Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information

for

Uranyl-catalysed C-H Alkynylation and Olefination

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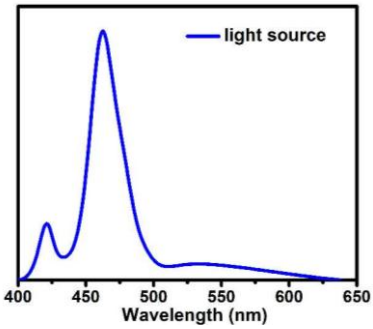
Supplementary Methods

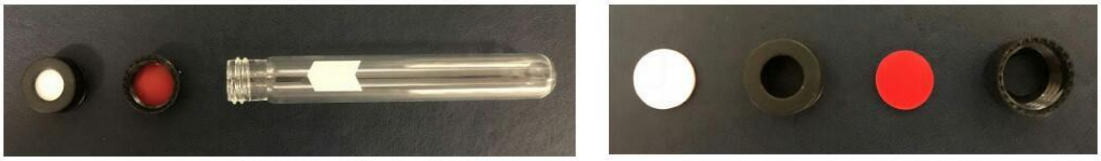
General Methods. All reactions were performed in flame-dried glassware with magnetic stirring bar and sealed with a rubber septum. The solvents were distilled by standard methods. Reagents were obtained from commercial suppliers and used without further purification unless otherwise noted. Silica gel column chromatography was carried out using silica Gel 60 (230–400 mesh). Analytical thin layer chromatography (TLC) was done using silica Gel (silica gel 60 F254). TLC was performed on pre-coated silica gel plated, using short-wave UV light as the visualizing agent, and phosphomolybdic acid, *p*-anisaldehyde, or $KMnO_4$ and heat as developing agents. NMR experiments were measured on a Bruker AVANCE III-400 or 500 spectrometer and carried out indeuterochloroform ($CDCl_3$) ^1H NMR and ^{13}C NMR spectra were recorded at 400 MHz or 500 MHz and 100 MHz or 125 MHz spectrometers respectively. 19F NMR spectra were recorded at 376 MHz or 470 MHz spectrometers. Chemical shifts are reported as δ valuesrelative to internal TMS (δ 0.00 for ^1H NMR), chloroform (δ 7.26 for ^1H NMR), chloroform (δ 77.00 for ^{13}C NMR). The following abbreviations are used for the multiplicities: s: singlet, d: doublet, dd:doublet of doublet, t: triplet, q: quadruplet, m: multiplet, br: broad signal for proton spectra; Coupling constants (J) are reported in Hertz (Hz). Melting points were uncorrected. HRMS were recorded on a Bruker microTOF-Q111. GC-MS spectra were performed on Shimadzu QP2010 (EI Source). A borosilicate glass tube was used as a reaction tube. The reaction mixture was irradiated with two Kessil LEDs (Saltwater Aquarium Light A360WE Series Tuna Blue; Rating: 19VDC 90W Max http://www.kessil.com/products/saltwater_A360.php) from 10 cm away. The emission spectrum of the lamp is shown below:



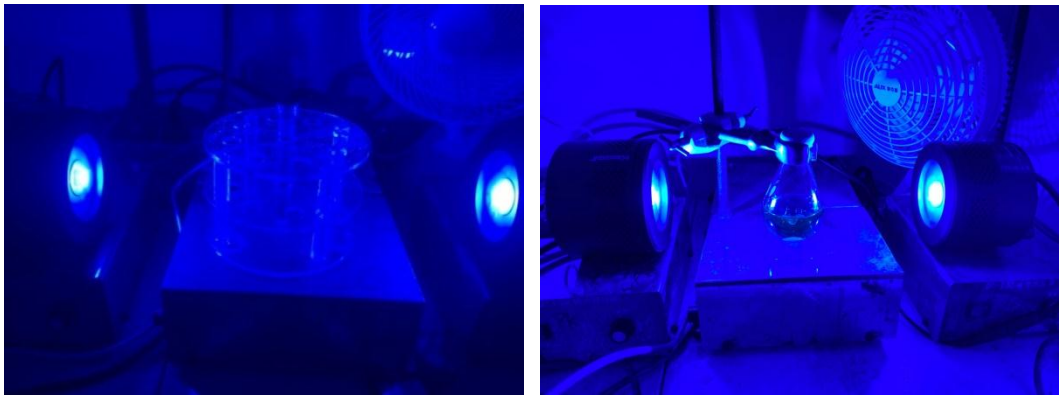
Supplementary Figure 1. Emission spectrum of the lamp

We have not used any filters. Unless otherwise noted, all reagents were weighed and handled in air, and all reactions were underargon.

Medium-sized screw-cap test tubes (8 mL) were used for all 0.20 mmol scale reactions: Fisher 13 x 100 mm tubes (Cat. No.1495935C), Cap with Septa: Thermo Scientific ASM PHN CAP w/PTFE/SIL (Cat. No.03378316)



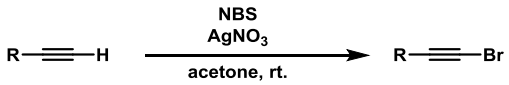
Reactor setup:



(left) 0.20 mmol scale reactions (right) gram scale reactions

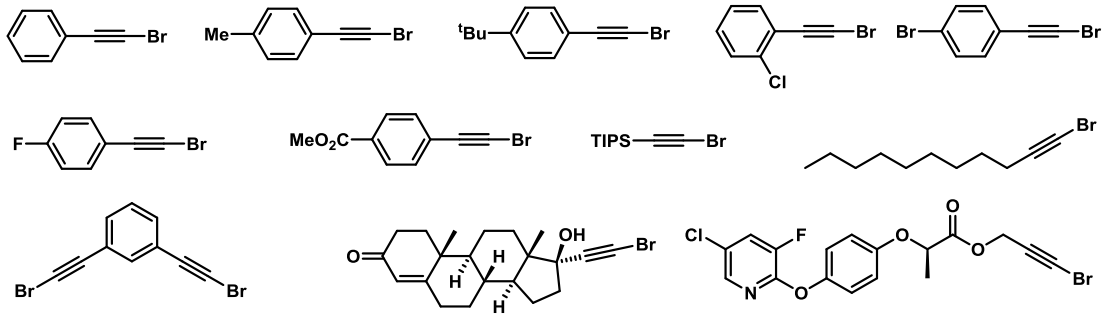
Synthesis of Starting Materials.

Synthesis of Alkynyl Bromides (Procedure A)



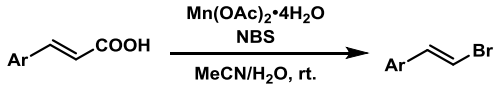
Alkynyl bromides were prepared according to a previously reported procedure[1]. Terminal alkynes (5.00 mmol, 1.00 equiv) was dissolved in acetone (30 mL). N-bromosuccinimide (5.80 mmol, 1.16 equiv) was added, followed by silver nitrate (0.50 mmol, 0.1 equiv). The resulting mixture was stirred at room temperature for 3 h and it was then poured onto ice. After ice being allowed to melt, the aqueous layer was extracted with pentane (3 x 30 mL, ethyl acetate instead of pentane if precipitate). The combined organic layers were dried over $MgSO_4$, filtered and concentrated in vacuo to afford bromoalkynes. If necessary, the product could be purified by column chromatography or recrystallization.

The bromoalkynes shown below were prepared according to **Procedure A**.



Synthesis of Alkenyl Bromides

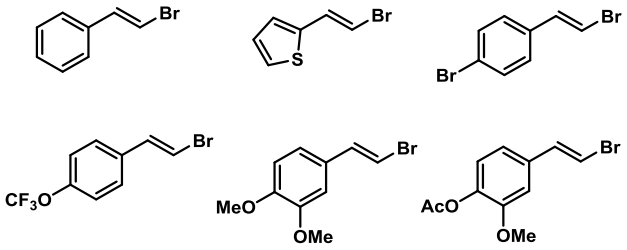
Method A (Procedure B)



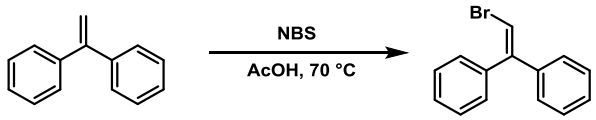
Alkenyl bromides were prepared according to a previously reported procedure[2]. A round-bottomed flask was charged with cinnamic acid (1.00 mmol, 1.00 equiv), N-bromosuccinimide (1.05 mmol, 1.05 equiv), Manganese(II) acetate tetrahydrate (0.20 mmol, 0.20 equiv), 2 mL of water and 2 mL of acetonitrile. The reaction mixture was stirred at room temperature and monitored by TLC analysis. After total conversion of substrates, acetonitrile was evaporated. The mixture was extracted by

diethyl ether (2 mL x 3). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by column chromatography to give the product.

The bromoalkynes shown below were prepared according to **Procedure B**.



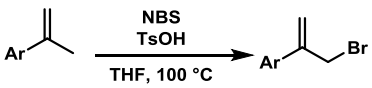
Method B (Procedure C)



(2-bromoethene-1,1-diyl)dibenzene was prepared according to a previously reported procedure[3]. To a suspension of 1, 1-diphenylethene (2.00 mmol, 1.00 equiv) in AcOH (2 mL) was added N-bromosuccinimide (2.00 mmol, 1.00 equiv). The resulting mixture was stirred at 70 ℃ for 4 h. After cooling down to room temperature naturally, the reaction was neutralized by slowly adding NaOH/$NaHCO_3$ (1:1) and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (petroleum ether / ethyl acetate 100:1) to afford 2,2-diarylvinyl bromides. (97%, 0.52 g).

Synthesis of Allyl Bromides

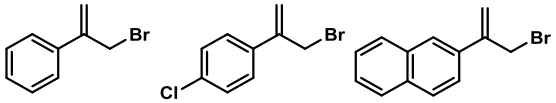
Method A (Procedure D)



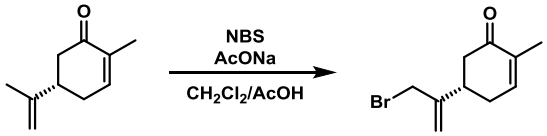
Allyl bromides were prepared according to a previously reported procedure[4]. In an oven dried flask 1-methylethylenebenzene (5.00 mmol, 1.00 equiv.) was taken and to this dry tetrahydrofuran (15 mL) was added. To the resulting solution N-bromosuccinimide (5.25 mmol, 1.05 equiv.) and *p*-toluenesulfonic acid (0.50 mmol, 0.10 equiv.) was added and the solution was refluxed at 100 ℃ for 4 h. Reaction

mixture was cooled to rt and the reaction mixture was taken in petroleum ether (15 mL/mmol), washed with water (15 mL x 3). Organic phase was dried over Na_2SO_4, concentrated under reduced pressure to obtain a yellow oil. Purification by column chromatography using petroleum ether as eluent afforded the product.

The allyl bromides shown below were prepared according to **Procedure D**.



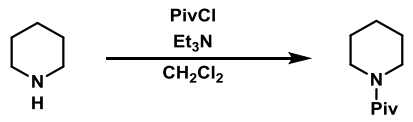
Method B (Procedure E)



Bromo carvone was prepared according to a previously reported procedure[5]. A solution of (S)-carvone (30.0 mmol, 1.00 equiv.) and sodium acetate (22.0 mmol, 0.73 equiv.) in 45 mL of a mixture of CH_2Cl_2 and acetic acid (40 mL, 3 : 2) was cooled in an ice bath. To the magnetically stirring solution was added N-bromosuccinimide (36.0 mmol, 1.20 equiv.) in small portions over a period of 90 min. The reaction mixture was stirred at room temperature for 5 h, diluted with 50 mL of CH_2Cl_2, washed successively with water (3 x 30 mL), aqueous $NaHCO_3$ (3 x 30 mL), and brine, and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel with 1:3 ethyl acetate-hexane as eluent furnished allyl bromide (1.25 g, 40%) as an oil.

Synthesis of Amide

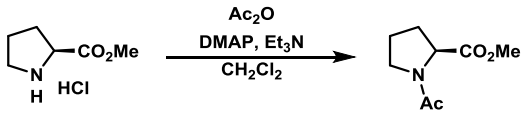
Synthesis of 2,2-dimethyl-1-(piperidin-1-yl)propan-1-one (Procedure F)



2,2-dimethyl-1-(piperidin-1-yl)propan-1-one was prepared according to a previously reported procedure[6]. To a 100 ml flask charged with a magnetic stirring bar and piperidine (0.92 mL, 1.0 equiv., 10 mmol) was added. Dichloromethane (50 ml, 0.2 M) was added and the mixture was cooled to 0 ℃ with an ice bath. Triethylamine (2.80

ml, 2.0 equiv., 20 mmol) was added in one portion. Pivaloyl chloride (1.35 ml, 1.1 equiv., 11 mmol) was then added dropwise and the reaction was stirred for 2 h before quenching with sat. $NaHCO_3$. The organic layer was separated, washed with brine, dried over anhydrous magnesium sulfate, and filtered to a yellowish oil (1.6 g, 95%), which was used without further purification.

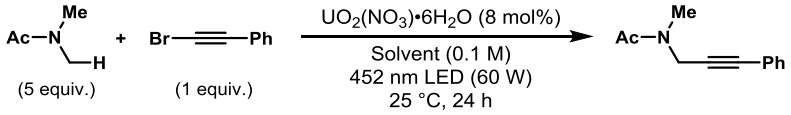
Synthesis of Methyl acetyl-L-prolinate (Procedure G)



Methyl acetyl-*L*-prolinate was prepared according to a previously reported procedure[7]. Into a flask were added methyl *L*-prolinate hydrochloride (490 mg, 2.96 mmol, 1.0 equiv), dichloromethane (30 mL, 0.1 M), and 4-(dimethylamino)pyridine (90 mg, 0.74 mmol, 0.25 equiv). The flask was capped with a rubber septum and maintained under a nitrogen atmosphere. To the flask were added triethylamine (1.64 mL, 11.86 mmol, 4.0 equiv) and acetic anhydride (0.56 mL, 5.92 mmol, 2.0 equiv). The mixture was stirred (2.5 h), diluted with dichloromethane (80 mL), washed with sodium carbonate (10% aqueous, 80 mL) and citric acid (10% aqueous, 80 mL), and dried with sodium sulfate. Volatiles were removed under reduced pressure, and the crude material was purified by column chromatography (silica gel, EtOAc) to yield acetamide (313 mg, 62%).

Optimization Tables

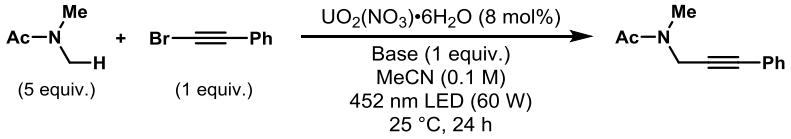
Supplementary Table 1. Optimization of Solvent



Entry	Solvent	Yield[a] (%)
1	acetonitrile	23
2	acetone	26
3	benzene	28
4	methanol	0
5	dimethyl sulfoxide	0

[a] Yields were determined by GC-FID using cyclododecane as internal standard.

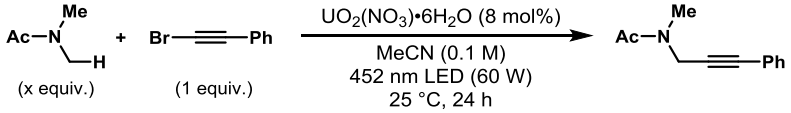
Supplementary Table 2. Optimization of Base



Entry	Base	Yield[a] (%)
1	K_2CO_3	8
2	K_3PO_4	0
3	Et_3N	0
4	LiOH $\cdot H_2O$	0

[a] Yields were determined by GC-FID using cyclododecane as internal standard.

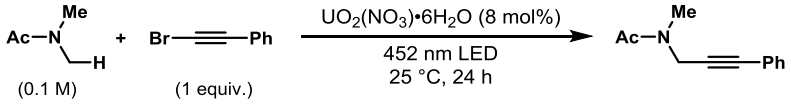
Supplementary Table 3. Optimization of Material Ratio



Entry	Material Ratio	Yield(%)
1	x = 5	23
2	x = 10	31
3	x = 20	49
4	DMAc as solvent	73

[a] Yields were determined by GC-FID using cyclododecane as internal standard.

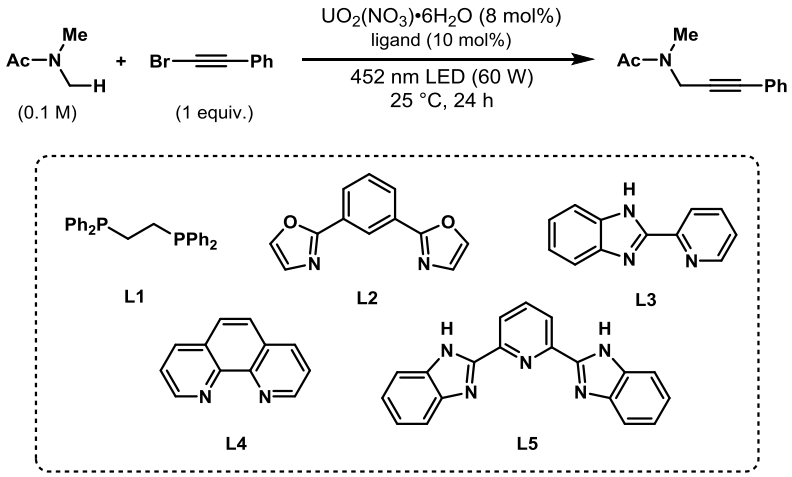
Supplementary Table 4. Optimization of Light Sources



Entry	Light sources	Yield(%)
1	30 W blue LEDs	59
2	90 W blue LEDs	72
3	in darkness	0

[a] Yields were determined by GC-FID using cyclododecane as internal standard.

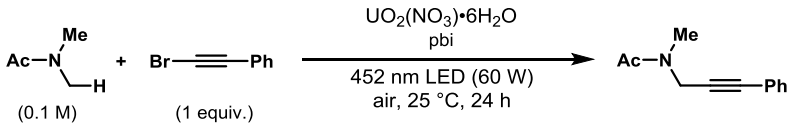
Supplementary Table 5. Optimization of Ligands



Entry	Ligands	Yield(%)
1	**L1**	7
2	**L2**	74
3	**L3**	98
4	**L4**	81
5	**L5**	86

[a] Yields were determined by GC-FID using cyclododecane as internal standard.

Supplementary Table 5. Optimization of Catalylst Quantity

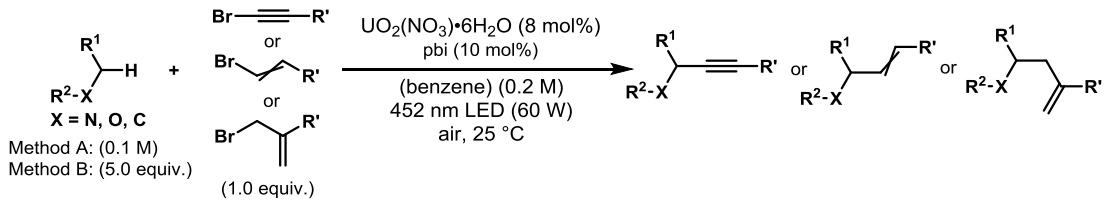


Entry	Catalylst Quantity	Yield(%)
1	[UO_2] (8 mol%) & pbi (10 mol%)	98
2	[UO_2] (4 mol%) & pbi (5 mol%)	51

[a] Yields were determined by GC-FID using cyclododecane as internal standard.

General Procedure

Procedure for C-H Alkynylation, Alkenylation and Allylation



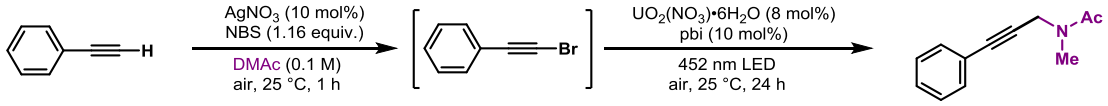
Method A (Procedure H)

Uranyl nitrate hexahydrate (8.0 mg, 8 mol%), 2-(2-pyridyl)benzimidazole (pbi) (3.9 mg, 10 mol%) and the bromide (if solid, 0.2 mmol, 1.0 equiv.) were added into a screw-cap test tube with stirring bar. The alkyl source (2 mL, 0.1 M) was injected into the tube, followed with the bromide (if liquid, 0.2 mmol, 1.0 equiv.). Afterwards, the tube was set between two lamps (10 cm away from the lamp, 60 W each) and stirred at room temperature (with a fan to cool down the reaction) for 24 h. The mixture was diluted with ethyl acetate and washed with saturated $NaHCO_3$ (10 mL), water (10 mL x 3) and brine (10 mL). The organic layer was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude material was purified by column chromatography to afford the corresponding product.

Method B (Procedure I)

Uranyl nitrate hexahydrate (8.0 mg, 8 mol%) and 2-(2-pyridyl)benzimidazole (3.9 mg, 10 mol%) were added into a screw-cap test tube with stirring bar. The bromide (0.2 mmol, 1.0 equiv.) and the alkyl source (1 mmol, 5.0 equiv.) were dissolved in benzene (1 mL, 0.2 M) and the solution was injected into the tube. Afterwards, the tube was set between two lamps (10 cm away from the lamp, 60 W each) and stirred at room temperature (with a fan to cool down the reaction) for 24-96 h. The mixture was diluted with ethyl acetate and washed with saturated $NaHCO_3$ (10 mL), water (10 mL x 3) and brine (10 mL). The organic layer was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude material was purified by column chromatography to afford the corresponding product.

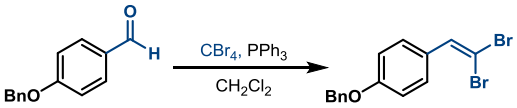
Procedure for One-pot Alkynylation with Terminal Alkynes (Procedure J)



In a screw-cap test tube, silver nitrate (3.4 mg, 10 mol%), N-bromosuccinimide (41.3 mg, 1.16 equiv.) and phenylacetylene (22 μL, 1.0 equiv.) were dissolved in N,N-dimethylacetamide (2 mL, 0.1 M). The mixture was stirred for 1 h and then uranyl nitrate hexahydrate (8.0 mg, 8 mol%) and 2-(2-pyridyl)benzimidazole (3.9 mg, 10 mol%) were added. Afterwards, the tube was set between two lamps (10 cm away from the lamp, 60 W each) and stirred at room temperature (with a fan to cool down the reaction) for 24 h. The mixture was diluted with ethyl acetate and washed with saturated $NaHCO_3$ (10 mL), water (10 mL x 3) and brine (10 mL). The organic layer was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude material was purified by column chromatography (silica, 50% ethyl acetate / petroleum ether) to afford the propargyl amide (colorless oil, 25.1 mg, 67%).

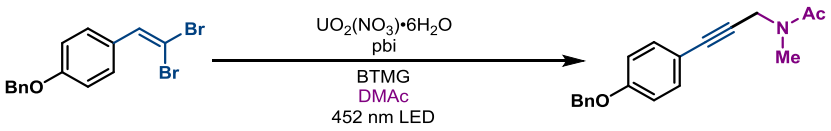
Procedure for Alkynylation with Aldehyde (Dibromoethene)

Synthesis of dibromoethene (Procedure K)



Dibromoethene was prepared according to a previously reported procedure[8]. Carbon tetrabromide (1.33 g, 4.0 mmol), 4-benzyloxybenzaldehyde (424 mg, 2.0 mmol) and triphenylphosphine (2.10 g, 8.0 mmol) was stirred at 0 ℃ in dichloromethane (6 mL). The ice bath was removed, and the reaction mixture was stirred at room temperature overnight. The reaction mixture was quenched with pentane (30 mL) and filtered through a silica plug (Et_2O). The solvent was removed under reduced pressure and the corresponding dibromoethene was isolated by flash column chromatography (5% ethyl acetate / petroleum ether) as a white solid (0.67 g, 91%).

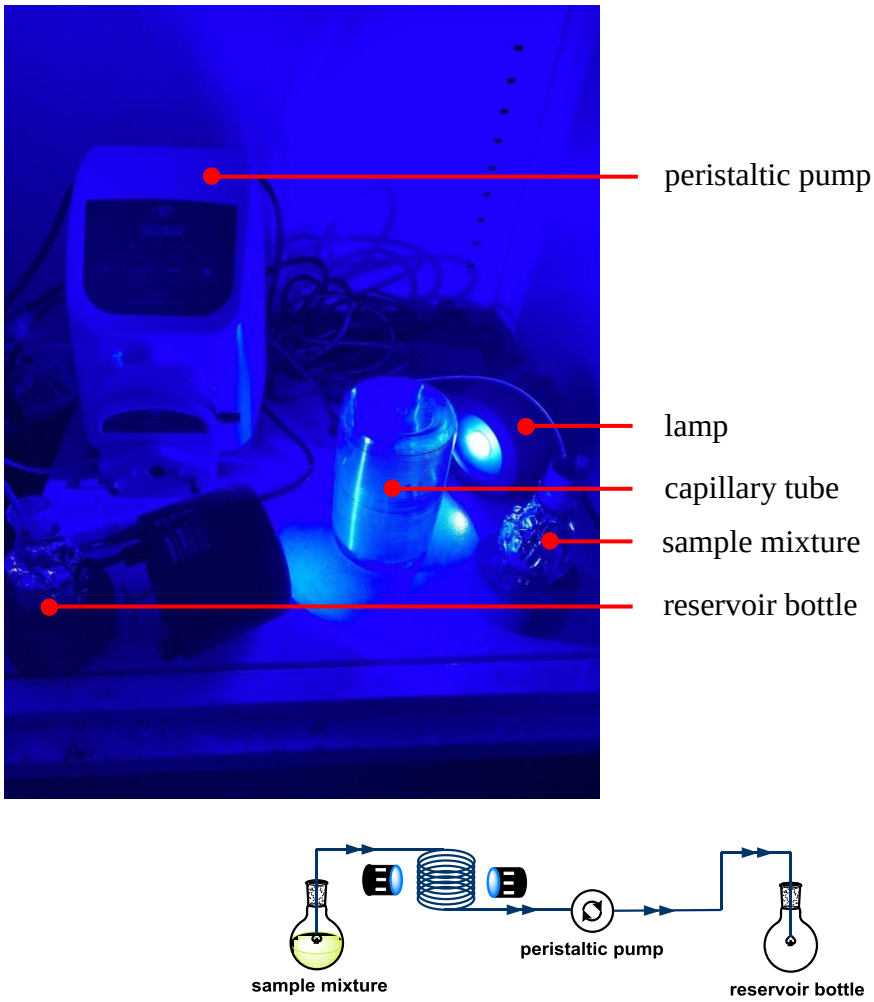
Alkynylation with dibromoethene (Procedure L)



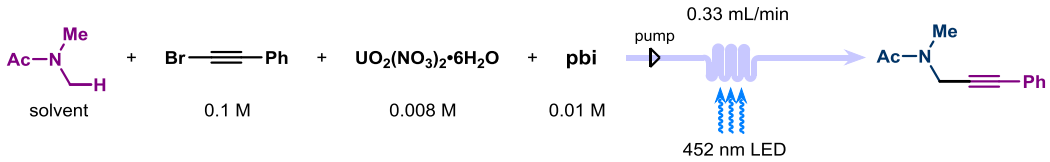
Uranyl nitrate hexahydrate (8.0 mg, 8 mol%), 2-(2-pyridyl)benzimidazole (pbi) (3.9 mg, 10 mol%) and the dibromoethene (58.7 mg, 0.2 mmol, 1.0 equiv.) were added into a screw-cap test tube with a stirring bar. 2-(tert-butyl)-1,1,3,3-tetramethylguanidine (40 μL, 1.0 equiv.) were dissolved in N,N-dimethylacetamide (2 mL, 0.1 M) and the solution was injected into the tube. Afterwards, the tube was set between two lamps (10 cm away from the lamp, 60 W each) and stirred at room temperature (with a fan to cool down the reaction) for 24 h. The mixture was diluted with ethyl acetate and washed with water (10 mL x 3) and brine (10 mL). The organic layer was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude material was purified by column chromatography to afford the corresponding propargyl amide.

Flowing Reaction

Flowing reaction is carried out with a homemade setup consisting of peristaltic pump (CM1000; purchased from Baoding Chuang Rui Precision Pump Co., Ltd), annular capillary tube (PTEF, ID 0.8 mm, ED 1.6 mm, length 40 m, volume 20 mL) and two Kessil LEDs (Saltwater Aquarium Light A360WE Series Tuna Blue; Rating: 19VDC 90W Max).

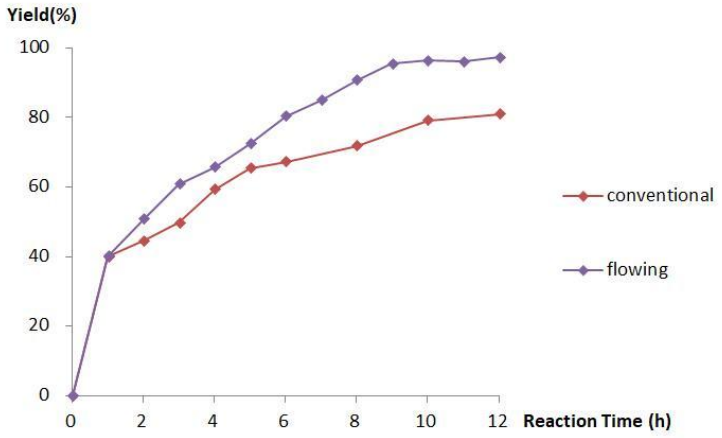


Supplementary Figure 2. Setting method of reactor



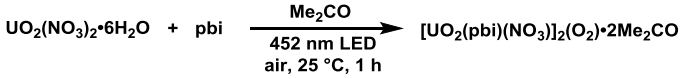
We selected (bromoethynyl)benzene to react in continuous flow in 2.0 mmol scale. Uranyl nitrate hexahydrate (80.3 mg, 8 mol%), 2-(2-pyridyl)benzimidazole (pbi) (39.0 mg, 10 mol%), (bromoethynyl)benzene (362 mg, 2.0 mmol, 1.0 equiv.) and

cyclododecane (84.2 mg, 0.25 equiv., internal standard) were dissolved in N,N-dimethylacetamide (20 mL). The yellow mixture was then transferred into a sample bottle (wrapped in aluminum foil). Next, the reaction mixture was flowing under the irradiation of two 60 W blue LEDs (distance app. 10.0 cm) in the mode of extraction at the speed of 0.33 mL/min. After 1 h, the sample would be completely transferred to the reservoir bottle (wrapped in aluminum foil). The position of two bottles could be exchanged so the reaction time could be extended. The products and the crude yields were monitored by GC-FID and GC-MS. The comparison of reaction rate with conventional reaction was shown below.



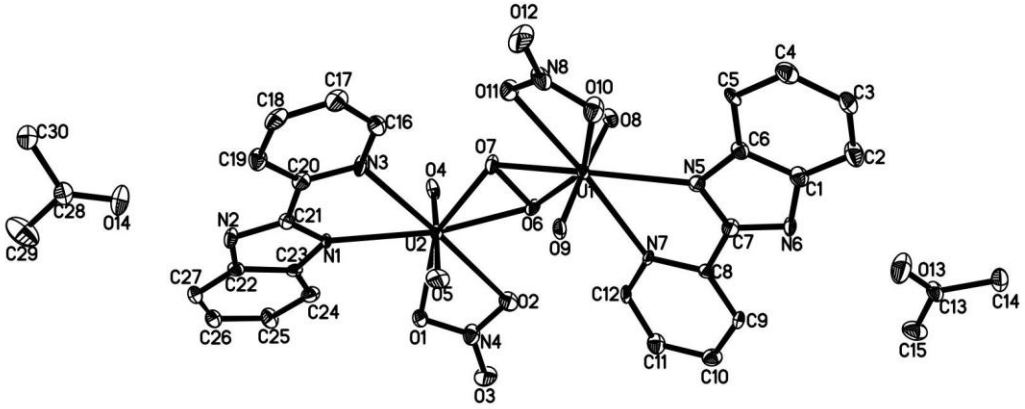
Supplementary Figure 3. Comparison between conventional and flowing reactor

Synthesis of the Uranyl Nitrate Peroxide Complex



Uranyl nitrate hexahydrate (25.1 mg, 0.05 mmol, 1.0 equiv.) and 2-(2-pyridyl)benzimidazole (pbi) (9.8 mg, 1.0 equiv.) were dissolved in acetone (2 mL, 0.1 M) in a screw-cap test tube with a stirring bar. The tube was set between two lamps (10 cm away from the lamp, 60 W each) and stirred under ambient conditions. The tube was pierced by a syringe needle and the solvent volatilized slowly for 1-2 weeks. The orange supernatant was decanted and the yellow crystals were harvested and dried under vacuum. Single crystals for structure determination were isolated manually from the initial crude precipitate. (10.5 mg, 35% based on U).

X-ray crystallography data for Uranyl Nitrate Peroxide



Supplementary Figure 4. X-ray structure of uranyl nitrate peroxide

Supplementary Table 6 Crystal data and structure refinement

Identification code	**Compound 52**
Empirical formula	$C_{30}H_{30}N_8O_{14}U_2$
Formula weight	1202.68
Temperature/K	193
Crystal system	orthorhombic
Space group	$Pca2_1$

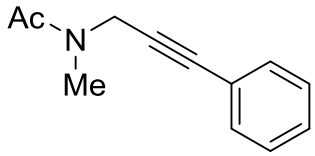
a/Å	14.6321(10)
b/Å	15.2595(7)
c/Å	16.1553(9)
α/	90
β/	90
γ/	90
Volume/$Å^3$	3607.1(4)
Z	4
$\rho_{calc}g/cm^3$	2.215
μ/mm^{-1}	9.046
F(000)	2248.0
Crystal size/mm^3	0.15 × 0.12 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/	4.608 to 58.134
Index ranges	$-18 \leq h \leq 17$, $-15 \leq k \leq 20$, $-19 \leq l \leq 19$
Reflections collected	22885
Independent reflections	8231 [R_{int}= 0.0743, R_{sigma}= 0.0846]
Data/restraints/parameters	8231/253/491
Goodness-of-fit on F^2	1.007
Final R indexes [I>=2σ (I)]	R_1= 0.0572, wR_2= 0.1347
Final R indexes [all data]	R_1= 0.0721, wR_2= 0.1456
Largest diff. peak/hole / e $Å^{-3}$	5.90/-3.33
Flack parameter	0.038(10)

Characterization Data for Products

General Information

NMR experiments were measured at room temperature. All the asymmetric tertiary amide derivatives are mixtures of two conformational products, giving a splitting of the signal in both ^{1}H NMR and ^{13}C NMR spectra.

Compound 3



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 1:1) afforded 36.0 mg (96%).

Physical State: colorless oil.

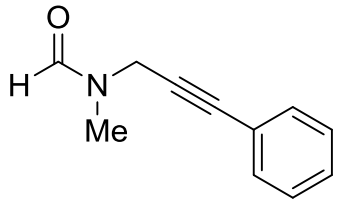
R_f= 0.40 (petroleum ether/ethyl acetate = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.36 (m, 2H), 7.36 – 7.24 (m, 3H), 4.44/4.24 (s, 2H), 3.11/3.03 (s, 3H), 2.20/2.11 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.6, 170.4, 131.8, 131.8, 128.7, 128.4, 128.4, 128.3, 122.8, 122.3, 84.6, 84.3, 83.7, 83.2, 41.2, 36.8, 35.2, 33.4, 21.8, 21.6 ppm.

This compound was previously reported[9].

Compound 4



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 2:1) afforded 19.1 mg (52%).

Physical State: colorless oil.

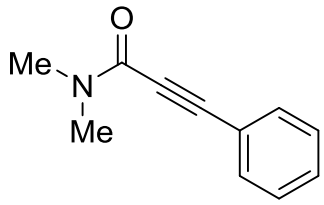
R_f= 0.26 (petroleum ether/ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 – 8.02 (m, 1H), 7.50 – 7.37 (m, 3H), 7.41 – 7.25 (m, 2H), 4.50 – 4.17 (m, 2H), 3.18 – 2.97 (m, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$):δ 162.4, 162.2, 131.9, 131.8, 128.9, 128.6, 128.5, 128.4, 122.5, 122.1, 85.5, 84.2, 82.9, 82.6, 40.1, 34.0, 34.0, 29.6 ppm.

This compound was previously reported[11].

Compound 5



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 2:1) afforded 10.5 mg (29%).

Physical State: colorless oil.

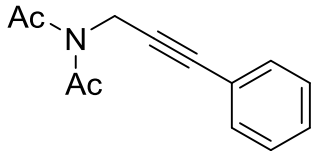
***R*$_f$**= 0.34 (petroleum ether/ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 – 7.52 (m, 2H), 7.43 – 7.33 (m, 3H), 3.29 (s, 3H), 3.03 (s, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 149.2, 132.3, 130.0, 128.5, 121.6, 90.2, 81.6, 38.4, 34.2. ppm.

This compound was previously reported[11].

Compound 6



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 1:1) afforded 21.1 mg (49%).

Physical State: colorless oil.

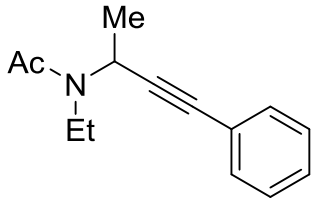
***R*$_f$**= 0.35 (petroleum ether/ethyl acetate = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 – 7.39 (m, 2H), 7.34 – 7.27 (m, 3H), 4.72 (s, 2H), 2.54 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.5, 131.8, 128.7, 128.3, 122.1, 83.8, 83.5, 34.6, 26.4 ppm.

HRMS (ESI-TOF): calculated for $C_{13}H_{13}NO_2$ $[M+Na]^+$: 238.0839, found: 238.0840.

Compound 7



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 1:1) afforded 34.9 mg (81%).

Physical State: colorless oil.

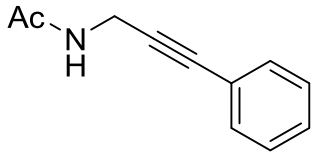
***R*$_f$**= 0.44 (petroleum ether/ethyl acetate = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.37 (m, 2H), 7.37 – 7.28 (m, 3H), 5.74/4.84 (q, *J* = 6.9 Hz, 1H), 3.69 – 3.34 (m, 2H), 2.18/2.14 (s, 3H), 1.55/1.43 (d, *J* = 7.0 Hz, 3H), 1.35/1.26 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 169.9, 169.5, 131.7, 131.7, 128.7, 128.5, 128.4, 128.4, 123.0, 122.5, 89.0, 83.7, 46.6, 42.0, 39.9, 38.1, 29.8, 21.9, 21.8, 21.1, 16.3, 14.7 ppm.

HRMS (ESI-TOF): calculated for $C_{14}H_{17}NO$ $[M+Na]^+$: 238.1203, found: 238.1201.

Compound 8



Following **Procedure I** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 1:1) afforded 14.6 mg (42%).

Physical State: colorless oil.

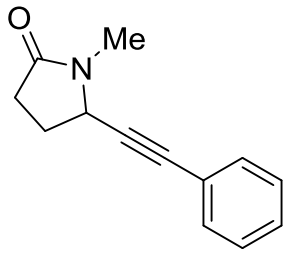
***R*$_f$**= 0.45 (petroleum ether/ethyl acetate = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.37 (m, 2H), 7.33 – 7.26 (m, 3H), 6.11 (s, 1H), 4.25 (d, *J* = 5.2 Hz, 2H), 2.02 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.0, 131.8, 128.5, 128.4, 122.6, 84.9, 83.4, 30.2, 23.1 ppm.

This compound was previously reported[9].

Compound 9



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 1:1) afforded 27.4 mg (69%).

Physical State: colorless oil.

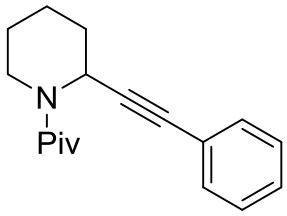
R_f= 0.35 (petroleum ether/ethyl acetate = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.39 (m, 2H), 7.36 – 7.30 (m, 3H), 4.62 – 4.33 (m, 1H), 2.94 (s, 3H), 2.63 – 2.51 (m, 1H), 2.48 – 2.36 (m, 2H), 2.25 – 2.15 (m, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$):δ 174.5, 131.8, 128.8, 128.5, 122.2, 86.5, 85.5, 52.0, 29.9, 28.2, 26.3 ppm.

This compound was previously reported[11].

Compound 10



Following **Procedure I** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 5:1) afforded 25.9 mg (48%).

Physical State: colorless oil.

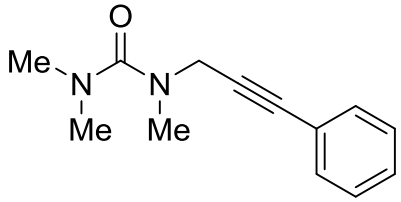
***R**_f*= 0.30 (petroleum ether/ethyl acetate = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.38 (m, 2H), 7.36 – 7.26 (m, 3H), 5.72 (s, 1H), 4.21 (d, *J* = 13.4 Hz, 1H), 3.35 (s, 1H), 2.02 – 1.85 (m, 2H), 1.78 – 1.66 (m, 3H), 1.44 (qt, *J* = 13.2, 4.1 Hz, 1H), 1.31 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 176.2, 131.9, 128.4, 128.3, 123.1, 87.7, 84.7, 77.5, 77.2, 76.8, 45.0, 42.4, 39.0, 31.1, 28.5, 26.1, 20.6 ppm.

HRMS (ESI-TOF): calculated for $C_{18}H_{23}NO$ $[M+Na]^+$: 292.1672, found: 292.1672.

Compound 11



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (ethyl acetate) afforded 38.1 mg (88%).

Physical State: colorless oil.

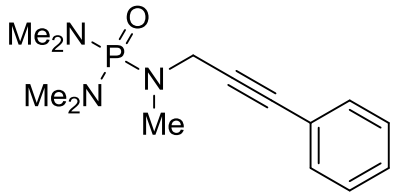
***R**_f*= 0.45 (ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 – 7.39 (m, 2H), 7.34 – 7.27 (m, 3H), 4.12 (s, 2H), 2.93 (s, 3H), 2.86 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 164.9, 131.8, 128.4, 128.3, 123.0, 85.2, 84.0, 41.1, 38.7, 36.4 ppm.

HRMS (ESI-TOF): calculated for $C_{13}H_{16}N_2O$ $[M+Na]^+$: 239.1155, found: 239.1154.

Compound 12



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography

(dichloromethane/methanol = 10:1) afforded 40.8 mg (73%).

Physical State: colorless oil.

R_f= 0.56 (dichloromethane/methanol = 10:1).

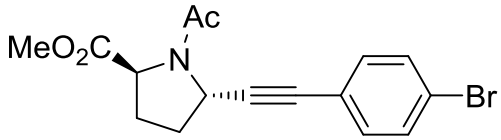
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.36 (m, 2H), 7.33 – 7.27 (m, 3H), 4.01 (d, *J* = 9.7 Hz, 2H), 2.78 (d, *J* = 8.9 Hz, 3H), 2.69 (d, *J* = 9.6 Hz, 12H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 131.7, 128.4, 128.3, 123.2, 86.2, 86.2, 83.9, 39.8, 39.7, 37.0, 37.0, 34.2, 34.2 ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ 25.0.

HRMS (ESI-TOF): calculated for $C_{14}H_{22}N_3OP$ $[M+Na]^+$: 302.1393, found: 302.1395.

Compound 13



Following **Procedure I** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 2:1) afforded 34.5 mg (49%).

Physical State: colorless oil.

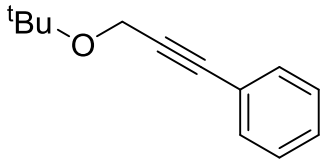
R_f= 0.40 (petroleum ether/ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.40 (m, 2H), 7.26 – 7.22 (m, 2H), 4.90 – 4.83 (m, 1H), 4.63 – 4.57 (m, 1H), 3.72 (s, 3H), 2.53 – 2.38 (m, 2H), 2.28 (s, 3H), 2.25 – 2.15 (m, 1H), 2.13 – 2.02 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.4, 170.0, 133.1, 131.7, 123.0, 121.0, 88.8, 82.9, 58.6, 52.4, 50.3, 32.6, 28.1, 22.4 ppm.

HRMS (ESI-TOF): calculated for $C_{16}H_{16}BrNO_3$ $[M+Na]^+$: 372.0206, found: 372.0202.

Compound 14



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 18.4 mg (49%).

Physical State: colorless oil.

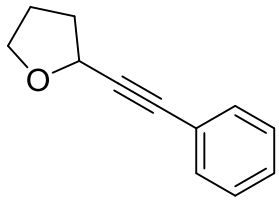
R_f= 0.32 (petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.41 (m, 2H), 7.34 – 7.27 (m, 3H), 4.32 (s, 2H), 1.29 (s, 9H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 131.9, 128.3, 128.3, 123.2, 87.2, 84.9, 51.3, 29.9, 27.7 ppm.

This compound was previously reported[13].

Compound 15



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 17.9 mg (52%).

Physical State: colorless oil.

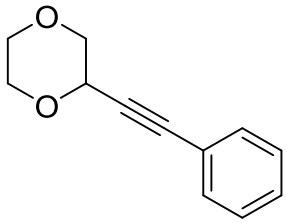
R_f= 0.42 (petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 – 7.39 (m, 2H), 7.35 – 7.27 (m, 3H), 4.81 (dd, *J* = 7.2, 4.9 Hz, 1H), 4.06 – 3.98 (m, 1H), 3.86 (td, *J* = 7.9, 5.4 Hz, 1H), 2.28 – 2.18 (m, 1H), 2.15 – 2.04 (m, 2H), 2.00 – 1.90 (m, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 131.8, 128.4, 128.3, 122.9, 89.2, 84.6, 68.7, 68.1, 33.5, 25.6 ppm.

This compound was previously reported[9].

Compound 16



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 23.6 mg (63%).

Physical State: colorless oil.

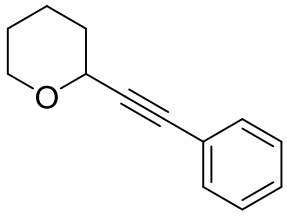
R_f= 0.33 (petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 – 7.43 (m, 2H), 7.35 – 7.28 (m, 3H), 4.57 (dd, *J* = 8.5, 2.9 Hz, 1H), 3.94 (ddd, *J* = 11.5, 5.5, 2.4 Hz, 2H), 3.79 – 3.66 (m, 4H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 132.0, 128.8, 128.4, 122.1, 86.7, 84.4, 70.5, 66.6, 66.5, 65.9 ppm.

This compound was previously reported[10].

Compound 17



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 18.9 mg (51%).

Physical State: colorless oil.

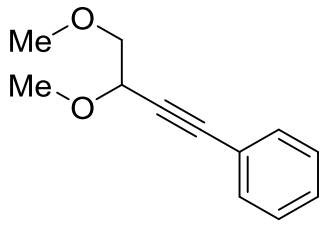
R_f= 0.40 (petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 – 7.40 (m, 2H), 7.36 – 7.23 (m, 3H), 4.51 (dd, *J* = 7.9, 2.9 Hz, 1H), 4.16 – 3.97 (m, 1H), 3.59 (ddd, *J* = 11.7, 8.3, 3.3 Hz, 1H), 1.99 – 1.83 (m, 2H), 1.85 – 1.72 (m, 1H), 1.70 – 1.53 (m, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 131.9, 128.4, 128.3, 122.9, 88.2, 85.3, 67.6, 66.8, 32.3, 25.8, 22.0 ppm.

This compound was previously reported[13].

Compound 18



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 20:1) afforded 19.3 mg (51%).

Physical State: colorless oil.

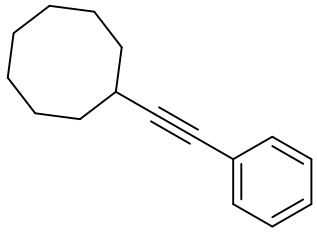
R_f= 0.35 (petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.42 (m, 2H), 7.31 (dd, *J* = 5.2, 2.1 Hz, 3H), 4.41 (dd, *J* = 7.3, 4.0 Hz, 1H), 3.73 – 3.60 (m, 2H), 3.53 (s, 3H), 3.45 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 132.0, 128.7, 128.4, 122.5, 87.0, 85.0, 75.1, 71.2, 59.5, 57.0 ppm.

This compound was previously reported[10].

Compound 19



Following **Procedure I** on 0.20 mmol scale, using 40 equiv. of cyclooctane, reaction for 96 h. Purification by column chromatography (petroleum ether) afforded 23.4 mg (55%).

Physical State: colorless oil.

R_f= 0.65 (petroleum ether).

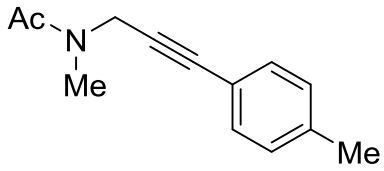
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.35 (m, 2H), 7.32 – 7.21 (m, 3H), 2.79 (tt, *J* = 8.2, 4.1 Hz, 1H), 2.00 – 1.89 (m, 2H), 1.84 – 1.71 (m, 4H), 1.65 – 1.49 (m, 8H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 131.7, 128.3, 127.5, 124.4, 95.6, 80.6, 31.8, 30.9,

27.6, 25.6, 24.7 ppm.

This compound was previously reported[14].

Compound 20



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 1:1) afforded 33.1 mg (82%).

Physical State: colorless oil.

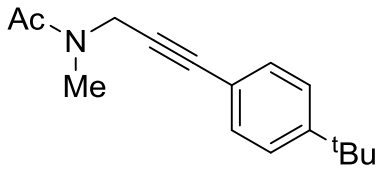
R_f= 0.40 (petroleum ether/ethyl acetate = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.28 (m, 2H), 7.13 – 7.07 (m, 2H), 4.43/4.23 (s, 2H), 3.11/3.03 (s, 3H), 2.34/2.33 (s, 3H), 2.20/2.11 (s, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 170.7, 170.4, 138.9, 138.5, 131.7, 131.7, 129.2, 129.1, 119.7, 119.2, 84.7, 83.8, 83.5, 82.5, 41.2, 36.8, 35.2, 33.4, 21.8, 21.5 ppm.

HRMS (ESI-TOF): calculated for $C_{13}H_{15}NO$ $[M+Na]^+$: 224.1046, found: 224.1045.

Compound 21



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 1:1) afforded 37.6 mg (77%).

Physical State: colorless oil.

R_f= 0.45 (petroleum ether/ethyl acetate = 1:1).

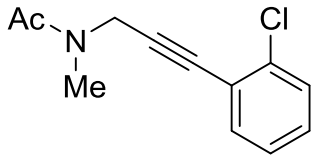
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.29 (m, 4H), 4.44/4.23 (s, 2H), 3.11/3.03 (s, 3H), 2.20/2.11 (s, 3H), 1.30/1.29 (s, 9H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 170.7, 170.3, 152.0, 151.7, 131.6, 131.5, 125.4, 125.3, 119.8, 119.3, 84.7, 83.8, 83.5, 82.5, 52.9, 49.1, 41.2, 36.8, 35.2, 33.4, 31.2,

31.2, 21.8, 21.6 ppm.

HRMS (ESI-TOF): calculated for $C_{16}H_{21}NO$ $[M+Na]^+$: 266.1516, found: 266.1512.

Compound 22



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 1:1) afforded 38.1 mg (86%).

Physical State: colorless oil.

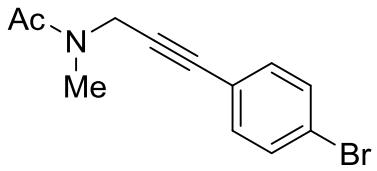
$\boldsymbol{R_f}$= 0.39 (petroleum ether/ethyl acetate = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (dt, J = 7.5, 2.3 Hz, 1H), 7.41 – 7.35 (m, 1H), 7.29 – 7.15 (m, 2H), 4.51/4.30 (s, 2H), 3.16/3.06 (s, 3H), 2.22/2.13 (m, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 170.8, 170.5, 136.2, 136.1, 133.5, 133.5, 129.8, 129.5, 129.4, 129.3, 126.6, 126.5, 122.7, 122.3, 89.7, 88.6, 81.5, 80.7, 41.3, 36.8, 35.3, 33.5, 21.8, 21.6 ppm.

HRMS (ESI-TOF): calculated for $C_{12}H_{12}ClNO$ $[M+Na]^+$: 244.0500, found: 244.0501.

Compound 23



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 1:1) afforded 41.9 mg (79%).

Physical State: colorless oil.

$\boldsymbol{R_f}$= 0.45 (petroleum ether/ethyl acetate = 1:1).

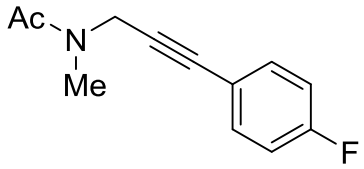
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.40 (m, 2H), 7.30 – 7.24 (m, 2H), 4.43/4.24 (s, 2H), 3.12/3.04 (s, 3H), 2.20/2.13 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.6, 170.5, 133.3, 133.2, 131.8, 131.6, 123.0,

122.7, 121.8, 121.2, 85.5, 84.4, 83.6, 82.6, 41.2, 36.8, 35.4, 33.5, 21.8, 21.6 ppm.

HRMS (ESI-TOF): calculated for $C_{12}H_{12}BrNO$ $[M+Na]^+$: 287.9995, found: 287.9991.

Compound 24



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 1:1) afforded 41.2 mg (98%).

Physical State: colorless oil.

***R*$_f$**= 0.40 (petroleum ether/ethyl acetate = 1:1).

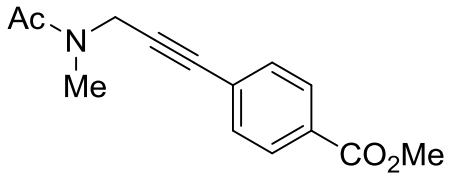
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 – 7.33 (m, 2H), 7.04 – 6.91 (m, 2H), 4.41/4.22 (s, 2H), 3.10/3.02 (s, 3H), 2.18/2.10 (s, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 170.6, 170.4, 163.7, 163.5, 161.7, 161.5, 133.8, 133.7, 133.7, 133.6, 118.9, 118.8, 118.4, 118.3, 115.8, 115.7, 115.6, 115.5, 84.0, 84.0, 83.5, 82.9, 82.5, 41.1, 36.7, 35.3, 33.4, 21.7, 21.5 ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ -110.3, -110.9 ppm.

HRMS (ESI-TOF): calculated for $C_{12}H_{12}FNO$ $[M+Na]^+$: 228.0796, found: 228.0794.

Compound 25



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 1:1) afforded 16.7 mg (34%).

Physical State: colorless oil.

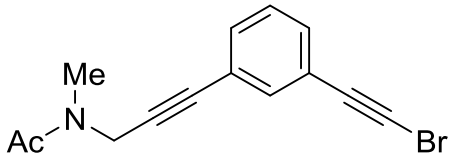
***R*$_f$**= 0.25 (petroleum ether/ethyl acetate = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 – 7.81 (m, 2H), 7.57 – 7.34 (m, 2H), 4.44/4.25 (s, 2H), 3.89/3.88 (s, 3H), 3.11/3.02 (s, 3H), 2.19/2.11 (s, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 170.6, 170.4, 166.5, 166.4, 131.8, 131.7, 130.0, 129.7, 129.6, 129.5, 127.5, 126.9, 87.4, 86.2, 83.9, 82.9, 52.3, 52.3, 41.2, 36.8, 35.4, 33.4, 21.7, 21.6 ppm.

HRMS (ESI-TOF): calculated for $C_{14}H_{15}NO_3$ $[M+Na]^+$: 268.0945, found: 268.0942.

Compound 26



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (dichloromethane/acetone = 10:1) afforded 30.3 mg (52%).

Physical State: colorless oil.

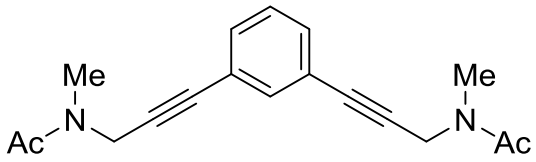
***R**$_f$*= 0.60 (dichloromethane/acetone = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 – 7.18 (m, 4H), 4.42/4.23 (s, 2H), 3.10/3.02 (s, 3H), 2.18/2.10 (s, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 170.6, 170.5, 136.1, 136.0, 135.3, 135.2, 132.2, 132.0, 131.9, 131.9, 128.5, 128.4, 123.2, 123.2, 85.2, 85.0, 83.1, 82.7, 79.3, 79.1, 51.1, 50.8, 41.2, 36.8, 35.3, 33.5, 21.8, 21.6 ppm.

HRMS (ESI-TOF): calculated for $C_{14}H_{12}BrNO$ $[M+Na]^+$: 311.9995, found: 311.9991.

Compound 27



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (dichloromethane/acetone = 5:1) afforded 26.8 mg (45%).

Physical State: colorless oil.

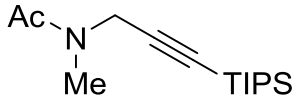
R_f= 0.42 (dichloromethane/acetone = 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 – 7.45 (m, 1H), 7.40 – 7.31 (m, 2H), 7.25 – 7.19 (m, 1H), 4.43/4.23 (s, 4H), 3.11/3.03 (s, 6H), 2.19/2.12 (d, 6H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 170.6, 170.4, 135.1, 135.0, 131.9, 131.8, 131.6, 131.5, 128.5, 128.4, 123.3, 123.1, 122.7, 122.6, 85.2, 85.0, 84.1, 83.9, 83.7, 83.6, 82.8, 82.6, 41.2, 36.8, 35.3, 33.4, 21.8, 21.6 ppm.

HRMS (ESI-TOF): calculated for $C_{18}H_{20}N_2O_2$ $[M+Na]^+$: 319.1417, found: 319.1419.

Compound 28



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 2:1) afforded 35.8 mg (67%).

Physical State: colorless oil.

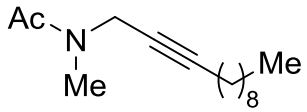
R_f= 0.30 (petroleum ether/ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.28/4.05 (s, 2H), 3.06/2.98 (s, 3H), 2.15/2.08 (s, 3H), 1.04 (s, 21H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 170.7, 170.3, 102.4, 101.4, 86.2, 85.1, 41.5, 36.9, 34.9, 33.3, 21.9, 21.5, 18.7, 18.7, 11.3, 11.2 ppm.

HRMS (ESI-TOF): calculated for $C_{15}H_{29}NOSi$ $[M+Na]^+$: 290.1911, found: 290.1912.

Compound 29



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 2:1) afforded 23.7 mg (50%).

Physical State: colorless oil.

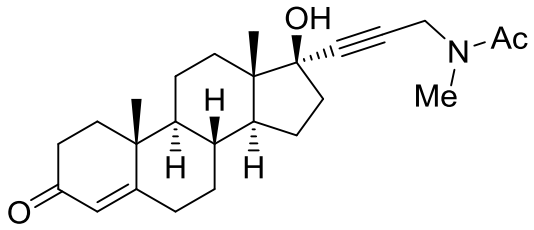
R_f= 0.42 (petroleum ether/ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.17/3.96 (t, *J* = 2.2 Hz, 2H), 3.02/2.94 (s, 3H), 2.17 – 2.11 (m, 2H), 2.12/2.06 (s, 3H), 1.50 – 1.41 (m, 2H), 1.24 (s, 12H), 0.89 – 0.83 (m, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): 170.8, 170.4, 85.4, 84.4, 74.7, 74.0, 53.7, 51.9, 48.2, 41.7, 41.6, 40.8, 36.4, 35.0, 33.2, 32.0, 29.8, 29.6, 29.5, 29.4, 29.3, 29.2, 29.2, 29.0, 28.9, 28.8, 28.7, 28.5, 28.0, 22.8, 21.8, 21.5, 18.8, 18.7, 14.2 ppm.

HRMS (ESI-TOF): calculated for $C_{15}H_{27}NO$ $[M+Na]^+$: 260.1985, found: 260.1983.

Compound 30



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (ethyl acetate) afforded 48.5 mg (61%).

Physical State: white solid.

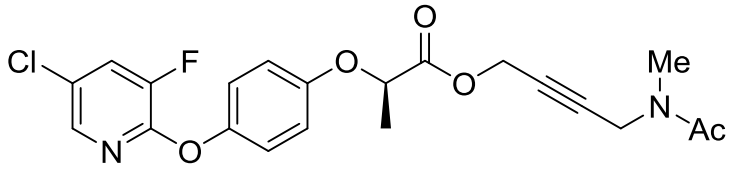
R_f= 0.55 (ethyl acetate).

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.72 (s, 1H), 4.25/4.07 (d/s, *J* = 5.0 Hz, 2H), 3.04/2.95 (s, 3H), 2.47 – 2.18 (m, 6H), 2.13/2.08 (s, 3H), 2.05 – 1.48 (m, 8H), 1.48 – 1.21 (m, 4H), 1.18 (s, 3H), 1.08 – 0.89 (m, 2H), 0.87/0.86 (s, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 199.7, 199.6, 171.3, 171.1, 170.6, 170.5, 124.0, 124.0, 88.3, 87.2, 80.9, 80.0, 79.8, 79.7, 53.7, 53.6, 50.3, 50.1, 47.0, 46.9, 40.7, 39.1, 39.0, 38.7, 38.7, 36.4, 36.3, 36.3, 35.8, 35.3, 34.1, 34.0, 33.4, 32.9, 32.8, 32.8, 31.6, 31.6, 29.8, 23.2, 21.8, 21.6, 20.8, 20.8, 17.5, 12.9 ppm.

HRMS (ESI-TOF): calculated for $C_{25}H_{35}NO_3$ $[M+Na]^+$: 420.2510, found: 420.2511.

Compound 31



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (ethyl acetate) afforded 42.9 mg (49%).

Physical State: colorless oil.

R_f= 0.41 (ethyl acetate).

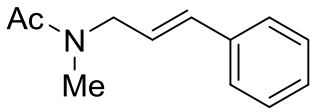
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85/7.85 (s 1H), 7.50/7.47 (d, *J* = 2.2 Hz, 1H), 7.11 – 7.02 (m, 2H), 6.96 – 6.85 (m, 2H), 4.82 – 4.70 (m, 3H), 4.27 – 4.02 (m, 2H), 3.01/2.94 (s, 3H), 2.12/2.08 (s, 3H), 1.63 (d, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.5, 171.4, 170.6, 170.5, 154.9, 151.4, 151.3, 148.4, 147.3, 147.3, 145.8, 140.3, 140.2, 129.8, 128.8, 125.2, 125.0, 122.5, 122.4, 122.4, 116.3, 116.2, 116.2, 82.7, 81.6, 78.1, 77.0, 73.1, 53.2, 52.9, 40.6, 36.3, 35.3, 33.4, 21.7, 21.5, 18.8, 18.6 ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ -134.3 ppm.

HRMS (ESI-TOF): calculated for $C_{21}H_{20}ClFN_2O_5$ $[M+Na]^+$: 457.0937, found: 457.0938.

Compound 32



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 1:1) afforded 24.6 mg (65%).

Physical State: colorless oil.

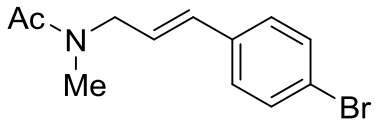
R_f= 0.45 (petroleum ether/ethyl acetate = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 – 7.17 (m, 5H), 6.56 – 6.40 (m, 1H), 6.21 – 6.07 (m, 1H), 4.06/4.15 (dd, *J* = 6.0, 1.5 Hz, 2H), 2.99/2.98 (s, 3H), 2.14/2.13 (s, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 171.0, 170.7, 136.7, 136.2, 132.9, 131.9, 128.8,

128.7, 128.1, 127.8, 126.5, 126.5, 124.7, 123.8, 52.8, 49.4, 35.6, 33.7, 22.0, 21.5 ppm. This compound was previously reported[9].

Compound 33



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 1:1) afforded 33.2 mg (62%).

Physical State: colorless oil.

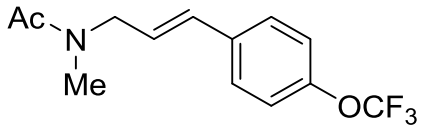
R_f= 0.50 (petroleum ether/ethyl acetate = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.39 (m, 2H), 7.25 – 7.18 (m, 2H), 6.44 – 6.36 (m, 1H), 6.17 – 6.07 (m, 1H), 4.12/4.03 (dd, *J* = 5.8, 1.6 Hz, 2H), 2.98/2.96 (s, 3H), 2.12/2.12 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.9, 170.6, 135.6, 135.2, 131.9, 131.8, 131.5, 130.6, 128.0, 128.0, 125.6, 124.7, 121.5, 52.6, 49.4, 35.7, 33.6, 21.9, 21.4 ppm.

HRMS (ESI-TOF): calculated for $C_{12}H_{14}BrNO$ $[M+Na]^+$: 290.0151, found: 290.0151.

Compound 34



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 1:1) afforded 32.5 mg (59%).

Physical State: colorless oil.

R_f= 0.41 (petroleum ether/ethyl acetate = 1:1).

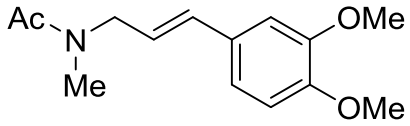
^{1}H NMR (400 MHz, $CDCl_3$): δ7.43 – 7.32 (m, 2H), 7.21 – 7.10 (m, 2H), 6.53 – 6.40 (m, 1H), 6.20 – 6.05 (m, 1H), 4.13/4.05 (dd, *J* = 5.9, 1.7 Hz, 2H), 2.98/2.97 (s, 3H), 2.13/2.12 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.9, 170.6, 148.9, 148.7, 135.5, 135.0, 131.3, 130.3, 127.8, 127.7, 125.9, 125.0, 121.3, 121.2, 52.6, 49.4, 35.7, 33.6, 21.9, 21.4 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ -57.9 ppm.

HRMS (ESI-TOF): calculated for $C_{13}H_{14}F_3NO_2$ $[M+Na]^+$: 296.0869, found: 296.0870.

Compound 35



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 1:1) afforded 43.9 mg (88%).

Physical State: colorless oil.

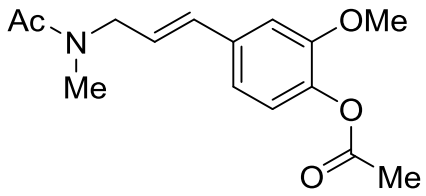
***R*$_f$**= 0.33 (petroleum ether/ethyl acetate = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95 – 6.77 (m, 3H), 6.49 – 6.34 (m, 1H), 6.07 – 5.92 (m, 1H), 4.11/4.03 (dd, *J* = 6.1, 1.5 Hz, 2H), 3.95 – 3.80 (m, 6H), 2.98/2.96 (s, 3H), 2.13/2.11 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.9, 170.6, 149.2, 149.2, 149.2, 149.0, 132.7, 131.6, 129.8, 129.3, 122.7, 121.7, 119.8, 119.6, 111.3, 111.2, 109.0, 108.8, 56.1, 56.0, 56.0, 55.9, 52.7, 49.5, 35.6, 33.6, 22.0, 21.4 ppm.

This compound was previously reported[16].

Compound 36



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (ethyl acetate) afforded 54.6 mg (98%).

Physical State: colorless oil.

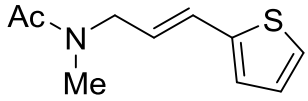
***R*$_f$**= 0.61 (ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.01 – 6.88 (m, 3H), 6.49 – 6.37 (m, 1H), 6.13 – 6.02 (m, 1H), 4.12/4.04 (dd, *J* = 5.9, 1.5 Hz, 2H), 3.84/3.82 (s, 3H), 2.97/2.96 (s, 3H), 2.29/2.29 (s, 3H), 2.12/2.11 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.9, 170.6, 169.1, 169.1, 151.3, 151.2, 139.6, 139.4, 135.7, 135.3, 132.3, 131.1, 125.0, 124.1, 123.0, 122.9, 119.3, 119.0, 110.4, 110.0, 56.0, 55.9, 52.6, 49.4, 35.6, 33.6, 21.9, 21.4, 20.7 ppm.

HRMS (ESI-TOF): calculated for $C_{15}H_{19}NO_4$ $[M+Na]^+$: 300.1207, found: 300.1206.

Compound 37



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 1:1) afforded 24.5 mg (63%).

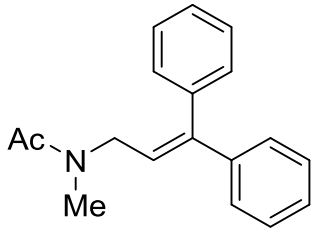
Physical State: colorless oil.

***R*$_f$**= 0.56 (petroleum ether/ethyl acetate = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 – 7.08 (m, 1H), 7.01 – 6.88 (m, 2H), 6.64 – 6.54 (m, 1H), 6.02 – 5.90 (m, 1H), 4.10/4.01 (dd, *J* = 6.0, 1.6 Hz, 2H), 2.97/2.96 (s, 3H), 2.12/2.11 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.9, 170.6, 141.8, 141.2, 127.6, 127.4, 126.2, 126.0, 125.7, 125.0, 124.7, 124.4, 124.3, 123.4, 52.4, 49.1, 35.6, 33.6, 21.9, 21.4 ppm. This compound was previously reported[16].

Compound 38



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 1:1) afforded 39.8 mg (75%).

Physical State: colorless oil.

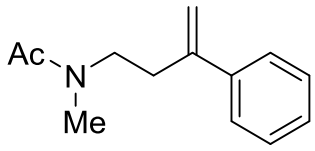
R_f= 0.43 (petroleum ether/ethyl acetate = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 – 7.13 (m, 10H), 6.04/6.01 (t, *J* = 6.7 Hz, 1H), 4.08/3.95 (d, *J* = 6.7 Hz, 2H), 2.91/2.87 (s, 3H), 2.08/1.97 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.6, 170.5, 145.4, 144.9, 141.6, 141.2, 139.1, 138.7, 129.8, 129.7, 128.6, 128.4, 128.4, 128.3, 127.9, 127.6, 127.5, 127.4, 127.3, 124.4, 123.3, 49.9, 46.2, 35.6, 33.3, 21.9, 21.4 ppm.

This compound was previously reported[15].

Compound 39



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 1:1) afforded 32.8 mg (81%).

Physical State: colorless oil.

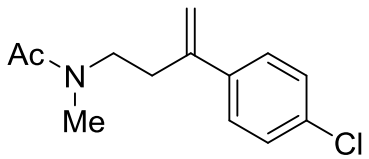
R_f= 0.47 (petroleum ether/ethyl acetate = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.24 (m, 5H), 5.37 (dd, *J* = 7.3, 1.3 Hz, 1H), 5.12 (t, *J* = 1.2 Hz, 1H), 3.51 – 3.33 (m, 2H), 2.91 (s, 3H), 2.81 – 2.73 (m, 2H), 2.02/1.91 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.5, 170.5, 145.8, 144.8, 140.5, 140.0, 128.7, 128.5, 128.0, 127.6, 126.1, 126.0, 115.0, 114.0, 49.8, 47.8, 37.0, 34.4, 33.2, 33.1, 22.0, 21.1 ppm.

HRMS (ESI-TOF): calculated for $C_{13}H_{17}NO$ $[M+Na]^+$: 226.1203, found: 226.1202.

Compound 40



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 1:1) afforded 38.4 mg (81%).

Physical State: colorless oil.

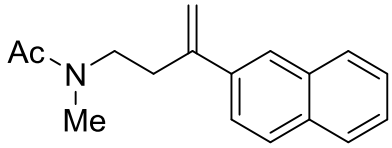
***R*$_f$**= 0.44 (petroleum ether/ethyl acetate = 1:1).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.41 – 7.25 (m, 4H), 5.35/5.33 (d, 1.0 Hz, 1H), 5.11/5.11 (q, *J* = 1.1 Hz, 1H), 3.42/3.34 (dd, *J* = 8.3, 6.7 Hz, 2H), 2.91/2.89 (s, 3H), 2.77 – 2.66 (m, 2H), 2.01/1.91 (s, 3H) ppm.

^{13}C NMR (101 MHz, CDCl$_3$): δ 170.6, 170.5, 144.6, 143.6, 138.9, 138.5, 133.9, 133.5, 128.9, 128.6, 127.4, 127.3, 115.6, 114.5, 49.7, 47.7, 37.0, 34.3, 33.3, 33.0, 22.0, 21.2 ppm.

HRMS (ESI-TOF): calculated for $C_{13}H_{16}ClNO$ $[M+Na]^+$: 260.0813, found: 260.0811.

Compound 41



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 1:1) afforded 45.5 mg (90%).

Physical State: colorless oil.

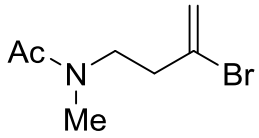
***R*$_f$**= 0.49 (petroleum ether/ethyl acetate = 1:1).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.94 – 7.77 (m, 4H), 7.65 – 7.41 (m, 3H), 5.53/5.52 (d, *J* = 1.1 Hz, 1H), 5.22/5.21 (d, *J* = 1.2 Hz, 1H), 3.57 – 3.37 (m, 2H), 2.94/2.91 (s, 3H), 2.90 – 2.85 (m, 2H), 2.03/1.91 (s, 3H) ppm.

^{13}C NMR (101 MHz, CDCl$_3$): δ 170.6, 170.6, 145.6, 144.5, 137.6, 137.1, 133.5, 133.4, 133.0, 132.9, 128.5, 128.4, 128.2, 128.1, 127.7, 127.6, 126.6, 126.3, 126.3, 126.0, 124.8, 124.7, 124.4, 124.3, 115.6, 114.6, 49.9, 48.0, 37.2, 34.4, 33.3, 33.1, 22.0, 21.2 ppm.

HRMS (ESI-TOF): calculated for $C_{17}H_{19}NO$ $[M+Na]^+$: 276.1359, found: 276.1360.

Compound 42



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 2:1) afforded 22.0 mg (53%).

Physical State: colorless oil.

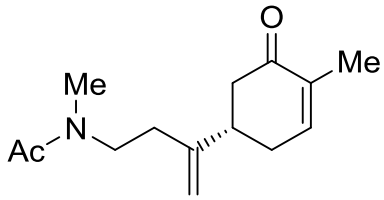
R_f= 0.36 (petroleum ether/ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.64 – 5.61 (m, 1H), 5.48/5.43 (d, *J* = 1.8 Hz, 1H), 3.54/3.51 (t, *J* = 7.0 Hz, 2H), 3.02/2.91 (s, 3H), 2.65 (t, *J* = 6.7 Hz, 2H), 2.12/2.05 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.8, 170.8, 131.4, 129.8, 119.8, 118.8, 49.2, 46.9, 40.6, 39.7, 37.5, 33.5, 22.0, 21.4 ppm.

HRMS (ESI-TOF): calculated for $C_7H_{12}BrNO$ $[M+Na]^+$: 227.9995, found: 227.9997.

Compound 43



Following **Procedure H** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 2:1) afforded 25.9 mg (55%).

Physical State: colorless oil.

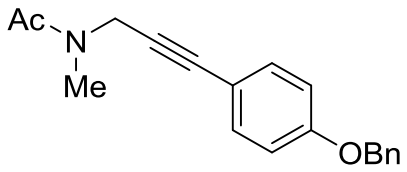
R_f= 0.41 (petroleum ether/ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.81 – 6.67 (m, 1H), 4.96 – 4.80 (m, 2H), 3.58 – 3.28 (m, 2H), 2.97/2.90 (s, 3H), 2.79 – 2.40 (m, 3H), 2.40 – 2.17 (m, 4H), 2.06/2.04 (s, 3H), 1.77/1.75 (dt, *J* = 2.7, 1.4 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 199.7, 199.2, 170.5, 170.3, 148.2, 147.4, 144.7, 144.2, 135.7, 135.5, 111.8, 111.1, 50.2, 46.8, 43.4, 43.4, 41.4, 41.0, 36.4, 33.5, 32.8, 31.8, 31.6, 30.0, 29.8, 22.0, 21.3, 15.8 ppm.

HRMS (ESI-TOF): calculated for $C_{14}H_{21}NO_2$ $[M+Na]^+$: 258.1465, found: 258.1461.

Compound 47



Following **Procedure L** on 0.20 mmol scale. Purification by column chromatography (petroleum ether/ethyl acetate = 1:1) afforded 38.4 mg (65%).

Physical State: colorless oil.

R_f= 0.38 (petroleum ether/ethyl acetate = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.30 (m, 7H), 6.97 – 6.86 (m, 2H), 5.06/5.06 (s, 2H), 4.43/4.23 (s, 2H), 3.12/3.04 (s, 3H), 2.21/2.12 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.6, 170.3, 159.0, 158.8, 136.6, 136.5, 133.3, 133.2, 128.7, 128.6, 128.1, 128.1, 127.5, 115.1, 114.9, 114.8, 114.6, 114.6, 114.5, 84.4, 83.5, 82.8, 81.8, 70.0, 70.0, 41.2, 36.8, 35.1, 33.3, 21.7, 21.5 ppm.

HRMS (ESI-TOF): calculated for $C_{19}H_{19}NO_2$ $[M+Na]^+$: 316.1308, found: 316.1307.

Quantum Yield Measurement

1. Determination of the light intensity at 452 nm:

According to the standard procedure for iron oxalate actinometry[17] and the works by Yoon and co-workers[18], the photon flux of the LED (λ_{max}= 452 nm) was first determined by standard ferrioxalate actinometry. For this, a 10 mL 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). A 20 mL buffered solution of 1, 10-phenanthroline was prepared by dissolving 1, 10- phenanthroline (20 mg) and sodium acetate (4.5 g) in H_2SO_4 (20 mL of a 0.5 M solution). Both solutions were stored in the dark. To determine the photon flux of the LED, the ferrioxalate solution (2.0 mL) was placed in a cuvette and irradiated for 10 seconds at λ_{max}= 452 nm. After irradiation, the phenanthroline solution (0.35 mL) was added to the cuvette and the mixture was stirred in the dark for 1.0 h to allow all the ferrous ions to be coordinated by phenanthroline. The absorption of the solution was measured at 510 nm. A non-irradiated sample was also prepared identically and the absorption at 510 nm was also measured. Each sample preparation and measurements were repeated two more times. The average of the absorption of the irradiated and non-irradiated samples were determined and used for the calculation of photon flux.

$$\text{mol } Fe^{2+} = \frac{V \times \Delta A\ (510\ nm)}{l \times \varepsilon}$$

Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in absorption at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.00 cm), and ε is the molar absorptivity of the ferrioxalate actinometer at 510 nm (11,100 L mol^{-1} cm^{-1}). The photon flux can be calculated based on the following equation:

$$\text{photon flux} = \frac{mol\ Fe^{2+}}{\Phi \times t \times f}$$

Where Φ is the quantum yield for the ferrioxalate actinometer (0.92 for a 0.15 M solution at λ = 452 nm)[17], t is the irradiation time (10 s), and f is the fraction of light absorbed at λ = 452 nm. This value is calculated using the following equation where

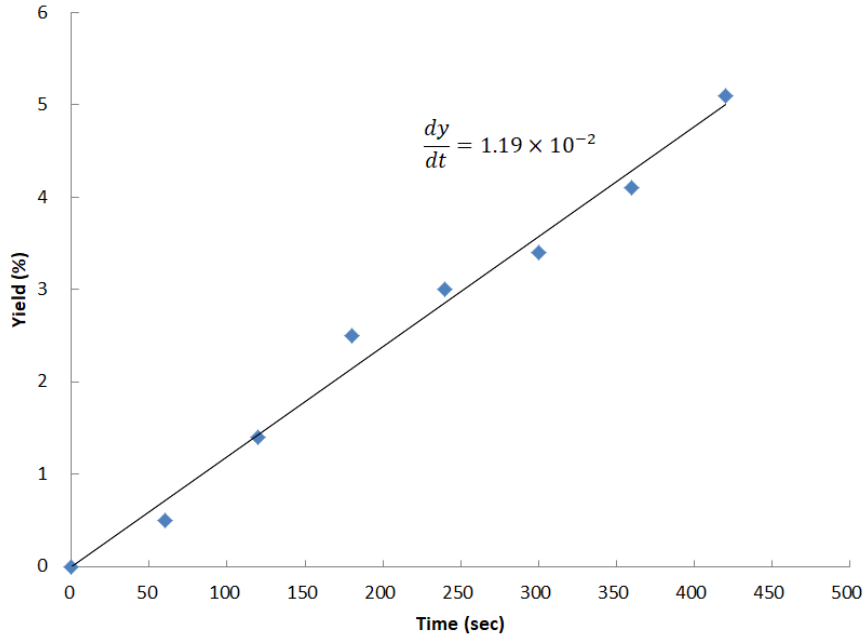
A(452 nm) is the absorption of the ferrioxalate solution at 452 nm. The absorbance of the above ferrioxalate solution at 452 nm was measured to be 2.6328.

$$f = 1 - 10^{-A(452\ \mathrm{nm})}$$

The average photon flux was thus calculated to be 4.48×10^{-8} einsteins s^{-1}

2. Determination of the reaction quantum yield:

Uranyl nitrate hexahydrate (8.0 mg, 8 mol%), 2-(2-pyridyl)benzimidazole (pbi) (3.9 mg, 10 mol%), (bromoethynyl)benzene (36.2 mg, 0.2 mmol, 1.0 equiv.) and cyclododecane (8.4 mg, 0.25 equiv., internal standard) were dissolved in N,N-dimethylacetamide (2 mL). The mixture was placed in a tube with a stirring bar. After that, the tube was exposed to two 60 W blue LEDs at room temperature After every 500 s, an aliquot of 20 μL was taken out from this solution to monitor the yield by GC-FID. From the time vs yield curve, an initial product formation rate of 1.19×10^{-2} was determined. This will give a product formation rate of 2.38×10^{-8} mol sec^{-1}.



The reaction quantum yield (Φ) was determined with the following formula:

$$\Phi = \frac{\text{mole of product formation rate}}{\text{photon flux} \times f}$$

Where, *f* is the fraction of light absorbed at λ_{max} = 452 nm by the reaction mixture. An absorption spectrum gave an *A*(452 nm) value of 0.3449, indicating that the fraction of absorbed light (*f*) is 0.5480.

$$\Phi = \frac{2.38\times10^{-8}}{4.481 \times 10^{-8} \times 0.5480} = 0.969$$

The reaction quantum yield (Φ) was thus determined to be Φ = 0.969 (96.9%). Thus, a radical chain pathway may be ruled out.

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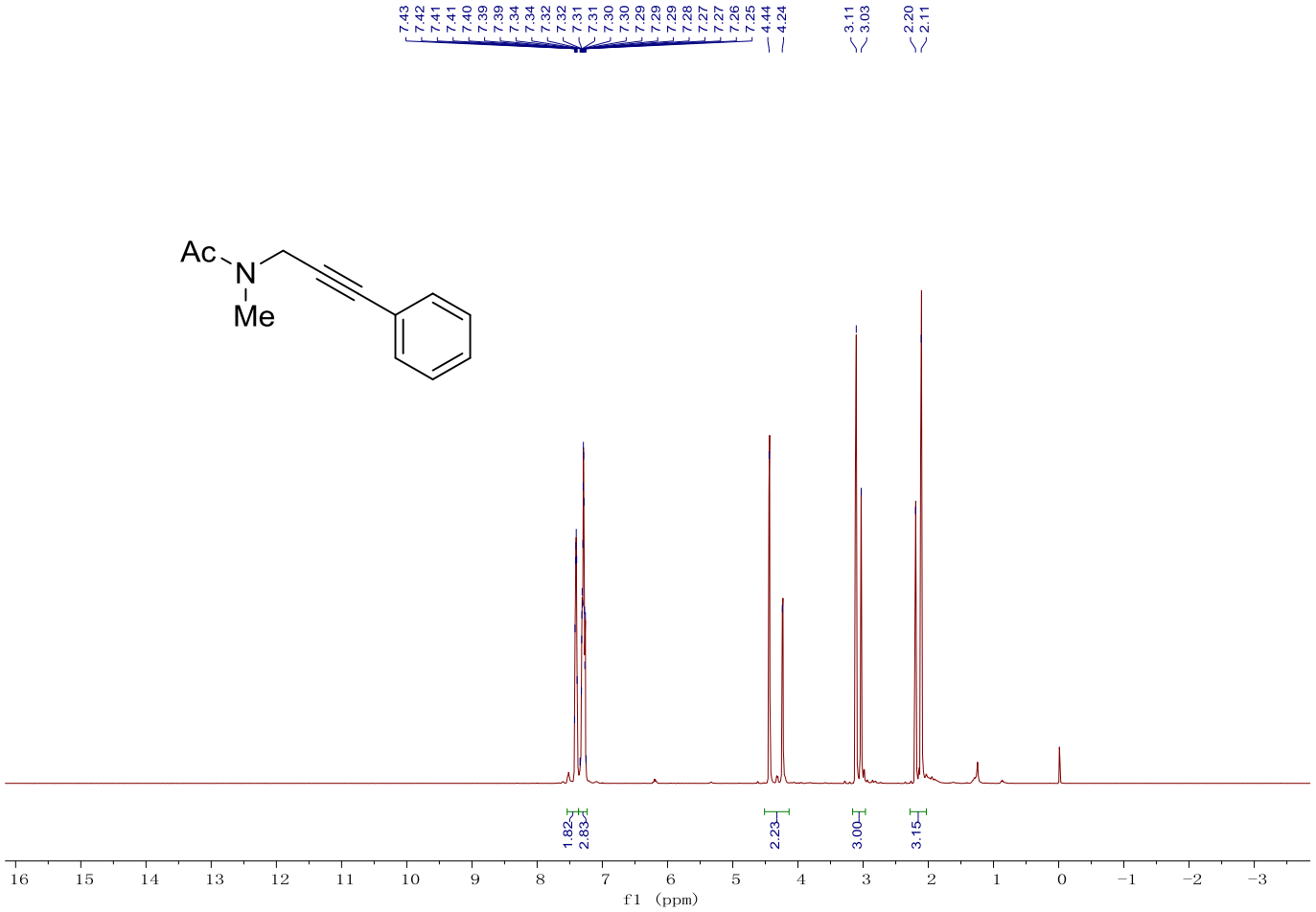
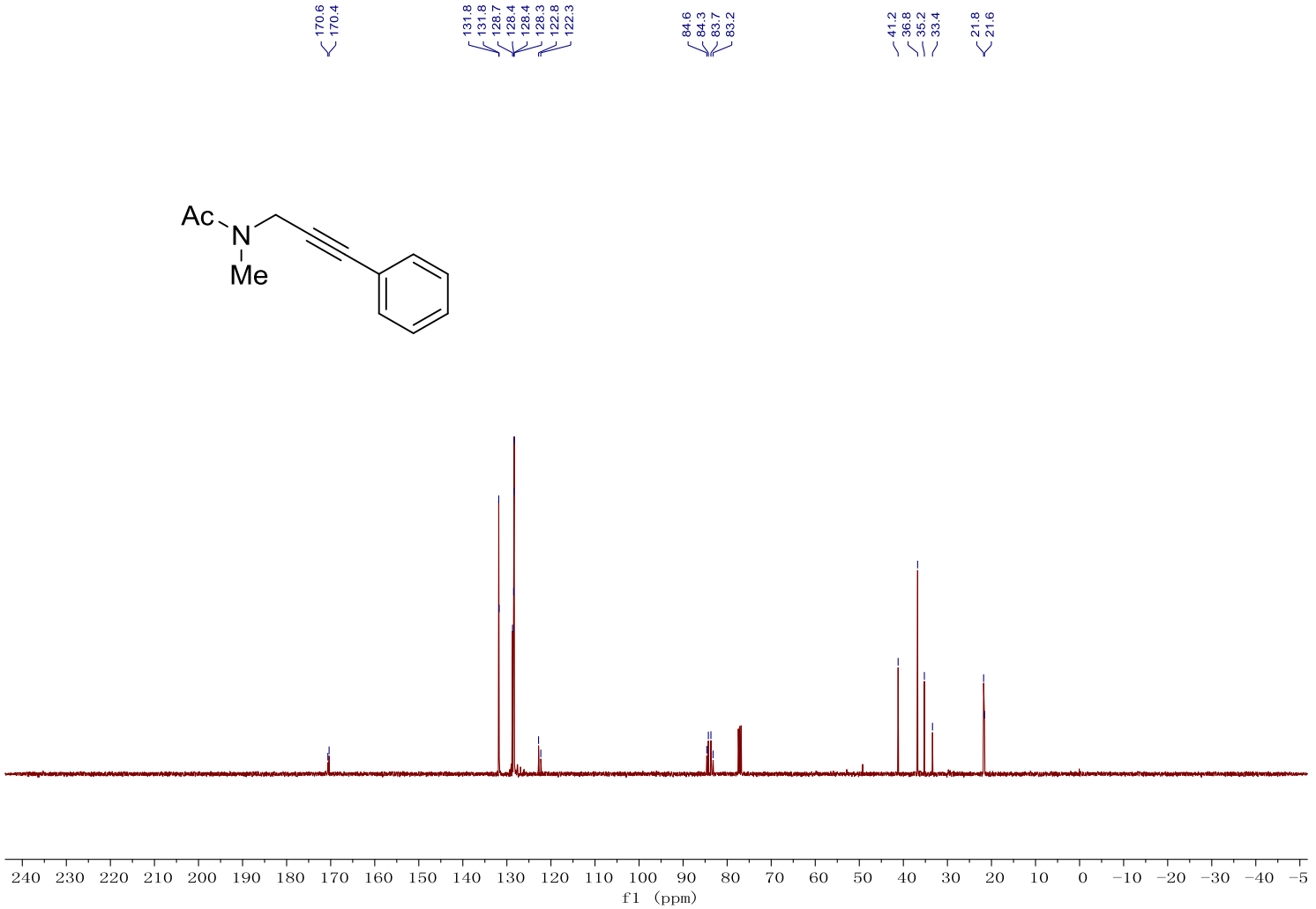
NMR Spectra

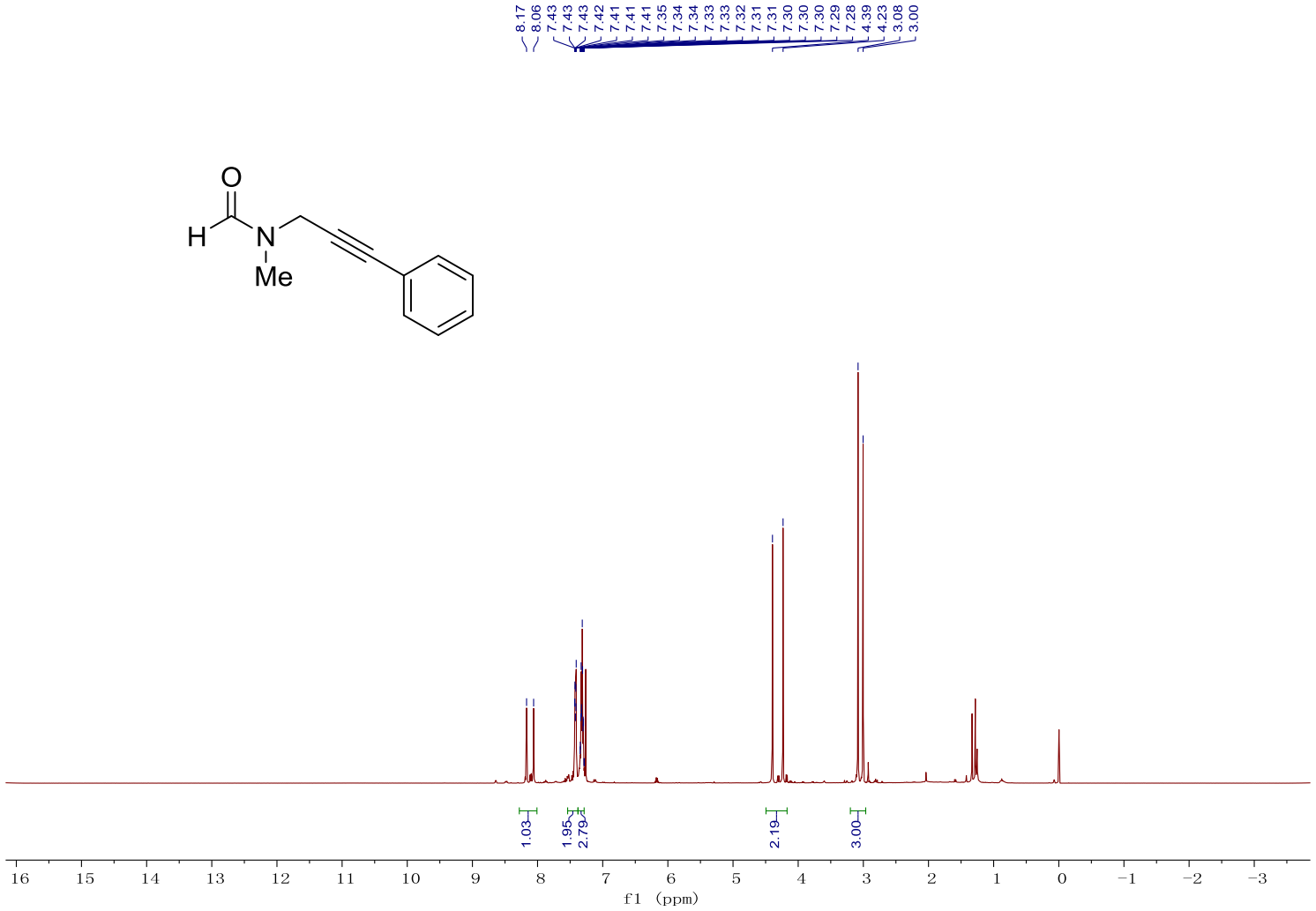
Supplementary Figure 5. Compound **3** ^{1}H NMR in $CDCl_3$



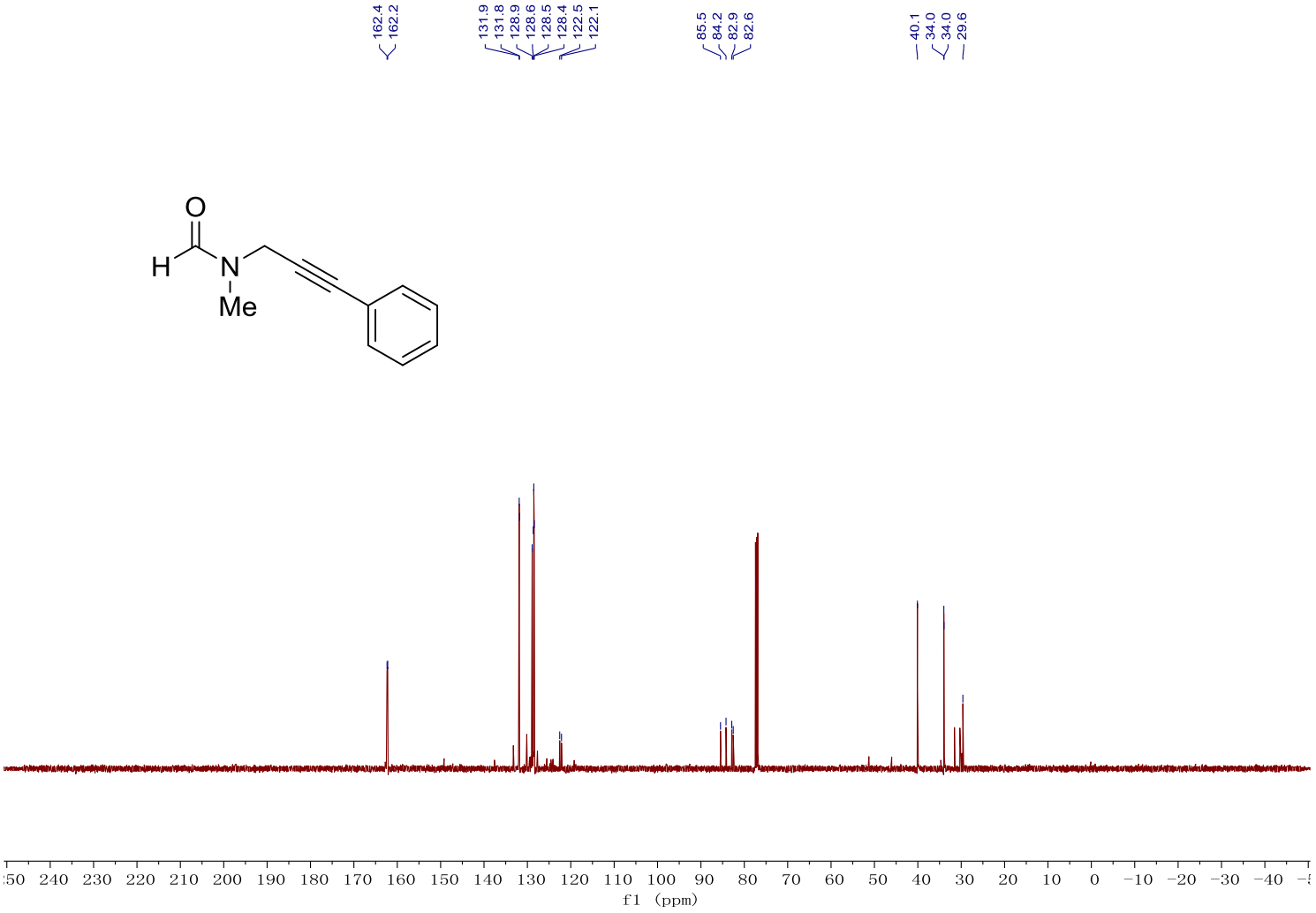
Supplementary Figure 6. Compound **3** ^{13}C NMR in $CDCl_3$



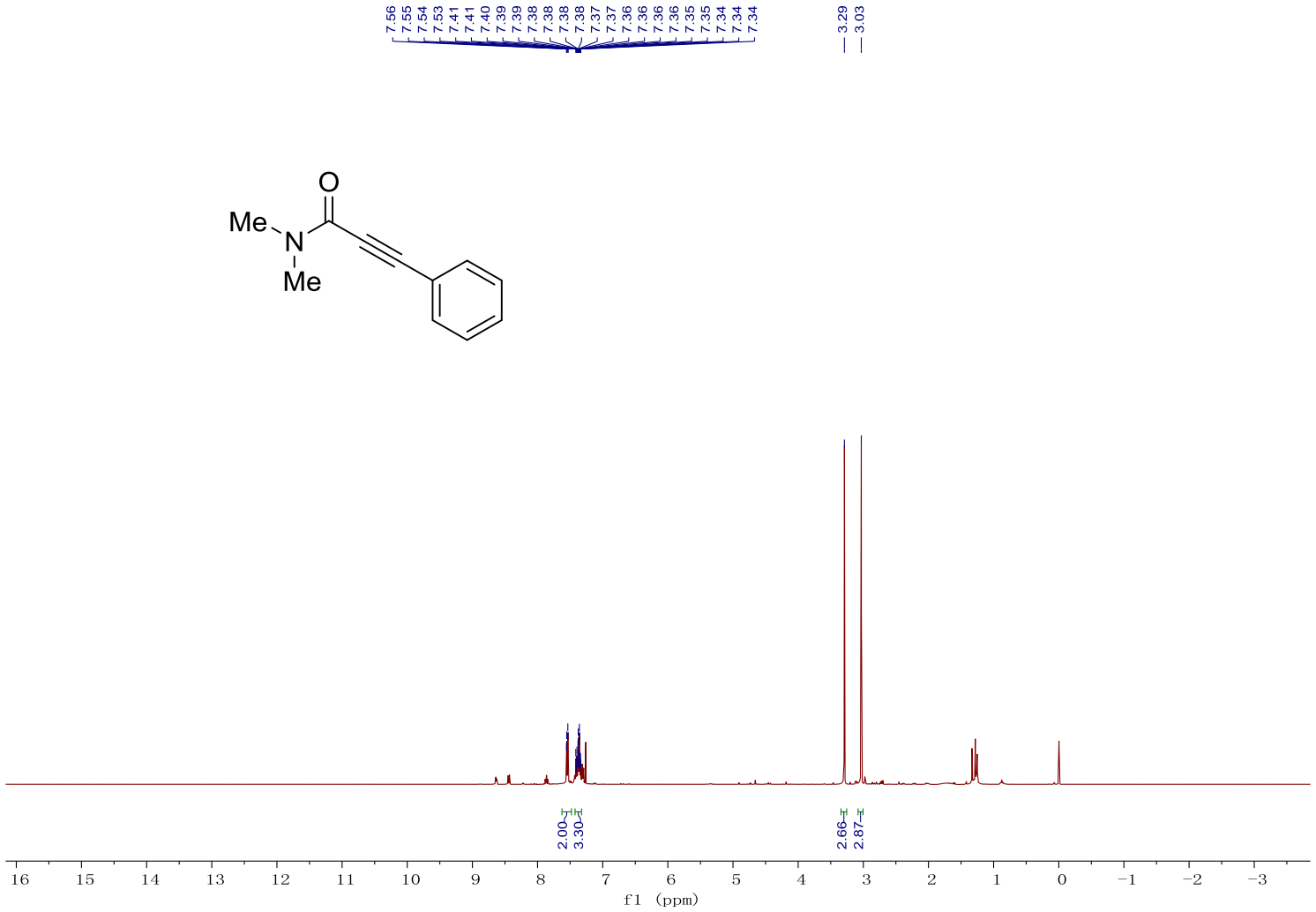
Supplementary Figure 7.Compound **4** ^{1}H NMR in $CDCl_3$



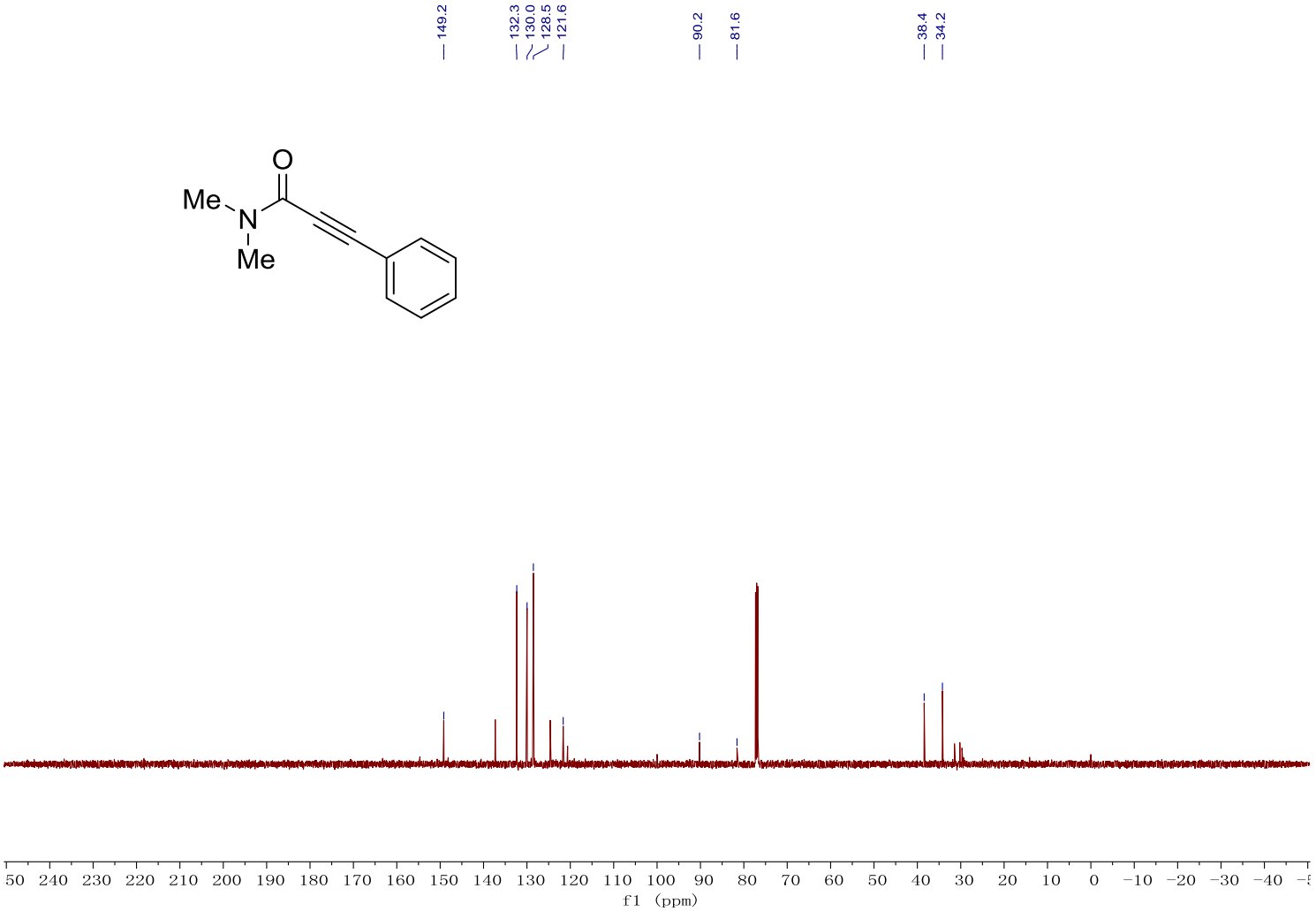
Supplementary Figure 8.Compound **4** ^{13}C NMR in $CDCl_3$



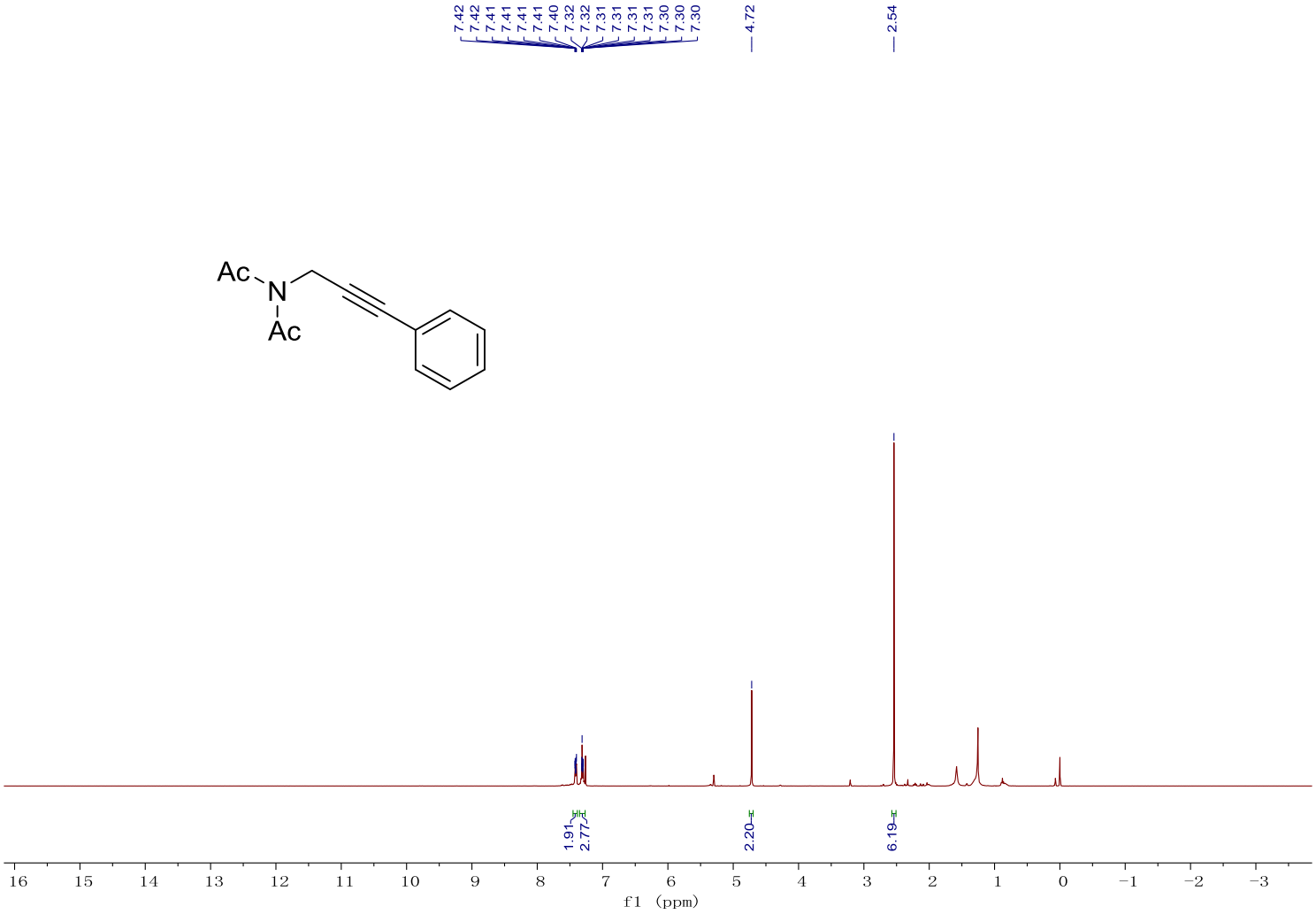
Supplementary Figure 9. Compound **5** ^{1}H NMR in $CDCl_3$



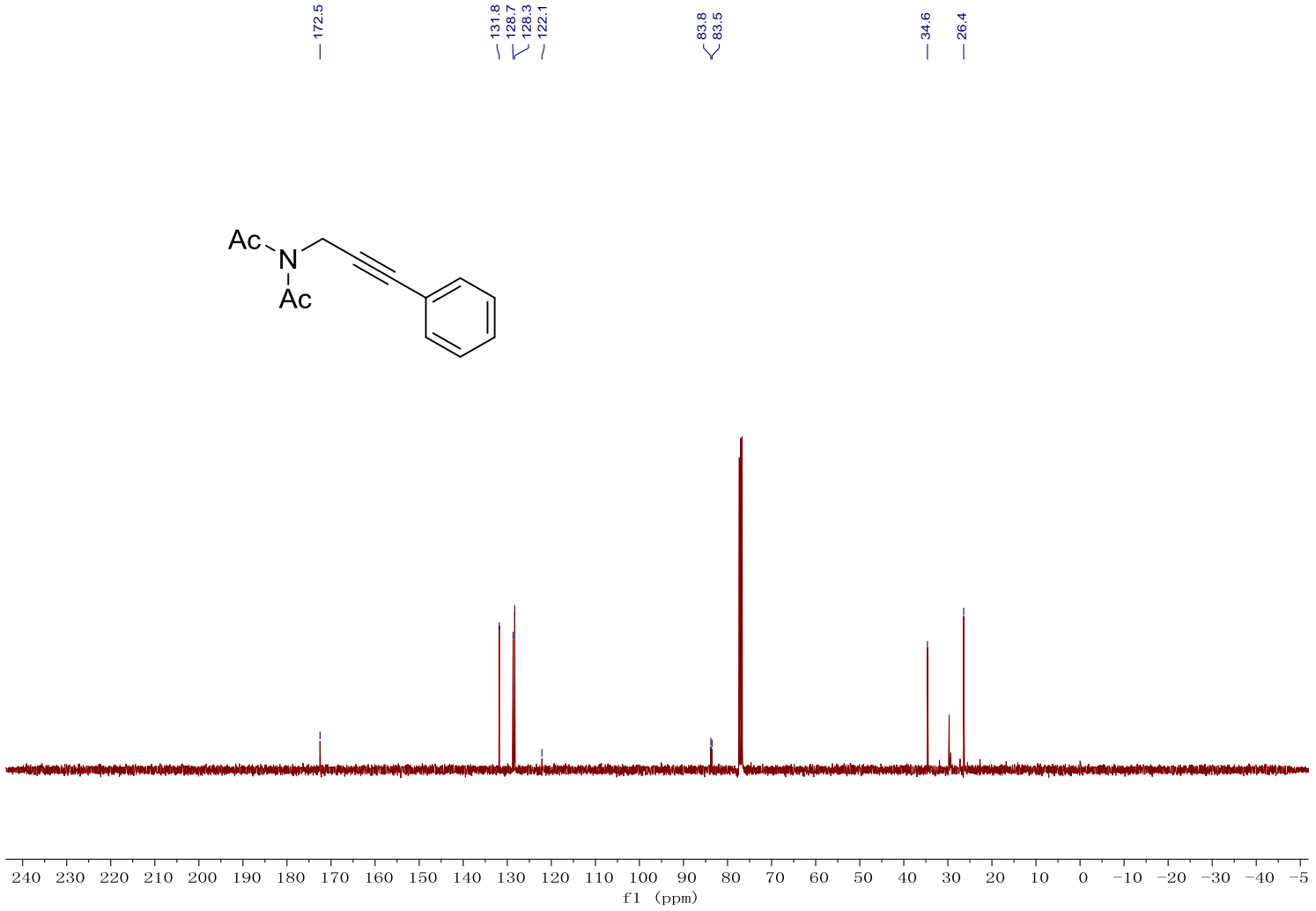
Supplementary Figure 10. Compound **5** ^{13}C NMR in $CDCl_3$



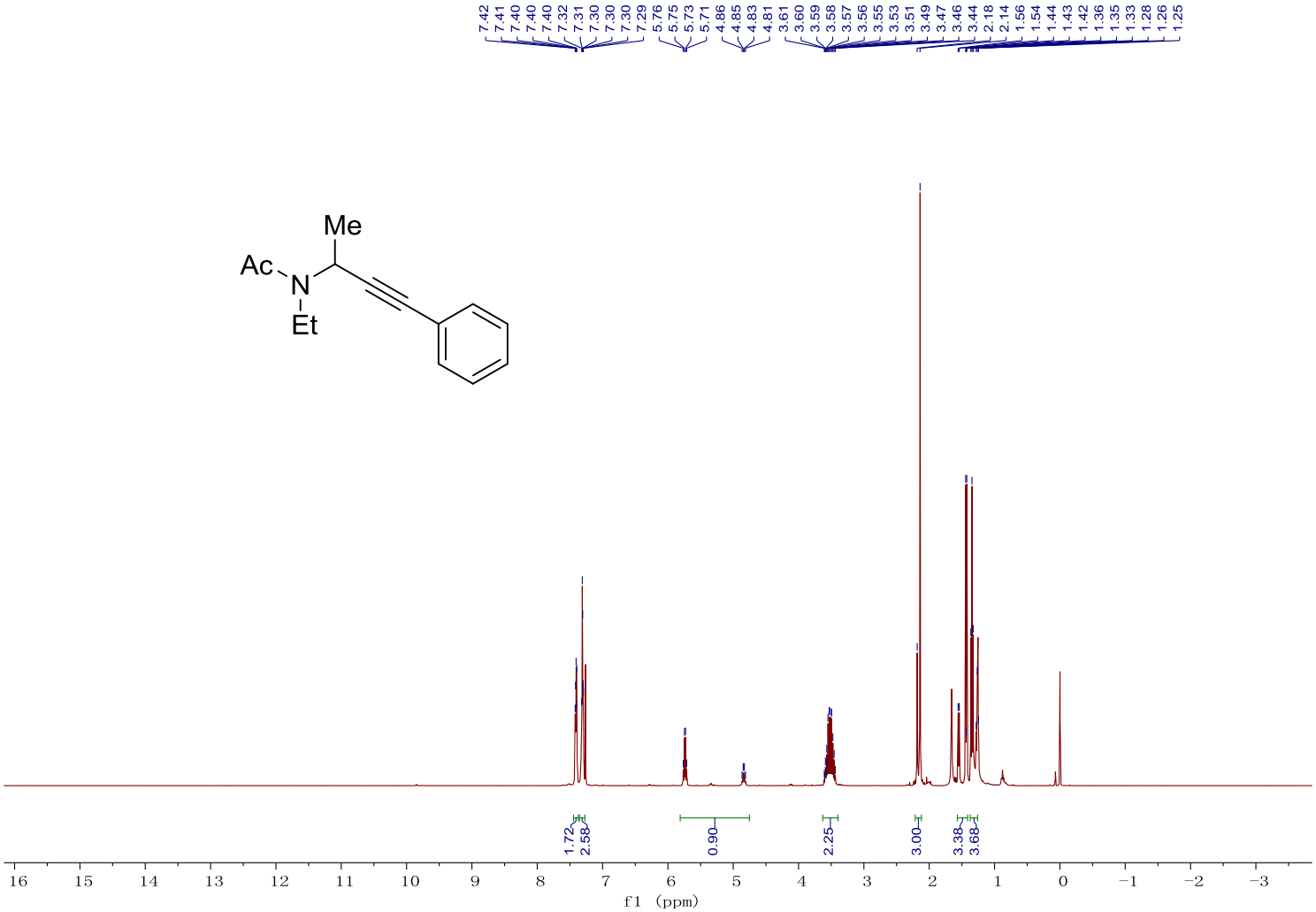
Supplementary Figure 11. Compound **6** ^{1}H NMR in $CDCl_3$



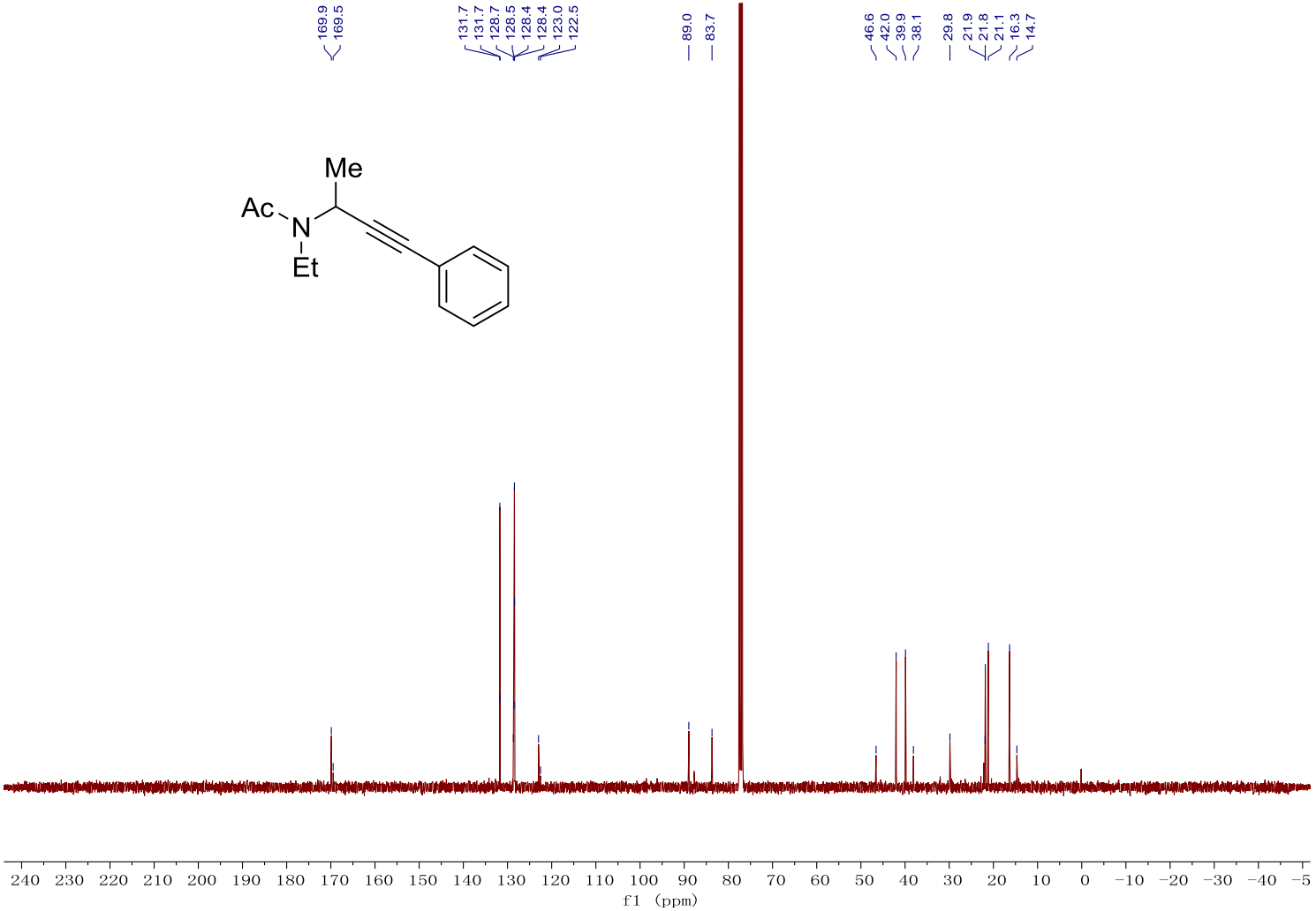
Supplementary Figure 12. Compound **6** ^{13}C NMR in $CDCl_3$



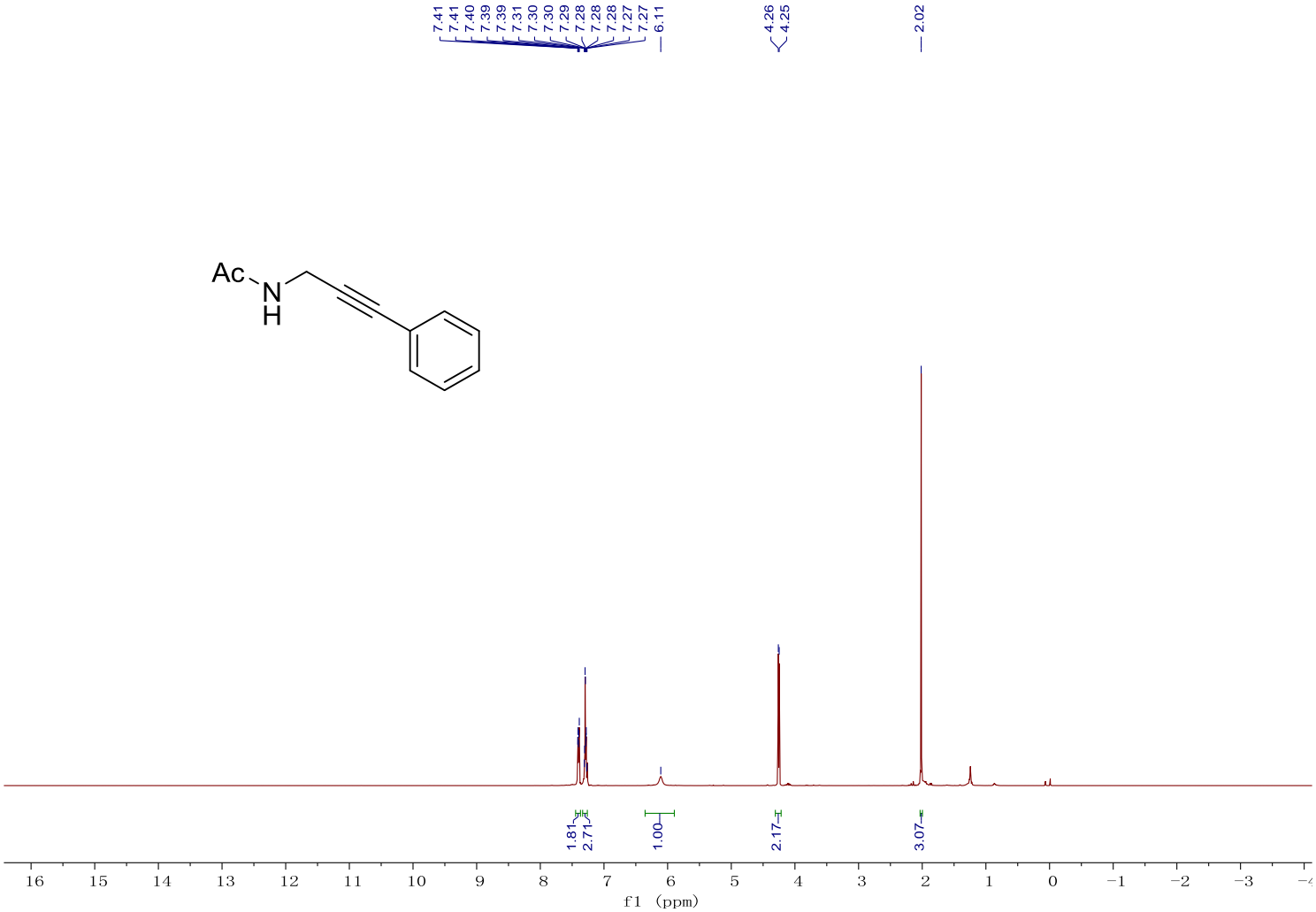
Supplementary Figure 13. Compound **7** ^{1}H NMR in $CDCl_3$



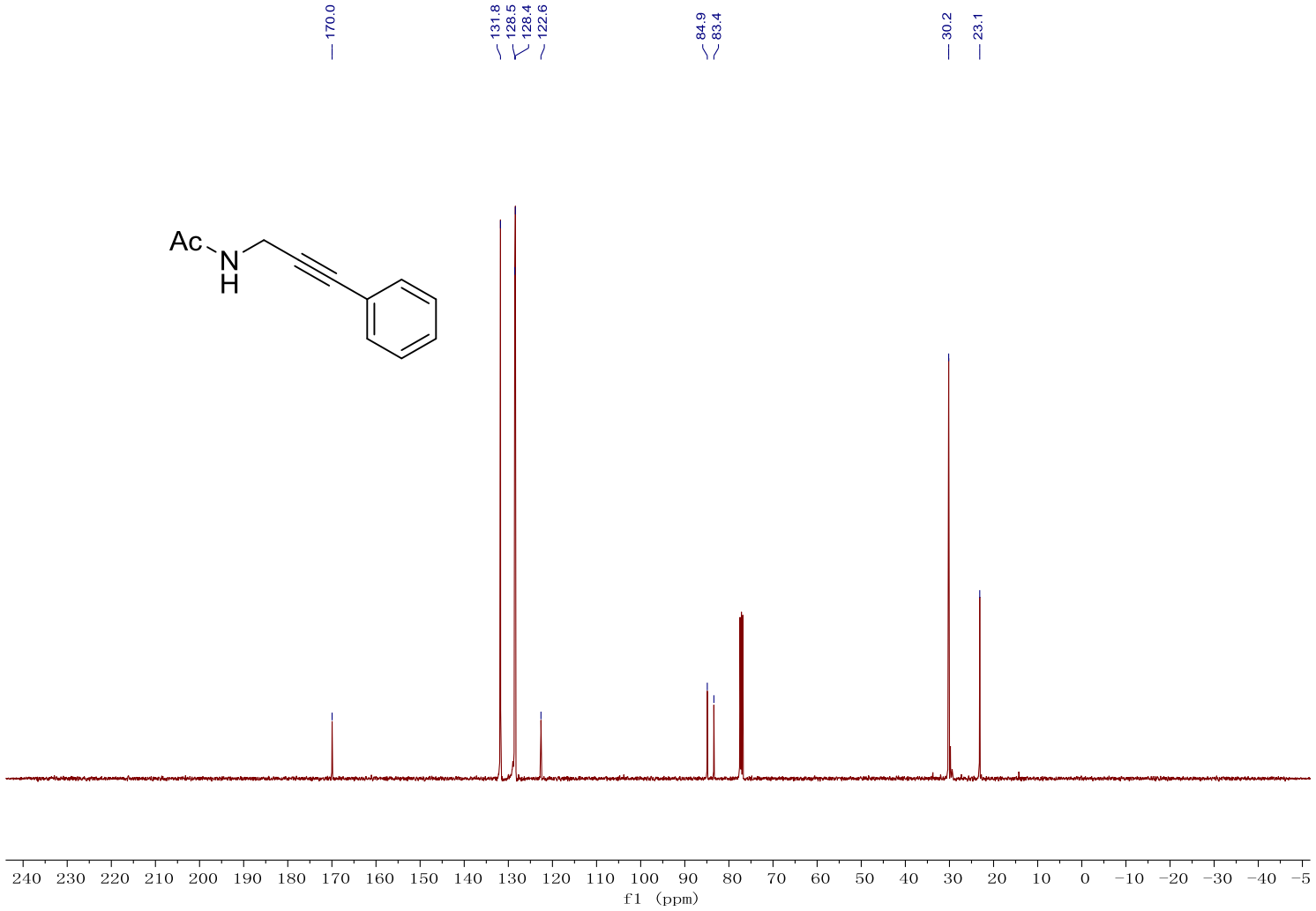
Supplementary Figure 14. Compound **7** ^{13}C NMR in $CDCl_3$



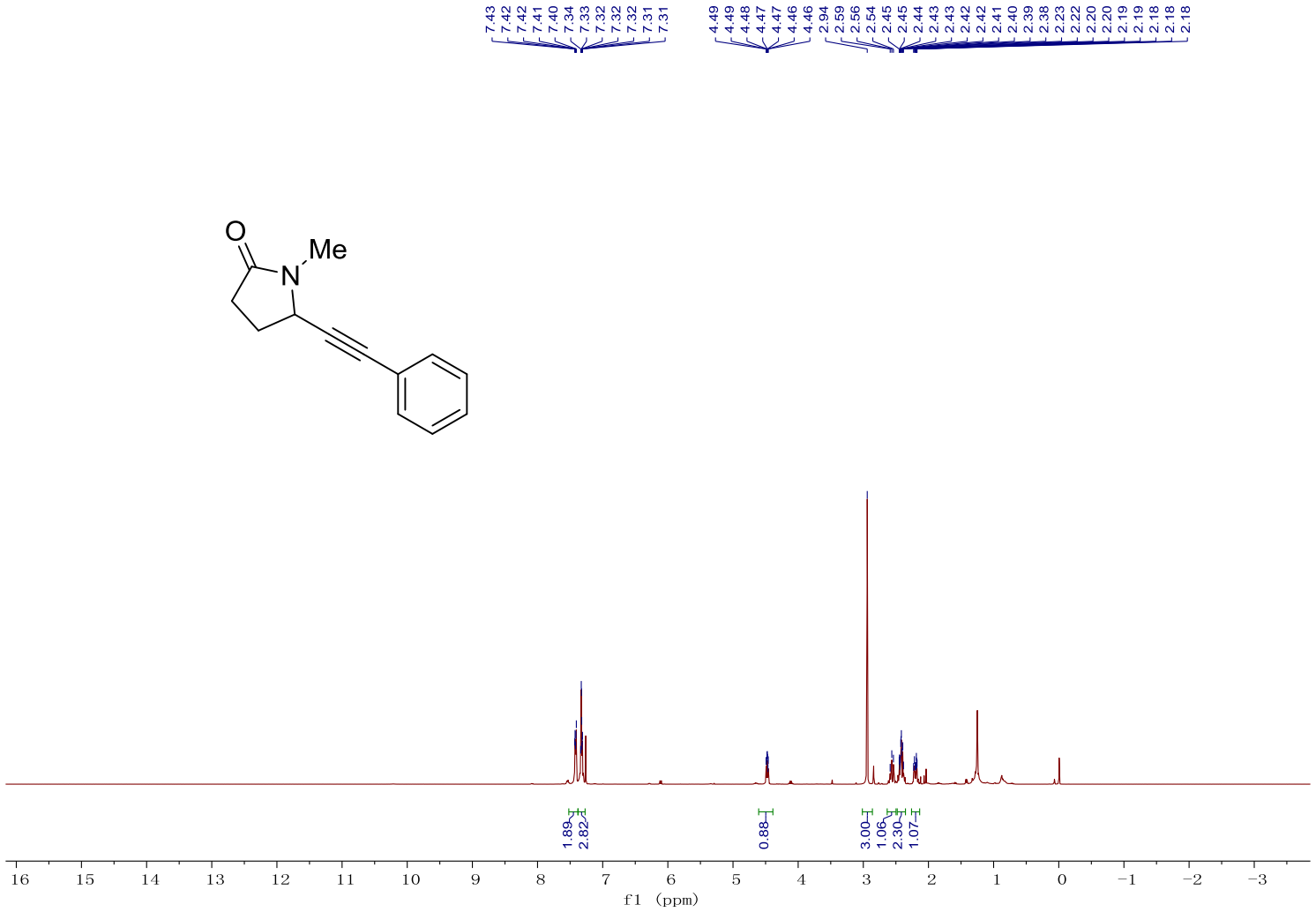
Supplementary Figure 15. Compound **8** ^{1}H NMR in $CDCl_3$



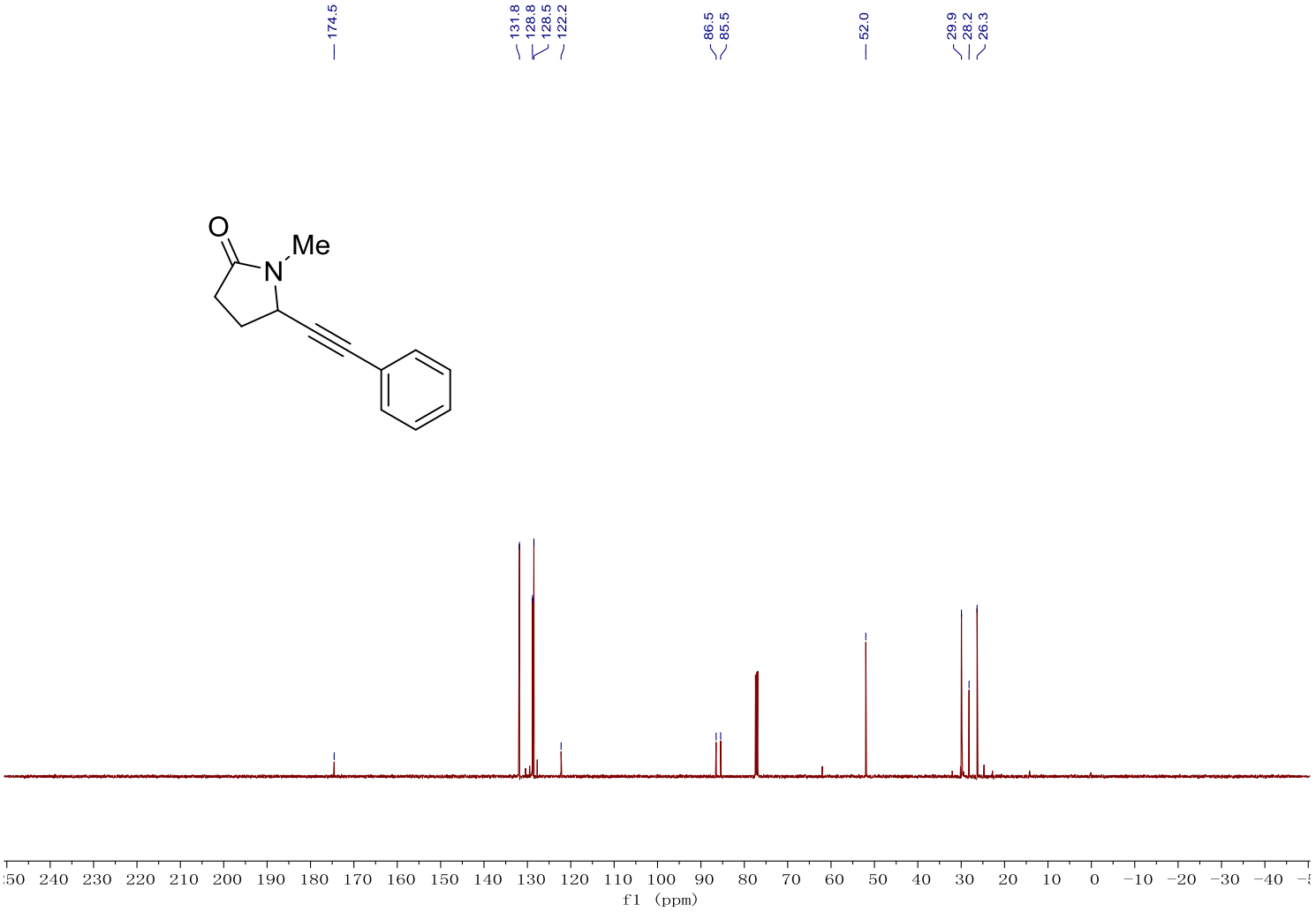
Supplementary Figure 16. Compound **8** ^{13}C NMR in $CDCl_3$



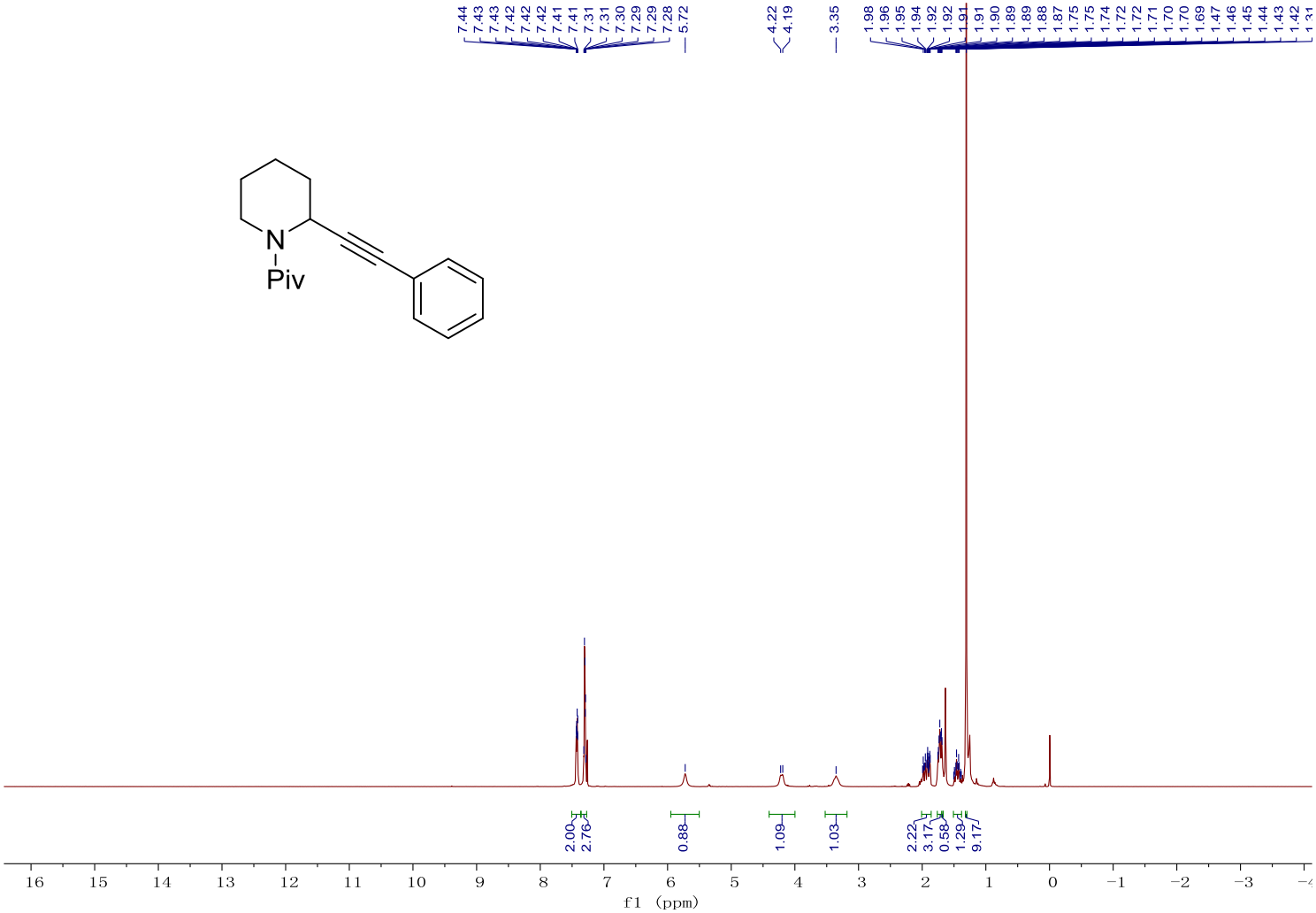
Supplementary Figure 17. Compound **9** ^{1}H NMR in $CDCl_3$



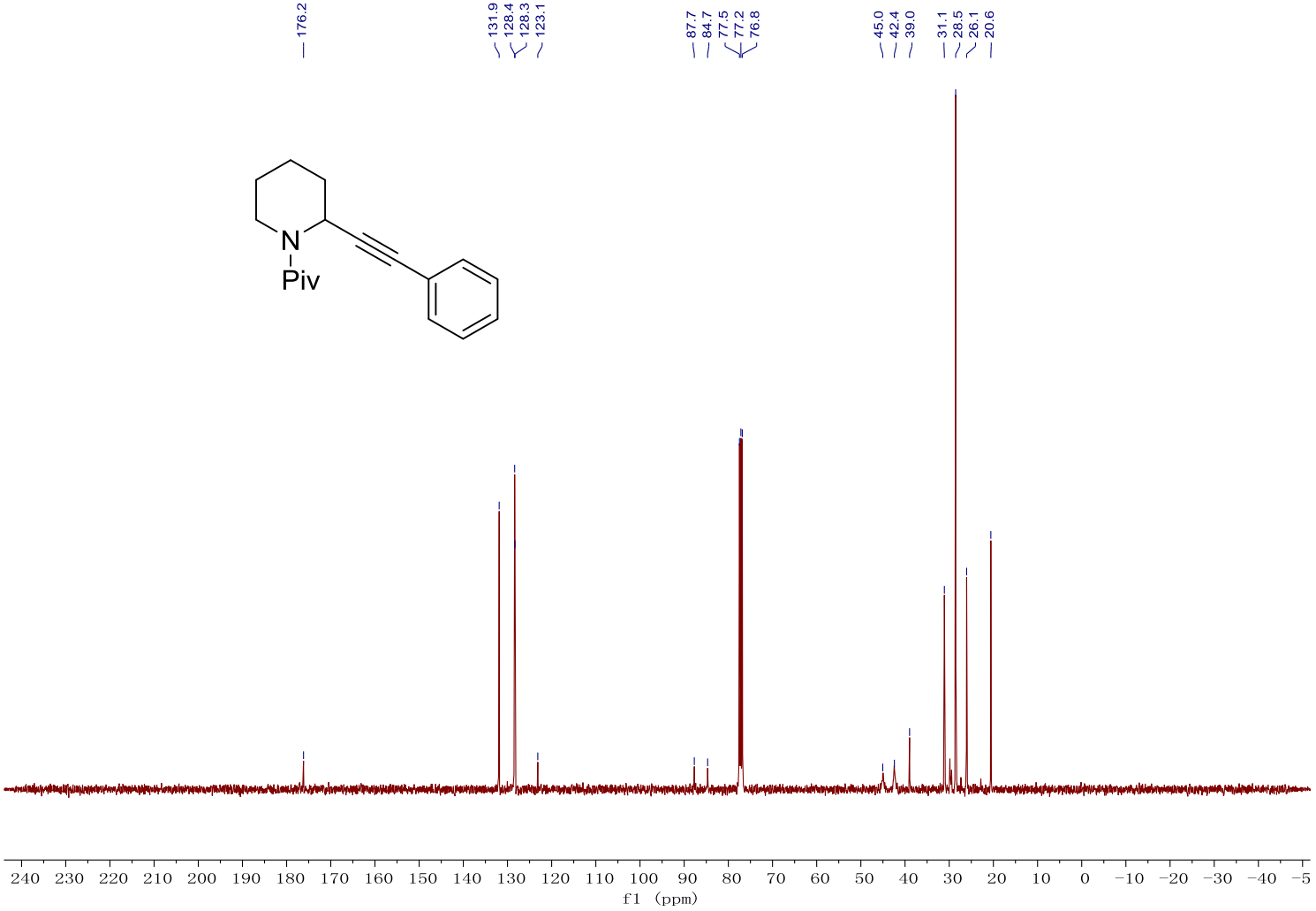
Supplementary Figure 18. Compound **9** ^{13}C NMR in $CDCl_3$



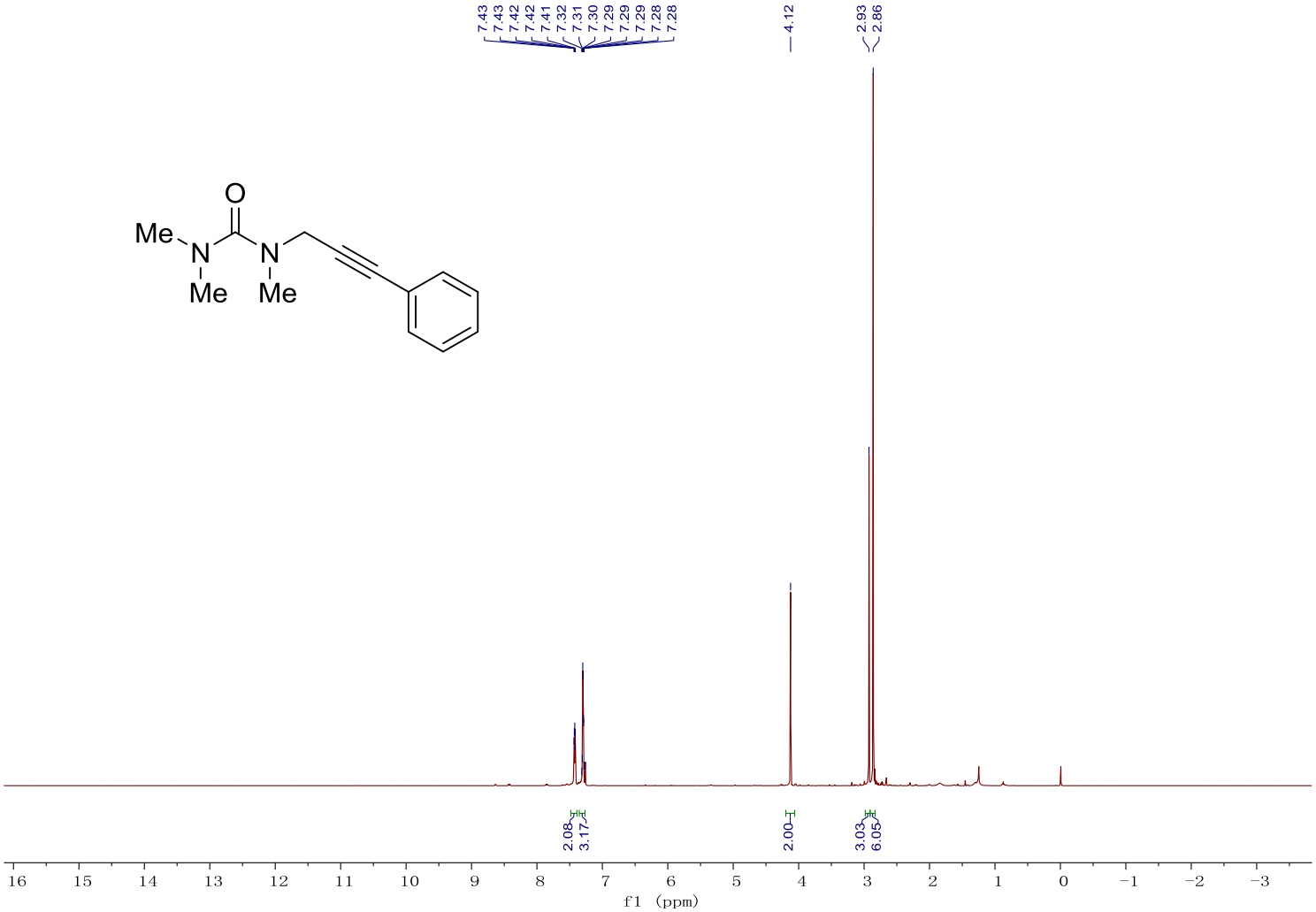
Supplementary Figure 19. Compound **10** ^{1}H NMR in $CDCl_3$



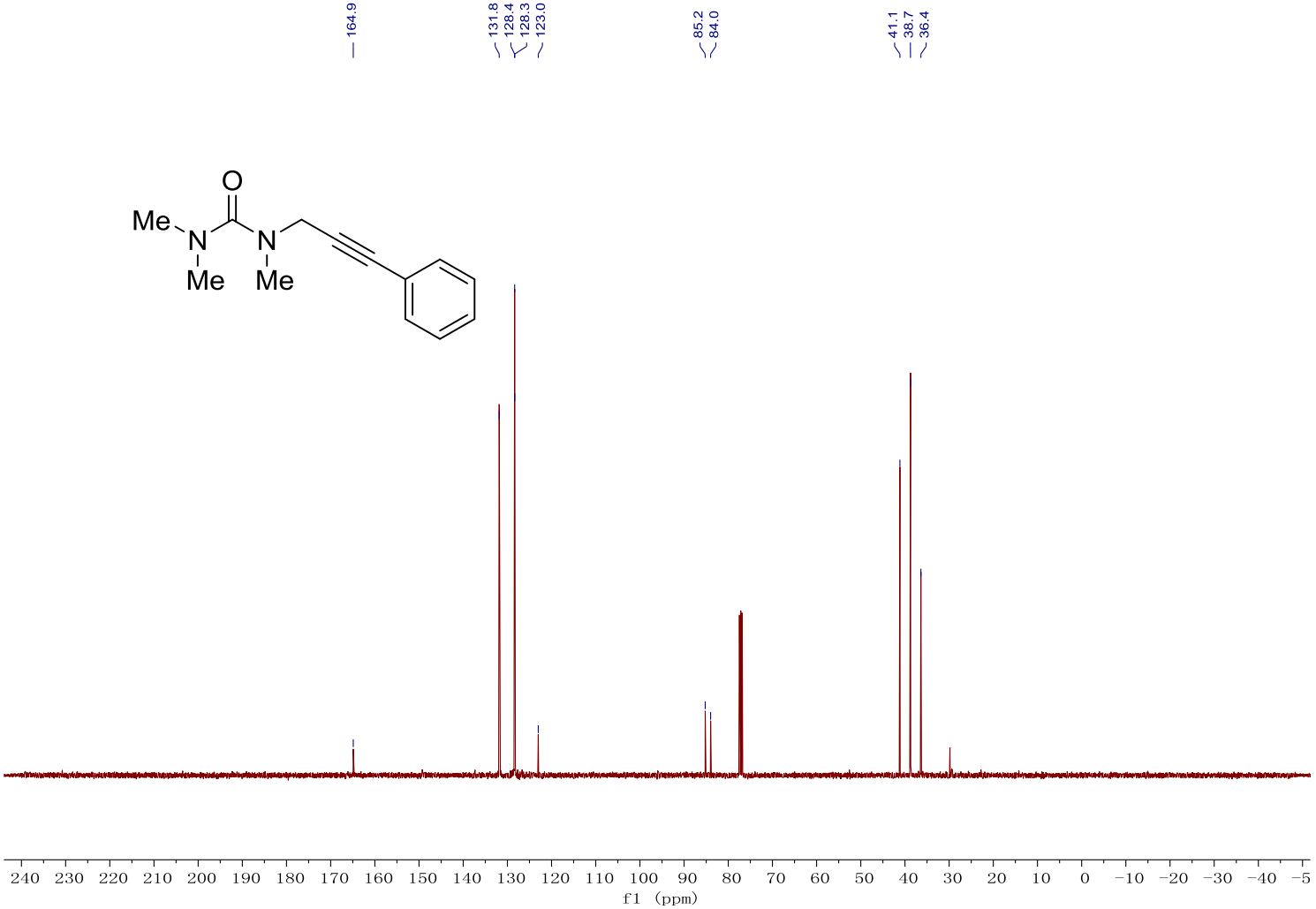
Supplementary Figure 20. Compound **10** ^{13}C NMR in $CDCl_3$



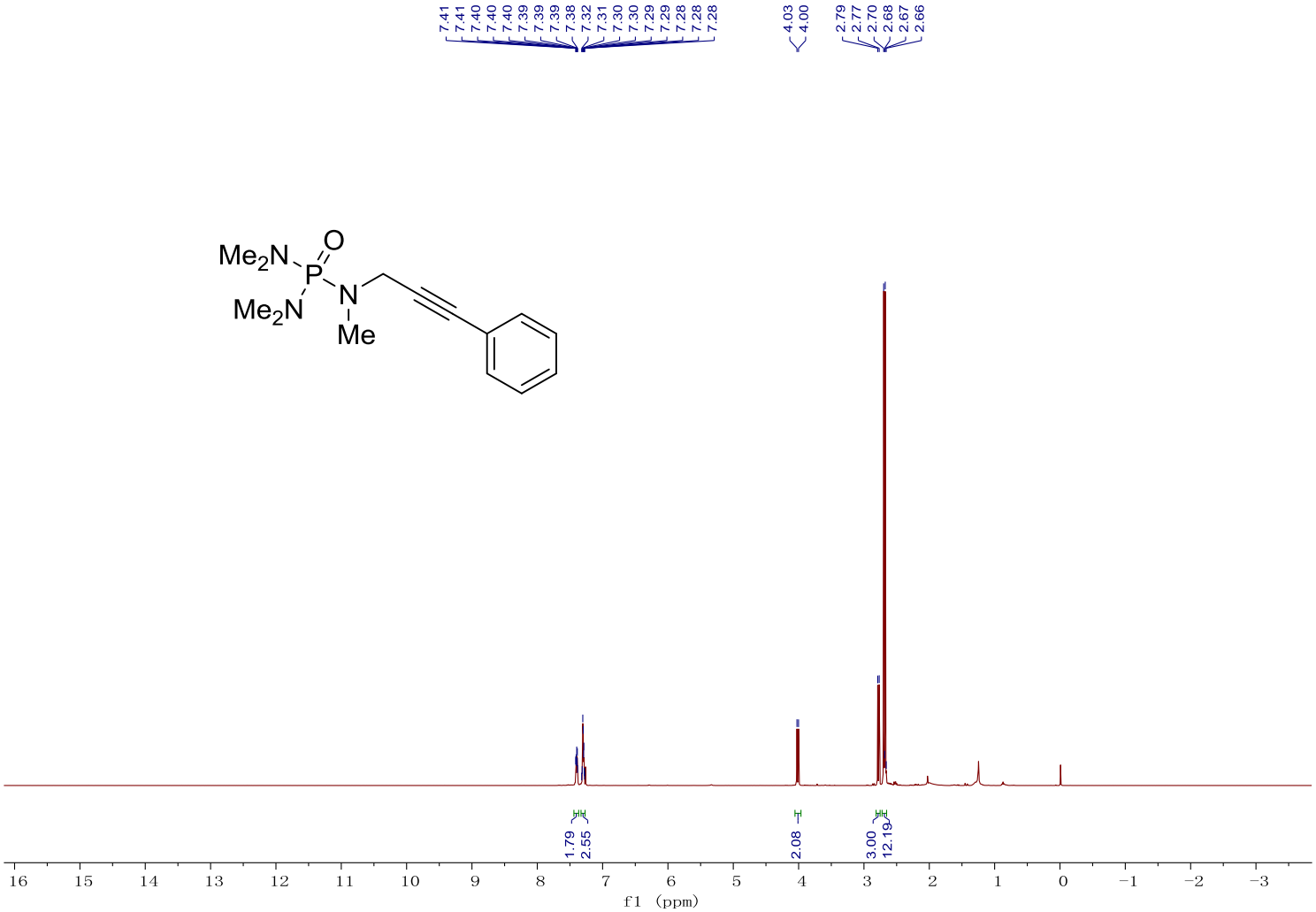
Supplementary Figure 21. Compound **11** ^{1}H NMR in $CDCl_3$



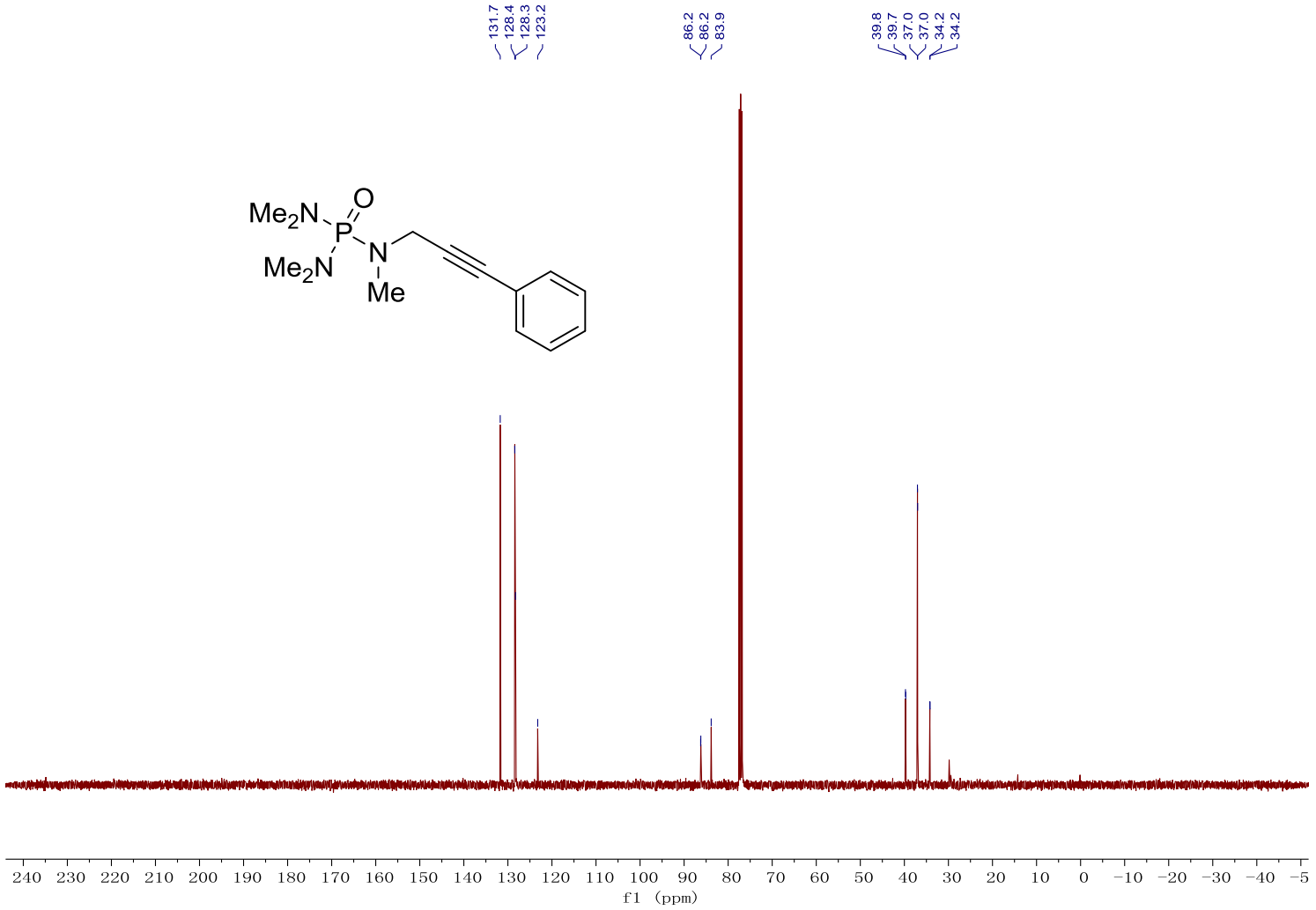
Supplementary Figure 22. Compound **11** ^{13}C NMR in $CDCl_3$



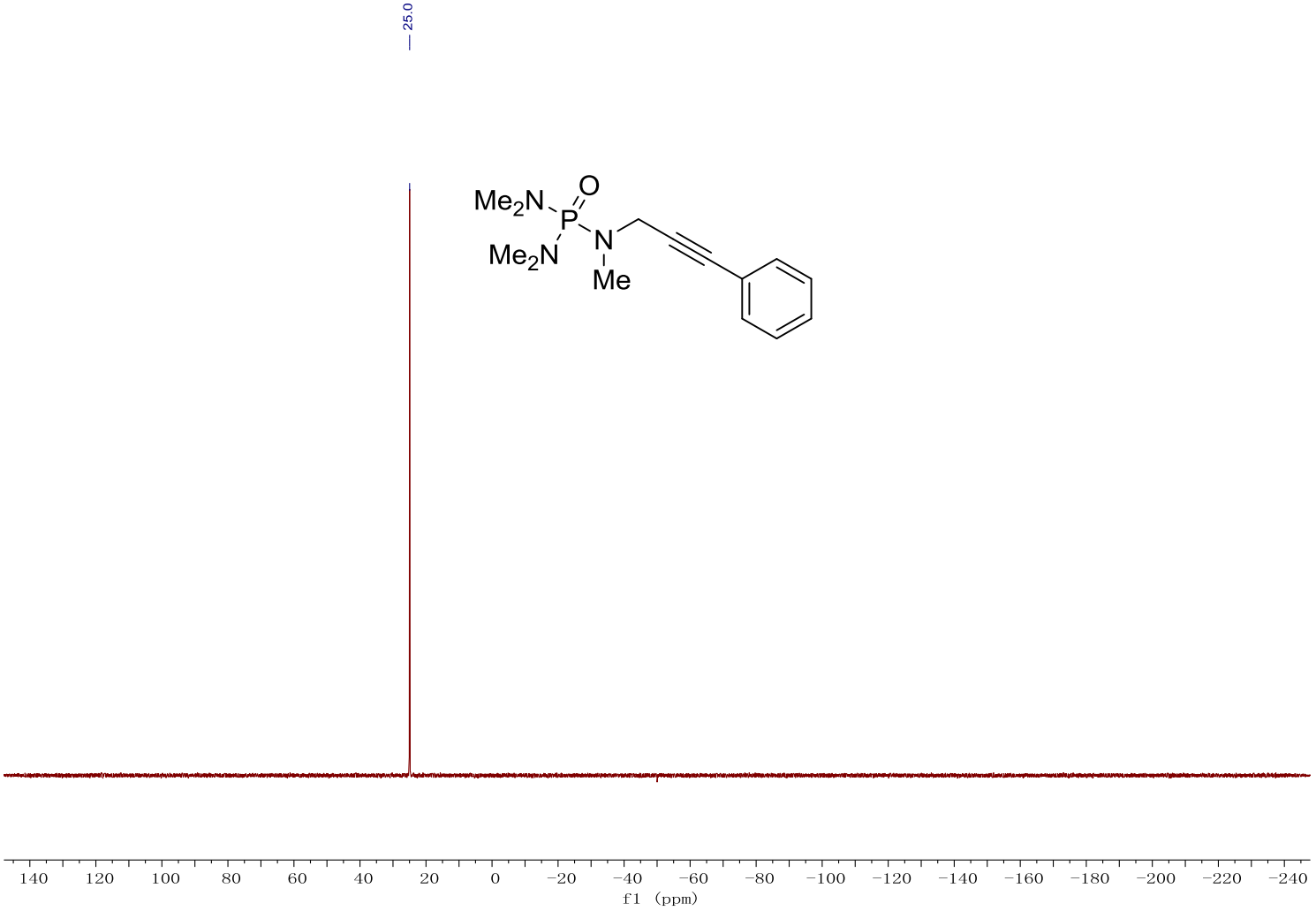
Supplementary Figure 23. Compound **12** ^{1}H NMR in $CDCl_3$



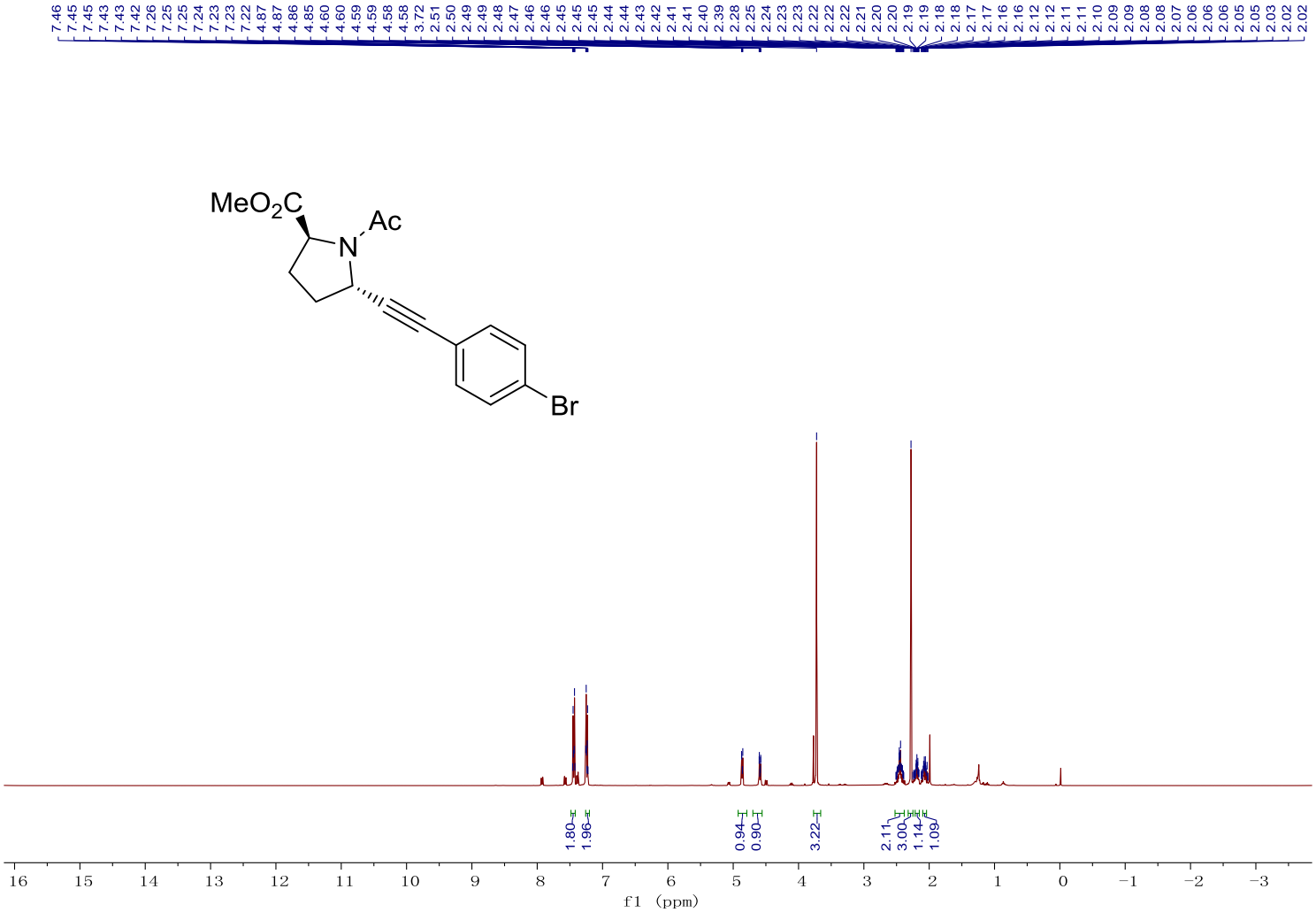
Supplementary Figure 24. Compound **12** ^{13}C NMR in $CDCl_3$



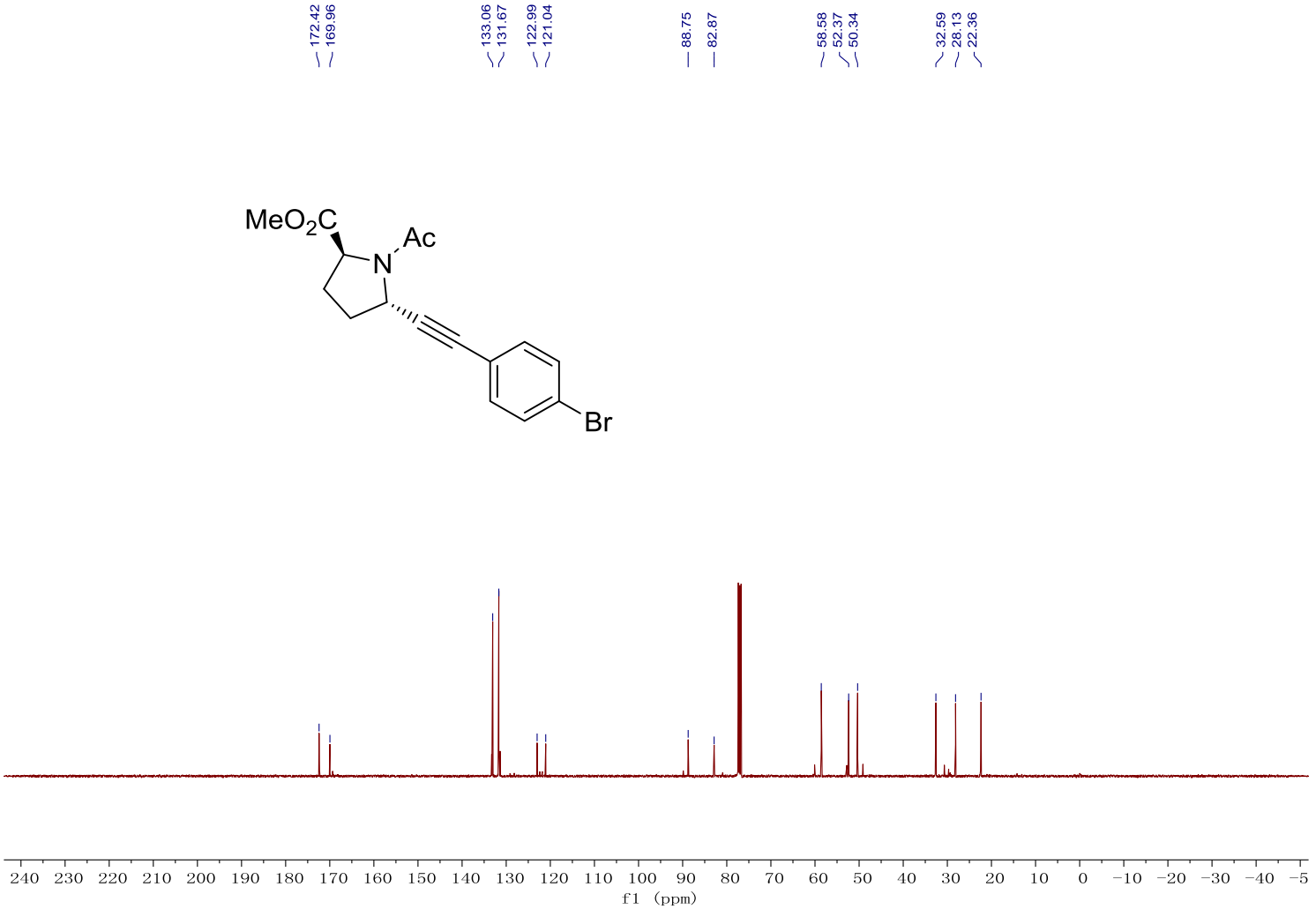
Supplementary Figure 25. Compound **12** ^{31}P NMR in $CDCl_3$



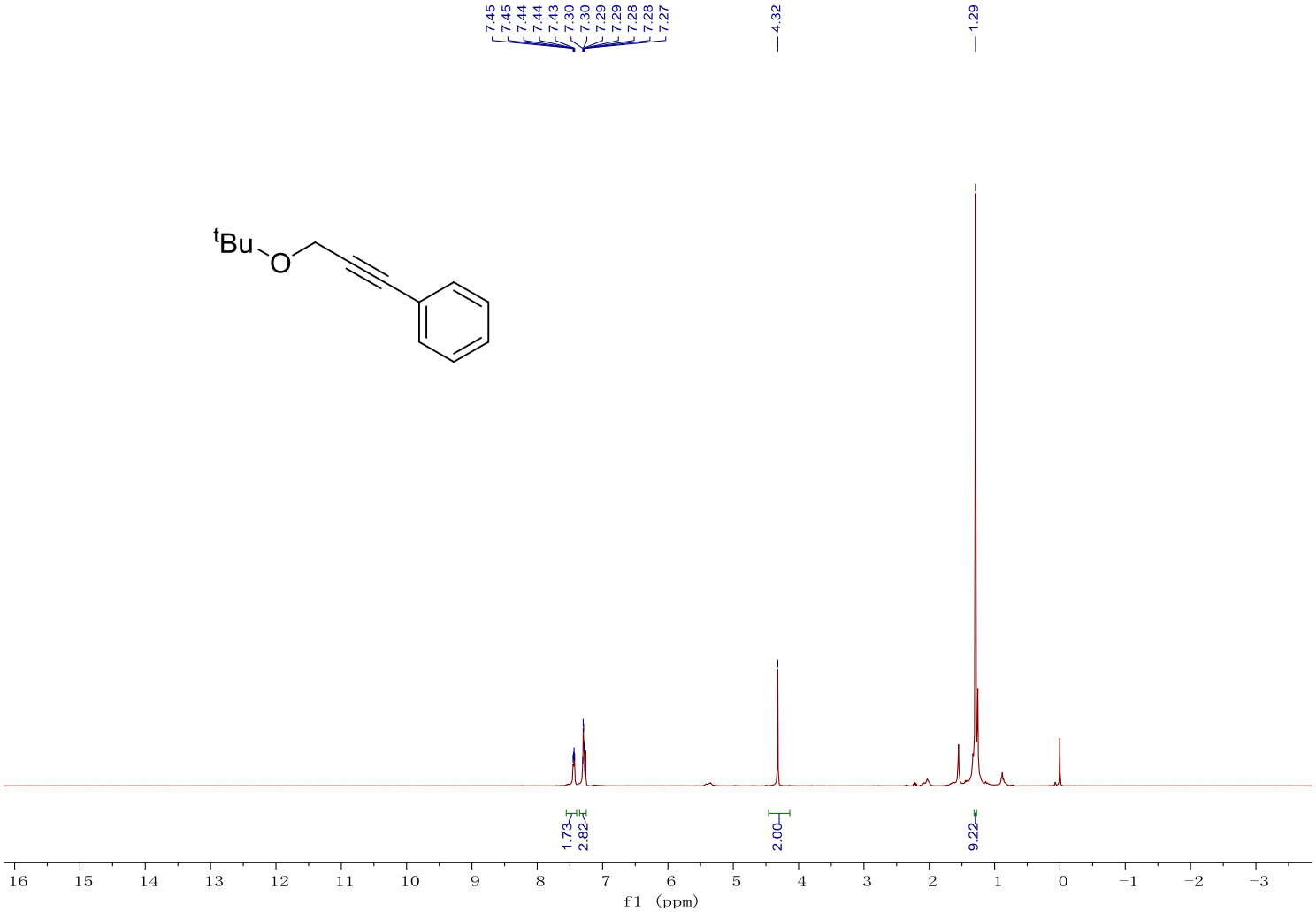
Supplementary Figure 26. Compound **13** ^{1}H NMR in $CDCl_3$



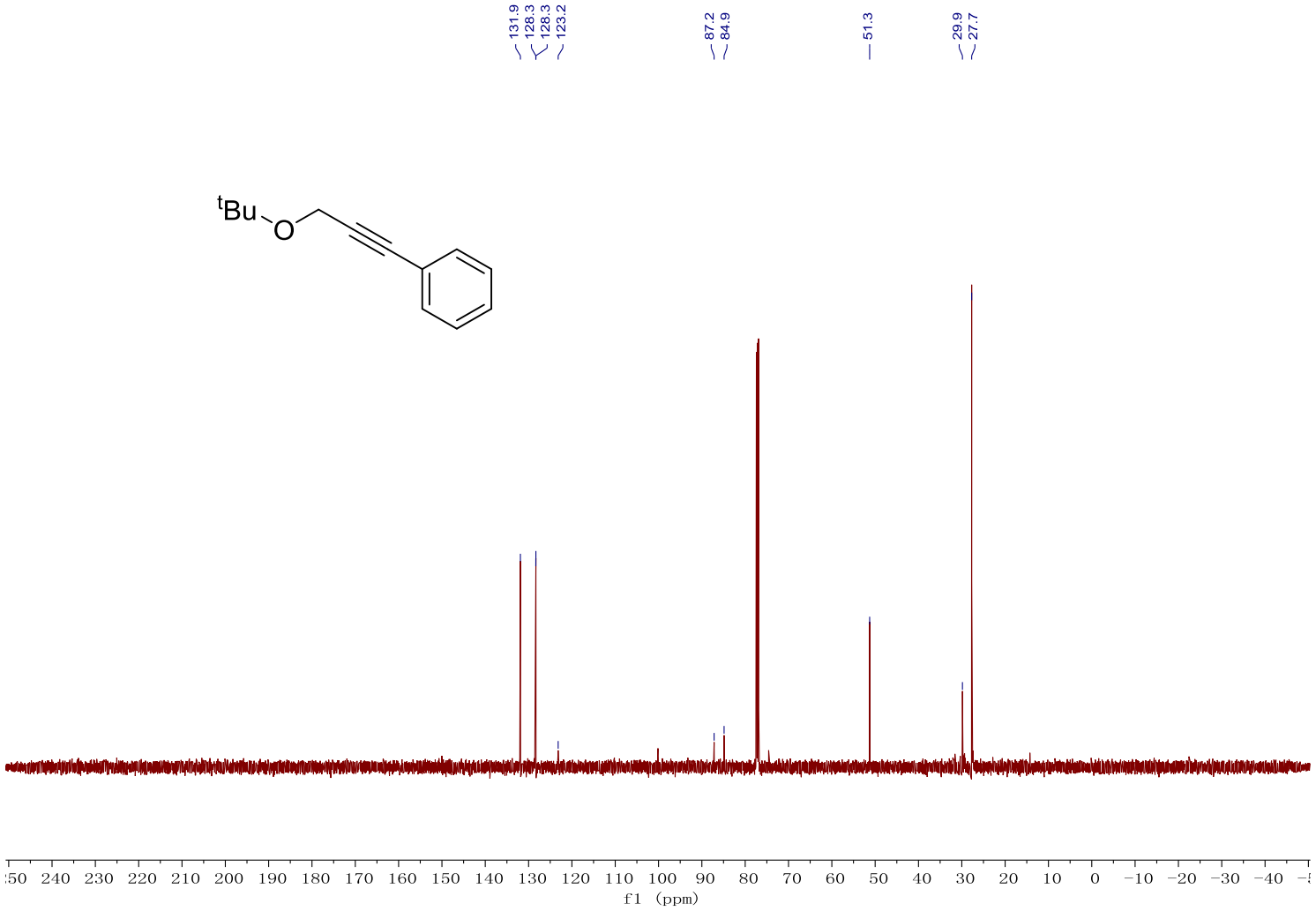
Supplementary Figure 27. Compound **13** ^{13}C NMR in $CDCl_3$



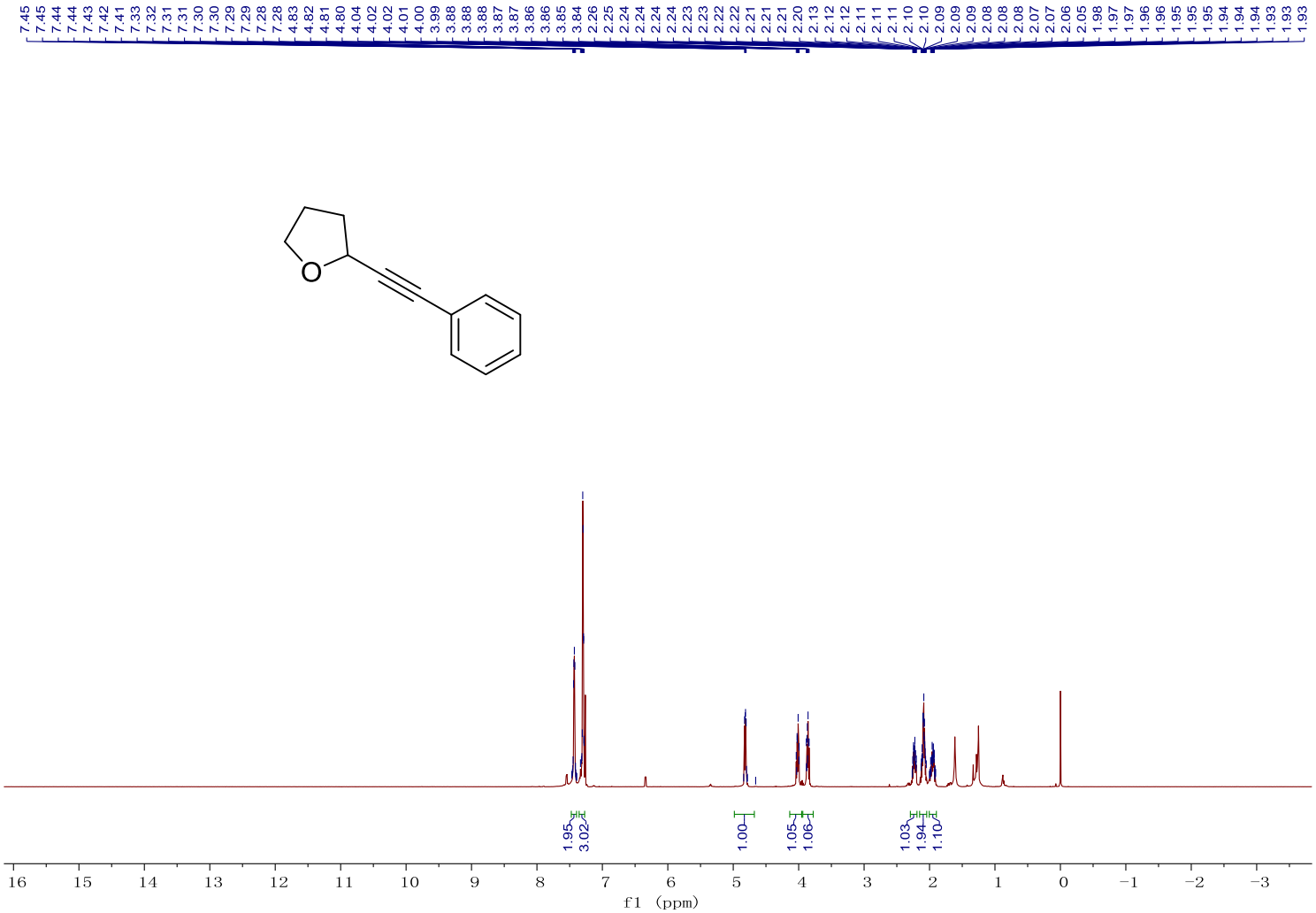
Supplementary Figure 28. Compound **14** ^{1}H NMR in $CDCl_3$



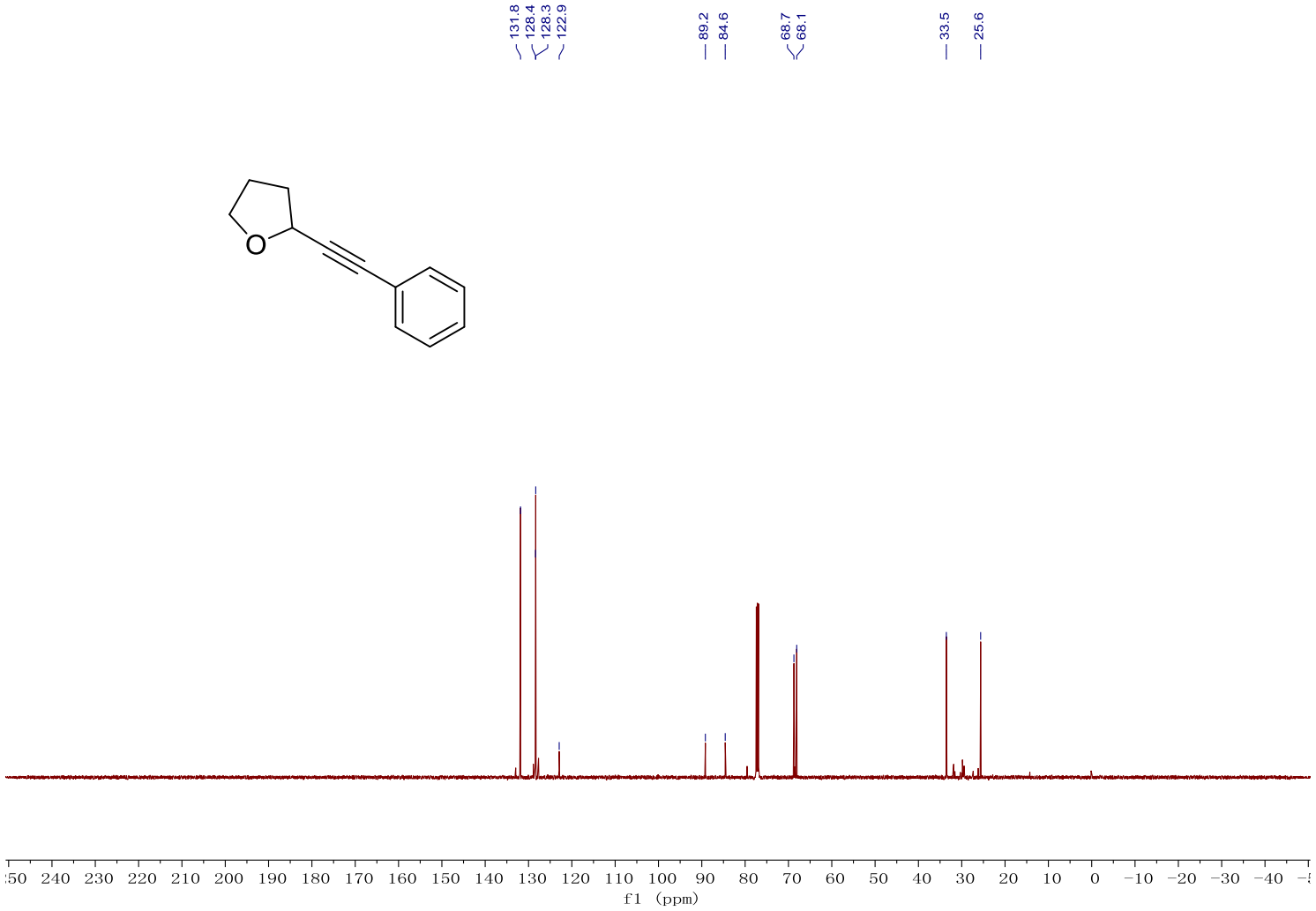
Supplementary Figure 29. Compound **14** ^{13}C NMR in $CDCl_3$



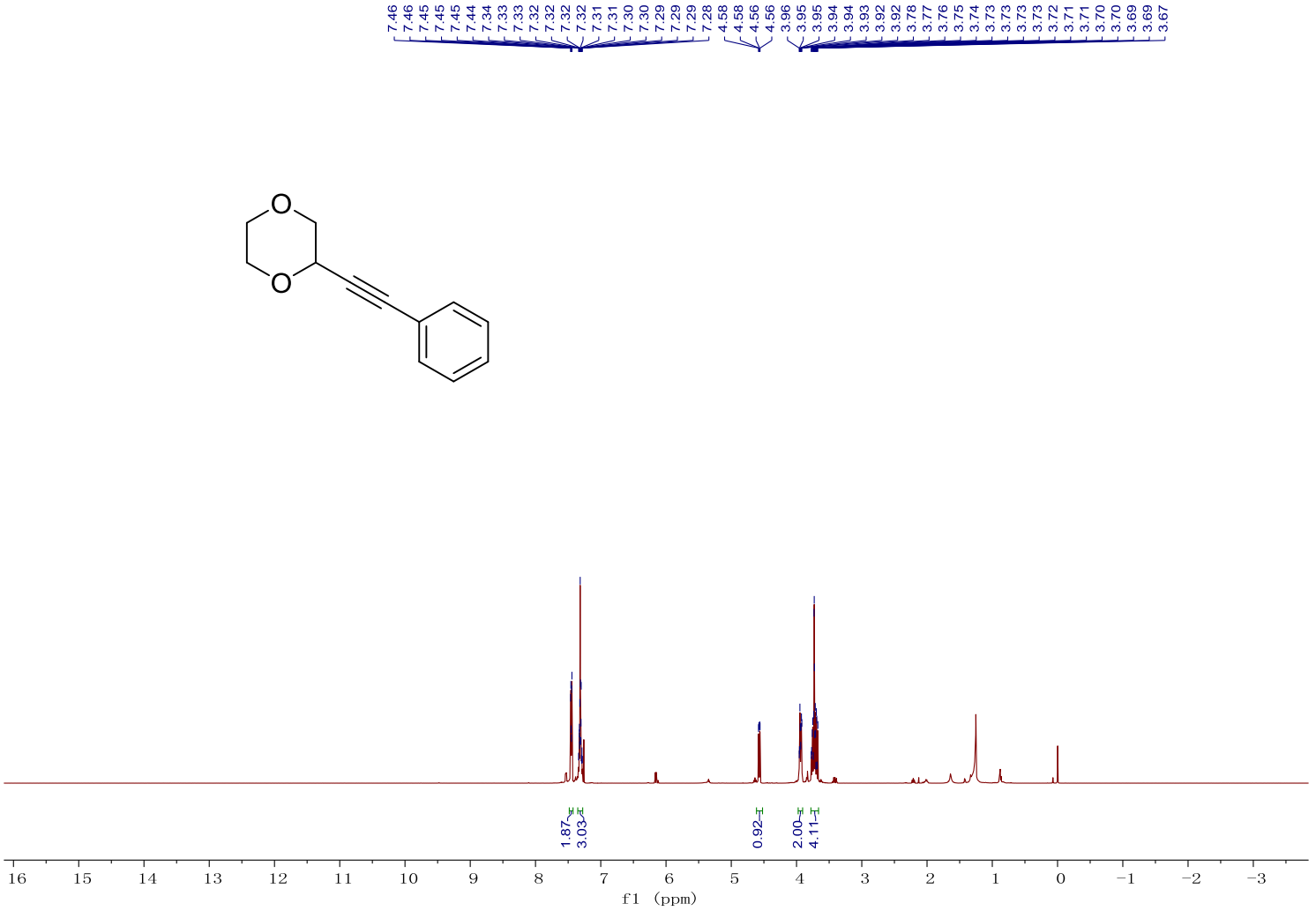
Supplementary Figure 30. Compound **15** ^{1}H NMR in $CDCl_3$



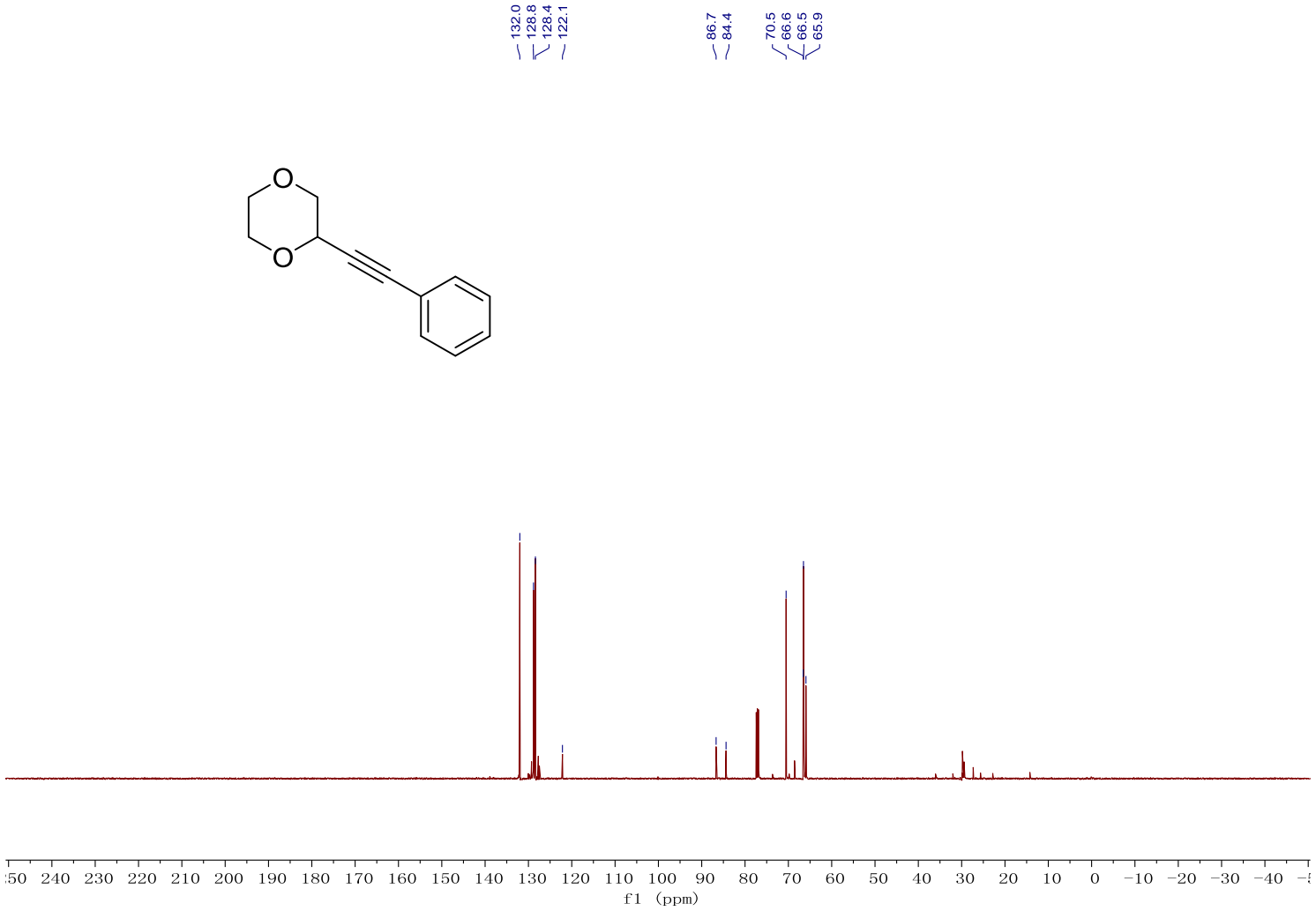
Supplementary Figure 31. Compound **15** ^{13}C NMR in $CDCl_3$



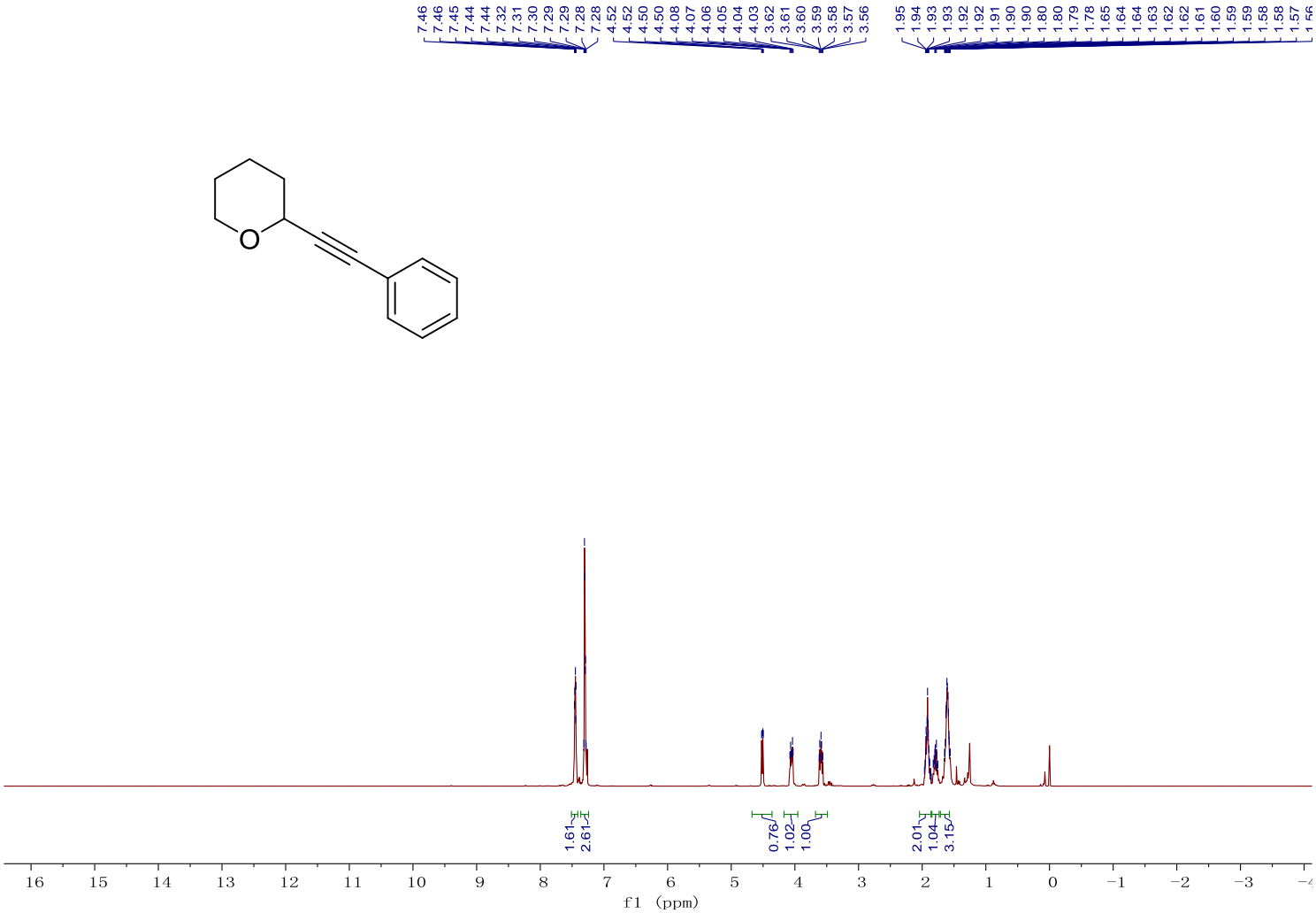
Supplementary Figure 32. Compound **16** ^{1}H NMR in $CDCl_3$



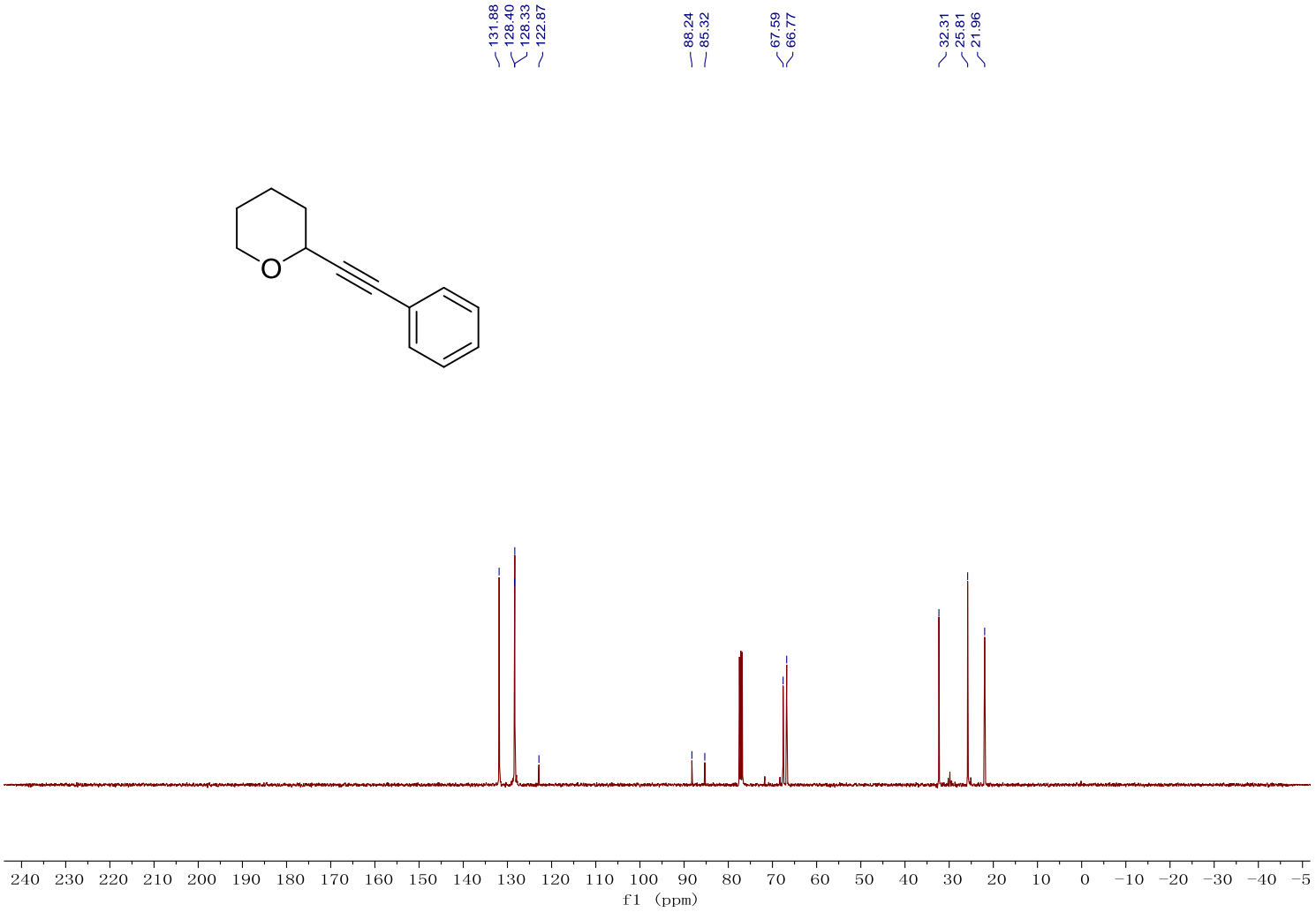
Supplementary Figure 33. Compound **16** ^{13}C NMR in $CDCl_3$



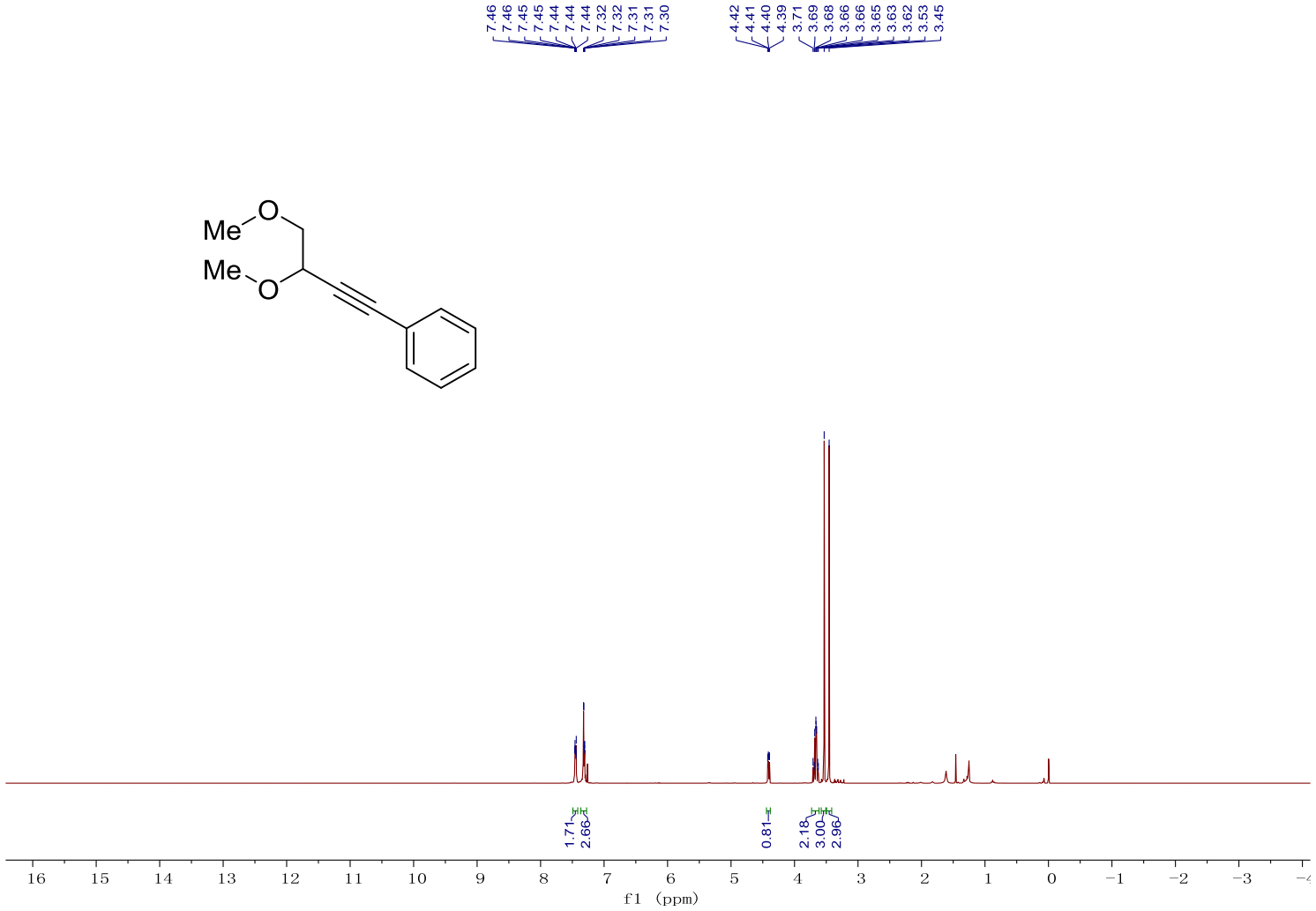
Supplementary Figure 34. Compound **17** ^{1}H NMR in $CDCl_3$



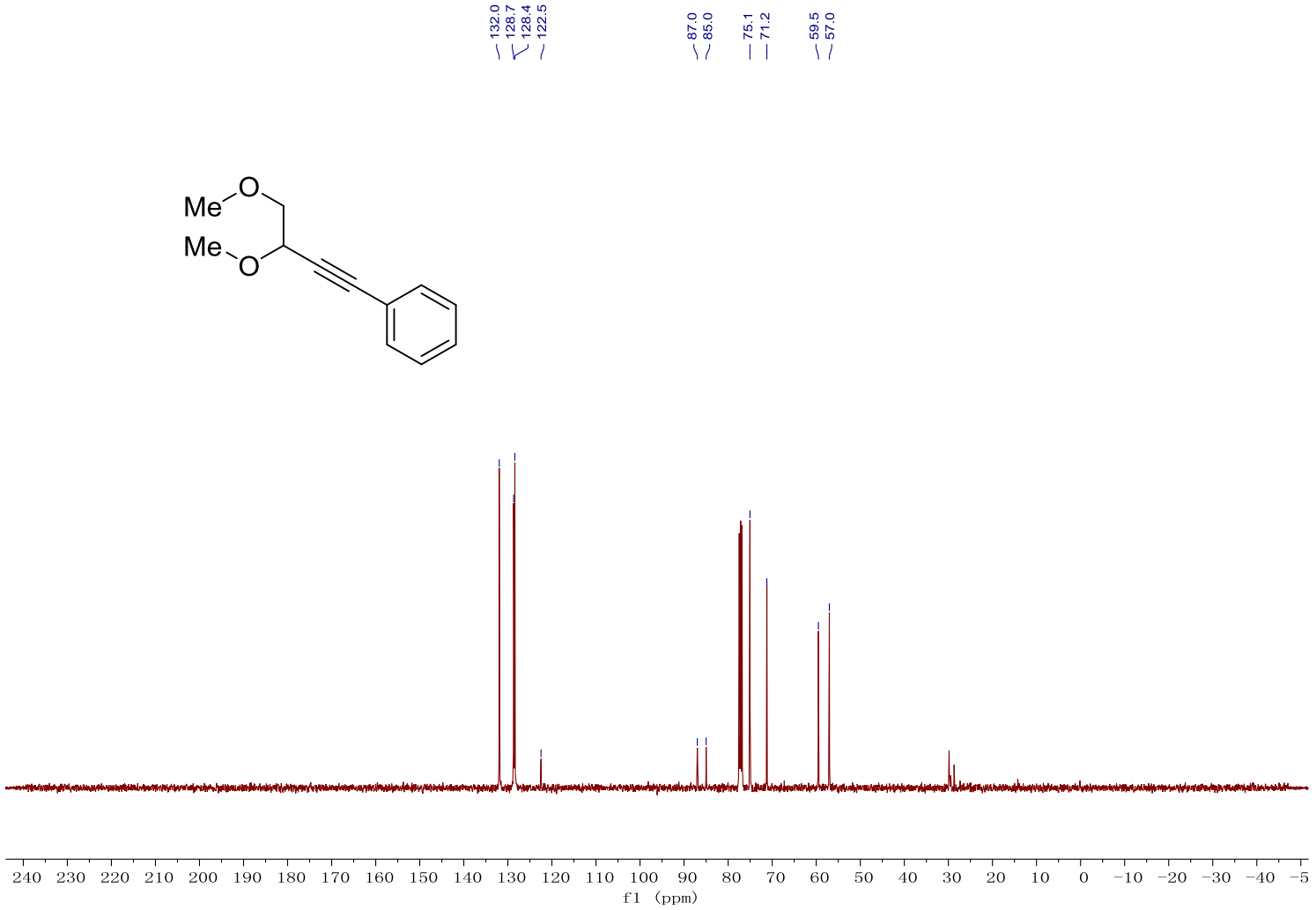
Supplementary Figure 35. Compound **17** ^{13}C NMR in $CDCl_3$



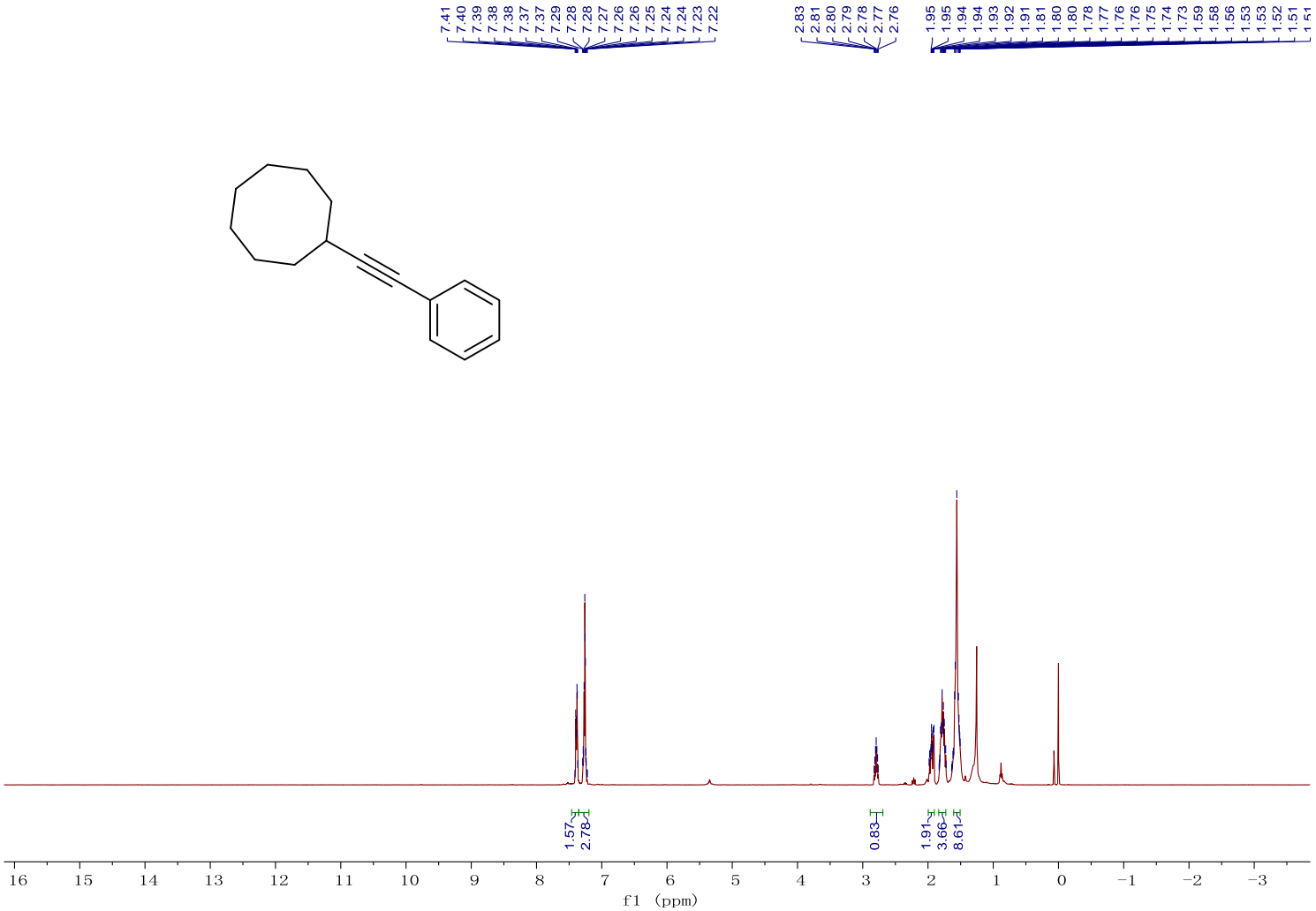
Supplementary Figure 36. Compound **18** ^{1}H NMR in $CDCl_3$



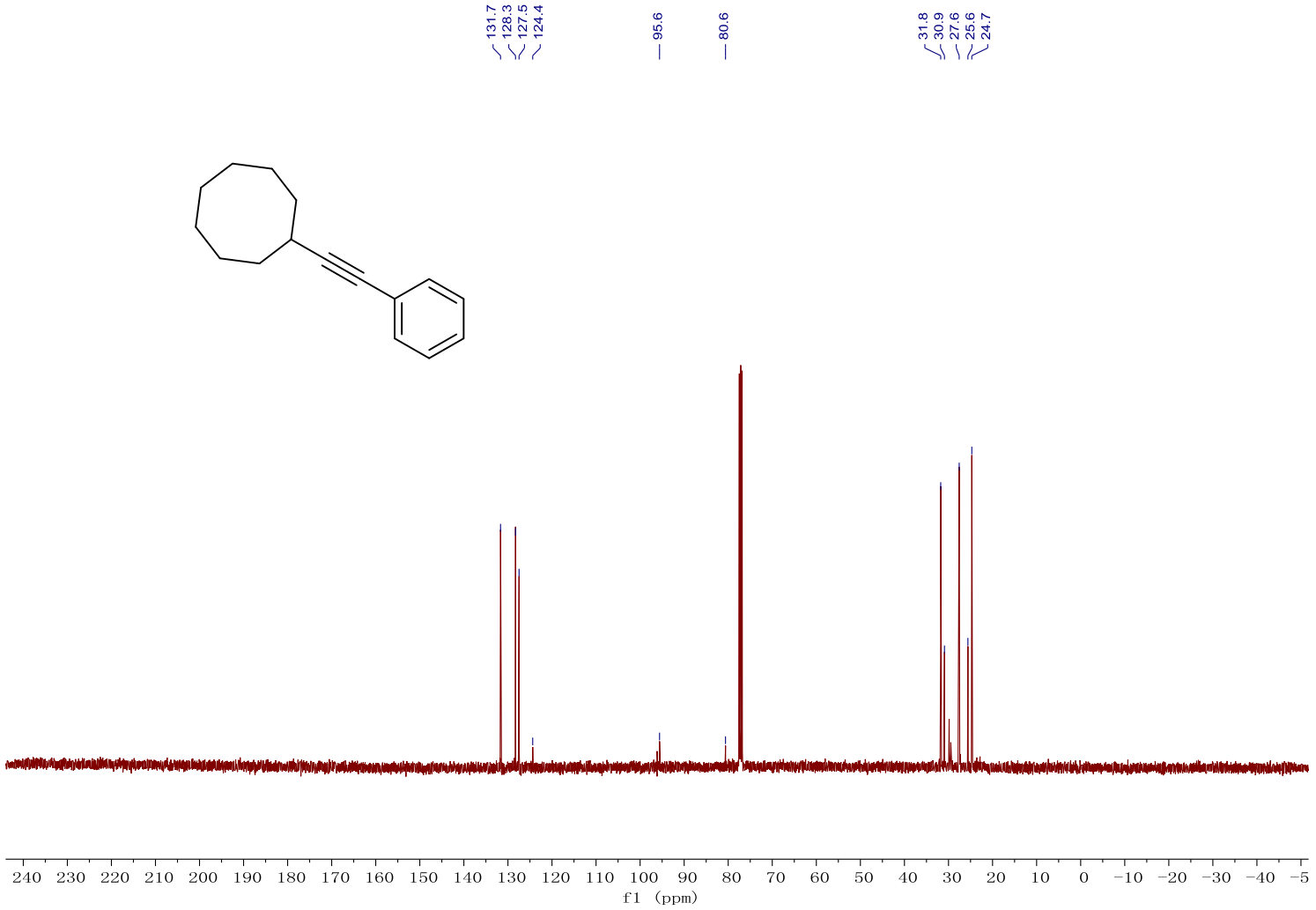
Supplementary Figure 37. Compound **18** ^{13}C NMR in $CDCl_3$



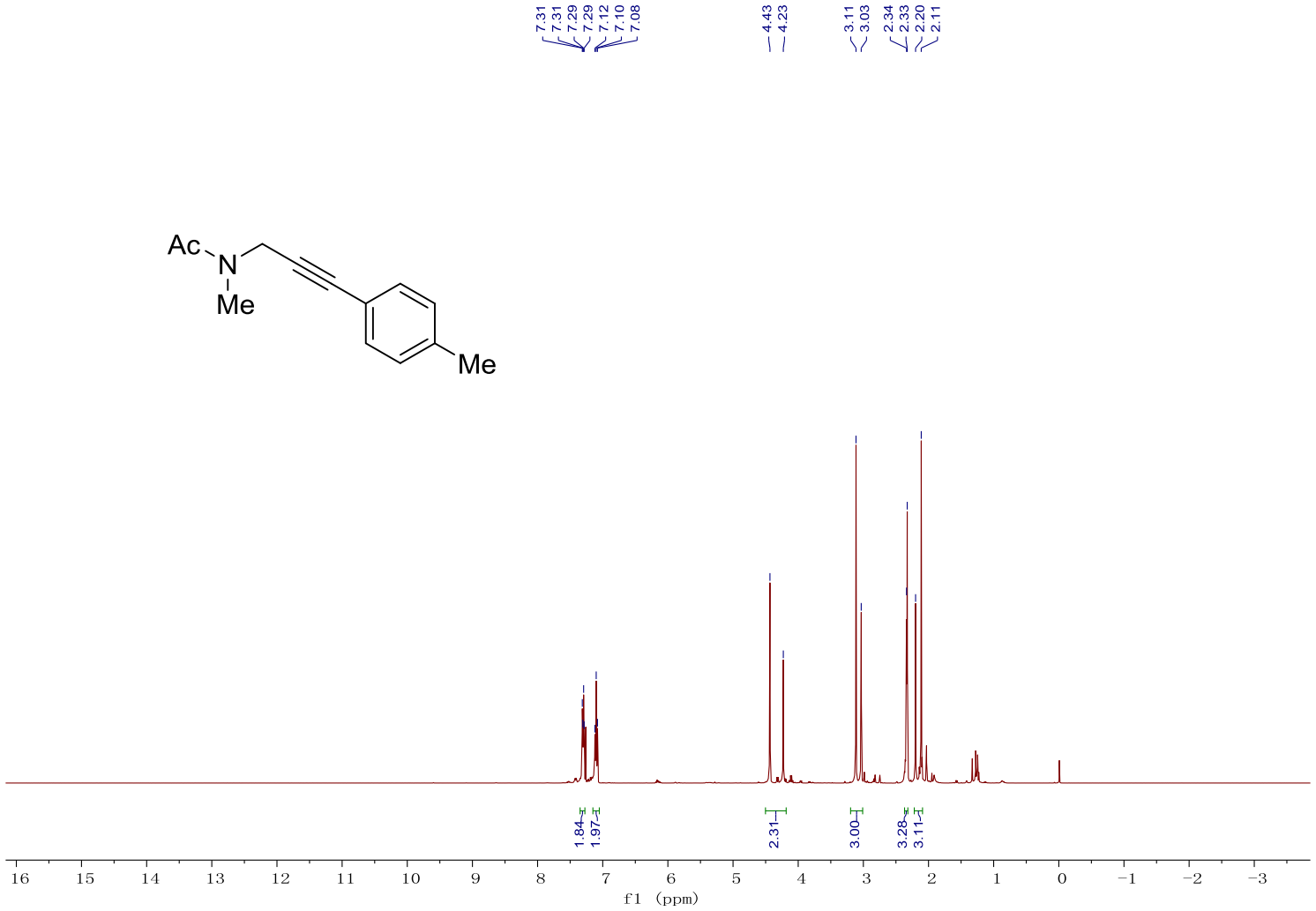
Supplementary Figure 38. Compound **19** ^{1}H NMR in $CDCl_3$



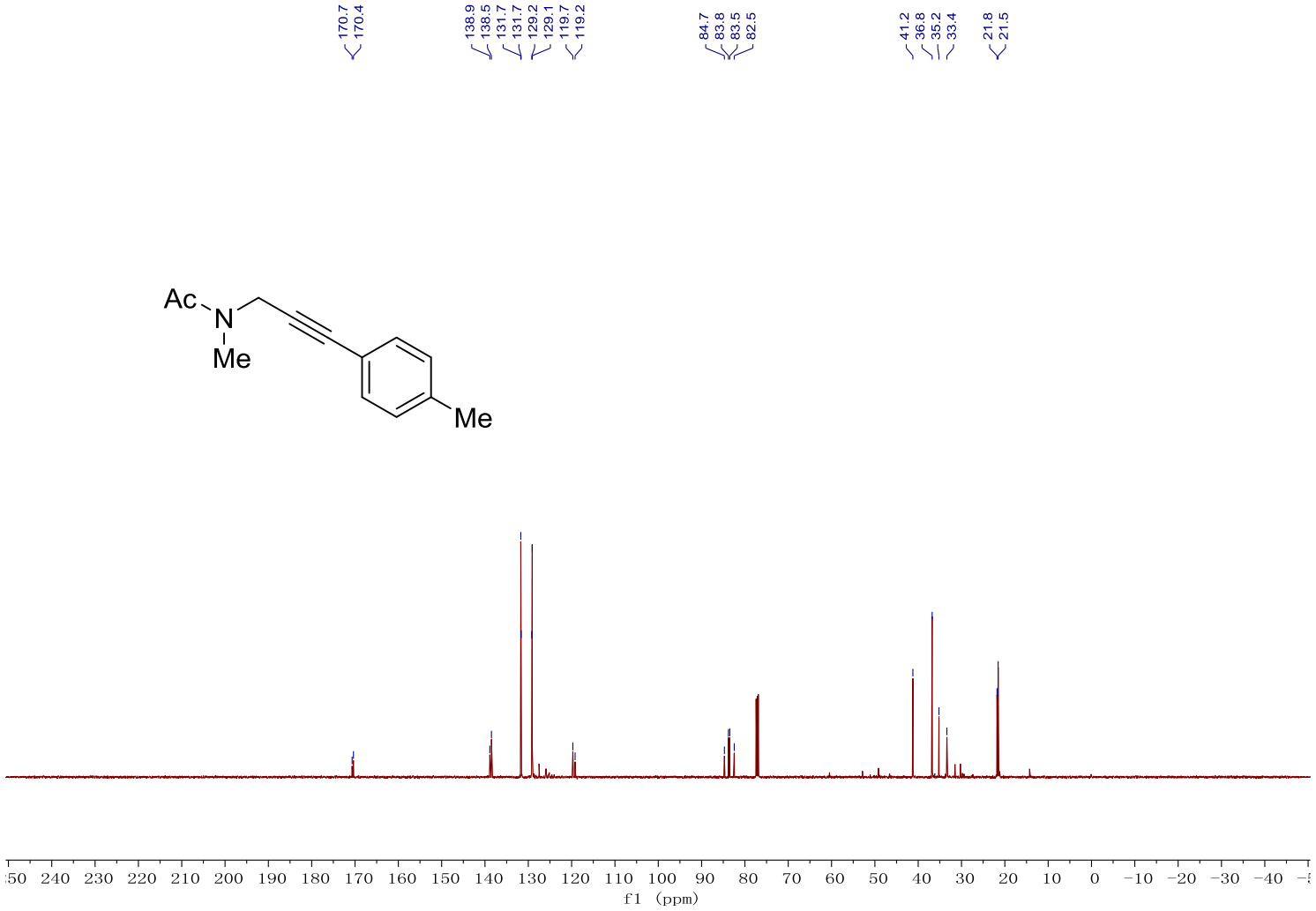
Supplementary Figure 39. Compound **19** ^{13}C NMR in $CDCl_3$



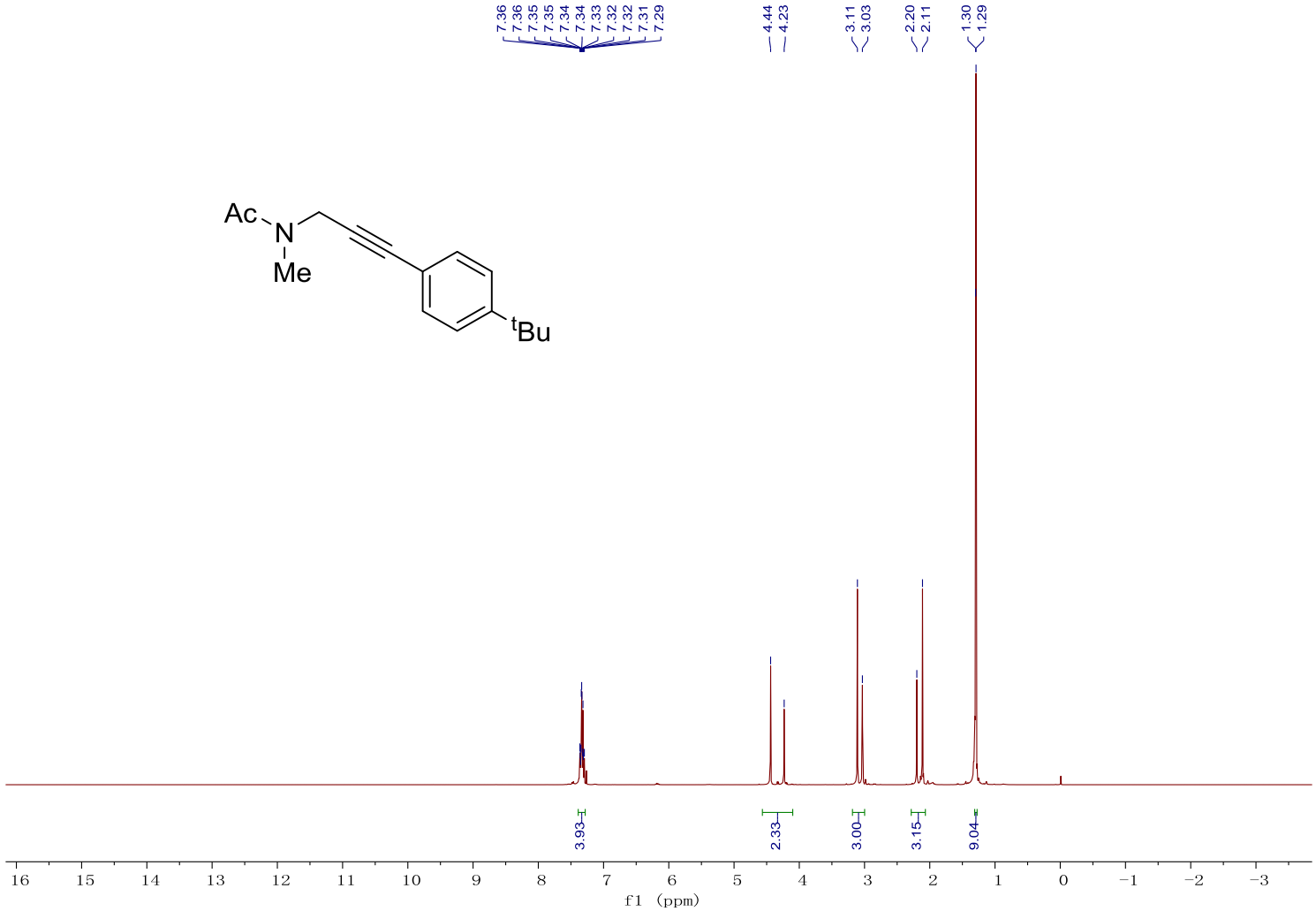
Supplementary Figure 40. Compound **20** ^{1}H NMR in $CDCl_3$



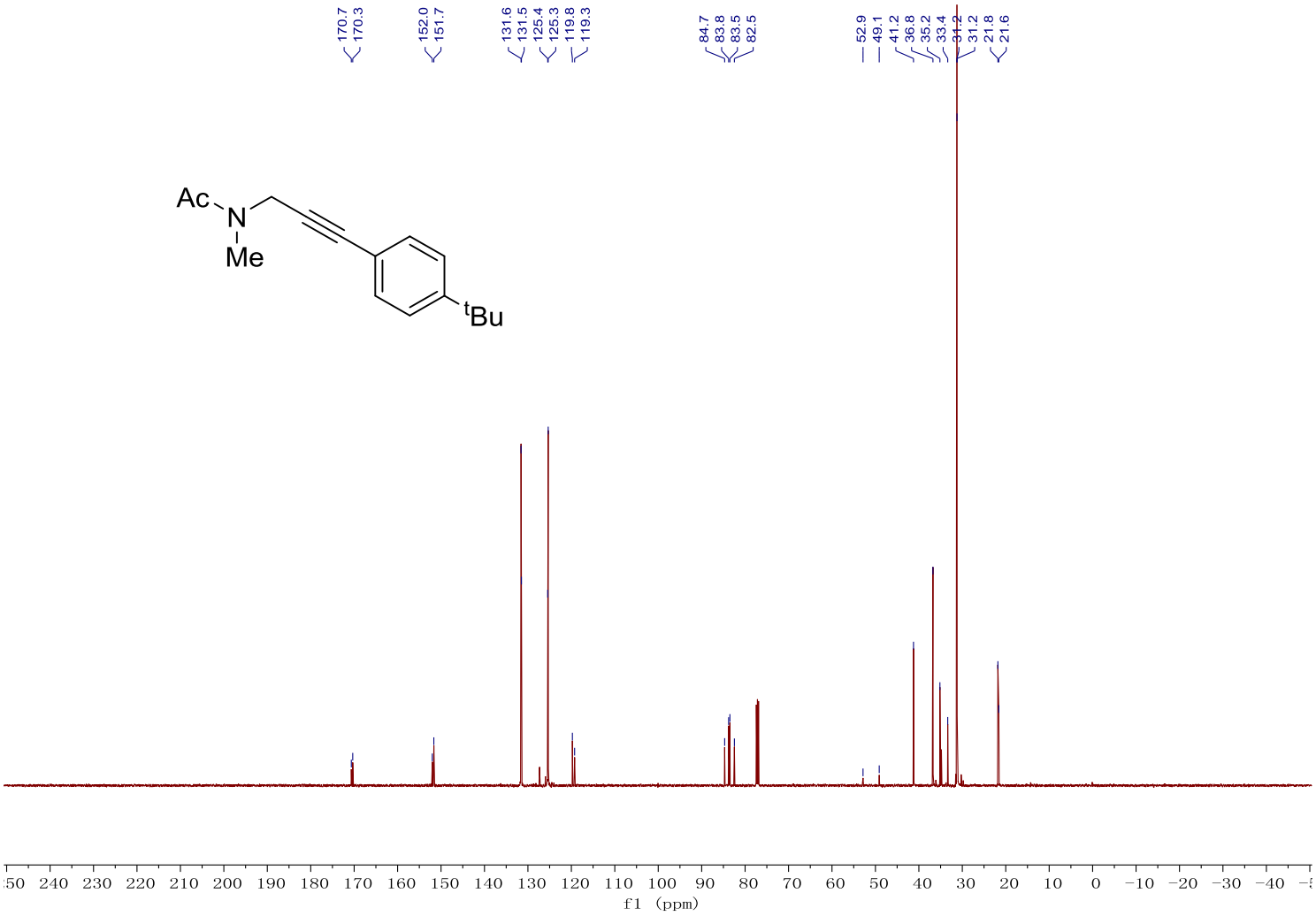
Supplementary Figure 41. Compound **20** ^{13}C NMR in $CDCl_3$



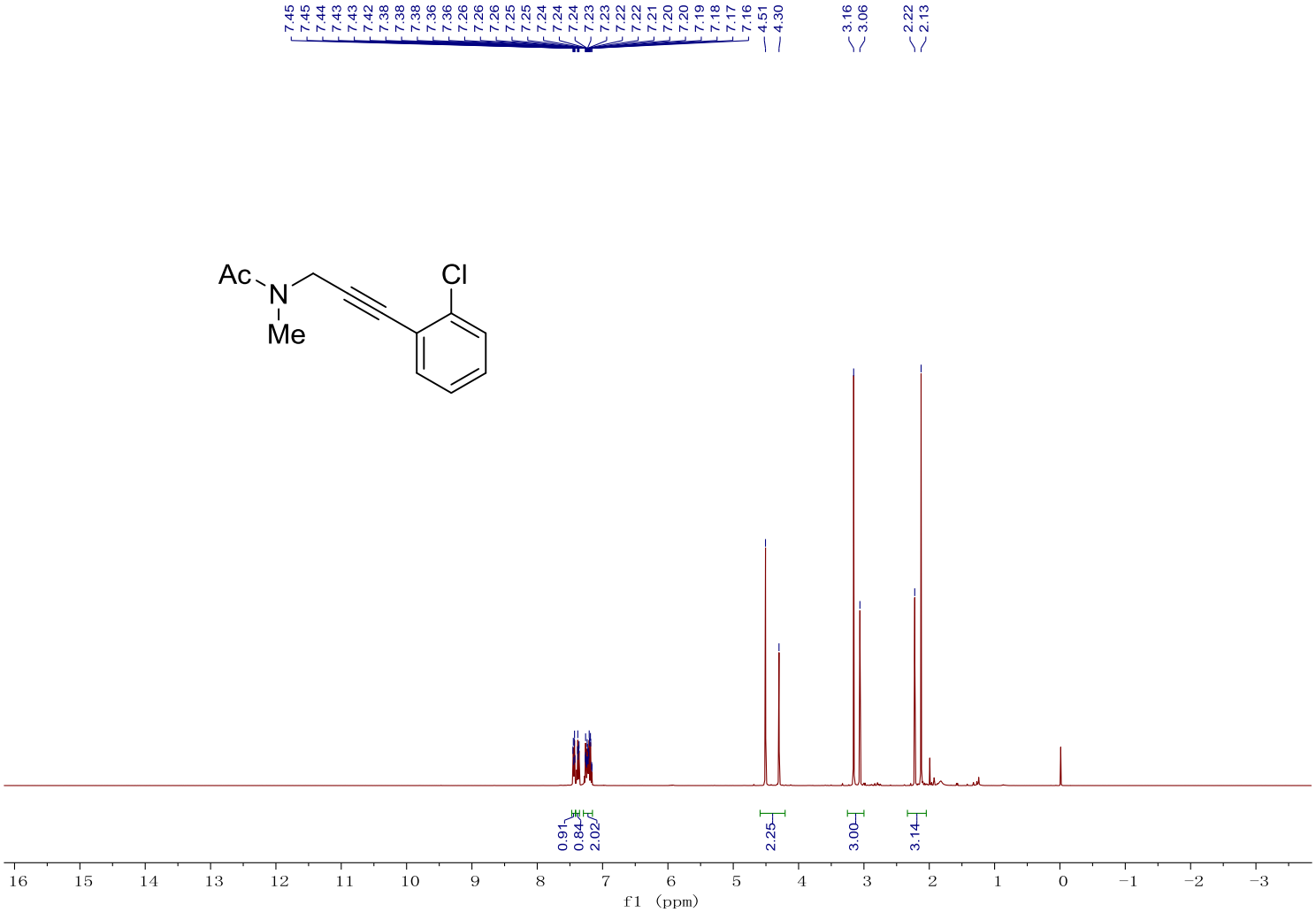
Supplementary Figure 42. Compound **21** ^{1}H NMR in $CDCl_3$



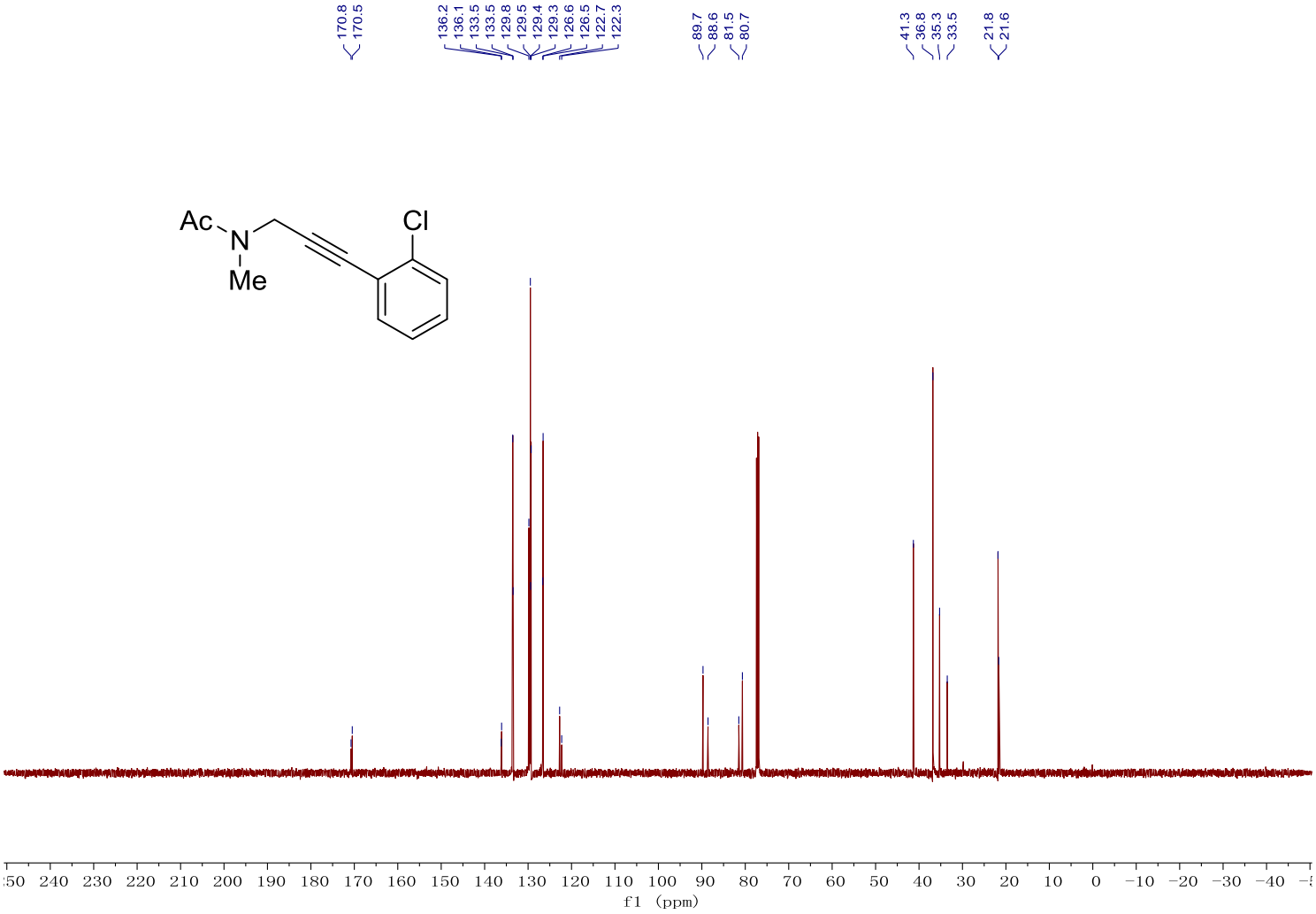
Supplementary Figure 43. Compound **21** ^{13}C NMR in $CDCl_3$



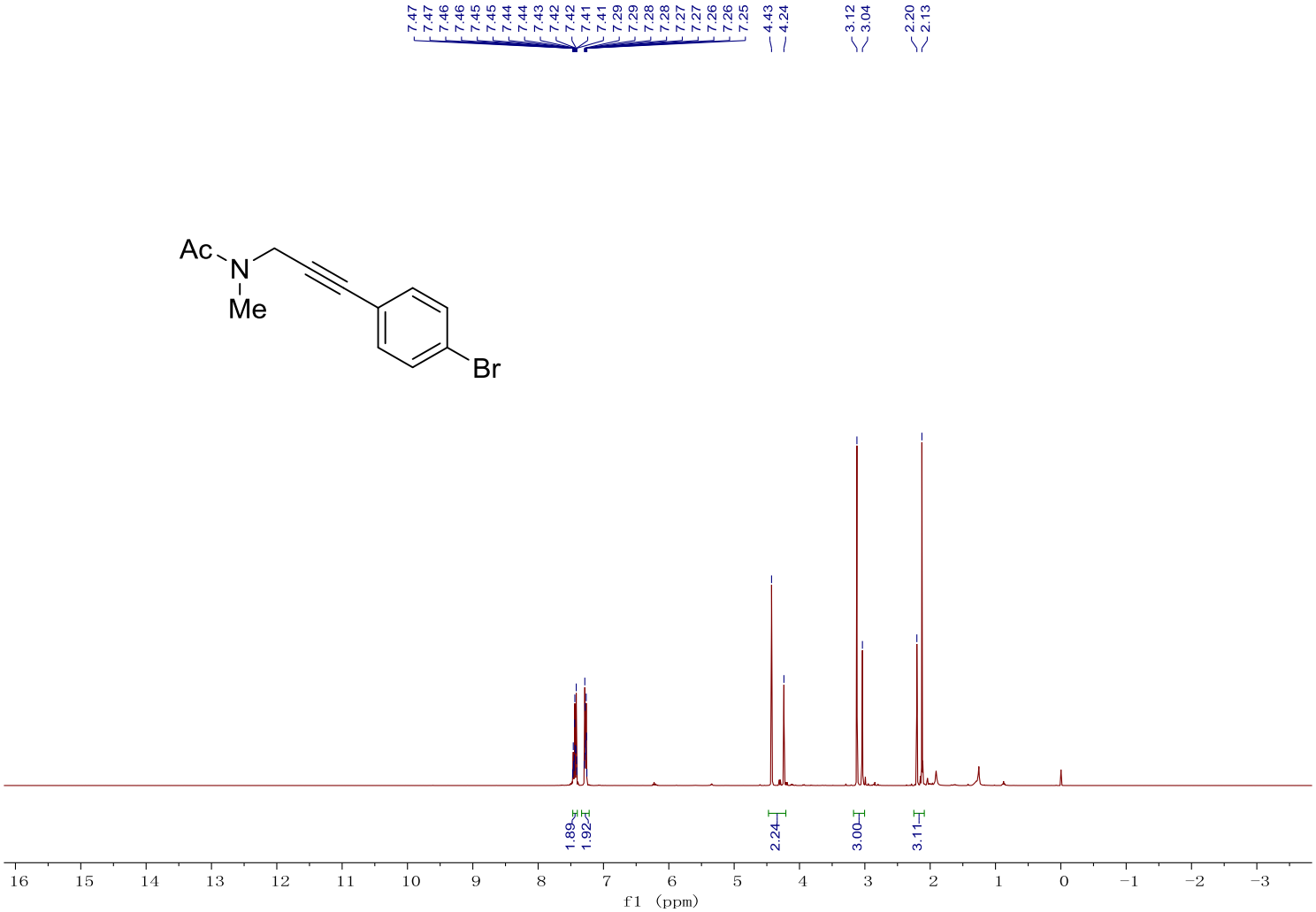
Supplementary Figure 44. Compound **22** ^{1}H NMR in $CDCl_3$



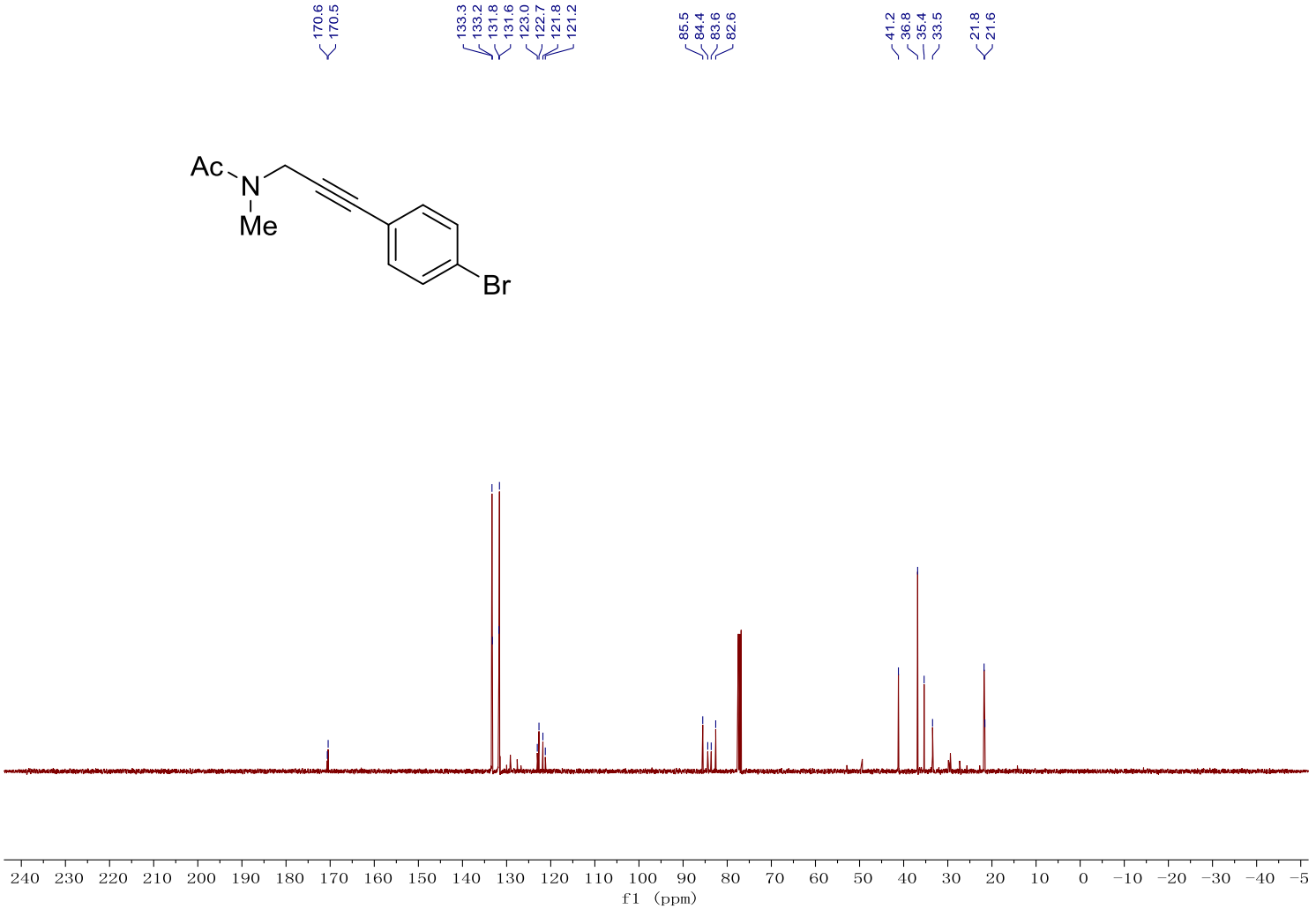
Supplementary Figure 45. Compound **22** ^{13}C NMR in $CDCl_3$



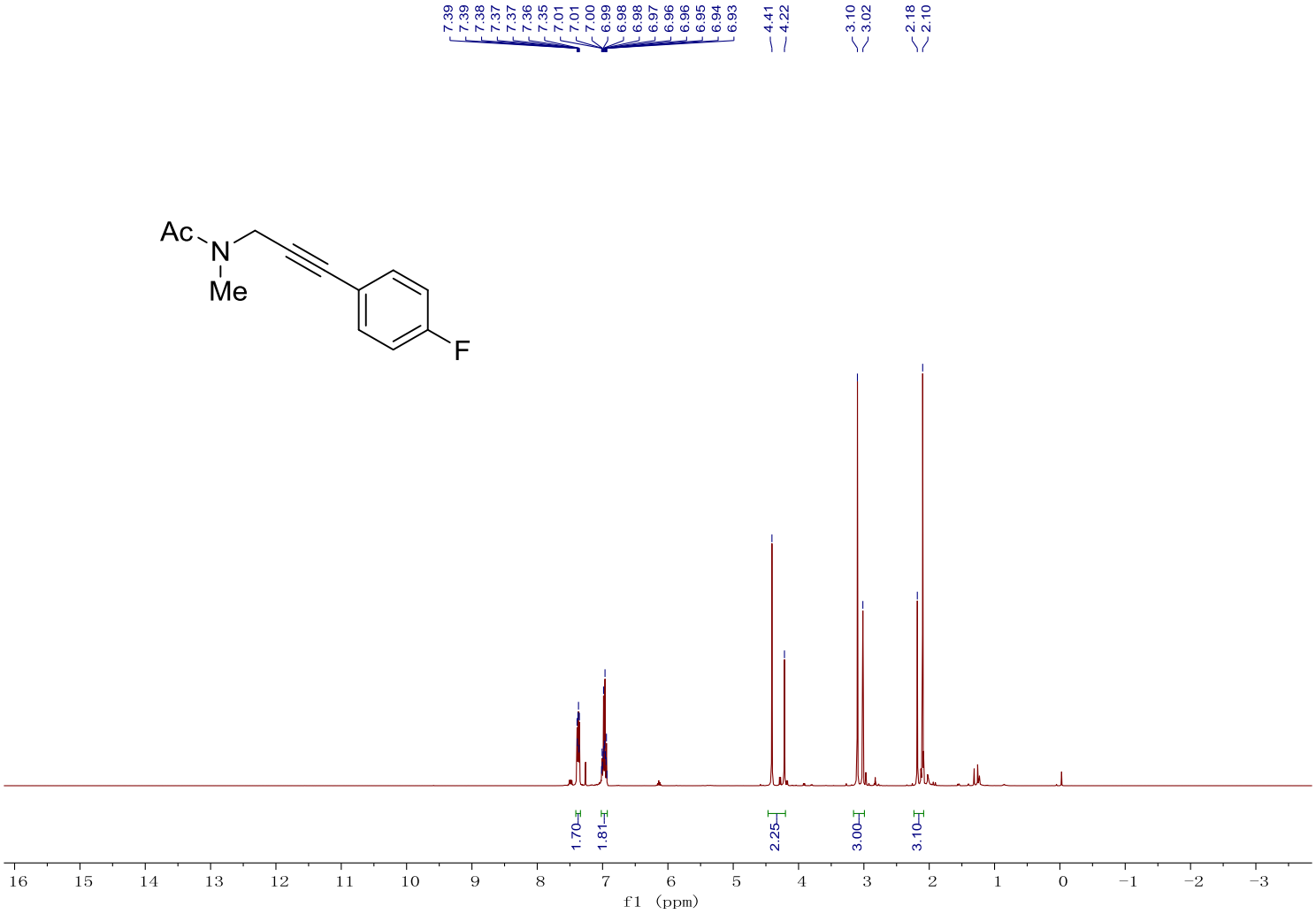
Supplementary Figure 46. Compound **23** ^{1}H NMR in $CDCl_3$



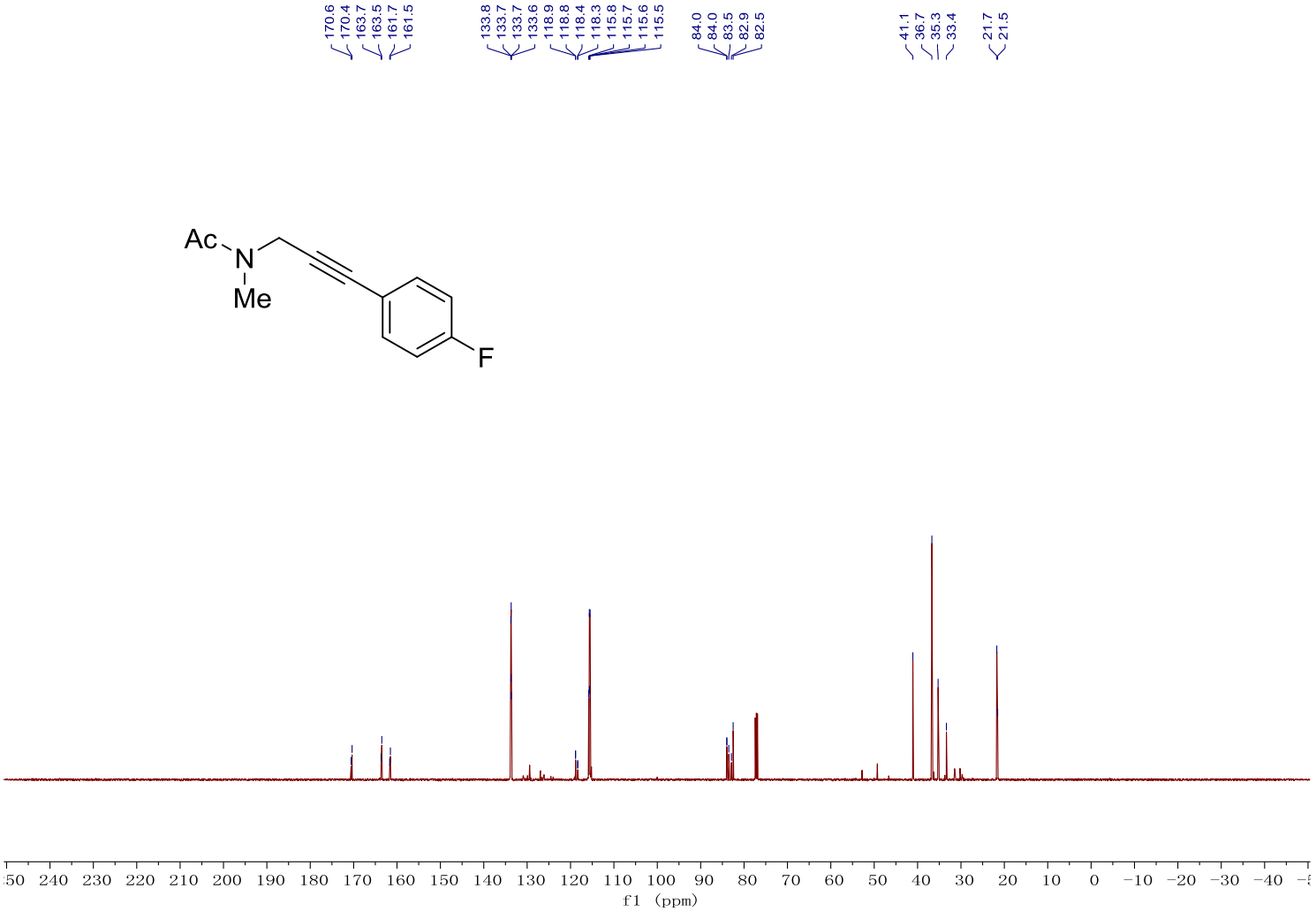
Supplementary Figure 47. Compound **23** ^{13}C NMR in $CDCl_3$



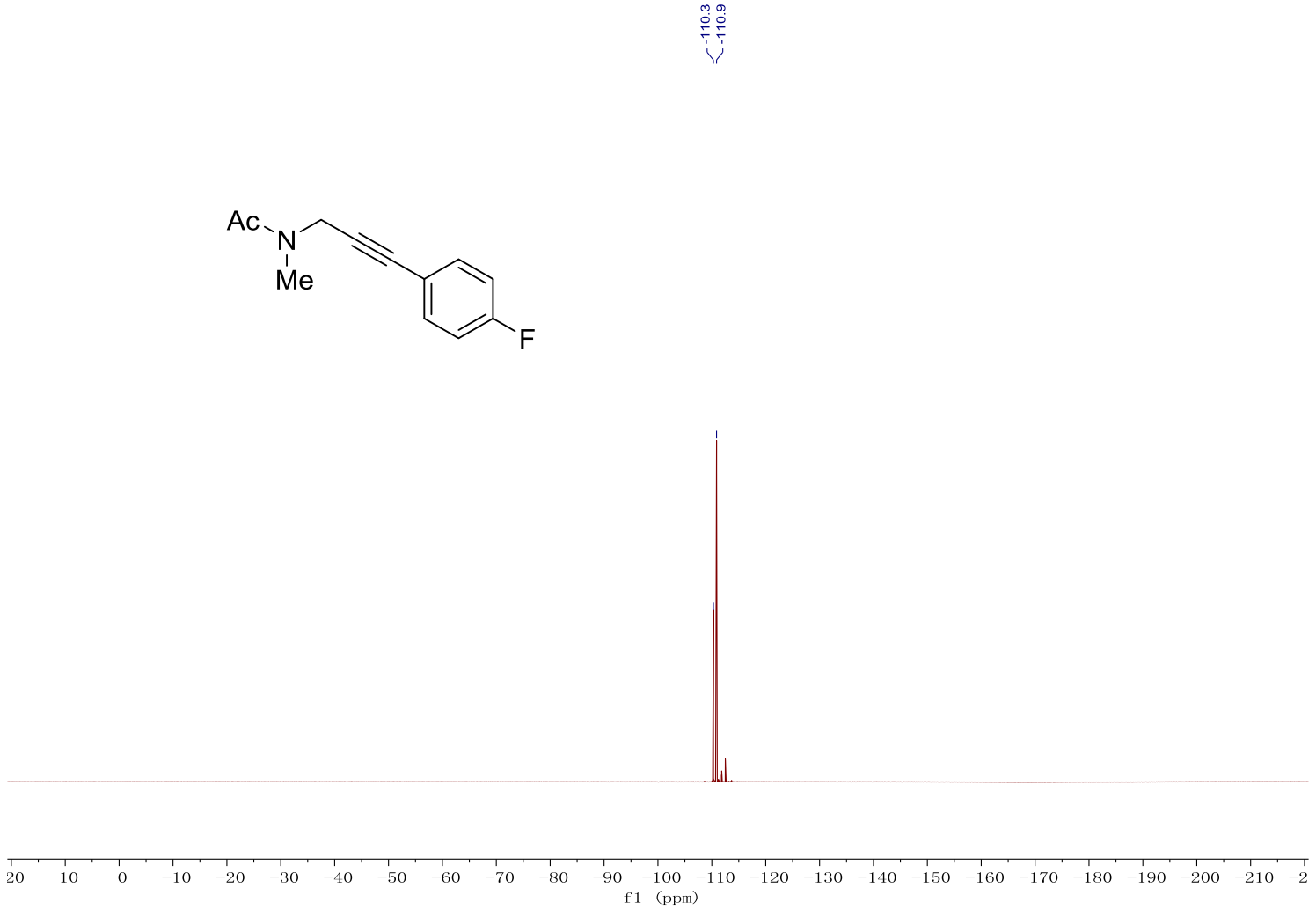
Supplementary Figure 48. Compound **24** ^{1}H NMR in $CDCl_3$



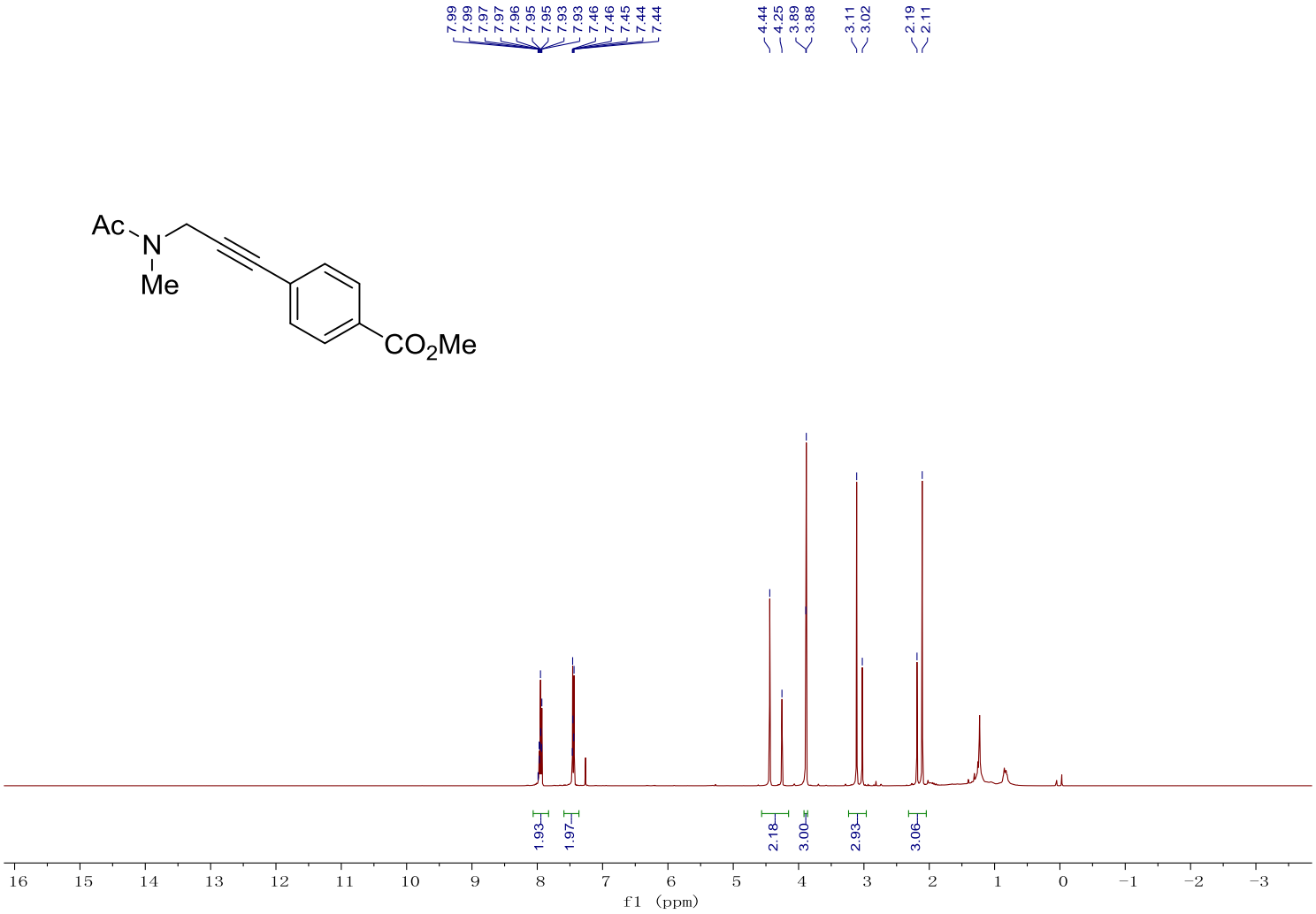
Supplementary Figure 49. Compound **24** ^{13}C NMR in $CDCl_3$



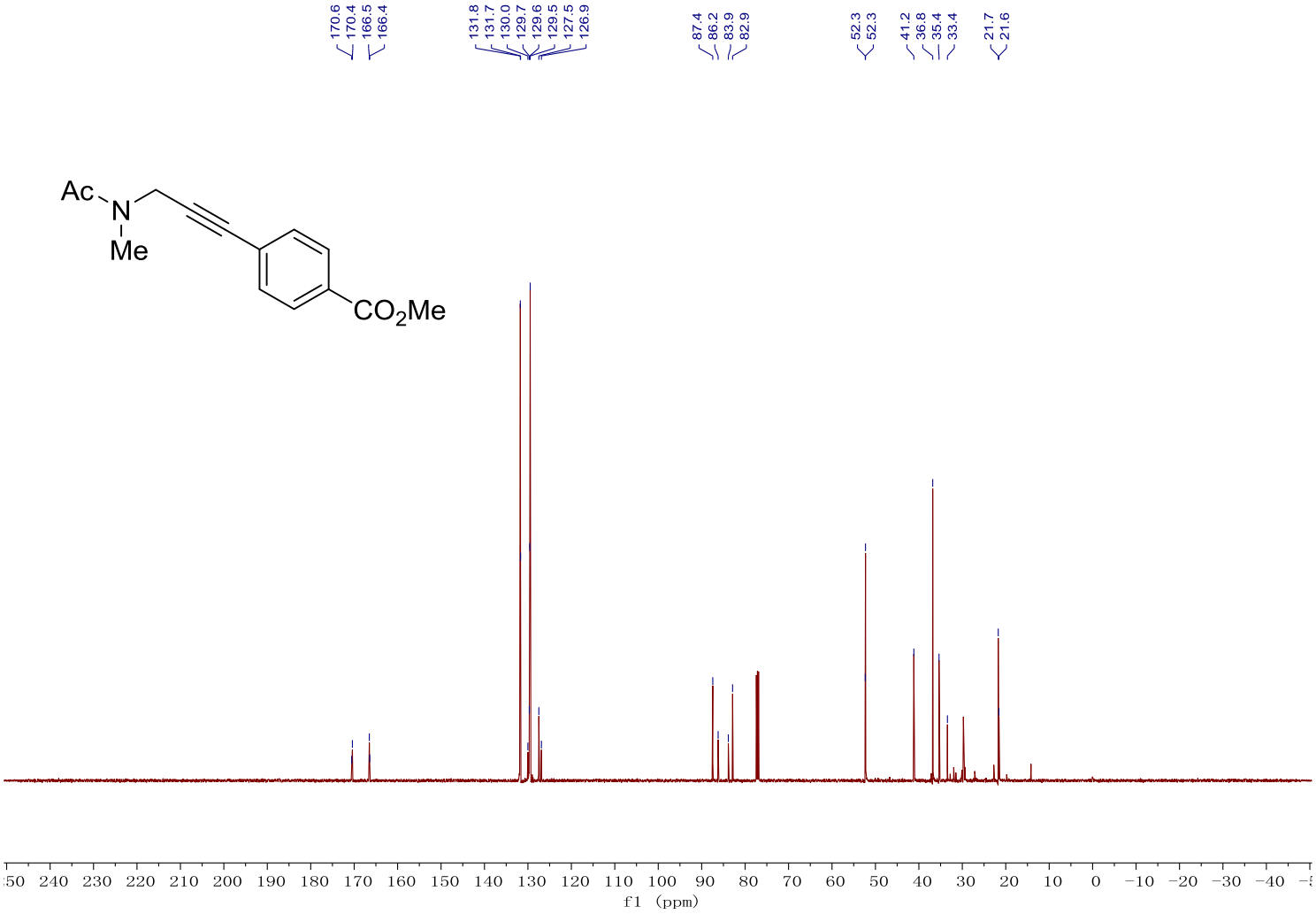
Supplementary Figure 50. Compound **24** ^{19}F NMR in $CDCl_3$



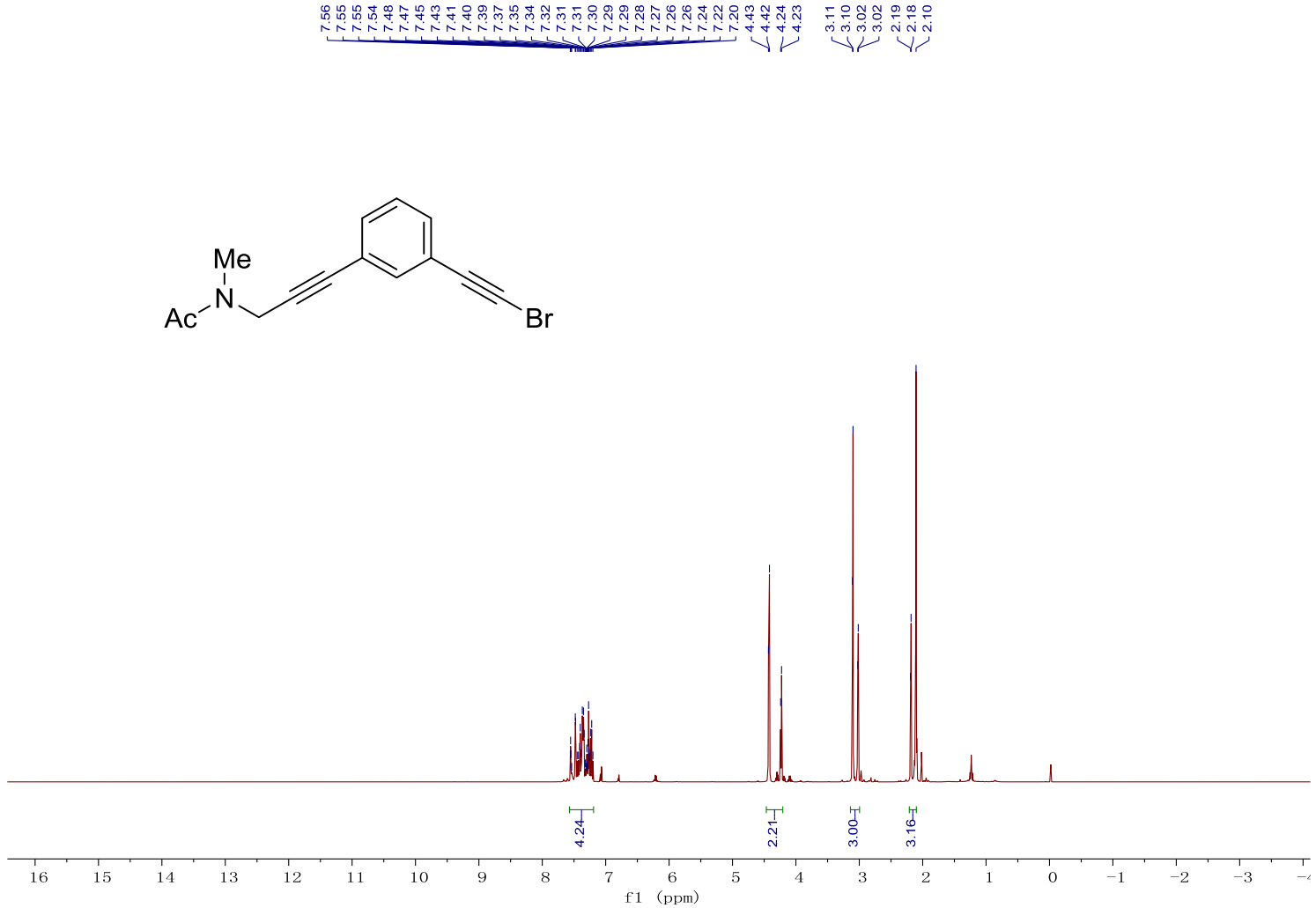
Supplementary Figure 51. Compound **25** ^{1}H NMR in $CDCl_3$



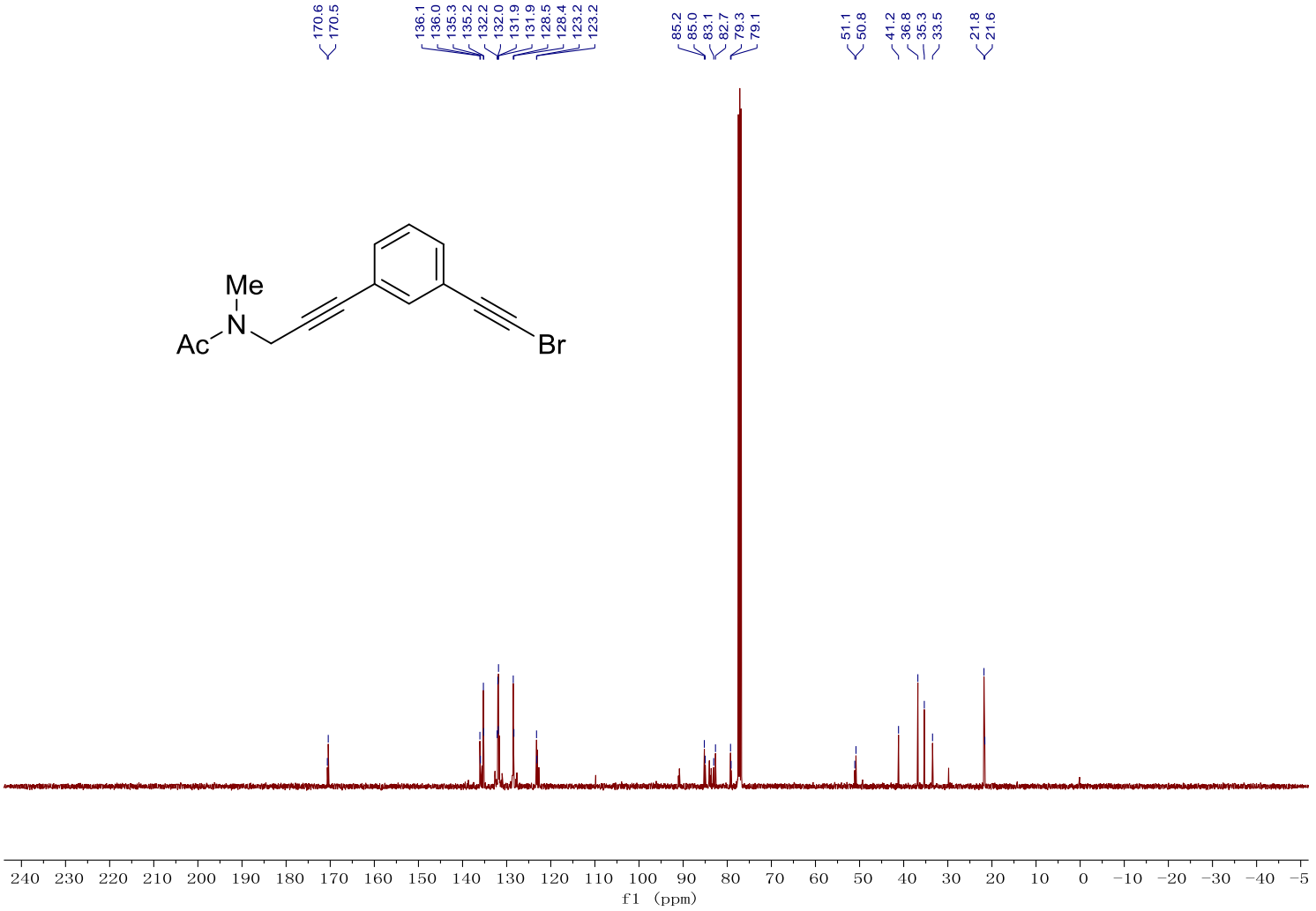
Supplementary Figure 52. Compound **25** ^{13}C NMR in $CDCl_3$



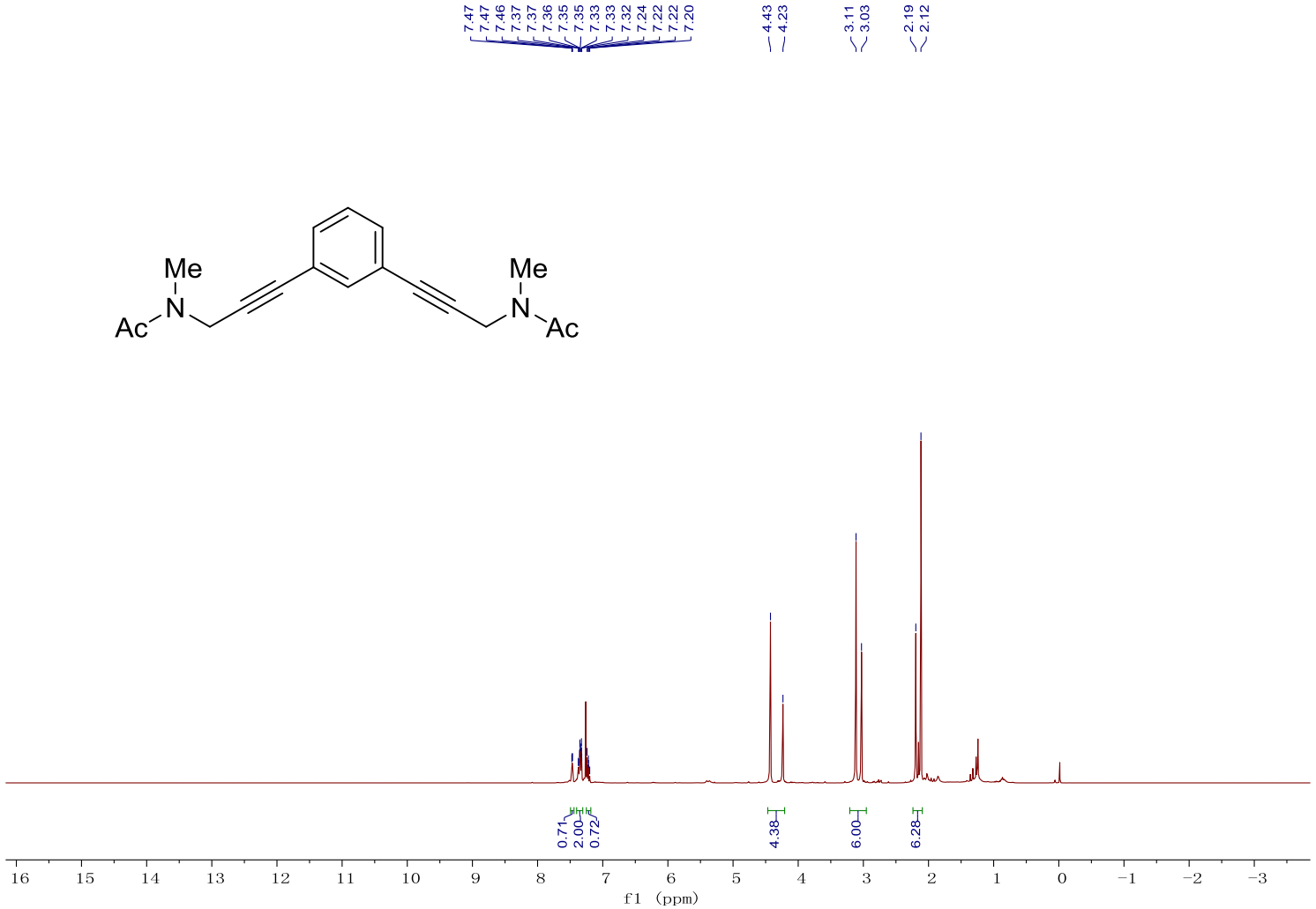
Supplementary Figure 53. Compound **26** ^{1}H NMR in $CDCl_3$



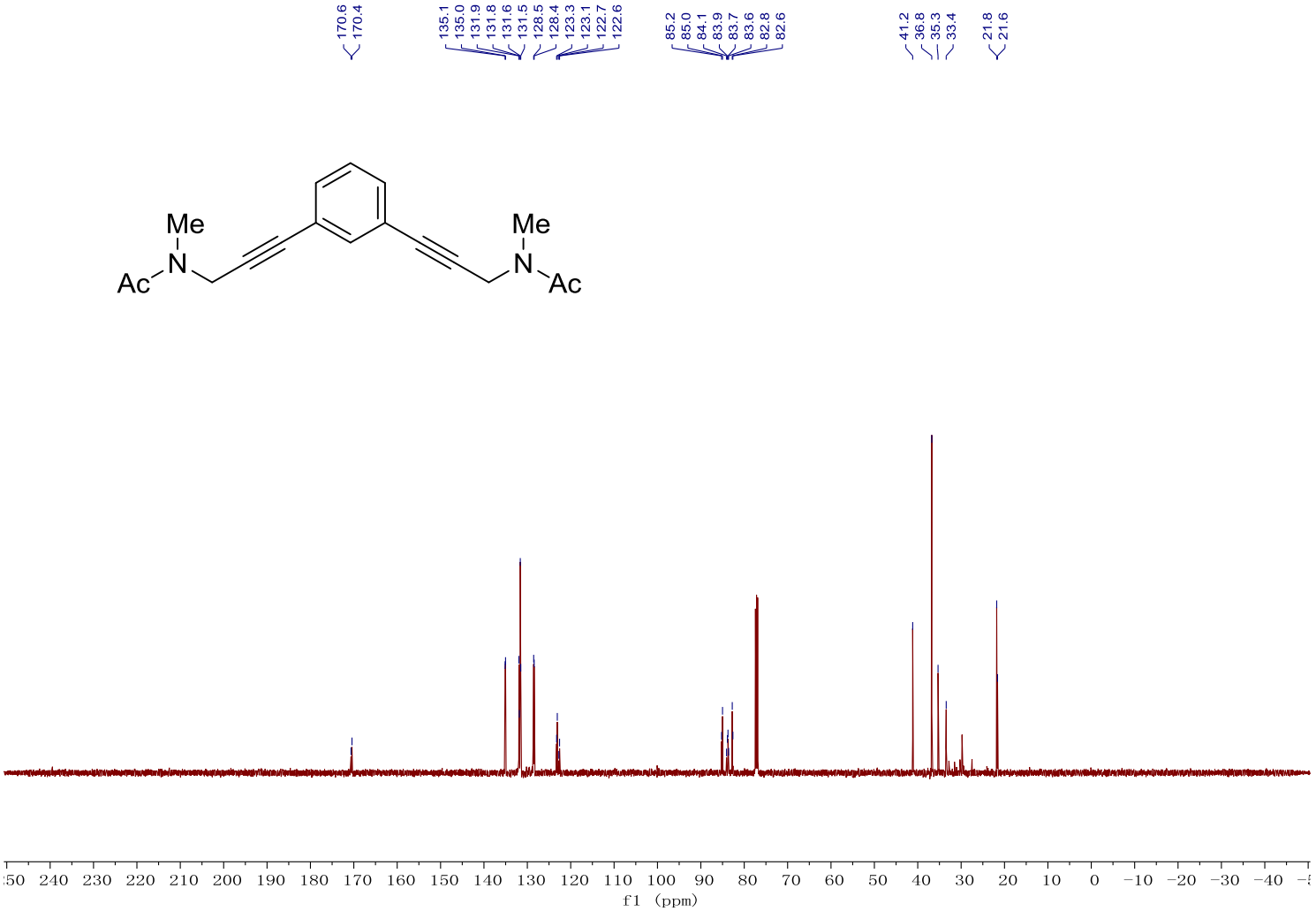
Supplementary Figure 54. Compound **26** ^{13}C NMR in $CDCl_3$



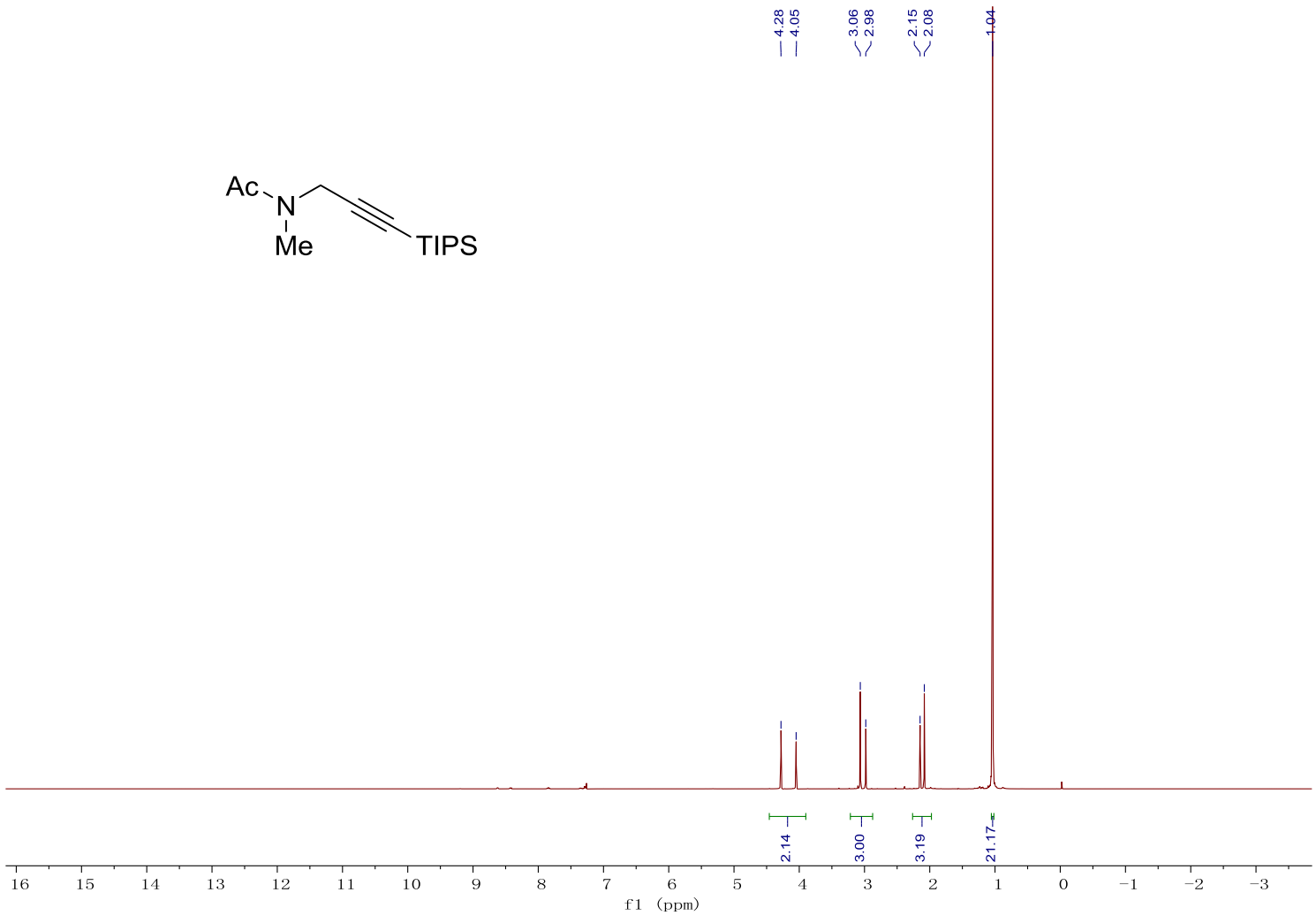
Supplementary Figure 55. Compound **27** ^{1}H NMR in $CDCl_3$



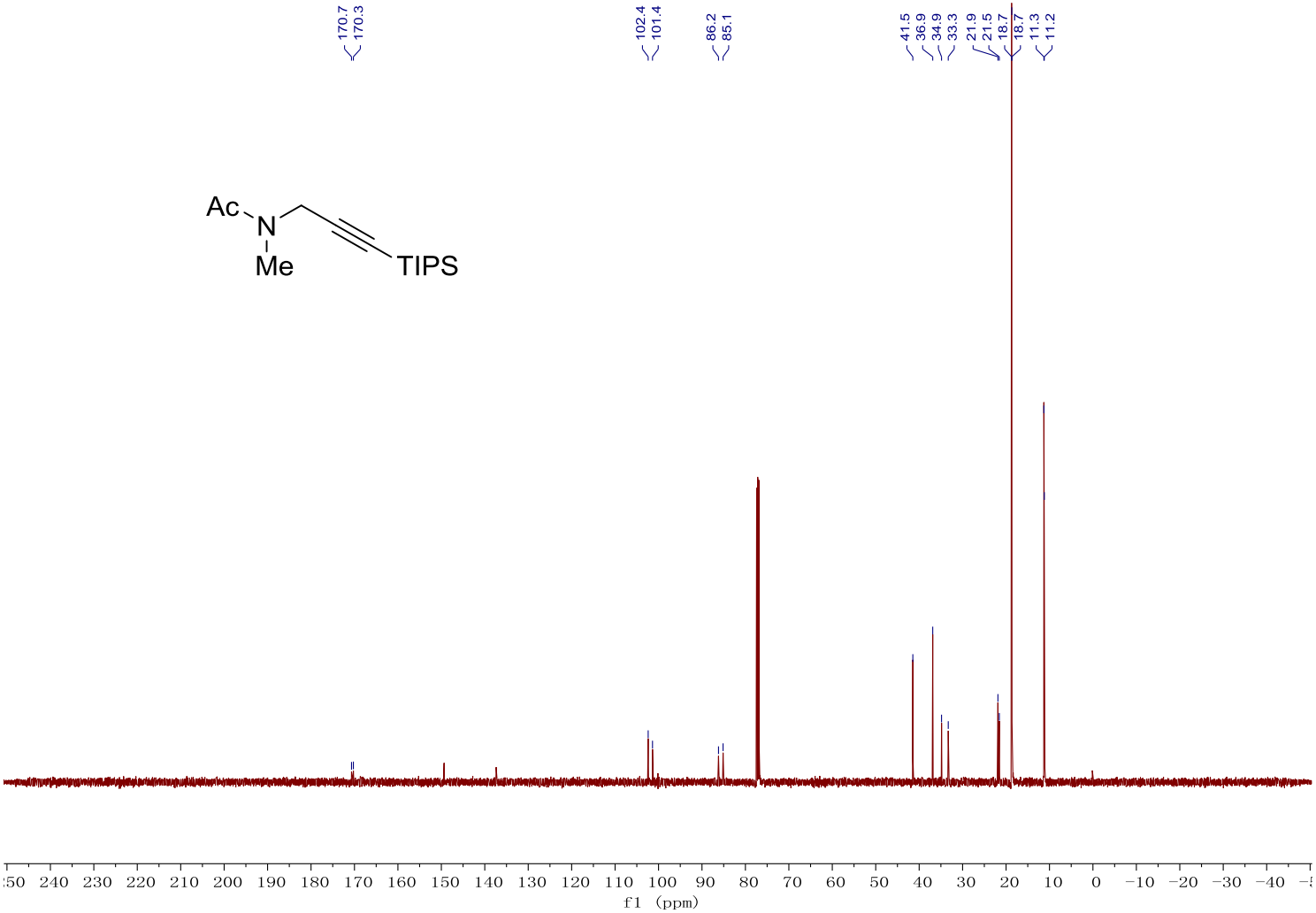
Supplementary Figure 56. Compound **27** ^{13}C NMR in $CDCl_3$



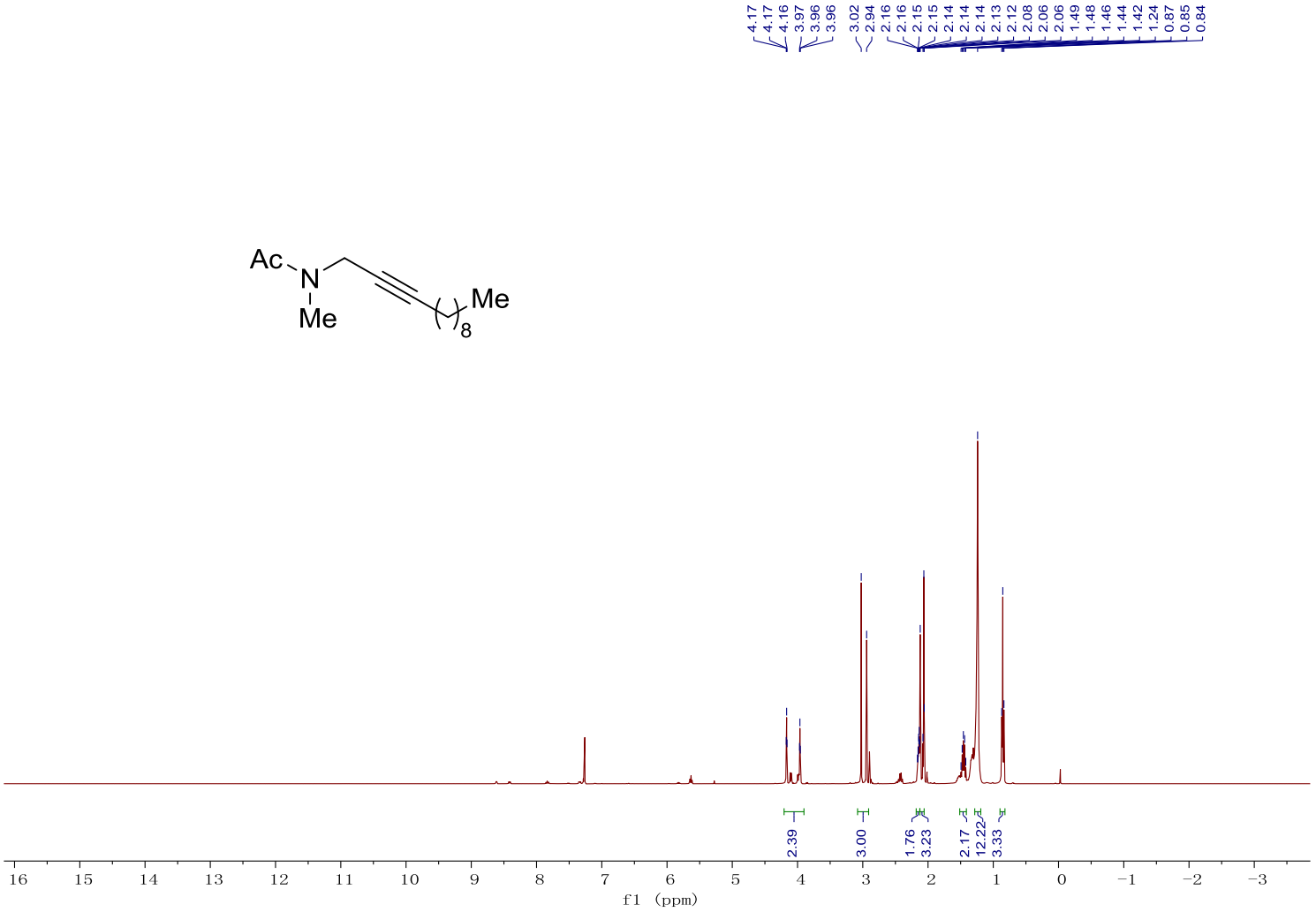
Supplementary Figure 57. Compound **28** ^{1}H NMR in $CDCl_3$



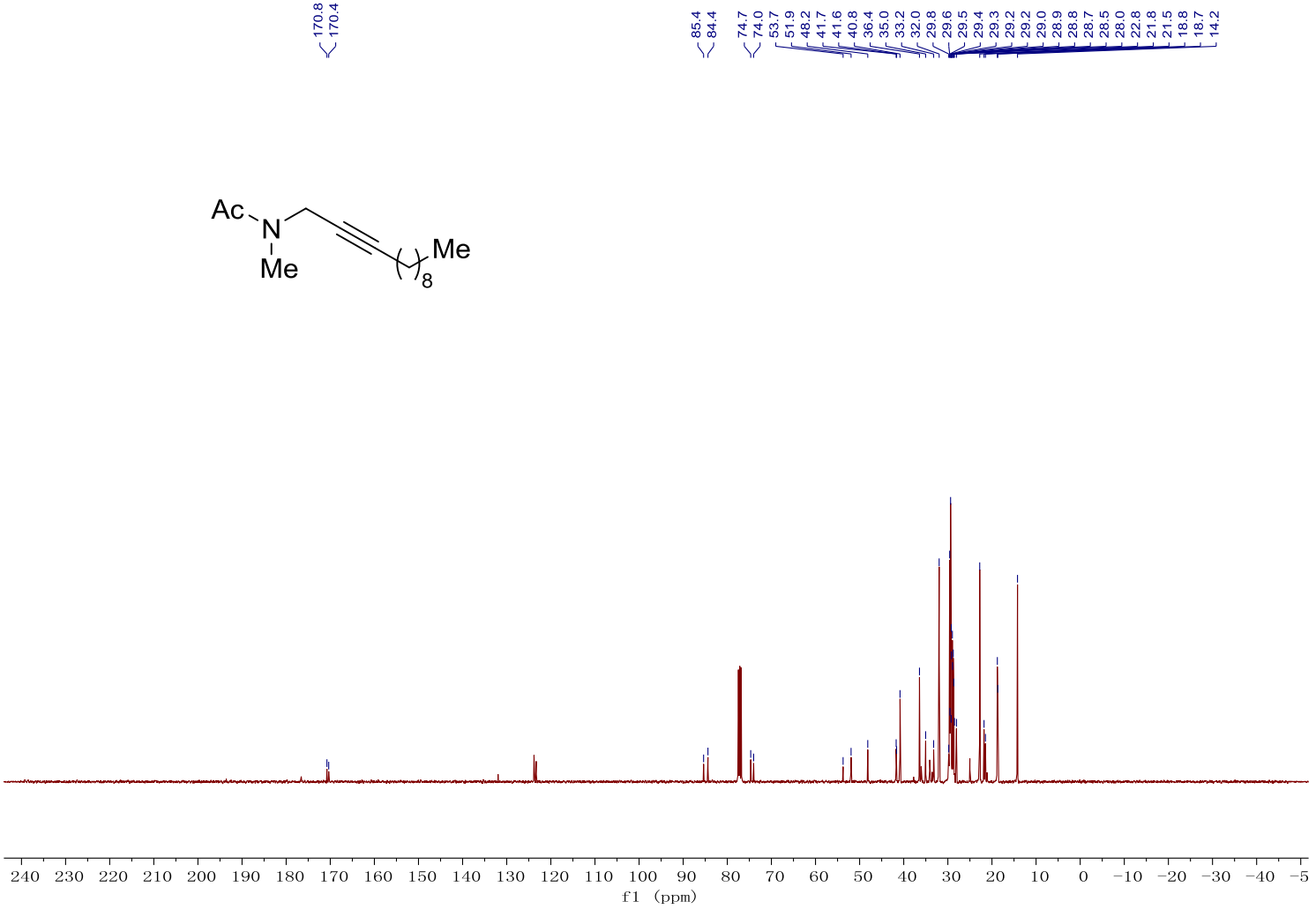
Supplementary Figure 58. Compound **28** ^{13}C NMR in $CDCl_3$



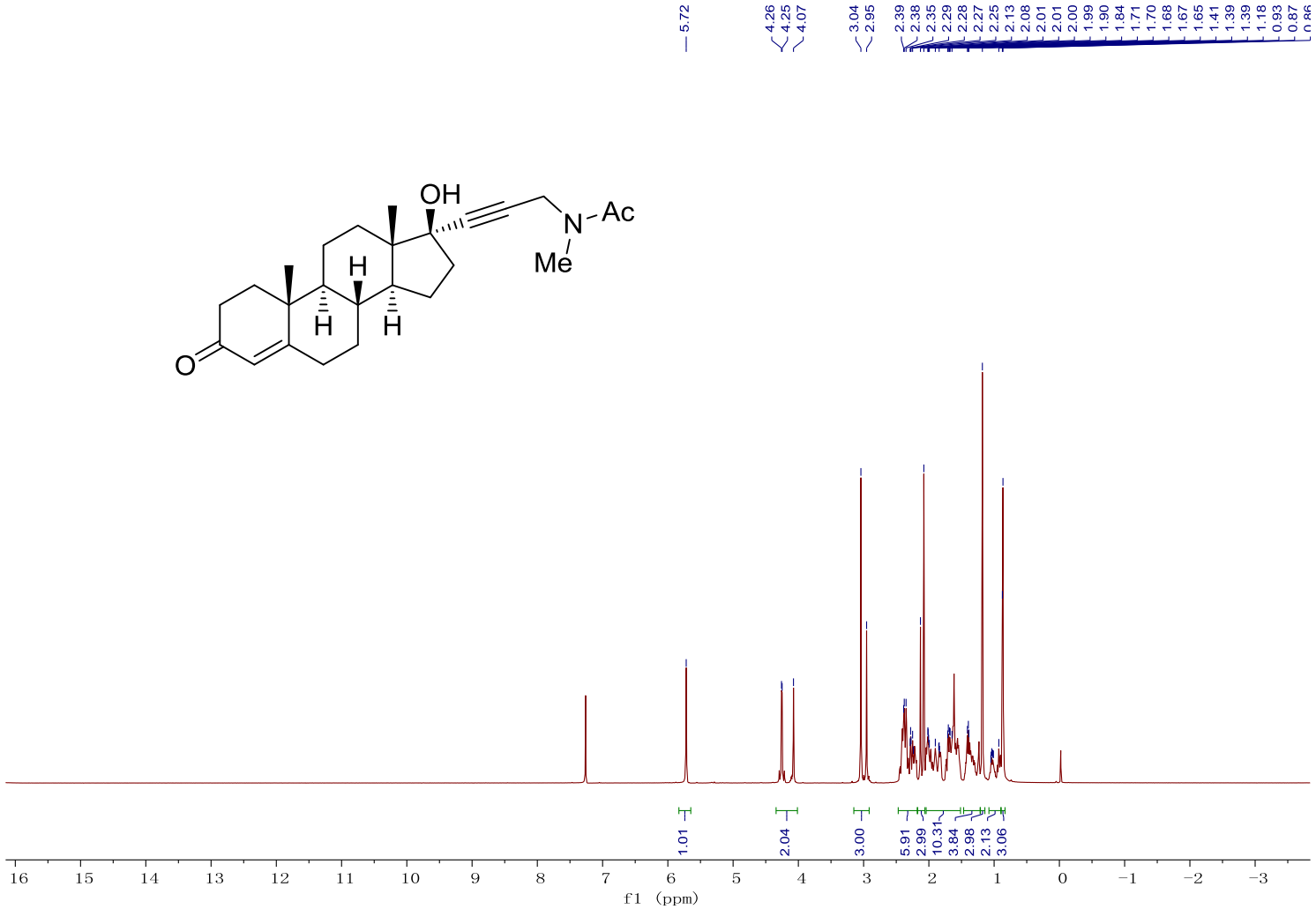
Supplementary Figure 59. Compound **29** ^{1}H NMR in $CDCl_3$



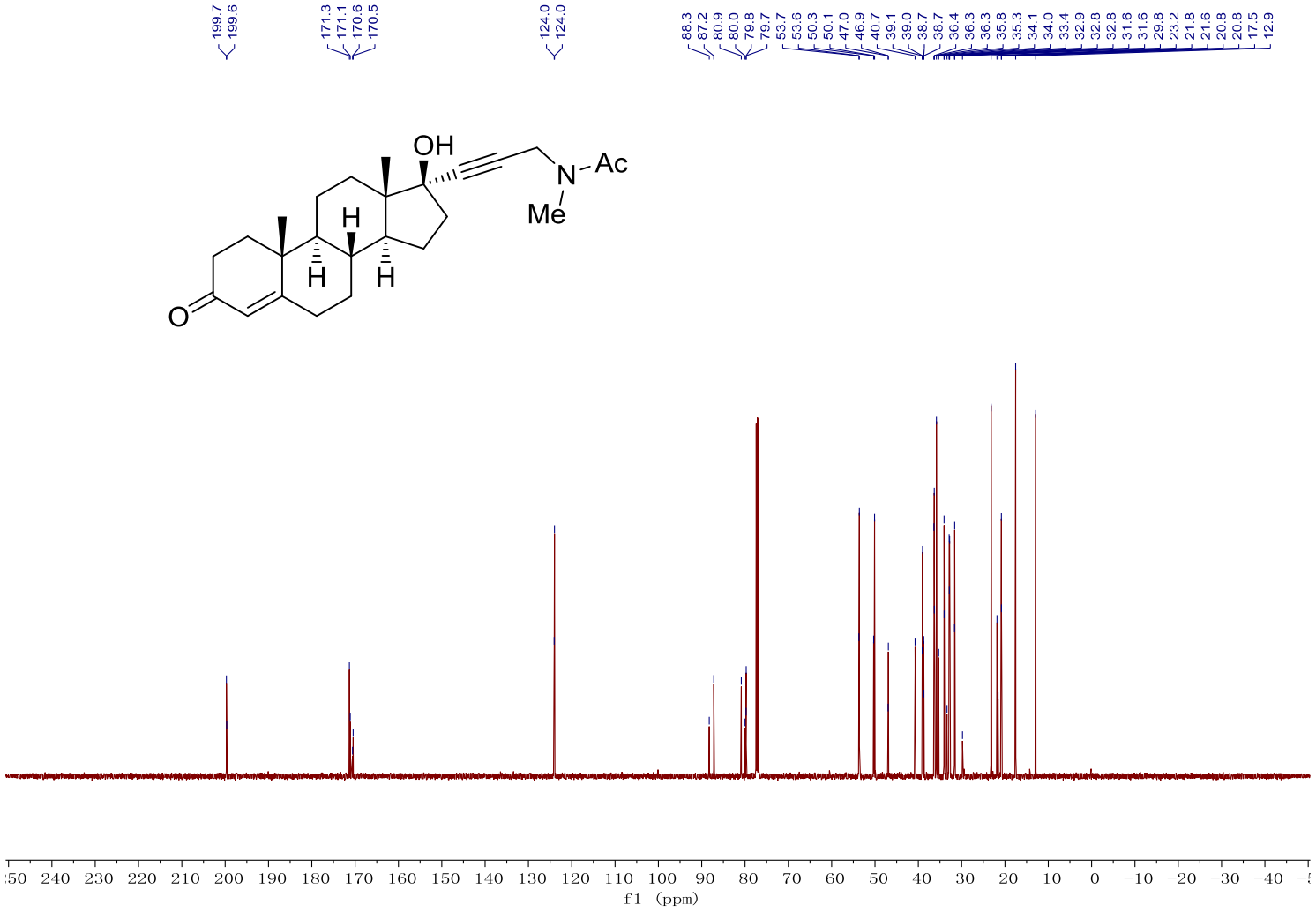
Supplementary Figure 60. Compound **29** ^{13}C NMR in $CDCl_3$



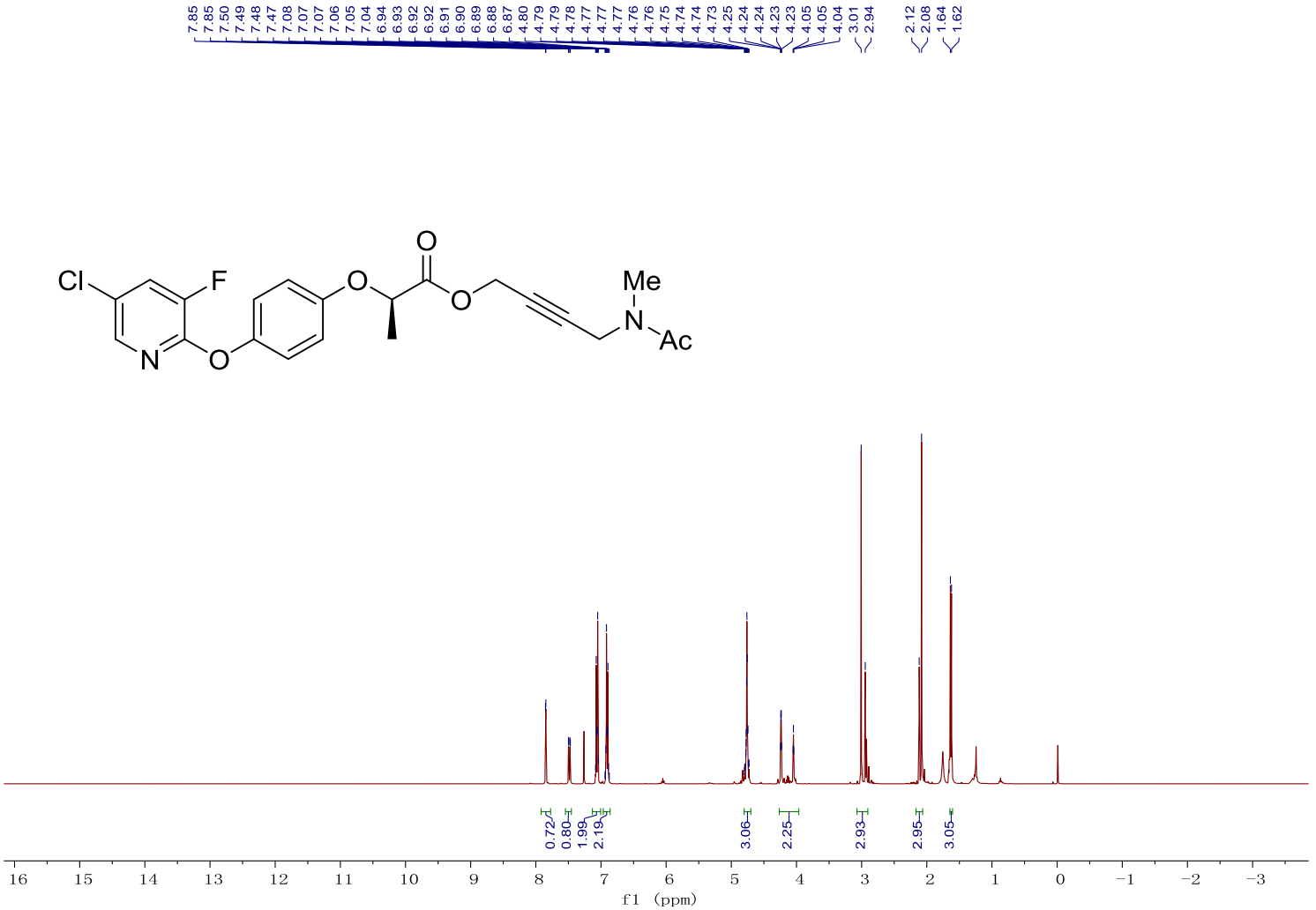
Supplementary Figure 61. Compound **30** ^{1}H NMR in $CDCl_3$



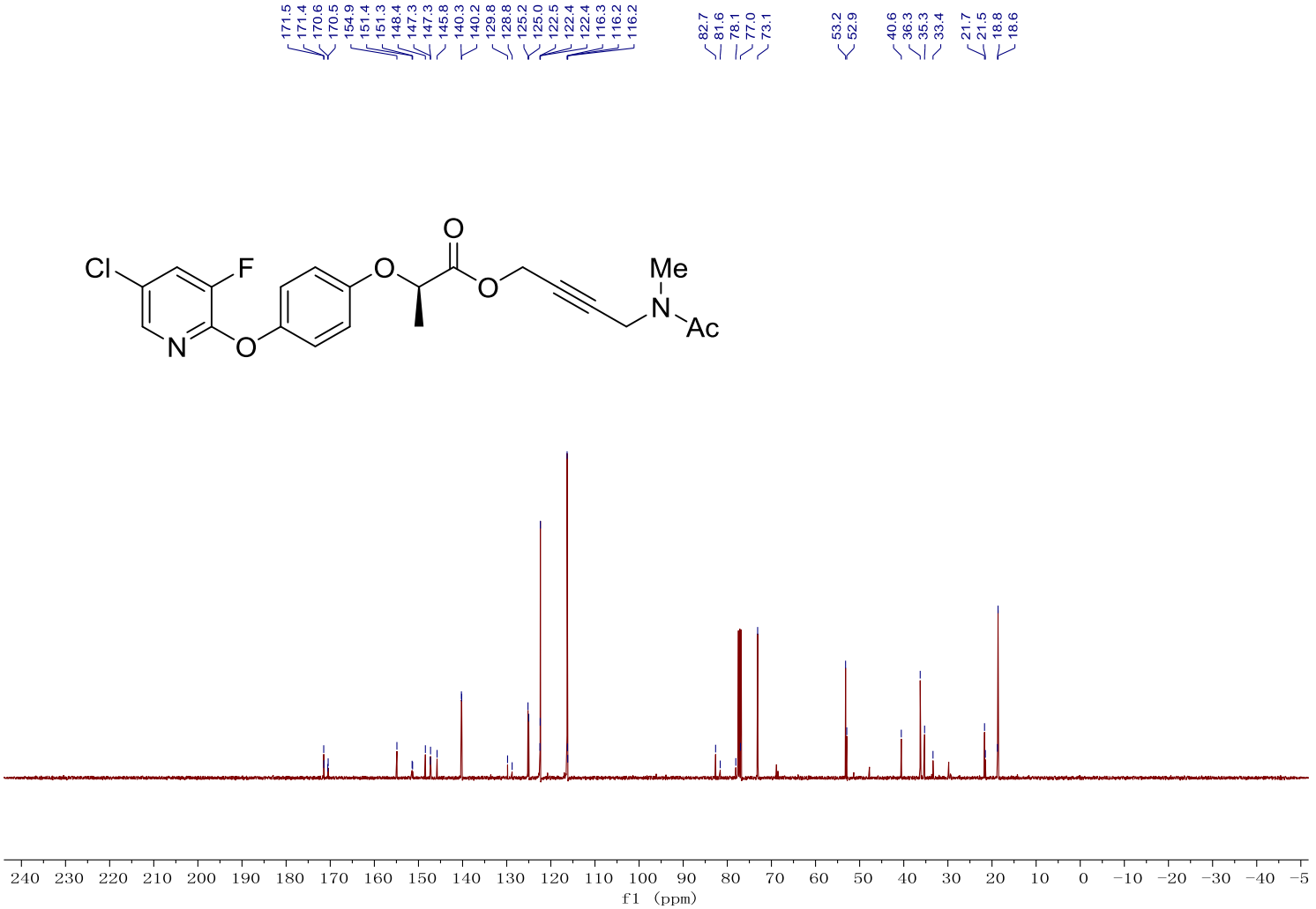
Supplementary Figure 62. Compound **30** ^{13}C NMR in $CDCl_3$



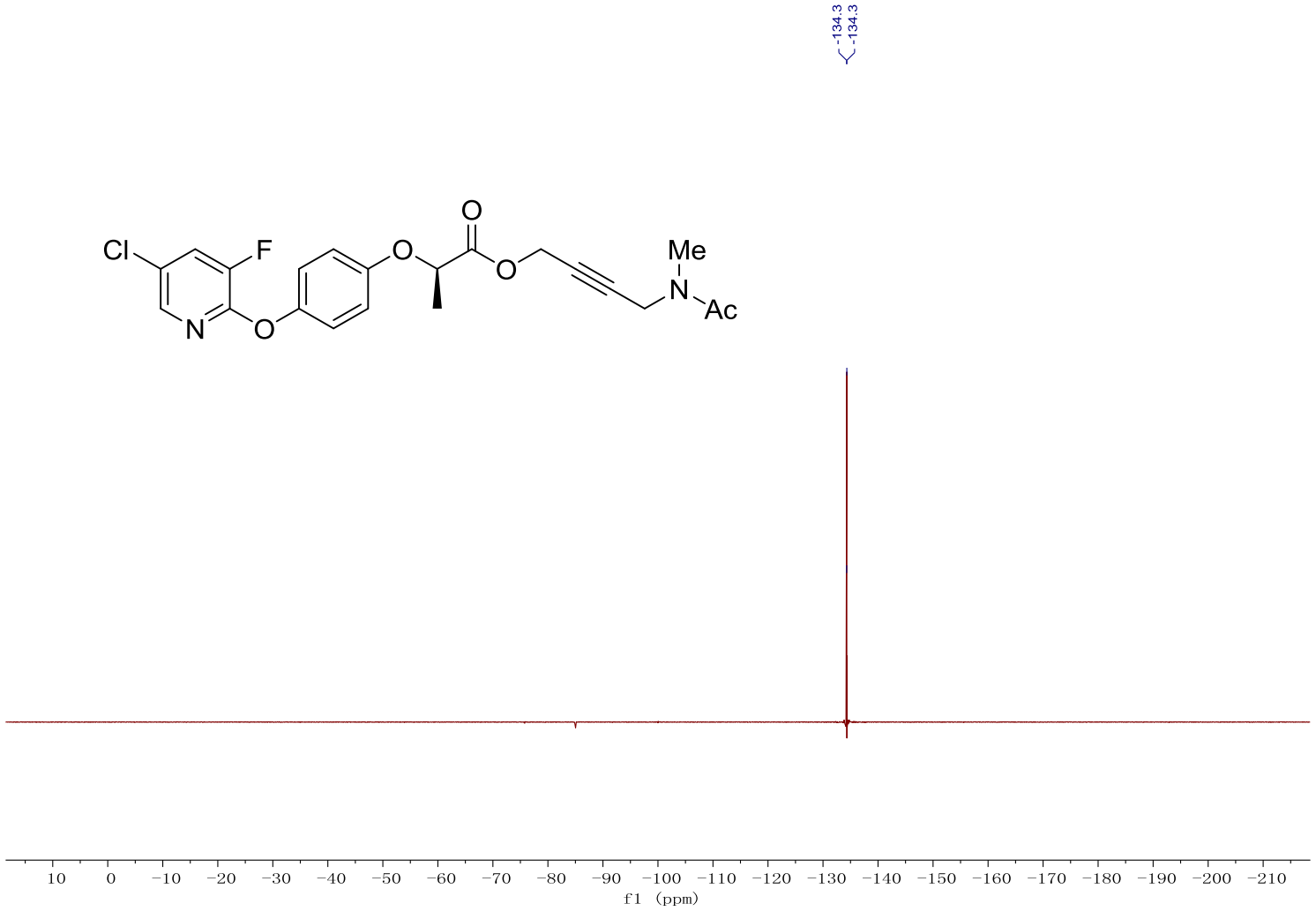
Supplementary Figure 63. Compound **31** ^{1}H NMR in $CDCl_3$



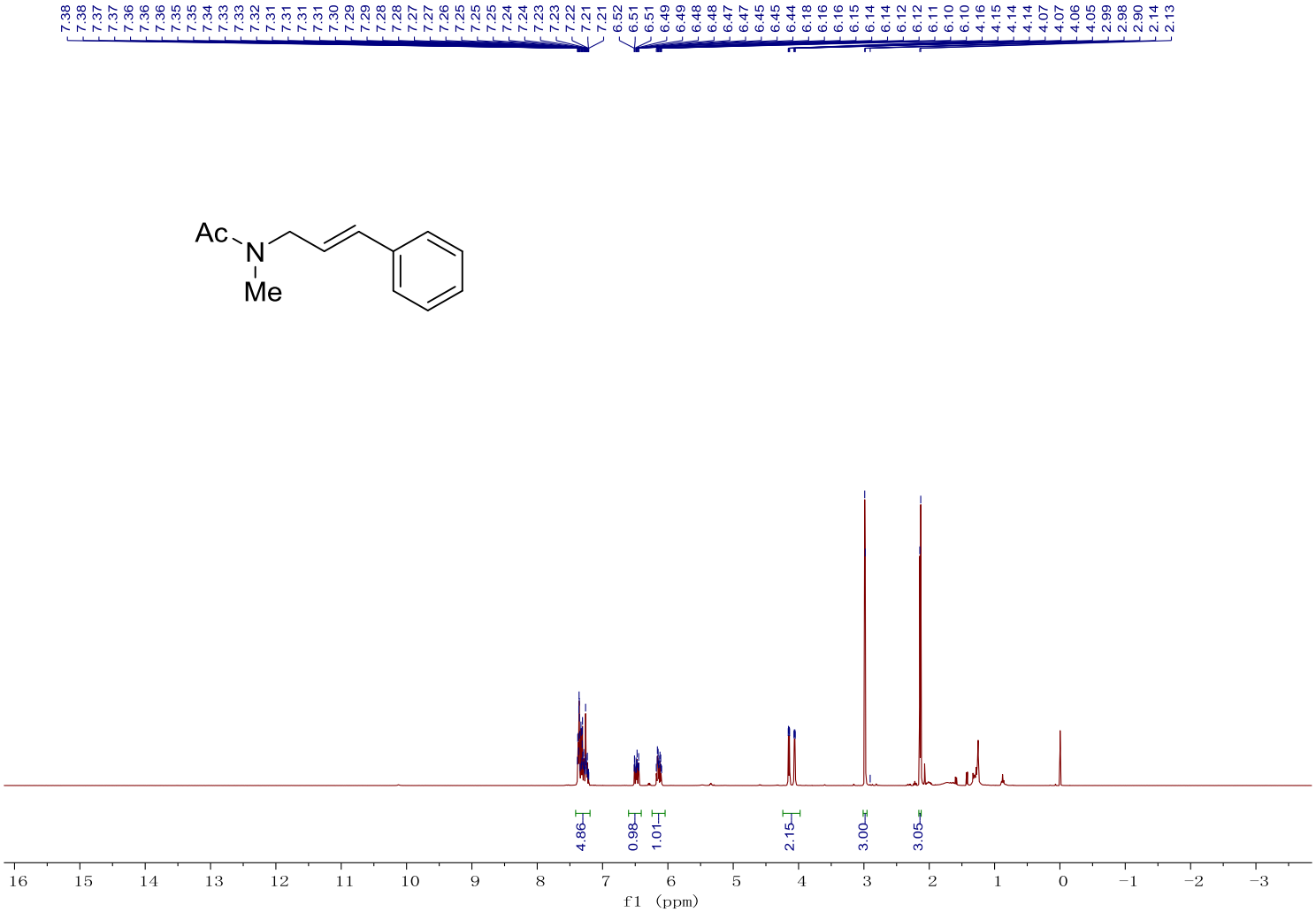
Supplementary Figure 64. Compound **31** ^{13}C NMR in $CDCl_3$



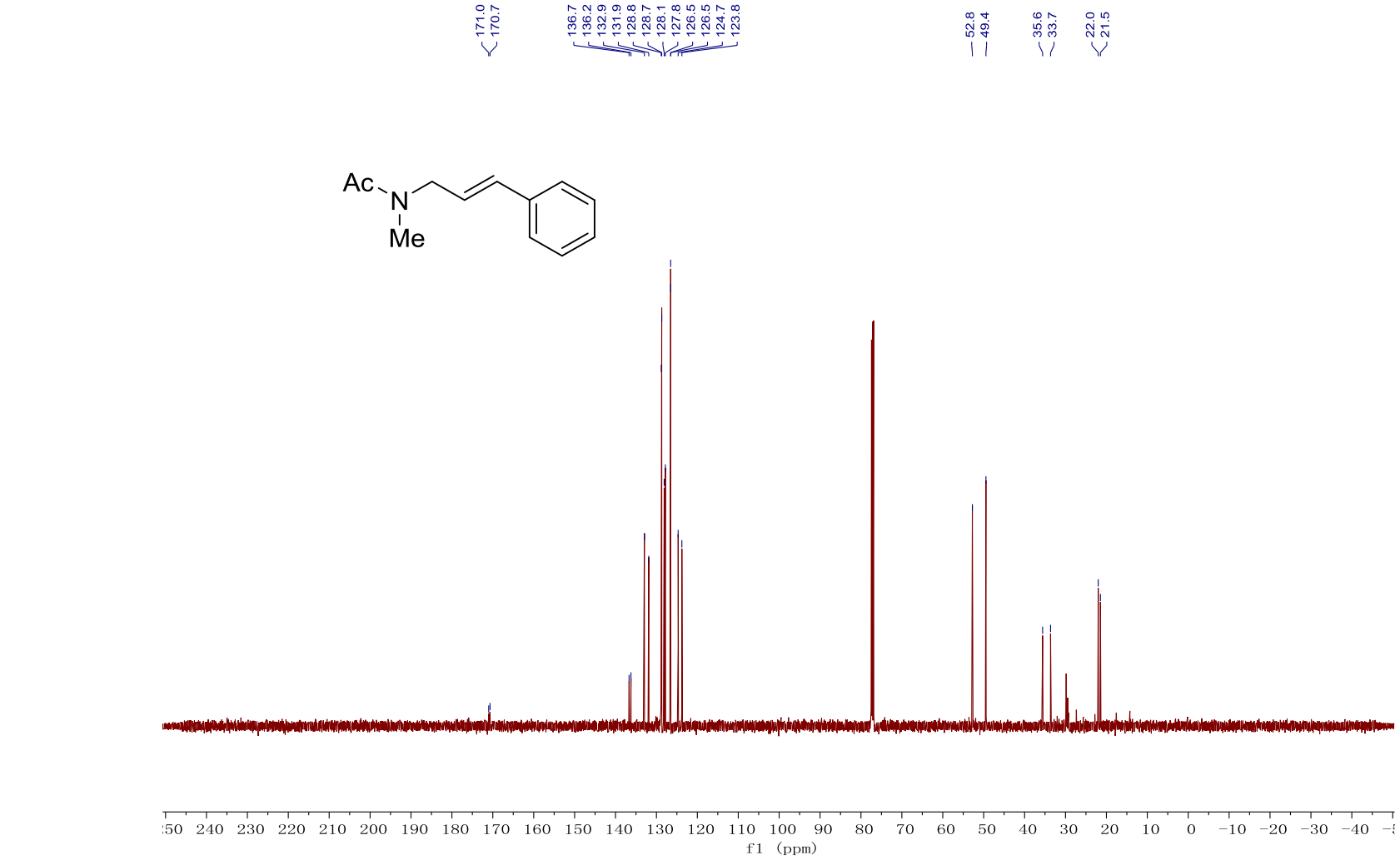
Supplementary Figure 65. Compound **31** ^{19}F NMR in $CDCl_3$



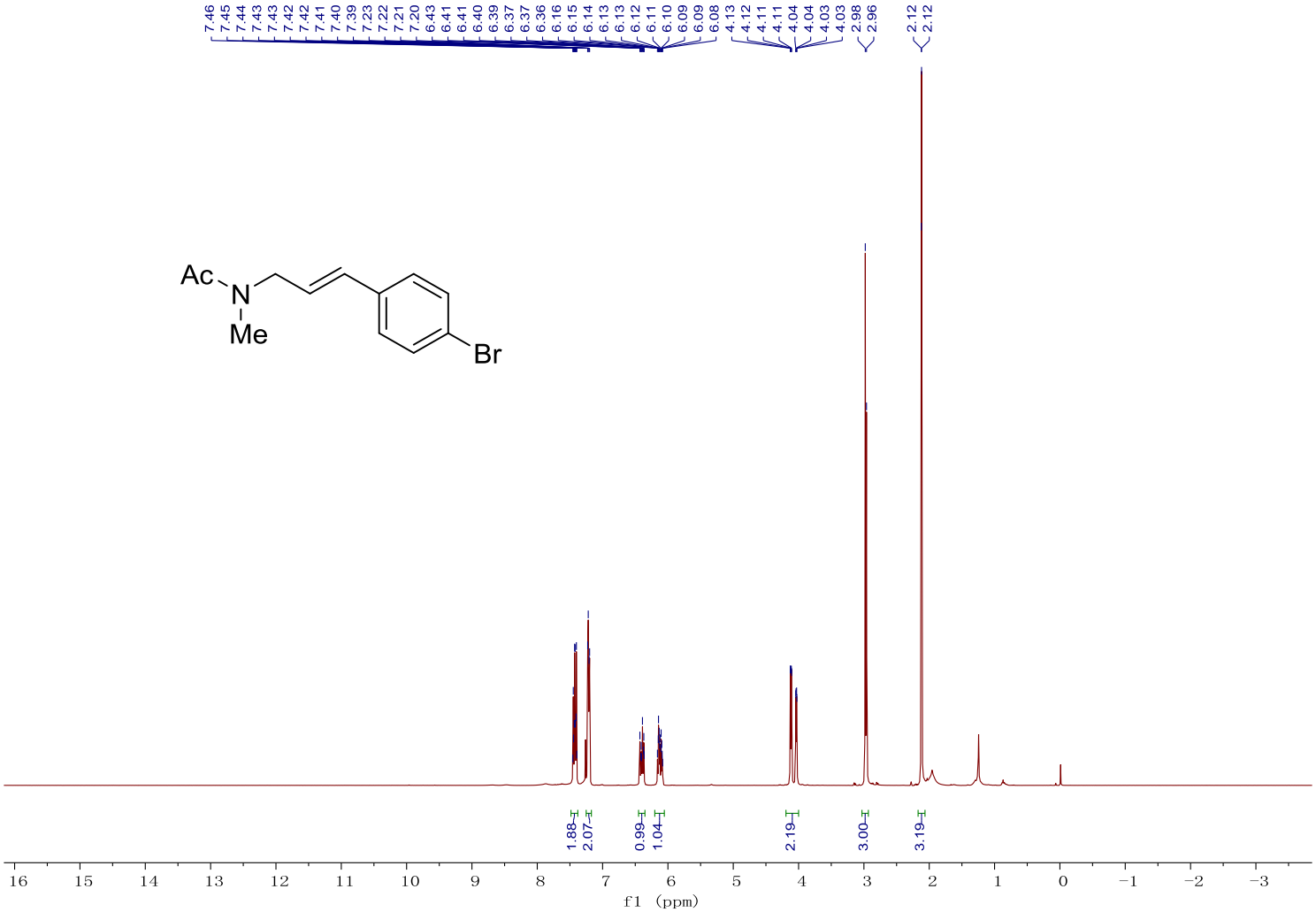
Supplementary Figure 66. Compound **32** ^{1}H NMR in $CDCl_3$



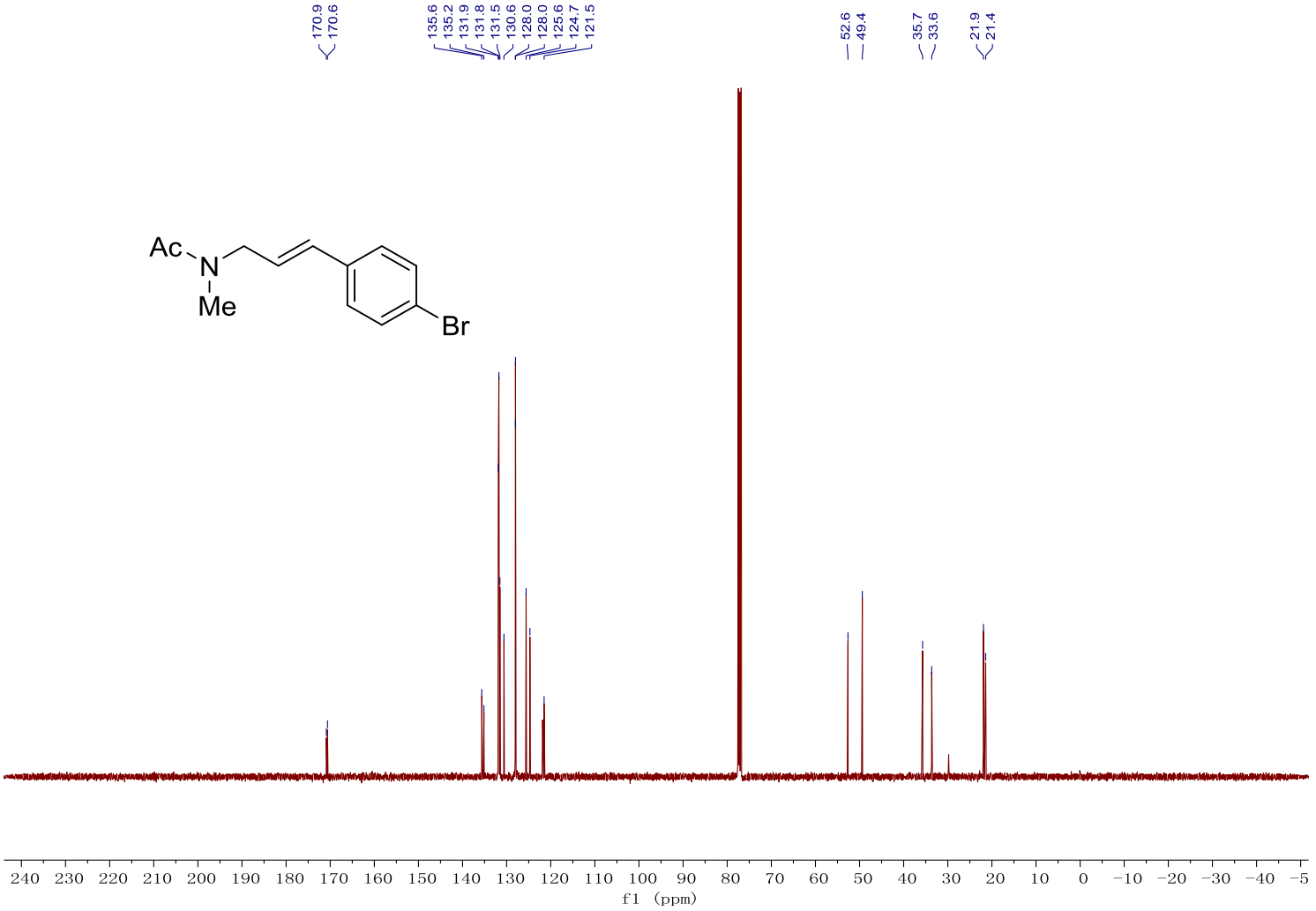
Supplementary Figure 67. Compound **32** ^{13}C NMR in $CDCl_3$



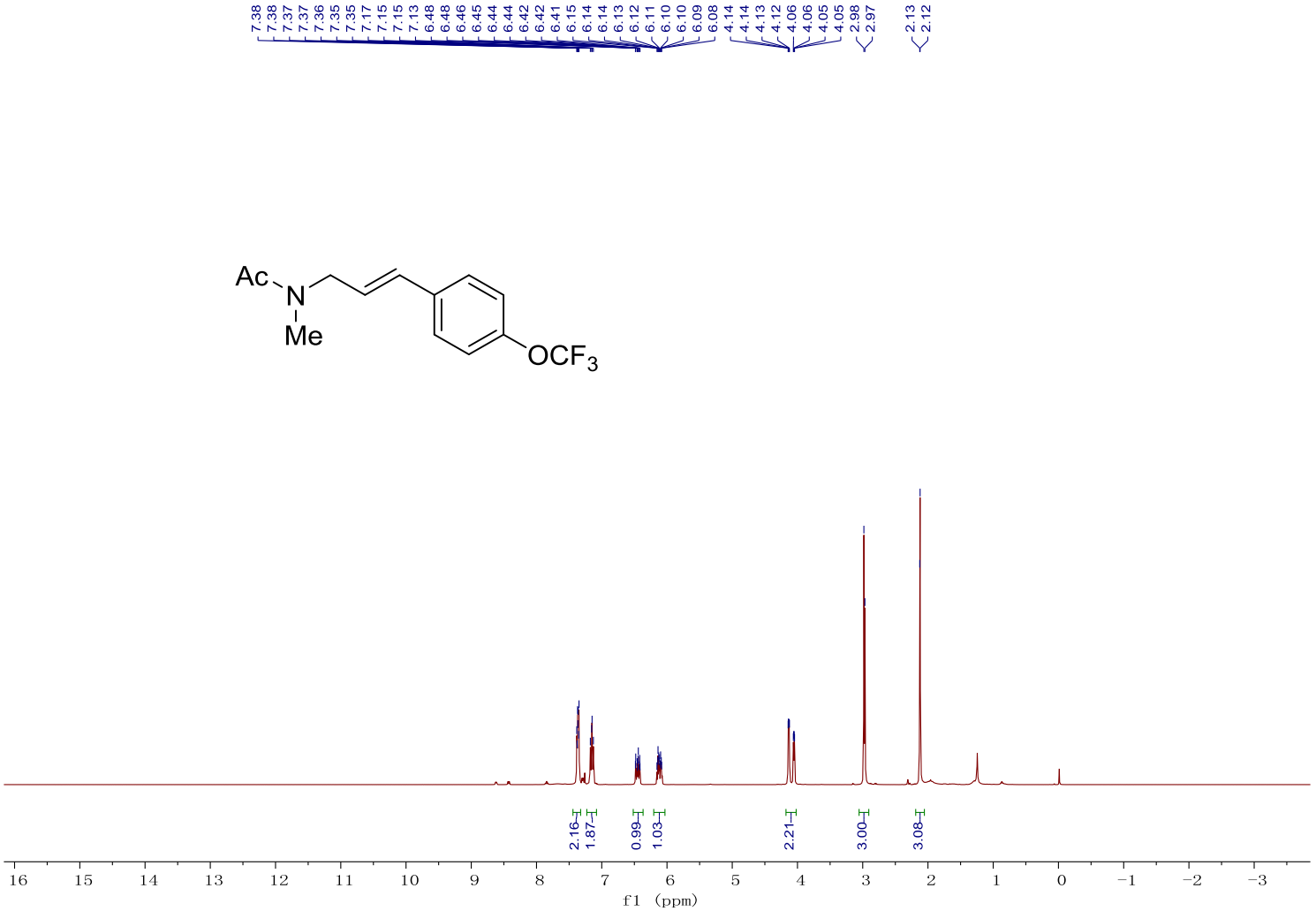
Supplementary Figure 68. Compound **33** ^{1}H NMR in $CDCl_3$



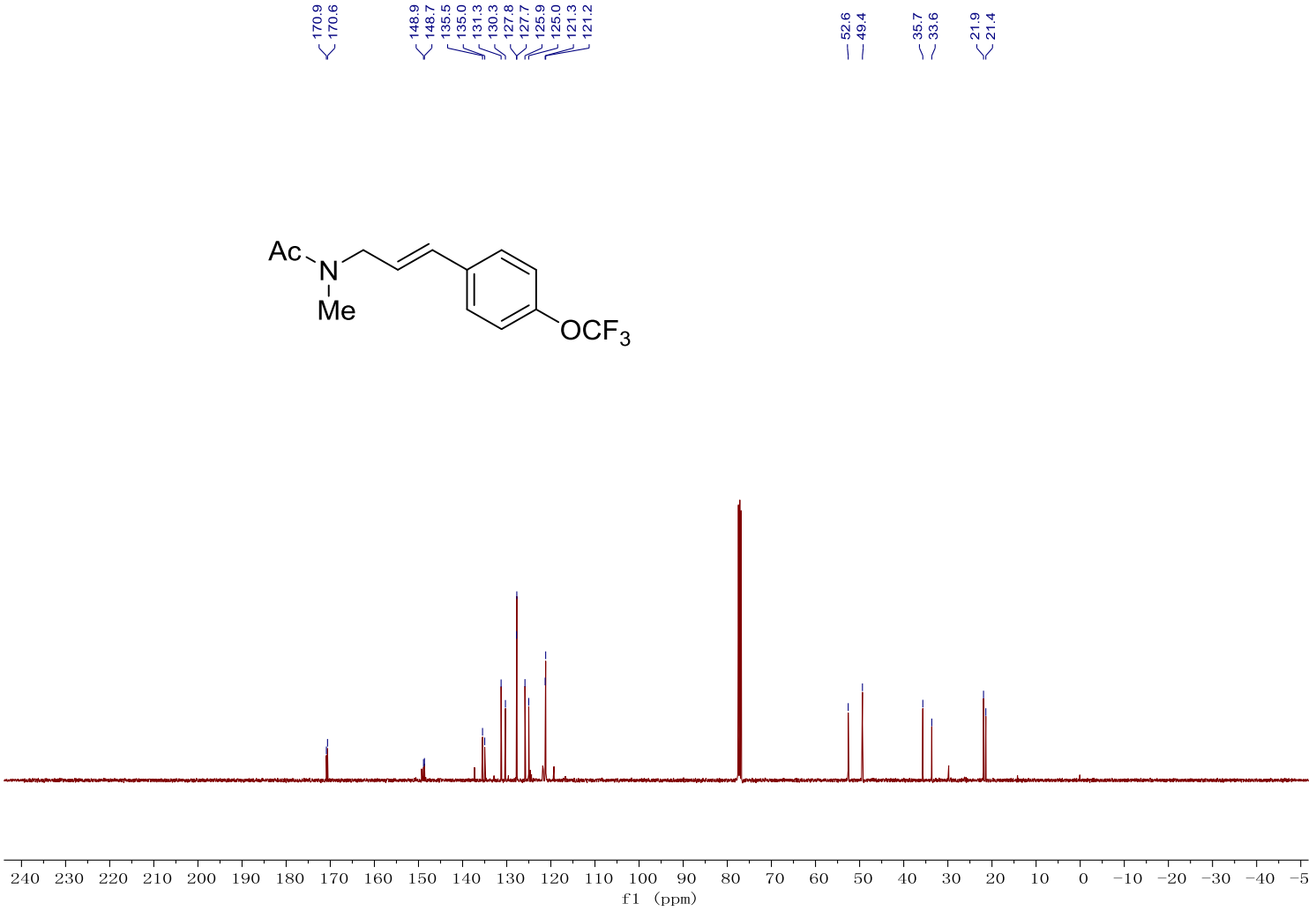
Supplementary Figure 69. Compound **33** ^{13}C NMR in $CDCl_3$



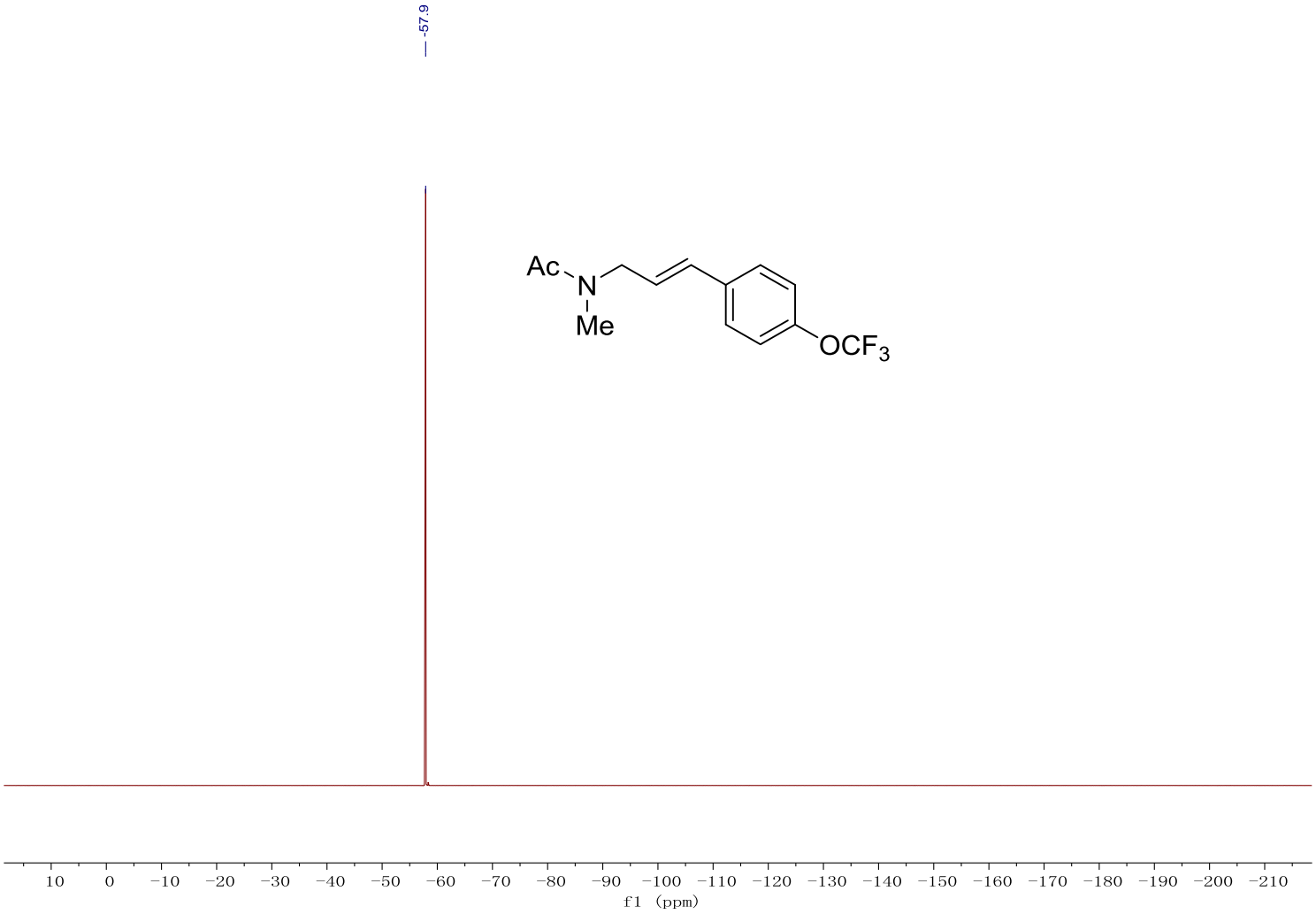
Supplementary Figure 70. Compound **34** ^{1}H NMR in $CDCl_3$



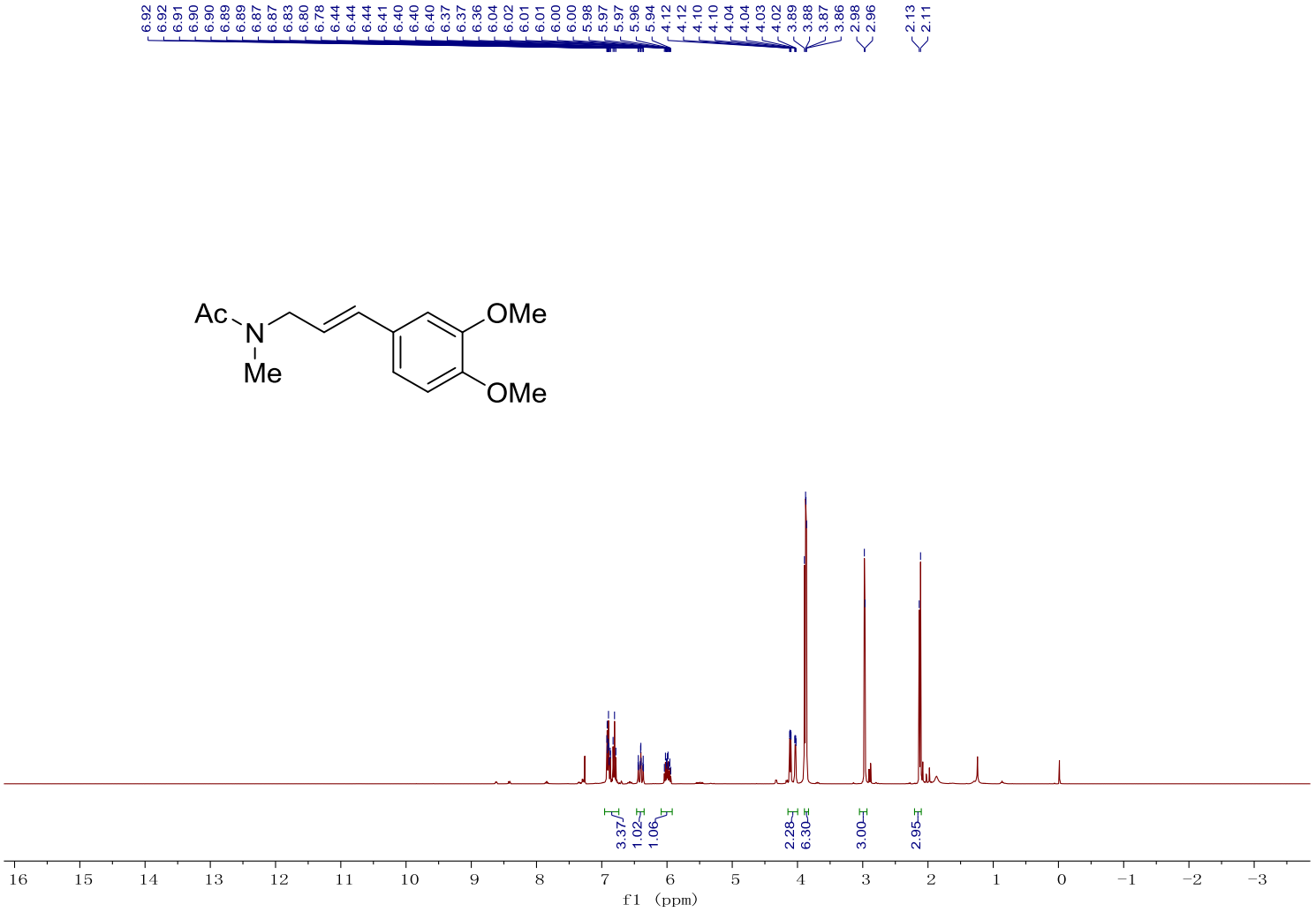
Supplementary Figure 71. Compound **34** ^{13}C NMR in $CDCl_3$



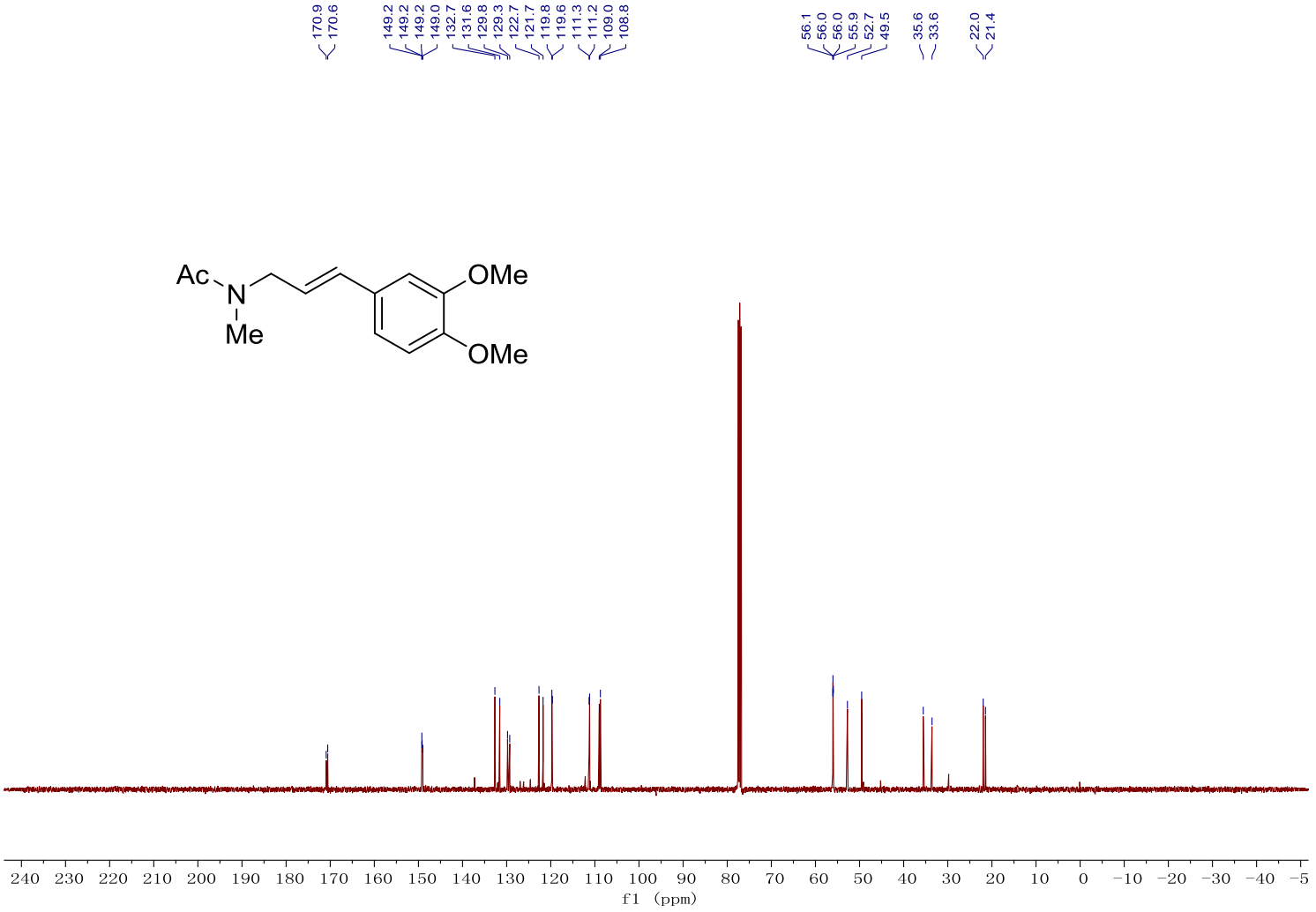
Supplementary Figure 72. Compound **34** ^{19}F NMR in $CDCl_3$



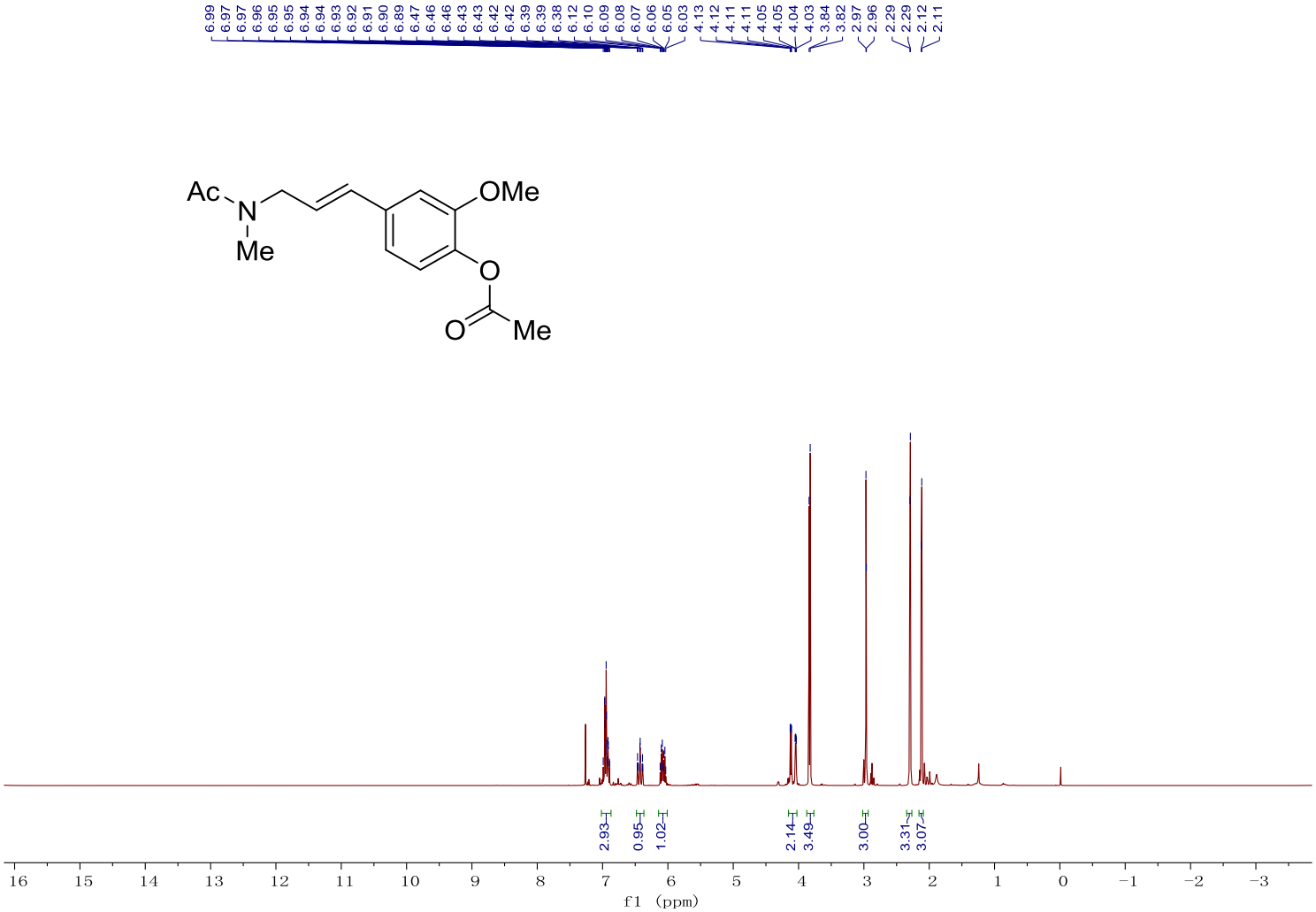
Supplementary Figure 73. Compound **35** ^{1}H NMR in $CDCl_3$



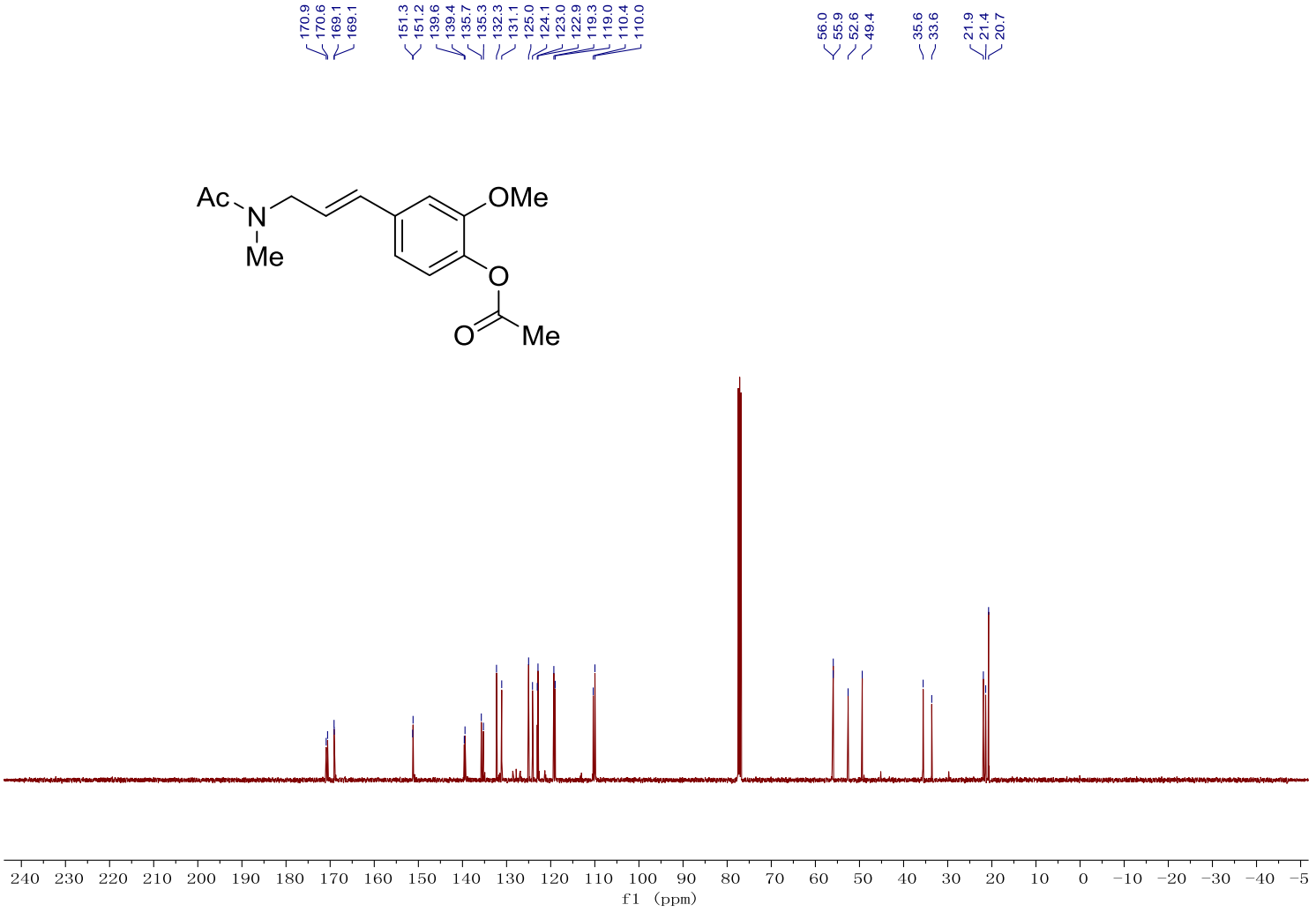
Supplementary Figure 74. Compound **35** ^{13}C NMR in $CDCl_3$



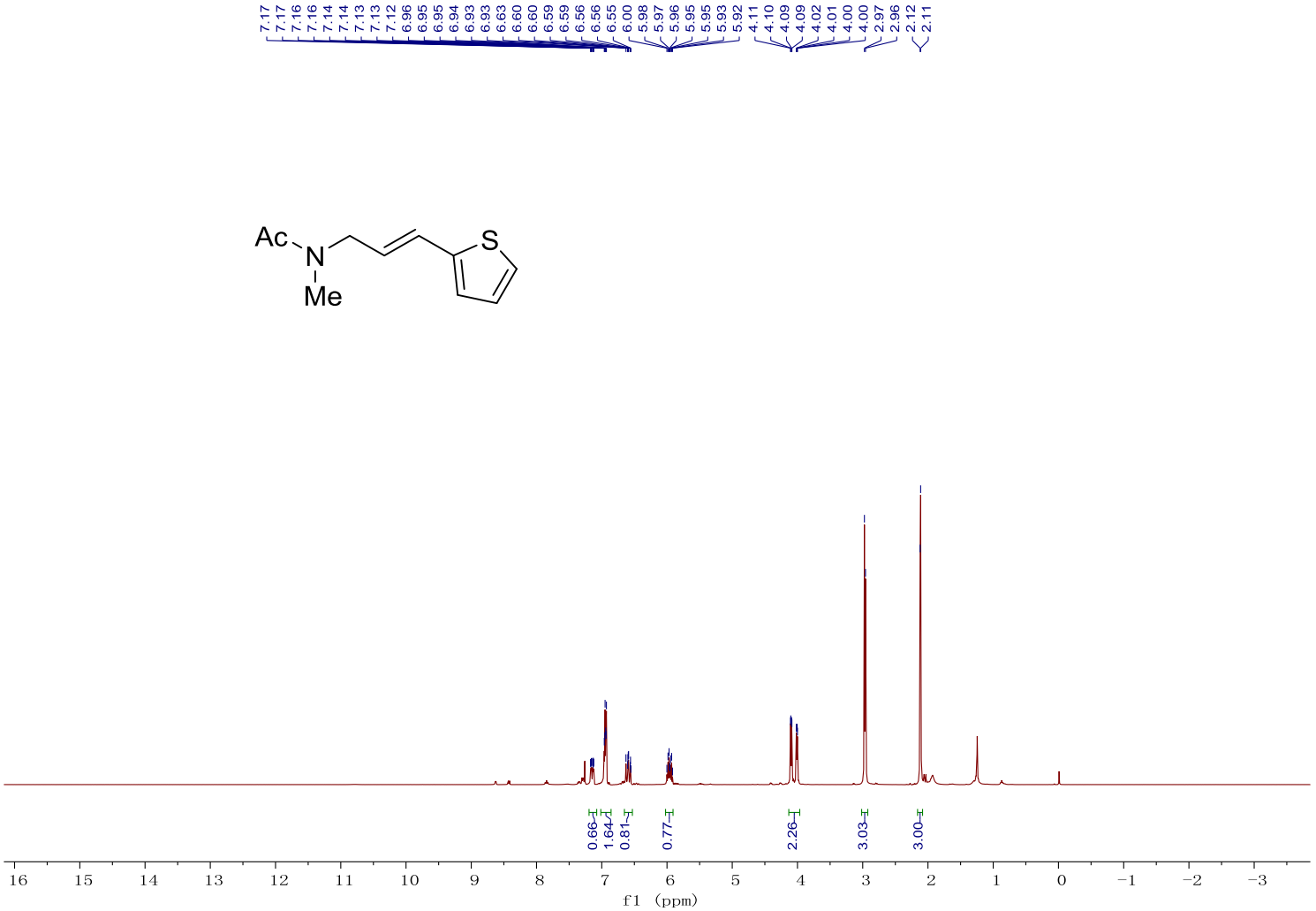
Supplementary Figure 75. Compound **36** ^{1}H NMR in $CDCl_3$



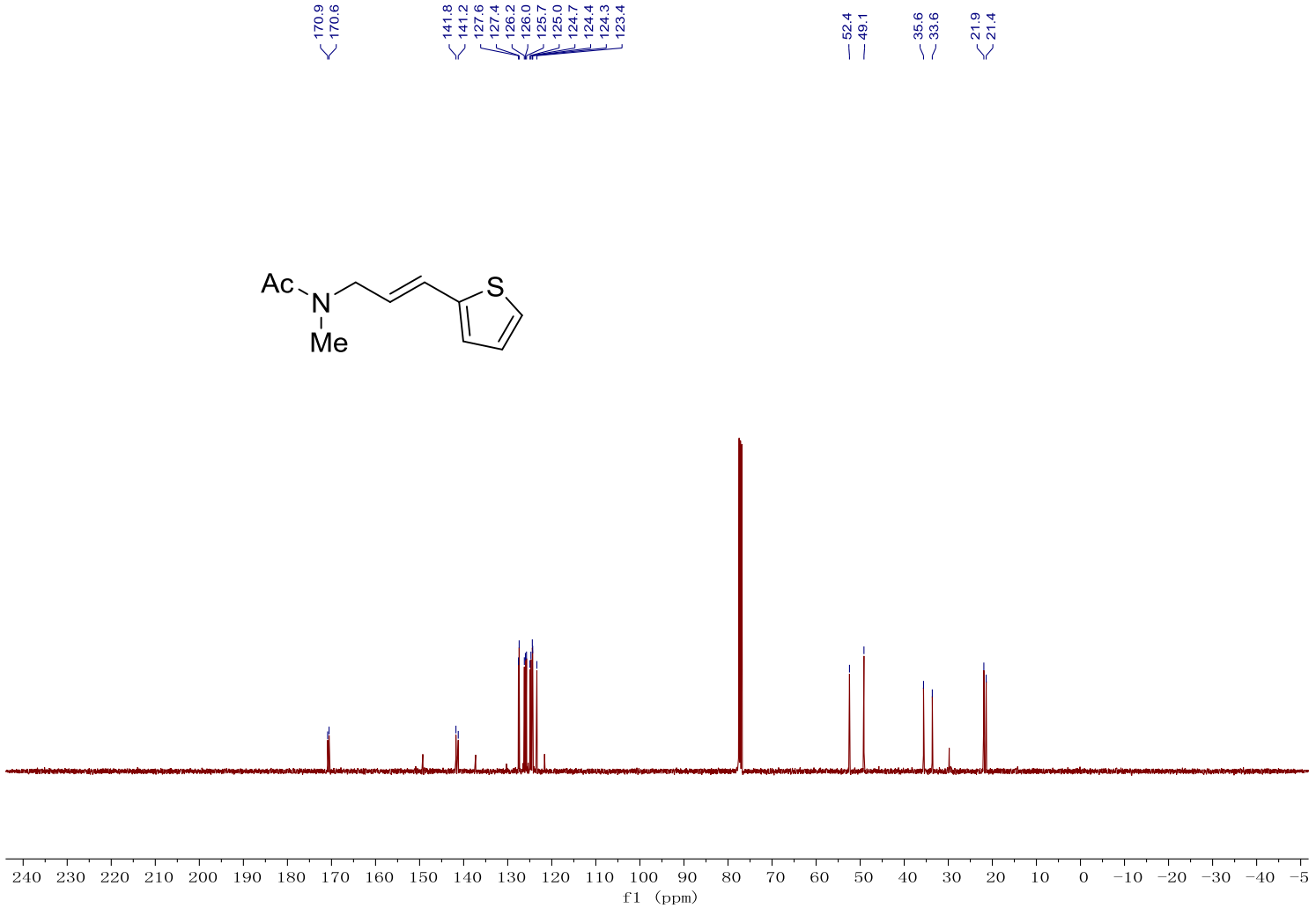
Supplementary Figure 76. Compound **36** ^{13}C NMR in $CDCl_3$



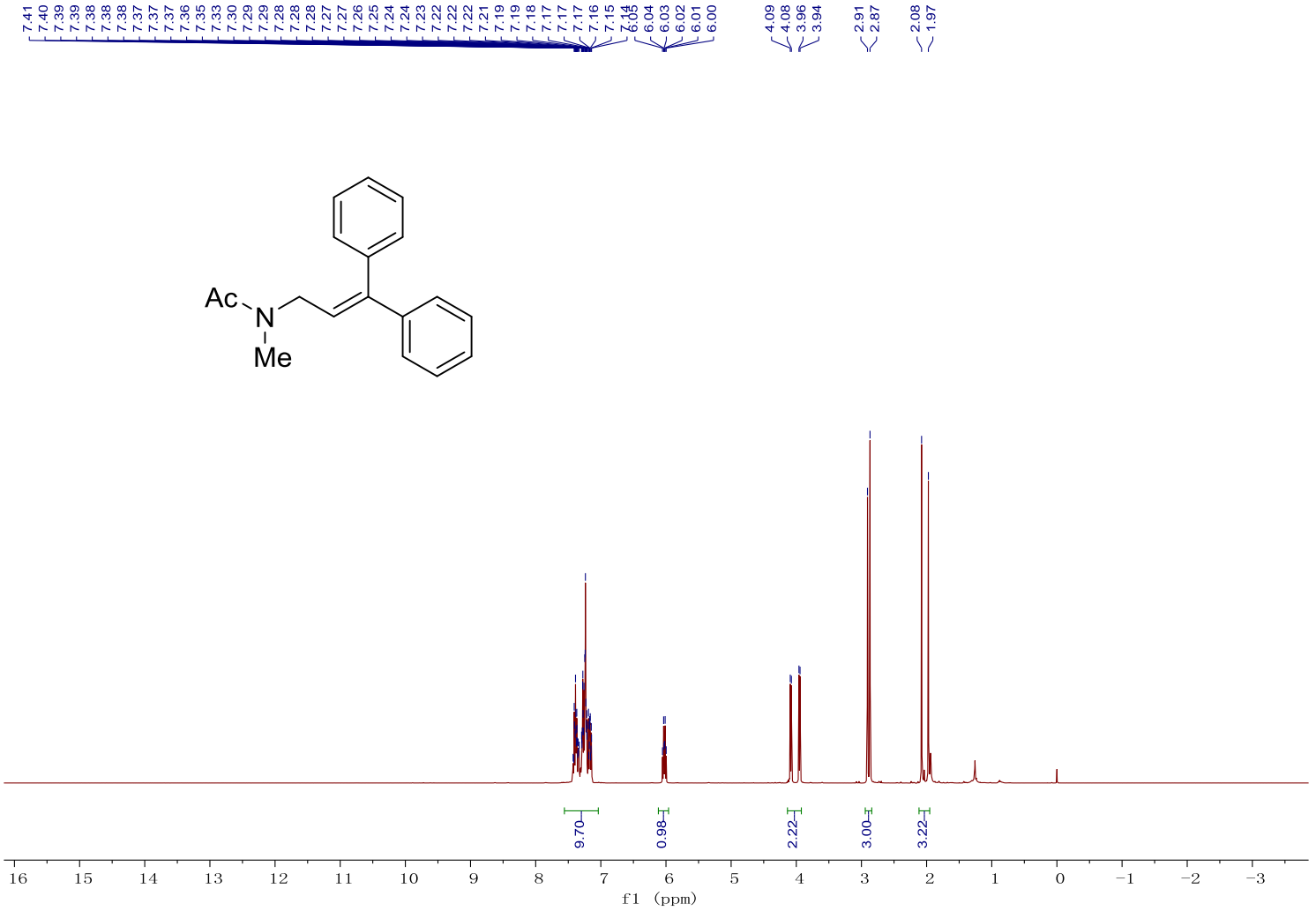
Supplementary Figure 77. Compound **37** ^{1}H NMR in $CDCl_3$



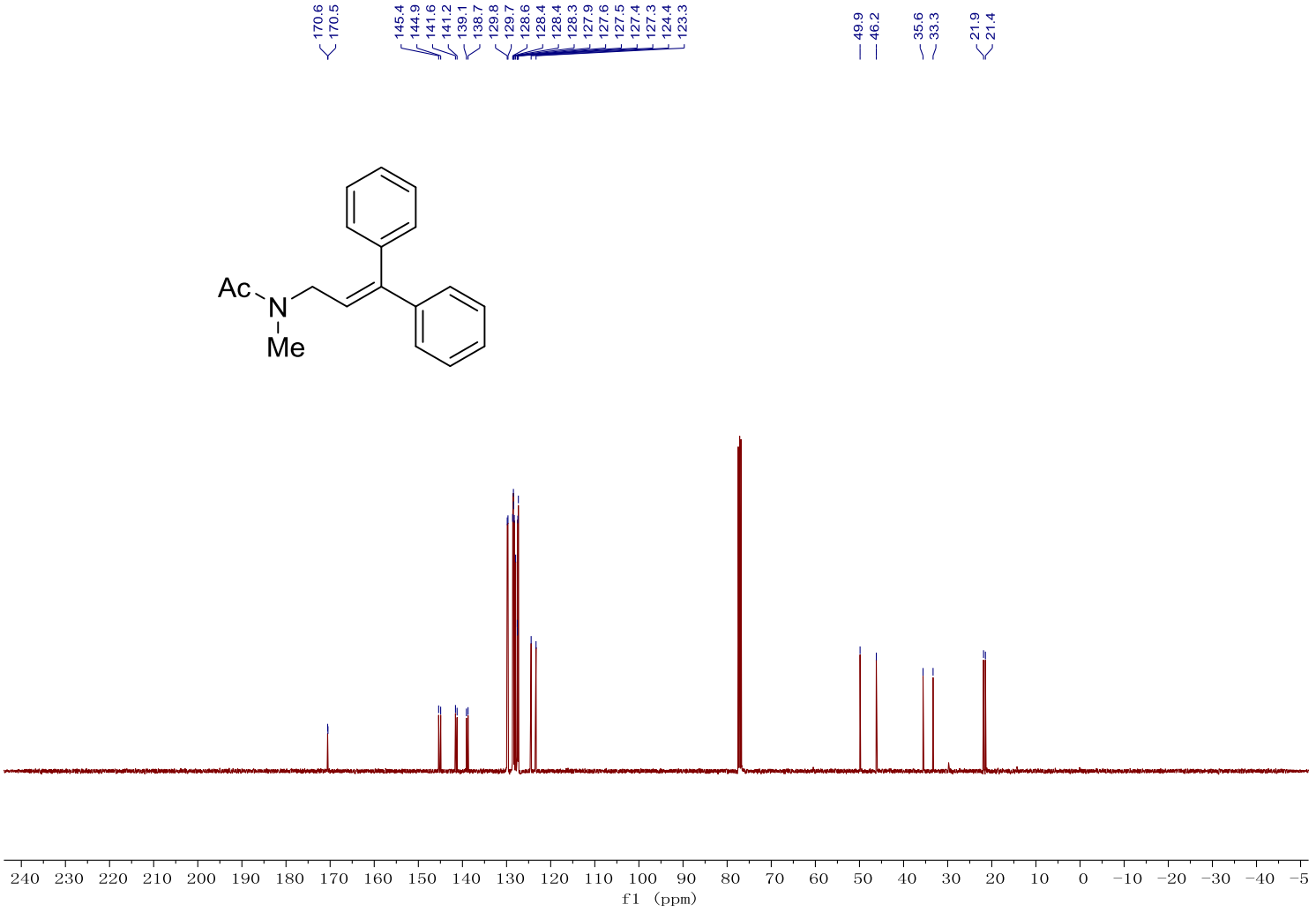
Supplementary Figure 78. Compound **37** ^{13}C NMR in $CDCl_3$



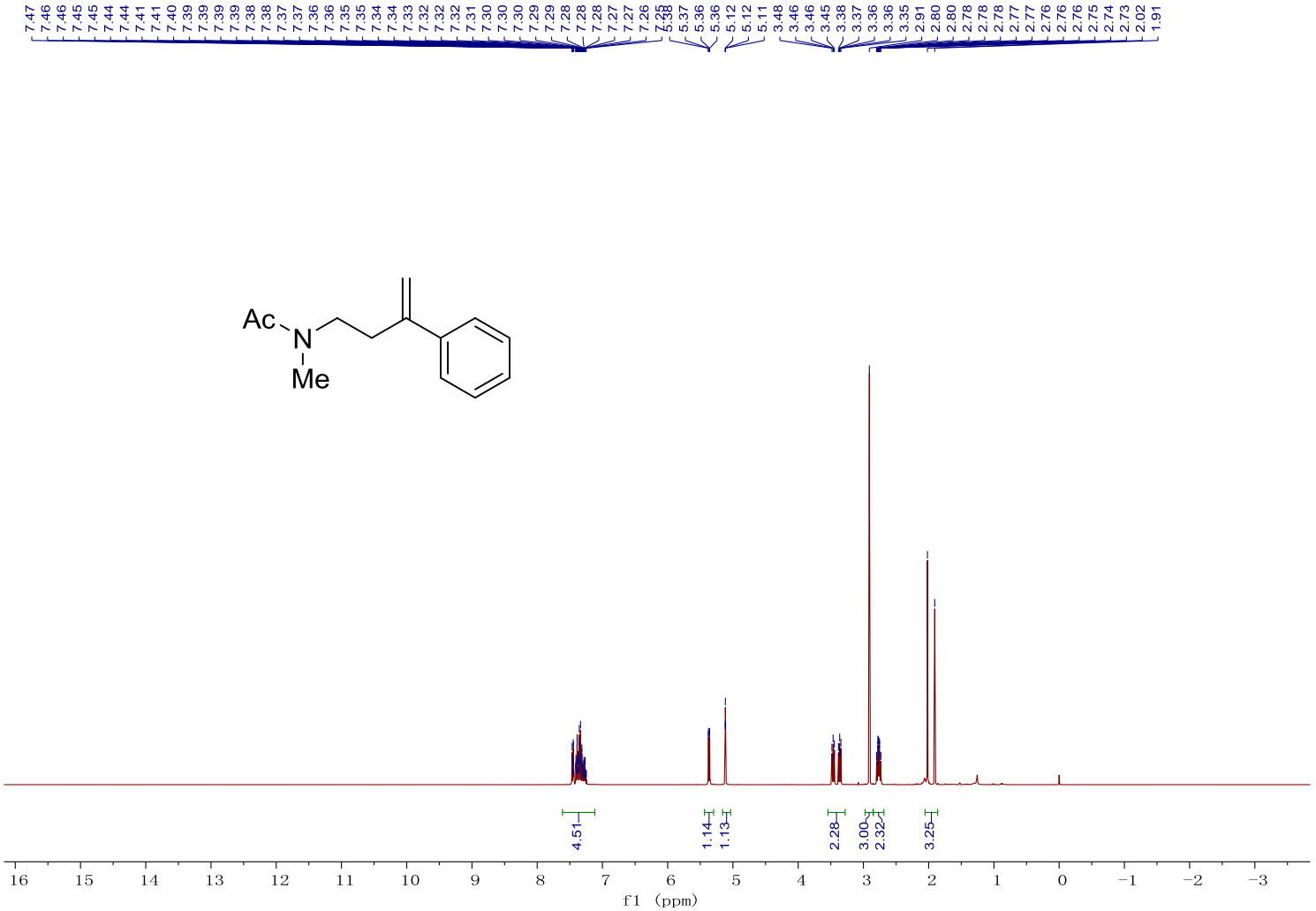
Supplementary Figure 79. Compound **38** ^{1}H NMR in $CDCl_3$



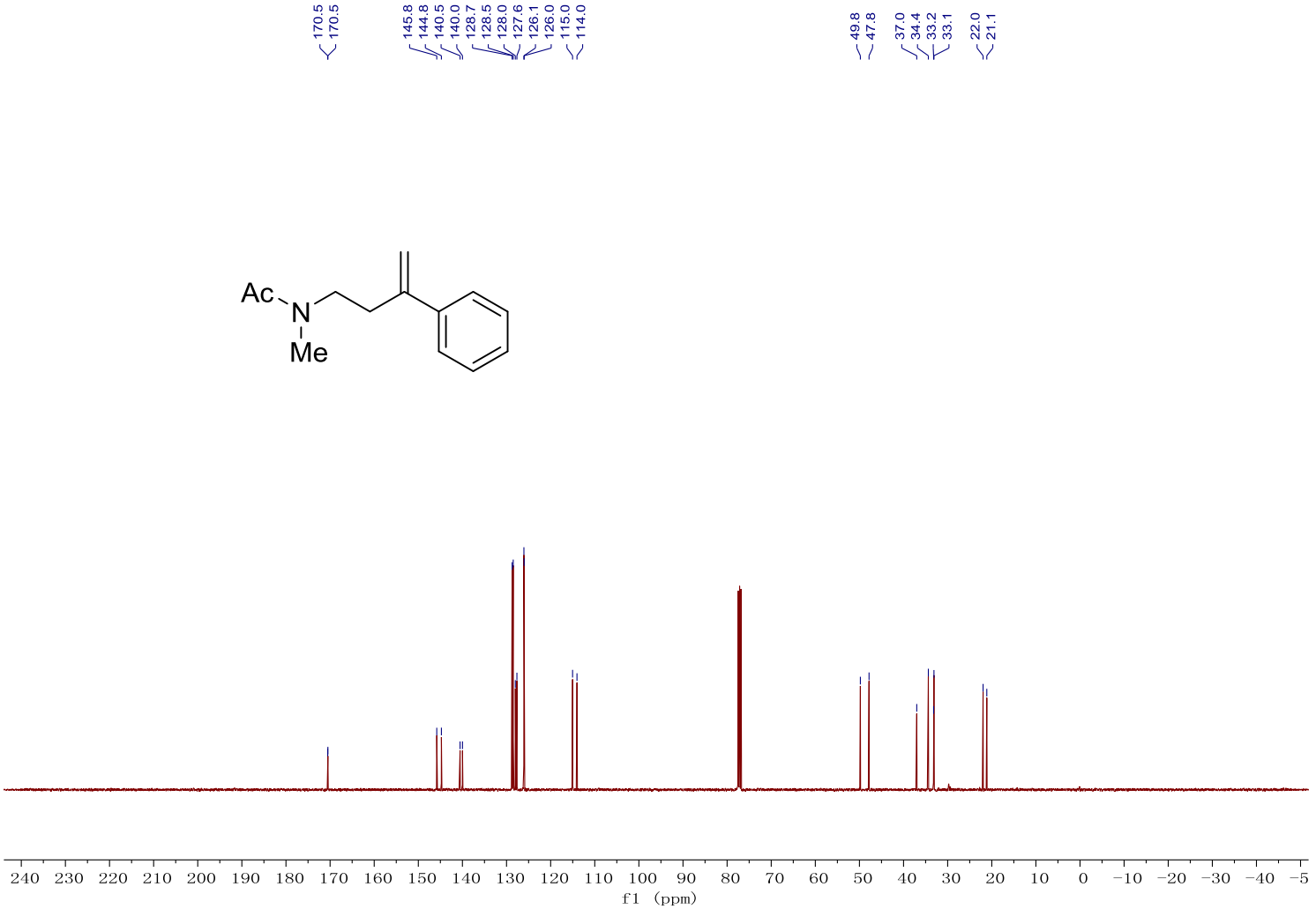
Supplementary Figure 80. Compound **38** ^{13}C NMR in $CDCl_3$



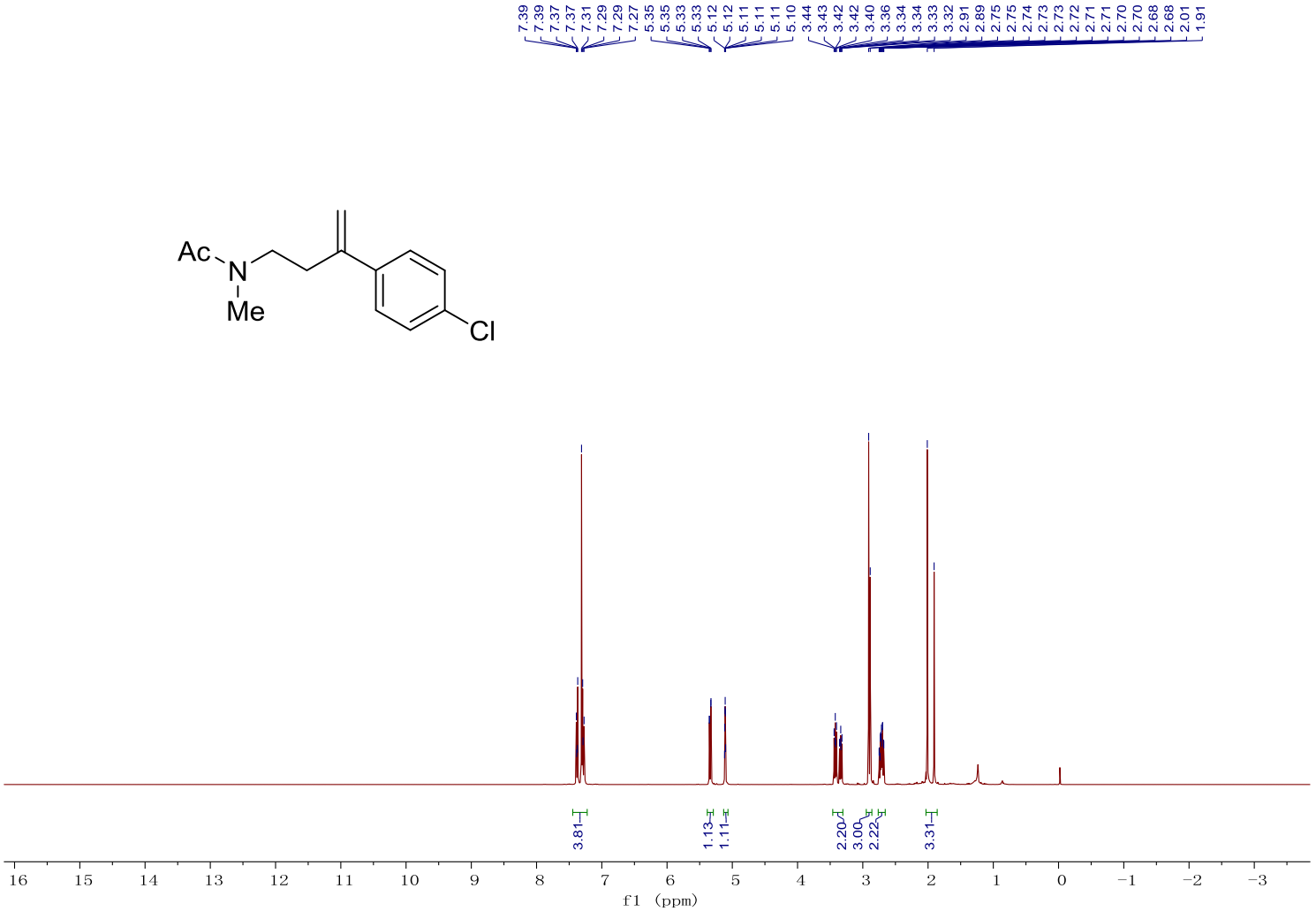
Supplementary Figure 81. Compound **39** ^{1}H NMR in $CDCl_3$



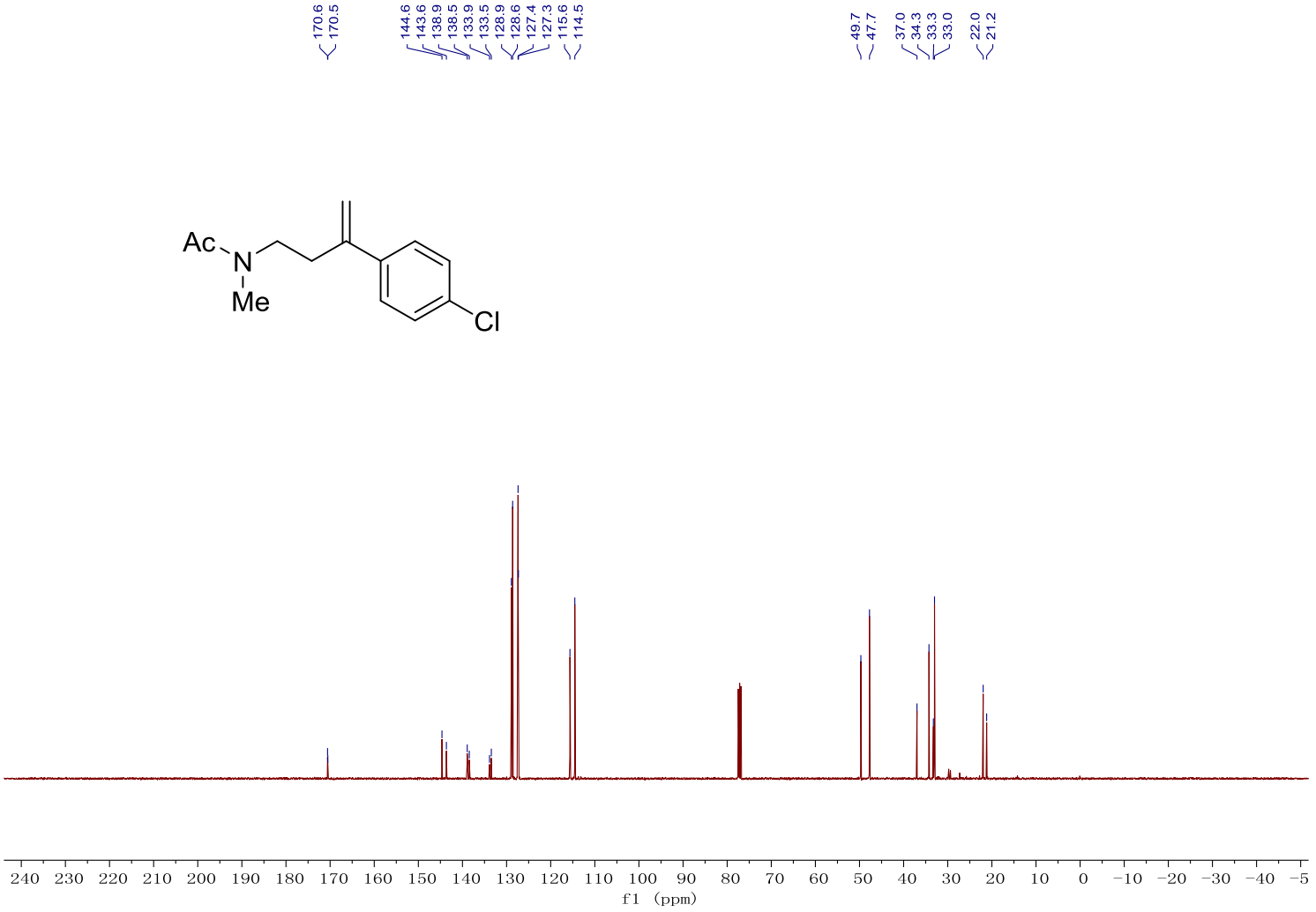
Supplementary Figure 82. Compound **39** ^{13}C NMR in $CDCl_3$



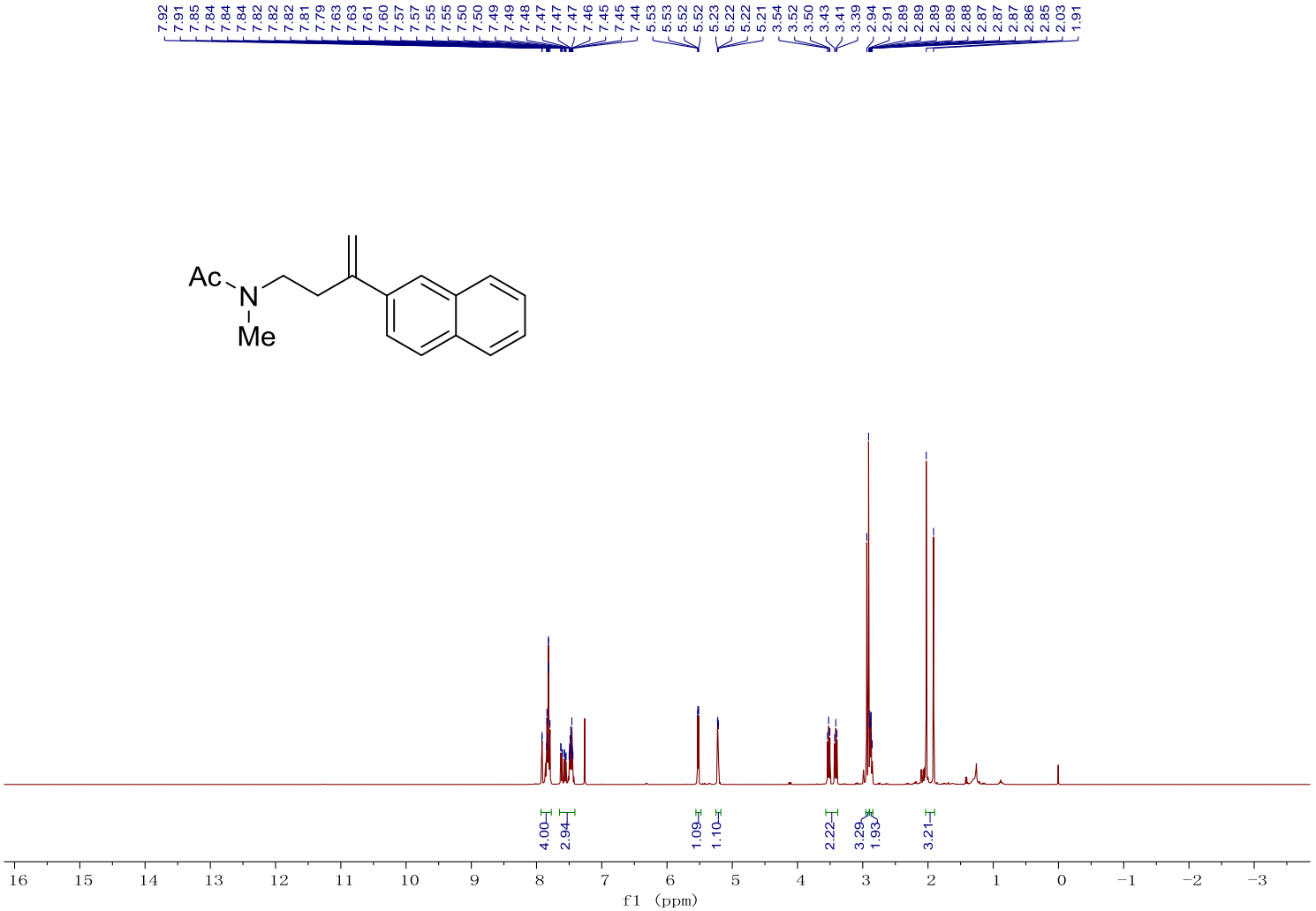
Supplementary Figure 83. Compound **40** ^{1}H NMR in $CDCl_3$



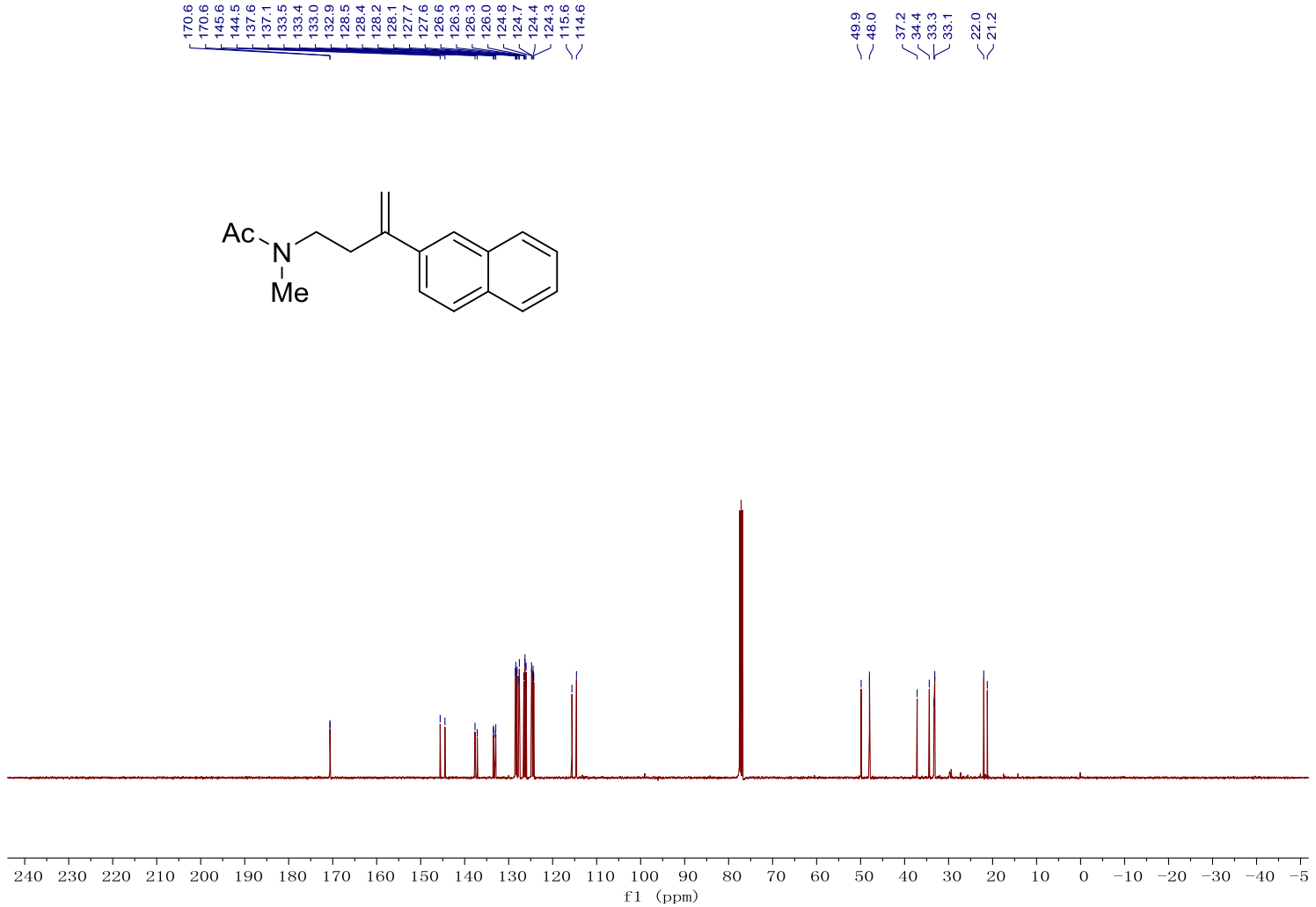
Supplementary Figure 84. Compound **40** ^{13}C NMR in $CDCl_3$



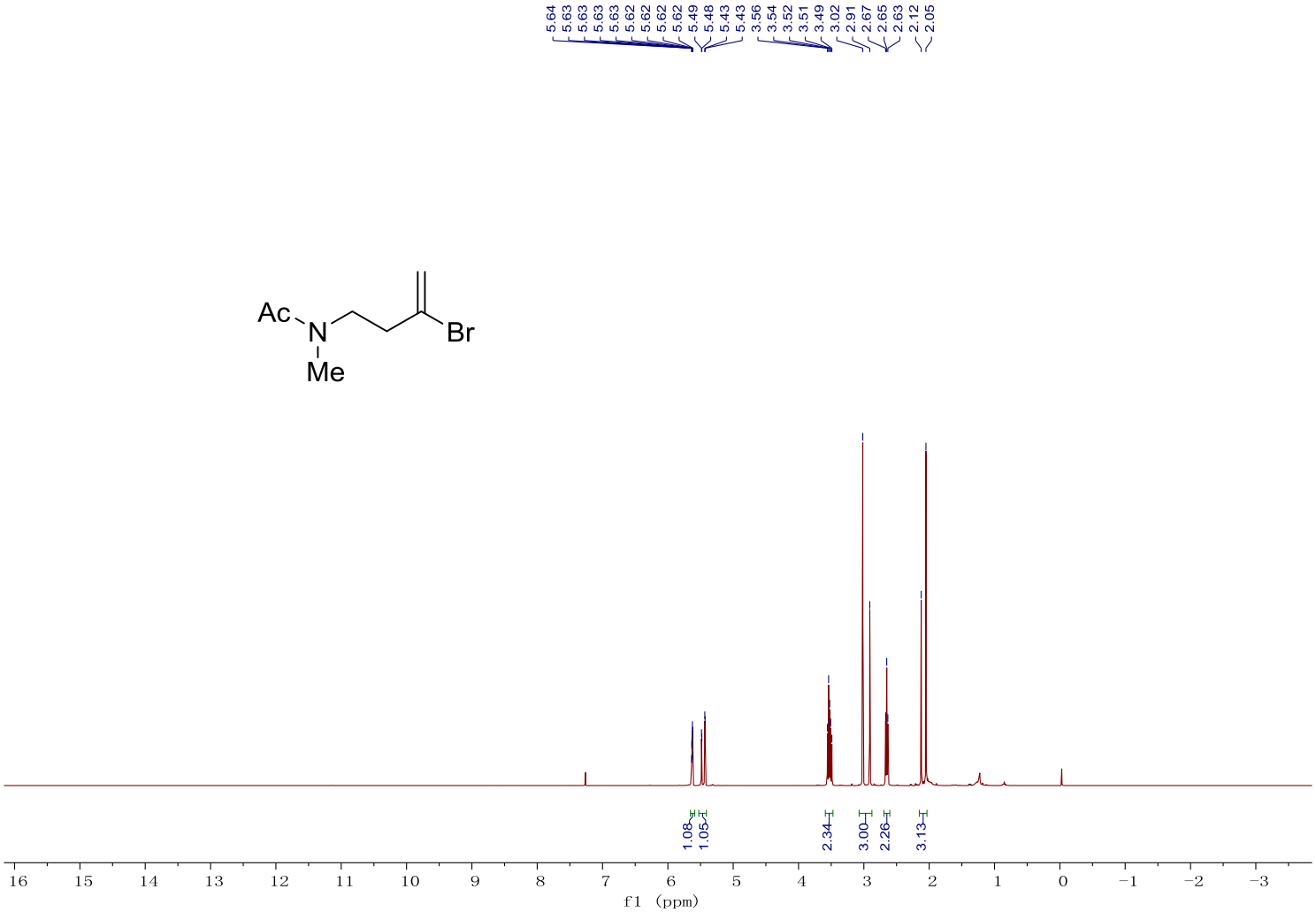
Supplementary Figure 85. Compound **41** ^{1}H NMR in $CDCl_3$



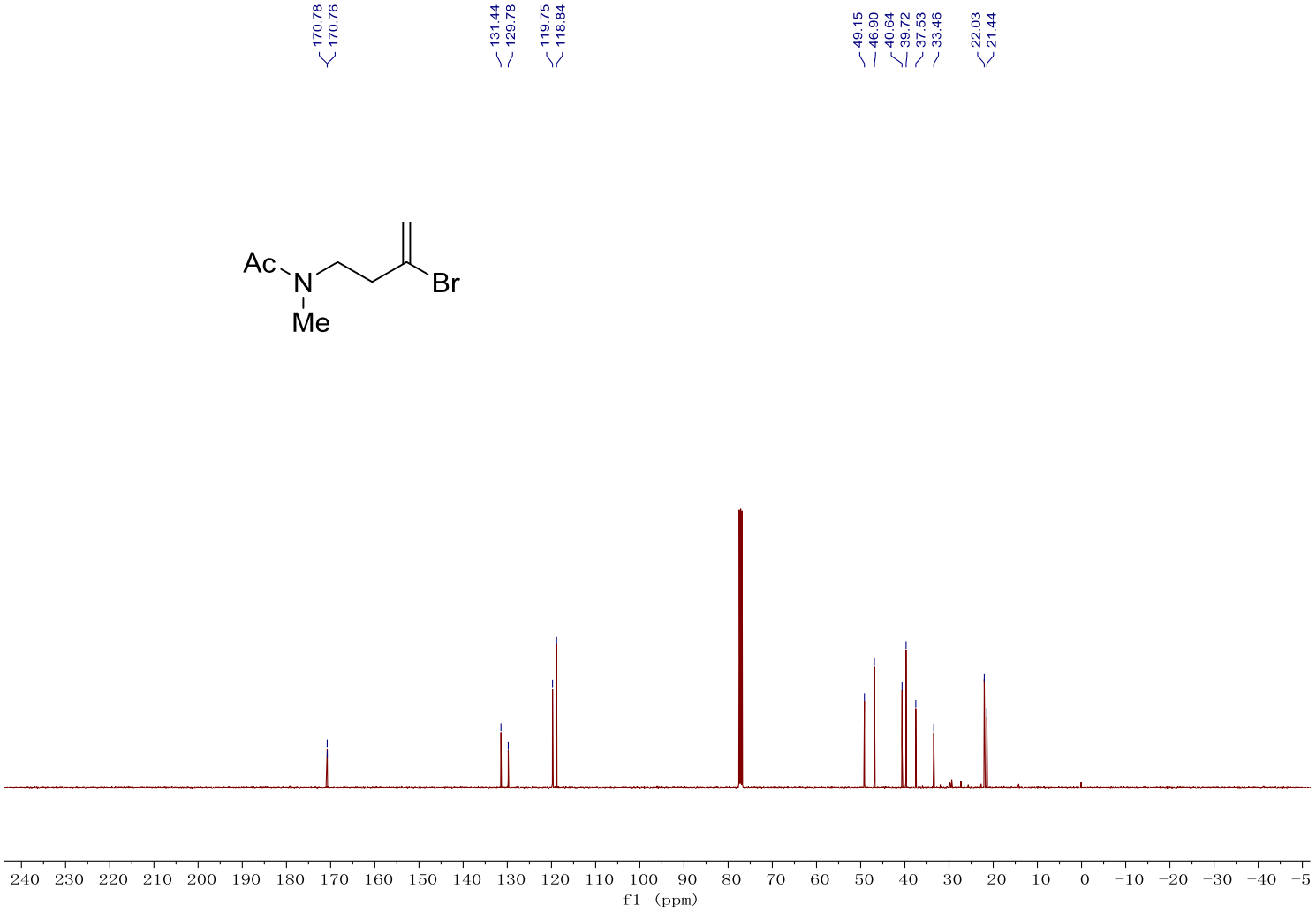
Supplementary Figure 86. Compound **41** ^{13}C NMR in $CDCl_3$



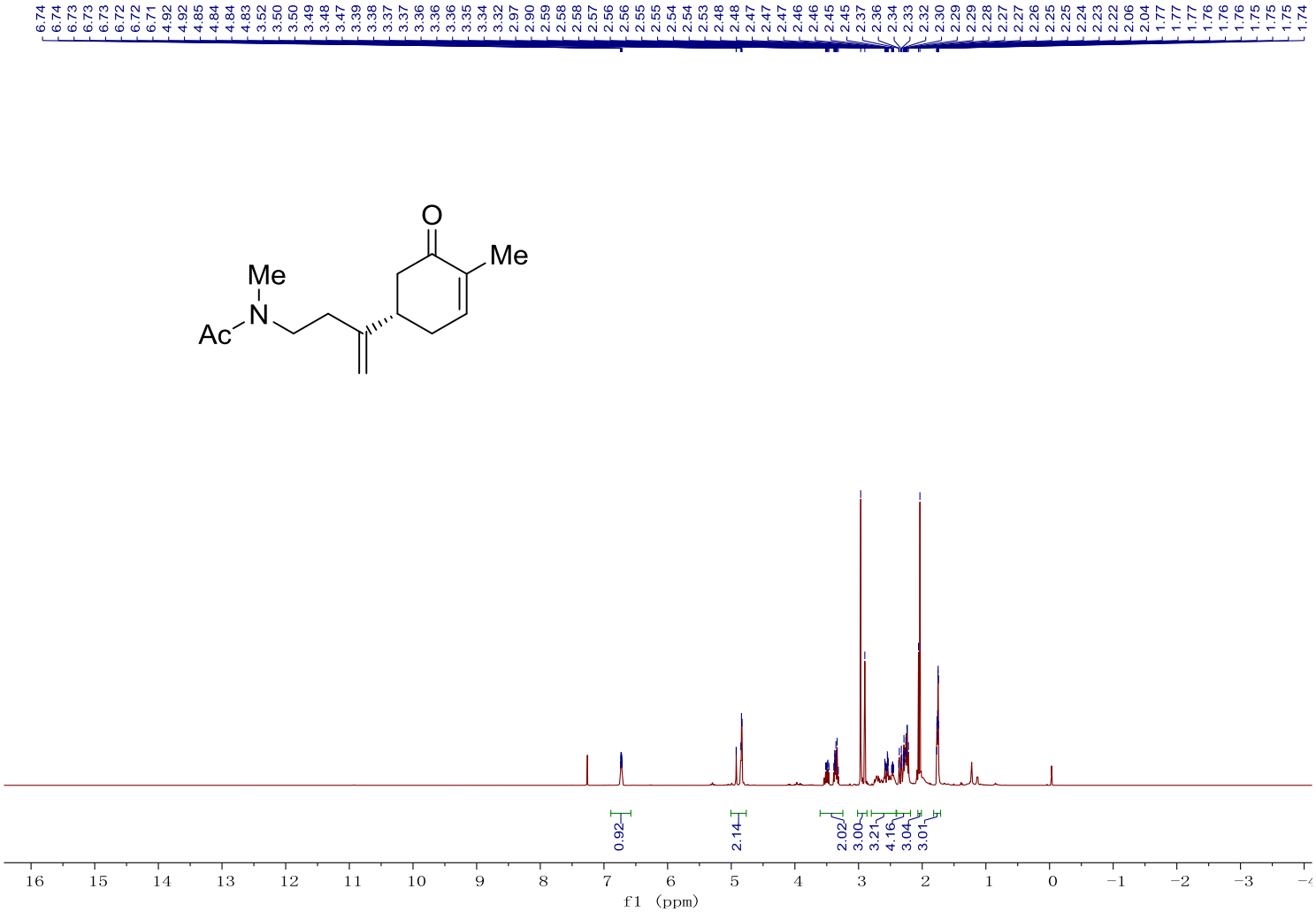
Supplementary Figure 87. Compound **42** ^{1}H NMR in $CDCl_3$



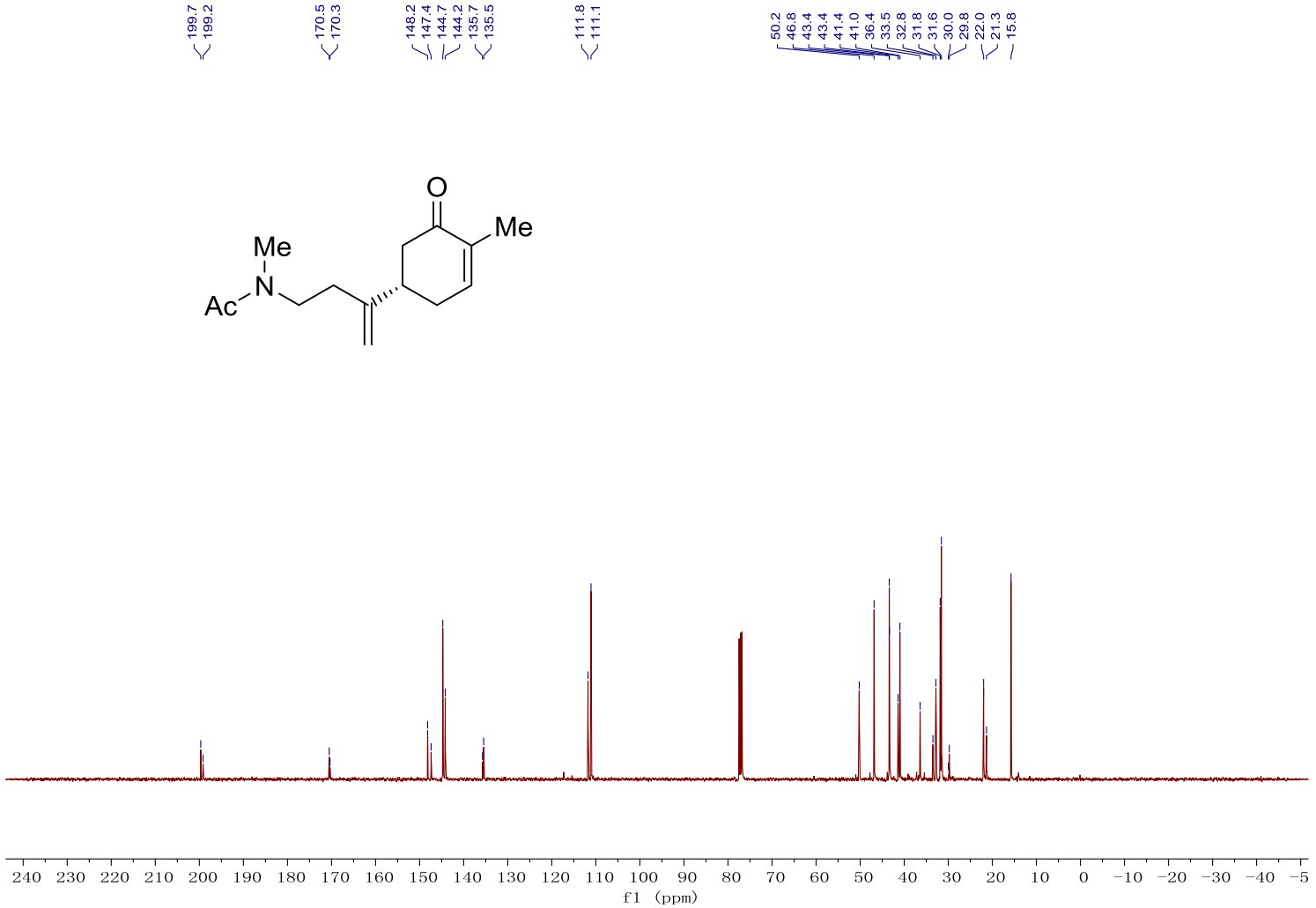
Supplementary Figure 88. Compound **42** ^{13}C NMR in $CDCl_3$



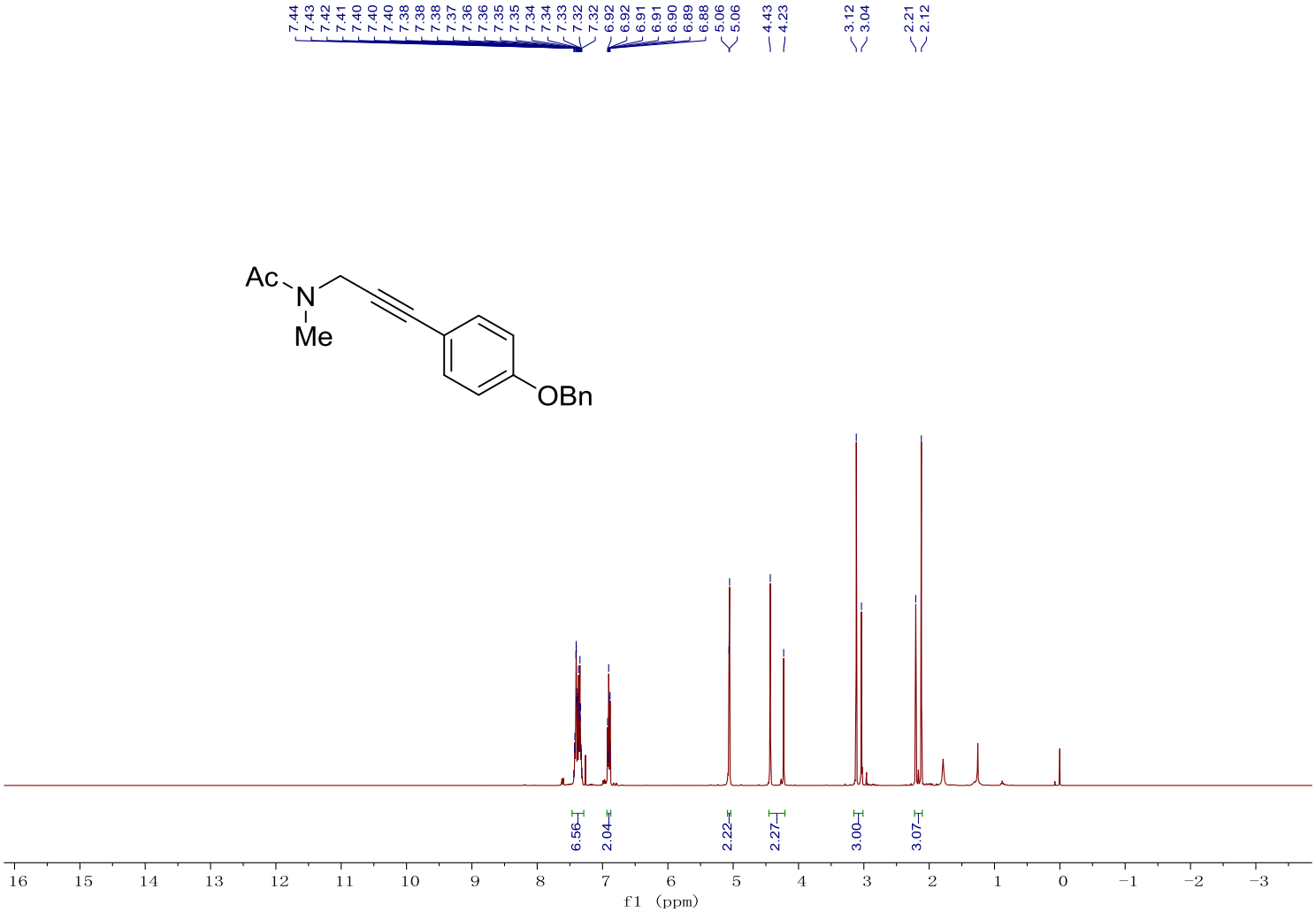
Supplementary Figure 89. Compound **43** ^{1}H NMR in $CDCl_3$



Supplementary Figure 90. Compound **43** ^{13}C NMR in $CDCl_3$



Supplementary Figure 91. Compound **47** ^{1}H NMR in $CDCl_3$



Supplementary Figure 92. Compound **47** ^{13}C NMR in $CDCl_3$