

Supporting Information

Pd(II)-Catalyzed hydroarylations/hydroalkenylations of terminal alkynes: regioselective synthesis of allylic, homoallylic and 1,3-diene systems

Jivan Shinde, Sundaram Suresh, Veerababurao Kavala, and Ching-Fa Yao*

Department of Chemistry, National Taiwan Normal University, 88, Sec. 4, Ting-Zhou Road, Taipei-11677,
Taiwan R.O.C.

* E-mail: cheyaocf@ntnu.edu.tw

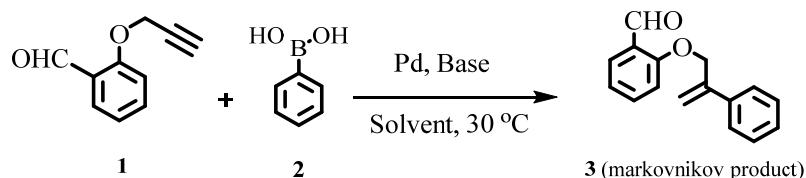
Table of Contents

I	General Remarks	S2
II	Optimization of the Reaction Conditions	S3
III	Experimental procedures	S3
IV	Control Experiments	S10
V	Single Crystal X-ray Analytical Data	S15
VI	Spectral Data	S18
VII	References	S32
VIII	Spectra Copies	S34

I. General Remarks:

Unless otherwise stated, all reagents were purchased from commercial suppliers and were used directly without any further purification. All solvents were dried according to known methods and distilled prior to use. All reactions were conducted under a nitrogen atmosphere on a dual-manifold Schlenk line unless otherwise mentioned and in oven-dried glassware. All reactions that require anhydrous conditions were conducted under an argon atmosphere. For reactions that required heating, an oil bath was used as the heat source. (Flash column chromatography was performed on 63-200 mesh silica gel using n-hexane (distilled) and ethyl acetate as eluents. ^1H and ^{13}C NMR spectra were recorded on a Bruker Ascend spectrometer at 400 and 100 MHz, respectively. Chemical shifts are reported in parts per million (ppm) on the δ scale by using CDCl_3 , as an internal standard. Multiplicities were indicated by using abbreviations s=singlet; d=doublet; t=triplet; q=quartet; and m=multiplet. Coupling constants are expressed in Hertz (Hz). High-Resolution Mass Spectra (HRMS) were recorded in JEOL JMS-700 M Station and ESI-TOF mode. The melting points (mp) were obtained on an Electro-Thermal FARGO MP-2D capillary melting point apparatus. The X-ray diffraction measurements were carried out at 200 K on either a Bruker D8 Venture or a Bruker KAPPA APEX II CCD area detector system equipped with a graphite monochromator and a Mo-K α fine-focus sealed tube ($k = 0.71073 \text{ \AA}$).

II. Table 1. Optimization of the Reaction Conditions.



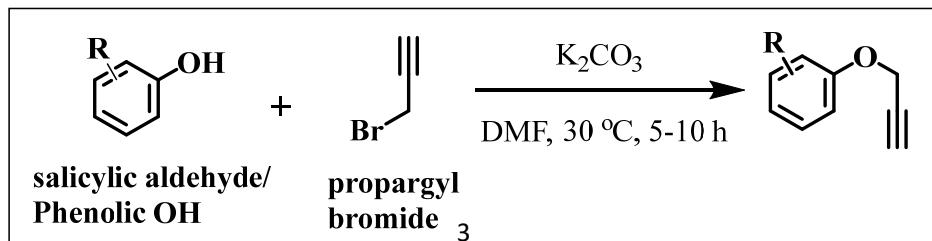
Entry ^a	Cat. (3 mol%)	Base (equiv.)	Solvent 2 mL	T(°C) /t (h)	Yield (%) ^b
01	-	KOAc	DCM	30/2.5	ND
02	PdCl ₂ (PPh ₃) ₂	KOAc	DCM	30/2.5	66
03	PdCl ₂ (PPh ₃) ₂	KOAc	DMSO	30/2.5	ND
04	PdCl ₂ (PPh ₃) ₂	KOAc	DMF	30/2.5	ND
05	PdCl ₂ (PPh ₃) ₂	KOAc	THF	30/2.5	14
06	PdCl ₂ (PPh ₃) ₂	KOAc	ACN	30/2.5	ND
07	PdCl ₂ (PPh ₃) ₂	KOAc	CHCl ₃	30/2.5	58
08	PdCl₂(PPh₃)₂	KOAc	DCE	30/2.5	98
09 ^c	PdCl ₂ (PPh ₃) ₂	KOAc	DCE	30/2.5	54
10	PdCl ₂ (PPh ₃) ₂	NaOAc	DCE	30/4.5	65
11	PdCl ₂ (PPh ₃) ₂	K ₂ CO ₃	DCE	30/2.5	ND
12	PdCl ₂ (PPh ₃) ₂	K ₃ PO ₄	DCE	30/2.5	ND
13	PdCl ₂	KOAc	DCE	30/2.5	06
14	Pd(OAc) ₂	KOAc	DCE	30/2.5	ND

^[a] **1** (0.4 mmol), **2** (0.6 mmol), catalyst (3 mol%), KOAc (0.8 mmol), solvent (2 mL) at 30 °C for 2.5 h. ^[b] Yields were calculated from the crude reaction mixtures by ¹H NMR using CH₂Br₂ as the internal standard. ^[c] 1 mol% of catalyst was used. The biphenyl compound was formed only in traces. ND-not detected.

III. Experimental Procedures

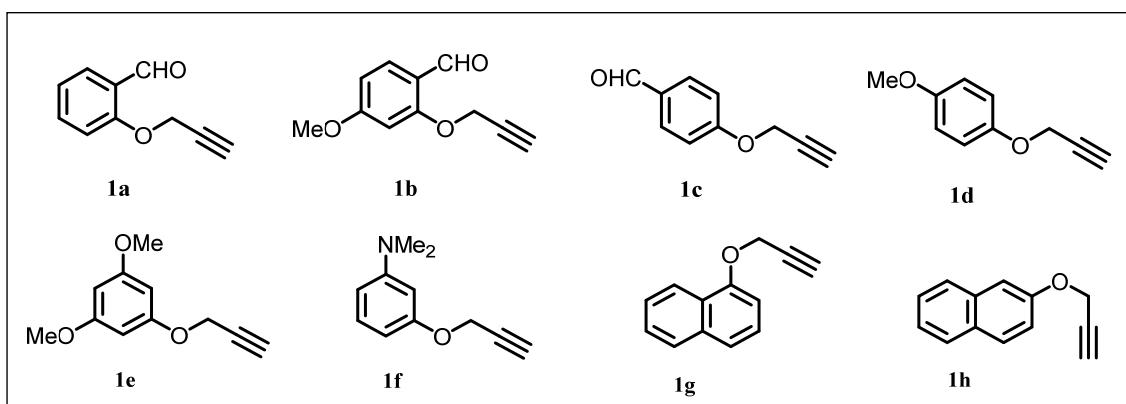
Synthesis of starting materials: -

- a) General procedure for the synthesis of propargyl aryl ethers¹

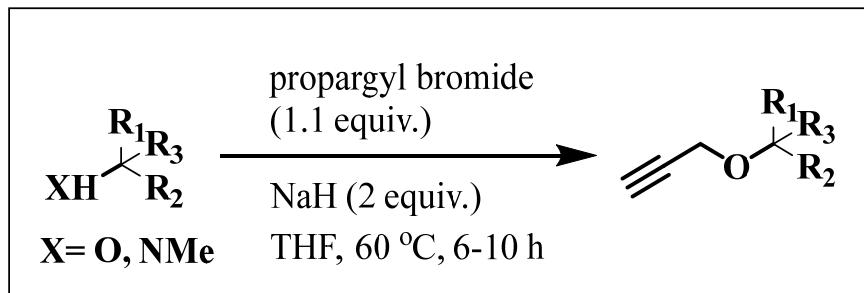


A 50 mL round bottom flask was charged with salicylic aldehyde (1220 mg, 10 mmol) in DMF (25 mL) then K₂CO₃ (2760 mg, 20 mmol) was added. Then, a propargyl bromide (1309 mg, 11 mmol) was added dropwise at 0 °C over 5 min. After completion of the addition, the reaction mixture was stirred at 30 °C for 5 h and quenched with crushed ice. The reaction mixture was extracted with EtOAc (30 mL × 3) and the organic phase was dried over anhydrous MgSO₄. The solvent was then removed under reduced pressure and the crude product was purified by flash chromatography with the eluent hexane-ethyl acetate.

List of Isolated molecules-



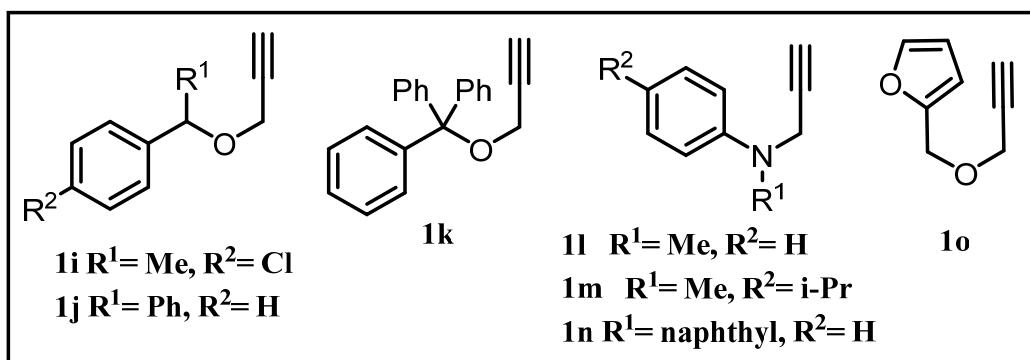
b) General procedure for propargyl aryl ethers/amine synthesis²



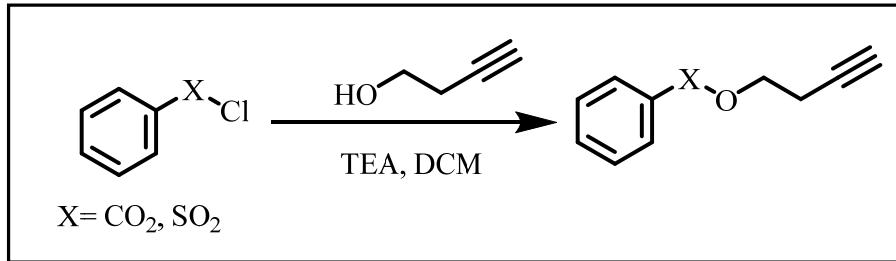
In a dried 50 mL flask containing alcohol/amine (3 mmol) in THF (25 mL), NaH (0.144 g, 6 mmol) was added. Then a solution of propargyl bromide (0.392 g, 3.3 mmol) in THF (5 mL) was added dropwise over 10 minutes. The reaction mixture was stirred at 60 °C for 6-10h, after completion of the reaction, NH₄Cl solution was added and the reaction mixture was dissolved

in ethyl acetate further organic layer was separated and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure, and the crude residue was subjected to flash column chromatography on silica gel (eluent hexane-ethyl acetate) to obtain the pure terminal alkynes.

List of Isolated molecules-

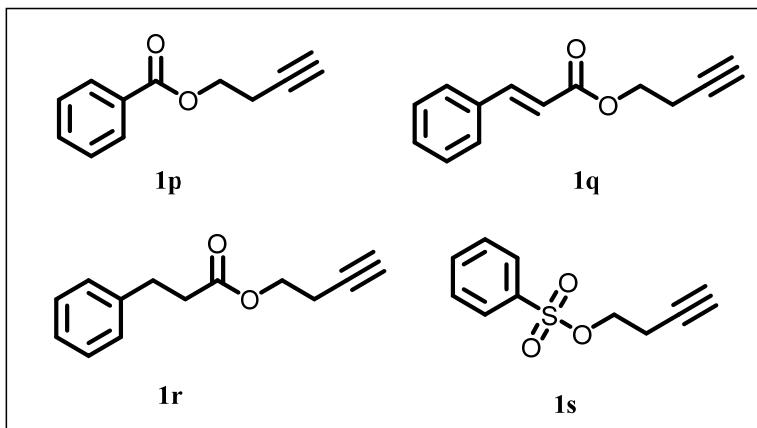


c) General procedure for But-3-yn-1-yl benzoate synthesis³

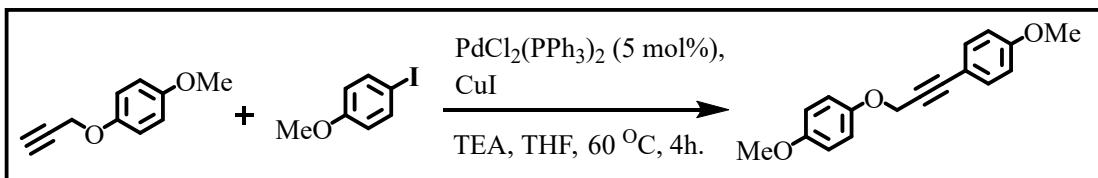


In a dried 50 mL flask containing but-3-yn-1-ol (0.77 g, 5.5 mmol) in DCM (25 mL) at 0 °C, TEA (2 mL, 15 mmol) was added. Then a solution of benzoyl chloride/sulfonyl chloride (5 mmol) was added. The reaction mixture was stirred at room temperature for 6 hours, after completion of the reaction crushed ice was added and the reaction mixture was washed by DCM. The organic layer was separated by a separatory funnel and further dried over anhydrous MgSO₄. The solvent was removed under reduced pressure, and the crude residue was subjected to flash column chromatography on silica gel (eluent hexane-ethyl acetate) to obtain the pure but-3-yn-1-yl benzoate.

List of Isolated molecules-

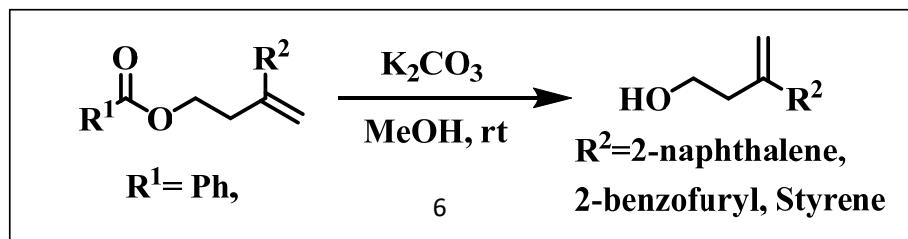


d) Synthesis of 1-methoxy-4-(3-(4-methoxyphenoxy)prop-1-yn-1-yl)benzene⁴



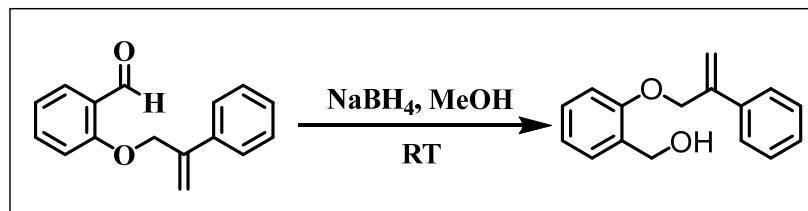
To a 50 mL round bottom flask was added 1-methoxy-4-(prop-2-yn-1-yloxy)benzene (0.648 g, 4 mmol,) and 1-iodo-4-methoxybenzene (1.1 g, 4.8 mmol). Later Triethyl amine (0.808 g, 8 mmol) and THF solvent (30 mL) were added to system then reaction mixture degassed by using nitrogen gas. Then CuI (0.038 g, 0.2 mmol). and PdCl₂(PPh₃)₂ (0.140 g 5 mol%) were added. The resulting mixture was heated for 4 h at 60 °C. After completion of the reaction, the reaction mixture extracted with ethyl acetate-water system, and the organic layer was separated and evaporated under reduced pressure. The crude residue was then subjected to flash column chromatography on silica gel (eluent hexane-ethyl acetate) to obtain the pure internal alkyne compound.

e) Synthesis of homoallylic alcohol



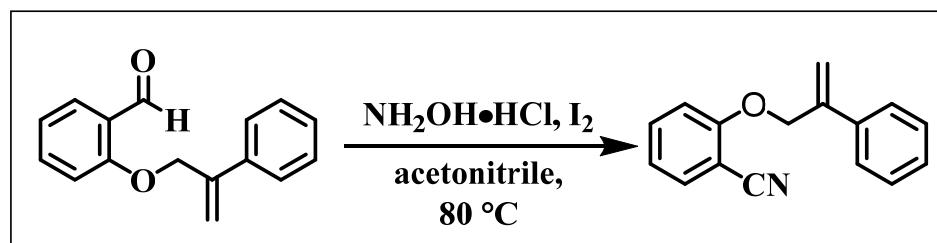
To a 25 mL round bottom flask was added 3-(naphthalen-2-yl)but-3-en-1-yl benzoate (0.060 g, 0.2 mmol,), K₂CO₃ (0.055 g, 0.4 mmol,) and MeOH 5 mL. The resulting mixture was stirred at room temperature. After completion of the reaction, the reaction mixture was evaporated on a rotatory evaporator and then extracted with ethyl acetate-water system, and the organic layer was separated and evaporated under reduced pressure. The crude residue was then subjected to flash column chromatography on silica gel (eluent hexane-ethyl acetate) to obtain the pure homoallylic alcohol.

f) Synthesis of (2-((2-Phenylallyl)oxy)phenyl)methanol



To a 25 mL round bottom flask **3a** (0.095 g, 0.4 mmol) and 2 mL MeOH were added. Next, NaBH₄ (0.030 g, 0.8 mmol) was added, and the resulting solution was stirred at room temperature for 1 h. The reaction mixture was quenched with ammonium chloride solution, and the organic layer was separated and evaporated under reduced pressure. The crude product was subjected to flash column chromatography on silica gel (eluent hexane-ethyl acetate) to obtain the pure target compound.

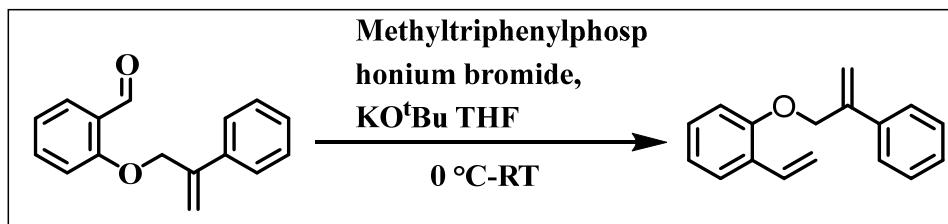
g) Synthesis of 2-((2-Phenylallyl)oxy)benzonitrile



To a 25 mL round bottom flask **3a** (0.095 g, 0.4 mmol), and 5 mL acetonitrile were added. Next, NH₂OH.HCl (0.083 g, 1.2 mmol) and Iodine (0.030 g, 0.12 mmol) were added, and the

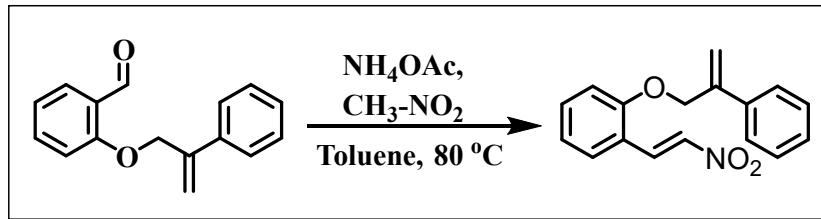
resulting solution was refluxed for 6 h. The resulting reaction mixture was quenched with cold water, and the organic layer was separated and evaporated under reduced pressure. The crude product was subjected to flash column chromatography on silica gel (eluent hexane-ethyl acetate) to obtain the pure target compound.

h) Synthesis of 1-((2-Phenylallyl)oxy)-2-vinylbenzene



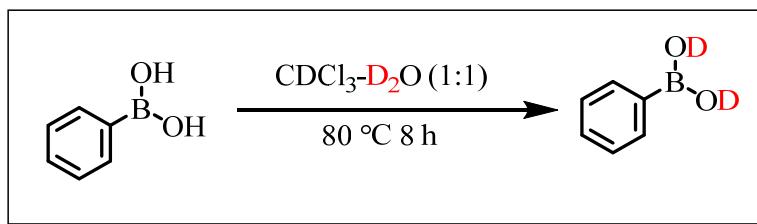
To a 25 mL round bottom flask Methyltriphenylphosphonium bromide (0.171 g, 0.48 mmol) and dry THF 5 mL were added under an inert atmosphere further Potassium tert-butoxide (0.089 g, 0.8 mmol) was added and reaction mixture was allowed to stir 1 h. Next, **3a** (0.095 g, 0.4 mmol) was added, and the resulting mixture was stirred at room temperature for 6 h. The reaction mixture was quenched with crushed ice, and the organic layer was separated and evaporated under reduced pressure. The crude product was subjected to flash column chromatography on silica gel (100 % hexane) to obtain the pure product.

i) Synthesis of (*E*)-1-(2-Nitrovinyl)-2-((2-phenylallyl)oxy)benzene



To a 25 mL round bottom flask **3a** (0.095 g, 0.4 mmol) and toluene 5 mL were added. Then NH₄OAc (0.062 g, 0.8 mmol) and nitromethane (0.037 g, 0.6 mmol) were added, and the reaction mixture was refluxed for 4 h. Next, the resulting mixture was quenched with water, and the organic layer was separated and evaporated under reduced pressure. The crude product was subjected to flash column chromatography on silica gel (eluent hexane-ethyl acetate) to obtain the pure product.

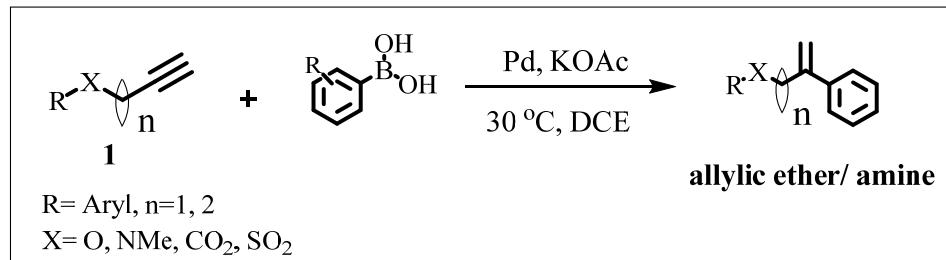
j) Synthesis of deuterated Phenylboronic acid⁵



To a 25 mL round bottom flask was added Phenyl boronic Acid (0.610 g, 5.0 mmol,) and $\text{CDCl}_3\text{-D}_2\text{O}$ (1:1) 3 mL. Then resulting solution was refluxed at 80 °C for 8 h in an oil bath. The reaction mixture was cooled and deuterated phenyl boronic acid was obtained. After filtration, the white solid was dried by using a high vacuum for 5 h. Deuterated phenylboronic acid (0.390 g, 63%, >85% D) was obtained. ^1H NMR (400 MHz, DMSO-d6) δ 7.90 – 7.78 (m, 2H), 7.42 – 7.30 (m, 3H), 8.02 (s, 0.30).

General Procedures-

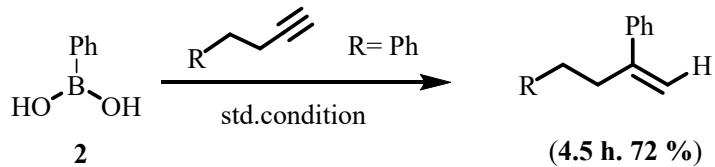
[A] Palladium (II)-Catalyzed regioselective hydroarylation of terminal alkyne:



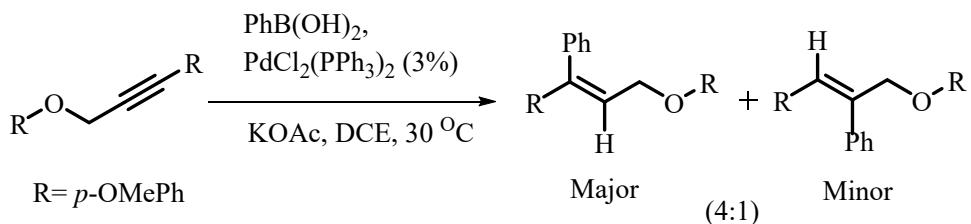
A 10 mL round bottom flask fitted with a septum containing alkyne substrate **1** (0.4 mmol), phenylboronic acid **2a** (0.073 g, 0.6 mmol) and KOAc (0.078 g, 0.8 mmol, 2 equiv), finally the catalyst $\text{PdCl}_2(\text{PPh}_3)_2$ (0.0084 g, 3 mol %) was added. Then DCE (2.0 mL) solvent was added to the system and the reaction mixture was stirred at 30 °C for 2-5 h. At the end of the reaction, the reaction mixture was filtered on a celite pad with CH_2Cl_2 (10 mL) solvent. The crude products were purified by silica gel column chromatography using n-hexane/EtOAc as eluent to afford the desired product.

IV Control Experiments:

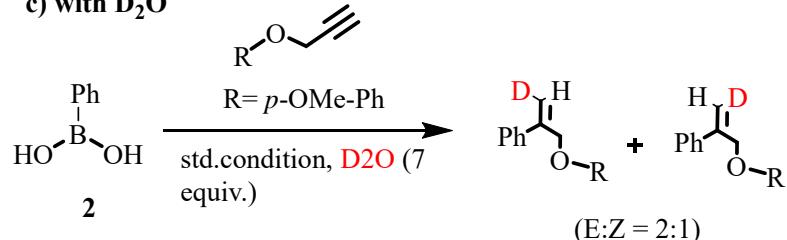
a) without heteroatom



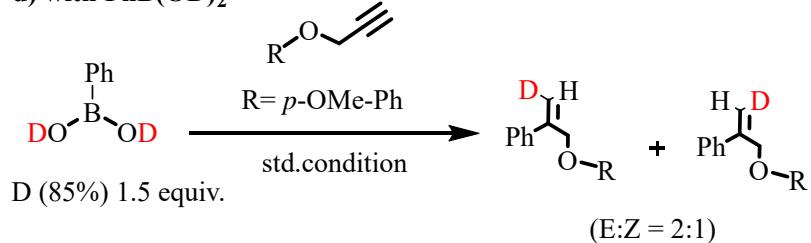
b) with internal alkyne



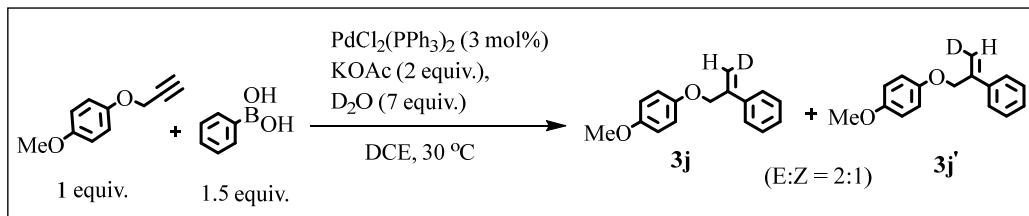
c) with D₂O



d) with PhB(OD)₂

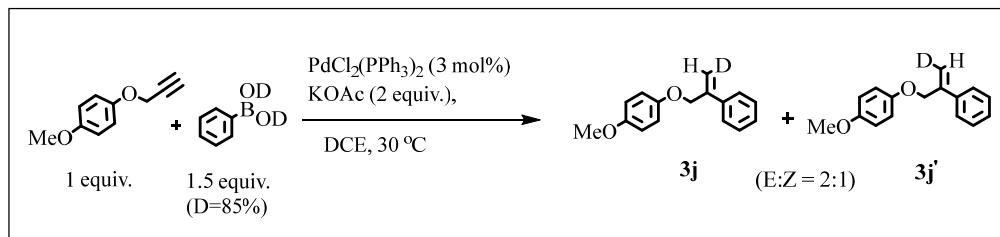


a) Studies with D₂O-⁶



A 10 mL round bottom flask fitted with a septum containing 1-methoxy-4-(prop-2-yn-1-yloxy)benzene (0.065 g, 0.4 mmol), phenylboronic acid **2** (0.073 g, 0.6 mmol), KOAc (0.078 g, 0.8 mmol, 2 equiv) and D₂O (7 equiv., 2.8 mmol) finally catalyst PdCl₂(PPh₃)₂ (0.0084, 3 mol %) was added, then DCE (2.0 mL) solvent was added to the system, and the reaction mixture was stirred at 30 °C for 1.5 h. At the end of the reaction, the reaction mixture was filtered on a celite pad with CH₂Cl₂ (10 mL) solvent. The crude products were purified by silica gel column chromatography using n-hexane/ EtOAc as eluent to afford desired products **3j** and **3j'** (E:Z= 2:1).

b) Studies with PhB(OD)₂-⁶



A 10 mL round bottom flask fitted with a septum containing 1-methoxy-4-(prop-2-yn-1-yloxy)benzene (0.065 g, 0.4 mmol), phenylboronic acid-d2 (D=85%) (0.087 g, 0.6 mmol) and KOAc (0.078 g, 0.8 mmol, 2 equiv), finally catalyst PdCl₂(PPh₃)₂ (3 mol %) was added to the system then DCE (2.0 mL) solvent was added and the reaction mixture was stirred at 30 °C for 1.5 h. At the end of the reaction, the reaction mixture was filtered on a celite pad with CH₂Cl₂ (10 mL) solvent. The crude products were purified by silica gel column chromatography using n-hexane/ EtOAc as eluent to afford desired products **3j** and **3j'** (E:Z= 2:1).

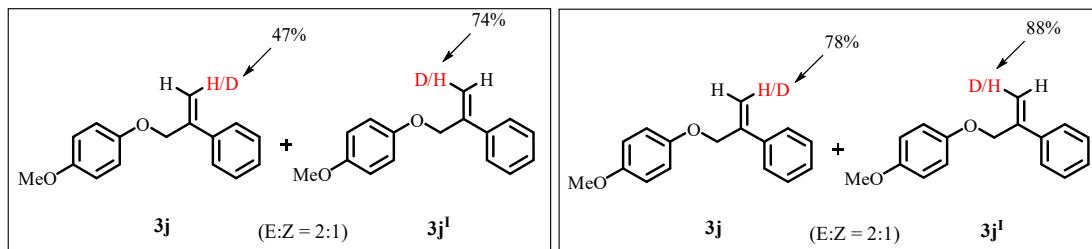
Deuteration % calculation-⁷

The equation below was used to determine the % of deuterium incorporation in allylic ether.

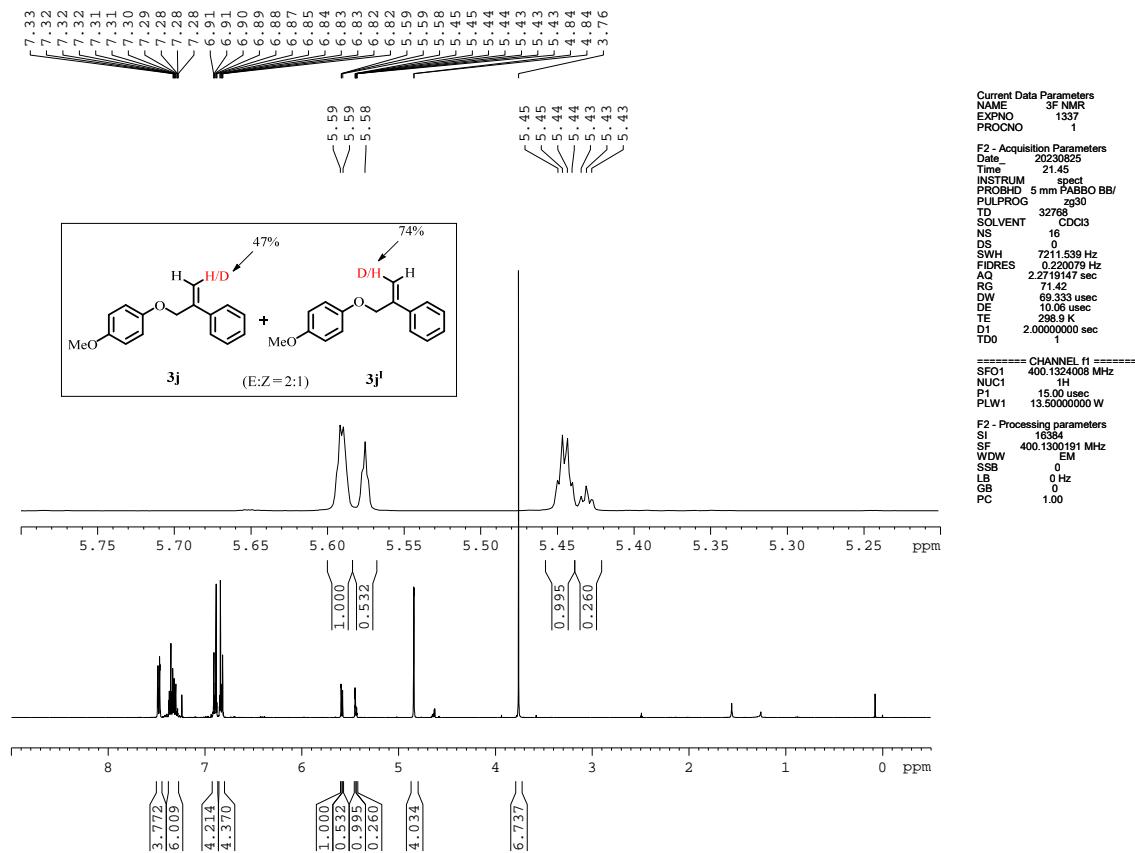
$$\% \text{ deuteration} = 100 - \left[\left(\frac{\text{residual integral}}{\text{no. labelling sites}} \right) \times 100 \right]$$

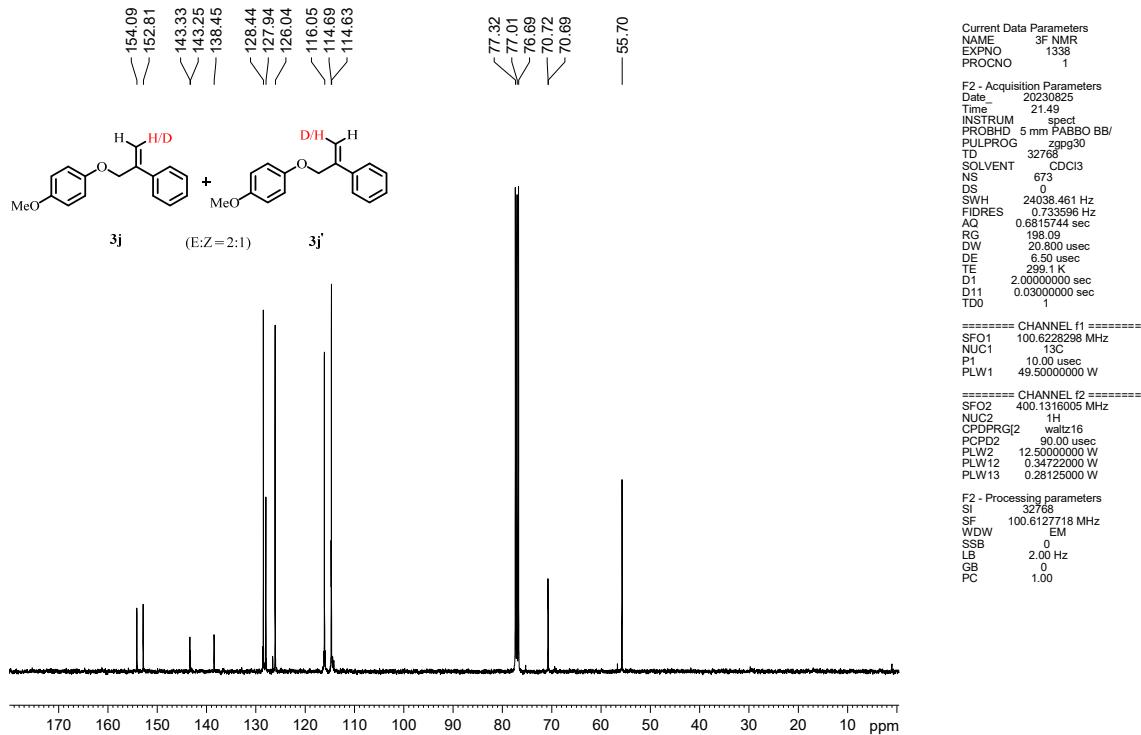
This experiment concluded boronic acid has more percentage of proton donor than water.

Studies with D₂O and PhB(OD)₂

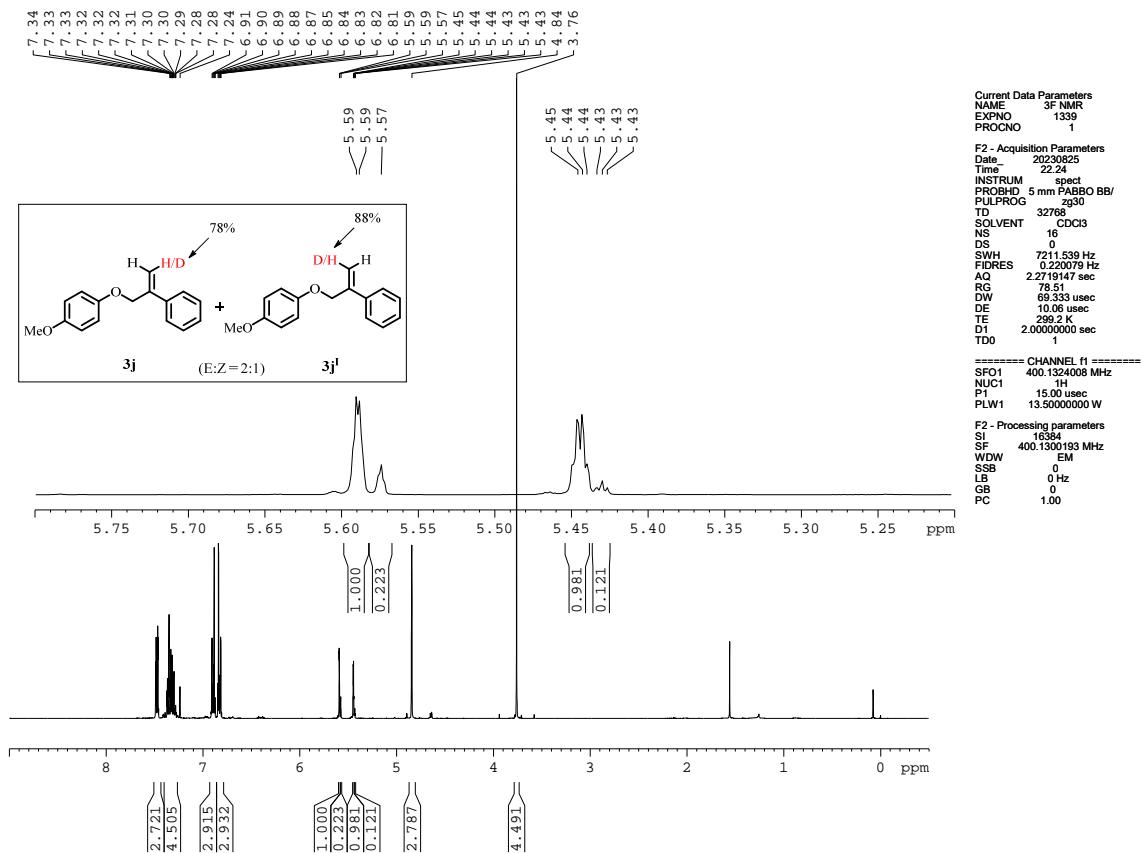


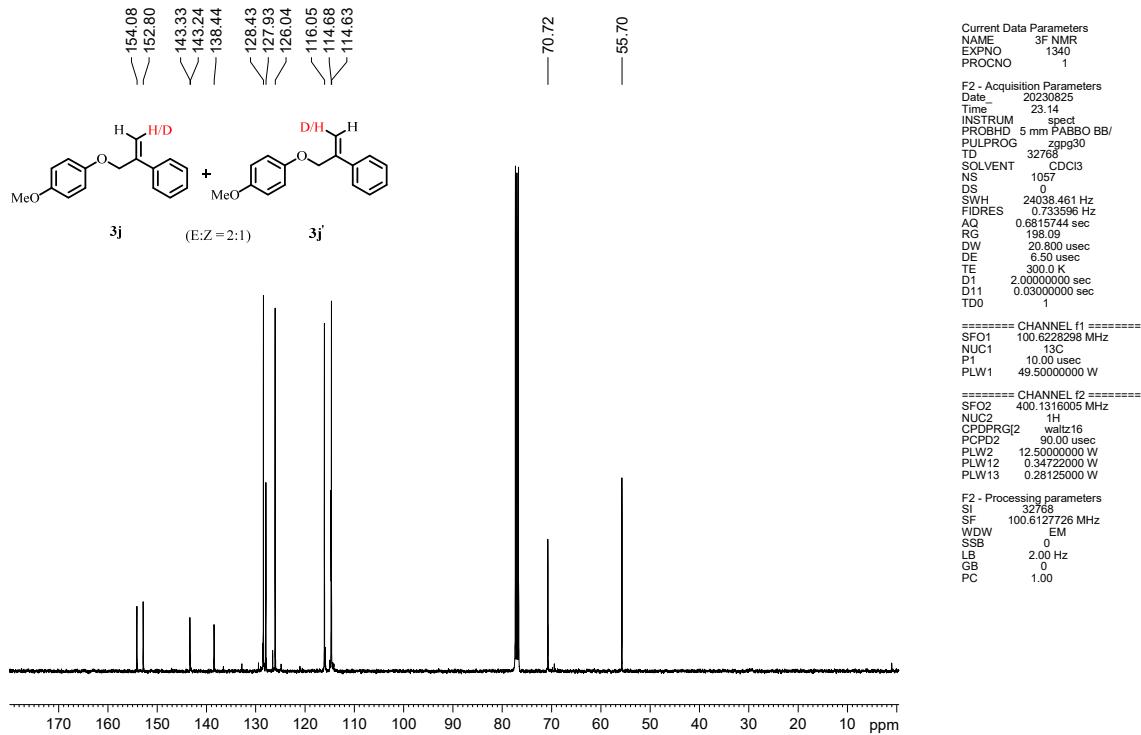
c) Studies with D₂O-





d) Studies with PhB(OD)₂-

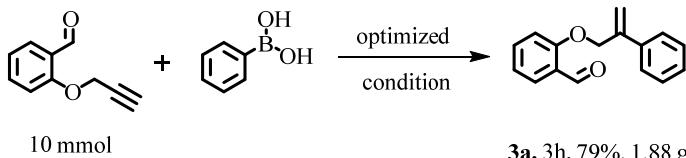




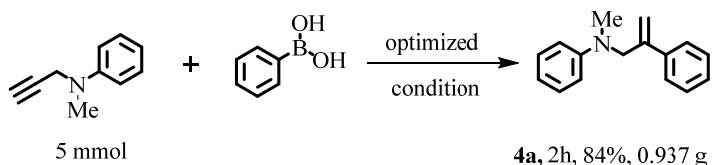
Gram scale synthesis.

Optimized reaction conditions were applied for large scale and successfully achieved good to moderate yields.

a) 10 mmol scale synthesis of allylic ether-

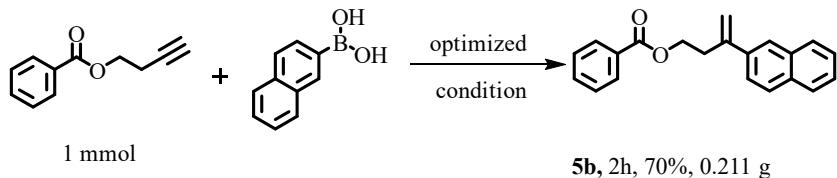


b) 5 mmol scale synthesis of allylic amine-

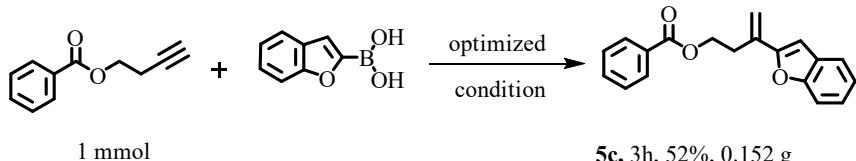


Scale-up on 1 mmol.

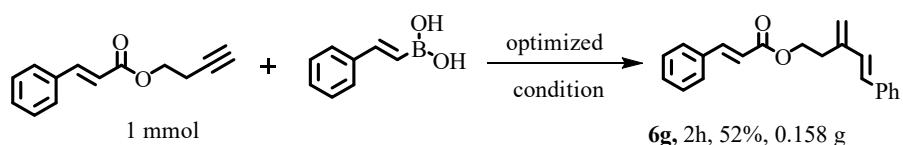
a) 1 mmol scale synthesis of allylic benzoate-



b) 1 mmol scale synthesis of allylic benzoate-



c) 1 mmol scale synthesis of diene derivative-



V. Single crystal X-ray Analytical Data

The Single crystals of isolated compounds **3a** and **6f** were obtained by slow evaporation of dichloromethane: hexane (1:2) solution at room temperature. X-ray reflections were collected using Mo K α X-radiation ($\lambda = 0.71073 \text{ \AA}$) on the single crystals at 200 K using a Bruker Kappa APEX-II diffractometer. All the crystal structures were solved and refined using SHELX-97.

- Crystal data and structure refinement for **3a** [CCDC number 2290697]. (ellipsoid counter 30% probability)

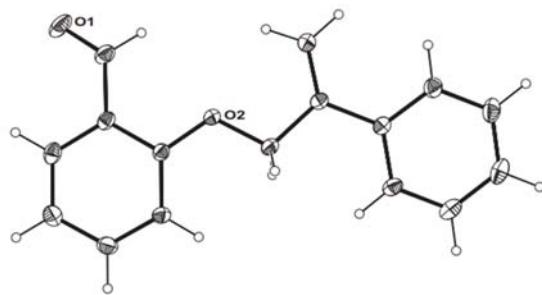


Table 1. Crystal data and structure refinement for d24491.

Identification code	d24491	
Empirical formula	C16 H14 O2	
Formula weight	238.27	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P n a 21	
Unit cell dimensions	a = 16.5657(15) Å b = 5.4295(4) Å c = 14.0697(11) Å	α= 90°. β= 90°. γ = 90°.
Volume	1265.48(18) Å ³	
Z	4	
Density (calculated)	1.251 Mg/m ³	
Absorption coefficient	0.081 mm ⁻¹	
F(000)	504	
Crystal size	0.72 x 0.06 x 0.02 mm ³	
Theta range for data collection	2.46 to 25.26°.	
Index ranges	-19<=h<=19, -6<=k<=5, -16<=l<=13	
Reflections collected	6361	
Independent reflections	1825 [R(int) = 0.1282]	
Completeness to theta = 25.26°	99.0 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.9984 and 0.9437	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1825 / 1 / 164	
Goodness-of-fit on F ²	1.028	
Final R indices [I>2sigma(I)]	R1 = 0.0528, wR2 = 0.1200	
R indices (all data)	R1 = 0.0701, wR2 = 0.1313	
Absolute structure parameter	-4(2)	
Extinction coefficient	0.034(8)	
Largest diff. peak and hole	0.171 and -0.155 e.Å ⁻³	

- Crystal data and structure refinement for **6f** [CCDC number 2290696]. (ellipsoid counter 30% probability)

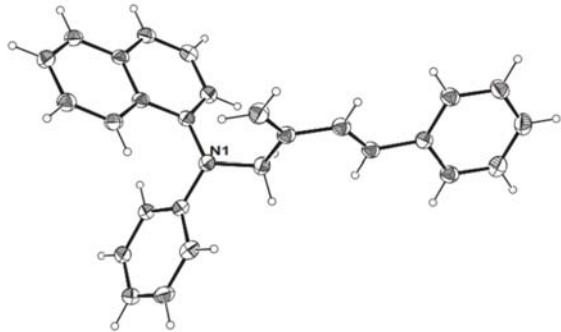
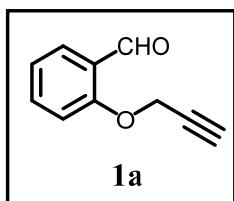


Table 1. Crystal data and structure refinement for d24673.

Identification code	d24673
Empirical formula	C27 H23 N O0
Formula weight	361.46
Temperature	200(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	P 21/n
Unit cell dimensions	a = 9.4988(2) Å $\alpha = 90^\circ$. b = 11.9651(3) Å $\beta = 97.1390(10)^\circ$. c = 17.3667(4) Å $\gamma = 90^\circ$.
Volume	1958.49(8) Å ³
Z	4
Density (calculated)	1.226 Mg/m ³
Absorption coefficient	0.534 mm ⁻¹
F(000)	768
Crystal size	0.57 x 0.40 x 0.13 mm ³
Theta range for data collection	5.98 to 66.74°.
Index ranges	-11<=h<=11, -14<=k<=14, -20<=l<=20
Reflections collected	14764
Independent reflections	3440 [R(int) = 0.0476]
Completeness to theta = 66.74°	98.7 %
Absorption correction	None
Max. and min. transmission	0.9338 and 0.7505
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3440 / 0 / 253
Goodness-of-fit on F ²	1.041
Final R indices [I>2sigma(I)]	R1 = 0.0492, wR2 = 0.1273
R indices (all data)	R1 = 0.0548, wR2 = 0.1342
Largest diff. peak and hole	0.181 and -0.187 e.Å ⁻³

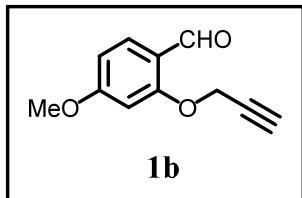
VI. Spectral Data

2-(Prop-2-yn-1-yloxy)benzaldehyde (**1a**):^{1a}



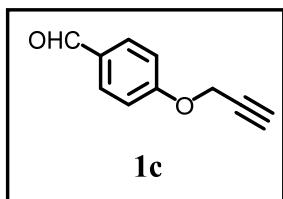
Eluent: n-hexane/ ethyl acetate (93/7); White solid; Yield: 1.21 g (76%);
¹H NMR (400 MHz, CDCl₃): δ 10.49 (s, 1H), 7.87-7.85 (m, 1H), 7.59-7.55 (m, 1H), 7.13-7.07 (m, 2H), 4.83 (d, *J* = 4 Hz, 2H), 2.57 (t, *J* = 2 Hz, 1H).

4-Methoxy-2-(prop-2-yn-1-yloxy)benzaldehyde (**1b**):^{1b}



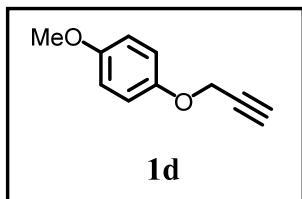
Eluent: n-hexane/ ethyl acetate (93/7); White solid; Yield: 1.36 g (72%); **¹H NMR** (400 MHz, CDCl₃): δ 10.30 (s, 1H), 7.84 (d, *J* = 8 Hz, 1H), 6.59 (d, *J* = 4 Hz, 2H), 4.80 (d, *J* = 2 Hz, 2H), 3.88 (s, 3H), 2.58 (t, *J* = 2 Hz, 1H).

4-(Prop-2-yn-1-yloxy)benzaldehyde (**1c**):^{1c}



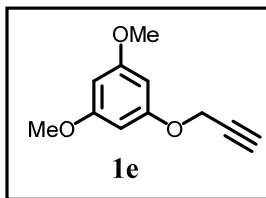
Eluent: n-hexane/ ethyl acetate (93/7); White solid; Yield: 1.02 g (64%); **¹H NMR** (400 MHz, CDCl₃): δ 9.90 (s, 1H), 7.86 (d, *J* = 8 Hz, 2H), 7.09 (d, *J* = 8 Hz, 2H), 4.78 (d, *J* = 2.4 Hz, 2H), 2.57 (t, *J* = 4 Hz 1H).

1-Methoxy-4-(prop-2-yn-1-yloxy)benzene (**1d**):^{1d}



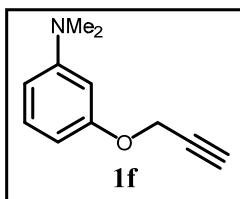
Eluent: n-hexane/ ethyl acetate (90/5); Yellow liquid; Yield: 1.36 g (84%); **¹H NMR** (400 MHz, CDCl₃): δ 6.93-6.90 (m, 2H), 6.86-6.83 (m, 2H), 4.63 (d, *J* = 2 Hz, 2H), 3.77 (s, 3H), 2.50 (t, *J* = 2 Hz 1H).

1,3-Dimethoxy-5-(prop-2-yn-1-yloxy)benzene (**1e**):^{1e}



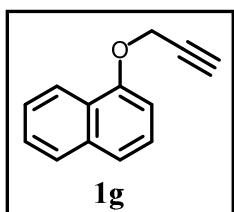
Eluent: n-hexane/ ethyl acetate (94/6); Gray solid; Yield: 1.11 g (58%); **¹H NMR** (400 MHz, CDCl₃): δ 6.15 (d, *J* = 8 Hz, 2H), 6.12 (d, *J* = 4 Hz, 1H), 4.64 (q, *J* = 1 Hz 2H), 3.76 (d, *J* = 1 Hz 6H), 2.52 (q, *J* = 4 Hz 1H).

N,N-Dimethyl-3-(prop-2-yn-1-yloxy)aniline (1f):^{1e}



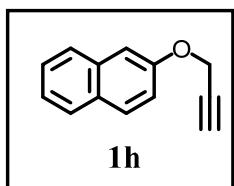
Eluent: n-hexane/ ethyl acetate (95/5); White solid; Yield: 1.15 g (66%);
¹H NMR (400 MHz, CDCl₃): δ 7.17-7.13 (m, 1H), 6.40-6.28 (m, 3H), 4.67 (d, *J* = 2 Hz, 2H), 2.93 (s, 6H), 2.50 (t, *J* = 2 Hz 1H).

1-(Prop-2-yn-1-yloxy)naphthalene (1g):^{1c}



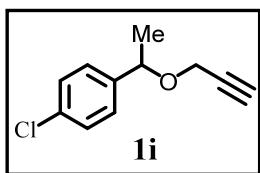
Eluent: n-hexane/ ethyl acetate (97/3); colorless liquid; Yield: 1.41 g (78%); **¹H NMR** (400 MHz, CDCl₃): δ 8.26 (t, *J* = 8 Hz, 1H), 7.80-7.78 (m, 1H), 7.50-7.45 (m, 3H), 7.37 (t, *J* = 8 Hz, 1H), 6.93 (d, *J* = 8 Hz, 1H), 4.88 (d, *J* = 2 Hz, 2H), 2.54 (t, *J* = 2 Hz 1H).

2-(Prop-2-yn-1-yloxy)naphthalene (1h):^{1f}



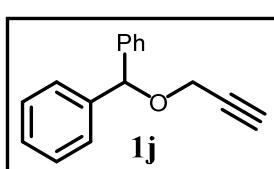
Eluent: n-hexane/ ethyl acetate (97/3); Gray solid; Yield: 1.25 g (69%);
¹H NMR (400 MHz, CDCl₃): δ 7.78-7.74 (m, 3H), 7.46-7.42 (m, 1H), 7.37-7.33 (m, 1H), 7.23 (d, *J* = 4 Hz, 1H), 7.20-7.17 (m, 1H), 4.80 (d, *J* = 4 Hz, 2H), 2.55 (t, *J* = 2 Hz 1H).

1-Chloro-4-(1-(prop-2-yn-1-yloxy)ethyl)benzene (1i):



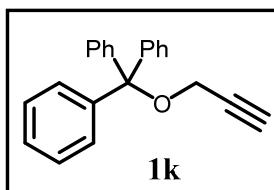
Eluent: n-hexane/ ethyl acetate (97/3); colorless liquid; Yield: 0.5 g (86%); **¹H NMR** (400 MHz, CDCl₃): δ 7.33-7.30 (m, 2H), 7.28-7.25 (m, 2H), 4.64 (q, *J* = 4 Hz, 1H), 4.07 (dd, *J* = 12 Hz, 4 Hz, 1H), 3.86 (dd, *J* = 12 Hz, 4 Hz, 1H), 2.40 (t, *J* = 4 Hz 1H), 1.44 (d, *J* = 4 Hz, 3H), **¹³C NMR** (100 MHz, CDCl₃): δ 141.0, 133.4, 128.7, 127.8, 79.7, 75.9, 74.2, 55.5, 23.6; **HRMS (EI)** m/z calcd. For [M]⁺ C₁₁H₁₁ClO 194.0498, found 194.0487.

((Prop-2-yn-1-yloxy)methylene)dibenzene (1j):^{2a}



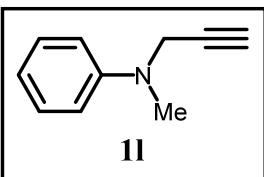
Eluent: n-hexane/ ethyl acetate (95/5); Yellow solid; Yield: 0.47 g (71%); **¹H NMR** (400 MHz, CDCl₃): δ 7.34-7.25 (m, 10H), 5.66 (s, 1H), 4.15 (s, 2H), 2.44 (s, 1H).

((Prop-2-yn-1-yloxy)methanetriyl)tribenzene (1k):^{2b}



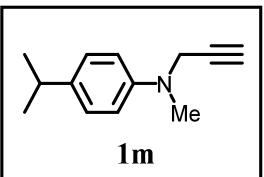
Eluent: n-hexane/ ethyl acetate (95/5); White solid; Yield: 0.46 g (52%); **¹H NMR** (400 MHz, CDCl₃): δ 7.47-7.44 (m, 5H), 7.33-7.28 (m, 5H), 7.26-7.22 (m, 5H), 3.74 (d, *J* = 2 Hz, 2H), 2.38 (t, *J* = 2 Hz 1H).

N-methyl-N-(prop-2-yn-1-yl)aniline (1l):^{2c}



Eluent: n-hexane/ ethyl acetate (97/3); brownish liquid; Yield: 1.7 g (81%); **¹H NMR** (400 MHz, CDCl₃): δ 7.28-7.24 (m, 2H), 6.87-6.79 (m, 3H), 4.04 (d, *J* = 2 Hz, 2H), 2.97 (s, 3H), 2.16 (t, *J* = 2 Hz, 1H).

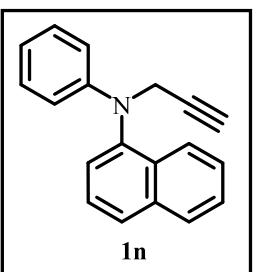
4-Isopropyl-N-methyl-N-(prop-2-yn-1-yl)aniline (1m):



Eluent: n-hexane/ ethyl acetate (96/4); colorless liquid; Yield: 0.35 g (64%); **¹H NMR** (400 MHz, CDCl₃): δ 7.13 (d, *J* = 8 Hz, 2H), 6.82 (d, *J* = 8 Hz, 2H), 4.02 (d, *J* = 1 Hz, 2H), 2.94 (s, 3H), 2.87-2.80 (m, 1H), 2.17 (t, *J* = 2 Hz, 1H), 1.22 (d, *J* = 8 Hz, 6 H); **¹³C NMR** (100 MHz, CDCl₃): δ 147.0, 139.0, 127.0, 114.7, 79.3, 72.1, 42.8, 38.8, 33.1, 24.1;

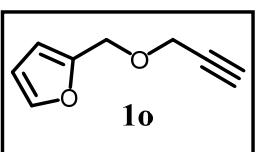
HRMS (EI) m/z calcd. For [M]⁺ C₁₃H₁₇N 187.1361, found 187.1357.

N-Phenyl-N-(prop-2-yn-1-yl)naphthalen-1-amine (1n):



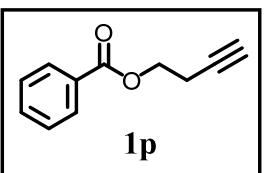
Eluent: n-hexane/ ethyl acetate (95/5); Brown liquid; Yield: 0.59 g (77%); **¹H NMR** (400 MHz, CDCl₃): δ 7.95 (d, *J* = 12 Hz, 1H), 7.90 (d, *J* = 12 Hz, 1H), 7.81 (d, *J* = 8 Hz, 1H), 7.53-7.41 (m, 4H), 7.20-7.15 (m, 2H), 6.78 (d, *J* = 8 Hz, 1H), 6.72 (d, *J* = 8 Hz, 2H), 4.45 (d, *J* = 2 Hz, 2H), 2.27 (t, *J* = 2 Hz, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 148.29, 143.63, 135.02, 131.31, 128.88, 128.40, 127.17, 126.51, 126.33, 126.28, 125.99, 123.53, 118.321, 114.49, 80.11, 72.49, 41.77 ; **HRMS (EI)** m/z calcd. For [M]⁺ C₁₉H₁₅N 257.1204, found 257.1202.

2-((Prop-2-yn-1-yloxy)methyl)furan (1o):^{2d}



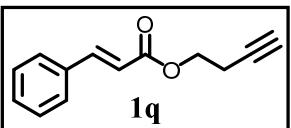
Eluent: n-hexane/ ethyl acetate (96/4); brownish liquid; Yield: 0.27 g (68%); **¹H NMR** (400 MHz, CDCl₃): δ 7.42 (s, 1H), 6.38-6.34 (m, 2H), 4.56 (s, 2H); 4.16 (d, *J* = 2 Hz, 2H), 2.46 (t, *J* = 2 Hz, 1H).

But-3-yn-1-yl benzoate (1p):^{1f}



Eluent: n-hexane/ ethyl acetate (98/2); colorless liquid; Yield: 0.72 g (83%); **¹H NMR** (400 MHz, CDCl₃): δ 8.06 (d, *J* = 4 Hz, 2H), 7.57 (t, *J* = 8 Hz, 1H), 7.44 (d, *J* = 8 Hz, 2H), 4.43 (t, *J* = 8 Hz, 2H), 2.69-2.65 (m, 2H), 2.04-2.02 (m, 1H).

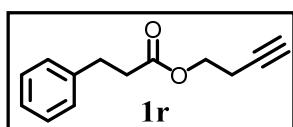
But-3-yn-1-yl cinnamate (1q):



Eluent: n-hexane/ ethyl acetate (96/4); colorless liquid; Yield: 0.68 g (62%); **¹H NMR** (400 MHz, CDCl₃): δ 7.71 (d, *J* = 16 Hz, 1H), 7.54-7.51 (m, 2H), 7.39-7.37 (m, 3H), 6.45 (d, *J* = 16 Hz, 1H), 4.32

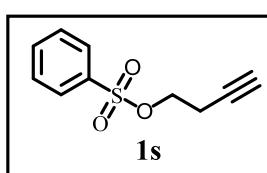
(t, $J = 4$ Hz, 2H), 2.63-2.59 (m, 2H), 2.03 (t, $J = 4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 166.6, 145.2, 134.3, 130.3, 128.86, 128.09, 117.6, 80.1, 69.9, 62.1, 19.0; HRMS (EI) m/z calcd. For $[\text{M}]^+$ $\text{C}_{13}\text{H}_{12}\text{O}_2$ 200.0837, found 200.0838.

But-3-yn-1-yl 3-phenylpropanoate (1r):³



Eluent: n-hexane/ ethyl acetate (97/3); colorless liquid; Yield: 0.59 g (59%); ^1H NMR (400 MHz, CDCl_3): δ 7.31-7.25 (m, 2H), 7.21-7.17 (m, 3H), 4.18 (t, $J = 8$ Hz, 2H), 2.96 (t, $J = 8$ Hz, 2H), 2.67-2.64 (m, 2H), 2.51-2.47 (m, 2H), 1.98 (t, $J = 4$ Hz, 1H).

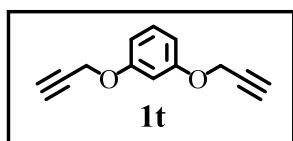
But-3-yn-1-yl benzenesulfonate (1s):



Eluent: n-hexane/ ethyl acetate (97/3); colorless liquid; Yield: 0.81g (78%); ^1H NMR (400 MHz, CDCl_3): δ 7.95-7.92 (m, 2H), 7.69-7.65 (m, 1H), 7.59-7.55 (m, 2H), 4.14 (t, $J = 8$ Hz, 1H), 2.59-2.55 (m, 2H), 1.96 (t, $J = 4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 135.8, 133.8, 129.2, 127.8, 78.2, 70.7, 67.5, 19.3; HRMS (EI) m/z calcd. For $[\text{M}]^+$

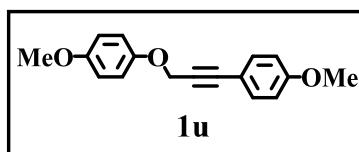
$\text{C}_{10}\text{H}_{10}\text{O}_3\text{S}$ 210.0350, found 210.0346.

1,3-Bis(prop-2-yn-1-yloxy)benzene (1t):⁸



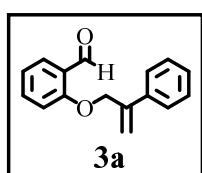
Eluent: n-hexane/ ethyl acetate (95/5); colorless liquid; Yield: 0.56 g (61%); ^1H NMR (400 MHz, CDCl_3): δ 7.23-7.19 (m, 1H), 7.63-7.61 (m, 3H), 4.67(d, $J = 1$ Hz, 4H), 2.52 (t, $J = 4$ Hz, 2H).

1-methoxy-4-(3-(4-methoxyphenoxy)prop-1-yn-1-yl)benzene (1u):⁴



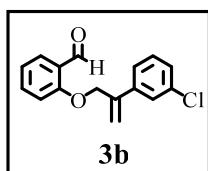
Eluent: n-hexane/ ethyl acetate (97/3); White solid; Yield: 0.73 g (69%); ^1H NMR (400 MHz, CDCl_3): δ 7.35-7.39 (m, 2H), 6.95-6.99 (m, 2H), 6.80-6.87 (m, 4H), 4.84 (s, 2H), 3.80 (s, 3H), 3.77 (s, 3H).

2-((2-Phenylallyl)oxy)benzaldehyde (3a):⁹



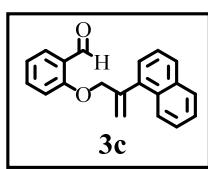
Eluent: n-hexane/ ethyl acetate (97/3); White solid; Yield: 90.4 mg (95%); M.p.: 55 °C; ^1H NMR (400 MHz, CDCl_3): δ 10.38 (s, 1H), 7.83 (dd, $J = 8.2$ Hz, 2 Hz, 1H), 7.57-7.52 (m, 1H), 7.45-7.44 (m, 2H), 7.39-7.32 (m, 3H), 7.07-7.02 (m, 2H), 5.63 (s, 1H), 5.49 (s, 1H), 5.03 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 189.7, 160.8, 142.6, 137.9, 135.8, 128.6, 128.4, 128.2, 126.0, 125.3, 121.1, 115.2, 113.1, 70.3; HRMS (EI) m/z calcd. For $[\text{M}]^+$ $\text{C}_{16}\text{H}_{14}\text{O}_2$ 238.0993, found 238.0992.

2-((2-(3-Chlorophenyl)allyl)oxy)benzaldehyde (3b):



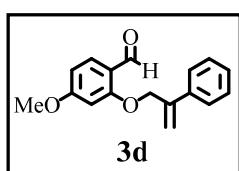
Eluent: n-hexane/ ethyl acetate (97/3); White solid; Yield: 82.6 mg (76%); M.p.: 58 °C; **1H NMR** (400 MHz, CDCl₃): δ 10.40 (s, 1H), 7.83 (dd, *J* = 8 Hz, 2 Hz, 1H), 7.57-7.53 (m, 1H), 7.44-7.43 (m, 1H), 7.34-7.29 (m, 3H), 7.06 (t, *J* = 12 Hz, 2H), 5.64 (s, 1H), 5.53 (s, 1H), 4.99 (s, 2H); **13C NMR** (100 MHz, CDCl₃): δ 189.5, 160.6, 141.5, 139.8, 135.8, 134.6, 129.8, 128.5, 128.3, 126.2, 125.3, 124.2, 121.2, 116.5, 113.0, 70.0; **HRMS (EI)** m/z calcd. For [M]⁺ C₁₆H₁₃ClO₂ 272.0604, found 272.0612.

2-((2-(Naphthalen-1-yl)allyl)oxy)benzaldehyde (3c):



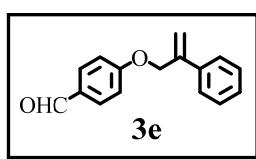
Eluent: n-hexane/ ethyl acetate (97/3); White solid; Yield: 110 mg (96%); M.p.: 125 °C; **1H NMR** (400 MHz, CDCl₃): δ 10.40 (s, 1H), 8.06-8.02 (m, 1H), 7.89-7.85 (m, 1H), 7.84-7.80 (m, 2H), 7.52-7.46 (m, 4H), 7.37 (d, *J* = 8 Hz, 1H), 7.03-6.97 (m, 2H), 5.86 (s, 1H), 5.42 (s, 1H), 4.94 (s, 2H); **13C NMR** (100 MHz, CDCl₃): δ 189.6, 160.7, 142.8, 137.2, 135.7, 133.6, 131.3, 128.4, 128.1, 126.2, 125.9, 125.8, 125.1, 125.1, 120.9, 117.8, 112.7, 71.5; **HRMS (EI)** m/z calcd. For [M]⁺ C₂₀H₁₆O₂ 288.1150, found 288.1142.

4-Methoxy-2-((2-phenylallyl)oxy)benzaldehyde (3d):¹⁰



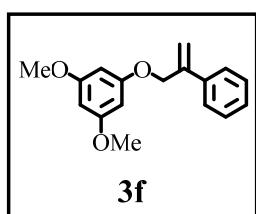
Eluent: n-hexane/ ethyl acetate (95/5); White solid; Yield: 84.6 mg (79%); M.p.: 81 °C; **1H NMR** (400 MHz, CDCl₃): δ 10.22 (s, 1H), 7.81 (d, *J* = 8 Hz, 1H), 7.46-7.43 (m, 2H), 7.38-7.29 (m, 3H), 6.5 (dd, *J* = 8 Hz, 2H), 6.52 (d, *J* = 4 Hz, 1H), 5.63 (s, 1H), 5.49 (s, 1H), 4.99 (s, 1H), 3.86 (s, 3H); **13C NMR** (100 MHz, CDCl₃): δ 188.1, 166.0, 162.5, 142.4, 137.9, 130.4, 128.5, 128.2, 126.0, 119.4, 115.2, 106.2, 99.2, 70.2, 55.6; **HRMS (EI)** m/z calcd. For [M]⁺ C₁₇H₁₆O₃ 268.1099, found 268.1109.

4-((2-Phenylallyl)oxy)benzaldehyde (3e):



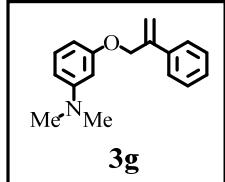
Eluent: n-hexane/ ethyl acetate (97/3); colorless liquid; Yield: 49.5 mg (52%); **1H NMR** (400 MHz, CDCl₃): δ 9.89 (s, 1H), 7.84 (d, *J* = 8 Hz, 2H), 7.46 (d, *J* = 8 Hz, 2H), 7.39-7.33 (m, 3H), 7.06 (d, *J* = 8 Hz, 2H), 5.64 (s, 1H), 5.46 (s, 1H), 4.99 (s, 2H); **13C NMR** (100 MHz, CDCl₃): δ 190.7, 163.5, 142.2, 137.9, 131.9, 130.2, 128.5, 128.2, 126.0, 115.3, 115.1, 70.0; **HRMS (EI)** m/z calcd. For [M]⁺ C₁₆H₁₄O₂ 238.0993, found 238.0991.

1,3-Dimethoxy-5-((2-phenylallyl)oxy)benzene (3f):



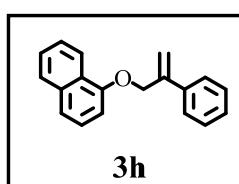
Eluent: n-hexane/ ethyl acetate (90/5); colorless liquid; Yield: 84.2 mg (78%); **1H NMR** (400 MHz, CDCl₃): δ 7.47 (d, *J* = 8 Hz, 2H), 7.35-7.30 (m, 3H), 6.15-6.10 (m, 3H), 5.61 (s, 1H), 5.46 (s, 1H), 4.85 (s, 2H), 3.76 (s, 6H); **13C NMR** (100 MHz, CDCl₃): δ 161.5, 160.5, 142.9, 138.3, 128.0, 126.0, 115.0, 93.8, 93.3, 69.9, 55.3; **HRMS (EI)** m/z calcd. For [M]⁺ C₁₇H₁₈O₃ 270.1255, found 270.1248.

N,N-Dimethyl-3-((2-phenylallyl)oxy)aniline (3g):



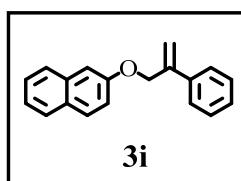
Eluent: n-hexane/ ethyl acetate (90/5); colorless liquid;; Yield: 76.9 mg (76%); M.p.:88 °C; **¹H NMR** (400 MHz, CDCl₃): δ 7.47 (d, *J* = 8 Hz, 2H), 7.36-7.27 (m, 3H), 7.14 (t, *J* = 8 Hz, 1H), 6.38-6.28 (m, 3H), 5.60 (s, 1H), 5.47 (s, 1H), 4.88 (s, 2H), 2.92 (s, 6H); **¹³C NMR** (100 MHz, CDCl₃): δ 159.8, 152.0, 143.3, 138.5, 129.7, 128.4, 127.9, 126.0, 114.8, 106.0, 102.3, 100.2, 69.8, 40.6; **HRMS (EI)** m/z calcd. For [M]⁺ C₁₇H₁₉NO 253.1466, found 253.1453.

1-((2-Phenylallyl)oxy)naphthalene (3h):¹¹



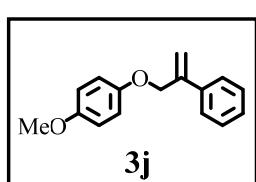
Eluent: n-hexane/ ethyl acetate (96/4); colorless liquid; Yield: 70.7 mg (68%); **¹H NMR** (400 MHz, CDCl₃): δ 8.23 (d, *J* = 8 Hz, 1H), 7.79 (d, *J* = 8 Hz, 1H), 7.53 (d, *J* = 8 Hz, 2H), 7.49-7.40 (m, 4H), 6.89 (d, *J* = 8 Hz, 1H), 5.66 (s, 1H), 5.59 (s, 1H), 5.06 (s, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 154.3, 143.0, 138.4, 134.5, 128.4, 128.0, 127.4, 126.4, 126.0, 125.7, 125.2, 122.1, 120.5, 114.7, 105.1, 70.0; **HRMS (EI)** m/z calcd. For [M]⁺ C₁₉H₁₆O 260.1201, found 260.1197.

2-((2-Phenylallyl)oxy)naphthalene (3i):



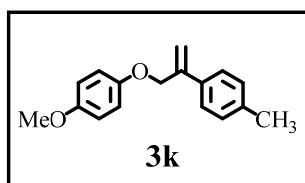
Eluent: n-hexane/ ethyl acetate (96/4); colorless liquid;; Yield: 56 mg (54%); **¹H NMR** (400 MHz, CDCl₃): δ 7.76-7.70 (m, 3H), 7.51-7.41 (m, 3H), 7.37-7.31 (m, 4H), 7.21 (s, 2H), 5.64 (s, 1H), 5.52 (s, 1H), 5.00 (s, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 156.5, 142.9, 138.3, 134.4, 129.4, 129.1, 128.5, 128.0, 127.6, 126.7, 126.3, 126.0, 123.7, 119.0, 114.9, 107.3, 69.8; **HRMS (EI)** m/z calcd. For [M]⁺ C₁₉H₁₆O 260.1201, found 260.1197.

1-Methoxy-4-((2-phenylallyl)oxy)benzene (3j):¹²



Eluent: n-hexane/ ethyl acetate (90/5); White solid; Yield: 72 mg (75%); M.p.:50 °C; **¹H NMR** (400 MHz, CDCl₃): δ 7.48-7.46 (m, 2H), 7.37-7.29 (m, 3H), 6.90-6.87 (m, 2H), 6.84-6.81 (m, 2H), 5.58 (s, 1H), 5.44 (d, *J* = 1.2 Hz, 1H), 4.48 (s, 2H), 3.75 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 154.0, 152.8, 143.3, 138.4, 128.4, 127.9, 126.0, 116.0, 114.75, 114.64, 70.72, 55.7; **HRMS (EI)** m/z calcd. For [M]⁺ C₁₆H₁₆O₂ 240.1150, found 240.1152.

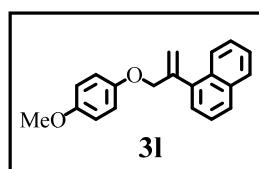
1-Methoxy-4-((2-(p-tolyl)allyl)oxy)benzene (3k):



Eluent: n-hexane/ ethyl acetate (90/5); White solid; Yield: 59 mg (58%); M.p.:61 °C; **¹H NMR** (400 MHz, CDCl₃): δ 7.37 (d, *J* = 8 Hz, 2H), 7.16 (d, *J* = 8 Hz, 2H), 6.90-6.87 (m, 2H), 6.84-6.81 (m, 2H), 5.56 (s, 1H), 5.39 (s, 1H), 4.82 (s, 2H), 3.76 (s, 3H), 2.35 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 154.0, 152.8, 143.0, 137.7,

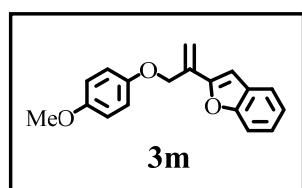
135.4, 129.1, 125.8, 116.0, 114.5, 113.8, 70.7, 55.6, 21.0; **HRMS (EI)** m/z calcd. For [M]⁺ C₁₇H₁₈O₂ 254.1306, found 254.1316.

1-(3-(4-Methoxyphenoxy)prop-1-en-2-yl)naphthalene (3l):



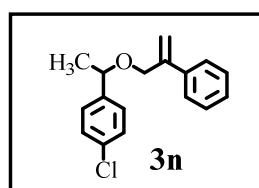
Eluent: n-hexane/ ethyl acetate (90/5); colorless liquid; Yield: 112.5 mg (97%); **¹H NMR** (400 MHz, CDCl₃): δ 8.07-8.05 (m, 1H), 7.87-7.79 (m, 2H), 7.49-7.43 (m, 3H), 7.36 (d, *J* = 8 Hz, 1H), 6.89-6.80 (m, 4H), 5.83 (s, 1H), 5.35 (s, 1H), 4.76 (s, 2H), 3.75 (s, 3H), **¹³C NMR** (100 MHz, CDCl₃): δ 154.0, 152.8, 147.7, 137.9, 133.7, 131.5, 128.3, 127.9, 126.1, 125.8, 125.8, 125.4, 125.2, 116.7, 115.8, 114.6, 71.7, 55.7; **HRMS (EI)** m/z calcd. For [M]⁺ C₂₀H₁₈O₂ 290.1306, found 290.1316.

2-(3-(4-Methoxyphenoxy)prop-1-en-2-yl)benzofuran (3m):



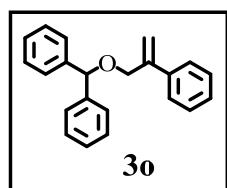
Eluent: n-hexane/ ethyl acetate (96/4); White solid; Yield: 65 mg (58%); M.p.: 57 °C; **¹H NMR** (400 MHz, CDCl₃): δ 7.53 (d, *J* = 8 Hz, 1H), 7.46 (d, *J* = 8 Hz, 1H), 7.30-7.26 (m, 2H), 7.22-7.18 (m, 1H), 6.94-6.91 (m, 2H), 6.86-6.83 (m, 2H), 6.77 (s, 1H), 6.03 (s, 1H), 5.54 (s, 1H), 4.48 (s, 2H), 3.77 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 154.6, 154.2, 153.9, 152.6, 133.5, 128.7, 124.7, 122.8, 121.1, 116.0, 115.2, 114.7, 111.0, 103.5, 69.1, 55.7; **HRMS (EI)** m/z calcd. For [M]⁺ C₁₈H₁₆O₃ 280.1099, found 280.1116.

1-Chloro-4-(1-((2-phenylallyloxy)ethyl)benzene (3n):



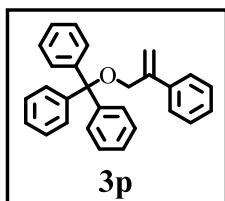
Eluent: n-hexane/ ethyl acetate (98/2); colorless liquid;; Yield: 99 mg (91%); **¹H NMR** (400 MHz, CDCl₃): δ 7.41-7.39 (m, 2H), 7.32-7.24 (m, 7H), 5.50 (s, 1H), 5.31 (s, 1H), 4.50 (q, *J* = 6.4 Hz, 1H), 4.28 (d, *J* = 12 Hz, 1H), 4.11 (d, *J* = 12 Hz, 1H), 1.40 (d, *J* = 6.4 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 144.4, 142.1, 138.8, 133.0, 128.5, 128.2, 127.6, 126.0, 114.0, 76.4, 70.2, 23.9; **HRMS (EI)** m/z calcd. For [M]⁺ C₁₇H₁₇ClO 272.0967, found 272.0961.

((2-Phenylallyloxy)methylene)dibenzene (3o):



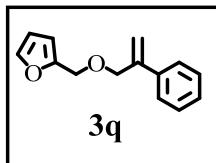
Eluent: n-hexane/ ethyl acetate (95/5); colorless liquid; Yield: 94.8 mg (79%); **¹H NMR** (400 MHz, CDCl₃): δ 7.45-7.43 (m, 2H), 7.33-7.26 (m, 11H), 7.24-7.20 (m, 3H), 5.54 (s, 1H), 5.48 (s, 1H), 5.38 (s, 1H), 4.37 (s, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 144.3, 142.1, 139.0, 128.4, 128.3, 127.7, 127.5, 127.2, 126.2, 114.2, 82.5, 70.5; **HRMS (EI)** m/z calcd. For [M]⁺ C₂₂H₂₀O 300.1514, found 300.1507.

((2-Phenylallyl)oxy)methanetriyltribenzene (3p):¹³



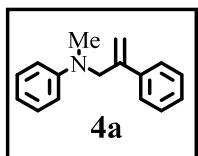
Eluent: n-hexane/ ethyl acetate (90/5); White solid; Yield: 63 mg (42%); M.p.: 102 °C; **¹H NMR** (400 MHz, CDCl₃): δ 7.50-7.47 (m, 5H), 7.31-7.20 (m, 15H), 5.66 (s, 1H), 5.53 (s, 1H), 3.96 (s, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 145.0, 144.1, 139.3, 128.6, 128.2, 127.8, 127.5, 127.0, 126.0, 112.5, 87.1, 65.5; **HRMS (EI)** m/z calcd. For [M]⁺ C₂₈H₂₄O 376.1827, found 376.1813.

2-((2-Phenylallyl)oxy)methyl)furan (3q):



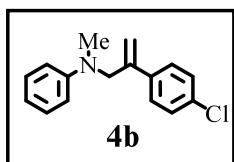
Eluent: n-hexane/ ethyl acetate (94/6); brownish liquid; Yield: 24 mg (28%); **¹H NMR** (400 MHz, CDCl₃): δ 7.46-7.45 (m, 1H), 7.44-7.43 (m, 1H), 7.41-7.40 (m, 1H), 7.34-7.25 (m, 3H), 6.34-6.33 (m, 1H), 6.30 (d, J = 4 Hz, 1H), 5.55 (s, 1H), 5.35 (d, J = 2 Hz, 1H), 4.50 (s, 2H), 4.39 (s, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 151.7, 143.8, 142.7, 138.6, 128.3, 127.7, 126.0, 114.7, 110.2, 109.3, 71.6, 63.6; **HRMS (EI)** m/z calcd. For [M]⁺ C₁₄H₁₄O₂ 214.0993, found 214.0990.

N-Methyl-N-(2-phenylallyl)aniline (4a):



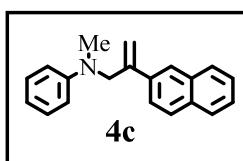
Eluent: n-hexane/ ethyl acetate (97/3); Yellow solid; Yield: 87 mg (98%); M.p.: 57 °C; **¹H NMR** (400 MHz, CDCl₃): δ 7.44-7.42 (m, 2H), 7.36-7.27 (m, 3H), 7.23-7.19 (m, 2H), 6.72-6.68 (m, 3H), 5.41 (s, 1H), 5.09 (s, 1H), 4.27 (s, 2H), 3.00 (s, 3H), **¹³C NMR** (100 MHz, CDCl₃): δ 149.4, 142.9, 139.7, 129.1, 128.4, 127.8, 126.0, 116.3, 112.4, 112.0, 56.7, 38.3; **HRMS (EI)** m/z calcd. For [M]⁺ C₁₆H₁₇N 223.1361, found 223.1356.

N-(2-(4-Chlorophenyl)allyl)-N-methylaniline (4b):



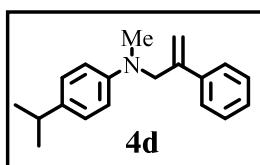
Eluent: n-hexane/ ethyl acetate (96/4); colorless liquid; Yield: 59.6 mg (58%); **¹H NMR** (400 MHz, CDCl₃): δ 7.37-7.29 (m, 4H), 7.24-7.20 (m, 2H), 6.73-6.69 (m, 3H), 5.41 (s, 1H), 5.13 (s, 1H), 4.23 (s, 2H), 2.99 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 149.3, 142.1, 136.0, 133.6, 129.1, 128.5, 127.3, 116.5, 113.2, 112.1, 56.6, 38.2; **HRMS (EI)** m/z calcd. For [M]⁺ C₁₆H₁₆ClN 257.0971, found 257.0966.

N-Methyl-N-(2-(naphthalen-2-yl)allyl)aniline (4c):



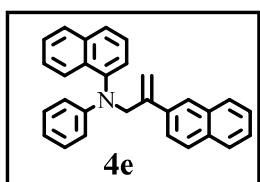
Eluent: n-hexane/ ethyl acetate (95/5); Yellow solid; Yield: 98 mg (90%); M.p.: 67 °C; **¹H NMR** (400 MHz, CDCl₃): δ 7.83-7.80 (m, 4H), 7.63-7.60 (m, 1H), 7.49-7.44 (m, 2H), 7.25-7.21 (m, 2H), 6.76-6.69 (m, 3H), 5.57 (s, 1H), 5.21 (s, 1H), 4.40 (s, 2H), 3.05 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 149.4, 142.6, 136.8, 133.3, 132.9, 129.0, 128.1, 127.9, 127.5, 126.2, 125.9, 124.4, 116.3, 112.9, 112.0, 56.7, 38.3; **HRMS (EI)** m/z calcd. For [M]⁺ C₂₀H₁₉N 273.1517, found 273.1506.

4-Isopropyl-N-methyl-N-(2-phenylallyl)aniline (4d):



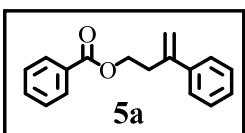
Eluent: n-hexane/ ethyl acetate (97/3); colorless liquid; Yield: 71 mg (67%); **¹H NMR** (400 MHz, CDCl₃): δ 7.44 (d, *J* = 8 Hz, 2H), 7.37-7.25 (m, 3H), 7.11-7.07 (m, 2H), 6.68 (d, *J* = 8 Hz, 2H), 5.43 (s, 1H), 5.15 (s, 1H), 4.24 (s, 2H), 2.98 (s, 3H), 2.85-2.78 (m, 1H), 1.21 (d, *J* = 8 Hz, 6H); **¹³C NMR** (100 MHz, CDCl₃): δ 147.7, 143.2, 139.7, 128.3, 127.7, 126.94, 126.03, 112.60, 112.21, 57.1, 38.3, 33.0, 24.2; **HRMS (ESI)** m/z calcd. For [M+H]⁺ C₁₉H₂₄N 266.1903, found 266.1913.

***N*-(2-(naphthalen-2-yl)allyl)-*N*-phenylnaphthalen-1-amine (4e):**



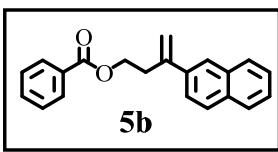
Eluent: n-hexane/ ethyl acetate (90/5); colorless liquid; Yield: 108 mg (70%); **¹H NMR** (400 MHz, CDCl₃): δ 7.89 (d, *J* = 8 Hz, 1H), 7.80-7.72 (m, 6H), 7.55-7.53 (m, 1H), 7.48-7.42 (m, 5H), 7.36-7.32 (m, 1H), 7.14-7.10 (m, 2H), 6.72 (t, *J* = 8 Hz, 1H), 6.62 (d, *J* = 8 Hz, 2H), 5.66 (s, 2H), 4.89 (s, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 149.3, 143.9, 143.2, 136.8, 135.3, 133.2, 132.9, 131.2, 128.8, 128.5, 128.1, 127.9, 127.5, 127.0, 126.4, 126.3, 126.2, 126.1, 126.0, 125.9, 124.7, 124.6, 123.9, 117.5, 114.0, 113.9, 57.1; **HRMS (EI)** m/z calcd. For [M]⁺ C₂₉H₂₃N 385.1830, found 385.1825.

3-Phenylbut-3-en-1-yl benzoate (5a):



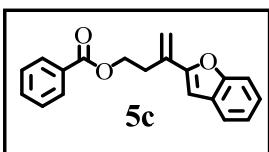
Eluent: n-hexane/ ethyl acetate (90/5); colorless liquid; Yield: 82.6 mg (82%); **¹H NMR** (400 MHz, CDCl₃): δ 7.97-7.95 (m, 2H), 7.56-7.51 (m, 1H), 7.46-7.39 (m, 4H), 7.36-7.26 (m, 3H), 5.40 (d, *J* = 1 Hz, 1H), 5.20 (q, *J* = 1 Hz, 1H), 4.43 (t, *J* = 6.8 Hz, 2H), 3.00 (m, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 166.5, 144.5, 140.6, 132.8, 130.3, 129.5, 128.4, 128.3, 127.6, 126.1, 114.5, 63.7, 43.6; **HRMS (EI)** m/z calcd. For [M]⁺ C₁₇H₁₆O₂ 252.1150, found 252.1145.

3-(Naphthalen-2-yl)but-3-en-1-yl benzoate (5b):



Eluent: n-hexane/ ethyl acetate (90/5); colorless liquid; Yield: 92 mg (76%); **¹H NMR** (400 MHz, CDCl₃): δ 7.93 (d, *J* = 8 Hz, 2H), 7.88 (s, 1H), 7.84-7.79 (m, 3H), 7.60 (dd, *J* = 12 Hz, 4 Hz 1H), 7.52-7.42 (m, 3H), 7.35 (t, *J* = 8 Hz, 2H), 5.55 (s, 1H), 5.30 (s, 1H), 4.48 (t, *J* = 8 Hz, 2H), 3.09 (t, *J* = 8 Hz, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 166.4, 144.4, 137.8, 133.3, 132.87, 132.81, 130.2, 129.5, 128.23, 128.18, 128.03, 127.5, 126.2, 125.9, 124.7, 124.4, 115.0, 63.8, 34.6; **HRMS (EI)** m/z calcd. For [M]⁺ C₂₁H₁₈O₂ 302.1306, found 302.1322.

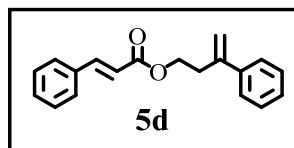
3-(Benzofuran-2-yl)but-3-en-1-yl benzoate (5c):



Eluent: n-hexane/ ethyl acetate (90/5); colorless liquid; Yield: 70 mg (60%); **¹H NMR** (400 MHz, CDCl₃): δ 8.01 (t, *J* = 8 Hz, 2H), 7.56-7.52 (m, 2H), 7.45-7.39 (m, 3H), 7.29-7.24 (m, 1H), 7.21-7.17 (m, 1H), 6.79 (s, 1H), 5.94 (s, 1H), 5.32 (s, 1H), 4.57 (t, *J* = 8 Hz, 2H), 2.93 (q, *J* = 8 Hz, 8 Hz, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 166.5, 155.7, 154.8, 133.5, 132.9,

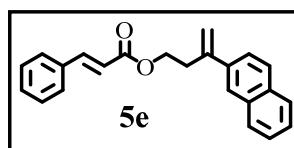
130.2, 129.6, 128.87, 128.37, 124.7, 122.8, 121.0, 114.8, 111.0, 103.1, 63.7, 32.6; **HRMS (EI)** m/z calcd. For $[M]^+$ C₁₉H₁₆O₃ 292.1099, found 292.1114.

3-Phenylbut-3-en-1-yl cinnamate (5d):



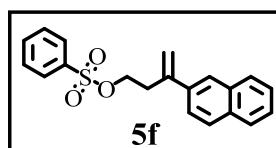
Eluent: n-hexane/ ethyl acetate (90/5); colorless liquid; Yield: 71 mg (64%); **¹H NMR** (400 MHz, CDCl₃): δ 7.62 (d, J = 16 Hz, 1H), 7.51-7.48 (m, 2H), 7.45-7.42 (m, 2H), 7.38-7.35 (m, 3H), 7.34-7.24 (m, 3H), 6.39 (d, J = 16 Hz, 1H), 5.39 (d, J = 4 Hz, 1H), 5.17 (d, J = 1 Hz, 1H), 4.32 (t, J = 8 Hz, 2H), 2.94 -2.90 (m, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 166.8, 144.72, 144.45, 140.5, 134.4, 130.2, 128.84, 128.40, 128.05, 127.6, 126.0, 118.0, 114.3, 63.3, 34.5; **HRMS (EI)** m/z calcd. For $[M]^+$ C₁₉H₁₈O₂ 278.1306, found 278.1316.

3-(Naphthalen-2-yl)but-3-en-1-yl cinnamate (5e):



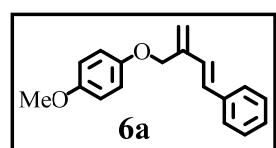
Eluent: n-hexane/ ethyl acetate (90/5); White solid; Yield: 101 mg (77%); M.p.: 78 °C; **¹H NMR** (400 MHz, CDCl₃): δ 7.87 (s, 1H), 7.84-7.79 (m, 3H), 7.61-7.55 (m, 2H), 7.48-7.41 (m, 4H), 7.36-7.33 (m, 3H), 6.37 (d, J = 16 Hz, 1H), 5.55 (s, 1H), 5.28 (s, 1H), 4.40-4.37 (m, 2H), 3.03 (t, J = 8 Hz, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 166.8, 144.7, 144.3, 137.7, 134.3, 133.3, 132.8, 130.2, 128.81, 128.20, 128.03, 127.5, 126.2, 125.9, 124.76, 124.43, 118.0, 114.9, 63.5, 34.5; **HRMS (EI)** m/z calcd. For $[M]^+$ C₂₃H₂₀O₂ 328.1463, found 328.1456.

3-(Naphthalen-2-yl)but-3-en-1-yl benzenesulfonate (5f):



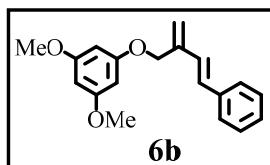
Eluent: n-hexane/ ethyl acetate (90/5); colorless liquid; Yield: 115 mg (85%); **¹H NMR** (400 MHz, CDCl₃): δ 7.81-7.73 (m, 5H), 6.67 (d, J = 1.2 Hz, 1H), 7.55-7.51 (m, 1H), 7.49-7.39 (m, 5H), 5.48 (s, 1H), 5.18 (d, J = 1 Hz, 1H), 4.17 (t, J = 8 Hz, 2H), 3.00-2.97 (m, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 142.5, 136.8, 135.9, 133.53, 133.19, 132.8, 129.0, 128.10, 128.05, 127.69, 127.46, 126.25, 126.06, 124.66, 124.12, 115.8, 68.8, 34.7; **HRMS (EI)** m/z calcd. For $[M]^+$ C₂₀H₁₈O₃S 338.0976, found 338.0962.

(E)-1-Methoxy-4-((2-methylene-4-phenylbut-3-en-1-yl)oxy)benzene (6a):



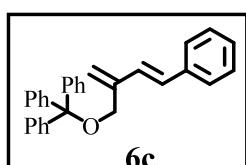
Eluent: n-hexane/ ethyl acetate (90/3); White solid; Yield: 89 mg (84%); M.p.: 85 °C; **¹H NMR** (400 MHz, CDCl₃): δ 7.43-7.41 (m, 2H), 7.33-7.29 (m, 2H), 7.25-7.21 (m, 2H), 6.93-6.89 (m, 2H), 6.87-6.82 (m, 3H), 6.67 (d, J = 16 Hz, 1H), 5.41 (s, 1H), 5.36 (s, 1H), 4.75 (s, 2H), 3.76 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 154.0, 152.7, 141.2, 137.0, 129.1, 128.5, 128.1, 127.7, 126.4, 118.1, 115.9, 114.6, 68.9, 55.6; **HRMS (EI)** m/z calcd. For $[M]^+$ C₁₈H₁₈O₂ 266.1298, found 266.1306.

(E)-1,3-Dimethoxy-5-((2-methylene-4-phenylbut-3-en-1-yl)oxy)benzene (6b):



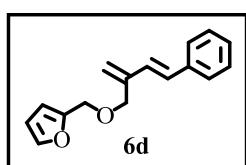
Eluent: n-hexane/ ethyl acetate (97/3); White solid; Yield: 107.7 mg (91%); M.p.: 70 °C; **¹H NMR** (400 MHz, CDCl₃): δ 7.43-7.41 (m, 2H), 7.34-7.30 (m, 2H), 7.24-7.21 (m, 1H), 6.85 (d, *J* = 16 Hz, 1H), 6.65 (d, *J* = 16 Hz, 1H), 6.17 (d, *J* = 2 Hz, 2H), 6.11 (t, *J* = 4 Hz, 1H), 5.42 (s, 1H), 5.39 (s, 1H), 4.75 (s, 2H), 3.77 (s, 6H); **¹³C NMR** (100 MHz, CDCl₃): δ 161.5, 160.5, 140.9, 137.0, 129.2, 128.6, 128.1, 127.7, 126.5, 118.3, 93.8, 93.2, 96.2, 55.3; **HRMS (EI)** m/z calcd. For [M]⁺ C₁₉H₂₀O₃ 296.1412, found 296.1401.

(E)-(((4-Phenylbuta-1,3-dien-2-yl)oxy)methanetriyl)tribenzene (6c):



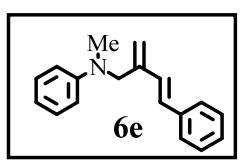
Eluent: n-hexane/ ethyl acetate (97/3); colorless liquid;; Yield: 101.3 mg (63%); **¹H NMR** (400 MHz, CDCl₃): δ 7.52-7.46 (m, 5H), 7.34-7.19 (m, 15H), 6.76 (d, *J* = 16 Hz, 1H), 6.28 (d, *J* = 16 Hz, 1H), 5.62 (d, *J* = 1.6 Hz, 1H), 5.34 (s, 1H), 3.87 (s, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 144.1, 142.9, 137.2, 128.83, 128.70, 128.54, 128.37, 127.87, 127.48, 127.06, 126.3, 116.4, 87.0, 63.7; **HRMS (EI)** m/z calcd. For [M]⁺ C₃₀H₂₆O 402.1983, found 402.1977.

(E)-2-(((2-Methylene-4-phenylbut-3-en-1-yl)oxy)methyl)furan (6d):



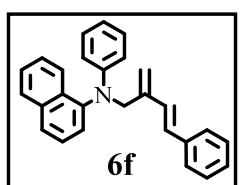
Eluent: n-hexane/ ethyl acetate (97/3); Yellowish liquid; Yield: 87.3 mg (91%); **¹H NMR** (400 MHz, CDCl₃): δ 7.43-7.39 (m, 3H), 7.33-7.29 (m, 2H), 7.25-7.20 (m, 1H), 6.79 (d, *J* = 16 Hz, 1H), 6.67 (d, *J* = 16 Hz, 1H), 6.36-6.34 (m, 2H), 5.32 (s, 2H), 4.50 (s, 2H), 4.29 (s, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 151.8, 142.82, 142.01, 137.2, 129.3, 128.58, 128.37, 127.6, 126.5, 118.2, 110.3, 109.4, 70.0, 63.7; **HRMS (EI)** m/z calcd. For [M]⁺ C₁₆H₁₆O₂ 240.1150, found 240.1136.

(E)-N-Methyl-N-(2-methylene-4-phenylbut-3-en-1-yl)aniline (6e):



Eluent: n-hexane/ ethyl acetate (97/3); colorless liquid; Yield: 81.6 mg (82%); **¹H NMR** (400 MHz, CDCl₃): δ 7.42-7.40 (m, 2H), 7.34-7.30 (m, 2H), 7.25-7.20 (m, 3H), 6.90 (d, *J* = 16 Hz, 1H), 6.71-6.69 (m, 3H), 5.59 (d, *J* = 16 Hz, 1H), 5.24 (s, 1H), 5.09 (s, 1H), 4.19 (s, 2H), 3.02 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 149.5, 140.4, 137.1, 129.3, 129.1, 128.6, 128.1, 127.6, 126.4, 116.2, 116.2, 111.9, 54.4, 38.3; **HRMS (EI)** m/z calcd. For [M]⁺ C₁₈H₁₉N 249.1517, found 249.1520.

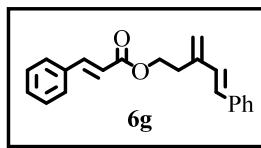
(E)-N-(2-Methylene-4-phenylbut-3-en-1-yl)-N-phenylnaphthalen-1-amine (6f):



Eluent: n-hexane/ ethyl acetate (97/3); Brown solid; Yield: 131.4 mg (91%); M.p.: 142 °C; **¹H NMR** (400 MHz, CDCl₃): δ 7.91 (d, *J* = 8 Hz, 1H), 7.86 (d, *J* = 8 Hz, 1H), 7.80 (dd, *J* = 8 Hz, 4 Hz 1H), 7.52-7.47 (m, 3H), 7.44-7.40 (m, 1H), 7.38-7.36 (m, 3H), 7.31-7.21 (m, 2H), 7.23-7.19 (m, 2H), 7.14-7.09 (m, 2H), 6.89 (d, *J* = 16 Hz, 1H), 6.73-6.69 (m, 1H),

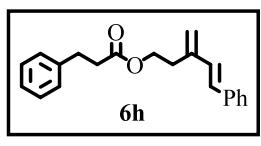
6.58-6.54 (m, 3H), 5.57 (s, 1H), 5.38 (s, 1H), 4.67 (s, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 149.3, 144.0, 140.6, 137.0, 135.3, 131.1, 129.2, 128.7, 128.6, 128.5, 128.0, 127.5, 126.9, 126.36, 126.32, 126.29, 126.25, 126.0, 123.9, 117.4, 117.1, 113.9, 54.7; **HRMS (EI)** m/z calcd. For [M]⁺ C₂₇H₂₃N 361.1830, found 361.1822.

(E)-3-Methylene-5-phenylpent-4-en-1-yl cinnamate (6g):



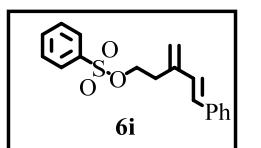
Eluent: n-hexane/ ethyl acetate (97/3); colorless liquid; Yield: 76 mg (63%); **¹H NMR** (400 MHz, CDCl₃): δ 7.69 (d, *J* = 16 Hz, 1H), 7.48-7.21 (m, 10H), 6.83 (d, *J* = 16 Hz, 1H), 6.67 (d, *J* = 16 Hz, 1H), 6.44 (d, *J* = 16 Hz, 1H), 5.26 (s, 1H), 5.16 (s, 1H), 4.41 (t, *J* = 8 Hz, 2H), 2.76 (t, *J* = 8 Hz, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 166.9, 144.9, 142.1, 137.1, 134.4, 130.47, 130.28, 128.88, 128.71, 128.66, 128.10, 127.6, 126.5, 118.12, 118.05, 63.4, 31.4; **HRMS (EI)** m/z calcd. For [M]⁺ C₂₁H₂₀O₂ 304.1463, found 304.1454.

(E)-3-Methylene-5-phenylpent-4-en-1-yl 3-phenylpropanoate (6h):



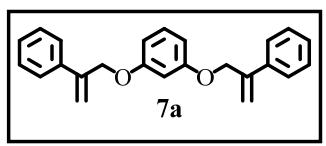
Eluent: n-hexane/ ethyl acetate (97/3); colorless liquid;; Yield: 111.3 mg (91%); **¹H NMR** (400 MHz, CDCl₃): δ 7.48-7.46 (m, 2H), 7.39-7.22 (m, 8H), 6.85 (d, *J* = 16 Hz, 1H), 6.66 (d, *J* = 16 Hz, 1H), 5.26 (s, 1H), 5.13 (s, 1H), 4.32 (t, *J* = 8 Hz, 2H), 3.0 (t, *J* = 8 Hz, 2H), 2.71-2.26 (m, 4H); **¹³C NMR** (100 MHz, CDCl₃): δ 172.8, 142.0, 140.5, 137.1, 130.4, 128.66, 128.62, 128.51, 128.32, 127.6, 126.53, 126.27, 117.9, 63.2, 35.9, 31.3, 31.0; **HRMS (EI)** m/z calcd. For [M]⁺ C₂₁H₂₂O₂ 306.1620, found 306.1607.

(E)-3-Methylene-5-phenylpent-4-en-1-yl benzenesulfonate (6i):



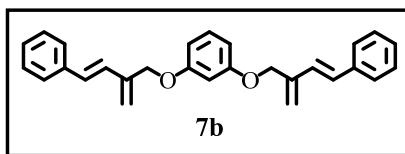
Eluent: n-hexane/ ethyl acetate (97/3); colorless liquid; Yield: 103 mg (82%); **¹H NMR** (400 MHz, CDCl₃): δ 7.92-7.89 (m, 2H), 7.64-7.60 (m, 1H), 7.54-7.50 (m, 2H), 7.37-7.29 (m, 4H), 7.25-7.21 (m, 1H), 6.68 (d, *J* = 16 Hz, 1H), 6.45 (d, *J* = 16 Hz, 1H), 5.19 (s, 1H), 5.05 (s, 1H), 4.23 (t, *J* = 8 Hz, 2H), 2.73-2.70 (m, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 140.4, 136.80, 136.23, 133.7, 129.78, 129.21, 128.6, 127.89, 127.80, 126.5, 118.7, 69.0, 31.7; **HRMS (EI)** m/z calcd. For [M]⁺ C₁₈H₁₈O₃S 314.0976, found 314.0968.

1,3-Bis((2-phenylallyl)oxy)benzene (7a):



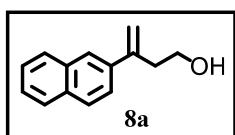
Eluent: n-hexane/ ethyl acetate (98/2); colorless liquid; Yield: 76 mg (56%); **¹H NMR** (400 MHz, CDCl₃): δ 7.47 (d, *J* = 8 Hz, 4H), 7.39-7.28 (m, 6H), 7.21-7.17 (m, 1H), 6.59 (d, *J* = 8 Hz, 3H), 5.60 (s, 2H), 5.46 (s, 2H), 4.86 (s, 4H); **¹³C NMR** (100 MHz, CDCl₃): δ 159.8, 143.0, 138.3, 129.8, 128.48, 128.00, 126.05, 114.8, 107.5, 102.4, 69.9; **HRMS (EI)** m/z calcd. For [M]⁺ C₂₄H₂₂O₂ 342.1619, found 342.1614.

1,3-Bis((*E*)-2-methylene-4-phenylbut-3-en-1-yl)oxy)benzene (7b):



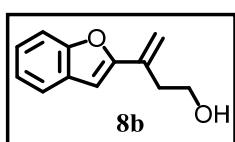
Eluent: n-hexane/ ethyl acetate (98/2); White solid; Yield: 56.7 mg (36%); M.p.: 92 °C; **¹H NMR** (400 MHz, CDCl₃): δ 7.43-7.41 (m, 4H), 7.33-7.29 (m, 4H), 7.25-7.19 (m, 3H), 6.85 (d, *J* = 16 Hz, 2H), 6.68-6.60 (m, 5H), 5.44 (s, 2H), 5.39 (s, 2H), 4.79 (s, 4H); **¹³C NMR** (100 MHz, CDCl₃): δ 159.9, 141.0, 137.0, 129.9, 129.2, 128.63, 128.15, 127.7, 126.5, 118.2, 107.5, 102.4, 68.2; **HRMS (EI)** m/z calcd. For [M]⁺ C₂₈H₂₆O₂ 394.1932, found 394.1928.

3-(Naphthalen-2-yl)but-3-en-1-ol (8a):¹⁴



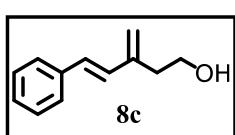
Eluent: n-hexane/ ethyl acetate (90/10); White solid; Yield: 36.4 mg (92%); M.p.: 51 °C; **¹H NMR** (400 MHz, CDCl₃): δ 7.83-7.79 (m, 4H), 7.57 (dd, *J* = 4 Hz, 4 Hz, 1H), 7.49-7.43 (m, 2H), 5.55 (d, *J* = 1.2 Hz, 1H), 5.26 (d, *J* = 1.2 Hz, 1H), 3.77 (t, *J* = 8 Hz, 2H), 2.92-2.88 (m, 2H), 1.50 (s, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 144.6, 137.6, 133.3, 132.9, 128.16, 128.03, 127.5, 126.25, 126.0, 124.83, 124.46, 115.0, 61.1, 38.6; **HRMS (ESI)** m/z calcd. For [M+H]⁺ C₁₄H₁₅O 199.1117, found 199.1125.

3-(Benzofuran-2-yl)but-3-en-1-ol (8b):¹⁵



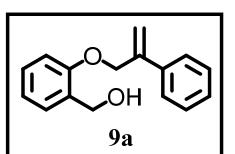
Eluent: n-hexane/ ethyl acetate (90/10); colorless liquid; Yield: 35.7 mg (95%); **¹H NMR** (400 MHz, CDCl₃): δ 7.52 (d, *J* = 4 Hz, 1H), 7.45-7.43 (m, 1H), 7.29-7.25 (m, 1H), 7.21-7.17 (m, 1H), 6.69 (s, 1H), 5.93 (d, *J* = 1 Hz, 1H), 5.27 (d, *J* = 1 Hz, 1H), 3.37 (q, *J* = 1 Hz, 1H), 2.76-2.72 (m, 2H), 1.54 (t, *J* = 8 Hz, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 155.7, 154.7, 133.9, 128.7, 124.7, 122.8, 121.0, 114.7, 110.9, 103.0, 61.4, 36.5; **HRMS (EI)** m/z calcd. For [M]⁺ C₁₂H₁₂O₂ 188.0837, found 188.0847.

(E)-3-Methylene-5-phenylpent-4-en-1-ol (8c):¹⁶



Eluent: n-hexane/ ethyl acetate (90/10); White solid; Yield: 32.3 mg (93%); M.p.: 54 °C; **¹H NMR** (400 MHz, CDCl₃): δ 7.43-7.41 (m, 2H), 7.34-7.30 (m, 2H), 7.25-7.21 (m, 1H), 6.81 (d, *J* = 16 Hz, 1H), 6.61 (d, *J* = 16 Hz, 1H), 5.26 (s, 1H), 5.14 (s, 1H), 3.82 (t, *J* = 8 Hz, 2H), 6.65-6.62 (m, 2H), 1.50 (s, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 142.4, 137.0, 130.3, 128.75, 128.64, 127.6, 126.4, 118.1, 61.2, 35.4; **HRMS (EI)** m/z calcd. For [M]⁺ C₁₂H₁₄O 174.1044, found 174.1025.

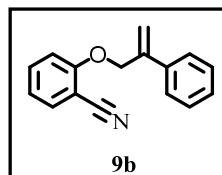
(2-((2-Phenylallyl)oxy)phenyl)methanol (9a):



Eluent: n-hexane/ ethyl acetate (93/7); colorless liquid; Yield: 86 mg (90%); **¹H NMR** (400 MHz, CDCl₃): δ 7.45 (d, *J* = 8 Hz, 2H), 7.38-7.25 (m, 5H), 6.96-6.93 (m, 2H), 5.60 (s, 1H), 5.45 (s, 1H), 4.96 (s, 2H), 4.57 (d, *J* = 8 Hz, 2H), 2.08 (q, *J* = 1.2 Hz, 1); **¹³C NMR** (100 MHz, CDCl₃): δ

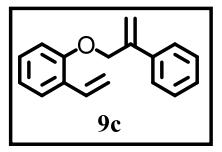
156.3, 143.1, 138.1, 129.5, 128.89, 128.86, 128.58, 128.17, 126.0, 121.0, 114.9, 111.4, 69.8, 62.0; **HRMS (EI)** m/z calcd. For $[M]^+$ C₁₆H₁₆O₂ 240.1150, found 240.1136.

2-((2-Phenylallyl)oxy)benzonitrile (9b):



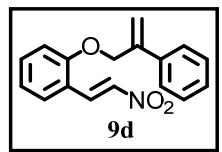
Eluent: n-hexane (94/6); colorless liquid; Yield: 63 mg (67%); **¹H NMR** (400 MHz, CDCl₃): δ 7.56-7.44 (m, 4H), 7.39-7.30 (m, 3H), 7.02-6.98 (m, 2H), 5.61 (d, *J* = 1 Hz, 1H), 5.54 (s, 1H), 5.00 (t, *J* = 4 Hz, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 160.1, 147.7, 137.8, 134.1, 133.7, 128.52, 128.16, 125.9, 121.0, 116.2, 114.8, 112.8, 102.3, 70.1; **HRMS (EI)** m/z calcd. For [M+H]⁺ C₁₆H₁₄NO 236.1069, found 236.1072.

1-((2-Phenylallyl)oxy)-2-vinylbenzene (9c):



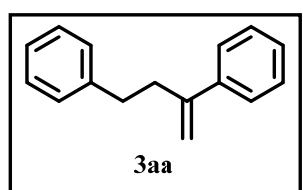
Eluent: n-hexane (100%); colorless liquid; Yield: 78 mg (83%); **¹H NMR** (400 MHz, CDCl₃): δ 7.50-7.45 (m, 3H), 7.37-7.28 (m, 3H), 7.24-7.20 (m, 1H), 7.05-6.92 (m, 3H), 5.69 (dd, *J* = 8 Hz, 1.6 Hz, 1H), 5.60 (d, *J* = 1 Hz, 1H), 5.47 (q, *J* = 4 Hz, 1H), 5.20 (dd, *J* = 1 Hz, 4 Hz, 1H), 4.91 (s, 1H), **¹³C NMR** (100 MHz, CDCl₃): δ 155.6, 143.1, 138.4, 131.5, 128.69, 128.41, 127.92, 127.20, 126.48, 126.02, 120.9, 114.53, 114.39, 112.4, 70.1; **HRMS (EI)** m/z calcd. For [M]⁺ C₁₇H₁₆O 236.1201, found 236.1206.

(E)-1-(2-Nitrovinyl)-2-((2-phenylallyl)oxy)benzene (9d):



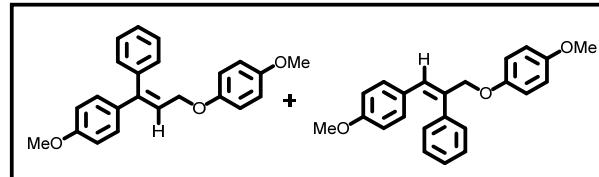
Eluent: n-hexane/ethyl acetate (95/5); colorless liquid; Yield: 86 mg (77%); **¹H NMR** (400 MHz, CDCl₃): δ 8.01 (d, *J* = 12 Hz, 1H), 7.62 (d, *J* = 12 Hz, 1H), 7.46-7.32 (m, 7H), 7.02 (t, *J* = 8 Hz, 1H), 5.62 (s, 1H), 7.02 (d, *J* = 1 Hz, 1H), 5.05 (s, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 158.4, 142.7, 138.5, 137.9, 135.1, 133.2, 132.6, 128.71, 128.39, 126.1, 121.4, 119.7, 115.8, 112.8, 70.7; **HRMS (EI)** m/z calcd. For [M]⁺ C₁₇H₁₅NO₃ 281.1051, found 281.1042.

But-3-ene-1,3-diyldibenzene (3aa):¹⁷



Eluent: n-hexane/ethyl acetate (97/3); colorless liquid; Yield: 60 mg (72%); **¹H NMR** (400 MHz, CDCl₃): δ 7.44-7.41 (m, 2H), 7.36-7.31 (m, 2H), 7.29-7.23 (m, 3H), 7.20-7.16 (m, 3H), 5.29 (d, *J* = 1.2 Hz, 1H), 5.06 (d, *J* = 1.2 Hz, 1H), 2.83-2.74 (m, 4H); **¹³C NMR** (100 MHz, CDCl₃): δ 147.8, 141.9, 141.1, 128.4, 128.36, 128.31, 127.4, 126.1, 125.8, 112.6, 37.2, 34.7; **HRMS (EI)** m/z calcd. For [M]⁺ C₁₆H₁₆ 208.1252, found 208.1238.

(E)-1-methoxy-4-(3-(4-methoxyphenoxy)-1-phenylprop-1-en-1-yl)benzene (3bb) and (E)-1-methoxy-4-(3-(4-methoxyphenoxy)-2-phenylprop-1-en-1-yl)benzene (3bb').



The products **3bb** and **3bb'** were isolated in a 4:1 ratio of inseparable mixture using eluent: *n*-hexane/ethyl acetate (96/4); White solid; Yield: 88 mg (64%); M.p.: 85 °C; **¹H NMR** (400 MHz, CDCl₃): δ 7.58 (d, *J* = 4 Hz, 0.51H), 7.35 (t, *J* = 8 Hz, 1H), 7.29–7.23 (m, 5.2H), 7.13 (t, *J* = 8 Hz, 2.3H), 6.90 (d, *J* = 8 Hz, 2.8H), 6.86–6.82 (m, 0.87H), 6.78 (s, 4H), 6.24 (t, *J* = 4 Hz, 1H), 4.88 (s, 0.5H), 4.55 (d, *J* = 4 Hz, 2H), 3.82 (s, 3.0H), 3.79 (s, 0.88H), 3.77 (s, 0.82H), 3.74 (s, 3.0H); **¹³C NMR** (100 MHz, CDCl₃): 159.1, 154.0, 153.8, 152.7, 145.1, 142.0, 141.2, 134.7, 132.9, 131.2, 130.9, 130.3, 129.3, 128.4, 128.0, 127.7, 127.6, 127.2, 126.1, 123.7, 115.8, 115.7, 114.6, 114.5, 113.8, 113.6, 66.8, 66.7, 55.6, 55.2. **HRMS (MALDI)** m/z calcd. For [M+H]⁺ C₂₃H₂₂O₃ 347.1642, found 347.1646.

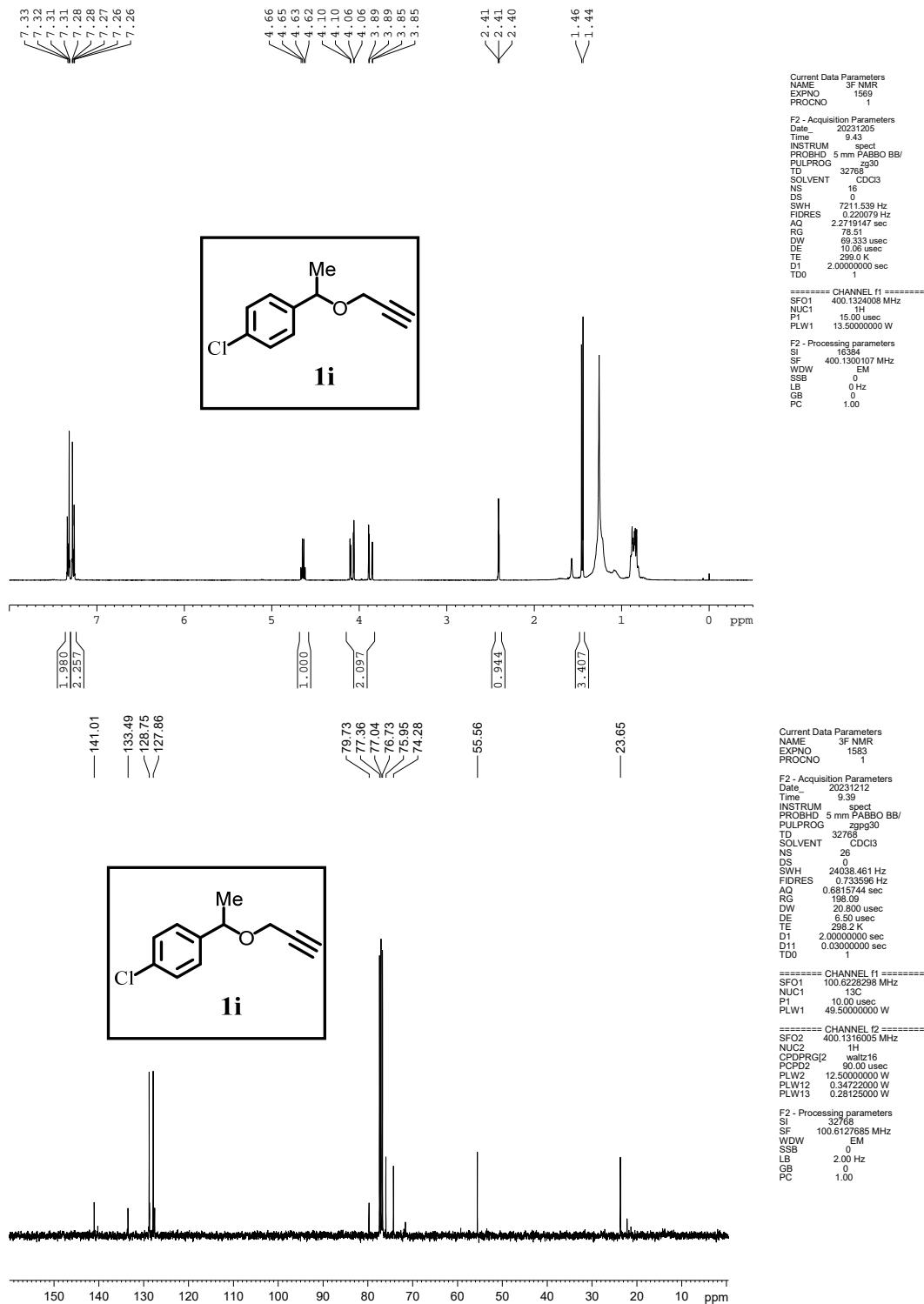
VII. References-

- 1) a) K. C. M. Kurtz, R. P. Hsung, Y. Zhang, *Org. Lett.* **2006**, *8*, 231–234. b) S. A. I. Sharif, E. D. D. Calder, A. H. Harkiss, M. Maduro, A. Sutherland, *J. Org. Chem.* **2016**, *81*, 9810–9819.
- c) D. Lasányi, G. L. Tolnai, *Org. Lett.* **2019**, *21*, 10057–10062. d) I. Volchkov, D. Lee, *J. Am. Chem. Soc.* **2013**, *135*, 5324–5327. e) Y-Y. Chen, K-L. Chen, Y-C. Tyan, C-F. Liang, P-C. Lin, *Tetrahedron*, **2015**, *71*, 6210–6218. f) Y-S. Feng, C-Q. Xie, W-L. Qiao, H-J. Xu, *Org. Lett.* **2013**, *15*, 936–939.
- 2) a) N. Iwasawa, S. Watanabe, A. Ario, H. Sogo, *J. Am. Chem. Soc.* **2018**, *140*, 7769–7772. b) V. Druais, M. J. Hall, C. Corsi, S. Wendeborn, C. Meyer, J. Cossy, *Org. Lett.* **2009**, *11*, 935–938. c) B. Rajagopal, C-H. Chou, C-C. Chung, P-C. Lin, *Org. Lett.* **2014**, *16*, 3752–3755. d) B. Martín-Matute, C. Nevado, D. J. Cárdenas, A. M. Echavarren, *J. Am. Chem. Soc.* **2003**, *125*, 5757–5766.
- 3) T. Nanjo, N. Kato, Y. Takemoto, *Org. Lett.* **2018**, *20*, 5766–5769.
- 4) J. Xu, Y-L. Wang, T-J. Gong, B. Xiao, Y. Fu, *Chem. Commun.*, **2014**, *50*, 12915—12918.
- 5) J. Zhong, Y. Long, X. Yan, S. He, R. Ye, H. Xiang, X. Zhou, *Org. Lett.*, **2019**, *21*, 9790–9794.
- 6) D., Ma, S. Hu, S., Chen, J., Pan, S., Tu, Y., Yin, Y., Gao, Y., Zhao, *Org. Lett.* **2020**, *22*, 8156–8160.
- 7) W. J. Kerr, D. M. Lindsay, P. K. Owens, M. Reid, T. Tuttle, S. Campos *ACS Catal.* **2017**, *7*, 7182–7186.
- 8) M. Srinivasan, S. Sankararaman, H. Hopf, I. Dix, P. G. Jones, *J. Org. Chem.* **2001**, *66*, 4299–4303.
- 9) I. Piel, M. Steinmetz, K. Hirano, R. Fröhlich, S. Grimme, F. Glorius, *Angew. Chem. Int. Ed.* **2011**, *50*, 4983 –4987.

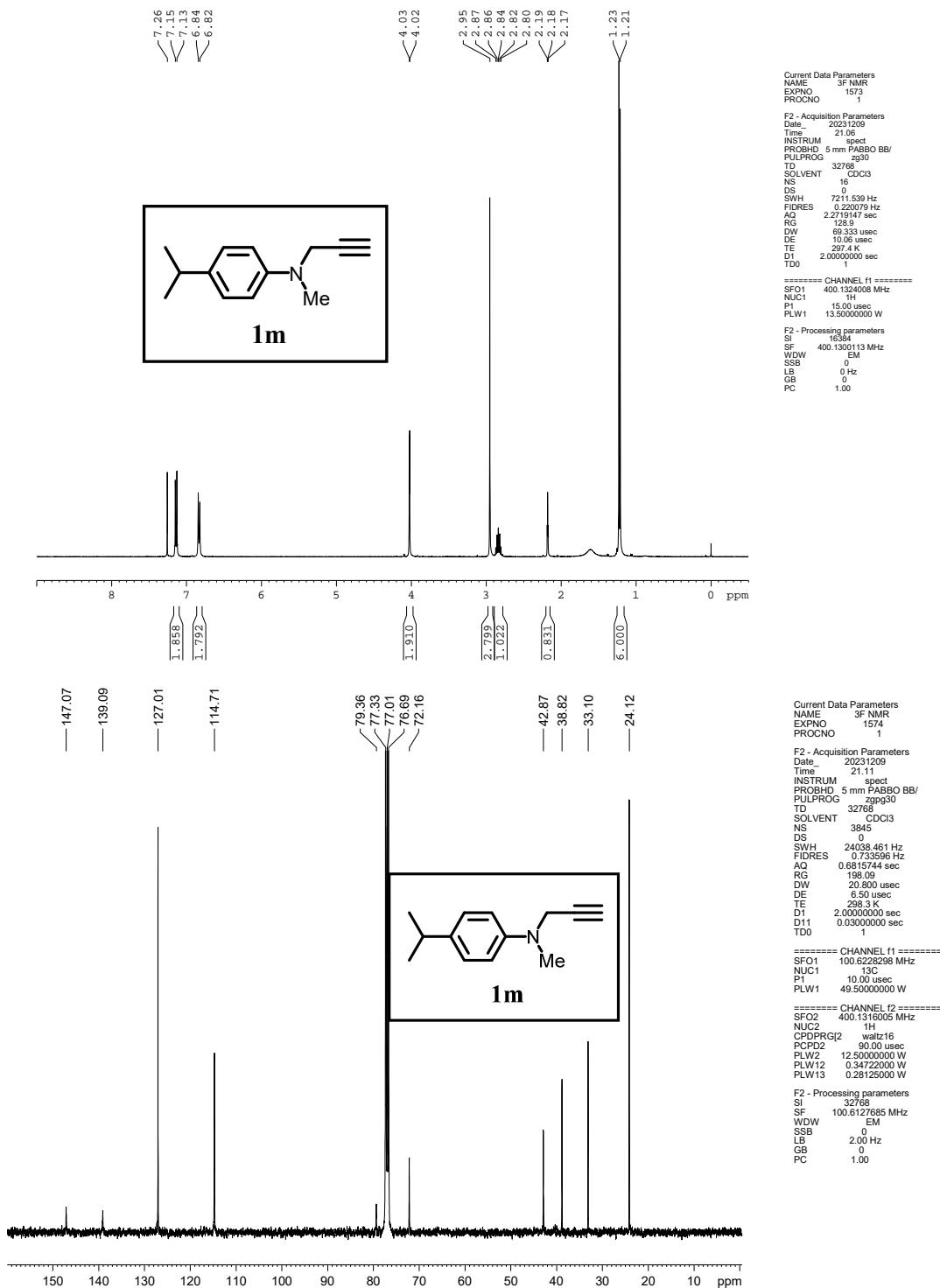
- 10) A. M. Martínez-Gualda, P. Domingo-Legarda, T. Rigotti, S. Díaz-Tendero, A. Fraile, J. Alemany, *Chem. Commun.*, **2021**, 57, 3046–3049.
- 11) J. Barluenga, F. J. Fanana's, R. Sanz, C. Marcos, J. M. Ignacio, *Chem. Commun.*, **2005**, 933–935.
- 12) X-F. Song, T-M. Ding, D. Zhu, J. Huang, Z-M. Chen, *Org. Lett.* **2020**, 22, 7052–7056.
- 13) W. Adam, M. Heil, *Eur JIC*, **1992**, 125, 235–241.
- 14) Q. Huang, A. Fazio, G. Dai, M. A. Campo, R. C. Larock, *J. Am. Chem. Soc.* **2004**, 126, 7460–7461.
- 15) C. Shu, R. S. Mega, B. J. Andreassen, A. Noble, V. K. Aggarwal, *Angew. Chem. Int. Ed.* **2018**, 57, 15430–15434.
- 16) S. M. Tan, A. C. Willis, M. N. Paddon-Row, M. S. Sherburn, *Angew. Chem. Int. Ed.* **2016**, 55, 3081–3085.
- 17) P. Lu, X. Ren, H. Xu, D. Lu, Y. Sun, Z. Lu, *J. Am. Chem. Soc.* **2021**, 143, 12433–12438.

VIII. Spectra Copies

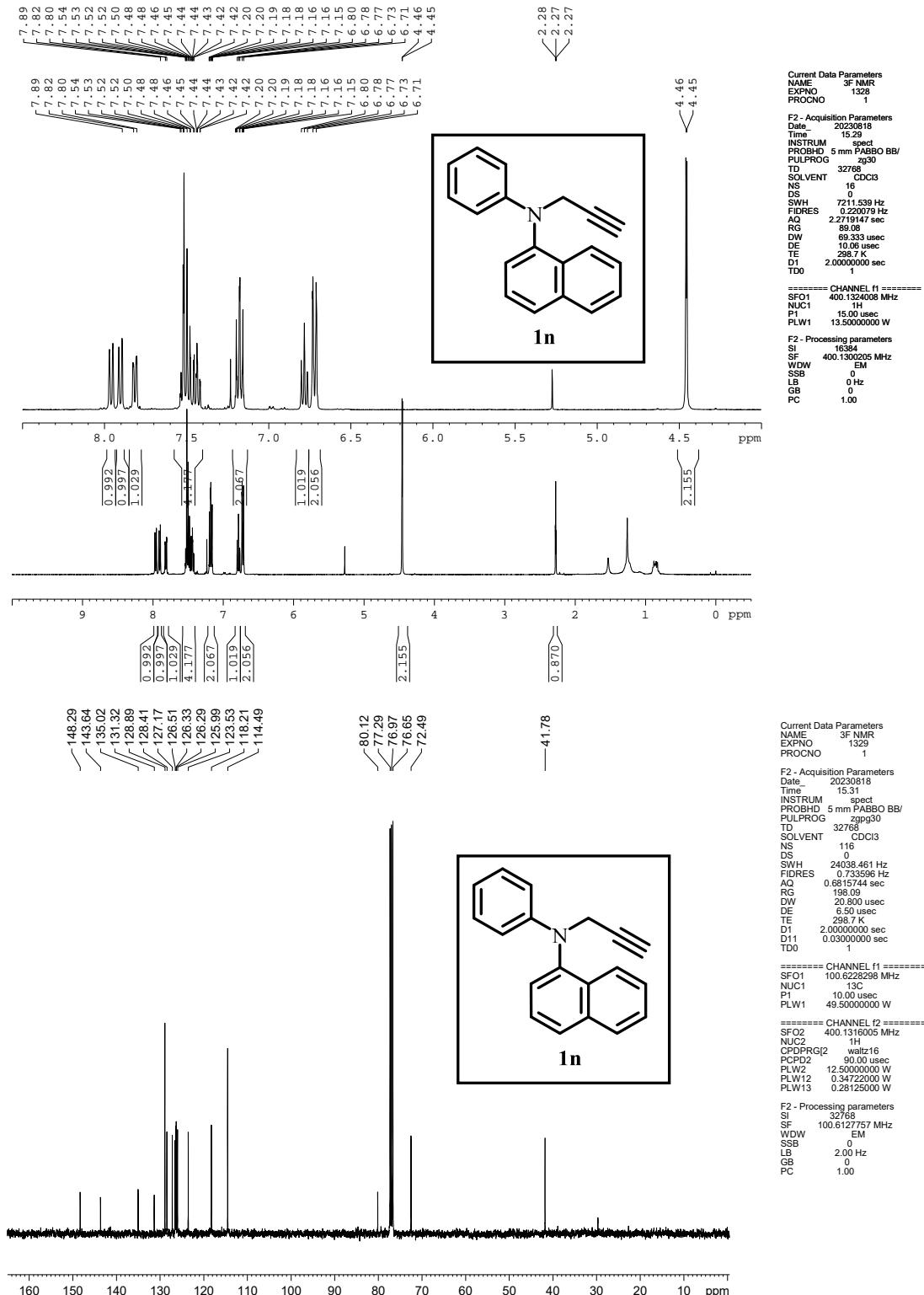
¹H and ¹³C NMR spectra of compound 1i.



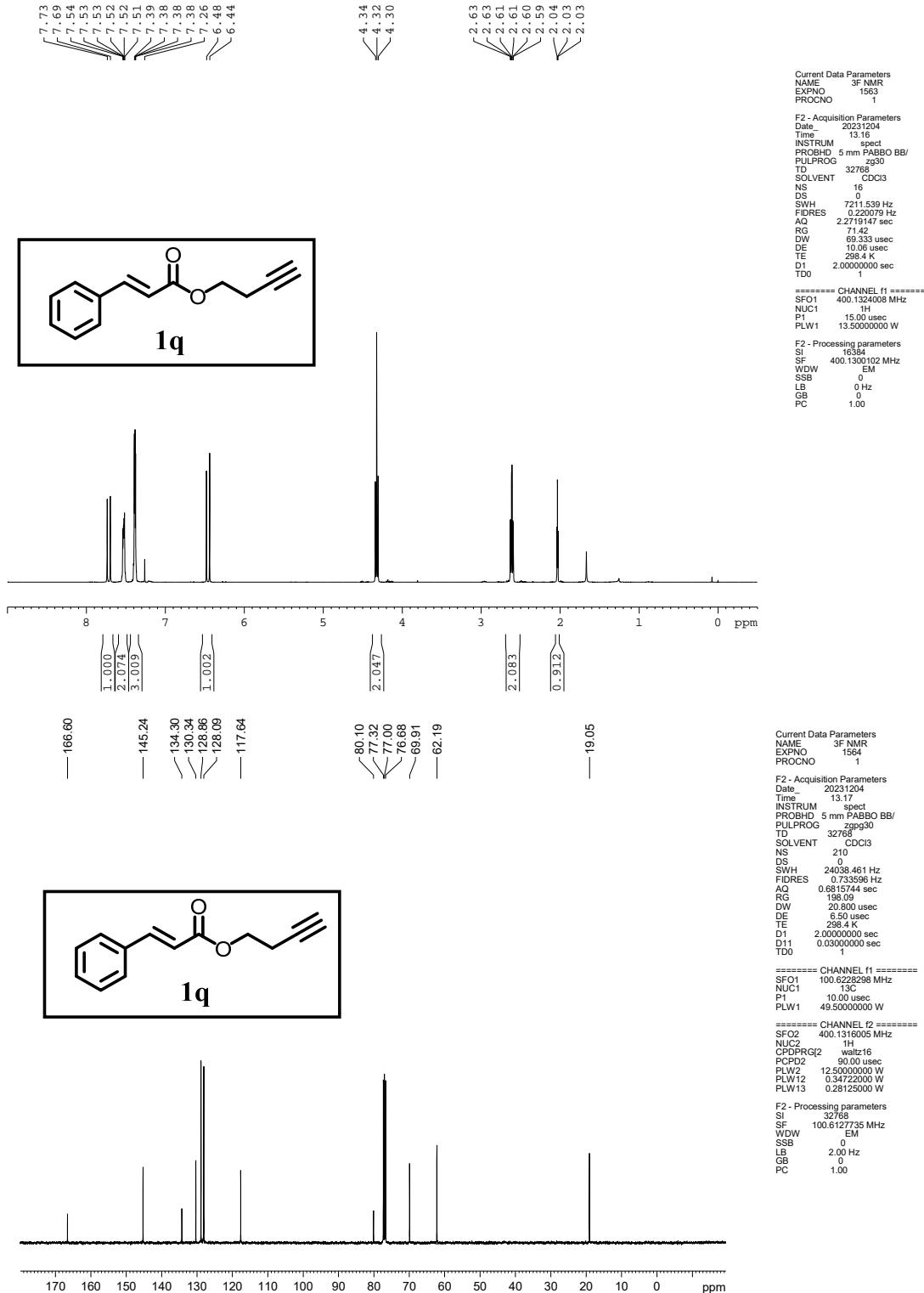
¹H and ¹³C NMR spectra of compound 1m.



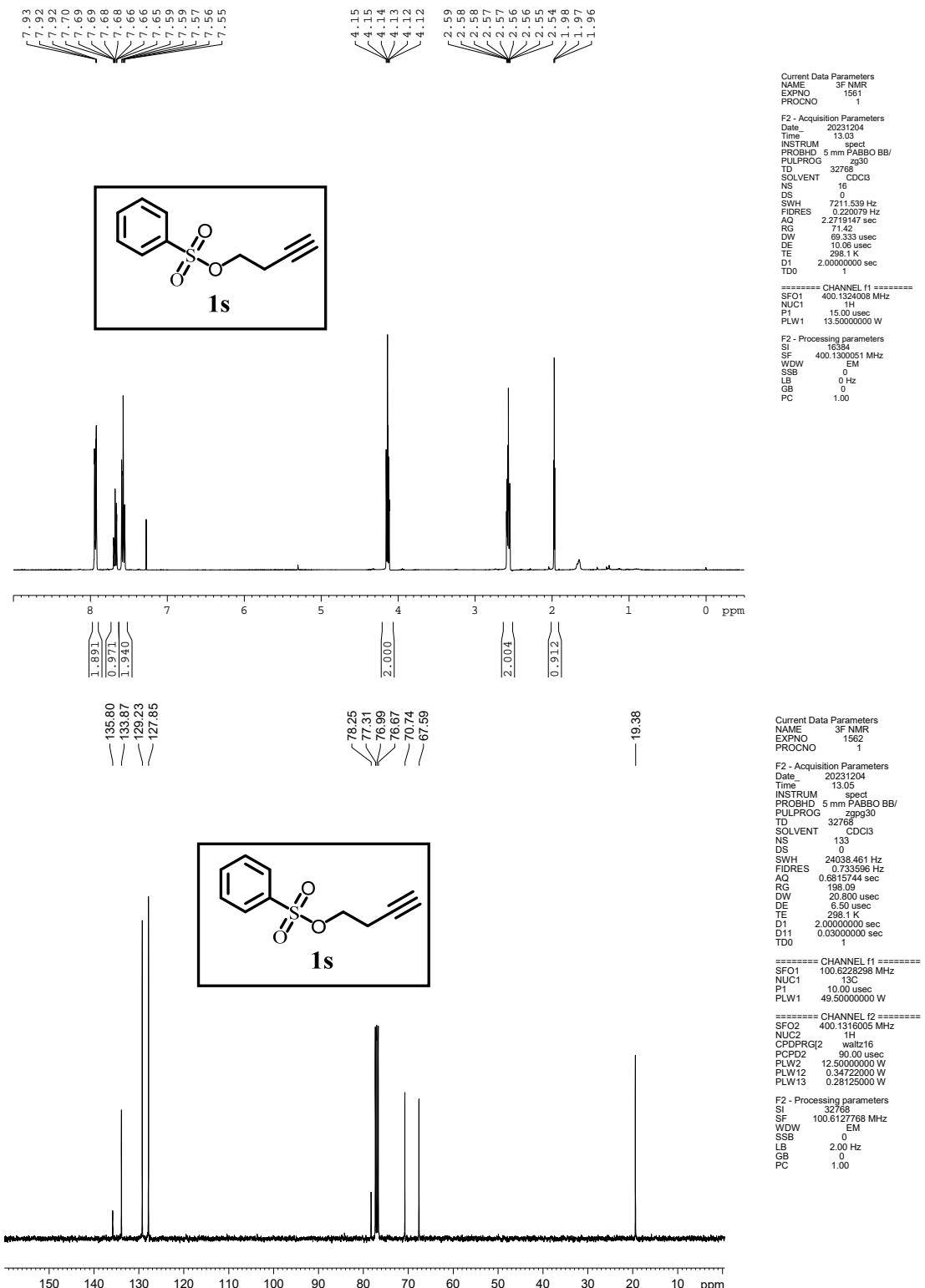
¹H and ¹³C NMR spectra of compound 1n.



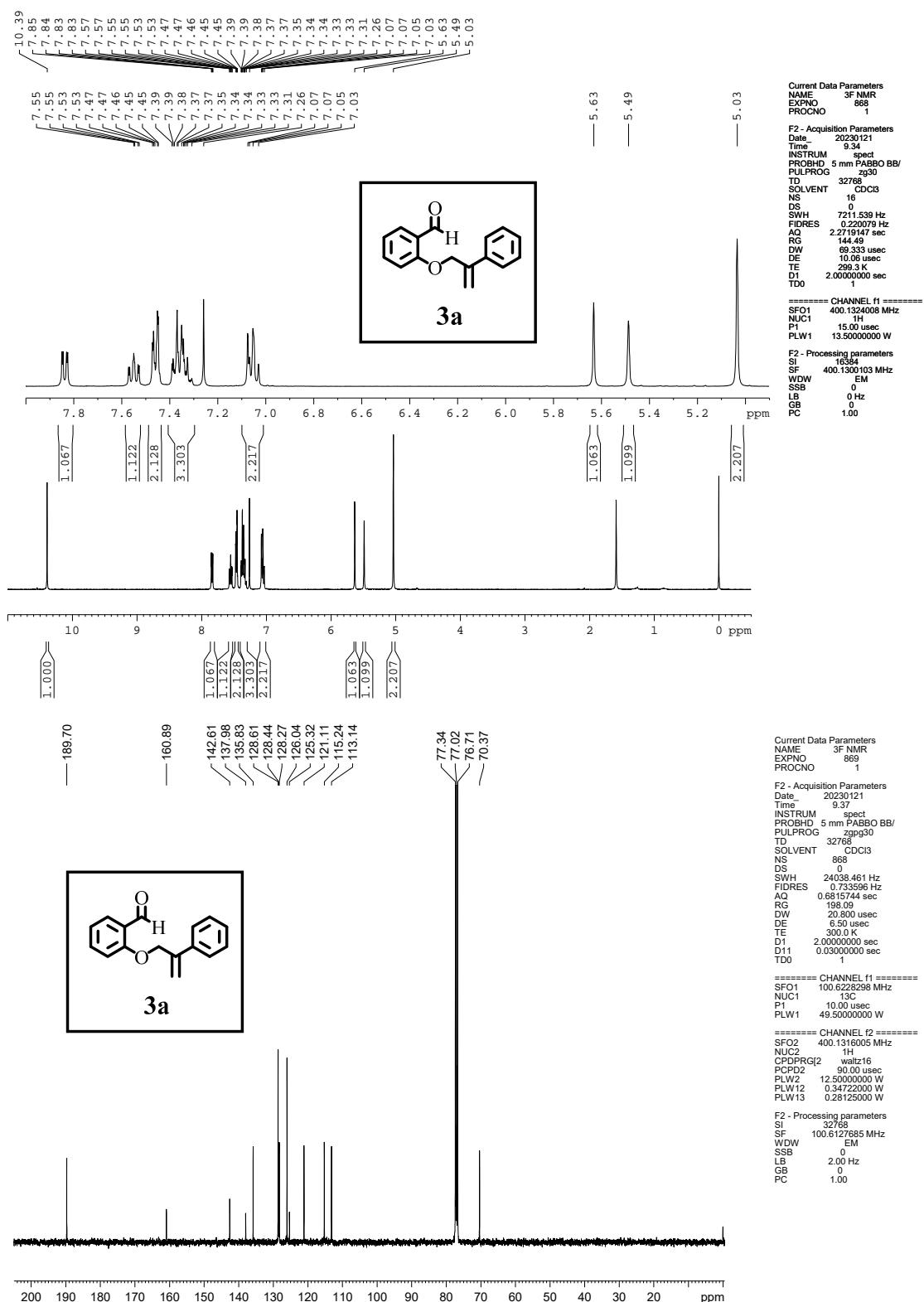
¹H and ¹³C NMR spectra of compound 1q.



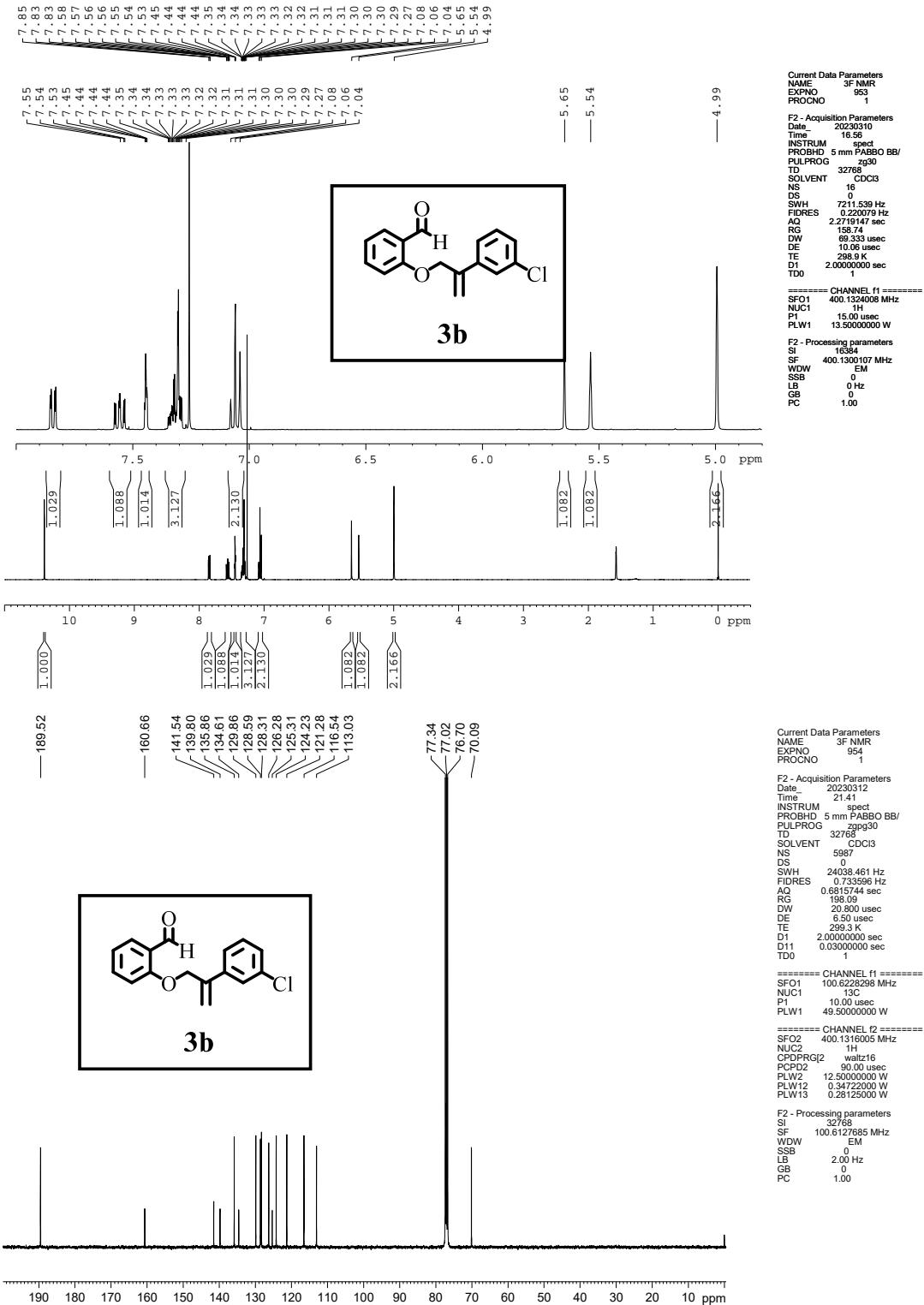
¹H and ¹³C NMR spectra of compound 1s.



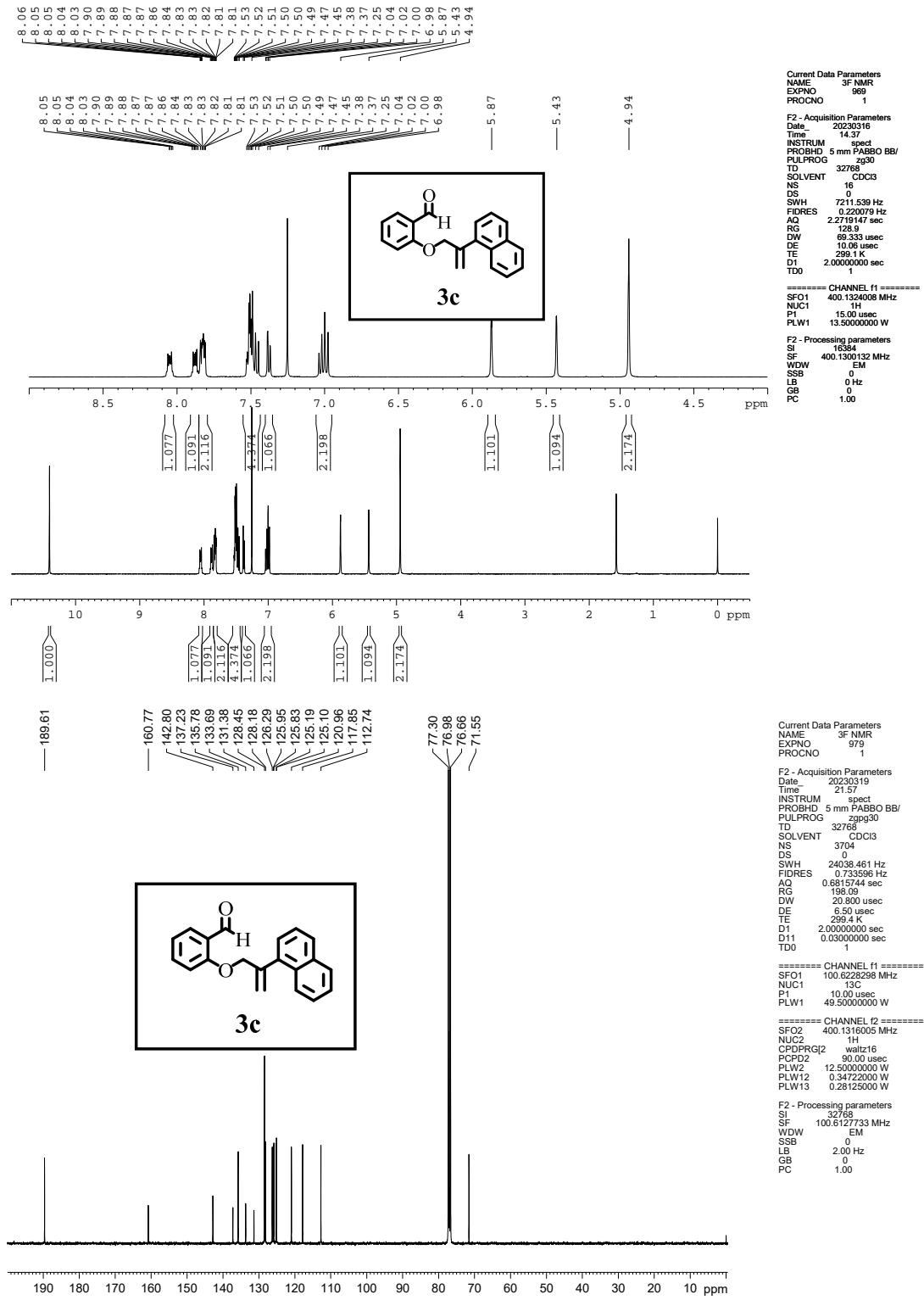
¹H and ¹³C NMR spectra of compound 3a.



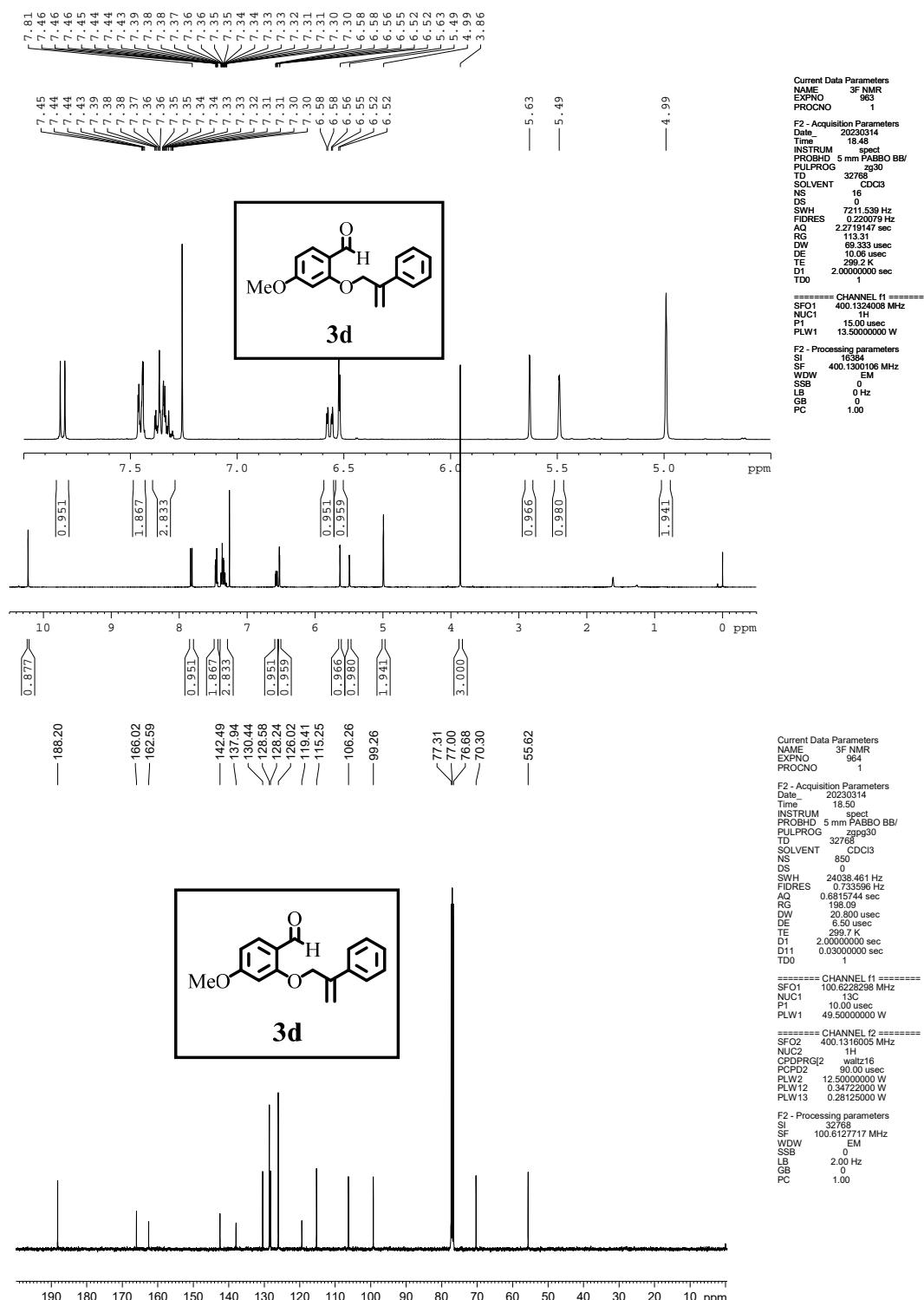
¹H and ¹³C NMR spectra of compound 3b



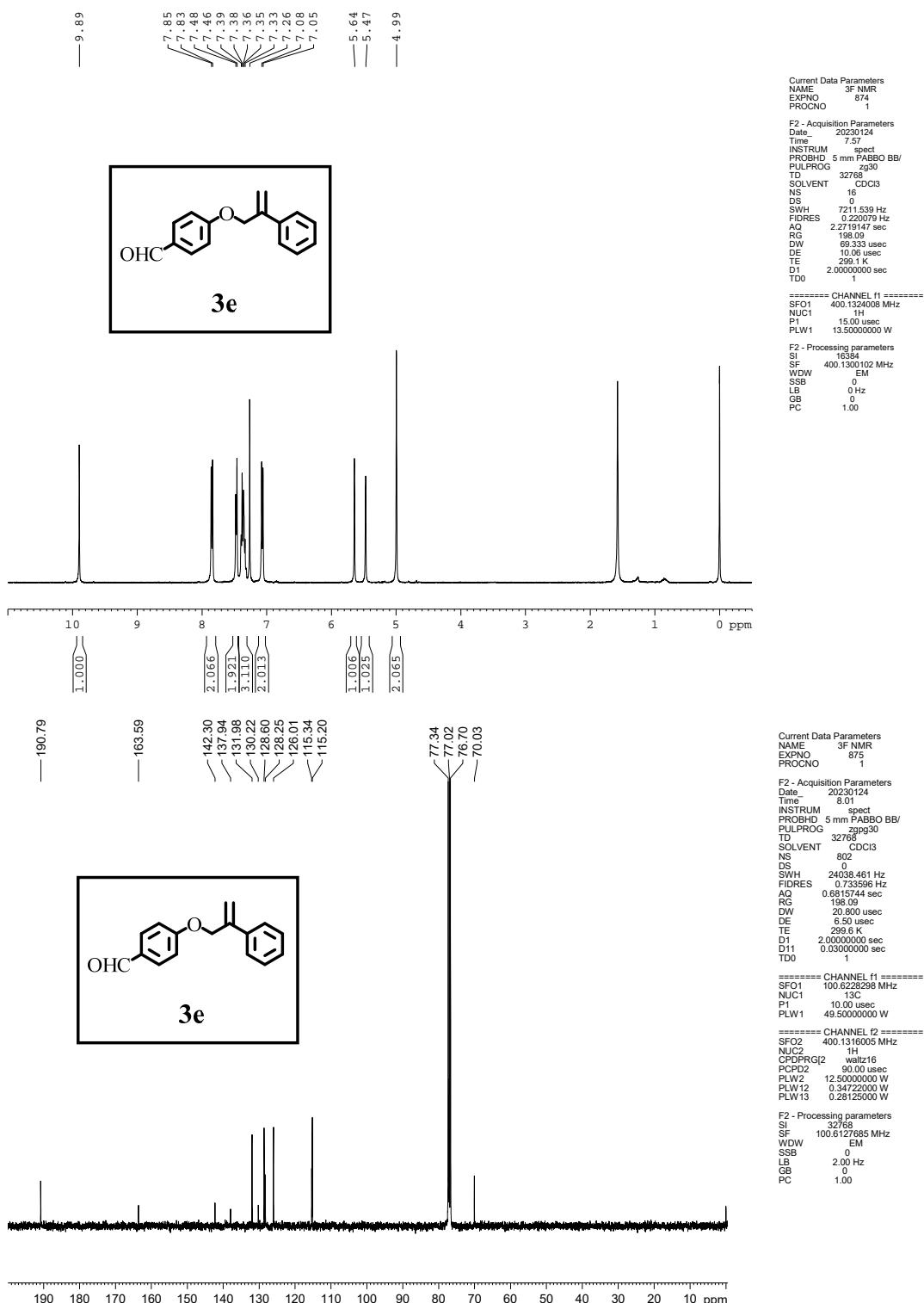
¹H and ¹³C NMR spectra of compound 3c



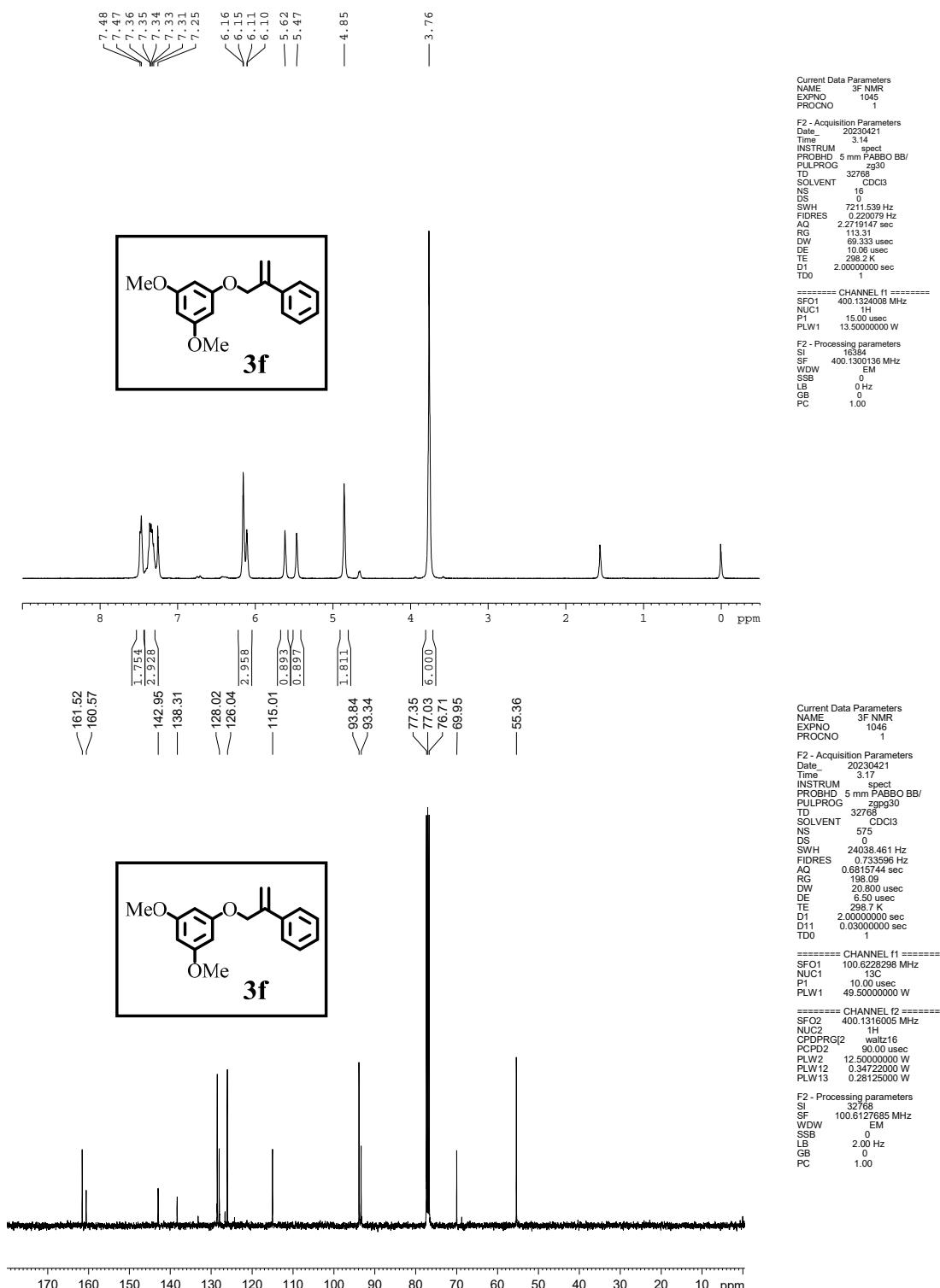
¹H and ¹³C NMR spectra of compound 3d



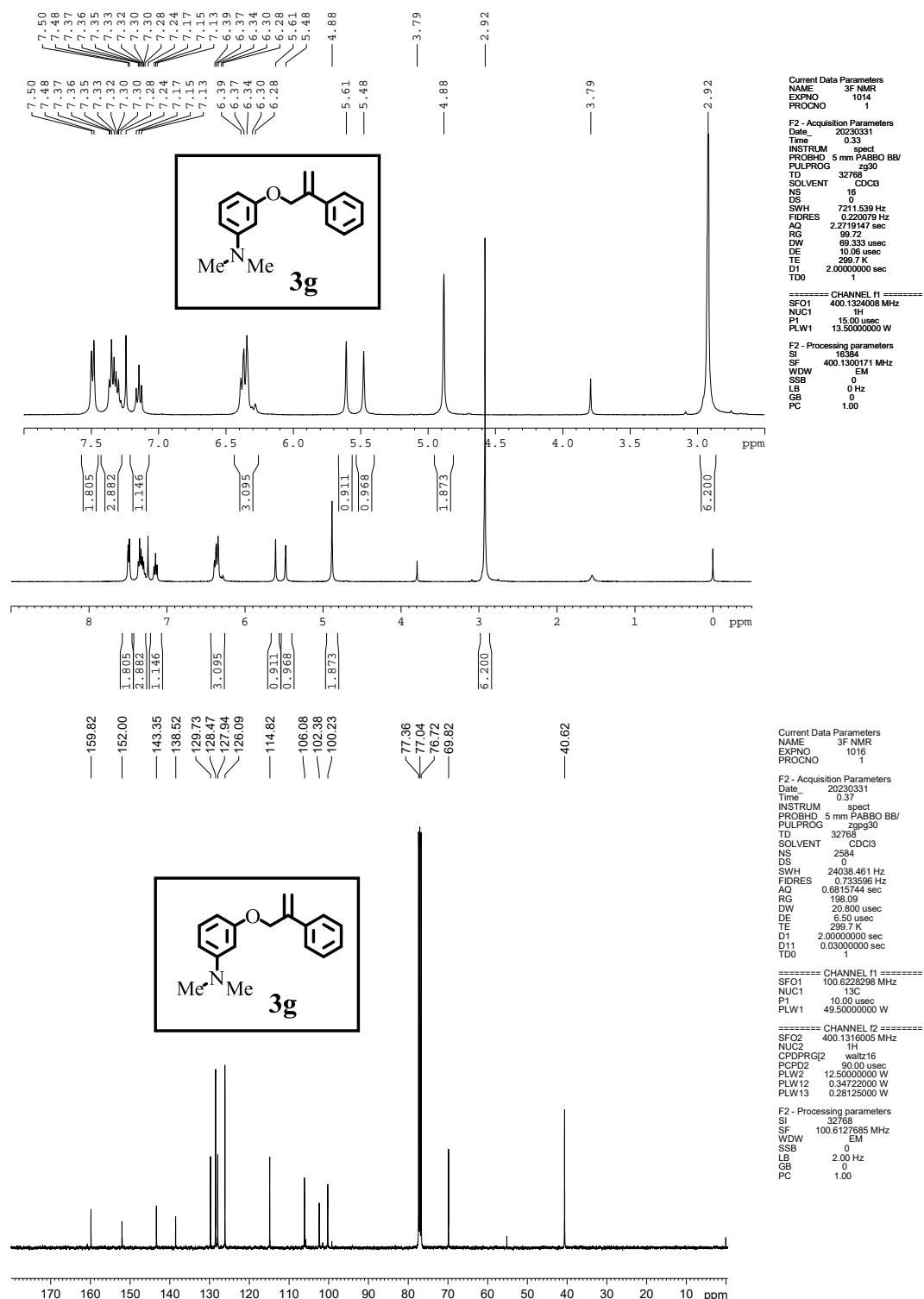
¹H and ¹³C NMR spectra of compound 3e.



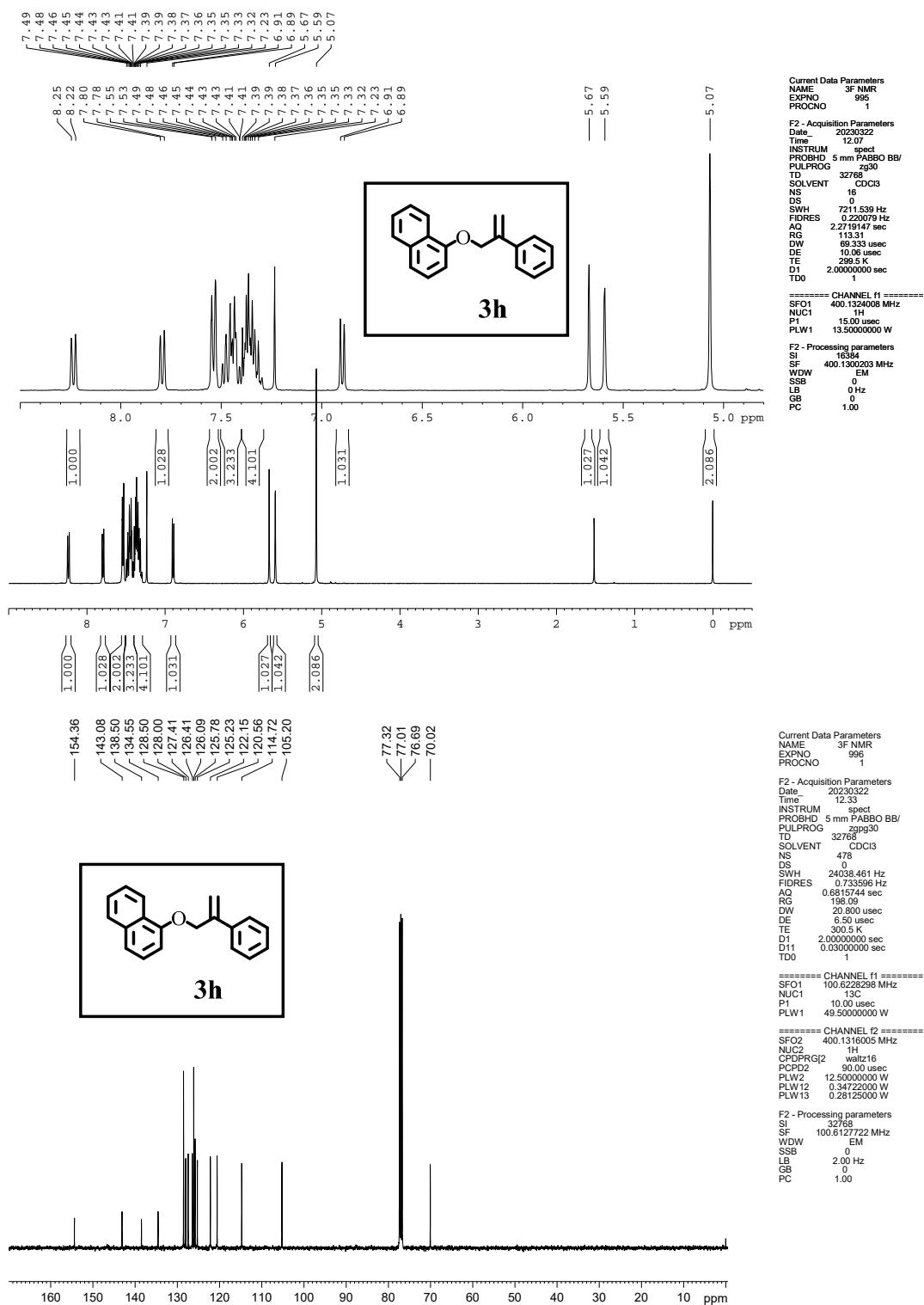
¹H and ¹³C NMR spectra of compound 3f.



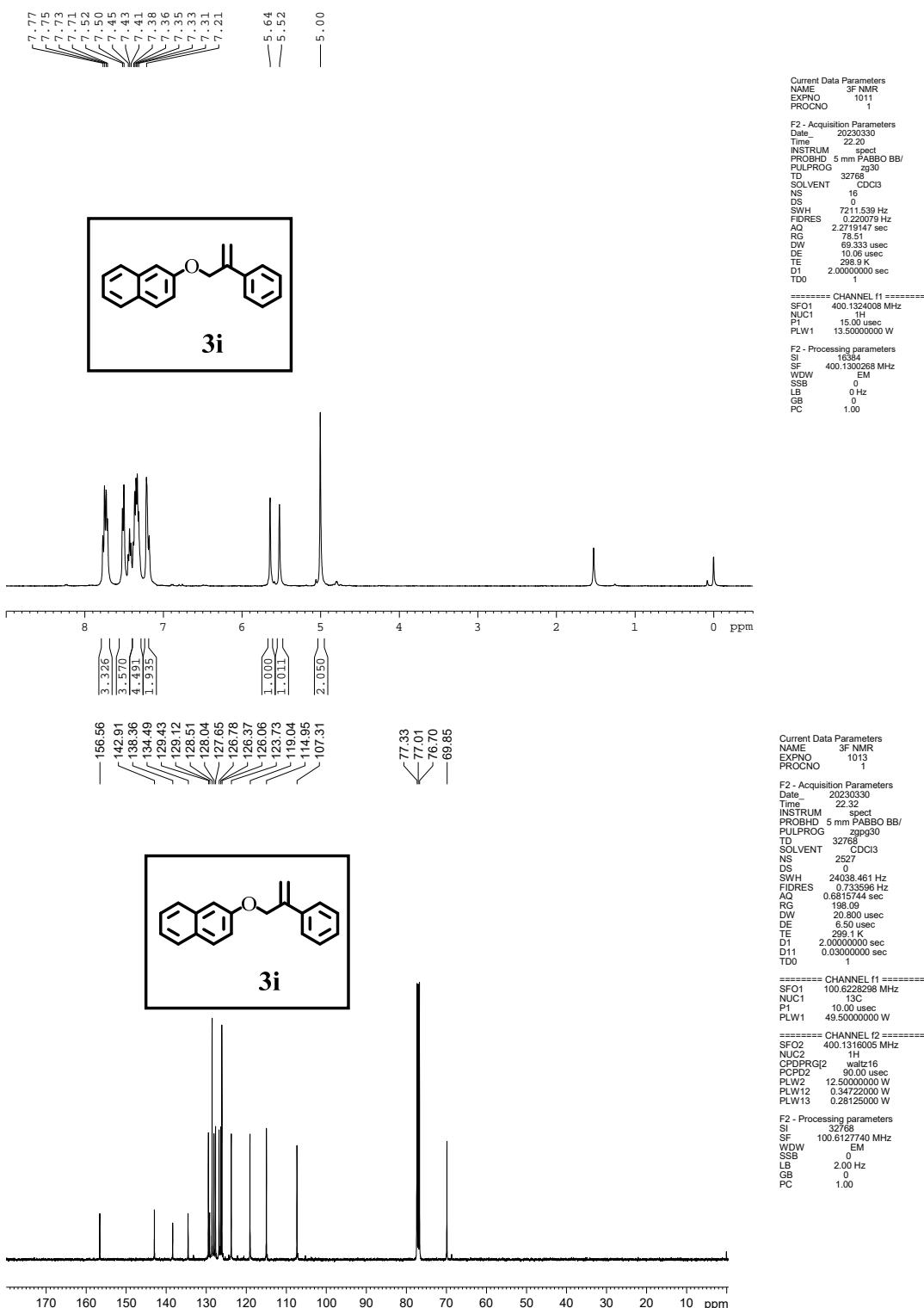
¹H and ¹³C NMR spectra of compound 3g.



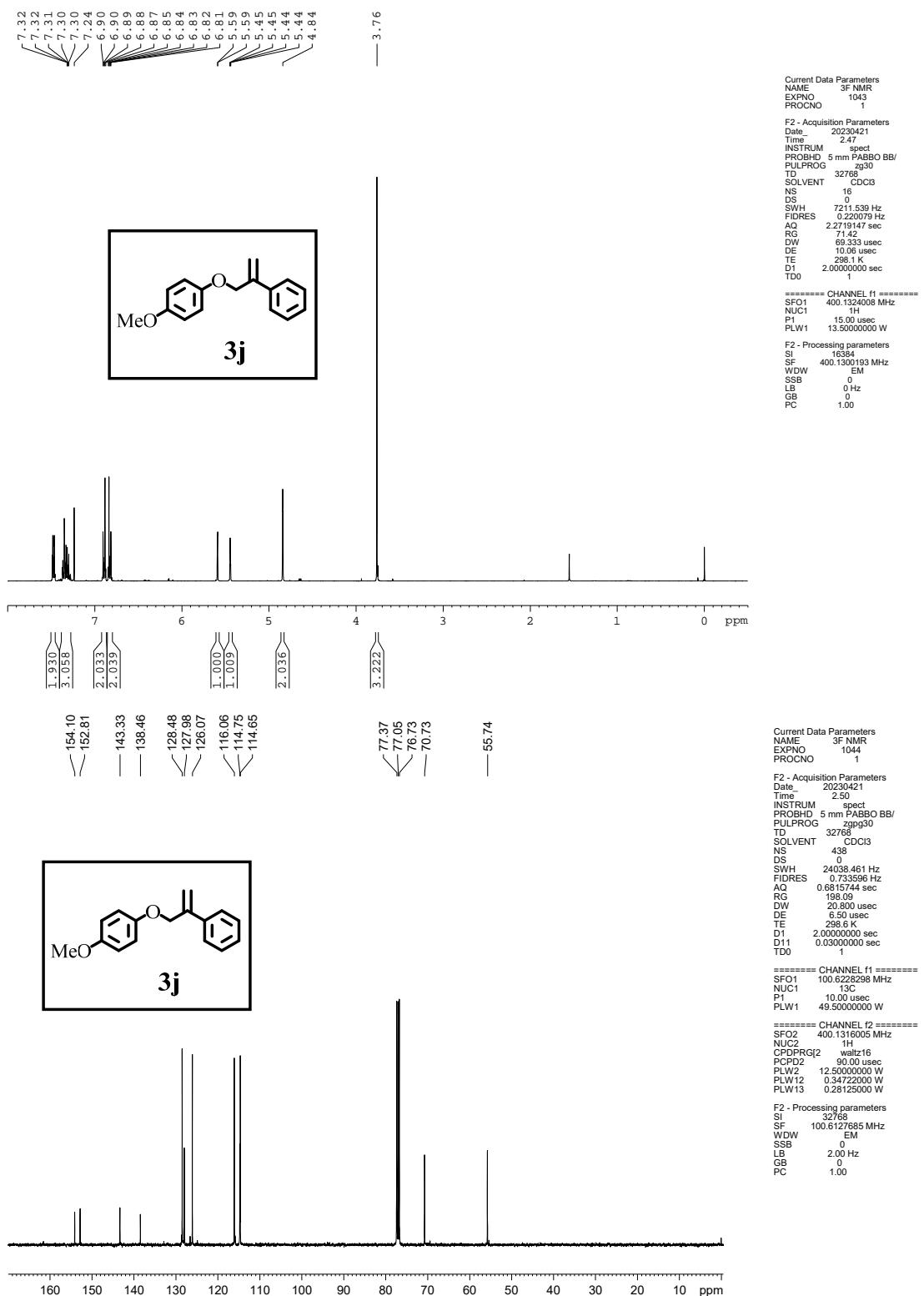
¹H and ¹³C NMR spectra of compound 3h.



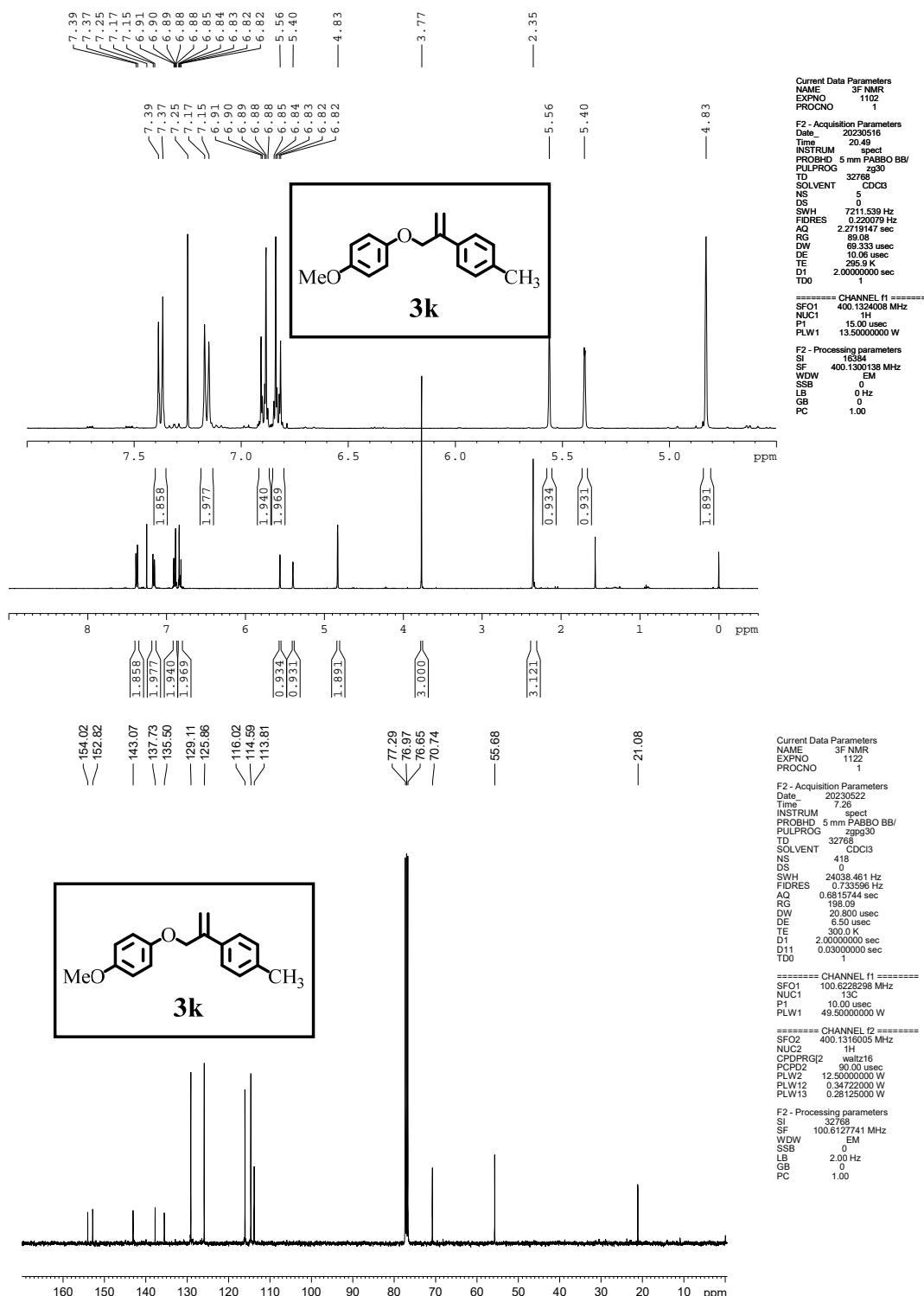
¹H and ¹³C NMR spectra of compound 3i.



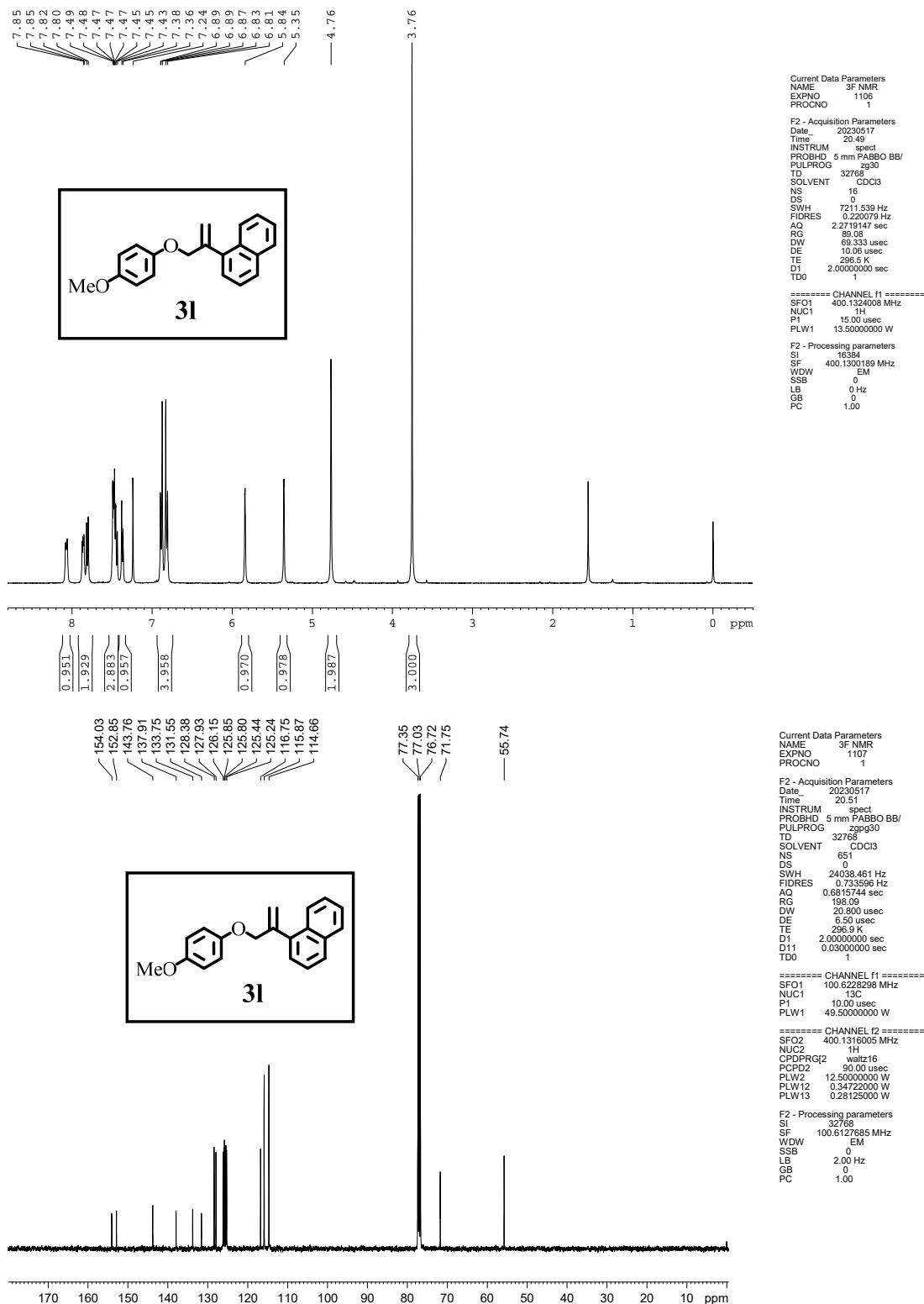
¹H and ¹³C NMR spectra of compound 3j.



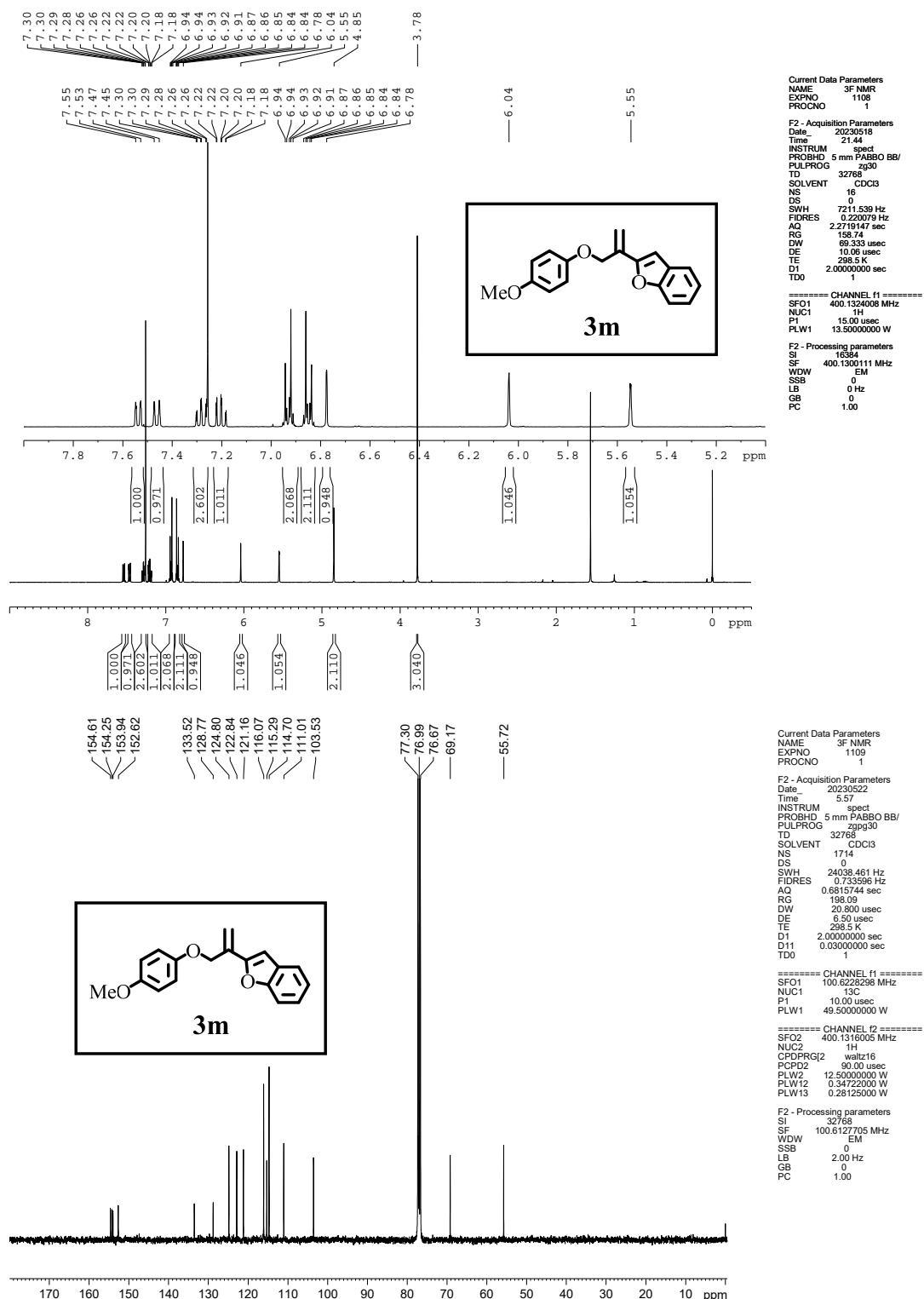
¹H and ¹³C NMR spectra of compound 3k.



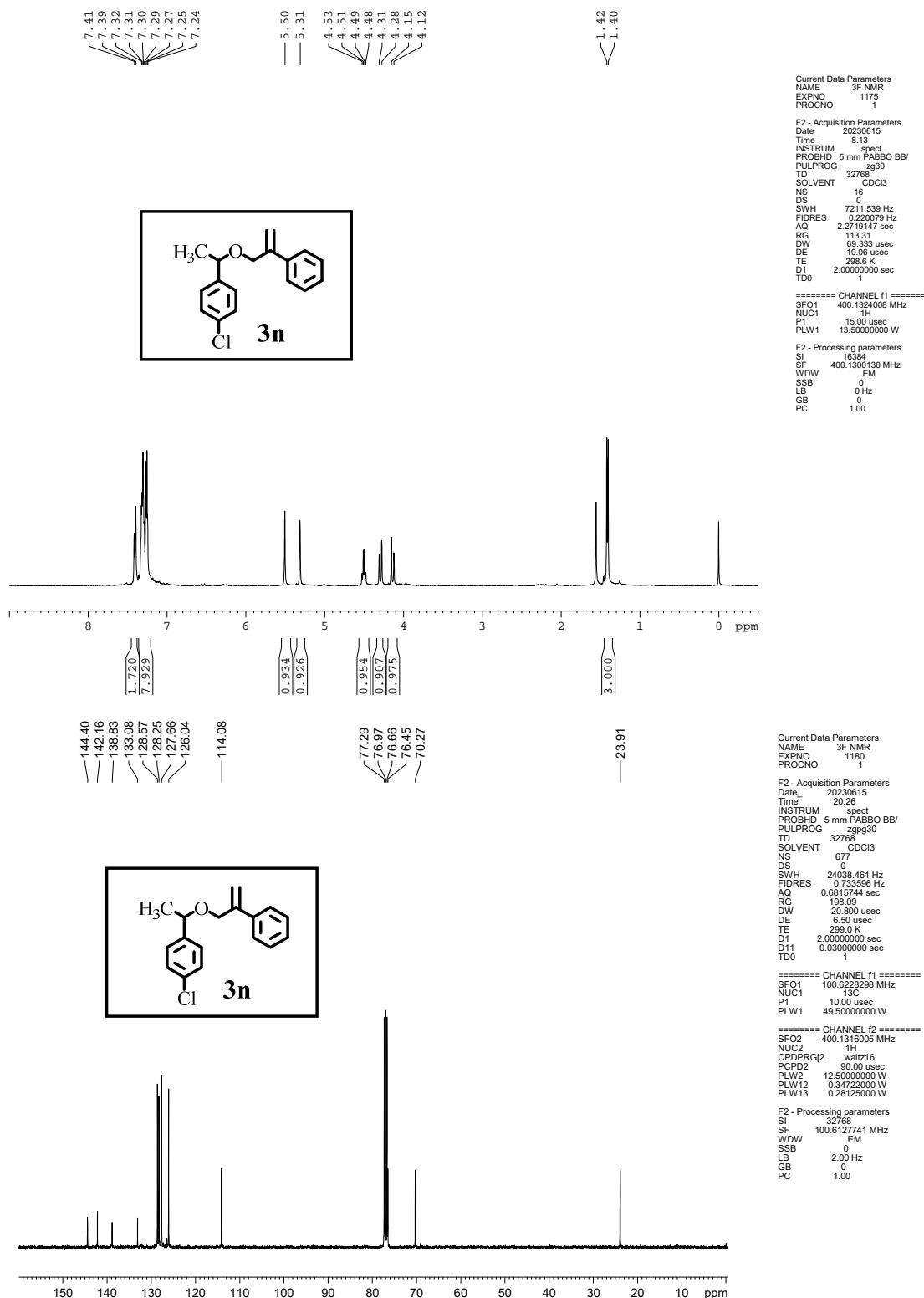
¹H and ¹³C NMR spectra of compound 3l.



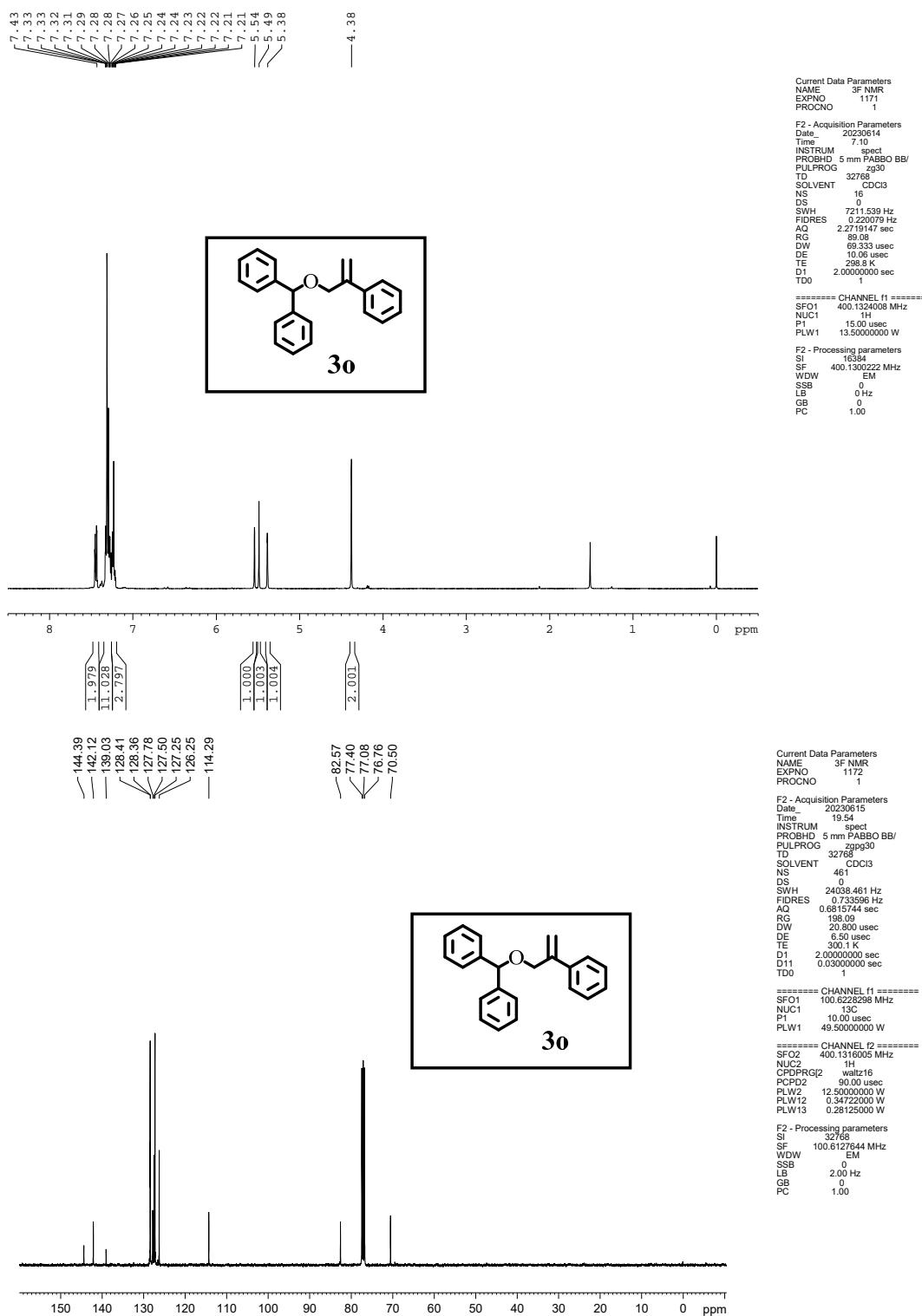
¹H and ¹³C NMR spectra of compound 3m.



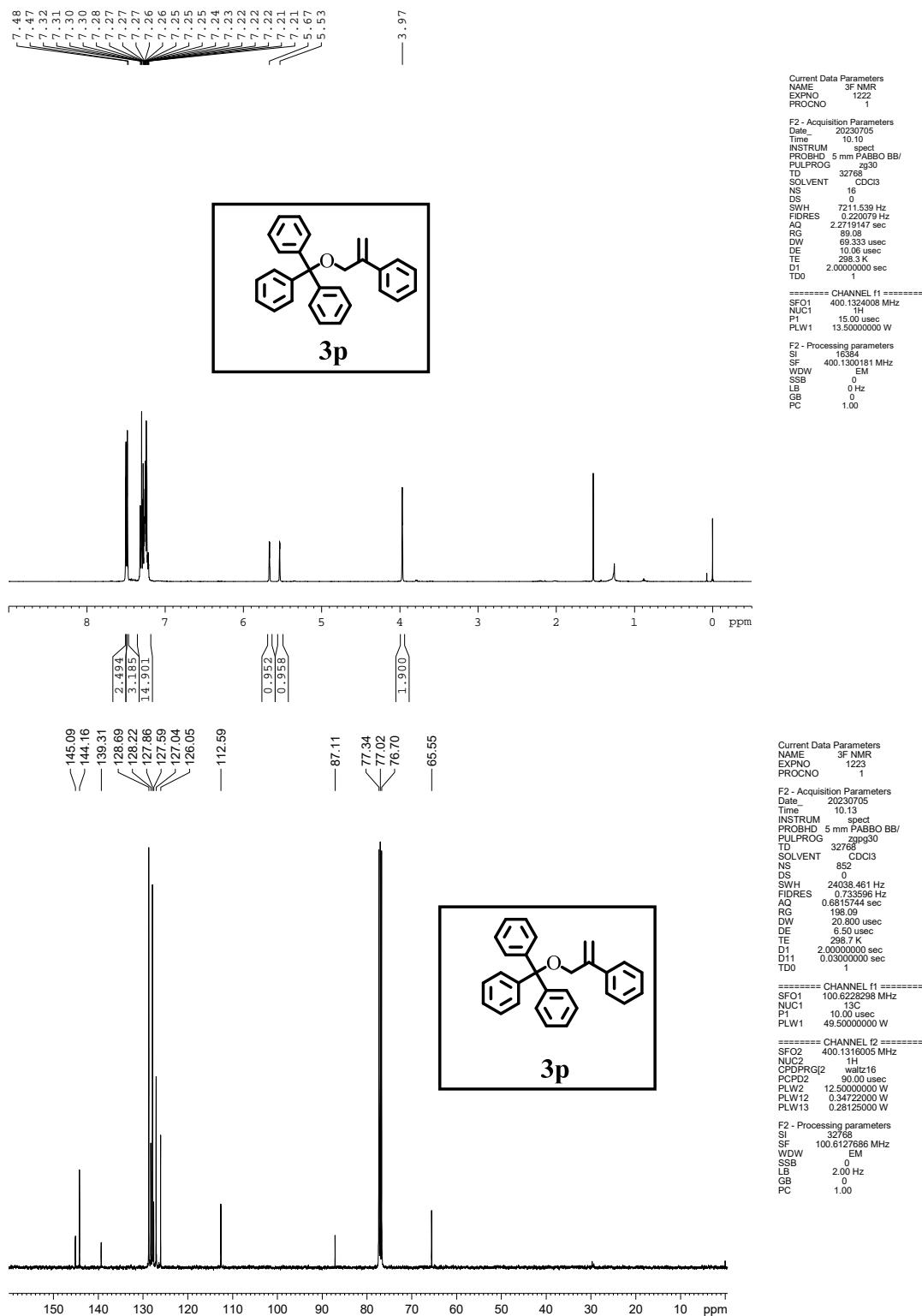
¹H and ¹³C NMR spectra of compound 3n.



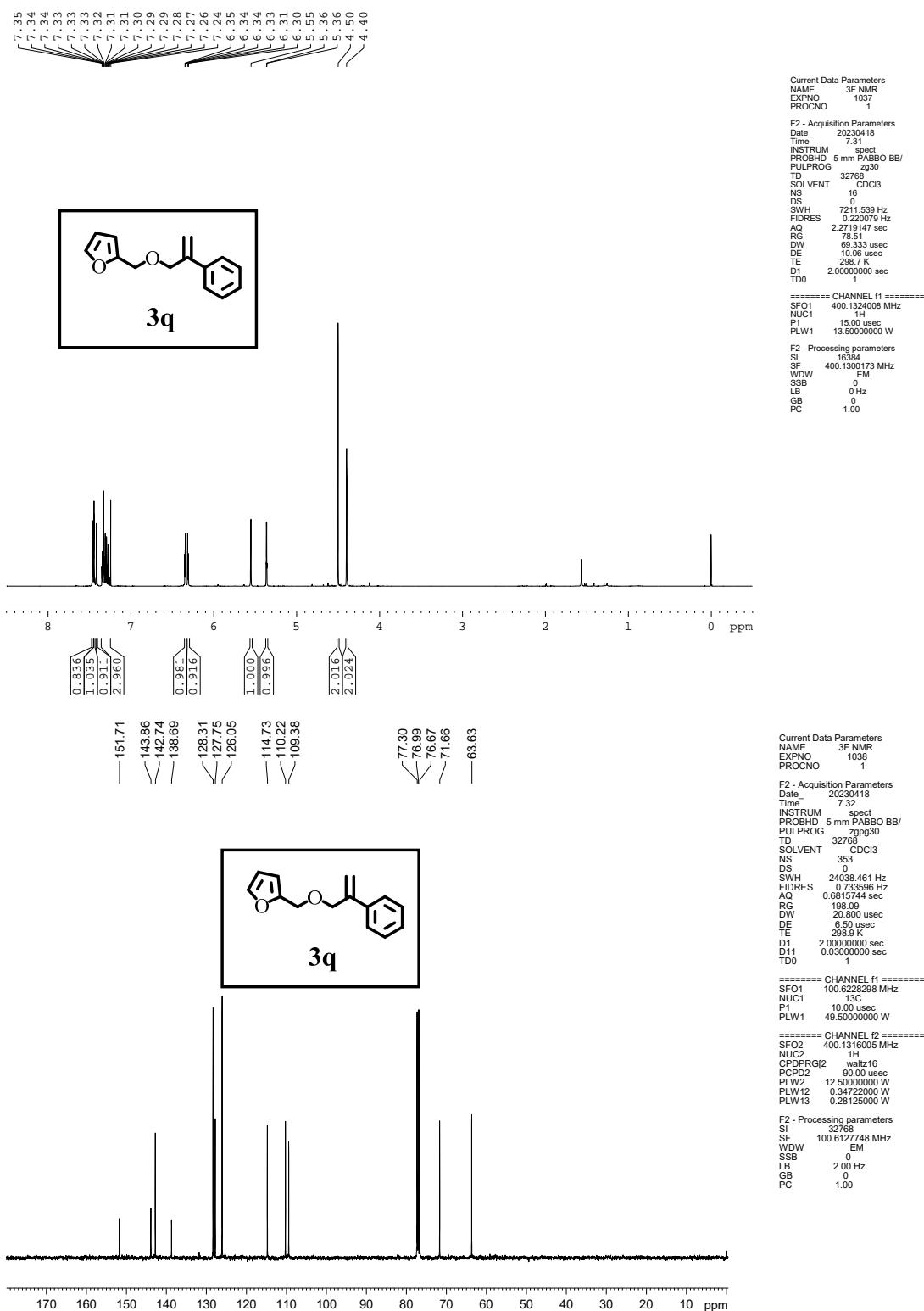
¹H and ¹³C NMR spectra of compound 3o.



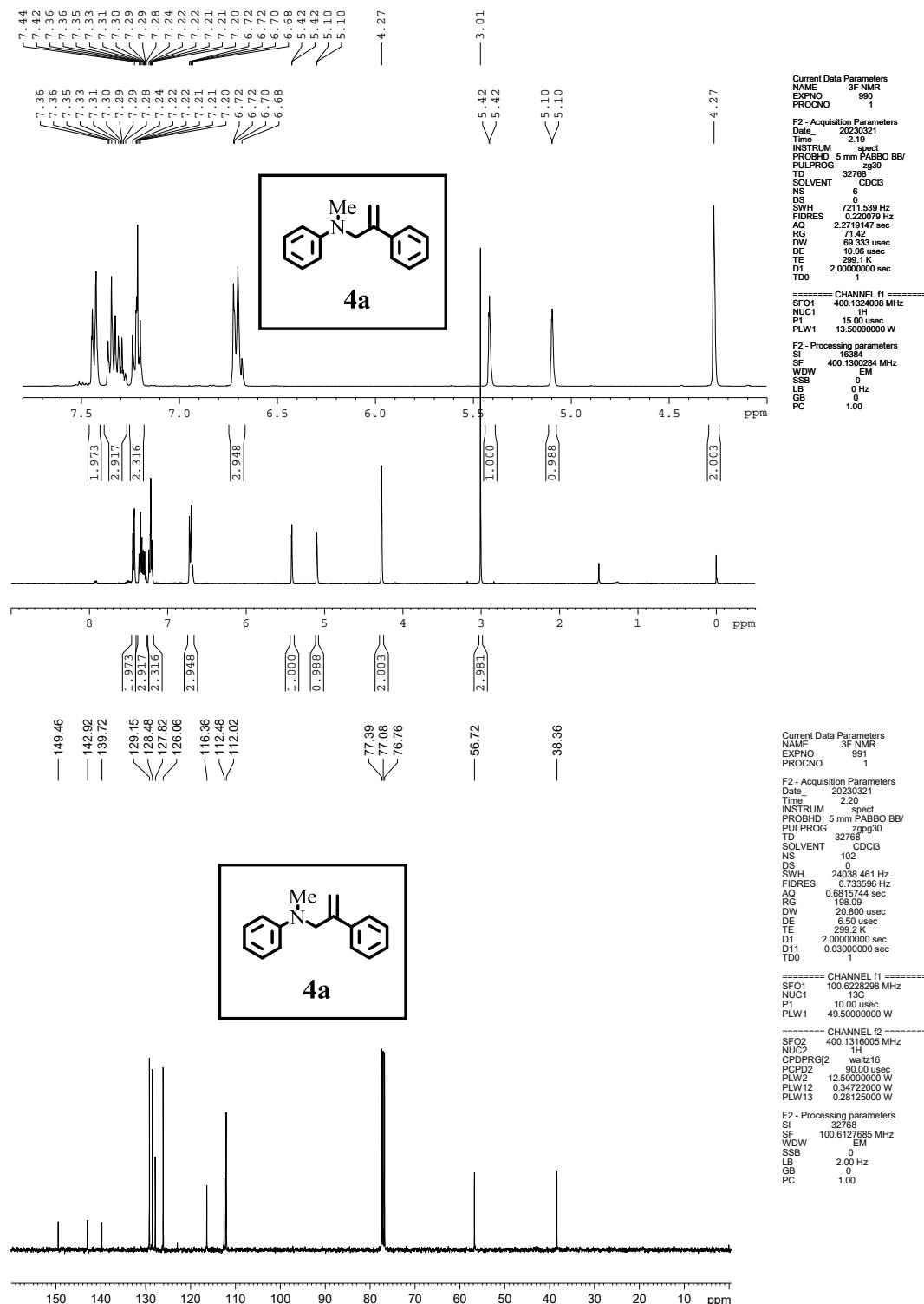
¹H and ¹³C NMR spectra of compound 3p.



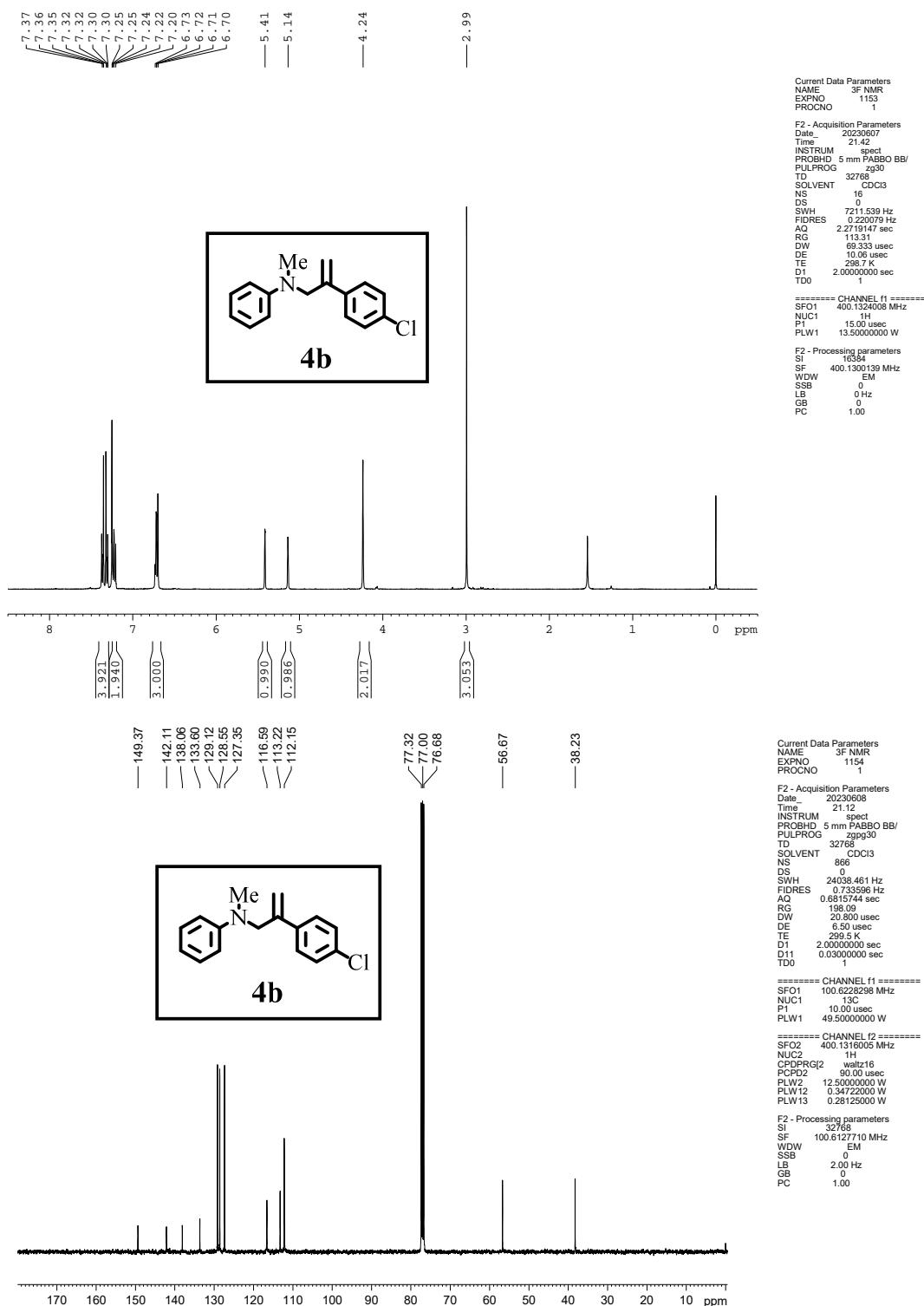
¹H and ¹³C NMR spectra of compound 3q.



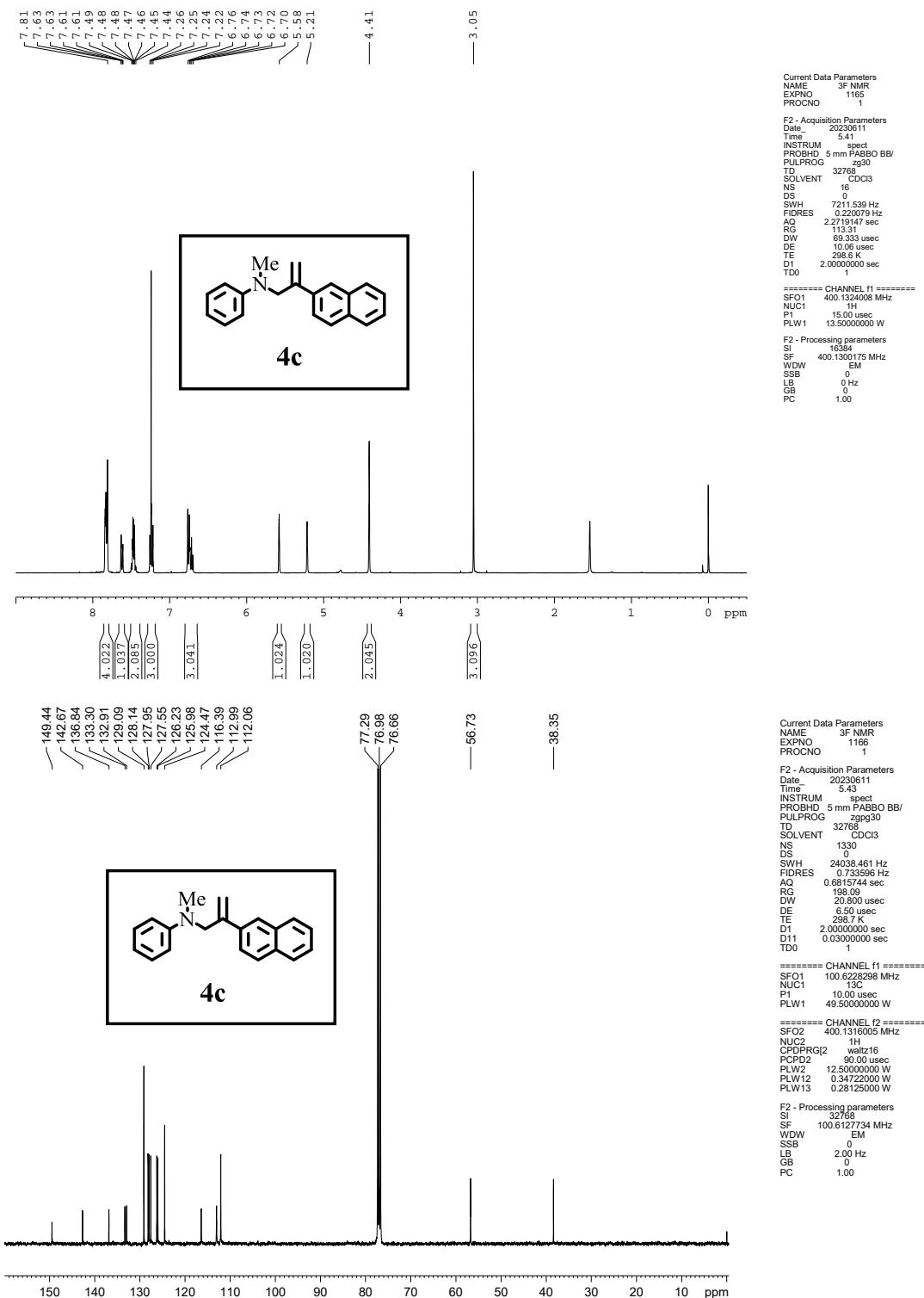
¹H and ¹³C NMR spectra of compound 4a.



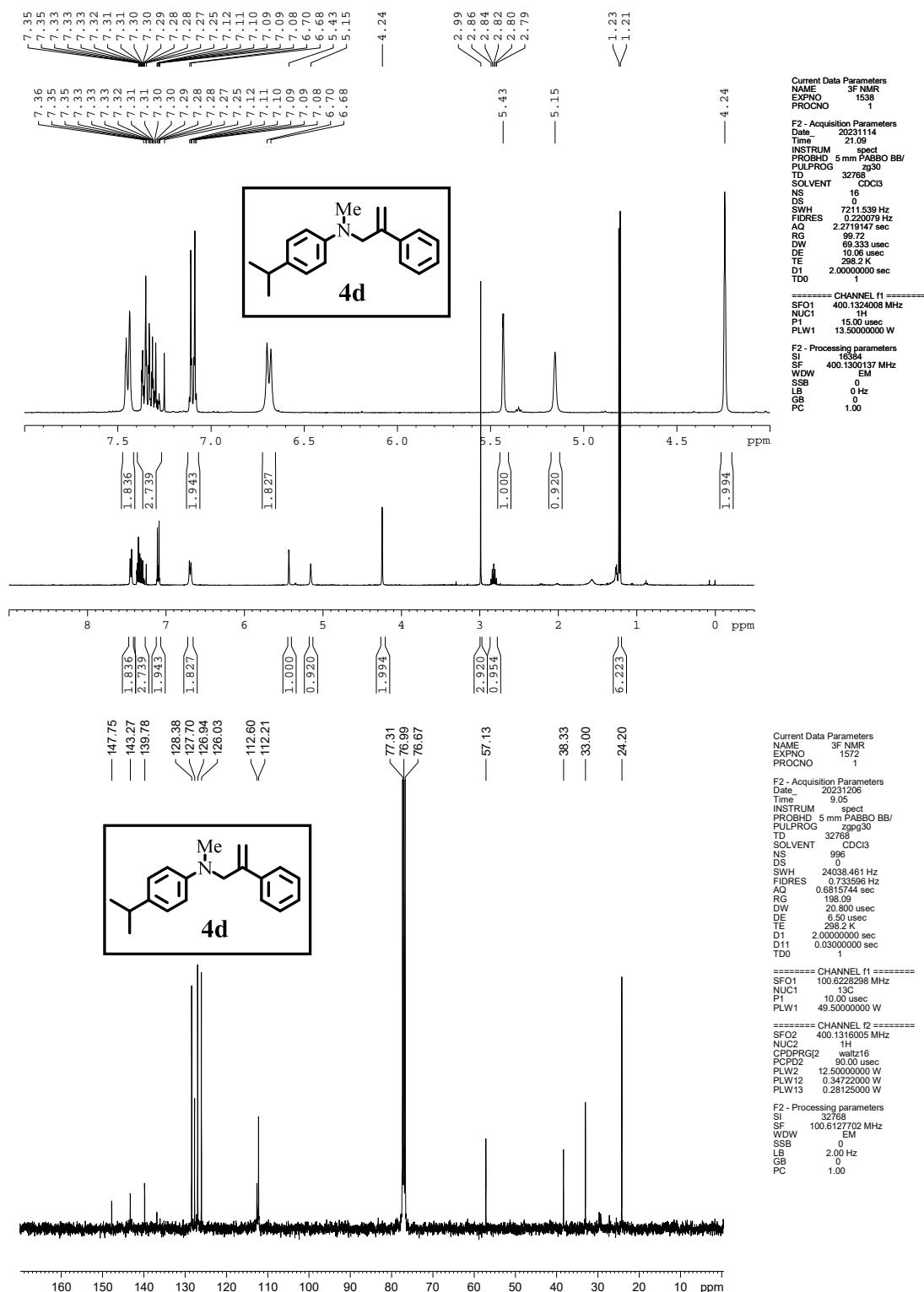
¹H and ¹³C NMR spectra of compound 4b.



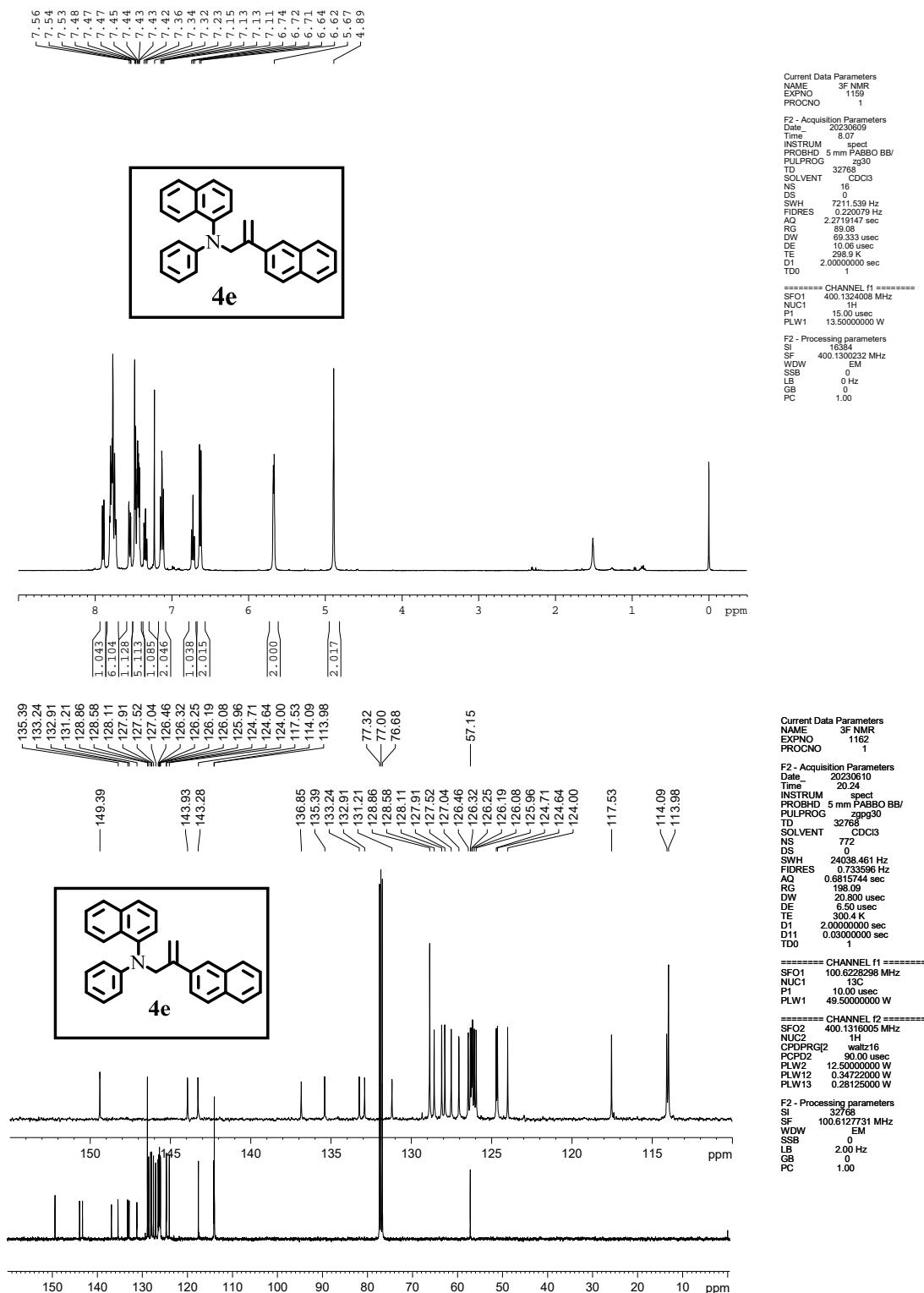
¹H and ¹³C NMR spectra of compound 4c.



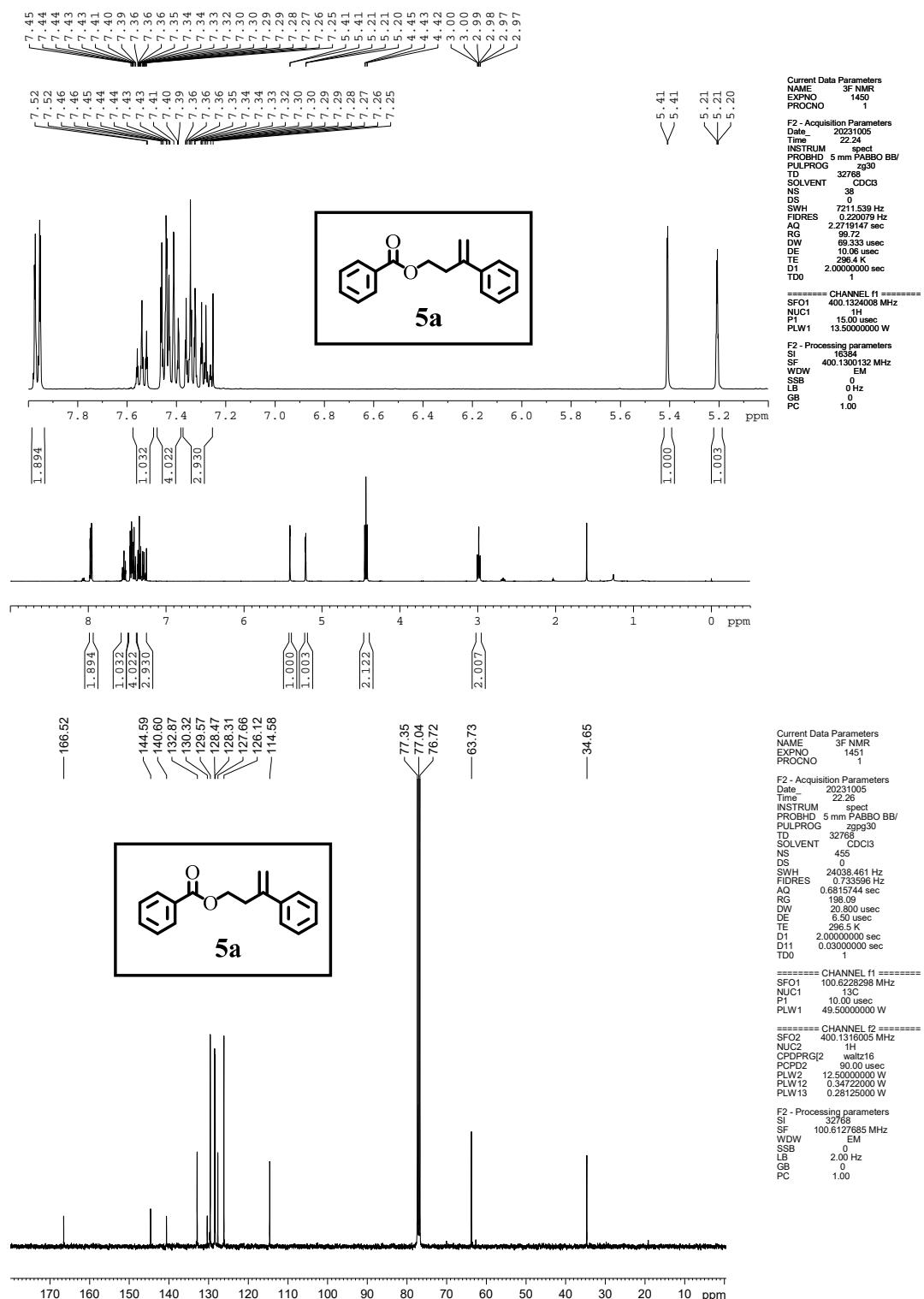
¹H and ¹³C NMR spectra of compound 4d.



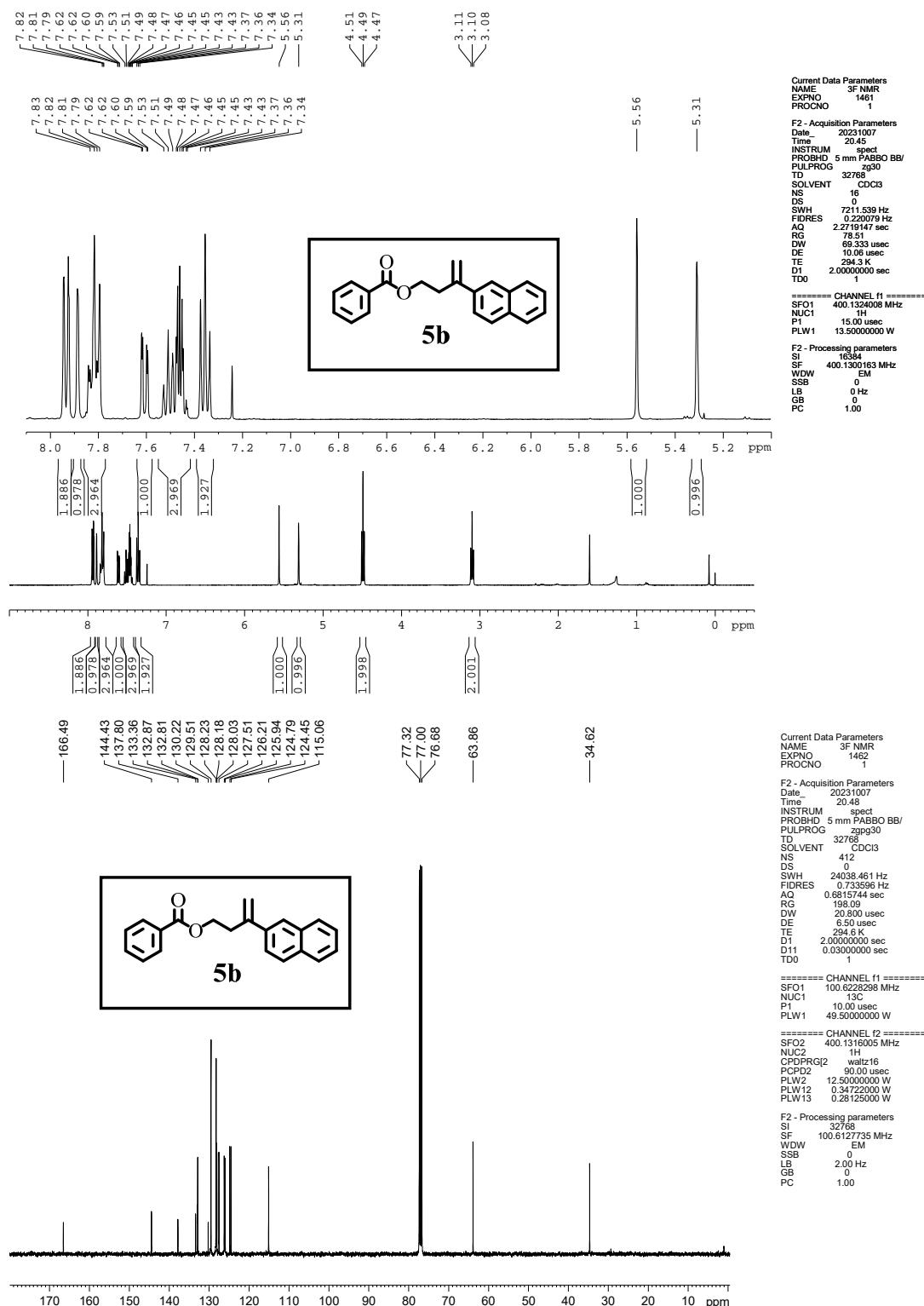
¹H and ¹³C NMR spectra of compound 4e.



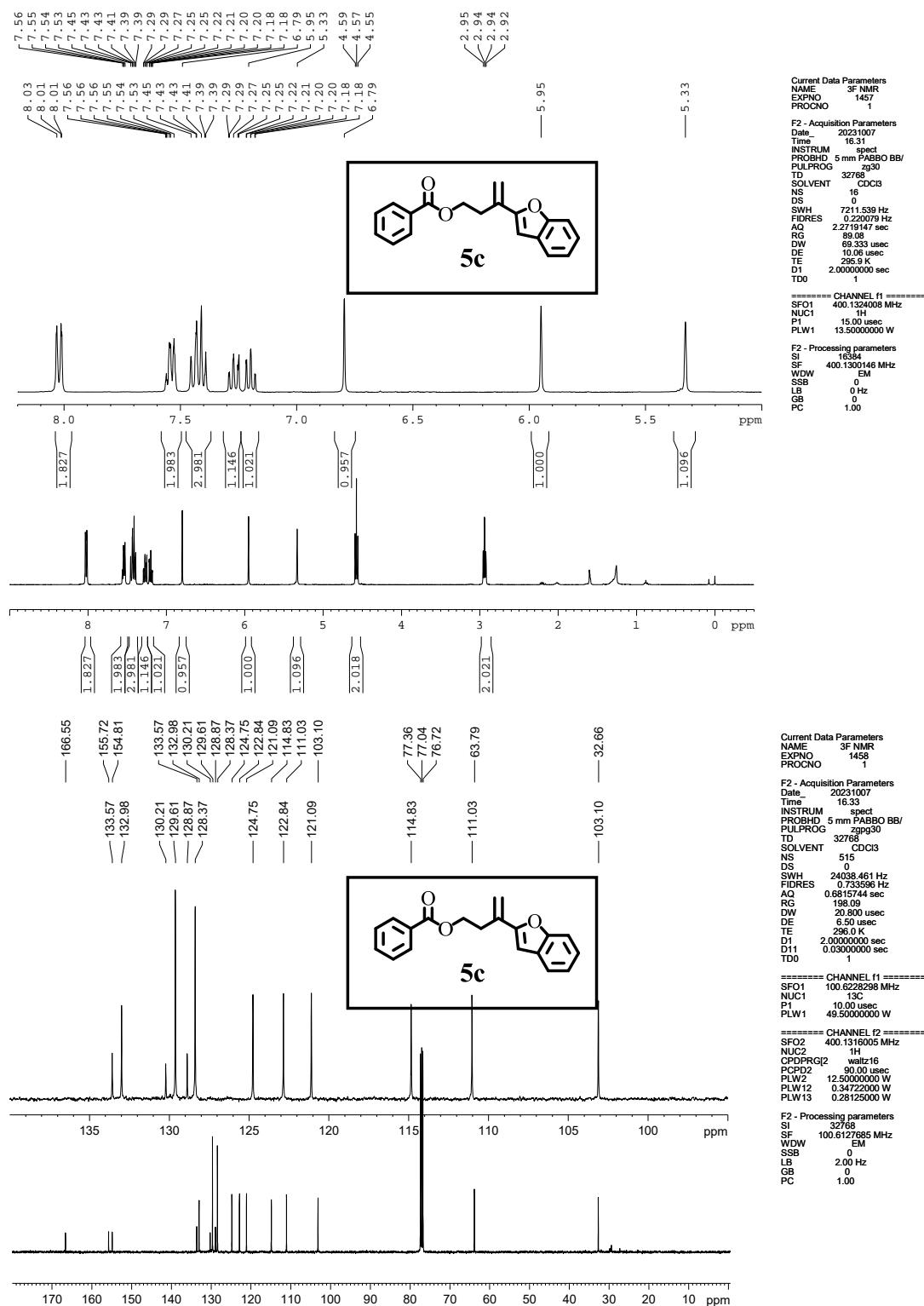
¹H and ¹³C NMR spectra of compound 5a.



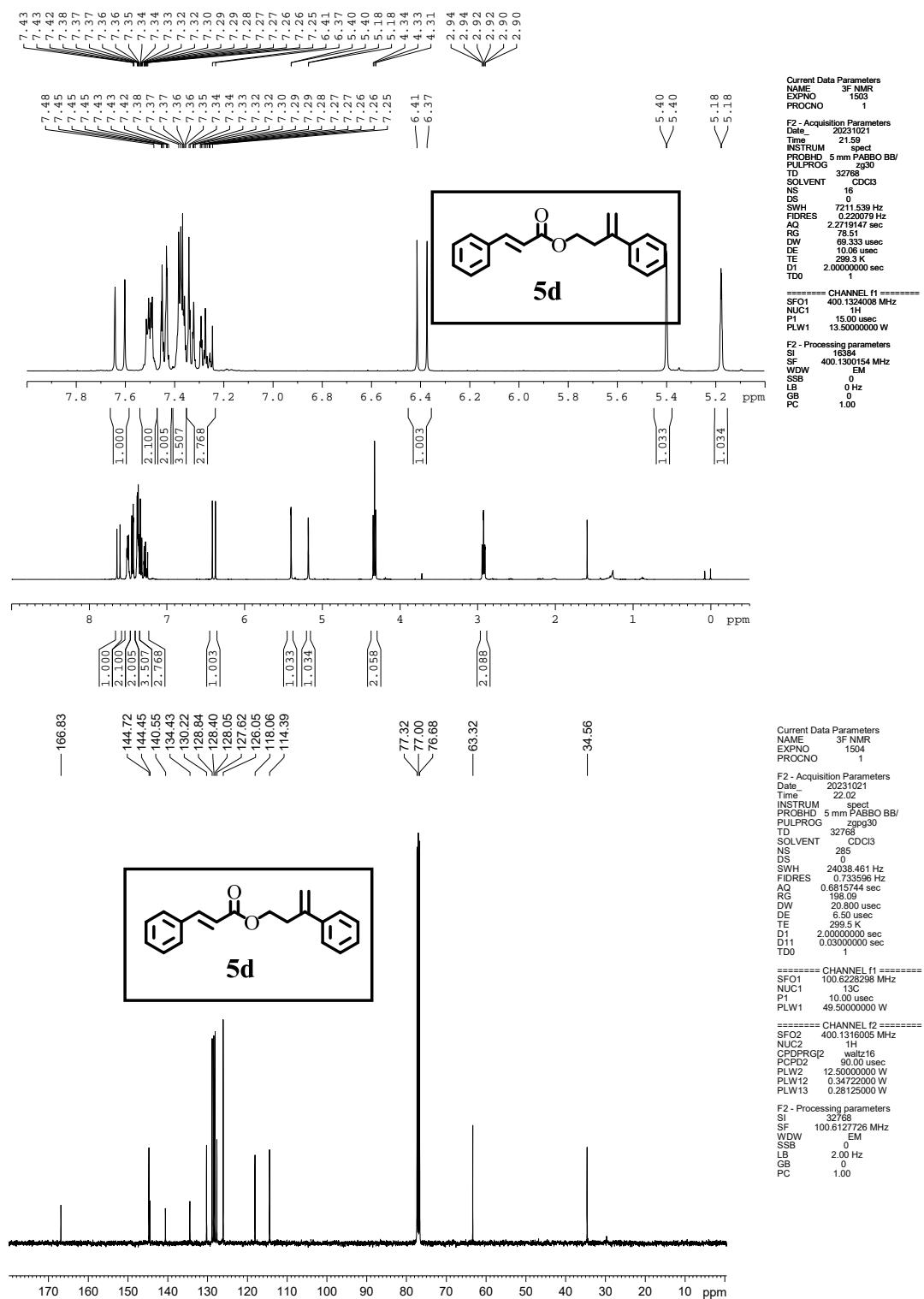
¹H and ¹³C NMR spectra of compound 5b.



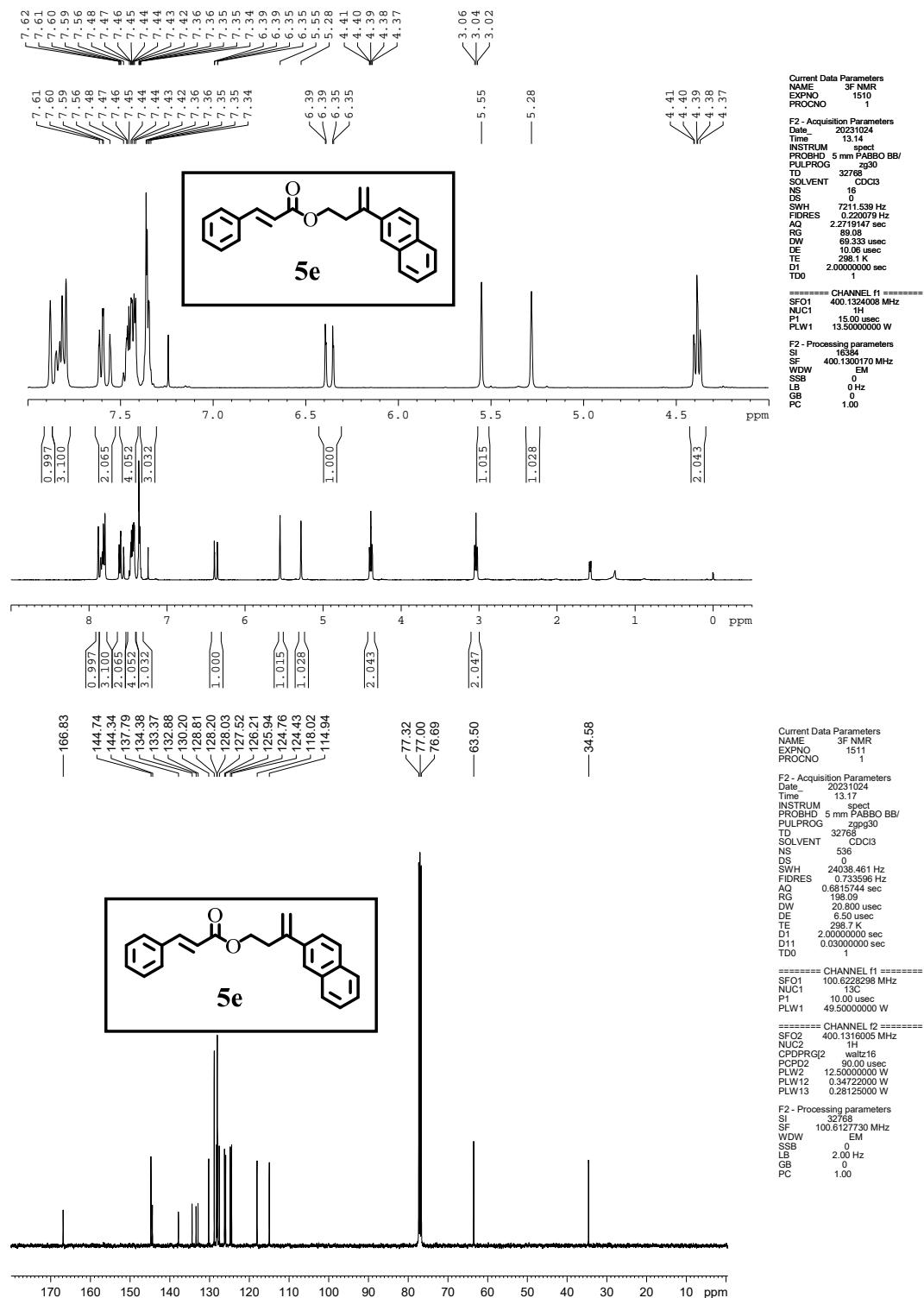
¹H and ¹³C NMR spectra of compound 5c.



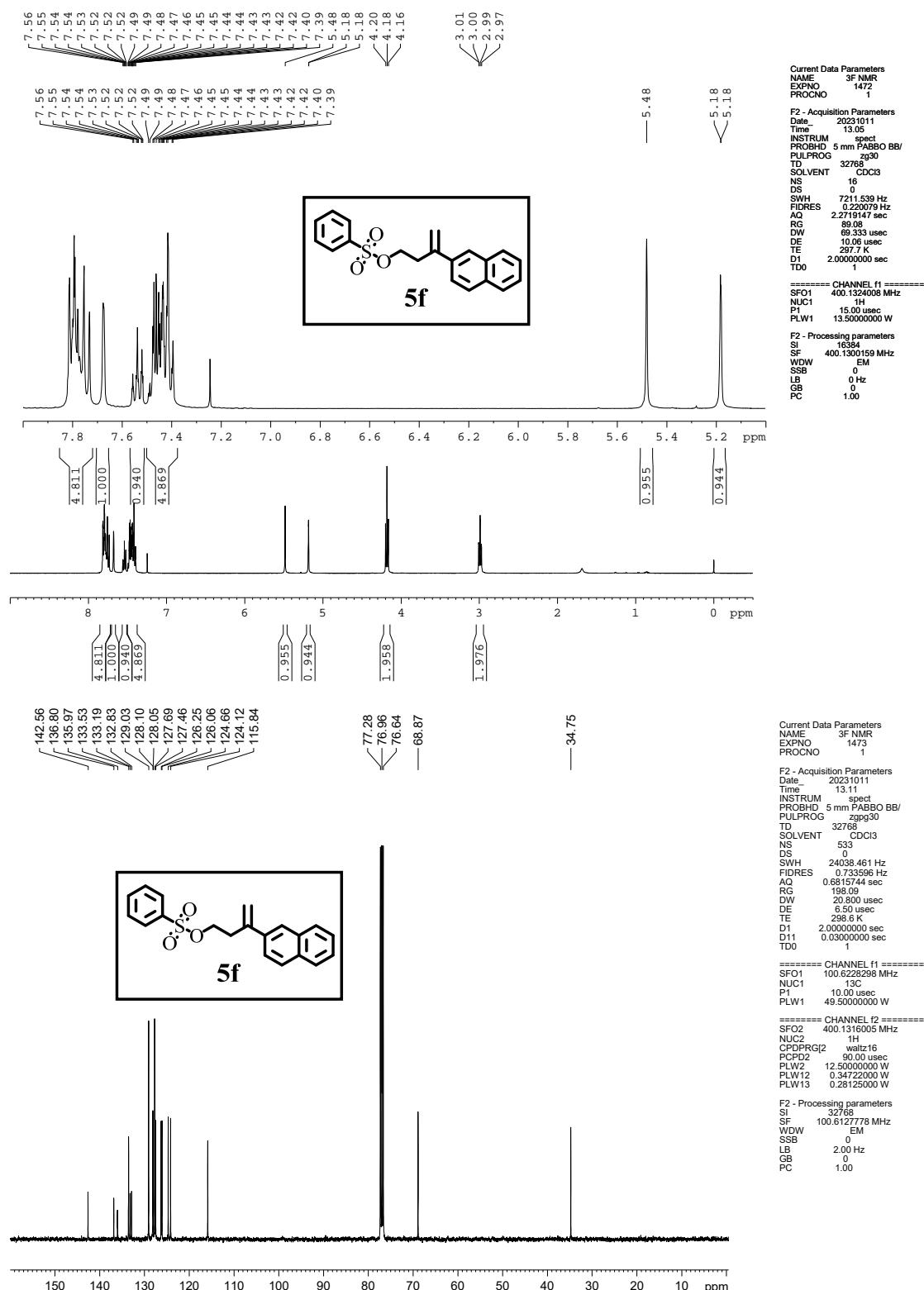
¹H and ¹³C NMR spectra of compound 5d.



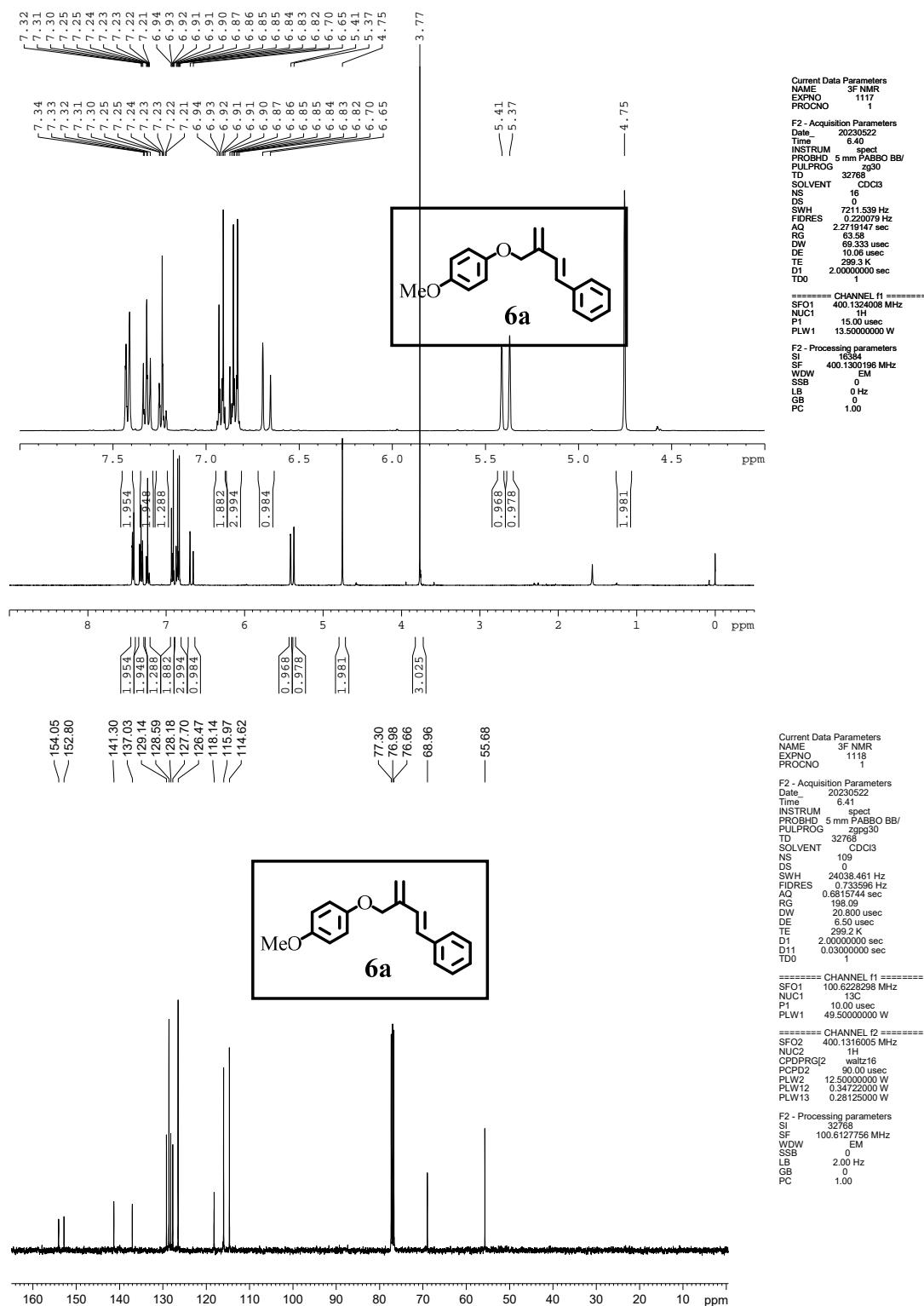
¹H and ¹³C NMR spectra of compound 5e.



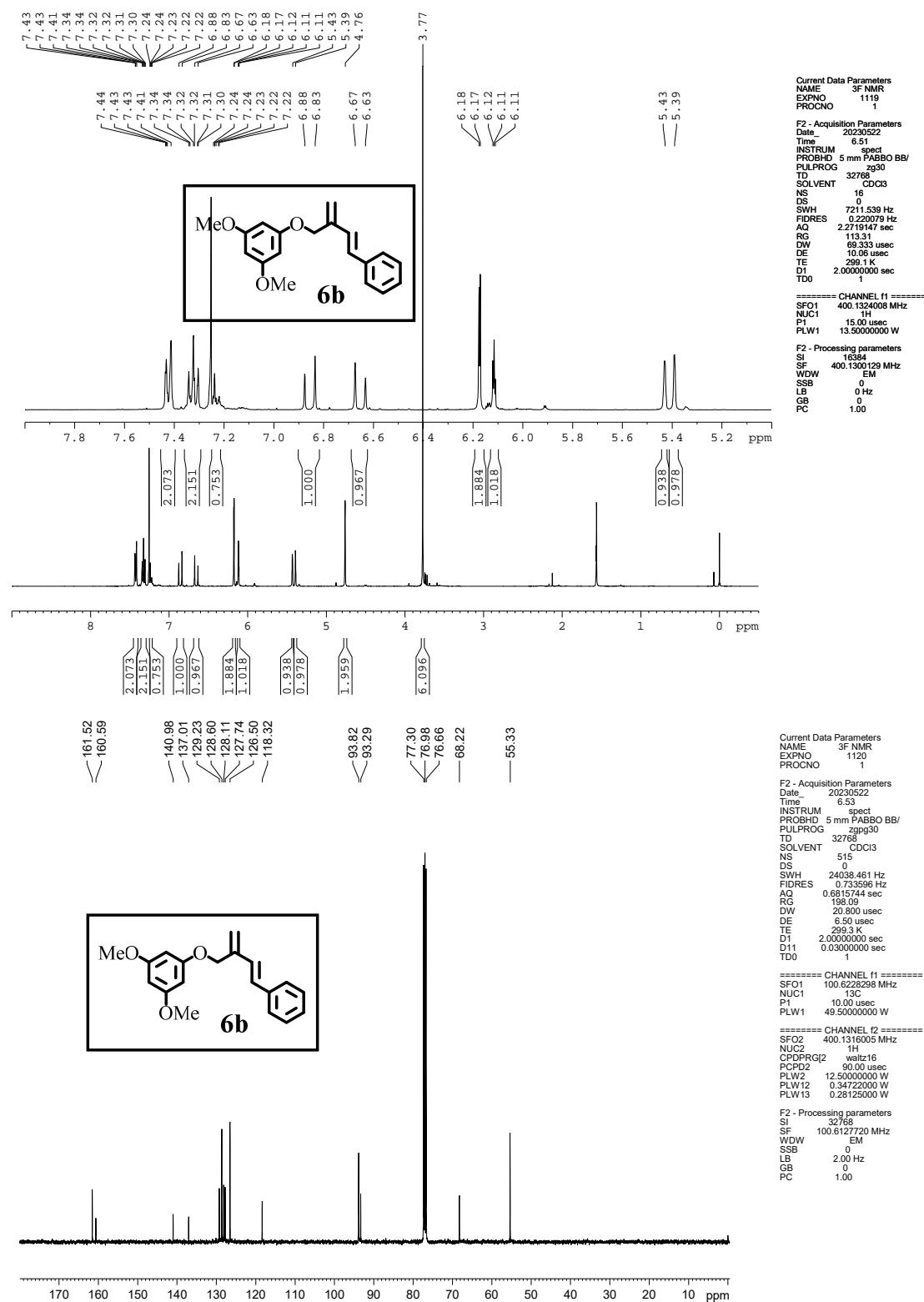
¹H and ¹³C NMR spectra of compound 5f.



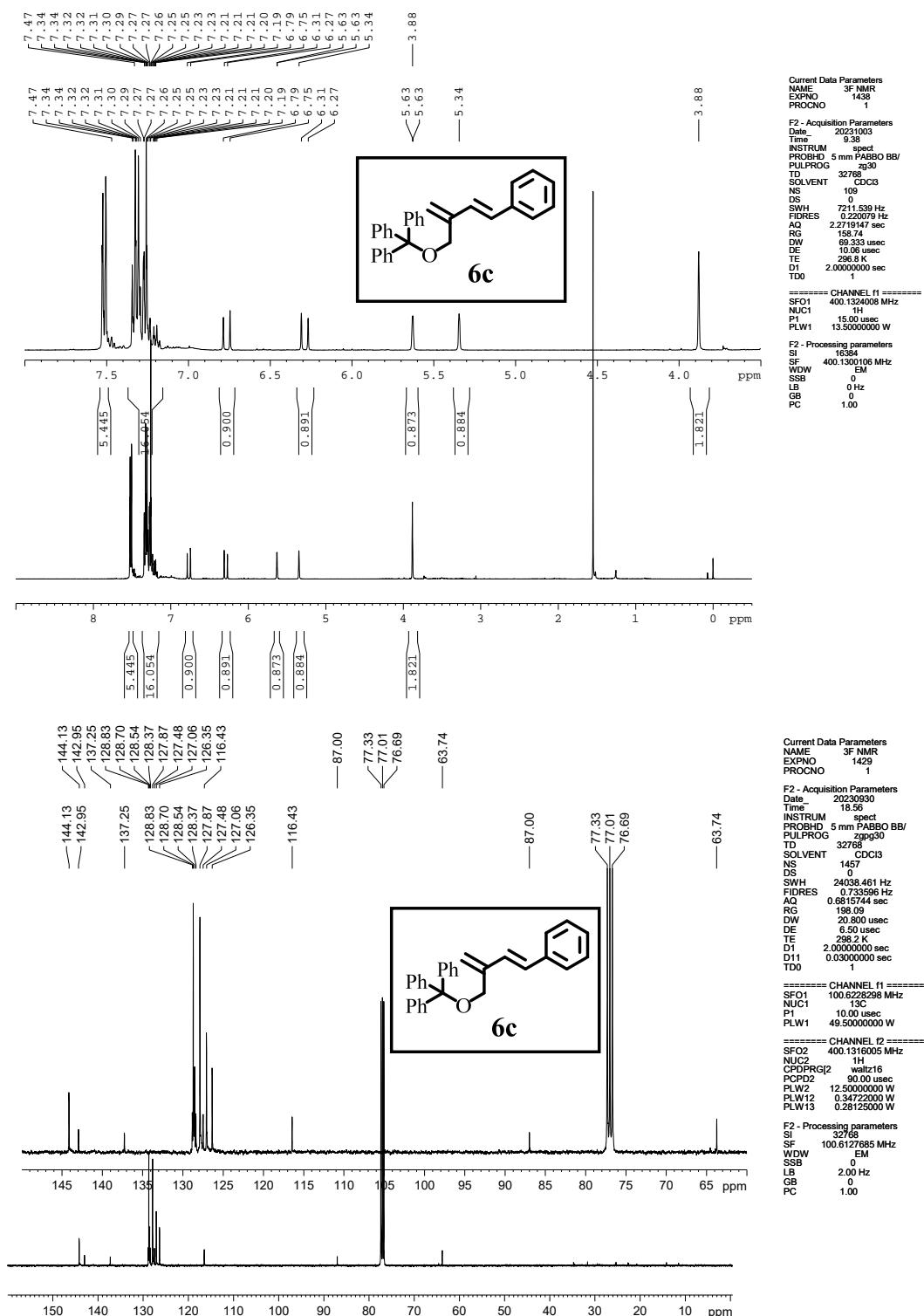
¹H and ¹³C NMR spectra of compound 6a.



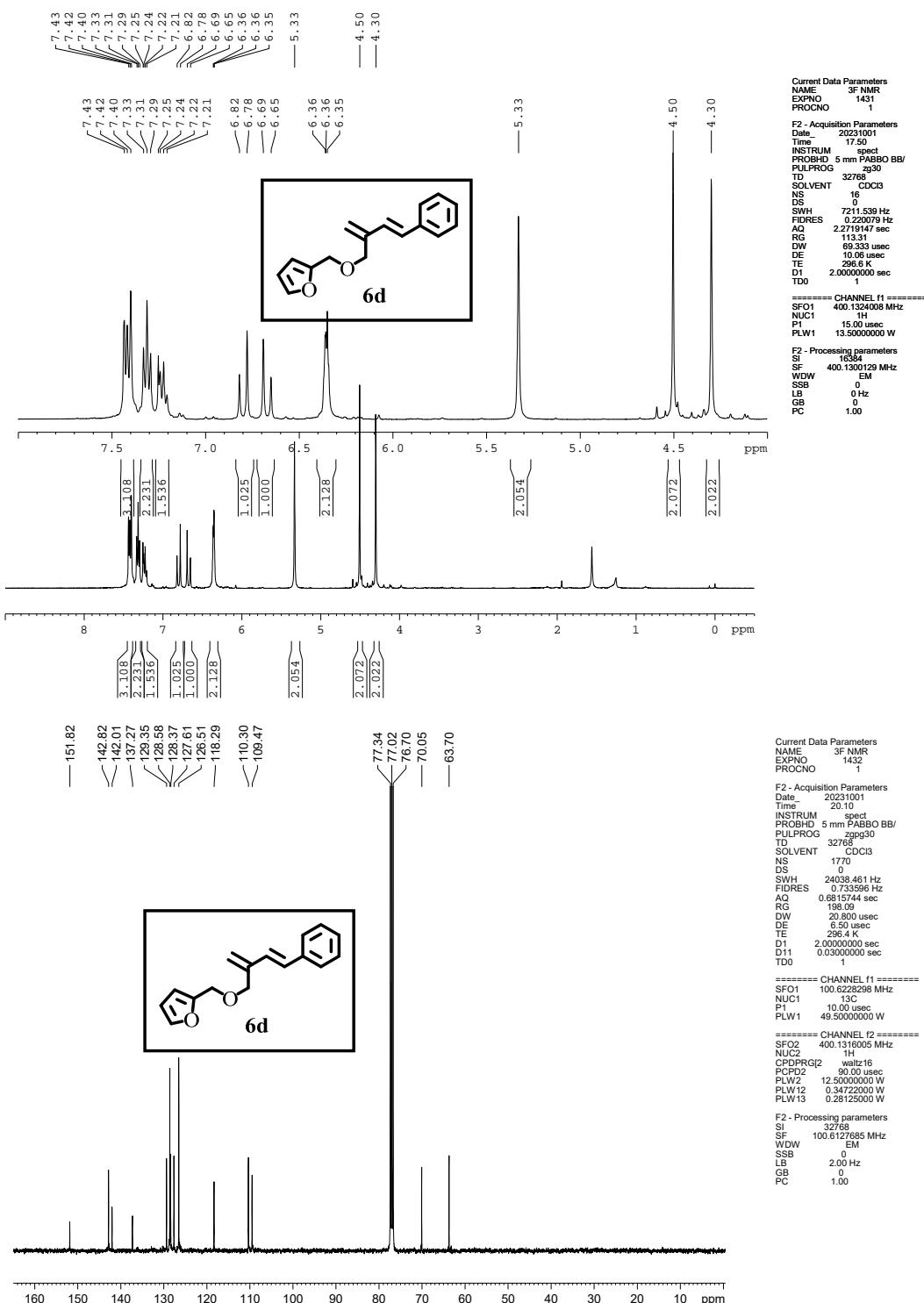
¹H and ¹³C NMR spectra of compound 6b.



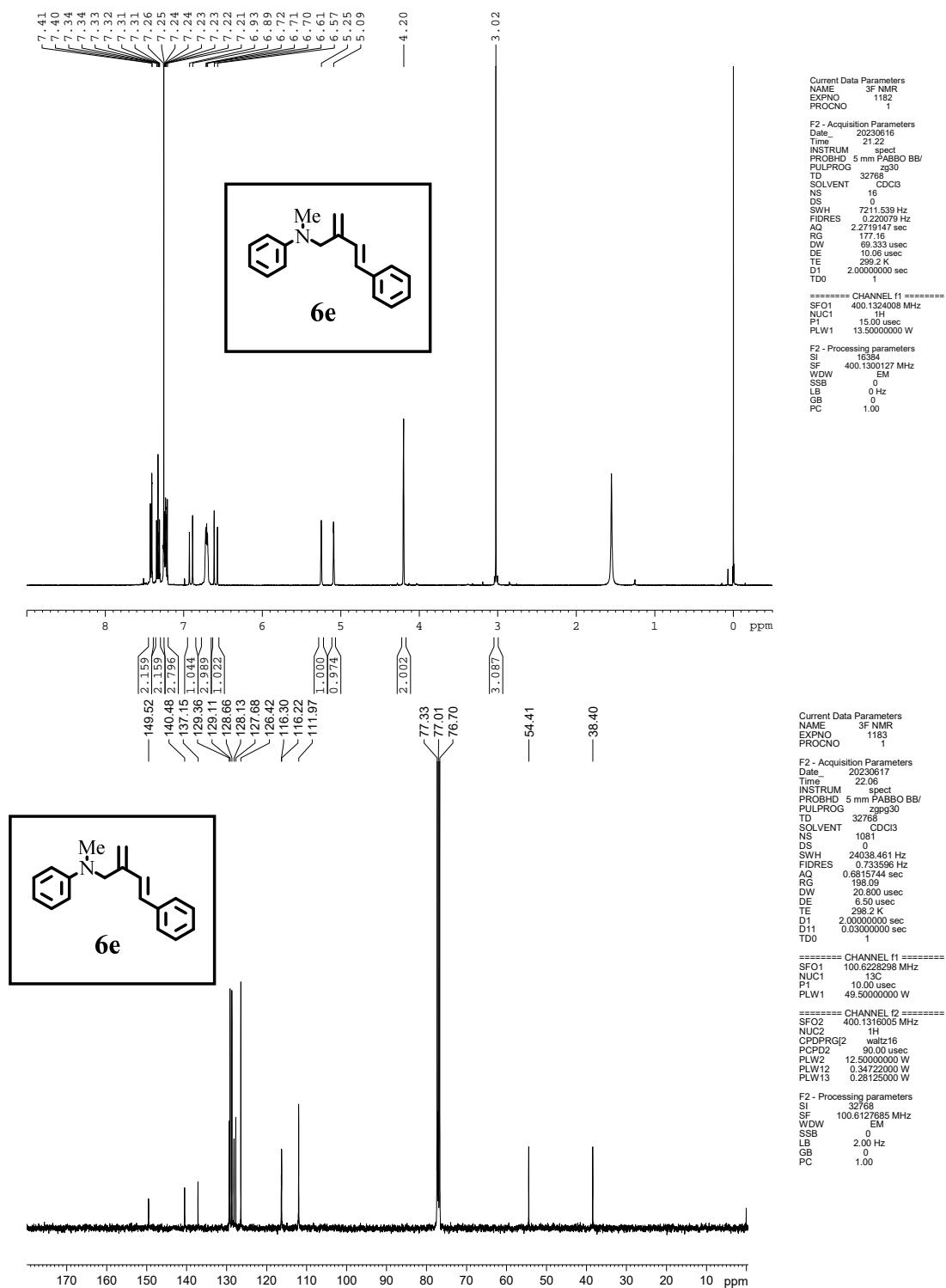
¹H and ¹³C NMR spectra of compound 6c.



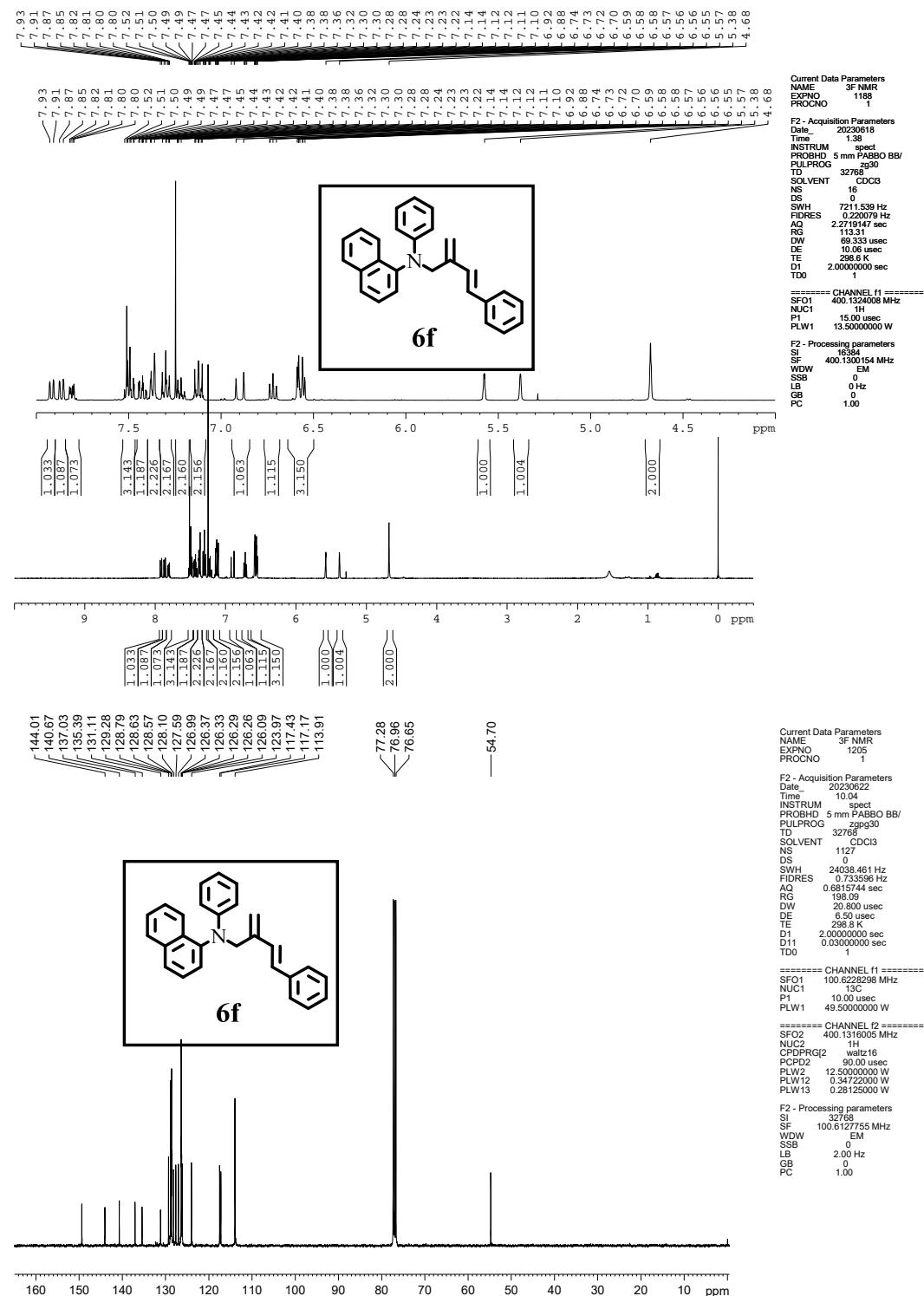
¹H and ¹³C NMR spectra of compound 6d.



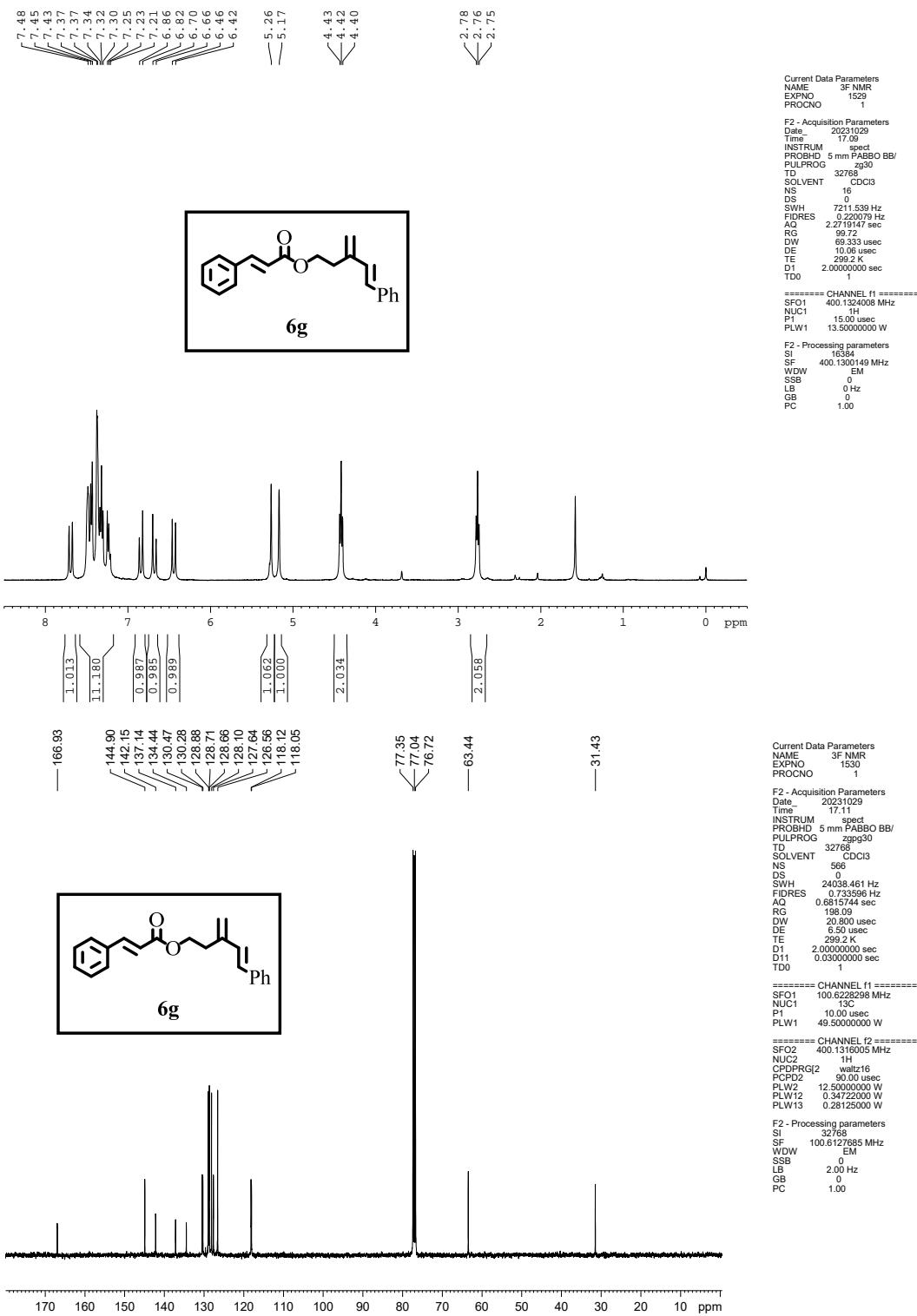
¹H and ¹³C NMR spectra of compound 6e.



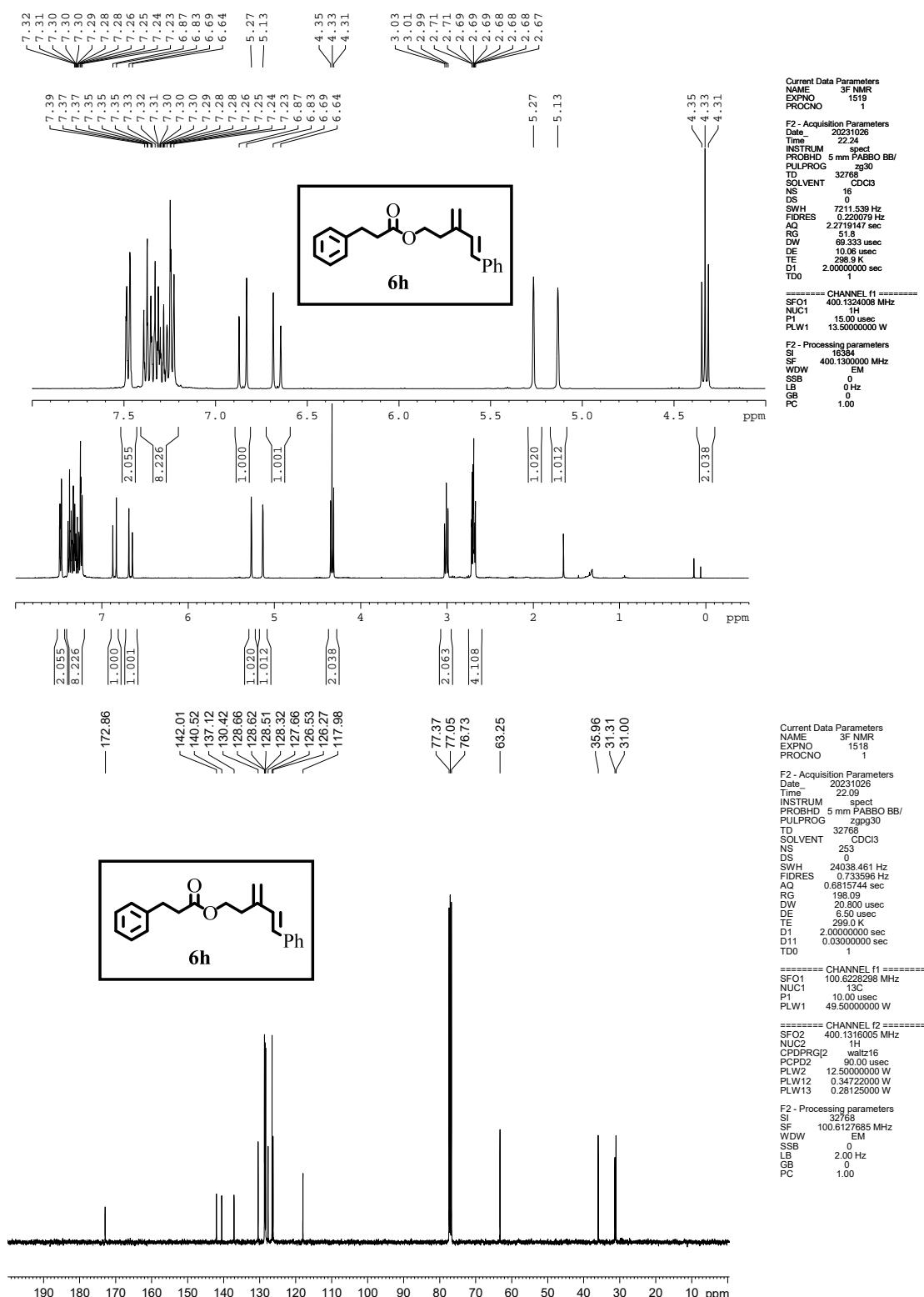
¹H and ¹³C NMR spectra of compound 6f.



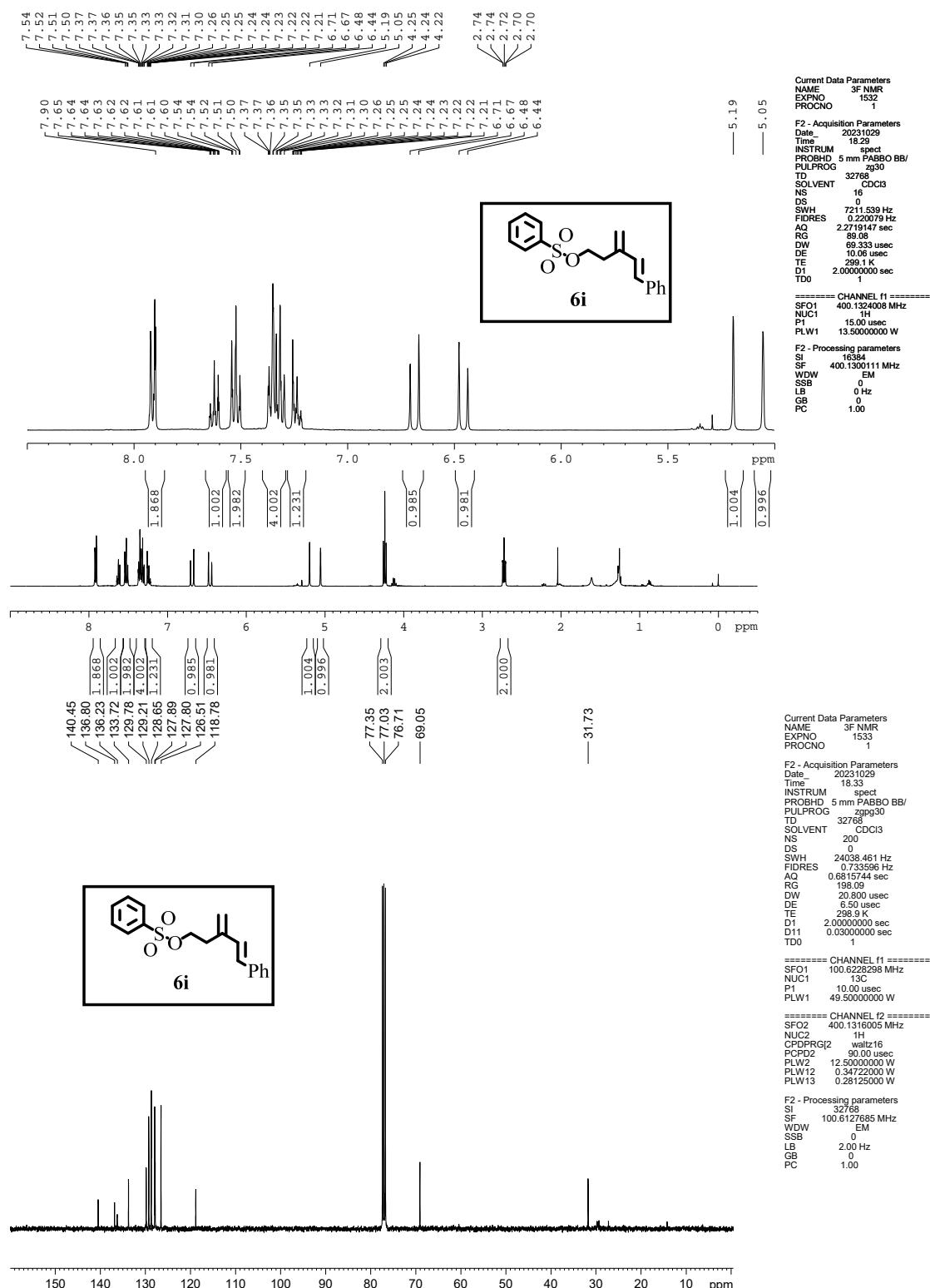
¹H and ¹³C NMR spectra of compound 6g.



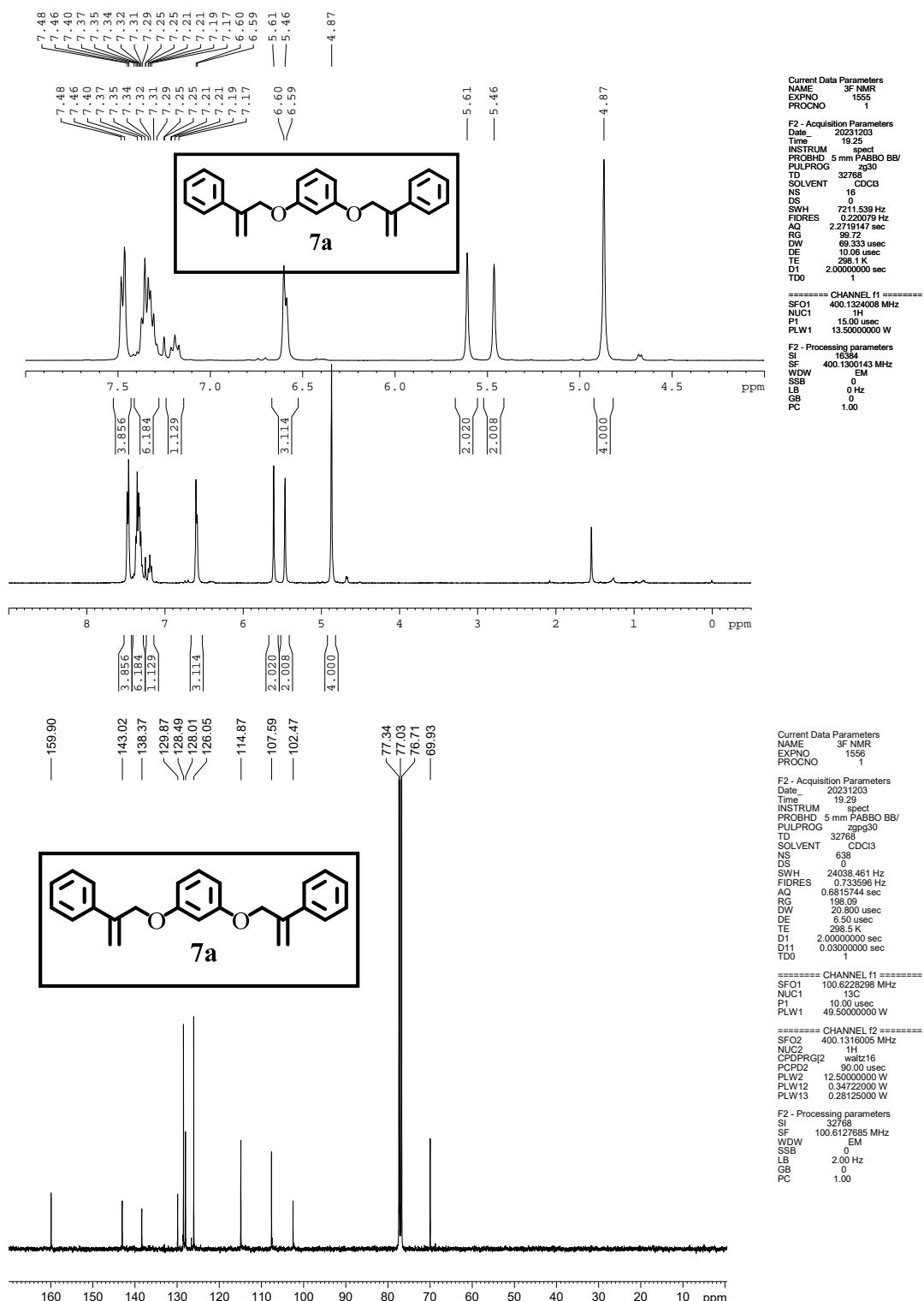
¹H and ¹³C NMR spectra of compound 6h.



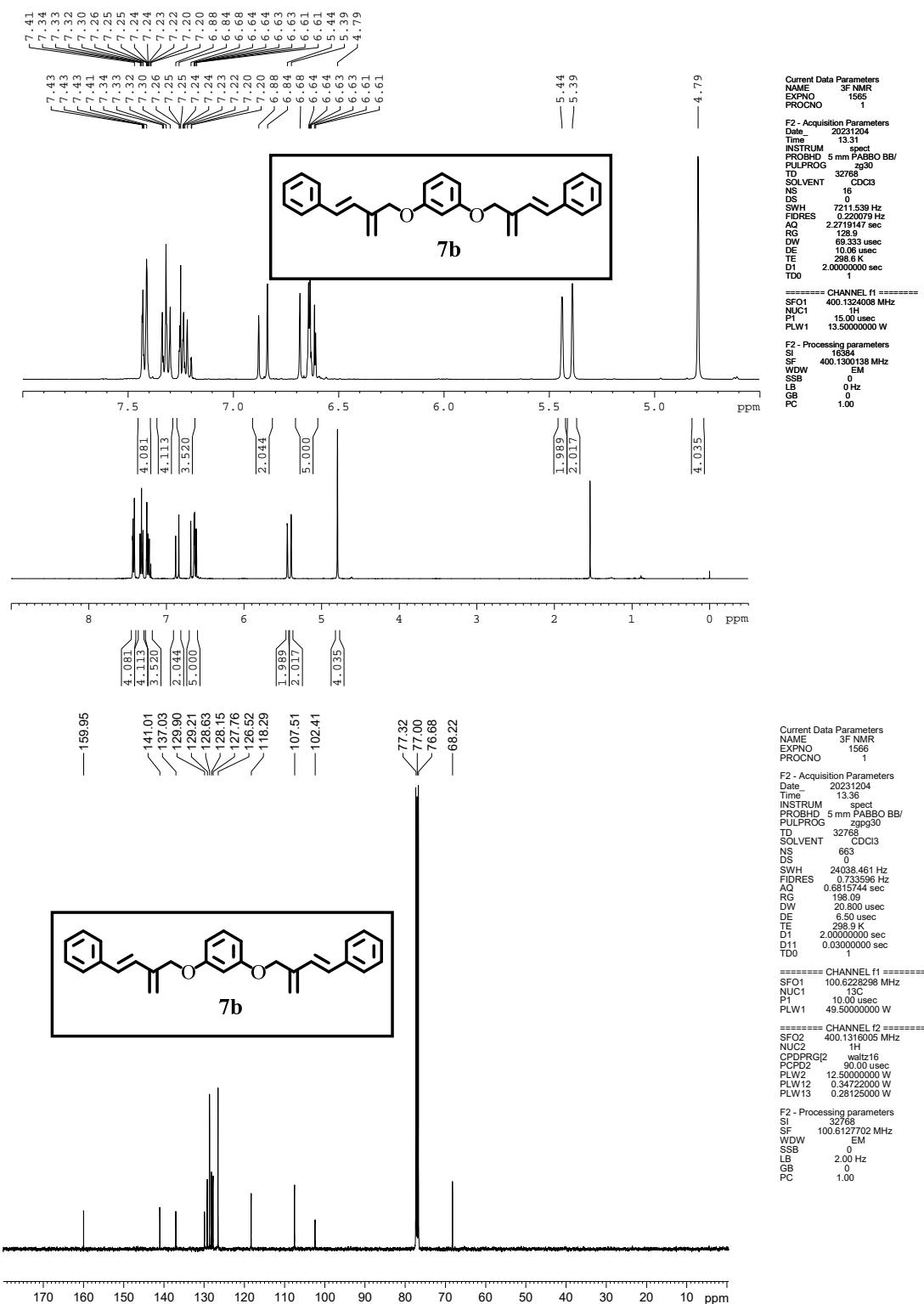
¹H and ¹³C NMR spectra of compound 6i.



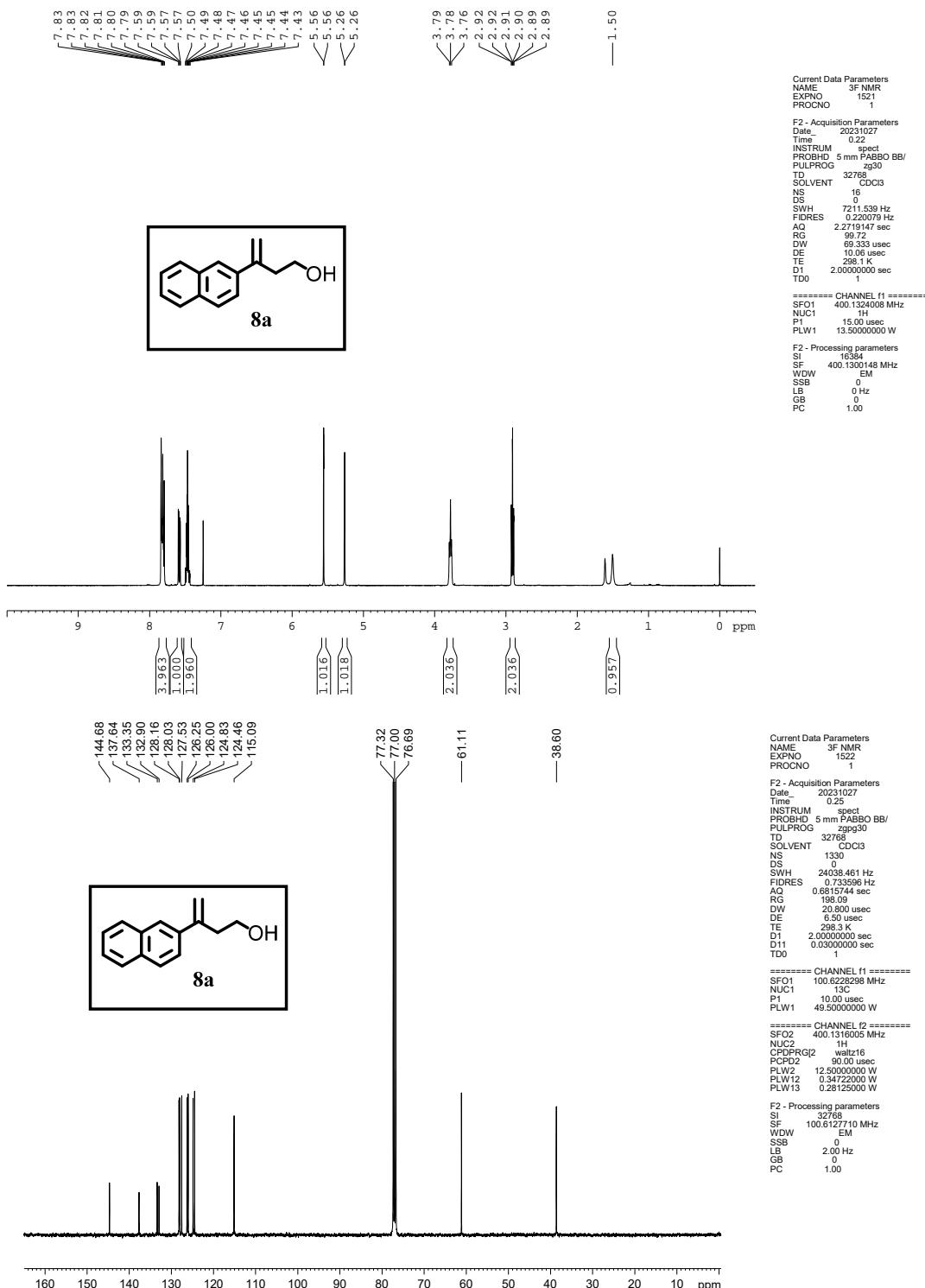
¹H and ¹³C NMR spectra of compound 7a.



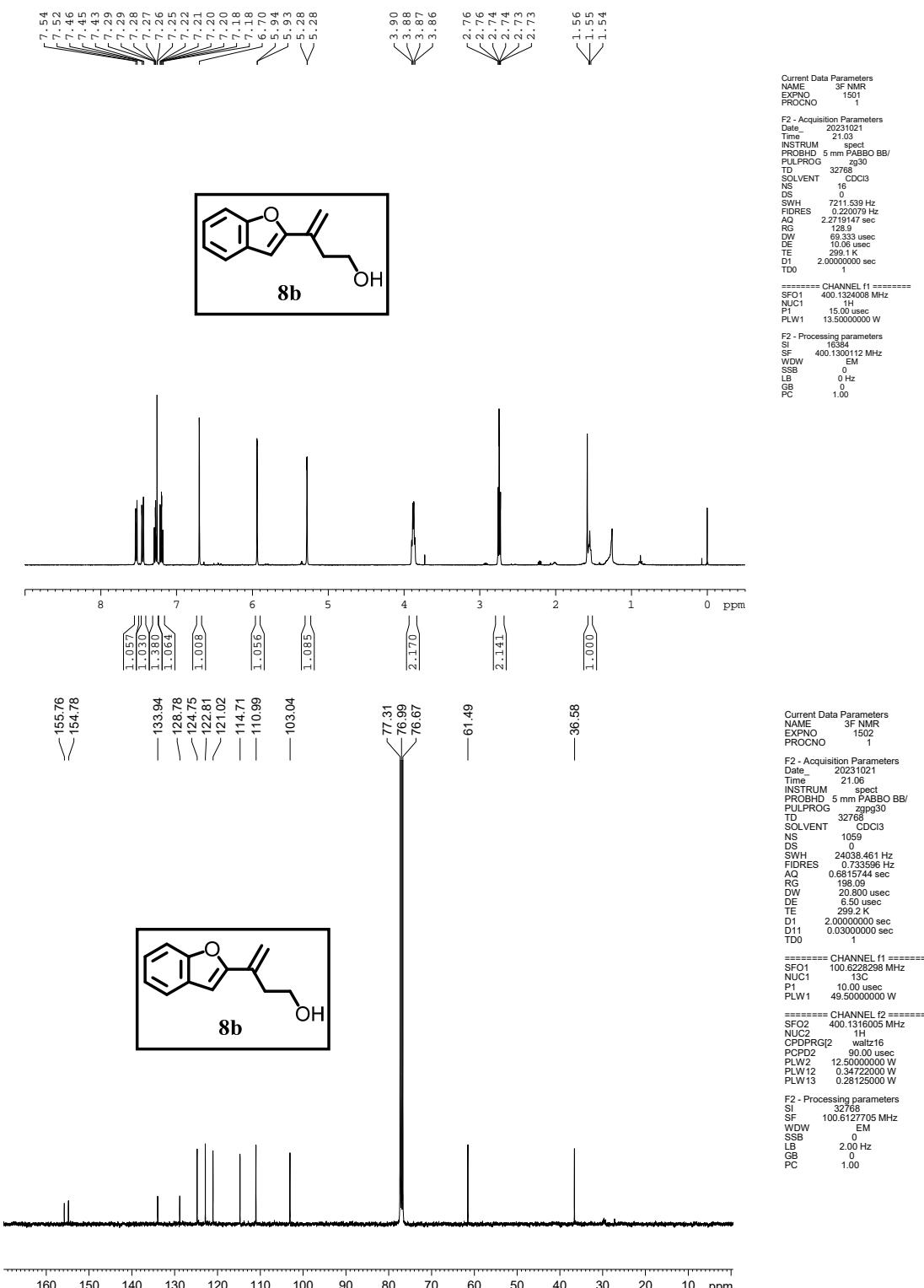
¹H and ¹³C NMR spectra of compound 7b.



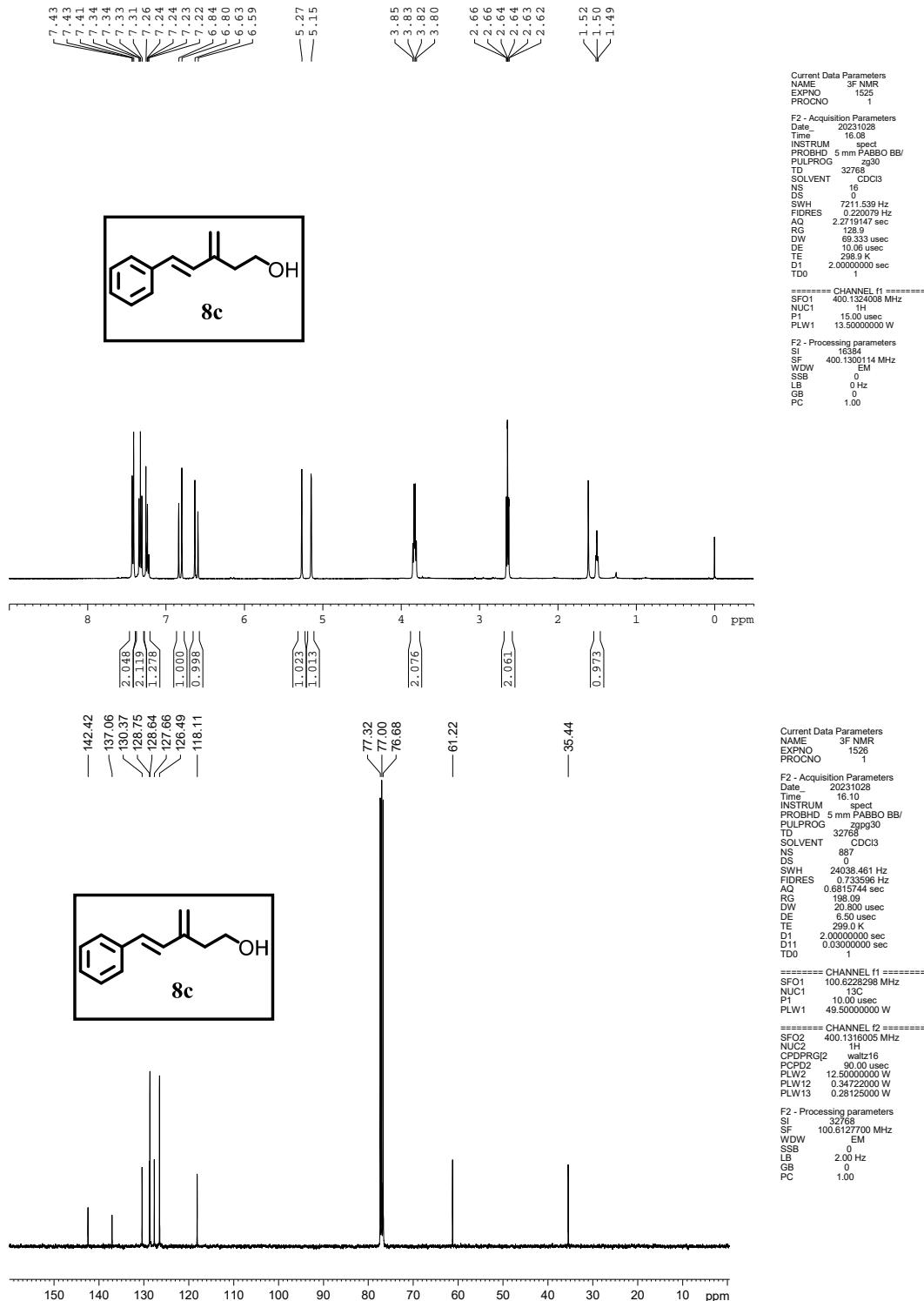
¹H and ¹³C NMR spectra of compound 8a.



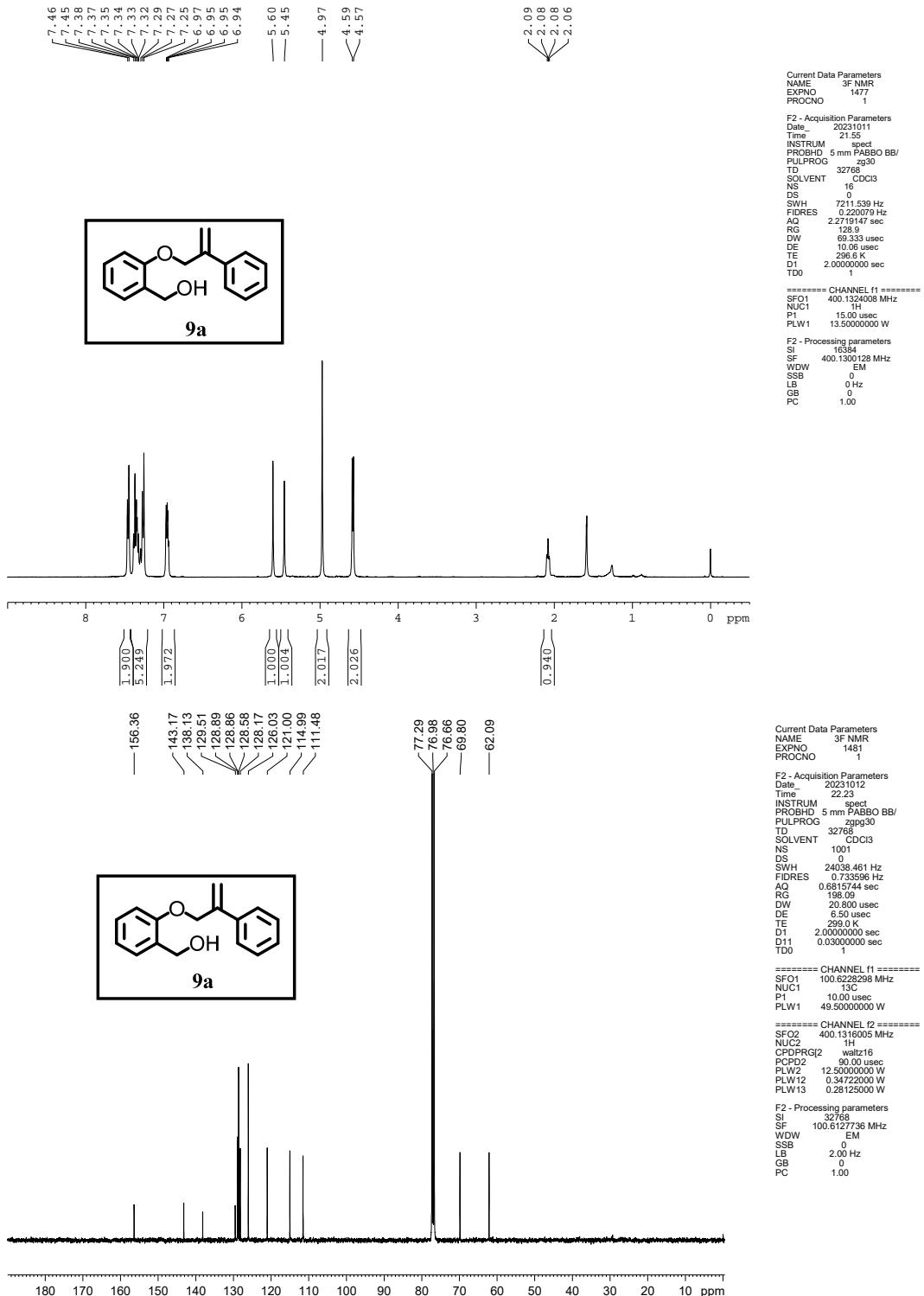
¹H and ¹³C NMR spectra of compound 8b.



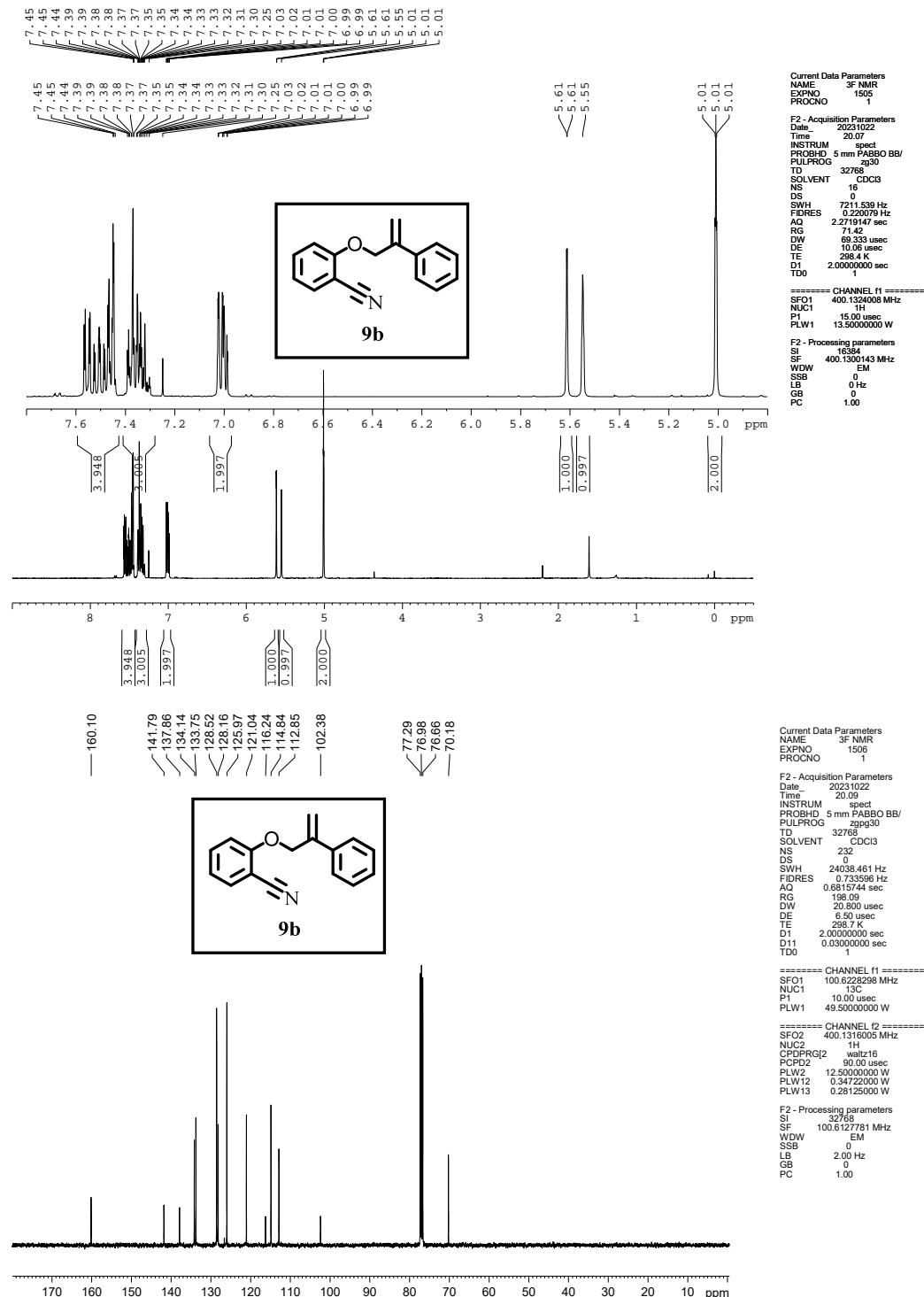
¹H and ¹³C NMR spectra of compound 8c.



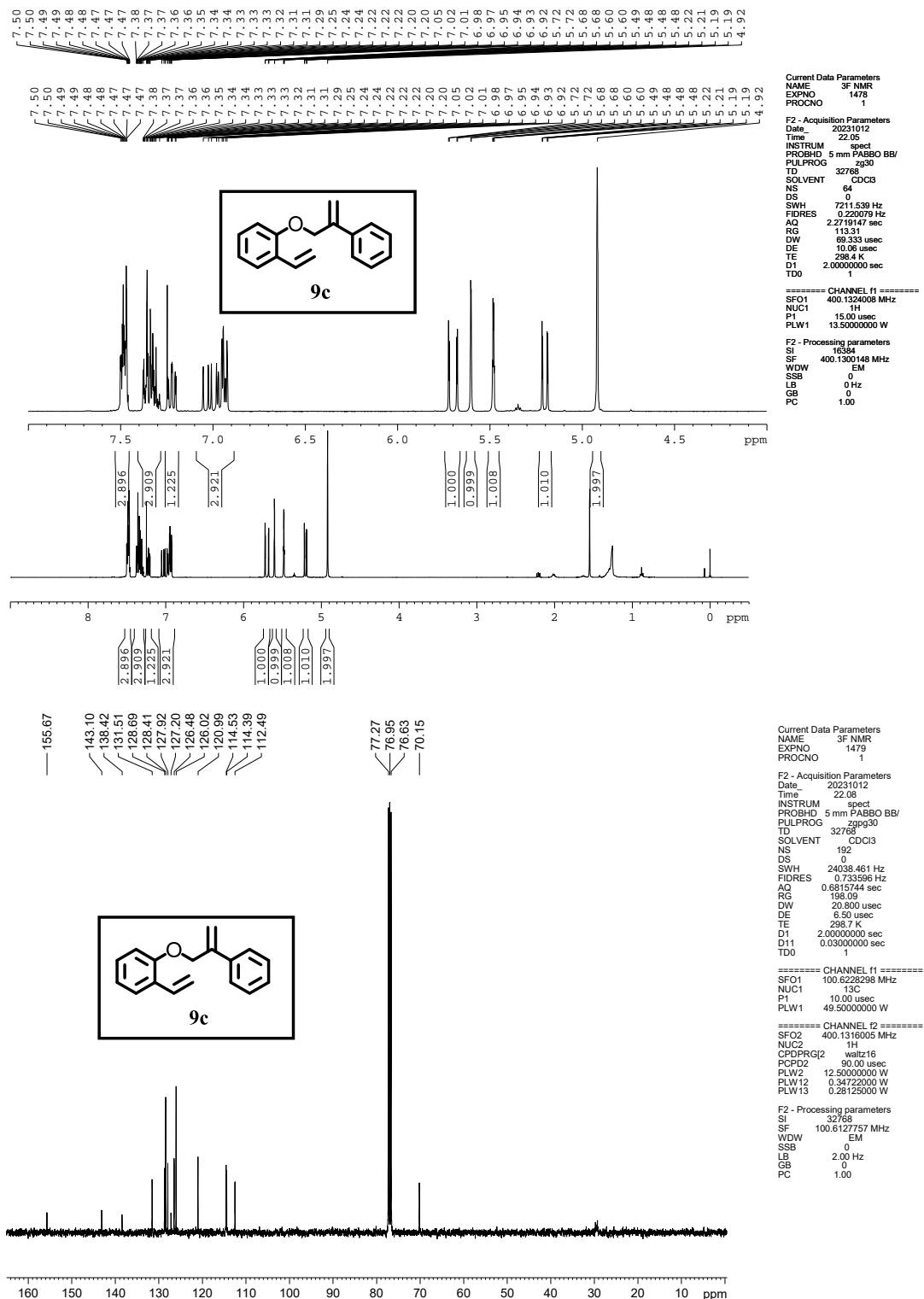
¹H and ¹³C NMR spectra of compound 9a.



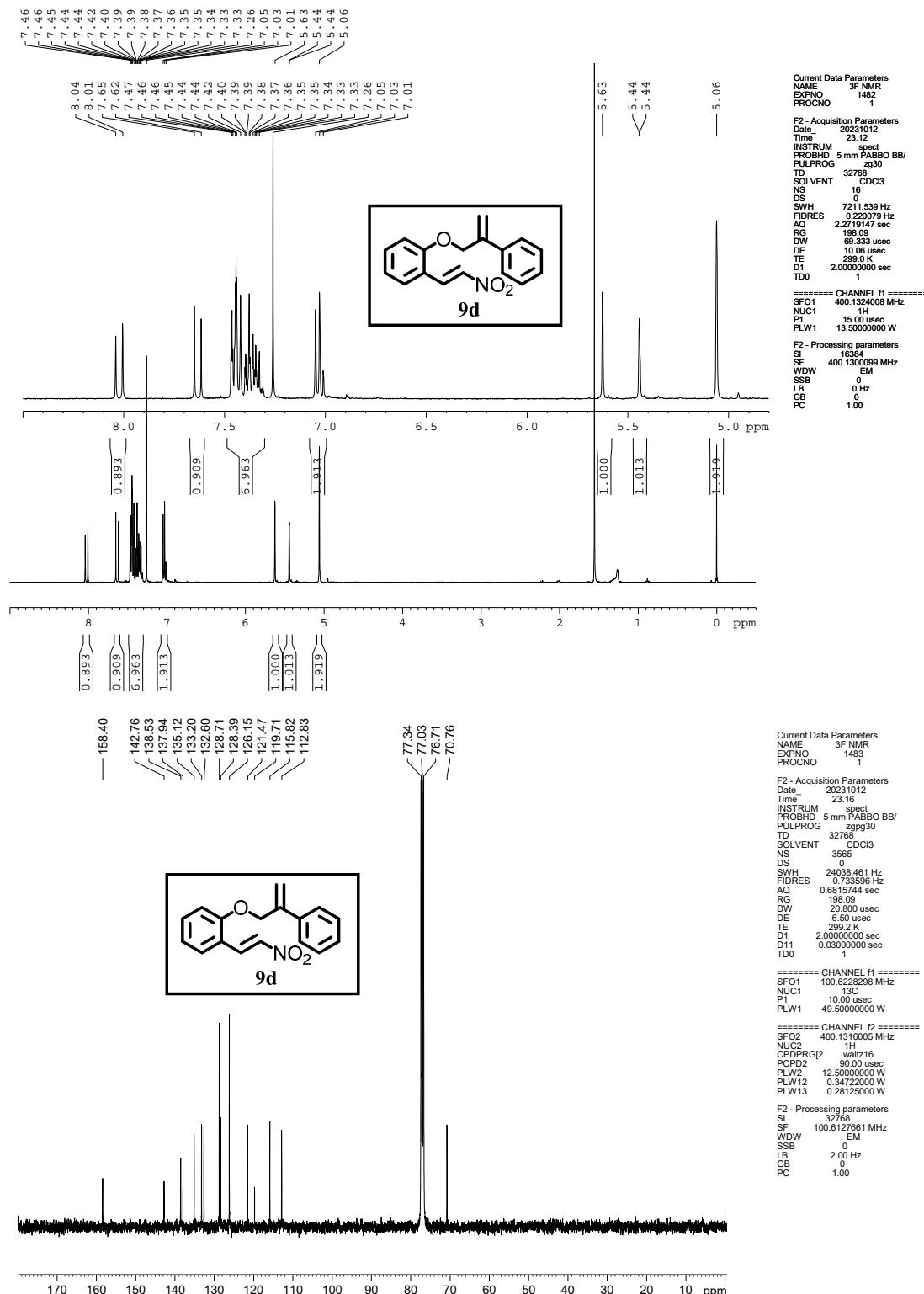
¹H and ¹³C NMR spectra of compound 9b.



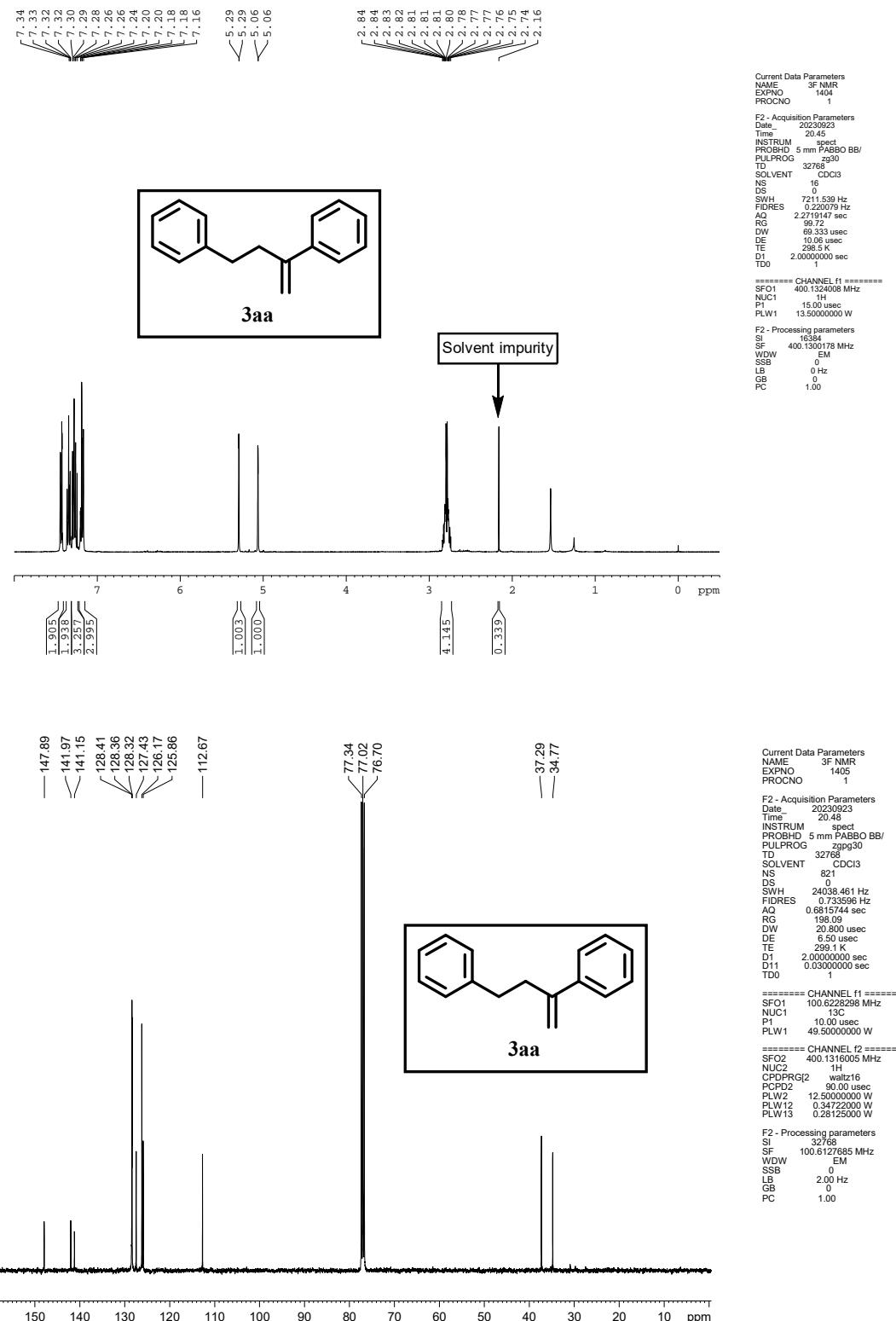
¹H and ¹³C NMR spectra of compound 9c.



¹H and ¹³C NMR spectra of compound 9d.



¹H and ¹³C NMR spectra of compound 3aa.



¹H and ¹³C NMR spectra of compound 3bb and 3bb' (4:1)

