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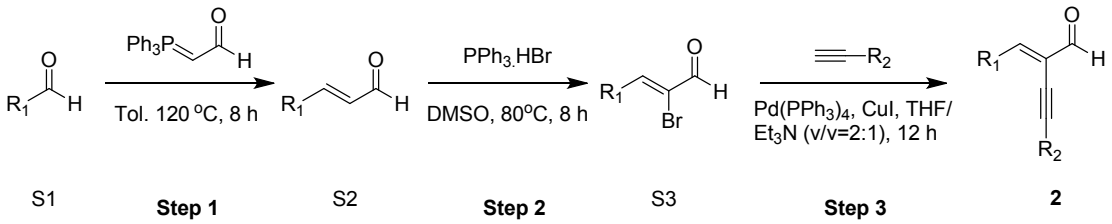
I. General information

Commercially available materials purchased from J&K or Bide were used as received. THF was distilled over sodium. Unless otherwise specified, all reactions were carried out under an atmosphere of nitrogen in 4 mL dry Schlenk tube. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker (AVANCE III HD 400 MHz) spectrometer. Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ 0.00) or chloroform (δ = 7.26, singlet). ^{1}H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets); m (multiplets), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker (AVANCE III HD 101 MHz) spectrometer. Fluorine (^{19}F) nuclear magnetic resonance (^{19}F NMR) spectra were recorded on a Bruker (AVANCE III HD 376 MHz) spectrometer. The melting points (m.p.) of the title compounds were determined when left untouched on an XT-4-MP apparatus from Beijing Tech. Instrument Co. (Beijing, China). High resolution mass spectral analysis (HRMS) was performed on a quadrupole/electrostatic field orbitrap mass spectrometer. Absolute configuration of the products was determined by X-ray crystallography. HPLC analyses were measured on Waters systems with Empower 3 system controller, Alliance 2695, and 2998 Diode Array Waters 2489 UV/Vis detector. Chiralcel brand chiral columns from Daicel Chemical Industries were used with models IA, IB, IC, ID, IF, AD-H, OD-H in 4.6 x 250 mm size and IA-U in 3.0 x 100 mm size. The racemic products used to determine the ee values were synthesized using racemic catalyst. Optical rotations were measured on an Insmark IP-digi Polarimeter in a 1 dm cuvette at 25 ^{o}C. The concentration (c) is given in g/100 mL. Analytical thin-layer chromatography (TLC) was carried out pre-coated silica gel plate (0.2 mm thickness). Visualization was performed using a UV lamp.

II. Preparation of substrates

Note: Starting materials **2** were prepared according to previous literature procedures .[1]



S1 **Step 1** S2 **Step 2** S3 **Step 3** **2**

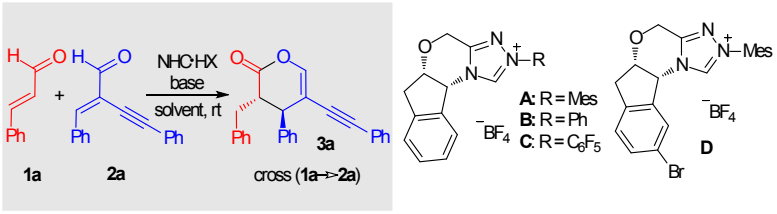
Step 1: To a suspension of aldehyde **S1**(10.50 mmol) in toluene (20.0 mL) was added 2-(triphenylphosphoranylidene)acetaldehyde (3.51 g, 11.55 mmol), the reaction mixture was heated to 120 °C and stirred for 8 h. Then the mixture was concentrated directly in vacuum and the residue was purified by silica gel chromatography with petroleum ether/EtOAc (100:1 to 20:1) to give **S2** as colorless liquid.

Step 2: The enals **S2** (10 mmol) were dissolved in DMSO (40.0 mL), PPh_3.HBr (6.86 g, 20 mmol) was added and the reaction mixture were heated to 80 °C and stirred for 8 h. After completion of reaction, monitored by TLC plate, the reaction mixture were poured into H_2O (50.0 mL), and extracted with EtOAc (50.0 mL*3), the combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum to give the residue. The residue was purified by silica gel chromatography with petroleum ether/EtOAc (100:1 to 20:1) to give **S3** as a yellow solid.[1b]

Step 3: To a suspension of (Z)-2-bromo-Cinnamaldehyde **S3** (2.0 mmol), $Pd(PPh_3)_4$ (0.1 mmol), CuI (0.2 mmol), substituted-ethynyl (2.4 mmol) was added THF (50.0 mL) and Et_3N (25.0 mL) under N_2 atmosphere at room temperature for 12 hours. After completion of reaction, monitored by TLC plate, the reaction mixture were poured into H_2O (50.0 mL), and extracted with EtOAc (50.0 mL*3), the combined organic layers were washed with H_2O (50.0 mL*2) and dried over anhydrous Na_2SO_4, filtered and concentrated in vacuum to give the residue. The residue was purified by silica gel chromatography with petroleum ether/EtOAc (100:1 to 20:1) to give **2** as red liquid.[1a]

III. Condition optimization for the synthesis of 3a

Table S1. Condition optimization.



Entry	NHC	Base	Solvent	Yield[%][b]	Ee [%][c]	Dr[d]
1	**A**	Et_3N	THF	52	99	> 20:1
2	**B**	Et_3N	THF	0	-	-
3	**C**	Et_3N	THF	0	-	-
4	**D**	Et_3N	THF	85	99	> 20:1
5	**D**	DIEA	THF	83	99	> 20:1
6	**D**	Na_2CO_3	THF	80	92	-
7	**D**	$NaHCO_3$	THF	50	98	-
8	**D**	NaOA	THF	75	95	
9	**D**	DABCO	THF	72	67	>20:1
10	**D**	K_3PO_4	THF	80	79	>20:1
11	**D**	DBU	THF	Trace	-	-
12	**D**	Cs_2CO_3	THF	45	50	-
13	**D**	K_2CO_3	THF	85	43	-
14	**D**	CsOAc	THF	85	5	-
15	**D**	KOAc	THF	85	37	-
16	**D**	DMAP	THF	60	79	
17	**D**	Et_3N	$CHCl_3$	64	97	> 20:1
18	**D**	Et_3N	EtOAc	68	99	>20:1
19	**D**	Et_3N	MeOH	0	-	-
20	**D**	Et_3N	EtOH	0	-	-
21	**D**	Et_3N	MeCN	70	88	-
22[e]	**D**	Et_3N	THF	62	99	>20:1
23[f]	**D**	DABCO	THF	0	-	-
24[f]	**D**	K_3PO_4	THF	0	-	-

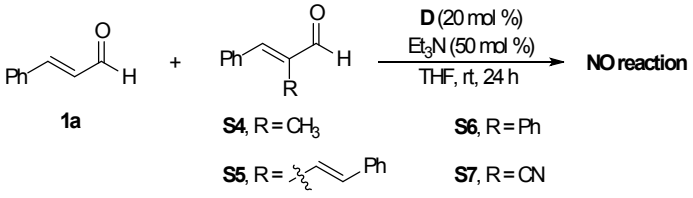
25 [f]	**D**	K_2CO_3	THF	0	-	-
26 [f]	**D**	KOAc	THF	0	-	-
27 [f]	**D**	DMAP	THF	0	-	-

[a] Unless otherwise specified, the reactions were carried using **1a** (0.15 mmol), **2a** (0.1 mmol), NHC (0.02 mmol), base (0.05 mmol) and solvent (1.0 mL) at rt for 24 h. [b] Isolated yield of 3a. [c] The ee values were determined via HPLC on chiral stationary phase. [d] Dr values were determined via ^{1}H NMR on the crude reaction mixture. [e] **1a** (0.1 mmol). [f] base (0.01 mmol). Mes = 2,4,6-Trimethylphenyl. THF = Tetrahydrofuran. DBU = 1,8-Dizabicyclo[5.4.0]undec-7-ene. MAP = 4-Dimethylaminopyridine. DABCO = 1,4-Diazabicyclo[2.2.2]octane;triethylenediamine. Et_3N = Triethylamine. DIEA = Diisopropylethy.

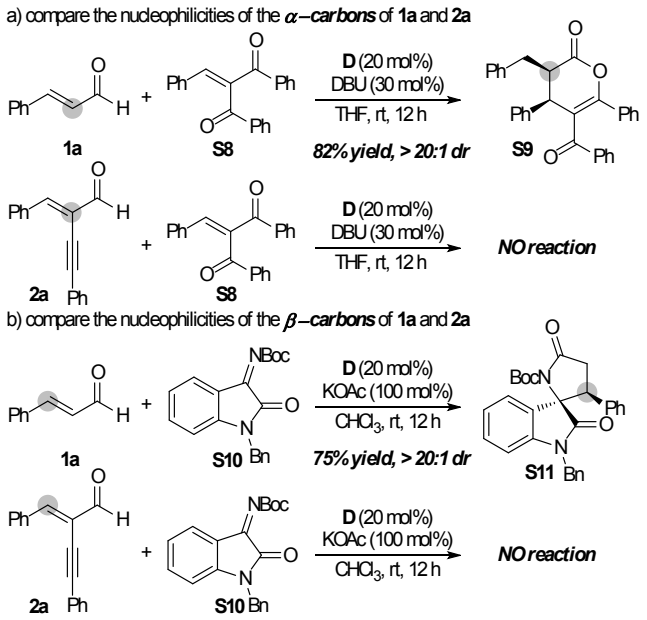
IV. Reaction mechanistic investigations

a) Replacing the alkynyl group with a methyl, vinyl, phenyl or cyano group

α-Substituted enals **S4** to **S7**[2] were used instead of the alkynyl enal **2** as the Michael acceptor in this protocol. No desired cross-coupling products were observed in these reactions. The results indicated that the α-alkynyl substituent is crucial to this NHC-catalyzed chemoselective [2 + 4] cycloaddition reaction.



b) Compare the nucleophilicities of the α- and β-carbons of 1a and 2a



The relative nucleophilicities of the α- and β-carbons of the enal substrates **1a** and **2a** have been studied with reported NHC organocatalytic reactions.[3] The α-carbon of cinnamaldehyde **1a** can react with the enone substrate **S8** through enolate activation pathway under the catalysis of NHC catalyst **D** to give the lactone **S9** as the product in 82% yield.[3a] The β-carbon of cinnamaldehyde **1a** can react with the imine substrate **S10** through homoenolate activation pathway under the catalysis of NHC catalyst **D** and afford the lactam **S11** in 75% yield.[3b] However, no reactions happened when using the alkynyl enal **2a** as the nucleophilic enolate or homoenolate precursors under the same catalytic reaction conditions. Therefore, it is more difficult for an NHC catalyst to react with the alkynyl enal **2a** than cinnamaldehyde **1a** to generate nucleophilic species through covalent pathways. Bode, Glorius and coworkers have also observed similar phenomenon when using α-branched enal substrates as the nucleophiles in NHC organocatalytic reactions.[4] It has been postulated that the steric effects caused by the α-substituent on the enal substrate could inhibit the nucleophilic addition of the NHC catalyst to the enal carbonyl carbon. Additionally, the conjugated planar of the trace amount of the α,β-unsaturated Breslow intermediate generated from α-substituted enals and the NHC catalysts can

be twisted due to steric reasons and the nucleophilicities of the α- and β-carbons of the enal substrates are therefore inhibited.

c) Non-linear effects of the ee values of the NHC catalyst D and the product 3a

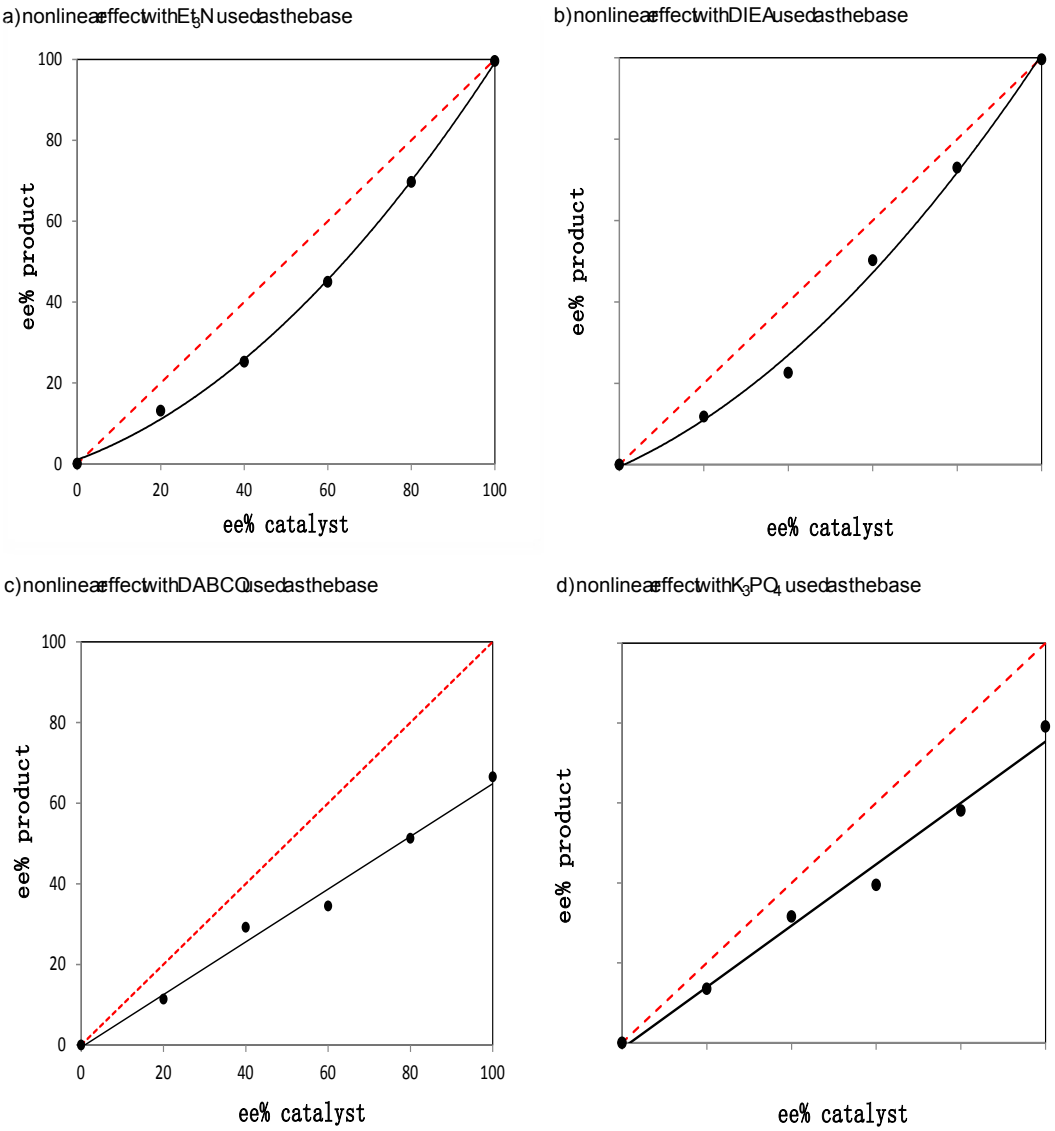


Figure S1. None-linear Effects.

We have also studied the NHC catalytic reaction of **1a** and **2a** by varying the enantiopurity of the NHC catalyst **D** under the optimized reaction conditions (Section III, Table S1, entry 4). The ee values of the products and the ee values of the catalysts showed a negative nonlinear effect (Figure S1, a). Nonlinear effects indicate at least two catalysts are involved in the enantiodifferentiating step of a reaction.[5] We therefore assume that both of the enal substrates have been activated by the NHC catalyst in this [2 + 4] process. It has been well established that cinnamaldehyde **1** could be activated by NHC organic catalysts through covalent bond formations and fragmentations. We have indicated that it was unlikely for the NHC catalyst to react with the alkynyl enal **2** through covalent activation modes in the chemoselective [2 + 4] reaction. Therefore, the alkynyl enal **2** might be activated by the NHC catalyst in a non-covalent hydrogen-

bonding interaction mode. Non-covalent activation reactions with chiral NHC organic catalysts have been reported by Huang, Guin, and others.[6]

The existence of the non-covalent hydrogen-bonding interactions in this NHC organocatalytic [2 + 4] reaction could be supported by the base effects on the product enantioselectivities. Bases with similar basicities to Et_3N could give the product **3a** in excellent enantioselectivities (Table S1, entries 5-8), with similar non-linear effects observed when using NHC catalyst **D** with different optical purities (e.g, Figure S1, b). Strong bases could destroy the hydrogen-bonding interactions existed in the catalytic system, and resulted in drops in the product ee values (Table S1, entries 11-16). Meanwhile, the non-linear effects disappeared when using strong bases (e.g., DABCO or K_3PO_4) for the NHC organocatalytic reactions (e.g., Figure S1, c & d). This is probably because that the hydrogen-bonding interactions have been destroyed by DABCO or K_3PO_4 with a stronger basicity.

Additionally, to exclude the possibility for the dual activation of the cinnamaldehyde **1** by two or more NHC catalysts, we have examined the non-linear effect of a known NHC-catalyzed enantioselective reaction of the substituted cinamaldehyde **S12** (Figure S2). Experimental results indicated an obvious linear relationship between the product ee values and the NHC's optical purities. Therefore, one molecule of the cinnamaldehydes are likely activated by a single molecule of the NHC catalyst and the non-covalent interactions between cinnamaldehydes **1** and the NHC organic catalysts are not likely to exist.[7]

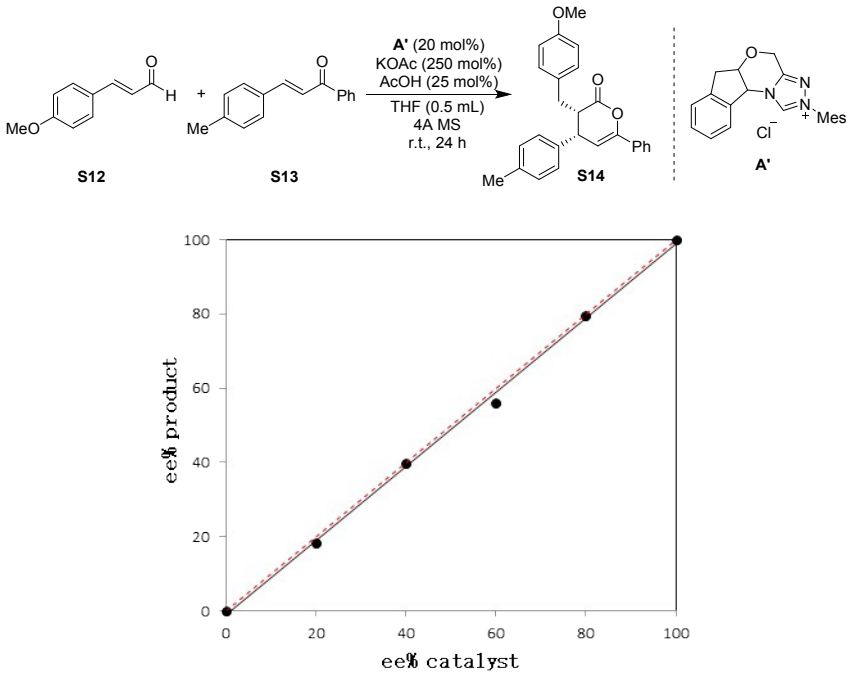


Figure S2. None-linear Effects.

d) ^{1}H NMR analysis of the catalytic system

The non-covalent H-bonding interactions between the NHC catalyst **D** and the alkynyl group of the α-alkynyl enal **2a** can also be supported by ^{1}H NMR analysis (Figures S3 & S4). A catalytic amount of the NHC catalyst **D** was added to the solution of the alkynyl enal **2a** in THF-d_8 in the presence of a sub-stoichiometric amount of TEA (Figure S3, a). Comparing with the reaction system without **2a** (Figure S3, b), an obvious change in the chemical shift of the acidic azolium

proton on the NHC precatalyst **D** was observed. Meanwhile, the aldehyde proton of the alkynyl enal **2a** was not changed in these reaction systems (Figures S3, a *v.s.* d). This is strong evidence for the existence of a non-covalent interaction between the acidic NHC azolium proton and the alkynyl enal **2a**.

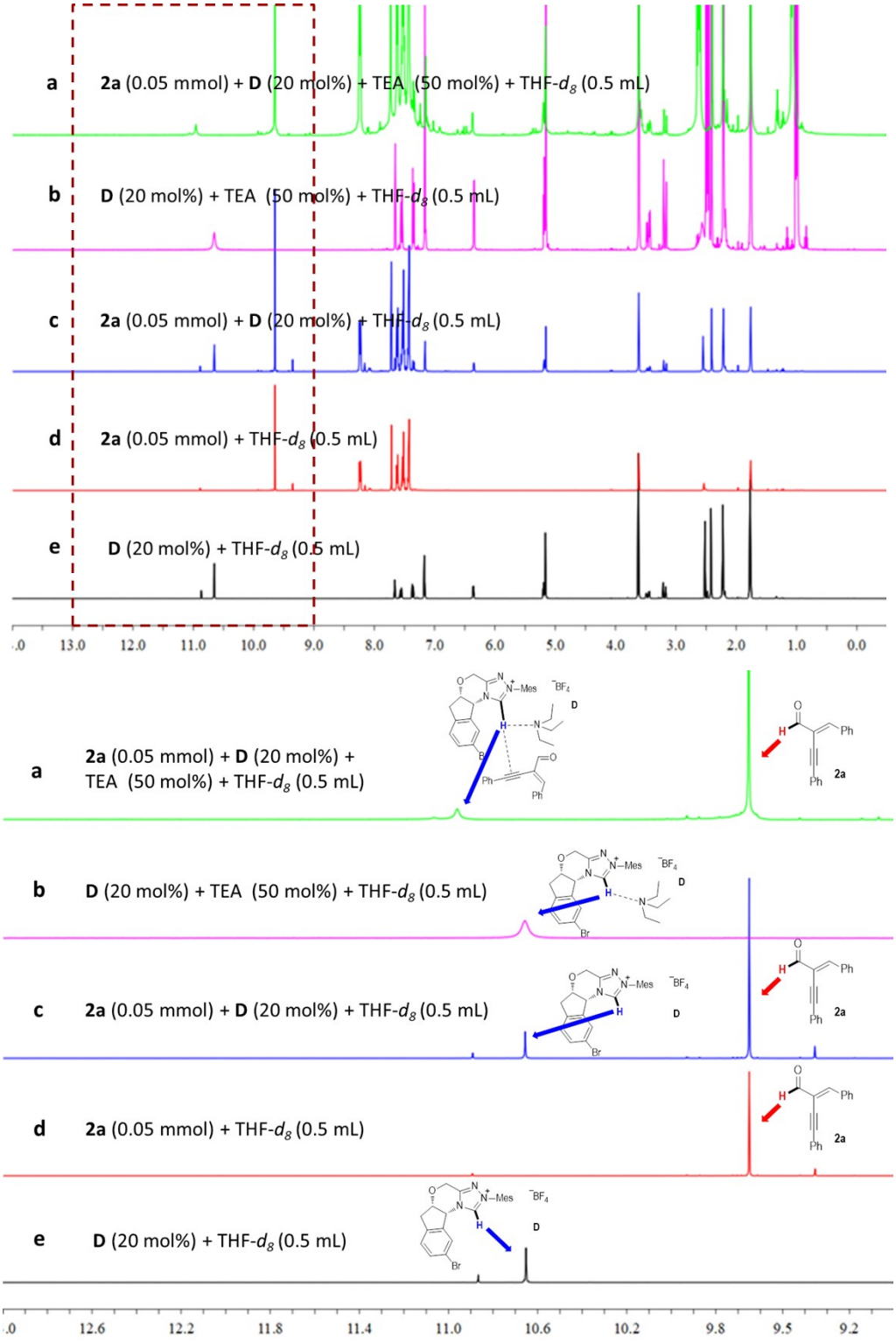


Figure S3. ^{1}H NMR analysis of the NHC pre-catalyst **D** with a catalytic amount of **2a**.

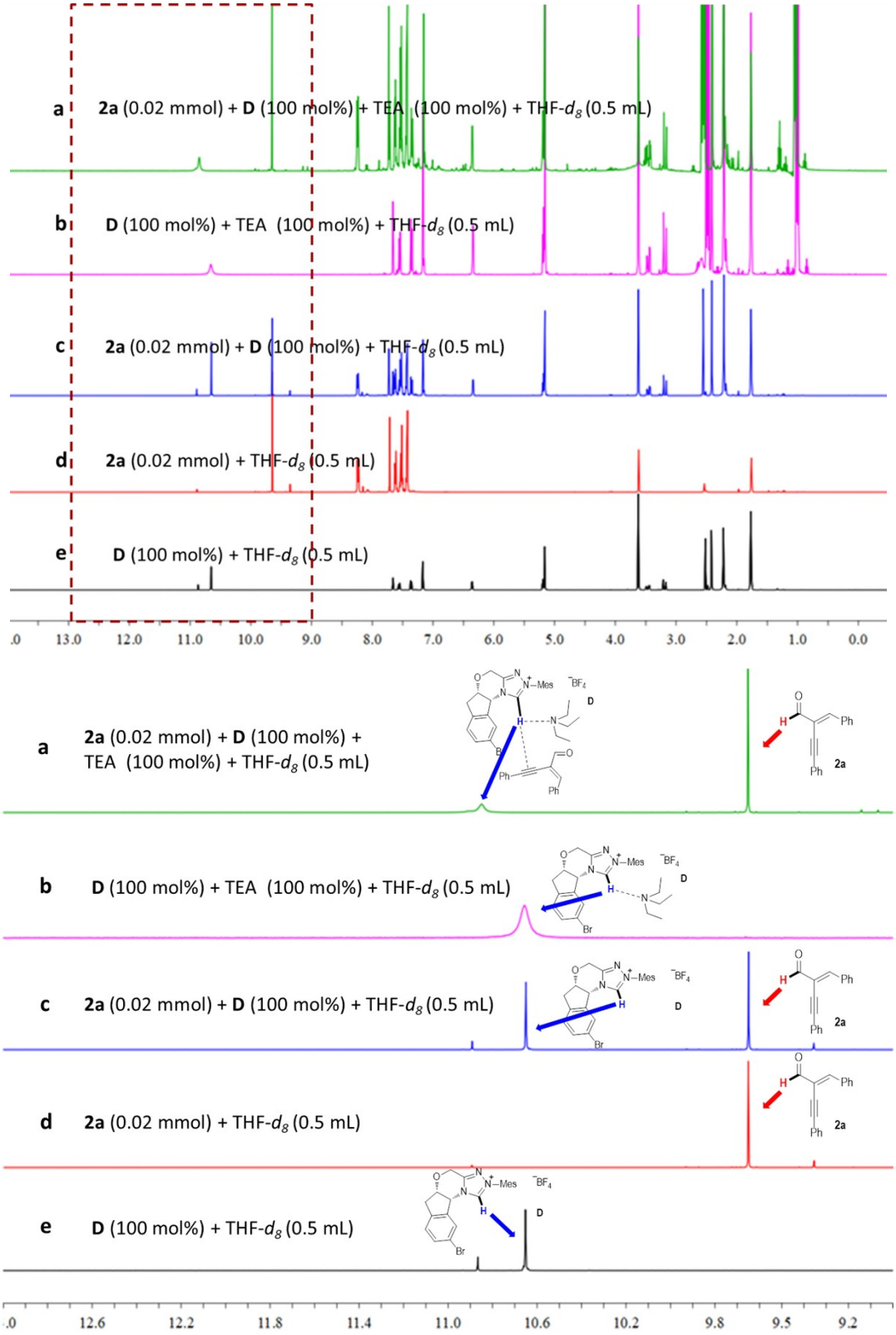


Figure S4. ^{1}H NMR analysis of the NHC pre-catalyst **D** with a stoichiometric amount of **2a**.

Similarly, changes in the chemical shift of the NHC pre-catalyst **D** can also be observed when mixing stoichiometric amount of **D** and **2a** in the precense of TEA (Figure S4). Therefore, the non-

covalent H-bonding interactions between **D** may exist in our NHC-catalyzed [2 + 4] cycloaddition reactions.

e) Shielding of the alkynyl units in the alkynyl enal 2

To show the critical roles of the alkynyl units in the chirality inductions of our NHC-catalyzed [2 + 4] cycloaddition reactions, we examined the [2 + 4] reactions using the alkynyl enals **2x** and **2y** (Figure S5). The alkynyl units of the substrates **2x** and **2y** were shielded by the steric bulky mesityl group and 2,4-diisopropyl group, and the H-bonding interactions between the NHC catalyst **D** and the alkynyl groups on **2x** or **2y** were therefore interupted. As a result, both of the ee values and the yields of the desired products **4x** and **4y** were droped.

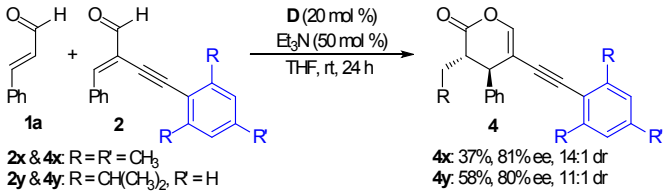


Figure S5. Reactions with enals **2** bearing bulky alkynyl substituents.

f) Hammett studies with substituted alkynyl enal substrate 2

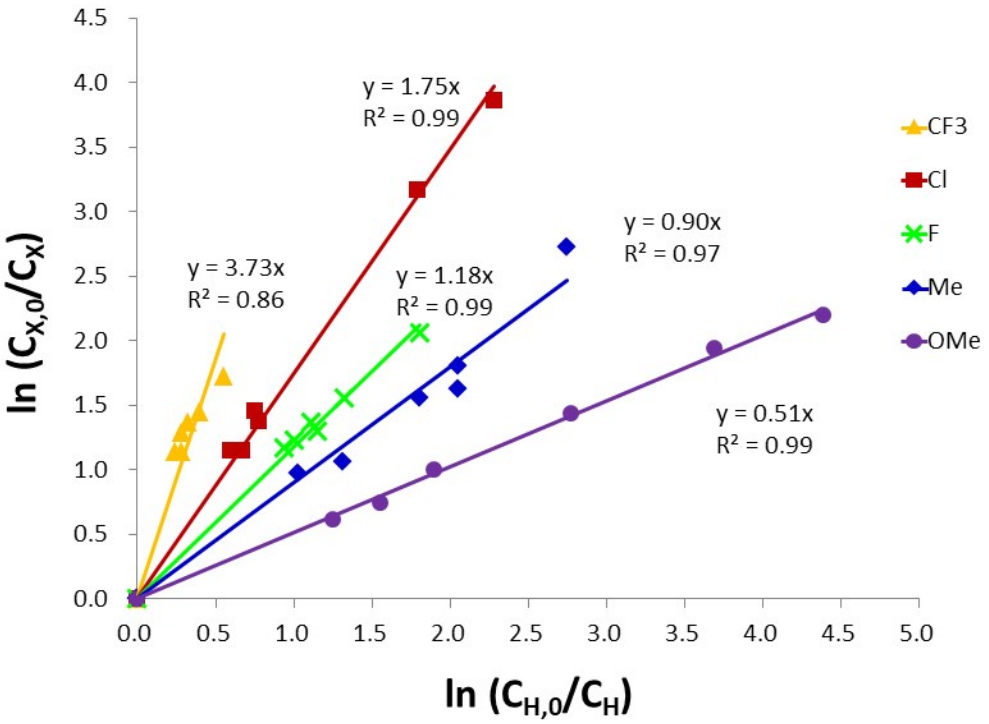


Figure S6. kinetic data obtained in the chemo-selective [2 + 4] cycloaddition reaction.

Hammett studies were carried out to get further insights into the reaction mechanism (Figures S6 & S7). Alkynyl enal substrates **2** bearing 4-F (**2i**), 4-Cl (**2j**), 4-CF_3 (**2k**), 4-CH_3 (**2l**), 4-OCH_3 (**2m**) groups were chosen as the target substrates to evaluate their relative reaction rates compared with the alkynyl enal **2a**. Kinetic studies showed that electron-withdrawing groups reacted faster

than the electron-donating groups (Figure S6). The Hammett plot of the relative reaction rates of the substrates **2i** to **2m** gave a positive slop (ρ = 1.0128) (Figure S7). Therefore, a negatively charged transition state should be built up in the rate determining step. This is in accordance with the non-covalent H-bonding interactions that we have proposed to exist between the acidic azolium proton of the NHC-precatalyst **D** and the alkynyl groups of the alkynyl enal substrates **2** (Figure S9).

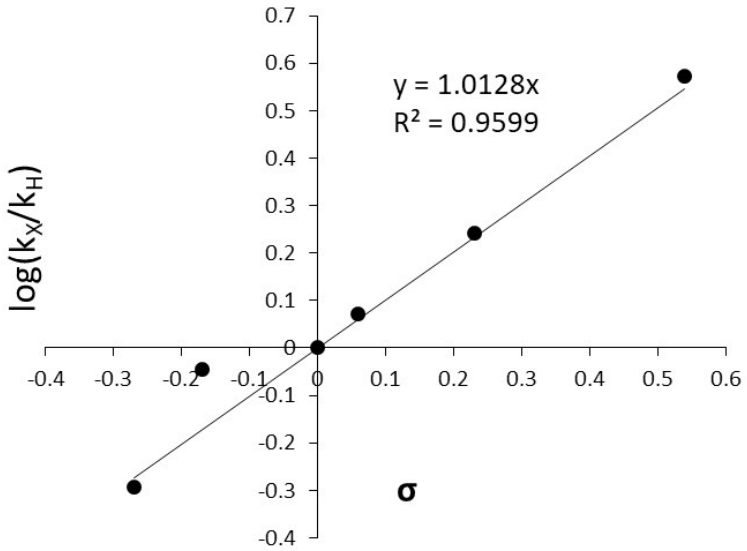


Figure S7. Hammett plot for the chemo-selective [2 + 4] cycloaddition reaction.

g) Effects of the counter anions of the NHC pre-catalysts on the reaction results

Finally, the effects of the counter anions of the NHC pre-catalysts were examined (Figure S8). We have examined the NHC pre-catalysts bearing different counter ions (BF_4^-, Cl^-, ClO_4^-, and Br^-) in our model reactions. The counter ions have significant impacts on the reaction yields. However, all the corresponding products are afforded in similar ee values.

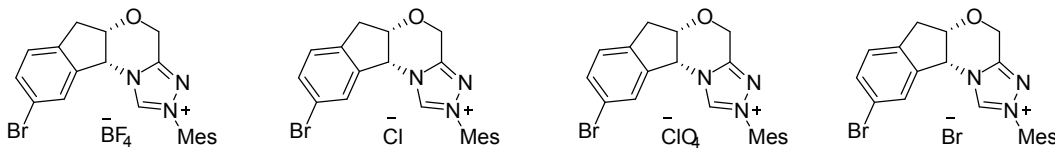


Figure S8. Effects of the counter ions of the NHC pre-catalysts on the reaction outcome.

Based on the above results, this NHC organocatalytic reaction is believed to go through a dual activation process (Figure S9). Cinnamaldehyde **1a** is activated by NHC catalysts via a covalent enolate activation pathway to generate the chiral intermediate **I**. Alkynyl enal **2a** is activated by NHC·HX via H-bonding interactions in the presence of TEA (trasition state-1, **TS-1**) and can react with intermediate **I** as an electrophilic Michael acceptor. The Re face of intermediate **I** is favored to react with the Si face of **2a** due to steric effects. The afforded Michael adduct **II** can then go through lactone formation process to give the desired product **3a** with elimination of the NHC catalyst for additional catalytic cycles.

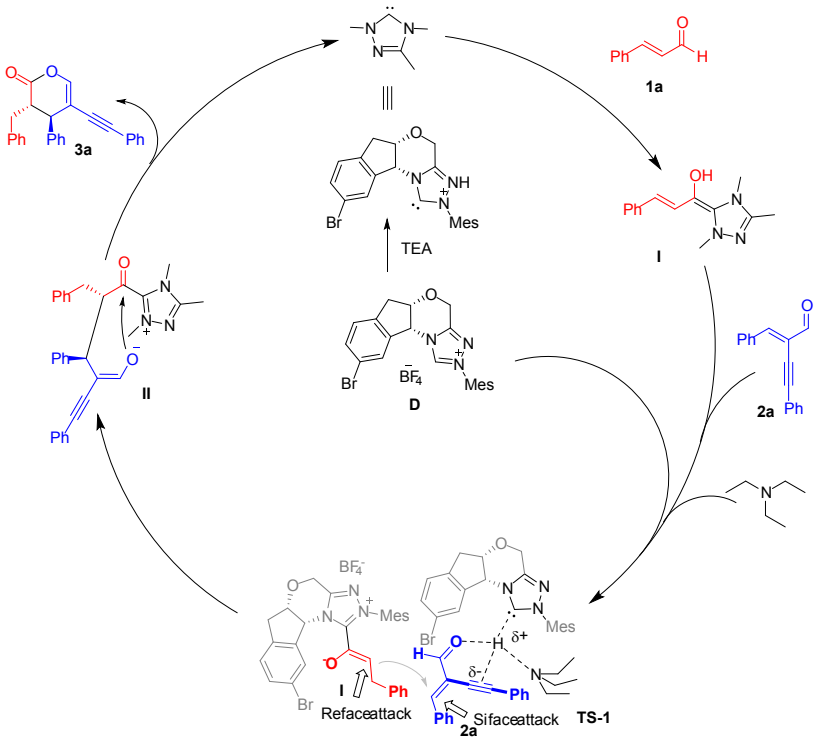
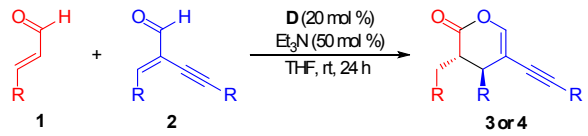


Figure S9. Proposed Reaction Pathway

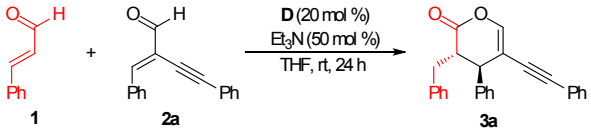
V. General procedure for reactions

1. General procedure for the catalytic reactions of Cinnamaldehyde 1 and (*E*)-2-benzy -lidene-4-phenylbut-3-ynal 2 to synthesize product 3 or 4



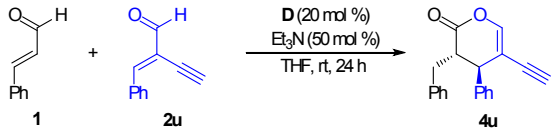
To a 4 mL dry Schlenk tube equipped with a magnetic stir bar, was added cinnamaldehyde **1** (0.15 mmol) and α-alkynyl enal **2** (0.1 mmol), triazolium salt **NHC-D** (0.02 mmol) and Et_3N (0.05 mmol). The tube was closed with a septum, evacuated, and refilled with nitrogen. Freshly distilled THF (0.5 mL) was added and the reaction mixture was then stirred at room temperature till cinnamaldehyde was completely consumed (monitored by TLC). The mixture was concentrated under reduced pressure. The residue was purified via column chromatography on silica gel (petroleum ether / ethyl acetate=100:1 to 20:1) to afford the desired product **3 or 4**.

2. Procedure for the synthesis 3a at 1 mmol



To a 50 mL dry Schlenk tube equipped with a magnetic stir bar, was added cinnamaldehyde **1a** (1.5 mmol, 198.2 mg) and (*E*)-2-benzylidene-4-phenylbut-3-ynal **2a** (1.0 mmol, 232.3 mg), triazolium salt **NHC-D** (0.2 mmol, 20 mol%, 99.6 mg) and Et_3N (0.5 mmol, 50 mol%, 50.6 mg). The tube was closed with a septum, evacuated, and refilled with nitrogen. Freshly distilled THF (5.0 mL) was added and the reaction mixture was then stirred at room temperature till cinnamaldehyde was completely consumed (monitored by TLC). The mixture was concentrated under reduced pressure. The residue was purified via column chromatography on silica gel (petroleum ether / ethyl acetate=100:1 to 20:1) to afford the desired product **3a** (83% yield, 99% ee, > 20:1 dr) as a white solid.

3. Procedure for the synthesis 4v at 1 g scale



To a 100 mL dry Schlenk tube equipped with a magnetic stir bar, was added cinnamaldehyde **1a** (9.6 mmol, 1.3 g) and (E)-2-benzylidenebut-3-ynal **2v** (6.40 mmol, 1.0 g),

triazolium salt **NHC-D** (1.3 mmol, 20 mol%, 0.64 g) and Et_3N (3.2 mmol, 50 mol%, 0.32 g). The tube was closed with a septum, evacuated, and refilled with nitrogen. Freshly distilled THF (20.0 mL) was added and the reaction mixture was then stirred at room temperature for 24 hours. After completely consumed (monitored by TLC), the reaction mixture was directly concentrated under reduced pressure to give a crude product. The crude product was purified via column chromatography on silica gel (petroleum ether / ethyl acetate=100:1 to 20:1) to afford the desired product **4v** (75% yield, 99% ee, > 20:1 dr) as a white solid.

4. Preparation of the NHC pre-catalyst D with varying ee values

The NHC pre-catalyst **D** with varying ee values were prepared by mixing the different enantiomers of **D** in different ratios:

NHC pre-catalyst **D** with a 80% ee value: optically pure **D** (0.18 mmol, 90.0 mg), optically pure ent-**D** (0.02 mmol, 10.0 mg).

NHC pre-catalyst **D** with a 60% ee value: optically pure **D** (0.16 mmol, 80.0 mg), optically pure ent-**D** (0.04 mmol, 20.0 mg).

NHC pre-catalyst **D** with a 40% ee value: optically pure **D** (0.14 mmol, 70.0 mg), optically pure ent-**D** (0.06 mmol, 30.0 mg).

NHC pre-catalyst **D** with a 20% ee value: optically pure **D** (0.12 mmol, 60.0 mg), optically pure ent-**D** (0.08 mmol, 40.0 mg).

NHC pre-catalyst **D** with a 0% ee value: optically pure **D** (0.10 mmol, 50.0 mg), optically pure ent-**D** (0.10 mmol, 50.0 mg).

5. Preparation of the NHC catalysts bearing different anions.

The NHC pre-catalyst **D-1** bearing the counter anion Cl^- was prepared according to the literature.[8]

The NHC pre-catalyst **D-2** bearing the counter anion ClO_4^- was prepared through the follow procedures:

The NHC pre-catalysts **D** (100 mg, 200.75 μmol) was dissolved in DCM (10.0 mL) and added to a solution of NaOH (160.6 mg, 4.02 mmol) in water (10.0 mL). The biphasic mixture was shaken vigorously and the organic layer was collected and quickly transferred to a solution of $HClO_4$ (576.2 mg, 4.02 mmol, 70% in water) in H_2O (10.0 mL). After stirring for 5 min the organic layer was separated and dried over anhydrous Na_2SO_4. After removing of the organic solvents the NHC pre-catalyst **D-2** bearing the counter anion ClO_4^- was afforded as a white solid and was used without further purification.

The NHC pre-catalyst **D-3** bearing the counter anion Br^- was prepared through similar procedures to the preparation of **D-2**. HBr (984.5 mg, 4.02 mmol, 33% in acetic acid) was used instead of the $HClO_4$ (576.2 mg, 4.02 mmol, 70% in water).

6. Experiment of a stoichiometric reaction of alkynyl enal and NHC·HX with Et_3N

Alkynyl enal **2a** (0.05 mmol), TEA (50 mol%) and NHC pre-catalyst **D** (20 mol% or 100 mol%) was dissolved in THF-d_8 (0.5 mL), and the solution was subjected to ^1H NMR analysis. Meanwhile, the solution of **D** (0.05 mmol) and TEA (50 mol%) in THF-d_8 (0.5 mL), the solution of **2a** (0.05 mmol) in THF-d_8 (0.5 mL), and the solution of **D** (0.05 mmol) in THF-d_8 (0.5 mL) were also

analyzed by ^{1}H NMR.

7. Competition experiment for the Hammett study

To a 4 mL dry Schlenk tube equipped with a magnetic stir bar, was added cinnamaldehyde **1** (0.15 mmol, 19.82 mg) and α-alkynyl enal **2a** (0.05 mmol), α-alkynyl bearing *para*-substituted enal (0.05 mmol) triazolium salt **NHC-D** (0.02 mmol, 9.96 mg) and Et_3N (0.05 mmol, 6.94 μL) and 1,3,5-Trimethoxybenzene (0.05 mmol, 8.41 mg) as internal standard. The tube was closed with a septum, evacuated, and refilled with nitrogen. Freshly distilled THF (1.0 mL) was added and the reaction mixture was then stirred at room temperature, this reaction was carried out four parallel samples at the same time. Samples of 0.5 mL each were withdrawn from the reaction mixture after 0, 0.5, 1, 2, 3, 5, and 10 hours reaction time and poured into water (2.0 mL) directly, extracted with EtOAc (2.0 mL*3) and concentrated under reduce pressure to give the residue. The residue was diluted with $CDCl_3$ (0.5 mL) and analyzed by ^{1}H NMR.[9]

Table S2: Date for the competition experiment involving **2a** and **2i.**

Reaction time (h)	C_H (M)	C_X (M)	ln ($C_{H,0}$ / C_H)	ln ($C_{x,0}$ / C_X)
0	0.0395	0.0275	0	0
0.5 h	0.0130	0.0070	1.1113	1.3682
1 h	0.0145	0.0080	1.0022	1.2347
2 h	0.0065	0.0035	1.8045	2.0614
3 h	0.0125	0.0075	1.1506	1.2993
5 h	0.0105	0.0055	1.3249	1.5563
10 h	0.0155	0.0085	0.9354	1.1741

Table S3: Date for the competition experiment involving **2a** and **2j.**

Reaction time (h)	C_H (M)	C_X (M)	ln ($C_{H,0}$ / C_H)	ln ($C_{x,0}$ / C_X)
0	0.0390	0.0475	0	0
0.5 h	0.0180	0.0120	0.7732	1.3758
1 h	0.0200	0.0150	0.6678	1.1526
2 h	0.0215	0.0150	0.5955	1.1526
3 h	0.0185	0.0110	0.7458	1.4628
5 h	0.0065	0.0020	1.7917	3.1675
10 h	0.0040	0.0010	2.2773	3.8607

Table S4: Date for the competition experiment involving **2a** and **2k.**

Reaction time (h)	C_H (M)	C_X (M)	ln ($C_{H,0}$ / C_H)	ln ($C_{x,0}$ / C_X)
0	0.0485	0.0449	0	0
0.5 h	0.0380	0.0143	0.2439	1.1442
1 h	0.0356	0.0144	0.2843	1.1372
2 h	0.0365	0.0123	0.2843	1.2948
3 h	0.0350	0.0114	0.3262	1.3708
5 h	0.0325	0.0105	0.4003	1.4530
10 h	0.0180	0.0080	0.5494	1.7250

Table S5: Date for the competition experiment involving **2a** and **2l.**

Reaction time (h)	C_H (M)	C_X (M)	ln ($C_{H,0}$ / C_H)	ln ($C_{x,0}$ / C_X)
0	0.0390	0.0305	0	0
0.5 h	0.0050	0.0060	2.0541	1.6259
1 h	0.0025	0.0020	2.7472	2.7246
2 h	0.0140	0.0115	1.0240	0.9754
3 h	0.0105	0.0105	1.3121	1.0664
5 h	0.0064	0.0064	1.8073	1.5614
10 h	0.0050	0.0050	2.0541	1.8082

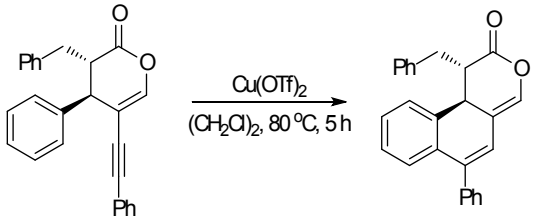
Table S6: Date for the competition experiment involving **2a** and **2m.**

Reaction time (h)	C_H (M)	C_X (M)	ln ($C_{H,0}$ / C_H)	ln ($C_{x,0}$ / C_X)
0	0.0400	0.0315	0	0
0.5 h	0.0060	0.0115	1.8971	1.0076
1 h	0.0085	0.0150	1.5488	0.7419
2 h	0.0115	0.0170	1.2465	0.6168
3 h	0.0010	0.0045	3.6889	1.9459
5 h	0.0025	0.0075	2.7725	1.4351
10 h	0.0005	0.0035	4.3820	2.1972

8. Synthetic transformation of chiral product of 3a

Preparation of **5** from product **3a**

To a solution of **3a** (20 mg, 54.88 μmol) in 1,2-dichloroethane (1.0 mL) was added $Cu(OTf)_2$ (1.98 mg, 5.49 μmol) at room temperature, then the reaction mixture was heated to 80 °C and stirred for 5 hours. After cooling to room temperature, H_2O (10 mL) was added. The mixture was extracted with EtOAc (10 mL), and the combined organic layers were concentrated to afford the residue, the residue was purification directly by column chromatography with petroleum ether / ethyl acetate (20:1) to give the desired product **5** in 71% yield.[10]



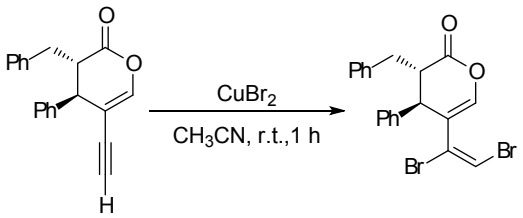
3a, 99% ee, > 20:1 dr **5**, 71%, > 99% ee, 3:1 dr

9. Synthetic transformation of chiral product of 4v

Preparation of **6** from product **4v**

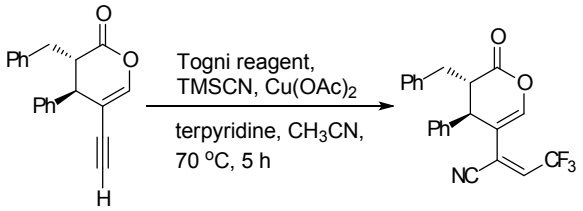
To a solution of **4v** (20 mg, 69.36 μmol) in CH_3CN (1.0 mL) was added $CuBr_2$ (30.98 mg, 138.73 μmol) at room temperature, the reaction mixture was stirred for 1 hour. Then the reaction mixture was concentrated and then directly subjected to column chromatography on silica gel with petroleum ethyl / ethyl acetate (20:1) to yield the desired product **6** in 84%

yield.[11a]



4v, 99% ee, > 20:1 dr **6**, 84%, > 99% ee, > 20:1 dr

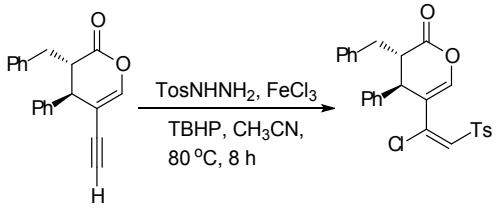
Preparation of **7** from product **4v**



4v, 99% ee, > 20:1 dr **7**, 53%, 97% ee, > 20:1 dr

To a 10 mL dry Schlenk tube was charged with **4v** (20 mg, 69.36 μmol), Togni reagent (26.30 mg, 83.24 μmol), TMSCN (13.76 mg, 138.73 μmol), terpyridine (3.24 mg, 0.94 μmol), $Cu(OAc)_2$ and CH_3CN(1.0 mL) at room temperature, then the reaction mixture was heated to 70 °C and stirred for 5 hours. After cooling to room temperature, the mixture was poured into water (5.0 mL) and extracted with EtOAc (10.0 mL*3), the combined organic layer concentrated under vacuum to afford a residue, the residue was purified by column chromatography on silica gel with petroleum ethyl / ethyl acetate (20:1) to give the desired product **7** in 53% yield.[11b]

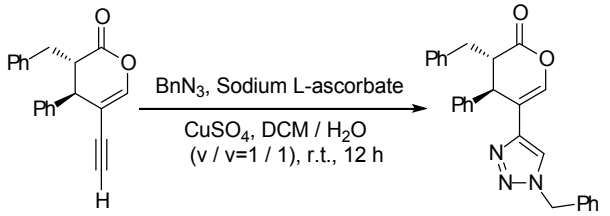
Preparation of **8** from product **4v**



4v, 99% ee, > 20:1 dr **8**, 49%, > 99% ee, > 20:1 dr

To a solution of **4v** (20 mg, 69.36 μmol) and $TosNHNH_2$ (18.08 mg, 138.93 μmol) in CH_3CN (1 mL) was added $FeCl_3$ (22.5 mg, 138.93 μmol) and TBHP (12.5 mg, 138.93 μmol), then the reaction mixture was heated to 80 °C and stirred for 8 hours. After completion, the mixture was added H_2O (5.0 mL) and extracted with EtOAc (10.0 mL*3), combined the organic layer and concentrated under vacuum. The crude product was directly subjected to column chromatography on silica gel with petroleum ethyl / ethyl acetate (5:1) to afford the desired product **8** in 49% yield.[11c]

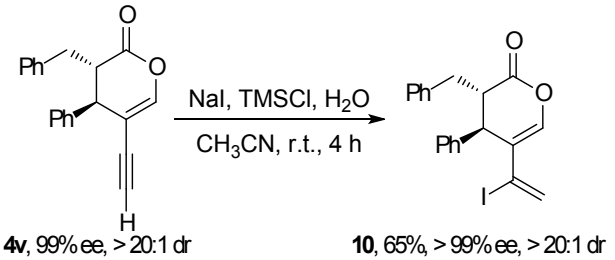
Preparation of **9** from product **4v**:



4v, 99% ee, > 20:1 dr **9**, 96%, 99% ee, > 20:1 dr

To a solution of **4v** (20 mg, 69.36 μmol) and BnN_3 (9.24 mg, 69.36 μmol) in DCM/H_2O (v / v=1/1, 1 mL) was added Sodium L-ascorbate (1.37 mg, 6.94 μmol) and $CuSO_4$ (0.55 mg, 3.47 μmol) at room temperature, and stirred for 12 hours. Then the solution was participated and the aqueous phase was extracted with DCM (1.0 mL*2), the combined organic layers were concentrated in vacuum to give the crude product. The crude product was purified by column chromatography on silica gel with petroleum ethyl / ethyl acetate (10:1) to afford the desired product **9** in 96% yield.[11d]

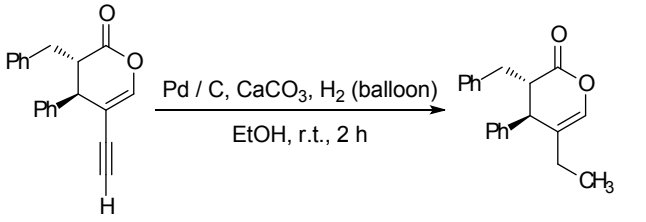
Preparation of **10** from product **4u**:



4v, 99% ee, > 20:1 dr **10**, 65%, > 99% ee, > 20:1 dr

To a solution of NaI (12.48 mg, 83.24 μmol) in CH_3CN (1.0 mL) was added TMSCl (9.04 mg, 83.24 μmol) and H_2O (0.75 mg, 41.62 μmol), the mixture was allowed stirred 10 minutes at room temperature, then **4v** (20 mg, 69.36 μmol) was added and the reaction mixture was stirred for 4 hours. After completion, monitored by TLC plate, the resulting mixture was directly purified by column chromatography on silica gel with petroleum ethyl / ethyl acetate (20:1) to give the desired product **10** in 65% yield.[11e]

Preparation of **11** from product **4v**:

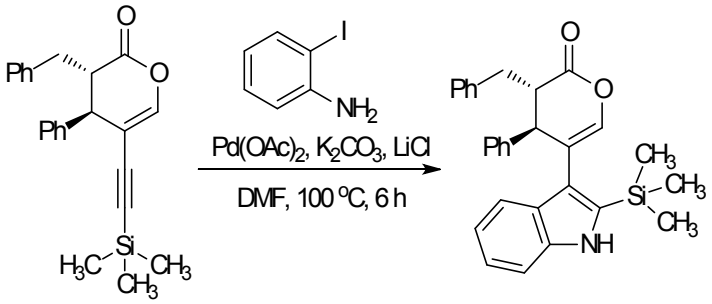


4v, 99% ee, > 20:1 dr **11**, 84%, > 99% ee, > 20:1 dr

To a 25 mL flask was added **4v** (30 mg, 104.04 μmol), Pd / C, $CaCO_3$ (2.45 mg) and EtOH (2.0 mL), the flask was flushed with hydrogen gas, then placed under a balloon of hydrogen. After 4 hours, the mixture was filtered with through Celite and concentrated in vacuum to give a crude product. The crude product was purified by column chromatography with petroleum ethyl / ethyl acetate (20:1) to afford the desired product **11** in 84% yield.

10. Synthetic transformation of chiral product of 4w:

Preparation of **12** form product **4w**:



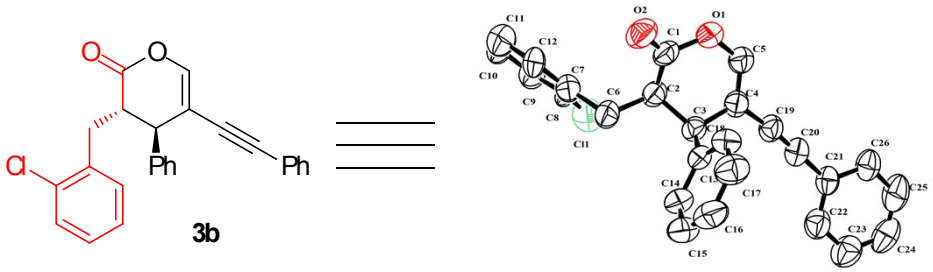
4t, 99% ee, 16:1 dr **12**, 50%, > 99% ee, 4:1 dr

To a 10 mL dry Schlenk tube equipped with a magnetic stir bar, was added **4w** (20 mg, 55.48 μmol), 2-iodoaniline (12.15 mg, 55.48 μmol), K_2CO_3 (15.33 mg, 110.95 μmol), $Pd(OAc)_2$ (0.62 mg, 2.77 μmol) and LiCl (2.35 mg, 55.48 μmol). The tube was charged with nitrogen, freshly distilled DMF (1.0 mL) was added, and then the reaction mixture was heated to 100 °C for 6 hours. After cooling to room temperature, the reaction was directly purified by column chromatography on silica gel with petroleum ethyl / ethyl acetate (5:1) as the eluent to afford the desired product **12** in 50% yield.[12]

VI. Stereochemistry determination via X-ray crystallographic analysis

A colorless needle crystal of **3b** was obtained by vaporization of its ethyl acetate / petroleum ethyl solution.

The absolute stereochemistry of **3b** was determined by the X-ray diffraction. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as **CCDC**: 1980067.



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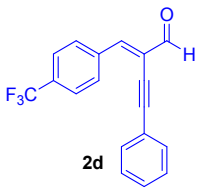
VII. Characterization of substrates and products

1. Characterization of substrates



(*E*)-4-phenyl-2-(4-(trifluoromethyl) benzylidene) but-3-ynal

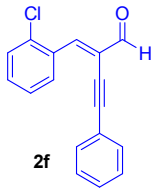
Red solid, 96% yield, 578.1 mg, m.p. 73-74 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77-9.66 (m, 1H), 8.24 (d, *J* = 8.5 Hz, 1H), 7.75-7.69 (m, 3H), 7.60-7.49 (m, 3H), 7.42-7.40 (m, 2H), 6.81-6.75 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.2, 189.3, 149.3, 147.1, 131.0 (2C), 129.6 (2C), 128.5, 127.6 (2C), 124.7, 123.5, 100.9, 82.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.0.

HRMS (ESI, m/z): Mass calcd. for $C_{18}H_{12}OF_3$ $[M+H]^+$, 301.0835; found: 301.0842.



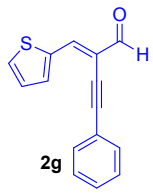
(*E*)-2-(2-chlorobenzylidene)-4-phenylbut-3-ynal

Red oil, 70% yield, 387.1 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (s, 1H), 8.75-8.58 (m, 1H), 8.00 (s, 1H), 7.60- 7.46 (m, 3H), 7.41-7.37 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.7, 145.5, 134.7, 131.1, 130.9 (2C), 129.2, 129.1, 128.3, 127.5 (2C), 125.8, 123.6, 121.5, 121.3, 100.2, 81.5.

HRMS (ESI, m/z): Mass calcd. for $C_{17}H_{12}OCl$ $[M+H]^+$, 267.0571; found: 267.0570.



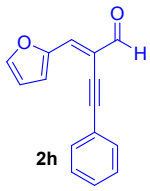
(*E*)-4-phenyl-2-(thiophen-2-ylmethylene) but-3-ynal

Reddish black solid, 73% yield, 350.6 mg, m.p. 41-42 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.80 (s, 1H), 7.73-7.56 (m, 4H), 7.44- 7.33 (m, 3H), 7.19 (dd, *J* = 5.0, 3.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.0, 142.5, 137.8, 134.3, 131.9, 130.8 (2C), 128.1, 127.4, 126.7, 121.6, 118.8, 102.1, 82.5.

HRMS (ESI, m/z): Mass calcd. for $C_{15}H_{11}OS$ $[M+H]^+$, 239.0528; found 286.0531



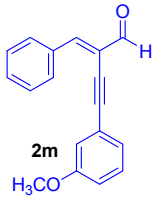
(*E*)-2-(furan-2-ylmethylene)-4-phenylbut-3-ynal

Red oil, 65% yield, 289.1 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.56 (s, 1H), 7.67 (dd, *J* = 1.7, 0.5 Hz, 1H), 7.61-7.59 (m, 2H), 7.55 (d, *J* = 3.6 Hz, 1H), 7.46 (s, 1H), 7.40-7.38 (m, 3H), 6.65-6.63 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.8, 150.3, 145.2, 135.9, 130.8 (2C), 128.1, 127.5 (2C), 121.5, 118.2, 116.9, 112.5, 100.5, 82.3.

HRMS (ESI, m/z): Mass calcd. for $C_{15}H_{11}O$ $[M+H]^+$, 223.0754; found: 223.0752.



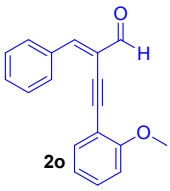
(*E*)-2-benzylidene-4-(3-methoxyphenyl) but-3-ynal

Red oil, 40% yield, 259.2 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.59 (s, 1H), 8.17-8.00 (m, 2H), 7.49 (s, 1H), 7.46- 7.39 (m, 3H), 7.25-7.18 (m, 1H), 7.15-7.13 (m, 1H), 7.06 (dd, *J* = 2.5, 1.4 Hz, 1H), 6.91-6.88 (m, *J* = 8.3, 2.6, 1.0 Hz, 1H), 3.78 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.0, 158.4, 150.4, 133.1, 130.7, 129.7 (2C), 128.5, 127.8 (2C), 123.4, 122.5, 121.6, 115.5, 114.8, 99.8, 82.0, 54.3.

HRMS (ESI, m/z): Mass calcd. for $C_{18}H_{15}O_2$ $[M+H]^+$, 263.1067; found: 263.1064.



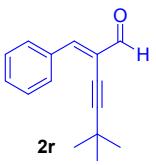
(*E*)-2-benzylidene-4-(2-methoxyphenyl) but-3-ynal

Red oil, 98% yield, 516.8 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.65 (s, 1H), 8.41-8.17 (m, 2H), 7.58 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.53-7.44 (m, 4H), 7.38-7.34 (m, 1H), 6.99-6.92 (m, 2H), 3.97 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.1, 159.5, 149.4, 133.2, 132.8, 130.5, 129.9 (2C), 129.7, 127.7 (2C), 121.6, 119.6, 110.8, 109.6, 97.0, 86.4, 54.8.

HRMS (ESI, m/z): Mass calcd. for $C_{18}H_{15}O_2$ $[M+H]^+$, 263.1067; found: 263.1065.



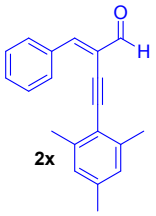
(*E*)-2-benzylidene-5,5-dimethylhex-3-ynal

Red oil, 71% yield, 250.3 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.55 (s, 1H), 8.10 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.53- 7.34 (m, 4H), 1.39 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5, 149.30, 133.32, 130.21, 129.4 (2C), 127.5 (2C), 122.3, 109.8, 72.3, 29.6 (3C), 27.7.

HRMS (ESI, m/z): Mass calcd. for $C_{15}H_{17}O$ $[M+H]^+$, 213.1274; found: 213.1275.



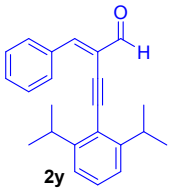
(*E*)-2-benzylidene-4-mesitylbut-3-ynal

Yellow oil, 82% yield, 565.0 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.68 (s, 1H), 8.32 – 8.12 (m, 2H), 7.58 – 7.35 (m, 4H), 6.92 (s, 2H), 2.55 (s, 6H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.2, 149.6, 141.0, 139.0, 134.3, 131.4 (2C), 130.5 (2C), 128.7 (2C), 127.9 (2C), 123.4, 119.4, 100.0, 90.6, 21.4, 21.2 (2C).

HRMS (ESI, m/z): Mass calcd. for $C_{20}H_{19}O$ $[M+H]^+$, 275.1430; found: 275.1437.



(*E*)-2-benzylidene-4-(2,6-diisopropylphenyl)but-3-ynal

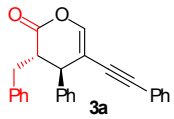
Yellow oil, 35% yield, 280.0 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (s, 1H), 8.18 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.51 (s, 1H), 7.47 (dd, *J* = 5.1, 1.9 Hz, 3H), 7.39 – 7.31 (m, 1H), 7.19 (d, *J* = 7.8 Hz, 2H), 3.76 (dt, *J* = 13.7, 6.9 Hz, 2H), 1.33 (s, 6H), 1.32 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.2, 151.6, 149.7, 134.3, 131.4, 130.4 (3C), 129.5, 128.8 (2C), 123.4, 122.3 (2C), 120.3, 99.0, 90.8, 31.8 (2C), 23.6 (4C).

HRMS (ESI, m/z): Mass calcd. for $C_{23}H_{25}O$ $[M+H]^+$, 317.1900; found: 317.1905.

2. Characterization of products



3a

(3*S*,4*R*)-3-benzyl-4-phenyl-5-(phenylethynyl)-3,4-dihydro-2*H*-pyran-2-one

White solid, 85% yield, 31.1 mg, m.p. 144-145 °C.

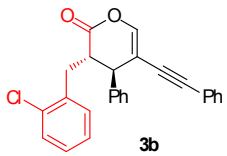
[α]$_D^{25}$ = -214.1 (c = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.33 (m, 3H), 7.32-7.28 (m, 4H), 7.27 (dd, *J* = 3.9, 3.0 Hz, 2H), 7.26-7.22 (m, 2H), 7.14-7.06 (m, 4H), 7.04 (s, 1H), 3.55 (d, *J* = 7.0 Hz, 1H), 3.45-3.39 (m, 1H), 3.28 (dd, *J* = 14.7, 4.7 Hz, 1H), 2.43 (dd, *J* = 14.7, 9.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 144.7, 138.2, 136.4, 131.4 (2C), 129.1 (2C), 129.0 (2C), 128.7 (2C), 128.5, 128.3 (4C), 128.2, 126.7, 122.6, 108.8, 92.8, 83.7, 45.1 (2C), 32.3.

HRMS (ESI, m/z): Mass calcd. for $C_{26}H_{21}O_2$ $[M+H]^+$, 365.1536; found: 365.1531.

HPLC analysis: 99% e.e. (Chiralcel ID, 25 °C, IPA/Hexane = 1/99, 0.5 mL/min, 254 nm), Rt (major) = 20.5 min, Rt (minor) = 22.3 min.



3b

(3*S*,4*R*)-3-(2-chlorobenzyl)-4-phenyl-5-(phenylethynyl)-3,4-dihydro-2*H*-pyran-2-one

White solid, 80% yield, 24.1 mg, m.p. 86-88 °C.

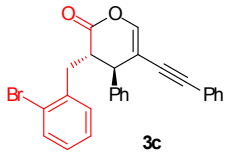
[α]$_D^{25}$ = -131.6 (c = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.30 (m, 6H), 7.30-7.26 (m, 3H), 7.23-7.08 (m, 5H), 7.02 (s, 1H), 3.63 (d, *J* = 7.1 Hz, 1H), 3.57 (dd, *J* = 13.3, 6.9 Hz, 1H), 3.16 (dd, *J* = 14.3, 6.2 Hz, 1H), 2.69 (dd, *J* = 14.3, 6.9 Hz, 1H).

^{13}C NMR (101 MHz, CDCl3) δ 168.8, 144.6, 136.7, 136.0, 134.1, 132.2, 131.4 (2C), 129.6, 129.2 (2C), 128.5, 128.3 (3C), 128.2 (3C), 126.7, 122.5, 108.5, 92.8, 83.6, 46.1, 42. 9, 31.3.

HRMS (ESI, m/z): Mass calcd. for $C_{26}H_{20}O_2Cl$ $[M+H]^+$, 399.1146; found: 399.1147.

HPLC analysis: > 99% e.e. (Chiralcel OD-H, 25 °C, IPA/Hexane = 1/99, 0.5 mL/min, 254 nm), Rt (major) = 22.3 min, Rt (minor) = 26.9 min.



3c

(3*S*,4*R*)-3-(2-bromobenzyl)-4-phenyl-5-(phenylethynyl)-3,4-dihydro-2*H*-pyran-2-one

White solid, 96% yield, 42.5 mg, m.p. 139-140 °C.

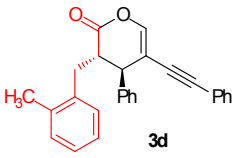
[α]$_D^{25}$ = -260.7 (c = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.33-7.41 (m, 5H), 7.31-7.26 (m, 3H), 7.24-7.18 (m, 3H), 7.17-7.07 (m, 2H), 7.02 (s, 1H), 3.67 (d, *J* = 7.1 Hz, 1H), 3.57 (q, *J* = 6.7 Hz, 1H), 3.14 (dd, *J* = 14.3, 6.5 Hz, 1H), 2.70 (dd, *J* = 14.3, 6.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 144.6, 137.8, 136.7, 132.9, 132.4 (2C), 131.4, 129.2 (2C), 128.6, 128.5, 128.3 (2C), 128.2 (3C), 127.4, 124.6, 122.6, 108.5, 92.9, 83.7, 46.3, 43.2, 33.7.

HRMS (ESI, m/z): Mass calcd. for $C_{26}H_{20}O_2Br$ $[M+H]^+$, 443.0641; found: 443.0641.

HPLC analysis: 99% e.e. (Chiralcel OD-H, 25 °C, IPA/Hexane = 1/99, 0.7 mL/min, 254 nm), Rt (major) = 18.2 min, Rt (minor) = 21.3 min.



3d

(3*S*,4*R*)-3-(2-methylbenzyl)-4-phenyl-5-(phenylethynyl)-3,4-dihydro-2*H*-pyran-2-one

White solid, 77% yield, 29.3 mg, m.p. 125-126 °C.

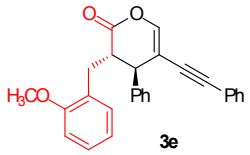
[α]$_D^{25}$ = -231.7 (c = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, CDCl3) δ 7.39 – 7.29 (m, 5H), 7.27 (s, 2H), 7.25 (s, 1H), 7.16 (d, *J* = 2.8 Hz, 3H), 7.12-7.08 (m, 2H), 7.07-7.00 (m, 2H), 3.61 (d, *J* = 7.0 Hz, 1H), 3.44-3.39 (m, 1H), 3.24 (dd, *J* = 15.1, 4.7 Hz, 1H), 2.51 (dd, *J* = 15.1, 9.4 Hz, 1H), 2.12 (s, 3H).

^{13}C NMR (101 MHz, CDCl3) δ 168.0, 143.5, 135.6, 135.5, 135.2, 130.3 (2C), 129.62, 128.1 (2C), 128.0, 127.4, 127.3 (2C), 127.1 (2C), 127.0, 125.7, 125.0, 121.5, 107.7, 91.8, 82.6, 44.1, 42.3, 28.2, 18.4.

HRMS (ESI, m/z): Mass calcd. for $C_{27}H_{23}O_2$ $[M+H]^+$, 379.1693; found: 379.1693.

HPLC analysis: 99% e.e. (Chiralcel OD-H, 25 °C, IPA/Hexane = 1/99, 0.5 mL/min, 254 nm), Rt (major) = 35.8 min, Rt (minor) = 48.8 min.



3e

(3*S*,4*R*)-3-(2-methoxybenzyl)-4-phenyl-5-(phenylethynyl)-3,4-dihydro-2*H*-pyran-2-one

White solid, 53% yield, 20.8 mg, m.p. 53-55 °C.

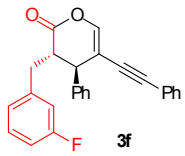
[α]$_D^{25}$ = -98.7 (c = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, CDCl3) δ 7.39-7.29 (m, 5H), 7.29-7.26 (m, 2H), 7.26-7.21 (m, 2H), 7.19-7.09 (m, 2H), 7.00 (s, 1H), 6.93-6.80 (m, 3H), 3.83 (s, 3H), 3.66-3.60 (m, 1H), 3.52 (d, *J* = 7.1 Hz, 1H), 3.22 (dd, *J* = 14.1, 5.0 Hz, 1H), 2.46 (dd, *J* = 14.1, 8.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 157.6, 144.6, 137.0, 131.7, 131.3 (2C), 129.0 (2C), 128.4, 128.3 (2C), 128.2 (2C), 128.0, 127.9, 126.2, 122.6, 120.2, 110.1, 108.7, 92.6, 84.0, 55.2, 45.5, 42.4, 28.4.

HRMS (ESI, m/z): Mass calcd. for $C_{27}H_{23}O_3$ $[M+H]^+$, 395.1642; found: 395.1643.

HPLC analysis: 99% e.e. (Chiralcel OD-H, 25 °C, IPA/Hexane = 1/99, 0.6 mL/min, 254 nm), Rt (major) = 15.7 min, Rt (minor) = 21.5 min.



3f

(3*S*,4*R*)-3-(3-fluorobenzyl)-4-phenyl-5-(phenylethynyl)-3,4-dihydro-2*H*-pyran-2-one

White solid, 89% yield, 34.2 mg, m.p. 140-141 °C.

[α]$_D^{25}$ = -199.2 (c = 1.0, $CHCl_3$).

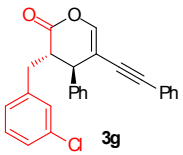
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.30 (m, 5H), 7.29-7.26 (m, 3H), 7.25-7.23 (m, 1H), 7.10 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.04 (s, 1H), 6.95 (t, *J* = 8.4, 2.4 Hz, 1H), 6.88 (d, *J* = 7.7 Hz, 1H), 6.81 (dd, *J* = 9.9, 1.9 Hz, 1H), 3.55 (d, *J* = 7.0 Hz, 1H), 3.41-3.39 (m, 1H), 3.24 (dd, *J* = 14.7, 5.0 Hz, 1H), 2.44 (dd, *J* = 14.7, 9.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 162.9 (d, *J* = 246.1 Hz), 144.6, 140.7 (d, *J* = 7.3 Hz), 136.3, 131.4 (2C), 130.1 (d, *J* = 8.4 Hz), 129.1 (2C), 128.5, 128.3 (3C), 128.2 (2C), 124.7, 124.6, 122.5, 115.9 (d, *J* = 21.3 Hz), 113. 7 (d, *J* = 20.9 Hz), 92.9, 83.5, 45.3, 44.9, 32.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.9.

HRMS (ESI, m/z): Mass calcd. for $C_{26}H_{20}O_2F$ $[M+H]^+$, 383.1442; found: 383.1440.

UPLC analysis: > 99% e.e. (Chiralcel IA-U, 25 °C, IPA/Hexane = 1/99, 0.5 mL/min, 254 nm), Rt (major) = 2.9 min, Rt (minor) = 3.1 min.



3g

(3*S*,4*R*)-3-(3-chlorobenzyl)-4-phenyl-5-(phenylethynyl)-3,4-dihydro-2*H*-pyran-2-one

White solid, 80% yield, 32.0 mg, m.p. 136-137 °C.

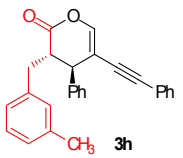
[α]$_D^{25}$ = -199.2 (c = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.31 (m, 5H), 7.30-7.27 (m, 3H), 7.25-7.22 (m, 2H), 7.14-7.07 (m, 3H), 7.04 (s, 1H), 7.01-6.94 (m, 1H), 3.54 (d, *J* = 7.0 Hz, 1H), 3.39 (m, 1H), 3.22 (dd, *J* = 14.7, 5.1 Hz, 1H), 2.42 (dd, *J* = 14.7, 9.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 144.6, 140.3, 136.2, 134.4 (3C), 129.9, 129.2 (3C), 128.5, 128.3 (3C), 128.2 (2C), 127.3, 127.0, 122.5, 108.6, 93.0, 83.5, 45.4, 44.9, 32.2.

HRMS (ESI, m/z): Mass calcd. for $C_{26}H_{20}O_2Cl$ $[M+H]^+$, 399.1146; found: 399.1148.

HPLC analysis: > 99% e.e. (Chiralcel OD-H, 25 °C, IPA/Hexane = 1/99, 0.5 mL/min, 254 nm), Rt (minor) = 41.6 min, Rt (major) = 45.8 min.



3h

(3*S*,4*R*)-3-(3-methylbenzyl)-4-phenyl-5-(phenylethynyl)-3,4-dihydro-2*H*-pyran-2-one

White solid, 69% yield, 26.2 mg, m.p. 105-107 °C.

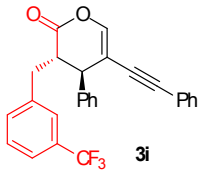
[α]$_D^{25}$ = -171.1 (c = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.28 (m, 2H), 7.26-7.08 (m, 8H), 7.08-6.90 (m, 5H), 6.82 (s, 2H), 3.47 (d, *J* = 6.4 Hz, 1H), 3.34-3.31 (m, 1H), 3.22-3.10 (m, 1H), 2.43-2.29 (m, 1H), 2.26 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 143.6, 137.2, 137.0, 135.4, 130.3 (2C), 128.8, 128.0 (2C), 127.5, 127.4, 127.3 (2C), 127.2 (2C), 127.1, 126.4, 125.0, 121.5, 107.7, 91.7, 82.7, 44.0, 43.9, 31.1, 20.4.

HRMS (ESI, m/z): Mass calcd. for $C_{27}H_{23}O_2$ $[M+H]^+$, 379.1693; found: 379.1691.

HPLC analysis: > 99% e.e. (Chiralcel OD-H, 25 °C, IPA/Hexane = 1/99, 0.5 mL/min, 254 nm), Rt (minor) = 30.8 min, Rt (major) = 32.5 min.



3i

(3*S*,4*R*)-4-phenyl-5-(phenylethynyl)-3-(3-(trifluoromethyl)benzyl)-3,4-dihydro-2*H*-pyran-2-one

White solid, 87% yield, 37.5 mg, m.p. 106-107 °C.

[α]$_D^{25}$ = -131.1 (c = 1.0, $CHCl_3$).

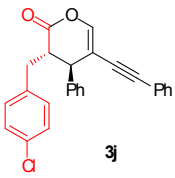
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.7 Hz, 1H), 7.48-7.34 (m, 4H), 7.31 (dd, *J* = 7.4, 2.4 Hz, 4H), 7.27 (t, *J* = 2.2 Hz, 2H), 7.26-7.22 (m, 1H), 7.09 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.04 (s, 1H), 3.51 (d, *J* = 7.1 Hz, 1H), 3.44-3.41 (m, 1H), 3.27 (dd, *J* = 14.6, 5.4 Hz, 1H), 2.52 (dd, *J* = 14.6, 8.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 144.6, 139.2, 136.2, 132.4, 131.4 (2C), 130.9 (d, *J* = 32.1 Hz), 129.2 (2C), 129.1, 128.6, 128.4, 128.3 (2C), 128.2 (2C), 126.1 (d, *J* = 3.8 Hz), 123.7 (d, *J* = 3.8 Hz), 122.7, 122.5, 108.5, 93.0, 83.5, 45.6, 44.9, 32.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6.

HRMS (ESI, m/z): Mass calcd. for $C_{27}H_{20}O_2F_3$ $[M+H]^+$, 433.1410; found: 433.1409.

HPLC analysis: 99% e.e. (Chiralcel IA, 25 °C, IPA/Hexane = 1/99, 0.5 mL/min, 254 nm), Rt (major) = 18.9 min, Rt (minor) = 19.5 min.



3j

(3*S*,4*R*)-3-(4-chlorobenzyl)-4-phenyl-5-(phenylethynyl)-3,4-dihydro-2*H*-pyran-2-one

White solid, 73% yield, 29.1 mg, m.p. 175-176 °C.

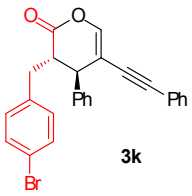
[α]$_D^{25}$ = -300.4 (c = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.27 (m, 7H), 7.25-7.21 (m, 3H), 7.08 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.01 (d, *J* = 7.4 Hz, 3H), 3.51 (d, *J* = 7.0 Hz, 1H), 3.39-3.33(m, 1H), 3.19 (dd, *J* = 14.7, 5.1 Hz, 1H), 2.41 (dd, *J* = 14.7, 9.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 144.6, 136.6, 136.2, 132.5, 131.4 (2C), 130.4 (2C), 129.2 (2C), 128.8 (2C), 128.5, 128.3 (2C), 128.2 (3C), 122.5, 108.7, 93.0, 83.5, 45.3, 44.9, 31.9.

HRMS (ESI, m/z): Mass calcd. for $C_{26}H_{20}O_2Cl$ $[M+H]^+$, 399.1146; found: 399.1147.

HPLC analysis: 98% e.e. (Chiralcel OD-H, 25 °C, IPA/Hexane = 1/99, 0.7 mL/min, 254 nm), Rt (minor) = 22.6 min, Rt (major) = 25.8 min.



3k

(3*S*,4*R*)-3-(4-bromobenzyl)-4-phenyl-5-(phenylethynyl)-3,4-dihydro-2*H*-pyran-2-one

White solid, 97% yield, 43.2 mg, m.p. 135-137 °C.

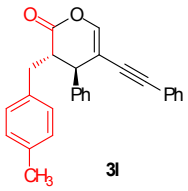
[α]$_D^{30}$ = -295.9 (c = 1 in $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.3 Hz, 2H), 7.39-7.30 (m, 5H), 7.27 (d, *J* = 1.7 Hz, 3H), 7.09 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.03 (s, 1H), 6.97 (d, *J* = 8.3 Hz, 2H), 3.52 (d, *J* = 7.0 Hz, 1H), 3.37 (m, 1H), 3.18 (dd, *J* = 14.7, 5.1 Hz, 1H), 2.40 (dd, *J* = 14.7, 9.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 144.6, 137.2, 136.2, 131.7 (2C), 131.4 (2C), 130.8 (2C), 129.2 (2C), 128.5, 128.3 (3C), 128.2 (2C), 122.5, 120.6, 108.6, 93.0, 83.5, 45.3, 44.9, 31.9.

HRMS (ESI, m/z): Mass calcd. for $C_{26}H_{20}O_2Br$ $[M+H]^+$, 443.0641; found: 443.0641.

HPLC analysis: 96% e.e. (Chiralcel OD-H, 25 °C, IPA/Hexane = 2/98, 0.3 mL/min, 254 nm), Rt (minor) = 57.2 min, Rt (major) = 69.1 min.



3l

(3*S*,4*R*)-3-(4-methylbenzyl)-4-phenyl-5-(phenylethynyl)-3,4-dihydro-2*H*-pyran-2-one

White solid, 51% yield, 19.2 mg, m.p. 121-122 °C.

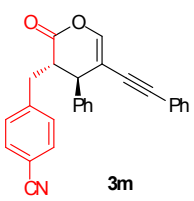
[α]$_D^{25}$ = -370.5 (c = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.27 (m, 5H), 7.27-7.22 (m, 3H), 7.15-7.06 (m, 4H), 7.01 (s, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 3.54 (d, *J* = 7.0 Hz, 1H), 3.35-3.40 (m,1H), 3.22 (dd, *J* = 14.7, 4.6 Hz, 1H), 2.41-2.35 (m, 1H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 144.7, 136.5, 136.3, 135.0, 131.4 (2C), 129.3 (2C), 129.0 (2C), 128.9 (2C), 128.5, 128.3 (2C), 128.3 (2C), 128.1, 122.6, 108.8, 92.8, 83.8, 45.2, 45.0, 31.8, 21.1.

HRMS (ESI, m/z): Mass calcd. for $C_{27}H_{23}O_2$ $[M+H]^+$, 379.1693; found: 379.1691.

HPLC analysis: 99% e.e. (Chiralcel IA, 25 °C, IPA/Hexane = 1/99, 0.5 mL/min, 254 nm), Rt (major) = 18.5 min, Rt (minor) = 20.3 min.



3m

(3*S*,4*R*)-3-(4-isocyanobenzyl)-4-phenyl-5-(phenylethynyl)-3,4-dihydro-2*H*-pyran-2-one

White solid, 51% yield, 19.8 mg, m.p. 162-163 °C.

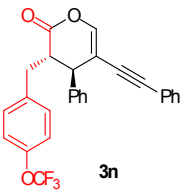
[α]$_D^{25}$ = -130.9 (c = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.9 Hz, 1H), 7.53-7.47 (m, 1H), 7.43- 7.31 (m, 7H), 7.30-7.26 (m, 3H), 7.22-7.15 (m, 2H), 7.04 (s, 1H), 3.75 (d, *J* = 7.2 Hz, 1H), 3.54 (t, *J* = 7.5, 5.8 Hz, 1H), 3.12 (dd, *J* = 14.5, 7.7 Hz, 1H), 2.85 (dd, *J* = 14.5, 5.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 144.6, 142.8, 136.1, 132.9, 132.8, 131.4 (2C), 131.3, 129.3 (2C), 128.5, 128.4, 128.3 (2C), 128.1 (2C), 127.4, 122.5, 117.8, 112.5, 108.4, 93.0, 83.4, 46.9, 44.3, 32.4.

HRMS (ESI, m/z): Mass calcd. for $C_{27}H_{20}NO_2$ $[M+H]^+$, 390.1489; found: 390.1491.

HPLC analysis: > 99% e.e. (Chiralcel IA, 25 °C, IPA/Hexane = 6/94, 0.5 mL/min, 254 nm), Rt (major) = 17.9 min, Rt (minor) = 19.5 min.



3n

(3*S*,4*R*)-4-phenyl-5-(phenylethynyl)-3-(4-(trifluoromethoxy)benzyl)-3,4-dihydro-2*H*-pyran-2-one

White solid, 74% yield, 33.4 mg, m.p. 158-159 °C.

[α]$_D^{25}$ = -178.6 (c = 1.0, $CHCl_3$).

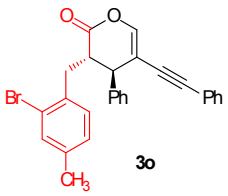
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.29 (m, 5H), 7.28 (dd, *J* = 4.5, 1.8 Hz, 3H), 7.20 – 7.07 (m, 6H), 7.04 (s, 1H), 3.56 (d, *J* = 7.0 Hz, 1H), 3.41-3.36 (m, 1H), 3.21 (dd, *J* = 14.7, 5.3 Hz, 1H), 2.46 (dd, *J* = 14.7, 8.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 148.0, 144.6, 137.0, 136.2, 131.4 (2C), 130.4 (2C), 129.2 (2C), 128.6, 128.3 (3C), 128.2 (2C), 122.5, 121.8, 121.1, 119.2, 108.6, 93.0, 83.5, 45.5, 45.0, 31.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.8.

HRMS (ESI, m/z): Mass calcd. for $C_{27}H_{20}O_3F_3$ $[M+H]^+$, 449.1359; found: 449.1352.

HPLC analysis: > 99% e.e. (Chiralcel IA, 25 °C, IPA/Hexane = 1/99, 0.7 mL/min, 254 nm), Rt (minor) = 15.8 min, Rt (major) = 18.3 min.



3o

(3*S*,4*R*)-3-(2-bromo-4-methylbenzyl)-4-phenyl-5-(phenylethynyl)-3,4-dihydro-2*H*-pyran-2-one

White solid, 78% yield, 35.8 mg, m.p. 65-66 °C.

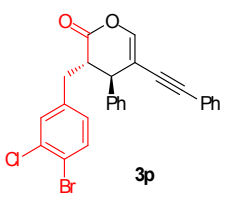
[α]$_D^{25}$ = -283.2 (c = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.26 (m, 4H), 7.25-7.23 (m, 2H), 7.22-7.16 (m, 3H), 7.15-7.08 (m, 2H), 6.96-6.89 (m, 3H), 3.57 (d, *J* = 7.1 Hz, 1H), 3.47 (q, *J* = 6.8 Hz, 1H), 3.03 (dd, *J* = 14.3, 6.4 Hz, 1H), 2.57 (dd, *J* = 14.3, 6.8 Hz, 1H), 2.22 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 143.6, 137.6, 135.6, 133.5, 132.3, 131.0, 130.3 (2C), 128.1 (2C), 127.4, 127.3 (2C), 127.2 (2C), 127.1, 127.1, 123.3, 121.5, 107.5, 91.8, 82. 7, 45.0, 42.1, 32.1, 19.6.

HRMS (ESI, m/z): Mass calcd. for $C_{27}H_{22}O_2$ $[M+H]^+$, 457.0783; found: 457.0781.

HPLC analysis: > 99% e.e. (Chiralcel OD-H, 25 °C, IPA/Hexane = 1/99, 0.7 mL/min, 254 nm), Rt (major) = 15.5 min, Rt (minor) = 17.5 min.



3p

(3*S*,4*R*)-3-(4-bromo-3-chlorobenzyl)-4-phenyl-5-(phenylethynyl)-3,4-dihydro-2*H*-pyran-2-one

White solid, 83% yield, 39.7 mg, m.p. 167-168 °C.

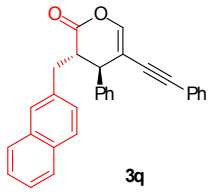
[α]$_D^{25}$ = -215.1 (c = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.2 Hz, 1H), 7.41-7.30 (m, 5H), 7.27 (dd, *J* = 5.0, 1.2 Hz, 3H), 7.18 (d, *J* = 2.0 Hz, 1H), 7.09 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.03 (s, 1H), 6.86 (dd, *J* = 8.2, 2.1 Hz, 1H), 3.53 (d, *J* = 7.1 Hz, 1H), 3.38-3.33 (m, 1H), 3.14 (dd, *J* = 14.7, 5.5 Hz, 1H), 2.40 (dd, *J* = 14.7, 8.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 144.6, 139.2, 136.1, 134.5, 133.8, 131.4 (2C), 131.0, 129.3 (2C), 128.7, 128.6, 128.4, 128.3 (2C), 128.2 (2C), 122.5, 120.6, 108.6, 93.1, 83.4, 45.5, 44.7, 32.0.

HRMS (ESI, m/z): Mass calcd. for $C_{26}H_{19}O_2BrCl$ $[M+H]^+$, 447.0251; found: 447.0251.

HPLC analysis: 98% e.e. (Chiralcel OD-H, 25 °C, IPA/Hexane = 2/98, 0.5 mL/min, 254 nm), Rt (minor) = 25.3 min, Rt (major) = 33.2 min.



3q

(3*S*,4*R*)-3-(naphthalen-2-ylmethyl)-4-phenyl-5-(phenylethynyl)-3,4-dihydro-2*H*-pyran-2-one

Colorless solid, 57% yield, 23.8 mg, m.p. 175-176 °C.

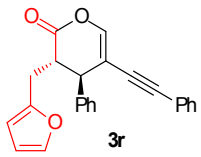
[α]$_D^{25}$ = -269.6 (c =0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.83 (m, 2H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.58-7.45 (m, 2H), 7.44-7.33 (m, 4H), 7.29-7.26 (m, 2H), 7.25-7.18 (m, 5H), 7.16 (d, *J* = 6.8 Hz, 1H), 6.98 (s, 1H), 3.89-3.78 (m, 1H), 3.60-3.51 (m, 2H), 2.94-2.84 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 144.4, 136.7, 134.0, 134.0, 131.5, 131.3 (2C), 129.2 (2C), 129.1, 128.4, 128.4 (2C), 128.3 (2C), 128.2, 127.7, 127.6, 126.4, 125.8, 125.3, 123.2, 122.5, 108.8, 92.9, 83.6, 45.3, 43.9, 29.3.

HRMS (ESI, m/z): Mass calcd. for $C_{30}H_{23}O_2$ $[M+H]^+$, 415.1693; found: 415.1693.

HPLC analysis: 99% e.e. (Chiralcel OD-H, 25 °C, IPA/Hexane = 2/98 0.5 mL/min, 254 nm), Rt (minor) = 39.1 min, Rt (major) = 45.6 min.



3r

(3*S*,4*R*)-3-(furan-2-ylmethyl)-4-phenyl-5-(phenylethynyl)-3,4-dihydro-2*H*-pyran-2-one

Yellow oil, 78% yield, 27.6 mg.

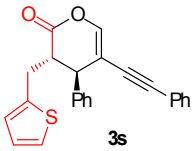
[α]$_D^{25}$ = -106.1 (c = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.26 (m, 3H), 7.25-7.23 (m, 3H), 7.20-7.17 (m, 3H), 7.10-7.04 (m, 2H), 7.01 (s, 1H), 6.26 (dd, *J* = 3.1, 1.9 Hz, 1H), 5.94 (d, *J* = 3.1 Hz, 1H), 3.60 (d, *J* = 7.0 Hz, 1H), 3.47-3.42 (m, 1H), 3.13 (dd, *J* = 15.8, 4.1 Hz, 1H), 2.39 (dd, *J* = 15.8, 9.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 150.8, 143.9, 140.6, 134.8, 130.4 (2C), 128.0 (2C), 127.5, 127.3 (4C), 127.2, 121.5, 109.3, 107.5, 106.3, 91.7, 82.6, 44.2, 41.7, 24.1

HRMS (ESI, m/z): Mass calcd. for $C_{24}H_{19}O_3$ $[M+H]^+$, 355.1329; found: 355.1328.

HPLC analysis: > 99% e.e. (Chiralcel OD-H, 25 °C, IPA/Hexane =2/98, 0.7 mL/min, 254 nm), Rt (major) = 13.0 min, Rt (minor) = 14.3 min.



3s

(3*S*,4*R*)-4-phenyl-5-(phenylethynyl)-3-(thiophen-2-ylmethyl)-3,4-dihydro-2*H*-pyran-2-one

Yellow solid, 51% yield, 18.8 mg, m.p. 102-104 °C.

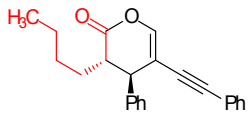
[α]$_D^{25}$ = -262.1 (c = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.30 (m, 5H), 7.29-7.27 (m, 3H), 7.20 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.17-7.12 (m, 2H), 7.06 (s, 1H), 6.96 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.76 (d, *J* = 3.4 Hz, 1H), 3.73 (d, *J* = 6.6 Hz, 1H), 3.50-3.26 (m, 2H), 2.78-2.55 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 144.7, 140.6, 135.9, 131.4 (2C), 129.1 (2C), 128.5, 128.3 (C), 128.30 (2C), 128.2, 127.0, 126.2, 124.1, 122.5, 108.6, 92.8, 83.6, 45.7, 45.0, 26.8.

HRMS (ESI, m/z): Mass calcd. for $C_{24}H_{19}O_2S$ $[M+H]^+$, 371.1100; found: 371.1101.

HPLC analysis: > 99% e.e. (Chiralcel OD-H, 25 °C, IPA/Hexane = 1/99, 0.5 mL/min, 254 nm), Rt (major) = 31.7 min, Rt (minor) = 37.4 min.



3t

(3*S*,4*R*)-3-butyl-4-phenyl-5-(phenylethynyl)-3,4-dihydro-2*H*-pyran-2-one

Yellow solid, 51% yield, 16.0 mg, m.p. 87-89 °C.

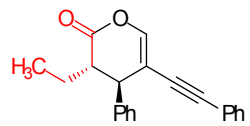
[α]$_D^{25}$ = -73.6 (c = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.33 (m, 3H), 7.33-7.26 (m, 5H), 7.21- 7.14 (m, 2H), 7.07 (s, 1H), 3.73 (d, *J* = 7.0 Hz, 1H), 3.01-2.96 (m, 1H), 1.83-1.63 (m, 1H), 1.46-1.13 (m, 5H), 0.87 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 144.9, 136.4, 131.4 (2C), 129.0 (2C), 128.4, 128.3 (2C), 128.0 (3C), 122.7, 108.4, 92.6, 83.9, 45.8, 43.7, 29.4, 26.2, 22.5, 13.9.

HRMS (ESI, m/z): Mass calcd. for $C_{23}H_{23}O_2$ $[M+H]^+$, 331.1693; found: 331.1693.

HPLC analysis: 98% e.e. (Chiralcel OD-H, 25 °C, IPA/Hexane = 1/99, 0.5 mL/min, 254 nm), Rt (minor) = 18.4 min, Rt (major) = 23.2 min.



3u

(3*S*,4*R*)-3-ethyl-4-phenyl-5-(phenylethynyl)-3,4-dihydro-2*H*-pyran-2-one

White solid, 51% yield, 19.1 mg, m.p. 146-147 °C.

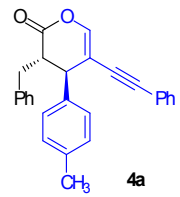
[α]$_D^{25}$ = -35.8 (c = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.32 (m, 3H), 7.32-7.26 (m, 5H), 7.21- 7.15 (m, 2H), 7.07 (s, 1H), 3.76 (d, *J* = 7.0 Hz, 1H), 2.96-2.86 (m, 1H), 1.87- 1.72 (m, 1H), 1.30-1.16 (m, 1H), 1.02 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 145.0, 136.4, 131.4 (2C), 129.0 (2C), 128.4, 128.3 (2C), 128.0 (3C), 122.7, 108.4, 92.7, 83.9, 45.6, 45.3, 19.9, 11.9.

HRMS (ESI, m/z): Mass calcd. for $C_{21}H_{19}O_2$ $[M+H]^+$, 303.1380; found: 303.1375.

HPLC analysis: > 99% e.e. (Chiralcel OD-H, 25 °C, IPA/Hexane = 1/99, 0.5 mL/min, 254 nm), Rt (minor) = 22.4 min, Rt (major) = 24.5 min.



4a

(3*S*,4*R*)-3-benzyl-5-(phenylethynyl)-4-(p-tolyl)-3,4-dihydro-2*H*-pyran-2-one

White solid, 86% yield, 32.5 mg, m.p. 164-166 °C.

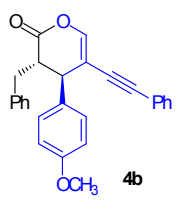
[α]$_D^{25}$ = -232.4 (c = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.26 (m, 5H), 7.24 (m, 3H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.1 Hz, 2H), 7.04-6.96 (m, 3H), 3.52 (d, *J* = 6.9 Hz, 1H), 3.42-3.36 (m, 1H), 3.26 (dd, *J* = 14.6, 4.7 Hz, 1H), 2.43 (dd, *J* = 14.6, 9.5 Hz, 1H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 144.6, 138.3, 137.9, 133.3, 131.4 (2C), 129.8 (2C), 129.1 (2C), 128.6 (2C), 128.4, 128.3 (2C), 128.2 (2C), 126.7, 122.6, 108.9, 92.7, 83.8, 45.2, 44.7, 32.3, 21.2.

HRMS (ESI, m/z): Mass calcd. for $C_{27}H_{23}O_2$ $[M+H]^+$, 379.1693; found: 379.1693.

HPLC analysis: > 99% e.e. (Chiralcel OD-H, 25 °C, IPA/Hexane = 1/99, 0.7 mL/min, 254 nm), Rt (major) = 21.7 min, Rt (minor) = 30.0 min.



4b

(3*S*,4*R*)-3-benzyl-4-(4-methoxyphenyl)-5-(phenylethynyl)-3,4-dihydro-2*H*-pyran-2-one

White solid, 74% yield, 29.2 mg, m.p. 81-82 °C.

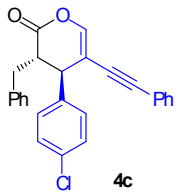
[α]$_D^{25}$ = -171.2 (c = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.18 (m, 4H), 7.17-7.10 (m, 4H), 7.04 -6.96 (m, 2H), 6.94-6.87 (m, 3H), 6.81-6.72 (m, 2H), 3.68 (s, 3H), 3.40 (d, *J* = 6.9 Hz, 1H), 3.31-3.26 (m, 1H), 3.16 (dd, *J* = 14.6, 4.7 Hz, 1H), 2.33 (dd, *J* = 14.6, 9.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 158.3, 143.4, 137.3, 130.3 (2C), 128.3 (2C), 128.0 (2C), 127.6 (2C), 127.4, 127.2 (2C), 127.2, 125.6, 121.5, 113.3 (2C), 107.9, 91.7, 82.8, 54.2, 44.2, 43.2, 31.2.

HRMS (ESI, m/z): Mass calcd. for $C_{27}H_{23}O_3$ $[M+H]^+$, 395.1642; found: 395.1640.

HPLC analysis: > 99% e.e. (Chiralcel IA, 25 °C, IPA/Hexane = 1/99, 0.7 mL/min, 254 nm), Rt (major) = 20.8 min, Rt (minor) = 24.6 min.



4c

(3*S*,4*R*)-3-benzyl-4-(4-chlorophenyl)-5-(phenylethynyl)-3,4-dihydro-2*H*-pyran-2-one

White solid, 58% yield, 23.2 mg, m.p. 154-155 °C.

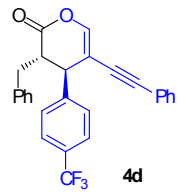
[α]$_D^{25}$ = -343.4 (c = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.26 (m, 9H), 7.24 (dd, *J* = 3.7, 2.4 Hz, 1H), 7.09 (d, *J* = 7.0 Hz, 2H), 7.06-6.99 (m, 3H), 3.53 (d, *J* = 7.0 Hz, 1H), 3.46-2.40 (m, 1H), 3.29 (dd, *J* = 14.7, 4.7 Hz, 1H), 2.40 (dd, *J* = 14.7, 9.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 144.8, 137.8, 134.9, 134.1, 131.4 (2C), 129.7 (2C), 129.3 (2C), 129.0 (2C), 128.8 (2C), 128.6, 128.4 (2C), 126.9, 122.4, 108.4, 93.1, 83.3, 44.8, 44.5, 32.3.

HRMS (ESI, m/z): Mass calcd. for $C_{26}H_{20}O_2Cl$ $[M+H]^+$, 399.1146; found: 399.1144.

HPLC analysis: 99% e.e. (Chiralcel IA, 25 °C, IPA/Hexane = 1/99, 0.7 mL/min, 254 nm), Rt (major) = 15.0 min, Rt (minor) = 17.1 min.



4d

(3*S*,4*R*)-3-benzyl-5-(phenylethynyl)-4-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2*H*-pyran-2-one

White solid, 44% yield, 19.1 mg, m.p. 117-118 °C.

[α]$_D^{25}$ = -173.8 (c = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.26 (m, 7H), 7.26-7.22 (m, 1H), 7.12-7.01 (m, 7H), 3.54 (d, *J* = 7.0 Hz, 1H), 3.46-3.40 (m, 1H), 3.29 (dd, *J* = 14.7, 4.7 Hz, 1H), 2.40 (dd, *J* = 14.7, 9.7 Hz, 1H).

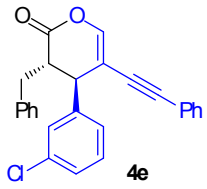
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 162.51 (d, *J* = 247.0 Hz), 144.7, 137.9, 132.2, 132.1, 131.4 (2C), 130.0, 129.9, 129.0 (2C), 128.7 (2C), 128.6, 128.3 (2C), 126.8, 122.4, 116.2, 115.9, 108.6, 93.0, 83.4, 44.9, 44.3, 32.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.8.

HRMS (ESI, m/z): Mass calcd. for $C_{27}H_{19}O_3F_3$ $[M+H]^+$, 432.1332; found: 432.1335.

HPLC analysis: > 99% e.e. (Chiralcel OD-H, 25 °C, IPA/Hexane = 1/99, 0.5 mL/min, 254 nm), Rt (major)

= 35.0 min, Rt (minor) = 42.1 min.



4e

(3*S*,4*R*)-3-benzyl-4-(3-chlorophenyl)-5-(phenylethynyl)-3,4-dihydro-2*H*-pyran-2-one

Yellow solid, 40% yield, 16.0 mg, m.p. 67-69 °C.

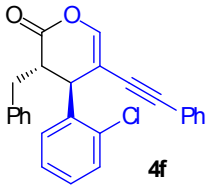
[α]$_D^{25}$ = -139.7 (c = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 1H), 7.24-7.14 (m, 9H), 7.02 (d, *J* = 7.3 Hz, 2H), 6.98 (s, 2H), 6.92 (d, *J* = 6.3 Hz, 1H), 3.52-3.41 (m, 1H), 3.41-3.31 (m, 1H), 3.29-3.15 (m, 1H), 2.33 (dd, *J* = 14.8, 9.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 144.0, 137.3, 136.7 133.7, 130.3 (2C), 129.4, 127.9 (2C), 127.7 (3C), 127.6, 127.4, 127.3 (2C), 125.8, 125.1, 121.3, 107.0, 92.0, 82.2, 43.7, 43.7, 31.2.

HRMS (ESI, m/z): Mass calcd. for $C_{26}H_{20}O_2Cl$ $[M+H]^+$, 399.1146; found: 399.1145.

HPLC analysis: 98% e.e. (Chiralcel IA, 25 °C, IPA/Hexane = 1/99, 0.3 mL/min, 254 nm), Rt (major) = 31.3 min, Rt (minor) = 33.5 min.



4f

(3*S*,4*S*)-3-benzyl-4-(2-chlorophenyl)-5-(phenylethynyl)-3,4-dihydro-2*H*-pyran-2-one

Yellow solid, 49% yield, 19.7 mg. m.p. 65-66 °C.

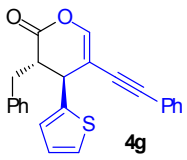
[α]$_D^{25}$ = -262.1 (c = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.38-7.26 (m, 9H), 7.25-7.15 (m, 2H), 7.05 (d, *J* = 7.1 Hz, 2H), 7.01 (s, 1H), 4.47 (s, 1H), 3.49-3.43 (m, *J* = 7.9, 6.1 Hz, 1H), 3.23-3.12 (m, 1H), 2.54 (dd, *J* = 14.5, 8.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 146.3, 144.7, 138.0, 134.7, 131.3 (2C), 130.2, 129.5, 129.2, 129.0 (2C), 128.7 (2C), 128.5, 128.3 (2C), 128.0, 126.7, 122.6, 103.2, 93.1, 83.3, 47.5, 44.9, 32.5.

HRMS (ESI, m/z): Mass calcd. for $C_{26}H_{20}O_2Cl$ $[M+H]^+$, 399.1146; found: 399.1143.

HPLC analysis: > 99% e.e. (Chiralcel OD-H, 25 °C, IPA/Hexane = 1/99, 1.0 mL/min, 254 nm), Rt (major) = 13.1 min, Rt (minor) = 17.6 min.



4g

(3*S*,4*S*)-3-benzyl-5-(phenylethynyl)-4-(thiophen-2-yl)-3,4-dihydro-2*H*-pyran-2-one

White solid, 73% yield, 27.0 mg, m.p. 149-150 °C.

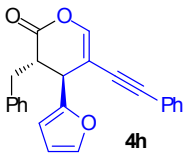
[α]$_D^{25}$ = -189.9 (c = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.30 (m, 4H), 7.28 (dd, *J* = 5.1, 3.3 Hz, 4H), 7.25 (s, 1H), 7.22- 7.14 (m, 2H), 7.05- 6.96 (m, 2H), 6.89 (dd, *J* = 3.5, 0.6 Hz, 1H), 3.83 (d, *J* = 6.2 Hz, 1H), 3.45-3.29 (m, 2H), 2.72-2.48 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 143.7, 137.5, 137.0, 130.4 (2C), 128.1 (2C), 127.7 (2C), 127.5, 127.3 (2C), 126.3, 125.8, 125.4, 124.3, 121.4, 108.0, 92.4, 82.2, 44.9, 38.8, 31.2.

HRMS (ESI, m/z): Mass calcd. for $C_{24}H_{19}O_2S$ $[M+H]^+$, 371.1100; found: 371.1098.

HPLC analysis: >99% e.e. (Chiralcel OD-H, 25 °C, IPA/Hexane = 1/99, 0.7 mL/min, 254 nm), Rt (major) = 37.0 min, Rt (minor) = 54.0 min.



4h

(3*S*,4*S*)-3-benzyl-4-(furan-2-yl)-5-(phenylethynyl)-3,4-dihydro-2*H*-pyran-2-one

White solid, 67% yield, 23.7 mg, m.p. 113-114 °C.

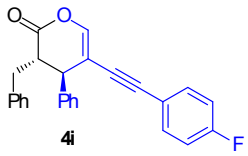
[α]$_D^{25}$ = -158.7 (c = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.40 (m, 1H), 7.38-7.31 (m, 4H), 7.31-7.26 (m, 4H), 7.23-7.14 (m, 2H), 7.00 (s, 1H), 6.37 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.22 (d, *J* = 3.2 Hz, 1H), 3.61 (d, *J* = 6.5 Hz, 1H), 3.40 (dd, *J* = 14.4, 4.1 Hz, 1H), 3.27-3.22 (m, 1H), 2.43 (dd, *J* = 14.4, 10.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 149.7, 145.7, 143.1, 138.1, 131.4 (2C), 129.2 (2C), 128.7 (2C), 128.6, 128.4 (2C), 126.8, 122.5, 110.5, 109.2, 105.7, 92.9, 83.3, 44.6, 38.1, 32.5.

HRMS (ESI, m/z): Mass calcd. for $C_{24}H_{19}O_3$ $[M+H]^+$, 355.1329; found: 355.1324.

HPLC analysis: > 99% e.e. (Chiralcel OD-H, 25 °C, IPA/Hexane = 1/99, 0.7 mL/min, 254 nm), Rt (major) = 31.3 min, Rt (minor) = 41.7 min.



4i

(3*S*,4*R*)-3-benzyl-5-((4-fluorophenyl)ethynyl)-4-phenyl-3,4-dihydro-2*H*-pyran-2-one

White solid, 69% yield, 26.5 mg, m.p. 145-146 °C.

[α]$_D^{25}$ = -263.4 (c = 0.5, $CHCl_3$).

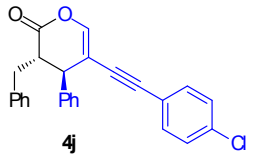
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.27 (m, 7H), 7.26-7.23 (m, 1H), 7.10 (dd, *J* = 7.9, 1.3 Hz, 4H), 7.03 (s, 1H), 6.99-6.89 (m, 2H), 3.54 (d, *J* = 7.0 Hz, 1H), 3.44-3.99 (m, 1H), 3.27 (dd, *J* = 14.7, 4.7 Hz, 1H), 2.42 (dd, *J* = 14.7, 9.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 162.6 (d, *J* = 250.1 Hz), 144.7, 138.2, 136.4, 133.4, 133.3, 129.1 (2C), 129.0 (2C), 128.7 (2C), 128.3 (2C), 128.2, 126.7, 118.7 (d, *J* = 3.5 Hz), 115.8, 115.5, 108.6, 91.7, 83.4, 45.1, 45.0, 32.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -110.4.

HRMS (ESI, m/z): Mass calcd. for $C_{26}H_{20}O_2F$ $[M+H]^+$, 383.1442; found: 383.1443.

HPLC analysis: 99% e.e. (Chiralcel IA, 25 °C, IPA/Hexane = 1/99, 1.0 mL/min, 254 nm), Rt (major) = 9.8 min, Rt (minor) = 11.1 min.



4j

(3*S*,4*R*)-3-benzyl-5-((4-chlorophenyl)ethynyl)-4-phenyl-3,4-dihydro-2*H*-pyran-2-one

White solid, 59% yield, 23.6 mg, m.p. 140-142 °C.

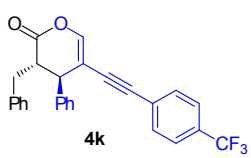
[α]$_D^{25}$ = -148.0 (c = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.30 (m, 5H), 7.28 (d, *J* = 1.2 Hz, 1H), 7.23 (s, 4H), 7.10 (d, *J* = 7.8 Hz, 4H), 7.05 (s, 1H), 3.55 (d, *J* = 7.0 Hz, 1H), 3.45-4.39 (m, 1H), 3.28 (dd, *J* = 14.7, 4.7 Hz, 1H), 2.42 (dd, *J* = 14.7, 9.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 145.0, 138.1, 136.3, 134.5, 132.6 (2C), 129.1 (2C), 129.0 (2C), 128.7 (2C), 128.6 (2C), 128.3 (2C), 128.2, 126.7, 121.1, 108.5, 91.7, 84.7, 45.1, 45.0, 32.3.

HRMS (ESI, m/z): Mass calcd. for $C_{26}H_{20}O_2Cl$ $[M+H]^+$, 399.1146; found: 399.1148.

HPLC analysis: 97% e.e. (Chiralcel IA, 25 °C, IPA/Hexane = 1/99, 0.5 mL/min, 254 nm), Rt (major) = 20.3 min, Rt (minor) = 24.8 min.



4k

(3*S*,4*R*)-3-benzyl-4-phenyl-5-((4-(trifluoromethyl)phenyl)ethynyl)-3,4-dihydro-2*H*-pyran-2-one

White solid, 77% yield, 33.3 mg, m.p. 115-116 °C.

[α]$_D^{25}$ = -165.0 (c = 1.0, $CHCl_3$).

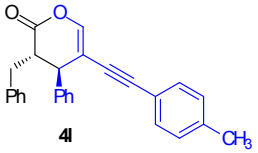
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.47 – 7.29 (m, 8H), 7.12 (dd, *J* = 10.4, 3.4 Hz, 5H), 3.59 (d, *J* = 7.0 Hz, 1H), 3.45 (m, 1H), 3.31 (dd, *J* = 14.7, 4.7 Hz, 1H), 2.46 (dd, *J* = 14.7, 9.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 145.5, 143.0, 138.1, 136.2, 131.6 (2C), 130.4, 130.3, 129.1 (2C), 129.0 (2C), 128.7 (2C), 128.3, 128.3 (2C), 126.8, 126.4, 125.2 (dd, *J* = 7.7, 3.7 Hz), 108.2, 91.4, 86.2, 45.1, 45.0, 32.3.

^{19}F NMR (377 MHz, $CDCl_3$) δ -62.9.

HRMS (ESI, m/z): Mass calcd. for $C_{27}H_{20}O_2F_3$ $[M+H]^+$, 433.1410 ; found: 433.1411.

HPLC analysis: 99% e.e. (Chiralcel IA, 25 °C, IPA/Hexane = 1/99, 0.5 mL/min, 254 nm), Rt (major) = 21.6 min, Rt (minor) = 23.4 min.



4l

(3*S*,4*R*)-3-benzyl-4-phenyl-5-(p-tolylethynyl)-3,4-dihydro-2*H*-pyran-2-one

White solid, 76% yield, 28.8 mg, m.p. 179-180 °C.

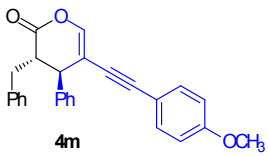
[α]$_D^{25}$ = -226.1 (c = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.28 (m, 5H), 7.24 (d, *J* = 8.1 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.09 (m, 6H), 7.01 (s, 1H), 3.54 (d, *J* = 7.0 Hz, 1H), 3.43-3.38 (m, 1H), 3.27 (dd, *J* = 14.7, 4.7 Hz, 1H), 2.42 (dd, *J* = 14.7, 9.6 Hz, 1H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 144.4, 138.7, 138.2, 136.5, 131.3 (2C), 129.1 (4C), 129.0 (2C), 128.7 (2C), 128.3 (2C), 128.1, 126.7, 119.5, 108.9, 93.0, 83.0, 45.1, 45.1, 32.3, 21.5.

HRMS (ESI, m/z): Mass calcd. for $C_{27}H_{23}O_2$ $[M+H]^+$, 379.1693; found: 379.1690.

HPLC analysis: 95% e.e. (Chiralcel OD-H, 25 °C, IPA/Hexane = 1/99, 0.7 mL/min, 254 nm), Rt (major) = 29.5 min, Rt (minor) = 36.5 min.



4m

(3*S*,4*R*)-3-benzyl-5-((4-methoxyphenyl)ethynyl)-4-phenyl-3,4-dihydro-2*H*-pyran-2-one

White solid, 60% yield, 23.6 mg, m.p. 137-138 °C.

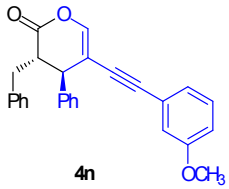
[α]$_D^{25}$ = -174.2 (c = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.26 (m, 5H), 7.26-7.22 (m, 3H), 7.14-7.04 (m, 4H), 7.00 (s, 1H), 6.80-6.72 (m, 2H), 3.76 (s, 3H), 3.53 (d, *J* = 7.0 Hz, 1H), 3.43-3.38 (m, 1H), 3.26 (dd, *J* = 14.6, 4.7 Hz, 1H), 2.41 (dd, *J* = 14.7, 9.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 159.7, 144.1, 138.2, 136.5, 132.8 (2C), 129.0 (2C), 129.0 (2C), 128.6 (2C), 128.3 (2C), 128.1, 126.7, 114.6, 113.9 (2C), 109.0, 92.8, 82.28, 55.3, 45.1, 45.1, 32.2.

HRMS (ESI, m/z): Mass calcd. for $C_{27}H_{23}O_3$ $[M+H]^+$, 395.1642; found:395.1643.

HPLC analysis: 99% e.e. (Chiralcel IA, 25 °C, IPA/Hexane = 1/99, 0.5 mL/min, 254 nm), Rt (major) = 28.1 min, Rt (minor) = 33.6 min.



4n

(3*S*,4*R*)-3-benzyl-5-((3-methoxyphenyl)ethynyl)-4-phenyl-3,4-dihydro-2*H*-pyran-2-one

White solid, 77% yield, 30.5 mg, m.p. 99-101 °C.

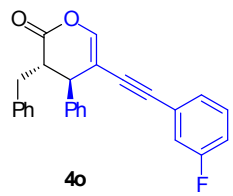
[α]$_D^{25}$ = -194.5 (c = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.29 (m, 5H), 7.26 (d, *J* = 7.2 Hz, 1H), 7.19-7.07 (m, 5H), 7.04 (s, 1H), 6.92-6.89 (m, 1H), 6.86-6.78 (m, 2H), 3.75 (s, 3H), 3.55 (d, *J* = 7.0 Hz, 1H), 3.44-3.39 (m, 1H), 3.27 (dd, *J* = 14.7, 4.7 Hz, 1H), 2.42 (dd, *J* = 14.7, 9.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 159.2, 144.8, 138.2, 136.4, 129.4, 129.1 (2C), 129.1 (2C), 128.7 (2C), 128.3(2C), 128.2, 126.7, 124.0, 123.5, 116.2, 115.1, 108.7, 92.7, 83.5, 55.3, 45.1, 45.0, 32.3.

HRMS (ESI, m/z): Mass calcd. for $C_{27}H_{23}O_3$ $[M+H]^+$, 395.1642; found: 395.1642.

HPLC analysis: 96% e.e. (Chiralcel IA, 25 °C, IPA/Hexane = 1/99, 0.5 mL/min, 254 nm), Rt (major) = 23.7 min, Rt (minor) = 31.2 min.



4o

(3*S*,4*R*)-3-benzyl-5-((3-fluorophenyl)ethynyl)-4-phenyl-3,4-dihydro-2*H*-pyran-2-one

Yellow solid, 65% yield, 25.0 mg, m.p. 86-87 °C.

[α]$_D^{25}$ = -184.7 (c = 1.0, $CHCl_3$).

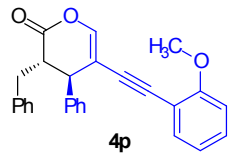
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.26 (m, 6H), 7.25-7.16 (m, 1H), 7.12-7.06 (m, 6H), 7.02-6.96 (m, 2H), 3.56 (d, *J* = 7.0 Hz, 1H), 3.46-3.40 (m, 1H), 3.29 (dd, *J* = 14.7, 4.7 Hz, 1H), 2.43 (dd, *J* = 14.7, 9.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 162.3 (d, *J* = 246.8 Hz), 145.2, 138.1, 136.3, 129.9 (d, *J* = 8.7 Hz), 129.2 (2C), 129.1 (2C), 128.7 (2C), 128.3 (2C), 128.3, 127.3 (d, *J* = 3.0 Hz), 126.8, 124.5 (d, *J* = 9.5 Hz), 118.2 (d, *J* = 22.9 Hz), 115.8 (d, *J* = 21.2 Hz), 108.4, 91.6, 84.7, 45.1, 45.0, 32.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.8.

HRMS (ESI, m/z): Mass calcd. for $C_{26}H_{20}O_2F$ $[M+H]^+$, 383.1442; found: 383.1442.

HPLC analysis: 99% e.e. (Chiralcel OD-H, 25 °C, IPA/Hexane = 1/99, 0.3 mL/min, 254 nm), Rt (minor) = 36.6 min, Rt (major) = 41.7 min.



4p

(3*S*,4*R*)-3-benzyl-4-phenyl-5-(thiophen-2-ylethynyl)-3,4-dihydro-2*H*-pyran-2-one

White solid, 50% yield, 19.7 mg, m.p. 148-150 °C.

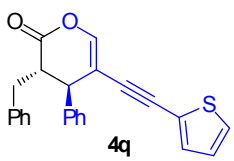
[α]$_D^{25}$ = -216.5 (c = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.28 (m, 5H), 7.26 (s, 1H), 7.24 (d, *J* = 5.5, 1.7 Hz, 2H), 7.15-7.08 (m, 4H), 7.05 (s, 1H), 6.88-6.80 (m, 2H), 3.81 (s, 3H), 3.59 (d, *J* = 7.0 Hz, 1H), 3.45-3.40 (m, 1H), 3.29 (dd, *J* = 14.6, 4.8 Hz, 1H), 2.45 (dd, *J* = 14.6, 9.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 159.7, 144.4, 138.2, 136.6, 133.3, 130.0, 129.1 (2C), 129.0 (2C), 128.6 (2C), 128.4 (2C), 128.1, 126.7, 120.4, 111.8, 110.6, 109.0, 89.3, 87.7, 55.7, 45.2, 45.0, 32.3.

HRMS (ESI, m/z): Mass calcd. for $C_{27}H_{23}O_3$ $[M+H]^+$, 395.1642; found: 395.1642.

HPLC analysis: > 99% e.e. (Chiralcel OD-H, 25 °C, IPA/Hexane = 1/99, 0.5 mL/min, 254 nm), Rt (major) = 12.9 min, Rt (minor) = 47.5 min.



4q

(3*S*,4*R*)-3-benzyl-4-phenyl-5-(thiophen-2-ylethynyl)-3,4-dihydro-2*H*-pyran-2-one

White solid, 59% yield, 21.8 mg, m.p. 135-137 °C.

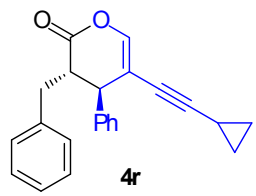
[α]$_D^{25}$ = -280.7 (c = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.25 (m, 6H), 7.24-7.19 (m, 1H), 7.13- 7.07 (m, 5H), 7.03 (s, 1H), 6.92 (dd, *J* = 5.1, 3.7 Hz, 1H), 3.55 (d, *J* = 6.9 Hz, 1H), 3.43-3.38 (m, 1H), 3.26 (dd, *J* = 14.7, 4.7 Hz, 1H), 2.42 (dd, *J* = 14.7, 9.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 144.9, 138.1, 136.3, 132.1, 129.1 (2C), 129.0 (2C), 128.7 (2C), 128.3 (2C), 128.2, 127.8, 127.1, 126.8, 122. 6, 108.6, 87.3, 85.9, 45.1, 44.9, 32.3.

HRMS (ESI, m/z): Mass calcd. for $C_{24}H_{19}O_2S$ $[M+H]^+$, 371.1100; found: 371.1100.

HPLC analysis: 96% e.e. (Chiralcel OD-H, 25 °C, IPA/Hexane = 1/99, 0.5 mL/min, 254 nm), Rt (major) = 50.8 min, Rt (minor) = 58.9 min.



4r

(3*S*,4*R*)-3-benzyl-5-(cyclopropylethynyl)-4-phenyl-3,4-dihydro-2*H*-pyran-2-one

White solid, 85% yield, 27.9 mg, m.p. 81-83 °C.

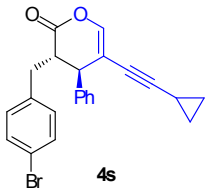
[α]$_D^{25}$ = -200.8 (c = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.32 (m, 3H), 7.32-7.27 (m, 2H), 7.24 (dd, *J* = 6.2, 3.4 Hz, 1H), 7.11-7.00 (m, 4H), 6.85 (s, 1H), 3.43-3.28 (m, 2H), 3.23 (dd, *J* = 14.6, 4.5 Hz, 1H), 2.36 (dd, *J* = 14.6, 9.3 Hz, 1H), 1.27-1.20 (m, 1H), 0.80-0.68 (m, 2H), 0.67-0.53 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 143.9, 138.2, 136.4, 128.9 (2C), 128.8 (2C), 128.5 (2C), 128.2 (2C), 127.9, 126.5, 109.0, 97.0, 69.8, 45.1, 44.9, 32.1, 8.5, 8.5, 0.1.

HRMS (ESI, m/z): Mass calcd. for $C_{23}H_{21}O_2$ $[M+H]^+$, 329.1536; found: 329.1536.

HPLC analysis: 99% e.e. (Chiralcel OD-H, 25 °C, IPA/Hexane = 1/99, 0.5 mL/min, 254 nm), Rt (minor) = 21.9 min, Rt (major) = 23.9 min.



4s

(3*S*,4*R*)-3-(4-bromobenzyl)-5-(cyclopropylethynyl)-4-phenyl-3,4-dihydro-2*H*-pyran-2-one

White solid, 75% yield, 23.7 mg, m.p. 138-140 °C.

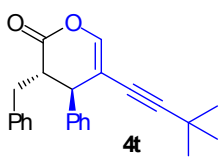
[α]$_D^{25}$ = -195.2 (c = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.38 (m, 2H), 7.38 – 7.28 (m, 3H), 7.06 – 6.99 (m, 2H), 6.94 (d, *J* = 8.3 Hz, 2H), 6.84 (s, 1H), 3.35 (d, *J* = 7.0 Hz, 1H), 3.27 (m, 1H), 3.14 (dd, *J* = 14.7, 5.0 Hz, 1H), 2.34 (dd, *J* = 14.7, 9.2 Hz, 1H), 1.24 (m, 1H), 0.74 (m, 2H), 0.61 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 143.9, 137.3, 136.3, 131.7 (2C), 130.7 (2C), 129.0 (2C), 128.2 (2C), 128.1, 120.5, 109.0, 97.3, 69.8, 45.4, 44.8, 31.9, 8.6, 8.6, 0.1.

HRMS (ESI, m/z): Mass calcd. for $C_{23}H_{20}O_2Br$ $[M+H]^+$, 407.0641; found: 407.0639.

HPLC analysis: >99% e.e. (Chiralcel OD-H, 25 °C, IPA/Hexane = 1/99, 0.8 mL/min, 254 nm), Rt (minor) = 14.5 min, Rt (major) = 24.9 min.



4t

(3*S*,4*R*)-3-benzyl-5-(3,3-dimethylbut-1-yn-1-yl)-4-phenyl-3,4-dihydro-2*H*-pyran-2-one

White solid, 74% yield, 25.4 mg, m.p. 70-72 °C.

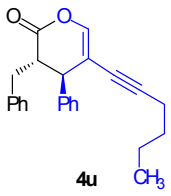
[α]$_D^{25}$ = -174.8 (c = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.27 (m, 1H), 7.26-7.12 (m, 5H), 7.05-6.93 (m, 4H), 6.75 (s, 1H), 3.34-3.22 (m, 2H), 3.18 (dd, *J* = 14.5, 4.4 Hz, 1H), 2.34 (dd, *J* = 14.5, 8.8 Hz, 1H), 1.05 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 142.3, 137.3, 135.7, 128.0 (2C), 127.9 (2C), 127.5 (2C), 127.2 (2C), 126.8, 125.5, 108.0, 101.2, 72.2, 44.4, 43.8, 31.3, 29.7 (3C), 26.9.

HRMS (ESI, m/z): Mass calcd. for $C_{24}H_{25}O_2$ $[M+H]^+$, 345.1849; found: 345.1848.

HPLC analysis: 99% e.e. (Chiralcel IC, 25 °C, IPA/Hexane = 4/96, 1.0 mL/min, 254 nm), Rt (minor) = 5.4 min, Rt (major) = 6.7 min.



4u

(3*S*,4*R*)-3-benzyl-5-(hex-1-yn-1-yl)-4-phenyl-3,4-dihydro-2*H*-pyran-2-one

White solid, 82% yield, 28.4 mg, m.p. 70-72 °C.

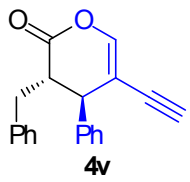
[α]$_D^{25}$ = -203.8 (c = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.26 (m, 5H), 7.25-7.22 (m, 1H), 7.13-6.97 (m, 4H), 6.86 (s, 1H), 3.40 (d, *J* = 7.0 Hz, 1H), 3.37-3.32 (m, 1H), 3.24 (dd, *J* = 14.6, 4.6 Hz, 1H), 2.38 (dd, *J* = 14.6, 9.3 Hz, 1H), 2.19 (t, *J* = 7.0 Hz, 2H), 1.46-1.35 (m, 2H), 1.35-1.22 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 143.7, 138.3, 136.6, 129.0 (2C), 128.9 (2C), 128.6 (2C), 128.3 (2C), 128.0, 126.6, 109.1, 94.1, 74.7, 45.3, 45.0, 32.2, 30.5, 21.9, 19.1, 13.5.

HRMS (ESI, m/z): Mass calcd. for $C_{24}H_{25}O_2$ $[M+H]^+$, 345.1849; found: 345.1848.

HPLC analysis: > 99% e.e. (Chiralcel ID, 25 °C, IPA/Hexane = 2/98, 0.3 mL/min, 254 nm), Rt (minor) = 19.8 min, Rt (major) = 21.7 min.



4v

(3*S*,4*R*)-3-benzyl-5-ethynyl-4-phenyl-3,4-dihydro-2*H*-pyran-2-one

White solid, 89% yield, 25.7 mg, m.p. 142-143 °C.

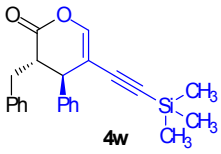
[α]$_D^{25}$ = -370.9 (c = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.30 (m, 4H), 7.29 (d, *J* = 1.2 Hz, 1H), 7.25-7.23 (m, 1H), 7.09-7.04 (m, 4H), 7.02-6.99 (m, 1H), 3.47 (d, *J* = 7.0 Hz, 1H), 3.41-3.31 (m, 1H), 3.24 (dd, *J* = 14.7, 4.7 Hz, 1H), 2.92 (s, 1H), 2.38 (dd, *J* = 14.7, 9.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 146.1, 138.0, 136.1, 129.1 (2C), 129.0 (2C), 128.7 (2C), 128.3 (3C), 126.8, 107.6, 80.9, 78.3, 45.0, 44.8, 32.2.

HRMS (ESI, m/z): Mass calcd. for $C_{20}H_{17}O_2$ $[M+H]^+$, 289.1223; found: 289.1221.

HPLC analysis: > 99% e.e. (Chiralcel IA, 25 °C, IPA/Hexane = 1/99, 1.0 mL/min, 254 nm), Rt (major) = 10.1 min, Rt (minor) = 11.5 min.



4w

(3*S*,4*R*)-3-benzyl-4-phenyl-5-((trimethylsilyl)ethynyl)-3,4-dihydro-2*H*-pyran-2-one

White solid, 82% yield, 29.6 mg, m.p. 91-93 °C.

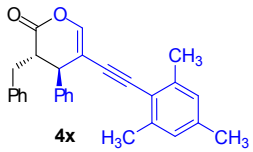
[α]$_D^{25}$ = -242.9 (c = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.27 (m, 5H), 7.25-7.21 (m, 1H), 7.11-7.02 (m, 4H), 6.96 (s, 1H), 3.44 (d, *J* = 7.0 Hz, 1H), 3.36-3.31 (m, 1H), 3.24 (dd, *J* = 14.6, 4.7 Hz, 1H), 2.40 (dd, *J* = 14.6, 9.4 Hz, 1H), 0.10 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 145.8, 138.4, 136.5, 129.3 (2C), 129.2 (2C), 128.8 (2C), 128.5 (2C), 128.3, 126.9, 108.9, 99.4, 98.7, 45.1, 45.1, 32.5, 0.0 (3C).

HRMS (ESI, m/z): Mass calcd. for $C_{23}H_{24}O_2Si$ $[M+H]^{+,}$ 361.1618; found: 361.1616.

HPLC analysis: 99% e.e. (Chiralcel IC, 25 °C, IPA/Hexane = 1/99, 1.0 mL/min, 254 nm), Rt (minor) = 7.1 min, Rt (major) = 10.5 min.



4x

(3*S*,4*R*)-3-benzyl-5-(mesitylethynyl)-4-phenyl-3,4-dihydro-2*H*-pyran-2-one

Colorless oil, 37% yield, 15.1 mg.

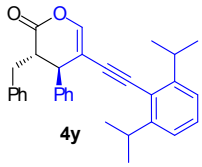
[α]$_D^{25}$ = -125.0 (c = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.30 (m, 5H), 7.26 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.13 (dd, *J* = 7.7, 1.4 Hz, 4H), 7.03 (s, 1H), 6.81 (s, 2H), 3.60 (d, *J* = 7.2 Hz, 1H), 3.47 (m, 1H), 3.30 (dd, *J* = 14.7, 4.9 Hz, 1H), 2.54 – 2.40 (m, 1H), 2.25 (s, 3H), 2.23 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 143.5, 139.8 (2C), 138.3, 138.0, 136.7, 129.0 (4C), 128.6 (2C), 128.4 (2C), 128.1, 127.6 (3C), 126.7, 119.3, 109.3, 91.1, 45.8, 45.0, 32.4, 21.3, 20.8 (2C).

HRMS (ESI, m/z): Mass calcd. for $C_{29}H_{27}O_2$ $[M+H]^+$, 407.2006; found: 407.2002.

HPLC analysis: 81% e.e. (Chiralcel IF, 25 °C, IPA/Hexane = 4/96, 0.5 mL/min, 254 nm), Rt (major) = 14.0 min, Rt (minor) = 15.5 min.



4y

(3*S*,4*R*)-3-benzyl-5-((2,6-diisopropylphenyl)ethynyl)-4-phenyl-3,4-dihydro-2*H*-pyran-2-one

Colorless oil, 58% yield, 26.1 mg.

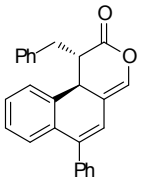
[α]$_D^{25}$ = -203.0 (c = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 5H), 7.22 (dd, *J* = 16.9, 9.1 Hz, 2H), 7.11 (m, 4H), 7.05 – 7.00 (m, 3H), 3.61 (d, *J* = 7.2 Hz, 1H), 3.47 (m, 1H), 3.27 (dd, *J* = 14.7, 5.0 Hz, 1H), 3.24 – 3.11 (m, 2H), 2.45 (dd, *J* = 14.7, 9.2 Hz, 1H), 1.14 (s, 3H), 1.12 (s, 3H), 1.07 (s, 3H), 1.05 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 150.5 (2C), 143.6 (2C), 138.3, 136.7, 129.0 (4C), 128.6, 128.6 (2C), 128.4 (2C), 128.1, 126.7, 122.1, 120.2, 109.2, 91.5, 90.3, 45.9, 45.0, 32.4, 31.7 (2C), 23.1 (2C), 23.0 (2C).

HRMS (ESI, m/z): Mass calcd. for $C_{32}H_{33}O_2$ $[M+H]^+$, 449.2475; found: 449.2466.

HPLC analysis: 80% e.e. (Chiralcel ODH, 25 °C, IPA/Hexane = 2/98, 0.6 mL/min, 254 nm), Rt (major) = 11.1 min, Rt (minor) = 10.0 min.



5

(1*S*,10*bR*)-1-benzyl-6-phenyl-1*H*-benzo[f]isochromen-2(10*bH*)-one

Yellow solid, 71% yield, 14.1 mg, m.p. 82-83 °C.

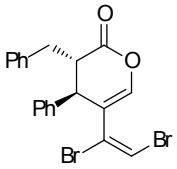
$[\alpha]_D^{25}$ = -280.1 (c = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.74 (s, 1H), 7.38-7.27 (m, 6H), 7.26 -7.17 (m, 3H), 7.14-6.94 (m, 5H), 4.08 (dd, *J* = 6.4, 3.5 Hz, 1H), 323-3.08 (m, 2H), 2.43-2.36 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.0, 187.2, 168.6, 166.6, 151.2, 137.9, 137.0, 136.6, 134.9, 133.9, 129.2, 129.0, 129.0, 128.7, 128.7, 128.4, 128.4, 128.0, 127.7, 127.1, 126.8, 124.7, 121.9, 45.1, 38.4, 32.3.

HRMS (ESI, m/z): Mass calcd. for $C_{26}H_{21}O_2$ $[M+H]^+$, 365.1536; found: 365.1535.

HPLC analysis: 99% e.e. (Chiralcel AD-H, 25 °C, IPA/Hexane = 8/92, 0.5 mL/min, 254 nm), Rt (major) = 20.7 min, Rt (minor) = 25.9 min.



6

(*3S*,*4R*)-3-benzyl-5-((Z)-1,2-dibromovinyl)-4-phenyl-3,4-dihydro-2*H*-pyran-2-one

Colorless oil, 84% yield, 26.2 mg.

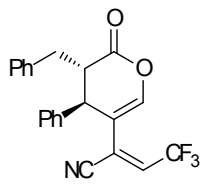
$[\alpha]_D^{25}$ = -259.1 (c = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.27 (m, 5H), 7.24 (t, *J* = 4.7 Hz, 1H), 7.13 (d, *J* = 7.2 Hz, 2H), 7.09-7.02 (m, 2H), 6.99 (s, 1H), 6.54 (s, 1H), 3.78 (d, *J* = 7.0 Hz, 1H), 3.47-3.42 (m, 1H), 3.20 (dd, *J* = 14.9, 5.3 Hz, 1H), 2.43 (dd, *J* = 14.9, 9.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 142.7, 138.1, 135.6, 128.9 (2C), 128.9 (2C), 128.7 (2C), 128.6 (2C), 128.3, 126.7, 120.2, 117.4, 106.0, 45.1, 43.4, 32.3.

HRMS (ESI, m/z): Mass calcd. for $C_{20}H_{17}O_2Br_2$ $[M+H]^+$, 446.9590; found: 446.9591.

HPLC analysis: > 99% e.e. (Chiralcel OD-H, 25 °C, IPA/Hexane = 1/99, 0.5 mL/min, 254 nm), Rt (minor) = 22.6 min, Rt (major) = 24.6 min.



7

(*E*)-2-((3*S*,4*R*)-3-benzyl-2-oxo-4-phenyl-3,4-dihydro-2*H*-pyran-5-yl)-4,4,4-trifluorobut-2-enenitrile

White solid, 53% yield, 14.1 mg, m.p. 125-126 °C.

$[\alpha]_D^{25}$ = -166.2 (c = 0.5, $CHCl_3$).

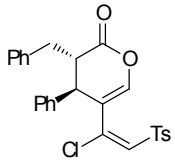
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.27 (m, 5H), 7.24 (s, 1H), 7.10 (d, *J* = 7.1 Hz, 2H), 7.05-6.98 (m, 2H), 6.97 (s, 1H), 6.28 (q, *J* = 7.5 Hz, 1H), 3.67 (d, *J* = 7.0 Hz, 1H), 3.47-3.41 (m, 1H), 3.20 (dd, *J* = 14.9, 5.3 Hz, 1H), 2.41 (dd, *J* = 14.9, 9.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 143.3, 143.2, 137.4, 134.4, 132.2 (d, *J* = 36.3 Hz), 129.3 (2C), 128.8, 128.8 (2C), 128.7 (2C), 128.3 (2C), 126.9, 121.9, 114.9, 114.8, 44.8, 43.8, 32.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.6 (d, *J* = 7.5 Hz).

HRMS (ESI, m/z): Mass calcd. for $C_{22}H_{17}O_2NF_3$ $[M+H]^+$, 384.1206; found: 384.1204.

HPLC analysis: > 99% e.e. (Chiralcel IB, 25 °C, IPA/Hexane = 2.5/97.5, 0.5 mL/min, 254 nm), Rt (minor) = 47.9 min, Rt (major) = 56.3 min.



8

(3*S*,4*R*)-3-benzyl-5-((Z)-1-chloro-2-tosylvinyl)-4-phenyl-3,4-dihydro-2*H*-pyran-2-one

White solid, 49% yield, 16.4 mg, m.p. 165-166 °C.

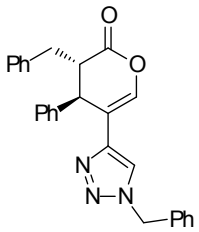
[α]$_D^{25}$ = -90.6 (c = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.41 (m, 2H), 7.40-7.30 (m, 5H), 7.30-7.21 (m, 3H), 7.15 (d, *J* = 7.2 Hz, 2H), 7.08-6.98 (m, 3H), 6.55 (s, 1H), 3.71 (d, *J* = 6.8 Hz, 1H), 3.67-3.62 (m, 1H), 3.24 (dd, *J* = 15.0, 4.9 Hz, 1H), 2.43 (s, 3H), 2.38 (dd, *J* = 15.0, 9.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 145.1, 143.5, 143.4, 137.8, 137.3, 136.0, 131.6, 130.1 (2C), 129.0 (4C), 128.6 (2C), 128.5 (2C), 128.2, 127.6 (2C), 126.7, 118.0, 44.5, 43.9, 32.1, 21.7.

HRMS (ESI, m/z): Mass calcd. for $C_{27}H_{24}O_4SCl$ $[M+H]^+$, 479.1082; found 479.1084.

HPLC analysis: > 99% e.e. (Chiralcel OD-H, 25 °C, IPA/Hexane = 0.5/99.5, 0.5 mL/min, 254 nm), Rt (minor) = 31.2 min, Rt (major) = 34.7 min.



9

(3*S*,4*R*)-3-benzyl-5-(1-benzyl-1H-1,2,3-triazol-4-yl)-4-phenyl-3,4-dihydro-2*H*-pyran-2-one

White solid, 96% yield, 28.3 mg, m.p. 176-177 °C.

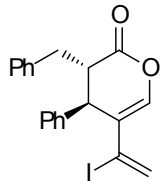
[α]$_D^{25}$ = -226.0 (c = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.35-7.27 (m, 7H), 7.27-7.19 (m, 2H), 7.19-7.08 (m, 7H), 5.54-5.18 (m, 2H), 3.97 (d, *J* = 7.0 Hz, 1H), 3.51-3.45 (m, 1H), 3.23 (dd, *J* = 14.8, 5.0 Hz, 1H), 2.40 (dd, *J* = 14.8, 9.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 145.1, 143.5, 143.4, 137.8, 137.3, 136.0, 131.6, 130.1 (2C), 129.0 (4C), 128.6 (2C), 128.5 (2C), 128.2, 127.6 (2C), 126.7, 118.0, 44.5, 43.9, 32.1, 21.7.

HRMS (ESI, m/z): Mass calcd. for $C_{27}H_{24}N_3O_2$ $[M+H]^+$, 422.1870; found 422.1869.

HPLC analysis: 99% e.e. (Chiralcel AD-H, 25 °C, IPA/Hexane = 20/80, 0.5 mL/min, 254 nm), Rt (major) = 24.2 min, Rt (minor) = 28.5 min.



10

(3*S*, 4*R*)-3-benzyl-5-(1-iodovinyl)-4-phenyl-3,4-dihydro-2*H*-pyran-2-one

Colorless solid, 65% yield, 18.9 mg, m.p. 134-135 °C.

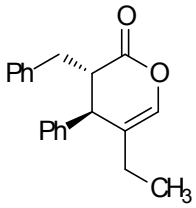
[α]$_D^{25}$ = -211.7 (c = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.30 (m, 5H), 7.29-7.26 (m, 1H), 7.21-7.12 (m, 3H), 7.09-6.97 (m, 2H), 6.12 (d, *J* = 2.1 Hz, 1H), 5.79 (d, *J* = 2.1 Hz, 1H), 3.87 (s, 1H), 3.39-3.34 (m, 1H), 3.18 (dd, *J* = 15.0, 5.1 Hz, 1H), 2.38 (dd, *J* = 15.0, 9.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 146.8, 138.1, 136.0, 129.2 (2C), 128.9 (2C), 128.7 (2C), 128.3, 128.2 (2C), 127.6, 126.8, 124.9, 99.9, 44.7, 42.5, 32.2.

HRMS (ESI, m/z): Mass calcd. for $C_{20}H_{18}O2I$ $[M+H]^+$, 417.0351; found 417.0361.

HPLC analysis: 96% e.e. (Chiralcel OD-H, 25 °C, IPA/Hexane = 0.5/99.5, 0.5 mL/min, 254 nm), Rt (minor) = 38.4 min, Rt (major) = 43.0 min.



11

(3*S*,4*R*)-3-benzyl-5-ethyl-4-phenyl-3, 4-dihydro-2*H*-pyran-2-one

Colorless oil, 84% yield, 25.6 mg.

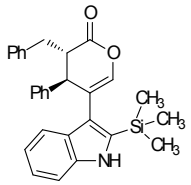
[α]$_D^{25}$ =-321.3 (c = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.27 (m, 5H), 7.25-7.19 (m, 1H), 7.11 (d, *J* = 7.2 Hz, 2H), 7.03 (dd, *J* = 7.6, 1.8 Hz, 2H), 6.45 (t, *J* = 1.6 Hz, 1H), 3.32-3.28 (m, 1H), 3.27-3.19 (m, 2H), 2.34 (dd, J = 14.7, 9.4 Hz, 1H), 1.98-1.87 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 138.8, 137.5, 135.2, 129.0 (2C), 128.9 (2C), 128.6 (2C), 128.5 (2C), 127.8, 126.5, 125.6, 45.4, 44.3, 32.3, 23.8, 12.1.

HRMS (ESI, m/z): Mass calcd. for $C_{20}H_{21}O_2$ $[M+H]^+$, 293.1536; found: 293.1532.

HPLC analysis: > 99% e.e. (Chiralcel OD-H, 25 °C, IPA/Hexane = 0.5/99.5, 0.5 mL/min, 254 nm), Rt (major) = 28.5 min, Rt (minor) = 30.4 min.



12

(3S,4R)-3-benzyl-4-phenyl-5-(2-(trimethylsilyl)-1H-indol-3-yl)-3,4-dihydro-2*H*-pyran-2-one

Colorless solid, 50% yield, 13.5 mg, m.p. 150-151 °C.

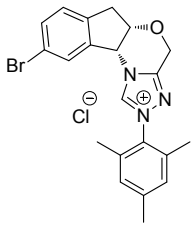
[α]$_D^{25}$ = - 170.9 (c = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 19.5 Hz, 1H), 7.45-7.18 (m, 7H), 7.17-7.06 (m, 3H), 7.04-6.96 (m, 2H), 6.96-6.79 (m, 2H), 6.65 (s, 1H), 3.70 (d, *J* = 6.8 Hz, 1H), 3.65-3.60 (m, 1H), 3.52-3.38 (m, 1H), 2.46 (dd, *J* = 14.5, 10.3 Hz, 1H), 0.11 (d, *J* = 23.2 Hz, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 139.1, 138.8, 138.3, 137.8, 135.7, 129.5 (2C), 129.4 (2C), 129.2 (2C), 129.1 (2C), 128.2, 127.8, 127.1, 123.1, 120.8, 120.3, 120.2, 119.7, 111.3, 46.3, 46.2, 32.9, 0.1, 0.0 (2C).

HRMS (ESI, m/z): Mass calcd. for $C_{29}H_{30}NO_2Si$ $[M+H]^+$, 452.2040; found: 452.2039.

HPLC analysis: > 99% e.e. (Chiralcel OD-H, 25 °C, IPA/Hexane = 2.5/97.5, 0.1 mL/min, 254 nm), Rt (minor) = 178.6 min, Rt (major) = 186.7 min.



(5a*S*,10b*R*)-9-bromo-2-mesityl-4,5a,6,10b-tetrahydroindeno[2,1-b][1,2,4]triazolo[4,3-d][1,4]oxazin-2-ium chloride

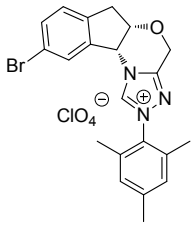
White solid, 37% yield, 1.24 g, m.p. 253-255 °C.

[α]$_D^{25}$ = -25.2 (c = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, DMSO) δ 11.58 (s, 1H), 7.98 (s, 1H), 7.58 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.21 (s, 2H), 6.22 (d, *J* = 2.9 Hz, 1H), 5.26 (d, *J* = 16.0 Hz, 1H), 5.09 (d, *J* = 16.0 Hz, 1H), 5.00 (s, 1H), 3.45 (dd, *J* = 17.1, 4.5 Hz, 1H), 3.13 (d, *J* = 17.2 Hz, 1H), 2.37 (s, 3H), 2.16 (s, 6H).

^{13}C NMR (101 MHz, DMSO) δ 150.5, 145.3, 141.8, 140.7, 139.2, 135.3 (2C), 132.6, 131.8, 129.9 (2C), 127.9 (2C), 120.5, 77.5, 61.3, 60.3, 37.2, 21.2, 17.6 (2C).

HRMS (ESI, m/z): Mass calcd. for $C_{21}H_{22}BrClN_3O$ $[M+H]^+$, 446.0567; found: 446.0564.



(5a*S*,10b*R*)-9-bromo-2-mesityl-4,5a,6,10b-tetrahydroindeno[2,1-b][1,2,4]triazolo[4,3-d][1,4]oxazin-2-ium perchlorate

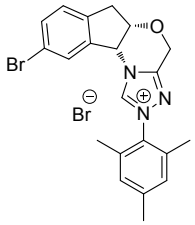
White solid, 82% yield, 84.1 mg, m.p. 282-283 °C.

$[\alpha]_D^{25}$ = -29.0 (c = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, DMSO) δ 11.06 (d, *J* = 10.3 Hz, 1H), 7.89 (s, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.22 (s, 2H), 6.09 (dd, *J* = 12.7, 3.7 Hz, 1H), 5.26 (d, *J* = 16.0 Hz, 1H), 5.02 (dd, *J* = 30.4, 10.1 Hz, 2H), 3.52 – 3.43 (m, 1H), 3.14 (d, *J* = 17.2 Hz, 1H), 2.38 (s, 3H), 2.14 (s, 6H).

^{13}C NMR (101 MHz, DMSO) δ 150.6, 145.0, 141.9, 140.7, 139.1, 135.2 (2C), 132.6, 131.7, 130.0 (2C), 128.0, 127.7, 120.5, 77.5, 61.3, 60.3, 37.2, 21.2, 17.5 (2C).

HRMS (ESI, m/z): Mass calcd. for $C_{21}H_{22}BrClN_3O_5$ $[M+H]^+$, 510.7685; found: 510.7683.



(5a*S*,10b*R*)-9-bromo-2-mesityl-4,5a,6,10b-tetrahydroindeno[2,1-b][1,2,4]triazolo[4,3-d][1,4]oxazin-2-ium bromide

White solid, 87% yield, 86.2 mg, m.p. 202-203 °C.

$[\alpha]_D^{25}$ = -38.5 (c = 0.5, $CHCl_3$).

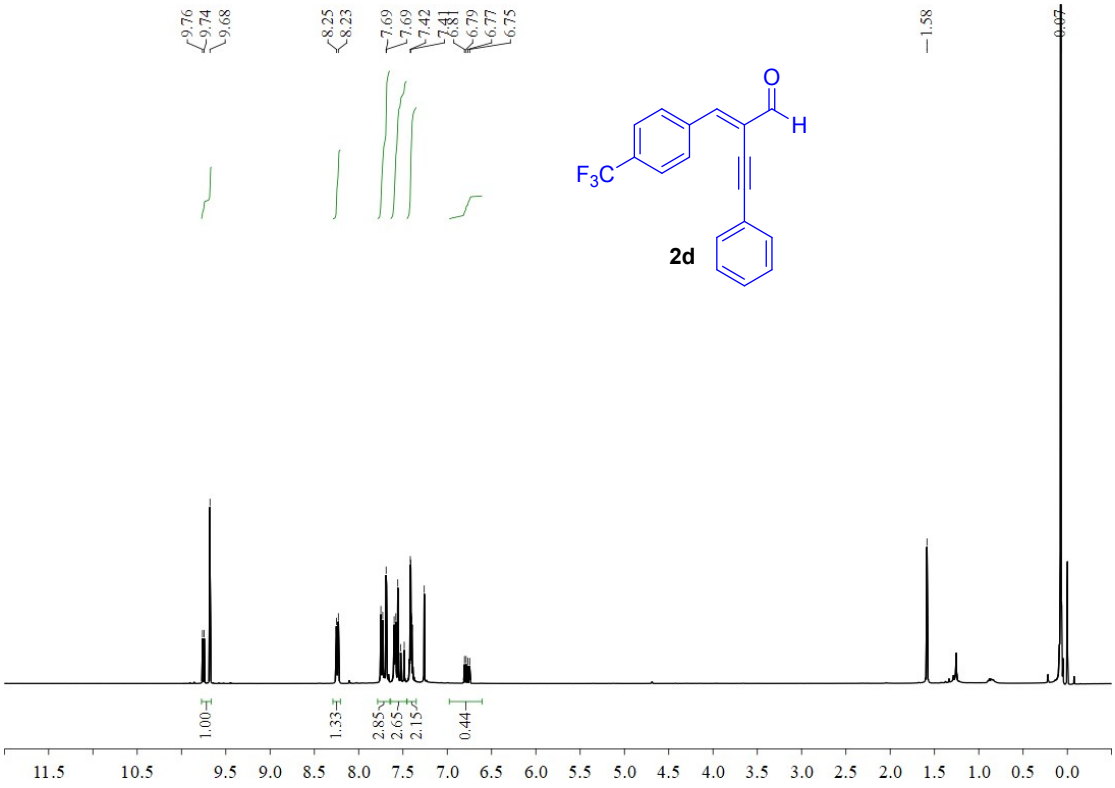
^{1}H NMR (400 MHz, DMSO) δ 11.15 (d, *J* = 5.6 Hz, 1H), 7.90 (d, *J* = 11.4 Hz, 1H), 7.69 – 7.54 (m, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.22 (s, 2H), 6.15 (dd, *J* = 10.4, 4.0 Hz, 1H), 5.26 (d, *J* = 16.0 Hz, 1H), 5.17 – 4.90 (m, 2H), 3.46 (dd, *J* = 17.1, 4.9 Hz, 1H), 3.14 (dd, *J* = 17.4, 3.3 Hz, 1H), 2.38 (s, 3H), 2.15 (s, 6H).

^{13}C NMR (101 MHz, DMSO) δ 150.6, 145.0, 141.9, 140.7, 139.2, 135.3 (2C), 132.6, 131.7, 130.0 (2C), 128.2, 128.0, 127.8, 120.5, 77.5, 61.3, 60.3, 37.2, 21.2, 17.6 (2C).

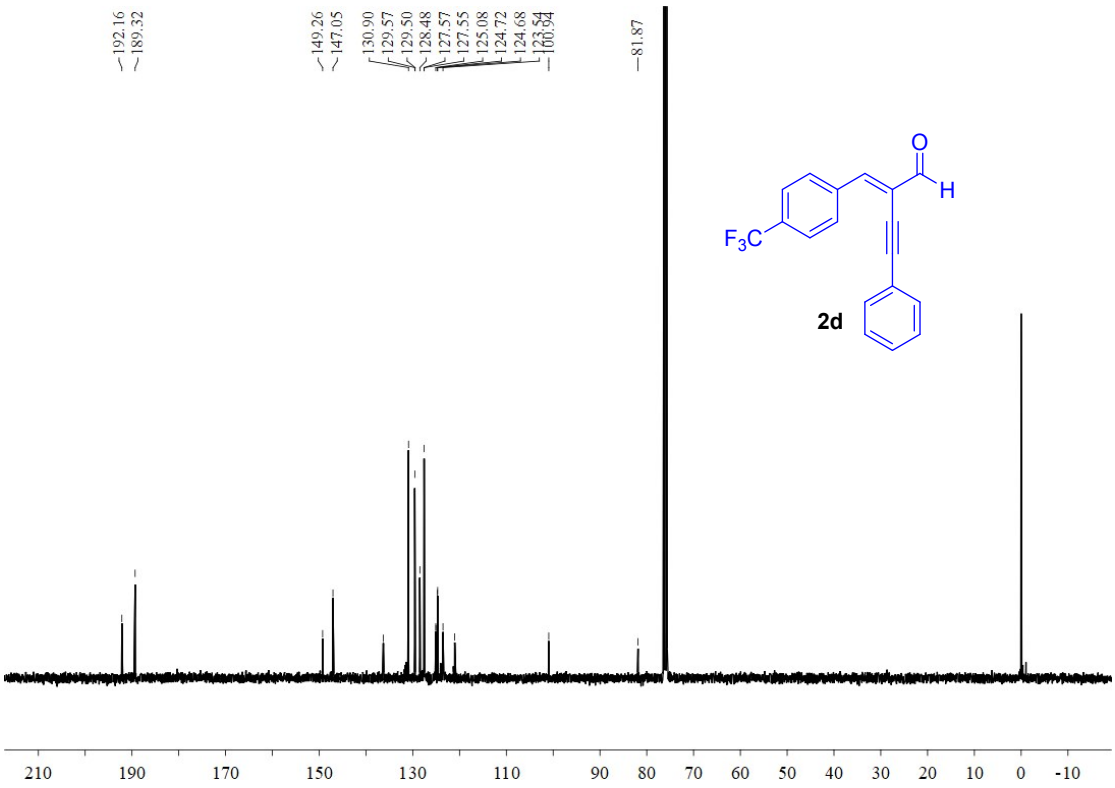
HRMS (ESI, m/z): Mass calcd. for $C_{21}H_{22}Br_2N_3O$ $[M+H]^+$, 489.0151; found: 489.0148.

VIII. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and HPLC Spectra

Figure S10. ^{1}H, ^{13}C and ^{19}F NMR spectrum of **2d**.



n



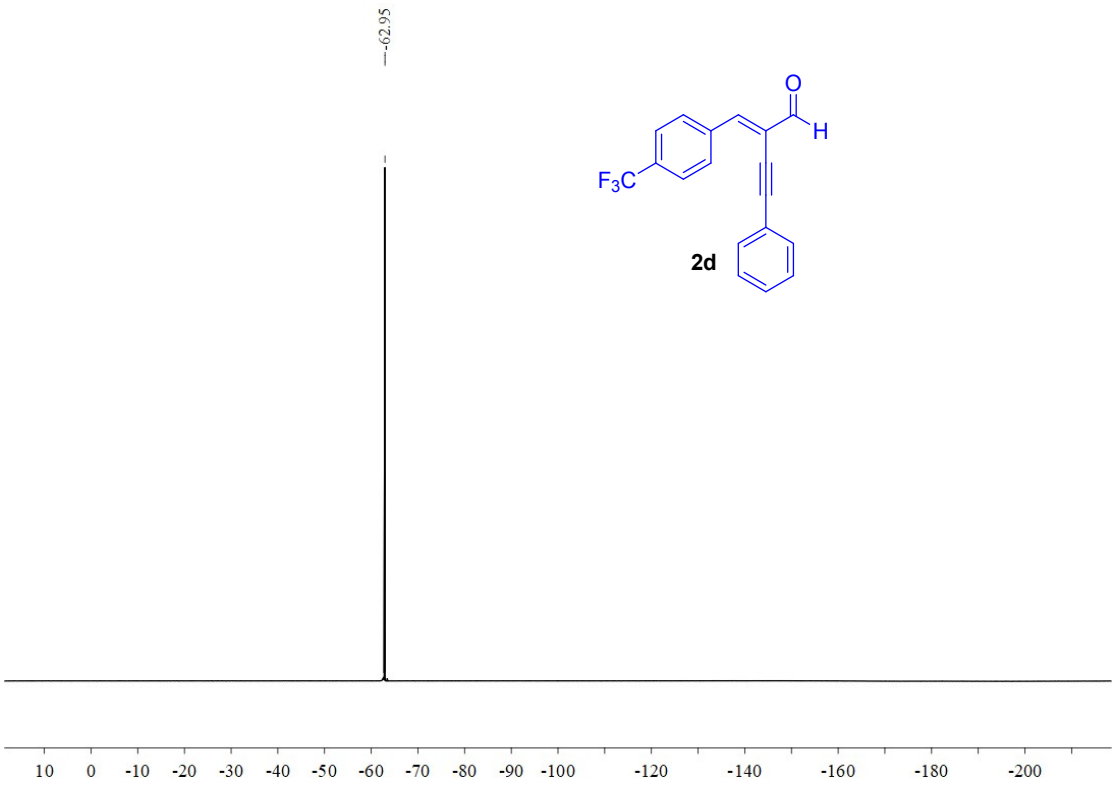
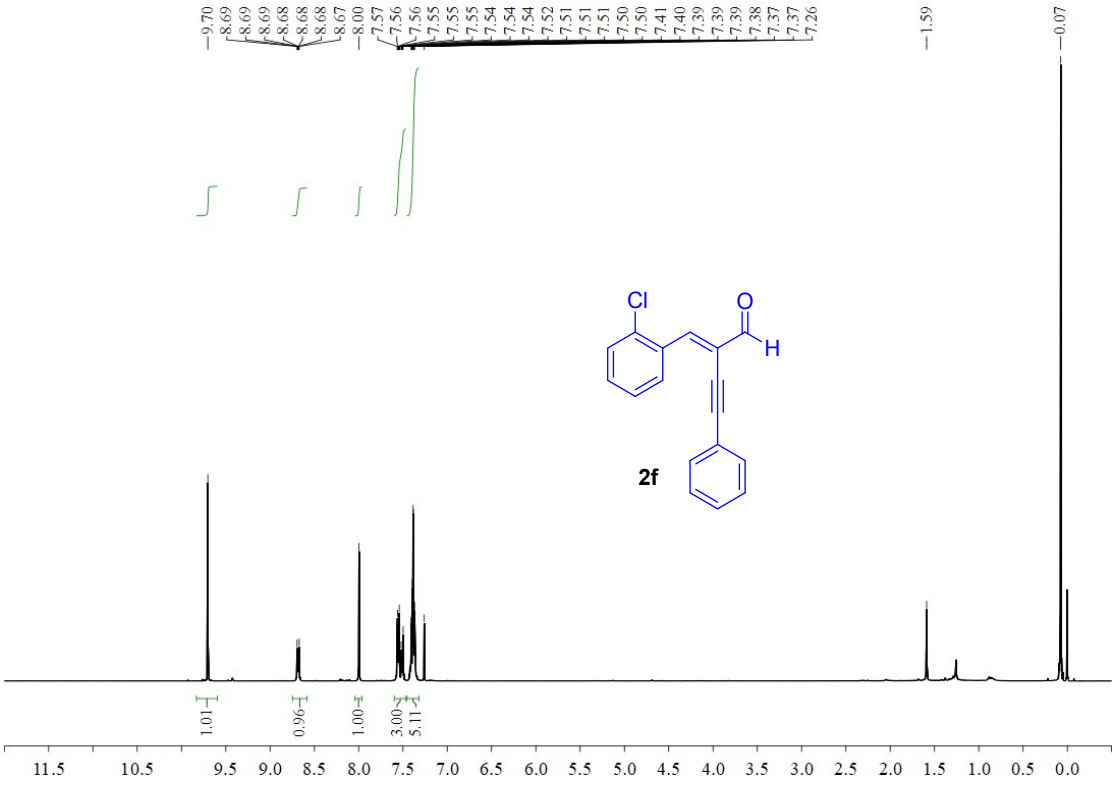

-62.95
O
H
F3C
2d
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

Figure S11. ^{1}H and ^{13}C NMR spectrum of **2f.**



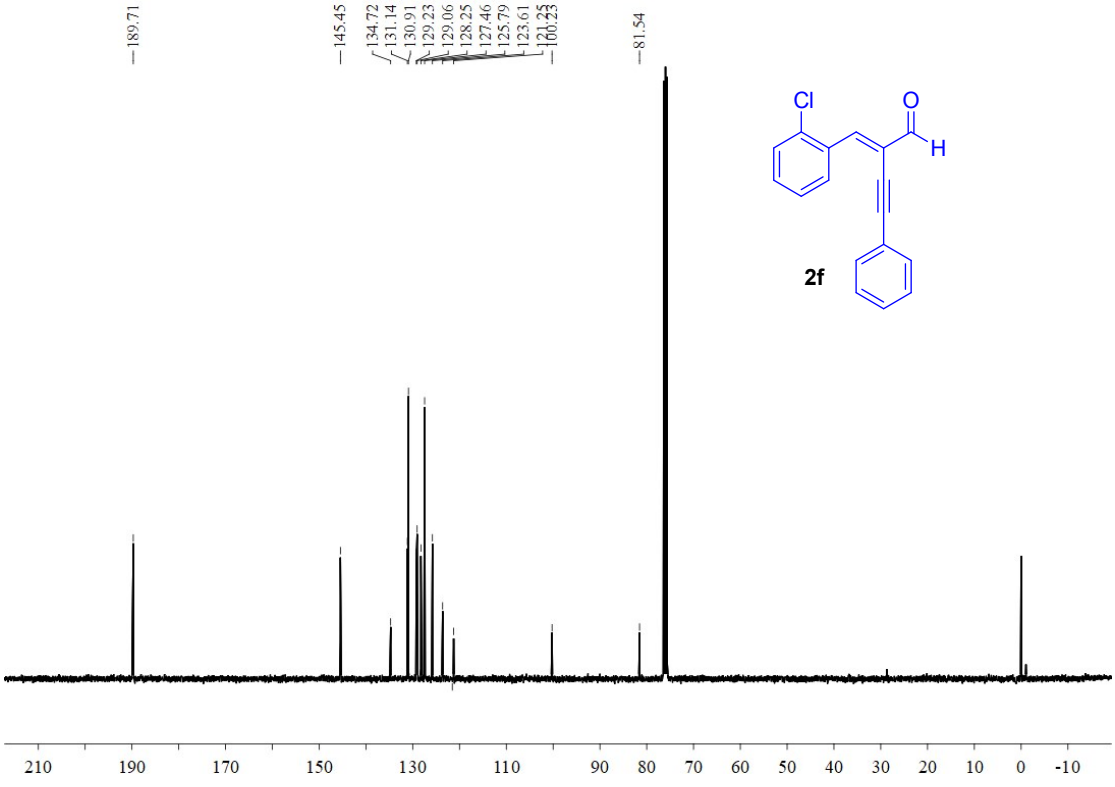


Figure S12. ^{1}H and ^{13}C NMR spectrum of **2g.**

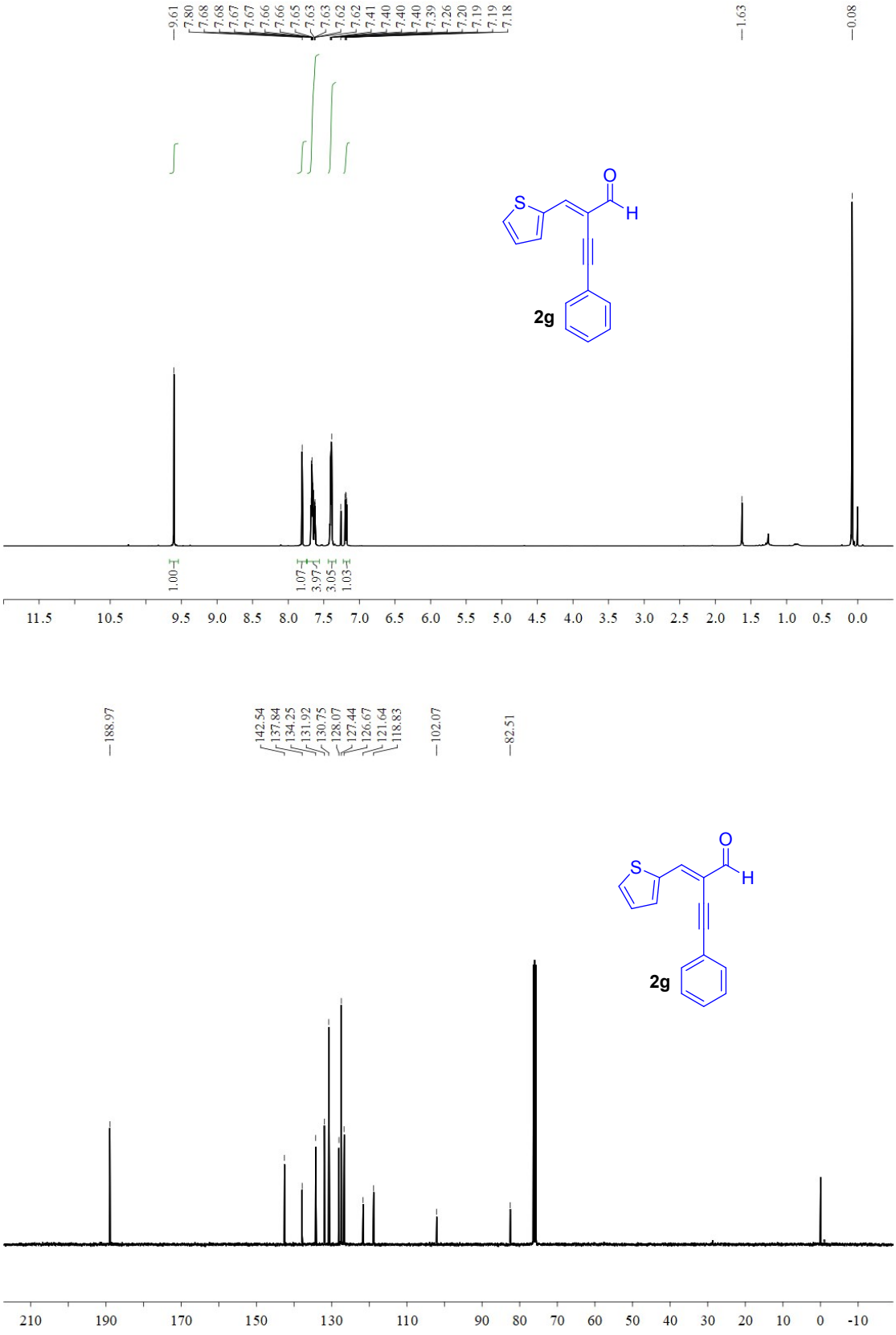


Figure S13. ^{1}H and ^{13}C NMR spectrum of **2h.**

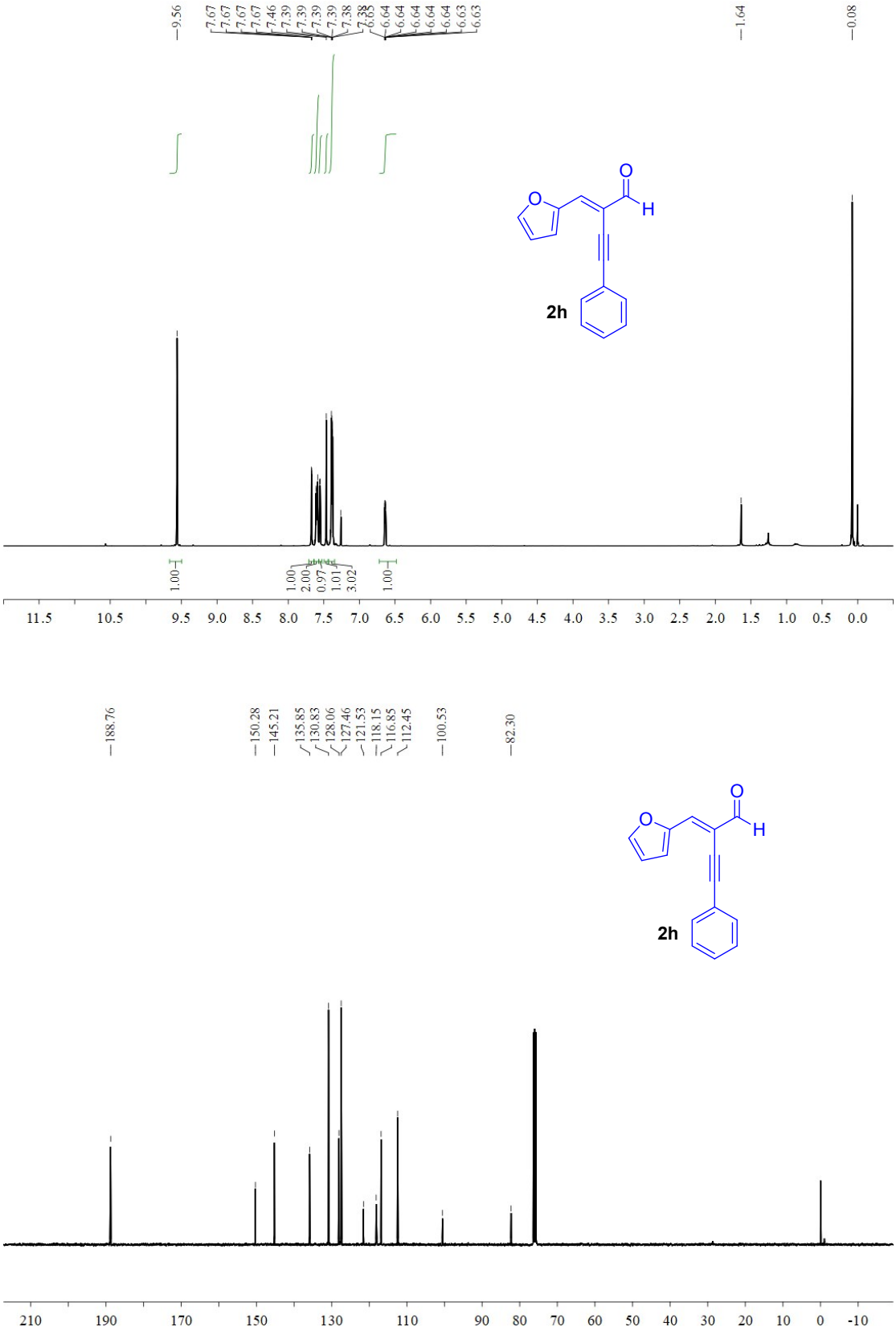


Figure S14. ^{1}H and ^{13}C NMR spectrum of **2m.**

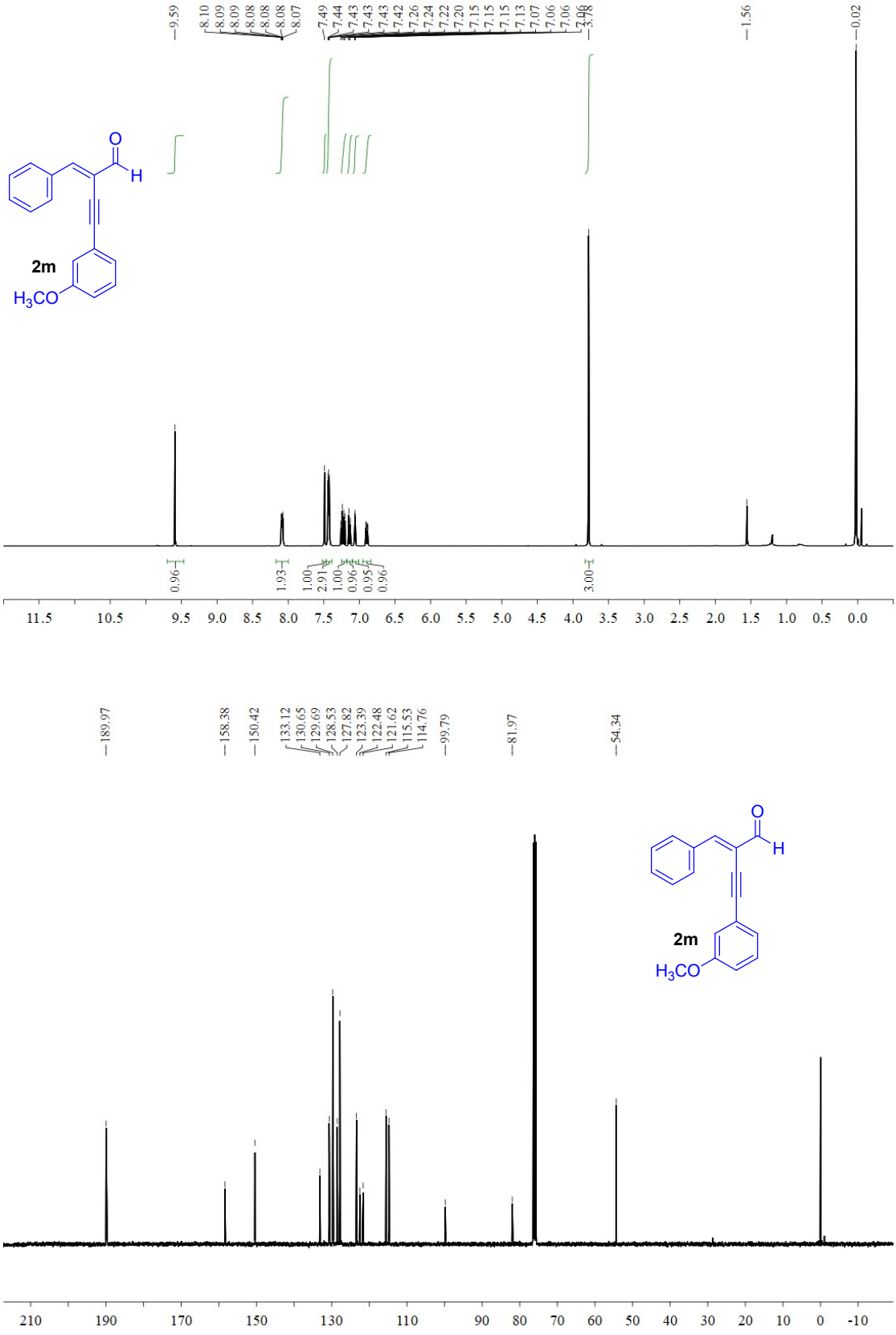


Figure S15. ^{1}H and ^{13}C NMR spectrum of **2o.**

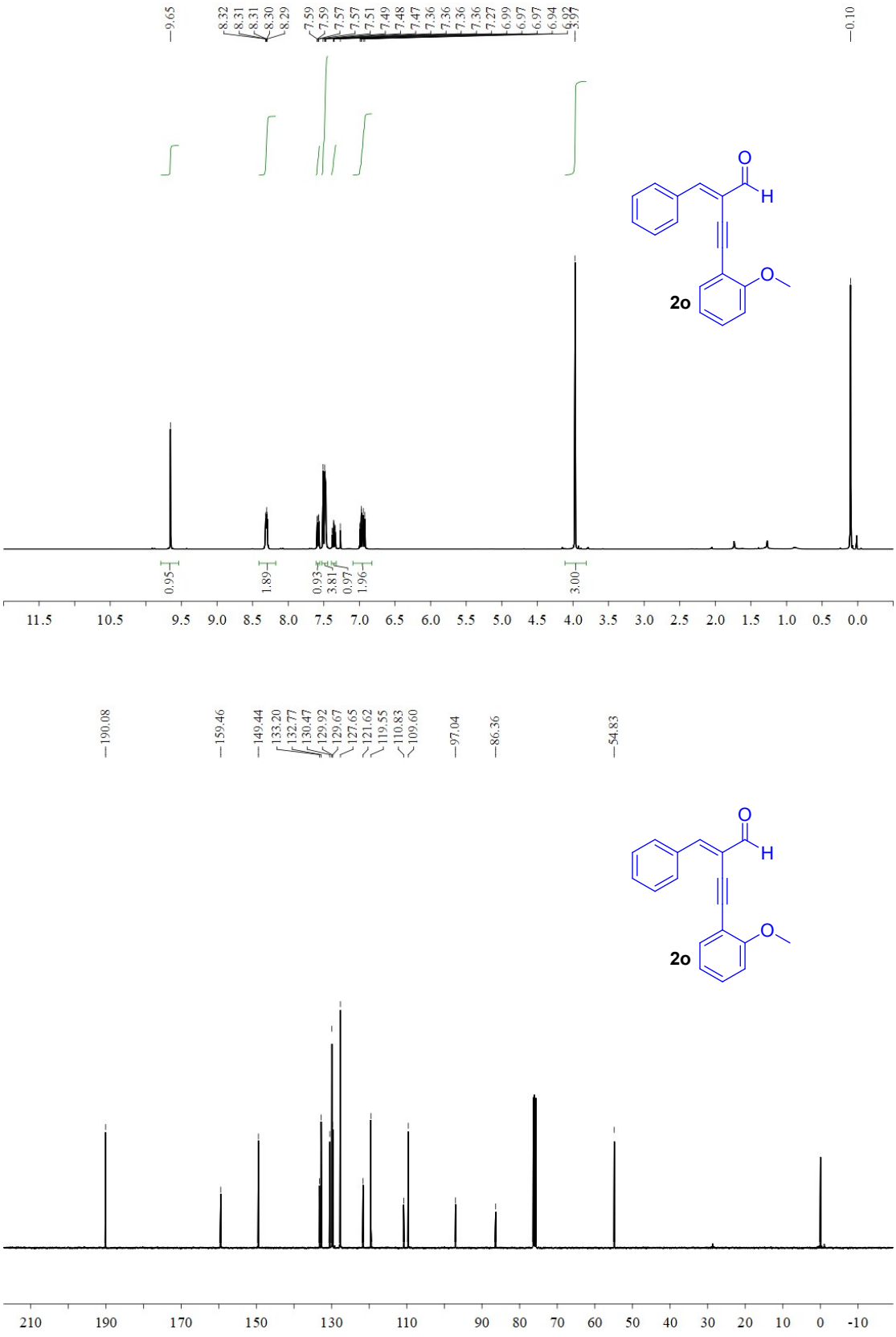


Figure S16. ^{1}H and ^{13}C NMR spectrum of **2r.**

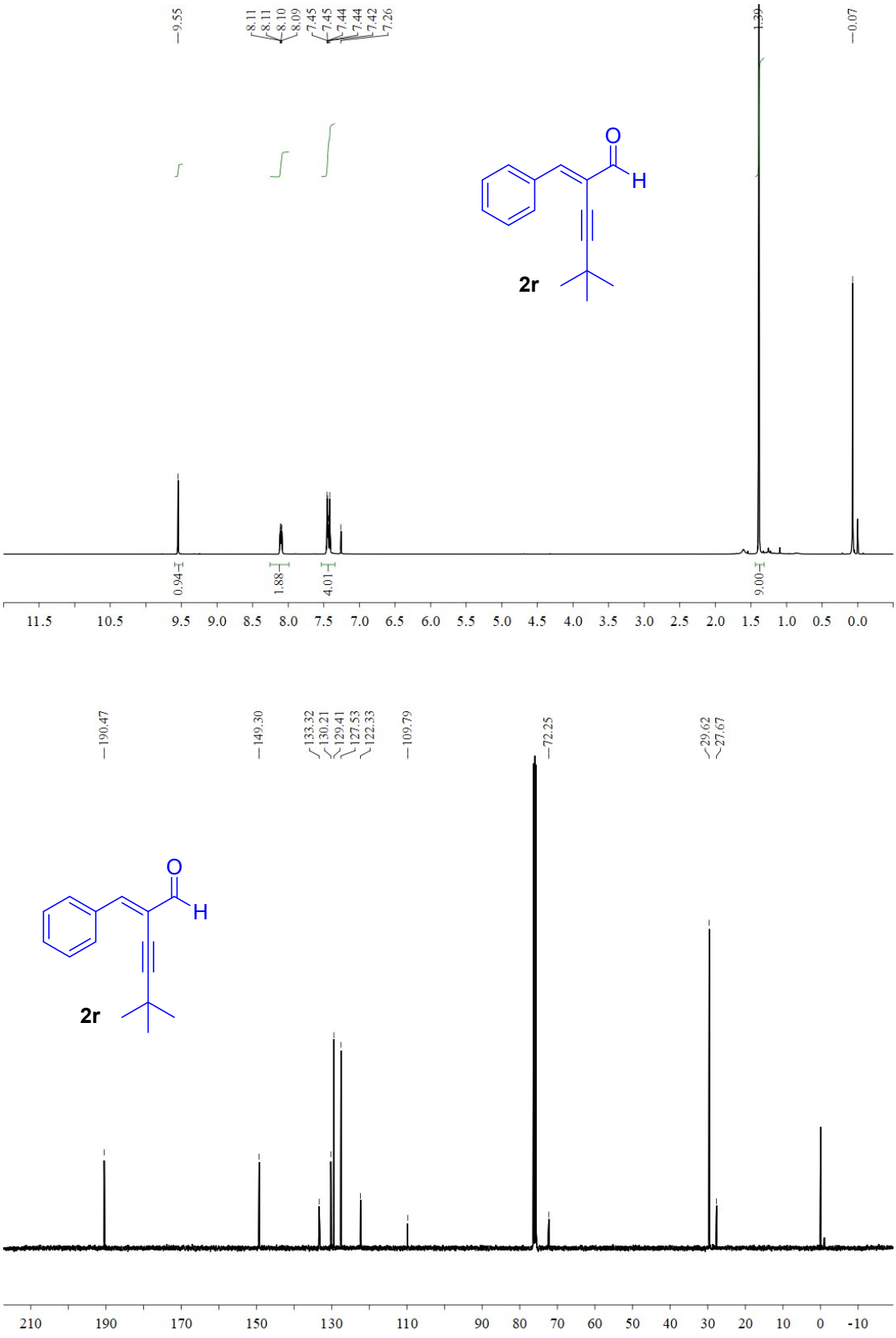


Figure S17. ^{1}H and ^{13}C NMR spectrum of **2x.**

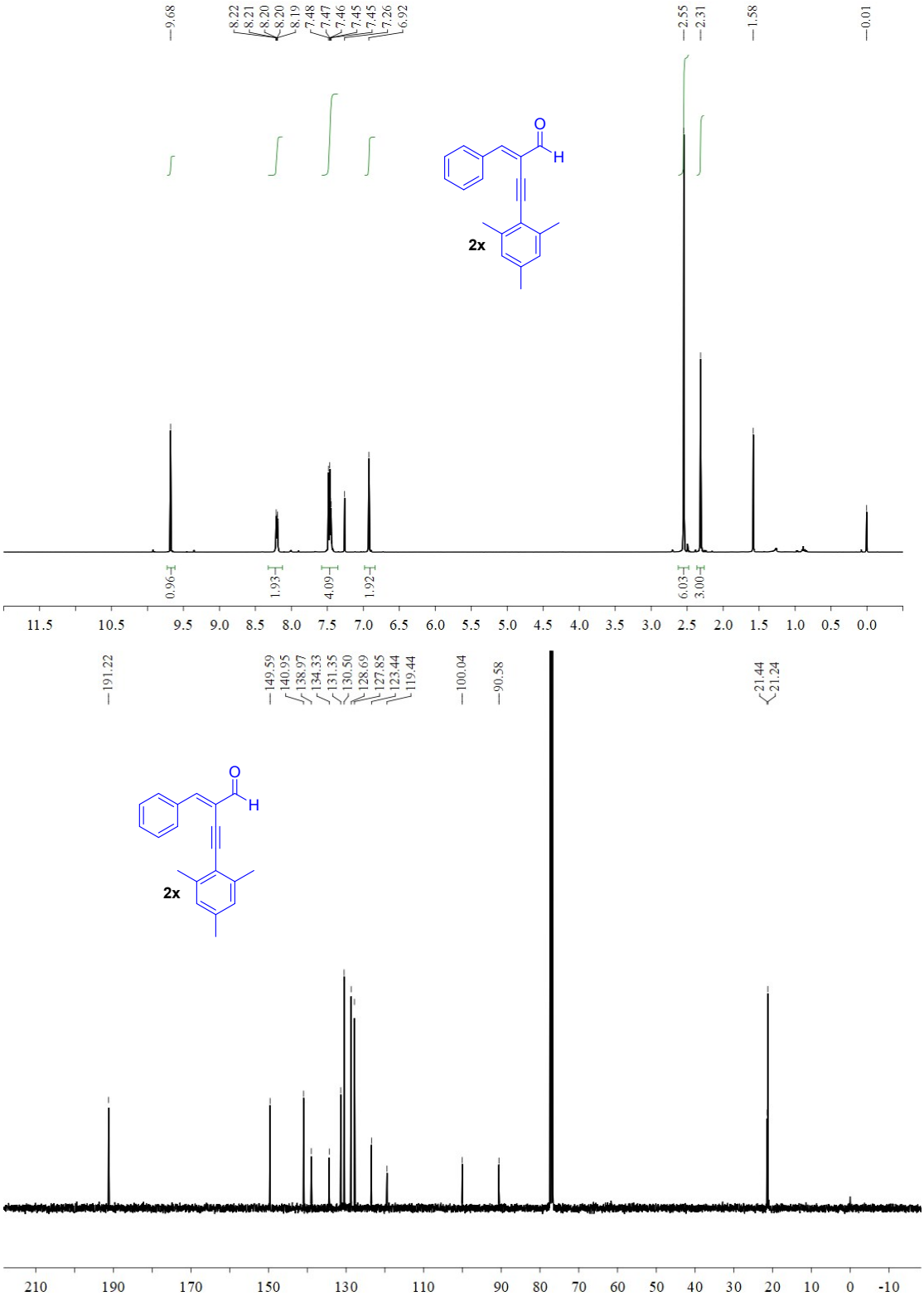


Figure S18. ^{1}H and ^{13}C NMR spectrum of **2y.**

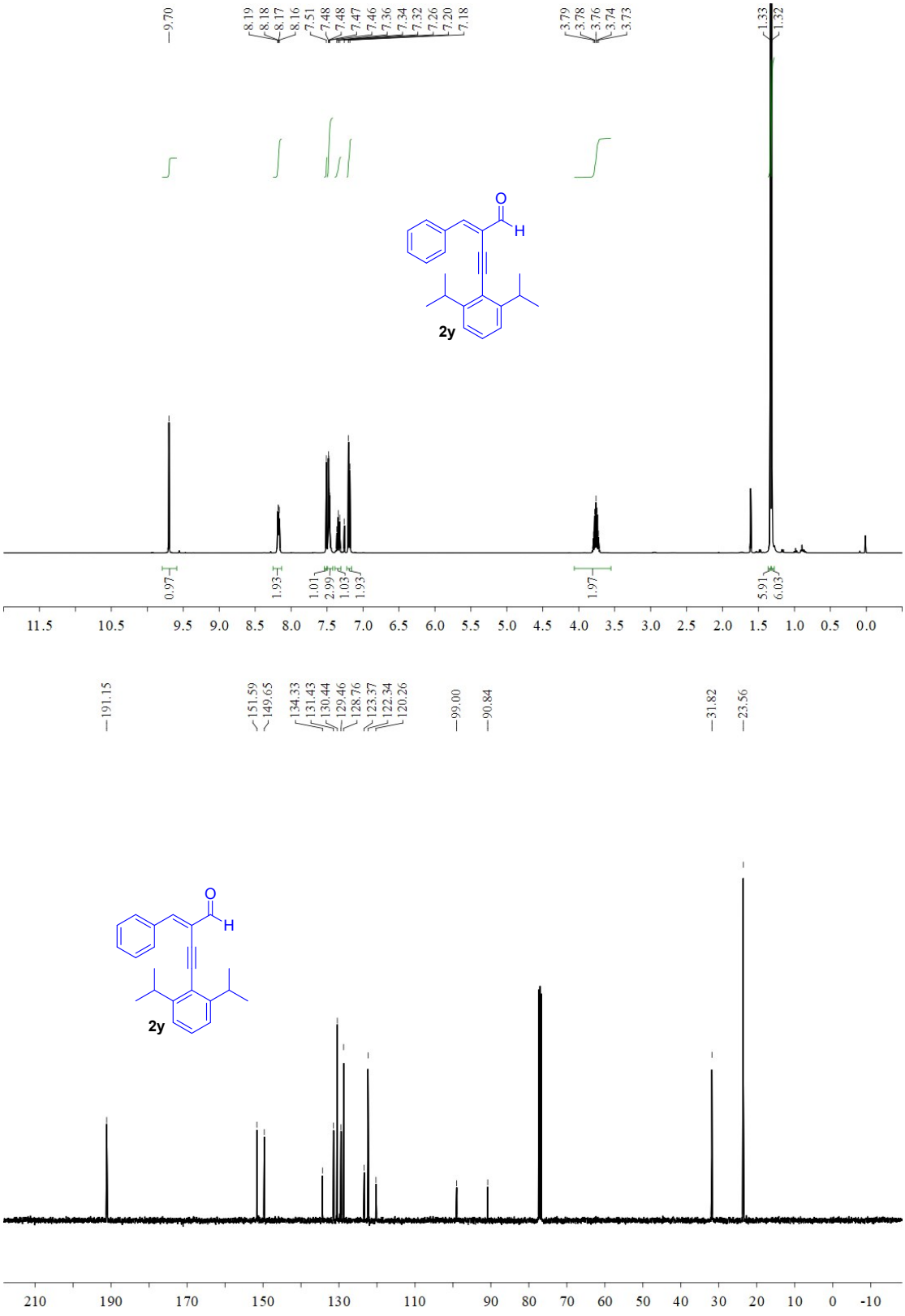


Figure S19. ^{1}H and ^{13}C NMR spectrum of **3a.**

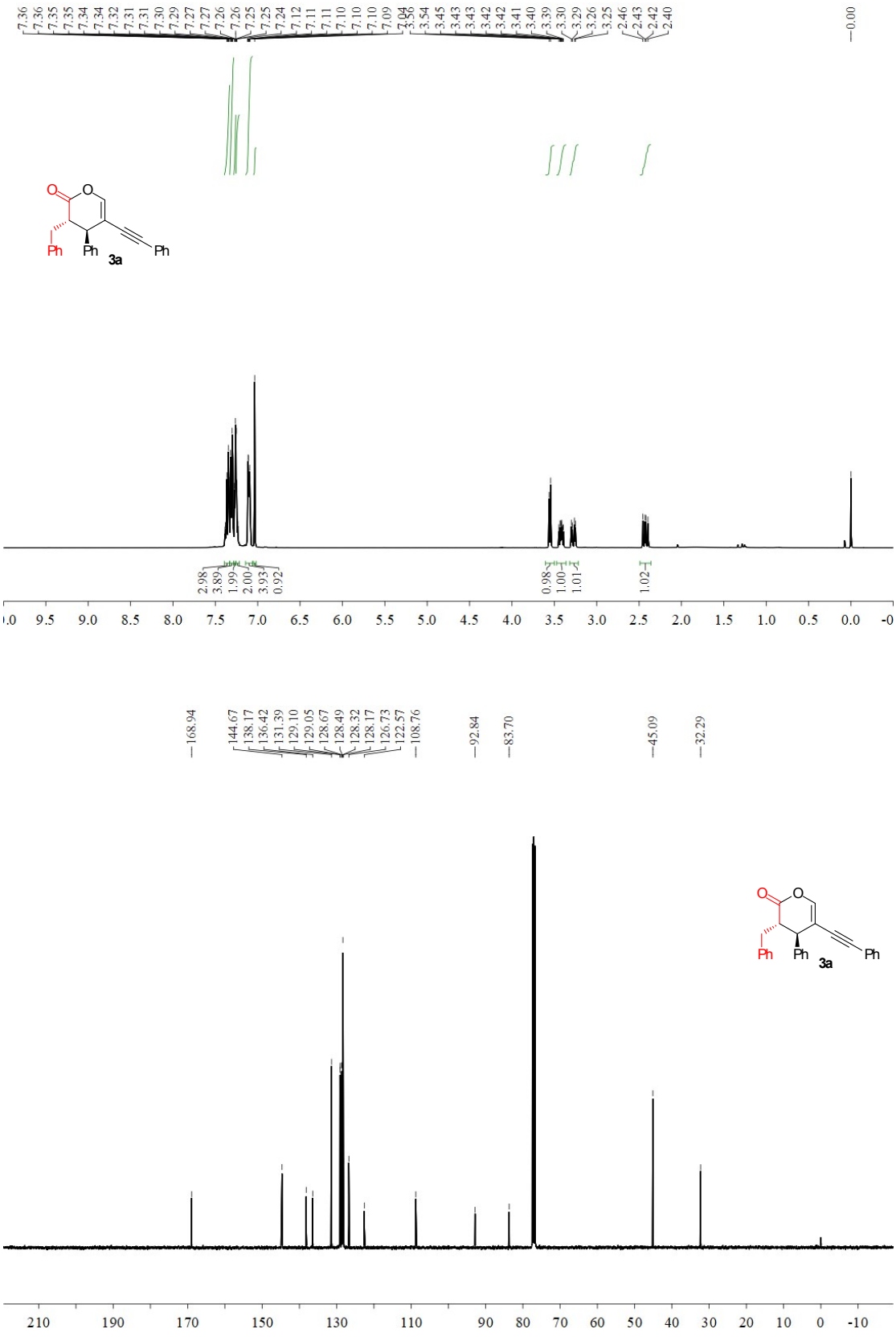
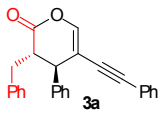
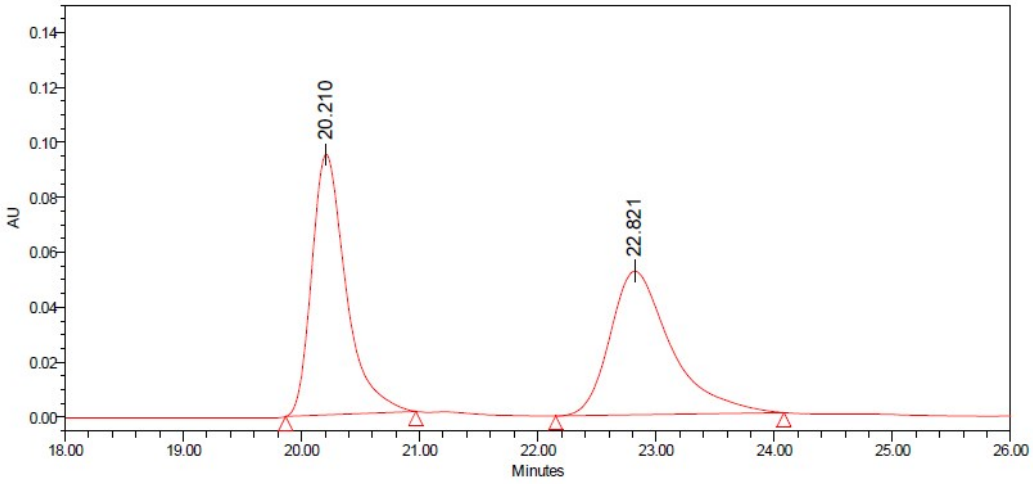


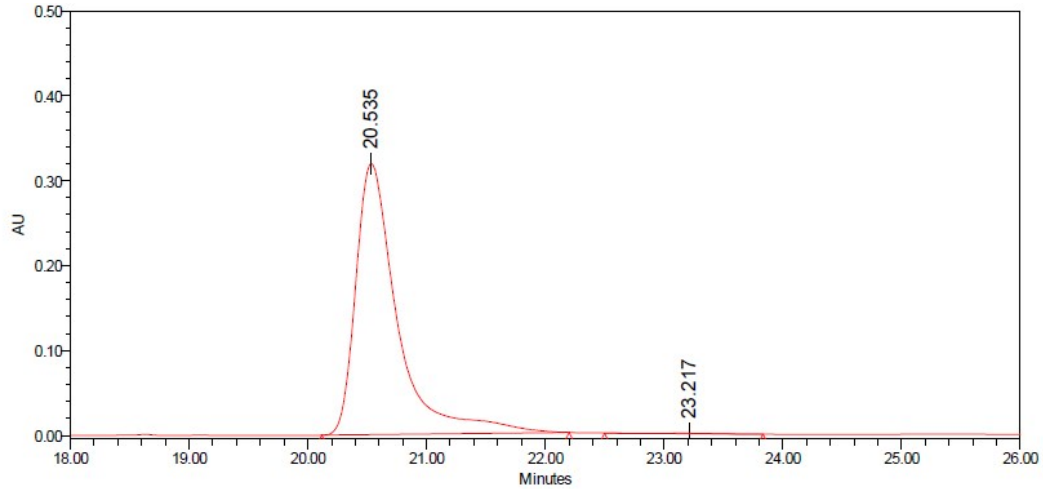
Figure S20. HPLC spectrum of **3a.**



3a



	Ret. Time	Height	Area	% Area
1	20.210	94946	1911225	50.50
2	22.821	52285	1873402	49.50



	Ret. Time	Height	Area	% Area
1	20.535	319648	7801899	99.80
2	23.217	547	15278	0.20

Figure S21. ^{1}H and ^{13}C NMR spectrum of **3b.**

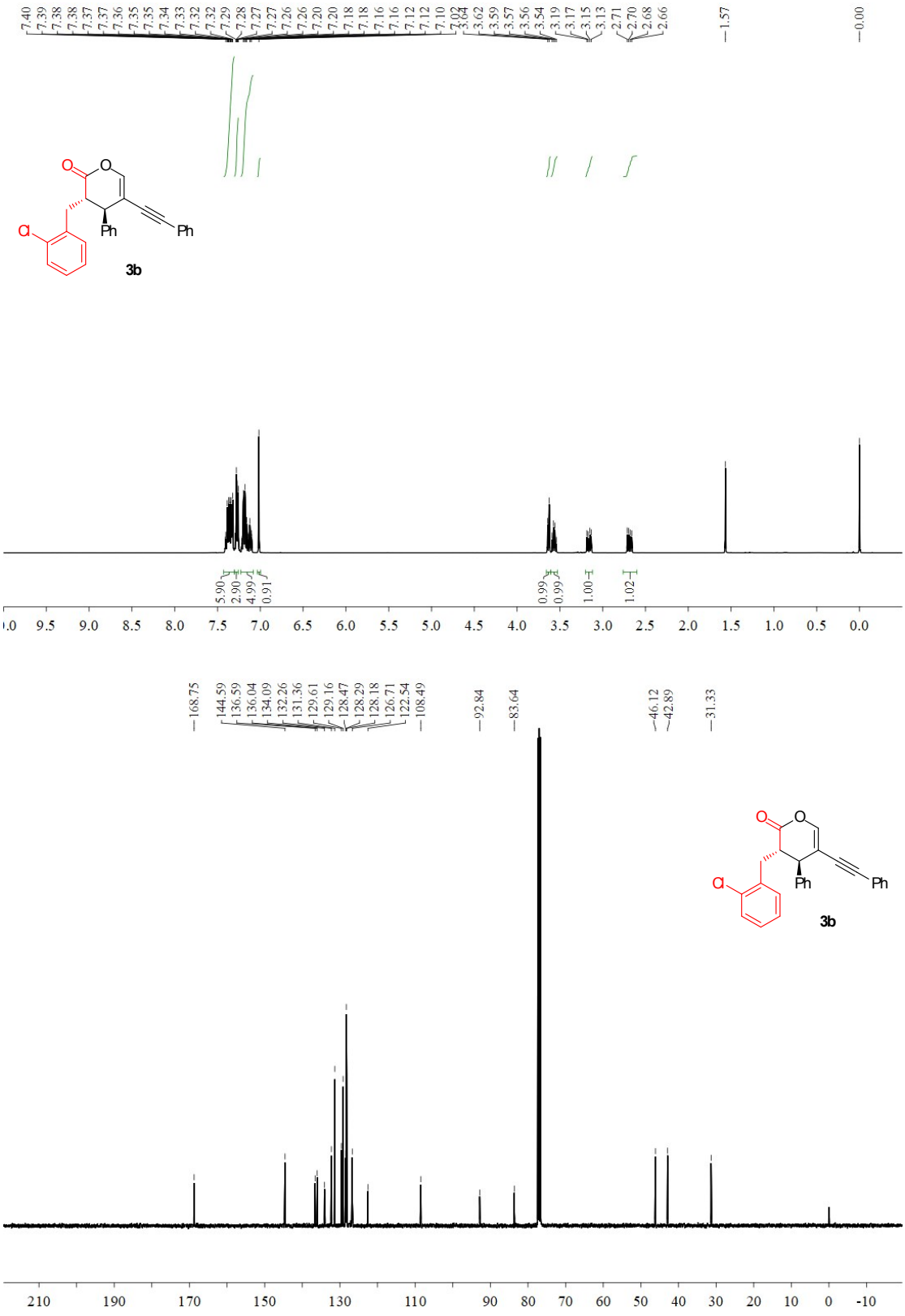
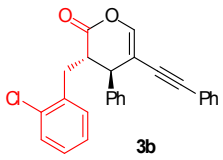
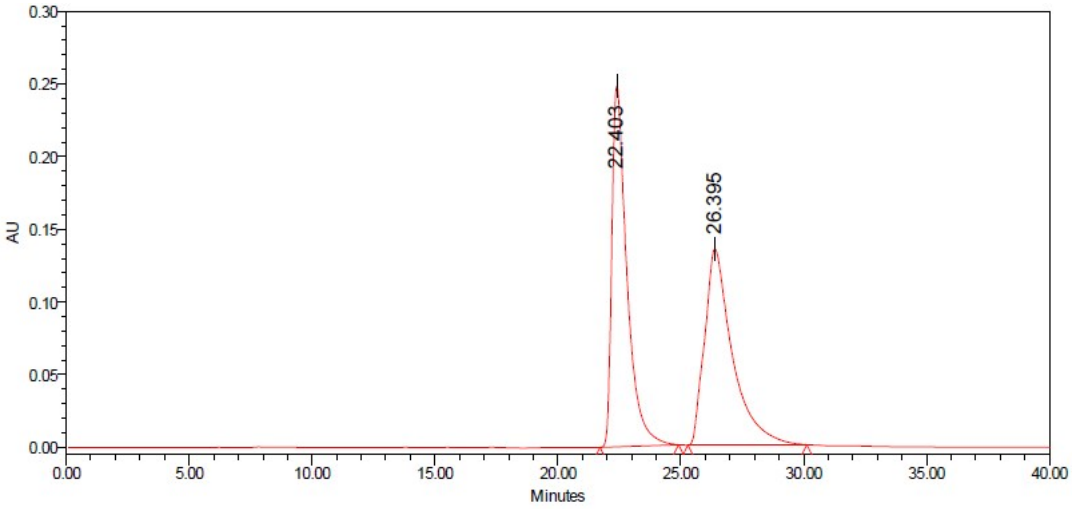


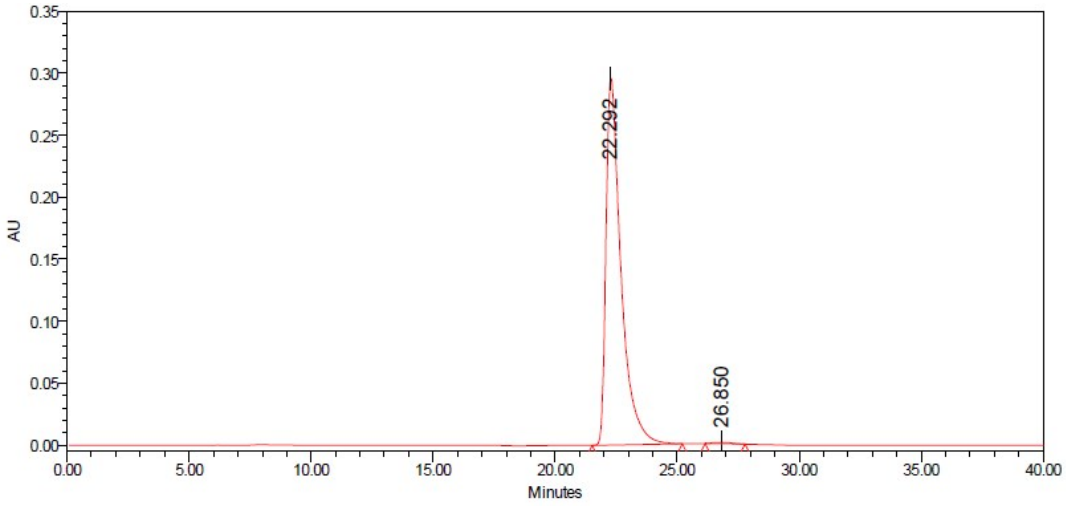
Figure S22. HPLC spectrum of **3b.**



3b



	Ret. Time	Height	Area	% Area
1	22.403	248115	10569262	50.00
2	26.395	134941	10569183	50.00



	Ret. Time	Height	Area	% Area
1	22.292	295812	12654256	99.55
2	26.850	1105	57128	0.45

Figure S23. ^{1}H and ^{13}C NMR spectrum of **3c.**

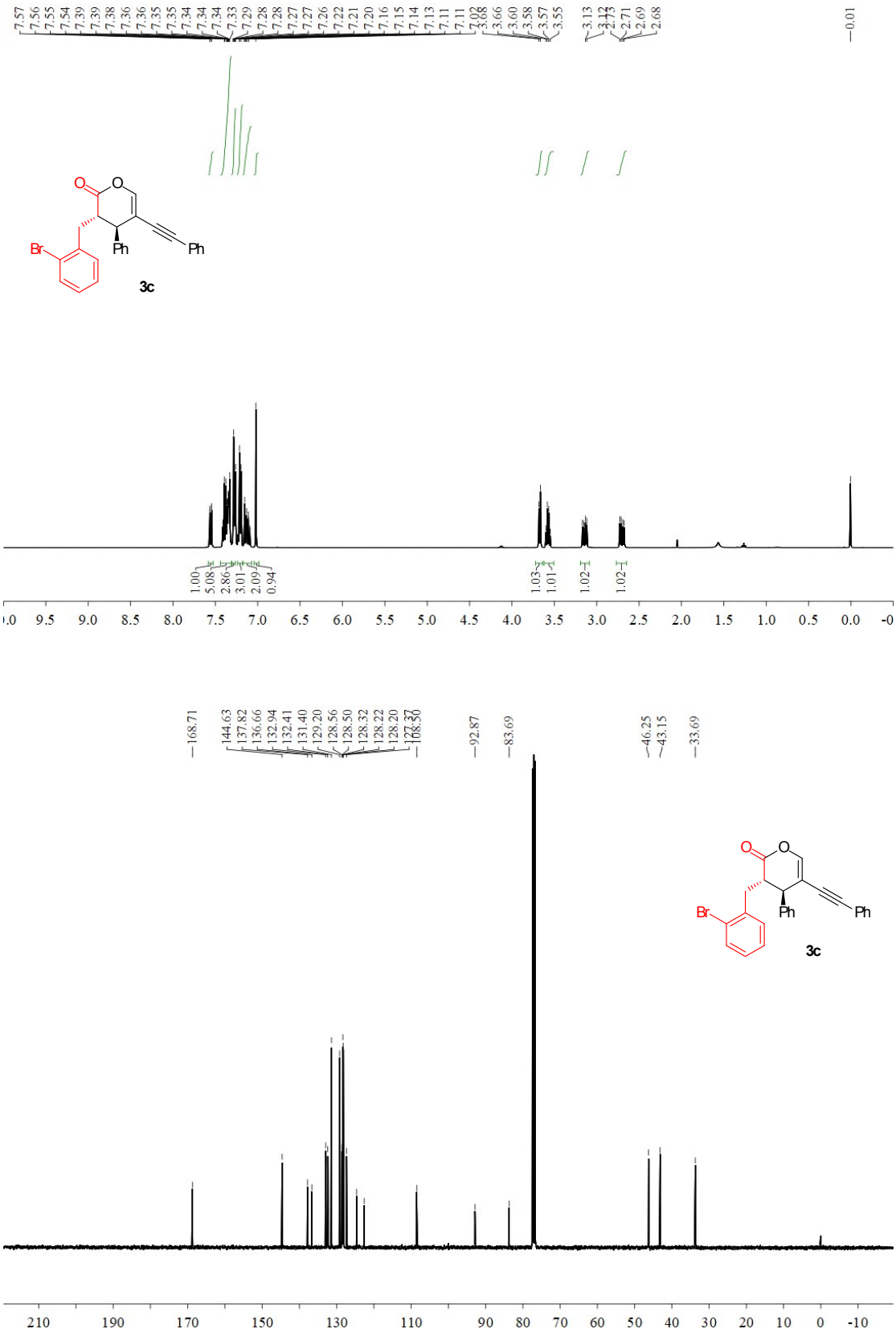
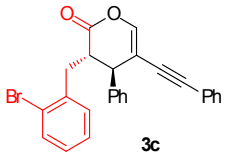
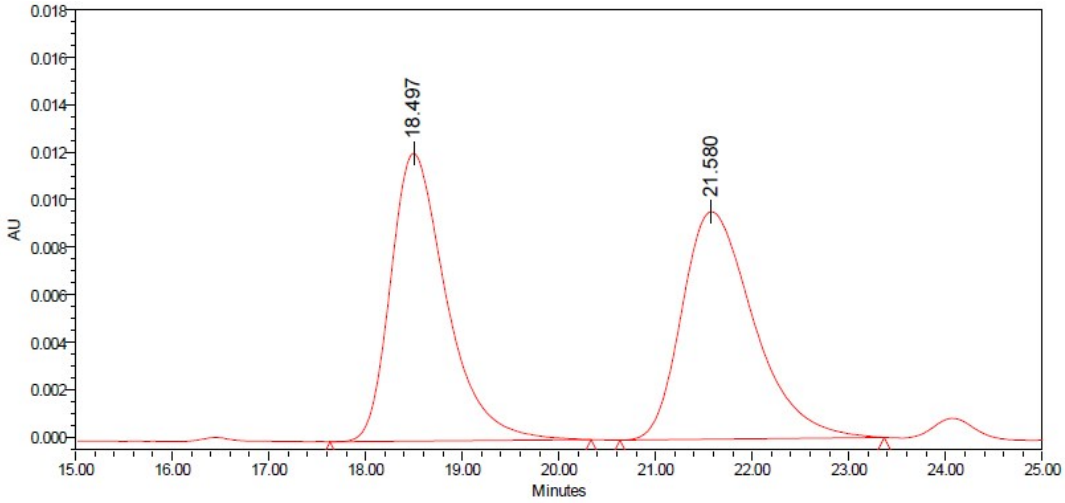


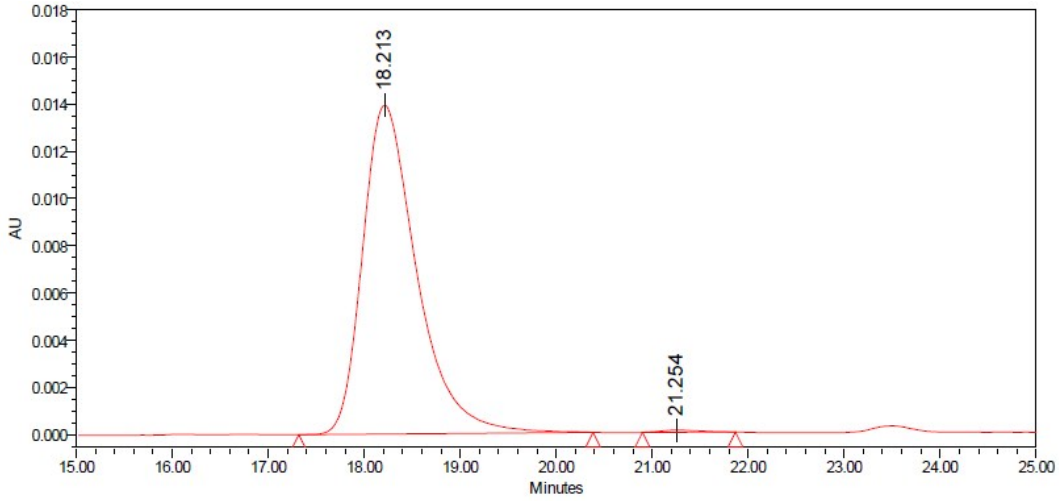
Figure S24. HPLC spectrum of **3c.**



3c



	Ret. Time	Height	Area	% Area
1	18.497	12119	485604	49.51
2	21.580	9583	495149	50.49



	Ret. Time	Height	Area	% Area
1	18.213	13936	546133	99.52
2	21.254	94	2618	0.48

Figure S25. ^{1}H and ^{13}C NMR spectrum of **3d.**

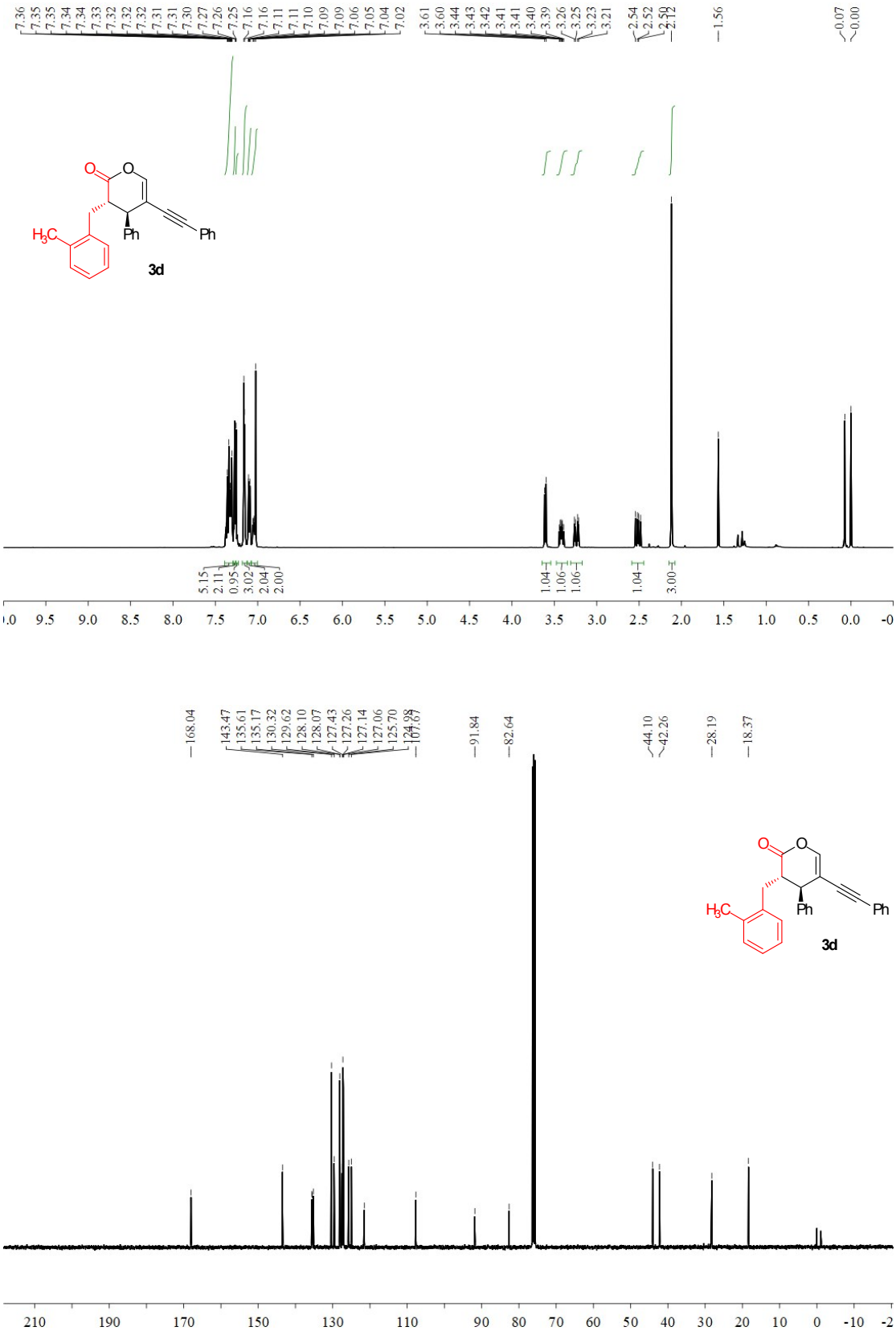
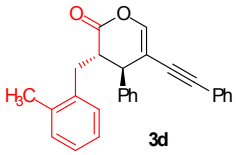
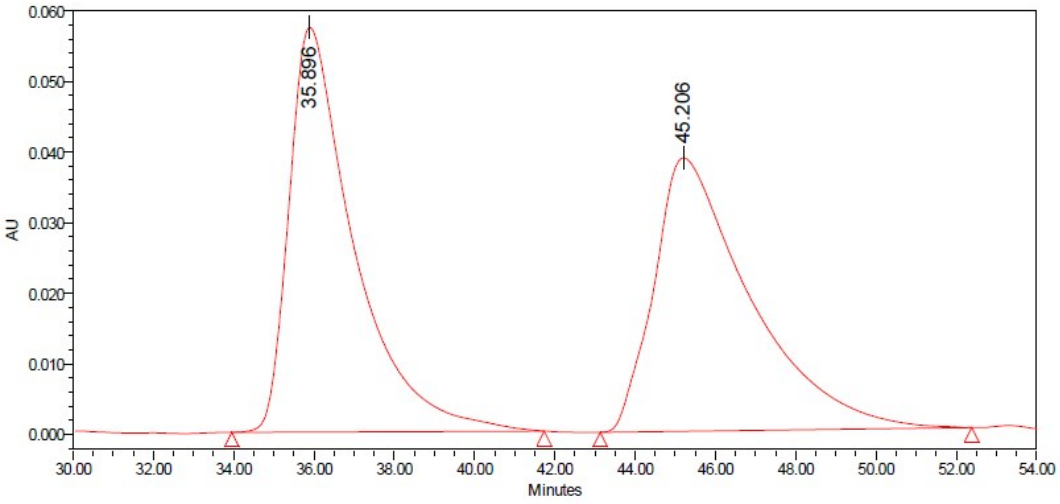


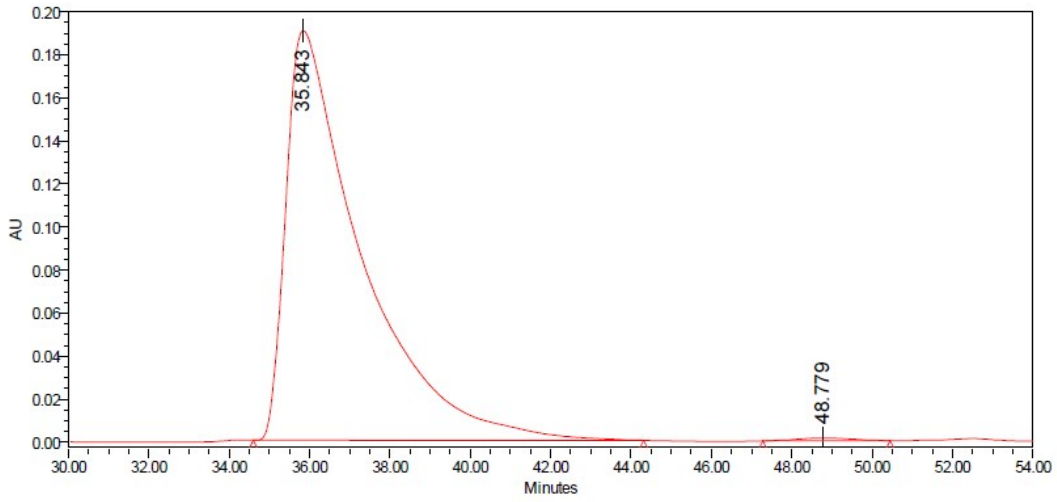
Figure S26. HPLC spectrum of **3d.**



3d



	Ret. Time	Height	Area	% Area
1	35.896	57324	6444861	50.00
2	45.206	38710	6445790	50.00



	Ret. Time	Height	Area	% Area
1	35.843	190301	24817155	99.52
2	48.779	1273	119998	0.48

Figure S27. ^{1}H and ^{13}C NMR spectrum of **3e.**

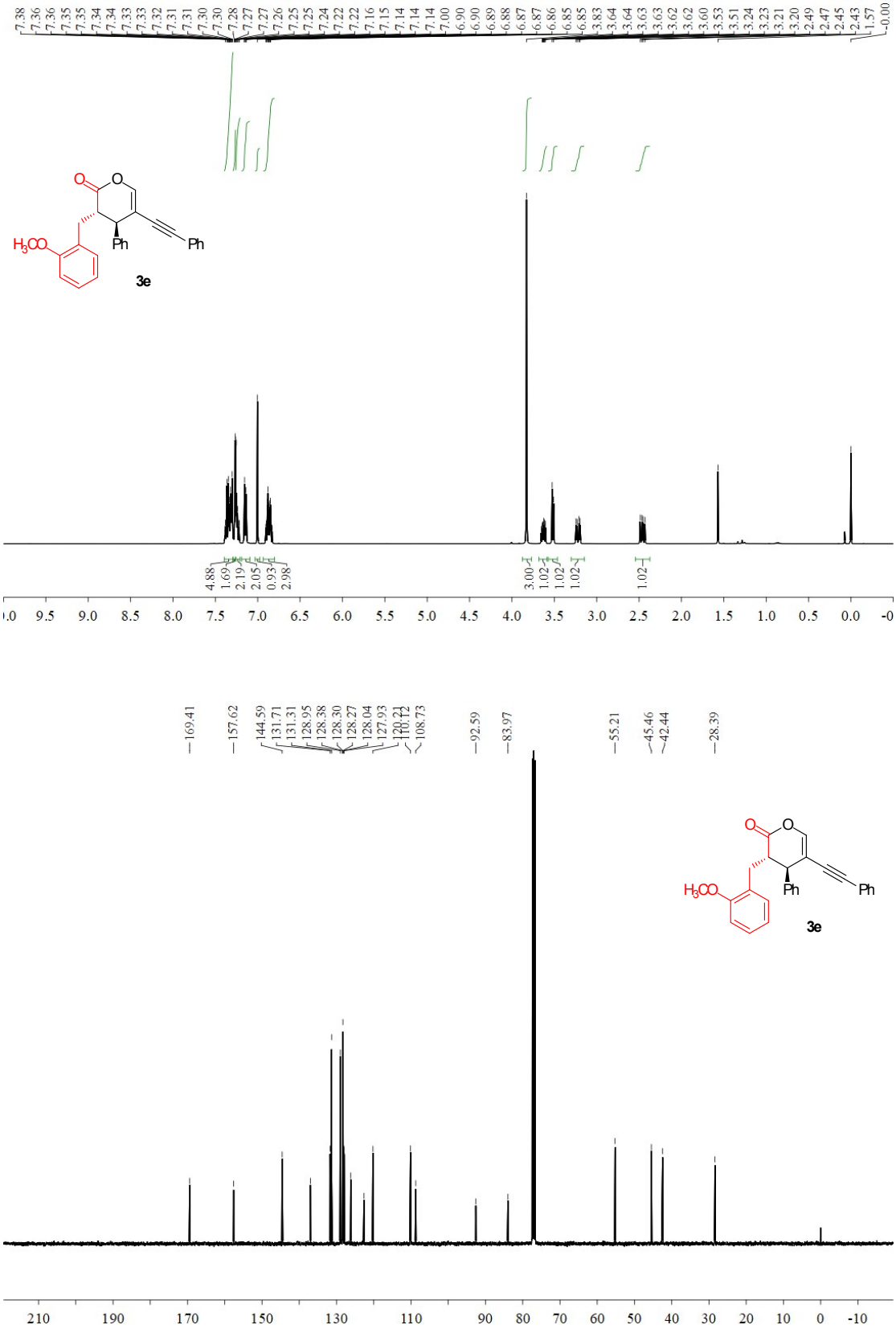
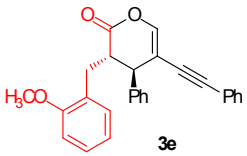
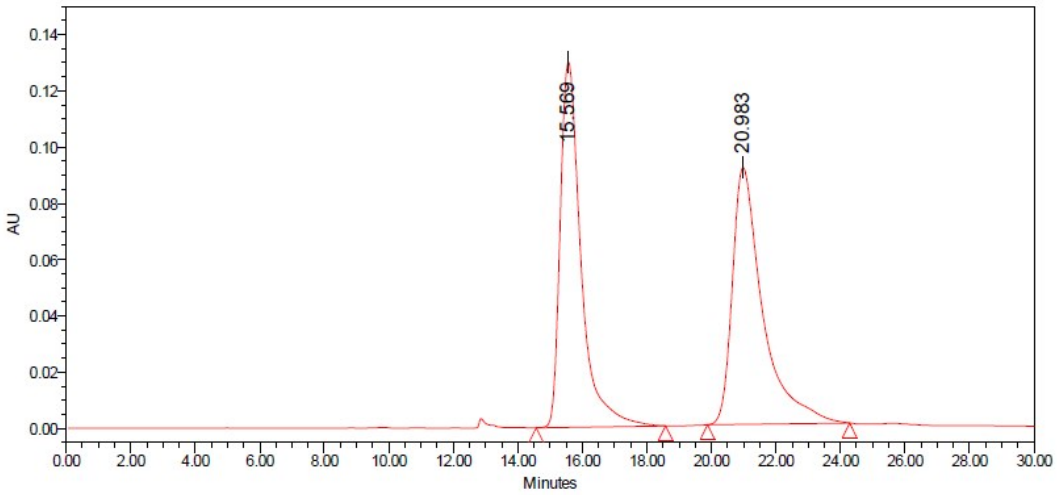


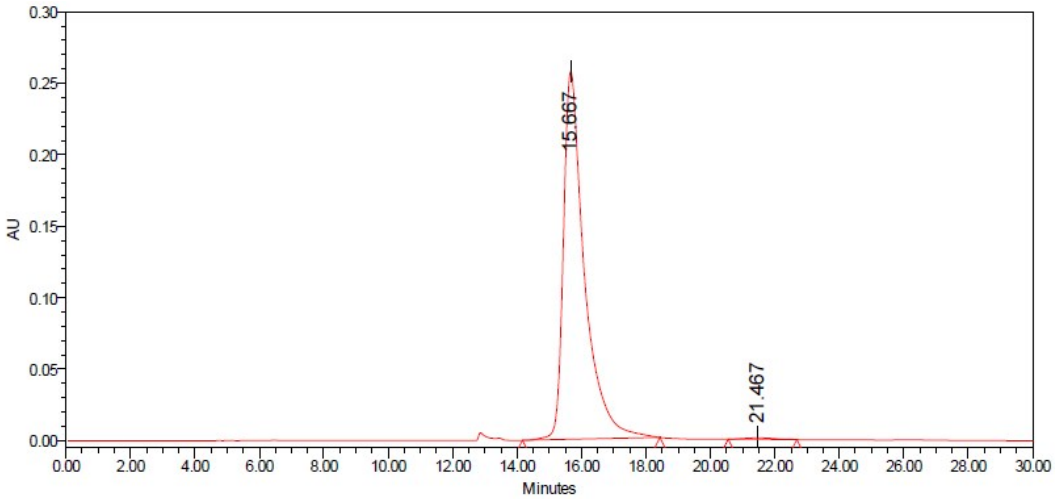
Figure S28. HPLC spectrum of **3e.**



3e

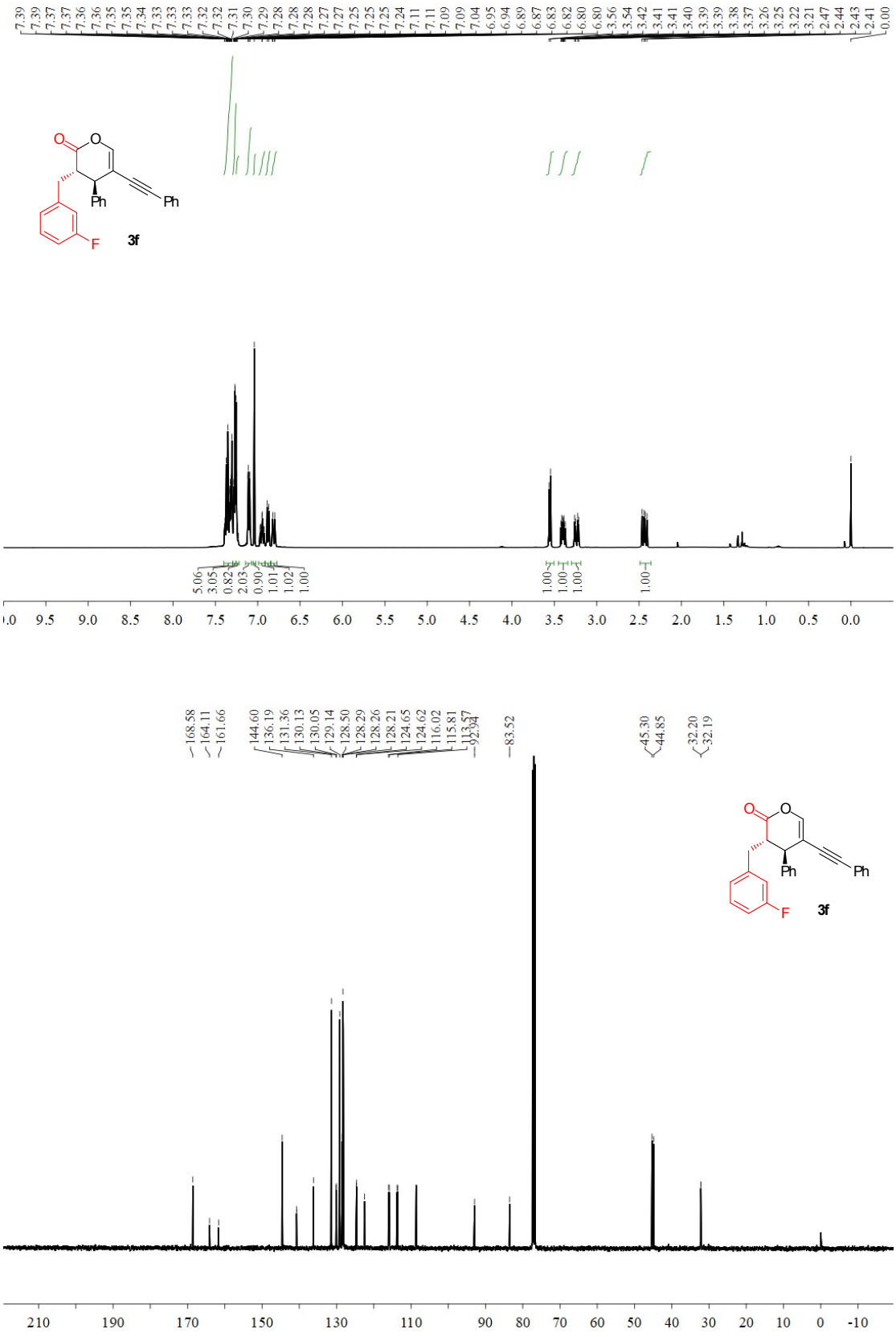


	Ret. Time	Height	Area	% Area
1	15.569	129799	5818301	49.33
2	20.983	91279	5977175	50.67



	Ret. Time	Height	Area	% Area
1	15.667	257284	11670765	99.51
2	21.467	969	57995	0.49

Figure S29. ^{1}H, ^{13}C and ^{19}F NMR spectrum of **3f.**



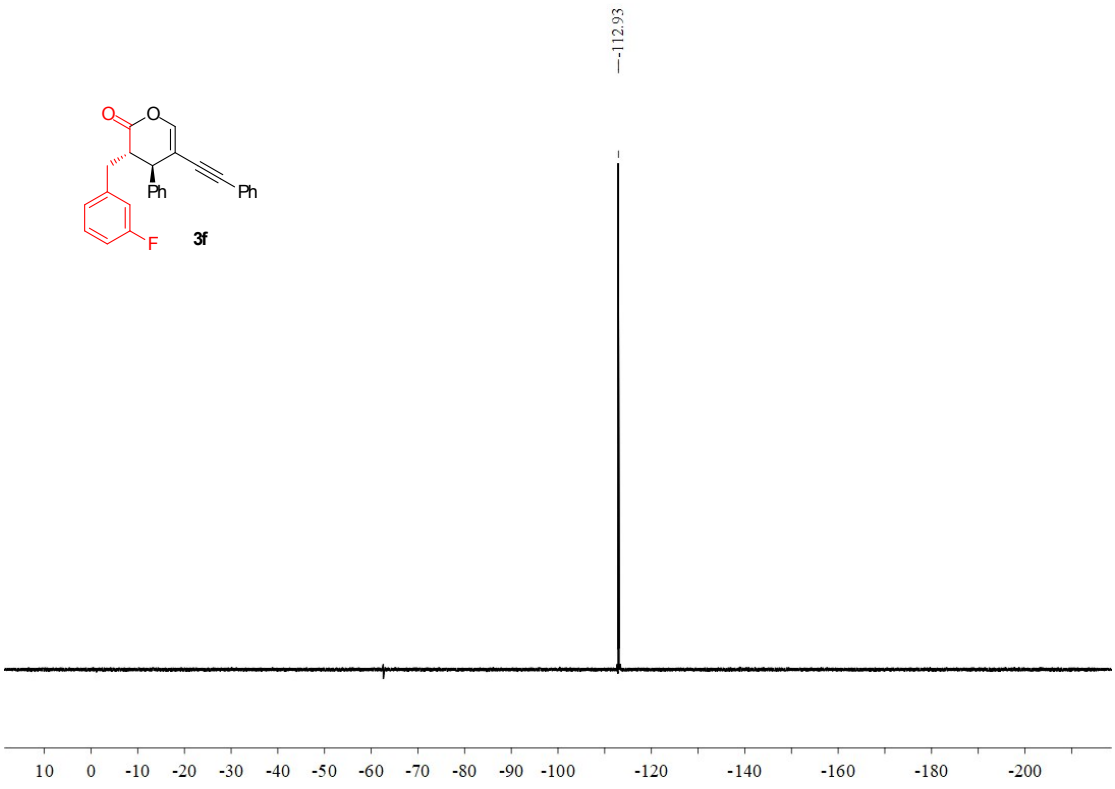
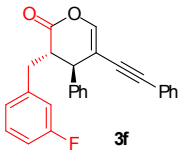
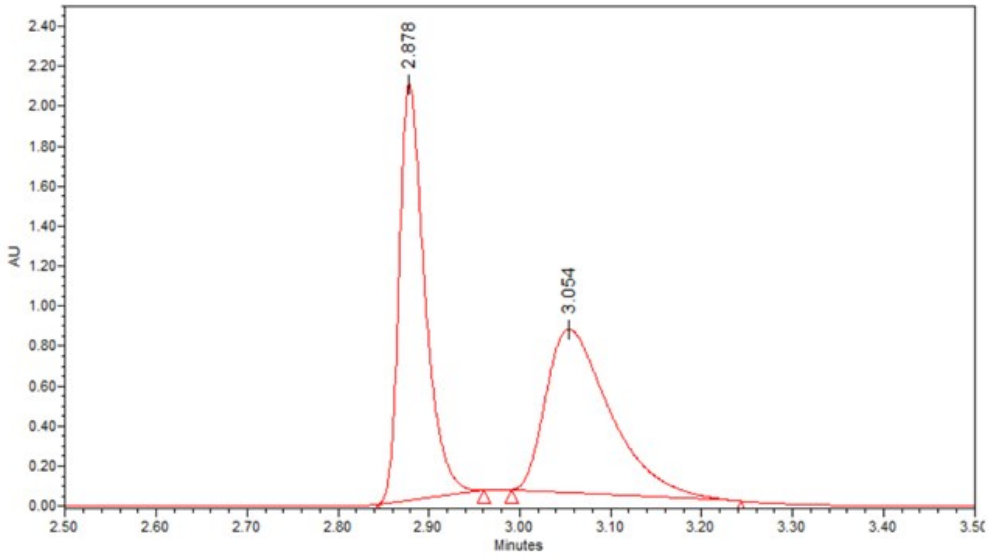

-112.93
O
O
Ph
Ph
F
3f
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

Figure S30. HPLC spectrum of **3f.**

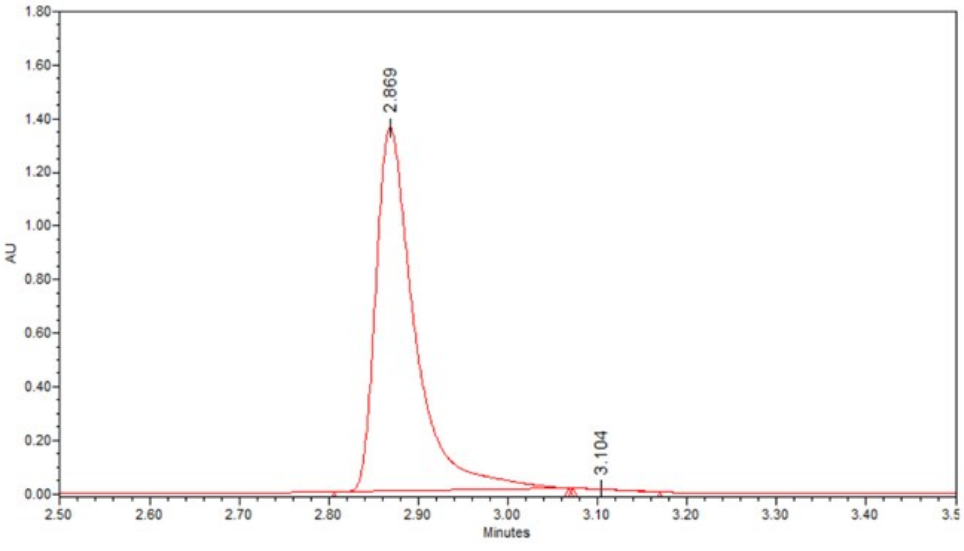


3f



Peak Results

	RT	Area	Height	% Area
1	2.878	4019209	2076606	51.29
2	3.054	3816385	808706	48.71



Peak Results

	RT	Area	Height	% Area
1	2.869	4102391	1359291	99.93
2	3.104	2783	980	0.07

Figure S31. ^{1}H and ^{13}C NMR spectrum of **3g.**

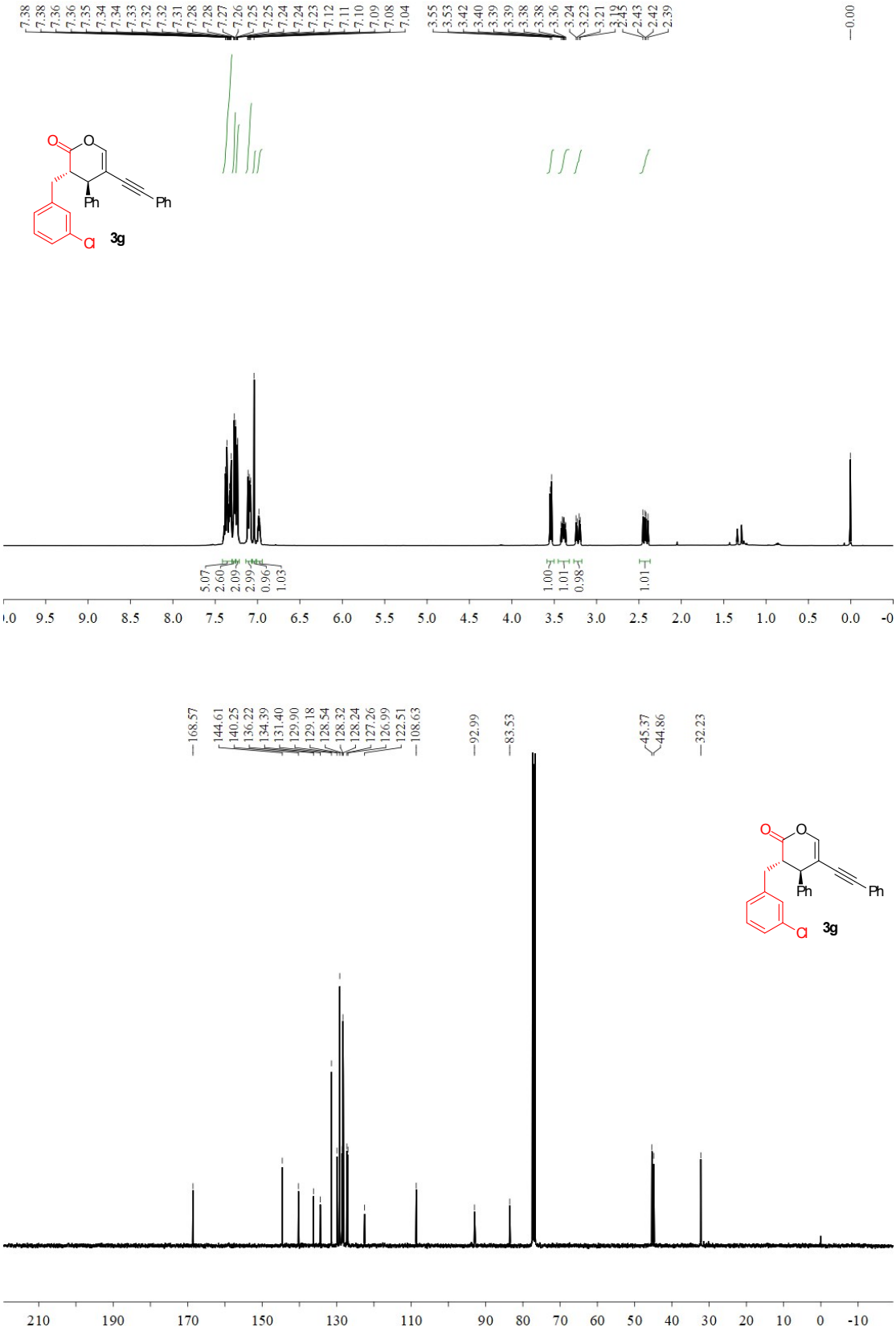
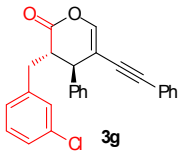
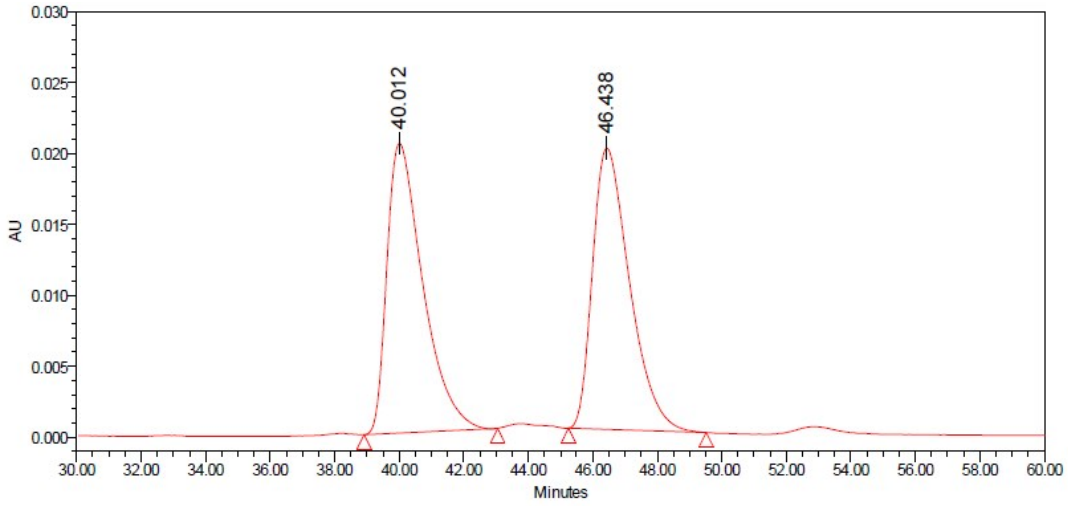


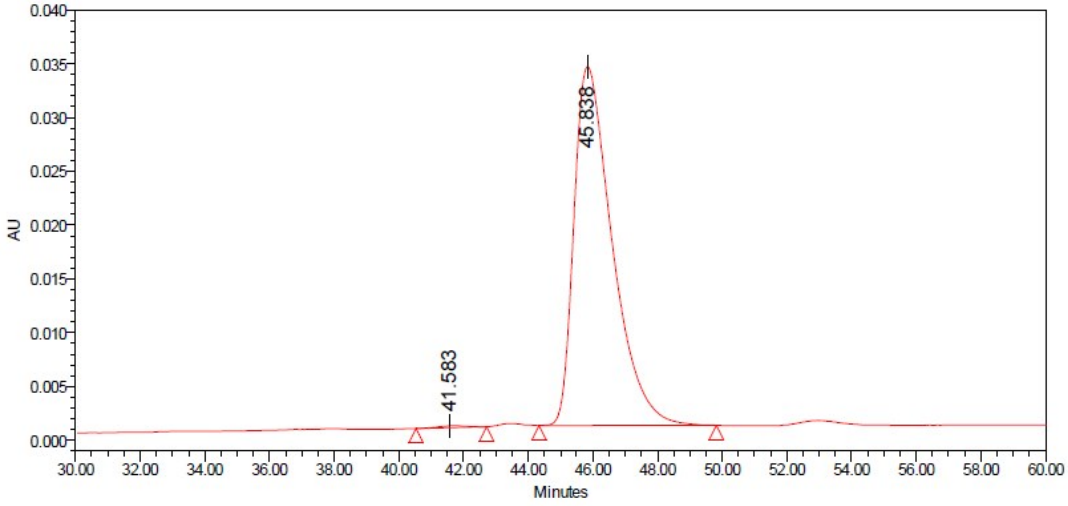
Figure S32. HPLC spectrum of **3g.**



3g



	Ret. Time	Height	Area	% Area
1	40.012	20414	1579663	49.90
2	46.438	19829	1585972	50.10



	Ret. Time	Height	Area	% Area
1	41.583	165	9916	0.36
2	45.838	33340	2733356	99.64

Figure S33. ^{1}H and ^{13}C NMR spectrum of **3h.**

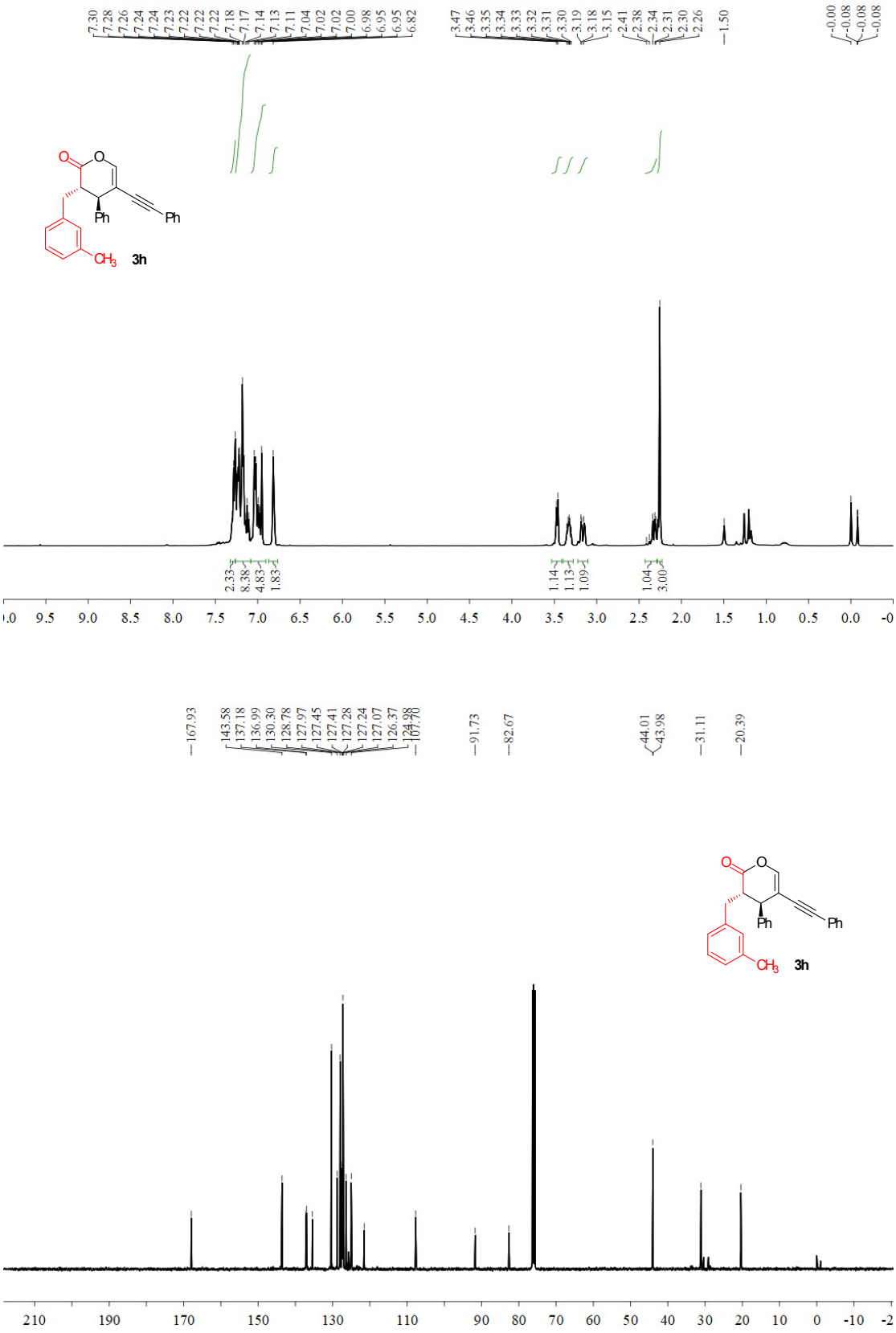
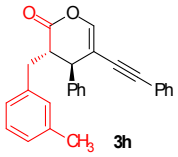
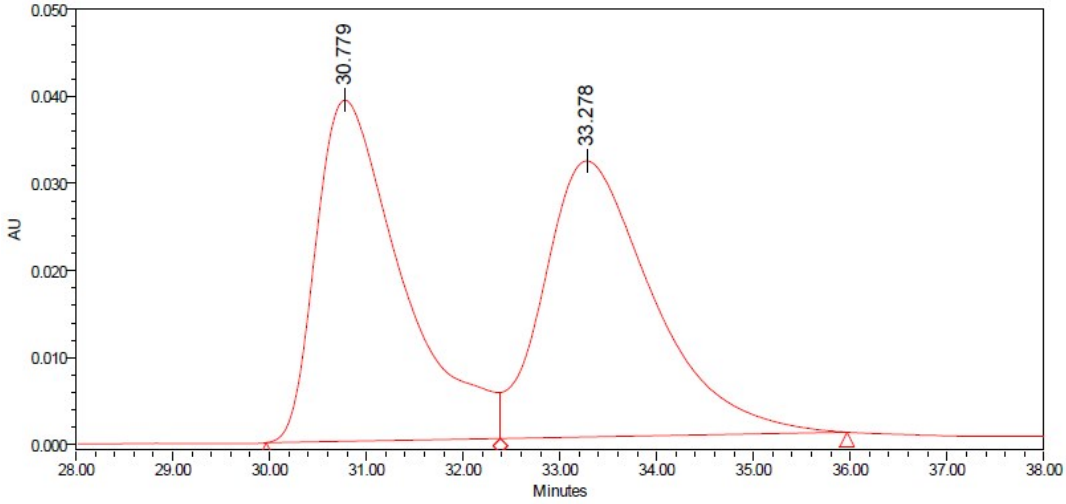


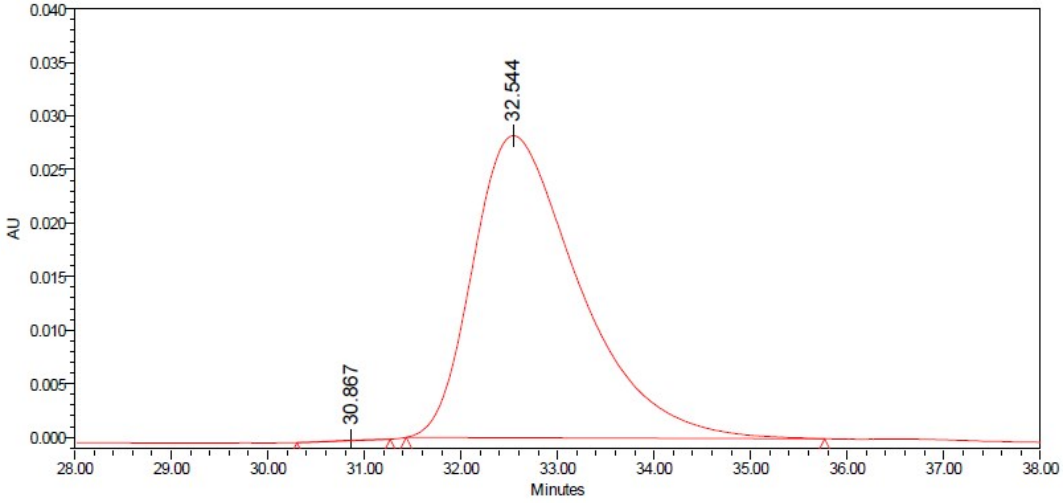
Figure S34. HPLC spectrum of **3h.**



3h

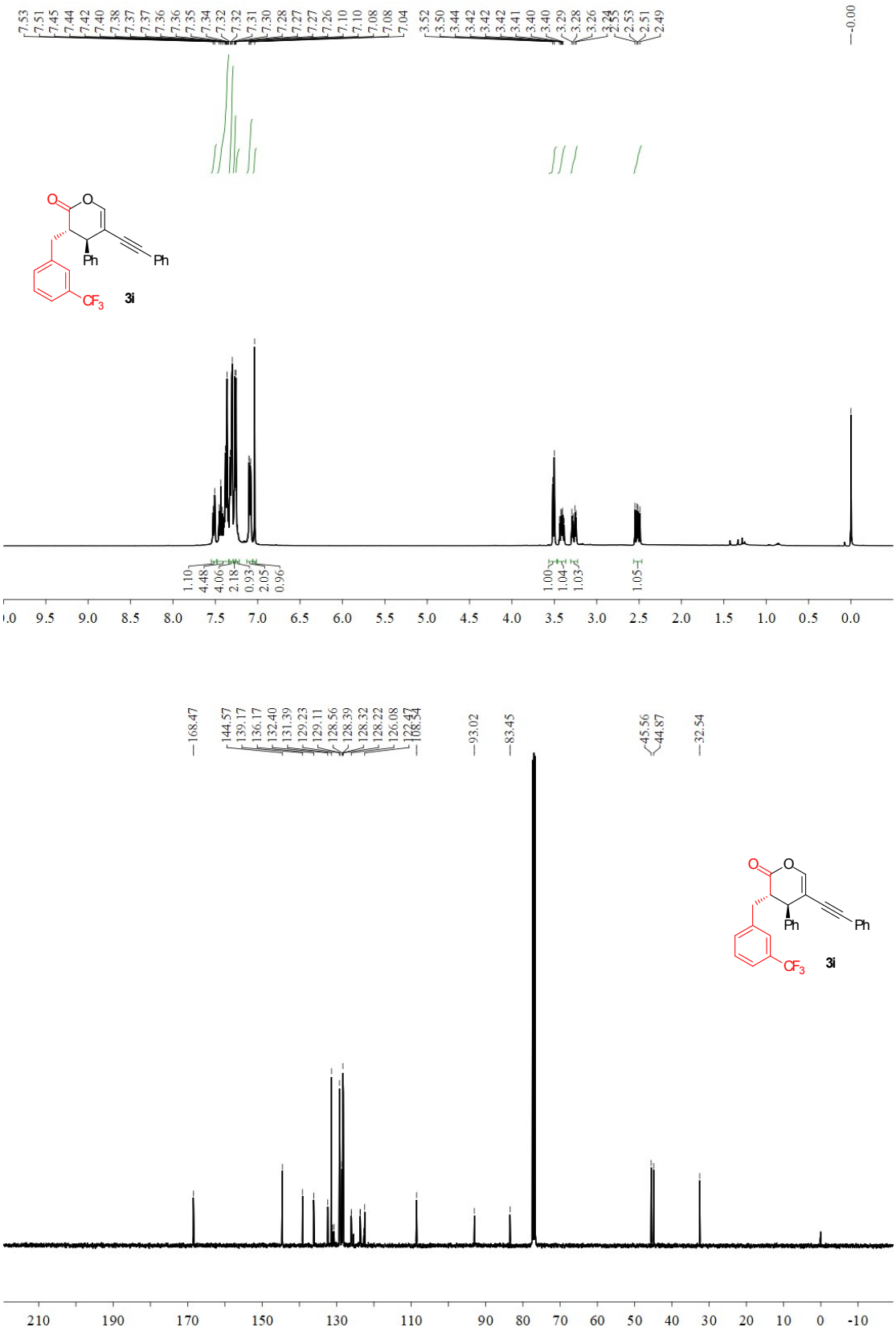


	Ret. Time	Height	Area	% Area
1	30.779	39166	2409859	49.21
2	33.278	31678	2486885	50.79



	Ret. Time	Height	Area	% Area
1	30.867	34	827	0.04
2	32.544	28197	2160009	99.96

Figure S35. ^{1}H, ^{13}C and ^{19}F NMR spectrum of **3i.**



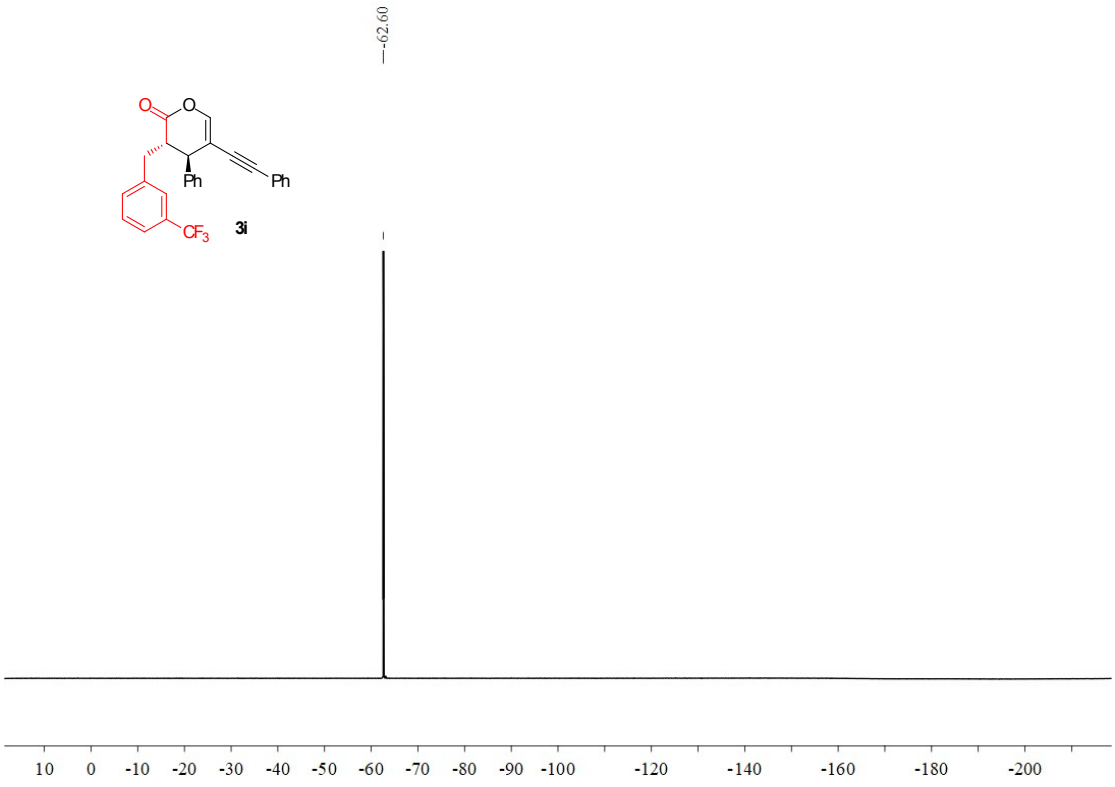
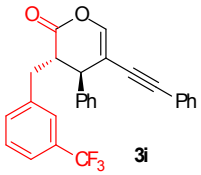
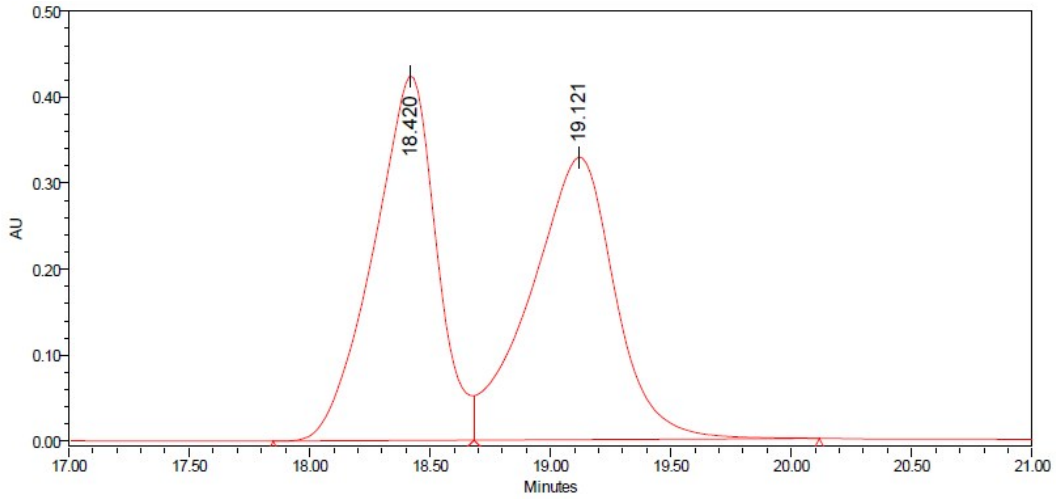

-62.60
O
O
Ph
Ph
CF3
3i
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

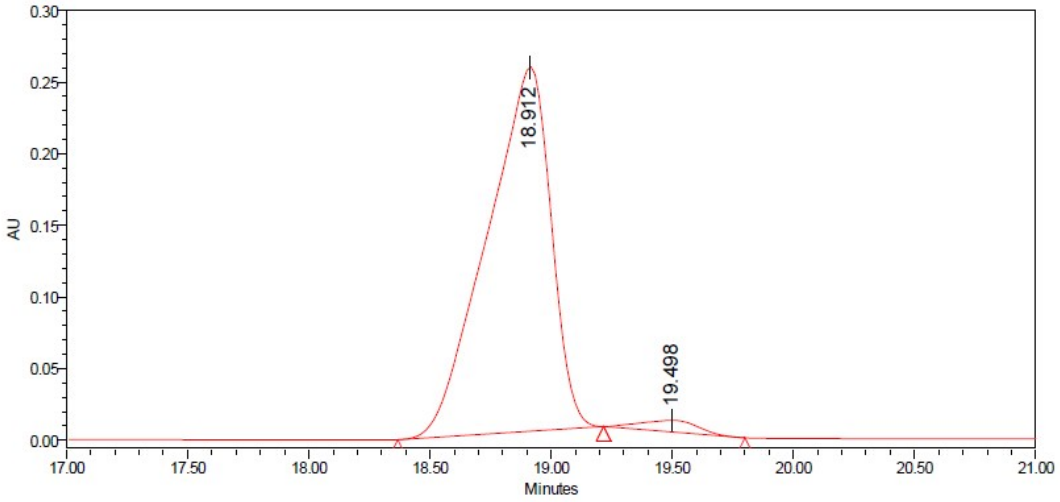
Figure S36. HPLC spectrum of **3i.**



3i



	Ret. Time	Height	Area	% Area
1	18.420	424004	7703568	49.02
2	19.121	328486	8011021	50.98



	Ret. Time	Height	Area	% Area
1	18.912	254645	4651385	97.24
2	19.498	8162	132261	2.76

Figure S37. ^{1}H and ^{13}C NMR spectrum of **3j.**

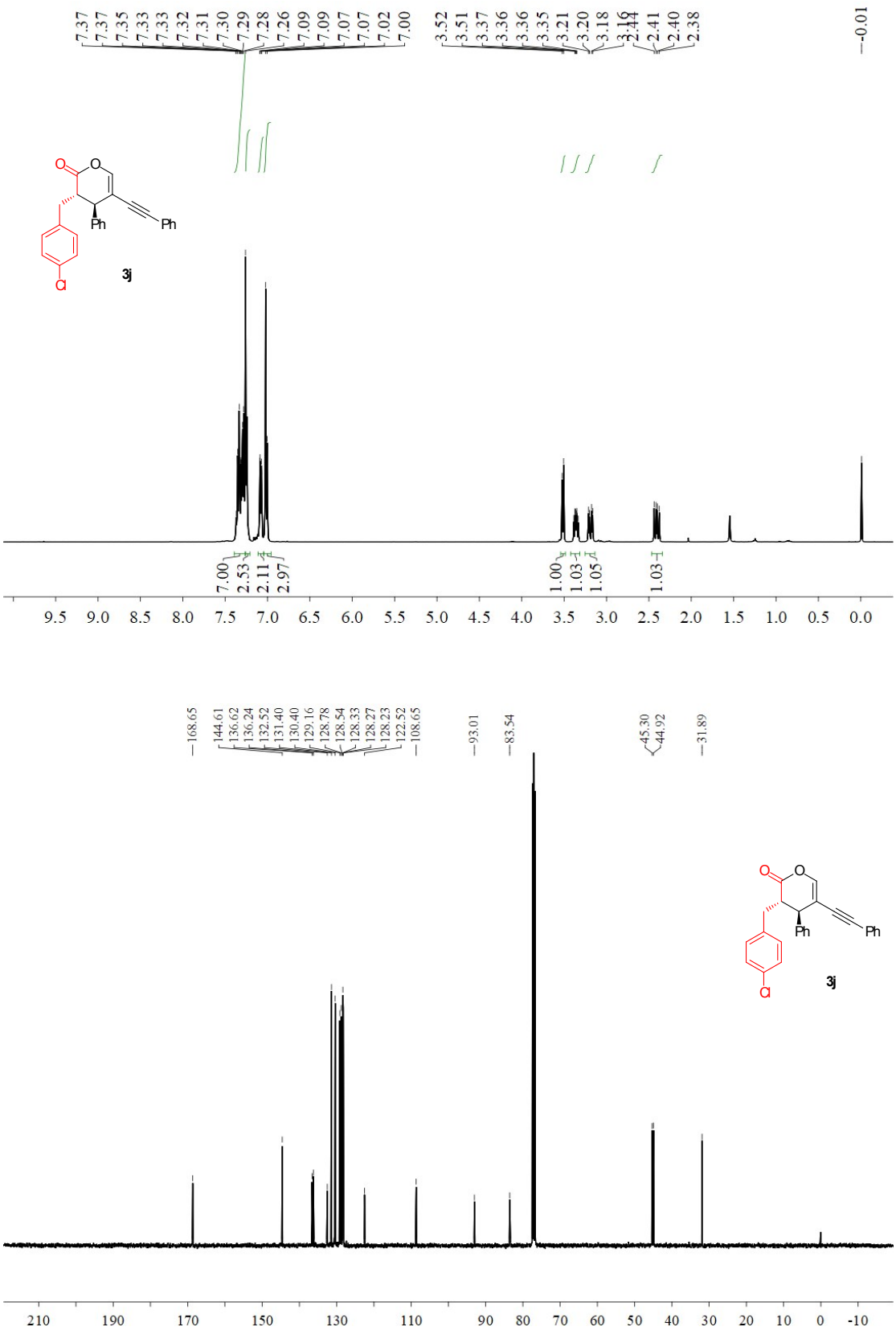
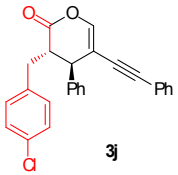
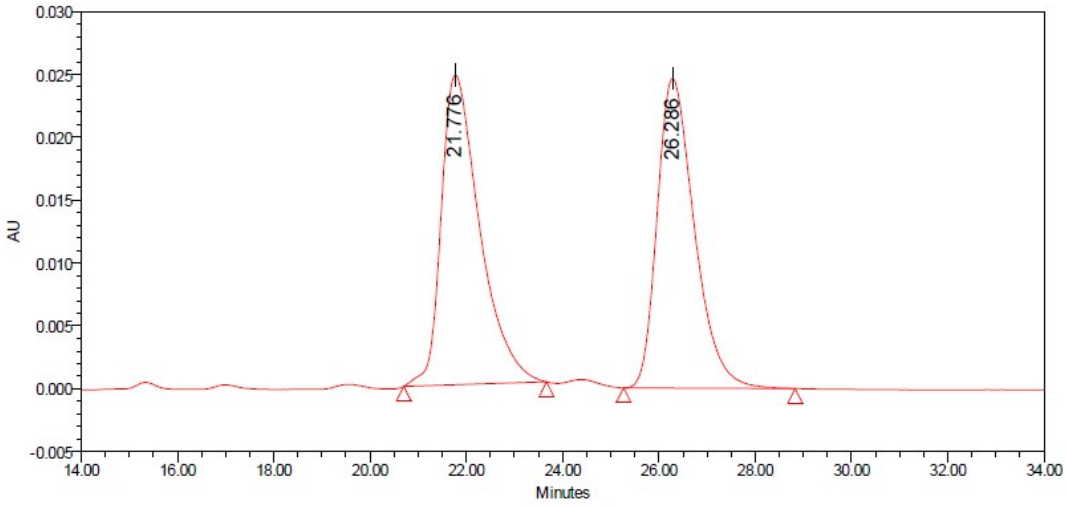


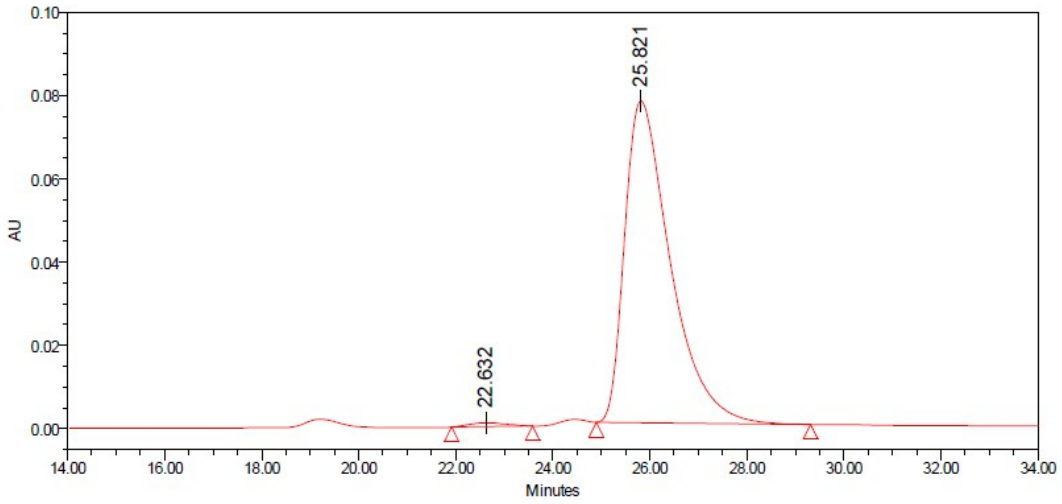
Figure S38. HPLC spectrum of **3j.**



3j



	Ret. Time	Height	Area	% Area
1	21.776	24634	1370601	50.88
2	26.286	24617	1323141	49.12



	Ret. Time	Height	Area	% Area
1	22.632	897	48602	0.95
2	25.821	77189	5052145	99.05

Figure S39. ^{1}H and ^{13}C NMR spectrum of **3k.**

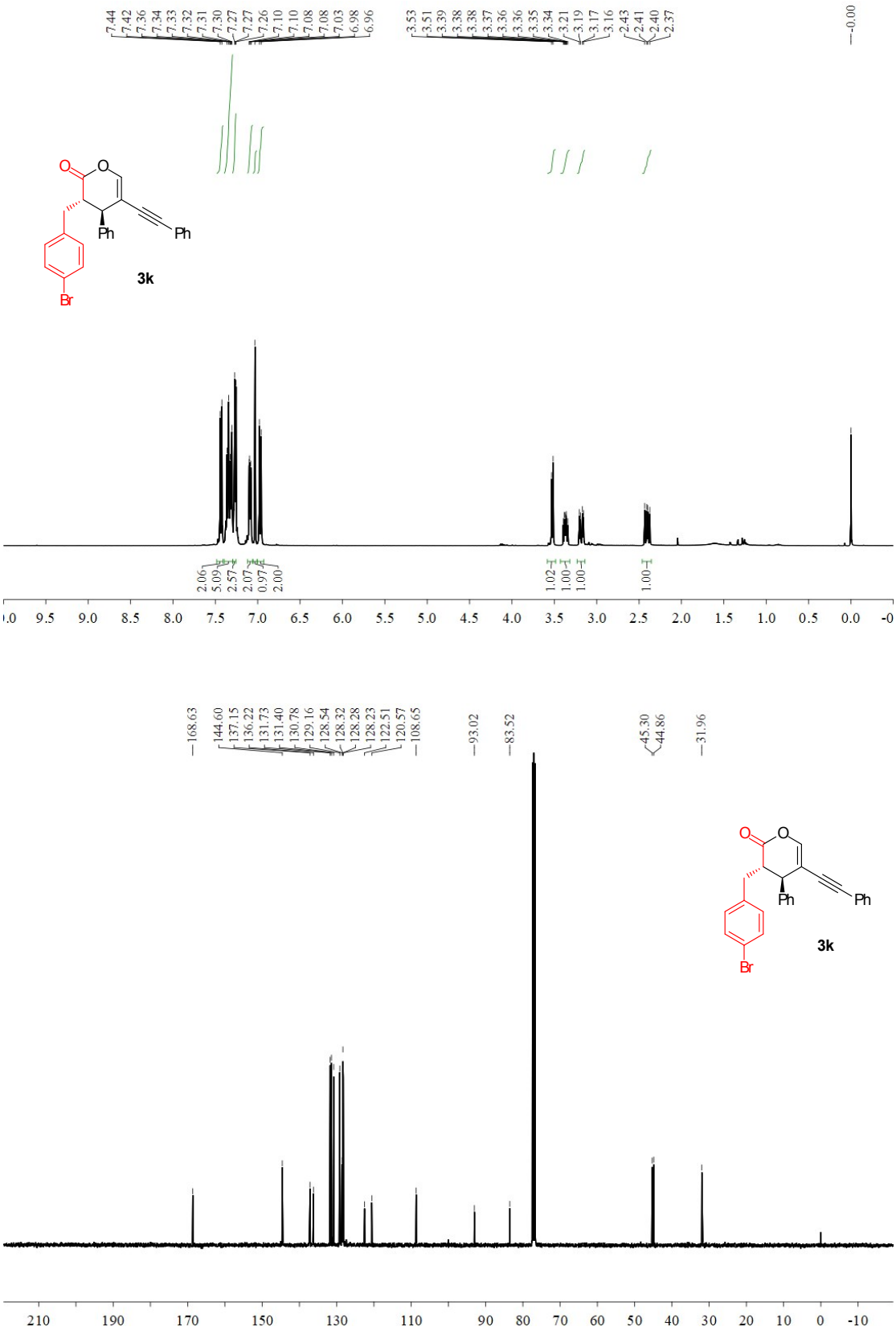
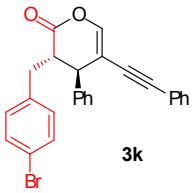
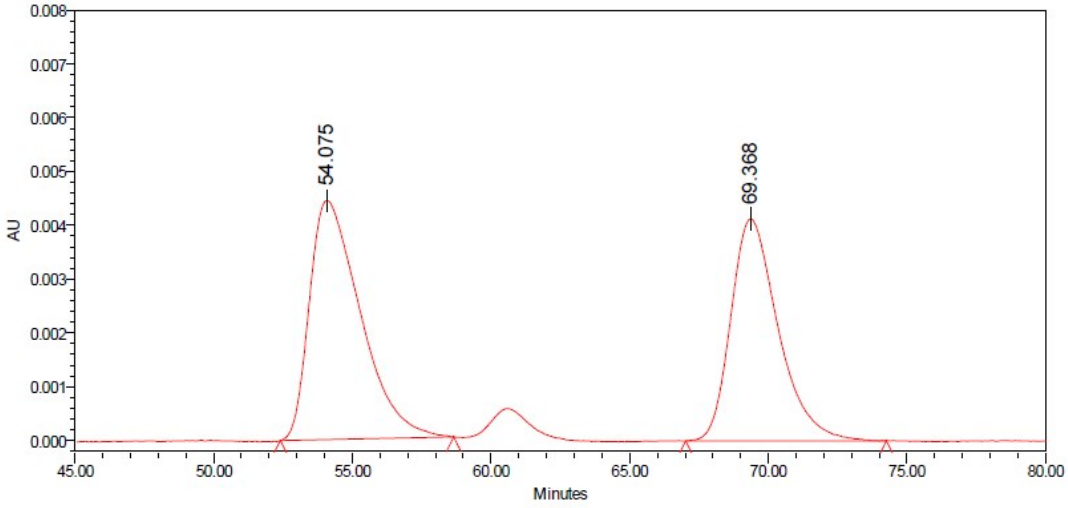


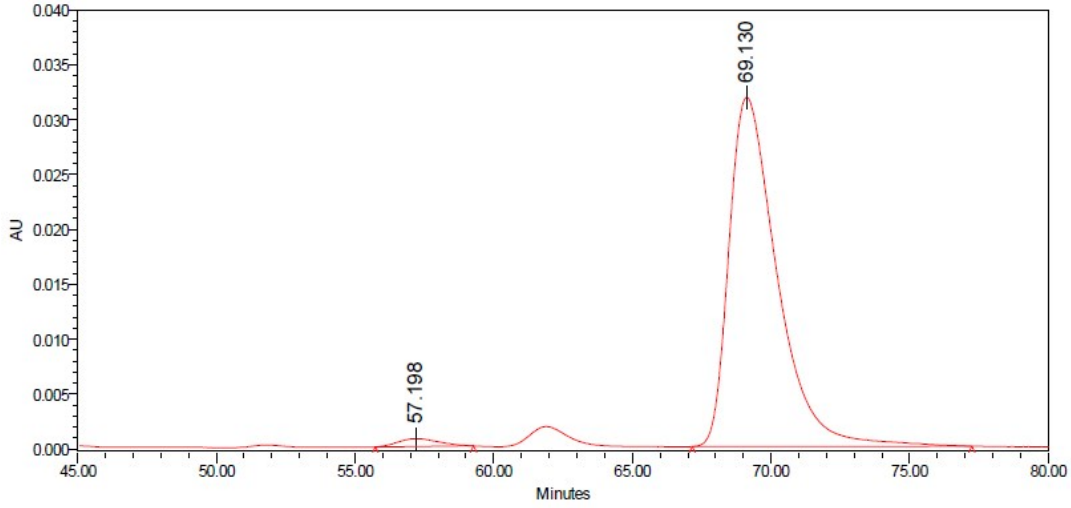
Figure S40. HPLC spectrum of **3k.**



3k



	Ret. Time	Height	Area	% Area
1	54.075	4445	567450	53.66
2	69.368	4127	490117	46.34



	Ret. Time	Height	Area	% Area
1	57.198	711	73156	1.87
2	69.130	31808	3844266	98.13

Figure S41. ^{1}H and ^{13}C NMR spectrum of **3l.**

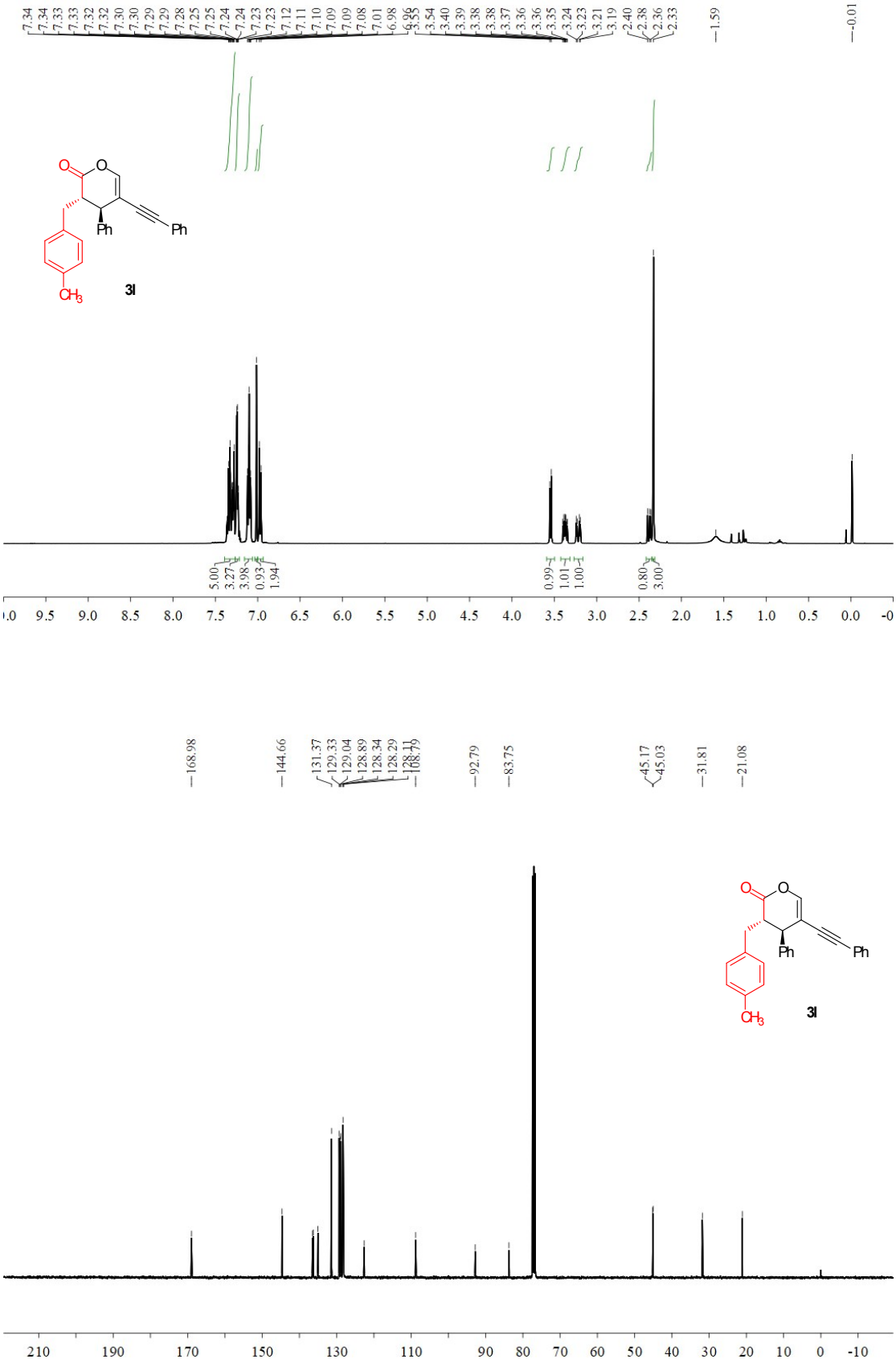
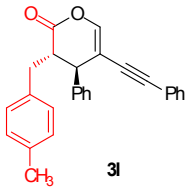
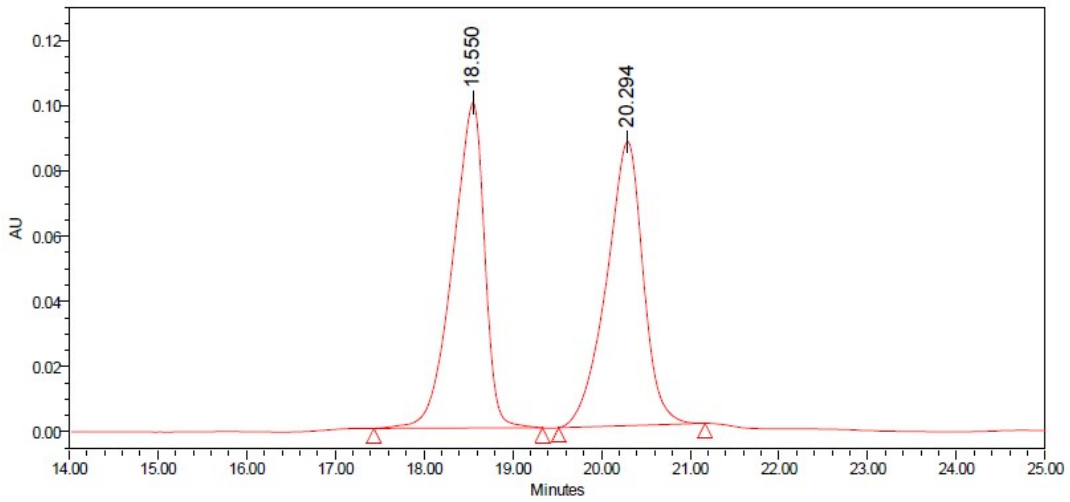


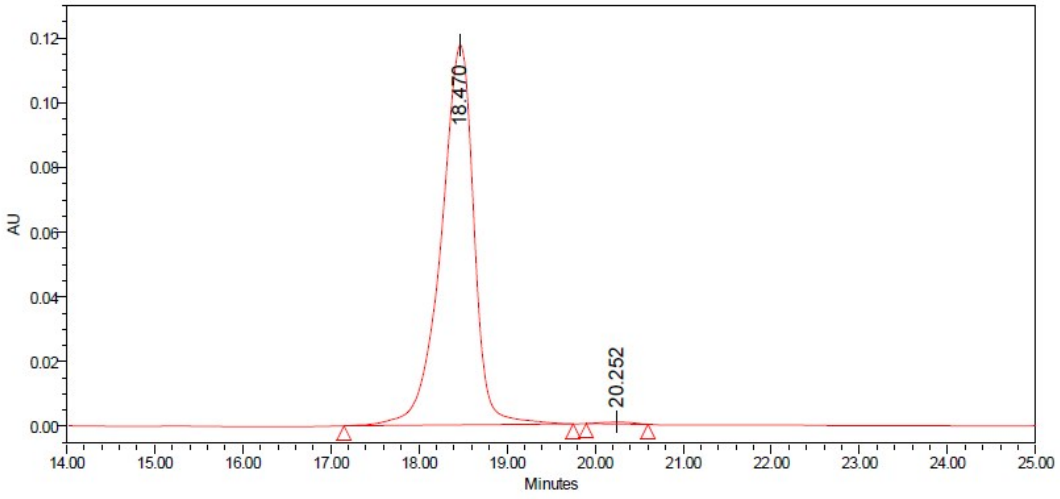
Figure S42. HPLC spectrum of **3l.**



3l



	Ret. Time	Height	Area	% Area
1	18.550	99841	2490852	49.79
2	20.294	87138	2511786	50.21



	Ret. Time	Height	Area	% Area
1	18.470	117521	3042481	99.51
2	20.252	618	14959	0.49

Figure S43. ^{1}H and ^{13}C NMR spectrum of **3m.**

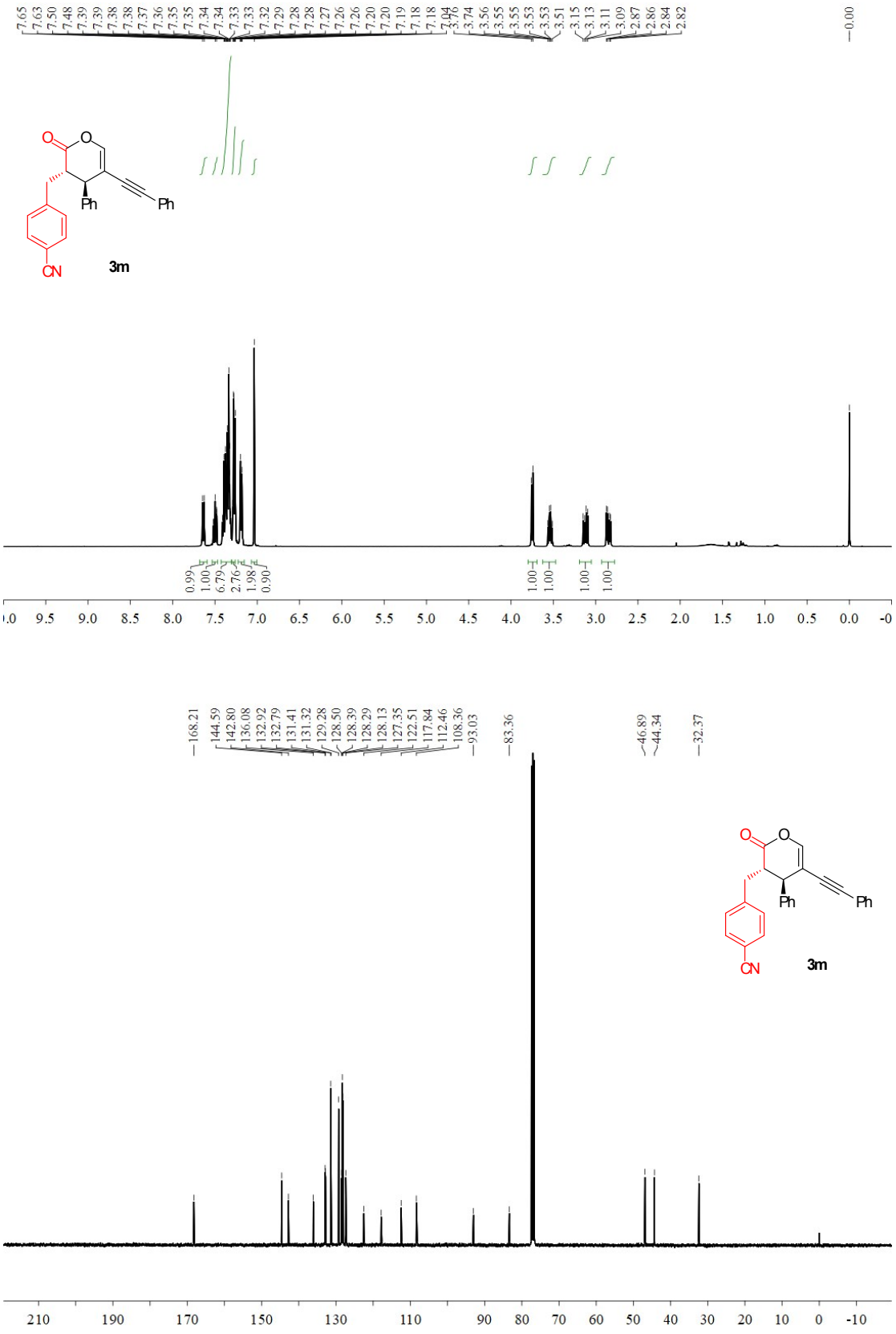
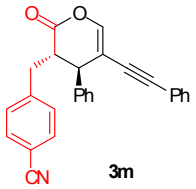
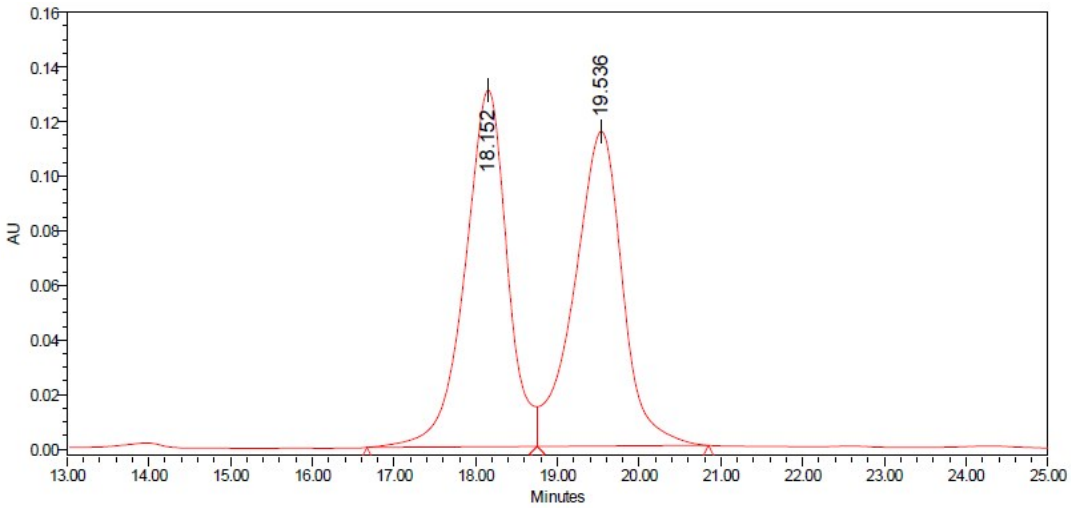


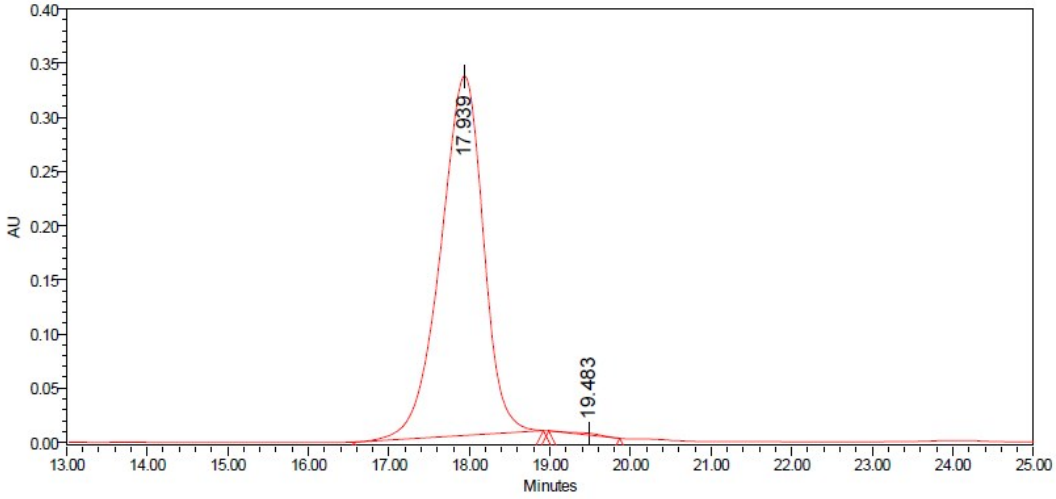
Figure S44. HPLC spectrum of **3m.**



3m

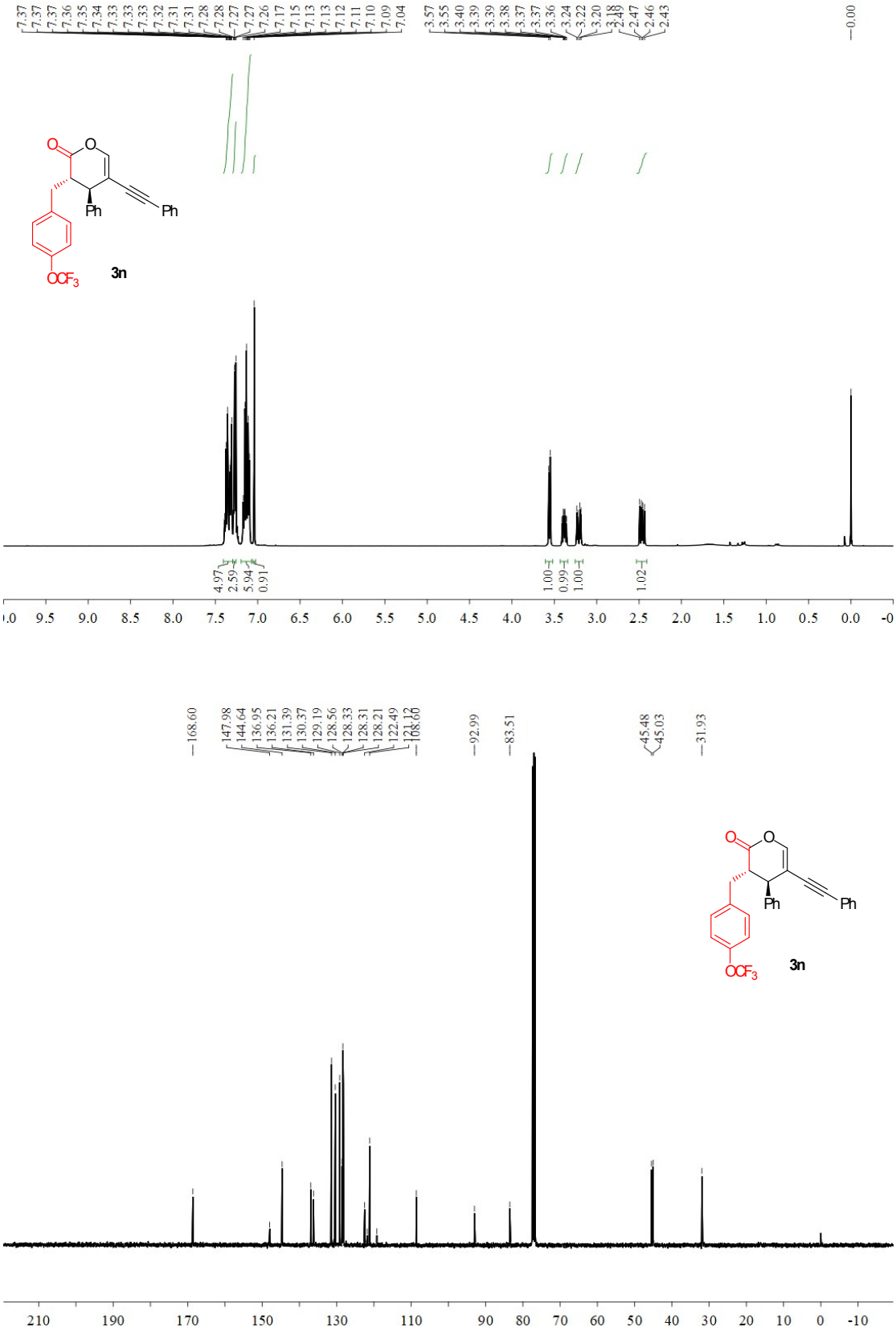


	Ret. Time	Height	Area	% Area
1	18.152	130669	4694734	49.82
2	19.536	115243	4729408	50.18



	Ret. Time	Height	Area	% Area
1	17.939	331715	12245734	99.67
2	19.483	1690	40751	0.33

Figure S45. ^{1}H, ^{13}C and ^{19}F NMR spectrum of **3n.**



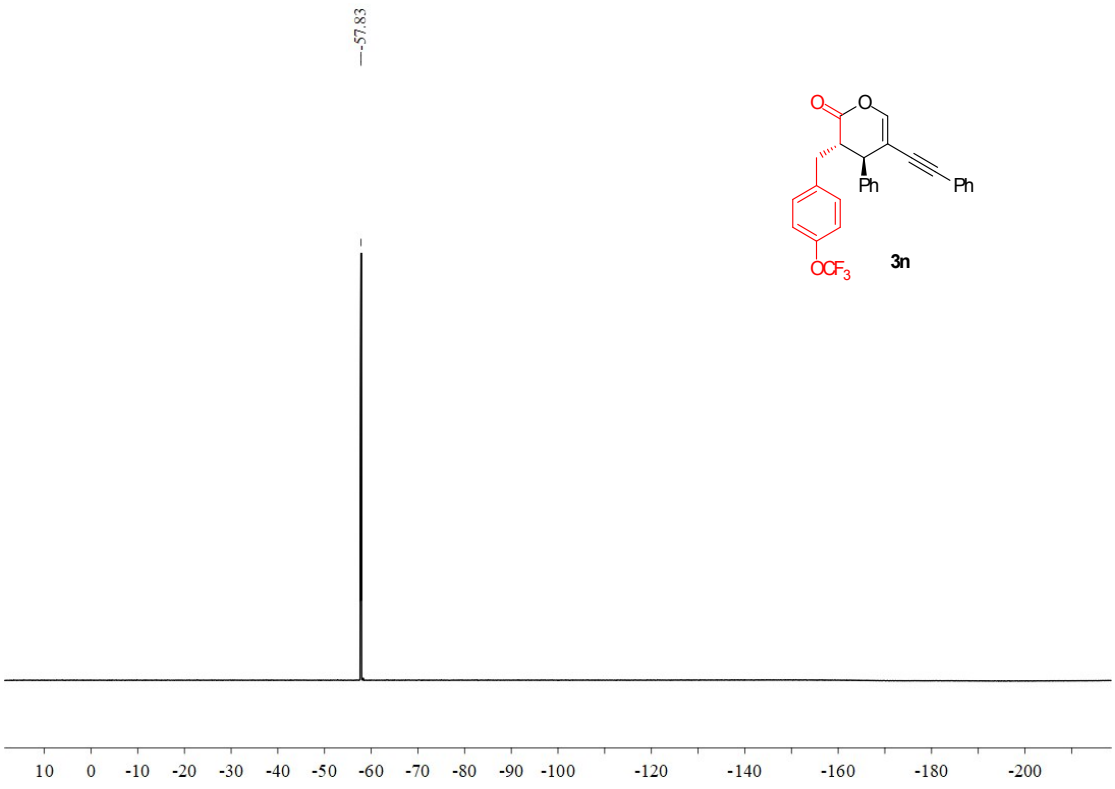
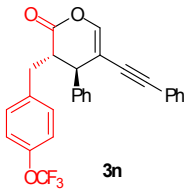
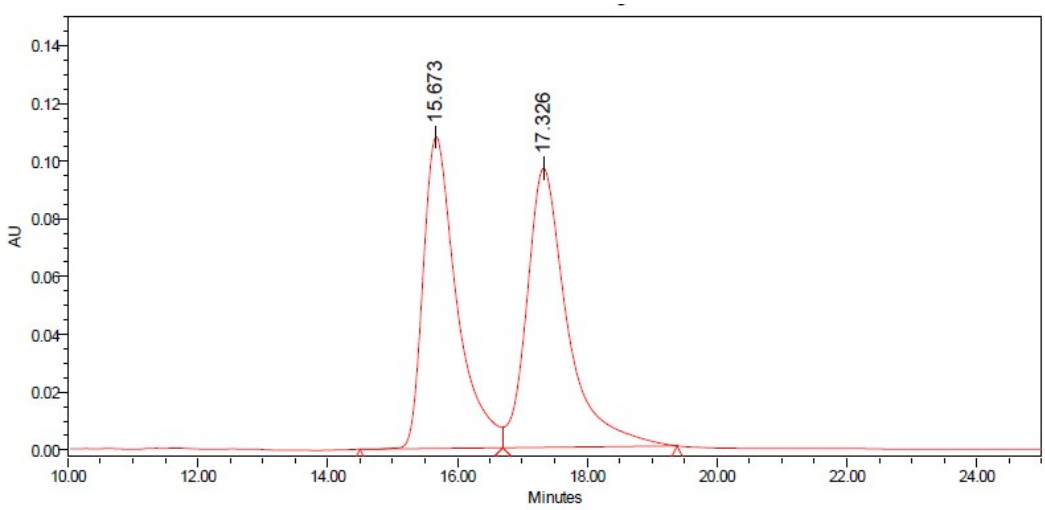

-57.83
O
O
Ph
Ph
OCF3
3n
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

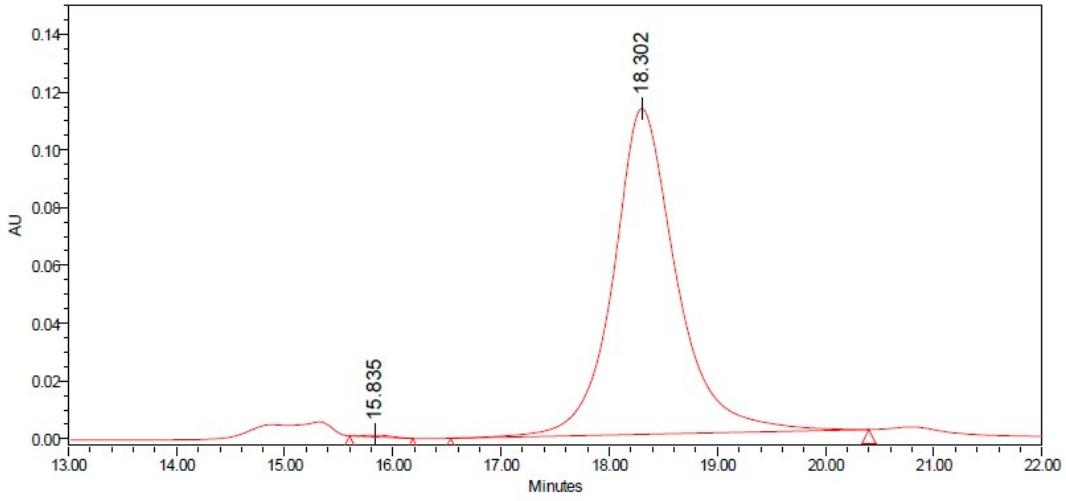
Figure S46. HPLC spectrum of **3n.**



3n



	Ret. Time	Height	Area	% Area
1	15.673	107997	3878495	48.20
2	17.326	96640	4168551	51.80



	Ret. Time	Height	Area	% Area
1	15.835	646	11120	0.24
2	18.302	112841	4596357	99.76

Figure S47. ^{1}H and ^{13}C NMR spectrum of **3o.**

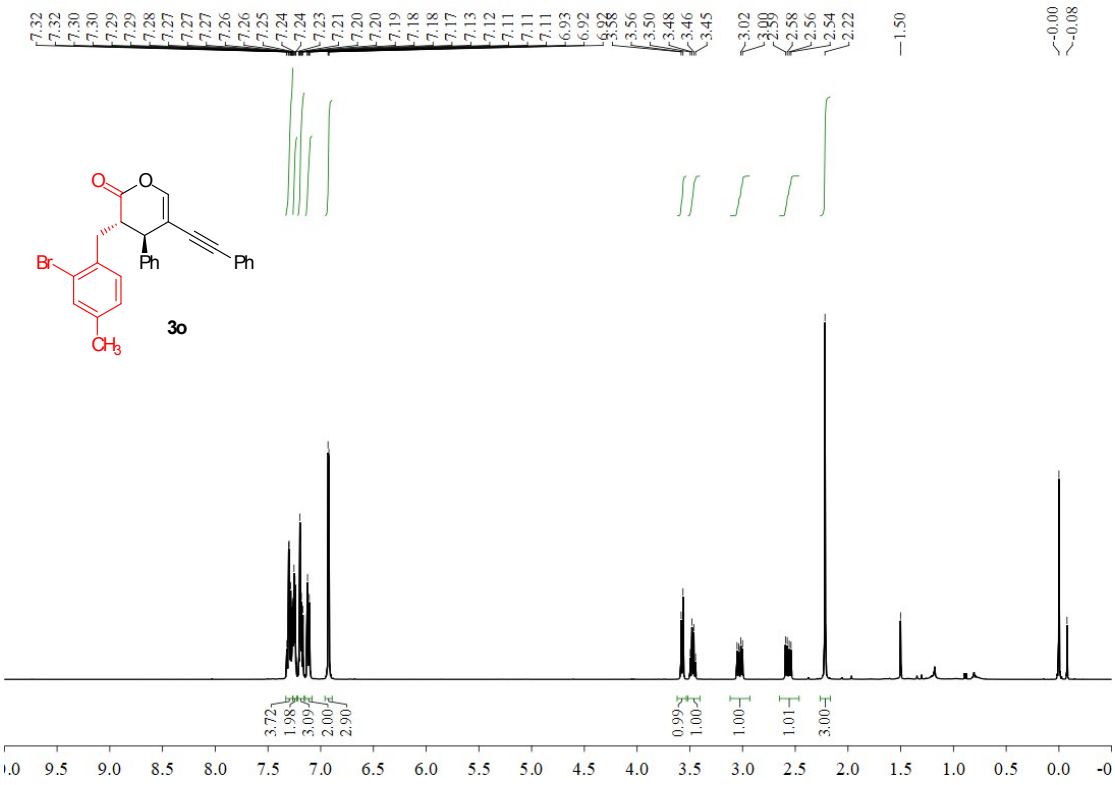


Figure S32. ^{1}H NMR spectrum of 3o.

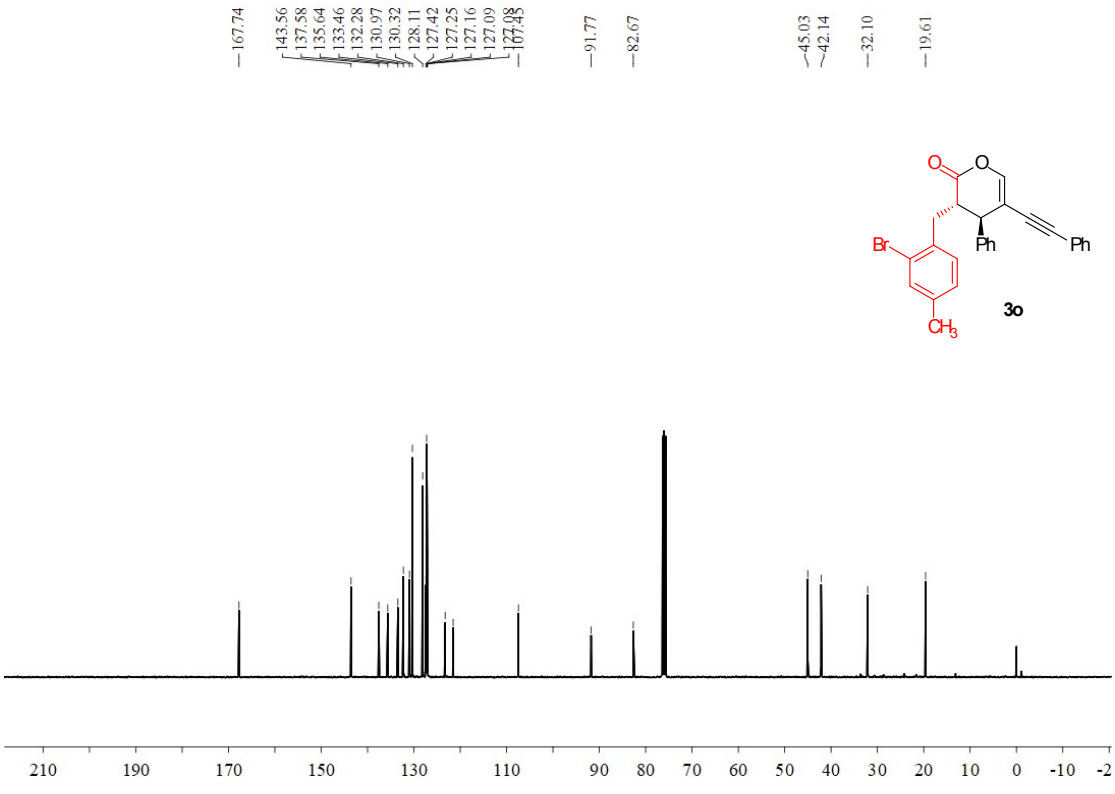
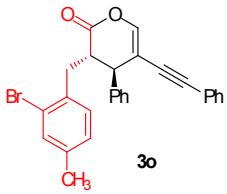
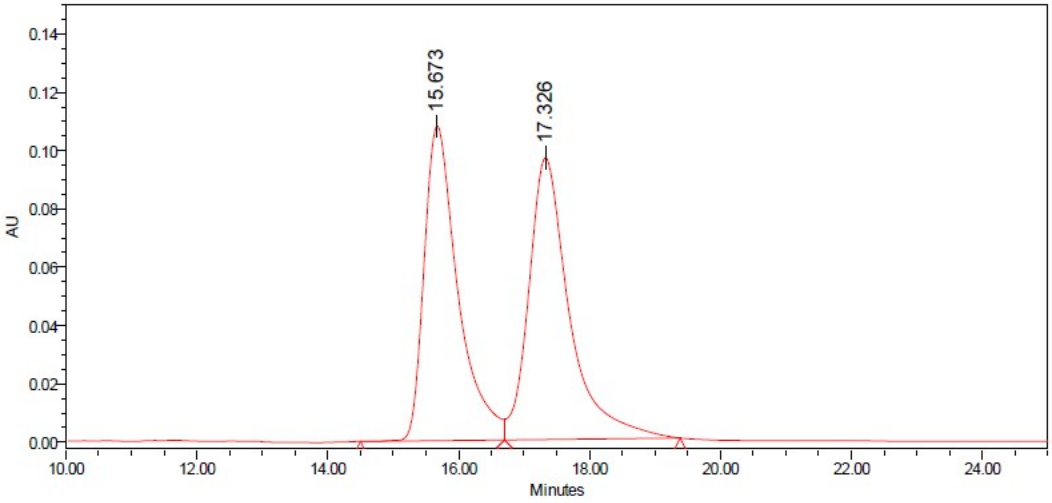


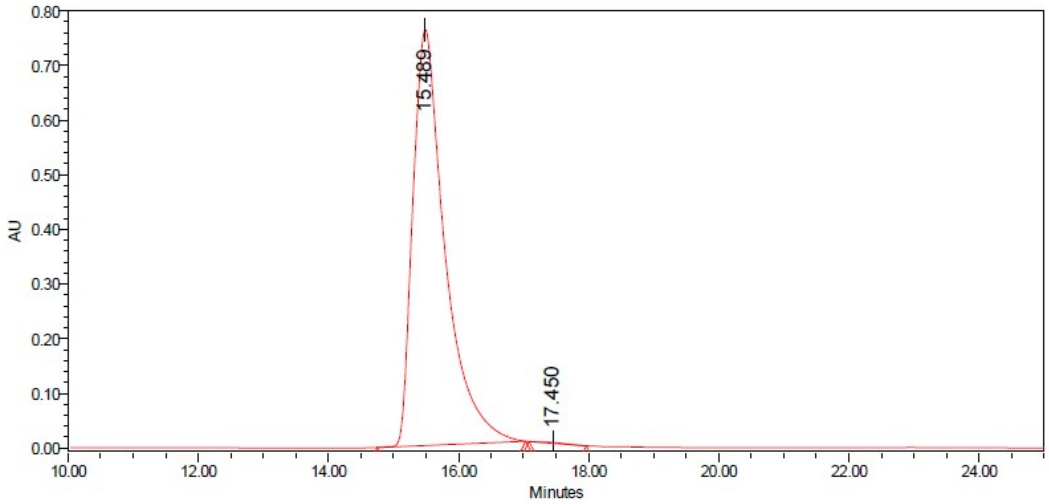
Figure S48. HPLC spectrum of **3o.**



3o



	Ret. Time	Height	Area	% Area
1	15.673	107997	3878495	48.20
2	17.326	96640	4168551	51.80



	Ret. Time	Height	Area	% Area
1	15.489	761697	26027907	99.87
2	17.450	1490	33590	0.13

Figure S49. ^{1}H and ^{13}C NMR spectrum of **3p.**

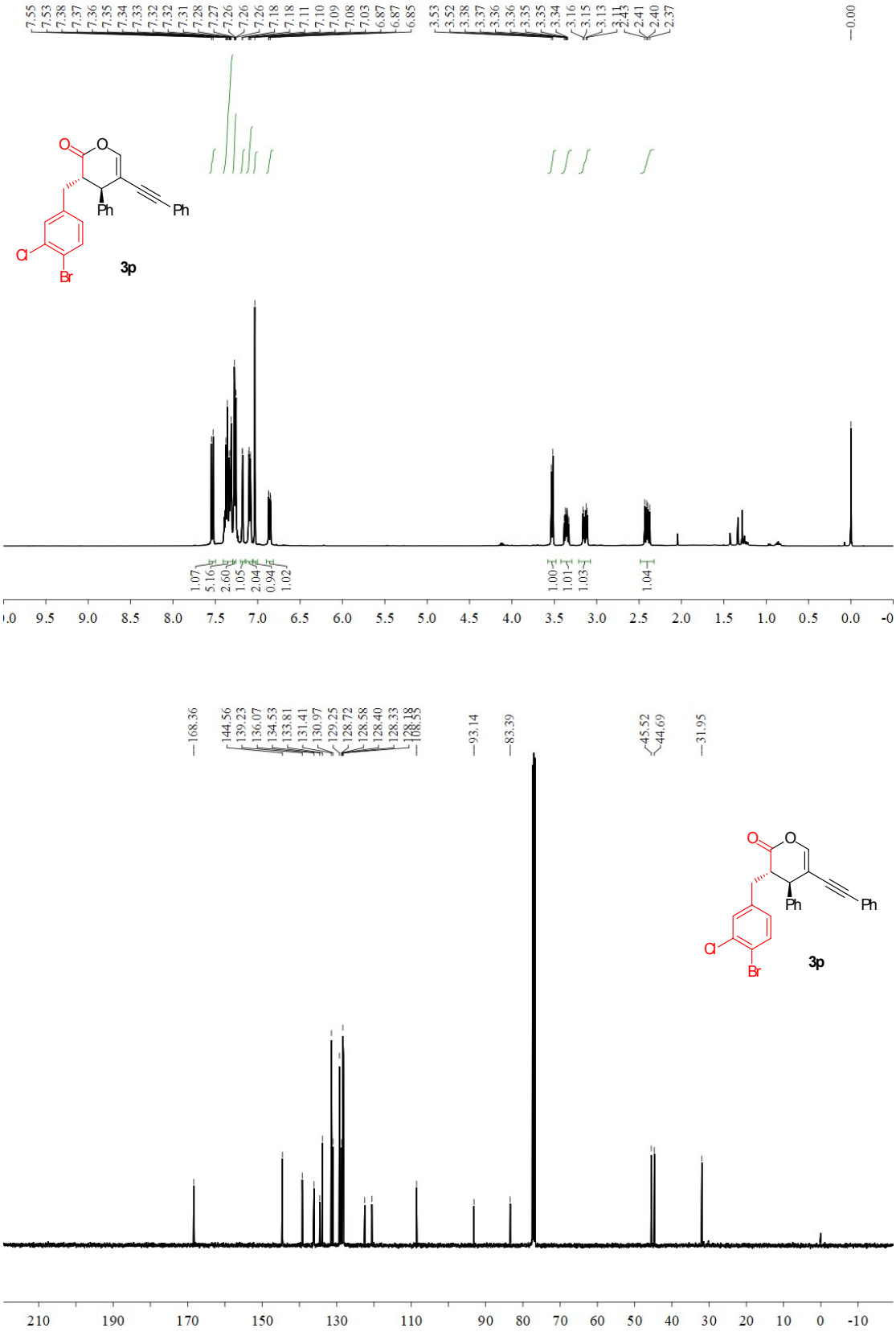
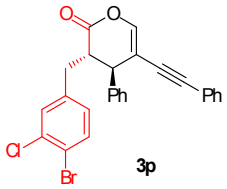
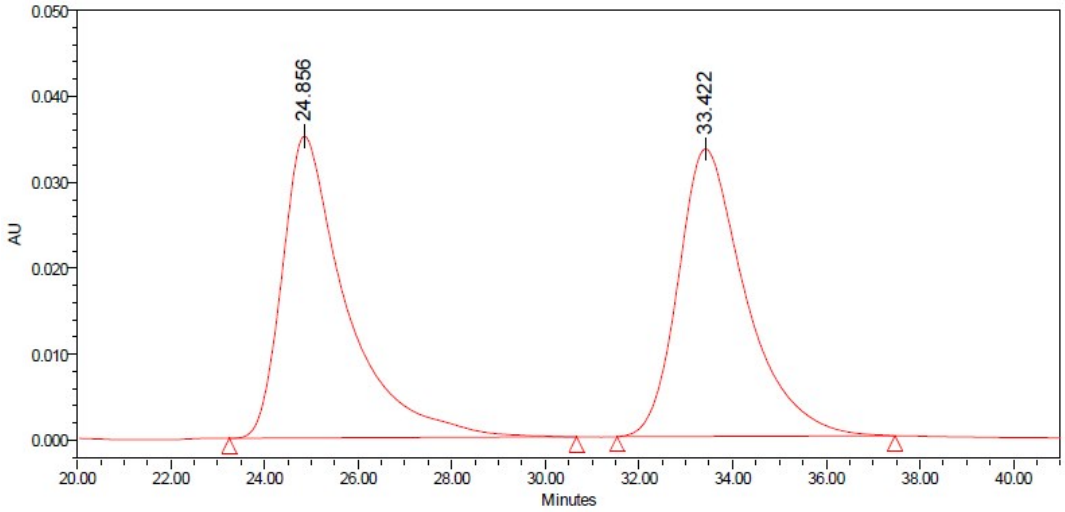


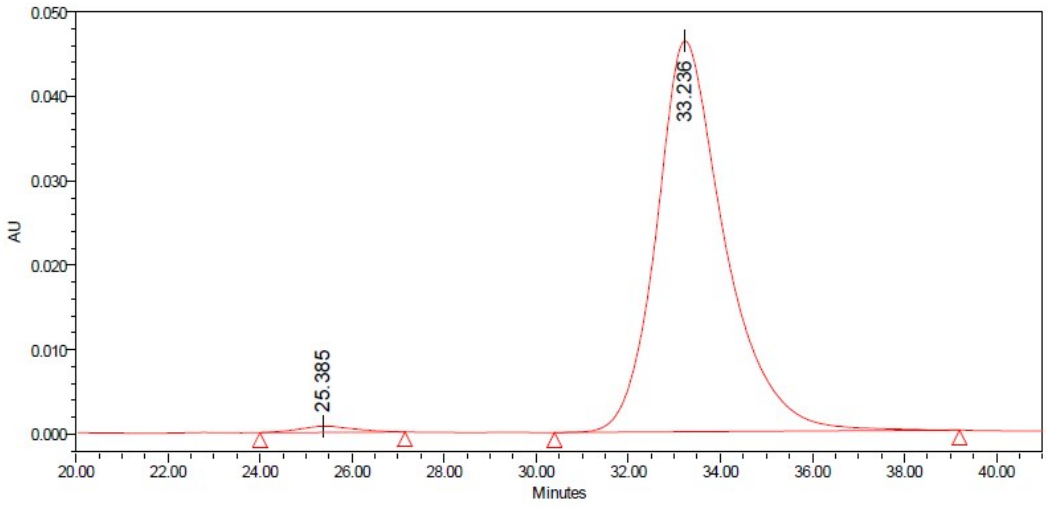
Figure S50. HPLC spectrum of **3p.**



3p



	Ret. Time	Height	Area	% Area
1	24.856	35109	3341382	49.96
2	33.422	33421	3346269	50.04



	Ret. Time	Height	Area	% Area
1	25.385	723	60362	1.25
2	33.236	46263	4785051	98.75

Figure S51. ^{1}H and ^{13}C NMR spectrum of **3q.**

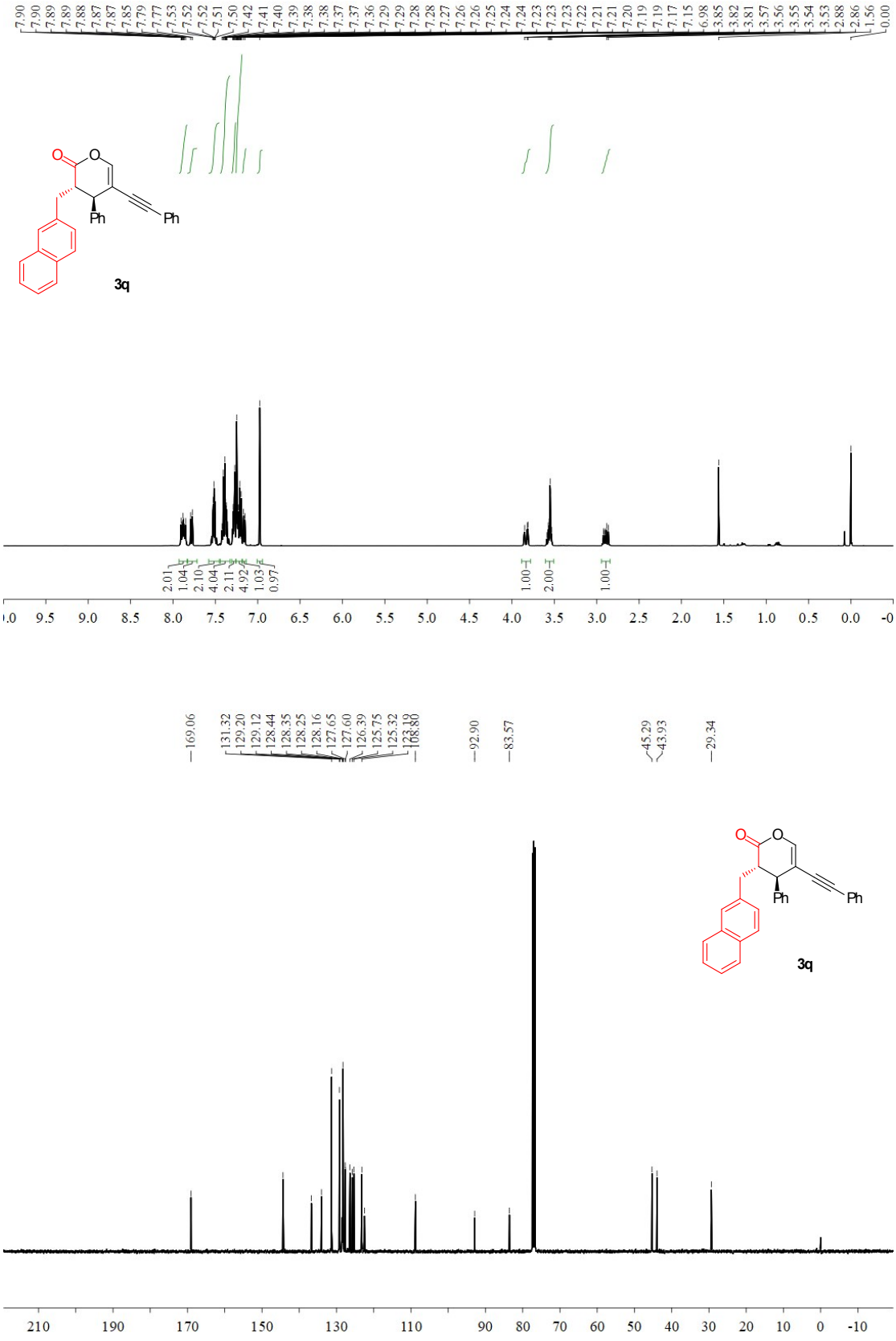
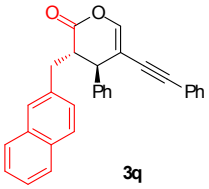
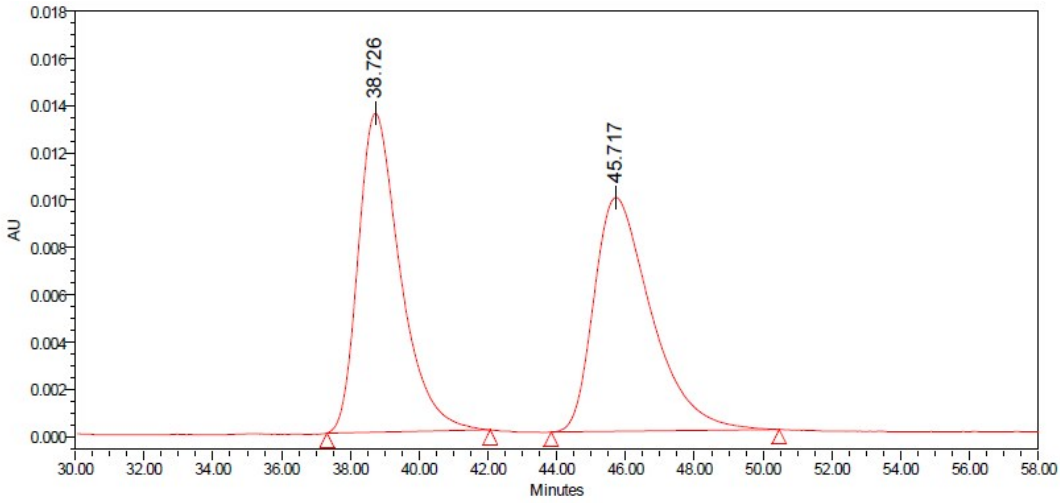


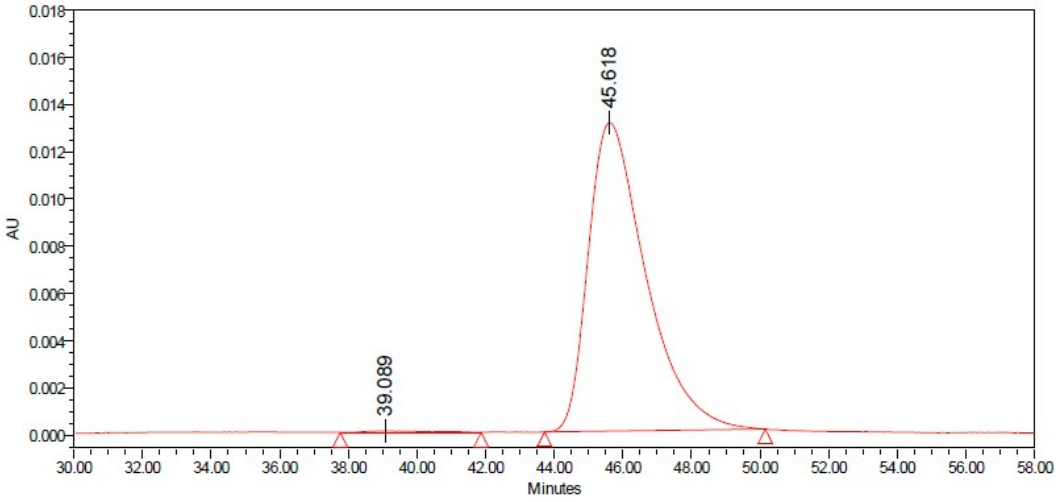
Figure S52. HPLC spectrum of **3q.**



3q



	Ret. Time	Height	Area	% Area
1	38.726	13485	1147376	50.00
2	45.717	9889	1147191	50.00



	Ret. Time	Height	Area	% Area
1	39.089	61	7122	0.46
2	45.618	13063	1524446	99.54

Figure S53.[1]H and [13]C NMR spectrum of **3r.**

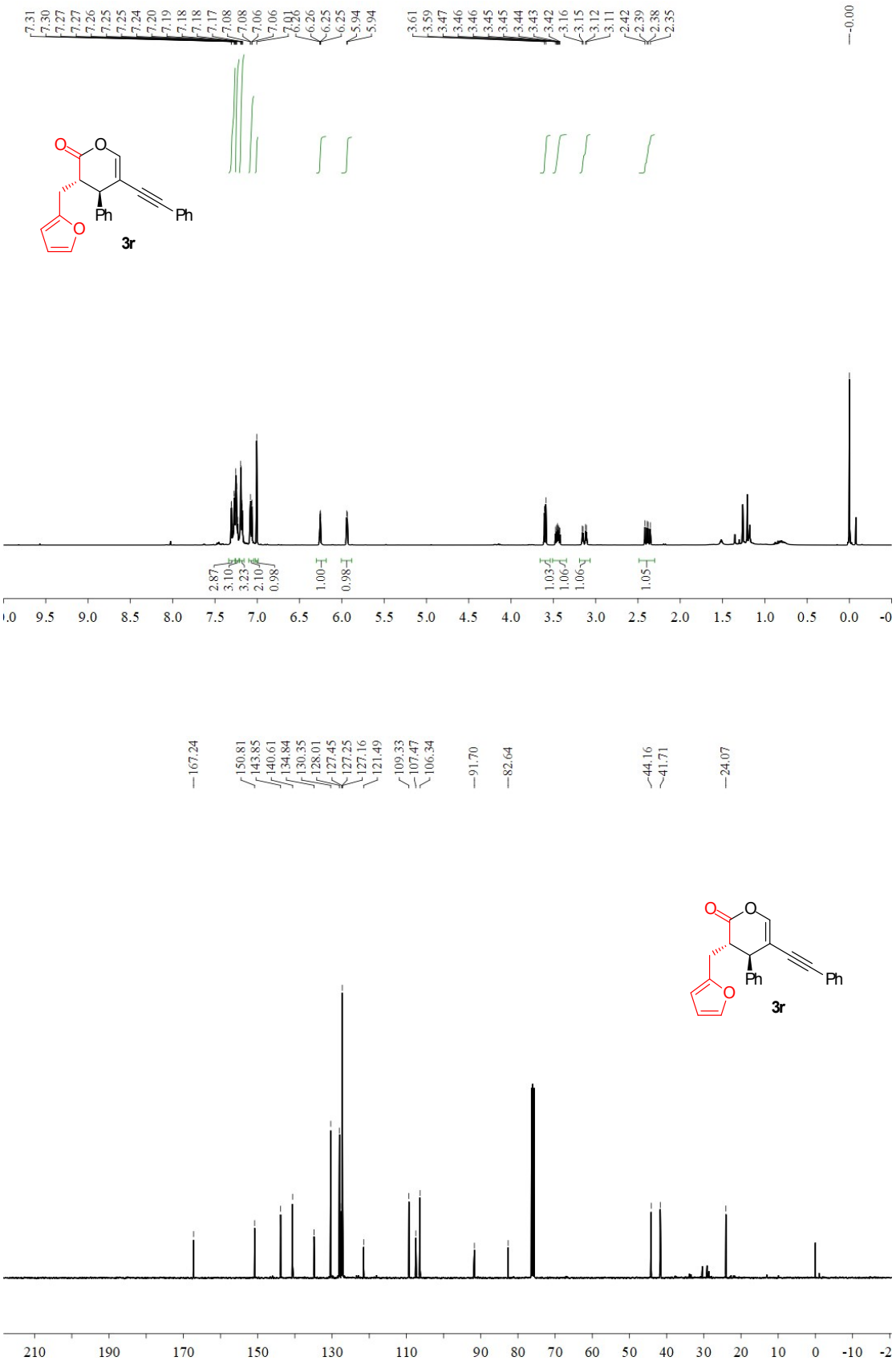
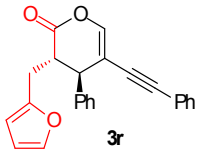
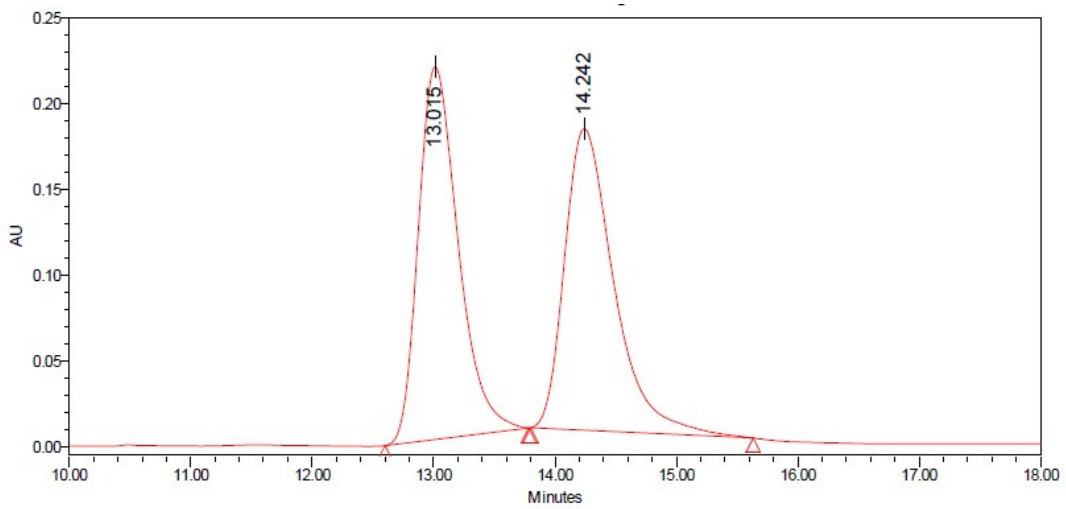


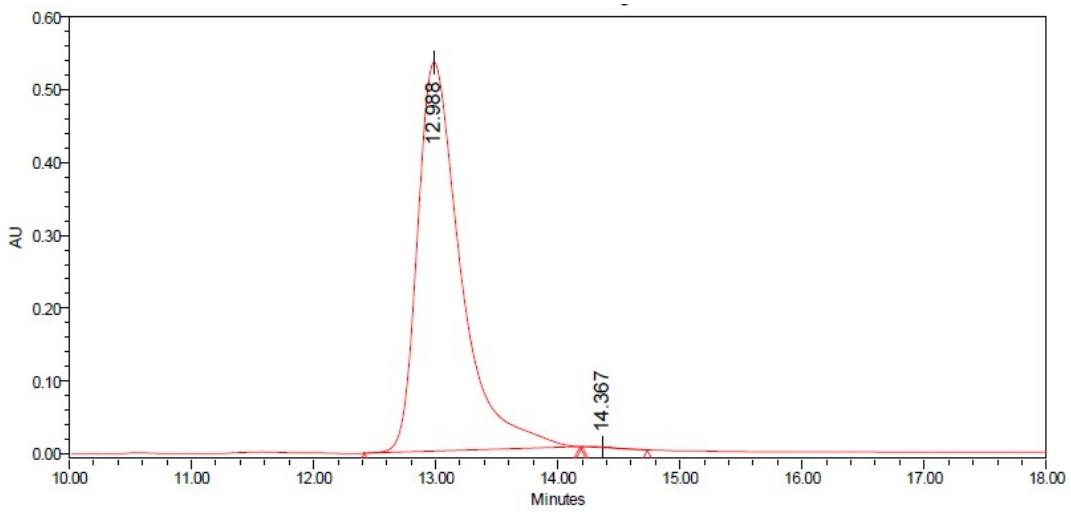
Figure S54. HPLC spectrum of **3r.**



3r



	Ret. Time	Height	Area	% Area
1	13.015	217383	4945299	49.92
2	14.242	175750	4960451	50.08



	Ret. Time	Height	Area	% Area
1	12.988	534586	13106577	99.89
2	14.367	948	13838	0.11

Figure S55. ^{1}H and ^{13}C NMR spectrum of **3s.**

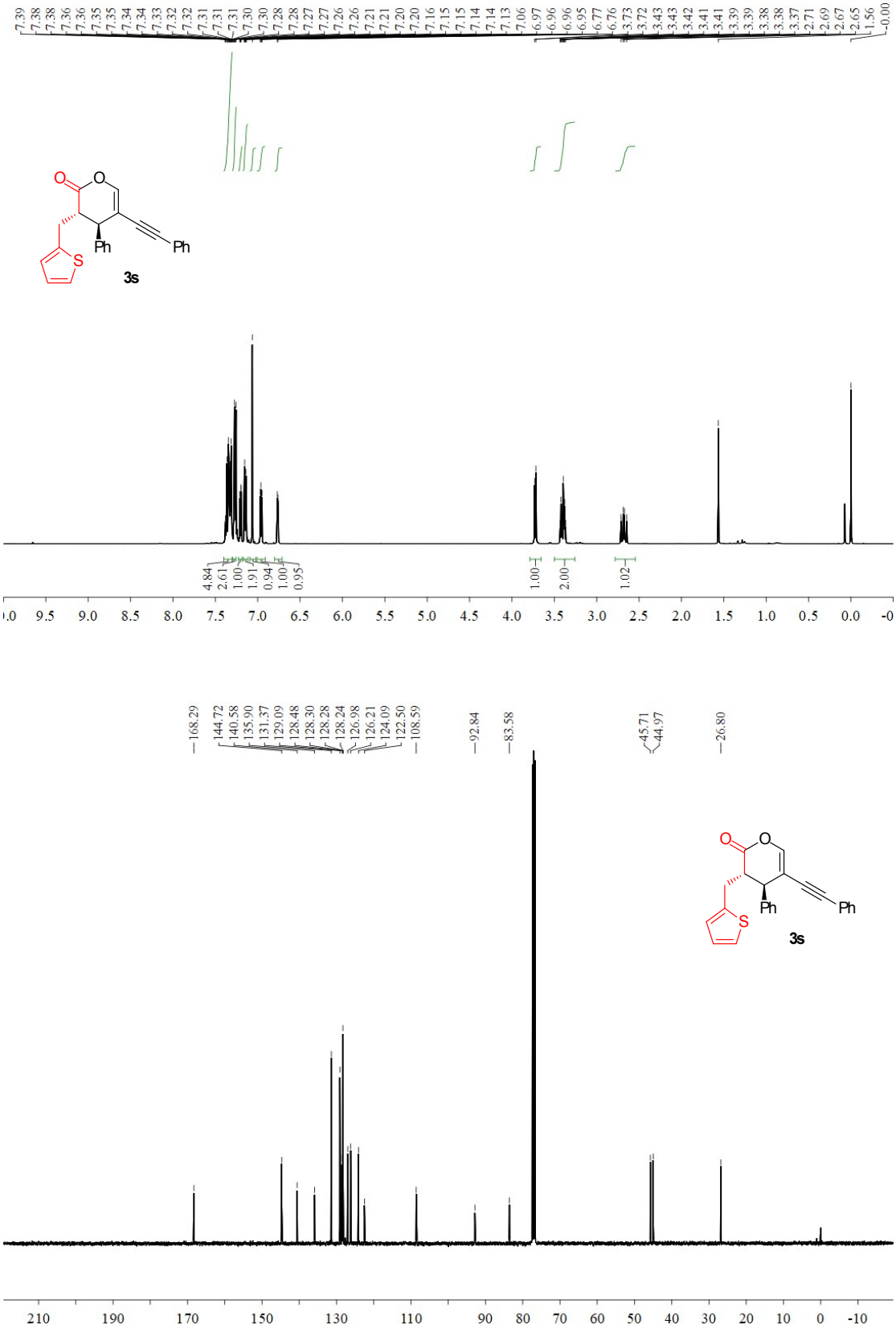
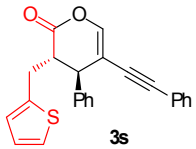
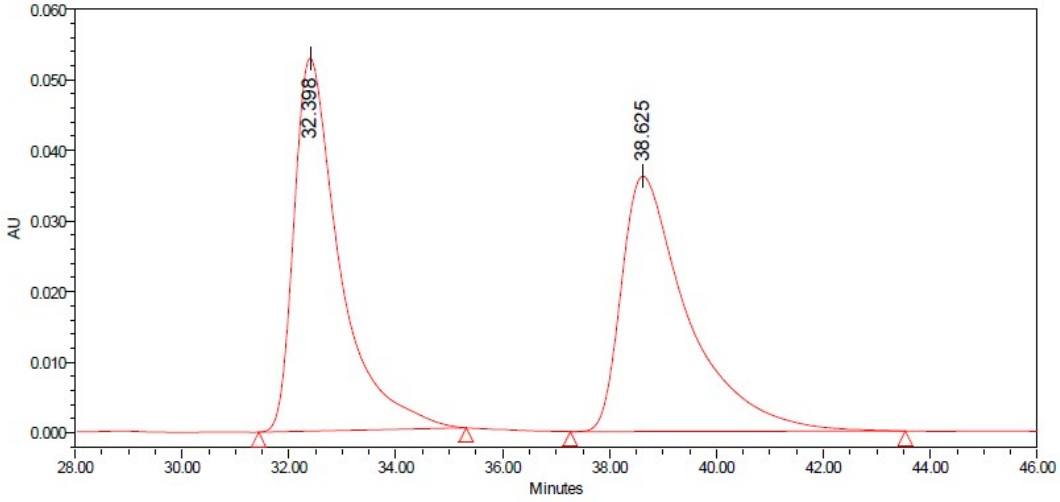


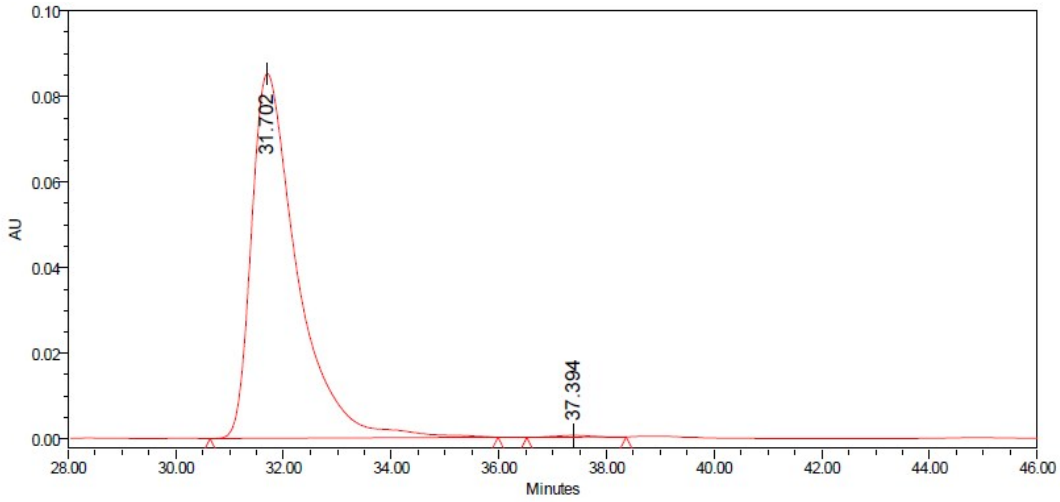
Figure S56. HPLC spectrum of **3s.**



3s



	Ret. Time	Height	Area	% Area
1	32.398	52829	3135531	50.08
2	38.625	36153	3125010	49.92



	Ret. Time	Height	Area	% Area
1	31.702	85185	5030972	99.64
2	37.394	403	18265	0.36

Figure S57. ^{1}H and ^{13}C NMR spectrum of **3t.**

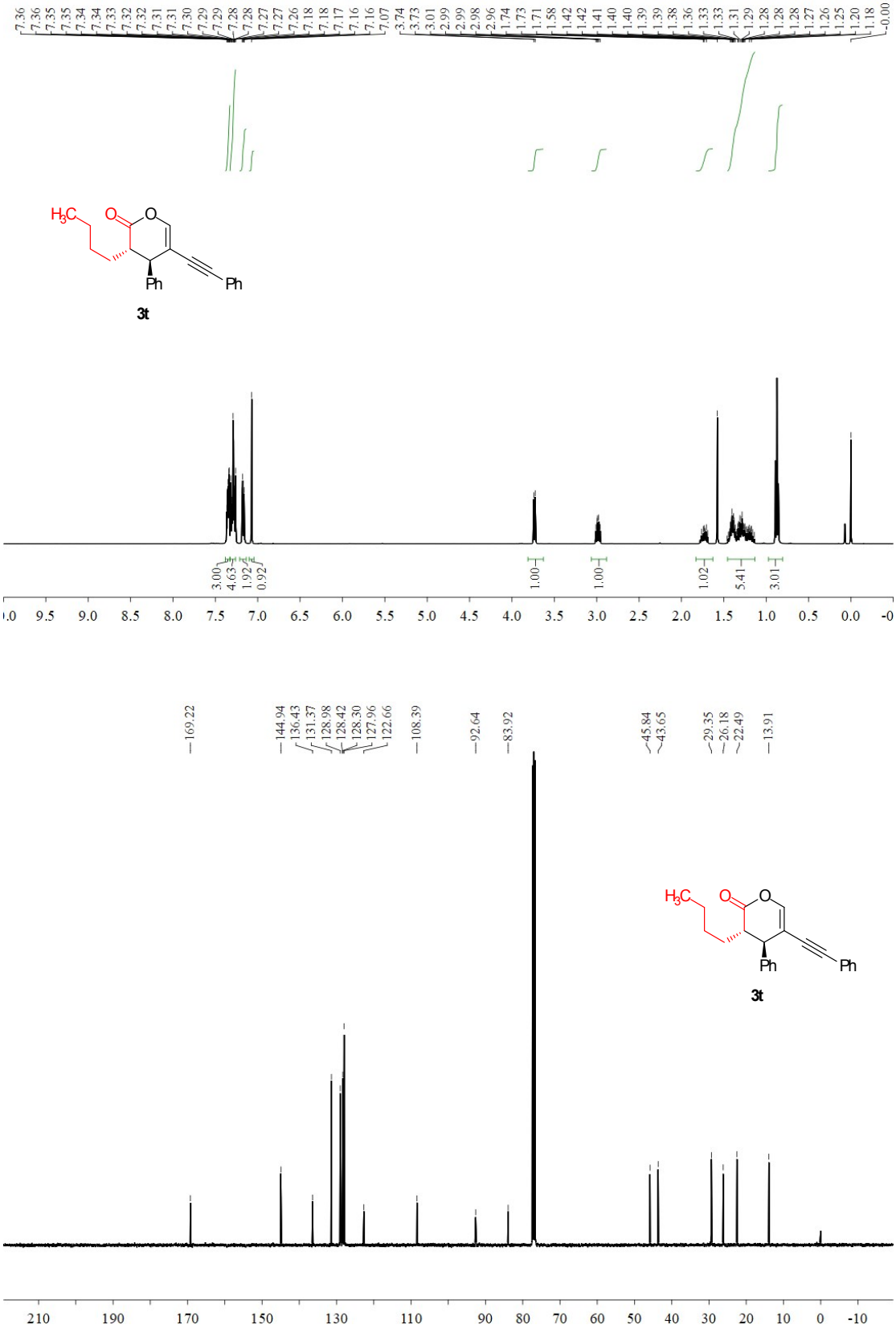
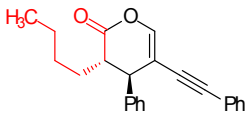
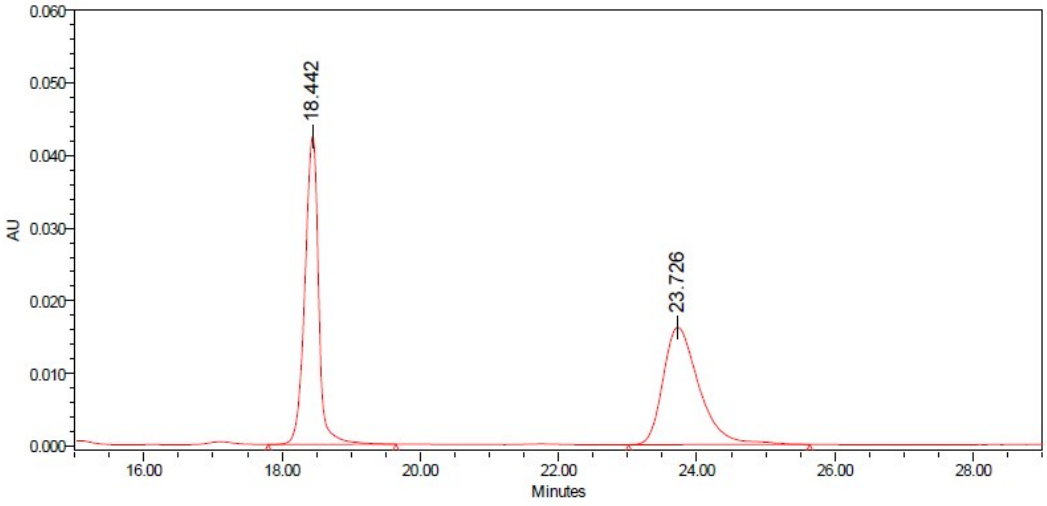


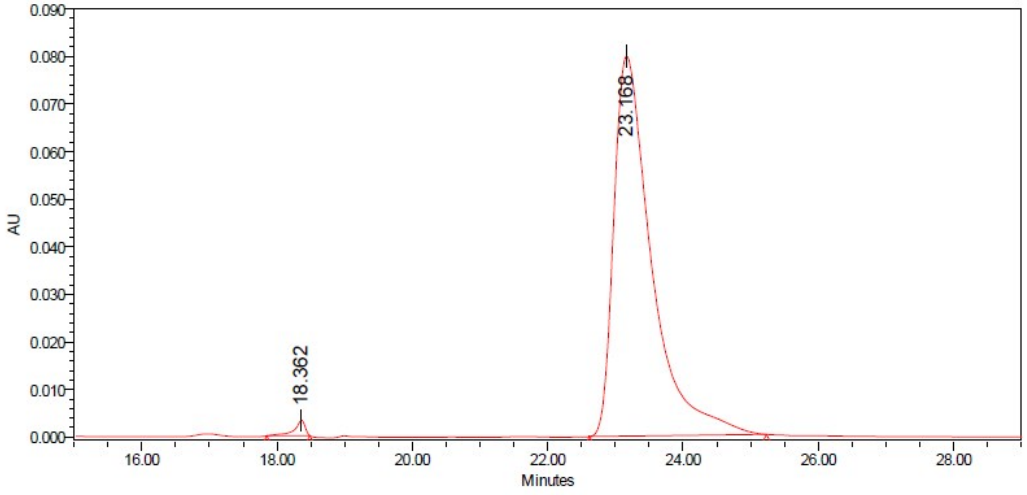
Figure S58. HPLC spectrum of **3t.**



3t



	Ret. Time	Height	Area	% Area
1	18.442	42606	583917	50.00
2	23.726	16130	583913	50.00



	Ret. Time	Height	Area	% Area
1	18.362	3263	35697	1.14
2	23.168	79844	3090479	98.86

Figure S59. ^{1}H and ^{13}C NMR spectrum of **3u.**

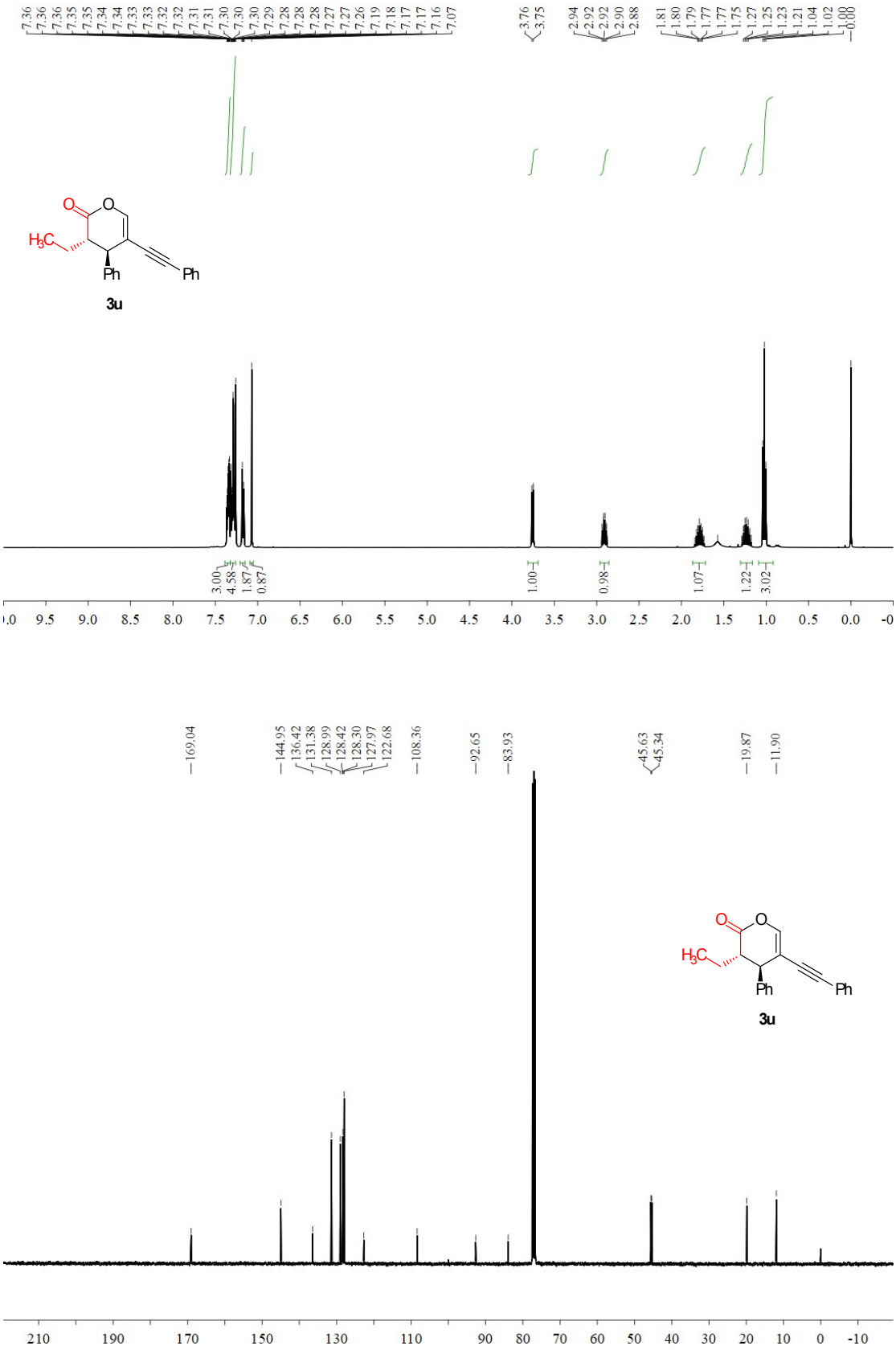
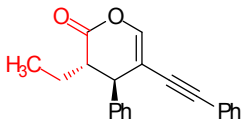
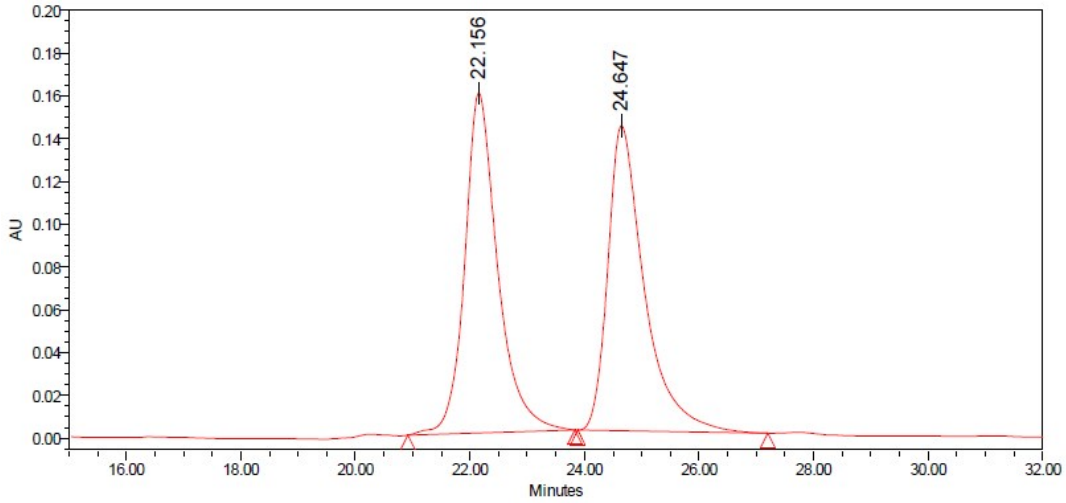


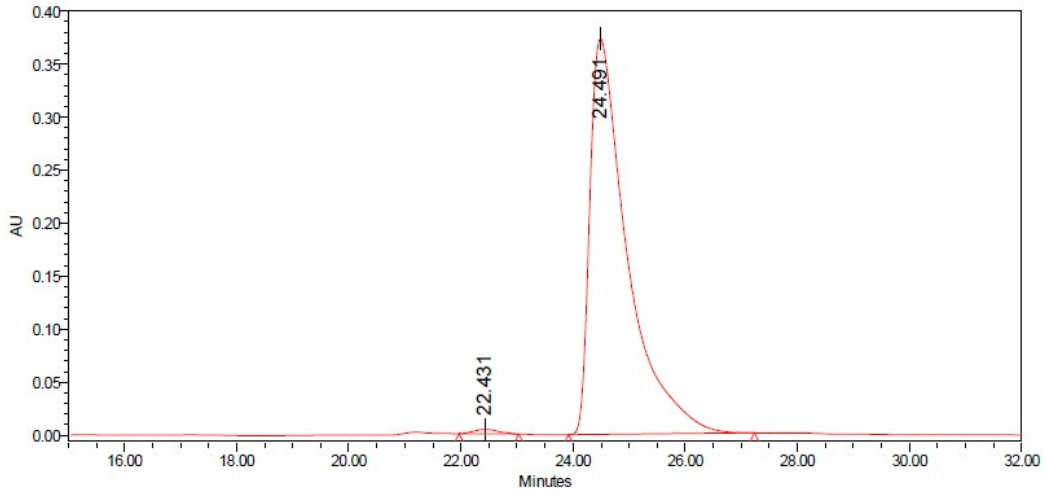
Figure S60. HPLC spectrum of **3u.**



3u



	Ret. Time	Height	Area	% Area
1	22.156	158845	6374542	50.16
2	24.647	142548	6333575	49.84



	Ret. Time	Height	Area	% Area
1	22.431	4168	126168	0.73
2	24.491	373270	17258947	99.27

Figure S61. ^{1}H and ^{13}C NMR spectrum of **4a.**

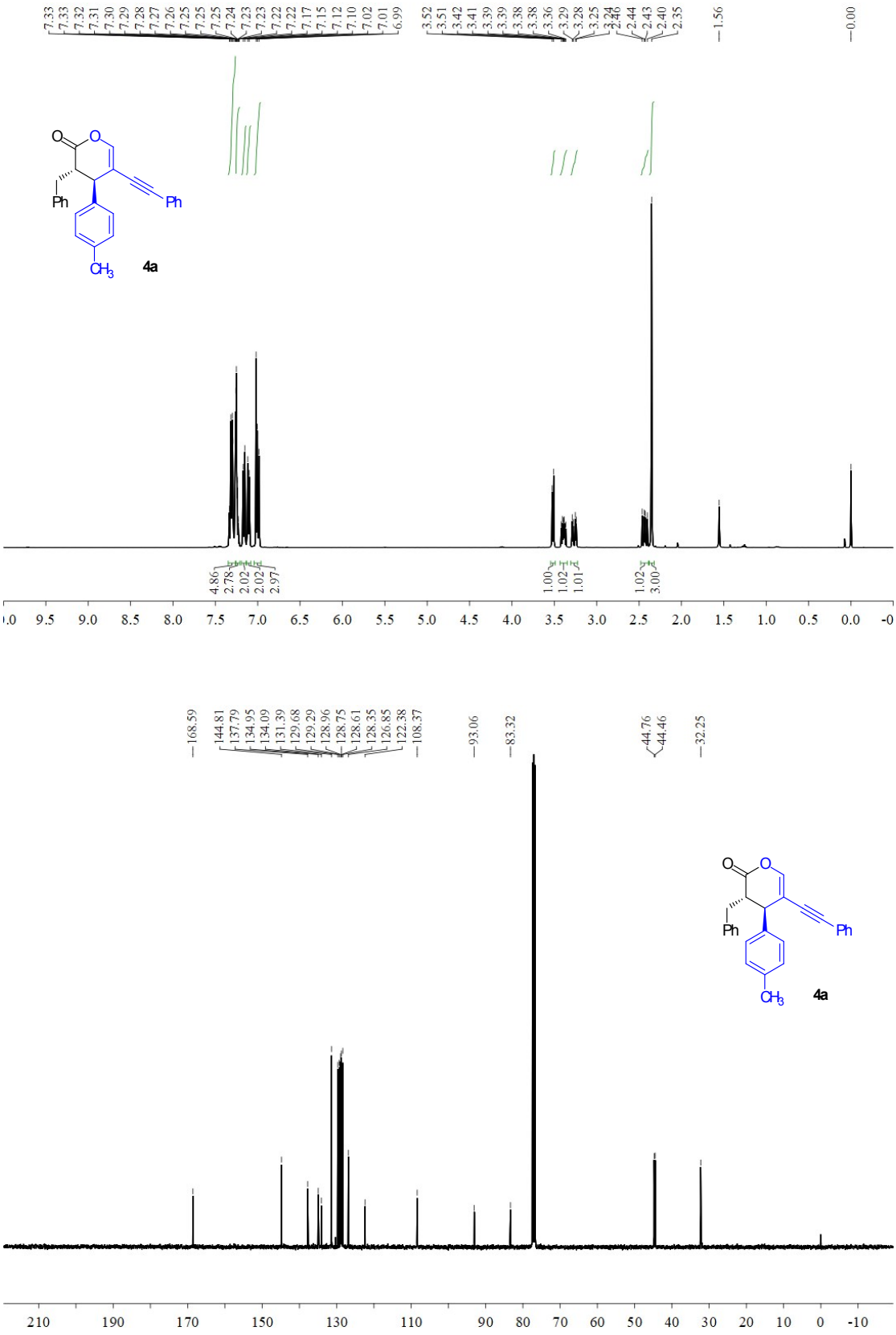
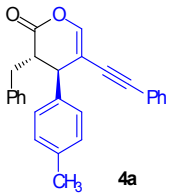
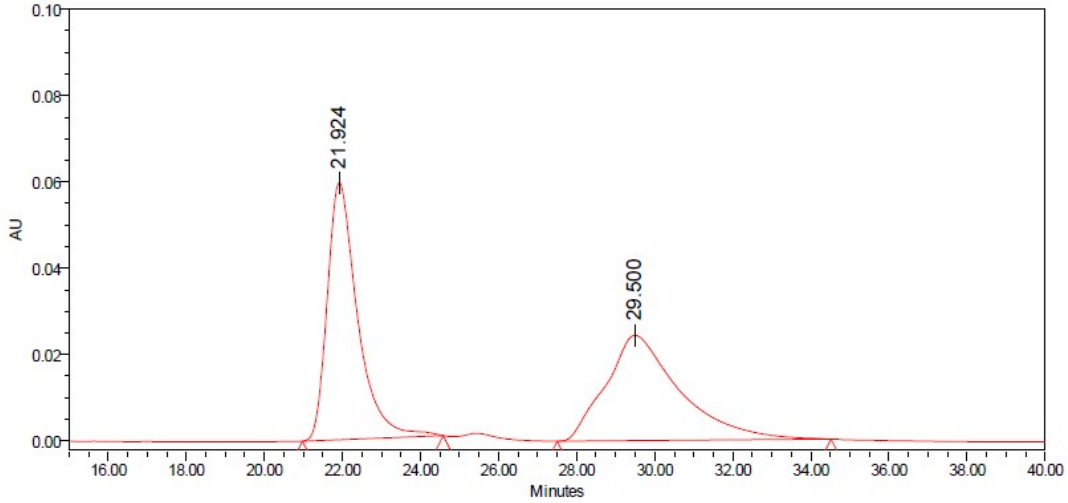


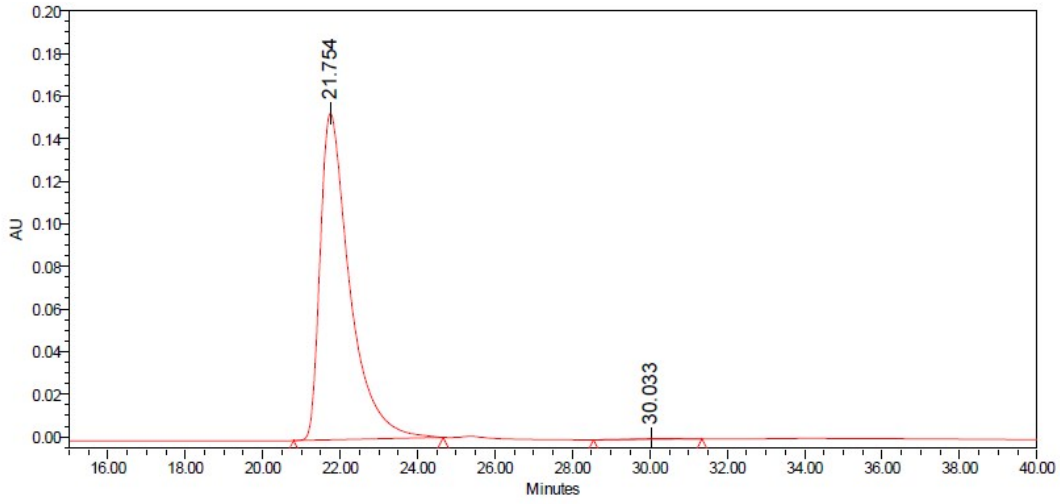
Figure S62. HPLC spectrum of **4a.**



4a



	Ret. Time	Height	Area	% Area
1	21.924	59561	3211655	50.04
2	29.500	24397	3206607	49.96



	Ret. Time	Height	Area	% Area
1	21.754	153210	8134112	99.70
2	30.033	303	24362	0.30

Figure S63. ^{1}H and ^{13}C NMR spectrum of **4b.**

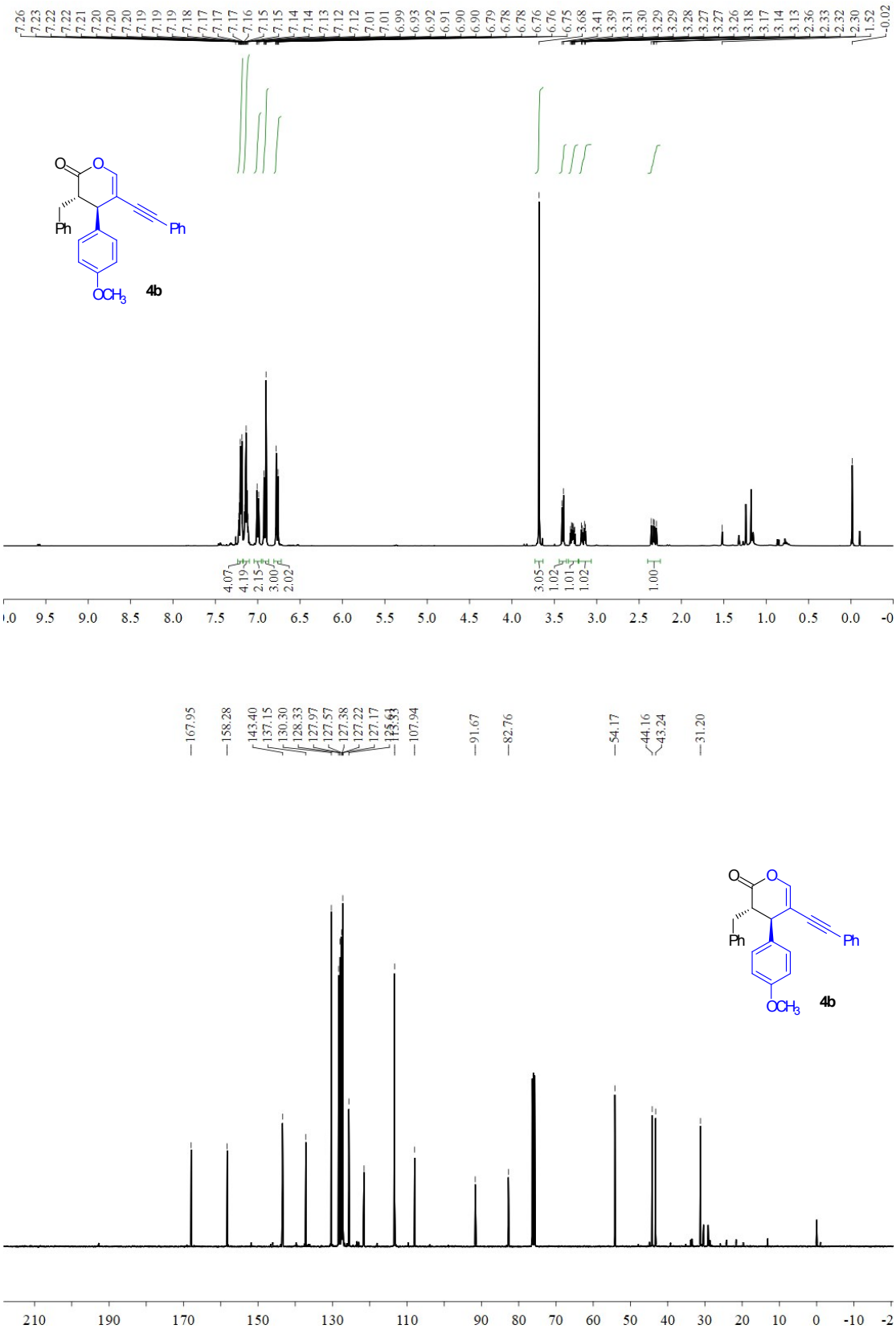
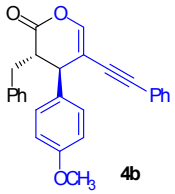
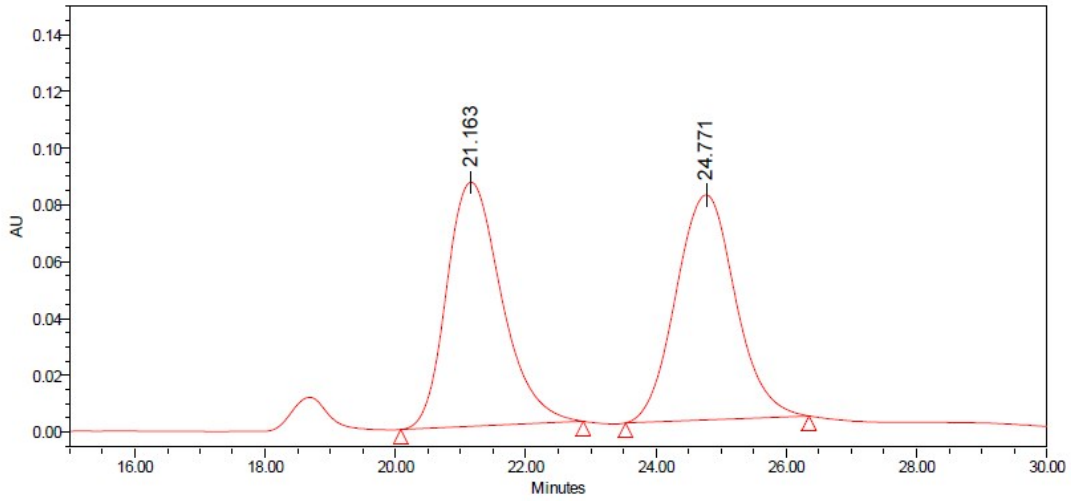


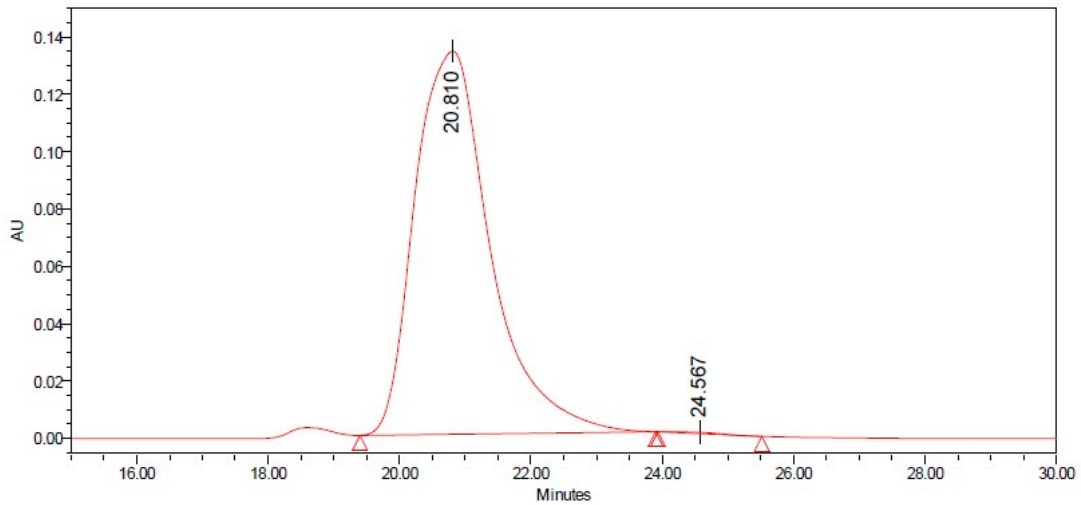
Figure S64. HPLC spectrum of **4b.**



4b

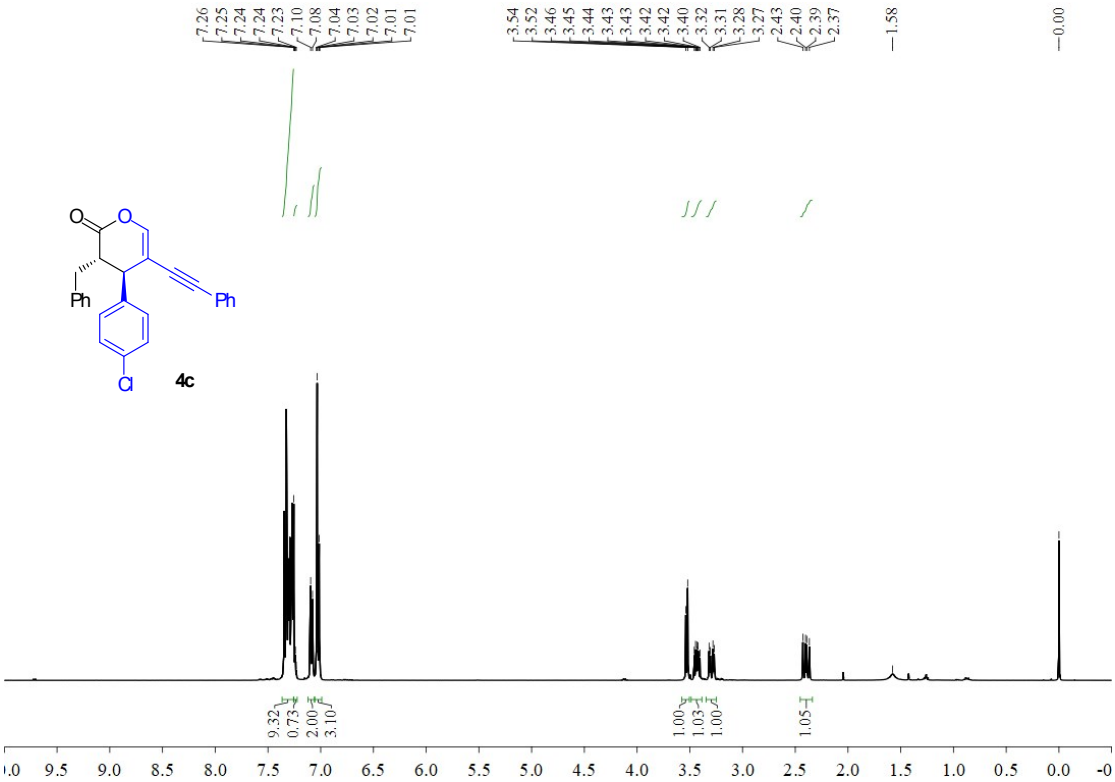


	Ret. Time	Height	Area	% Area
1	21.163	86033	5044885	50.06
2	24.771	79245	5033237	49.94



	Ret. Time	Height	Area	% Area
1	20.810	133643	10723351	99.80
2	24.567	502	21052	0.20

Figure S65. ^{1}H and ^{13}C NMR spectrum of **4c.**



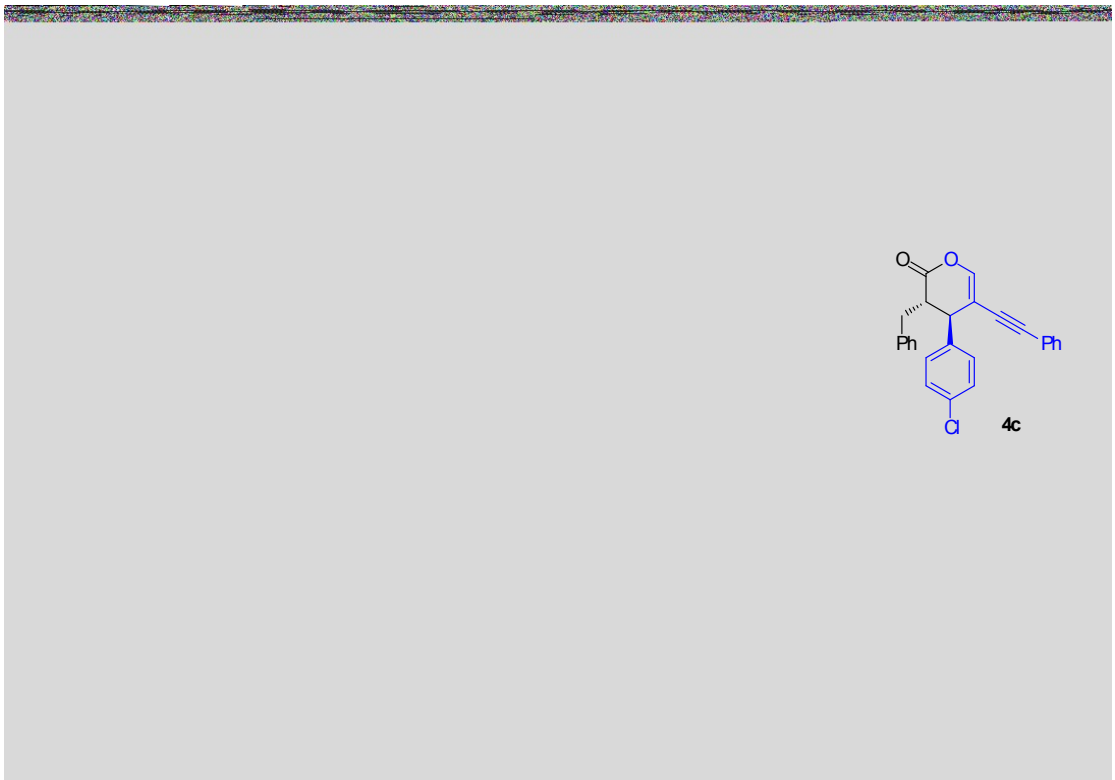
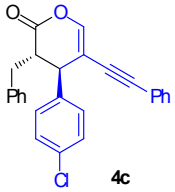
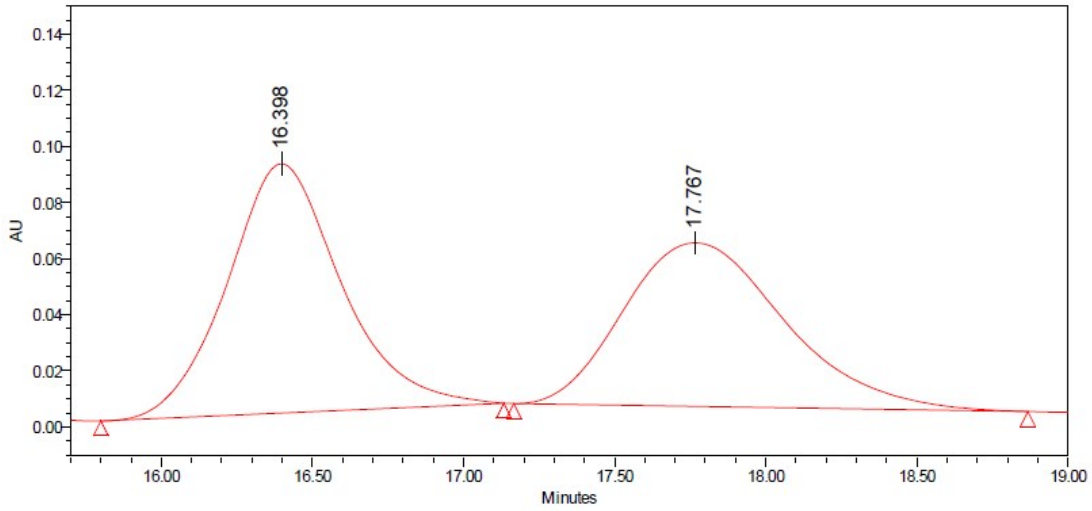


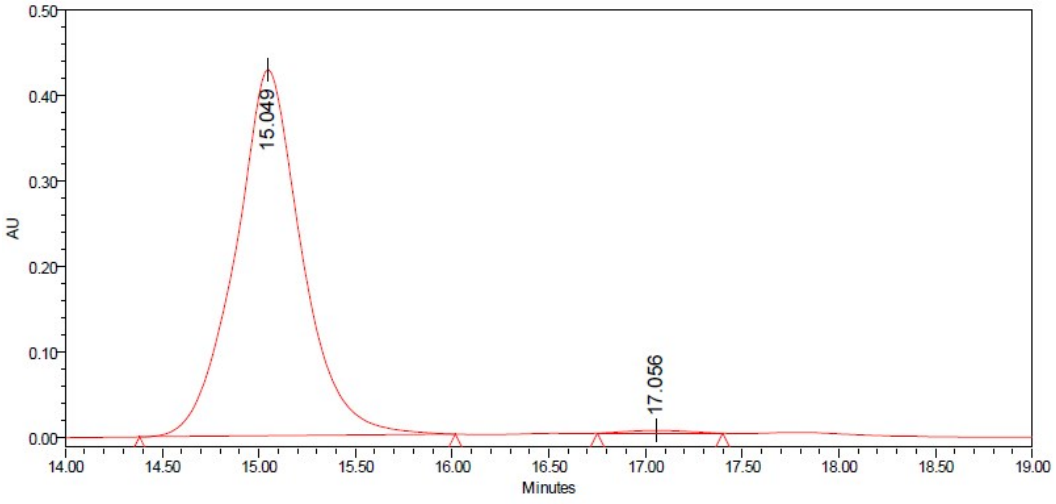
Figure S66. HPLC spectrum of **4c.**



4c

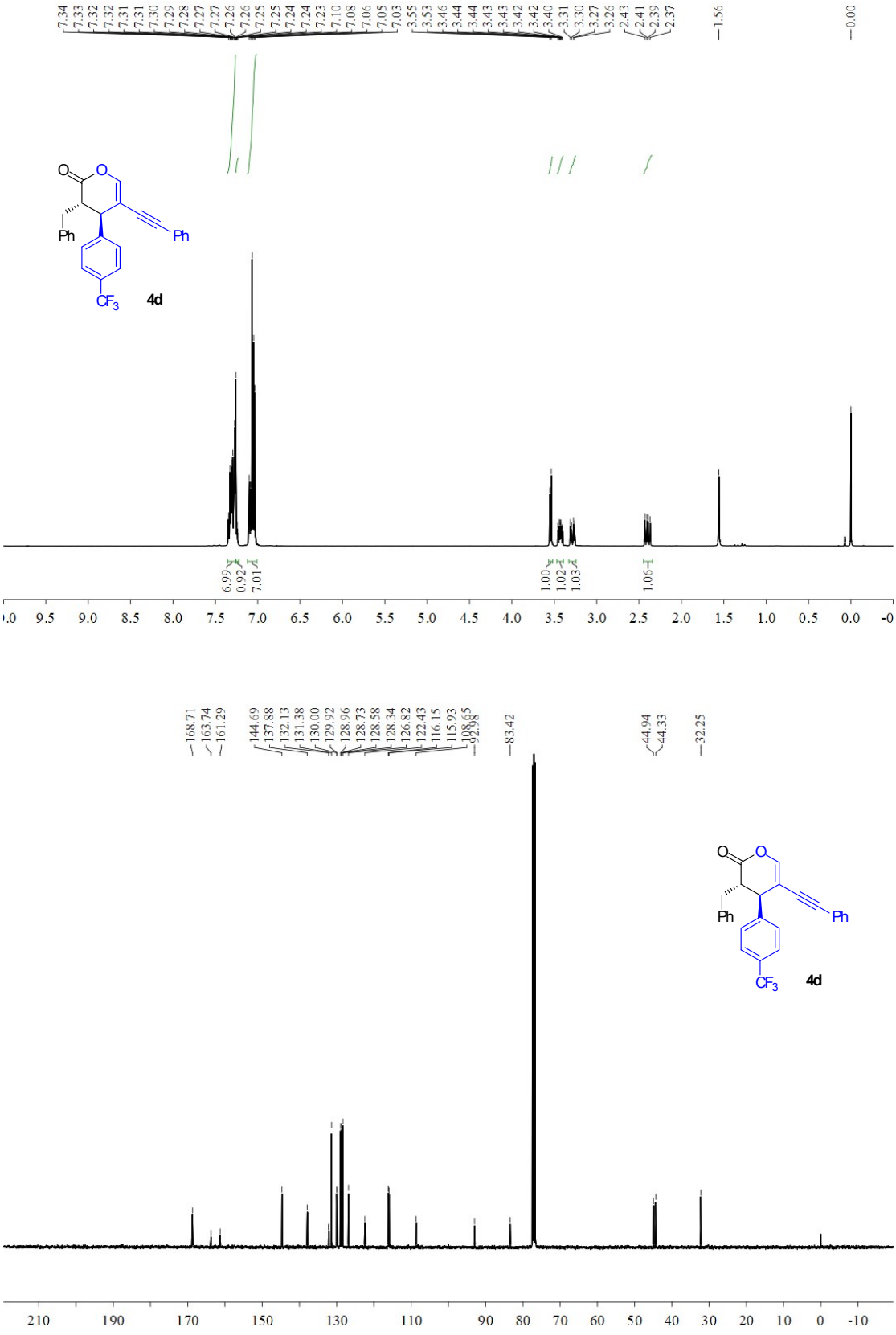


	Ret. Time	Height	Area	% Area
1	16.398	88832	2325365	51.88
2	17.767	58273	2157211	48.12



	Ret. Time	Height	Area	% Area
1	15.049	428117	10232015	99.31
2	17.056	3290	71424	0.69

Figure S67.^{1}H, ^{13}C and ^{19}9F NMR spectrum of **4d.**



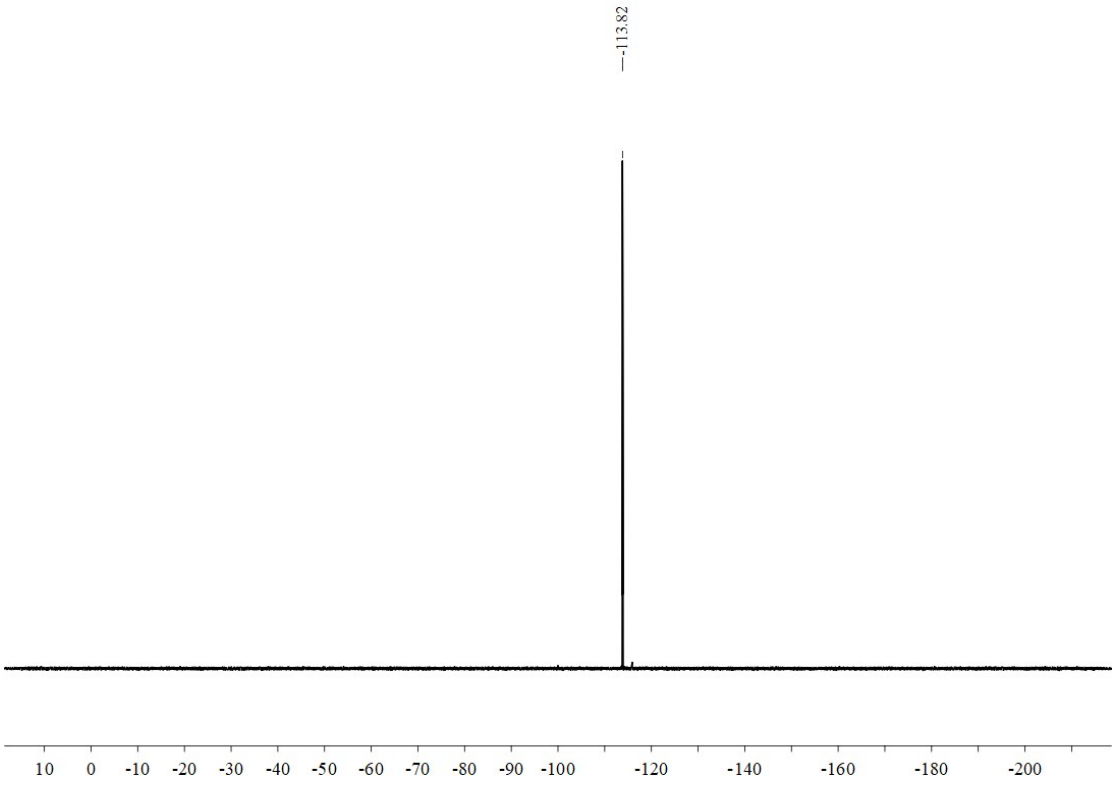
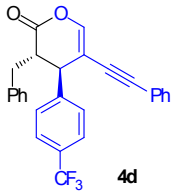
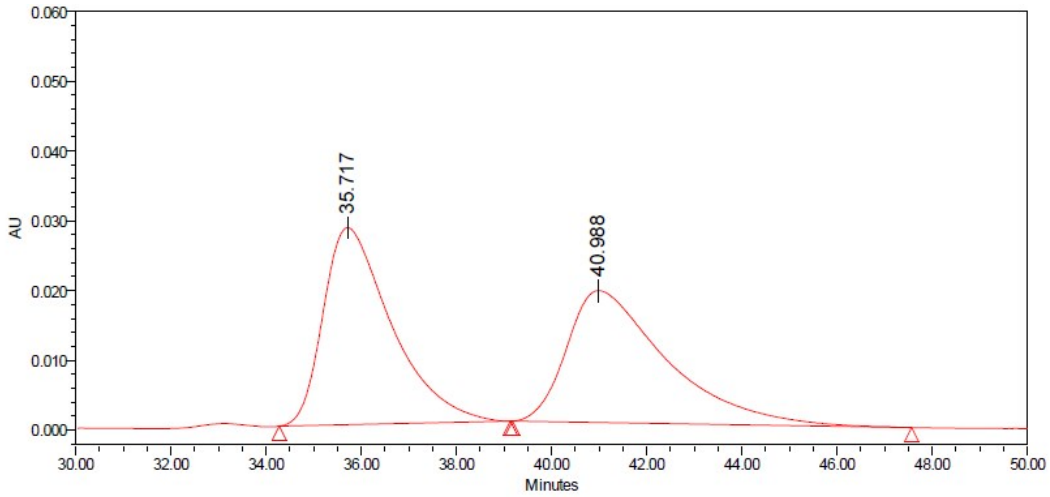

-113.82
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

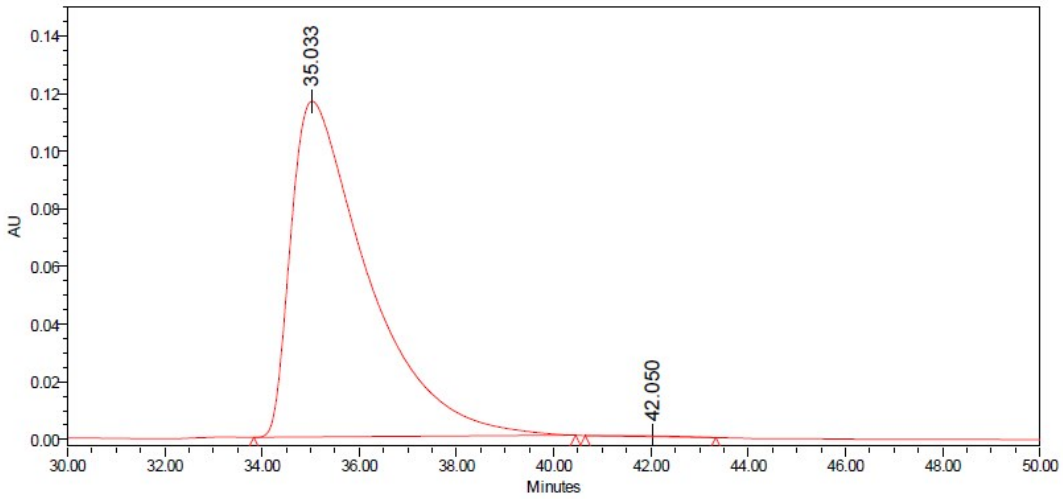
Figure S68. HPLC spectrum of **4d.**



4d



	Ret. Time	Height	Area	% Area
1	35.717	28236	2813185	50.59
2	40.988	18909	2747612	49.41



	Ret. Time	Height	Area	% Area
1	35.033	116575	12810792	99.80
2	42.050	308	25859	0.20

Figure S69. ^{1}H and ^{13}C NMR spectrum of **4e.**

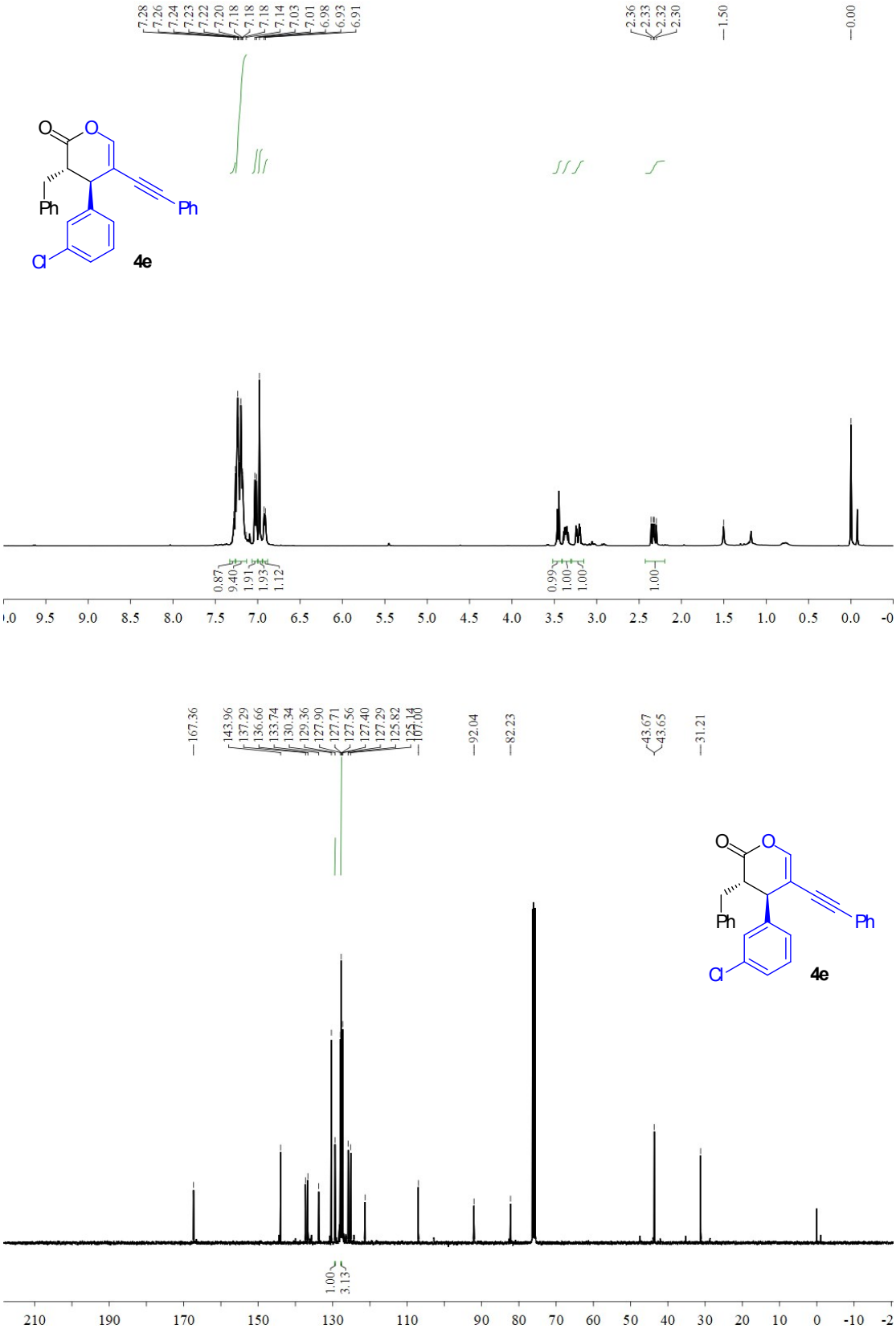
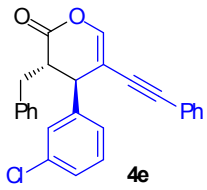
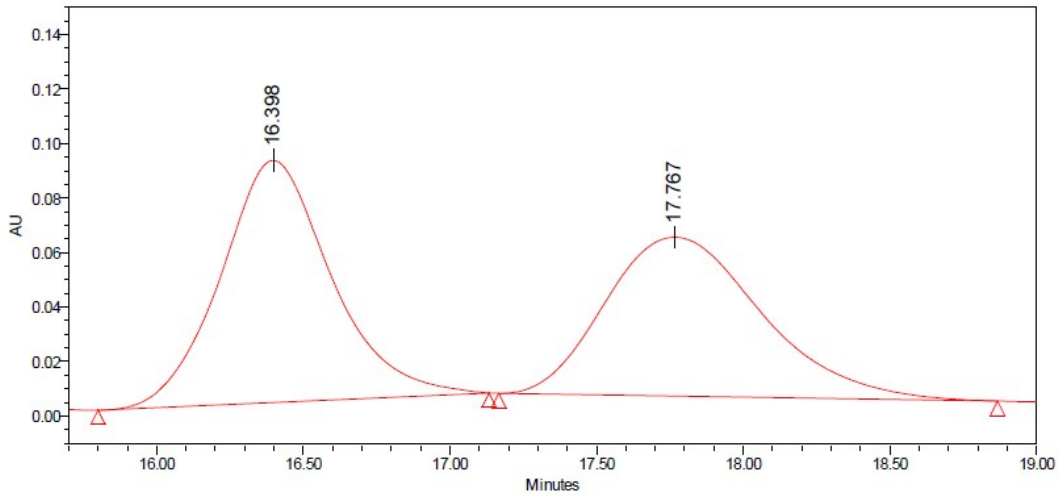


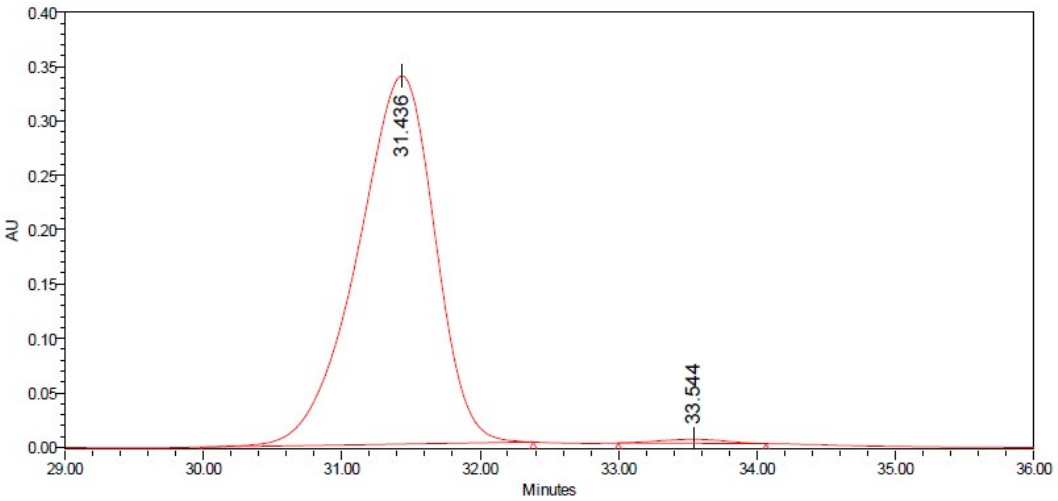
Figure S70. HPLC spectrum of **4e.**



4e



	Ret. Time	Height	Area	% Area
1	16.398	88832	2325365	51.88
2	17.767	58273	2157211	48.12



	Ret. Time	Height	Area	% Area
1	31.436	338640	13143366	99.08
2	33.544	3780	121959	0.92

Figure S71. ^{1}H and ^{13}C NMR spectrum of **4e.**

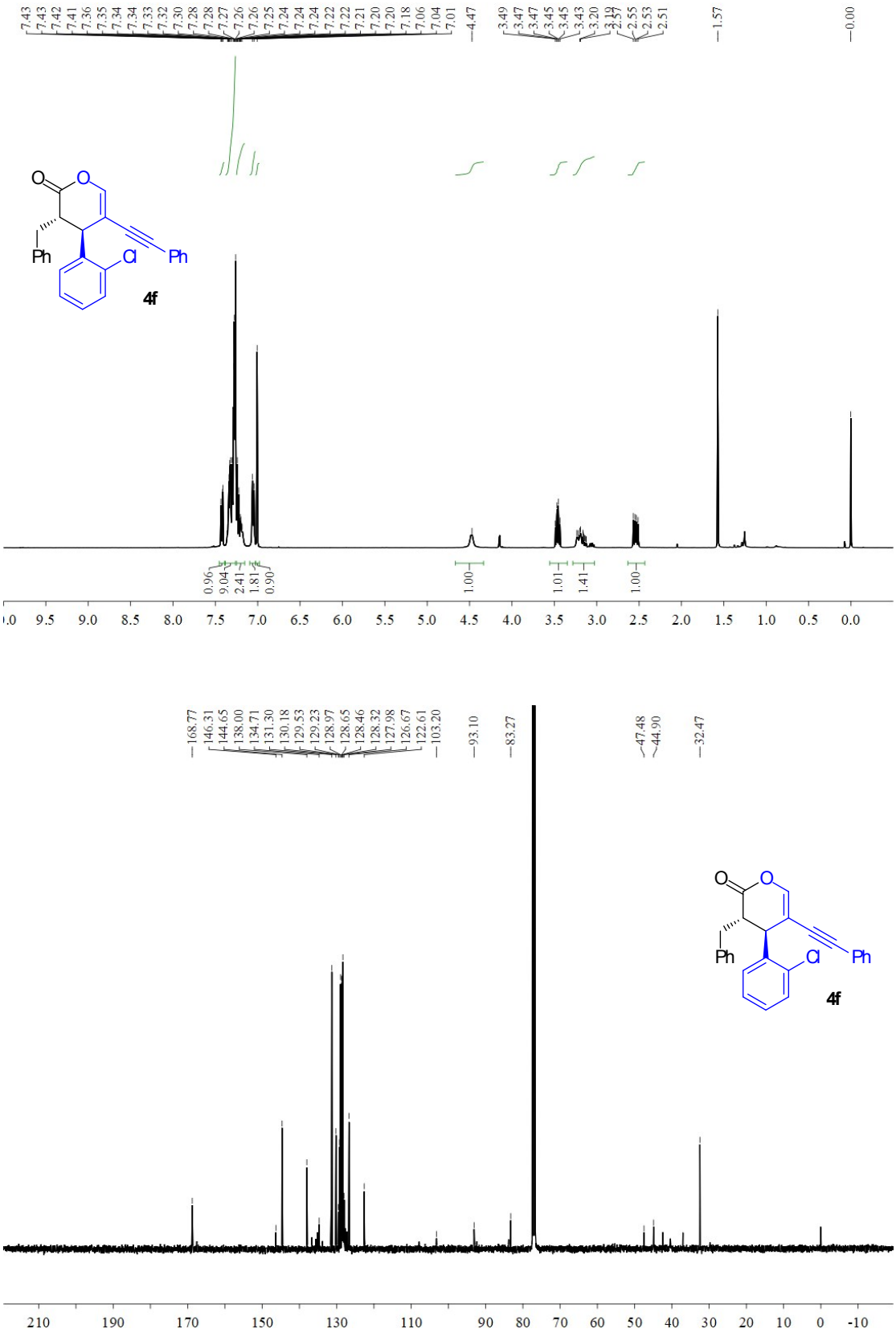
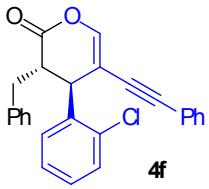
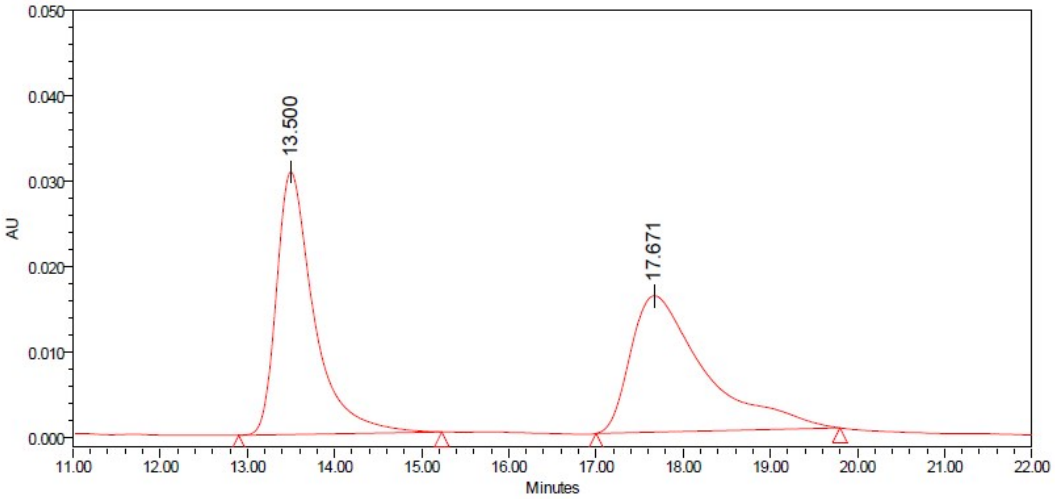


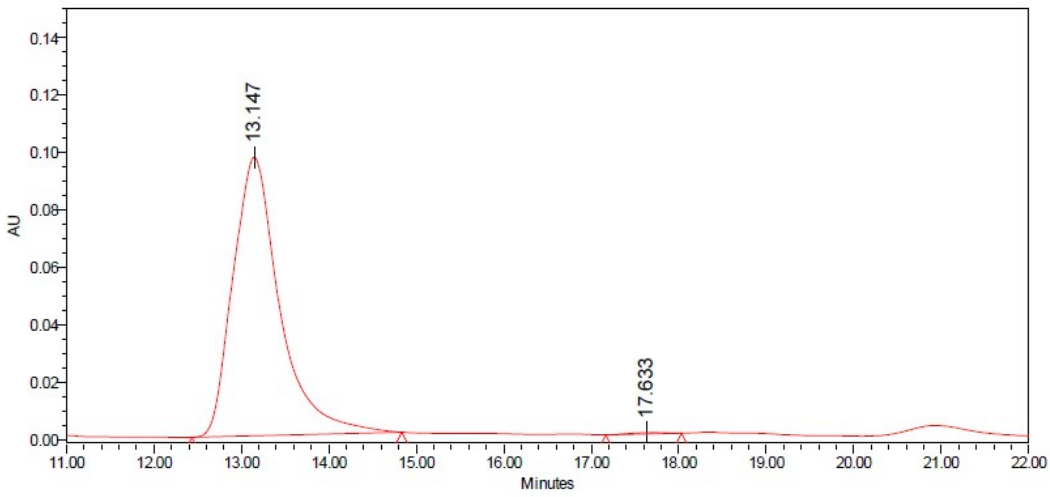
Figure S72. HPLC spectrum of **4e.**



4f



	Ret. Time	Height	Area	% Area
1	13.500	30732	917980	49.38
2	17.671	15942	941200	50.62



	Ret. Time	Height	Area	% Area
1	13.147	97037	3601554	99.68
2	17.633	440	11676	0.32

Figure S73. ^{1}H and ^{13}C NMR spectrum of **4g.**

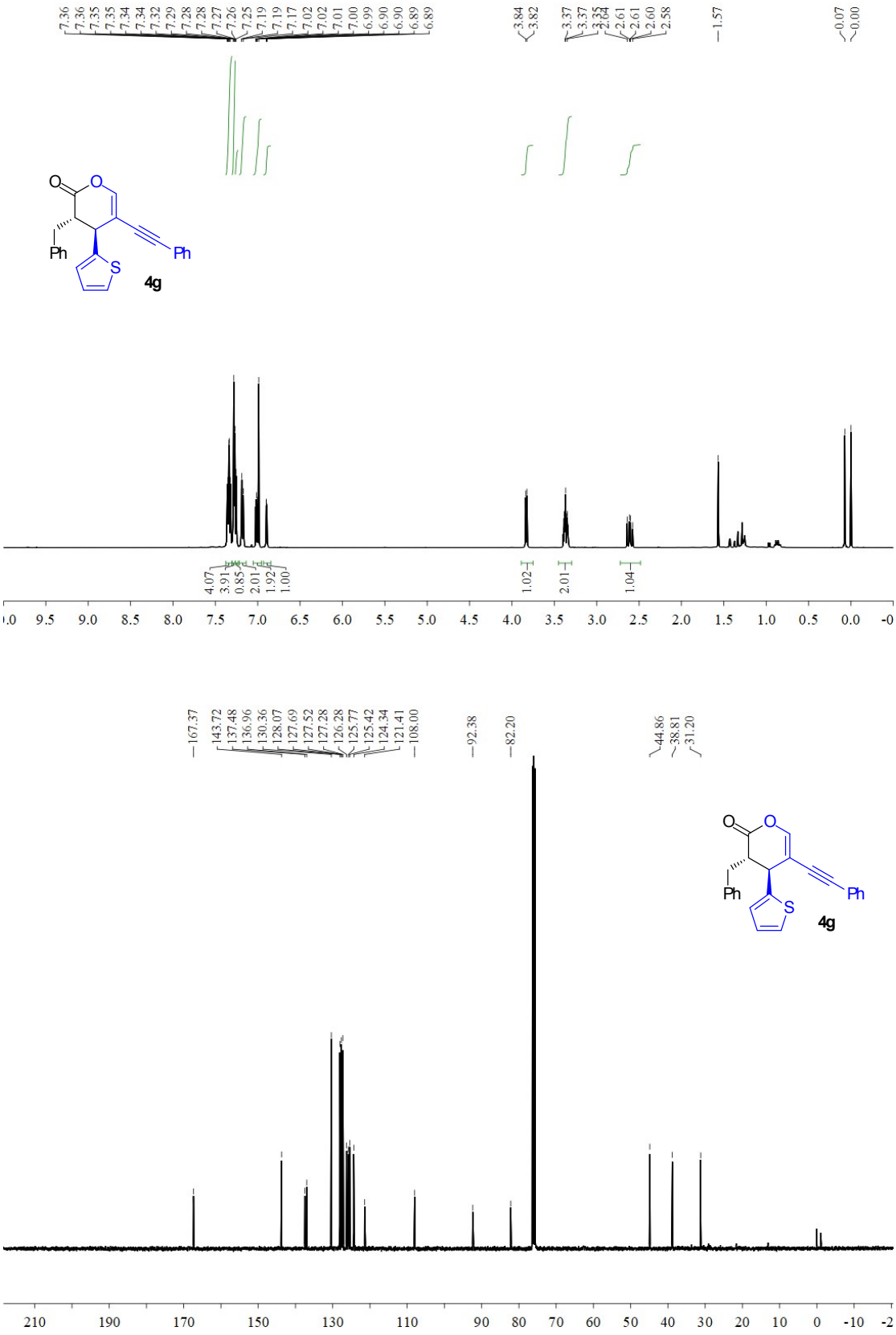
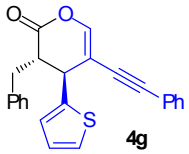
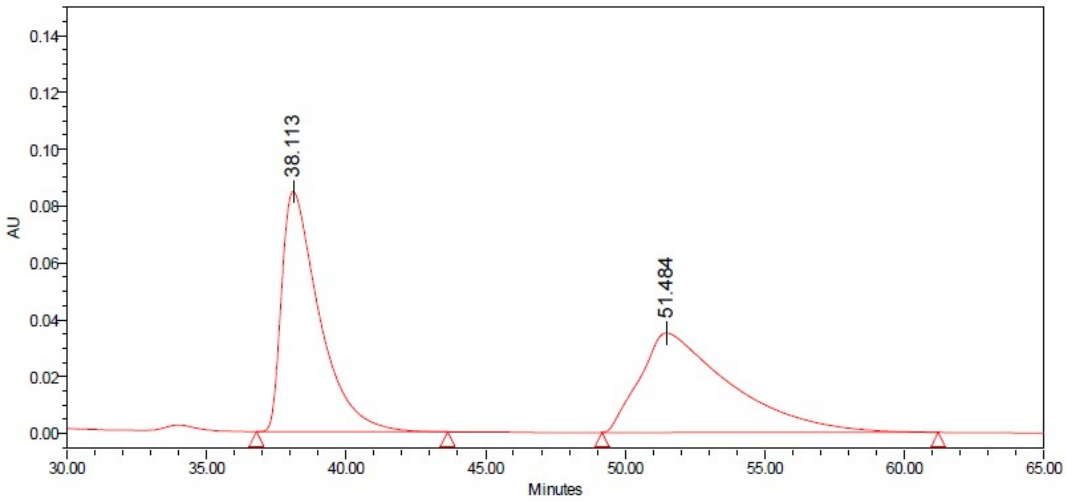


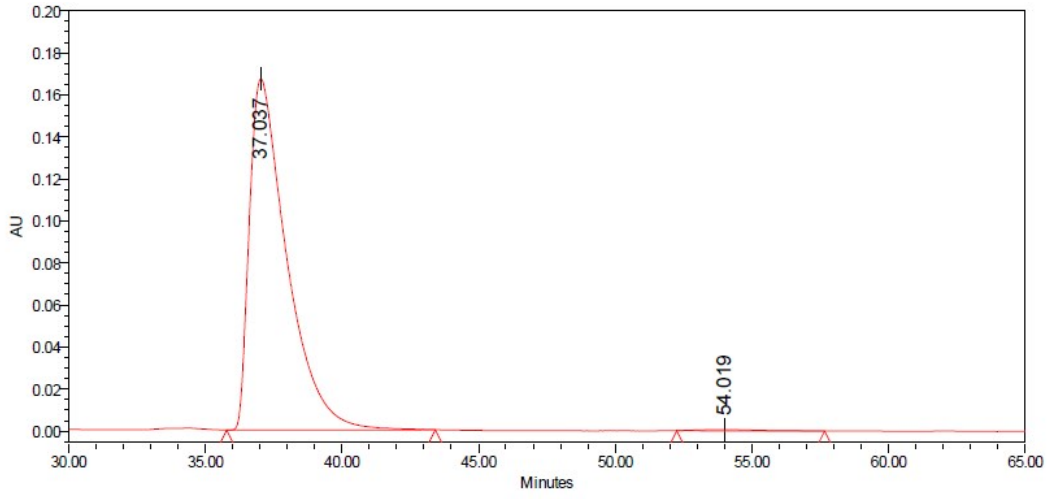
Figure S74. HPLC spectrum of **4g.**



4g



	Ret. Time	Height	Area	% Area
1	38.113	84523	7920508	50.11
2	51.484	35072	7886105	49.89



	Ret. Time	Height	Area	% Area
1	37.037	167086	15892998	99.55
2	54.019	495	71686	0.45

Figure S75. ^{1}H and ^{13}C NMR spectrum of **4h.**

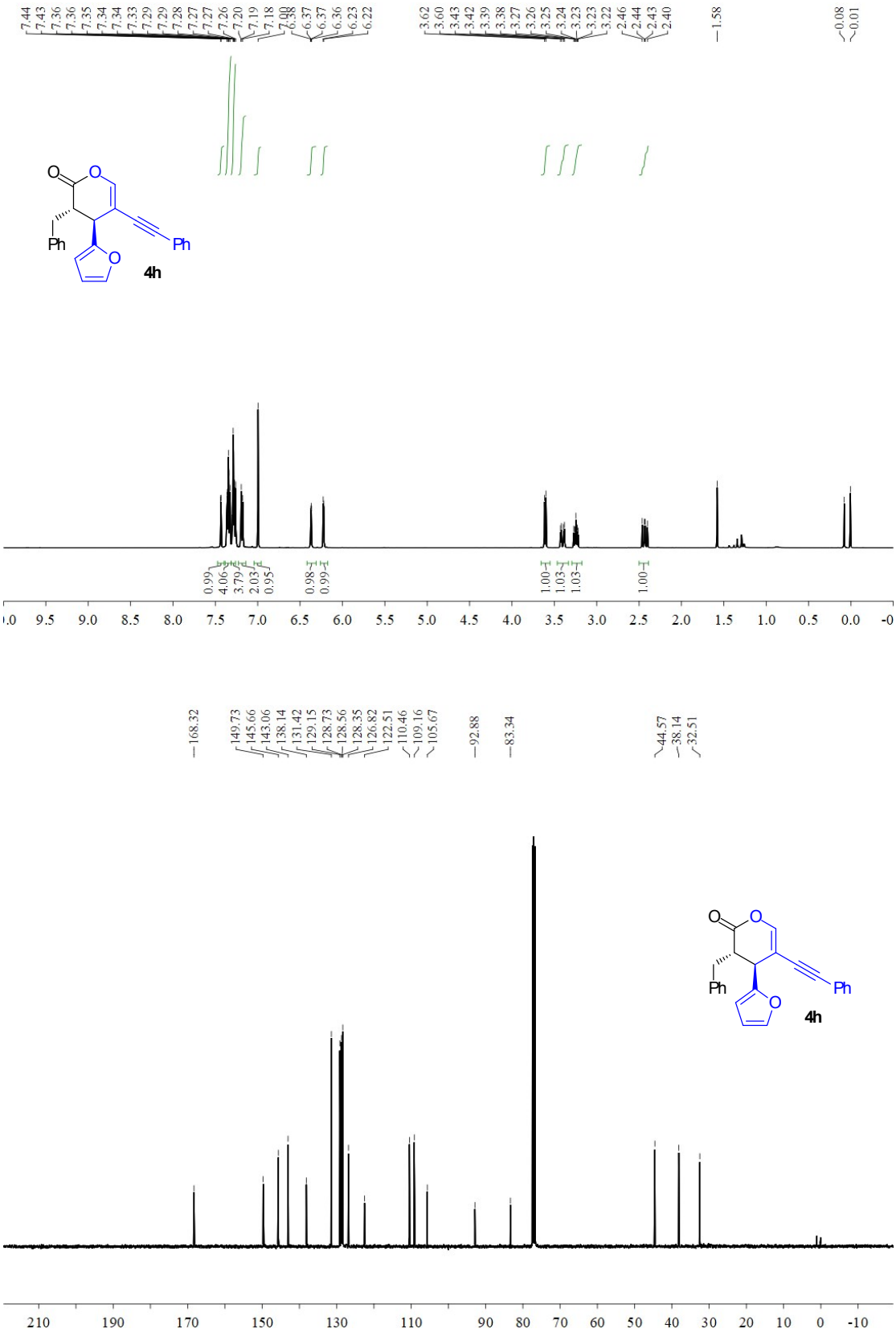
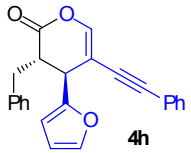
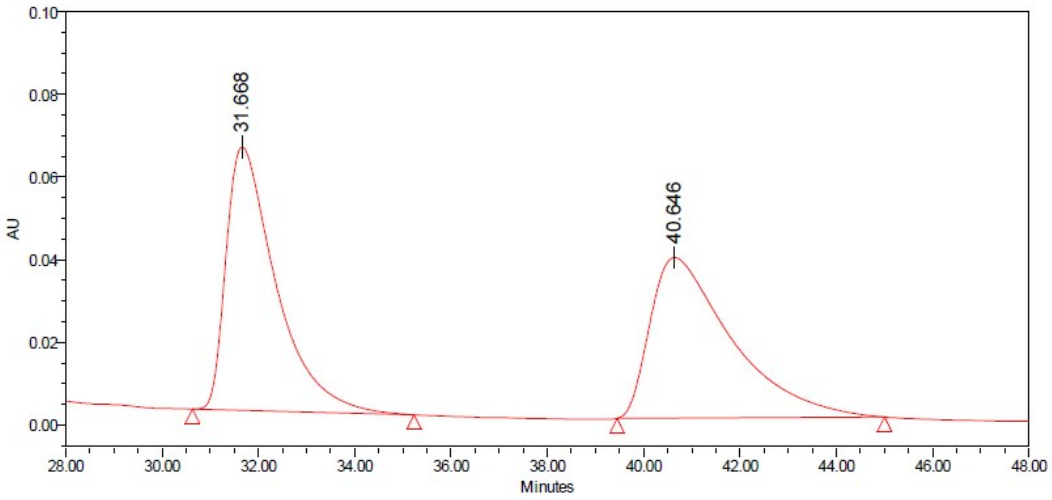


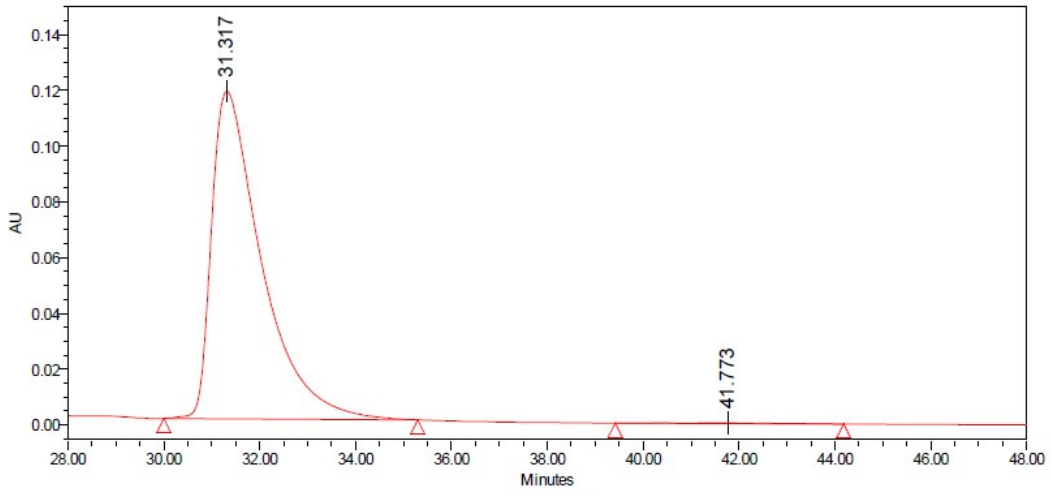
Figure S76. HPLC spectrum of **4h.**



4h

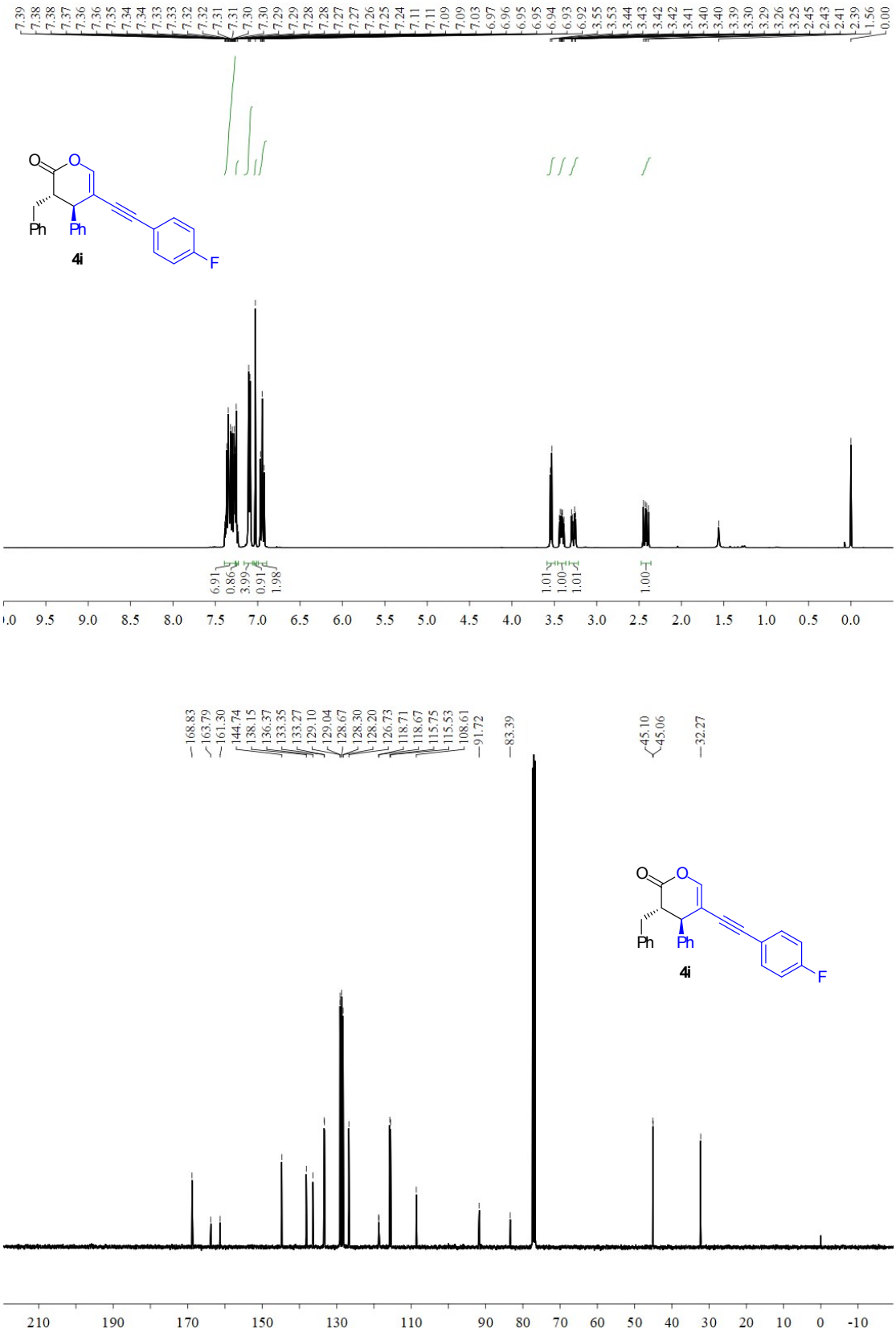


	Ret. Time	Height	Area	% Area
1	31.668	63731	4586685	50.15
2	40.646	38837	4559302	49.85



	Ret. Time	Height	Area	% Area
1	31.317	117526	8497013	99.58
2	41.773	243	36080	0.42

Figure S77. ^{1}H, ^{13}C and ^{19}F NMR spectrum of **4i.**



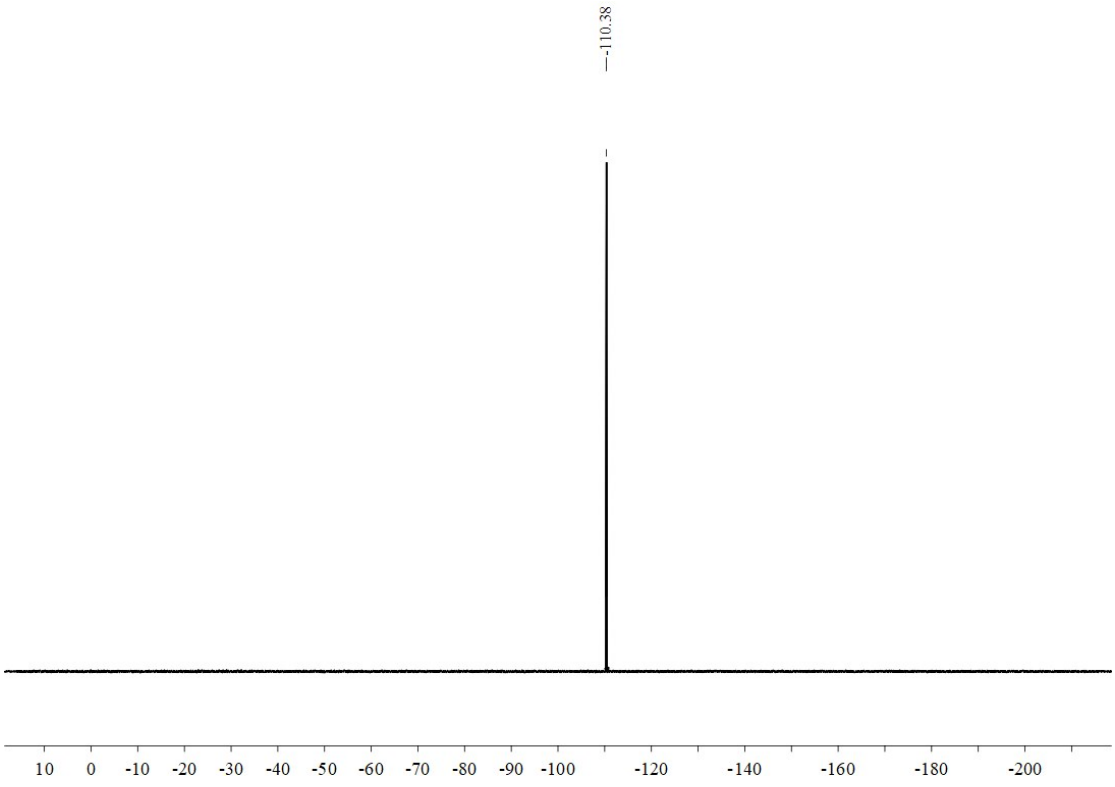
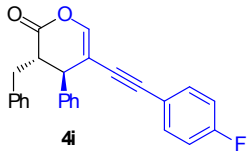
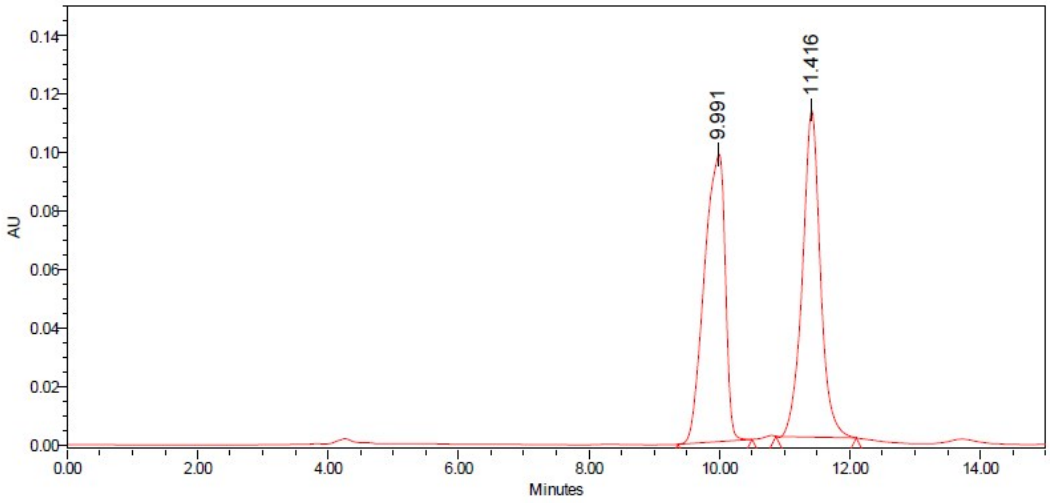

-110.38
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

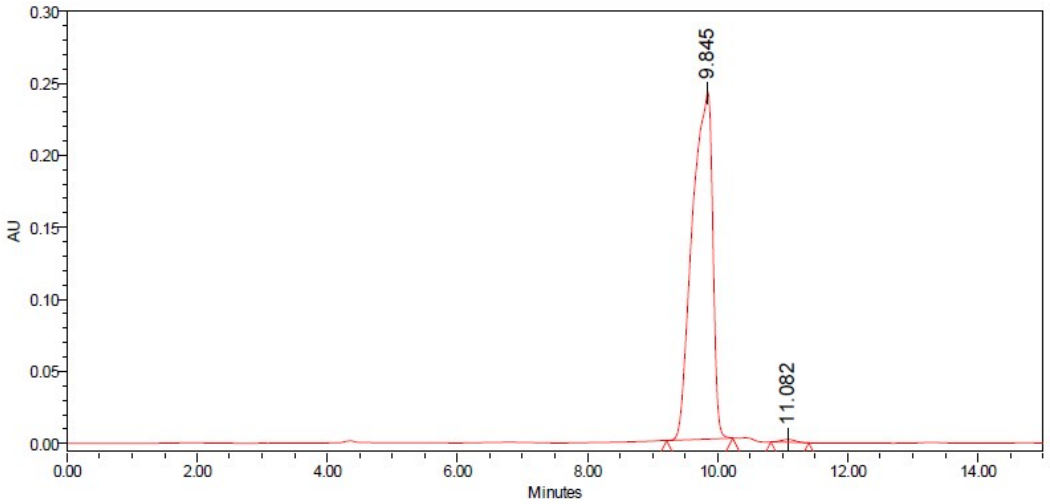
Figure S78. HPLC spectrum of **4i.**



4i



	Ret. Time	Height	Area	% Area
1	9.991	98504	2170378	50.36
2	11.416	111871	2139514	49.64



	Ret. Time	Height	Area	% Area
1	9.845	241291	5187858	99.41
2	11.082	2025	30848	0.59

Figure S79. ^{1}H and ^{13}C NMR spectrum of **4j.**

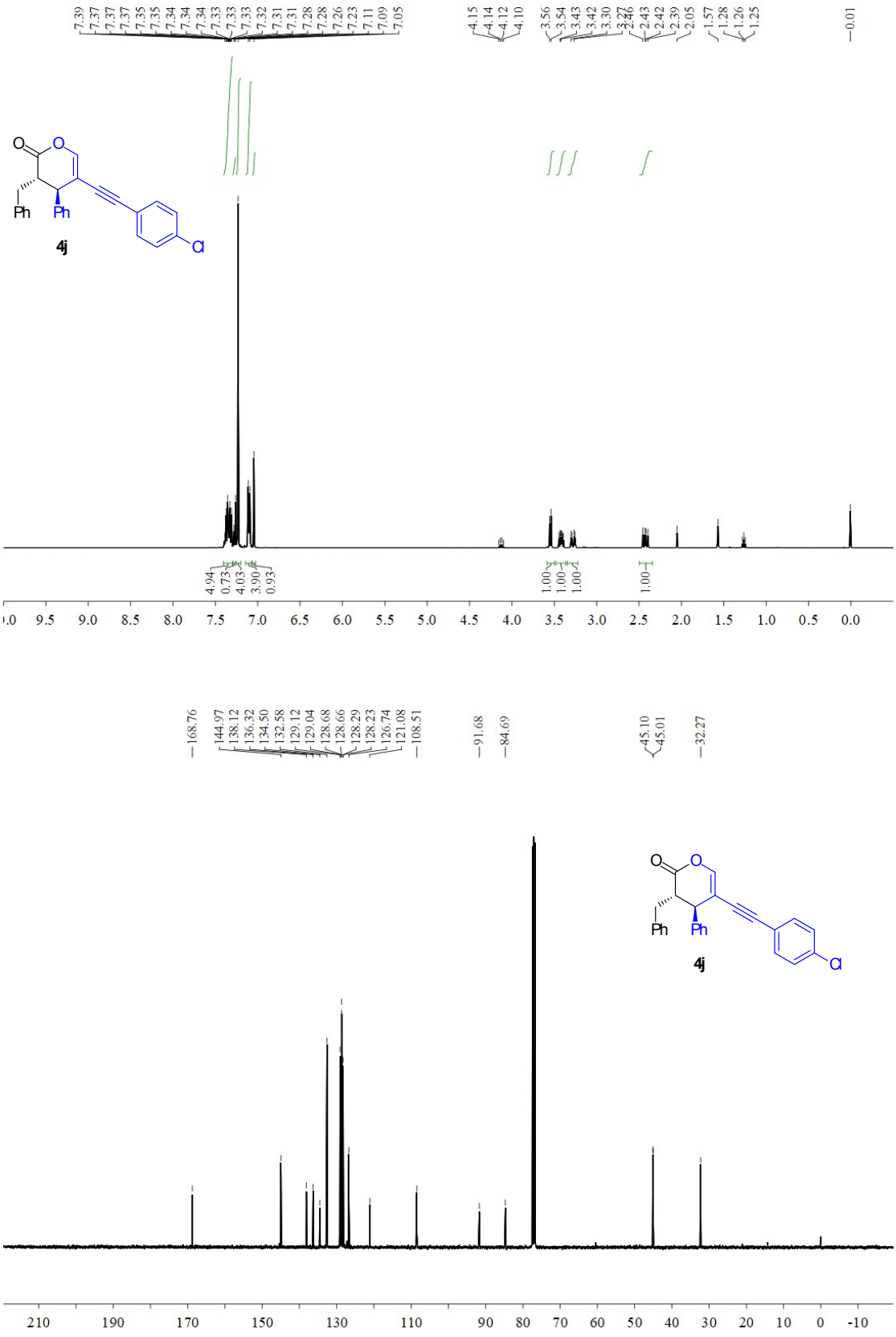
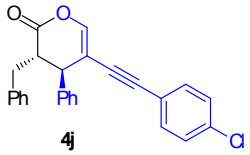
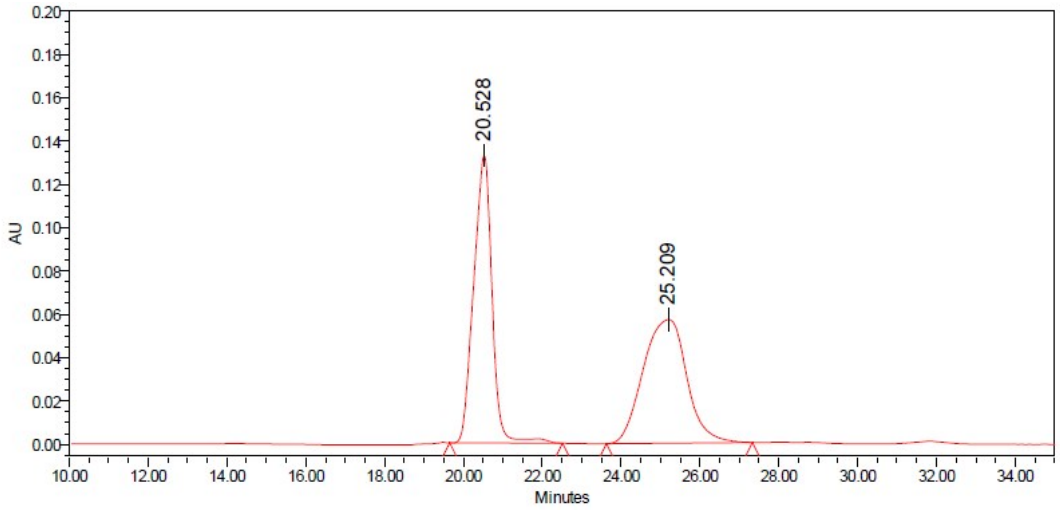


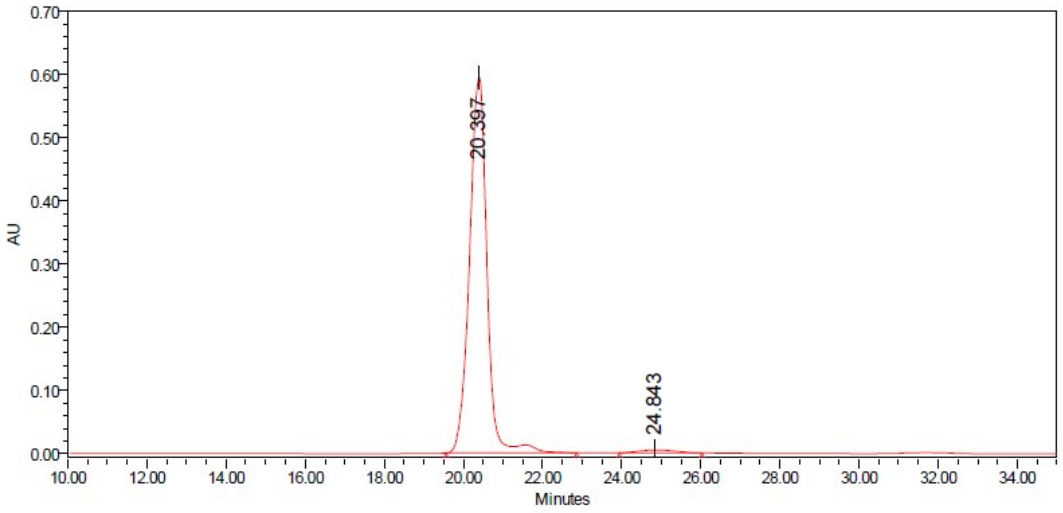
Figure S80. HPLC spectrum of **4j.**



4j

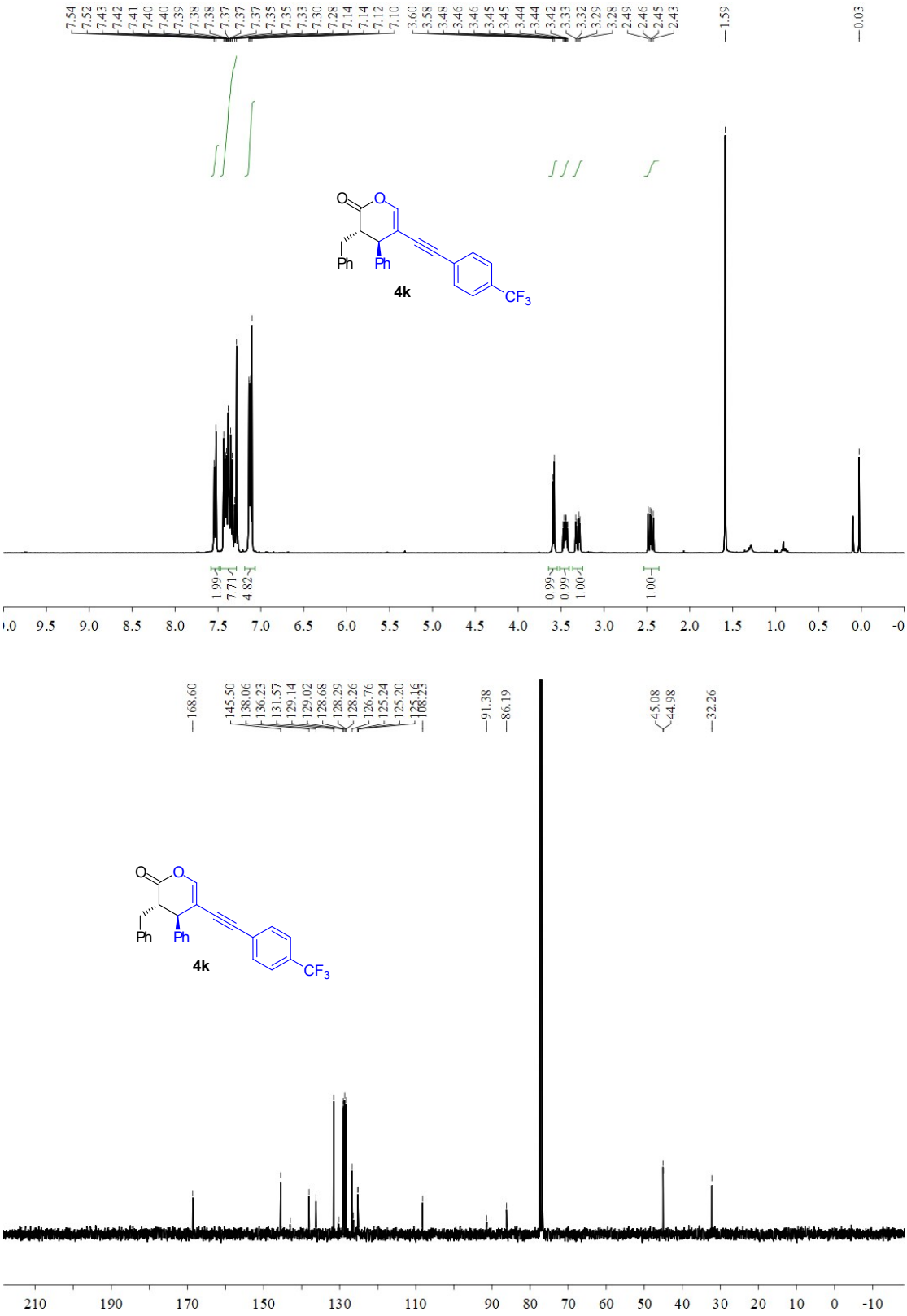


	Ret. Time	Height	Area	% Area
1	20.528	132808	4285595	49.42
2	25.209	56989	4386910	50.58



	Ret. Time	Height	Area	% Area
1	20.397	594827	18185964	98.53
2	24.843	4115	270854	1.47

Figure S81. ^{1}H and ^{13}C NMR spectrum of **4k.**



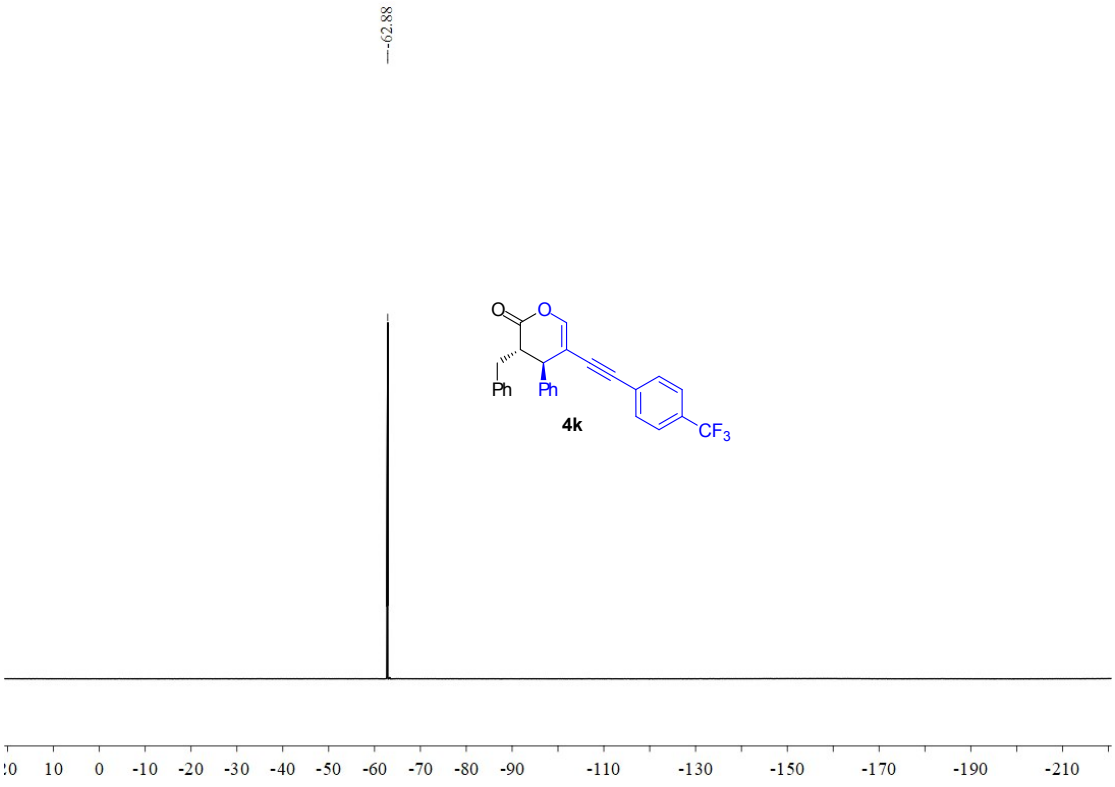
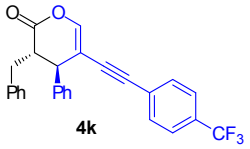
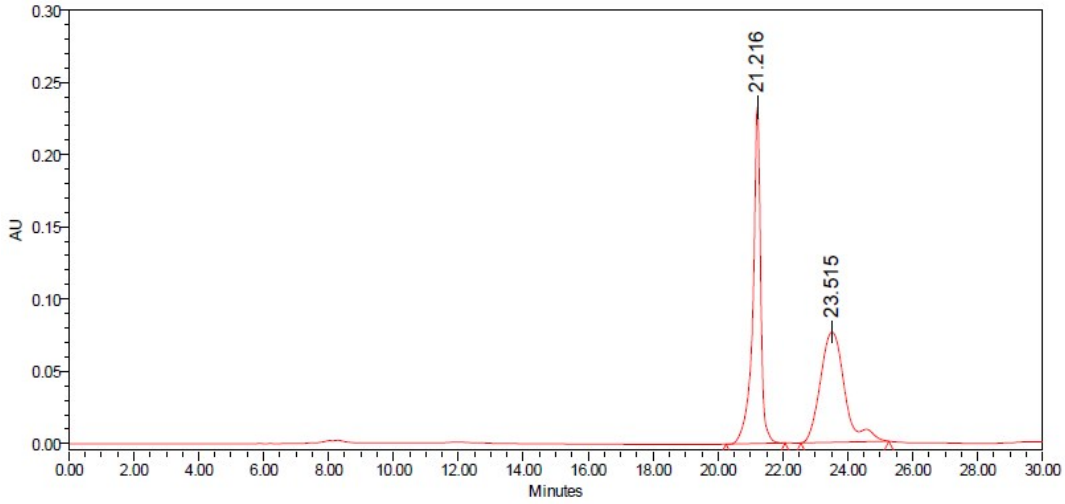

-62.88
O
O
Ph
Ph
4k
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210

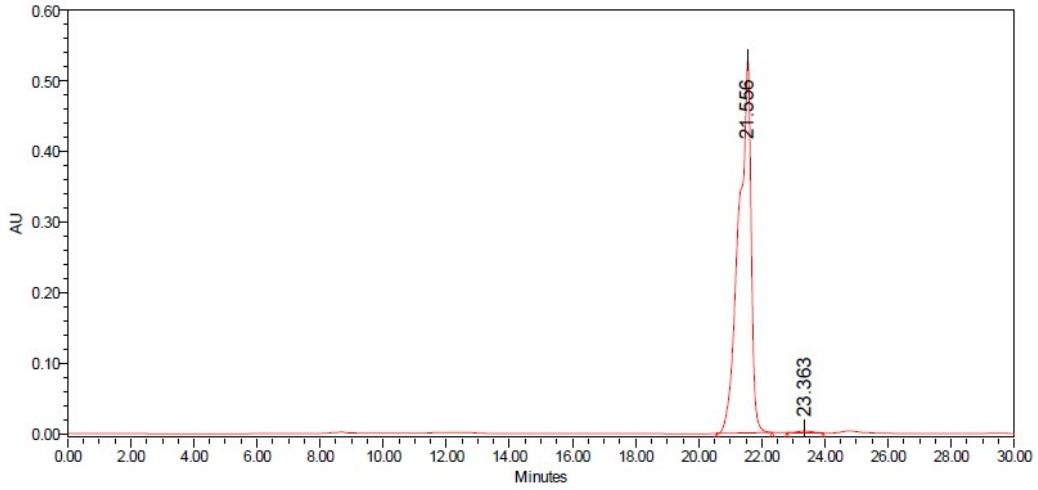
Figure S82. HPLC spectrum of **4k.**



4k



	Ret. Time	Height	Area	% Area
1	21.216	232789	3875781	49.34
2	23.515	76381	3979894	50.66



	Ret. Time	Height	Area	% Area
1	21.556	529236	14322684	99.42
2	23.363	2529	83244	0.58

Figure S83. ^{1}H and ^{13}C NMR spectrum of **4l.**

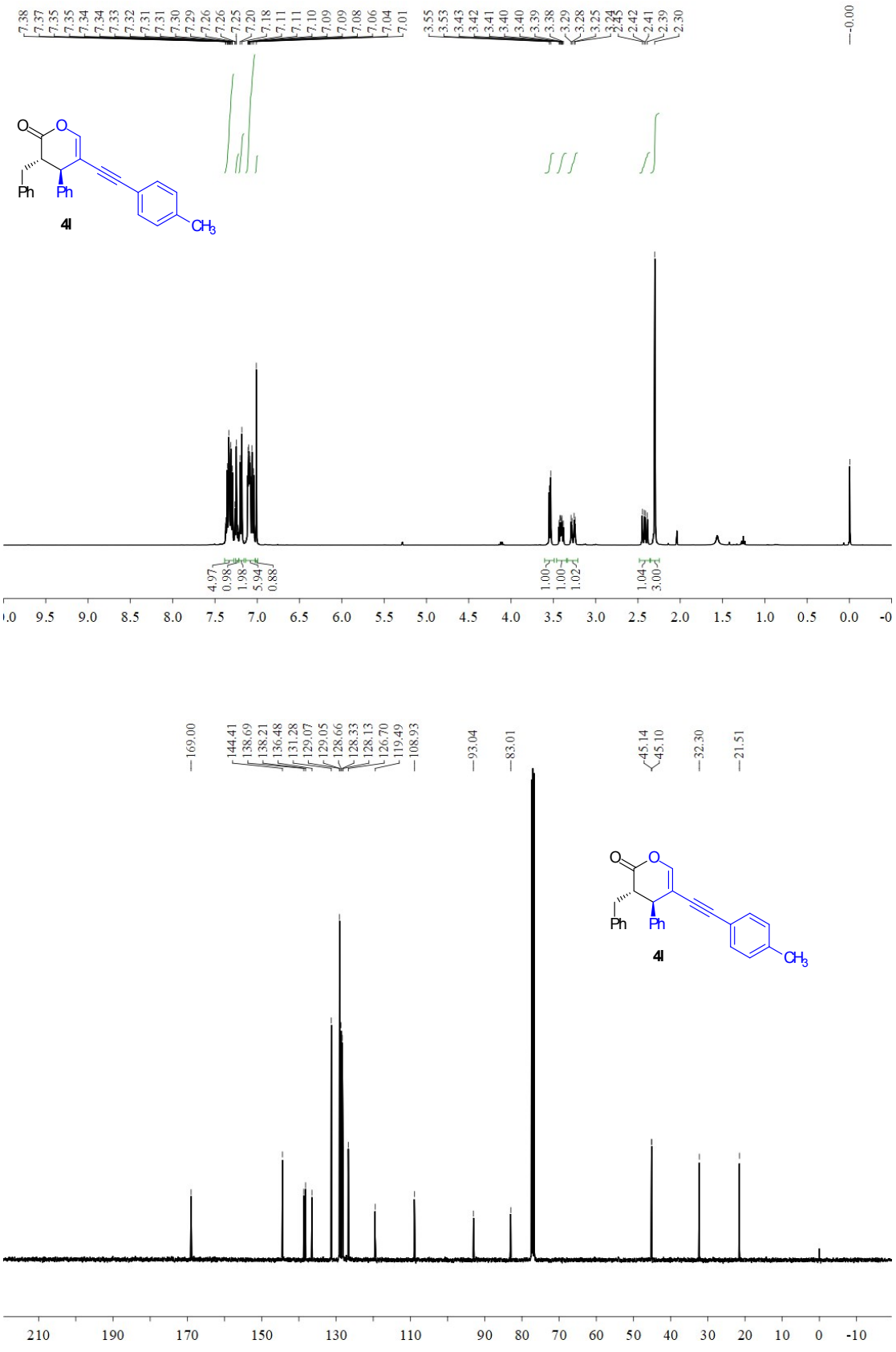
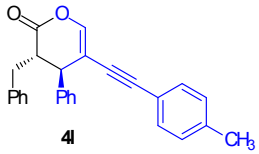
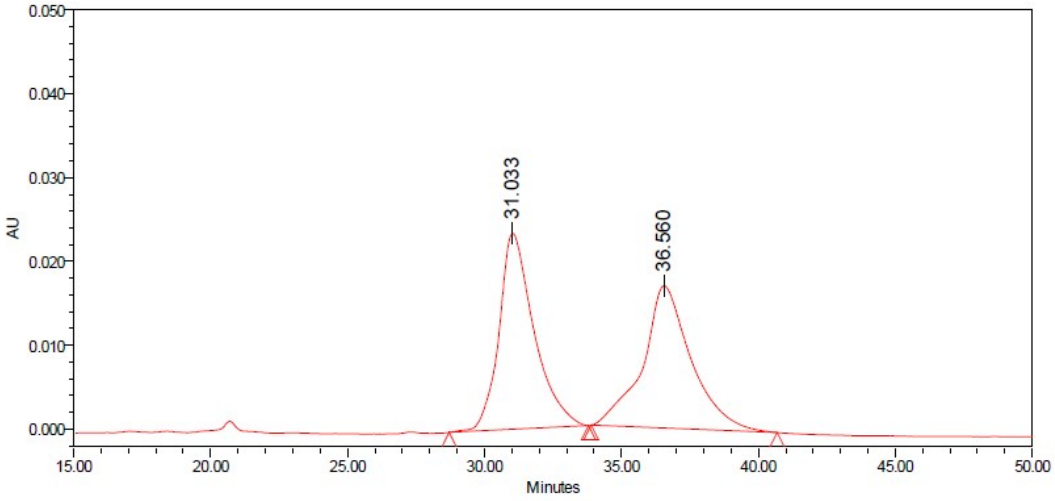


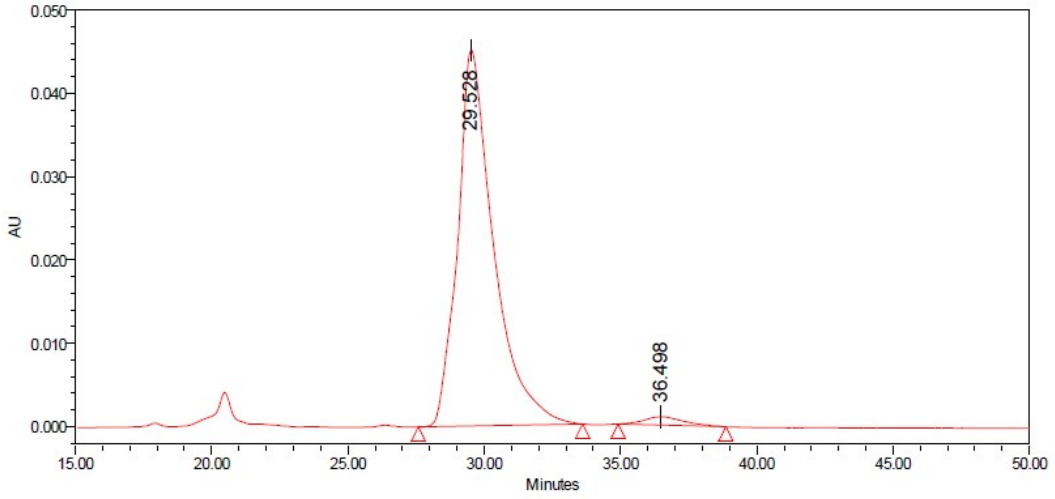
Figure S84. HPLC spectrum of **4l.**



4l



	Ret. Time	Height	Area	% Area
1	31.033	23363	2074597	49.80
2	36.560	16957	2091235	50.20



	Ret. Time	Height	Area	% Area
1	29.528	45105	4148048	97.65
2	36.498	995	99875	2.35

Figure S85. ^{1}H and ^{13}C NMR spectrum of **4m.**

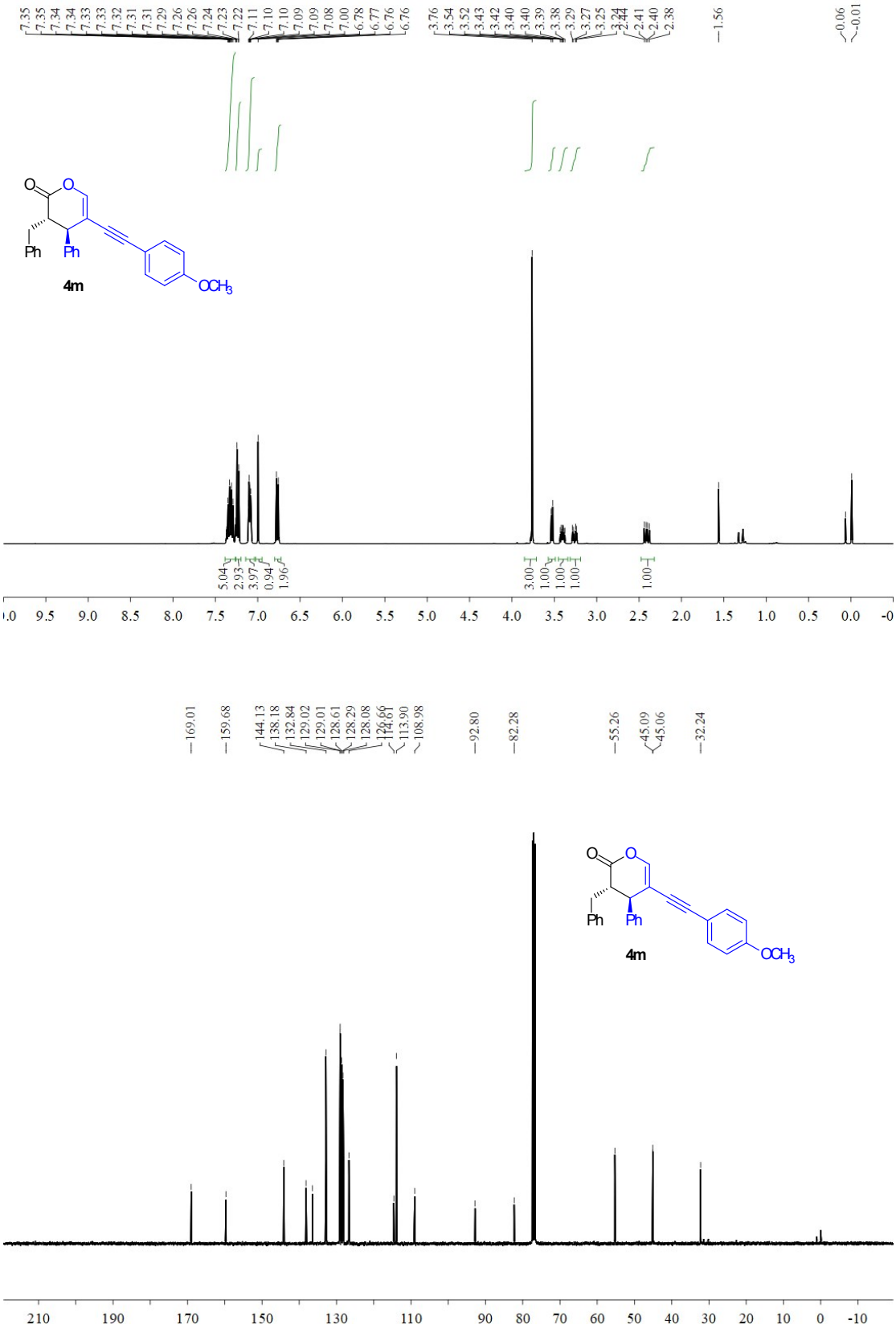
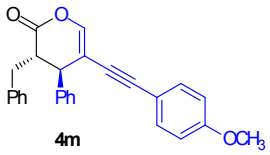
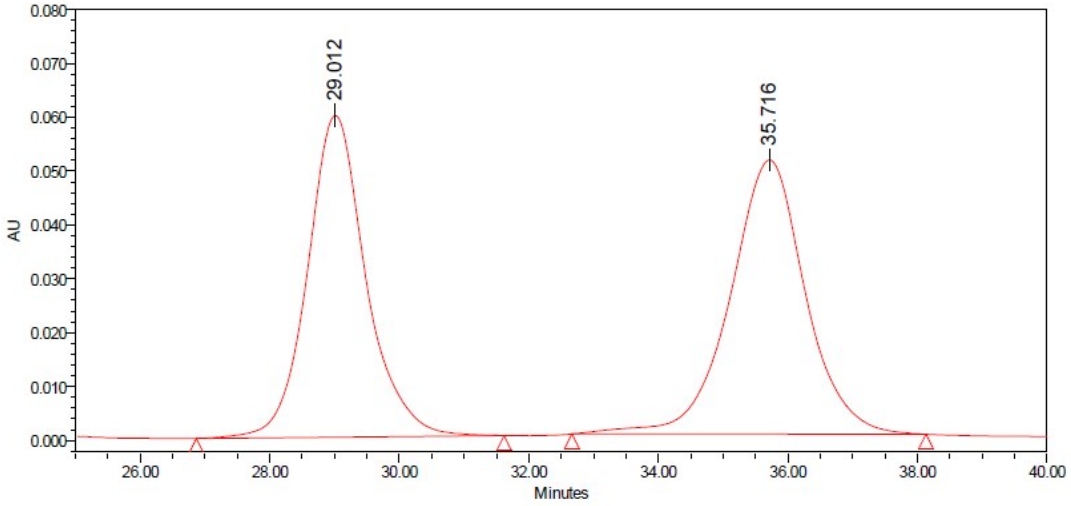


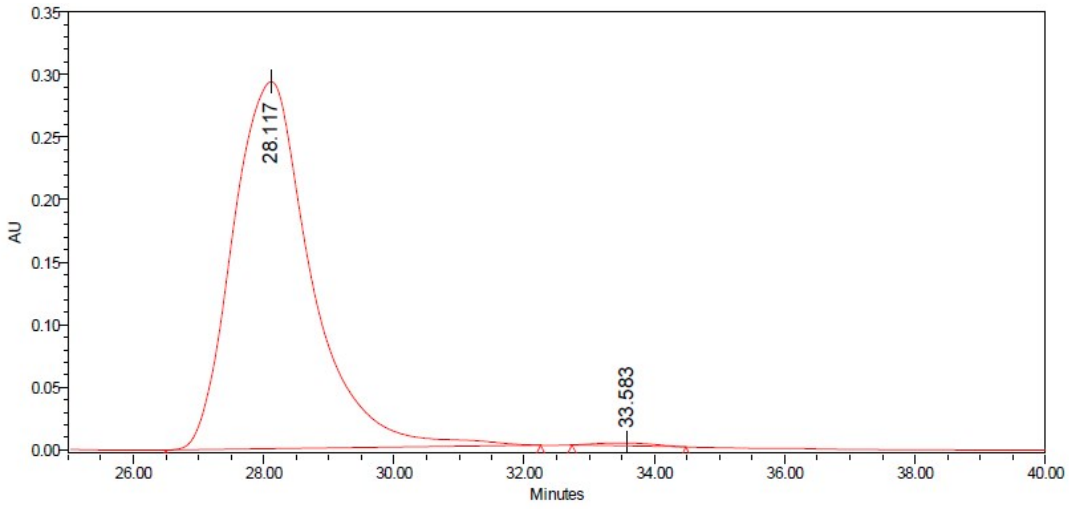
Figure S86. HPLC spectrum of **4m.**



4m



	Ret. Time	Height	Area	% Area
1	29.012	59720	3751145	47.69
2	35.716	50887	4114962	52.31



	Ret. Time	Height	Area	% Area
1	28.117	293385	24585098	99.44
2	33.583	2305	138436	0.56

Figure S87. ^{1}H and ^{13}C NMR spectrum of **4n.**

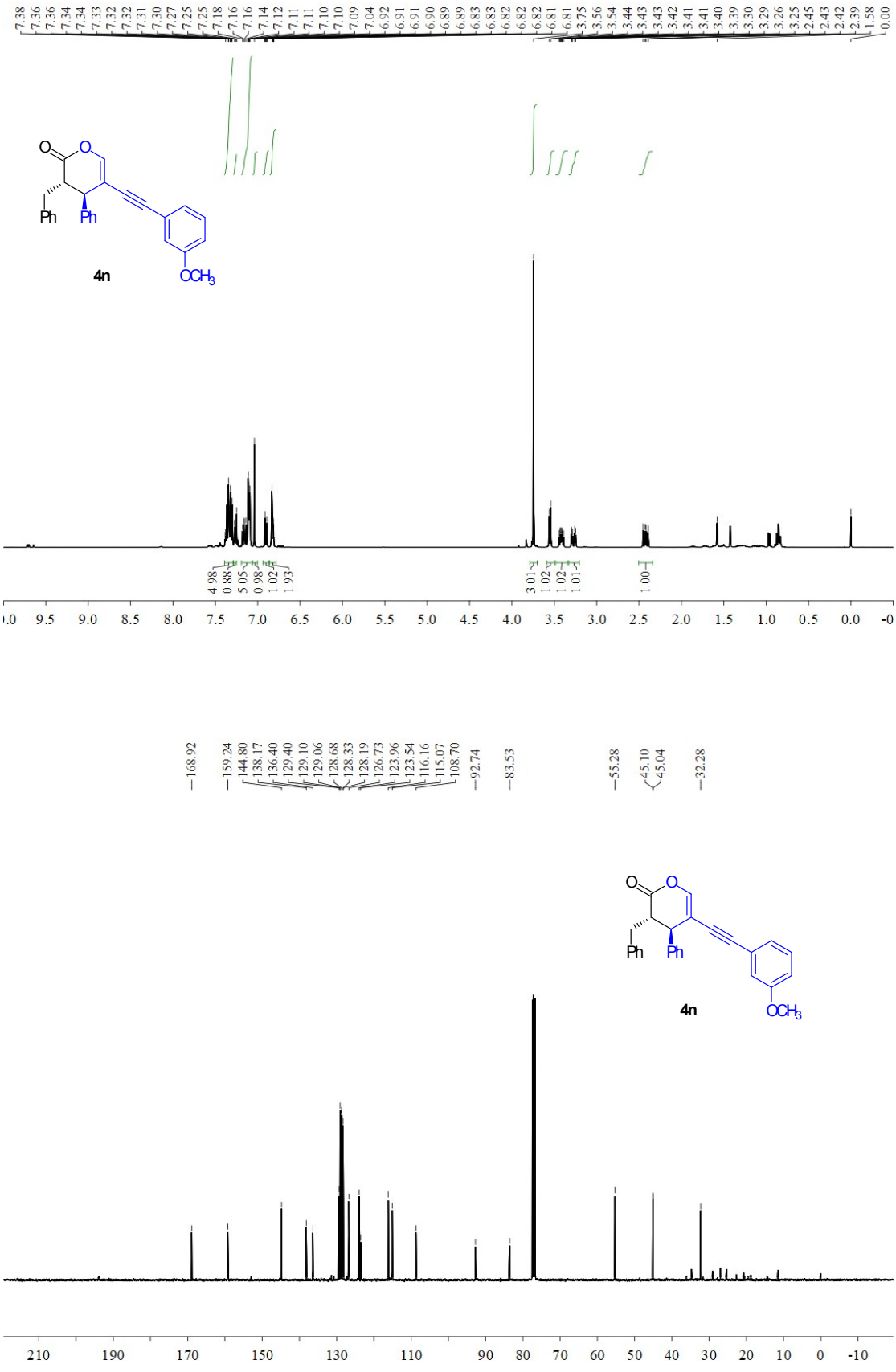
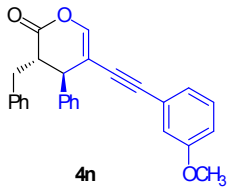
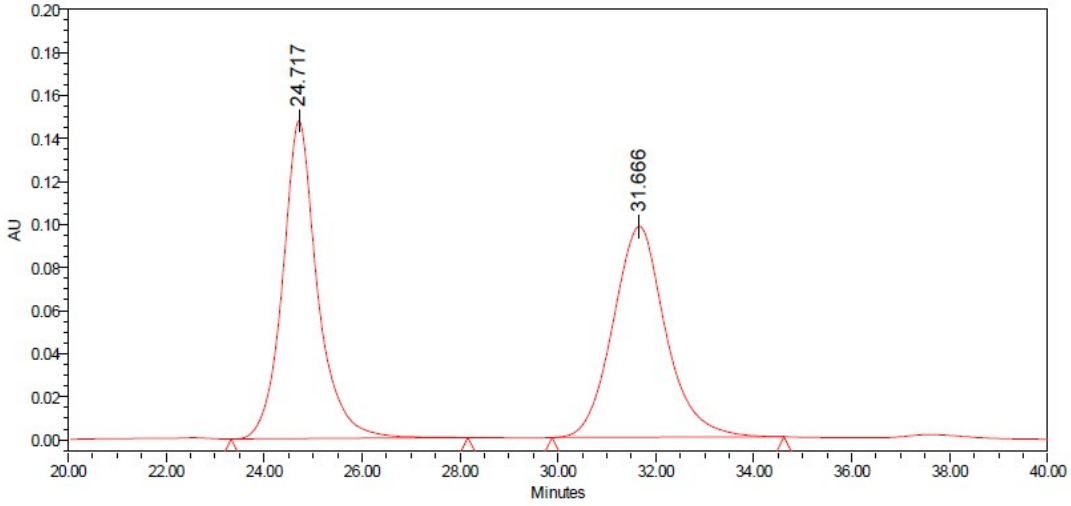


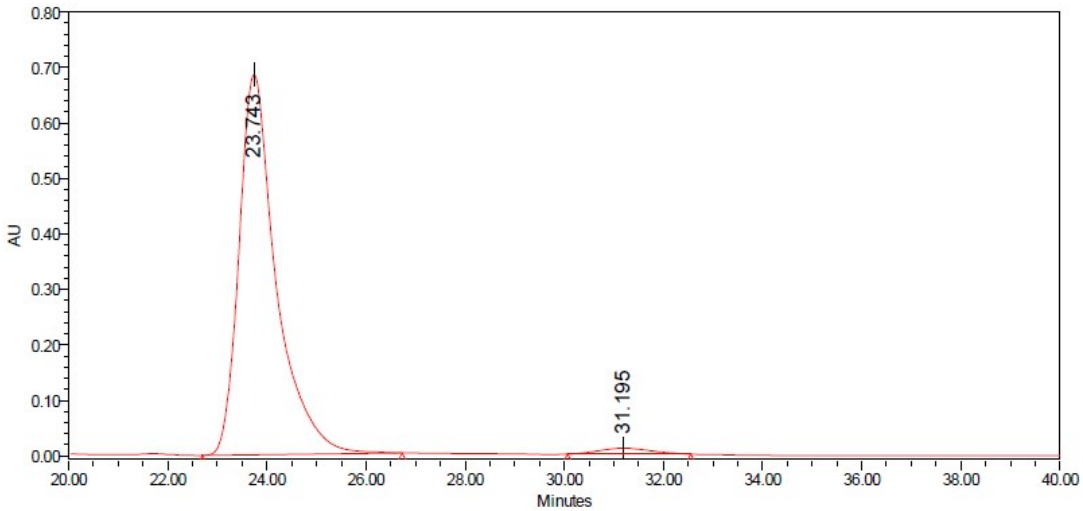
Figure S88. HPLC spectrum of **4n.**



4n

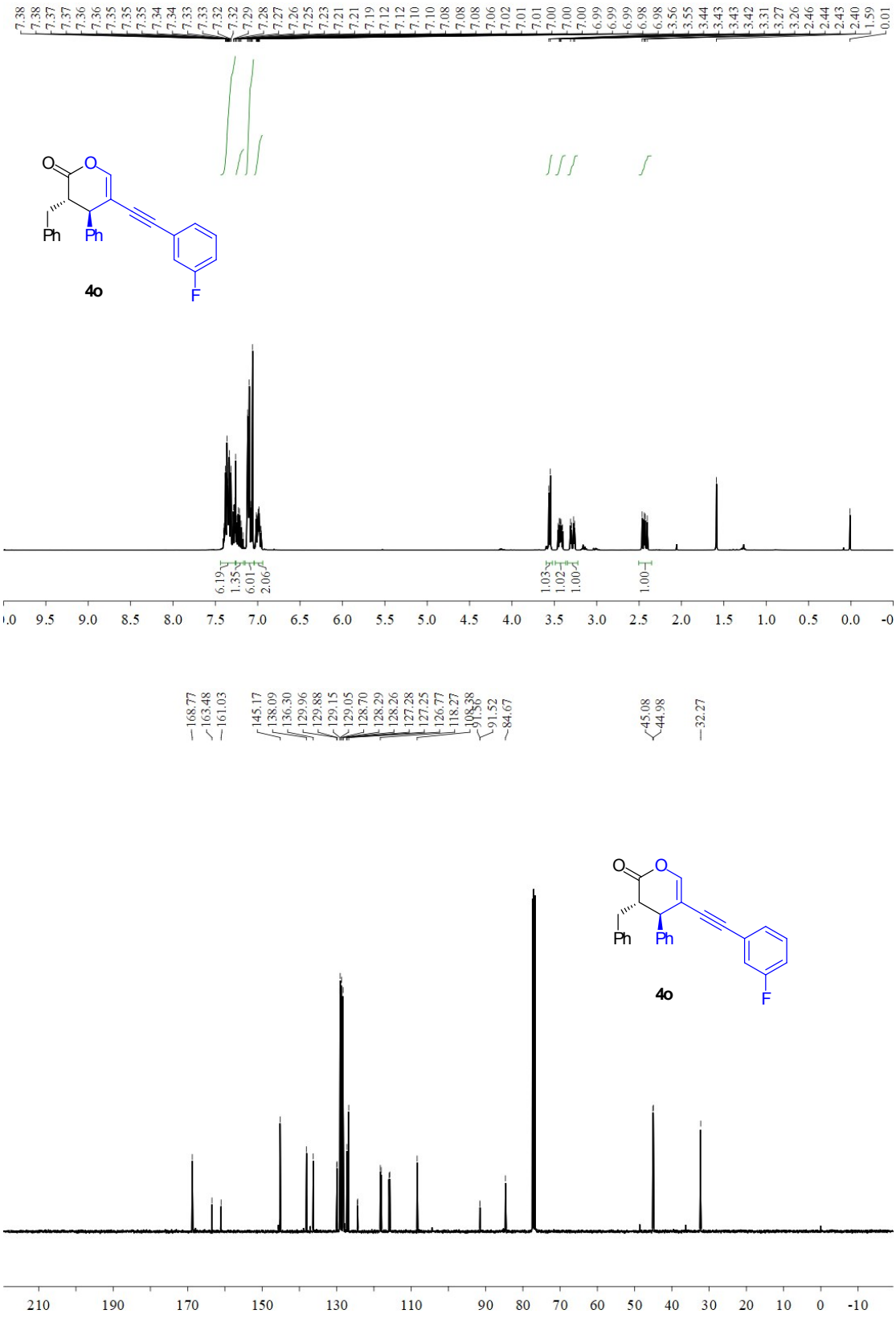


	Ret. Time	Height	Area	% Area
1	24.717	147619	7325814	49.99
2	31.666	98040	7329078	50.01



	Ret. Time	Height	Area	% Area
1	23.743	685422	35621364	97.92
2	31.195	10519	757155	2.08

Figure S89. ^{1}H and ^{13}C NMR spectrum of **4o.**



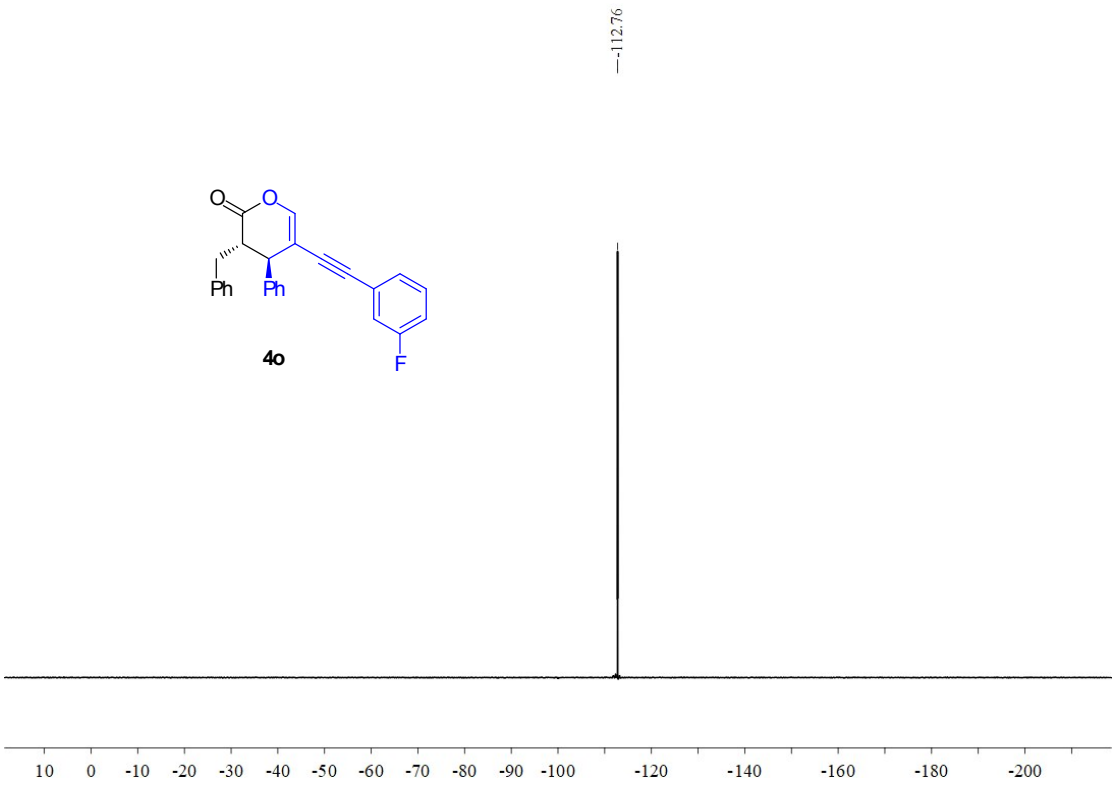
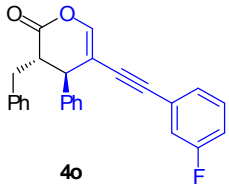
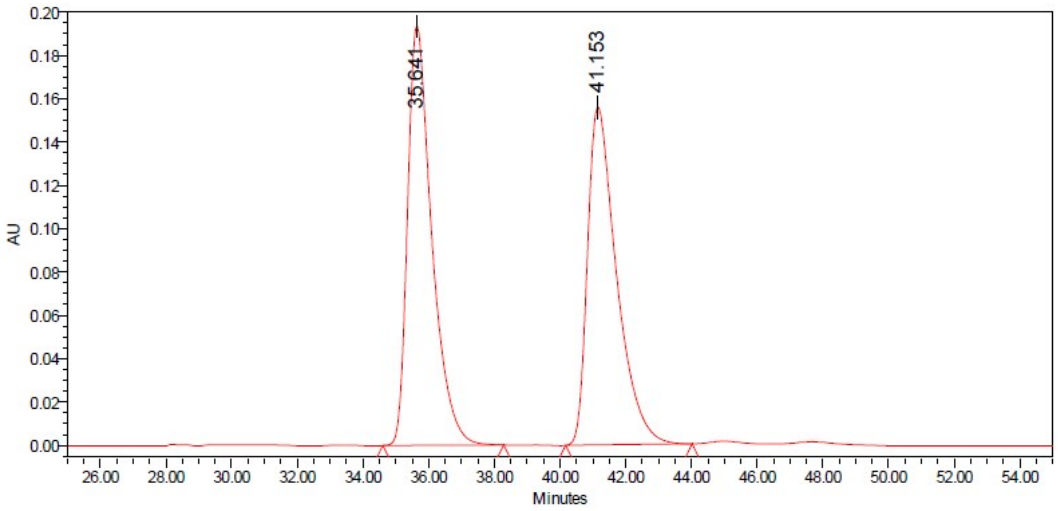

-112.76
O
O
Ph
Ph
F
4o
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

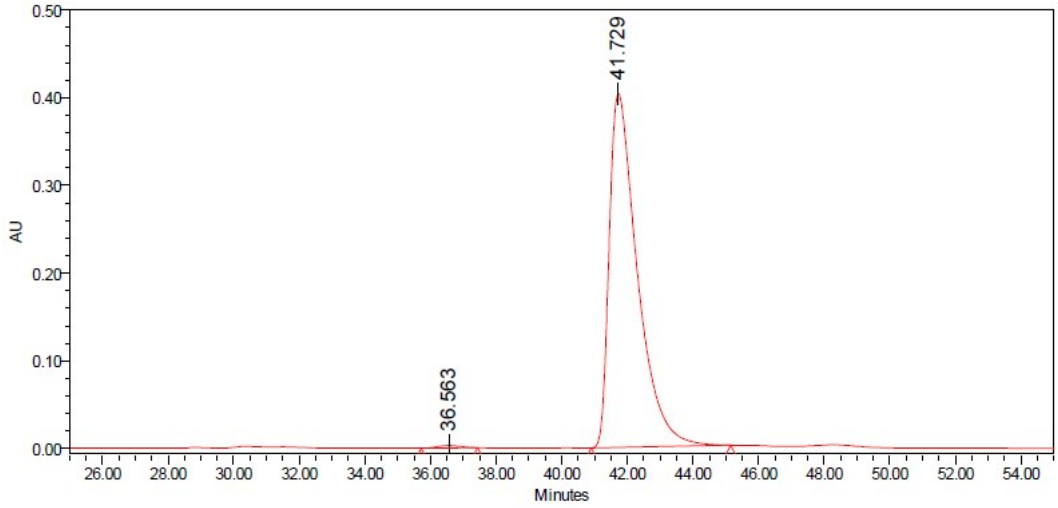
Figure S90. HPLC spectrum of **4o.**



4o



	Ret. Time	Height	Area	% Area
1	35.641	193577	9914818	50.87
2	41.153	155859	9574539	49.13



	Ret. Time	Height	Area	% Area
1	36.563	2677	132390	0.55
2	41.729	403236	24033008	99.45

Figure S91. ^{1}H and ^{13}C NMR spectrum of **4p.**

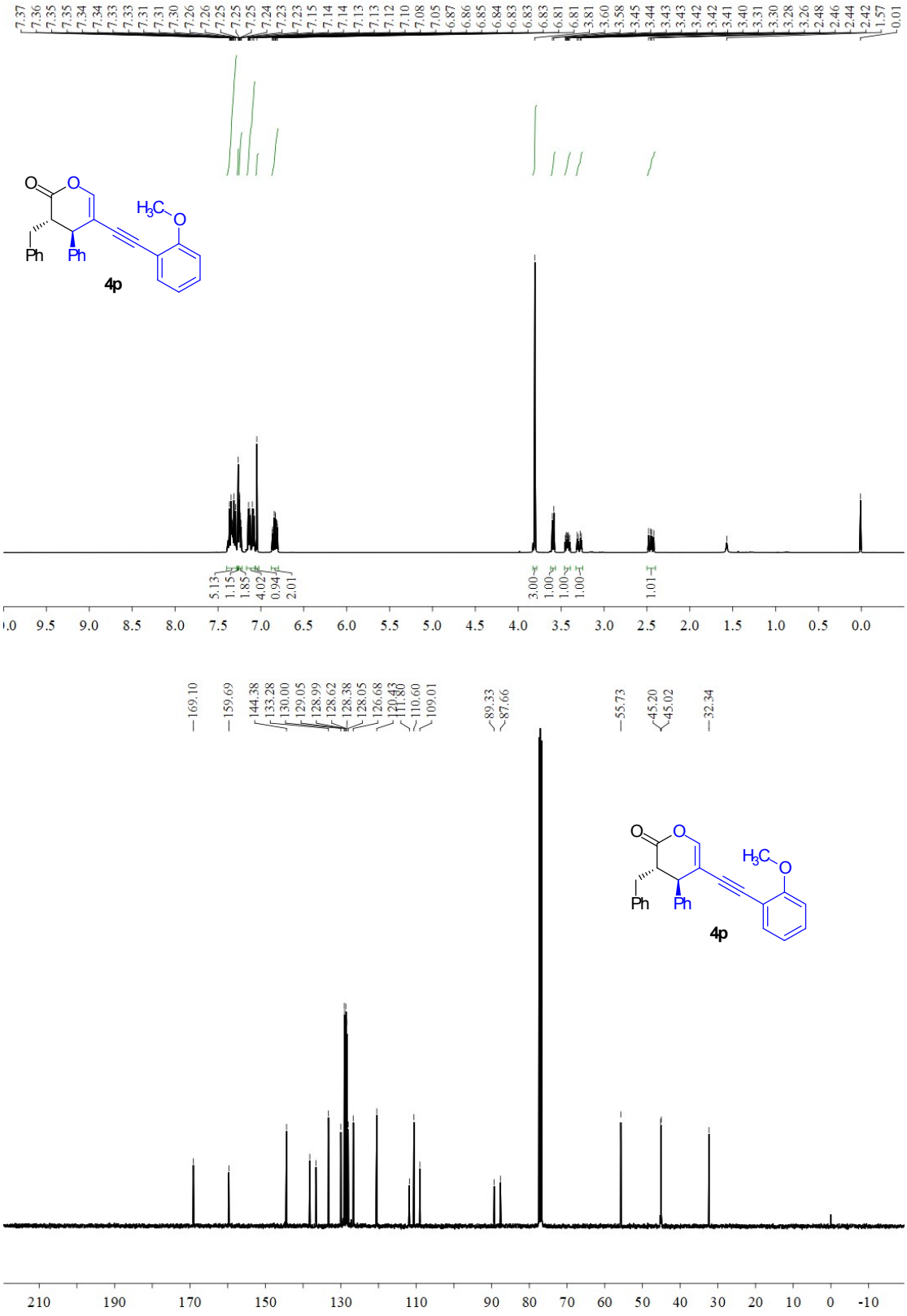
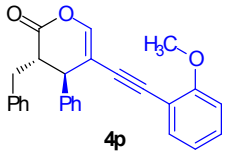
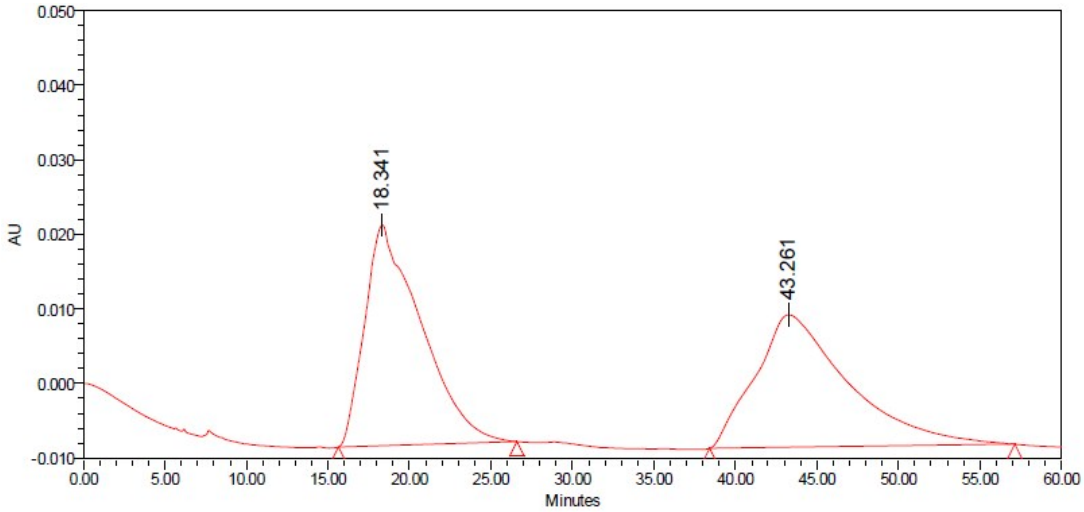


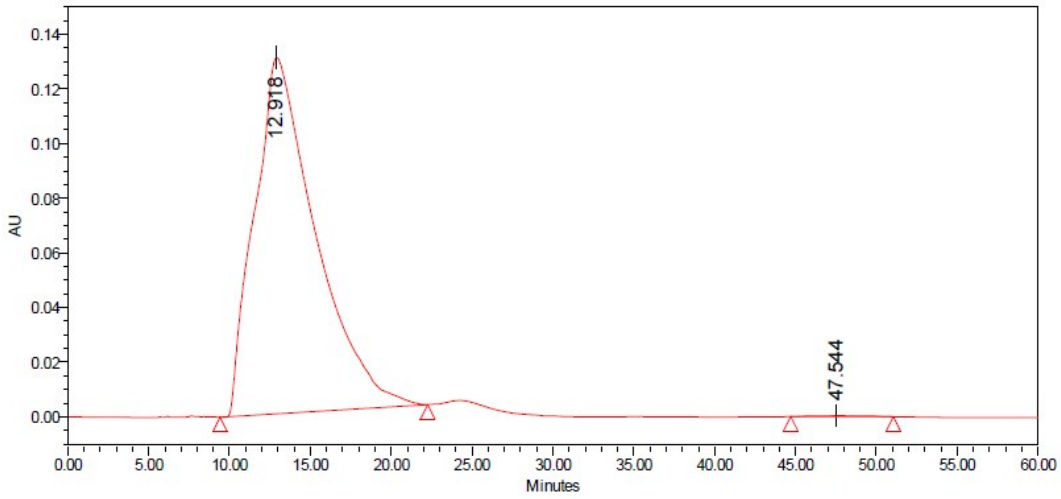
Figure S92. HPLC spectrum of **4p.**



4p



	Ret. Time	Height	Area	% Area
1	18.341	29580	7137049	50.32
2	43.261	17766	7046587	49.68



	Ret. Time	Height	Area	% Area
1	12.918	130244	34267248	99.76
2	47.544	364	82397	0.24

Figure S93. ^{1}H and ^{13}C NMR spectrum of **4q.**

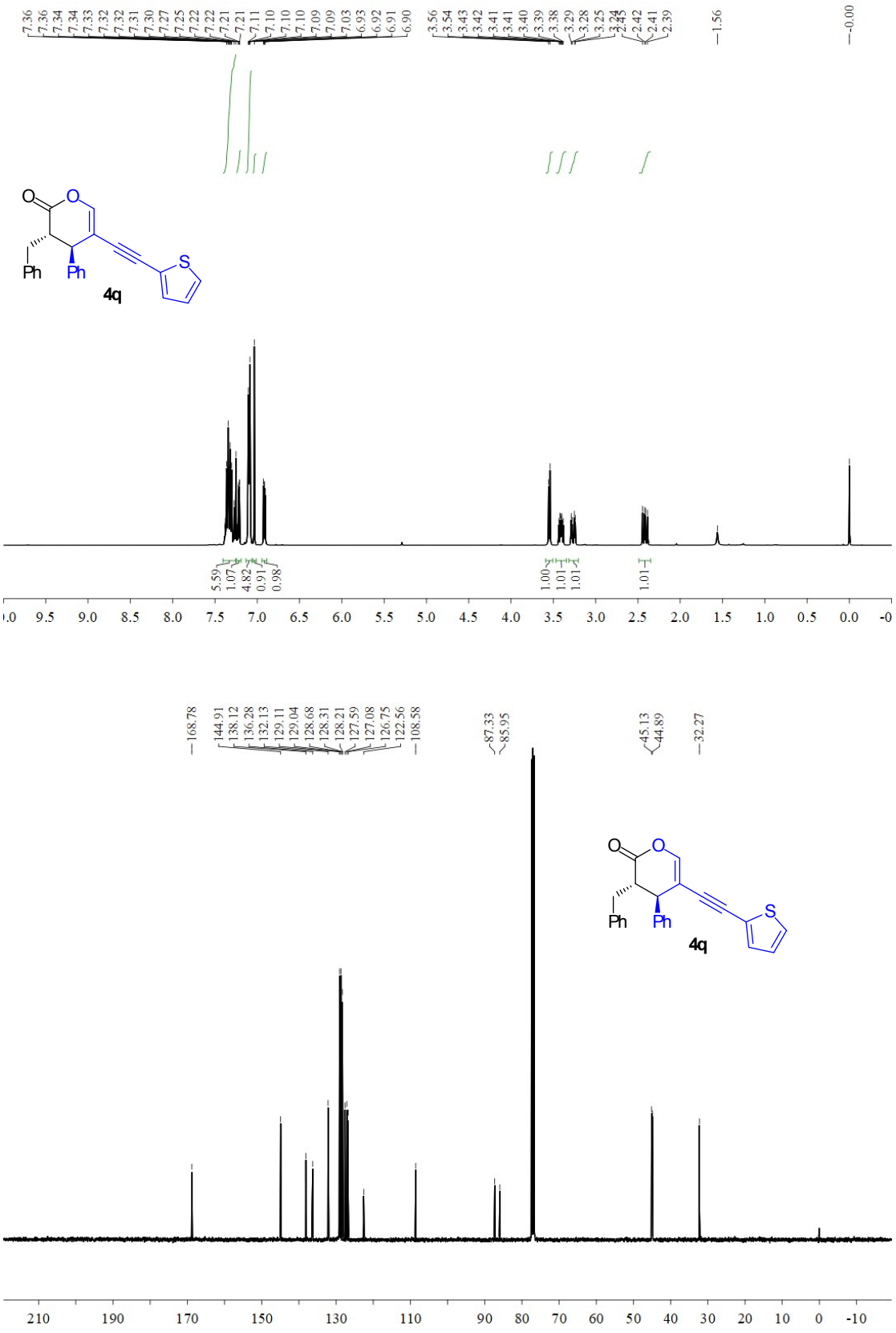
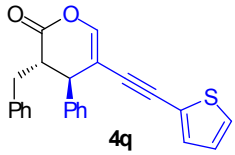
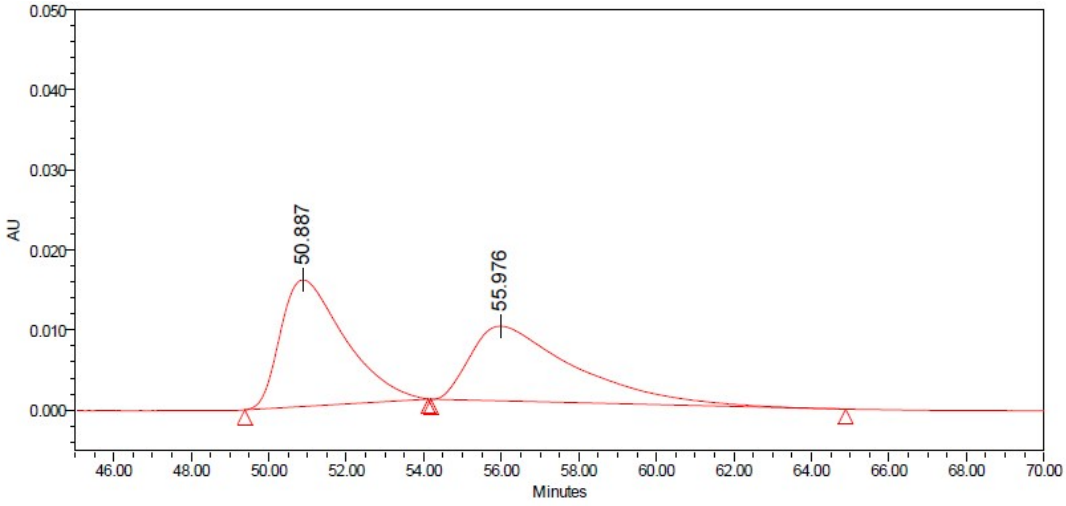


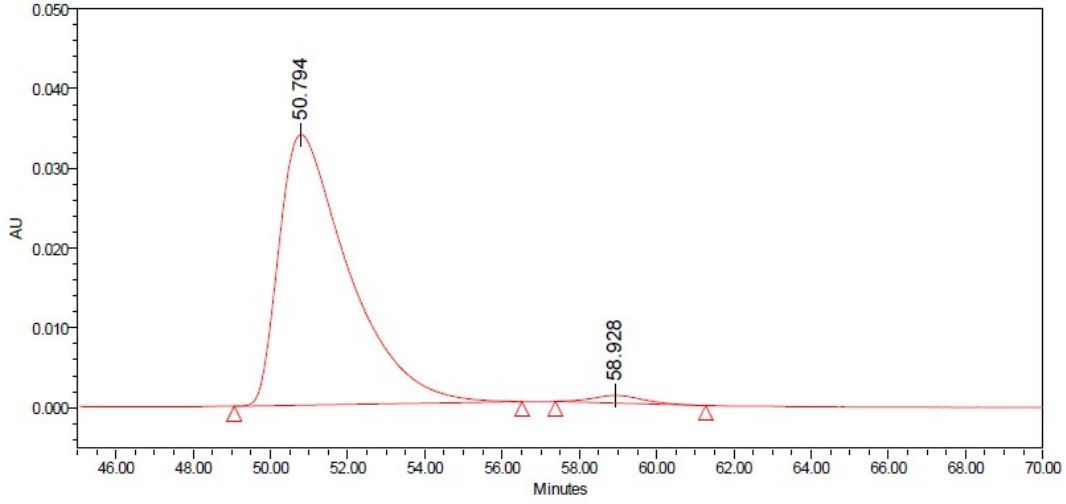
Figure S94. HPLC spectrum of **4p.**



4q



	Ret. Time	Height	Area	% Area
1	50.887	15812	1818518	51.05
2	55.976	9343	1743511	48.95



	Ret. Time	Height	Area	% Area
1	50.794	33926	4249565	98.00
2	58.928	943	86868	2.00

Figure S95. ^{1}H and ^{13}C NMR spectrum of **4r.**

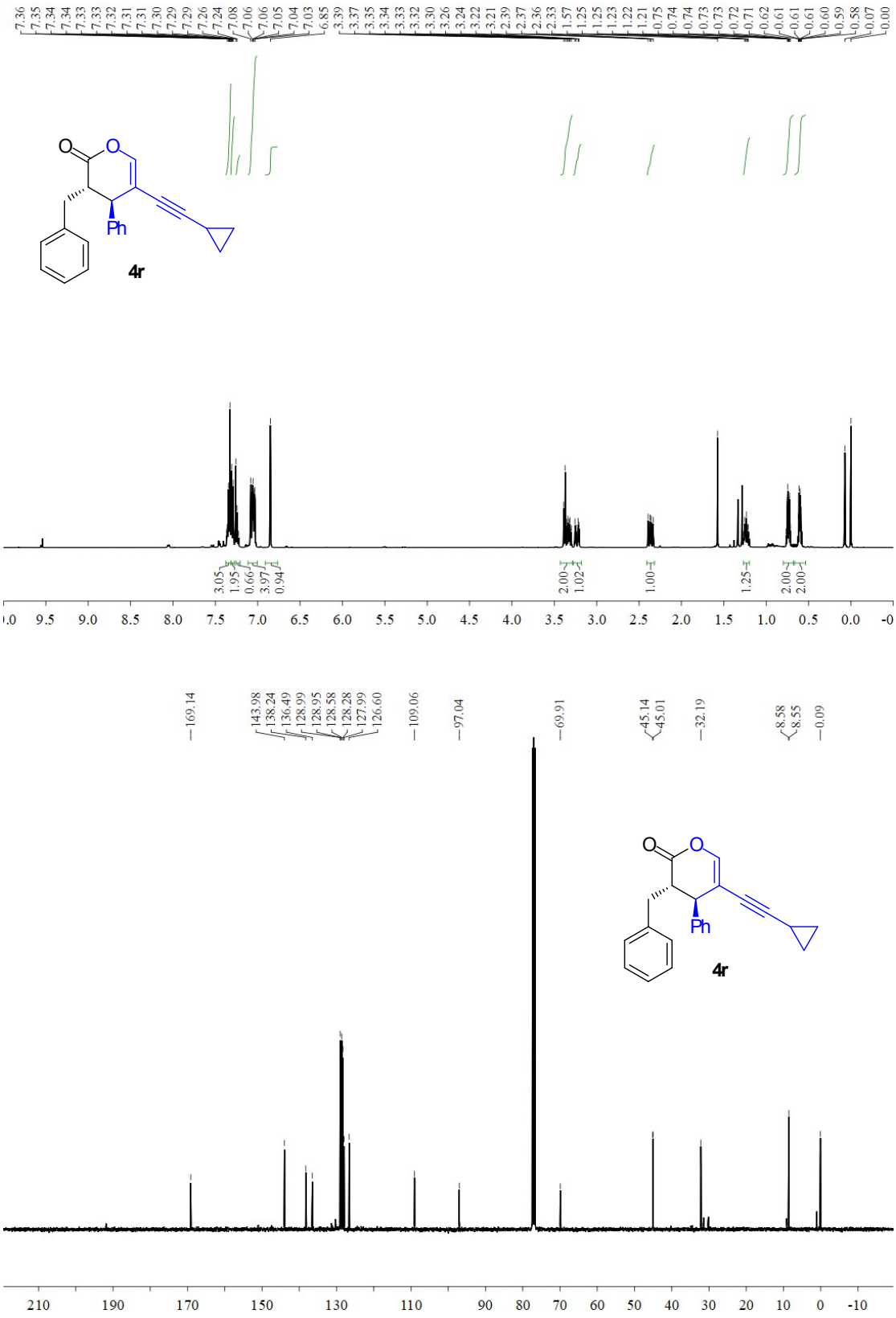
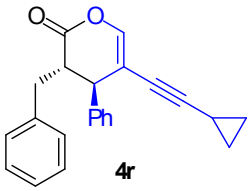
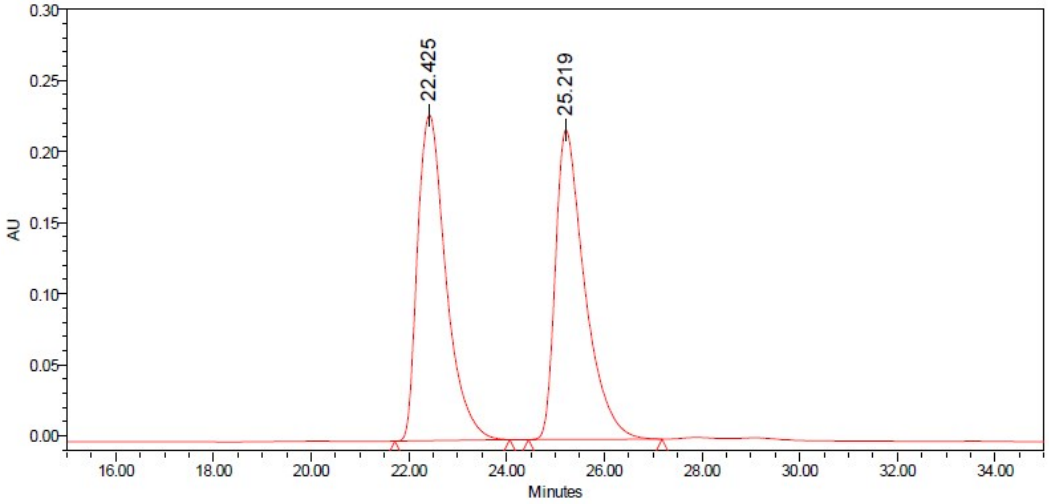


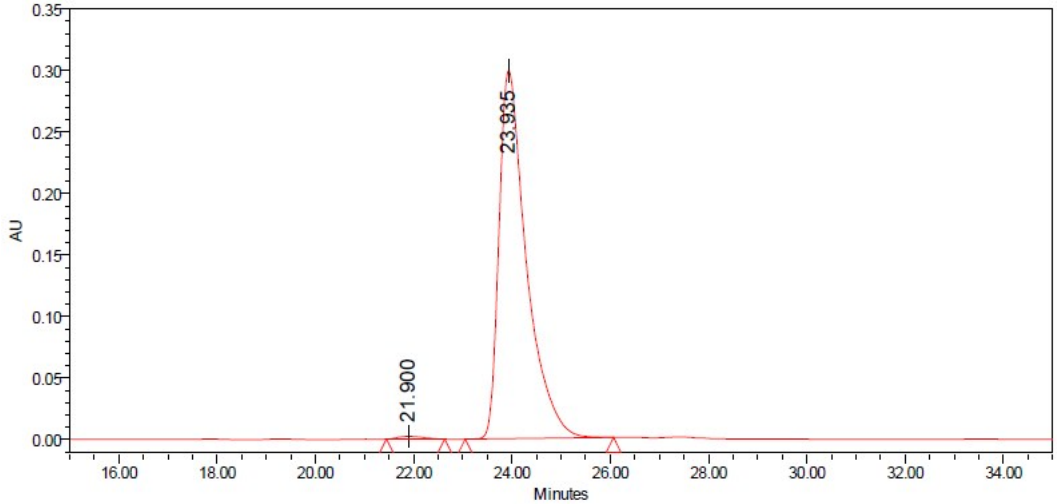
Figure S96. HPLC spectrum of **4r.**



4r

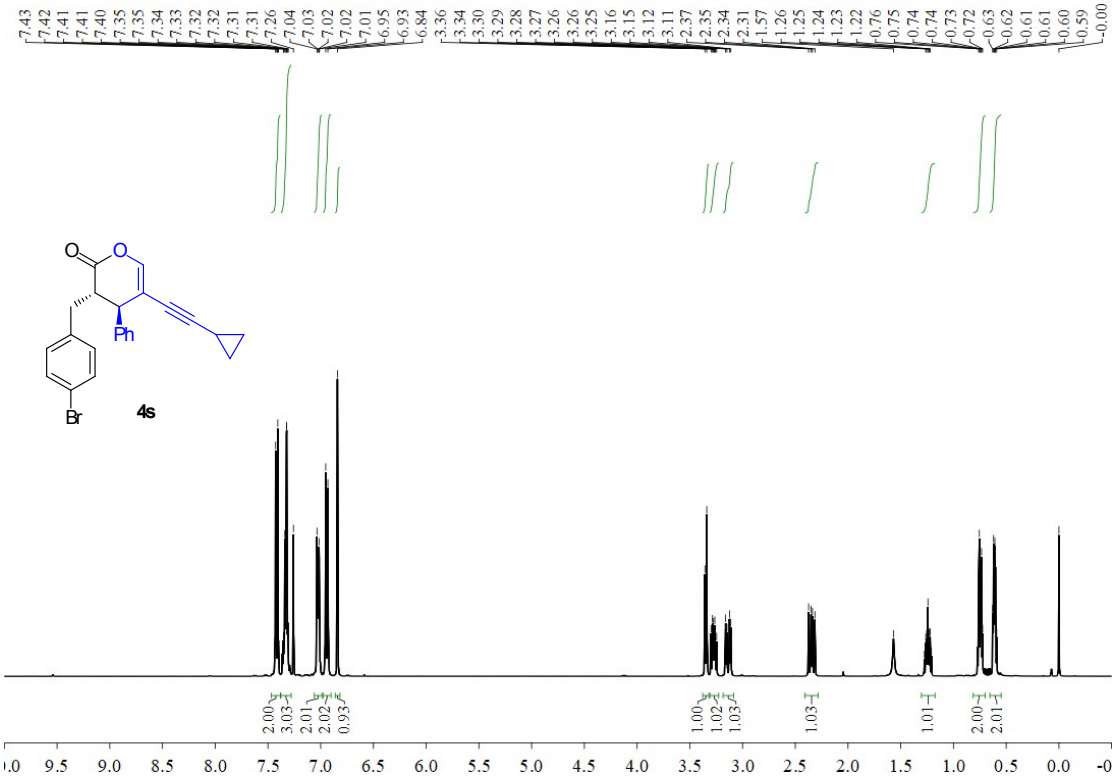


	Ret. Time	Height	Area	% Area
1	22.425	229015	9261397	50.48
2	25.219	217733	9084852	49.52



	Ret. Time	Height	Area	% Area
1	21.900	2167	79385	0.68
2	23.935	298963	11595660	99.32

Figure S97. ^{1}H and ^{13}C NMR spectrum of **4s.**



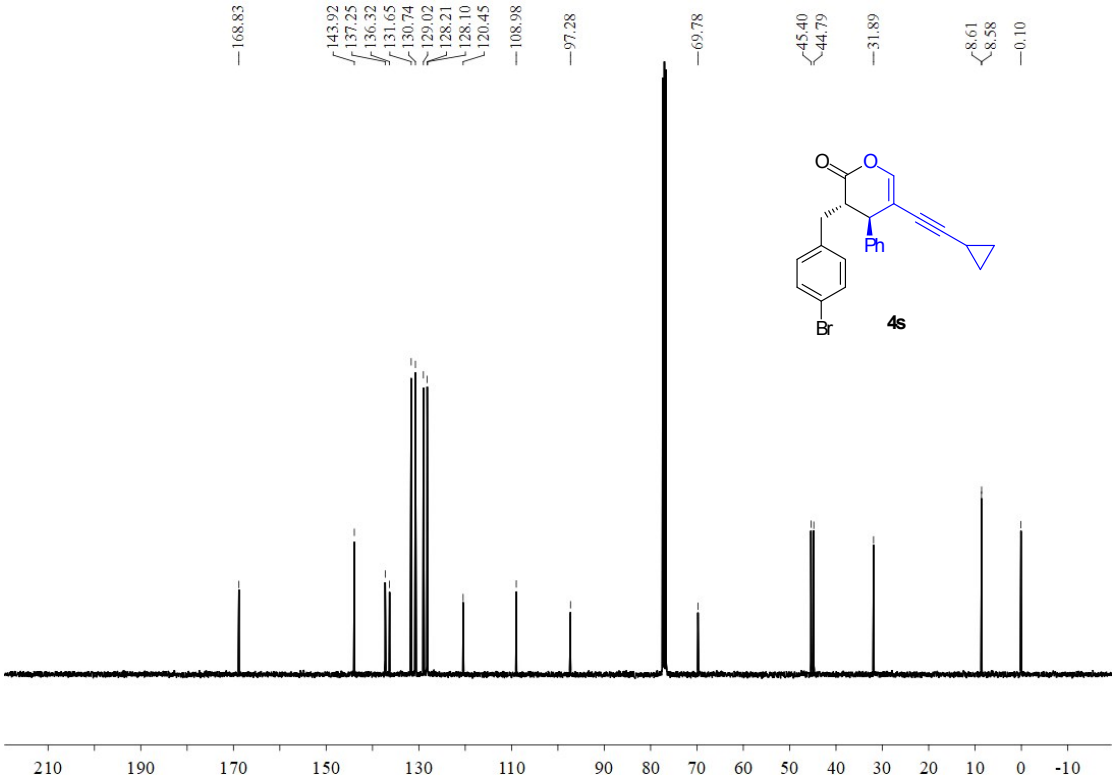
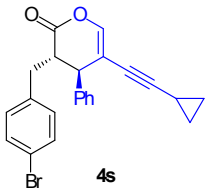
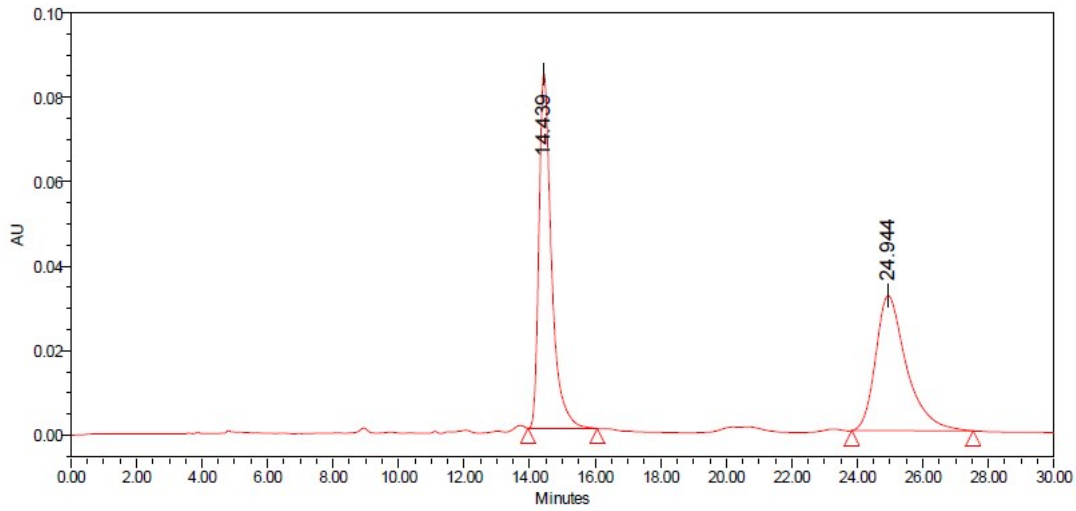


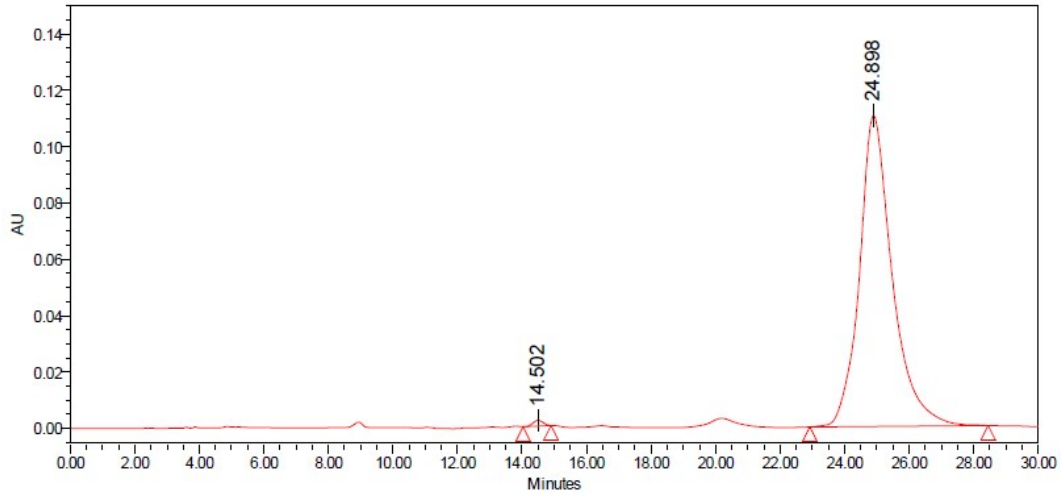
Figure S98. HPLC spectrum of **4s.**



4s



	Ret. Time	Height	Area	% Area
1	14.439	84084	2231609	51.64
2	24.944	31985	2089885	48.36



	Ret. Time	Height	Area	% Area
1	14.502	2005	43765	0.56
2	24.898	110328	7809406	99.44

Figure S99. ^{1}H and ^{13}C NMR spectrum of **4t.**

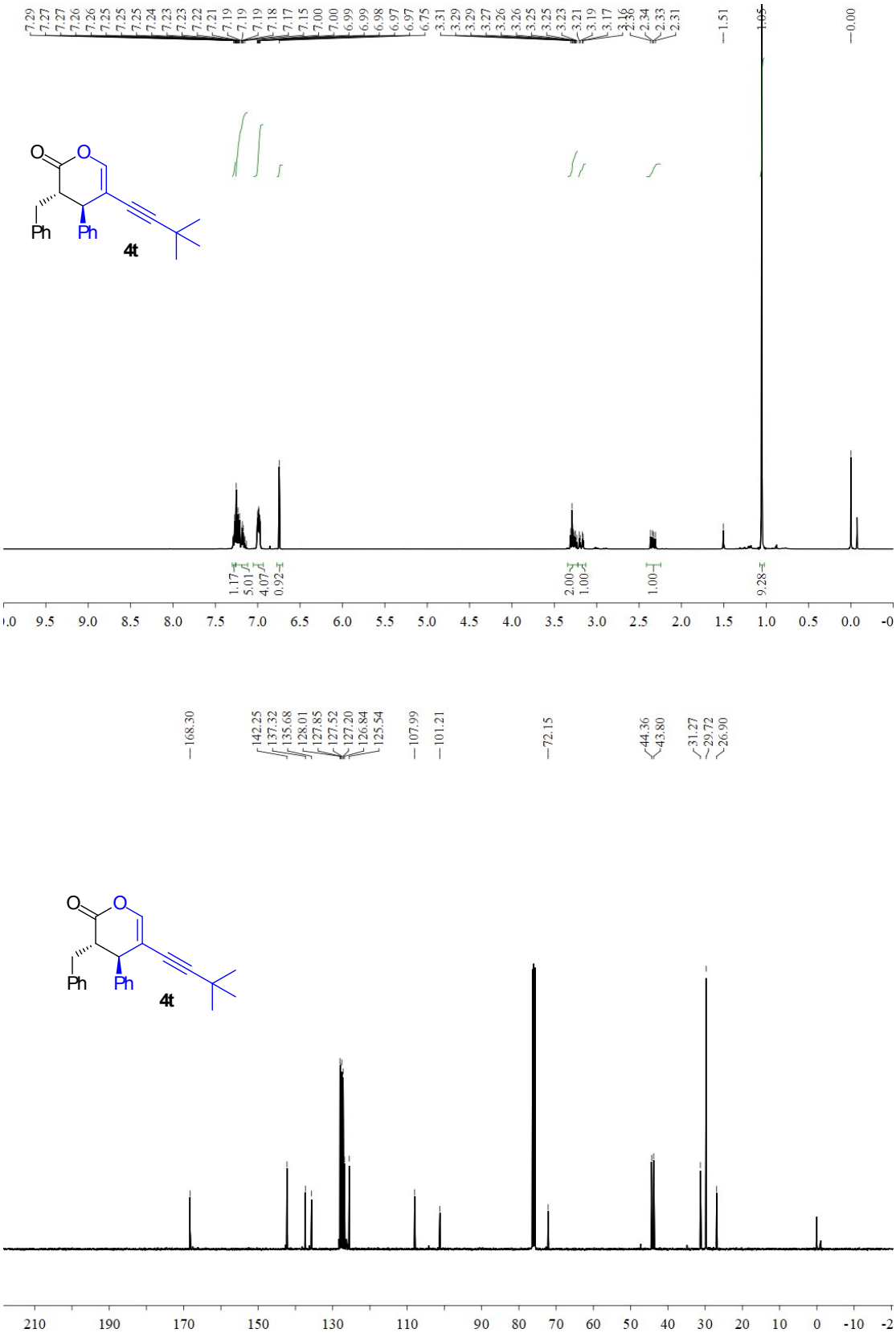
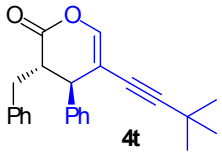
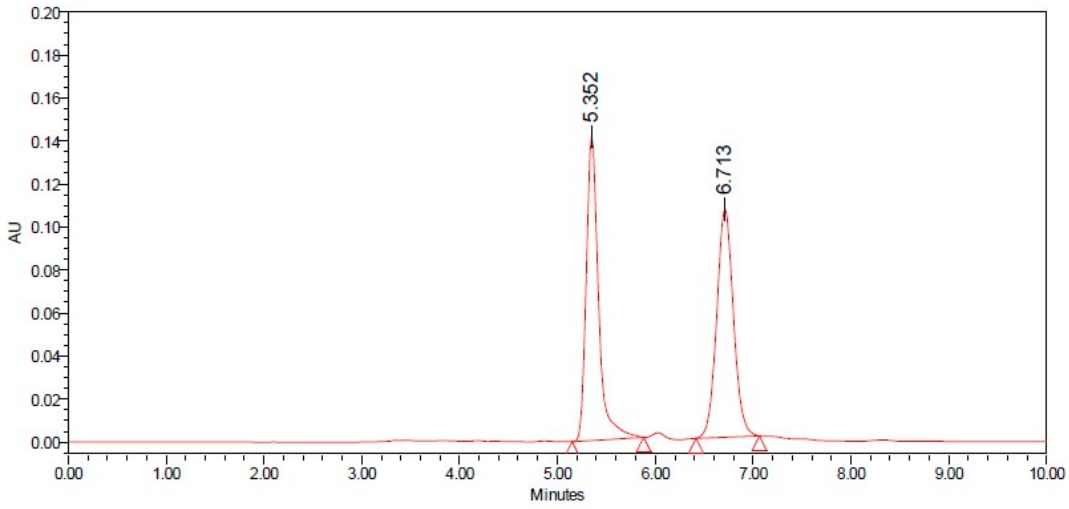


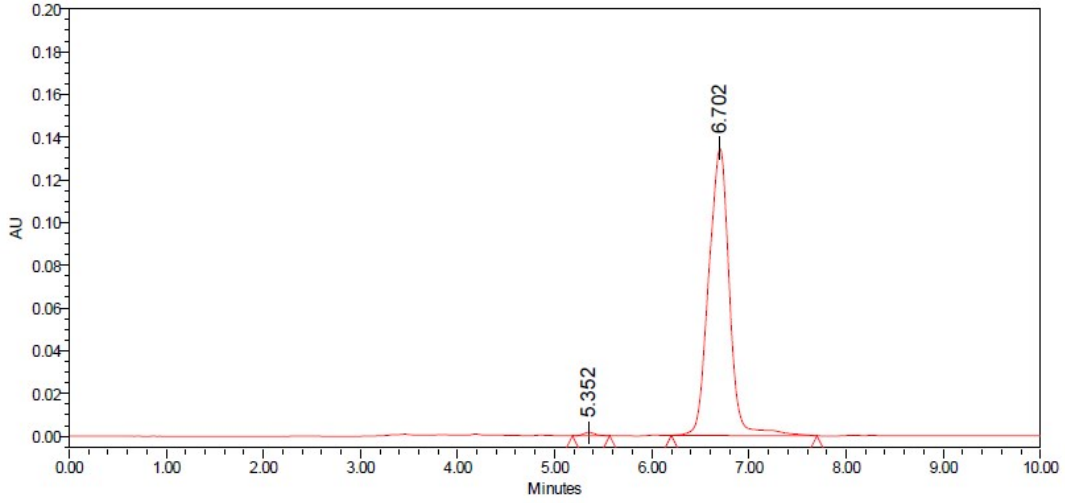
Figure S100. HPLC spectrum of **4t.**



4t



	Ret. Time	Height	Area	% Area
1	5.352	141537	1232803	49.52
2	6.713	106208	1256516	50.48



	Ret. Time	Height	Area	% Area
1	5.352	1590	12927	0.65
2	6.702	134474	1984418	99.35

Figure S101. ^{1}H and ^{13}C NMR spectrum of **4u.**

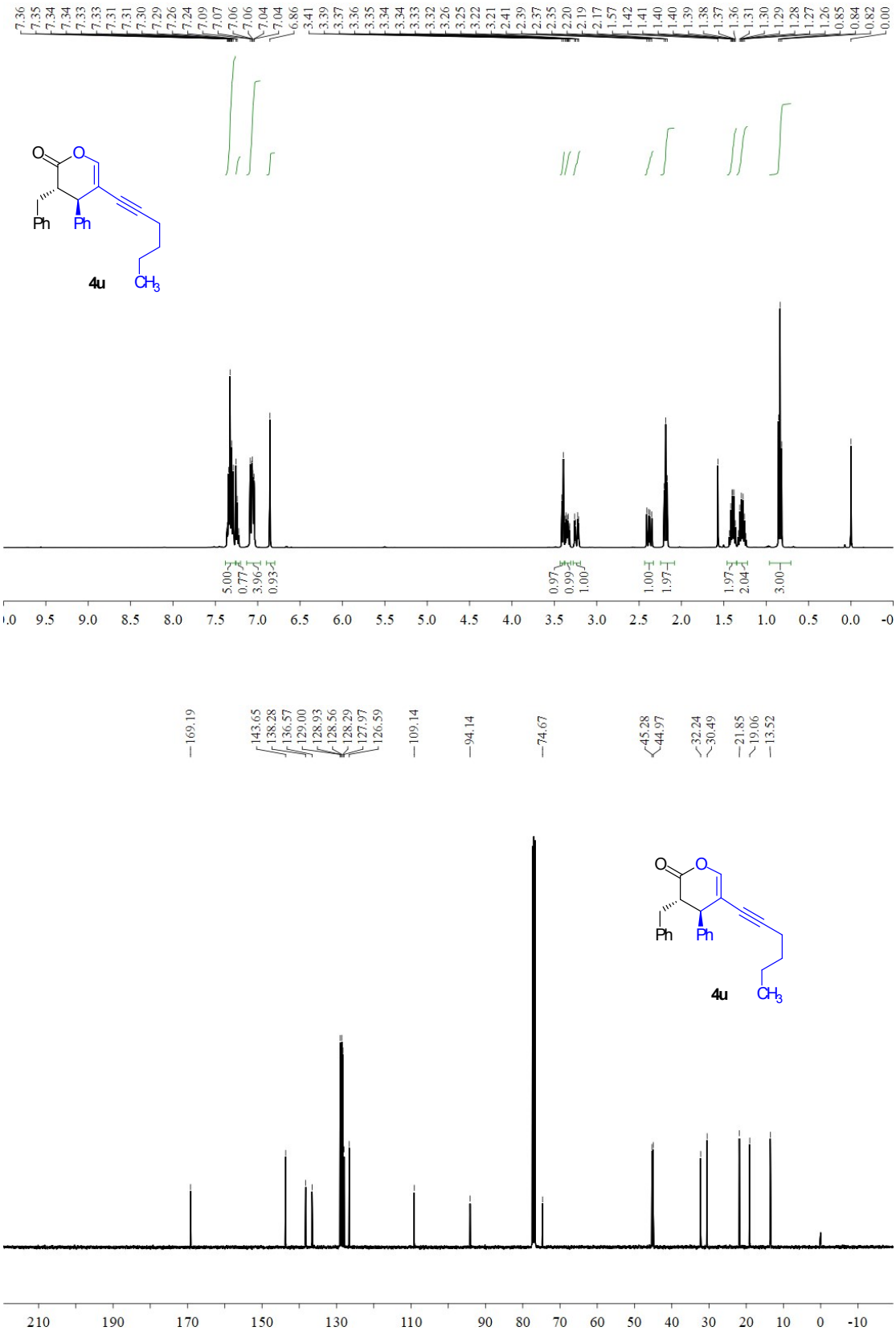
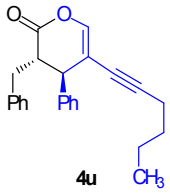
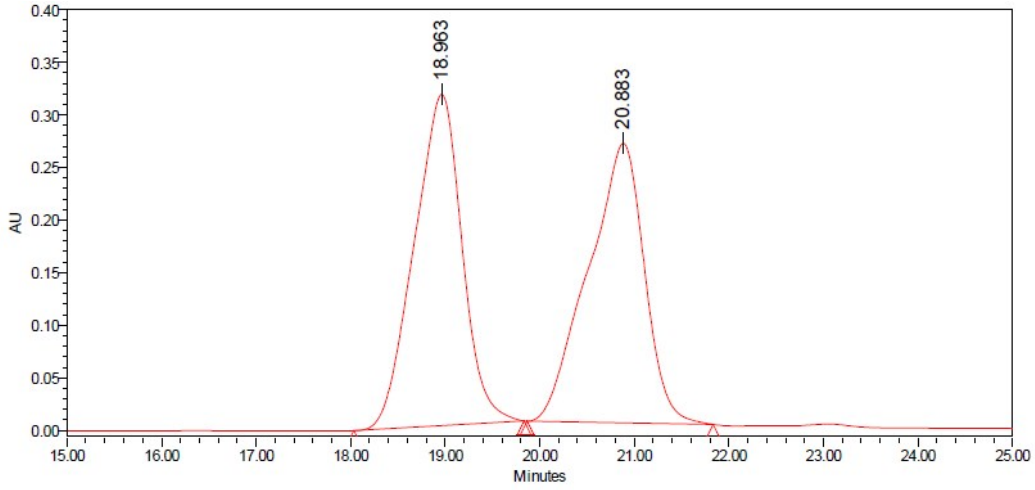


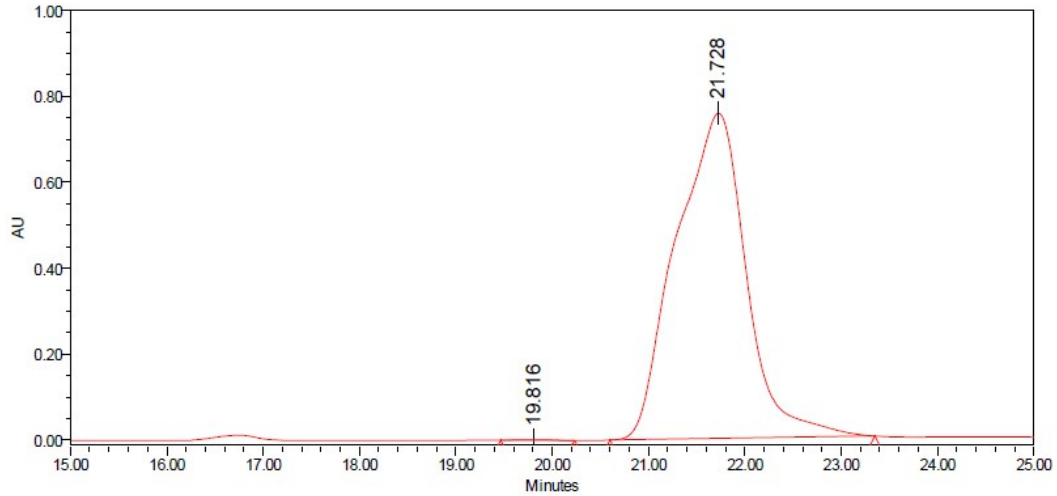
Figure S102. HPLC spectrum of **4u.**



4u



	Ret. Time	Height	Area	% Area
1	18.963	315107	11098850	50.26
2	20.883	265839	10982065	49.74



	Ret. Time	Height	Area	% Area
1	19.816	775	17919	0.05
2	21.728	757167	38329173	99.95

Figure S103. ^{1}H and ^{13}C NMR spectrum of **4v.**

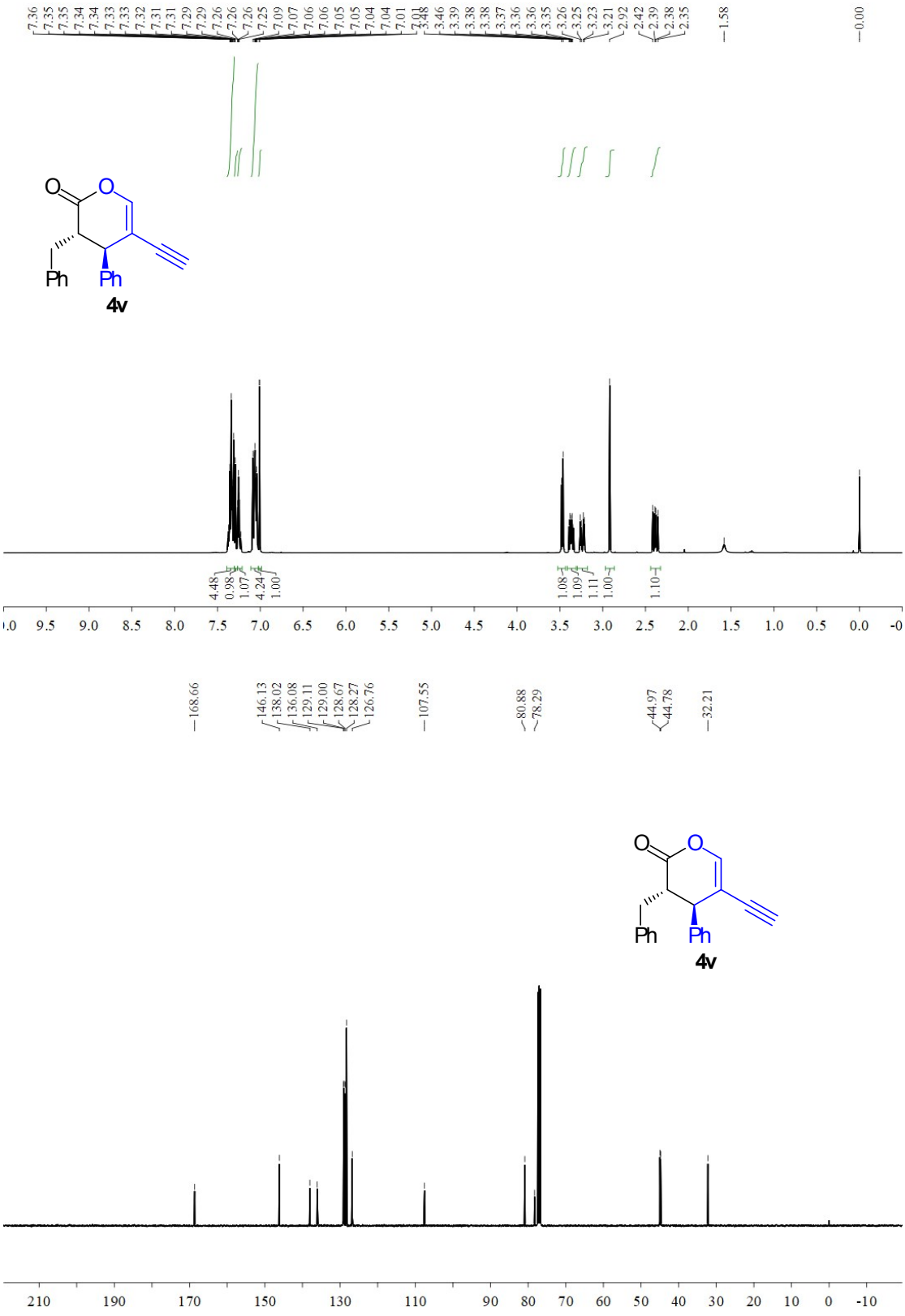
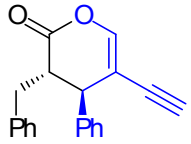
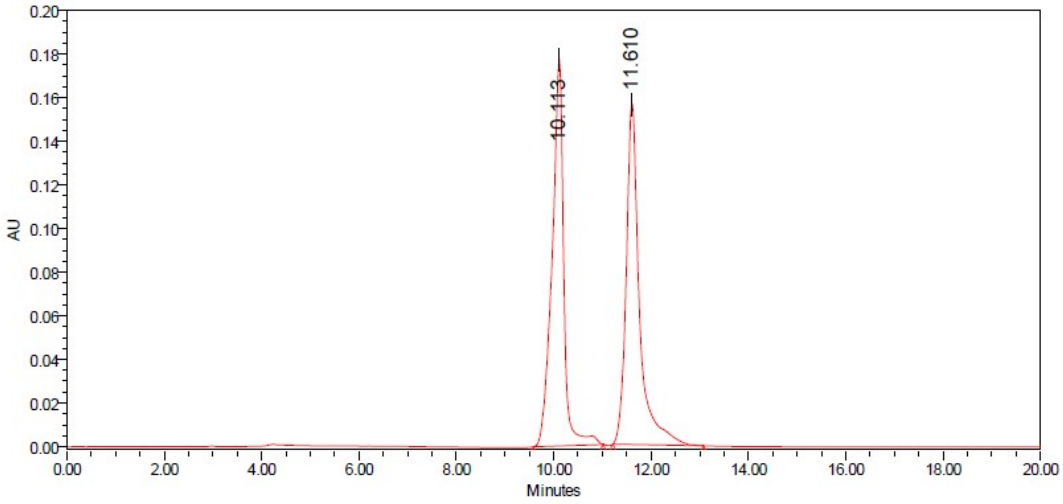


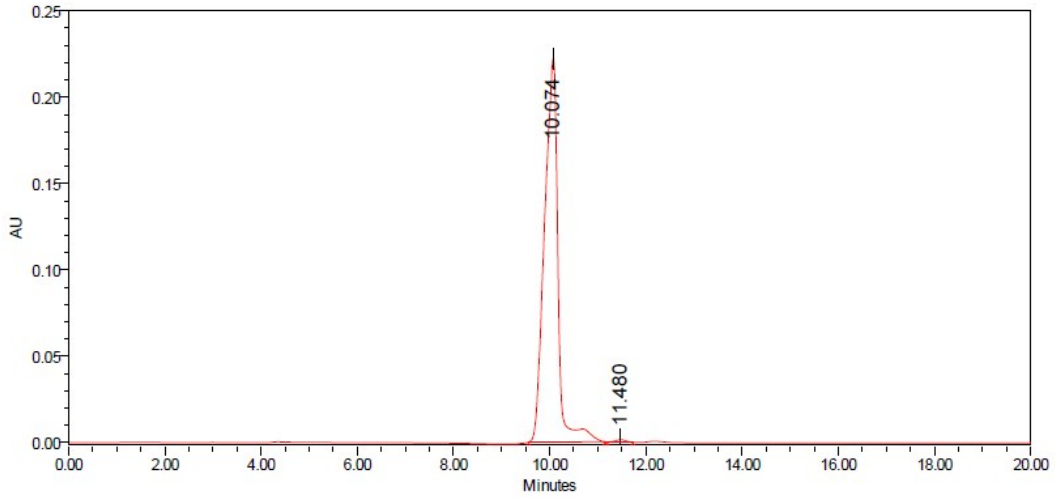
Figure S104. HPLC spectrum of **4v.**



4v



	Ret. Time	Height	Area	% Area
1	10.113	177589	2950094	49.89
2	11.610	156380	2962840	50.11



	Ret. Time	Height	Area	% Area
1	10.074	223066	4324170	99.57
2	11.480	1309	18586	0.43

Figure S105. ^{1}H and ^{13}C NMR spectrum of **4w.**

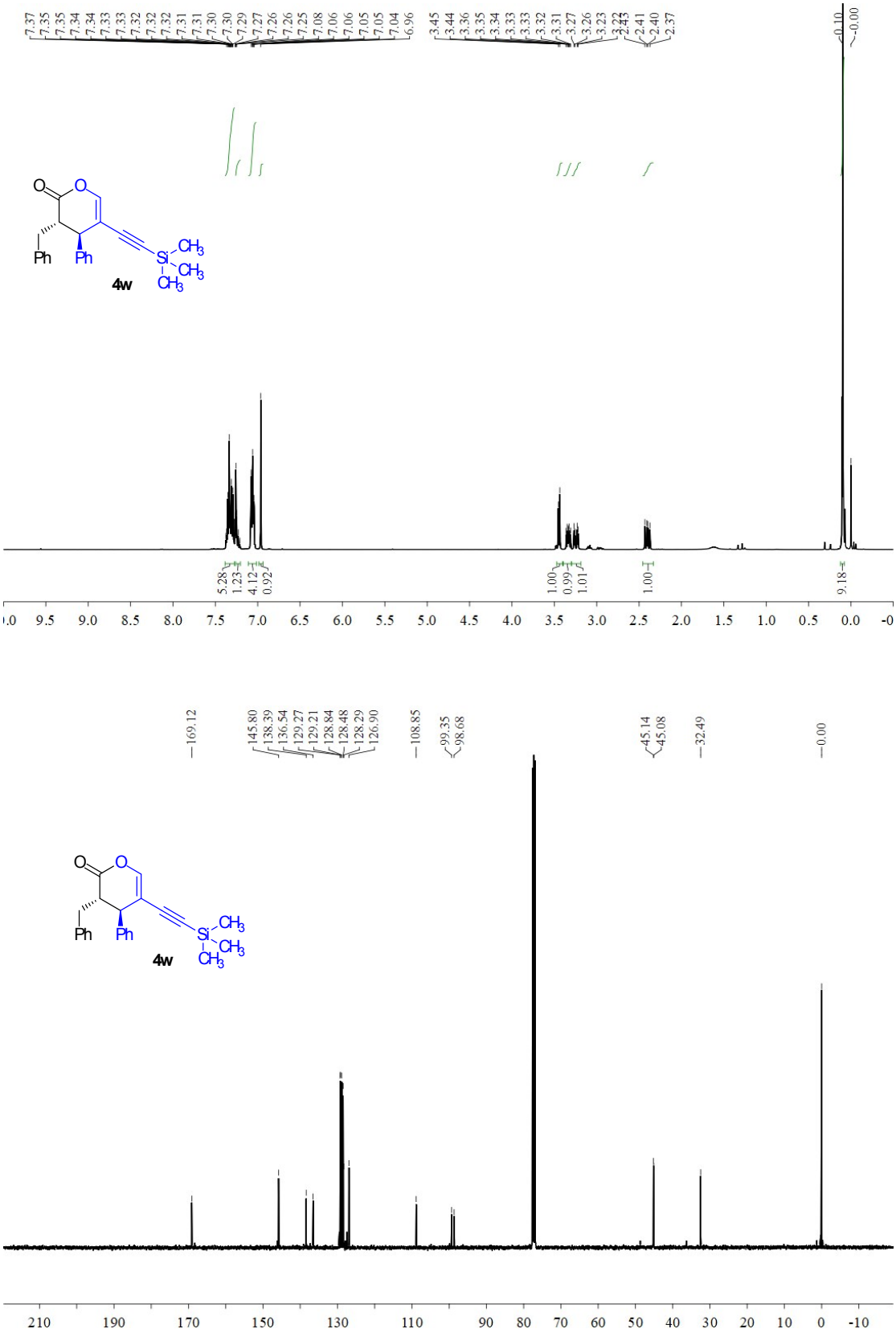
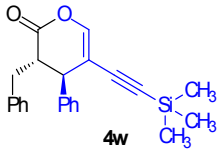
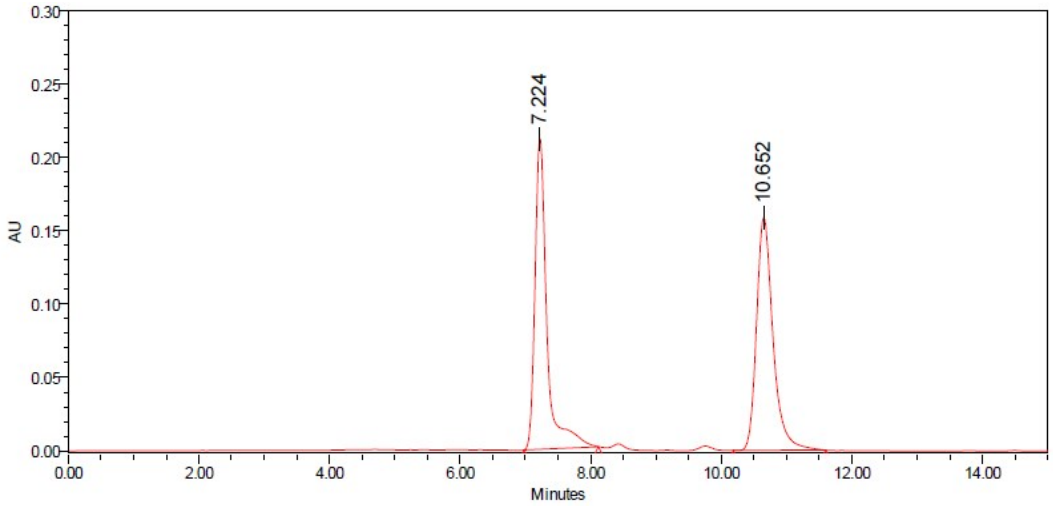


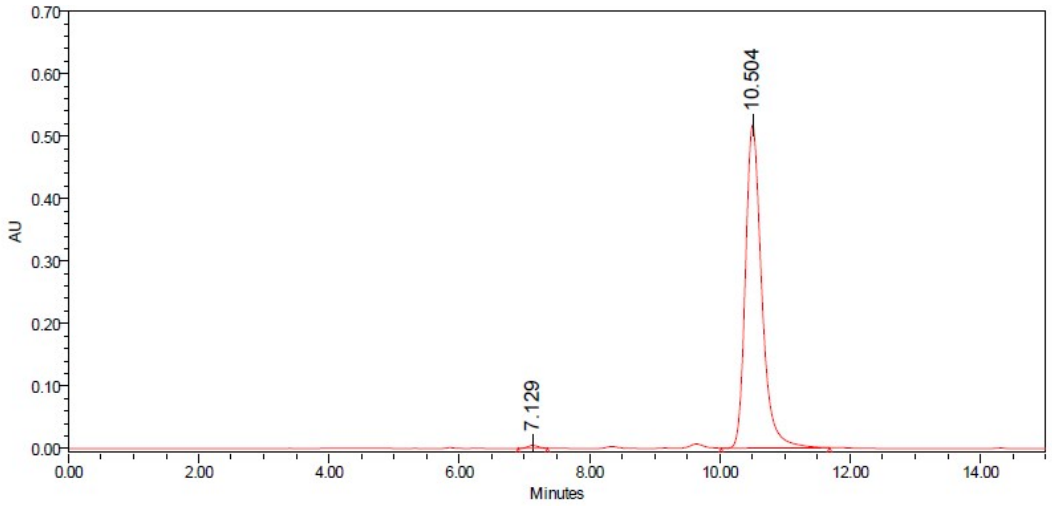
Figure S106. HPLC spectrum of **4w.**



4w



	Ret. Time	Height	Area	% Area
1	7.224	212653	2668717	49.03
2	10.652	158853	2774295	50.97



	Ret. Time	Height	Area	% Area
1	7.129	4749	49286	0.55
2	10.504	517947	8976088	99.45

Figure S107. ^{1}H and ^{13}C NMR spectrum of **4x.**

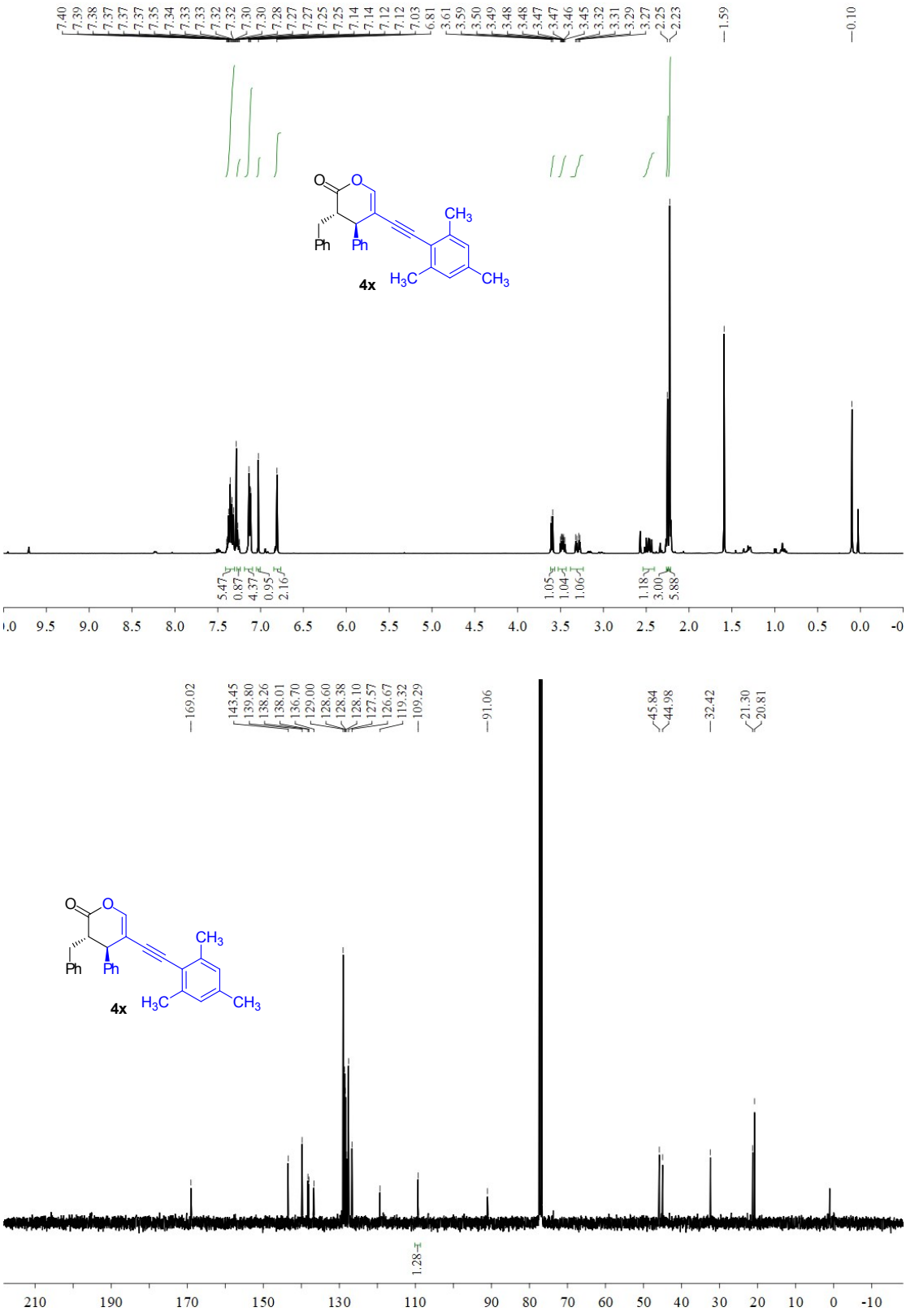
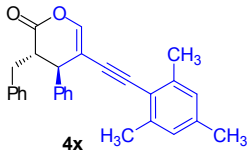
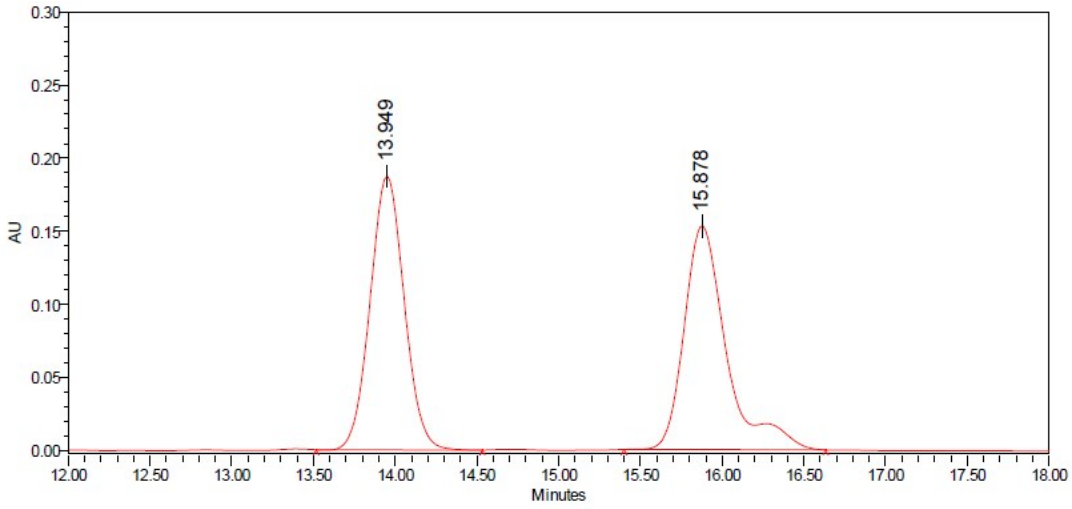


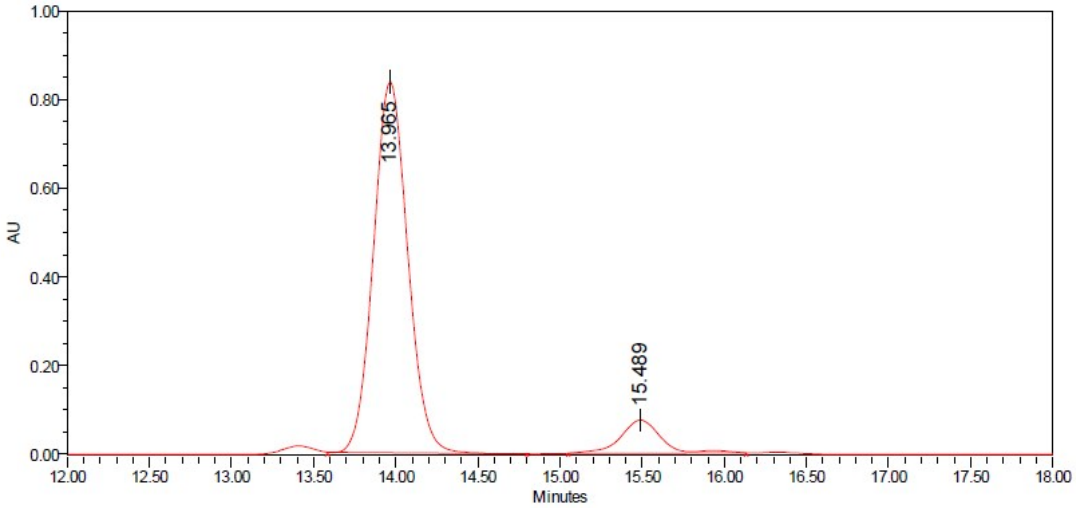
Figure S108. HPLC spectrum of **4x.**



4x



	Ret. Time	Height	Area	% Area
1	13.949	187134	2715017	49.71
2	15.878	152906	2746456	50.29



	Ret. Time	Height	Area	% Area
1	13.965	837815	12133676	90.55
2	15.489	74421	1266847	9.45

Figure S109. ^{1}H and ^{13}C NMR spectrum of **4y.**

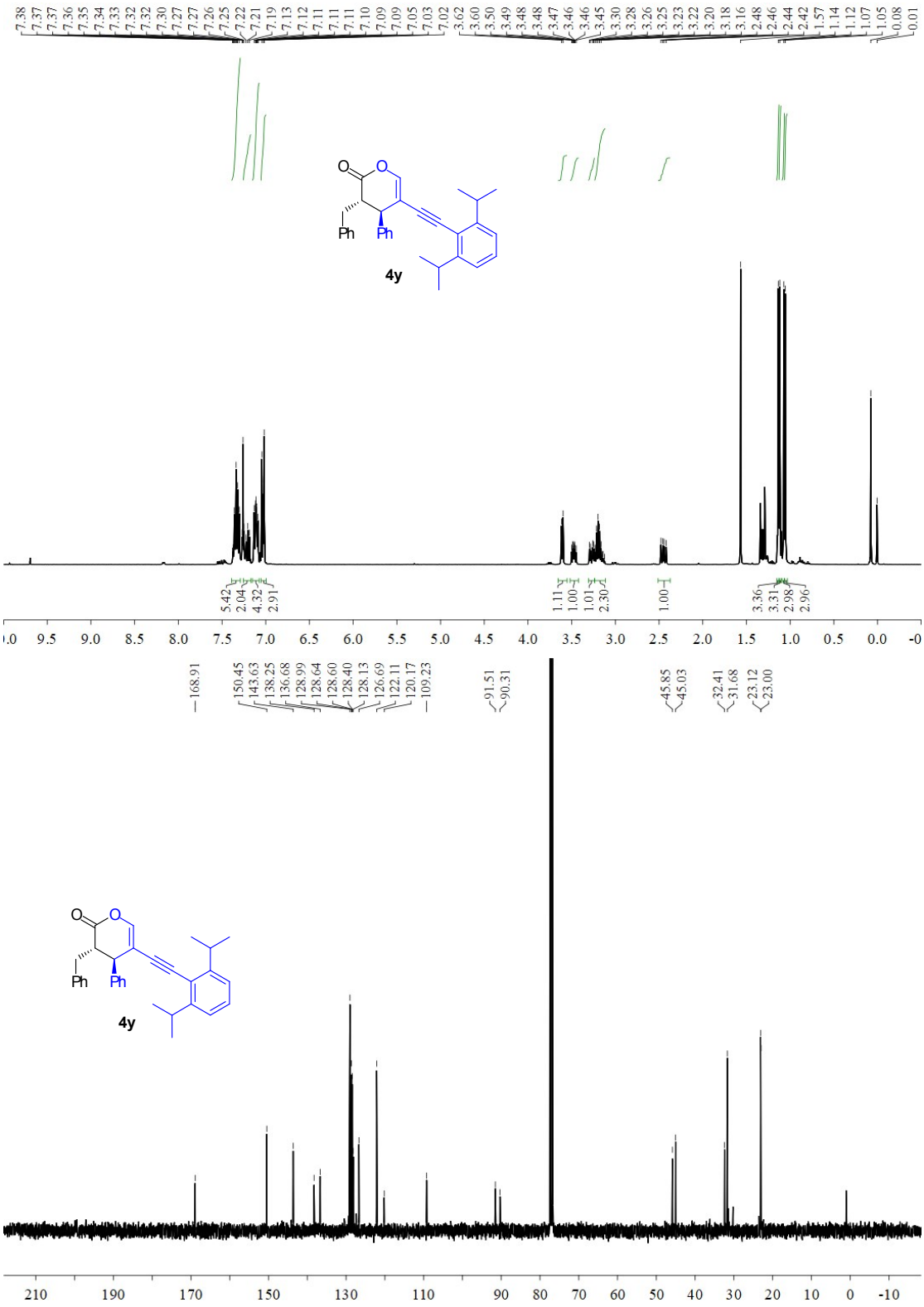
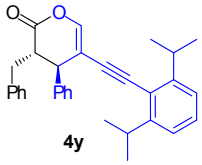
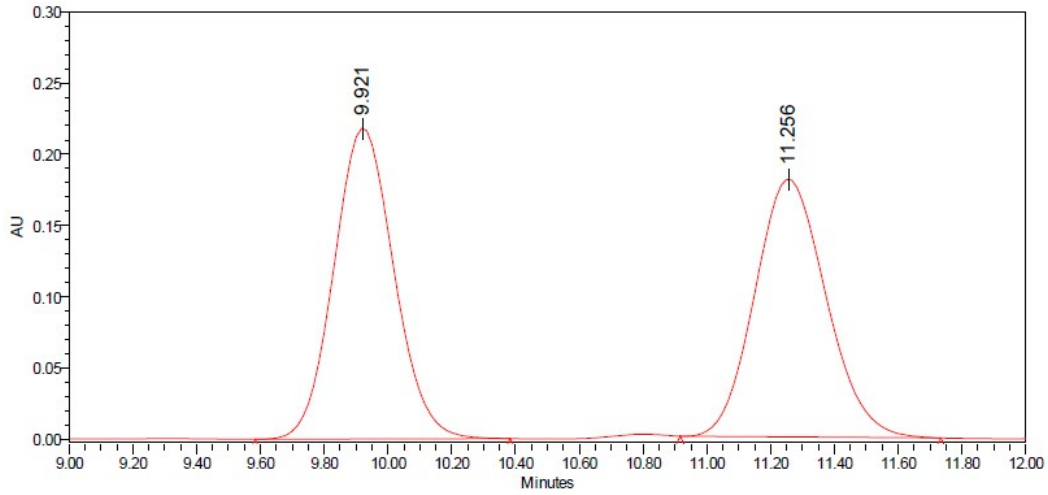


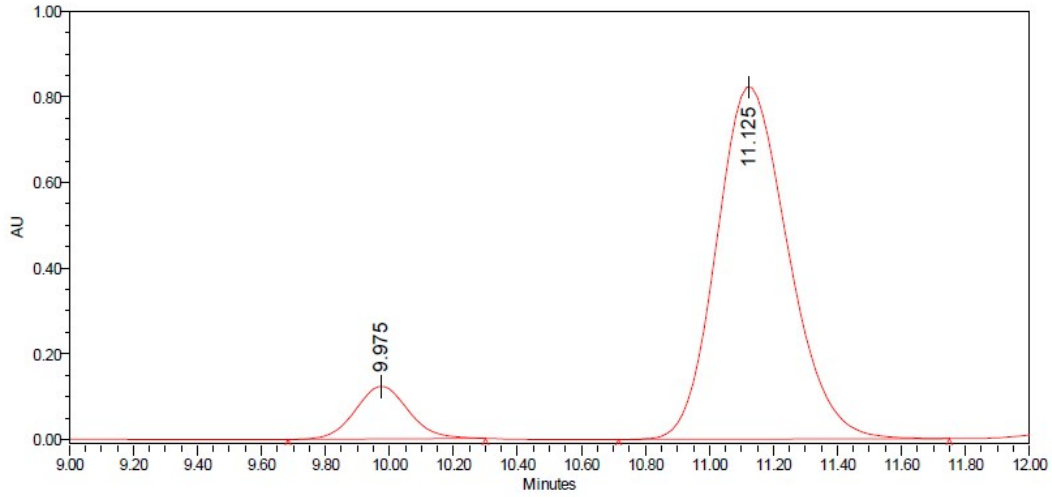
Figure S110. HPLC spectrum of **4y.**



4y



	Ret. Time	Height	Area	% Area
1	9.921	218062	2854026	50.41
2	11.256	180850	2807462	49.59



	Ret. Time	Height	Area	% Area
1	9.975	123287	1419548	9.99
2	11.125	823468	12788591	90.01

Figure S111. ^{1}H and ^{13}C NMR spectrum of **5**

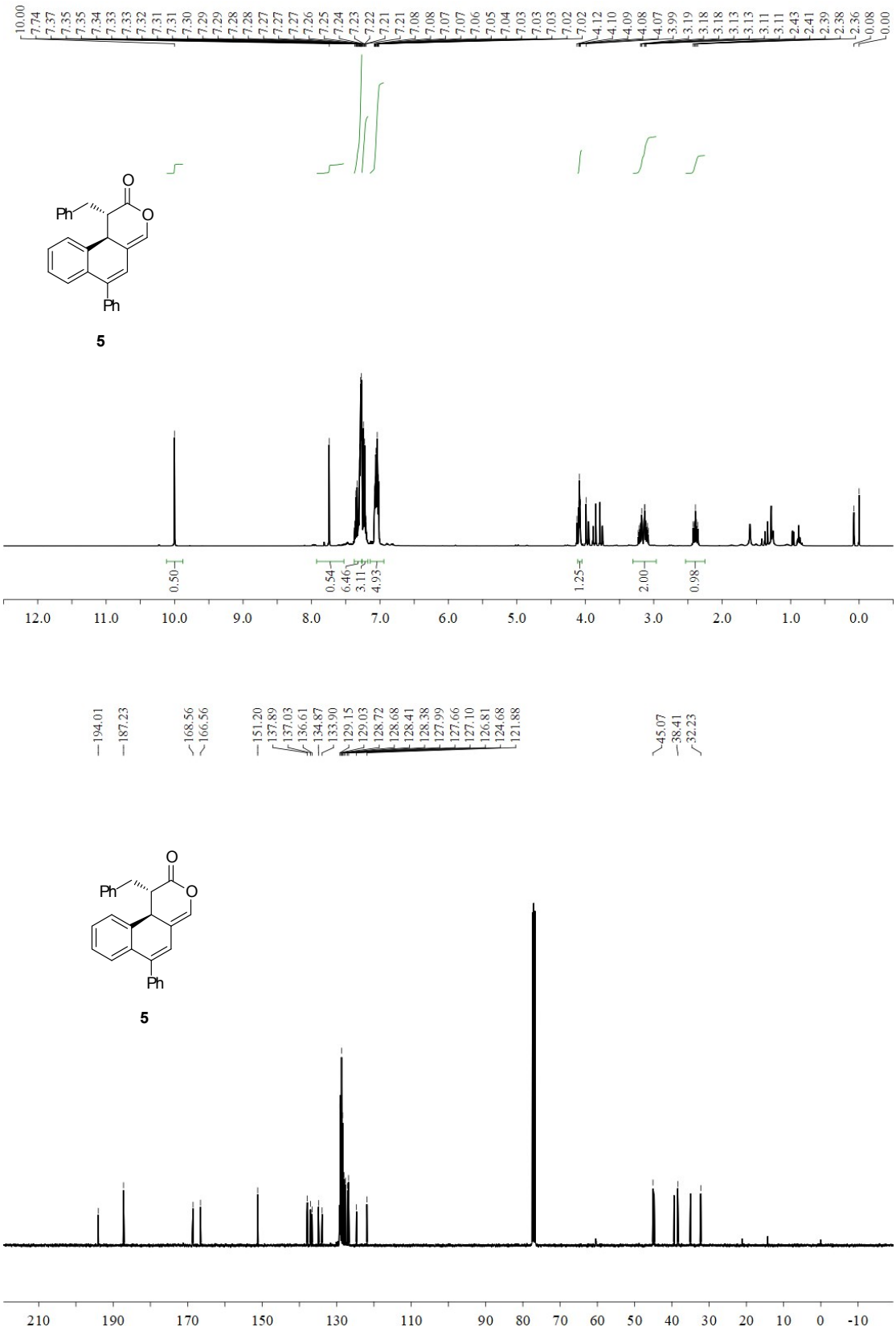
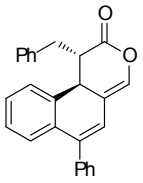
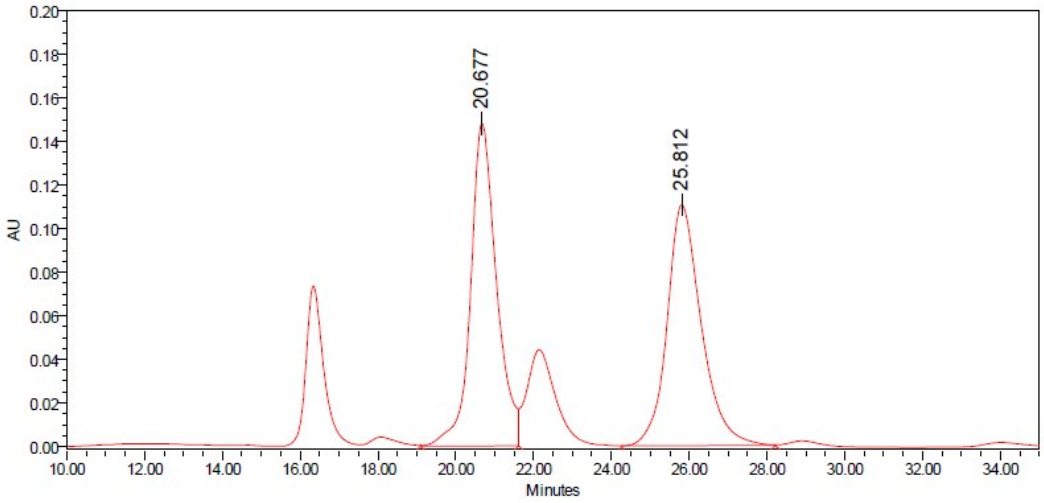


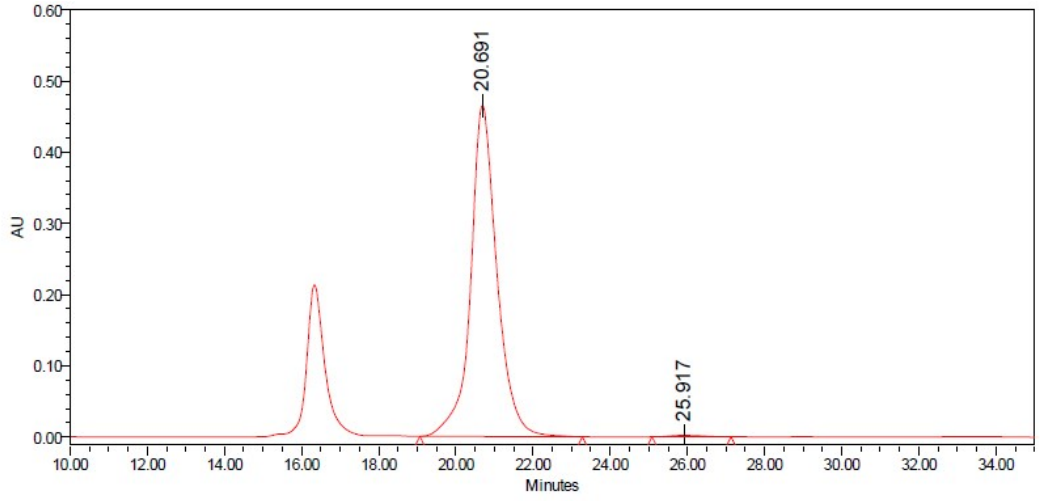
Figure S112. HPLC spectrum of **5.**



5

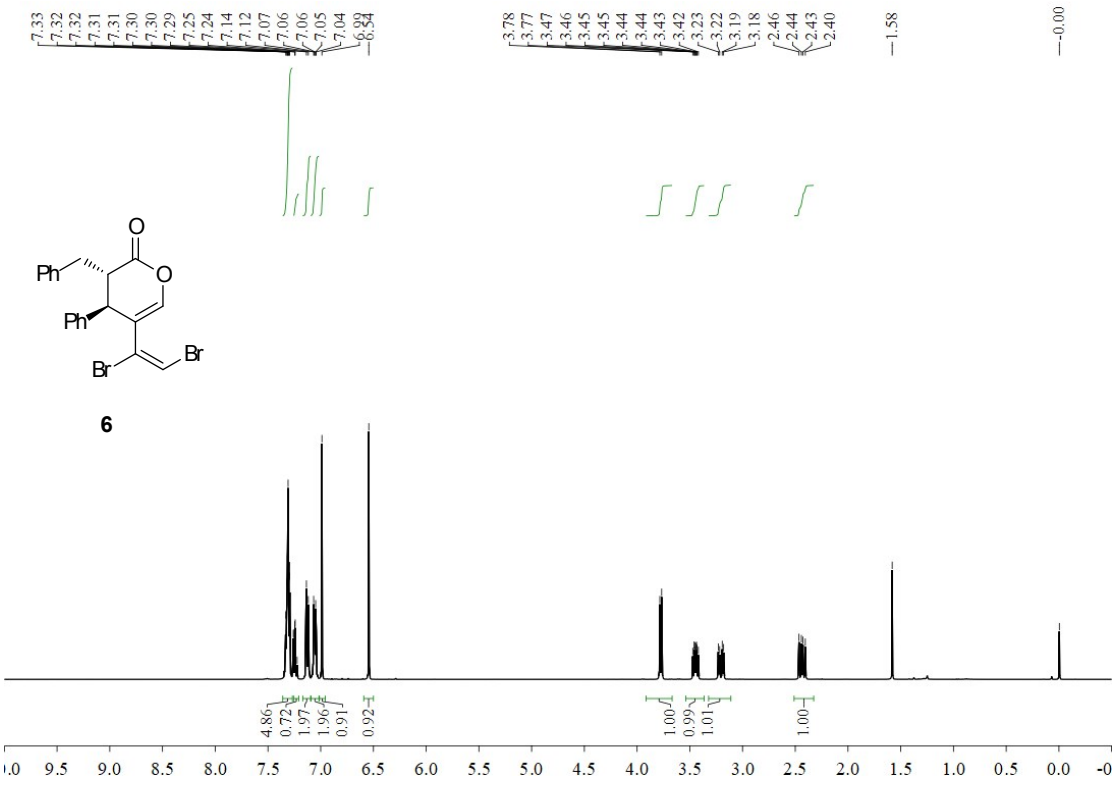


	Ret. Time	Height	Area	% Area
1	20.677	148011	6849823	50.29
2	25.812	110583	6771039	49.71



	Ret. Time	Height	Area	% Area
1	20.691	465084	22064918	99.46
2	25.917	2092	119116	0.54

Figure S113. ^{1}H and ^{13}C NMR spectrum of **6.**



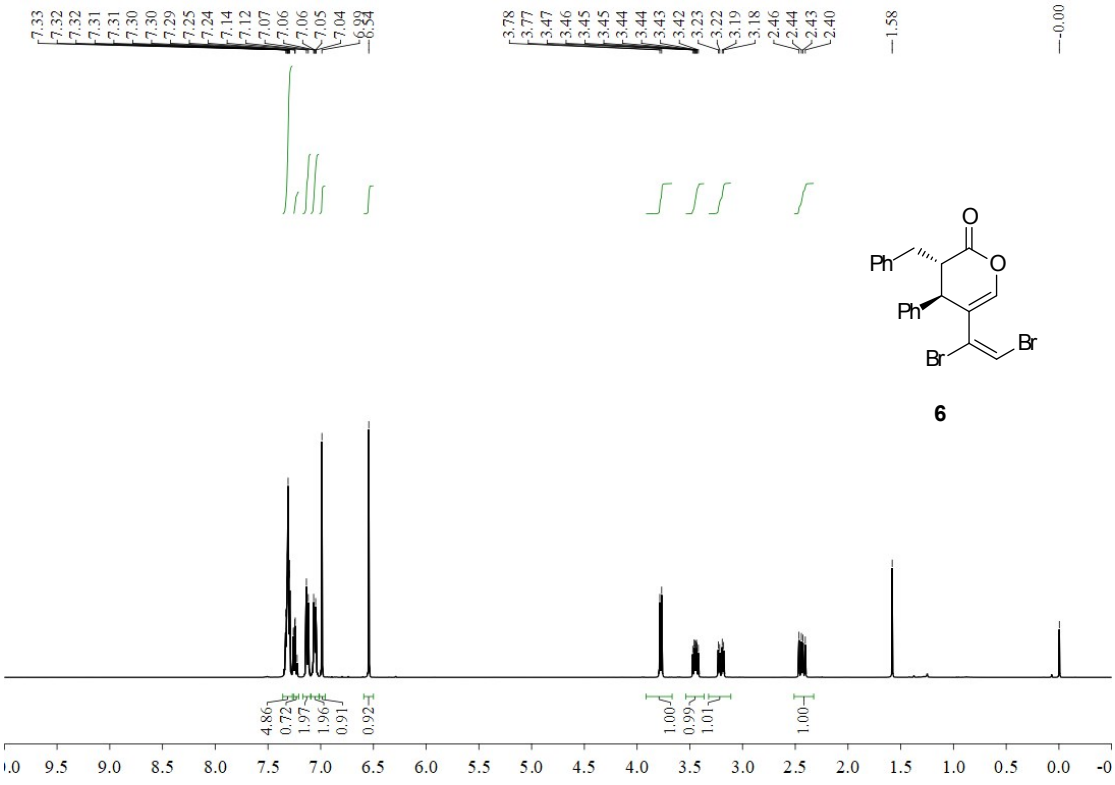
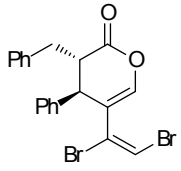
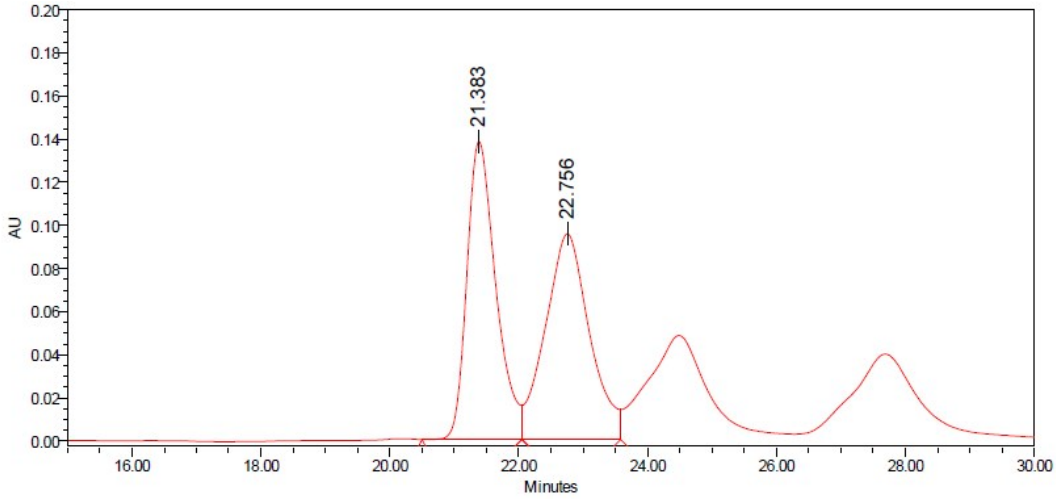


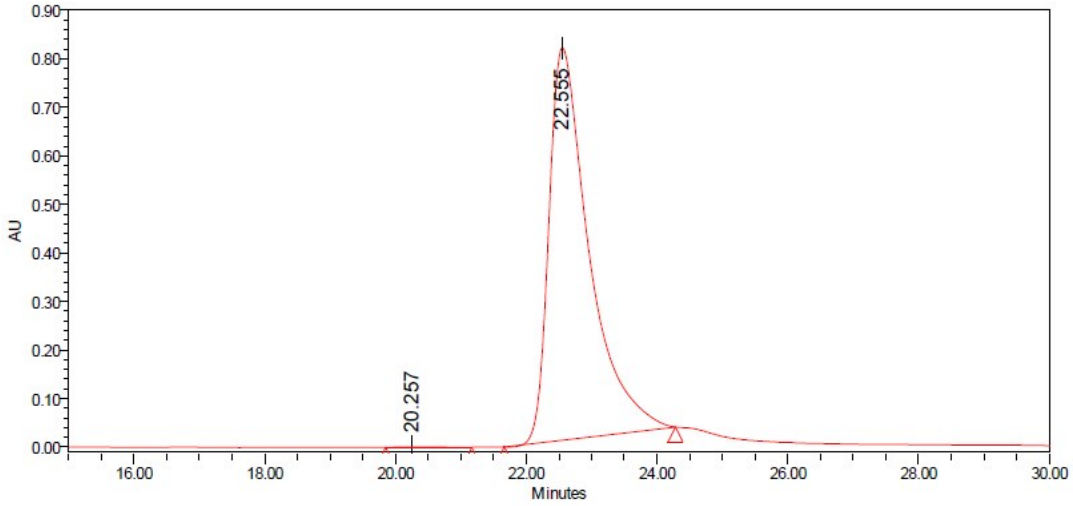
Figure S114. HPLC spectrum of **6.**



6

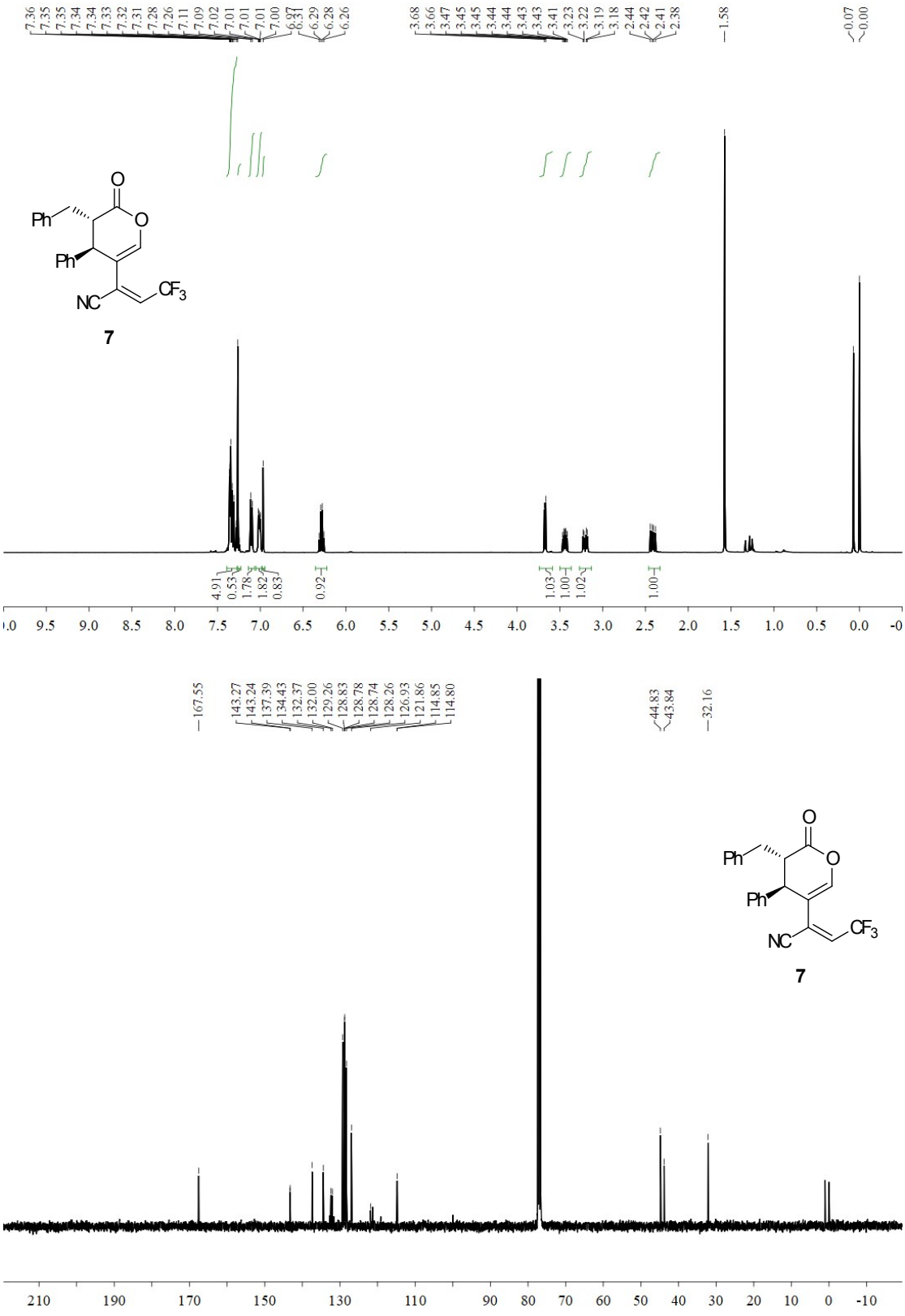


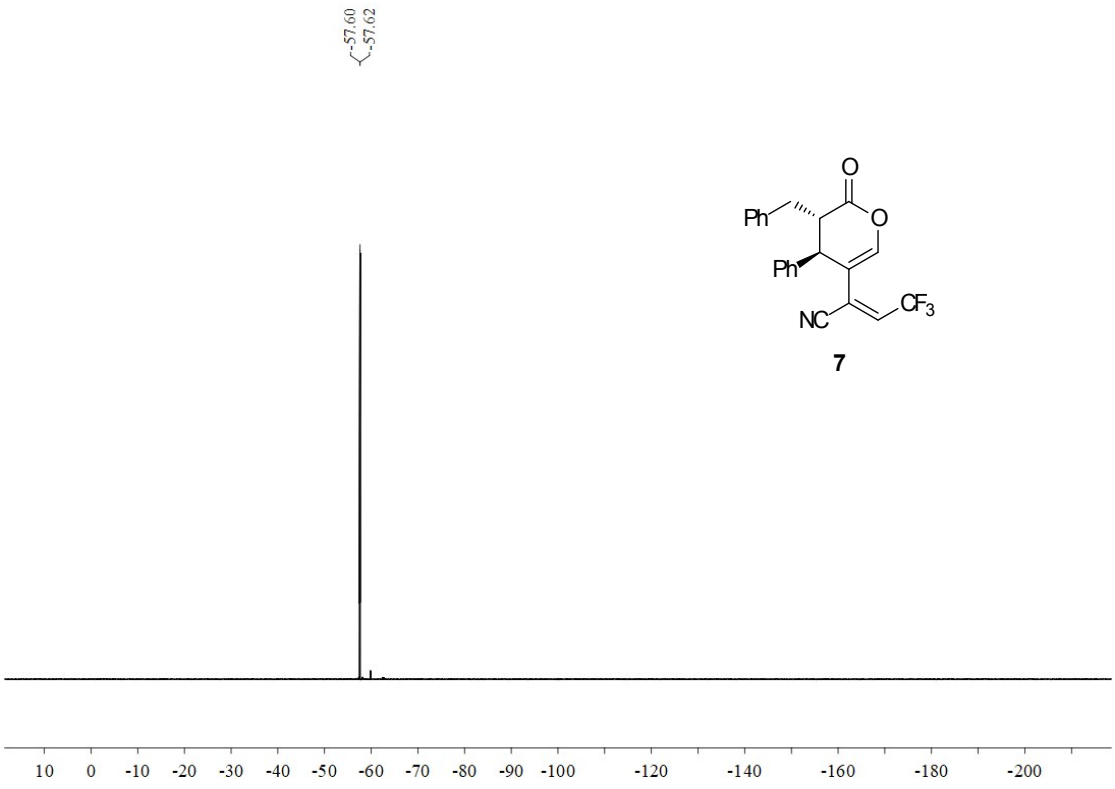
	Ret. Time	Height	Area	% Area
1	21.383	138198	4307218	48.65
2	22.756	95358	4546501	51.35



	Ret. Time	Height	Area	% Area
1	20.257	164	5436	0.02
2	22.555	808778	34548880	99.98

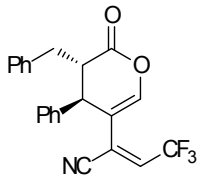
Figure S115. ^{1}H and ^{13}C NMR spectrum of **7.**



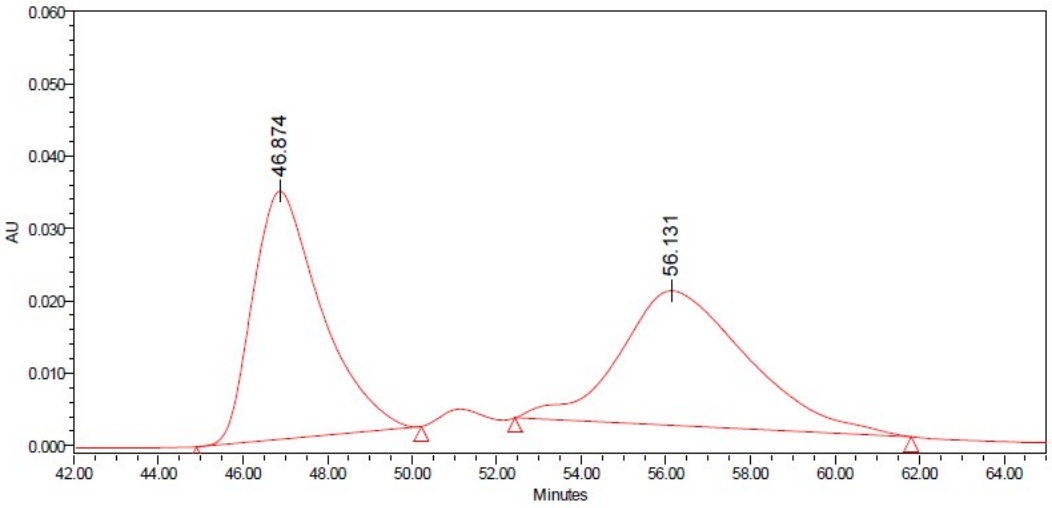

-57.60
-57.62
O
Ph
O
Ph
NC
CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

7

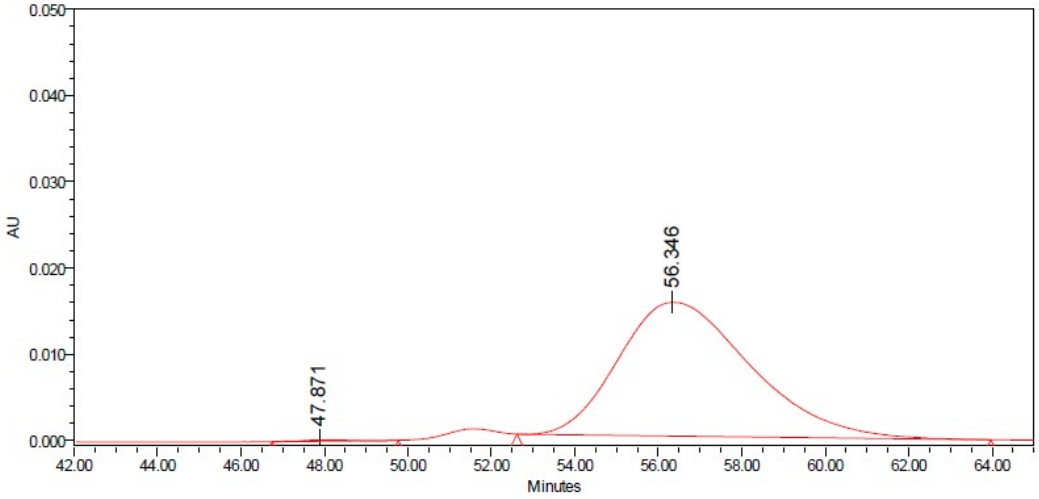
Figure S116. HPLC spectrum of **7.**



7



	Ret. Time	Height	Area	% Area
1	46.874	34261	3860367	49.54
2	56.131	18563	3932291	50.46



	Ret. Time	Height	Area	% Area
1	47.871	125	9420	0.28
2	56.346	15491	3409407	99.72

Figure S117. ^{1}H and ^{13}C NMR spectrum of **8.**

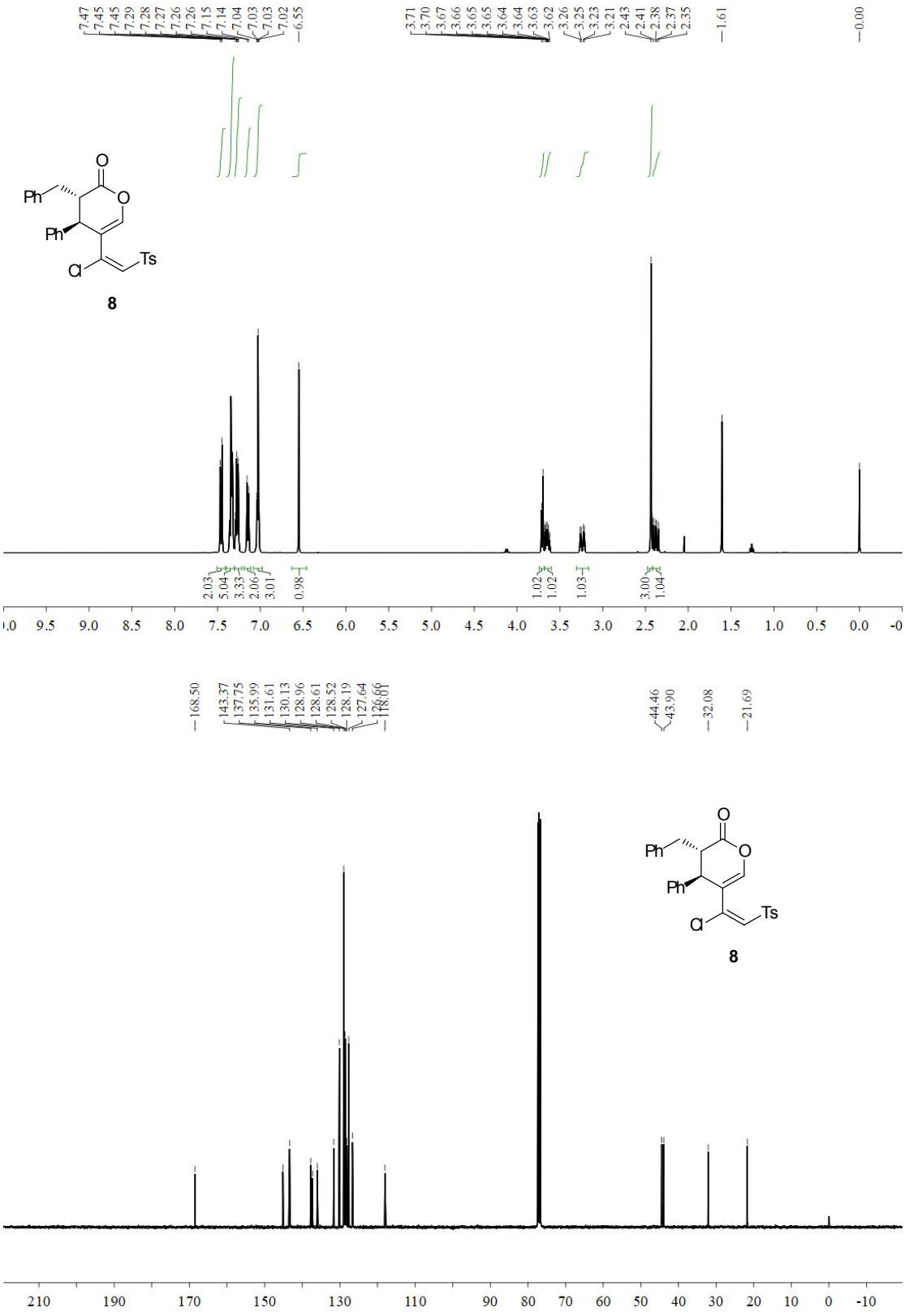
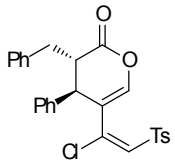
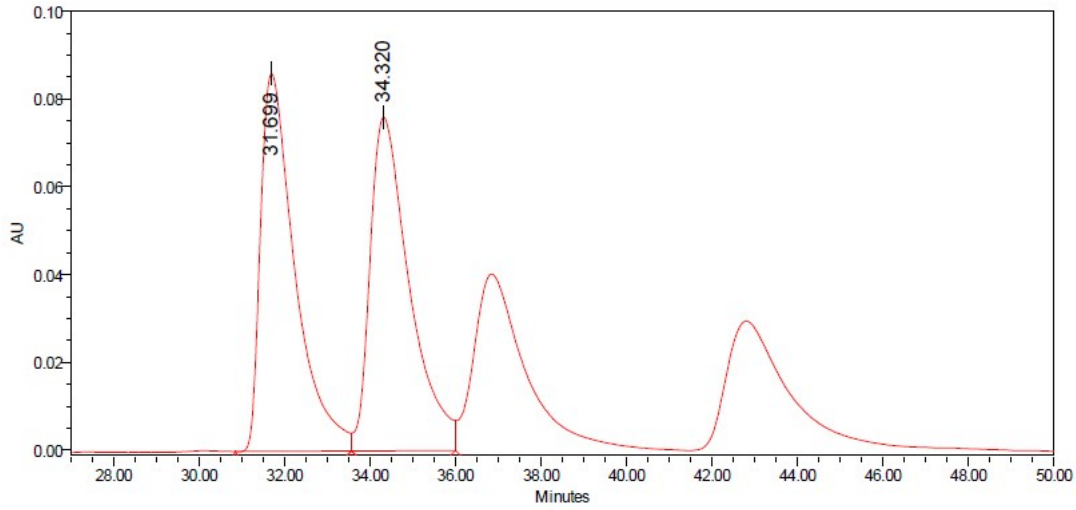


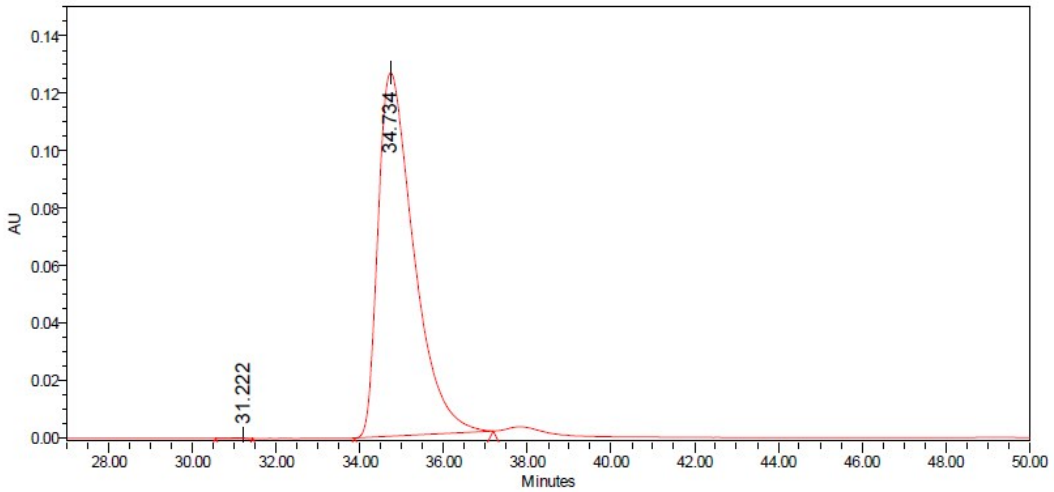
Figure S118. HPLC spectrum of **8.**



8



	Ret. Time	Height	Area	% Area
1	31.699	86064	4802965	49.66
2	34.320	76012	4868420	50.34



	Ret. Time	Height	Area	% Area
1	31.222	62	1766	0.02
2	34.734	126553	7499382	99.98

Figure S119. ^{1}H and ^{13}C NMR spectrum of **9.**

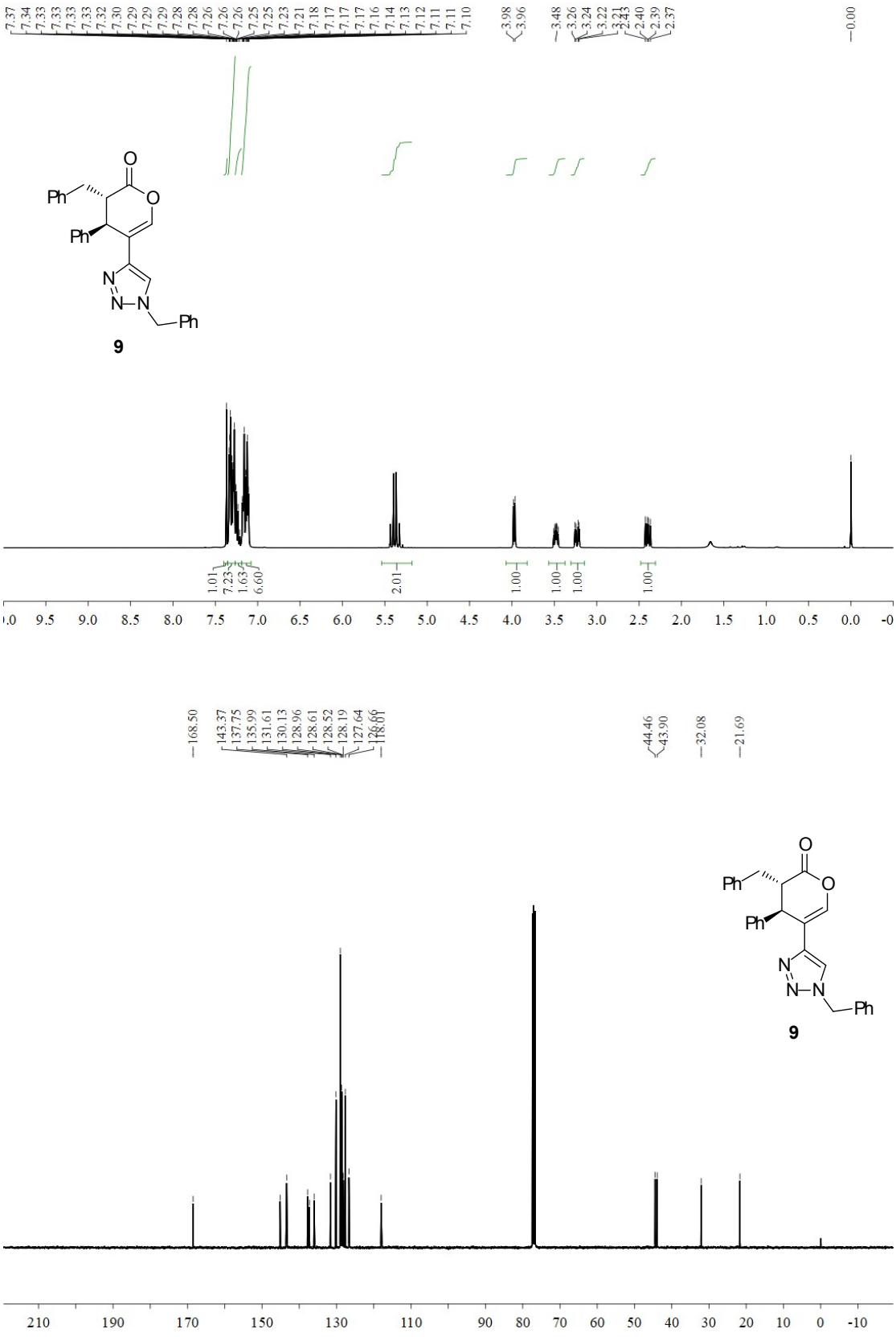
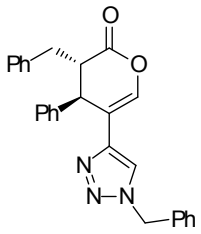
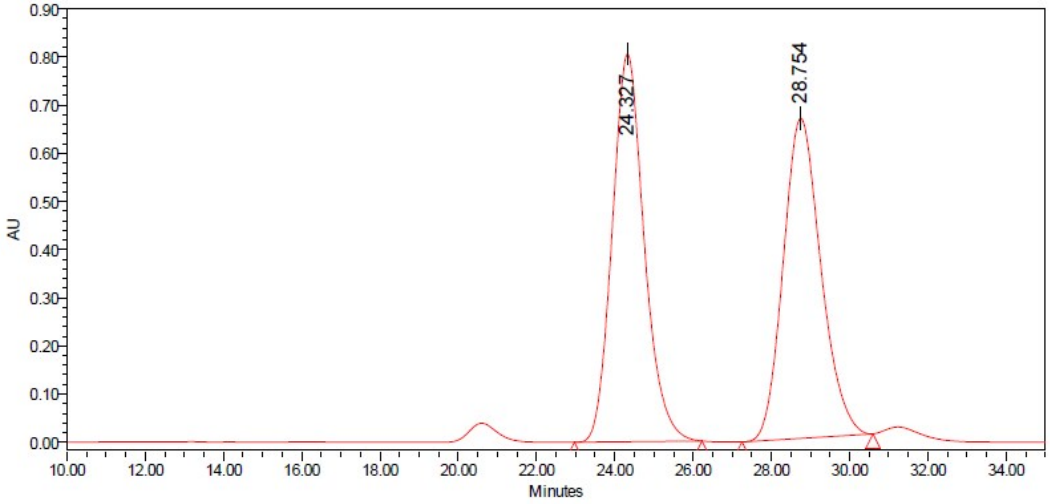


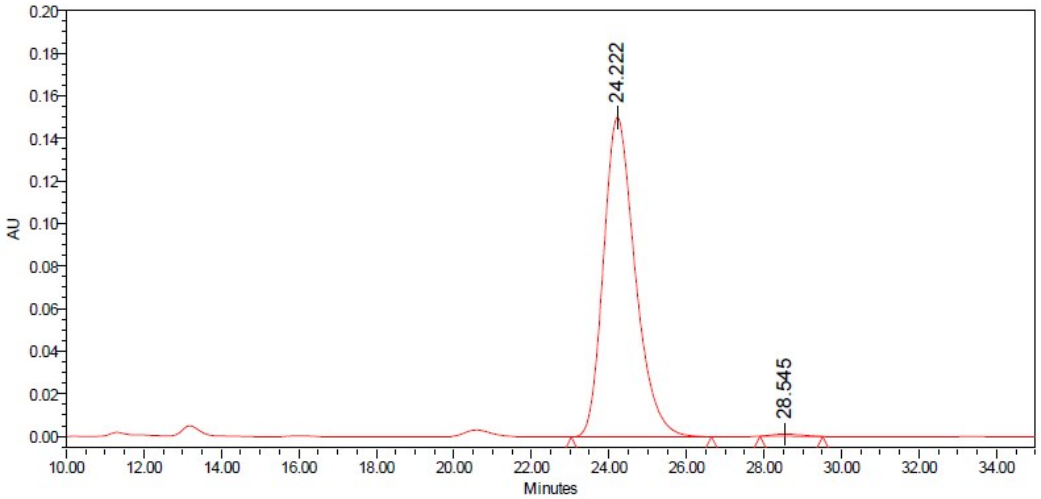
Figure S120. HPLC spectrum of **9.**



9



	Ret. Time	Height	Area	% Area
1	24.327	805346	45784576	50.72
2	28.754	664999	44476485	49.28



	Ret. Time	Height	Area	% Area
1	24.222	150104	8543208	99.37
2	28.545	1054	53769	0.63

Figure S121. ^{1}H and ^{13}C NMR spectrum of **10.**

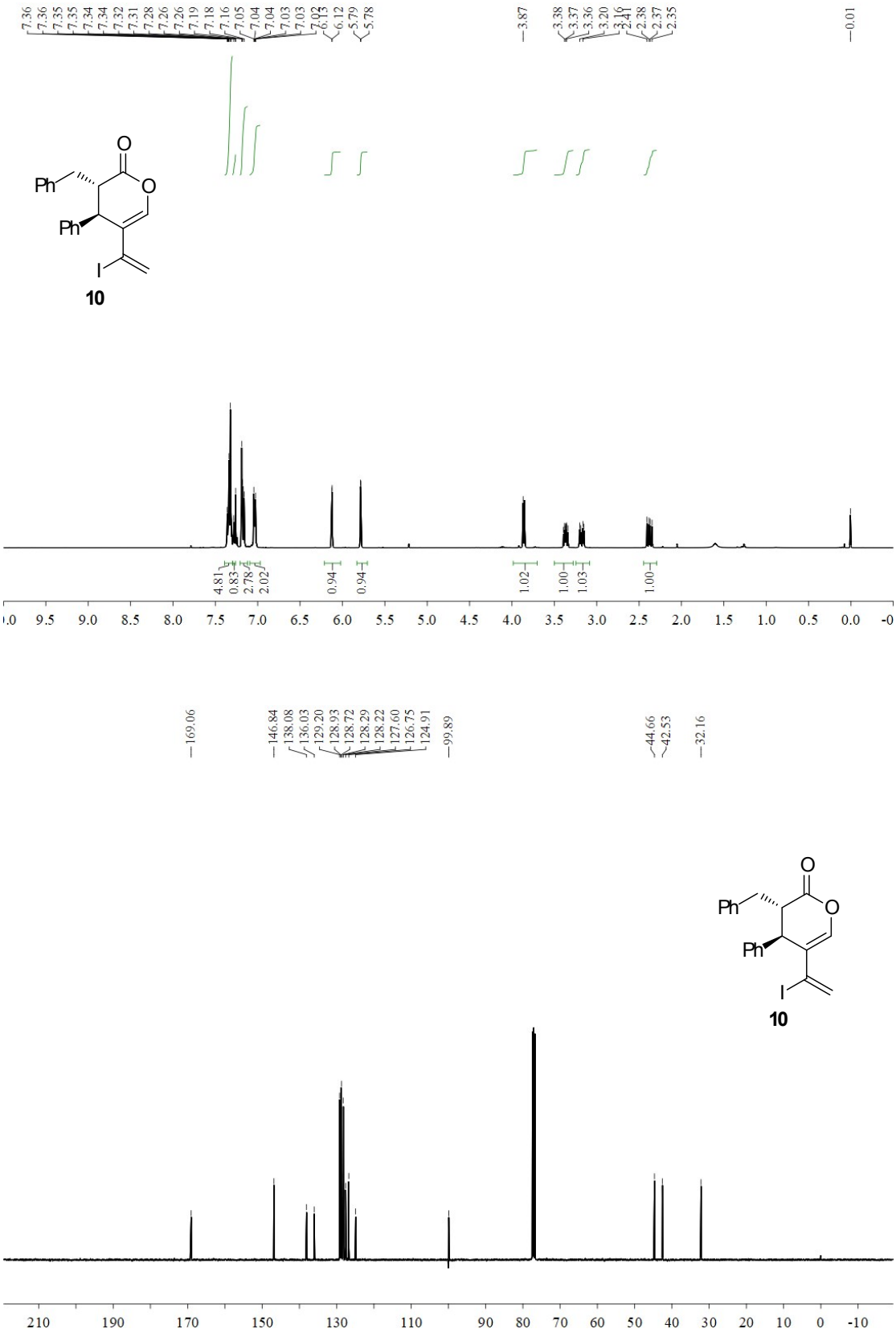
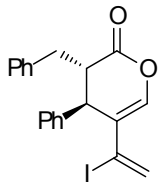
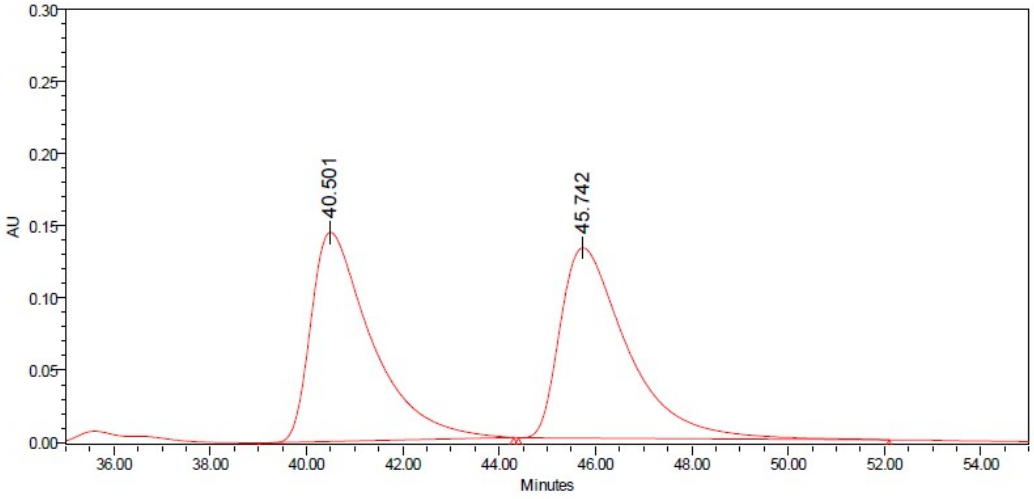


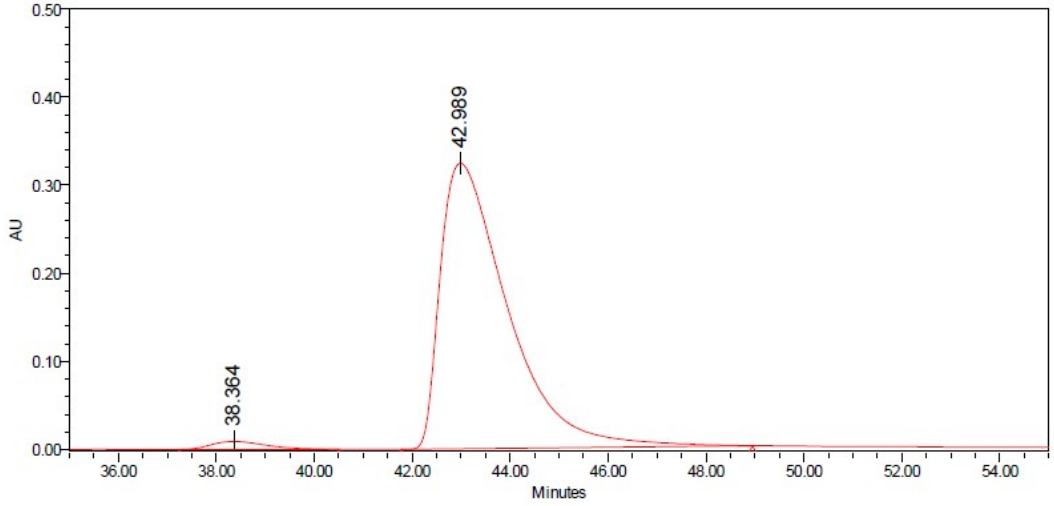
Figure S122. HPLC spectrum of **10.**



10



	Ret. Time	Height	Area	% Area
1	40.501	144979	12727699	49.92
2	45.742	131795	12768641	50.08



	Ret. Time	Height	Area	% Area
1	38.364	9042	701571	2.22
2	42.989	324064	30961258	97.78

Figure S123. ^{1}H and ^{13}C NMR spectrum of **11.**

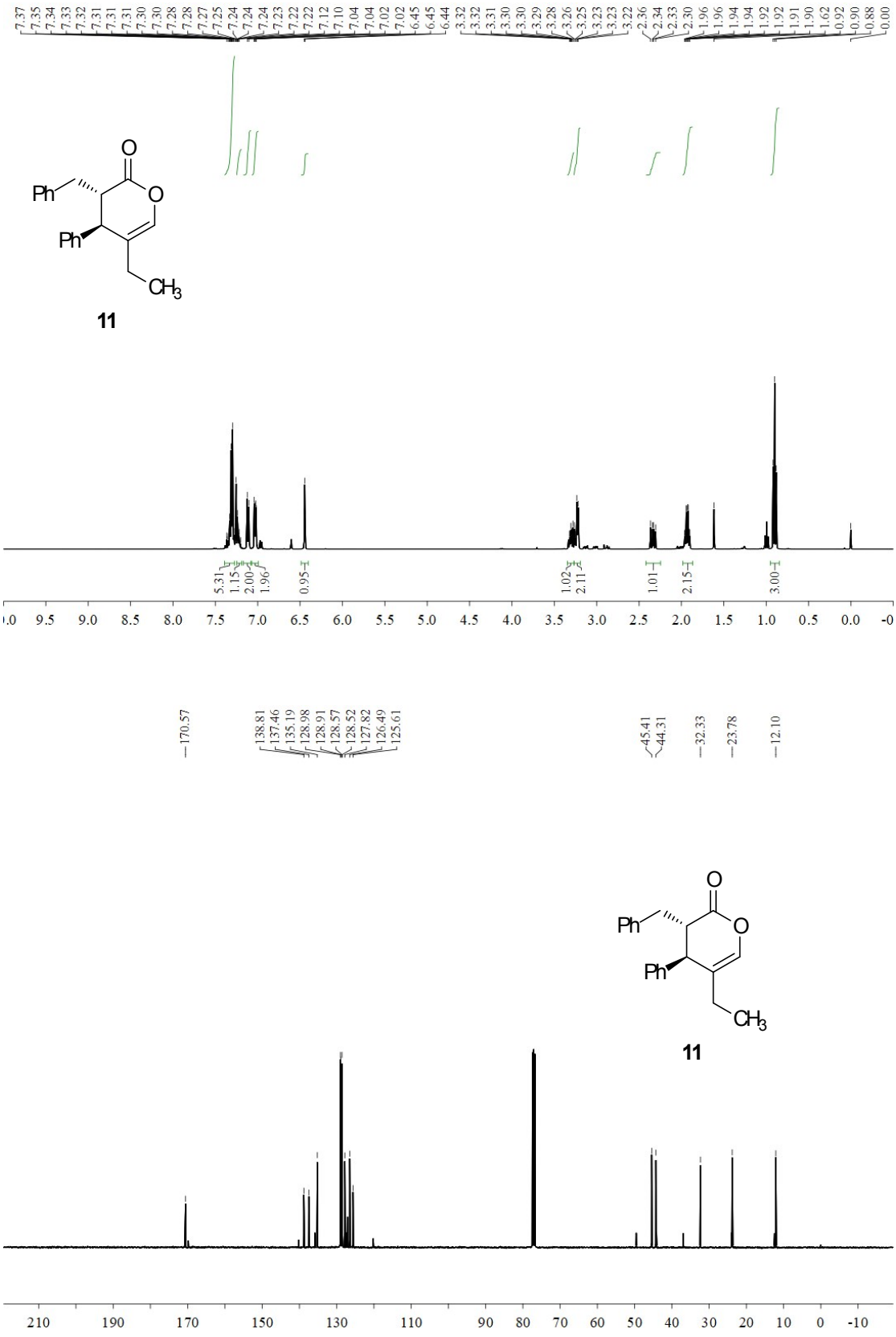
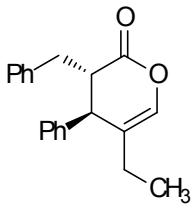
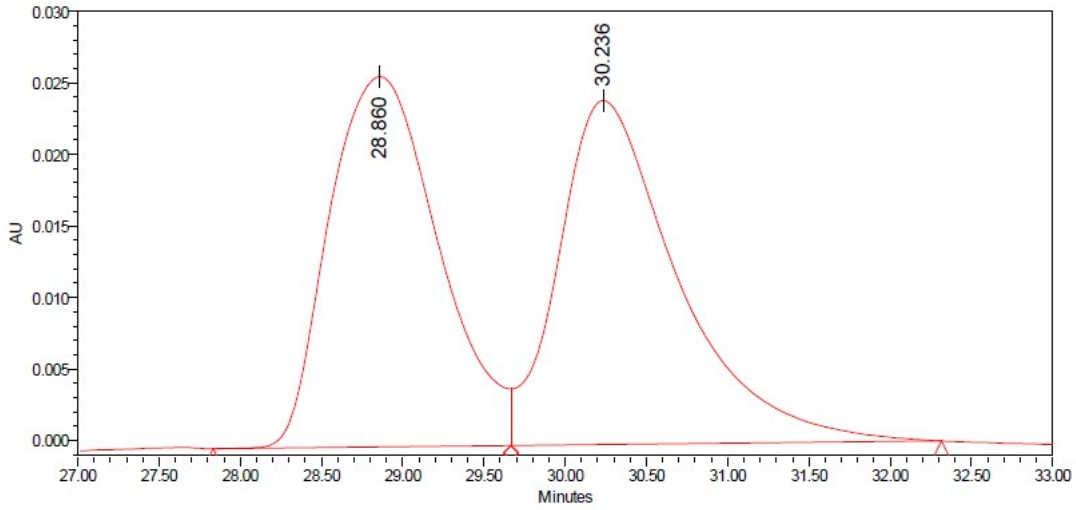


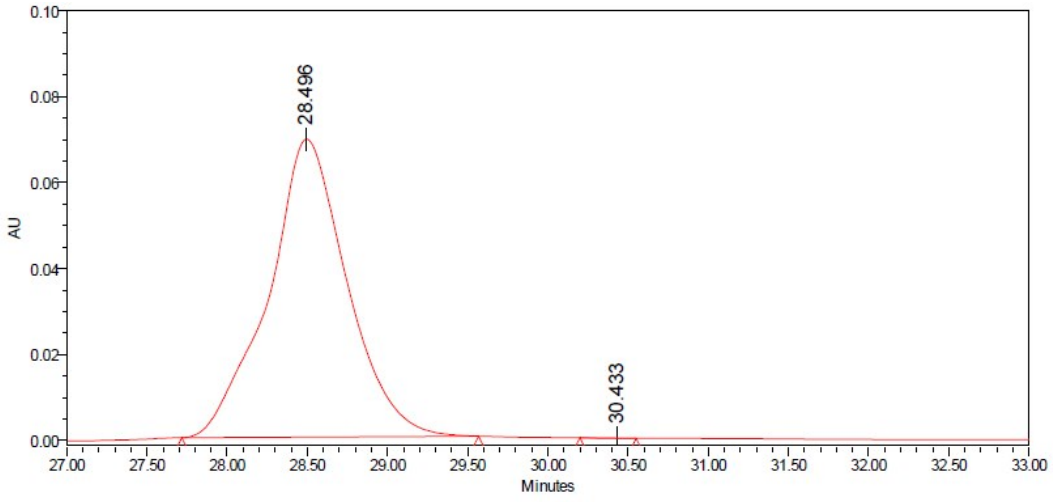
Figure S124. HPLC spectrum of **11.**



11



	Ret. Time	Height	Area	% Area
1	28.860	25887	1211500	49.67
2	30.236	24054	1227705	50.33



	Ret. Time	Height	Area	% Area
1	28.496	69361	2359141	99.99
2	30.433	13	146	0.01

Figure S125. ^{1}H and ^{13}C NMR spectrum of **12.**

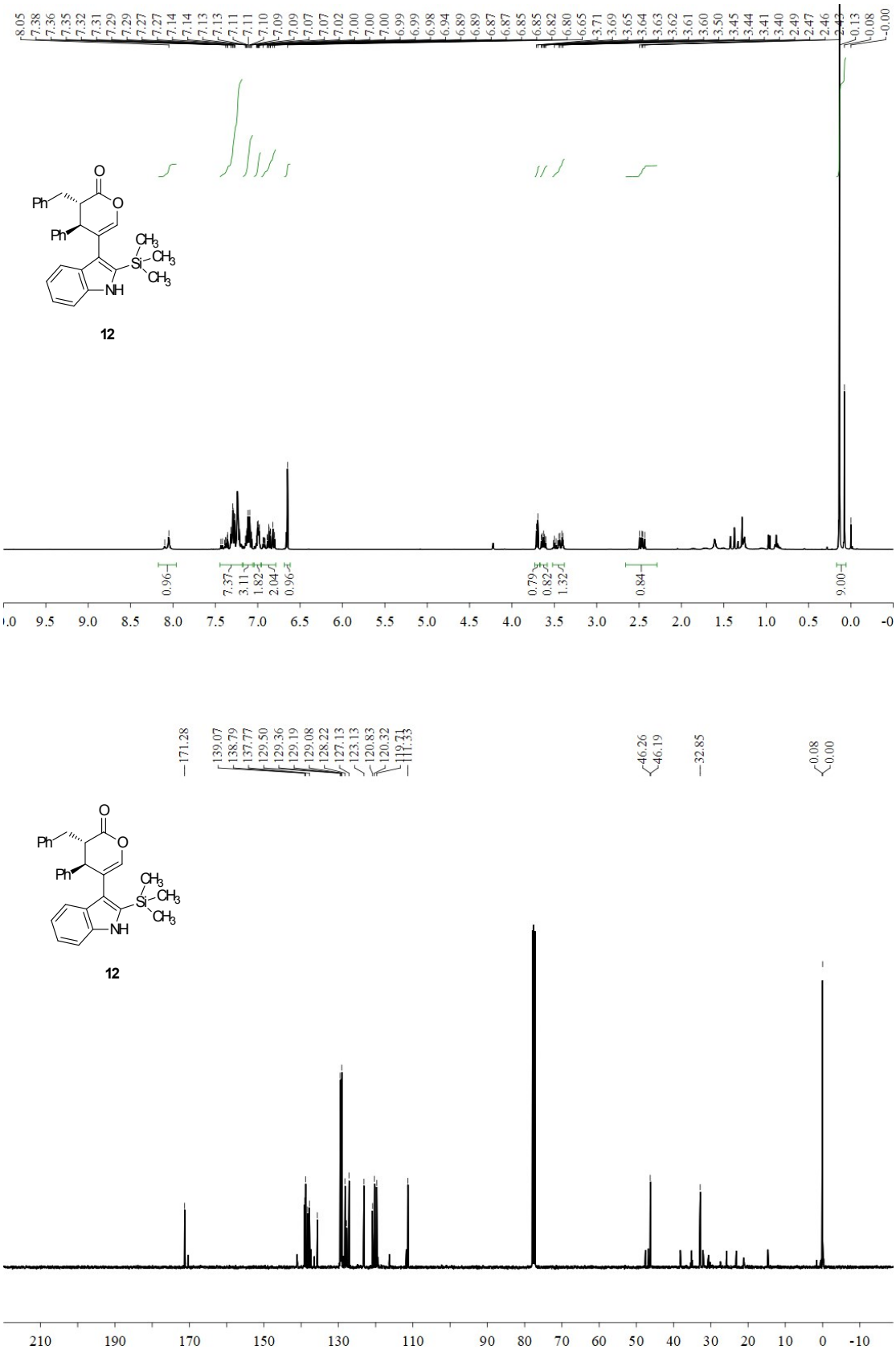
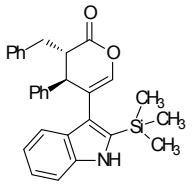
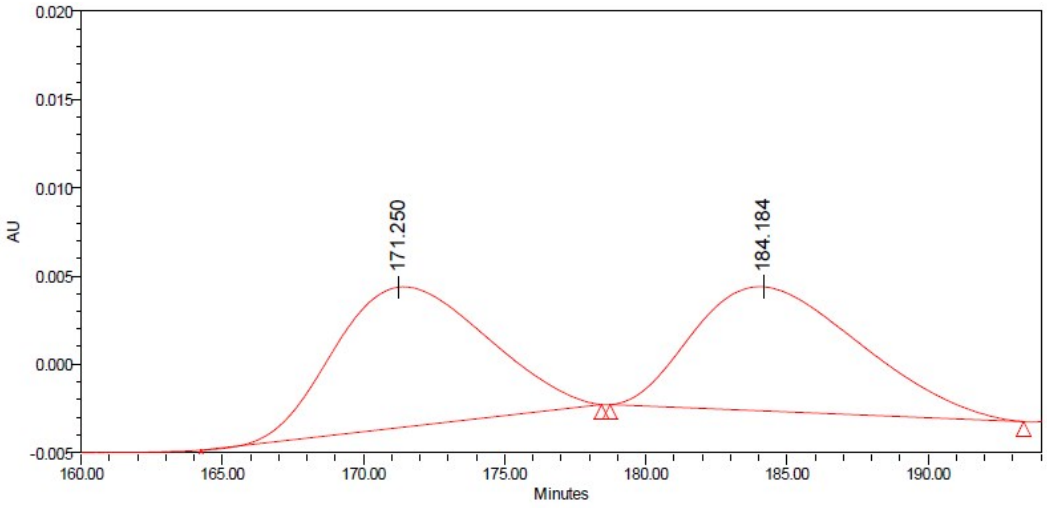


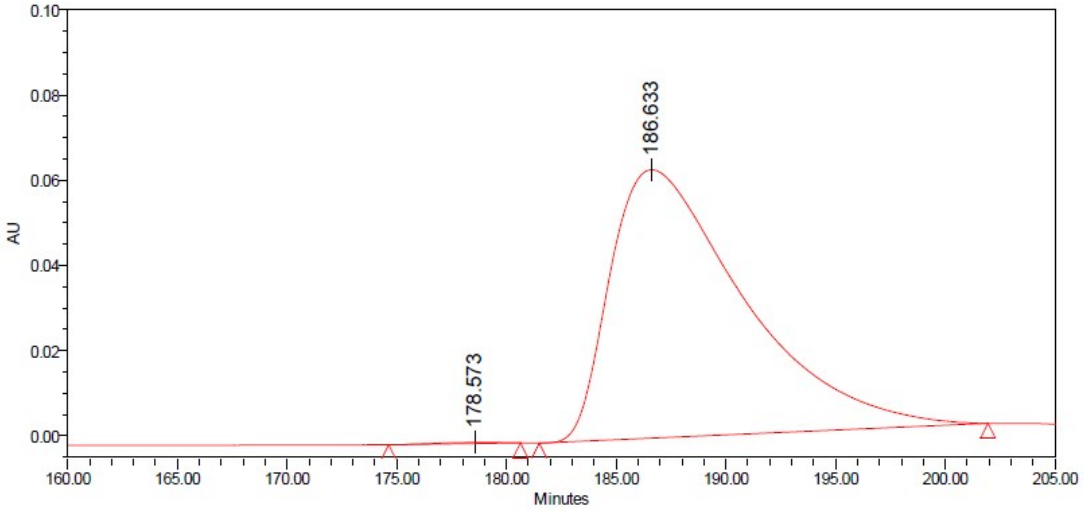
Figure S126. HPLC spectrum of **12.**



12



	Ret. Time	Height	Area	% Area
1	171.250	7965	2987339	50.76
2	184.184	7032	2897454	49.24



	Ret. Time	Height	Area	% Area
1	178.573	286	55859	0.21
2	186.633	63076	26780095	99.79

Figure S127. ^{1}H and ^{13}C NMR spectrum of the NHC pre-catalysts D bearing counter ions (Cl-).

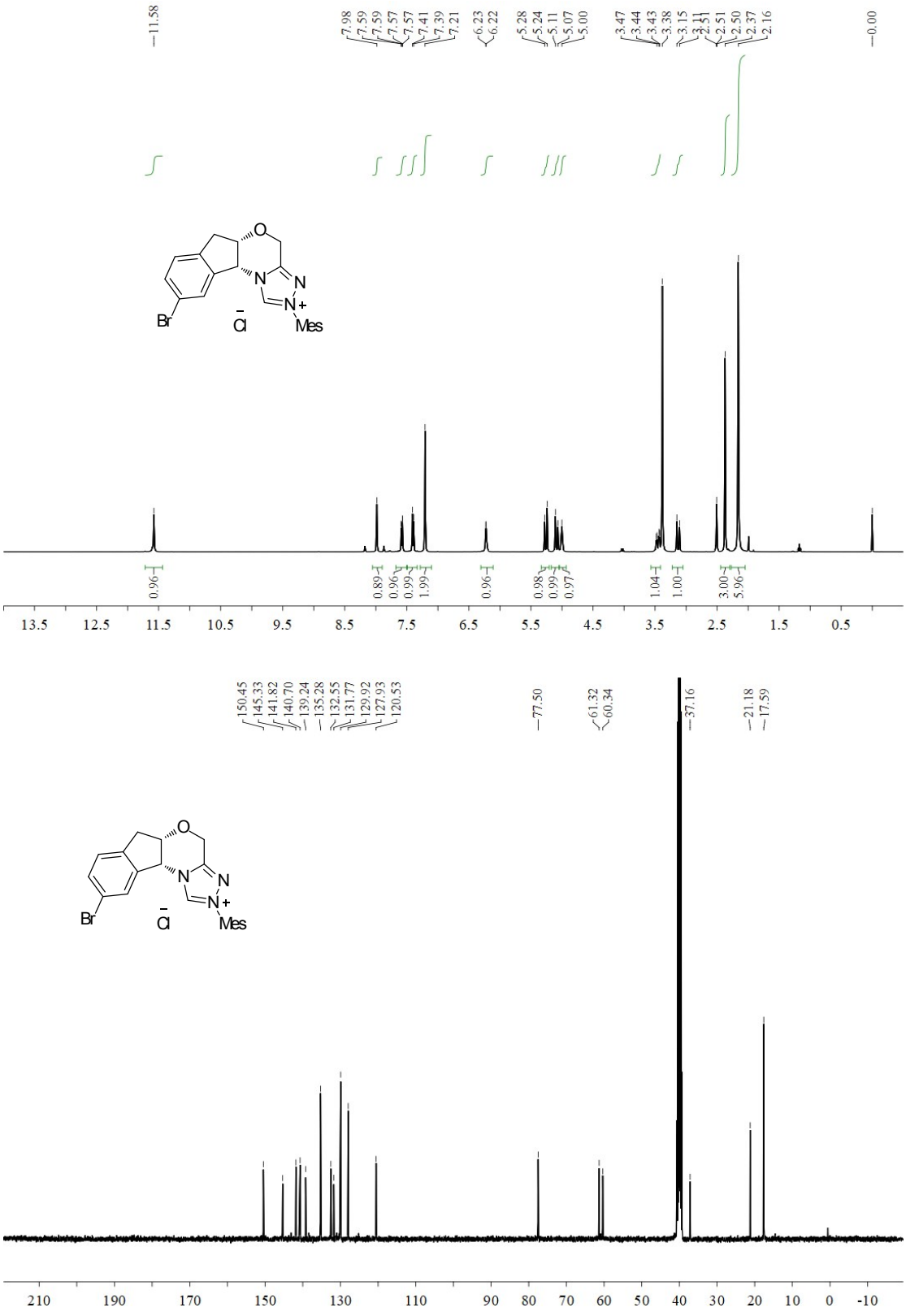
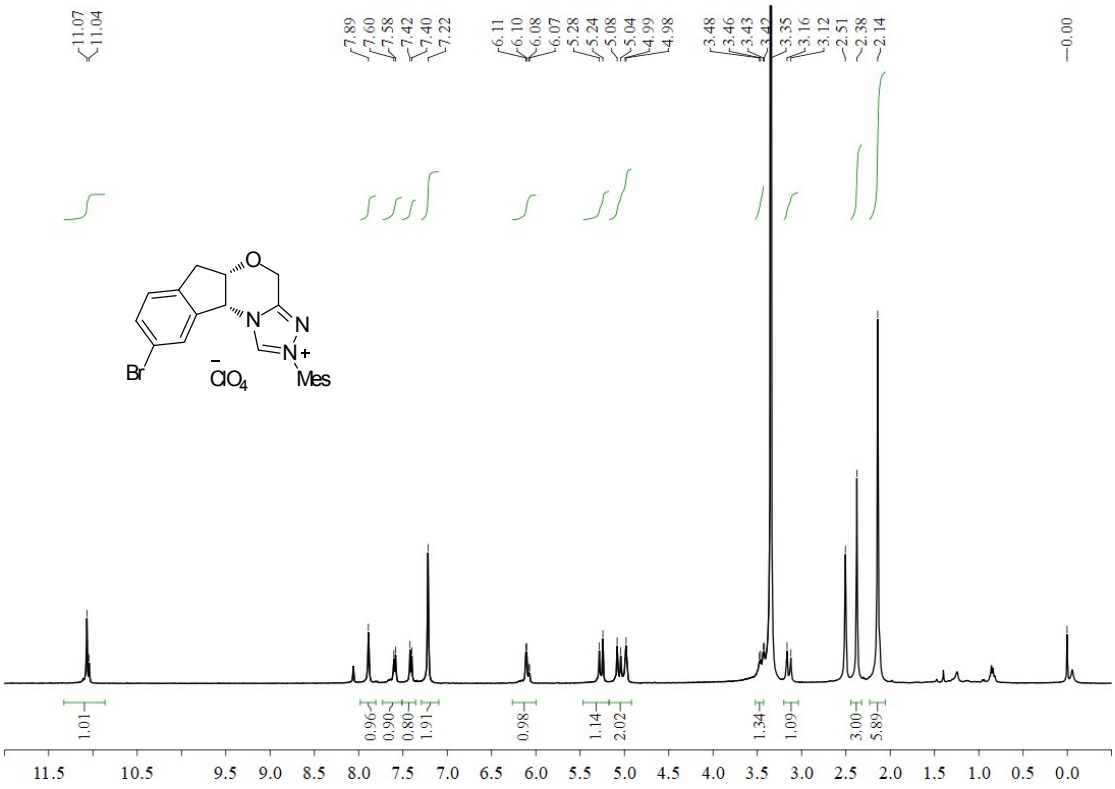


Figure S128. ^{1}H and ^{13}C NMR spectrum of the NHC pre-catalysts D bearing counter ions (ClO_4^-).



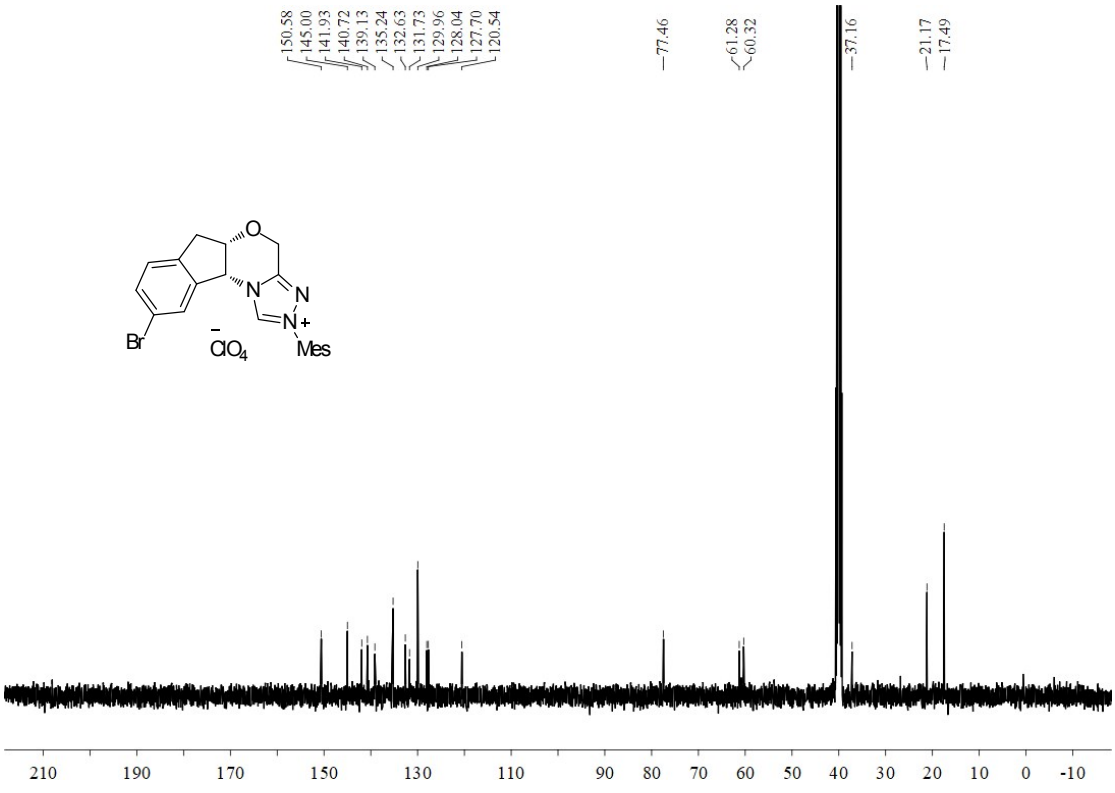


Figure S129. ^{1}H and ^{13}C NMR spectrum of the NHC pre-catalysts D bearing counter ion (Br^-).