

Supporting Information

Regio- and Diastereoselective 1,2-Hydroalkylation of 1,3-Enynes via Dual Photoredox/Ti Catalysis

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1. General remarks

^1H NMR spectra were recorded on a 500 MHz spectrometer. Chemical shifts are reported in delta (δ) units in parts per million (ppm) and the spectra are calibrated to the resonance resulting from incomplete deuteration of the solvent (CDCl_3 : 7.26 ppm). ^{13}C NMR spectra were recorded on the same spectrometer (126 MHz) with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CDCl_3 : 77.0 ppm). Data are reported as follows: chemical shift δ /ppm, integration (^1H only), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet; ^{13}C signals are singlets unless otherwise stated), coupling constants J in Hz, assignment. ^{19}F NMR spectra were recorded on the same spectrometer (471 MHz) and fully decoupled by broad band proton decoupling. High Resolution Mass Spectrometry (HRMS) were recorded on HPLC-Q-TOF mass spectrometer. Measured values are reported to 4 decimal places of the calculated value. The fluorescence emission spectra were collected on a Hitachi F-70000 fluorescence spectrometer.

Unless otherwise noted, the commercially available reagents were used directly without further purification. All reactions were performed under nitrogen gas atmosphere. Anhydrous solvents were directly purchased from Energy Chemical and stored under nitrogen gas. Thin layer chromatography (TLC) was performed using Huanghai TLC silica gel plates HSGF254 and visualized using UV light or potassium permanganate (KMnO_4). Flash column chromatography was performed using 200-300 mesh silica gel.

2. The parameters of the blue LEDs

The photocatalytic reactions were performed on RLH-18CU Light Reactor (Figure S1, left, Beijing Rogertech Ltd.). The maximum emission of the LED strips at 455 nm (Figure S1, right). The Quartz glass was used as reaction vessel at room temperature.

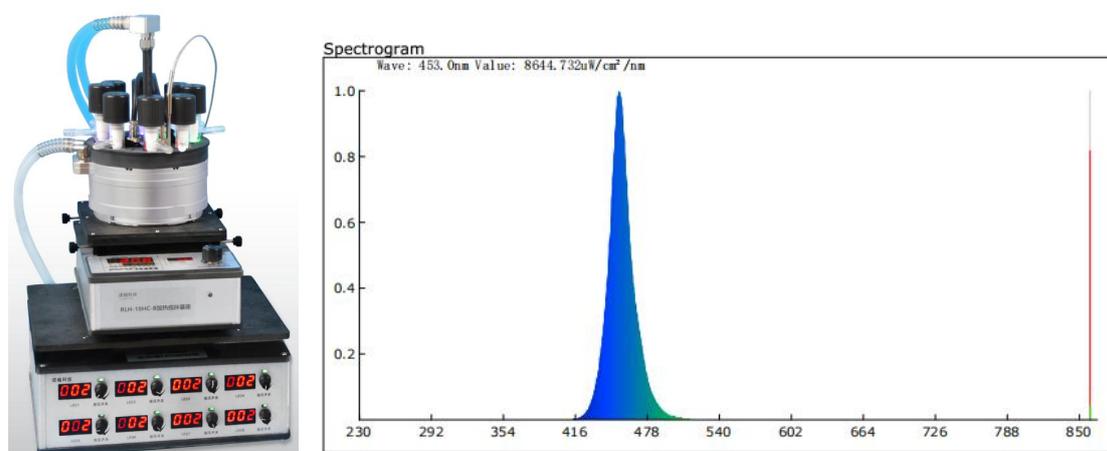
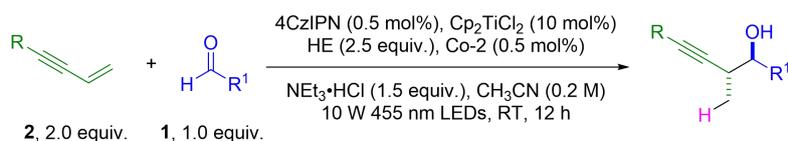


Figure S1. Reaction setup (left) and the emission spectra (right)

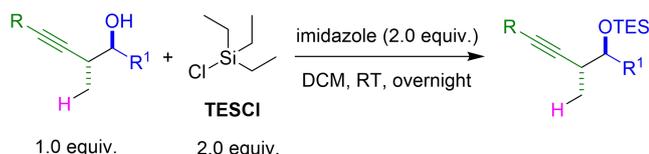
3. General procedures of the reaction



In an oven-dried 15 mL Schlenk tube, 4CzIPN (0.5 mol%), Cp₂TiCl₂ (10 mol%), Hantzsch ester (HE, 2.5 equiv.), NEt₃·HCl (1.5 equiv.) and Co-2 (0.5 mol%) were combined. The tube was subjected to three freeze-pump-thaw cycles and backfilled with nitrogen. For liquid substrates: Aldehyde **1** (0.2 mmol, 1.0 equiv.), 1,3-enyne **2** (0.4 mmol, 2.0 equiv.), and anhydrous CH₃CN (0.2 M) were added under nitrogen. For solid substrates, **1** and **2** were introduced prior to degassing. The reaction mixture was stirred at room temperature under irradiation with blue LEDs (10 W, 455 nm) for 12 h. Upon completion, the solution was concentrated in vacuo and purified by flash chromatography on silica gel (pentane/EtOAc gradient) to afford the desired product.

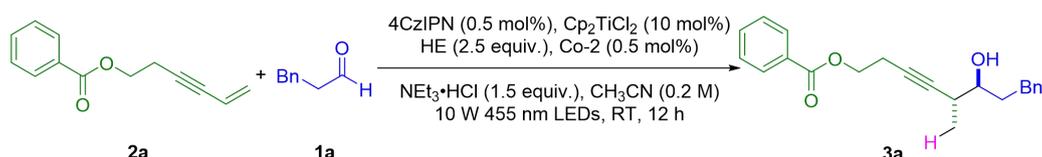
All 1,3-enynes were prepared from the alkynes according to the previous reports.^[1-2]

4. The procedure of TES protection



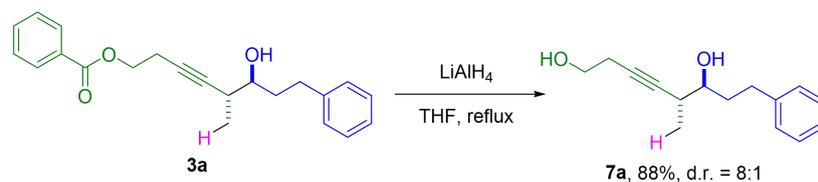
To facilitate purification and mitigate co-elution issues with Hantzsch ester oxidation byproducts, the crude products were converted to triethylsilyl (TES) ether derivatives. In an oven-dried round-bottom flask equipped with a magnetic stir bar, homopropargylic alcohol (1.0 equiv.), triethylsilyl chloride (TESCl, 2.0 equiv.), and imidazole (2.0 equiv.) were dissolved in anhydrous dichloromethane (DCM, 0.2 M). The reaction mixture was stirred at room temperature for 3 h under nitrogen atmosphere. Upon completion (monitored by TLC), the solution was concentrated under reduced pressure and purified by flash chromatography on silica gel (gradient elution: pentane/EtOAc 50:1 to 20:1) to yield the desired TES-protected products.

5. The synthetic transformations

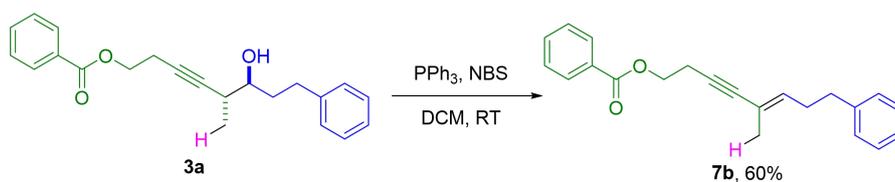


Following the general protocol, a mixture of 3-phenylpropionaldehyde (**1a**, 5 mmol), 1,3-enyne **2a** (10 mmol), 4CzIPN (0.025 mmol), Cp₂TiCl₂ (0.5 mmol), Hantzsch ester (HE, 12.5 mmol), NEt₃·HCl (7.5 equiv.) and Co-2 (0.025 mmol) in anhydrous CH₃CN (0.2 M, 25 mL) was irradiated with blue LEDs (10 W, 455 nm) at room temperature for 48 h under N₂. Upon completion, the solution was concentrated

in vacuo, the crude product was purified by flash chromatography to afford homopropargylic alcohol **3a** as a colourless oil (1.21 g, 72% yield).



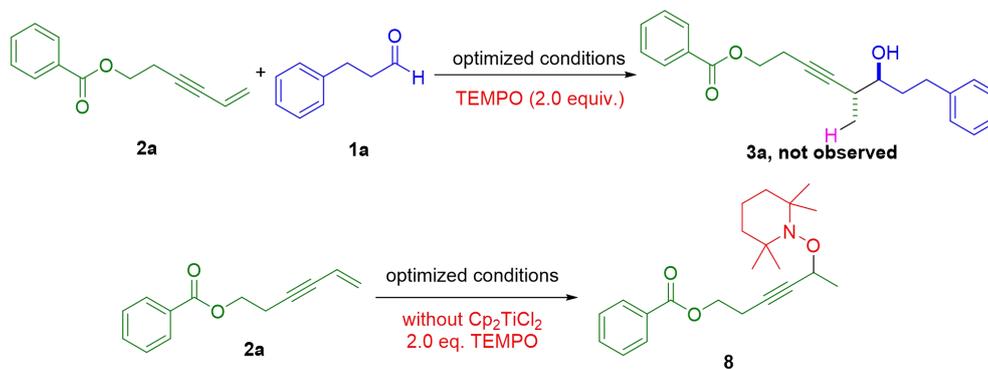
The procedure was modified from the reported literature,^[3] to a solution of compound **3a** (33.6 mg, 0.1 mmol) in THF (5 mL) was added LiAlH₄ (2.5 equiv.) at 0 °C and then the reaction was refluxed for 12 h. After cooling to room temperature, the reaction was diluted with 20% NaOH solution, and then extracted with EtOAc three times. The organic phase was removed and then the residue was purified by flash chromatography using pentane/EtOAc as eluent to give the product **7a** (20.42 mg, 88%).



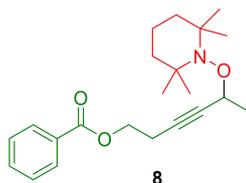
According to a modified literature procedure,^[4] to the cooled solution of **3a** (0.1 mmol, 1.0equiv.) in DCM at 0 °C. Subsequently, NBS (1.5 equiv.) was added under air in one portion and then PPh₃ (1.5 equiv.) was added slowly. The resulting mixture was stirred at room temperature for overnight. After completion of the reaction, the mixture was concentrated and then purified by column chromatography to afford the desired product **7b** in 60% yield.

6. Mechanistic investigation

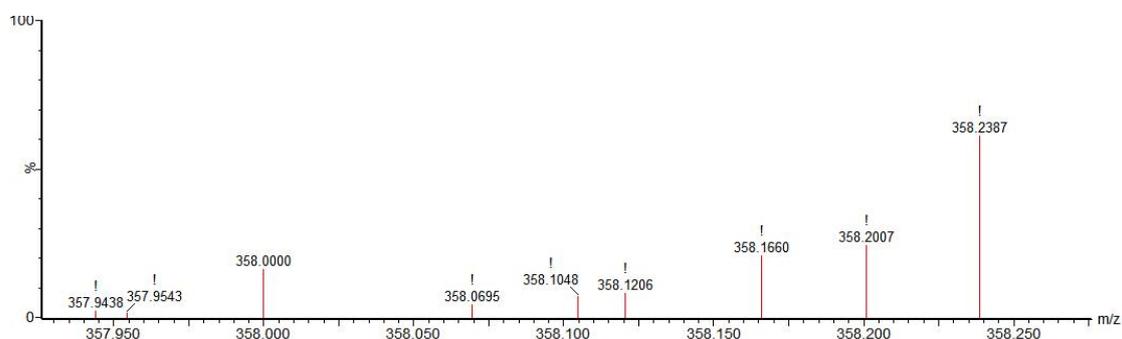
6.1 Radical trapping experiment



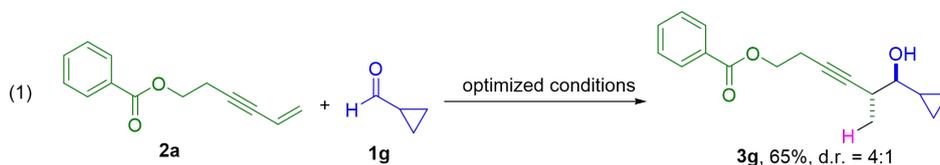
Following the general protocol, the reaction was performed in the presence of radical scavengers (2.0 equiv. of TEMPO), the reaction was inhibited (top). Additionally, the reaction was carried out using 2.0 equivalents of TEMPO in the absence of Cp_2TiCl_2 . The TEMPO adduct **8** could be detected through HRMS. These results demonstrated that the propargyl radical species should be involved in the current transformation and the propargyl radical intermediates could be produced via Co(III)-H catalyzed MHAH.



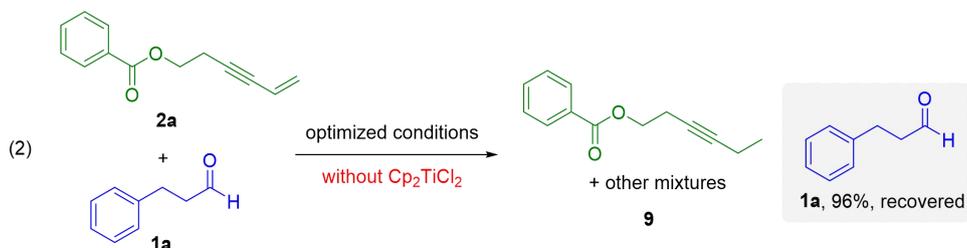
HRMS (ESI) calcd. for $\text{C}_{22}\text{H}_{32}\text{NO}_3$, $[\text{M}+\text{H}^+]$: 358.2377, found: 358.2387



6.2 Radical probing experiment

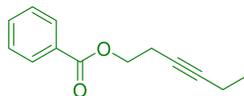


According to the general procedure, cyclopropanecarbaldehyde **1i** was used for the reaction and the corresponding product **3i** could be obtained smoothly without the radical ring-opening coupling product. This results depict that the ketyl radical intermediates may not occur.

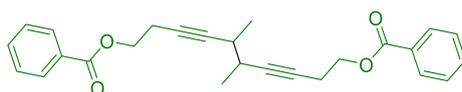
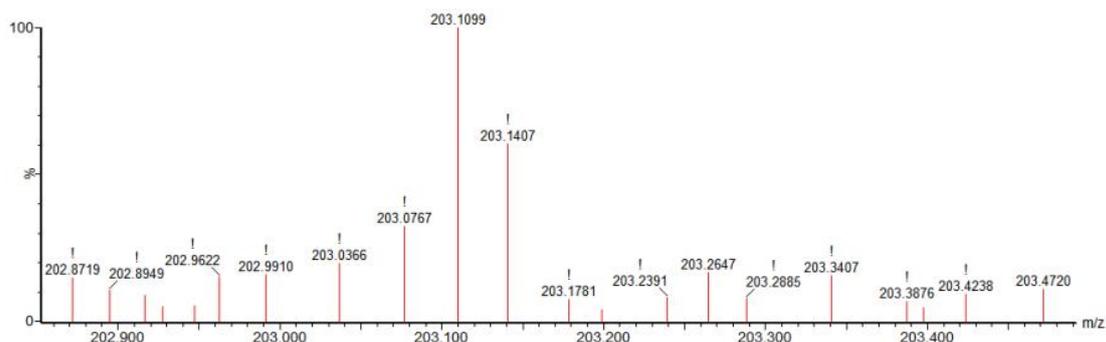


According to the general procedure, the reaction was performed in the absence of Cp_2TiCl_2 . The mixed reduction hydrogenation products and dimerization products of

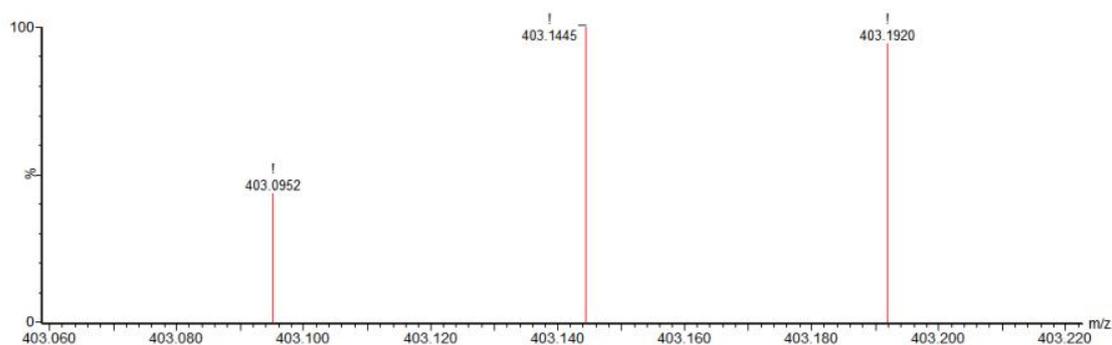
1,3-enynes **2a** could be detected through HRMS. This results further demonstrate that the propargyl radical intermediates could be produced via Co(III)-H catalyzed MHAH and the propargyl radical addition pathway to aldehydes appeared to be energetically unfavorable.



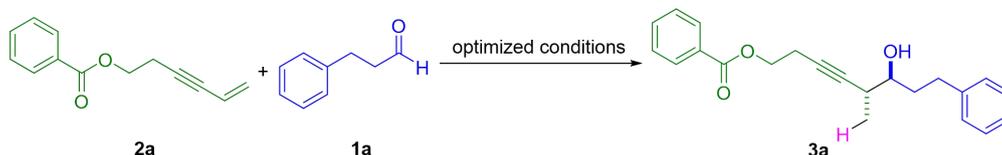
HRMS (ESI) calcd. for $C_{13}H_{15}O_2$, $[M+H]^+$: 203.1067, Found: 203.1099



HRMS (ESI) calcd. for $C_{26}H_{27}O_4$, $[M+H]^+$: 403.1904, Found: 403.1920



6.3 Light on/off experiment



Following the general protocol, light on/off control experiments were conducted for the model reaction at 0.5 mmol scale, using 1,3,5-trimethoxybenzene (0.2 equiv.) as an internal standard. Quantitative 1H NMR analysis of the reaction mixture demonstrated complete suppression of product **3a** formation in the absence of light, unambiguously confirming the photoredox nature of this transformation.

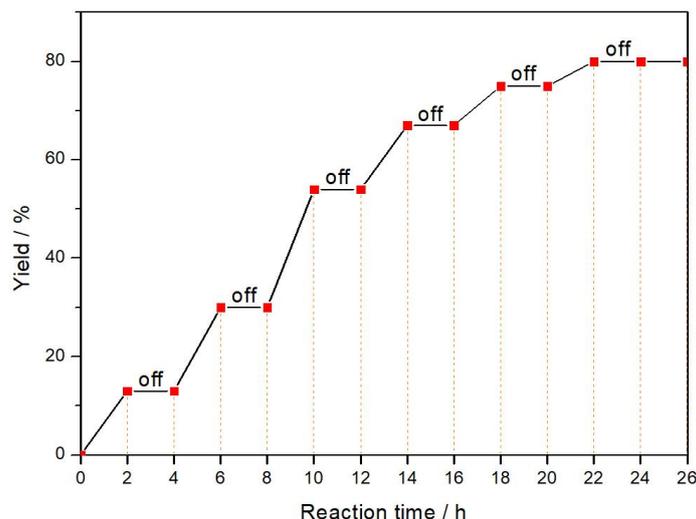


Figure S2. Time profile of the transformation with light on/off over time

6.4 Determination of the reaction quantum yield

Determination of the light intensity at 455 nm:

According to the procedure of the previous reports^[5-6], the photon flux of the blue LED ($\lambda_{\max} = 455$ nm) was determined by standard ferrioxalate actinometry.

Two solutions were prepared and stored in the dark.

Solution 1: A 0.15 M solution of ferrioxalate was prepared by dissolving potassium ferrioxalate hydrate (0.737 g) in H_2SO_4 (10 mL of a 0.05 M).

Solution 2: A buffered solution of 1,10-phenanthroline was prepared by dissolving 1,10-phenanthroline (10.0 mg) and sodium acetate (2.25 g) in 10 mL of 0.5 M H_2SO_4 .

To determine the photon flux of the spectrophotometer, 3.0 mL of ferrioxalate solution was placed in a cuvette and irradiated for 90 seconds at $\lambda_{\max} = 455$ nm. After irradiation, 0.525 mL of phenanthroline solution was added to the cuvette and the mixture was allowed to stir in the dark for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm was measured. Conversion was calculated using eq.1.

$$n(\text{Fe}^{2+}) = \frac{V \times \Delta A}{l \times \varepsilon} \quad (1)$$

Where V is the total volume (0.003525 L) of the solution after addition of phenanthroline; ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions; l is the path length (1.000 cm); ε is the molar absorptivity at 510 nm (11,100 L mol⁻¹ cm⁻¹). The photon flux (F) is obtained by using the following eq.2:

$$F = \frac{n(\text{Fe}^{2+})}{\Phi \times t \times f} \quad (2)$$

Where Φ is the quantum yield for the ferrioxalate actinometer (0.9 at $\lambda = 457.9$ nm); t is the irradiation time (90.0 s); f is the fraction of light absorbed at $\lambda = 455$ nm (0.98) by the ferrioxalate actinometer. So the photon flux (F) was calculated to be 2.29×10^{-9} einstein s^{-1} .

Following the model reaction, after 18000 s, the target product was isolated in 1.49×10^{-5} mol, f is the fraction of light absorbed at $\lambda = 455$ nm by the mixed reaction ($f \approx 1$). The reaction quantum yield Φ can be calculated using eq3 ($\Phi = 0.36$).

$$\Phi = \frac{n(\text{product})}{F \times t \times f} \quad (3)$$

6.5 Stern-Volmer quenching study

Photoluminescence quenching experiments were recorded using Hitachi F-7000 fluorescence spectrometer. All 4CzIPN solutions were excited at 455 nm and the emission intensity was collected at 500-750 nm. In a typical experiment, the THF solution of 4CzIPN (10^{-5} M) was added the appropriate amount of quencher in a screw-top 4.5 cm quartz cuvette. After degassing with nitrogen for 15 min, the emission spectra of the samples were collected. I_0 and I represent the intensities of the emission in the absence and presence of the quencher at 525 nm. The results showed that HE, Cp_2TiCl_2 , and CoPc quenched the photoexcited 4CzIPN* effectively. Comparative quenching studies revealed the following quenching efficiency order was $\text{Cp}_2\text{TiCl}_2 > \text{HE} > \text{Co-2}$, demonstrating that both the reductive and oxidation quenching pathway were involved in this transformation.

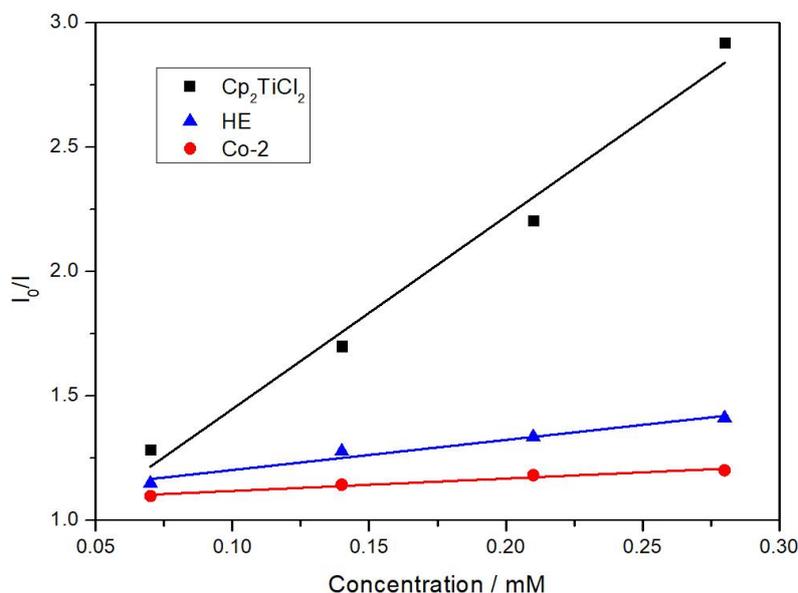


Figure S3. The Stern-Volmer plot.

7. DFT calculations

Computational Methods: All density functional theory (DFT) calculations were performed using the Gaussian 09 software^[7]. Geometry optimizations were carried out employing the hybrid PBE0 exchange-correlation functional^[8], augmented with Grimme's D3 dispersion correction and Becke–Johnson damping to account for long-range interactions^[9-10]. A mixed basis set approach was adopted: the Stuttgart/Dresden (SDD) effective core potential was applied to the titanium center^[11], while the Def2-SVP basis set was used for all other atoms^[12]. Harmonic vibrational frequency analyses were performed at the same level of theory to confirm the nature of each stationary point—either as a local minimum (no imaginary frequencies) or a transition state (one imaginary frequency), and to obtain thermal corrections for Gibbs free energy calculations.

Subsequent single-point energy refinements were conducted on the optimized geometries using the PBE0-D3 functional in conjunction with the Def2-TZVP basis set to improve energetic accuracy^[12]. Solvent effects were modeled using the SMD implicit solvation model with acetonitrile as the solvent^[13]. To ensure the validity of each transition state, intrinsic reaction coordinate (IRC) calculations were performed to confirm proper connectivity between the corresponding reactant and product species.

Cartesian (\AA) Coordinates and Energies of Optimized Structures.

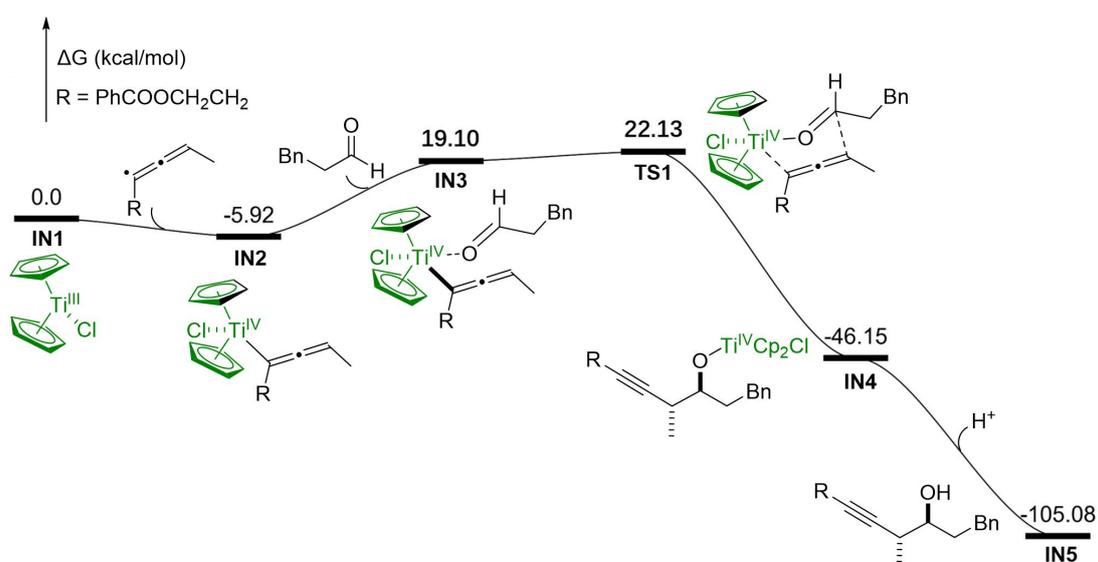


Figure S4. Computational investigations of 1,4-hydrocarbonation process.

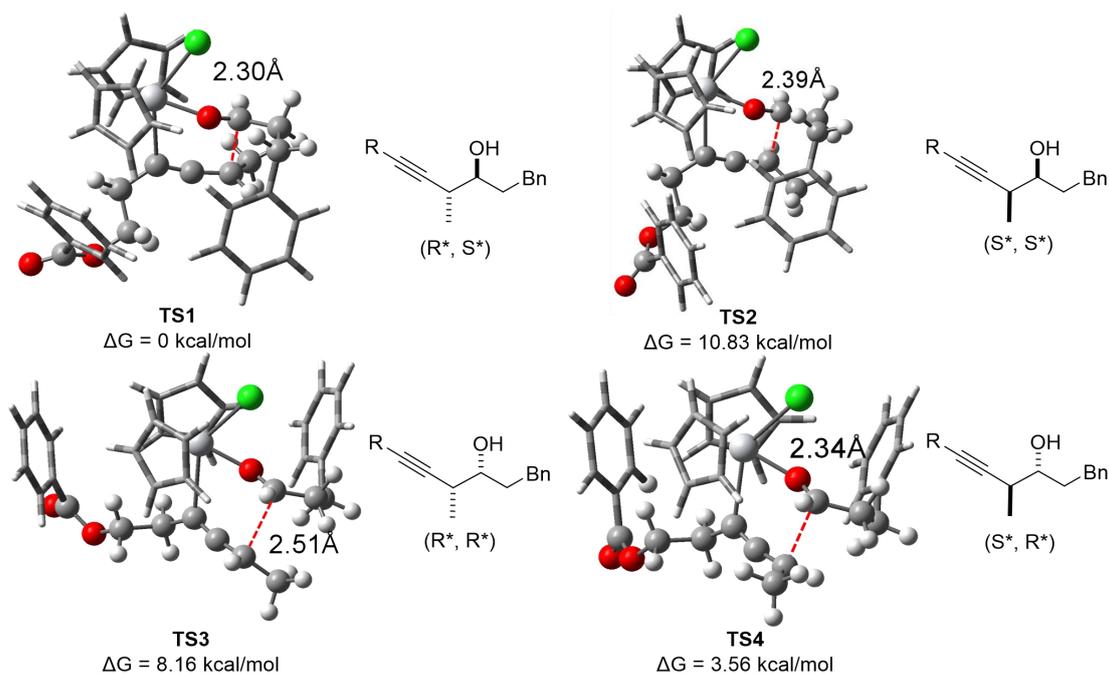


Figure S5. The relative Gibbs free energy of transition states in 1,2-Addition Process.

IN2				C	-1.09555800	-4.50190000	3.85399200
Ti	0.27213300	-1.67768300	1.64230000	H	-0.50720200	-4.67315500	4.77021300
C	2.07397200	-2.09001600	0.18703100	O	-2.16779800	-5.45016100	3.80338500
C	1.09237900	-3.07747100	-0.09644000	C	-3.09040900	-5.52387500	4.76694600
C	1.54455500	-0.83293400	-0.17274800	O	-3.69809600	-6.55366100	4.92629400
H	3.05755300	-2.27042500	0.61951900	C	-3.36350800	-4.30829100	5.59442800
C	-0.04610600	-2.42205500	-0.59893900	C	-3.47344600	-4.45738300	6.98148400
H	1.20227100	-4.15014300	0.04279400	C	-3.60276600	-3.05829900	5.00870100
C	0.21847000	-1.02795000	-0.62238600	C	-3.78219900	-3.35864000	7.78011600
H	2.05930800	0.12186400	-0.08614400	H	-3.30724700	-5.43944100	7.43064300
H	-0.98080700	-2.89879400	-0.88468800	C	-3.93385300	-1.96706700	5.80948100
H	-0.47767400	-0.24587700	-0.92564700	H	-3.54402300	-2.93475700	3.92437100
C	-0.27079800	-0.77766900	3.79486000	C	-4.01313800	-2.11267300	7.19526700
C	1.11736700	-1.02988700	3.77439100	H	-3.84980700	-3.47699500	8.86440600
C	-0.54724200	0.22472300	2.83344700	H	-4.13020700	-0.99698800	5.34586700
H	-1.00280500	-1.27606000	4.42903200	H	-4.26280600	-1.25244600	7.82163100
C	1.69696000	-0.22346500	2.76962100	H	-1.48123400	-3.47676200	3.87491800
H	1.64580000	-1.74008700	4.40354300	C	0.80522500	-3.59739900	2.55247200
C	0.66085700	0.56990100	2.19903300	C	-0.23846100	-4.69085400	2.62231100
H	-1.53017700	0.62415800	2.58943900	H	0.23578200	-5.68626000	2.65062100
H	2.75078500	-0.20046200	2.49442900	H	-0.89419700	-4.65526400	1.73811800
H	0.77500200	1.31189700	1.41076100	C	3.28890000	-3.92744000	3.33217600
Cl	-2.05486100	-2.09772500	1.57920000	C	4.41534900	-4.35451800	2.43558800
C	2.02865600	-3.79381500	2.96039300	H	3.55069500	-3.70557700	4.37806000

H	4.93381600	-5.24146800	2.83804900	H	0.35844000	-2.12709000	5.55780000
H	4.05961800	-4.59828200	1.42369800	H	0.30737600	-2.75893400	3.91794400
H	5.17654300	-3.55953900	2.34839300	C	0.48879200	-3.66518800	-0.17085400
IN3				C	-1.81536500	-2.91270300	1.50942500
Ti	1.77687400	-0.72105800	-0.10754900	H	-1.46664100	-3.95045100	1.40629900
C	1.36877600	-0.45223900	-2.40888700	O	-3.24484000	-2.99608700	1.41919700
C	0.10068700	-0.57084800	-1.81167300	C	-4.06116200	-2.47648200	2.33968900
C	1.96233300	0.75562600	-1.94308200	O	-5.13930900	-2.98119600	2.53224800
H	1.80119600	-1.15575600	-3.11784700	C	-3.63919200	-1.23124000	3.05339800
C	-0.08866500	0.54902000	-0.95611600	C	-3.77352000	-1.16188900	4.44534500
H	-0.61943700	-1.35637700	-2.01683200	C	-3.25657100	-0.09243500	2.33478700
C	1.03990600	1.38314300	-1.08485300	C	-3.49773000	0.02866000	5.11358800
H	2.94067400	1.14526400	-2.21951400	H	-4.09195800	-2.04722000	5.00068300
H	-0.96760100	0.76290100	-0.35008300	C	-3.00623300	1.10428500	3.00543800
H	1.19379000	2.32438300	-0.56767700	H	-3.19115600	-0.12923500	1.24565800
C	3.71148200	-1.45036700	1.04762200	C	-3.11799100	1.16422100	4.39424300
C	3.06508600	-2.59411500	0.55400100	H	-3.58639200	0.07369300	6.20177700
C	4.15622600	-0.68287500	-0.06283200	H	-2.72390600	1.99407300	2.43726700
H	3.80565700	-1.17365400	2.09498400	H	-2.91158500	2.09998800	4.91970600
C	3.08351900	-2.53110100	-0.86588100	H	-1.52584300	-2.55701600	2.50913400
H	2.59537600	-3.36638000	1.15536100	C	0.20719900	-2.40882100	0.04089100
C	3.80010400	-1.37203200	-1.23579400	C	-1.22803700	-2.05214600	0.40511900
H	4.67176100	0.27297700	-0.01435000	H	-1.87080900	-2.18129400	-0.48226900
H	2.64645400	-3.25711600	-1.54745400	H	-1.31293200	-0.99600200	0.68815400
H	4.00812900	-1.04853100	-2.25353400	C	0.78794100	-4.93342600	-0.39183700
Cl	2.51677000	1.36500200	1.39377100	C	0.72047800	-5.61451100	-1.72861900
O	0.97394000	-0.93959600	1.89575500	H	1.13160100	-5.54559500	0.45599000
C	0.31719900	-0.25195900	2.66019400	H	0.04181400	-6.48465000	-1.70594400
C	0.08089200	-0.62722000	4.07334600	H	0.36732600	-4.92849000	-2.51323100
C	0.70577600	-1.93428900	4.52835400	H	1.71045600	-5.99829400	-2.03167200
C	2.21270700	-2.00191700	4.50474200	IN4			
C	3.01370600	-0.90864700	4.85892100	Ti	2.23057900	-0.72805300	0.36569600
C	2.84891400	-3.20125400	4.15809200	C	0.70143700	-0.65102200	-1.41287600
C	4.40533700	-1.01142400	4.86485400	C	0.00507200	-0.20817700	-0.26762600
H	2.55030000	0.04319200	5.13084500	C	1.70585700	0.31277200	-1.71332200
C	4.23888700	-3.31005200	4.16655300	H	0.49000100	-1.55841600	-1.97687000
H	2.23924600	-4.06303600	3.87027700	C	0.60363000	0.99155300	0.17384200
C	5.02511600	-2.21273200	4.51969000	H	-0.80971100	-0.73942500	0.22269400
H	5.00967300	-0.14267700	5.13966600	C	1.64334100	1.31846400	-0.73426400
H	4.71070900	-4.25593800	3.88703300	H	2.41312900	0.26981500	-2.54010800
H	6.11527400	-2.29176100	4.52110400	H	0.33257600	1.55707900	1.06452400
H	-0.13192400	0.69739500	2.31128800	H	2.30545600	2.17851700	-0.66237600
H	0.39892300	0.24127500	4.67866900	C	4.32295500	-1.91372800	0.68983200
H	-1.01400500	-0.64909600	4.21225000	C	3.29430800	-2.84314900	0.89116500

C	4.27046200	-1.47808600	-0.66681900	C	-0.52685800	-2.30256100	2.89894100
H	5.02663800	-1.56722300	1.44344000	C	-1.57049800	-2.18071900	4.00760500
C	2.55993500	-2.95483500	-0.31401700	H	-1.06224200	-2.34652700	1.93328200
H	3.02973600	-3.30680800	1.83851900	H	-2.30223900	-2.99920000	3.94218100
C	3.20703500	-2.15207400	-1.29175000	H	-1.10619000	-2.22058000	5.00415800
H	4.93042200	-0.74555200	-1.13096000	H	-2.11519600	-1.22806200	3.91751900
H	1.67811300	-3.57519400	-0.47334700	C	0.86072500	-4.58773200	3.04998800
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Cl	3.56264200	0.90094000	1.54020900	C	1.77111200	-6.42742100	1.67990100
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O	2.55872900	-7.61194500	1.74791100	H	2.67682400	-5.56865900	3.43448600
C	3.89840900	-7.58076400	1.66092000	H	2.19213500	-5.70264400	0.96982900
O	4.54758000	-8.40152900	2.25804900	H	0.78375000	-6.73744600	1.31152800
C	4.52921500	-6.56958100	0.76036900	IN5			
C	5.68562300	-5.91311900	1.19641300	C	3.10873100	-3.47300500	-0.91778600
C	4.04988300	-6.34820900	-0.53694800	O	7.44915800	-2.52642000	-2.67633500
C	6.34128600	-5.02126400	0.35150300	C	8.64306300	-3.01193400	-2.31090500
H	6.06224900	-6.10240600	2.20427600	O	9.63550300	-2.57687600	-2.83908200
C	4.72453900	-5.47524600	-1.38767500	C	8.70731400	-4.10335600	-1.28990100
H	3.15771700	-6.87264000	-0.88861200	C	9.69287900	-4.02073600	-0.29921800
C	5.86451500	-4.80518800	-0.94252300	C	7.88840300	-5.23748100	-1.36021900
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H	4.35468600	-5.31391100	-2.40304100	H	10.33939600	-3.14109600	-0.25886800
H	6.38365800	-4.11037900	-1.60733400	C	8.05301200	-6.27307700	-0.44277800
O	1.36111200	-1.27253800	1.84812400	H	7.13351400	-5.32568600	-2.14478000
C	0.37386300	-1.04693700	2.79409000	C	9.02248900	-6.17745400	0.55574900
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C	2.04494100	-1.52954700	4.70195600	H	7.41788700	-7.15980900	-0.50742400
C	2.86257200	-0.87803000	5.78253500	H	9.14054200	-6.98566200	1.28122100
C	3.91243400	-0.00870100	5.45009200	O	3.02442800	-1.91638000	1.39371300
C	2.57839600	-1.08857300	7.13737400	C	2.54930100	-3.23714800	1.51039400
C	4.65691700	0.62697200	6.44245600	C	3.56368600	-4.14392700	2.20549700
H	4.14162500	0.17077900	4.39454400	C	4.91299700	-4.30394300	1.50402500
C	3.32139200	-0.45361400	8.13419700	C	5.94647800	-4.95654700	2.37911000
H	1.76299400	-1.76415900	7.41338700	C	6.95689500	-4.20112700	2.98641400
C	4.36400300	0.40666000	7.79014900	C	5.90694200	-6.33595800	2.62945400
H	5.47413300	1.29765700	6.16273000	C	7.89997200	-4.80189600	3.82176200
H	3.08488600	-0.63433100	9.18643200	H	7.00717100	-3.12522400	2.79396600
H	4.94857800	0.90306500	8.56924600	C	6.84498500	-6.94009700	3.46523100
H	-0.30035300	-0.23102400	2.46498700	H	5.13058900	-6.94454400	2.15555500
H	1.54233100	0.37601500	3.83619600	C	7.84586000	-6.17390400	4.06650400
H	0.24985900	-0.31265100	4.82192200	H	8.68420500	-4.19392700	4.28108600
H	2.71228700	-1.88689300	3.90193200	H	6.79875000	-8.01769800	3.64499900
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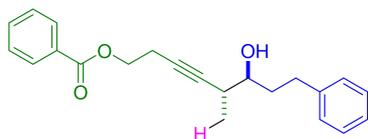
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H	4.78518400	-4.89856700	0.58693700	C	-1.89841900	0.53715400	0.07795800
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C	3.97086700	-3.33581300	-1.76178500	H	-5.03087200	-0.73641100	-0.37314000
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C	6.29057300	-2.59461300	-1.85184300	H	-0.70381200	-0.13019500	3.76329100
H	4.88660900	-2.51632100	-3.49226800	H	0.72170500	0.89218200	3.67368100
H	5.41092900	-4.15052700	-3.06317800	H	-1.06579100	2.21104000	2.81718300
H	6.48304600	-3.18858200	-0.94846500	H	-0.02878700	1.78948400	1.44471900
H	6.05741500	-1.56653200	-1.53371700	C	-0.22015500	-2.57645400	0.81672100
TS1				C	-1.27176000	-3.30137800	-1.88227300
Ti	2.61059200	-1.12055400	-0.05586100	H	-1.90468100	-3.76535100	-1.11393600
C	2.50690200	-1.24727200	-2.38012300	O	-1.54255300	-4.03836800	-3.07749800
C	1.36399800	-0.51767800	-1.96370700	C	-1.10743200	-3.64562900	-4.28126900
C	3.65334600	-0.45766900	-2.10338200	O	-0.96890800	-4.46867500	-5.15197600
H	2.51504000	-2.21912000	-2.86902300	C	-0.84223400	-2.19329900	-4.51973800
C	1.80953900	0.68830300	-1.38727200	C	-1.76303900	-1.20071700	-4.16180300
H	0.32657200	-0.82212300	-2.07224500	C	0.32935800	-1.83908400	-5.19849600
C	3.22115400	0.73239400	-1.49617300	C	-1.49828200	0.13487700	-4.45819300
H	4.68694200	-0.72610500	-2.31456700	H	-2.69931100	-1.47121700	-3.66813800
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C	3.99169000	-2.12882200	1.60967100	C	-0.31261700	0.48710500	-5.10438600
C	2.95324100	-3.03199600	1.35891600	H	-2.22304800	0.90465100	-4.18205000
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C	3.06644300	-3.47000400	0.00840100	H	-1.58175400	-2.25300700	-1.98142600
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H	5.59798700	-1.31505800	0.27134400	H	0.46266800	-4.44485400	-1.33738500
H	2.43526000	-4.20457800	-0.48335700	H	0.79972500	-3.04701600	-2.34988600
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Cl	3.74633100	0.79624300	1.36262400	H	-1.63307800	-1.62526500	2.01401600
O	1.24327100	-0.41144100	1.18680800	C	-0.64280800	-3.18939700	3.23116600
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TS2				C	-0.94496400	-3.44220000	-2.06902400
Ti	2.94725000	-1.25518800	0.18240300	H	-1.49655500	-4.03978100	-1.32673900
C	4.26534000	-0.68021700	-1.73473100	O	-1.11981900	-4.09474300	-3.32754200
C	3.08582900	-1.35902100	-2.13972900	C	-1.80088500	-3.54137800	-4.33750100
C	3.88446800	0.53626000	-1.14864300	O	-2.30626800	-4.25206400	-5.16971200
H	5.28634700	-1.04223500	-1.84110800	C	-1.86736300	-2.04879000	-4.42748300
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C	4.93396000	-2.26869900	0.90305100	H	0.12389500	0.71527100	-4.54107600
H	4.09620500	-1.88658700	2.94532900	H	-2.08667700	1.79975700	-4.92554200
C	3.22375100	-3.62570200	0.23607400	H	-1.39081600	-2.43773200	-2.08800500
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C	4.46054900	-3.07822300	-0.15281500	C	0.52324000	-3.36585000	-1.69148600
H	5.84574900	-1.67429100	0.90025500	H	0.93769000	-4.38656300	-1.63196700
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H	4.94439100	-3.22804800	-1.11573500	C	-0.65232800	-2.59302700	1.86951600
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O	1.43724500	-0.58452500	1.23633500	H	-2.35546300	-1.39239500	1.27466000
C	0.85375600	-0.79325000	2.32534500	H	-2.75845200	-2.92570300	2.08306500
C	0.01394200	0.28905200	2.93296700	H	-2.16290500	-1.56884800	3.04101900
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C	-1.50566800	1.14370600	1.06100100	TS3			
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C	-3.89249300	1.03913300	0.59732400	C	0.33065000	-0.79836200	-1.94048500
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H	1.27644900	-1.52345800	3.03479400	H	1.85330800	2.06042500	-1.15947900
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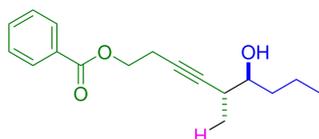
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O	1.03336200	-0.57961800	1.47724700	H	-2.38561100	-0.23898900	0.53952400
C	0.15522300	0.14834400	1.97724200	H	-3.73617700	-1.53687800	2.30614400
C	-0.02675500	0.19803100	3.45760100	H	-2.24004800	-1.84864500	3.20888800
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H	2.48627200	0.58080000	4.68329800	C	1.98838800	0.83335300	-2.26325800
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H	1.40291200	-3.54670100	4.11427900	C	-0.00864800	0.83723600	-1.15156600
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O	-0.25402600	-5.39216600	-2.34976600	H	4.86841800	-0.18875900	-0.30431700
C	0.76322000	-5.79522900	-3.12148800	H	2.14859500	-3.11309300	-1.99919000
O	1.08625500	-6.95642700	-3.11658600	H	3.91594900	-1.19553000	-2.60039100
C	1.43131000	-4.78685200	-4.00201100	Cl	3.02529000	1.39126800	0.85920600
C	0.69167600	-3.92647000	-4.82326500	O	1.03718200	-0.48714700	1.42783900
C	2.82933000	-4.76464900	-4.05092500	C	0.11510500	0.08803000	2.04151600
C	1.34964600	-3.05034800	-5.68338000	C	0.04158800	0.03385200	3.53611000
H	-0.40081200	-3.94734600	-4.79682100	C	0.41556700	-1.28995300	4.19292400
C	3.48354000	-3.86587300	-4.89091400	C	1.86139300	-1.71176300	4.12708400
H	3.40031700	-5.44641300	-3.41646500	C	2.90108900	-0.82978400	4.45075900
C	2.74465500	-3.01079800	-5.71010000	C	2.19412200	-3.03372700	3.80547900
H	0.76935400	-2.38873000	-6.33101900	C	4.22866500	-1.25700300	4.45581400
H	4.57576100	-3.83759000	-4.91108900	H	2.67277800	0.20913300	4.70425900

C	3.52006000	-3.46780700	3.81444800
H	1.39563500	-3.73421900	3.54304400
C	4.54505600	-2.58001300	4.14096600
H	5.02348800	-0.55008700	4.70895800
H	3.75307100	-4.50478700	3.55781800
H	5.58565700	-2.91433700	4.14466900
H	-0.40833400	0.93652100	1.56787200
H	0.70840600	0.84420300	3.88886300
H	-0.96948700	0.33882900	3.84510500
H	0.13291600	-1.21588800	5.25724100
H	-0.20635300	-2.09633300	3.77454700
C	-1.08089000	-1.84704200	0.63968000
C	-0.67177200	-3.55116400	-2.30458900
H	-1.65546600	-3.06679400	-2.37388600
O	-0.86646500	-4.85247900	-2.86196800
C	0.14286900	-5.64512800	-3.24422900
O	-0.02596500	-6.83882500	-3.26758200
C	1.43128900	-5.02203600	-3.67410600
C	1.47439300	-3.95011000	-4.57496400
C	2.62474400	-5.58926300	-3.21190100
C	2.70316000	-3.43970700	-4.99009300
H	0.54856700	-3.52406200	-4.96899300
C	3.84986400	-5.06400500	-3.61456100
H	2.58382200	-6.43703900	-2.52418100
C	3.89025300	-3.98728300	-4.50179800
H	2.73251900	-2.60897700	-5.69939000
H	4.77831400	-5.49800000	-3.23577300
H	4.85195000	-3.57652600	-4.81931100
H	0.03950600	-2.96842400	-2.90282500
C	-0.19030600	-2.34887800	-0.12264300
C	-0.22640800	-3.65879400	-0.85496600
H	-0.92933800	-4.33857700	-0.34542000
H	0.75408000	-4.16055300	-0.83063300
C	-1.80984200	-1.14465500	1.52874100
C	-2.89549700	-0.17341900	1.16585700
H	-2.83978200	0.12651100	0.10955400
H	-3.89519600	-0.60588400	1.34318800
H	-2.83224900	0.73663600	1.78649800
H	-1.82493400	-1.51909000	2.55990500

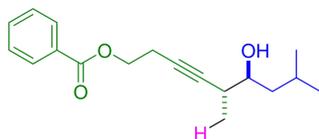
8. Report of the NMR spectra



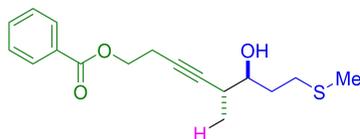
3a, $R_f = 0.5$ (EA:PE=1:5), column solvent: hexane/EtOAc = 10/1, 78%, colourless oil, ^1H NMR (500 MHz, CDCl_3) δ 8.07 (d, $J = 7.2$ Hz, 2H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.43 (t, $J = 7.8$ Hz, 2H), 7.30 – 7.24 (m, 2H), 7.22 – 7.14 (m, 3H), 4.43 (t, $J = 6.7$ Hz, 2H), 3.55 – 3.33 (m, 1H), 2.88 – 2.76 (m, 1H), 2.72 – 2.60 (m, 3H), 2.57 – 2.46 (m, 1H), 1.95 (s, 1H), 1.87 – 1.76 (m, 2H), 1.17 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 166.40, 141.95, 133.04, 129.90, 129.58, 128.39, 128.34, 128.30, 125.72, 82.42, 78.94, 77.25, 77.00, 76.75, 73.60, 62.98, 36.93, 33.28, 32.00, 19.51, 17.71. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{22}\text{H}_{25}\text{O}_3$, 337.1798, found 337.1803.



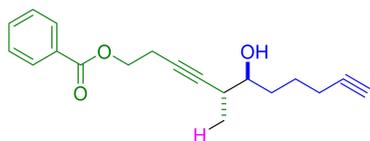
3b, $R_f = 0.5$ (EA:PE=1:5), column solvent: hexane/EtOAc = 10/1, 80%, colourless oil, ^1H NMR (500 MHz, CDCl_3) δ 8.06 (d, $J = 8.4$ Hz, 2H), 7.57 (t, $J = 6.8$ Hz, 1H), 7.44 (t, $J = 7.8$ Hz, 2H), 4.42 (t, $J = 6.7$ Hz, 2H), 3.54 – 3.34 (m, 1H), 2.70 – 2.62 (m, 2H), 2.53 – 2.45 (m, 1H), 1.53 – 1.34 (m, 4H), 1.18 (d, $J = 7.0$ Hz, 3H), 0.88 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 166.44, 133.06, 129.98, 129.63, 128.37, 82.61, 78.75, 74.21, 63.05, 37.44, 33.17, 19.54, 18.95, 17.82, 13.99. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{17}\text{H}_{23}\text{O}_3$, 275.1642, found 275.1655.



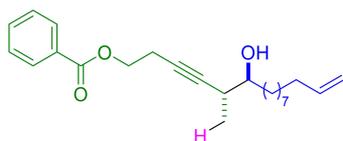
3c, $R_f = 0.5$ (EA:PE=1:5), column solvent: hexane/EtOAc = 10/1, 75%, colourless oil, ^1H NMR (500 MHz, CDCl_3) δ 8.06 (d, $J = 7.1$ Hz, 2H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.44 (t, $J = 7.7$ Hz, 2H), 4.43 (t, $J = 6.7$ Hz, 2H), 3.61 – 3.41 (m, 1H), 2.71 – 2.61 (m, 2H), 2.49 – 2.40 (m, 1H), 1.83 – 1.73 (m, 1H), 1.48 – 1.40 (m, 1H), 1.28 – 1.22 (m, 1H), 1.18 (d, $J = 7.0$ Hz, 3H), 0.88 (d, $J = 6.4$ Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 166.44, 133.07, 129.64, 128.38, 82.63, 78.83, 72.50, 63.06, 44.55, 33.63, 24.57, 23.48, 21.89, 19.54, 17.85. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{18}\text{H}_{25}\text{O}_3$, 289.1798, found 289.1807.



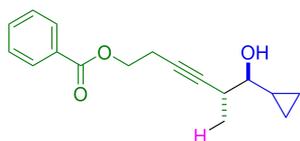
3d, $R_f = 0.5$ (EA:PE=1:5), column solvent: hexane/EtOAc = 10/1, 70%, colourless oil, ^1H NMR (500 MHz, CDCl_3) δ 8.05 (d, $J = 7.2$ Hz, 2H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.44 (t, $J = 7.8$ Hz, 2H), 4.42 (t, $J = 5.8$ Hz, 2H), 3.66 – 3.47 (m, 1H), 2.68 – 2.47 (m, 5H), 2.08 (s, 3H), 1.81 – 1.72 (m, 2H), 1.18 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 166.43, 133.08, 129.92, 129.61, 128.38, 82.31, 79.03, 73.25, 62.97, 34.27, 33.21, 30.75, 19.52, 17.57, 15.47. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{17}\text{H}_{23}\text{O}_3\text{S}$, 307.1362, found 307.1377.



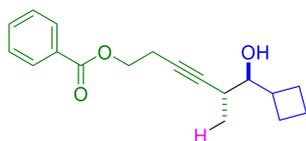
3e, $R_f = 0.5$ (EA:PE=1:5), column solvent: hexane/EtOAc = 10/1, 72%, colourless oil, ^1H NMR (500 MHz, CDCl_3) δ 8.06 (d, $J = 7.3$ Hz, 2H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.45 (t, $J = 7.7$ Hz, 2H), 4.43 (t, $J = 6.7$ Hz, 2H), 3.54 – 3.33 (m, 1H), 2.70 – 2.62 (m, 2H), 2.55 – 2.45 (m, 1H), 2.21 – 2.14 (m, 2H), 1.98 – 1.91 (m, 1H), 1.83 (s, 1H), 1.71 – 1.51 (m, 4H), 1.18 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 166.44, 133.11, 129.94, 129.62, 128.39, 84.27, 82.43, 79.00, 73.99, 68.49, 63.00, 34.16, 33.36, 24.69, 19.54, 18.23, 17.75. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{19}\text{H}_{23}\text{O}_3$, 299.1642, found 299.1651.



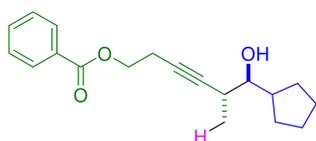
3f, $R_f = 0.5$ (EA:PE=1:5), column solvent: hexane/EtOAc = 10/1, 77%, colourless oil, ^1H NMR (500 MHz, CDCl_3) δ 8.12 – 7.99 (m, 2H), 7.60 – 7.51 (m, 1H), 7.44 (t, $J = 7.7$ Hz, 2H), 5.90 – 5.61 (m, 1H), 5.20 – 4.87 (m, 2H), 4.46 – 4.29 (m, 2H), 3.50 – 3.29 (m, 1H), 2.90 – 2.30 (m, 3H), 2.10 – 1.98 (m, 2H), 1.68 – 1.58 (m, 4H), 1.30 – 1.21 (m, 10H), 1.14 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 166.44, 139.23, 133.07, 129.98, 129.64, 128.37, 114.09, 82.61, 78.76, 74.49, 63.06, 35.32, 33.79, 33.14, 29.56, 29.54, 29.42, 29.11, 28.91, 25.79, 19.54, 17.84. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{24}\text{H}_{35}\text{O}_3$, 371.2581, found 371.2592.



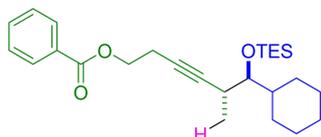
3g, $R_f = 0.5$ (EA:PE=1:5), column solvent: hexane/EtOAc = 10/1, 65%, colourless oil, ^1H NMR (500 MHz, CDCl_3) δ 8.05 (d, $J = 7.2$ Hz, 2H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.44 (t, $J = 7.8$ Hz, 2H), 4.49 – 4.38 (m, 2H), 2.84 – 2.58 (m, 4H), 1.22 (d, $J = 6.5$ Hz, 3H), 1.04 – 0.92 (m, 1H), 0.59 – 0.40 (m, 2H), 0.38 – 0.17 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 166.42, 133.05, 129.98, 129.62, 128.35, 83.08, 79.33, 63.04, 33.83, 19.54, 17.92, 16.43, 15.87, 3.09, 2.42. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{17}\text{H}_{21}\text{O}_3$, 273.1485, found 273.1495.



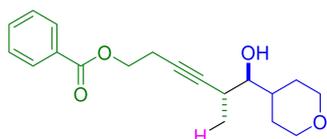
3h, $R_f = 0.5$ (EA:PE=1:5), column solvent: hexane/EtOAc = 10/1, 67%, colourless oil, ^1H NMR (500 MHz, CDCl_3) δ 8.06 (d, $J = 7.2$ Hz, 2H), 7.56 (t, $J = 7.7$ Hz, 1H), 7.44 (t, $J = 7.7$ Hz, 2H), 4.41 (t, $J = 6.7$ Hz, 2H), 3.48 – 3.20 (m, 1H), 2.70 – 2.58 (m, 2H), 2.49 – 2.43 (m, 1H), 1.98 – 1.67 (m, 7H), 1.16 (d, $J = 7.1$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 166.40, 133.04, 129.97, 129.60, 128.34, 82.40, 78.47, 63.01, 39.75, 30.47, 24.80, 24.65, 19.51, 18.14, 17.96. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{18}\text{H}_{23}\text{O}_3$, 287.1642, found 287.1653.



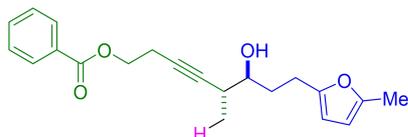
3i, $R_f = 0.5$ (EA:PE=1:5), column solvent: hexane/EtOAc = 10/1, 61%, colourless oil, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.05 (d, $J = 7.1$ Hz, 2H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.44 (t, $J = 7.7$ Hz, 2H), 4.42 (t, $J = 6.7$ Hz, 2H), 3.10 – 3.02 (m, 1H), 2.69 – 2.63 (m, 2H), 2.62 – 2.57 (m, 1H), 2.02 – 1.95 (m, 1H), 1.75 – 1.65 (m, 4H), 1.59 – 1.54 (m, 2H), 1.49 – 1.42 (m, 2H), 1.20 (d, $J = 7.0$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 166.43, 133.06, 129.97, 129.61, 128.36, 82.26, 78.91, 63.06, 44.96, 31.85, 29.27, 29.13, 25.51, 25.40, 19.56, 18.58. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{19}\text{H}_{25}\text{O}_3$, 301.1798, found 301.1809.



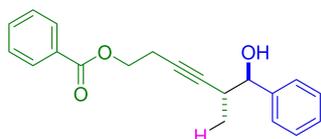
3j, $R_f = 0.6$ (EA:PE=1:20), column solvent: hexane/EtOAc = 50/1, 71%, colourless oil, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.06 (d, $J = 7.1$ Hz, 2H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.44 (t, $J = 7.7$ Hz, 2H), 4.38 (t, $J = 7.0$ Hz, 2H), 3.39 – 3.30 (m, 1H), 2.72 – 2.52 (m, 3H), 1.80 – 1.57 (m, 6H), 1.26 (s, 1H), 1.20 – 1.14 (m, 2H), 1.13 (d, $J = 7.0$ Hz, 3H), 1.11 – 1.04 (m, 2H), 0.97 (t, $J = 7.9$ Hz, 9H), 0.62 (q, $J = 7.9$ Hz, 6H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 166.35, 132.91, 130.14, 129.62, 128.29, 84.86, 79.58, 76.78, 63.33, 41.64, 31.07, 30.35, 28.38, 26.53, 26.46, 26.21, 19.54, 17.41, 7.07, 5.41. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{26}\text{H}_{41}\text{O}_3\text{Si}$, 429.2819, found 429.2828.



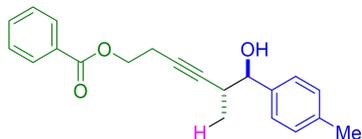
3k, $R_f = 0.3$ (EA:PE=1:5), column solvent: hexane/EtOAc = 5/1, 78%, colourless oil, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.05 (d, $J = 7.2$ Hz, 2H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.44 (t, $J = 7.7$ Hz, 2H), 4.49 – 4.36 (m, 2H), 4.00 – 3.84 (m, 2H), 3.33 – 3.14 (m, 2H), 3.12 – 2.86 (m, 1H), 2.76 – 2.55 (m, 3H), 1.82 – 1.74 (m, 2H), 1.66 – 1.57 (m, 1H), 1.46 (m, 1H), 1.38 – 1.27 (m, 2H), 1.21 (d, $J = 6.9$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 166.42, 133.13, 129.86, 129.57, 128.38, 81.62, 79.21, 78.26, 67.79, 67.45, 62.94, 39.48, 29.38, 29.16, 29.03, 19.56, 18.43. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{19}\text{H}_{25}\text{O}_4$, 317.1747, found 317.1759.



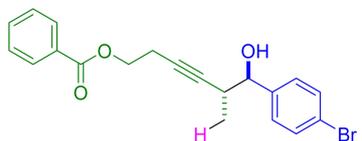
3l, $R_f = 0.4$ (EA:PE=1:5), column solvent: hexane/EtOAc = 10/1, 73%, colourless oil, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.05 (d, $J = 7.3$ Hz, 2H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.43 (t, $J = 7.7$ Hz, 2H), 5.83 (d, $J = 4.6$ Hz, 2H), 4.42 (t, $J = 6.7$ Hz, 2H), 3.58 – 3.34 (m, 1H), 2.78 – 2.60 (m, 4H), 2.55 – 2.47 (m, 1H), 2.24 (s, 3H), 1.89 (s, 1H), 1.84 – 1.69 (m, 2H), 1.18 (d, $J = 7.0$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 166.41, 153.80, 150.28, 133.05, 129.93, 129.61, 128.36, 105.77, 105.51, 82.40, 78.97, 73.65, 62.99, 33.72, 33.25, 24.42, 19.53, 17.75, 13.48. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{21}\text{H}_{25}\text{O}_4$, 341.1747, found 341.1767.



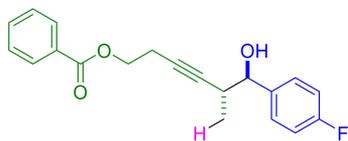
4a, $R_f = 0.4$ (EA:PE=1:5), column solvent: hexane/EtOAc = 10/1, 62%, colourless oil, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.08 – 8.02 (m, 2H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.47 – 7.41 (m, 2H), 7.37 – 7.27 (m, 5H), 4.72 – 4.33 (m, 3H), 2.82 – 2.56 (m, 3H), 1.05 (d, $J = 7.0$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 166.47, 141.55, 133.09, 129.96, 129.65, 128.39, 128.23, 127.86, 126.60, 82.89, 79.29, 77.64, 63.00, 35.48, 19.56, 17.66. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{20}\text{H}_{21}\text{O}_3$, 309.1485, found 309.1499.



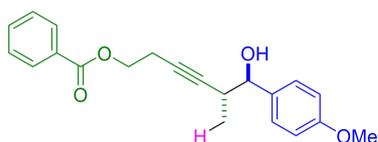
4b, $R_f = 0.4$ (EA:PE=1:5), column solvent: hexane/EtOAc = 10/1, 65%, colourless oil, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.08 – 8.02 (m, 2H), 7.57 (t, $J = 6.8$ Hz, 1H), 7.47 – 7.41 (m, 2H), 7.22 (d, $J = 8.1$ Hz, 2H), 7.12 (d, $J = 7.9$ Hz, 2H), 4.66 – 4.34 (m, 3H), 2.76 – 2.57 (m, 3H), 2.32 (s, 3H), 1.04 (d, $J = 7.0$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 166.46, 138.59, 137.51, 133.07, 129.98, 129.65, 128.90, 128.38, 126.50, 83.04, 79.15, 77.48, 63.02, 35.41, 21.12, 19.55, 17.67. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{21}\text{H}_{23}\text{O}_3$, 323.1642, found 323.1655.



4c, $R_f = 0.4$ (EA:PE=1:5), column solvent: hexane/EtOAc = 10/1, 57%, colourless oil, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.07 – 8.02 (m, 2H), 7.58 (t, $J = 7.4$ Hz, 1H), 7.48 – 7.40 (m, 4H), 7.24 – 7.17 (m, 2H), 4.65 – 4.34 (m, 3H), 2.81 – 2.58 (m, 3H), 1.05 (d, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 166.49, 140.63, 133.14, 131.29, 129.91, 129.63, 128.42, 128.30, 121.65, 82.36, 79.72, 76.88, 62.92, 35.42, 19.57, 17.54. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{20}\text{H}_{20}\text{O}_3\text{Br}$, 387.0590, found 387.0606.

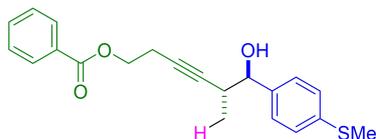


4d, $R_f = 0.4$ (EA:PE=1:5), column solvent: hexane/EtOAc = 10/1, 60%, colourless oil, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.08 – 8.01 (m, 2H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.48 – 7.41 (m, 2H), 7.35 – 7.27 (m, 2H), 7.04 – 6.94 (m, 2H), 4.66 – 4.33 (m, 3H), 2.80 – 2.59 (m, 3H), 1.03 (d, $J = 6.9$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 166.48, 162.33 (d, $J = 246.0$ Hz), 137.31 (d, $J = 3.3$ Hz), 133.12, 129.91, 129.63, 128.40, 128.21 (d, $J = 8.2$ Hz), 115.04 (d, $J = 21.2$ Hz), 82.63, 79.52, 76.92, 62.93, 35.54, 19.55, 17.52. $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ -114.49 – -115.03 (m, 1F). HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{20}\text{H}_{20}\text{O}_3\text{F}$, 327.1391, found 327.1407.

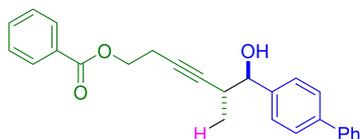


4e, $R_f = 0.3$ (EA:PE=1:5), column solvent: hexane/EtOAc = 8/1, 67%, colourless oil, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.07 – 7.97 (m, 2H), 7.54 (t, $J = 7.4$ Hz, 1H), 7.45 – 7.38 (m, 2H), 7.26 – 7.19 (m, 2H), 6.86 – 6.77 (m, 2H), 4.59 – 4.31 (m, 3H), 3.75 (s, 3H), 2.81 – 2.56 (m, 3H), 1.00 (d, $J = 6.9$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 166.43, 159.19, 133.69, 133.05, 129.96, 129.62, 128.36, 127.76, 113.58,

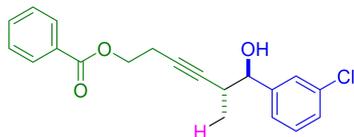
83.13, 79.10, 76.12, 63.00, 55.19, 35.42, 19.54, 17.59. HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{21}H_{23}O_4$, 339.1591, found 339.1602.



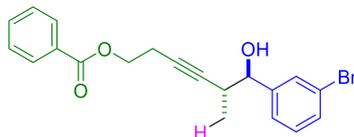
4f, $R_f = 0.3$ (EA:PE=1:5), column solvent: hexane/EtOAc = 8/1, 66%, colourless oil, 1H NMR (500 MHz, $CDCl_3$) δ 8.07 – 7.99 (m, 2H), 7.55 (t, $J = 7.4$ Hz, 1H), 7.46 – 7.38 (m, 2H), 7.25 – 7.21 (m, 2H), 7.19 – 7.12 (m, 2H), 4.65 – 4.31 (m, 3H), 2.83 – 2.56 (m, 3H), 2.43 (s, 3H), 1.08 – 0.93 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.47, 138.47, 137.93, 133.10, 129.95, 129.64, 128.40, 127.12, 126.37, 82.79, 79.40, 77.21, 62.98, 35.42, 19.57, 17.60, 15.81. HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{21}H_{23}O_3S$, 355.1362, found 355.1374.



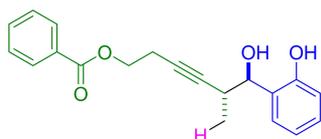
4g, $R_f = 0.4$ (EA:PE=1:5), column solvent: hexane/EtOAc = 10/1, 50%, colourless oil, 1H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, $J = 7.7$ Hz, 2H), 7.61 – 7.51 (m, 5H), 7.47 – 7.39 (m, 6H), 7.34 (t, $J = 7.3$ Hz, 1H), 4.63 – 4.34 (m, 3H), 2.84 – 2.63 (m, 3H), 1.10 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.50, 140.78, 140.73, 140.62, 133.10, 129.96, 129.65, 128.72, 128.40, 127.26, 127.06, 127.04, 126.96, 82.85, 79.43, 77.37, 63.01, 35.45, 19.59, 17.71. HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{26}H_{25}O_3$, 385.1798, found 385.1804.



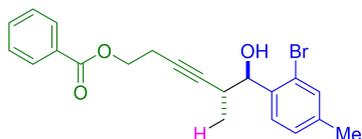
4h, $R_f = 0.4$ (EA:PE=1:5), column solvent: hexane/EtOAc = 10/1, 70%, colourless oil, 1H NMR (500 MHz, $CDCl_3$) δ 8.08 – 8.02 (m, 2H), 7.58 (t, $J = 7.4$ Hz, 1H), 7.48 – 7.42 (m, 2H), 7.33 – 7.27 (m, 4H), 4.66 – 4.33 (m, 3H), 2.76 – 2.60 (m, 3H), 1.05 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.49, 140.10, 133.48, 133.13, 129.89, 129.63, 128.63, 128.41, 128.33, 128.11, 127.94, 82.41, 79.66, 76.83, 62.92, 35.44, 19.56, 17.53. HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{20}H_{20}O_3Cl$, 343.1095, found 343.1110.



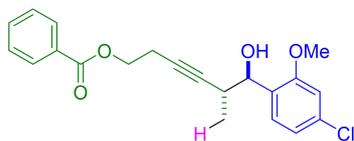
4i, $R_f = 0.4$ (EA:PE=1:5), column solvent: hexane/EtOAc = 10/1, 61%, colourless oil, 1H NMR (500 MHz, $CDCl_3$) δ 8.05 (t, $J = 7.2$ Hz, 2H), 7.60 – 7.49 (m, 2H), 7.48 – 7.42 (m, 2H), 7.38 (t, $J = 8.7$ Hz, 1H), 7.26 (s, 1H), 7.19 – 7.13 (m, 1H), 4.68 – 4.35 (m, 3H), 2.81 – 2.59 (m, 3H), 1.07 (d, $J = 7.2$ Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.49, 143.97, 133.12, 130.87, 129.92, 129.73, 129.68, 129.64, 128.40, 125.26, 122.36, 82.28, 79.78, 76.81, 62.91, 35.45, 19.56, 17.54. HRMS-ESI (m/z) $[M+H]^+$ calculated for $C_{20}H_{20}O_3Br$, 387.0590, found 387.0606.



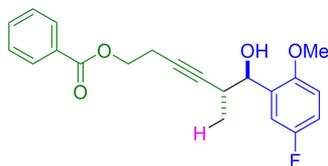
4j, $R_f = 0.2$ (EA:PE=1:5), column solvent: hexane/EtOAc = 3/1, 66%, colourless oil, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.32 (s, 0.5H), 8.12 – 8.01 (m, 2H), 7.92 (s, 0.5H), 7.63 – 7.54 (m, 1H), 7.50 – 7.40 (m, 2H), 7.21 – 7.09 (m, 1H), 6.99 – 6.74 (m, 3H), 5.00 – 4.29 (m, 3H), 3.56 (s, 0.5H), 3.39 (s, 0.5H), 2.98 – 2.79 (m, 1H), 2.74 – 2.56 (m, 2H), 1.12 (d, $J = 7.0$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 166.80, 156.04, 133.22, 129.84, 129.64, 129.36, 128.84, 128.44, 123.64, 119.38, 117.20, 83.25, 79.41, 78.51, 62.86, 34.49, 19.68, 17.54. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{20}\text{H}_{21}\text{O}_4$, 325.1434, found 325.1450.



4k, $R_f = 0.4$ (EA:PE=1:5), column solvent: hexane/EtOAc = 10/1, 75%, colourless oil, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.05 (d, $J = 7.6$ Hz, 2H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.48 – 7.41 (m, 3H), 7.32 (s, 1H), 7.09 (d, $J = 7.8$ Hz, 1H), 5.09 (d, $J = 4.3$ Hz, 1H), 4.41 (t, $J = 6.2$ Hz, 2H), 3.05 – 2.94 (m, 1H), 2.69 – 2.60 (m, 2H), 2.28 (s, 3H), 1.03 (d, $J = 7.0$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 166.50, 139.07, 137.05, 133.05, 132.91, 130.00, 129.65, 128.37, 128.26, 128.02, 122.06, 83.58, 78.38, 74.42, 62.98, 32.04, 20.66, 19.56, 14.70. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{21}\text{H}_{22}\text{O}_3\text{Br}$, 401.0747, found 401.0759.

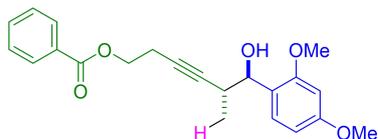


4l, $R_f = 0.3$ (EA:PE=1:5), column solvent: hexane/EtOAc = 7/1, 54%, colourless oil, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.05 (d, $J = 7.1$ Hz, 2H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.44 (t, $J = 7.8$ Hz, 2H), 7.15 – 7.10 (m, 1H), 6.92 – 6.87 (m, 1H), 6.79 – 6.73 (m, 1H), 4.79 (d, $J = 5.6$ Hz, 1H), 4.45 – 4.36 (m, 2H), 3.79 (s, 3H), 2.88 – 2.80 (m, 1H), 2.69 – 2.61 (m, 2H), 1.15 (d, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 166.47, 156.16, 152.37, 133.04, 132.35, 129.98, 129.65, 128.37, 114.21, 114.02, 111.12, 82.45, 79.22, 71.69, 63.05, 55.80, 34.14, 19.53, 18.19. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{21}\text{H}_{22}\text{O}_4\text{Cl}$, 373.1201, found 373.1218.

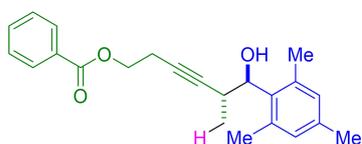


4m, $R_f = 0.3$ (EA:PE=1:5), column solvent: hexane/EtOAc = 7/1, 60%, colourless oil, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.04 (d, $J = 7.1$ Hz, 2H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.45 (t, $J = 7.8$ Hz, 2H), 7.34 (d, $J = 8.2$ Hz, 1H), 6.90 (dd, $J = 8.2, 1.9$ Hz, 1H), 6.82 (d, $J = 1.9$ Hz, 1H), 4.87 (d, $J = 5.4$ Hz, 1H), 4.36 (t, $J = 6.8$ Hz, 2H), 3.80 (s, 3H), 2.97 – 2.90 (m, 1H), 2.65 – 2.58 (m, 2H), 1.04 (d, $J = 7.0$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 166.54, 162.54, 160.55, 136.10, 133.11, 129.95, 129.64, 129.60, 128.40, 119.58 (d, $J = 24.6$ Hz), 114.39 (d, $J = 20.9$ Hz), 83.26, 78.71, 73.98, 62.90, 32.06, 30.11, 19.60, 14.58.

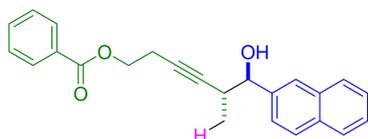
^{19}F NMR (471 MHz, CDCl_3) δ -112.95 (s, 1F). HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{21}\text{H}_{22}\text{O}_4\text{F}$, 357.1497, found 357.1505.



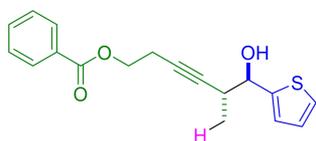
4n, $R_f = 0.3$ (EA:PE=1:5), column solvent: hexane/EtOAc = 5/1, 62%, colourless oil, ^1H NMR (500 MHz, CDCl_3) δ 8.04 (d, $J = 7.9$ Hz, 2H), 7.56 (t, $J = 7.1$ Hz, 1H), 7.44 (t, $J = 7.6$ Hz, 2H), 7.03 – 6.99 (m, 1H), 6.78 – 6.72 (m, 2H), 4.85 (d, $J = 5.6$ Hz, 1H), 4.34 (t, $J = 6.9$ Hz, 2H), 3.77 (s, 3H), 3.76 (s, 3H), 3.00 – 2.91 (m, 1H), 2.66 – 2.57 (m, 2H), 1.09 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 166.40, 153.38, 150.50, 133.00, 130.56, 130.05, 129.63, 128.34, 114.31, 112.71, 111.16, 84.25, 77.96, 73.14, 63.08, 55.70, 32.20, 19.48, 15.64. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{22}\text{H}_{25}\text{O}_5$, 369.1697, found 369.1710.



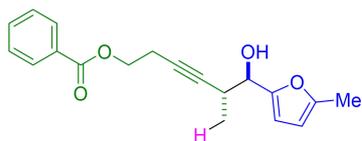
4o, $R_f = 0.4$ (EA:PE=1:5), column solvent: hexane/EtOAc = 10/1, 65%, colourless oil, ^1H NMR (500 MHz, CDCl_3) δ 8.09 (d, $J = 8.3$ Hz, 2H), 7.57 (t, $J = 8.0$ Hz, 1H), 7.45 (t, $J = 7.7$ Hz, 2H), 6.80 (s, 2H), 4.88 (d, $J = 10.0$ Hz, 1H), 4.54 – 4.42 (m, 2H), 3.18 – 3.10 (m, 1H), 2.77 – 2.69 (m, 2H), 2.39 (s, 6H), 2.24 (s, 3H), 0.93 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 166.47, 136.86, 136.79, 133.14, 133.04, 130.14, 129.95, 129.62, 128.35, 84.34, 78.47, 74.30, 62.90, 32.91, 20.93, 20.70, 19.60, 17.38. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{23}\text{H}_{27}\text{O}_3$, 351.1955, found 351.1971.



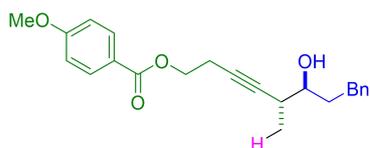
4p, $R_f = 0.4$ (EA:PE=1:5), column solvent: hexane/EtOAc = 10/1, 73%, colourless oil, ^1H NMR (500 MHz, CDCl_3) δ 8.14 – 7.99 (m, 2H), 7.89 – 7.73 (m, 4H), 7.59 – 7.53 (m, 1H), 7.52 – 7.33 (m, 5H), 4.91 – 4.57 (m, 1H), 4.49 – 4.31 (m, 2H), 2.98 – 2.82 (m, 1H), 2.76 – 2.58 (m, 2H), 1.14 – 0.99 (m, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 166.48, 138.99, 133.08, 133.04, 129.94, 129.64, 128.39, 128.05, 127.95, 127.65, 126.07, 125.88, 125.82, 125.34, 124.33, 82.86, 79.41, 77.77, 62.99, 35.42, 19.58, 17.72. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{24}\text{H}_{23}\text{O}_3$, 359.1642, found 359.1653.



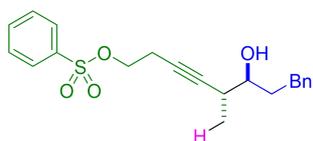
4q, $R_f = 0.4$ (EA:PE=1:5), column solvent: hexane/EtOAc = 10/1, 50%, colourless oil, ^1H NMR (500 MHz, CDCl_3) δ 8.05 (d, $J = 8.4$ Hz, 2H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.47 – 7.40 (m, 2H), 7.24 – 7.17 (m, 1H), 7.00 (d, $J = 3.4$ Hz, 1H), 6.94 – 6.90 (m, 1H), 4.91 – 4.69 (m, 1H), 4.46 – 4.38 (m, 2H), 2.96 – 2.76 (m, 1H), 2.72 – 2.63 (m, 2H), 1.16 – 1.09 (m, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 166.47, 145.39, 133.09, 129.95, 129.66, 128.39, 126.37, 124.91, 124.79, 82.34, 79.88, 73.64, 62.94, 35.77, 19.57, 17.76. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{18}\text{H}_{19}\text{O}_3\text{S}$, 315.1049, found 315.1057.



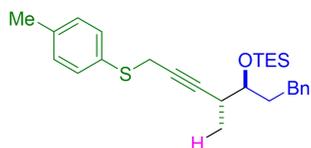
4r, $R_f = 0.4$ (EA:PE=1:5), column solvent: hexane/EtOAc = 10/1, 77%, colourless oil, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.05 (d, $J = 7.1$ Hz, 2H), 7.57 (t, $J = 8.6$ Hz, 1H), 7.44 (t, $J = 7.7$ Hz, 2H), 6.17 (d, $J = 3.0$ Hz, 1H), 5.86 (d, $J = 4.0$ Hz, 1H), 4.45 – 4.34 (m, 3H), 3.02 – 2.92 (m, 1H), 2.69 – 2.62 (m, 2H), 2.25 (s, 3H), 1.11 (d, $J = 7.0$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 166.47, 152.19, 151.85, 133.07, 129.95, 129.64, 128.38, 108.31, 106.00, 82.53, 79.20, 71.24, 63.00, 32.70, 19.55, 17.76, 13.53. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{19}\text{H}_{21}\text{O}_4$, 313.1434, found 313.1434.



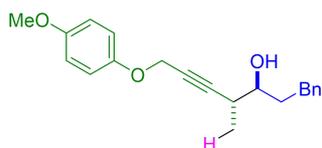
5a, $R_f = 0.4$ (EA:PE=1:10), column solvent: hexane/EtOAc = 5/1, 70%, colourless oil, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.01 (d, $J = 8.9$ Hz, 2H), 7.28 (t, $J = 6.3$ Hz, 2H), 7.22 – 7.15 (m, 3H), 6.91 (d, $J = 8.9$ Hz, 2H), 4.40 (t, $J = 6.7$ Hz, 2H), 3.85 (s, 3H), 3.44 – 3.33 (m, 1H), 2.85 – 2.76 (m, 1H), 2.71 – 2.60 (m, 3H), 2.56 – 2.47 (m, 1H), 1.86 – 1.77 (m, 2H), 1.18 (d, $J = 7.0$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 166.16, 163.41, 141.98, 131.63, 128.39, 128.29, 125.71, 122.29, 113.58, 82.31, 79.09, 73.64, 62.68, 55.36, 36.93, 33.27, 32.01, 19.57, 17.74. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{23}\text{H}_{27}\text{O}_4$, 367.1904, found 367.1920.



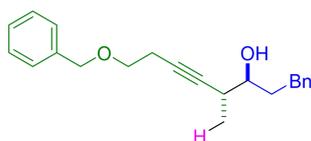
5b, $R_f = 0.4$ (EA:PE=1:10), column solvent: hexane/EtOAc = 5/1, 60%, colourless oil, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.92 (d, $J = 7.3$ Hz, 2H), 7.65 (t, $J = 7.5$ Hz, 1H), 7.55 (t, $J = 7.8$ Hz, 2H), 7.29 (t, $J = 7.5$ Hz, 2H), 7.24 – 7.17 (m, 3H), 4.11 (t, $J = 6.9$ Hz, 2H), 3.52 – 3.35 (m, 1H), 2.88 – 2.78 (m, 1H), 2.72 – 2.62 (m, 1H), 2.60 – 2.54 (m, 2H), 2.50 – 2.40 (m, 1H), 1.84 – 1.76 (m, 2H), 1.15 (d, $J = 7.0$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 141.93, 135.93, 133.84, 129.25, 128.43, 128.34, 127.79, 125.78, 83.31, 77.19, 73.53, 68.21, 36.88, 33.23, 32.01, 19.80, 17.58. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{21}\text{H}_{25}\text{O}_4\text{S}$, 373.1468, found 373.1480.



5c, $R_f = 0.7$ (EA:PE=1:10), column solvent: hexane/EtOAc = 50/1, 55%, colourless oil, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.36 (d, $J = 8.1$ Hz, 2H), 7.31 – 7.27 (m, 2H), 7.20 (t, $J = 7.4$ Hz, 3H), 7.09 (d, $J = 8.2$ Hz, 2H), 3.86 – 3.68 (m, 1H), 3.58 (s, 2H), 2.78 – 2.69 (m, 1H), 2.67 – 2.58 (m, 1H), 2.58 – 2.48 (m, 1H), 2.31 (s, 3H), 1.97 – 1.85 (m, 1H), 1.74 – 1.64 (m, 1H), 1.11 (d, $J = 7.1$ Hz, 3H), 0.99 (t, $J = 7.9$ Hz, 9H), 0.63 (q, $J = 8.0$ Hz, 6H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 142.42, 136.88, 131.66, 130.99, 129.55, 128.33, 128.27, 125.65, 85.79, 77.48, 74.18, 34.68, 32.54, 23.87, 21.02, 17.49, 14.64, 6.94, 5.09. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{27}\text{H}_{39}\text{OSSi}$, 439.2485, found 439.2495.



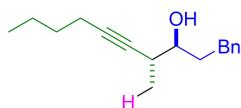
5d, $R_f = 0.4$ (EA:PE=1:10), column solvent: hexane/EtOAc = 5/1, 62%, colourless oil, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.31 – 7.26 (m, 2H), 7.18 (t, $J = 8.5$ Hz, 3H), 6.91 (d, $J = 9.1$ Hz, 2H), 6.83 (d, $J = 9.2$ Hz, 2H), 4.65 (d, $J = 1.9$ Hz, 2H), 3.76 (s, 3H), 3.46 – 3.37 (m, 1H), 2.82 – 2.62 (m, 2H), 2.60 – 2.54 (m, 1H), 1.82 – 1.74 (m, 2H), 1.20 (d, $J = 7.0$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 154.36, 151.62, 141.83, 128.42, 128.36, 125.82, 116.30, 114.54, 88.25, 78.28, 73.52, 57.09, 55.65, 36.88, 33.35, 32.00, 17.27. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{21}\text{H}_{25}\text{O}_3$, 325.1798, found 325.1808.



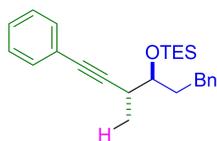
5e, $R_f = 0.4$ (EA:PE=1:10), column solvent: hexane/EtOAc = 5/1, 76%, colourless oil, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.36 (d, $J = 4.4$ Hz, 4H), 7.31 – 7.28 (m, 3H), 7.23 – 7.19 (m, 3H), 4.56 (s, 2H), 3.58 (t, $J = 6.8$ Hz, 2H), 3.43 – 3.37 (m, 1H), 2.86 – 2.67 (m, 2H), 2.55 – 2.47 (m, 3H), 1.87 – 1.81 (m, 2H), 1.20 (d, $J = 6.9$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 142.06, 138.00, 128.43, 128.38, 128.32, 127.66, 125.74, 81.72, 80.25, 73.72, 72.91, 68.65, 36.94, 33.39, 32.05, 20.13, 17.76. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{22}\text{H}_{27}\text{O}_2$, 323.2006, found 323.2012.



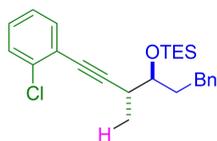
5f, $R_f = 0.4$ (EA:PE=1:10), column solvent: hexane/EtOAc = 5/1, 49%, colourless oil, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.31 – 7.26 (m, 4H), 7.20 (t, $J = 7.4$ Hz, 1H), 7.16 (d, $J = 7.4$ Hz, 2H), 6.88 (d, $J = 8.1$ Hz, 2H), 6.84 (t, $J = 7.3$ Hz, 1H), 4.07 (s, 2H), 3.48 – 3.29 (m, 1H), 2.95 (s, 3H), 2.78 – 2.55 (m, 2H), 2.52 – 2.45 (m, 1H), 1.76 – 1.66 (m, 2H), 1.50 (s, 1H), 1.16 (d, $J = 7.0$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 141.90, 129.09, 129.05, 128.43, 128.32, 125.75, 118.44, 114.60, 84.79, 78.40, 73.56, 43.17, 38.78, 36.98, 33.25, 31.99, 17.63. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{21}\text{H}_{26}\text{NO}$, 308.2009, found 308.2012.



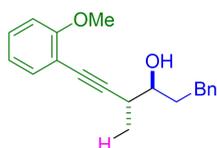
5g, $R_f = 0.6$ (EA:PE=1:10), column solvent: hexane/EtOAc = 10/1, 57%, colourless oil, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.28 (d, $J = 7.5$ Hz, 2H), 7.23 – 7.19 (m, 3H), 3.41 – 3.36 (m, 1H), 2.86 – 2.81 (m, 1H), 2.71 – 2.67 (m, 1H), 2.54 – 2.49 (m, 1H), 2.21 – 2.16 (m, 2H), 1.86 – 1.81 (m, 2H), 1.49 – 1.45 (m, 2H), 1.43 – 1.38 (m, 2H), 1.18 (d, $J = 7.0$ Hz, 3H), 0.91 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 142.13, 128.44, 128.34, 125.75, 83.78, 80.23, 73.82, 36.99, 33.40, 32.08, 31.10, 21.93, 18.37, 17.92, 13.58. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{17}\text{H}_{25}\text{O}$, 245.1900, found 245.1911.



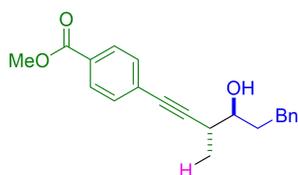
5h, $R_f = 0.7$ (EA:PE=1:10), column solvent: hexane/EtOAc = 50/1, 54%, colourless oil, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.41 – 7.37 (m, 2H), 7.31 – 7.27 (m, 5H), 7.24 – 7.17 (m, 3H), 3.91 – 3.85 (m, 1H), 2.88 – 2.62 (m, 3H), 2.11 – 2.02 (m, 1H), 1.86 – 1.76 (m, 1H), 1.25 (d, $J = 7.1$ Hz, 3H), 1.00 (t, $J = 7.9$ Hz, 9H), 0.66 (q, $J = 8.0$ Hz, 6H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 142.46, 131.55, 128.37, 128.33, 128.14, 127.56, 125.70, 123.88, 92.11, 82.08, 74.27, 35.06, 33.12, 32.47, 14.92, 6.97, 5.16. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{25}\text{H}_{35}\text{OSi}$, 379.2452, found 379.2456.



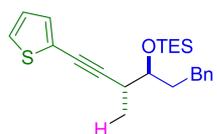
5i, $R_f = 0.7$ (EA:PE=1:10), column solvent: hexane/EtOAc = 50/1, 60%, colourless oil, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.43 – 7.40 (m, 1H), 7.38 – 7.35 (m, 1H), 7.30 – 7.26 (m, 2H), 7.22 (d, $J = 7.0$ Hz, 2H), 7.20 – 7.16 (m, 3H), 3.93 – 3.88 (m, 1H), 2.95 – 2.87 (m, 1H), 2.84 – 2.76 (m, 1H), 2.69 – 2.62 (m, 1H), 2.19 – 2.10 (m, 1H), 1.85 – 1.77 (m, 1H), 1.28 (d, $J = 7.1$ Hz, 3H), 1.00 (t, $J = 7.9$ Hz, 9H), 0.65 (q, $J = 8.0$ Hz, 6H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 142.45, 135.91, 133.17, 129.10, 128.57, 128.39, 128.32, 126.26, 125.68, 123.66, 97.67, 79.09, 74.22, 35.08, 33.33, 32.67, 14.65, 6.97, 5.15. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{19}\text{H}_{20}\text{OCl}$, 299.1197, found 299.1200.



5j, $R_f = 0.5$ (EA:PE=1:10), column solvent: hexane/EtOAc = 10/1, 63%, colourless oil, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.37 – 7.34 (m, 1H), 7.29 (t, $J = 7.6$ Hz, 3H), 7.24 (d, $J = 7.0$ Hz, 2H), 7.19 (t, $J = 7.2$ Hz, 1H), 6.91 – 6.84 (m, 2H), 3.86 (s, 3H), 3.55 – 3.48 (m, 1H), 2.92 – 2.72 (m, 3H), 1.98 – 1.89 (m, 2H), 1.31 (d, $J = 7.0$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 160.13, 142.18, 132.76, 129.30, 128.48, 128.35, 125.76, 120.39, 112.36, 110.38, 94.94, 79.80, 74.05, 55.72, 37.08, 34.40, 32.13, 17.51. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{20}\text{H}_{23}\text{O}_2$, 295.1693, found 295.1699.

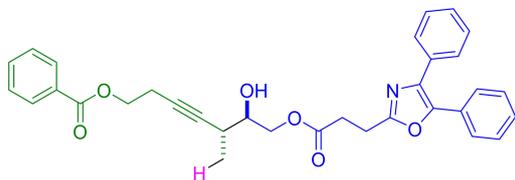


5k, $R_f = 0.4$ (EA:PE=1:10), column solvent: hexane/EtOAc = 8/1, 51%, colourless oil, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.96 (d, $J = 8.2$ Hz, 2H), 7.46 (d, $J = 8.2$ Hz, 2H), 7.30 (t, $J = 7.5$ Hz, 2H), 7.23 (d, $J = 7.3$ Hz, 2H), 7.20 (t, $J = 7.3$ Hz, 1H), 3.91 (s, 3H), 3.58 – 3.54 (m, 1H), 2.88 – 2.73 (m, 3H), 1.96 – 1.90 (m, 2H), 1.31 (d, $J = 7.0$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 166.56, 141.80, 131.60, 129.40, 129.23, 128.44, 128.41, 128.04, 125.89, 93.58, 82.84, 73.64, 52.16, 36.91, 34.01, 32.06, 17.25. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{21}\text{H}_{23}\text{O}_3$, 323.1642, found 323.1653.

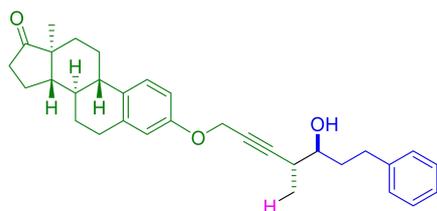


5l, $R_f = 0.7$ (EA:PE=1:10), column solvent: hexane/EtOAc = 50/1, 56%, colourless oil, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.34 – 7.32 (m, 1H), 7.30 – 7.26 (m, 2H), 7.24 – 7.20 (m, 3H), 7.18 (t, $J = 7.3$ Hz, 1H),

7.05 (d, $J = 4.9$ Hz, 1H), 3.87 – 3.82 (m, 1H), 2.85 – 2.75 (m, 2H), 2.66 – 2.58 (m, 1H), 2.07 – 2.00 (m, 1H), 1.83 – 1.75 (m, 1H), 1.23 (d, $J = 7.0$ Hz, 3H), 0.99 (t, $J = 7.9$ Hz, 9H), 0.65 (q, $J = 8.0$ Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 142.46, 130.00, 128.36, 128.33, 127.64, 125.71, 124.93, 91.59, 83.60, 74.24, 35.05, 33.12, 32.43, 14.91, 6.97, 5.15. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{23}\text{H}_{33}\text{OSSi}$, 385.2016, found 385.2027.



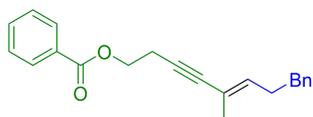
6a, $R_f = 0.3$ (EA:PE=1:10), column solvent: hexane/EtOAc = 5/1, 70%, colourless oil, ^1H NMR (500 MHz, CDCl_3) δ 8.05 (d, $J = 8.3$ Hz, 2H), 7.63 – 7.59 (m, 2H), 7.55 (t, $J = 7.4$ Hz, 3H), 7.44 (t, $J = 7.7$ Hz, 2H), 7.38 – 7.29 (m, 6H), 4.42 – 4.37 (m, 2H), 4.26 – 4.15 (m, 2H), 3.72 – 3.62 (m, 1H), 3.23 – 3.14 (m, 2H), 2.94 – 2.88 (m, 2H), 2.67 – 2.56 (m, 3H), 1.15 (d, $J = 6.8$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 171.74, 166.40, 161.71, 145.48, 135.08, 133.05, 132.14, 129.62, 128.62, 128.51, 128.36, 128.09, 127.97, 127.91, 126.44, 81.47, 79.11, 71.70, 66.97, 62.92, 31.32, 29.71, 23.57, 19.49, 17.30. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{33}\text{H}_{32}\text{NO}_6$, 538.2224, found 538.2231.



6b, $R_f = 0.3$ (EA:PE=1:10), column solvent: hexane/EtOAc = 5/1, 55%, colourless oil, ^1H NMR (500 MHz, CDCl_3) δ 7.28 (t, $J = 7.4$ Hz, 2H), 7.22 – 7.15 (m, 4H), 6.78 (d, $J = 8.6$ Hz, 1H), 6.72 (s, 1H), 4.70 – 4.64 (m, 2H), 3.54 – 3.40 (m, 1H), 2.91 – 2.86 (m, 2H), 2.82 – 2.75 (m, 1H), 2.68 – 2.58 (m, 2H), 2.54 – 2.47 (m, 1H), 2.40 – 2.35 (m, 1H), 2.27 – 2.21 (m, 1H), 2.18 – 2.10 (m, 1H), 2.07 – 1.93 (m, 4H), 1.84 – 1.78 (m, 2H), 1.65 – 1.57 (m, 2H), 1.54 – 1.46 (m, 3H), 1.45 – 1.38 (m, 1H), 1.21 (d, $J = 7.1$ Hz, 3H), 0.90 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 155.52, 141.76, 137.70, 132.74, 128.34, 128.28, 126.24, 125.75, 115.09, 115.06, 112.53, 88.31, 78.13, 73.44, 56.24, 50.28, 47.91, 43.86, 38.17, 36.75, 35.78, 33.26, 31.97, 31.46, 29.54, 26.42, 25.78, 21.49, 17.18, 13.75. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{32}\text{H}_{39}\text{O}_3$, 471.2894, found 471.2903.



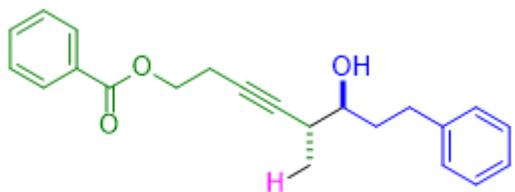
7a, $R_f = 0.3$ (EA:PE=1:10), column solvent: hexane/EtOAc = 5/1, 88%, colourless oil, ^1H NMR (500 MHz, CDCl_3) δ 7.29 (t, $J = 7.5$ Hz, 2H), 7.23 – 7.18 (m, 3H), 3.69 (t, $J = 6.1$ Hz, 2H), 3.46 – 3.36 (m, 1H), 2.87 – 2.79 (m, 1H), 2.73 – 2.65 (m, 1H), 2.55 – 2.50 (m, 1H), 2.46 – 2.42 (m, 4H), 1.89 – 1.82 (m, 2H), 1.19 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 141.95, 128.40, 128.34, 125.78, 82.75, 79.89, 73.73, 61.15, 36.88, 33.22, 32.03, 23.02, 17.86. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{15}\text{H}_{21}\text{O}_2$, 233.1536, found 233.1541.



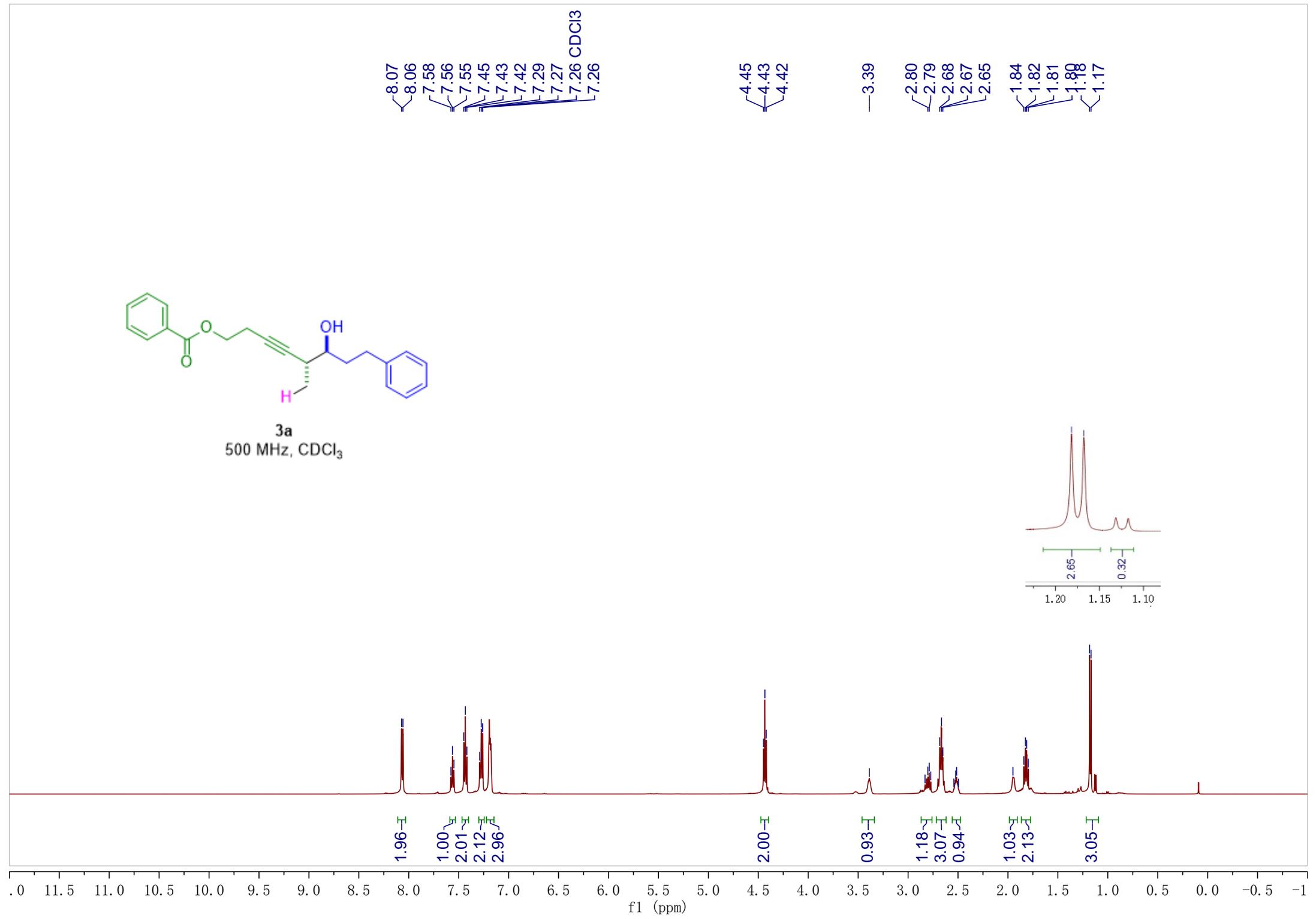
7b, $R_f = 0.6$ (EA:PE=1:10), column solvent: hexane/EtOAc = 50/1, 60%, colourless oil, ^1H NMR (500 MHz, CDCl_3) δ 8.06 (d, $J = 7.1$ Hz, 2H), 7.55 (t, $J = 8.0$ Hz, 1H), 7.41 (t, $J = 7.8$ Hz, 2H), 7.29 – 7.25 (m, 2H), 7.18 (t, $J = 7.2$ Hz, 3H), 5.64 (t, $J = 7.2$ Hz, 1H), 4.44 (t, $J = 6.9$ Hz, 2H), 2.83 (t, $J = 6.9$ Hz, 2H), 2.65 (t, $J = 7.7$ Hz, 2H), 2.56 – 2.49 (m, 2H), 1.80 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 166.3, 141.8, 136.3, 133.0, 130.0, 129.6, 128.4, 128.3, 128.3, 125.8, 118.4, 89.0, 81.31, 63.0, 35.3, 32.1, 23.2, 20.1. HRMS-ESI (m/z) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{22}\text{H}_{23}\text{O}_2$, 319.1693, found 319.1698.

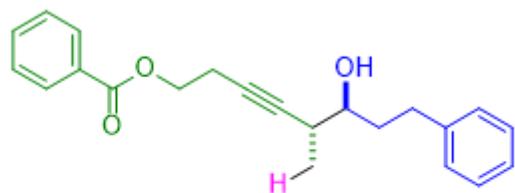
Reference:

- [1] Wu J, Xu X, Duan C, et al. Diastereoselective 1, 2-difunctionalization of 1, 3-enynes enabled by merging photoexcited Hantzsch ester with chromium catalysis[J]. *Organic Chemistry Frontiers*, 2024, 11: 284-289.
- [2] He J, Yoon W S, Yun J. Cu-Catalyzed diastereo- and enantioselective synthesis of homopropargyl amines bearing all-carbon quaternary stereocenters via chirality transfer of hindered allenylcopper species[J]. *ACS Catalysis*, 2024, 15: 578-584.
- [3] Li J, Li S, Cui G H, et al. Photoinduced copper-catalyzed regio- and enantioselective alkynylation of epoxides[J]. *ACS Catalysis*, 2024, 14: 7553-7561.
- [4] Zhang F H, Guo X, Zeng X, et al. Catalytic enantioconvergent allenylation of aldehydes with propargyl halides[J]. *Angewandte Chemie International Edition*, 2022, 61(10): e202117114.
- [5] Cismesia, M. A.; Yoon, T. P. Characterizing chain processes in visible light photoredox catalysis. *Chemical Science*. 2015, 6, 5426-5434.
- [6] Kim S, Lee Y, Cho E J. Photoredox selective homocoupling of propargyl bromides[J]. *The Journal of Organic Chemistry*, 2022, 88: 6382-6389.
- [7] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
- [8] Adamo, C.; Barone, V. Toward Reliable Density Functional Methods without Adjustable Parameters: The PBE0 Model. *J. Chem. Phys.* 1999, 110, 6158.
- [9] Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* 2010, 132, 154104.
- [10] Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *J. Comput. Chem.* 2011, 32, 1456.
- [11] Igelmann, G.; Stoll, H.; and Preuss, H. Pseudopotentials for main group elements (IIIa through VIIa). *Mole. Phys.* 2006, 65, 1321.
- [12] Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* 2005, 7, 3297.
- [13] Marenich, A. V.; Cramer, C. J.; and Truhlar, D. G. Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. *J. Phys. Chem. B* 2009, 113, 6378.



3a
500 MHz, CDCl₃





3a
126 MHz, CDCl₃

— 166.40

— 141.95
— 133.04
— 129.90
— 129.58
— 128.39
— 128.34
— 128.30
— 125.72

— 82.42
— 78.94
— 77.25
— 77.00 CDCl₃
— 76.75
— 73.60
— 62.98

— 36.93
— 33.28
— 32.00

— 19.51
— 17.71

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)



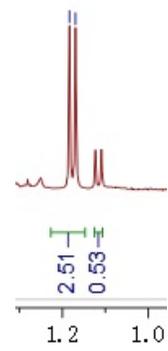
3b
500 MHz, CDCl₃

8.06
8.05
7.58
7.57
7.55
7.46
7.44
7.43
7.26 CDCl₃

4.44
4.42
4.41

3.39
3.37
3.34
2.68
2.66
2.65
2.50
2.48
2.46

1.48
1.47
1.46
1.44
1.18
1.17
0.90
0.88
0.87



2.21

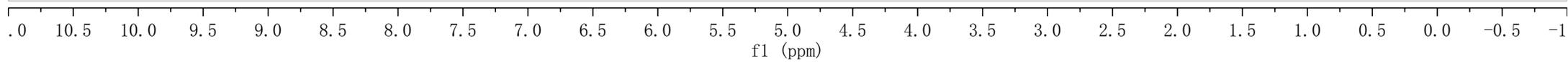
1.12
2.06

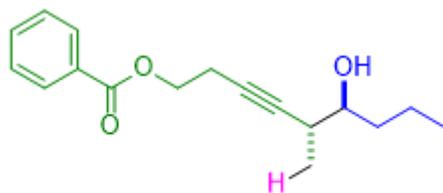
1.99

1.00

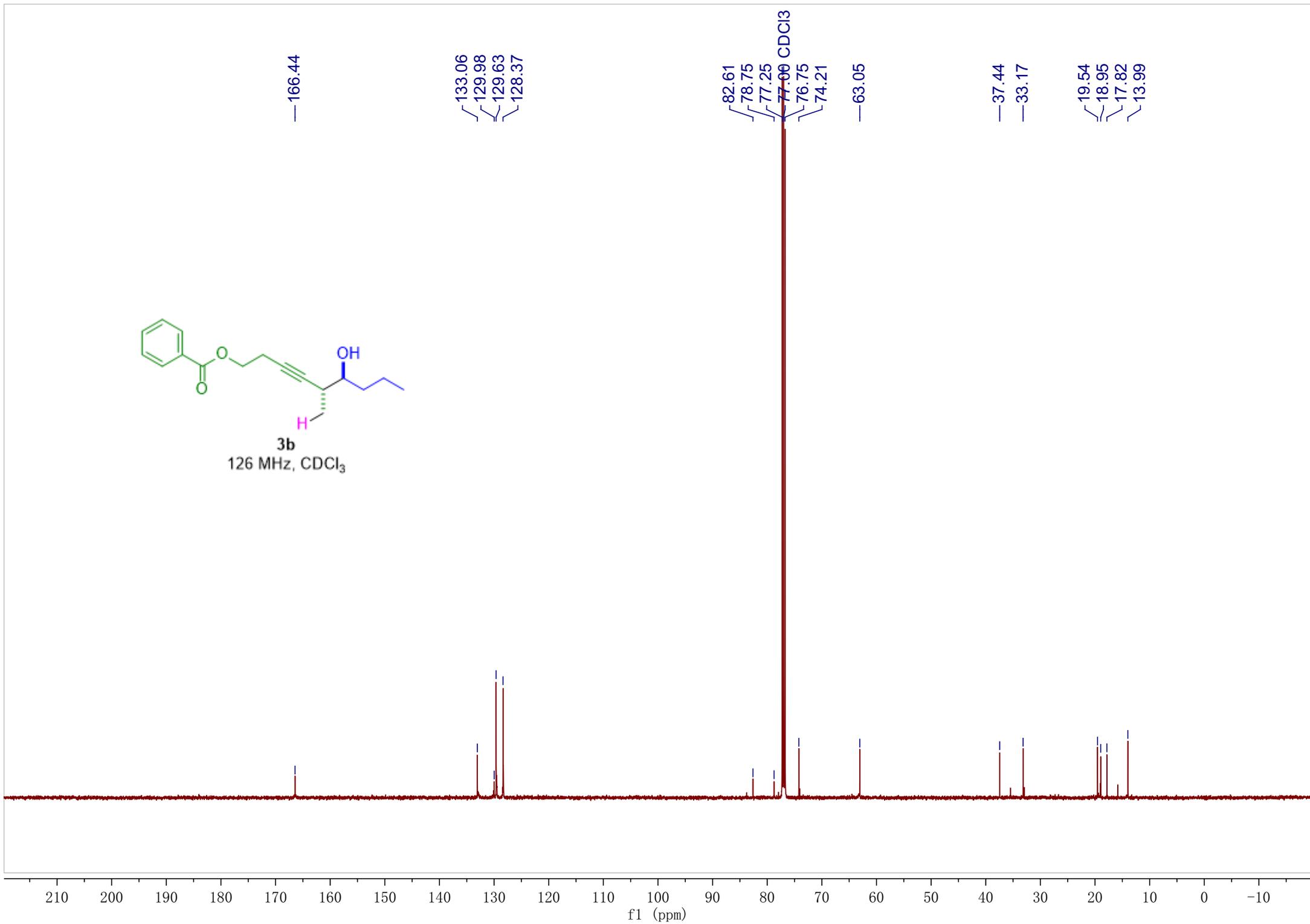
2.06
0.99

4.22
3.09
3.13





3b
126 MHz, CDCl₃





3c

500 MHz, CDCl₃

8.07
8.05
7.58
7.57
7.55
7.46
7.44
7.43
7.26 CDCl₃

4.44
4.43
4.41

3.45
3.42
3.40

2.68
2.66
2.65
2.64

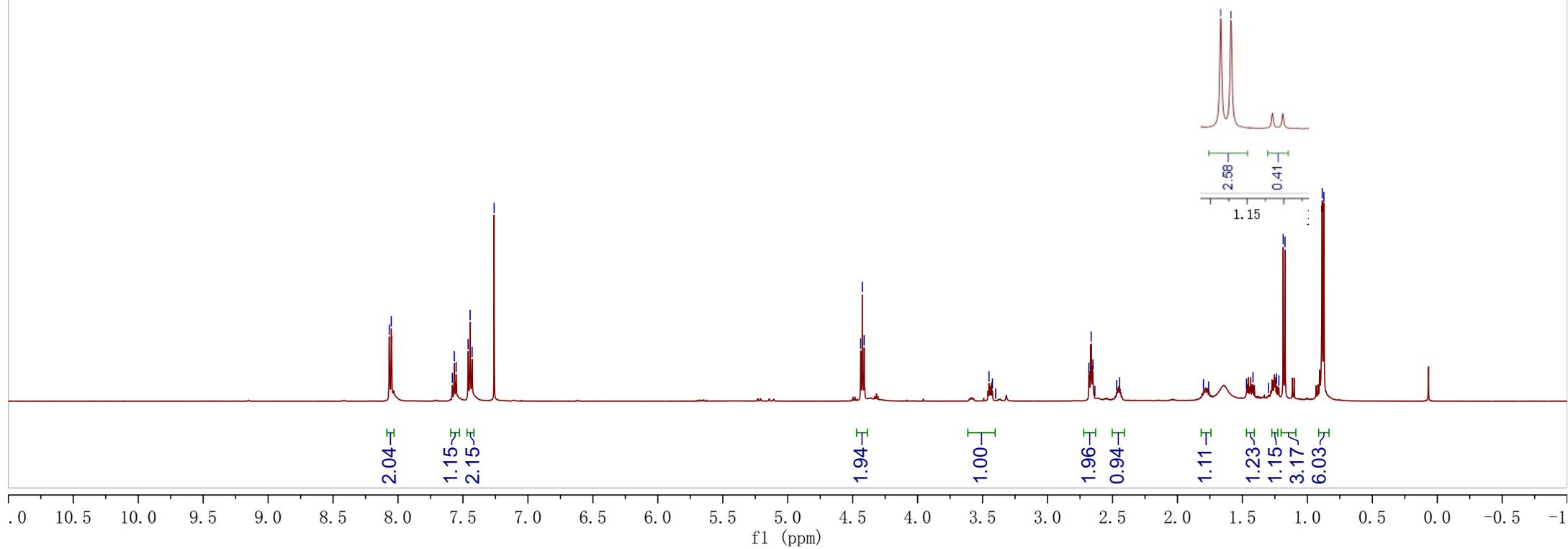
2.47
2.45

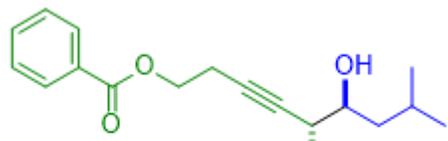
1.80
1.76
1.47

1.42
1.30

1.24
1.22
1.19
1.17

0.89
0.87





3c
126 MHz, CDCl₃

— 166.44

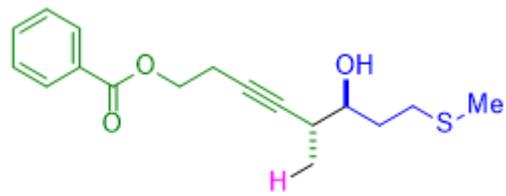
— 133.07
— 129.64
— 128.38

— 82.63
— 78.83
— 77.25
— 77.00 CDCl₃
— 76.75
— 72.50
— 63.06

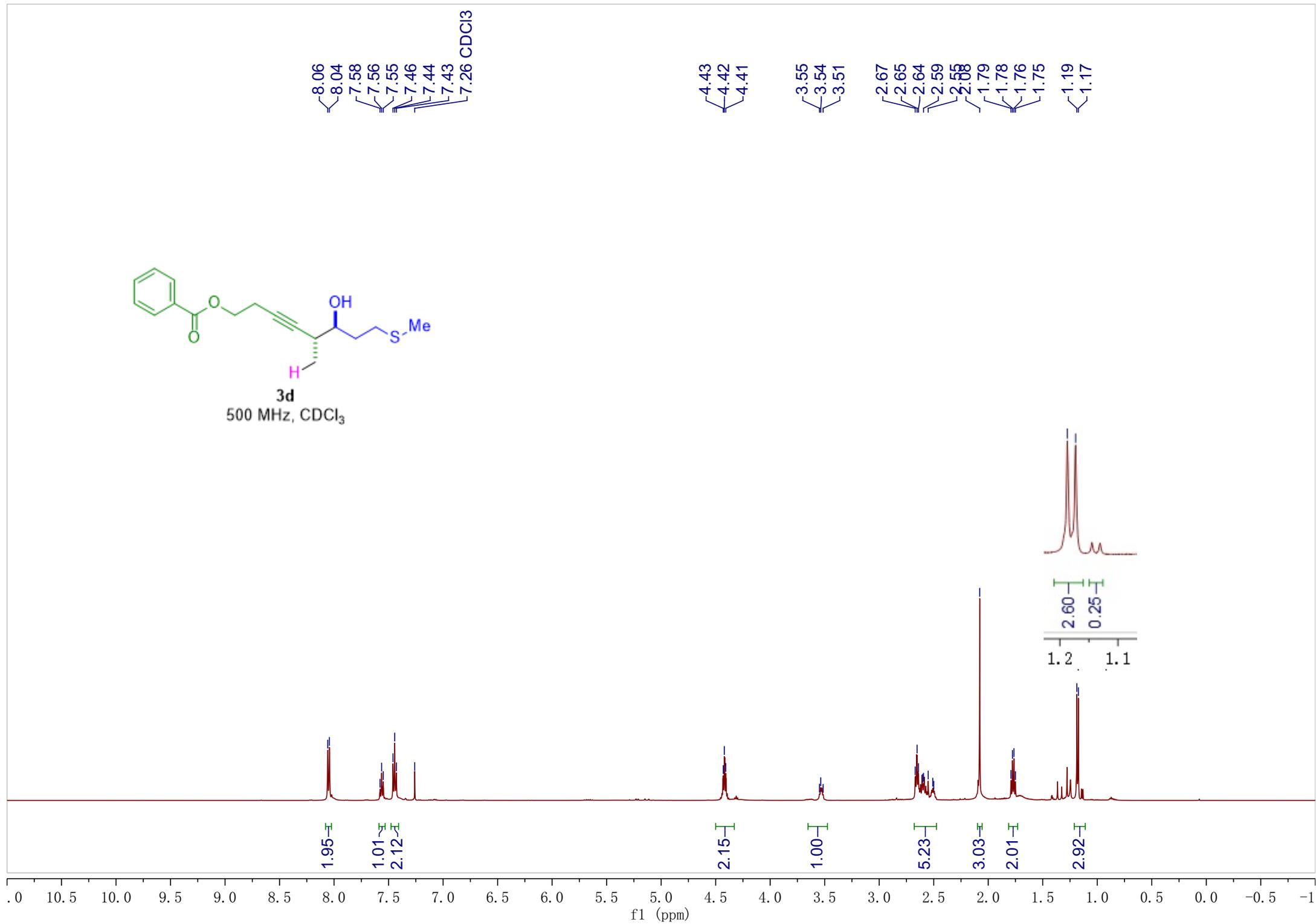
— 44.55

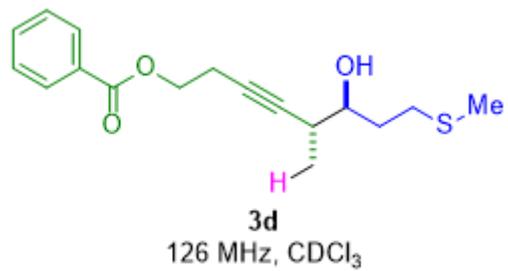
— 33.63
— 24.57
— 23.48
— 21.89
— 19.54
— 17.85

f1 (ppm)



3d
500 MHz, CDCl₃





—166.43

133.08
129.92
129.61
128.38

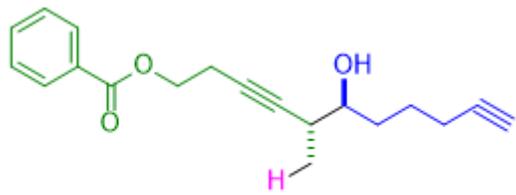
82.31
79.03
77.25
77.00 CDCl₃
76.75
73.25
—62.97

34.27
33.21
30.75

19.52
17.57
15.47

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)



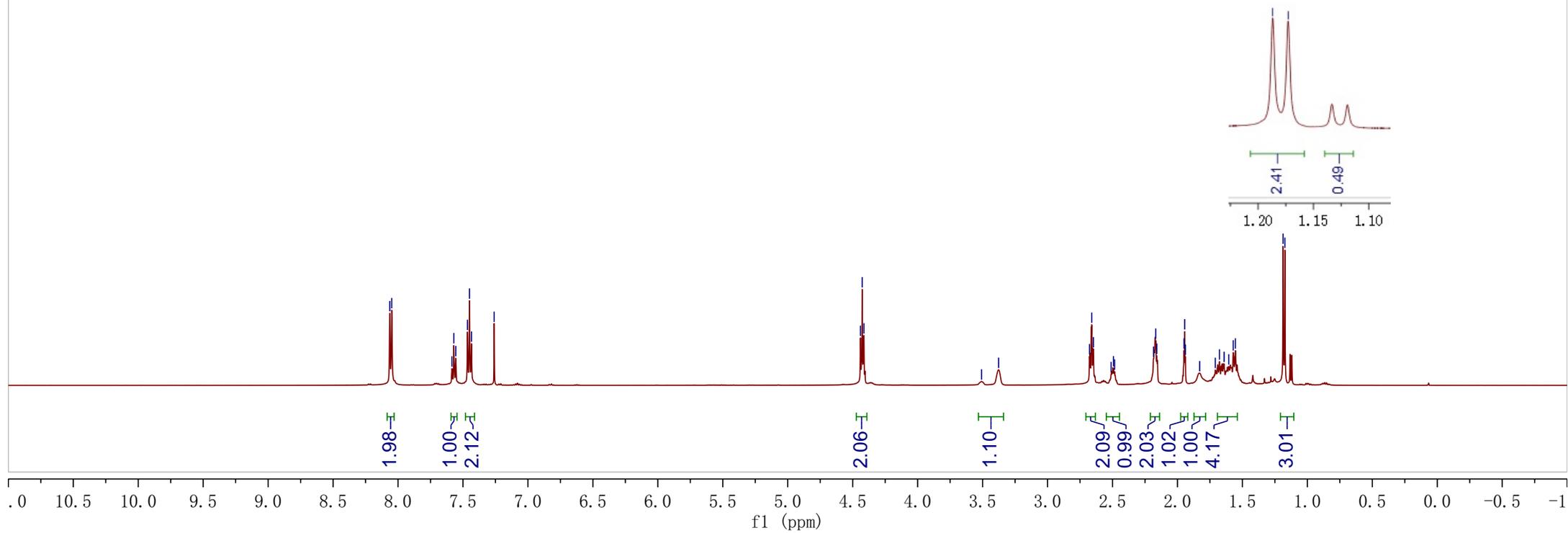
3e
500 MHz, CDCl₃

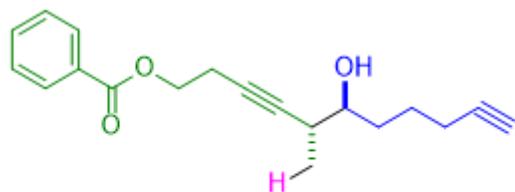
8.06
8.05
7.58
7.57
7.56
7.47
7.45
7.43
7.26 CDCl₃

4.44
4.43
4.41

3.51
3.38

2.68
2.66
2.65
2.18
2.17
2.16
1.95
1.94
1.94
1.57
1.55
1.17





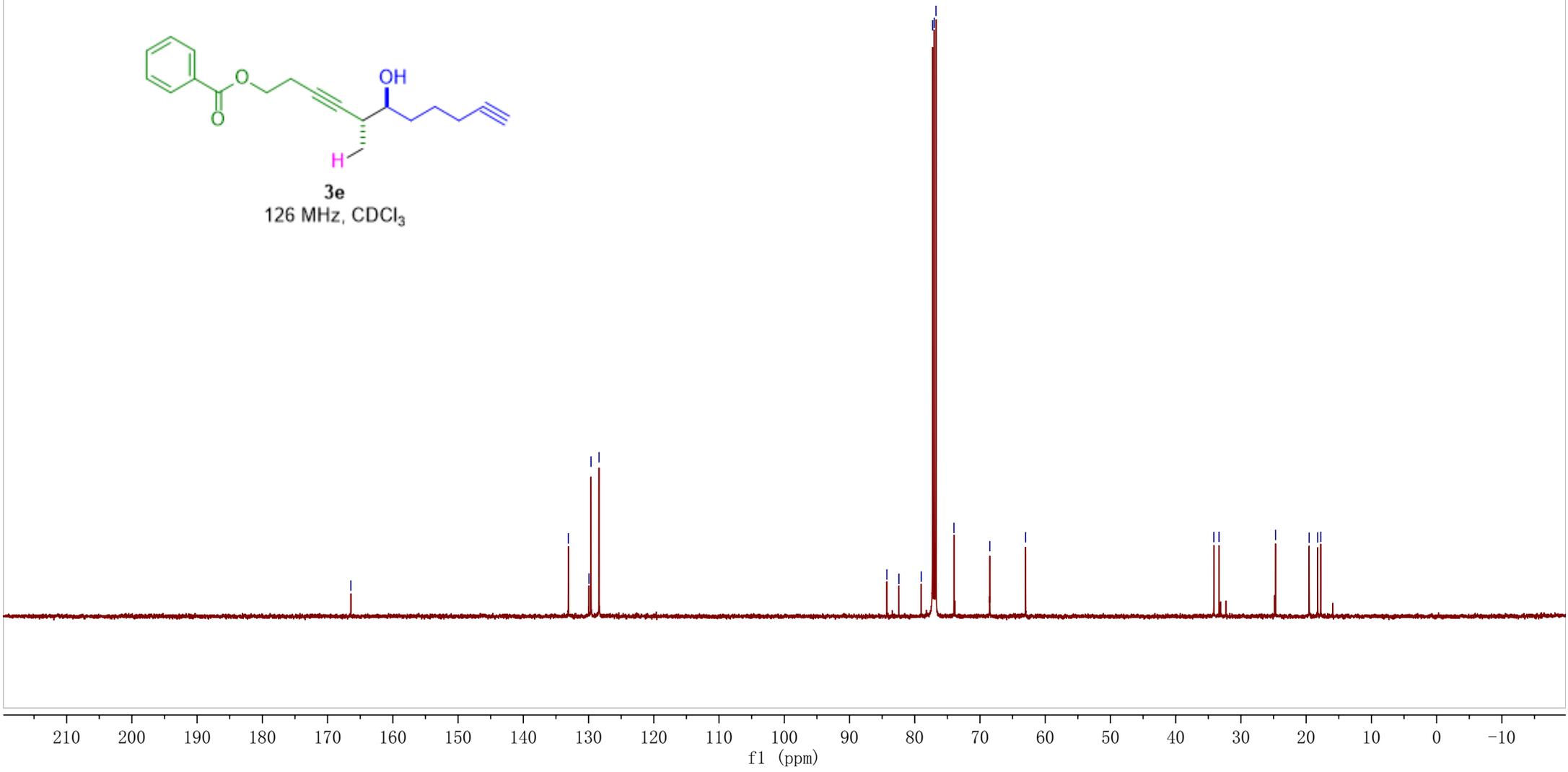
3e
126 MHz, CDCl₃

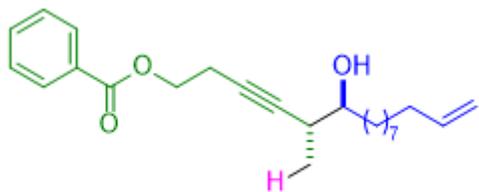
166.44

133.11
129.94
129.62
128.39

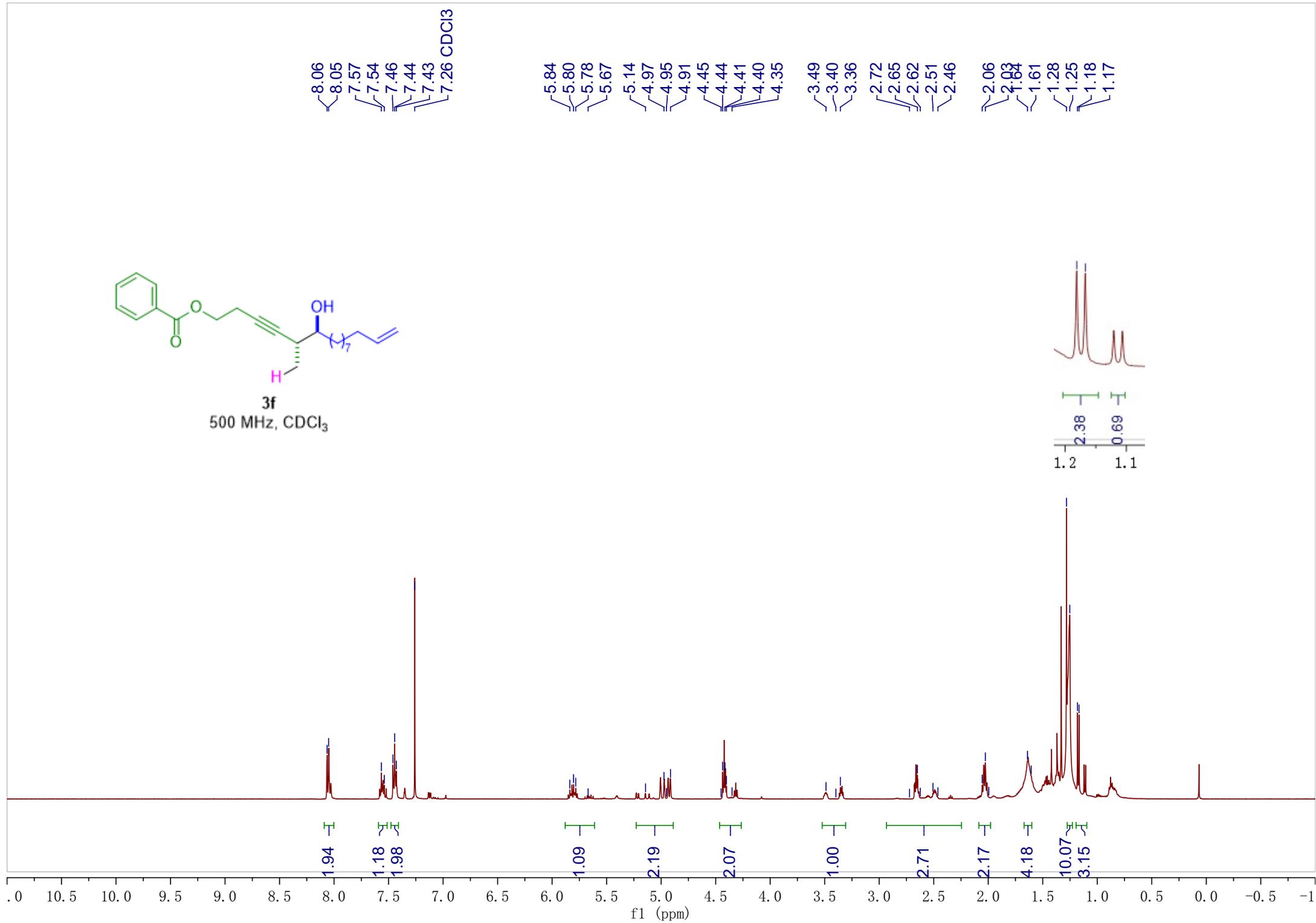
84.27
82.43
79.00
77.25
77.00 CDCl₃
76.75
73.99
68.49
63.00

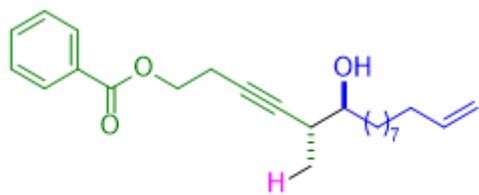
34.16
33.36
24.69
19.54
18.23
17.75



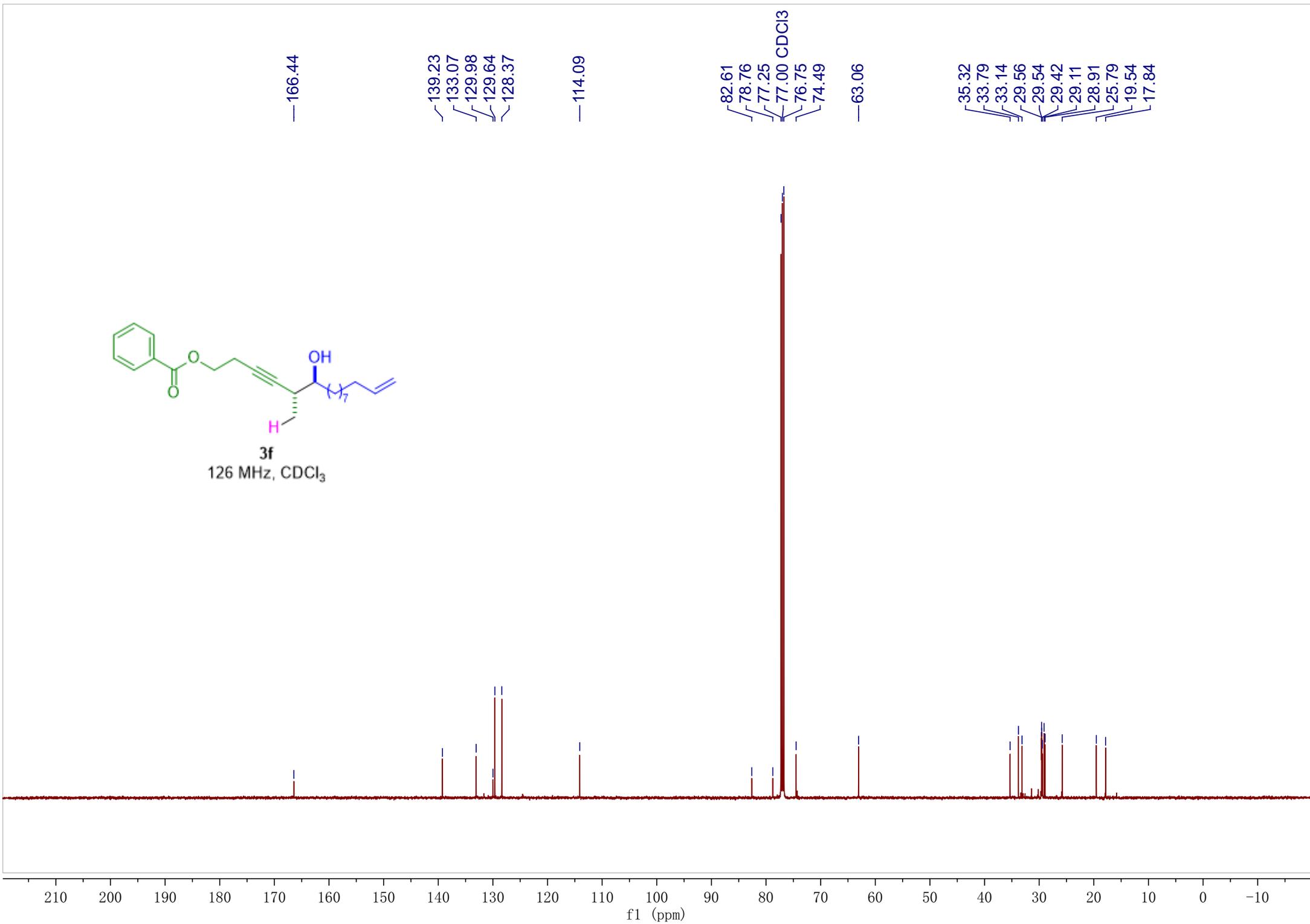


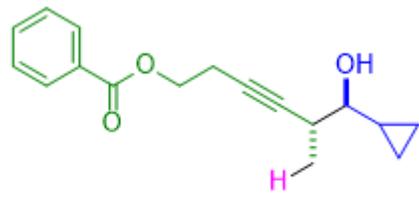
3f
500 MHz, CDCl₃



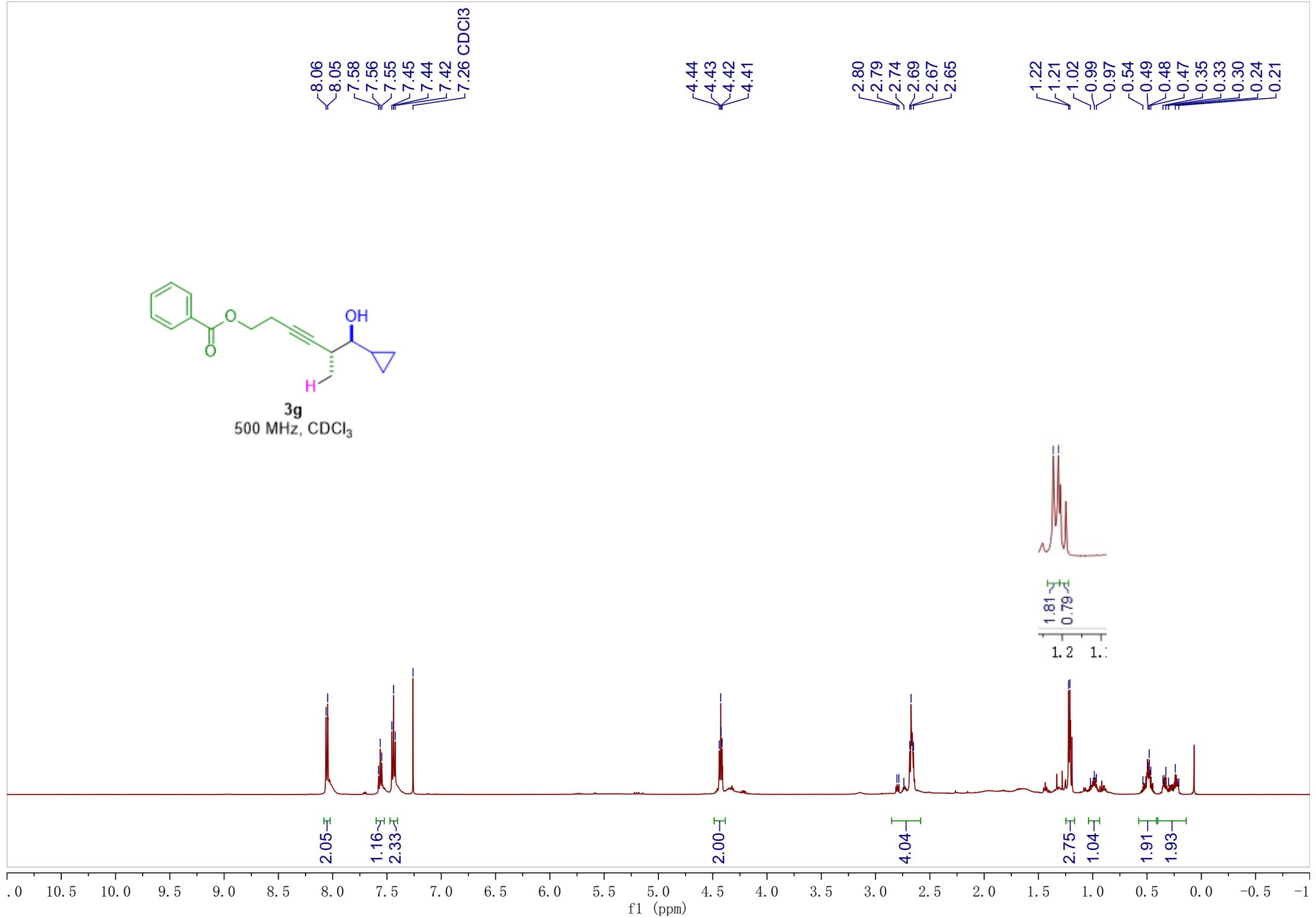


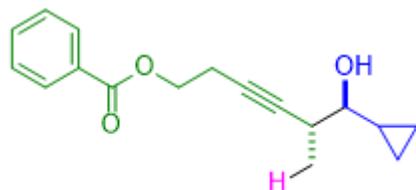
3f
126 MHz, CDCl₃



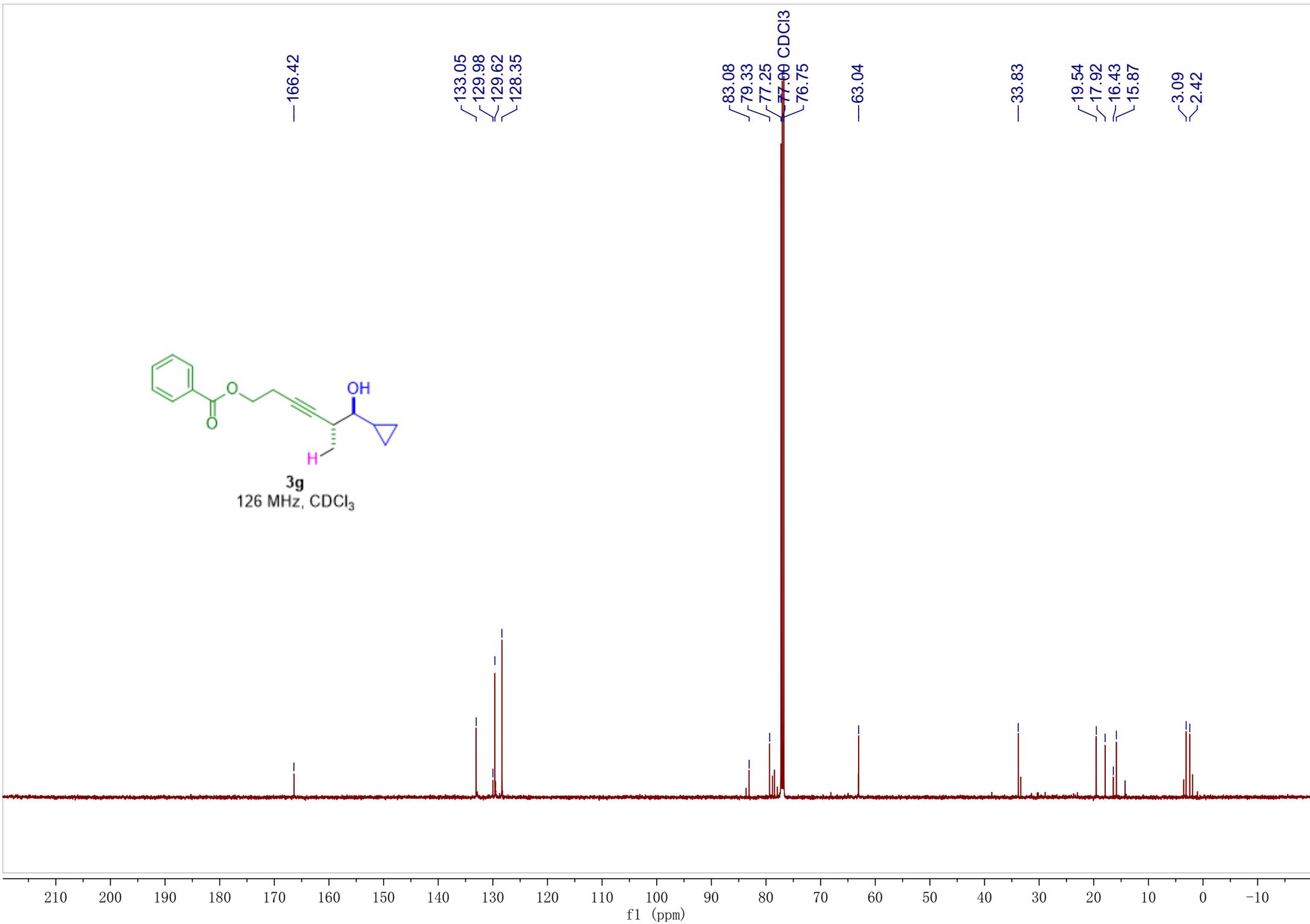


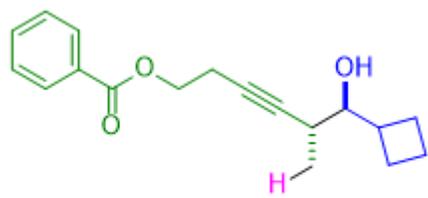
3g
500 MHz, CDCl₃



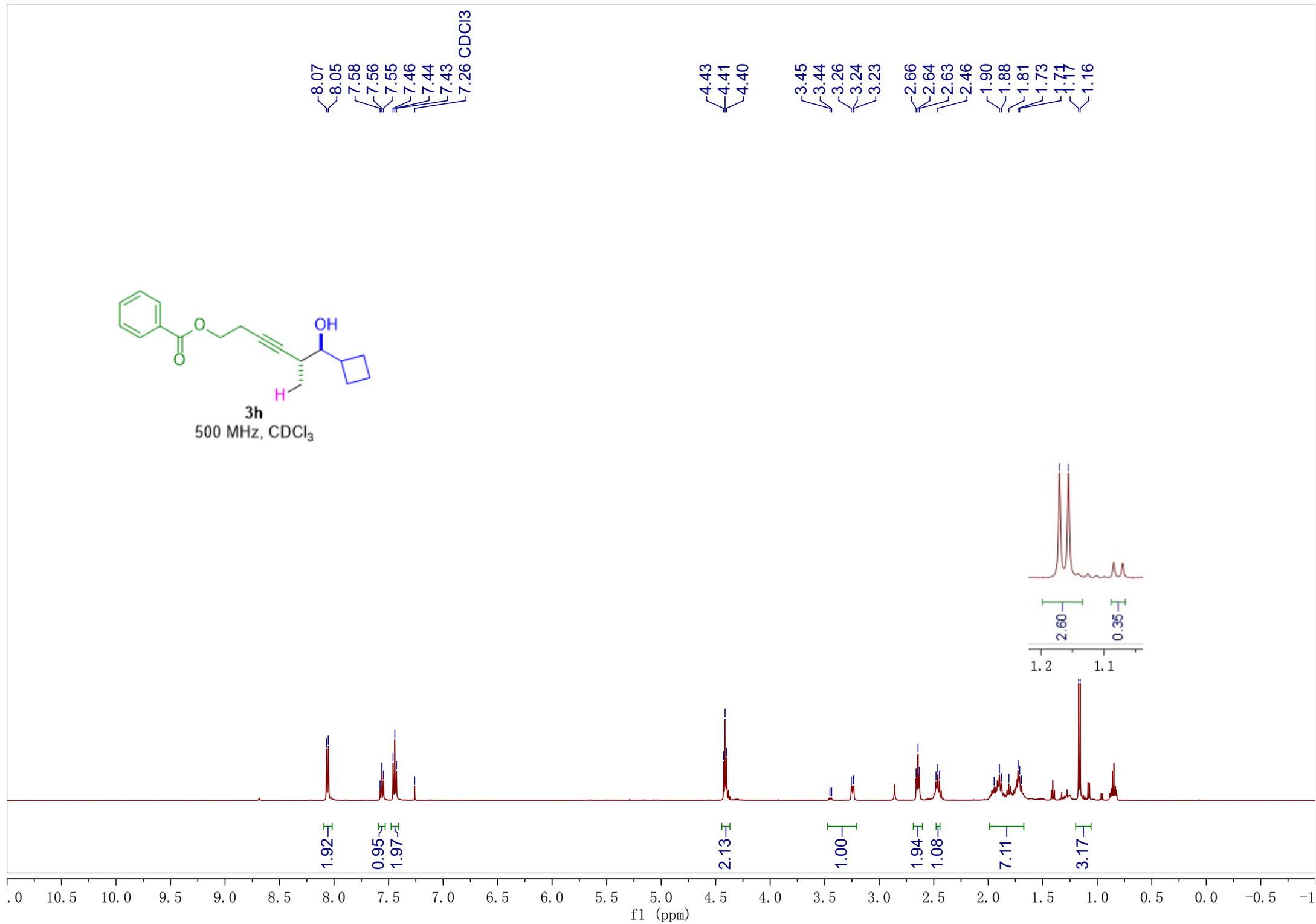


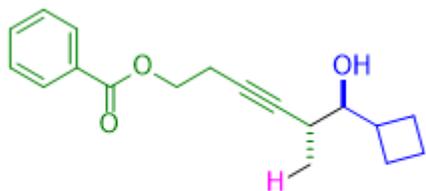
3g
126 MHz, CDCl₃





3h
500 MHz, CDCl₃





3h
126 MHz, CDCl₃

—166.40

133.04
129.97
129.60
128.34

82.40
78.47
77.25
77.00 CDCl₃
76.75

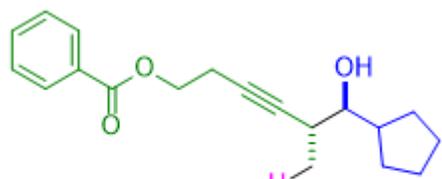
—63.01

—39.75

30.47
24.80
24.65
19.51
18.14
17.96

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)



3i
500 MHz, CDCl₃

8.06
8.05
7.58
7.56
7.55
7.46
7.44
7.43
7.26 CDCl₃

4.44
4.42
4.41

3.08
3.05

2.68
2.66
2.65
1.98
1.96
1.75
1.74
1.67
1.64
1.58
1.56
1.48
1.46
1.45
1.21
1.20



3.27
0.48
1.2
1

2.11

1.19

2.03

2.12

1.00

2.11

0.97

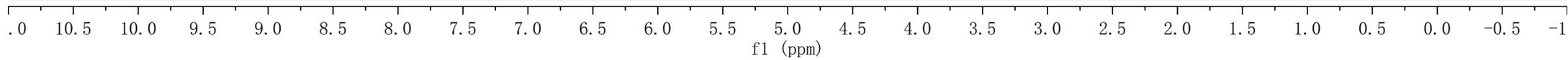
1.11

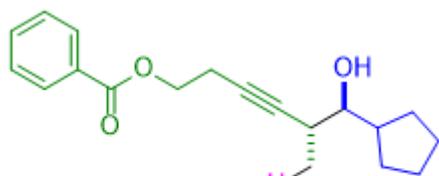
4.01

2.08

1.96

3.13





3i
126 MHz, CDCl₃

—166.43

133.06
129.97
129.61
128.36

82.26
78.91
77.25
77.00 CDCl₃
76.75

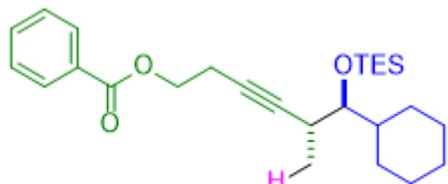
—63.06

—44.96

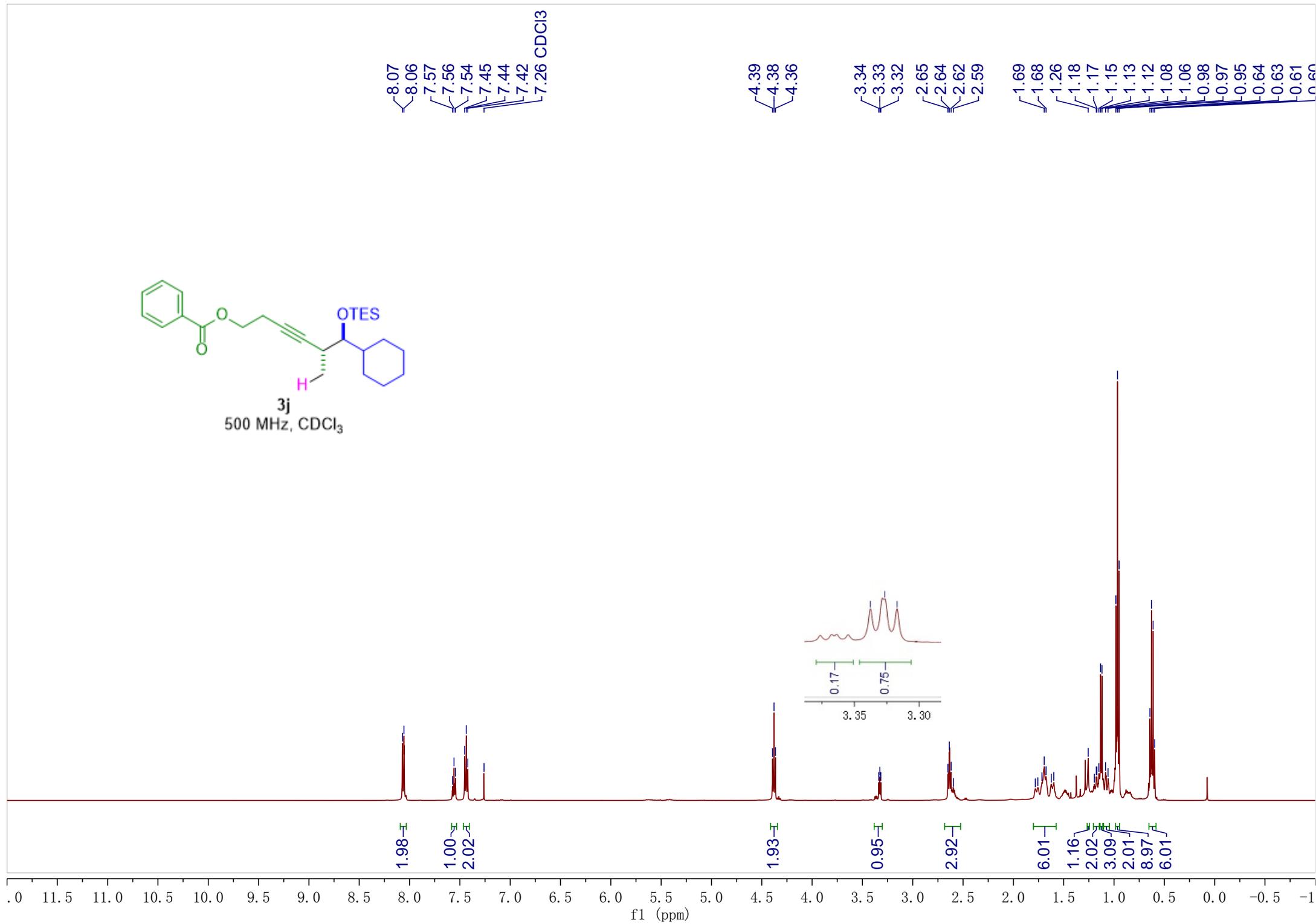
31.85
29.27
29.13
25.51
25.40
19.56
18.58

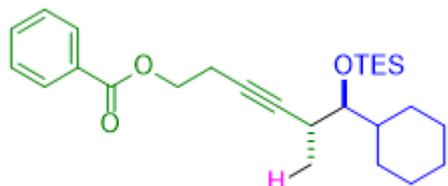
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)



3j
500 MHz, CDCl₃





3j
126 MHz, CDCl₃

—166.3

132.9
130.1
129.6
128.3

84.9
79.6
77.3
77.0 CDCl₃
76.8
76.7

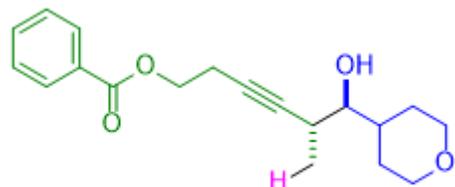
—63.3

—41.6

31.1
30.4
28.4
26.5
26.5
26.2
19.5
17.4
7.1
5.4

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

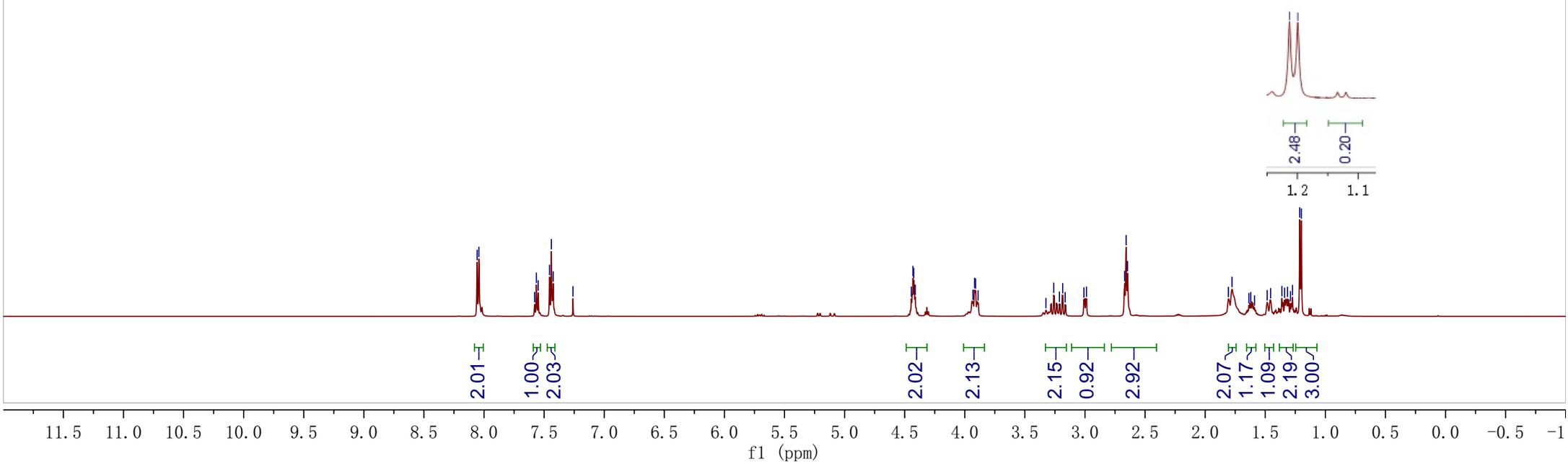
f1 (ppm)

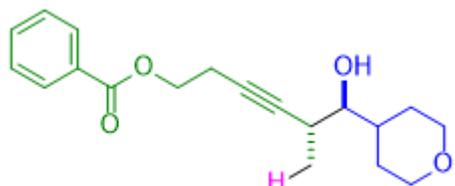


3k
500 MHz, CDCl₃

8.06
8.04
7.58
7.56
7.55
7.46
7.44
7.42
7.26 CDCl₃

4.44
4.43
4.43
4.41
3.93
3.92
3.91
3.26
3.19
3.01
2.99
2.67
2.66
2.65
1.87
1.78
1.64
1.62
1.59
1.48
1.46
1.36
1.34
1.31
1.29
1.27
1.21
1.20





3k
126 MHz, CDCl₃

— 166.42

133.13
129.86
129.57
128.38

81.62
79.21
78.26
77.25
77.00 CDCl₃
76.75
67.79
67.45
62.94

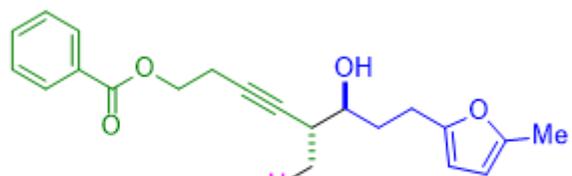
— 39.48

29.38
29.16
29.03

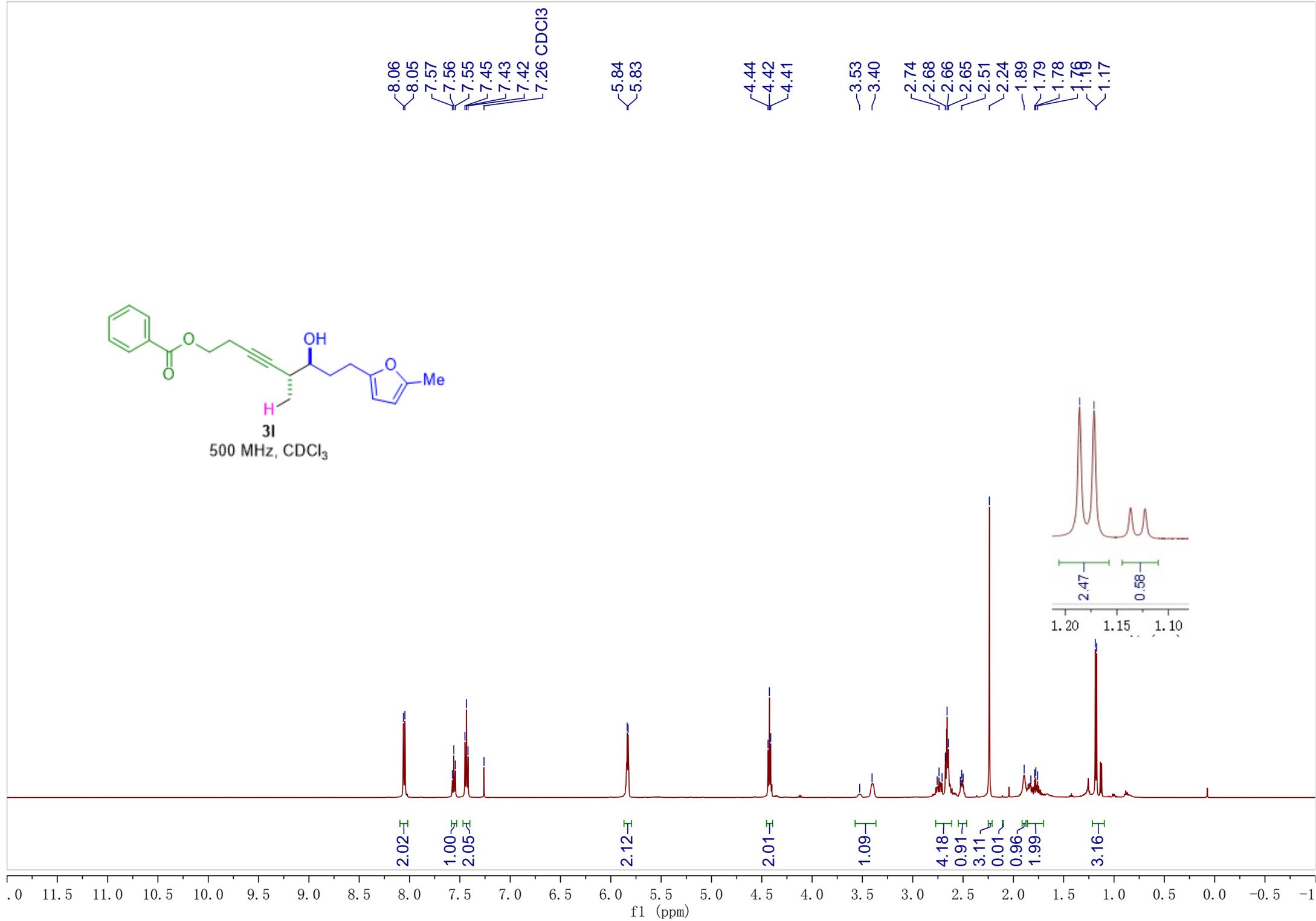
19.56
18.43

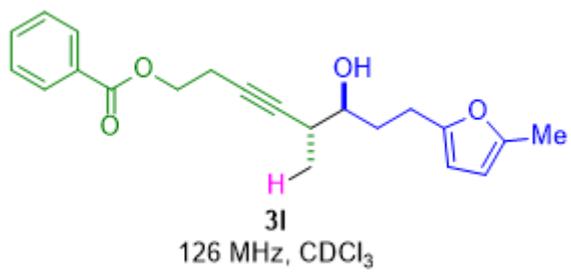
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)



3I
500 MHz, CDCl₃





—166.4

—153.8

—150.3

133.0

129.9

129.6

128.4

105.8

105.5

82.4

79.0

77.3

77.0 CDCl₃

76.7

73.7

—63.0

33.7

33.3

24.4

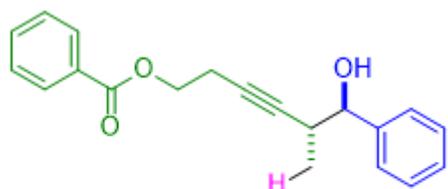
19.5

17.7

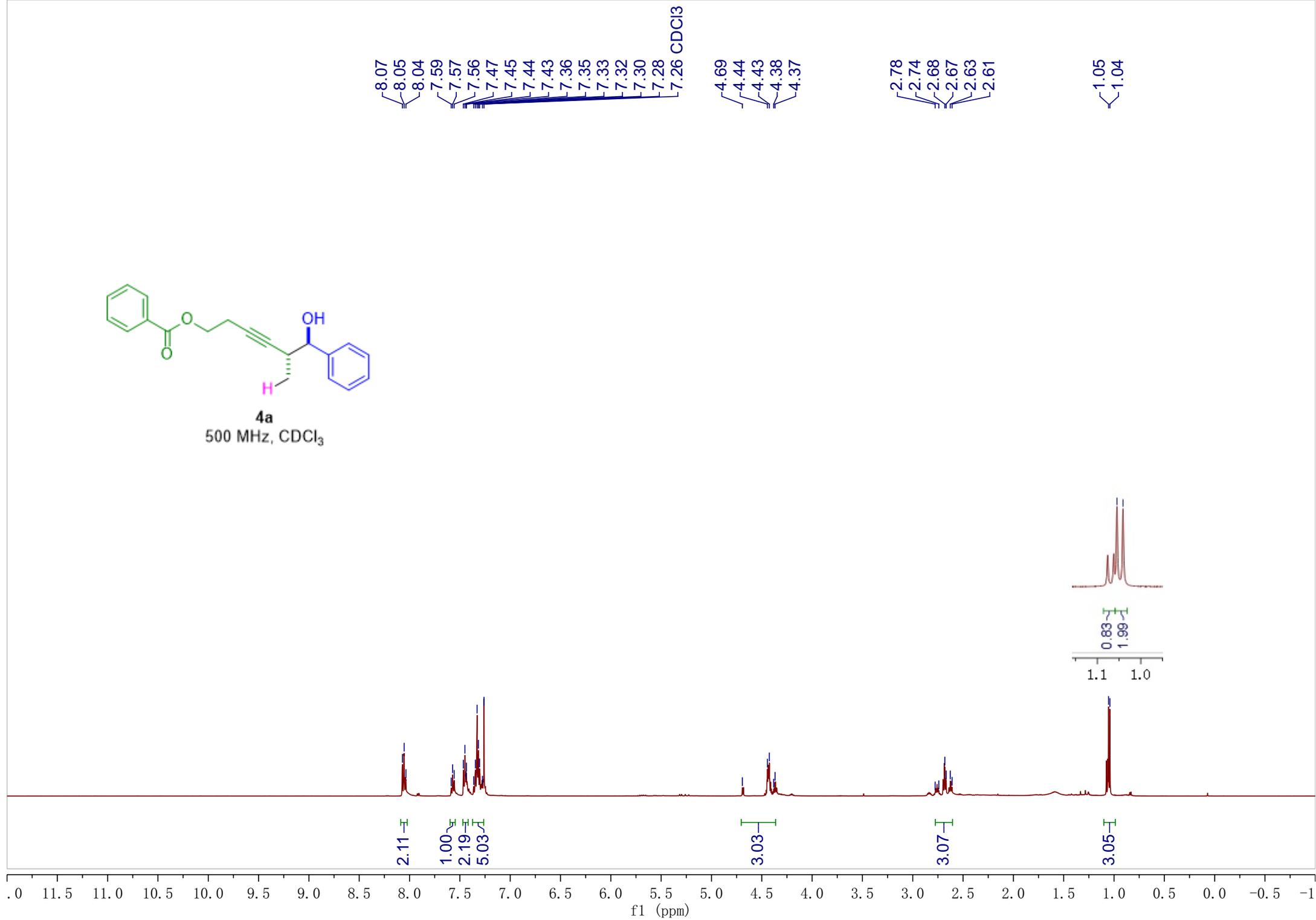
13.5

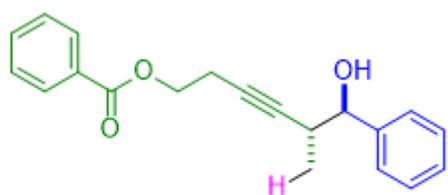
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)



4a
500 MHz, CDCl₃





4a

126 MHz, CDCl₃

166.47

141.55

133.09

129.96

129.65

128.39

128.23

127.86

126.60

82.89

79.29

77.64

77.25

77.00 CDCl₃

76.75

63.00

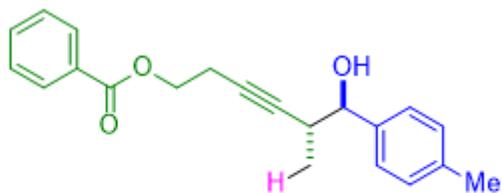
35.48

19.56

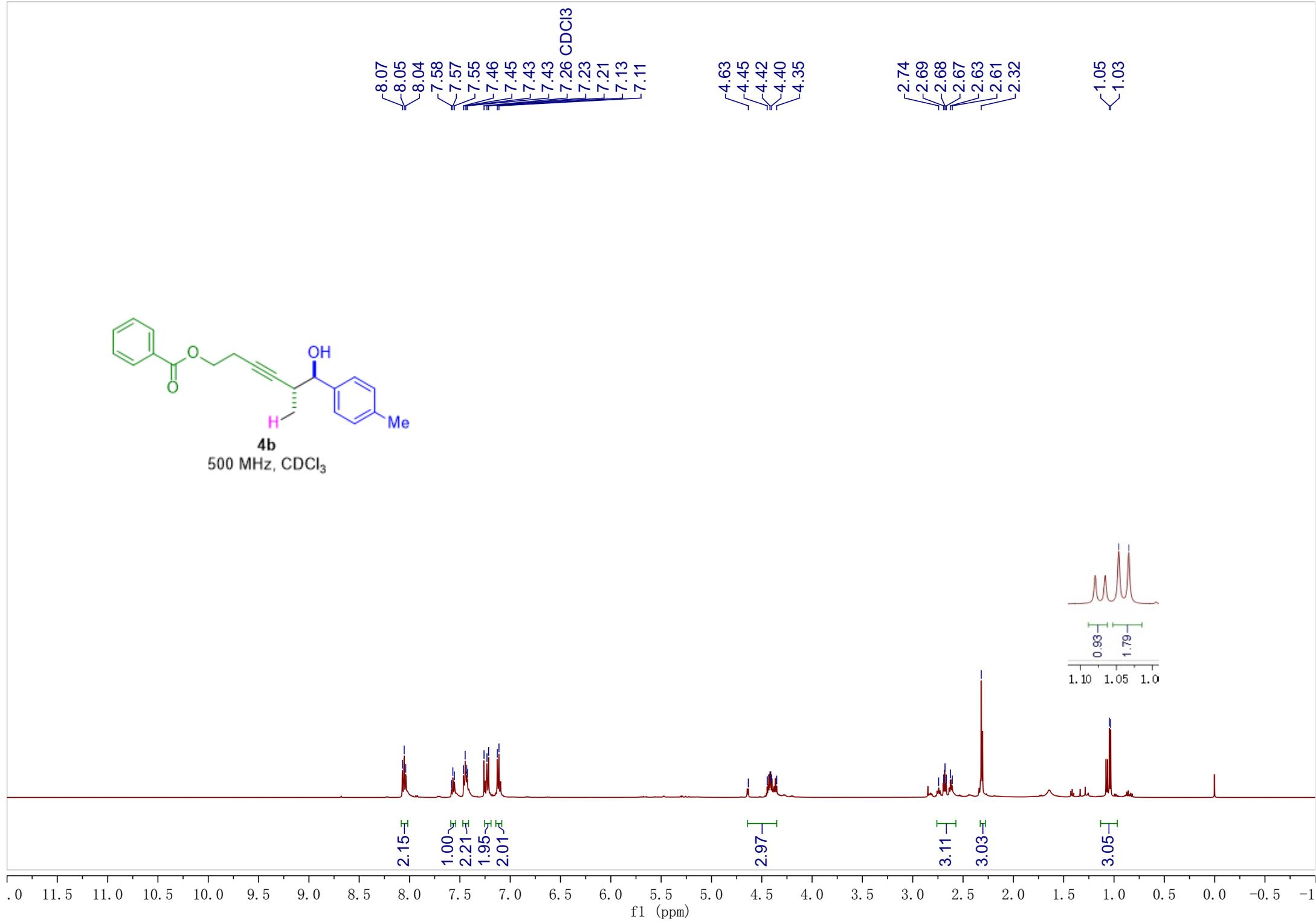
17.66

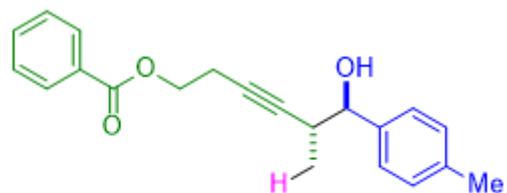
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)



4b
500 MHz, CDCl₃





4b

126 MHz, CDCl₃

166.46

138.59
137.51
133.07
129.98
129.65
128.90
128.38
126.50

83.04
79.15
77.48
77.25
77.00 CDCl₃
76.75

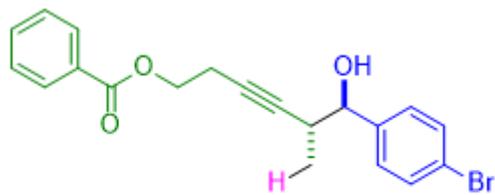
63.02

35.41

21.12
19.55
17.67

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)



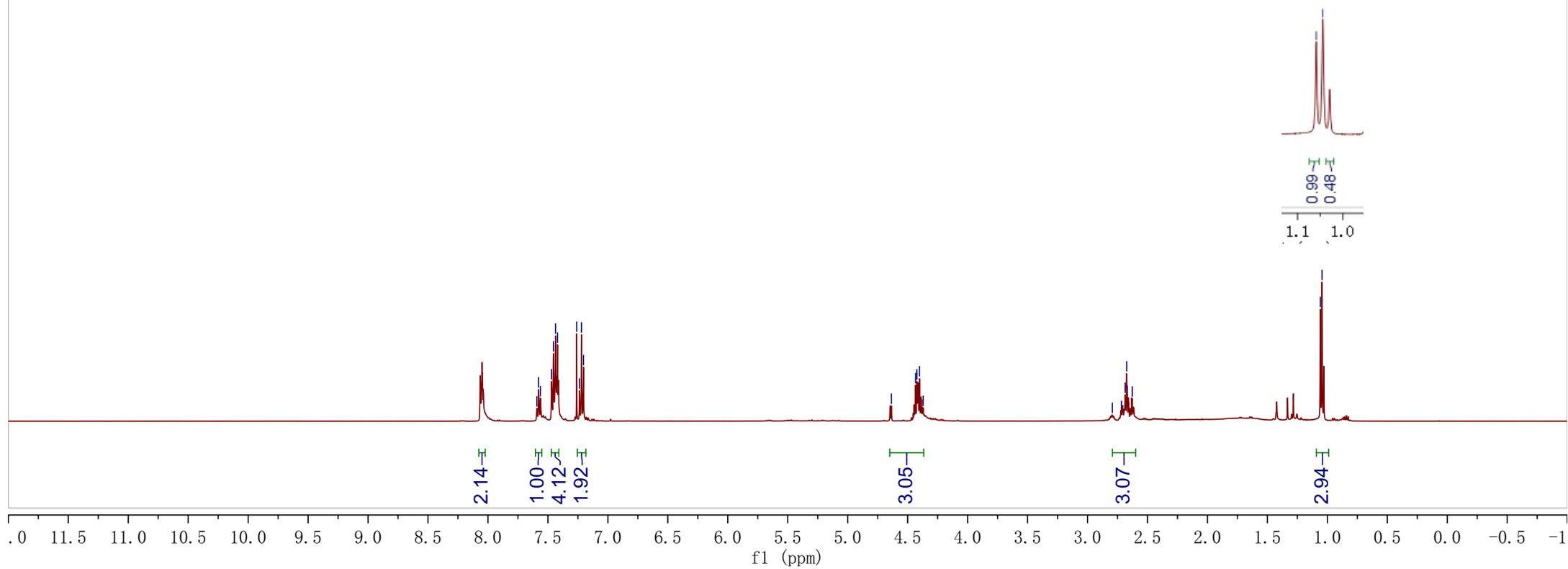
4c
500 MHz, CDCl₃

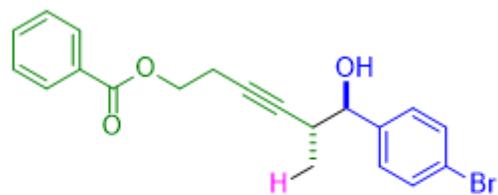
7.59
7.58
7.56
7.47
7.45
7.44
7.42
7.26 CDCl₃
7.24
7.22
7.20

4.64
4.43
4.42
4.40
4.37

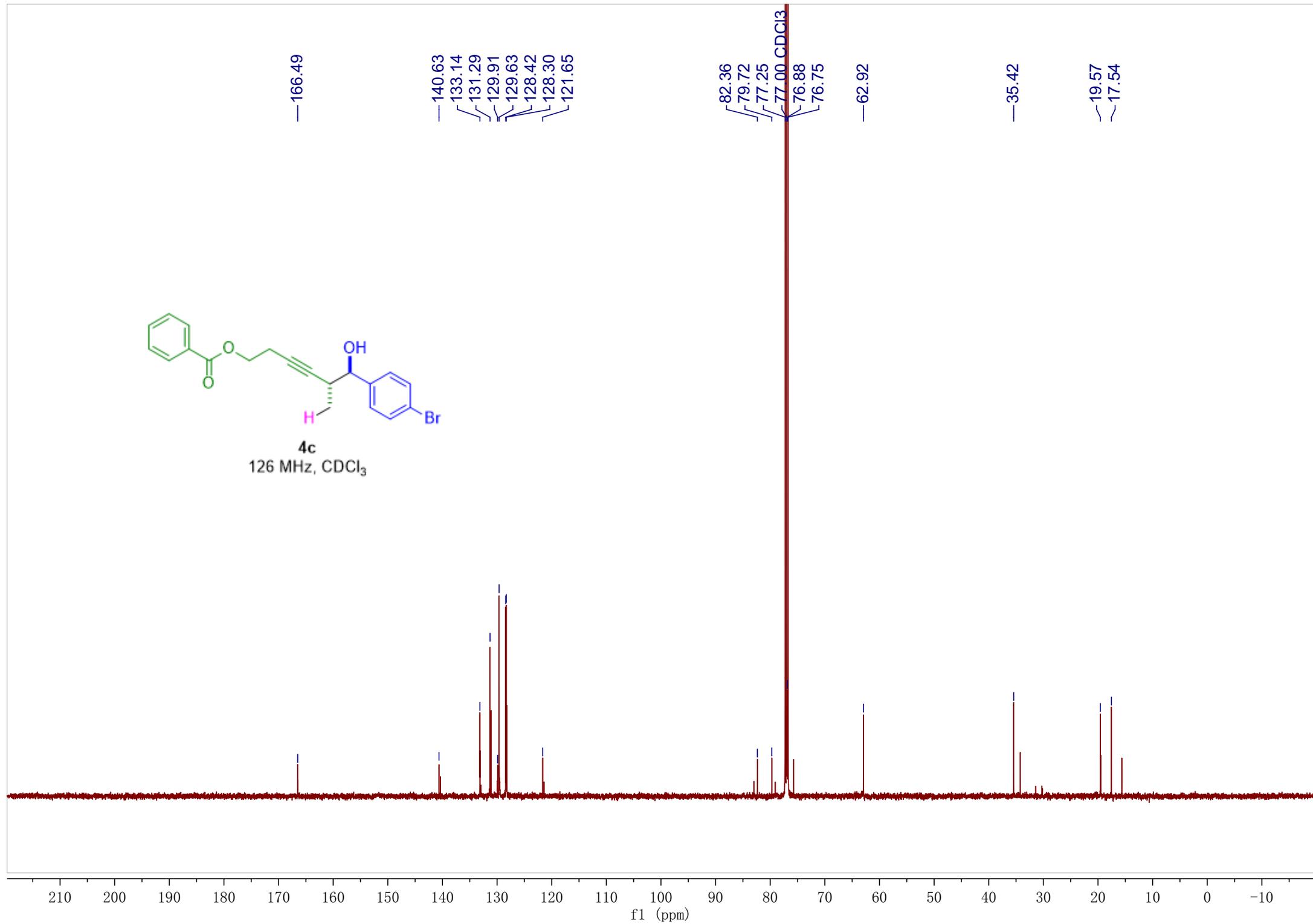
2.79
2.72
2.69
2.67
2.63

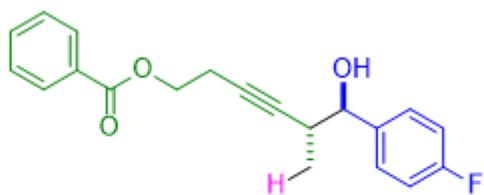
1.06
1.04





4c
126 MHz, CDCl₃





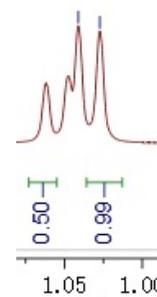
4d
500 MHz, CDCl₃

8.06
8.05
8.03
7.59
7.57
7.56
7.46
7.45
7.43
7.33
7.32
7.30
7.29
7.26 CDCl₃
7.01
6.99
6.98
6.96

4.65
4.43
4.42
4.38
4.36

2.81
2.72
2.69
2.68
2.63
2.62
2.61

1.04
1.03



1.95

1.00

2.11

2.06

2.07

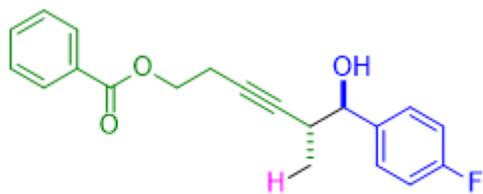
3.11

3.09

2.93

10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1

f1 (ppm)



4d
126 MHz, CDCl₃

~166.48
~163.31
~161.35

137.32
137.30
133.12
129.91
129.63
128.40
128.24
128.17
115.13
114.96

82.63
79.52
77.25
77.00 CDCl₃
76.92
76.75

—62.93

—35.54

~19.55
~17.52

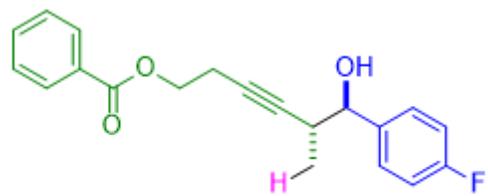
A (d)
162.33

B (d)
137.31

D (d)
128.21

C (d)
115.04

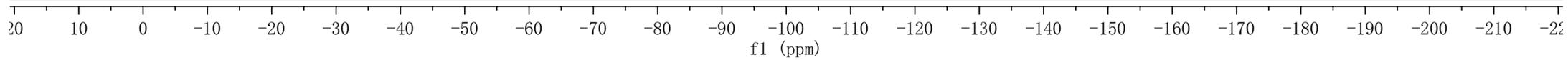
f1 (ppm)

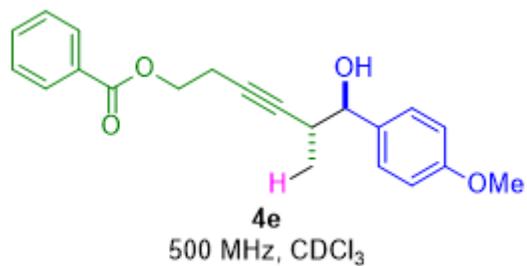


4d
471 MHz, CDCl₃

114.61
114.61
114.65
114.98

1.00





8.08
8.06
8.05
7.46
7.28
7.26
7.26
6.86
6.85
6.83

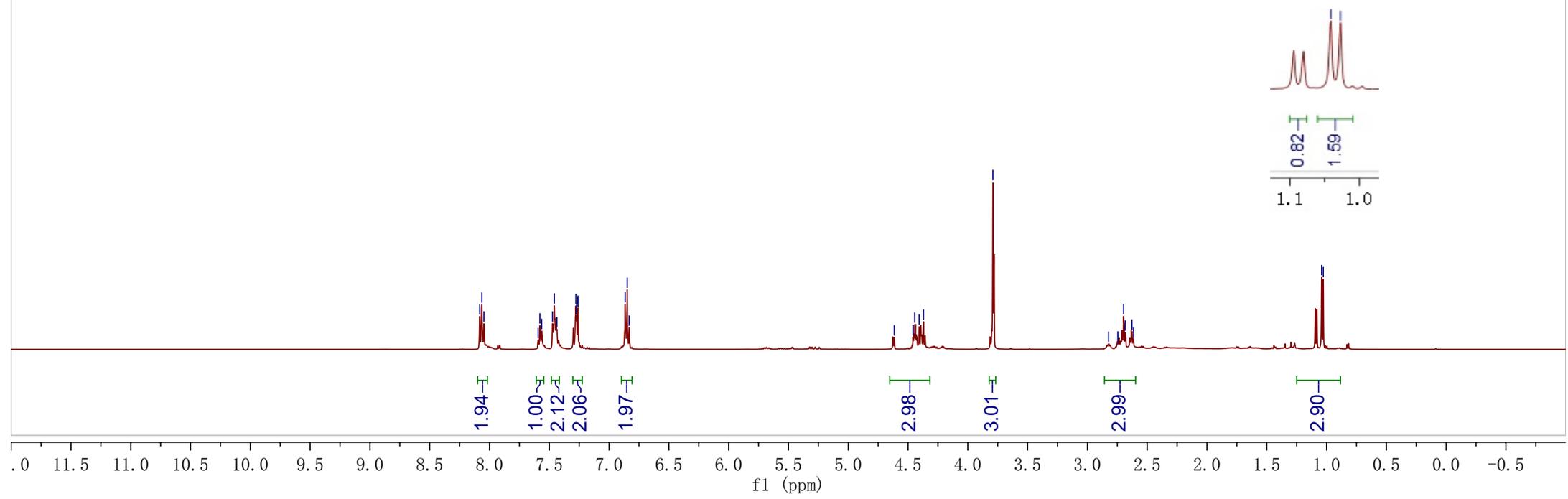
CDCl₃

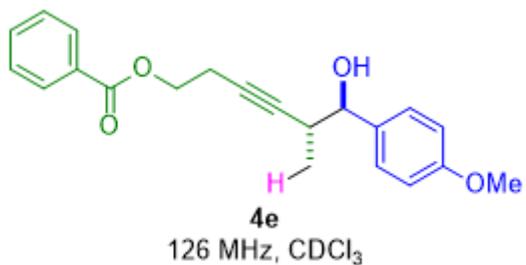
4.61
4.46
4.44
4.41
4.37

— 3.79

2.82
2.75
2.70
2.68
2.63
2.61

1.04
1.03





—166.43

—159.19

133.69

133.05

129.96

129.62

128.36

127.76

—113.58

83.13

79.10

77.25

77.00 CDCl₃

76.75

76.12

—63.00

—55.19

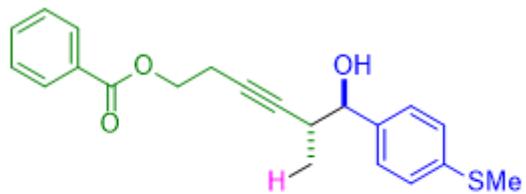
—35.42

~19.54

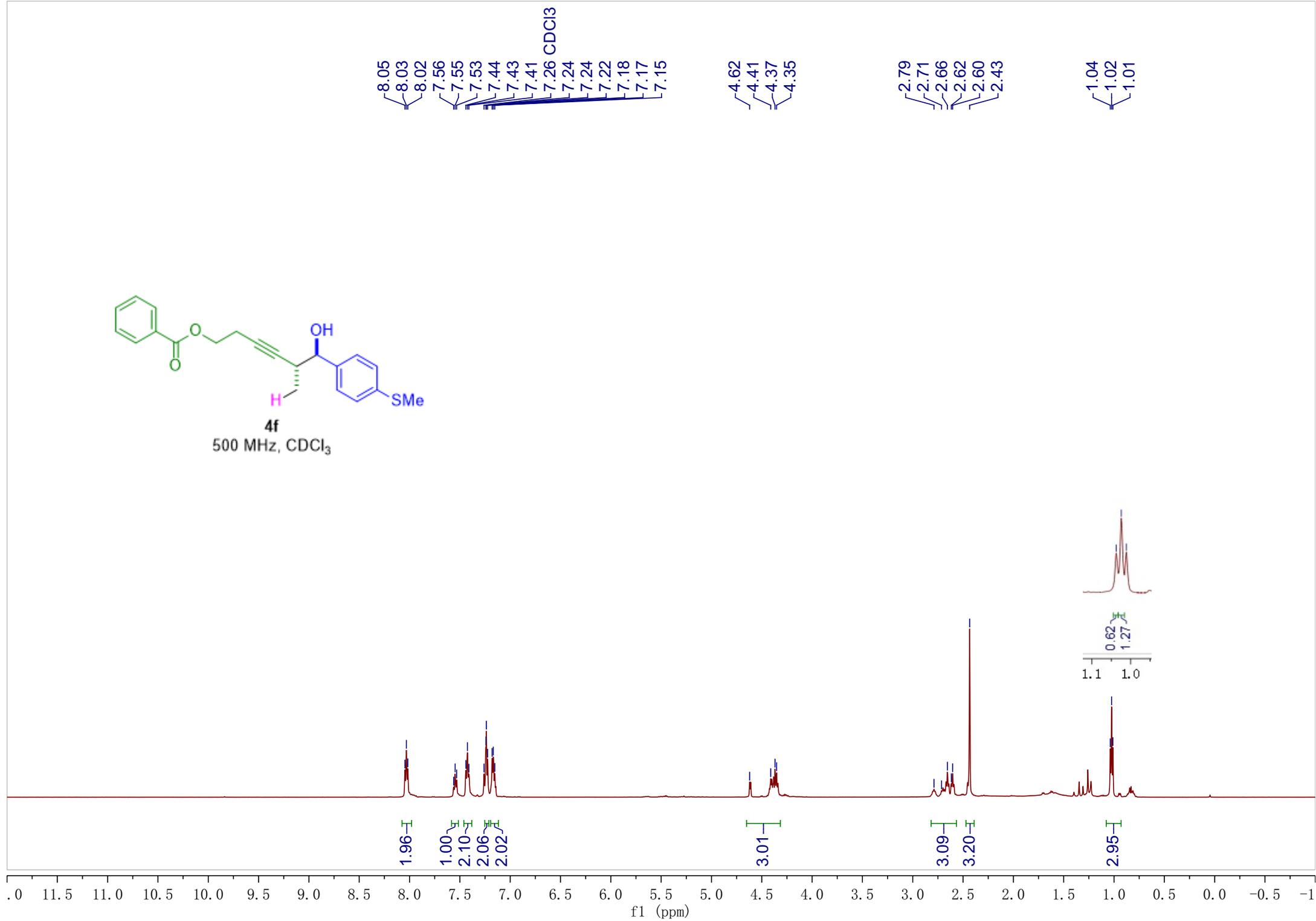
~17.59

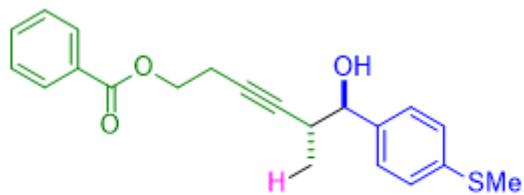
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)



4f
500 MHz, CDCl₃





4f
126 MHz, CDCl₃

— 166.47

138.47
137.93
133.10
129.95
129.64
128.40
127.12
126.37

82.79
79.40
77.25
77.21
77.00 CDCl₃
76.75

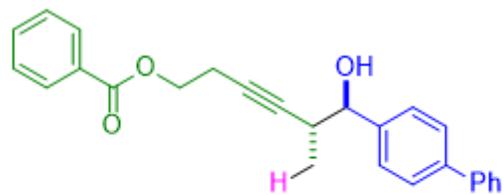
— 62.98

— 35.42

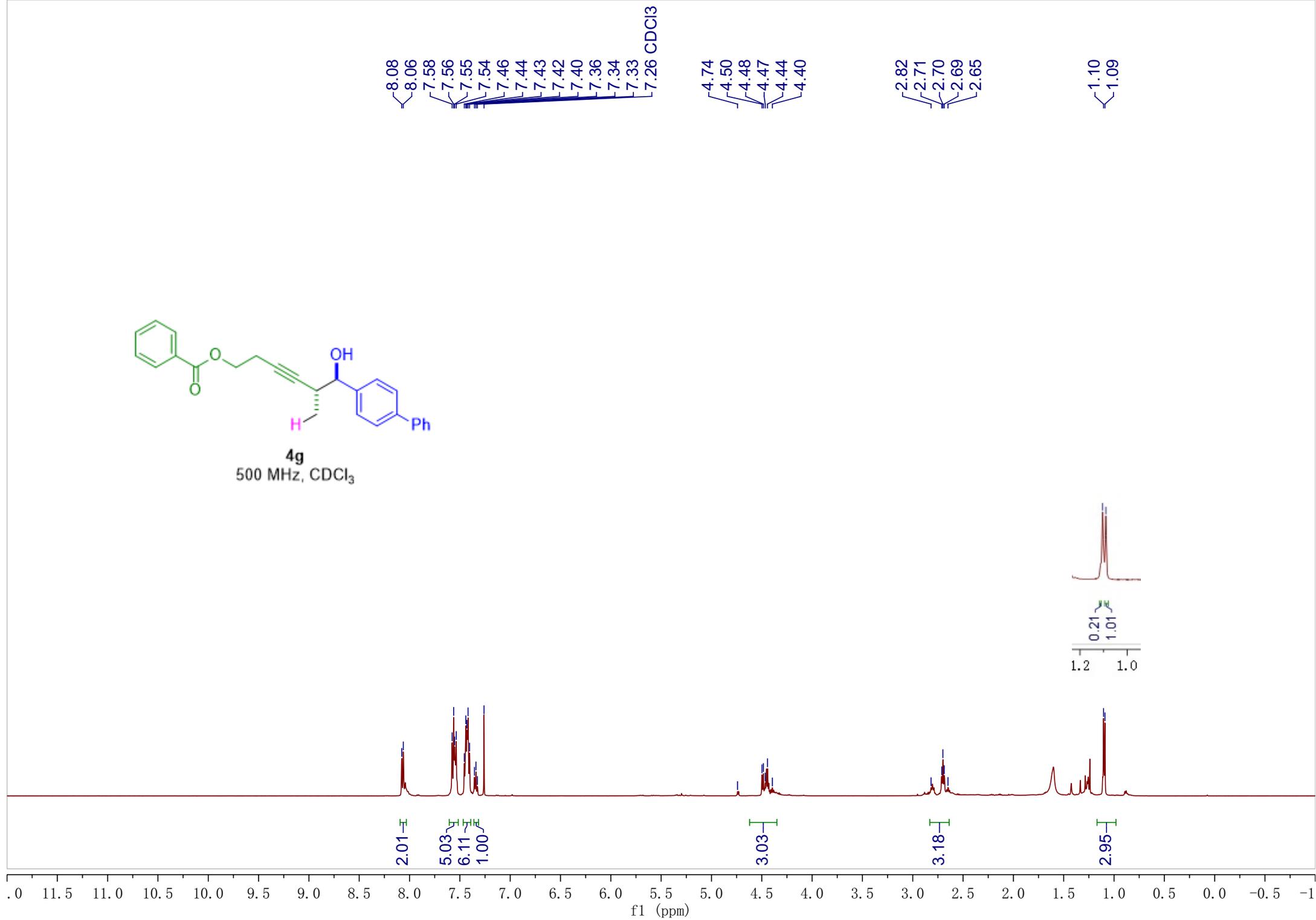
19.57
17.60
15.81

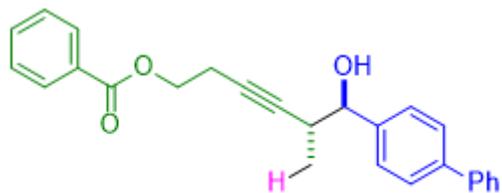
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)



4g
500 MHz, CDCl₃





4g
126 MHz, CDCl₃

—166.50

140.78

140.73

140.62

133.10

129.96

129.65

128.72

128.40

127.26

127.06

127.04

126.96

82.85

79.43

77.37

77.25

77.00 CDCl₃

76.75

—63.01

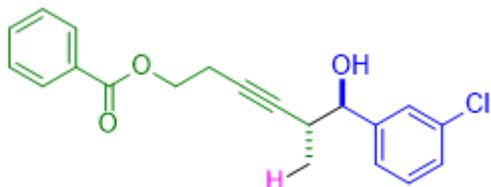
—35.45

~19.59

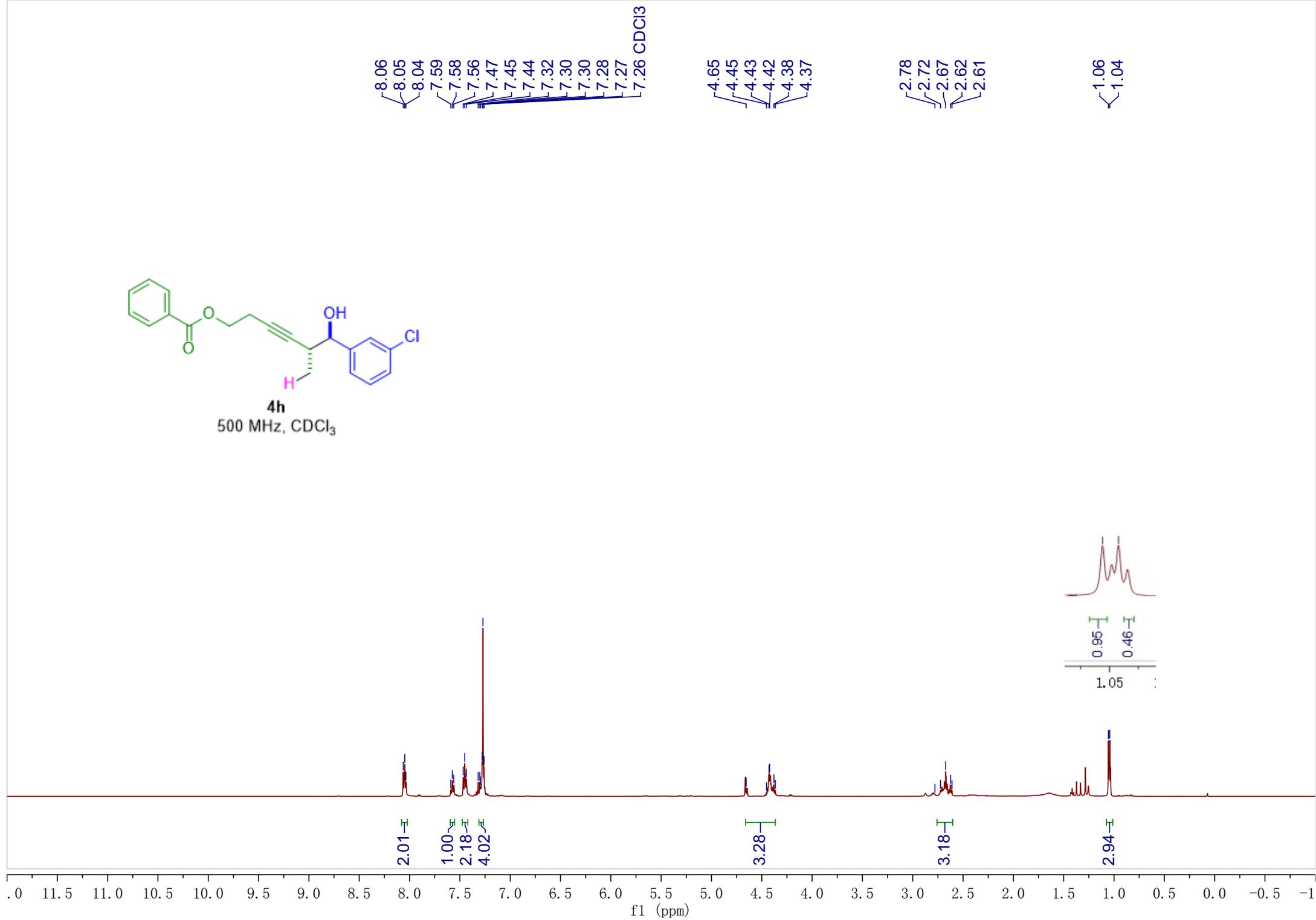
~17.71

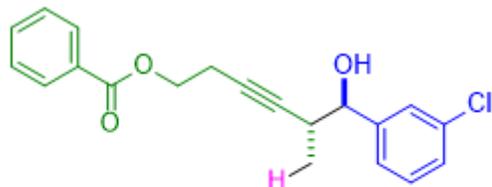
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

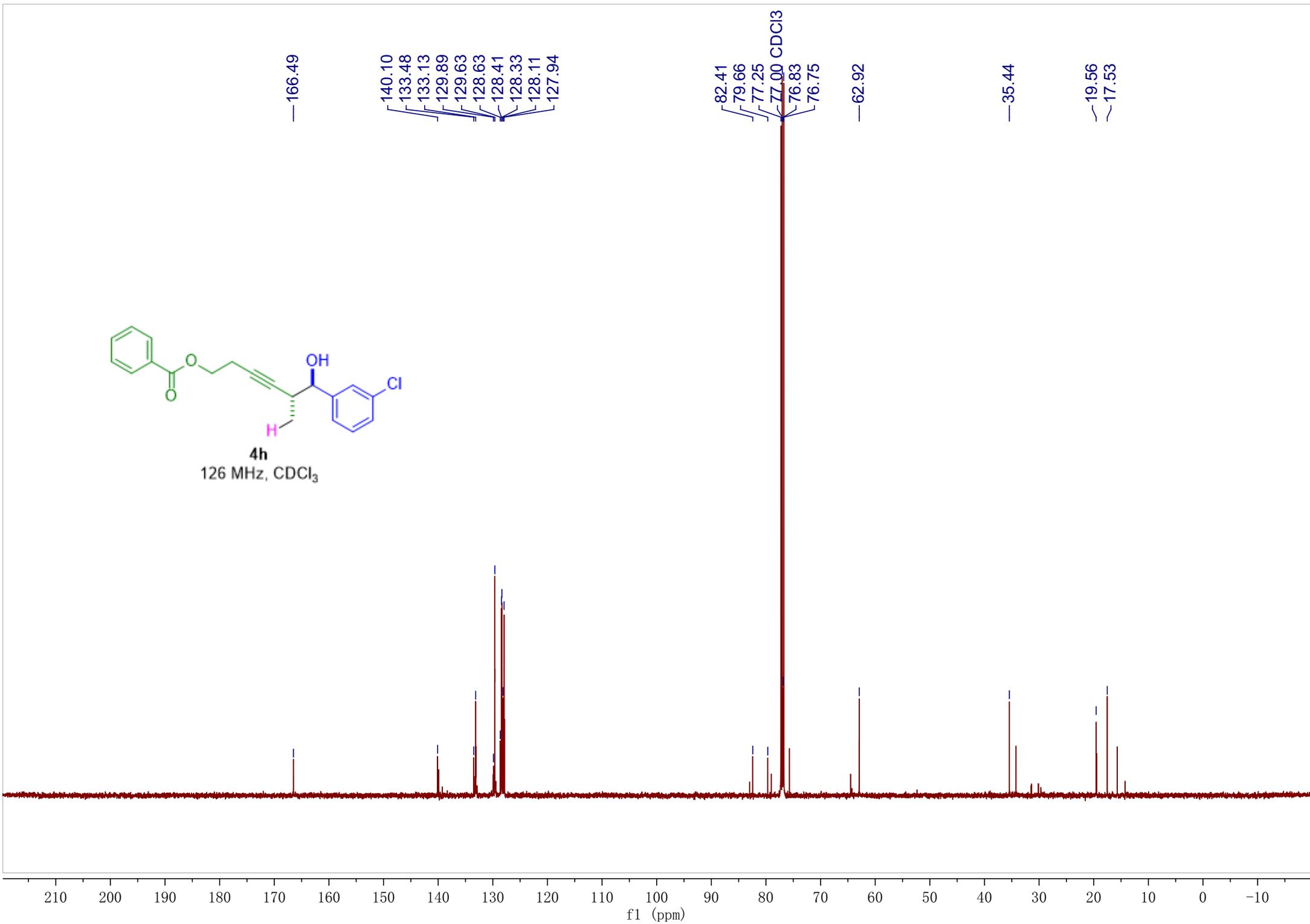


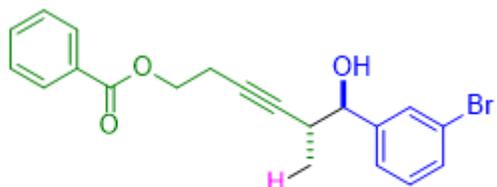
4h
500 MHz, CDCl₃



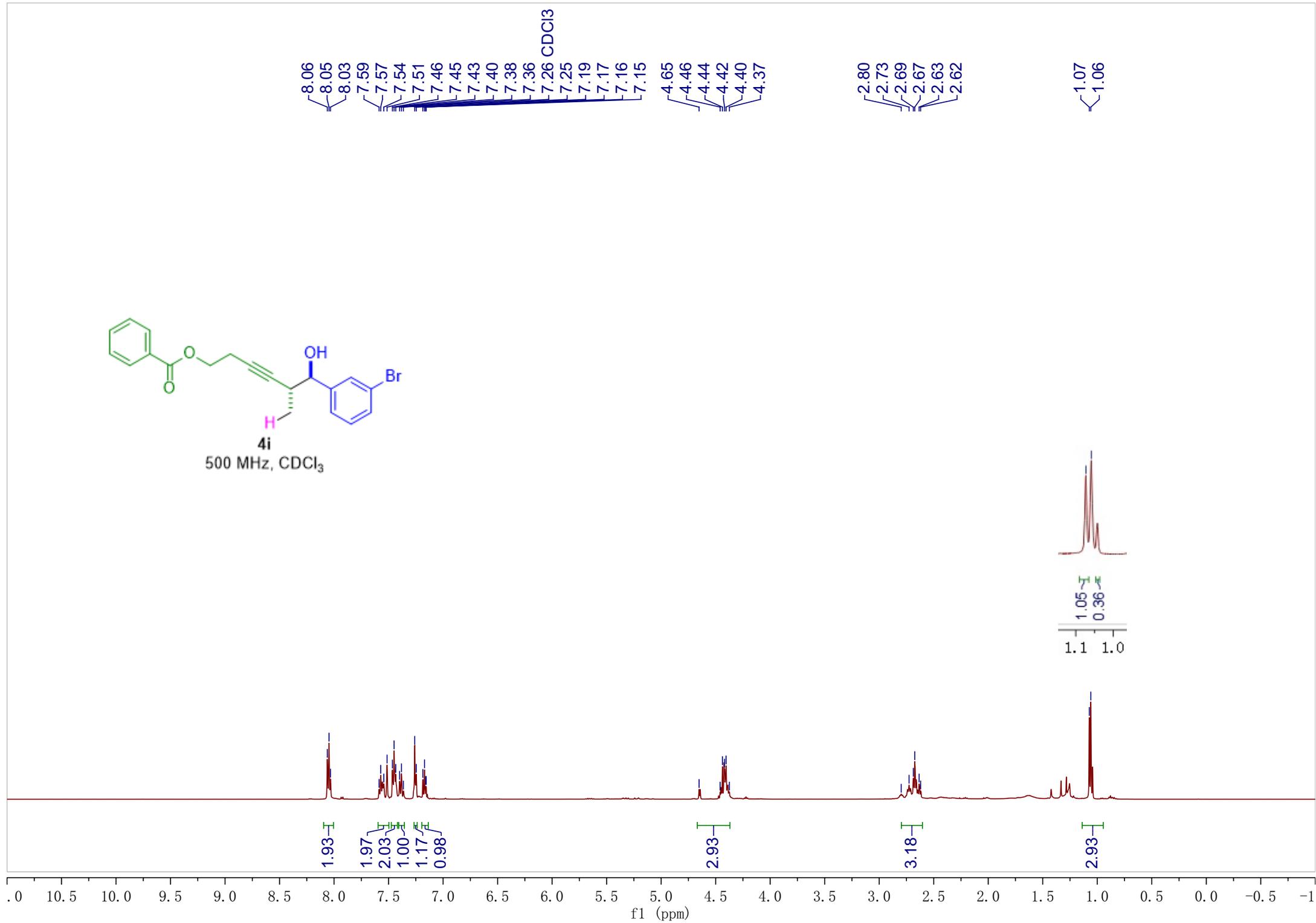


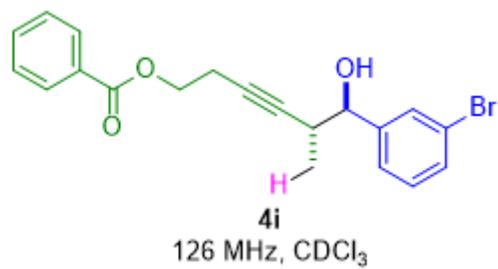
4h
126 MHz, CDCl₃





4i
500 MHz, CDCl₃





—166.49

—143.97
133.12
130.87
129.92
129.73
129.68
129.64
128.40
125.26
122.36

82.28
79.78
77.25
77.00 CDCl₃
76.81
76.75

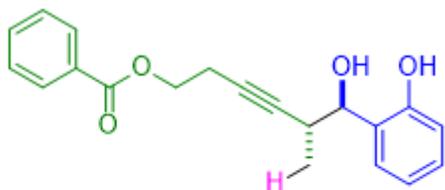
—62.91

—35.45

~19.56
~17.54

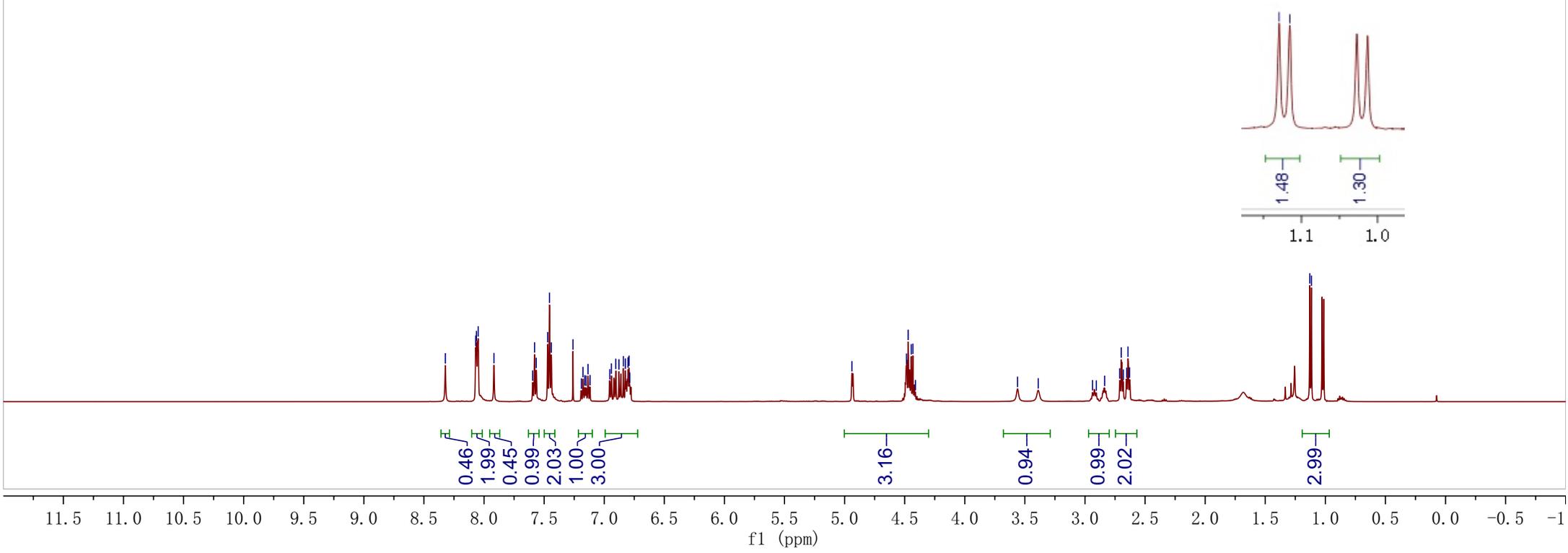
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

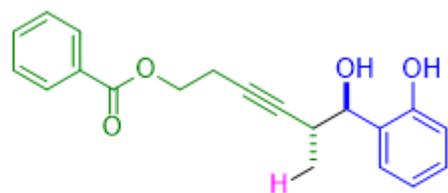
f1 (ppm)



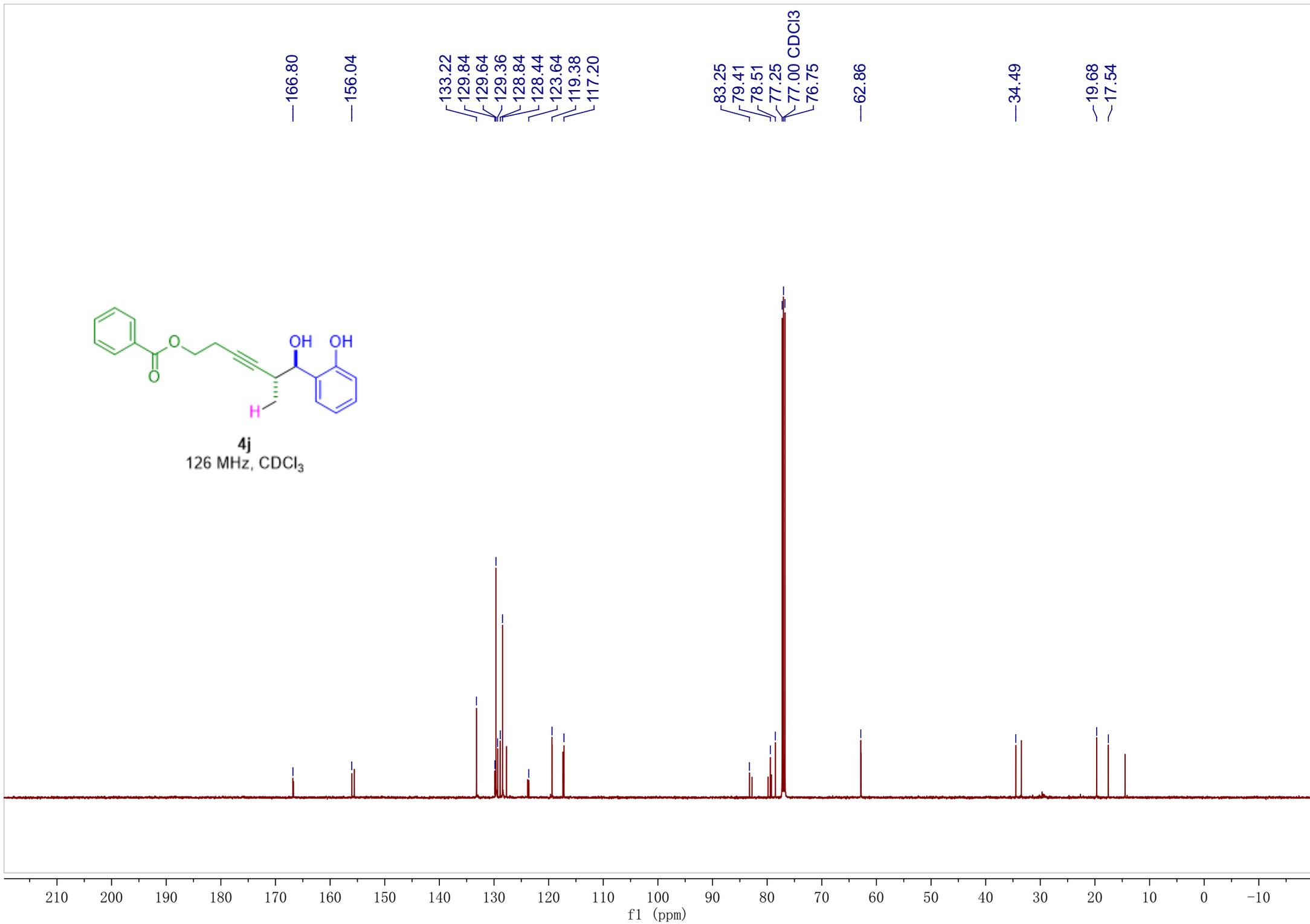
4j
500 MHz, CDCl₃

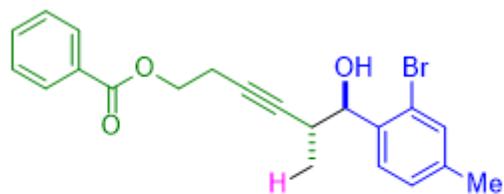
8.32
8.07
8.06
8.05
7.92
7.60
7.58
7.57
7.47
7.46
7.44
7.26 CDCl₃
7.19
7.18
7.16
7.15
7.14
7.12
6.95
6.94
6.90
6.88
6.84
6.82
6.80
6.79
6.79
4.94
4.49
4.47
4.45
4.43
4.41
3.56
3.39
2.94
2.91
2.84
2.71
2.70
2.68
2.65
2.64
2.63
1.13
1.12





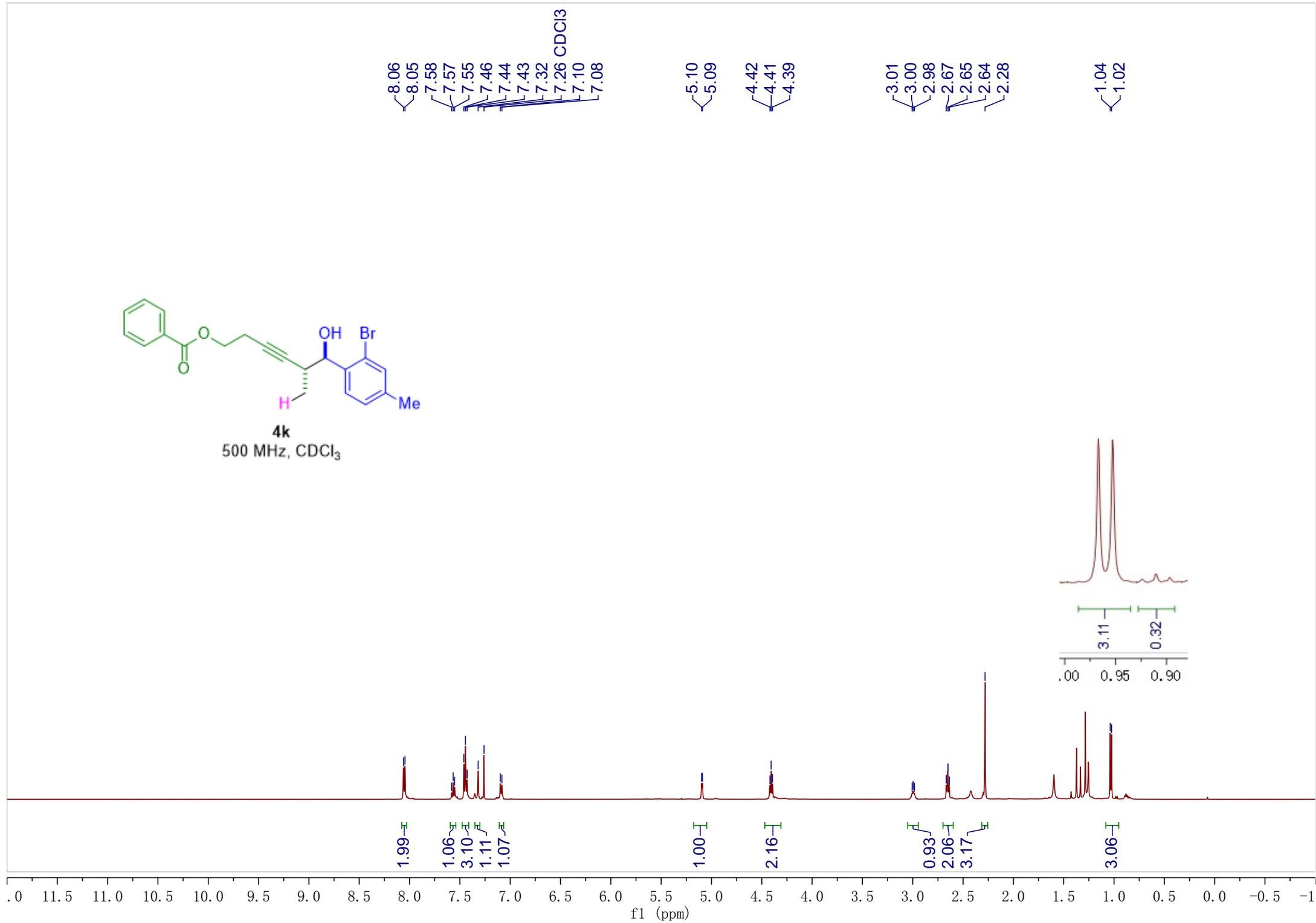
4j
126 MHz, CDCl₃

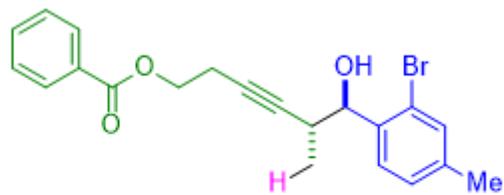




4k

500 MHz, CDCl₃





4k

126 MHz, CDCl₃

166.50

139.07

137.05

133.05

132.91

130.00

129.65

128.37

128.26

128.02

122.06

83.58

78.38

77.25

77.00 CDCl₃

76.75

74.42

62.98

32.04

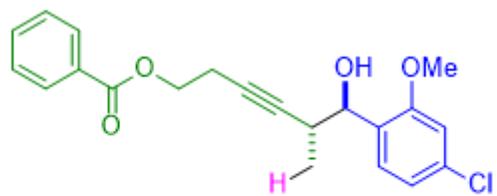
20.66

19.56

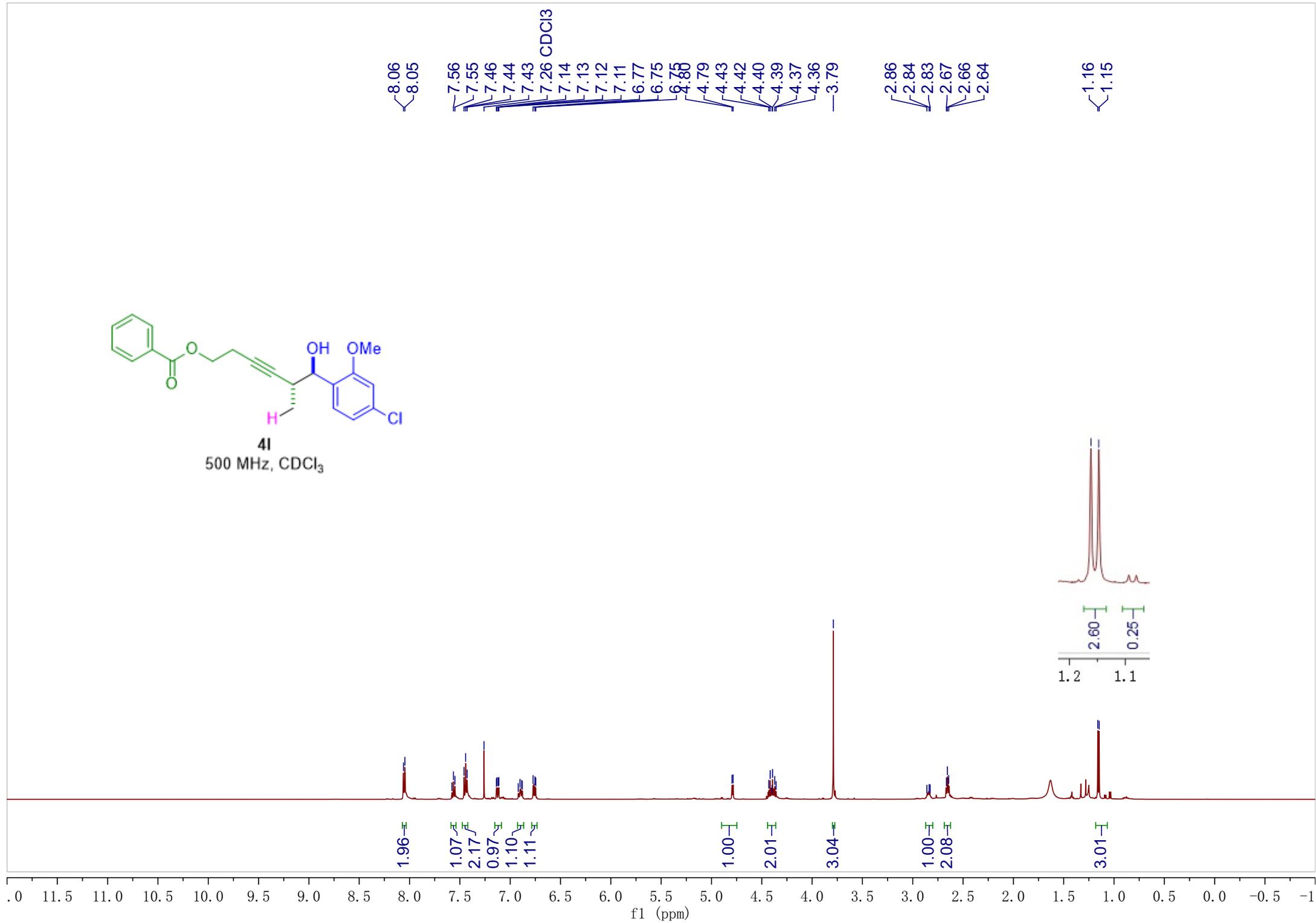
14.70

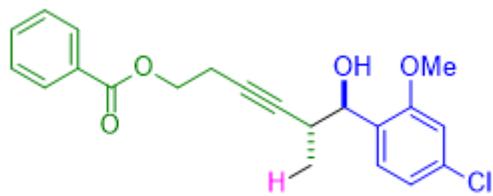
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

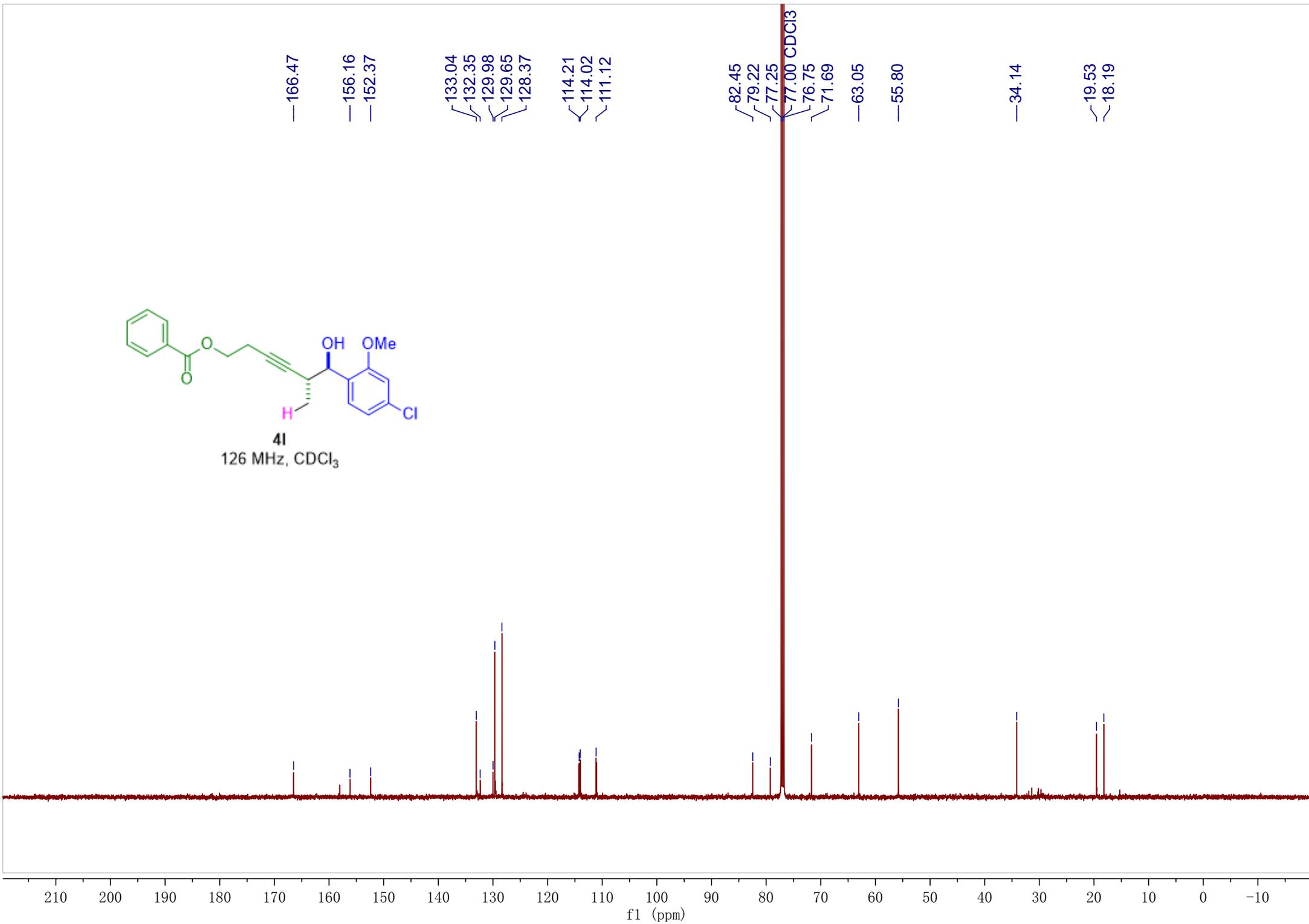


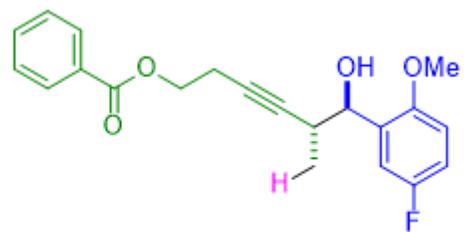
4I
500 MHz, CDCl₃



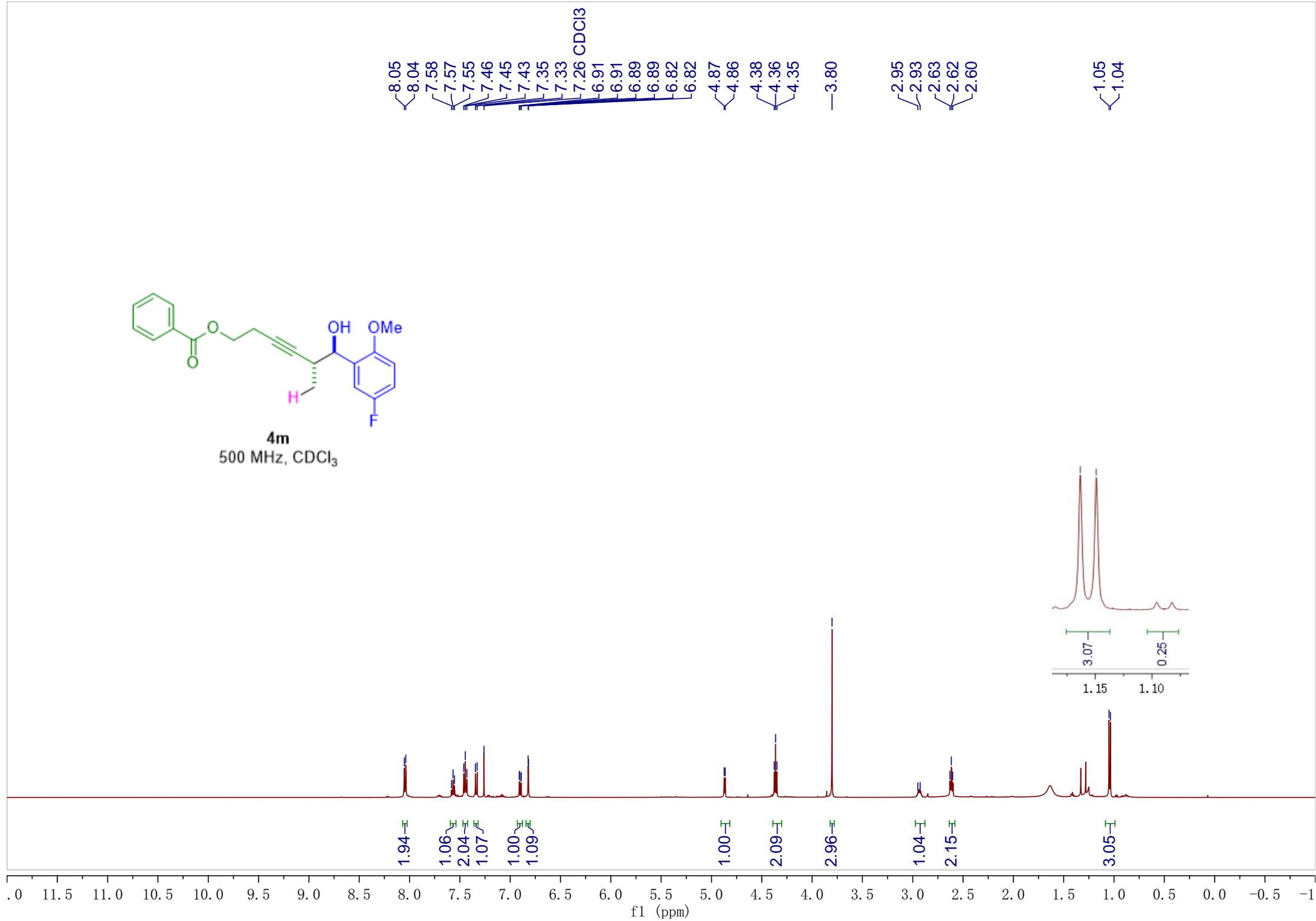


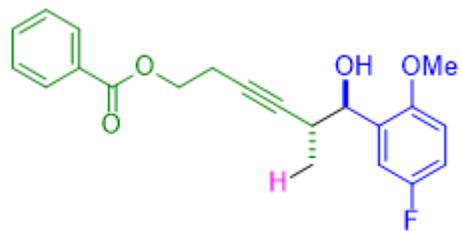
4I
126 MHz, CDCl₃





4m
500 MHz, CDCl₃





4m
126 MHz, CDCl₃

166.54
162.54
160.55

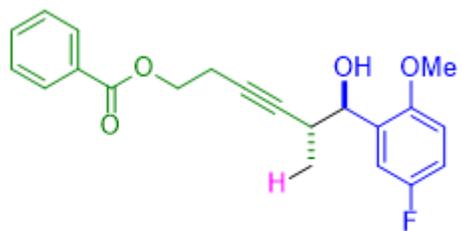
136.10
133.11
129.95
129.64
129.60
128.40
119.68
119.48
114.48
114.31

83.26
78.71
77.25
77.00 CDCl₃
76.75
73.98
62.90

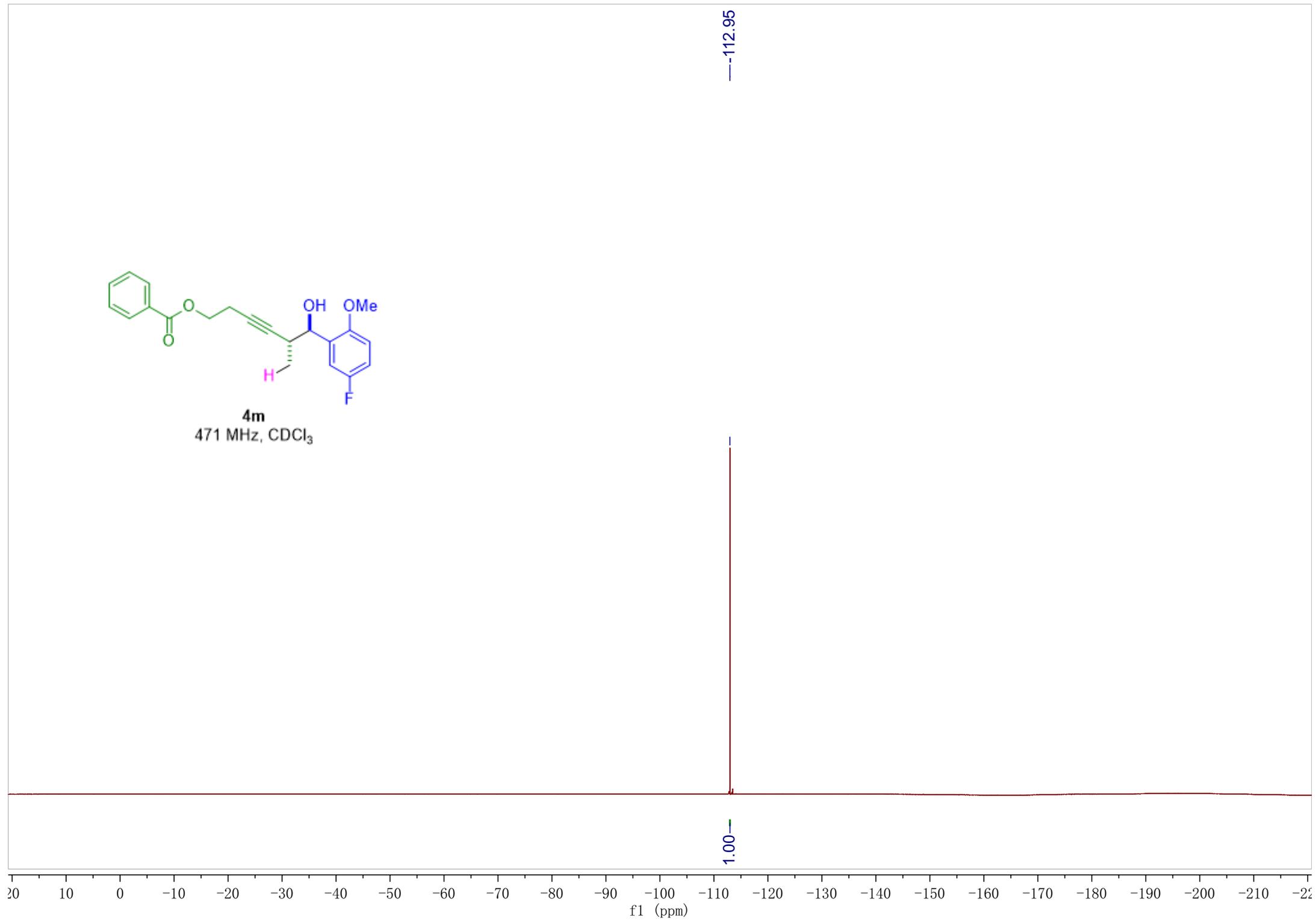
32.06
30.11
19.60
14.58

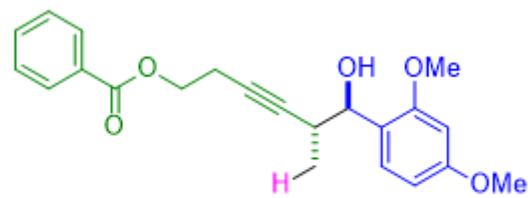
B (d)
114.39
A (d)
119.58

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

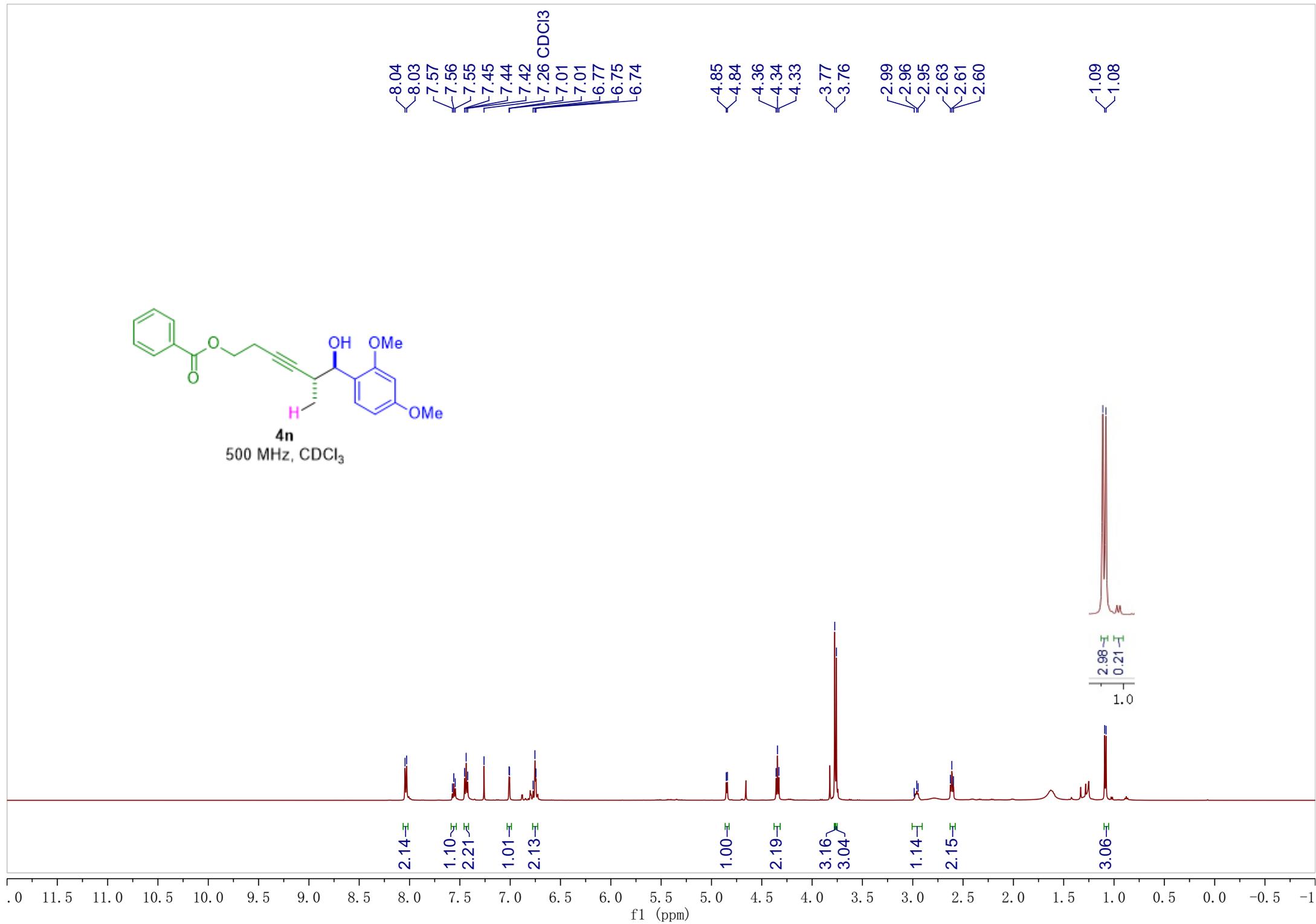


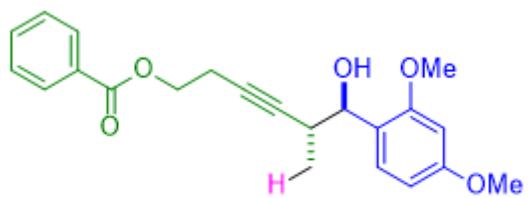
4m
471 MHz, CDCl₃





4n
500 MHz, CDCl₃





4n
126 MHz, CDCl₃

166.40
153.38
150.50
133.00
130.56
130.05
129.63
128.34
114.31
112.71
111.16

84.25
77.96
77.25
77.00 CDCl₃
76.75
73.14

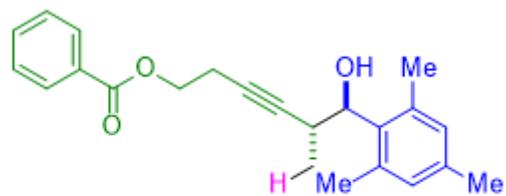
63.08
55.70

32.20

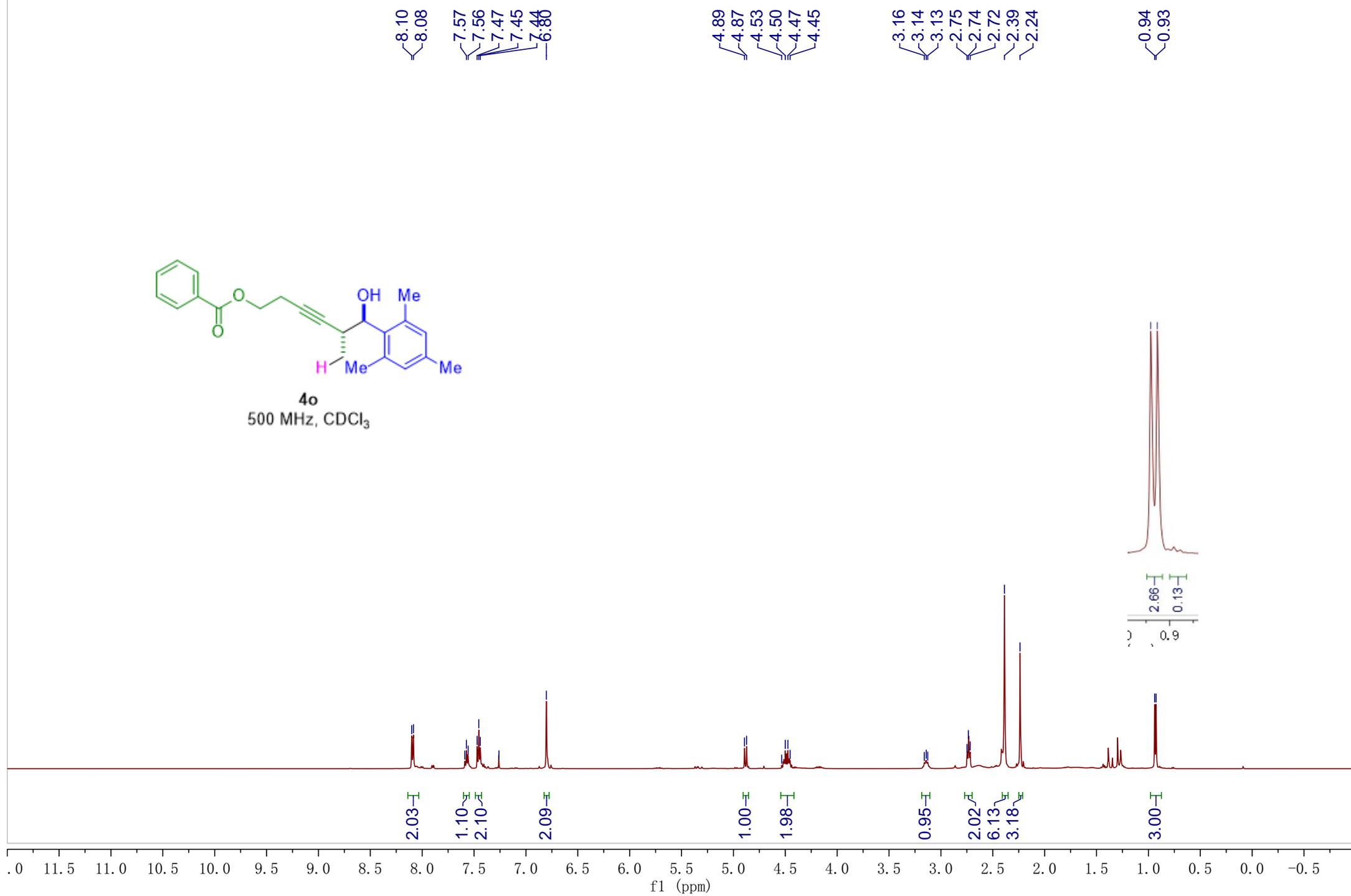
19.48
15.64

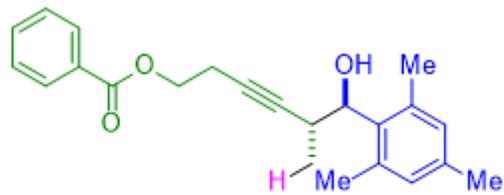
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)



4o
500 MHz, CDCl₃





4o
126 MHz, CDCl₃

—166.47

136.86
136.79
133.14
133.04
130.14
129.95
129.62
128.35

84.34
78.47
77.25
77.00 CDCl₃
76.75
74.30

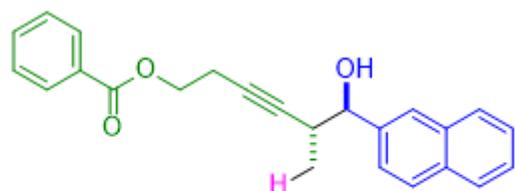
—62.90

—32.91

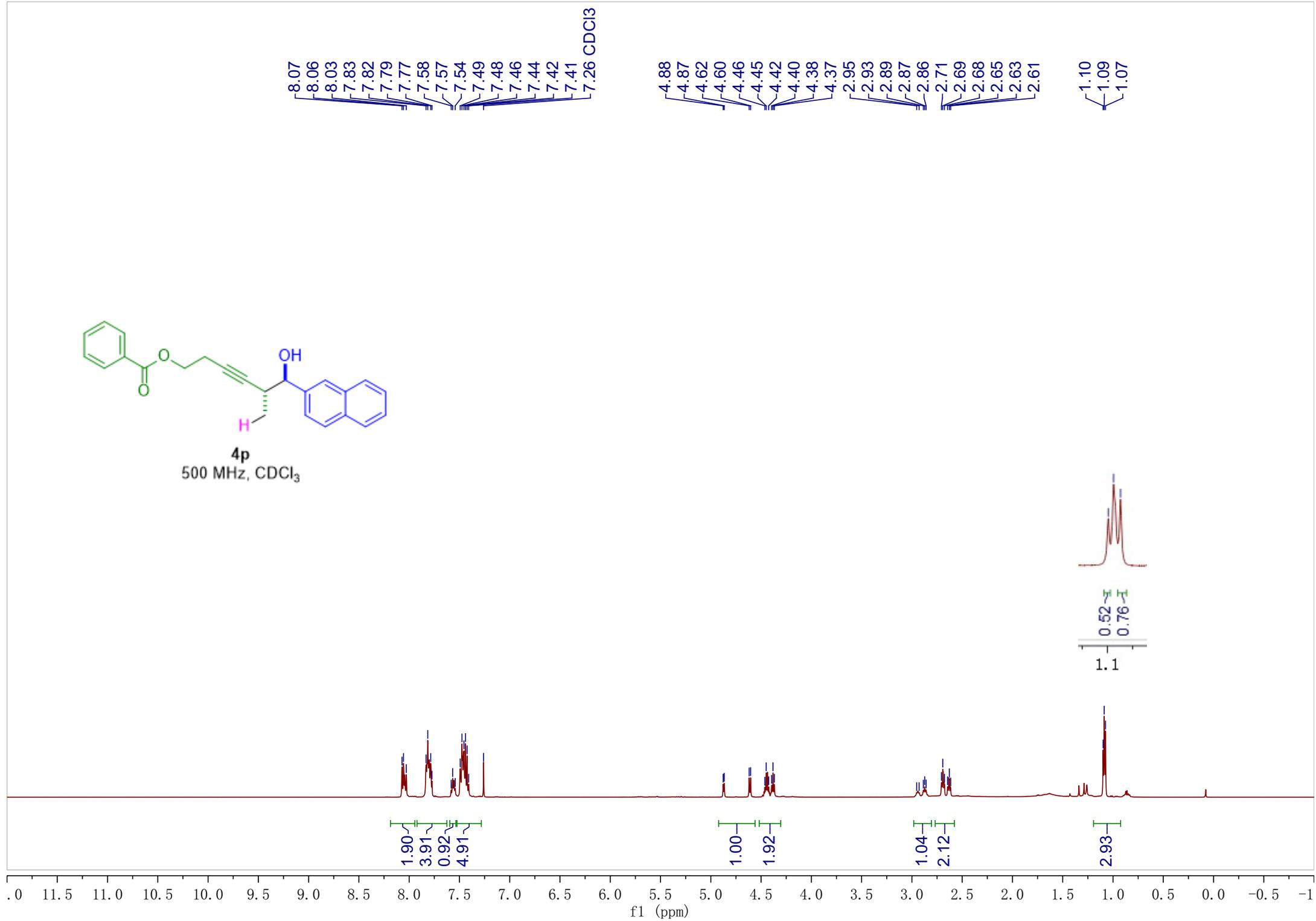
20.93
20.70
19.60
17.38

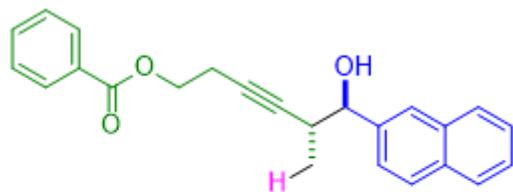
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

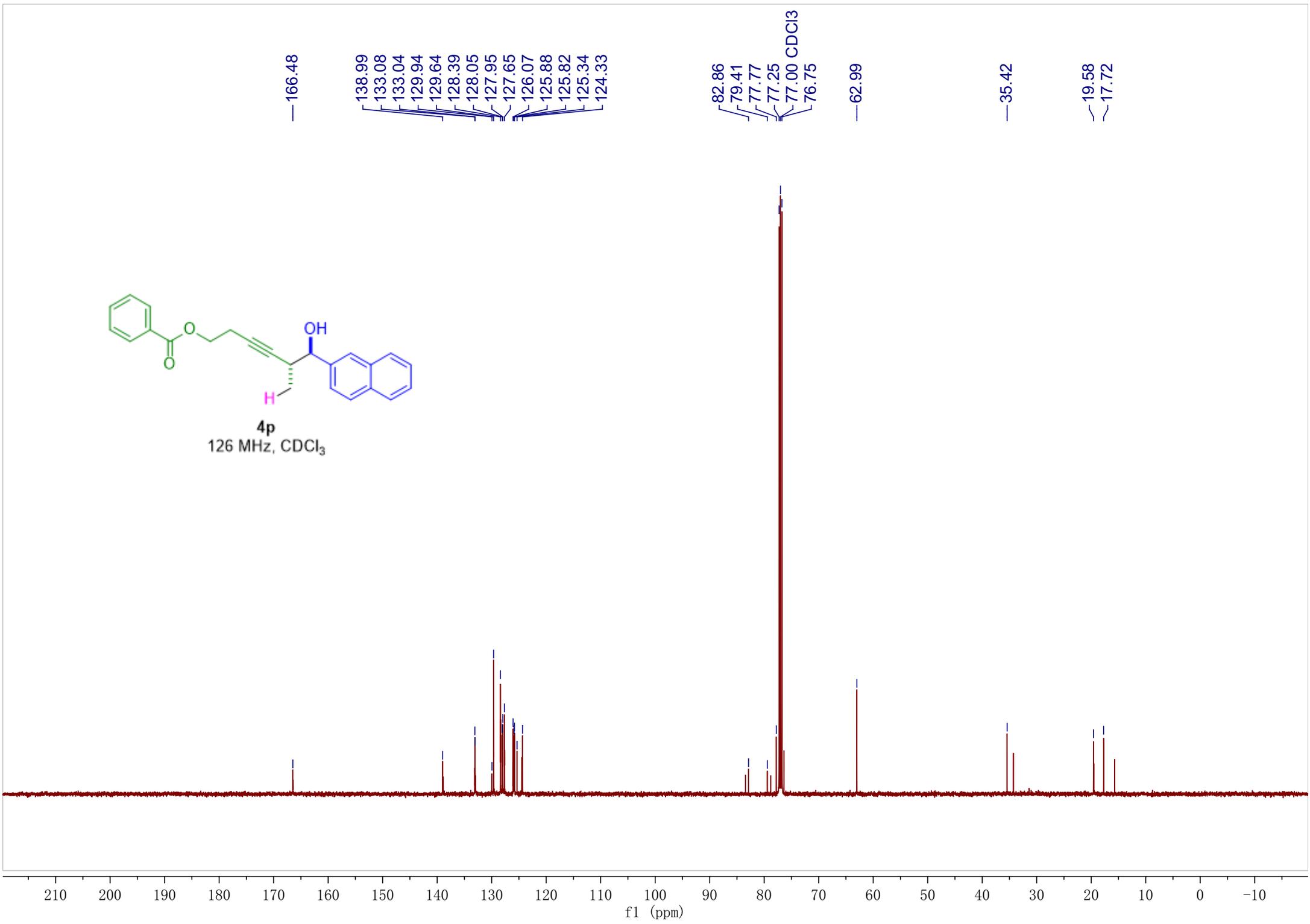


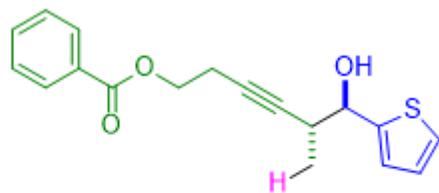
4p
500 MHz, CDCl₃



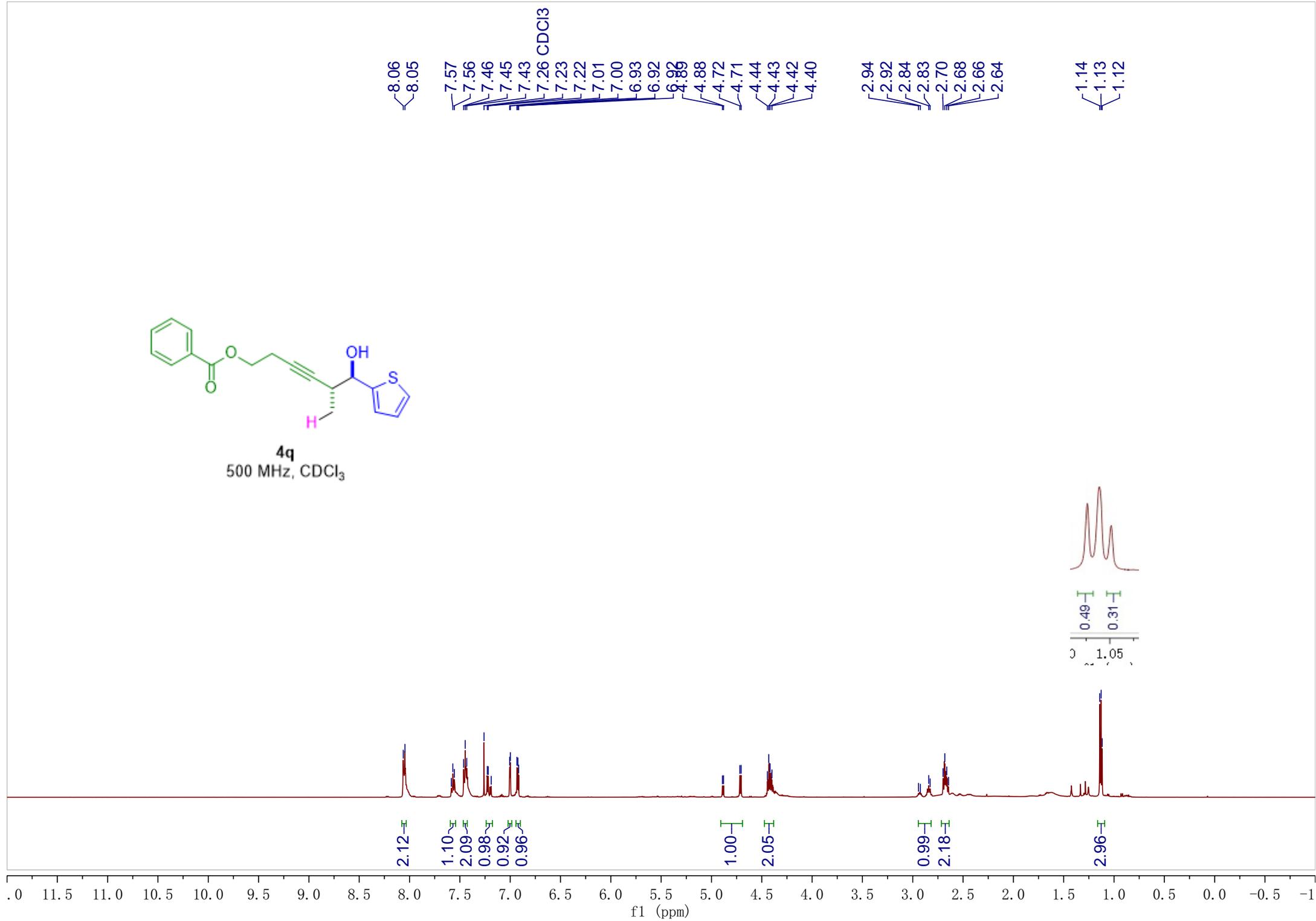


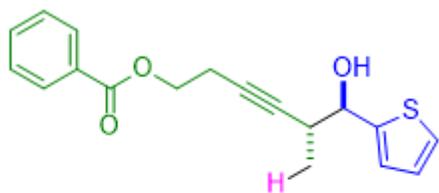
4p
126 MHz, CDCl₃





4q
500 MHz, CDCl₃





4q
126 MHz, CDCl₃

— 166.47

— 145.39

133.09

129.95

129.66

128.39

126.37

124.91

124.79

82.34

79.88

77.25

77.00 CDCl₃

76.75

73.64

— 62.94

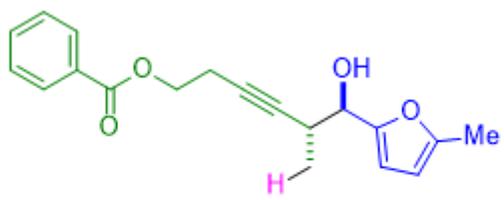
— 35.77

~ 19.57

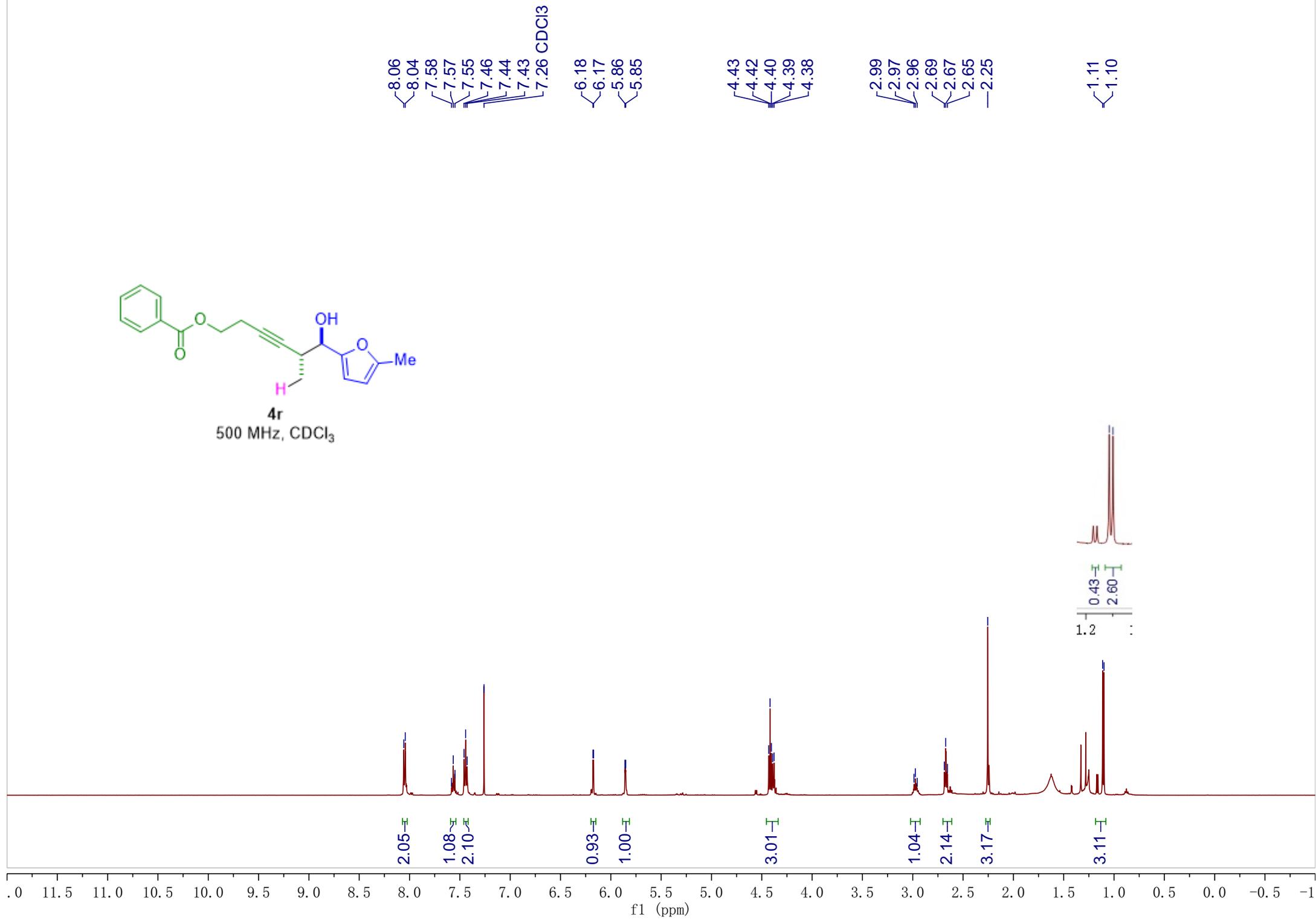
~ 17.76

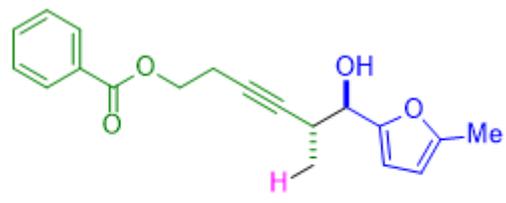
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)



4r
500 MHz, CDCl₃





4r
126 MHz, CDCl₃

166.47

152.19
151.85

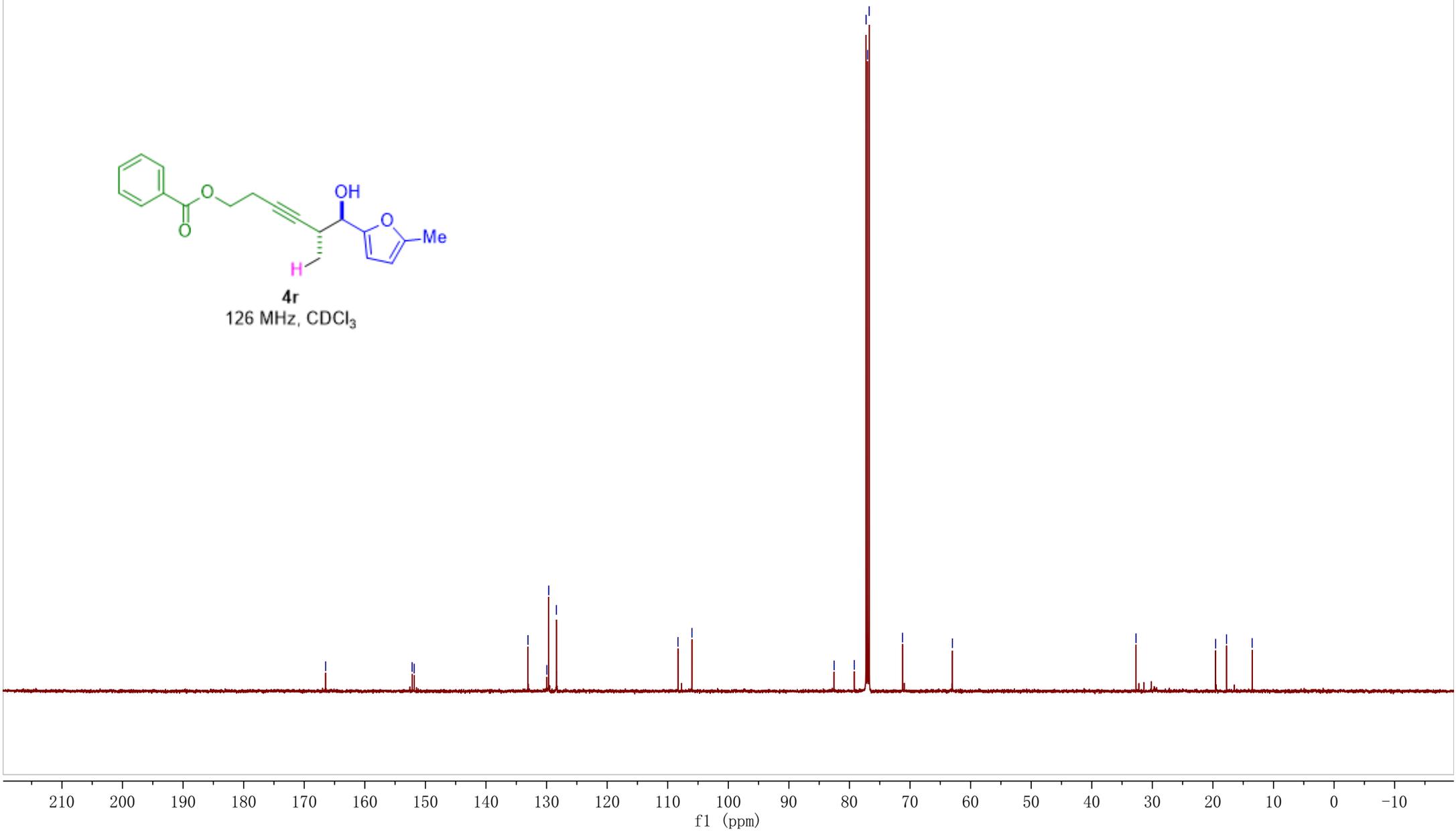
133.07
129.95
129.64
128.38

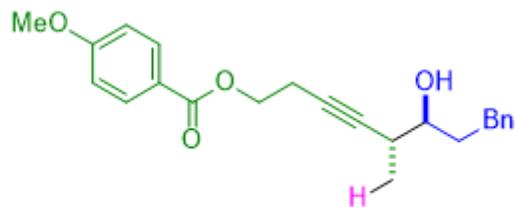
108.31
106.00

82.53
79.20
77.25
77.00 CDCl₃
76.75
71.24
63.00

32.70

19.55
17.76
13.53





5a
500 MHz, CDCl₃

8.02
8.01
7.29
7.27
7.26
7.26 CDCl₃
7.19
7.18
7.18
6.92
6.90

4.42
4.40
4.39
— 3.85
3.40
3.39
3.37
2.79
2.69
2.67
2.65
2.64
1.82
1.81
1.80
1.18
1.17

2.10

2.15

3.02

2.08

2.04

3.06

1.00

1.12

3.12

1.04

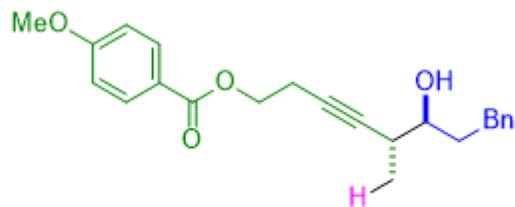
2.16

3.08

2.57
1.10
0.51
1.05

11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1

f1 (ppm)



5a
126 MHz, CDCl₃

166.2
163.4

142.0

131.6
128.4
128.3
125.7
122.3

113.6

82.3
79.1
77.3
77.0 CDCl₃
76.7
73.6

62.7

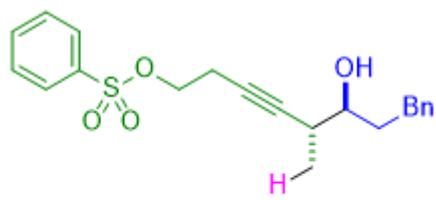
55.4

36.9
33.3
32.0

19.6
17.7

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

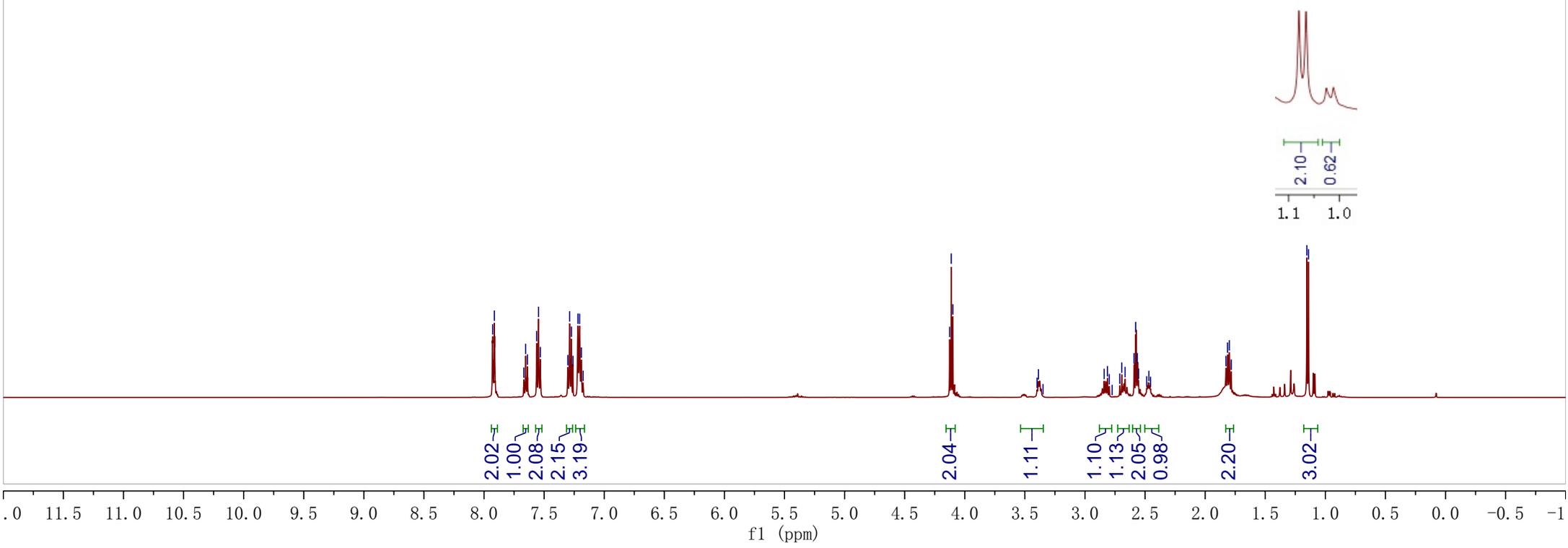
f1 (ppm)

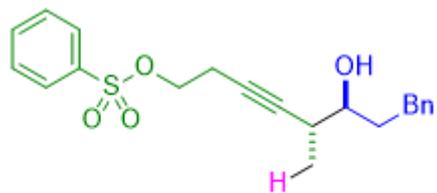


5b
500 MHz, CDCl₃

7.93
7.91
7.67
7.65
7.64
7.56
7.55
7.53
7.30
7.29
7.27
7.26 CDCl₃
7.22
7.20
7.19
7.18

4.13
4.11
4.10
3.40
3.39
3.35
2.81
2.69
2.59
2.58
2.56
1.81
1.80
1.78
1.15
1.14





5b
126 MHz, CDCl₃

141.9
135.9
133.8
129.3
128.4
128.3
127.8
125.8

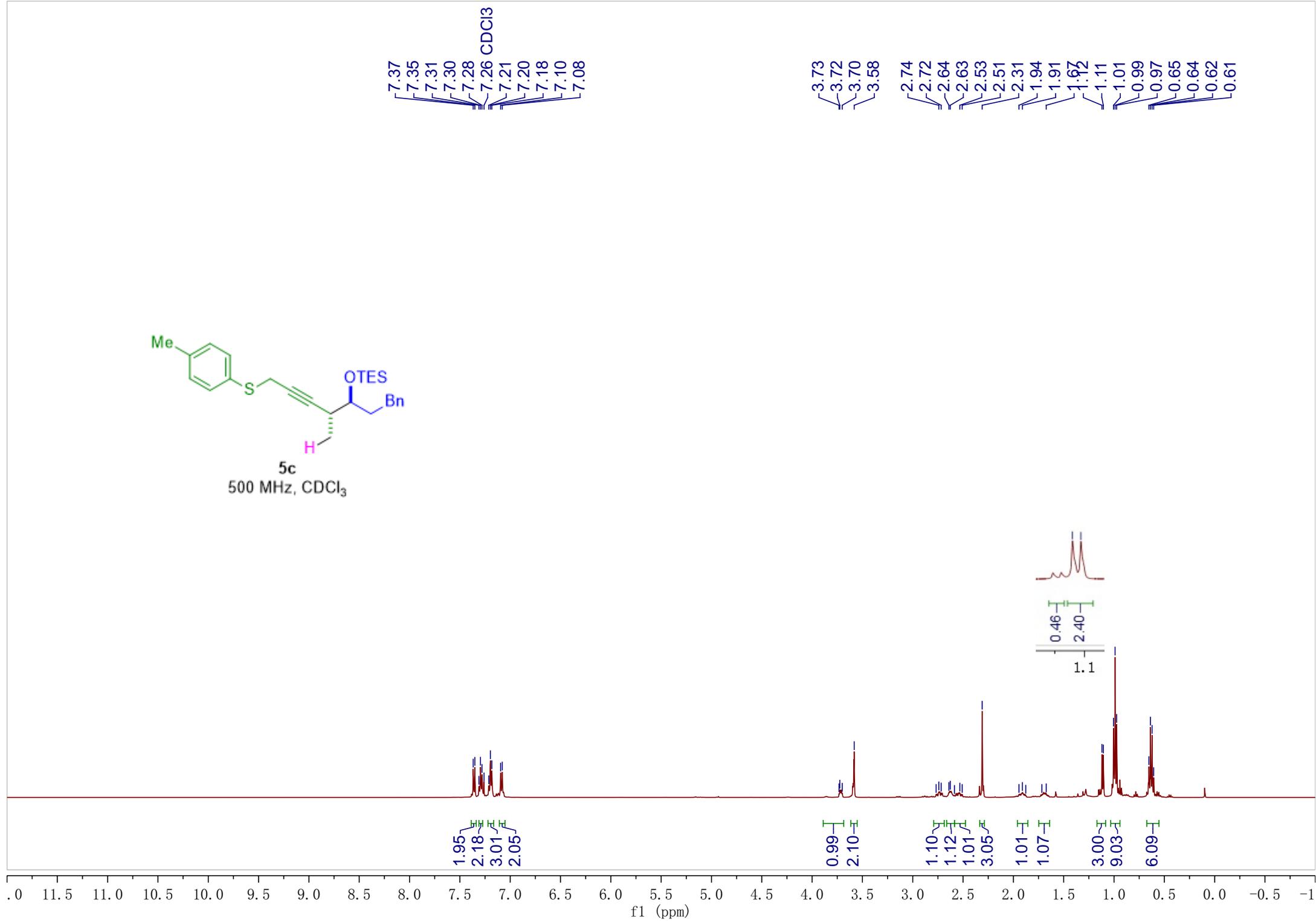
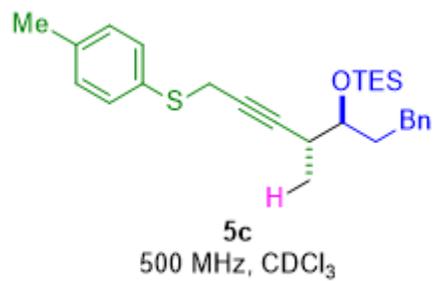
83.3
77.3
77.2
77.0 CDCl₃
76.7
73.5
68.2

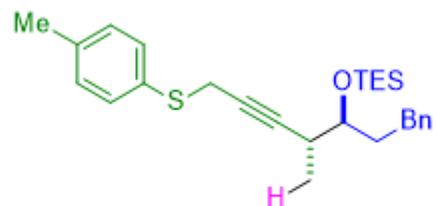
36.9
33.2
32.0

19.8
17.6

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)





5c
126 MHz, CDCl₃

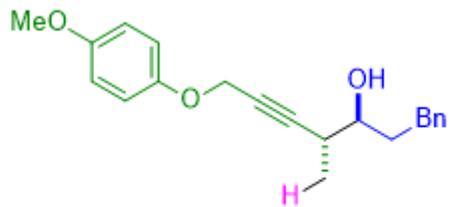
142.4
136.9
131.7
131.0
129.5
128.3
128.3
125.7

85.8
77.5
77.3
77.0 CDCl₃
76.7
74.2

34.7
32.5
23.9
21.0
17.5
14.6
6.9
5.1

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)



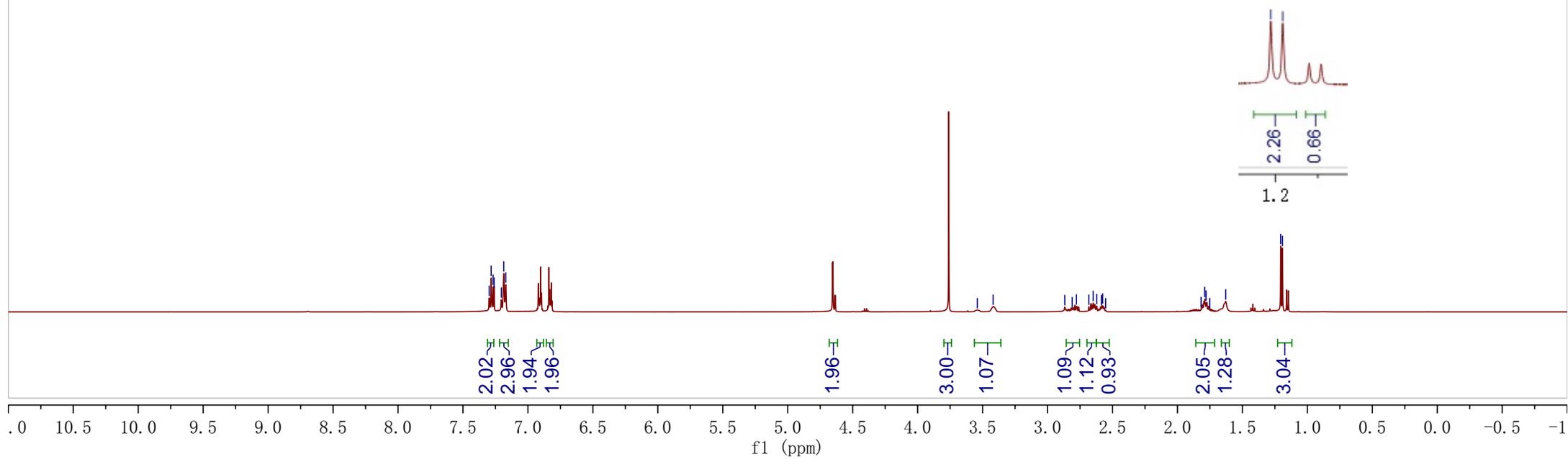
5d
500 MHz, CDCl₃

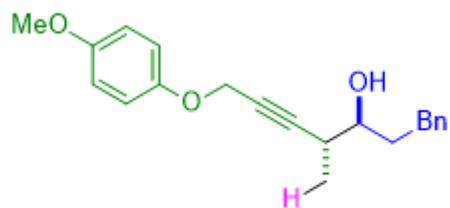
7.30
7.28
7.27
7.26 CDCl₃
7.20
7.19
7.17

3.54
3.42

2.87
2.78
2.68
2.65
2.62
2.58

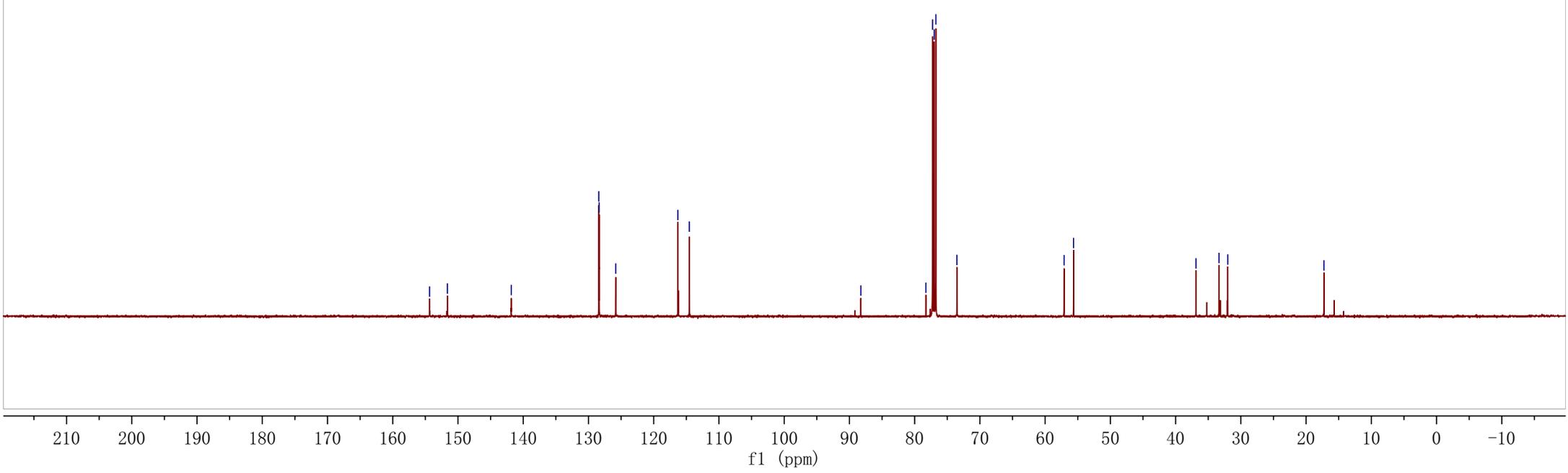
1.82
1.79
1.78
1.63
1.21
1.19

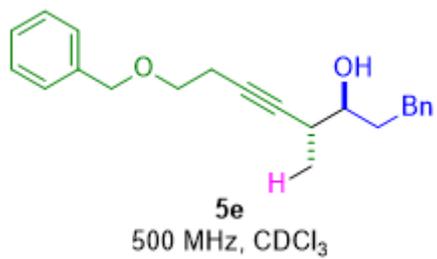




5d
126 MHz, CDCl₃

154.4
151.6
141.8
128.4
128.4
125.8
116.3
114.5
88.2
78.3
77.3
77.0 CDCl₃
76.7
73.5
57.1
55.6
36.9
33.3
32.0
17.3





7.36
 7.35
 7.31
 7.30
 7.28
 7.26 CDCl₃
 7.23
 7.22
 7.20

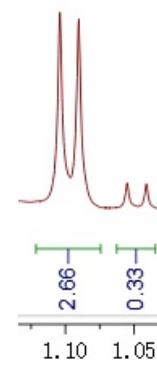
— 4.56

3.60
 3.58
 3.57
 3.42
 3.39

2.83
 2.83
 2.53
 2.52

1.87
 1.85
 1.84
 1.82

1.20
 1.19



4.12
 2.98
 2.96

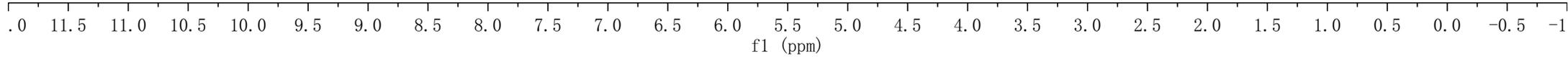
2.18

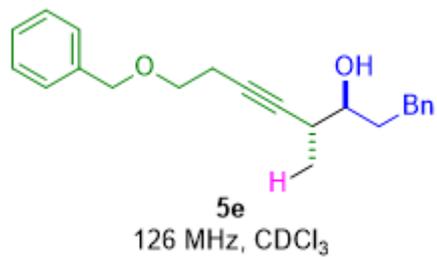
2.12
 1.00

2.10
 3.10

2.05

3.12





— 142.06
— 138.00
128.43
128.38
128.32
127.66
125.74

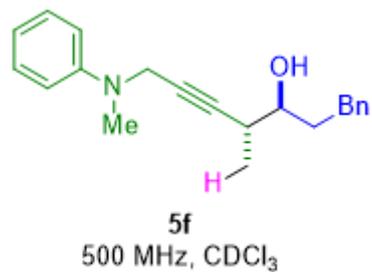
81.72
80.25
77.25
77.00 CDCl₃
76.75
73.72
72.91
68.65

36.94
33.39
32.05

20.13
17.76

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)



7.31
 7.30
 7.29
 7.28
 7.28
 7.27
 7.26 CDCl₃
 7.22
 7.20
 7.19
 7.17
 7.15
 6.88
 6.87
 6.85
 6.84
 6.82

4.07
 3.34
 2.95
 2.77
 2.74
 2.73
 2.62
 2.59
 2.58
 2.50
 2.49
 1.74
 1.73
 1.71
 1.69
 1.68
 1.50
 1.17
 1.15

4.16
 1.14
 2.12
 2.00
 1.00

2.19

1.13

3.19

2.11

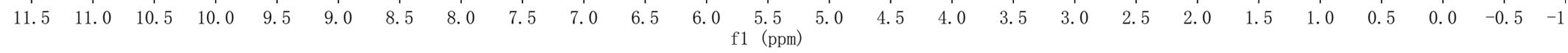
0.94

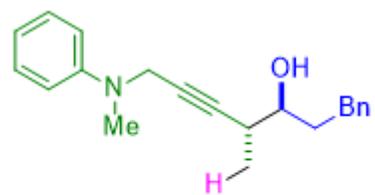
2.07

1.03

3.31

2.71
 0.53
 1.05





5f
126 MHz, CDCl₃

141.9
129.1
129.0
128.4
128.3
125.8
118.4
114.6

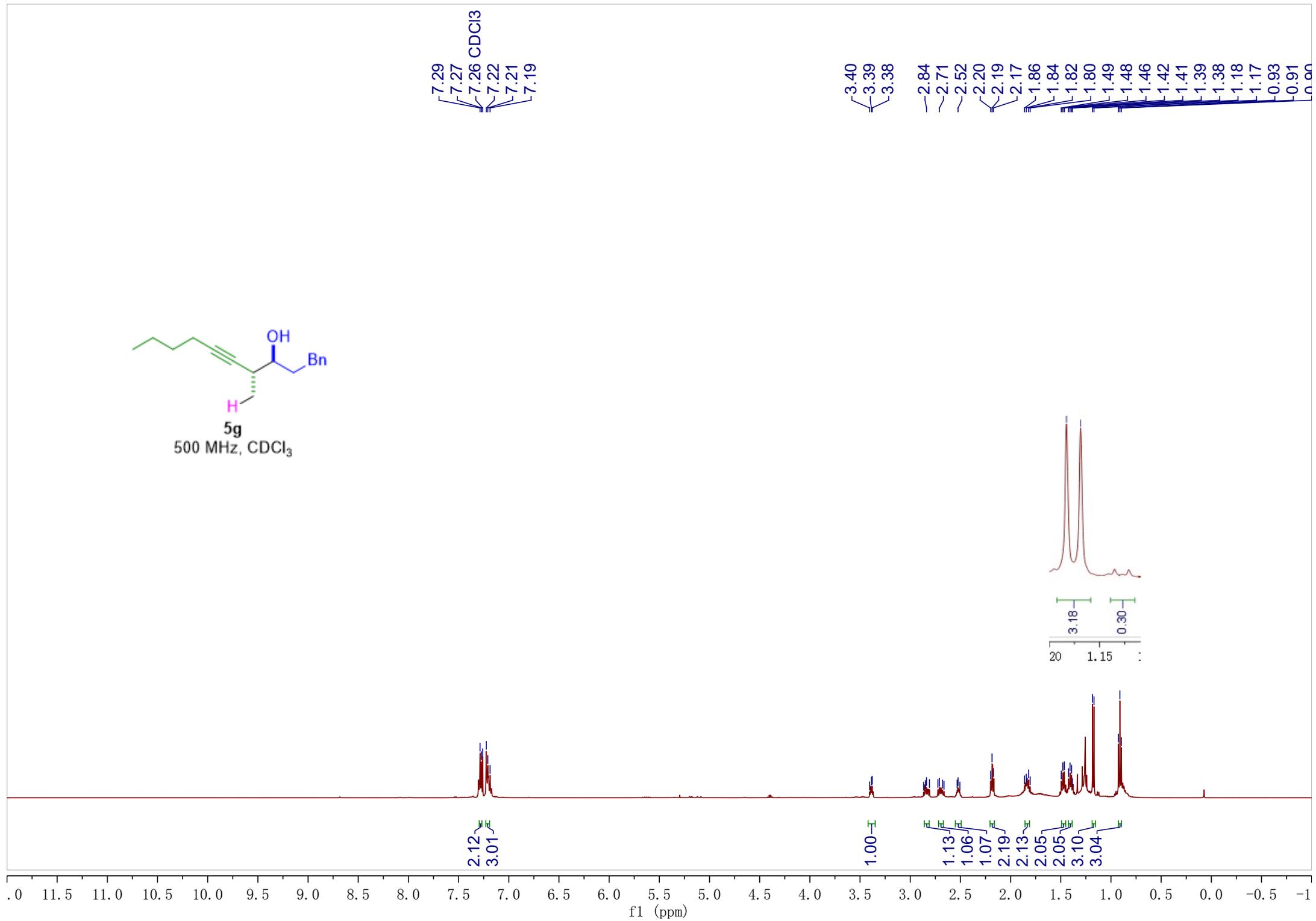
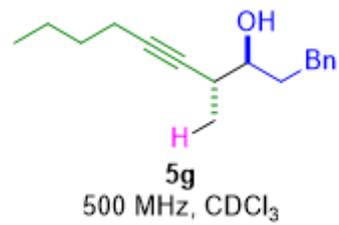
84.8
78.4
77.3
77.0 CDCl₃
76.7
73.6

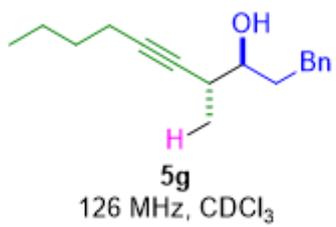
43.2
38.8
37.0
33.3
32.0

17.6

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)





142.13

128.44
128.34
125.75

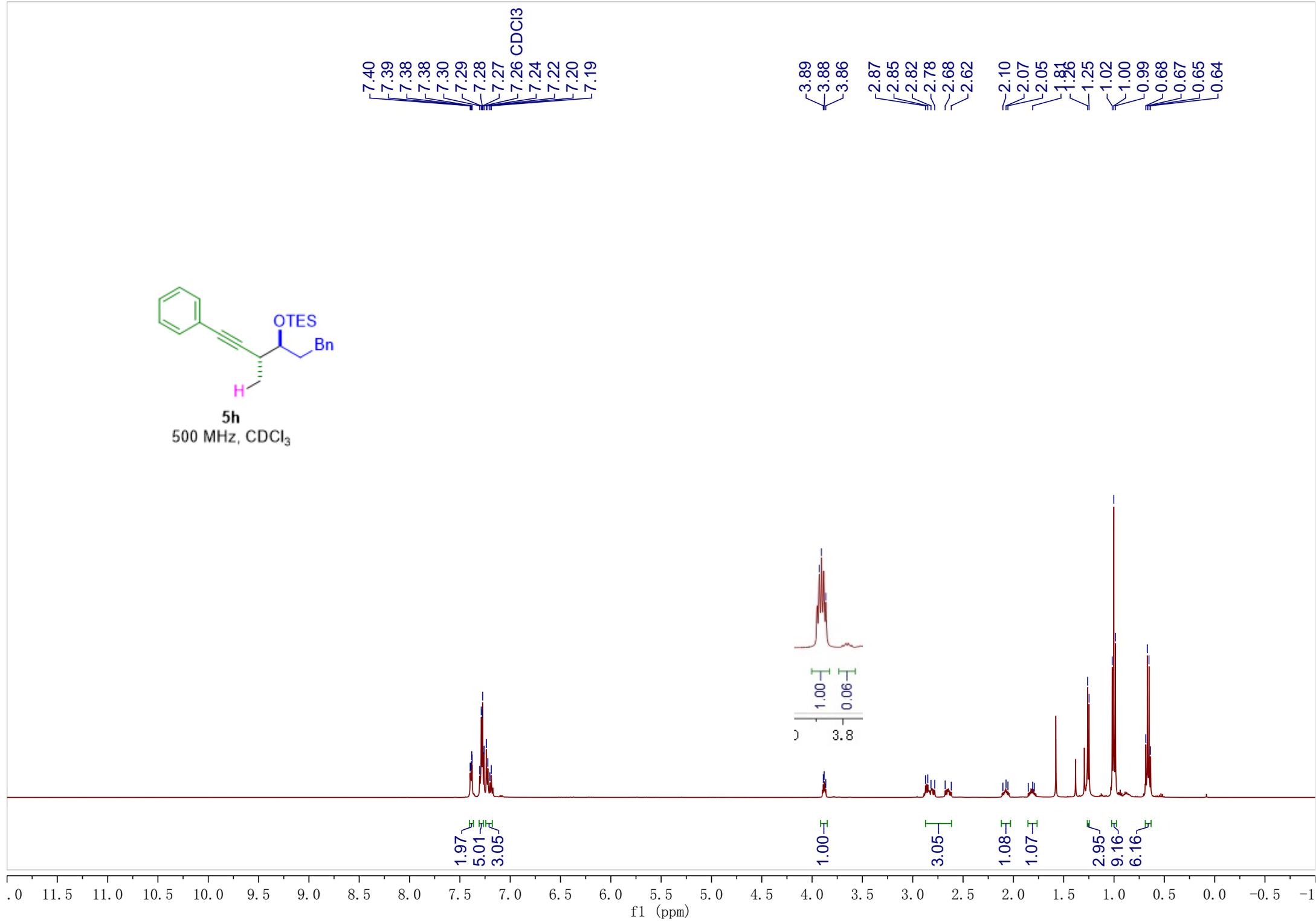
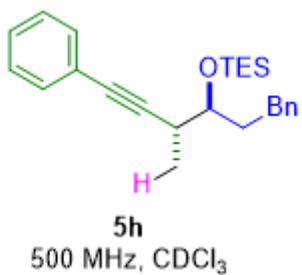
83.78
80.23
77.25
77.00 CDCl₃
76.75
73.82

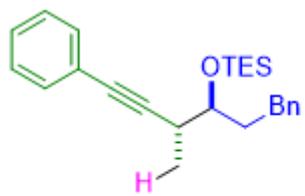
36.99
33.40
32.08
31.10

21.93
18.37
17.92
13.58

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)





5h
126 MHz, CDCl₃

142.46
131.55
128.37
128.33
128.14
127.56
125.70
123.88

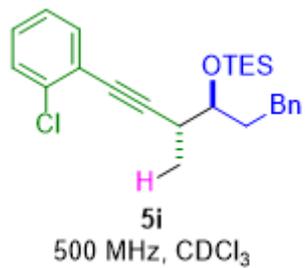
92.11
82.08
77.25
77.00 CDCl₃
76.75
74.27

35.06
33.12
32.47

14.92
6.97
5.16

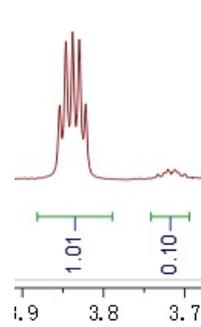
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)



7.42
 7.41
 7.40
 7.38
 7.38
 7.36
 7.29
 7.28
 7.26 CDCl₃
 7.23
 7.22

3.93
 3.92
 3.90
 3.90
 2.93
 2.91
 2.79
 2.77
 2.68
 2.65
 2.16
 2.13
 1.81
 1.28
 1.27
 1.01
 1.00
 0.98
 0.68
 0.66
 0.65
 0.63



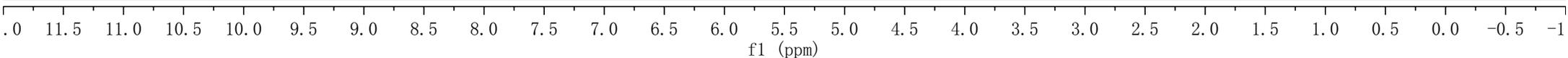
1.14
 1.13
 1.98
 2.12
 3.07

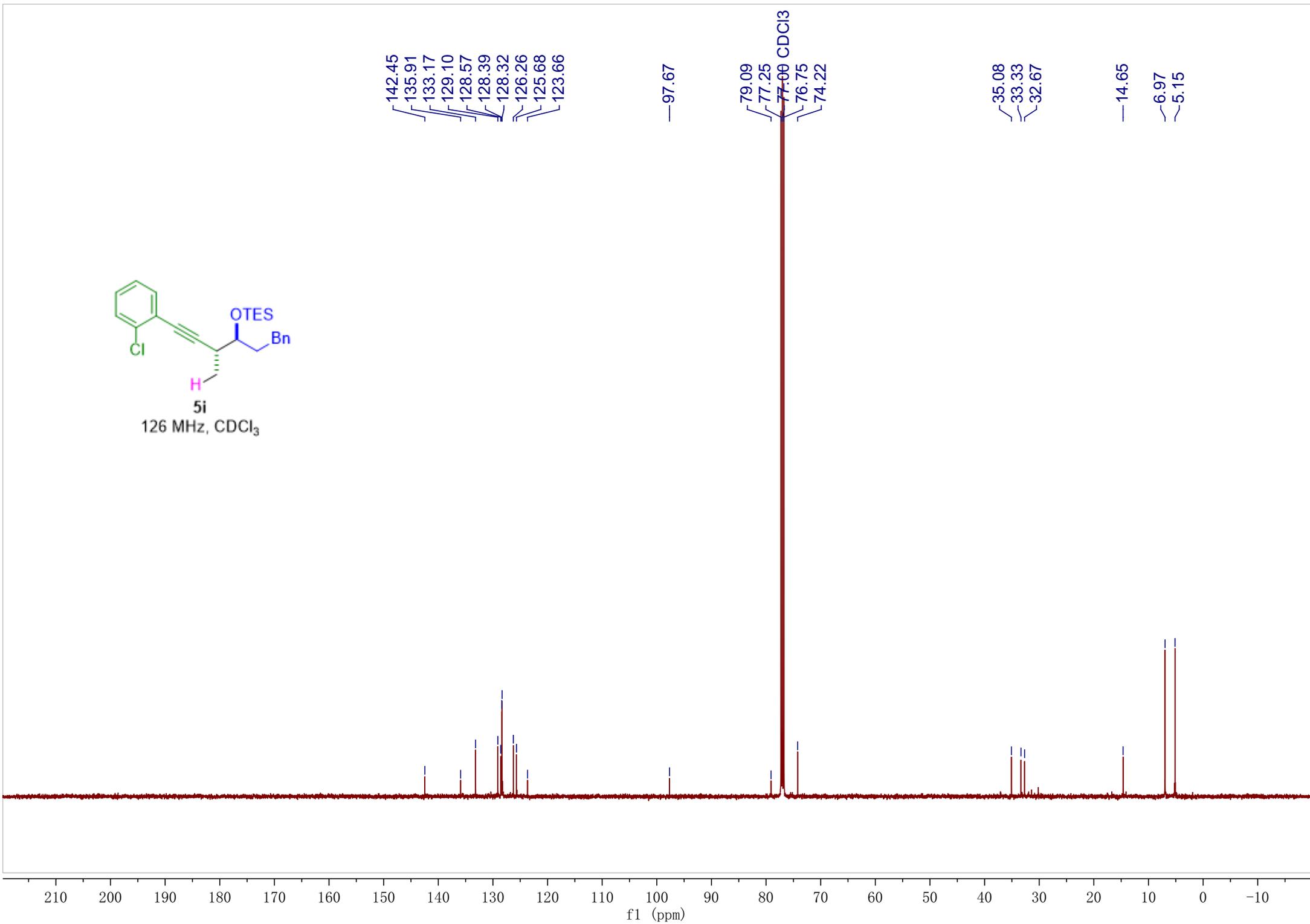
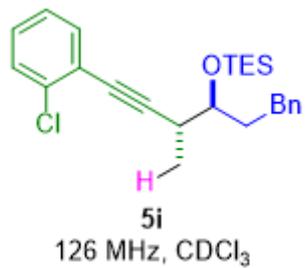
1.00

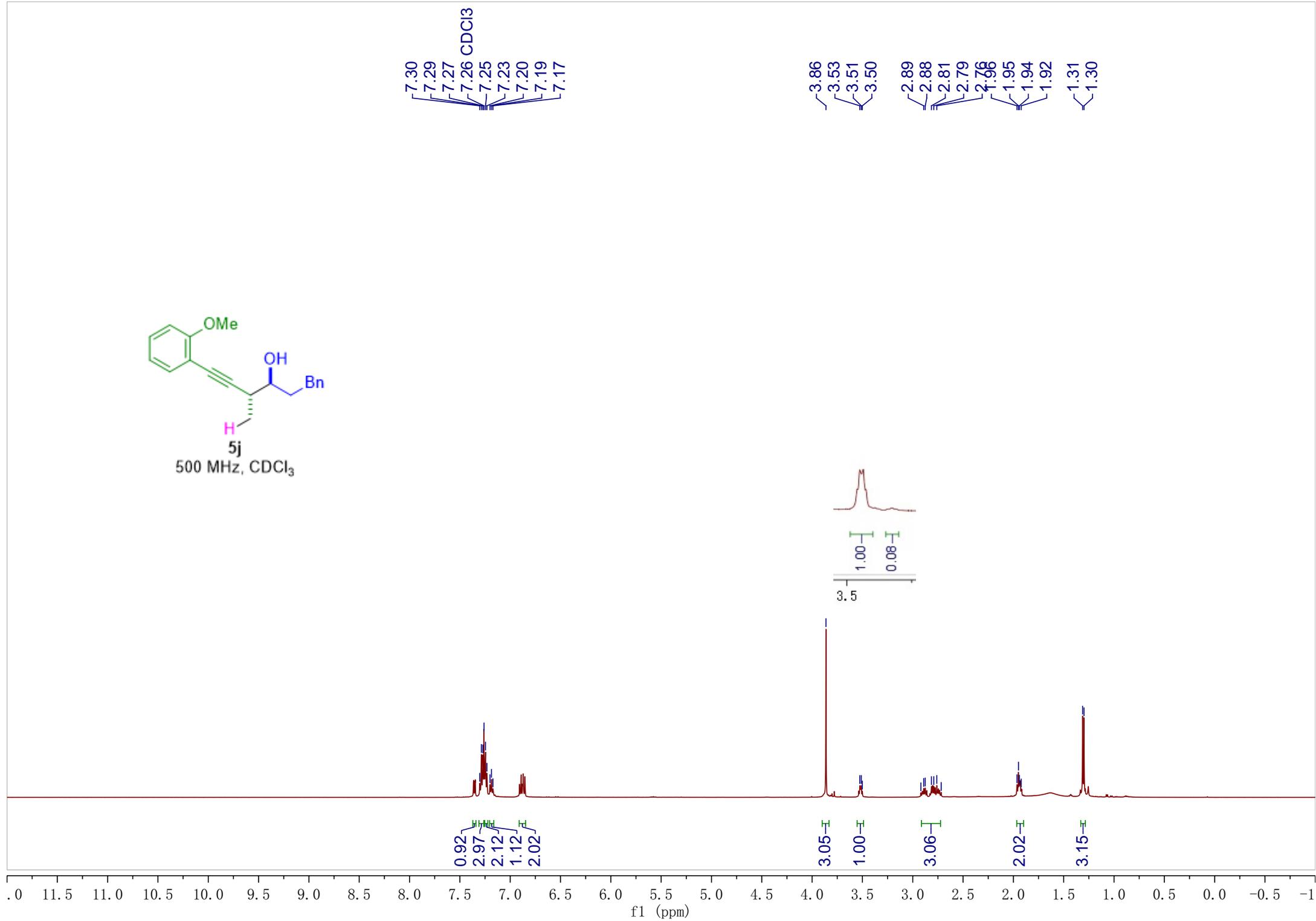
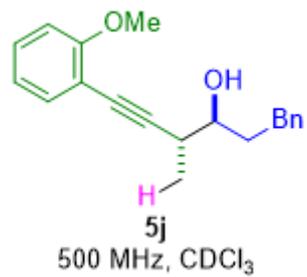
1.08
 1.12
 1.15

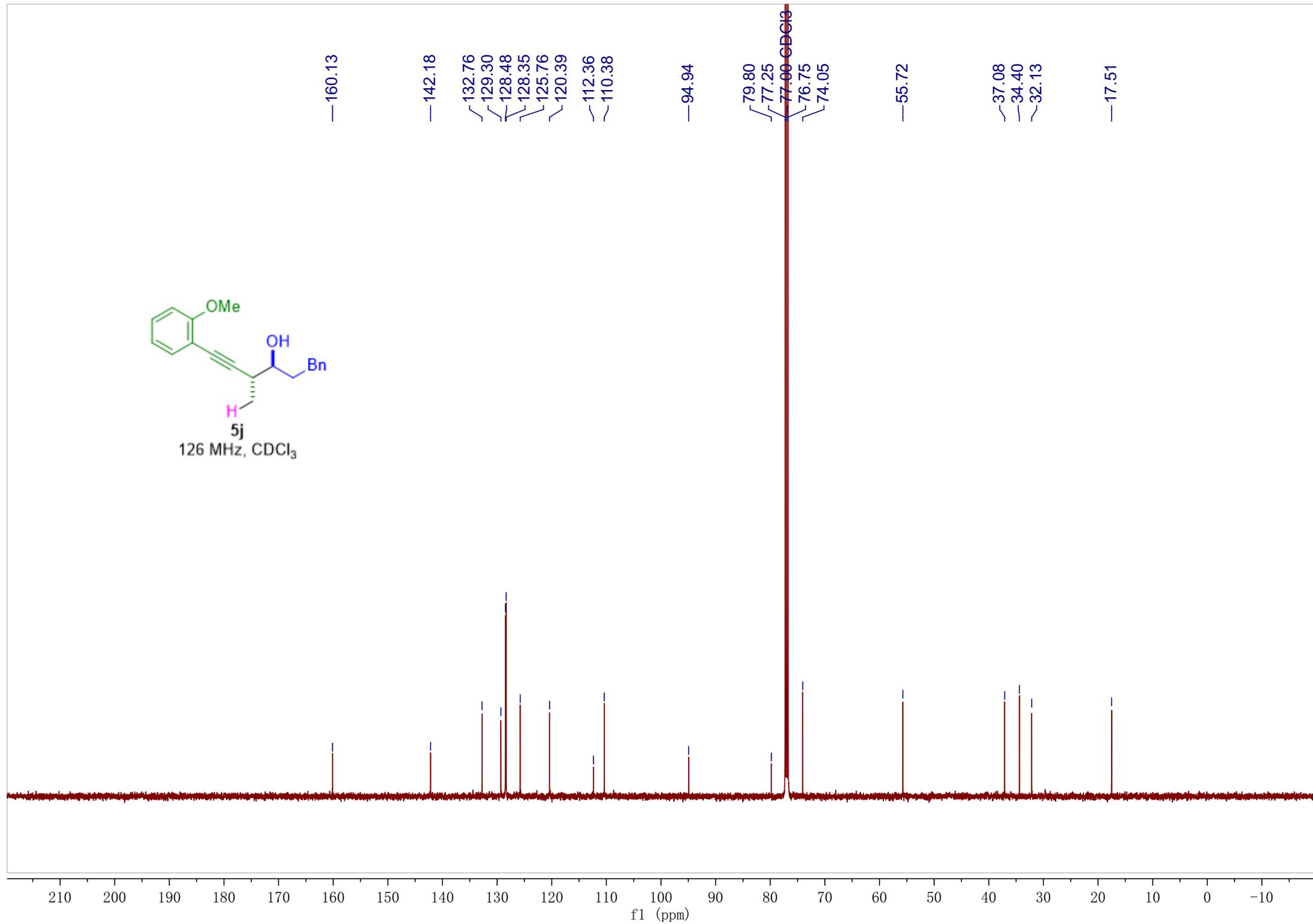
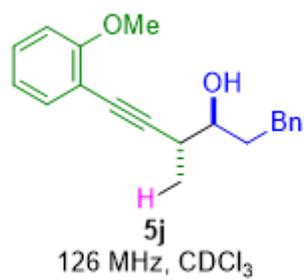
1.12
 1.14

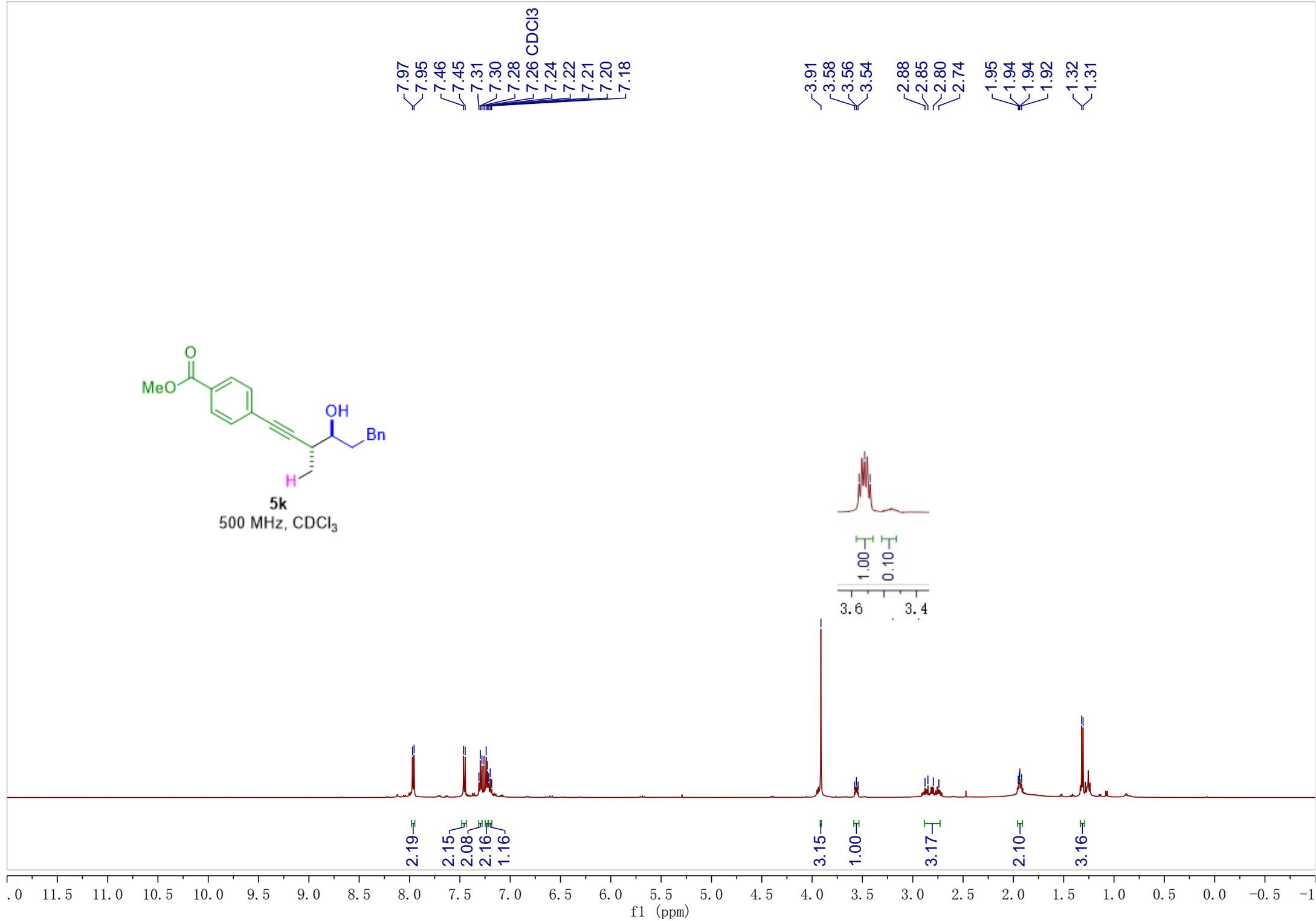
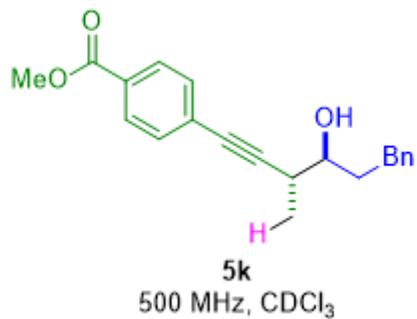
3.12
 9.19
 6.15

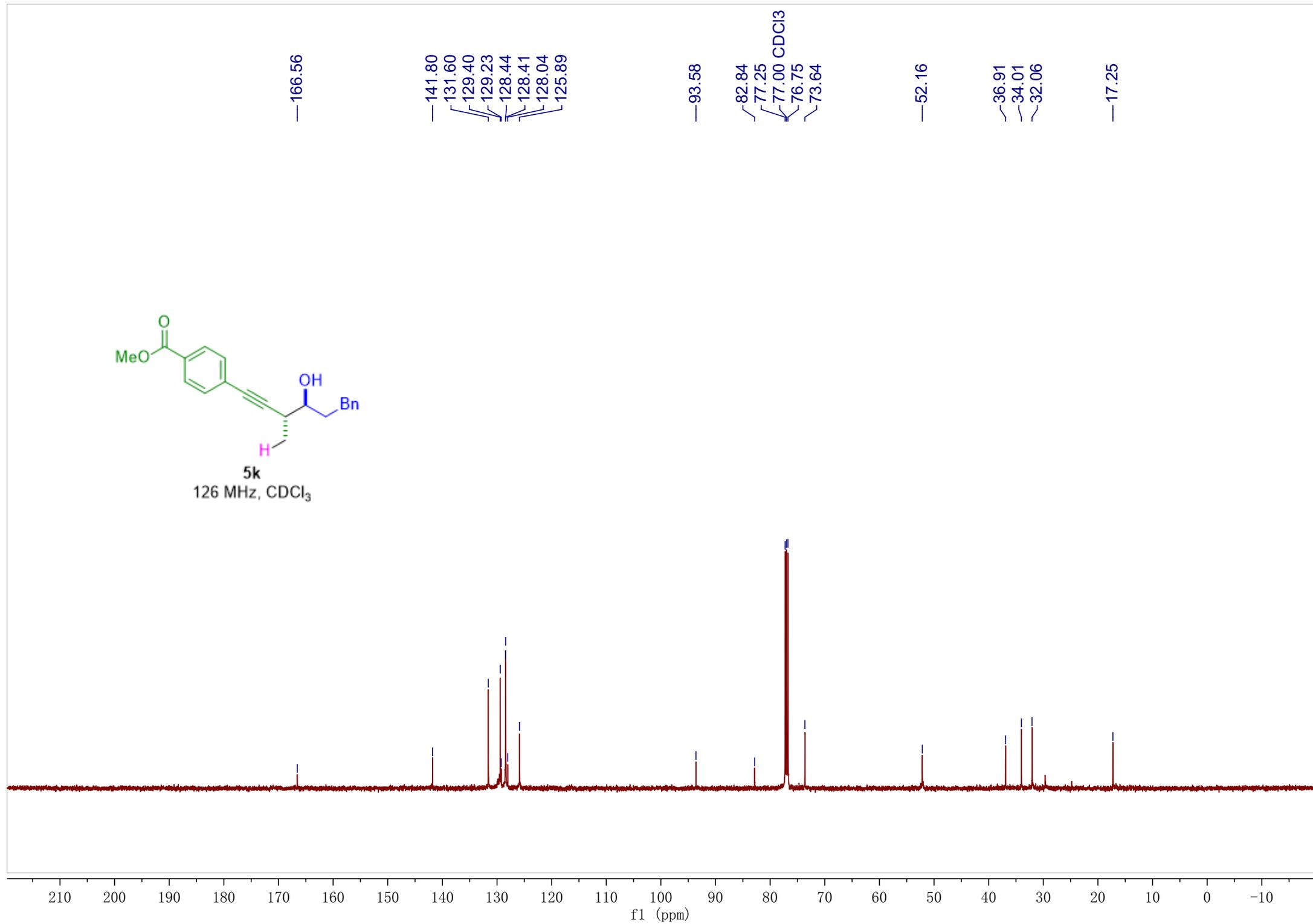
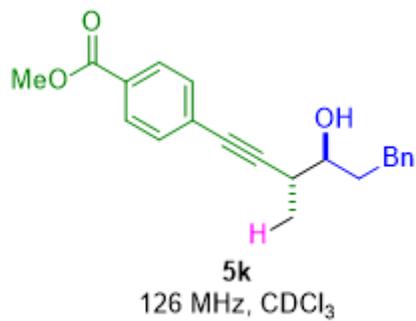


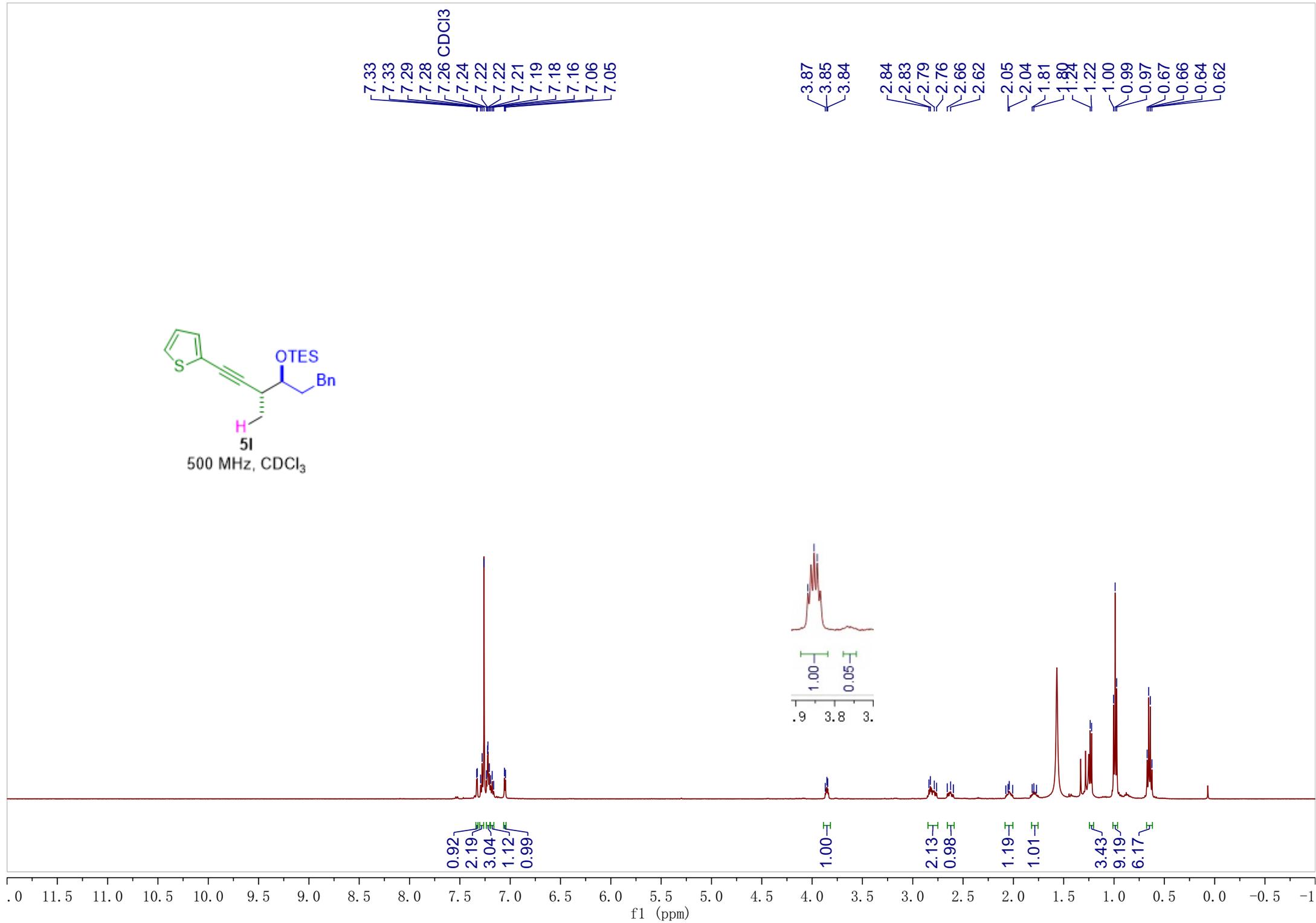
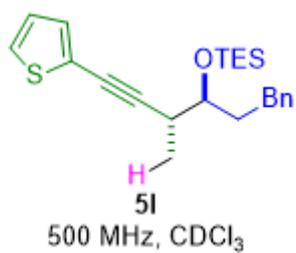


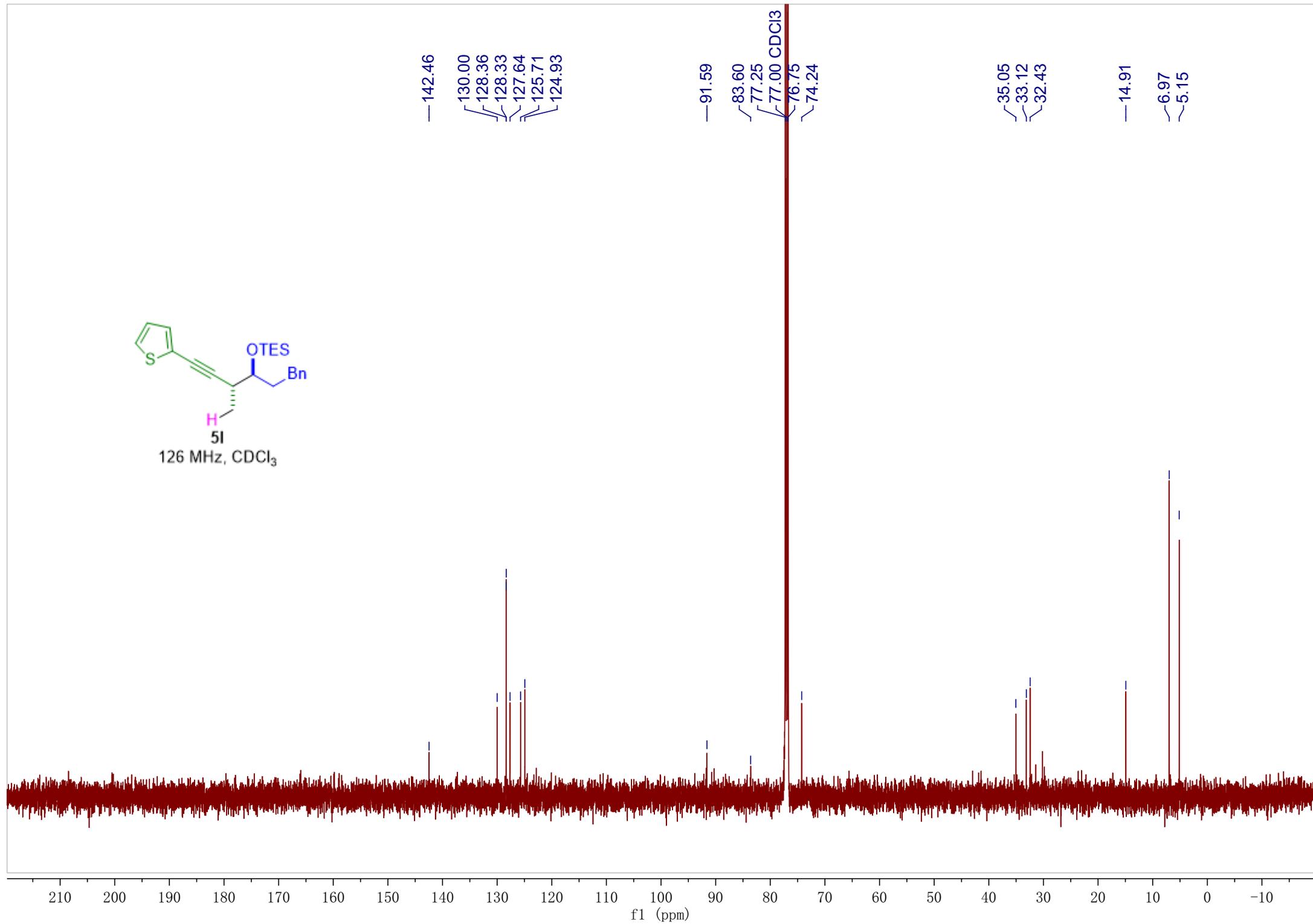
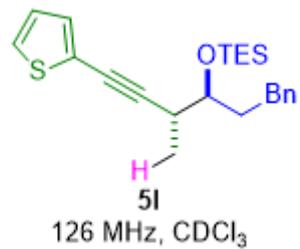


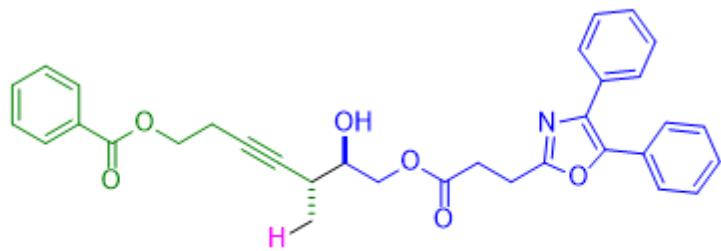




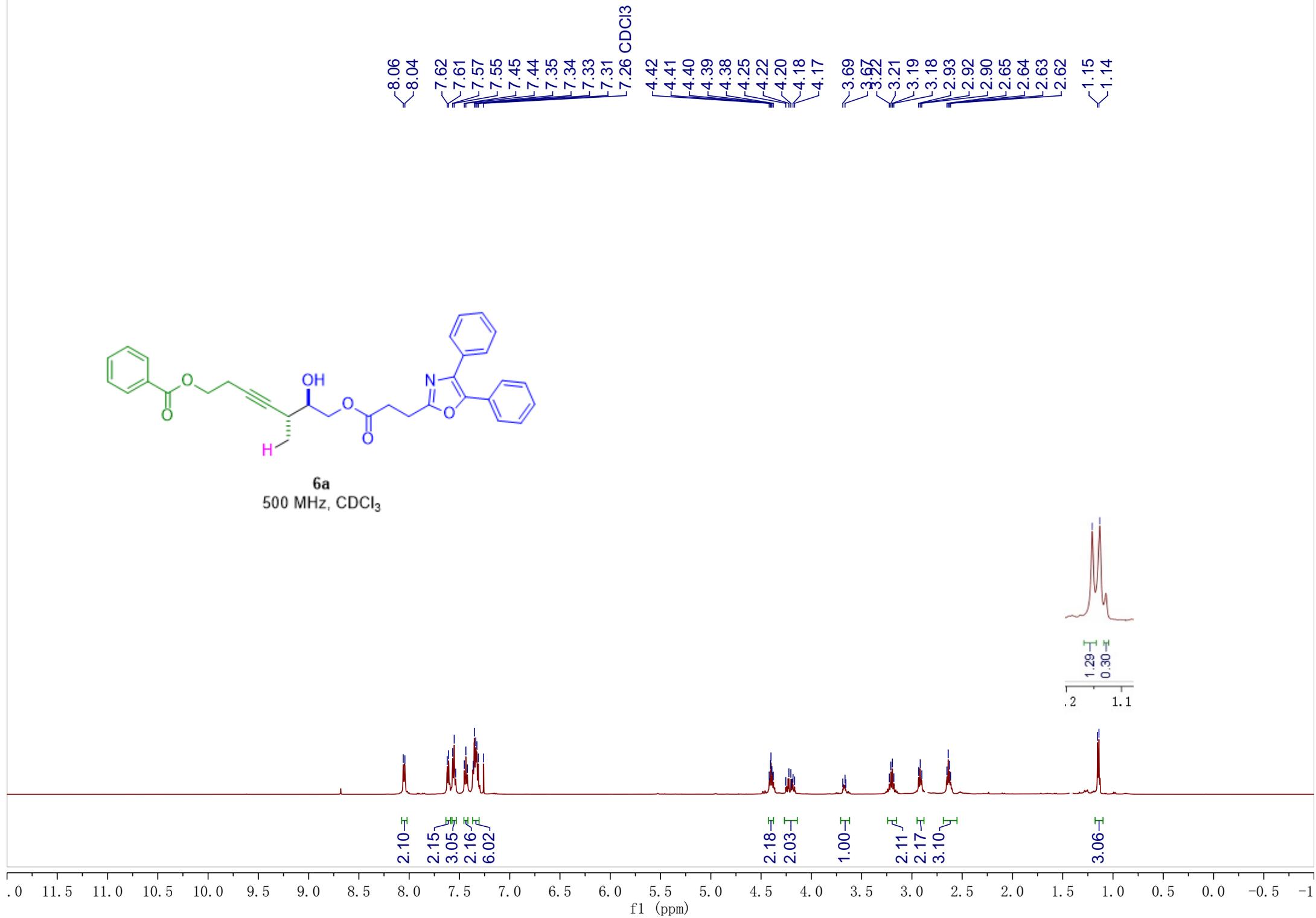


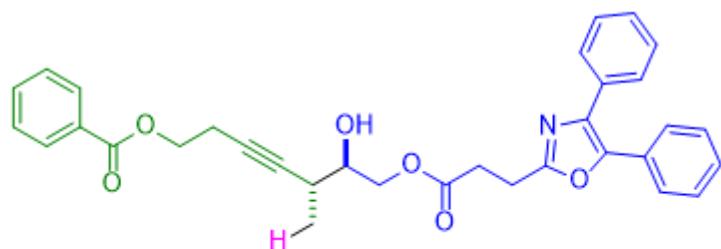






6a
500 MHz, CDCl₃





6a
126 MHz, CDCl₃

171.74
166.40
161.71

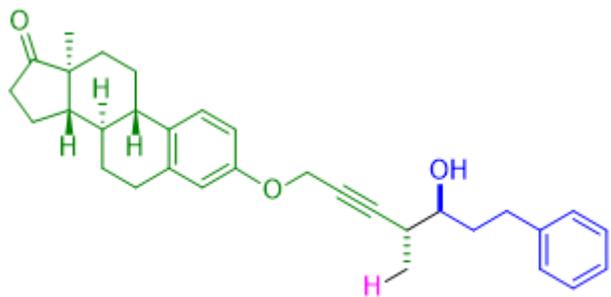
145.48
135.08
133.05
132.14
129.62
128.62
128.51
128.36
128.09
127.97
127.91
126.44

81.47
79.11
77.25
77.00 CDCl₃
76.75
71.70
66.97
62.92

31.32
29.71
23.57
19.49
17.30

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

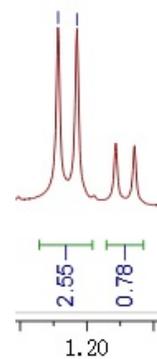


6b
500 MHz, CDCl₃

7.29
7.28
7.26
7.26
7.20
7.19
7.18
7.17
6.79
6.77
6.72

4.68
4.67
4.65

3.54
3.45
3.42
2.90
2.86
2.81
2.78
2.76
2.68
2.65
2.63
2.61
2.58
1.22
1.21
0.90



2.19
4.19

1.12
1.00

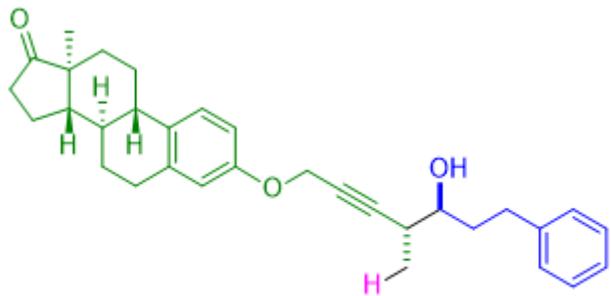
2.18

1.11

2.10
0.98
2.07
1.09
1.09
1.18
1.23
4.06
2.06
2.08
3.13
1.07
3.11
3.19

11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1

f1 (ppm)



6b
126 MHz, CDCl₃

—155.5

141.8

137.7

132.7

128.3

128.3

126.2

125.8

115.1

115.1

112.5

—88.3

78.1

77.3

77.0 CDCl₃

76.7

73.4

56.2

50.3

47.9

43.9

38.2

36.7

35.8

33.3

32.0

31.5

29.5

26.4

25.8

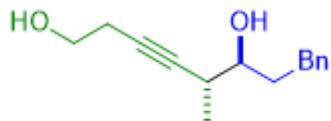
21.5

17.2

13.8

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)



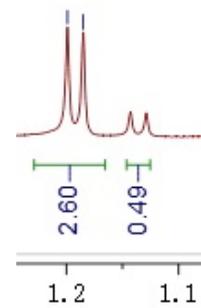
7a
500 MHz, CDCl₃

7.30
7.29
7.27
7.26 CDCl₃
7.22
7.21
7.19
7.18

3.70
3.69
3.68
3.43
3.42
3.41
3.40

2.85
2.82
2.71
2.69
1.86
1.85
1.83

1.20
1.18



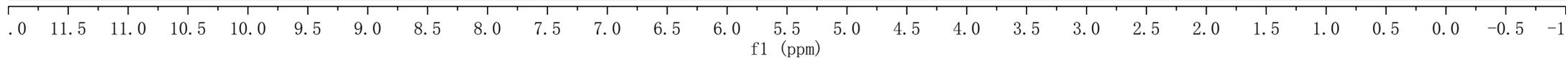
2.27
3.18

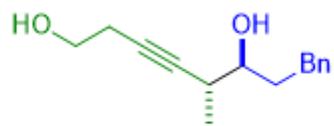
2.01
1.00

0.96
1.19
1.20
4.14

2.15

3.09





7a
126 MHz, CDCl₃

—141.9

128.4
128.3
125.8

82.8
79.9
77.3
77.0 CDCl₃
76.7
73.7

—61.1

36.9
33.2
32.0

—23.0

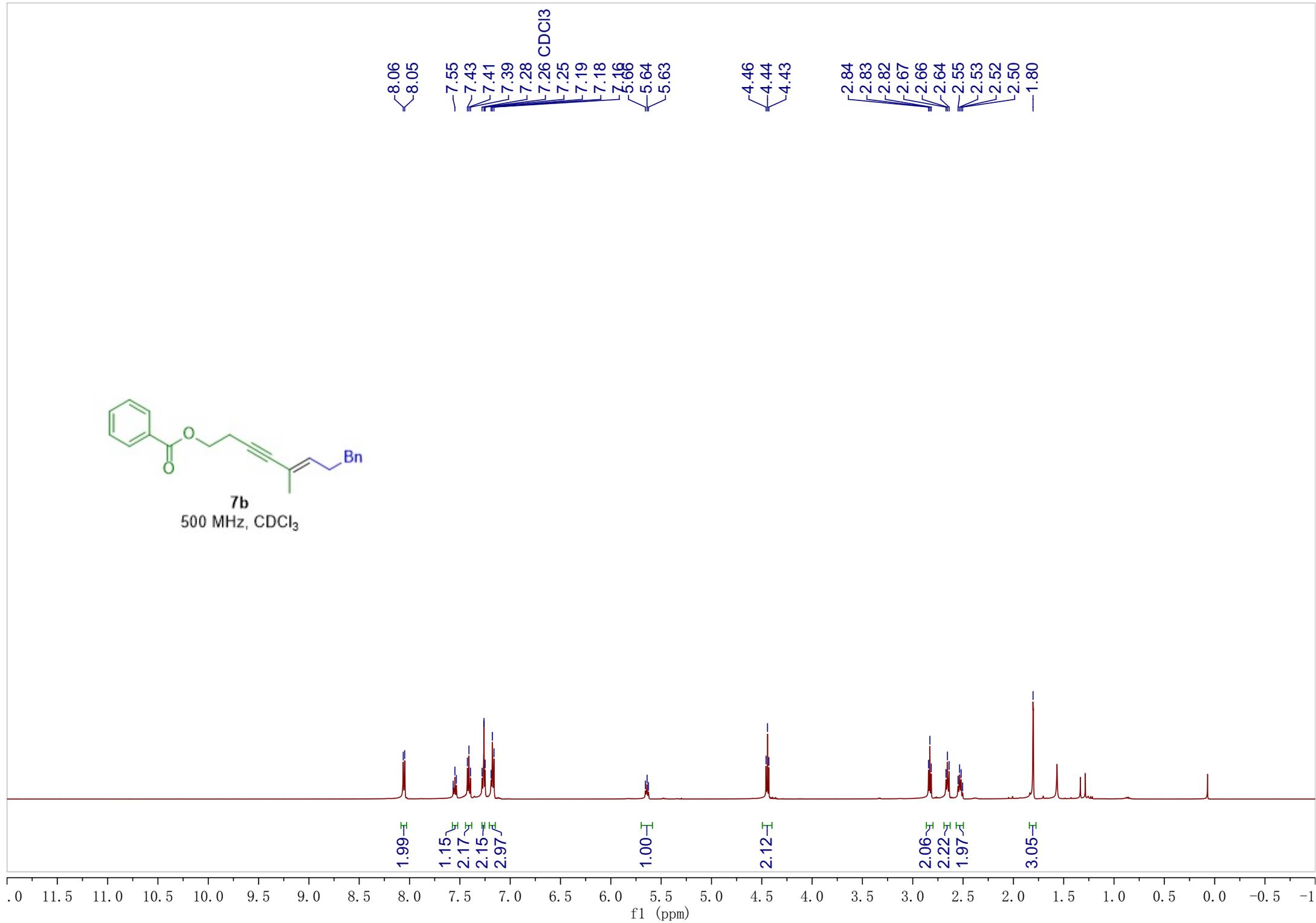
—17.9

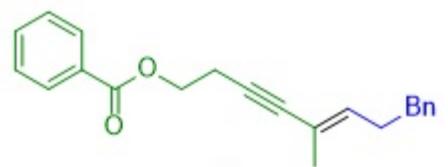
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)



7b
500 MHz, CDCl₃





7b
126 MHz, CDCl₃

166.3
141.8
136.3
133.0
130.0
129.6
128.4
128.3
128.3
125.8
118.4

89.0
81.3
77.3
77.0 CDCl₃
76.7

63.0

35.3
32.1
23.2
20.1

