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Copper and palladium bimetallic sub-nanoparticles were stabilized on modified polyaniline materials as an efficient catalyst to promote C-C coupling reactions in aqueous solution

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1 General experimental condition

All reagents are more than 98% pure and the solvent is A.R. It is used directly after purchase. Unless otherwise stated, the reaction is carried out in air. The ^{1}H and ^{13}C NMR were recorded by Bruker 400 MHz spectrometer. The ICP-MS measurements were conducted by Agilent 7800. The morphology of the materials was obtained on JEOL JEM-2010F High Resolution Transmission Electron Microscope (HRTEM). The powder X-ray diffraction (XRD) patterns were recorded by a D/max 2200 PC03030502 X-ray diffractometer using Cu-Karadiation. Fourier transform infrared (FT-IR) spectra were recorded in the range of 400-4000 cm^{-1} using a Spectrum Two03040404 FT-IR spectrometer. The X-ray photoemission (XPS) spectra were performed at room temperature using a Thermo ESCALAB 250xi hemispherical electron energy analyzer. The solid-state NMR spectra were obtained on Agilent 600M. Raman spectra were recorded using a laser at 785 nm to assess the structure of the catalysts (Thermo Fisher DXR). The online infrared spectrum were obtained by METTLER TOLEDO ReactIR^{TM} iC10. The TA Q-600 thermogravimetric analysis (TGA) was carried out under nitrogen with a temperature ramp of 10℃ min^{-1}.

1.1 Preparation of the 3-hydroxy polyaniline materials

3-hydroxy-aniline (20 mmol) and HCl (1M, 200 mL) were added to the reactor, stir at room temperature until 3-hydroxy-aniline is dissolved. Then the $(NH_4)_2S_2O_8$ (1M, 20 mL) were added, continuous stirring until the solution was completely blue-black (about 48 hours). Generated 3-hydroxy polyaniline was isolated by centrifugalization, washed by deionized water and ethanol to neutral, vacuum dried at 60℃ for 8 h, collection for use (PANI-3OH).

1.2 Preparation of the modified PANI-3OH materials

PANI-3OH (500 mg) and DMF (15 mL) were added to a 100 mL reactor, heat to 80°C to react for 2 hours and then cool to room temperature. Add 1,1-carbonyldiimidazole (CDI: 5 mmol, 0.85 g) under the protection of argon, and continue to stir and react for 4 hours. Then the propargyl ammonia (5 mmol) was added and stirred for 16 hours. Add NH_4H_2O (4 mL) dropwise to the solution, after reacting for 1 hour, the solution is concentrated by rotary evaporation to a viscous shape. Add ethanol (50 mL) and let stand for precipitation. Generated modified PANI-3OH materials were isolated by centrifugalization, washed by

deionized water and ethanol to neutral, vacuum dried at 60℃ for 8 h, collection for use (Mod-PANI-3OH).

1.3 Preparation of the Cu/Pd@Mod-PANI-3OH materials

Add DMF solution (1 mL) to the reaction flask containing Mod-PANI-3OH composite material (200 mg), disperse uniformly by, and record it as A solution. Add $PdCl_2$ (10 mg) and $CuCl_2$ (10 mg) to the reaction flask containing hydrochloric acid (1M, 0.5 mL) and DMF solution (0.5 mL), dissolve by ultrasonic, and record it as B solution. Then the solution B were added to solution A, after mix well by ultrasonic for 20 min, let stand for 4 hours to react. The Cu/Pd@Mod-PANI-3OH materials were isolated by centrifugalization, washed by deionized water and ethanol, vacuum dried at 60℃, collection for use.

1.4 Typical procedure for the Sonogashira coupling reaction

To a 15 mL reaction tube, ArI (1.0 mmol), Phenylacetylene (1.2 mmol), Et_3N (2 mmol), H_2O (1.0 mL) and 5 mg of Cu/Pd@Mod-PANI-3OH were added. The reaction mixture was stirred at 80℃ under air for 8 h. After the reaction, the catalyst was isolated by centrifugalization, washed by deionized water and ethnol, vacuum dried at 60℃ and then reused in the next round of reaction. Organic phase was collected, add saturated salt water (2 mL), extracted with ethyl acetate (3*5 mL), then the organic phase was dried with anhydrous Na2SO4. The product was separated and purified by silica gel column chromatography (eluent: Petroleum ether and Ethyl acetate).

1.5 Typical procedure for Suzuki–Miyaura coupling reaction

ArI (1 mmol), phenylboronic acid (1.2 mmol), K_3PO_4 (1.2 mmol), H_2O: EtOH=1:1 (2 mL) and 3 mg of Cu/Pd@Mod-PANI-3OH. The reaction mixture was stirred at 80℃ under air for 5h. After the reaction, the catalyst was isolated by centrifugalization, washed by ethyl acetate, and then the organic phase was collected. The product was separated and purified by silica gel column chromatography (Eluent: Petroleum ether).

1.6 TON and TOF value calculation method

$$\mathrm{TON} = \frac{\text{Number of moles of reactant conversion}}{\text{moles of catalyst active centers}} = \frac{\mathrm{D}*\mathrm{Y}}{\mathrm{B}} \qquad \left(B = \frac{m*C}{M}\right) \qquad (1)$$

$$\mathrm{TOF} = \frac{\mathrm{TON}}{\text{Reaction time}} \qquad (2)$$

TON is the turnover number, indicating the molar amount of reactants converted per unit of active site (Eq. (1)). “D” represents the mole fraction of the reactants added (mmol), “Y” represents the conversion rate of the reactants, “m” represents the mass of the catalyst added in the reaction (mg), “C” represents the percentage of active sites contained in the catalyst (In this paper, the active center of the catalyst is approximately equal to the Pd content obtained by ICP test), “M” represents the mass fraction of metal palladium. TOF is the turnover frequency, represents the amount of reactant that is converted per unit time by the unit active site (Eq. (2))”

2 Th e characterization results and experimental data

Figure S1. Cu/Pd@Mod-PANI-3OH material

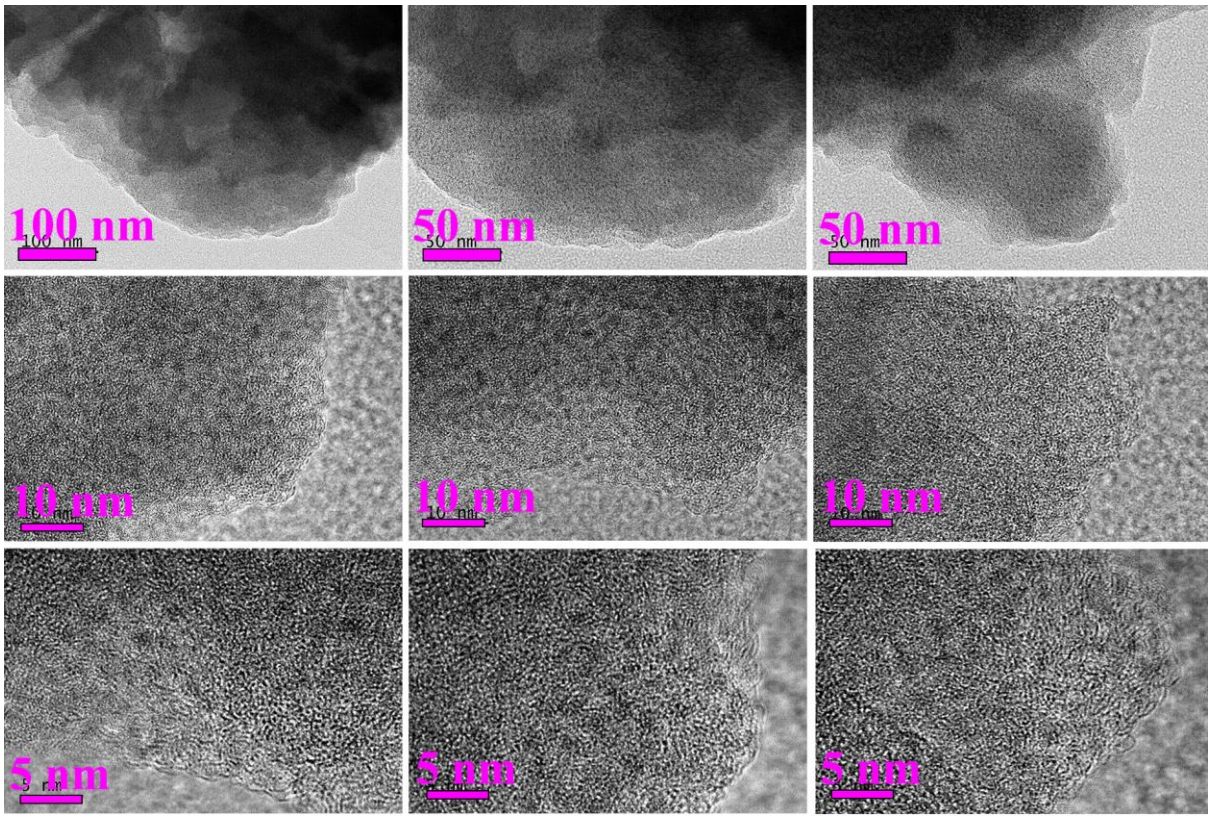


Figure S2. HR-TEM image of the Cu/Pd@Mod-PANI-3OH material

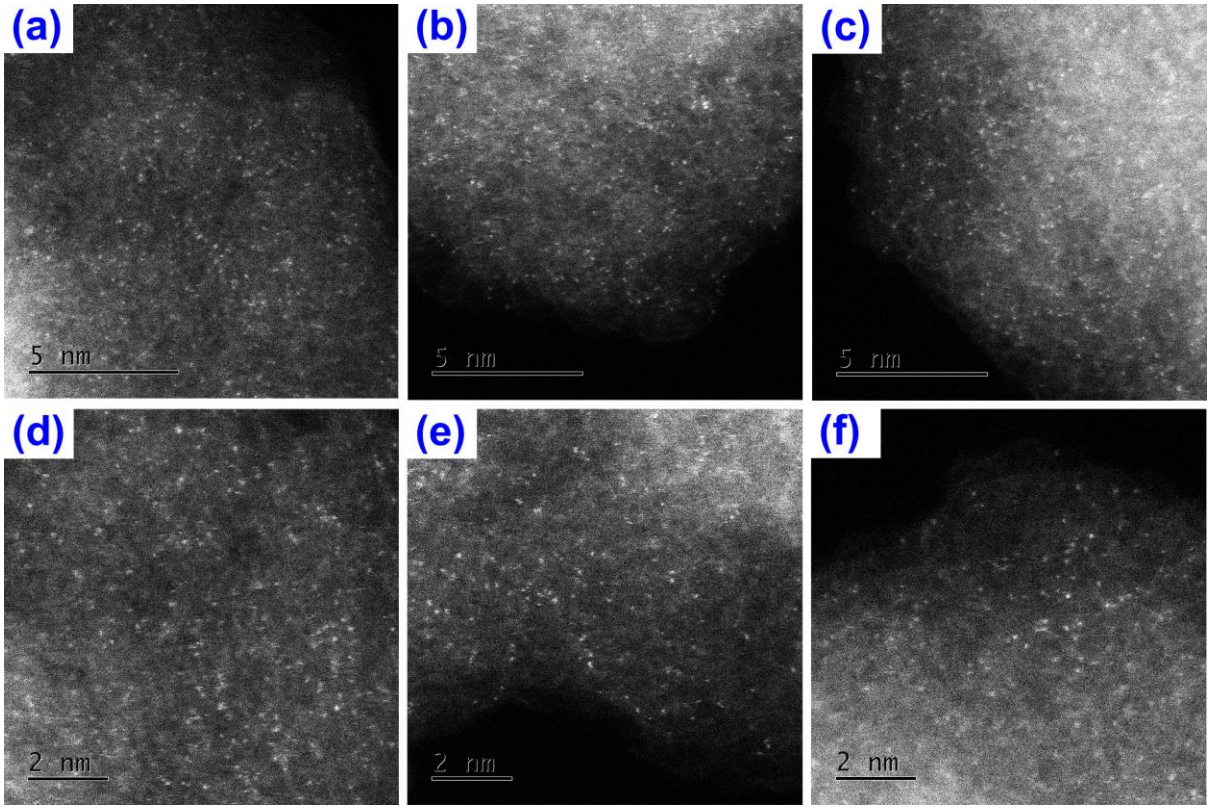


Figure S3. STEM image of the Cu/Pd@Mod-PANI-3OH material

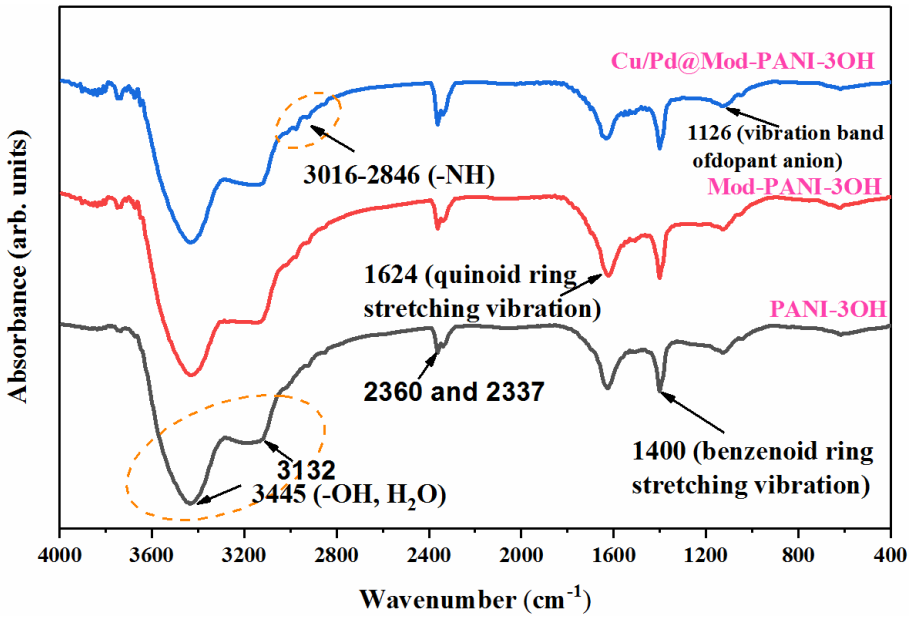


Figure S4. The infrared spectrum of Cu/Pd@Mod-PANI-3OH material

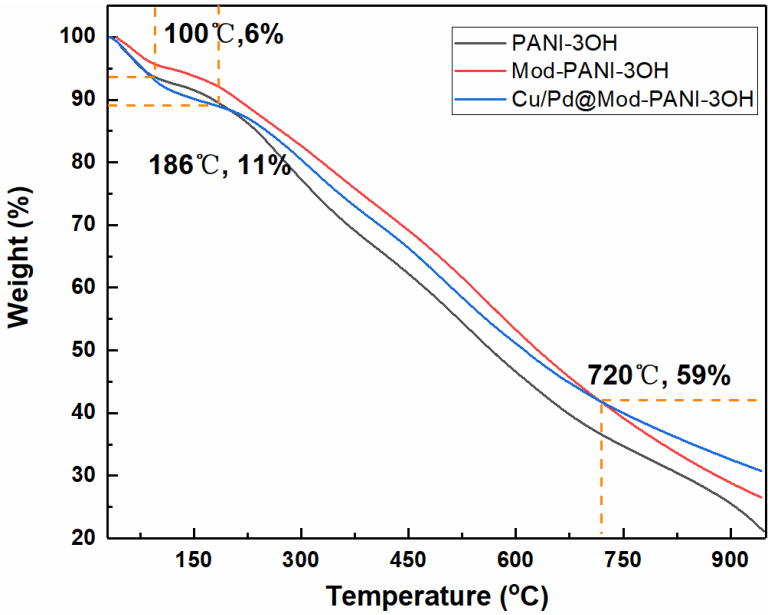


Figure S5. The thermogravimetric test results of Cu/Pd@Mod-PANI-3OH material

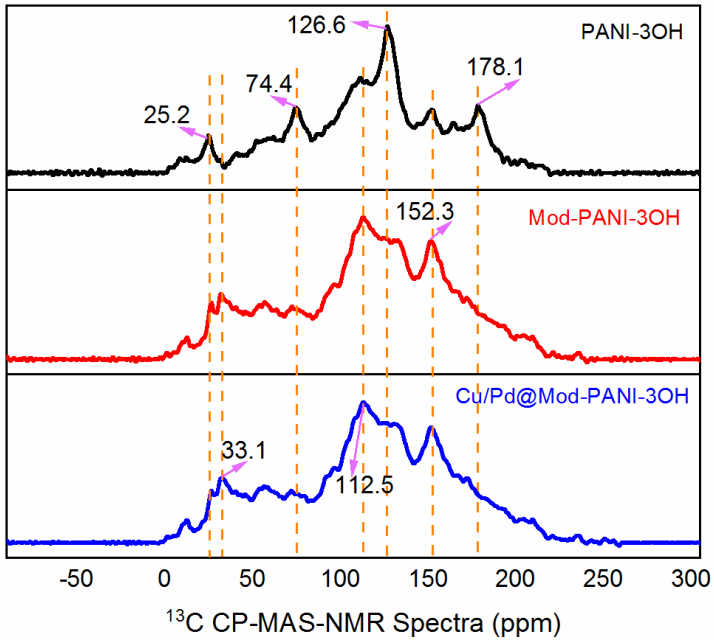


Figure S6. The ^{13}C CP-MAS-NMR Spectra of Cu/Pd@Mod-PANI-3OH material

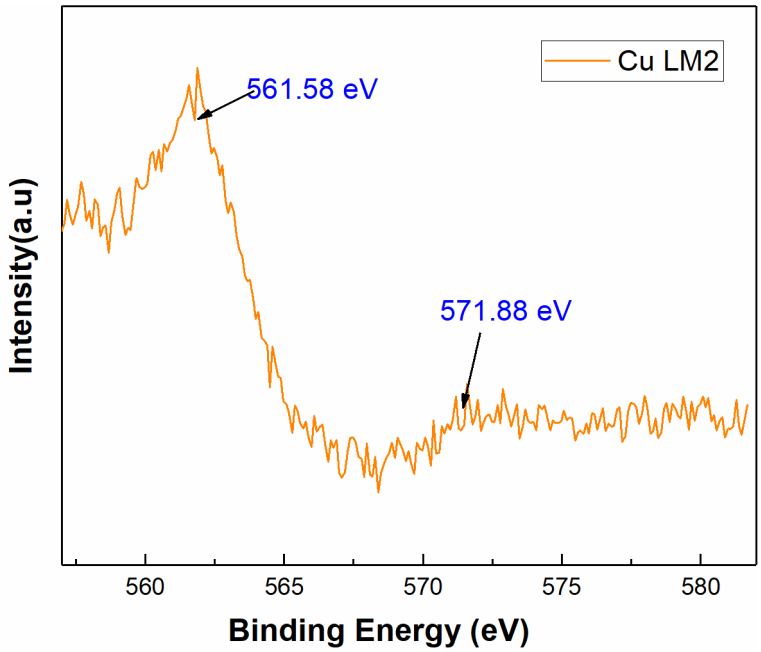


Figure S7. The Cu-LM2 XPS analysis of Cu/Pd@Mod-PANI-3OH materials

Table S1. The content of palladium and copper in the catalyst

Entyr	m_0（g)	V_0	element	C_o（μg/L)	(f)	C_1（μg/L)	C_x（μg/kg)	W(%)
Fresh	0.0494	25	Cu	176	100	17600	8906883	**0.89%**
catalyst	0.0494	25		175	100	17500	8856275	**0.89%**
Fresh	0.0494	25	Pd	400	100	40000	20242915	**2.02%**
catalyst	0.0494	25		403	100	40300	20394737	**2.04%**
Repeated	0.0615	25	Cu	102	100	10200	4146341	**0.41%**
6 times	0.0615	25		103	100	10300	4186992	**0.42%**
Repeated	0.0615	25	Pd	341	100	34100	13861789	**1.39%**
6 times	0.0615	25		342	100	34200	13902439	**1.39%**

m_0: Sample quality

V_0: Constant volume

f: Dilution times

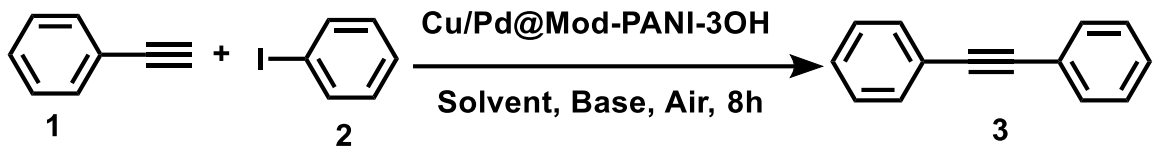
C_0: Test solution element concentration

C_1: Digestion solution original solution element concentration

C_x: Sample element content

W%: Sample element content

Table S2. Condition optimization of Sonogashira reaction by Cu/Pd@Mod-PANI-3OH catalysts [a]



Entry	Solvent	Base	Temp. (℃)	Catalyst （）	Yield (%) [b]
1	CH_3CN	Et_3N	80	Cu/Pd@Mod-PANI-3OH	45
2	CH_3CN	$(i\text{-}Pr)_2NEt$	80	Cu/Pd@Mod-PANI-3OH	17
3	CH_3CN	Cs_2CO_3	80	Cu/Pd@Mod-PANI-3OH	21
4	CH_3CN	K_3PO_4	80	Cu/Pd@Mod-PANI-3OH	15
5	CH_3CN	K_2CO_3	80	Cu/Pd@Mod-PANI-3OH	Trace [c]
6	DMF	Et_3N	80	Cu/Pd@Mod-PANI-3OH	56
7	NMP	Et_3N	80	Cu/Pd@Mod-PANI-3OH	45
8	THF	Et_3N	80	Cu/Pd@Mod-PANI-3OH	20
9	DMSO	Et_3N	80	Cu/Pd@Mod-PANI-3OH	74
10	H_2O	Et_3N	80	Cu/Pd@Mod-PANI-3OH	90
11	EtOH	Et_3N	80	Cu/Pd@Mod-PANI-3OH	50
12	H_2O	-	80	Cu/Pd@Mod-PANI-3OH	Trace [c]
13	-	Et_3N	80	Cu/Pd@Mod-PANI-3OH	13
14	H_2O	Cs_2CO_3	80	Cu/Pd@Mod-PANI-3OH	48
15	H_2O	K_3PO_4	80	Cu/Pd@Mod-PANI-3OH	43
16	H_2O	Et_3N	100	Cu/Pd@Mod-PANI-3OH	68
17	H_2O	Et_3N	60	Cu/Pd@Mod-PANI-3OH	73
18	H_2O	Et_3N	RT	Cu/Pd@Mod-PANI-3OH	23
19	H_2O	Et_3N	80	Cu/Pd@Mod-PANI-3OH (2)	63
20	H_2O	Et_3N	80	Cu/Pd@Mod-PANI-3OH (10)	81

Reaction Conditions: [a] Iodobenzene (1 mmol), Phenylacetylene (1.2 mmol), Solvent (1.0 mL), Base (2.0 eq), react for 8 hours at air atmosphere; [b] Isolated yields; [c] Yield <3%.

In order to explore the catalytic performance of Cu/Pd@Mod-PANI-3OH composite material, the sonogashira coupling reaction of iodobenzene and phenylacetylene was selected as the probe. The results of the optimization of the reaction conditions are shown in Table 1. Firstly, the different kinds of bases were screened (Table S2, entries 1-5), and it was found that the organic base triethylamine has the best catalytic effect. According to our previous research, triethylamine has a special reducing effect, which can reduce the divalent palladium to zero valence under a specific environment, thereby improving the catalytic

activity. Next, the solvent effect of different solvents with triethylamine as the base was investigated (items 6-11), and the results showed that this type of reaction can be carried out in different solvents, especially when water is used as the solvent, the yield of 90% can be obtained (entry 10). This phenomenon occurs because the material contains a large number of hydroxyl and amide bonds, so the material will have better hydrophilic properties. In addition, the presence of a large number of carbon branches in the material structure will make the surface of the material rougher, which is conducive to the adsorption and contact of the reaction substrate, thereby realizing water phase catalysis. The blank experiment confirms that both solvent and base are necessary in the reaction process (entries 12, 13). Subsequently, we optimized the reaction temperature and the amount of catalyst separately (Table S2), and finally determined the optimal reaction conditions as follows: by using water as the solvent and triethylamine as the base, 90% yield can be obtained by reacting at 80°C after 8 hours. During the reaction, only 0.094 mol% of palladium needs to be added, which is much lower than the value given in most reported literatures. The reason for this phenomenon is that the metal copper and palladium are uniformly distributed in the Pd@Mod-PANI-3OH micro-nano reactor. The surface of the micro-nano reactor provides a place for the adsorption and transformation of the reactant molecules, and the metal inside the reactor promotes the ability of the material to transmit electrons, so the Pd@Mod-PANI-3OH micro-nano reactor exhibits such excellent catalytic activity.

The definitions and calculations of yield, conversion and selectivity.

Reaction conditions: Iodobenzene (1 mmol), Phenylacetylene (1.2 mmol). As shown in the diagram, the three products of the reaction are present, the self-coupling product (Marked as 4 and 5) and the cross-coupling product (Marked as 3). Their molecular weights are denoted by M_3, M_4 and M_5 respectively. After the reaction was completed, the product was separated and purified by silica gel column chromatography. Three products were obtained with masses m_3 (161 mg, 0.9 mmol), m_4 (5 mg, 0.032 mmol), m_5 (8 mg, 0.039 mmol), respectively. Where m_3 is the cross-coupling product of the target.

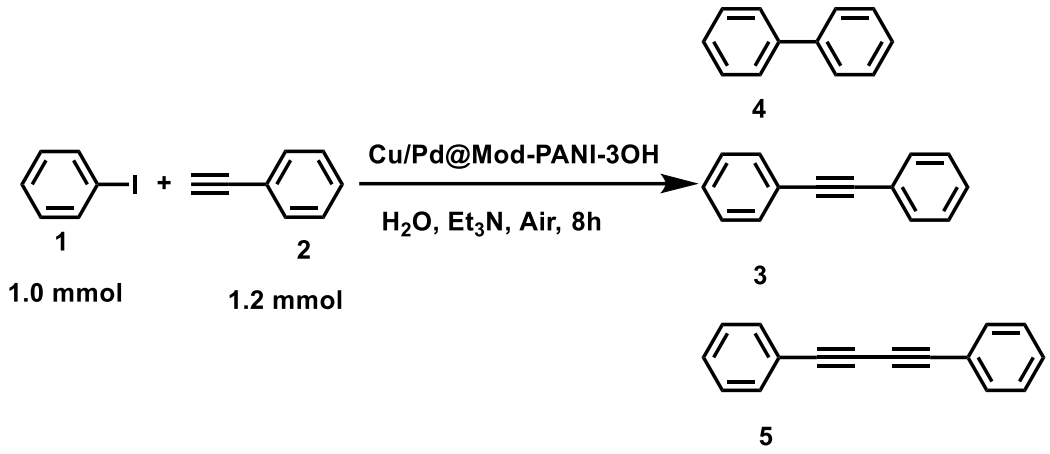


Figure S8. Sonogashira reaction catalysis by Cu/Pd@Mod-PANI-3OH

1. Conversion rate calculation scheme

Iodobenzene is used as the basis for calculating the conversion. Since iodobenzene is a liquid and cannot easily be weighed accurately at the end of the reaction, the amount of iodobenzene consumed to produce products 3 and 4 is used as a proxy for the amount of iodobenzene converted. The conversion rate can be calculated using Formula 1.

Conversion of Iodobenzene:

$$\frac{\left(\frac{m_3}{M_3}\right)+\left(\frac{m_4}{M_4}\times 2\right)}{1.0}\times 100\% = \frac{\left(\frac{161}{178.08}\right)+\left(\frac{5}{154.08}\times 2\right)}{1.0}\times 100\% = \frac{0.964}{1}\times 100\% = 96.4\% \quad (1)$$

2. The calculation method of Selectivity

As an example, selectivity is calculated to generate target compound 3.

Selectivity of 1,2-diphenylethyne:

$$\frac{\left(\frac{m_3}{M_3}\right)}{\left(\frac{m_3}{M_3}\right)+\left(\frac{m_4}{M_4}\times 2\right)}=\frac{0.9}{0.9+(0.032\times 2)}=\frac{0.9}{0.964}\times 100\%$$

$$=93.4\% \qquad (2)$$

3. The calculation method of Yield

As an example, yield is calculated to generate target compound 3.

$$\text{Yield}\,(1,2-\text{diphenylethyne}):\frac{m_3}{M_3}\times 100\%=\frac{161}{178.08}\times 100\%=90.4\% \qquad (3)$$

Because of the extremely low amounts of products 4 and 5 during the reaction, the catalytic performance of the catalysts is still mainly described in terms of yield in the paper.

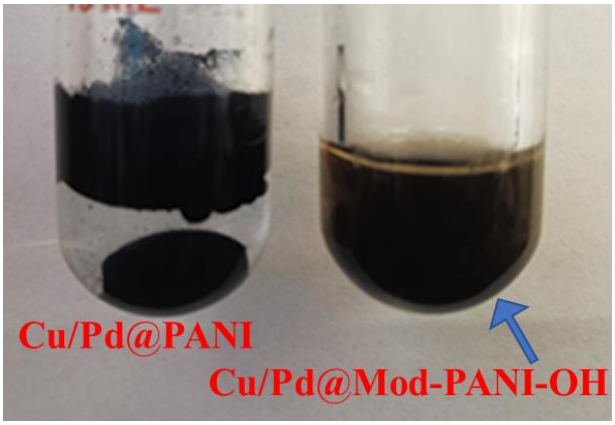
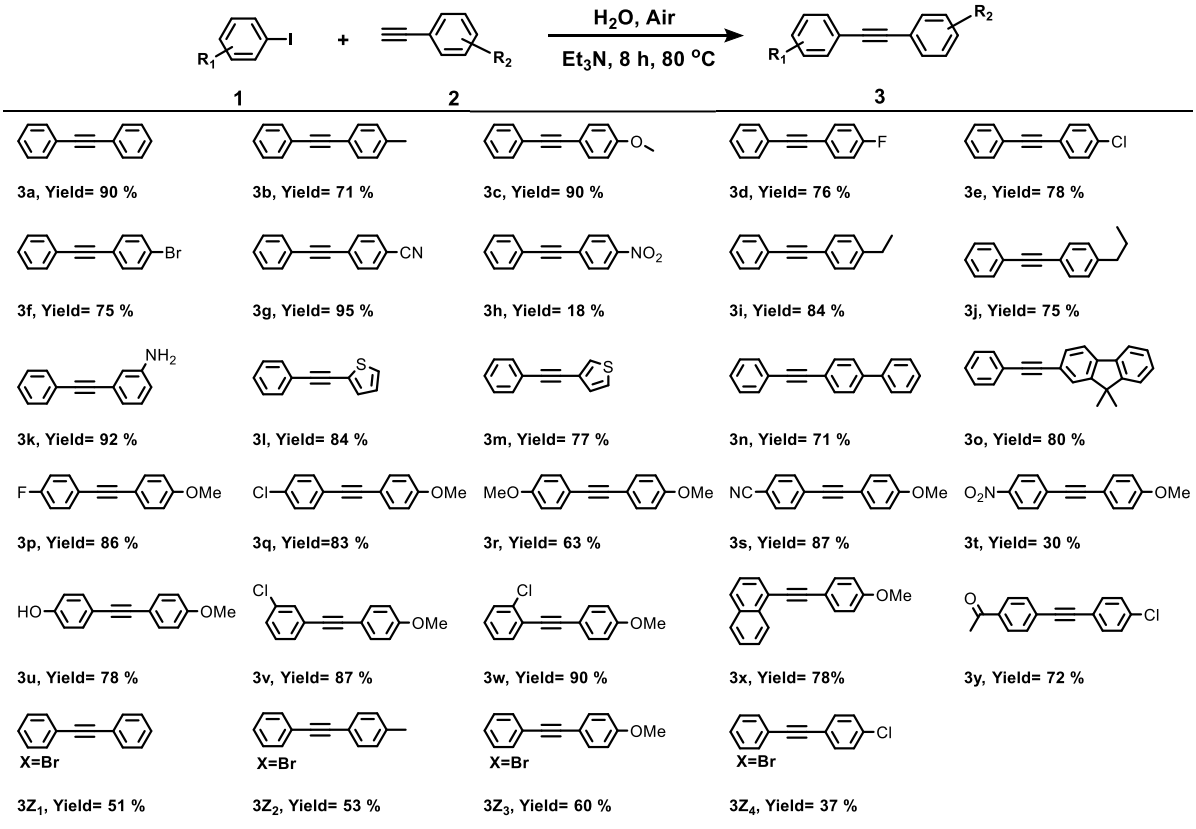


Figure S9. The picture of the reaction state

Table S3. Sonogashira coupling reaction of aryl iodide and phenylacetylene over Cu/Pd@Mod-PANI-3OH catalysts [a].

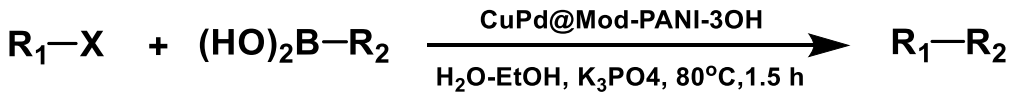


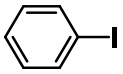
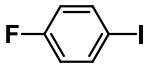
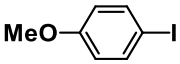
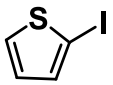
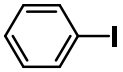
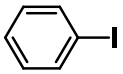
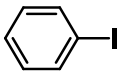
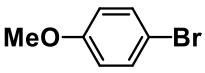
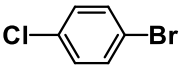
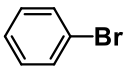
Reaction Conditions: [a] Iodobenzene (1 mmol), Phenylacetylene (1.2 mmol), H_2O (1.0 mL), Et_3N (2.0 eq), react for 8 hours at air atmosphere; [b] Isolated yields.

After obtaining the optimal reaction conditions, we investigated the universality of the catalytic Sonogashira reaction of Cu/Pd@Mod-PANI-3OH catalyst. It was found that the substituent group on the benzene ring has a certain influence on the reaction. When changing the substituents on the phenylacetylene, it can be found that the reaction yield of the electron-donating group is generally better than that of the electron-withdrawing group (Table **S3**, 3b-3h). This is because when the electron-donating group is introduced into the phenylacetylene, the electron cloud density on the benzene ring will increase, so that the H atom of the terminal alkynyl group in the phenylacetylene is easily activated. Moreover, we found that when different halogens are used as the substituent groups, the reaction yield does not change much (Table **S3**, 3d-3f, 75-78%), but when the cyano group is used as the substituent group, the reaction effect is particularly excellent (Table **S3**, 3g, 95%). Of course,

the reactivity of some heterocyclic alkynes has also been studied, and it has been found that 2-thiophene alkynes can react better (Table **S3**, 3l, 84%). Unfortunately, when 2-alkynylpyridine was used as the substrate, the target compound was not obtained. The steric hindrance of different functional groups does not affect the catalytic activity of the catalytic system. For example, when 2-Ethynyl-9,9-Dimethyl-9H-Fluorene is used as the substrate, 80% yield can still be obtained (Table **S3**, 3o). In addition, different substituent groups on halogenated aromatic hydrocarbons have also been investigated, and the result shows that the reactivity of the electron-withdrawing group on the halogenated aromatic hydrocarbon is stronger than that of the electron-donating group (Table **S3**, 3p-3u). When the substituent group is chlorine, the relationship of catalytic activity is: ortho position>meta position>para position. Under the original reaction conditions, when brominated aromatic hydrocarbons are used as the reaction substrate, the results show that the reaction can proceed smoothly (Table **S3**, $3Z_1$-Z_4).

Table S4. Suzuki coupling reactions of aryl iodide and aryl bromide over Cu/Pd@Mod-PANI-3OH catalysts [a]



Entry	1(R_1)	2(R_2)	Product(R_3)	Yield (%)[b]	TOF (h^{-1})
1		Ph	1,1'-biphenyl	93	659.6
2		Ph	4-fluoro-1,1'-biphenyl	93	659.6
3		Ph	4-methoxy-1,1'-biphenyl	95	673.7
4		Ph	2-phenylthiophene	85	602.8
5		4-MeC_6H_4	4-methyl-1,1'-biphenyl	86	609.9
6		4-FC_6H_4	4-fluoro-1,1'-biphenyl	98	695.0
7		4-ClC_6H_4	4-chloro-1,1'-biphenyl	89	631.2
8		Ph	4-methoxy-1,1'-biphenyl	87	617.0
9		Ph	4-chloro-1,1'-biphenyl	62	439.7
10		Ph	1,1'-biphenyl	83	588.6

Reaction Conditions: [a] 1 mmol of R-X, 1.2 mmol of phenylboronic acid, 1.2 mmol of K_3PO_4, 2 mL of solvent (H_2O:EtOH=1:1), CuPd@Mod-PANI-3OH (0.094 mol% Pd), 80 ℃. [b] Isolated yields.

In addition to the Sonogashira reaction, the catalytic performance of the Cu/Pd@Mod-PANI-3OH composite material in the Suzuki coupling reaction was also tested (Table S4). After simple optimization of conditions, the reaction was carried out in a relatively clean ethanol-water system, and the corresponding target compound could be obtained with a yield of 95% within 1.5 hours. The reactant molecules of different

substituent groups can be reacted, and the yield is between 85-98%. Furthermore, the reaction product of brominated aromatics was obtained with a yield of 62-87% (Table S4). The CuPd@Mod-PANI-3OH nanoreactor catalyst can be reused at least 8 times in the Suzuki coupling reaction. This is a gratifying result, because it once again proves that CuPd@Mod-PANI-3OH composite material has a wide range of application value in the field of green organic synthesis.

Table S5. The quality of the catalyst changes during use

Repeated times	Add amount (mg)	Recycling quality (mg)	Change value (mg)	Change value (%)
1	**201.3**	**208.5**	**+7.2**	**+3.57**
2	**200.6**	**197.0**	**-3.6**	**-1.79**
3	**201.8**	**196.5**	**-5.3**	**-2.63**
4	**201.4**	**194.7**	**-6.7**	**-3.33**
5	**200.3**	**192.5**	**-7.8**	**-3.89**
6	**200.6**	**193.3**	**-7.3**	**-3.63**

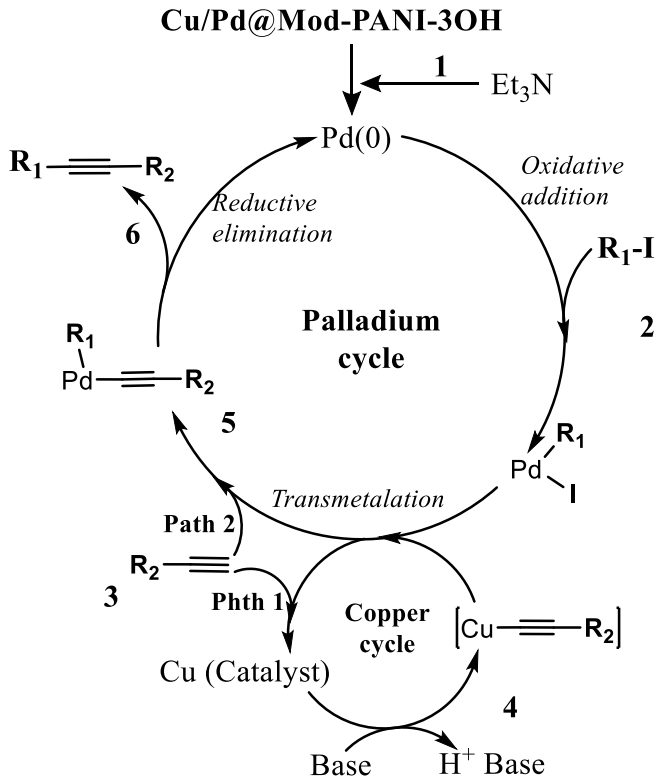
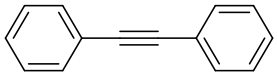


Figure S10. A possible mechanism for Sonogashira coupling reaction over Cu/Pd@Mod-PANI-3OH catalyst

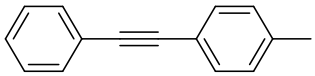
A possible mechanism for Sonogashira coupling reaction over Cu/Pd@Mod-PANI-3OH catalyst is shown in Figure S10. The catalytic process can be divided into two steps: the palladium cycle and copper cycle. The copper cycle only promotes and accelerates the reaction, because it cannot complete the entire catalytic process alone (Figure 4). Firstly, the Cu/Pd@Mod-PANI-3OH composite material undergoes reduction under the action of a nitrogen-containing organic base (triethylamine) to produce a true active center zero-valent palladium. Then zero-valent palladium undergoes an oxidative insertion reaction with iodobenzene, which is one of the raw materials for the reaction. At the same time, phenylacetylene generates active intermediate of phenylethynylcopper(I) on the metal copper in the catalyst through the action of alkali. Next, the activated phenylacetylene group is transported to the metal palladium to undergo a reduction and elimination reaction. During this period, the metal palladium and copper are removed to participate in the next

cycle, and the final product 1,2-diphenylacetylene is produced at the same time. It is worth mentioning that the process can also be carried out without copper, and phenylacetylene is directly involved in the circulation through the insertion reaction with palladium by step 2 (it can be confirmed by the result of Figure 4). However, the energy required for the reaction in step 2 is higher than that in step 1, so the reaction yield of the Pd@Mod-PANI-3OH catalyst is only 71%, and the reaction yield of the Cu/Pd@Mod-PANI-3OH catalyst can be increased to 90%. In addition, the modified polyaniline material in the composite catalyst not only functions as a support for the carrier, but also functions as a macromolecular organic ligand, which synergistically improves the reactivity together with copper and palladium atoms.

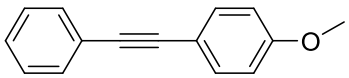
3 Characterization data of the products：



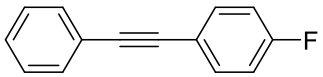
1,2-diphenylethyne (Table 2, 3a): White solid, 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 7.3, 2.5 Hz, 4H), 7.45 (p, *J* = 4.1, 3.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.54, 128.28, 128.19, 123.20, 89.37.



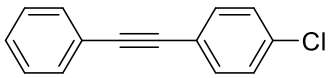
1-methyl-4-(phenylethynyl)benzene (Table 2, 3b): White solid, 71%. 1H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, J = 37.0, 7.5 Hz, 4H), 7.26 (d, J = 7.3 Hz, 3H), 7.08 (d, J = 7.6 Hz, 2H), 2.28 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 138.23, 131.44, 131.40, 129.03, 128.22, 127.97, 123.39, 120.10, 89.58, 88.72, 21.34.



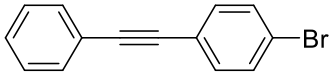
1-methoxy-4-(phenylethynyl)benzene (Table 2, 3c): White solid, 90%. 1H NMR (400 MHz, $CDCl_3$) δ 7.52 (ddt, J = 16.3, 6.4, 1.6 Hz, 4H), 7.41 – 7.28 (m, 3H), 6.97 – 6.82 (m, 2H), 3.83 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 159.56, 133.01, 131.40, 128.27, 127.90, 123.54, 115.31, 113.95, 89.34, 88.03, 55.24, 55.22.



1-fluoro-4-(phenylethynyl)benzene (Table 2, 3d): White solid, 76%. 1H NMR (400 MHz, $CDCl_3$) δ 7.50 (ddt, J = 9.1, 5.7, 2.7 Hz, 4H), 7.33 (q, J = 3.4, 2.2 Hz, 3H), 7.02 (t, J = 8.5 Hz, 2H). 13C NMR (100 MHz, CDCl3) δ 163.69, 161.21, 133.48, 133.40, 131.52, 128.34, 128.30, 123.05, 119.34, 119.31, 115.71, 115.49, 89.02, 88.27.

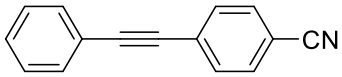


1-chloro-4-(phenylethynyl)benzene (Table 2, 3e): White solid, 78%. 1H NMR (400 MHz, $CDCl_3$) δ 7.89 (dt, J = 6.0, 3.8 Hz, 2H), 7.82 (d, J = 8.2 Hz, 2H), 7.74 – 7.65 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.20, 132.76, 131.56, 128.65, 128.44, 128.36, 122.88, 121.72, 90.29, 88.22.

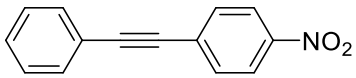


1-bromo-4-(phenylethynyl)benzene (Table 2, 3f): White solid, 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ

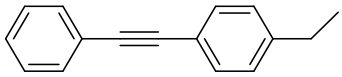
7.49 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.35 – 7.25 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.89, 131.48, 128.39, 128.29, 122.80, 122.38, 122.09, 90.48, 88.31.



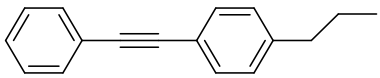
4-(phenylethynyl)benzonitrile (Table 2, 3g): White solid, 95%. 1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 6.9 Hz, 6H), 7.41 – 7.32 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.74, 131.71, 131.50, 128.88, 128.26, 127.81, 121.91, 118.23, 111.11, 93.51, 87.56.



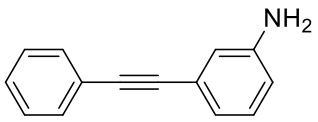
1-nitro-4-(phenylethynyl)benzene (Table 2, 3h): Yellow solid, 18%. 1H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H), 7.56 (dd, J = 7.0, 2.7 Hz, 2H), 7.39 (d, J = 5.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.89, 132.21, 131.79, 130.20, 129.24, 128.50, 123.58, 122.03, 94.66, 87.51.



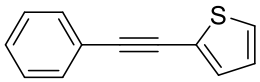
1-ethyl-4-(phenylethynyl)benzene (Table 2, 3i): Oily liquid, 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 2H), 7.47 – 7.40 (m, 2H), 7.32 – 7.23 (m, 3H), 7.12 (d, *J* = 7.8 Hz, 2H), 2.59 (q, *J* = 7.6 Hz, 2H), 1.19 (td, *J* = 7.6, 1.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.54, 131.52, 131.47, 128.23, 127.98, 127.84, 123.43, 120.37, 89.59, 88.71, 28.74, 15.27.



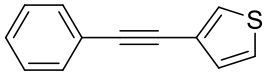
1-(phenylethynyl)-4-propylbenzene (Table 2, 3j): Light yellow liquid, 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dt, *J* = 7.1, 1.7 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.23 (m, 3H), 7.12 (d, *J* = 7.8 Hz, 2H), 2.56 (t, *J* = 7.7 Hz, 2H), 1.62 (h, *J* = 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.00, 131.46, 131.43, 128.43, 128.22, 127.96, 123.44, 120.38, 89.60, 88.74, 37.85, 24.25, 13.68.



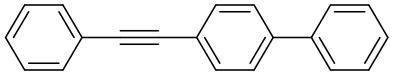
3-(phenylethynyl)aniline (Table 2, 3k): Brown solid, 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.44 (m, 2H), 7.27 (d, *J* = 6.0 Hz, 3H), 7.07 (t, *J* = 7.8 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 2.3 Hz, 1H), 6.55 (dd, *J* = 8.2, 2.4 Hz, 1H), 3.58 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.20, 131.38, 129.11, 128.18, 128.03, 123.57, 123.06, 121.70, 117.55, 115.22, 89.62, 88.66.



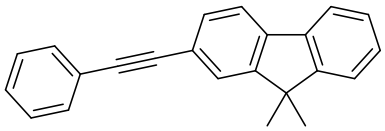
2-(phenylethynyl)thiophene (Table 2, 3l): White solid, 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.44 (m, 2H), 7.31 (d, *J* = 5.2 Hz, 3H), 7.25 (dd, *J* = 8.4, 4.4 Hz, 2H), 6.97 (t, *J* = 4.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.84, 131.34, 128.36, 128.31, 127.20, 127.05, 123.23, 122.84, 93.01, 82.61.



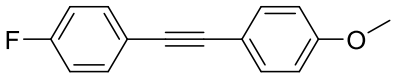
3-(phenylethynyl)thiophene (Table 2, 3m): White solid, 77%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.46 (m, 3H), 7.34 – 7.27 (m, 3H), 7.24 (t, *J* = 4.2 Hz, 1H), 7.18 (d, *J* = 4.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.46, 129.80, 128.56, 128.29, 128.15, 125.32, 123.13, 122.21, 88.86, 84.51.



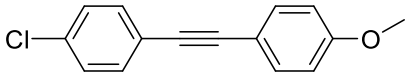
4-(phenylethynyl)-1,1'-biphenyl (Table 2, 3n): White solid, 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.53 (m, 8H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.42 – 7.30 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.94, 140.33, 132.01, 131.60, 128.85, 128.35, 128.26, 127.62, 127.01, 123.27, 122.15, 90.04, 89.28.



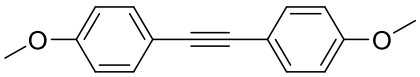
9,9-dimethyl-2-(phenylethynyl)-9H-fluorene (Table 2, 3o): Oily liquid, 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.65 (m, 2H), 7.61 (d, *J* = 1.3 Hz, 1H), 7.54 (ddt, *J* = 15.1, 7.8, 1.7 Hz, 3H), 7.46 – 7.38 (m, 1H), 7.40 – 7.27 (m, 5H), 1.49 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.97, 153.66, 139.50, 138.58, 131.64, 130.79, 128.42, 128.22, 127.75, 127.18, 125.98, 123.48, 122.72, 121.72, 120.35, 120.02, 90.32, 89.51, 46.92, 27.10.



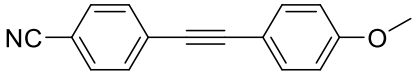
1-fluoro-4-((4-methoxyphenyl)ethynyl)benzene (Table 2, 3p): White solid, 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.41 (m, 4H), 7.04 (t, *J* = 8.5 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 3.82 (d, *J* = 1.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.48, 161.00, 159.61, 133.27, 133.18, 132.95, 119.66, 119.62, 115.63, 115.41, 115.10, 113.97, 89.00, 88.98, 86.94, 55.20.



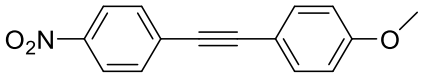
1-chloro-4-((4-methoxyphenyl)ethynyl)benzene (Table 2, 3q): White solid, 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.38 (m, 4H), 7.33 – 7.25 (m, 2H), 6.92 – 6.81 (m, 2H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.75, 133.83, 133.04, 132.61, 128.61, 122.09, 114.97, 114.02, 90.33, 86.96, 55.28.



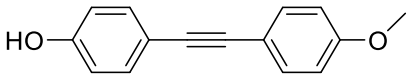
1,2-bis(4-methoxyphenyl)ethyne (Table 2, 3r): White solid, 63%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.5 Hz, 4H), 6.87 (d, *J* = 8.4 Hz, 4H), 3.82 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.34, 132.84, 115.66, 113.92, 87.91, 55.26, 55.24.



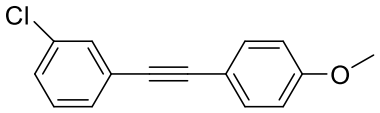
4-((4-methoxyphenyl)ethynyl)benzonitrile (Table 2, 3s): White solid, 87%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (q, *J* = 8.3 Hz, 4H), 7.53 – 7.42 (m, 2H), 6.96 – 6.79 (m, 2H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.25, 133.34, 131.99, 131.82, 128.61, 118.63, 114.21, 114.14, 110.99, 94.07, 86.70, 55.33.



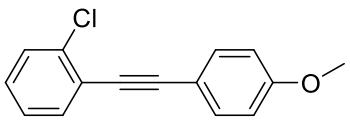
1-methoxy-4-((4-nitrophenyl)ethynyl)benzene (Table 2, 3t): Light yellow solid, 30%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.07 (m, 2H), 7.65 – 7.54 (m, 2H), 7.52 – 7.41 (m, 2H), 6.95 – 6.82 (m, 2H), 3.83 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.34, 146.56, 133.36, 131.89, 130.59, 123.53, 114.12, 114.00, 95.09, 86.58, 55.27.



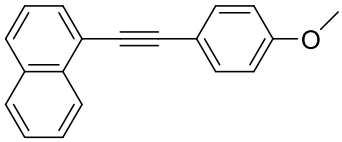
4-((4-methoxyphenyl)ethynyl)phenol (Table 2, 3u): White solid, 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.30 (m, 4H), 6.96 – 6.68 (m, 4H), 5.00 (s, 1H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.39, 155.39, 133.12, 132.91, 116.00, 115.68, 115.49, 114.01, 87.98, 87.84, 55.34.



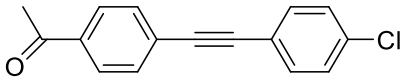
1-chloro-3-((4-methoxyphenyl)ethynyl)benzene (Table 2, 3v): White solid, 87%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.40 (m, 3H), 7.35 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.28 – 7.16 (m, 2H), 6.88 – 6.79 (m, 2H), 3.76 (d, *J* = 1.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.78, 134.02, 133.07, 131.15, 129.44, 128.03, 125.28, 114.70, 113.97, 90.64, 86.67, 55.15, 55.14.



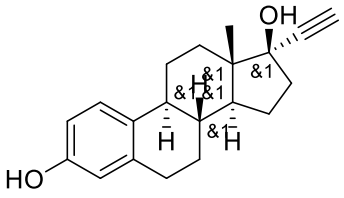
1-chloro-2-((4-methoxyphenyl)ethynyl)benzene (Table 2, 3w): White solid, 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.41 (m, 3H), 7.38 (dt, *J* = 5.4, 3.7 Hz, 1H), 7.23 – 7.11 (m, 2H), 6.92 – 6.75 (m, 2H), 3.77 (d, *J* = 1.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.83, 135.54, 133.13, 132.92, 129.14, 128.82, 126.36, 123.40, 114.85, 113.94, 94.64, 84.93, 55.17, 55.16.



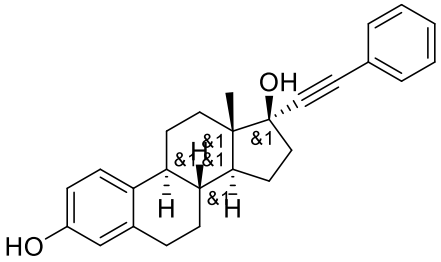
1-((4-methoxyphenyl)ethynyl)naphthalene (Table 2, 3x): White solid, 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.73 (t, *J* = 8.3 Hz, 2H), 7.59 – 7.49 (m, 3H), 7.50 – 7.42 (m, 1H), 7.42 – 7.33 (m, 1H), 6.91 – 6.71 (m, 2H), 3.69 (d, *J* = 1.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.62, 133.12, 133.01, 129.97, 128.31, 128.21, 126.59, 126.28, 126.16, 125.21, 121.15, 115.34, 113.97, 94.40, 86.20, 55.09, 55.08.



1-(4-((4-chlorophenyl)ethynyl)phenyl)ethan-1-one (Table 2, 3y): White solid, 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 2.62 – 2.56 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.13, 136.23, 134.78, 132.85, 131.59, 128.72, 128.20, 127.67, 121.04, 91.40, 89.44, 26.53.

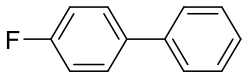


17α-Ethinylestradiol (Scheme 2, raw material): White solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.99 (s, 1H), 7.04 (d, *J* = 8.5 Hz, 1H), 6.56 – 6.36 (m, 2H), 5.34 (s, 1H), 3.31 (s, 1H), 2.78 – 2.58 (m, 2H), 2.28 (dq, *J* = 12.9, 3.7 Hz, 1H), 2.08 (dddd, *J* = 26.2, 14.3, 9.5, 4.4 Hz, 2H), 1.93 – 1.72 (m, 3H), 1.72 – 1.54 (m, 3H), 1.27 (dtq, *J* = 23.6, 11.7, 5.1 Hz, 4H), 0.76 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 154.89, 137.08, 130.25, 126.04, 114.87, 112.69, 88.92, 78.12, 74.96, 48.95, 46.65, 43.28, 39.19, 38.77, 32.55, 29.16, 26.99, 26.11, 22.44, 12.70.

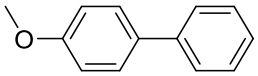


17α-(phenylethynyl)-Estradiol (Scheme 2, product): White solid, 56%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.01 (s, 1H), 7.52 – 7.29 (m, 5H), 7.07 (d, *J* = 8.5 Hz, 1H), 6.58 – 6.37 (m, 2H), 5.48 (s, 1H), 2.84 – 2.62 (m, 2H), 2.33 (dd, *J* = 13.3, 3.8 Hz, 1H), 2.22 (ddd, *J* = 13.6, 8.8, 5.4 Hz, 1H), 2.16 – 2.05 (m, 1H), 2.05 – 1.61 (m, 6H), 1.30 (dh, *J* = 23.7, 8.5, 5.8 Hz, 4H), 0.82 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 155.39, 137.61, 131.68, 130.71, 129.09, 128.62, 126.59, 123.42, 115.39, 113.21, 95.54,

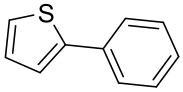
84.50, 79.06, 49.85, 47.73, 43.88, 39.41, 33.40, 29.70, 27.48, 26.72, 23.08, 13.39.



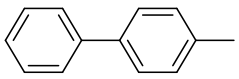
4-fluoro-1,1'-biphenyl (Table S4, entry 2): White solid, 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.5 Hz, 4H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.07 (t, *J* = 8.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.83, 161.38, 140.35, 137.46, 137.43, 128.97, 128.85, 128.77, 127.41, 127.15, 115.86, 115.64. known compound



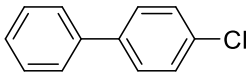
4-methoxy-1,1'-biphenyl (Table S4, entry 3): White solid, 95%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (t, *J* = 9.2 Hz, 4H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 2H), 3.70 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.06, 140.72, 133.64, 128.67, 128.07, 126.65, 126.59, 114.12, 55.21. known compound.



2-phenylthiophene (Table S4, entry 4): White solid, 85%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.6, 2.3 Hz, 2H), 7.34 (td, *J* = 7.7, 2.0 Hz, 2H), 7.29 – 7.19 (m, 3H), 7.03 (p, *J* = 2.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.34, 134.31, 128.82, 127.95, 127.39, 125.87, 124.74, 123.01. known compound.

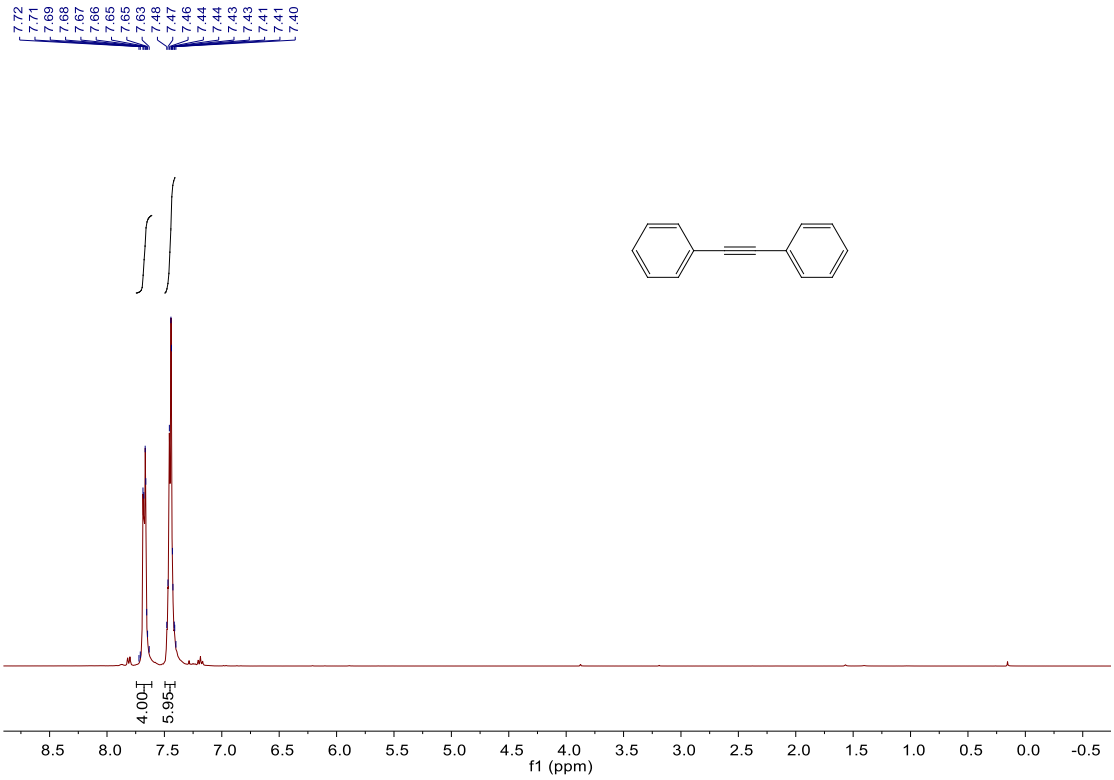


4-methyl-1,1'-biphenyl (Table S4, entry 5): White solid, 86%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dt, *J* = 7.0, 1.9 Hz, 2H), 7.47 (dt, *J* = 8.1, 1.9 Hz, 2H), 7.39 (tt, *J* = 8.0, 1.7 Hz, 2H), 7.29 (ddd, *J* = 9.0, 5.3, 1.7 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 2H), 2.36 (t, *J* = 1.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.08, 138.28, 136.93, 129.44, 128.67, 126.94, 126.92, 21.05. known compound



4-chloro-1,1'-biphenyl (Table S4, entry 7): White solid, 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 –

7.47 (m, 2H), 7.47 – 7.43 (m, 2H), 7.44 – 7.26 (m, 5H).^{13}C NMR (100 MHz, $CDCl_3$) δ 139.86, 139.55, 133.30, 128.83, 128.32, 127.53, 126.90. known compound.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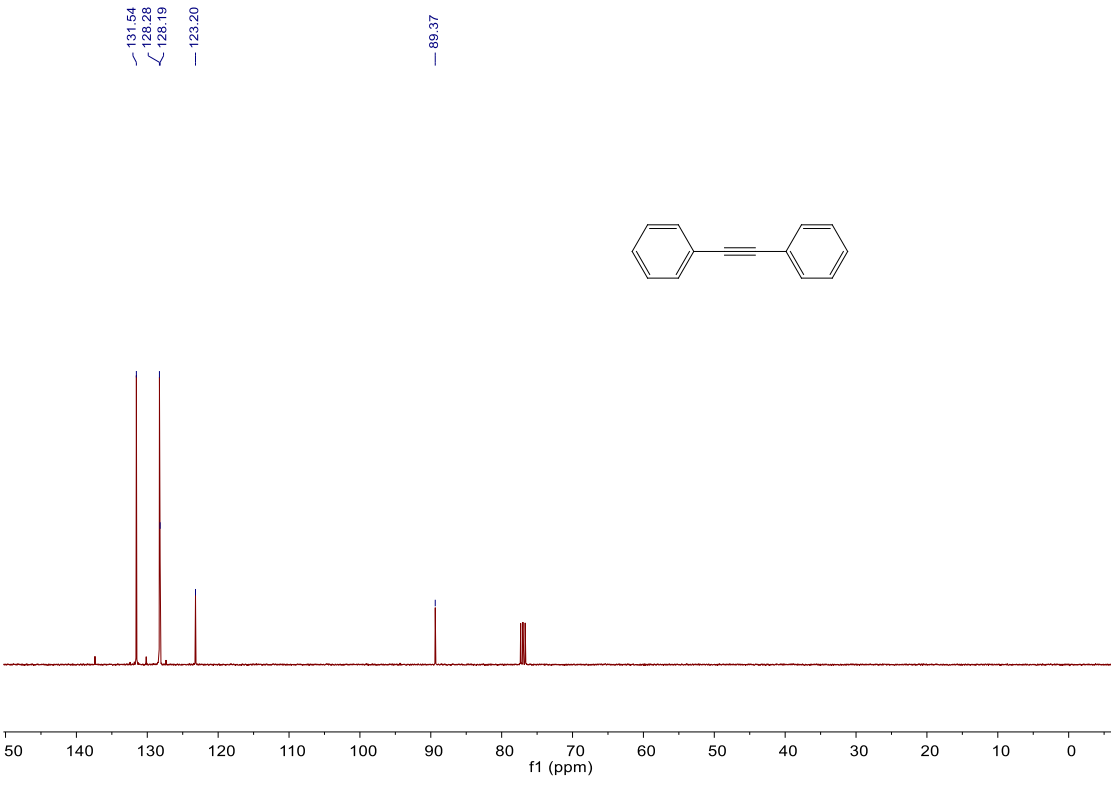
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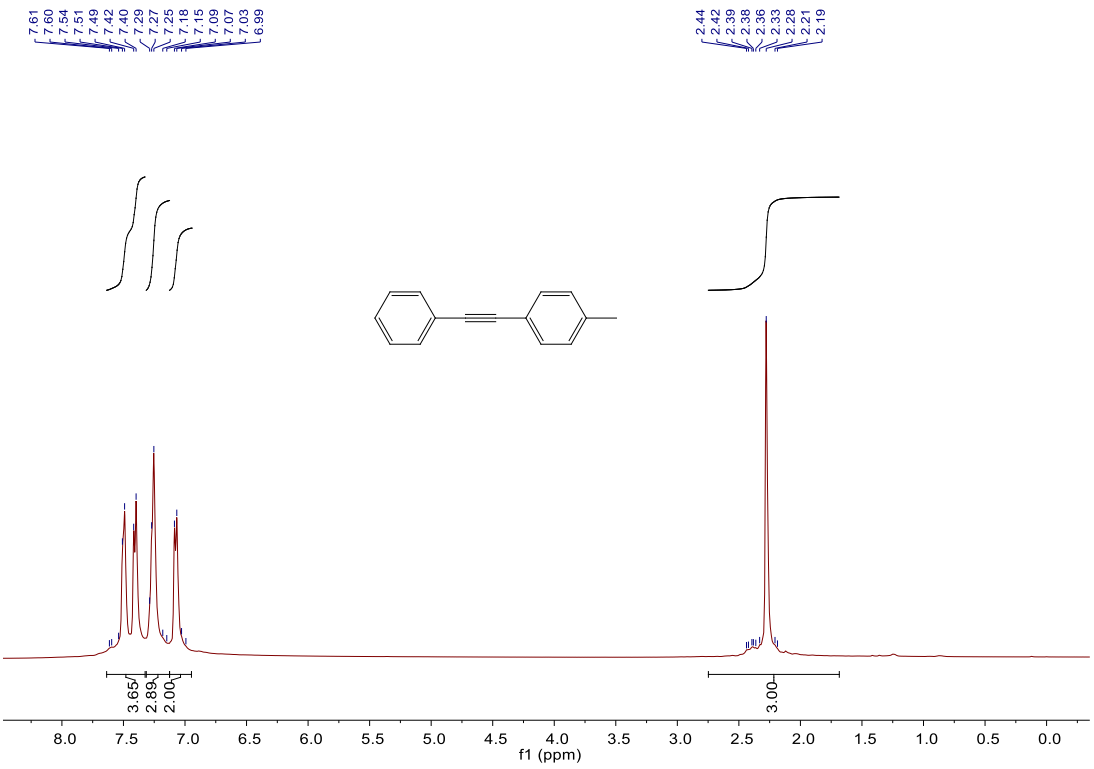
f1 (ppm)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7.07
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2.42
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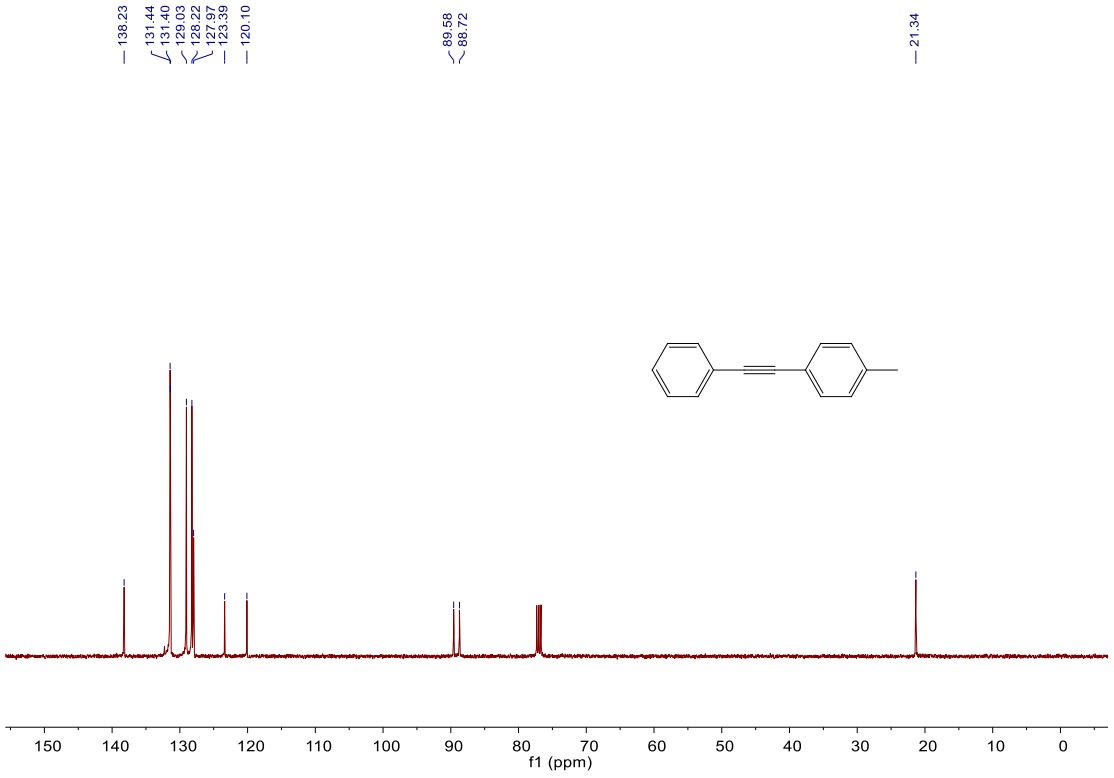
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f1 (ppm)

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7.54
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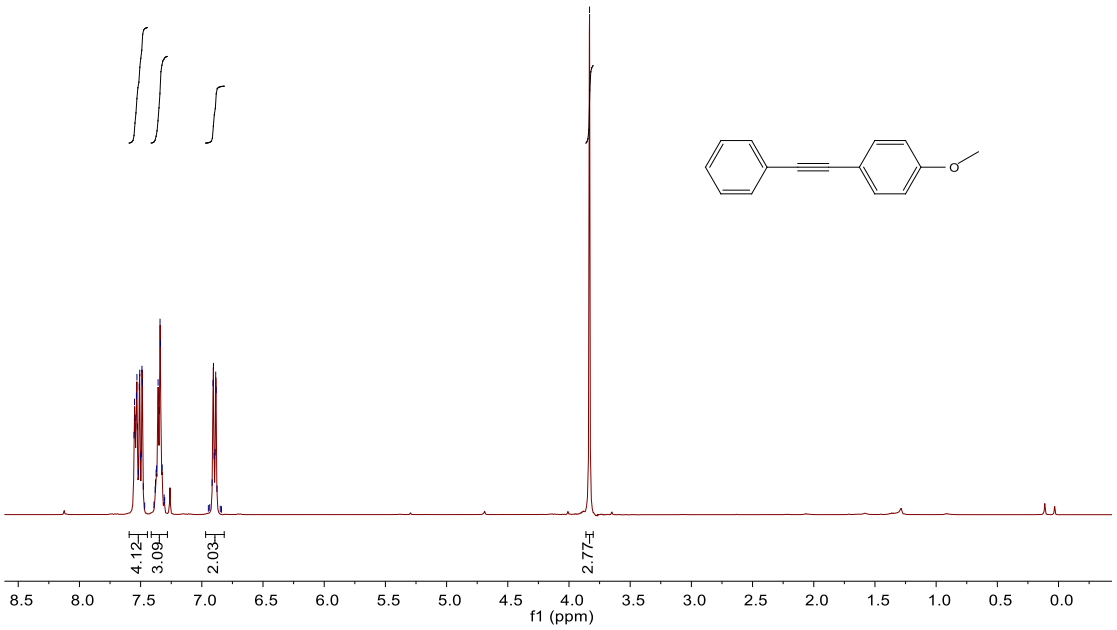
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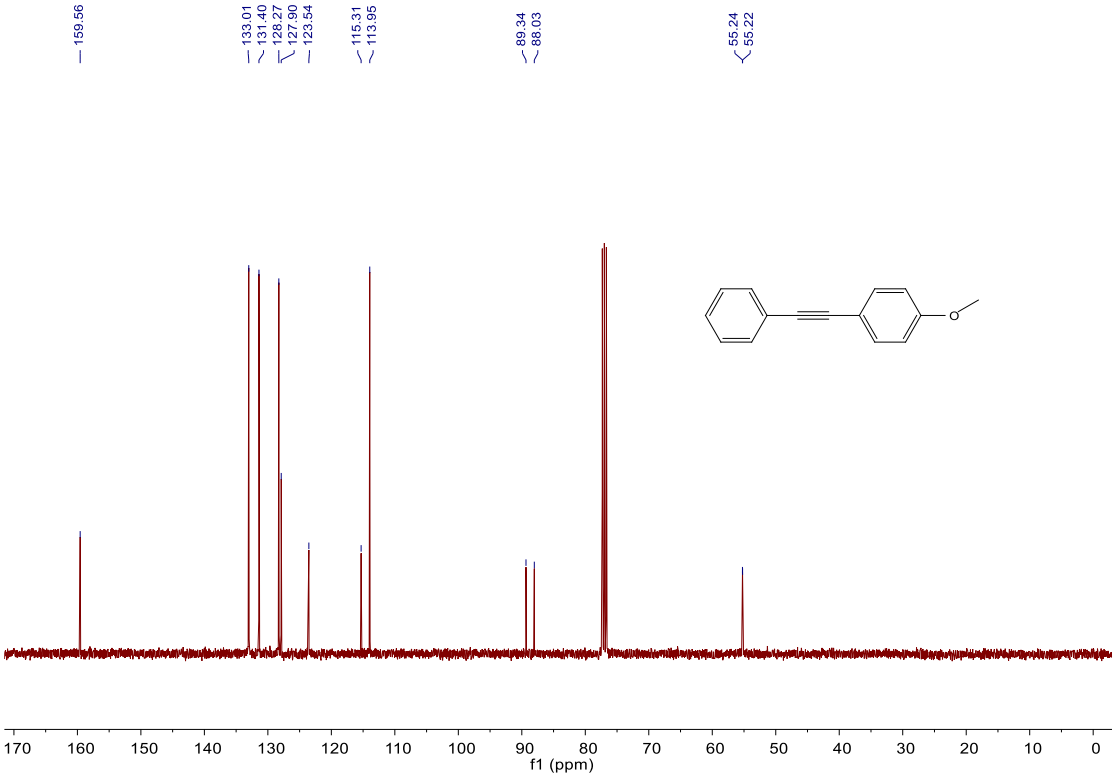
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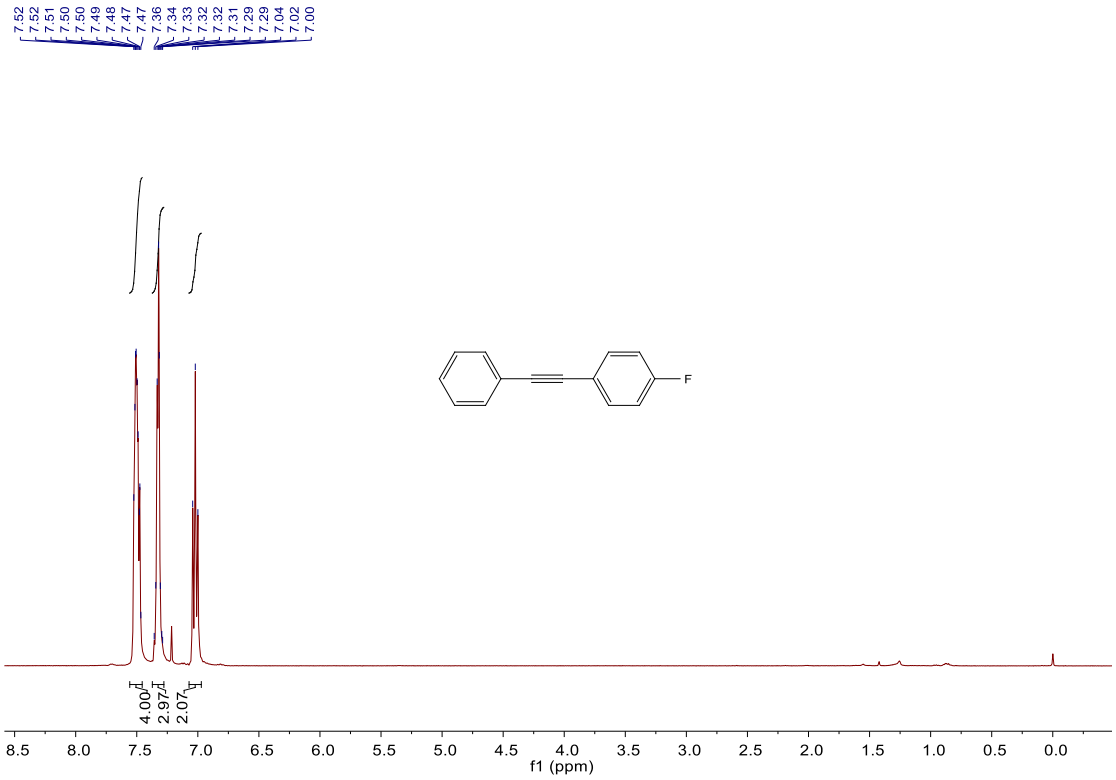
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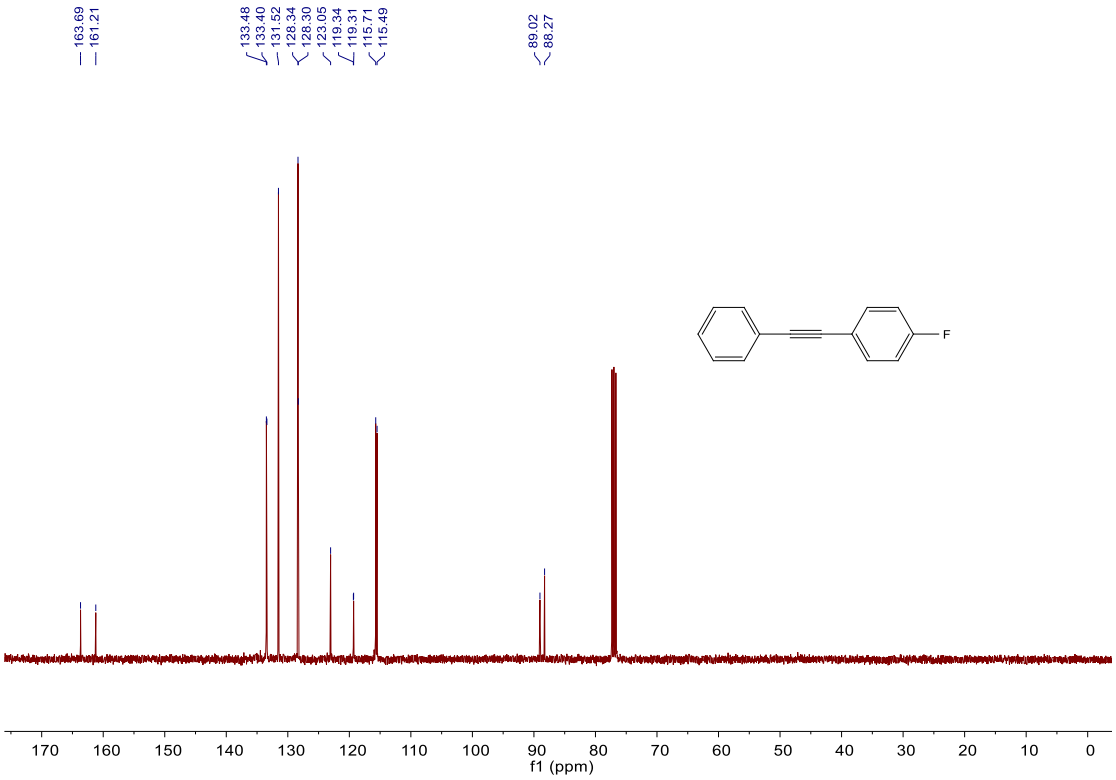
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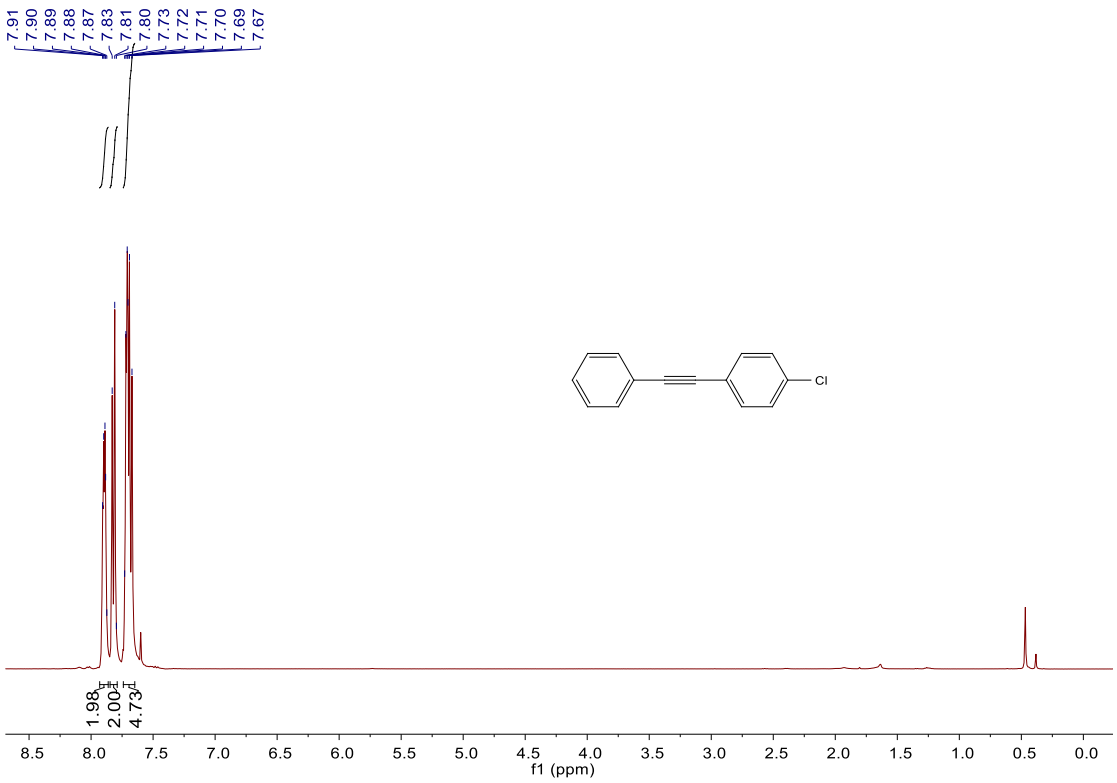
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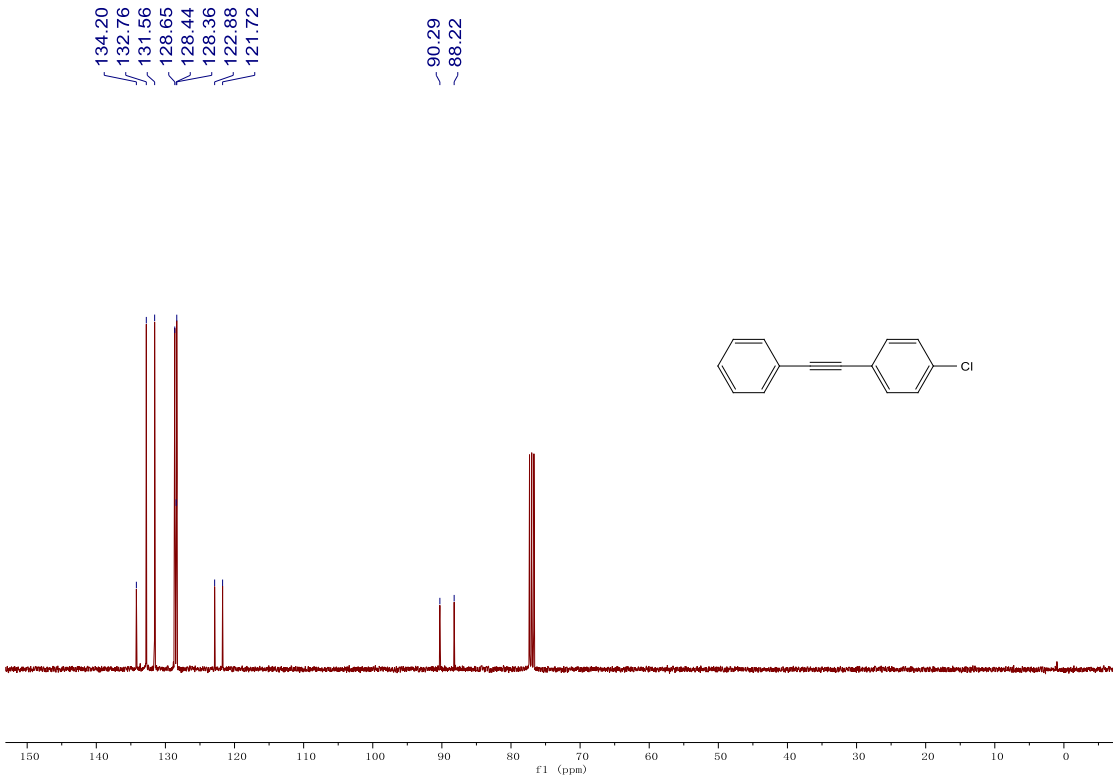
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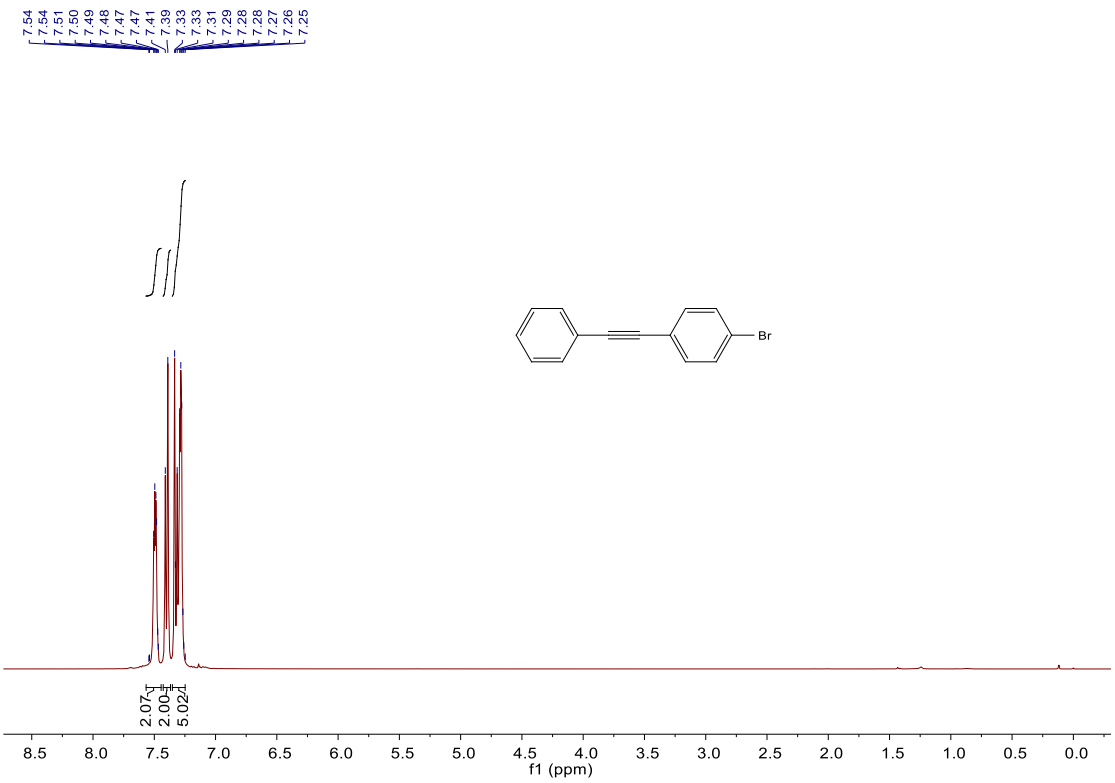
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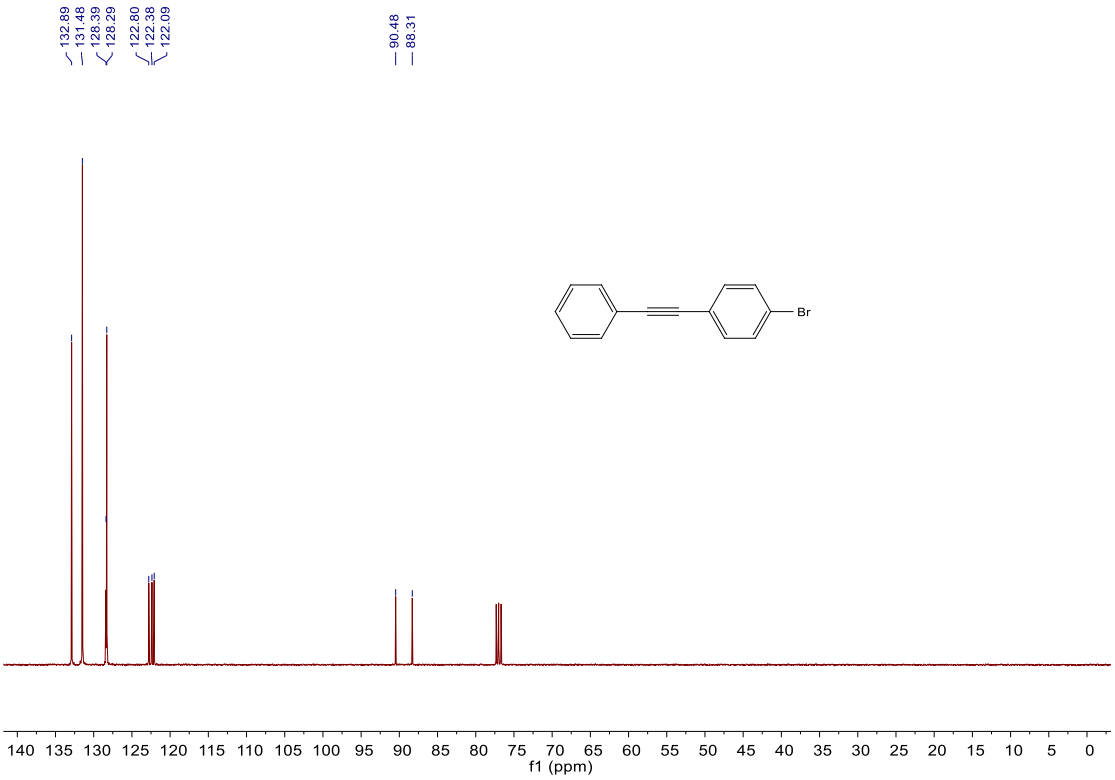
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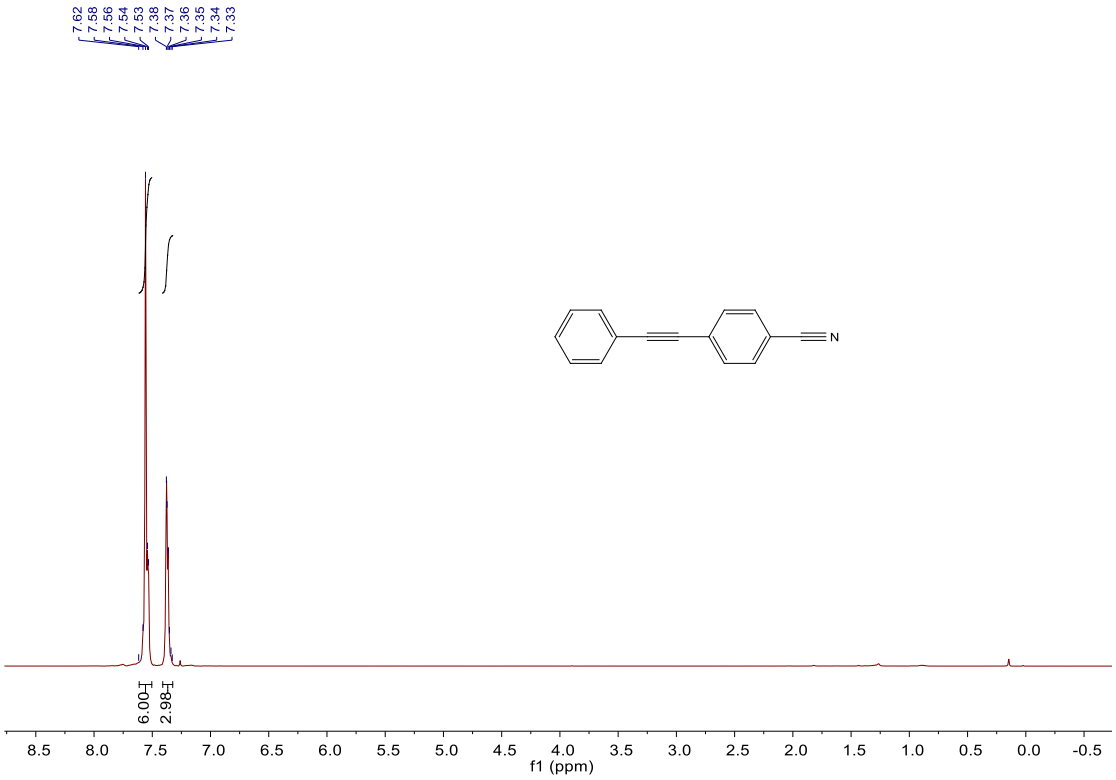
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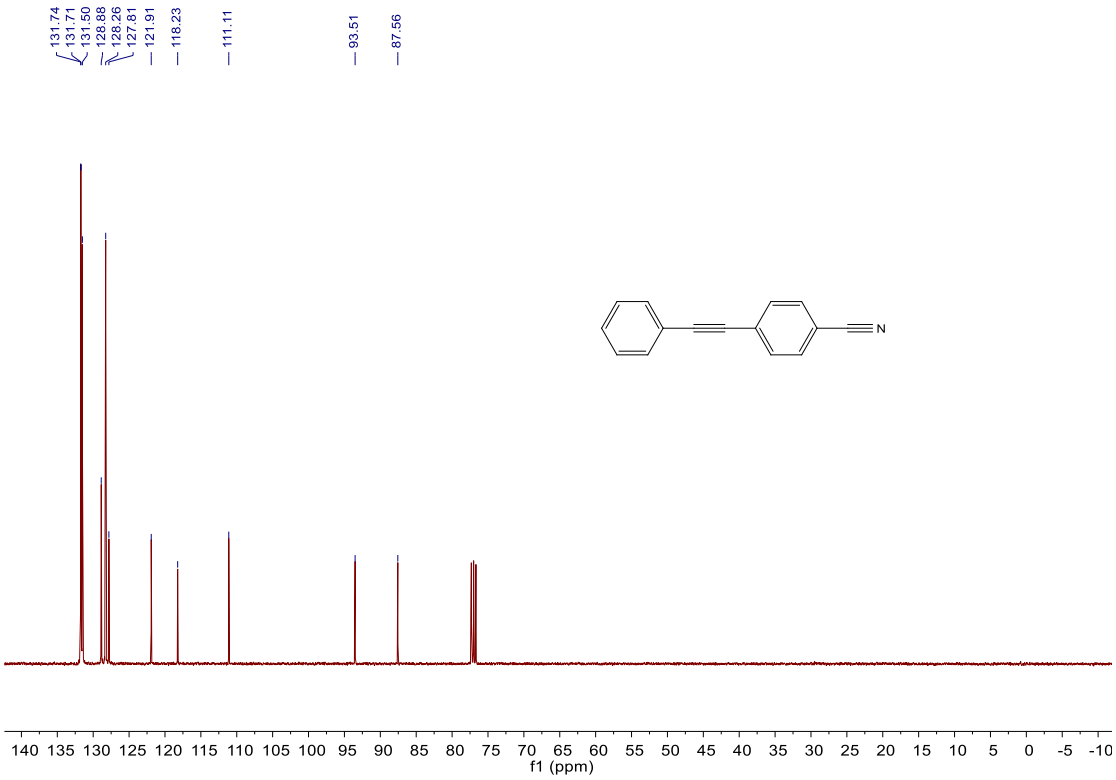
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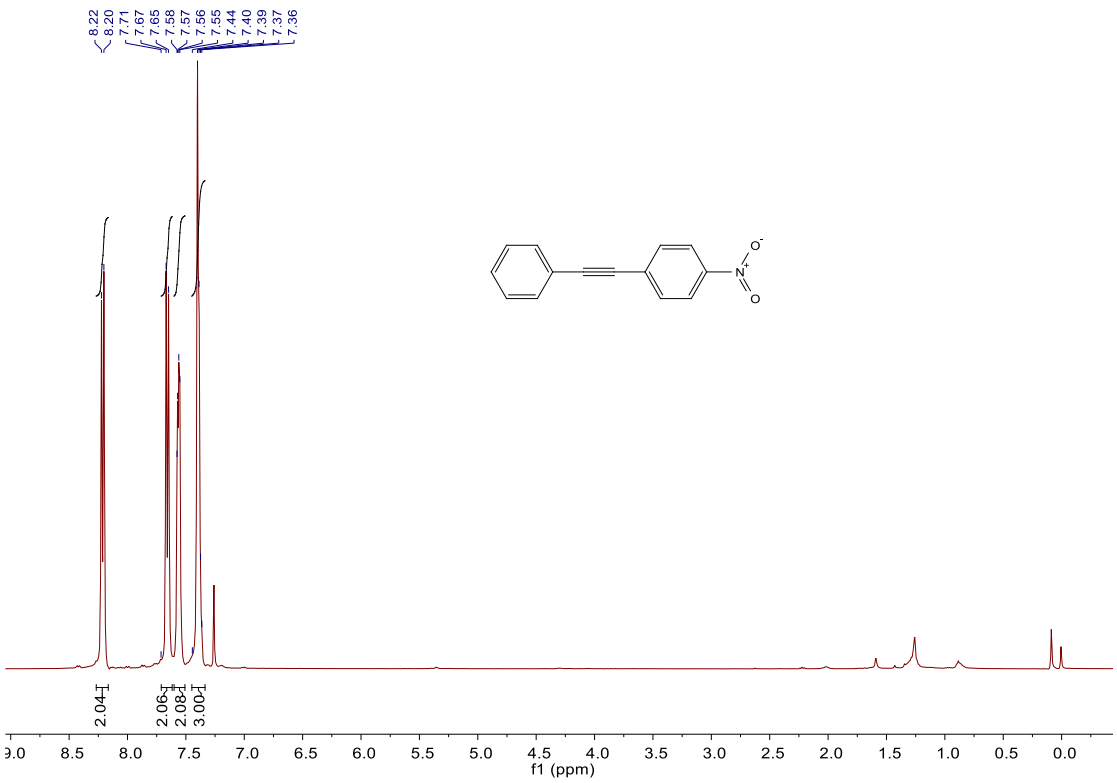
f1 (ppm)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7.37
7.36
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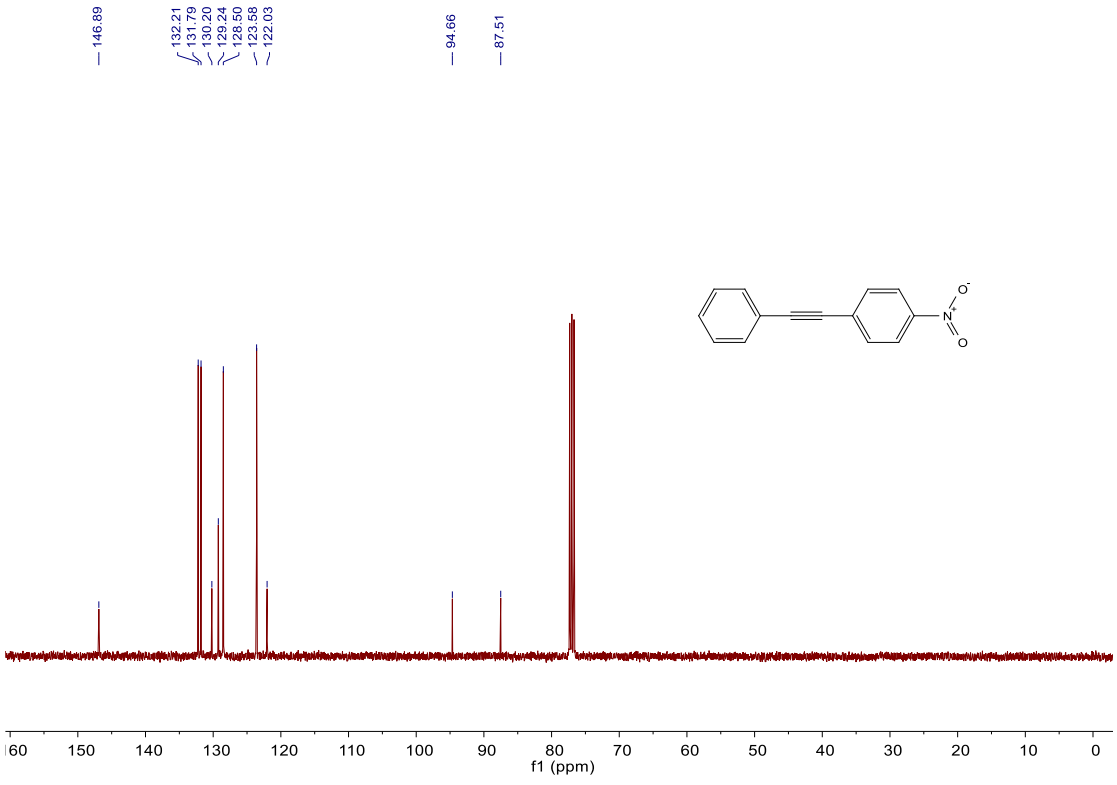
2.06
2.08
3.00
f1 (ppm)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130.20
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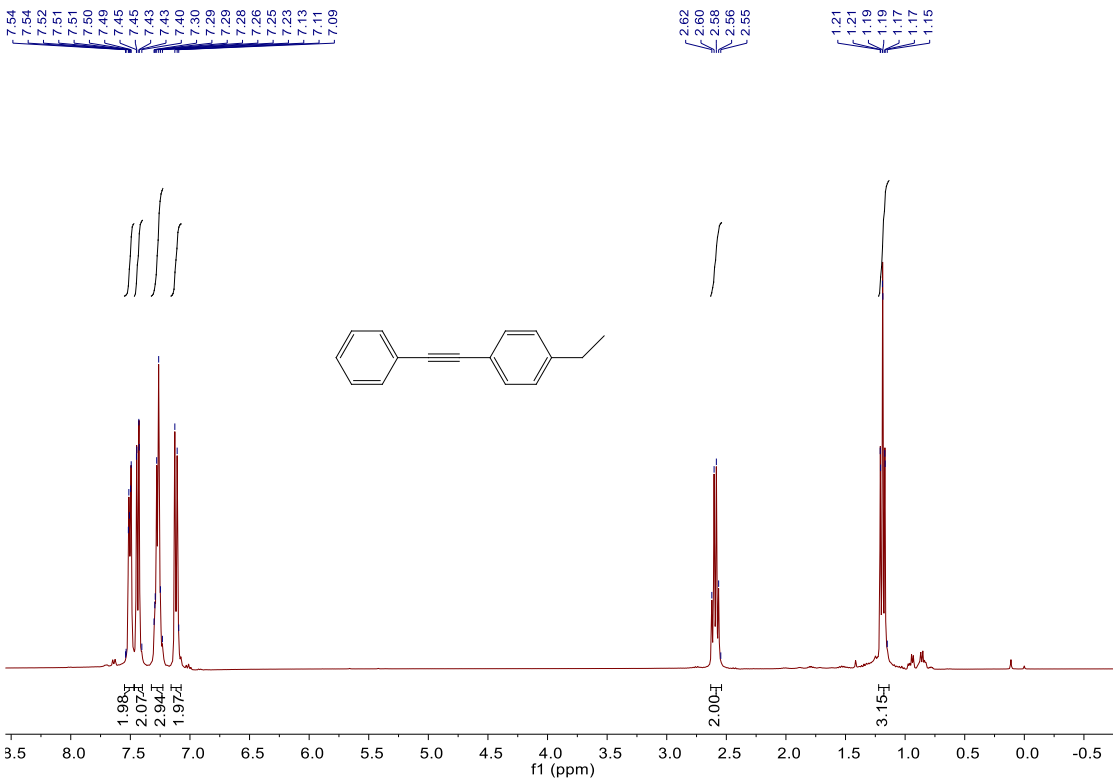
128.50
123.58
122.03
94.66
87.51
f1 (ppm)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7.29
7.28
7.26
7.25
7.23
7.13
7.11
7.09
2.62
2.60
2.58
2.56
2.55
1.21
1.21
1.19
1.19
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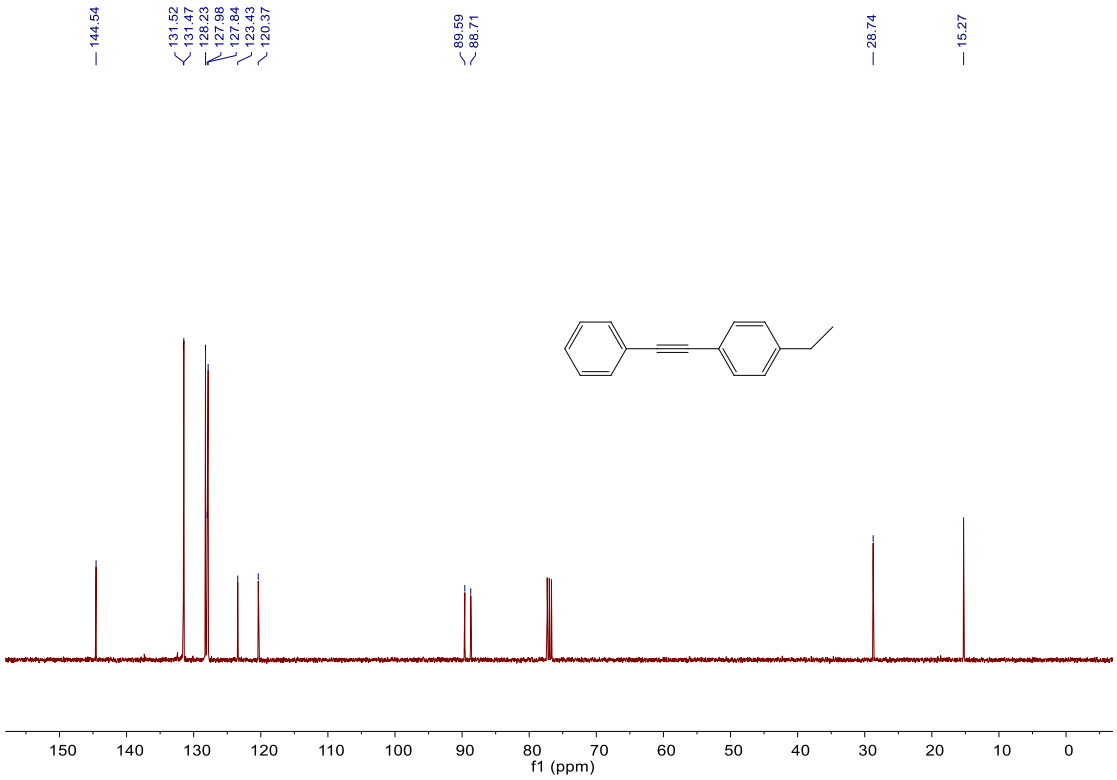
1.17
1.15
1.98
2.07
2.94
1.97
2.00
3.15
f1 (ppm)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120.37
89.59
88.71
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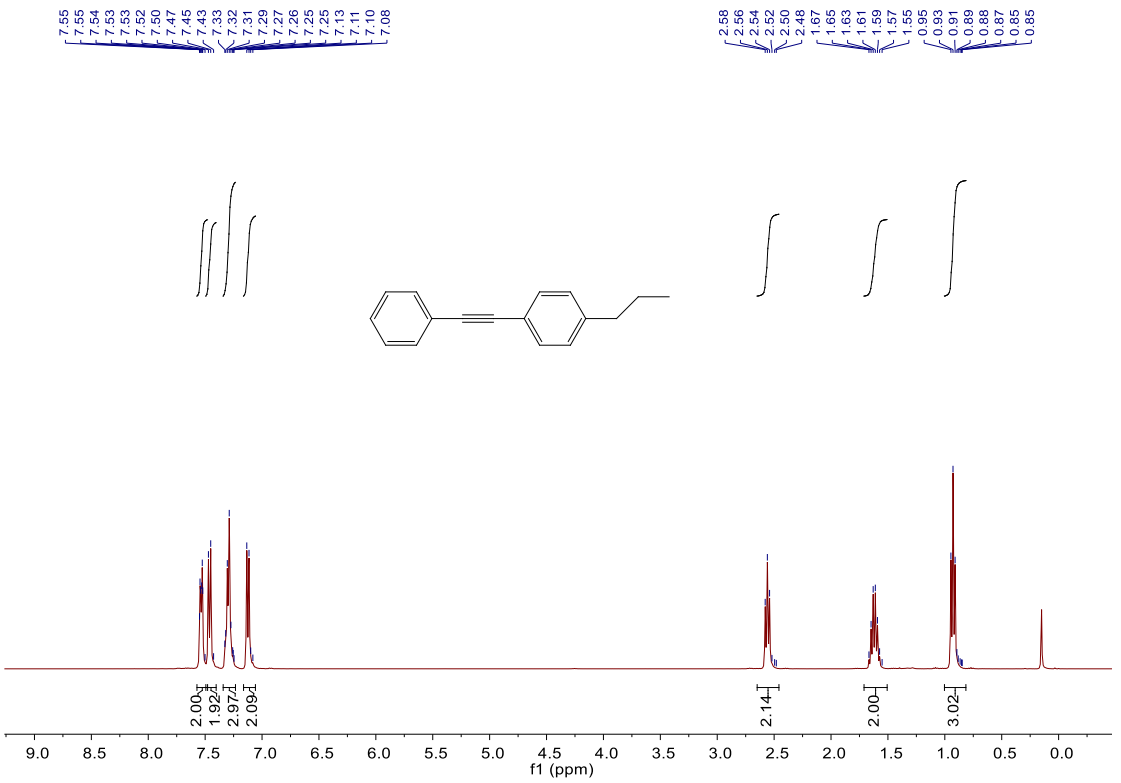
15.27
f1 (ppm)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7.29
7.27
7.26
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7.25
7.13
7.11
7.10
7.08
2.58
2.56
2.54
2.52
2.50
2.48
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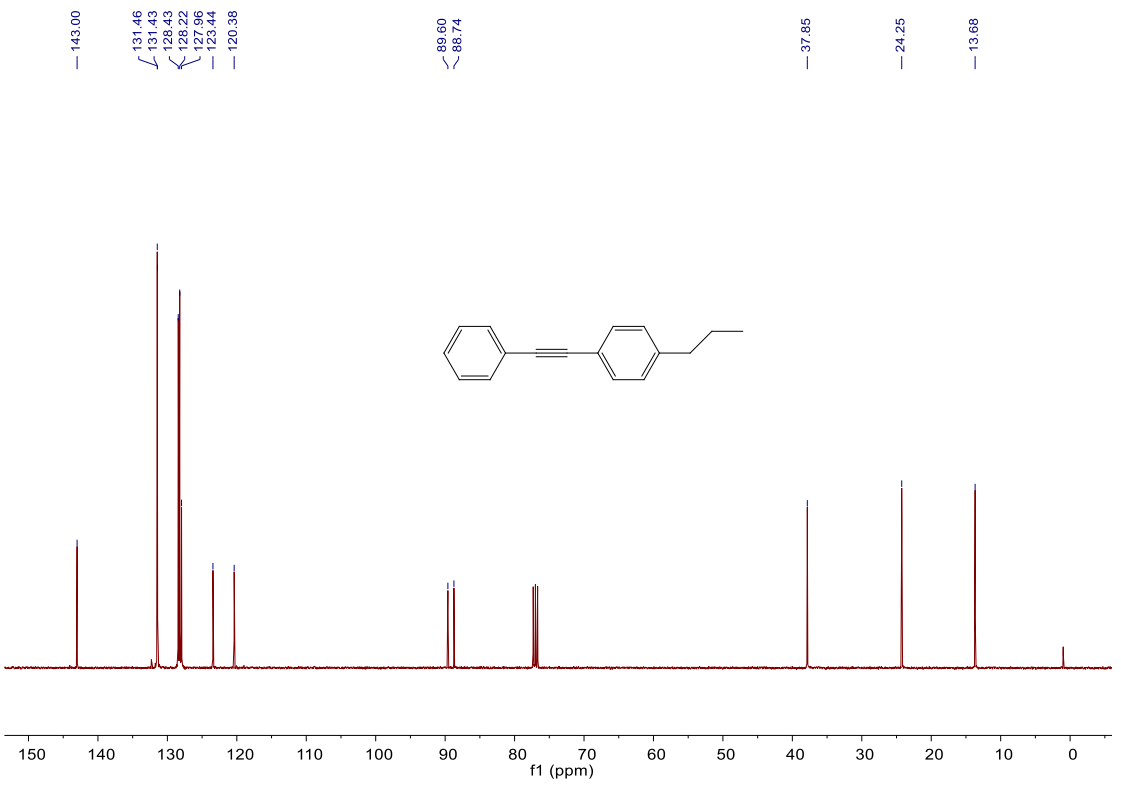
1.65
1.63
1.61
1.59
1.57
1.55
0.95
0.93
0.91
0.89
0.88
0.87
0.85
0.85
2.00
1.92
2.97
2.09
2.14
2.00
3.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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131.46
131.43
128.43
128.22
127.96
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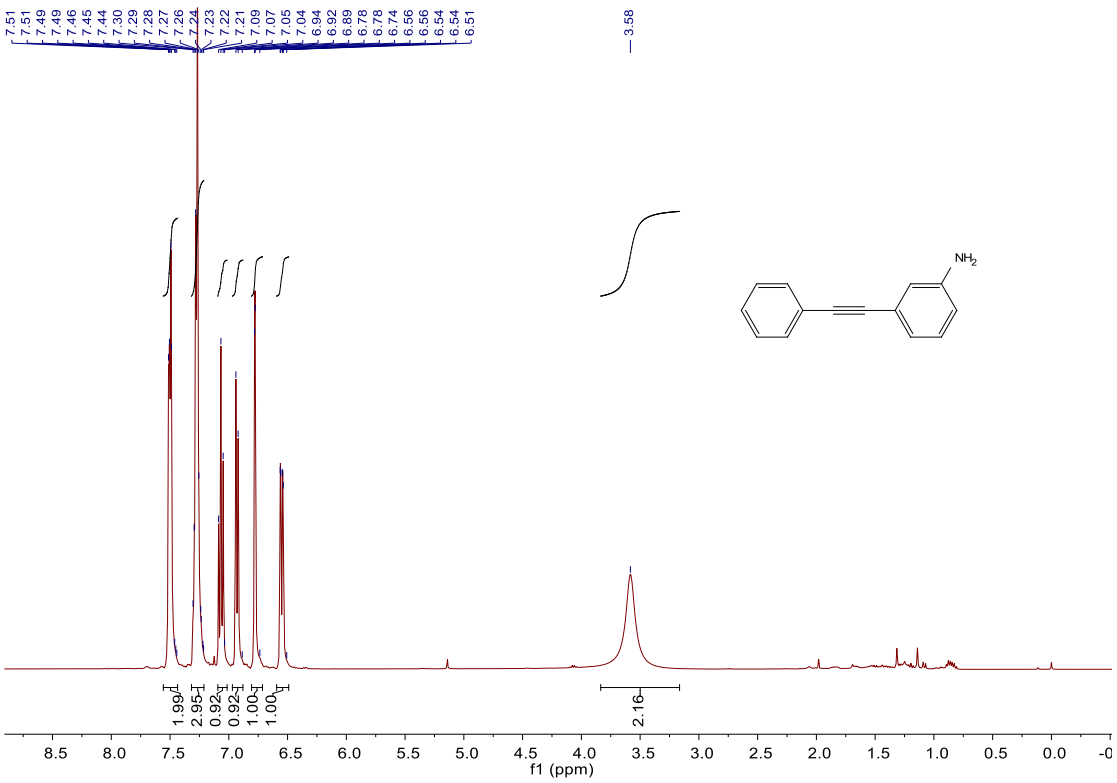
120.38
89.60
88.74
37.85
24.25
13.68
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.49
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7.30
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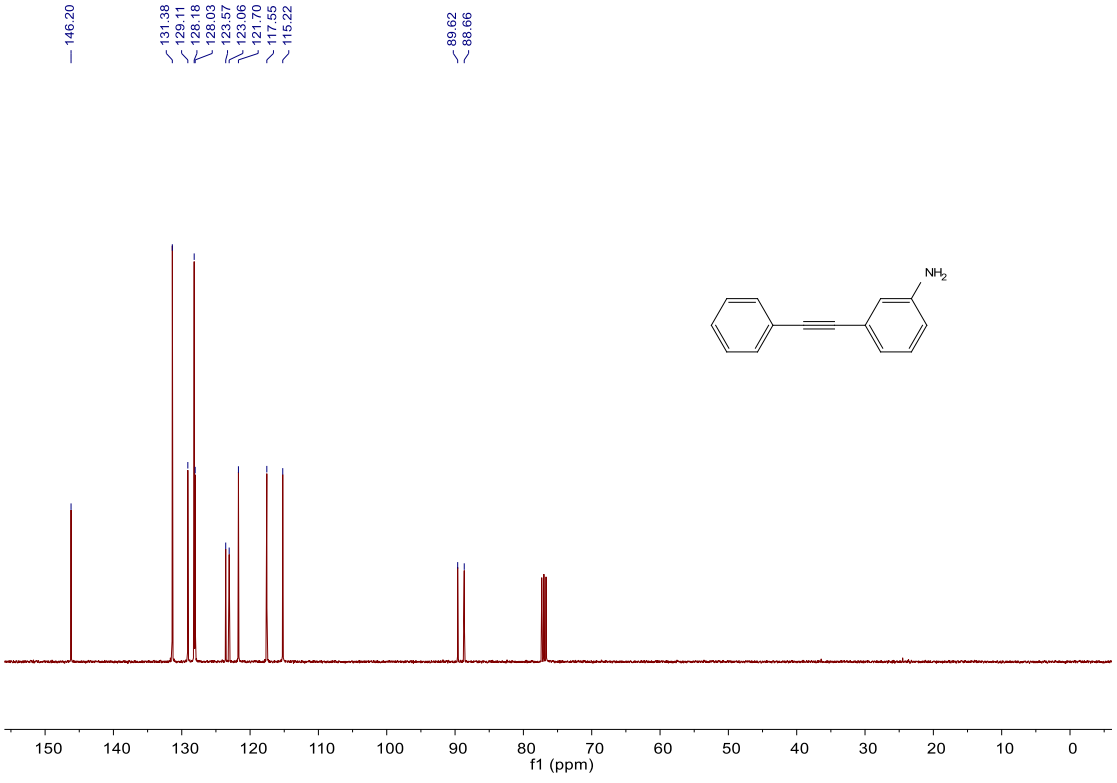
7.26
7.24
7.23
7.22
7.21
7.09
7.07
7.05
7.04
6.94
6.92
6.89
6.78
6.78
6.74
6.56
6.56
6.54
6.54
6.51
3.58
NH2
1.99
2.95
0.92
0.92
1.00
1.00
2.16
f1 (ppm)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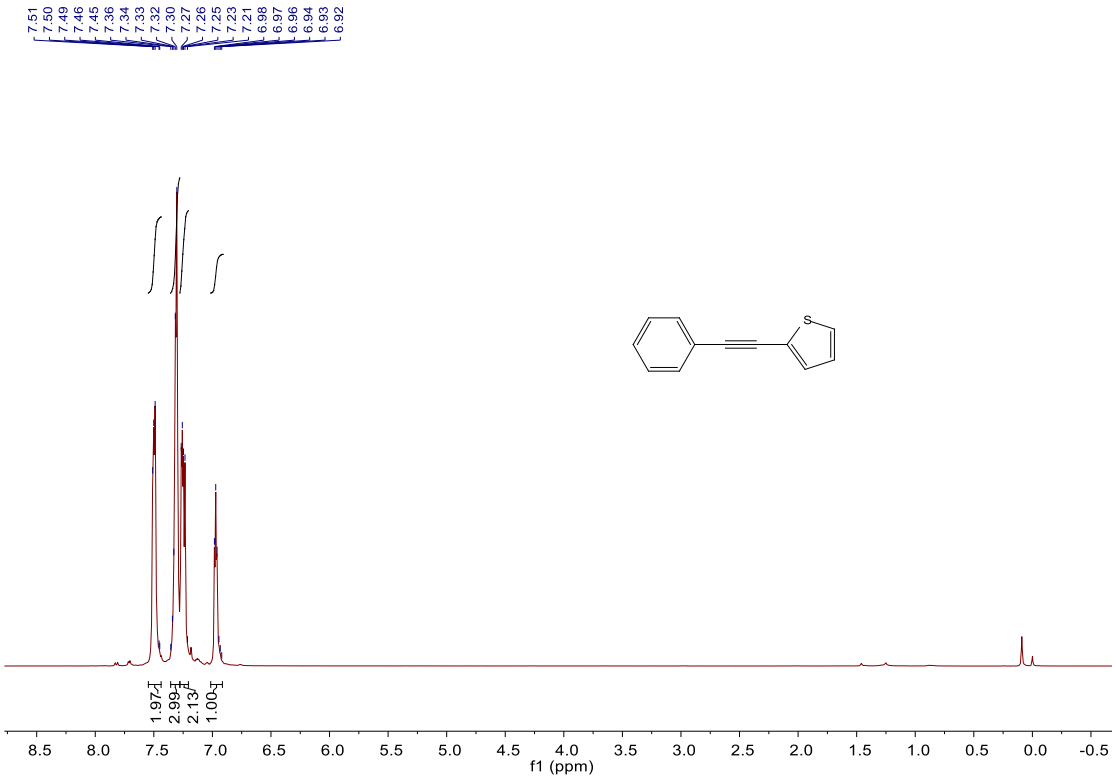
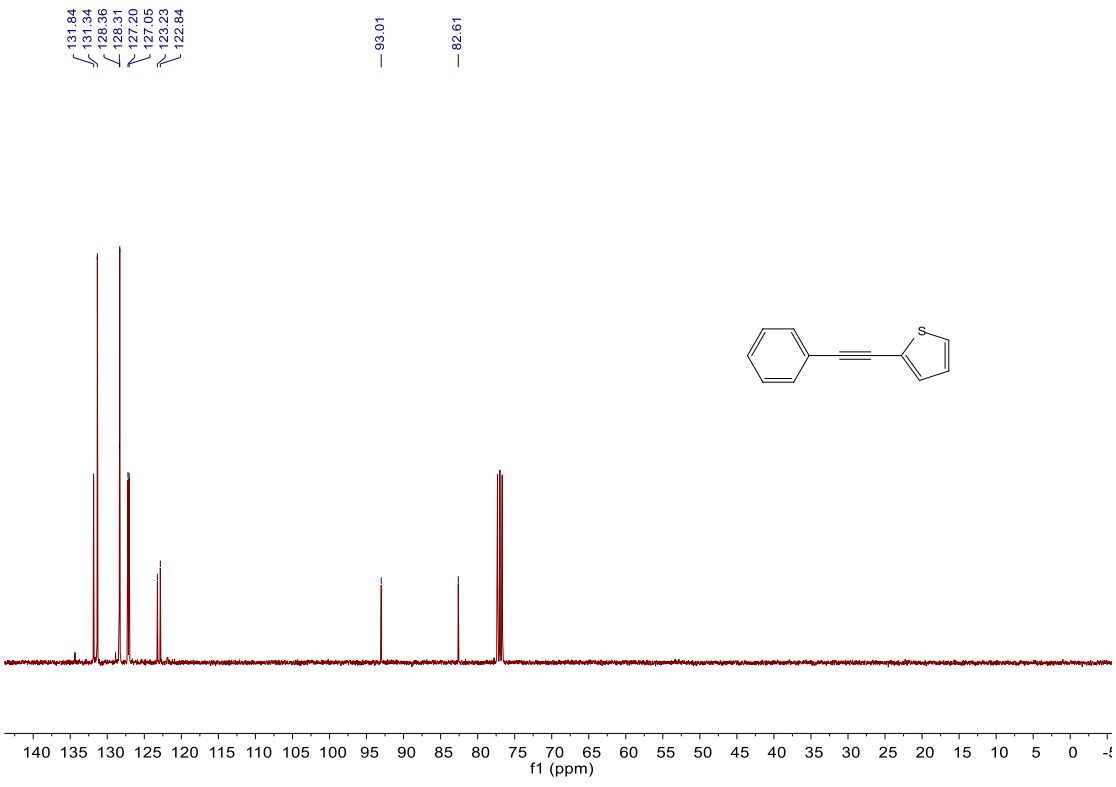
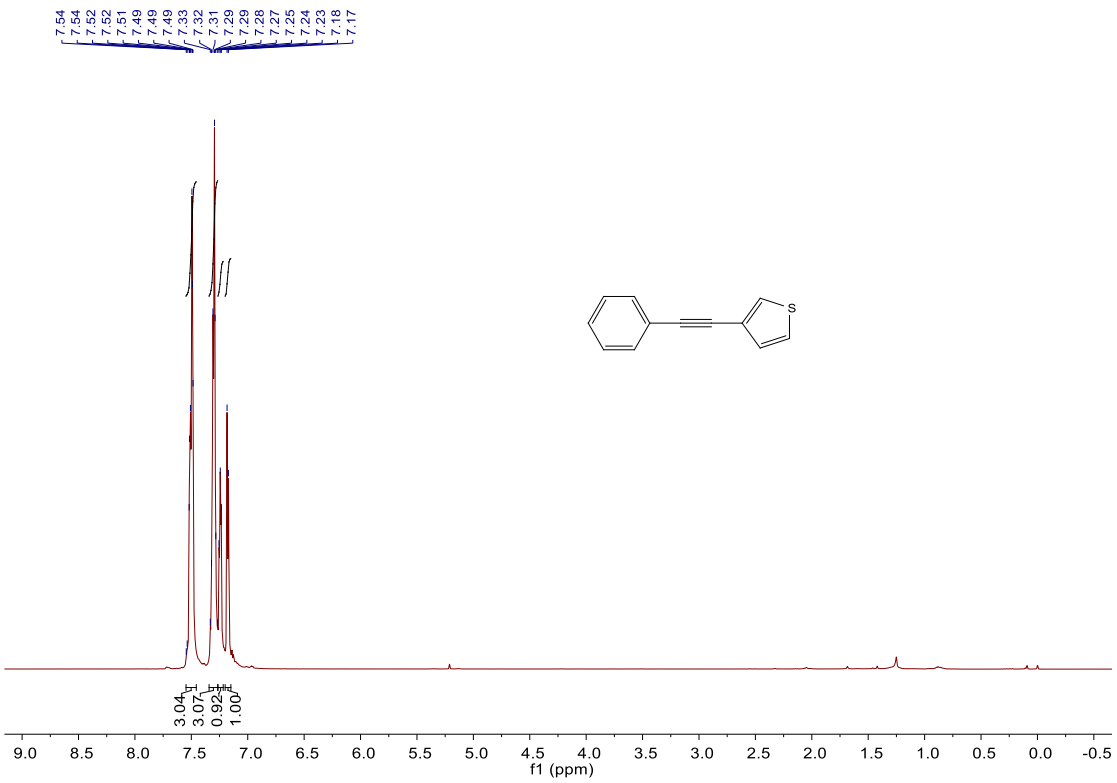
131.38
129.11
128.18
128.03
123.57
123.06
121.70
117.55
115.22
89.62
88.66
NH2
f1 (ppm)


7.51
7.50
7.49
7.46
7.45
7.36
7.34
7.33
7.32
7.30
7.27
7.26
7.25
7.23
7.21
6.98
6.97
6.96
6.94
6.93
6.92
1.97
2.99
2.13
1.00
S
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


131.84
131.34
128.36
128.31
127.20
127.05
123.23
122.84
93.01
82.61
S
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)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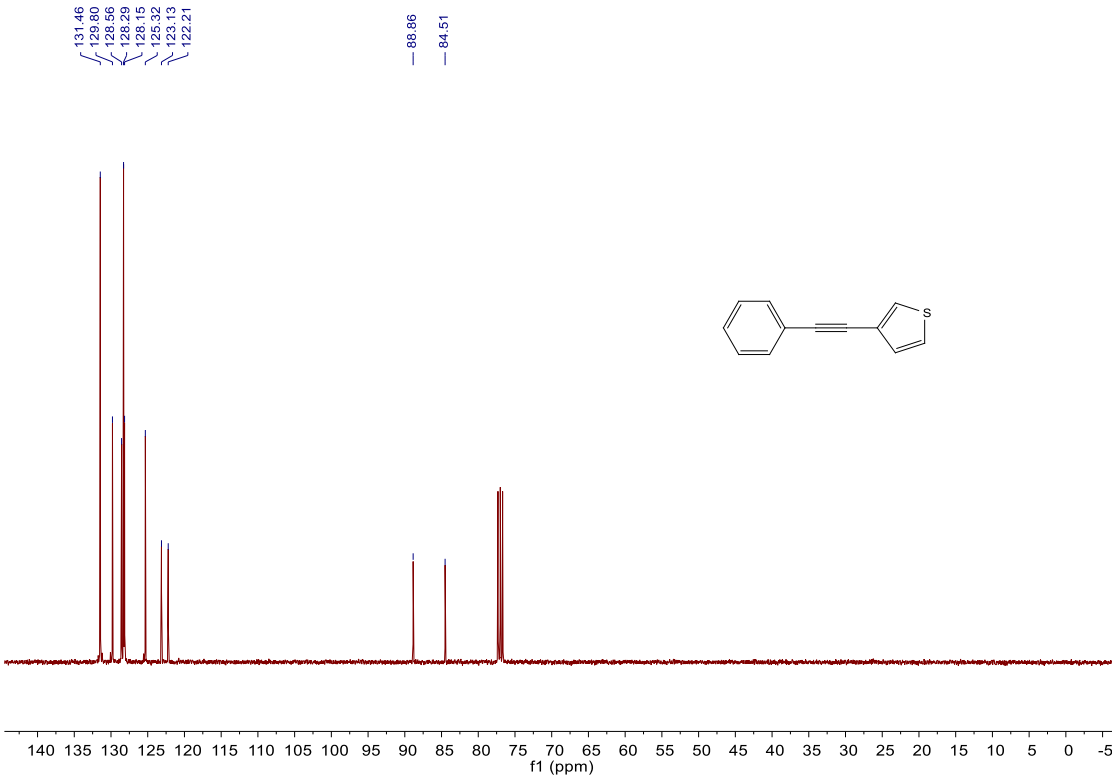
7.49
7.33
7.32
7.31
7.29
7.29
7.28
7.27
7.25
7.24
7.23
7.18
7.17
3.04
3.07
0.92
1.00
S
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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128.29
128.15
125.32
123.13
122.21
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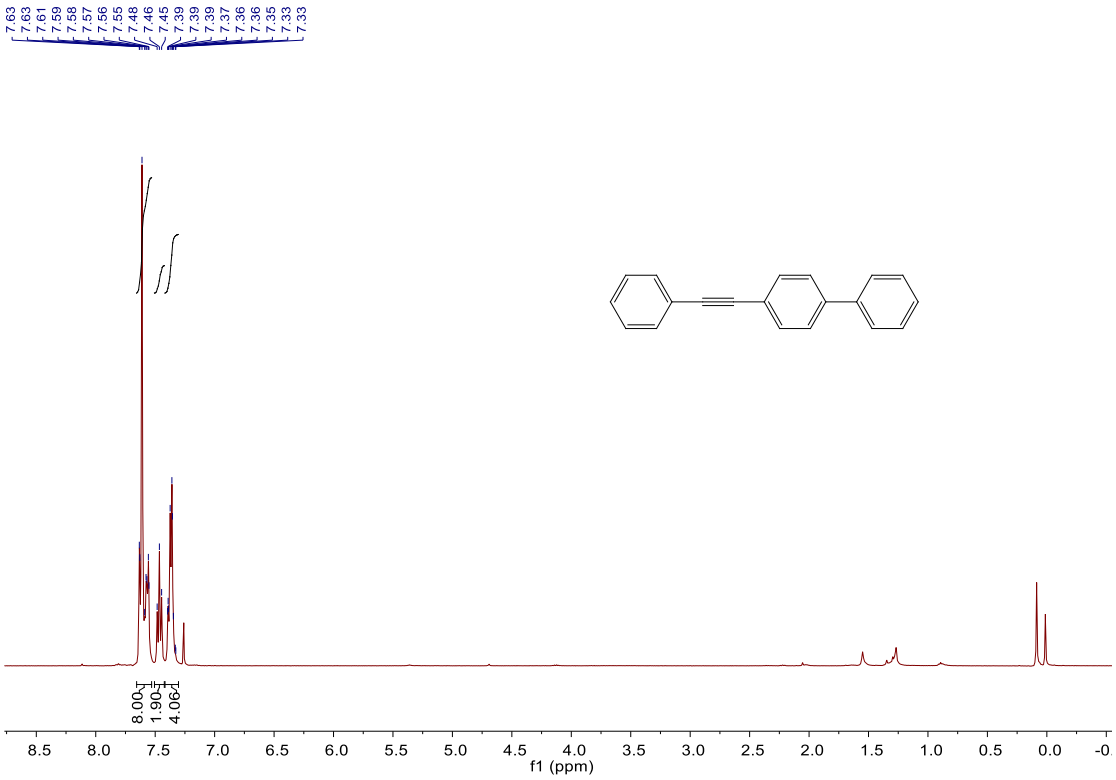
84.51
S
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5
f1 (ppm)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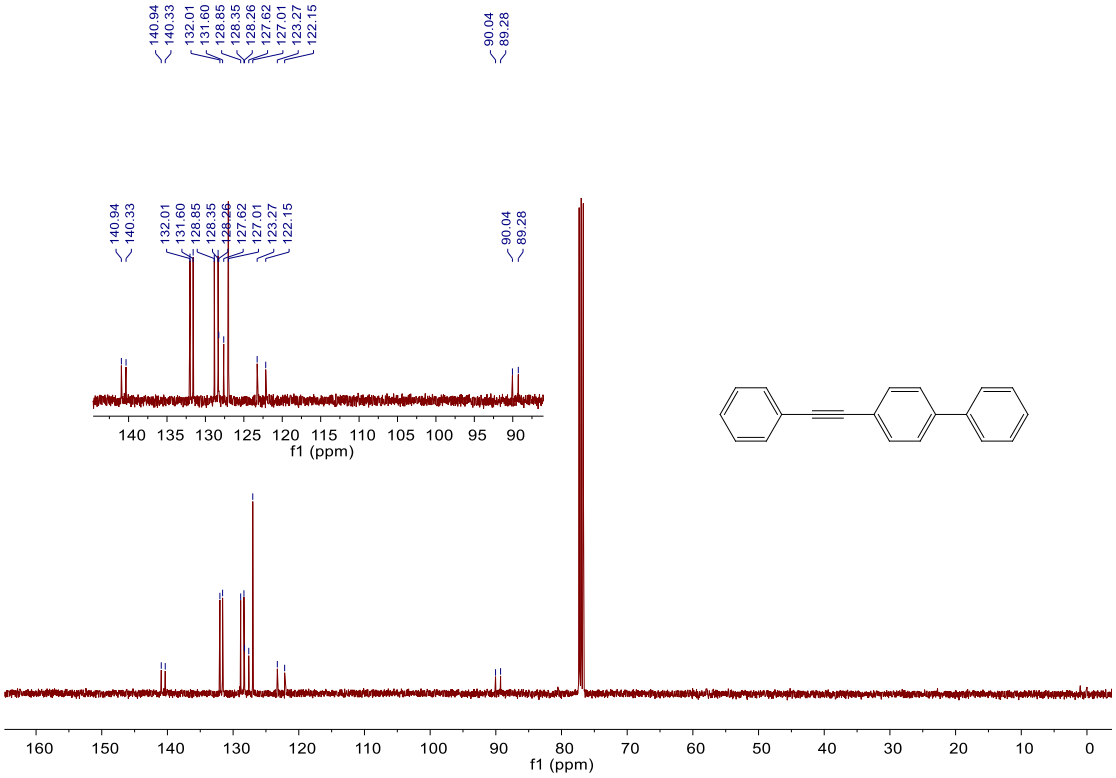
7.57
7.56
7.55
7.48
7.46
7.45
7.39
7.39
7.39
7.37
7.36
7.36
7.35
7.33
7.33
8.00
1.90
4.06
f1 (ppm)


140.94
140.33
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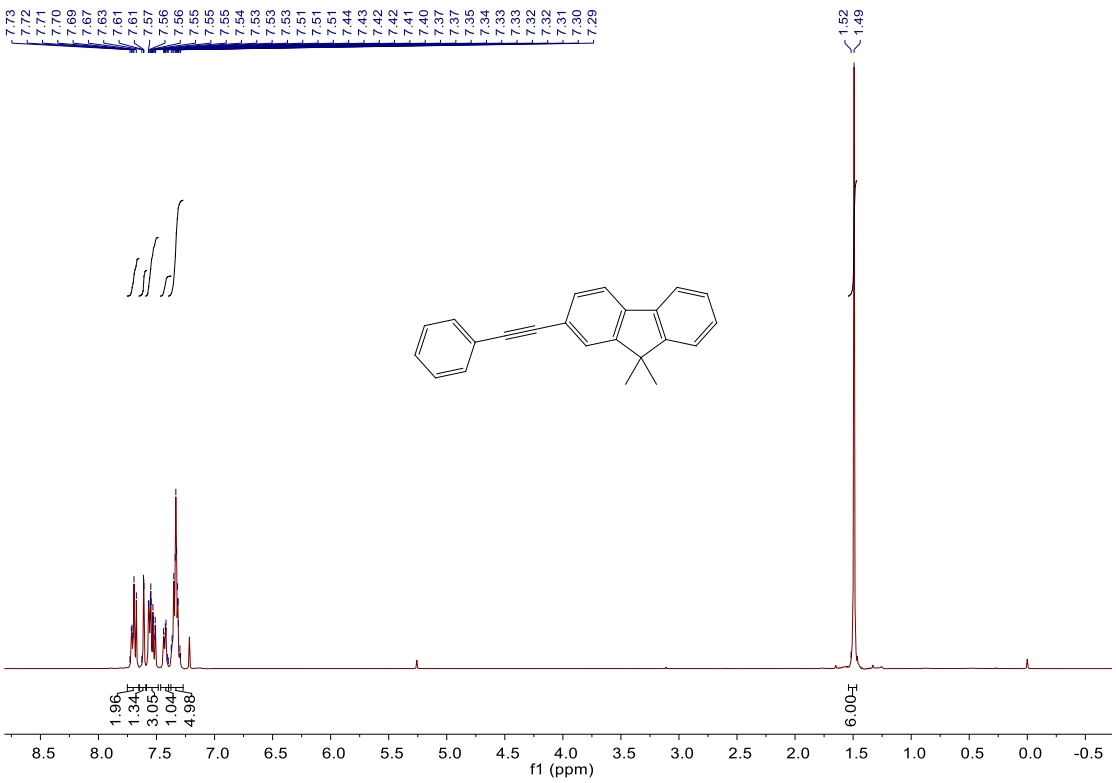
131.60
128.85
128.35
128.26
127.62
127.01
123.27
122.15
90.04
89.28
f1 (ppm)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7.42
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7.33
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7.32
7.32
7.31
7.30
7.29
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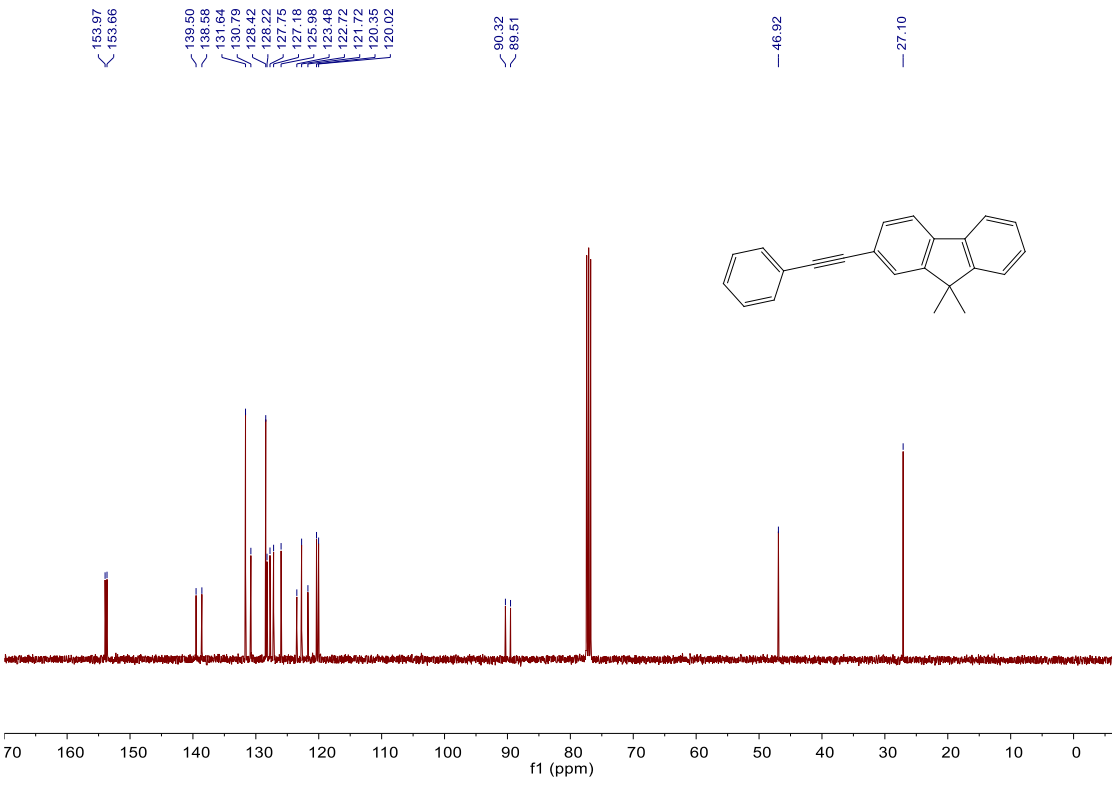
1.49
1.96
1.34
3.05
1.04
4.98
6.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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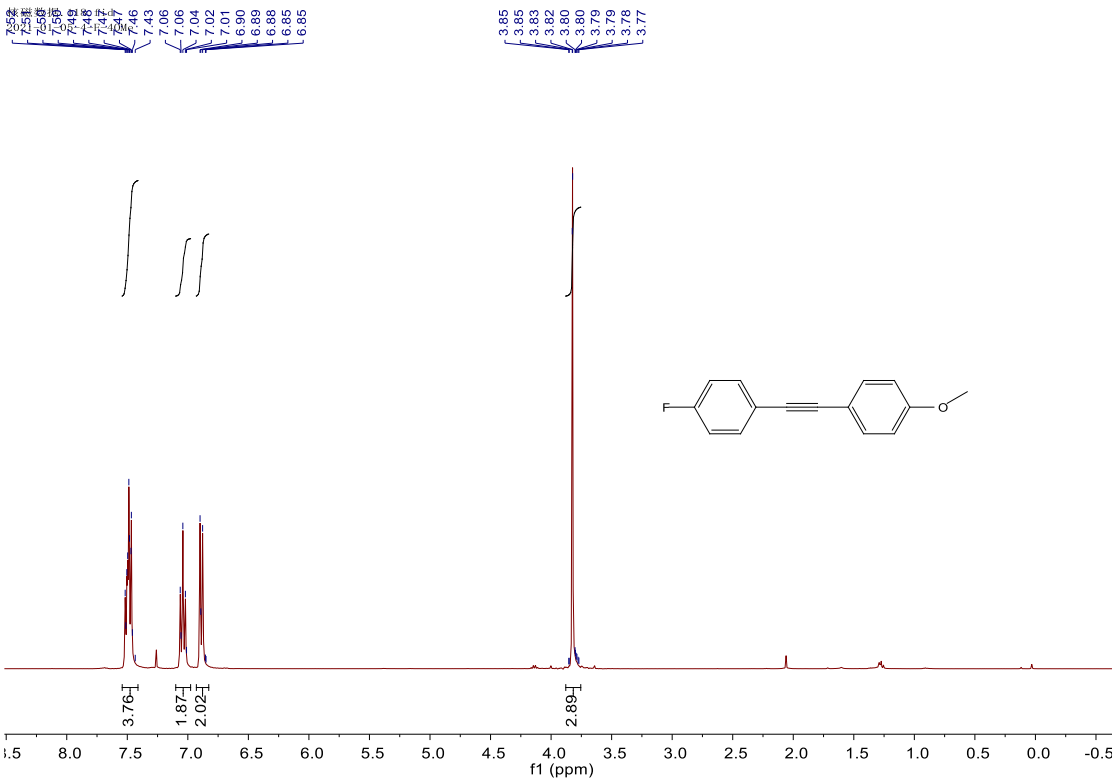
128.42
128.22
127.75
127.18
125.98
123.48
122.72
121.72
120.35
120.02
90.32
89.51
46.92
27.10
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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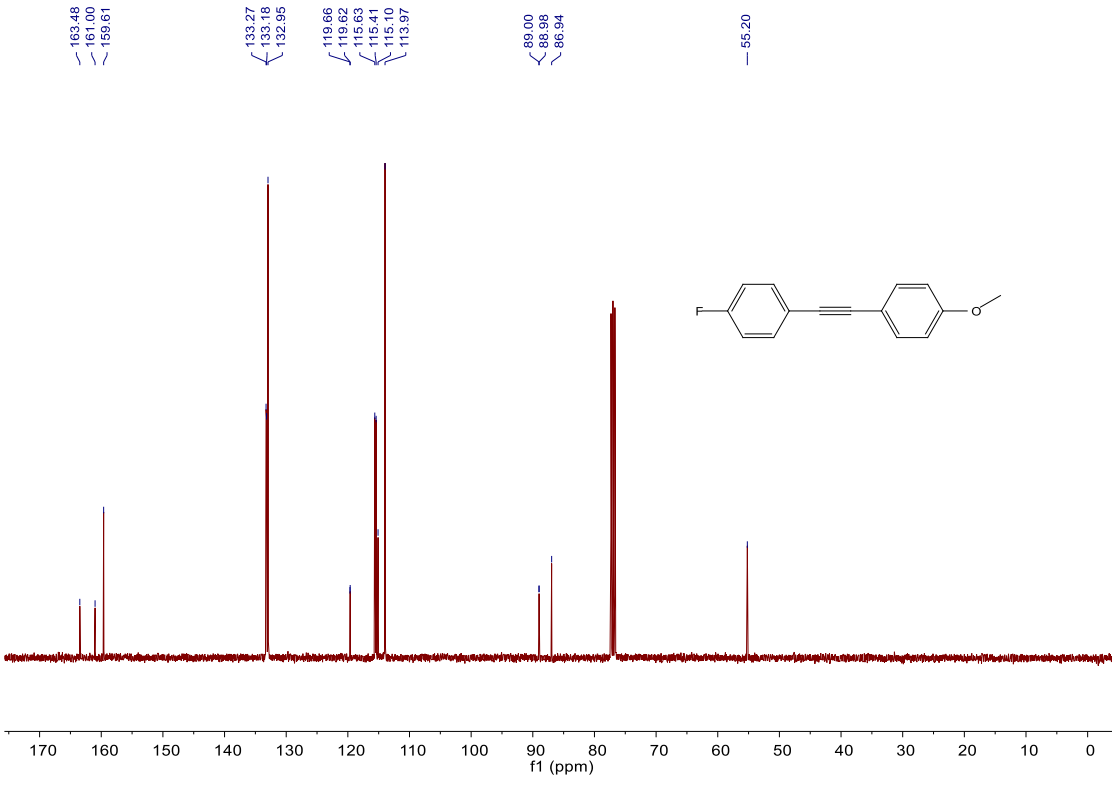
7.43
7.06
7.04
7.02
7.01
6.90
6.89
6.88
6.85
6.85
3.85
3.83
3.82
3.80
3.80
3.79
3.79
3.78
3.77
F
O
3.76
1.87
2.02
2.89
f1 (ppm)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161.00
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133.27
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119.62
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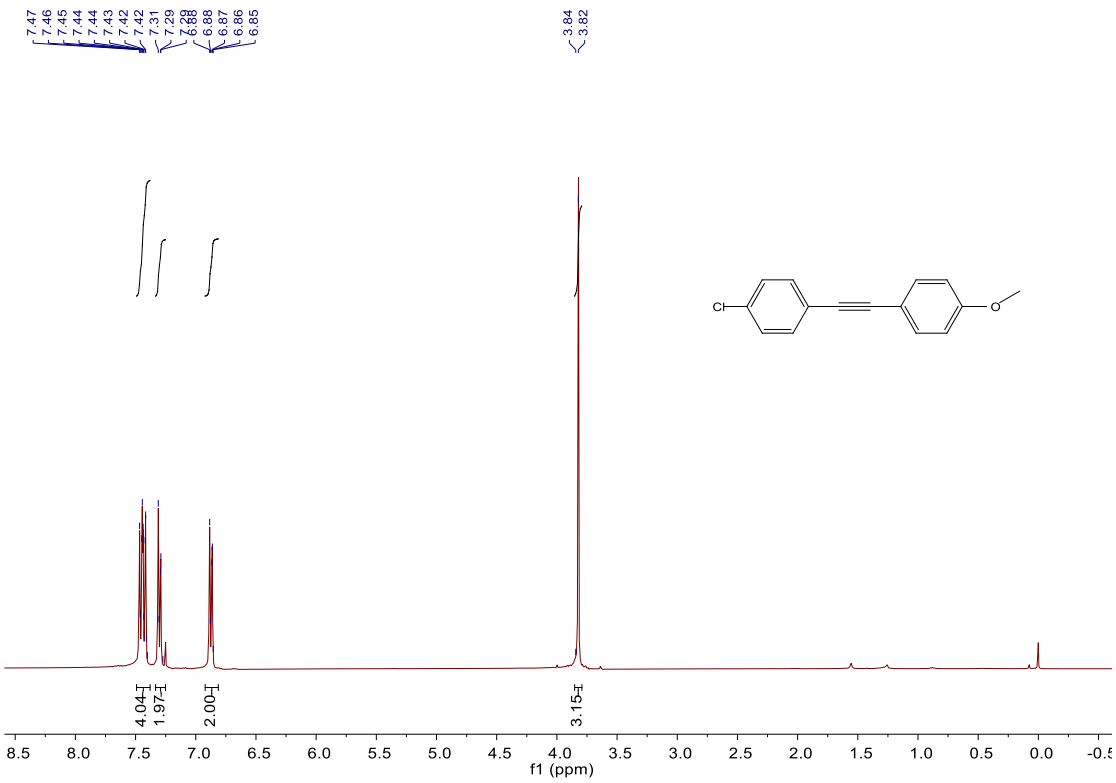
115.41
115.10
113.97
89.00
88.98
86.94
55.20
F
O
f1 (ppm)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7.43
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7.42
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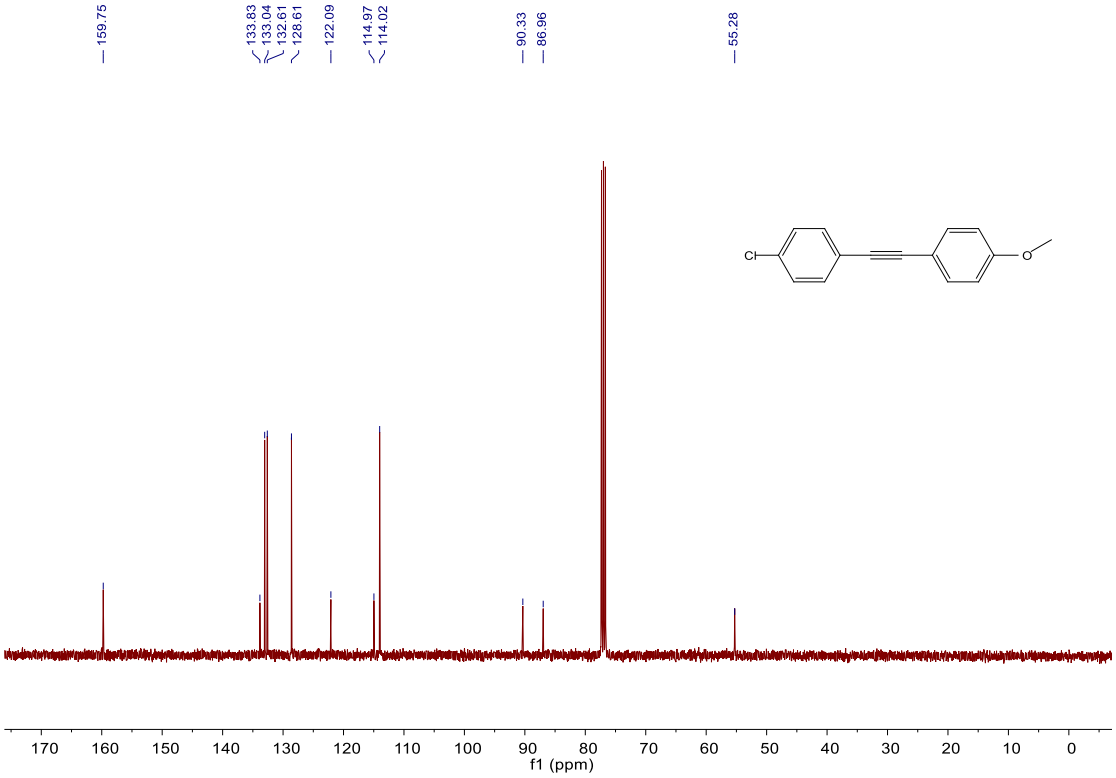
7.29
6.88
6.88
6.87
6.86
6.85
3.84
3.82
Cl
O
4.04
1.97
2.00
3.15
f1 (ppm)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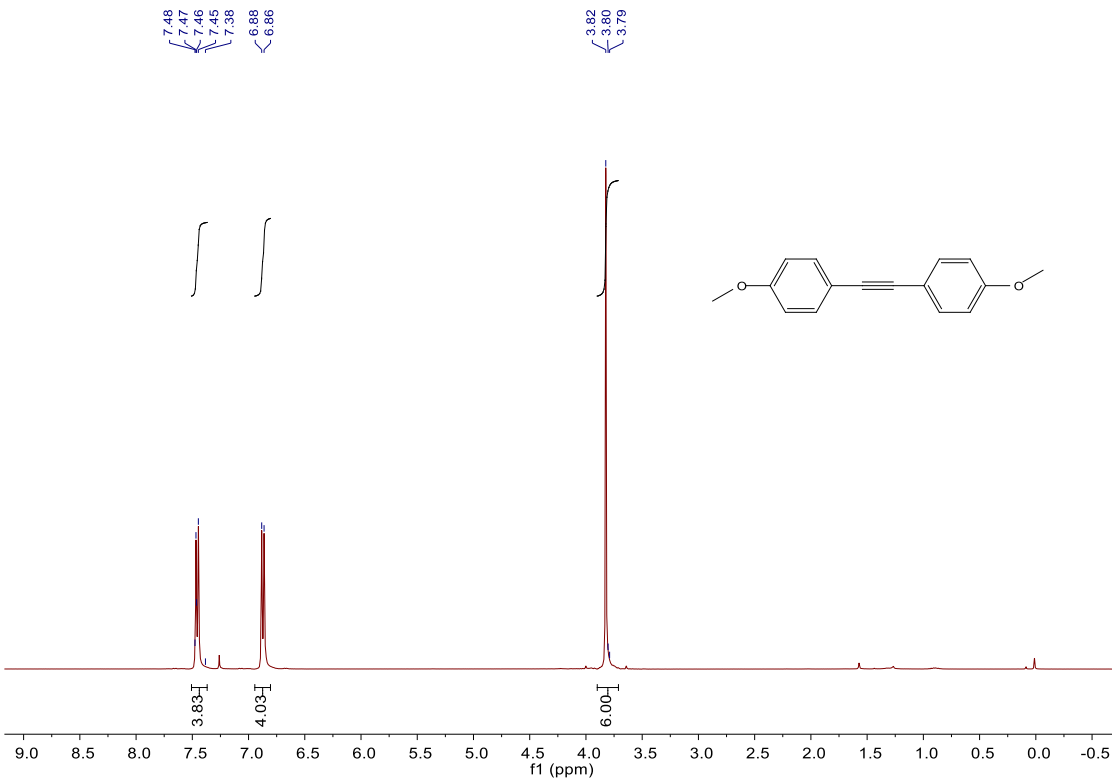
122.09
114.97
114.02
90.33
86.96
55.28
Cl
O
f1 (ppm)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7.47
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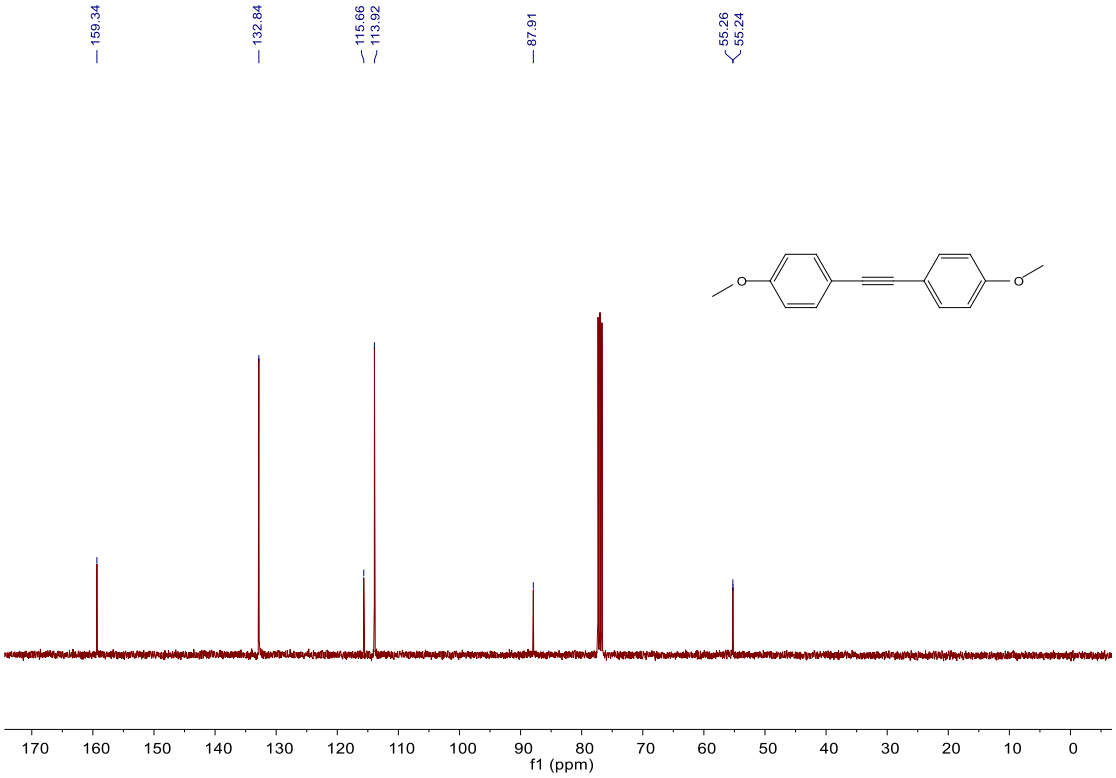
6.86
3.82
3.80
3.79
3.83
4.03
6.00
f1 (ppm)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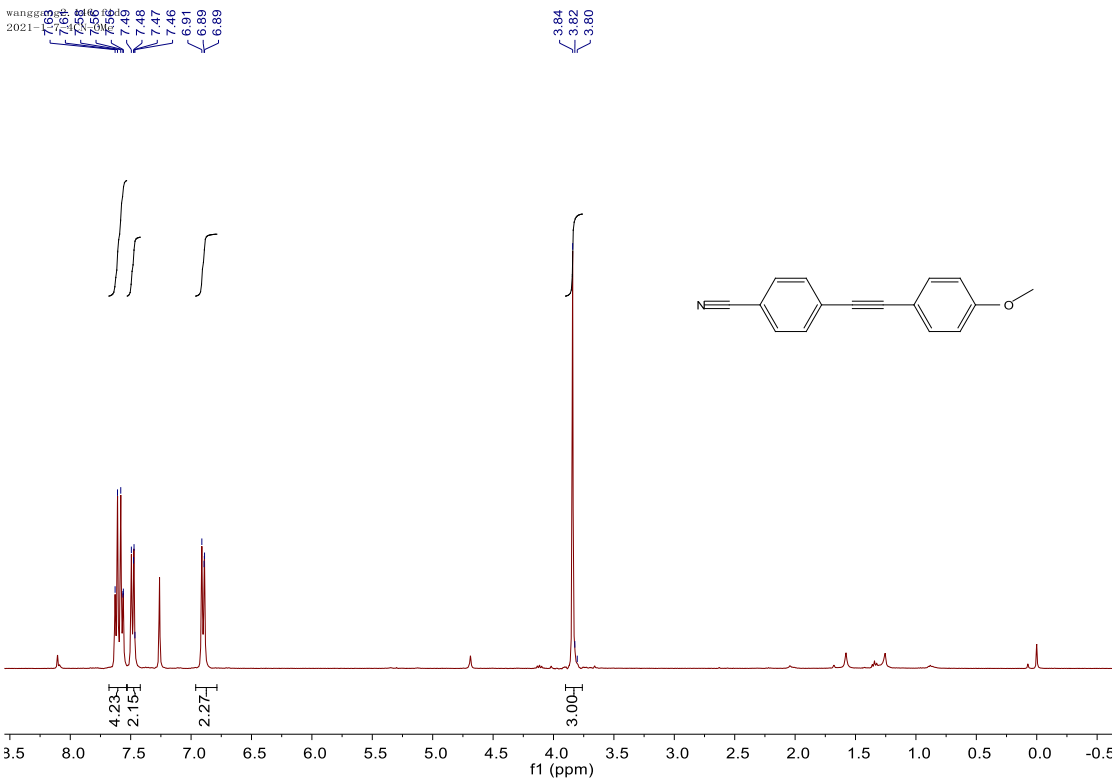
113.92
87.91
55.26
55.24
f1 (ppm)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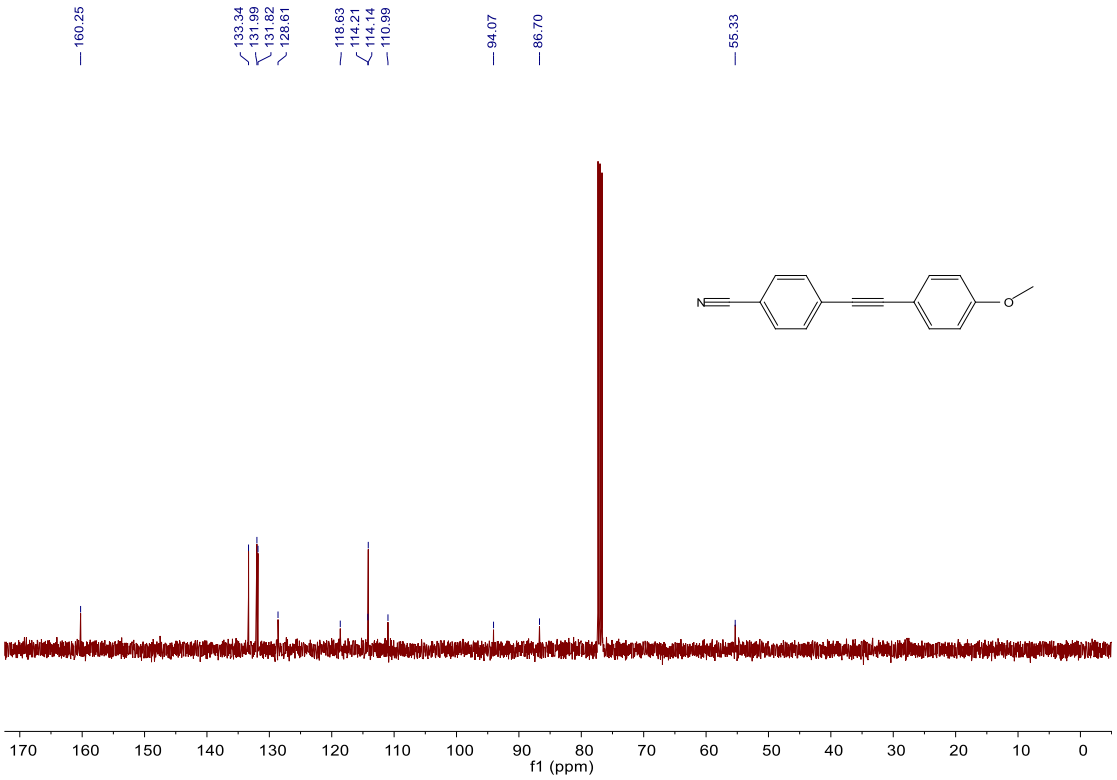
7.56
7.49
7.48
7.47
7.46
6.91
6.89
6.89
3.84
3.82
3.80
N
O
4.23
2.15
2.27
3.00
f1 (ppm)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114.14
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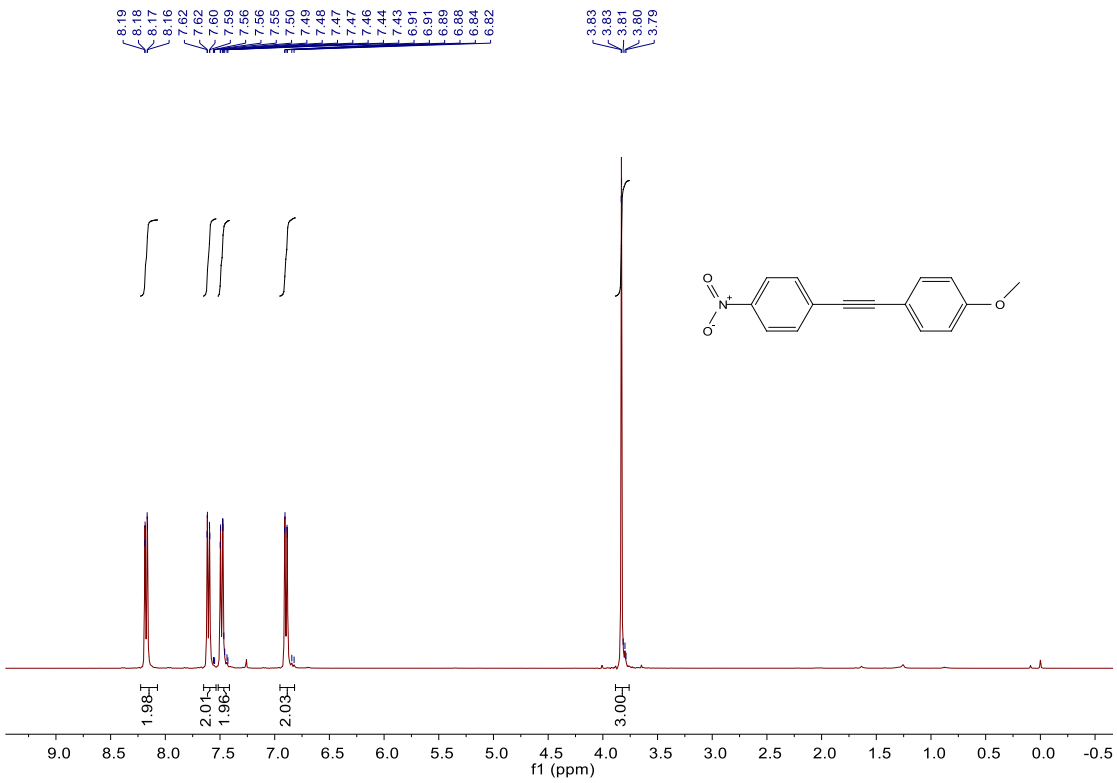
94.07
86.70
55.33
N
O
f1 (ppm)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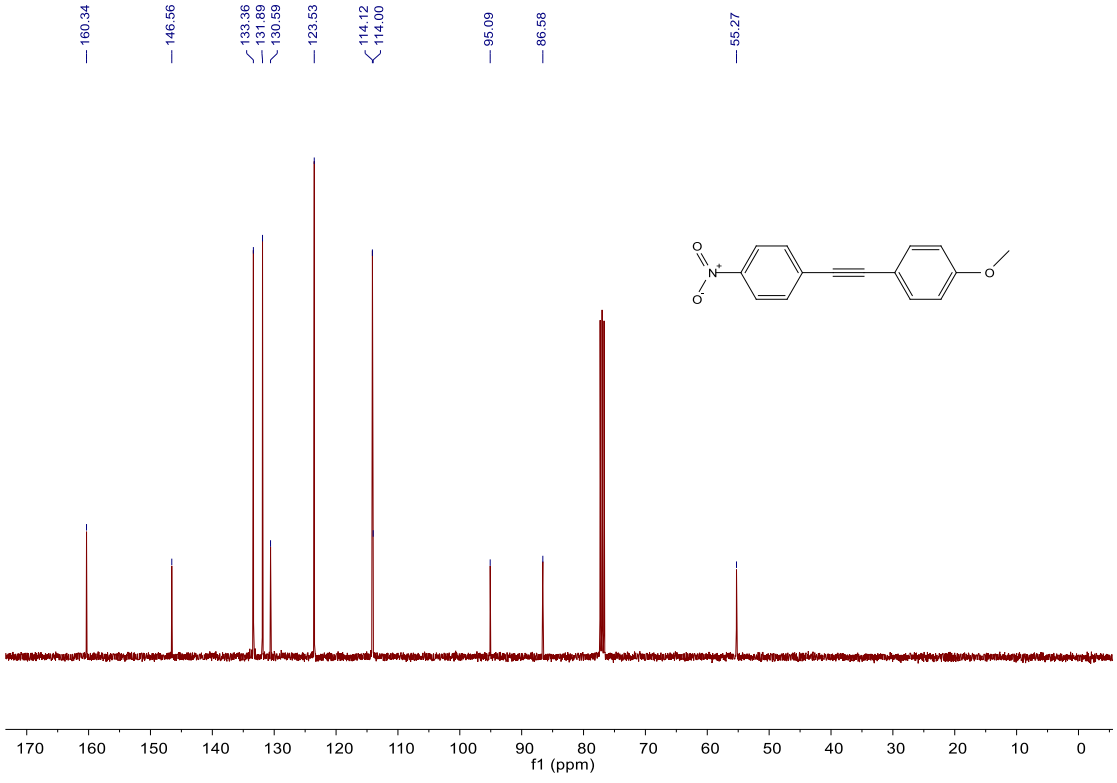
7.46
7.44
7.43
6.91
6.91
6.89
6.88
6.84
6.82
3.83
3.83
3.81
3.80
3.79
1.98
2.01
1.96
2.03
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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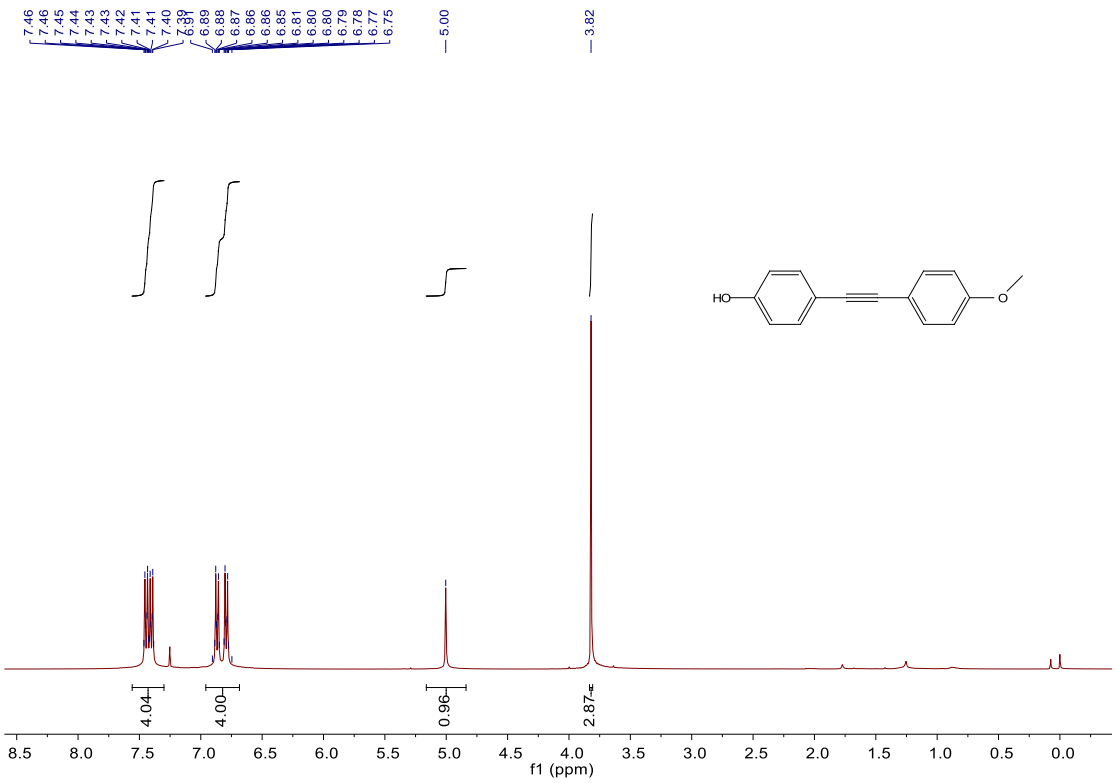
114.00
95.09
86.58
55.27
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.40
7.39
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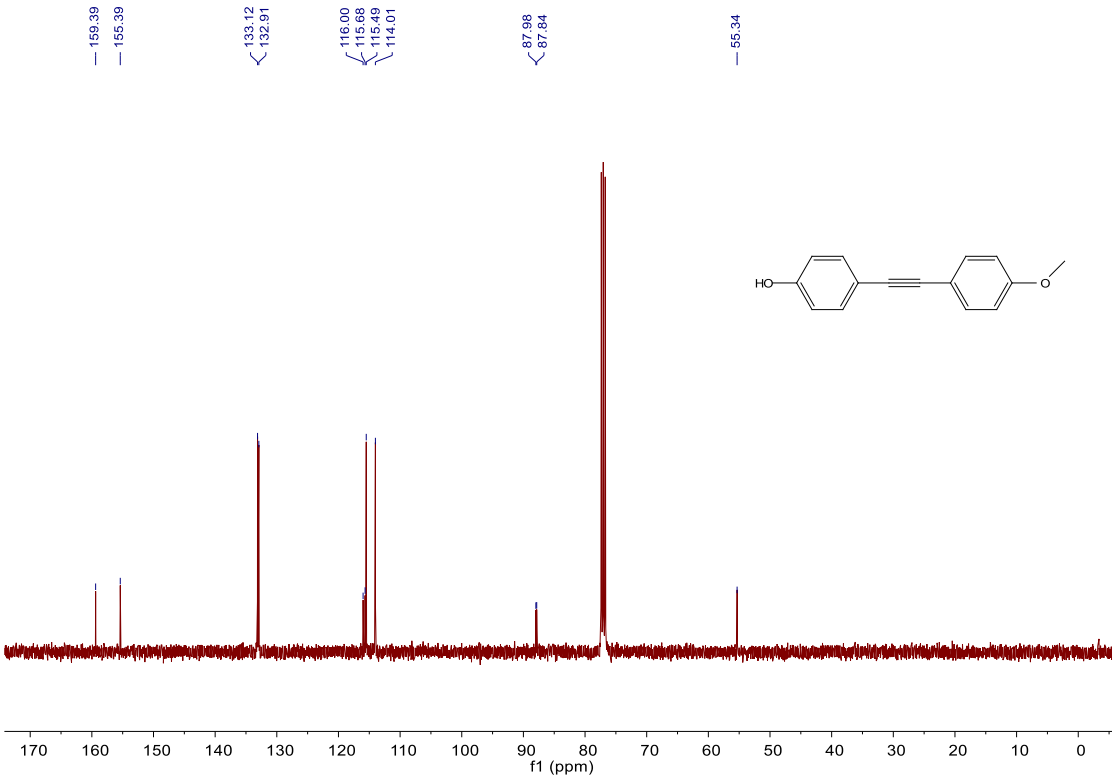
6.88
6.87
6.86
6.86
6.85
6.81
6.80
6.80
6.79
6.78
6.77
6.75
5.00
3.82
HO
O
4.04
4.00
0.96
2.87
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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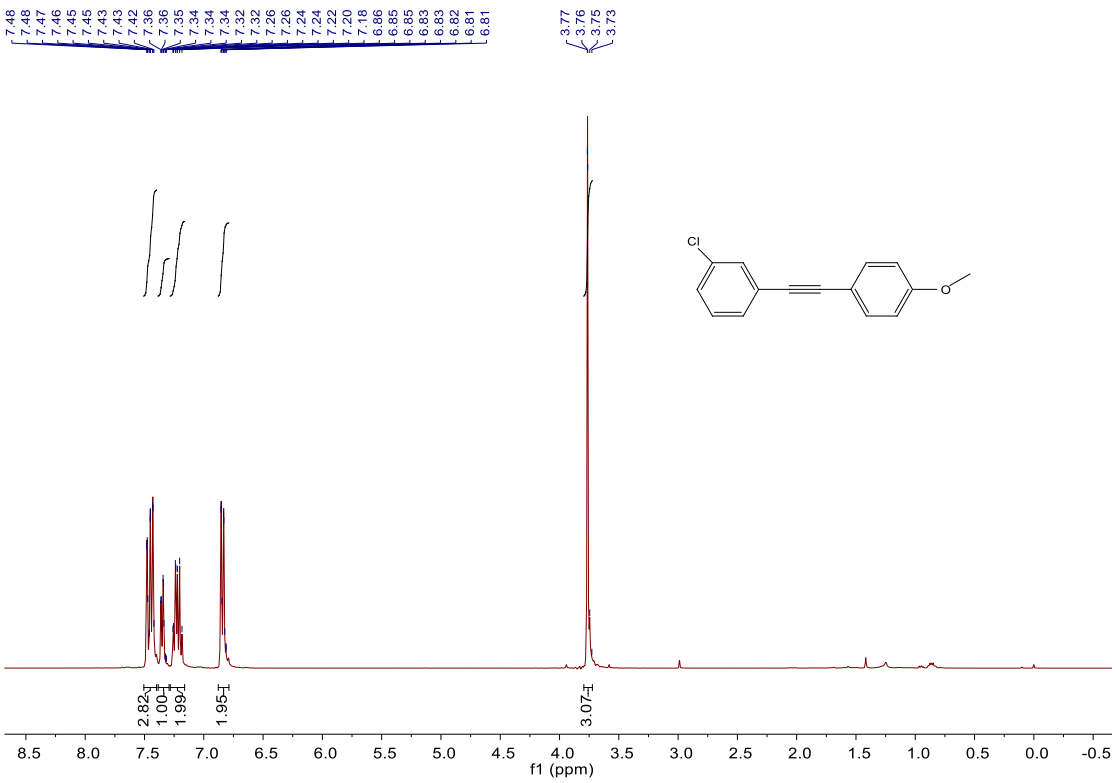
116.00
115.68
115.49
114.01
87.98
87.84
55.34
HO
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.48
7.47
7.46
7.45
7.45
7.43
7.43
7.42
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7.36
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7.34
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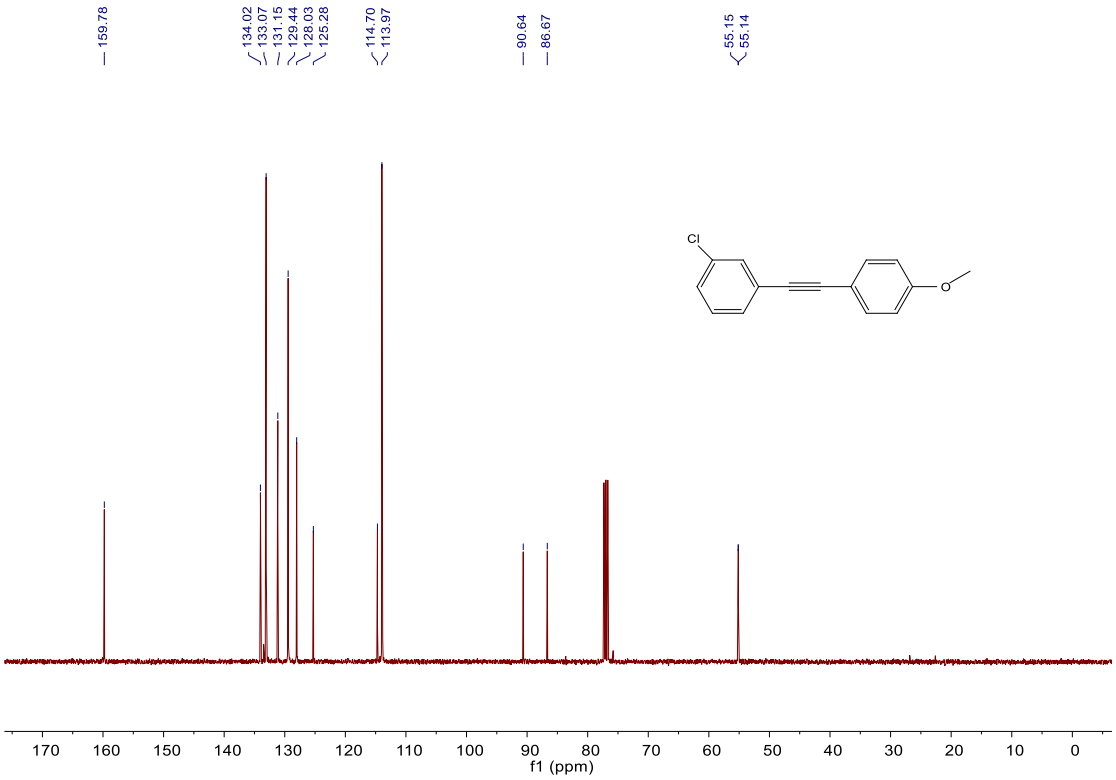
6.85
6.85
6.83
6.83
6.82
6.81
6.81
3.77
3.76
3.75
3.73
Cl
O
2.82
1.00
1.99
1.95
3.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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134.02
133.07
131.15
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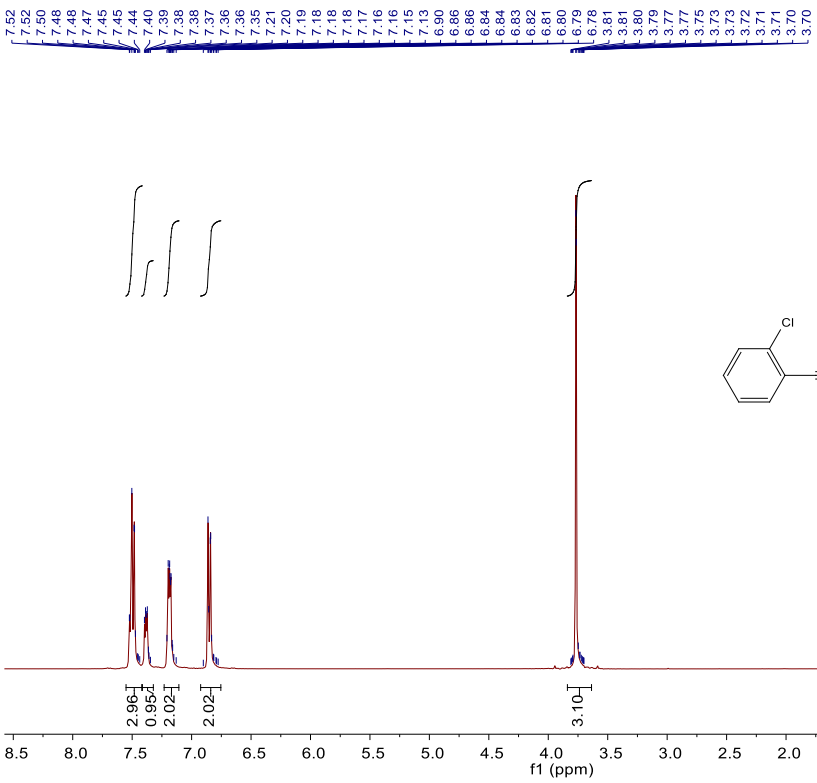
128.03
125.28
114.70
113.97
90.64
86.67
55.15
55.14
Cl
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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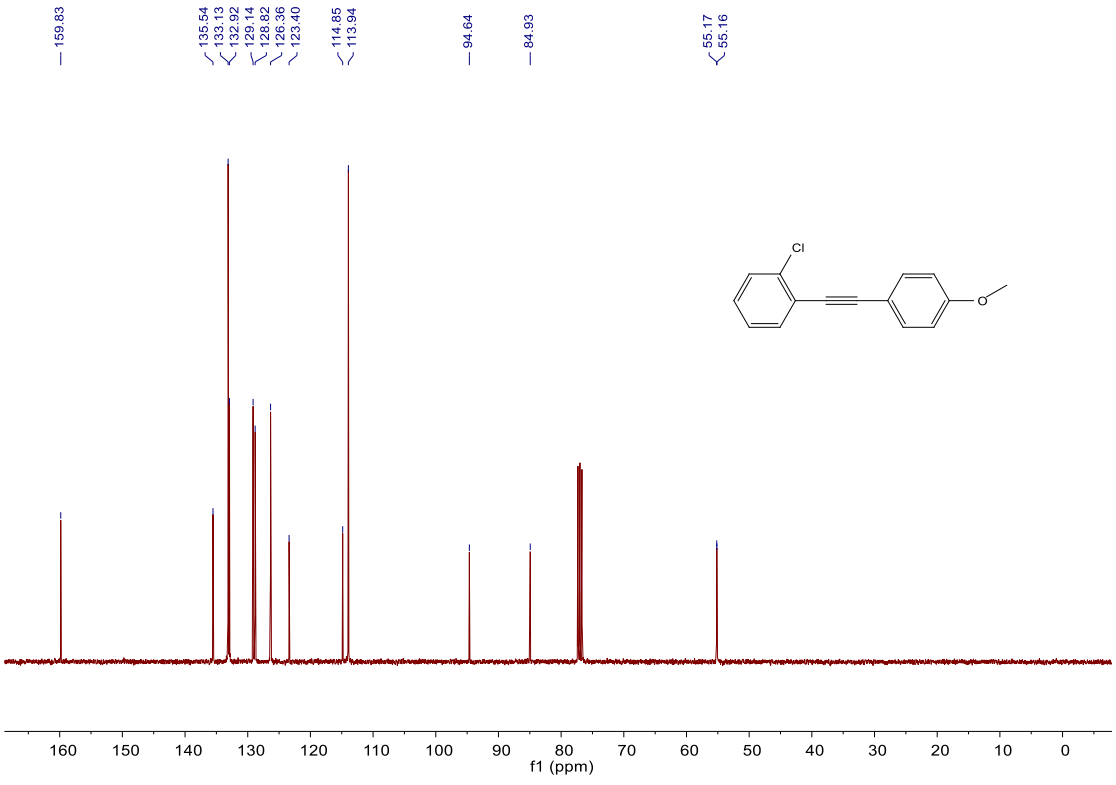
7.39
7.38
7.38
7.37
7.36
7.35
7.21
7.20
7.19
7.18
7.18
7.18
7.17
7.16
7.16
7.15
7.13
6.90
6.86
6.86
6.84
6.84
6.83
6.82
6.81
6.80
6.79
6.78
3.81
3.81
3.80
3.79
3.77
3.77
3.75
3.73
3.73
3.72
3.71
3.71
3.70
3.70
Cl
O
2.96
0.95
2.02
2.02
3.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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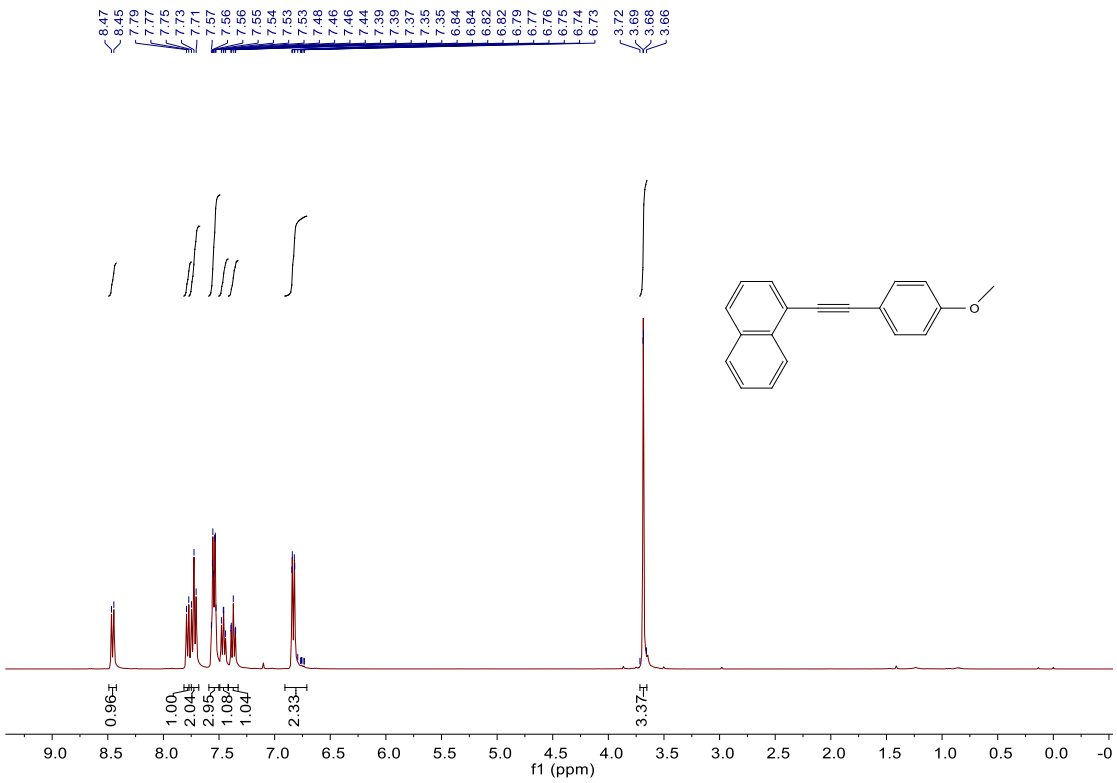
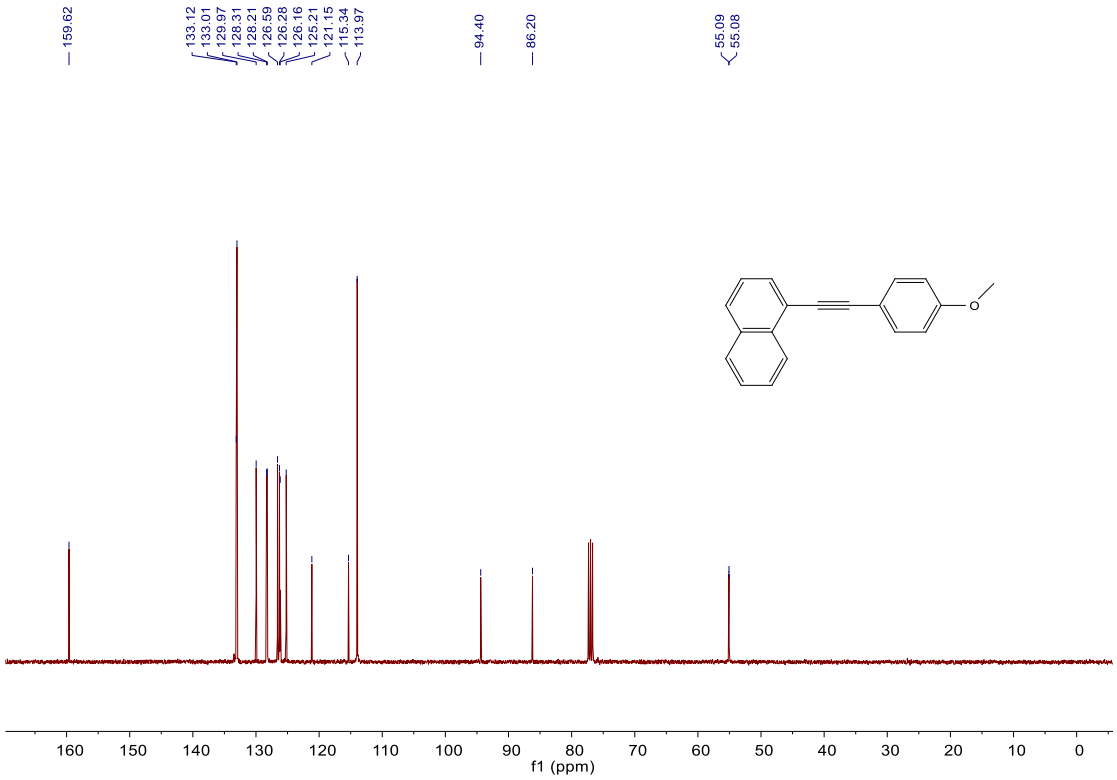
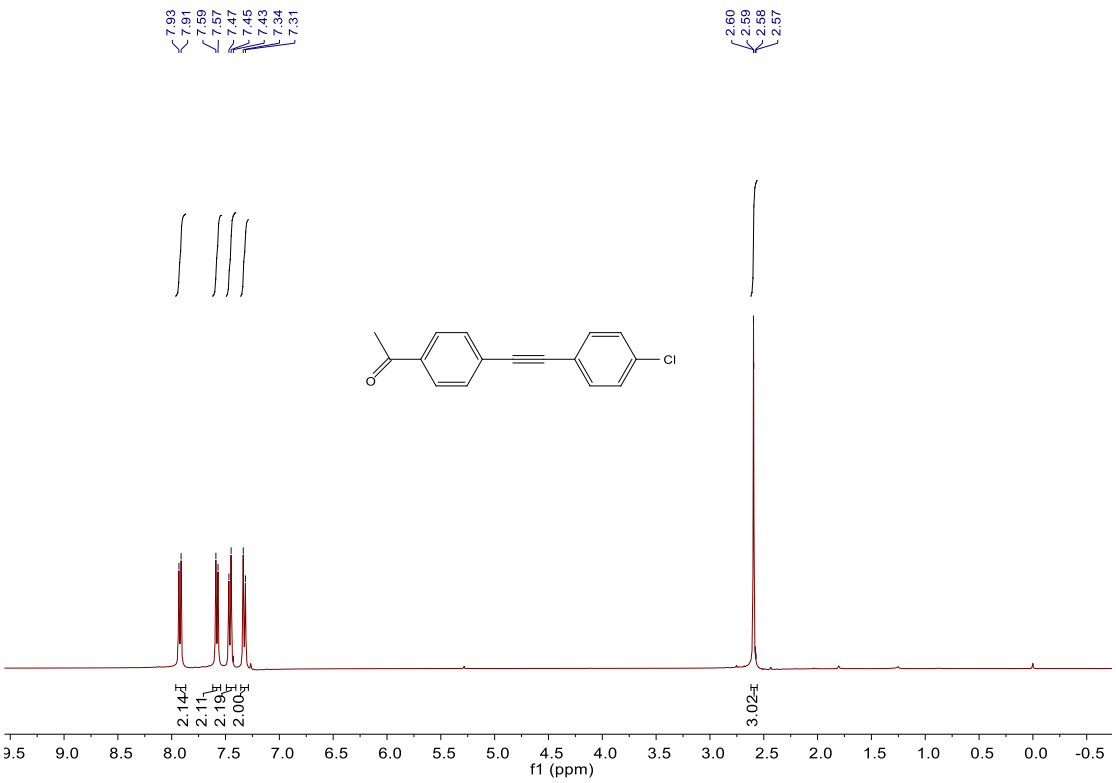
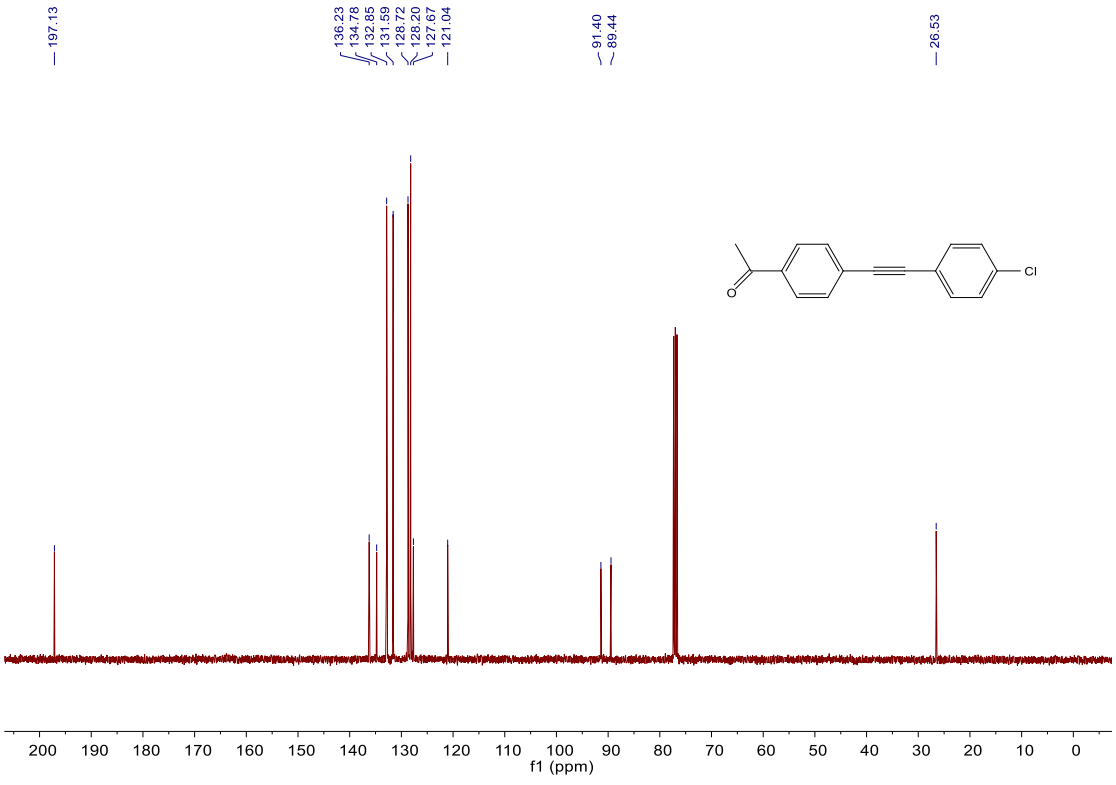
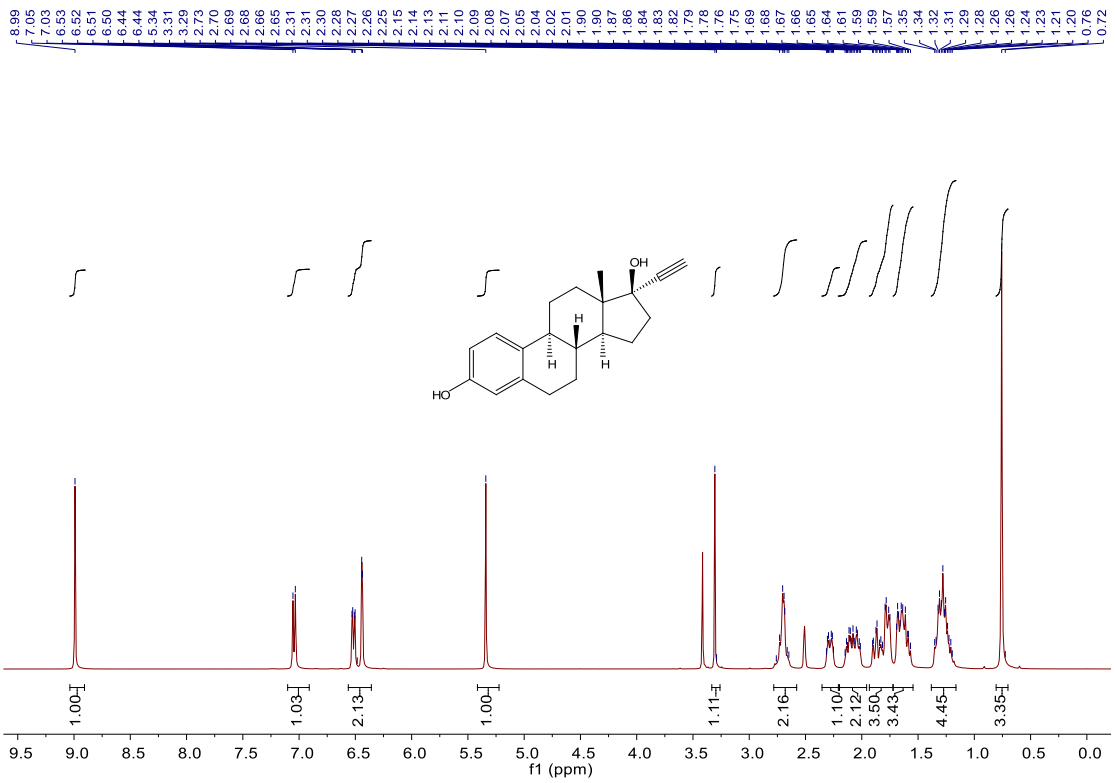
135.54
133.13
132.92
129.14
128.82
126.36
123.40
114.85
113.94
94.64
84.93
55.17
55.16
Cl
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

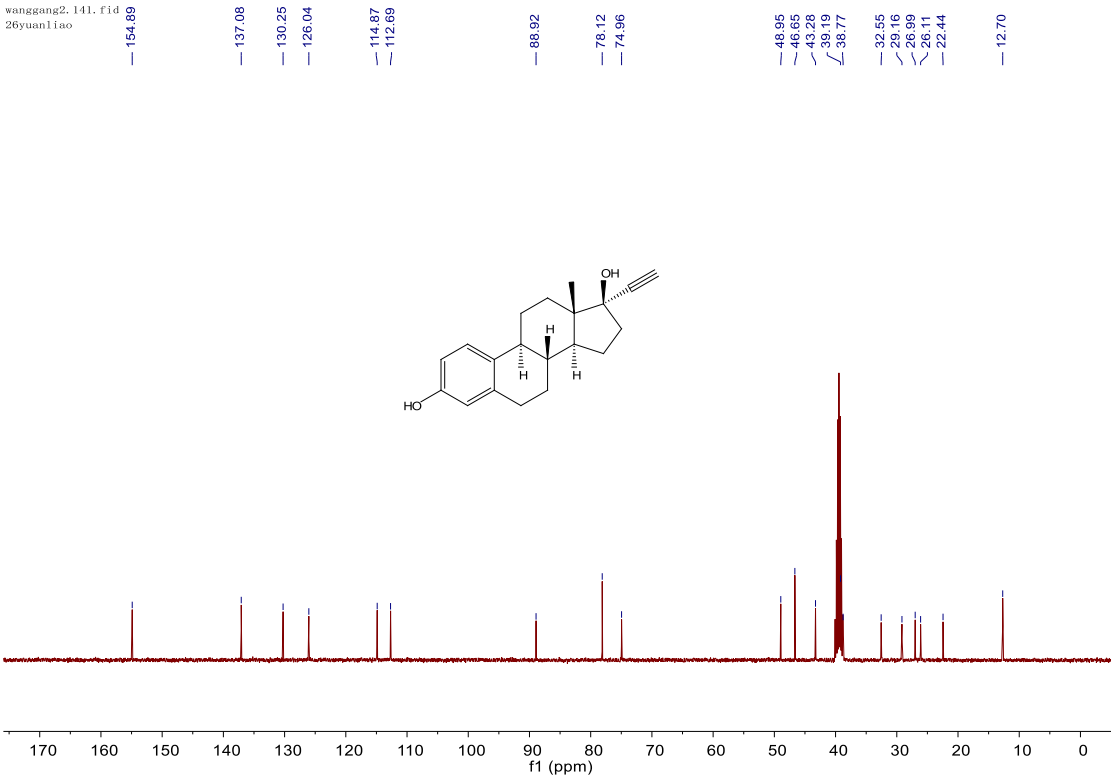

8.47
8.45
7.79
7.77
7.75
7.73
7.71
7.57
7.56
7.56
7.55
7.54
7.53
7.53
7.48
7.46
7.46
7.44
7.39
7.39
7.37
7.35
7.35
6.84
6.84
6.82
6.82
6.79
6.77
6.76
6.75
6.74
6.73
3.72
3.69
3.68
3.66
0.96
1.00
2.04
2.95
1.08
1.04
2.33
3.37
f1 (ppm)

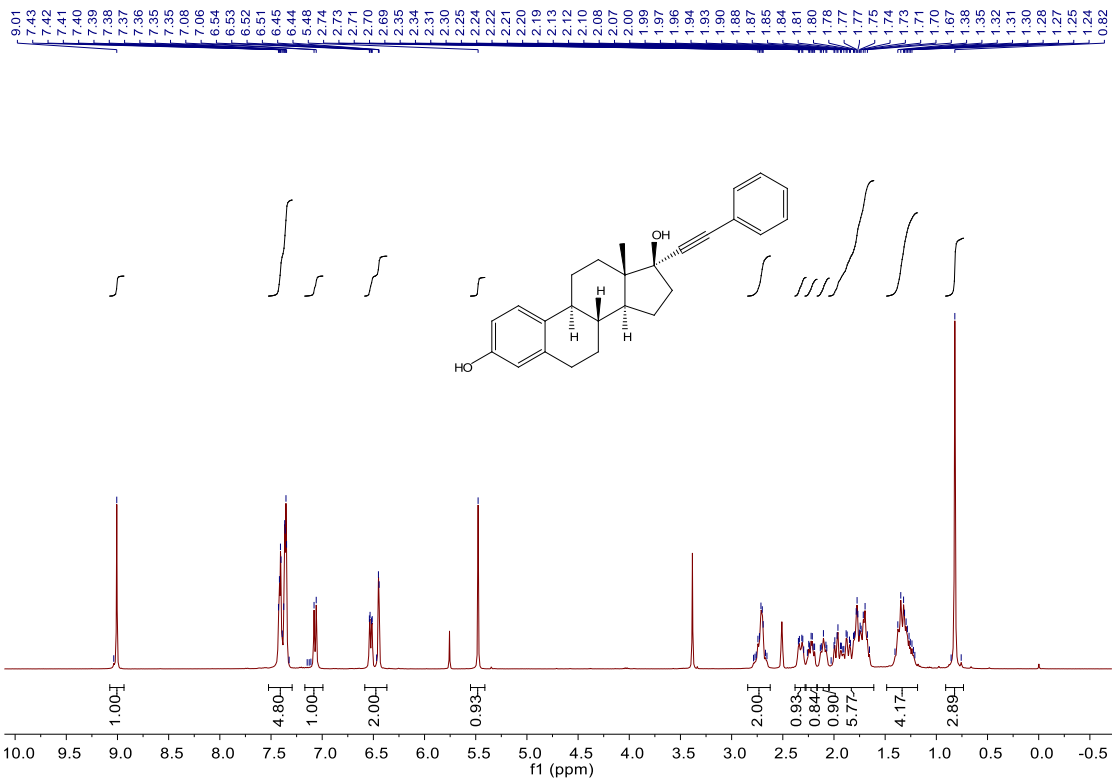

159.62
133.12
133.01
129.97
128.31
128.21
126.59
126.28
126.16
125.21
121.15
115.34
113.97
94.40
86.20
55.09
55.08
f1 (ppm)

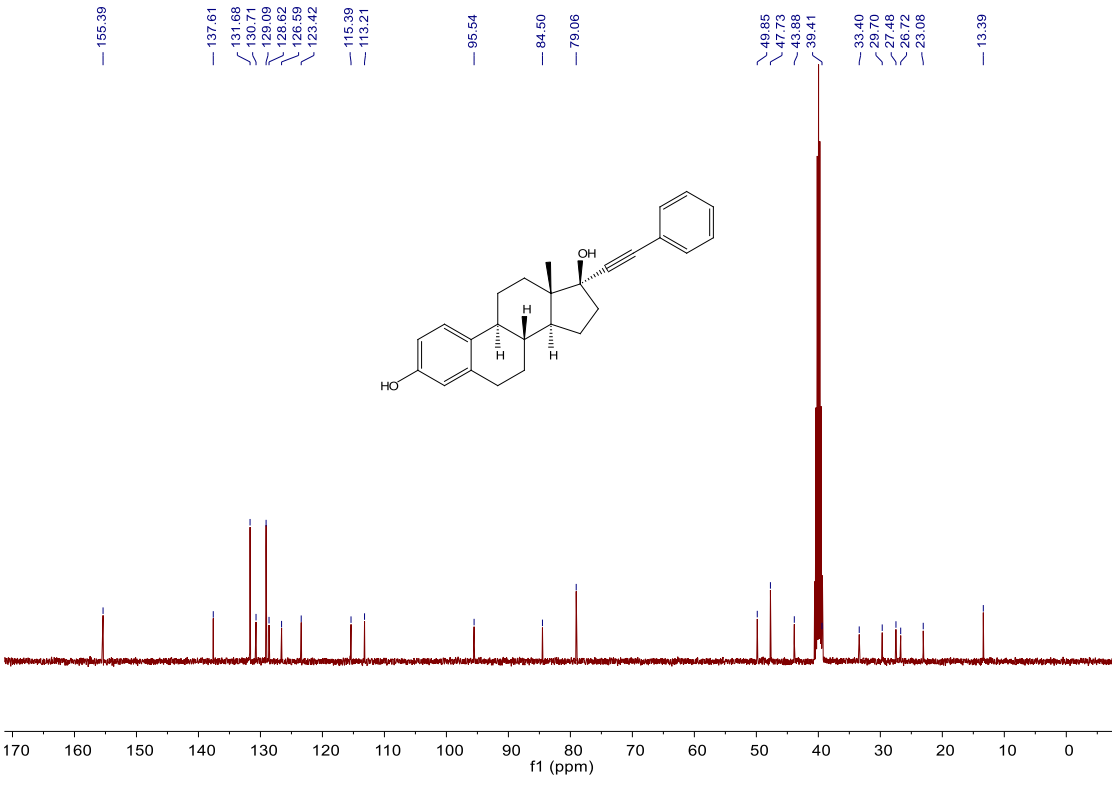

7.93
7.91
7.59
7.57
7.47
7.45
7.43
7.34
7.31
2.60
2.59
2.58
2.57
O
Cl
2.14
2.11
2.19
2.00
3.02
f1 (ppm)

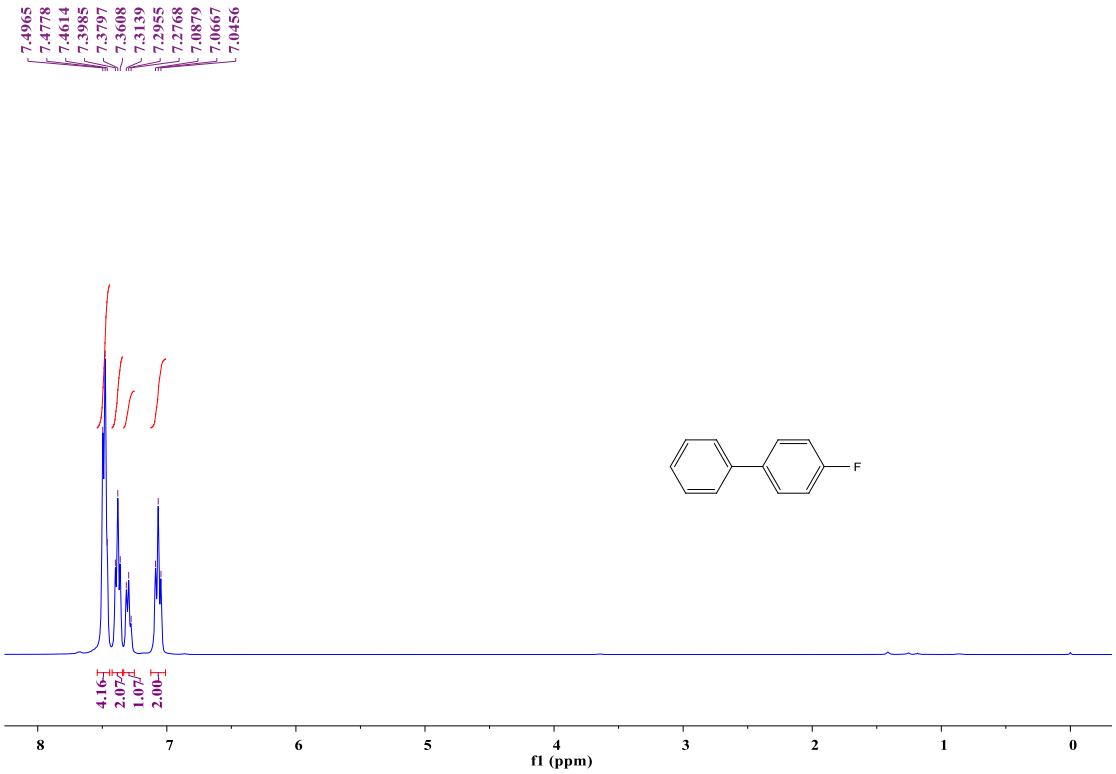

197.13
136.23
134.78
132.85
131.59
128.72
128.20
127.67
121.04
91.40
89.44
26.53
O
Cl
f1 (ppm)

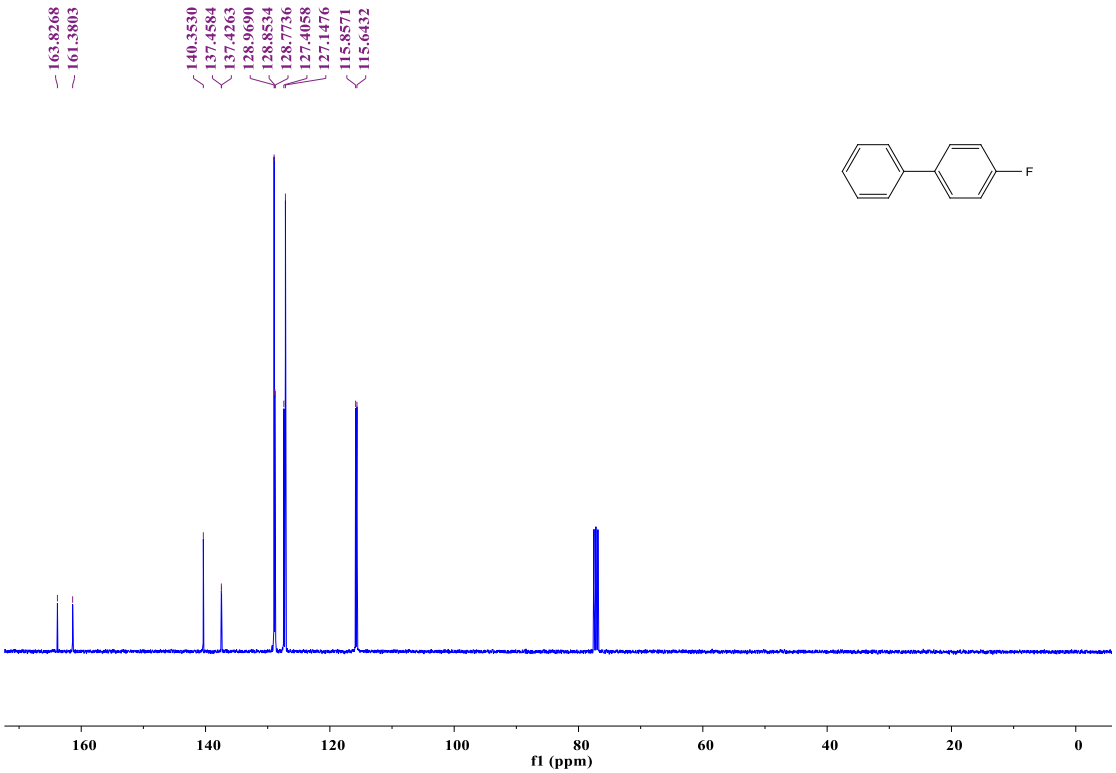

8.99 7.05 7.03 6.53 6.52 6.51 6.50 6.44 6.44 5.34 3.31 3.29 2.73 2.70 2.69 2.68 2.66 2.65 2.31 2.31 2.30 2.28 2.27 2.26 2.25 2.15 2.14 2.13 2.11 2.10 2.09 2.08 2.07 2.05 2.04 2.02 2.01 1.90 1.90 1.87 1.86 1.84 1.83 1.82 1.79 1.78 1.76 1.75 1.69 1.68 1.67 1.66 1.65 1.64 1.61 1.59 1.59 1.57 1.35 1.34 1.32 1.31 1.29 1.28 1.26 1.26 1.24 1.23 1.21 1.20 0.76 0.72
OH
H
H
H
HO
1.00 1.03 2.13 1.00 1.11 2.16 1.10 2.12 3.50 3.43 4.45 3.35
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

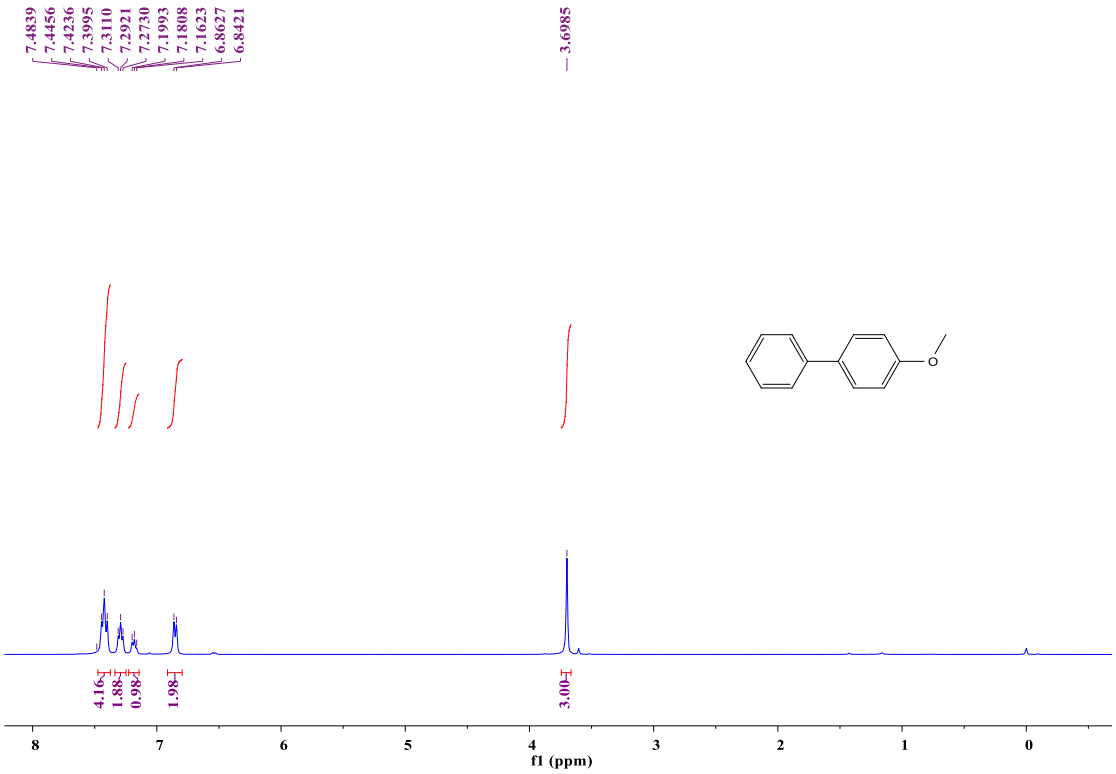

wanggang2.141.fid
26yuanliao
154.89 137.08 130.25 126.04 114.87 112.69 88.92 78.12 74.96 48.95 46.65 43.28 39.19 38.77 32.55 29.16 26.99 26.11 22.44 12.70
OH
H
H
H
HO
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


9.01 7.43 7.42 7.41 7.40 7.39 7.38 7.37 7.36 7.35 7.35 7.08 7.06 6.54 6.53 6.52 6.51 6.45 6.44 5.48 2.74 2.73 2.71 2.70 2.69 2.35 2.34 2.31 2.30 2.25 2.24 2.22 2.21 2.20 2.19 2.13 2.12 2.10 2.08 2.07 2.00 1.99 1.97 1.96 1.94 1.93 1.90 1.88 1.87 1.85 1.84 1.81 1.80 1.78 1.77 1.77 1.75 1.74 1.73 1.71 1.70 1.67 1.38 1.35 1.32 1.31 1.30 1.28 1.27 1.25 1.24 0.82
OH
H
H
H
HO
1.00 4.80 1.00 2.00 0.93 2.00 0.93 0.84 0.90 5.77 4.17 2.89
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


155.39 137.61 131.68 130.71 129.09 128.62 126.59 123.42 115.39 113.21 95.54 84.50 79.06 49.85 47.73 43.88 39.41 33.40 29.70 27.48 26.72 23.08 13.39
OH
H
H
H
HO
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.4965
7.4778
7.4614
7.3985
7.3797
7.3608
7.3139
7.2955
7.2768
7.0879
7.0667
7.0456
F
4.16
2.07
1.07
2.00
8
7
6
5
4
3
2
1
0
f1 (ppm)


163.8268
161.3803
140.3530
137.4584
137.4263
128.9690
128.8534
128.7736
127.4058
127.1476
115.8571
115.6432
F
160
140
120
100
80
60
40
20
0
f1 (ppm)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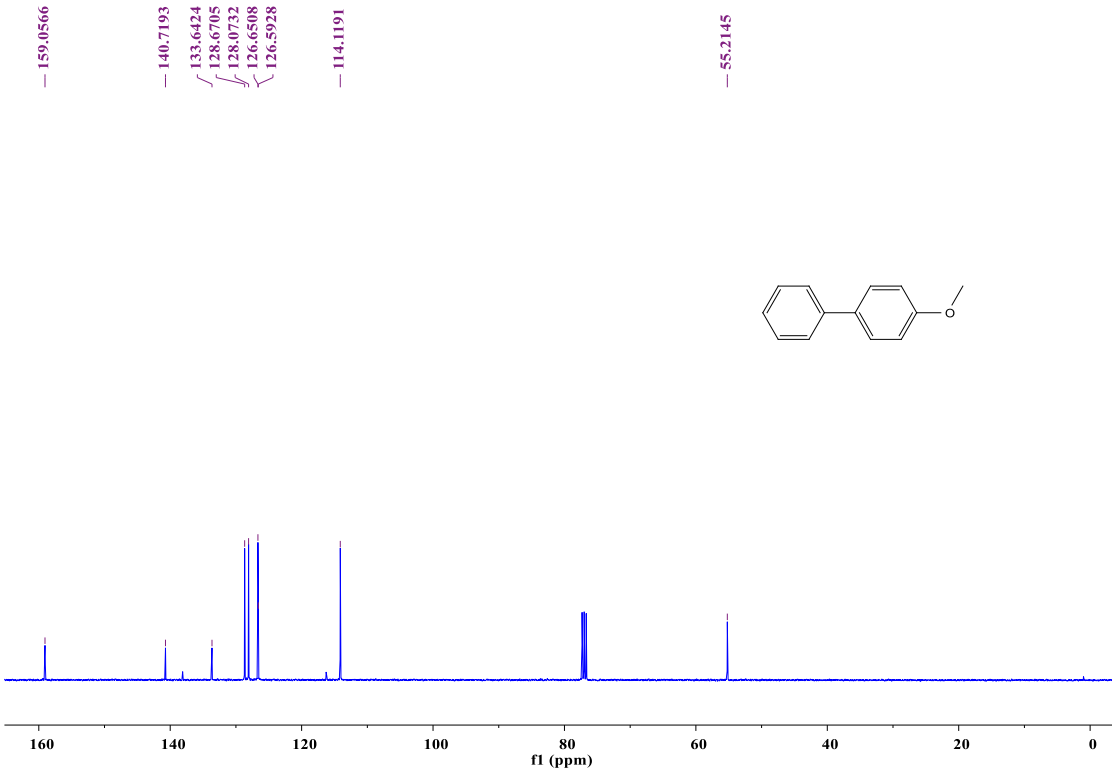
7.4456
7.4236
7.3995
7.3110
7.2921
7.2730
7.1993
7.1808
7.1623
6.8627
6.8421
3.6985
4.16
1.88
0.98
1.98
3.00
8
7
6
5
4
3
2
1
0
f1 (ppm)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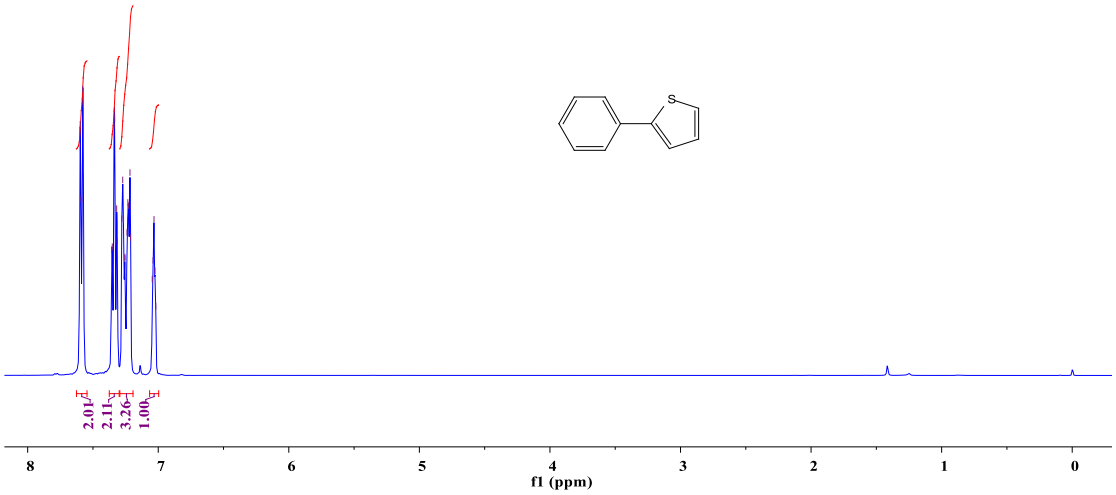
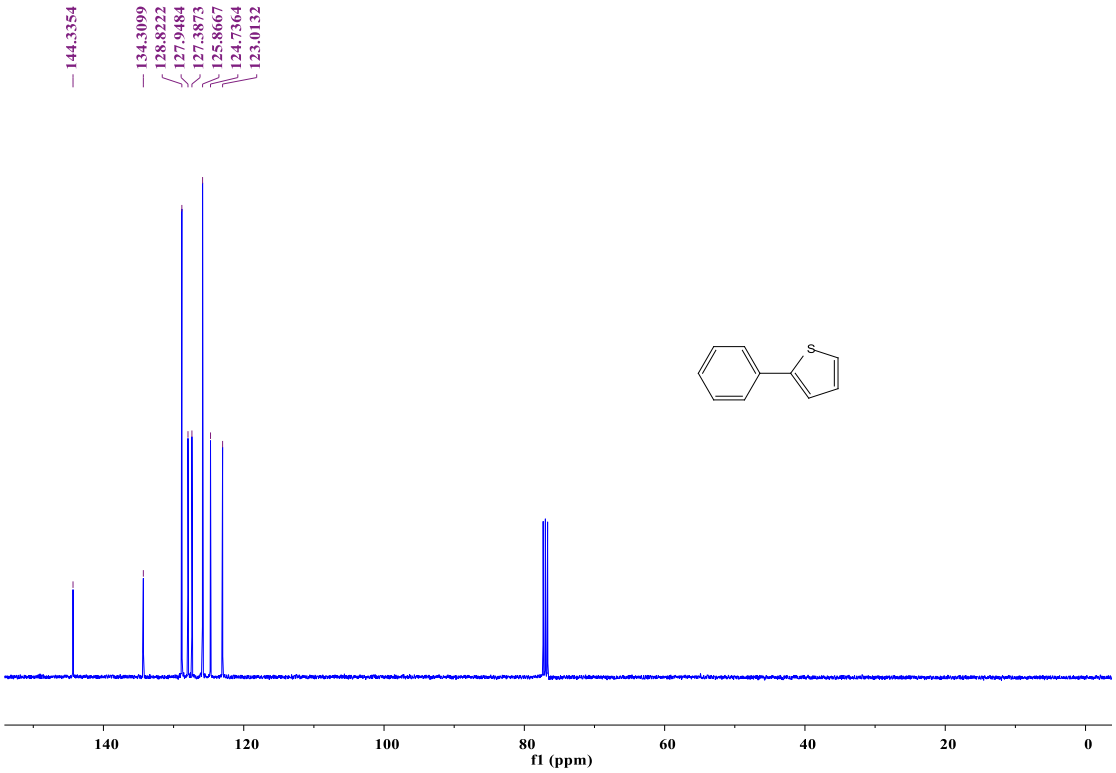
133.6424
128.6705
128.0732
126.6508
126.5928
114.1191
55.2145
160
140
120
100
80
60
40
20
0
f1 (ppm)

7.5976
7.5916
7.5786
7.5729
7.3569
7.3519
7.3384
7.3335
7.3183
7.3133
7.2792
7.2721
7.2656
7.2557
7.2551
7.2392
7.2327
7.2272
7.2165
7.2115
7.0459
7.0393
7.0325
7.0249
7.0187


S
2.01
2.11
3.26
1.00
8
7
6
5
4
3
2
1
0
f1 (ppm)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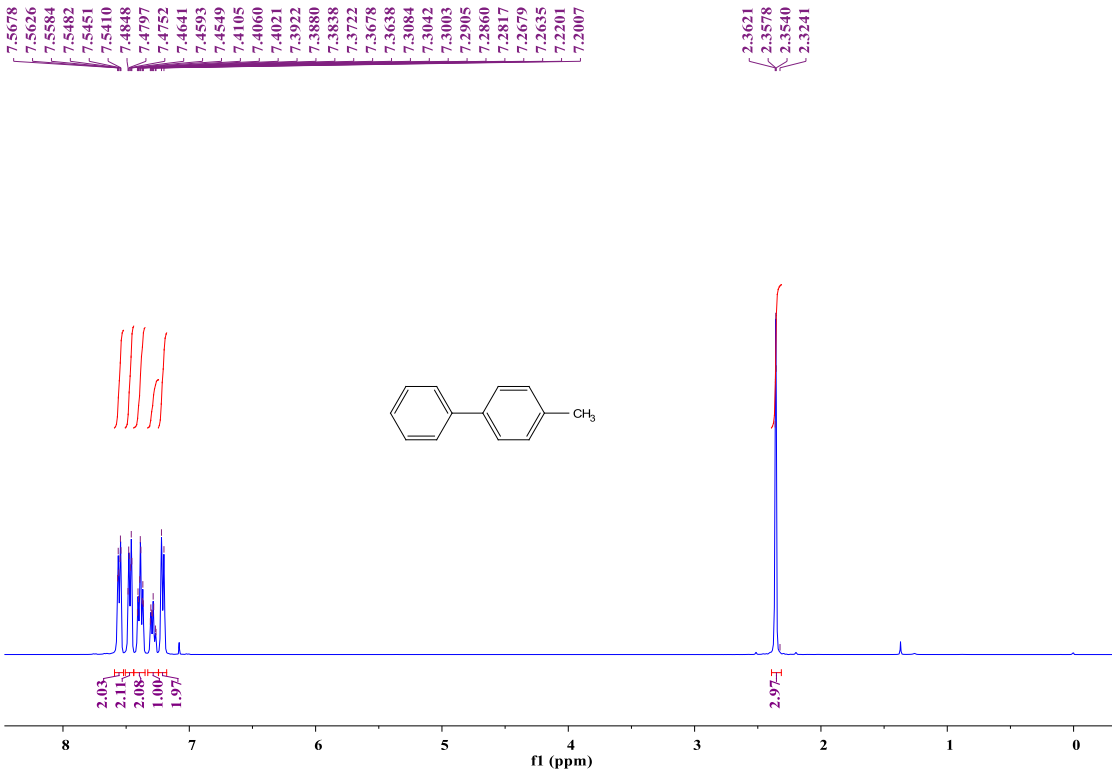
134.3099
128.8222
127.9484
127.3873
125.8667
124.7364
123.0132
S
140
120
100
80
60
40
20
0
f1 (ppm)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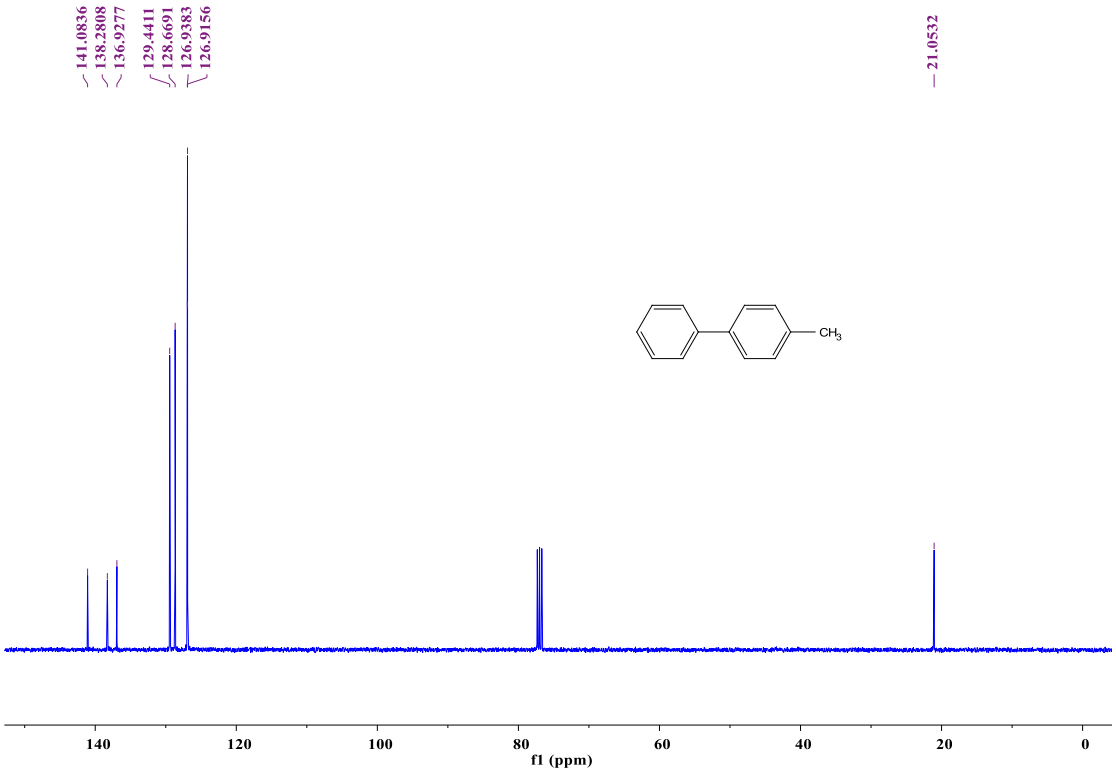
7.5584
7.5482
7.5451
7.5410
7.4848
7.4797
7.4752
7.4641
7.4593
7.4549
7.4105
7.4060
7.4021
7.3922
7.3880
7.3838
7.3722
7.3678
7.3638
7.3084
7.3042
7.3003
7.2905
7.2860
7.2817
7.2679
7.2635
7.2201
7.2007
2.3621
2.3578
2.3540
2.3241
CH3
2.03
2.11
2.08
1.00
1.97
2.97
8
7
6
5
4
3
2
1
0
f1 (ppm)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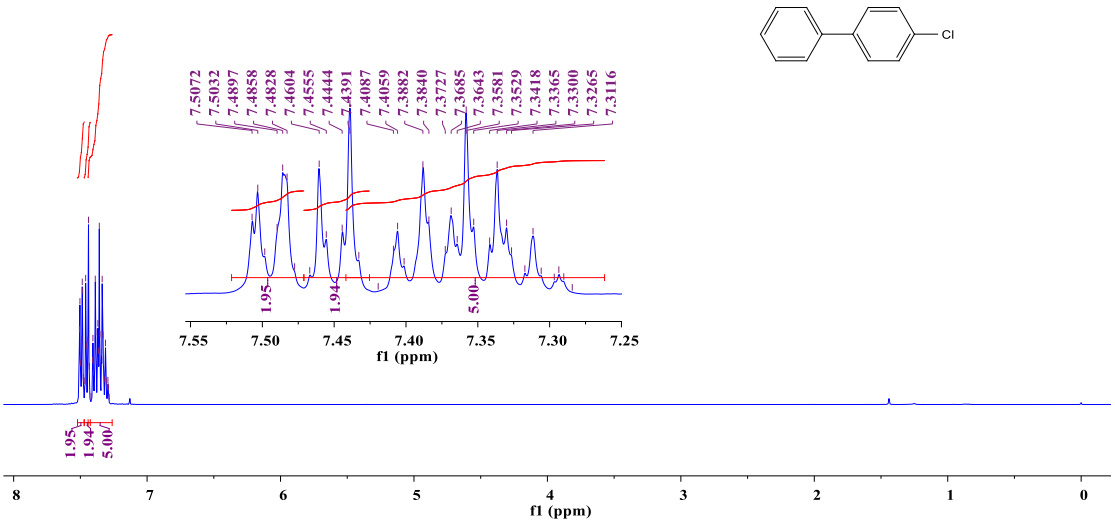
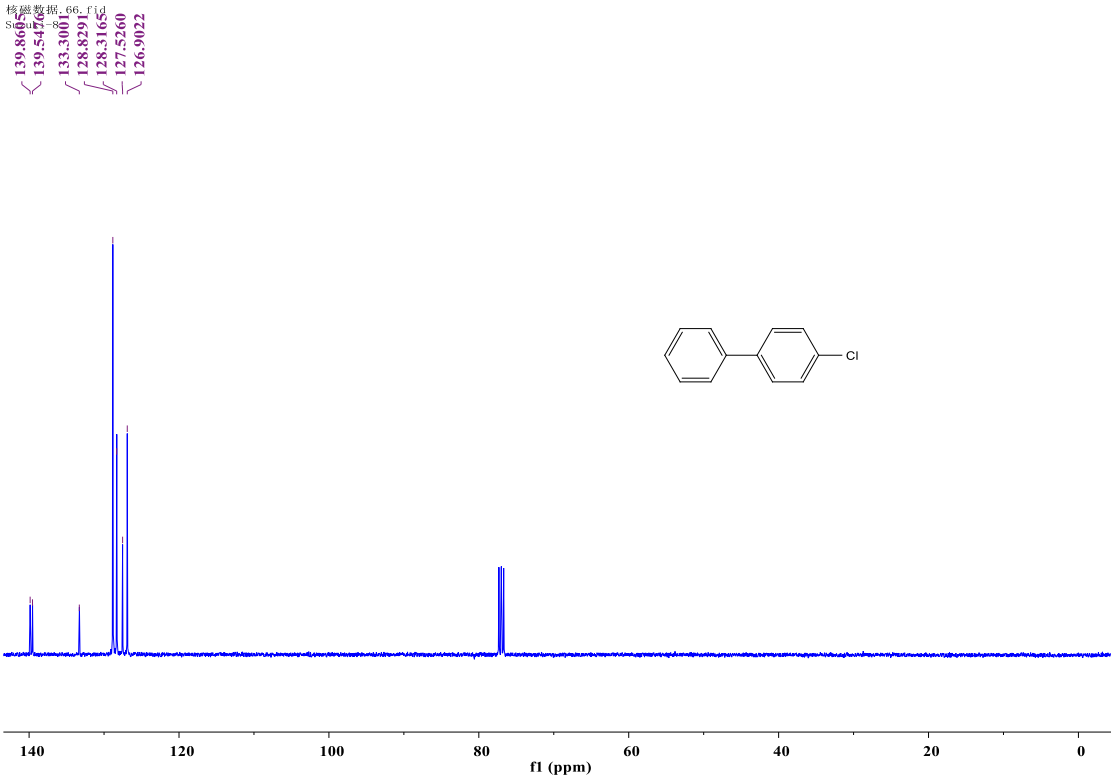
136.9277
129.4411
128.6691
126.9383
126.9156
21.0532
CH3
140
120
100
80
60
40
20
0
f1 (ppm)

7.5072
7.5032
7.4983
7.4897
7.4858
7.4828
7.4775
7.4670
7.4604
7.4555
7.4444
7.4391
7.4328
7.4193
7.4087
7.4059
7.4013
7.3882
7.3840
7.3727
7.3685
7.3643
7.3581
7.3529
7.3418
7.3365
7.3300
7.3265
7.3172
7.3116
7.3059
7.2968
7.2936
7.2901
7.2842


Cl
7.5072
7.5032
7.4897
7.4858
7.4828
7.4604
7.4555
7.4444
7.4391
7.4087
7.4059
7.3882
7.3840
7.3727
7.3685
7.3643
7.3581
7.3529
7.3418
7.3365
7.3300
7.3265
7.3116
1.95
1.94
5.00
7.55
7.50
7.45
7.40
7.35
7.30
7.25
f1 (ppm)
8
7
6
5
4
3
2
1
0
f1 (ppm)


核磁数据.66.fid
139.8661
139.5474
133.3001
128.8291
128.3165
127.5260
126.9022
Cl
140
120
100
80
60
40
20
0
f1 (ppm)