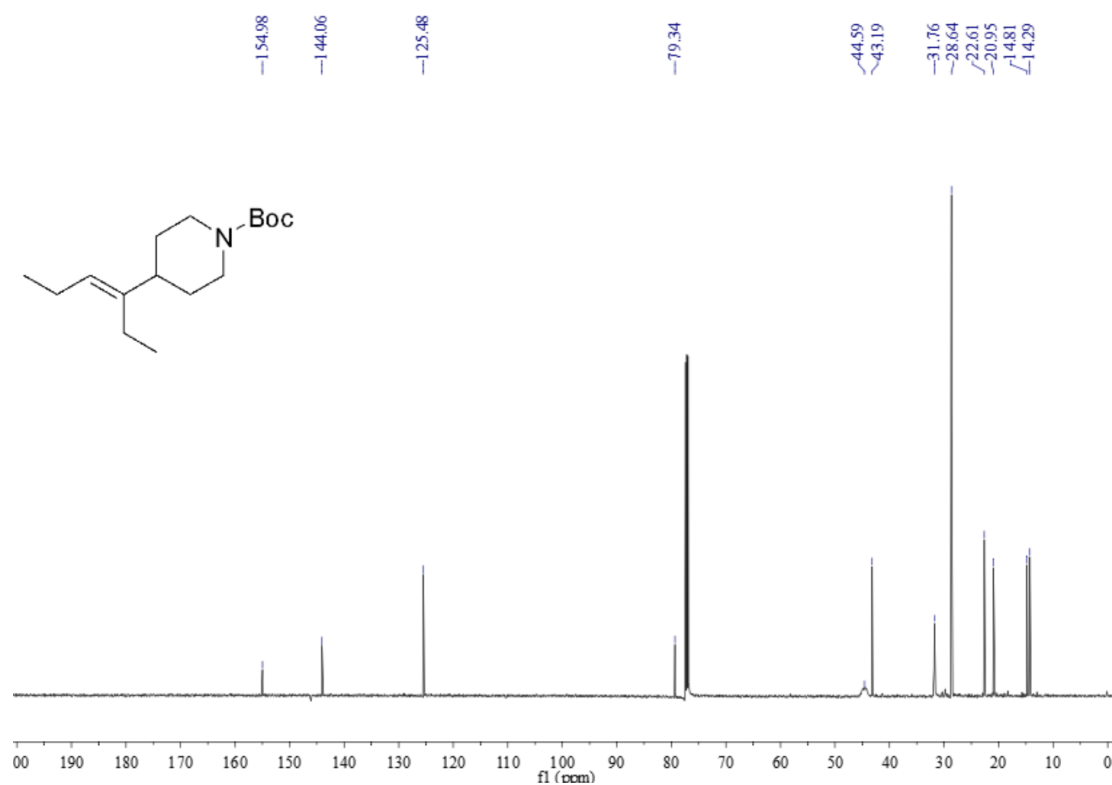
^{13}C NMR of **4r**



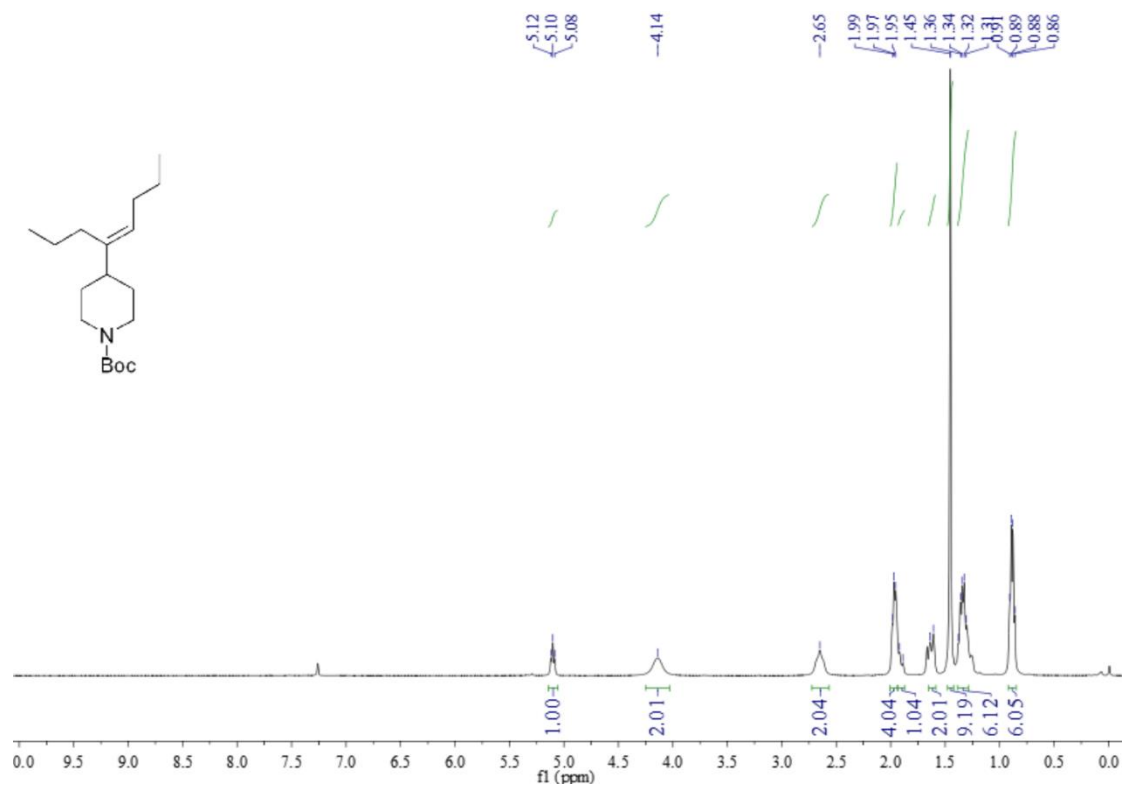
^1H NMR of **4s**



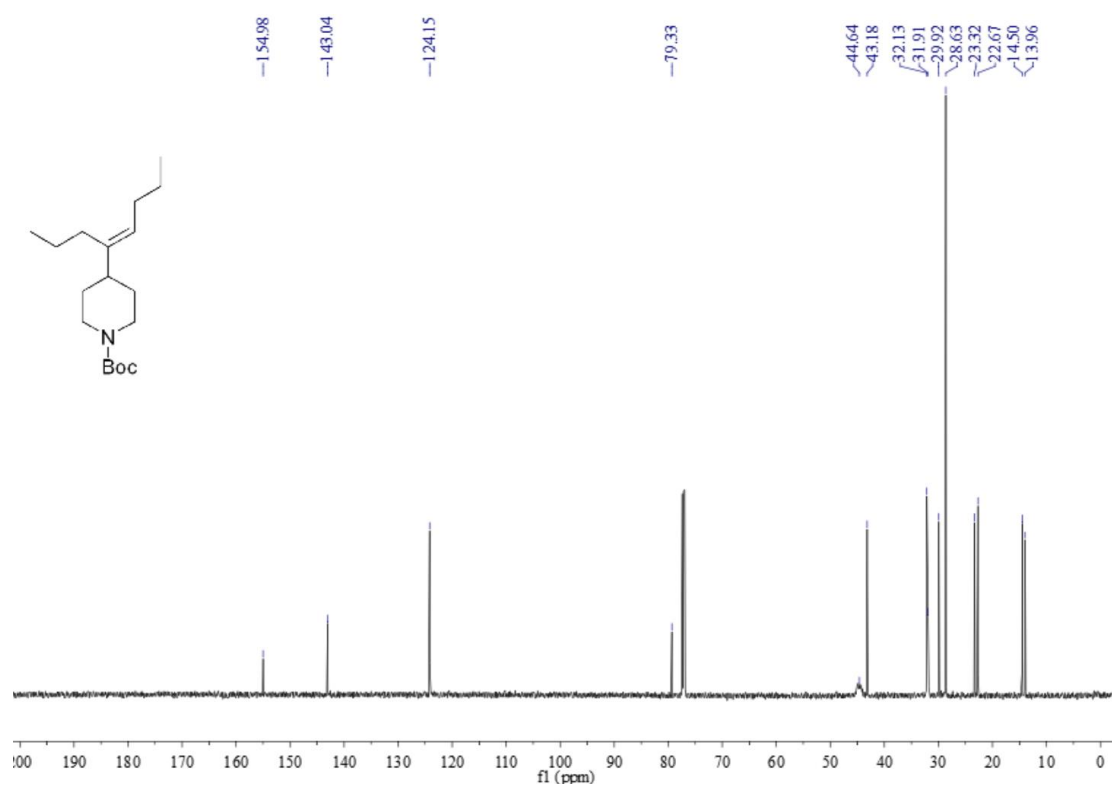
^{13}C NMR of **4s**



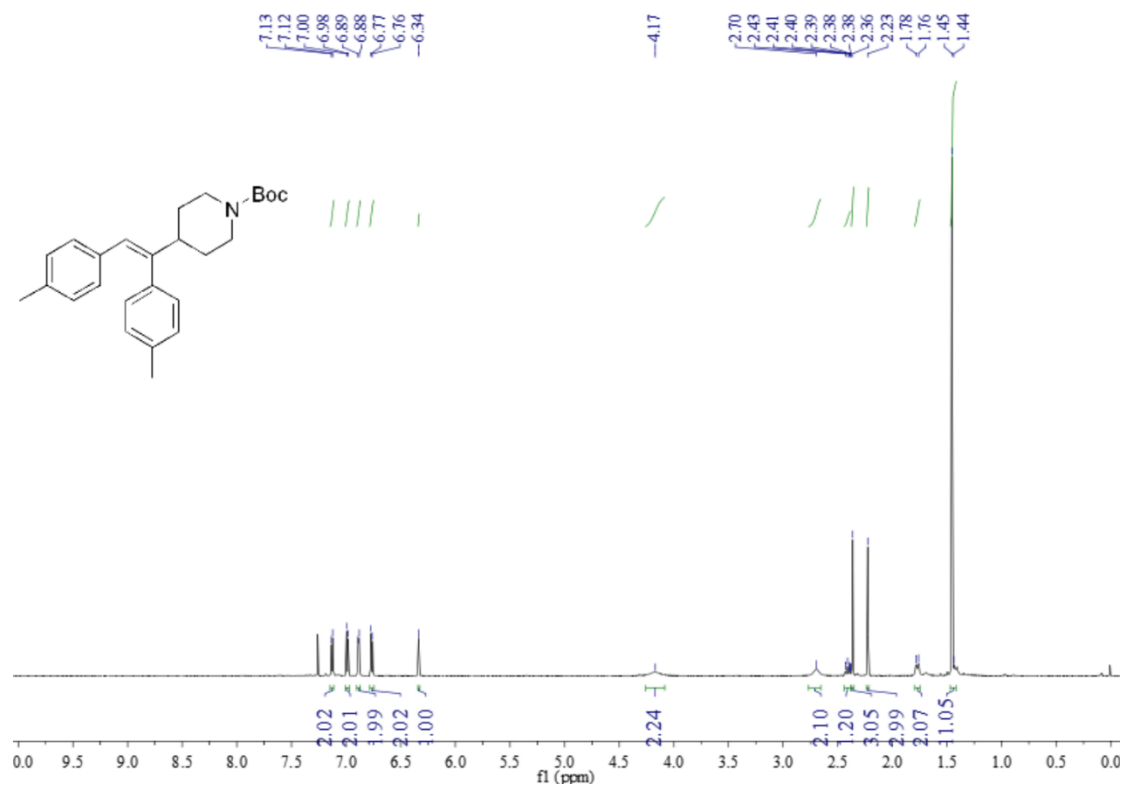
^1H NMR of **4t**



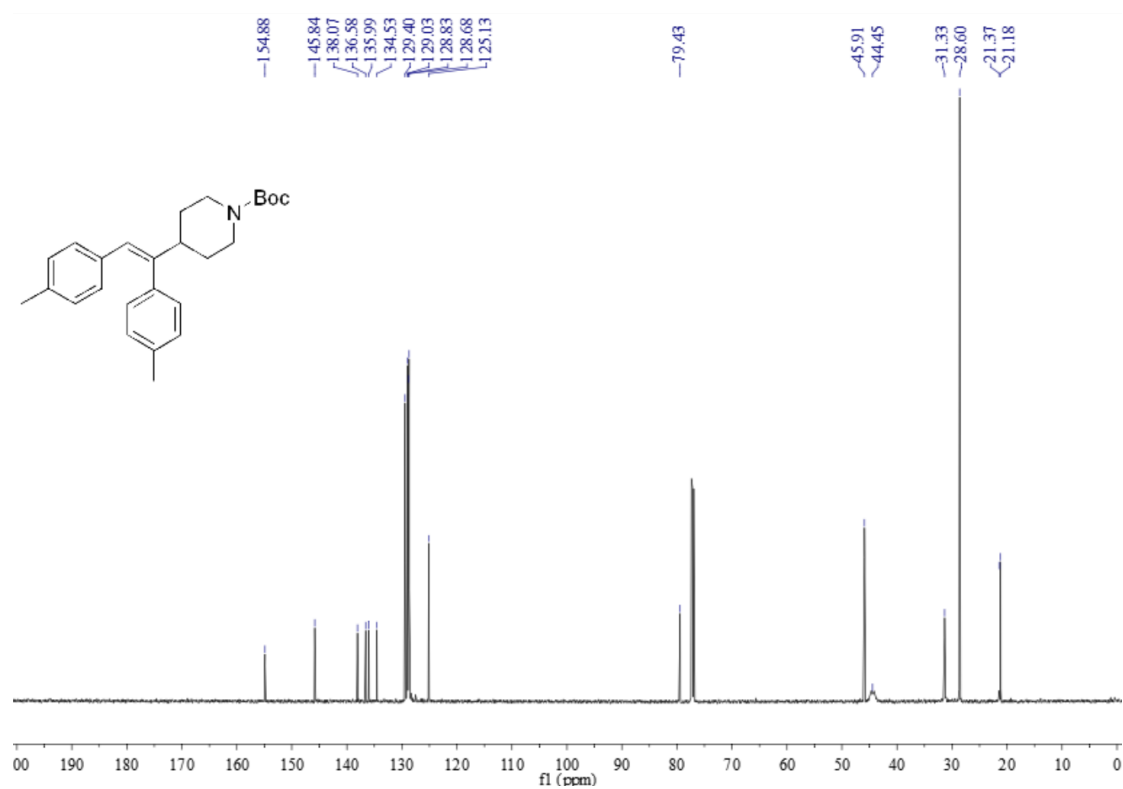
¹³C NMR of **4t**



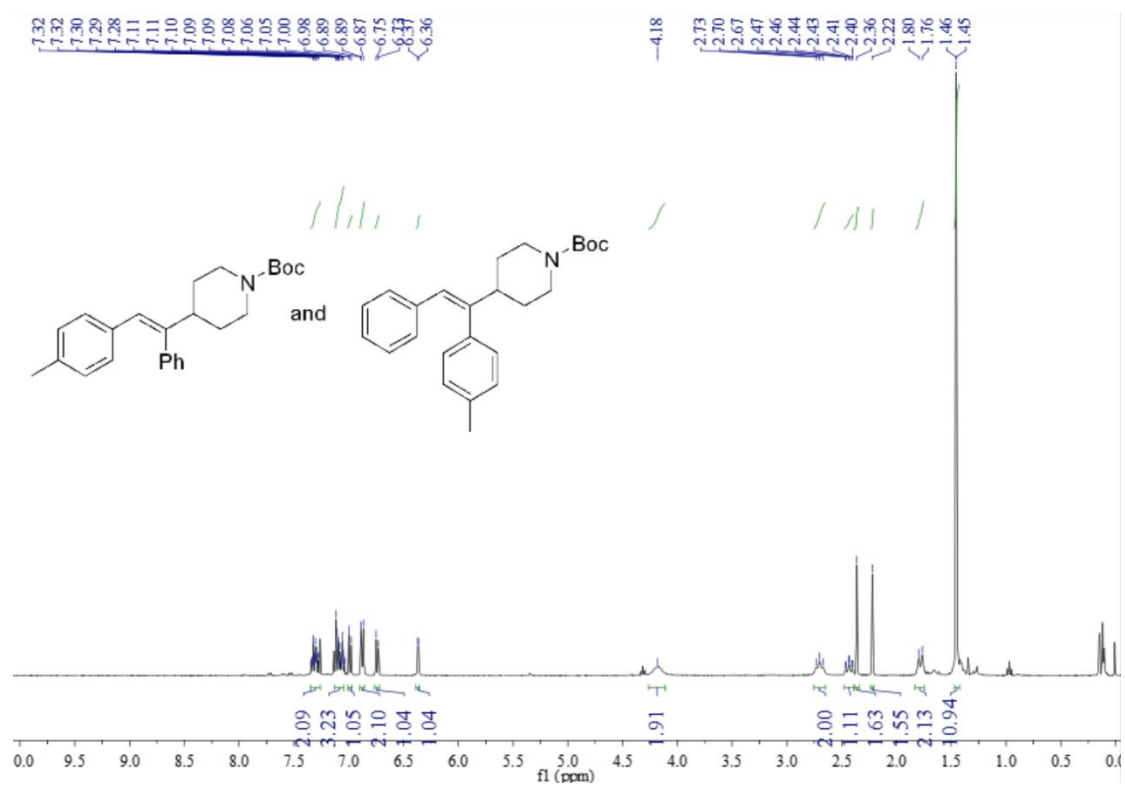
¹H NMR of **4u**



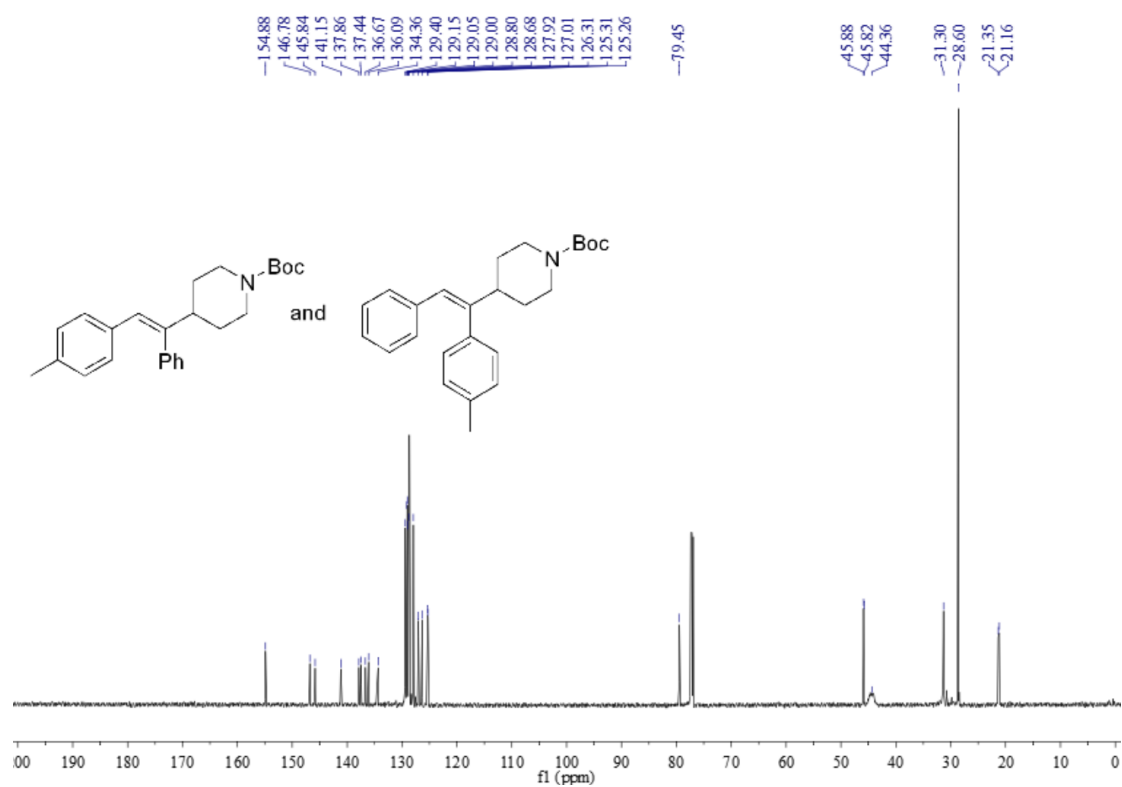
¹³C NMR of **4u**



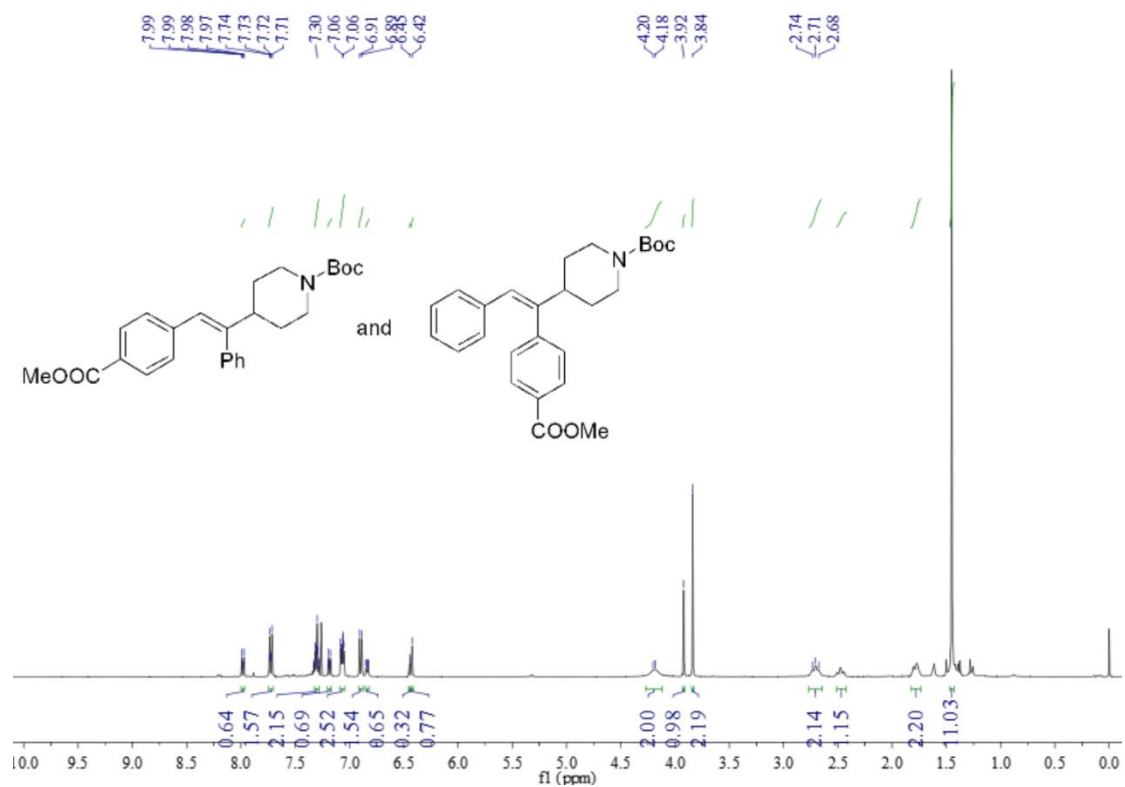
¹H NMR of **4v**



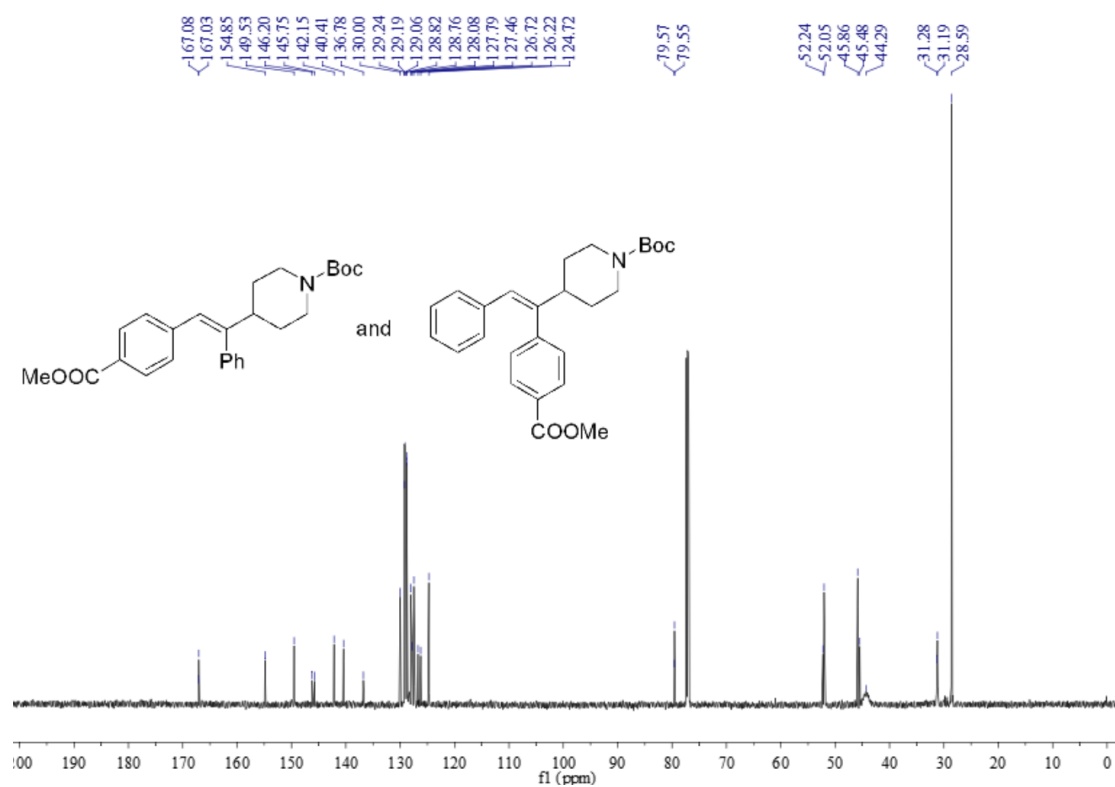
¹³C NMR of **4v**



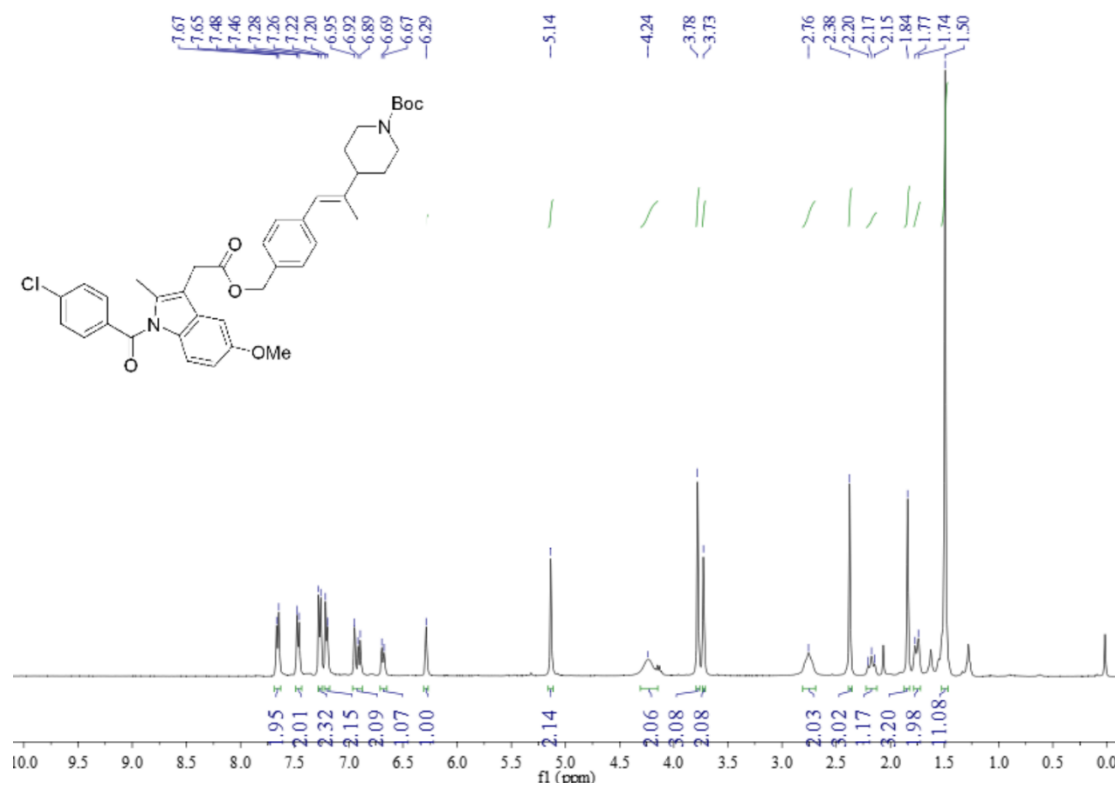
¹H NMR of **4w**



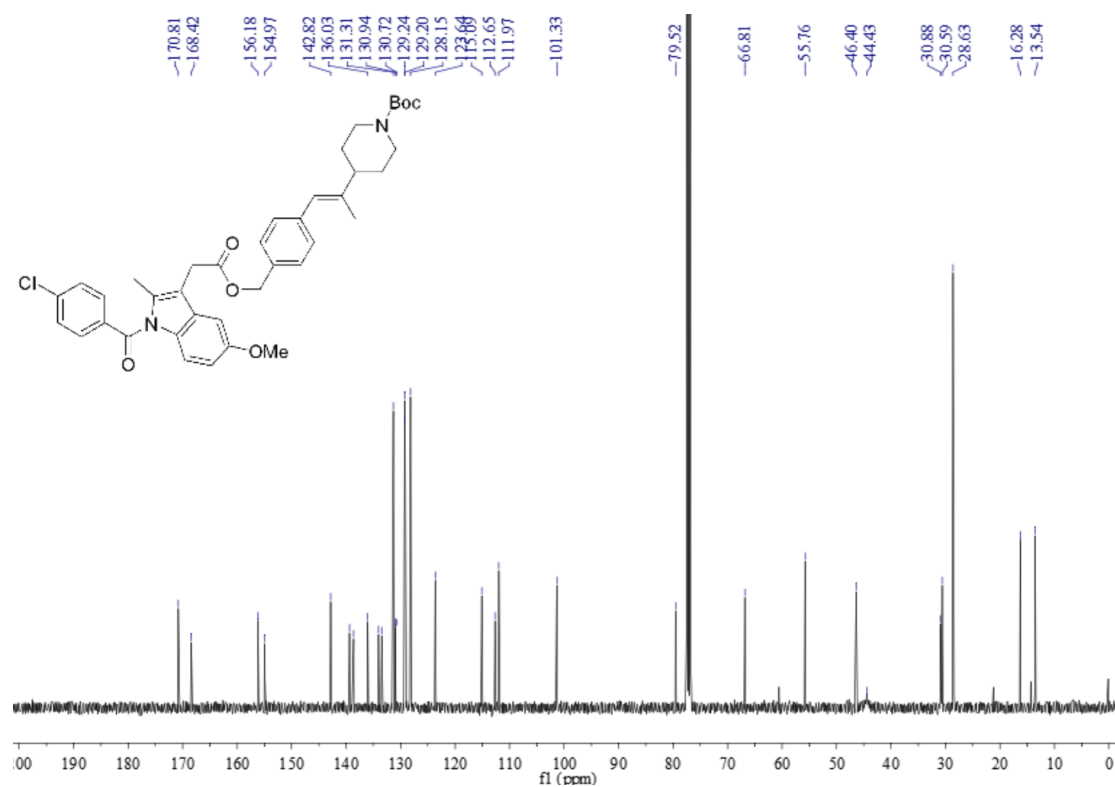
¹³C NMR of **4w**



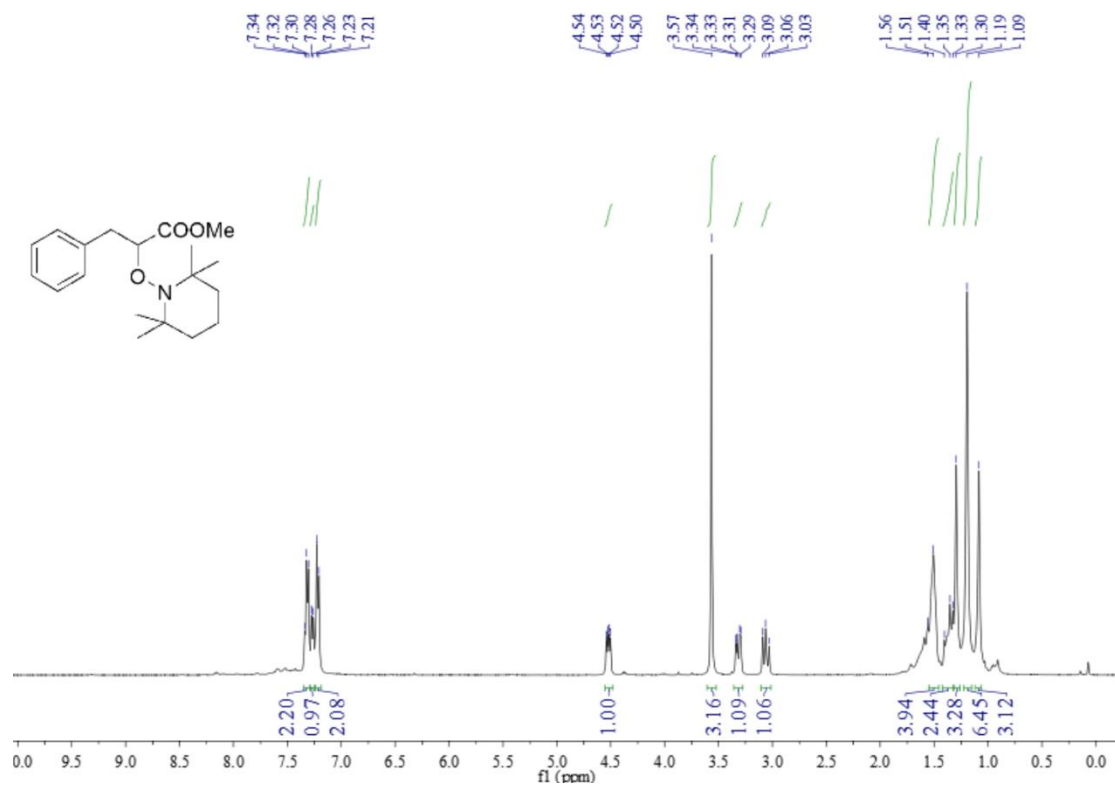
¹H NMR of **4x**



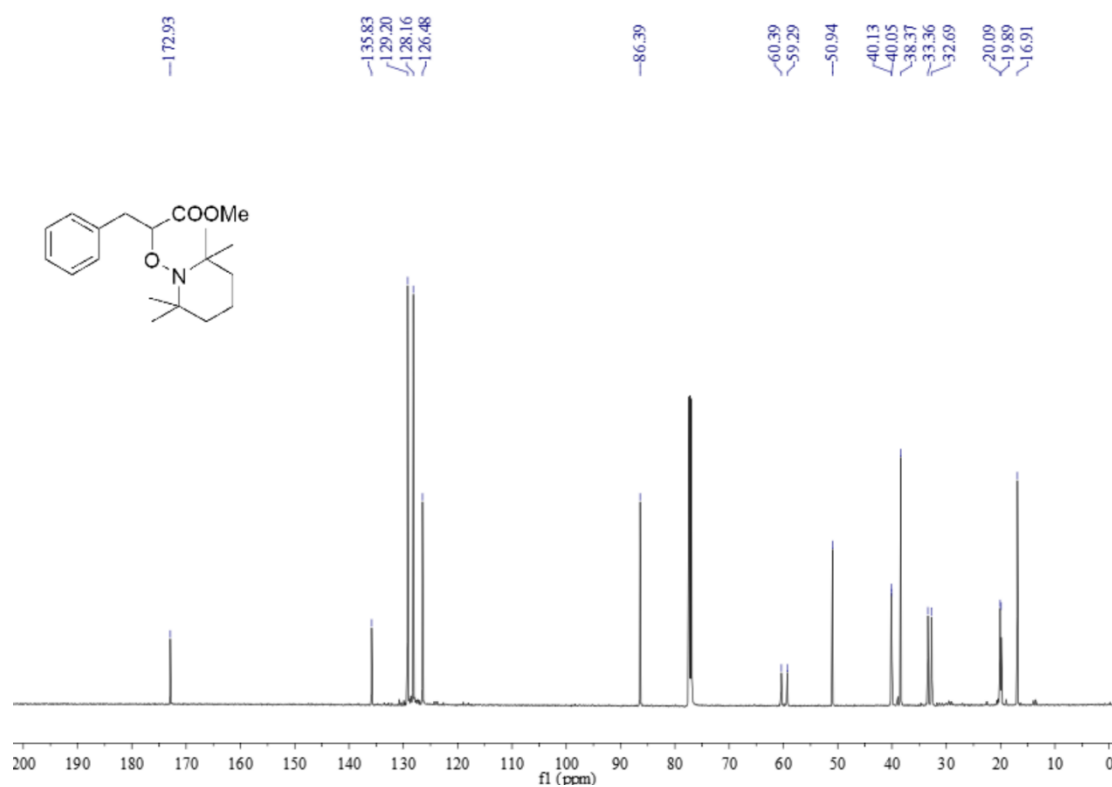
¹³C NMR of **4x**



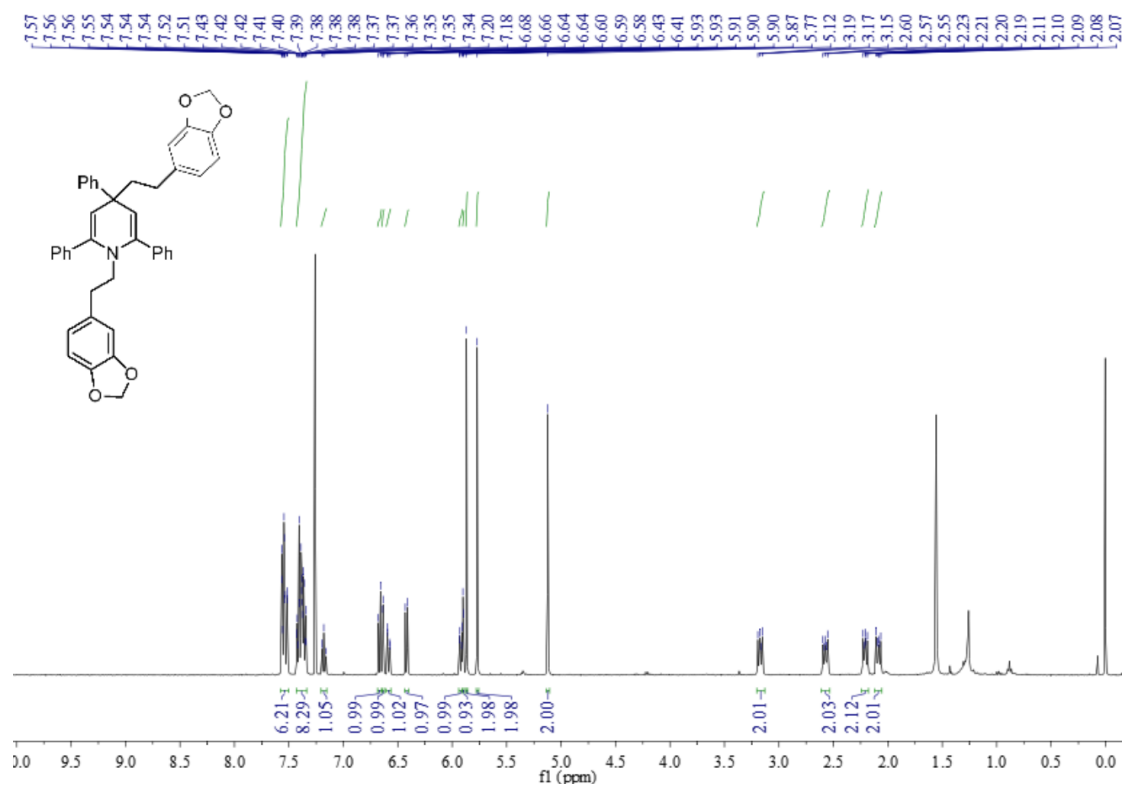
¹H NMR of **5**



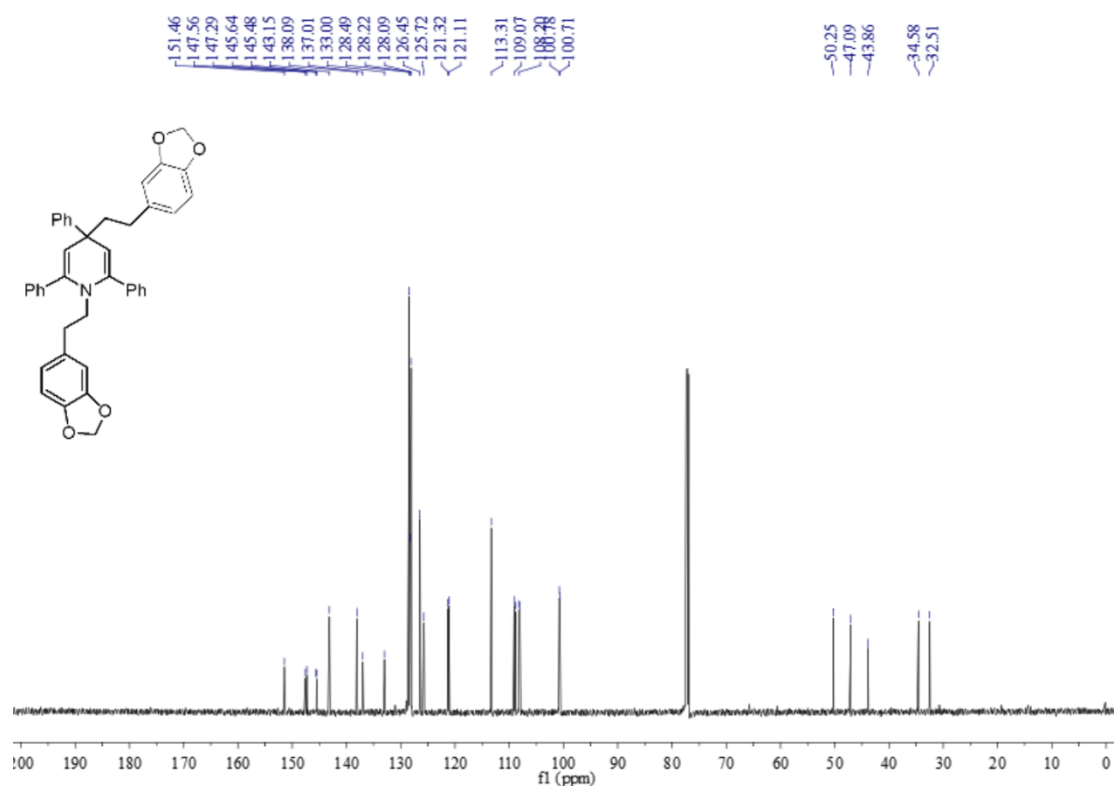
¹³C NMR of 5



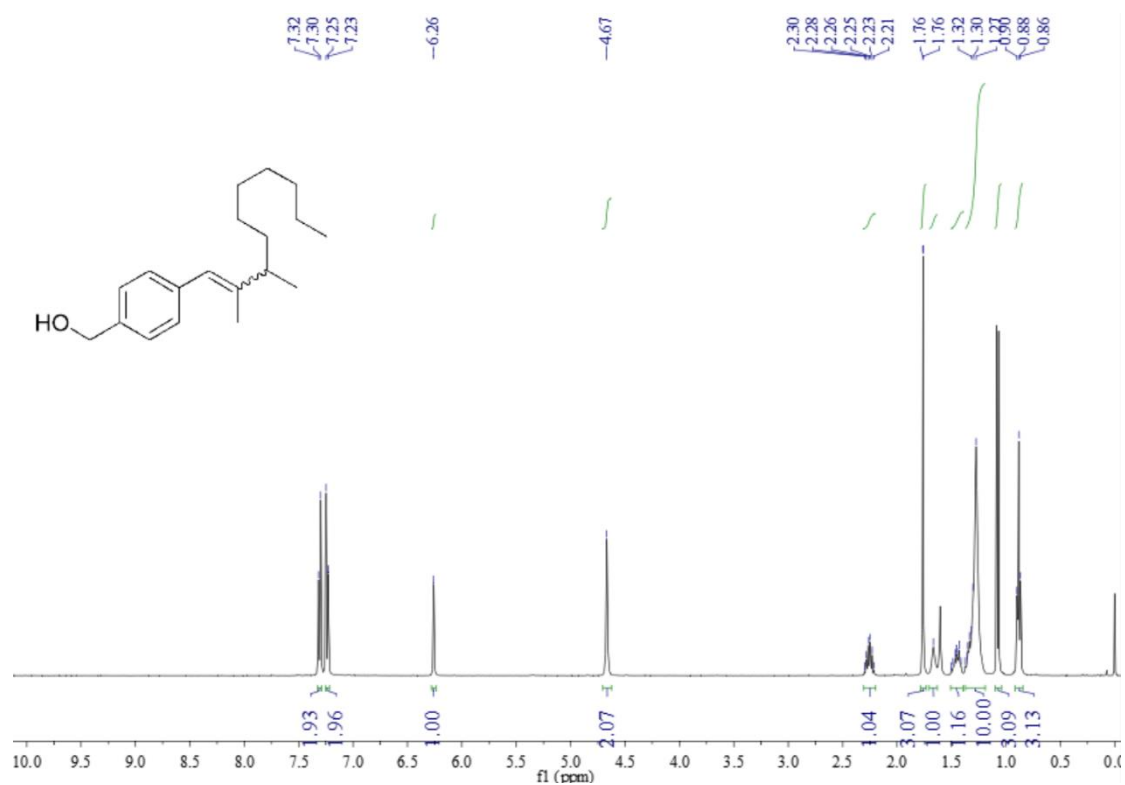
¹H NMR of 6



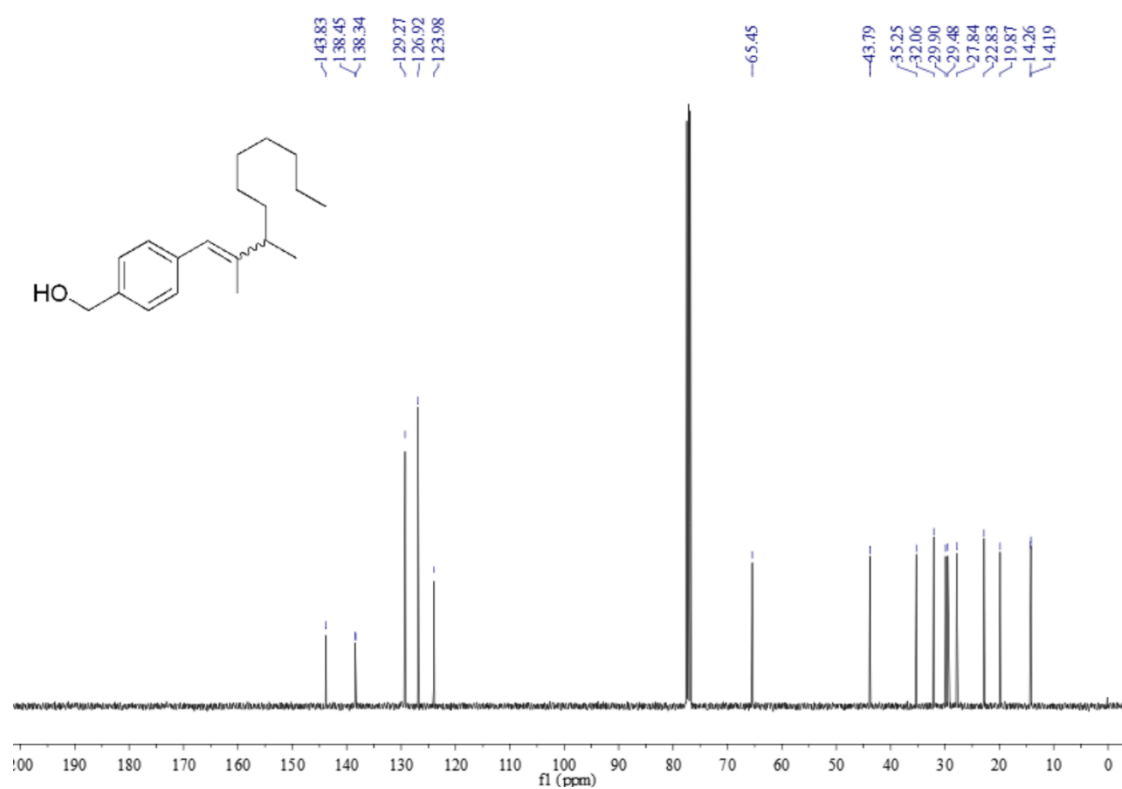
¹³C NMR of **6**



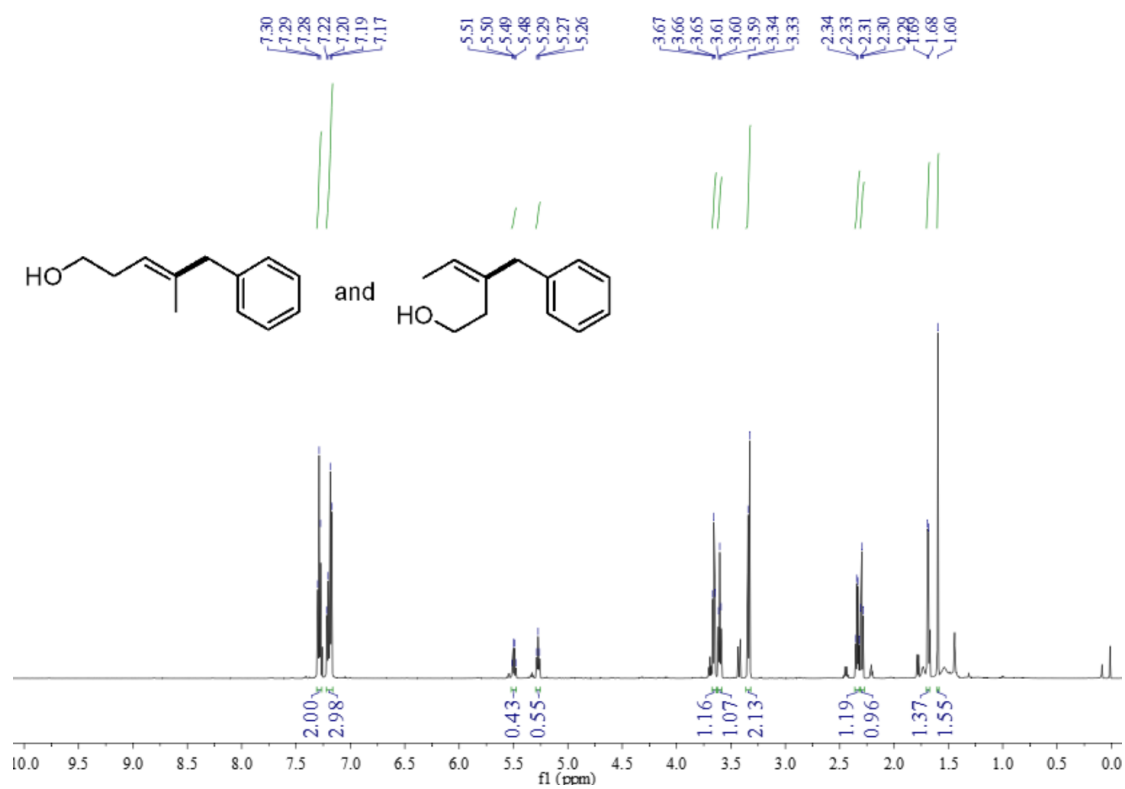
¹H NMR of **7**



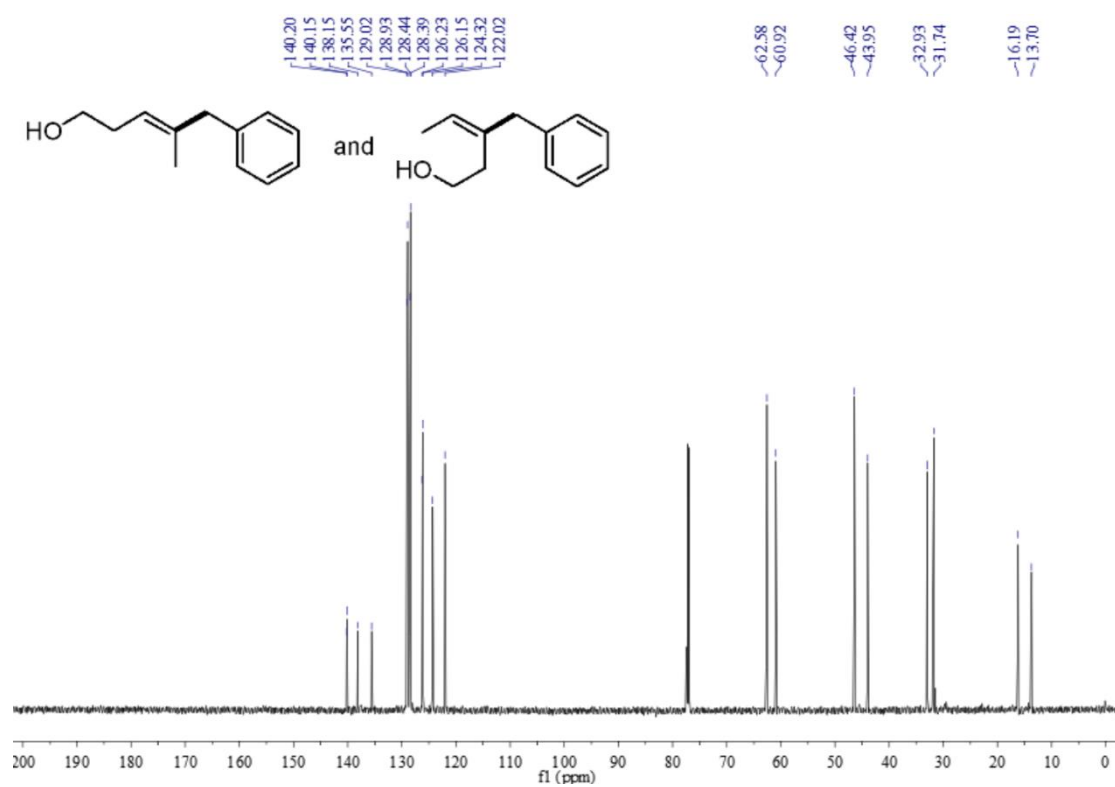
^{13}C NMR of **7**



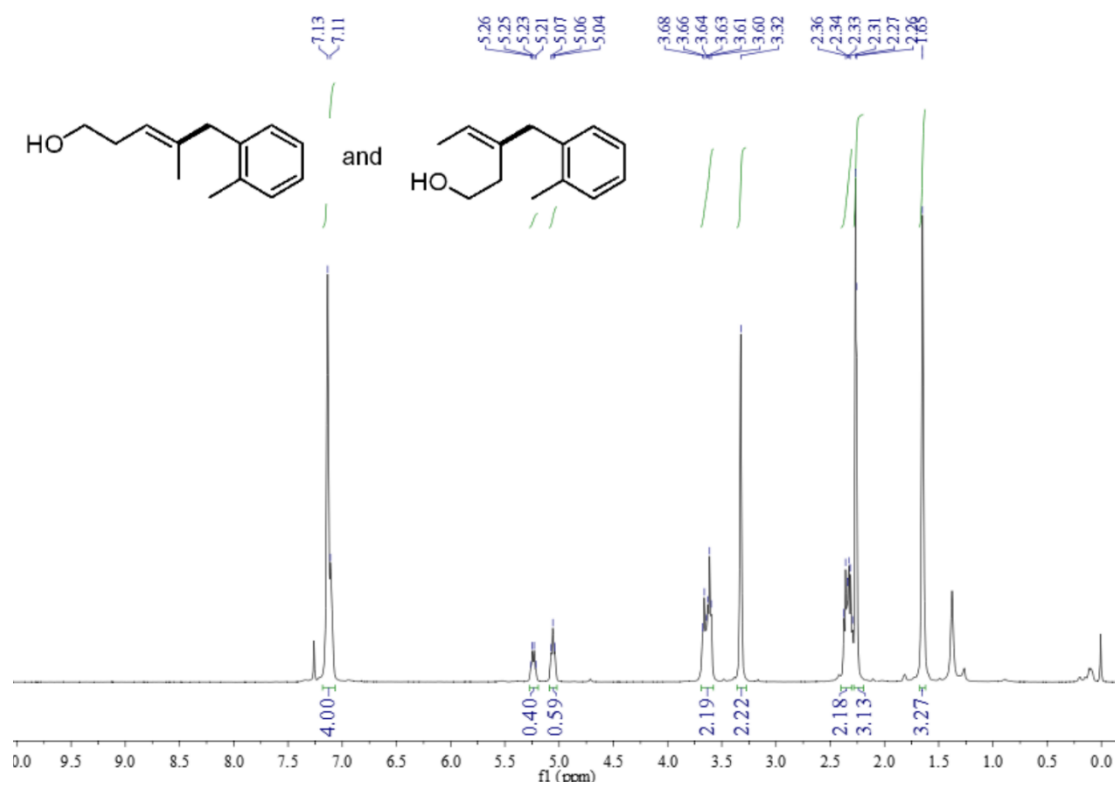
^1H NMR of **8a**



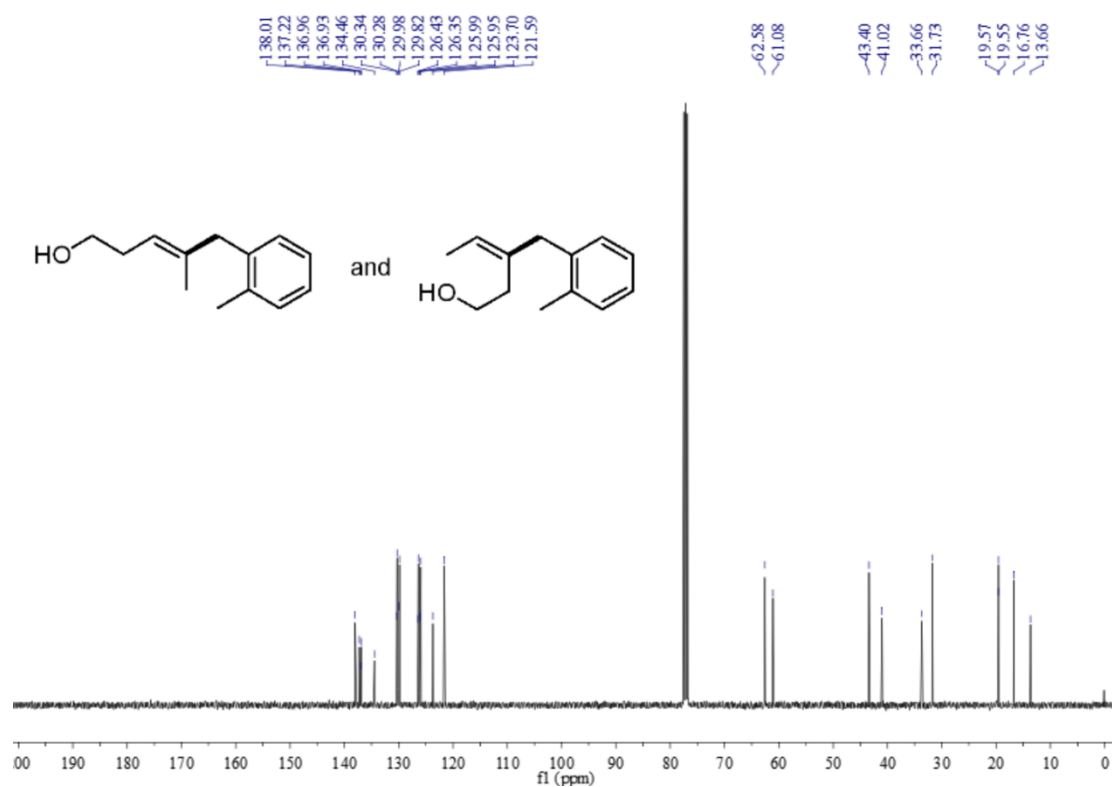
^{13}C NMR of **8a**



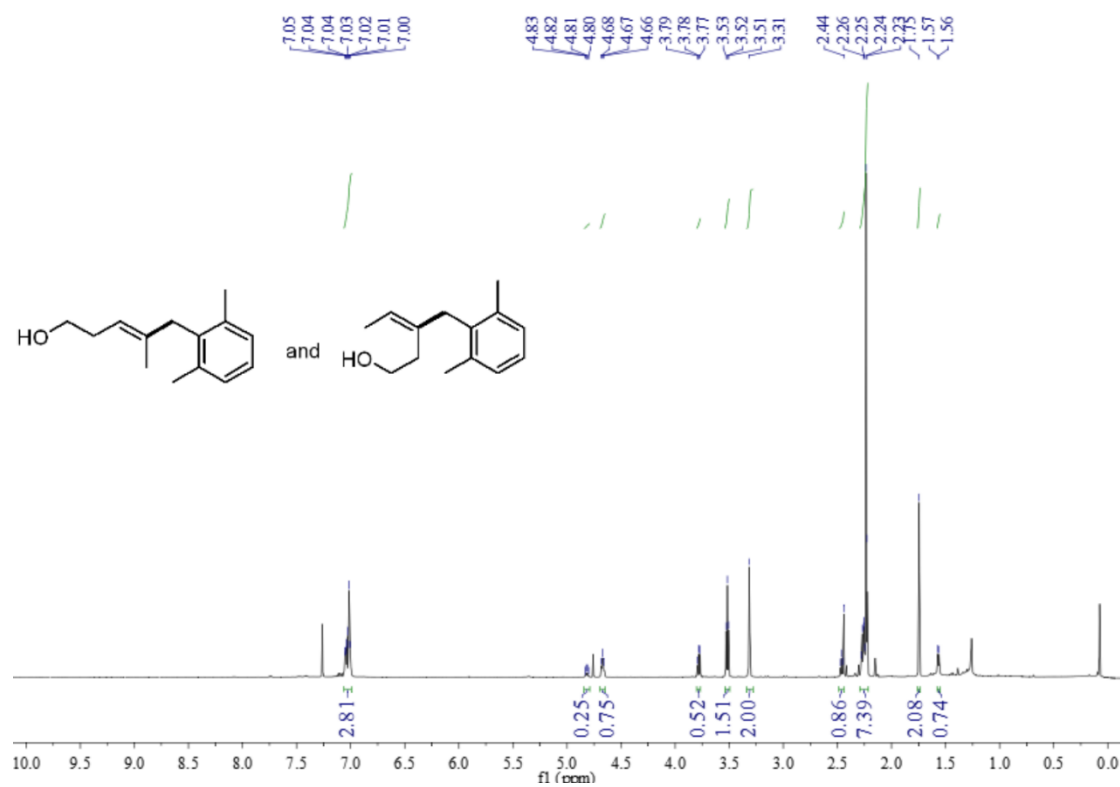
^1H NMR of **8b**



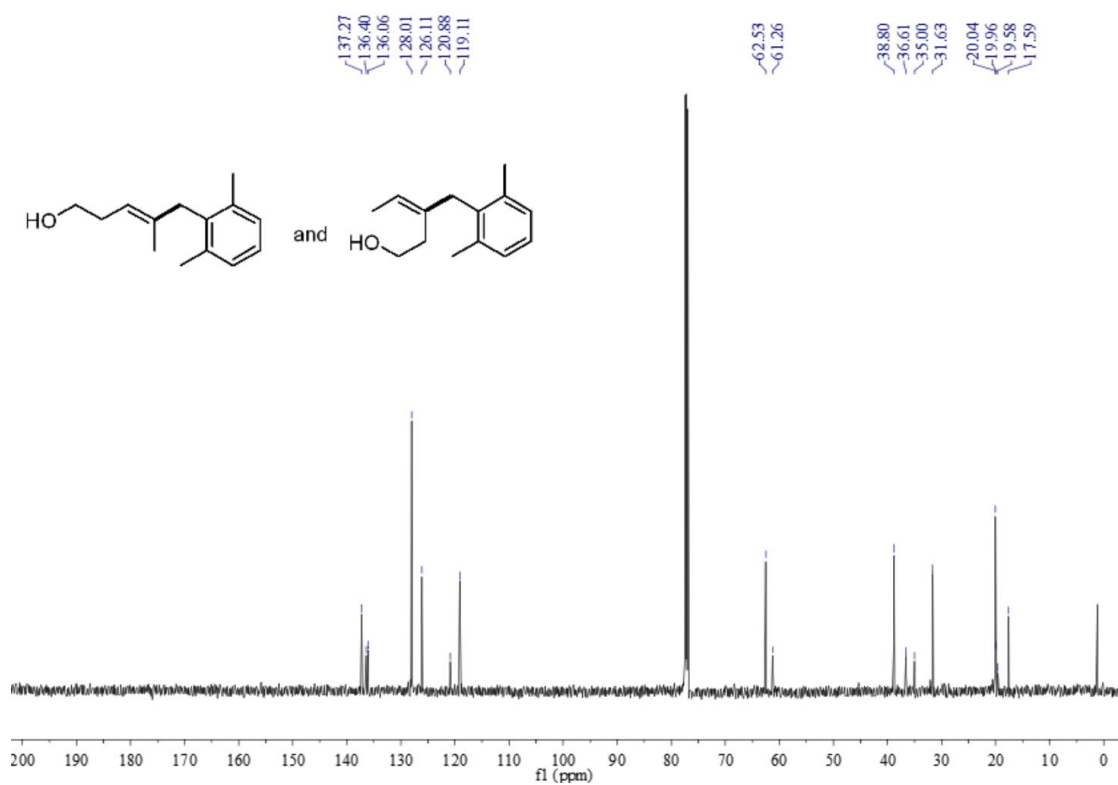
^{13}C NMR of **8b**



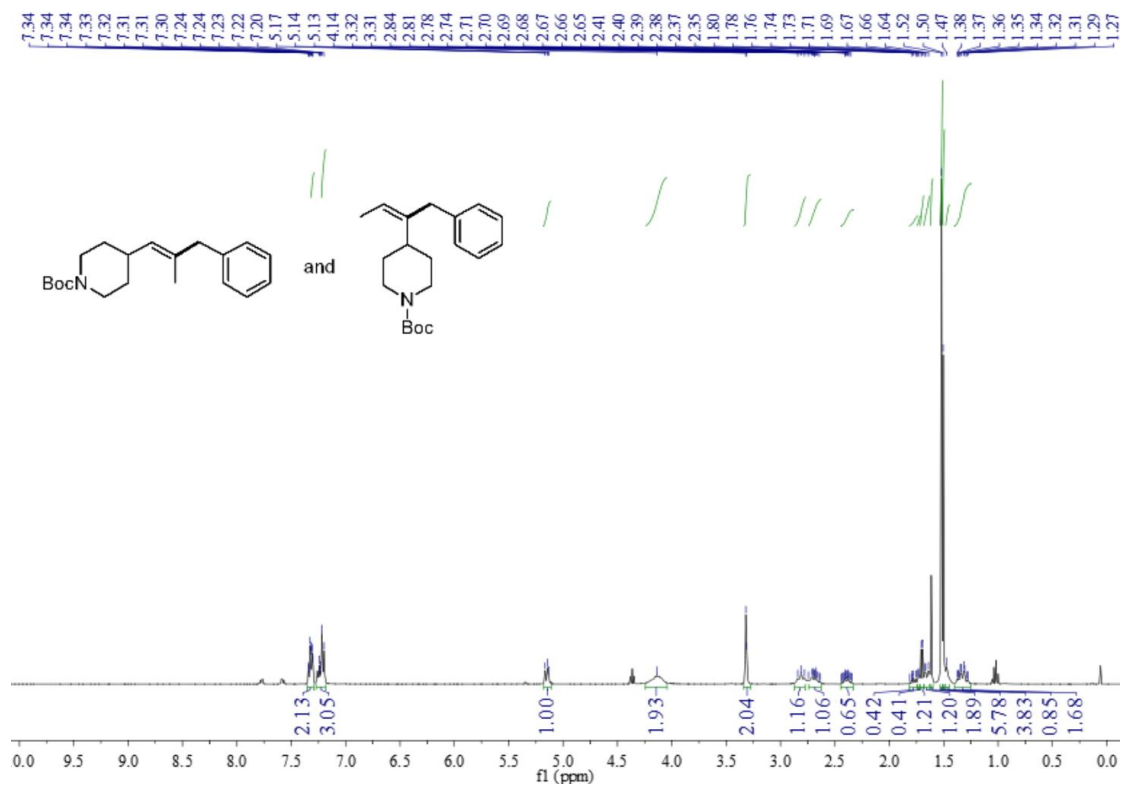
^1H NMR of **8c**



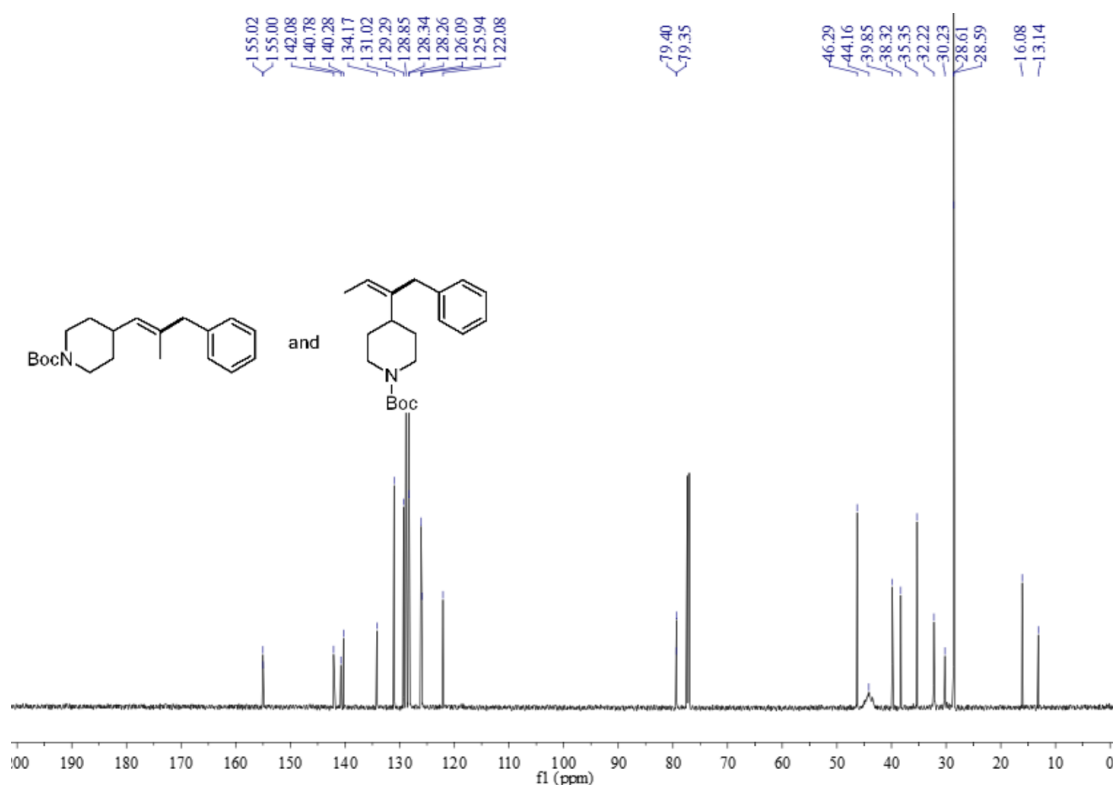
^{13}C NMR of **8c**



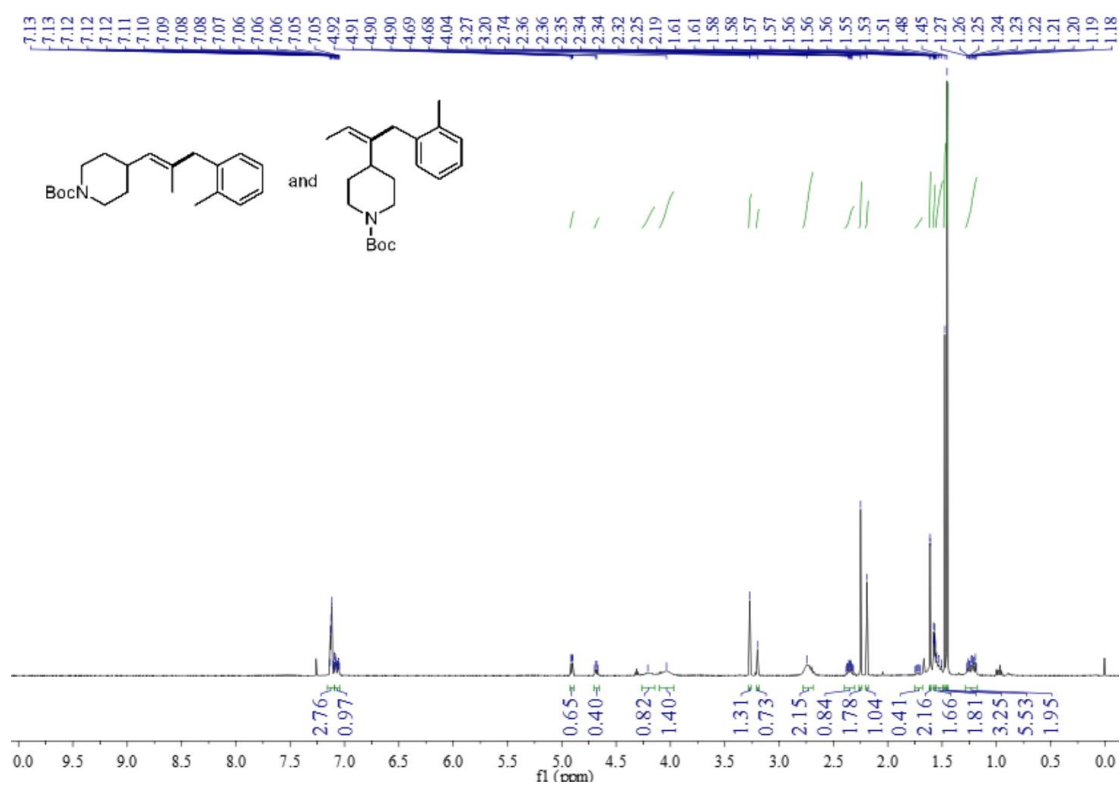
^1H NMR of **9a**



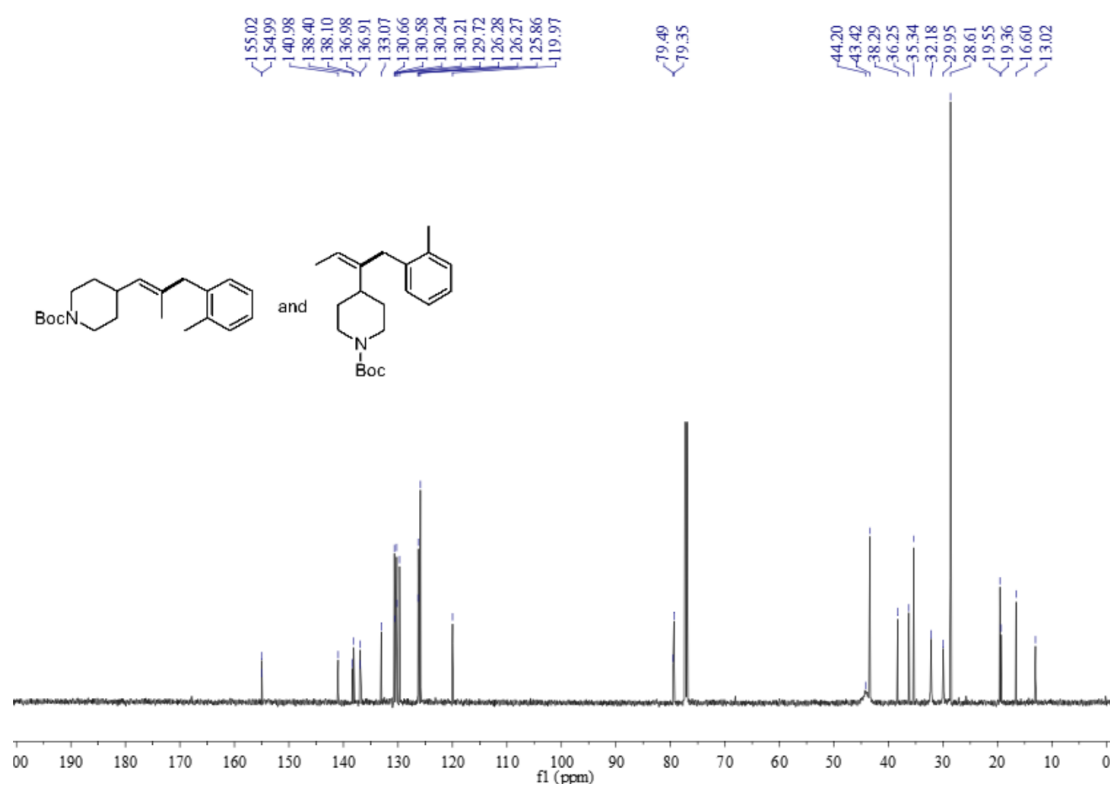
¹³C NMR of **9a**



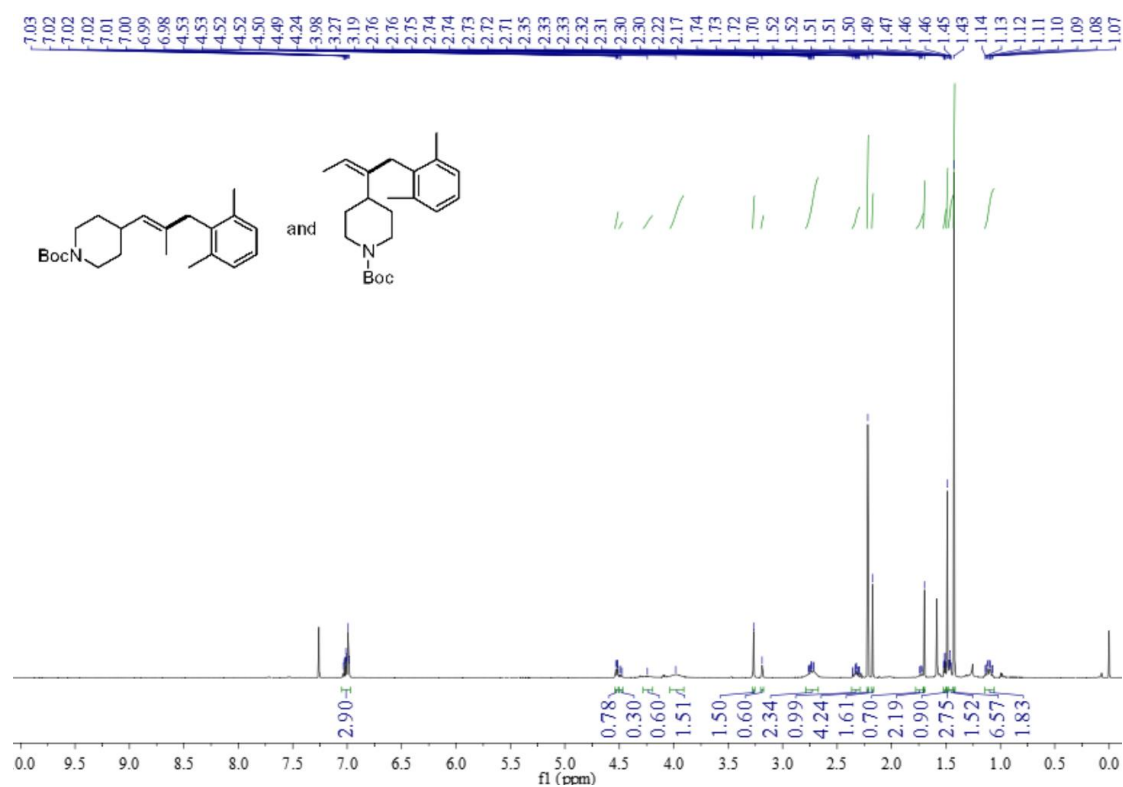
¹H NMR of **9b**



¹³C NMR of **9b**



¹H NMR of **9c**



^{13}C NMR of **9c**

