SUPPORTING INFORMATION

Visible-light-mediated Propargylation of Phenols/ Thiophenols via Organic Photocatalysis

Ting Zhang,[c] Delin Wu,[a] Tianbao Liu,[a] Kaiyuan Zhou,[b] Shuguang Chen,*[b] Yongjia Shang*[b] and Hao Wu*[a]

[a] Anhui Engineering Research Center of Highly Reactive Micro-Nano Powders; Key Laboratory of Micro-Nano Powder and Advanced Energy Materials of Anhui Higher Education Institutes; School of Chemistry and Materials Engineering; Chizhou University, Chizhou, 247000, P. R. China

[b] Key Laboratory of Functional Molecular Solids, Ministry of Education, Anhui Laboratory of Molecule-Based Materials (State Key Laboratory Cultivation Base), College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241000, P. R. China

[c] State Key Laboratory of Fine Chemicals, Frontiers Science Center for Smart Materials, Dalian University of Technology, Linggong Road, Dalian, 116024, P. R. China

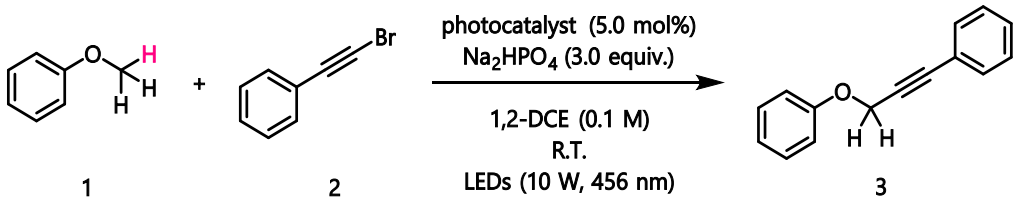
Contents

General Information

Unless otherwise specified, all reagents and starting materials were purchased from commercial sources and used as received, and the solvents were purified and dried using standard procedures. The chromatography solvents were technical grade and distilled prior to use. The NMR spectra were recorded with a Bruker Avance 400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C and 376 MHz for ^{19}F) with $CDCl_3$ as solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts are given in δ relative to TMS or residual $CHCl_3$, the coupling constants J are given in Hz. HRMS spectra were obtained with an Agilent 6200 using a quadrupole time-of-flight mass spectrometer equipped with an ESI source. Photoreaction was carried out using light lamp (456 nm, 40 W) purchased from Xuzhou Ai Jia electronic technology Co. LTD. The reaction tubes are F580810ND from Synthware and were about 5 cm away from the light source. The material of the irradiation vessel is borosilicate glass and no filters were used. All NMR yields were determined by crude ^{1}H-NMR using CH_2Br_2 as internal standard.

Optimization of conditions for alkynylation

Table S1. Screening photocatalysts[a]



1 2 3

Entry	Photocatalyst (5.0 mol%)	NMR Yield (%)[b]
1	Mes-Acr-Ph$^+$$ClO_4^-$	57
2	Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6	N.R.
3	4CzIPN	N.R.
4	*fac*-Ir(ppy)$_3$	N.R.
5	Eosin Y	N.R.
6	Perylene	N.R.
7	**Mes-Acr-Ph$^+$$BF_4^-$**	**88**
8	Mes-Acr-Ph$^+$$PF_6^-$	61
9	Mes-Acr-Me$^+$$BF_4^-$	48
10	**Mes-Acr-Ph$^+$$BF_4^-$**	63[c]
11	**Mes-Acr-Ph$^+$$BF_4^-$**	34[d]

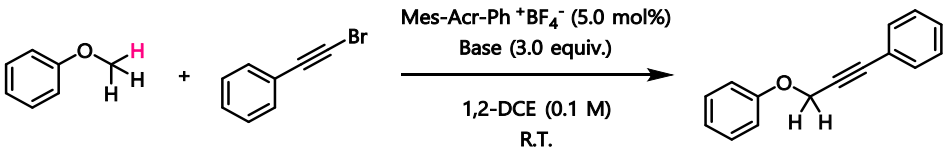
(a) 1 (0.1 mmol, 1.0 equiv.), 2 (3.0 equiv.), PC, Na_2HPO_4 (3.0 equiv.), 1,2-DCE (0.1 M), LEDs (10 W, 456 nm), R.T., 24 hrs.

(b) Isolated yield.

(c) Using Photocatalyst (10.0 mol%)

(d) Using Photocatalyst (2.5 mol%)

Table S2. Screening bases[a]



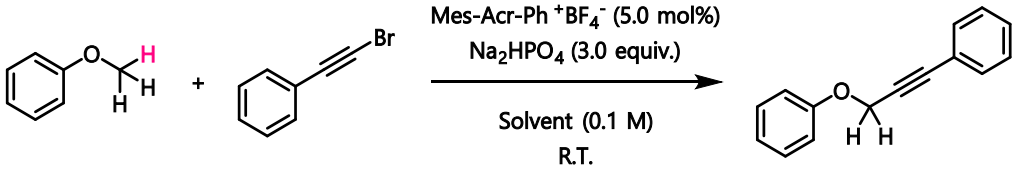
1 2 3

Entry	Base (3.0 equiv.)	NMR Yield (%)[b]
1	**Na_2HPO_4**	**88**
2	$NaHCO_3$	24
3	K_2HPO_4	28
4	Na_3PO_4	30
5	NaH_2PO_4	N.R.
6	Pyridine	69
7	2,6-lutidine	79
8	4-DMAP	N.R.

a) 1 (0.1 mmol, 1.0 equiv.), 2 (3.0 equiv.), Mes-Acr$^{+}BF_4^{-}$ (5.0 mol%), Base (3.0 equiv.), 1,2-DCE (0.1 M), LEDs (10 W, 456 nm), R.T., 24 hrs

b) Isolated yield.

Table S3. Screening solvents[a]



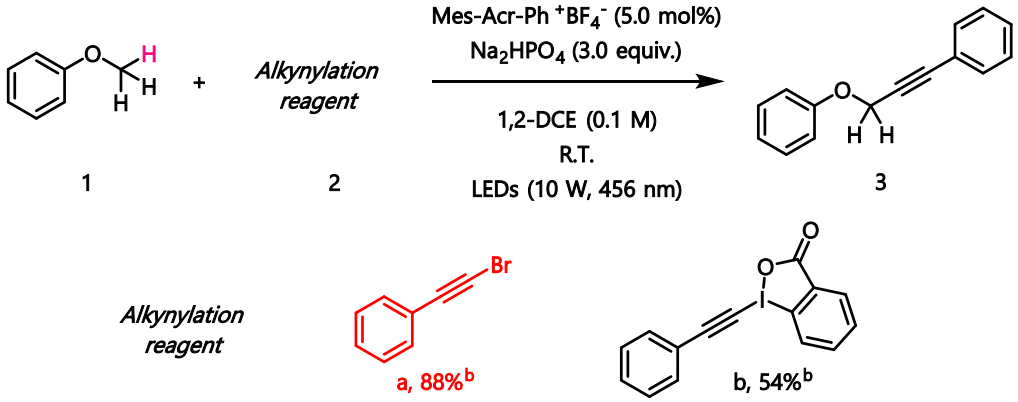
1 2 3

Entry	Solvent	NMR Yield (%)[b]
1	**1,2-DCE**	**88**
2	DCM	80
3	Chloroform	20
4	MeCN	< 5
5	Ethyl acetate	N.R.
6	Toluene	N.R.
7	DMF	N.R.
8	THF	N.R.
9	1,4-Dioxane	N.R.

a) 1 (0.1 mmol, 1.0 equiv.), 2 (3.0 equiv.), Mes-Acr$^{+}BF_4^{-}$ (5.0 mol%), Na_2HPO_4 (3.0 equiv.), Solvent (0.1 M), LEDs (10 W, 456 nm), R.T., 24 hrs

b) Isolated yield.

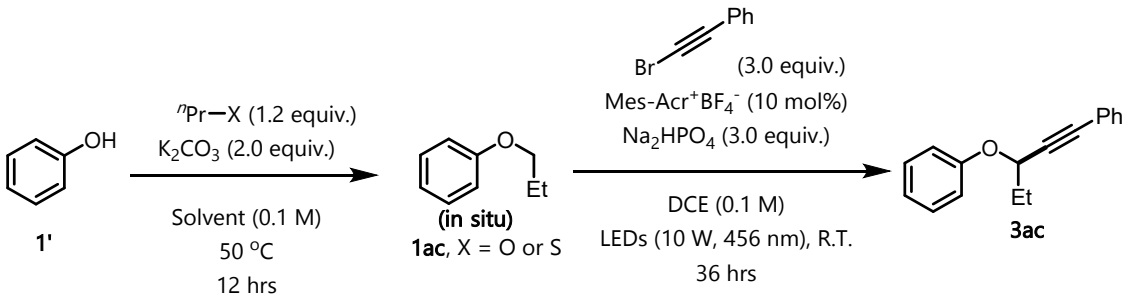
Table S4. Screening alkynylation reagent[a, b]



a) 1 (0.1 mmol, 1.0 equiv.), 2 (3.0 equiv.), Mes-Acr$^{+}BF_4^{-}$ (5.0 mol%), Na_2HPO_4 (3.0 equiv.), 1,2-DCE (0.1 M), LEDs (10 W, 456 nm), R.T., 24 hrs

b) Isolated yield.

Table S5. Screening one-pot method[b]



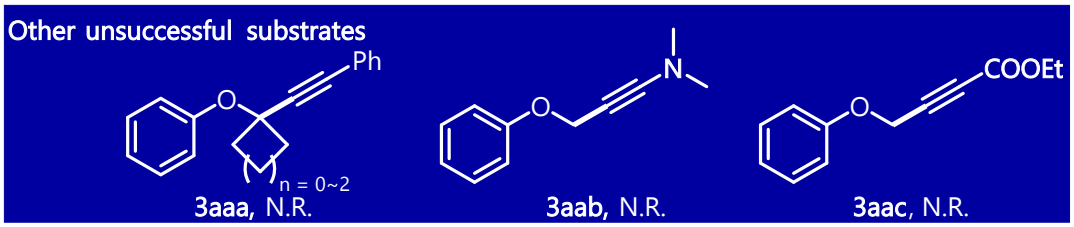
Entry	Solvent	X	NMR Yield (%)[a]
1	DMF	Br	70
2	Acetone	Br	68
3	DMF	OTf	44
4	**DMF**	**I**	**75**

a) Total yield of two steps

b) 1′ (0.2 mmol, 1.0 equiv.), ^{n}Pr-X (0.24 mmol, 1.2 equiv.), K_2CO_3 (0.4 mmol, 2.0 equiv.), Solvent (0.1 M), 50 °C, 12 hrs; 1 (0.1 mmol, 1.0 equiv.), 2 (3.0 equiv.), Mes-Acr$^{+}BF_4^{-}$ (5.0 mol%), Na_2HPO_4 (3.0 equiv.), 1,2-DCE (0.1 M), LEDs (10 W, 456 nm), R.T., 24 hrs

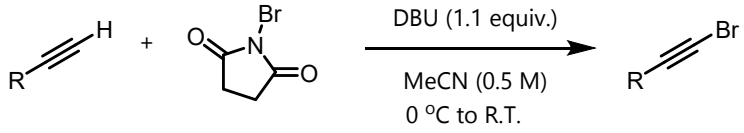
c) Isolated yield.

Unsuccessful substrates



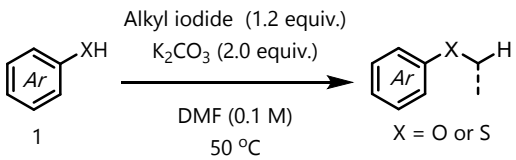
General Procedure A for the Synthesis of crude raw materials I&II

General Procedure A-1 for the Synthesis of crude product I



A 100 mL flame-dried single-neck flask with stirring bar was charged with terminal alkyne (5.0 mmol, 1.0 equiv.), DBU (0.822 mL, 5.5 mmol, 1.1 equiv.) and MeCN (2.5 mL, 0.5 M). The mixture was cooled to 0 °C in an ice bath and NBS (978.9 mg, 5.5 mmol, 1.1 equiv.) dissolved in MeCN (1.1 mL, 5.0 M) was added dropwise to the reaction mixture in 10 mins, then the temperature was slowly raised from 0 °C to room temperature. The reaction was stirred at room temperature for 1-5 min and monitored by TLC analysis. After the aryl acetylene was totally consumed, the mixture was transferred to a 200 mL beaker. Water (50 mL) was added to the mixture and extracted with PE (3 × 20 mL). The combined organic solution was dried over Na_2SO_4 for 1 h, filtered with Buchner funnel and concentrated *in vacuo*. The residue was directly loaded onto a short silica gel column (5 cm) and the column was washed with PE (50 mL). The eluent was collected and concentrated *in vacuo* to give out the crude product **I**. The crude product **I** was directly used for next step without any purification.[*Caution: The selection of an eluent was contingent upon the compound's polarity, with optimal systems typically yielding an R_f of approximately 0.4-0.7 on silica gel thin-layer chromatography (TLC) plates. When eluent mixtures exceeding a PE:EA ratio of 5:1 (v/v) were generally incompatible with this method. Highly polar compounds necessitate purification by column chromatography to ensure the complete removal of residual DBU.*]

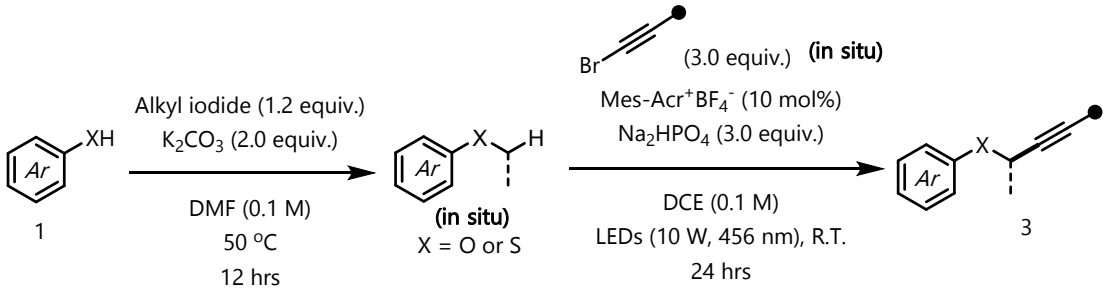
General Procedure A-2 for the Synthesis of crude product II



To a 10 mL Schlenk tube equipped with a magnetic stir bar was added arylphenol or arylthiophenol (5.0 mmol, 1.0 equiv.), K_2CO_3 (1382.1 mg, 10.0 mmol, 2.0 equiv.), DMF (10.0 mL, 0.5 M) under N_2. The reaction mixture was stirred at R.T. for about 30 minutes. Alkyl iodide (6.0 mmol, 1.2 equiv.) was added to the tube by syringe over 2 minutes. The mixture was stirred for 24 hrs at 50 °C with monitoring by TLC analysis. After this period, the mixture was transferred to a 200 mL beaker. Water (50 mL) was added to the mixture and extracted with EtOAc (3 × 20 mL). The combined organic solution was washed with brine (3 × 20 mL) and dried over Na_2SO_4

for 1 h. The solution was filtered with Buchner funnel and concentrated *in vacuo* to give out the crude product **II**. The crude product **II** was directly used for next step without any purification. [*Caution: brine washing and extraction steps are indispensable, as residual potassium carbonate in the reaction system will impair the yield of the subsequent step.*]

General Procedure B for the Synthesis of Aryl Propargyl Ether



Crude product **I** and crude product **II** were all prepared by general procedure A

To a 10 mL Schlenk tube equipped with a magnetic stir bar was added crude product **I** (0.9 mmol, 3.0 equiv.), Mes-Acr-Ph$^{+}BF_4^{-}$ (8.6 mg, 5 mol%), Na_2HPO_4 (127.8 mg, 0.9 mmol, 3.0 equiv.) and DCE (2.5 mL, 0.1 M) under N_2. The reaction vial was sealed with rubber stopper and placed in the light reactor with blue LEDs (456 nm, 10 W). Crude product **II** (0.3 mmol, 1.0 equiv.) was dissolved in DCE (0.5 mL) and the mixture was added to the tube in 5 minutes by syringe pump. The reaction mixture was stirred at R.T. for about 24 hrs with monitoring by TLC analysis. After this period, the mixture was transferred to a 100 mL beaker. Water (50 mL) was added to the mixture and extracted with EtOAc (3 × 50 mL). The combined organic solution was dried over Na_2SO_4 for 1 h and filtered with Buchner funnel. The filtrate was collected and then concentrated *in vacuo.* The resulting crude product was purified by flash column chromatography.

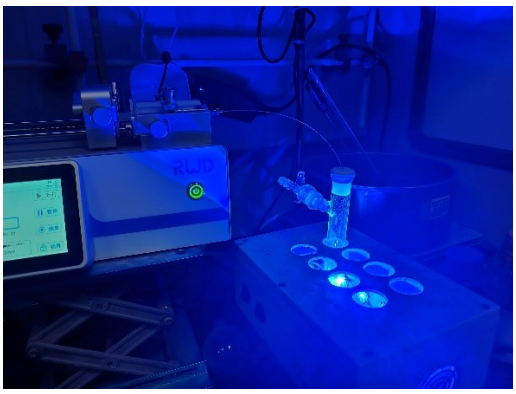
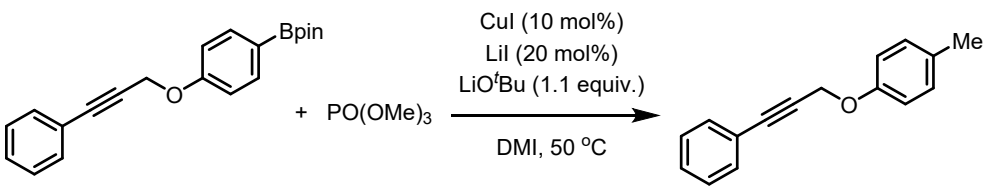


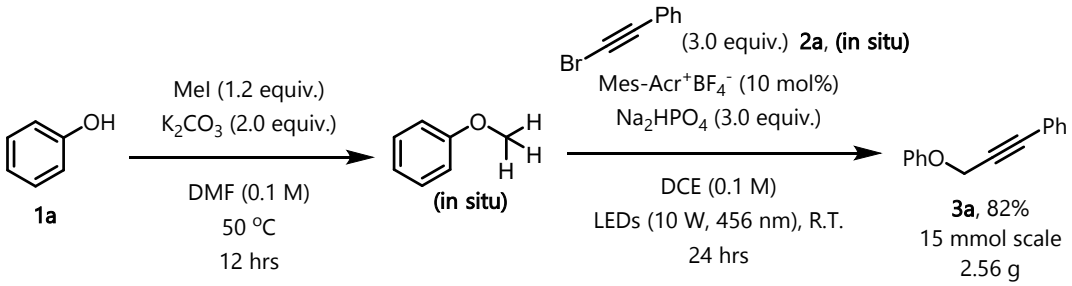
Figure S1. Reactions in light reactor and reaction workup

Procedure C for the Synthesis of Aryl Propargyl Ether (3p-2)



To a 10 mL Schlenk tube equipped with a magnetic stir bar was added 4,4,5,5-tetramethyl-2-(4-((3-phenylprop-2-yn-1-yl)oxy)phenyl)-1,3,2-dioxaborolane (62.1 mg, 0.3 mmol, 1.0 equiv.), LiO^tBu (26.4 mg, 0.33 mmol, 1.1 equiv.), lithium iodide (8.0 mg, 20 mol %), copper iodide (5.7 mg, 10 mol%), trimethyl phosphate (40.9 mg, 0.33 mmol, 1.1 equiv.) and 1,3-dimethylimidazolidin-2-one (DMI, 0.5 mL) under N_2. The reaction vial was sealed with rubber stopper and stirred at 50 ºC for 24 hrs. After this period, the mixture was transferred to a 200 mL beaker. Water (50 mL) was added to the mixture and extracted with EtOAc (3 × 20 mL). The combined organic solution was washed with brine (3 × 20 mL), dried over Na_2SO_4 for 1 h and filtered with Buchner funnel. The filtrate was collected and then concentrated *in vacuo.* The resulting crude product was purified by flash column chromatography.

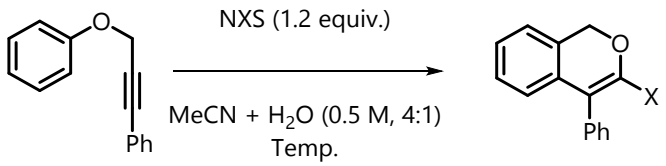
Procedure D for the Synthesis of (3-phenoxyprop-1-yn-1-yl)benzene (3a, 15 mmol scale)



Crude product **1a** and crude product **2a** were all prepared by general procedure A

To a 250 mL Schlenk tube equipped with a magnetic stir bar was added crude product **2a** (45.0 mmol, 3.0 equiv.), Mes-Acr-$Ph^+BF_4^-$ (430.0 mg, 5 mol%), Na_2HPO_4 (6390.0 mg, 0.9 mmol, 3.0 equiv.) and DCE (110.0 mL, 0.1 M) under N_2. The reaction vial was sealed with rubber stopper and placed in the light reactor with blue LEDs (456 nm, 10 W). Crude product **1a** (15.0 mmol, 1.0 equiv.) was dissolved in DCE (15.0 mL) and the mixture was added to the tube in 20 minutes by syringe pump. The reaction mixture was stirred at R.T. for about 48 hrs with monitoring by TLC analysis. After this period, the mixture was transferred to a 1000 mL beaker. Water (500 mL) was added to the mixture and extracted with EtOAc (3 × 100 mL). The combined organic solution was dried over Na_2SO_4 for 1 h and filtered with Buchner funnel. The filtrate was collected and then concentrated *in vacuo.* The resulting crude product was purified by flash column chromatography.

Procedure E for the Synthesis of 3-Halochromenes



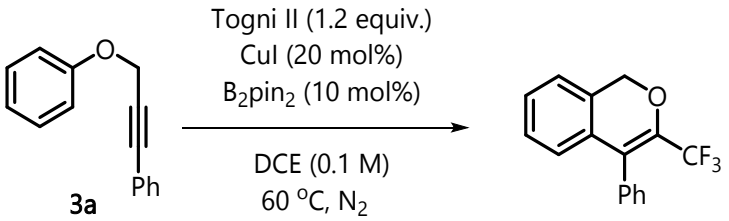
3a

3aa': X = Cl, 80%
3ab': X = Br, 74%

To a 10 mL Schlenk tube equipped with a magnetic stir bar was added **3a** (62.4 mg, 0.3 mmol, 1.0 equiv.), NXS (0.36 mmol, 1.2 equiv,) and MeCN-H_2O solvent mixture (0.6 mL, 0.5 M, 4:1) under air. The reaction vial was sealed with rubber stopper and the mixture was stirred at corresponding temperature (X = Cl, 130 °C, 3 hrs; X = Br, R.T., 10 mins) with monitoring by TLC analysis. After this period, the mixture was transferred to a 100 mL beaker. Water (50 mL) was added to the mixture and extracted with EtOAc (3 × 20 mL). The combined organic solution was

dried over Na_2SO_4 for 1 h and filtered with Buchner funnel. The filtrate was collected and then concentrated *in vacuo.* The resulting crude product was purified by flash column chromatography.

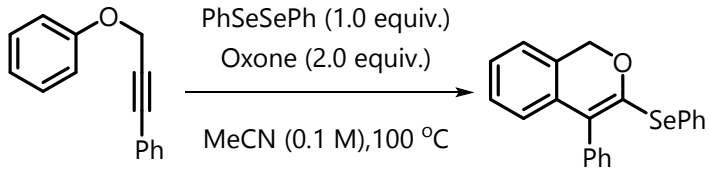
Procedure F for the Synthesis of 4-Phenyl-3-(Trifluoromethyl)-1*H*-Isochromene



3a

To a 10 mL Schlenk tube equipped with a magnetic stir bar was added **3a** (62.4 mg, 0.3 mmol, 1.0 equiv.), Togni II (113.8 mg, 0.36 mmol, 1.2 equiv.), CuI (11.4 mg, 20 mol%), B_2pin_2 (7.6 mg, 10 mol%) and DCE (3.0 mL, 0.1 M) under N_2. The reaction vial was sealed with rubber stopper and the mixture was stirred at 60 °C for about 4 hrs with monitoring by TLC analysis. After this period, the mixture was transferred to a 100 mL beaker. Water (50 mL) was added to the mixture and extracted with EtOAc (3 × 20 mL). The combined organic solution was dried over Na_2SO_4 for 1 h and filtered with Buchner funnel. The filtrate was collected and then concentrated *in vacuo.* The resulting crude product was purified by flash column chromatography.

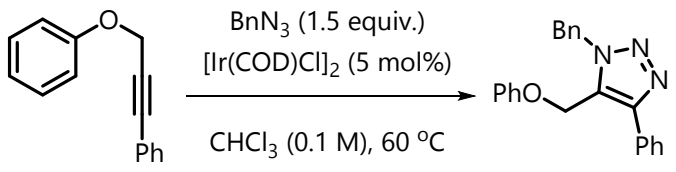
Procedure G for the Synthesis of 4-Phenyl-3-(Phenylselanyl)-1*H*-Isochromene



3a, 2.0 equiv.

To a 10 mL sealed tube equipped with a magnetic stir bar was added **3a** (124.8 mg, 0.6 mmol, 2.0 equiv.), PhSeSePh (93.6 mg, 0.3 mmol, 1.0 equiv.), Oxone (207.8 mg, 0.6 mmol, 2.0 equiv.) and DCE (3.0 mL, 0.1 M) under air. The reaction vial was sealed and the mixture was stirred at 100 °C for about 1 h with monitoring by TLC analysis. After this period, the mixture was transferred to a 100 mL beaker. Water (50 mL) was added to the mixture and extracted with EtOAc (3 × 20 mL). The combined organic solution was dried over Na_2SO_4 for 1 h and filtered with Buchner funnel. The filtrate was collected and then concentrated *in vacuo.* The resulting crude product was purified by flash column chromatography.

Procedure H for the Synthesis of 1-Benzyl-5-(Phenoxymethyl)-4-Phenyl-1*H*-1,2,3-Triazole



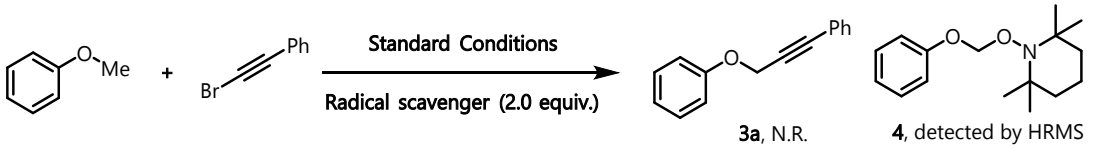
3a

To a 10 mL Schlenk tube equipped with a magnetic stir bar was added **3a** (62.4 mg, 0.3 mmol, 1.0 equiv.), BnN_3 (60.0 mg, 0.45 mmol, 1.5 equiv.), $[Ir(COD)Cl]_2$ (10.1 mg, 5 mol%) and $CHCl_3$ (3.0

mL, 0.1 M) under N_2. The reaction vial was sealed with rubber stopper and the mixture was stirred at 60 °C for about 24 hrs with monitoring by TLC analysis. After this period, the mixture was transferred to a 100 mL beaker. Water (50 mL) was added to the mixture and extracted with EtOAc (3 × 20 mL). The combined organic solution was dried over Na_2SO_4 for 1 h and filtered with Buchner funnel. The filtrate was collected and then concentrated *in vacuo.* The resulting crude product was purified by flash column chromatography.

Mechanism Study

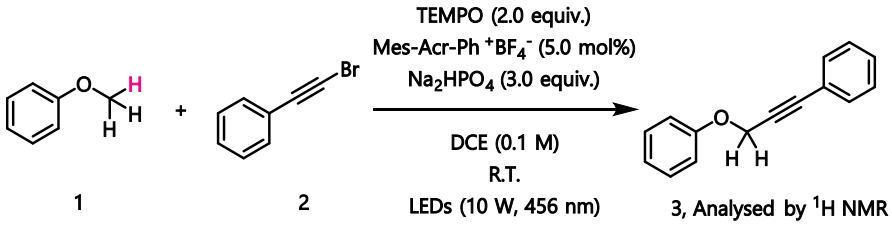
Procedure for Radical-Trapping Experiment



Entry	Radical scavenger	Yields of 3a
1	TEMPO	N.R.
2	BHT	N.R.
3	DPE	N.R.

To a 10 mL Schlenk tube equipped with a magnetic stir bar was added (bromoethynyl)benzene (162.0 mg, 0.9 mmol, 3.0 equiv.), 2,6-lutidine (96.4 mg, 0.9 mmol, 3.0 equiv.), TEMPO (93.7 mg, 0.6 mmol, 2.0 equiv.) and DCE (2.5 mL, 0.1 M) under N_2. The reaction vial was sealed with rubber stopper and placed in the light reactor with blue LEDs (456 nm, 10 W). Anisole (32.4 mg, 0.3 mmol, 1.0 equiv.) was dissolved in DCE (0.5 mL) and the mixture was added to the tube in 5 minutes by syringe pump. The reaction mixture was stirred at R.T. for about 24 hrs with monitoring by TLC analysis. After this period, the mixture was transferred to a 100 mL beaker. Water (50 mL) was added to the mixture and extracted with EtOAc (3 × 100 mL). The combined organic solution was dried over Na_2SO_4 for 1 h and filtered with Buchner funnel. The filtrate was collected and then concentrated *in vacuo.* The resulting crude product was analyzed by GC-MS.

Procedure for Light on/off Experiment



To a 10 mL Schlenk tube equipped with a magnetic stir bar was added (bromoethynyl)benzene (162.0 mg, 0.9 mmol, 3.0 equiv.), 2,6-lutidine (96.4 mg, 0.9 mmol, 3.0 equiv.) and DCE (2.5 mL, 0.1 M) under N_2. The reaction vial was sealed with rubber stopper and placed in the light reactor with blue LEDs (456 nm, 10 W). Anisole (32.4 mg, 0.3 mmol, 1.0 equiv.) was dissolved in DCE (0.5 mL) and the mixture was added to the tube in 5 minutes hrs by syringe pump. The reaction mixture was stirred at R.T. for about 24 hrs. 0.5 mL sample was taken every 4 hrs by 1 mL syringe in the glove box under nitrogen atompshere and the reaction vial was resealed again. The solution in the syringe was transferred to another 25 mL vial with 5 mL ethyl acetate, and the 25 ml vial and reaction vial both were taken out of glovebox. The reaction vial was palced in the

light reactor again. The cap of 25 mL vial was removed and reaction was quenched by addition of H_2O (2 mL) in air. The resulting mixture was transferred to 50 mL separatory funnel and extracted with EtOAc (3 × 20 mL). The combined organic solution was dried over Na_2SO_4 for 1 h and filtered with Buchner funnel. The resuting solution was concentrated in vacuo, and the residual solvent was removed by pump. 0.5 mL $CDCl_3$ and 7 uL CH_2Br_2 (internal standard) were added to dissolve the mixture, and the resulting solution was transferred to the NMR tube to be analyzed.

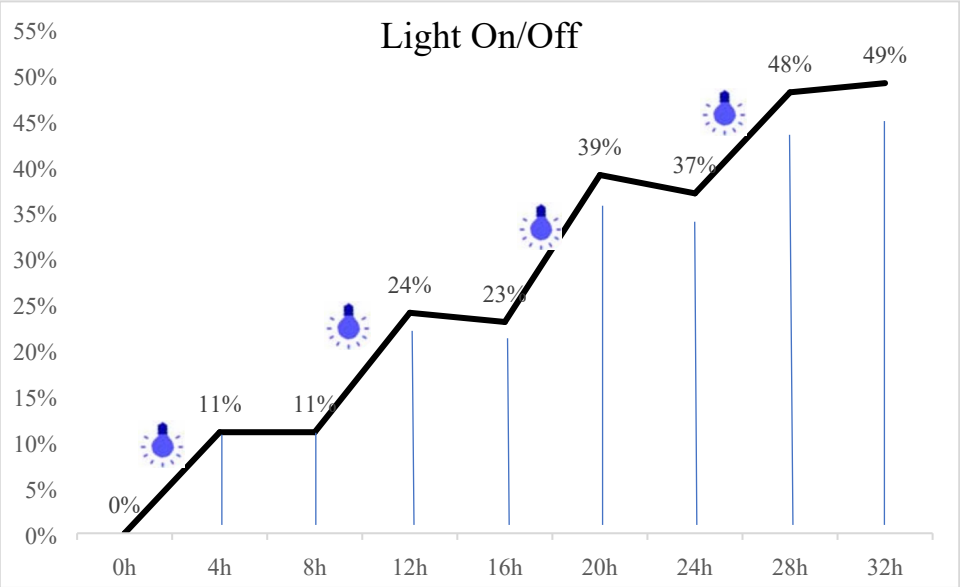
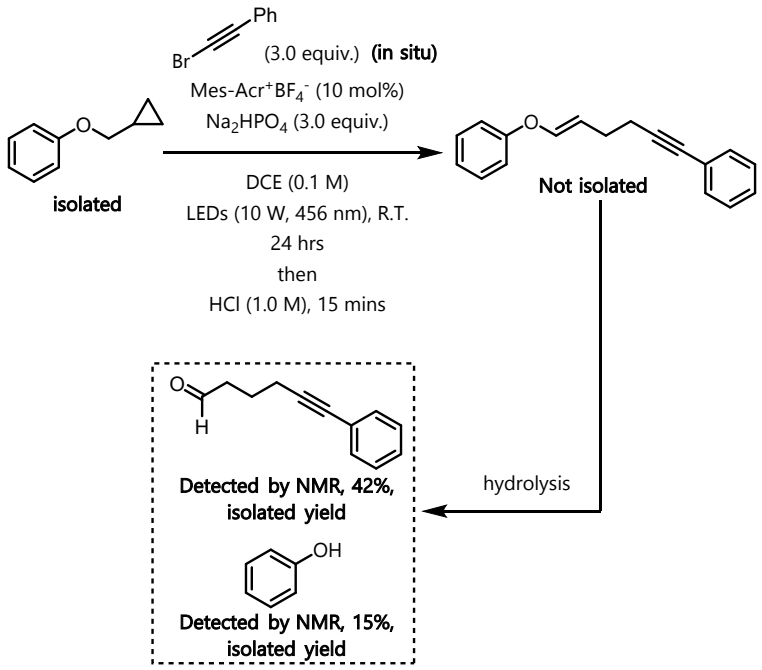


Figure S2: switch light experiments

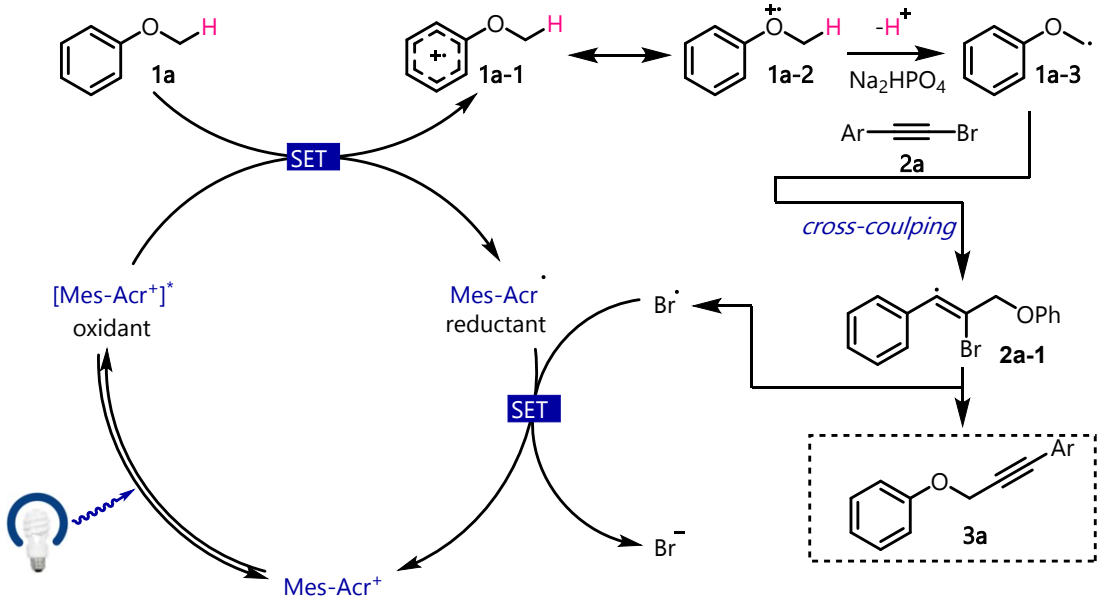
Procedure for Radical Clock Experiment



To a 10 mL Schlenk tube equipped with a magnetic stir bar was added (bromoethynyl)benzene (162.0 mg, 0.9 mmol, 3.0 equiv.), Mes-Acr-Ph$^+BF_4^-$ (8.6 mg, 5 mol%), Na_2HPO_4 (127.8 mg, 0.9 mmol, 3.0 equiv.) and DCE (2.5 mL, 0.1 M) under N_2. The reaction vial was sealed with rubber

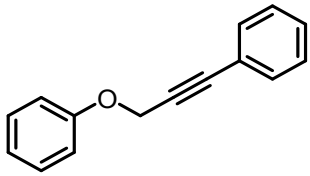
stopper and placed in the light reactor with blue LEDs (456 nm, 10 W). (cyclopropylmethoxy)benzene (44.4 mg, 0.3 mmol, 1.0 equiv.) was dissolved in DCE (0.5 mL) and the mixture was added to the tube in 5 minutes by syringe pump. The reaction mixture was stirred at R.T. for about 24 hrs with monitoring by TLC analysis. After this period, the mixture was transferred to a 100 mL beaker. Water (50 mL) was added to the mixture and extracted with EtOAc (3 × 50 mL). The combined organic solution was dried over Na_2SO_4 for 1 h and filtered with Buchner funnel. The filtrate was collected and then concentrated *in vacuo*. The resulting crude product was purified by flash column chromatography.

Plausible Mechanismc



Characterization Data

Experimental procedures and NMR spectra (PDF) FAIR data, including the primary NMR FID files, for compounds **3a**-**3az, 3aa'-3ae'**.



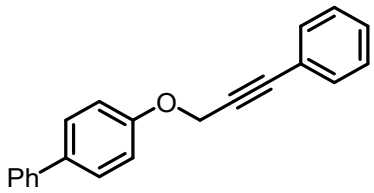
(3-phenoxyprop-1-yn-1-yl)benzene (3a): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (54.9 mg, 88% yield) as a pale yellow soild.[1]

M.p.: 45-46 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.41 (m, 2H), 7.39 – 7.21 (m, 5H), 7.10 – 6.94 (m, 3H), 4.91 (s, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.9, 131.9, 129.6, 128.7, 128.4, 122.4, 121.5, 115.1, 87.2, 84.1, 56.7.

HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{15}H_{13}O$ 209.0961, found 209.0955.



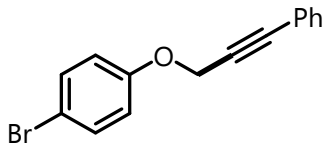
4-((3-phenylprop-2-yn-1-yl)oxy)-1,1'-biphenyl (3b): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (75.9 mg, 89% yield) as a white soild.[2]

M.p.: 113-114 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.49 (m, 4H), 7.48 – 7.37 (m, 4H), 7.34 – 7.23 (m, 4H), 7.12 – 7.03 (m, 2H), 4.91 (s, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.4, 140.8, 134.6, 131.9, 128.84, 128.80, 128.4, 128.3, 126.9, 122.3, 115.3, 87.4, 84.0, 56.8 with one peaks missing due to overlap.

HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{21}H_{17}O$ 285.1274, found 285.1280.



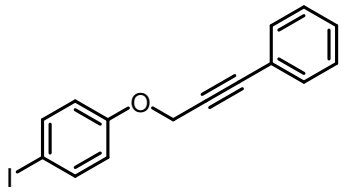
1-bromo-4-((3-phenylprop-2-yn-1-yl)oxy)benzene (3c): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (56.6 mg, 66% yield) as a white soild.[3]

M.p.: 83-84 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.40 (m, 2H), 7.39 – 7.31 (m, 4H), 7.30 – 7.24 (m, 3H), 3.80 (s, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 134.4, 132.12, 132.07, 131.7, 128.43, 128.37, 122.8, 121.1, 84.9, 84.0, 23.9.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{15}H_{12}BrO$ 287.0066, found 287.0058.



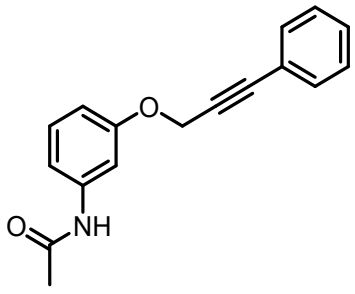
1-iodo-4-((3-phenylprop-2-yn-1-yl)oxy)benzene (3d): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (64.1 mg, 64% yield) as a white soild.[4]

M.p.: 88-89 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.52 (m, 2H), 7.45 – 7.37 (m, 2H), 7.35 – 7.24 (m, 3H), 6.83 – 6.72 (m, 2H), 4.85 (s, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.7, 138.3, 131.9, 128.9, 128.4, 122.1, 117.5, 87.6, 83.8, 83.4, 56.7.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{15}H_{12}IO$ 334.9927 found 334.9934.



***N*-(3-((3-phenylprop-2-yn-1-yl)oxy)phenyl)acetamide (3e)**: The compound was prepared by

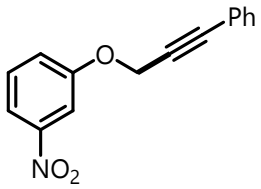
General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (55.7 mg, 70% yield) as a white soild.

M.p.: 110-111 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 (s, 1H), 7.46 – 7.38 (m, 2H), 7.35 (t, *J* = 2.0 Hz, 1H), 7.31 – 7.23 (m, 3H), 7.19 (t, *J* = 8.4 Hz, 1H), 7.14 – 7.03 (m, 1H), 6.75 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.83 (s, 2H), 2.10 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.2, 158.2, 139.4, 131.8, 129.7, 128.7, 128.3, 122.2, 113.1, 110.7, 107.0, 87.2, 83.9, 56.7, 24.5.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{17}H_{16}NO_2$ 266.1176, found 266.1181.



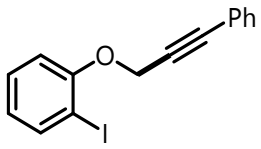
1-nitro-3-((3-phenylprop-2-yn-1-yl)oxy)benzene (3f): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (38.7 mg, 51% yield) as a yellow soild.[3]

M.p.: 69-70 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (t, *J* = 2.4 Hz, 1H), 7.88 – 7.83 (m, 1H), 7.50 – 7.41 (m, 3H), 7.36 – 7.26 (m, 4H), 4.99 (s, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.2, 149.2, 132.0, 130.1, 129.1, 128.5, 122.1, 121.8, 116.5, 109.7, 88.4, 82.6, 57.2.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{15}H_{12}NO_3$ 254.0812, found 254.0820.



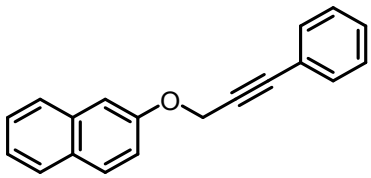
1-iodo-2-((3-phenylprop-2-yn-1-yl)oxy)benzene (3g): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (52.1 mg, 52% yield) as a colorless oil.[5]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.48 – 7.37 (m, 2H), 7.35 – 7.24 (m, 4H), 7.07 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.83 – 6.64 (m, 1H), 4.96 (s, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.6, 139.7, 131.9, 129.5, 128.8, 128.4, 123.4, 122.2,

113.4, 87.8, 86.8, 83.5, 57.9.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{15}H_{12}IO$ 334.9927, found 334.9920.



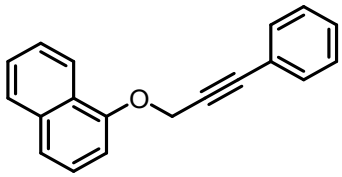
2-((3-phenylprop-2-yn-1-yl)oxy)naphthalene (3h): The compound was prepared by General Procedure B and Procedure C. The crude product was purified by chromatography on silica gel (petroleum ether) to give the target product (58.8 mg, 76% yield) as a white soild.[6]

M.p.: 93-94 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.69 (m, 3H), 7.52 – 7.40 (m, 3H), 7.39 – 7.22 (m, 6H), 5.03 (s, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.9, 134.5, 132.0, 129.7, 129.4, 128.8, 128.4, 127.8, 127.1, 126.6, 124.1, 122.4, 119.0, 107.8, 87.5, 83.9, 56.9.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{19}H_{15}O$ 259.1117, found 259.1120.



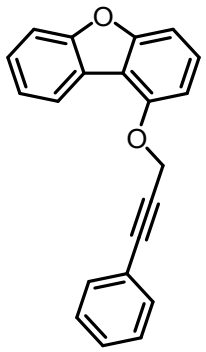
1-((3-phenylprop-2-yn-1-yl)oxy)naphthalene (3i): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (65.0 mg, 84% yield) as a white soild.[6]

M.p.: 51-52 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.37 – 8.27 (m, 1H), 7.84 – 7.73 (m, 1H), 7.51 – 7.40 (m, 5H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.31 – 7.23 (m, 3H), 6.98 (d, *J* = 7.6 Hz, 1H), 5.06 (s, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 153.7, 134.6, 131.9, 128.8, 128.4, 127.6, 126.6, 125.84, 125.79, 125.5, 122.4, 122.2, 121.1, 105.7, 87.3, 84.1, 57.1.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{19}H_{15}O$ 259.1117, found 259.1122.



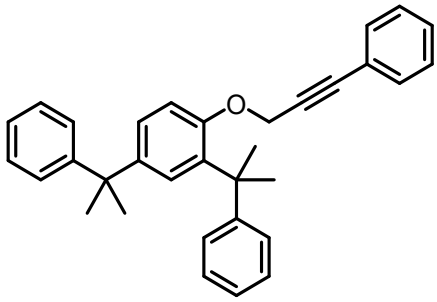
1-((3-phenylprop-2-yn-1-yl)oxy)dibenzo[*b,d*]furan (3j): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (63.5 mg, 71% yield) as a white soild.

M.p.: 110-111 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (dd, *J* = 6.0, 0.8 Hz, 1H), 7.51 (d, *J* = 6.8 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.40 – 7.36 (m, 1H), 7.36 – 7.29 (m, 2H), 7.29 – 7.22 (m, 3H), 7.20 (d, *J* = 6.4 Hz, 1H), 6.92 (d, *J* = 6.4 Hz, 1H), 5.08 (s, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.4, 155.6, 154.0, 131.9, 128.8, 128.4, 127.8, 126.4, 123.5, 123.2, 122.9, 122.3, 114.1, 111.1, 105.4, 105.1, 87.6, 83.9, 57.2.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{21}H_{15}O_2$ 299.1067, found 299.1073.



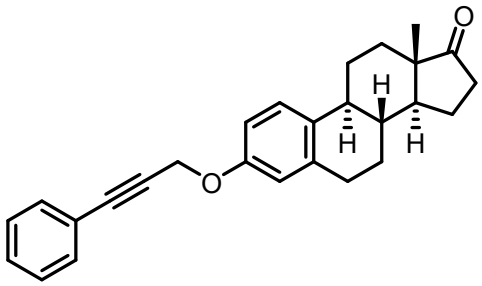
((4-((3-phenylprop-2-yn-1-yl)oxy)-1,3-phenylene)bis(propane-2,2-diyl))dibenzene (3k): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (114.6 mg, 86% yield) as a white soild.

M.p.: 124-125 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.31 (m, 3H), 7.30 – 7.24 (m, 7H), 7.21 – 7.13 (m, 5H), 7.10 – 7.04 (m, 2H), 6.91 (d, *J* = 6.8 Hz, 1H), 4.17 (s, 2H), 1.71 (s, 6H), 1.63 (s, 6H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 154.6, 151.5, 151.1, 143.4, 138.6, 131.8, 128.5, 128.3, 128.1, 127.7, 126.9, 125.77, 125.75, 125.7, 125.5, 125.0, 122.8, 114.3, 86.3, 85.0, 57.3, 42.8, 42.1, 31.1, 29.7.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{33}H_{33}O$ 445.2526, found 445.2520.



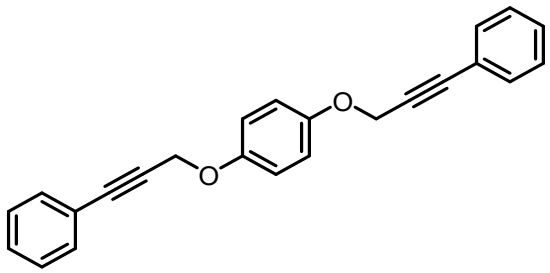
(8*R*,9*S*,13*S*,14*S*)-13-methyl-3-((3-phenylprop-2-yn-1-yl)oxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (3l): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (87.6 mg, 76% yield) as a white soild.[4]

M.p.: 160-161 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.40 (m, 2H), 7.33 – 7.27 (m, 3H), 7.21 (d, *J* = 6.8 Hz, 1H), 6.84 (dd, *J* = 7.0, 2.4 Hz, 1H), 6.80 – 6.73 (m, 1H), 4.86 (s, 2H), 2.96 – 2.82 (m, 2H), 2.48 (dd, *J* = 15.4, 7.2 Hz, 1H), 2.41 – 2.33 (m, 1H), 2.30 – 2.20 (m, 1H), 2.18 – 2.07 (m, 1H), 2.07 – 1.90 (m, 3H), 1.64 – 1.39 (m, 6H), 0.89 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 221.0, 155.9, 137.9, 132.9, 131.9, 128.7, 128.3, 126.4, 122.4, 115.1, 112.5, 87.0, 84.3, 56.7, 50.4, 48.0, 44.0, 38.3, 35.9, 31.6, 29.7, 26.6, 25.9, 21.6, 13.9.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{27}H_{29}O_2$ 385.2162, found 385.2166.



1,4-bis((3-phenylprop-2-yn-1-yl)oxy)benzene (3m): The compound was prepared by Procedure using hydroquinone (33.0 mg, 0.3 mmol, 1.0 equiv.), MeI (102.2 mg, 0.72 mmol, 2.4 equiv.), K_2CO_3 (165.8 mg, 1.2 mmol, 4.0 equiv.) and DMF (3 mL, 0.1 M), then (bromoethynyl)benzene (323.9 mg, 1.8 mmol, 6.0 equiv.), Mes-Acr-Ph$^+$BF$_4^-$ (8.6 mg, 5 mol%), Na_2HPO_4 (255.5 mg, 1.8 mmol, 6.0 equiv), DCE (3 mL, 0.1 M). The crude product was purification by chromatography on silica gel (petroleum ether) to give the target product (66.9 mg, 66% yield) as a white soild.

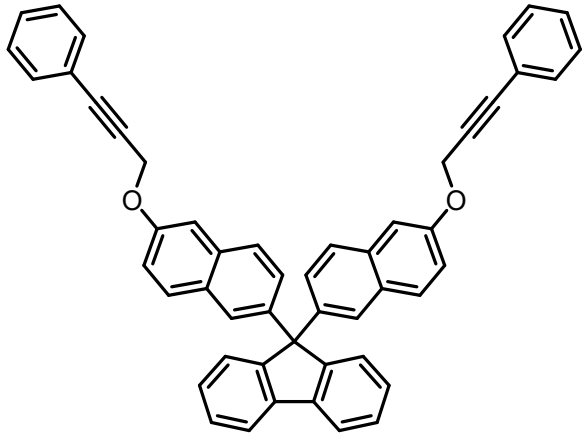
M.p.: 57-58 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.36 (m, 4H), 7.35 – 7.23 (m, 6H), 6.99 (s, 4H), 4.85

(s, 4H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 152.6, 131.9, 128.7, 128.4, 122.4, 116.2, 87.2, 84.3, 57.5.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{24}H_{19}O_2$ 339.1380, found 339.1388.



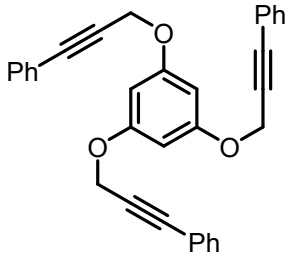
9,9-bis(6-((3-phenylprop-2-yn-1-yl)oxy)naphthalen-2-yl)-9*H*-fluorene (3n): The compound was prepared by Procedure using 6,6'-(9*H*-fluorene-9,9-diyl)bis(naphthalen-2-ol) (135.0 mg, 0.3 mmol, 1.0 equiv.), MeI (102.2 mg, 0.72 mmol, 2.4 equiv.), K_2CO_3 (165.8 mg, 1.2 mmol, 4.0 equiv.) and DMF (3 mL, 0.1 M), then (bromoethynyl)benzene (323.9 mg, 1.8 mmol, 6.0 equiv.), Mes-Acr-Ph$^+$BF$_4^-$ (8.6 mg, 5 mol%), Na_2HPO_4 (255.5 mg, 1.8 mmol, 6.0 equiv), DCE (3 mL, 0.1 M). The crude product was purification by chromatography on silica gel (petroleum ether) to give the target product (138.4 mg, 68% yield) as a white soild.

M.p.: 118-119 ^{o}C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 6.0 Hz, 2H), 7.63 (d, *J* = 6.8 Hz, 2H), 7.58 – 7.54 (m, 2H), 7.53 – 7.46 (m, 4H), 7.44 – 7.37 (m, 6H), 7.36 – 7.32 (m, 2H), 7.28 – 7.19 (m, 10H), 7.11 (dd, *J* = 7.2, 2.0 Hz, 2H), 4.92 (s, 4H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.8, 151.2, 141.3, 140.3, 133.3, 131.9, 129.7, 129.0, 128.8, 128.4, 127.9, 127.8, 127.7, 127.2, 126.4, 126.1, 122.3, 120.4, 118.9, 107.4, 87.4, 83.9, 65.5, 56.7.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{51}H_{35}O_2$ 679.2632, found 679.2641.



1,3,5-tris((3-phenylprop-2-yn-1-yl)oxy)benzene (3o): The compound was prepared by Procedure using benzene-1,3,5-triol (37.8 mg, 0.3 mmol, 1.0 equiv.), MeI (153.3 mg, 1.08 mmol, 3.6 equiv.), K_2CO_3 (248.8 mg, 1.8 mmol, 6.0 equiv.) and DMF (3 mL, 0.1 M), then (bromoethynyl)benzene (485.9 mg, 2.7 mmol, 9.0 equiv.), Mes-Acr-$Ph^+BF_4^-$ (8.6 mg, 5 mol%), 2,6-lutidine (289.1 mg, 2.7 mmol, 9.0 equiv), DCE (3 mL, 0.1 M). The crude product was purification by chromatography on silica gel (petroleum ether) to give the target product (85.7 mg, 61% yield) as a white soild.[7]

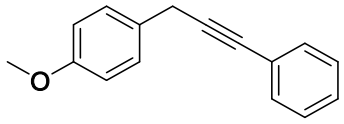
NOTE: The use of Na_2HPO_4 afforded the product in only 27% isolated yield; this low yield was presumably attributable to reduced transmittance caused by an excessive amount of insoluble base. Consequently, 2,6-lutidine was employed.

M.p.: 64-65 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.38 (m, 6H), 7.34 – 7.22 (m, 9H), 6.38 (s, 3H), 4.87 (s, 6H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.8, 132.0, 128.8, 128.4, 122.3, 95.6, 87.4, 83.7, 57.0.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{33}H_{25}O_3$ 469.1798, found 469.1789.

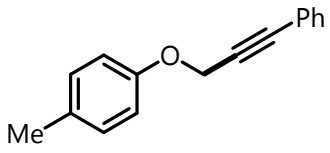


1-methoxy-4-(3-phenylprop-2-yn-1-yl)benzene (3p-1): The compound was prepared by Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (35.3 mg, 53% yield) as a yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.41 (m, 2H), 7.36 – 7.26 (m, 5H), 6.90 – 6.85 (m, 2H), 3.80 (s, 3H), 3.77 (s, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.5, 131.8, 129.1, 128.9, 128.4, 127.9, 123.9, 114.1, 88.1, 82.5, 55.5, 25.0.

HRMS (ESI-TOF): m/z [M + H]+ calcd for $C_{16}H_{15}O$ 223.1117, found 223.1110.



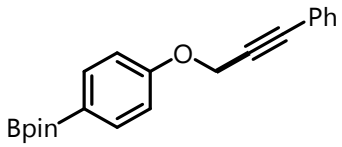
1-methyl-4-((3-phenylprop-2-yn-1-yl)oxy)benzene (3p-2): The compound was prepared by Procedure C and purified by chromatography on silica gel (petroleum ether) to give the target product (57.3 mg, 86% yield) as a pale yellow soild.[3]

M.p.: 71-72 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.38 (m, 2H), 7.35 – 7.26 (m, 3H), 7.17 – 7.08 (m, 2H), 7.00 – 6.90 (m, 2H), 4.87 (s, 2H), 2.30 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.8, 131.9, 130.8, 130.0, 128.7, 128.4, 122.5, 115.0, 87.1, 84.3, 56.9, 20.6.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{16}H_{15}O$ 223.1117, found 223.1120.



4,4,5,5-tetramethyl-2-(4-((3-phenylprop-2-yn-1-yl)oxy)phenyl)-1,3,2-dioxaborolane (3q): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (106.9 mg, 64% yield, 0.5 mmol scale) as a white soild.[8]

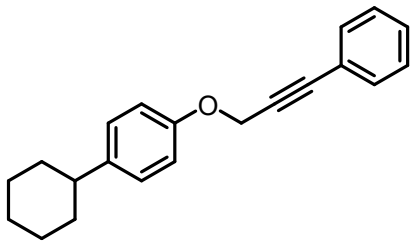
M.p.: 64-65 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.75 (m, 2H), 7.46 – 7.38 (m, 2H), 7.29 (m, 3H), 7.02 (d, *J* = 7.2 Hz, 2H), 4.92 (s, 2H), 1.33 (s, 12H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.4, 136.6, 131.9, 128.8, 128.4, 122.3, 114.3, 87.4, 83.8, 83.7, 77.4, 77.2, 76.9, 56.5, 25.0.

^{11}B NMR (160 MHz, Chloroform-*d*) δ 31.1.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{21}H_{24}BO_3$ 335.1813, found 335.1807.



1-cyclohexyl-4-((3-phenylprop-2-yn-1-yl)oxy)benzene (3r): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (45.3 mg, 52% yield) as a white soild.

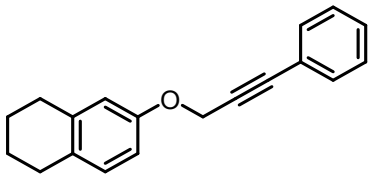
M.p.: 68-69 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.37 (m, 2H), 7.36 – 7.22 (m, 3H), 7.20 – 7.07 (m, 2H), 7.02 – 6.88 (m, 2H), 4.86 (s, 2H), 2.53 – 2.37 (m, 1H), 1.94 – 1.80 (m, 4H), 1.75 – 1.71 (m,

1H), 1.43 – 1.31 (m, 4H), 1.28 – 1.21 (m, 1H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.1, 141.3, 131.9, 128.7, 128.4, 127.8, 122.5, 114.9, 87.1, 84.4, 56.9, 43.9, 34.8, 27.1, 26.3.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{21}H_{23}O$ 291.1743, found 291.1750.



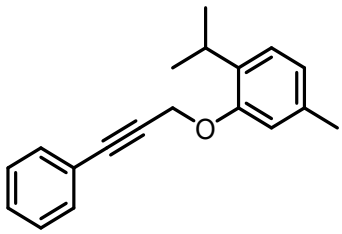
6-((3-phenylprop-2-yn-1-yl)oxy)-1,2,3,4-tetrahydronaphthalene (3s): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (44.8 mg, 57% yield) as a white soild.

M.p.: 55-56 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.37 (m, 2H), 7.32 – 7.23 (m, 3H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.78 (dd, *J* = 8.4, 2.8 Hz, 1H), 6.74 – 6.68 (m, 1H), 4.83 (s, 2H), 2.79 – 2.66 (m, 4H), 1.78 – 1.70 (m, 4H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.7, 138.3, 131.9, 130.2, 130.0, 128.7, 128.3, 122.5, 115.1, 112.7, 87.0, 84.4, 56.8, 29.8, 28.7, 23.5, 23.2.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{19}H_{19}O$ 263.1430, found 263.1435.



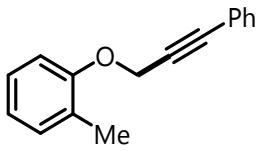
1-isopropyl-4-methyl-2-((3-phenylprop-2-yn-1-yl)oxy)benzene (3t): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (49.9 mg, 63% yield) as a pale yellow soild.[10]

M.p.: 53-54 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.38 (m, 2H), 7.27 – 7.21 (m, 3H), 7.10 (d, *J* = 6.4 Hz, 1H), 6.85 – 6.81 (m, 1H), 6.79 – 6.74 (m, 1H), 4.85 (s, 2H), 3.40 – 3.32 (m, 1H), 2.31 (s, 3H), 1.25 – 1.20 (m, 6H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.1, 136.3, 134.8, 131.9, 128.6, 128.3, 126.1, 122.6, 122.2, 113.4, 86.8, 84.7, 26.5, 23.0, 21.4 with one peaks missing due to overlap.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{19}H_{21}O$ 265.1587, found 265.1593.

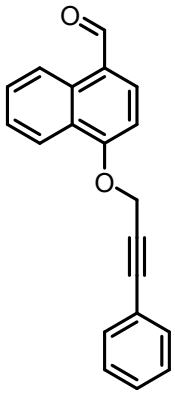


1-methyl-2-((3-phenylprop-2-yn-1-yl)oxy)benzene (3u): The compound was prepared by General Procedure B and purified by the following procedure: 1) purified by chromatography on silica gel (*n*-hexane); 2) purified by PTLC (Al_2O_3 as stationary phase, *n*-hexane); 3) recrystallization from *n*-pentane (1.5 mL) at -40 °C in low-temperature refrigerator to give the target product (54% yield, NMR yield; 10.7 mg, 16% yield, isolated yield) as a colorless oil.[9](Note: **3s** exists as a white solid in *n*-hexane at −40 °C and as a colorless oil at room temperature.)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.38 (m, 2H), 7.33 – 7.24 (m, 3H), 7.10 (d, *J* = 6.8 Hz, 2H), 6.96 – 6.89 (m, 2H), 4.87 (s, 2H), 2.29 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.8, 131.9, 130.8, 130.0, 128.7, 128.4, 122.5, 115.0, 87.1, 84.3, 56.9, 20.6.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{16}H_{15}O$ 223.1117, found 223.1122.



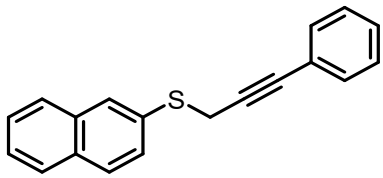
4-((3-phenylprop-2-yn-1-yl)oxy)-1-naphthaldehyde (3v): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (56.6 mg, 66% yield) as a white soild.

M.p.: 69-70 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.17 (s, 1H), 9.29 (d, *J* = 6.8 Hz, 1H), 8.35 (d, *J* = 6.8 Hz, 1H), 7.86 (d, *J* = 6.4 Hz, 1H), 7.73 – 7.62 (m, 1H), 7.60 – 7.50 (m, 1H), 7.47 – 7.36 (m, 2H), 7.33 – 7.21 (m, 3H), 7.05 (d, *J* = 6.4 Hz, 1H), 5.14 (s, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.4, 158.8, 139.3, 132.0, 131.9, 129.6, 129.0, 128.4, 126.6, 125.6, 125.4, 124.9, 122.5, 121.9, 104.4, 88.2, 82.8, 57.3.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{20}H_{15}O_2$ 287.1067, found 287.1062.



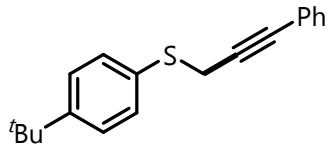
naphthalen-2-yl(3-phenylprop-2-yn-1-yl)sulfane (3w): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (73.2 mg, 89% yield) as a white soild.

M.p.: 89-90 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.93 (m, 1H), 7.86 – 7.73 (m, 3H), 7.55 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.50 – 7.39 (m, 2H), 7.37 – 7.29 (m, 2H), 7.28 – 7.18 (m, 3H), 3.92 (s, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 133.8, 132.7, 132.3, 131.8, 128.9, 128.6, 128.3, 128.2, 127.8, 127.5, 126.7, 126.2, 123.0, 85.3, 83.9, 23.9 with one peaks missing due to overlap.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{19}H_{15}S$ 275.0889, found 275.0882.



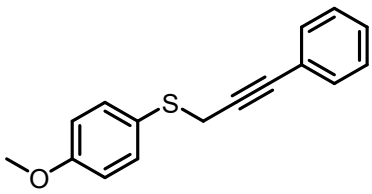
(4-(*tert*-butyl)phenyl)(3-phenylprop-2-yn-1-yl)sulfane (3x): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (74.0 mg, 88% yield) as a white soild.

M.p.: 63-64 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.44 (m, 2H), 7.38 – 7.31 (m, 4H), 7.29 – 7.25 (m, 3H), 3.80 (s, 2H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.5, 131.8, 131.1, 128.3, 128.2, 126.1, 124.6, 123.1, 85.7, 83.8, 34.6, 31.4, 24.4.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{19}H_{21}S$ 281.1358, found 281.1364.



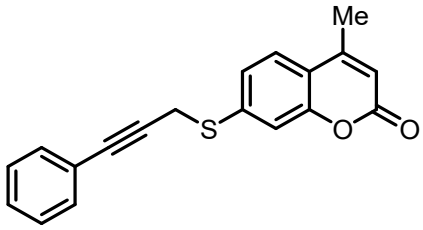
(4-methoxyphenyl)(3-phenylprop-2-yn-1-yl)sulfane (3y): The compound was prepared by

General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (65.6 mg, 86% yield) as a brown oil.[11]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.47 (m, 2H), 7.37 – 7.31 (m, 2H), 7.31 – 7.24 (m, 3H), 6.91 – 6.83 (m, 2H), 3.77 (s, 3H), 3.71 (s, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.8, 134.9, 131.7, 128.3, 128.2, 125.1, 123.1, 114.6, 85.8, 83.9, 55.4, 25.9.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{16}H_{15}OS$ 255.0838, found 255.0841.



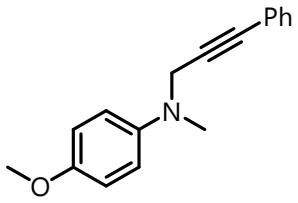
4-methyl-7-((3-phenylprop-2-yn-1-yl)thio)-2*H*-chromen-2-one (3z): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether : ethyl acetate = 5 : 1) to give the target product (44.1 mg, 48% yield) as a white soild.

M.p.: 81-82 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 8.7 Hz, 1H), 7.48 – 7.45 (m, 2H), 7.37 – 7.32 (m, 3H), 7.07 – 6.98 (m, 2H), 6.19 (s, 1H), 5.01 (s, 2H), 2.43 (s, 3H).

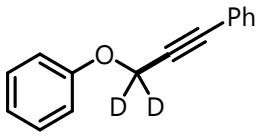
^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.4, 160.8, 155.2, 152.6, 132.0, 129.1, 128.5, 125.7, 121.9, 114.3, 113.0, 112.4, 102.3, 88.2, 82.7, 57.2, 18.8.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{19}H_{15}O_2S$ 307.0787, found 307.0778.



4-methoxy-*N*-methyl-*N*-(3-phenylprop-2-yn-1-yl)aniline (3aa-1)[12]: The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether : ethyl acetate = 20 : 1) to give the target product (6.8 mg, 9% yield) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 2H), 7.28 – 7.26 (m, 3H), 7.01 – 6.92 (m, 2H), 6.90 – 6.83 (m, 2H), 4.18 (s, 2H), 3.78 (s, 3H), 2.96 (s, 3H).



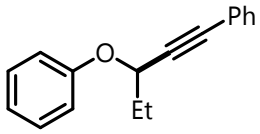
(3-phenoxyprop-1-yn-1-yl-3,3-*d*$_2$)benzene (3ab): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (49.8 mg, 79% yield) as a white soild.[13]

M.p.: 43-44 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.41 (m, 2H), 7.36 – 7.27 (m, 5H), 7.10 – 6.95 (m, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.9, 132.0, 129.6, 128.8, 128.4, 122.4, 121.5, 115.1, 87.2, 84.0, 56.2 (t, $J_{D\text{-}C}$ = 18.2 Mhz).

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{15}H_{11}D_2O$ 211.1086, found 211.1080.



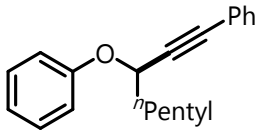
(3-phenoxyhex-1-yn-1-yl)benzene (3ac): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (53.1 mg, 75% yield) as a white soild.

M.p.: 59-60 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.36 (m, 2H), 7.34 – 7.24 (m, 5H), 7.12 – 7.05 (m, 2H), 6.97 (m, 1H), 4.88 (t, *J* = 6.4 Hz, 1H), 2.13 – 1.99 (m, 2H), 1.17 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.9, 131.9, 129.5, 128.6, 128.3, 122.6, 121.3, 116.0, 87.5, 86.5, 69.8, 29.3, 9.9.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{17}H_{17}O$ 267.1743, found 267.1734.



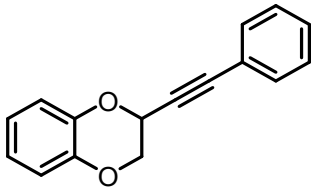
(3-phenoxyoct-1-yn-1-yl)benzene (3ad): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (57.6 mg, 69% yield) as a colurless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.36 (m, 2H), 7.34 – 7.24 (m, 5H), 7.12 – 7.04 (m,

2H), 7.02 – 6.93 (m, 1H), 4.93 (t, *J* = 6.4 Hz, 1H), 2.10 – 1.92 (m, 2H), 1.72 – 1.58 (m, 2H), 1.44 – 1.34 (m, 4H), 0.97 – 0.85 (m, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.0, 131.9, 129.5, 128.5, 128.3, 122.7, 121.3, 116.0, 87.8, 86.4, 68.6, 36.0, 31.6, 25.2, 22.7, 14.2.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{20}H_{23}O$ 279.1743, found 279.1735.

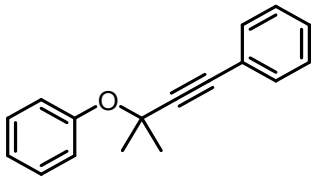


2-(phenylethynyl)-2,3-dihydrobenzo[*b*][1,4]dioxine (3ae): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (37.5 mg, 53% yield) as a yellow oil.[14]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.43 (m, 2H), 7.36 – 7.27 (m, 3H), 6.99 – 6.86 (m, 4H), 5.10 (dd, *J* = 7.4, 2.4 Hz, 1H), 4.42 (dd, *J* = 11.2, 2.4 Hz, 1H), 4.20 (dd, *J* = 11.2, 7.6 Hz, 1H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.8, 142.5, 132.1, 129.2, 128.4, 122.1, 121.9, 121.7, 117.8, 117.3, 87.8, 82.6, 67.5, 64.7.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{16}H_{13}O_2$ 237.0910, found 237.0915.

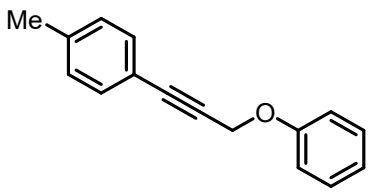


(3-methyl-3-phenoxybut-1-yn-1-yl)benzene (3af): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (45.3 mg, 64% yield) as a yellow oil.[15]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.34 (m, 2H), 7.33 – 7.22 (m, 7H), 7.09 – 7.01 (m, 1H), 1.72 (s, 6H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.8, 131.6, 129.0, 128.5, 128.4, 123.0, 122.8, 121.8, 91.7, 85.8, 73.3, 29.9.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{17}H_{17}O$ 237.1274, found 237.1266.



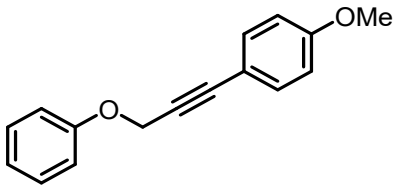
1-methyl-4-(3-phenoxyprop-1-yn-1-yl)benzene (3ag): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (56.6 mg, 85% yield) as a white soild.[16]

M.p.: 49-50°C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.25 (m, 4H), 7.13 – 7.05 (m, 2H), 7.05 – 6.92 (m, 3H), 4.87 (s, 2H), 2.31 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.9, 138.9, 131.8, 129.5, 129.1, 121.4, 119.3, 115.0, 87.4, 83.4, 56.7, 21.6.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{16}H_{15}O$ 223.1117, found 223.1125.



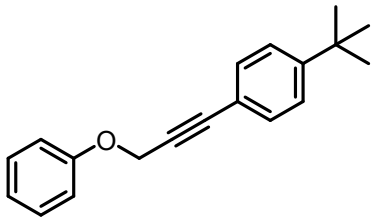
1-methoxy-4-(3-phenoxyprop-1-yn-1-yl)benzene (3ah): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (43.6 mg, 61% yield) as a white soild.[16]

M.p.: 48-49 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.24 (m, 4H), 7.10 – 6.92 (m, 3H), 6.87 – 6.72 (m, 2H), 4.83 (s, 2H), 3.69 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.9, 157.9, 133.3, 129.5, 121.3, 115.0, 114.4, 113.9, 87.1, 82.7, 56.7, 55.2.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{16}H_{15}O_2$ 239.1067, found 239.1076.



1-(*tert*-butyl)-4-(3-phenoxyprop-1-yn-1-yl)benzene (3ai): The compound was prepared by

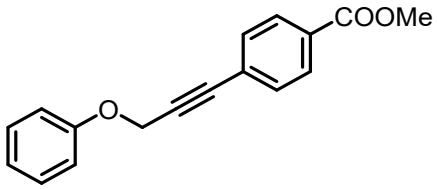
General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (49.1 mg, 62% yield) as a white soild.[16]

M.p.: 59-60 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.34 (m, 2H), 7.34 – 7.27 (m, 4H), 7.07 – 6.95 (m, 3H), 4.90 (s, 2H), 1.29 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.9, 152.1, 131.7, 129.6, 125.4, 121.5, 119.4, 115.1, 87.4, 83.4, 56.8, 34.9, 31.3.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{19}H_{21}O$ 265.1587, found 265.1580.



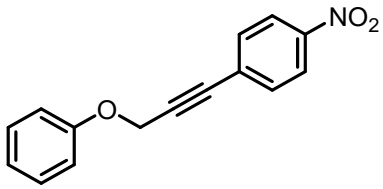
methyl 4-(3-phenoxyprop-1-yn-1-yl)benzoate (3aj): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (55.9 mg, 70% yield) as a white soild.[17]

M.p.: 78-79 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 6.4 Hz, 2H), 7.47 (d, *J* = 6.4 Hz, 2H), 7.31 (t, *J* = 6.4 Hz, 2H), 7.07 – 6.93 (m, 3H), 4.90 (s, 2H), 3.88 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.4, 157.7, 131.8, 130.0, 129.6, 129.5, 127.0, 121.6, 115.0, 87.0, 86.3, 56.5, 52.3.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{17}H_{15}O_3$ 267.1016, found 267.1022.



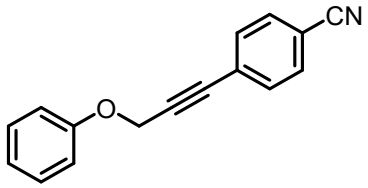
1-nitro-4-(3-phenoxyprop-1-yn-1-yl)benzene (3ak): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (57.7 mg, 76% yield) as a yellow soild.[16]

M.p.: 64-65 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.29 – 8.05 (m, 2H), 7.65 – 7.43 (m, 2H), 7.42 – 7.23 (m, 2H), 7.16 – 6.83 (m, 3H), 4.95 (s, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.6, 147.3, 132.5, 129.6, 129.1, 123.5, 121.8, 114.9, 89.4, 85.2, 56.3.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{15}H_{12}NO_3$ 254.0812, found 254.0804.



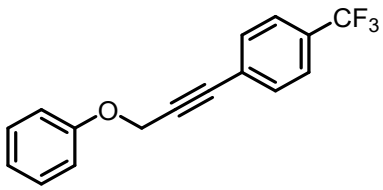
4-(3-phenoxyprop-1-yn-1-yl)benzonitrile (3al): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (52.4 mg, 75% yield) as a white soild.[16]

M.p.: 63-64 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.49 (m, 2H), 7.48 – 7.40 (m, 2H), 7.36 – 7.25 (m, 2H), 7.10 – 6.92 (m, 3H), 4.89 (s, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.5, 132.2, 131.9, 129.5, 127.0, 121.6, 118.2, 114.9, 112.0, 88.5, 85.3, 56.3.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{16}H_{12}NO$ 234.0913, found 234.0922.



1-(3-phenoxyprop-1-yn-1-yl)-4-(trifluoromethyl)benzene (3am): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (59.6 mg, 72% yield) as a white soild.[17]

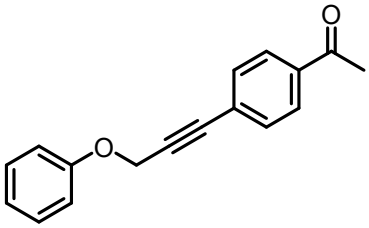
M.p.: 54-55 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.47 (m, 4H), 7.39 – 7.26 (m, 2H), 7.09 – 6.97 (m, 3H), 4.91 (s, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.8, 132.2, 130.6 (q, J_{F-C} = 26.0 Hz), 129.7, 126.3, 125.4 (q, J_{F-C} = 3.1 Hz), 121.8, 124.0(q, J_{F-C} = 216.4 Hz), 115.1, 86.6, 85.9, 56.6.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.90.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{19}H_{21}O$ 265.1587, found 265.1594.



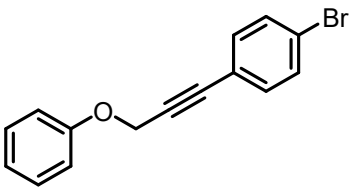
1-(4-(3-phenoxyprop-1-yn-1-yl)phenyl)ethan-1-one (3an): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (40.5 mg, 54% yield) as a white soild.[17]

M.p.: 91-92 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.82 (m, 2H), 7.54 – 7.43 (m, 2H), 7.36 – 7.26 (m, 2H), 7.08 – 6.90 (m, 3H), 4.91 (s, 2H), 2.55 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.3, 157.7, 136.6, 131.9, 129.6, 128.2, 127.1, 121.6, 115.0, 87.4, 86.3, 56.5, 26.6.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{17}H_{15}O_2$ 251.1067, found 251.1077.



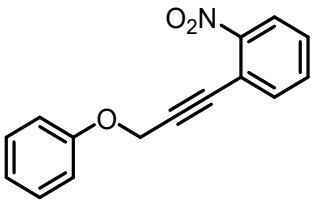
1-bromo-4-(3-phenoxyprop-1-yn-1-yl)benzene (3ao): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (76.4 mg, 89% yield) as a white soild.[16]

M.p.: 73-74 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.38 (m, 2H), 7.34 – 7.24 (m, 4H), 7.04 – 6.93 (m, 3H), 4.86 (s, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.8, 133.3, 131.7, 129.6, 123.1, 121.6, 121.3, 115.0, 86.1, 85.3, 56.6.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{15}H_{12}BrO$ 287.0066, found 287.0060.



1-nitro-2-(3-phenoxyprop-1-yn-1-yl)benzene (3ap): The compound was prepared by General

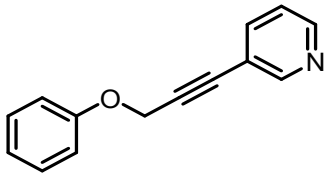
Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (47.1 mg, 62% yield) as a white soild.[18]

M.p.: 62-63 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.57 (dd, *J* = 7.8, 2.0 Hz, 1H), 7.54 – 7.47 (m, 1H), 7.46 – 7.39 (m, 1H), 7.35 – 7.28 (m, 2H), 7.07 – 6.97 (m, 3H), 4.95 (s, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.7, 135.1, 132.9, 129.6, 129.2, 124.6, 121.7, 117.7, 115.1, 92.0, 82.3, 56.6 with one peaks missing due to overlap.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{15}H_{12}NO_3$ 254.0812, found 254.0804.



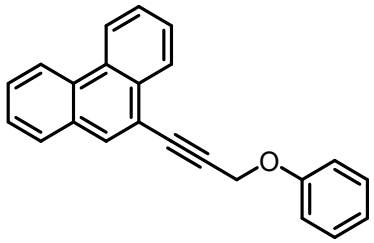
3-(3-phenoxyprop-1-yn-1-yl)pyridine (3aq): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (46.4 mg, 74% yield) as a pale yellow soild.

M.p.: 74-75 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.67 (s, 1H), 8.59 – 8.48 (m, 1H), 7.74 – 7.66 (m, 1H), 7.38 – 7.30 (m, 2H), 7.27 – 7.21 (m, 1H), 7.08 – 6.99 (m, 3H), 4.93 (s, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.7, 152.5, 149.1, 138.9, 129.6, 123.1, 121.7, 119.5, 115.0, 87.5, 83.9, 56.5.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{14}H_{12}NO$ 210.0913, found 210.0922.



9-(3-phenoxyprop-1-yn-1-yl)phenanthrene (3ar): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (84.1 mg, 91% yield) as a white soild.

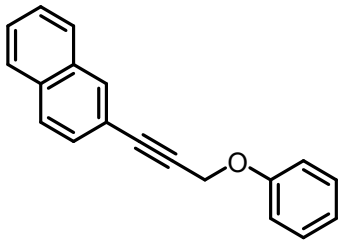
M.p.: 121-122 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.47 – 8.34 (m, 2H), 8.27 – 8.16 (m, 1H), 7.81 (s, 1H), 7.61 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.54 – 7.36 (m, 4H), 7.33 – 7.25 (m, 2H), 7.13 – 7.01 (m, 2H), 7.00 – 6.93

(m, 1H), 4.93 (s, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.8, 132.3, 130.9, 130.9, 130.3, 129.9, 129.6, 128.5, 127.6, 127.0, 126.9, 126.8, 122.7, 122.5, 121.5, 118.6, 115.2, 88.5, 85.5, 56.7 with one peaks missing due to overlap.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{23}H_{16}O$ 309.1274, found 309.1266.



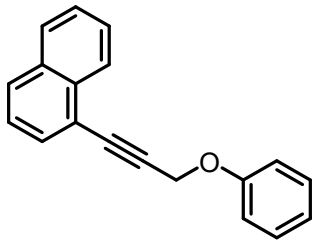
2-(3-phenoxyprop-1-yn-1-yl)naphthalene (3as): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (67.4 mg, 87% yield) as a white soild.[13]

M.p.: 74-75 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.75 – 7.64 (m, 3H), 7.47 – 7.37 (m, 3H), 7.35 – 7.25 (m, 2H), 7.09 – 7.01 (m, 2H), 7.01 – 6.94 (m, 1H), 4.90 (s, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.9, 133.0, 132.9, 132.0, 129.6, 128.4, 128.1, 127.85, 127.81, 126.9, 126.6, 121.5, 119.6, 115.0, 87.5, 84.4, 56.7.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{19}H_{15}O$ 259.1117, found 259.1109.

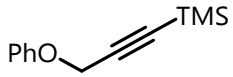


1-(3-phenoxyprop-1-yn-1-yl)naphthalene (3at): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (55.8 mg, 72% yield) as a yellow oil.[19]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 – 8.16 (m, 1H), 7.83 – 7.72 (m, 2H), 7.67 – 7.60 (m, 1H), 7.51 – 7.43 (m, 2H), 7.38 – 7.28 (m, 3H), 7.13 – 7.05 (m, 2H), 7.04 – 6.93 (m, 1H), 5.01 (s, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.9, 133.4, 133.2, 130.9, 129.6, 129.3, 128.4, 127.0, 126.6, 126.2, 125.2, 121.6, 120.0, 115.3, 89.0, 85.5, 56.9.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{19}H_{15}O$ 259.1117, found 259.1121.

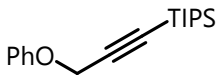


trimethyl(3-phenoxyprop-1-yn-1-yl)silane (3au): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (50.8 mg, 83% yield) as a colorless oil.[20]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.25 (m, 2H), 7.02 – 6.91 (m, 3H), 4.66 (s, 2H), 0.17 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.9, 129.5, 121.5, 115.1, 100.3, 92.8, 56.8, -0.2.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{12}H_{17}OSi$ 205.1043, found 205.1048.



triisopropyl(3-phenoxyprop-1-yn-1-yl)silane (3av): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (64.0 mg, 74% yield) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.24 (m, 2H), 7.06 – 6.92 (m, 3H), 4.71 (m, 2H), 1.07 – 1.01 (m, 21H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.8, 129.4, 121.4, 115.4, 102.2, 102.2, 89.2, 56.8, 18.6, 11.2.

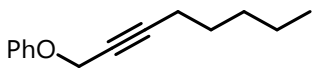
HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{18}H_{29}OSi$ 289.1982, found 289.1980.

(hex-2-yn-1-yloxy)benzene (3aw): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (35.5 mg, 68% yield) as a colorless oil.[21]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.18 (m, 2H), 7.07 – 6.88 (m, 3H), 4.67 (t, *J* = 2.4 Hz, 2H), 2.26 – 2.10 (m, 2H), 1.58 – 1.46 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.9, 129.5, 121.3, 115.0, 88.2, 75.1, 56.5, 22.0, 20.9, 13.6.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{12}H_{15}O$ 175.1117, found 175.1124.



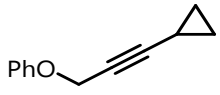
(oct-2-yn-1-yloxy)benzene (3ax): The compound was prepared by General Procedure B and

purified by chromatography on silica gel (petroleum ether) to give the target product (44.9 mg, 74% yield) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.26 (m, 2H), 7.06 – 6.92 (m, 3H), 4.67 (t, *J* = 2.4 Hz, 2H), 2.31 – 2.15 (m, 2H), 1.55 – 1.46 (m, 2H), 1.35 – 1.25 (m, 4H), 0.88 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.0, 129.5, 121.3, 115.0, 88.5, 75.0, 56.5, 31.1, 28.3, 22.3, 18.9, 14.1.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{14}H_{19}O$ 203.1430, found 203.1438.

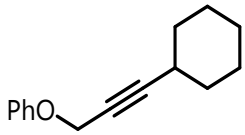


((3-cyclopropylprop-2-yn-1-yl)oxy)benzene (3ay): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (31.5 mg, 61% yield) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.23 (m, 2H), 7.04 – 6.87 (m, 3H), 4.62 (d, *J* = 2.0 Hz, 2H), 1.32 – 1.18 (m, 1H), 0.82 – 0.63 (m, 4H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.9, 129.5, 121.3, 114.9, 91.3, 70.3, 56.5, 8.4, -0.4.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{12}H_{13}O$ 173.0961, found 173.0966.

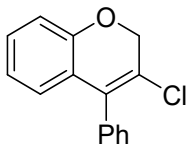


((3-cyclohexylprop-2-yn-1-yl)oxy)benzene (3az): The compound was prepared by General Procedure B and purified by chromatography on silica gel (petroleum ether) to give the target product (45.0 mg, 70% yield) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.26 (m, 2H), 7.04 – 6.90 (m, 3H), 4.68 (d, *J* = 2.0 Hz, 2H), 2.53 – 2.29 (m, 1H), 1.86 – 1.74 (m, 2H), 1.73 – 1.63 (m, 2H), 1.52 – 1.38 (m, 3H), 1.31 – 1.24 (m, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.0, 129.5, 121.3, 115.1, 92.4, 75.0, 56.7, 32.5, 29.2, 25.9, 24.9.

HRMS (ESI-TOF) m/z [M + H]+ calcd for $C_{15}H_{19}O$ 215.1430, found 215.1439.

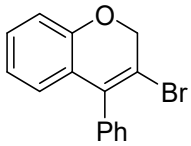


3-chloro-4-phenyl-2*H*-chromene (3aa'): The compound was prepared by Procedure E and purified by chromatography on silica gel (petroleum ether) to give the target product (58.1 mg, 80% yield) as a yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.36 (m, 3H), 7.32 – 7.24 (m, 2H), 7.16 – 7.08 (m, 1H), 6.88 (dd, *J* = 6.4, 0.8 Hz, 1H), 6.84 – 6.77 (m, 1H), 6.68 (dd, *J* = 6.2, 1.2 Hz, 1H), 4.92 (s, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 152.8, 134.7, 132.8, 129.8, 129.2, 128.6, 128.2, 126.1, 124.2, 122.2, 121.8, 116.0, 69.4.

HRMS (ESI-TOF): m/z [M + H]+ calcd for $C_{15}H_{12}ClO$ 243.0571, found 243.0563.

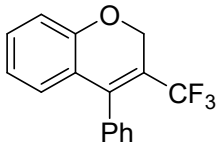


3-bromo-4-phenyl-2*H*-chromene (3ab'): The compound was prepared by Procedure E and purified by chromatography on silica gel (petroleum ether) to give the target product (63.5 mg, 74% yield) as a yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.39 (m, 3H), 7.27 – 7.25 (m, 2H), 7.18 – 7.11 (m, 1H), 6.87 (dd, *J* = 6.4, 0.8 Hz, 1H), 6.83 – 6.77 (m, 1H), 6.65 (dd, *J* = 6.2, 1.2 Hz, 1H), 5.03 (s, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 153.0, 136.6, 135.9, 129.7, 129.4, 128.6, 128.3, 126.3, 124.4, 121.8, 116.1, 113.8, 71.2.

HRMS (ESI-TOF): m/z [M + H]+ calcd for $C_{15}H_{12}BrO$ 287.0066, found 287.0075.



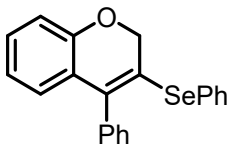
4-phenyl-3-(trifluoromethyl)-2*H*-chromene (3ac'): The compound was prepared by Procedure F and purified by chromatography on silica gel (petroleum ether) to give the target product (53.8 mg, 65% yield) as a yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.40 (m, 3H), 7.25 – 7.20 (m, 3H), 6.93 (dd, *J* = 6.4, 1.2 Hz, 1H), 6.87 – 6.79 (m, 1H), 6.68 (dd, *J* = 6.2, 1.2 Hz, 1H), 4.91 (s, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 154.6, 140.7 (d, *J* = 3.2 Hz), 134.7, 131.5, 128.9, 128.4, 128.3, 128.2, 123.8, 121.97, 121.95 (d, *J* = 216.9 Hz), 117.5 (d, *J* = 23.9 Hz), 116.3, 63.3 (d, *J* = 3.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.29.

HRMS (ESI-TOF): m/z [M + H]+ calcd for $C_{16}H_{12}F_3O$ 277.0835, found 277.0842.

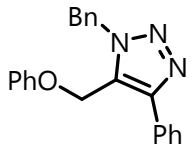


4-phenyl-3-(phenylselanyl)-2*H*-chromene (3ad'): The compound was prepared by Procedure G and purified by chromatography on silica gel (petroleum ether) to give the target product (83.0 mg, 76% yield) as a yellow oil.

^1H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.47 (m, 2H), 7.46 – 7.37 (m, 3H), 7.31 – 7.24 (m, 5H), 7.15 – 7.09 (m, 1H), 6.84 (dd, *J* = 6.4, 1.2 Hz, 1H), 6.82 – 6.77 (m, 1H), 6.70 (dd, *J* = 6.0, 1.2 Hz, 1H), 4.73 (s, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 153.7, 138.4, 137.6, 133.6, 133.5, 129.8, 129.5, 129.2, 128.7, 128.5, 128.2, 127.9, 126.3, 125.1, 122.7, 121.6, 116.0, 69.6.

HRMS (ESI-TOF): m/z [M + H]+ calcd for $C_{21}H_{17}OSe$ 365.0439, found 365.0442.

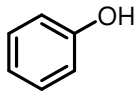


1-benzyl-5-(phenoxymethyl)-4-phenyl-1*H*-1,2,3-triazole (3ae'): The compound was prepared by Procedure H and purified by chromatography on silica gel (petroleum ether : ethyl acetate = 1:1) to give the target product (65.5 mg, 64% yield) as a yellow oil.

^1H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.37 (m, 3H), 7.29 – 7.21 (m, 7H), 7.13 – 7.03 (m, 2H), 7.02 – 6.87 (m, 3H), 5.47 (s, 2H), 5.05 (s, 2H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.5, 141.4, 137.6, 135.4, 129.9, 129.8, 129.5, 129.0, 128.9, 128.3, 127.5, 126.4, 121.2, 115.1, 61.3, 52.2.

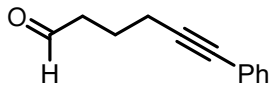
HRMS (ESI-TOF): m/z [M + H]+ calcd for $C_{22}H_{20}N_3O$ 342.1601, found 342.1595.



phenol (1)[23]: The compound was prepared by Procedure and purified by chromatography on silica gel (petroleum ether) to give the target product (4.2 mg, 15% yield) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.23 (m, 2H), 6.95 – 6.91 (m, 1H), 6.86 – 6.82 (m, 2H), 5.10 (s, 1H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.6, 129.8, 120.9, 115.4.



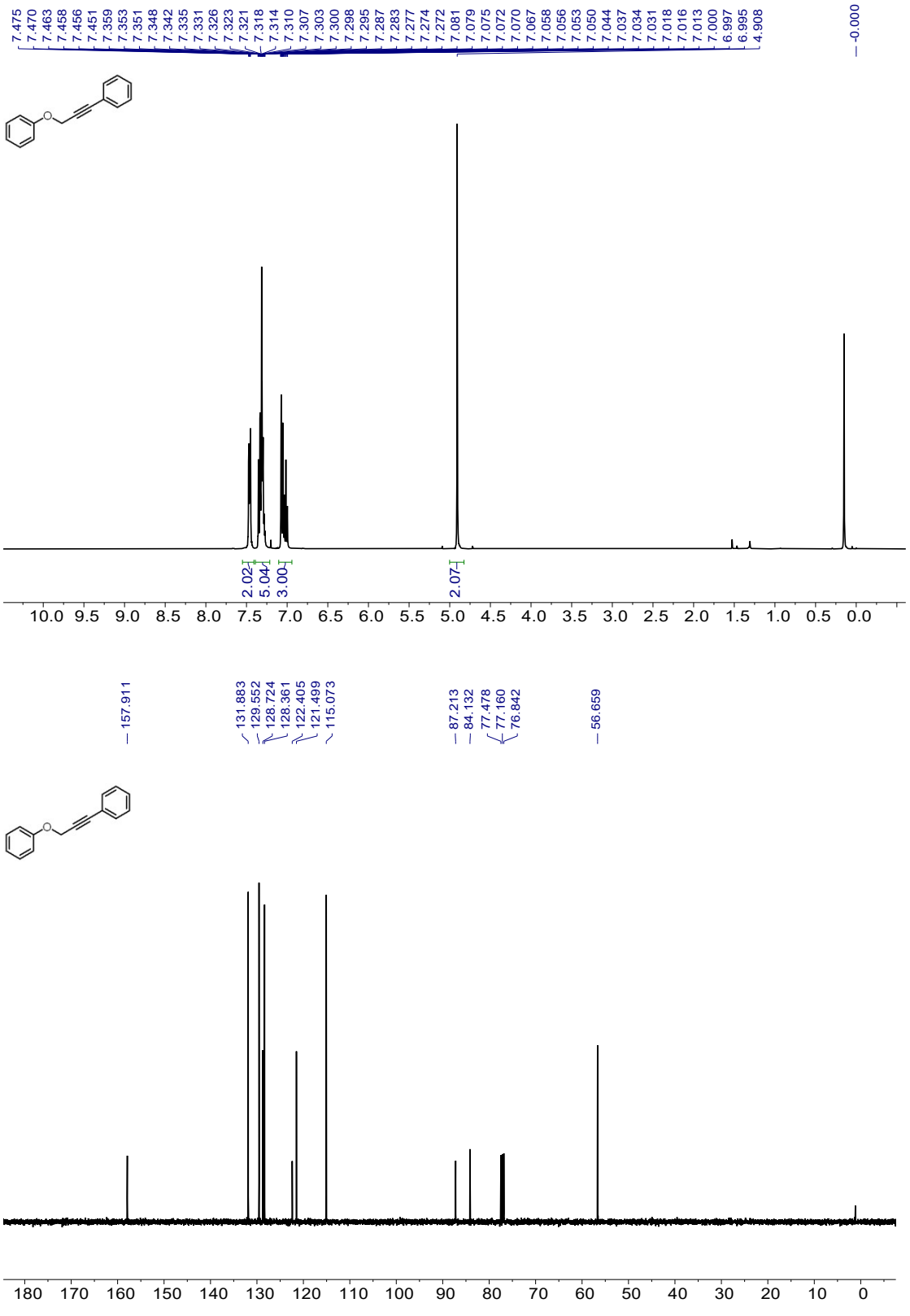
6-phenylhex-5-ynal (4)[24]: The compound was prepared by Procedure and purified by chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) to give the target product (21.7 mg, 42% yield) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.85 (s, 1H), 7.40 – 7.38 (m, 2H), 7.31 – 7.27 (m, 3H), 2.67 (t, *J* = 6.0 Hz, 2H), 2.50 (t, *J* = 5.6 Hz, 2H), 1.98 – 1.92 (m, 2H).

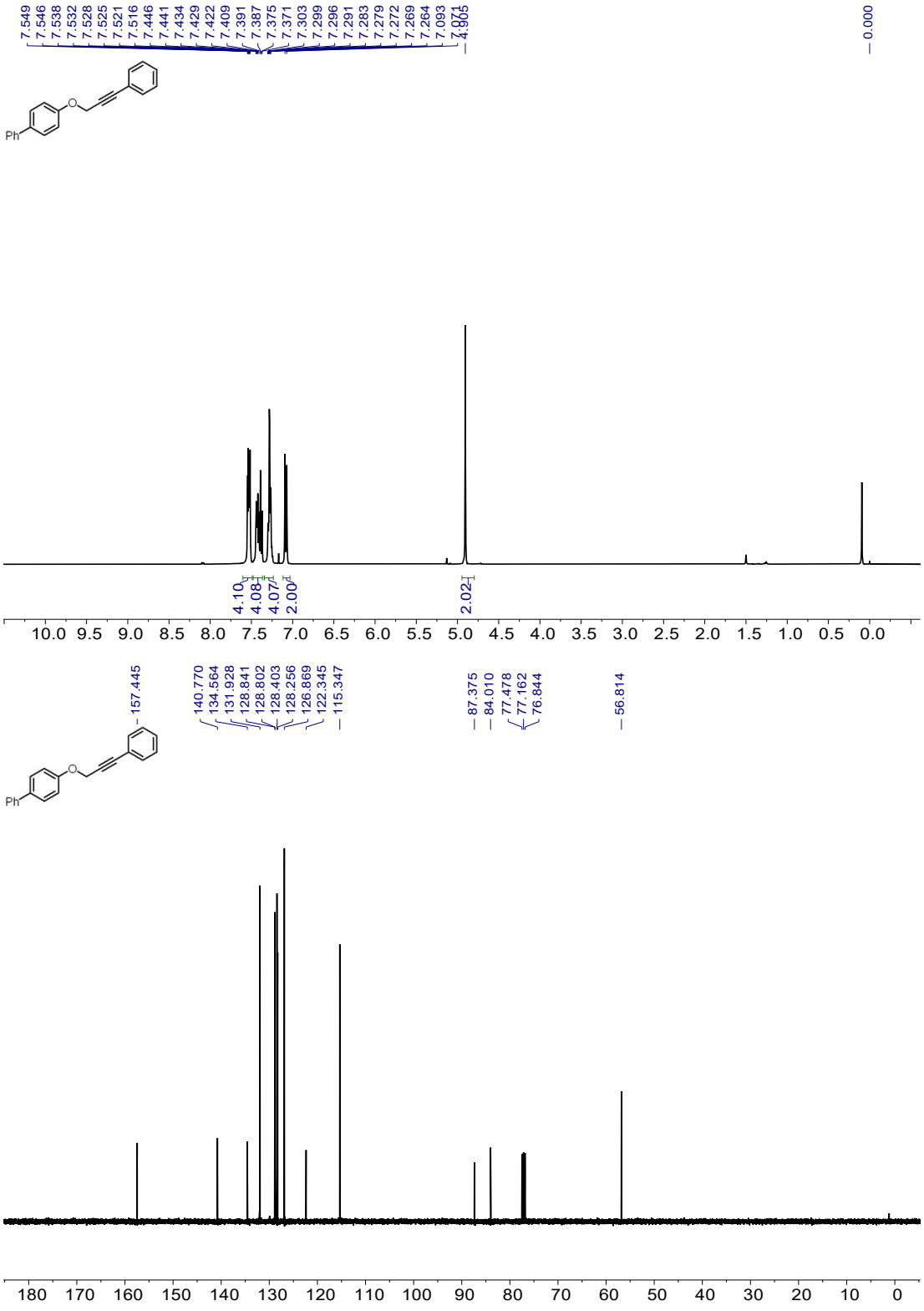
^{13}C NMR (100 MHz, Chloroform-*d*) δ 202.1, 131.7, 128.4, 127.9, 123.7, 88.9, 81.8, 43.0, 21.3, 19.0.

NOTE: Compound 5 decomposes within 5 hrs at room temperature. The phenomenon observed is a color transition from colorless to yellow.

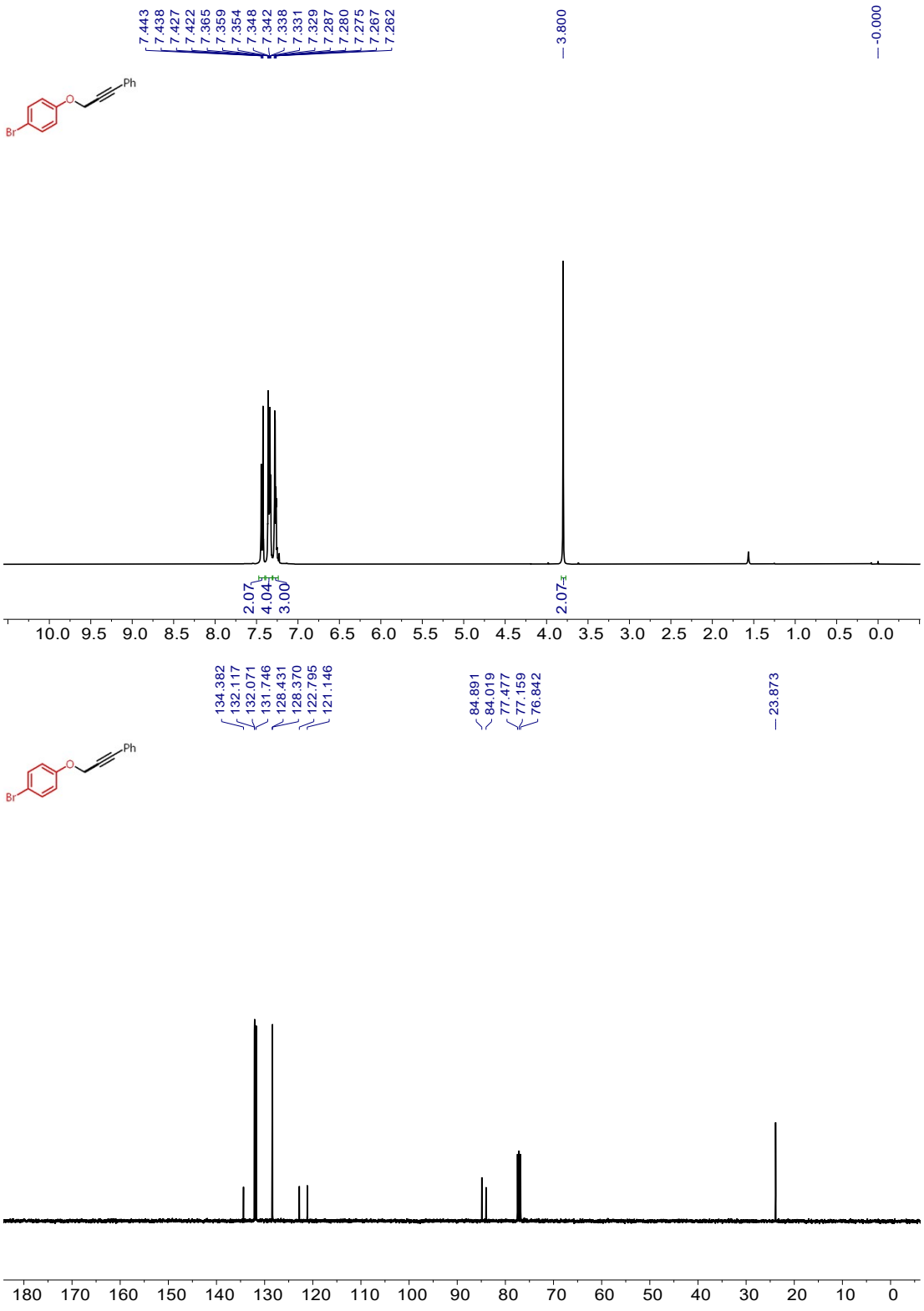
NMR Spectra for compounds 3a-3az, 3aa'-3ae'



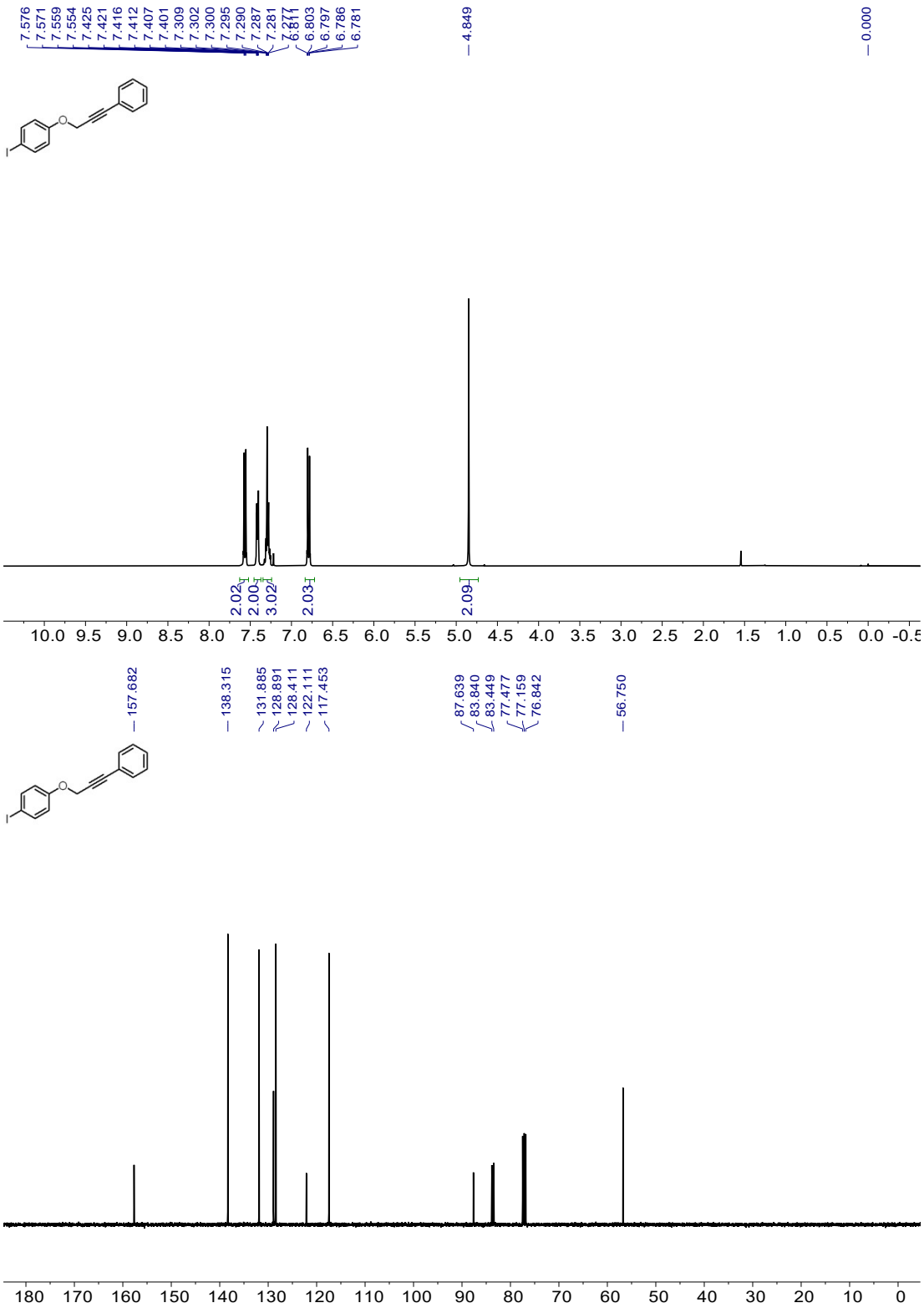
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3a**



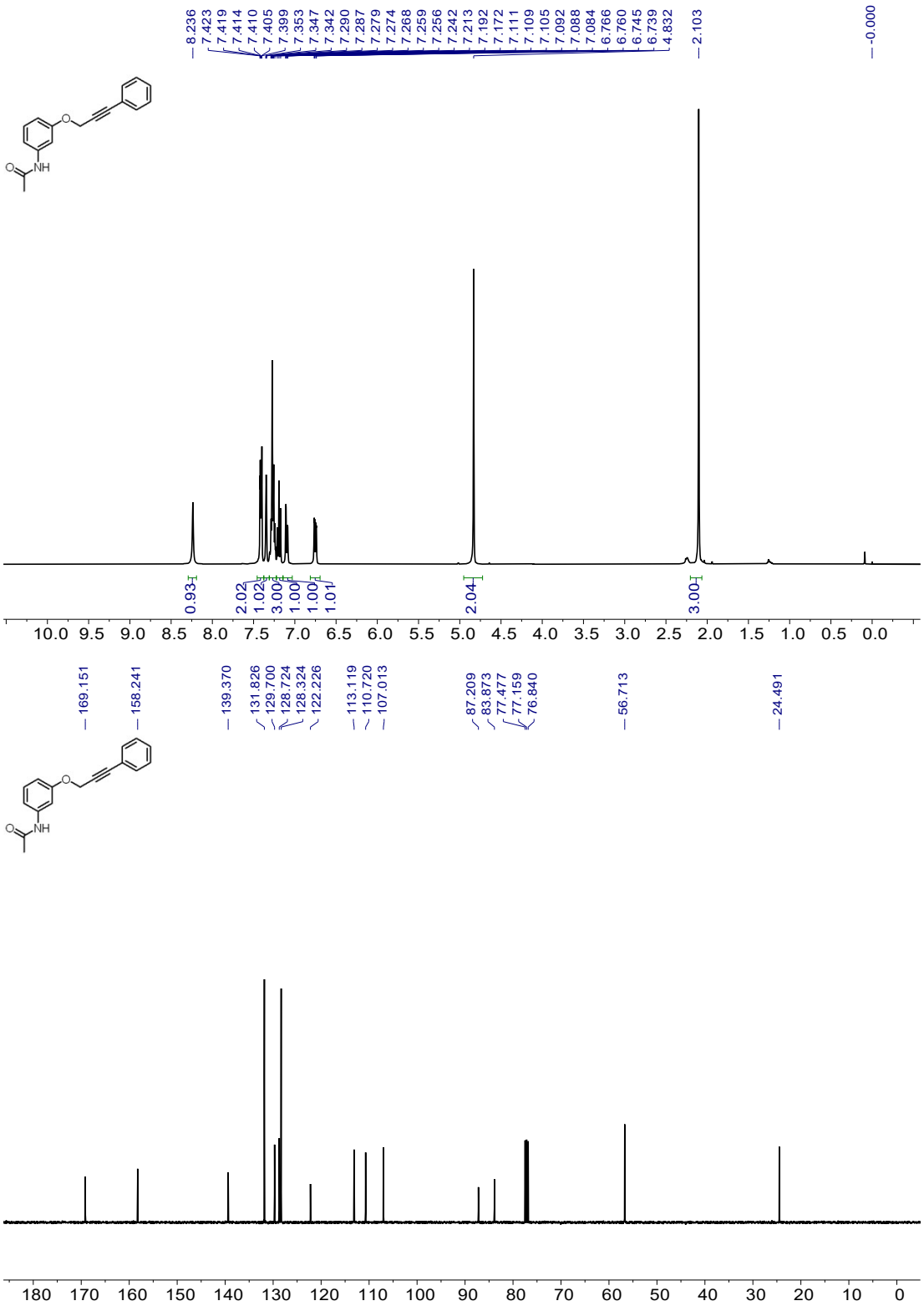
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3b**



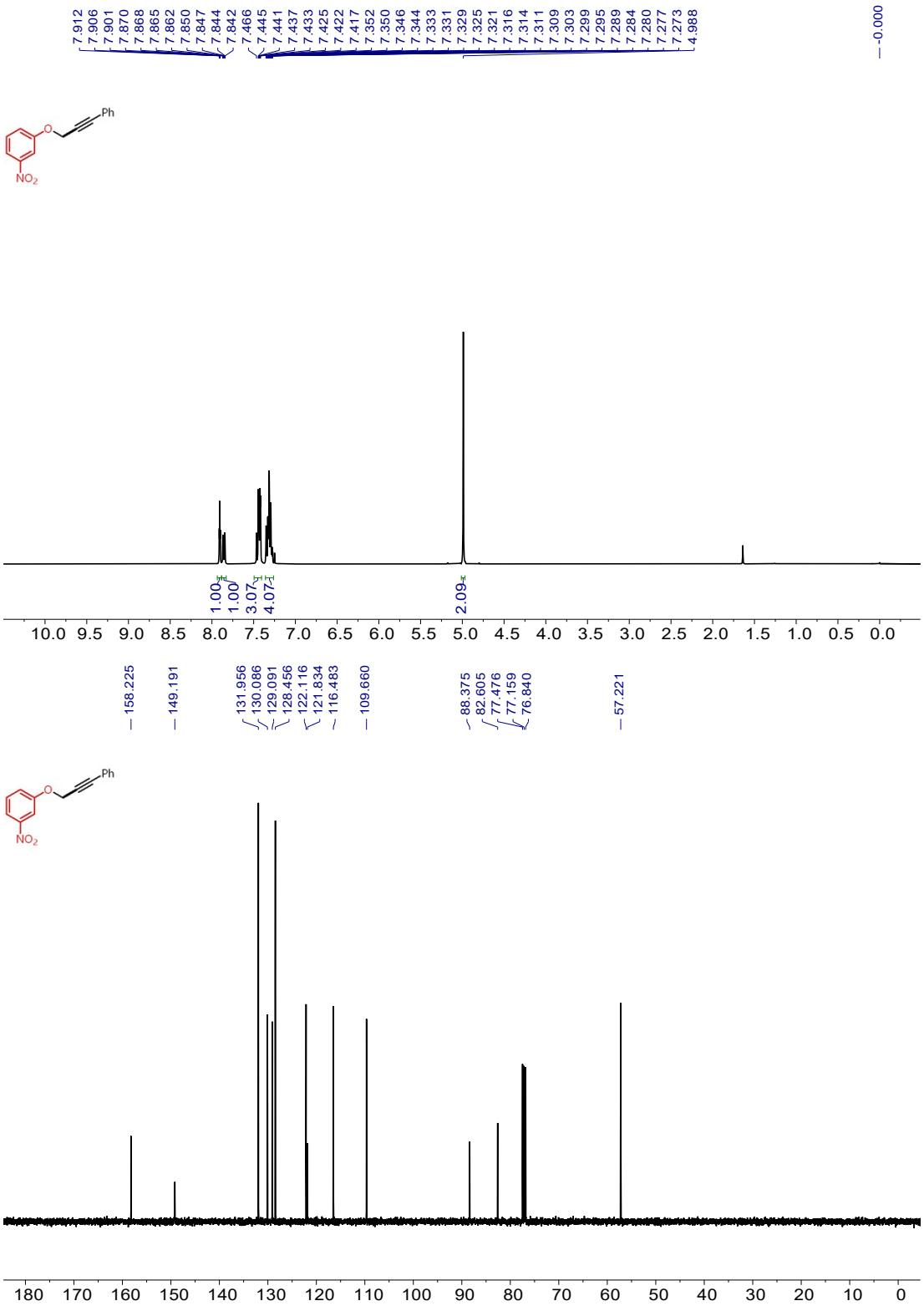
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3c**



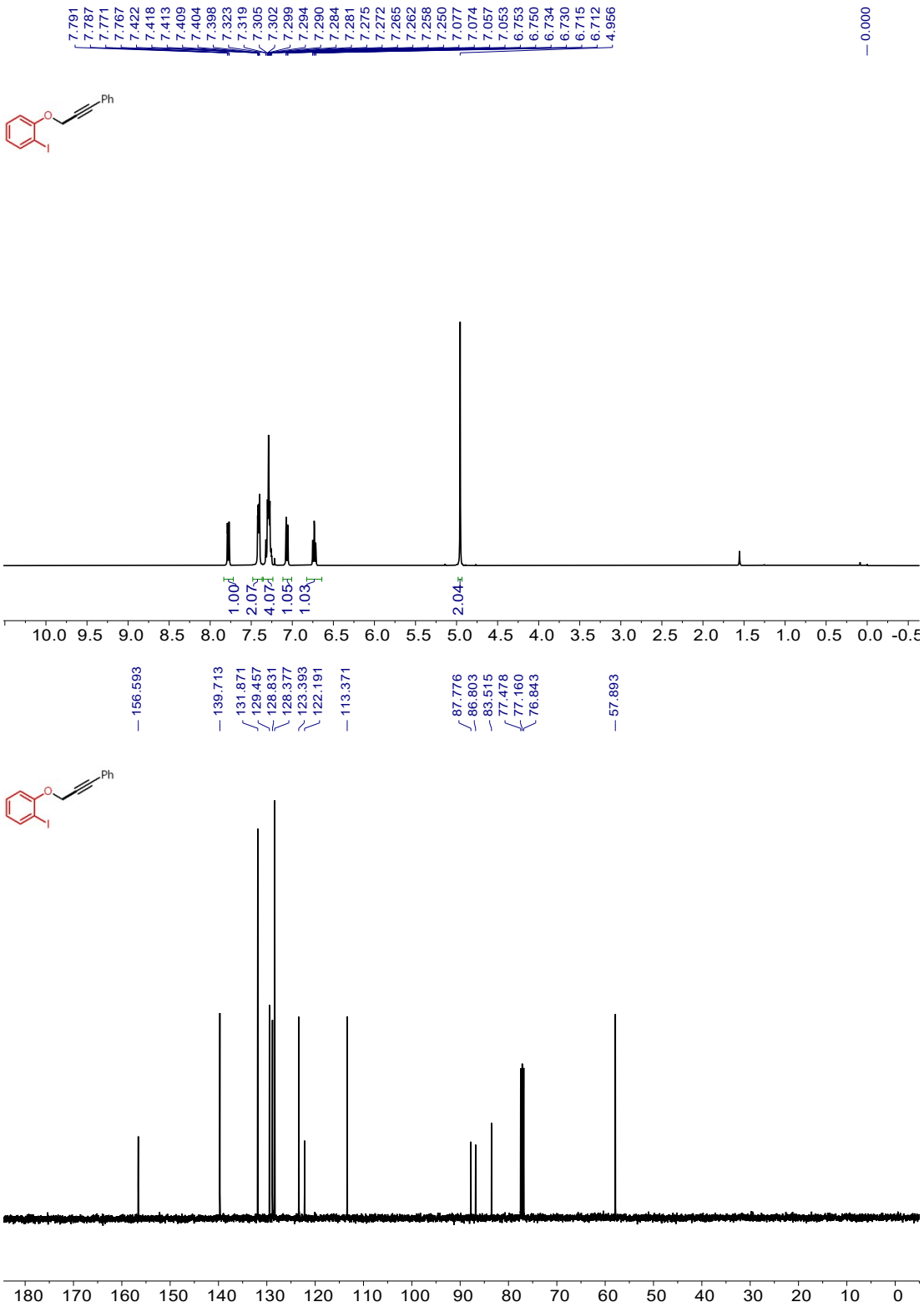
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3d**



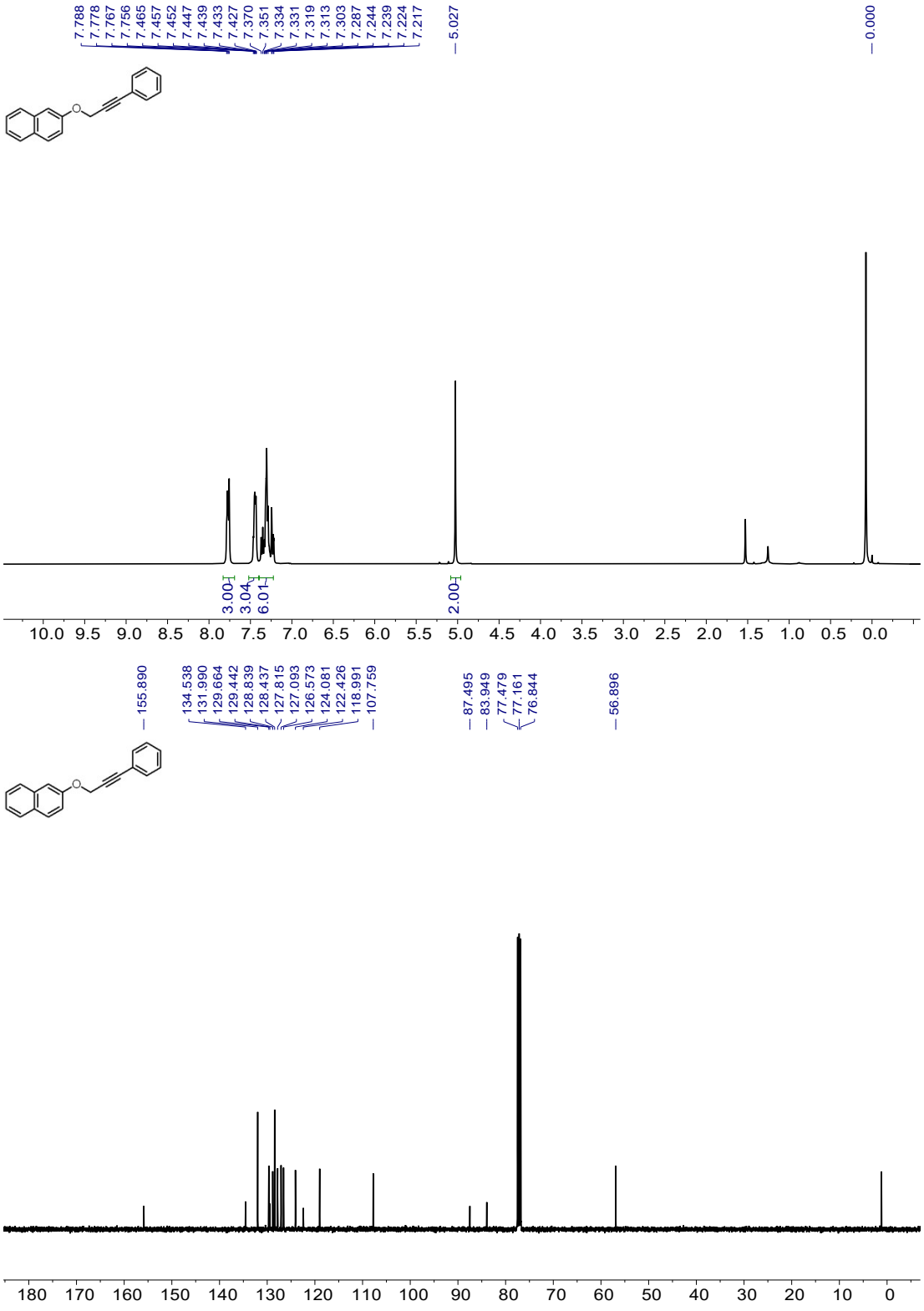
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3e**



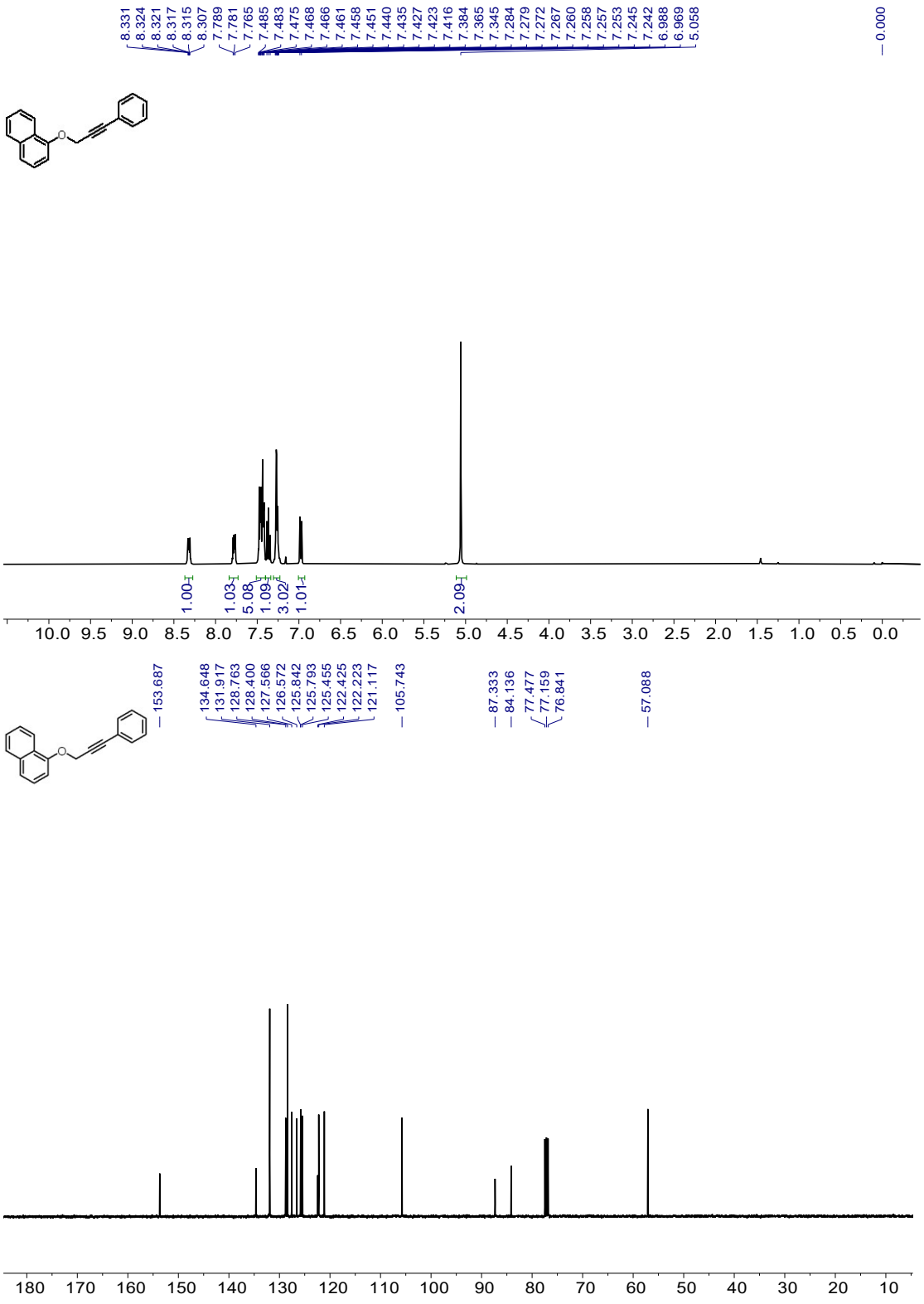
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3f**



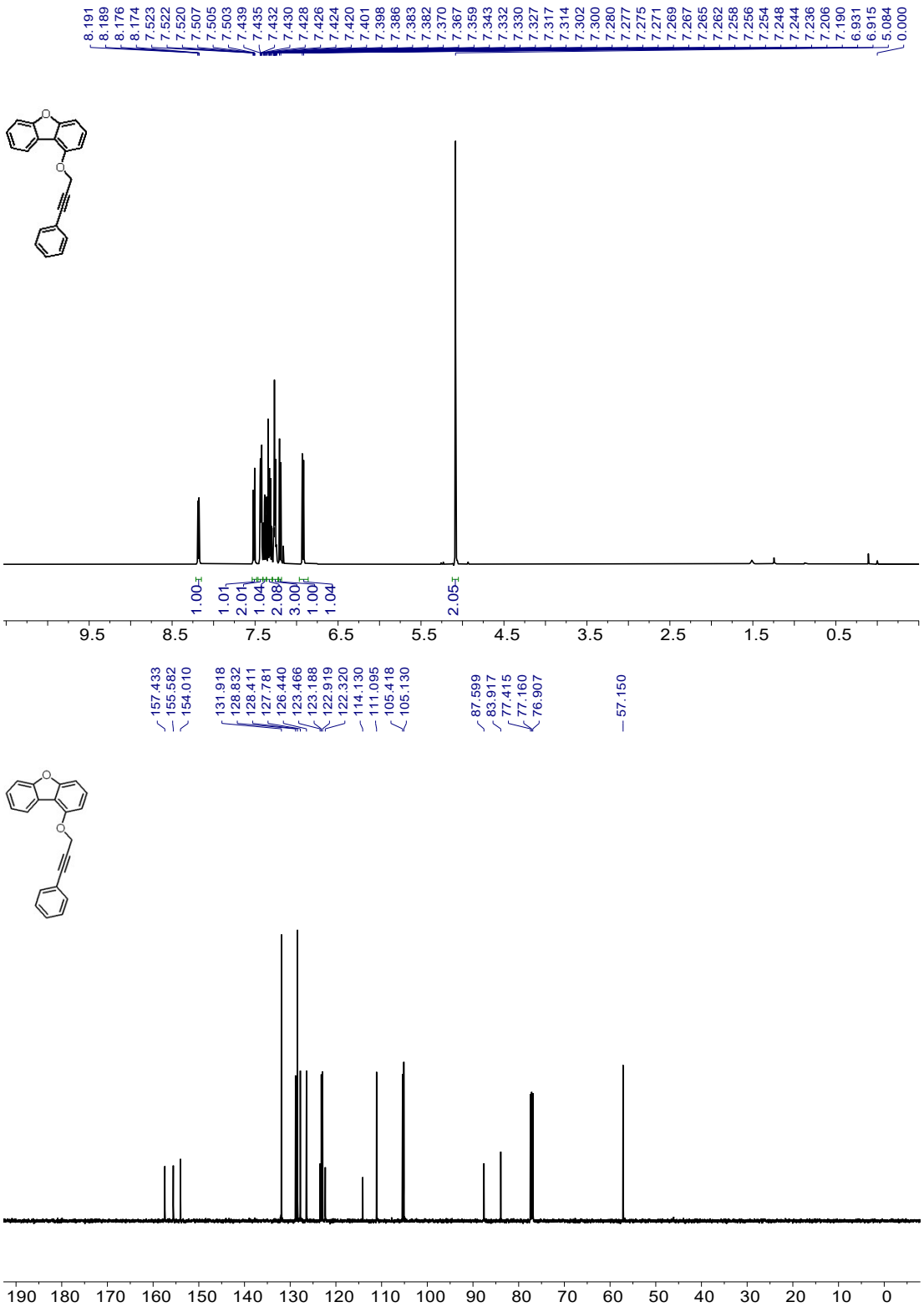
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3g**



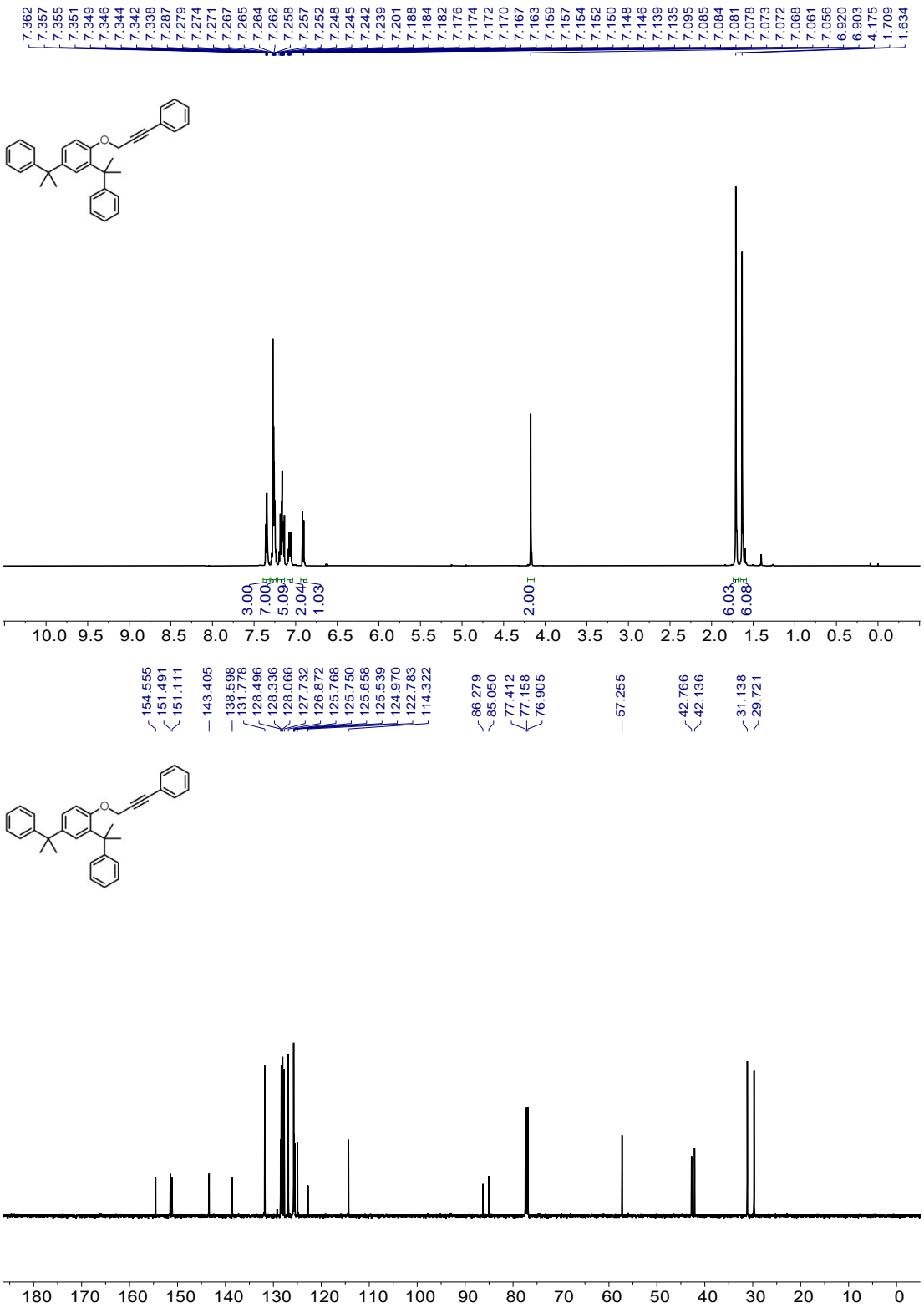
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3h**



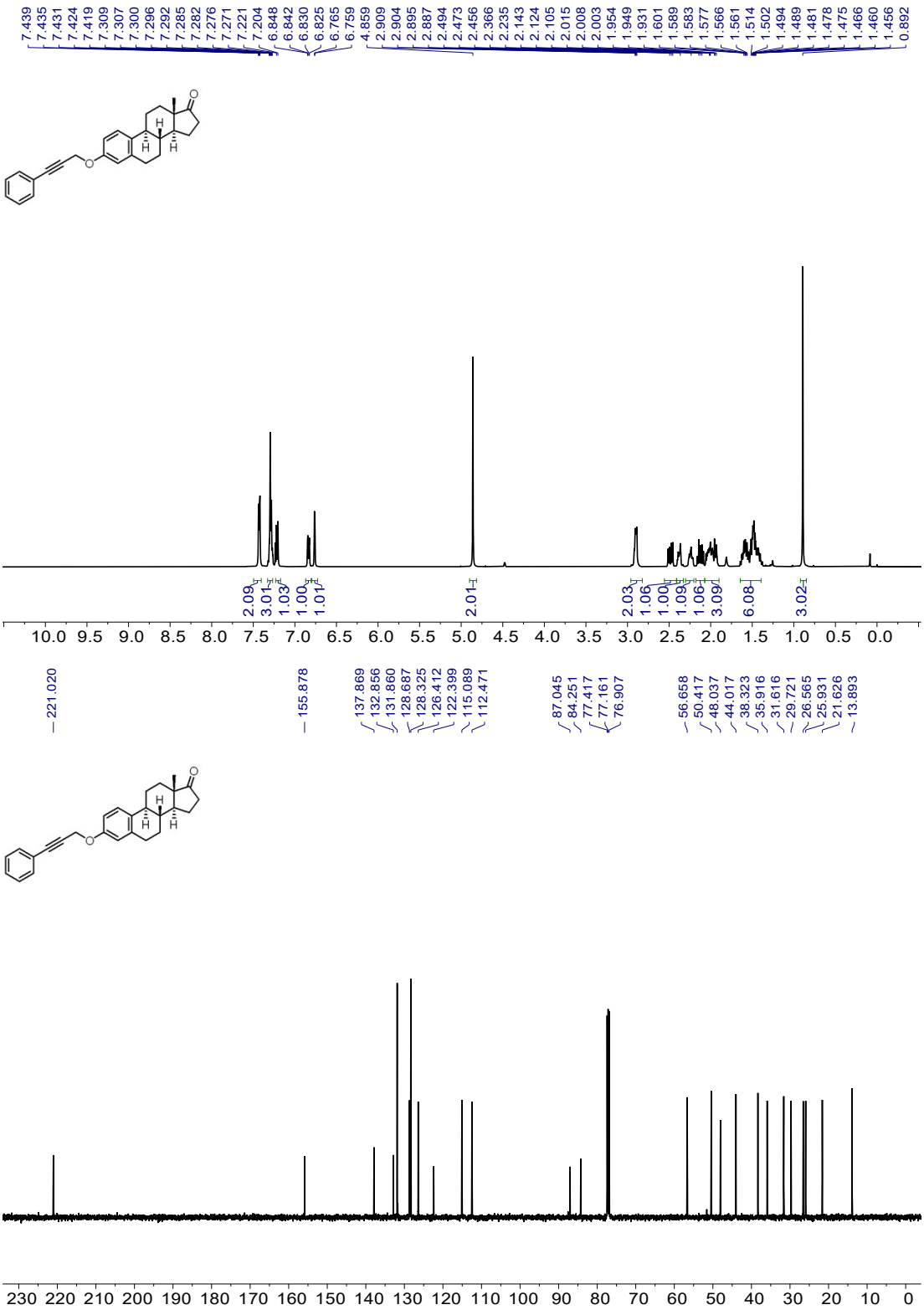
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3i**



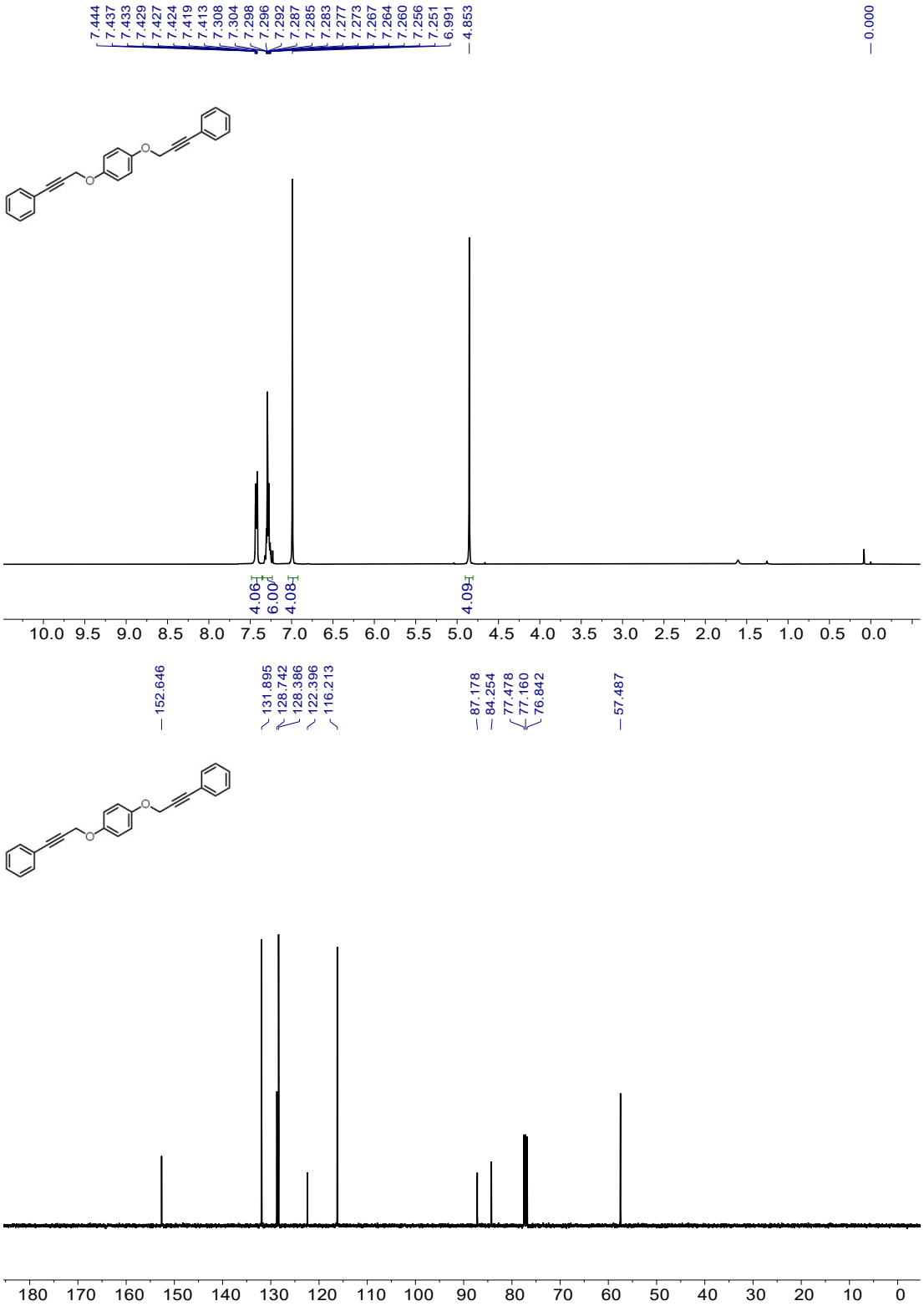
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3j**



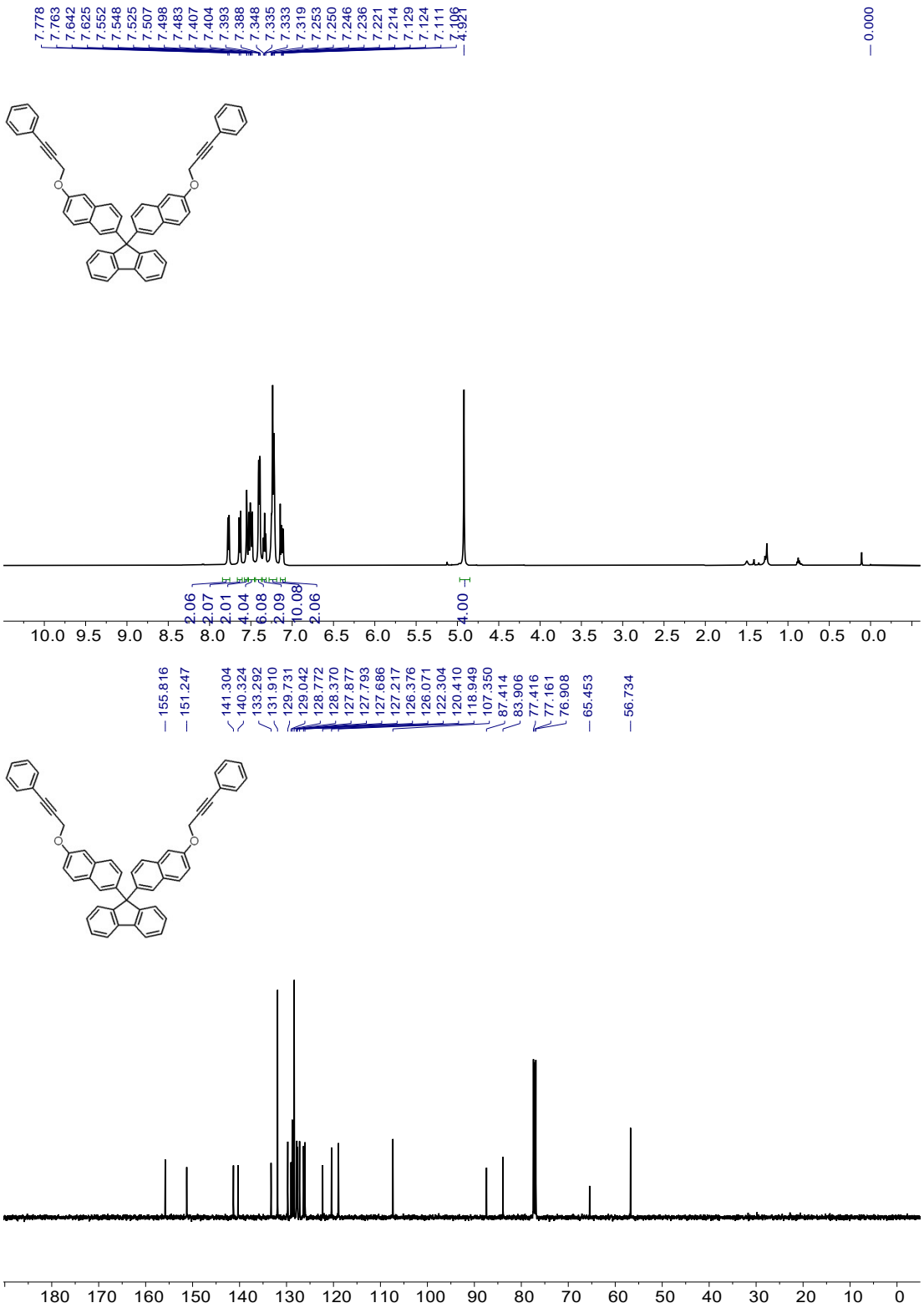
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3k**



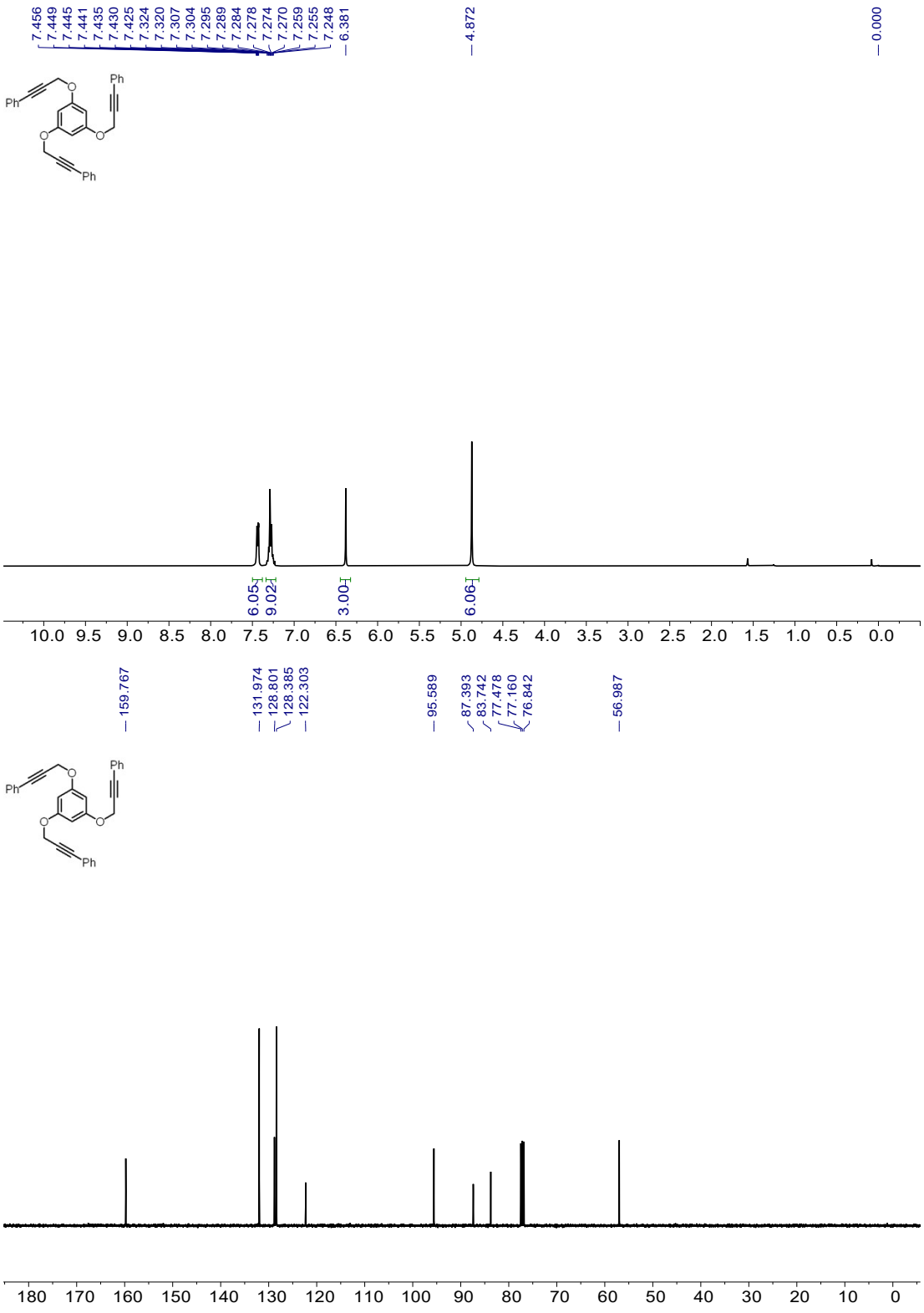
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3l**



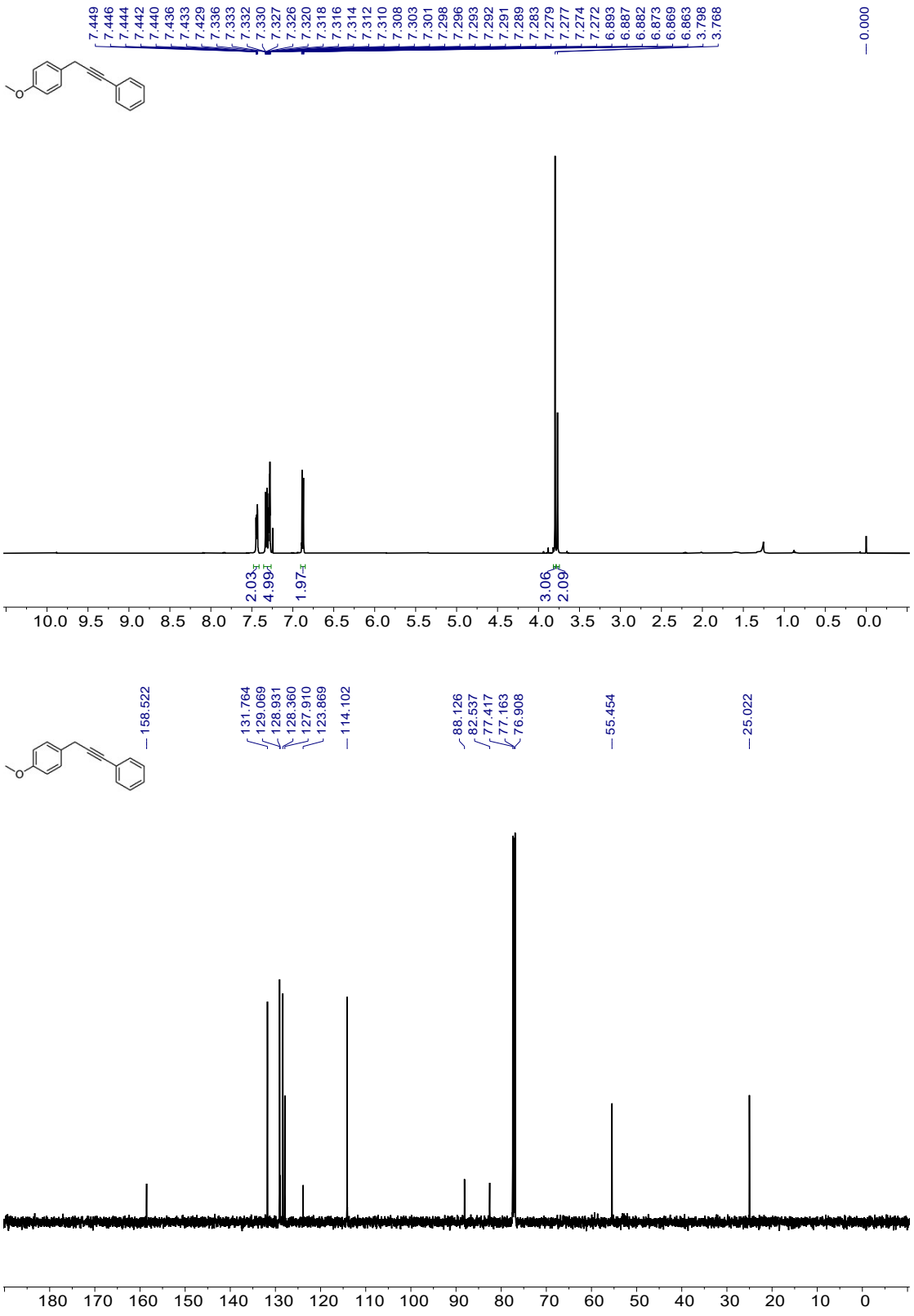
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3m**



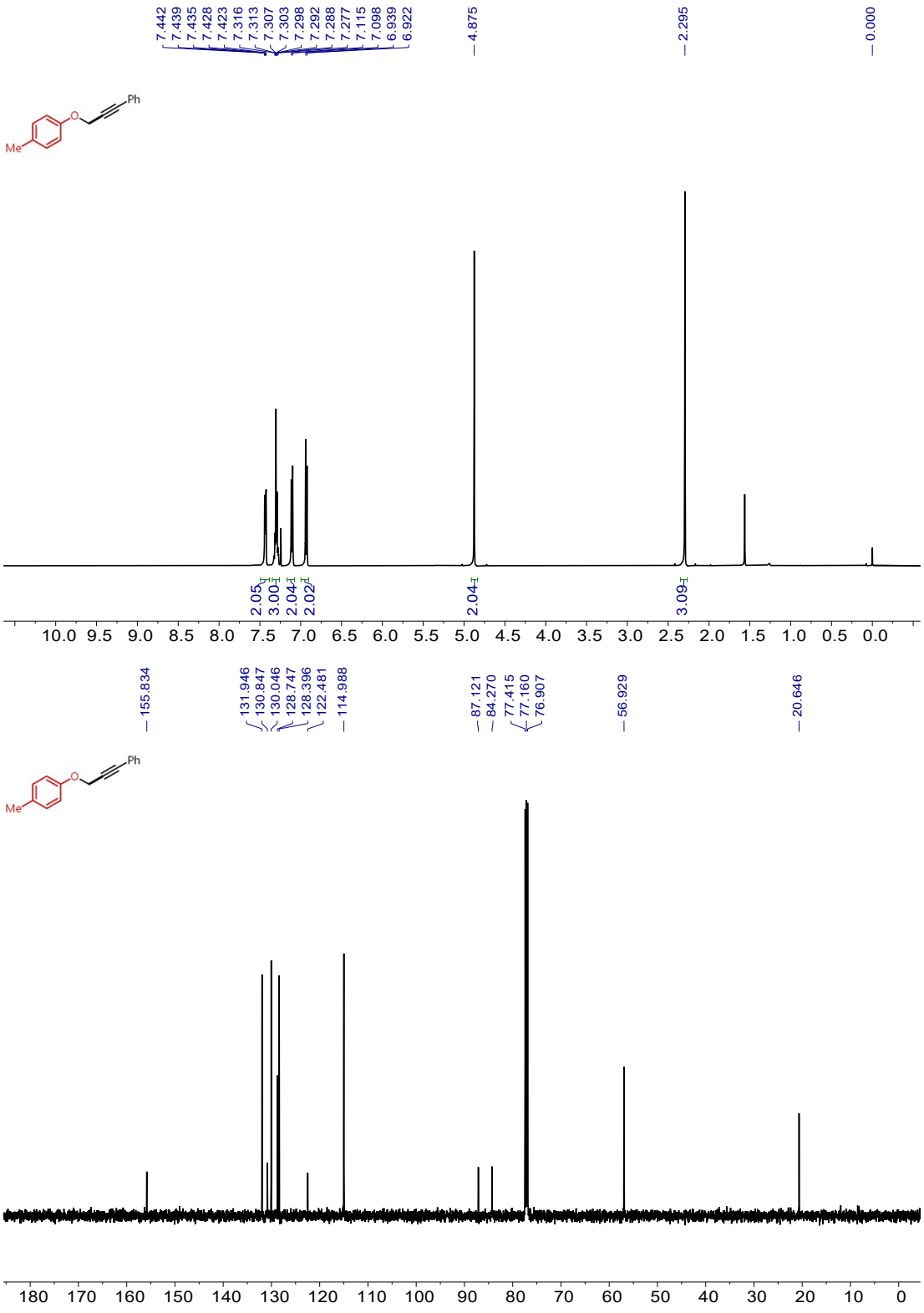
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3n**



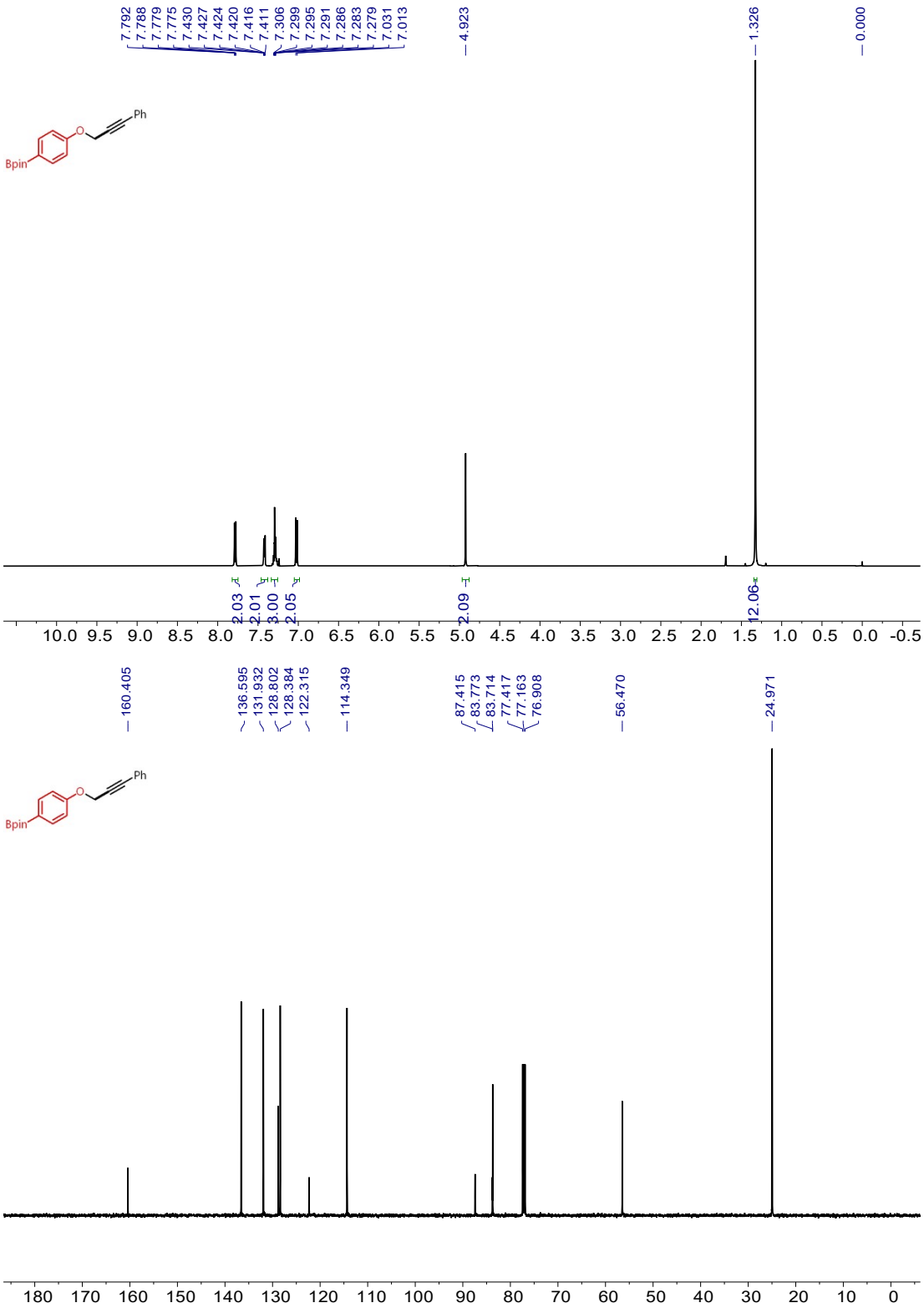
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3o**



^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3p-1**



^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3p-2**


7.792
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7.775
7.430
7.427
7.424
7.420
7.416
7.411
7.306
7.299
7.295
7.291
7.286
7.283
7.279
7.031
7.013
4.923
1.326
0.000
Ph
O
Bpin
2.03
2.01
3.00
2.05
2.09
12.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
160.405
136.595
131.932
128.802
128.384
122.315
114.349
87.415
83.773
83.714
77.417
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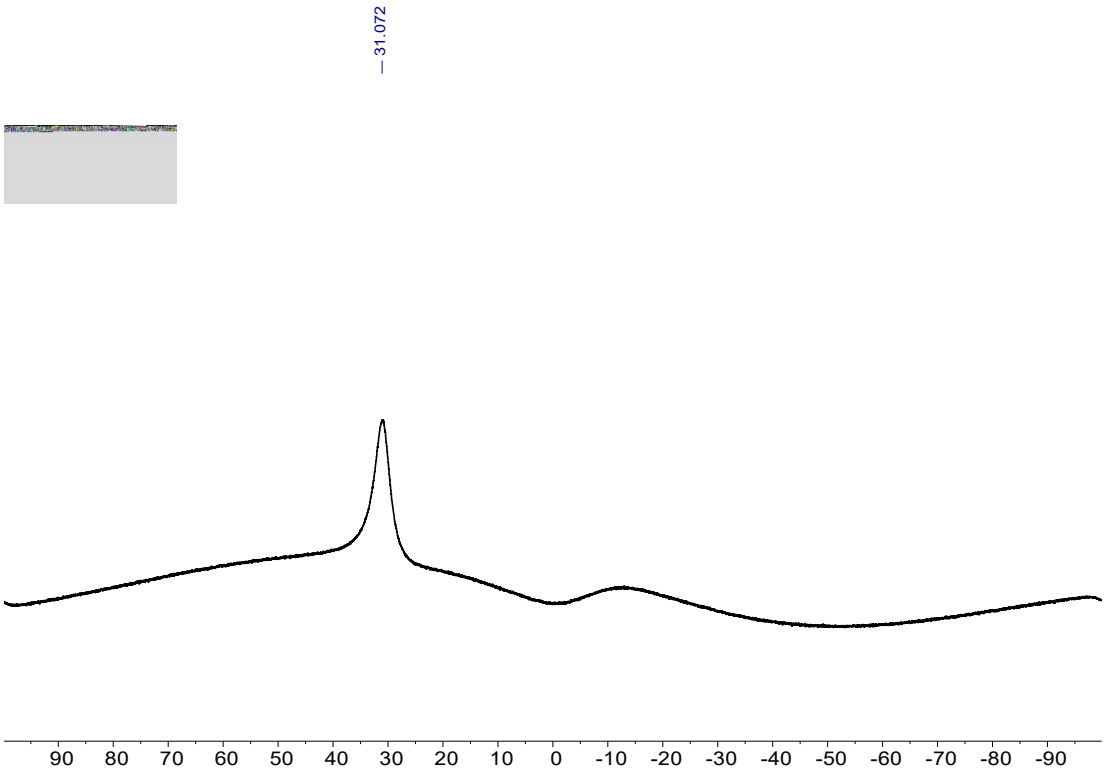
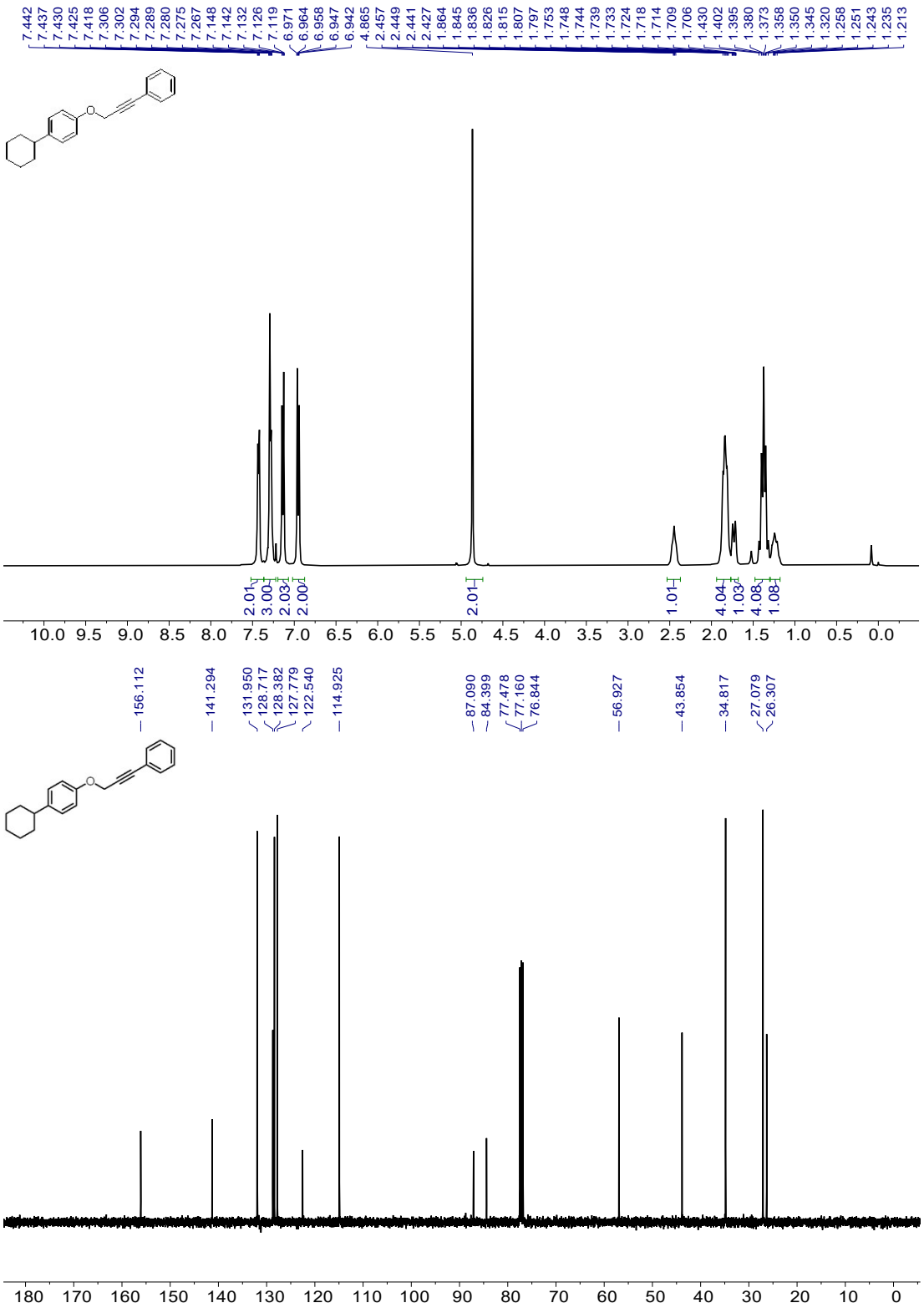
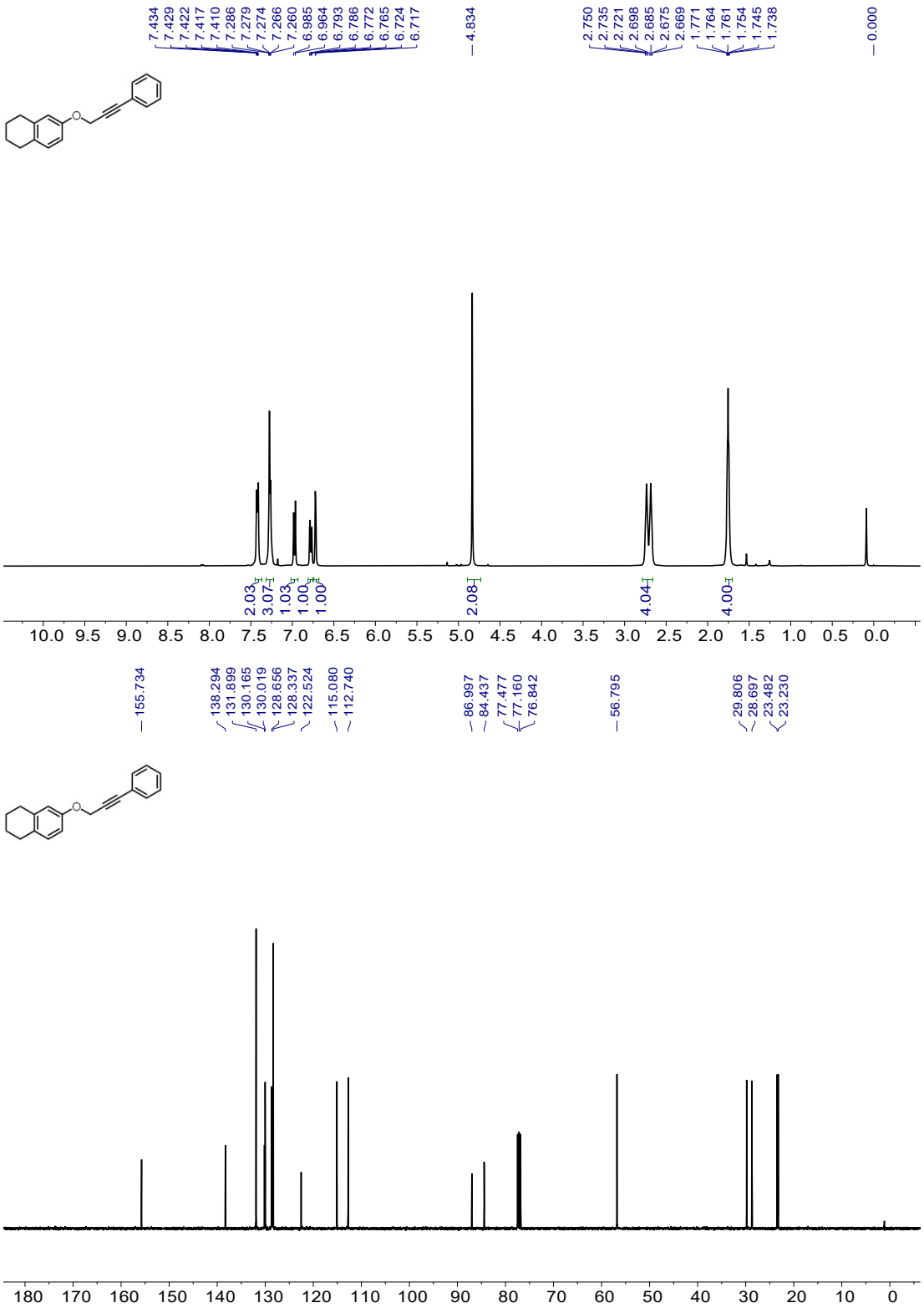
76.908
56.470
24.971
Ph
O
Bpin
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



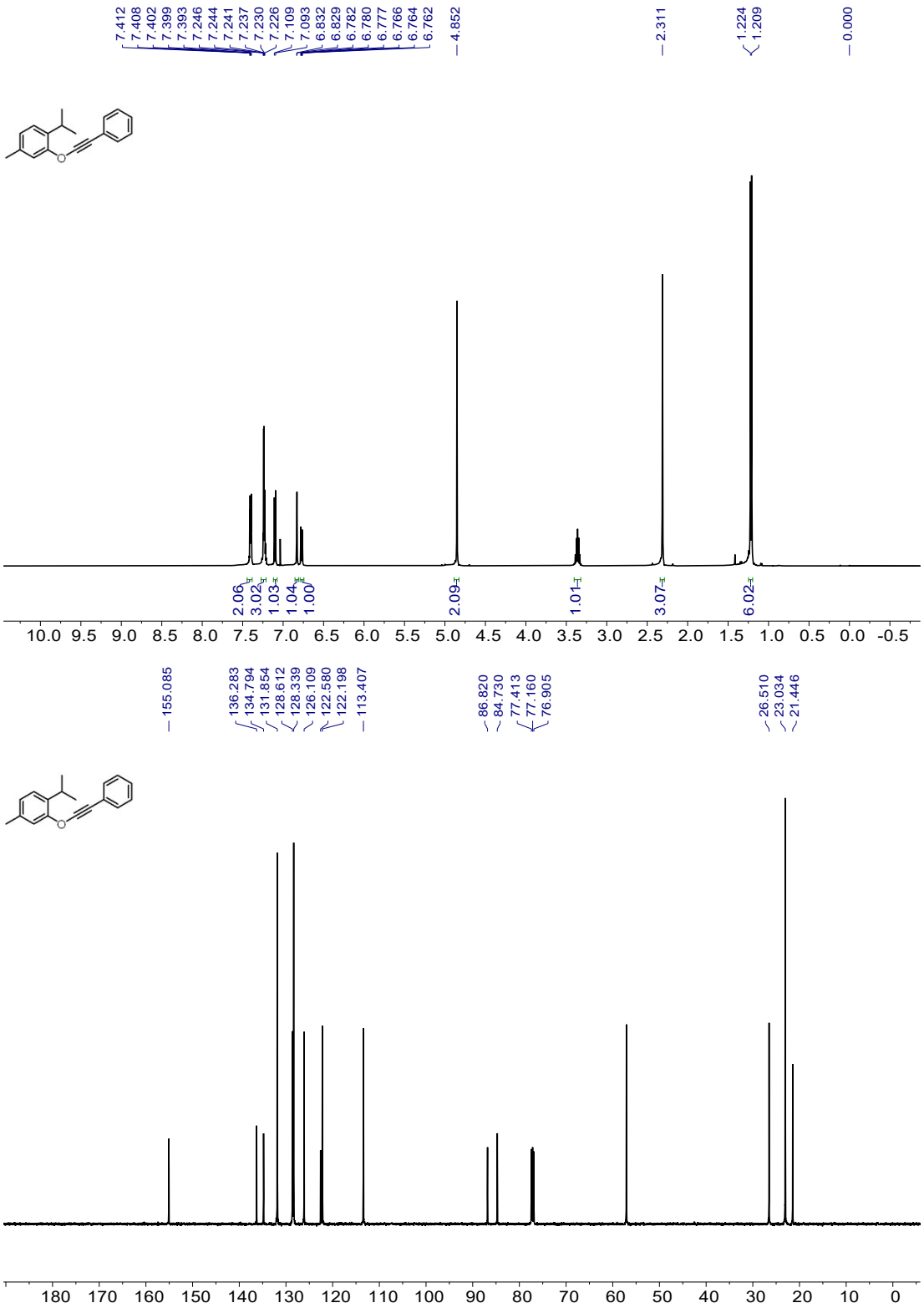
^{1}H NMR ($CDCl_3$, 400 MHz),^{13}C NMR ($CDCl_3$, 100 MHz) and ^{11}B NMR (160 MHz) spectrum of **3q**



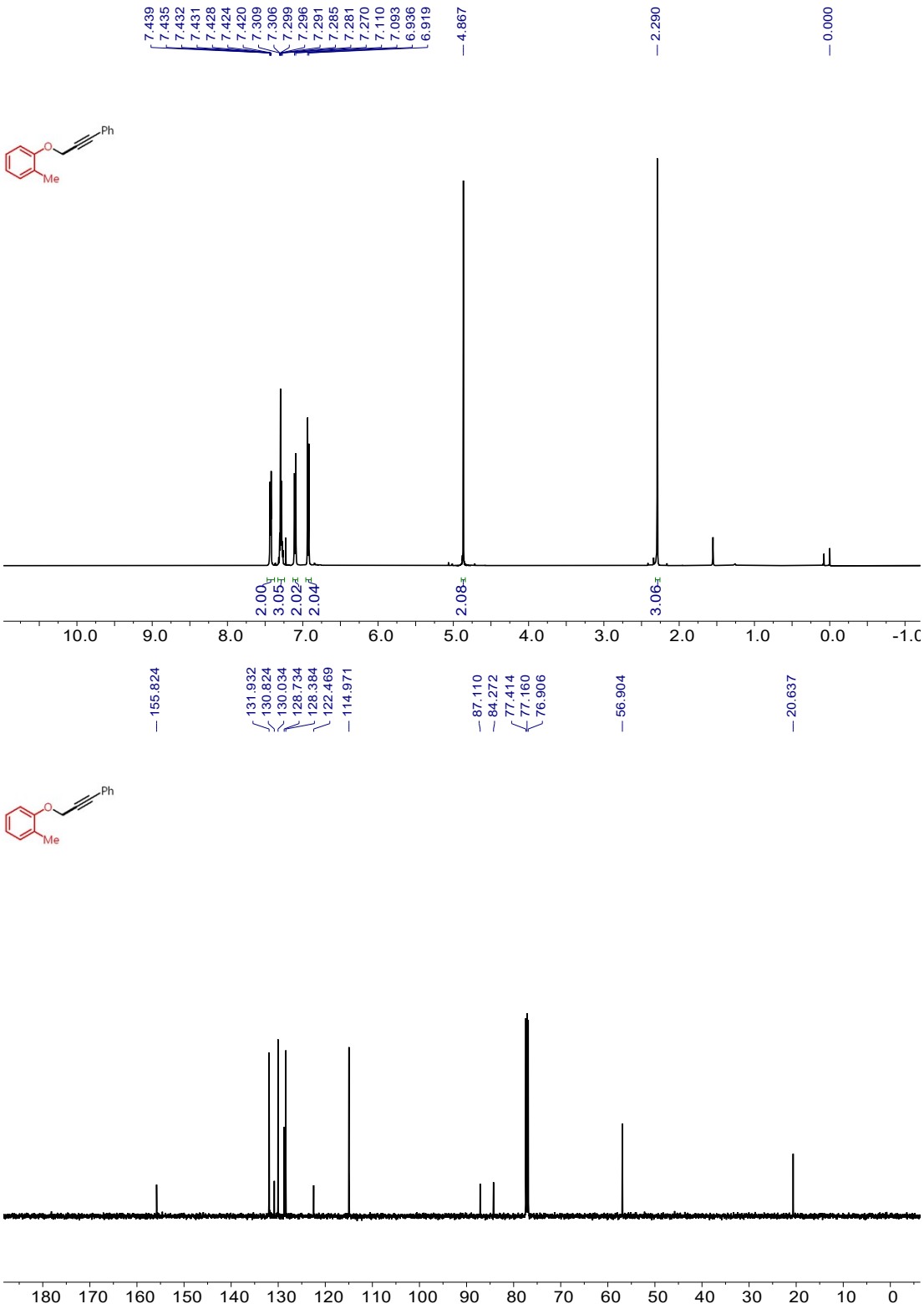
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3r**



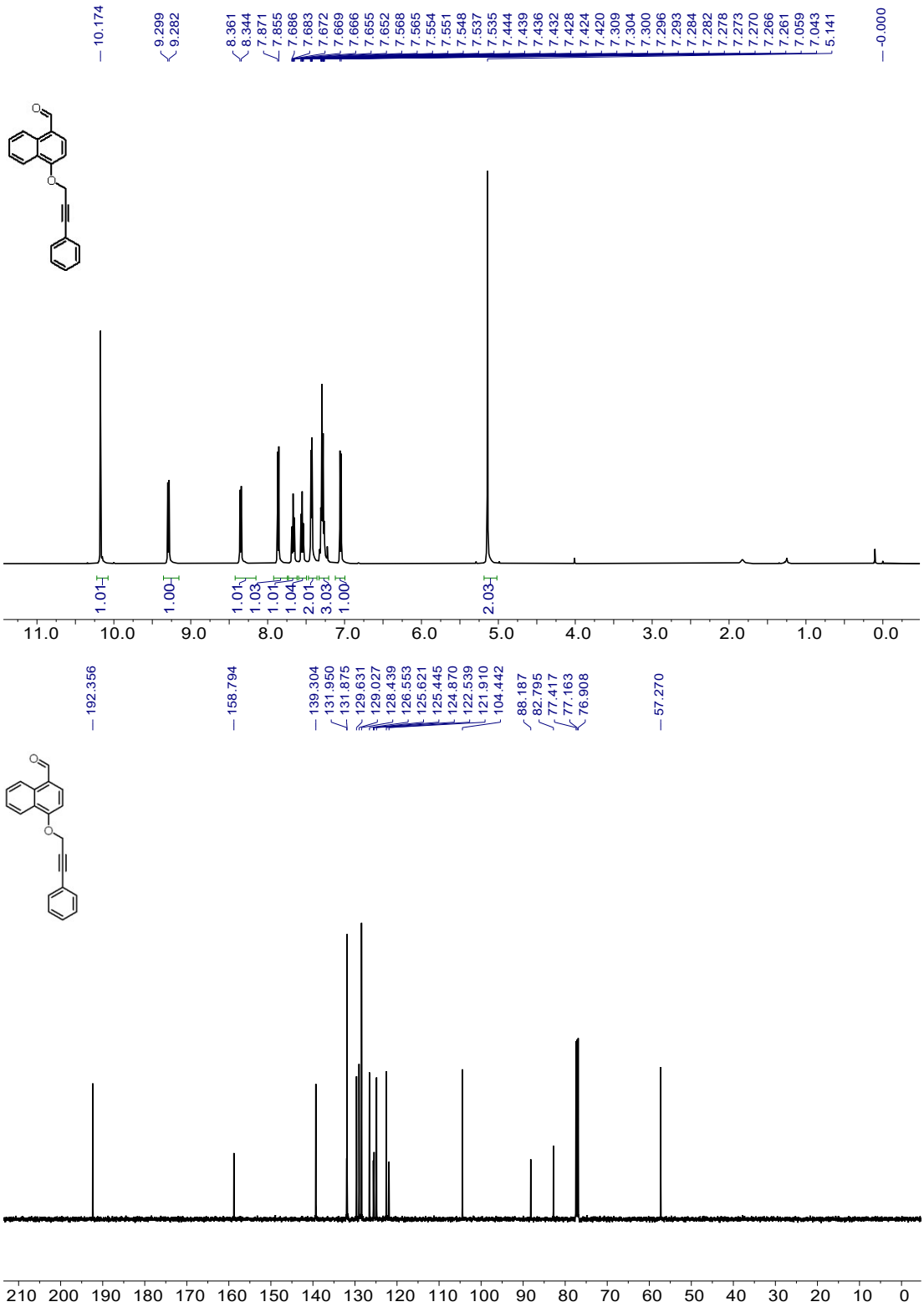
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3s**



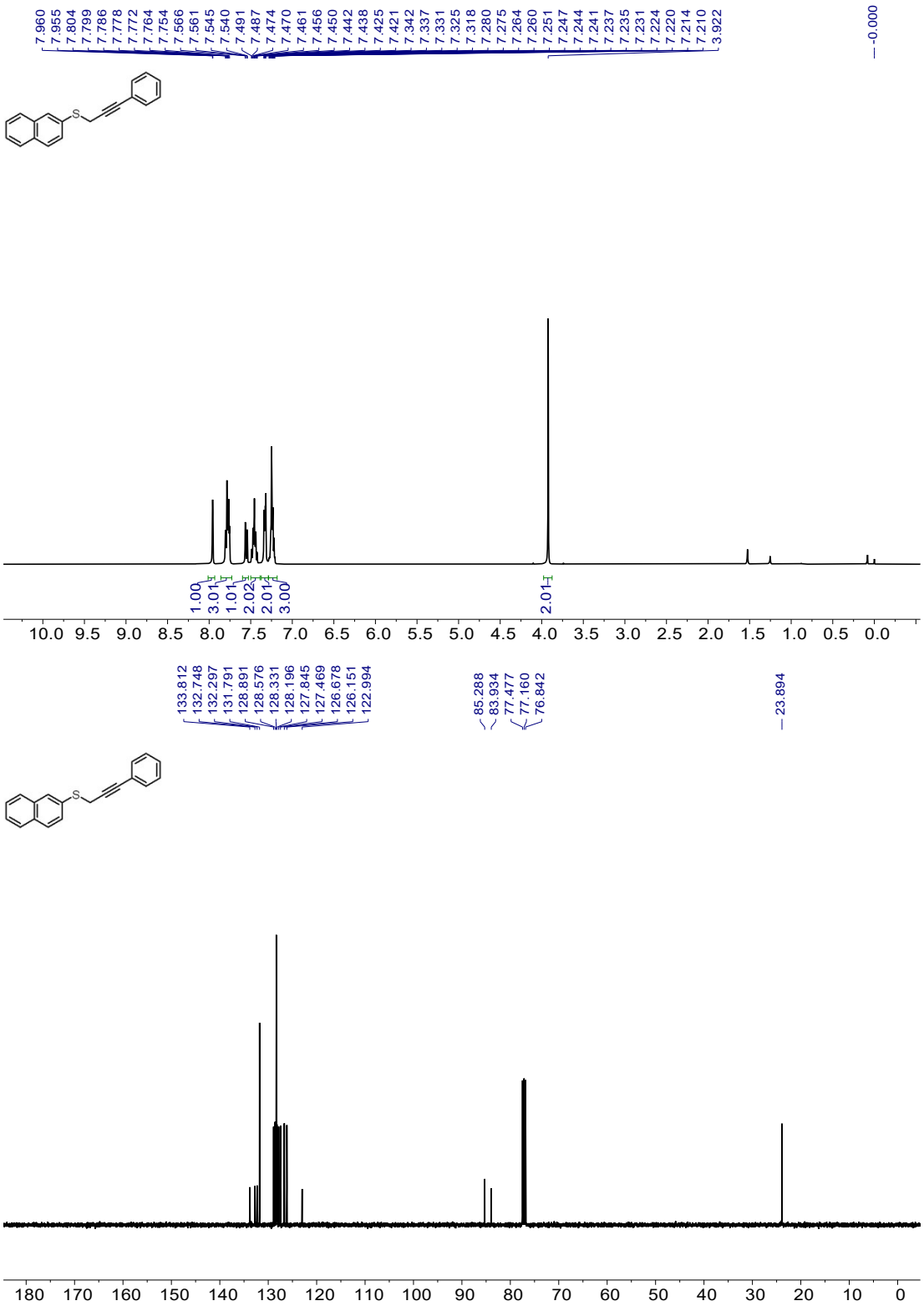
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3t**



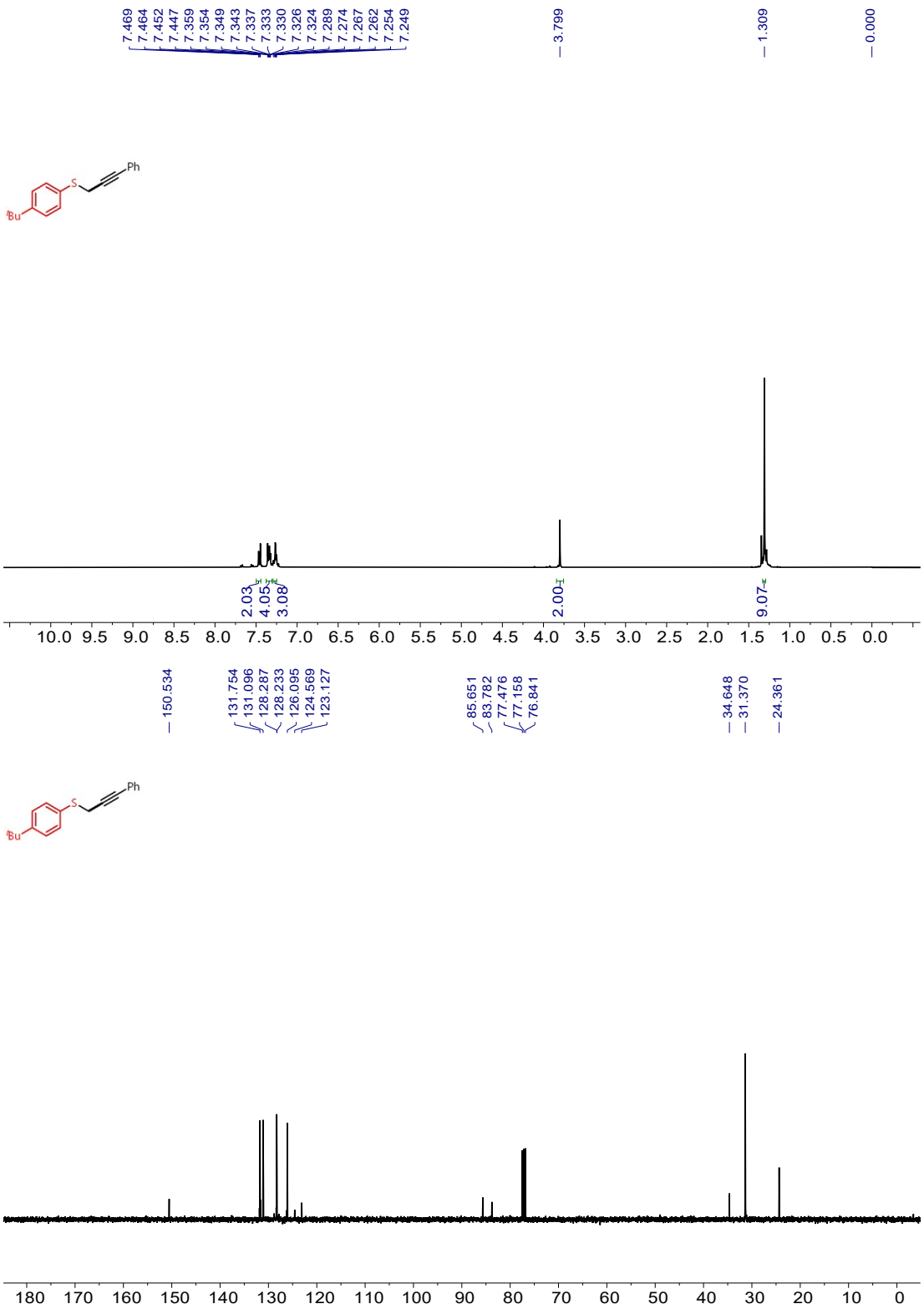
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3u**



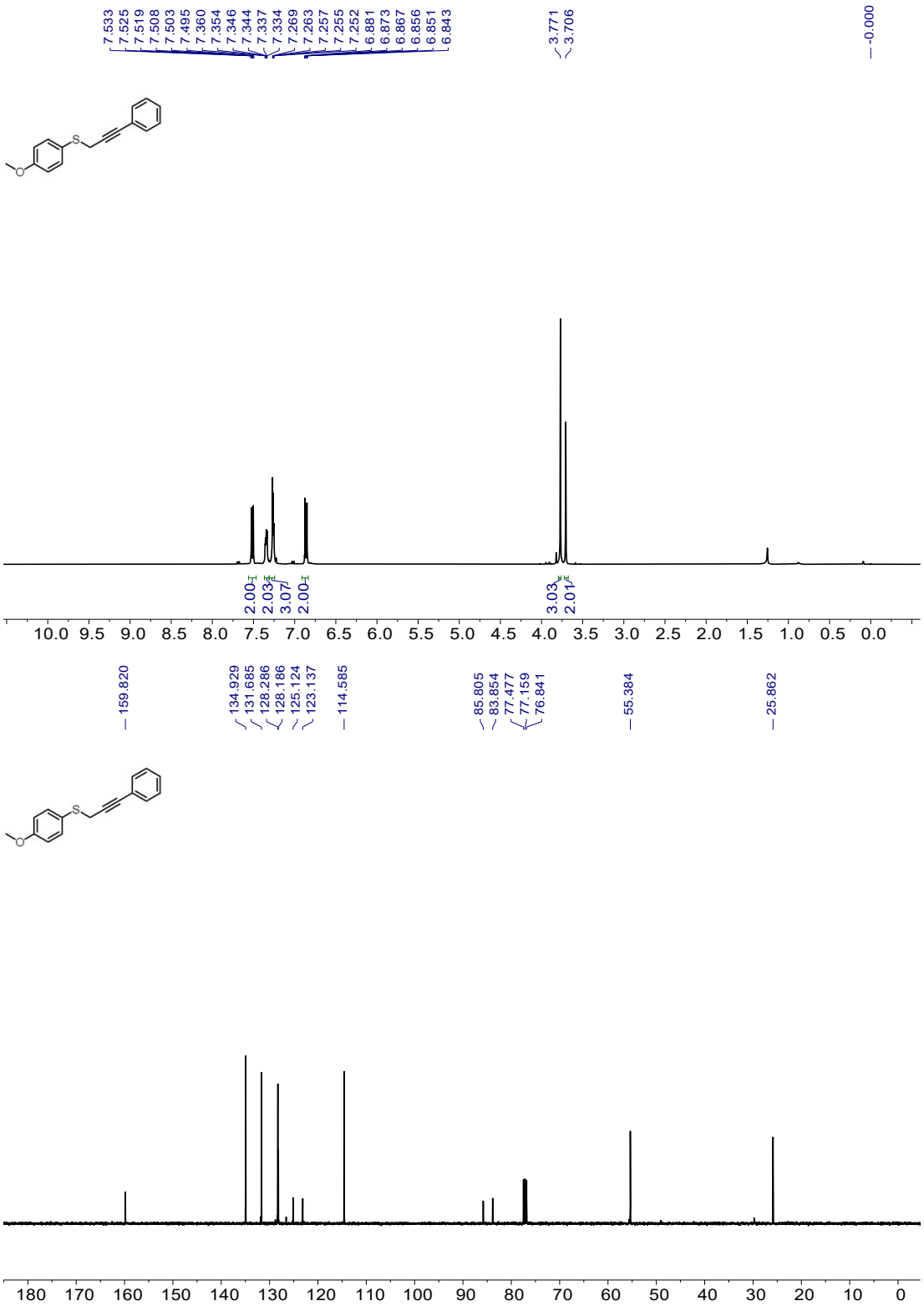
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3v**



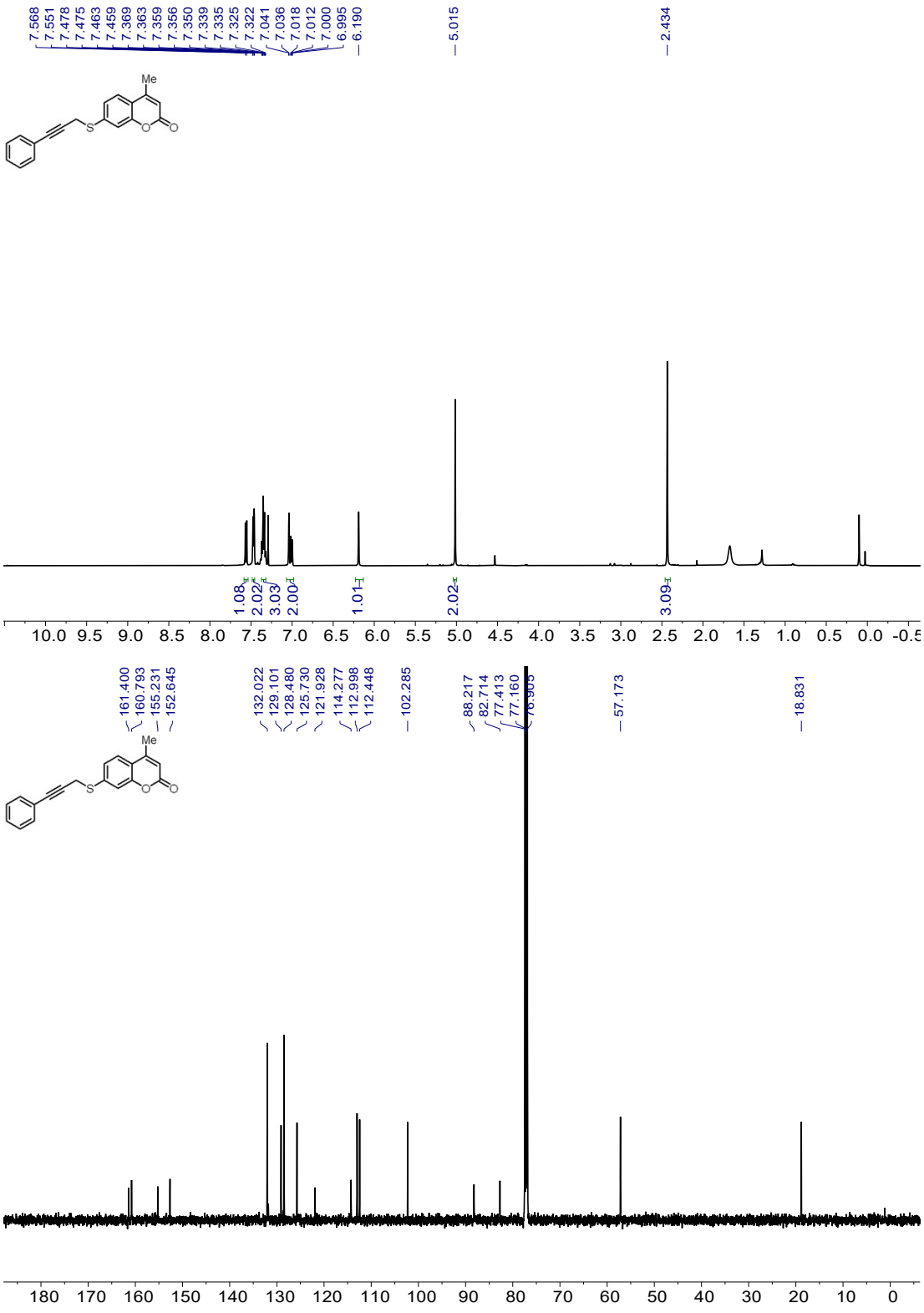
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3w**



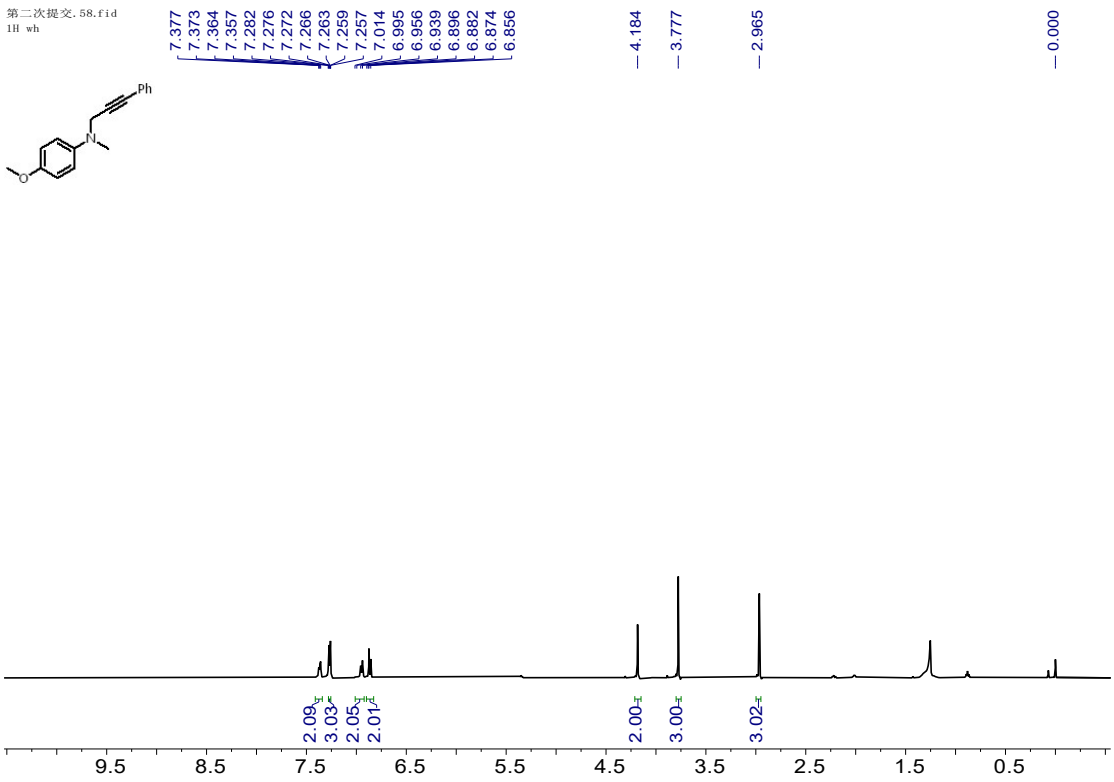
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3x**



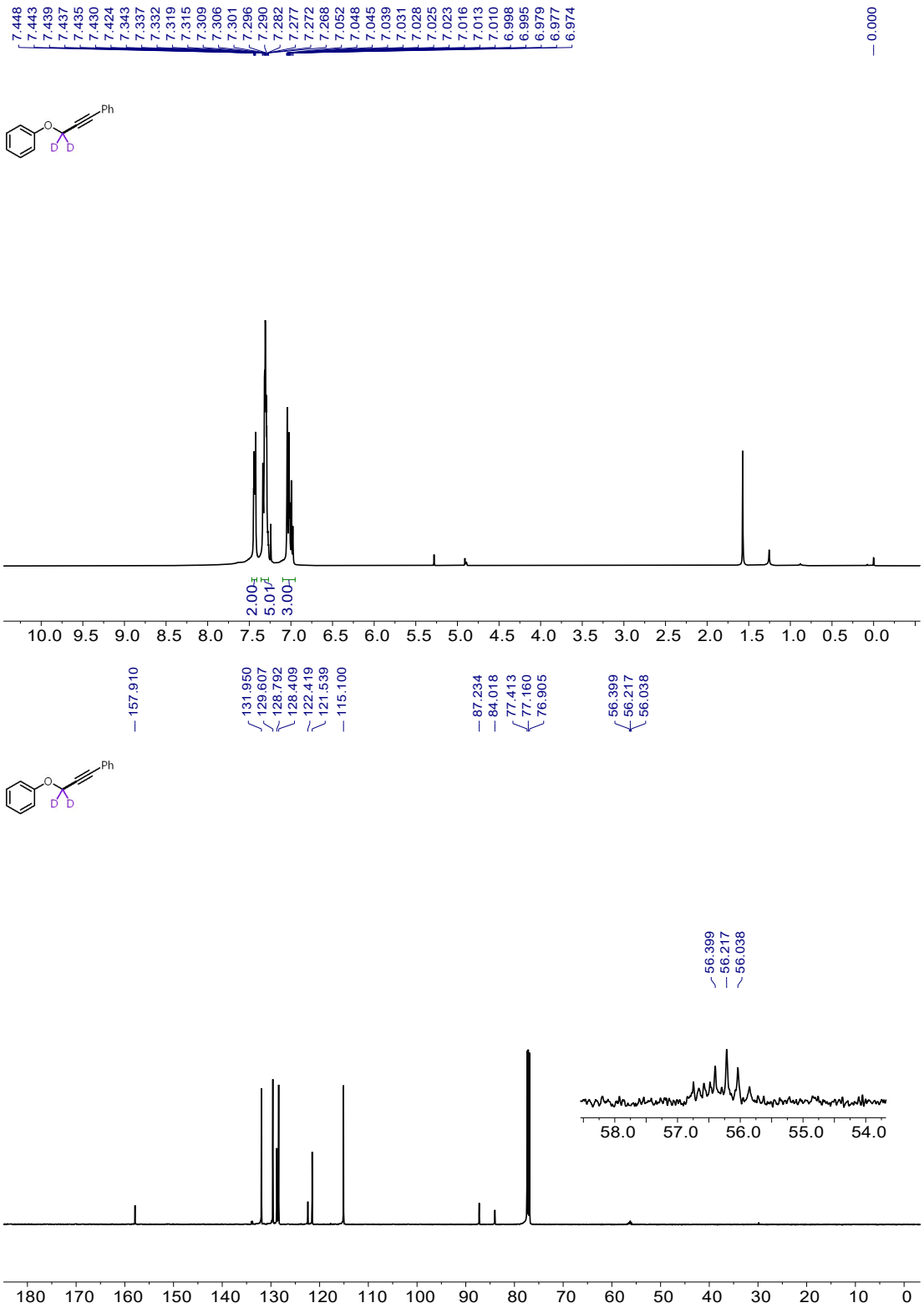
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3y**



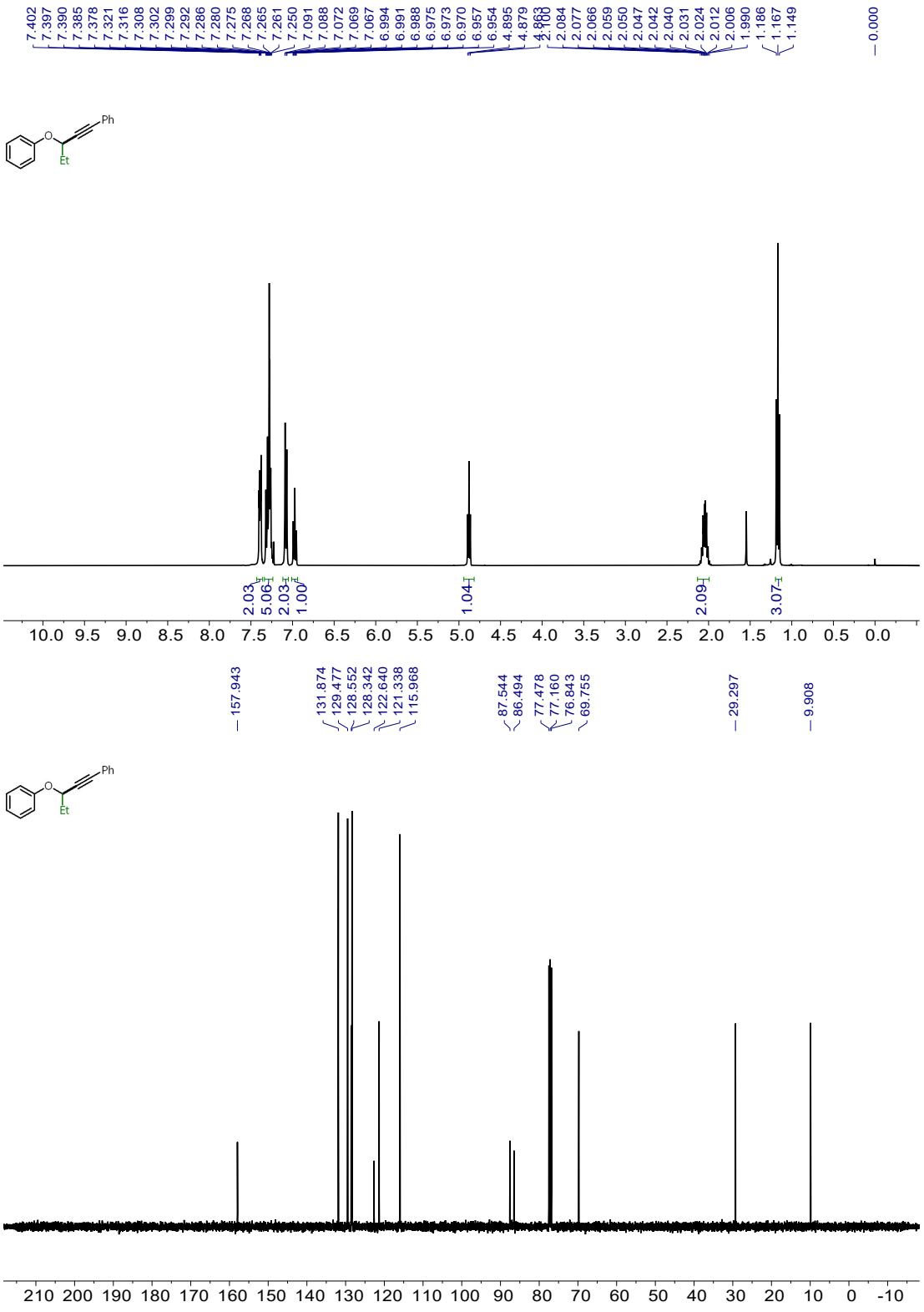
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3z**



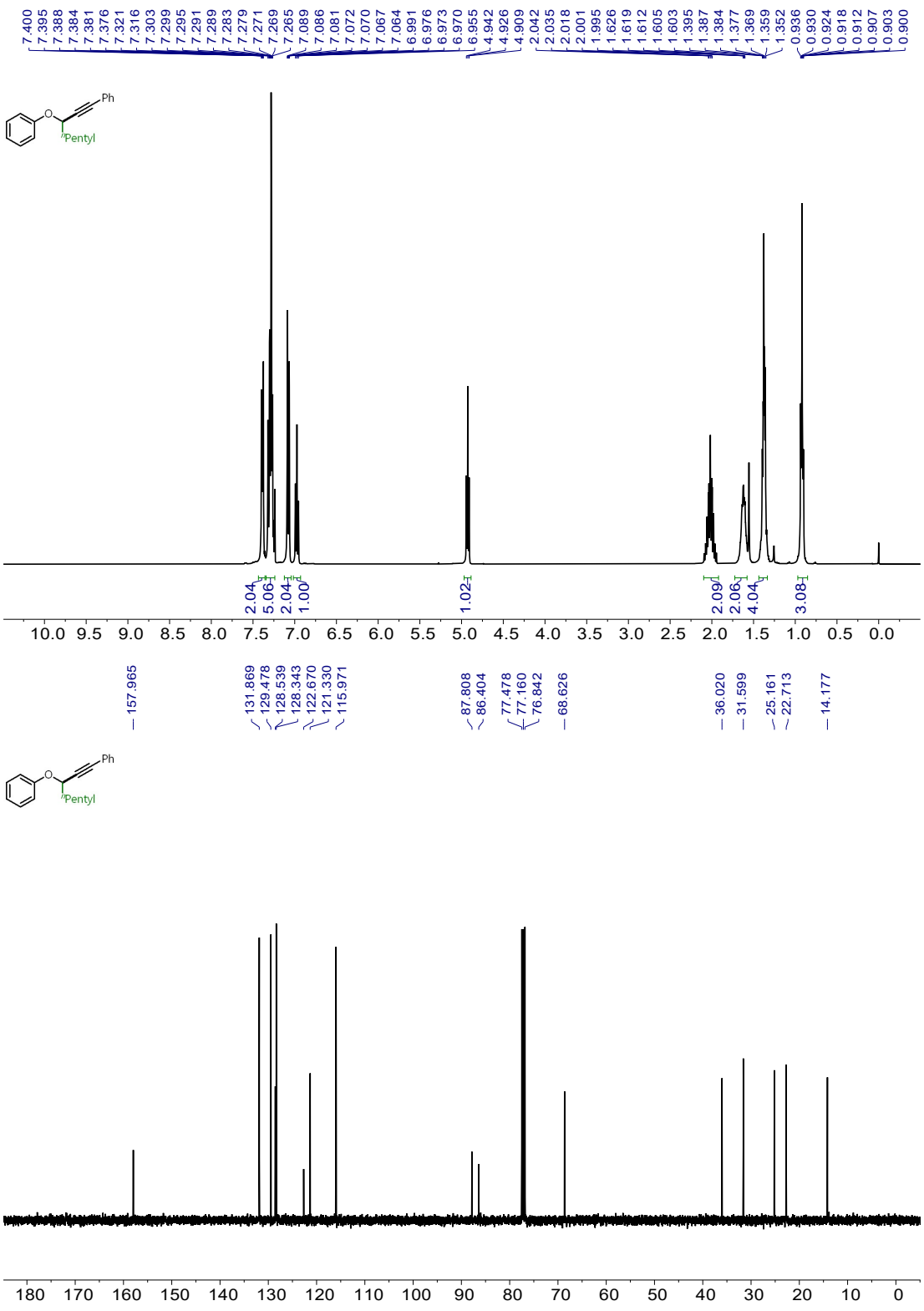
^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of **3aa**



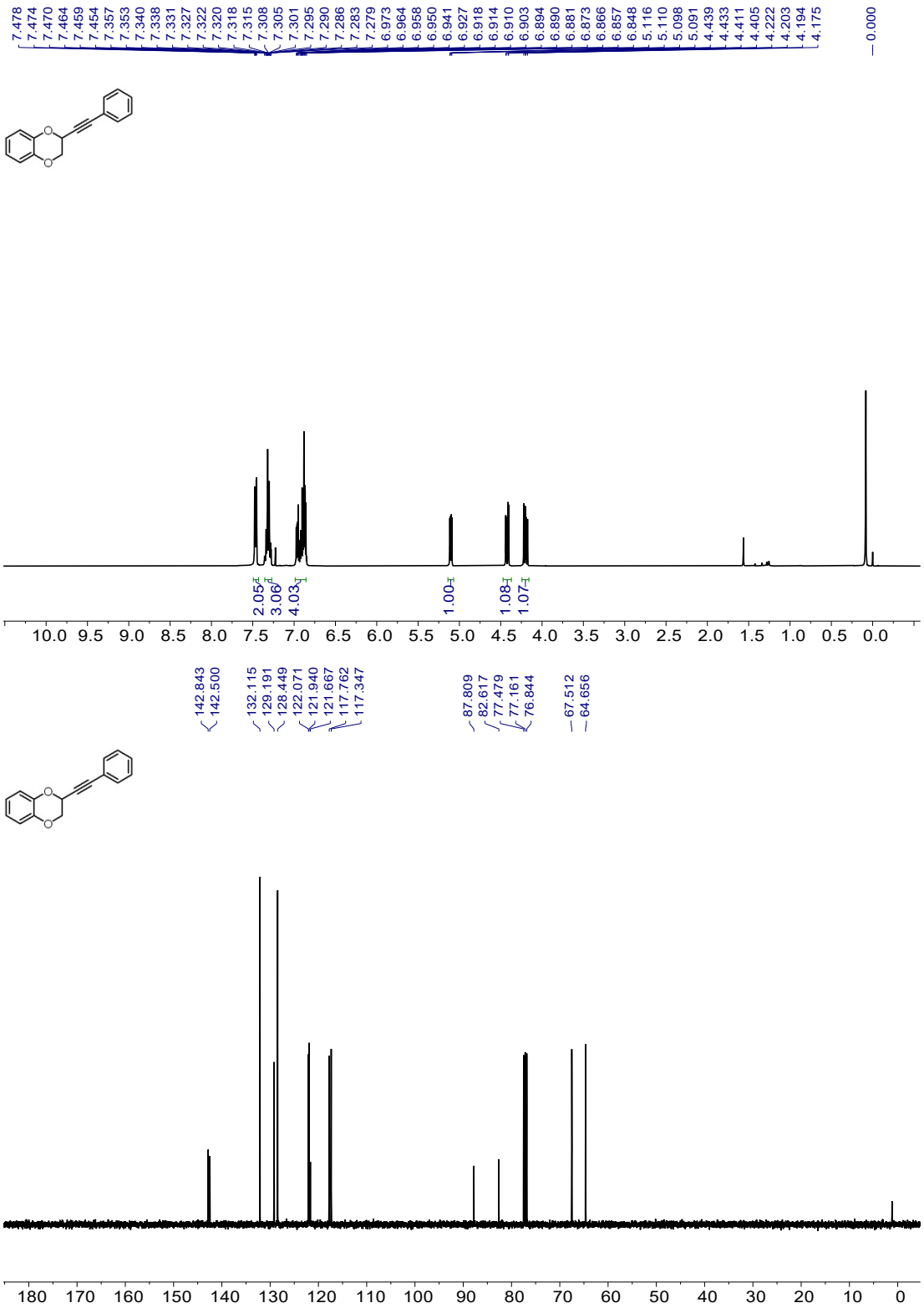
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3ab**



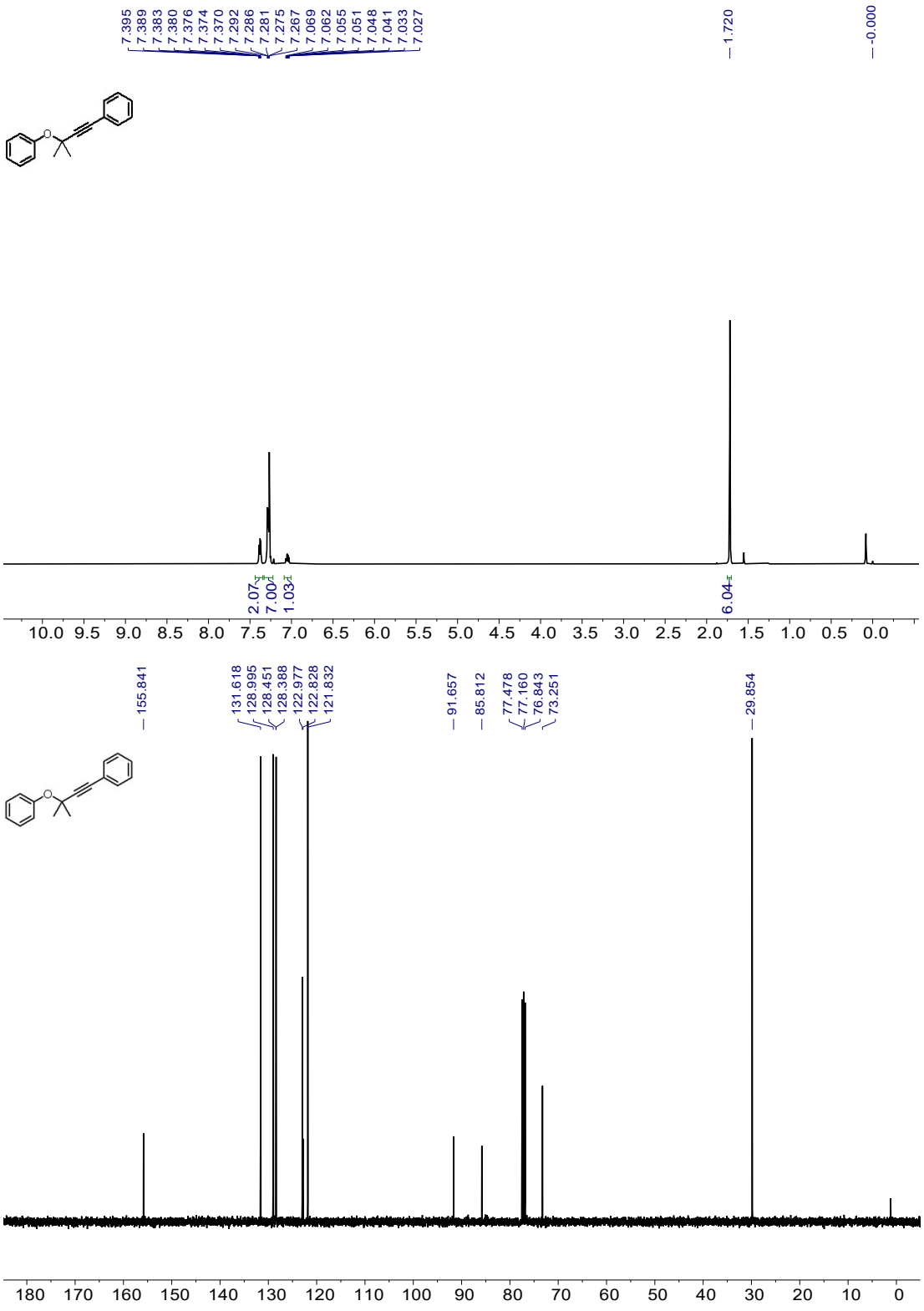
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3ac**



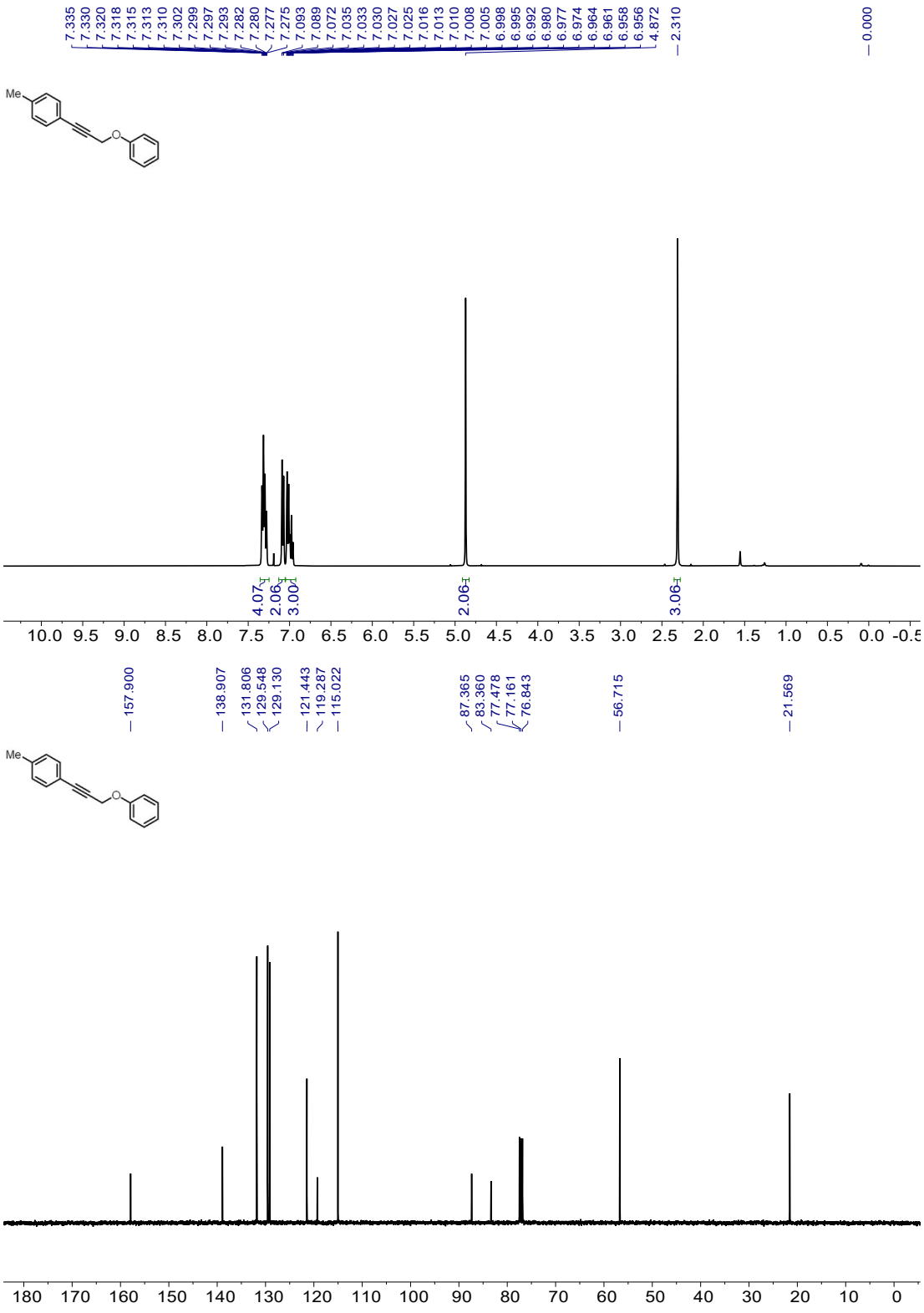
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3ad**



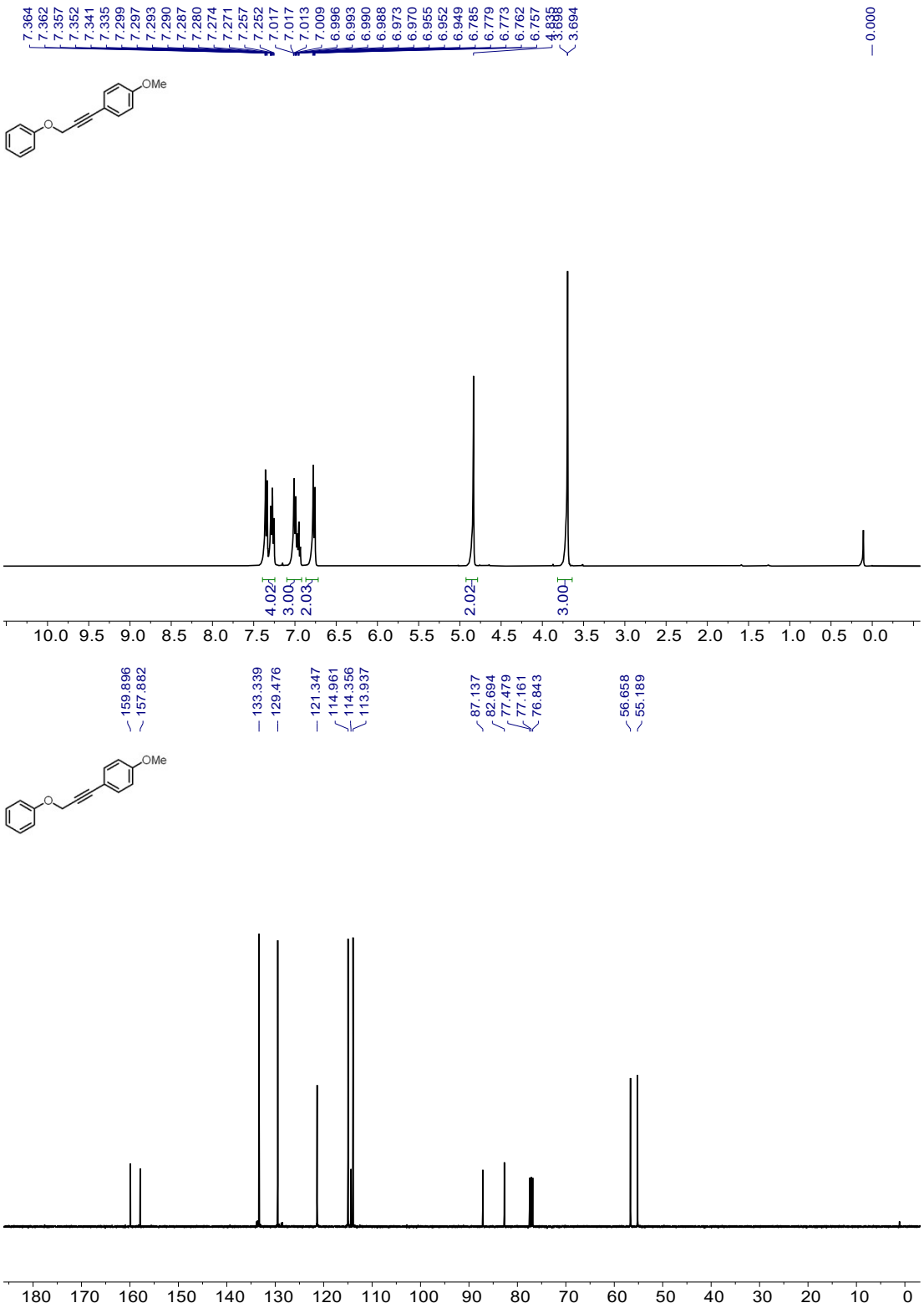
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3ae**



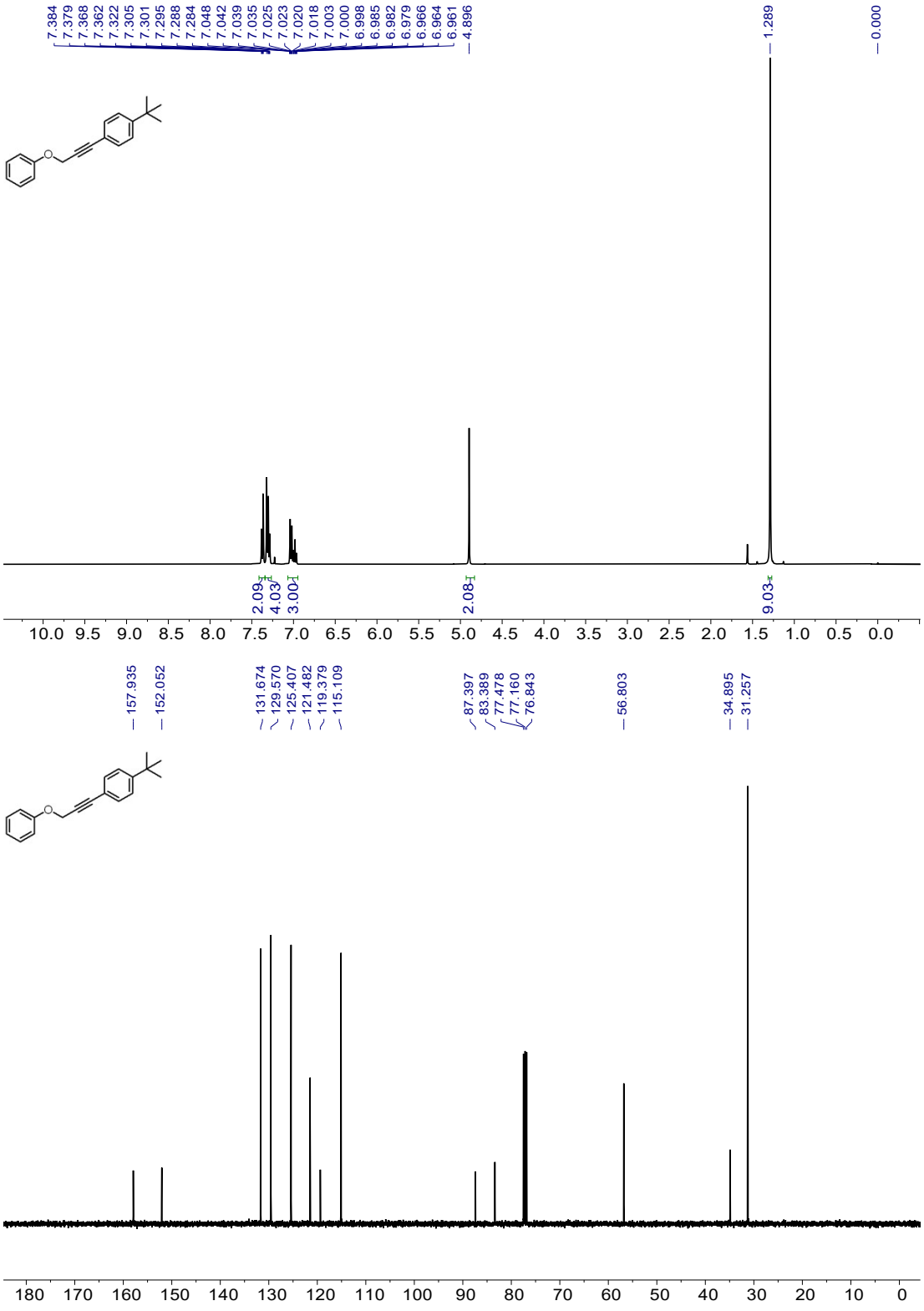
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3af**



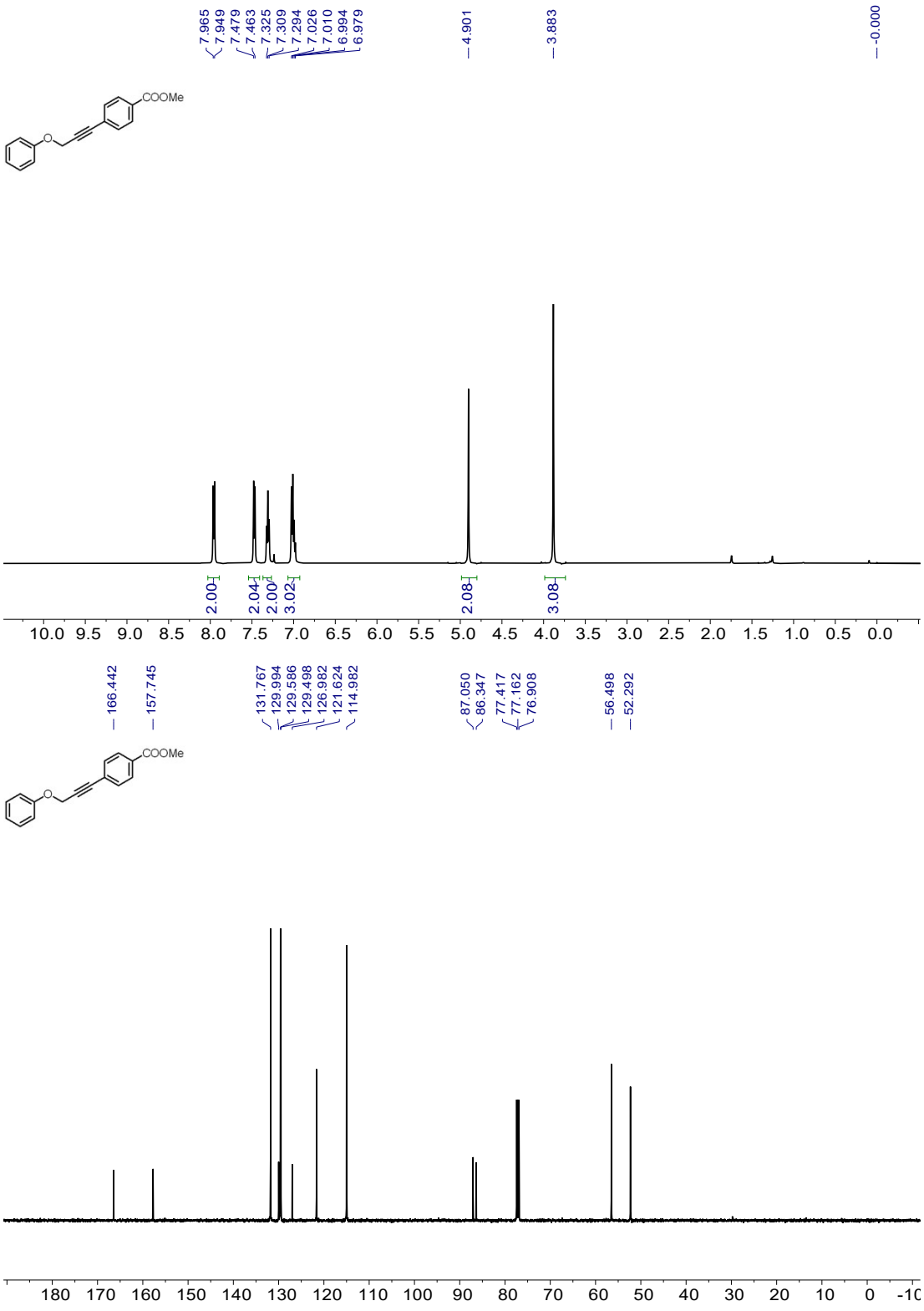
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3ag**



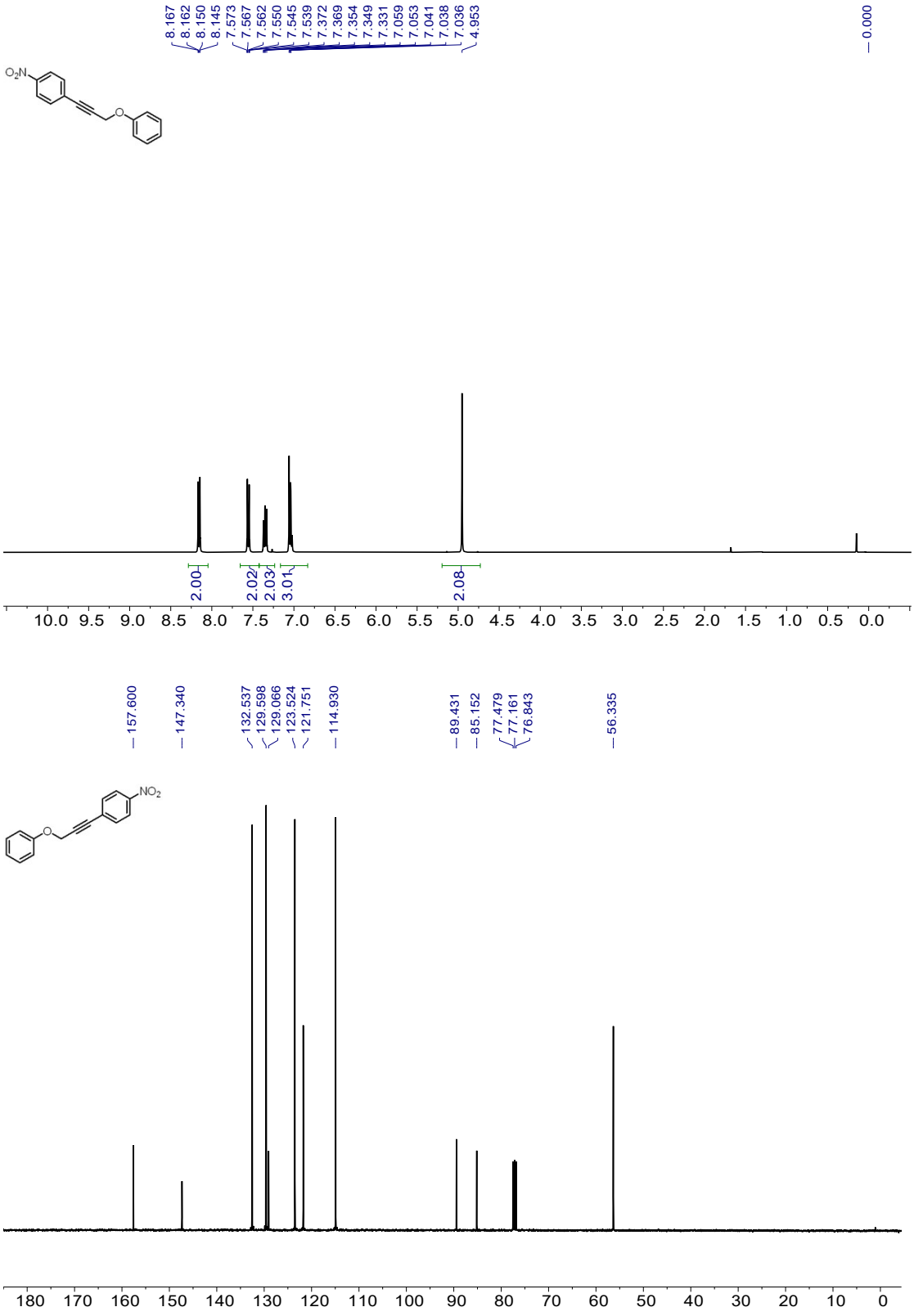
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3ah**



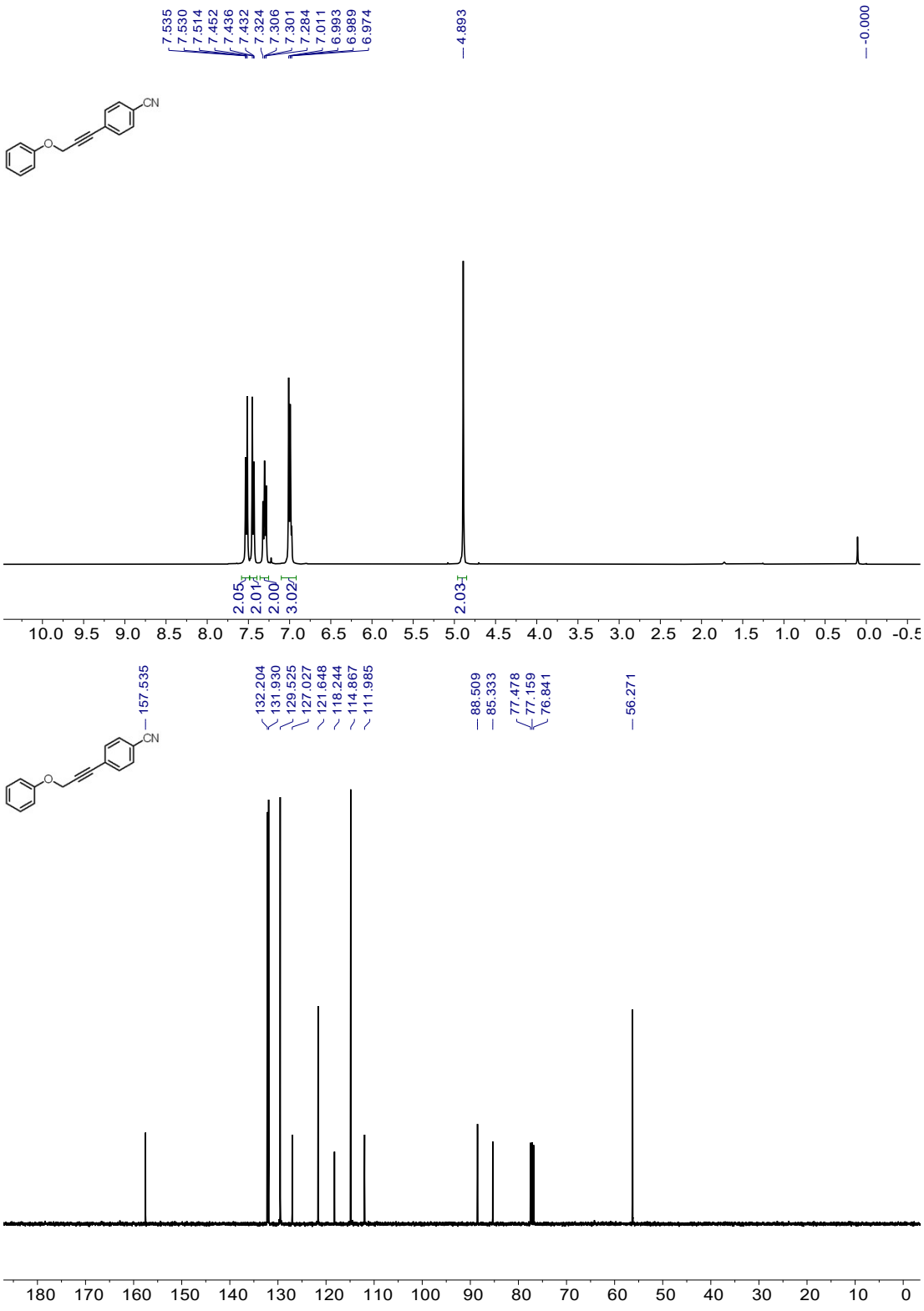
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3ai**



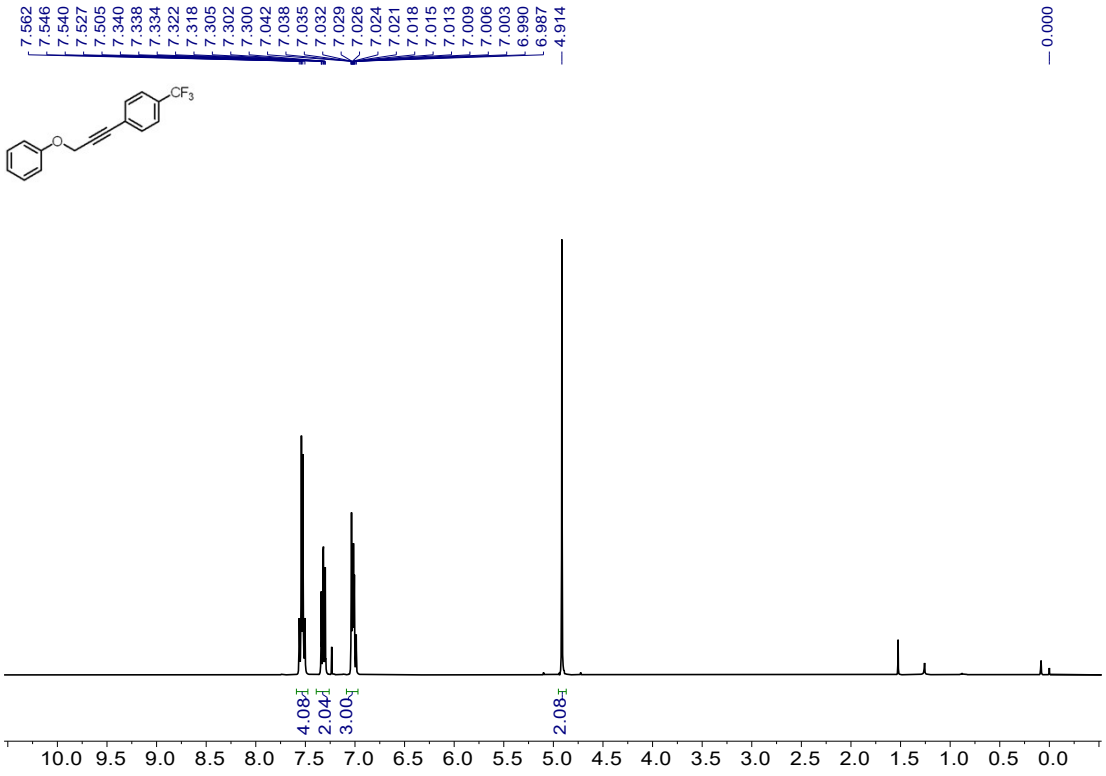
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3aj**



^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3ak**



^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3al**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3.00
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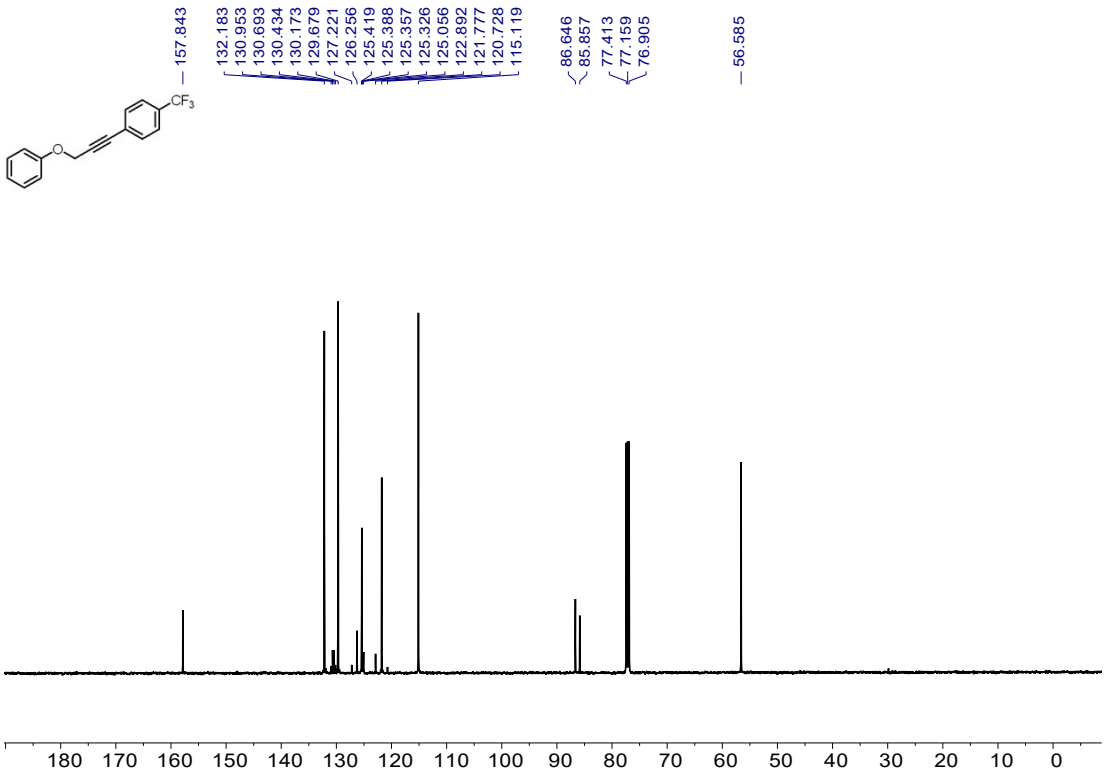
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125.056
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120.728
115.119
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CF3
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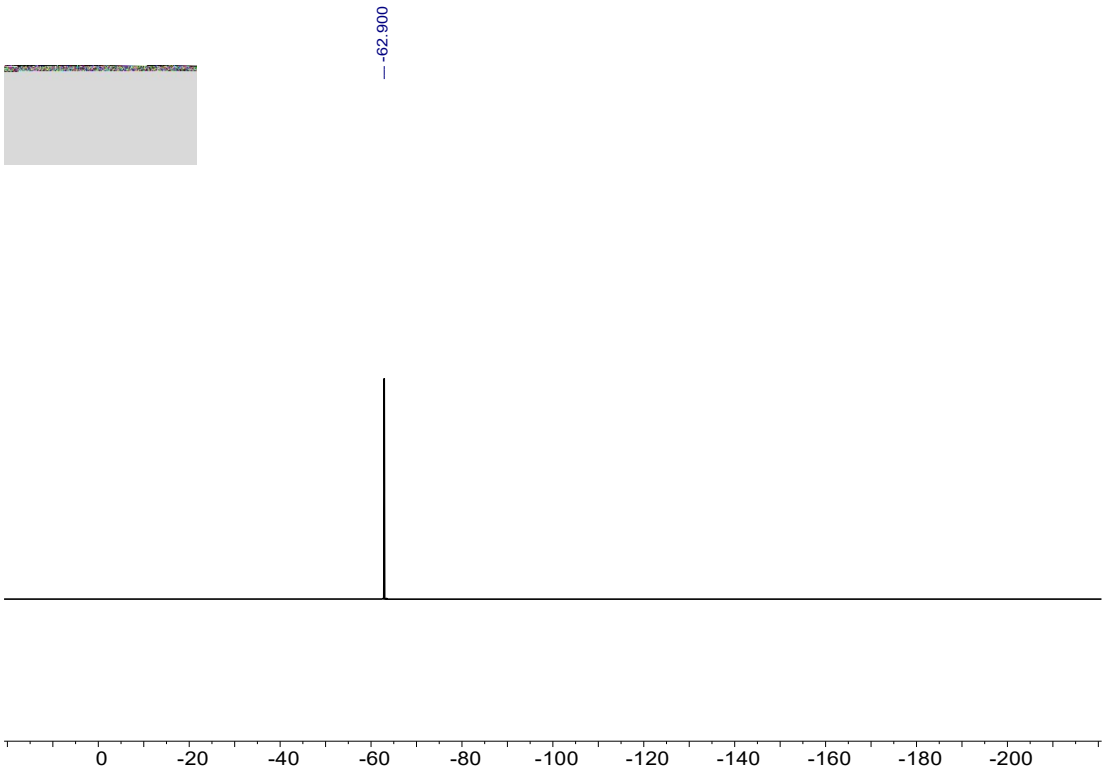
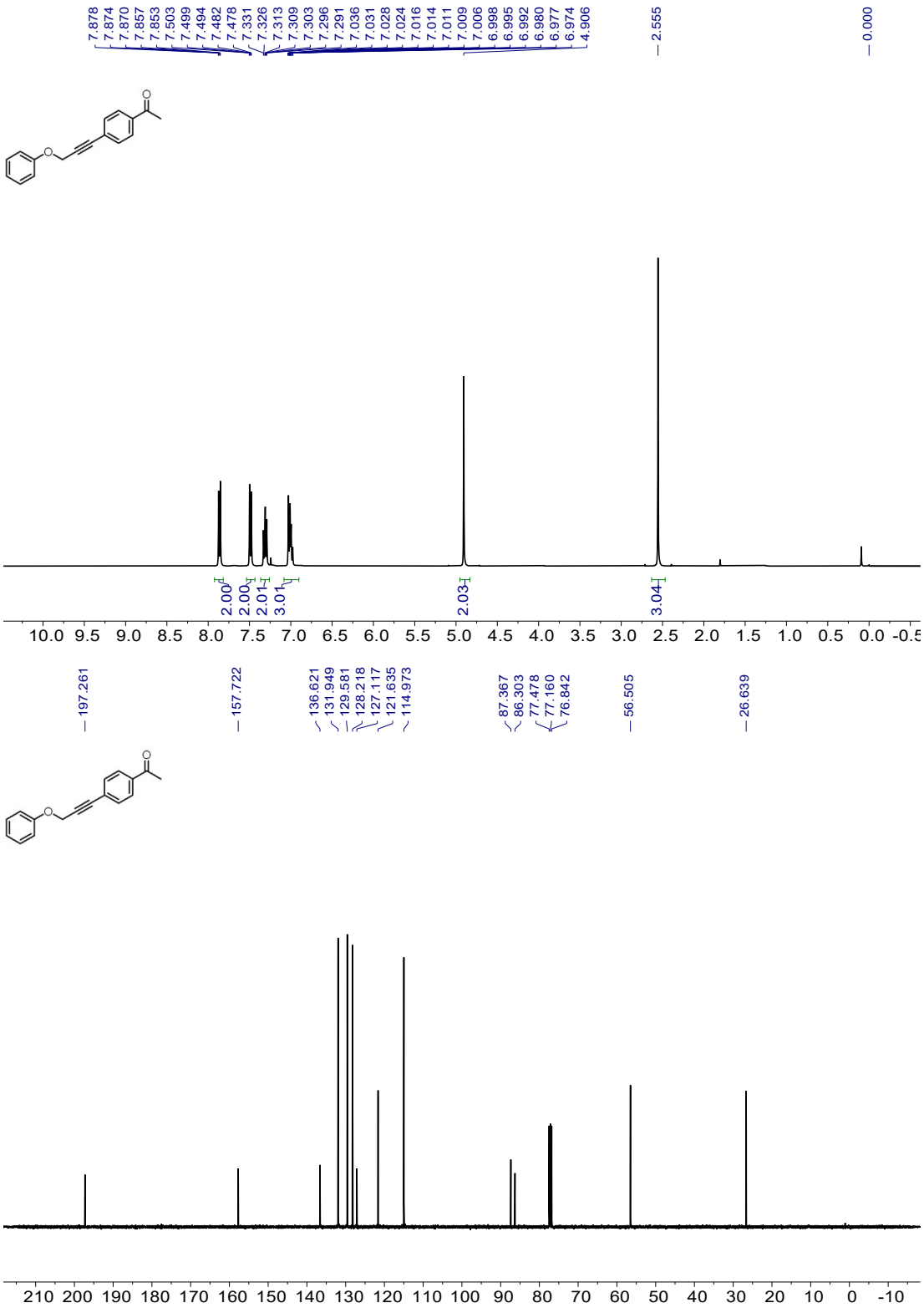
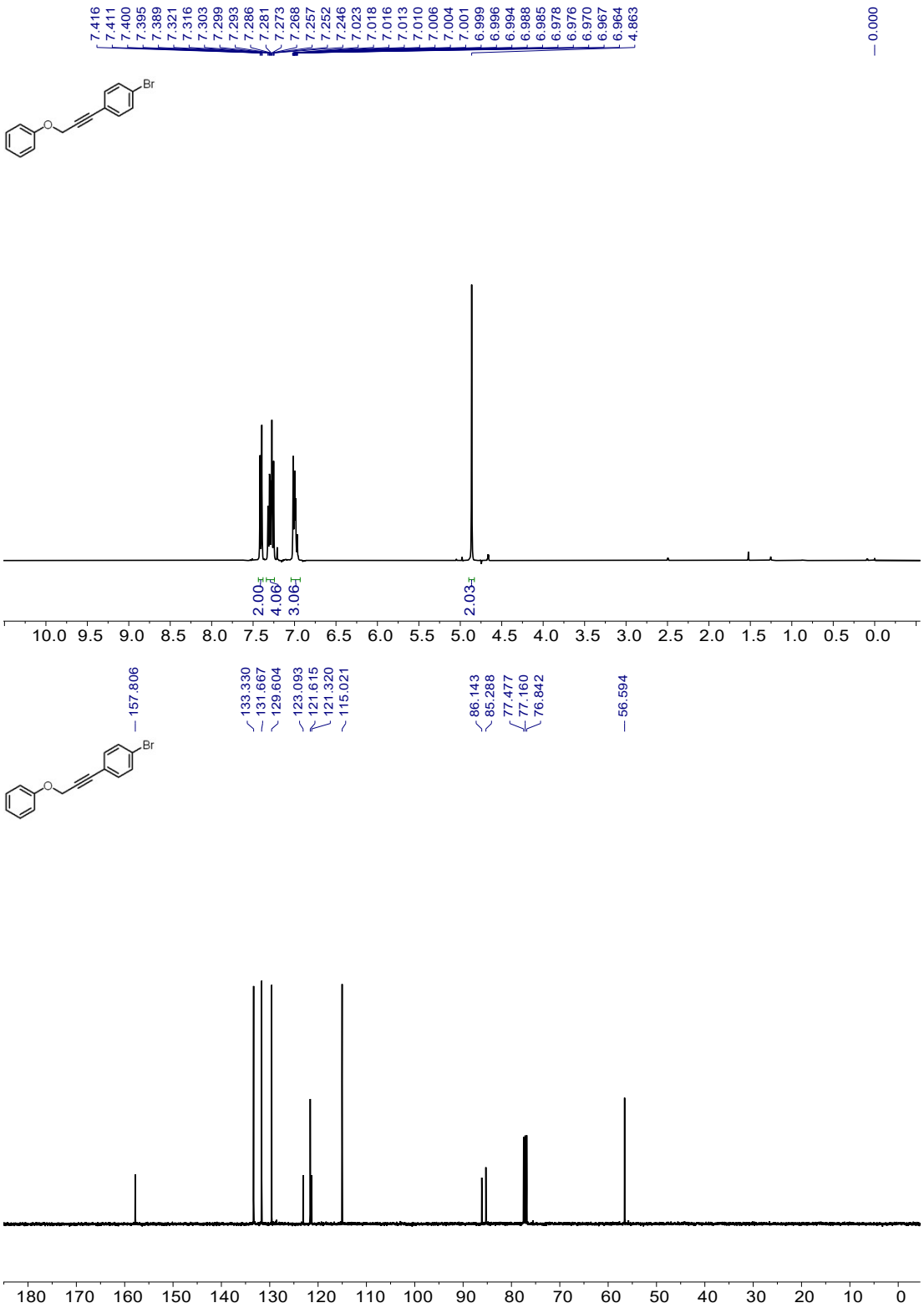


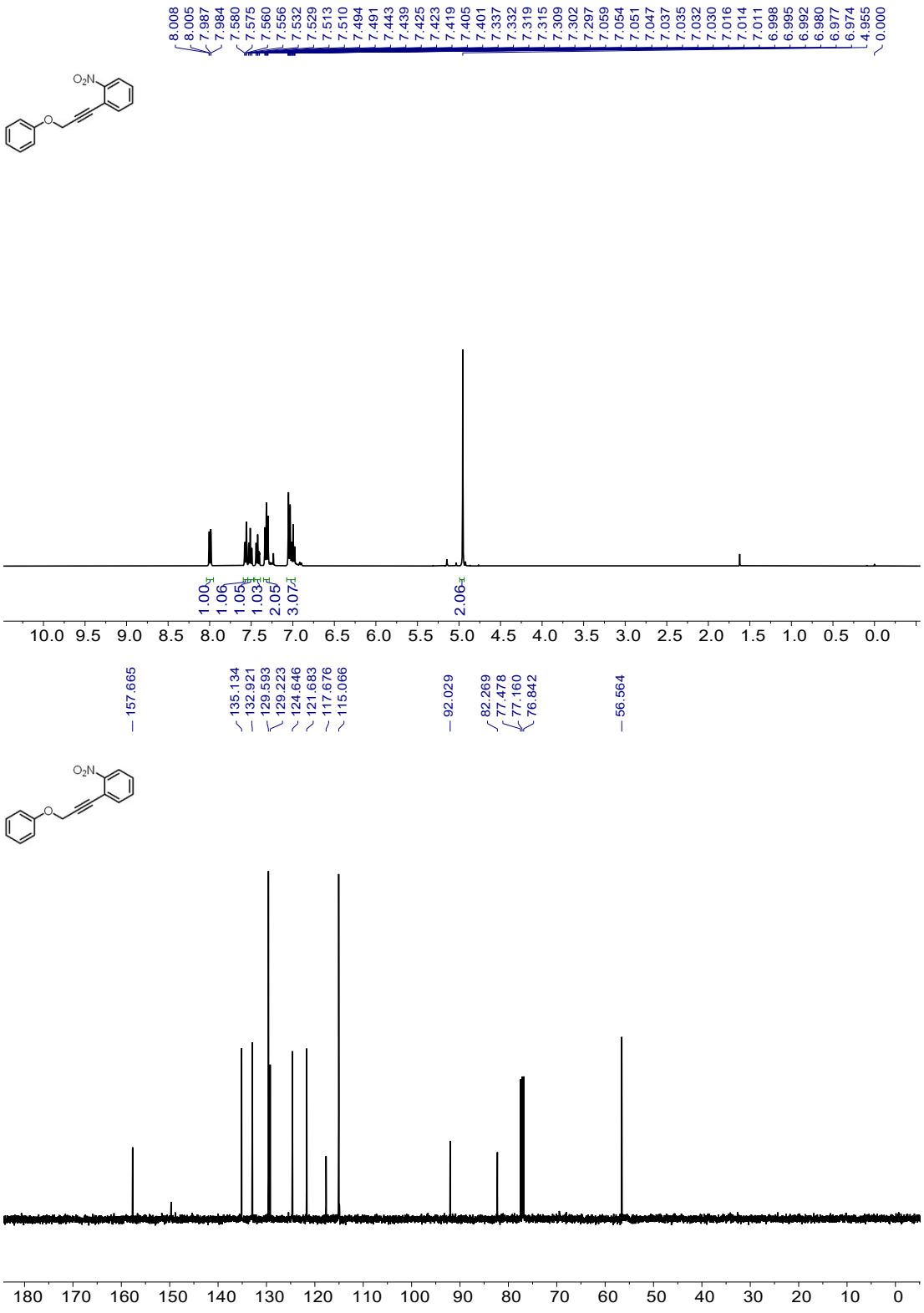
^{1}H NMR ($CDCl_3$, 400 MHz), ^{13}C NMR ($CDCl_3$, 100 MHz) and ^{19}F NMR ($CDCl_3$, 376 MHz) spectrum of **3am**



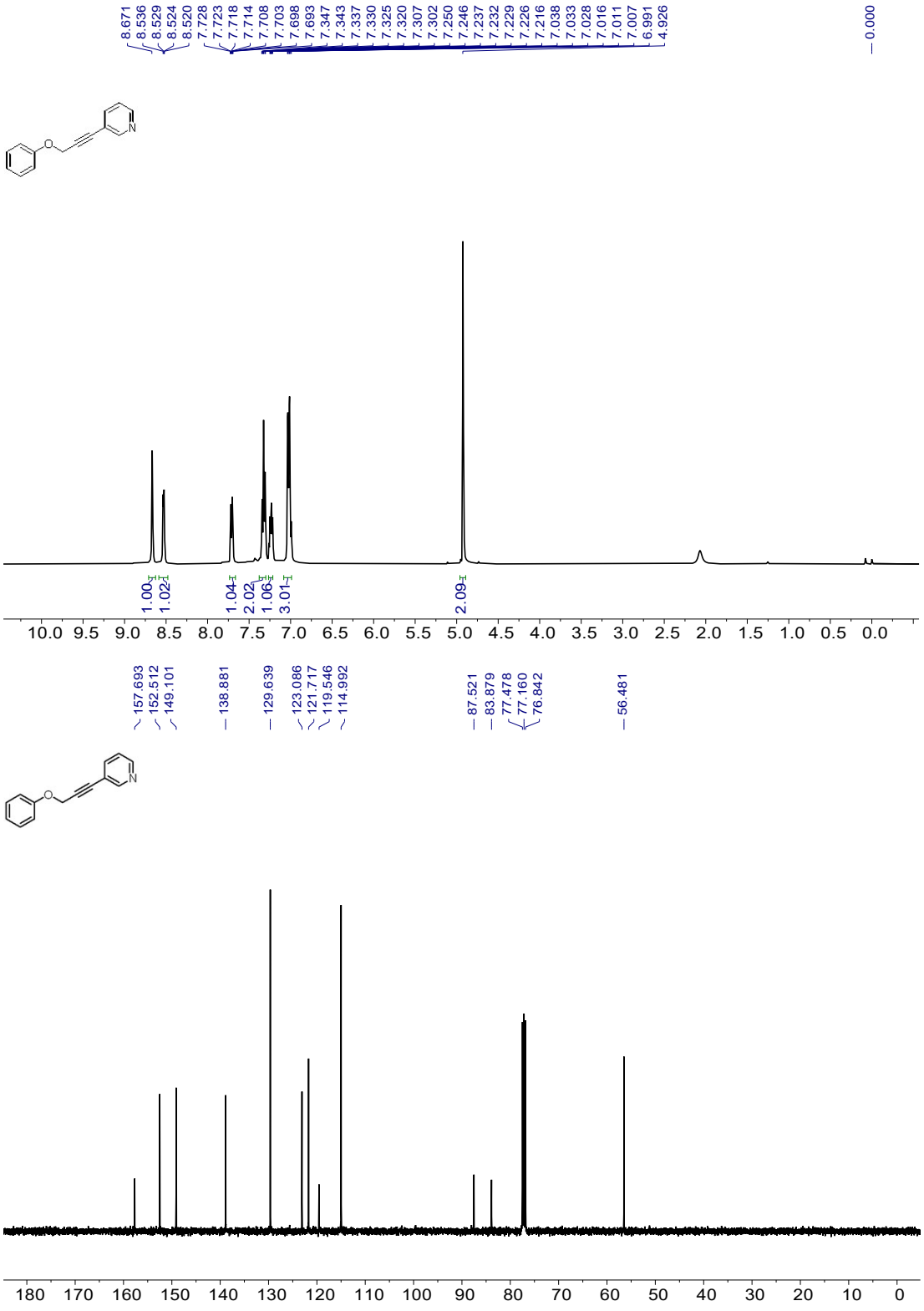
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3an**



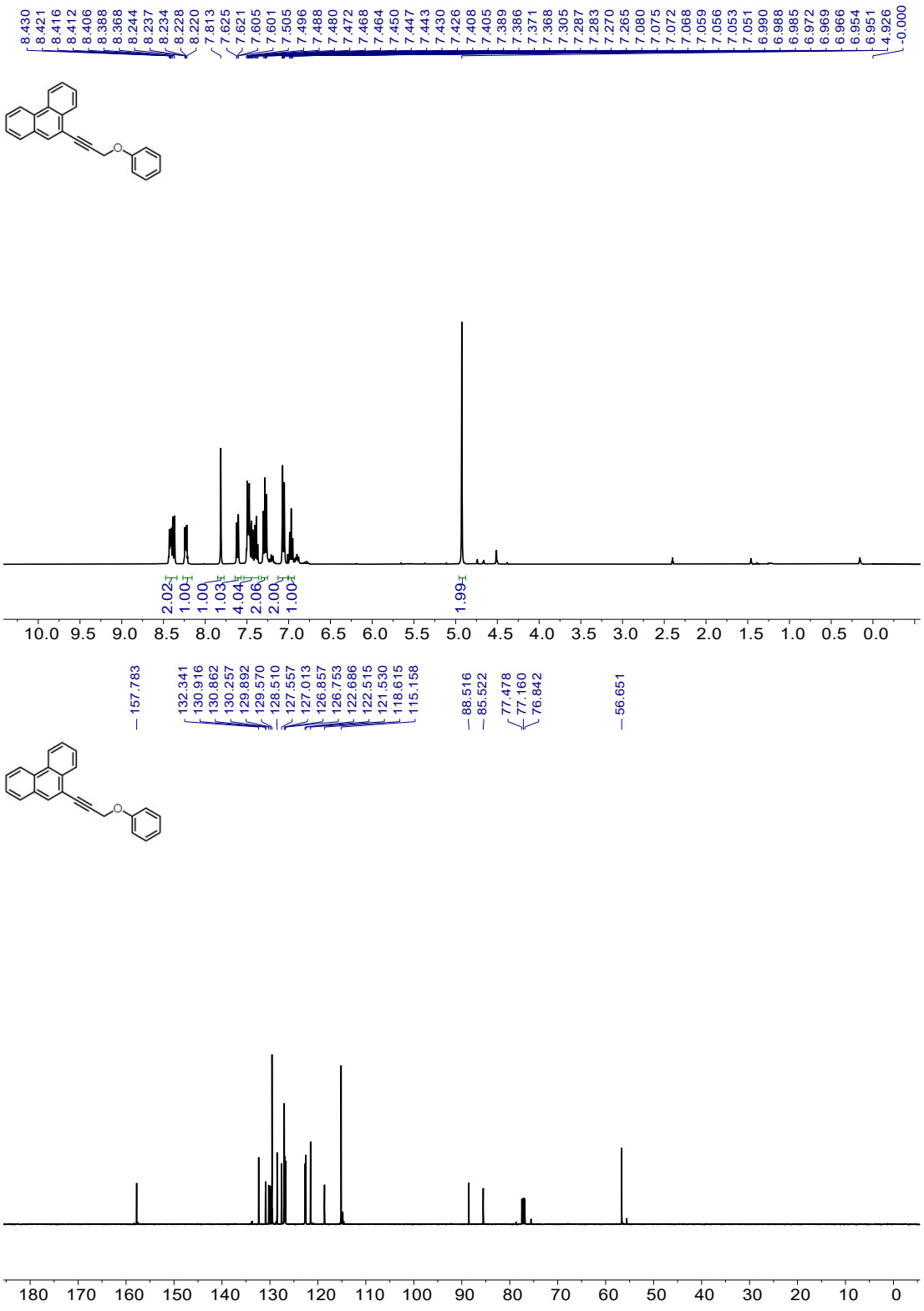
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3ao**



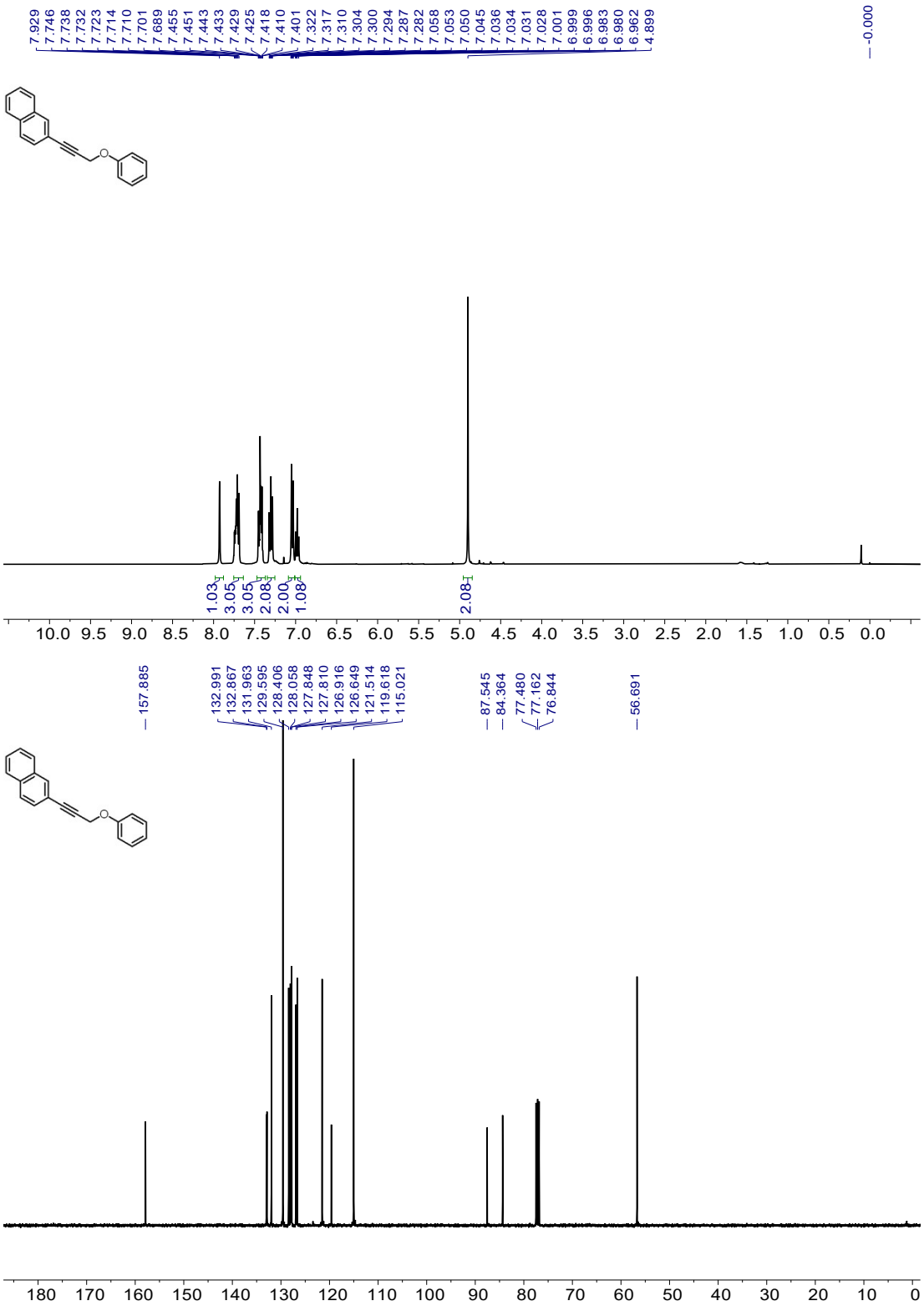
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3ap**



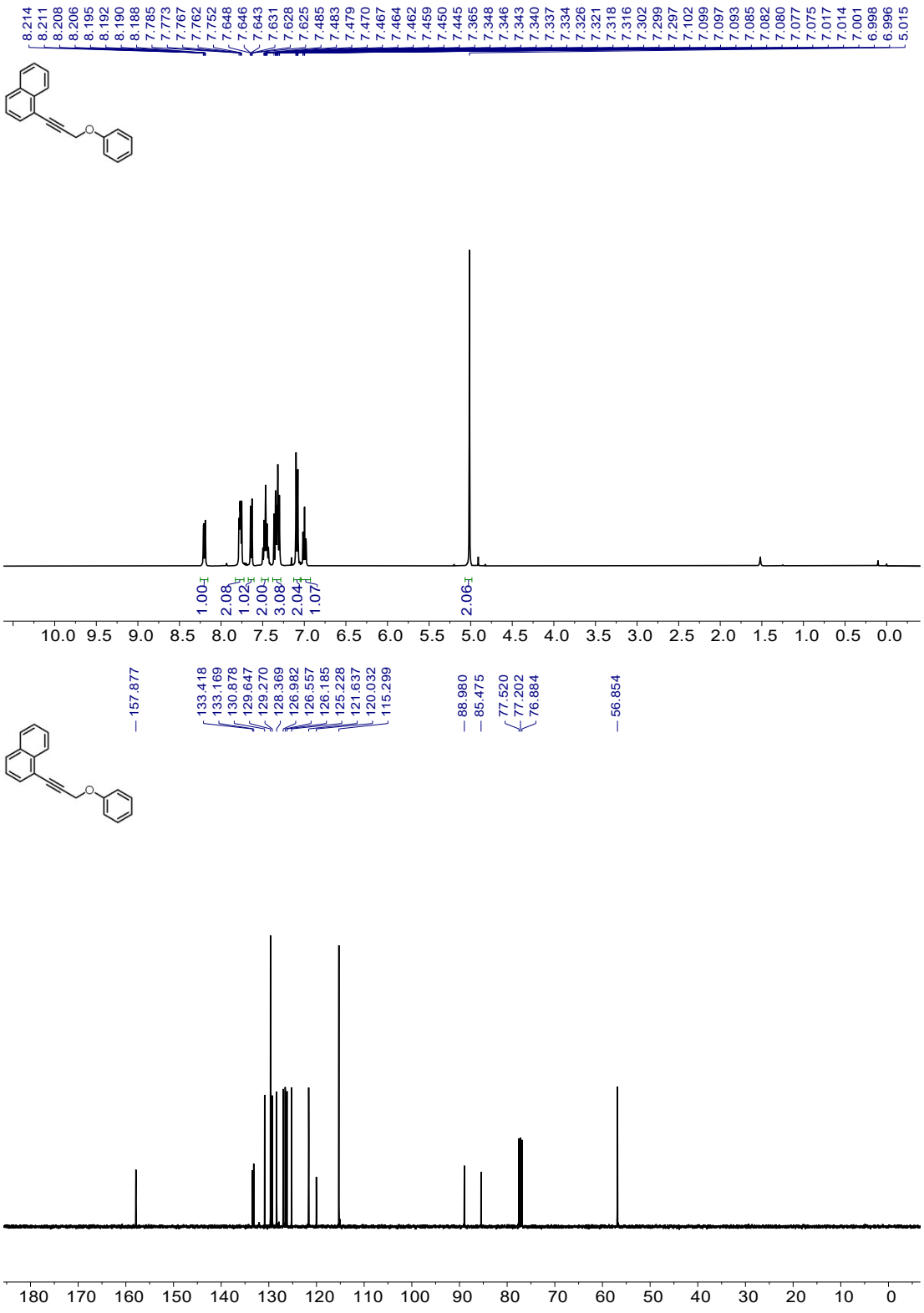
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3aq**



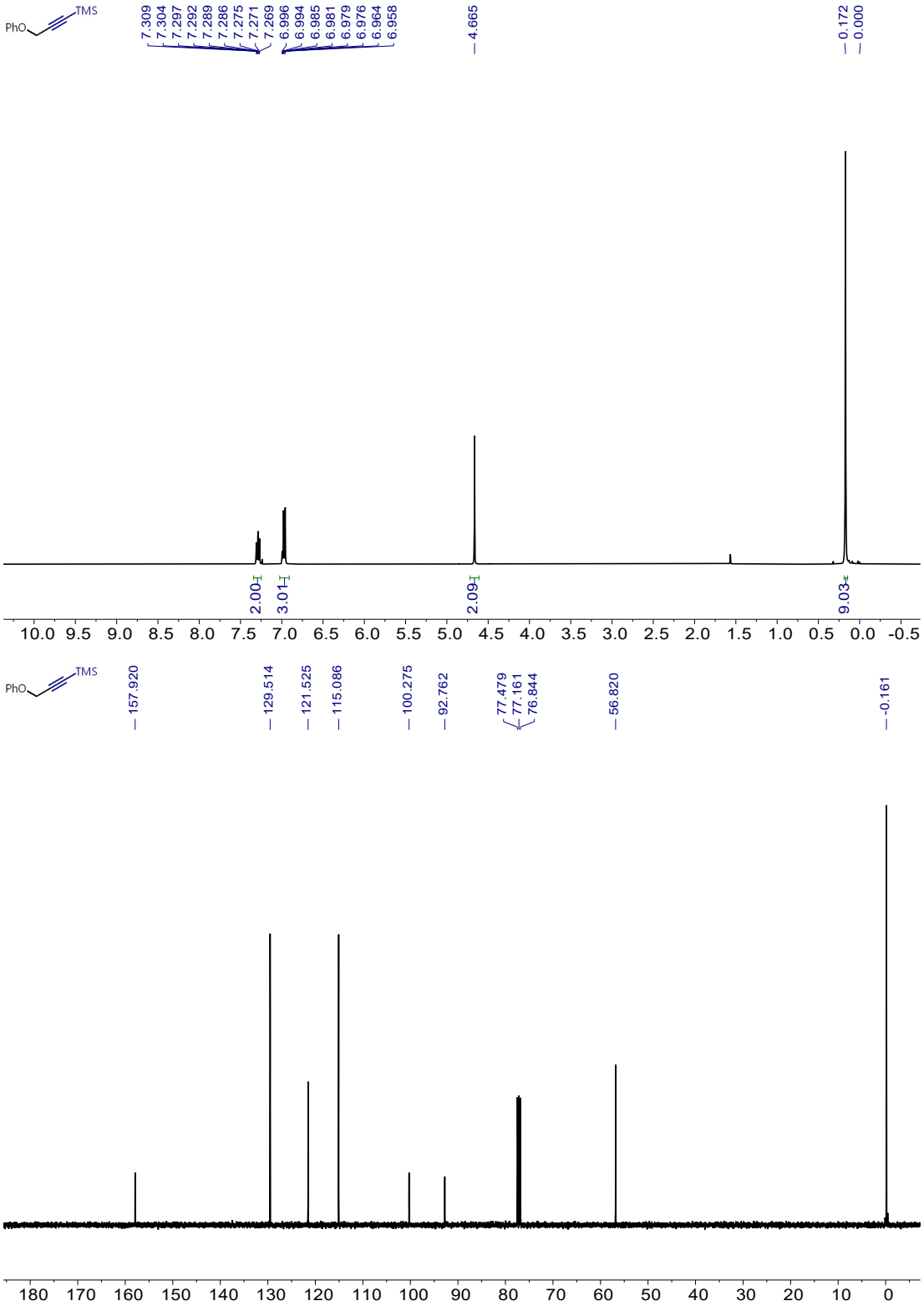
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3ar**



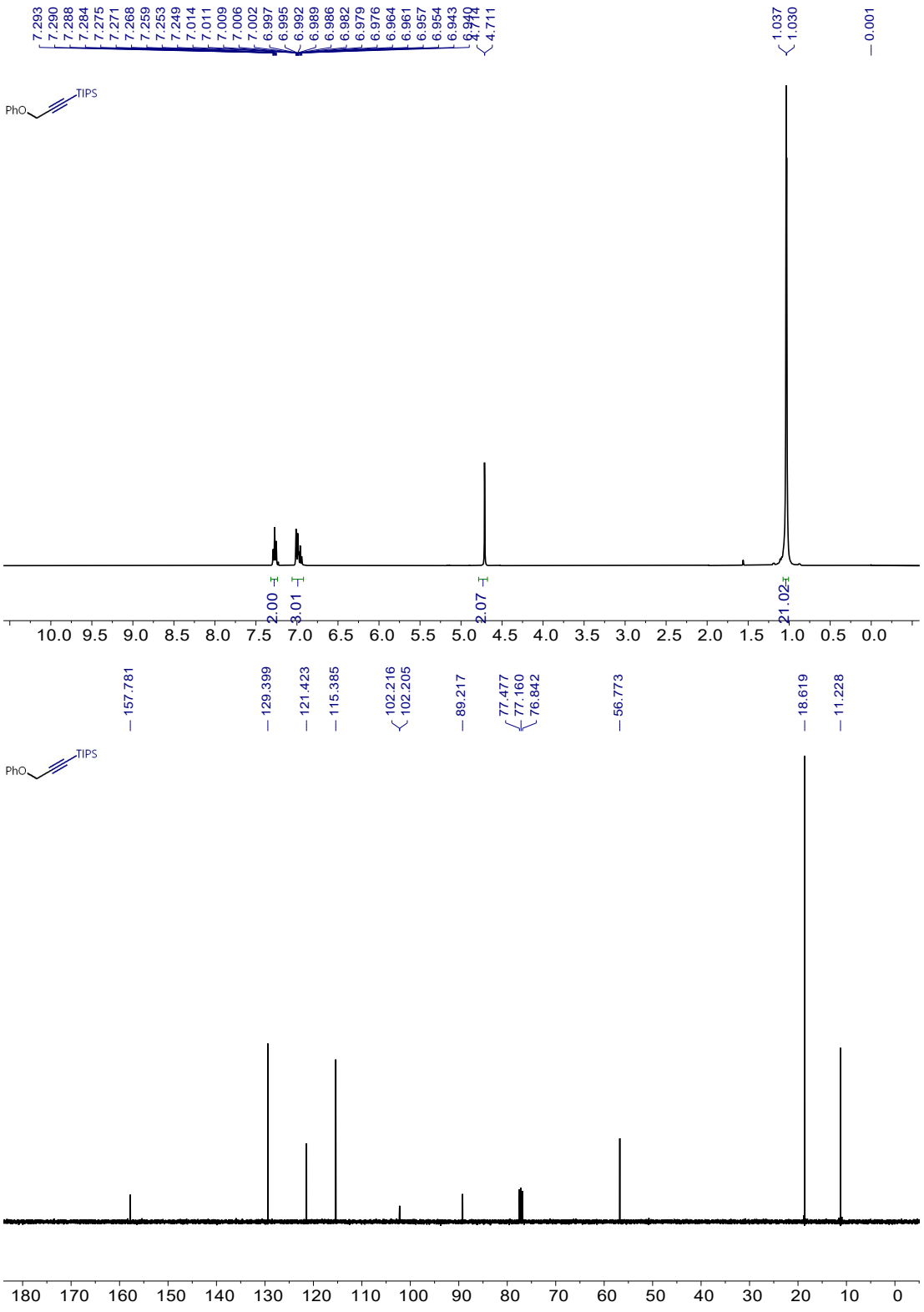
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3as**



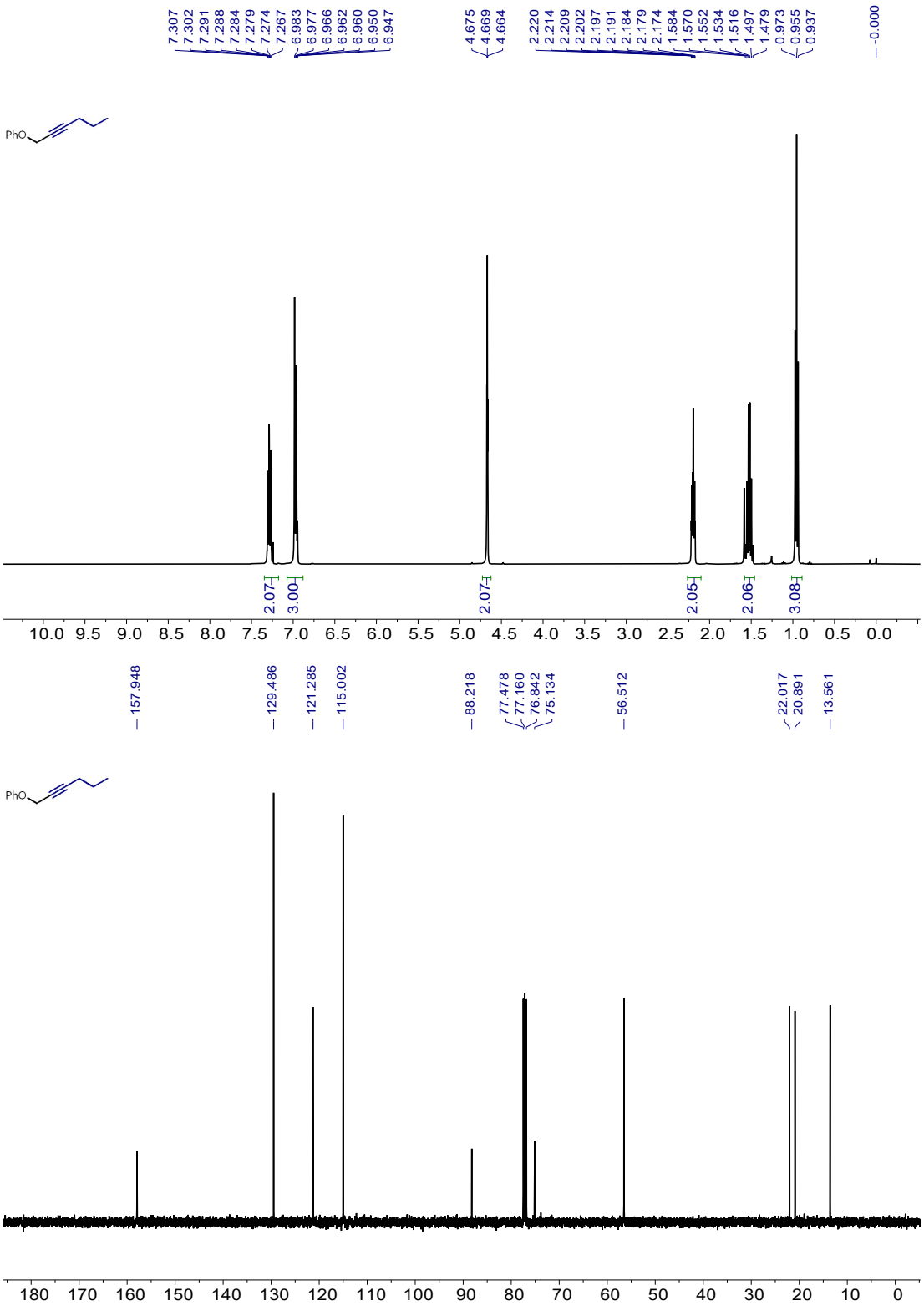
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3at**



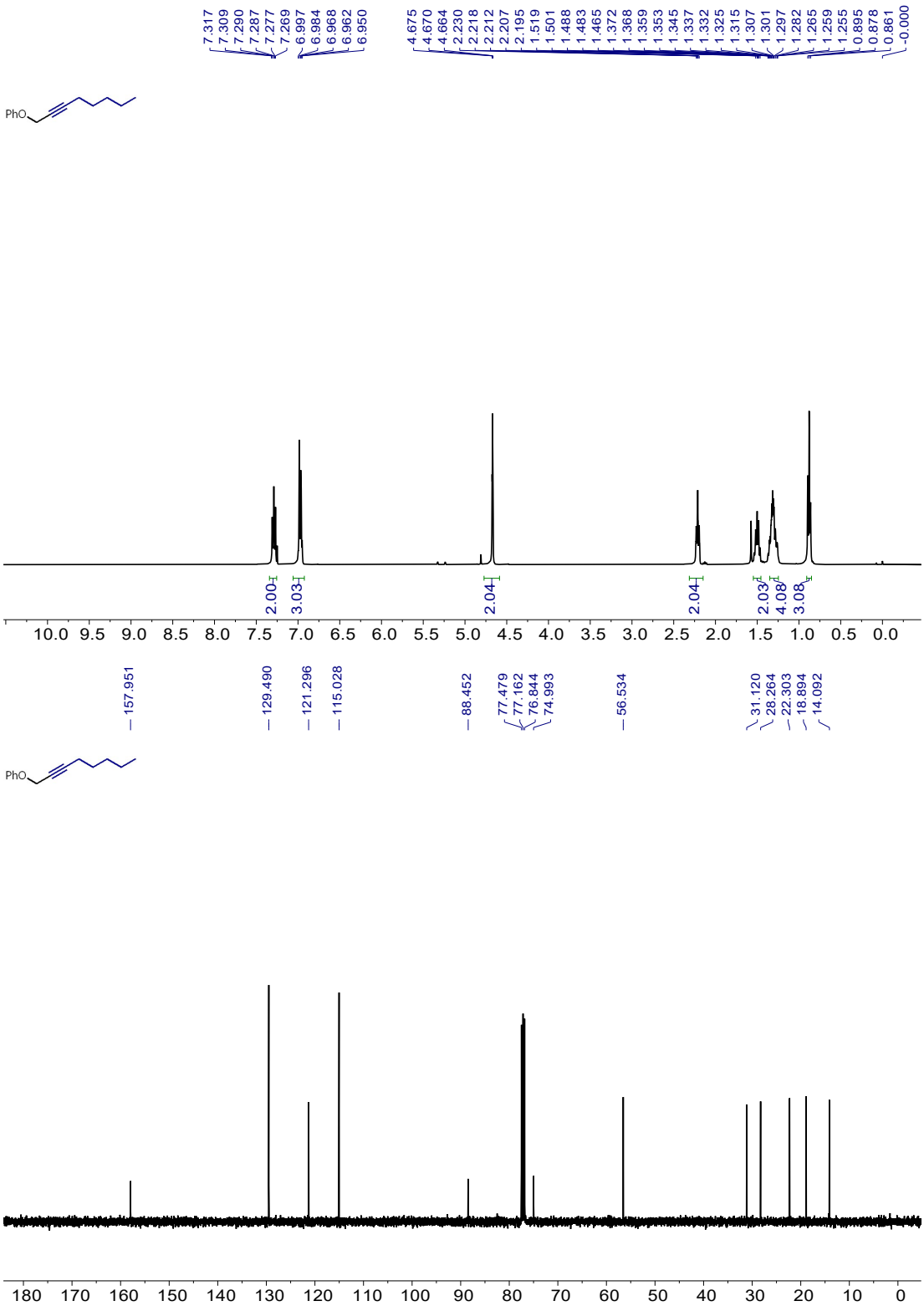
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3au**



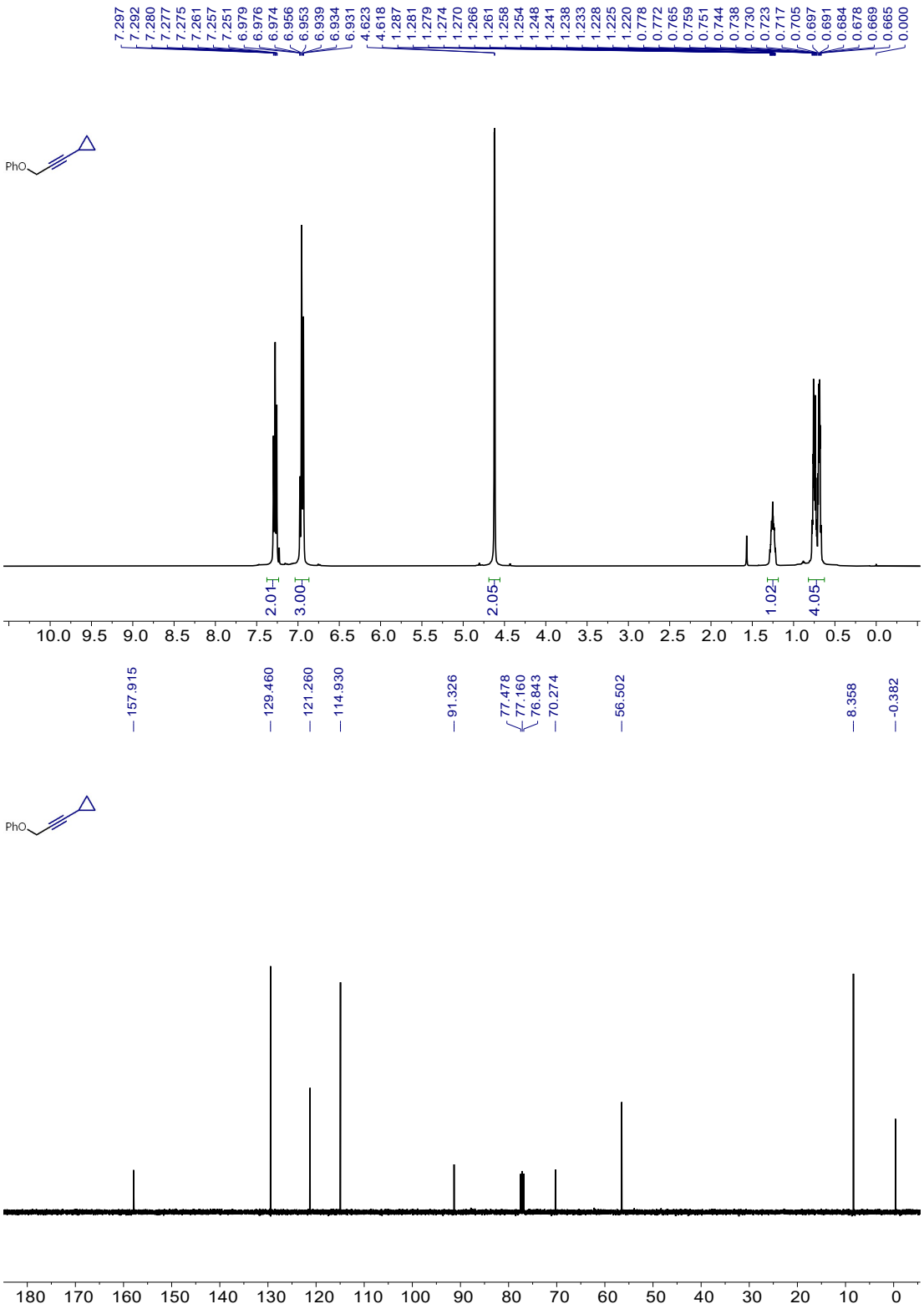
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3av**



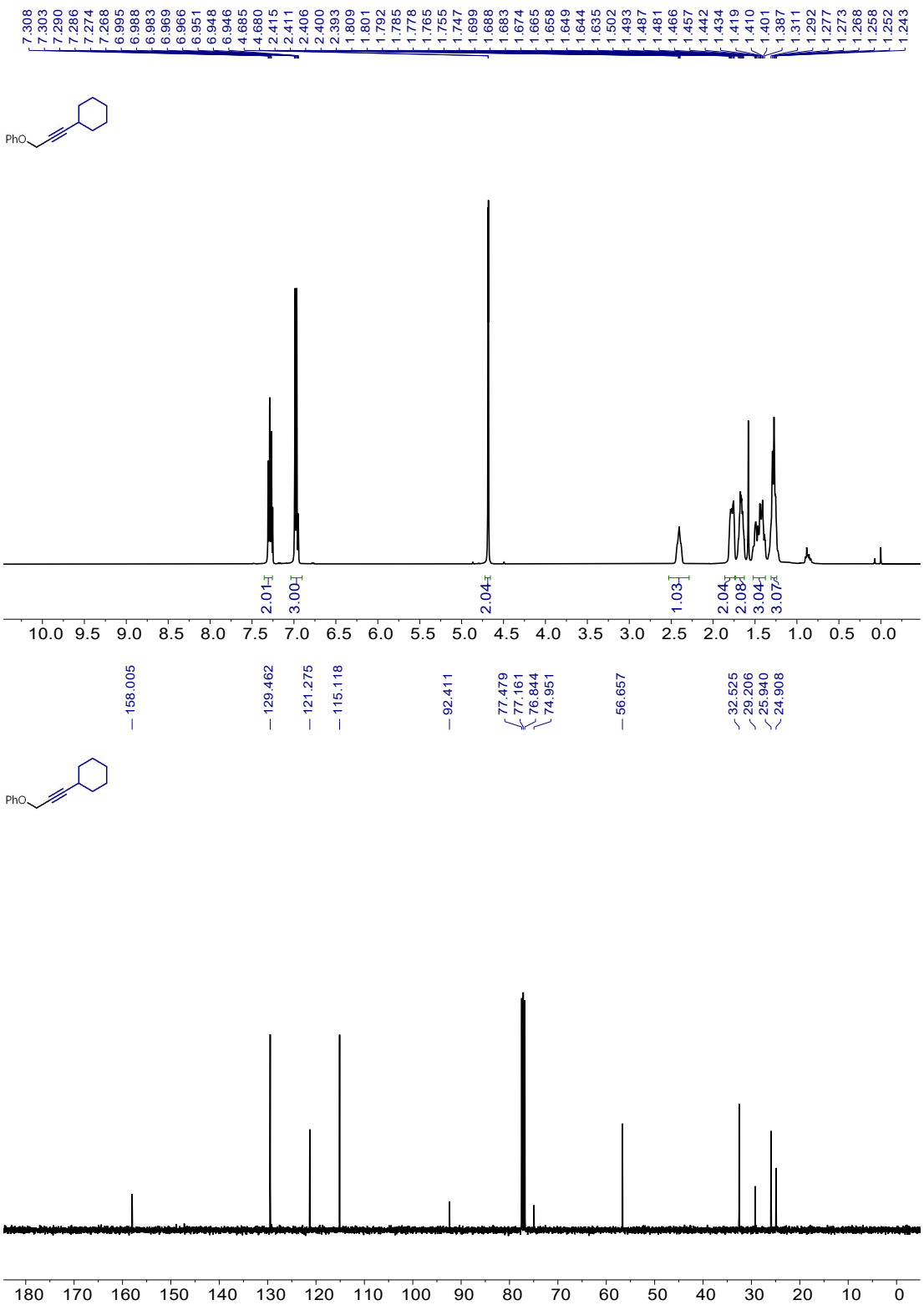
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3aw**



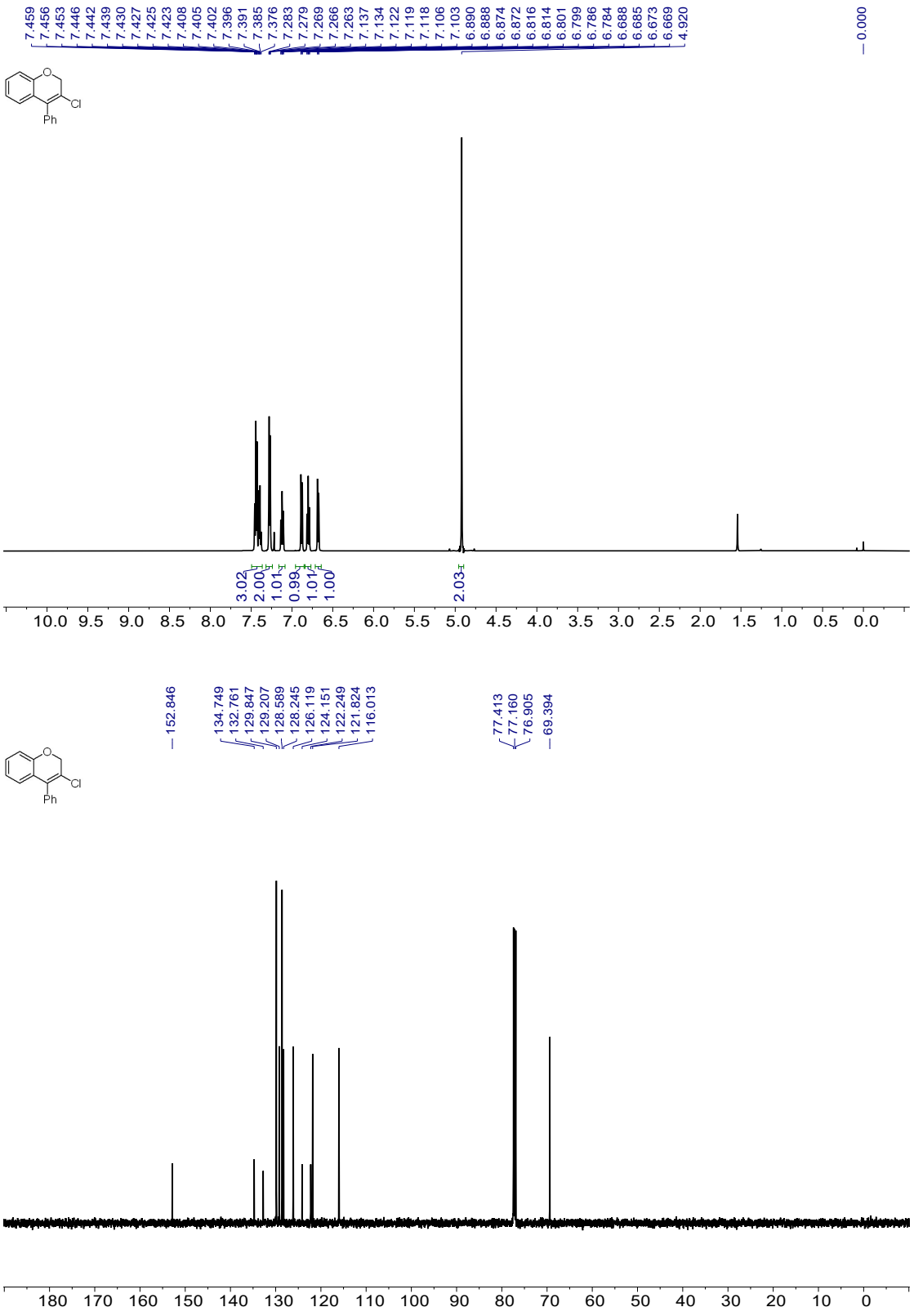
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3ax**



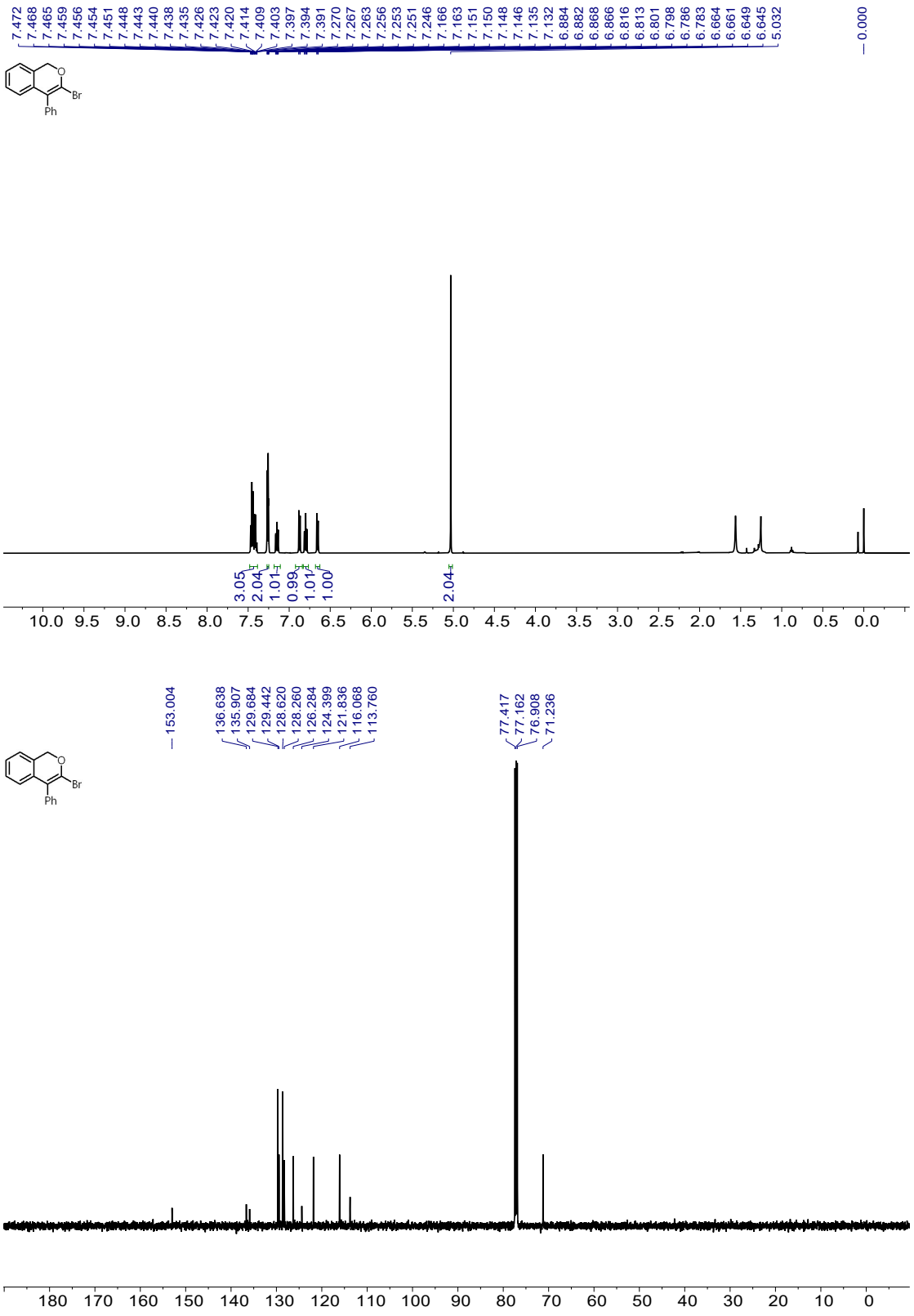
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3ay**



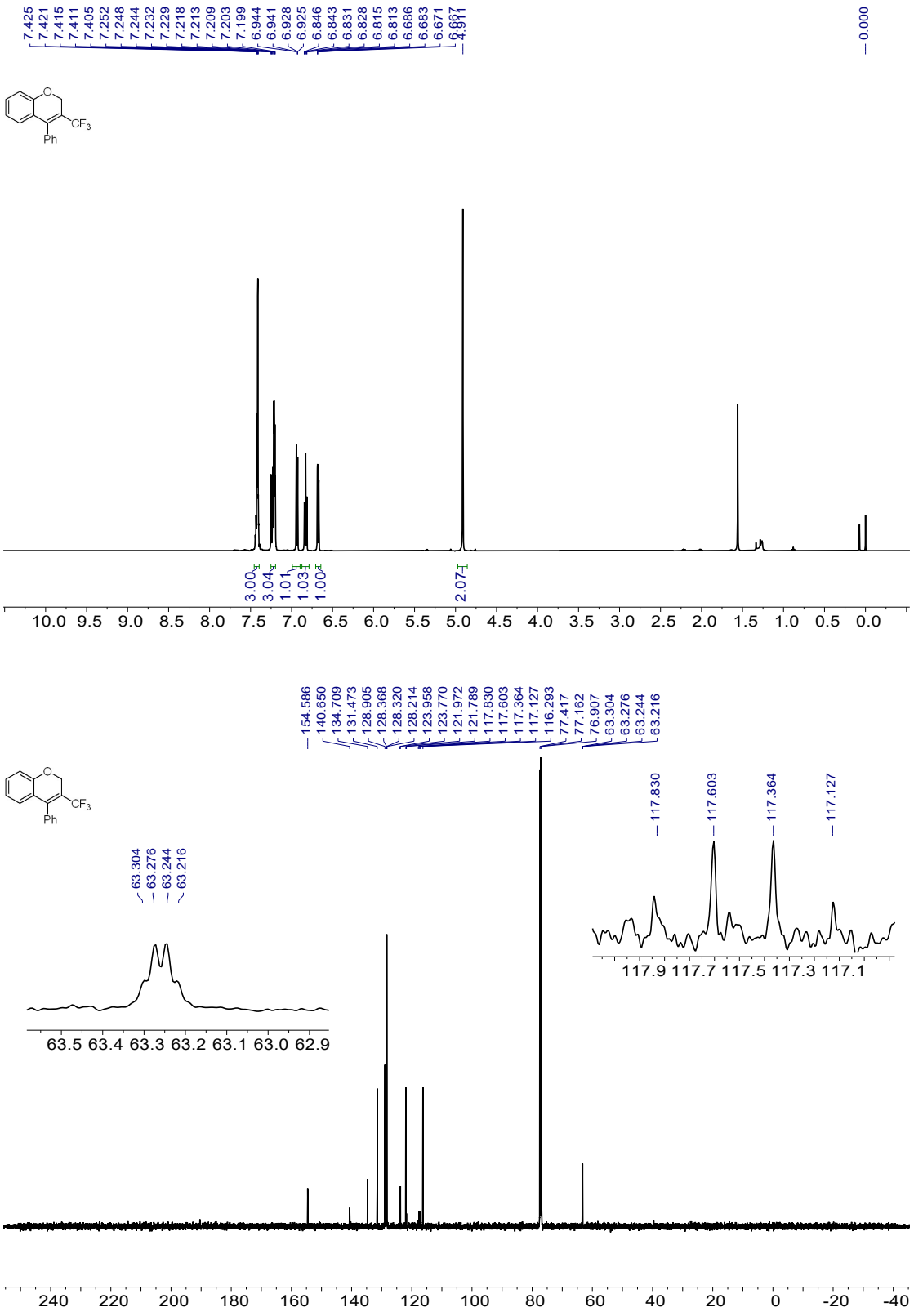
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3az**



^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3aa'**



^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3ab'**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1.01
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154.586
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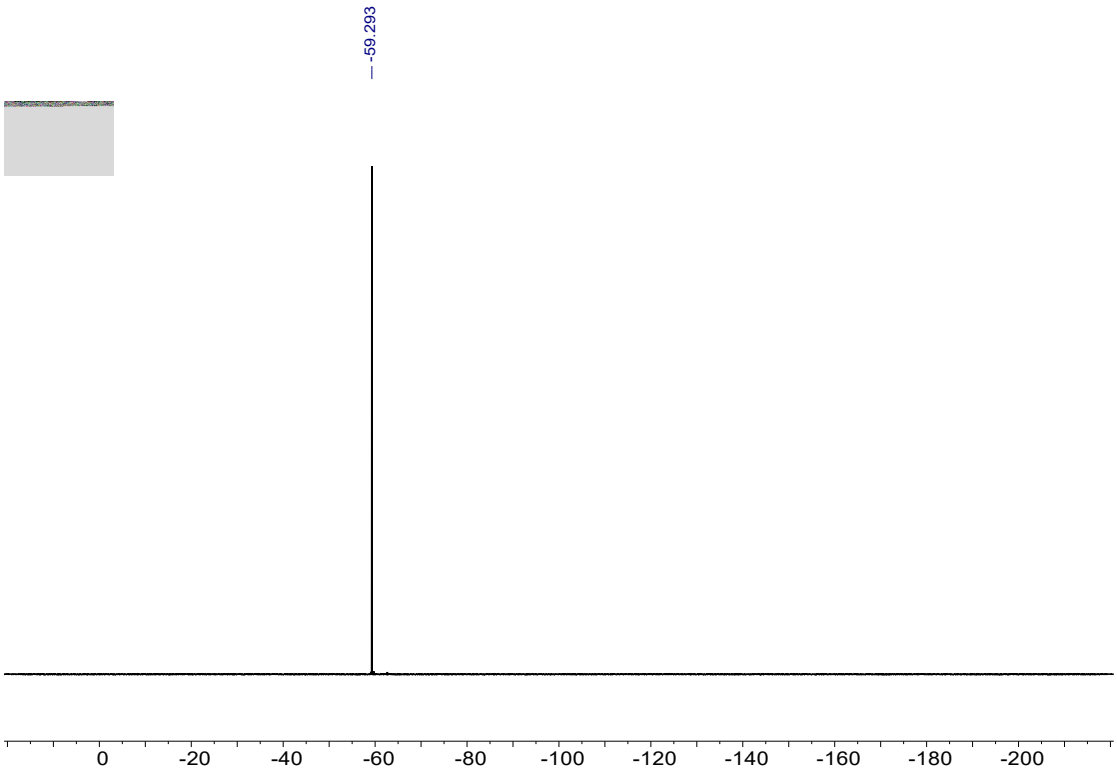
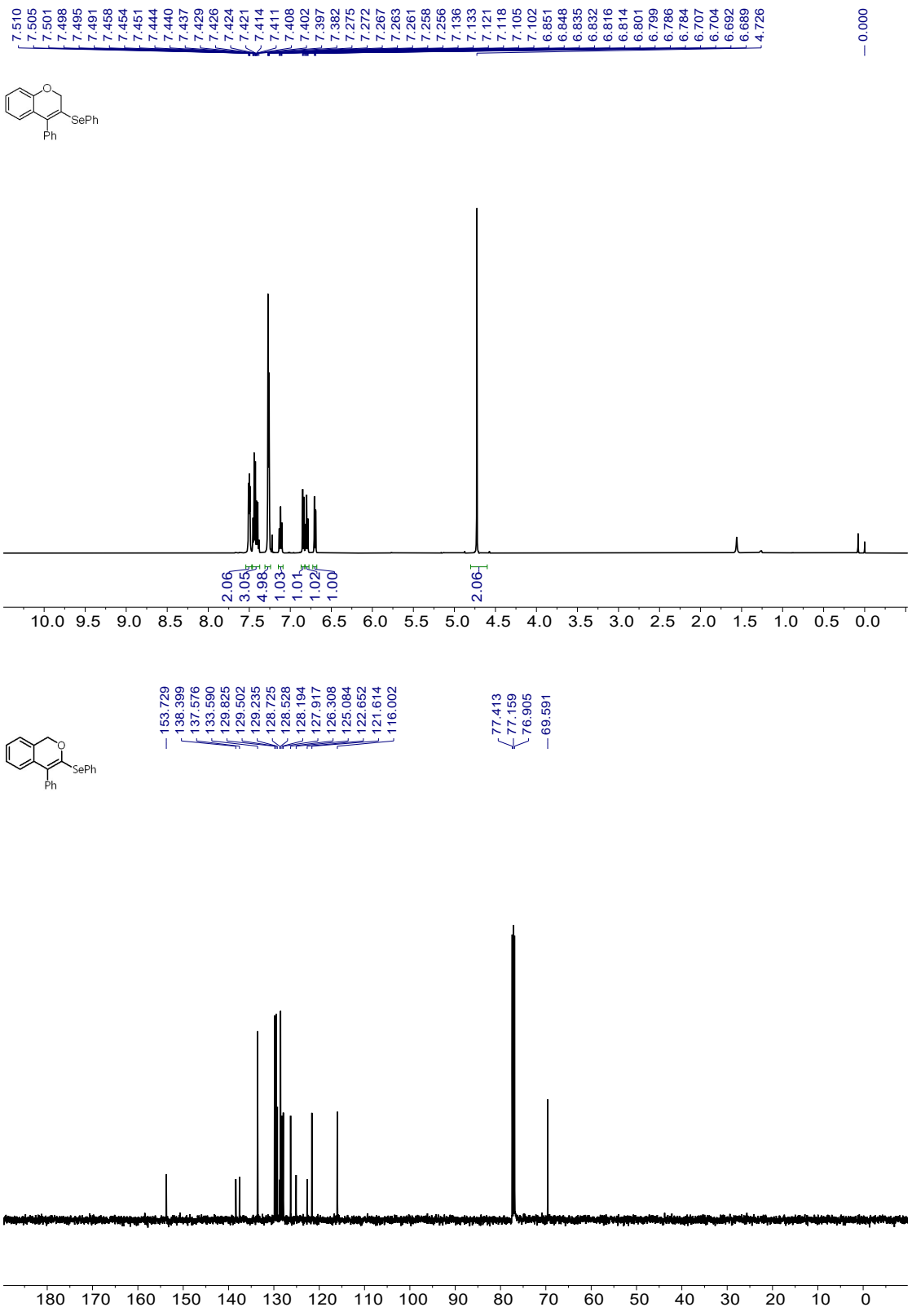
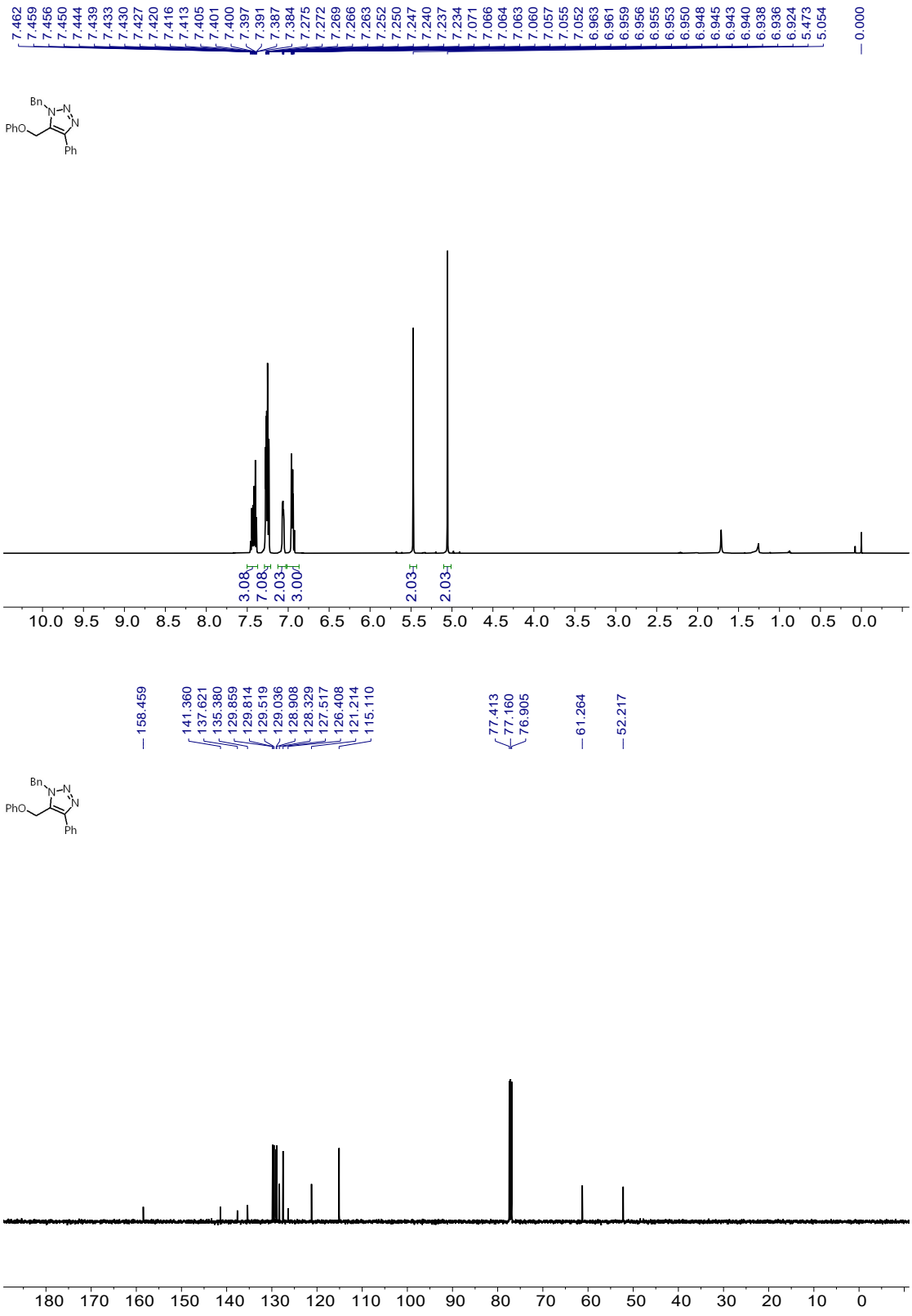


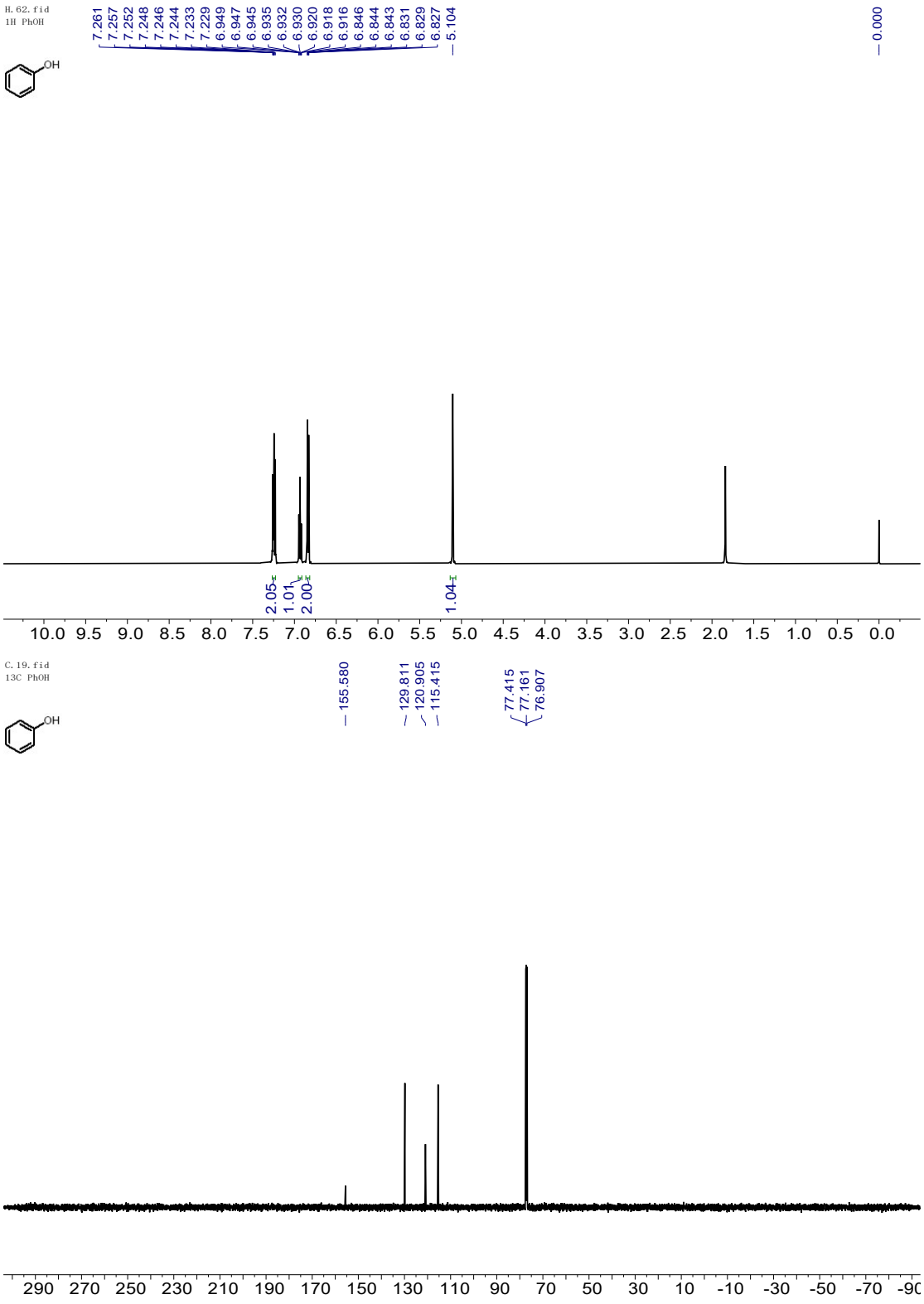
^{1}H NMR ($CDCl_3$, 400 MHz), ^{13}C NMR ($CDCl_3$, 100 MHz) and ^{9}F NMR ($CDCl_3$, 376 MHz) spectrum of **3ac'**



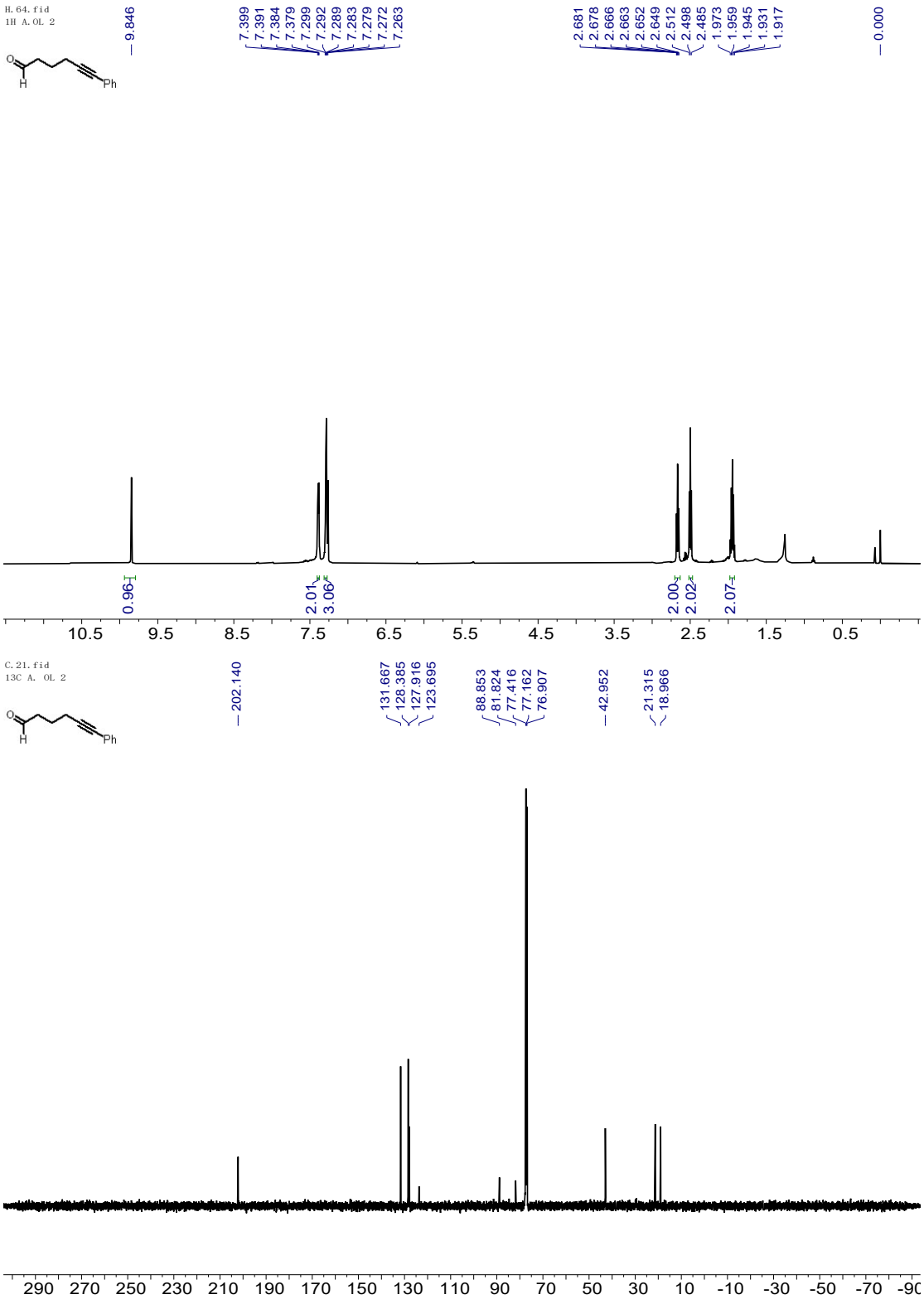
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3ad'**



^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **3ae'**



^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **1**



^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **4**

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