Supporting Information for

Rhodium-catalysed homo-coupling of terminal alkynes: divergent synthesis of bioactive 1,3-diyne and conjugated enediynes

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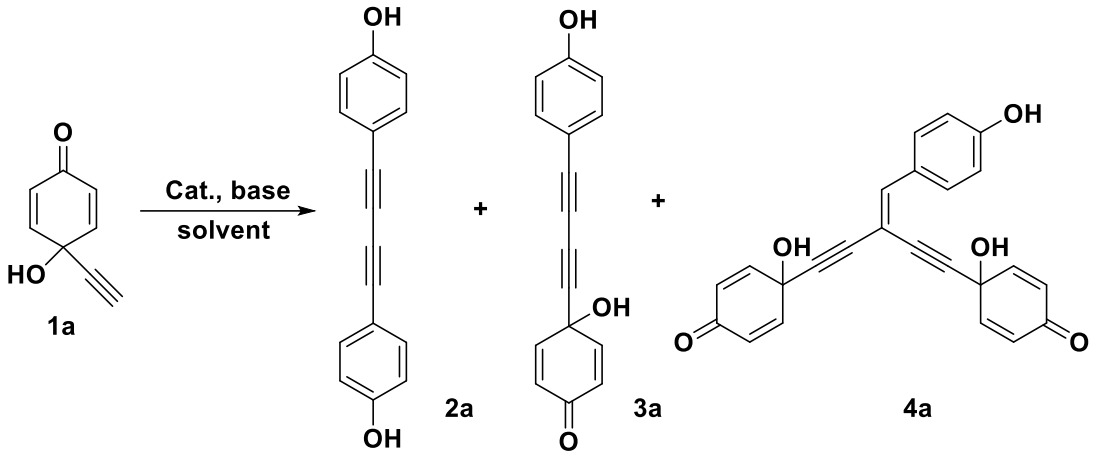
1. General methods

NMR spectra were recorded on a Bruker AVANCE III 600 instrument using $CDCl_3$ and DMSO-d_6 as solvent. The ^1H and ^{13}C chemical shifts are reported in parts per million relatives to tetramethylsilane as an internal standard. Data for ^1H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, brs = broad singlet, coupling constant (s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). High-resolution mass spectra (HRMS) were performed on Vanquish flex+oribit rap exploris 120 (Thermo Scientific). For chromatography, analytical TLC plates and 100-400 mesh silica gel were used. All the solvents and chemicals were purchased and used as available. Unless otherwise stated, all reagents were purchased from commercial suppliers (Energy-chemical, Adamas, Innochem, Macklin) and used without further purification.

2. Preliminary screening of reaction conditions

Table S1: Optimization of the reaction conditions[a]

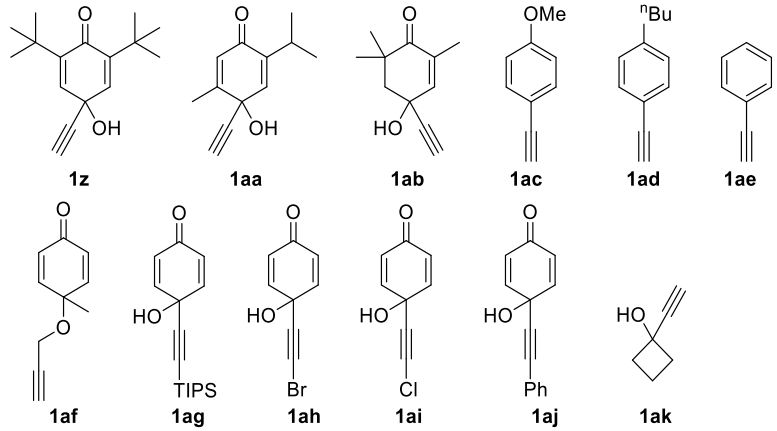


Entry	Cat.	Base	Solvent	T (°C)	*t* (h)	Yield[b] of (2a/3a/4a) %
1	[Ru(*p*-cymene)Cl_2]$_2$	AgOTf	DMF	rt-50	6	ND
2	[RhCl(COD)]$_2$	AgOTf	DMF	rt-50	6	NA
3	Grubbs(I)	AgOTf	DMF	rt	24	NA
4	Co(acac)$_2$	AgOTf	DMF	rt	24	NA
5	[Cp*IrCl_2]$_2$	AgOTf	DMF	rt	8	ND
6	Au(PPh_3)Cl	AgOTf	DMF	rt	8	NA
7	[Cp*RhCl_2]$_2$	AgOTf	DMF	rt	4	0/18/67
8	[Cp*RhCl_2]$_2$	$AgSbF_6$	DMF	rt	4	0/18/67
9	[Cp*RhCl_2]$_2$	$AgNTf_2$	DMF	rt	4	0/18/67
10	[Cp*RhCl_2]$_2$	Zn(OTf)$_2$	DMF	rt-60	24	NA
11	[Cp*RhCl_2]$_2$	Zn(NTf_2)$_2$	DMF	rt	24	NA
12	[Cp*RhCl_2]$_2$	Ag_2CO_3	DMF	rt	24	ND
13	[Cp*RhCl_2]$_2$	AgOAc	DMF	rt	24	ND
14	[Cp*RhCl_2]$_2$	AgF	DMF	rt	24	ND
15	[Cp*RhCl_2]$_2$	Ag_2O	DMF	rt	24	ND
16	[Cp*RhCl_2]$_2$	Sc(OTf)$_3$	DMF	rt	24	NA
17	[Cp*RhCl_2]$_2$	AgOTf	DMAc	rt	overnight	0/0/74

18	$[Cp^*RhCl_2]_2$	AgOTf	1,4-dioxane	rt	24	0/90/0
19	$[Cp^*RhCl_2]_2$	AgOTf	1,4-dioxane	50	4	0/62/0
20	$[Cp^*RhCl_2]_2$	AgOTf	$PhCF_3$	rt	24	ND
21	$[Cp^*RhCl_2]_2$	AgOTf	THF	rt	24	ND
22	$[Cp^*RhCl_2]_2$	AgOTf	Et_2O	rt	24	ND
23	$[Cp^*RhCl_2]_2$	AgOTf	PhCl	rt	24	ND
24	$[Cp^*RhCl_2]_2$	AgOTf	EtOH	rt	24	NA
25	$[Cp^*RhCl_2]_2$	AgOTf	MeOH	rt	24	NA
26	$[Cp^*RhCl_2]_2$	AgOTf	DCE	rt-50	24	NA
27	$[Cp^*RhCl_2]_2$	AgOTf	$CHCl_3$	rt	24	NA
28	$[Cp^*RhCl_2]_2$	AgOTf	CH_3CN	rt	24	NA
29	$[Cp^*RhCl_2]_2$	AgOTf	acetone	rt	16	0/71/0
30	$[Cp^*RhCl_2]_2$	$Zn(OTf)_2$	acetone	rt	24	NA
31	$[Cp^*RhCl_2]_2$	AgOTf	acetone	50	16	0/60/0
32	$[Cp^*RhCl_2]_2$	AgOTf	DMSO	rt-50	24	NA
33	$[Cp^*RhCl_2]_2$	--	DMF	rt	36	NR
34	--	AgOTf	DMF	rt	36	NR
35	$[Cp^*RhCl_2]_2$	-	1,4-dioxane	50	36	NR
36	-	AgOTf	1,4-dioxane	50	36	NR

[a]The reaction conditions: **1a (**0.15 mmol**)**, catalyst (5 mol %), Base (2.0 equiv), and 1 mL of solvent were mixed in a Schlenk tube under argon atmosphere; [b]Isolated yield. ND = Not detected, NA = not applicable.

Table S2: Incompatible substrates



These substrates are incompatible with the standard conditions in Table 2 and Table 3 of the manuscript.

Experimental details for the incompatible substrates:

(1) Under standard reaction conditions, the reaction was complex in TLC (1z, **1aa**); there was no desired compound was observed, and remained only the starting materials (**1ad, 1ae, 1af**).

(2) The reaction didn't proceed when prolonging the reaction time overnight. (**1ab,1ag,1ah,1ai,1aj**)

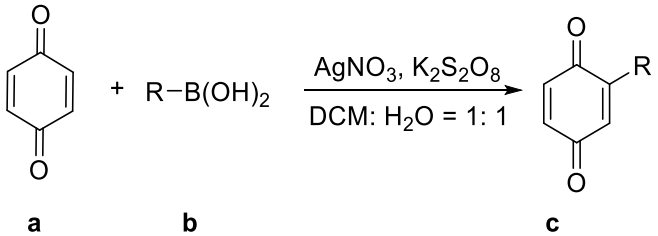
(3) The reaction didn't proceed at 80 ^{o}C for 4 h. (**1ac**)

(4) The reaction didn't proceed at 50 ^{o}C overnight. (**1ak**)

3. General procedure for the preparation of starting materials.

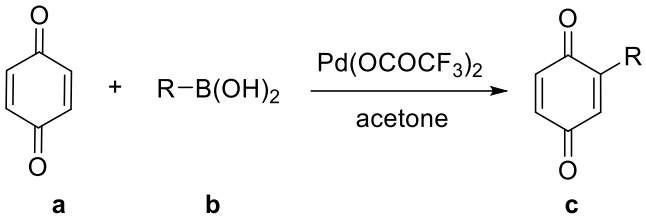
General methods for the synthesis of substituted benzoquinone

Method A[1]



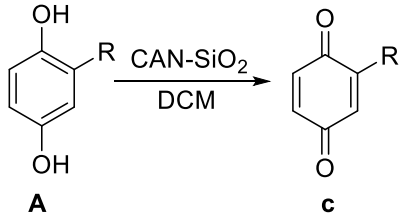
To a solution of benzoquinone **a** (10 mmol, 1.0 equiv) in dichloromethane (50 mL) was added the boronic acid **b** (15 mmol, 1.5 equiv), water (50 mL), and silver(I) nitrate (0.1 M solution in water, 344 mg, 2 mmol, 0.2 equiv). Potassium persulfate (8.08 g, 30 mmol, 3.0 equiv) was then added and the solution was stirred vigorously at room temperature and monitored by thin-layer chromatography. Upon consumption of quinone (10 to 24 h), the reaction was diluted with dichloromethane (3 mL) and washed with 5% sodium bicarbonate. The aqueous layer was extracted with dichloromethane (3 × 15 mL), dried over sodium sulfate, and evaporated in vacuo. Purification was performed by silica gel chromatography to get the substituted benzoquinone **c**.

Method B[2]



Benzoquinone **a** (3 equiv, 15 mmol), boronic acid **b** (1 equiv, 5 mmol), and palladium trifluoroacetate (7.5 mol%) was added to a round-bottom flask equipped with a magnetic stir bar, acetone (60 mL) was then added and the reaction was stirred at room temperature for 18-24 h until the completion of the reaction. The mixture was then evaporated, and purified by flash column chromatography to afford the targeted product **c**.

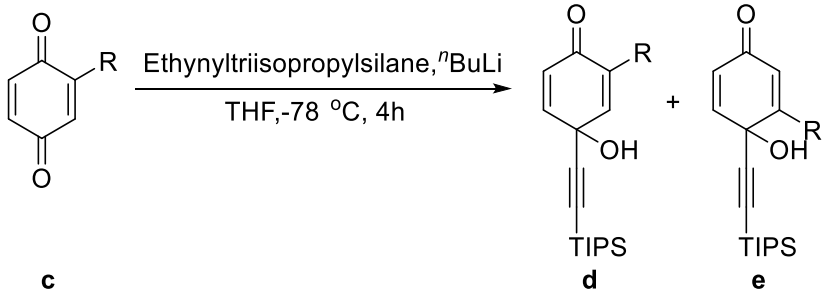
Method C[3]



A 100-mL round-bottom flask was charged with 6 g of silica gel (300-400 mesh particle size) and fitted with a rubber septum. A solution of 2.75 g of CAN (5.0 mmol) in 2.5 mL of water was added dropwise and kept stirring until a free-flowing yellow solid was generated. Dichloromethane (25 mL) was then added to the flask, followed by the addition of phenol **A** (1.96 mmol in 2 mL of CH_2Cl_2). The reaction mixture (yellow color) turned dark orange immediately. Upon completion of the reaction, the reaction mixture was filtered and the obtained solid crude was diluted and extracted with CH_2Cl_2 (75 mL). The combined organic phase was then evaporated and purified with chromatography to afford the targeted product **c** as orange solids.

General procedure for the synthesis of alkyl-ol 1

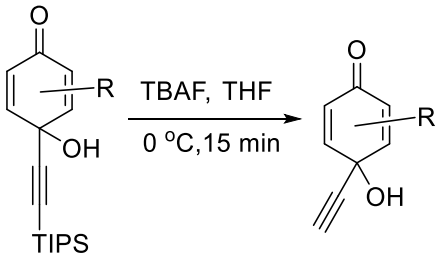
Step 1:



A flame-dried round-bottom flask was charged with *n*-BuLi (2.5 M, 1.2 equiv, 4.8 mmol) in anhydrous THF (0.5 M, 8 mL) under an argon atmosphere, and the reaction was cooled to -78 °C. The silyl acetylene (1.3, 5.2 mmol) was then added dropwise. The reaction was kept at -78 °C for 1 hour. Substituted benzoquinone **c** (1 equiv, 4 mmol) was then added dropwise in CH_2Cl_2 and the

reaction mixture was stirred at -78 °C for 3 hours. After completion, saturated NH_4Cl solution was added to quench the reaction. The mixture was extracted with ethyl acetate three times, and the combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered through a pad of celite, and concentrated under reduced pressure. The crude product was purified by column chromatography to get the titled compounds **d** and **e**.

Step 2:[4]



d or e **1**

To a solution of **d** or **e** (1 equiv) in THF (0.1 M) was added TBAF (1.2 equiv, 1.0 M in THF) at 0 °C. After stirring for 15 min, the reaction was quenched with sat. aq. NH_4Cl and the aqueous layer were extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude product was purified by column chromatography to yield the alkyne-ol **1**.

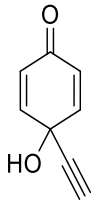
[1] Y. Fujiwara, V. Domingo, I. B. Seiple, R. Gianatassio, M. Del Bel and P. S. Baran, *J. Am. Chem. Soc.*, **2011**, *133*, 3292-3295.

[2] S. E. Walker, J. A. Jordan-Hore, D. G. Johnson, S. A. Macgregor and A. L. Lee, *Angew. Chem.*, **2014**, *126*, 14096-14099.

[3] M. Hashmat Ali, M. Niedbalski, G. Bohnert and D. Bryant, *Synth. Commun.*, **2006**, *36*, 1751-1759.

[4] J.-L. Shih, S. Jansone-Popova, C. Huynh and J. A. May, *Chem. Sci.*, **2017**, *8*, 7132-7137.

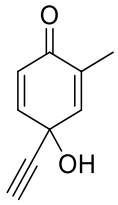
4-ethynyl-4-hydroxycyclohexa-2,5-dien-1-one **(1a)**



The compound **1a** was prepared using method A followed by the general procedure for the synthesis of alkyl-ol. The compound was isolated in 63% yield (2 steps) as a white solid. All spectral data were found to be in accordance with those reported in the literature.

^{1}H NMR (**600 MHz, $CDCl_3$**) δ 6.9 (d, *J* = 9.9 Hz, 2H), 6.2 (d, *J* = 9.9 Hz, 2H), 3.1 (s, 1H), 2.6 (s, 1H). **HRMS** (ESI) calculated for $C_8H_5O_2^-$ ([M-H]$^-$):133.0295, found 133.0295.

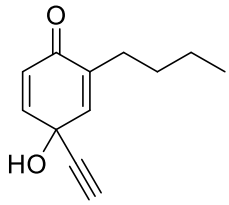
4-ethynyl-4-hydroxy-2-methylcyclohexa-2,5-dien-1-one **(1b)**



The compound **1b** was prepared using method C followed by the general procedure for the synthesis of alkyl-ol. The compound was isolated in 37% yield (3 steps) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.9 (dd, *J* = 9.9, 3.0 Hz, 1H), 6.7 (s, *J* = 3.0, 1.5 Hz, 1H), 6.2 (d, *J* = 9.9 Hz, 1H), 2.6 (s, 1H), 1.9 (d, *J* = 1.5 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 185.6, 146.3, 142.0, 134.4, 127.3, 81.0, 73.8, 62.6, 15.6. **HRMS** (ESI) calculated for $C_9H_7O_2^-$ ([M-H]$^-$):147.0452, found 147.0450.

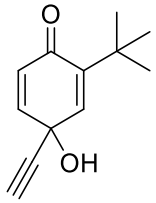
2-butyl-4-ethynyl-4-hydroxycyclohexa-2,5-dien-1-one**(1c)**



The compound **1d** was prepared using method A followed by the general procedure for the synthesis of alkyl-ol. The compound was isolated in 17% yield (3 steps) as brown oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.8 (dd, *J* = 9.9, 3.0 Hz, 1H), 6.6 (s, *J* = 3.0, 1.5 Hz, 1H), 6.2 (d, *J* = 9.9 Hz, 1H), 3.4 (s, 1H), 2.6 (s, 1H), 2.3 – 2.2 (m, 2H), 1.5 – 1.4 (m, 2H), 1.4 – 1.3 (m, 2H), 0.9 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 184.6, 145.3, 143.0, 139.7, 128.0, 81.3, 73.8, 62.8, 35.8, 32.2, 26.6, 26.3. **HRMS** (ESI) calculated for $C_{12}H_{13}O_2^-$ ([M-H]$^-$):189.0921, found 189.0921.

2-(tert-butyl)-4-ethynyl-4-hydroxycyclohexa-2,5-dien-1-one **(1d)**

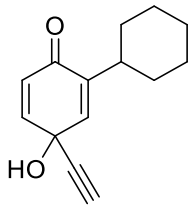


The compound **1d** was prepared using method A followed by the general procedure for the synthesis of alkyl-ol. The compound was isolated in 71% yield (3 steps) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.8 (dd, *J* = 9.9, 3.0 Hz, 1H), 6.7 (s, *J* = 3.0 Hz, 1H), 6.1 (d, *J* = 9.9 Hz, 1H), 2.6 (s, 1H), 1.2 (s, 9H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 185.3,

144.6, 144.3, 140.7, 129.1, 81.4, 73.7, 62.9, 34.6, 29.1. **HRMS** (ESI) calculated for $C_{12}H_{13}O_2^-$ ([M-H]$^-$): 189.0921, found 189.0922.

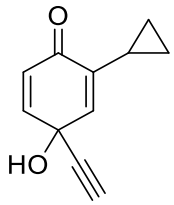
5-ethynyl-5-hydroxy-[1,1'-bi(cyclohexane)]-3,6-dien-2-one **(1e)**



The compound **1e** was prepared using method A followed by the general procedure for the synthesis of alkyl-ol. The compound was isolated in 11% yield (3 steps) as colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.8 (dd, *J* = 9.9, 3.0 Hz, 1H), 6.6 (s, 1H), 6.1 (d, *J* = 9.9 Hz, 1H), 3.7 (s, 1H), 2.5 (m, 2H), 1.8 – 1.6 (m, 5H), 1.4 – 1.3 (m, 2H), 1.2 – 1.1 (m, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 186.0, 165.9, 146.8, 126.4, 124.0, 80.7, 73.8, 64.9, 40.4, 34.5, 34.1, 26.5, 26.4, 25.8. **HRMS** (ESI) calculated for $C_{14}H_{15}O_2^-$ ([M-H]$^-$):215.1078, found 215.1073.

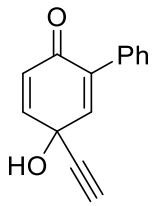
2-cyclopropyl-4-ethynyl-4-hydroxycyclohexa-2,5-dien-1-one **(1f)**



The compound **1f** was prepared using method A followed by the general procedure for the synthesis of alkyl-ol. The compound was isolated in 23% yield (3 steps) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.8 (dd, *J* = 9.9, 3.0 Hz, 1H), 6.3 (s, 1H), 6.2 (m, 1H), 2.6 (s, 1H), 1.9 (s, 1H), 0.9 (d, *J* = 7.8 Hz, 2H), 0.6 – 0.5 (m, 2H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 185.0, 145.8, 139.5, 137.1, 127.4, 81.0, 73.7, 62.6, 8.9, 7.3, 7.1. **HRMS** (ESI) calculated for $C_{11}H_9O_2^-$ ([M-H]$^-$):174.0681, found 174.0680.

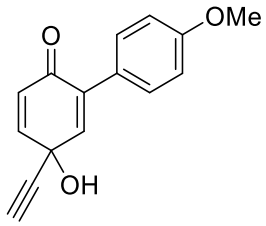
5-ethynyl-5-hydroxy-[1,1'-biphenyl]-2(5H)-one **(1g)**



The compound **1g** was prepared using method A followed by the general procedure for the synthesis of alkyl-ol. The compound was isolated in 17% yield (3 steps) as a white solid.

^{1}H NMR (**600 MHz, $CDCl_3$**) δ 7.4 – 7.4 (m, 5H), 6.9 (d, *J* = 8.3 Hz, 2H), 6.3 (d, *J* = 9.9 Hz, 1H), 2.7 (s, 1H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 183.7, 145.1, 142.9, 137.7, 134.3, 129.0, 128.8, 128.4, 128.3, 80.8, 74.7, 62.9. **HRMS** (ESI) calculated for $C_{14}H_9O_2^-$([M-H]$^-$): 209.0608, found 209.0607.

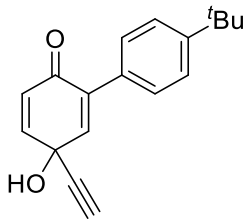
5-ethynyl-5-hydroxy-4'-methoxy-[1,1'-biphenyl]-2(5H)-one **(1h)**



The compound **1h** was prepared using method A followed by the general procedure for the synthesis of alkyl-ol. The compound was isolated in 17% yield (3 steps) as a white solid.

^{1}H NMR (**600 MHz, $CDCl_3$**) δ 7.9 (d, *J* = 9.0 Hz, 2H), 7.0 (d, *J* = 9.0 Hz, 3H), 6.4 (d, *J* = 1.8 Hz, 1H), 6.2 (dd, *J* = 9.9, 1.8 Hz, 1H), 3.9 (s, 3H), 2.7 (s, 1H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 185.7, 161.4, 155.2, 147.2, 130.2, 126.1, 124.1, 114.2, 81.8, 76.1, 64.5, 55.5. **HRMS** (ESI) calculated for $C_{15}H_{11}O_3^-$ ([M-H]$^-$): 239.0714, found 239.0711.

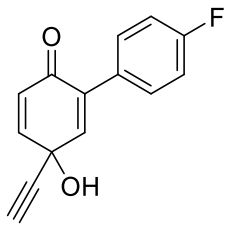
4'-(*tert*-butyl)-5-ethynyl-5-hydroxy-[1,1'-biphenyl]-2(5*H*)-one **(1i)**



The compound **1i** was prepared using method A followed by the general procedure for the synthesis of alkyl-ol. The compound was isolated in 25% yield (3 steps) as a white solid.

^{1}H NMR (**600 MHz, $CDCl_3$**) δ 7.8 (d, *J* = 8.4 Hz, 2H), 7.5 (d, *J* = 8.4 Hz, 2H), 7.0 (d, *J* = 9.9 Hz, 1H), 6.5 (d, *J* = 1.8 Hz, 1H), 6.3 (dd, *J* = 9.9, 1.8 Hz, 1H), 2.7 (s, 1H), 1.4 (s, 9H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 185.9, 156.0, 154.0, 147.6, 128.6, 126.4, 126.0, 125.2, 81.9, 76.3, 64.6, 35.2, 31.5. **HRMS** (ESI) calculated for $C_{18}H_{17}O_2^-$([M-H]$^-$): 265.1234, found 265.1229.

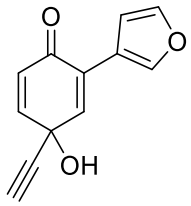
5-ethynyl-4'-fluoro-5-hydroxy-[1,1'-biphenyl]-2(5H)-one **(1j)**



The compound **1j** was prepared using method A followed by the general procedure for the synthesis of alkyl-ol. The compound was isolated in 7% yield (3 steps) as a brown solid.

^{1}H NMR (**600 MHz, $CDCl_3$**) δ 7.4 (dd, *J* = 8.7, 4.5, 1.5 Hz, 2H), 7.1 – 7.0 (m, 2H), 6.9 – 6.9 (m, 2H), 6.3 (dd, *J* = 9.9, 1.5 Hz, 1H), 3.2 – 3.1 (m, 1H), 2.7 (d, *J* = 1.5 Hz, 1H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 183.8, 164.0, 162.3, 145.5, 145.5, 143.1, 136.6, 130.9, 130.8, 130.2, 128.0, 115.4, 115.3, 80.7, 74.7, 62.7. **HRMS** (ESI) calculated for $C_{14}H_8FO_2^-$ ([M-H]$^-$): 227.0514, found 227.0511.

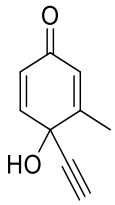
4-ethynyl-2-(furan-3-yl)-4-hydroxycyclohexa-2,5-dien-1-one **(1k)**



The compound **1l** was prepared using method B followed by the general procedure for the synthesis of alkyl-ol. The compound was isolated in 12% yield (3 steps) as a brown solid.

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.2 (s, 1H), 7.7 (t, *J* = 1.8 Hz, 1H), 7.2 (d, *J* = 3.0 Hz, 1H), 7.0 (dd, *J* = 9.9, 3.0 Hz, 1H), 7.0 (dd, *J* = 1.8, 0.9 Hz, 1H), 6.7 (s, 1H), 6.2 (d, *J* = 9.9 Hz, 1H), 3.7 (s, 1H). **^{13}C NMR (150 MHz, DMSO-d_6)** δ 183.4, 147.8, 143.3, 142.4, 142.2, 127.1, 126.2, 118.6, 108.4, 81.9, 75.7, 61.6. **HRMS** (ESI) calculated for $C_{12}H_7O_3^-$ ([M-H]$^-$): 199.0401, found 199.0400.

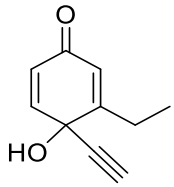
4-ethynyl-4-hydroxy-3-methylcyclohexa-2,5-dien-1-one (**1l**)



The compound **1l** was prepared using method B followed by the general procedure for the synthesis of alkyl-ol. The compound was isolated in 37% yield (2 steps) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.9 (d, *J* = 9.9 Hz, 1H), 6.1 (dd, *J* = 9.9, 1.8 Hz, 1H), 6.0 (s,1H), 2.6 (s, 1H), 2.2 (s, 3H). **^{13}C NMR (150 MHz, DMSO-d_6)** δ 186.0, 157.8, 147.6, 126.5, 125.7, 81.0, 74.3, 64.5, 18.7. HRMS (ESI) calculated for $C_9H_7O_2^-$ ([M-H]-):147.0452, found 147.0455.

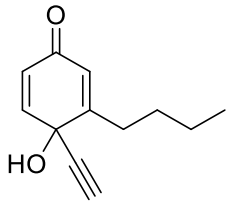
3-ethyl-4-ethynyl-4-hydroxycyclohexa-2,5-dien-1-one **(1m)**



The compound **1m** was prepared using method A followed by the general procedure for the synthesis of alkyl-ol. The compound was isolated in 19% yield (3 steps) as a white solid.

^{1}H NMR (600 MHz, CDCl$_3$) δ 6.9 (d, *J* = 9.9 Hz, 1H), 6.2 (dd, *J* = 9.9, 1.8 Hz, 1H), 6.1 (s,1H), 3.5 (s, 1H), 2.6 (dd, *J* = 9.0, 7.2, 1.8 Hz, 2H), 1.2 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (150 MHz, CDCl$_3$)** δ 183.0, 162.1, 120.1, 81.2,73.1, 65.0, 21.6, 9.9. **HRMS** (ESI) calculated for $C_{10}H_9O_2^-$ ([M-H]$^-$):161.0608, found 161.0607.

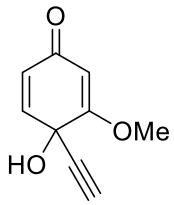
3-butyl-4-ethynyl-4-hydroxycyclohexa-2,5-dien-1-one **(1n)**



The compound **1n** was prepared using method C followed by the general procedure for the synthesis of alkyl-ol. The compound was isolated in 25% yield (3 steps) as brown oil.

^{1}H NMR (600 MHz, CDCl$_3$) δ 6.9 (d, *J* = 9.9 Hz, 1H), 6.1 (dd, *J* = 9.9, 1.8 Hz, 1H), 6.1 (s, *J* = 1.8 Hz, 1H), 3.4 (s, 1H), 2.6 – 2.5 (m, 3H), 1.6 (t, *J* = 8.1, 7.2 Hz, 2H), 1.5 – 1.4 (m, 2H), 0.9 (t, *J* = 7.5 Hz, 3H). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 186.1, 161.7, 147.8, 126.3, 126.3, 124.0, 124.0, 81.4, 81.3, 74.2, 74.1, 64.8, 30.6, 29.1, 22.5, 14.0. **HRMS** (ESI) calculated for $C_{14}H_{13}O_2^-$ ([M-H]$^-$):189.0921, found 189.0923.

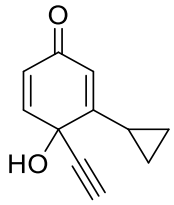
4-ethynyl-4-hydroxy-3-methoxycyclohexa-2,5-dien-1-one **(1o)**



The compound **1o** was prepared using method C followed by the general procedure for the synthesis of alkyl-ol. The compound was isolated in 57% yield (3 steps) as a white solid.

^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ 6.9 (s, 1H), 6.7 (d, *J* = 9.9 Hz, 1H), 6.0 (dd, *J* = 9.9, 1.6 Hz, 1H), 5.5 (d, *J* = 1.8 Hz, 1H), 3.8 (s, 3H), 3.6 (s, 1H).). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 186.0, 172.3, 144.5, 125.0, 99.8, 81.8, 75.7, 62.6, 56.4. **HRMS** (ESI) calculated for $C_9H_7O_3^-$ ([M-H]$^-$): 163.0401, found 163.0405.

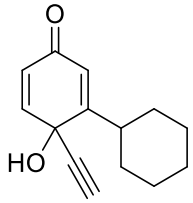
3-cyclopropyl-4-ethynyl-4-hydroxycyclohexa-2,5-dien-1-one **(1p)**



The compound **1p** was prepared using method A followed by the general procedure for the synthesis of alkyl-ol. The compound was isolated in 15% yield (3 steps) as colorless oil.

^{1}H NMR (**600 MHz, CDCl$_3$**) δ 6.9 (d, *J* = 9.9 Hz, 1H), 6.2 – 6.0 (m, 1H), 5.6 (s, 1H), 2.6 (d, *J* = 2.4 Hz, 1H), 2.1 – 1.8 (m, 1H), 1.1 (d, *J* = 1.8 Hz, 2H), 0.8 – 0.6 (m, 2H). **^{13}C NMR (150 MHz, CDCl$_3$)** δ 186.1, 165.4, 147.7, 126.2, 118.1, 81.3, 74.2, 64.8, 12.8, 11.2, 10.8. **HRMS** (ESI) calculated for $C_{11}H_{11}O_2^+$([M+H]$^+$): 175.0754, found 175.0755.

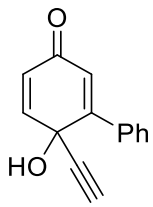
6-ethynyl-6-hydroxy-[1,1'-bi(cyclohexane)]-1,4-dien-3-one **(1q)**



The compound **1q** was prepared using method A followed by the general procedure for the synthesis of alkyl-ol. The compound was isolated in 19% yield (3 steps) as colorless oil.

^{1}H NMR (**600 MHz, CDCl$_3$**) δ 6.8 (d, *J* = 9.8 Hz, 1H), 6.2 – 6.1 (m, 2H), 2.9 (s, 1H), 2.6 – 2.5 (m, 2H), 2.0 – 1.9 (m, 2H), 1.9 – 1.6 (m, 4H), 1.4 – 1.3 (m, 2H), 1.3 – 1.2 (m, 2H).**^{13}C NMR (150 MHz, CDCl$_3$)** δ 186.1, 166.0, 147.0, 126.6, 124.2, 80.9, 74.0, 65.1, 40.5, 34.6, 34.3, 26.7, 26.6, 26.0. **HRMS** (ESI) calculated for $C_{14}H_{17}O_2^+$([M+H]$^+$): 217.1223, found 217.1226.

6-ethynyl-6-hydroxy-[1,1'-biphenyl]-3(6H)-one **(1r)**

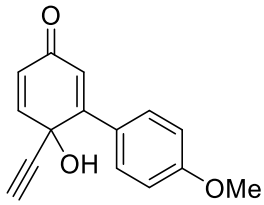


The compound **1p** was prepared using method A followed by the general procedure for the synthesis of alkyl-ol. The compound was isolated in 22% yield (3 steps) as a white solid.

^{1}H NMR (**600 MHz, CDCl$_3$**) δ 7.9 – 7.8 (m, 2H), 7.4 (s, 3H), 7.0 (d, *J* = 9.9 Hz, 1H), 6.4 (s, *J* = 1.8 Hz, 1H), 6.2 (dd, *J* = 9.9, 1.8 Hz, 1H), 3.2 (s, 1H), 2.7 (s, 1H). **^{13}C NMR**

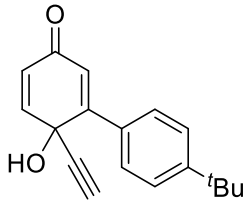
(150 MHz, $CDCl_3$) δ 185.7, 156.1, 147.5, 135.4, 130.2, 128.7, 128.6, 126.1, 125.8, 81.4, 76.1, 64.4. **HRMS** (ESI) calculated for $C_{14}H_{11}O_2^+$([M+H]$^+$): 211.0754, found 211.0707.

6-ethynyl-6-hydroxy-4'-methoxy-[1,1'-biphenyl]-3(6H)-one **(1s)**



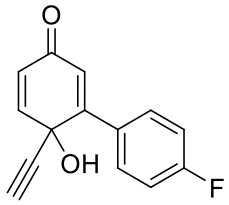
The compound **1s** was prepared using method A followed by the general procedure for the synthesis of alkyl-ol. The compound was isolated in 23% yield (3 steps) as a white solid.
1H NMR **(600 MHz, $CDCl_3$)** δ 7.9 (d, *J* = 8.7 Hz, 2H), 7.0 – 6.9 (m, 3H), 6.4 (d, *J* = 1.8 Hz, 1H), 6.2 (dd, *J* = 9.8, 1.8 Hz, 1H), 3.9 (s, 3H), 2.7 (s, 1H). **^{13}C NMR (150 MHz, $CDCl_3$) ^{13}C NMR (150 MHz, $CDCl_3$)** δ 185.7, 161.4, 155.2, 147.2, 130.2, 126.1, 124.1, 114.2, 81.8, 76.1, 64.5, 55.5. **HRMS** (ESI) calculated for $C_{15}H_{11}O_3^-$ ([M-H]$^-$): 239.0714, found 239.0714.

4'-(tert-butyl)-6-ethynyl-6-hydroxy-[1,1'-biphenyl]-3(6H)-one **(1t)**



The compound **1t** was prepared using method A followed by the general procedure for the synthesis of alkyl-ol. The compound was isolated in 25% yield (3 steps) as a white solid.
^{1}H NMR (**600 MHz, $CDCl_3$**) 8 (d, *J* = 8.5 Hz, 2H), 7.5 (d, *J* = 8.6 Hz, 2H), 7.0 (d, *J* = 9.8 Hz, 1H), 6.5 (d, *J* = 1.8 Hz, 1H), 6.2 (dd, *J* = 9.8, 1.8 Hz, 1H), 3.1 (s, 1H), 2.7 (s, 1H), 1.3 (s, 9H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 185.7, 155.8, 153.7, 147.3, 132.1, 128.4, 126.2, 125.8, 125.0, 81.7, 76.0, 64.4, 35.0, 31.3. **HRMS** (ESI) calculated for $C_{18}H_{17}O_2^-$([M-H]$^-$): 265.1234, found 265.1236.

6-ethynyl-4'-fluoro-6-hydroxy-[1,1'-biphenyl]-3(6H)-one **(1u)**

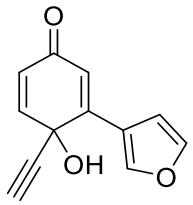


The compound **1u** was prepared using method A followed by the general procedure for

the synthesis of alkyl-ol. The compound was isolated in 7% yield (3 steps) as a white solid.

^{1}H NMR (**600 MHz, $CDCl_3$**) δ 7.8 (dd, *J* = 9.0, 5.4 Hz, 1H), 7.5 – 7.4 (m, 2H), 7.1 – 7.1 (m, 2H), 6.8 – 6.7 (m, 1H), 6.4 – 6.2 (m, 1H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 183.8, 164.0, 162.3, 145.7, 143.1, 143.1, 136.6, 130.9, 130.8, 130.2, 128.0, 128.0, 115.4, 115.3, 80.7, 74.7, 62.6. **HRMS** (ESI) calculated for $C_{14}H_8FO_2^-$ ([M-H]$^-$): 227.0514, found 227.0513.

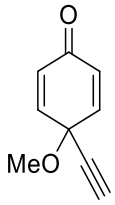
4-ethynyl-3-(furan-3-yl)-4-hydroxycyclohexa-2,5-dien-1-one **(1v)**



The compound **1v** was prepared using method A followed by the general procedure for the synthesis of alkyl-ol. The compound was isolated in 9% yield (3 steps) as a white solid.

^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ 8.3 – 8.3 (m, 1H), 7.8 (s, 1H), 7.1 – 7.1 (m, 1H), 7.0 (d, *J* = 9.9 Hz, 1H), 6.9 (s, 1H), 6.5 (d, *J* = 1.8 Hz, 1H), 6.2 (dd, *J* = 9.9, 1.8 Hz, 1H), 3.7 (s, 1H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 184.9, 149.5, 148.8, 144.8, 143.7, 124.7, 121.3, 121.0, 109.0, 83.1, 76.6, 62.7. **HRMS** (ESI) calculated for $C_{12}H_7O_3^-$ ([M-H]$^-$): 199.0401, found 199.0384.

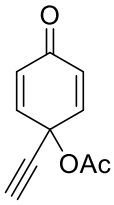
4-ethynyl-4-methoxycyclohexa-2,5-dien-1-one **(1w)**



To a solution of **1a** (1.0 equiv) in THF under N_2 which was stirred at 0℃, then was added sodium hydride. The resulting mixture was stirred at room temperature for 1 hour. Then, MeI (1.2 equiv) was added dropwise. The reaction mixture was stirred at 0 °C for 3 hours. After completion, the mixture was extracted with ethyl acetate three times, and the organic phases were combined and washed with brine, dried over anhydrous Na_2SO_4, filtered through a pad of celite, and concentrated under reduced pressure. After flash chromatography, the compound **1w** was isolated in 75% (2 steps) yield as a white solid.

^{1}H NMR (**600 MHz, $CDCl_3$**) δ 6.86 (d, *J* = 1.8 Hz, 1H), 6.84 (d, *J* = 1.8 Hz, 1H), 6.32 (d, *J* = 1.8 Hz, 1H), 6.31 (d, *J* = 1.8 Hz, 1H), 3.37 (s, 3H), 2.62 (s, 1H).

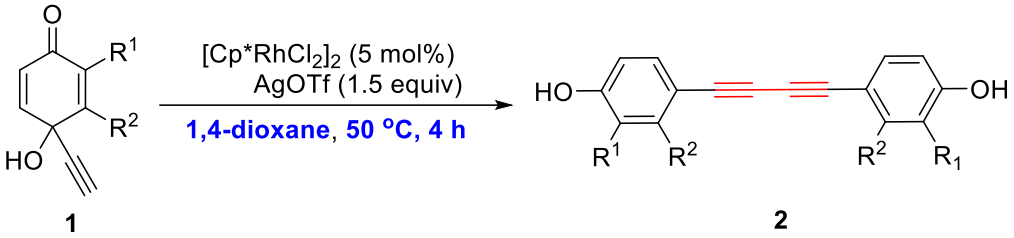
1-ethynyl-4-oxocyclohexa-2,5-dien-1-yl acetate **(1x)**



To a solution of **1a** (1.0 equiv) in CH_2Cl_2 at 0°C under Argon was added DMAP. After stirring for 30 minutes, Ac_2O and Et_3N were added slowly. The resulting mixture was stirred at room temperature for 4 hours. After completion, the mixture was extracted with CH_2Cl_2 three times, and the organic phases were combined and washed with brine, dried over anhydrous Na_2SO_4, filtered through a pad of celite, and concentrated under reduced pressure. After flash chromatography, the compound **1x** was isolated in 76% yield as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.0 (d, *J* = 10.5 Hz, 2H), 6.3 (d, *J* = 10.5 Hz, 2H), 2.7 (s, 1H), 2.1 (s, 3H).**^{13}C NMR (150 MHz, $CDCl_3$)** δ 184.1, 168.6, 142.4, 128.5, 76.8, 76.2, 67.0, 21.3.

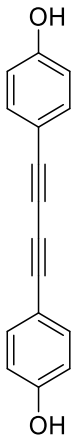
4. General procedure for the synthesis of symmetrical 1,3-diynes 2



1 **2**

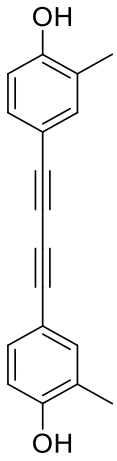
To a dried Schlenk flask charged with the alkyne-ol **1** (1.0 equiv, 0.3 mmol), AgOTf (1.5 equiv, 0.45mmol), $[Cp^*RhCl_2]_2$ (0.05 equiv, 0.015mmol), and anhydrous 1,4-dioxane (2mL). The reaction was vigorously stirred at 50 °C for 4 h under argon. After the reaction was completed, the reaction was diluted with ethyl acetate, washed with brine, dried over sodium sulfate, and evaporated in vacuo. After column chromatography, the symmetrical 1,3-diynes **2** were obtained as solids.

4,4'-(buta-1,3-diyne-1,4-diyl)diphenol **(2a)**



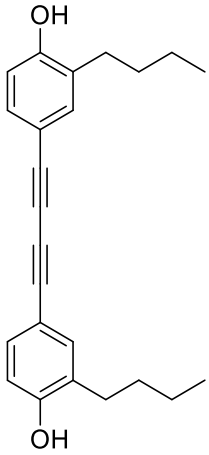
brown solid, 21 mg, 62% yield. Purification by silica gel column chromatography (PE/EA = 5:1). mp:217.6-219.3 ℃; **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 10.1 (s, 2H), 7.4 (d, *J* = 8.7 Hz, 4H), 6.8 (d, *J* = 8.7 Hz, 4H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 158.9, 134.1, 115.9, 110.8, 81.8, 72.3. **HRMS** (ESI) calculated for $C_{16}H_9O_2^-$ ([M-H]$^-$): 233.0608, found 233.0604.

4'-(buta-1,3-diyne-1,4-diyl)bis(2-methylphenol) **(2b)**



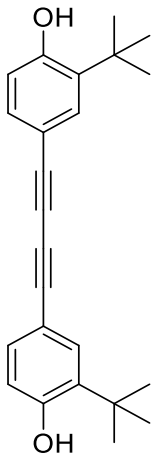
Brown solid, 34 mg, 89% yield. Purification by silica gel column chromatography (PE/EA = 4:1). mp:209.2-210.6 ℃; **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 10.0 (s, 2H), 7.4 (d, *J* = 8.4 Hz, 2H), 6.7 (d, *J* = 1.8 Hz, 2H), 6.6 (dd, *J* = 8.4, 2.4 Hz, 2H), 2.3 (s, 6H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 158.7, 143.0, 134.4, 116.7, 113.5, 111.0, 81.3, 75.8, 20.5. **HRMS** (ESI) calculated for $C_{18}H_{13}O_2^-$ ([M-H]$^-$): 261.0921, found 261.0920.

4,4'-(buta-1,3-diyne-1,4-diyl)bis(2-butylphenol) **(2c)**



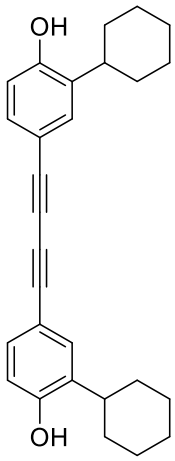
Brown oil, 22 mg, 63% yield. Purification by silica gel column chromatography (PE/EA = 4:1). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.30 (d, *J* = 2.1 Hz, 2H), 7.26 – 7.22 (m, 2H), 6.70 (d, *J* = 8.1 Hz, 2H), 4.99 (s, 2H), 2.61 – 2.51 (m, 4H), 1.60 – 1.56 (m, 4H), 1.43 – 1.34 (m, 4H), 0.94 (t, J = 7.3 Hz, 6H). **^{13}C NMR (150 MHz, CDCl$_3$)** δ 154.7, 134.6, 131.7, 129.2, 115.5, 114.1, 81.5, 72.7, 31.7, 29.5, 22.6, 14.1. **HRMS** (ESI) calculated for $C_{24}H_{25}O_2^-$ ([M-H]$^-$): 345.1860, found 345.1857.

4,4'-(buta-1,3-diyne-1,4-diyl)bis(2-(tert-butyl)phenol) **(2d)**



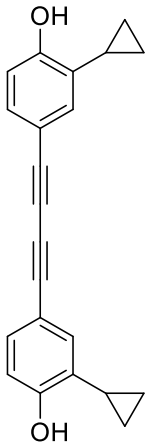
Brown solid, 23 mg, 42% yield. Purification by silica gel column chromatography (PE/EA = 4:1). mp:187.2-188.5 °C; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.5 (d, *J* = 2.1 Hz, 2H), 7.2 (dd, *J* = 8.1, 2.1 Hz, 2H), 6.6 (d, *J* = 8.1 Hz, 2H), 5.2 (s, 2H), 1.4 (s, 18H). **^{13}C NMR (150 MHz, CDCl$_3$)** δ 155.2, 136.5, 131.8, 131.4, 116.7, 113.8, 81.6, 72.4, 34.6, 29.3. **HRMS** (ESI) calculated for $C_{24}H_{27}O_2^+$([M+H]$^+$): 347.2006, found 347.2000.

4'-(buta-1,3-diyne-1,4-diyl)bis(2-cyclohexylphenol) **(2e)**



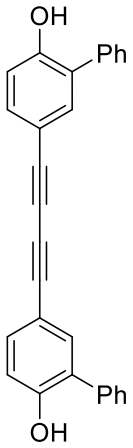
Brown solid, 23 mg, 53% yield. Purification by silica gel column chromatography (PE/EA = 4:1). mp:125.2-128.6 ℃;**^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.4 (d, *J* = 2.1 Hz, 2H), 7.2 (dd, *J* = 8.2, 2.1 Hz, 2H), 6.7 (d, *J* = 8.2 Hz, 2H), 5.2 – 5.1 (m, 2H), 2.8 (dd, *J* = 11.5, 8.7, 2.7 Hz, 2H), 1.9 (dd, *J* = 10.8, 2.7 Hz, 8H), 1.5 – 1.4 (m, 8H), 1.3 – 1.3 (m, 4H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 153.9, 134.2, 131.8, 131.3, 115.6, 114.3, 81.7, 72.7, 37.2, 33.0, 27.0, 26.4. **HRMS** (ESI) calculated for $C_{28}H_{29}O_2^-$([M-H]$^-$): 397.2173, found 397.2177.

4,4'-(buta-1,3-diyne-1,4-diyl)bis(2-cyclopropylphenol) **(2f)**



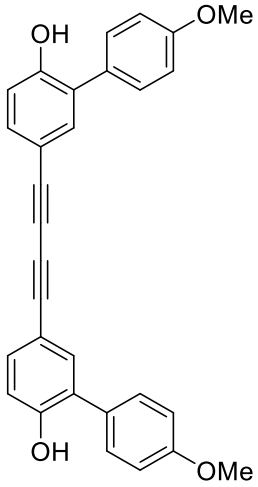
Brown solid, 24 mg, 55% yield. Purification by silica gel column chromatography (PE/EA = 4:1). mp:115.2-117.9℃; **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 10.1 (s, 2H), 7.2 (dd, *J* = 8.4, 2.1 Hz, 2H), 6.9 (d, *J* = 2.1 Hz, 2H), 6.8 (d, *J* = 8.4 Hz, 2H), 2.1 – 2.0 (m, 2H), 0.9 – 0.8 (m, 4H), 0.7 – 0.6 (m, 4H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 157.5, 130.8, 130.5, 128.9, 115.0, 110.9, 82.2, 72.2, 9.1, 7.8. **HRMS** (ESI) calculated for $C_{22}H_{17}O_2^-$([M-H]$^-$): 313.1234, found 313.1236.

5,5''-(buta-1,3-diyne-1,4-diyl)bis(([1,1'-biphenyl]-2-ol)) **(2g)**



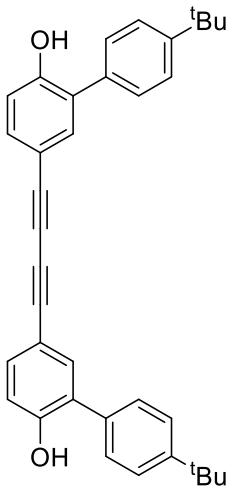
Brown solid, 46 mg, 79% yield. Purification by silica gel column chromatography (PE/EA = 4:1). mp:218.5-219.9 ℃; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.51 m, 4H), 7.44 (m, 10H), 6.97 – 6.93 (m, 2H), 5.48 (s, 2H).**^{13}C NMR (150 MHz, CDCl$_3$)** δ 153.6, 135.9, 134.7, 133.7, 129.6, 129.1, 128.7, 128.5, 116.4, 114.4, 81.2, 73.1. **HRMS** (ESI) calculated for $C_{28}H_{17}O_2^-$([M-H]$^-$): 385.1234, found 385.1229.

5,5''-(buta-1,3-diyne-1,4-diyl)bis(4'-methoxy-[1,1'-biphenyl]-2-ol) **(2h)**



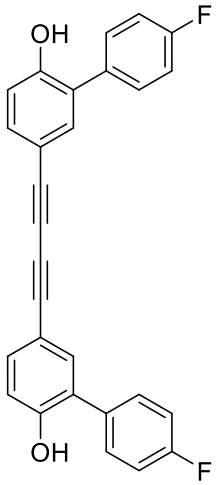
Brown solid, 31 mg, 47% yield. Purification by silica gel column chromatography (PE/EA = 4:1). mp:188.0-190.4 ℃; **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 10.2 (s, 2H), 7.5 – 7.5 (m, 4H), 7.4 (d, *J* = 2.1 Hz, 2H), 7.4 (dd, *J* = 8.4, 2.1 Hz, 2H), 7.0 (dd, *J* = 9.0, 7.5 Hz, 6H), 3.8 (s, 6H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 158.4, 156.0, 134.1, 132.5, 130.2, 129.4, 128.2, 116.6, 113.5, 111.3, 81.9, 72.5, 55.1. **HRMS** (ESI) calculated for $C_{30}H_{21}O_4^-$([M-H]$^-$): 445.1445, found: 445.1443.

5,5''-(buta-1,3-diyne-1,4-diyl)bis(4'-(tert-butyl)-[1,1'-biphenyl]-2-ol) **(2i)**



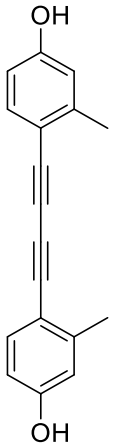
Brown solid, 34 mg, 56% yield. Purification by silica gel column chromatography (PE/EA = 4:1). mp:209.2-211.6 ℃; **^{1}H NMR** (**600 MHz, $CDCl_3$**) δ 7.6 – 7.5 (m, 4H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.46 – 7.42 (m, 4H), 6.9 (d, *J* = 2.7 Hz, 2H), 6.7 (dd, *J* = 8.4, 2.6 Hz, 2H), 5.7 (s, 2H), 1.4 (s, 18H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 153.7, 151.6, 134.6, 133.5, 132.9, 128.8, 128.6, 126.6, 116.3, 114.3, 73.1, 34.9, 31.4. **HRMS** (ESI) calculated for $C_{36}H_{33}O_2^-$([M-H]$^-$): 497.2486, found : 497.2488.

5,5''-(buta-1,3-diyne-1,4-diyl)bis(4'-fluoro-[1,1'-biphenyl]-2-ol) **(2j)**



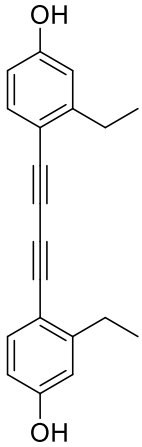
Brown oil, 20 mg, 32% yield. Purification by silica gel column chromatography (PE/EA = 4:1). **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 10.27 (s, 2H), 7.56 – 7.50 (m, 4H), 7.48 (d, J = 8.2 Hz, 2H), 7.26 (t, J = 8.8 Hz, 4H), 6.83 – 6.75 (m, 4H). **^{13}C NMR (150 MHz, DMSO-*d6*)** δ 162.71, 161.09, 158.86, 145.14, 135.89, 135.87, 135.82, 130.79, 130.73, 116.45, 115.14, 115.00, 109.41, 81.55, 74.78. **HRMS** (ESI) calculated for $C_{28}H_{15}F_2O_2^-$ ([M-H]$^-$): 421.1046, found : 421.1043.

4,4'-(buta-1,3-diyne-1,4-diyl)bis(3-methylphenol) **(2k)**



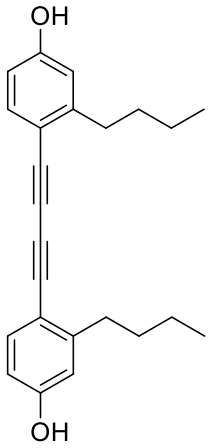
Brown oil, 34 mg, 89% yield. Purification by silica gel column chromatography (PE/EA = 4:1). **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 10.0 (s, 2H), 7.3 (dd, *J* = 2.1, 0.9 Hz, 2H), 7.2 (dd, *J* = 8.4, 2.1 Hz, 2H), 6.8 (d, *J* = 8.4 Hz, 2H), 2.1 (s, 6H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 13C NMR (151 MHz, DMSO) δ 157.6, 135.1, 132.0, 125.4, 115.5, 111.0, 82.5, 72.6, 16.1. **HRMS** (ESI) calculated for $C_{18}H_{13}O_2^-$ ([M-H]$^-$): 261.0921, found 261.0921.

4,4'-(buta-1,3-diyne-1,4-diyl)bis(3-ethylphenol) **(2l)**



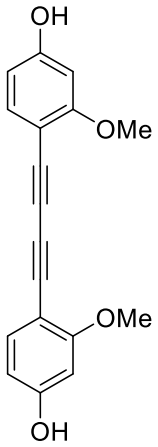
Brown solid, 23 mg, 48% yield. Purification by silica gel column chromatography (PE/EA = 4:1). mp:239.1-240.6 ℃; **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 10.0 (s, 2H), 7.4 (d, *J* = 8.4 Hz, 2H), 6.7 (d, *J* = 2.4 Hz, 2H), 6.6 (dd, *J* = 8.4, 2.5 Hz, 2H), 2.67 (q, *J* = 7.5 Hz, 4H) 1.17 (t, *J* = 7.5 Hz, 6H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 159.0, 149.1, 134.9, 115.2, 113.6, 110.3, 81.0, 75.5, 27.2, 14.9. **HRMS** (ESI) calculated for $C_{20}H_{17}O_2^-$ ([M-H]$^-$): 289.1234, found : 289.1232.

4,4'-(buta-1,3-diyne-1,4-diyl)bis(3-butylphenol) **(2m)**



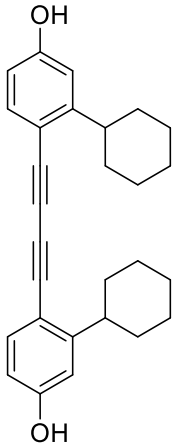
Brown oil, 22 mg, 47% yield. Purification by silica gel column chromatography (PE/EA = 4:1). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.4 (d, *J* = 8.4 Hz, 2H), 6.7 (d, *J* = 2.6 Hz, 2H), 6.6 (dd, *J* = 8.4, 2.6 Hz, 2H), 5.2 (s, 2H), 2.8 – 2.7 (m, 4H), 1.7 – 1.6 (m, 4H), 1.4 – 1.4 (m, 4H), 1.0 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR (150 MHz, CDCl$_3$)** δ 156.4, 148.9, 134.9, 115.9, 113.2, 80.6, 76.3, 34.4, 32.8, 22.6, 14.1. **HRMS** (ESI) calculated for $C_{24}H_{25}O_2^-$ ([M-H]$^-$): 345.1860, found 345.1858.

4,4'-(buta-1,3-diyne-1,4-diyl)bis(3-methoxyphenol) **(2n)**



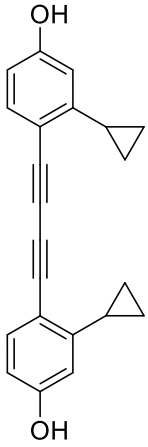
Brown solid, 29 mg, 68% yield. Purification by silica gel column chromatography (PE/EA = 3:1). mp:219.3-221.6 ℃; **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 10.1 (s, 2H), 7.3 (dd, *J* = 8.4, 1.2 Hz, 2H), 6.5 – 6.4 (m, 2H), 6.4 (d, *J* = 8.4, 1.8 Hz, 2H), 3.8 (m, 6H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** 162.7, 160.5, 134.9, 108.0, 100.5, 99.2, 79.2, 76.3, 55.5. **HRMS** (ESI) calculated for $C_{18}H_{13}O_4^-$ ([M-H]$^-$): 293.0819, found 293.0820.

4'-(buta-1,3-diyne-1,4-diyl)bis(2-cyclohexylphenol) **(2o)**



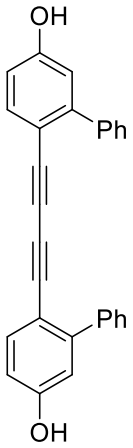
Brown solid, 29 mg, 58% yield. Purification by silica gel column chromatography (PE/EA = 4:1). mp:208.3-209.5 ℃; **^{1}H NMR (600 MHz, CDCl$_3$)** 7.40 (d, *J* = 8.4 Hz, 2H), 6.73 (d, *J* = 2.7 Hz, 2H), 6.62 (dd, *J* = 8.4, 2.7 Hz, 2H), 5.27 (s, 2H), 3.06 – 2.98 (m, 2H), 1.96 – 1.90 (m, 4H), 1.86 (dt, *J* = 13.2, 3.3 Hz, 4H), 1.81 – 1.72 (m, 2H), 1.53 – 1.43 (m, 4H), 1.41 – 1.31 (m, 4H), 1.30 – 1.21 (m, 2H).**^{13}C NMR (150 MHz, CDCl$_3$)** δ 156.7, 153.7, 135.1, 113.1, 113.1, 80.6, 77.4, 77.2, 76.9, 76.5, 42.4, 33.7, 27.0, 26.4. **HRMS** (ESI) calculated for $C_{28}H_{29}O_2^-$([M-H]$^-$): 397.2173, found 397.2164.

4,4'-(buta-1,3-diyne-1,4-diyl)bis(2-butylphenol) **(2p)**



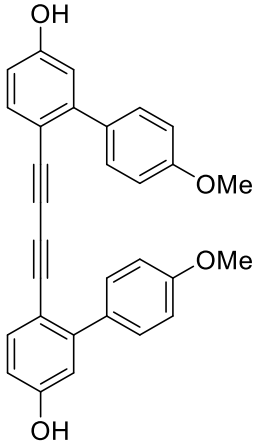
Brown solid, 25 mg, 49% yield. Purification by silica gel column chromatography (PE/EA = 4:1). mp:199.3-200.5 ℃; **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ 10.0 (s, 2H), 7.3 (d, *J* = 8.4 Hz, 2H), 6.6 (dd, *J* = 8.4, 2.4 Hz, 2H), 6.2 (d, *J* = 2.4 Hz, 2H), 2.3 – 2.2 (m, 2H), 1.0 (dd, *J* = 8.3, 2.2 Hz, 4H), 0.7 (dd, *J* = 5.1, 2.0 Hz, 4H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 159.1, 148.9, 134.5, 113.2, 109.8, 81.3, 75.7, 13.6, 9.7. **HRMS** (ESI) calculated for $C_{22}H_{17}O_2^-$([M-H]$^-$): 313.1234, found 1234.

6,6''-(buta-1,3-diyne-1,4-diyl)bis(([1,1'-biphenyl]-3-ol)) **(2q)**



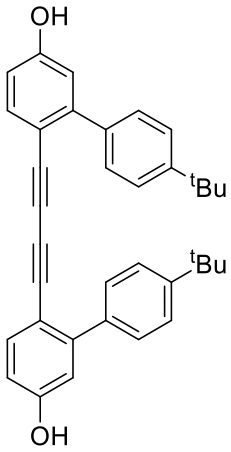
Brown solid, 30 mg, 53% yield. Purification by silica gel column chromatography (PE/EA = 3:1). mp:287.3-289.2 ℃; **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 10.2 (s, 2H), 7.5 – 7.4 (m, 12H), 6.8 – 6.7 (m, 4H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 158.8, 146.2, 139.5, 135.9, 128.6, 128.2, 127.9, 116.4, 115.0, 109.4, 81.6, 74.7. **HRMS** (ESI) calculated for $C_{28}H_{17}O_2^-$([M-H]$^-$): 385.1234, found 385.1229.

6,6''-(buta-1,3-diyne-1,4-diyl)bis(4'-methoxy-[1,1'-biphenyl]-3-ol) **(2r)**



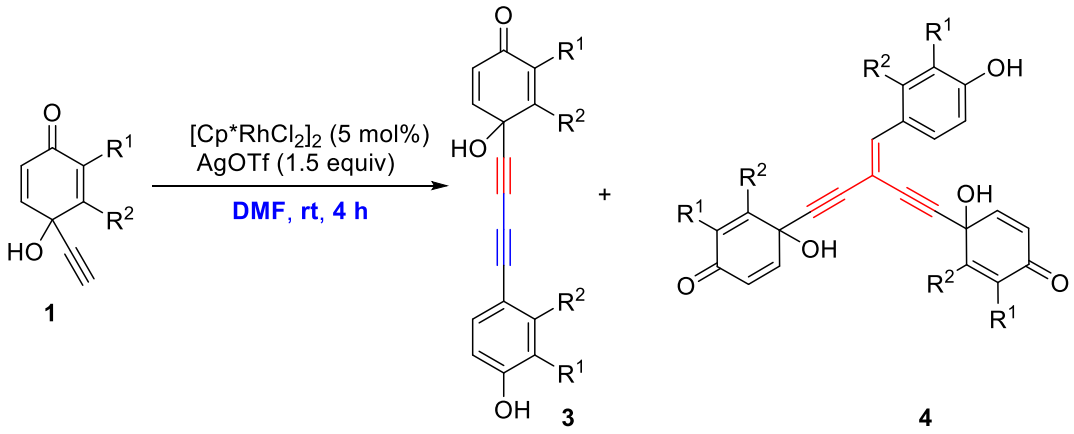
Brown solid, 37 mg, 56% yield. Purification by silica gel column chromatography (PE/EA = 4:1). mp:227.2-230.6 ℃; **^{1}H NMR** (**600 MHz, CDCl$_3$**) δ 10.2 (s, 2H), 7.5 – 7.5 (m, 4H), 7.4 (d, *J* = 2.1 Hz, 2H), 7.4 (dd, *J* = 8.4, 2.1 Hz, 2H), 7.0 (dd, *J* = 9.0, 7.5 Hz, 6H), 3.8 (s, 6H).**^{13}C NMR (150 MHz, CDCl$_3$)** δ 158.4, 156.0, 134.1, 132.5, 130.2, 129.4, 128.2, 116.6, 113.5, 111.3, 81.9, 72.5, 55.1. **HRMS** (ESI) calculated for $C_{30}H_{21}O_4^-$([M-H]$^-$): 445.1445, found : 445.1443.

6,6''-(buta-1,3-diyne-1,4-diyl)bis(4'-(tert-butyl)-[1,1'-biphenyl]-3-ol) **(2s)**



Brown solid, 48 mg, 80% yield. Purification by silica gel column chromatography (PE/EA = 4:1). mp:209.8-211.9 ℃; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.6 – 7.5 (m, 4H), 7.5 (d, *J* = 8.4 Hz, 2H), 7.4 – 7.4 (m, 4H), 6.8 (d, *J* = 2.7 Hz, 2H), 6.7 (dd, *J* = 8.4, 2.7 Hz, 2H), 5.9 (brs, 2H), 1.4 (s, 18H). **^{13}C NMR (150 MHz, CDCl$_3$)** δ 153.6, 151.5, 134.5, 133.4, 132.7, 128.6, 128.4, 126.5, 116.1, 114.2, 72.9, 34.7, 31.3. **HRMS** (ESI) calculated for $C_{36}H_{33}O_2^-$([M-H]$^-$): 497.2486, found : 497.2484.

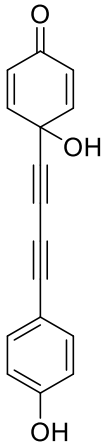
5. General procedure for the synthesis of unsymmetrical 1,3-diynes 3 and conjugated enediynes 4



To a dried Schlenk flask charged with the alkyne-ol **1** (1.0 equiv, 0.3 mmol), AgOTf (1.5 equiv, 0.45 mmol), [Cp*RhCl$_2$]$_2$ (0.05 equiv, 0.015 mmol), and anhydrous DMF

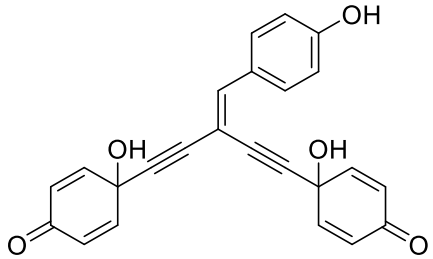
(2 mL) were added. The reaction was vigorously stirred at room temperature for 4-6 h under argon. After the reaction was completed, the reaction was diluted with ethyl acetate, washed with brine, dried over sodium sulfate, and evaporated in vacuo. After column chromatography, the unsymmetrical 1,3-diynes **3** and conjugated enediynes **4** were obtained as solids.

4-hydroxy-4-((4-hydroxyphenyl)buta-1,3-diyn-1-yl)cyclohexa-2,5-dien-1-one **(3a)**



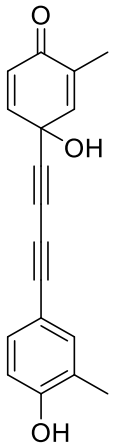
Pale yellow solid, 7 mg, 18% yield. Purification by silica gel column chromatography (PE/EA = 5:1). mp:274.6-279.7 ℃; **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 10.2 (s, 1H), 7.4 (d, *J* = 8.7 Hz, 2H), 7.0 (d, *J* = 9.9 Hz, 2H), 6.9 (s, 1H), 6.8 (d, J = 8.7 Hz, 1H), 6.2 (d, *J* = 9.9 Hz, 1H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 184.3, 159.4, 147.4, 134.6, 126.2, 116.0, 109.6, 80.7, 79.7, 70.9, 69.0, 61.8. **HRMS** (ESI) calculated for $C_{16}H_9O_3^-$ ([M-H]$^-$): 249.0557, found 249.0556.

4,4'-(3-(4-hydroxybenzylidene)penta-1,4-diyne-1,5-diyl)bis(4-hydroxycyclohexa-2,5-dien-1-one) **(4a)**



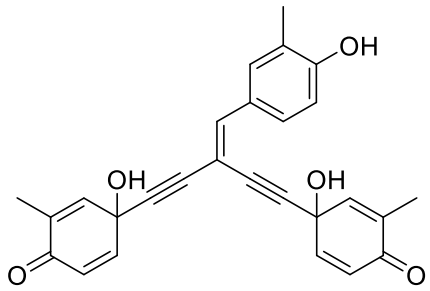
Pale yellow solid, 25 mg, 67% yield. Purification by silica gel column chromatography (PE/EA = 1:1). mp:295.9-296.9 ℃; **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** *δ* = 7.68 (d, *J* = 8.7 Hz, 2H), 7.16 (s, 1H), 7.08 (d, *J* = 9.6 Hz, 2H), 7.00 (d, *J* = 9.9 Hz, 2H), 6.93 (s, 1H), 6.81 (s, 1H), 6.73 (d, *J* = 8.7 Hz, 2H), 6.21 (d, *J* = 9.9 Hz, 2H), 6.15 (d, *J* = 9.9 Hz, 2H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** *δ* = 184.5, 184.4, 159.6, 148.3, 148.1, 131.1, 126.0, 125.8, 125.8, 115.5, 95.3, 91.8, 85.3, 83.2, 62.1, 61.6. **HRMS** (ESI) calculated for $C_{24}H_{15}O_5^-$ ([M-H]$^-$): 383.0925, found 383.0924.

4-hydroxy-4-((4-hydroxy-3-methylphenyl)buta-1,3-diyn-1-yl)-2-methylcyclohexa-2,5-dien-1-one **(3b)**



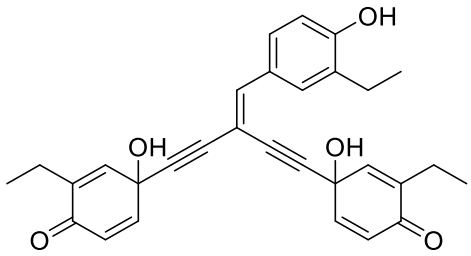
Brown oil, 8 mg, 22% yield. Purification by silica gel column chromatography (PE/EA = 4:1). **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 10.1 (s, 1H), 7.4 (d, *J* = 8.4 Hz, 1H), 7.0 (d, *J* = 9.9 Hz, 1H), 6.9 (s, 1H), 6.7 (d, *J* = 2.4 Hz, 1H), 6.6 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.1 (dd, *J* = 9.9, 1.8 Hz, 1H), 6.1 (p, *J* = 1.5 Hz, 1H), 2.3 (s, 3H), 2.1 (d, *J* = 1.5 Hz, 3H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 184.9, 157.7, 147.3, 142.7, 135.0, 132.6, 132.0, 126.0, 125.0, 115.1, 109.4, 80.7, 80.2, 70.8, 68.4, 62.2, 15.6, 15.0. **HRMS** (ESI) calculated for $C_{18}H_{13}O_3^-$ ([M-H]$^-$): 277.0870, found 277.0871.

4,4'-(3-(4-hydroxy-3-methylbenzylidene)penta-1,4-diyne-1,5-diyl)bis(4-hydroxy-2-methylcyclohexa-2,5-dien-1-one) **(4b)**



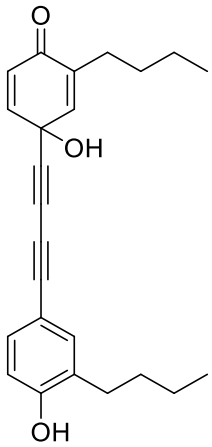
white solid, 26 mg, 60% yield. Purification by silica gel column chromatography (PE/EA = 1:2). mp:173.4 -174.8 ℃; **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 9.9 (s, 1H), 7.9 (d, *J* = 8.7 Hz, 1H), 7.2 (s, 1H), 7.0 (dd, *J* = 9.9, 6.9Hz, 2H), 6.8 (s, 1H), 6.7 (s, 1H), 6.6 (d, *J* = 2.7 Hz, 1H), 6.5 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.1 (dd, *J* = 9.9, 8.1, 1.8 Hz, 2H), 6.0 (dt, *J* = 3.3, 1.5 Hz, 2H), 2.2 (s, 3H), 2.1 (d, *J* = 1.5 Hz, 3H), 2.1 (d, *J* = 1.5 Hz, 3H).**^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 184.7, 184.5, 159.1, 158.1, 158.0, 148.4, 148.1, 143.8, 139.6, 129.1, 125.3, 125.2, 124.6, 124.6, 124.1, 117.2, 112.7, 96.7, 91.7, 86.1, 83.4, 80.8, 64.3, 64.0, 19.5, 18.3, 18.2. **HRMS** (ESI) calculated for $C_{27}H_{21}O_5^-$([M-H]$^-$): 425.1394, found 425.1395.

4,4'-(3-(3-ethyl-4-hydroxybenzylidene)penta-1,4-diyne-1,5-diyl)bis(2-ethyl-4-hydroxycyclohexa-2,5-dien-1-one) **(4c)**



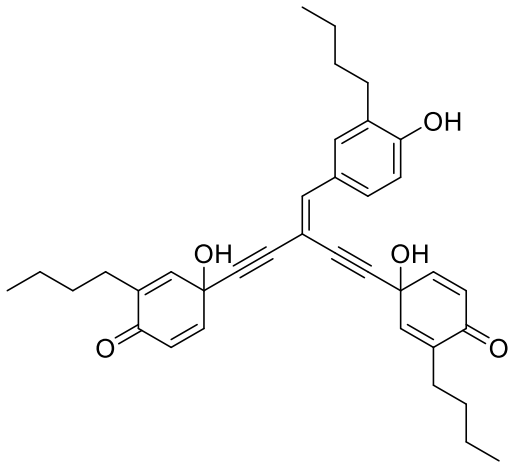
brown solid, 16 mg, 36% yield. Purification by silica gel column chromatography (PE/EA = 1:2). mp:157.2-159.9 ℃; **^{1}H NMR** (**600 MHz, DMSO-*d*$_6$)** δ 10.0 (s, 1H), 7.9 (d, *J* = 8.7 Hz, 1H), 7.0 (dd, *J* = 17.2, 9.9, 2.4 Hz, 2H), 6.8 (s, 1H), 6.7 (s, 1H), 6.64 (d, *J* = 2.6 Hz, 1H), 6.56 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.1 (mf, 2H), 6.0 – 5.9 (m, 2H), 2.57 (q, *J* = 7.9 Hz, 5H), 2.44 – 2.33 (m, 1H), 1.19 – 1.12 (m, 4H), 1.10 (t, *J* = 7.5 Hz, 3H), 1.07 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 185.0, 184.8, 163.3, 163.1, 159.5, 148.7, 148.5, 145.7, 143.8, 129.6, 125.3, 125.2, 123.3, 122.4, 122.4, 115.6, 112.8, 97.2, 91.9, 86.4, 83.3, 80.8, 64.5, 64.2, 31.2, 29.9, 25.8, 23.7, 15.5, 11.2 **HRMS** (ESI) calculated for $C_{30}H_{29}O_5^+$([M+H]$^+$): 469.5565, found: 469.5583.

2-butyl-4-((3-butyl-4-hydroxyphenyl)buta-1,3-diyn-1-yl)-4-hydroxycyclohexa-2,5-dien-1-one **(3d)**



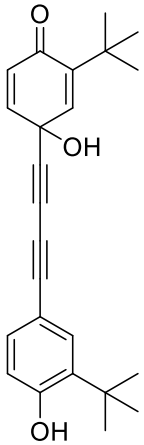
Brown oil, 12 mg, 24% yield. Purification by silica gel column chromatography (PE/EA = 4:1). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.26 (s, 1H), 7.21 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.9 (dd, *J* = 9.9, 3.0 Hz, 1H), 6.7 (d, *J* = 8.4 Hz, 1H), 6.6 (d, *J* = 3.0, 1.2 Hz, 1H), 6.2 (d, *J* = 9.9 Hz, 1H), 5.9 (s, 1H), 3.0 (s, 1H), 2.6 (dd, *J* = 8.4, 7.2 Hz, 2H), 2.3 – 2.3 (m, 2H), 1.6 – 1.5 (m, 2H), 1.4 (dd, *J* = 7.8, 5.4 Hz, 2H), 1.4 – 1.3 (m, 4H), 0.9 (d, *J* = 7.2, 3.3 Hz, 6H). **^{13}C NMR (150 MHz, CDCl$_3$)** δ 185.2, 155.5, 145.3, 140.7, 138.5, 134.9, 132.1, 129.5, 127.7, 115.6, 112.5, 81.2, 77.7, 71.3, 70.7, 63.5, 31.6, 30.1, 29.5, 28.6, 22.6, 14.1, 14.0. **HRMS** (ESI) calculated for $C_{24}H_{25}O_3^-$([M-H]$^-$): 361.1809, found 361.1807.

4,4'-(3-(3-butyl-4-hydroxybenzylidene)penta-1,4-diyne-1,5-diyl)bis(2-butyl-4-hydroxycyclohexa-2,5-dien-1-one) **(4d)**



Brown oil, 26 mg, 48% yield. Purification by silica gel column chromatography (PE/EA = 4:1). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.54 – 7.49 (m, 2H), 7.03 (s, 1H), 6.89 (ddd, *J* = 9.9, 3.0 Hz, 2H), 6.69 – 6.63 (m, 3H), 6.22 (dd, *J* = 9.9 Hz, 2H), 5.33 (s, 1H), 2.58 – 2.54 (m, 2H), 2.32 (m, 4H), 1.57 (d, *J* = 7.8 Hz, 4H), 1.49 – 1.44 (m, 4H), 1.42 (d, *J* = 3.3 Hz, 2H), 1.38 (d, J = 2.3 Hz, 2H), 0.96 – 0.91 (m, 9H), 0.91 – 0.88 (m, 3H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 185.3, 185.2, 156.0, 147.6, 145.9, 145.8, 141.2, 141.1, 138.4, 138.1, 132.0, 129.2, 128.4, 127.6, 127.5, 115.4, 96.8, 90.6, 84.7, 84.3, 82.4, 63.6, 63.3, 32.0, 31.6, 30.3, 30.2, 30.1, 29.9, 29.8, 28.7, 28.7, 22.7, 22.6, 14.1. **HRMS** (ESI) calculated for $C_{36}H_{41}O_5^+$ ([M+H]$^+$): 553.2949, found 553.2941.

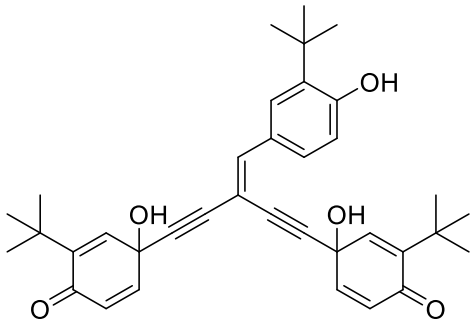
2-(tert-butyl)-4-((3-(tert-butyl)-4-hydroxyphenyl)buta-1,3-diyn-1-yl)-4-hydroxycyclohexa-2,5-dien-1-one **(3e)**



Brown solid, 14 mg, 27% yield. Purification by silica gel column chromatography (PE/EA = 3:1). mp:187.2-190.4 ℃; **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 10.2 (s, 1H), 7.3 (d, *J* = 2.1 Hz, 1H), 7.3 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.9 (dd, *J* = 9.9, 3.0 Hz, 1H), 6.83 (s, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 6.7 (d, *J* = 3.0 Hz, 1H), 6.1 (d, *J* = 9.9 Hz, 1H), 1.3 (s, 9H), 1.2 (s, 9H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 184.6, 158.2, 145.3, 142.7, 141.0, 136.2, 131.9, 131.2, 127.8, 116.7, 109.4, 81.1, 80.4, 70.9, 68.4, 62.5, 34.4, 34.1, 29.0, 28.8. **HRMS** (ESI) calculated for $C_{24}H_{25}O_3^-$([M-H]$^-$): 361.1809, found 361.1803.

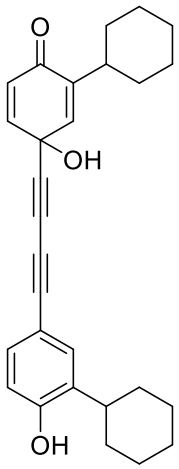
4,4'-(3-(3-(tert-butyl)-4-hydroxybenzylidene)penta-1,4-diyne-1,5-diyl)bis(2-(tert-

butyl)-4-hydroxycyclohexa-2,5-dien-1-one) **(4e)**



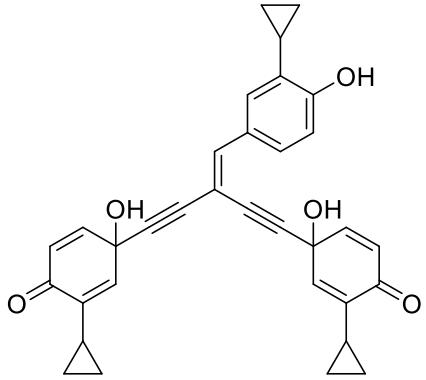
Brown solid, 19 mg, 36% yield. Purification by silica gel column chromatography (PE/EA = 1:1). mp:195.2-196.4 ℃; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.61 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.47 (s, 1H), 7.04 (s, 1H), 6.86 – 6.78 (m, 2H), 6.73 (d, *J* = 3.0 Hz, 1H), 6.69 (d, *J* = 3.0 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 1H), 6.16 – 6.10 (m, 2H), 5.77 (s, 1H), 1.37 (s, 9H), 1.26 (s, 9H), 1.25 (s, 9H).**^{13}C NMR (150 MHz, CDCl$_3$)** δ 185.2, 185.2, 156.6, 144.9, 144.7, 144.1, 144.1, 140.3, 140.3, 136.6, 129.9, 129.2, 129.1, 127.6, 127.4, 116.8, 96.8, 90.8, 84.8, 84.4, 82.5, 63.9, 63.6, 34.8, 34.8, 34.8, 29.6, 29.2.**HRMS** (ESI) calculated for $C_{36}H_{41}O_5^+$([M+H]$^+$): 553.2849, found 553.2867.

5-((3-cyclohexyl-4-hydroxyphenyl)buta-1,3-diyn-1-yl)-5-hydroxy-[1,1'-bi(cyclohexane)]-3,6-dien-2-one **(3f)**



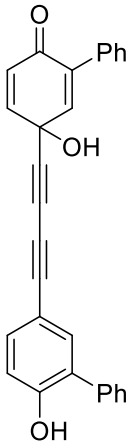
Brown solid, 22 mg, 58% yield. Purification by silica gel column chromatography (PE/EA = 4:1). mp:221.6-223.7 ℃; **^{1}H NMR** (**600 MHz, CDCl$_3$**) δ 7.4 (d, *J* = 8.4 Hz, 1H), 6.9 (d, *J* = 9.9 Hz, 1H), 6.7 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.6 – 6.6 (m, 1H), 6.2 (dd, *J* = 9.9, 1.8 Hz, 1H), 6.1 (d, *J* = 1.8 Hz, 1H), 2.9 (t, *J* = 11.7, 3.0 Hz, 1H), 2.6 (t, *J* = 11.7, 3.3 Hz, 1H), 2.0 – 1.9 (m, 2H), 1.9 – 1.8 (m, 6H), 1.78 –1.74 (m, 2H), 1.44 – 1.40 (m, 2H), 1.39 – 1.36 (m, 2H), 1.35 – 1.32 (m, 2H), 1.29 – 1.26 (m, 4H). **^{13}C NMR (150 MHz, CDCl$_3$)** δ 186.0, 165.5, 157.7, 154.4, 146.2, 135.6, 135.0, 126.7, 124.3, 113.3, 113.3, 113.1, 113.1, 79.6, 74.8, 71.0, 66.0, 42.4, 40.7, 34.6, 34.3, 33.7, 33.6, 27.0, 26.9, 26.6, 26.0. **HRMS** (ESI) calculated for $C_{28}H_{29}O_3^-$([M-H]$^-$): 413.2112, found 413.2118.

4,4'-(3-(3-cyclopropyl-4-hydroxybenzylidene)penta-1,4-diyne-1,5-diyl)bis(2-cyclopropyl-4-hydroxycyclohexa-2,5-dien-1-one) **(4g)**



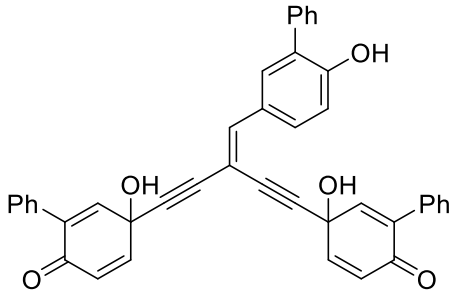
Brown solid, 6 mg, 19% yield. Purification by silica gel column chromatography (PE/EA = 4:1). mp:271.6-272.7 ℃; **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 10.0 (s, 1H), 8.0 (d, *J* = 8.7 Hz, 1H), 7.6 (s, 1H), 7.0 – 7.0 (m, 2H), 6.9 (s, 1H), 6.8 (s, 1H), 6.5 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.5 (d, *J* = 2.4 Hz, 1H), 6.1 (dd, *J* = 9.9, 4.2, 1.8 Hz, 2H), 5.7 (dd, *J* = 7.5, 1.8 Hz, 2H), 2.0 – 1.8 (m, 3H), 1.0 – 0.7 (m, 10H), 0.6 (q, *J* = 2.1 Hz, 2H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 186.0, 165.5, 157.7, 154.4, 146.2, 135.6, 135.0, 126.7, 124.3, 113.3, 113.3, 113.1, 113.1, 79.6, 74.8, 71.0, 66.0, 42.4, 40.7, 34.6, 34.3, 33.7, 33.6, 31.6, 30.3, 29.8. **HRMS** (ESI) calculated for $C_{33}H_{29}O_5^+$([M+H]$^+$): 505.5895, found 505.5891.

5-hydroxy-5-((6-hydroxy-[1,1'-biphenyl]-3-yl)buta-1,3-diyn-1-yl)-[1,1'-biphenyl]-2(5H)-one **(3h)**



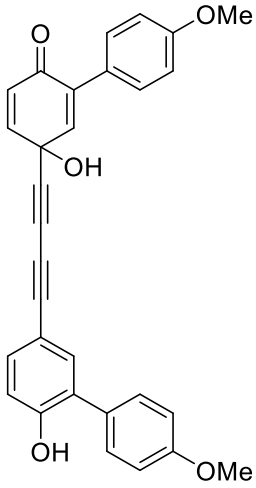
Brown solid, 18 mg, 30% yield. Purification by silica gel column chromatography (PE/EA = 4:1). mp:225.6 -226.9℃; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.5 – 7.5 (m, 2H), 7.4 – 7.4 (m, 11H), 7.0 – 6.9 (m, 3H), 6.4 – 6.3 (m, 1H), 5.7 (brs, 1H). **^{13}C NMR (150 MHz, CDCl$_3$)** δ 183.5, 154.2, 144.5, 142.3, 137.6, 134.9, 134.2, 133.9, 129.5, 129.0, 128.7, 128.5, 128.3, 128.1, 116.4, 112.9, 81.0, 77.6, 71.7, 71.3, 63.7. **HRMS** (ESI) calculated for $C_{28}H_{19}O_3^+$([M+H]$^+$): 403.1329, found : 403.1325.

5,5''-(3-((6-hydroxy-[1,1'-biphenyl]-3-yl)methylene)penta-1,4-diyne-1,5-diyl)bis(5-hydroxy-[1,1'-biphenyl]-2(5H)-one) **(4h)**



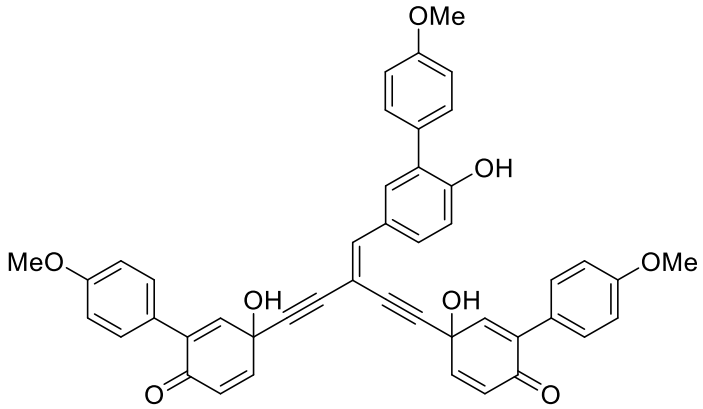
Brown solid, 9 mg, 15% yield. Purification by silica gel column chromatography (PE/EA = 1:1). mp:121.6-124.7 ℃;. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.8 (d, *J* = 2.4 Hz, 1H), 7.6 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.5 – 7.3 (m, 17H), 7.1 (d, *J* = 3.6 Hz, 1H), 7.0 – 6.9 (m, 2H), 6.9 – 6.9 (m, 2H), 6.8 (dd, *J* = 9.9, 3.0 Hz, 1H), 6.3 – 6.3 (m, 1H), 6.1 (d, *J* = 9.9 Hz, 1H), 5.8 (s, 1H). **^{13}C NMR (150 MHz, CDCl$_3$)** δ 183.9, 183.7, 154.7, 147.4, 145.3, 144.8, 143.1, 142.7, 137.6, 137.4, 136.3, 134.4, 131.4, 130.9, 129.6, 129.1, 129.0, 128.8, 128.6, 128.4, 128.1, 128.0, 127.8, 124.6, 124.1, 116.3, 97.5, 90.7, 85.2, 84.3, 82.8, 63.6, 63.4. **HRMS** (ESI) calculated for $C_{42}H_{29}O_5^+$([M+H]$^+$): 613.2010, found : 613.2009.

5-hydroxy-5-((6-hydroxy-4'-methoxy-[1,1'-biphenyl]-3-yl)buta-1,3-diyn-1-yl)-4'-methoxy-[1,1'-biphenyl]-2(5H)-one **(3i)**



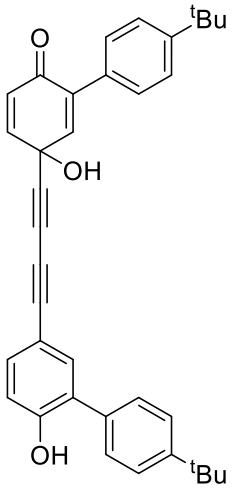
Brown solid, 15 mg, 23% yield. Purification by silica gel column chromatography (PE/EA = 4:1). mp:234.6-236.1 ℃. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.4 – 7.3 (m, 6H), 7.0 – 7.0 (m, 2H), 6.9 – 6.9 (m, 4H), 6.8 (d, *J* = 3.0 Hz, 1H), 6.3 (d, *J* = 9.9 Hz, 1H), 5.8 (s, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 3.2 (s, 1H). **^{13}C NMR (150 MHz, CDCl$_3$)** δ 184.0, 160.1, 159.8, 154.4, 145.7, 144.6, 141.3, 137.1, 135.0, 133.7, 130.3, 130.2, 128.6, 128.2, 127.8, 127.5, 126.7, 116.4, 115.0, 114.4, 113.9, 112.9, 81.0, 77.8, 71.7, 71.1, 63.7, 55.5, 55.5. **HRMS** (ESI) calculated for $C_{30}H_{23}O_5^+$([M+H]$^+$): 463.1540, found : 463.1542.

5,5''-(3-((6-hydroxy-4'-methoxy-[1,1'-biphenyl]-3-yl)methylene)penta-1,4-diyne-1,5-diyl)bis(5-hydroxy-4'-methoxy-[1,1'-biphenyl]-2(5H)-one) **(4i)**



Brown solid, 28 mg, 37% yield. Purification by silica gel column chromatography (PE/EA = 1:1). mp:134.9-136.2℃ ;**^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 10.2 (s, 1H), 8.0 (dd, *J* = 9.0, 1.2 Hz, 2H), 7.9 – 7.8 (m, 3H), 7.1 – 7.1 (m, 2H), 7.0 (dd, *J* = 9.9, 0.9. Hz, 2H), 7.0 – 6.9 (m, 7H), 6.9 – 6.8 (m, 2H), 6.8 (d, *J* = 1.2 Hz, 1H), 6.7 – 6.6 (m, 2H), 6.5 (dd, *J* = 12.6, 9.0, 1.8 Hz, 2H), 6.4 – 6.4 (m, 1H), 6.2 (dd, *J* = 9.9, 3.9, 1.8 Hz, 1H), 6.2 (dd, *J* = 9.9, 4.2, 1.8 Hz, 1H), 3.8 – 3.8 (m, 9H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 186.3, 186.0, 157.6, 156.8, 156.7, 154.0, 153.9, 153.6, 151.0, 147.9, 147.9, 147.4, 147.3, 144.8, 136.7, 132.4, 131.9, 130.3, 129.6, 128.4, 126.0, 125.9, 1 125.8, 125.7, 125.3, 125.0, 124.9, 124.3, 124.2, 117.2, 114.3, 97.9, 90.1, 86.1, 85.6, 84.1, 65.2, 65.1, 64.9. **HRMS** (ESI) calculated for $C_{45}H_{33}O_8^-$([M-H]$^-$): 701.2181, found : 701.2181.

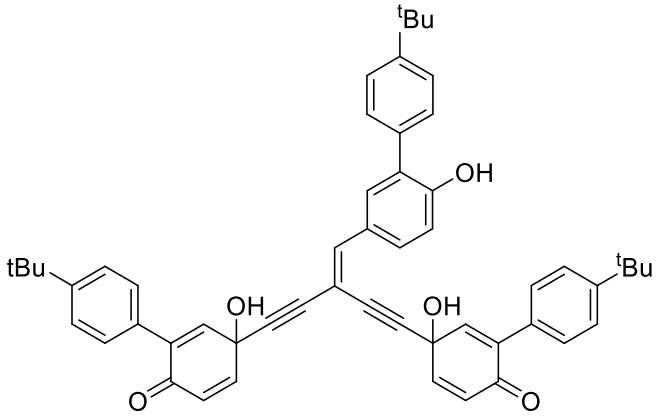
4'-(tert-butyl)-5-((4'-(tert-butyl)-6-hydroxy-[1,1'-biphenyl]-3-yl)buta-1,3-diyn-1-yl)-5-hydroxy-[1,1'-biphenyl]-2(5H)-one **(3j)**



Brown solid, 24 mg, 32% yield. Purification by silica gel column chromatography (PE/EA = 4:1). mp:301.6-304.2 ℃; **^{1}H NMR** (**600 MHz, CDCl$_3$**) δ 7.6 – 7.5 (m, 5H), 7.5 – 7.3 (m, 7H), 6.9 – 6.8 (m, 2H), 6.8 (dd, *J* = 8.4, 2.6 Hz, 1H), 5.6 – 5.5 (m, 1H), 1.37 (s, 9H), 1.36 (s, 9H). **^{13}C NMR (150 MHz, CDCl$_3$)** δ 185.6, 157.2, 155.7, 153.6, 151.0, 147.2, 146.6, 136.6, 136.3, 131.7, 128.5, 128.1, 125.9, 125.8, 125.1, 124.7, 116.6, 114.4, 111.0, 81.2, 78.1, 73.8, 72.7, 65.0, 34.8, 34.6, 31.3, 31.1. **HRMS** (ESI) calculated for $C_{36}H_{33}O_3^-$([M-H]$^-$): 513.2435, found : 513.2432.

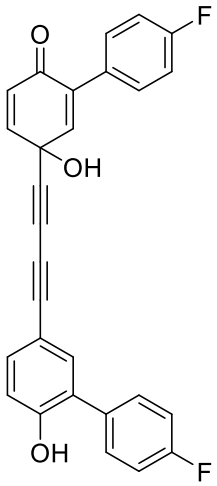
5,5''-(3-((4'-(tert-butyl)-6-hydroxy-[1,1'-biphenyl]-3-yl)methylene)penta-1,4-diyne-

1,5-diyl)bis(4'-(tert-butyl)-5-hydroxy-[1",1'"-biphenyl]-2(5H)-one) **(4j)**



Brown solid, 24 mg, 31% yield. Purification by silica gel column chromatography (PE/EA = 1:1). mp:154.8-156.2℃; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.8 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.8 – 7.7 (m, 4H), 7.4 (dd, *J* = 8.4, 2.4 Hz, 2H), 7.4 – 7.3 (m, 4H), 7.2 (dd, *J* = 8.3, 1.5 Hz, 2H), 7.0 – 7.0 (m, 1H), 7.0 – 7.0 (m, 1H), 6.9 (dd, *J* = 9.9, 6.9 Hz, 1H), 6.8 – 6.8 (m, 1H), 6.5 (dt, *J* = 8.7, 2.4 Hz, 1H), 6.4 (dd, *J* = 9.9, 1.8 Hz, 1H), 6.4 (dd, *J* = 6.0, 1.8 Hz, 1H), 6.2 (dd, *J* = 9.9, 6.3, 4.2, 1.8 Hz, 2H), 1.3 (d, *J* = 1.8 Hz, 9H), 1.3 – 1.3 (m, 18H). **^{13}C NMR (150 MHz, CDCl$_3$)** δ 186.0, 185.8, 157.5, 156.6, 153.9, 153.9, 153.6, 153.5, 151.1, 147.6, 147.6, 147.3, 147.2, 144.9, 136.8, 132.5, 132.0, 132.0, 130.3, 129.6, 128.4, 126.1, 125.9, 125.9, 125.8, 125.8, 125.4, 125.14, 125.08, 124.6, 124.5, 117.2, 114.3, 98.1, 90.3, 86.2, 85.7, 84.1, 65.2, 65.0, 34.9, 34.8, 31.5, 31.3. **HRMS** (ESI) calculated for $C_{54}H_{51}O_5^-$([M-H]$^-$): 779.3742, found: 779.3742.

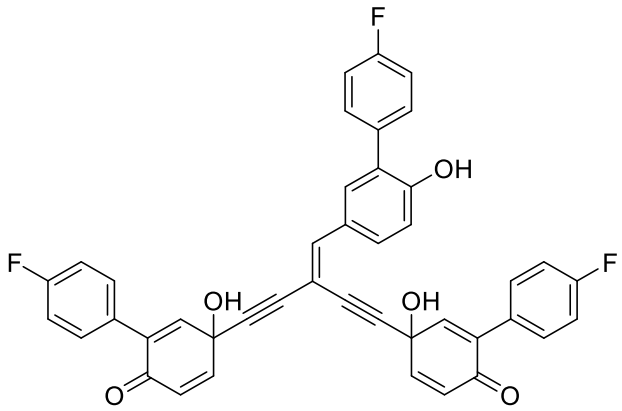
4'-fluoro-5-((4'-fluoro-6-hydroxy-[1,1'-biphenyl]-3-yl)buta-1,3-diyn-1-yl)-5-hydroxy-[1,1'-biphenyl]-2(5H)-one **(3k)**



Brown oil, 8 mg, 15% yield. Purification by silica gel column chromatography (PE/EA = 4:1). **^{1}H NMR (600 MHz, DMSO-*d6*)** δ 10.37 (s, 1H), 8.05 – 7.92 (m, 2H), 7.57 – 7.45 (m, 3H), 7.33 – 7.20 (m, 4H), 7.10 (s, 1H), 7.04 (d, J = 9.8 Hz, 1H), 6.82 – 6.74 (m, 2H), 6.52 (d, J = 1.8 Hz, 1H), 6.23 (dd, J = 9.8, 1.8 Hz, 1H). **^{13}C NMR (150 MHz, DMSO-*d$_6$*)** δ 184.9, 163.8, 162.8, 162.1, 161.1, 159.4, 153.7, 148.2, 145.7, 136.4, 135.6, 135.6, 131.7, 131.6, 130.9, 130.8, 130.7, 130.7, 124.6, 124.1, 116.5, 115.3, 115.2, 115.2,

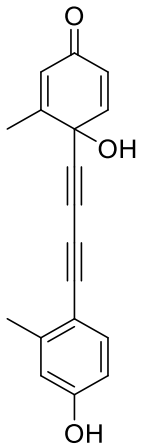
115.2, 115.1, 108.2, 80.6, 80.5, 73.2, 70.4, 64.0.**HRMS** (ESI) calculated for $C_{28}H_{15}F_2O_2^-$([M-H]$^-$): 437.0995, found : 437.0991.

5,5''-(3-((4'-fluoro-6-hydroxy-[1,1'-biphenyl]-3-yl)methylene)penta-1,4-diyne-1,5-diyl)bis(4'-fluoro-5-hydroxy-[1,1'-biphenyl]-2(5H)-one) **(4k)**



Brown oil, 43 mg, 55% yield. Purification by silica gel column chromatography (PE/EA = 4:1). **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 10.25 (s, 1H), 8.03 (m, 2H), 7.94 – 7.87 (m, 2H), 7.83 (dd, *J* = 8.7, 5.4 Hz, 1H), 7.28 – 7.18 (m, 6H), 7.12 – 7.04 (m, 4H), 6.97 (dd, *J* = 11.4, 9.8 Hz, 1H), 6.90 (d, J = 1.8 Hz, 1H), 6.66 (d, *J* = 1.8 Hz, 1H), 6.61 – 6.54 (m, 3H), 6.44 (dd, J = 10.1, 1.8 Hz, 1H), 6.26 (dd, *J* = 9.8, 1.8 Hz, 1H), 6.19 (m, *J* = 9.8, 3.0, 1.8 Hz, 1H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 185.1, 185.1, 163.9, 163.6, 162.7, 162.2, 162.0, 161.1, 159.1, 154.6, 154.3, 148.8, 148.8, 144.8, 144.8, 143.4, 135.7, 131.9, 131.7, 131.5, 131.4, 131.0, 131.0, 131.0, 130.9, 130.9, 130.8, 129.4, 124.6, 124.5, 124.0, 123.9, 122.9, 116.8, 115.4, 115.3, 115.2, 115.0, 114.9, 114.6, 96.6, 92.4, 86.6, 84.7, 82.0, 64.1, 63.7, 55.0. **HRMS** (ESI) calculated for $C_{42}H_{24}F_3O_5^-$([M-H]$^-$): 665.1581, found : 665.1579.

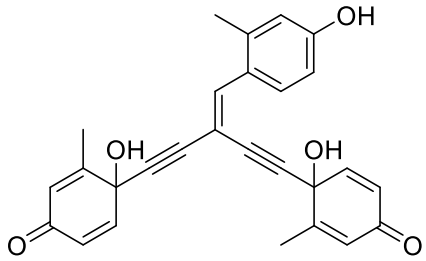
4-hydroxy-4-((4-hydroxy-2-methylphenyl)buta-1,3-diyn-1-yl)-3-methylcyclohexa-2,5-dien-1-one **(3l)**



Brown oil, 10 mg, 28% yield. Purification by silica gel column chromatography (PE/EA = 4:1). **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** *δ* 10.1 (s, 1H), 7.4 – 7.2 (m, 1H), 7.0 (dd, *J* = 9.9, 3.0 Hz, 1H), 6.8 – 6.7 (m, 3H), 6.2 (d, *J* = 9.9 Hz, 1H), 2.1 (s, 3H), 1.8 (d, *J* = 1.5 Hz, 3H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** *δ* =184.9, 157.7, 147.3, 142.7, 135.0, 132.6,

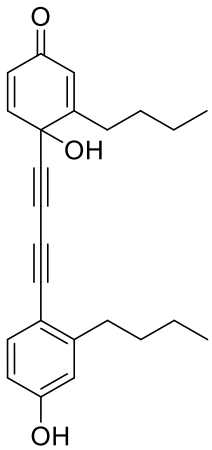
132.0, 126.0, 125.0, 115.1, 109.4, 80.7, 80.2, 70.8, 68.4, 62.2., 15.6, 15.0. **HRMS** (ESI) calculated for $C_{18}H_{13}O_3^-$ ([M-H]$^-$): 277.0870, found 277.0868.

4,4'-(3-(4-hydroxy-2-methylbenzylidene)penta-1,4-diyne-1,5-diyl)bis(4-hydroxy-3-methylcyclohexa-2,5-dien-1-one) **(4l)**



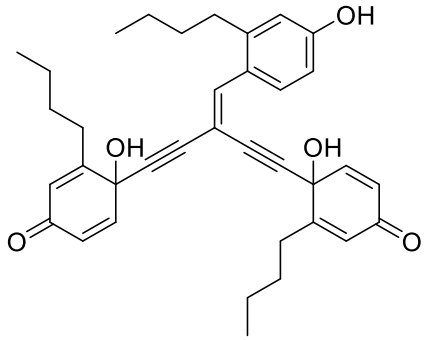
Brown oil, 9 mg, 21% yield. Purification by silica gel column chromatography (PE/EA = 4:1). **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 10.0 (brs, 1H), 7.9 (d, *J* = 8.6 Hz, 1H), 7.2 (s, 1H), 7.0 – 7.0 (m, 2H), 6.8 (s, 1H), 6.7 (s, 1H), 6.6 (d, *J* = 2.6 Hz, 1H), 6.5 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.1 (dd, *J* = 9.9, 7.8, 1.8 Hz, 2H), 6.0 (q, *J* = 3.0, 1.8 Hz, 2H), 2.2 (s, 3H), 2.1 (d, *J* = 1.4 Hz, 3H), 2.1 (d, *J* = 1.4 Hz, 3H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 184.8, 184.7, 159.2, 158.3, 158.1, 148.5, 148.3, 144.0, 139.8, 129.2, 125.4, 125.3, 124.7, 124.7, 124.2, 117.3, 112.8, 96.7, 91.7, 86.2, 83.4, 80.9, 64.3, 64.0, 19.6, 18.4, 18.3. **HRMS** (ESI) calculated for $C_{27}H_{21}O_5^-$([M-H]$^-$): 425.1394, found 425.1391.

3-butyl-4-((2-butyl-4-hydroxyphenyl)buta-1,3-diyn-1-yl)-4-hydroxycyclohexa-2,5-dien-1-one **(3m)**



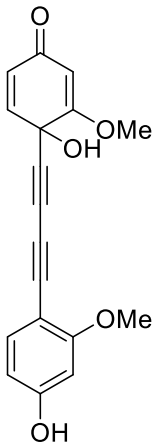
Brown oil, 11 mg, 20% yield. Purification by silica gel column chromatography (PE/EA = 4:1). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.4 (d, *J* = 8.4 Hz, 1H), 6.9 (d, *J* = 9.9 Hz, 1H), 6.7 (d, *J* = 2.7 Hz, 1H), 6.6 (dd, *J* = 8.4, 2.7 Hz, 1H), 6.2 (dd, *J* = 9.9, 1.8 Hz, 1H), 6.1 (q, *J* = 1.5 Hz, 1H), 5.9 (brs, 1H), 2.78 (s, 1H), 2.8 – 2.7 (m, 2H), 2.7 – 2.5 (m, 2H), 1.7 – 1.6 (m, 2H), 1.6 (t, *J* = 7.8 Hz, 2H), 1.5 – 1.4 (m, 2H), 1.4 – 1.4 (m, 2H), 1.0 (t, *J* = 7.4 Hz, 3H), 1.0 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (150 MHz, CDCl$_3$)** δ 185.8, 160.8, 157.6, 149.5, 146.8, 135.5, 126.6, 124.3, 116.1, 113.5, 112.0, 79.9, 74.5, 71.2, 66.0, 34.3, 32.8, 30.9, 29.3, 22.5, 22.5, 14.0. **HRMS** (ESI) calculated for $C_{24}H_{27}O_3^+$ ([M+H]$^+$): 363.1955, found 363.1952.

4,4'-(3-(2-butyl-4-hydroxybenzylidene)penta-1,4-diyne-1,5-diyl)bis(3-butyl-4-hydroxycyclohexa-2,5-dien-1-one) **(4m)**



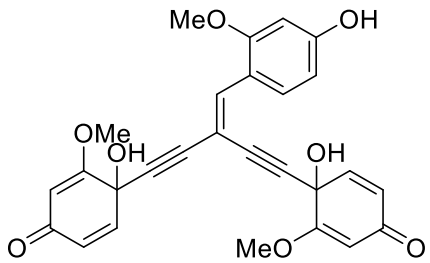
Brown oil, 15 mg, 28% yield. Purification by silica gel column chromatography (PE/EA = 4:1). **^{1}H NMR (600 MHz, DMSO-d$_6$)** δ 10.0 (d, *J* = 1.5 Hz, 1H), 7.9 (dd, *J* = 8.6, 2.7 Hz, 1H), 7.0 (dd, *J* = 9.9, 5.7, 2.1 Hz, 2H), 6.8 – 6.7 (m, 2H), 6.7 (d, *J* = 2.6 Hz, 1H), 6.6 (dt, *J* = 8.8, 2.0 Hz, 1H), 6.2 – 6.1 (m, 2H), 6.0 – 6.0 (m, 2H), 2.6 – 2.5 (m, 6H), 1.7 – 1.6 (m, 2H), 1.6 – 1.5 (m, 2H), 1.4 – 1.4 (m, 4H), 1.3 – 1.3 (m, 4H), 0.9 – 0.8 (m, 9H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 184.8, 184.7, 161.9, 161.8, 159.2, 148.6, 148.4, 144.2, 144.1, 129.5, 125.2, 125.1, 123.5, 123.09, 123.06, 116.4, 112.8, 97.1, 91.9, 86.2, 83.2, 80.7, 64.5, 64.2, 33.1, 32.3, 30.3, 29.0, 21.9, 13.8, 13.74, 13.73. **HRMS** (ESI) calculated for $C_{36}H_{41}O_5^+$ ([M+H]$^+$): 553.2949, found 553.2945.

4-hydroxy-4-((4-hydroxy-2-methoxyphenyl)buta-1,3-diyn-1-yl)-3-methoxycyclohexa-2,5-dien-1-one **(3n)**



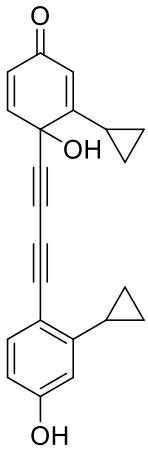
Brown solid, 6 mg, 13% yield. Purification by silica gel column chromatography (PE/EA = 3:1). mp:325.6-326.7 ℃; **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 6.8 (d, *J* = 10.1 Hz, 2H), 6.8 (dd, *J* = 10.1, 2.4 Hz, 2H), 6.1 (s, 1H), 6.1 (s, 1H), 3.8 (s, 6H), 3.7 (brs, 1H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 186.0, 171.8, 163.4, 161.2, 143.6, 135.5, 125.5, 108.3, 100.1, 99.3, 99.1, 80.4, 77.7, 74.7, 69.2, 63.4, 56.6, 55.7. **HRMS** (ESI) calculated for $C_{18}H_{13}O_5^-$ ([M-H]$^-$): 309.0768, found 309.0764.

4,4'-(3-(4-hydroxy-2-methoxybenzylidene)penta-1,4-diyne-1,5-diyl)bis(4-hydroxy-3-methoxycyclohexa-2,5-dien-1-one) **(4n)**



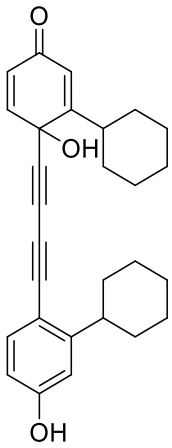
Brown solid, 30 mg, 64% yield. Purification by silica gel column chromatography (PE/EA = 3:1). mp:191.5-193.5 ℃; **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 8.00 (d, *J* = 8.7 Hz, 1H), 7.31 (s, 1H), 7.06 (s, 1H), 7.00 – 6.94 (m, 1H), 6.78 (dd, *J* = 9.8, 8.9 Hz, 2H), 6.42 (d, *J* = 2.3 Hz, 1H), 6.33 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.07 (dd, *J* = 9.8, 1.6 Hz, 1H), 6.03 (dd, *J* = 9.8, 1.6 Hz, 1H), 5.57 (d, *J* = 1.6 Hz, 1H), 5.54 – 5.47 (m, 1H), 3.81 (s, 6H), 3.77 (s, 3H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 185.5, 185.4, 171.8, 171.7, 161.1, 158.3, 143.9, 143.5, 139.9, 128.3, 124.7, 124.5, 113.8, 107.0, 99.4, 99.4, 98.3, 94.0, 91.5, 84.6, 82.9, 80.3, 62.9, 62.6, 56.0, 55.9, 55.1. **HRMS** (ESI) calculated for $C_{27}H_{21}O_8^-$ ([M-H]$^-$): 474.1315, found 474.1313.

3-cyclopropyl-4-((2-cyclopropyl-4-hydroxyphenyl)buta-1,3-diyn-1-yl)-4-hydroxycyclohexa-2,5-dien-1-one **(3o)**



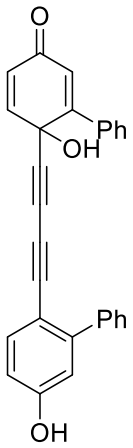
Brown solid, 20 mg, 35% yield. Purification by silica gel column chromatography (PE/EA = 3:1). mp:286.6-289.1 ℃; **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 10.1 (s, 1H), 7.3 (d, *J* = 8.4 Hz, 1H), 7.0 – 6.9 (m, 2H), 6.6 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.2 (d, *J* = 2.4 Hz, 1H), 6.1 (dd, *J* = 9.9, 1.8 Hz, 1H), 5.7 (d, *J* = 1.8 Hz, 1H), 2.2 – 2.1 (m, 1H), 1.9 – 1.8 (m, 1H), 1.2 (d, *J* = 3.8 Hz, 2H), 1.0 – 1.0 (m, 2H), 0.8 (dd, *J* = 5.1, 2.1 Hz, 2H), 0.6 (dd, *J* = 5.1, 2.1 Hz, 2H).. **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 185.0, 165.4, 160.1, 150.1, 148.0, 135.5, 125.9, 117.8, 113.8, 110.4, 110.3, 81.6, 79.9, 74.8, 69.4, 65.1, 14.1, 13.2, 12.0, 11.0, 10.2. **HRMS** (ESI) calculated for $C_{12}H_{19}O_3^+$([M+H]$^+$): 331.3905, found 331.3900.

6-((2-cyclohexyl-4-hydroxyphenyl)buta-1,3-diyn-1-yl)-6-hydroxy-[1,1'-bi(cyclohexane)]-1,4-dien-3-one **(3p)**



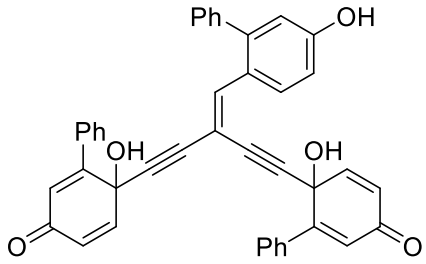
Brown oil, 15 mg, 25% yield. Purification by silica gel column chromatography (PE/EA = 4:1). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.3 (d, *J* = 2.1 Hz, 1H), 7.2 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.8 (dd, *J* = 9.9, 3.0 Hz, 1H), 6.7 (d, *J* = 8.3 Hz, 1H), 6.5 (dd, *J* = 3.0, 1.2 Hz, 1H), 6.2 (d, *J* = 9.9 Hz, 1H), 5.4 – 5.2 (m, 1H), 2.8 (dd, *J* = 11.7, 8.4, 3.0 Hz, 1H), 2.7 – 2.6 (m, 1H), 1.9 – 1.7 (m, 10H), 1.4 – 1.4 (m, 6H), 1.3 (d, *J* = 2.4 Hz, 4H). **^{13}C NMR (150 MHz, CDCl$_3$)** δ 186.0, 165.5, 157.7, 154.4, 146.2, 135.6, 135.0, 126.7, 124.3, 113.3, 113.3, 113.1, 113.1, 79.6, 78.2, 74.8, 71.0, 66.0, 42.4, 40.7, 34.6, 34.3, 33.7, 33.6, 27.0, 26.9, 26.9, 26.7, 26.6, 26.3, 26.0. **HRMS** (ESI) calculated for $C_{28}H_{29}O_3^-$([M-H]$^-$): 413.2122, found 413.2118.

6-hydroxy-6-((5-hydroxy-[1,1'-biphenyl]-2-yl)buta-1,3-diyn-1-yl)-[1,1'-biphenyl]-3(6H)-one **(3q)**



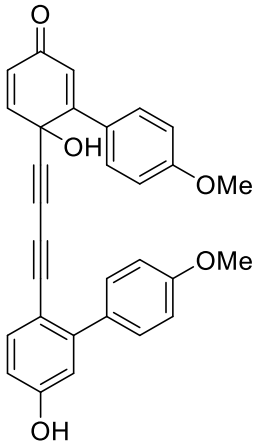
Brown solid, 10 mg, 17% yield. Purification by silica gel column chromatography (PE/EA = 3:1). mp:215.8-216.7 ℃; **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 10.3 (s, 1H), 8.0 – 7.9 (m, 2H), 7.5 – 7.4 (m, 9H), 7.1 – 7.0 (m, 2H), 6.8 – 6.8 (m, 2H), 6.5 (d, *J* = 1.8 Hz, 1H), 6.2 (dd, *J* = 9.8, 1.8 Hz, 1H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 184.9, 159.3, 155.0, 148.4, 146.8, 139.3, 136.4, 135.3, 129.8, 128.6, 128.4, 128.3, 128.0, 124.6, 124.2, 116.5, 115.1, 108.3, 80.6, 80.6, 73.1, 70.4, 64.0. **HRMS** (ESI) calculated for $C_{28}H_{19}O_3^+$([M+H]$^+$): 403.1329, found : 403.1325.

6,6''-(3-((5-hydroxy-[1,1'-biphenyl]-2-yl)methylene)penta-1,4-diyne-1,5-diyl)bis(6-hydroxy-[1,1'-biphenyl]-3(6H)-one) **(4q)**



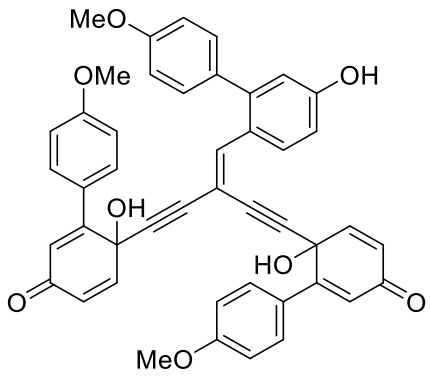
Brown solid, 18 mg, 30% yield. Purification by silica gel column chromatography (PE/EA = 1:1). mp:131.5-133.4 ℃; **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 10.22 (s, 1H), 8.01 – 7.96 (m, 2H), 7.88 (d, *J* = 8.7 Hz, 1H), 7.82 – 7.75 (m, 2H), 7.49 – 7.32 (m, 7H), 7.27 (td, *J* = 7.5, 6.8, 1.2 Hz, 2H), 7.19 – 7.14 (m, 2H), 7.08 (dd, *J* = 9.8, 3.0 Hz, 1H), 7.01 (d, *J* = 1.5 Hz, 1H), 6.97 (t, *J* = 9.8 Hz, 1H), 6.83 (d, *J* = 2.8 Hz, 1H), 6.67 (d, *J* = 2.6 Hz, 1H), 6.63 (d, *J* = 2.2 Hz, 1H), 6.57 (ddd, *J* = 13.4, 9.2, 2.2 Hz, 2H), 6.40 (dd, *J* = 14.5, 1.8 Hz, 1H), 6.27 (dt, *J* = 9.8, 1.8 Hz, 1H), 6.19 (ddd, *J* = 9.8, 2.9, 1.8 Hz, 1H), 2.88 (s, 1H), 2.73 (d, *J* = 0.7 Hz, 1H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 185.1, 185.1, 162.3, 159.0, 156.1, 156.1, 155.6, 149.0, 148.9, 144.6, 144.6, 144.5, 139.4, 135.5, 135.5, 135.3, 129.8, 129.5, 129.5, 129.3, 128.5, 128.5, 128.4, 128.4, 128.2, 128.0, 127.9, 127.8, 124.4, 124.4, 124.0, 124.0, 122.8, 116.7, 114.5, 96.5, 92.5, 86.6, 84.6, 82.0, 64.1, 63.7. **HRMS** (ESI) calculated for $C_{42}H_{29}O_5^+$([M+H]$^+$): 613.2010, found : 613.2000.

6-hydroxy-6-((5-hydroxy-4'-methoxy-[1,1'-biphenyl]-2-yl)buta-1,3-diyn-1-yl)-4'-methoxy-[1,1'-biphenyl]-3(6H)-one **(3r)**



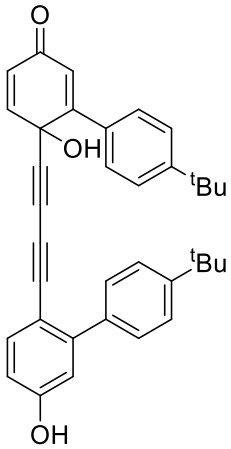
Brown solid, 19 mg, 28% yield. Purification by silica gel column chromatography (PE/EA = 4:1). mp:250.0-253.9 ℃; **^{1}H NMR** (**600 MHz, CDCl$_3$**) δ 7.39 – 7.36 (m, 4H), 7.35 – 7.32 (m, 2H), 7.03 – 7.01 (m, 2H), 6.93 – 6.89 (m, 4H), 6.85 (d, *J* = 3.1 Hz, 1H), 6.32 (d, *J* = 9.8 Hz, 1H), 5.55 (s, 1H), 3.86 (s, 3H), 3.83 (s, 3H). **^{13}C NMR (150 MHz, CDCl$_3$)** δ 185.7, 161.4, 159.6, 157.4, 155.2, 147.3, 146.6, 136.6, 132.0, 130.2, 127.1, 126.2, 124.0, 116.6, 114.4, 114.4, 113.8, 81.4, 78.4,73.9, 72.9, 65.1, 55.5, 55.4. **HRMS** (ESI) calculated for $C_{30}H_{23}O_5^+$([M+H]$^+$): 463.1540, found: 463.1532.

6,6''-(3-((5-hydroxy-4'-methoxy-[1,1'-biphenyl]-2-yl)methylene)penta-1,4-diyne-1,5-diyl)bis(6-hydroxy-4'-methoxy-[1,1'-biphenyl]-3(6H)-one) **(4r)**



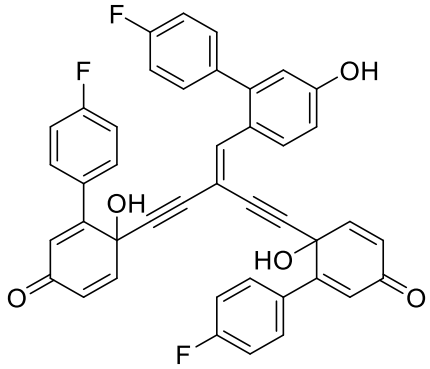
Brown solid, 24 mg, 32% yield. Purification by silica gel column chromatography (PE/EA = 4:1). mp:237.9-239.2℃; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.8 (d, *J* = 2.3 Hz, 1H), 7.6 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.4 (d, *J* = 8.6 Hz, 2H), 7.3 (d, *J* = 8.7 Hz, 2H), 7.3 (d, *J* = 8.6 Hz, 2H), 7.1 (s, 1H), 7.0 (d, *J* = 8.7 Hz, 2H), 6.9 – 6.9 (m, 2H), 6.9 – 6.9 (m, 3H), 6.9 – 6.9 (m, 2H), 6.8 (d, *J* = 3.0 Hz, 1H), 6.8 (dd, *J* = 9.8, 3.1 Hz, 1H), 6.3 (d, *J* = 9.8 Hz, 1H), 6.1 (d, *J* = 9.8 Hz, 1H), 3.8 – 3.8 (m, 9H). **^{13}C NMR (150 MHz, CDCl$_3$)** δ 186.3, 186.0, 157.6, 156.8, 156.7, 154.0, 153.9, 153.6, 153.5, 151.0, 147.9, 147.9, 147.4, 147.3, 144.8, 136.7, 132.4, 131.9, 131.8, 130.3, 129.6, 128.4, 128.4, 126.0, 125.9, 125.9, 125.8, 125.8, 125.7, 125.3, 125.0, 124.9, 124.3, 124.2, 117.2, 114.3, 97.9, 90.1, 86.1, 85.6, 84.1, 65.2, 65.1, 64.9. **HRMS** (ESI) calculated for $C_{45}H_{33}O_8^-$([M-H]$^-$): 701.2181, found: 701.2179.

4'-(tert-butyl)-6-((4'-(tert-butyl)-5-hydroxy-[1,1'-biphenyl]-2-yl)buta-1,3-diyn-1-yl)-6-hydroxy-[1,1'-biphenyl]-3(6H)-one **(3s)**



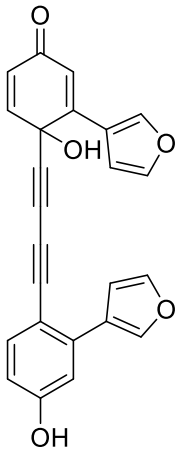
Brown solid, 7 mg, 25% yield. Purification by silica gel column chromatography (PE/EA = 4:1). mp:304.1-306.7 ℃; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.8 (d, *J* = 8.5 Hz, 2H), 7.5 – 7.4 (m, 7H), 6.9 (d, *J* = 9.8 Hz, 1H), 6.9 (d, *J* = 2.6 Hz, 1H), 6.8 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.4 (d, *J* = 1.8 Hz, 1H), 6.3 – 6.2 (m, 1H), 5.8 (brs, 1H),1.4 (s, 9H), 1.3 (s, 9H). **^{13}C NMR (150 MHz, CDCl$_3$)** δ 185.8, 157.4, 155.9, 153.8, 151.2, 147.4, 146.8, 136.9, 136.6, 132.0, 128.7, 128.3, 126.2, 126.0, 125.4, 124.9, 116.8, 114.6, 111.2, 81.4, 78.3, 74.1, 73.0, 65.1, 35.0, 34.8, 31.5, 31.3. **HRMS** (ESI) calculated for $C_{36}H_{35}O_3^+$([M+H]$^+$): 515.2581, found : 515.2580.

6,6''-(3-((4'-fluoro-5-hydroxy-[1,1'-biphenyl]-2-yl)methylene)penta-1,4-diyne-1,5-diyl)bis(4'-fluoro-6-hydroxy-[1,1'-biphenyl]-3(6H)-one) **(4t)**



Brown solid, 16 mg, 26% yield. Purification by silica gel column chromatography (PE/EA = 1:1). mp:301.6-303.4 ℃; **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 10.39 (s, 1H), 7.81 (d, *J* = 2.1 Hz, 1H), 7.74 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.55 (dd, *J* = 8.7, 5.6 Hz, 2H), 7.44 (dd, *J* = 8.7, 5.7 Hz, 2H), 7.37 (dd, *J* = 8.7, 5.7 Hz, 2H), 7.27 (s, 1H), 7.25 – 7.20 (m, 4H), 7.18 (t, *J* = 8.7 Hz, 2H), 7.08 (ddd, *J* = 9.8, 3.0, 1.2 Hz, 1H), 7.05 – 7.00 (m, 3H), 6.98 (s, 1H), 6.92 – 6.87 (m, 2H), 6.28 (dd, *J* = 9.8, 1.2 Hz, 1H), 6.20 – 6.16 (m, 1H).**^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 183.4, 183.2, 163.0, 162.1, 161.3, 160.5, 156.6, 147.5, 147.1, 146.7, 144.8, 144.3, 134.6, 134.3, 133.9, 133.9, 132.0, 131.0, 131.0, 130.9, 130.9, 130.8, 130.8, 130.7, 130.6, 130.6, 129.7, 127.0, 126.4, 126.3, 116.1, 115.1, 115.1, 115.0, 115.0, 114.9, 114.8, 95.9, 92.1, 85.5, 83.5, 81.1, 62.5, 62.2.**HRMS** (ESI) calculated for $C_{42}H_{24}F_3O_5^-$([M-H]$^-$): 665.1581, found : 665.1579.

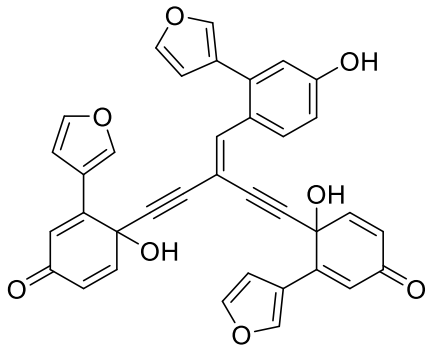
3-(furan-3-yl)-4-((2-(furan-3-yl)-4-hydroxyphenyl)buta-1,3-diyn-1-yl)-4-hydroxycyclohexa-2,5-dien-1-one **(3u)**



Brown solid, 10 mg, 18% yield. Purification by silica gel column chromatography (PE/EA = 1:1). mp:251.4-253.9 ℃; ^{1}**H NMR (600 MHz, DMSO-*d*$_6$)** δ 10.84 (s, 1H), 8.27 (s, 1H), 8.18 (s, 1H), 7.81 (d, *J* = 2.1 Hz, 1H), 7.72 (dt, *J* = 15.6, 1.8 Hz, 2H), 7.32 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.29 (d, *J* = 3.0 Hz, 1H), 7.08 (d, *J* = 1.7 Hz, 1H), 7.05 (dd, *J* = 9.8, 2.9 Hz, 1H), 7.02 – 6.99 (m, 1H), 6.98 (s, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.27 (d, *J* = 9.8 Hz, 1H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 183.7, 156.9, 147.2, 143.8, 143.5, 143.1, 142.2, 141.5, 132.7, 132.7, 127.9, 127.1, 121.3, 120.1, 119.0, 116.8, 110.5, 109.6, 108.8, 81.1, 80.4, 71.6, 69.1, 62.8, 40.2, 40.0, 39.9, 39.8, 39.6. **HRMS** (ESI) calculated

for $C_{24}H_{13}O_5^-$([M-H]$^-$): 381.0768, found: 381.0764.

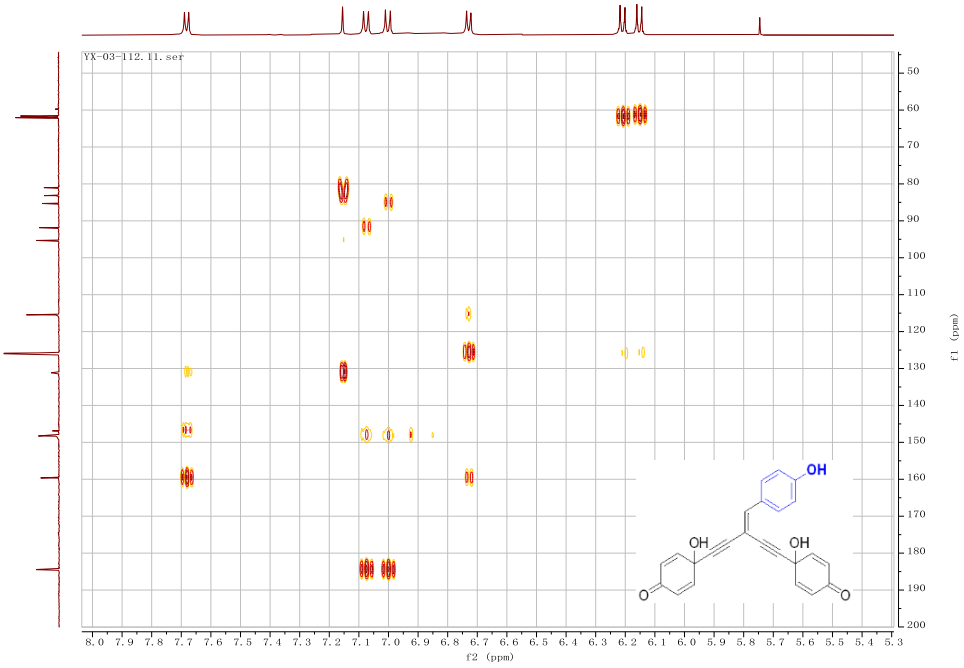
4,4'-(3-(2-(furan-3-yl)-4-hydroxybenzylidene)penta-1,4-diyne-1,5-diyl)bis(3-(furan-3-yl)-4-hydroxycyclohexa-2,5-dien-1-one) **(4u)**



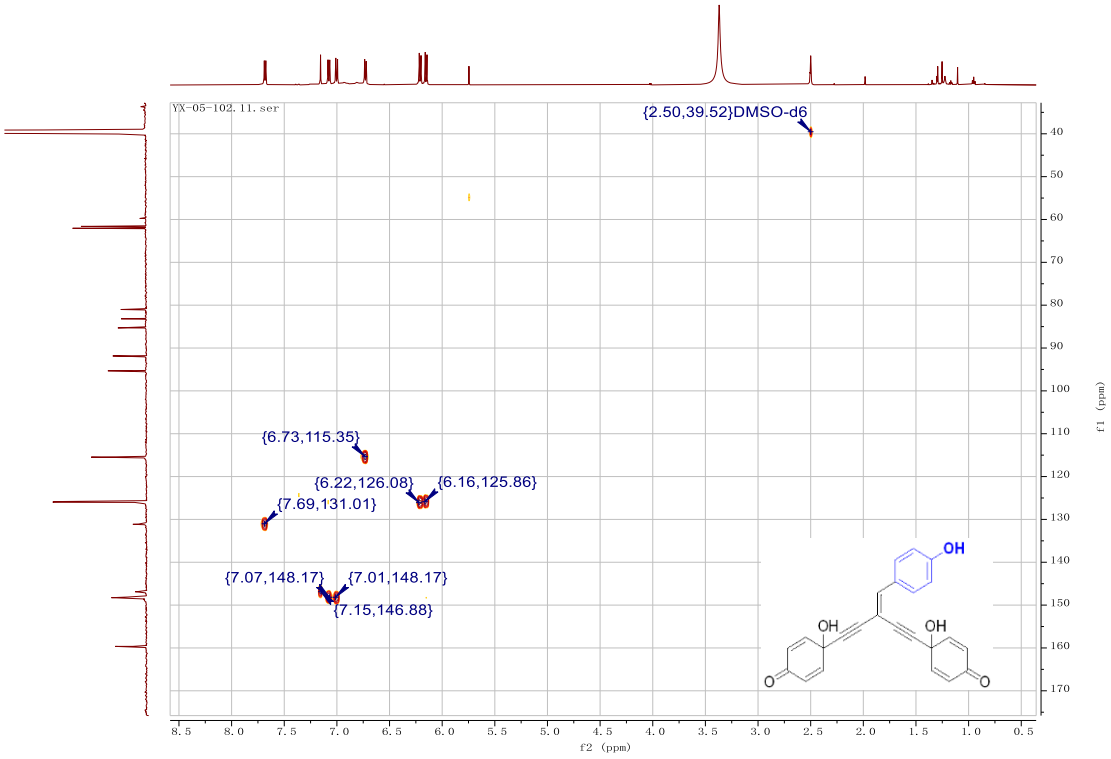
Brown solid, 18 mg, 31% yield. Purification by silica gel column chromatography (PE/EA = 1:1). mp:159.2-161.7 ℃; **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 10.21 (s, 1H), 8.27 (d, *J* = 8.2 Hz, 1H), 8.25 (d, *J* = 5.3 Hz, 1H), 7.82 (dd, *J* = 8.7, 6.3 Hz, 1H), 7.77 (q, *J* = 1.5 Hz, 3H), 7.69 (s, 1H), 7.10 (dd, *J* = 2.0, 0.8 Hz, 1H), 7.08 – 7.04 (m, 2H), 7.02 – 6.93 (m, 3H), 6.93 (d, *J* = 2.4 Hz, 1H), 6.74 (d, *J* = 2.6 Hz, 1H), 6.59 (dd, *J* = 5.2, 1.8 Hz, 1H), 6.57 – 6.52 (m, 3H), 6.21 (ddd, *J* = 9.9, 5.7, 1.8 Hz, 1H), 6.18 (dt, *J* = 9.8, 1.5 Hz, 1H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 185.7, 185.7, 171.4, 159.5, 150.2, 149.9, 149.9, 148.8, 148.6, 145.4, 145.2, 144.4, 144.3, 144.3, 141.5, 135.5, 130.0, 125.5, 125.4, 124.3, 123.5, 121.8, 121.8, 121.5, 121.4, 116.6, 114.9, 112.1, 109.4, 109.3, 97.4, 93.2, 87.7, 84.5, 81.6, 64.1, 64.0, 63.6. **HRMS** (ESI) calculated for $C_{36}H_{23}O_8^+$([M+H]$^+$): 583.1387, found : 583.1389.

6. 2D NMR of 4a (HMBC and HSQC)

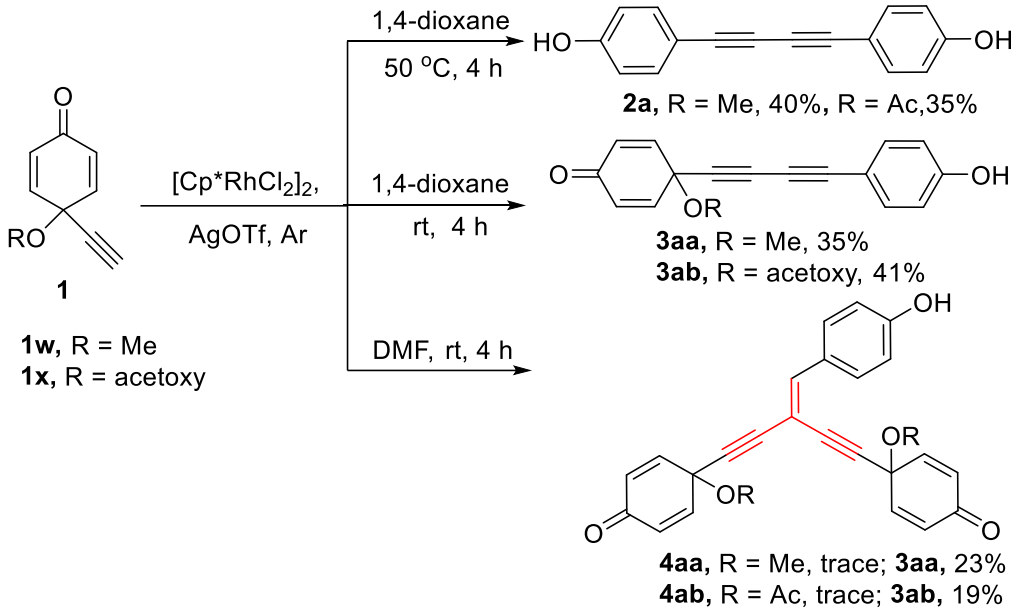
HMBC spectra of compound **4a**



HSQC spectra of compound **4a**

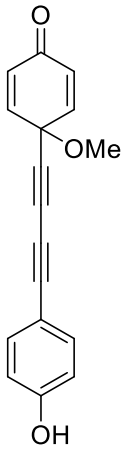


7. General procedure for the control experiments



To a dried Schlenk flask charged with the **1** (synthesized following the procedure as mentioned earlier (1.0 equiv) was added AgOTf (1.5 equiv), $[Cp^*RhCl_2]_2$ (0.05 equiv), and anhydrous 1,4-dioxane /DMF (2 mL). The reaction was vigorously stirred at 50°C or rt for 4 h at Argon. After the reaction was completed, the reaction was diluted with ethyl acetate. The layers were separated, and the aqueous layer was extracted with ethyl acetate, washed with brine, dried over sodium sulfate, and evaporated in vacuo. Purification was performed by silica gel chromatography to yield chromatographically and spectroscopically pure product.

4-((4-hydroxyphenyl)buta-1,3-diyn-1-yl)-4-methoxycyclohexa-2,5-dien-1-one **(3aa)**



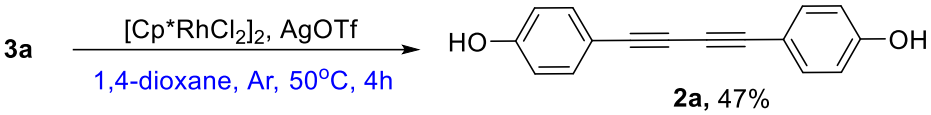
White solid, 14 mg, 35% yield. Purification by silica gel column chromatography (PE/EA = 4:1). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 6.88 (d, *J* = 10.2 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 6.33 (d, *J* = 10.2 Hz, 2H), 3.42 (s, 3H).**^{13}C NMR (150 MHz, $CDCl_3$)** δ 184.6, 157.4, 144.4, 134.8, 129.4, 115.9, 112.7, 80.6, 75.5, 72.3, 71.5, 68.3, 52.6.

HRMS (ESI) calculated for $C_{17}H_{13}O_3^+$([M+H]$^+$): 265.0859, found : 265.0850.

1-((4-hydroxyphenyl)buta-1,3-diyn-1-yl)-4-oxocyclohexa-2,5-dien-1-yl acetate**(3ab)**

White solid, 17 mg, 41% yield. Purification by silica gel column chromatography (PE/EA = 4:1). ^{1}**H NMR (600 MHz, DMSO-*d*$_6$)** δ 10.1 (s, 1H), 7.8 (d, *J* = 8.7 Hz, 2H), 7.4 (d, *J* = 8.7 Hz, 2H), 6.9 (d, *J* = 8.7 Hz, 2H), 6.8 (d, *J* = 8.7 Hz, 2H), 2.1 (s, 3H). ^{13}**C NMR (150 MHz, DMSO-*d*$_6$)** δ 184.0, 168.7, 159.7, 143.0, 134.8, 128.3, 122.5, 116.1, 109.2, 82.3, 74.4, 71.8, 70.6, 67.5, 21.0. **HRMS** (ESI) calculated for $C_{18}H_{13}O_4^+$([M+H]$^+$): 293.0808, found : 293.0798.

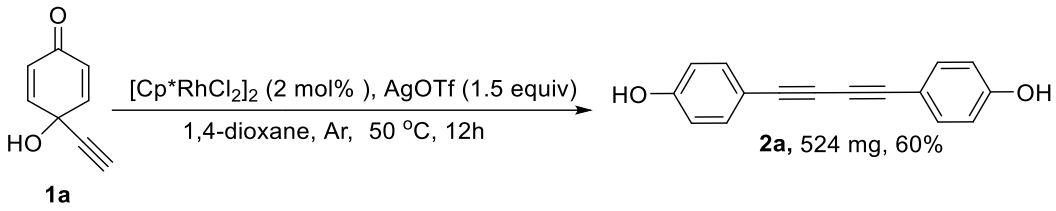
8. General procedure for the aromatization of 3a



To a dried Schlenk flask charged with the **3a** (synthesized following the procedure as mentioned earlier (1.0 equiv) was added AgOTf (1.5 equiv), $[Cp^*RhCl_2]_2$ (0.05 equiv) and anhydrous 1,4-dioxane (2 mL). The reaction was vigorously stirred at 50 °C for 12 h under Argon. After the reaction was completed, the reaction was diluted with ethyl acetate. The layers were separated, and the aqueous layer was extracted with ethyl acetate, washed with brine, dried over sodium sulfate, and evaporated in vacuo. Purification was performed by silica gel chromatography to yield chromatographically and spectroscopically pure product.

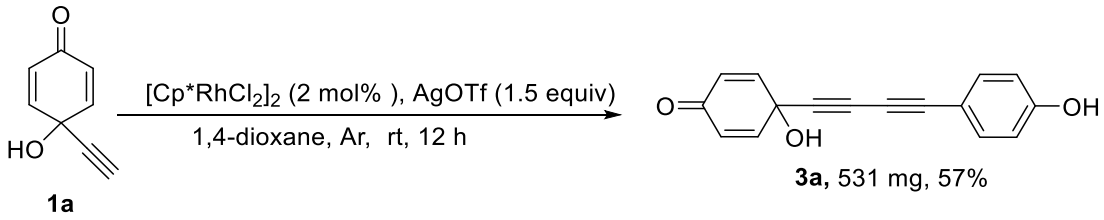
9. General procedure for the scale-up synthesis and transformations

(1) Scale-up synthesis of **2a**



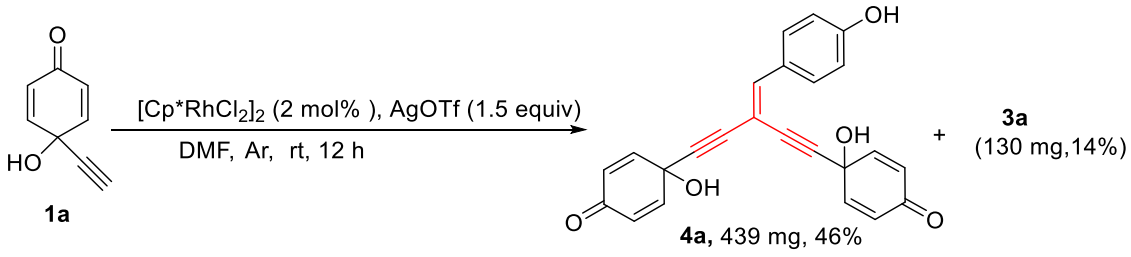
To a dried Schlenk flask charged with the **1a** (synthesized following the procedure as mentioned earlier (1.0 equiv) was added AgOTf (1.5 equiv), $[Cp^*RhCl_2]_2$ (0.02eq), and anhydrous 1,4-dioxane (2 mL). The reaction was vigorously stirred at 50 °C for 12 h at Argon. After the reaction was completed. the reaction was diluted with ethyl acetate. The layers were separated, and the aqueous layer was extracted with ethyl acetate, washed with brine, dried over sodium sulfate, and evaporated in vacuo. Purification was performed by silica gel chromatography to yield chromatographically and spectroscopically pure product.

(2) Scale-up synthesis of **3a**



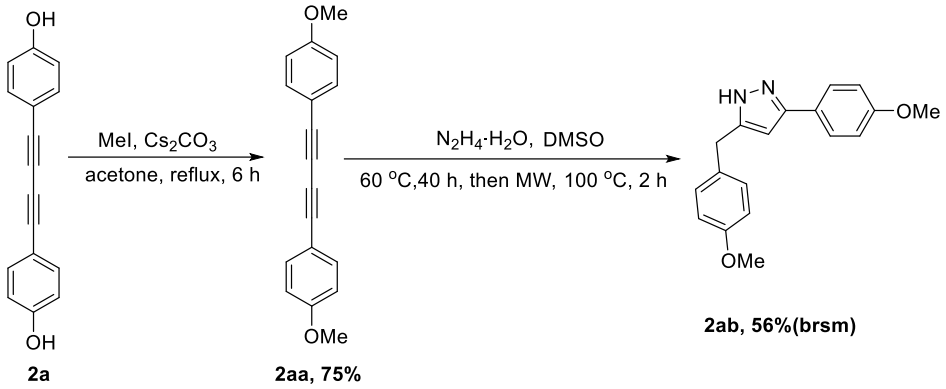
To a dried Schlenk flask charged with the **1a** (synthesized following the procedure as mentioned earlier (1.0 equiv) was added AgOTf (1.5 equiv), $[Cp^*RhCl_2]_2$ (0.02 equiv), and anhydrous 1,4-dioxane (2 mL). The reaction was vigorously stirred at rt for 12 h under Argon. After the reaction was completed. the reaction was diluted with ethyl acetate. The layers were separated, and the aqueous layer was extracted with ethyl acetate, washed with brine, dried over sodium sulfate, and evaporated in vacuo. Purification was performed by silica gel chromatography to yield chromatographically and spectroscopically pure product.

(3) Scale-up synthesis of **4a**



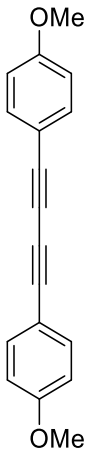
To a dried Schlenk flask charged with the **1a** (synthesized following the procedure as mentioned earlier (1.0 equiv) was added AgOTf (1.5 equiv), $[Cp^*RhCl_2]_2$ (0.02 equiv), and anhydrous DMF (2 mL). The reaction was vigorously stirred at rt for 12 h at Argon. After the reaction was completed. the reaction was diluted with ethyl acetate. The layers were separated, and the aqueous layer was extracted with ethyl acetate, washed with brine, dried over sodium sulfate, and evaporated in vacuo. Purification was performed by silica gel chromatography to yield chromatographically and spectroscopically pure product.

(4) Transformation of **2a**



Step1: To a solution of **2a** (1.0 equiv) in acetone under N_2 at 0℃ was added Cs_2CO_3. The resulting mixture was stirred at rt for 10 minutes. Then, MeI (4.0 equiv) was added dropwise. The reaction mixture was stirred at 60 °C for 8 hours. After completion, The mixture was extracted with ethyl acetate three times, and the organic phases were combined and washed with brine, dried over anhydrous Na_2SO_4, filtered through a pad of celite, and concentrated under reduced pressure.

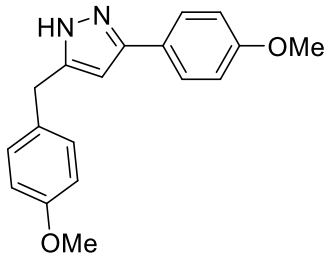
1,4-bis(4-methoxyphenyl)buta-1,3-diyne **(2aa)**



White solid, 25 mg, 76% yield. Purification by silica gel column chromatography (PE/EA = 8:1). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.5 – 7.4 (m, 4H), 6.9 – 6.8 (m, 4H), 3.8 (s, 6H). All spectral data were found to be in accordance with the literature.

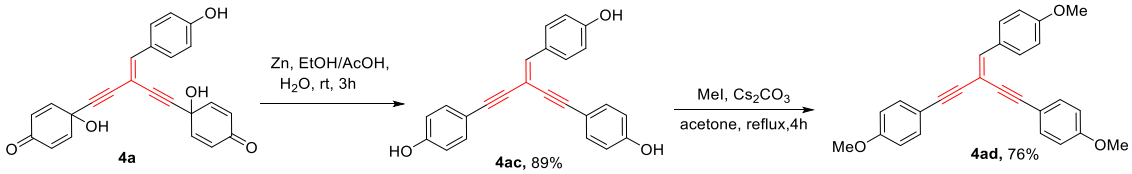
Step 2: A reaction flask was charged with a mixture of **2aa** (1.0 equiv), aqueous hydrazine solution (50 wt %, 3.0 equiv), and DMSO (1.0 mL). The reaction mixture was sealed and stirred at 60 °C for 40 h and then moved to the microwave reactor for 2 hours at 100 °C. After the reaction was completed, water (10 mL) was added to the resultant mixture. The product was extracted with ethyl acetate (10 mL × 3), and the combined organic layers were washed with brine (10 mL × 2) and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue obtained was purified via silica gel chromatography to afford product.

5-(4-methoxybenzyl)-3-(4-methoxyphenyl)-1H-pyrazole **(2ab)**

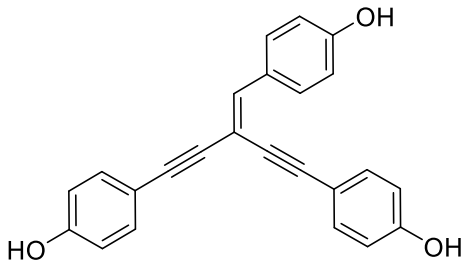


White solid, 7 mg, 56%(brsm) yield. Purification by silica gel column chromatography (PE/EA = 1:4). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.6 – 7.6 (m, 2H), 7.2 – 7.1 (m, 2H), 6.9 – 6.9 (m, 2H), 6.9 – 6.8 (m, 2H), 6.3 (s, 1H), 4.0 (s, 2H), 3.8 (s, 3H), 3.8 (s, 3H). All spectral data were found to be in accordance with the literature.

(5) Transformation of **4a**



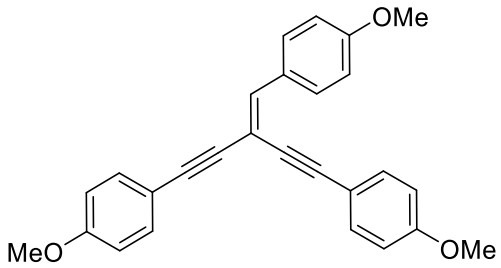
Step1: To a solution of **4a** (38 mg, 0.1 mmol) in EtOH/AcOH (4:1) and H_2O was added Zn (4.0 equiv). The reaction mixture was stirred at rt for 3 h. After the reaction was completed, the reaction was neutralized by saturated $NaHCO_3$ and diluted with ethyl acetate. The layers were separated, and the aqueous layer was extracted with ethyl acetate, washed with brine, dried over sodium sulfate, and evaporated in vacuo. Purification was performed by silica gel chromatography to yield chromatographically and spectroscopically pure product.



Compound **4ac,** white solid, 31 mg, 89% yield. Purification by silica gel column chromatography (PE/EA = 8:1).**^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 10.0 (s, 3H), 7.8 (d, *J* = 8.8 Hz, 2H), 7.4 (d, *J* = 8.7 Hz, 2H), 7.3 (d, *J* = 8.6 Hz, 2H), 7.1 (s, 1H), 6.8 (dd, *J* = 8.7, 1.5 Hz, 4H), 6.8 (d, *J* = 8.6 Hz, 2H). **^{13}C NMR (150 MHz, DMSO-*d*$_6$)** δ 158.8, 158.5, 158.1, 141.7, 133.1, 133.0, 130.7, 126.9, 116.1, 115.9, 115.6, 112.5, 112.2, 98.9, 94.6, 87.9, 87.8, 85.7.

Step 2: To a solution of **4ac** (1.0 equiv) in acetone under N_2 at 0 °C was added Cs_2CO_3. The resulting mixture was stirred at rt for 10 minutes. Then, MeI (4.0 equiv) was added dropwise. The reaction mixture was a stirred at 60 °C for 4 hours. After completion, the mixture was extracted with ethyl acetate three times, and the organic phase was combined and washed with brine, dried over anhydrous Na_2SO_4, filtered through a pad of celite, and concentrated under reduced pressure. Purification was performed by silica gel chromatography to yield chromatographically and spectroscopically pure product.

4,4'-(2-((4-methoxyphenyl)ethynyl)but-1-en-3-yne-1,4-diyl)bis(methoxybenzene) **(4ad)**



white solid, 29 mg, 76%. Purification by silica gel column chromatography (PE/EA = 8:1) **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.9 (d, *J* = 8.8 Hz, 2H), 7.5 – 7.4 (m, 4H), 7.1 (s, 1H), 6.9 (d, *J* = 9.2 Hz, 4H), 6.9 (d, *J* = 8.8 Hz, 2H), 3.8 (d, *J* = 3.4 Hz, 6H), 3.8 (s, 3H). **^{13}C NMR (150 MHz, CDCl$_3$)** δ 160.2, 160.0, 159.7, 141.8, 133.2, 130.7, 129.1, 115.5, 115.4, 114.2, 114.1, 114.0, 101.2, 94.4, 88.5, 87.7, 86.3, 55.5, 55.4, 31.6, 30.3, 29.8. All spectral data were found to be in accordance with the literature.

10. General information for the evaluation of anti-ferroptotic activity

Cell culture

HT-1080, HepG2 and MDA-MB-231 cells (ATCC) were cultured in DMEM. A549 and

K562 cells were grown in RPMI1640. All media were supplemented with 10% fetal bovine serum and 1% penicillin/streptomycin. And all cell lines were grown at 37 °C with 5% CO_2.

Cell viability assay

A total of 10,000 HT-1080 cells were seeded into 96-well plates. Cells were treated with RSL3 or Erastin in the presence or absence of **2a** for 24 h. And cell viability was detected via CellTiter-Lumi Plus Luminescent Cell Viability Assay Kit (Beyotime Biotechnology, C0057S) according to the manufacturer's instructions by a microplate reader. All data were analyzed using GraphPad Prism.

Measurement of cellular lipid ROS

HT-1080 cells were seeded into six-well plates. Cells were treated with RSL3 in the presence or absence of 2a. After treatment, cells were stained with C11- BODIPY$^{581/591}$ (D3861; Thermo Fisher Scientific) for 30 min at 37 °C and then harvested by trypsinization. Cells were resuspended in PBS, and then analyzed using a flow cytometer (Accuri C6; BD Biosciences). A minimum of 10,000 cells were analyzed per condition. Data analysis was performed using FlowJo_V10 software.

DPPH assay

The stable radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) was dissolved in methanol to a final concentration of 0.05 mM. 1 mL of DPPH solution was added to 1 μL of each test compound dissolved in DMSO. Samples were inverted several times and incubated at room temperature for 30 min. The absorbance at 517 nm was recorded via a microplate reader and normalized to background (methanol only).

11. General information for the measurement of cell viability and proliferation

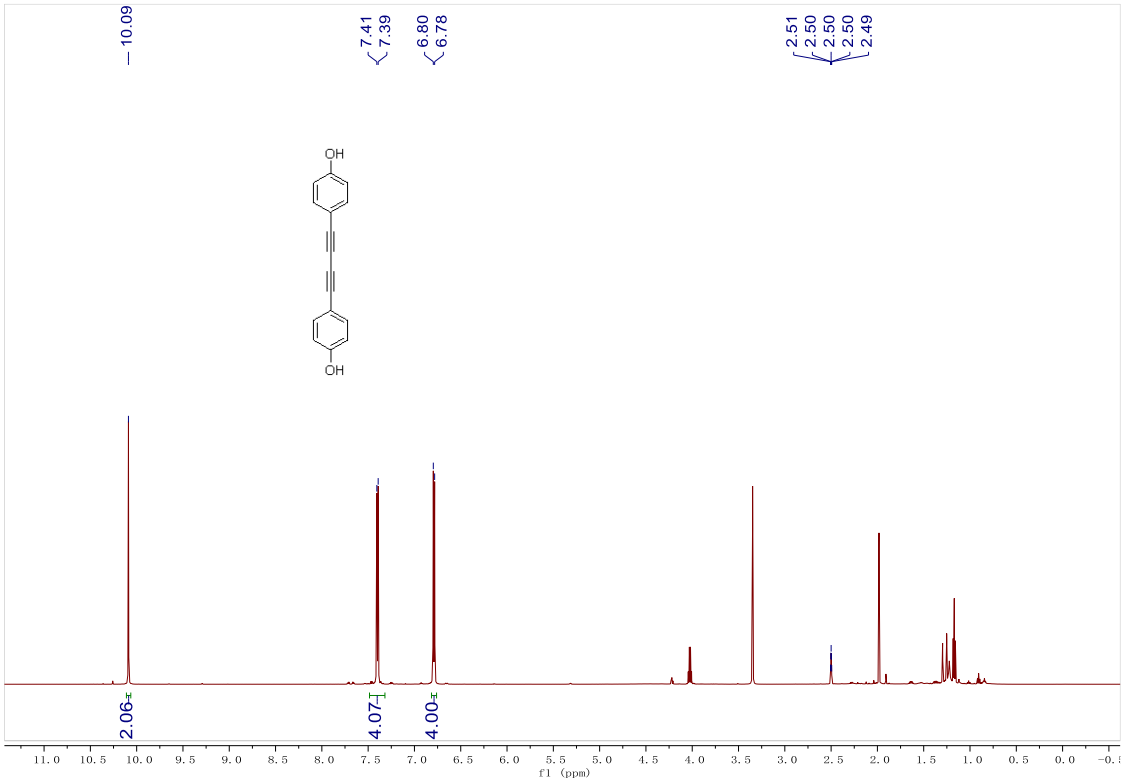
A549 (Lung Carcinoma), K562 (Bone Chronic Myelogenous Leukemia Cml), MDA-MB-231 (breast adenocarcinoma), and HepG2 (Hcuman hepatoellular carcinomas) were all purchased from American Type Culture Collection (ATCC, Manassas, VA, USA). A549 and K562 cells were cultured in RPMl medium modified (Gibco, C11875500BT, USA) medium, MDA-MB-231 and HepG2 cells were cultured in high-glucose DMEM (Gibco, C11995500BT, USA) medium with 10% bovine fetal serum (FBS, Biosera, 010321-UY, Uruguay Origin) and 1% penicillin/streptomycin (Thermo, 15140122, USA) at 37 ℃ in a humidified incubator containing 5% CO_2.

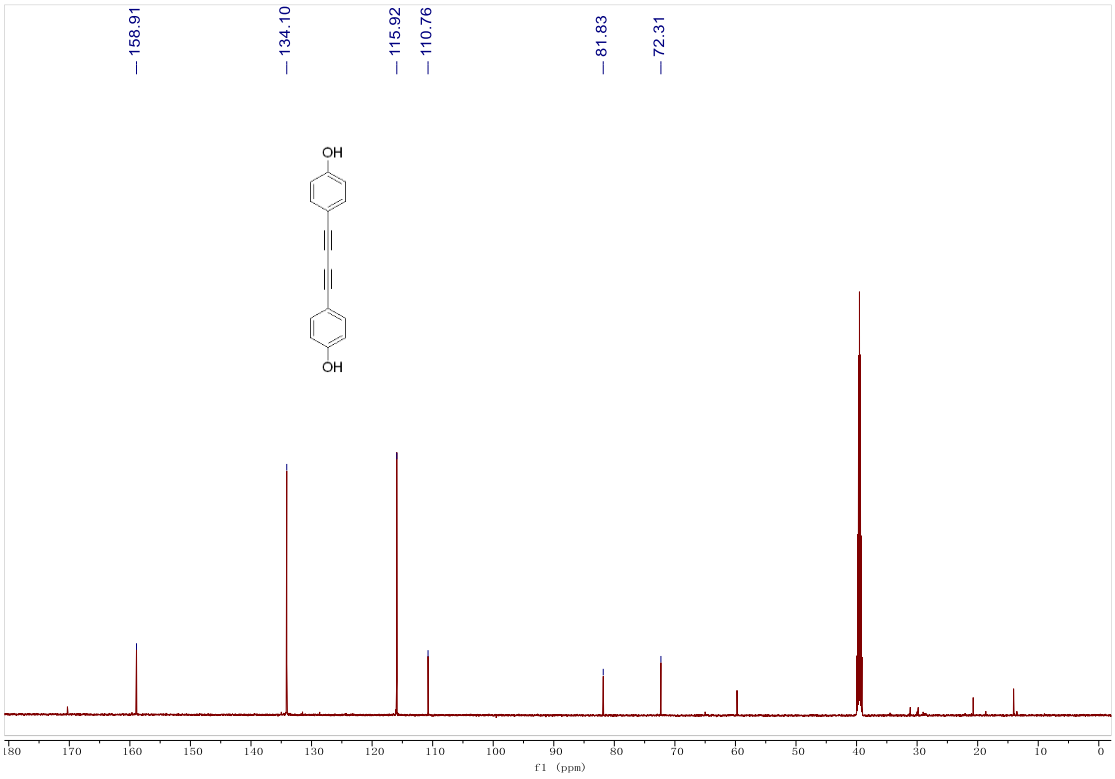
The effects of compounds on the inhibition of cell proliferation were measured by CellTiter-Glo® luminescent cell viability assay (Promega, G7572, USA). Briefly, cancer cells were seeded on the 96 well-plates at a density of 1×103 cells per well with 200 μL complete medium. Then, cells were treated with compounds at a concentration of 40 μM for 72 h after incubating for 12-16 h. After that, 100 μL of the medium was removed, and each well was added 40 μL CellTiter-Glo® reagent. The 96 well-plates were then placed on an oscillator with gentle shaking to mix for 2 min and incubated

for 10 min at room temperature.The chemiluminescent signals were detected using a multimode plate reader (EnSight™, PerkinElmer, USA).The luminescence value of the control wells was used as 100%, and the luminescence values of all compounds were calculated by GraphPad Prism 9, and the experiments were repeated three times.

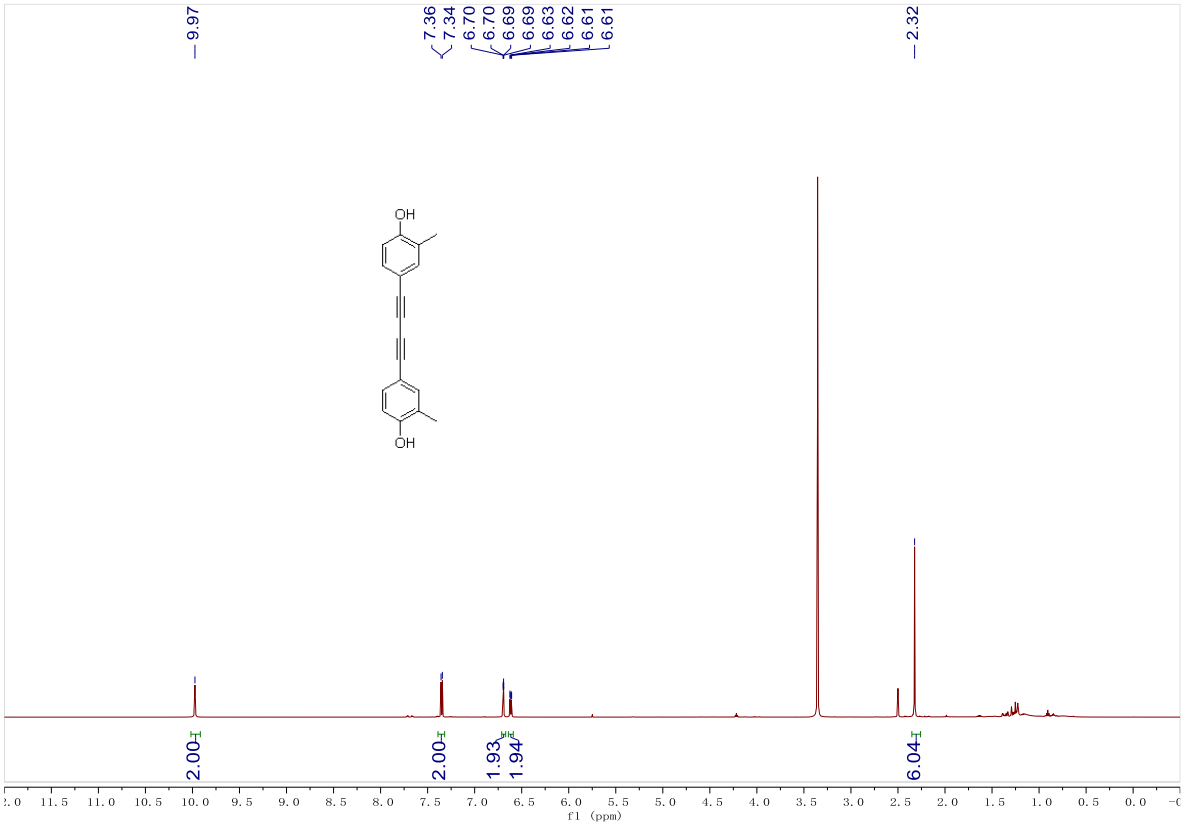
12. Copies of NMR spectra（symmetrical 1,3-diynes 2）

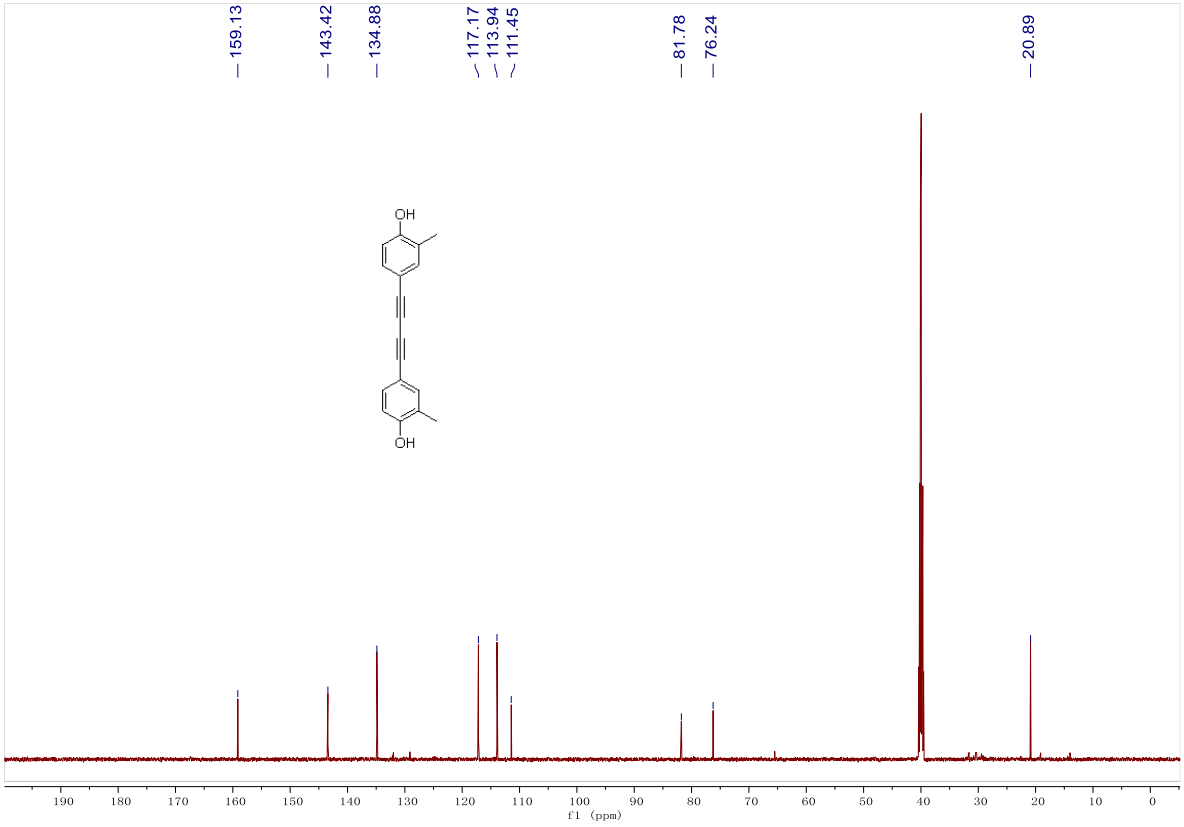
^{1}H and ^{13}C NMR spectra of compound **(2a)**



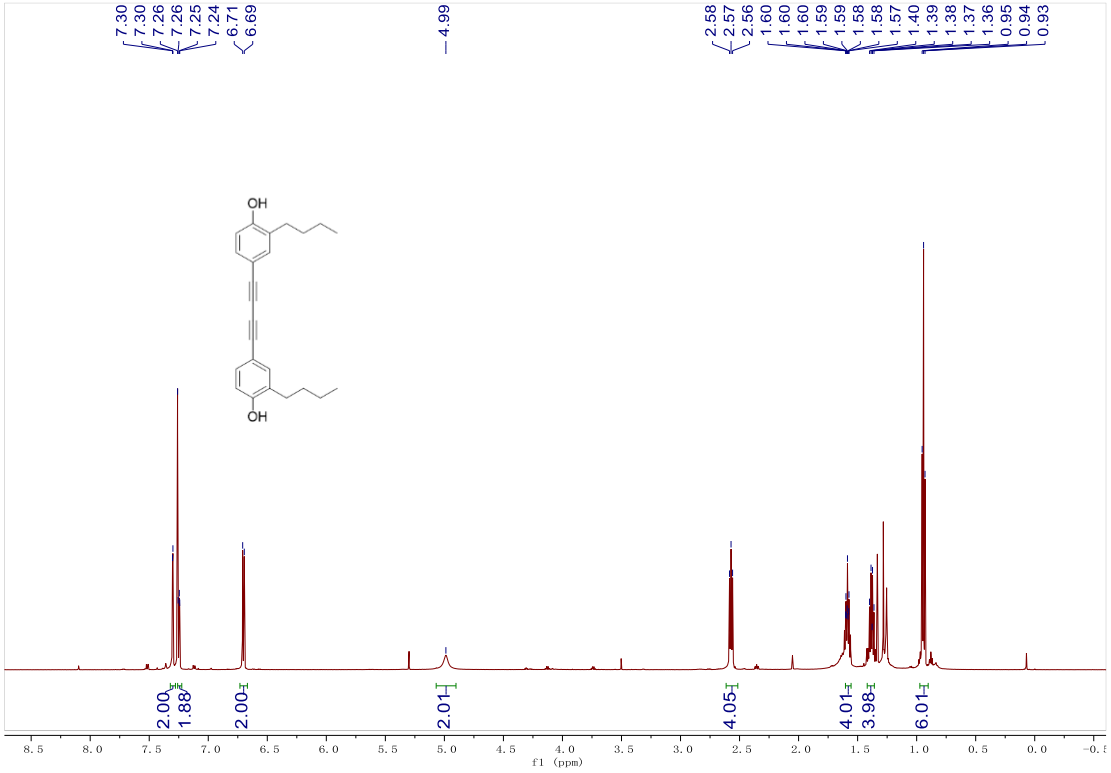


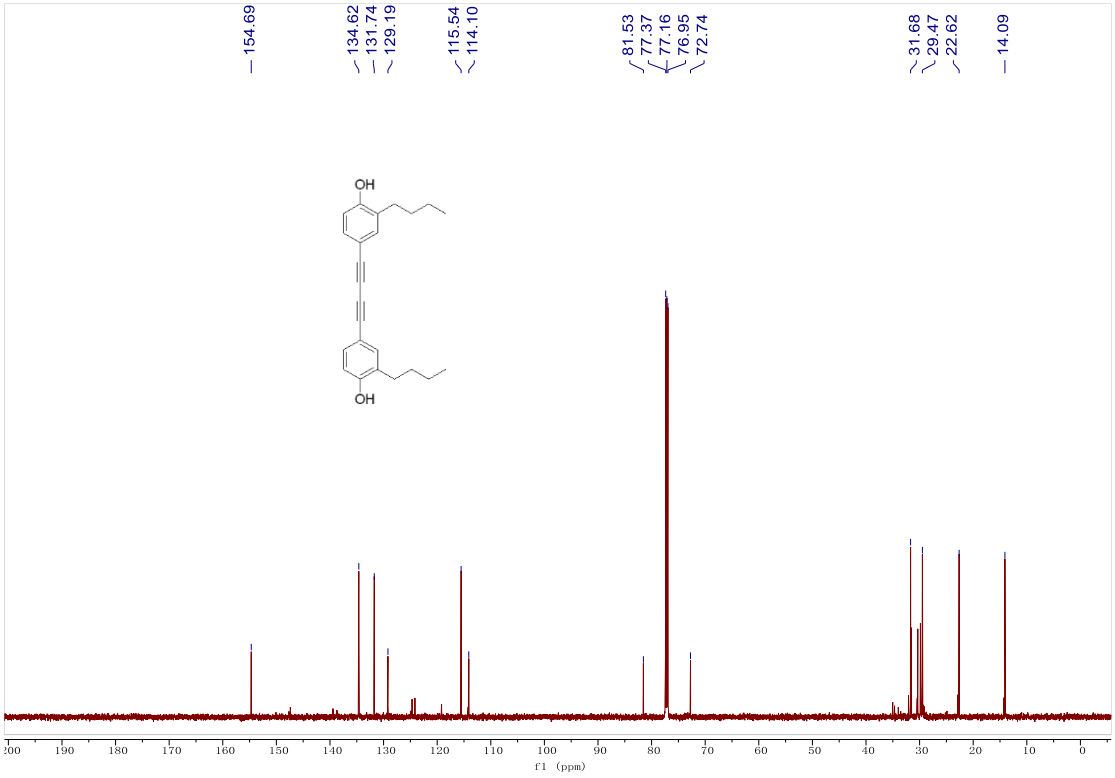
^{1}H and ^{13}C NMR spectra of compound **(2b)**



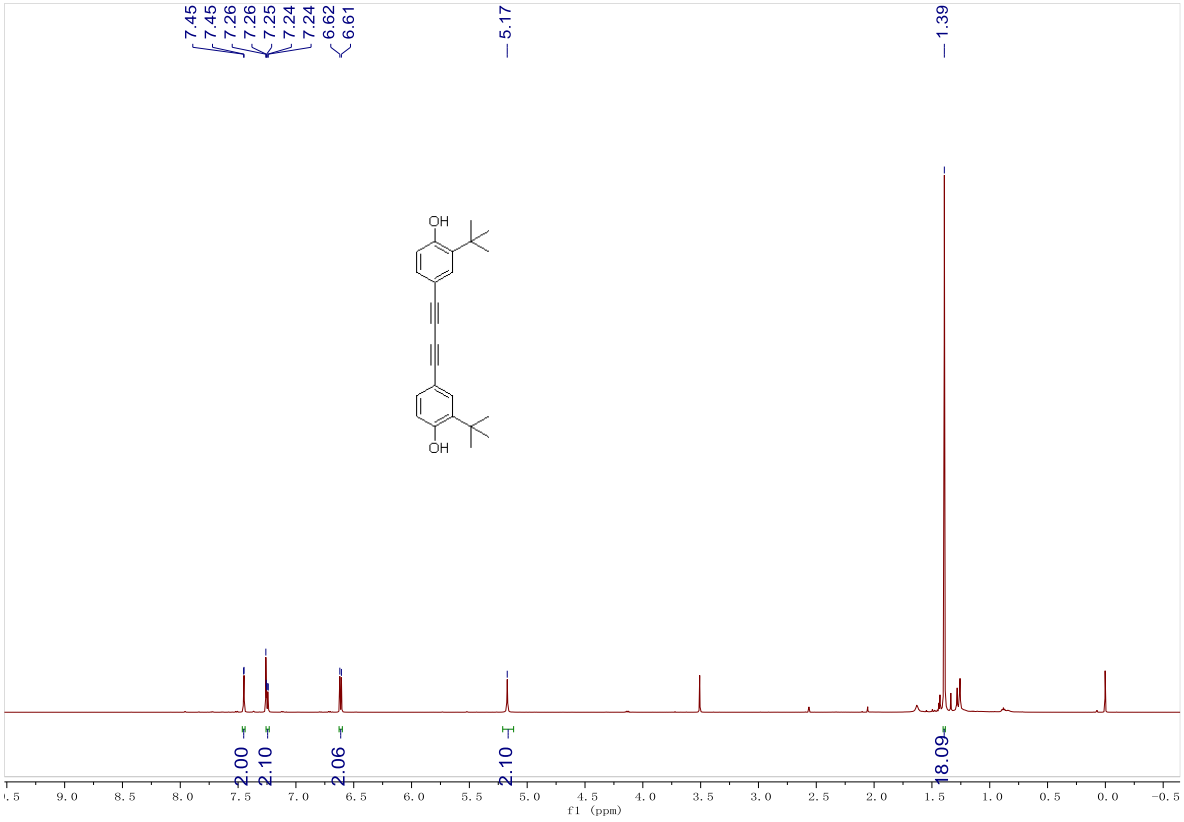


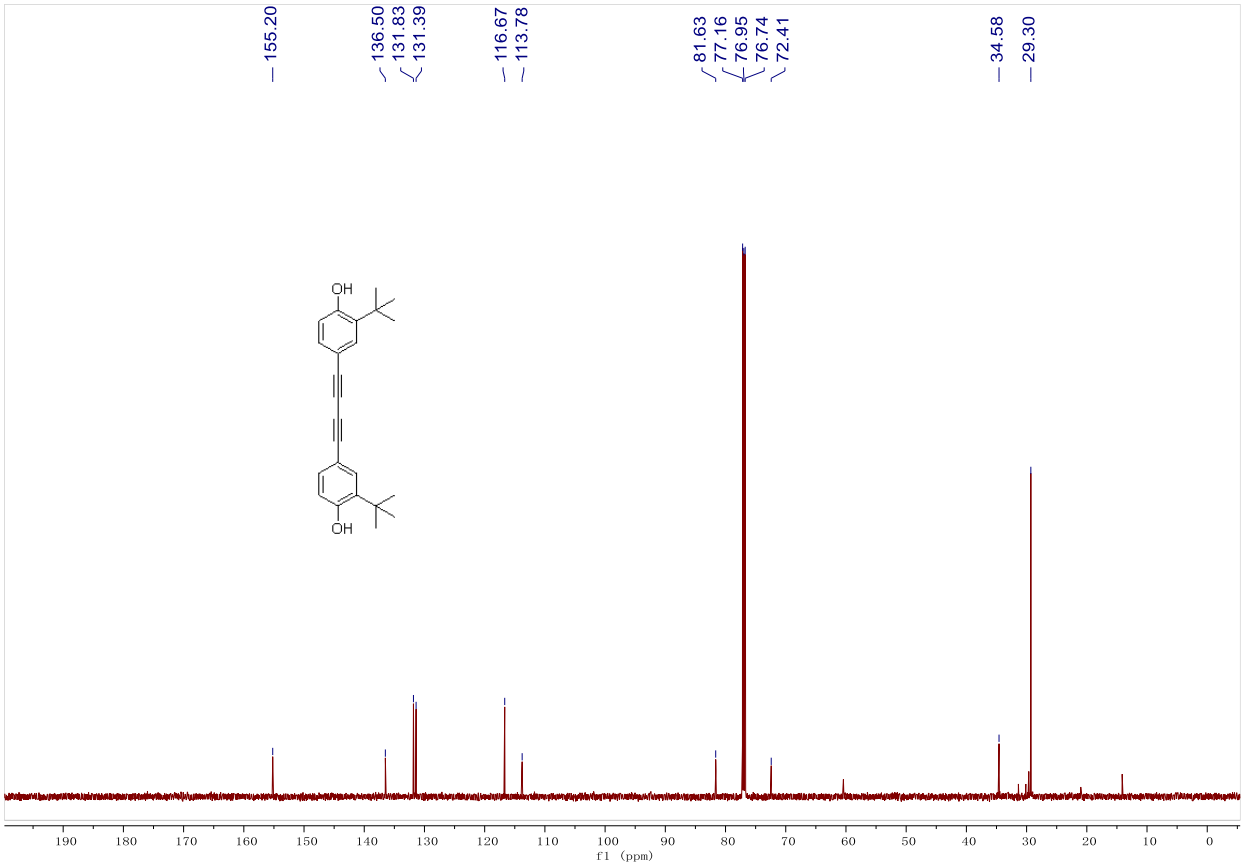
^{1}H and ^{13}C NMR spectra of compound **(2c)**



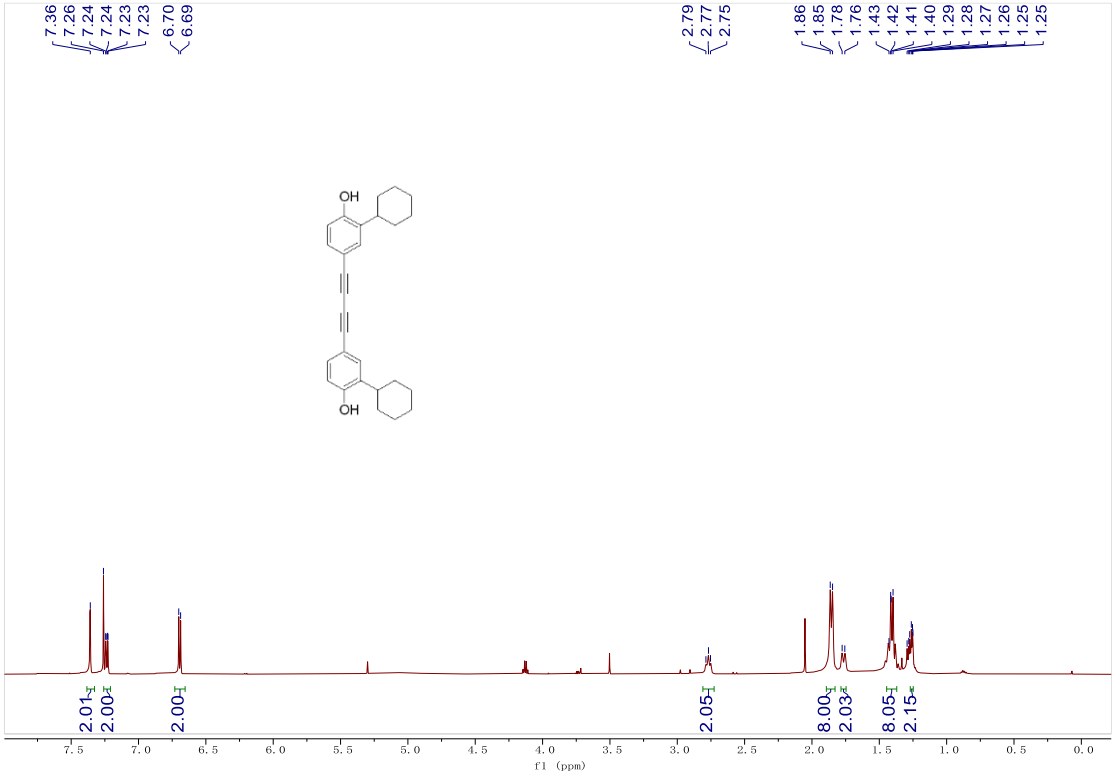


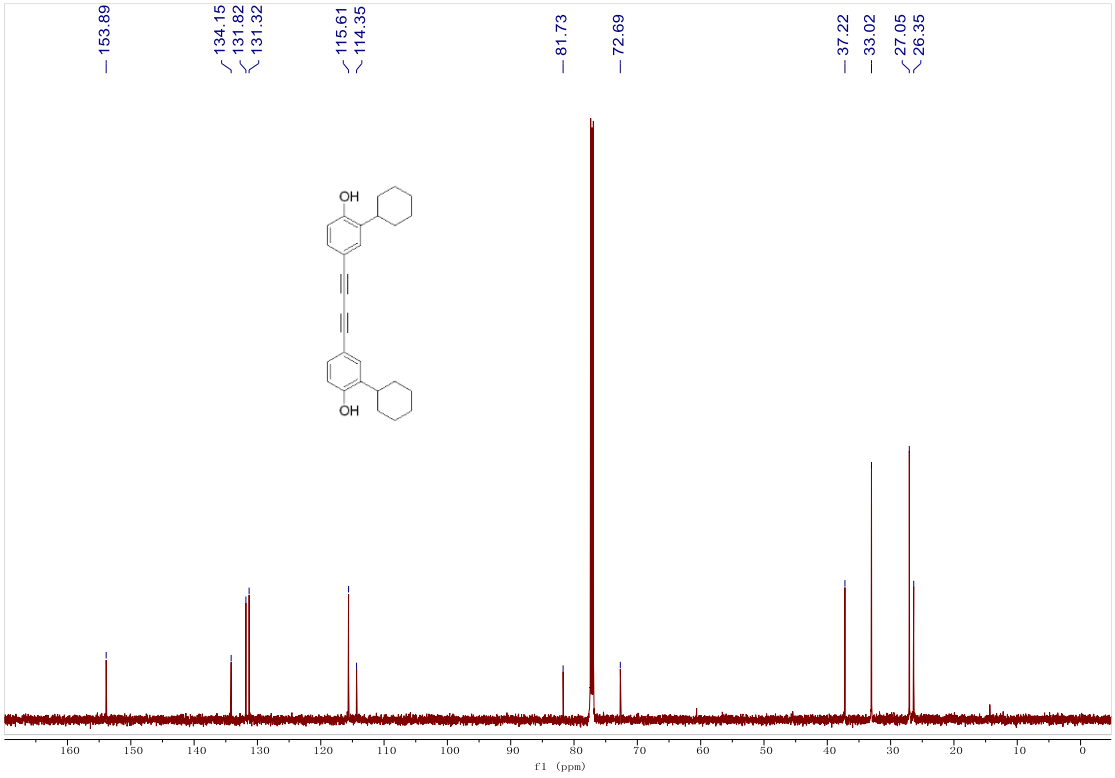
^{1}H and ^{13}C NMR spectra of compound **(2d)**



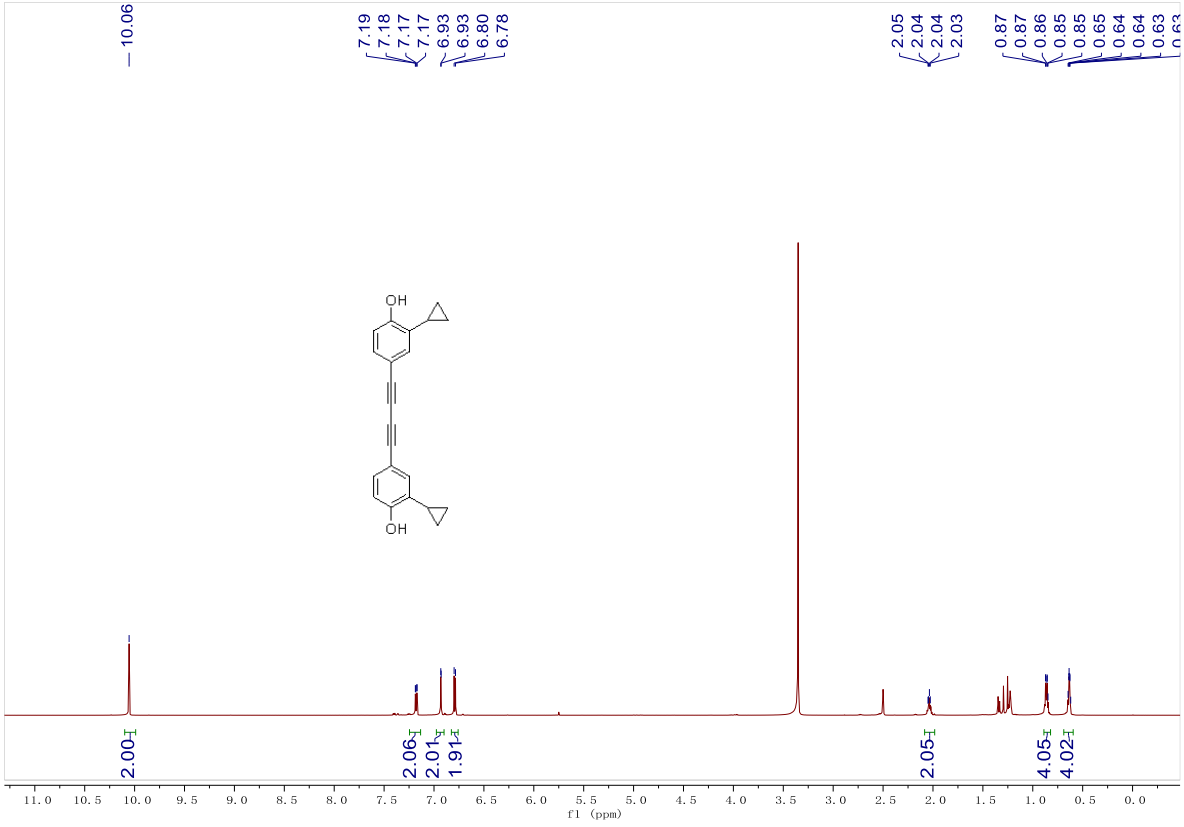


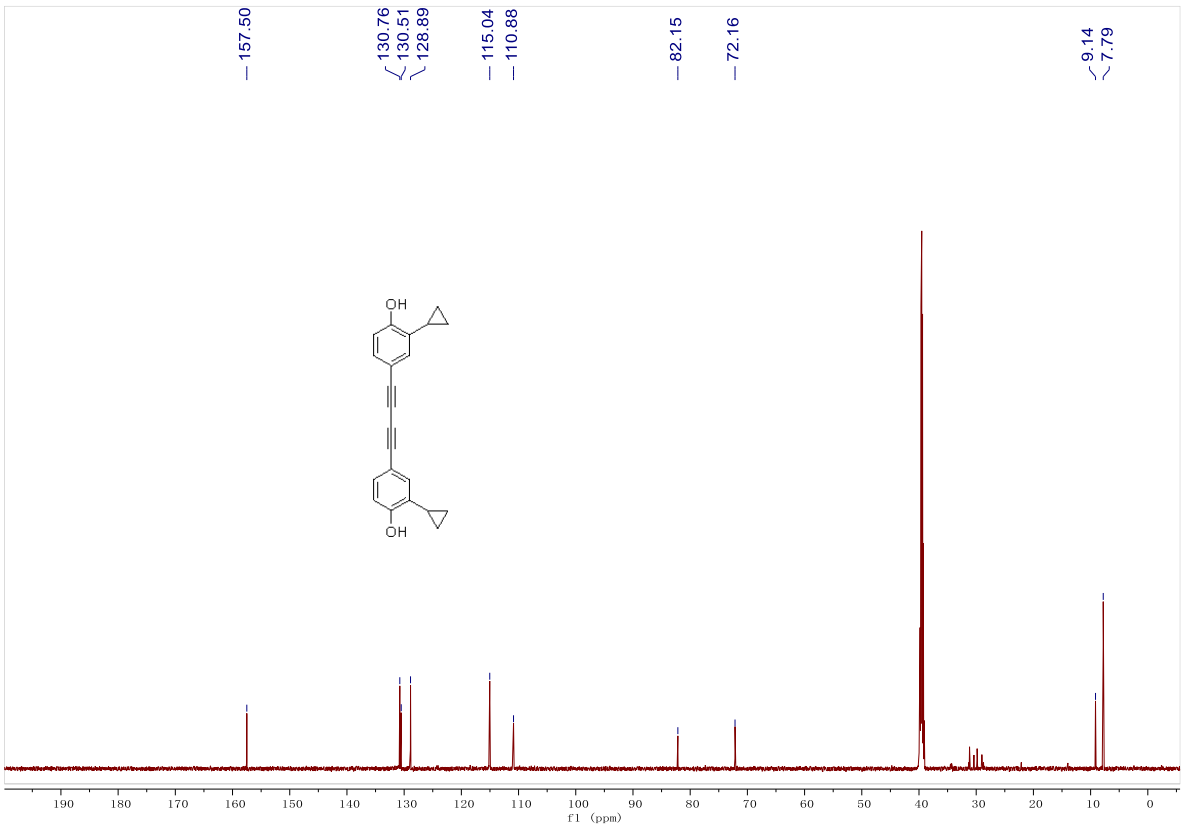
^{1}H and ^{13}C NMR spectra of compound **(2e)**



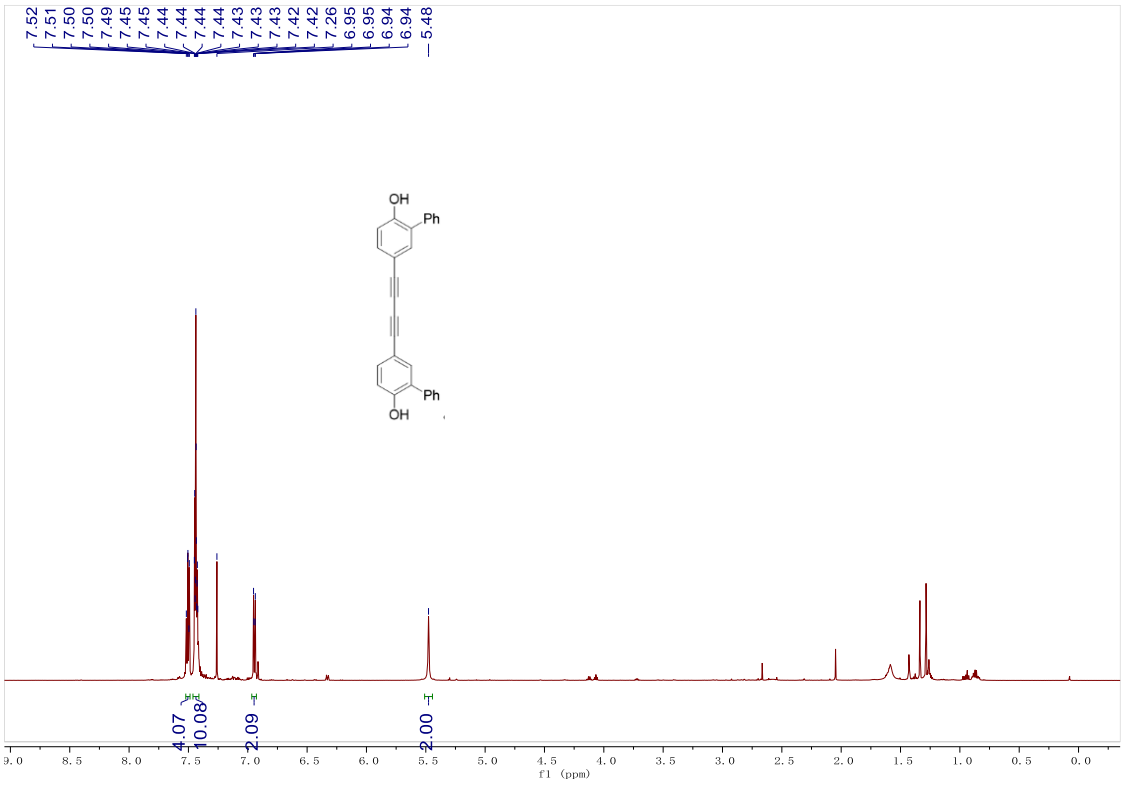


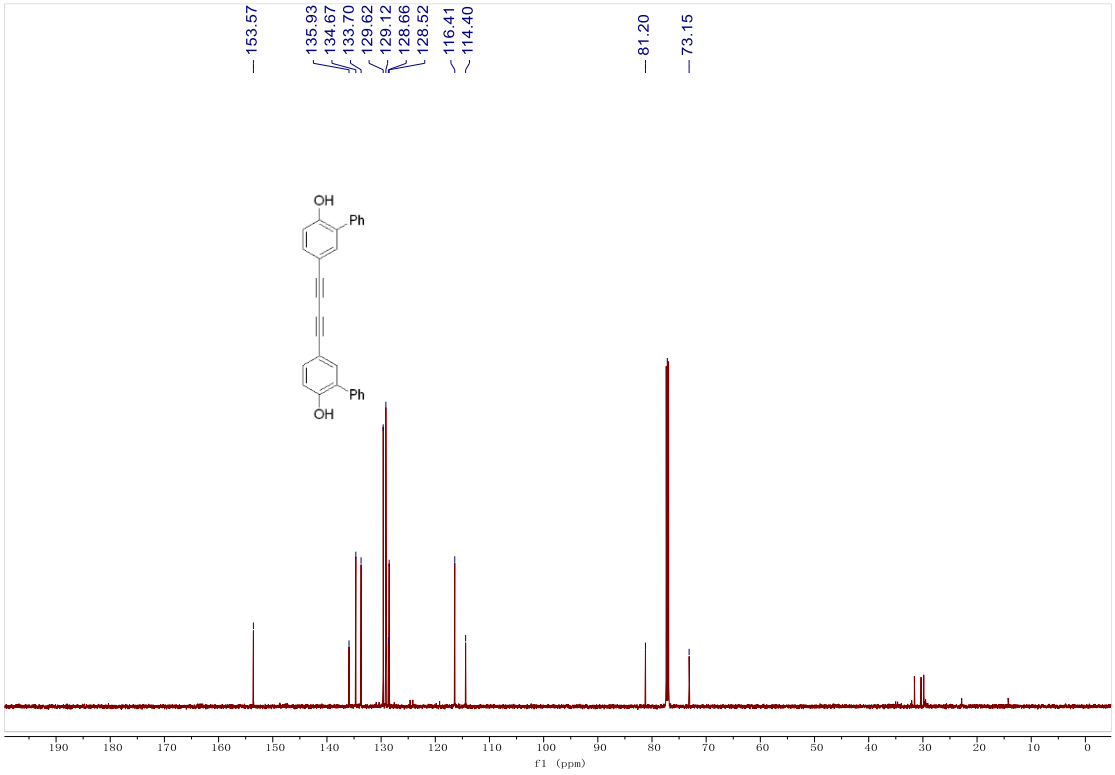
^{1}H and ^{13}C NMR spectra of compound **(2f)**



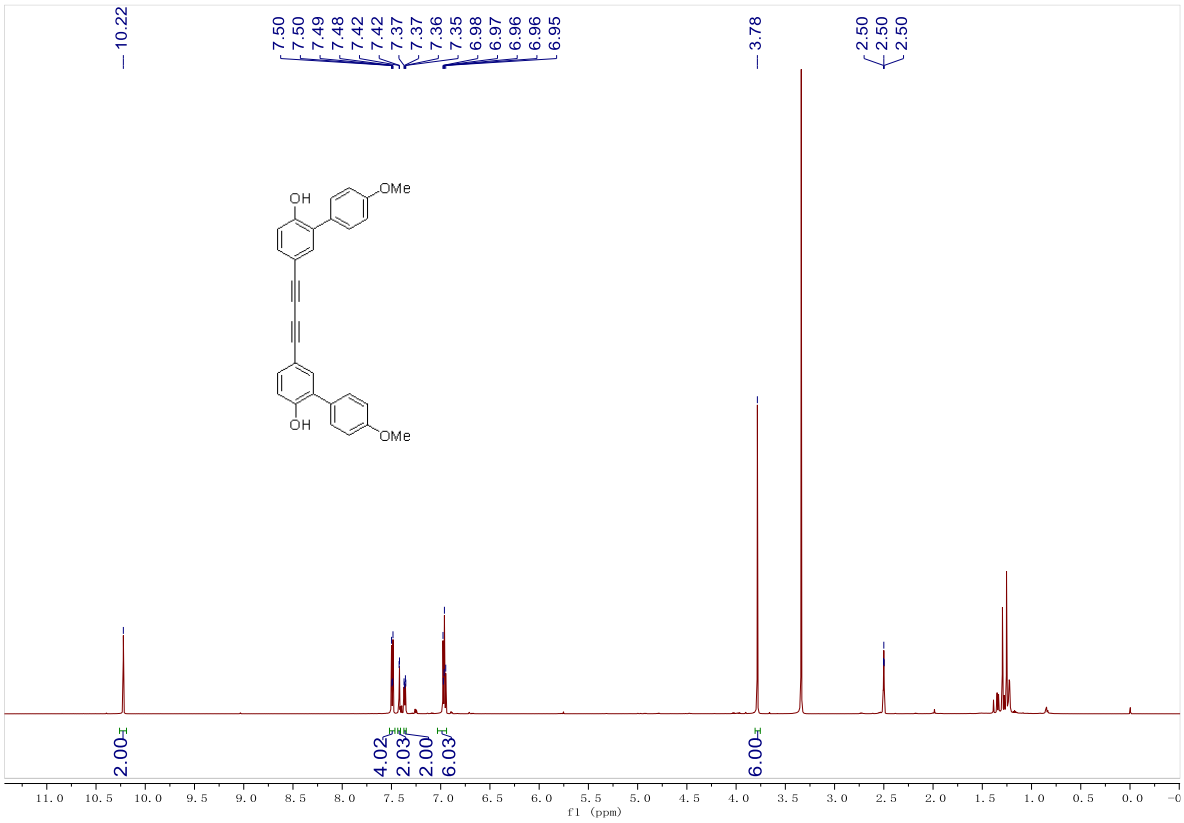


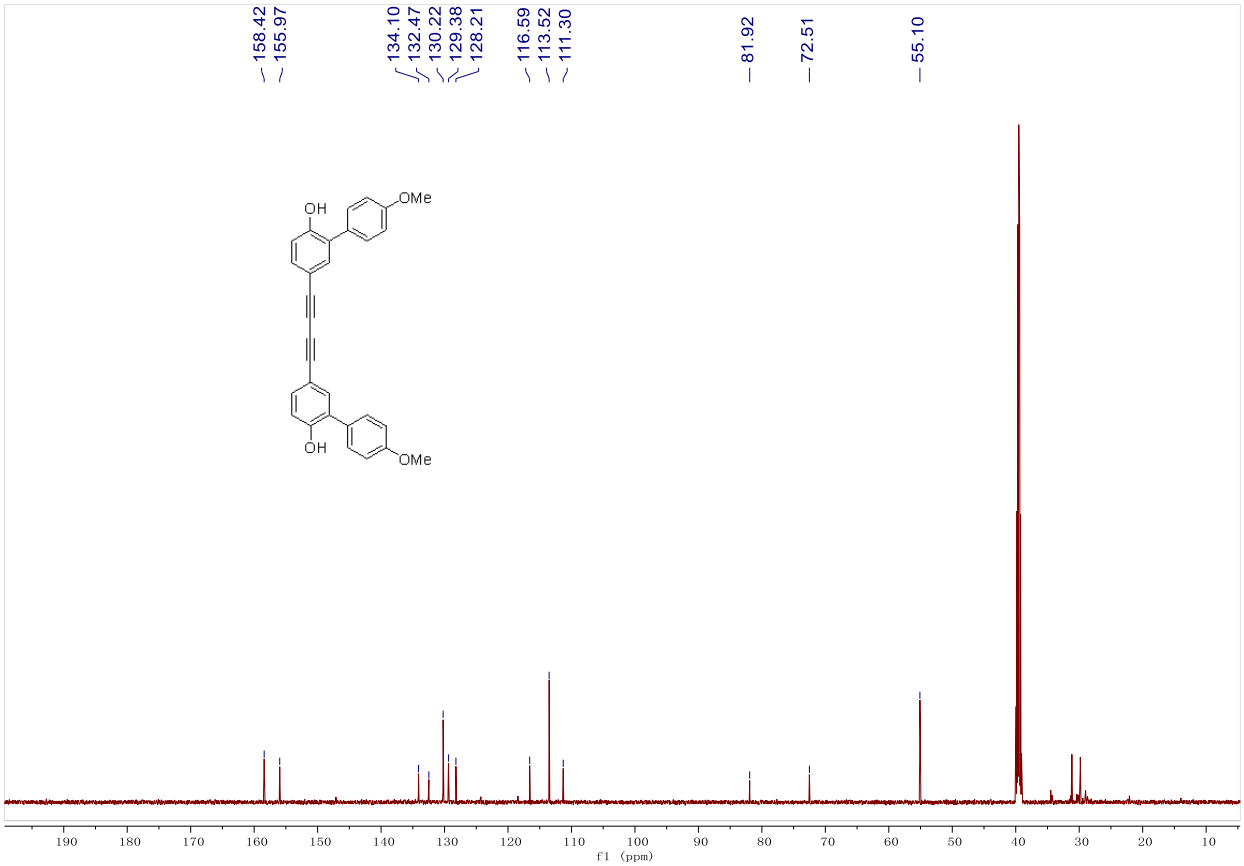
^{1}H and ^{13}C NMR spectra of compound **(2g)**



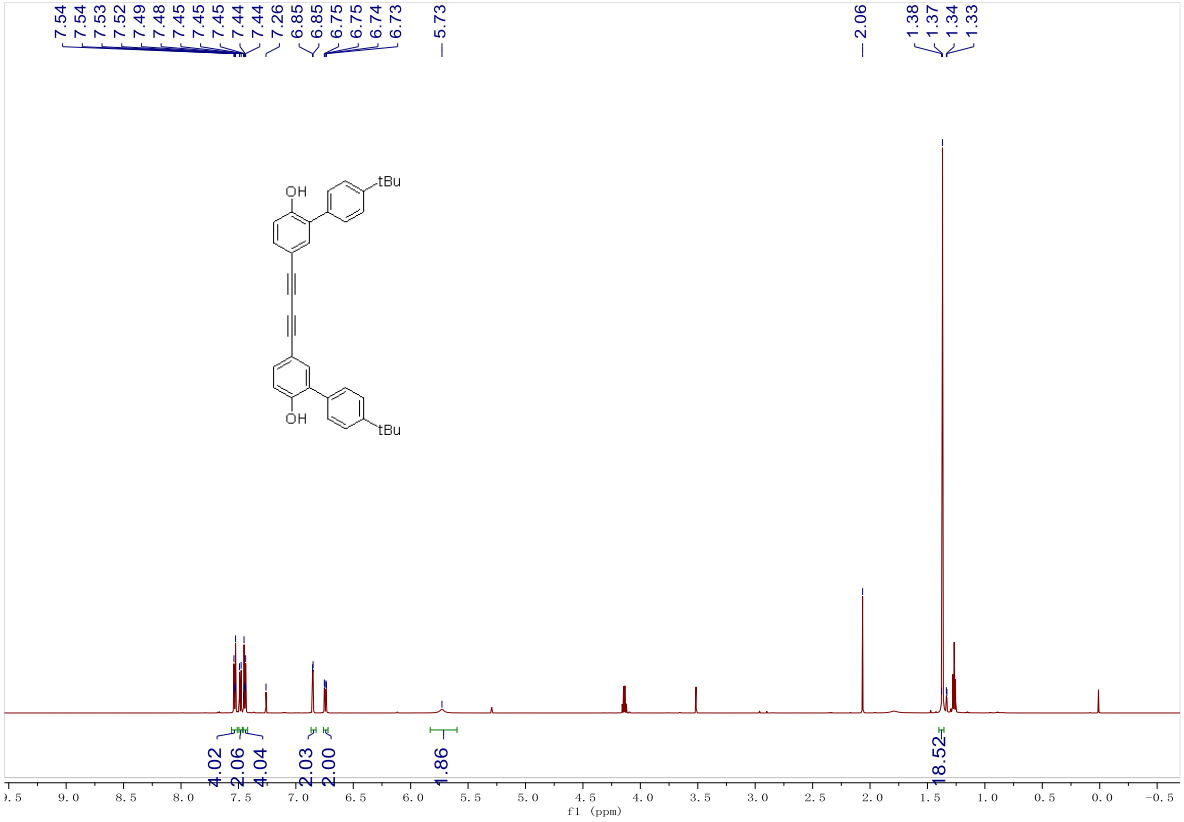


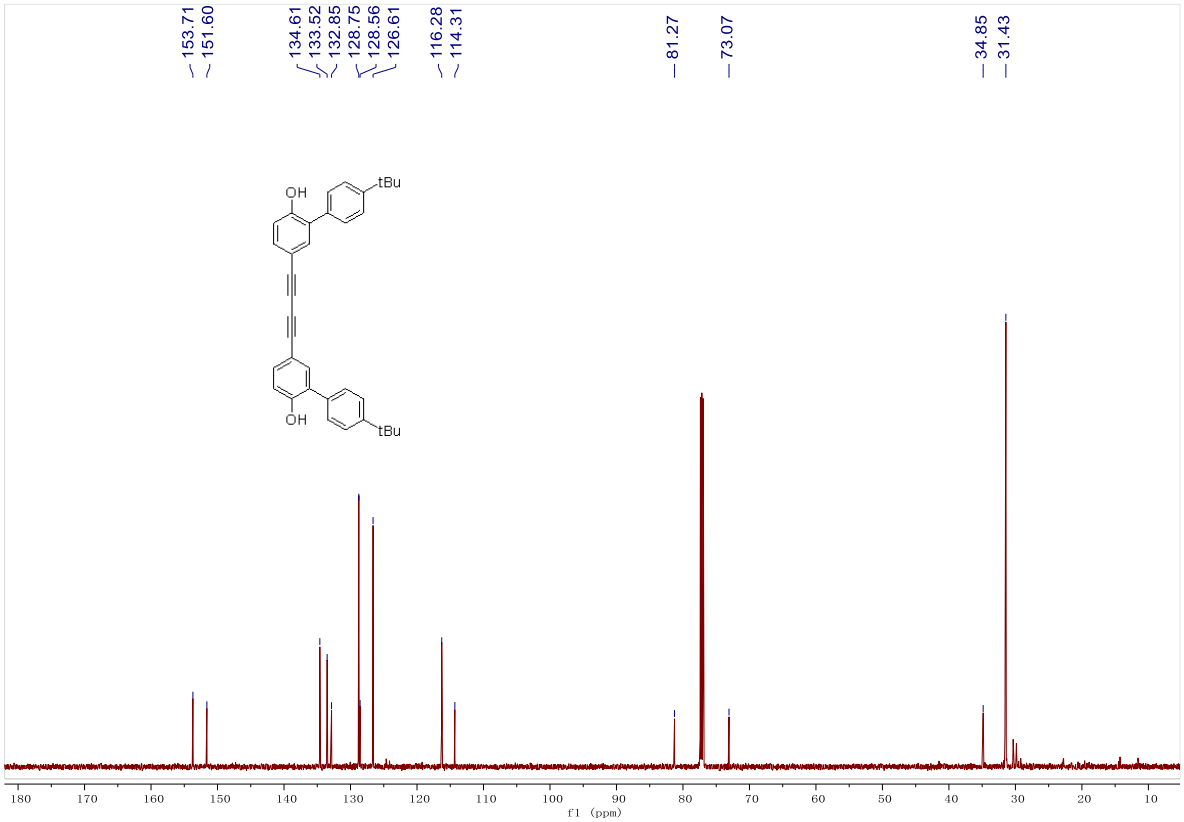
^{1}H and ^{13}C NMR spectra of compound **(2h)**



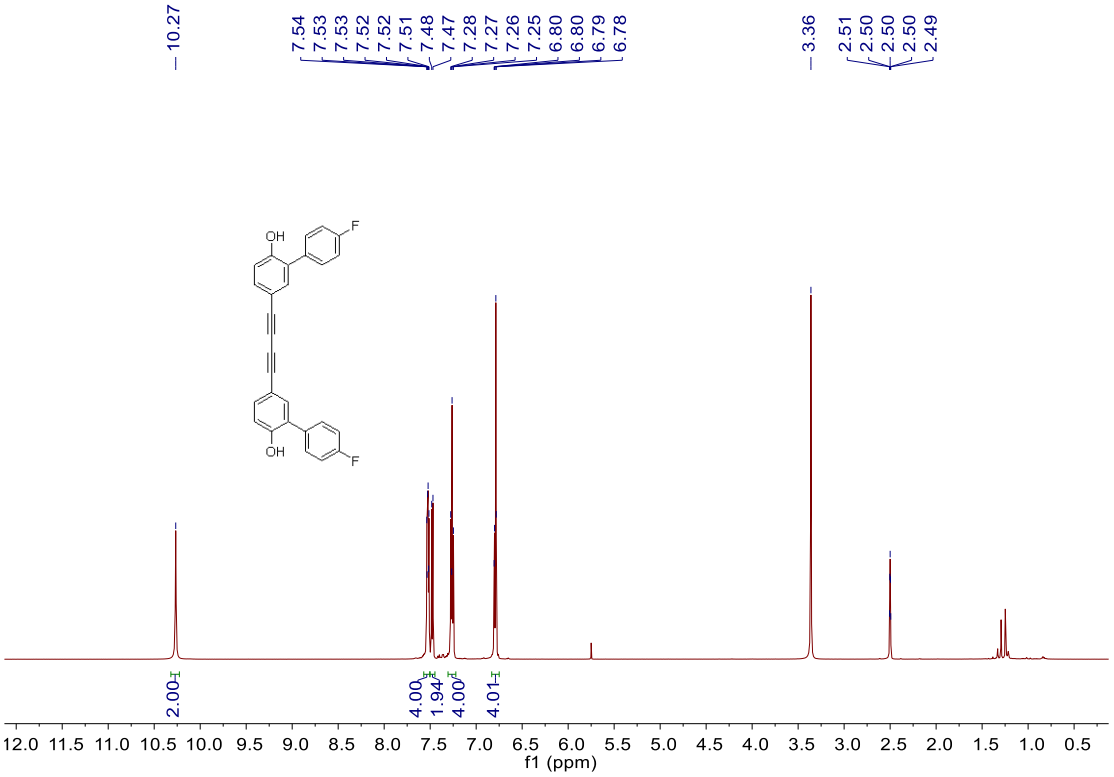


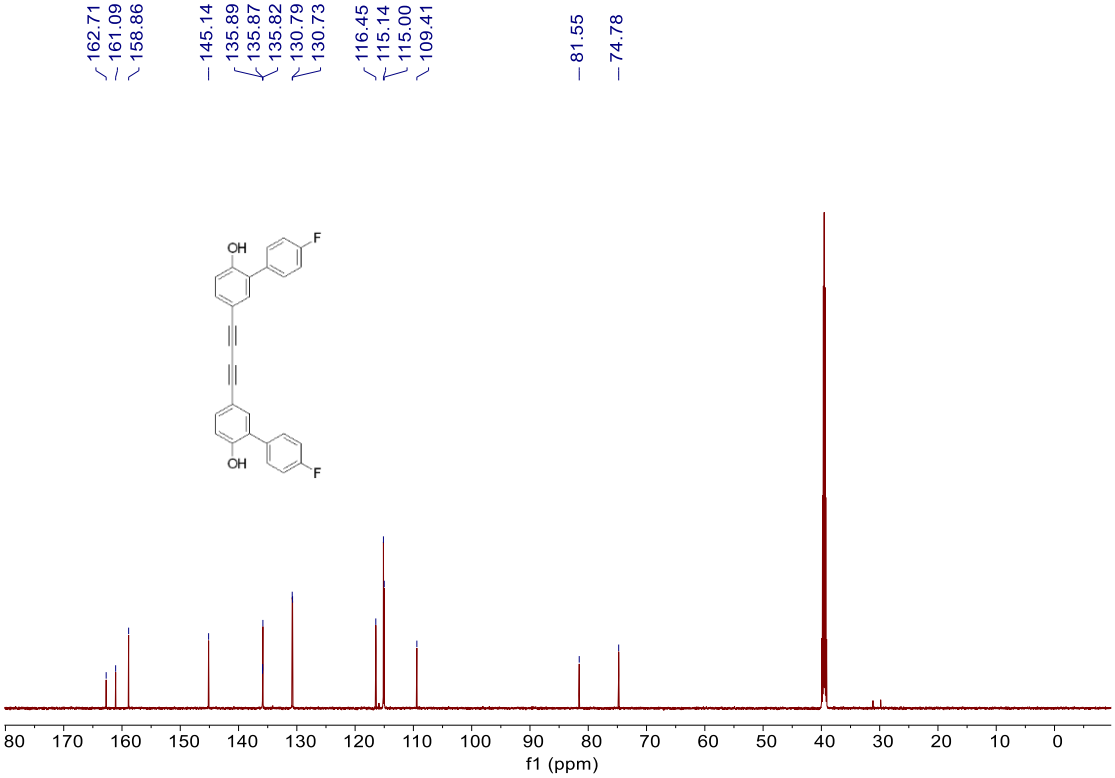
^{1}H and ^{13}C NMR spectra of compound **(2i)**



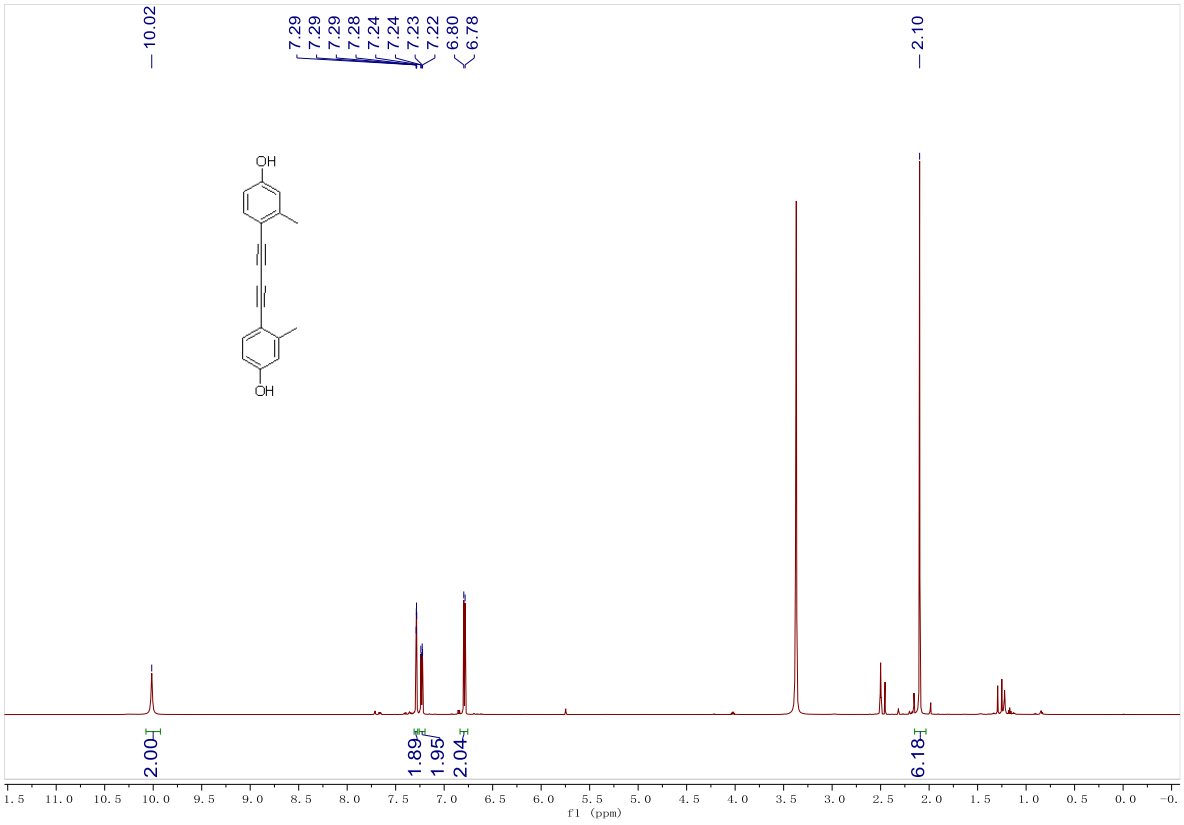


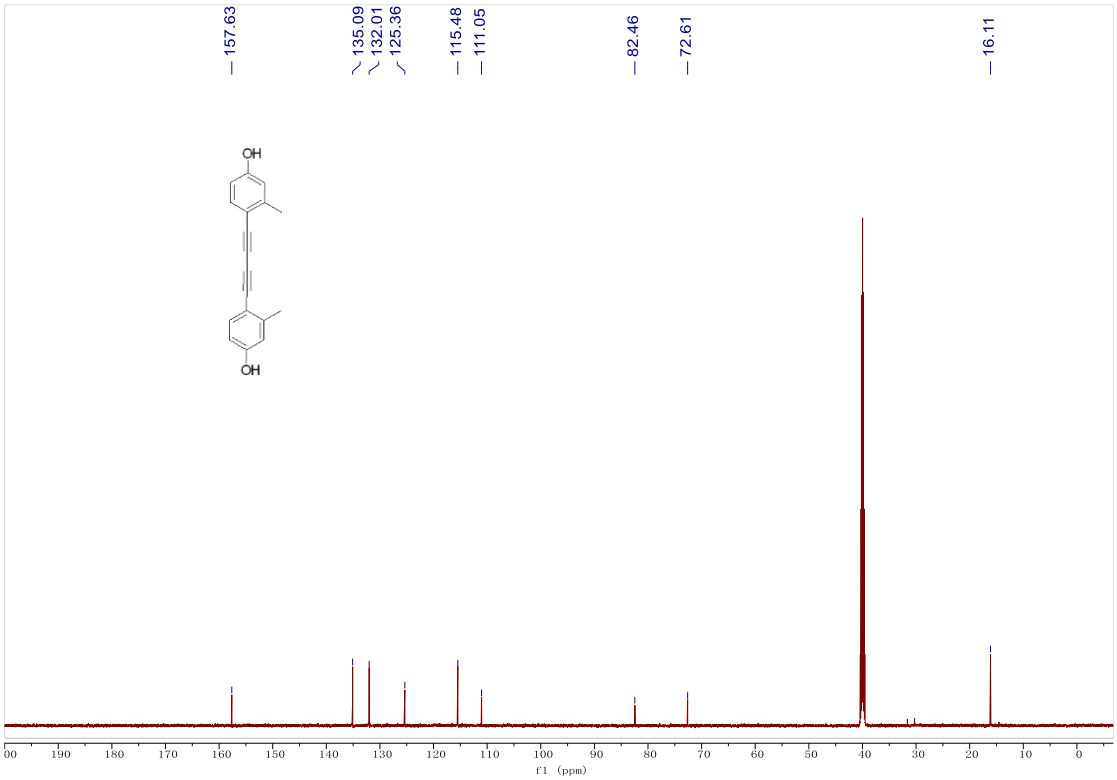
^{1}H and ^{13}C NMR spectra of compound **(2j)**



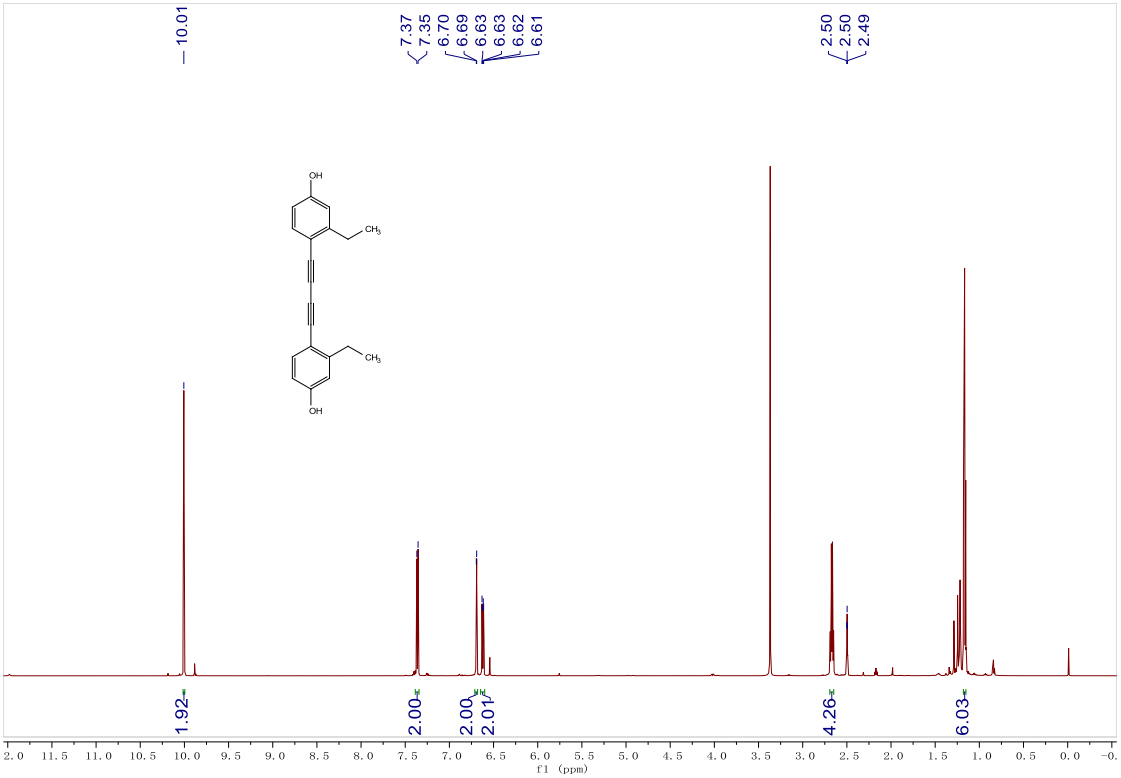


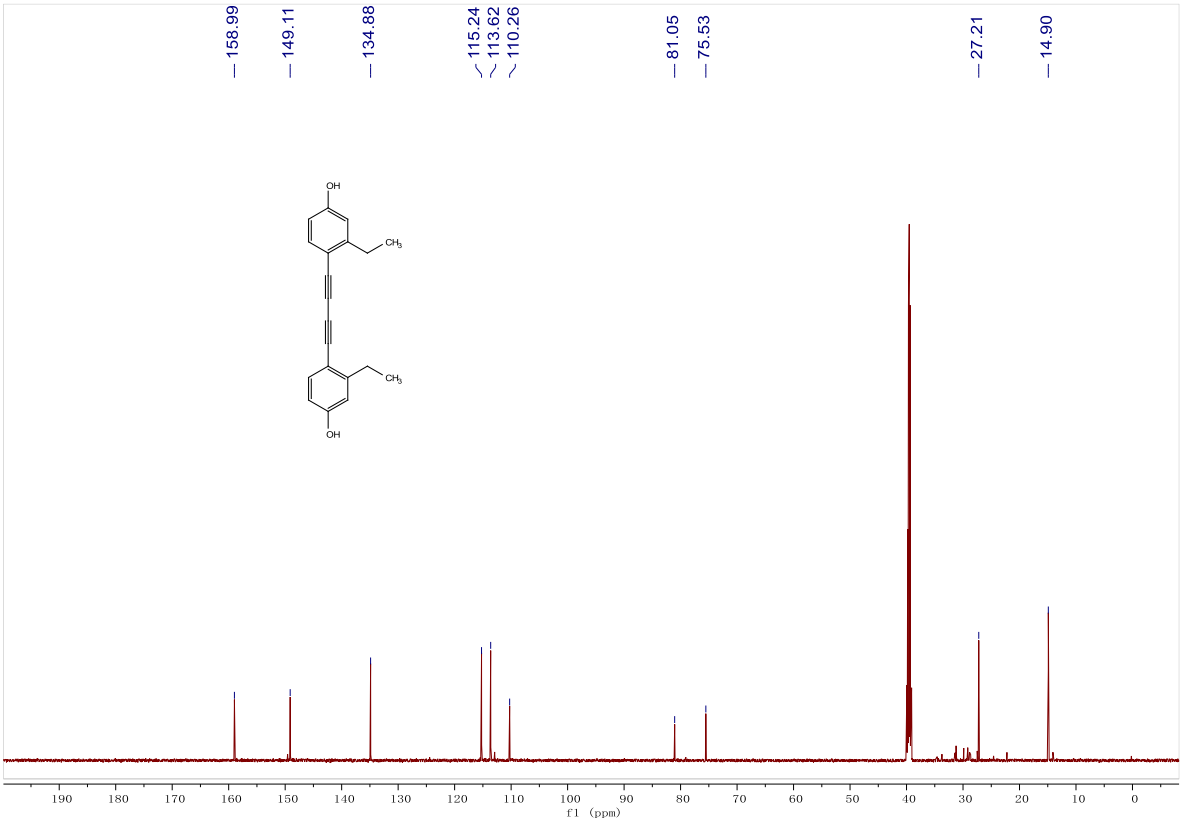
^{1}H and ^{13}C NMR spectra of compound **(2k)**



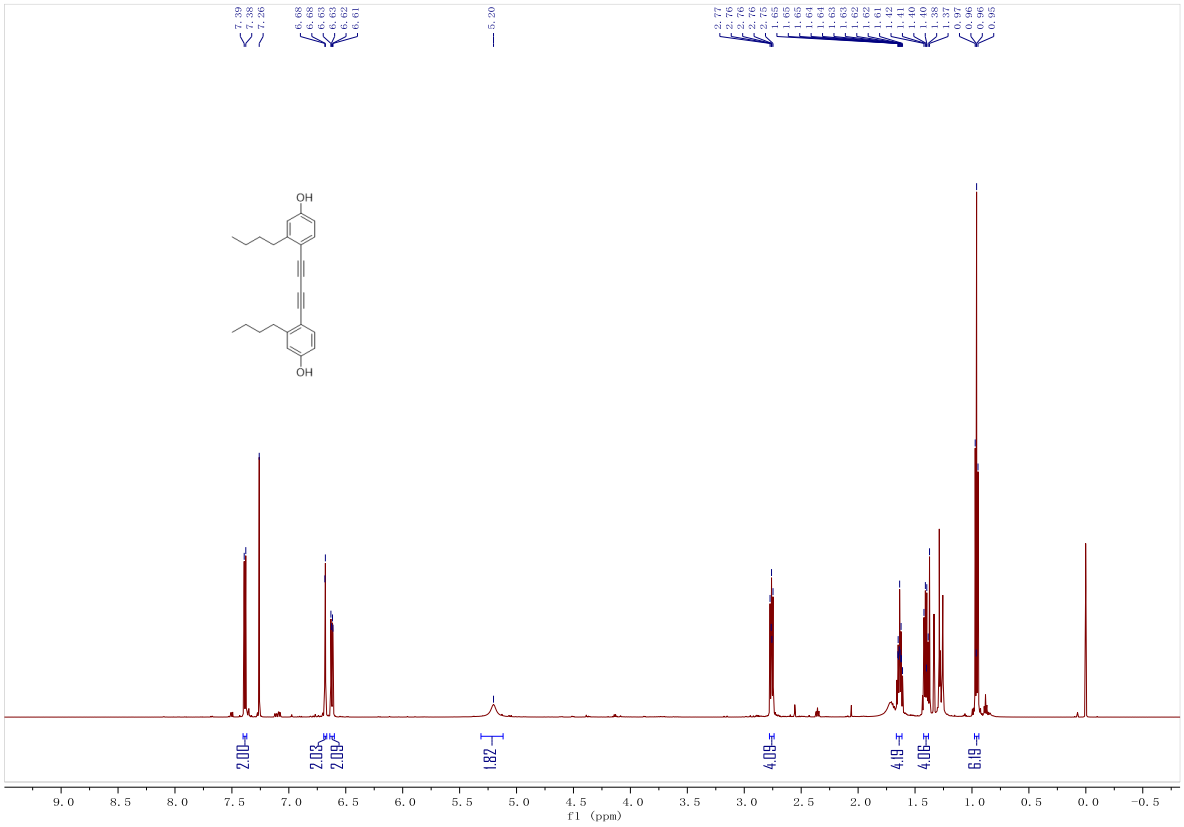


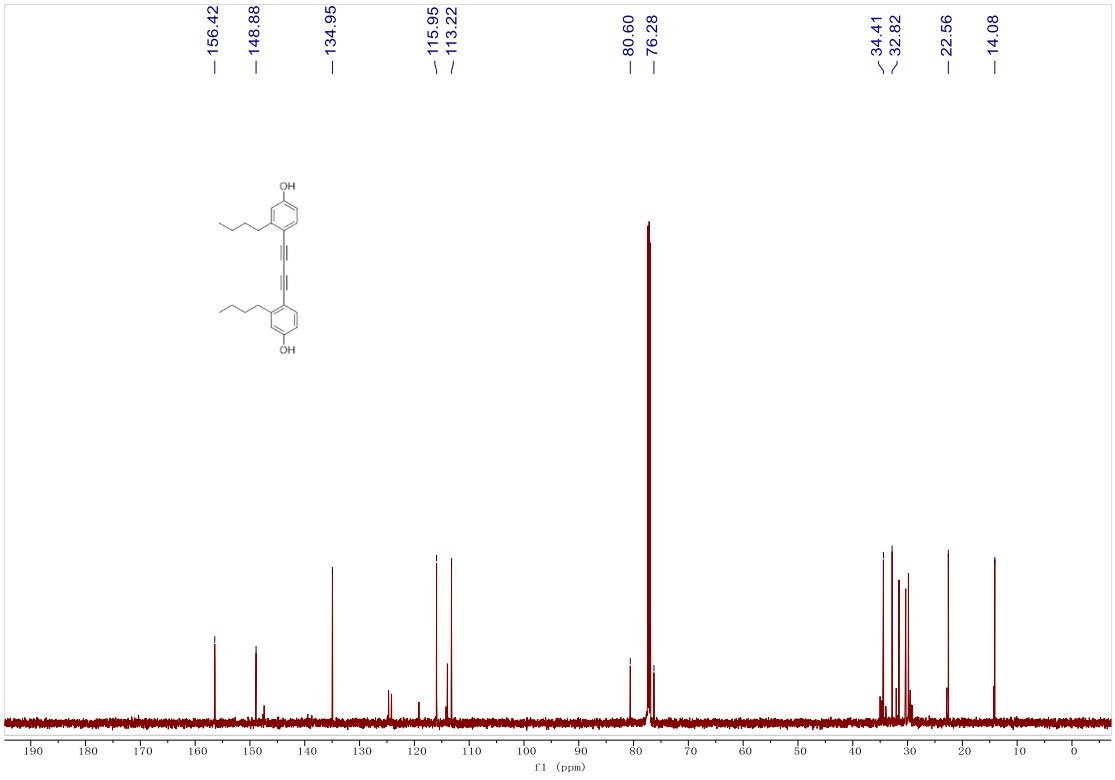
^{1}H and ^{13}C NMR spectra of compound **(2l)**



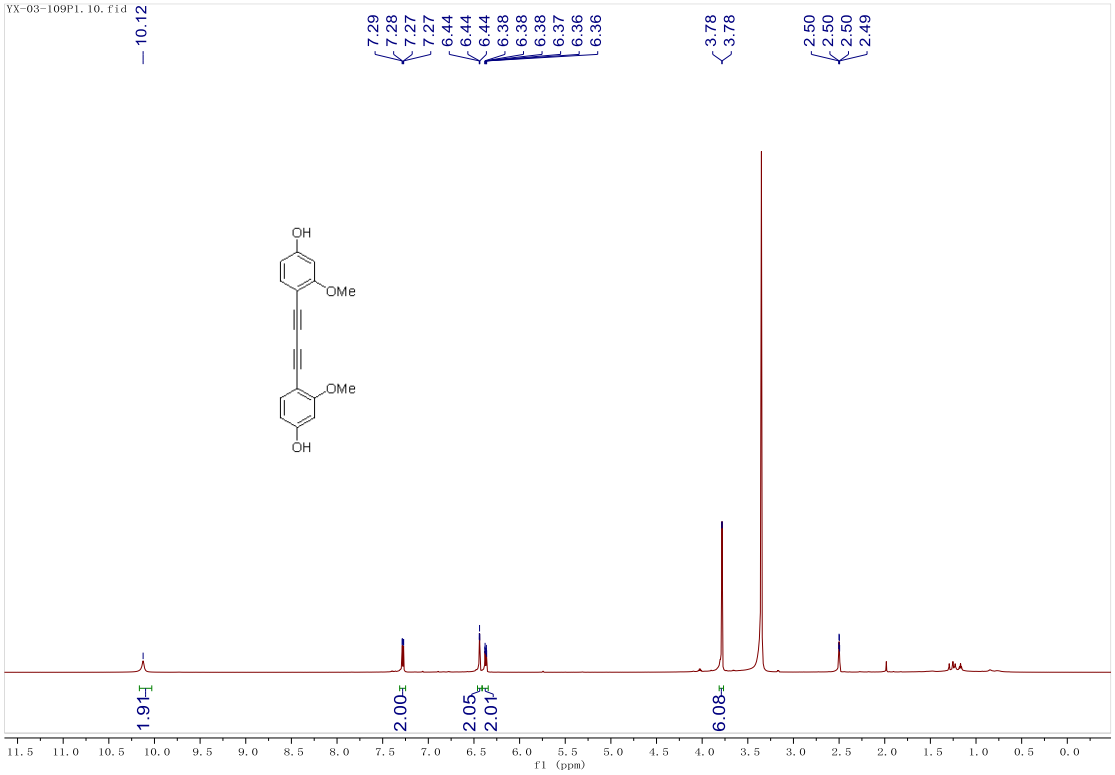


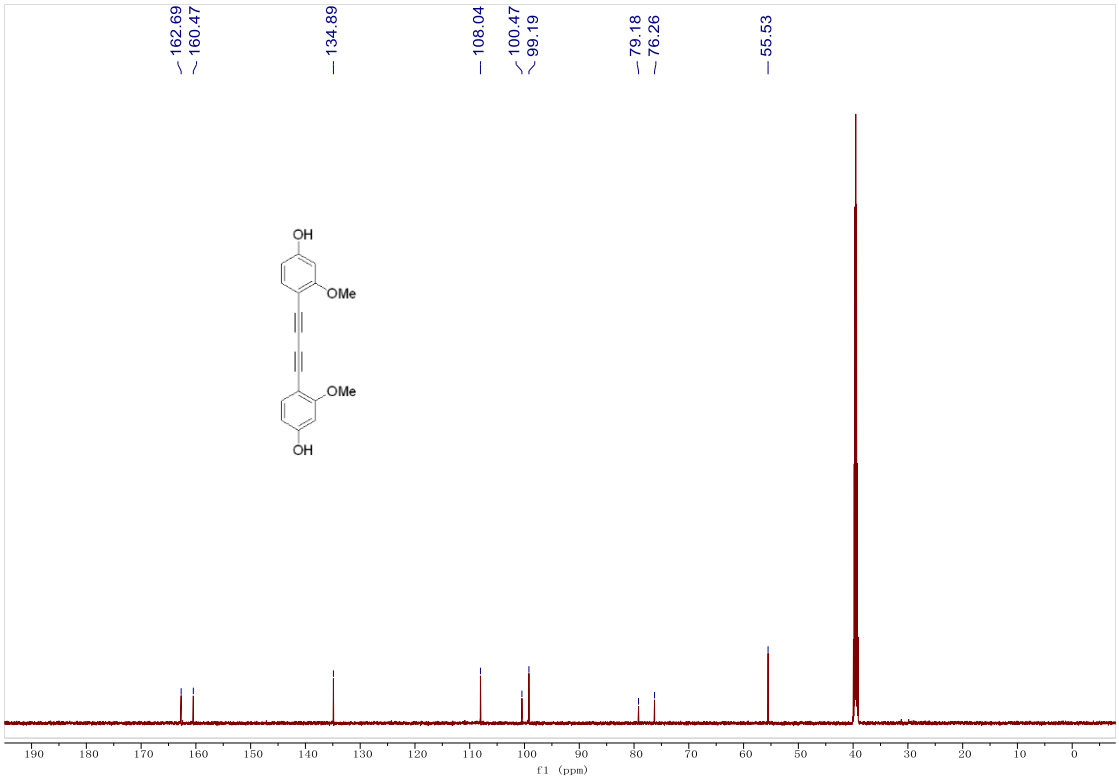
^{1}H and ^{13}C NMR spectra of compound **(2m)**



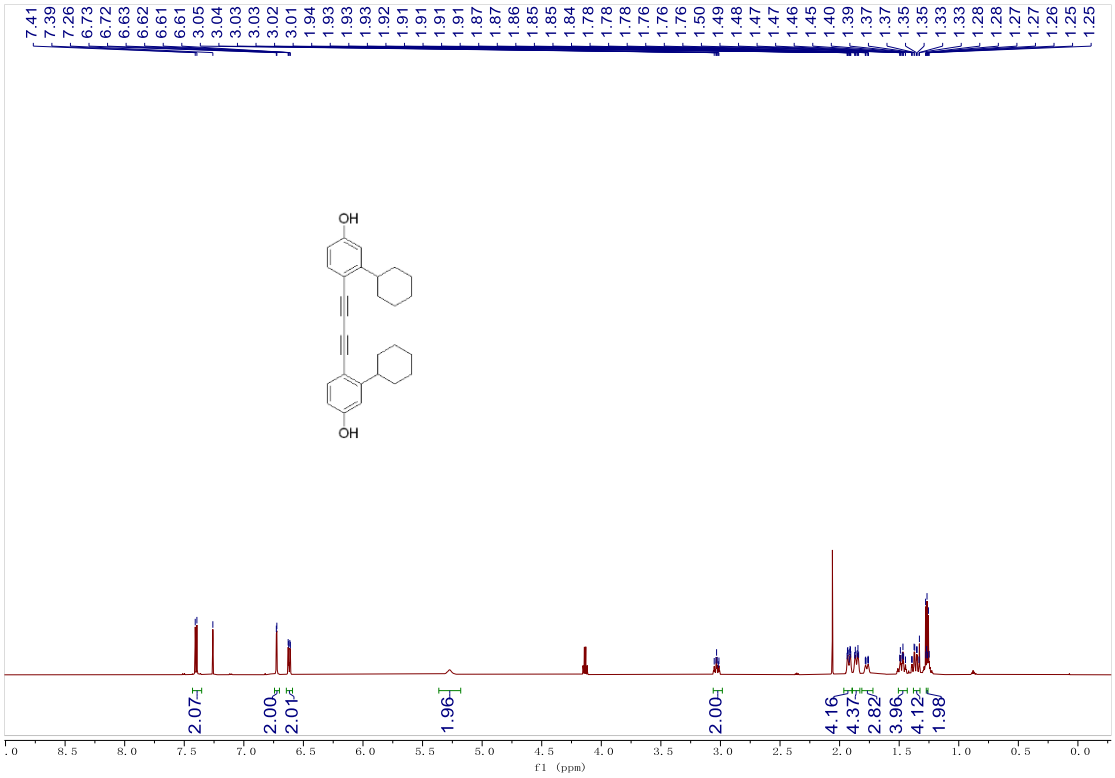


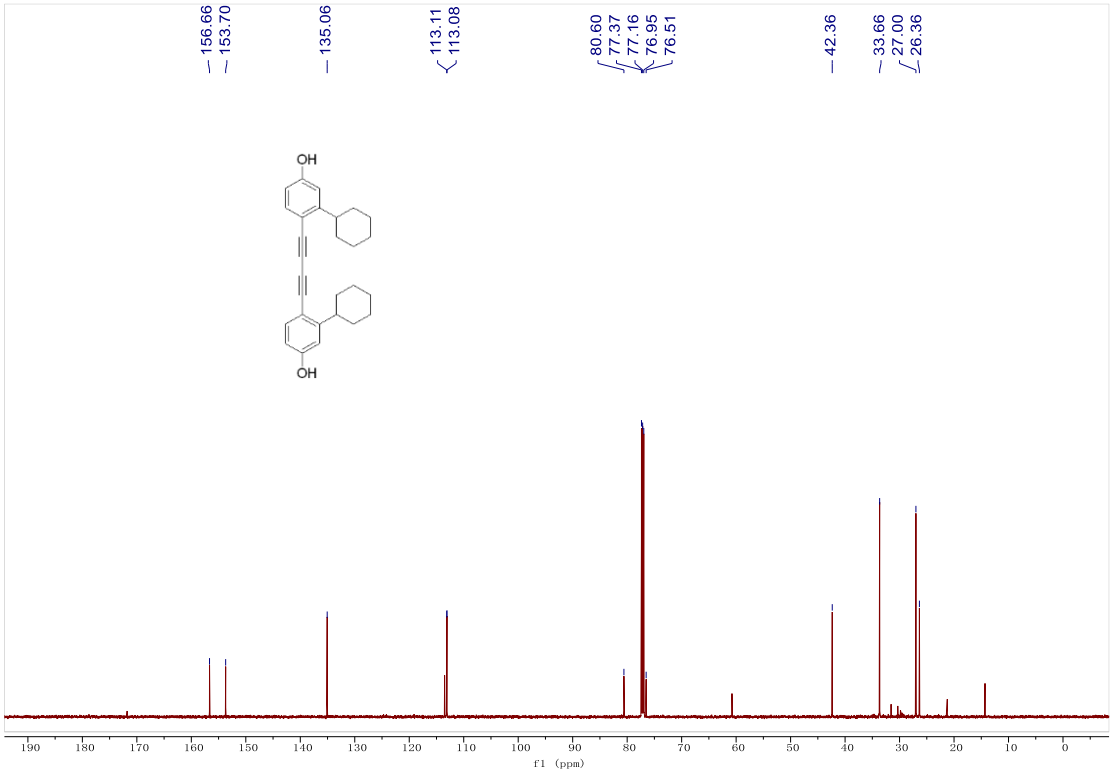
^{1}H and ^{13}C NMR spectra of compound **(2n)**



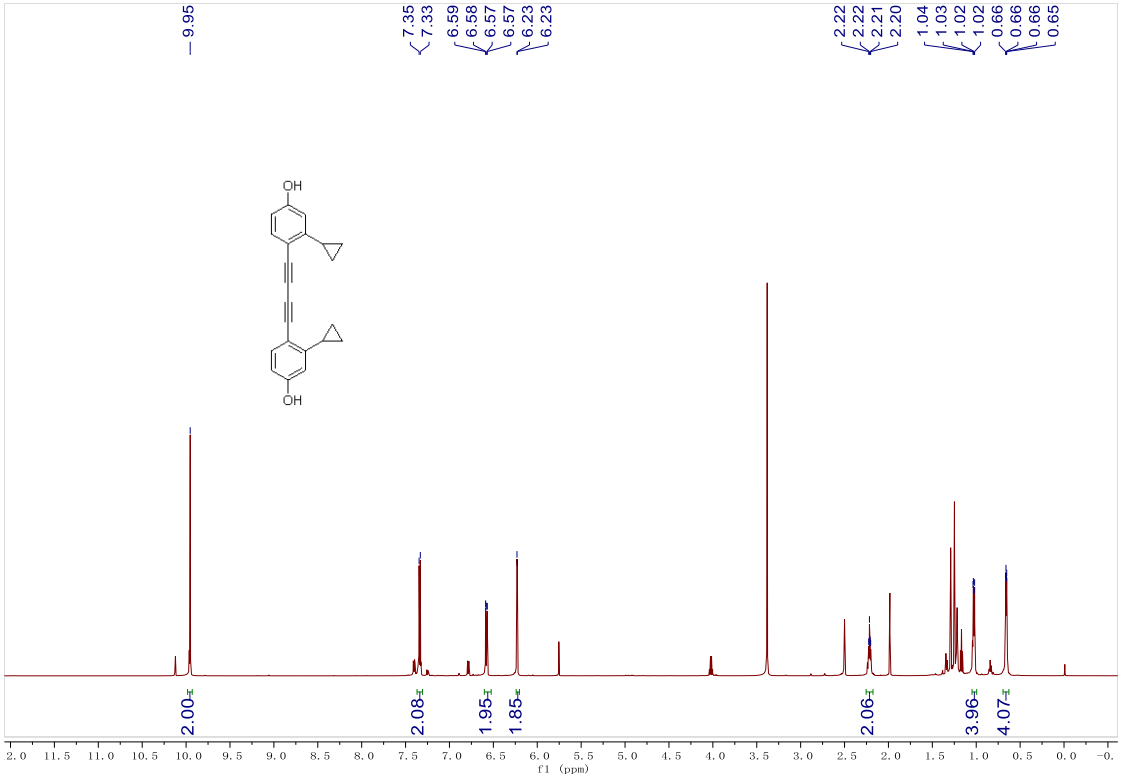


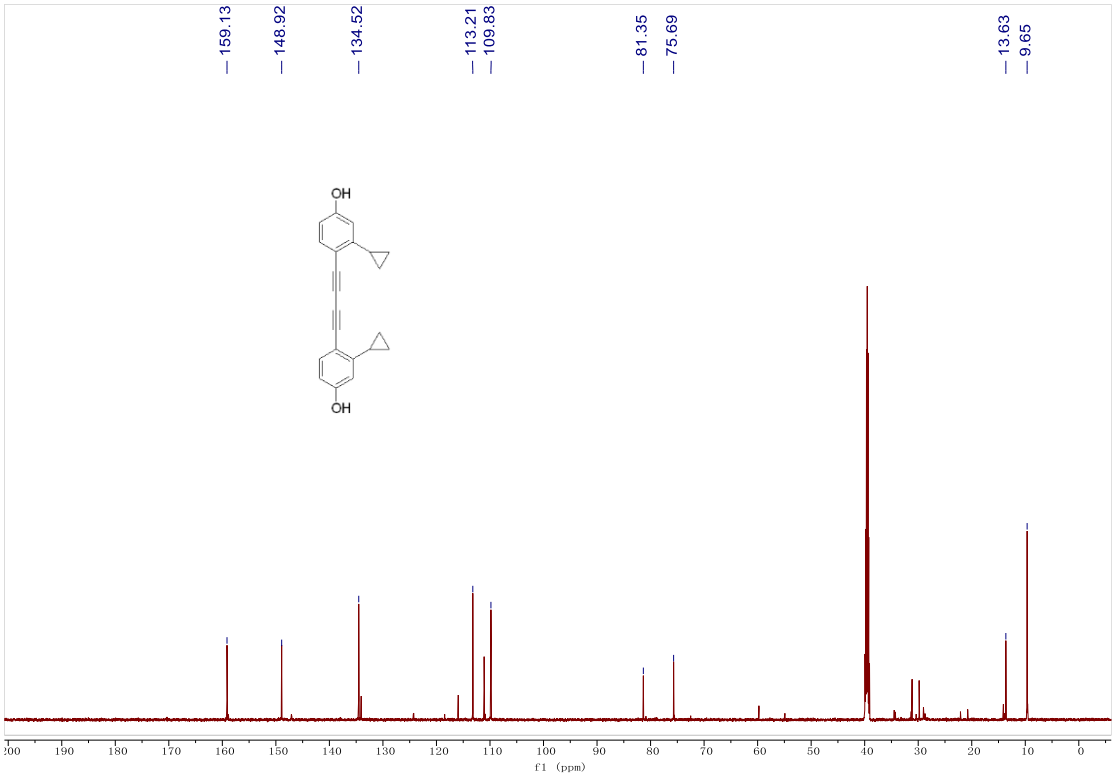
^{1}H and ^{13}C NMR spectra of compound **(2o)**



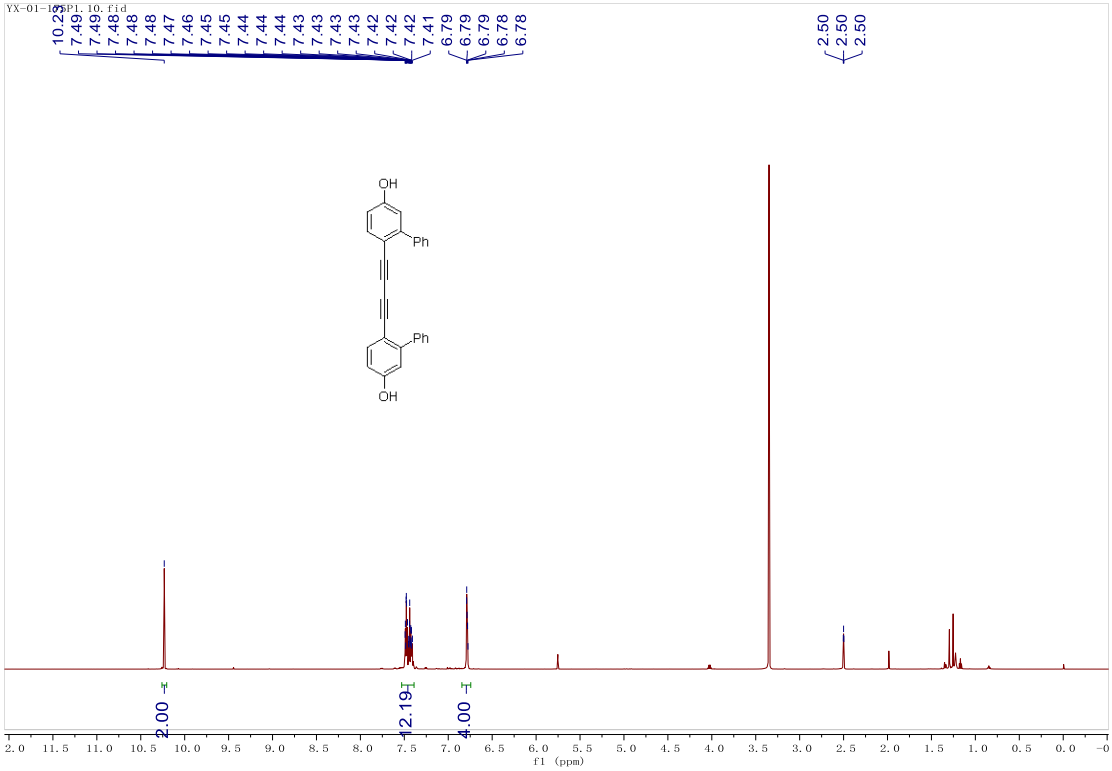


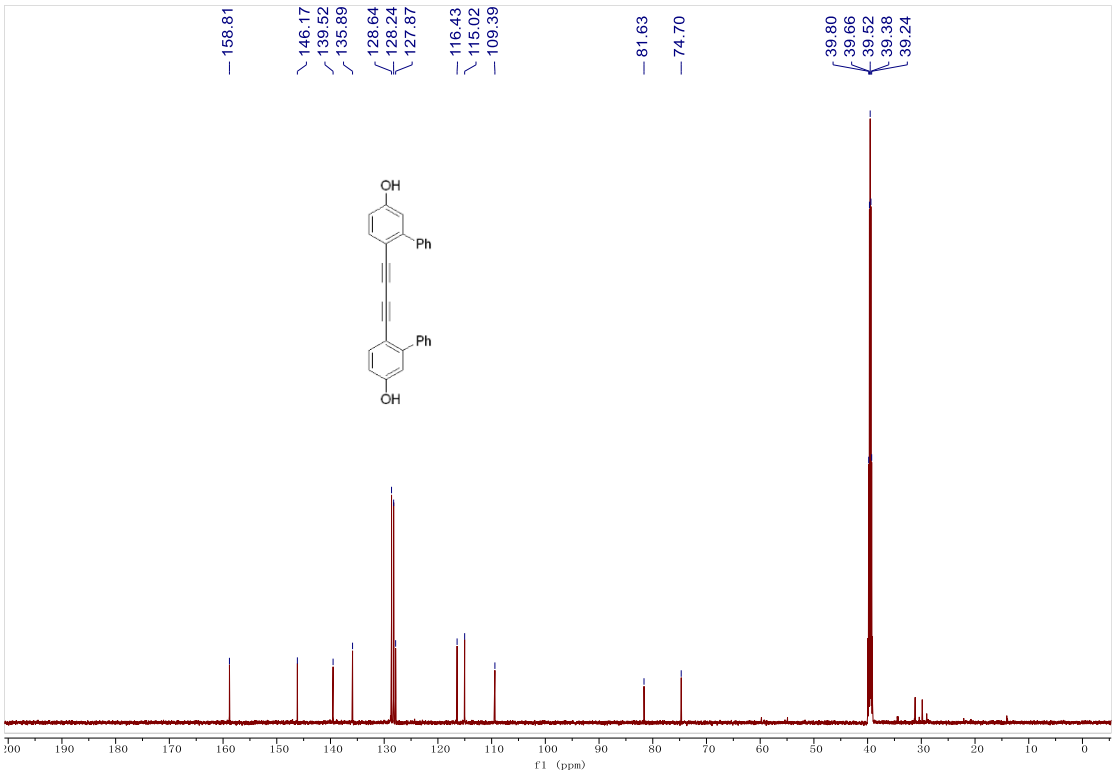
^{1}H and ^{13}C NMR spectra of compound **(2p)**



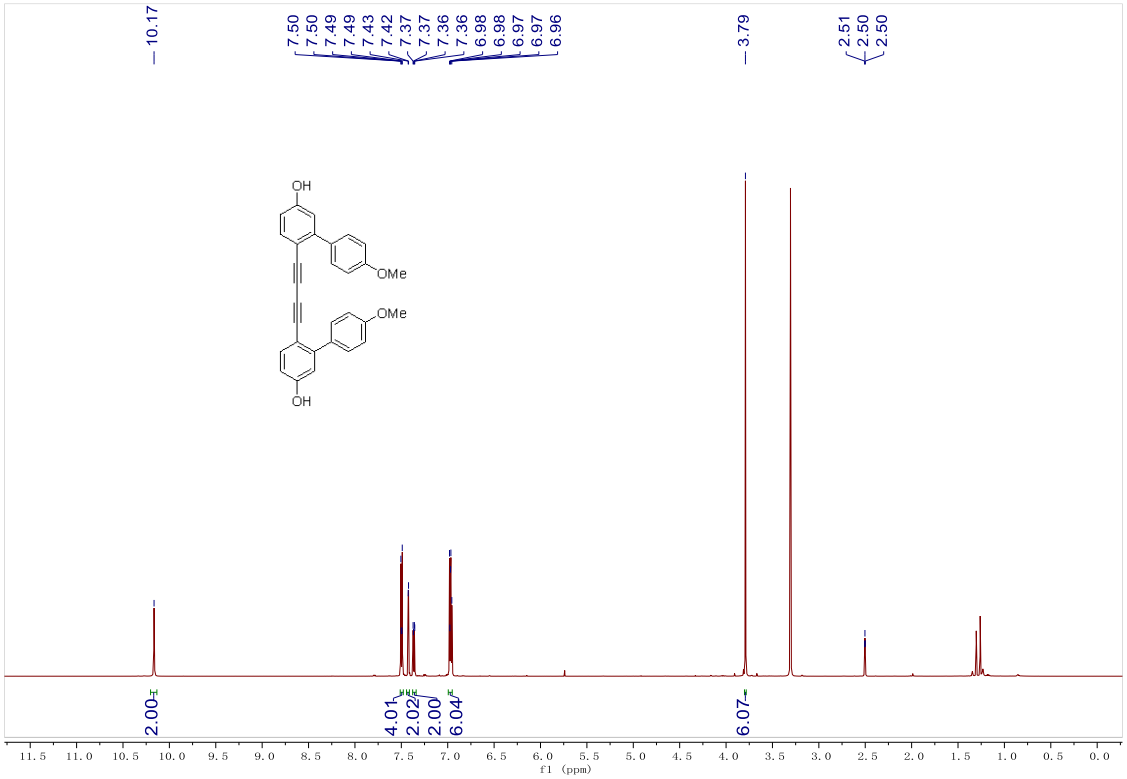


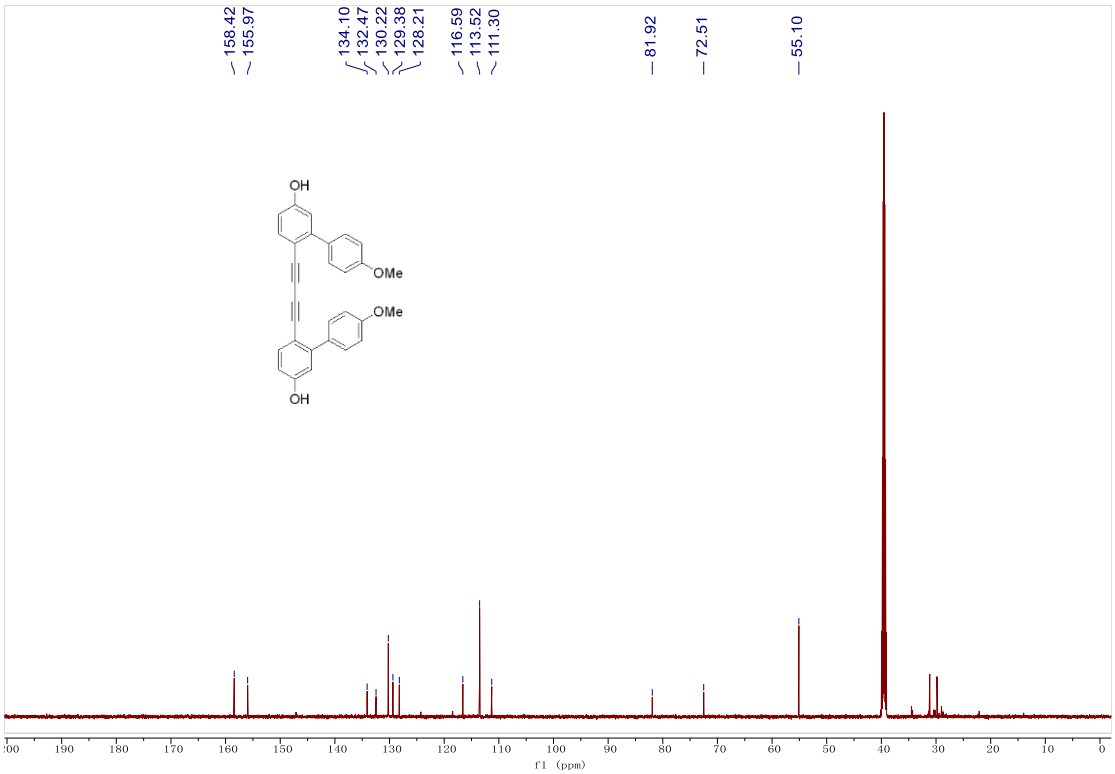
^{1}H and ^{13}C NMR spectra of compound **(2q)**



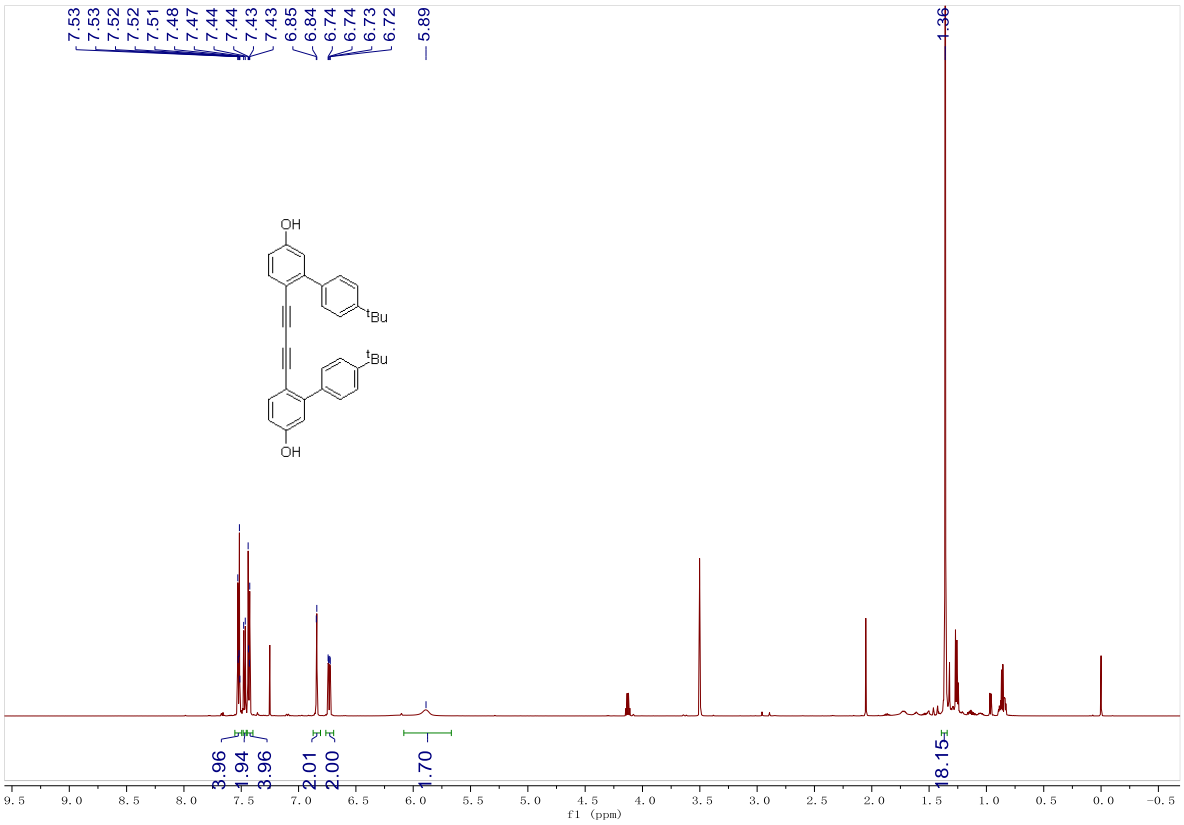


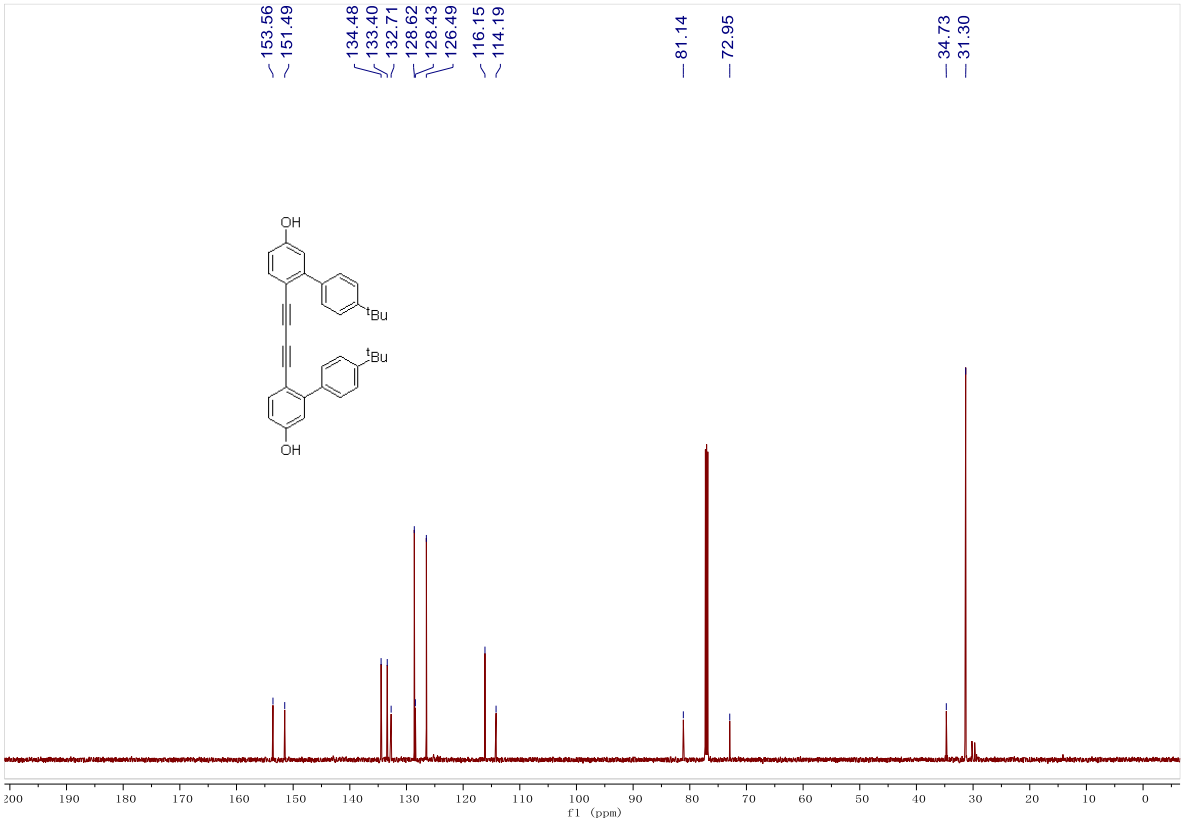
^{1}H and ^{13}C NMR spectra of compound **(2r)**





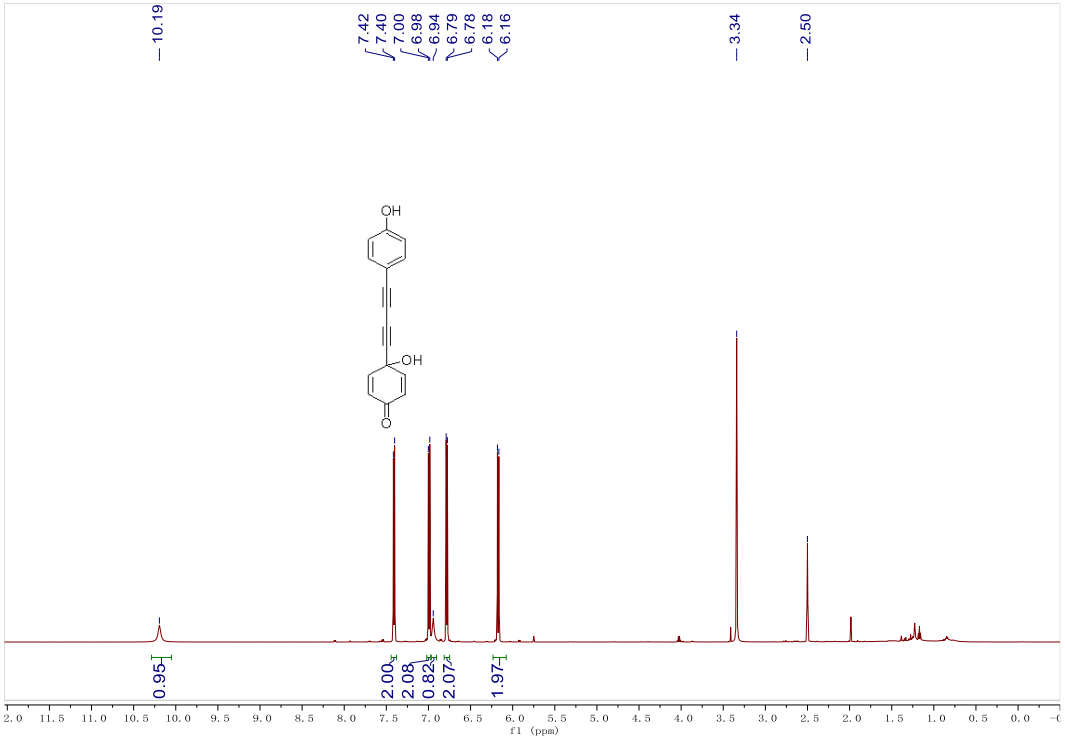
^{1}H and ^{13}C NMR spectra of compound **(2s)**

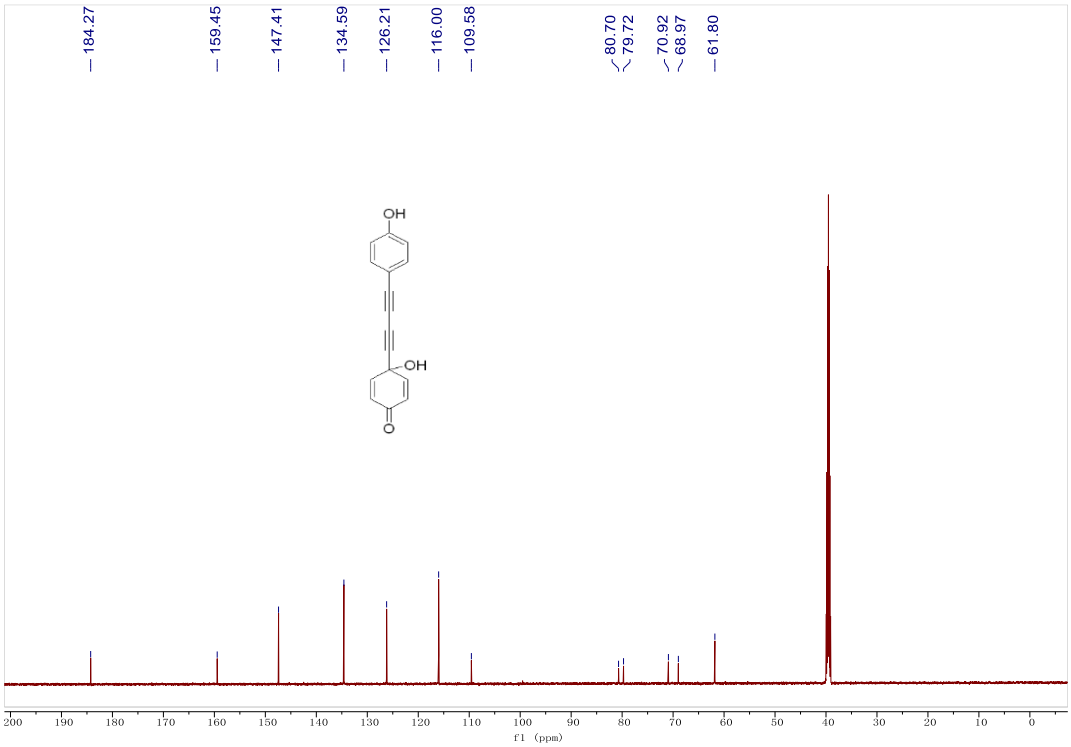




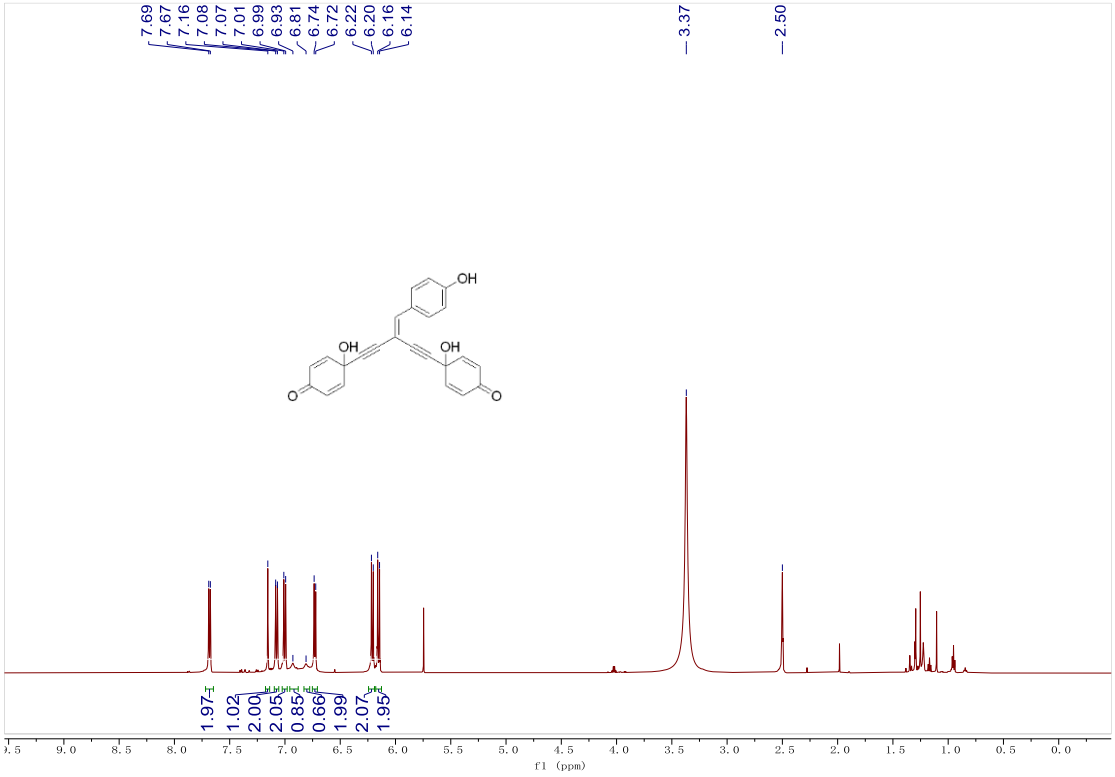
13. Copies of NMR spectra（unsymmetrical 1,3-diynes 3 and conjugated enediynes 4）

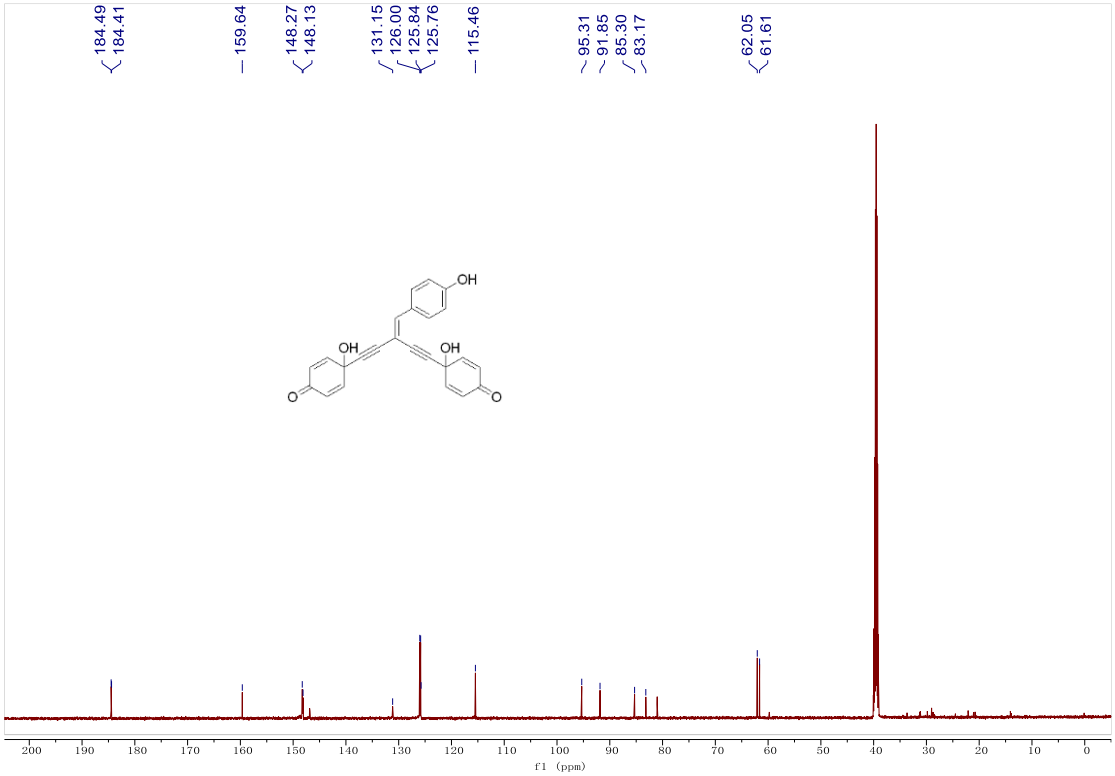
^{1}H and ^{13}C NMR spectra of compound **(3a)**



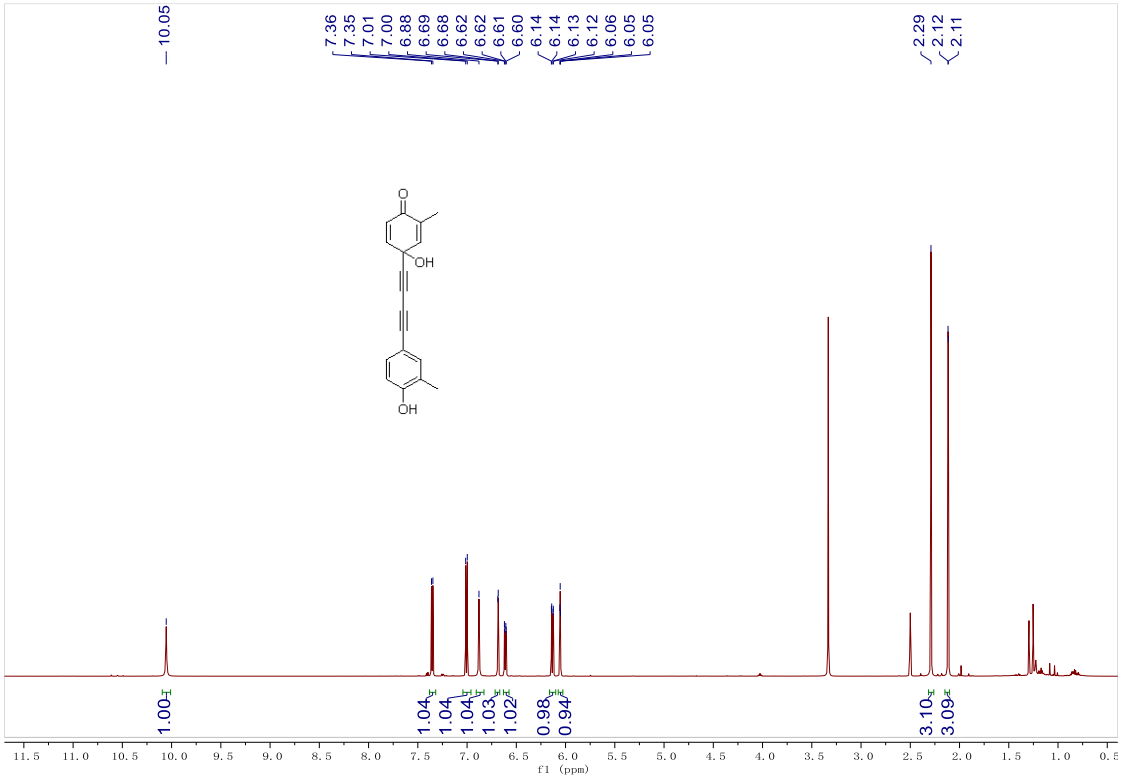


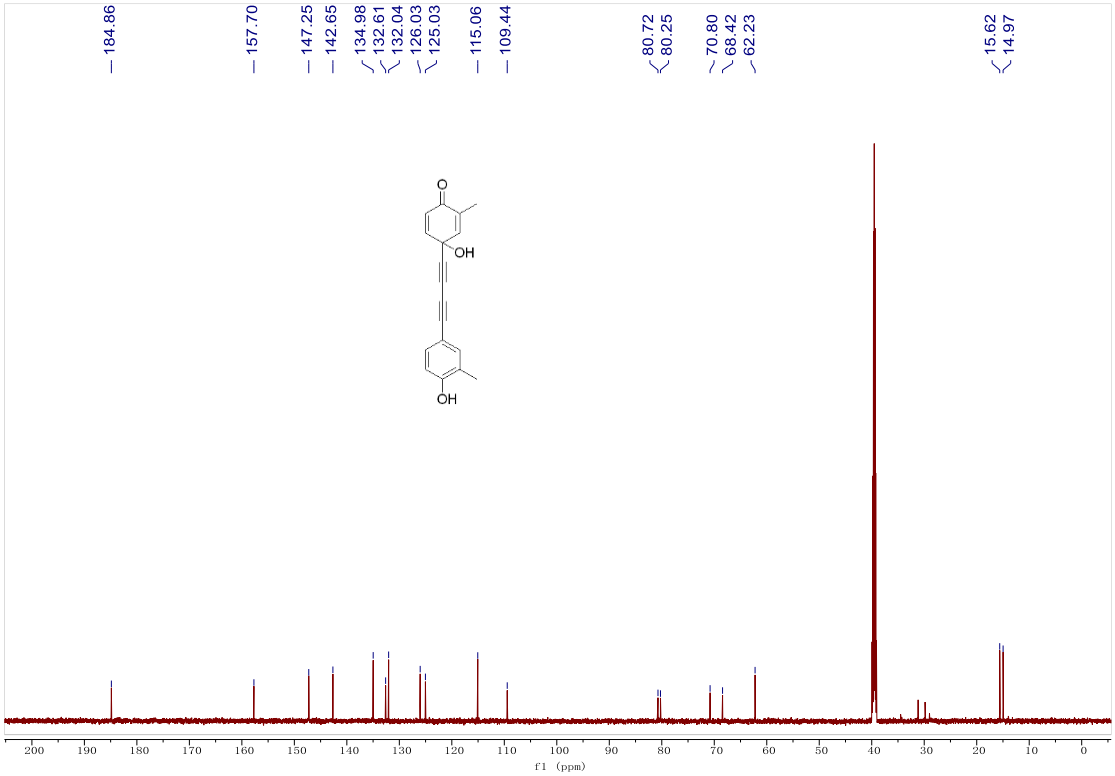
^{1}H and ^{13}C NMR spectra of compound **(4a)**



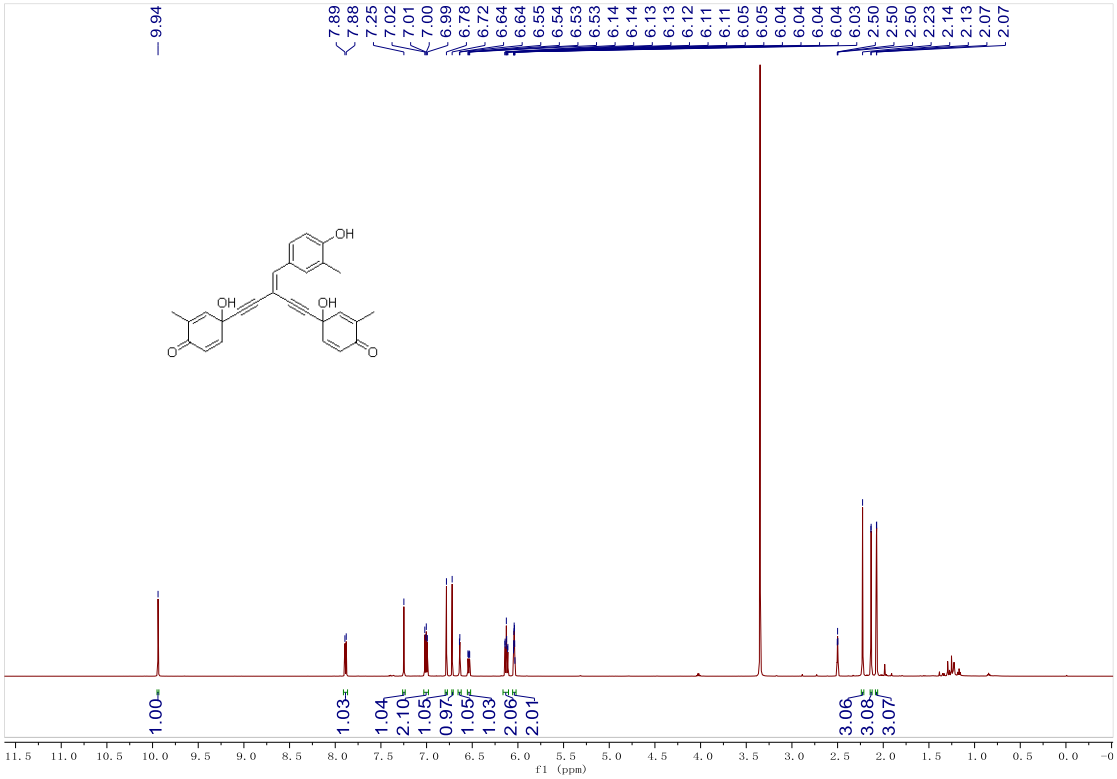


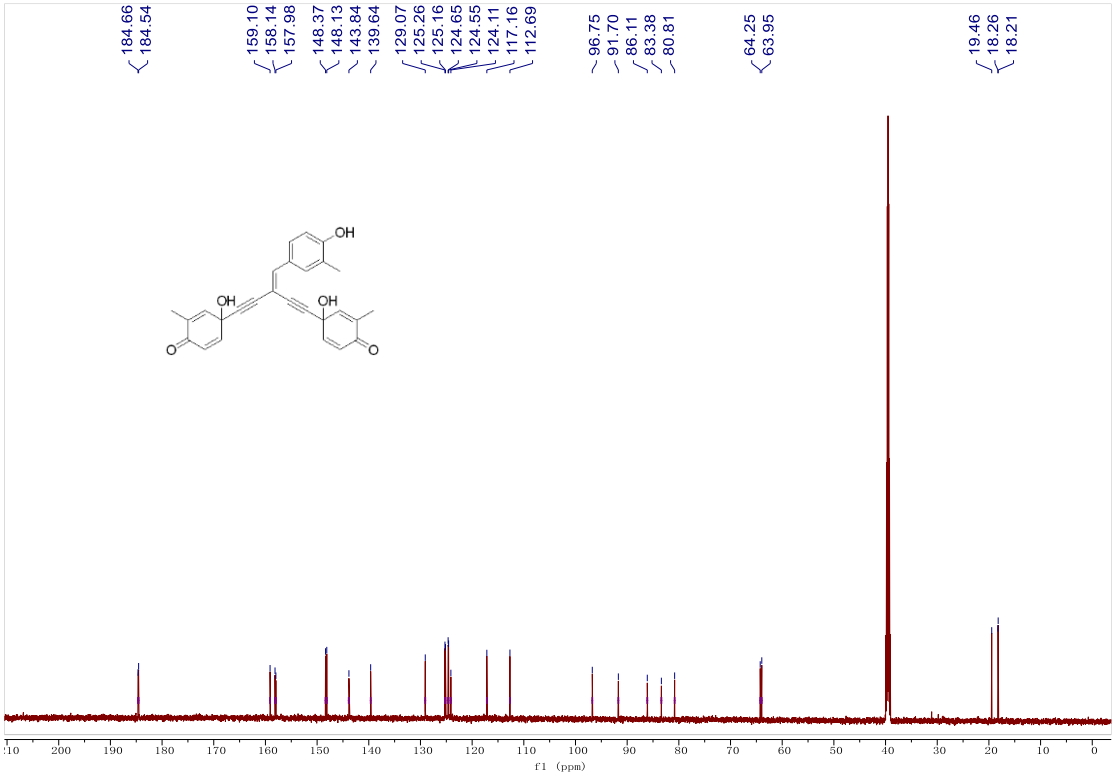
^{1}H and ^{13}C NMR spectra of compound **(3b)**



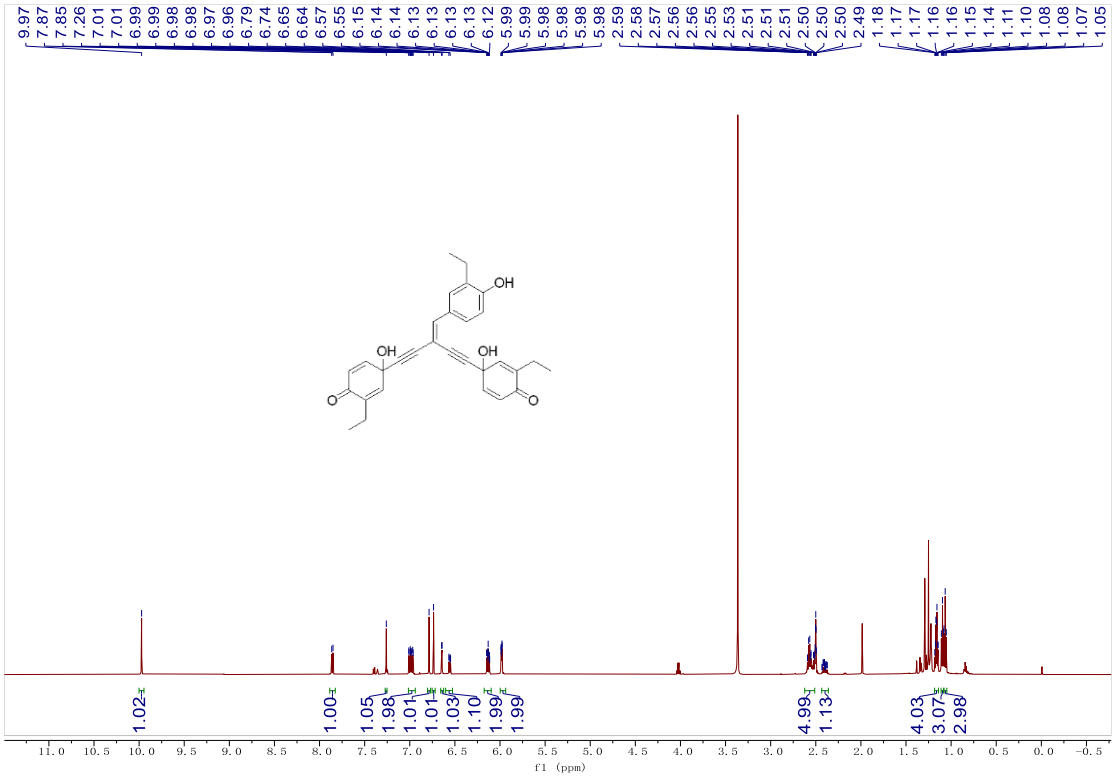


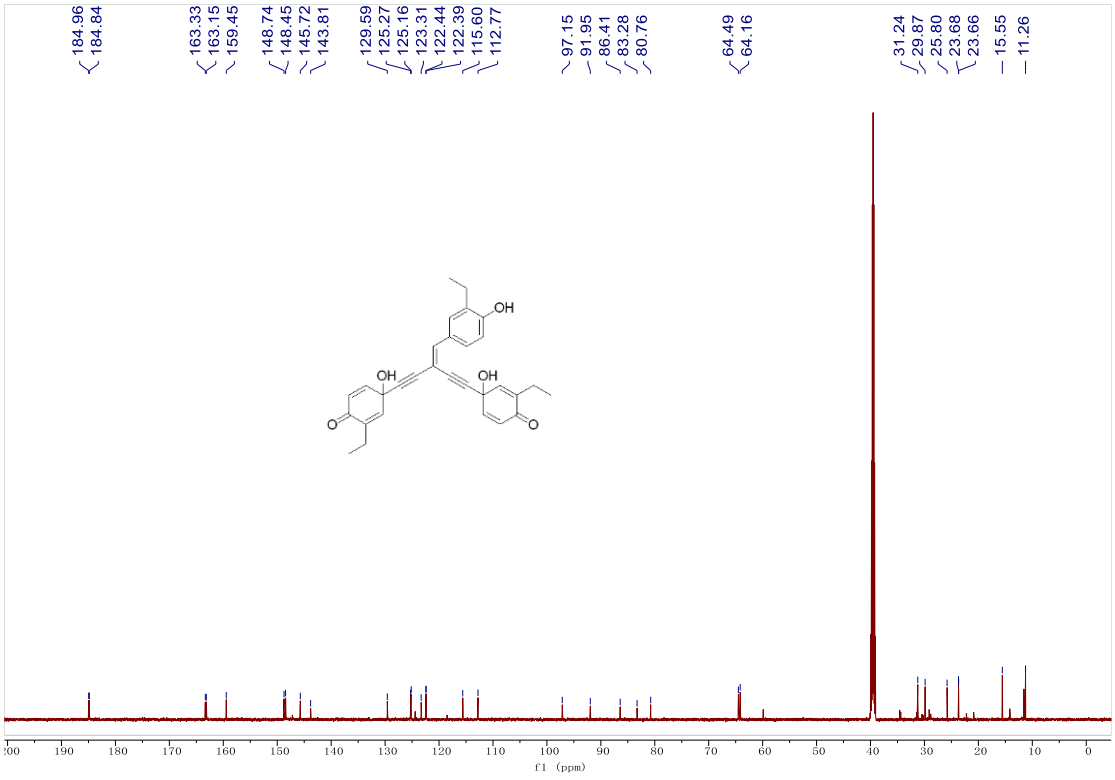
^{1}H and ^{13}C NMR spectra of compound **(4b)**



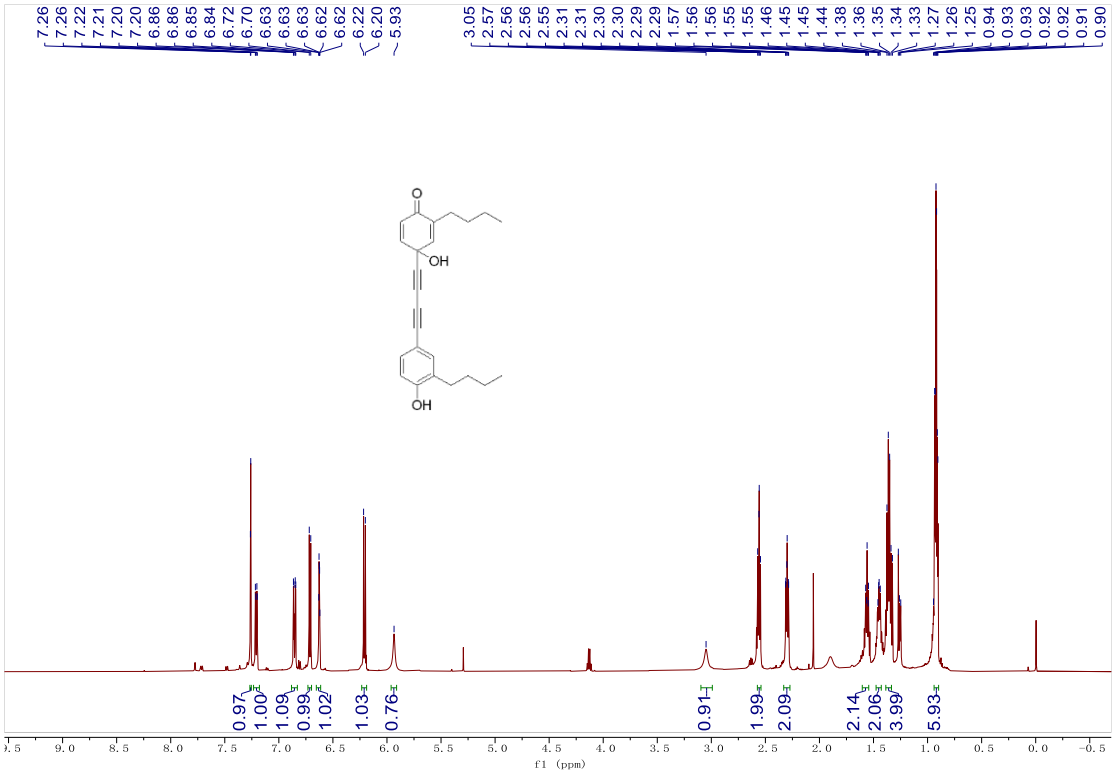


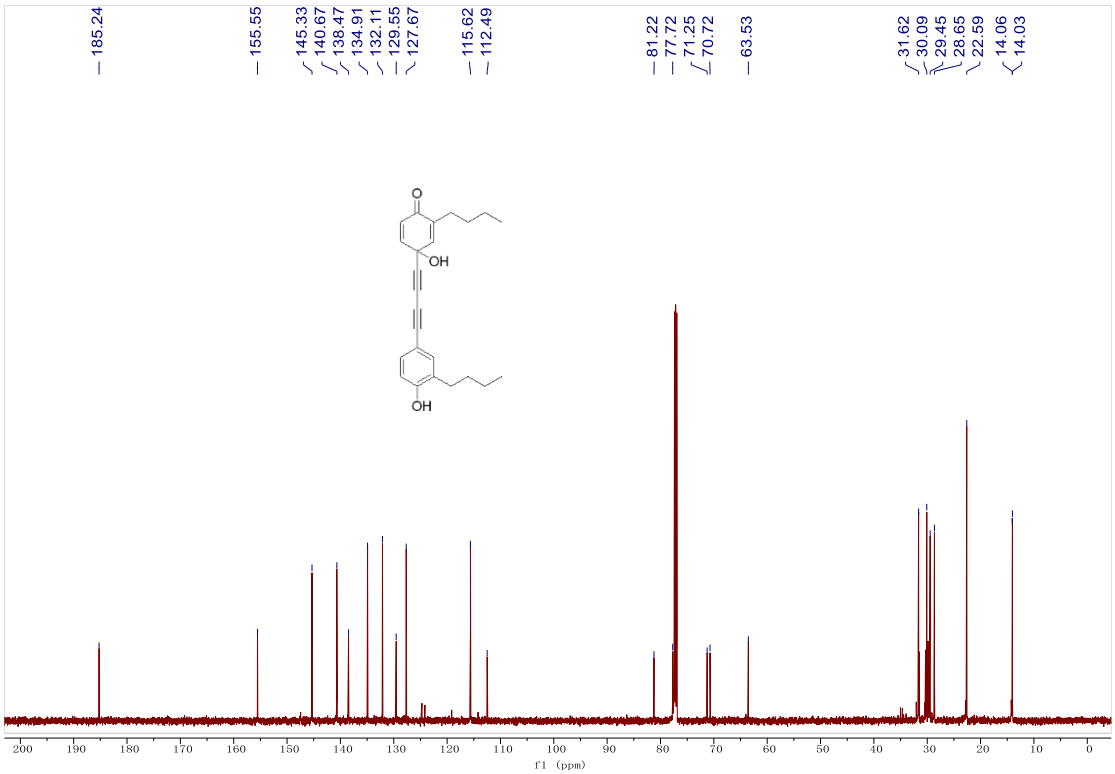
^{1}H and ^{13}C NMR spectra of compound **(4c)**



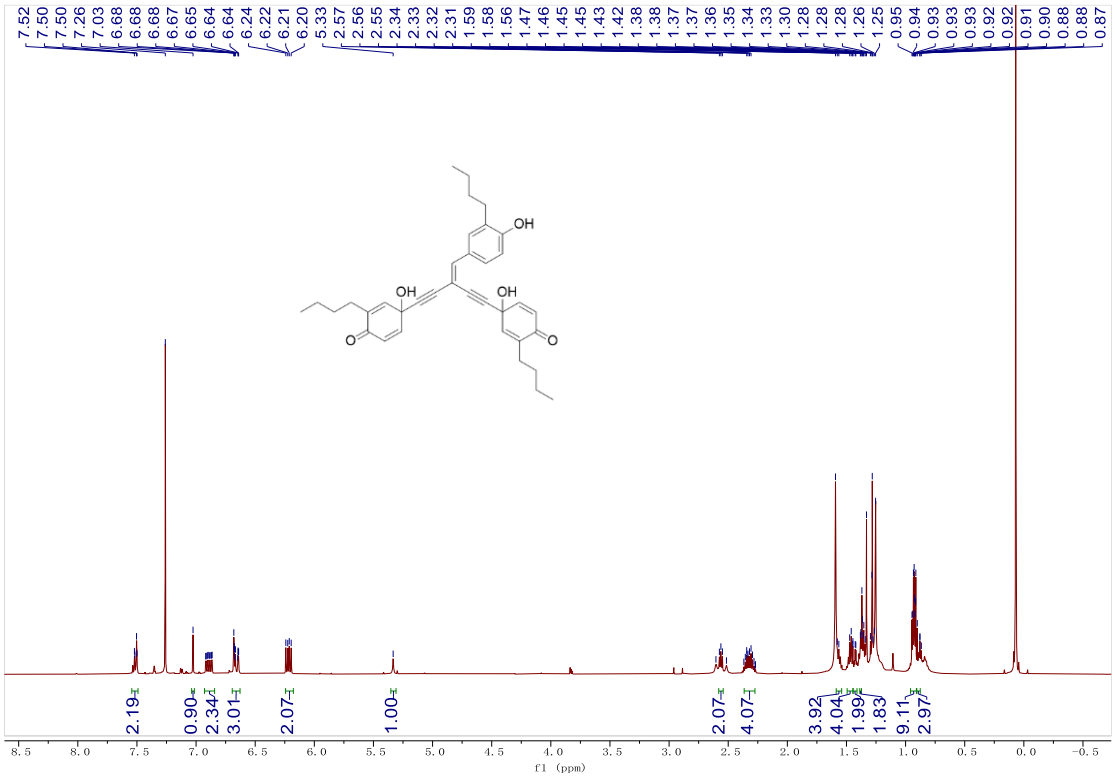


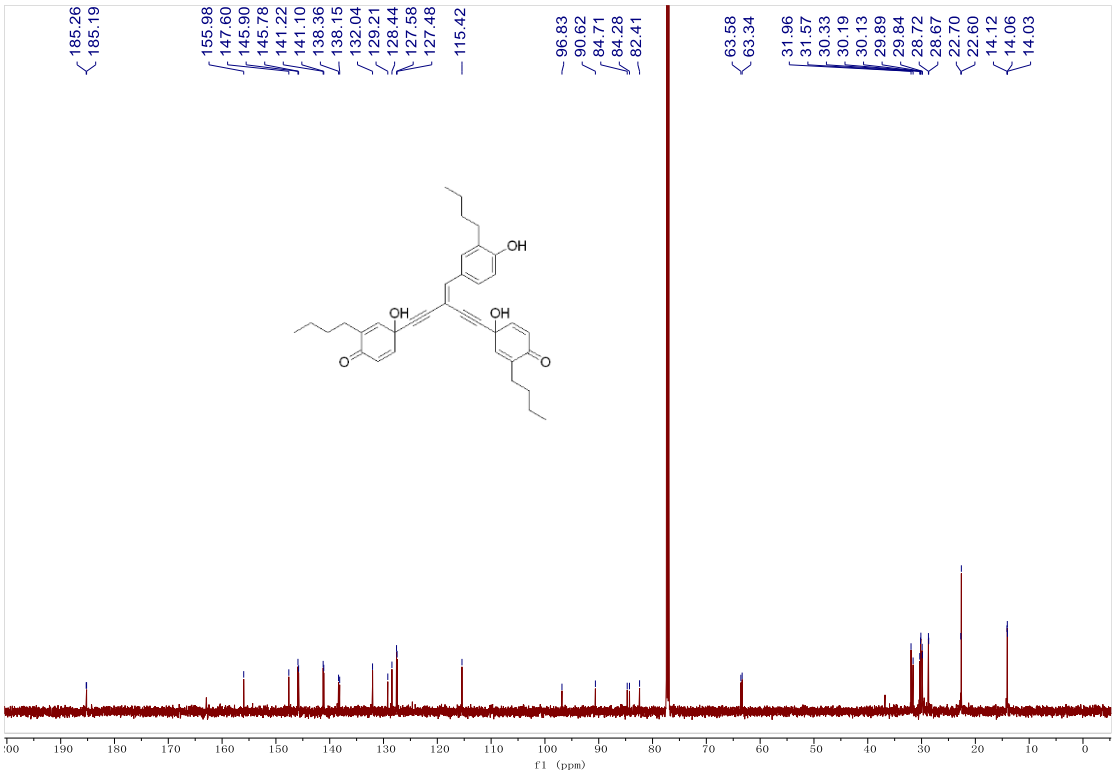
^{1}H and ^{13}C NMR spectra of compound **(3d)**



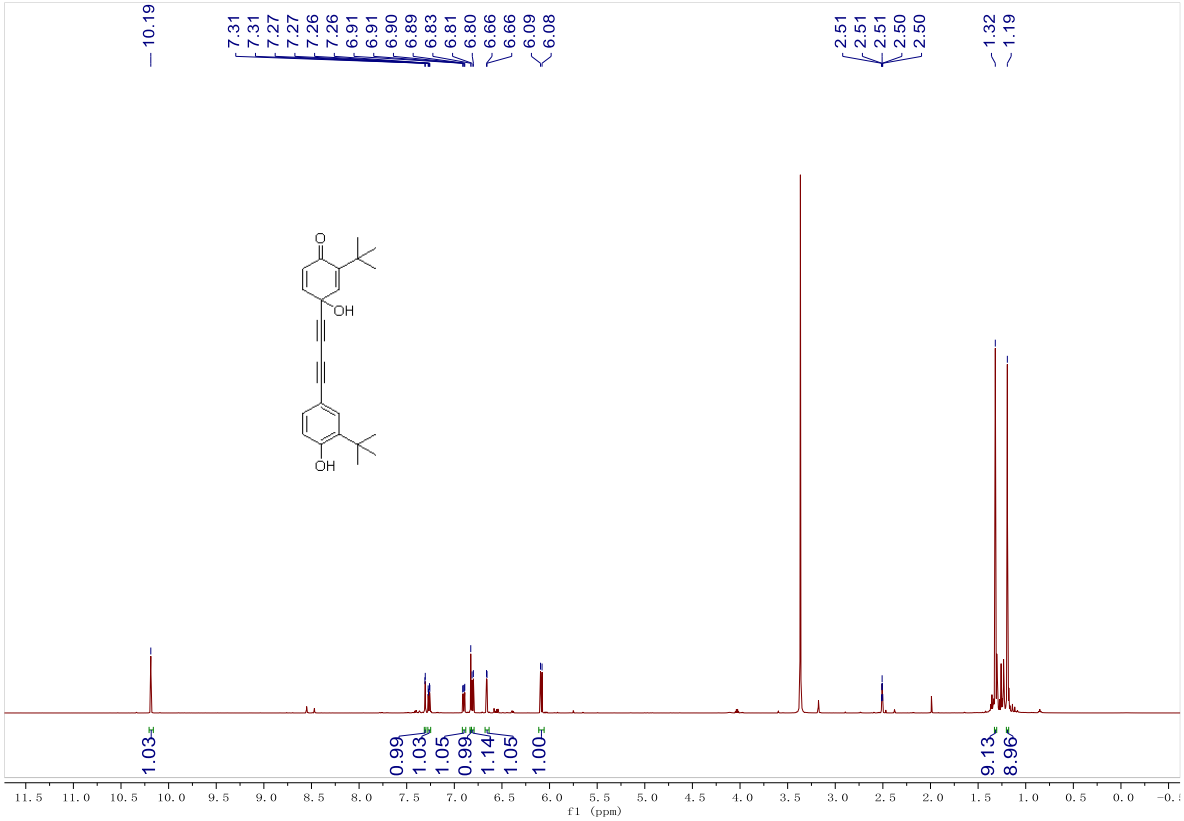


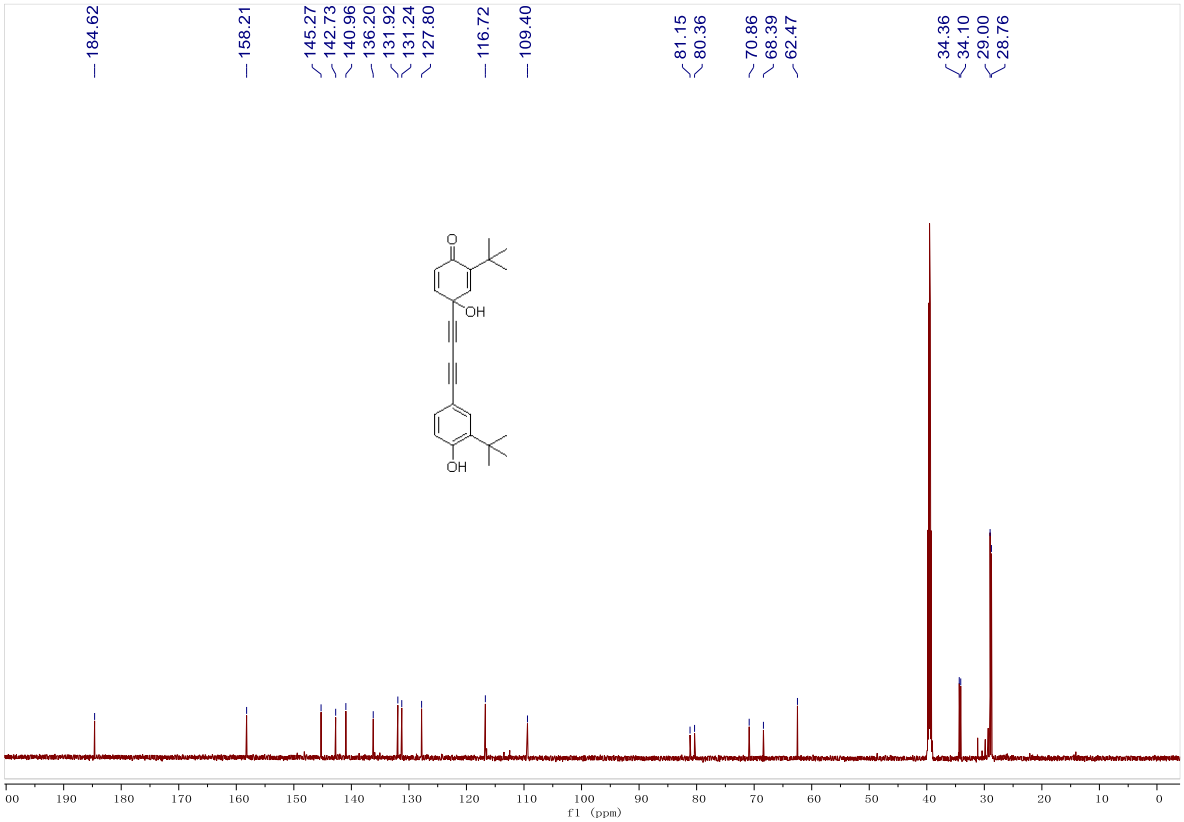
^{1}H and ^{13}C NMR spectra of compound **(4d)**



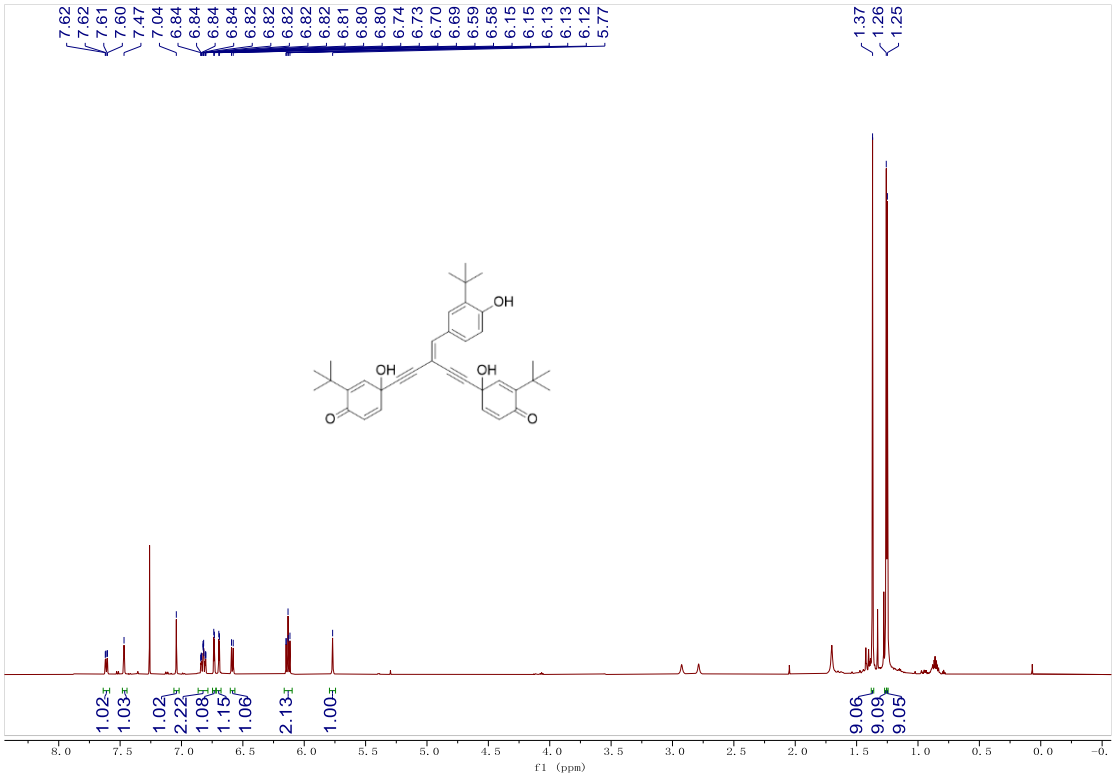


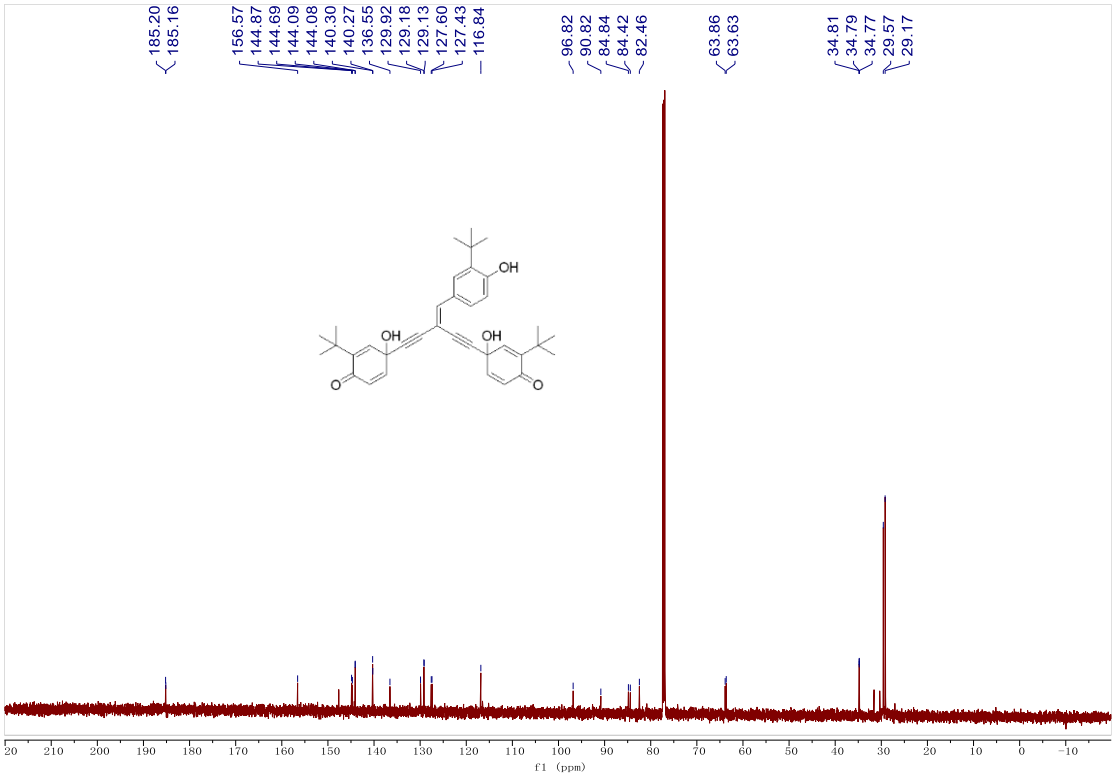
^{1}H and ^{13}C NMR spectra of compound **(3e)**



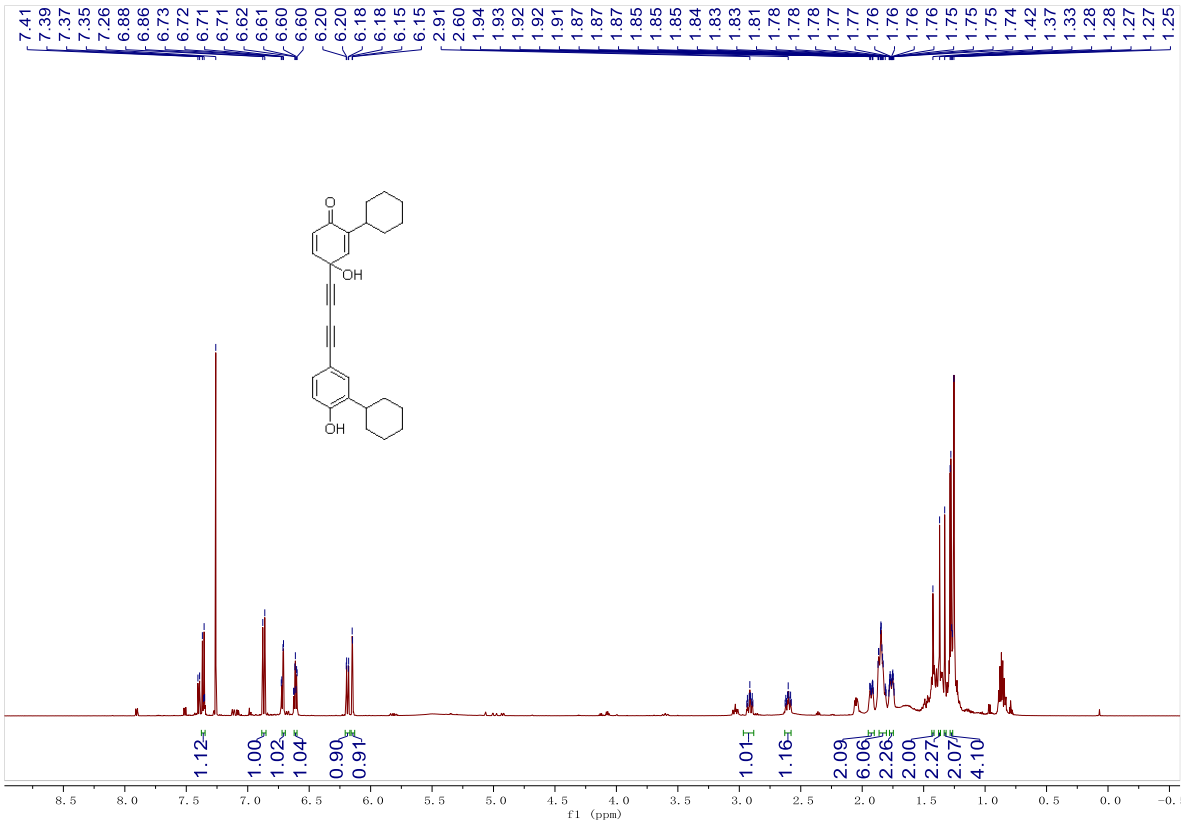


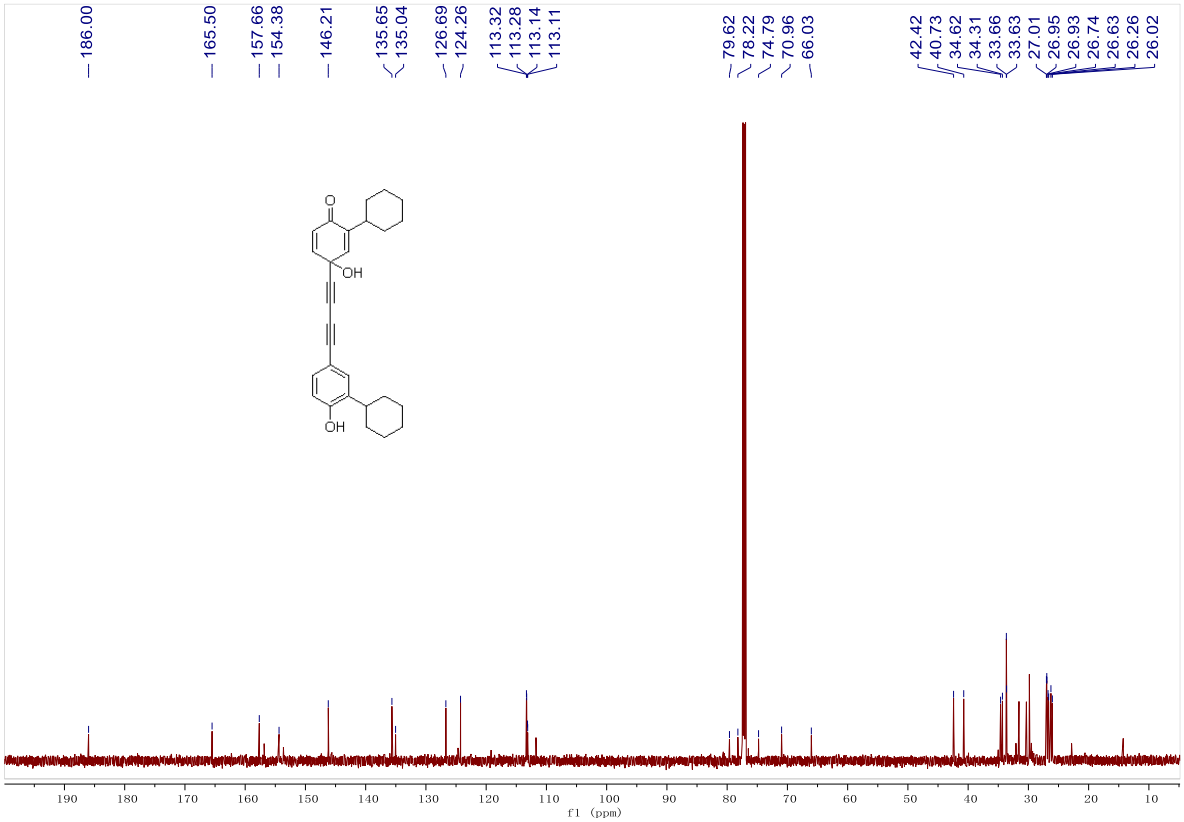
^{1}H and ^{13}C NMR spectra of compound **(4e)**



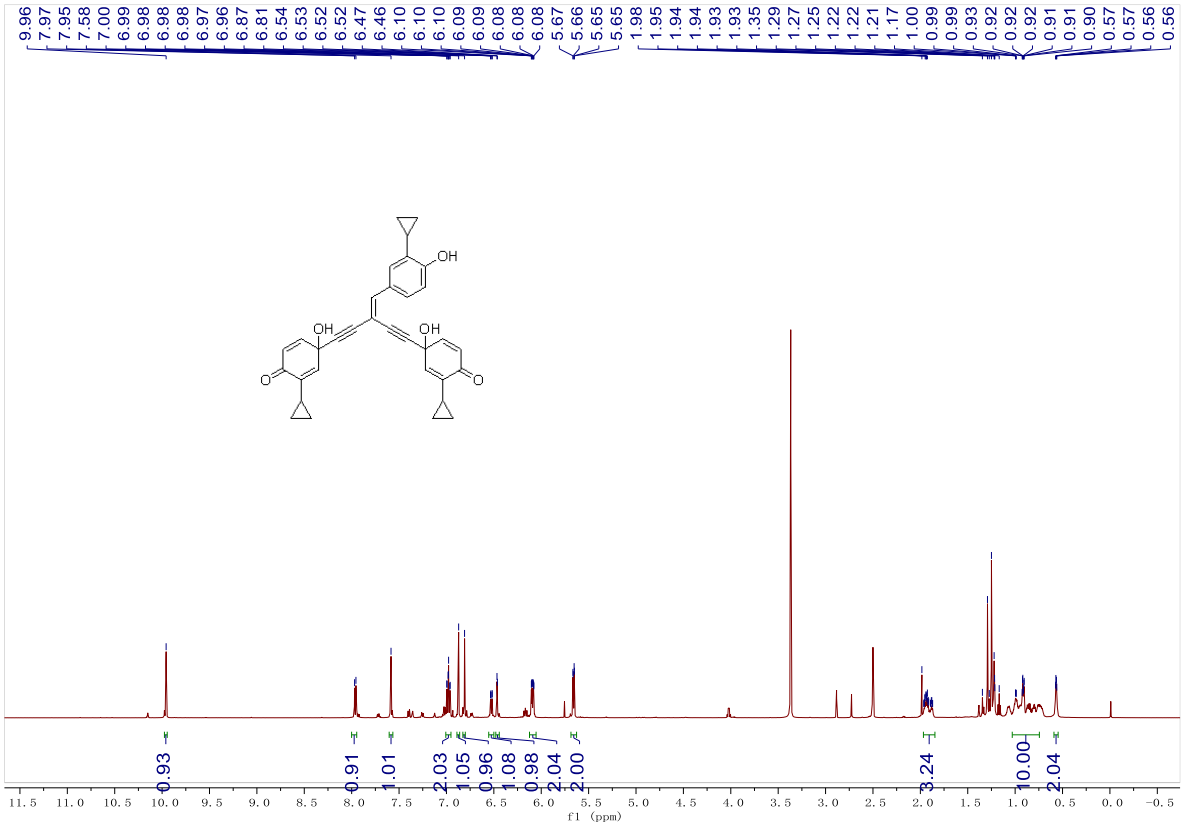


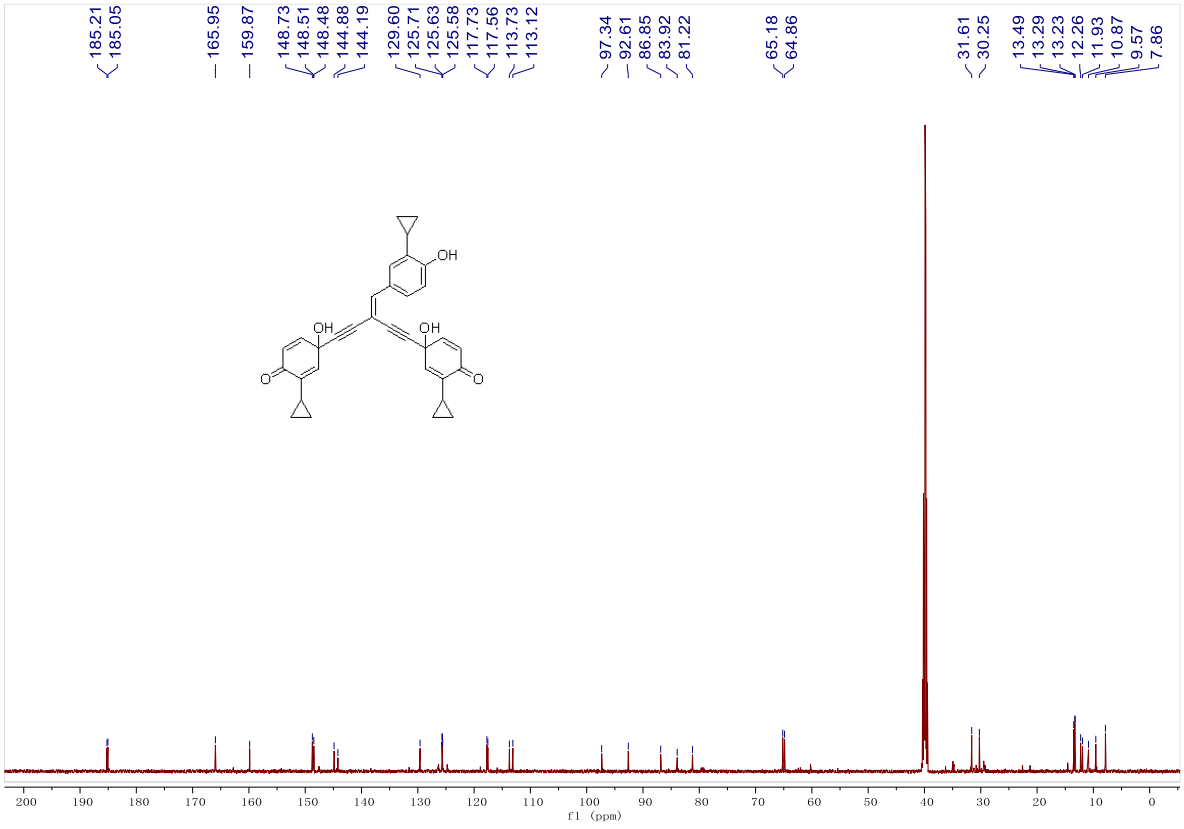
^{1}H and ^{13}C NMR spectra of compound **(3f)**



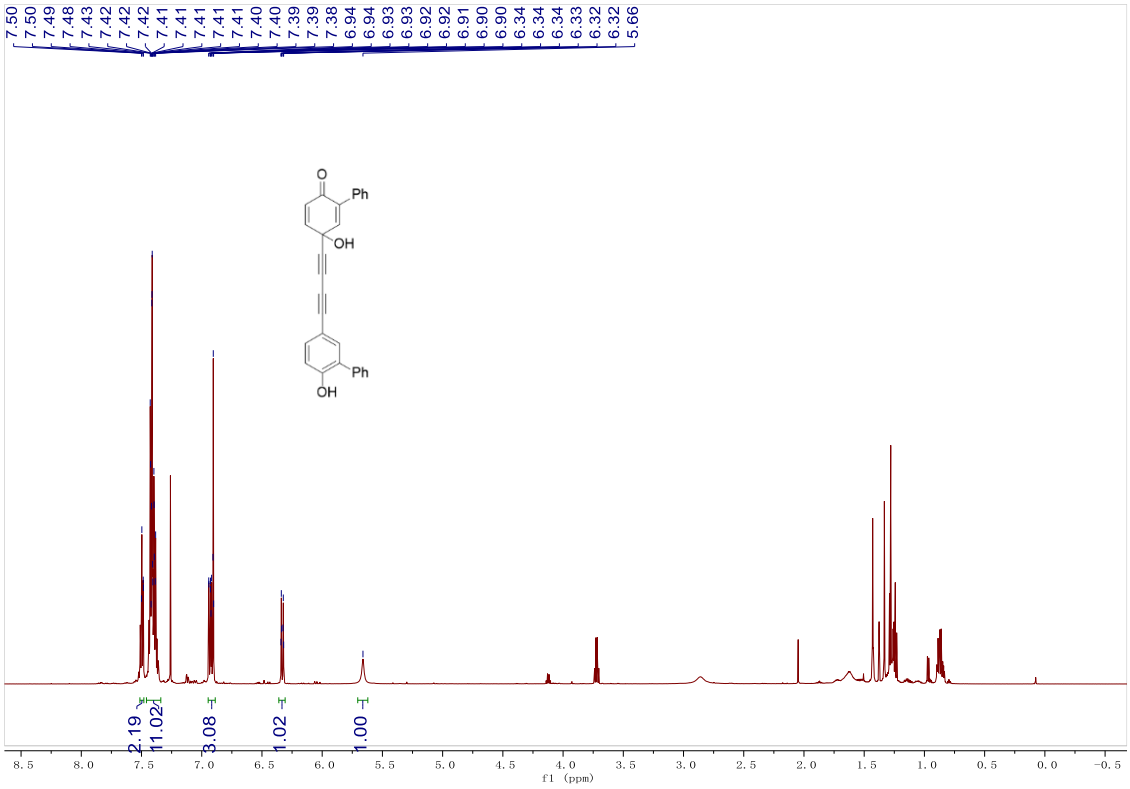


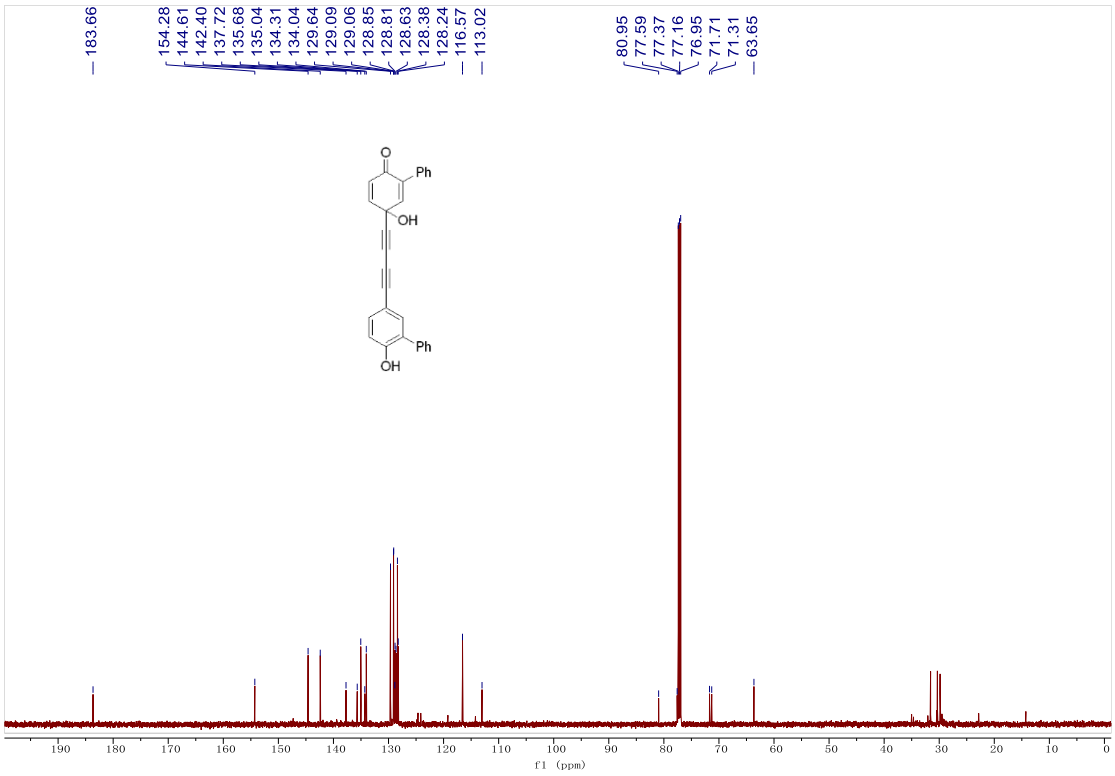
^{1}H and ^{13}C NMR spectra of compound **(4g)**



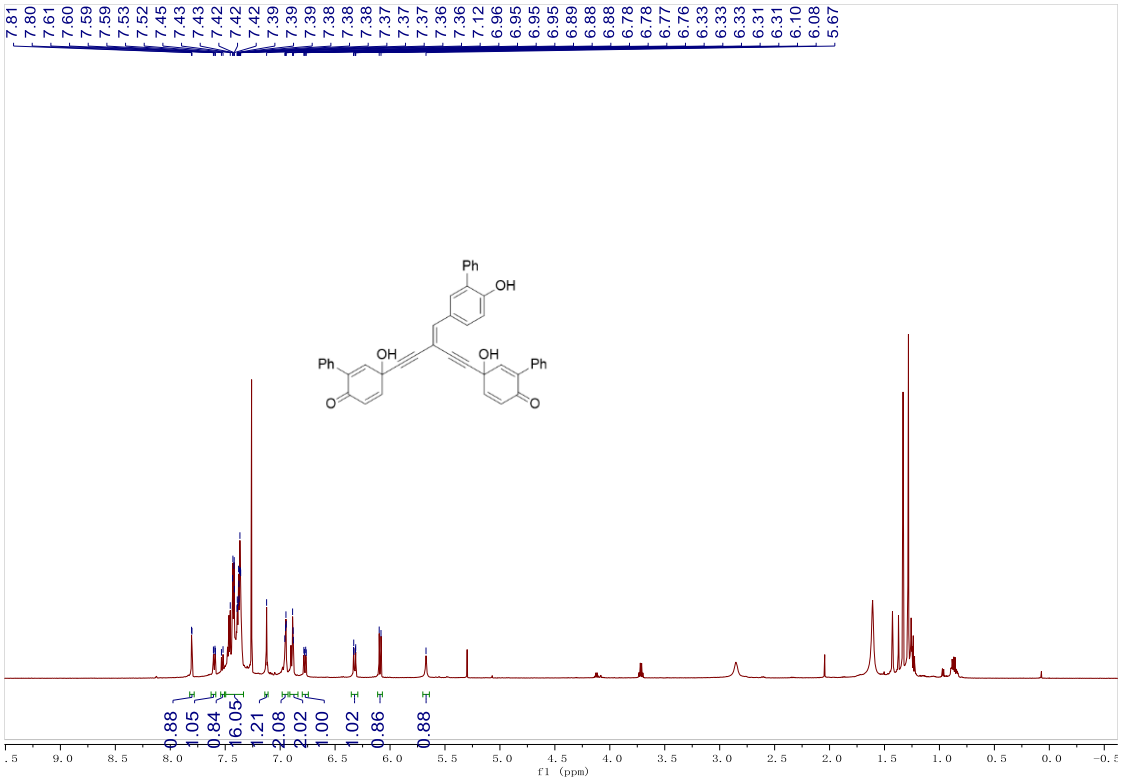


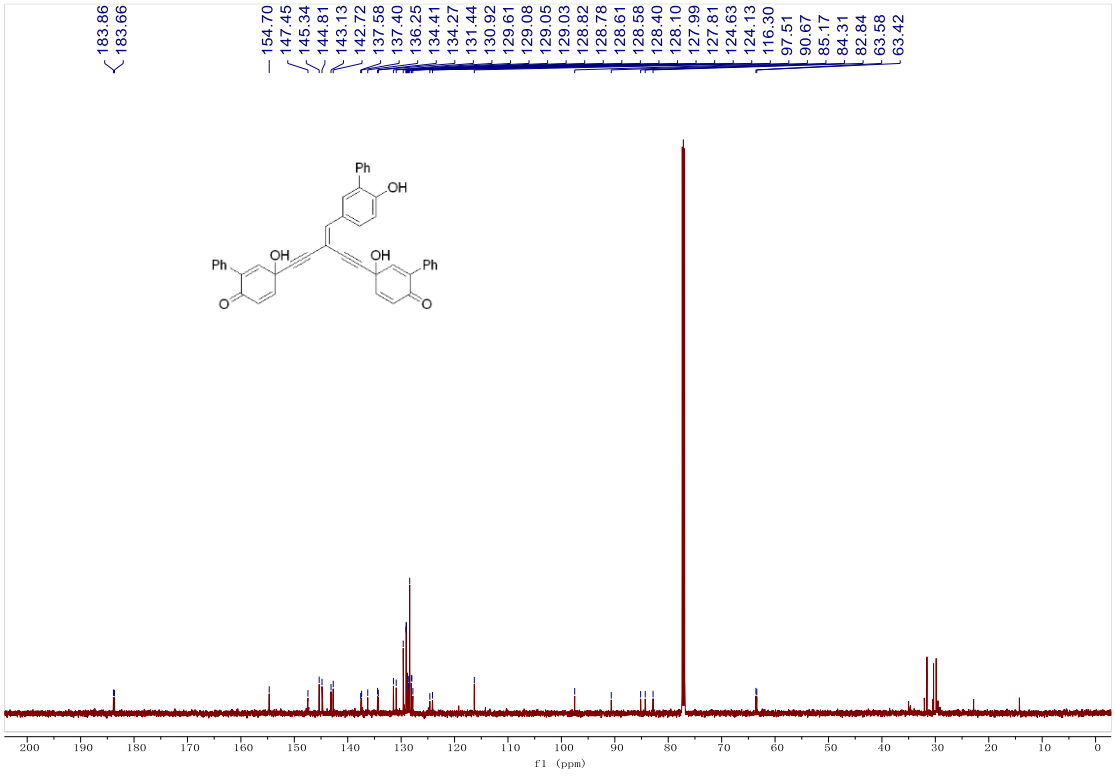
^{1}H and ^{13}C NMR spectra of compound **(3h)**



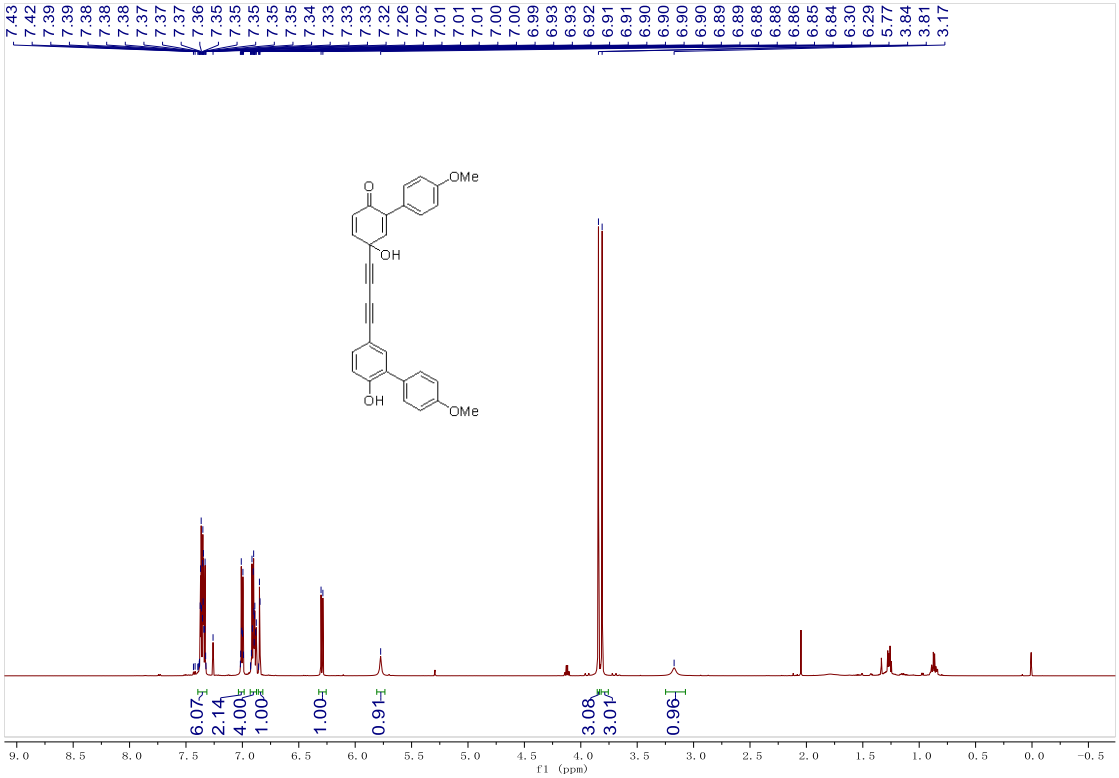


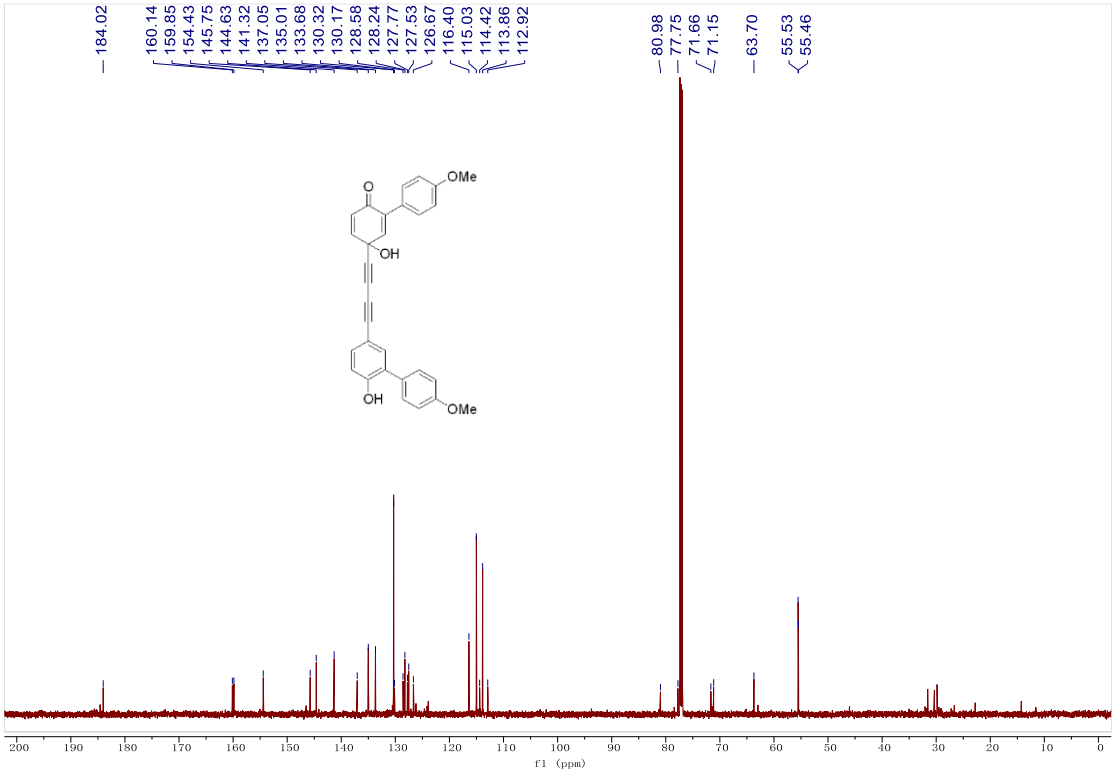
^{1}H and ^{13}C NMR spectra of compound **(4h)**



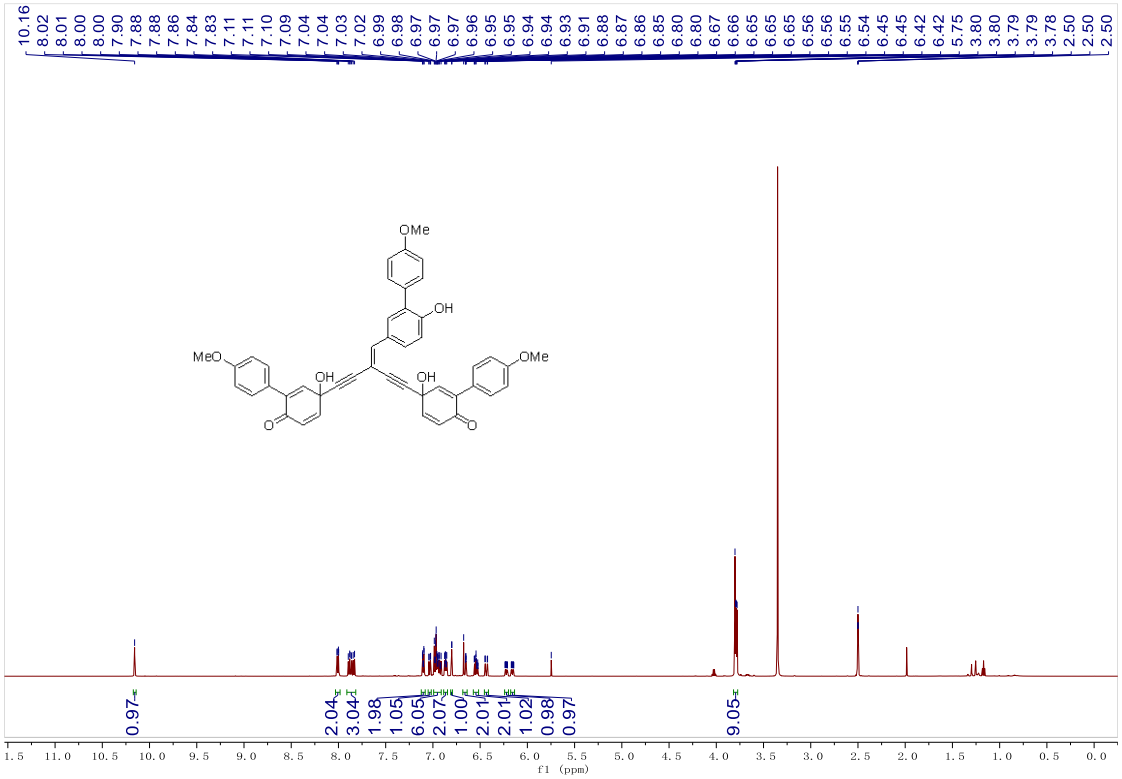


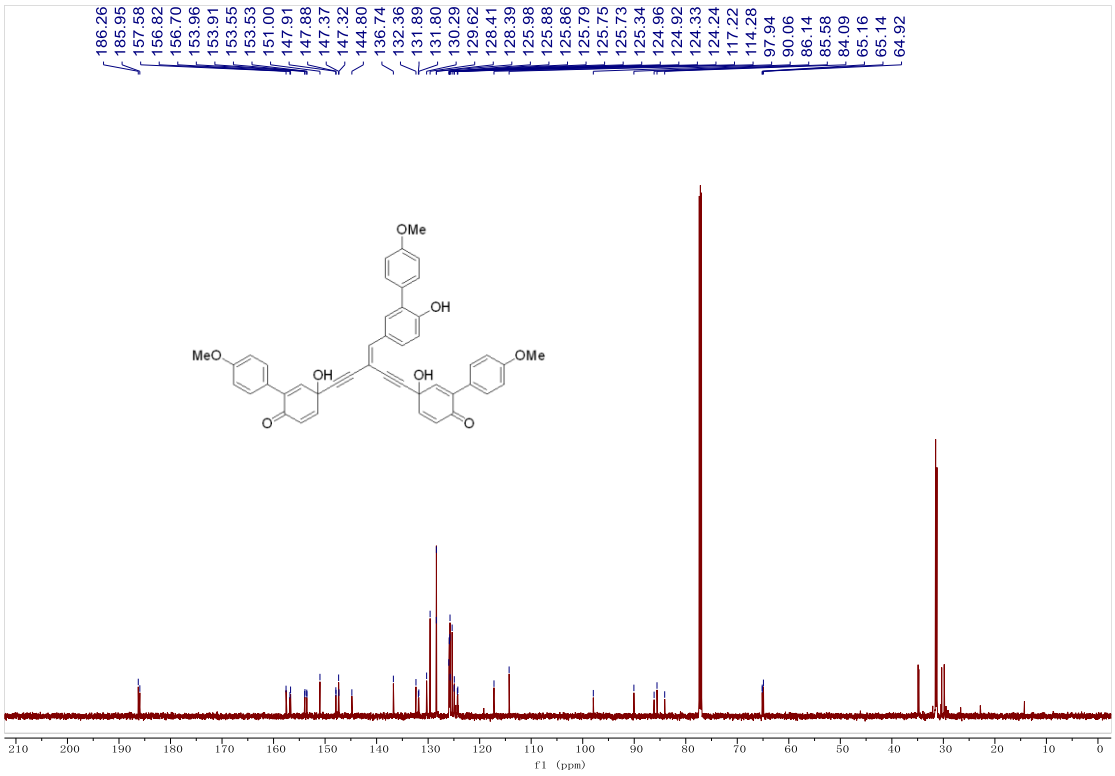
^{1}H and ^{13}C NMR spectra of compound **(3i)**



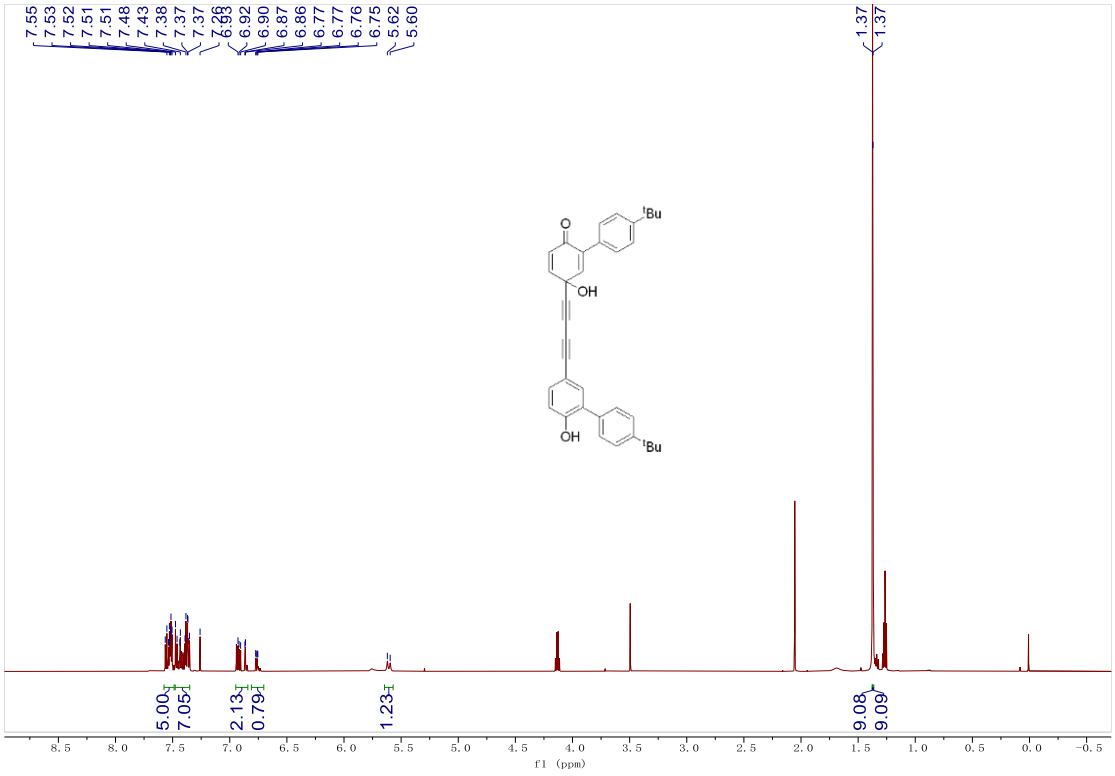


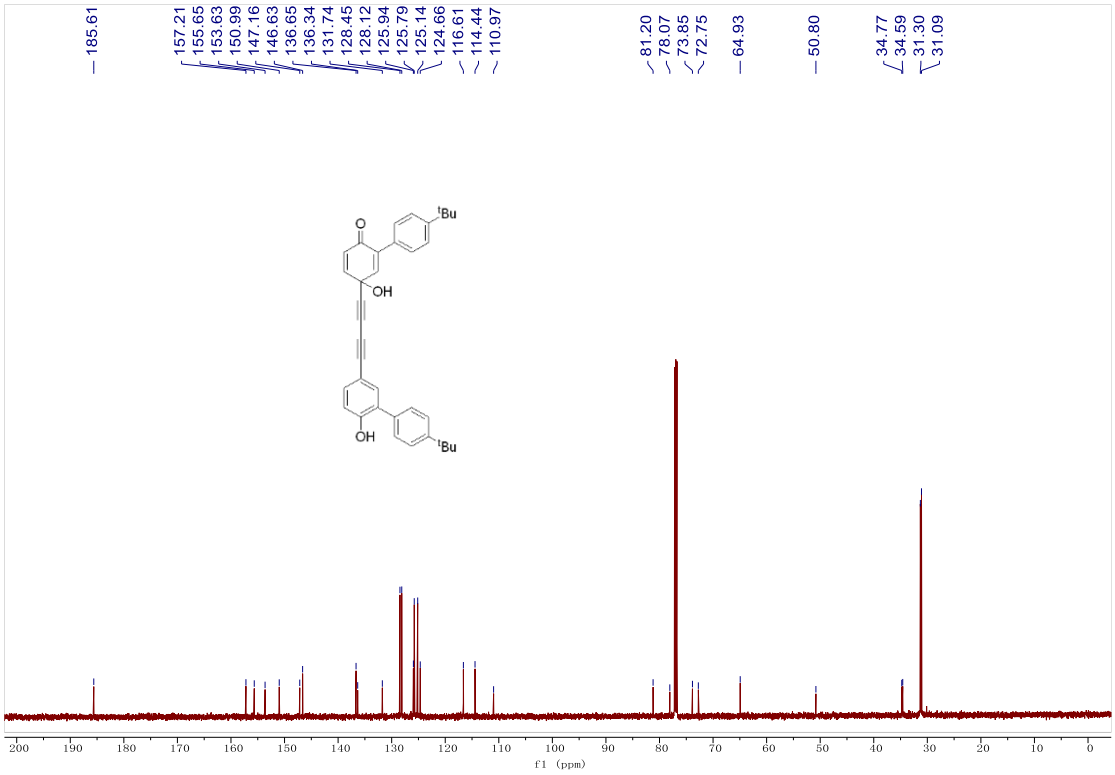
^{1}H and ^{13}C NMR spectra of compound **(4i)**



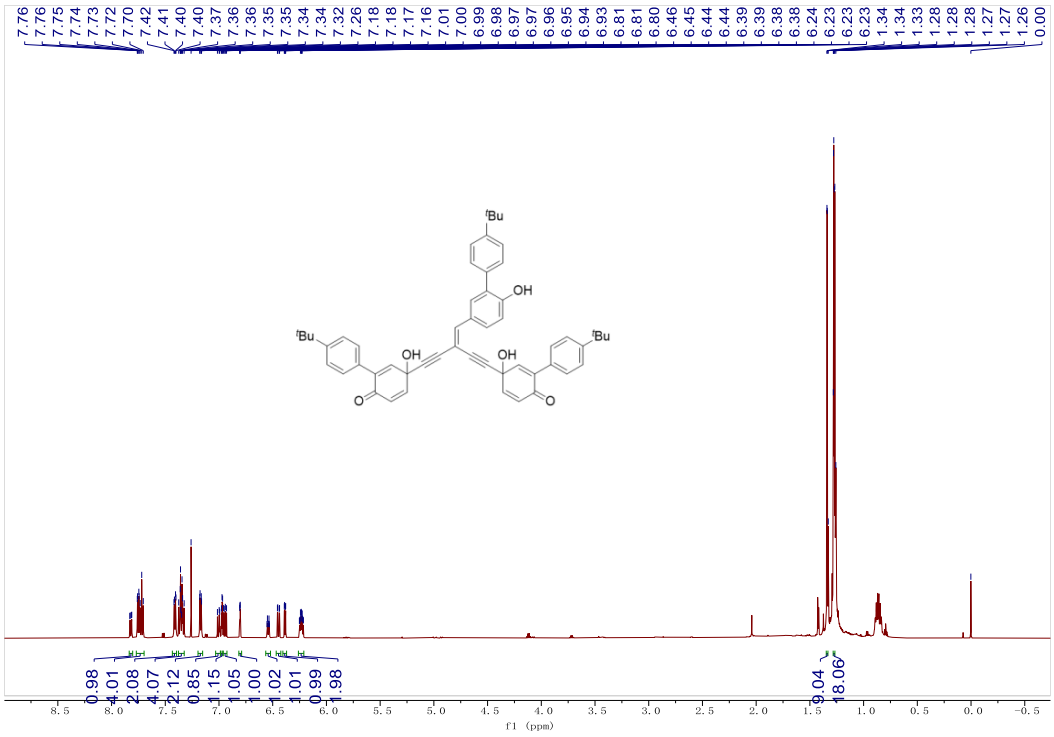


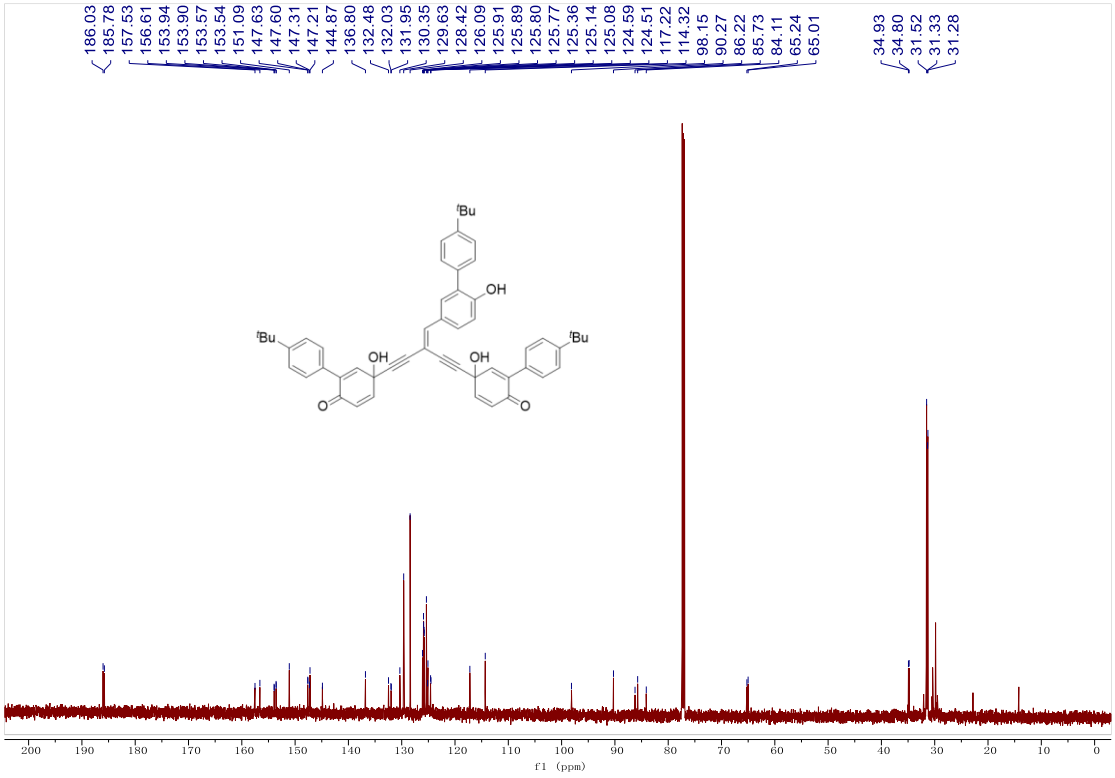
^{1}H and ^{13}C NMR spectra of compound **(3j)**



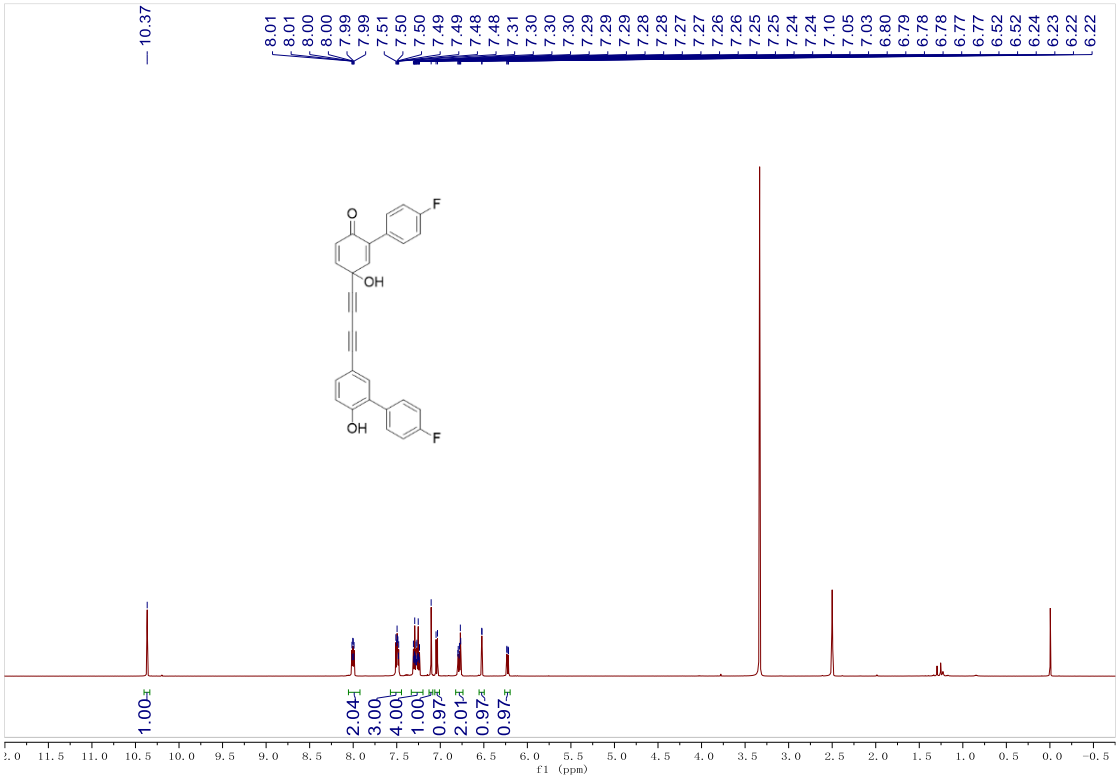


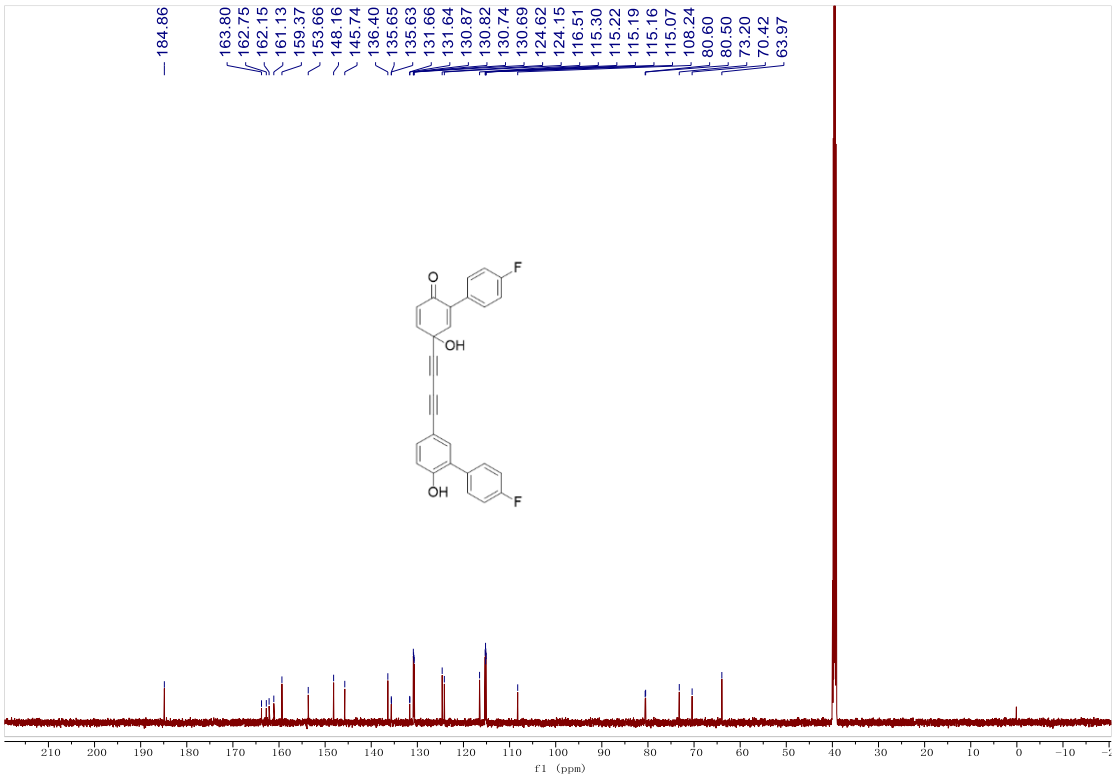
^{1}H and ^{13}C NMR spectra of compound **(4j)**



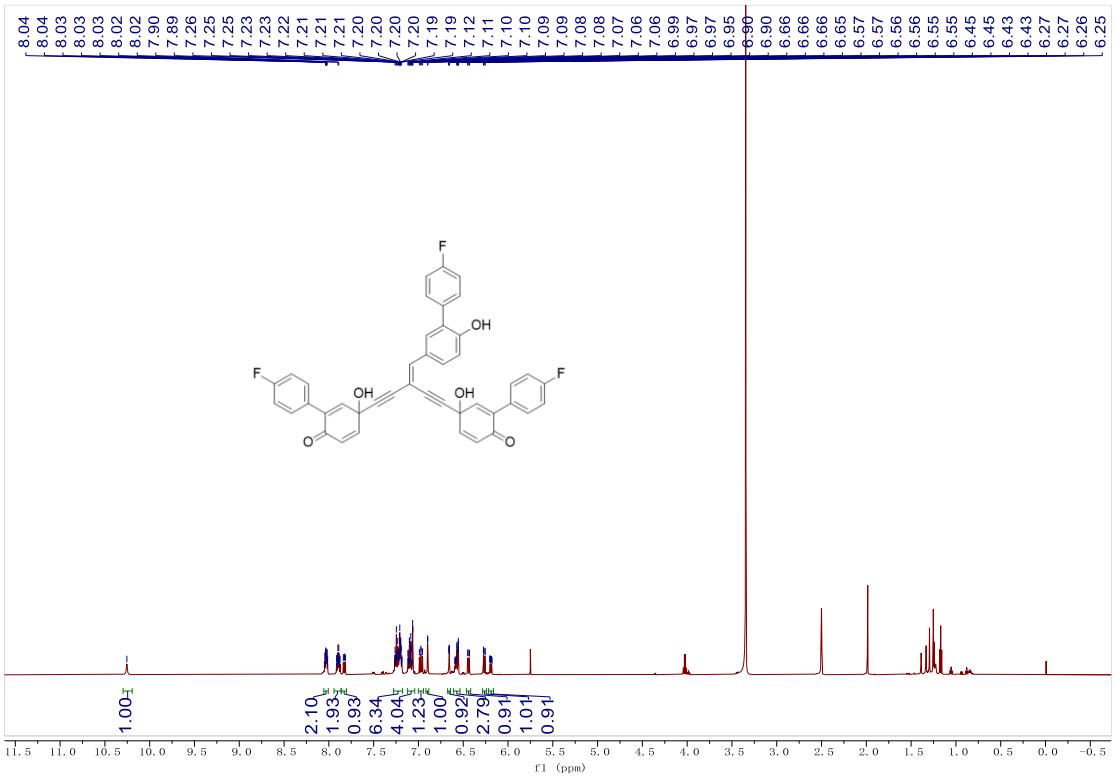


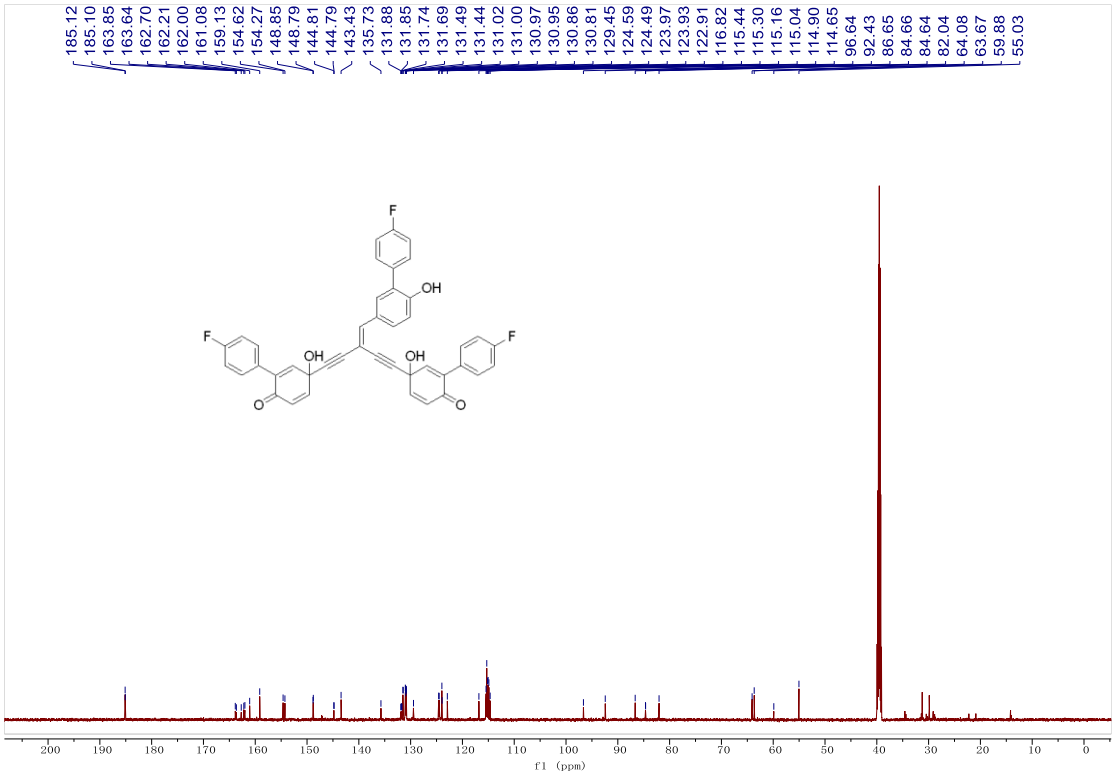
^{1}H and ^{13}C NMR spectra of compound **(3k)**



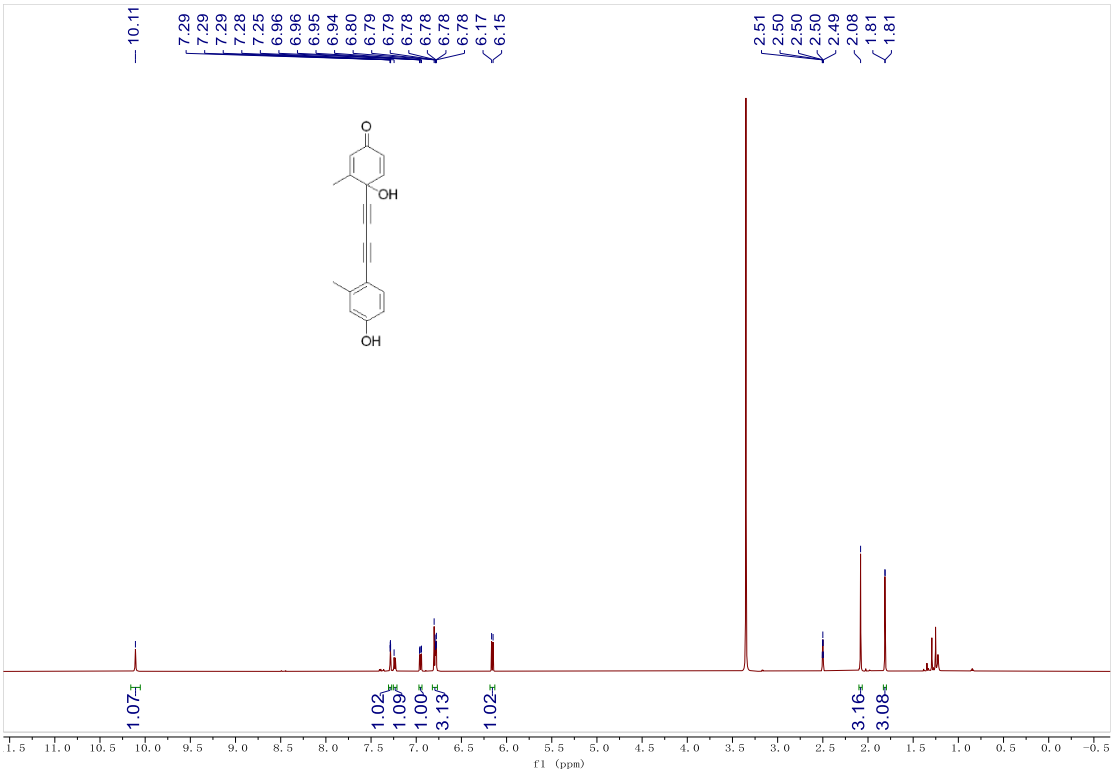


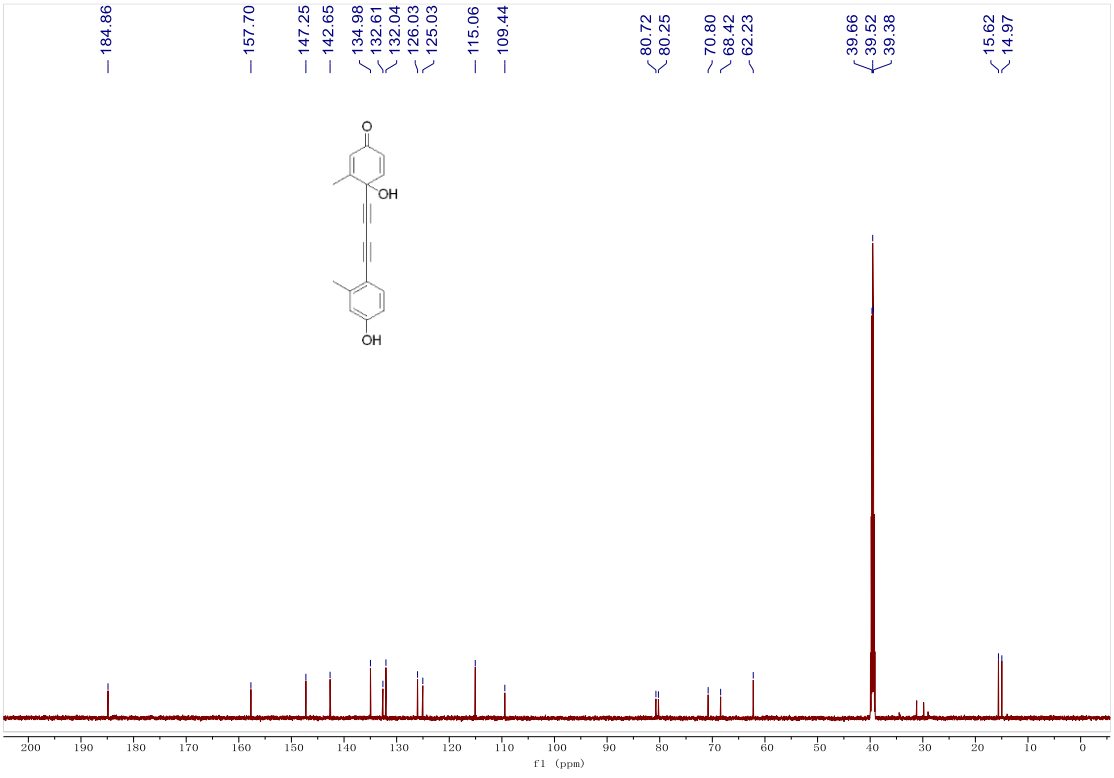
^{1}H and ^{13}C NMR spectra of compound **(4k)**



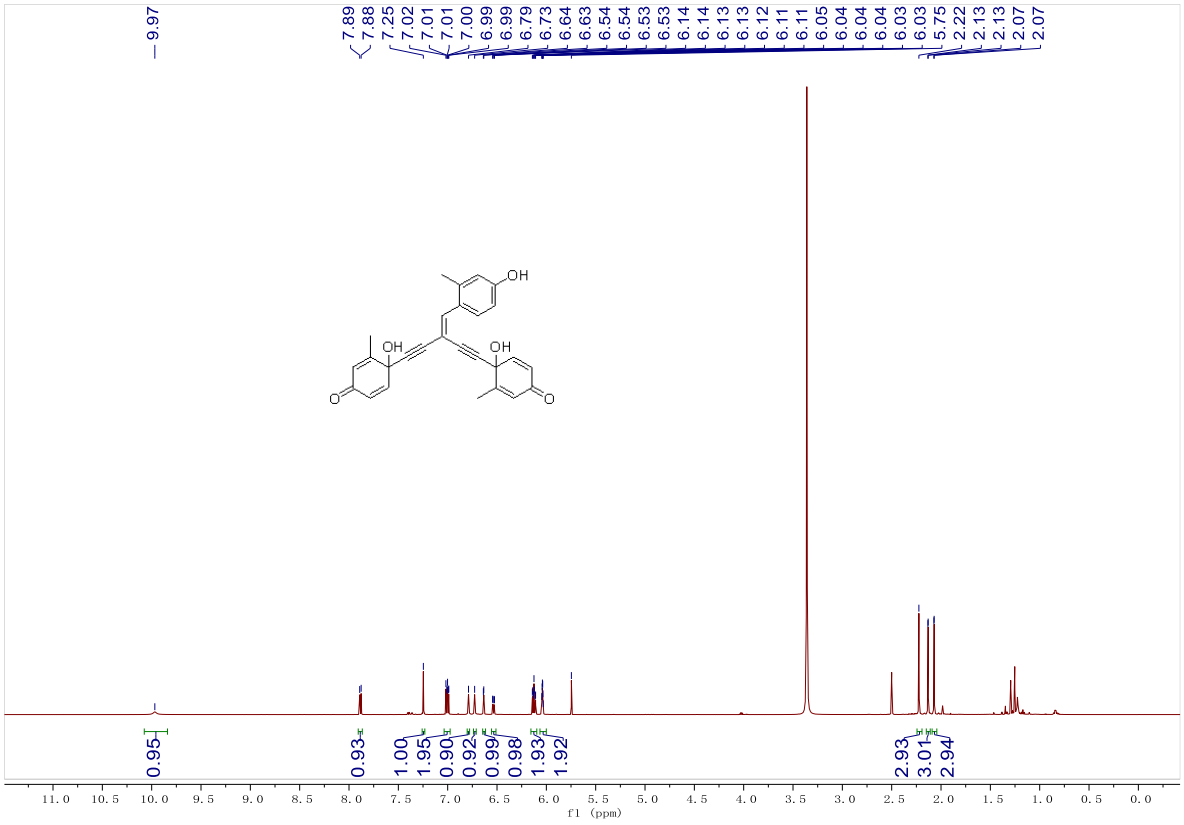


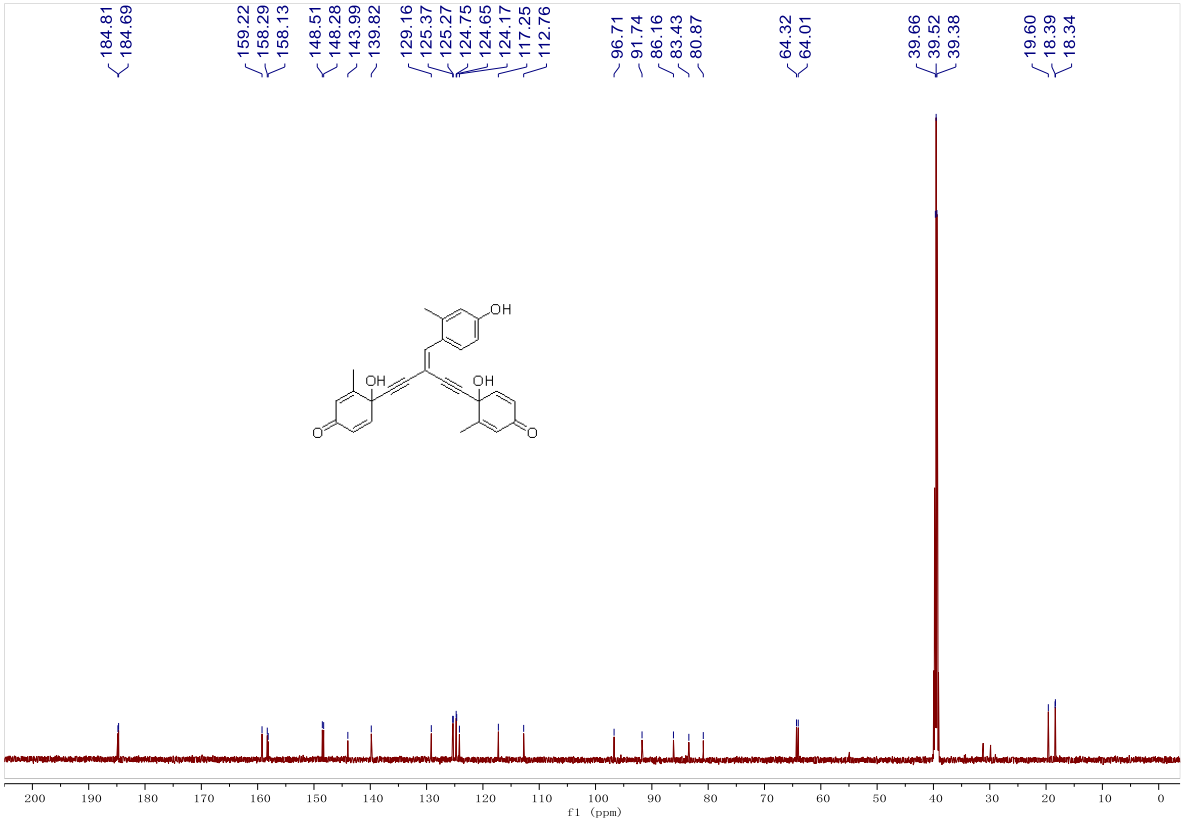
^{1}H and ^{13}C NMR spectra of compound **(3l)**



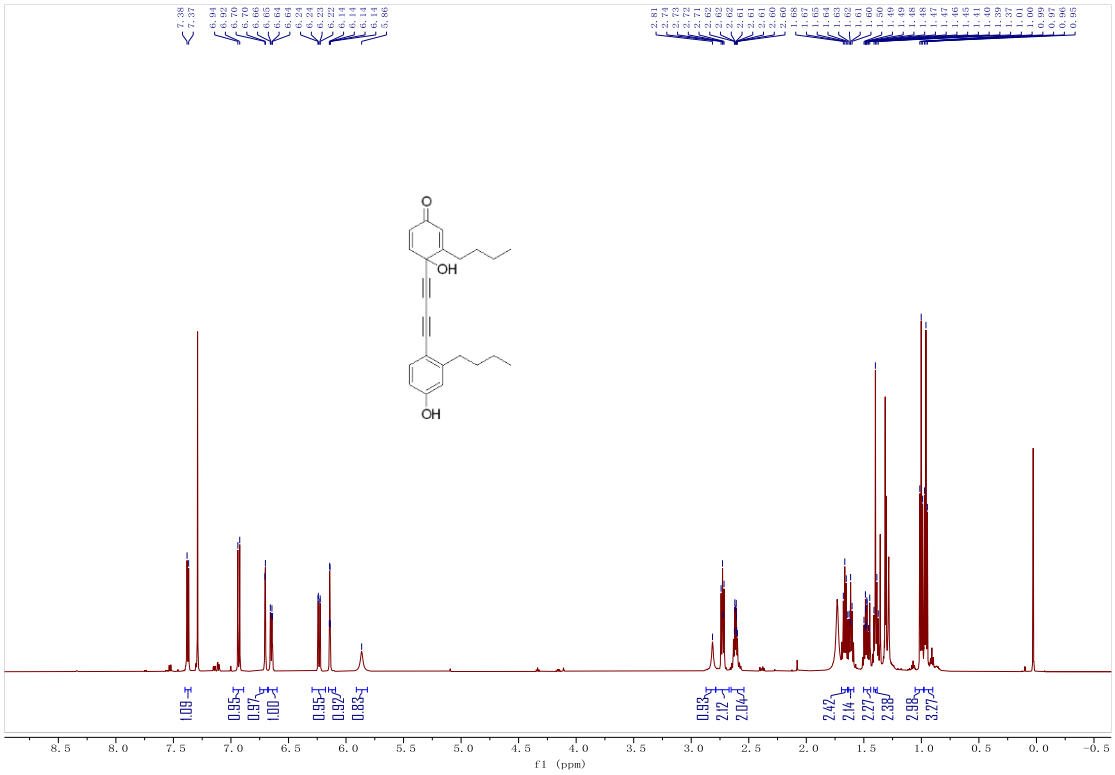


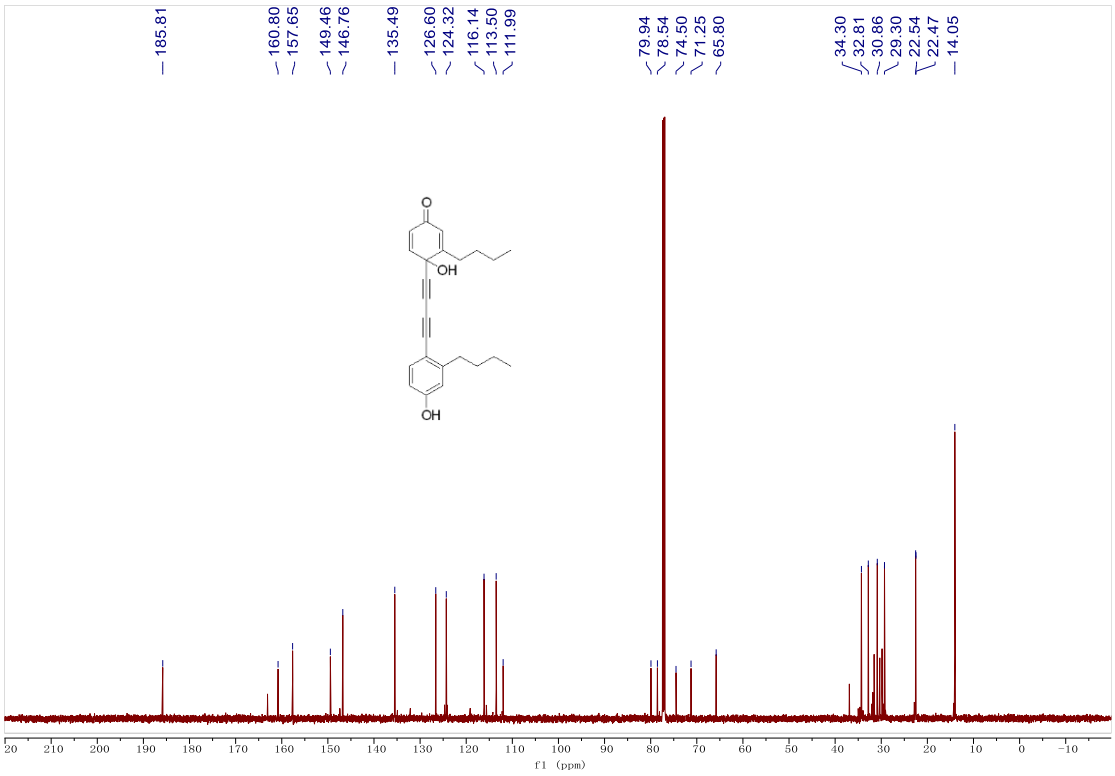
^{1}H and ^{13}C NMR spectra of compound **(4l)**



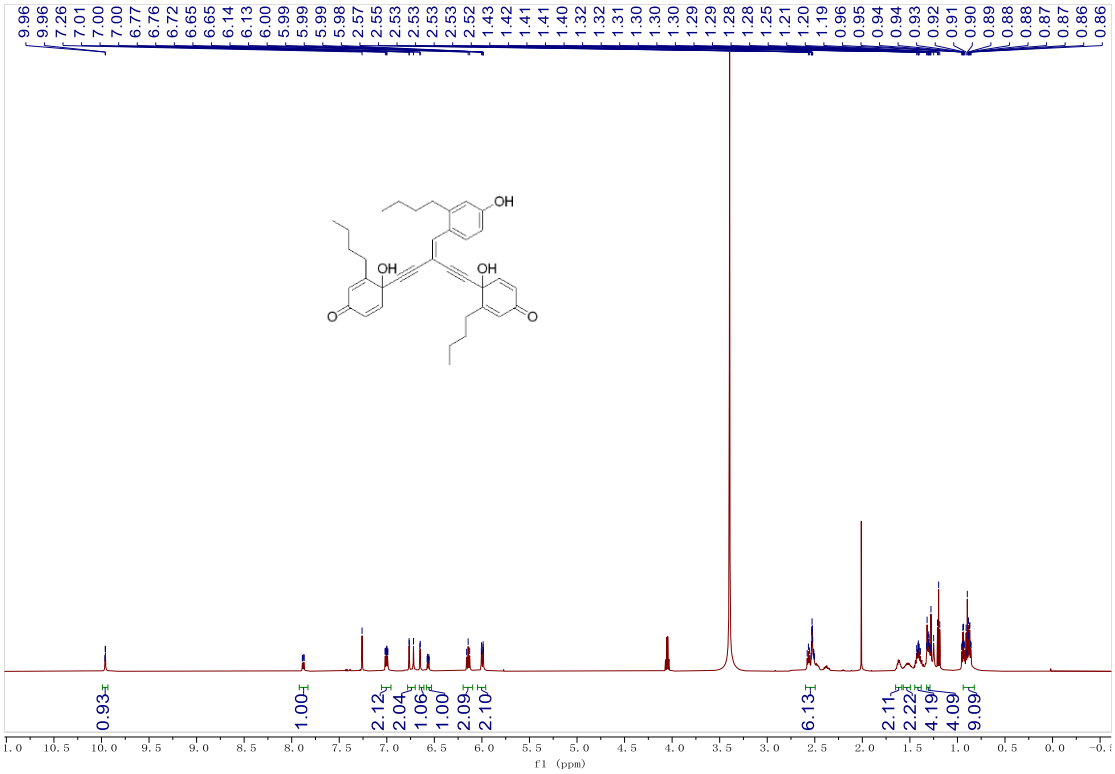


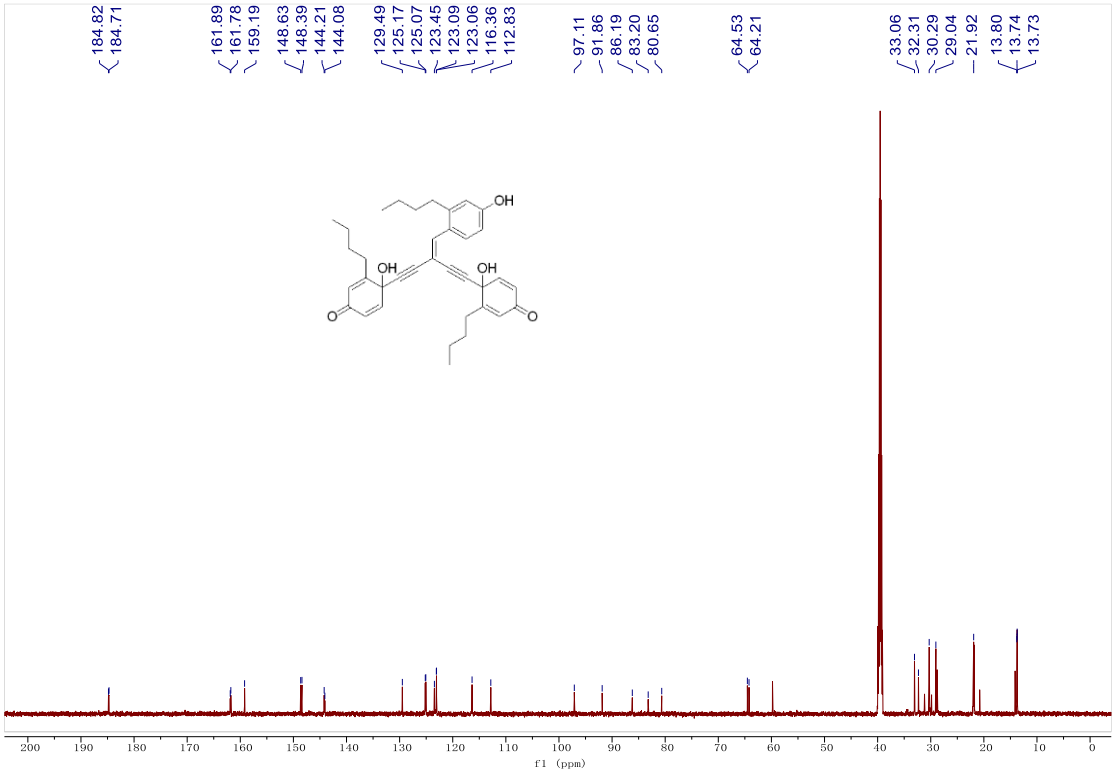
^{1}H and ^{13}C NMR spectra of compound **(3m)**



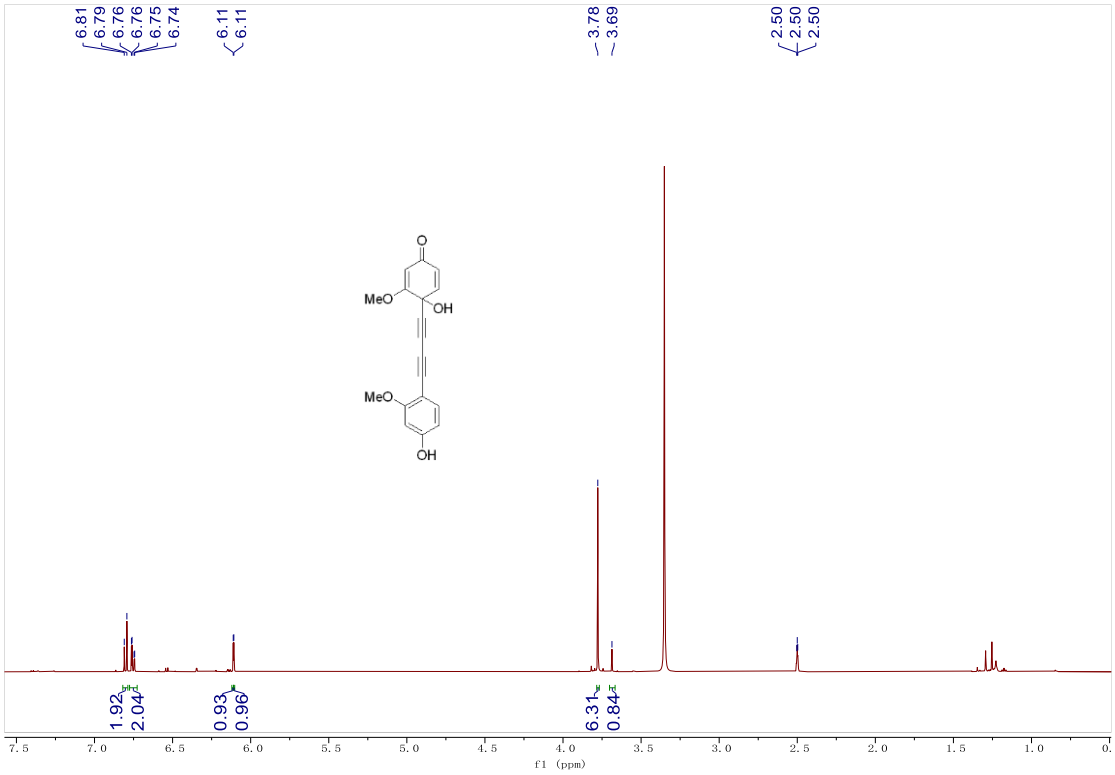


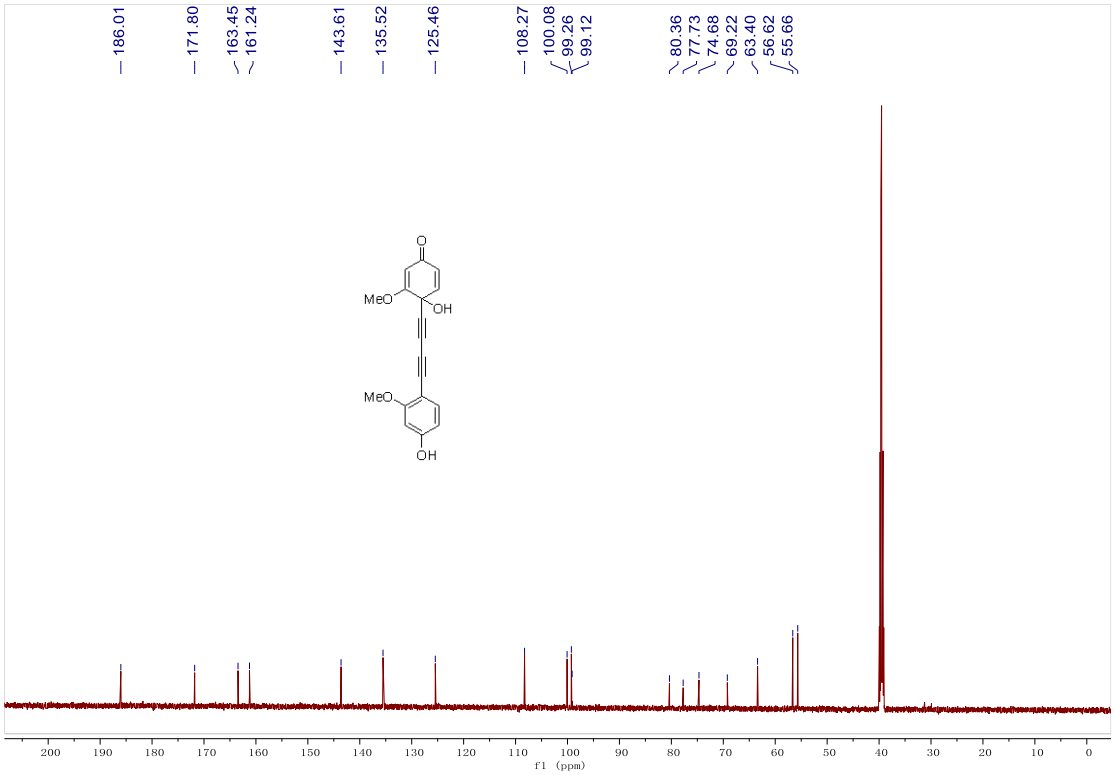
^{1}H and ^{13}C NMR spectra of compound **(4m)**



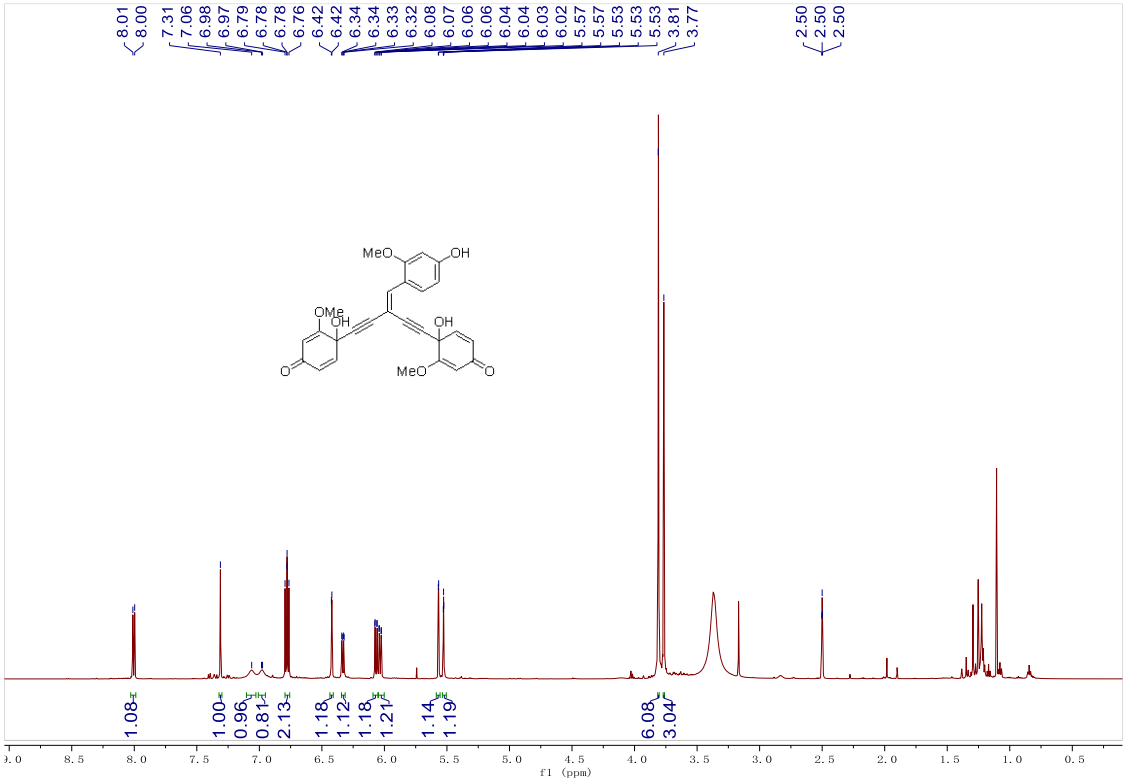


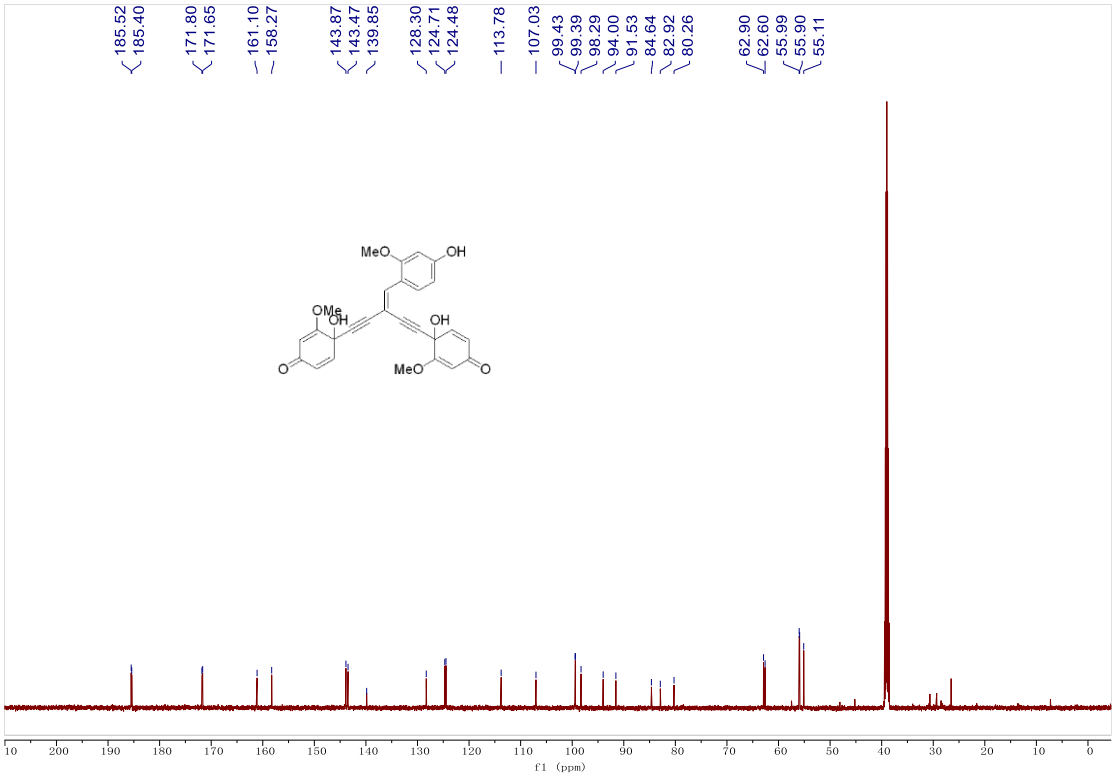
^{1}H and ^{13}C NMR spectra of compound **(3n)**



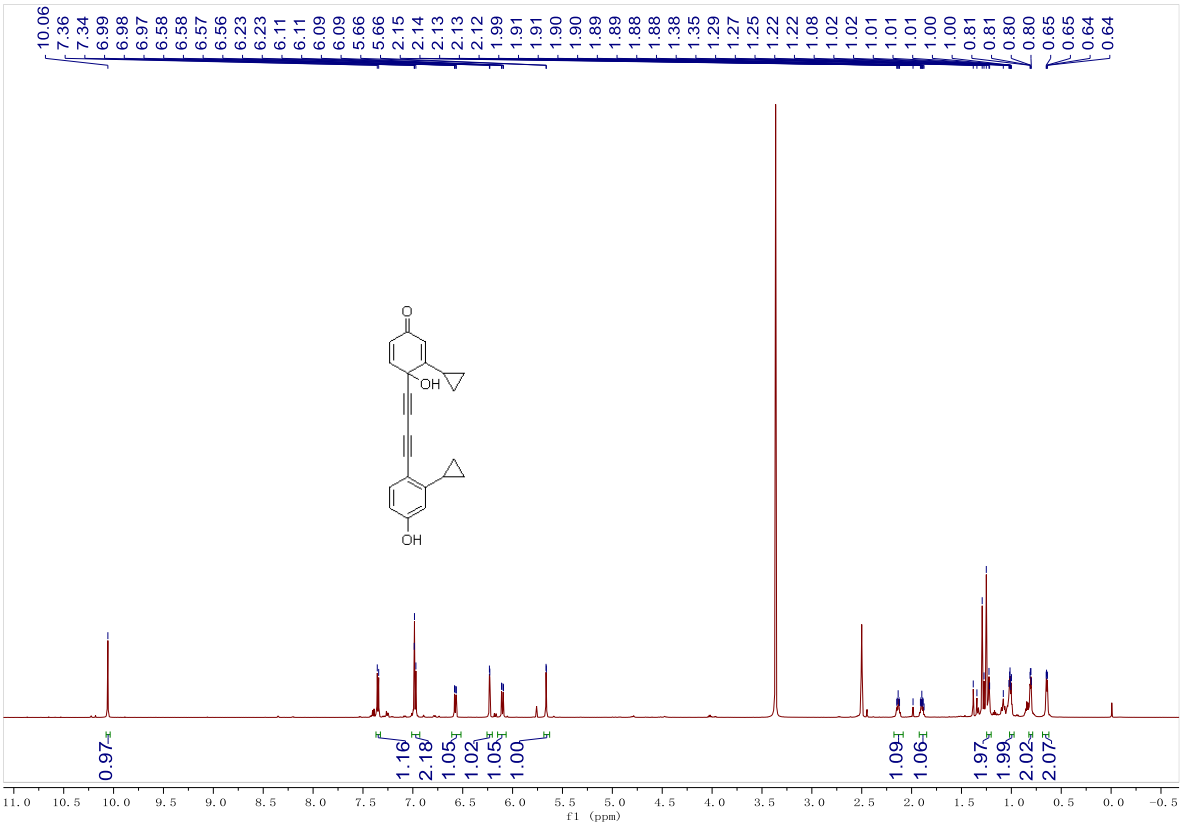


^{1}H and ^{13}C NMR spectra of compound **(4n)**





^{1}H and ^{13}C NMR spectra of compound **(3o)**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6.99
6.98
6.97
6.58
6.58
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6.56
6.23
6.23
6.11
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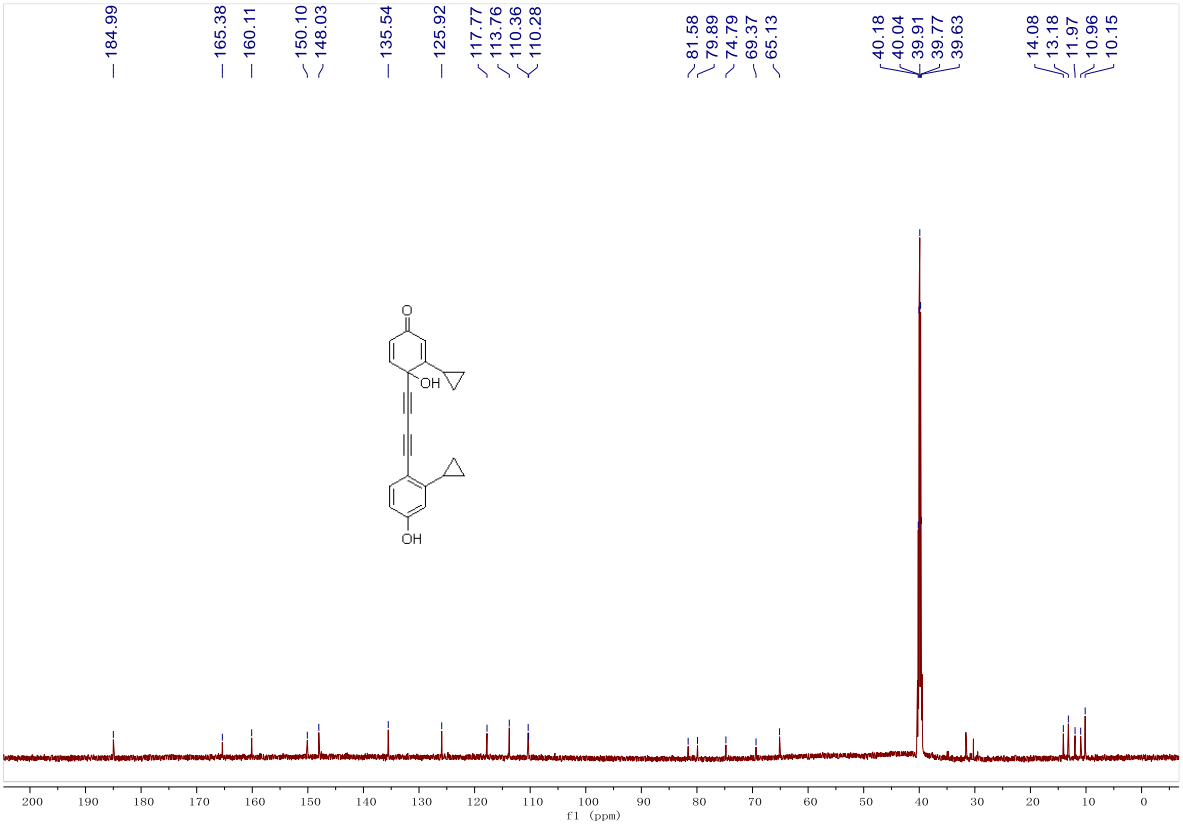
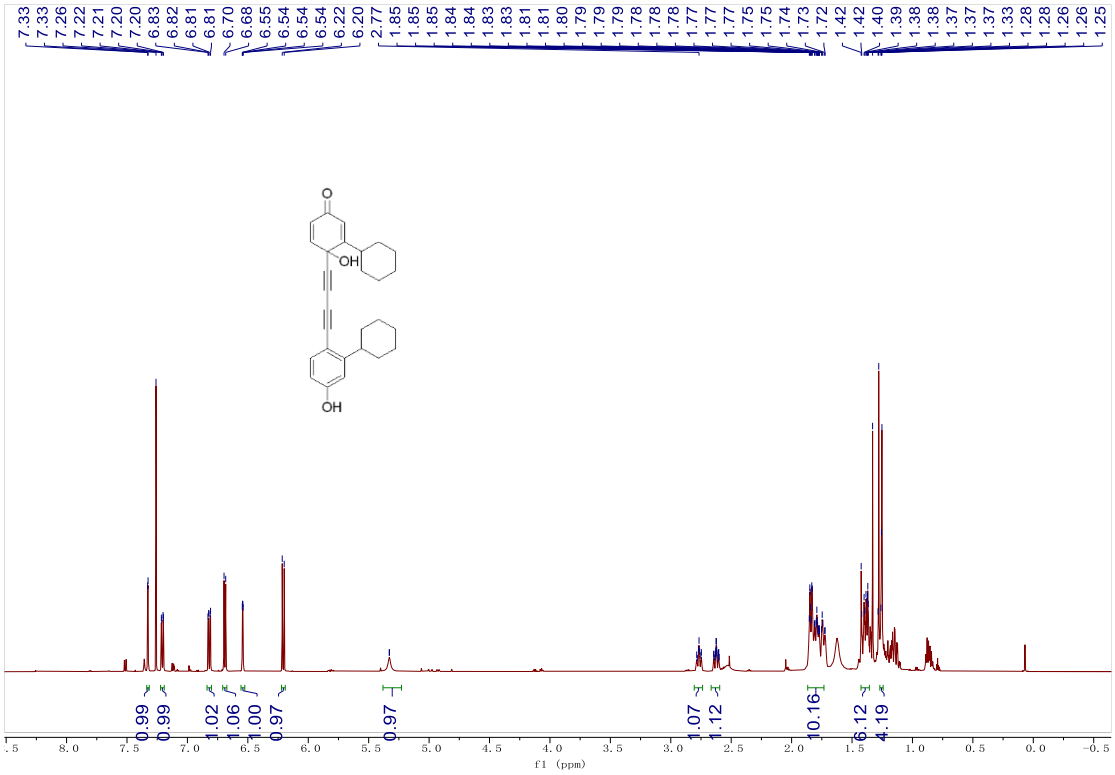
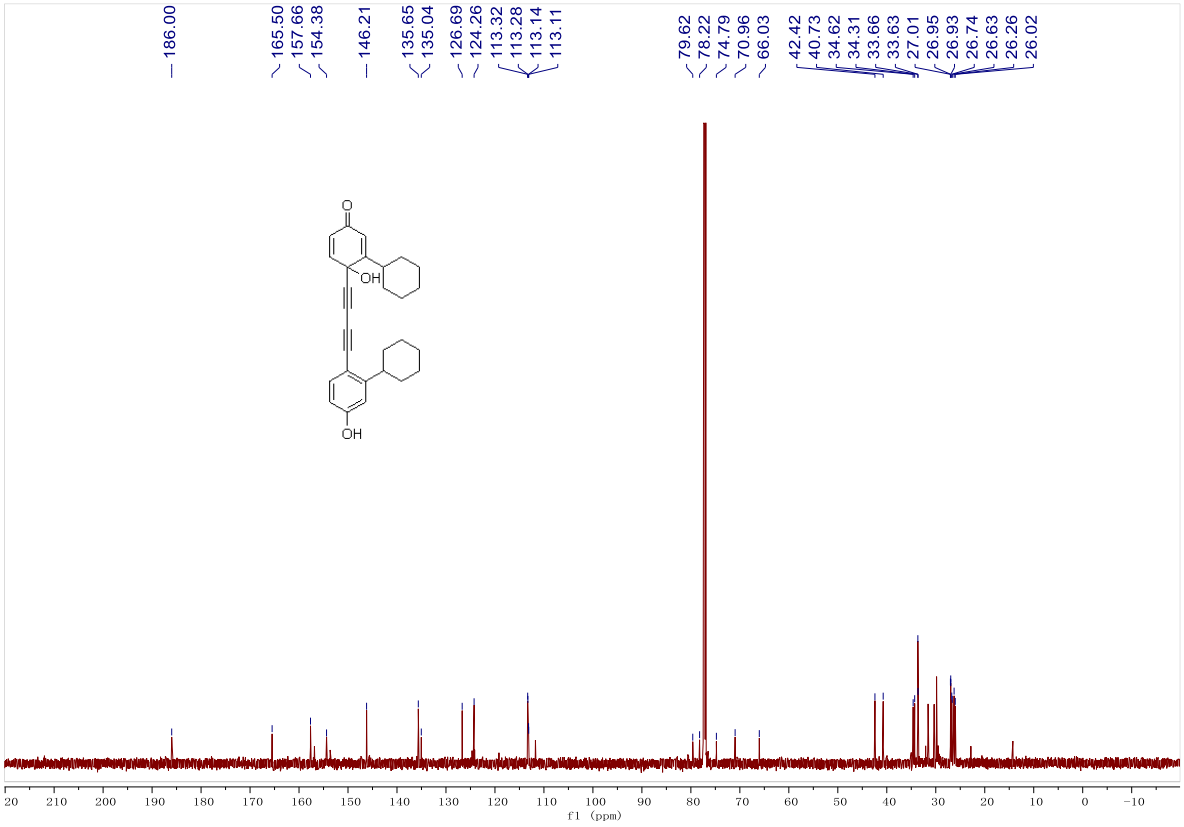
6.09
6.09
5.66
2.15
2.14
2.13
2.13
2.12
1.99
1.91
1.91
1.90
1.90
1.89
1.89
1.88
1.88
1.38
1.35
1.29
1.27
1.25
1.22
1.22
1.08
1.02
1.02
1.01
1.01
1.01
1.00
1.00
0.81
0.81
0.80
0.80
0.65
0.65
0.64
0.64
O
OH
OH
0.97
1.16
2.18
1.05
1.02
1.05
1.00
1.09
1.06
1.97
1.99
2.02
2.07
f1 (ppm)

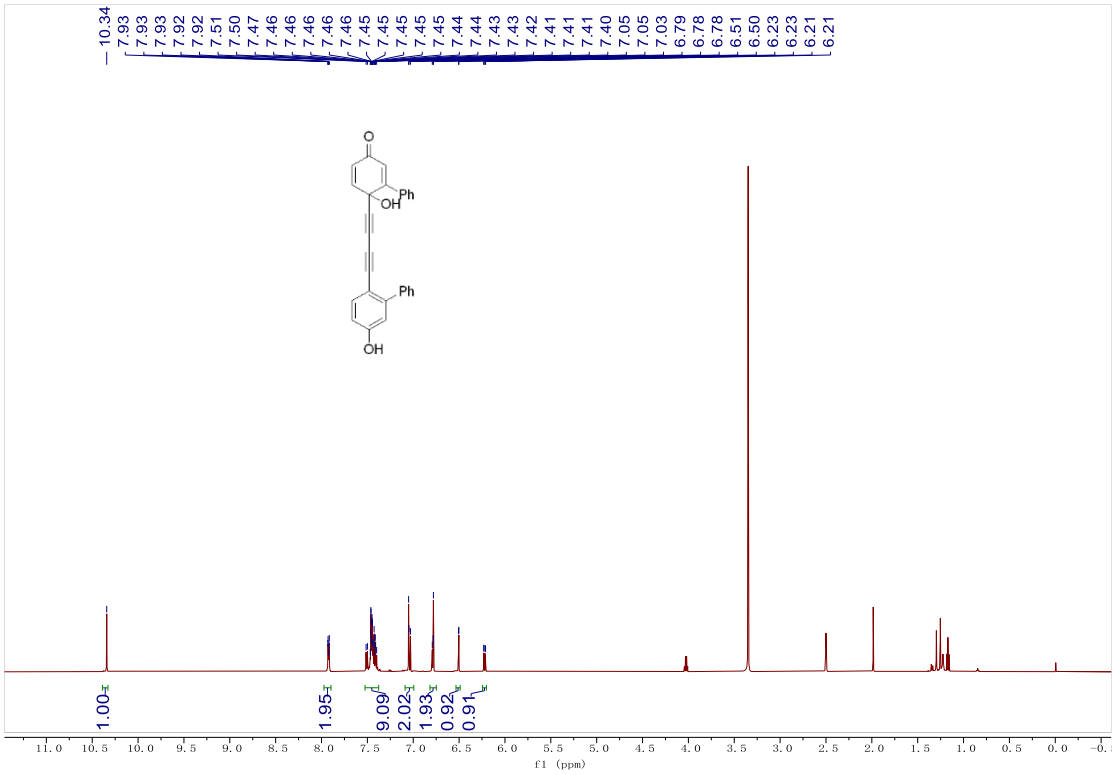

184.99
165.38
160.11
150.10
148.03
135.54
125.92
117.77
113.76
110.36
110.28
81.58
79.89
74.79
69.37
65.13
40.18
40.04
39.91
39.77
39.63
14.08
13.18
11.97
10.96
10.15
O
OH
OH
f1 (ppm)

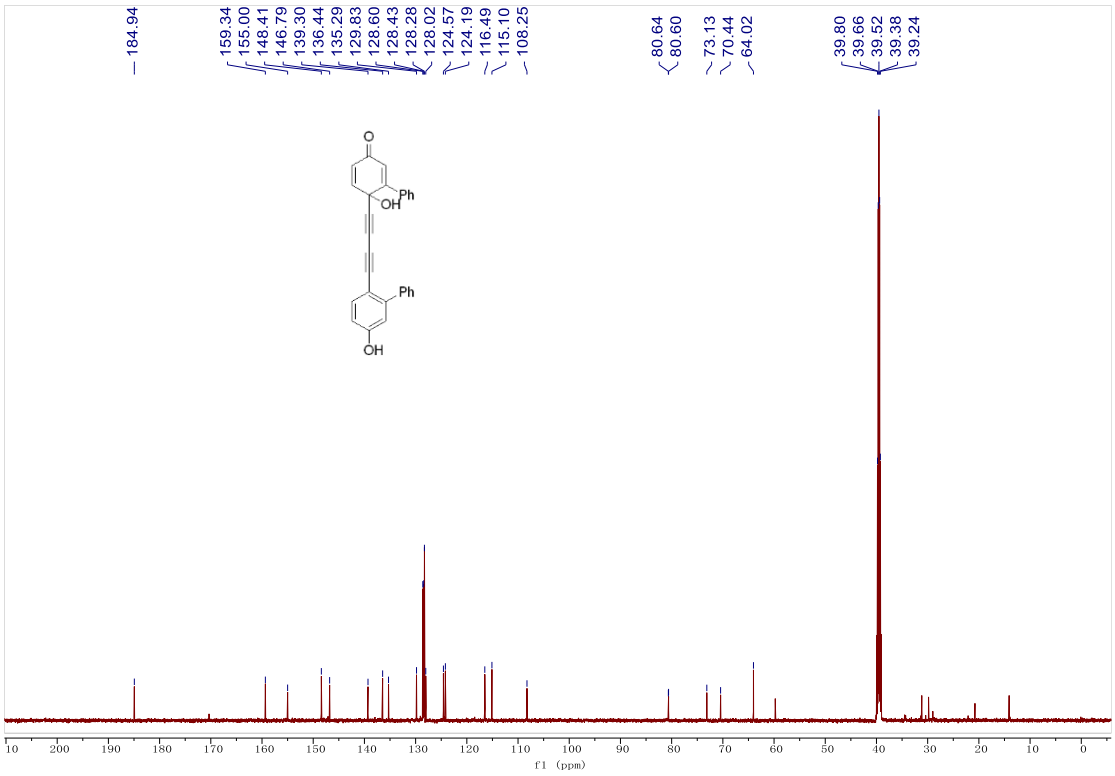
^{1}H and ^{13}C NMR spectra of compound **(3p)**



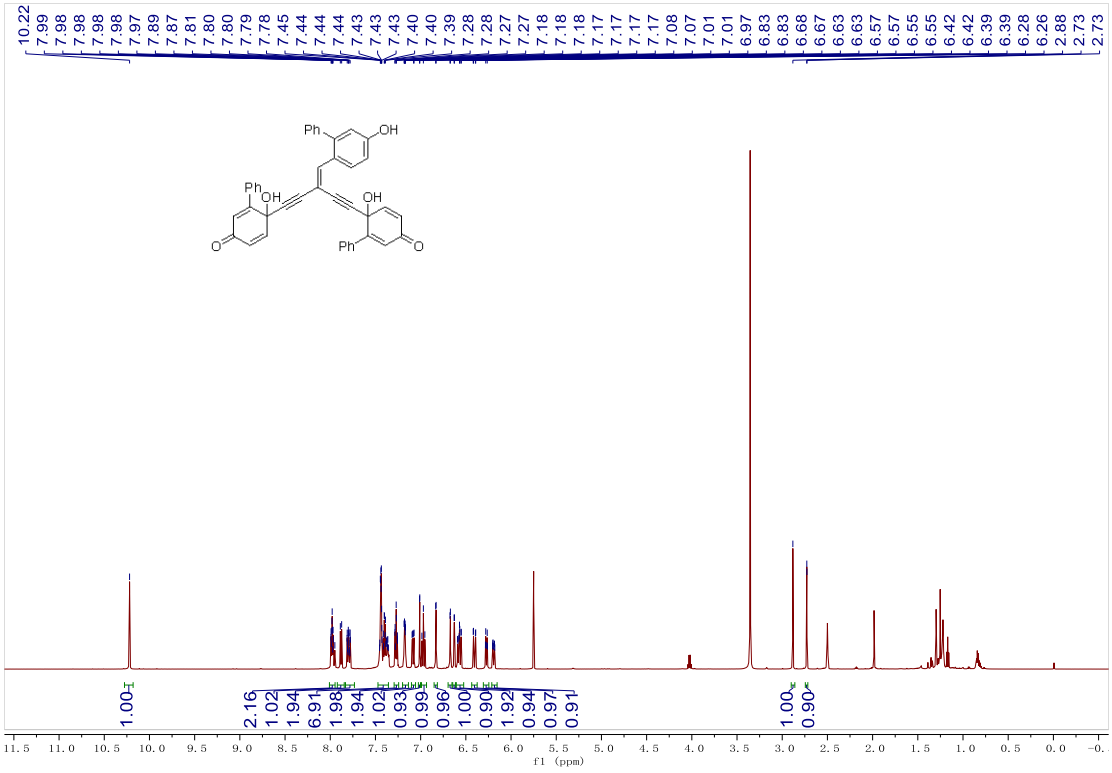


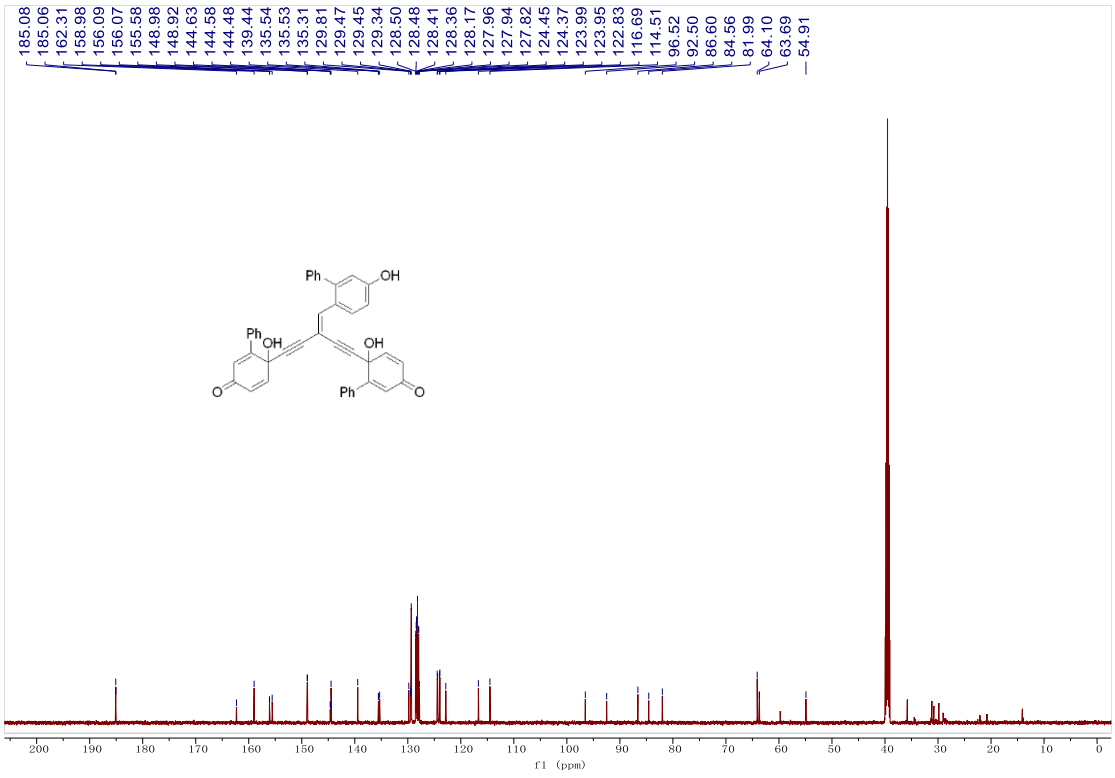
^{1}H and ^{13}C NMR spectra of compound **(3q)**



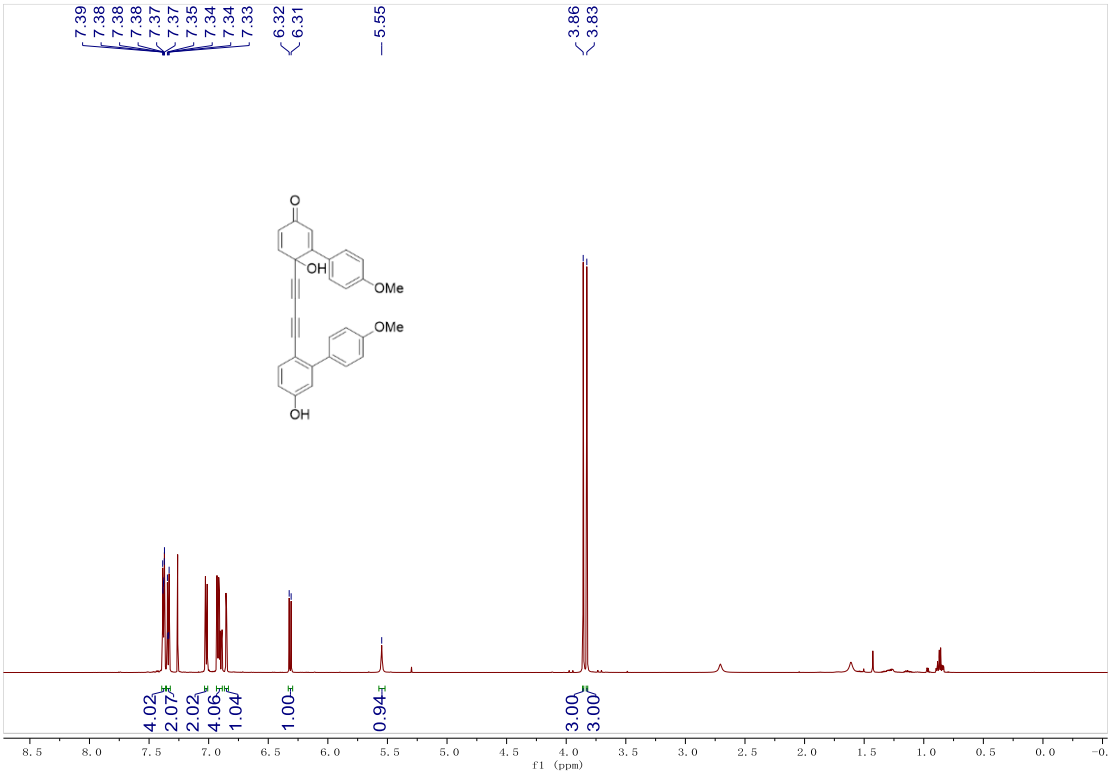


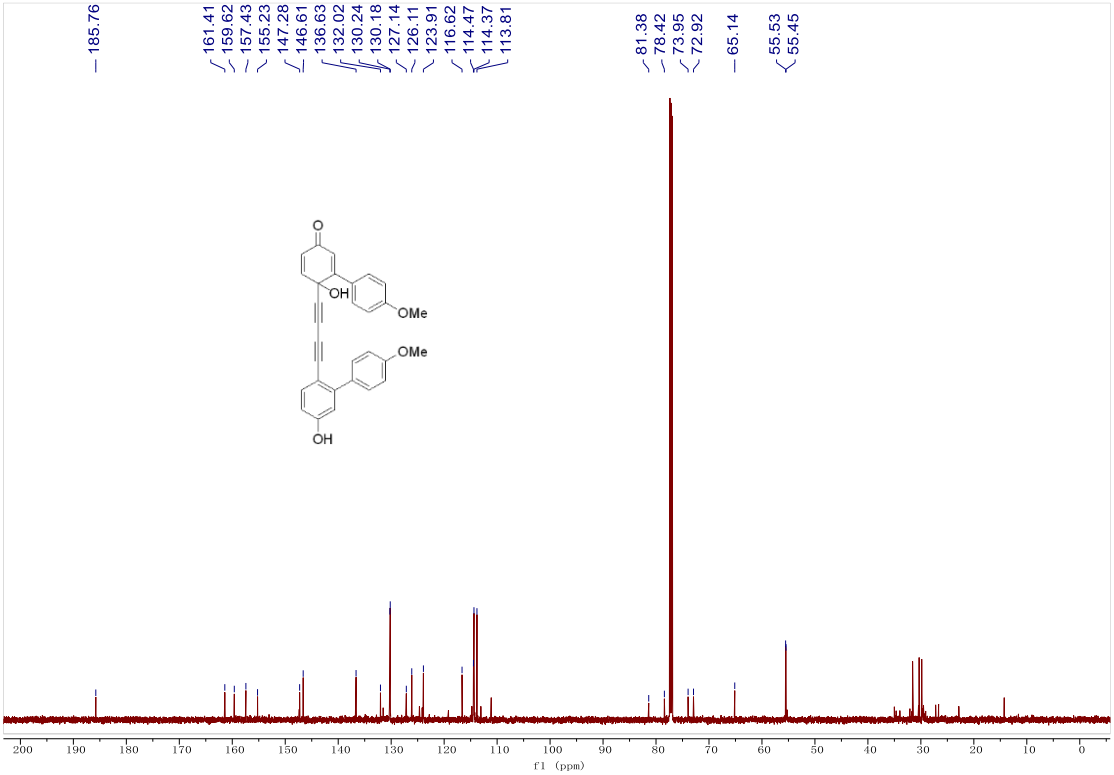
^{1}H and ^{13}C NMR spectra of compound **(4q)**



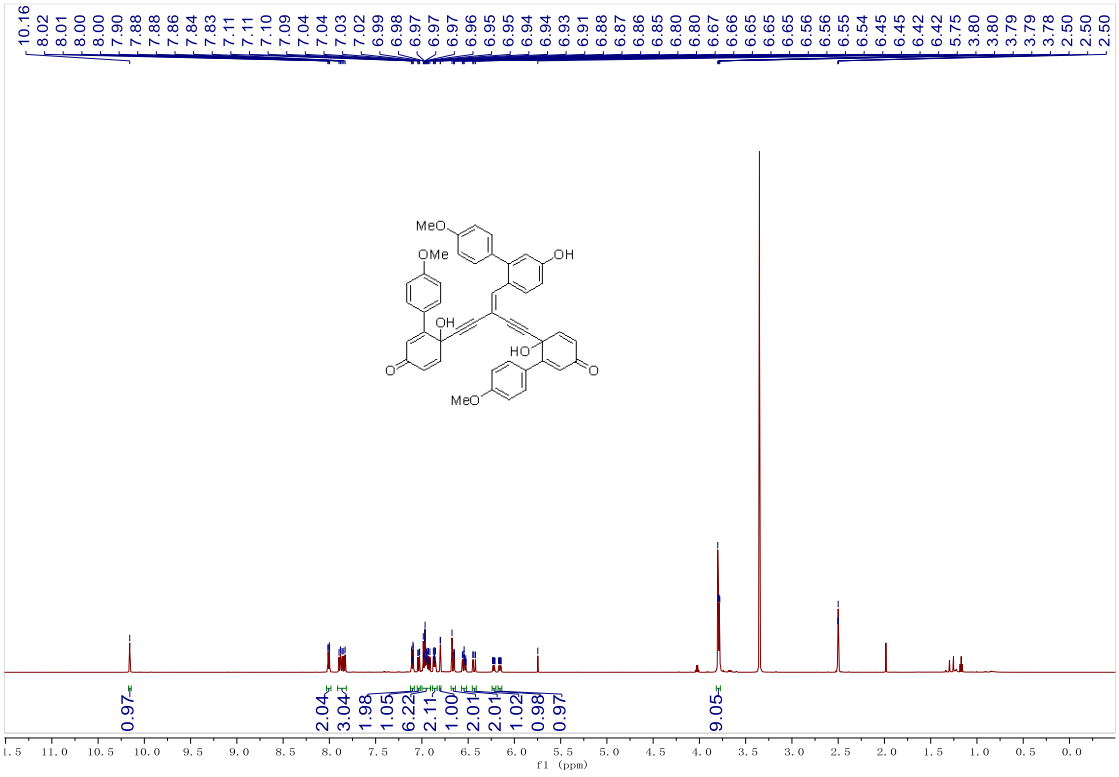


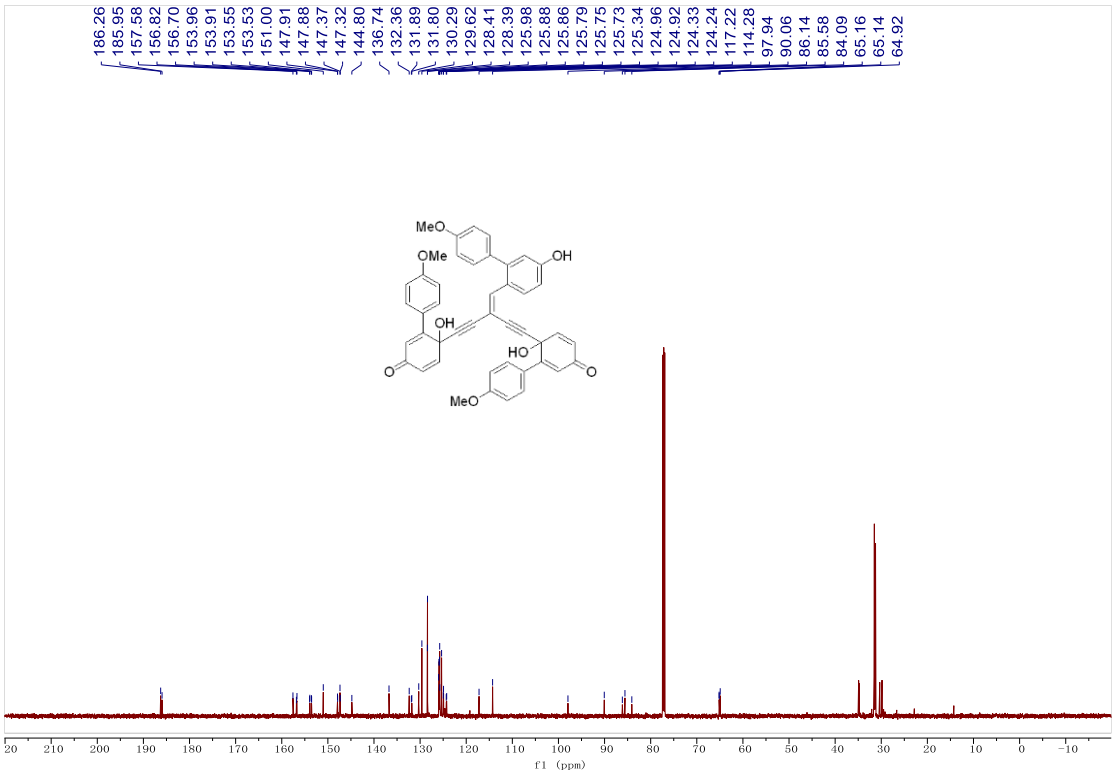
^{1}H and ^{13}C NMR spectra of compound **(3r)**



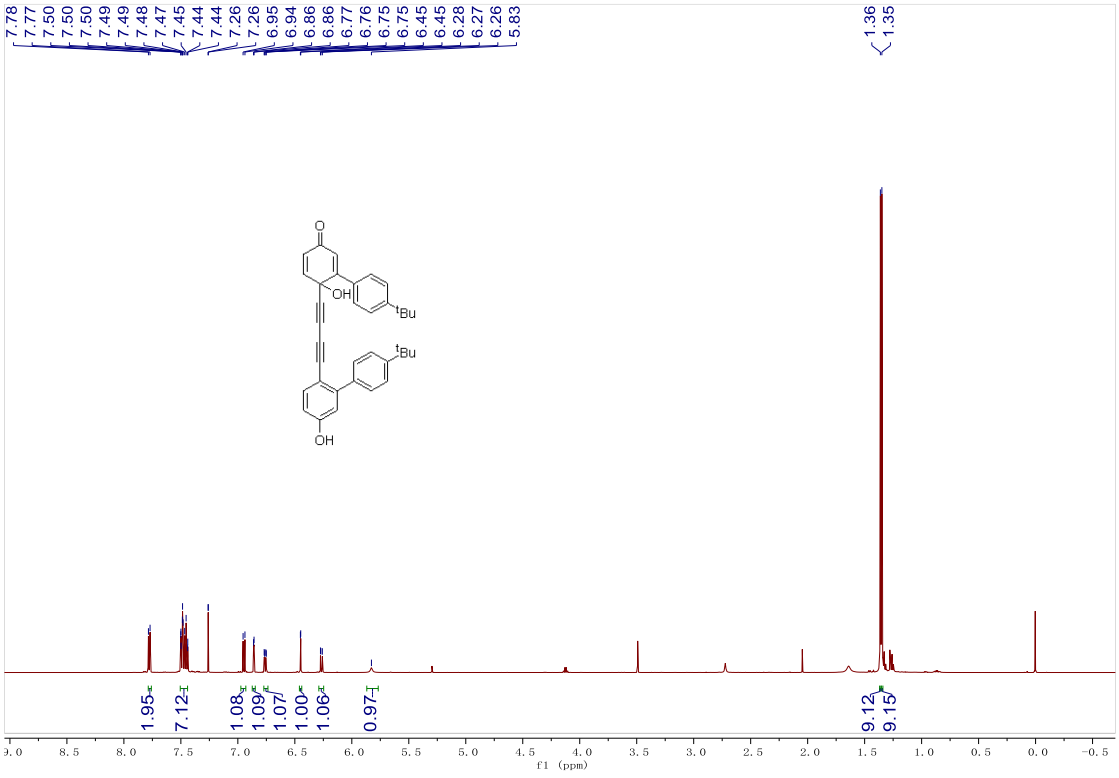


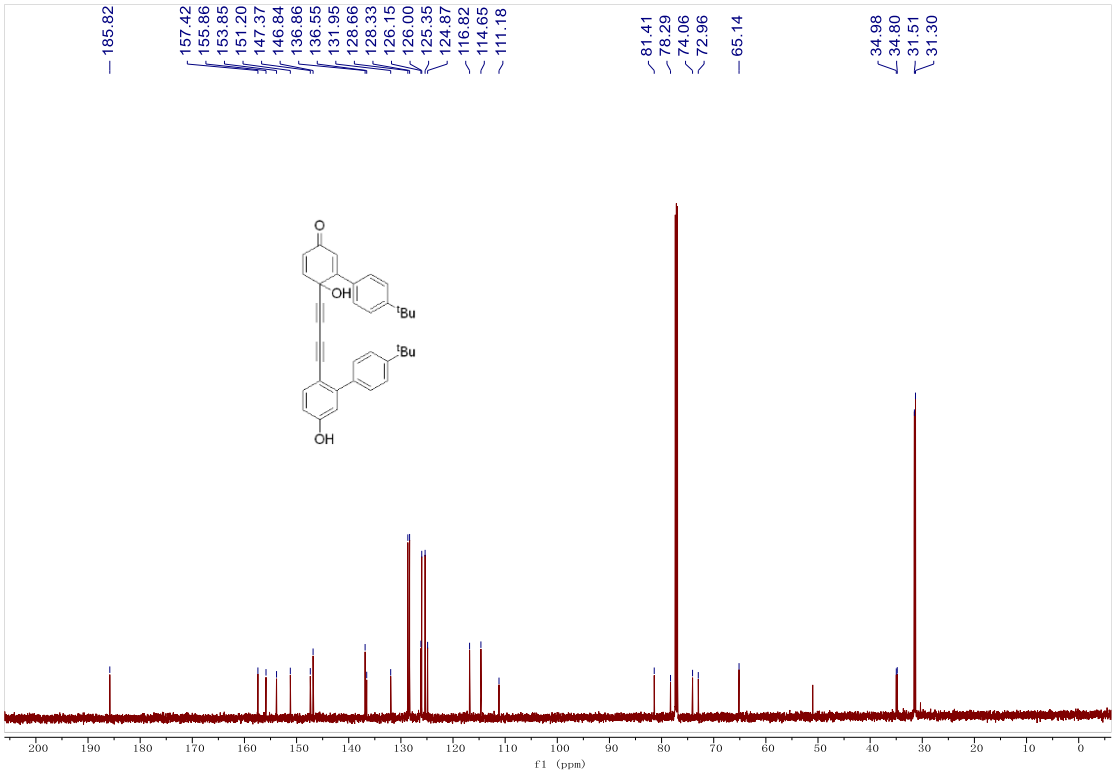
^{1}H and ^{13}C NMR spectra of compound **(4r)**



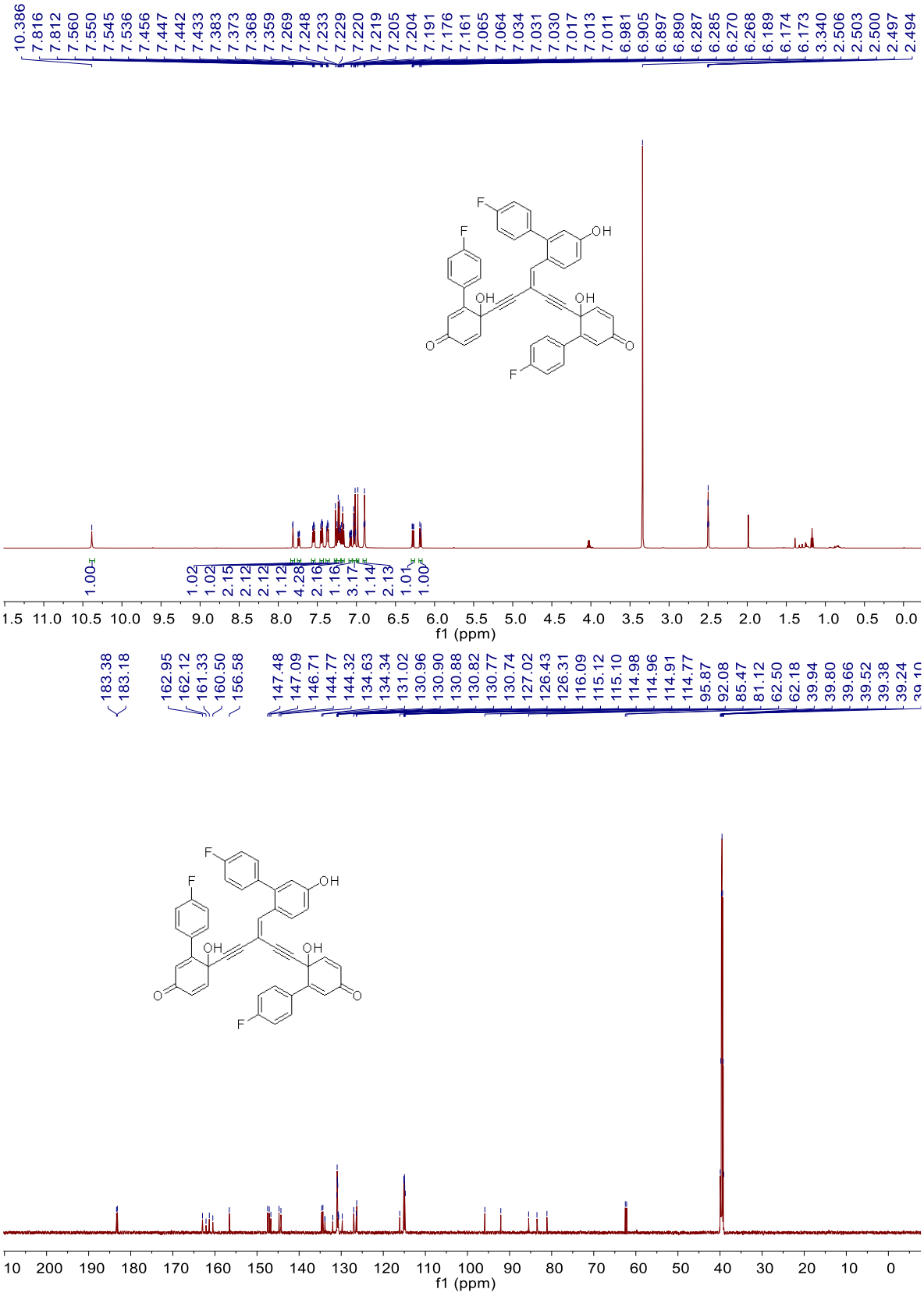


^{1}H and ^{13}C NMR spectra of compound **(3s)**

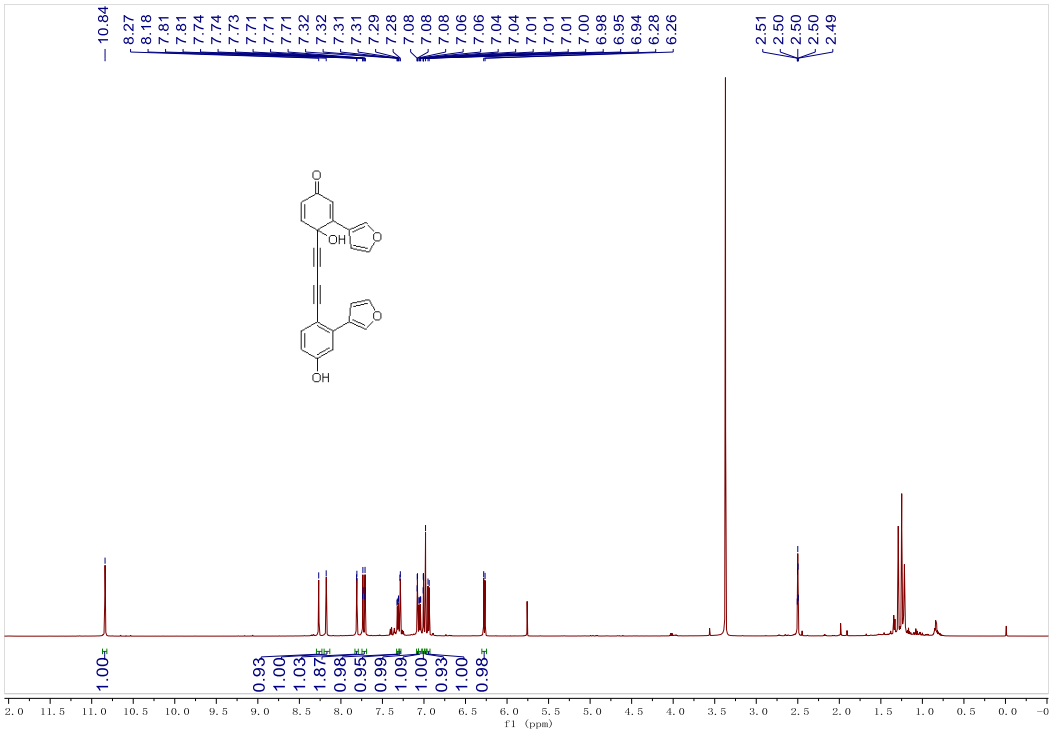


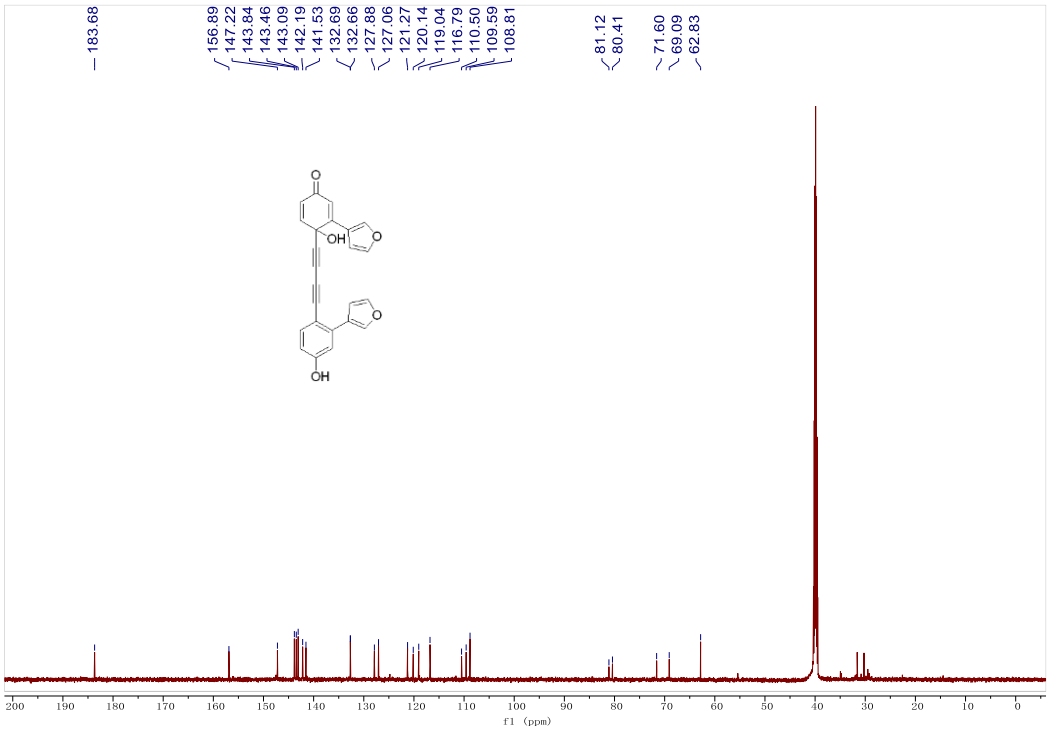


^{1}H and ^{13}C NMR spectra of compound **(4t)**

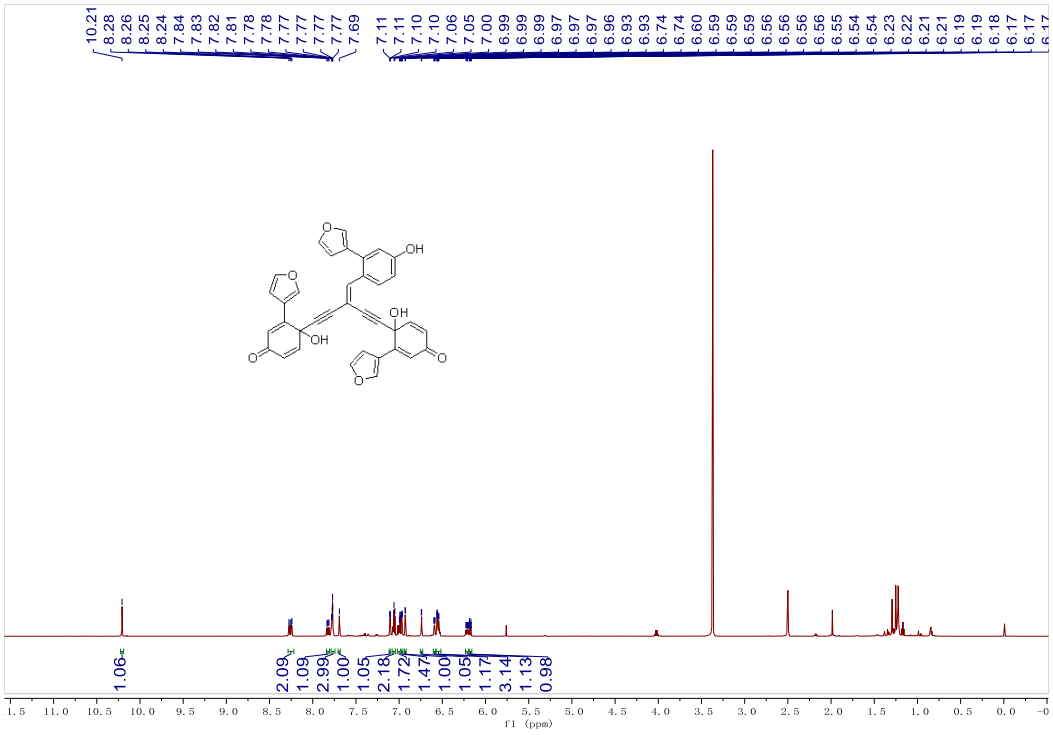


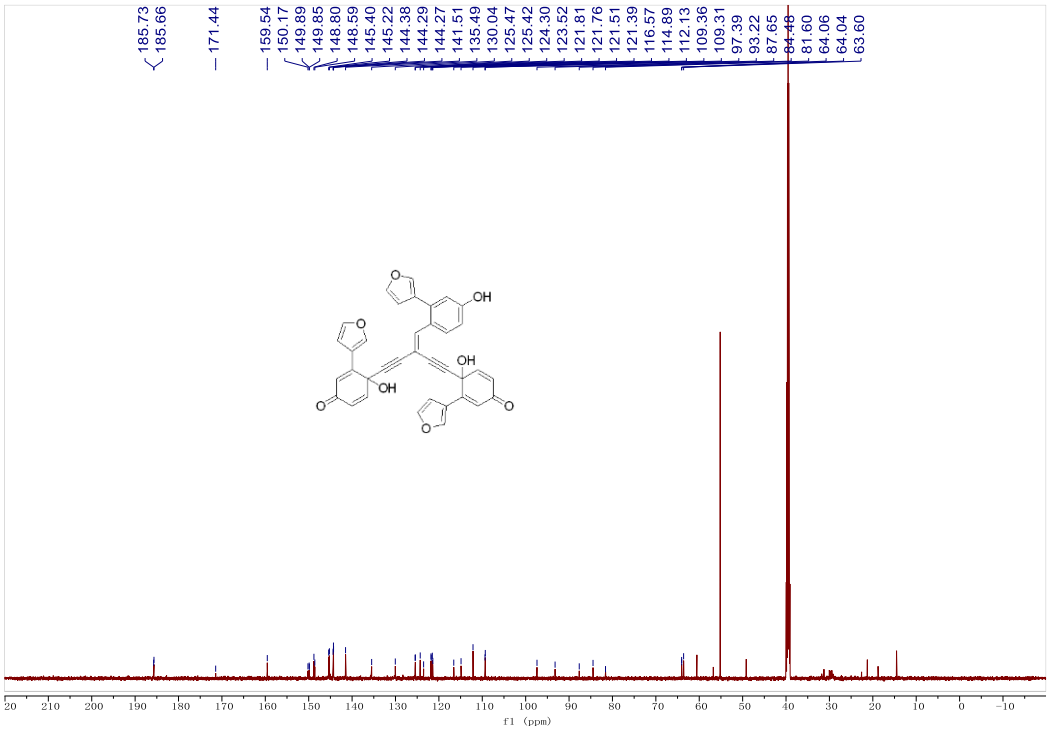
^{1}H and ^{13}C NMR spectra of compound **(3u)**





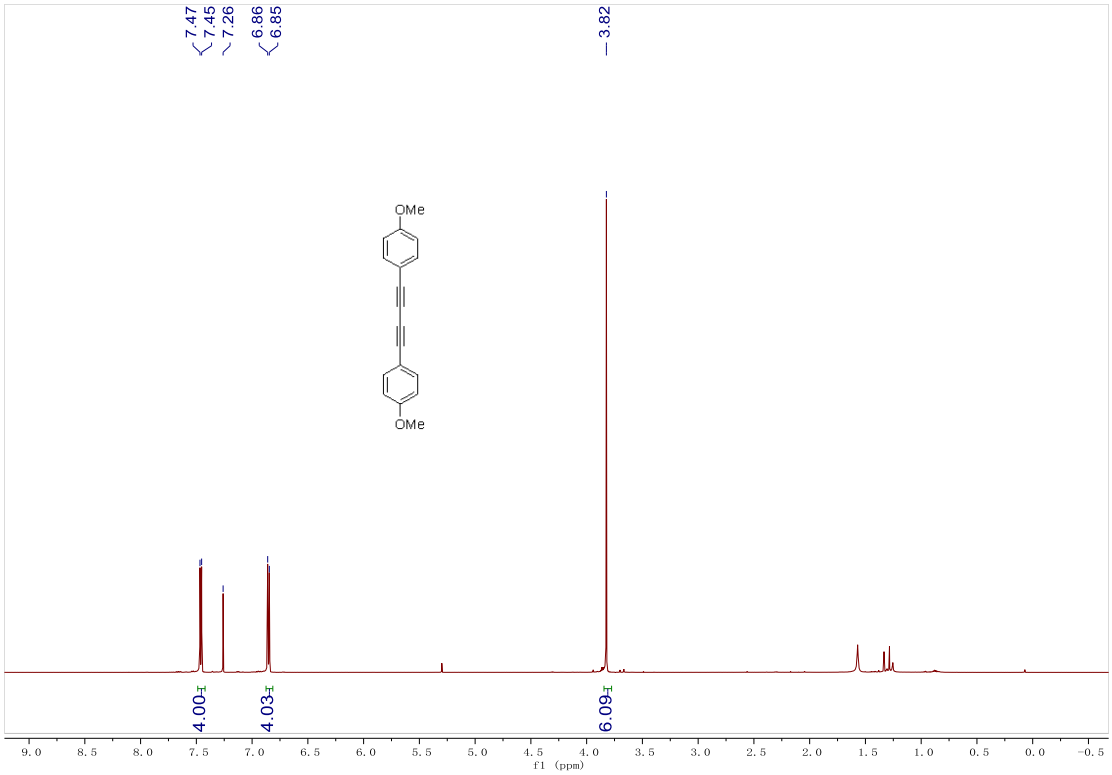
^{1}H and ^{13}C NMR spectra of compound **(4u)**



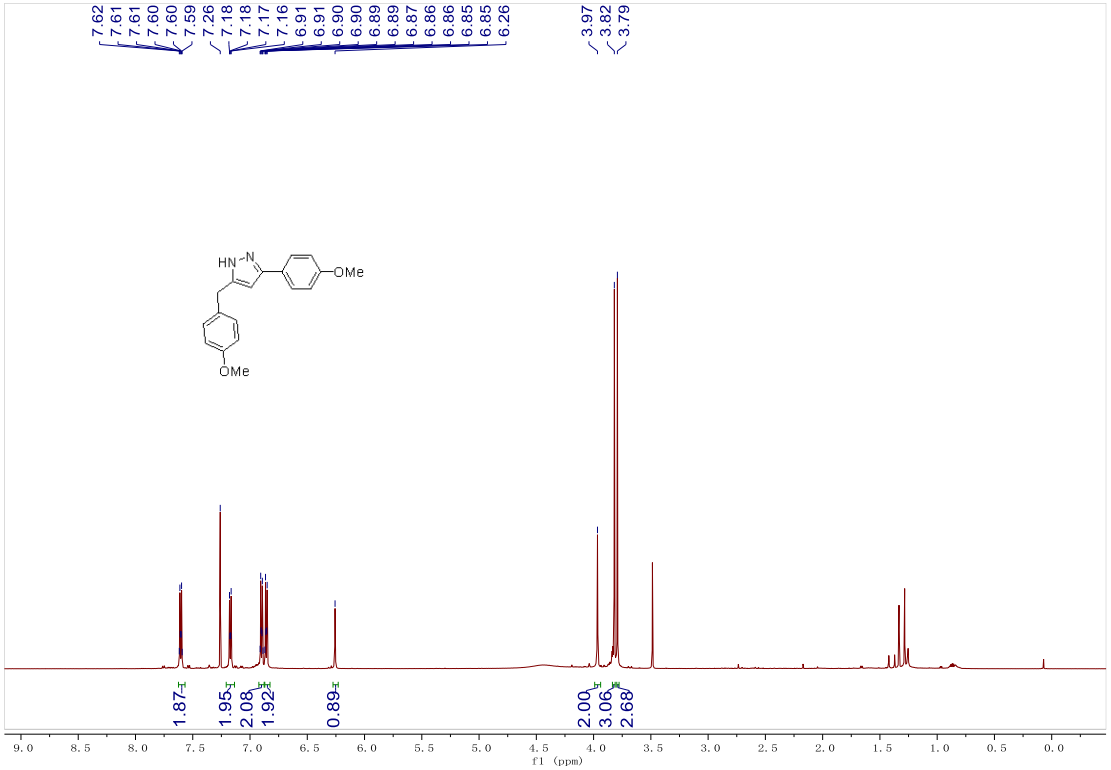


14. Copies of NMR spectra (transformations)

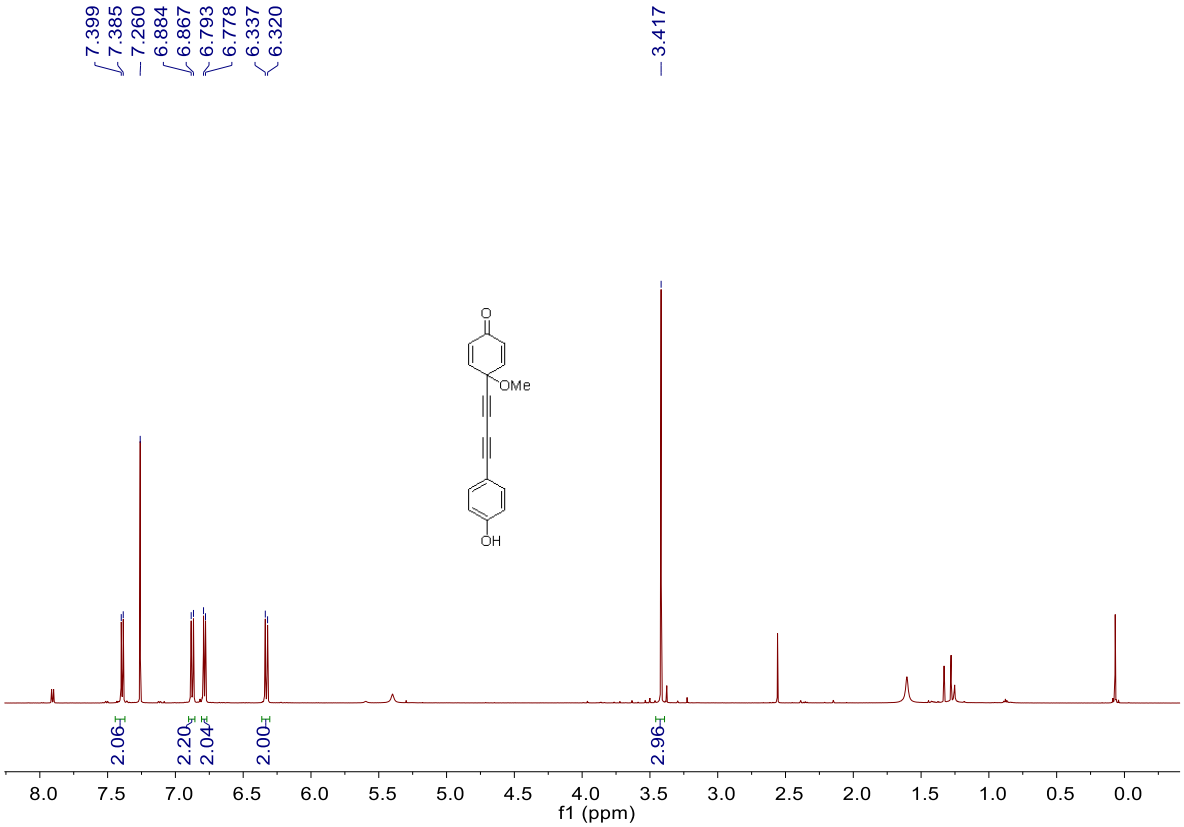
^{1}H spectra of compound **(2aa)**

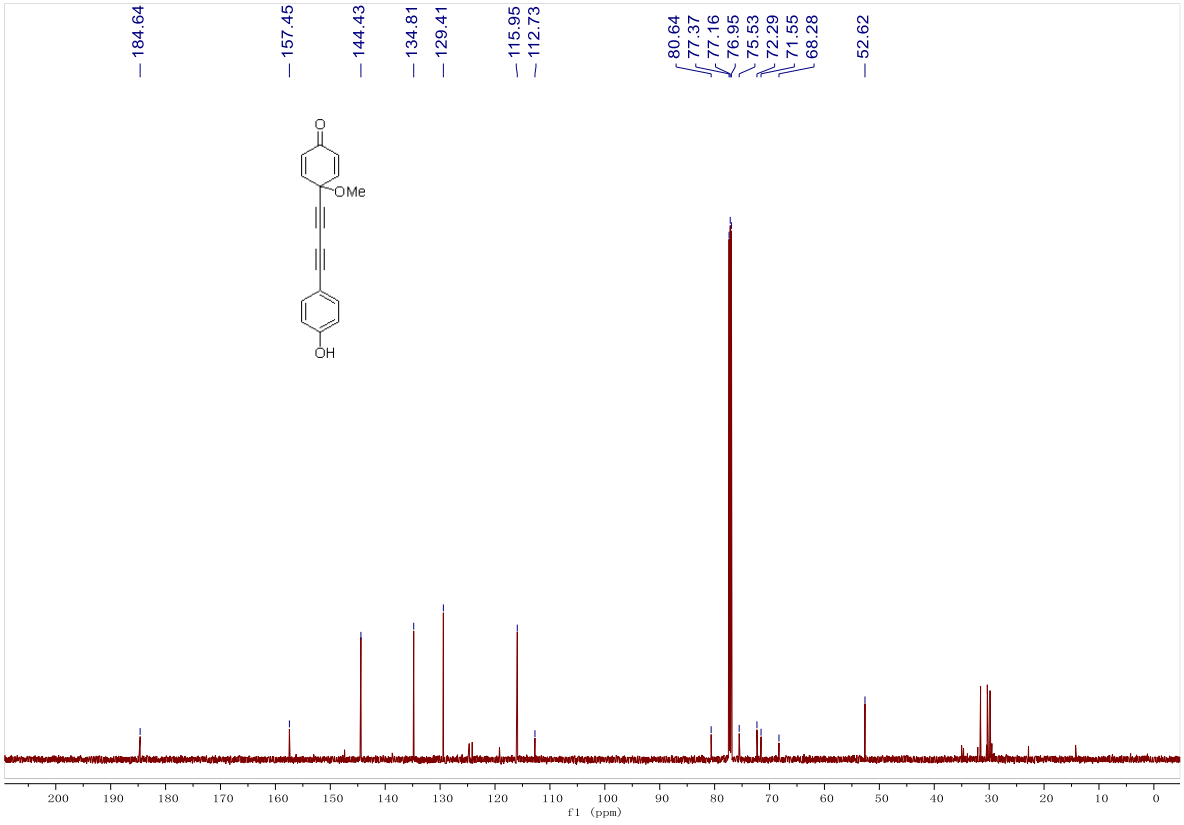


^{1}H spectra of compound **(2ab)**

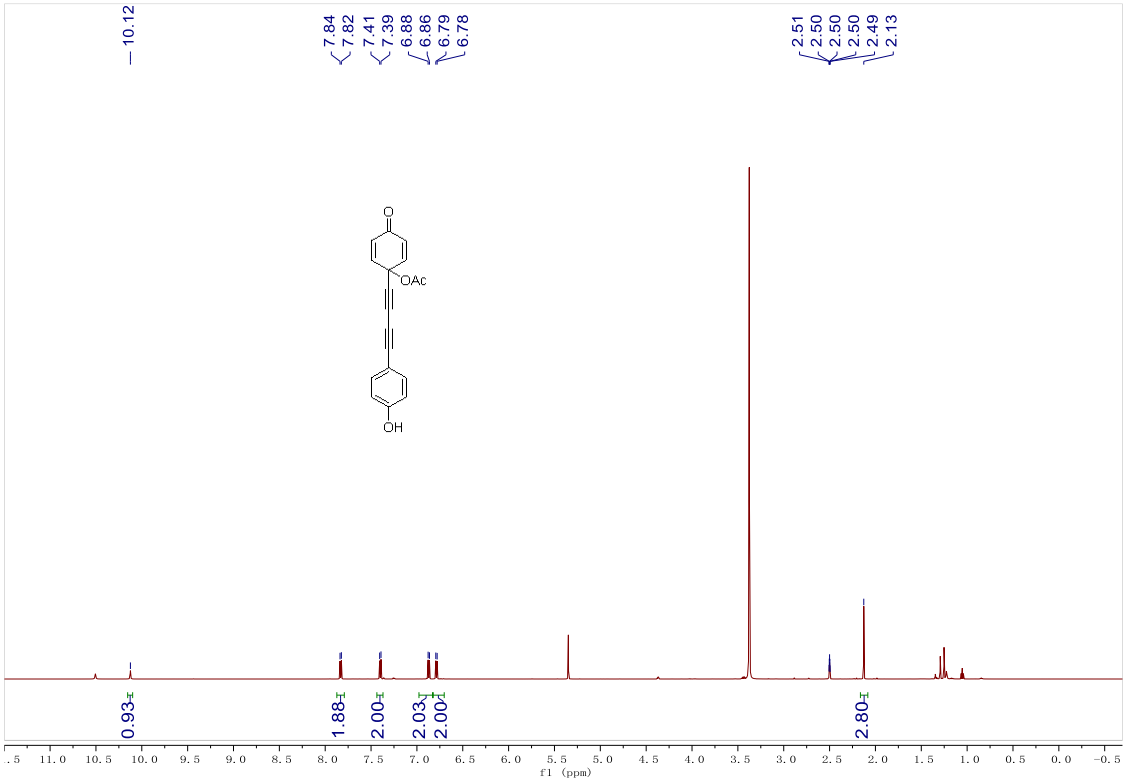


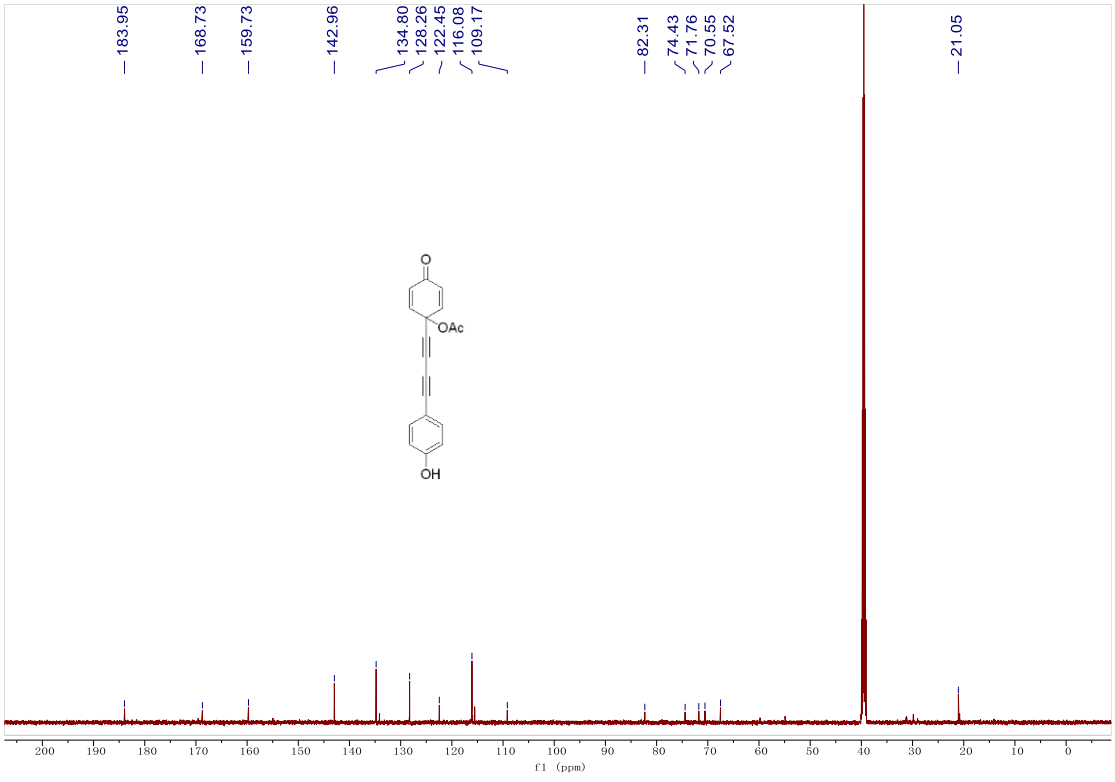
^{1}H and ^{13}C NMR spectra of compound **(3aa)**



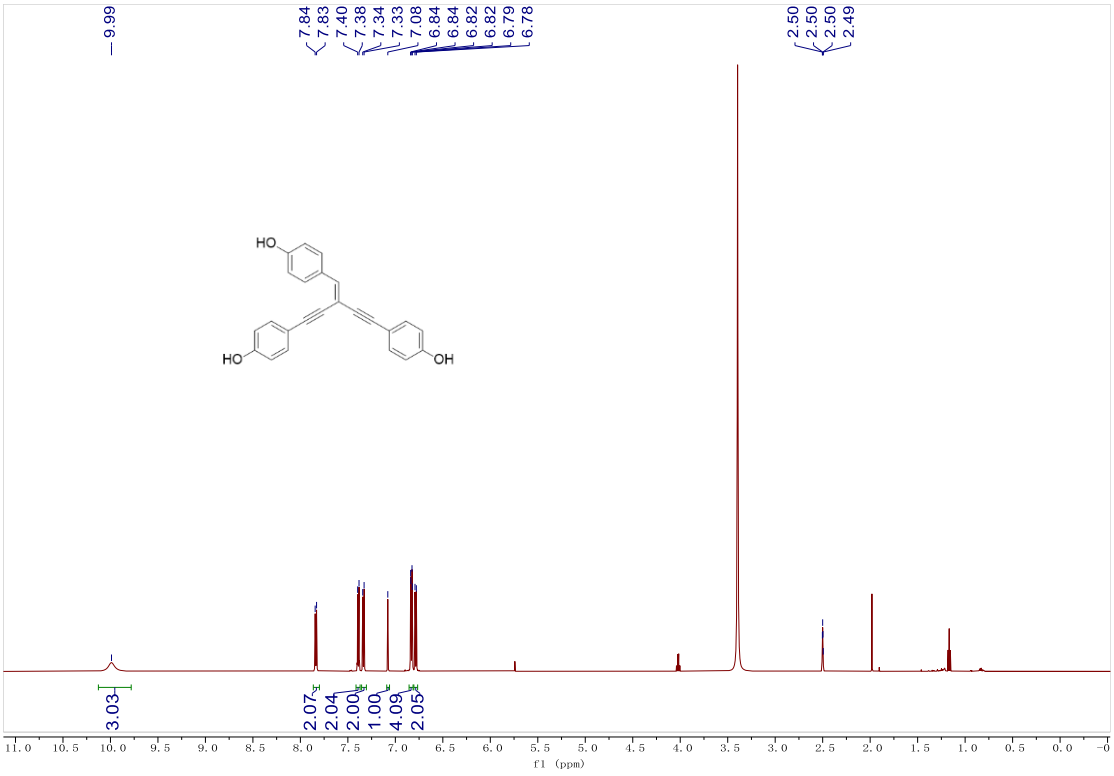


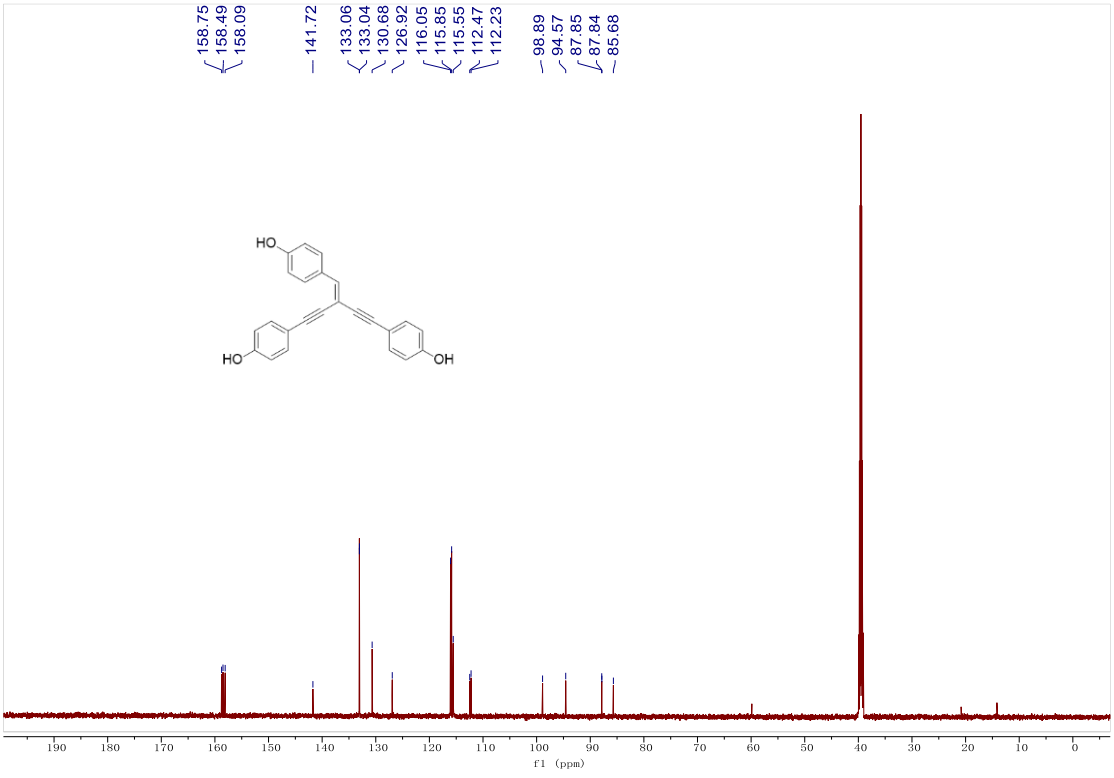
^{1}H and ^{13}C NMR spectra of compound **(3ab)**



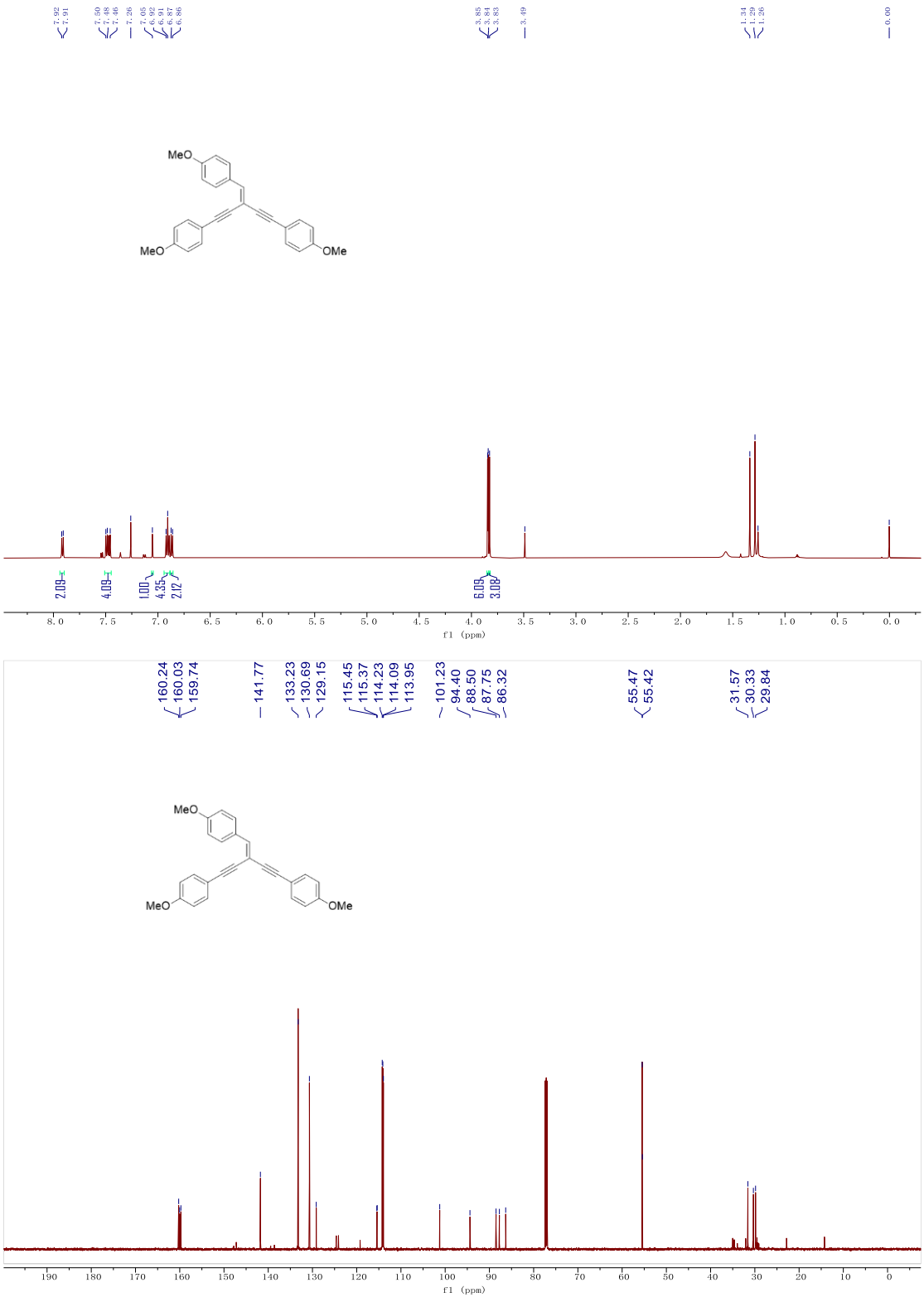


^{1}H and ^{13}C NMR spectra of compound **(4ac)**



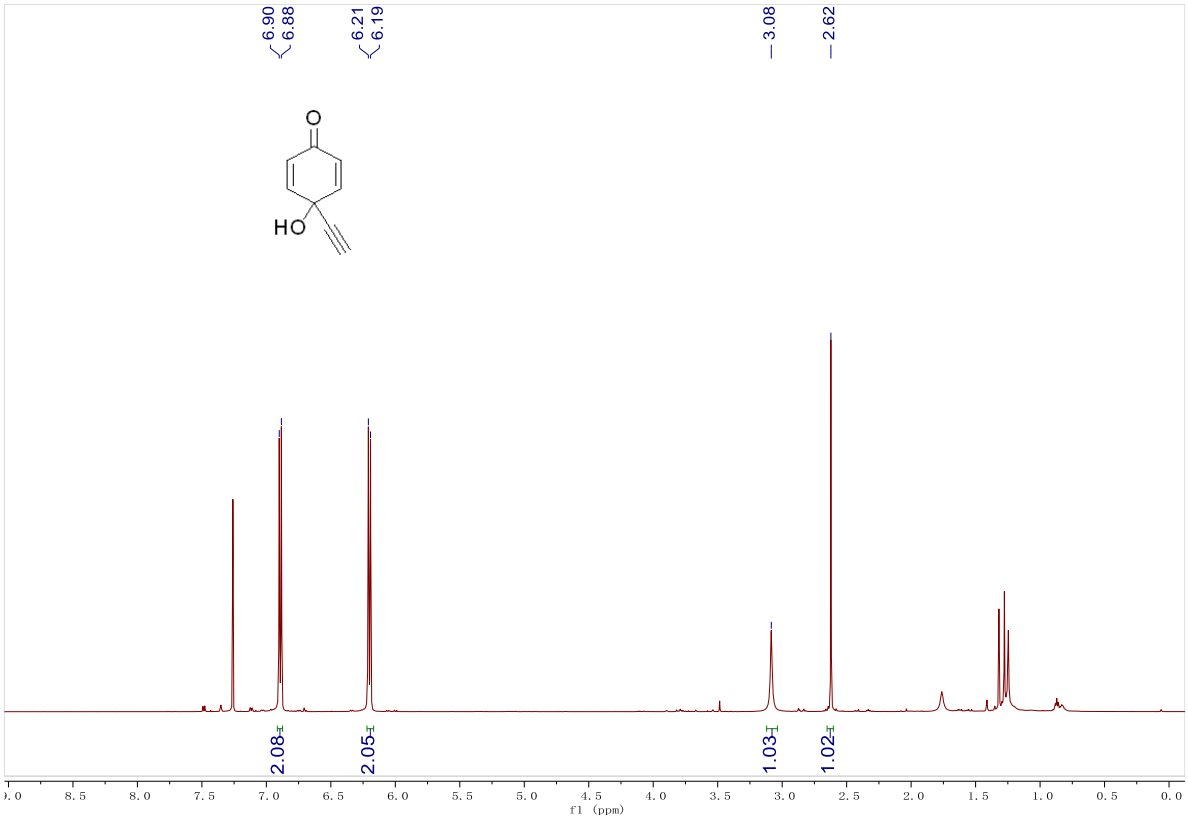


^{1}H and ^{13}C NMR spectra of compound **(4ad)**

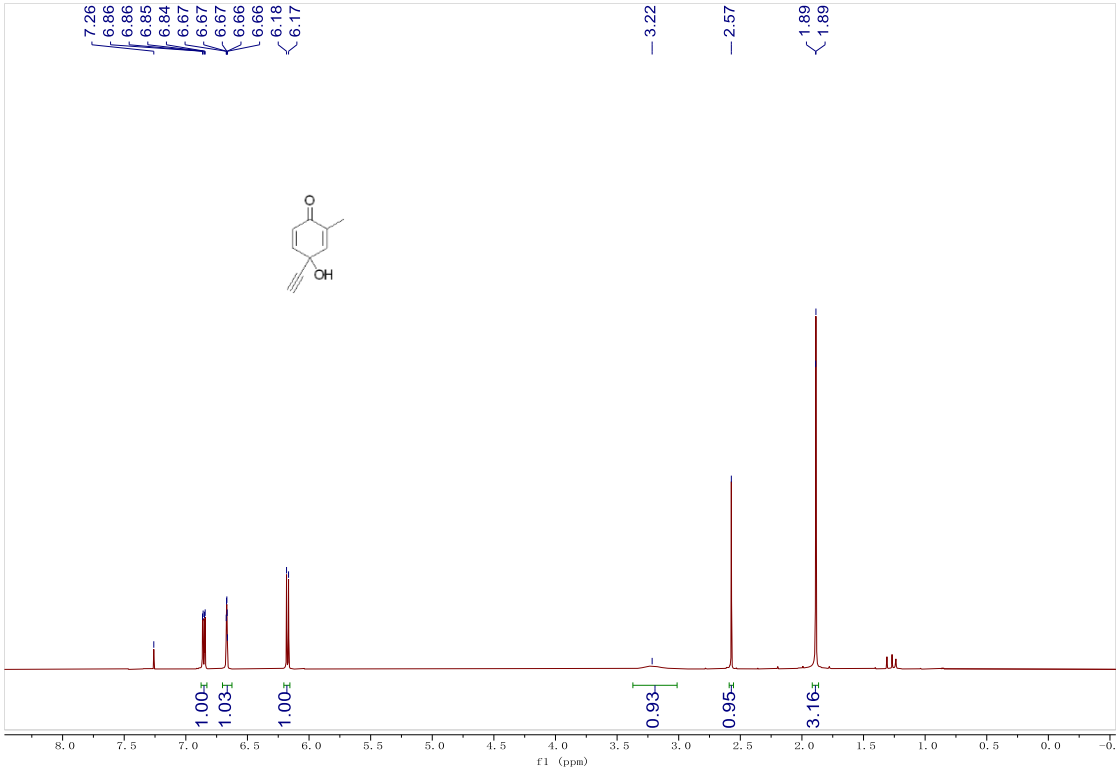


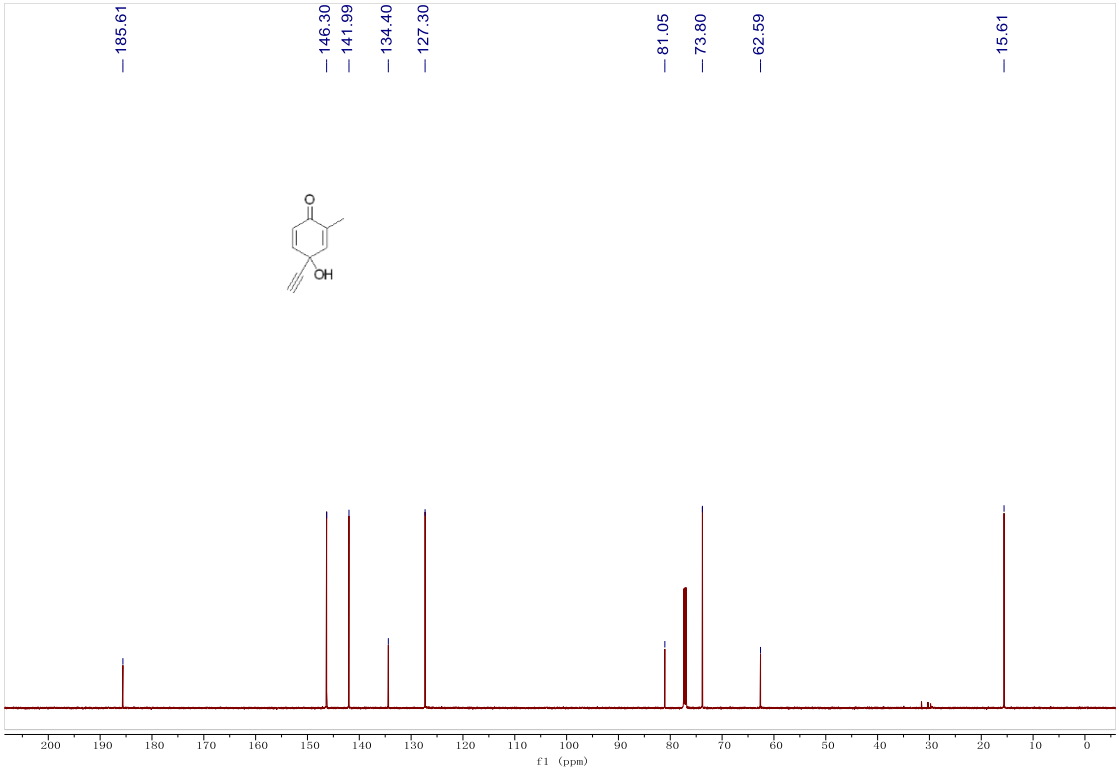
15. Copies of NMR spectra (starting materials)

^{1}H and ^{13}C NMR spectra of compound (**1a**)

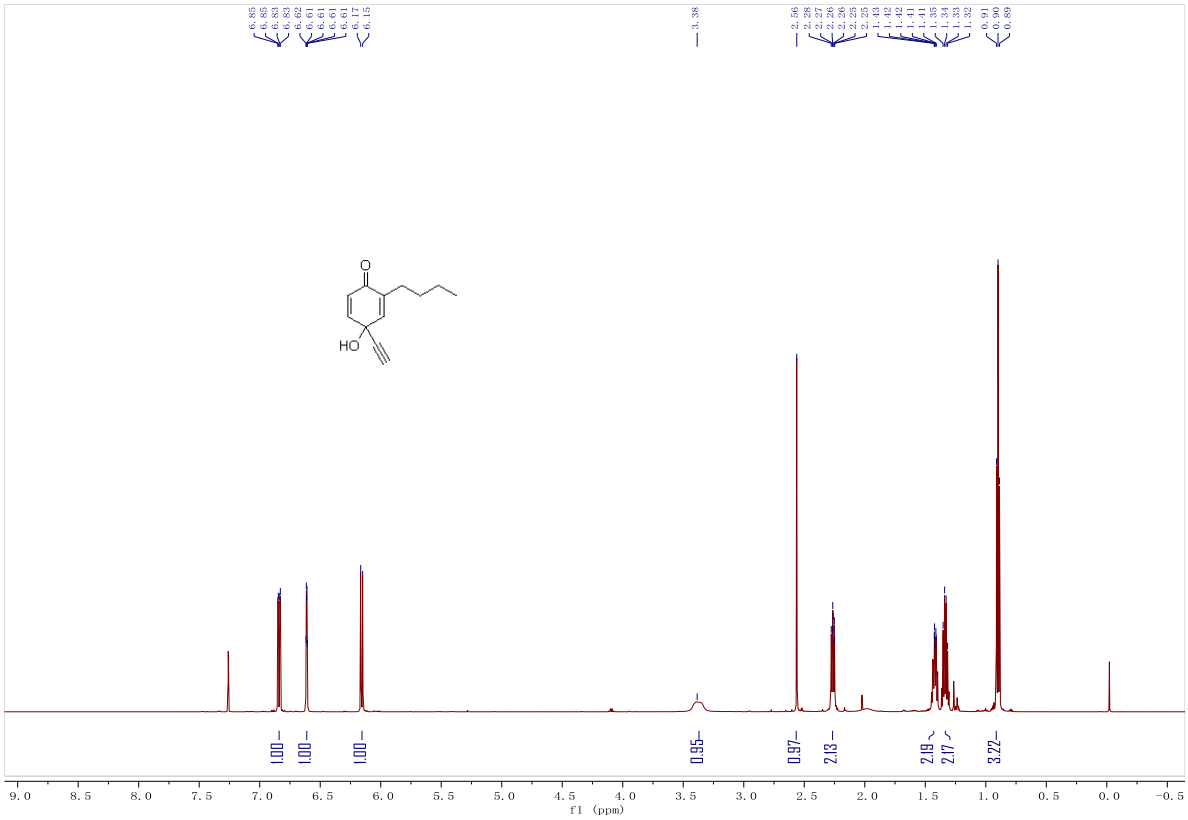


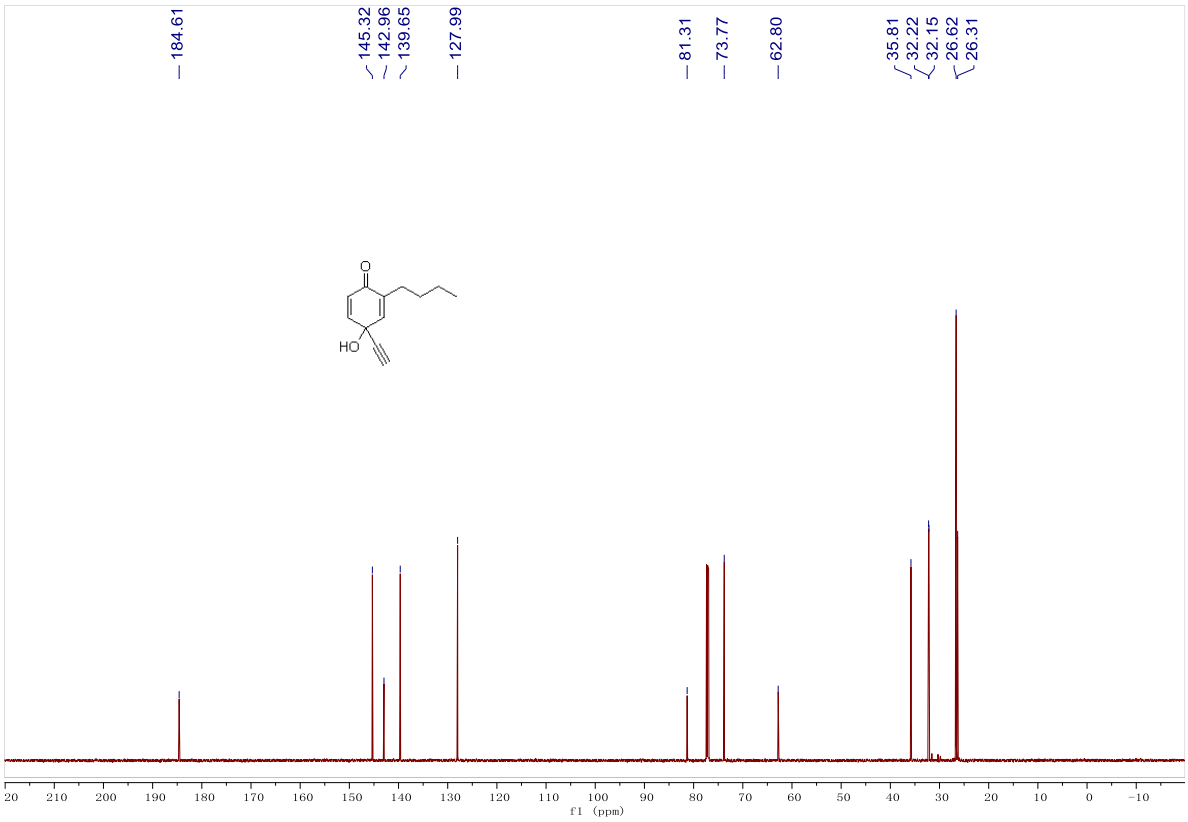
^{1}H and ^{13}C NMR spectra of compound (**1b**)



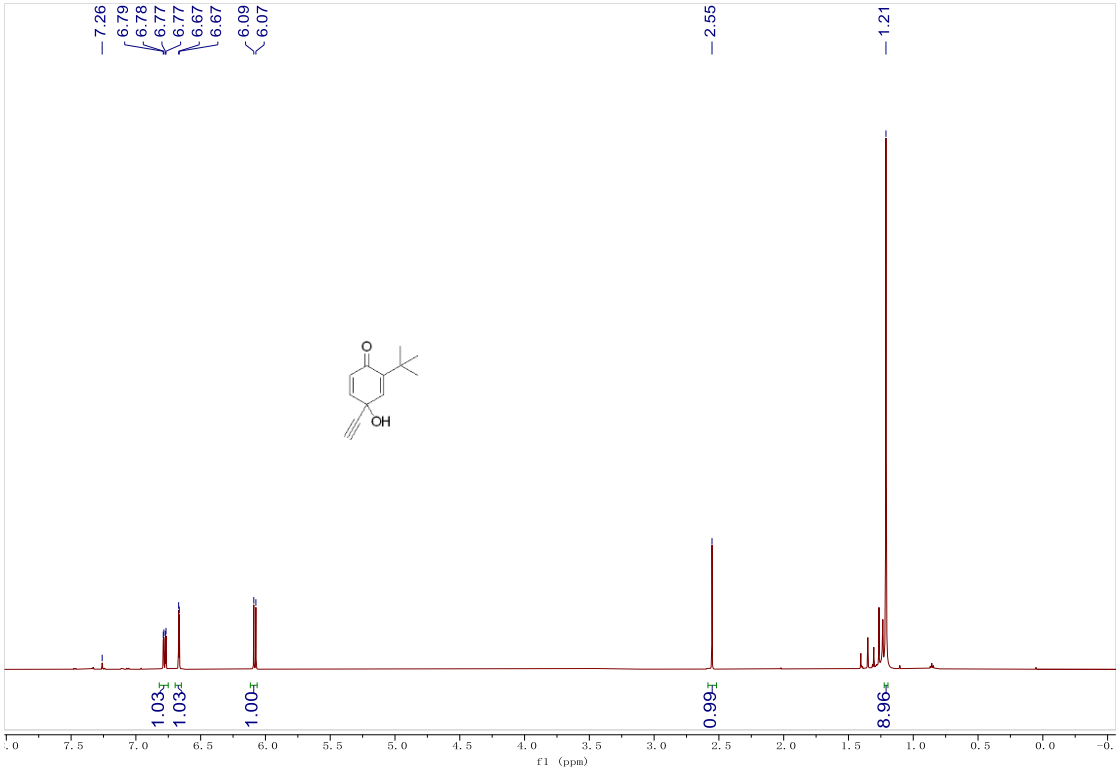


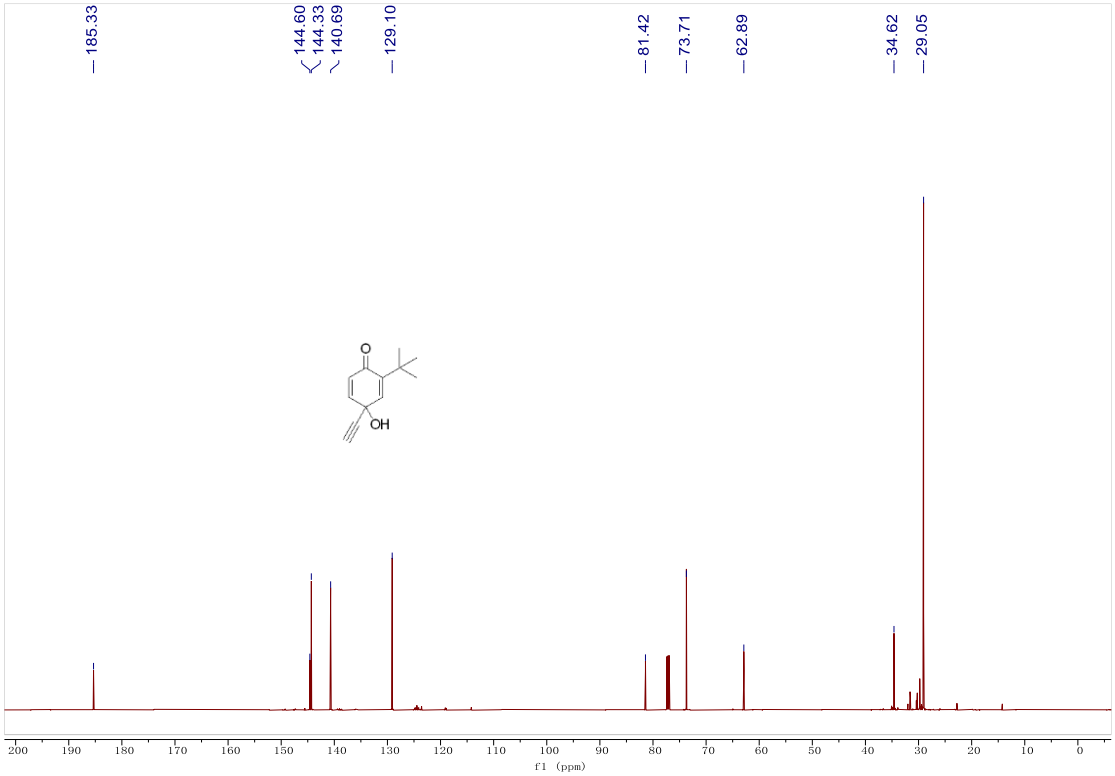
^{1}H and ^{13}C NMR spectra of compound (**1c**)



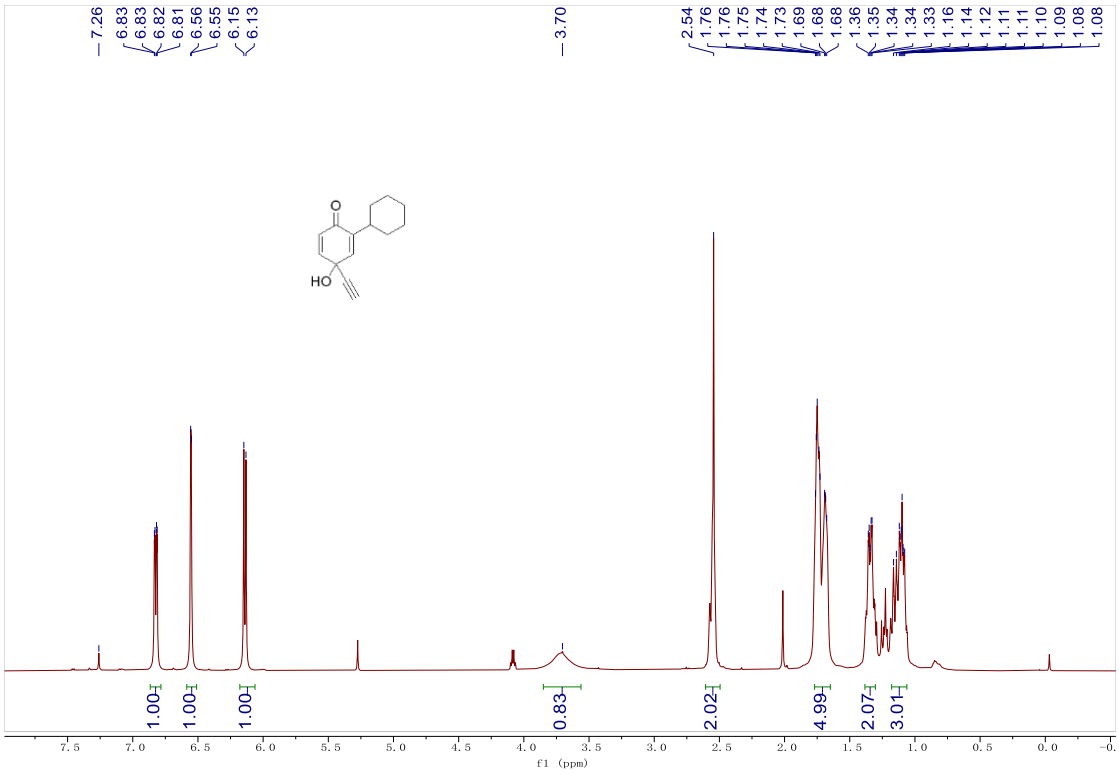


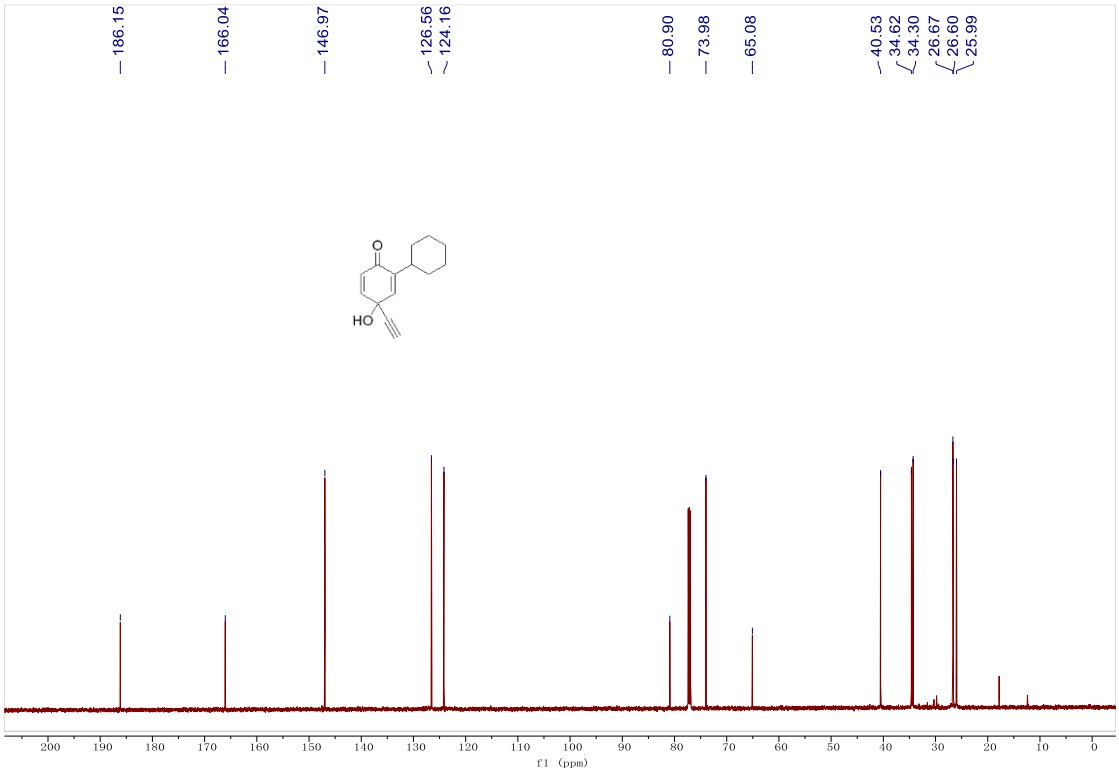
^{1}H and ^{13}C NMR spectra of compound (**1d**)



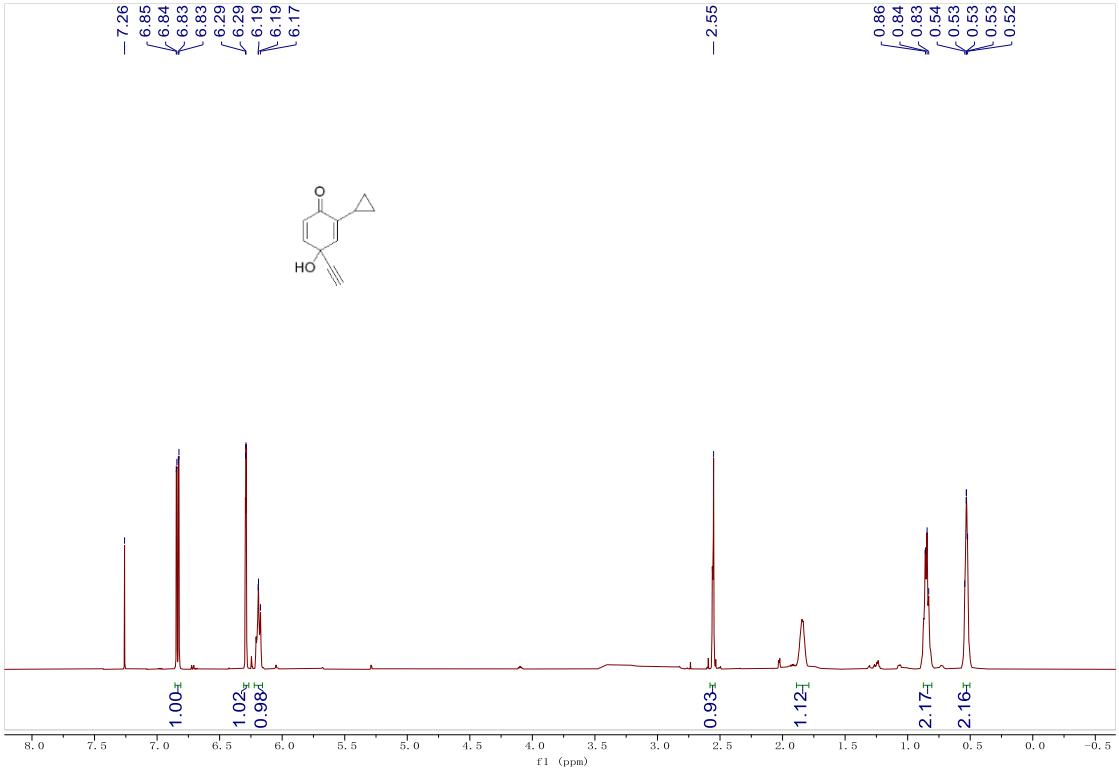


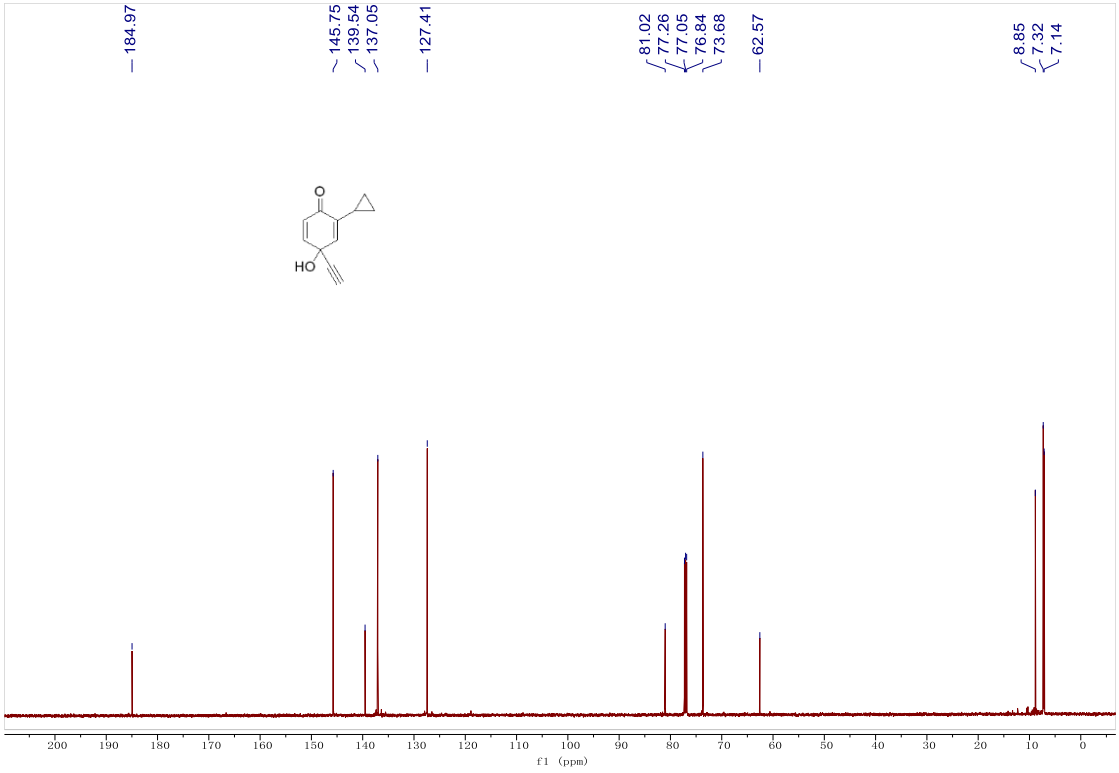
^{1}H and ^{13}C NMR spectra of compound (**1e**)



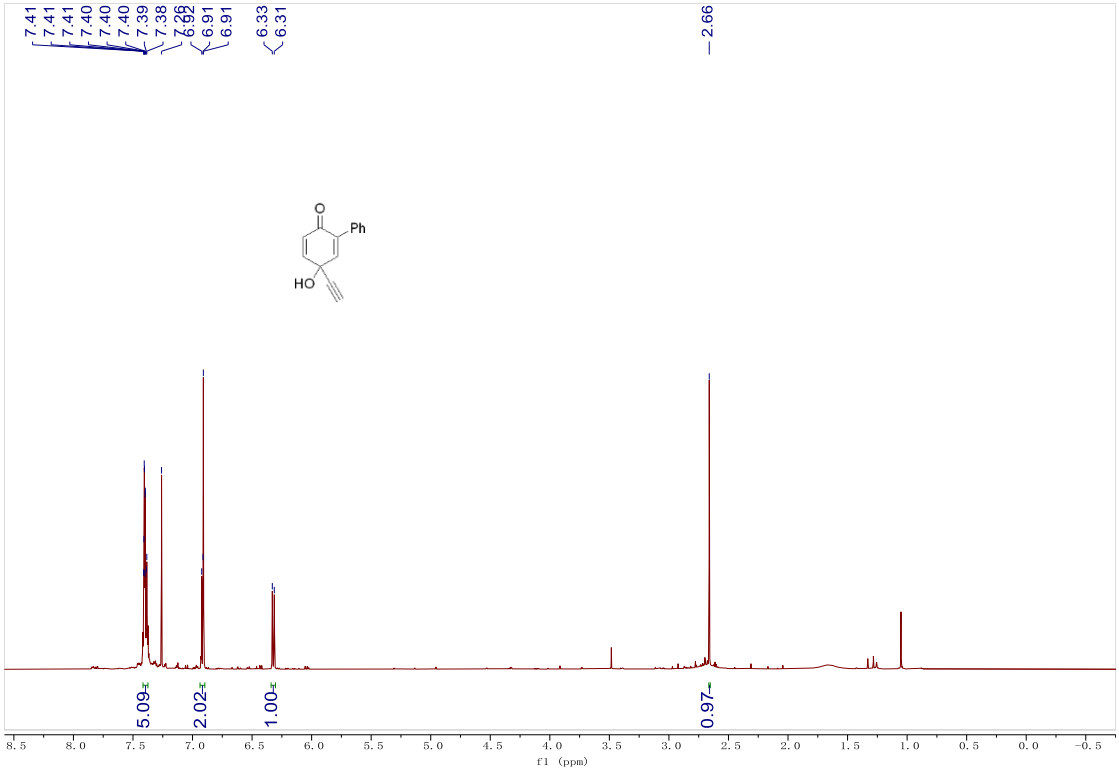


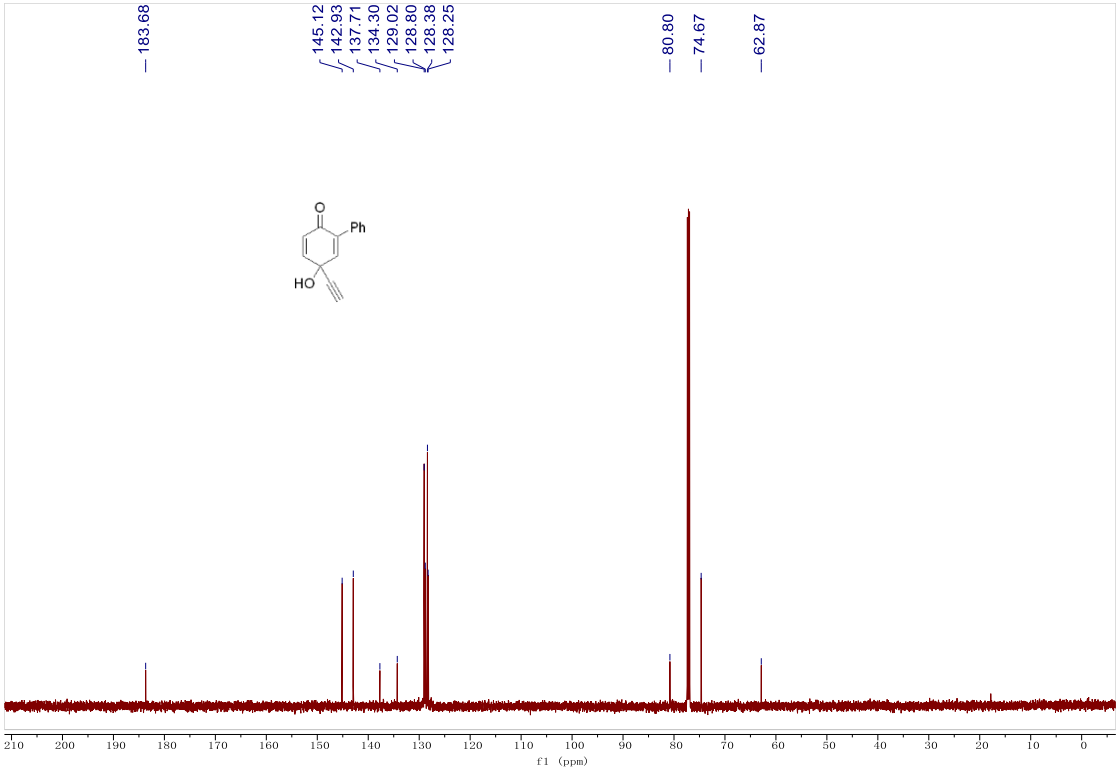
^{1}H and ^{13}C NMR spectra of compound (**1f**)



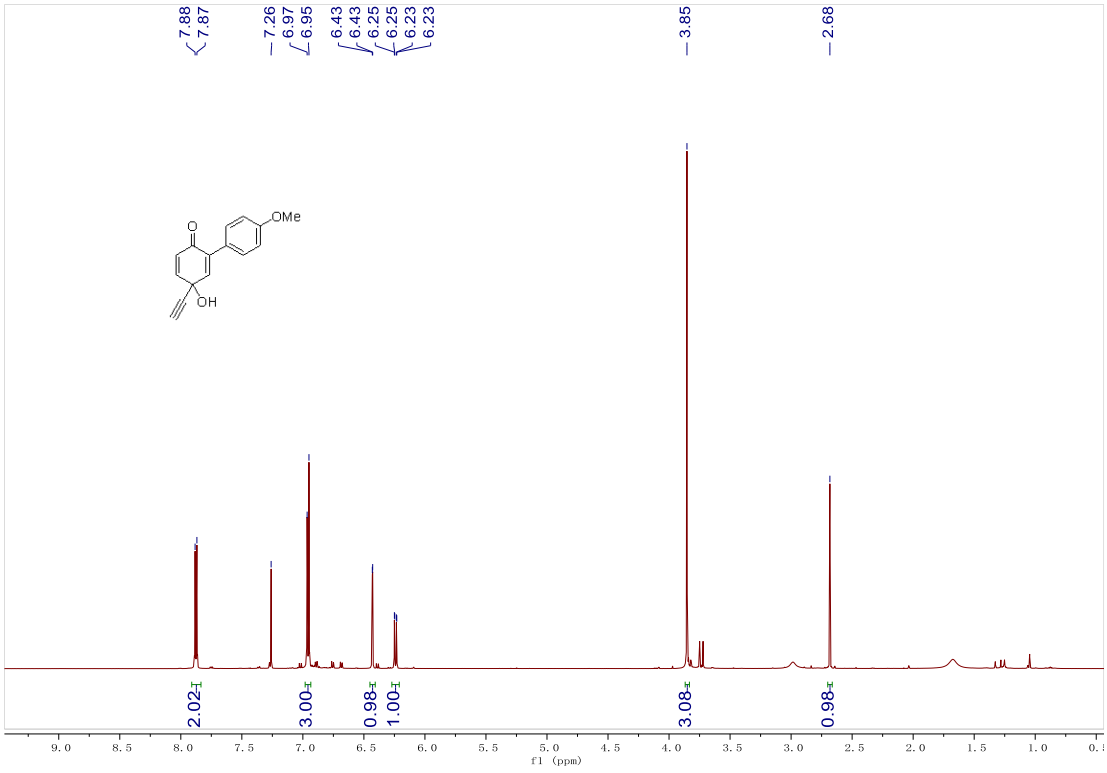


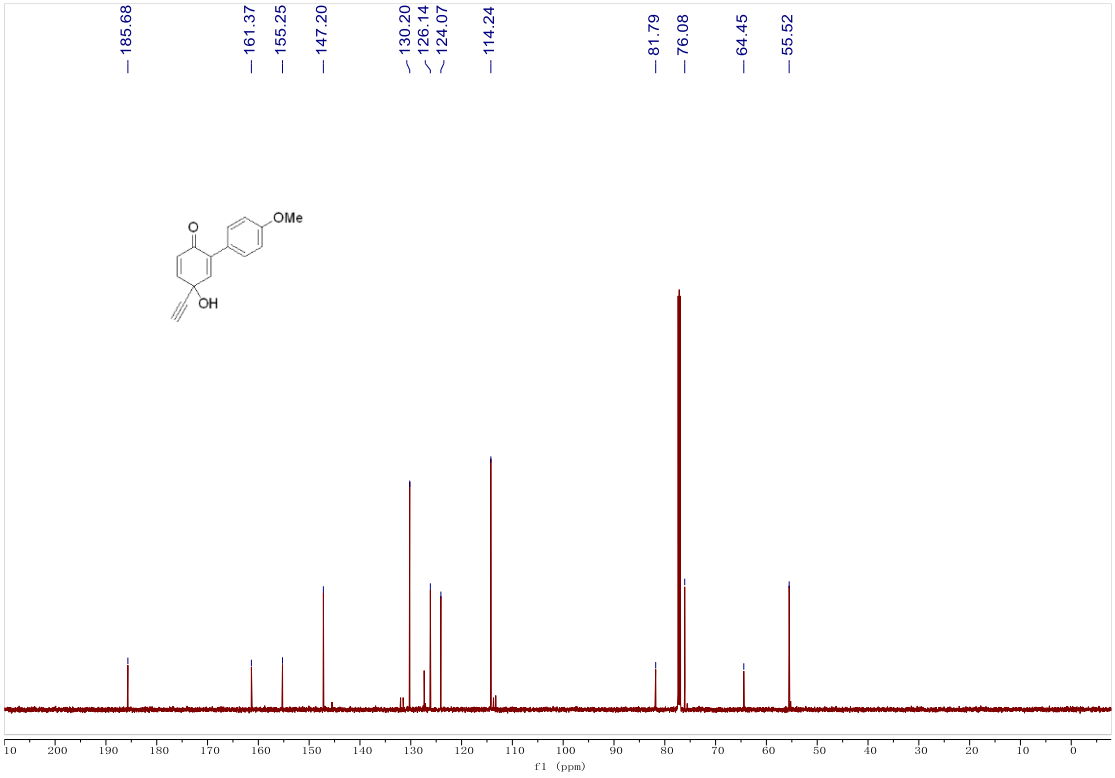
^{1}H and ^{13}C NMR spectra of compound (**1g**)



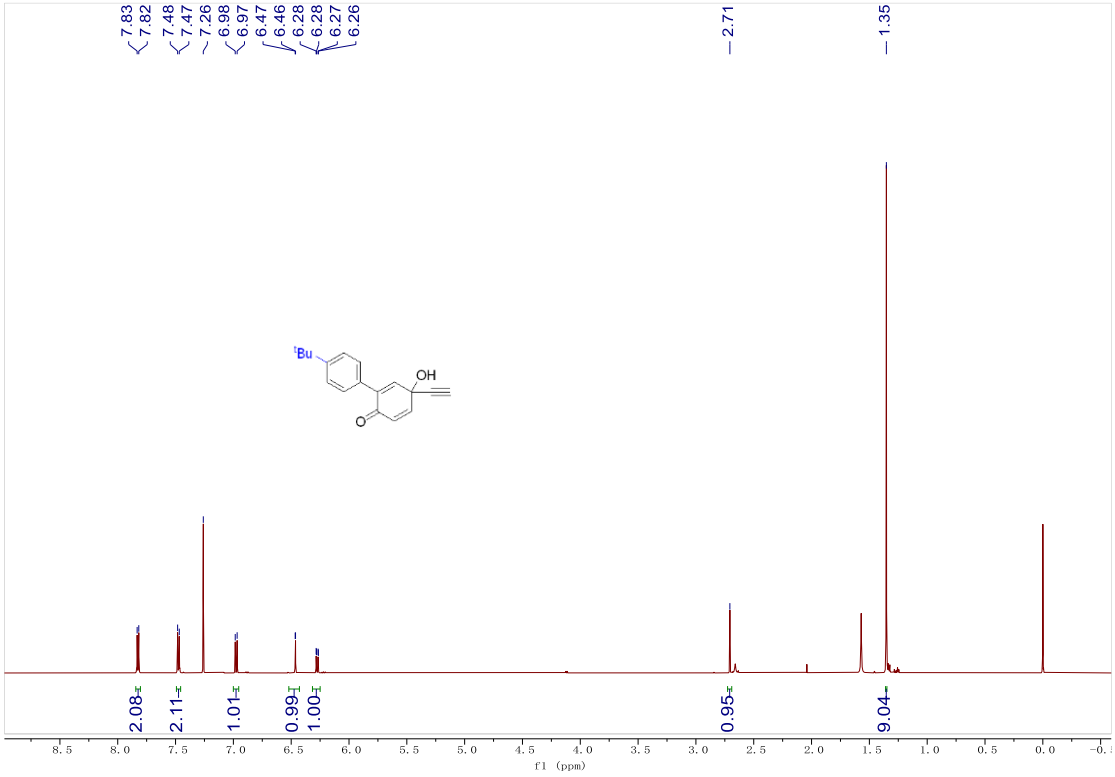


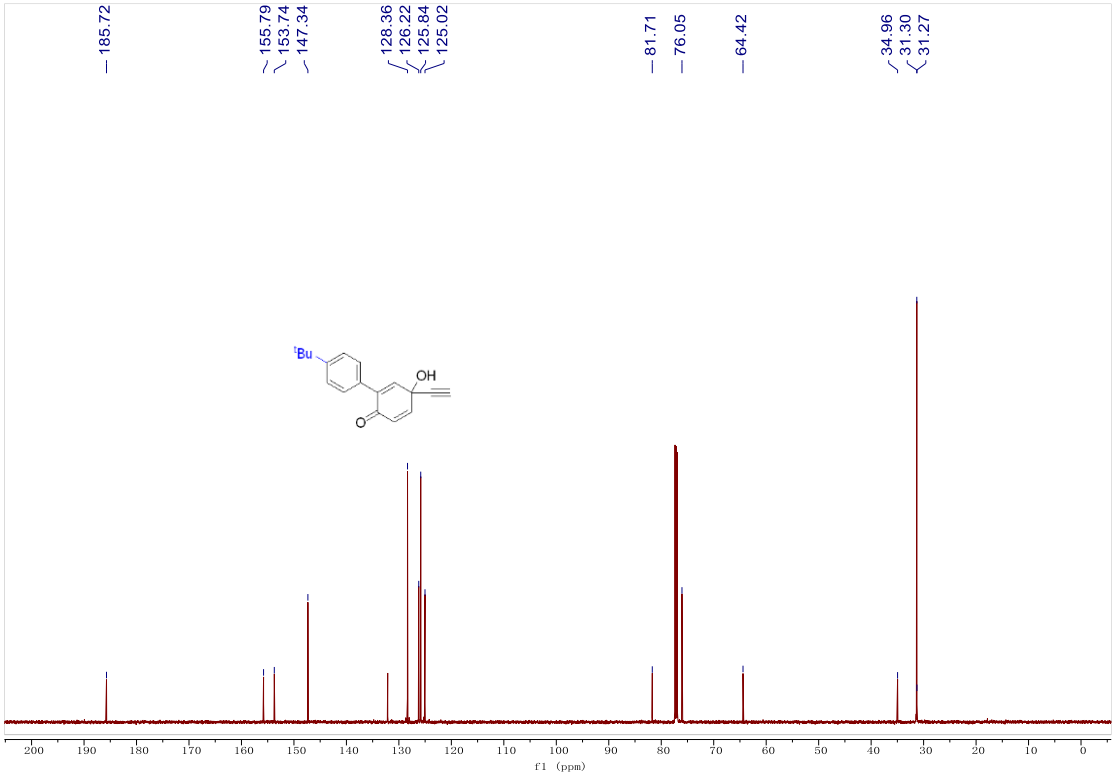
^{1}H and ^{13}C NMR spectra of compound (**1h**)



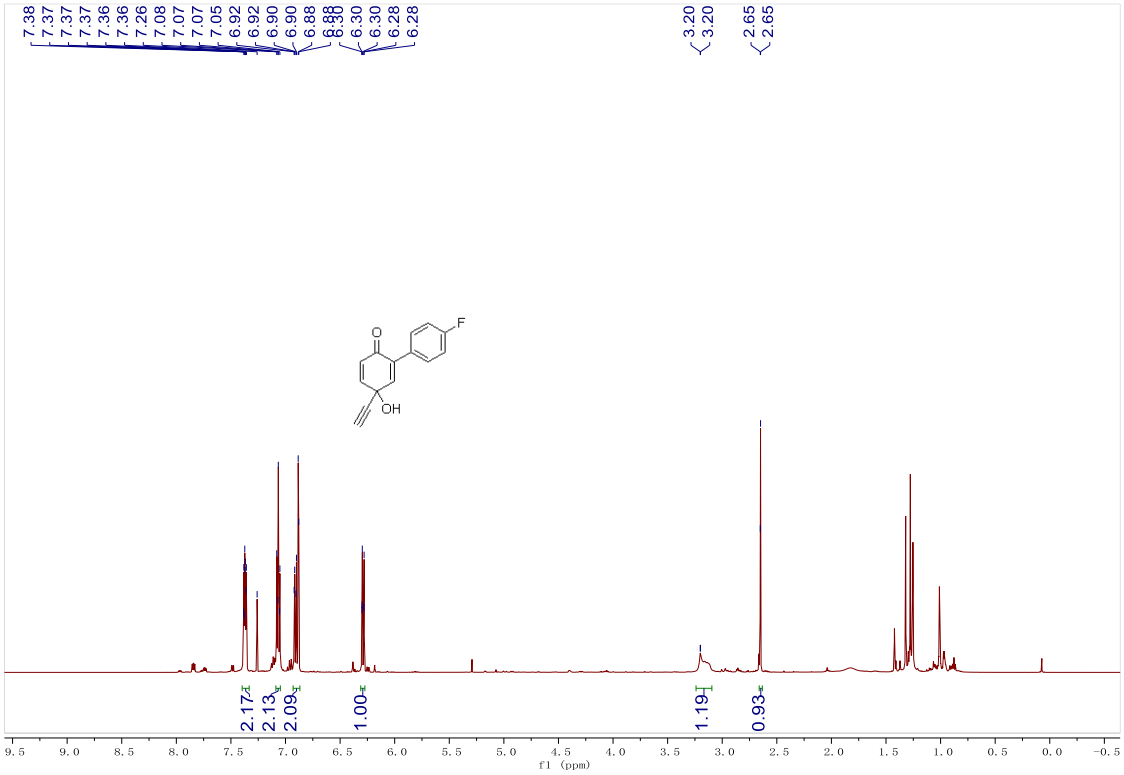


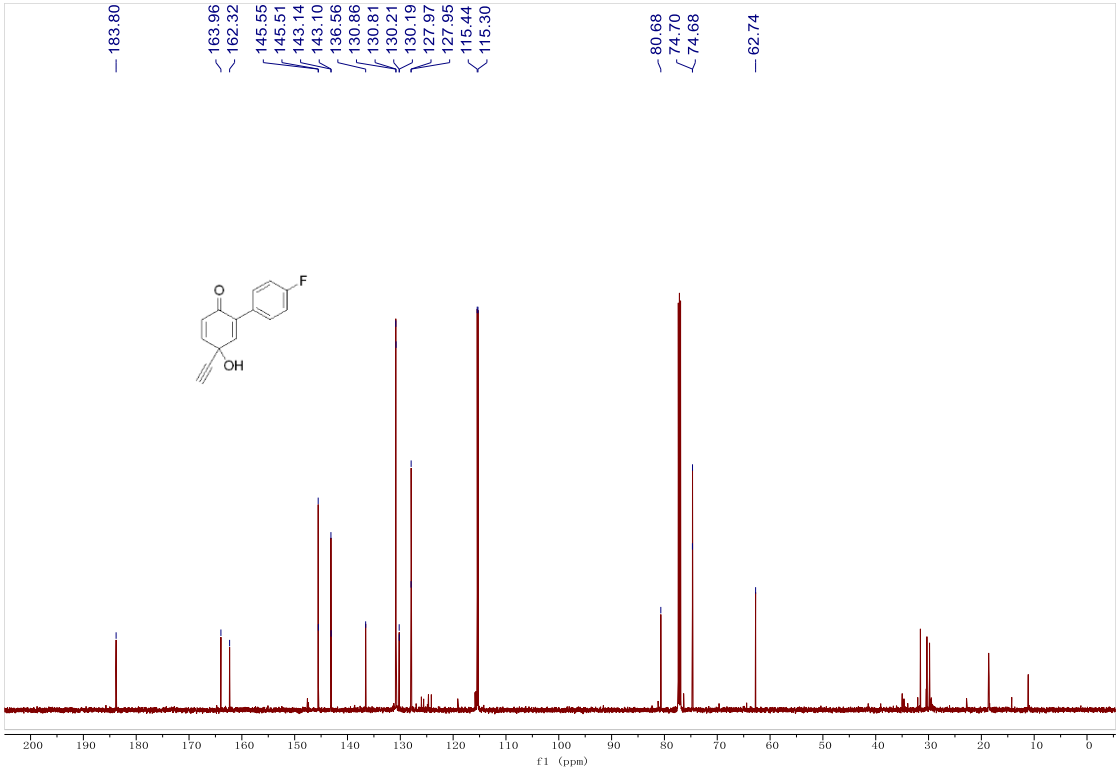
^{1}H and ^{13}C NMR spectra of compound **(1i)**



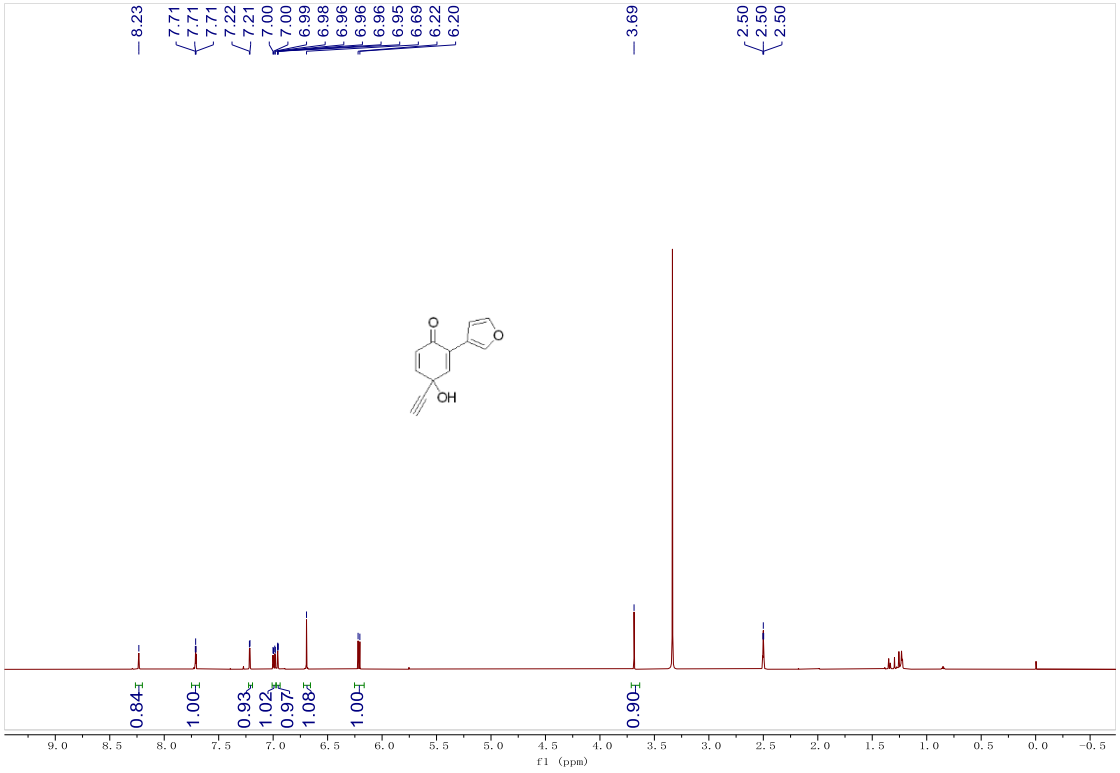


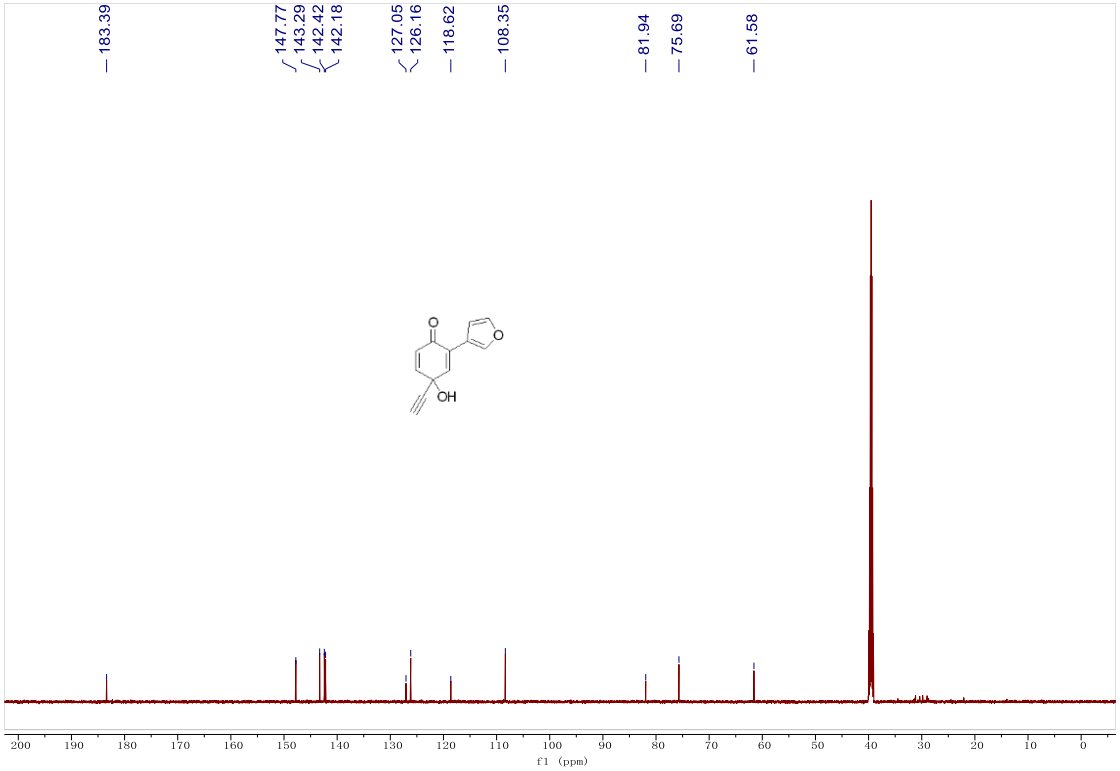
^{1}H and ^{13}C NMR spectra of compound (**1j**)



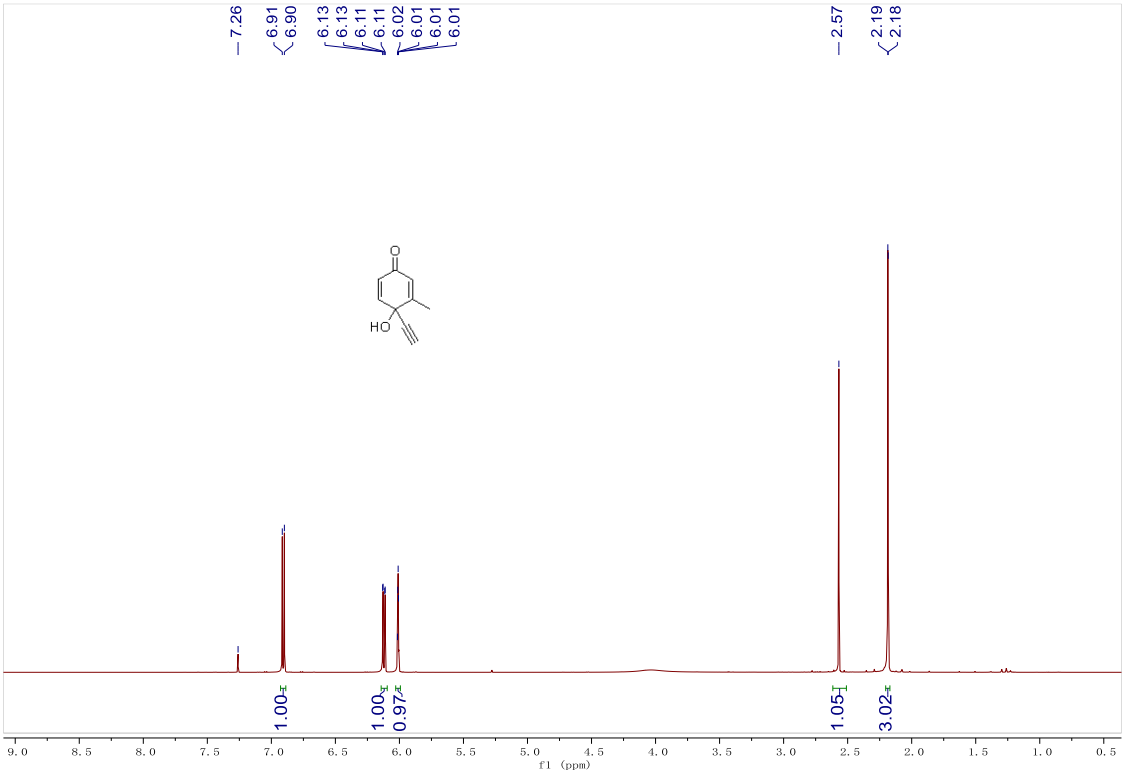


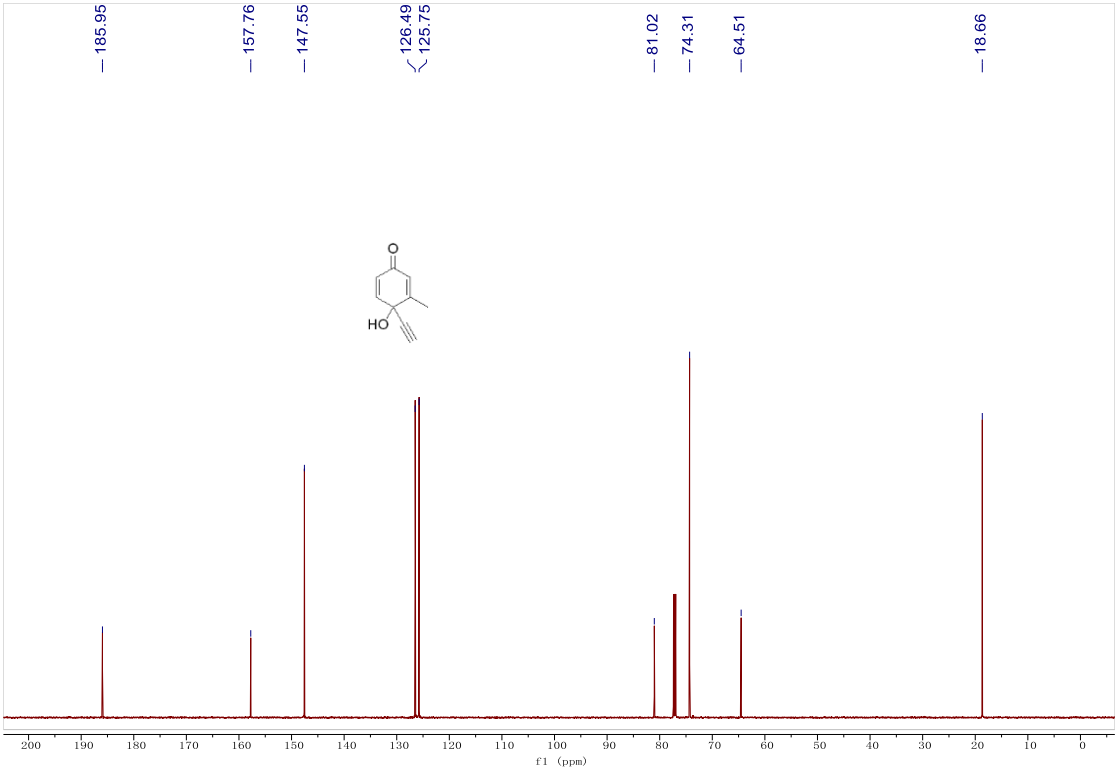
^{1}H and ^{13}C NMR spectra of compound **(1k)**



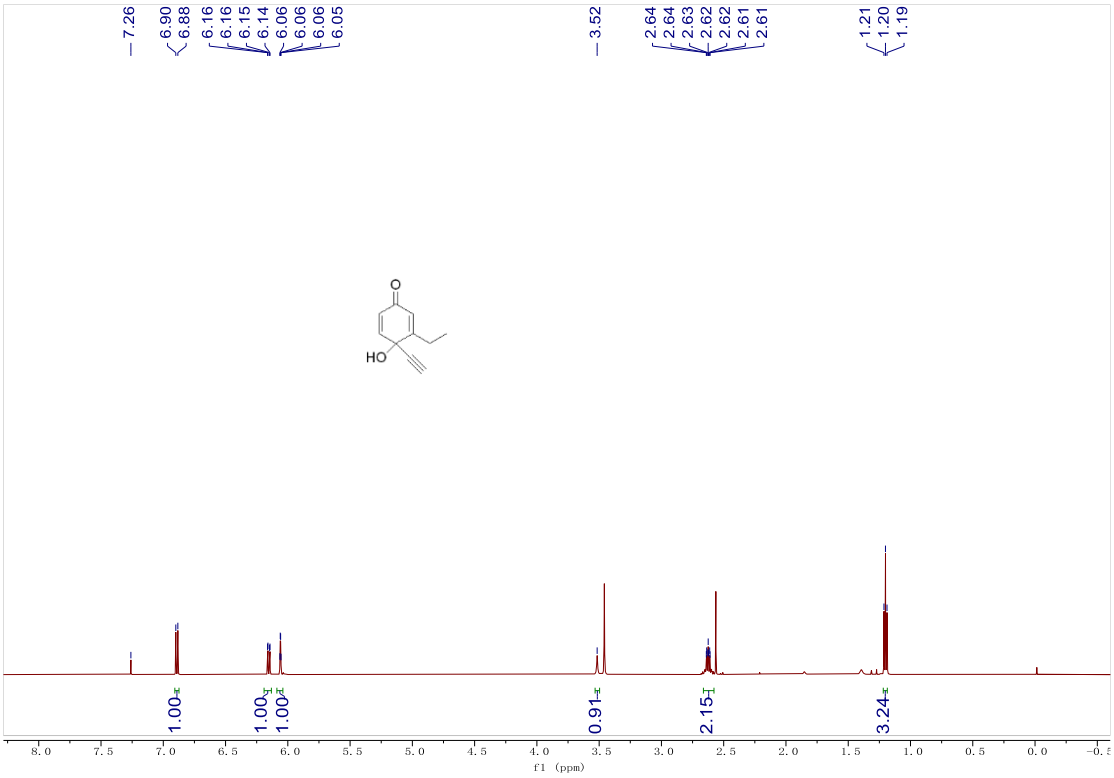


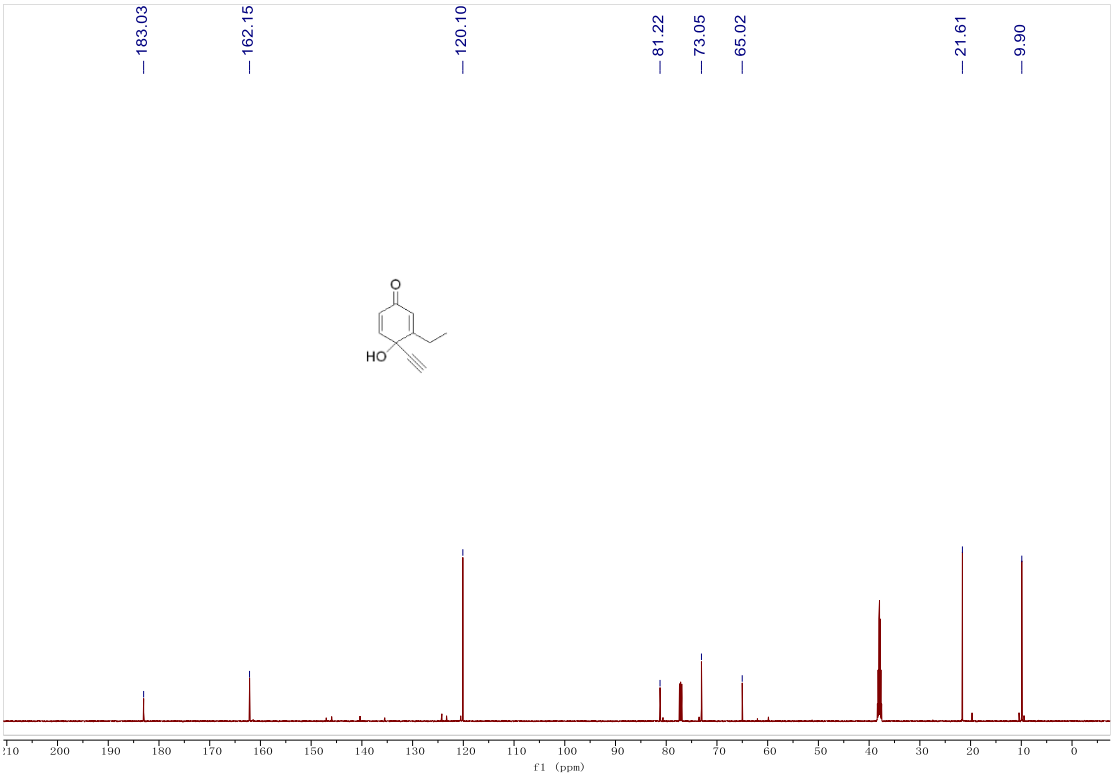
^{1}H and ^{13}C NMR spectra of compound (**1l**)



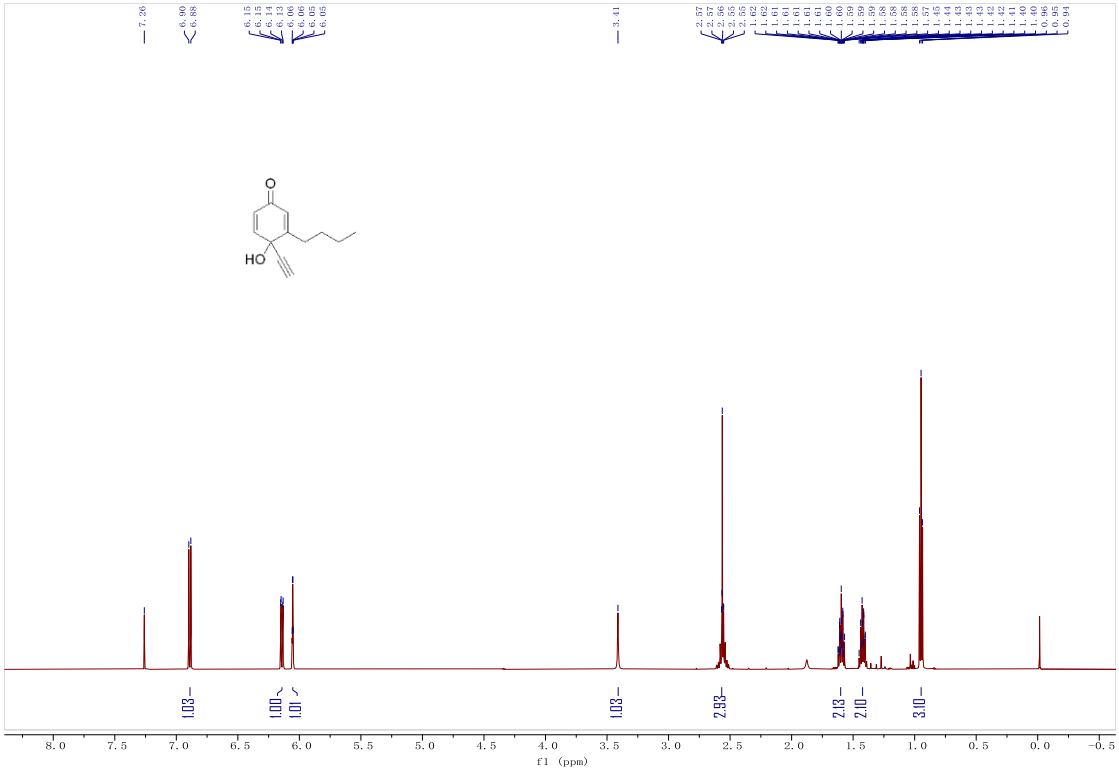


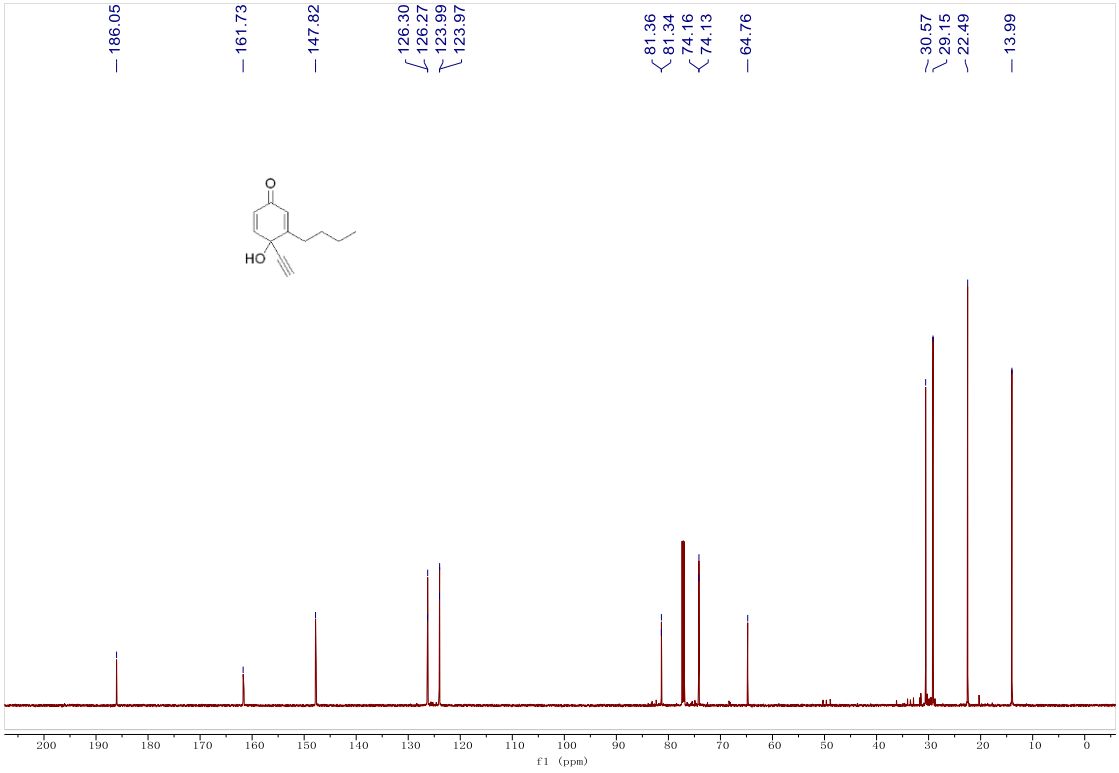
^{1}H and ^{13}C NMR spectra of compound (**1m**)



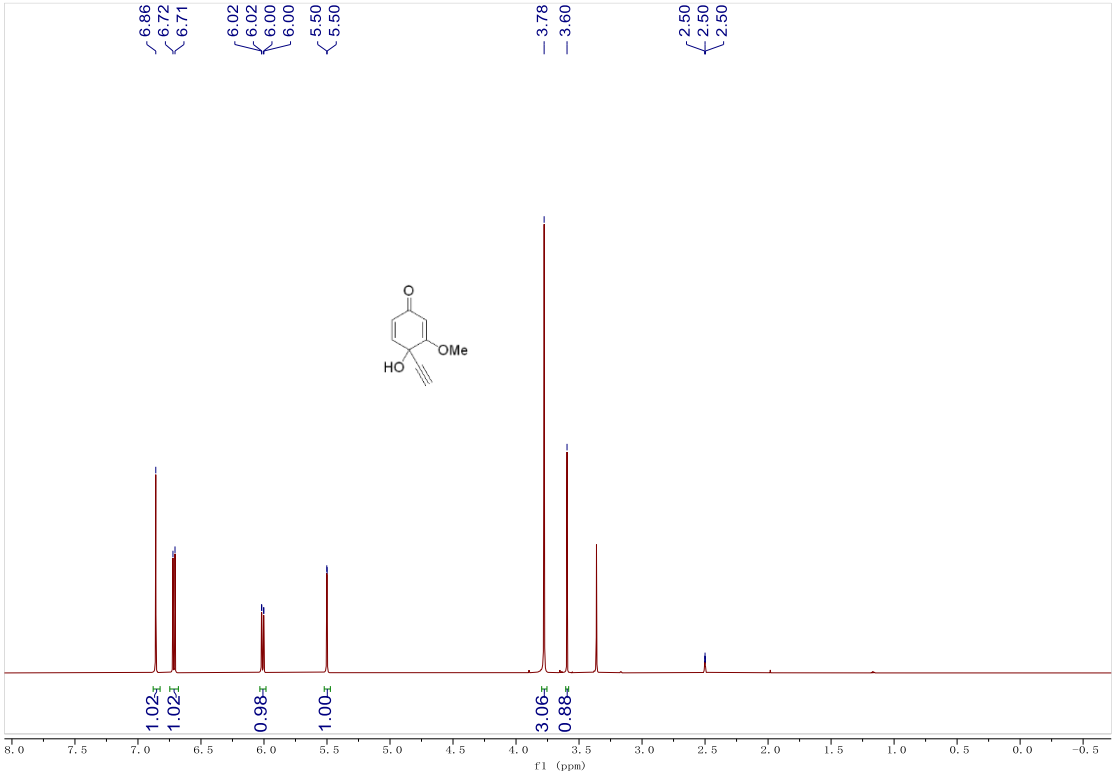


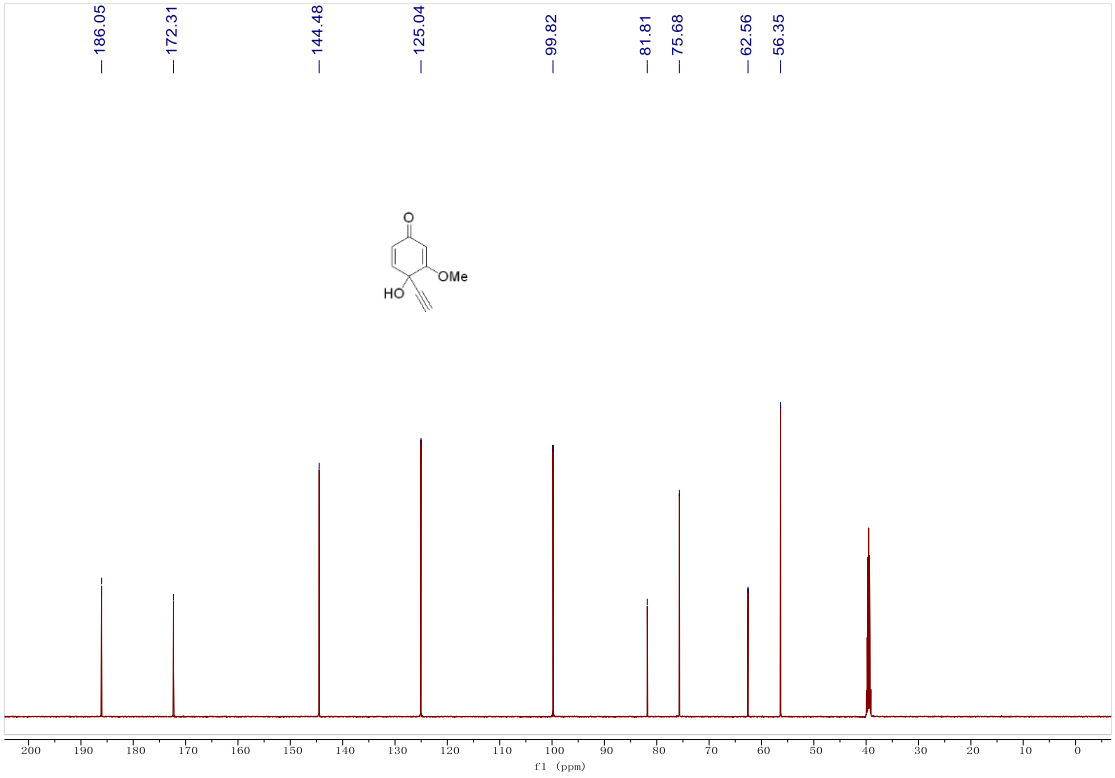
^{1}H and ^{13}C NMR spectra of compound **(1n)**



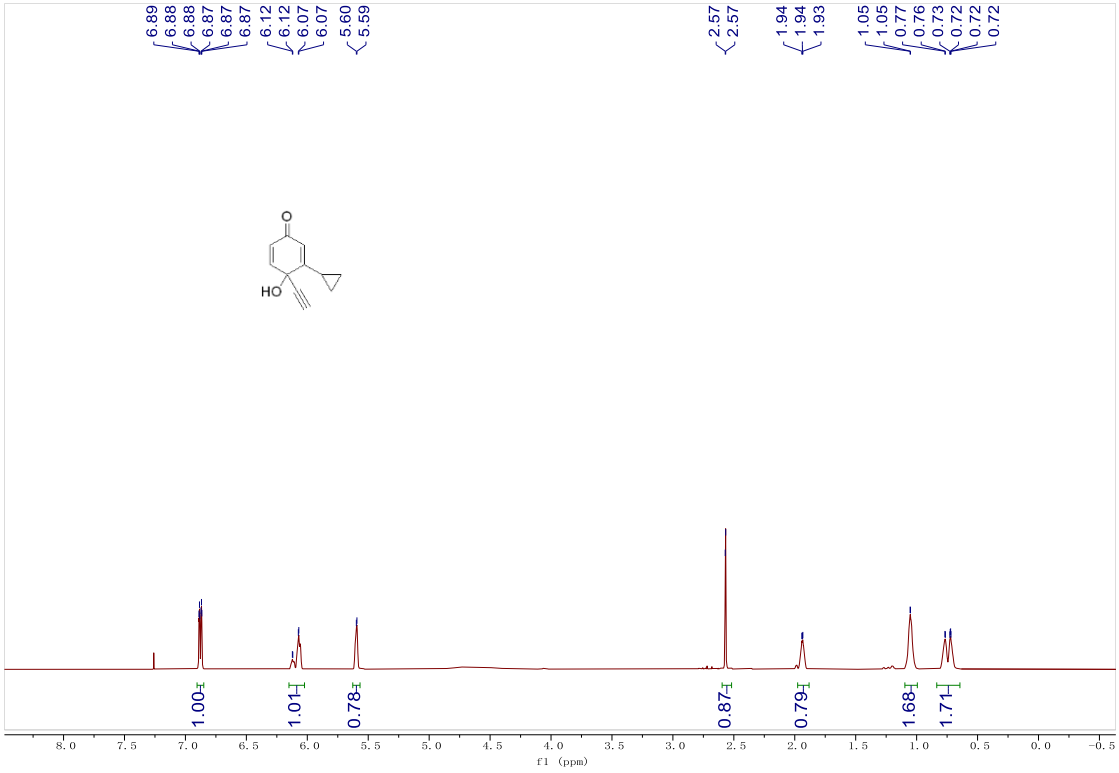


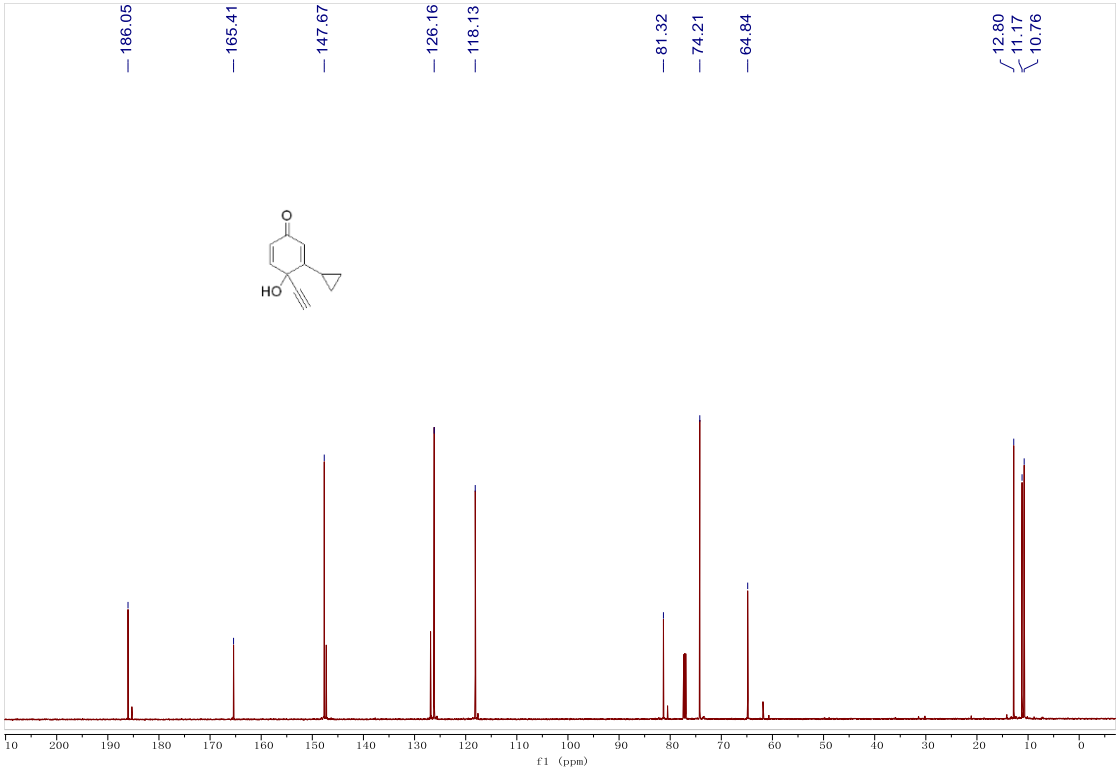
^{1}H and ^{13}C NMR spectra of compound **(1o)**



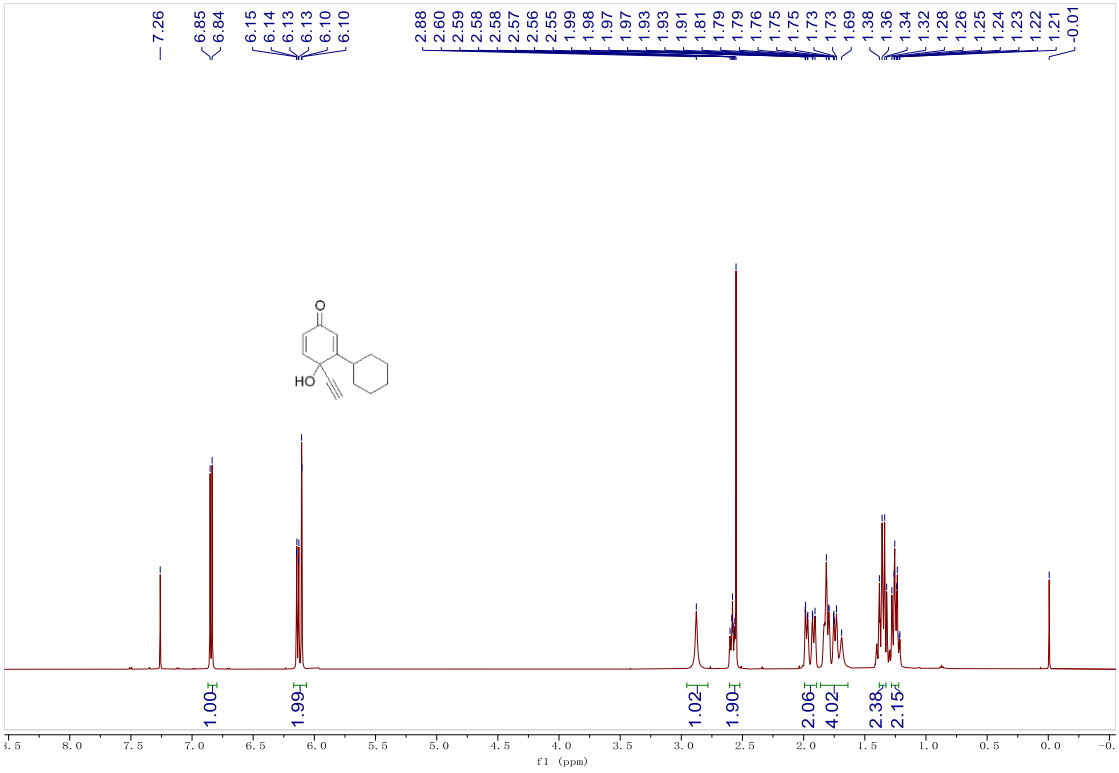


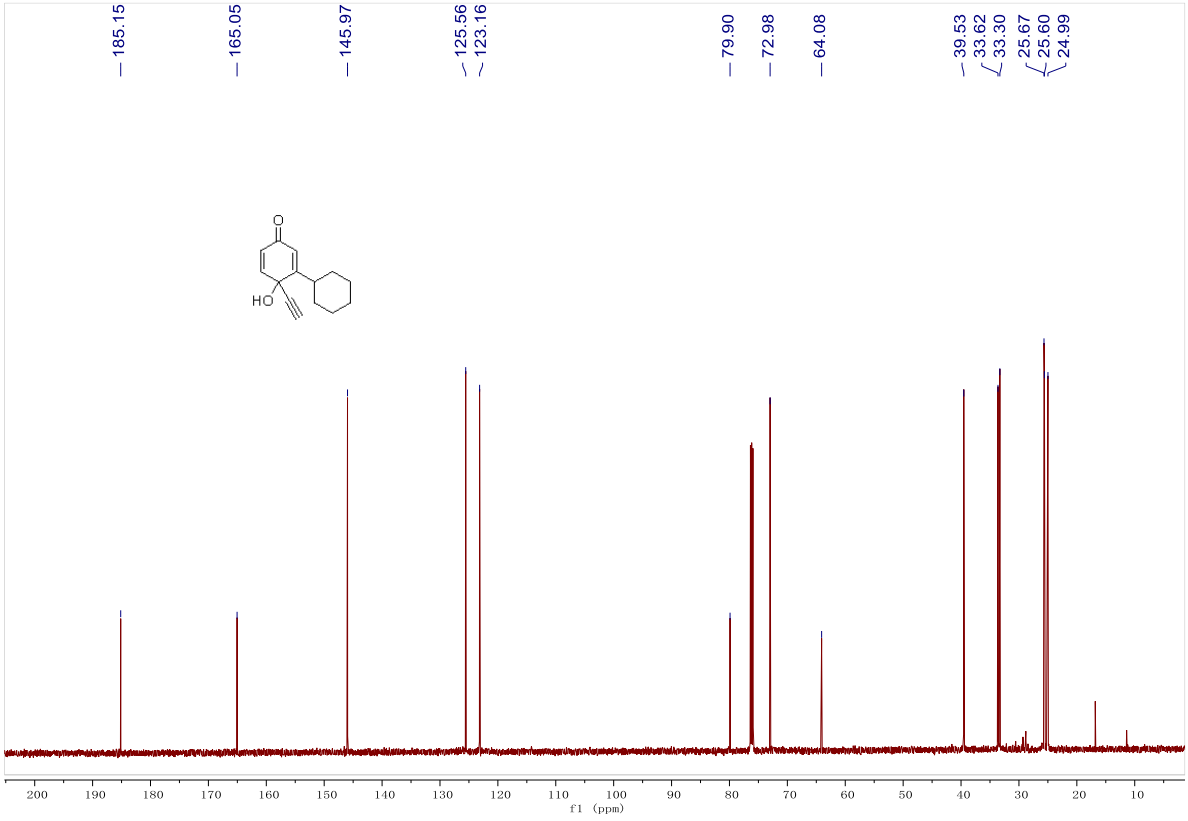
^{1}H and ^{13}C NMR spectra of compound **(1p)**



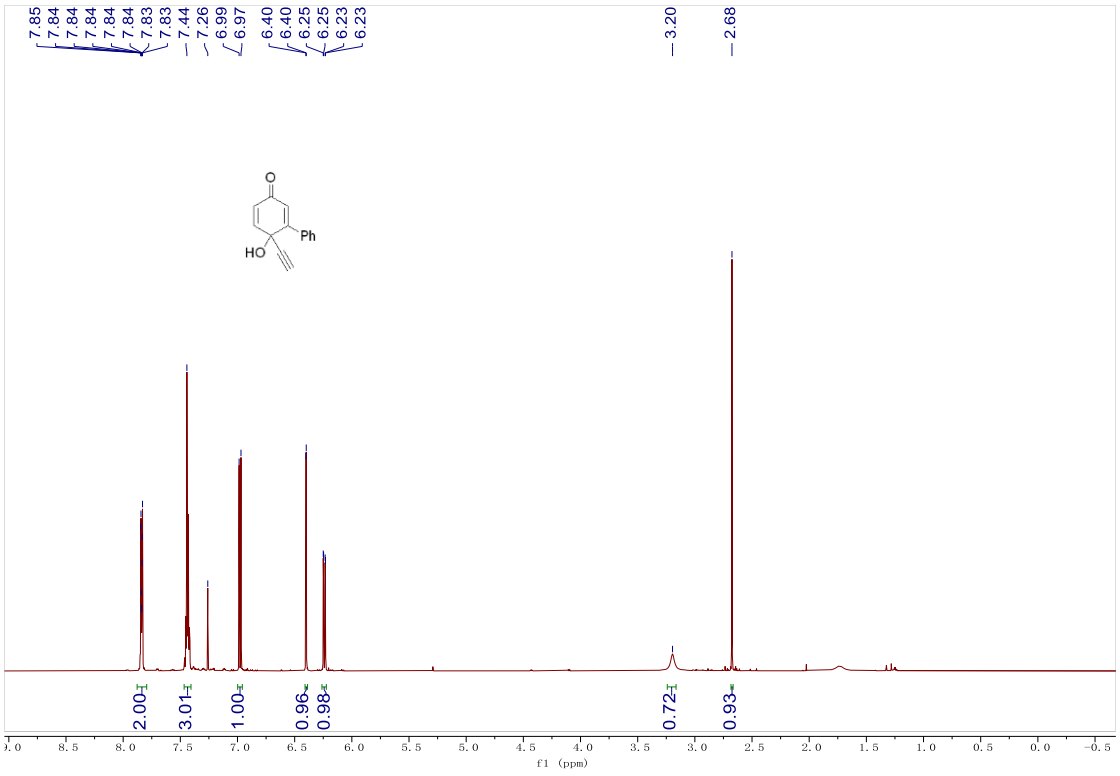


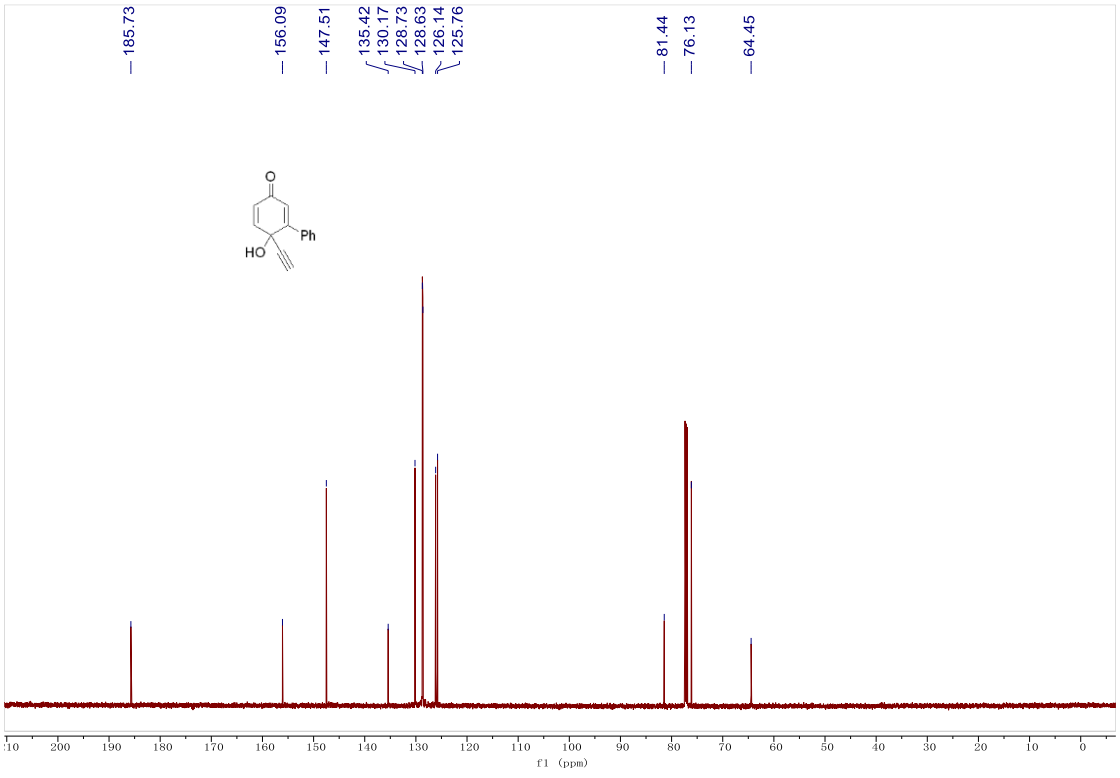
^{1}H and ^{13}C NMR spectra of compound **(1q)**



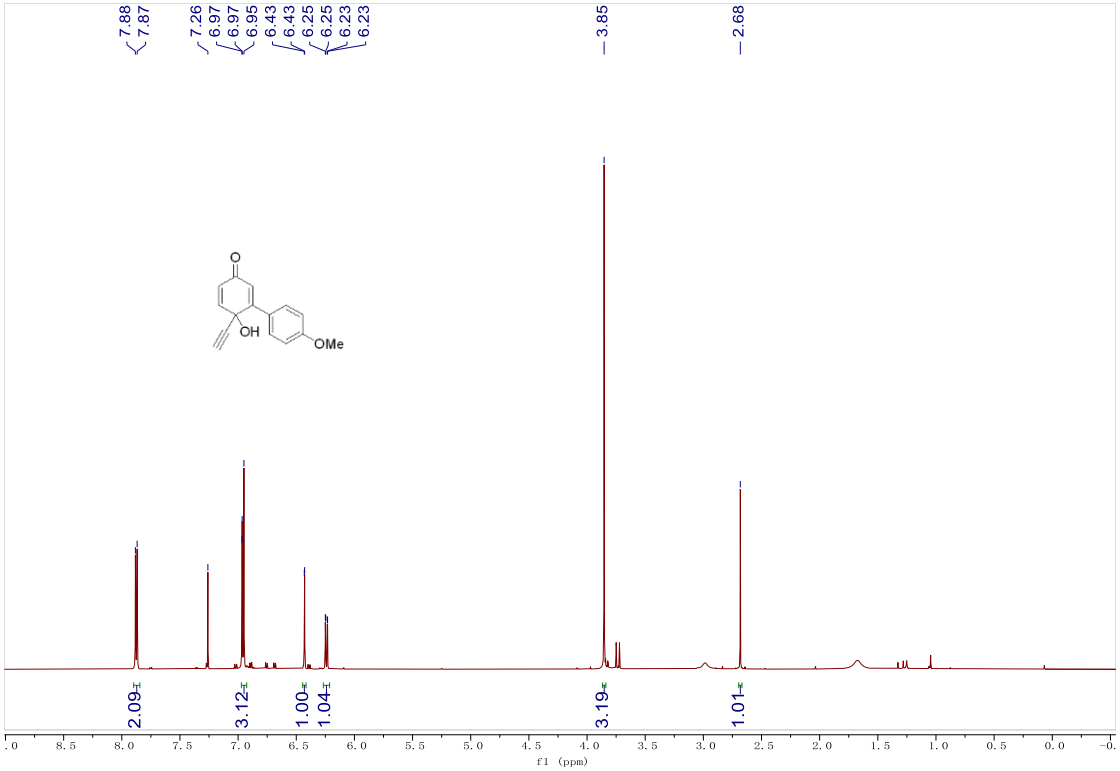


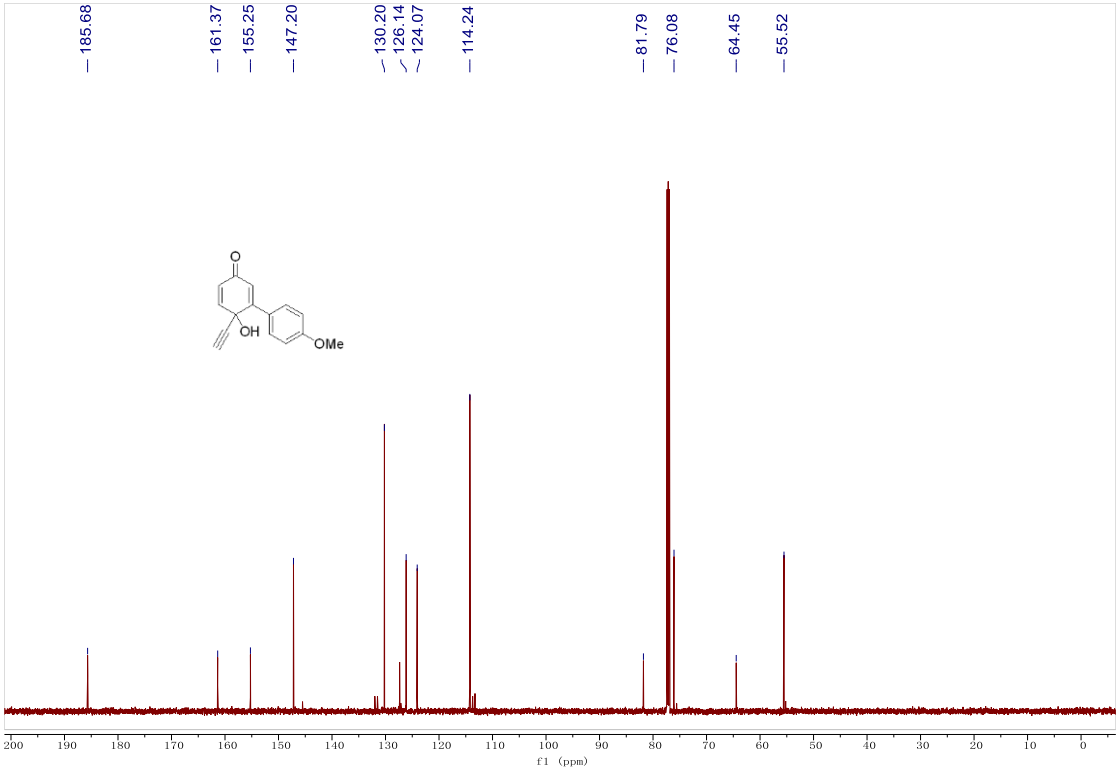
^{1}H and ^{13}C NMR spectra of compound **(1r)**



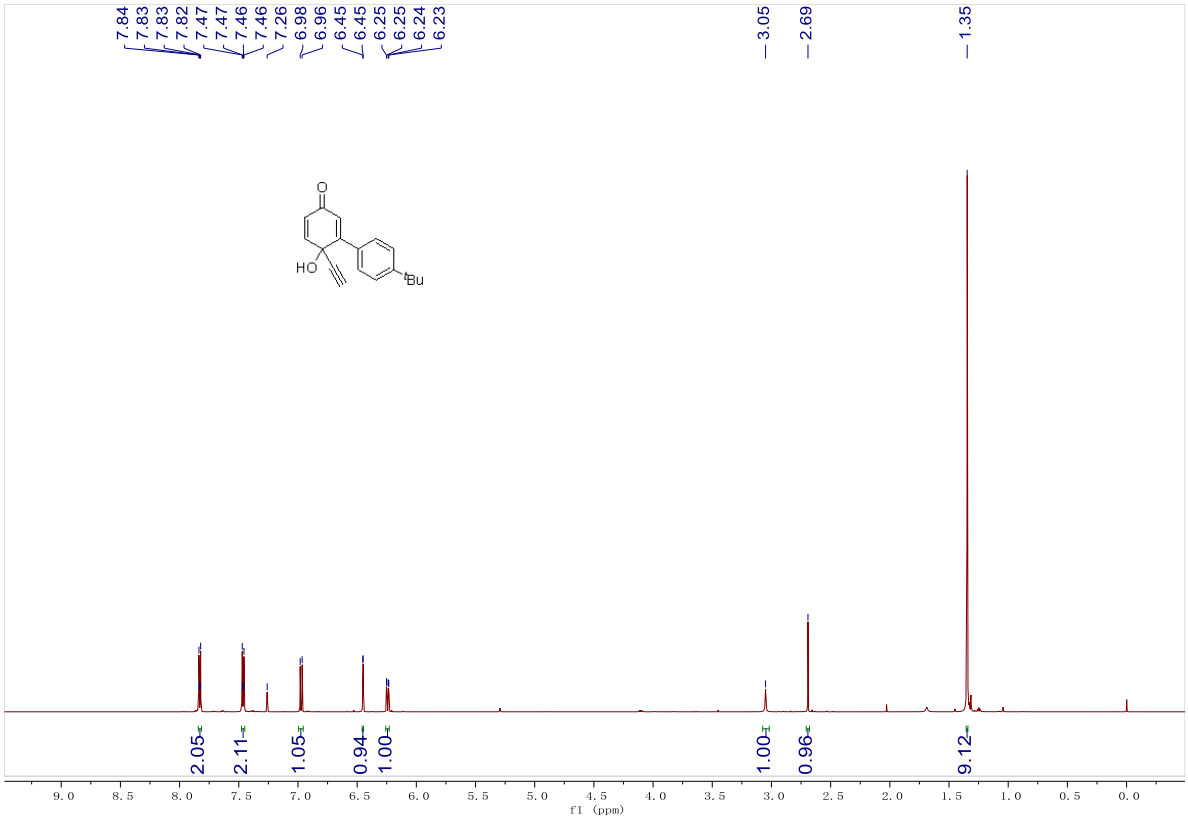


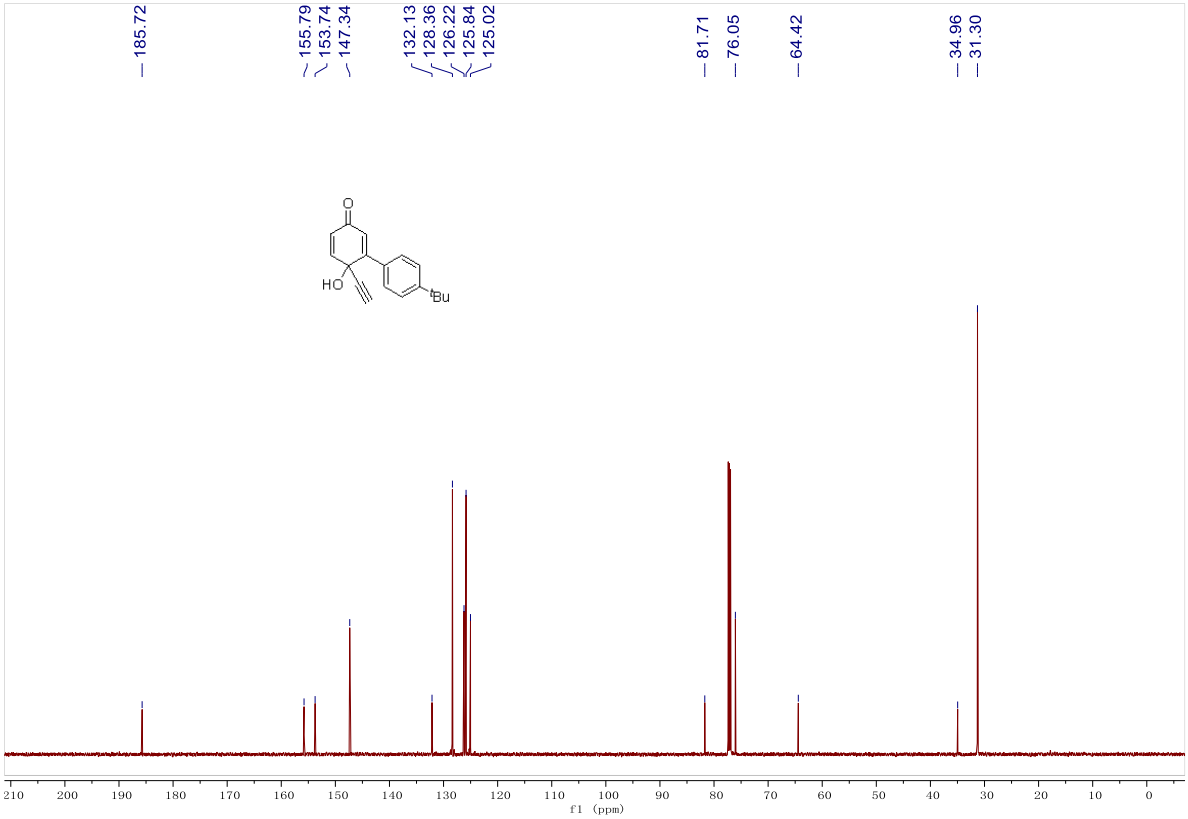
^{1}H and ^{13}C NMR spectra of compound (**1s**)



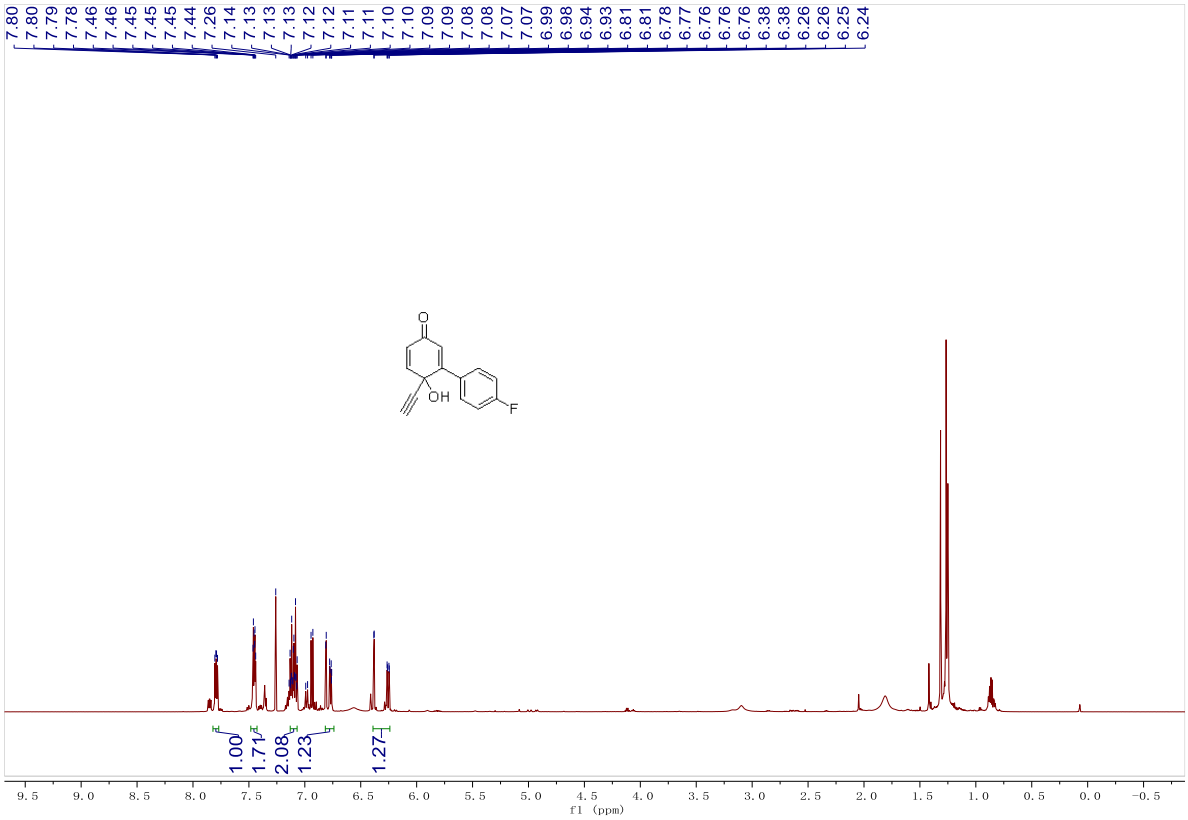


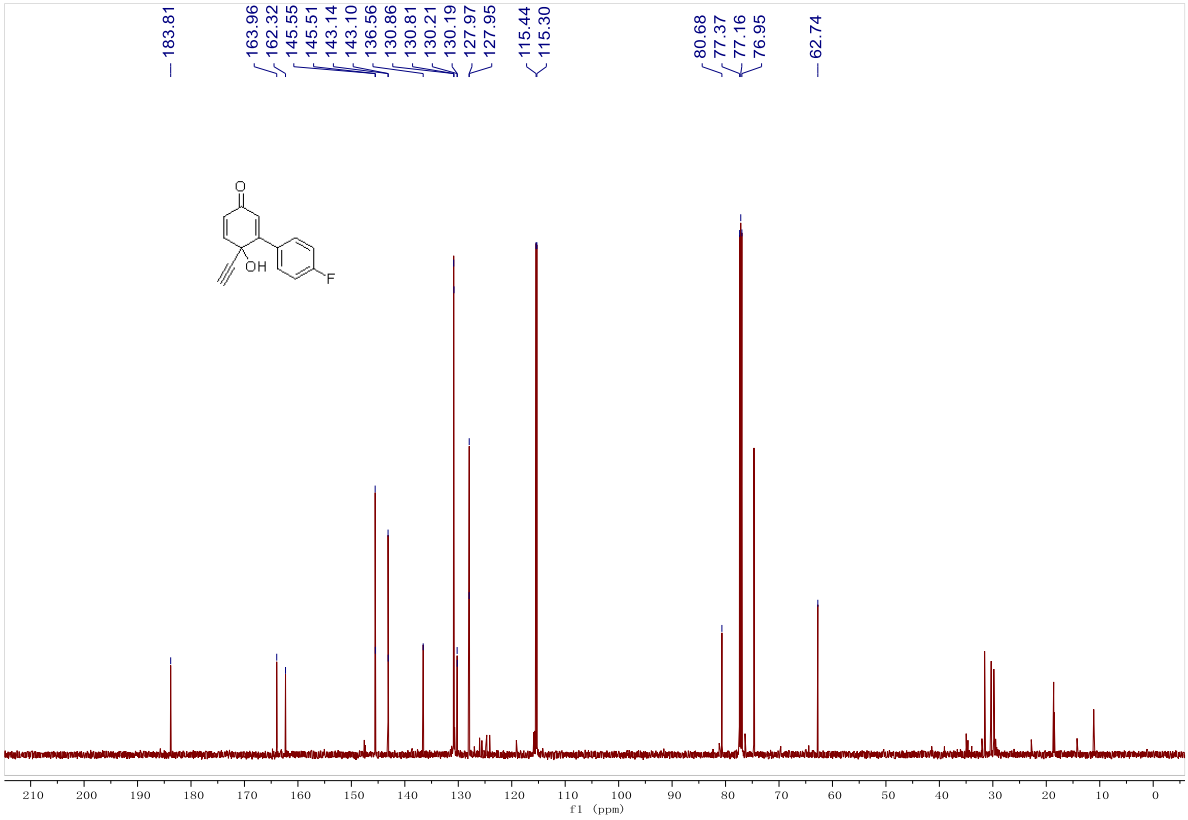
^{1}H and ^{13}C NMR spectra of compound **(1t)**



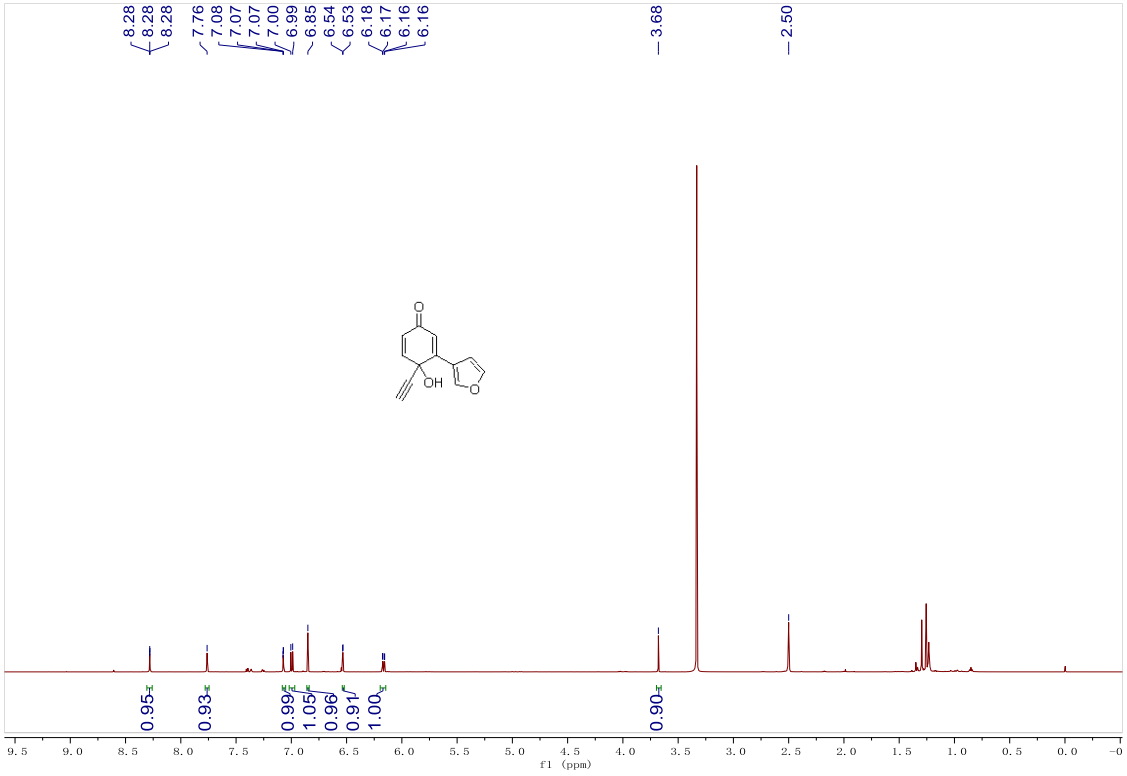


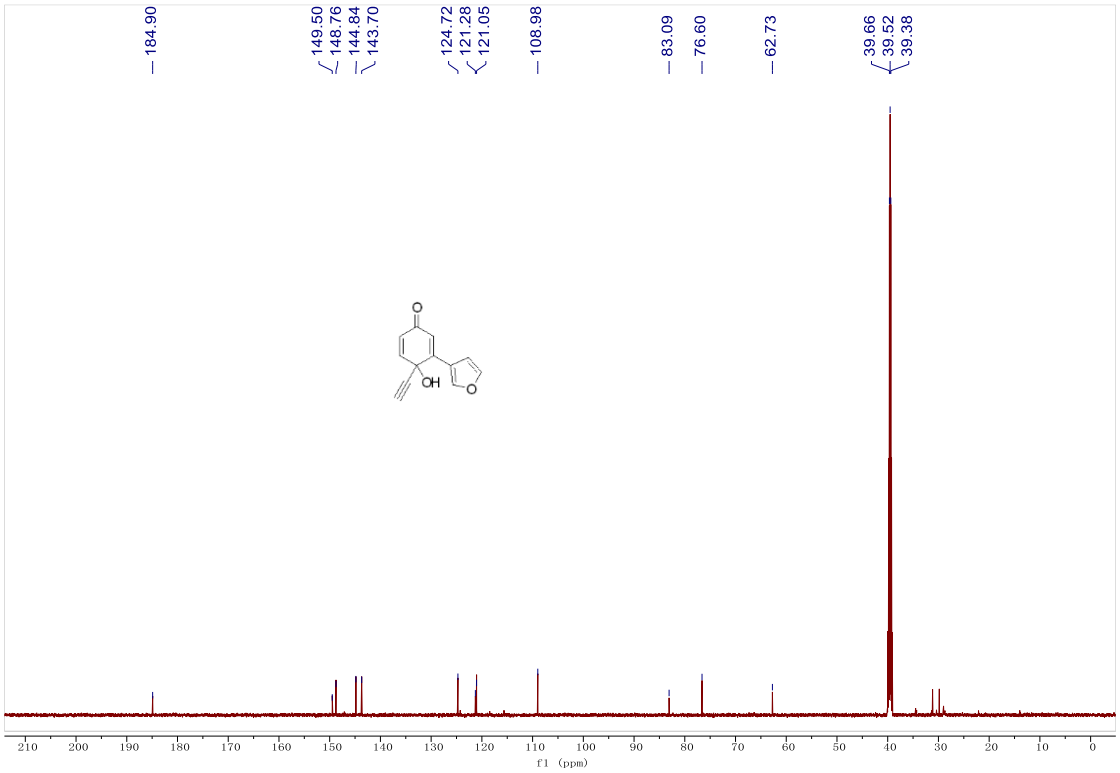
^{1}H and ^{13}C NMR spectra of compound **(1u)**



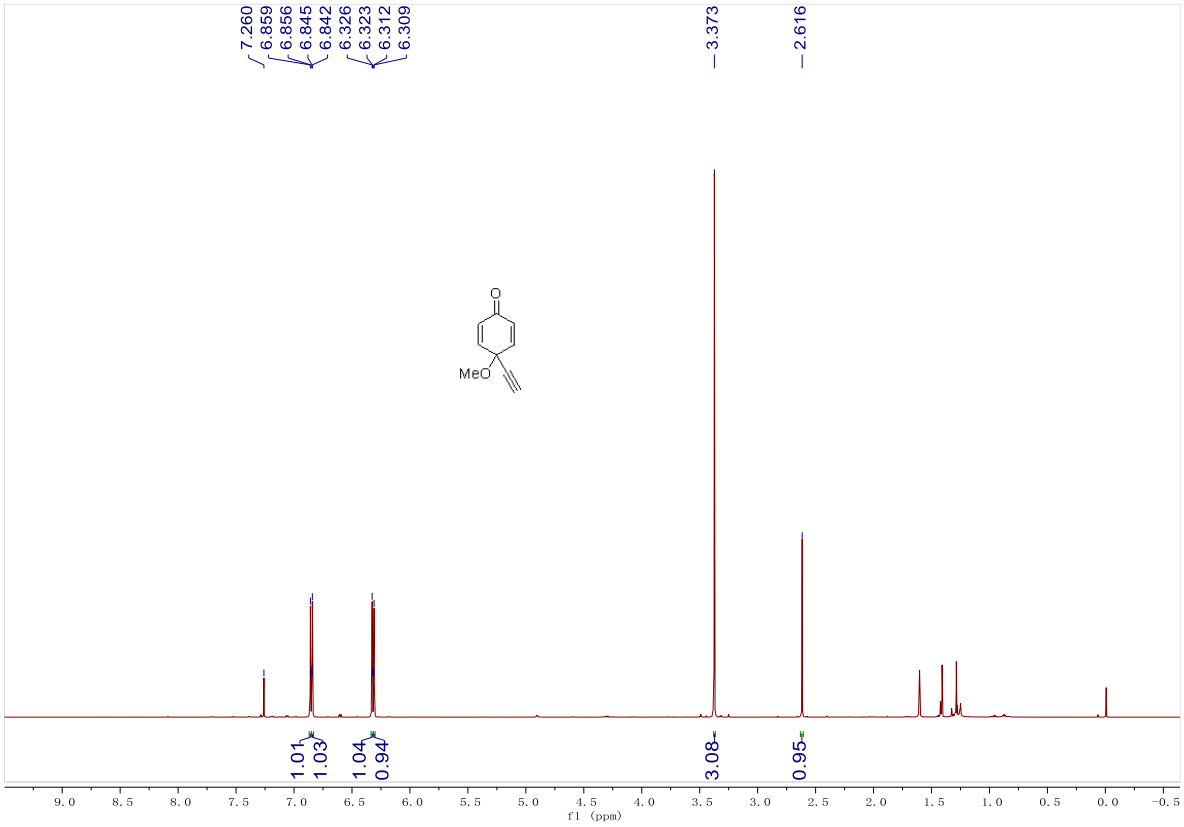


^{1}H and ^{13}C NMR spectra of compound **(1v)**

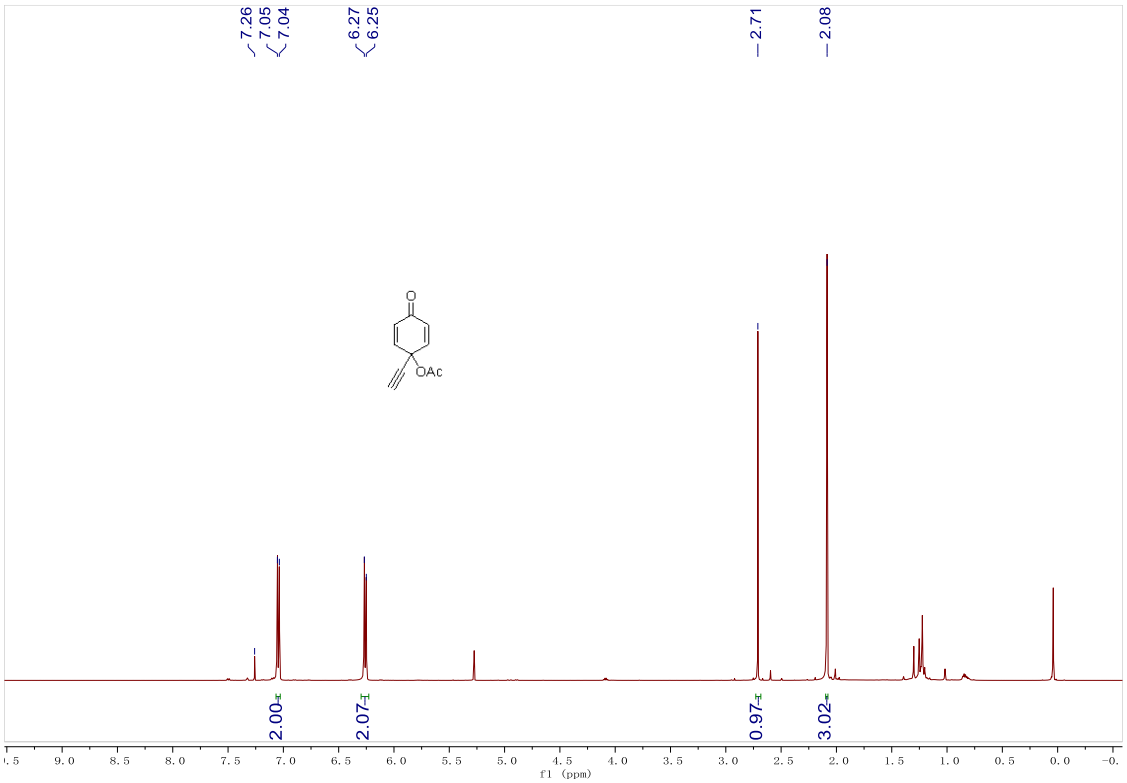


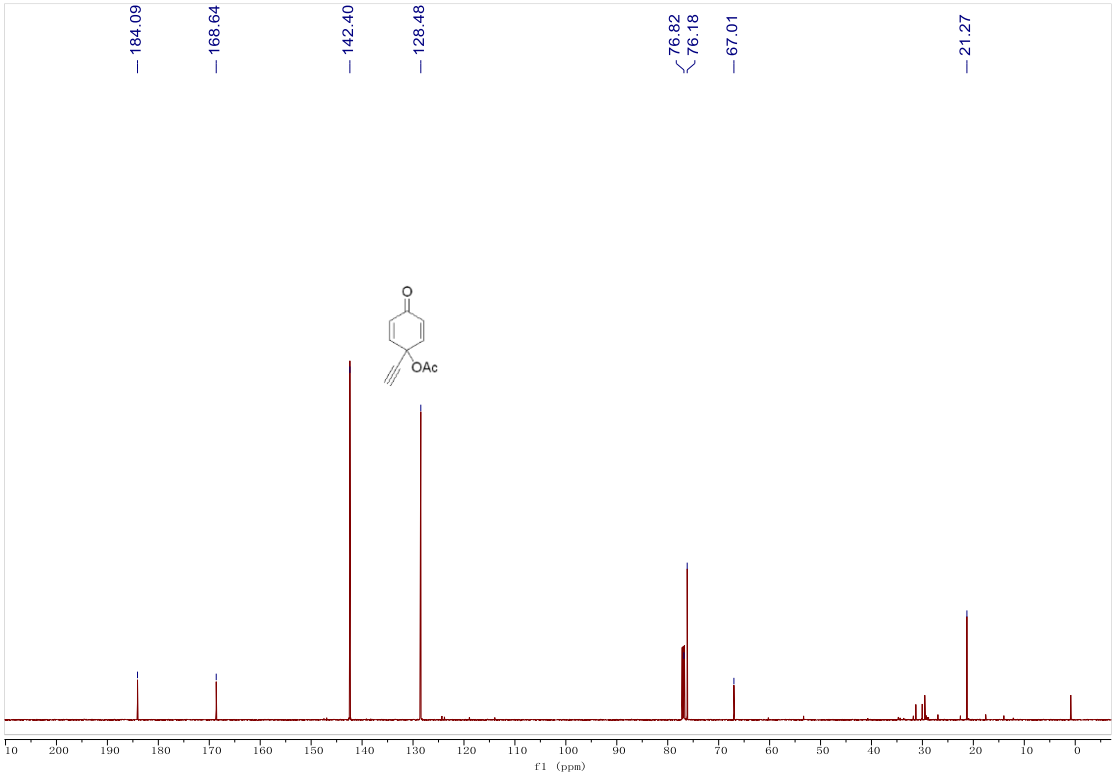


^{1}H and ^{13}C NMR spectra of compound **(1w)**



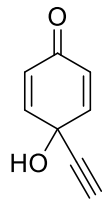
^{1}H and ^{13}C NMR spectra of compound **(1x)**



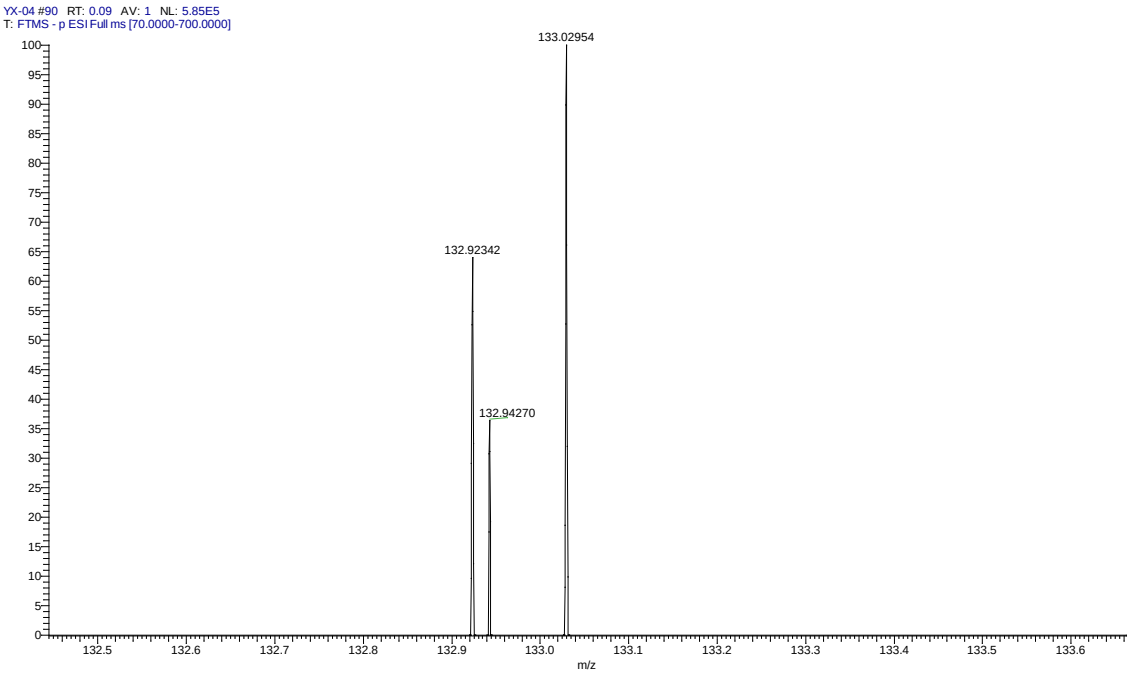


16. Selected HRMS spectra of starting materials, 1,3-diyne and conjugated enediynes

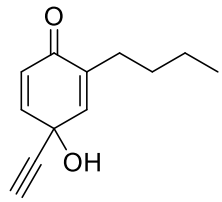
1a



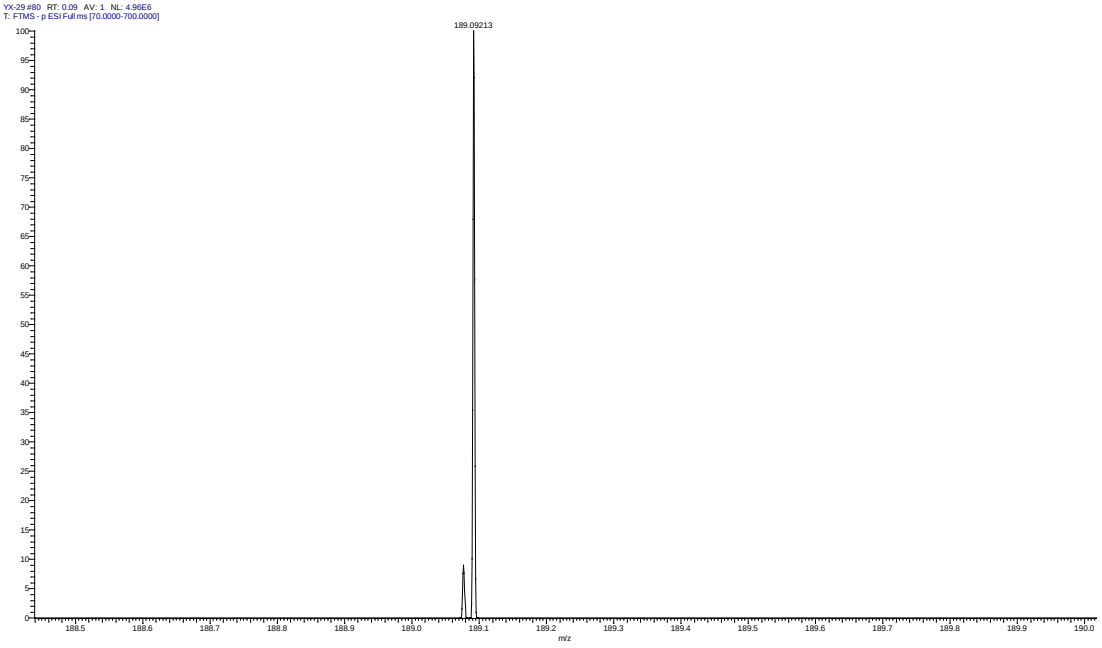
HRMS (ESI) calculated for $C_8H_5O_2^-$ ([M-H]$^-$):133.0295, found 133.0295.



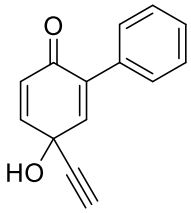
1c



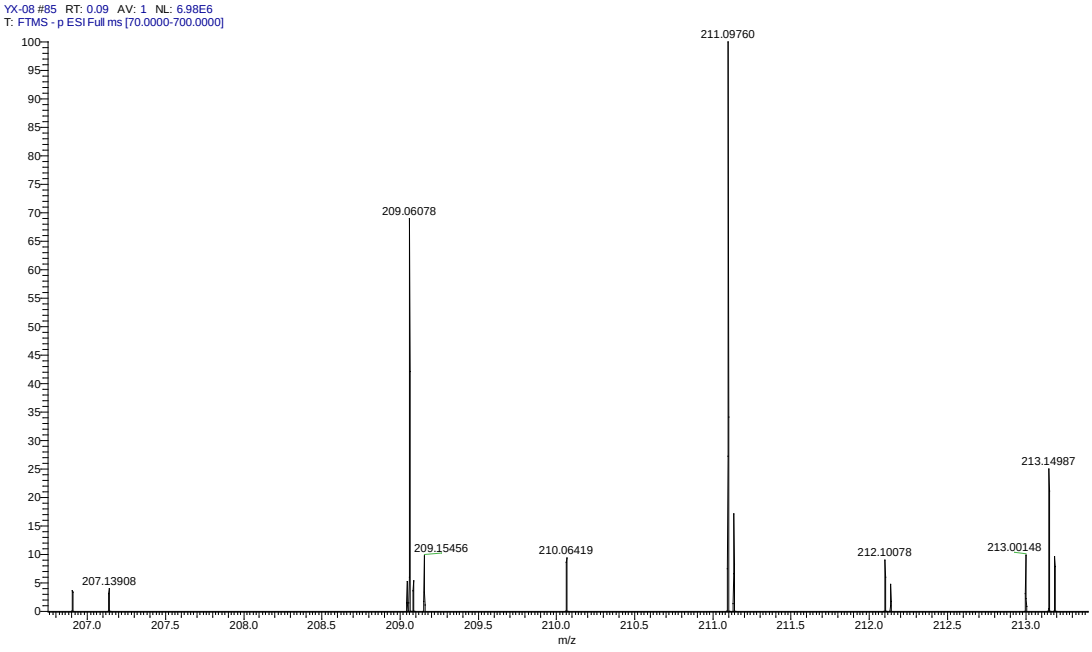
HRMS (ESI) calculated for $C_{12}H_{13}O_2^-$ ([M-H]$^-$):189.0921, found 189.0921.



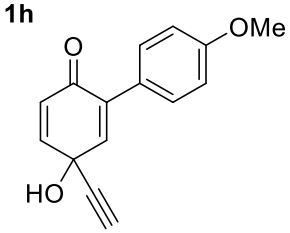
1g



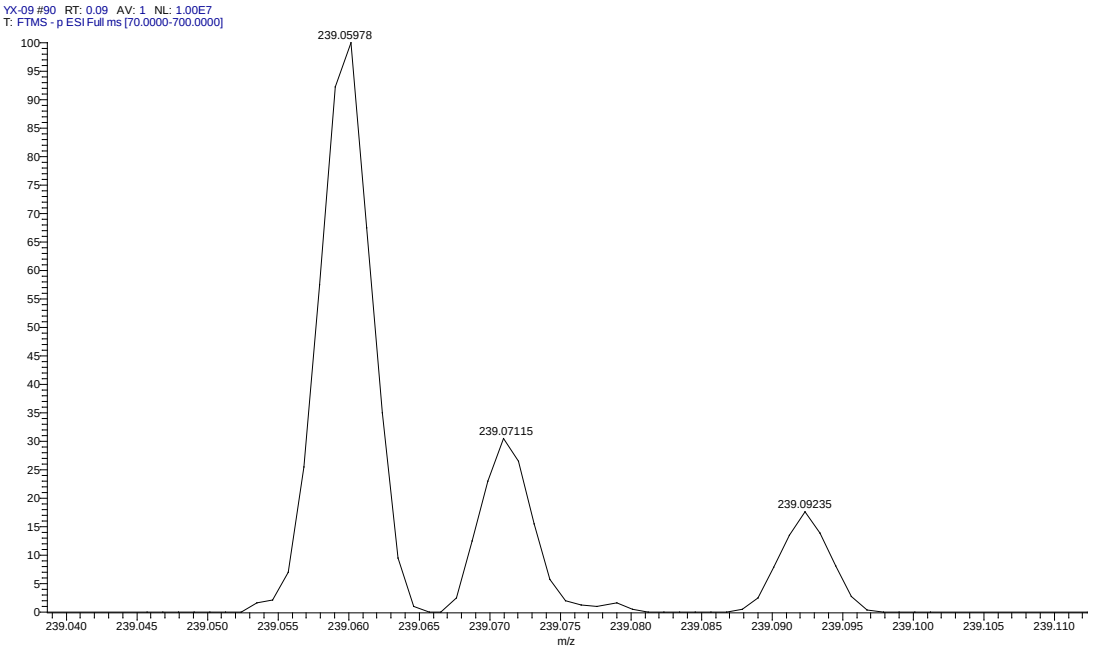
HRMS (ESI) calculated for $C_{14}H_9O_2^-$([M-H]$^-$): 209.0608, found 209.0607.



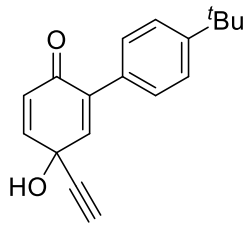
1h



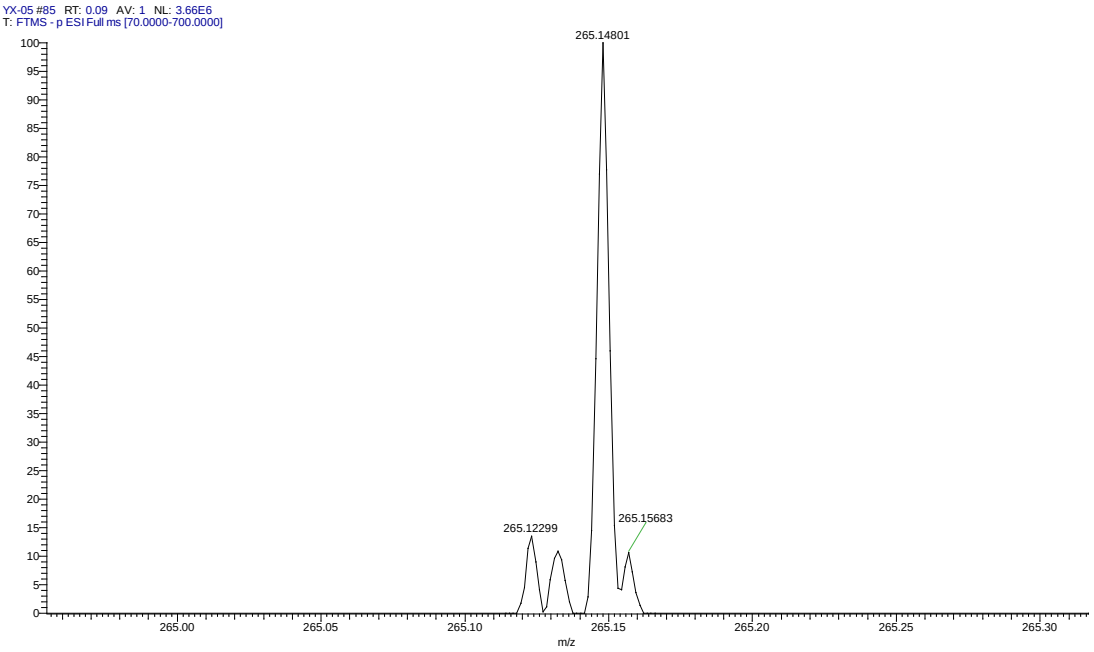
HRMS (ESI) calculated for $C_{15}H_{11}O_3^-$ ([M-H]$^-$): 239.0714, found 239.0711.



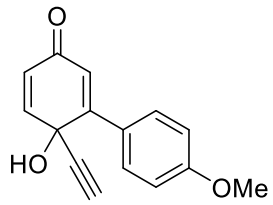
1i



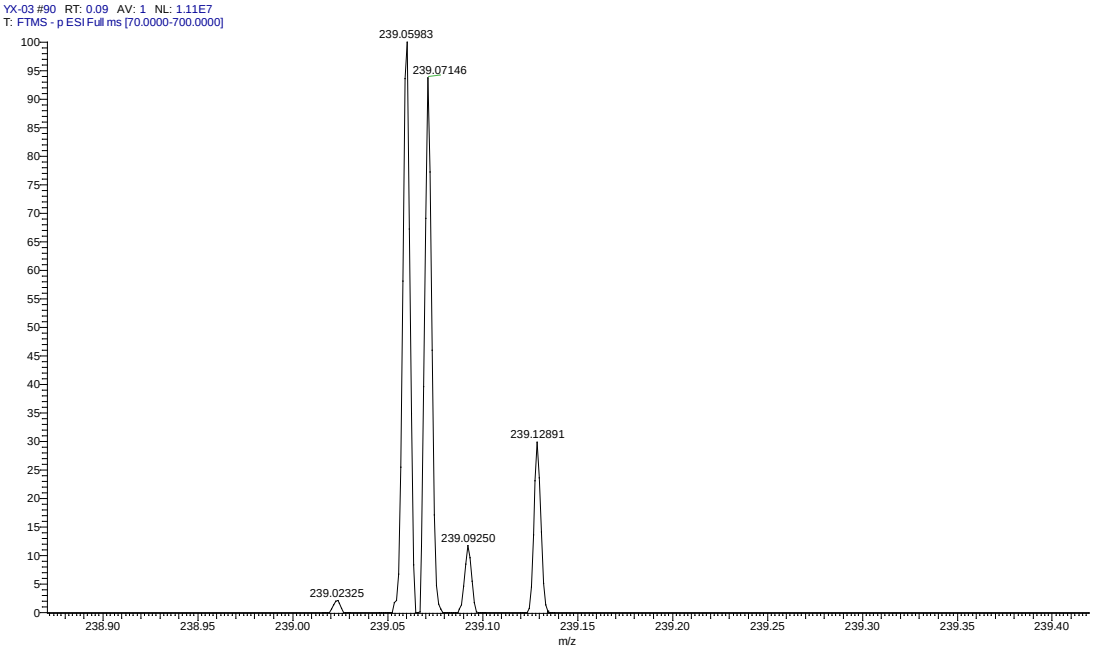
HRMS (ESI) calculated for $C_{18}H_{17}O_2^-$([M-H]$^-$): 265.1234, found 265.1229.



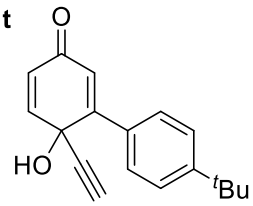
1s



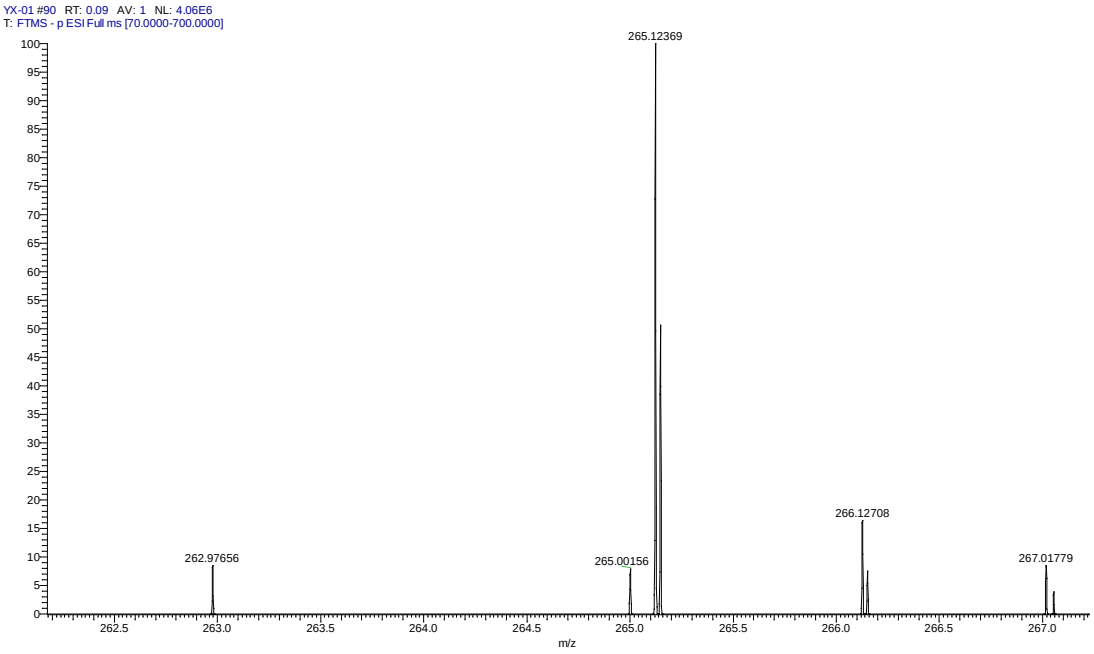
HRMS (ESI) calculated for $C_{15}H_{11}O_3^-$ ([M-H]$^-$): 239.0714, found 239.0714.



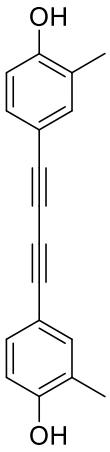
1t



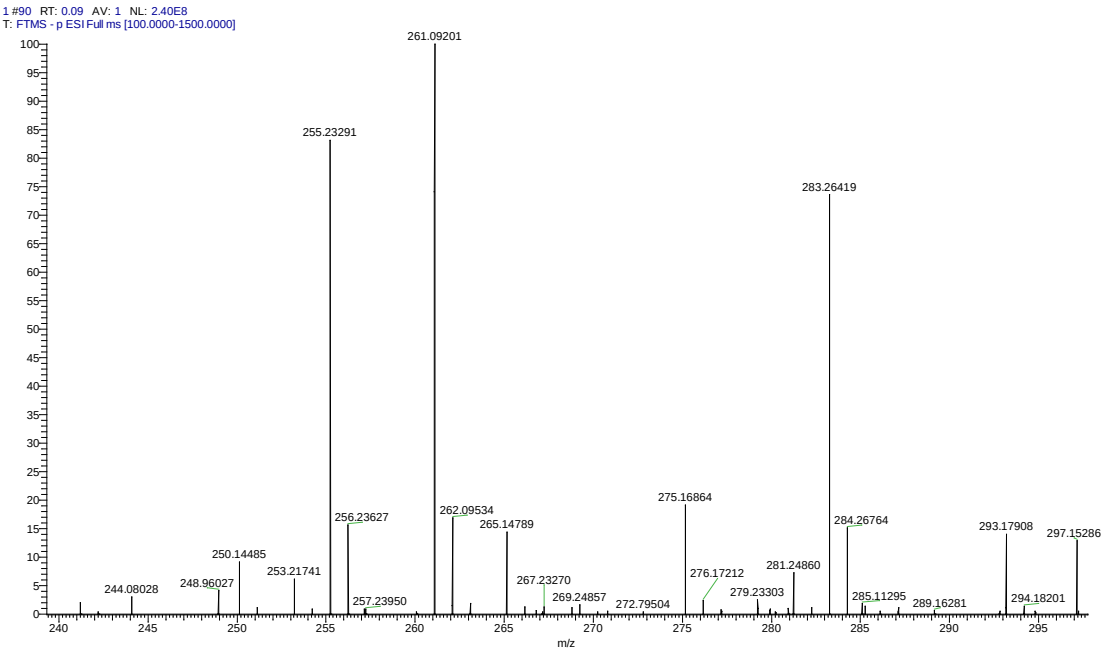
HRMS (ESI) calculated for $C_{18}H_{17}O_2^-$([M-H]$^-$): 265.1234, found 265.1236.



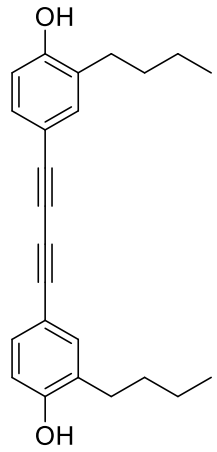
2b



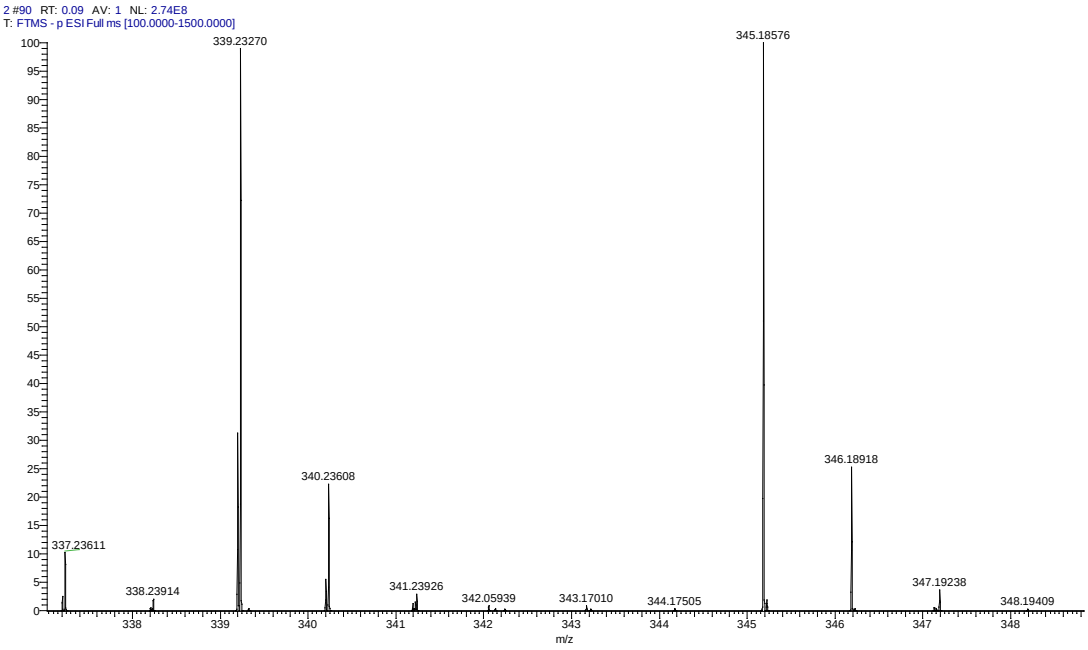
HRMS (ESI) calculated for $C_{18}H_{13}O_2^-$ ([M-H]$^-$): 261.0921, found 261.0920.



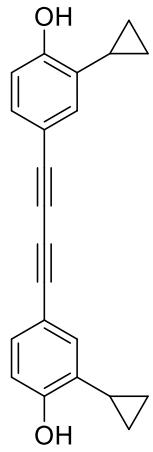
2c



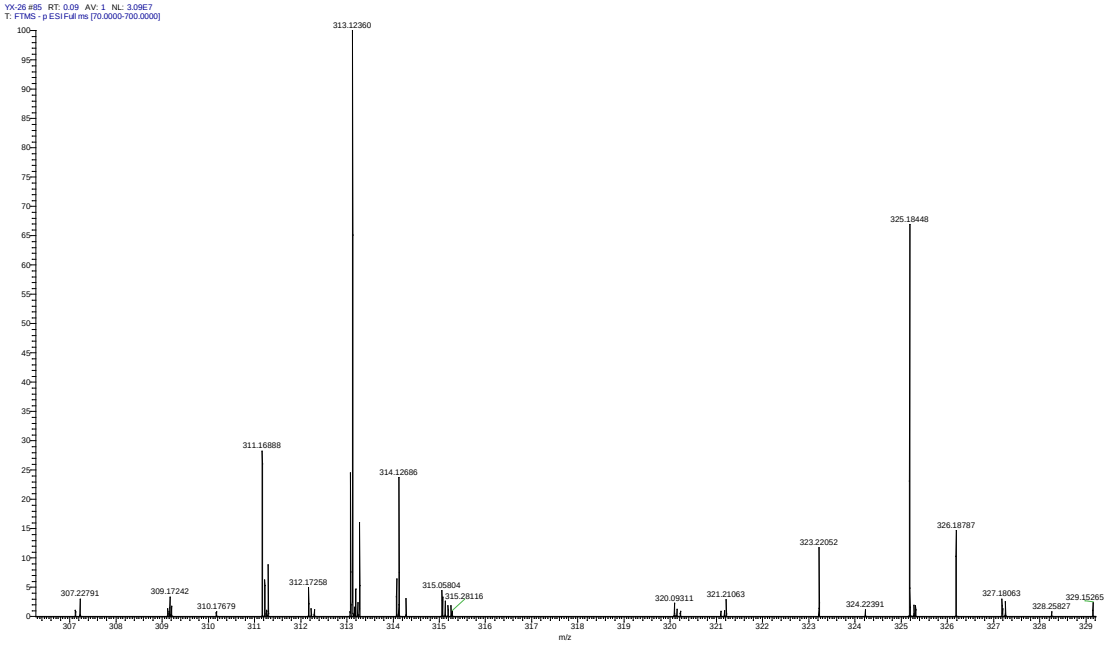
HRMS (ESI) calculated for $C_{24}H_{25}O_2^-$ ([M-H]$^-$): 345.1860, found 345.1857.



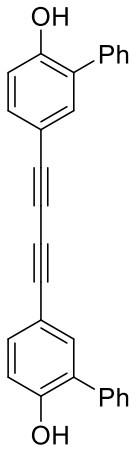
2f



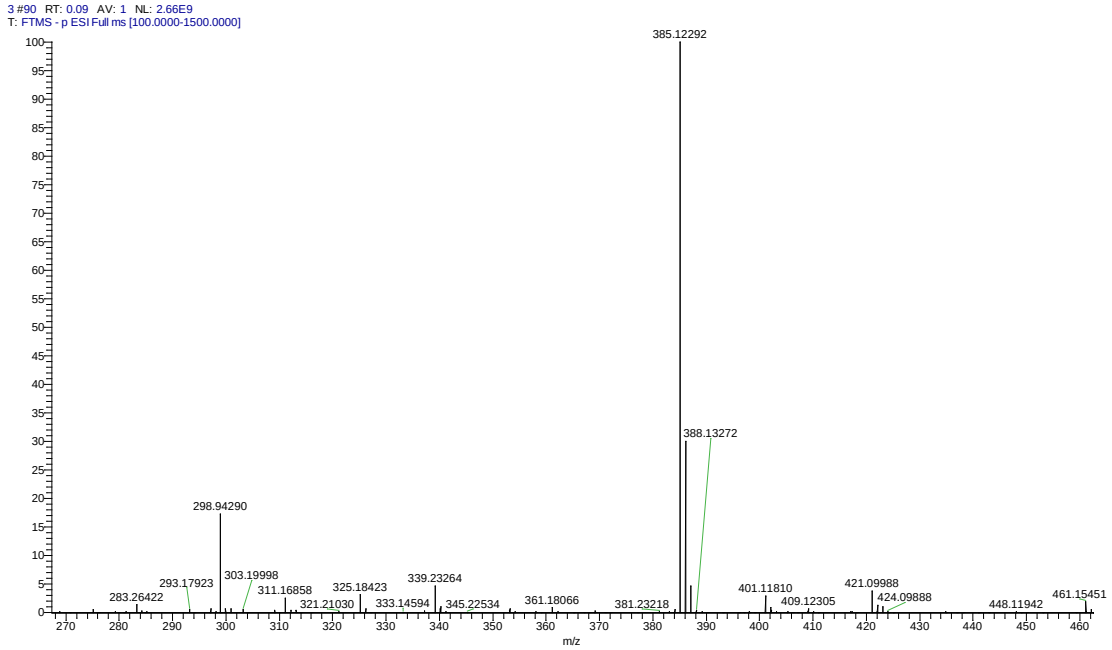
HRMS (ESI) calculated for $C_{22}H_{17}O_2^-$([M-H]$^-$): 313.1234, found 313.1236.



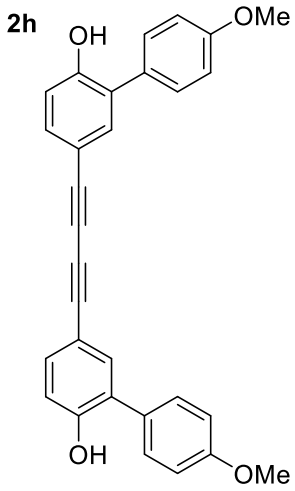
2g



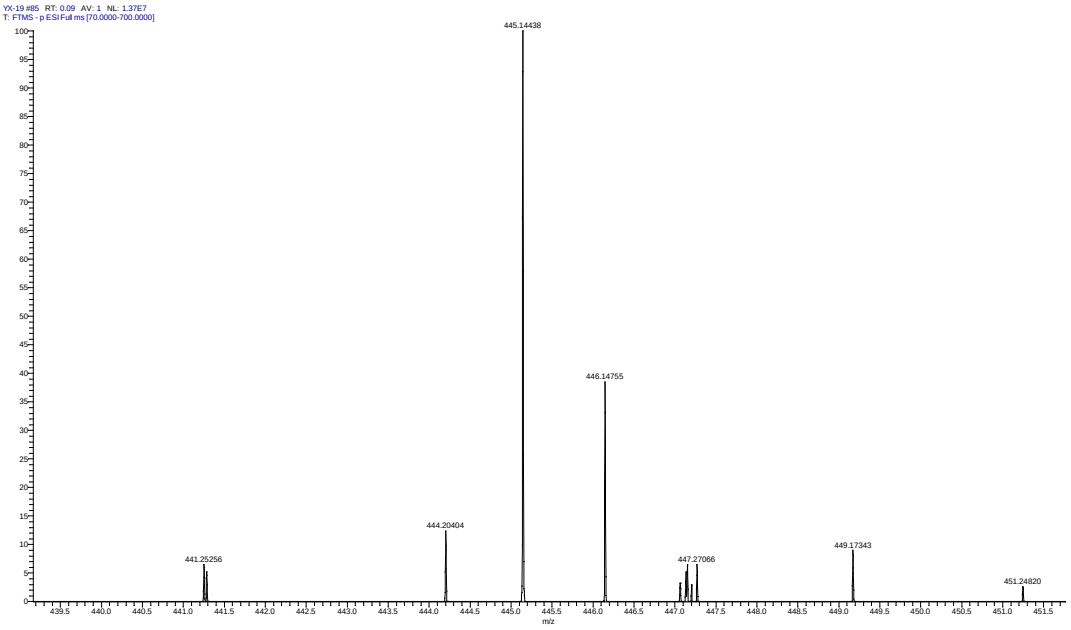
HRMS (ESI) calculated for $C_{28}H_{17}O_2^-$([M-H]$^-$): 385.1234, found 385.1229.



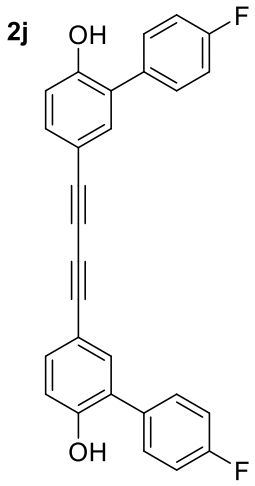
2h



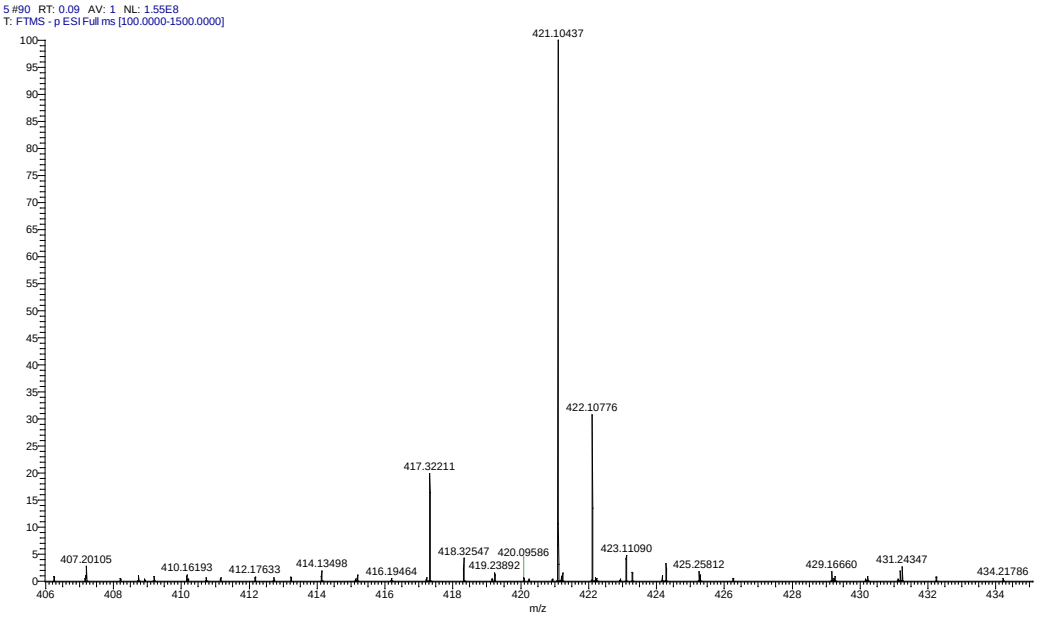
HRMS (ESI) calculated for $C_{30}H_{21}O_4^-$([M-H]$^-$): 445.1445, found: 445.1443.



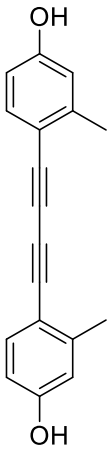
2j



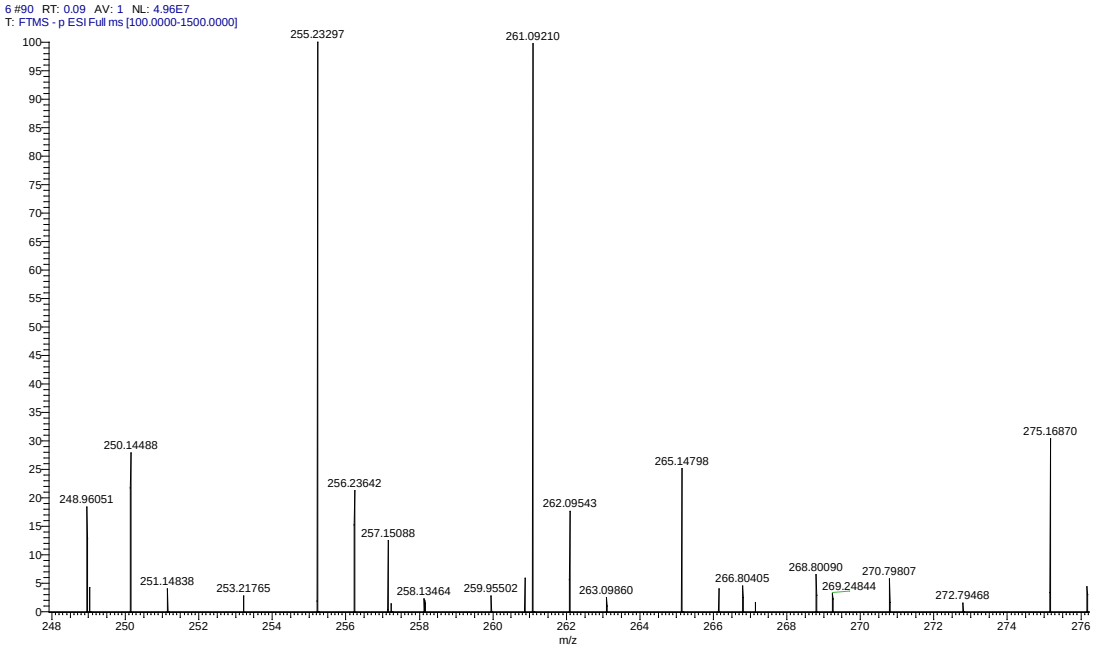
HRMS (ESI) calculated for $C_{28}H_{15}F_2O_2^-$([M-H]$^-$): 421.1046, found : 421.1043.



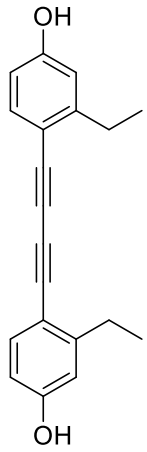
2k



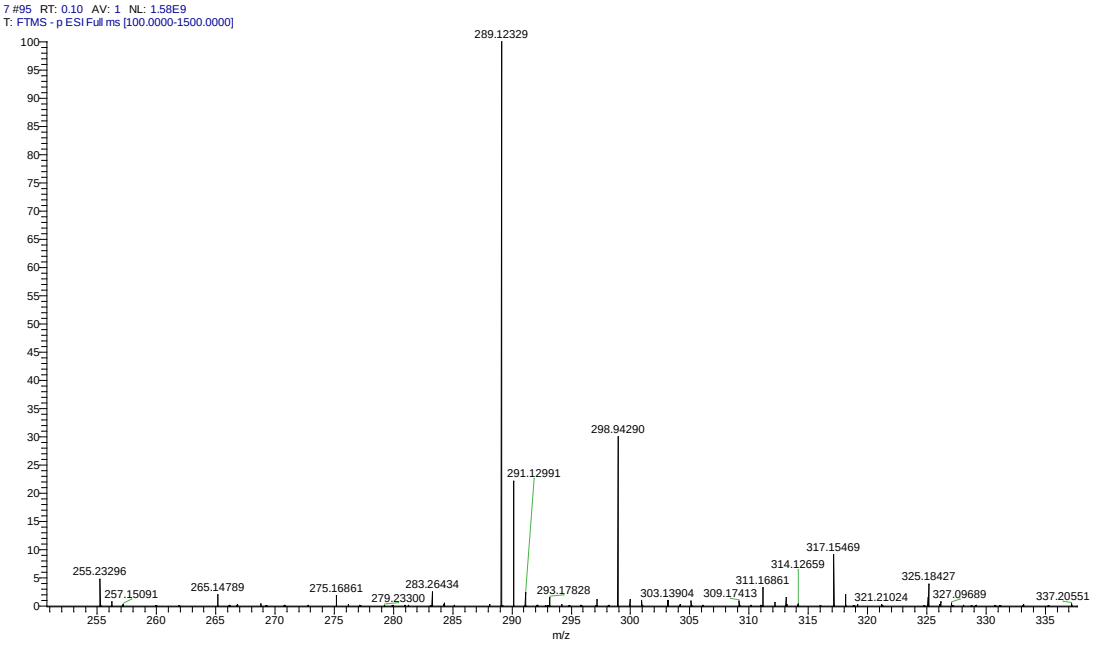
HRMS (ESI) calculated for $C_{18}H_{13}O_2^-$ ([M-H]$^-$): 261.0921, found 261.0921.



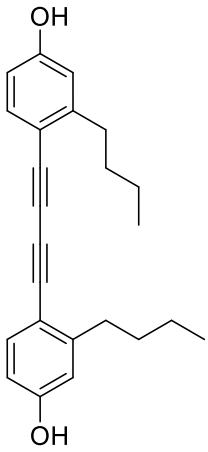
2l



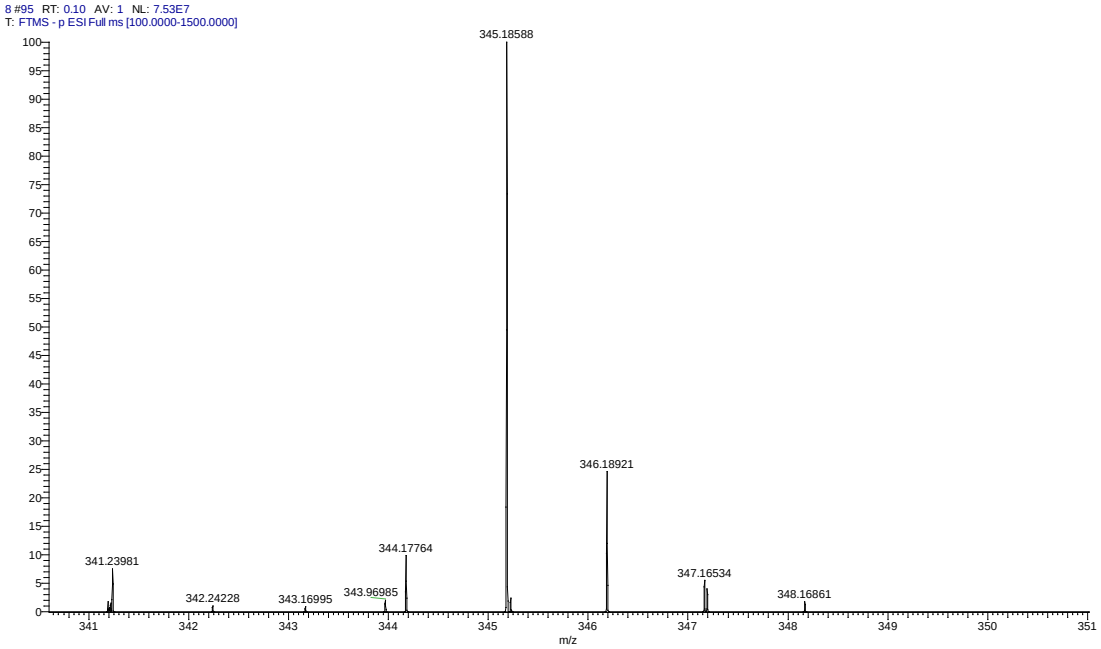
HRMS (ESI) calculated for $C_{20}H_{17}O_2^-$([M-H]$^-$): 289.1234, found : 289.1232.



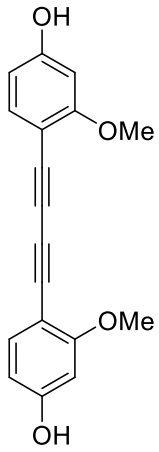
2m



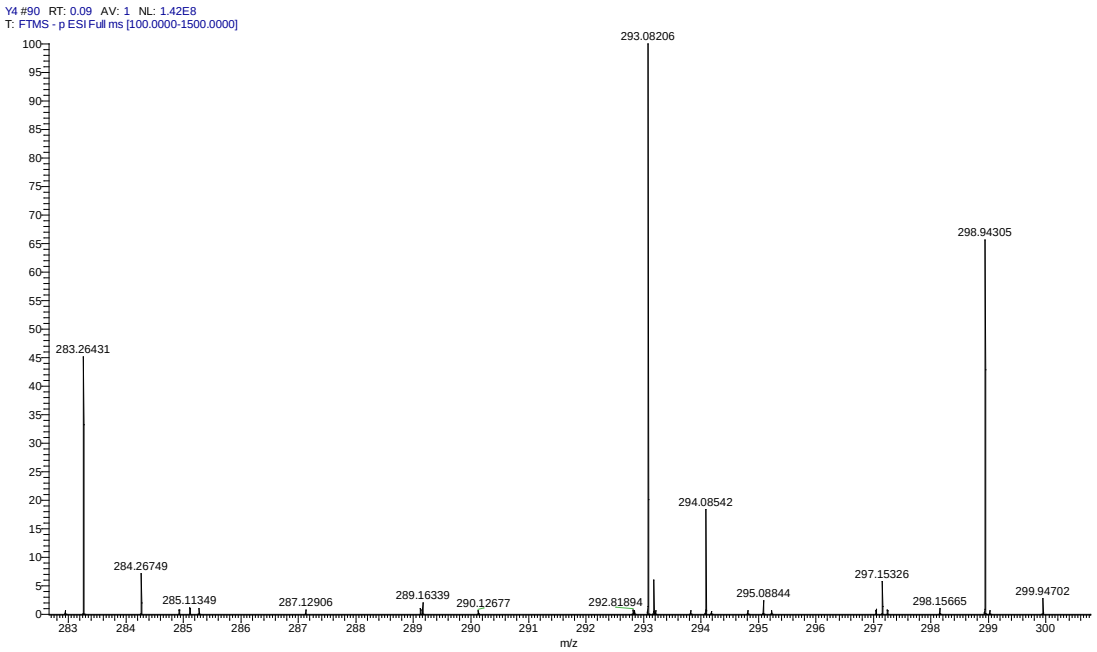
HRMS (ESI) calculated for $C_{24}H_{25}O_2^-$ ([M-H]$^-$): 345.1860, found 345.1858.



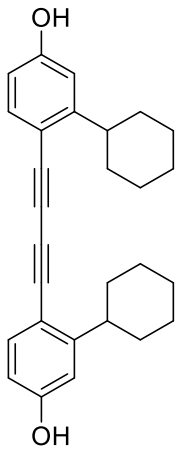
2n



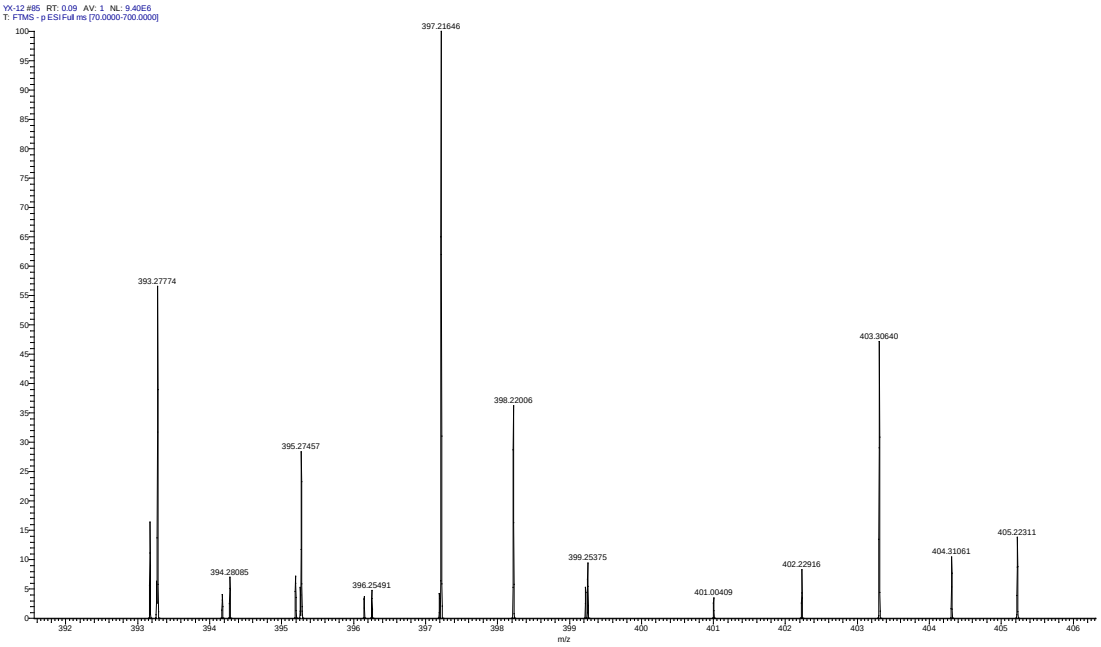
HRMS (ESI) calculated for $C_{18}H_{13}O_4^-$ ([M-H]$^-$): 293.0819, found 293.0820.



2o



HRMS (ESI) calculated for $C_{28}H_{29}O_2^-$([M-H]$^-$): 397.2173, found 397.2164.



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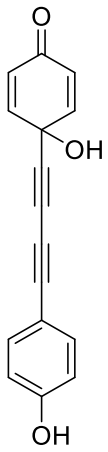
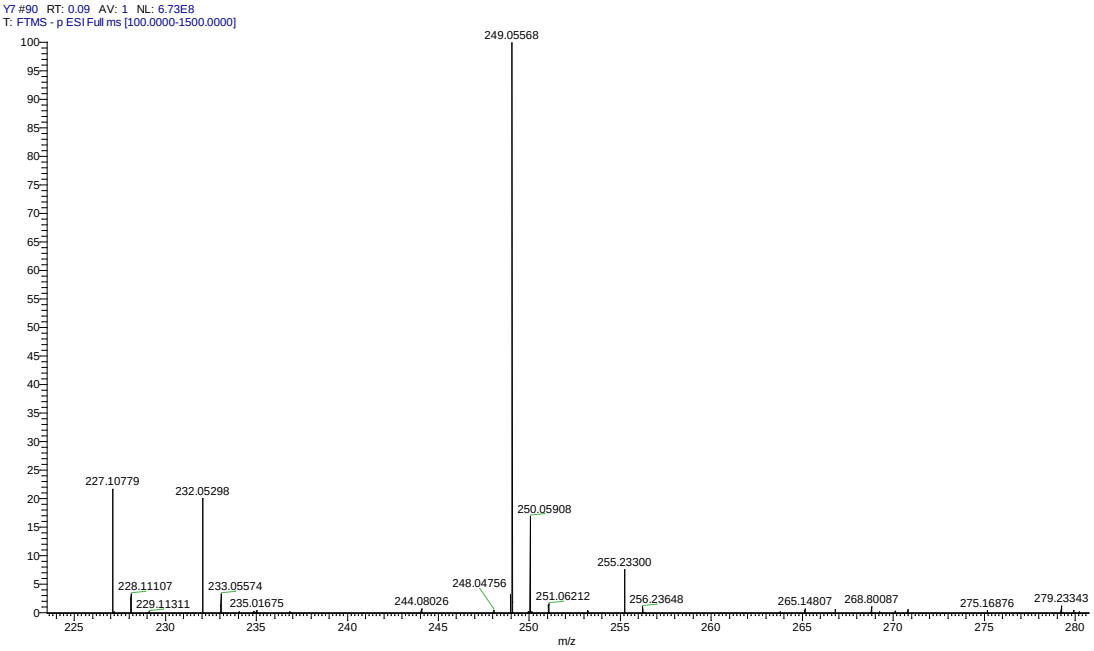
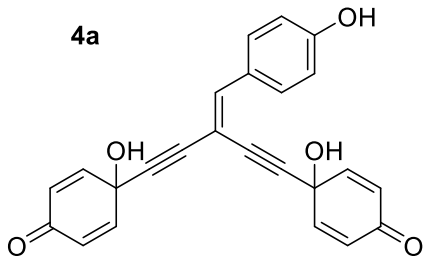
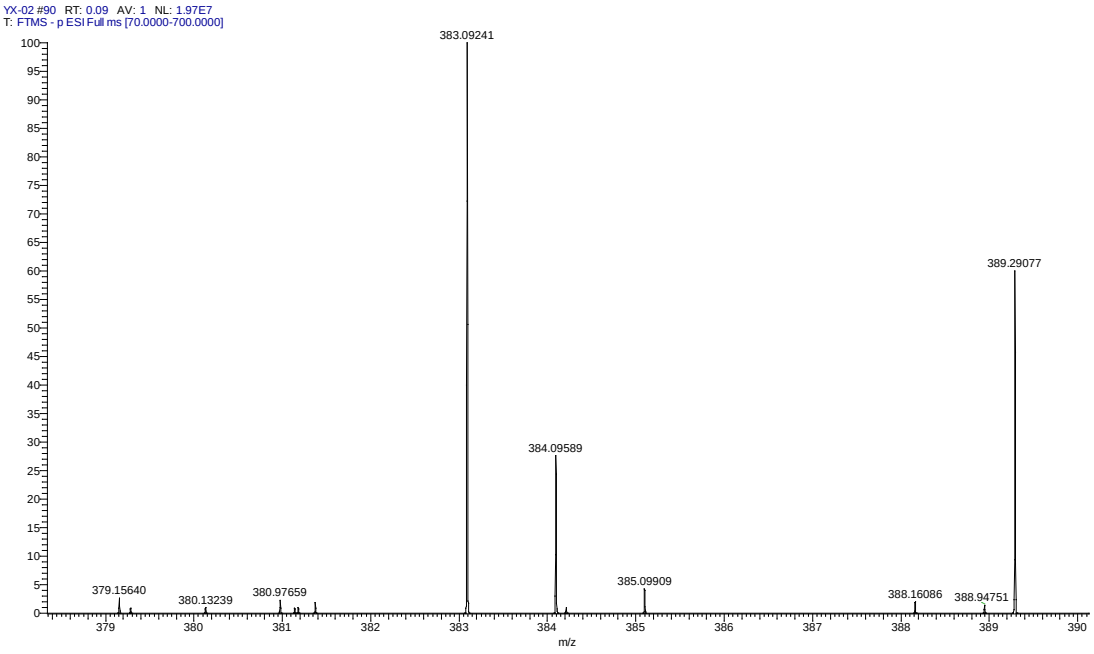


HRMS (ESI) calculated for $C_{16}H_9O_3^-$ ([M-H]$^-$): 249.0557, found 249.0556.

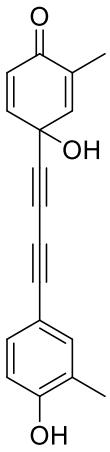




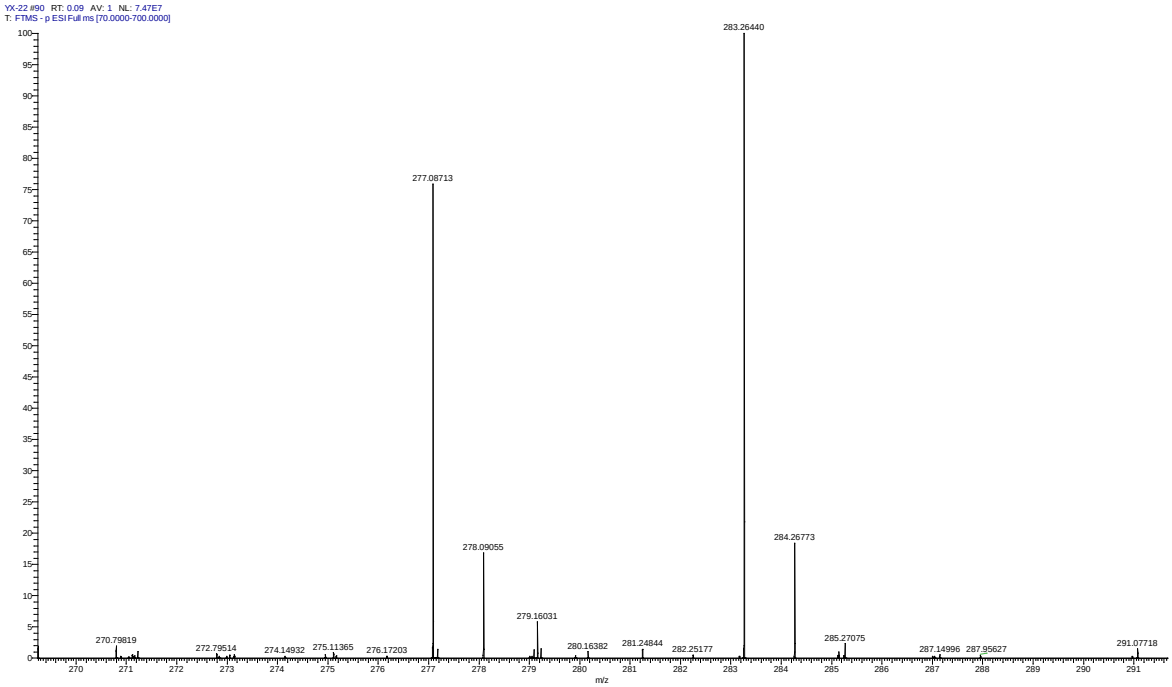
HRMS (ESI) calculated for $C_{24}H_{15}O_5^-$ ([M-H]$^-$): 383.0925, found 383.0924.



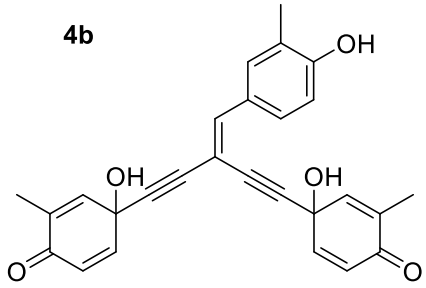
3b



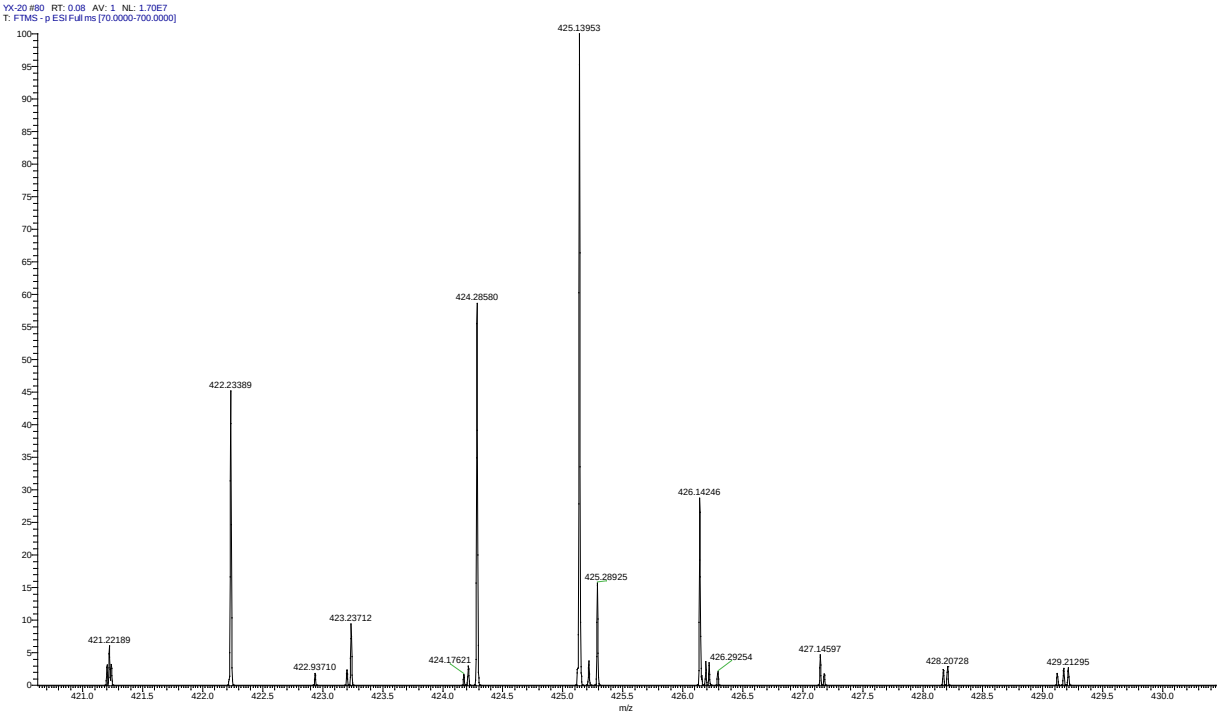
HRMS (ESI) calculated for $C_{18}H_{13}O_3^-$ ([M-H]$^-$): 277.0870, found 277.0871.



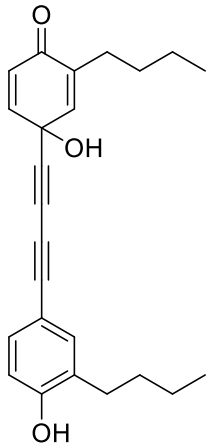
4b



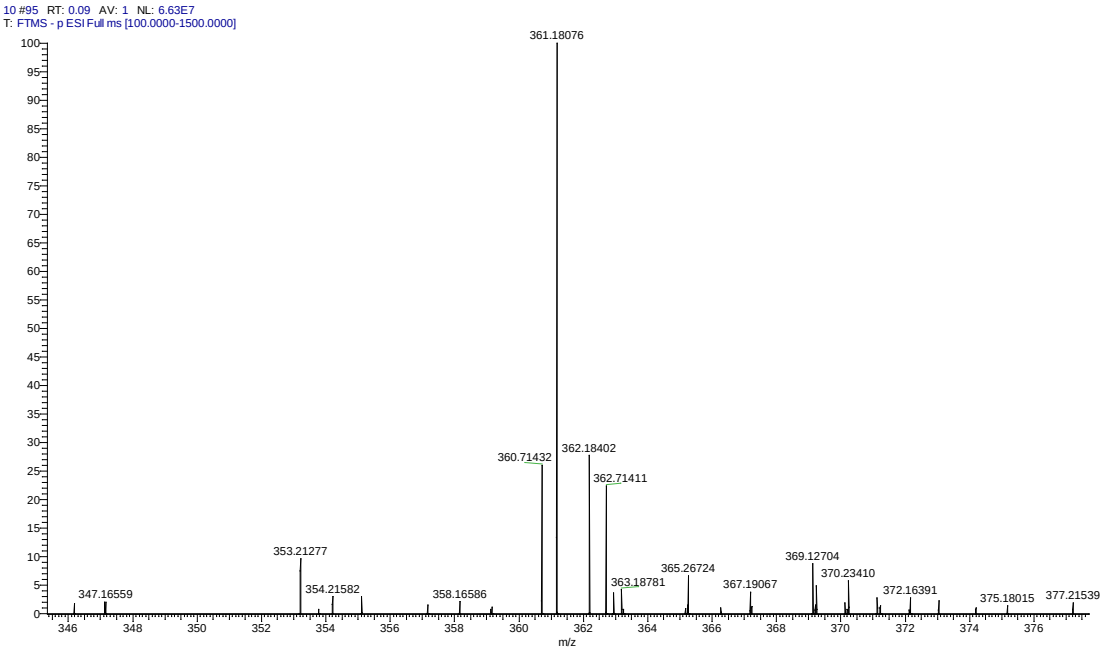
HRMS (ESI) calculated for $C_{27}H_{21}O_5^-$([M-H]$^-$): 425.1394, found:425.1395.



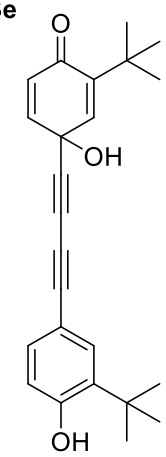
3d



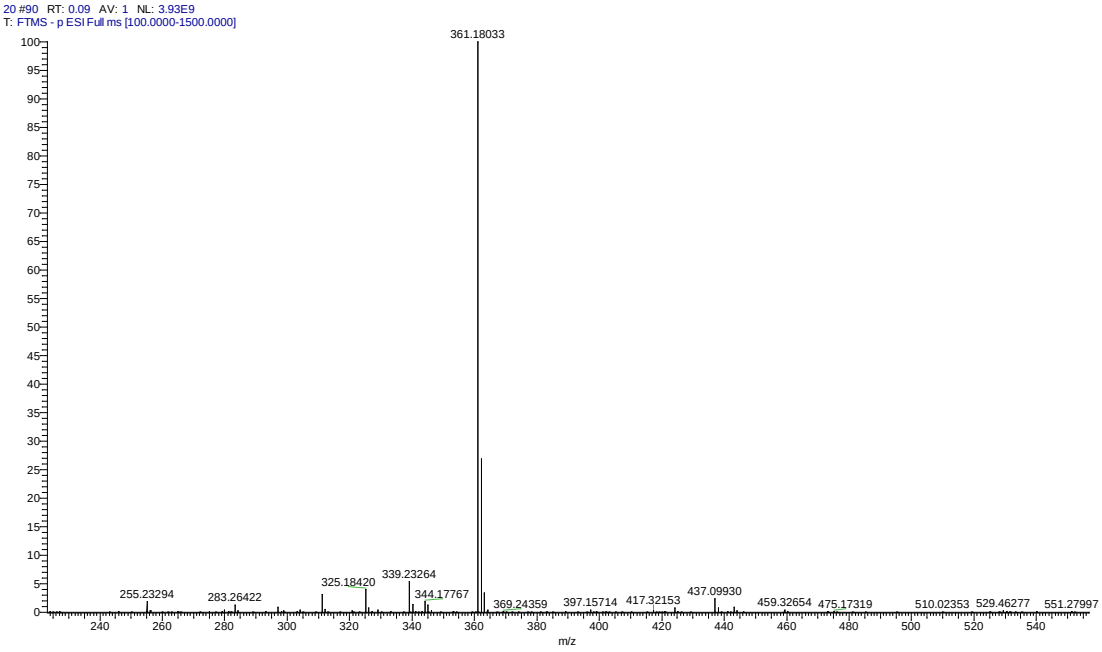
HRMS (ESI) calculated for $C_{24}H_{25}O_3^-$([M-H]$^-$): 361.1809, found 361.1807.



3e



HRMS (ESI) calculated for $C_{24}H_{25}O_3^-$([M-H]$^-$): 361.1809, found 361.1803.



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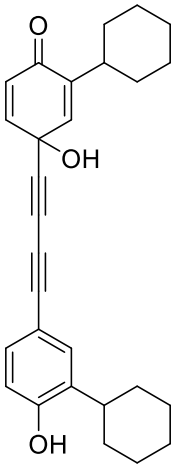
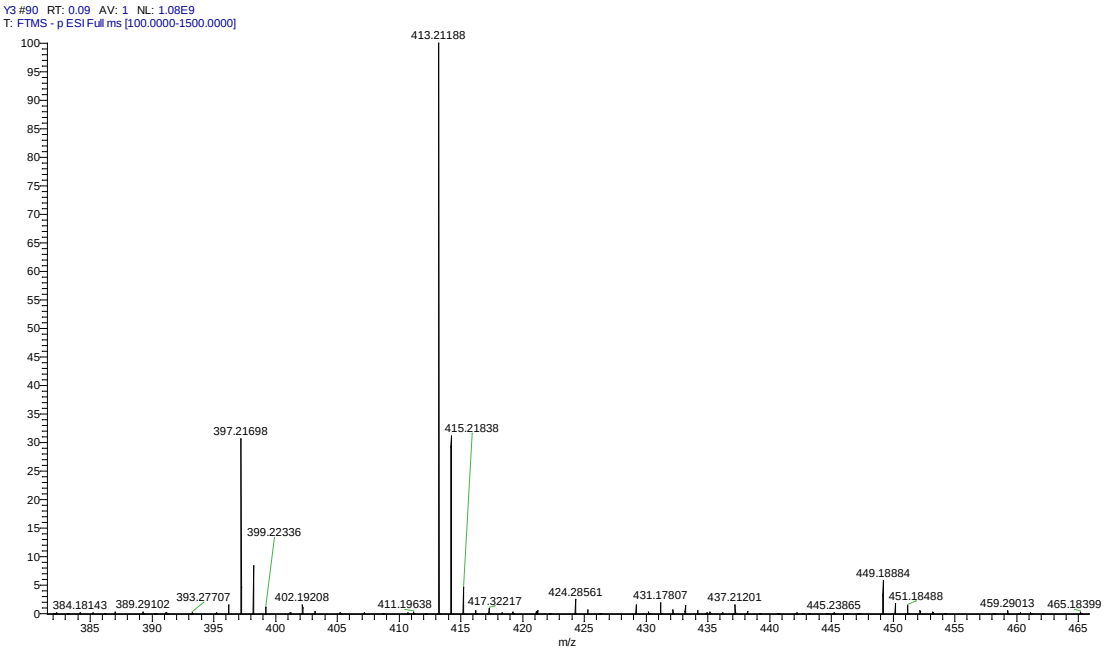
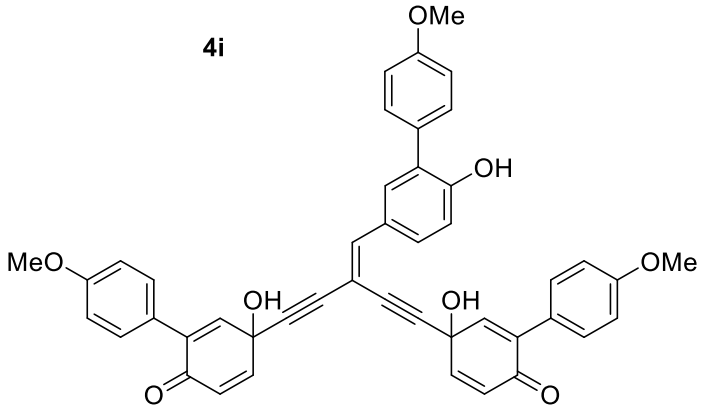


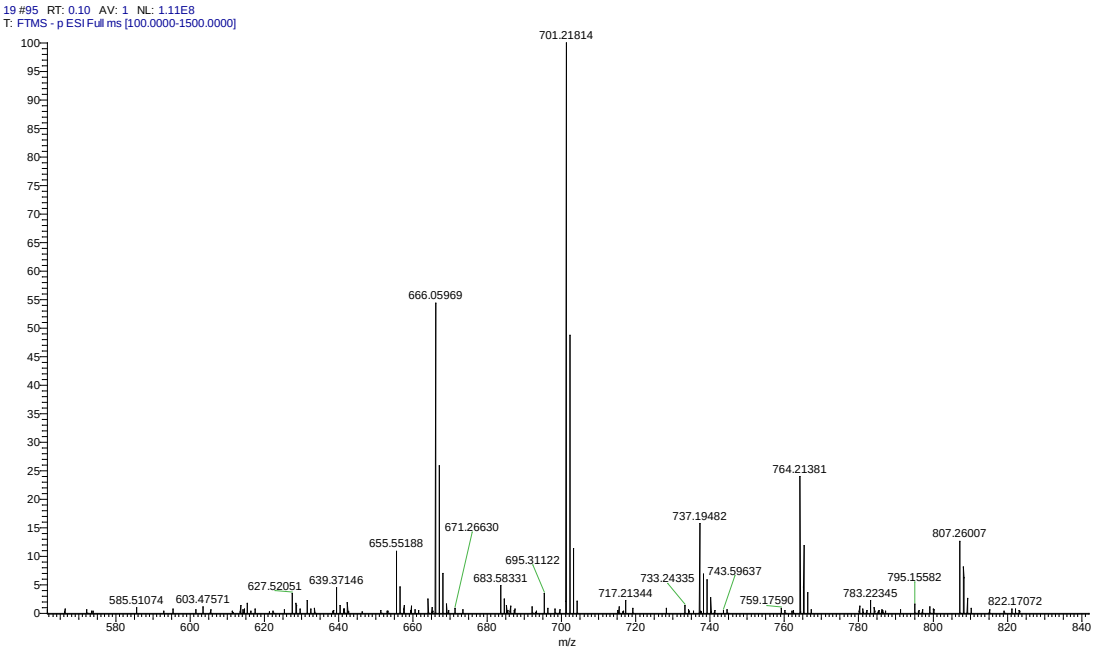
HRMS (ESI) calculated for $C_{28}H_{29}O_3^-$([M-H]$^-$): 413.2112, found 413.2118.



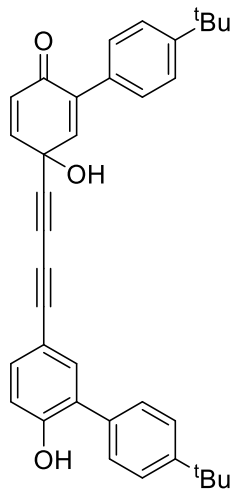
4i



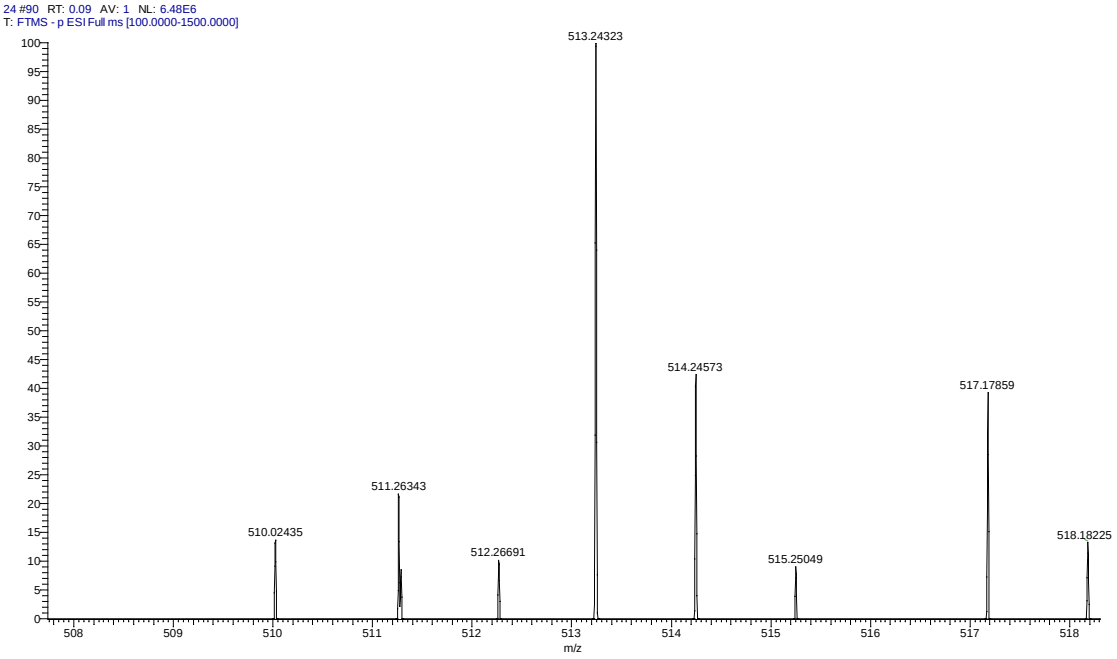
HRMS (ESI) calculated for $C_{45}H_{33}O_8^-$([M-H]$^-$): 701.2181, found : 701.2181.



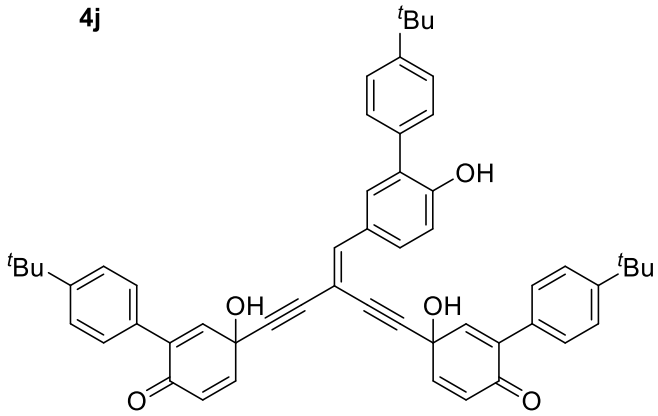
3j



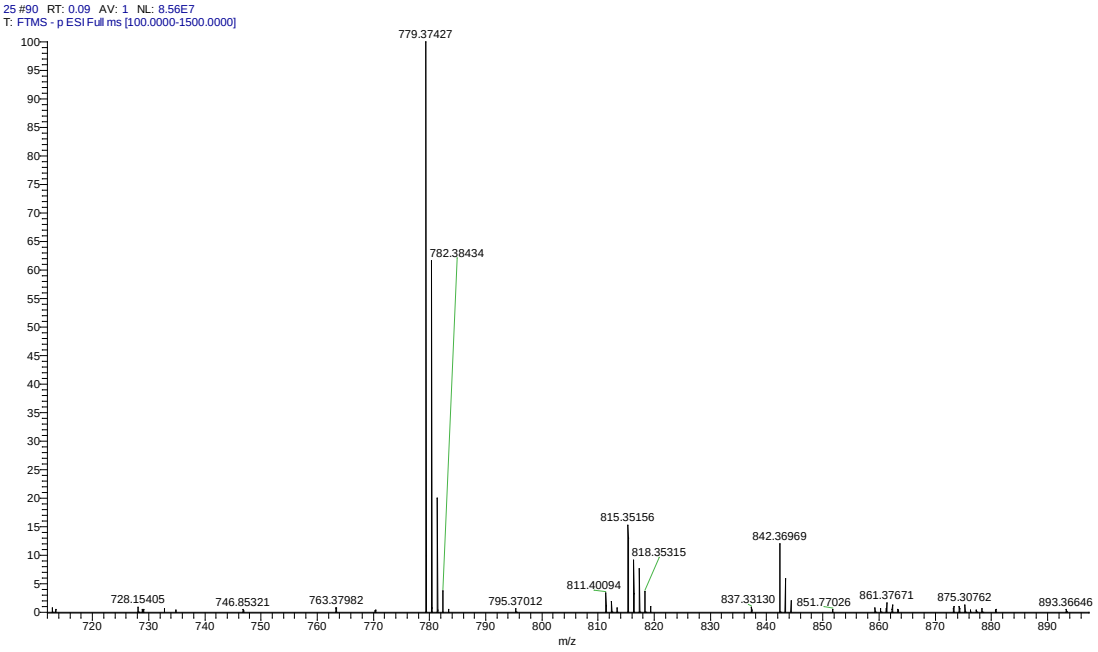
HRMS (ESI) calculated for $C_{36}H_{33}O_3^-$([M-H]$^-$): 513.2435, found : 513.2432.



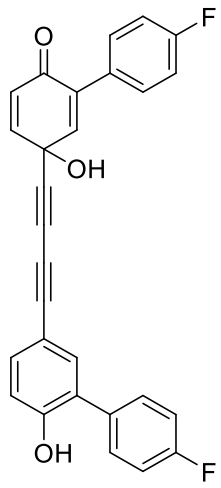
4j



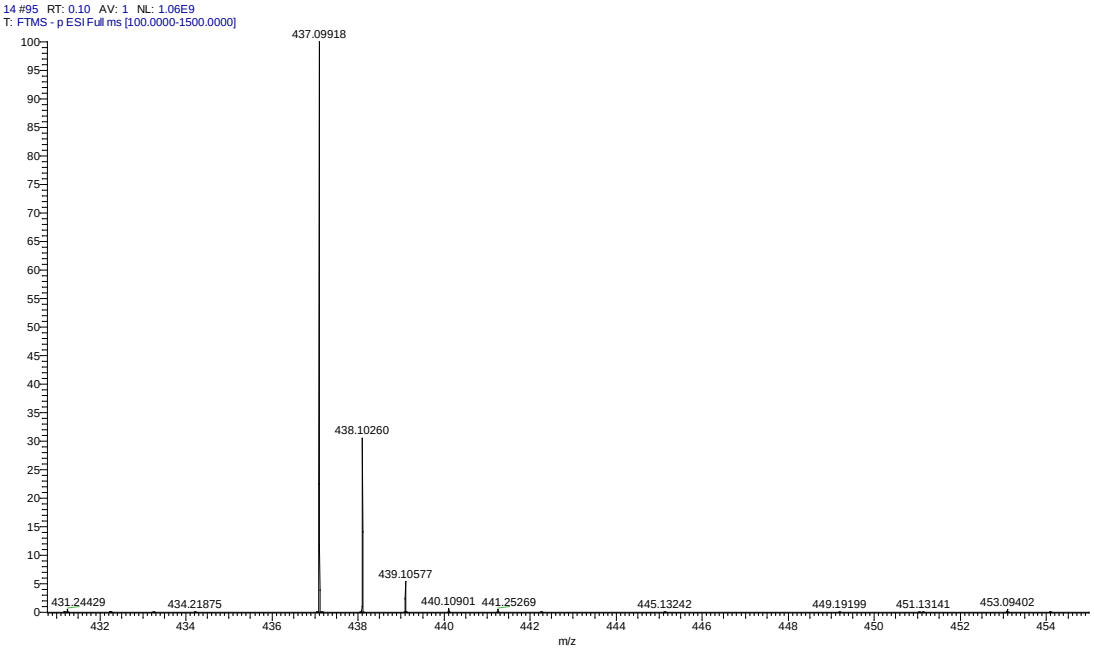
HRMS (ESI) calculated for $C_{54}H_{51}O_5^-$([M-H]$^-$): 779.3742, found: 779.3742.



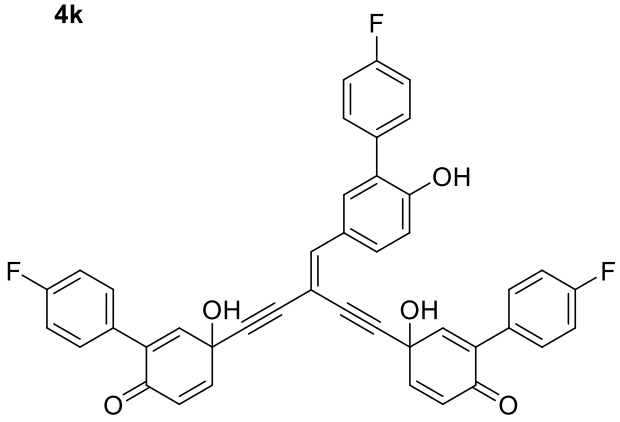
3k



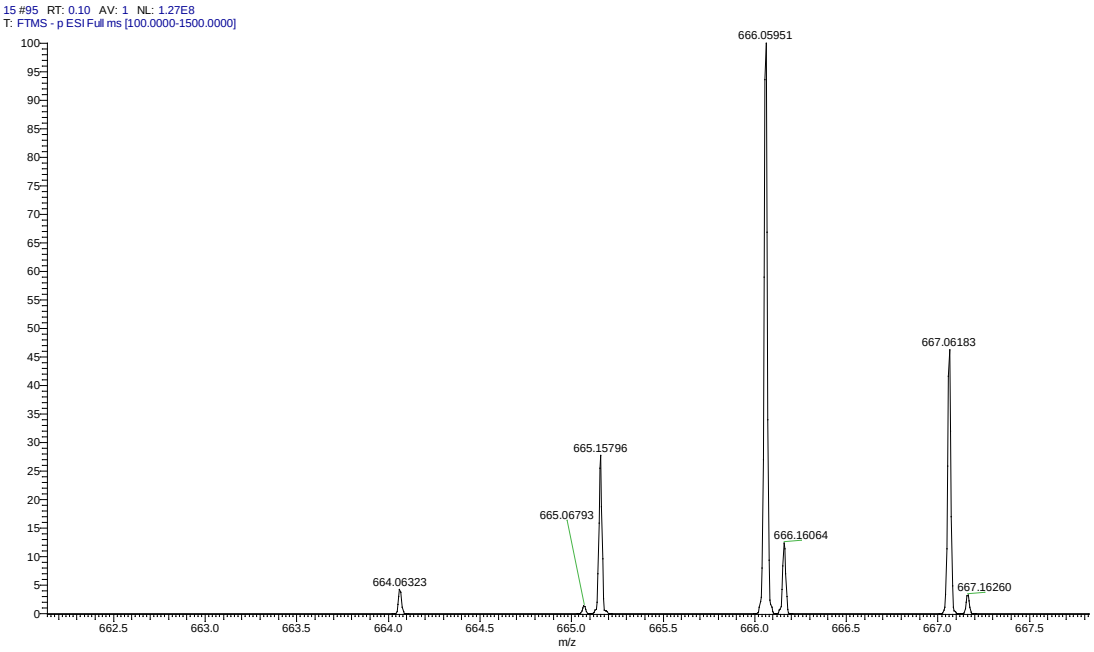
HRMS (ESI) calculated for $C_{28}H_{15}F_2O_2^-$([M-H]$^-$): 437.0995, found : 437.0991.



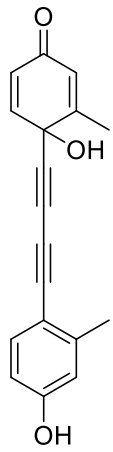
4k



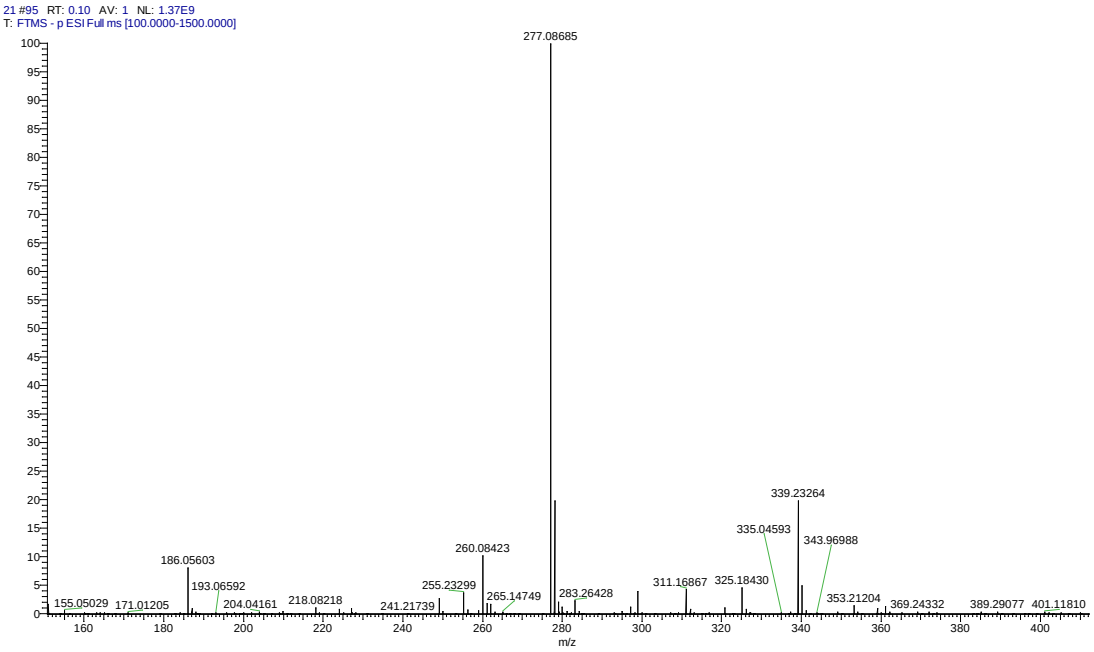
HRMS (ESI) calculated for $C_{42}H_{24}F_3O_5^-$([M-H]$^-$): 665.1581, found : 665.1579.



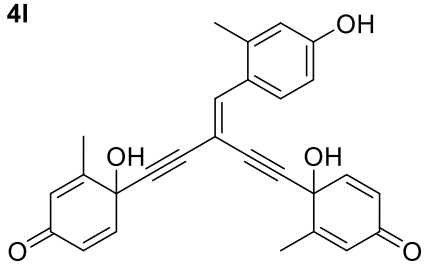
3l



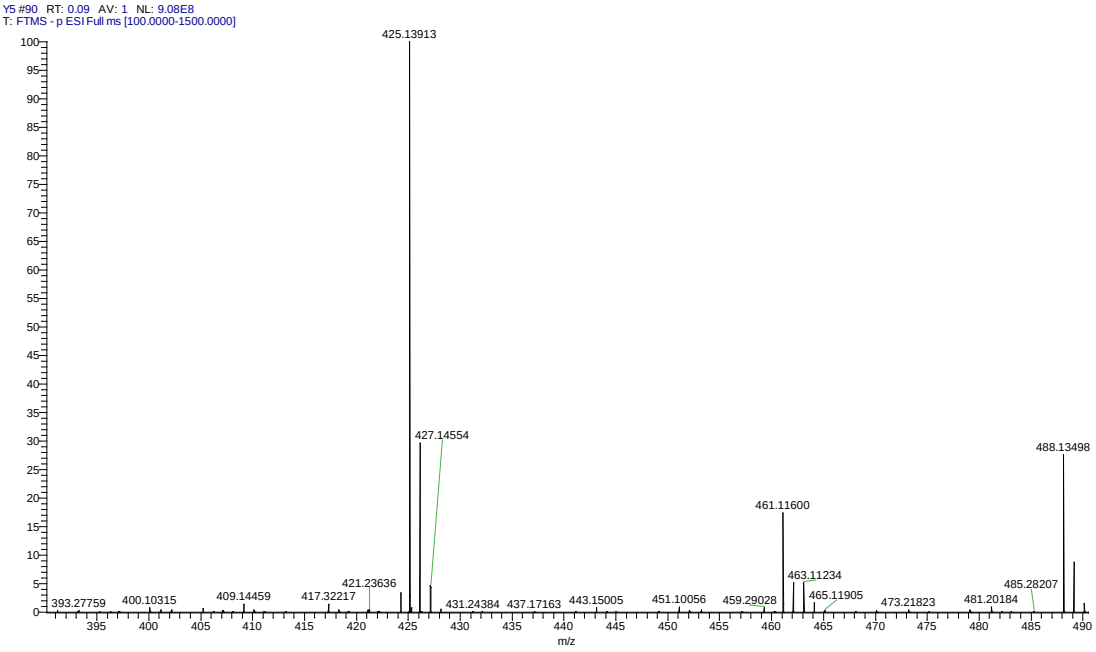
HRMS (ESI) calculated for $C_{18}H_{13}O_3^-$ ([M-H]$^-$): 277.0870, found 277.0868.



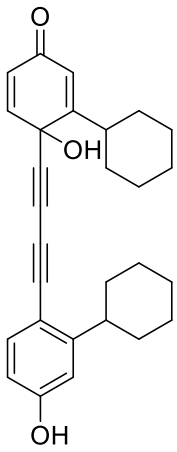
4l



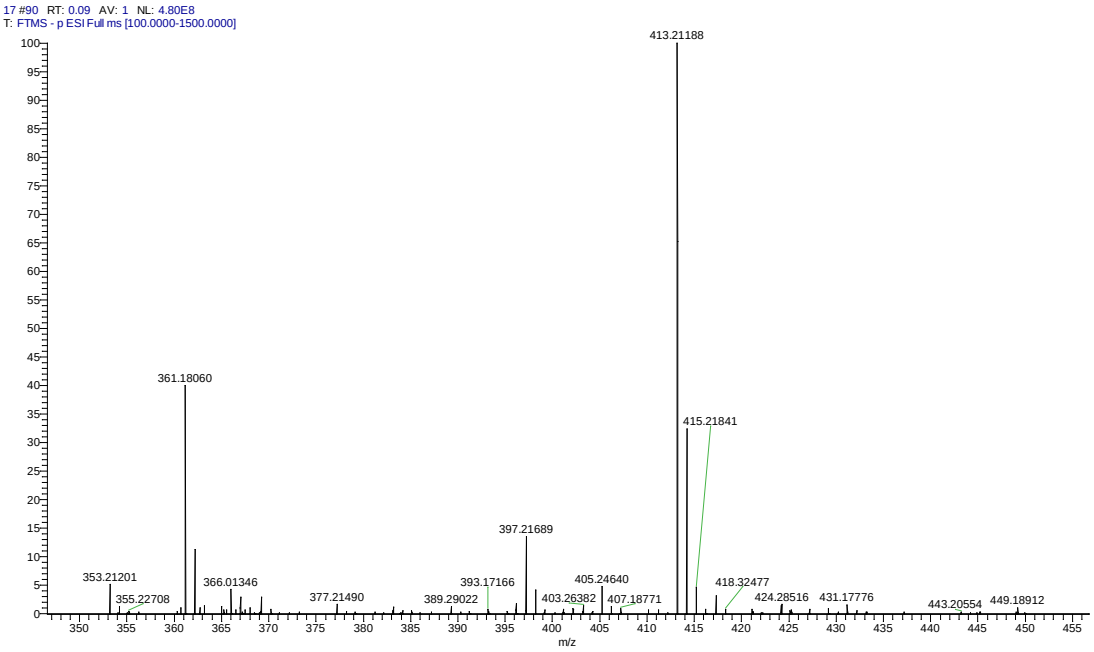
HRMS (ESI) calculated for $C_{27}H_{21}O_5^-$([M-H]$^-$): 425.1394, found 425.1391.



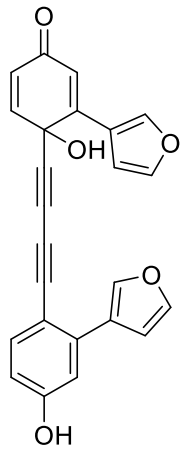
3p



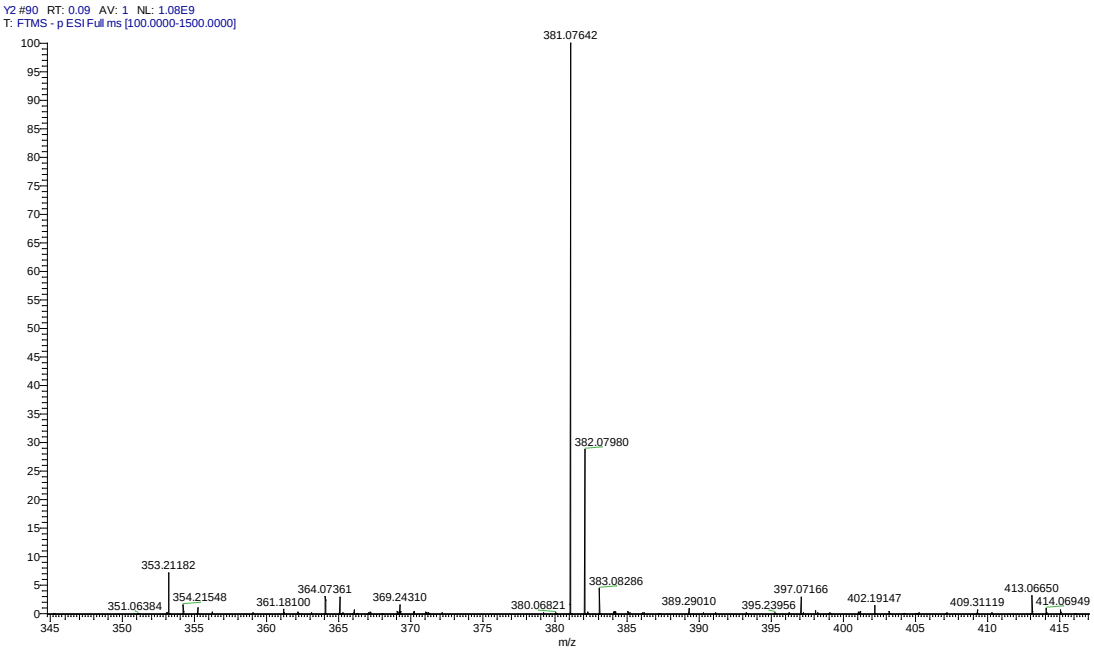
HRMS (ESI) calculated for $C_{28}H_{29}O_3^-$([M-H]$^-$): 413.2122, found 413.2118.



3u

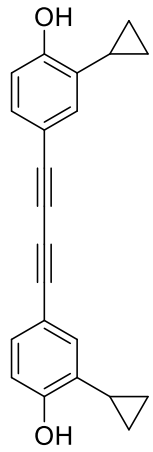


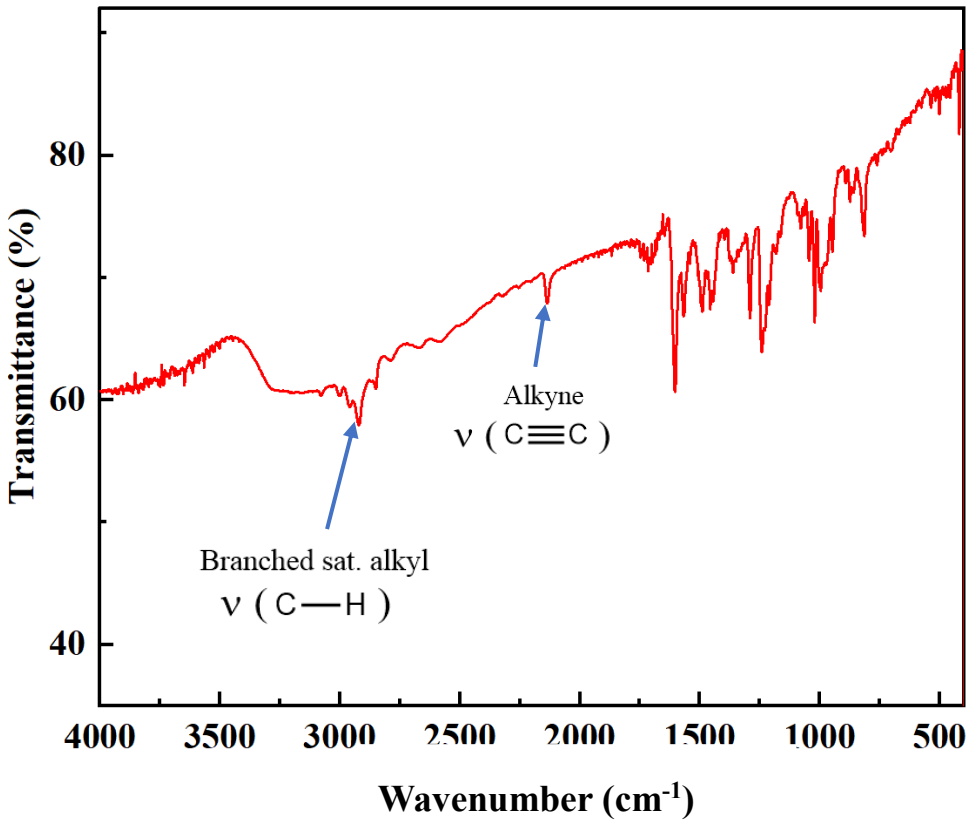
HRMS (ESI) calculated for $C_{24}H_{13}O_5^-$([M-H]$^-$): 381.0768, found: 381.0764.



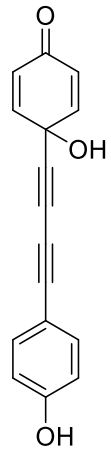
17. Selected IR spectra for 1,3-diyne and conjugated enediynes

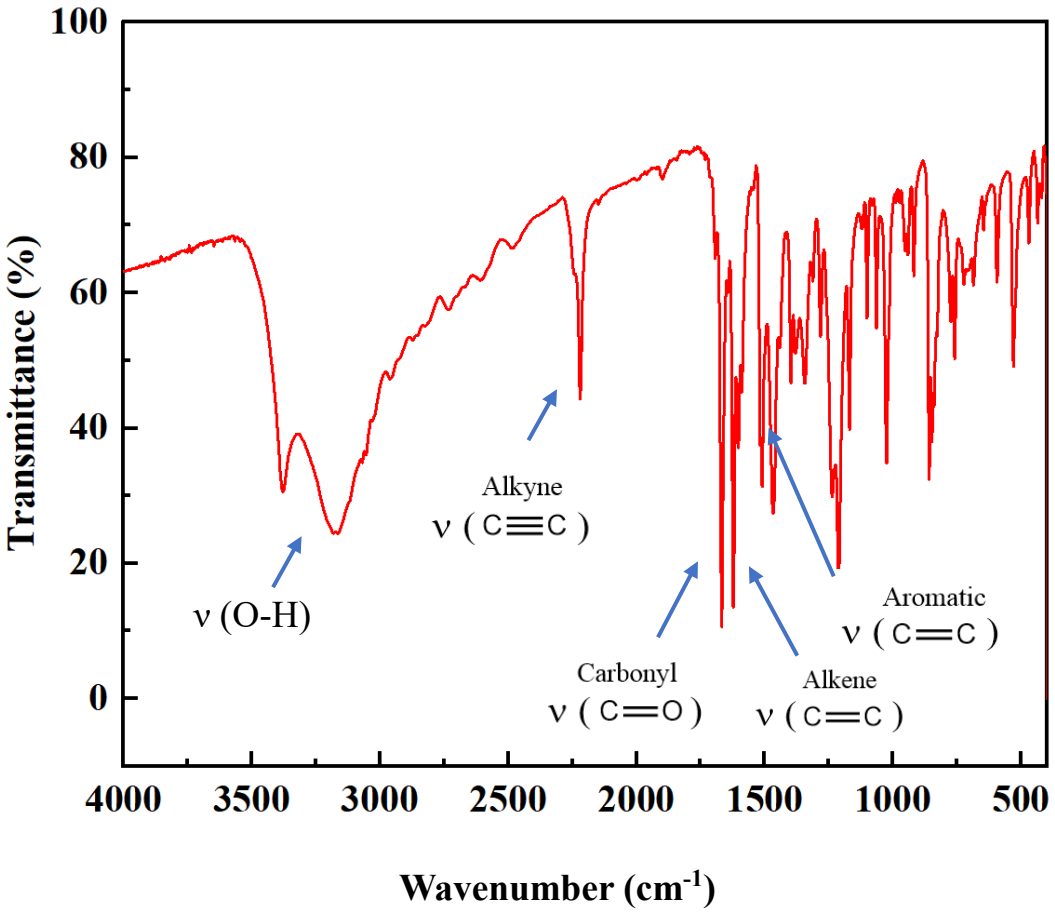
2f



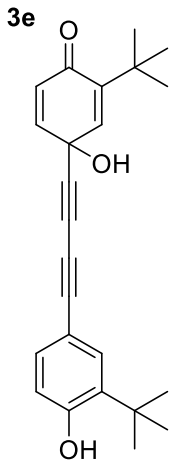


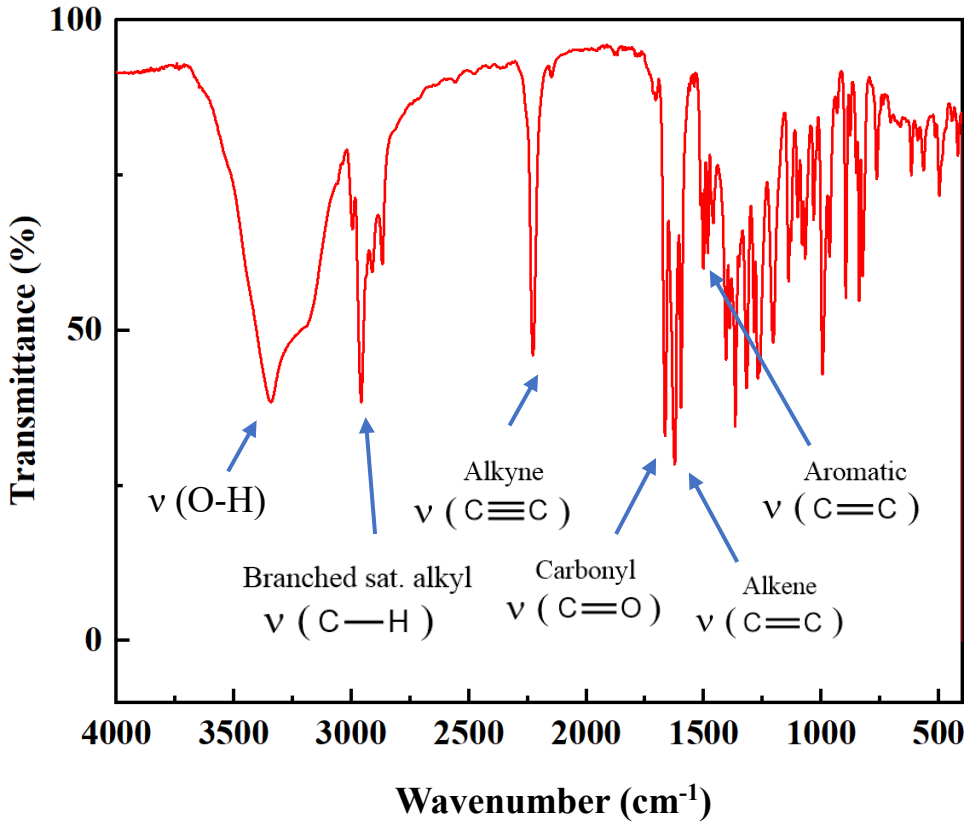
3a


O
OH
OH

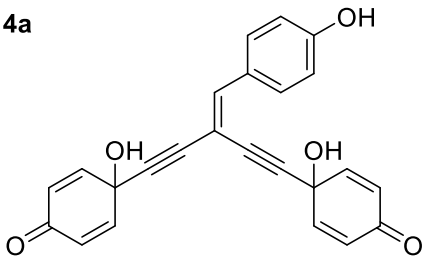

100
80
60
40
20
0
Transmittance (%)
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)
ν (O-H)
Alkyne
ν (C≡C)
Carbonyl
ν (C=O)
Alkene
ν (C=C)
Aromatic
ν (C=C)

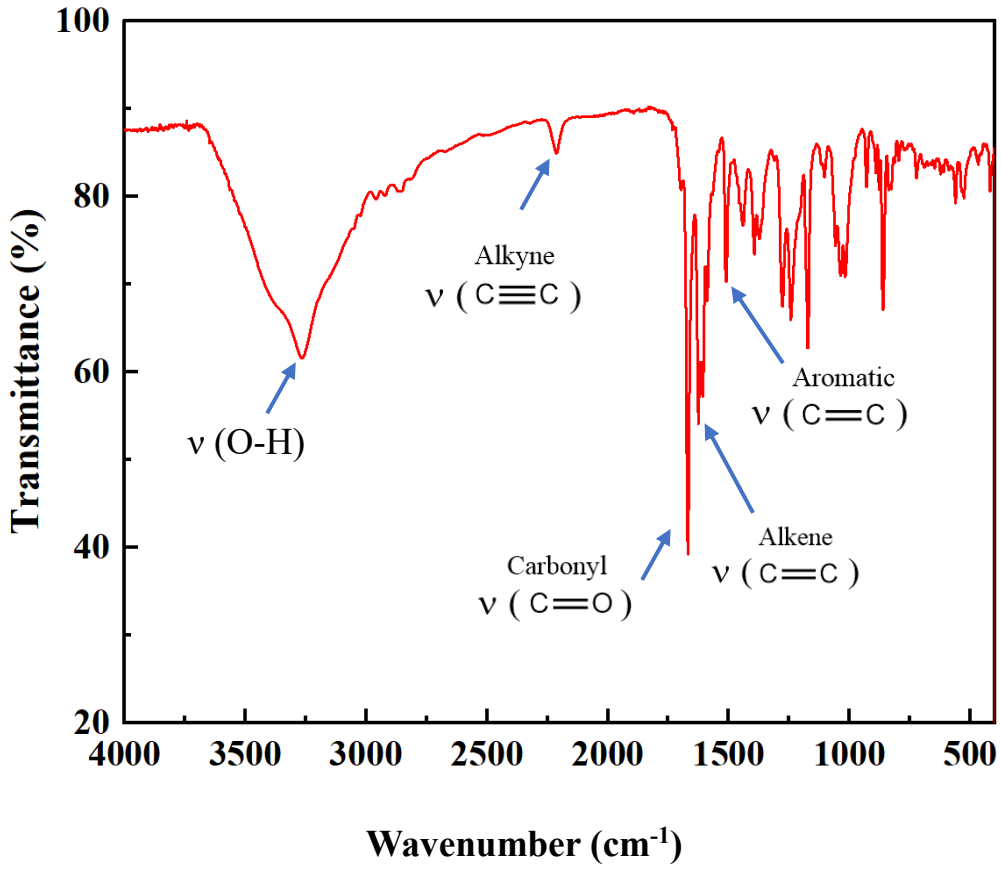
3e


O
OH
OH


100
50
0
Transmittance (%)
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)
ν (O-H)
Branched sat. alkyl
ν (C—H)
Alkyne
ν (C≡C)
Carbonyl
ν (C═O)
Alkene
ν (C═C)
Aromatic
ν (C═C)

4a


OH
OH
OH
O
O


100
80
60
40
20
Transmittance (%)
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)
ν (O-H)
Alkyne
ν (C≡C)
Carbonyl
ν (C=O)
Alkene
ν (C=C)
Aromatic
ν (C=C)