Supplementary Information

Visible light-mediated gold-catalyzed alkynylative cyclization of allenoates with iodoalkynes for the synthesis of β-alkynyl-γ-butenolides

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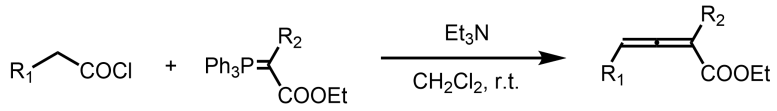
I. General Information

All reactions involving air sensitive reagents or intermediates were carried out in pre-heated glassware under an argon atmosphere using standard Schlenk techniques. All solvents and chemicals were used as received from suppliers (Adamas-beta, Leyan, Energy Chemical, Bidepharm). All other gold complexes were commercially available in Bidepharm and used as received. Acriflavine (CAS: 8048-52-0) was purchased from Aladdin. Unless stated otherwise, all reactions were carried out under argon. Column chromatography was performed using silica gel (200-300 mesh) or thin layer chromatography was performed using silica gel (GF254). ^{1}H NMR spectra were recorded using a Bruker 400 MHz instrument with tetramethylsilane (TMS) as an internal standard. ^{13}C NMR spectra were obtained at 101 MHz and referenced to the internal solvent signals. ^{19}F NMR spectra were obtained at 376 MHz. ^{31}P NMR spectra were obtained at 162 MHz. Abbreviations used in the NMR follow-up experiments: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. High resolution mass spectra (HRMS) were performed on a VG Autospec-3000 spectrometer TOF MS (100-1500) and LCMS-IT-TOF mass spectrometer (Shimadzu, Ky oto, Japan). Column chromatography was performed with silica gel (200-300 mesh) with petroleum ether and ethyl acetate as eluents. Commercially available reagents were used without further purification unless indicated otherwise.

II. Substrate Synthesis

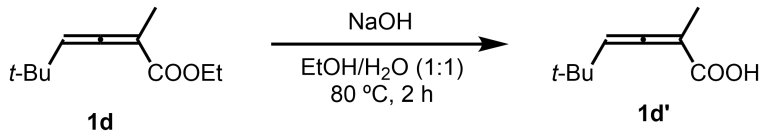
1. Synthesis of allenoates derivatives 1

General Procedure **1** (**GP1**): Synthesis of **1a**-**1h**.[1,2] **1d'**.[10b]



S1 **1**

A 25 mL, three-necked, round-bottomed flask is equipped with a nitrogen inlet, a 5 mL, pressure-equalizing dropping funnel fitted with a gas outlet, and a Teflon-coated magnetic stirring bar. The flask is charged with 8.0 mL of dichloromethane and 2.0 g (5.5 mmol) of ethyl (triphenylphosphoranylidene) acetate and flushed with nitrogen. The yellow solution is stirred at room temperature as 1.1 mL (8.0 mmol) of triethylamine is added. After 5 min, octanoyl chloride (0.8 g, 5.0 mmol) in 2.0 mL of dichloromethane is added dropwise to the vigorously stirred solution. Stirring is continued for an additional 12 h, after completion of the reaction (monitored by TLC), reaction mass quenched with ice-cold water and extracted into dichloromethane. The combined organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the crude product. The obtained crude product was passed through flash column chromatography to give pure product **1**.

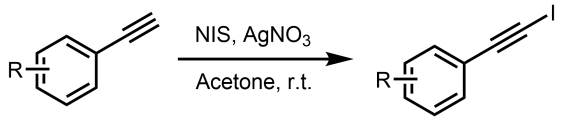


1d **1d'**

In a round- bottomed flask, NaOH (0.174 g, 4.35 mmol) was dissolved in 1:1 EtOH:H_2O (14 mL) and ethyl 2,5,5-trimethylhexa-2,3-dienoate **1d** (0.689 g, 2.9 mmol) and a stir bar were added. The resulting suspension was heated to 80 ºC for 2 h. The consumption of **1d** was monitored by TLC (20:1 hexanes: ethyl acetate). The round-bottomed flask was allowed to cool to ambient temperature and 1 M HCl was added dropwise until the solution reached pH 2. The acidic solution was extracted with DCM (3 × 10 mL). The combined organic layers were dried with Na_2SO_4, filtered, and concentrated in vacuo. The resulting solid was recrystallized in hexane. Excess solvent was removed by filtration to afford 2,5,5-trimethylhexa-2,3-dienoic acid **1d'** in 85% yield as a yellow solid.

2. Synthesis of Iodoalkynes Derivatives 2

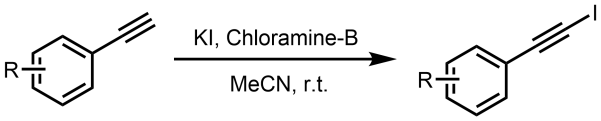
General Procedure **2** (**GP2**): Synthesis of **2a-2f**, **2h-2m, 2o, 2q-2s, 2x** and **2y**.[3]



S2 **2**

To a stirred solution of the terminal alkyne **S2** (5 mmol, 1.0 equiv.) in acetone (10 mL) was added NIS (5.5 mmol, 1.1 equiv.) and $AgNO_3$ (0.5 mmol, 10 mol%). The reaction mixture was stirred at room temperature for 3-5 h. After completion, the solvent was removed under reduced pressure and the residue was filtered through a pad of celite with petroleum ether. Removal of the solvent under reduced pressure followed by purification by flash column chromatography on silica gel (petroleum ether as eluent) afforded products **2a-2f**, **2h-2m, 2o, 2q-2s, 2x** and **2y**.

General Procedure **3** (**GP3**): Synthesis of **2g, 2n, 2p** and **2u-2w**.[4]

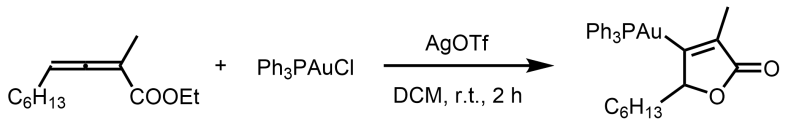


S2 **2**

To a stirred solution of the terminal alkyne **S2** (5 mmol, 1.0 equiv.) in MeCN (10 mL) was added KI (6.0 mmol, 1.2 equiv.) and Chloramine-B (7.5 mmol, 1.5 equiv.). The reaction mixture was stirred at room temperature for 2-6 h. After completion, the solvent was removed under reduced pressure and the residue was filtered through a pad of celite with petroleum ether. Removal of the solvent under reduced pressure followed by purification by flash column chromatography on silica gel (petroleum ether as eluent) afforded products **2g, 2n, 2p** and **2u-2w**.

3. Synthesis of Vinylgold(I) Complex 5

General Procedure **4** (**GP4**): Synthesis of **5**.[5]



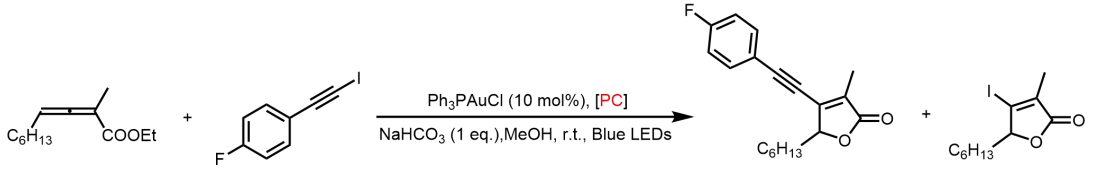
1a **5**

To a solution of ethyl 2-methyldeca-2,3-dienoate **1a** (50.0 mg, 0.24 mmol) in dichloromethane (2.0 mL) was add Ph_3PAuCl (99.0 mg, 0.20 mmol) and AgOTf (51.0 mg, 0.20 mmol). The mixture was stirred for 2 h at room temperature, afterwards the solvent was removed under reduced pressure and the residue was subjected to a flash column chromatography.

Following general procedure **GP4** with **1a** (50.0 mg, 0.24 mmol) to afford **5** (1.43 g, 4.6 mmol, 92 %) as colorless oil. The spectroscopic data match those previously reported in the literature.[17] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.56 (15H, m), 4.94 (1H, s), 2.04 (3H, s), 1.84-1.90 (1H, m), 1.65-1.71 (1H, m), 1.55-1.61 (2H, m), 1.24-1.36 (6H, m), 0.85 (t, J = 7.0 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 44.25.

III. Optimization of Reaction Conditions

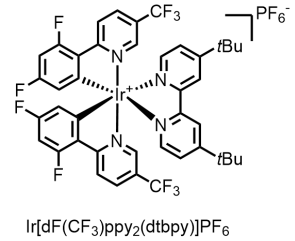
1. Screening of photocatalysts



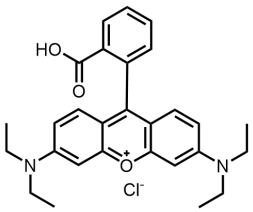
1a **2a** **3a** **3aa**

Entry	[PC] (mol%)	Yield of **3a** (%)	Yield of **3aa** (%)
1	$Ru(bpy)_3Cl_2$ (2.5)	30	11
2	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (1)	37	10
3	Rhodamine B (10)	46	17
4	Eosin Y (10)	35	14
5	4CzIPN (10)	45	20
6	Acriflavine (5)	53	18
7	Acriflavine (10)	44	18
8	Fukuzumi catalyst (5)	40	16
9	**PC1** (5)	42	17
10	**PC2** (5)	38	15

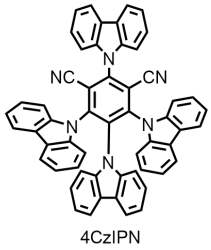
Reaction conditions: **1a** (0.2 mmol), **2a** (1.5 equiv.), Ph_3PAuCl catalyst (10 mol %), photocatalyst, $NaHCO_3$ (1 equiv.), degassed MeOH (2 mL), r.t., Blue LEDs, overnight. Yields are determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.



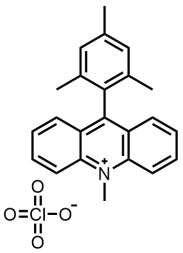
Ir[dF(CF$_3$)ppy$_2$(dtbpy)]PF$_6$



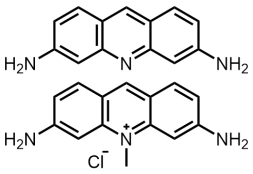
Rhodamine B (RB)



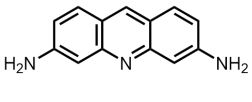
4CzIPN



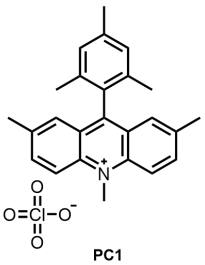
Fukuzumi catalyst



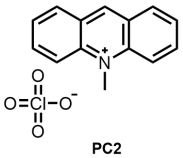
Acriflavine (ACF)



Proflavine

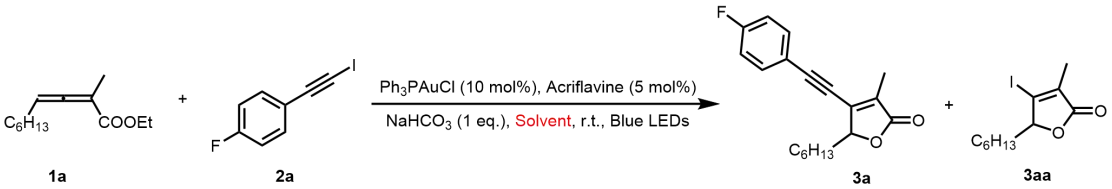


PC1



PC2

2. Screening of solvent

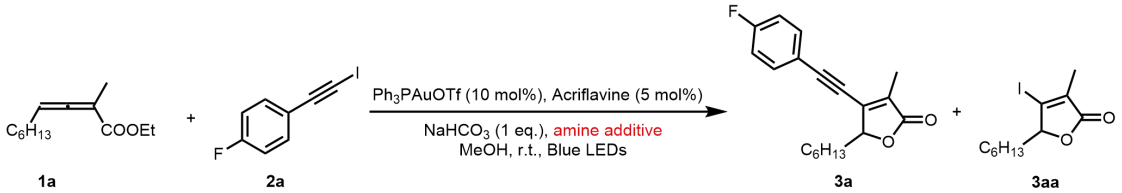


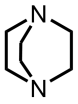
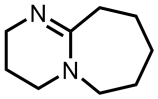
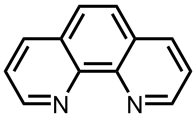
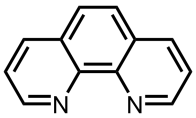
1a **2a** **3a** **3aa**

Entry	Solvent (2 mL)	Yield of **3a** (%)	Yield of **3aa** (%)
1	MeCN	12	13
2	DCM	21	9
3	THF	17	11
4	DMSO	19	10
5	Toluene	16	14
6	Acetone	22	13

Reaction conditions: **1a** (0.2 mmol), **2a** (1.5 equiv), Ph_3PAuCl catalyst (10 mol %), Acriflavine (5 mol%), $NaHCO_3$ (1 equiv), degassed solvent (2 mL), r.t., Blue LEDs, overnight. Yields are determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard.

3. Screening of amines

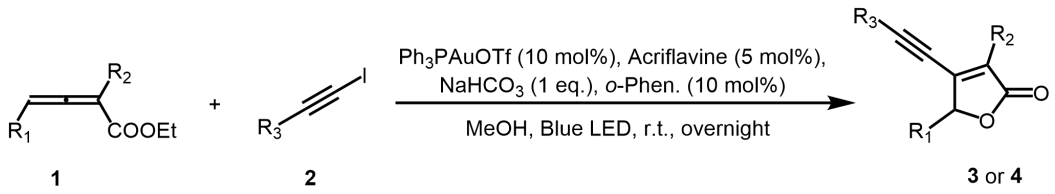


Entry	Amines additive (mol%)	Yield of **3a** (%)	Yield of **3aa** (%)
1	 DABCO (10)	27	13
2	 DBU (10)	31	8
3	 Phen. (10)	80	15
4	 Phen. (20)	60	17

Reaction conditions: **1a** (0.2 mmol), **2a** (1.5 equiv), Ph_3PAuCl catalyst (10 mol %), Acriflavine (5 mol%), $NaHCO_3$ (1 equiv), amines additive, degassed MeOH (2 mL), r.t., Blue LEDs, overnight. Yields are determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard.

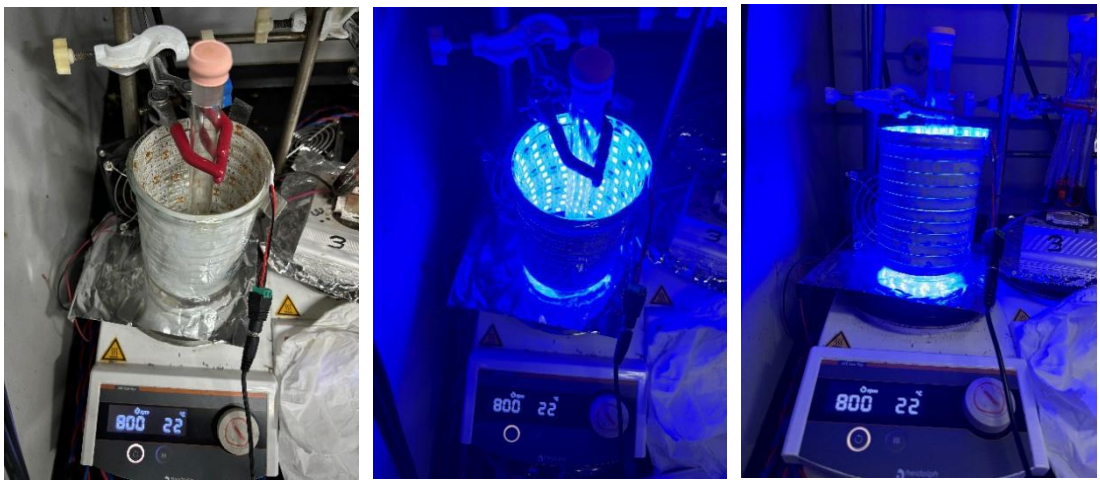
IV. General Procedure for Alkynylative Cyclization of Allenoates with Iodoalkynes

General Procedure **5** (**GP5**): Alkynylative cyclization of allenoates derivatives with iodoalkynes



The photocatalyst acriflavine (5 mol%), the gold (I) catalyst $Ph_3PAuOTf$ (10 mol %), $NaHCO_3$ (1 equiv.), 1,10-Phenanthroline (10 mol %), the appropriate iodoalkynes **2** (0.3 mmol, 1.5 equiv.) and allenoates **1** (0.2 mmol, 1 equiv.) were introduced in a Schlenk-tube equipped with a magnetic stirring bar in which MeOH (2 mL) was added. The mixture was degassed using three freeze pump-thaw cycles and purged with Ar, then irradiated with Blue LEDs (a very simple irradiating setup used as depicted in pictures below) for 24 h (unless mentioned). The stirring speed is equal

or more than 800 rpm. The reaction was quenched with EtOAc (3 mL) and a 2 M HCl solution (3 mL) and the solution was extracted by EtOAc (3 × 5 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the crude product. The residue was purified by FC on silica gel to afford the desired product or determined by ^1H NMR using 1,3,5-trimethoxybenzene as internal standard.

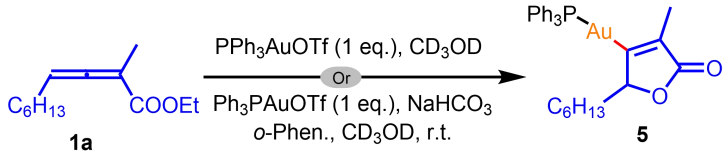


The simple photoreactor which is equipped with LED stripes (λ_{max} = 450 nm) on a beaker (the diameter is 7.5 cm and the height is 9.5 cm). An aluminum paper is put between the stirring plate and the beaker to reflect the light.

V. Mechanistic Investigations

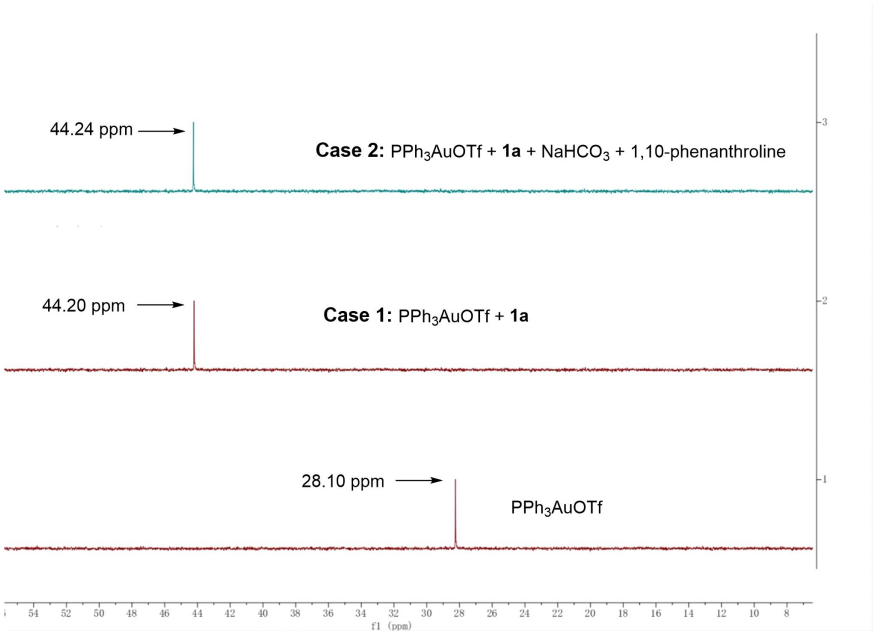
1. ^{31}P NMR studies:

(a) Cyclization of allenoate 1a in presence of cationic gold(I) complex in CD_3OD:

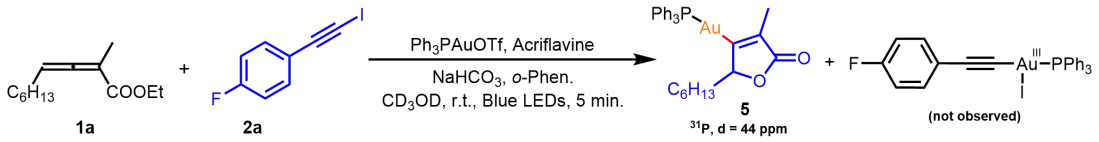


Case 1: A screw-cap NMR tube was charged with PPh_3AuOTf (12 mg, 0.02 mmol, 1.0 equiv.) and ethyl 2-methyldeca-2,3-dienoate **1a** (5.8 mg, 0.03 mmol, 1.5 equiv.) in CD_3OD (0.5 mL). Then, the ^{31}P NMR was then recorded instantly, and only a single peak at 44.20 ppm corresponding to vinyl gold (I) **5** was observed.

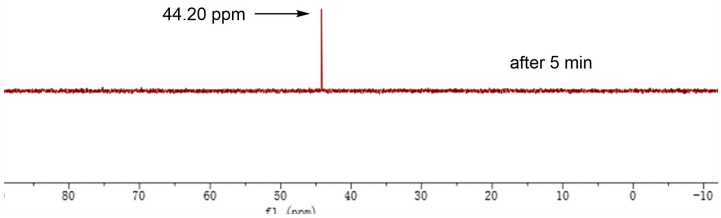
Case 2: A screw-cap NMR tube was charged with PPh_3AuOTf (12 mg, 0.02 mmol, 1.0 equiv.), $NaHCO_3$ (0.02 mmol, 1.0 equiv), and 1,10-phenanthroline (3.6 mg) in CD_3OD (0.2 mL). In another vial, ethyl 2-methyldeca-2,3-dienoate **1a** (6.3 mg, 0.03 mmol, 1.5 equiv.) was dissolved in CD_3OD (0.3 mL). Then, the prepared solution was added to the NMR tube using a plastic syringe equipped with stainless steel needle. Then, the ^{31}P NMR was recorded instantly, and only a single peak at 44.24 ppm corresponding to vinyl gold (I) **5** was observed.



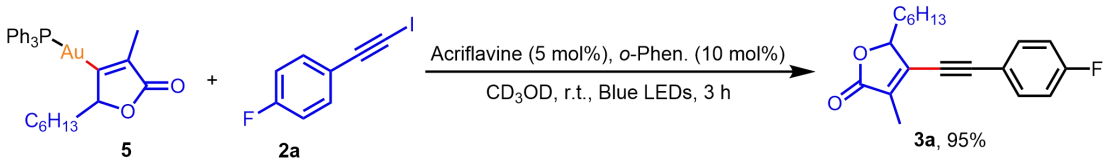
(b) ^{31}P NMR monitoring for the reaction of allenoate 1a and iodoalkynes 2a in standard reaction conditions:



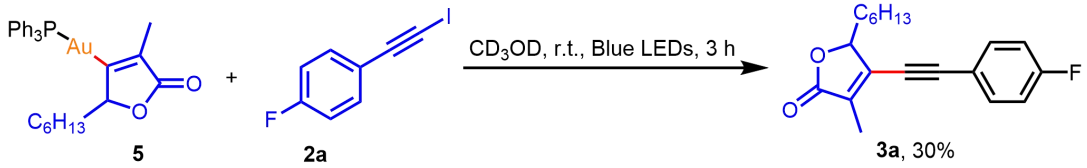
The photocatalyst acriflavine (5 mol%), the gold (I) catalyst $Ph_3PAuOTf$ (10 mol %), $NaHCO_3$ (1 equiv.), 1,10-Phenanthroline (10 mol %), the appropriate iodoalkynes **2a** (0.3 mmol) and allenoates **1a** (0.2 mmol) were introduced in a Schlenk-tube equipped with a magnetic stirring bar in which CD_3OD (2 mL) was added. The mixture was degassed using three freeze pump-thaw cycles and purged with Ar, then irradiated with Blue LEDs. Then, the ^{31}P NMR was recorded at interval of time. The ^{31}P NMR spectra recorded after 5 minutes, revealed a single peak at 44.20 ppm, corresponding to vinyl gold (I) **5**. But no other detectable peak was observed. These results strongly suggest that the cyclization of allenoate **1a** proceeds rapidly, even in the presence of iodoalkynes **2a**.



2. Control experiments



Case 1: The photocatalyst acriflavine (5 mol%), the vinyl gold (I) complex **5** (0.1 mmol, 1 equiv.), 1,10-Phenanthroline (10 mol %), the appropriate iodoalkynes **2a** (0.15 mmol, 1.5 equiv.) were introduced in a Schlenk-tube equipped with a magnetic stirring bar in which CD_3OD (1 mL) was added. The mixture was degassed using three freeze pump-thaw cycles and purged with Ar, then irradiated with Blue LEDs for 3 h. Then added 1,3,5-trimethoxybenzene (16.8 mg, 0.1 mmol) as internal standard to obtain product **3a** in 95% yield.

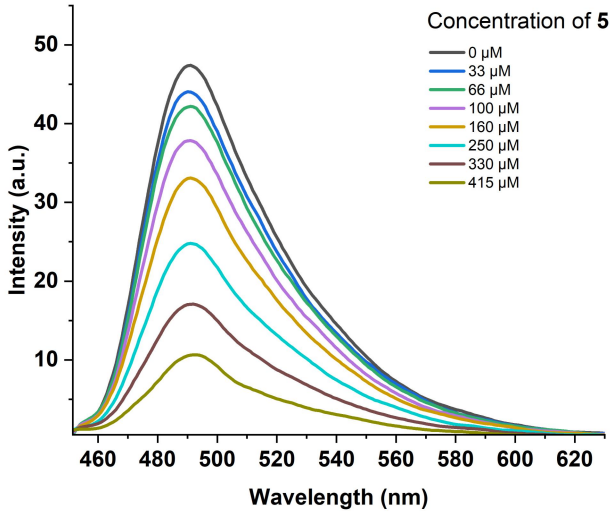


Case 1: The vinyl gold (I) complex **5** (0.1 mmol, 1 equiv.), the appropriate iodoalkynes **2a** (0.15 mmol, 1.5 equiv.) were introduced in a Schlenk-tube equipped with a magnetic stirring bar in which CD_3OD (1 mL) was added. The mixture was degassed using three freeze pump-thaw cycles and purged with Ar, then irradiated with Blue LEDs for 3 h. Then added 1,3,5-trimethoxybenzene (16.8 mg, 0.1 mmol) as internal standard to obtain product **3a** in 30% yield.

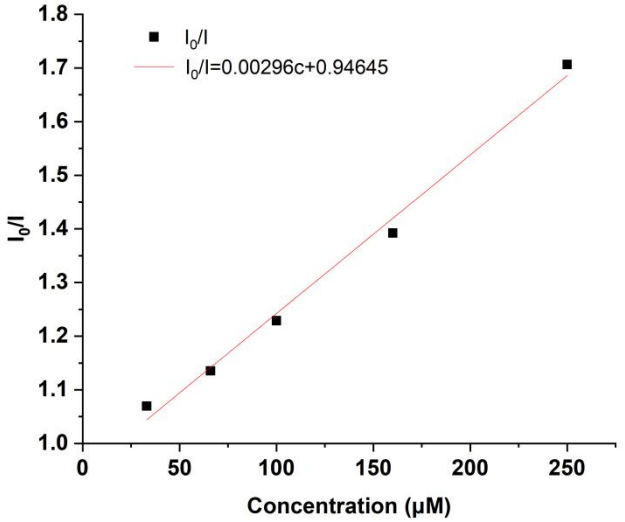
These results suggest that the reaction includes an energy transfer process.

3. Luminescence study

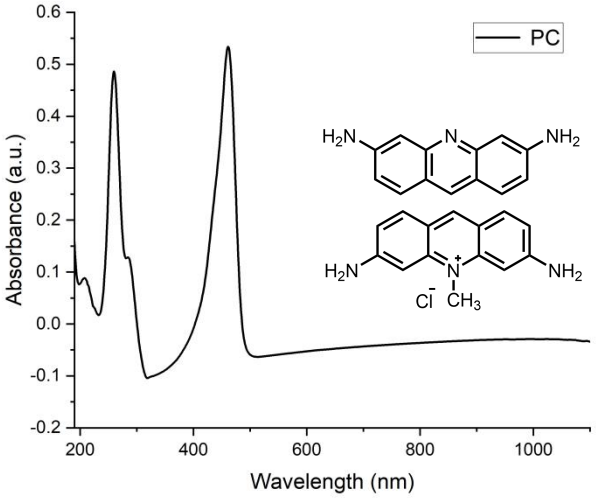
We proceeded by monitoring the evolution of the steady-state luminescence emission spectra of acriflavine solutions containing various concentrations of vinylgold (I) **5**. We observed a drop of the acriflavine luminescence signal upon increasing the **5** concentration, which suggested that the vinylgold (I) **5** acts as a quencher for the acriflavine triplet state (Supplementary Figure 1).



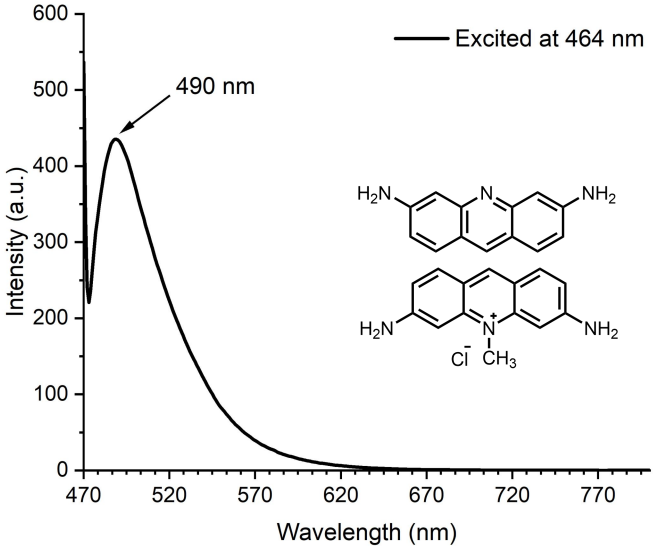
Supplementary Figure 1. Quenching of acriflavine by vinylgold(I) **5** monitored by steady-state fluorimetry. The luminescence spectrum of acriflavine (0.01 µM in N_2-saturated acetonitrile) was measured under 450 nm illumination, in the presence of increasing amounts of vinylgold(I) **5**.



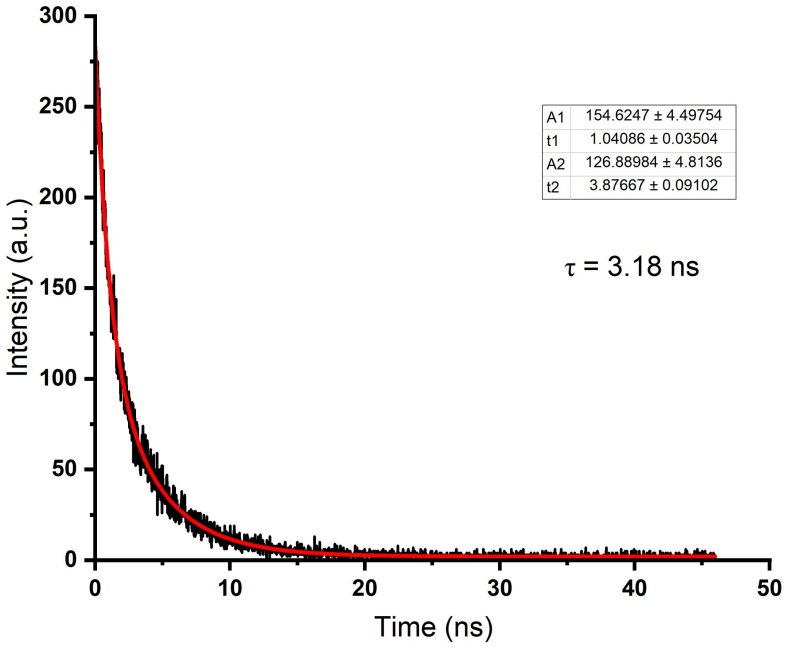
Supplementary Figure 2. Stern-Volmer plots for the quenching of acriflavine by vinylgold(I) complex **5** as monitored by steady-state fluorimetry.



Supplementary Figure 3. UV-visible spectrum of photocatalyst acriflavine (Maximum absorption wavelength is 464 nm).



Supplementary Figure 4. The fluorescence emission spectrum of acriflavine excited at 464 nm. The maximum fluorescence emission wavelength of acriflavine is 490 nm.

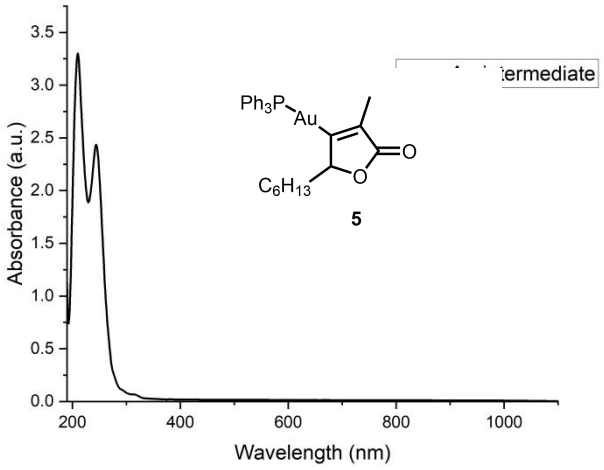


Supplementary Figure 5: Fluorescence lifetime decay (λ_{ex} = 450 nm, λ_{em} = 636 nm) curve of acriflavine.

By the test of fluorescence lifetime:

$$\tau = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2}$$

Where τ_1 and τ_2 are the fitted life, A_1 and A_2 are the proportions corresponding to the fitted lifetime, and τ is the excited state lifetime in the absence of quencher. So, τ = 3.18 ns.



Supplementary Figure 6. UV-visible spectrum of vinylgold (I) complex **5**.

4. Quantum yield reaction measurement[6,7]

The photon flux of blue LED was determined by standard ferrioxalate actinometry.
0.15 mol/L solution of ferrioxalate was prepared by dissolving potassium ferrioxalate hydrate (328 mg, 0.750 mmol) in 5.0 mL of 0.20 mol/L aqueous sulfuric acid.
0.15 mol/L buffered solution of 1,10-phenanthroline was prepared by dissolving 1,10-phenanthroline (54.1 mg, 0.3 mmol) and sodium acetate (1.23 g, 15.0 mmol) in 20 mL of 0.20 mol/L aqueous sulfuric acid. The actinometry measurements were done as follows: To a reaction tube equipped with a stir bar was added 0.50 mL of the ferrioxalate solution. The reaction tube was sealed and placed 2.0 cm away from a 450 nm blue LED. After irradiation for 5 seconds, 1.5 mL of the aqueous sulfuric acid and 2.0 mL of the buffered solution was added to the reaction tube. The solution was then allowed to rest for 1 hour to allow the resultant ferrous ions to react completely with 1,10-phenanthroline. 50.0 μL of the resulting solution was taken as an aliquot and diluted with 3.0 mL of 0.20 mol/L aqueous sulfuric acid. The absorbance of the resulting solution in a cuvette (l = 1.0 cm) at 510 nm was measured by UV-Vis spectrometer. A non-irradiated sample was also prepared and the absorbance at 510 nm was measured.
The amount of ferrous ion formed was calculated as follows:

$$\text{mol } Fe^{2+} = \frac{v \times \Delta A}{l \times \varepsilon}$$

Where V is the total volume (0.02 L) of the solution that was analyzed, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated samples, l is the path length (1.0 cm), and ε is the molar absorptivity at 510 nm (11100 L/(mol•cm)).
The photon flux was calculated as follows:

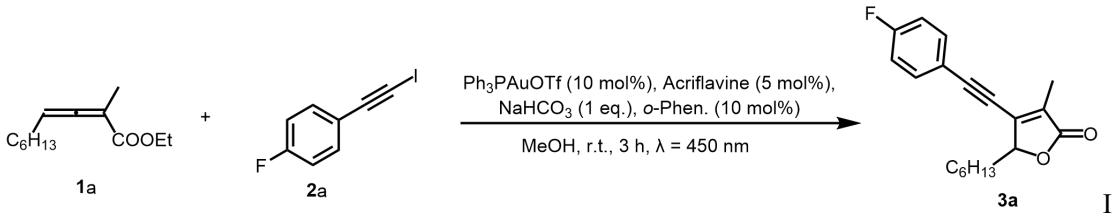
$$\text{photo flux} = \frac{\text{mol } Fe^{2+}}{\Phi \times t \times f}$$

Where Φ is the quantum yield for the ferrioxalate actinometer (approximated as 0.845, which was reported for a 0.15 mol/L solution at λ = 457.9 nm), t is the irradiation time, and f is the fraction of light absorbed at 450 nm (0.9921).
The fraction of light absorbed was determined by the following equation:

$$f = 1\text{-}10^{-A}$$

Where A is the measured absorbance (0.284) of the 0.15 mol/L solution of potassium ferrioxalate at 450 nm.
The photon flux was calculated to be 3.2×10^{-6} Einstein/s.

Determination of quantum yield:



I

In a screw capped quartz cuvette was introduced acriflavine (5 mol%), the gold (I) catalyst $Ph_3PAuOTf$ (10 mol %), $NaHCO_3$ (1 equiv.), 1,10-Phenanthroline (10 mol %), the appropriate iodoalkynes 2 (0.3 mmol, 1.5 equiv.), allenoates **1a** (0.2 mmol, 1 equiv.) and degassed MeOH (2 mL) under argon. The sample was placed in the spectrofluorometer and irradiated at 450 nm (excitation slit width at 10 nm and emission slit width at 10 nm) for 10800 seconds under vigorous stirring. The reaction mixture was transferred in an NMR tube protected from light. The reaction yield was 14.4% determined by ^1H NMR using 1,3,5-trimethoxybenzene as a standard. Under these conditions, the fraction of light absorbed at 450 nm (f) has a value of 0.047.

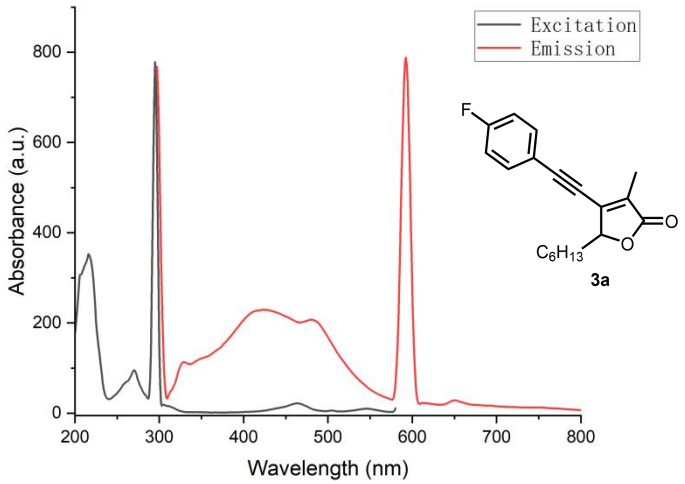
The quantum yield was calculated as follows:

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

where flux is the photon flux determined by ferrioxalate actinometry (3.2×10^{-6} Einstein/s), t is the time, and f is the fraction of light absorbed by the irradiated reaction system at 450 nm, and the absorbance of the irradiated reaction system at 450 nm was 0.021. The fraction of light absorbed at 450 nm was calculated: $f = 1\text{-}10^{-A} = 1\text{-}10^{-0.021} = 0.047$.

The quantum yield was calculated: $\Phi = 0.18$

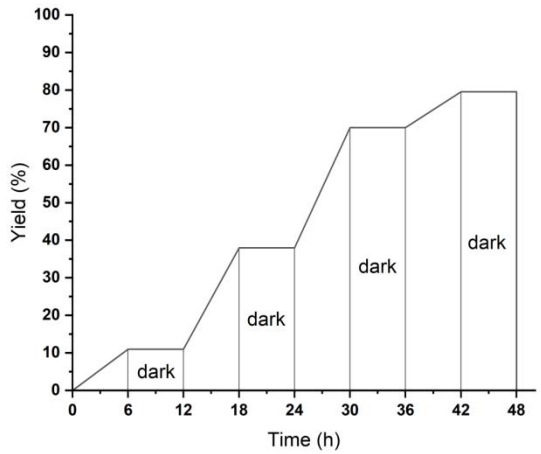
5. Fluorescence property of product 3a



Supplementary Figure 7. Excitation (blue line) and emission (red line) spectra of **3a**.

6. Light/dark experiments

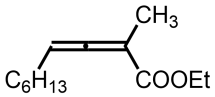
Eight standard reaction mixtures in 10 mL schlenk tube were equipped with a magnetic stir bar, added the photocatalyst acriflavine (5 mol%), the gold (I) catalyst $Ph_3PAuOTf$ (10 mol %), $NaHCO_3$ (1 equiv.), 1,10-Phenanthroline (10 mol %), 1-fluoro-4-(iodoethynyl)benzene **2a** (0.3 mmol, 1.5 equiv.), ethyl 2-methyldeca-2,3-dienoate **1a** (0.2 mmol, 1 equiv.) and MeOH (2 mL). Then the mixture was stirred and irradiated by blue LEDs at room temperature. After 6 h, the blue LEDs were turned off, and one schlenk tube was removed from the irradiation setup for analysis. The remaining seven schlenk tubes were stirred in the absence of light for an additional 6 h. Then, one schlenk tube was removed for analysis, and the blue LEDs were turned back on to irradiate the remaining six reaction mixtures. After an additional 6 h of irradiation, the blue LEDs were turned off, and one schlenk tube was removed for analysis. The remaining five schlenk tubes were stirred in the absence of light for an additional 6 h. Then, schlenk tube was removed for analysis, and the blue LEDs were turned back on to irradiate the remaining four reaction mixtures. After 6 h, the blue LEDs were turned off, and one schlenk tube was removed for analysis. The remaining three schlenk tubes were stirred in the absence of light for an additional 6 h, then, a schlenk tube was removed for analysis and the blue LEDs were turned back on to 8 irradiate the remaining two reaction mixtures. After 6 h, the blue LEDs were turned off, and one schlenk tube was removed for analysis. The last schlenk tube was stirred in the absence of light for an additional 6 h, and then it was analyzed. The yield was determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard.



Supplementary Figure 8. Light/dark experiment

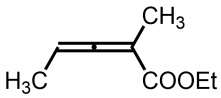
VI. Characterizations of Substrates 1 and 2

ethyl 2-methyldeca-2,3-dienoate (1a)



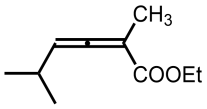
Following general procedure **GP1** with octanoyl chloride (0.81 g, 5.0 mmol) to afford **1a** (1.01 g, 4.8 mmol, 96 %) as colorless oil. The spectroscopic data match those previously reported in the literature.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.39 (dtq, J = 12.6, 6.4, 2.9 Hz, 1H), 4.13 (ddh, J = 14.2, 7.1, 3.4 Hz, 2H), 2.04 (p, J = 7.2 Hz, 2H), 1.85 – 1.73 (m, 3H), 1.44 – 1.17 (m, 11H), 0.84 (q, J = 6.8 Hz, 3H).

ethyl 2-methylpenta-2,3-dienoate (1b)



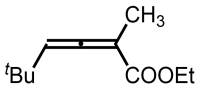
Following general procedure **GP1** with propionyl chloride (0.46 g, 5.0 mmol) to afford **1b** (0.67 g, 4.8 mmol, 97 %) as colorless oil. The spectroscopic data match those previously reported in the literature.[8] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.36 (dddtd, *J* = 10.2, 7.2, 6.0, 2.9, 1.5 Hz, 1H), 4.12 (qd, *J* = 7.1, 0.9 Hz, 2H), 1.79 (dd, *J* = 2.9, 1.0 Hz, 3H), 1.68 (dd, *J* = 7.3, 1.0 Hz, 3H), 1.24 – 1.19 (m, 3H).

ethyl 2,5-dimethylhexa-2,3-dienoate (1c)



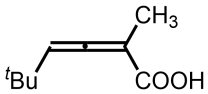
Following general procedure **GP1** with 3-methylbutanoyl chloride (0.60 g, 5.0 mmol) to afford **1c** (0.79 g, 4.7 mmol, 94 %) as colorless oil. The spectroscopic data match those previously reported in the literature.[9] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43 – 5.36 (m, 1H), 4.20 – 4.00 (m, 2H), 2.43 – 2.30 (m, 1H), 1.80 (dt, *J* = 3.0, 1.5 Hz, 3H), 1.20 (tt, *J* = 7.2, 1.5 Hz, 3H), 1.00 (dt, *J* = 6.8, 1.5 Hz, 6H).

ethyl 2,5,5-trimethylhexa-2,3-dienoate (1d)



Following general procedure **GP1** with 3,3-dimethylbutanoyl chloride (0.67 g, 5.0 mmol) to afford **1d** (0.89 g, 4.9 mmol, 97 %) as colorless oil. The spectroscopic data match those previously reported in the literature.[10a] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.41 – 5.35 (m, 1H), 4.23 – 4.01 (m, 2H), 1.82 (dd, *J* = 2.8, 1.5 Hz, 3H), 1.21 (td, *J* = 7.1, 1.5 Hz, 3H), 1.04 (d, *J* = 1.7 Hz, 9H).

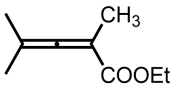
2,5,5-trimethylhexa-2,3-dienoic acid (1d')



Following general procedure **GP1** with ethyl 2,5,5-trimethylhexa-2,3-dienoate **1d** (0.689 g, 2.9 mmol) to afford **1d'** (0.38g, 2.5 mmol, 85 %) as yellow solid. The spectroscopic data match those previously

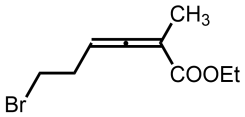
reported in the literature.[10b] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74 – 5.25 (m, 1H), 1.85 (s, 3H), 1.15 – 0.99 (m, 10H).

ethyl 2,4-dimethylpenta-2,3-dienoate (1e)



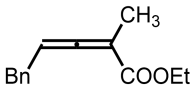
Following general procedure **GP1** with isobutyryl chloride (0.53 g, 5.0 mmol) to afford **1e** (0.69 g, 4.5 mmol, 91 %) as colorless oil. The spectroscopic data match those previously reported in the literature.[11] ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.15 (q, *J* = 7.1 Hz, 2H), 1.81 (s, 3H), 1.75 (s, 6H), 1.25 (t, *J* = 7.1 Hz, 3H).

ethyl 6-bromo-2-methylhexa-2,3-dienoate (1f)



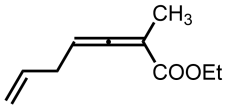
Following general procedure **GP1** with 4-bromobutanoyl chloride (0.93g, 5.0 mmol) to afford **1f** (1.01 g, 4.4 mmol, 88 %) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.45 (tt, *J* = 6.7, 3.0 Hz, 1H), 4.12 (dtt, *J* = 9.1, 6.9, 3.2 Hz, 2H), 3.46 (dddt, *J* = 58.7, 8.7, 6.9, 2.1 Hz, 2H), 2.67 – 2.42 (m, 2H), 1.82 (h, *J* = 2.6 Hz, 3H), 1.21 (dtd, *J* = 7.3, 5.4, 2.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.00, 167.09, 96.66, 91.01, 60.65, 31.07, 30.99, 14.76, 14.01; HRMS (APCI) calc. for $C_9H_{13}BrO_2^+$ $[M+H]^+$: 233.0099, found 233.0097.

ethyl 2-methyl-5-phenylpenta-2,3-dienoate (1g)



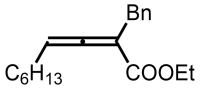
Following general procedure **GP1** with 3-phenylpropanoyl chloride (0.84 g, 5.0 mmol) to afford **1g** (0.89 g, 4.1 mmol, 82 %) as yellow oil. The spectroscopic data match those previously reported in the literature.[9] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.10 (m, 5H), 5.57 (tq, *J* = 7.7, 2.9 Hz, 1H), 4.27 – 4.10 (m, 2H), 3.50 – 3.30 (m, 2H), 1.84 (dd, *J* = 2.9, 1.0 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H).

ethyl 2-methylhepta-2,3,6-trienoate (1h)



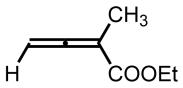
Following general procedure **GP1** with pent-4-enoyl chloride (0.59 g, 5.0 mmol) to afford **1h** (0.74 g, 4.5 mmol, 89 %) as colorless oil. The spectroscopic data match those previously reported in the literature.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82 (ddt, *J* = 16.5, 10.1, 6.2 Hz, 1H), 5.43 (ddt, *J* = 9.9, 7.0, 2.9 Hz, 1H), 5.18 – 4.96 (m, 2H), 4.15 (dtt, *J* = 10.8, 7.3, 3.7 Hz, 2H), 2.86 – 2.75 (m, 2H), 1.83 (d, *J* = 2.9 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).

ethyl 2-benzyldeca-2,3-dienoate (1i)



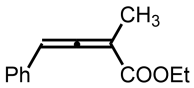
Following general procedure **GP1** with octanoyl chloride (0.81 g, 5.0 mmol) to afford **1i** (1.12 g, 3.9 mmol, 78 %) as colorless oil. The spectroscopic data match those previously reported in the literature.[8] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.06 (m, 5H), 5.36 (tt, *J* = 7.0, 2.5 Hz, 1H), 4.08 (qd, *J* = 6.3, 5.3, 1.8 Hz, 2H), 3.52 – 3.39 (m, 2H), 1.95 (s, 2H), 1.20 – 1.16 (m, 8H), 0.81 – 0.77 (m, 6H).

ethyl 2-methylbuta-2,3-dienoate (1j)



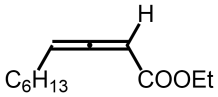
Following general procedure **GP1** with acetyl chloride (0.39 g, 5.0 mmol) to afford **1j** (0.30 g, 2.4 mmol, 47 %) as colorless oil. The spectroscopic data match those previously reported in the literature.[11] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.11 – 4.93 (m, 2H), 4.17 (qd, *J* = 7.2, 1.7 Hz, 2H), 1.83 (t, *J* = 3.1 Hz, 3H), 1.28 – 1.17 (m, 3H).

ethyl 2-methyl-4-phenylbuta-2,3-dienoate (1k)



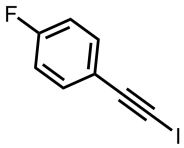
Following general procedure **GP1** with phenylacetyl chloride (0.77 g, 5.0 mmol) to afford **1k** (0.77 g, 3.8 mmol, 76 %) as yellow oil. The spectroscopic data match those previously reported in the literature.[9] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.16 (m, 5H), 6.45 (q, *J* = 2.9 Hz, 1H), 4.19 (qd, *J* = 7.1, 1.8 Hz, 2H), 1.99 (d, *J* = 3.0 Hz, 3H), 1.23 (t, *J* = 7.2 Hz, 3H).

ethyl deca-2,3-dienoate (1l)



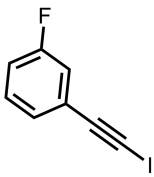
Following general procedure **GP1** with octanoyl chloride (0.81 g, 5.0 mmol) to afford **1l** (0.56 g, 2.9 mmol, 57 %) as colorless oil. The spectroscopic data match those previously reported in the literature.[11] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.65 – 5.52 (m, 1H), 4.23 – 4.14 (m, 2H), 3.23 (t, *J* = 2.5 Hz, 1H), 2.25 – 2.06 (m, 2H), 1.54 – 1.38 (m, 2H), 1.38 – 1.21 (m, 8H), 0.91 – 0.84 (m, 3H).

1-fluoro-4-(iodoethynyl)benzene (2a)



Following general procedure **GP2** with 1-ethynyl-4-fluorobenzene (0.60 g, 5.0 mmol) to afford **2a** (1.16 g, 4.7 mmol, 94 %) as yellow oil. The spectroscopic data match those previously reported in the literature.[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.33 (m, 2H), 7.11 – 6.94 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.72.

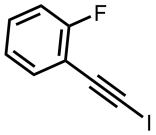
1-fluoro-3-(iodoethynyl)benzene (2b)



Following general procedure **GP2** with 1-ethynyl-3-fluorobenzene (0.60 g, 5.0 mmol) to afford **2b** (1.21 g, 4.9 mmol, 98 %) as yellow oil. The spectroscopic data match those previously reported in the

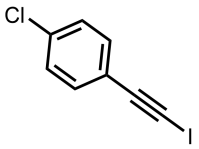
literature.[13] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 1H), 7.23 – 7.19 (m, 1H), 7.12 (ddd, *J* = 9.3, 2.7, 1.4 Hz, 1H), 7.03 (tdd, *J* = 8.4, 2.6, 1.2 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.61.

1-fluoro-2-(iodoethynyl)benzene (2c)



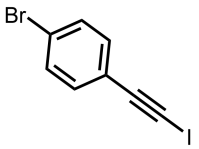
Following general procedure **GP2** with 1-ethynyl-2-fluorobenzene (0.60 g, 5.0 mmol) to afford **2c** (0.98 g, 4.0 mmol, 90 %) as yellow oil. The spectroscopic data match those previously reported in the literature.[14] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (td, *J* = 7.3, 1.8 Hz, 1H), 7.30 (tdd, *J* = 7.4, 5.2, 1.8 Hz, 1H), 7.13 – 7.03 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.05.

1-chloro-4-(iodoethynyl)benzene (2d)



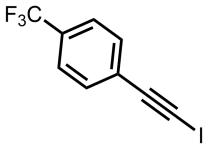
Following general procedure **GP2** with 4-chlorophenylacetylene (0.68 g, 5.0 mmol) to afford **2d** (1.25 g, 4.8 mmol, 95 %) as a yellow solid. The spectroscopic data match those previously reported in the literature.[15] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 2H), 7.31 – 7.26 (m, 2H).

1-bromo-4-(iodoethynyl)benzene (2e)



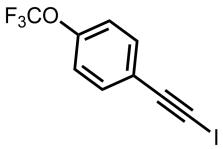
Following general procedure **GP2** with 4-bromophenylacetylene (0.91 g, 5.0 mmol) to afford **2e** (1.20 g, 3.9 mmol, 78 %) as a white solid. The spectroscopic data match those previously reported in the literature.[14] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 2H), 7.31 – 7.26 (m, 2H).

1-(iodoethynyl)-4-(trifluoromethyl)benzene (2f)



Following general procedure **GP2** with 4'-trifluoromethylphenyl acetylene (0.85 g, 5.0 mmol) to afford **2f** (1.21 g, 4.1 mmol, 81 %) as a yellow solid. The spectroscopic data match those previously reported in the literature.[13] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (q, *J* = 8.4 Hz, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.94.

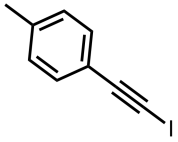
1-(iodoethynyl)-4-(trifluoromethoxy)benzene (2g)



Following general procedure **GP3** with 4-(trifluoromethoxy)phenylacetylene (0.93 g, 5.0 mmol) to afford **2g** (1.28 g, 4.1 mmol, 82 %) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 2H), 7.16 (dp, *J* = 7.8, 1.1 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.23, 149.21, 133.84, 122.01, 121.59,

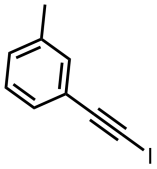
120.64, 119.03, 92.71, 7.93; ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.83; HRMS (APCI) calc. for $C_9H_4F_3IO^+$ $[M+H]^+$: 312.9256, found 312.9255.

1-(iodoethynyl)-4-methylbenzene (2h)



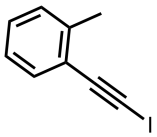
Following general procedure **GP2** with 4-ethynyltoluene (0.58 g, 5.0 mmol) to afford **2h** (1.17 g, 4.8 mmol, 97 %) as a yellow solid. The spectroscopic data match those previously reported in the literature.[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.23 (m, 2H), 7.16 – 7.08 (m, 2H), 2.34 (s, 3H).

1-(iodoethynyl)-3-methylbenzene (2i)



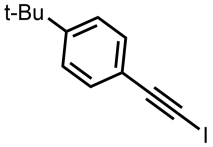
Following general procedure **GP2** with 3-ethynyltoluene (0.58 g, 5.0 mmol) to afford **2i** (1.11 g, 4.6 mmol, 92 %) as yellow oil. The spectroscopic data match those previously reported in the literature.[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.23 – 7.07 (m, 3H), 2.42 (s, 3H).

1-(iodoethynyl)-2-methylbenzene (2j)



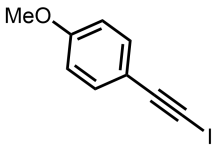
Following general procedure **GP2** with 2-ethynyltoluene (0.58 g, 5.0 mmol) to afford **2j** (1.09 g, 4.5 mmol, 90 %) as yellow oil. The spectroscopic data match those previously reported in the literature.[13] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.06 (m, 5H), 2.29 (s, 3H).

1-(tert-butyl)-4-(iodoethynyl)benzene (2k)



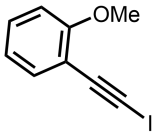
Following general procedure **GP2** with 4-(tert-butyl)phenylacetylene (0.79 g, 5.0 mmol) to afford **2k** (1.11 g, 3.9 mmol, 78 %) as a white solid. The spectroscopic data match those previously reported in the literature. [12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.36 (m, 2H), 7.34-7.32 (m, 2H), 1.30 (s, 9H).

1-(iodoethynyl)-4-methoxybenzene (2l)



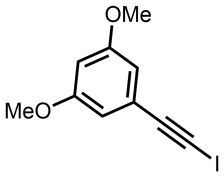
Following general procedure **GP2** with 4-methoxyphenylacetylene (0.66 g, 5.0 mmol) to afford **2l** (1.08 g, 4.2 mmol, 84 %) as an orange solid. The spectroscopic data match those previously reported in the literature.[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.25 (m, 2H), 6.98 – 6.67 (m, 2H), 3.78 (d, *J* = 19.1 Hz, 3H).

1-(iodoethynyl)-2-methoxybenzene (2m)



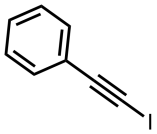
Following general procedure **GP2** with 2'-methoxyphenyl acetylene (0.66 g, 5.0 mmol) to afford **2m** (0. 80 g, 3.1 mmol, 62 %) as yellow oil. The spectroscopic data match those previously reported in the literature.[16] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.17 (ddd, *J* = 8.3, 7.4, 1.7 Hz, 1H), 6.81 – 6.72 (m, 2H), 3.74 (s, 3H).

1-(iodoethynyl)-3,5-dimethoxybenzene (2n)



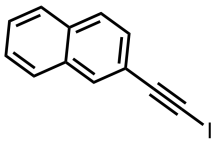
Following general procedure **GP3** with 3,5-dimethoxyphenyl acetylene (0.81 g, 5.0 mmol) to afford **2n** (1.07 g, 3.7 mmol, 74 %) as a brown solid. The spectroscopic data match those previously reported in the literature.[16] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.59 (d, *J* = 2.3 Hz, 2H), 6.44 (t, *J* = 2.4 Hz, 1H), 3.77 (s, 6H).

(iodoethynyl)benzene (2o)



Following general procedure **GP2** with phenylacetylene (0.51 g, 5.0 mmol) to afford **2o** (1.09 g, 4.8 mmol, 96 %) as yellow oil. The spectroscopic data match those previously reported in the literature.[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H), 7.32 (dd, *J* = 5.2, 2.0 Hz, 3H).

2-(iodoethynyl)naphthalene (2p)

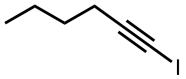


Following general procedure **GP3** with naphthylene-2-acetylene (0.76 g, 5.0 mmol) to afford **2p** (1.06 g, 3.8 mmol, 76 %) as a white solid. The spectroscopic data match those previously reported in the literature.[16] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 1.6 Hz, 1H), 7.86 – 7.75 (m, 3H), 7.55 – 7.45 (m, 3H).

(iodoethynyl)cyclopropane (2q)

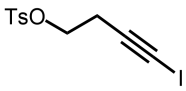
Following general procedure **GP2** with ethynylcyclopropane (0.33 g, 5.0 mmol) to afford **2q** (0.67 g, 3.5 mmol, 70 %) as colorless oil. The spectroscopic data match those previously reported in the literature.[13] ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (tt, *J* = 8.2, 5.2 Hz, 1H), 0.79 – 0.68 (m, 4H).

1-iodohept-1-yne (2r)



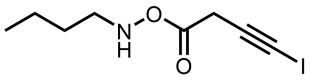
Following general procedure **GP2** with 1-hexyne (0.41 g, 5.0 mmol) to afford **2r** (0.73 g, 3.5 mmol, 71 %) as colorless oil. The spectroscopic data match those previously reported in the literature.[13] ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (t, *J* = 7.0 Hz, 2H), 1.55 – 1.35 (m, 4H), 0.91 (t, *J* = 7.3 Hz, 3H).

4-iodobut-3-yn-1-yl 4-methylbenzenesulfonate (2s)



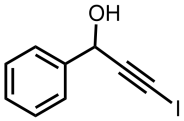
Following general procedure **GP2** with 3-butynyl p-toluenesulfonate (1.12 g, 5.0 mmol) to afford **2s** (1.30 g, 3.7 mmol, 73 %) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.06 (t, *J* = 6.8 Hz, 2H), 2.69 (t, *J* = 6.8 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.89, 132.13, 129.77, 127.65, 88.26, 67.29, 21.47, 21.31, -2.43. HRMS (APCI) calc. for $C_{11}H_{11}IO_3S^+$ $[M+H]^+$: 350.9474, found 350.9478.

***N*-butyl-*O*-(4-iodobut-3-ynoyl)hydroxylamine (2t)**



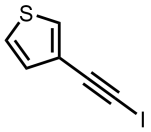
2t was used as received from Adamas-beta.

3-iodo-1-phenylprop-2-yn-1-ol (2u)



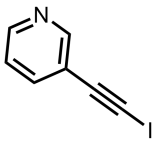
Following general procedure **GP3** with 1-phenyl-2-propyn-1-ol (0.66 g, 5.0 mmol) to afford **2u** (0.95 g, 3.7 mmol, 74 %) as colorless oil. The spectroscopic data match those previously reported in the literature.[17] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.47 (m, 2H), 7.42 – 7.32 (m, 3H), 5.52 (s, 1H), 3.37 (s, 1H).

3-(iodoethynyl)thiophene (2v)



Following general procedure **GP3** with 3-ethynylthiophene (0.54 g, 5.0 mmol) to afford **2v** (1.04 g, 4.5 mmol, 89 %) as a brown solid. The spectroscopic data match those previously reported in the literature.[13] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 3.0, 1.2 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.11 (dd, *J* = 5.0, 1.2 Hz, 1H).

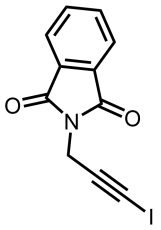
3-(iodoethynyl)pyridine (2w)



Following general procedure **GP3** with 3-ethynylpyridine (0.52 g, 5.0 mmol) to afford **2w** (0.91 g, 4.0 mmol, 79 %) as a yellow solid. The spectroscopic data match those previously reported in the literature.

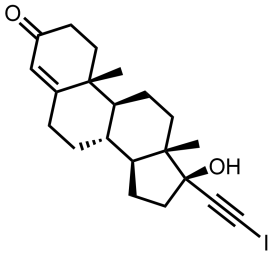
[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (dd, *J* = 2.2, 0.9 Hz, 1H), 8.53 (dd, *J* = 4.9, 1.7 Hz, 1H), 7.71 (dt, *J* = 7.9, 1.9 Hz, 1H), 7.27 – 7.22 (m, 1H).

2-(3-iodoprop-2-yn-1-yl)isoindoline-1,3-dione (2x)



Following general procedure **GP2** with 2-(prop-2-yn-1-yl)isoindoline-1,3-dione (0.93 g, 5.0 mmol) to afford **2x** (1.43 g, 4.6 mmol, 92 %) as a white solid. The spectroscopic data match those previously reported in the literature.[18] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.73 (dd, *J* = 5.5, 3.1 Hz, 2H), 4.57 (s, 2H).

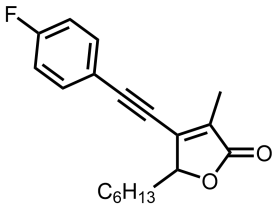
(8R,9S,10R,13S,14S,17S)-17-hydroxy-17-(iodoethynyl)-10,13-dimethyl-1,2,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-3*H*-cyclopenta[a]phenanthren-3-one (2y)



Following general procedure **GP2** with ethisterone (1.56 g, 5.0 mmol) to afford **2y** (1.91 g, 4.3 mmol, 87 %) as a white solid. Mp 145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.68 (d, *J* = 1.7 Hz, 1H), 2.69 (s, 3H), 2.37 – 2.29 (m, 2H), 2.26 – 2.15 (m, 2H), 2.02 – 1.86 (m, 2H), 1.58 (ddtd, *J* = 32.4, 21.5, 12.3, 10.9, 6.5 Hz, 6H), 1.42 – 1.23 (m, 3H), 1.13 (s, 3H), 1.07 – 0.86 (m, 2H), 0.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.89, 178.34, 171.66, 123.52, 97.77, 81.09, 52.99, 49.72, 46.98, 38.41, 35.93, 35.32, 33.65, 32.58, 31.18, 29.43, 22.92, 20.48, 17.19, 12.60, 1.95. HRMS (APCI) calc. for $C_{21}H_{27}IO_2^+$ $[M+H]^+$: 439.1058, found 439.1058.

VII. Characterization of Products 3 and 4

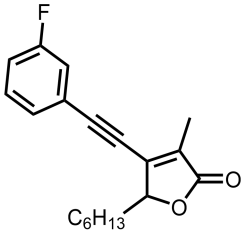
4-((4-fluorophenyl)ethynyl)-5-hexyl-3-methylfuran-2(5*H*)-one (3a)



Following general procedure **GP5** with ethyl 2-methyldeca-2,3-dienoate **1a** (42.1 mg, 0.2 mmol) and 1-fluoro-4-(iodoethynyl)benzene **2a** (73.8 mg, 0.3 mmol), the crude product was purified by flash column chromatography (Petroleum ether : EtOAc = 50 : 1) to afford **3a** as yellow oil (46.9 mg, 78 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.42 (m, 2H), 7.05 (t, *J* = 8.6 Hz, 2H), 4.87 (dq, *J* = 5.9, 1.9 Hz, 1H), 1.99 (d, *J* = 1.9 Hz, 3H), 1.60 (td, *J* = 14.2, 13.4, 8.8 Hz, 1H), 1.49 – 1.39 (m, 2H), 1.36 – 1.20 (m, 7H), 0.83 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.47, 164.49, 161.98, 143.10, 133.88,

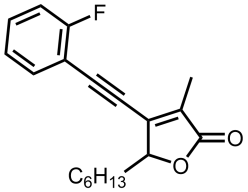
131.88, 117.48, 116.02, 115.80, 104.60, 82.12, 79.44, 32.93, 31.43, 28.79, 24.36, 22.35, 13.86, 10.15; ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.90; HRMS (APCI) calc. for $C_{19}H_{21}FO_2^+$ $[M+H]^+$: 301.1525, found 301.1527.

4-((3-fluorophenyl)ethynyl)-5-hexyl-3-methylfuran-2(5*H*)-one (3b)



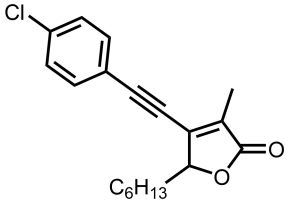
Following general procedure **GP5** with ethyl 2-methyldeca-2,3-dienoate **1a** (42.1 mg, 0.2 mmol) and 1-fluoro-3-(iodoethynyl)benzene **2b** (73.8 mg, 0.3 mmol), the crude product was purified by flash column chromatography (Petroleum ether : EtOAc = 50 : 1) to afford **3b** (42.3 mg, 70 %) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (td, *J* = 8.0, 5.6 Hz, 1H), 7.30 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.21 (ddd, *J* = 9.0, 2.7, 1.5 Hz, 1H), 7.13 (tdd, *J* = 8.4, 2.6, 1.2 Hz, 1H), 4.91 (ddd, *J* = 7.8, 3.8, 2.0 Hz, 1H), 2.04 (d, *J* = 1.9 Hz, 3H), 1.68 – 1.60 (m, 1H), 1.47 (q, *J* = 7.5, 5.5 Hz, 2H), 1.41 – 1.23 (m, 7H), 0.90 – 0.85 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.49, 163.56, 161.09, 142.83, 132.80, 127.75, 123.26, 118.70, 117.31, 104.12, 82.25, 80.40, 33.04, 31.55, 28.91, 24.48, 22.47, 13.98, 10.36; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.98; HRMS (APCI) calc. for $C_{19}H_{21}FO_2^+$ $[M+H]^+$: 301.1525, found 301.1526.

4-((2-fluorophenyl)ethynyl)-5-hexyl-3-methylfuran-2(5*H*)-one (3c)



Following general procedure **GP5** with ethyl 2-methyldeca-2,3-dienoate **1a** (42.1 mg, 0.2 mmol) and 1-fluoro-2-(iodoethynyl)benzene **2c** (73.8 mg, 0.3 mmol), the crude product was purified by flash column chromatography (Petroleum ether : EtOAc = 30 : 1) to afford **3c** (39.2 mg, 65 %) as a white solid. Mp 72 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (td, *J* = 7.3, 1.8 Hz, 1H), 7.40 (tdd, *J* = 7.4, 5.2, 1.7 Hz, 1H), 7.20 – 7.09 (m, 2H), 4.92 (ddd, *J* = 7.9, 3.9, 2.0 Hz, 1H), 2.03 (d, *J* = 2.0 Hz, 3H), 1.64 (td, *J* = 14.4, 8.0 Hz, 1H), 1.47 (h, *J* = 7.2, 6.3 Hz, 2H), 1.39 – 1.22 (m, 7H), 0.86 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.50, 163.84, 161.32, 142.95, 133.31, 132.57, 131.76, 124.20, 115.83, 110.30, 98.95, 82.19, 32.91, 31.46, 28.84, 24.36, 22.42, 13.93, 10.26; ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.45. HRMS (APCI) calc. for $C_{19}H_{21}FO_2^+$ $[M+H]^+$: 301.1525, found 301.1524.

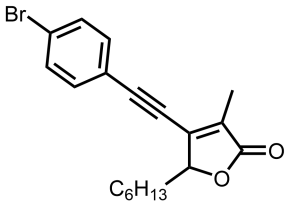
4-((4-chlorophenyl)ethynyl)-5-hexyl-3-methylfuran-2(5*H*)-one (3d)



Following general procedure **GP5** with ethyl 2-methyldeca-2,3-dienoate **1a** (42.1 mg, 0.2 mmol) and 1-chloro-4-(iodoethynyl)benzene **2d** (78.7 mg, 0.3 mmol), the crude product was purified by flash column chromatography (Petroleum ether : EtOAc = 50 : 1) to afford **3d** (44.1 mg, 69 %) as a white solid. Mp 67 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.41 (m, 2H), 7.39 – 7.34 (m, 2H), 4.90 (ddd, *J*

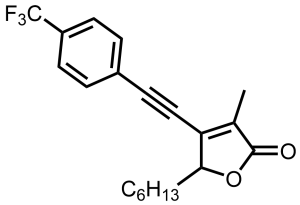
= 7.8, 3.8, 1.9 Hz, 1H), 2.03 (d, *J* = 1.9 Hz, 3H), 1.66 – 1.59 (m, 1H), 1.52 – 1.43 (m, 2H), 1.40 – 1.21 (m, 7H), 0.90 – 0.85 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.57, 143.01, 136.10, 133.03, 132.44, 129.02, 119.92, 104.47, 82.25, 80.64, 33.07, 31.56, 28.92, 24.50, 22.49, 14.00, 10.37. HRMS (APCI) calc. for $C_{19}H_{21}ClO_2^+$ $[M+H]^+$: 317.1230, found 317.1234.

4-((4-bromophenyl)ethynyl)-5-hexyl-3-methylfuran-2(5*H*)-one (3e)



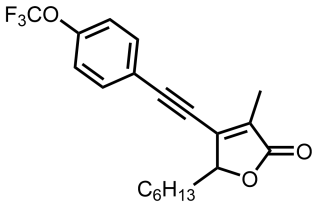
Following general procedure **GP5** with ethyl 2-methyldeca-2,3-dienoate **1a** (42.1 mg, 0.2 mmol) and 1-bromo-4-(iodoethynyl)benzene **2e** (92.1 mg, 0.3 mmol), the crude product was purified by flash column chromatography (Petroleum ether : EtOAc = 50 : 1) to afford **3e** (54.2 mg, 75 %) as a white solid. Mp 72 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.40 – 7.33 (m, 2H), 4.90 (ddd, *J* = 7.8, 3.8, 1.9 Hz, 1H), 2.02 (d, *J* = 1.9 Hz, 3H), 1.68 – 1.57 (m, 1H), 1.52 – 1.42 (m, 2H), 1.33 – 1.25 (m, 7H), 0.87 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.50, 142.96, 133.13, 132.41, 131.89, 124.34, 120.31, 104.48, 82.18, 80.73, 33.01, 31.51, 28.87, 24.45, 22.44, 13.97, 10.34. HRMS (APCI) calc. for $C_{19}H_{21}BrO_2^+$ $[M+H]^+$: 361.0715, found 361.0722.

5-hexyl-3-methyl-4-((4-(trifluoromethyl)phenyl)ethynyl)furan-2(5*H*)-one (3f)



Following general procedure **GP5** with ethyl 2-methyldeca-2,3-dienoate **1a** (42.1 mg, 0.2 mmol) and 1-(iodoethynyl)-4-(trifluoromethyl)benzene **2f** (88.8 mg, 0.3 mmol), the crude product was purified by flash column chromatography (Petroleum ether : EtOAc = 40 : 1) to afford **3f** (43.9 mg, 73 %) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.56 (m, 4H), 4.92 (ddd, *J* = 7.9, 3.9, 2.0 Hz, 1H), 2.04 (d, *J* = 1.9 Hz, 3H), 1.69 – 1.58 (m, 1H), 1.53 – 1.43 (m, 2H), 1.40 – 1.22 (m, 7H), 0.86 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.31, 142.51, 133.27, 132.05, 125.53, 125.50, 125.46, 125.16, 103.65, 82.19, 81.60, 33.02, 31.50, 28.86, 24.46, 22.43, 13.93, 10.37; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.06; HRMS (APCI) calc. for $C_{20}H_{21}F_3O_2^+$ $[M+H]^+$: 351.1529, found 351.1525.

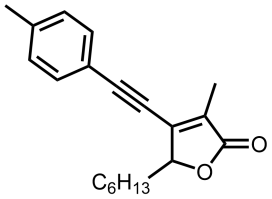
5-hexyl-3-methyl-4-((4-(trifluoromethoxy)phenyl)ethynyl)furan-2(5*H*)-one (3g)



Following general procedure **GP5** with ethyl 2-methyldeca-2,3-dienoate **1a** (42.1 mg, 0.2 mmol) and 1-(iodoethynyl)-4-(trifluoromethoxy)benzene **2g** (93.6 mg, 0.3 mmol), the crude product was purified by flash column chromatography (Petroleum ether : EtOAc = 40 : 1) to afford **3g** (54.6 mg, 74 %) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.50 (m, 2H), 7.26 – 7.19 (m, 2H), 4.91 (ddd, *J* = 7.9, 3.8, 2.0 Hz, 1H), 2.03 (d, *J* = 1.9 Hz, 3H), 1.68 – 1.58 (m, 1H), 1.52 – 1.42 (m, 2H), 1.30 (dtd, *J* = 20.4, 11.8, 10.5, 3.8 Hz, 7H), 0.89 – 0.84 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.50, 149.96,

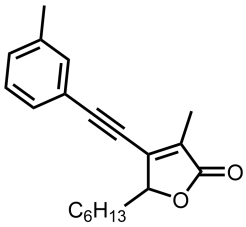
149.94, 142.89, 133.46, 132.59, 121.55, 120.96, 120.12, 118.98, 104.01, 82.22, 80.42, 33.03, 31.53, 28.89, 24.46, 22.45, 13.95, 10.32; ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.80; HRMS (APCI) calc. for $C_{20}H_{21}F_3O_3^+$ $[M+H]^+$: 367.1433, found 367.1430.

5-hexyl-3-methyl-4-(p-tolylethynyl)furan-2(5*H*)-one (3h)



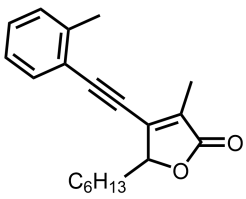
Following general procedure **GP5** with ethyl 2-methyldeca-2,3-dienoate **1a** (42.1 mg, 0.2 mmol) and 1-(iodoethynyl)-4-methylbenzene **2h** (72.6 mg, 0.3 mmol), the crude product was purified by flash column chromatography (Petroleum ether : EtOAc = 60 : 1) to afford **3h** (37.4 mg, 63 %) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 4.90 (ddd, *J* = 7.8, 3.8, 1.9 Hz, 1H), 2.39 (s, 3H), 2.03 (d, *J* = 1.9 Hz, 3H), 1.67 – 1.60 (m, 1H), 1.54 – 1.43 (m, 2H), 1.42 – 1.22 (m, 7H), 0.90 – 0.85 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.87, 143.72, 140.35, 131.78, 131.43, 129.36, 118.42, 106.33, 82.35, 79.35, 33.06, 31.57, 28.94, 24.49, 22.49, 21.62, 14.00, 10.28; HRMS (APCI) calc. for $C_{20}H_{24}O_2^+$ $[M+H]^+$: 297.1766, found 297.1767.

5-hexyl-3-methyl-4-(m-tolylethynyl)furan-2(5*H*)-one (3i)



Following general procedure **GP5** with ethyl 2-methyldeca-2,3-dienoate **1a** (42.1 mg, 0.2 mmol) and 1-(iodoethynyl)-3-methylbenzene **2i** (72.6 mg, 0.3 mmol), the crude product was purified by flash column chromatography (Petroleum ether : EtOAc = 60 : 1) to afford **3i** (44.5 mg, 75 %) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.35 – 7.17 (m, 3H), 4.92 (ddd, *J* = 7.7, 3.8, 2.0 Hz, 1H), 2.47 (s, 3H), 2.04 (d, *J* = 1.9 Hz, 3H), 1.71 – 1.60 (m, 1H), 1.52 – 1.43 (m, 2H), 1.36 – 1.25 (m, 7H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.74, 143.64, 140.44, 132.22, 131.51, 129.91, 129.72, 125.83, 121.26, 104.94, 83.57, 82.23, 32.99, 31.51, 28.89, 24.34, 22.45, 20.68, 13.96, 10.28; HRMS (APCI) calc. for $C_{20}H_{24}O_2^+$ $[M+H]^+$: 297.1766, found 297.1765.

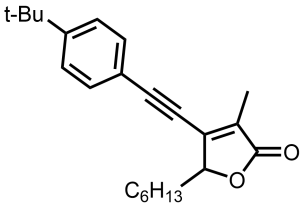
5-hexyl-3-methyl-4-(o-tolylethynyl)furan-2(5*H*)-one (3j)



Following general procedure **GP5** with ethyl 2-methyldeca-2,3-dienoate **1a** (42.1 mg, 0.2 mmol) and 1-(iodoethynyl)-2-methylbenzene **2j** (72.6 mg, 0.3 mmol), the crude product was purified by flash column chromatography (Petroleum ether : EtOAc = 40 : 1) to afford **3j** (38.5 mg, 65 %) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.19 (m, 4H), 4.89 (ddd, *J* = 7.8, 3.8, 2.0 Hz, 1H), 2.35 (s, 3H), 2.02 (d, *J* = 1.9 Hz, 3H), 1.67 – 1.57 (m, 1H), 1.51 – 1.41 (m, 2H), 1.30 (dtd, *J* = 18.9, 10.6, 8.8, 5.1 Hz, 7H), 0.88 – 0.83 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.80, 143.57, 138.38, 132.32, 131.72,

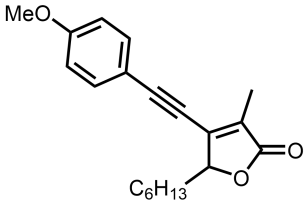
130.74, 128.94, 128.47, 121.24, 106.19, 82.33, 79.42, 33.02, 31.55, 28.91, 24.47, 22.47, 21.15, 13.99, 10.28; HRMS (APCI) calc. for $C_{20}H_{24}O_2^+$ $[M+H]^+$: 297.1766, found 297.1766.

4-((4-(tert-butyl)phenyl)ethynyl)-5-hexyl-3-methylfuran-2(5*H*)-one (3k)



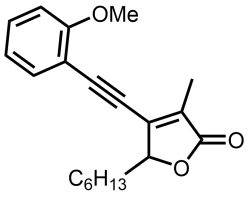
Following general procedure **GP5** with ethyl 2-methyldeca-2,3-dienoate **1a** (42.1 mg, 0.2 mmol) and 1-(tert-butyl)-4-(iodoethynyl)benzene **2k** (85.2 mg, 0.3 mmol), the crude product was purified by flash column chromatography (Petroleum ether : EtOAc = 50 : 1) to afford **3k** (46.1 mg, 68 %) as a white solid. Mp 76 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 4H), 4.90 (ddd, *J* = 7.8, 3.8, 1.9 Hz, 1H), 2.03 (d, *J* = 1.9 Hz, 3H), 1.69 – 1.59 (m, 1H), 1.52 – 1.43 (m, 2H), 1.38 – 1.26 (m, 16H), 0.87 (t, *J* = 3.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.85, 153.44, 143.72, 131.62, 131.43, 125.60, 118.41, 106.29, 82.33, 79.29, 34.94, 33.02, 31.54, 31.04, 28.92, 24.44, 22.47, 13.98, 10.26; HRMS (APCI) calc. for $C_{23}H_{30}O_2^+$ $[M+H]^+$: 339.2246, found 339.2248.

5-hexyl-4-((4-methoxyphenyl)ethynyl)-3-methylfuran-2(5*H*)-one (3l)



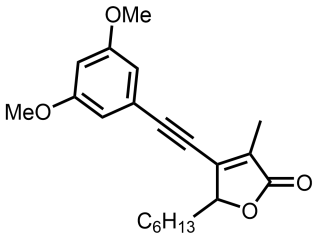
Following general procedure **GP5** with ethyl 2-methyldeca-2,3-dienoate **1a** (42.1 mg, 0.2 mmol) and 1-(iodoethynyl)-4-methoxybenzene **2l** (77.4 mg, 0.3 mmol), the crude product was purified by flash column chromatography (Petroleum ether : EtOAc = 50 : 1) to afford **3l** (43.8 mg, 70 %) as a white solid. Mp 74 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 2H), 6.92 – 6.88 (m, 2H), 4.89 (ddd, *J* = 7.8, 3.8, 1.9 Hz, 1H), 3.84 (s, 3H), 2.02 (d, *J* = 1.9 Hz, 3H), 1.68 – 1.58 (m, 1H), 1.52 – 1.42 (m, 2H), 1.31 (dtt, *J* = 17.0, 10.2, 5.8 Hz, 7H), 0.89 – 0.85 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.95, 160.84, 143.89, 133.52, 130.80, 114.26, 113.43, 106.44, 82.31, 78.95, 55.35, 33.05, 31.54, 28.91, 24.46, 22.46, 13.98, 10.21; HRMS (APCI) calc. for $C_{20}H_{24}O_3^+$ $[M+H]^+$: 313.1726, found 313.1724.

5-hexyl-4-((2-methoxyphenyl)ethynyl)-3-methylfuran-2(5*H*)-one (3m)



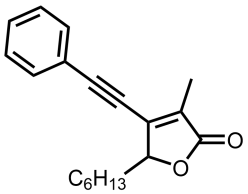
Following general procedure **GP5** with ethyl 2-methyldeca-2,3-dienoate **1a** (42.1 mg, 0.2 mmol) and 1-(iodoethynyl)-2-methoxybenzene **2m** (77.4 mg, 0.3 mmol), the crude product was purified by flash column chromatography (Petroleum ether : EtOAc = 30 : 1) to afford **3m** (42.5 mg, 67 %) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.36 (m, 2H), 6.94 (dd, *J* = 17.7, 8.0 Hz, 2H), 4.92 (ddd, *J* = 7.8, 3.9, 2.0 Hz, 1H), 3.90 (s, 3H), 2.04 (d, *J* = 1.9 Hz, 3H), 1.71 – 1.61 (m, 1H), 1.54 – 1.44 (m, 2H), 1.34 – 1.26 (m, 7H), 0.89 – 0.85 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.95, 160.27, 143.99, 133.43, 131.47, 131.18, 120.52, 110.73, 102.78, 83.86, 82.35, 55.73, 32.96, 31.50, 28.92, 24.42, 22.47, 13.97, 10.22; HRMS (APCI) calc. for $C_{20}H_{24}O_3^+$ $[M+H]^+$: 313.1726, found 313.1725.

4-((3,5-dimethoxyphenyl)ethynyl)-5-hexyl-3-methylfuran-2(5*H*)-one (3n)



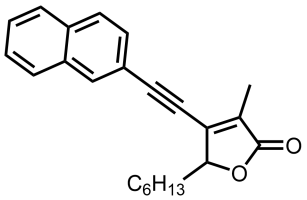
Following general procedure **GP5** with ethyl 2-methyldeca-2,3-dienoate **1a** (42.1 mg, 0.2 mmol) and 1-(iodoethynyl)-3,5-dimethoxybenzene **2n** (86.4 mg, 0.3 mmol), the crude product was purified by flash column chromatography (Petroleum ether : EtOAc = 30 : 1) to afford **3n** (37.7 mg, 55 %) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.64 (d, *J* = 2.3 Hz, 2H), 6.52 (t, *J* = 2.3 Hz, 1H), 4.90 (ddd, *J* = 7.9, 3.9, 2.0 Hz, 1H), 3.81 (s, 6H), 2.03 (d, *J* = 1.9 Hz, 3H), 1.69 – 1.58 (m, 1H), 1.47 (td, *J* = 9.6, 5.1 Hz, 2H), 1.42 – 1.19 (m, 7H), 0.90 – 0.84 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.71, 160.68, 143.30, 132.16, 122.65, 109.64, 105.78, 102.98, 82.32, 79.18, 55.48, 33.06, 31.57, 28.93, 24.50, 22.49, 14.00, 10.35; HRMS (APCI) calc. for $C_{21}H_{26}O_4^+$ $[M+H]^+$: 343.1832, found 343.1834.

5-hexyl-3-methyl-4-(phenylethynyl)furan-2(5*H*)-one (3o)



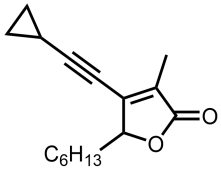
Following general procedure **GP5** with ethyl 2-methyldeca-2,3-dienoate **1a** (42.1 mg, 0.2 mmol) and (iodoethynyl)benzene **2o** (68.4 mg, 0.3 mmol), the crude product was purified by flash column chromatography (Petroleum ether : EtOAc = 60 : 1) to afford **3o** (36.8 mg, 65 %) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 2H), 7.45 – 7.35 (m, 3H), 4.91 (ddd, *J* = 7.8, 3.8, 1.9 Hz, 1H), 2.04 (d, *J* = 1.9 Hz, 3H), 1.68 – 1.61 (m, 1H), 1.53 – 1.43 (m, 2H), 1.41 – 1.21 (m, 7H), 0.90 – 0.85 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.74, 143.44, 131.94, 131.83, 129.83, 128.59, 121.47, 105.86, 82.33, 79.76, 33.05, 31.56, 28.93, 24.48, 22.48, 14.00, 10.31; HRMS (APCI) calc. for $C_{19}H_{22}O_2^+$ $[M+H]^+$: 283.1621, found 283.1623.

5-hexyl-3-methyl-4-(naphthalen-2-ylethynyl)furan-2(5*H*)-one (3p)



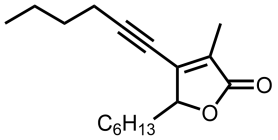
Following general procedure **GP5** with ethyl 2-methyldeca-2,3-dienoate **1a** (42.1 mg, 0.2 mmol) and 2-(iodoethynyl)naphthalene **2p** (83.4 mg, 0.3 mmol), the crude product was purified by flash column chromatography (Petroleum ether : EtOAc = 40 : 1) to afford **3p** (47.9 mg, 72 %) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 1.4 Hz, 1H), 7.85 (dt, *J* = 7.4, 2.1 Hz, 3H), 7.59 – 7.50 (m, 3H), 4.95 (ddq, *J* = 7.6, 3.7, 1.8 Hz, 1H), 2.09 (d, *J* = 1.9 Hz, 3H), 1.68 (dddd, *J* = 14.1, 10.1, 7.9, 5.4 Hz, 1H), 1.52 (ddq, *J* = 13.2, 10.2, 5.6 Hz, 2H), 1.46 – 1.22 (m, 7H), 0.92 – 0.85 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.80, 143.48, 133.40, 132.73, 132.39, 131.93, 128.37, 127.96, 127.84, 127.81, 127.55, 126.96, 118.62, 106.33, 82.35, 80.03, 33.08, 31.57, 28.93, 24.52, 22.49, 14.02, 10.38; HRMS (APCI) calc. for $C_{23}H_{24}O_2^+$ $[M+H]^+$: 333.1778, found 333.1777.

4-(cyclopropylethynyl)-5-hexyl-3-methylfuran-2(5*H*)-one (3q)



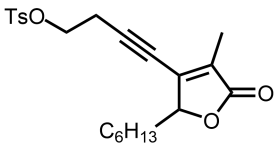
Following general procedure **GP5** with ethyl 2-methyldeca-2,3-dienoate **1a** (42.1 mg, 0.2 mmol) and (iodoethynyl)cyclopropane **2q** (57.6 mg, 0.3 mmol), the crude product was purified by flash column chromatography (Petroleum ether : EtOAc = 50 : 1) to afford **3q** (19.2 mg, 39 %) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.73 (ddd, *J* = 7.8, 3.7, 1.9 Hz, 1H), 1.90 (d, *J* = 1.9 Hz, 3H), 1.51 (tt, *J* = 8.6, 5.2 Hz, 2H), 1.44 – 1.37 (m, 2H), 1.28 (dtd, *J* = 12.8, 9.6, 8.5, 4.7 Hz, 9H), 0.98 (ddd, *J* = 8.1, 5.0, 1.8 Hz, 2H), 0.89 – 0.84 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.31, 144.53, 130.55, 112.02, 82.48, 67.03, 32.92, 31.55, 28.91, 24.43, 22.49, 14.02, 10.00, 9.64, 9.62; HRMS (APCI) calc. for $C_{16}H_{22}O_2^+$ $[M+H]^+$: 245.1622, found 245.1623.

4-(hex-1-yn-1-yl)-5-hexyl-3-methylfuran-2(5*H*)-one (3r)



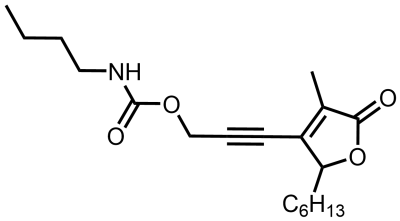
Following general procedure **GP5** with ethyl 2-methyldeca-2,3-dienoate **1a** (42.1 mg, 0.2 mmol) and 1-iodohept-1-yne **2r** (62.4 mg, 0.3 mmol), the crude product was purified by flash column chromatography (Petroleum ether : EtOAc = 50 : 1) to afford **3r** (31.0 mg, 59 %) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.77 (ddd, *J* = 7.8, 3.9, 2.0 Hz, 1H), 2.49 (t, *J* = 7.0 Hz, 2H), 1.93 (d, *J* = 1.9 Hz, 3H), 1.64 – 1.58 (m, 2H), 1.55 (d, *J* = 8.3 Hz, 1H), 1.46 (dq, *J* = 13.4, 6.6 Hz, 3H), 1.36 – 1.24 (m, 7H), 0.95 (t, *J* = 7.3 Hz, 3H), 0.88 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.29, 144.59, 130.79, 108.68, 82.52, 71.85, 32.85, 31.55, 30.28, 28.92, 24.38, 22.50, 21.91, 19.62, 14.03, 13.51, 10.03; HRMS (APCI) calc. for $C_{17}H_{26}O_2^+$ $[M+H]^+$: 263.1935, found 263.1934.

4-(2-hexyl-4-methyl-5-oxo-2,5-dihydrofuran-3-yl)but-3-yn-1-yl 4-methylbenzenesulfonate (3s)



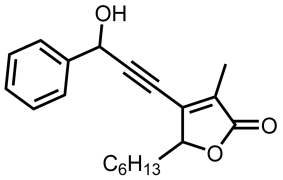
Following general procedure **GP5** with ethyl 2-methyldeca-2,3-dienoate **1a** (42.1 mg, 0.2 mmol) and 4-iodobut-3-yn-1-yl 4-methylbenzenesulfonate **2s** (105.1 mg, 0.3 mmol), the crude product was purified by flash column chromatography (Petroleum ether : EtOAc = 15 : 1) to afford **3s** (36.4 mg, 45 %) as a white solid. Mp 71 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.74 (ddd, *J* = 7.9, 3.7, 1.9 Hz, 1H), 4.18 (t, *J* = 6.7 Hz, 2H), 2.87 (t, *J* = 6.7 Hz, 2H), 2.45 (s, 3H), 1.89 (d, *J* = 1.8 Hz, 3H), 1.54 – 1.44 (m, 1H), 1.39 (td, *J* = 9.7, 8.7, 4.8 Hz, 2H), 1.35 – 1.20 (m, 7H), 0.87 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.78, 145.19, 143.24, 132.75, 132.38, 129.93, 127.86, 101.57, 82.36, 73.67, 66.75, 32.82, 31.54, 28.87, 24.46, 22.48, 21.64, 20.97, 14.01, 10.11; HRMS (APCI) calc. for $C_{22}H_{28}O_5S^+$ $[M+H]^+$: 405.1657, found 405.1655.

3-(2-hexyl-4-methyl-5-oxo-2,5-dihydrofuran-3-yl)prop-2-yn-1-yl butylcarbamate (3t)



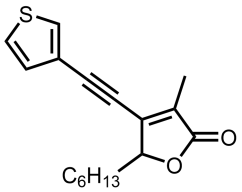
Following general procedure **GP5** with ethyl 2-methyldeca-2,3-dienoate **1a** (42.1 mg, 0.2 mmol) and *N*-butyl-*O*-(4-iodobut-3-ynoyl)hydroxylamine **2t** (84.3 mg, 0.3 mmol), the crude product was purified by flash column chromatography (Petroleum ether : EtOAc = 20 : 1) to afford **3t** (36.4 mg, 54 %) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.91 (s, 2H), 4.81 (ddd, *J* = 8.2, 3.9, 2.1 Hz, 1H), 3.25 – 3.12 (m, 2H), 1.95 (d, *J* = 1.9 Hz, 3H), 1.67 (s, 1H), 1.59 – 1.21 (m, 14H), 0.92 (t, *J* = 7.3 Hz, 3H), 0.87 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.55, 155.16, 142.50, 133.26, 100.60, 82.27, 52.59, 40.91, 32.84, 31.88, 31.52, 29.66, 28.88, 24.47, 22.48, 19.80, 14.01, 13.67, 10.25; HRMS (APCI) calc. for $C_{19}H_{29}NO_4^+$ $[M+H]^+$: 336.2098, found 336.2099.

5-hexyl-4-(3-hydroxy-3-phenylprop-1-yn-1-yl)-3-methylfuran-2(5*H*)-one (3u)



Following general procedure **GP5** with ethyl 2-methyldeca-2,3-dienoate **1a** (42.1 mg, 0.2 mmol) and 3-iodo-1-phenylprop-2-yn-1-ol **2u** (77.4 mg, 0.3 mmol), the crude product was purified by flash column chromatography (Petroleum ether : EtOAc = 20 : 1) to afford **3u** (28.7 mg, 46 %) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 2H), 7.44 – 7.35 (m, 3H), 5.72 (s, 1H), 4.84 (ddq, *J* = 7.8, 3.9, 2.0 Hz, 1H), 2.73 (s, 1H), 1.97 (d, *J* = 1.9 Hz, 3H), 1.56 (dddd, *J* = 19.6, 9.8, 5.2, 1.8 Hz, 1H), 1.48 – 1.36 (m, 2H), 1.36 – 1.17 (m, 7H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.64, 142.72, 139.49, 133.06, 133.05, 128.85, 126.51, 105.67, 105.64, 82.35, 65.06, 32.85, 31.49, 28.86, 24.39, 22.47, 14.00, 10.31; HRMS (APCI) calc. for $C_{20}H_{24}O_3^+$ $[M+H]^+$: 313.1725, found 313.1724.

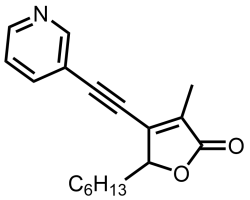
5-hexyl-3-methyl-4-(thiophen-3-ylethynyl)furan-2(5*H*)-one (3v)



Following general procedure **GP5** with ethyl 2-methyldeca-2,3-dienoate **1a** (42.1 mg, 0.2 mmol) and 3-(iodoethynyl)thiophene **2v** (70.4 mg, 0.3 mmol), the crude product was purified by flash column chromatography (Petroleum ether : EtOAc = 30 : 1) to afford **3v** (33.4 mg, 58 %) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.5, 1.8 Hz, 2H), 7.44 – 7.37 (m, 3H), 5.73 (d, *J* = 4.8 Hz, 1H), 4.84 (ddd, *J* = 7.9, 3.8, 2.0 Hz, 1H), 2.64 (d, *J* = 5.8 Hz, 1H), 1.97 (d, *J* = 1.8 Hz, 3H), 1.63 – 1.51 (m, 1H), 1.41 (ddd, *J* = 10.2, 7.6, 4.7 Hz, 2H), 1.36 – 1.19 (m, 7H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.53, 142.57, 139.44, 133.25, 133.24, 128.97, 128.93, 126.61, 126.55, 105.42,

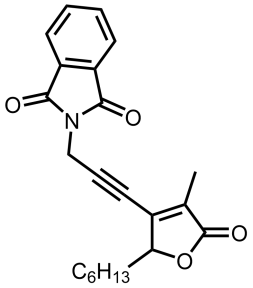
105.40, 82.30, 65.18, 32.91, 31.53, 28.90, 24.43, 22.51, 14.03, 10.37; HRMS (APCI) calc. for $C_{17}H_{20}O_2S^+$ $[M+H]^+$: 289.1185, found 289.1184.

5-hexyl-3-methyl-4-(pyridin-3-ylethynyl)furan-2(5*H*)-one (3w)



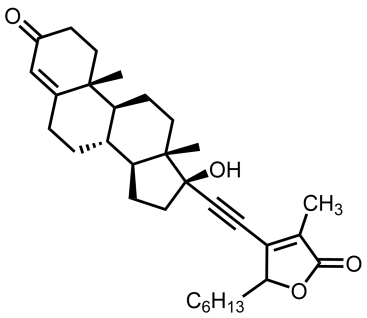
Following general procedure **GP5** with ethyl 2-methyldeca-2,3-dienoate **1a** (42.1 mg, 0.2 mmol) and 3-(iodoethynyl)pyridine **2w** (73.8 mg, 0.3 mmol), the crude product was purified by flash column chromatography (Petroleum ether : EtOAc = 40 : 1) to afford **3w** (34.1 mg, 60 %) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 – 8.71 (m, 1H), 8.62 (dd, *J* = 4.9, 1.7 Hz, 1H), 7.80 (dt, *J* = 7.9, 1.9 Hz, 1H), 7.36 – 7.30 (m, 1H), 4.92 (ddd, *J* = 7.8, 3.8, 1.9 Hz, 1H), 2.04 (d, *J* = 1.9 Hz, 3H), 1.63 (dddd, *J* = 14.1, 9.9, 7.9, 5.5 Hz, 1H), 1.46 (dtd, *J* = 11.3, 6.6, 6.2, 3.2 Hz, 2H), 1.30 (ttd, *J* = 15.3, 7.9, 2.8 Hz, 7H), 0.89 – 0.83 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.32, 152.20, 149.93, 142.45, 138.63, 133.21, 123.19, 118.71, 101.87, 82.71, 82.18, 33.02, 31.51, 28.87, 24.46, 22.44, 13.96, 10.41; HRMS (APCI) calc. for $C_{18}H_{21}NO_2^+$ $[M+H]^+$: 284.1572, found 284.1571.

2-(3-(2-hexyl-4-methyl-5-oxo-2,5-dihydrofuran-3-yl)prop-2-yn-1-yl)isoindoline-1,3-dione (3x)



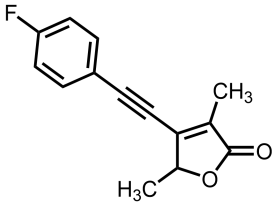
Following general procedure **GP5** with ethyl 2-methyldeca-2,3-dienoate **1a** (42.1 mg, 0.2 mmol) and 2-(3-iodoprop-2-yn-1-yl)isoindoline-1,3-dione **2x** (89.1 mg, 0.3 mmol), the crude product was purified by flash column chromatography (Petroleum ether : EtOAc = 15 : 1) to afford **3x** (25.5 mg, 35 %) as a white solid. Mp 74 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dt, *J* = 7.4, 3.7 Hz, 2H), 7.76 (dd, *J* = 5.5, 3.0 Hz, 2H), 4.77 (ddd, *J* = 8.0, 3.8, 2.0 Hz, 1H), 4.71 (s, 2H), 1.91 (d, *J* = 1.8 Hz, 3H), 1.55 – 1.45 (m, 1H), 1.37 (dq, *J* = 13.5, 5.8, 4.5 Hz, 2H), 1.33 – 1.17 (m, 7H), 0.83 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.84, 164.59, 162.08, 148.39, 134.00, 133.91, 130.51, 117.61, 117.57, 116.17, 115.95, 105.28, 85.65, 38.10, 31.21, 29.67, 25.49, 14.11, 10.43; HRMS (APCI) calc. for $C_{18}H_{21}NO_2^+$ $[M+H]^+$: 366.1628, found 366.1626.

5-hexyl-4-(((8R,9S,10R,13S,14S,17S)-17-hydroxy-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-17-yl)ethynyl)-3-methylfuran-2(5H)-one (3y)



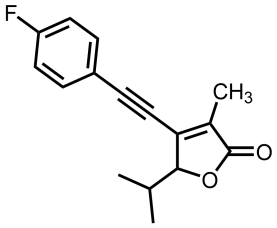
Following general procedure **GP5** with ethyl 2-methyldeca-2,3-dienoate **1a** (42.1 mg, 0.2 mmol) and (8R,9S,10R,13S,14S,17S)-17-hydroxy-17-(iodoethynyl)-10,13-dimethyl-1,2,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-3H-cyclopenta[a]phenanthren-3-one **2y** (131.8 mg, 0.3 mmol), the crude product was purified by flash column chromatography (Petroleum ether : EtOAc = 10 : 1) to afford **3y** (39.5 mg, 40 %) as a white solid. Mp 117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.76 – 5.70 (m, 1H), 4.82 (dq, *J* = 5.8, 1.9 Hz, 1H), 2.49 – 2.25 (m, 5H), 2.18 – 2.01 (m, 3H), 1.95 (d, *J* = 1.8 Hz, 3H), 1.87 (ddt, *J* = 14.1, 5.0, 2.9 Hz, 1H), 1.79 – 1.52 (m, 8H), 1.42 (dt, *J* = 14.6, 10.5 Hz, 5H), 1.34 – 1.23 (m, 7H), 1.21 (s, 3H), 1.09 – 0.97 (m, 1H), 0.95 (s, 3H), 0.86 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.31, 173.62, 170.65, 143.06, 131.99, 123.96, 109.97, 82.18, 82.15, 80.27, 53.70, 50.58, 47.26, 39.09, 38.52, 36.13, 35.69, 33.82, 32.84, 32.60, 31.52, 31.47, 28.98, 24.26, 24.19, 23.10, 22.47, 20.66, 17.34, 13.98, 12.75, 10.32; HRMS (APCI) calc. for $C_{32}H_{44}O_4^+$ $[M+H]^+$: 493.3239, found 493.3236.

4-((4-fluorophenyl)ethynyl)-3,5-dimethylfuran-2(5*H*)-one (4a)



Following general procedure **GP5** with ethyl 2-methylpenta-2,3-dienoate **1b** (28.0 mg, 0.2 mmol) and 1-fluoro-4-(iodoethynyl)benzene **2a** (73.8 mg, 0.3 mmol), the crude product was purified by flash column chromatography (Petroleum ether : EtOAc = 50 : 1) to afford **4a** (36.9 mg, 80 %) as a white solid. Mp 77 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 7.13 – 7.05 (m, 2H), 4.98 (dddd, *J* = 8.6, 6.7, 4.9, 1.8 Hz, 1H), 2.03 (d, *J* = 1.8 Hz, 3H), 1.53 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.47, 164.61, 162.10, 144.27, 134.00, 133.91, 131.68, 117.50, 116.17, 115.95, 104.74, 78.62, 18.93, 10.35; ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.85; HRMS (APCI) calc. for $C_{14}H_{11}FO_2^+$ $[M+H]^+$: 231.0744, found 231.0745.

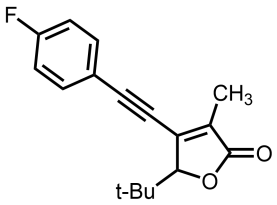
4-((4-fluorophenyl)ethynyl)-5-isopropyl-3-methylfuran-2(5*H*)-one (4b)



Following general procedure **GP5** with ethyl 2,5-dimethylhexa-2,3-dienoate **1c** (33.6 mg, 0.2 mmol) and 1-fluoro-4-(iodoethynyl)benzene **2a** (73.8 mg, 0.3 mmol), the crude product was purified by flash column chromatography (Petroleum ether : EtOAc = 50 : 1) to afford **4b** (30.1 mg, 59 %) as yellow oil.

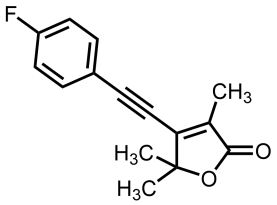
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 2H), 7.13 – 7.03 (m, 2H), 4.83 (dq, *J* = 3.8, 2.0 Hz, 1H), 2.26 (dqd, *J* = 14.4, 7.2, 2.8 Hz, 1H), 2.04 (d, *J* = 1.9 Hz, 3H), 1.15 (d, *J* = 6.9 Hz, 3H), 0.87 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.81, 164.63, 162.13, 142.16, 133.88, 132.80, 117.60, 116.17, 115.95, 104.78, 86.29, 79.81, 30.88, 18.92, 14.88, 10.28; ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.90; HRMS (APCI) calc. for $C_{16}H_{15}FO_2^+$ $[M+H]^+$: 259.1056, found 259.1055.

5-(tert-butyl)-4-((4-fluorophenyl)ethynyl)-3-methylfuran-2(5*H*)-one (4c)



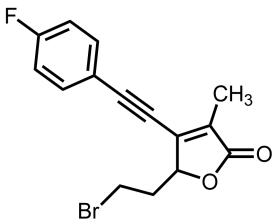
Following general procedure **GP5** with ethyl 2,5,5-trimethylhexa-2,3-dienoate **1d** (36.5 mg, 0.2 mmol) and 1-fluoro-4-(iodoethynyl)benzene **2a** (73.8 mg, 0.3 mmol), the crude product was purified by flash column chromatography (Petroleum ether : EtOAc = 50 : 1) to afford **4c** (27.1 mg, 50 %) as a white solid. Mp 84 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.43 (m, 2H), 7.11 – 7.03 (m, 2H), 4.63 (q, *J* = 1.9 Hz, 1H), 2.04 (d, *J* = 1.9 Hz, 3H), 1.08 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.39, 164.57, 162.07, 141.31, 134.02, 133.68, 133.60, 117.72, 117.69, 116.16, 115.94, 105.48, 89.26, 81.23, 35.71, 25.60, 10.31; ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.90; HRMS (APCI) calc. for $C_{17}H_{17}FO_2^+$ $[M+H]^+$: 273.1213, found 273.1215.

4-((4-fluorophenyl)ethynyl)-3,5,5-trimethylfuran-2(5*H*)-one (4d)



Following general procedure **GP5** with ethyl 2,4-dimethylpenta-2,3-dienoate **1e** (30.8 mg, 0.2 mmol) and 1-fluoro-4-(iodoethynyl)benzene **2a** (73.8 mg, 0.3 mmol), the crude product was purified by flash column chromatography (Petroleum ether : EtOAc = 50 : 1) to afford **4d** (18.6 mg, 38 %) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.47 (m, 2H), 7.15 – 7.04 (m, 2H), 2.01 (s, 3H), 1.55 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.49, 166.73, 142.45, 134.39, 133.45, 131.75, 123.65, 99.35, 82.22, 73.88, 32.76, 31.44, 28.80, 27.87, 24.36, 22.43, 13.96, 10.25; ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.93; HRMS (APCI) calc. for $C_{15}H_{13}FO_2^+$ $[M+H]^+$: 245.0911, found 245.0909.

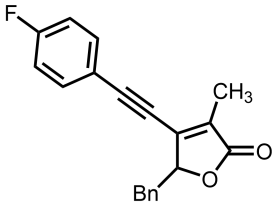
5-(2-bromoethyl)-4-((4-fluorophenyl)ethynyl)-3-methylfuran-2(5*H*)-one (4e)



Following general procedure **GP5** with ethyl 6-bromo-2-methylhexa-2,3-dienoate **1f** (46.4 mg, 0.2 mmol) and 1-fluoro-4-(iodoethynyl)benzene **2a** (73.8 mg, 0.3 mmol), the crude product was purified by flash column chromatography (Petroleum ether : EtOAc = 30 : 1) to afford **4e**(34.8 mg, 54 %) as a white solid. Mp 77 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (ddd, *J* = 7.9, 5.0, 2.3 Hz, 2H), 7.14 – 7.05 (m, 2H), 5.11 (ddd, *J* = 9.2, 3.2, 1.8 Hz, 1H), 3.68 – 3.49 (m, 2H), 2.57 – 2.44 (m, 1H), 2.17 – 2.06 (m,

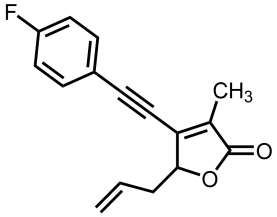
1H), 2.04 (d, *J* = 1.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.01, 164.76, 162.24, 142.27, 134.02, 132.31, 117.30, 116.24, 105.55, 79.86, 40.21, 36.62, 27.92, 10.39; ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.42; HRMS (APCI) calc. for $C_{15}H_{12}BrFO_2^+$ $[M+H]^+$: 323.0005, found 323.0006.

5-benzyl-4-((4-fluorophenyl)ethynyl)-3-methylfuran-2(5H)-one (4f)



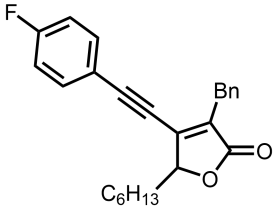
Following general procedure **GP5** with ethyl 2-methyl-5-phenylpenta-2,3-dienoate **1g** (43.3 mg, 0.2 mmol) and 1-fluoro-4-(iodoethynyl)benzene **2a** (73.8 mg, 0.3 mmol), the crude product was purified by flash column chromatography (Petroleum ether : EtOAc = 40 : 1) to afford **4f** (41.0 mg, 67 %) as a white solid. Mp 92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.29 – 7.21 (m, 5H), 7.12 – 7.05 (m, 2H), 5.13 (tt, *J* = 4.6, 2.1 Hz, 1H), 3.28 (dd, *J* = 14.4, 4.6 Hz, 1H), 3.03 (dd, *J* = 14.4, 6.5 Hz, 1H), 1.93 (d, *J* = 1.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.14, 164.64, 162.13, 142.20, 134.71, 134.05, 133.96, 132.85, 129.68, 128.32, 127.03, 117.50, 117.46, 116.15, 115.92, 105.33, 82.01, 79.60, 79.59, 39.08, 10.23; ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.72; HRMS (APCI) calc. for $C_{20}H_{15}FO_2^+$ $[M+H]^+$: 307.1058, found 307.1059.

5-allyl-4-((4-fluorophenyl)ethynyl)-3-methylfuran-2(5H)-one (4g)



Following general procedure **GP5** with ethyl 2-methylhepta-2,3,6-trienoate **1h** (33.2 mg, 0.2 mmol) and 1-fluoro-4-(iodoethynyl)benzene **2a** (73.8 mg, 0.3 mmol), the crude product was purified by flash column chromatography (Petroleum ether : EtOAc = 40 : 1) to afford **4g** (33.3 mg, 65 %) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.45 (m, 2H), 7.15 – 7.04 (m, 2H), 5.78 (ddt, *J* = 17.1, 10.1, 7.0 Hz, 1H), 5.28 – 5.12 (m, 2H), 4.97 (ddq, *J* = 6.2, 4.0, 1.9 Hz, 1H), 2.84 – 2.71 (m, 1H), 2.47 (dtt, *J* = 14.7, 6.8, 1.3 Hz, 1H), 2.03 (d, *J* = 1.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.41, 164.64, 162.13, 142.40, 133.90, 132.62, 130.83, 119.60, 117.52, 116.20, 115.97, 104.98, 81.23, 79.38, 36.88, 10.34; ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.78; HRMS (APCI) calc. for $C_{16}H_{13}FO_2^+$ $[M+H]^+$: 257.0989, found 257.0988.

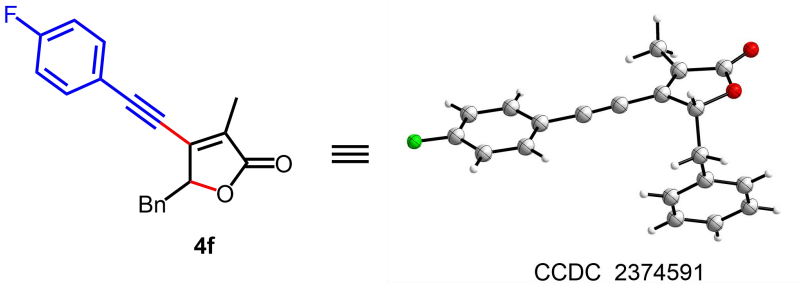
3-benzyl-4-((4-fluorophenyl)ethynyl)-5-hexylfuran-2(5H)-one (4h)



Following general procedure **GP5** with ethyl 2-benzyldeca-2,3-dienoate **1i** (57.3 mg, 0.2 mmol) and 1-fluoro-4-(iodoethynyl)benzene **2a** (73.8 mg, 0.3 mmol), the crude product was purified by flash column chromatography (Petroleum ether : EtOAc = 30 : 1) to afford **4h** (33.9 mg, 45 %) as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 2H), 7.37 – 7.27 (m, 4H), 7.25 – 7.20 (m, 1H), 7.13 – 7.05 (m, 2H), 4.93 (dd, *J* = 7.8, 3.6 Hz, 1H), 3.77 (s, 2H), 1.68 – 1.61 (m, 1H), 1.51 – 1.41 (m, 2H), 1.37 – 1.23 (m, 7H), 0.91 – 0.83 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.24, 170.50, 144.57, 135.70, 130.75, 121.42, 108.67, 85.51, 82.48, 71.82, 32.82, 31.52, 30.25, 28.89, 24.34, 22.47, 21.88, 19.59, 13.99, 13.47, 9.99; ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.58; HRMS (APCI) calc. for $C_{25}H_{25}FO_2^+$ $[M+H]^+$: 377.1836, found 377.1835.

VIII. Crystallographic Data of Substrate 4f



Single crystal diffraction data by XtaLAB AFC12 (RINC) single crystal diffractometer was then collected under 100 K. The light source of the single crystal diffractometer adopts Cu-Kα (λ = 1.54184) monochromatized by a graphite monochromator.

Suitable single crystals of **4f** were mounted with nylon loops. Data was collected on an Oxford Diffraction XtalAB [Rigaku (Cu) Xray dual wavelength source, Kα, λ = 1.5418 Å] equipped with a monochromator and CCD plate detector (CrysAlisPro CCD, Oxford Diffraction Ltd) at 100 K. The structure was solved by direct methods and refined by full-matrix least-squares refinements based on F^2. Single-crystal structures of compounds **4f** were solved by direct methods by ShelXS in Olex2 1.2. All non-hydrogen atoms were refined with anisotropic thermal parameters, and all hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those of the parent atoms.

Crystal data and structure refinement parameters were summarized in following Table. CCDC Number 2374591 (**4f**) contain the supplementary crystallographic data for this paper.

These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Bond precision: C-C = 0.0020 A Wavelength=1.54184

Cell: a=8.4867(3) b=9.8286(4) c=10.2689(5)

alpha=104.731(4) beta=100.536(4) gamma=100.806(3)

Temperature: 100 K

	Calculated	Reported
Volume	789.39(6)	789.39(6)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C20 H15 F O2	C20 H15 F O2
Sum formula	C20 H15 F O2	C20 H15 F O2
Mr	306.32	306.32
Dx,g cm-3	1.289	1.289
Z	2	2
Mu (mm-1)	0.738	0.738
F000	320.0	320.0
F000’	321.03	
h,k,lmax	10,12,12	10,12,12
Nref	3341	3203
Tmin,Tmax	0.737,0.801	0.907,1.000
Tmin’	0.659	

Correction method= # Reported T Limits: Tmin=0.907 Tmax=1.000

AbsCorr = MULTI-SCAN

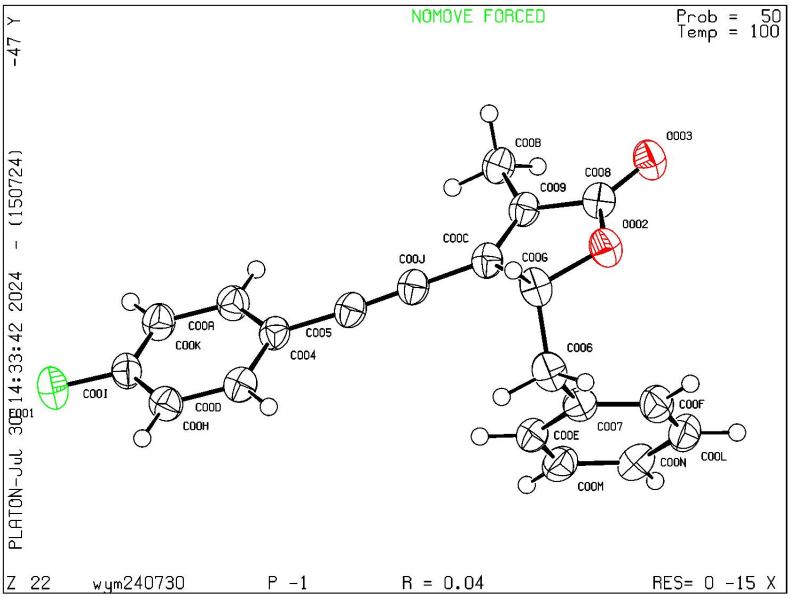
Data completeness= 0.959 Theta(max)= 77.262

R(reflections)= 0.0441(2747)

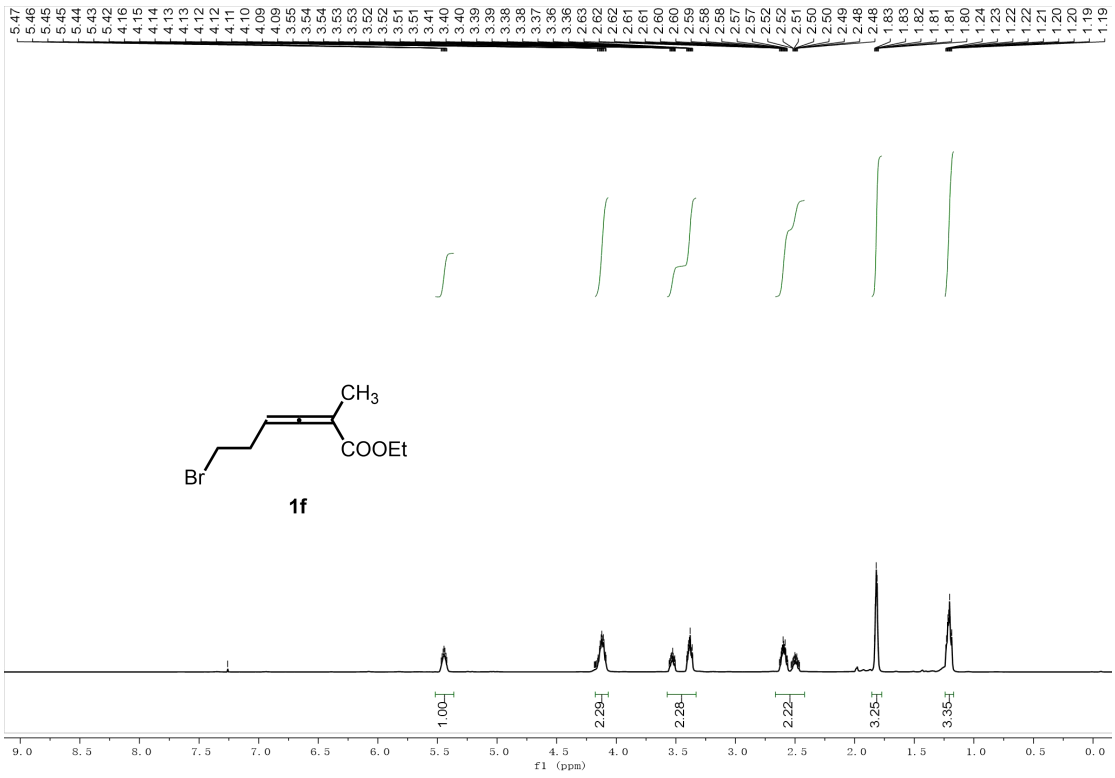
wR2(reflections)= 0.1269(3203)

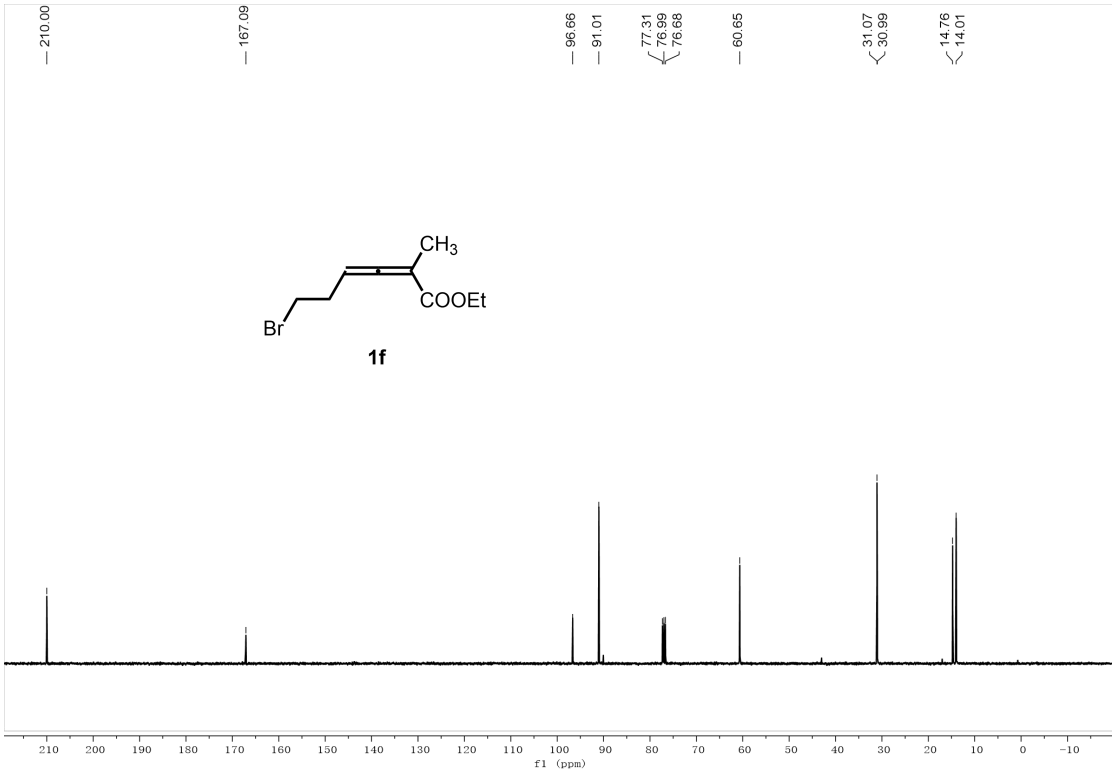
S = 1.104 Npar= 209

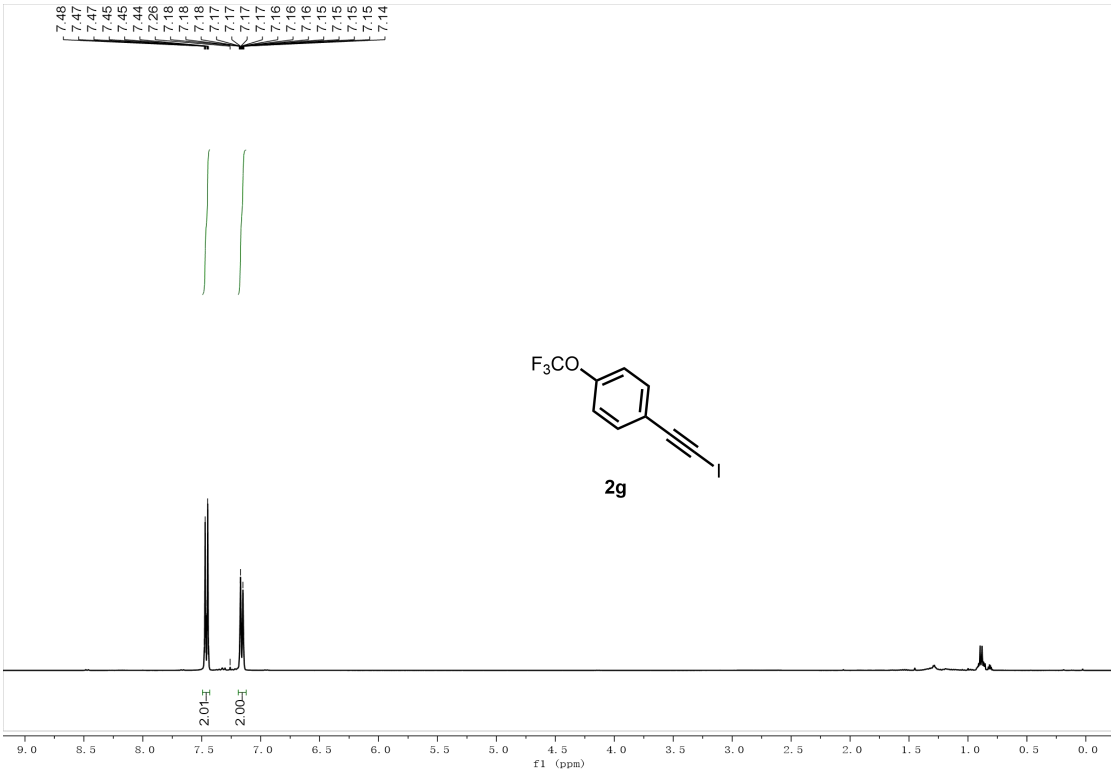
X-ray structure of 4f



IX. NMR Spectral Data



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7.47
7.47
7.45
7.45
7.44
7.26
7.18
7.18
7.18
7.17
7.17
7.17
7.17
7.16
7.16
7.16
7.15
7.15
7.15
7.15
7.14
F3CO
I
2g
2.01
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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2.5
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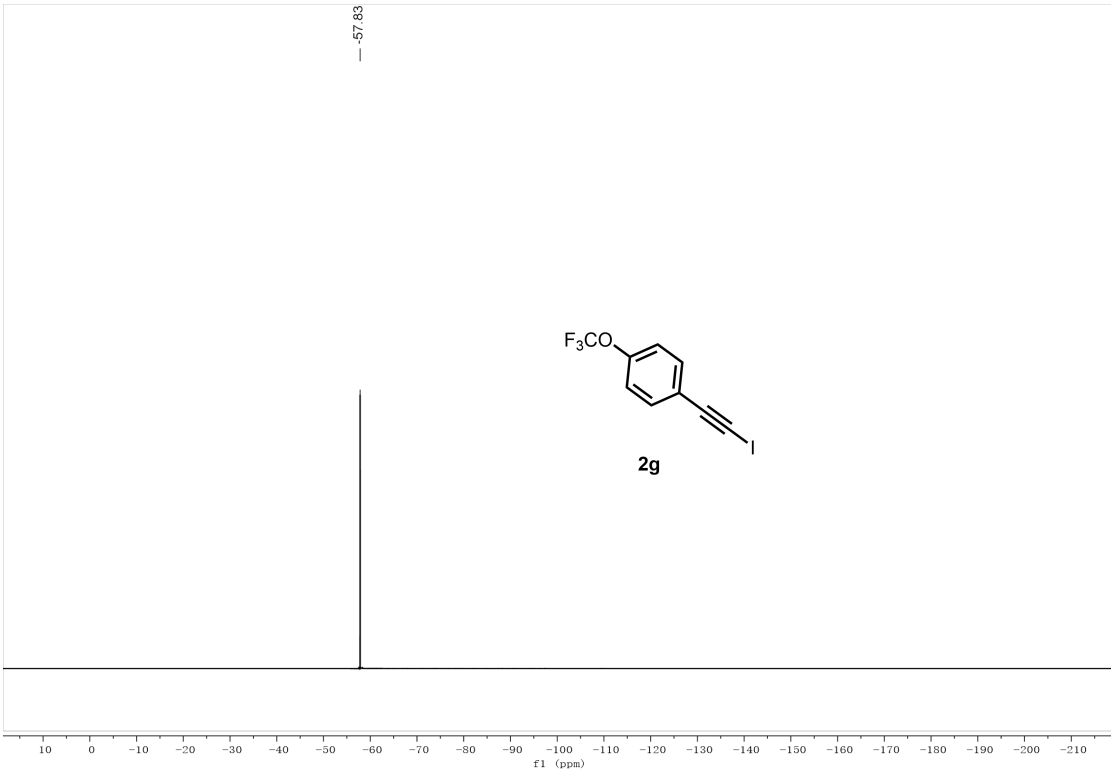
0.0
f1 (ppm)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F3CO
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-60
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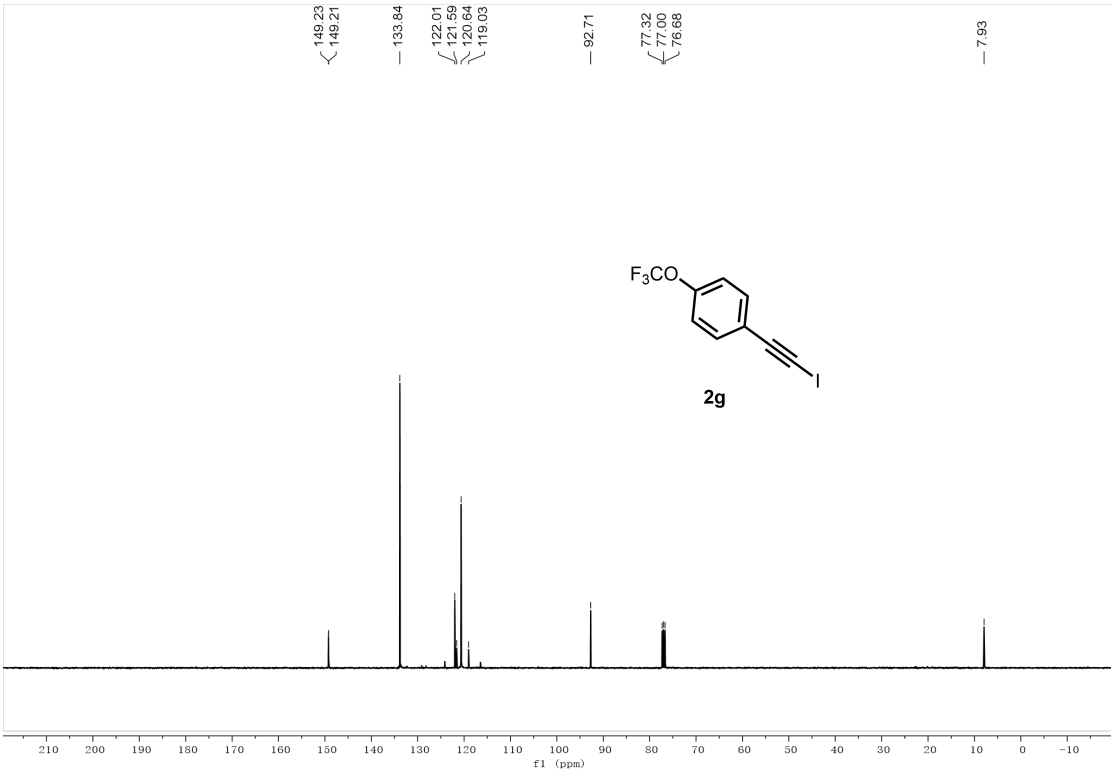
-170
-180
-190
-200
-210
f1 (ppm)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149.21
133.84
122.01
121.59
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119.03
92.71
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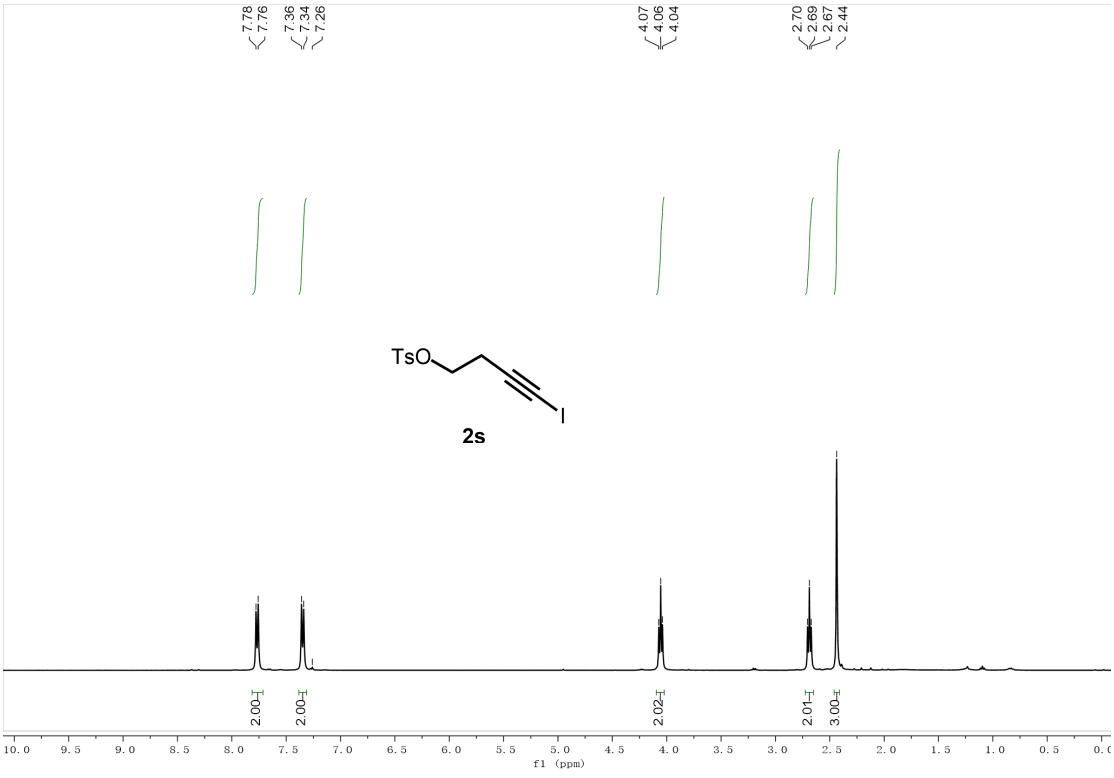
77.00
76.68
7.93
F3CO
I
2g
f1 (ppm)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4.04
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I
2s
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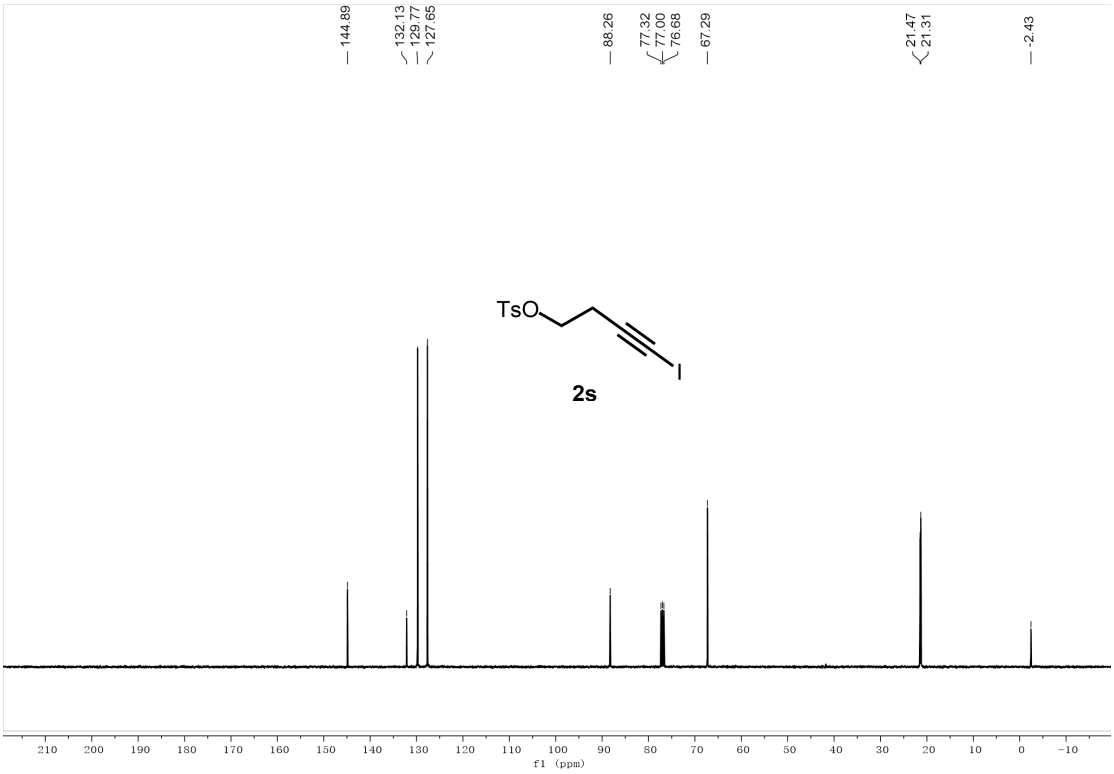
2.00
2.02
2.01
3.00
f1 (ppm)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127.65
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77.32
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76.68
67.29
21.47
21.31
-2.43
TsO
I
2s
f1 (ppm)


5.68
5.68
2.69
2.37
2.35
2.33
2.32
2.31
2.31
2.30
2.28
2.28
2.25
2.24
2.23
2.23
2.22
2.21
2.20
2.19
2.18
1.99
1.99
1.98
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1.96
1.95
1.94
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1.92
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1.31
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1.28
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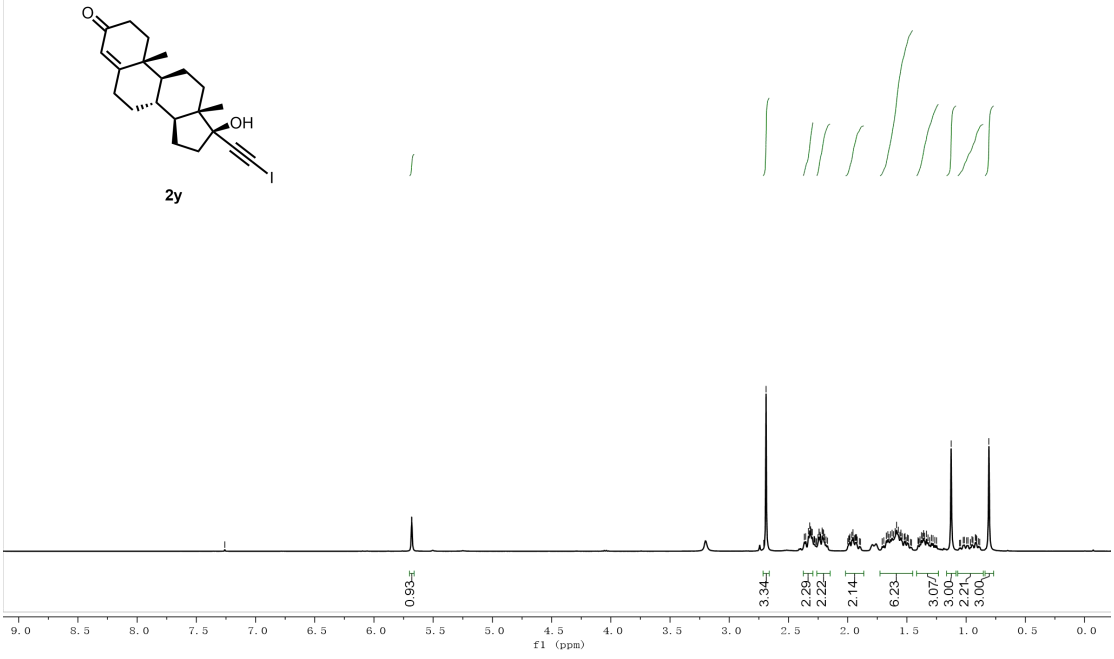
0.81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2.21
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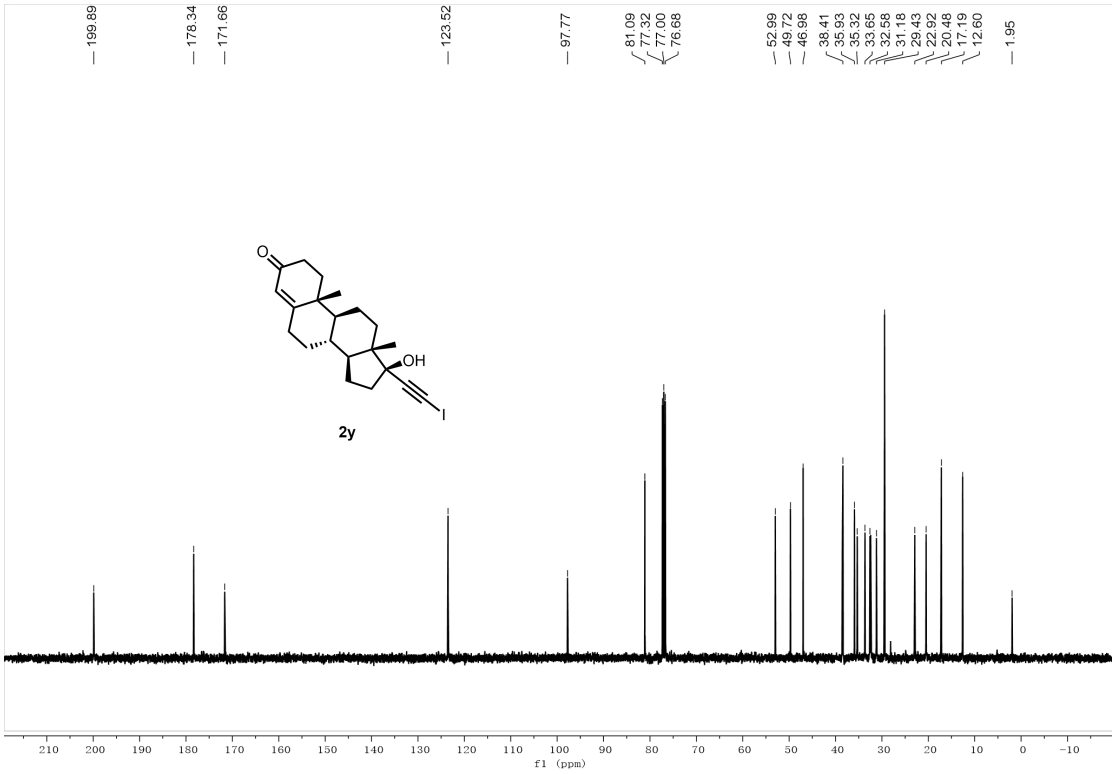
f1 (ppm)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123.52
97.77
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77.00
76.68
52.99
49.72
46.98
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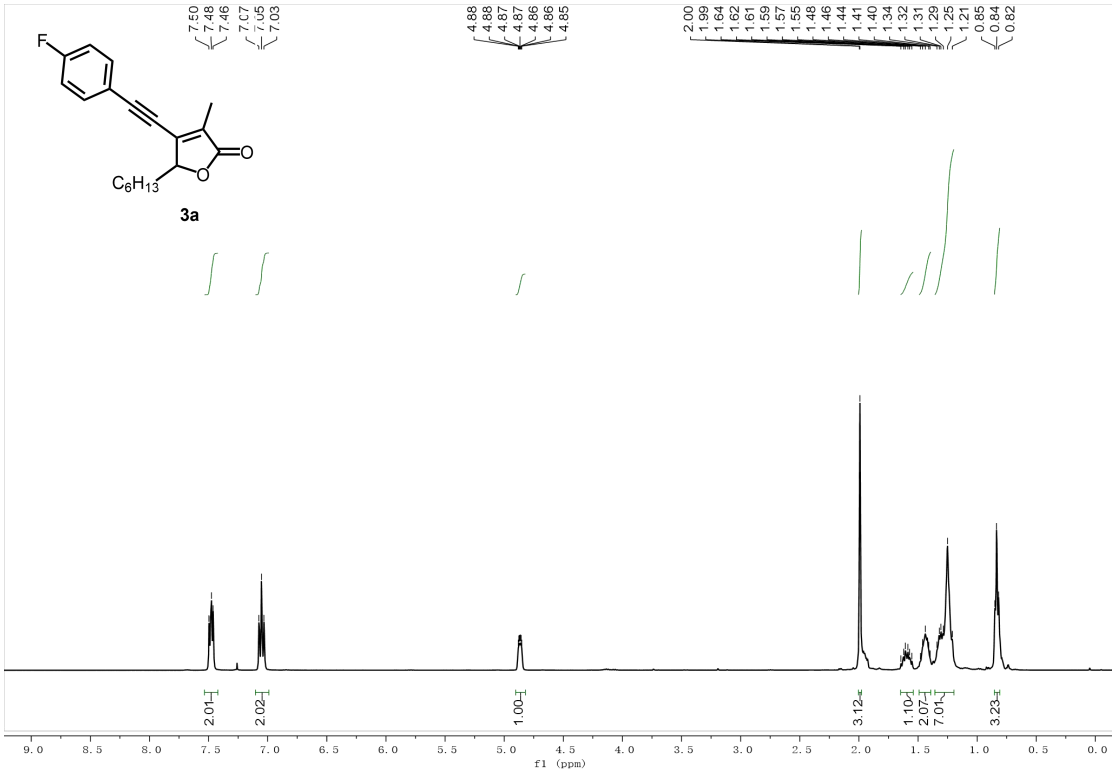
2y
f1 (ppm)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4.87
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4.86
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1.55
1.48
1.46
1.44
1.41
1.40
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1.32
1.31
1.29
1.25
1.21
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0.84
0.82
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C6H13
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2.02
1.00
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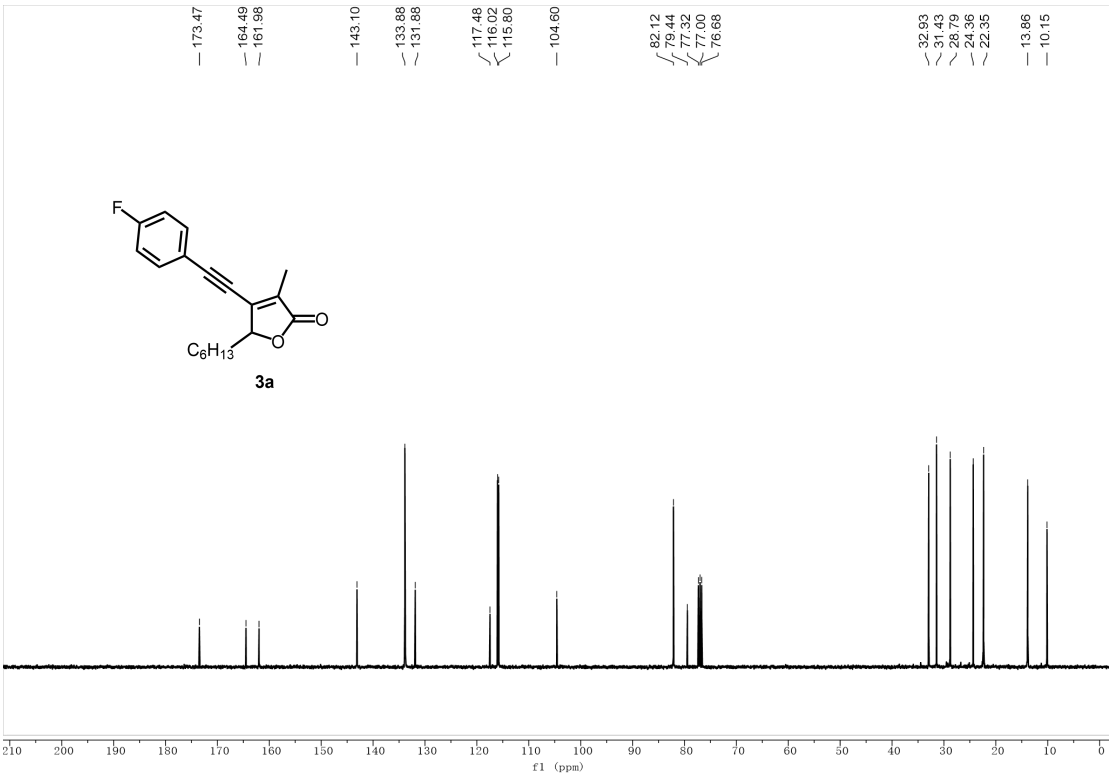
2.07
7.01
3.23
f1 (ppm)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131.88
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116.02
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82.12
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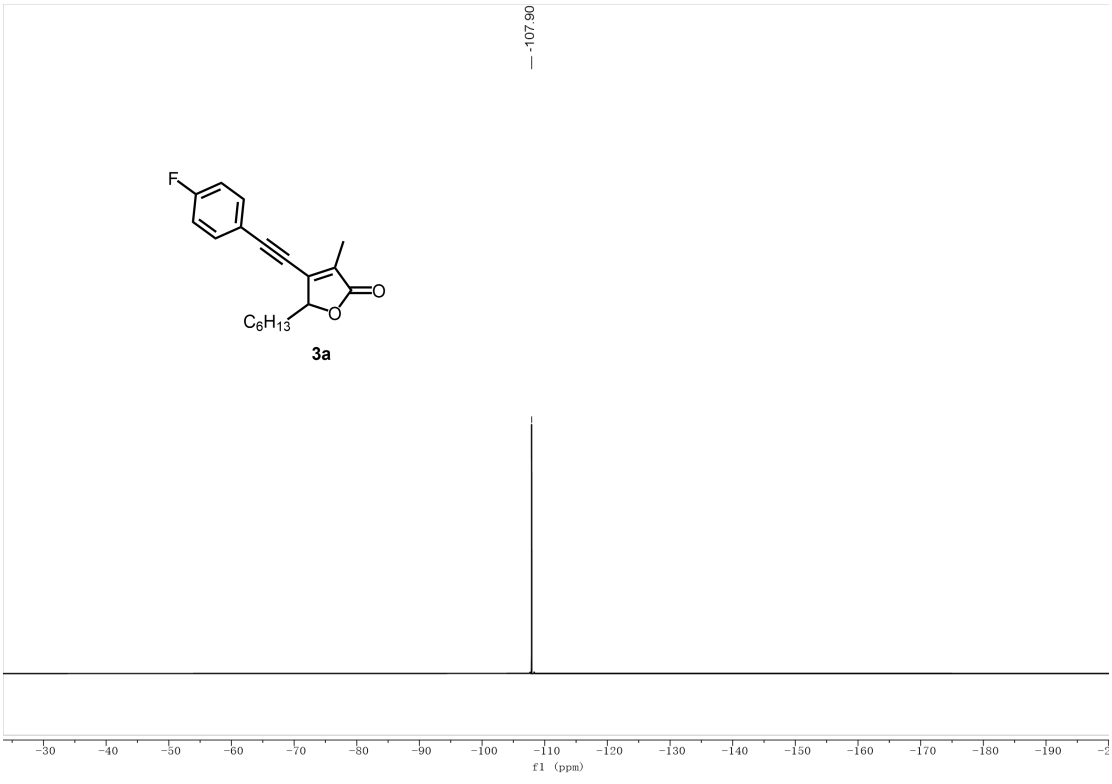
77.32
77.00
76.68
32.93
31.43
28.79
24.36
22.35
13.86
10.15
F
O
O
C6H13
f1 (ppm)

3a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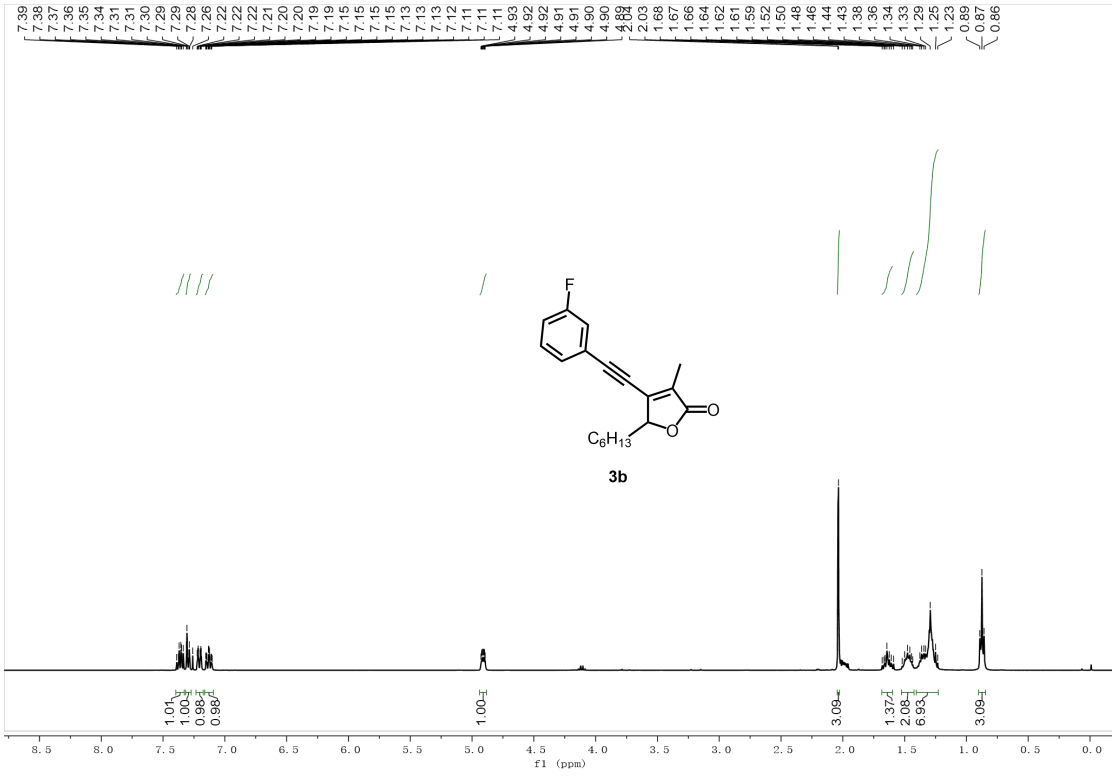
3a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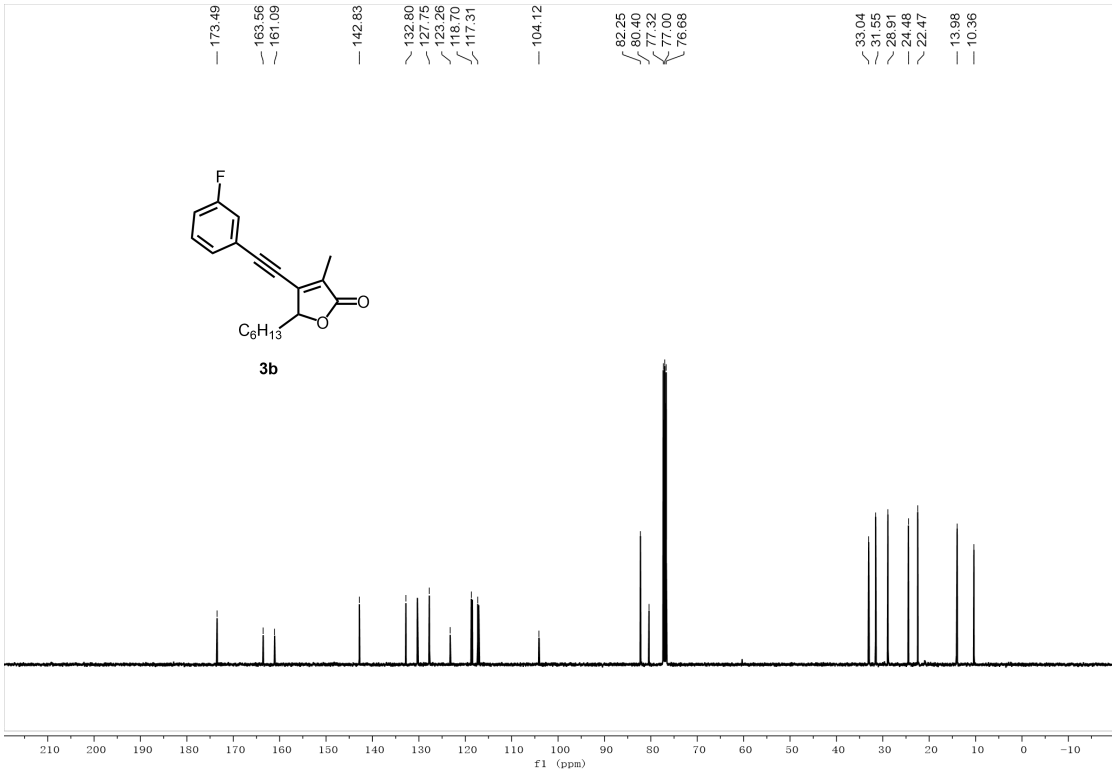
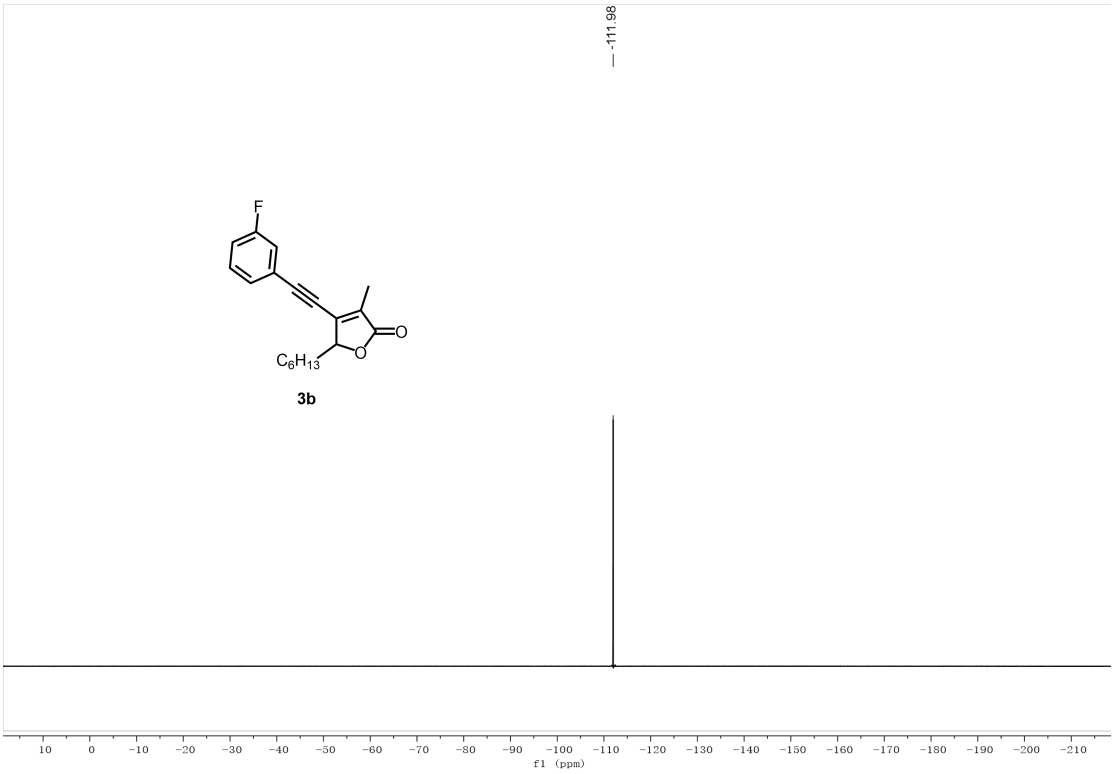
O
O
C6H13
3b
f1 (ppm)


F
O
O
C6H13
3b
f1 (ppm)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F
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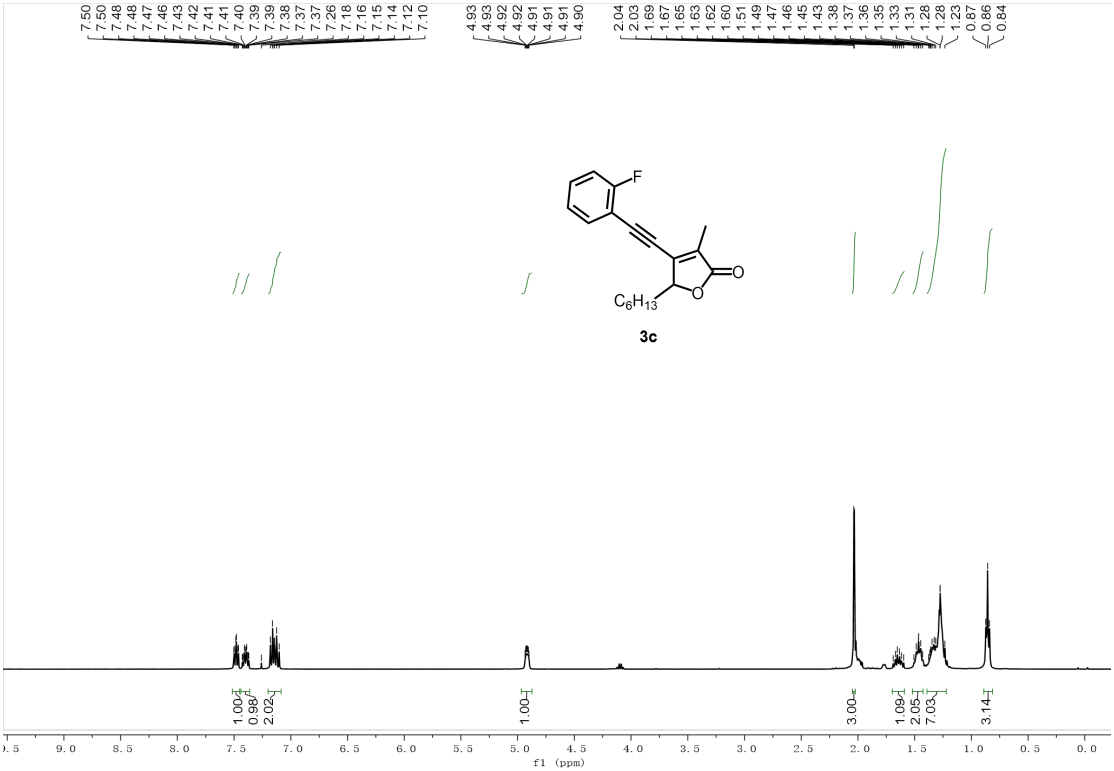
O
C6H13
3b
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)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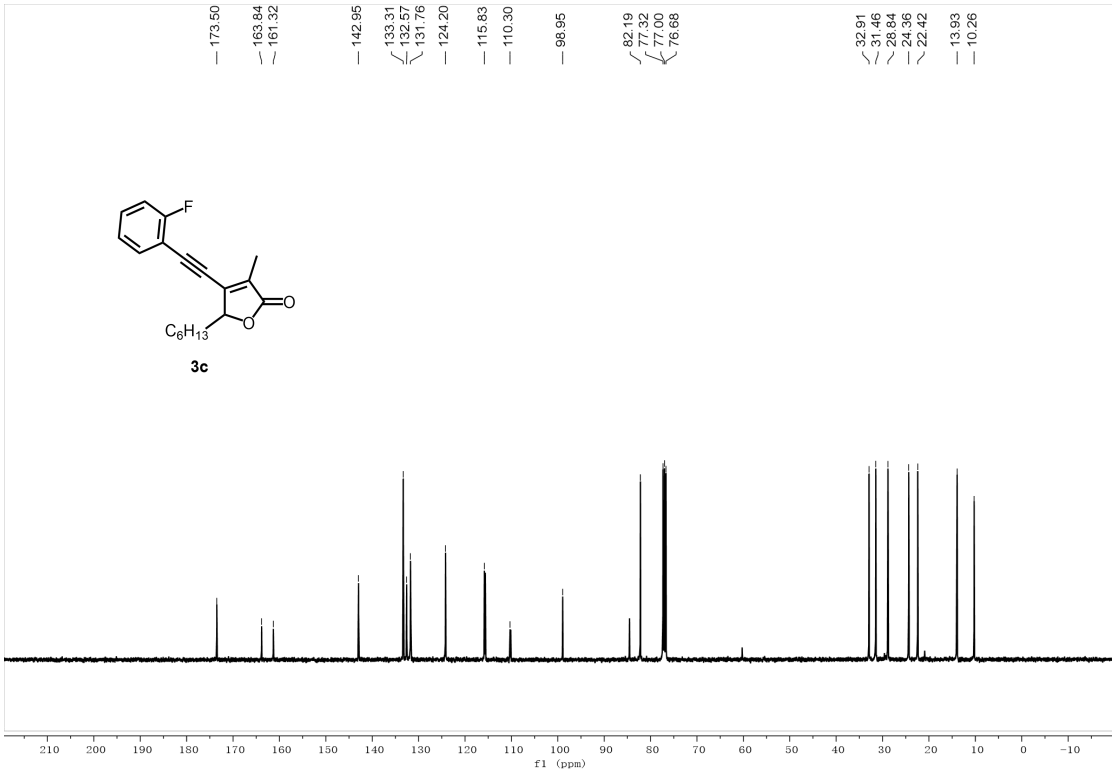
4.93 4.93 4.92 4.92 4.91 4.91 4.91 4.90
2.04 2.03 1.69 1.67 1.65 1.63 1.62 1.60 1.51 1.49 1.47 1.46 1.45 1.43 1.38 1.37 1.36 1.35 1.33 1.31 1.28 1.28 1.23 0.87 0.86 0.84
F
O
O
C6H13
3c
1.00 0.98 2.02 1.00 3.00 1.09 2.05 7.03 3.14
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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161.32
142.95
133.31
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124.20
115.83
110.30
98.95
82.19
77.32
77.00
76.68
32.91
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10.26
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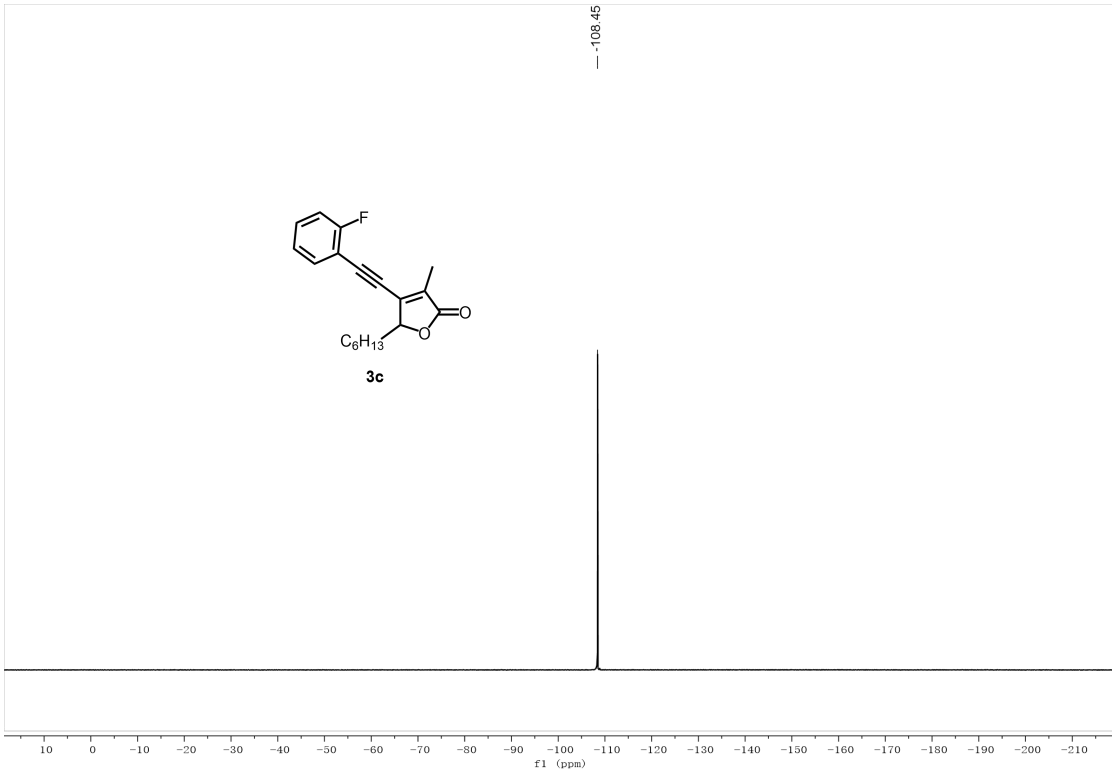
O
O
C6H13
3c
f1 (ppm)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O
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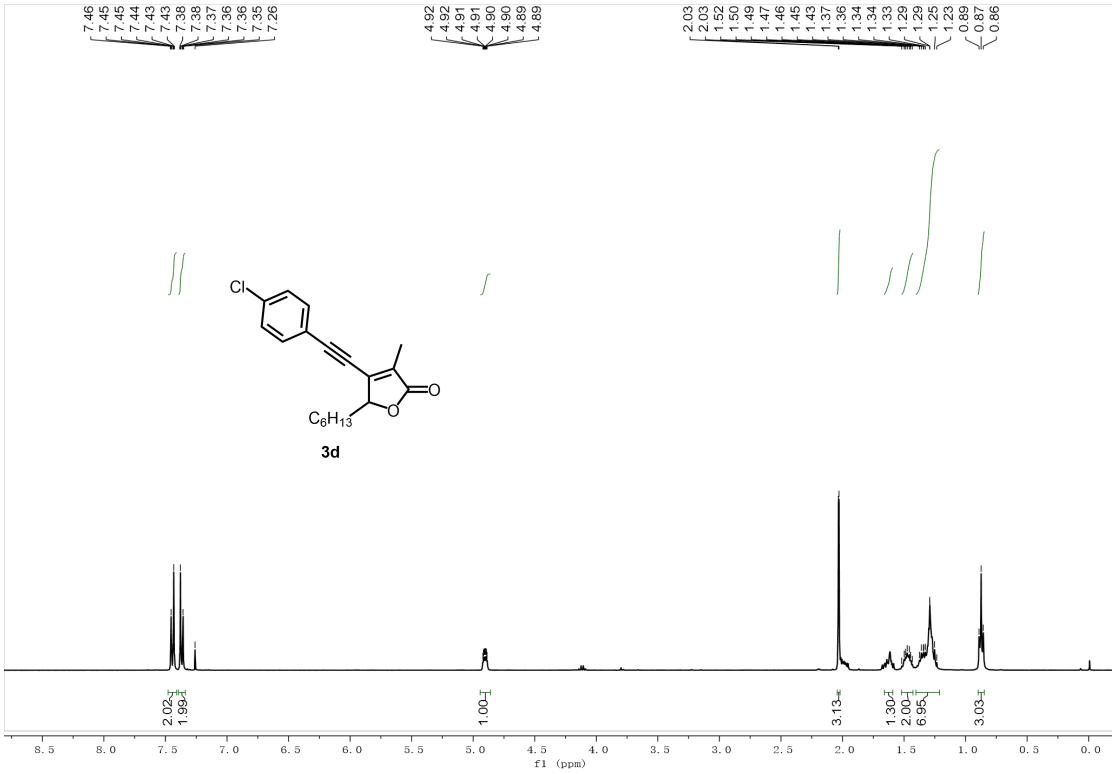
3c
f1 (ppm)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4.92
4.91
4.91
4.90
4.90
4.89
4.89
2.03
2.03
1.52
1.50
1.49
1.47
1.46
1.45
1.43
1.37
1.36
1.34
1.34
1.33
1.29
1.29
1.25
1.23
0.89
0.87
0.86
Cl
O
O
C6H13
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2.02
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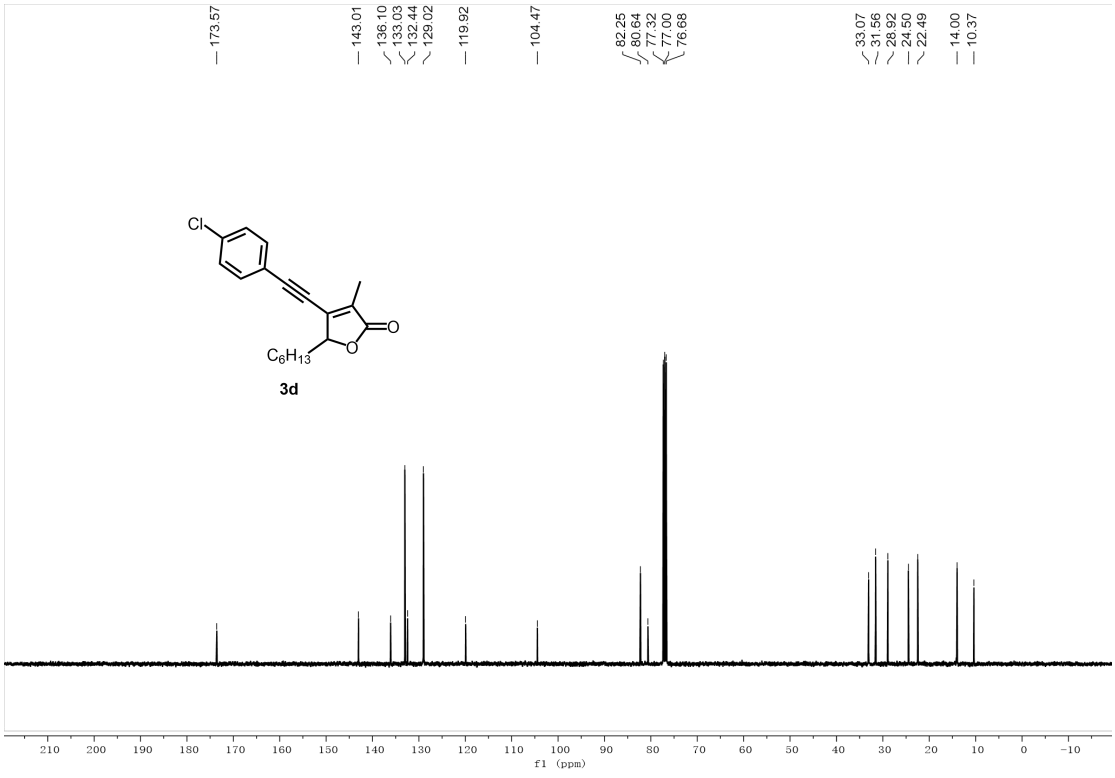
1.00
3.13
1.30
2.00
6.95
3.03
f1 (ppm)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104.47
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80.64
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77.00
76.68
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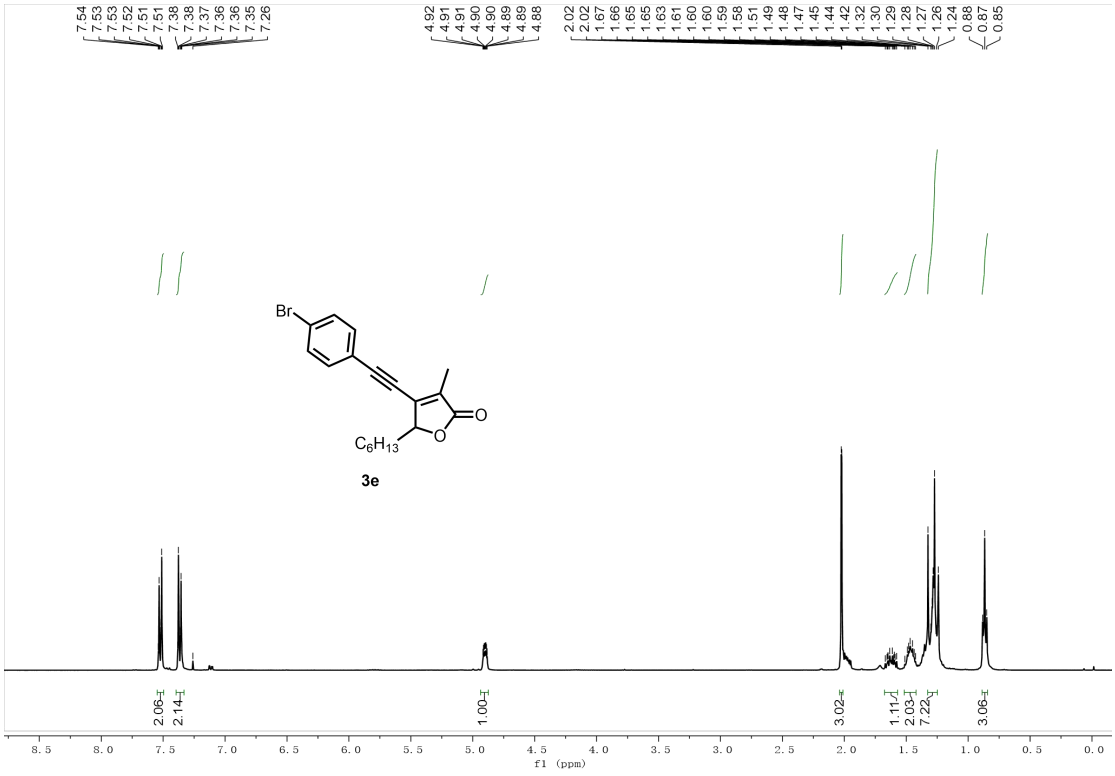
24.50
22.49
14.00
10.37
Cl
O
O
C6H13
3d
f1 (ppm)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7.38
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4.91
4.91
4.90
4.90
4.89
4.89
4.88
2.02
2.02
1.67
1.66
1.65
1.65
1.63
1.61
1.60
1.60
1.59
1.58
1.51
1.49
1.48
1.47
1.45
1.44
1.42
1.32
1.30
1.29
1.28
1.27
1.26
1.24
0.88
0.87
0.85
Br
O
O
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2.06
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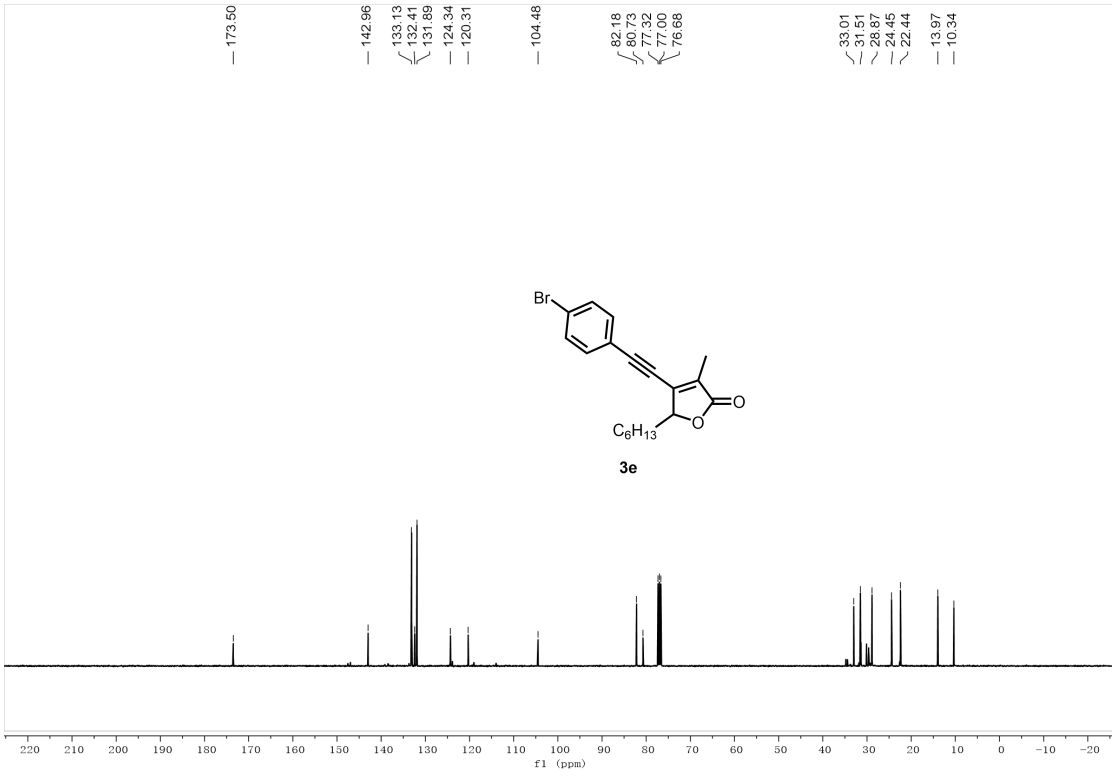
1.00
3.02
1.11
2.03
7.22
3.06
f1 (ppm)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104.48
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80.73
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77.00
76.68
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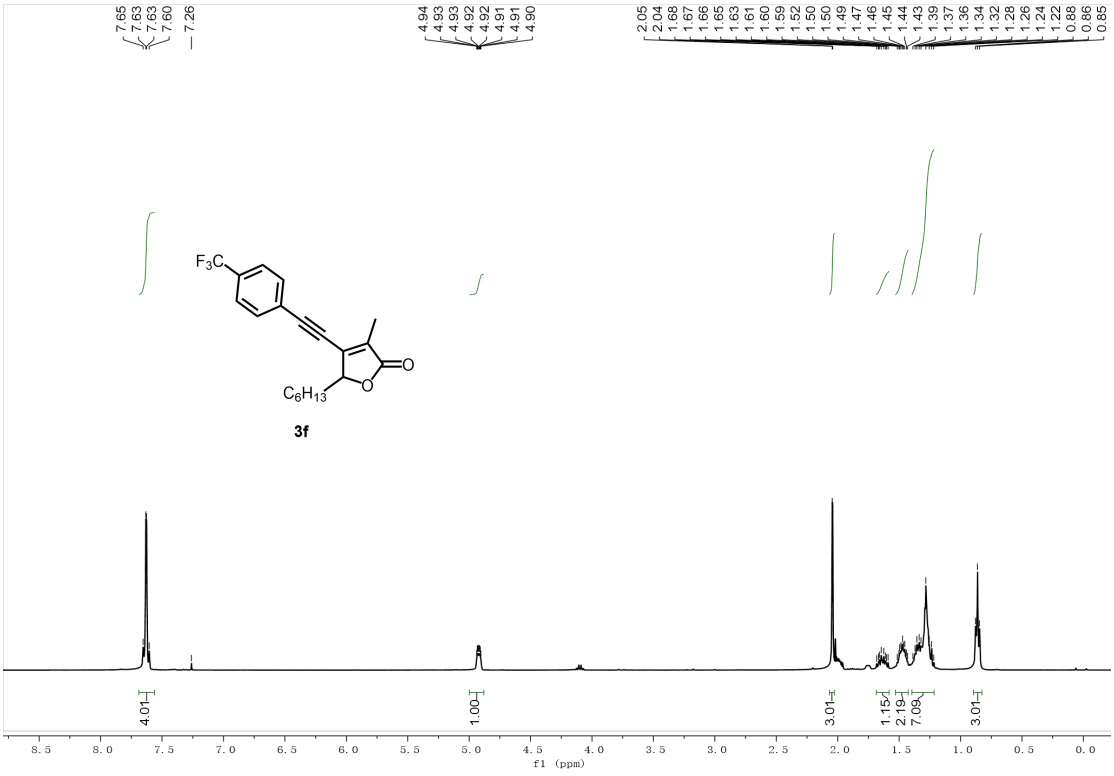
24.45
22.44
13.97
10.34
Br
O
O
C6H13
3e
f1 (ppm)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4.93
4.92
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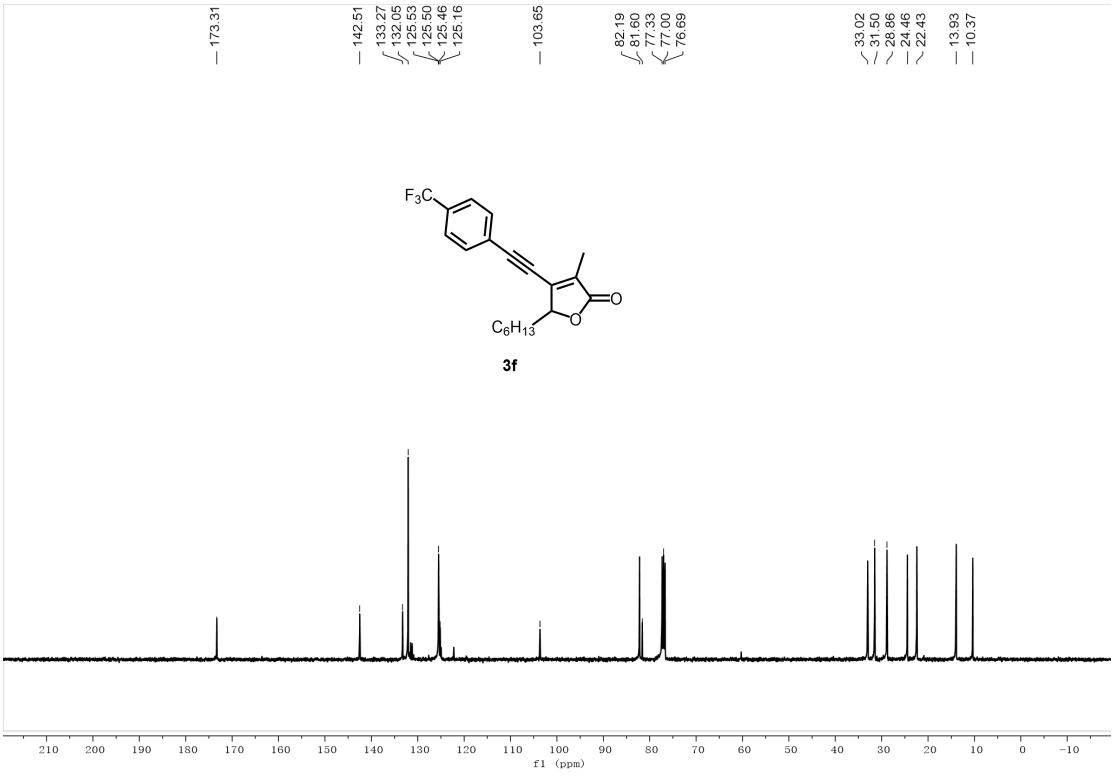
4.91
4.91
4.90
2.05
2.04
1.68
1.67
1.66
1.65
1.63
1.61
1.60
1.59
1.52
1.50
1.50
1.49
1.47
1.46
1.45
1.44
1.43
1.39
1.37
1.36
1.34
1.32
1.28
1.26
1.24
1.22
0.88
0.86
0.85
F3C
O
O
C6H13
3f
4.01
1.00
3.01
1.15
2.19
7.09
3.01
f1 (ppm)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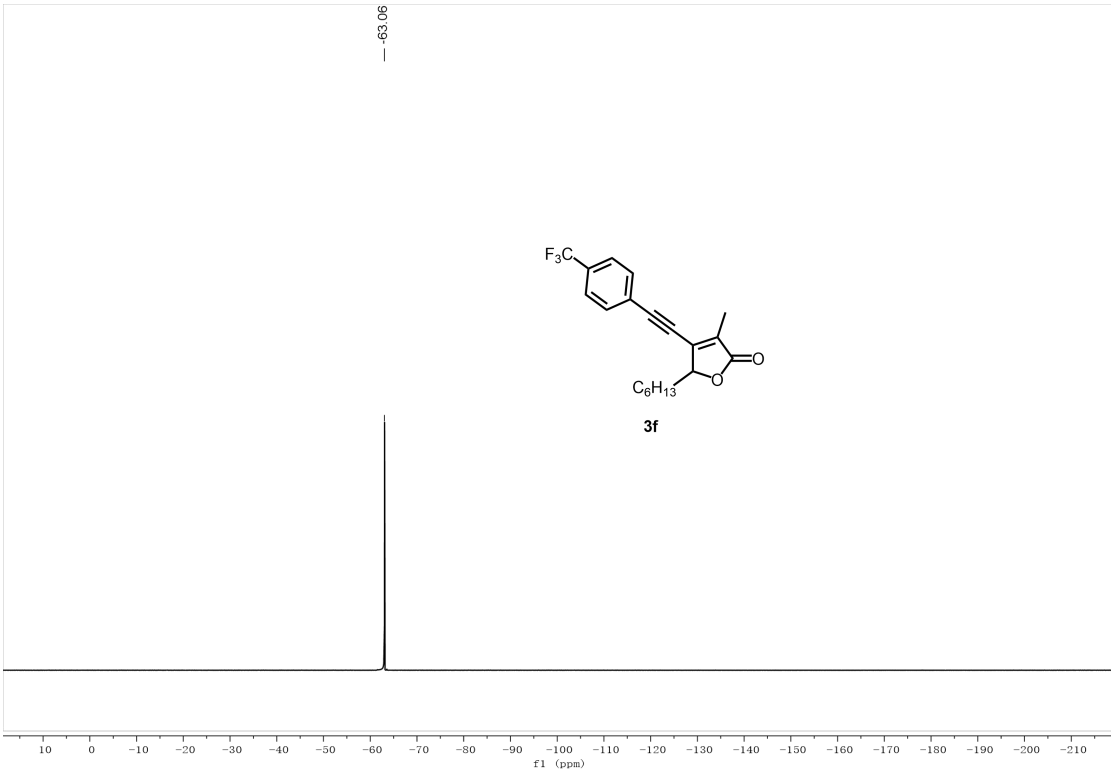
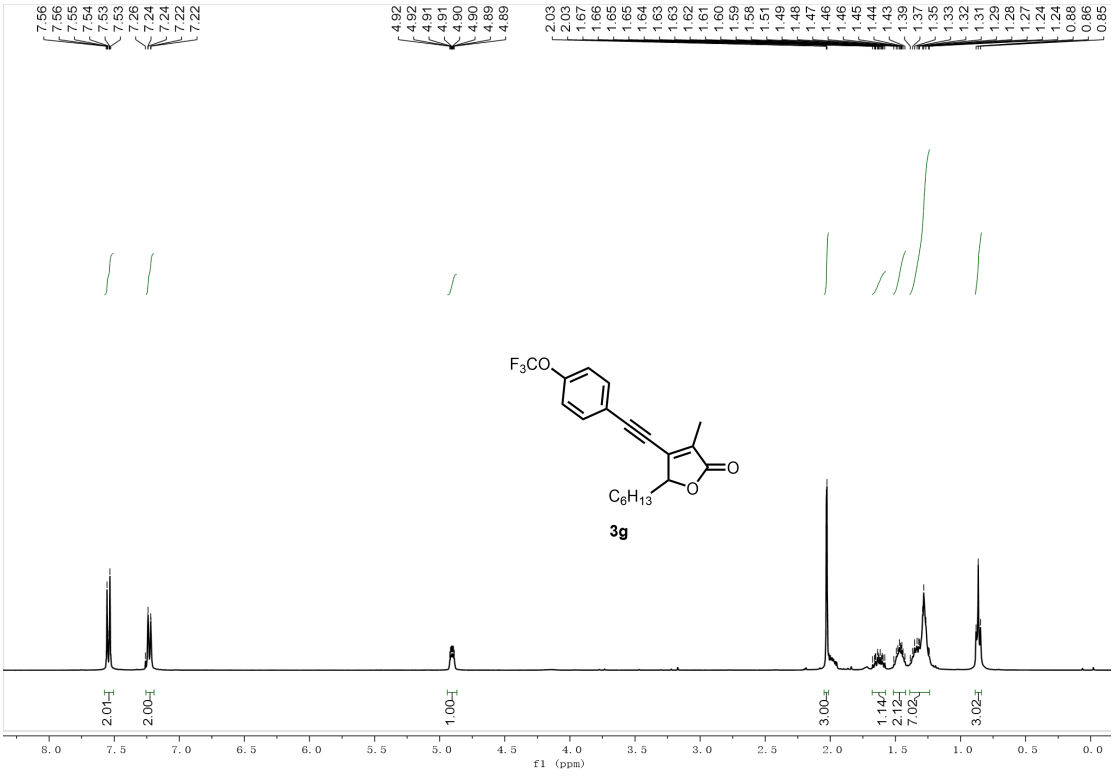
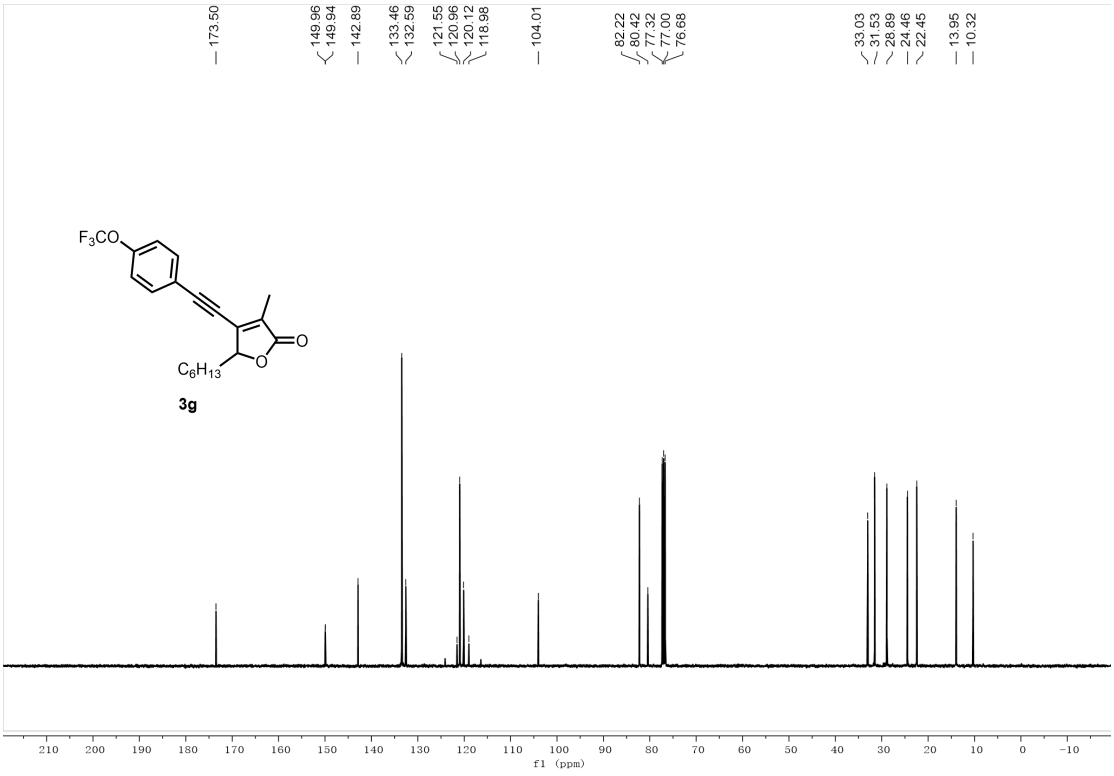
125.50
125.46
125.16
103.65
82.19
81.60
77.33
77.00
76.69
33.02
31.50
28.86
24.46
22.43
13.93
10.37
F3C
O
O
C6H13
3f
f1 (ppm)


-63.06
F3C
C6H13
O
O
3f
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)


7.56 7.56 7.55 7.54 7.53 7.53 7.26 7.24 7.24 7.22 7.22
4.92 4.92 4.91 4.91 4.90 4.90 4.89 4.89
2.03 2.03 1.67 1.66 1.65 1.65 1.64 1.63 1.63 1.62 1.61 1.60 1.59 1.58 1.51 1.49 1.48 1.47 1.46 1.46 1.45 1.44 1.43 1.39 1.37 1.35 1.33 1.32 1.31 1.29 1.28 1.27 1.24 1.24 0.88 0.86 0.85
F3CO
C6H13
O
O
3g
2.01 2.00 1.00 3.00 1.14 2.12 7.02 3.02
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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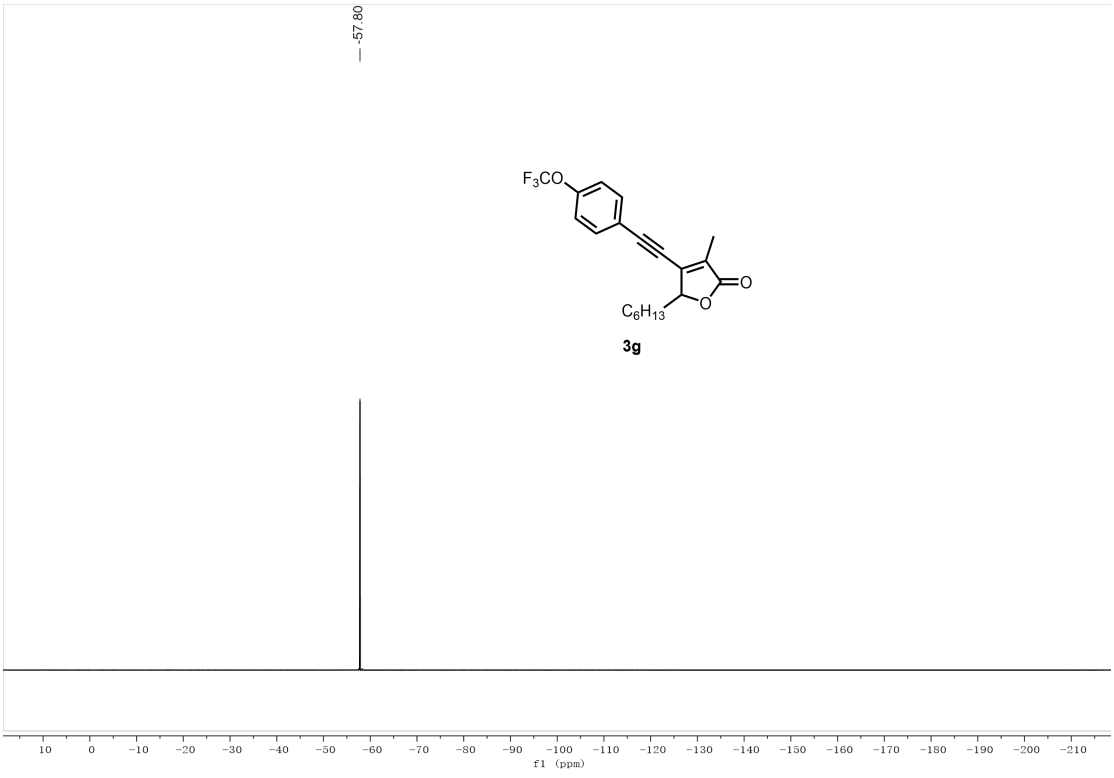
120.96
120.12
118.98
104.01
82.22
80.42
77.32
77.00
76.68
33.03
31.53
28.89
24.46
22.45
13.95
10.32
F3CO
C6H13
O
O
3g
f1 (ppm)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O
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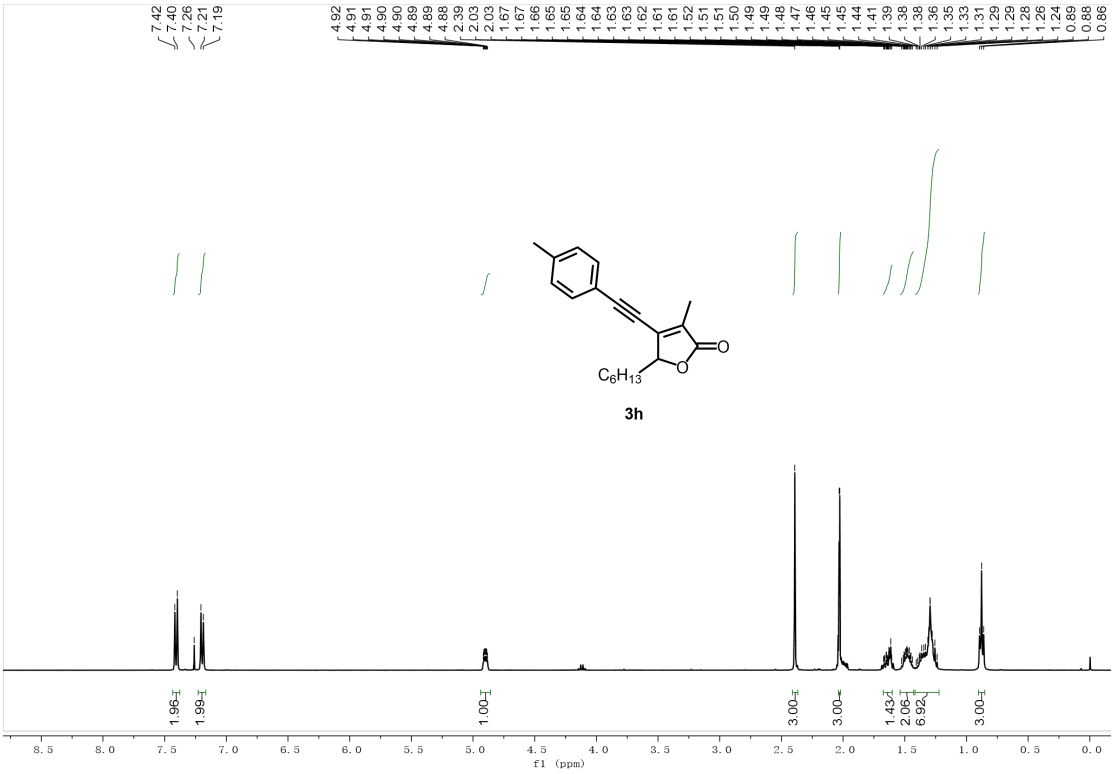
3g
f1 (ppm)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4.91
4.91
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4.90
4.89
4.89
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1.63
1.63
1.62
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1.61
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1.50
1.49
1.49
1.48
1.47
1.46
1.45
1.45
1.44
1.41
1.39
1.38
1.38
1.36
1.35
1.33
1.31
1.29
1.29
1.28
1.26
1.24
0.89
0.88
0.86
O
O
C6H13
3h
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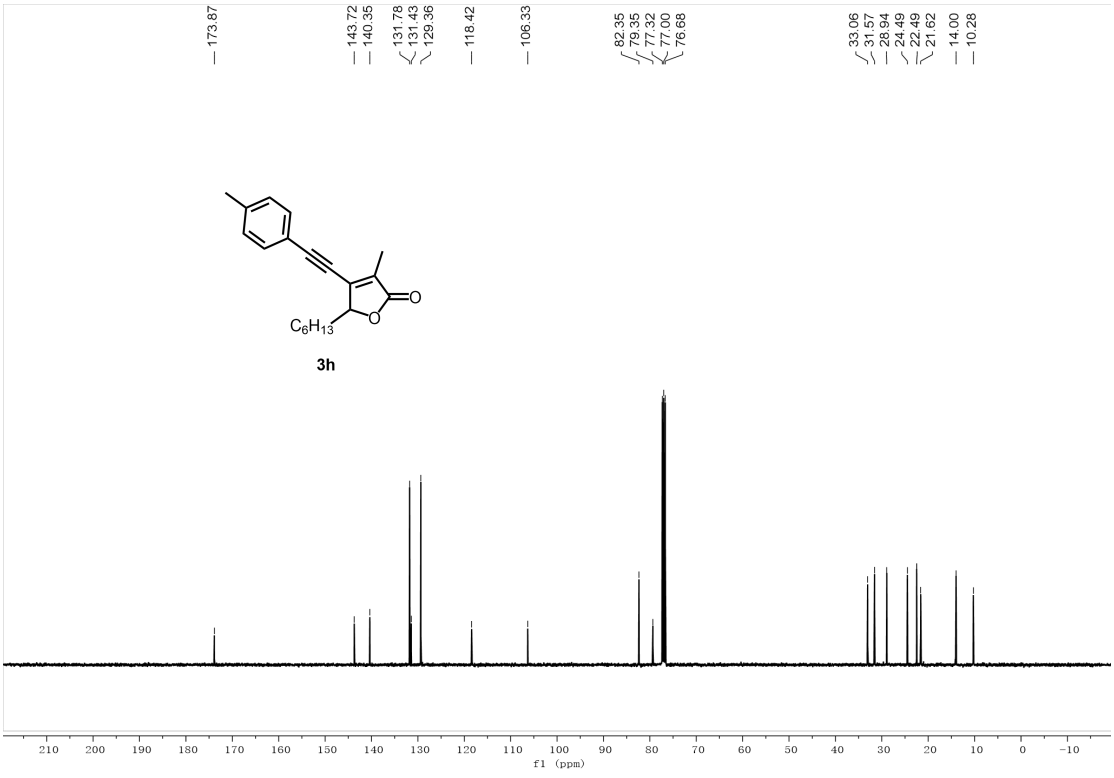
1.99
1.00
3.00
3.00
1.43
2.06
6.92
3.00
f1 (ppm)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106.33
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79.35
77.32
77.00
76.68
33.06
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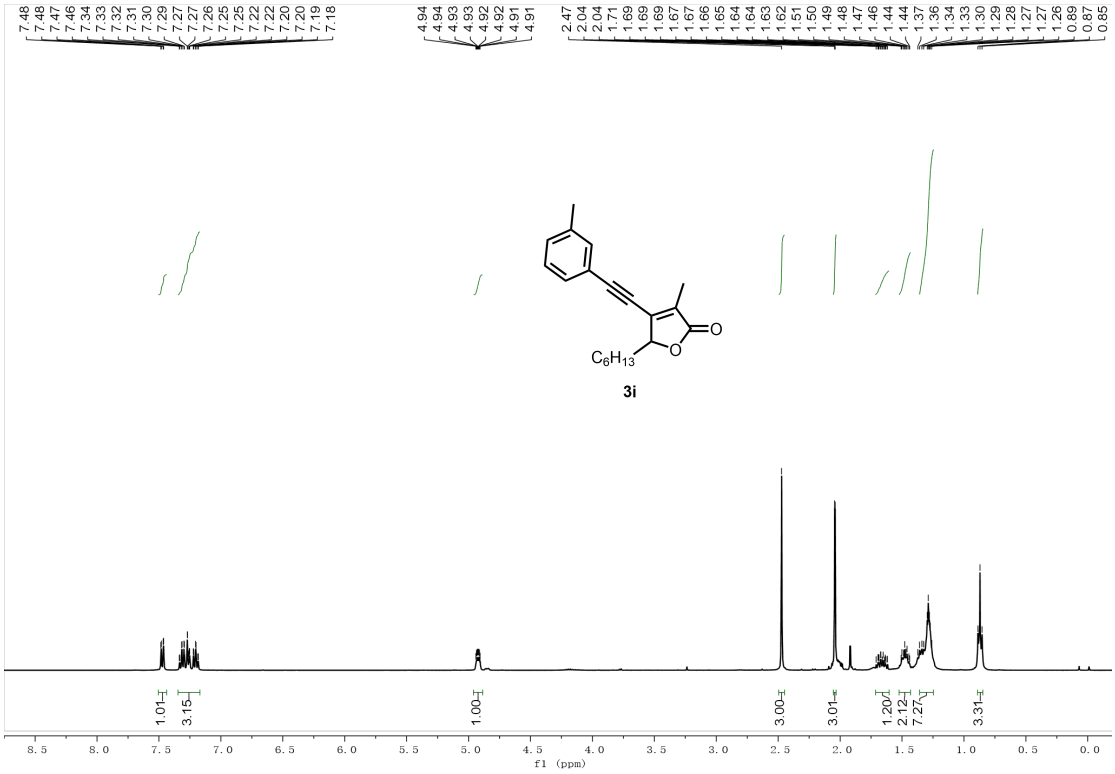
24.49
22.49
21.62
14.00
10.28
O
O
C6H13
3h
f1 (ppm)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7.25
7.22
7.22
7.20
7.20
7.19
7.18
4.94
4.94
4.93
4.93
4.92
4.92
4.91
4.91
2.47
2.04
2.04
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1.44
1.44
1.37
1.36
1.34
1.33
1.30
1.29
1.28
1.27
1.27
1.26
0.89
0.87
0.85
O
O
C6H13
1.01
3.15
1.00
3.00
3.01
1.20
2.12
7.27
3.31
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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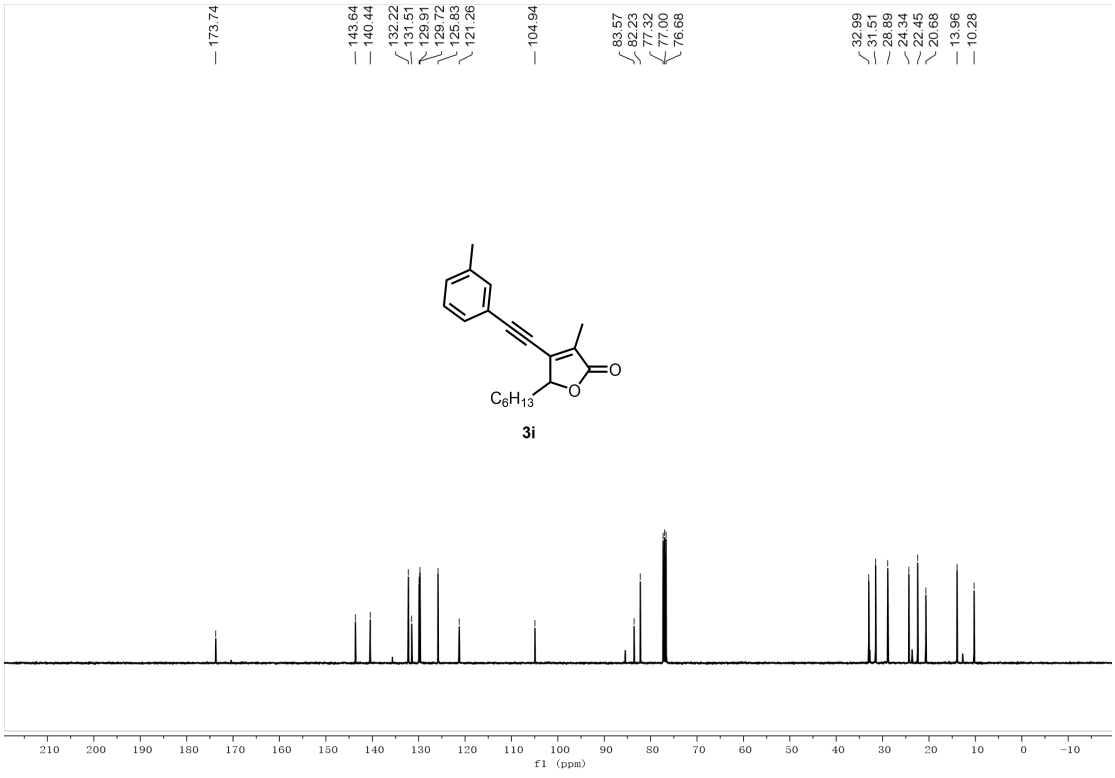
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3i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104.94
83.57
82.23
77.32
77.00
76.68
32.99
31.51
28.89
24.34
22.45
20.68
13.96
10.28
O
O
C6H13
210
200
190
180
170
160
150
140
130
120
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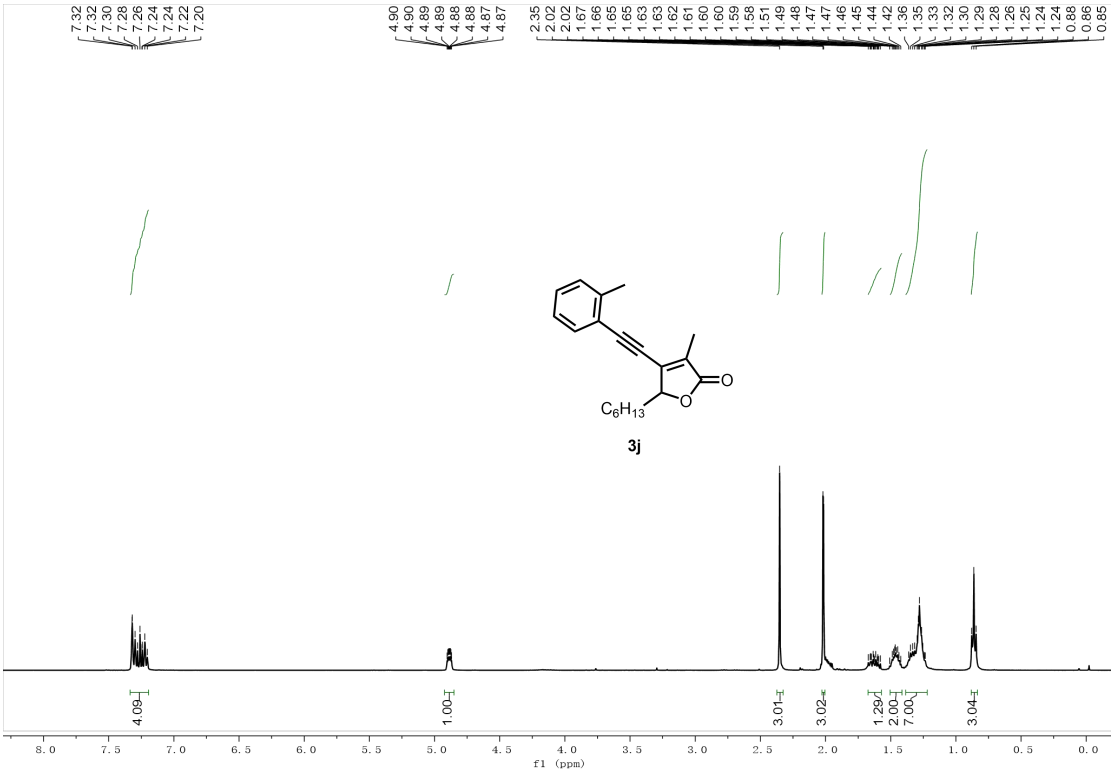
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

3i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4.90
4.89
4.89
4.88
4.88
4.87
4.87
2.35
2.02
2.02
1.67
1.66
1.65
1.65
1.63
1.63
1.62
1.61
1.60
1.60
1.59
1.58
1.51
1.49
1.48
1.47
1.47
1.46
1.45
1.44
1.42
1.36
1.35
1.33
1.32
1.30
1.29
1.28
1.26
1.25
1.24
1.24
0.88
0.86
0.85
O
O
C6H13
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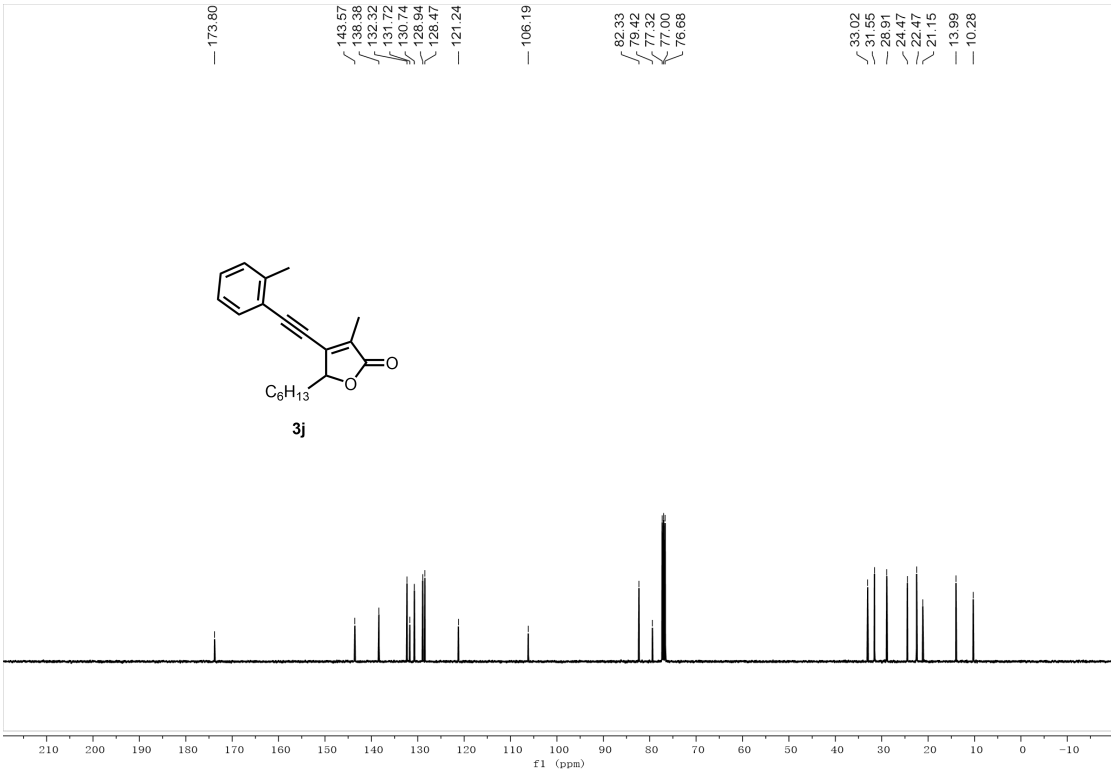
1.00
3.01
3.02
1.29
2.00
7.00
3.04
f1 (ppm)

3j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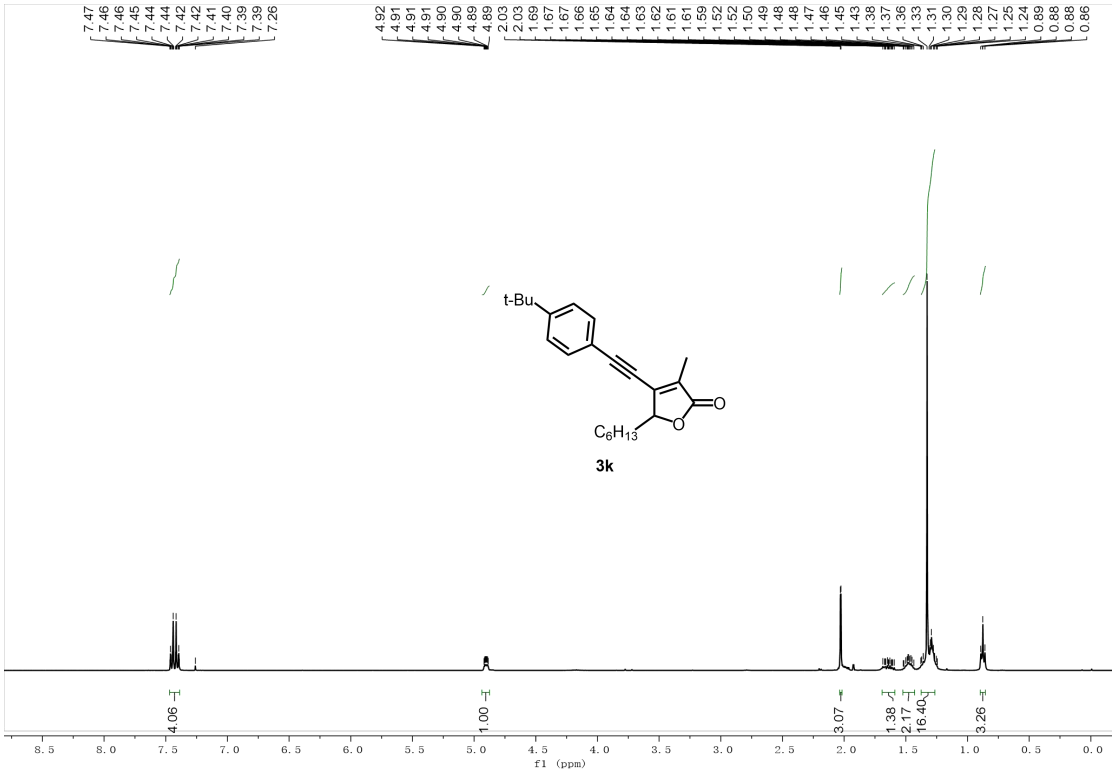
128.47
121.24
106.19
82.33
79.42
77.32
77.00
76.68
33.02
31.55
28.91
24.47
22.47
21.15
13.99
10.28
O
O
C6H13
f1 (ppm)

3j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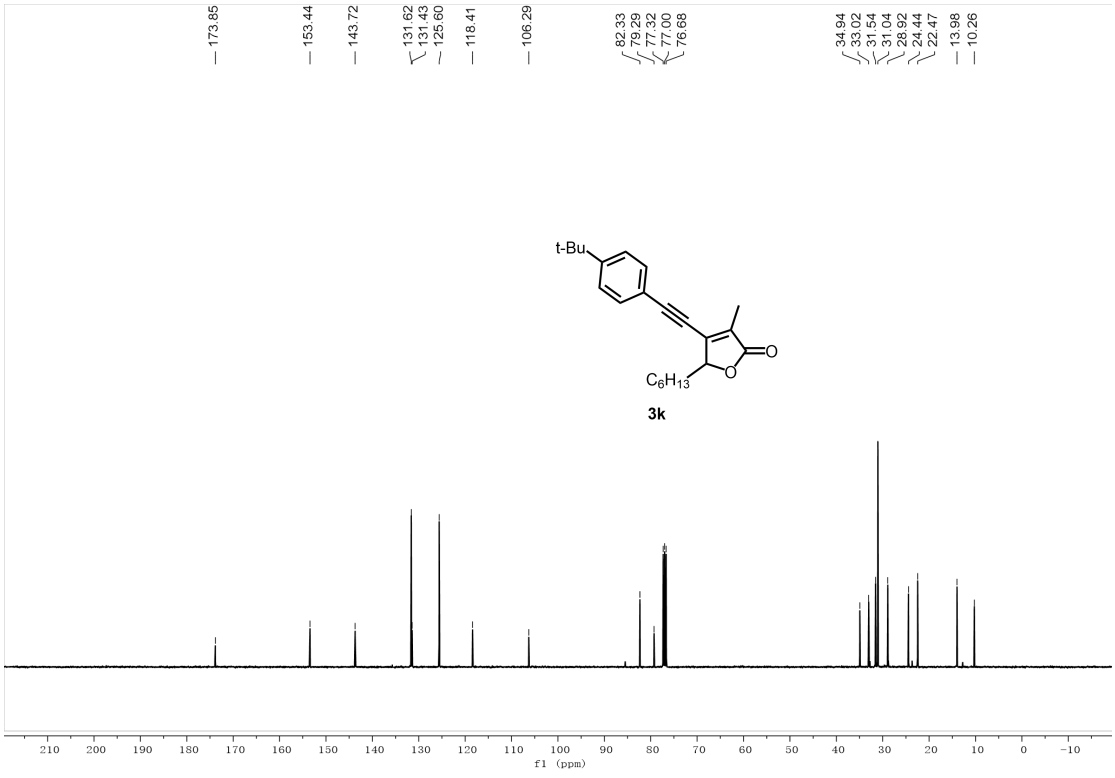
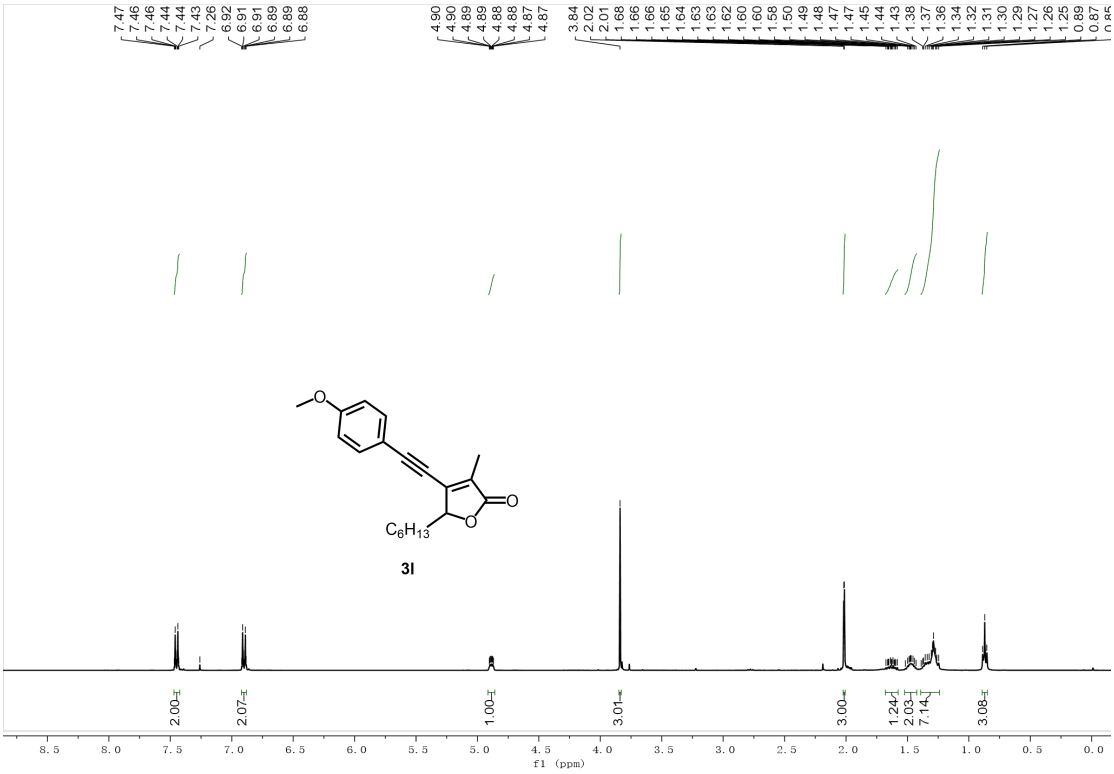
4.92 4.91 4.91 4.91 4.90 4.90 4.89 4.89 2.03 2.03 1.69 1.67 1.67 1.66 1.65 1.64 1.64 1.63 1.62 1.61 1.61 1.59 1.52 1.52 1.50 1.49 1.48 1.48 1.47 1.46 1.45 1.43 1.38 1.37 1.36 1.33 1.31 1.30 1.29 1.28 1.27 1.25 1.24 0.89 0.88 0.88 0.86
t-Bu
O
O
C6H13
3k
4.06
1.00
3.07
1.38
2.17
16.40
3.26
f1 (ppm)


173.85 153.44 143.72 131.62 131.43 125.60 118.41 106.29 82.33 79.29 77.32 77.00 76.68 34.94 33.02 31.54 31.04 28.92 24.44 22.47 13.98 10.26
t-Bu
O
O
C6H13
3k
f1 (ppm)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7.44
7.44
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6.91
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6.89
6.88
4.90
4.90
4.89
4.89
4.88
4.88
4.87
4.87
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1.48
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1.43
1.38
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1.36
1.34
1.32
1.31
1.30
1.29
1.27
1.26
1.25
0.89
0.87
O
O
O
C6H13
3l
2.00
2.07
1.00
3.01
3.00
1.24
2.03
7.14
3.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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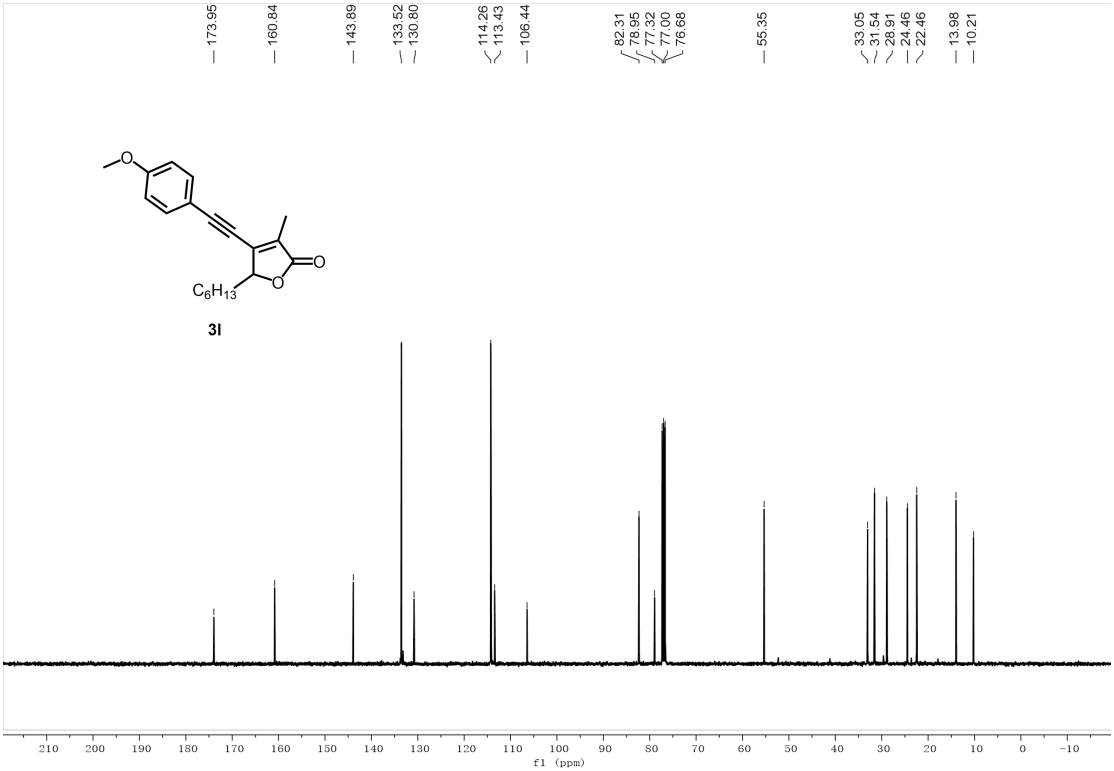
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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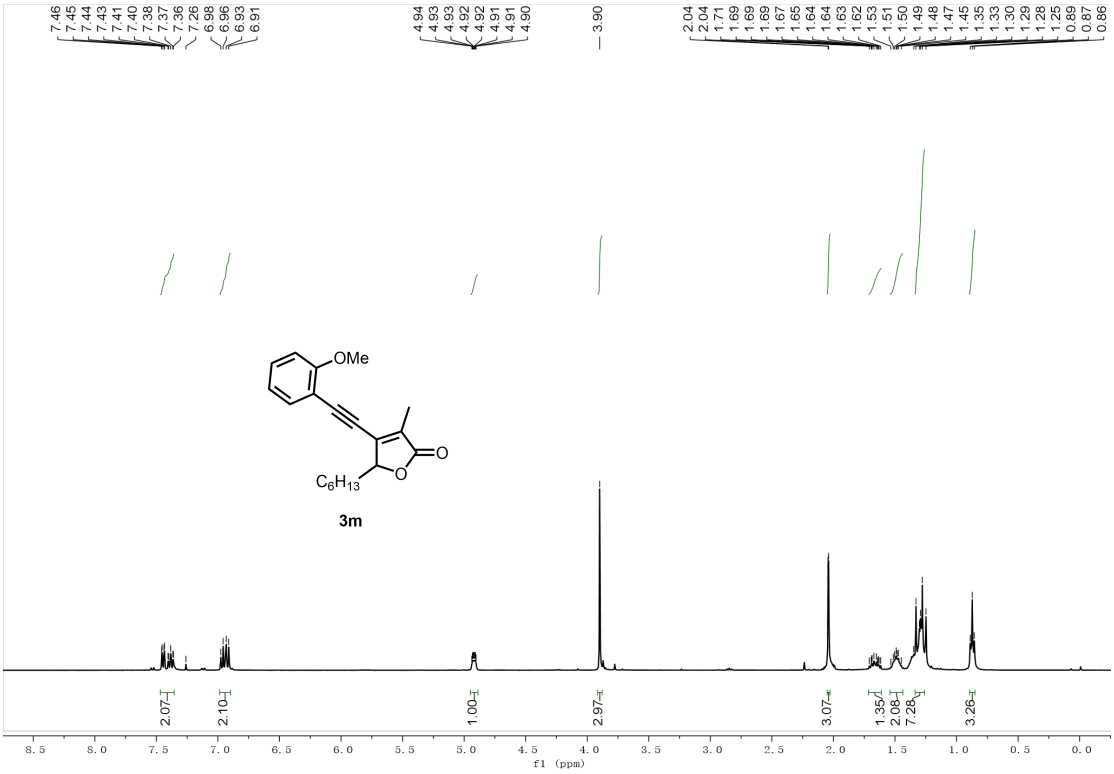
106.44
82.31
78.95
77.32
77.00
76.68
55.35
33.05
31.54
28.91
24.46
22.46
13.98
10.21
O
O
O
C6H13
3l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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7.26
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6.93
6.91
4.94
4.93
4.93
4.92
4.92
4.91
4.91
4.90
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2.04
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1.69
1.69
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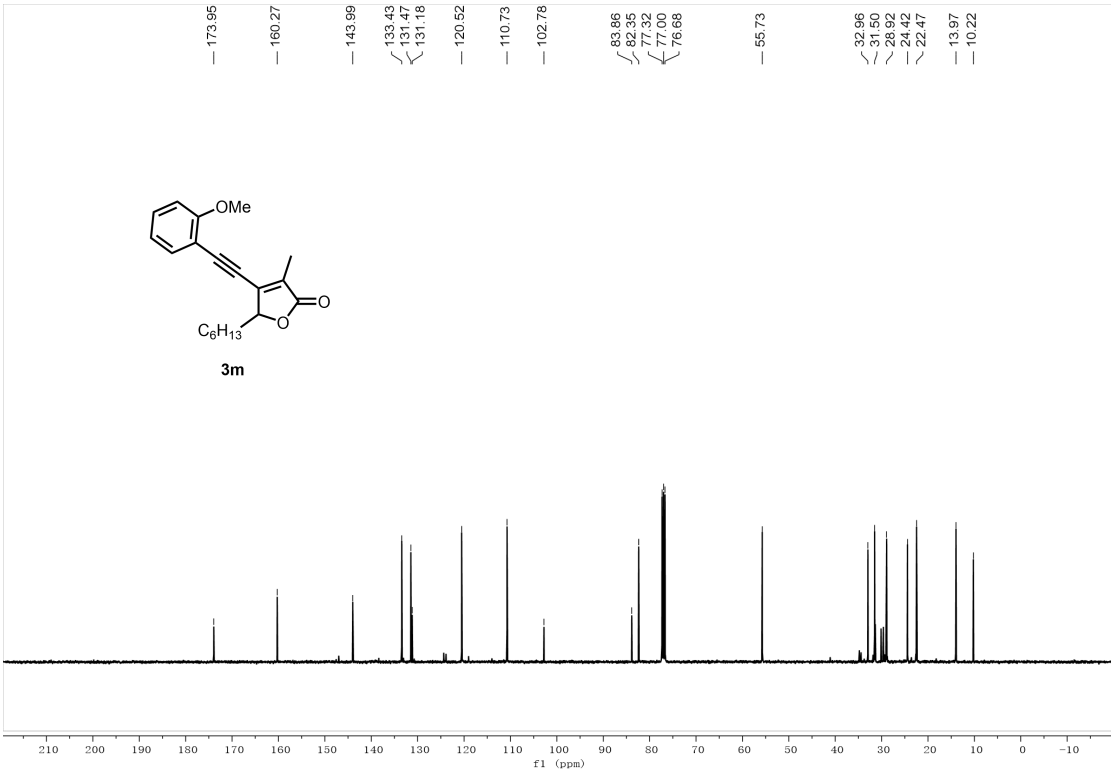
1.51
1.50
1.49
1.48
1.47
1.45
1.35
1.33
1.30
1.29
1.28
1.25
0.89
0.87
0.86
OMe
O
O
C6H13
3m
2.07
2.10
1.00
2.97
3.07
1.35
2.08
7.28
3.26
f1 (ppm)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133.43
131.47
131.18
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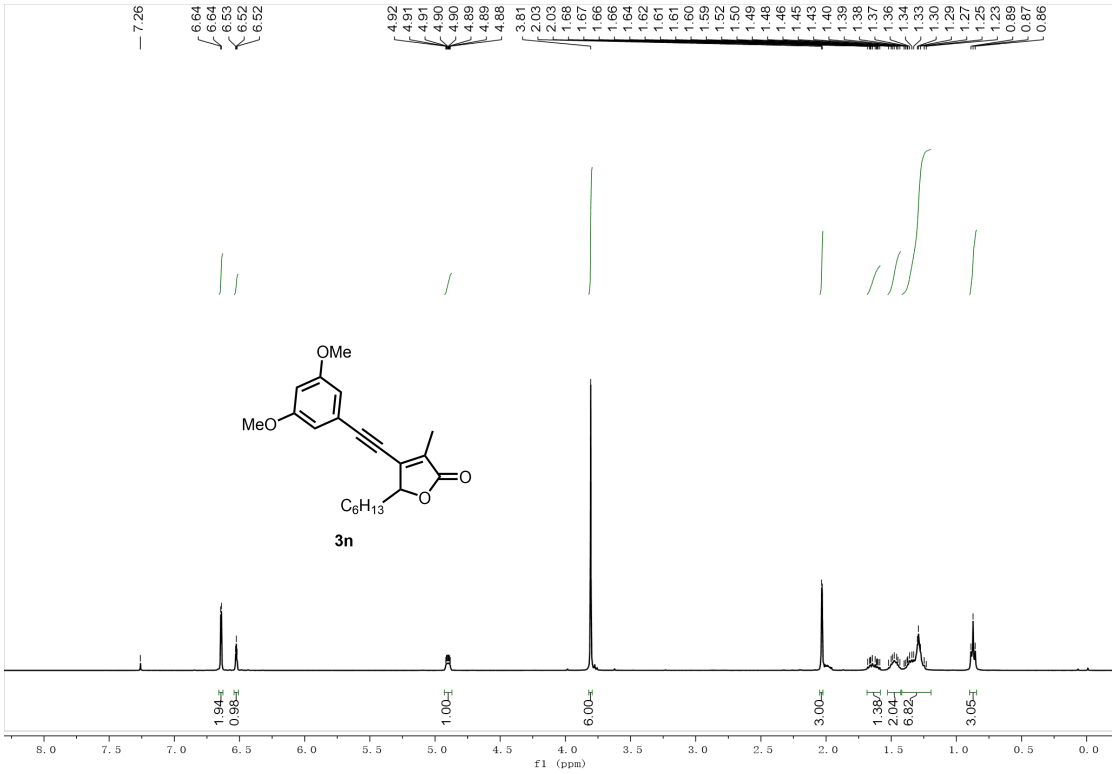
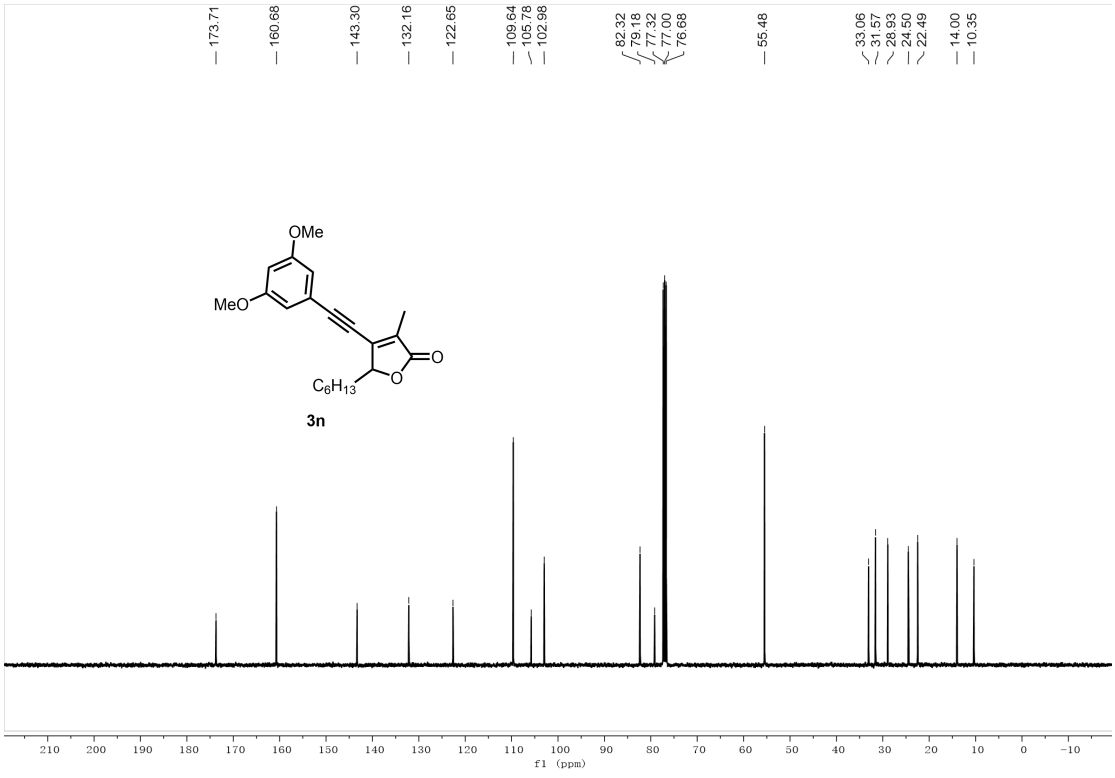
110.73
102.78
83.86
82.35
77.32
77.00
76.68
55.73
32.96
31.50
28.92
24.42
22.47
13.97
10.22
OMe
O
O
C6H13
3m
f1 (ppm)


7.26
6.64
6.64
6.53
6.52
6.52
4.92
4.91
4.91
4.90
4.90
4.89
4.89
4.88
3.81
2.03
2.03
1.68
1.67
1.66
1.66
1.64
1.62
1.61
1.61
1.60
1.59
1.52
1.50
1.49
1.48
1.46
1.45
1.43
1.40
1.39
1.38
1.37
1.36
1.34
1.33
1.30
1.29
1.27
1.25
1.23
0.89
0.87
0.86
OMe
MeO
O
O
C6H13
3n
1.94
0.98
1.00
6.00
3.00
1.38
2.04
6.82
3.05
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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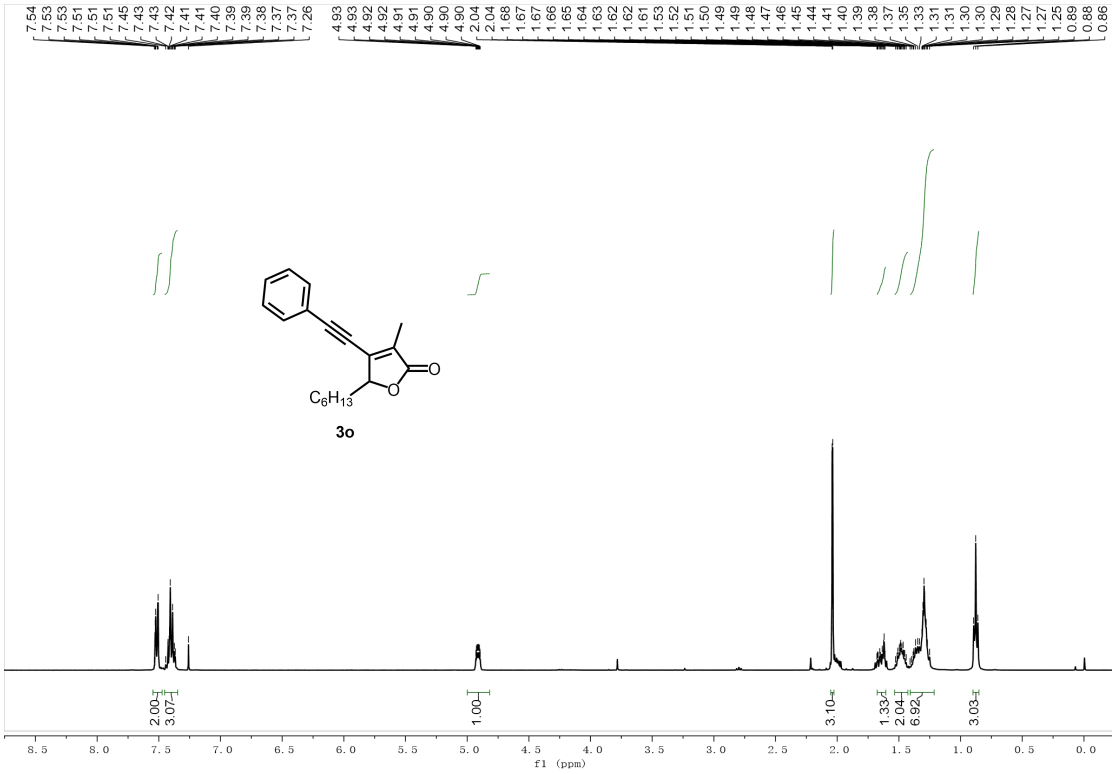
160.68
143.30
132.16
122.65
109.64
105.78
102.98
82.32
79.18
77.32
77.00
76.68
55.48
33.06
31.57
28.93
24.50
22.49
14.00
10.35
OMe
MeO
O
O
C6H13
3n
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.54 7.53 7.53 7.51 7.51 7.51 7.45 7.43 7.43 7.42 7.41 7.41 7.40 7.39 7.39 7.38 7.37 7.37 7.26
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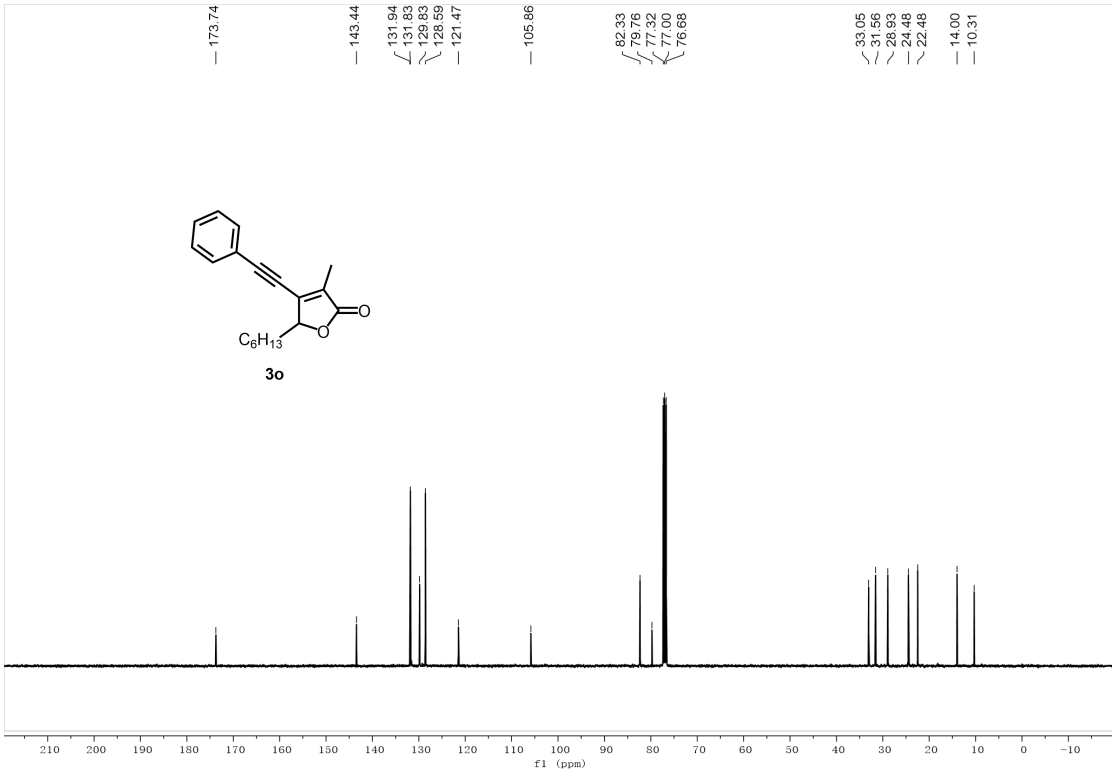
O
O
C6H13
3o
2.00 3.07 1.00 3.10 1.33 2.04 6.92 3.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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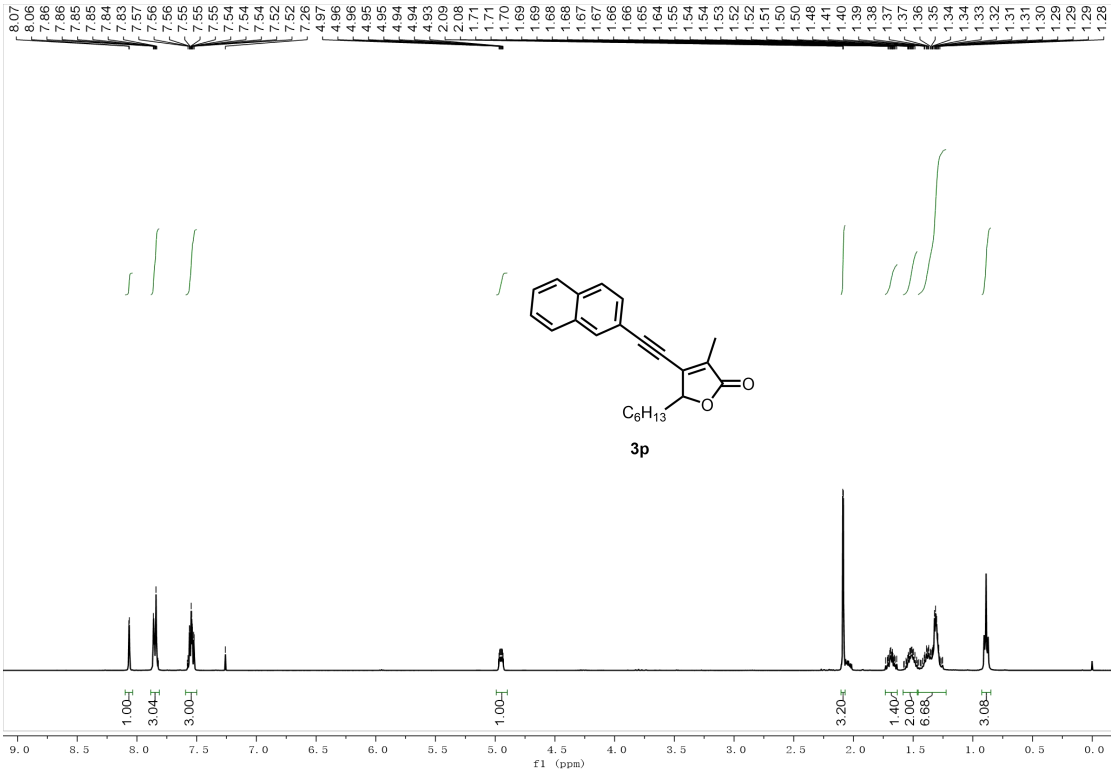
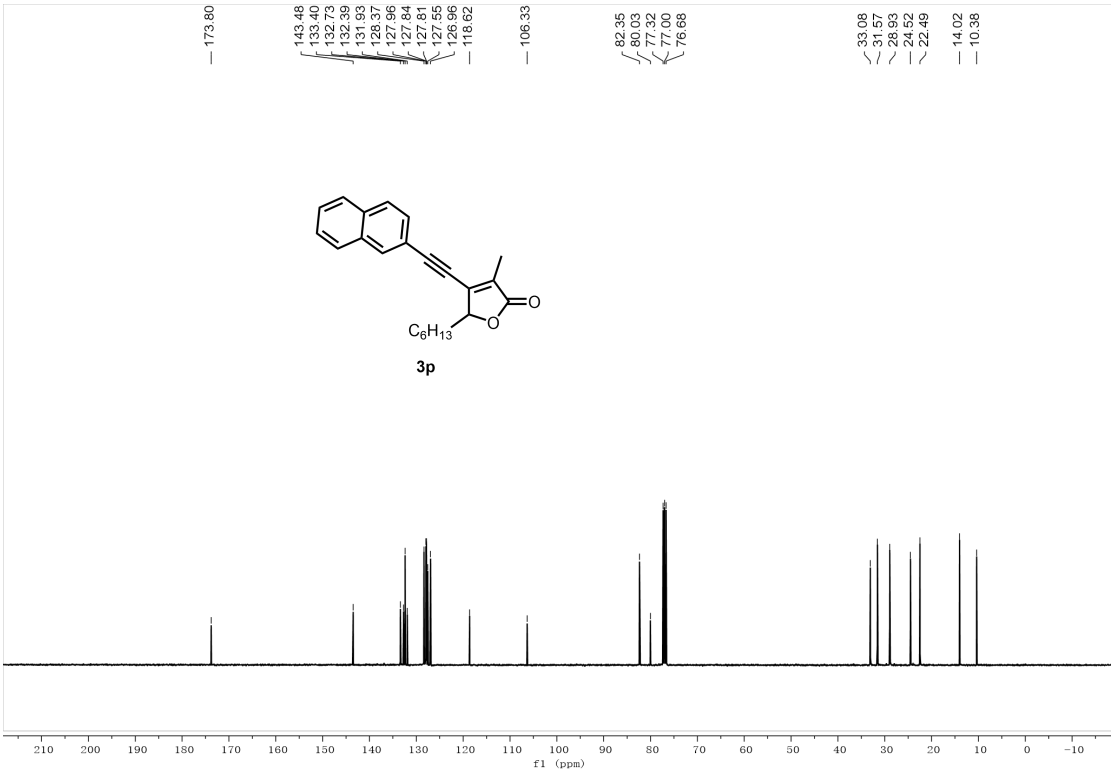
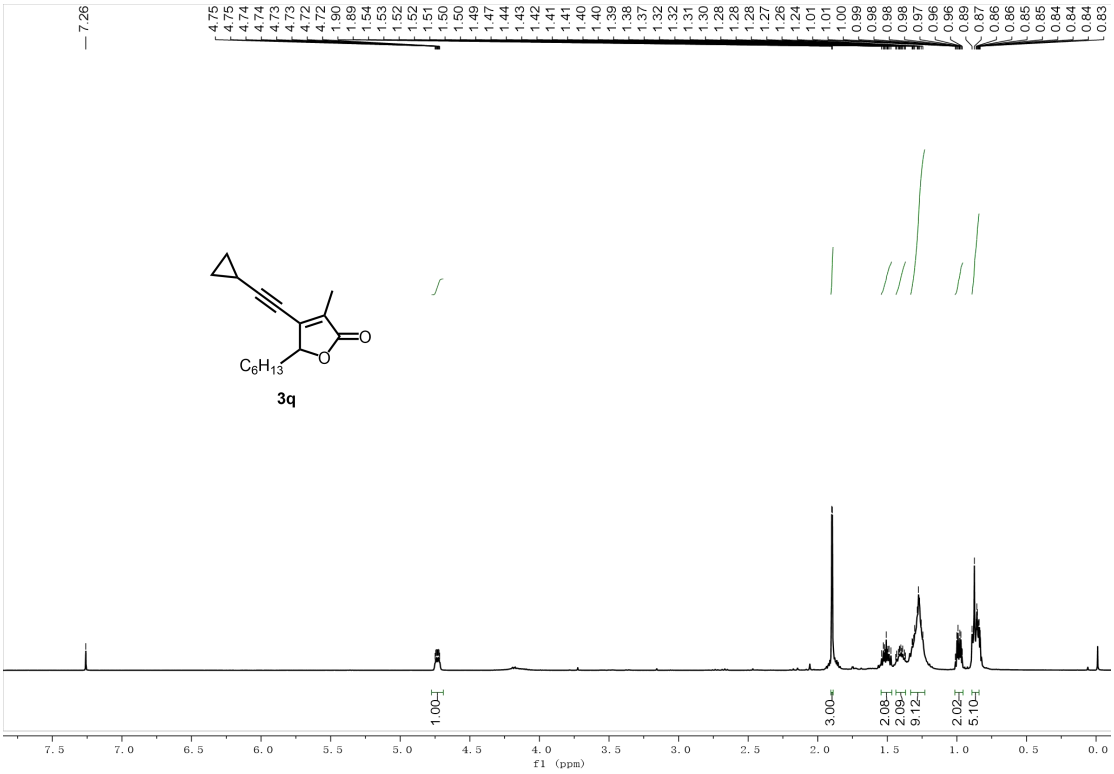
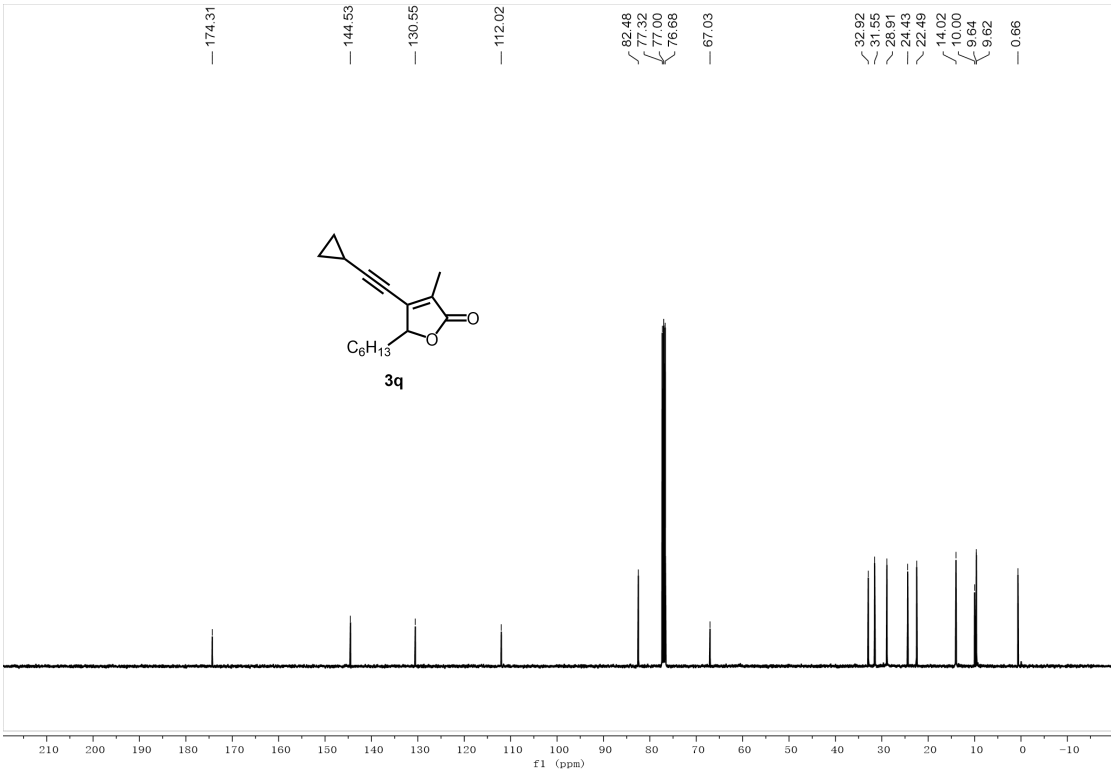
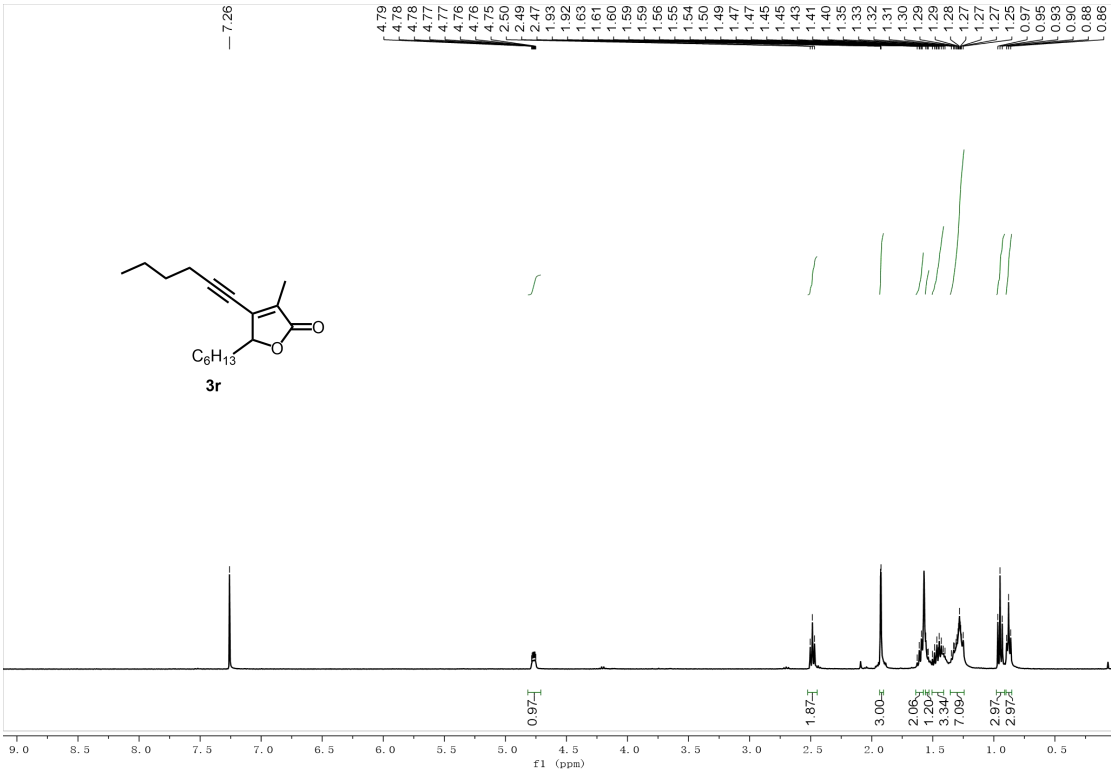
143.44
131.94
131.83
129.83
128.59
121.47
105.86
82.33
79.76
77.32
77.00
76.68
33.05
31.56
28.93
24.48
22.48
14.00
10.31
O
O
C6H13
3o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

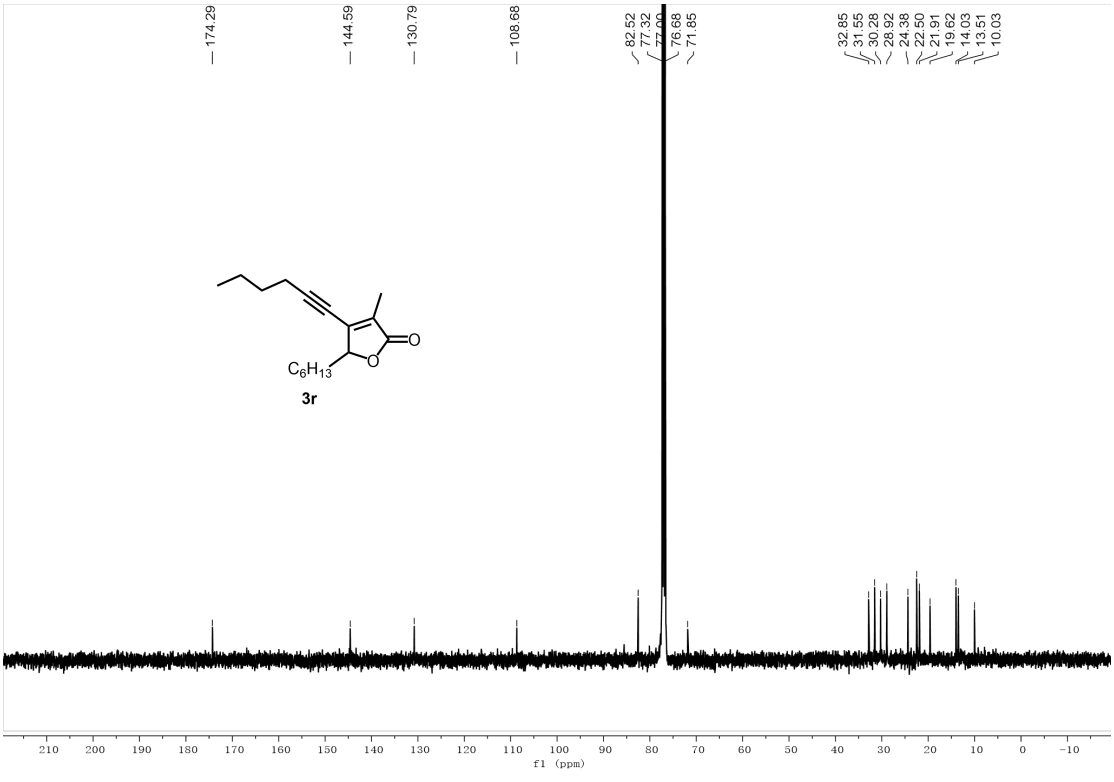

8.07 8.06 7.86 7.86 7.85 7.85 7.84 7.83 7.57 7.56 7.56 7.55 7.55 7.55 7.54 7.54 7.54 7.52 7.52 7.26
4.97 4.96 4.96 4.95 4.95 4.94 4.94 4.93 2.09 2.08 1.71 1.71 1.70 1.69 1.69 1.68 1.68 1.67 1.67 1.66 1.66 1.65 1.64 1.55 1.54 1.54 1.53 1.52 1.52 1.51 1.50 1.50 1.48 1.41 1.40 1.39 1.38 1.37 1.37 1.36 1.35 1.34 1.34 1.33 1.32 1.31 1.31 1.30 1.29 1.29 1.29 1.28
O
O
C6H13
3p
1.00 3.04 3.00 1.00 3.20 1.40 2.00 6.68 3.08
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)

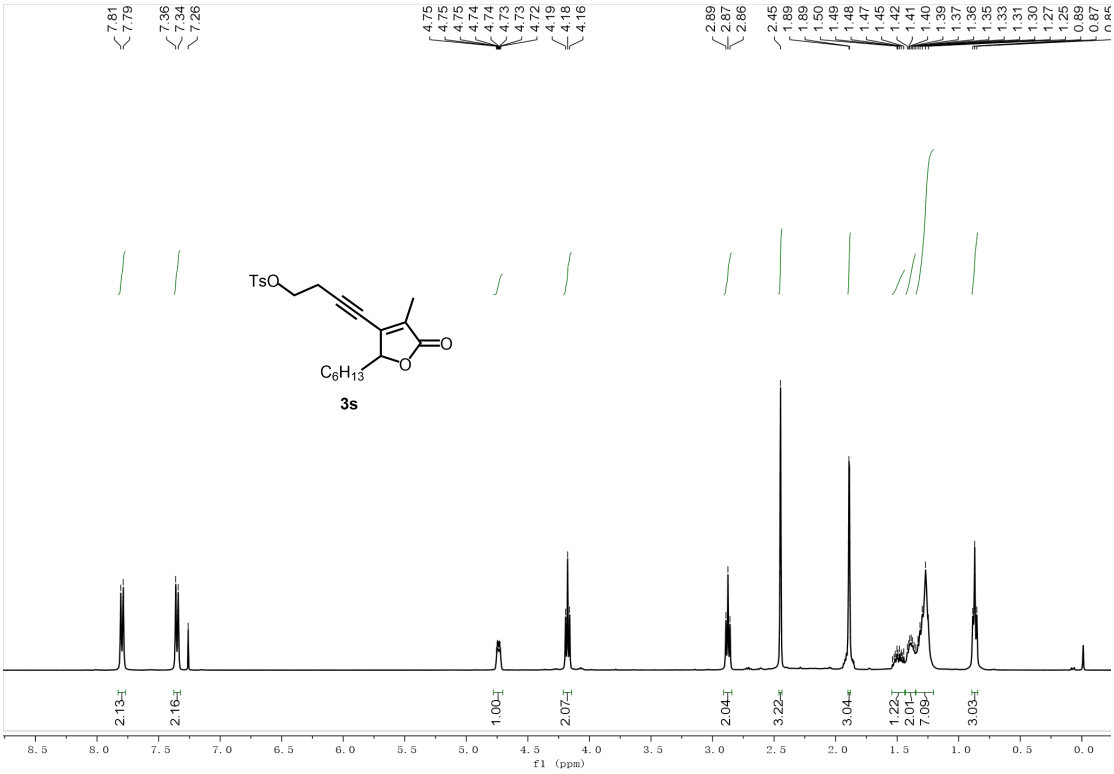

173.80
143.48 133.40 132.73 132.39 131.93 128.37 127.96 127.84 127.61 127.55 126.96 118.62
106.33
82.35 80.03 77.32 77.00 76.68
33.08 31.57 28.93 24.52 22.49
14.02 10.38
O
O
C6H13
3p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

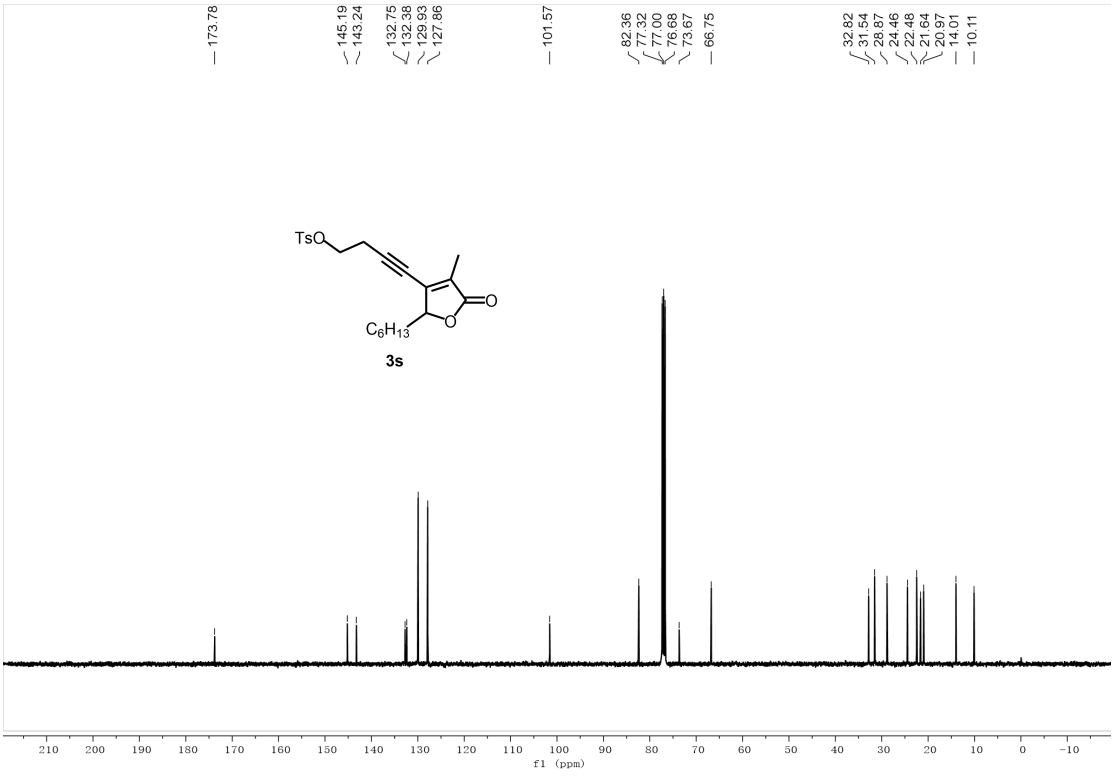

7.26
4.75 4.75 4.74 4.74 4.73 4.73 4.72 4.72 1.90 1.89 1.54 1.53 1.52 1.52 1.51 1.50 1.50 1.49 1.47 1.44 1.43 1.42 1.41 1.41 1.40 1.40 1.39 1.38 1.37 1.32 1.32 1.31 1.30 1.28 1.28 1.28 1.27 1.26 1.24 1.01 1.01 1.00 0.99 0.98 0.98 0.98 0.97 0.96 0.96 0.89 0.87 0.86 0.86 0.85 0.85 0.84 0.84 0.84 0.83
O
O
C6H13
3q
1.00
3.00
2.08
2.09
9.12
2.02
5.10
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)

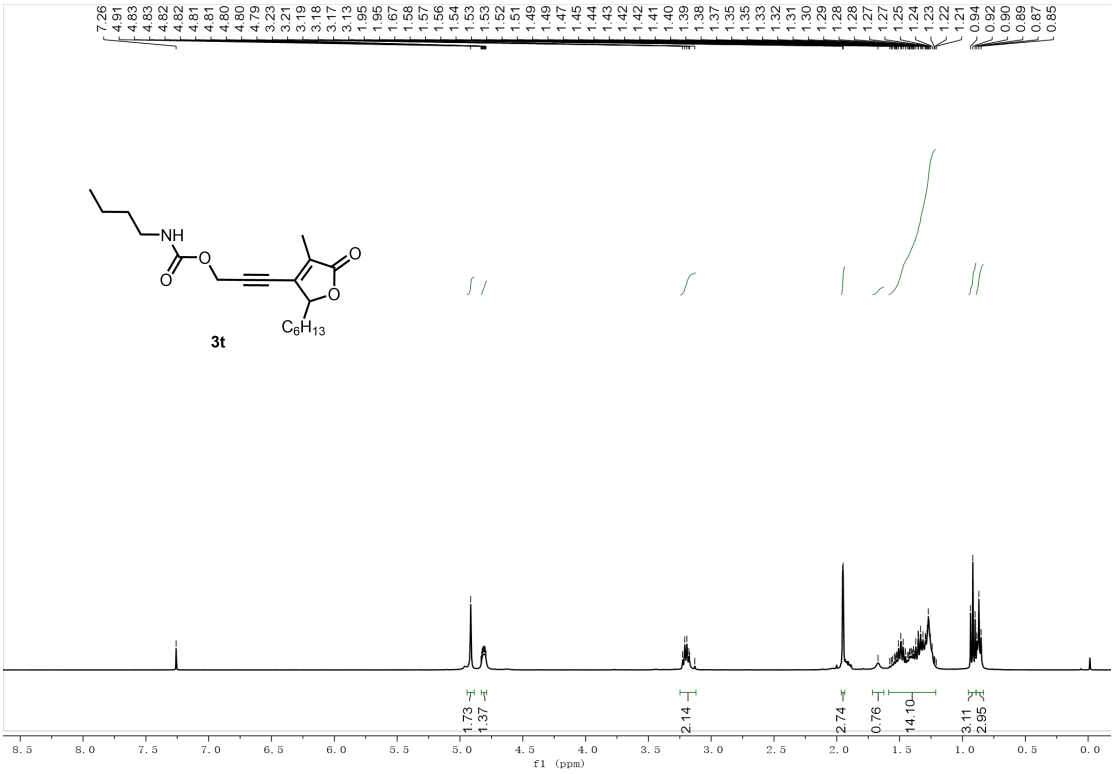

174.31
144.53
130.55
112.02
82.48
77.32
77.00
76.68
67.03
32.92
31.55
28.91
24.43
22.49
14.02
10.00
9.64
9.62
0.66
O
O
C6H13
3q
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

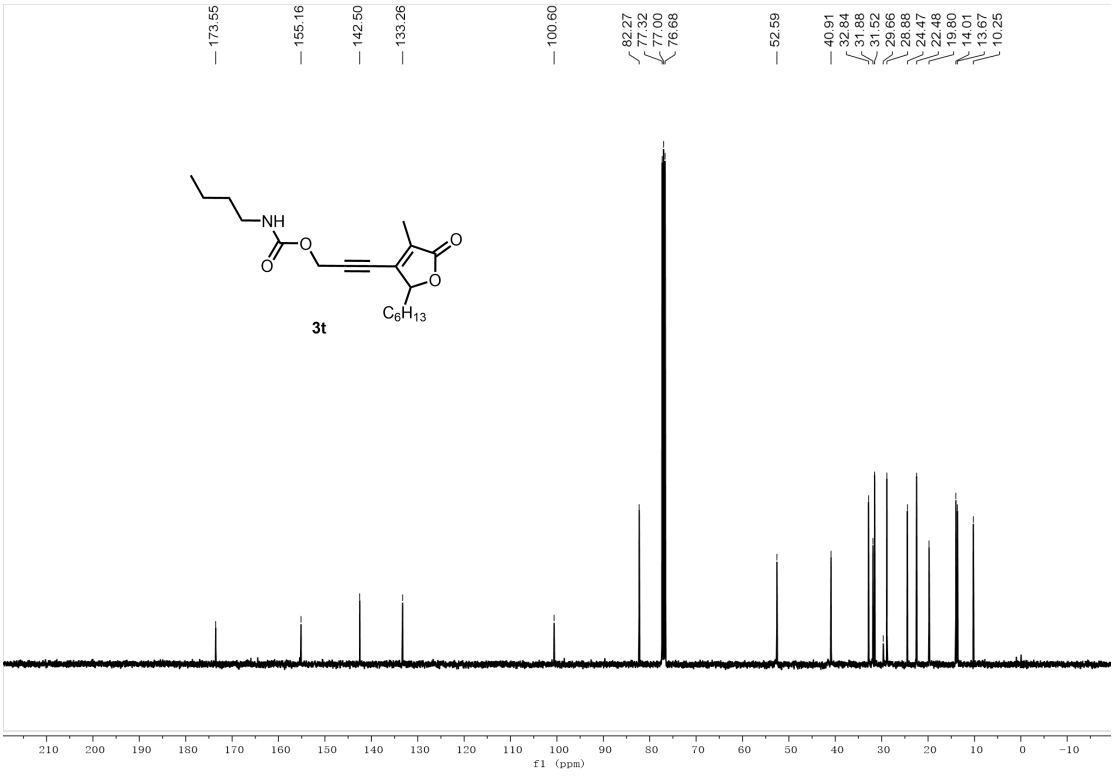

7.26
4.79 4.78 4.78 4.77 4.77 4.76 4.76 4.75 2.50 2.49 2.47 1.93 1.92 1.63 1.61 1.60 1.59 1.59 1.56 1.55 1.54 1.50 1.49 1.47 1.47 1.45 1.45 1.43 1.41 1.40 1.35 1.33 1.32 1.31 1.30 1.29 1.29 1.28 1.27 1.27 1.27 1.25 0.97 0.95 0.93 0.90 0.88 0.86
O
O
C6H13
3r
0.97 1.87 3.00 2.06 1.20 3.34 7.09 2.97 2.97
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
f1 (ppm)

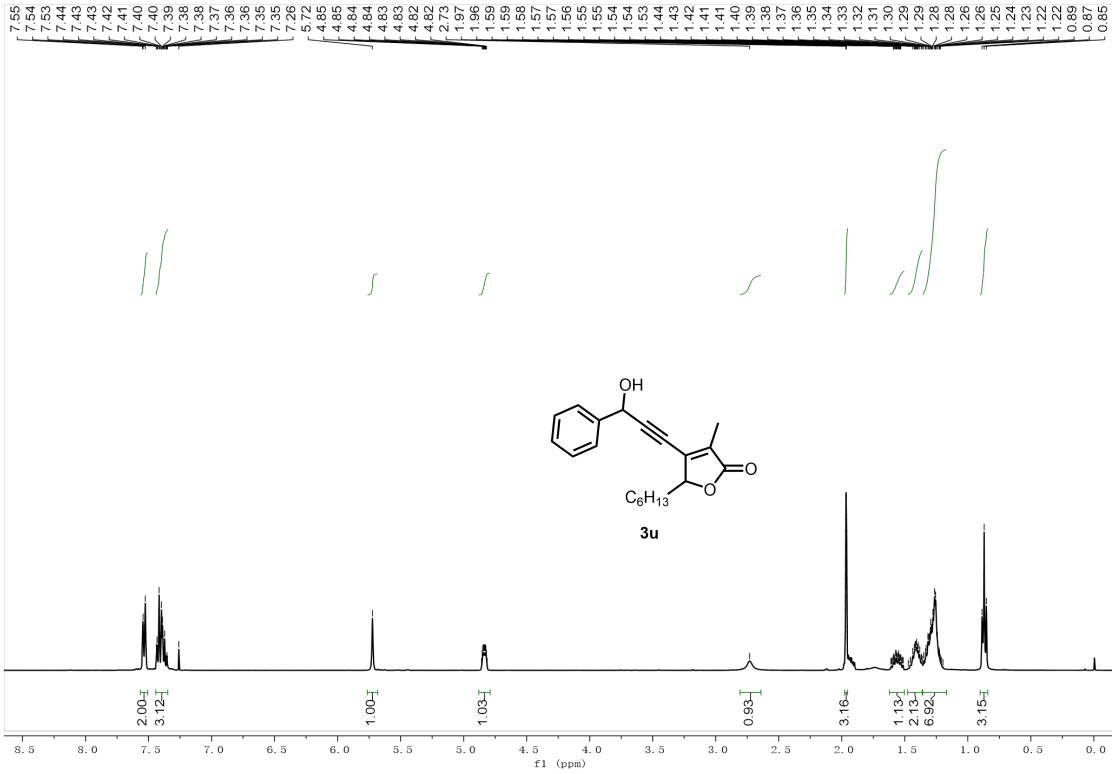

174.29
144.59
130.79
108.68
82.52
77.32
77.00
76.68
71.85
32.85
31.55
30.28
28.92
24.38
22.50
21.91
19.62
14.03
13.51
10.03
O
O
C6H13
3r
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

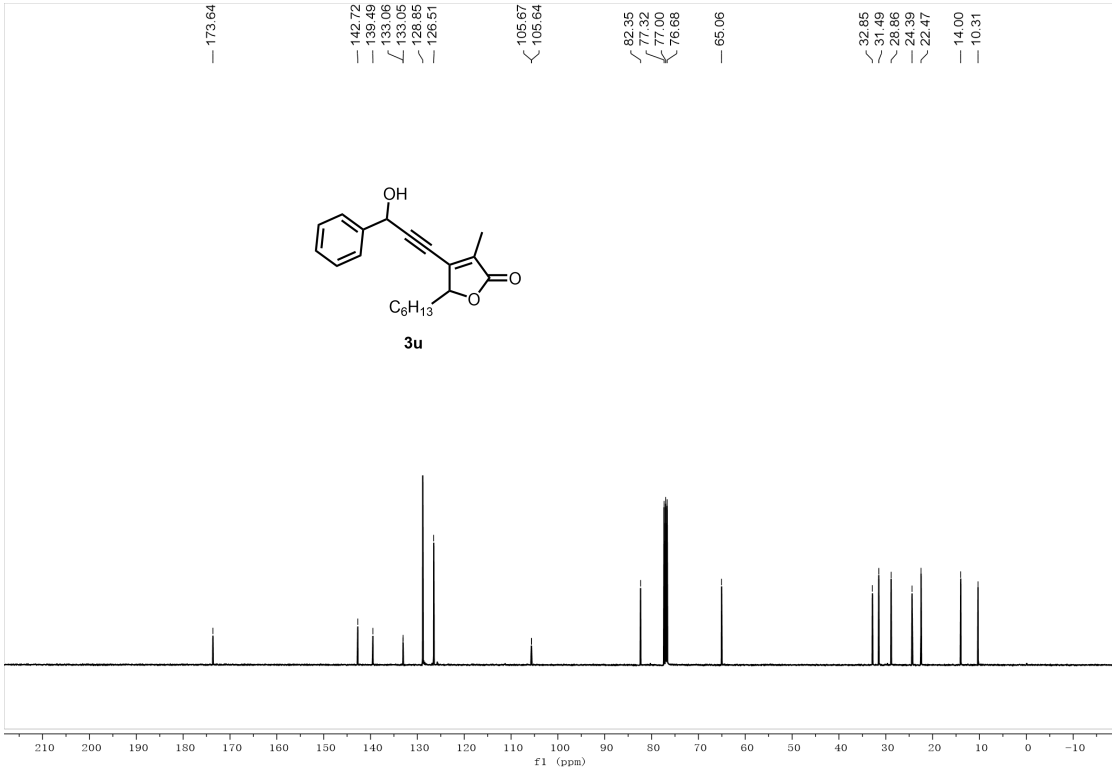

7.81
7.79
7.36
7.34
7.26
4.75
4.75
4.75
4.74
4.74
4.73
4.72
4.19
4.18
4.16
2.89
2.87
2.86
2.45
1.89
1.89
1.50
1.49
1.48
1.47
1.45
1.42
1.41
1.40
1.39
1.37
1.36
1.35
1.33
1.31
1.30
1.27
1.25
0.89
0.87
TsO
O
O
C6H13
3s
2.13
2.16
1.00
2.07
2.04
3.22
3.04
1.22
2.01
7.09
3.03
f1 (ppm)

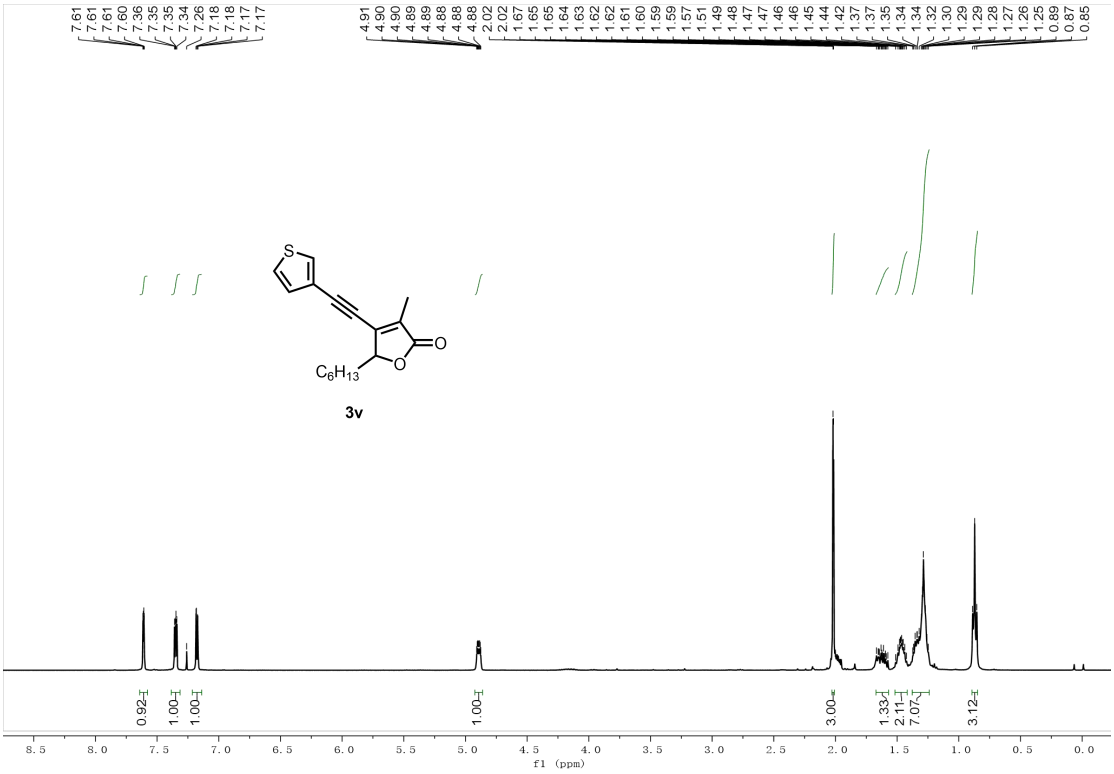

173.78
145.19
143.24
132.75
132.38
129.93
127.86
101.57
82.36
77.32
77.00
76.68
73.67
66.75
32.82
31.54
28.87
24.46
22.48
21.64
20.97
14.01
10.11
TsO
O
O
C6H13
3s
f1 (ppm)

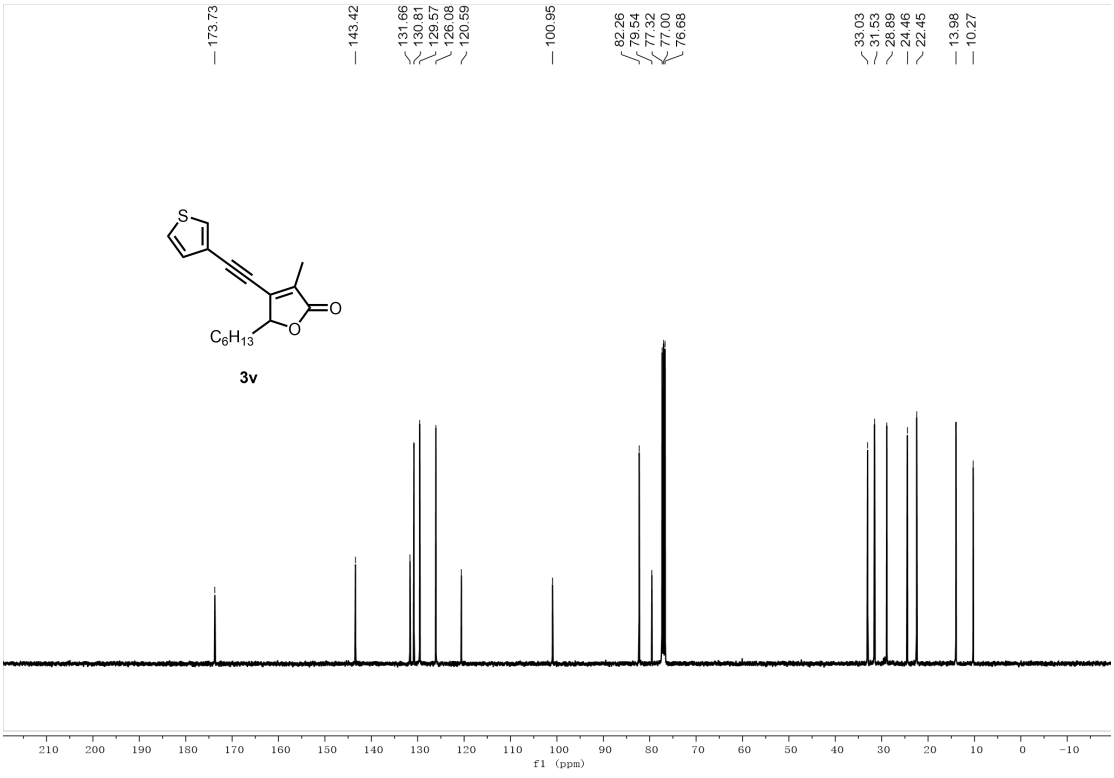

7.26 4.91 4.83 4.83 4.82 4.82 4.81 4.81 4.80 4.80 4.79 3.23 3.21 3.19 3.18 3.17 3.13 1.95 1.95 1.67 1.58 1.57 1.56 1.54 1.53 1.53 1.52 1.51 1.49 1.49 1.47 1.45 1.44 1.43 1.42 1.42 1.41 1.40 1.39 1.38 1.37 1.35 1.35 1.33 1.32 1.31 1.30 1.29 1.28 1.28 1.27 1.27 1.25 1.24 1.23 1.22 1.21 0.94 0.92 0.90 0.89 0.87 0.85
NH
O
O
O
O
C6H13
3t
1.73
1.37
2.14
2.74
0.76
14.10
3.11
2.95
f1 (ppm)

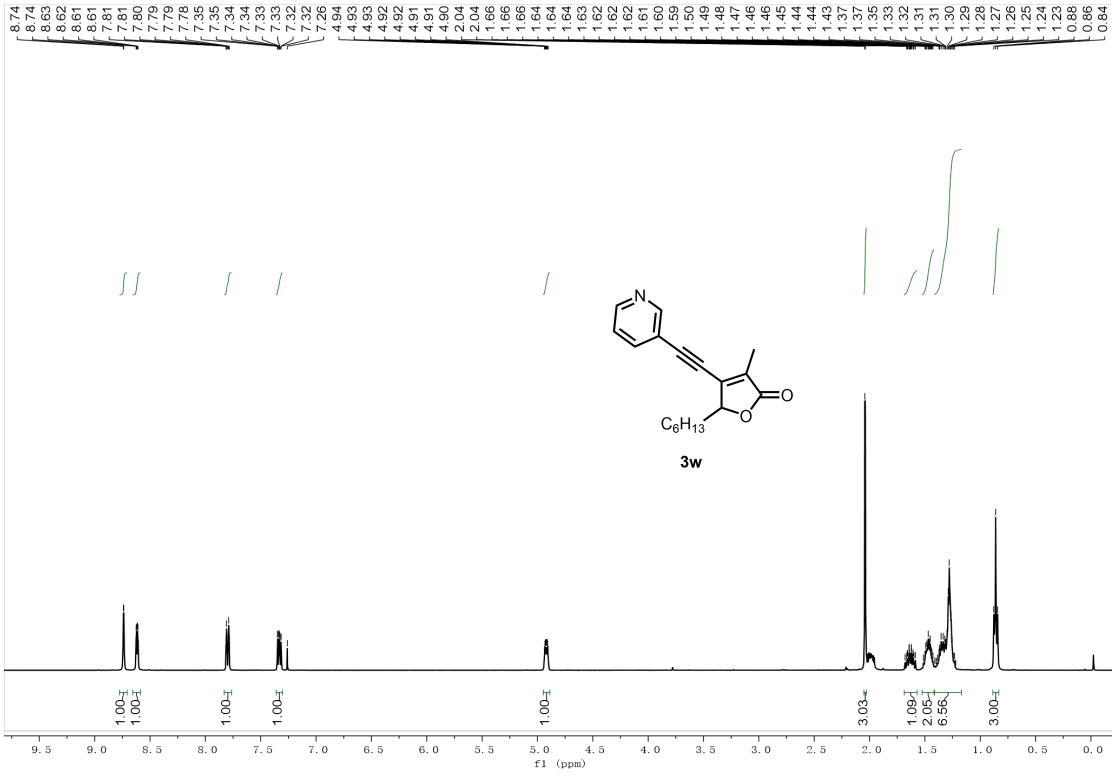

173.55 155.16 142.50 133.26 100.60 82.27 77.32 77.00 76.68 52.59 40.91 32.84 31.88 31.52 29.66 28.88 24.47 22.48 19.80 14.01 13.67 10.25
NH
O
O
O
O
C6H13
3t
f1 (ppm)

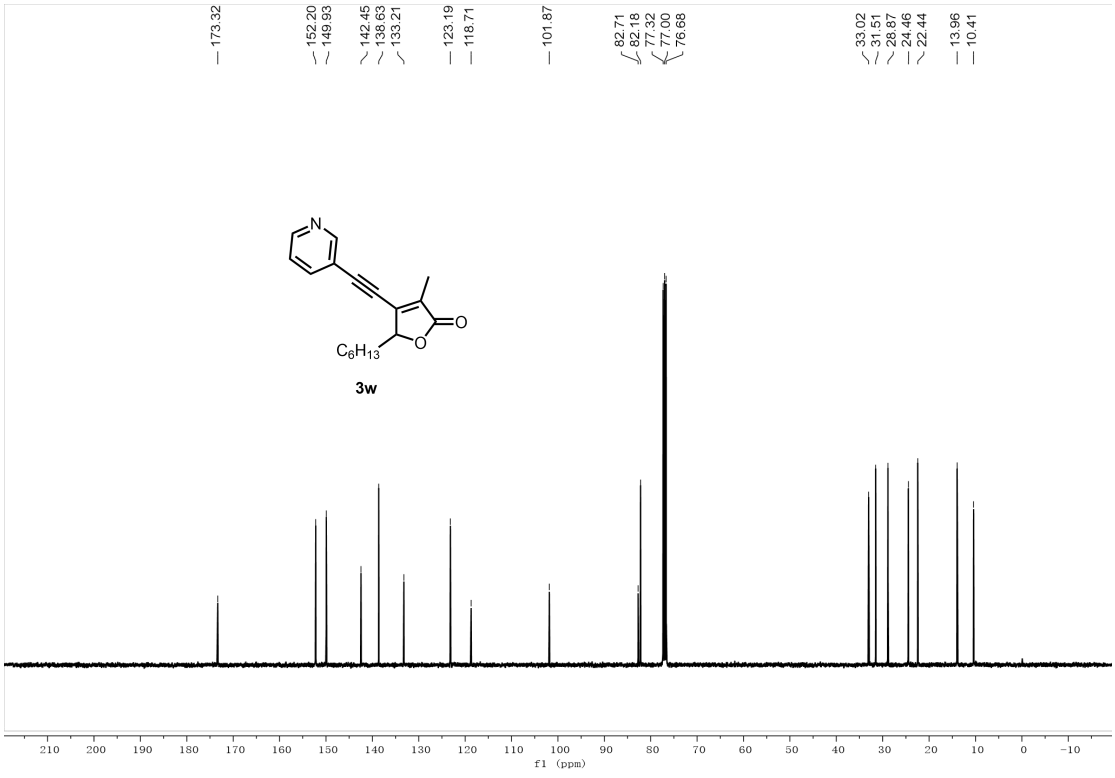

OH
O
O
C6H13
3u
f1 (ppm)

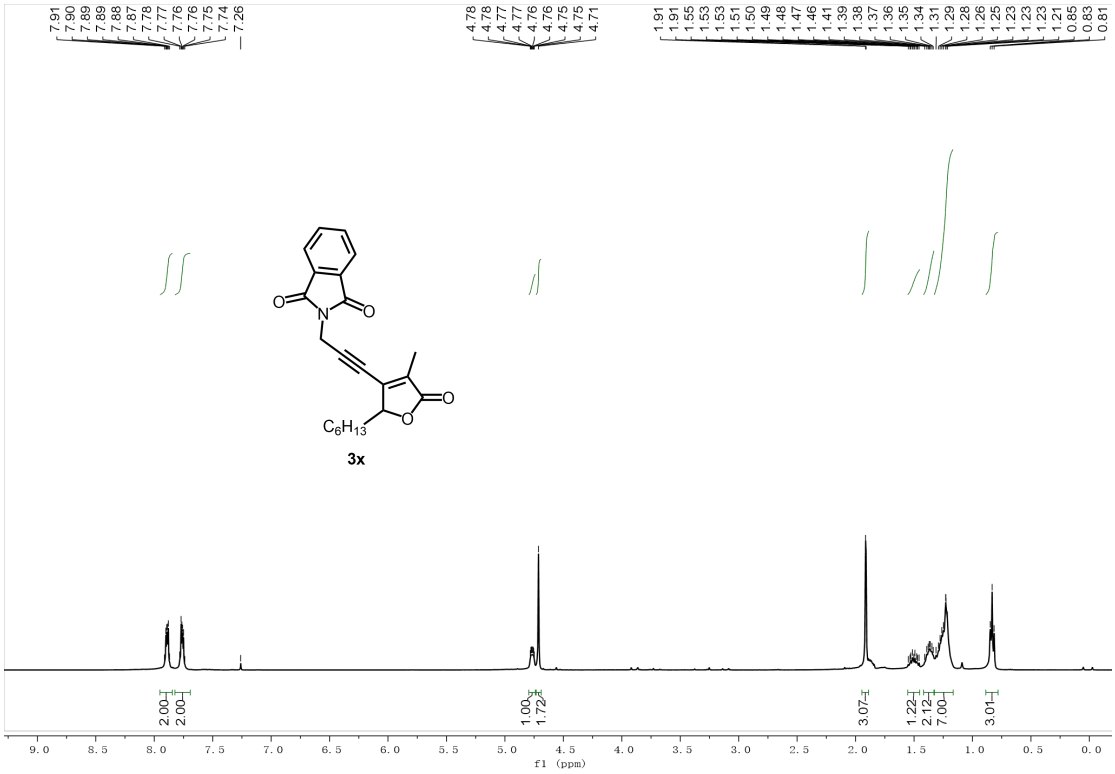

OH
O
O
C6H13
3u
f1 (ppm)


7.61 7.61 7.61 7.60 7.36 7.35 7.35 7.34 7.26 7.18 7.18 7.17 7.17
4.91 4.90 4.90 4.89 4.89 4.88 4.88 4.88 2.02 2.02 1.67 1.65 1.65 1.64 1.63 1.62 1.62 1.61 1.60 1.59 1.59 1.57 1.51 1.49 1.48 1.47 1.47 1.46 1.46 1.45 1.44 1.42 1.37 1.37 1.35 1.34 1.34 1.32 1.30 1.29 1.29 1.28 1.27 1.26 1.25 0.89 0.87 0.85
S
O
O
C6H13
3v
0.92 1.00 1.00 1.00 3.00 1.33 2.11 7.07 3.12
f1 (ppm)


173.73 143.42 131.66 130.81 129.57 126.08 120.59 100.95 82.26 79.54 77.32 77.00 76.68 33.03 31.53 28.89 24.46 22.45 13.98 10.27
S
O
O
C6H13
3v
f1 (ppm)


8.74 8.74 8.63 8.62 8.61 8.61 7.81 7.81 7.80 7.79 7.79 7.78 7.35 7.34 7.34 7.33 7.33 7.32 7.32 7.26
4.94 4.93 4.93 4.92 4.92 4.91 4.91 4.90 2.04 2.04 1.66 1.66 1.64 1.64 1.64 1.63 1.62 1.62 1.62 1.61 1.60 1.59 1.50 1.49 1.48 1.47 1.46 1.46 1.45 1.44 1.44 1.43 1.37 1.37 1.35 1.33 1.32 1.31 1.31 1.30 1.29 1.28 1.27 1.26 1.25 1.24 1.23 0.88 0.86 0.84
N
O
O
C6H13
3w
1.00 1.00 1.00 1.00 1.00 3.03 1.09 2.05 6.56 3.00
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)


173.32
152.20 149.93 142.45 138.63 133.21 123.19 118.71 101.87 82.71 82.18 77.32 77.00 76.68
33.02 31.51 28.87 24.46 22.44 13.96 10.41
N
O
O
C6H13
3w
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.91
7.90
7.89
7.89
7.88
7.87
7.78
7.77
7.76
7.76
7.75
7.74
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4.78
4.78
4.77
4.77
4.76
4.76
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4.75
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1.53
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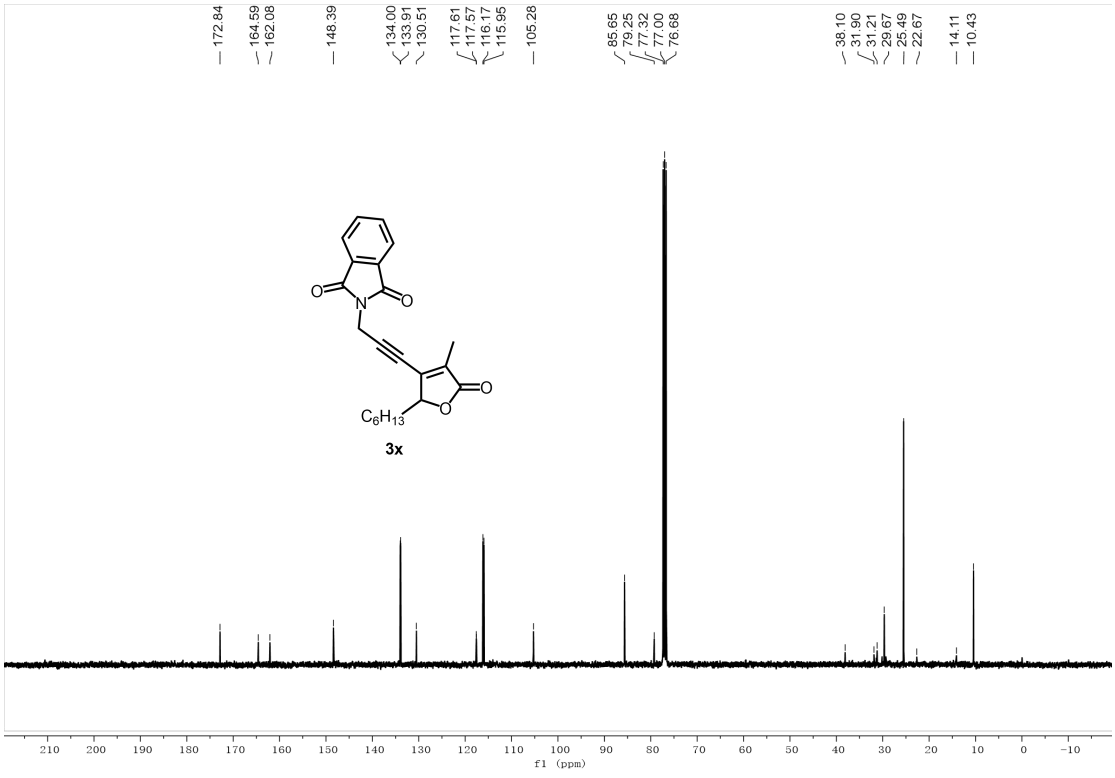
1.41
1.39
1.38
1.37
1.36
1.35
1.34
1.31
1.29
1.28
1.26
1.25
1.23
1.23
1.23
1.21
0.85
0.83
0.81
O
N
O
O
O
C6H13
3x
2.00
2.00
1.00
1.72
3.07
1.22
2.12
7.00
3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


172.84
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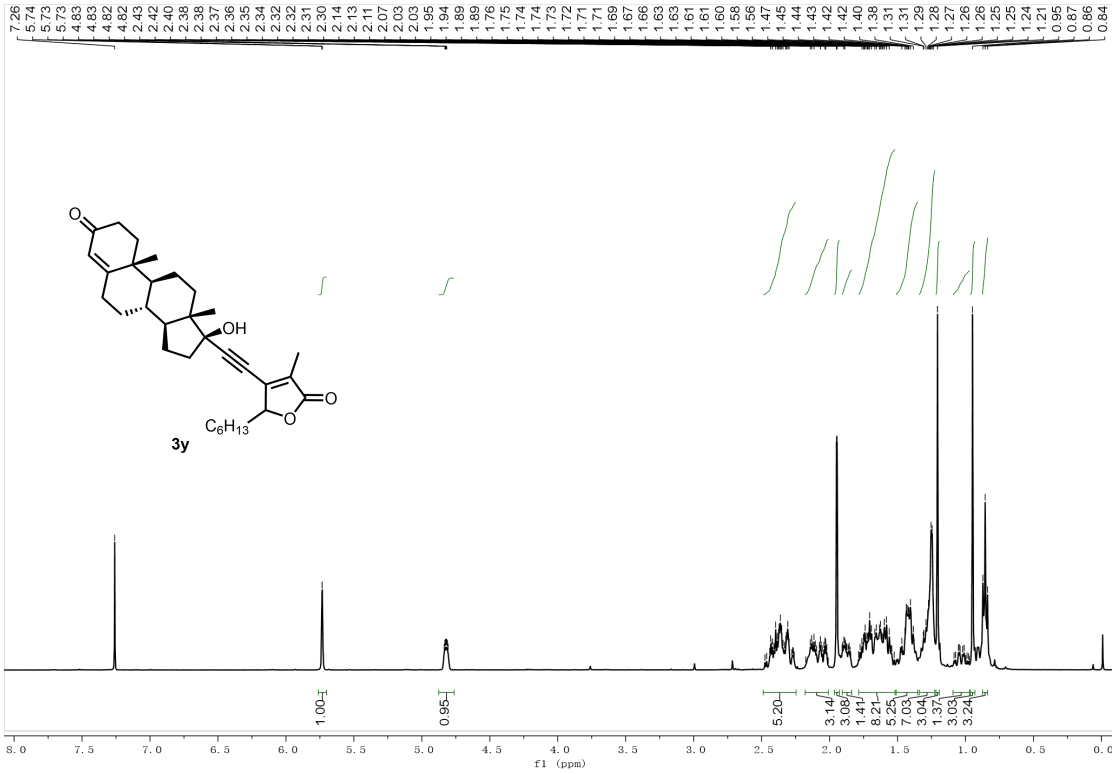
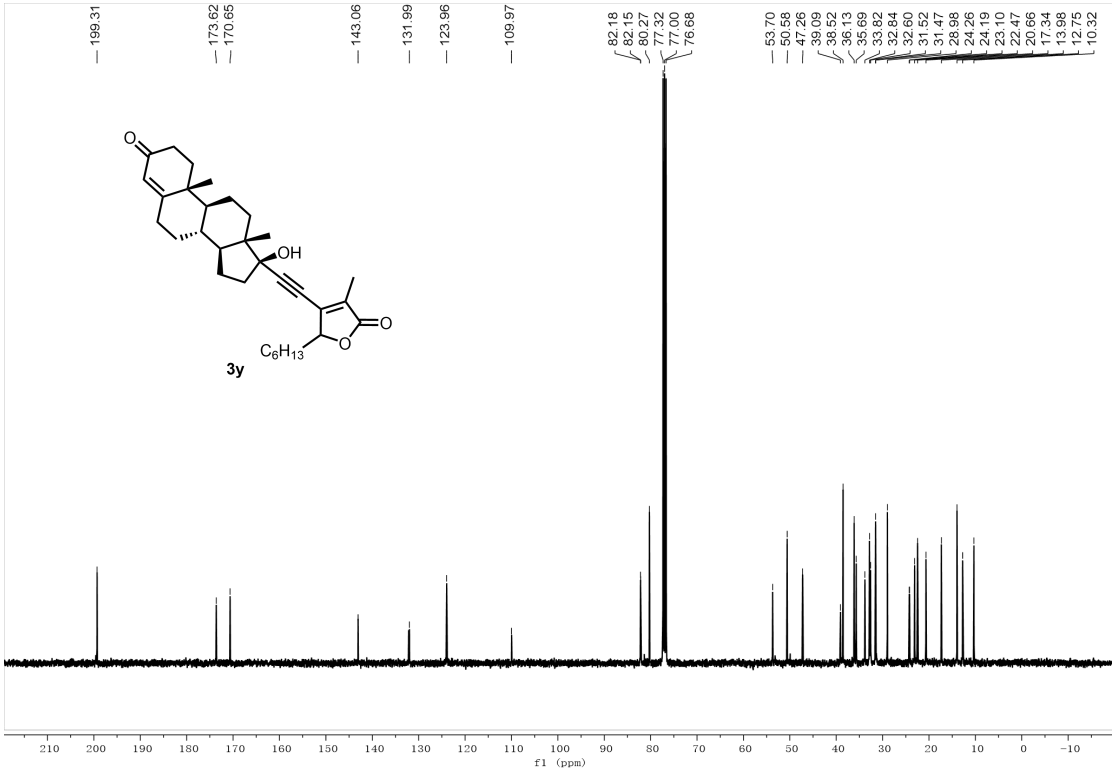
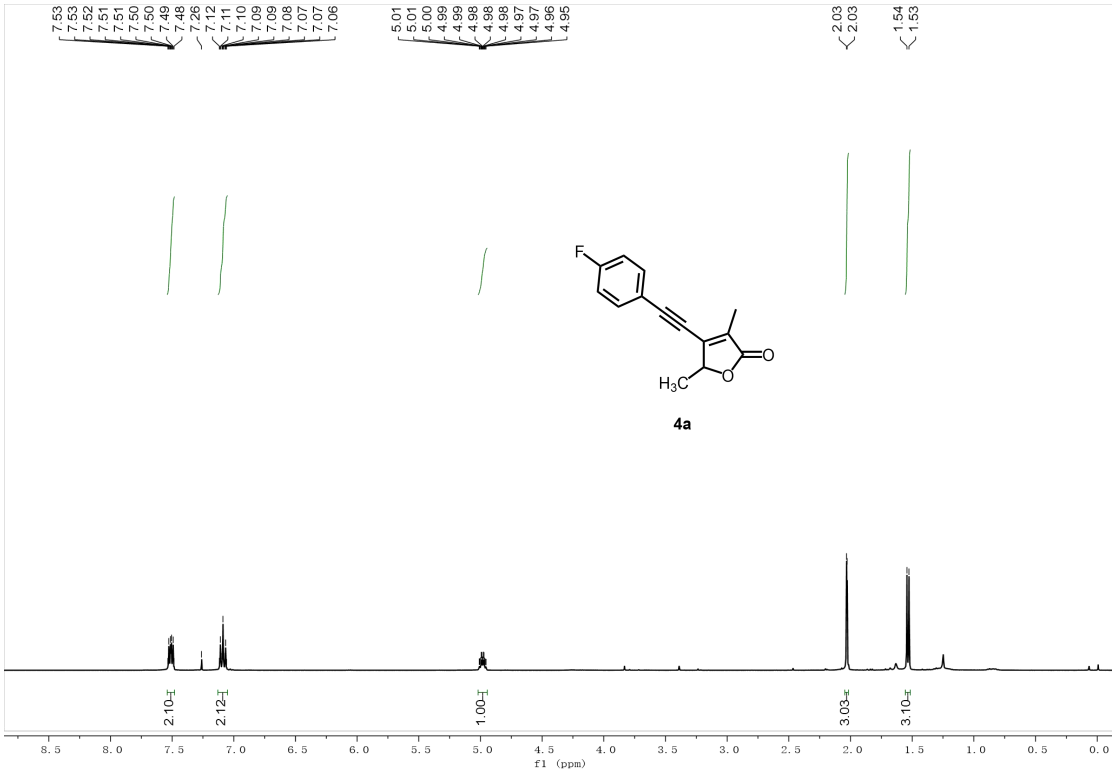
162.08
148.39
134.00
133.91
130.51
117.61
117.57
116.17
115.95
105.28
85.65
79.25
77.32
77.00
76.68
38.10
31.90
31.21
29.67
25.49
22.67
14.11
10.43
O
N
O
O
O
C6H13
3x
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.26 5.74 5.73 5.73 4.83 4.83 4.82 4.82 2.43 2.42 2.40 2.38 2.38 2.37 2.36 2.35 2.34 2.32 2.32 2.31 2.30 2.14 2.13 2.11 2.07 2.03 2.03 1.95 1.94 1.89 1.89 1.76 1.75 1.74 1.74 1.74 1.73 1.72 1.71 1.71 1.69 1.67 1.66 1.63 1.63 1.61 1.61 1.60 1.58 1.56 1.47 1.45 1.44 1.43 1.42 1.42 1.40 1.38 1.31 1.31 1.29 1.28 1.27 1.26 1.26 1.25 1.25 1.24 1.21 0.95 0.87 0.86 0.84
O
OH
O
O
C6H13
3y
1.00 0.95 5.20 3.14 3.08 1.41 8.21 5.25 7.03 3.04 1.37 3.03 3.24
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
f1 (ppm)


199.31 173.62 170.65 143.06 131.99 123.96 109.97 82.18 82.15 80.27 77.32 77.00 76.68 53.70 50.58 47.26 39.09 38.52 36.13 35.69 33.82 32.84 32.60 31.52 31.47 28.98 24.26 24.19 23.10 22.47 20.66 17.34 13.98 12.75 10.32
O
OH
O
O
C6H13
3y
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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7.53
7.52
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7.12
7.11
7.10
7.09
7.09
7.08
7.07
7.07
7.06
5.01
5.01
5.00
4.99
4.99
4.98
4.98
4.98
4.97
4.97
4.96
4.95
2.03
2.03
1.54
1.53
F
O
O
H3C
4a
2.10
2.12
1.00
3.03
3.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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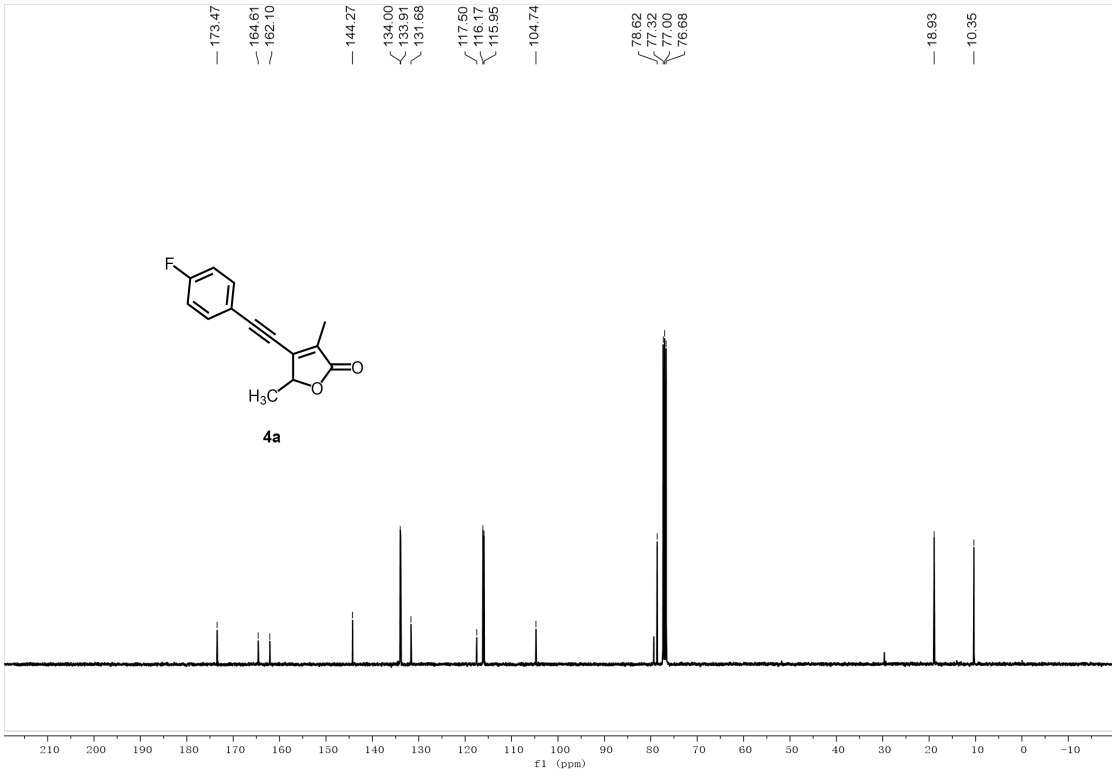
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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144.27
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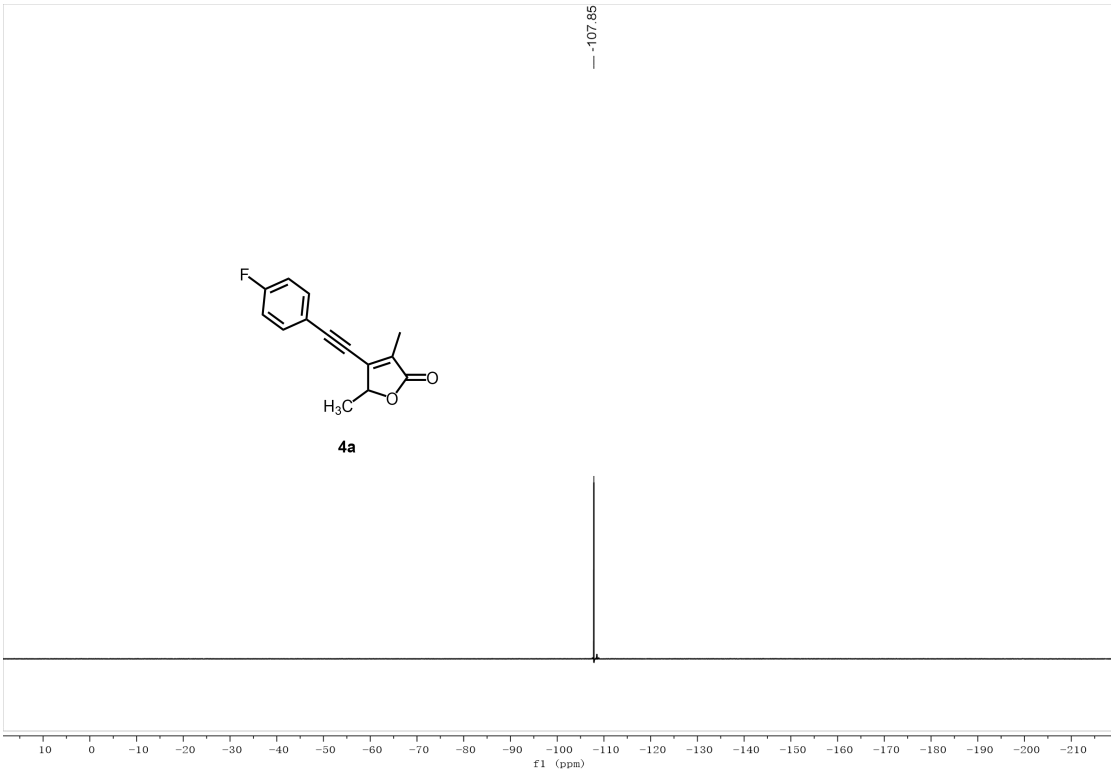
133.91
131.68
117.50
116.17
115.95
104.74
78.62
77.32
77.00
76.68
18.93
10.35
F
O
O
H3C
4a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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O
O
H3C
4a
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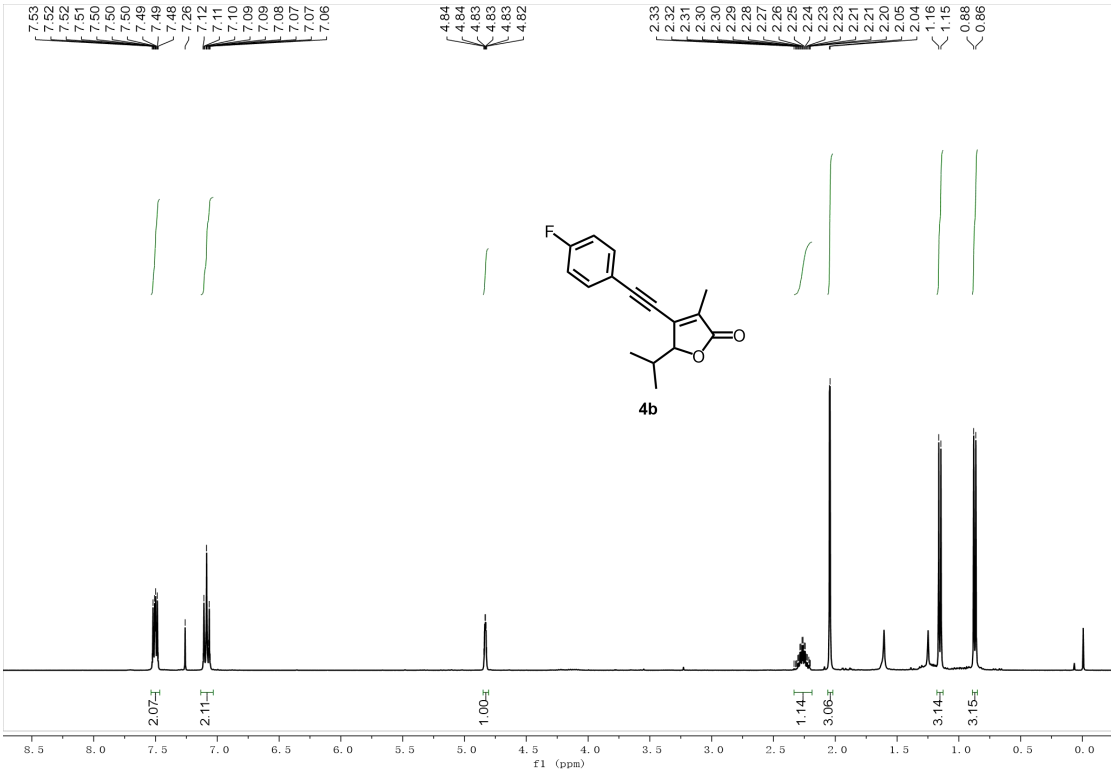
f1 (ppm)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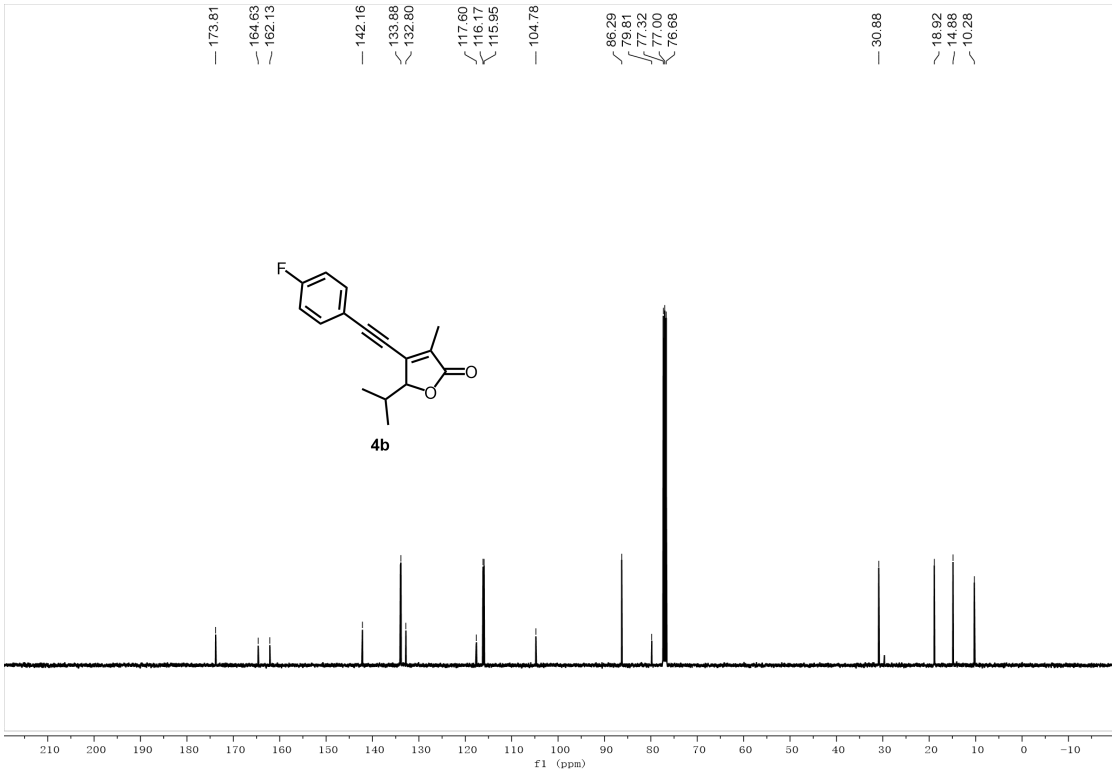
4.84 4.84 4.83 4.83 4.83 4.82
2.33 2.32 2.31 2.30 2.30 2.29 2.28 2.27 2.26 2.25 2.24 2.23 2.23 2.21 2.21 2.20 2.05 2.04 1.16 1.15 0.88 0.86
F
O
O
4b
2.07 2.11 1.00 1.14 3.06 3.14 3.15
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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142.16
133.88
132.80
117.60
116.17
115.95
104.78
86.29
79.81
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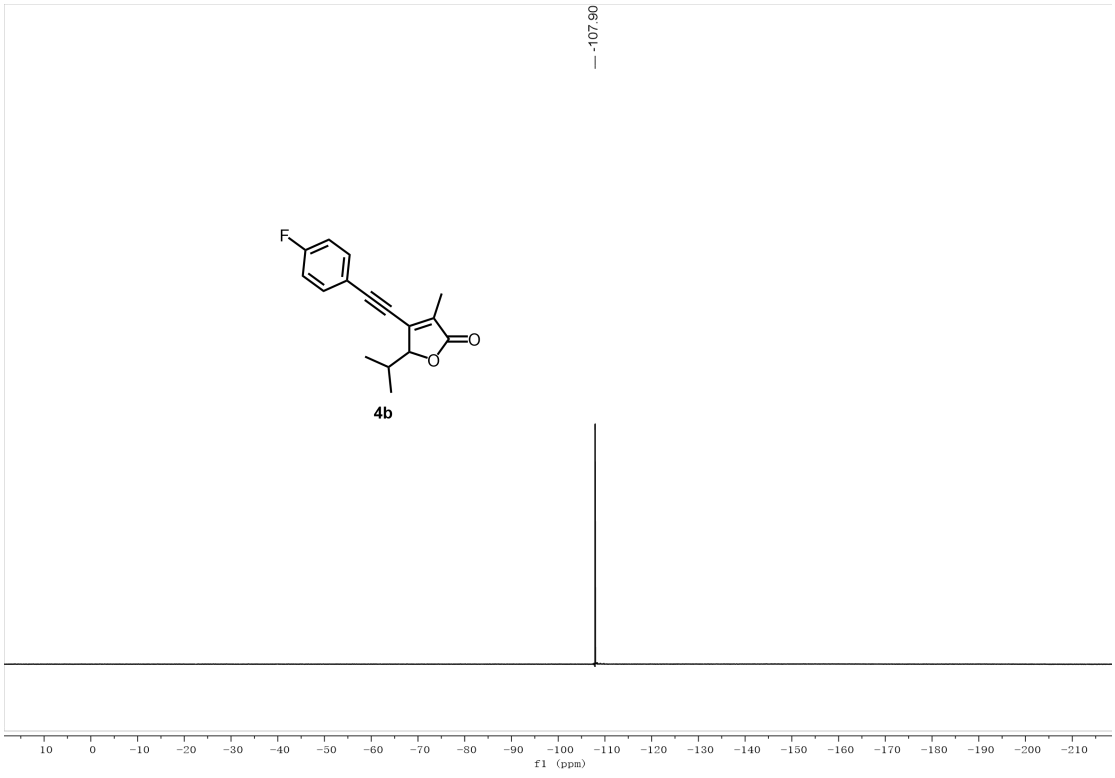
14.88
10.28
F
O
O
4b
f1 (ppm)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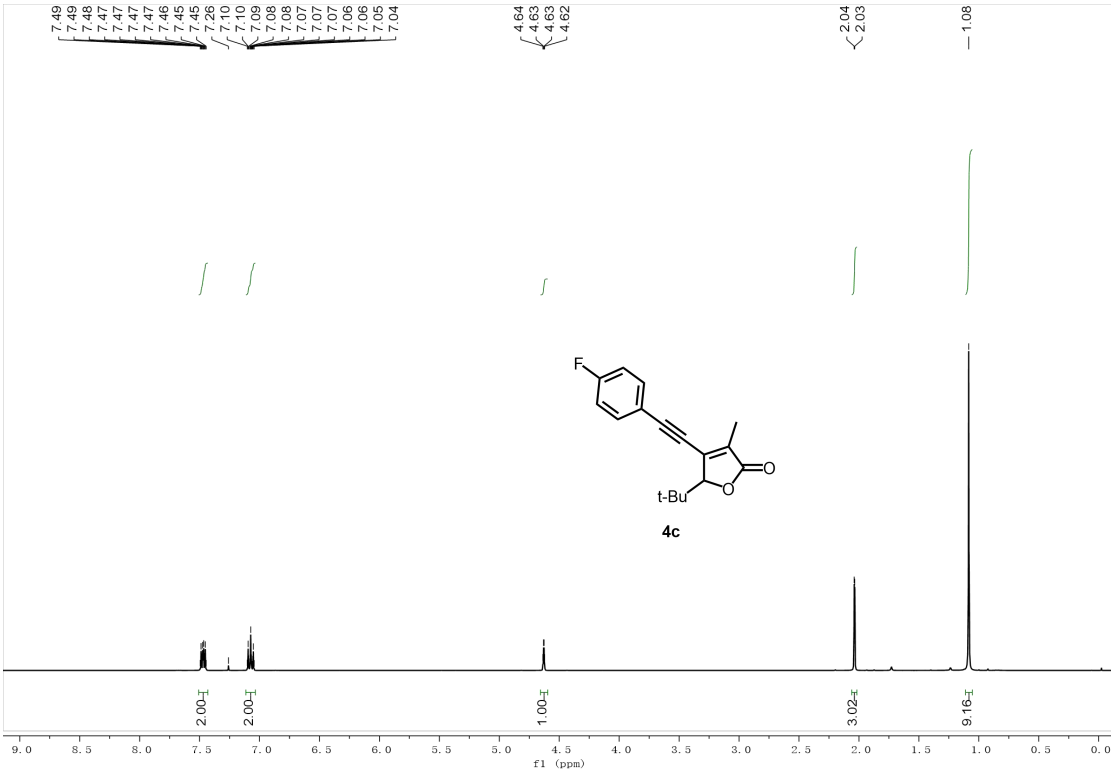
F
O
O
4b
f1 (ppm)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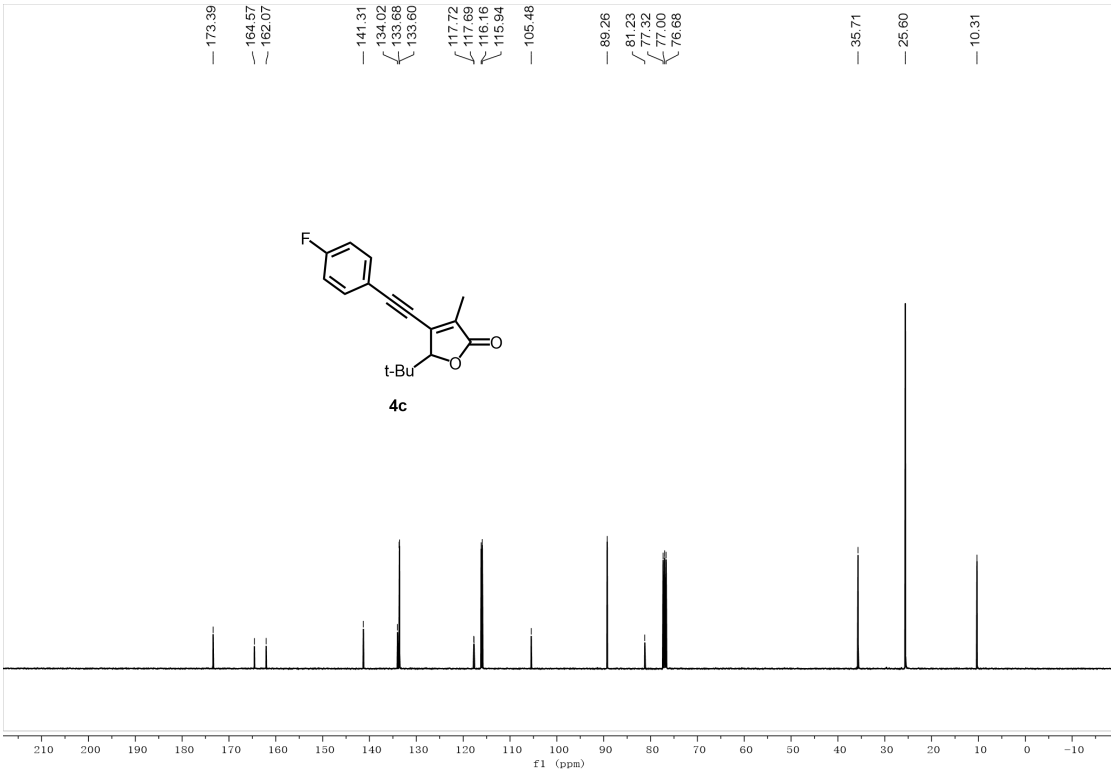
7.46
7.45
7.45
7.26
7.10
7.10
7.09
7.08
7.08
7.07
7.07
7.07
7.06
7.06
7.05
7.04
4.64
4.63
4.63
4.62
2.04
2.03
1.08
F
O
O
t-Bu
2.00
2.00
1.00
3.02
9.16
f1 (ppm)

4c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162.07
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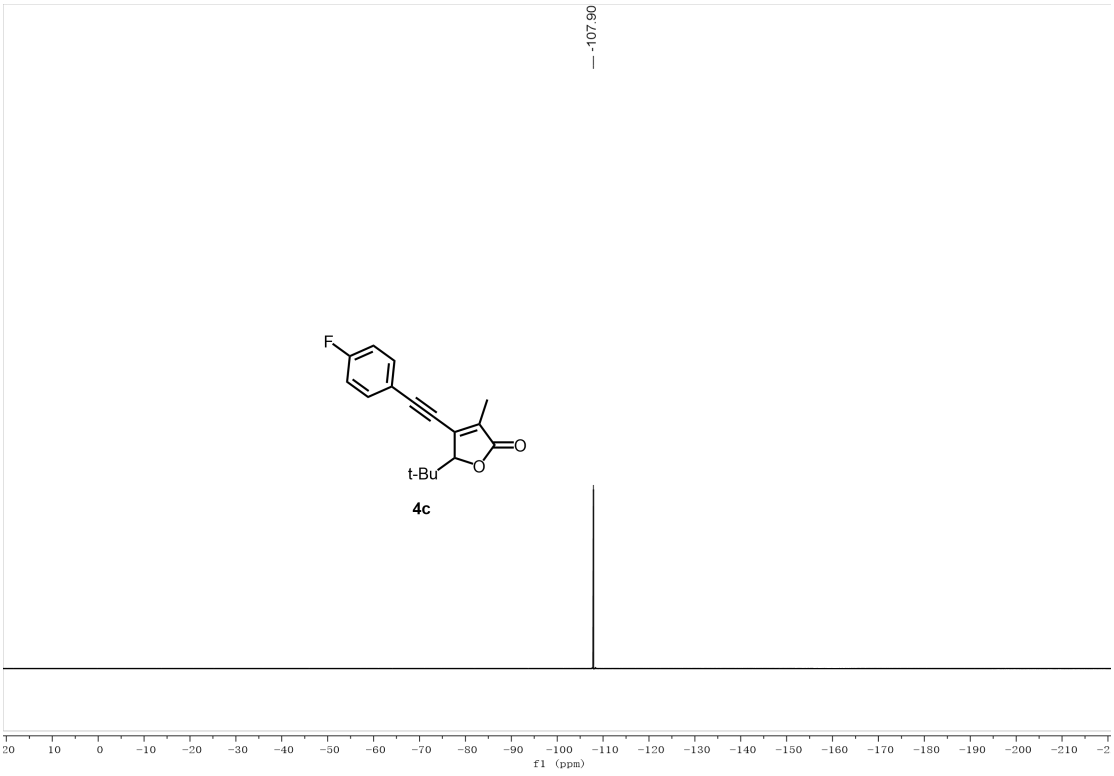
134.02
133.68
133.60
117.72
117.69
116.16
115.94
105.48
89.26
81.23
77.32
77.00
76.68
35.71
25.60
10.31
F
O
O
t-Bu
f1 (ppm)

4c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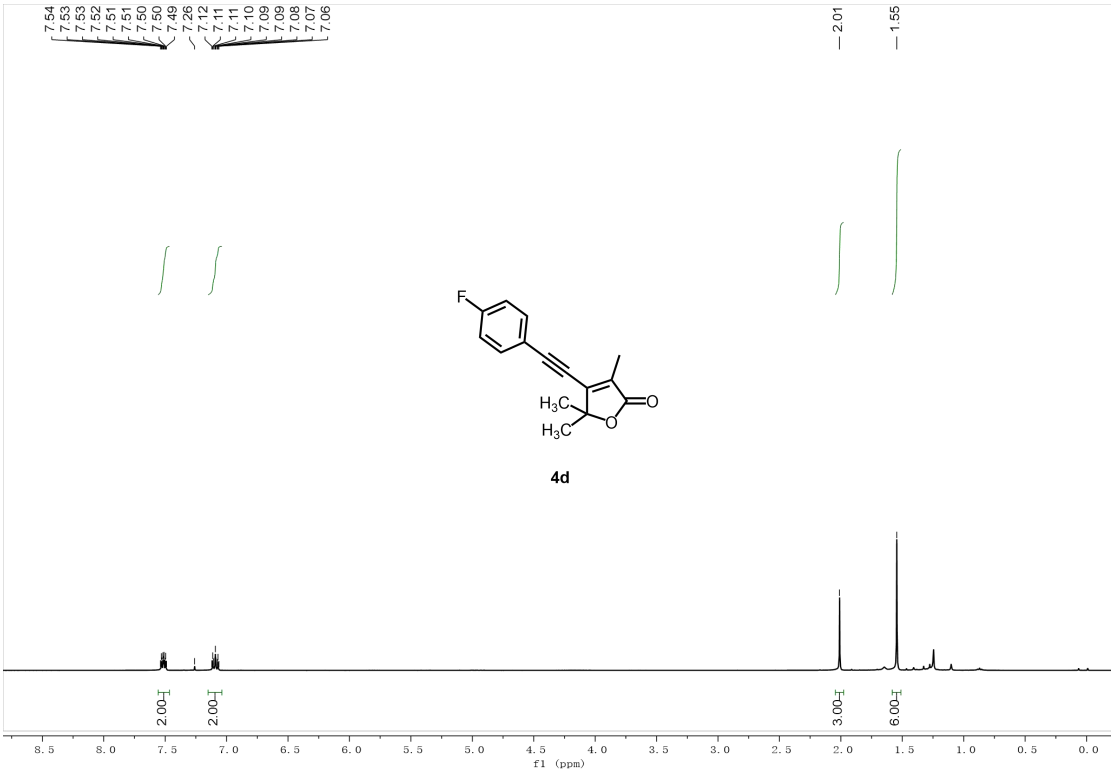
F
O
O
t-Bu
4c
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)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7.50
7.49
7.26
7.12
7.11
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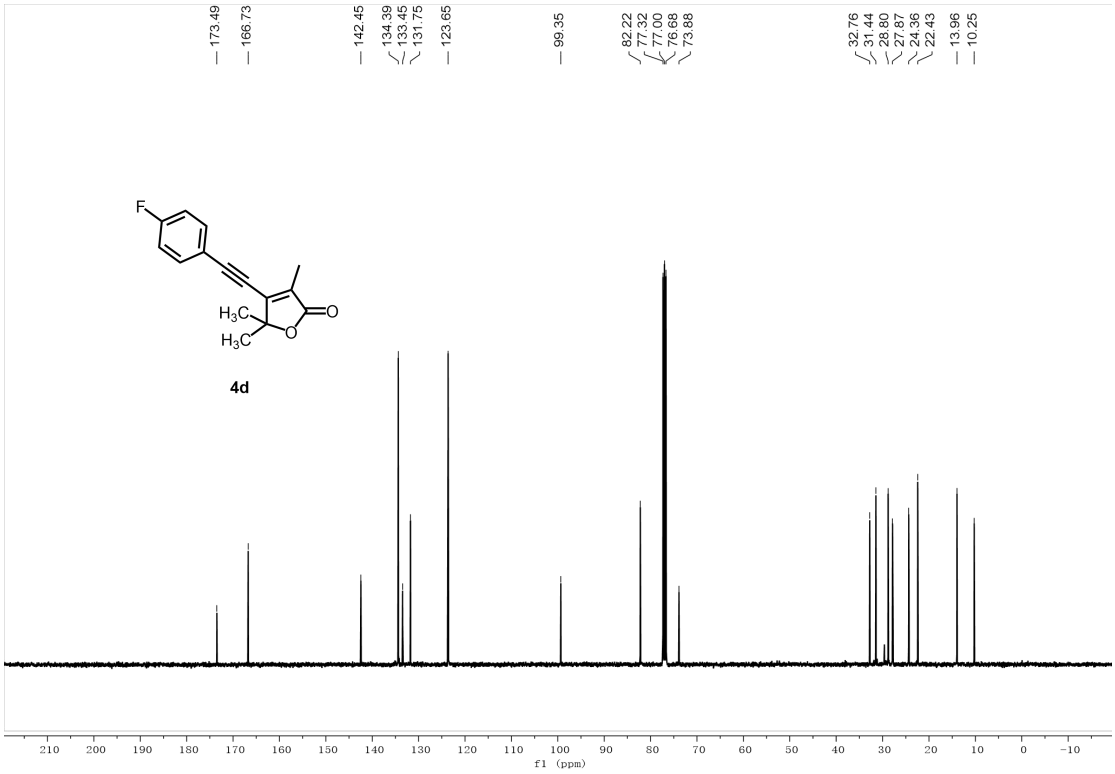
7.10
7.09
7.09
7.08
7.07
7.06
2.01
1.55
F
O
O
H3C
H3C
4d
2.00
2.00
3.00
6.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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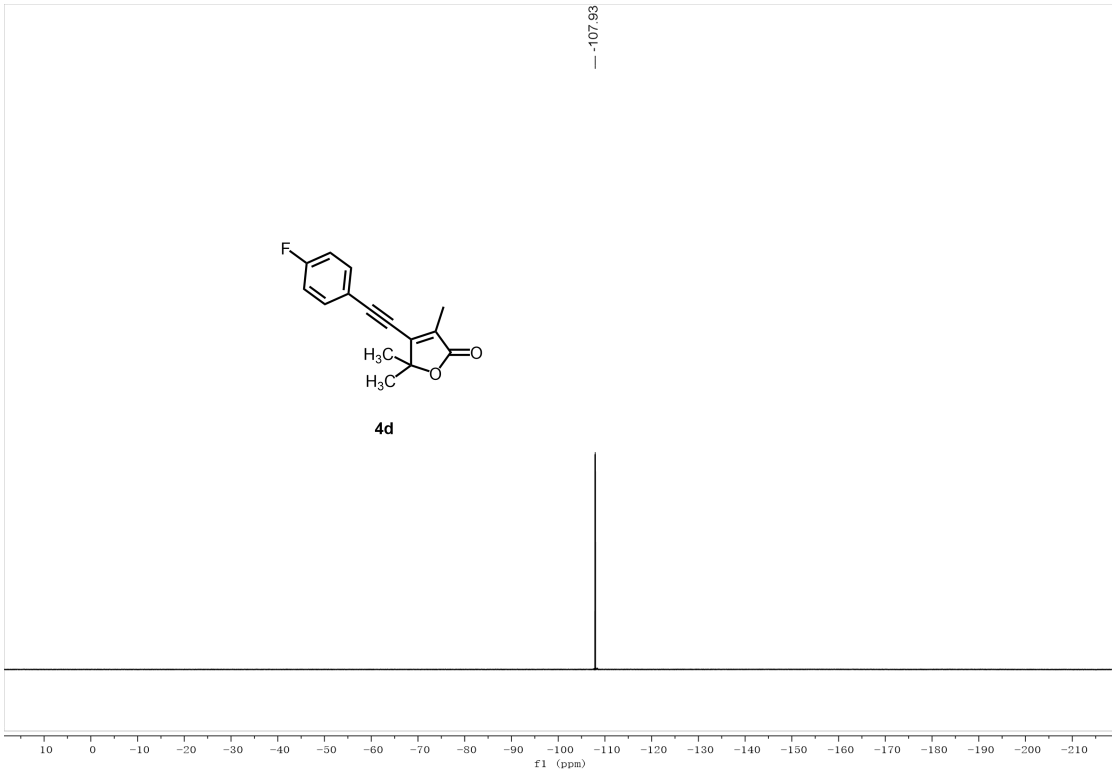
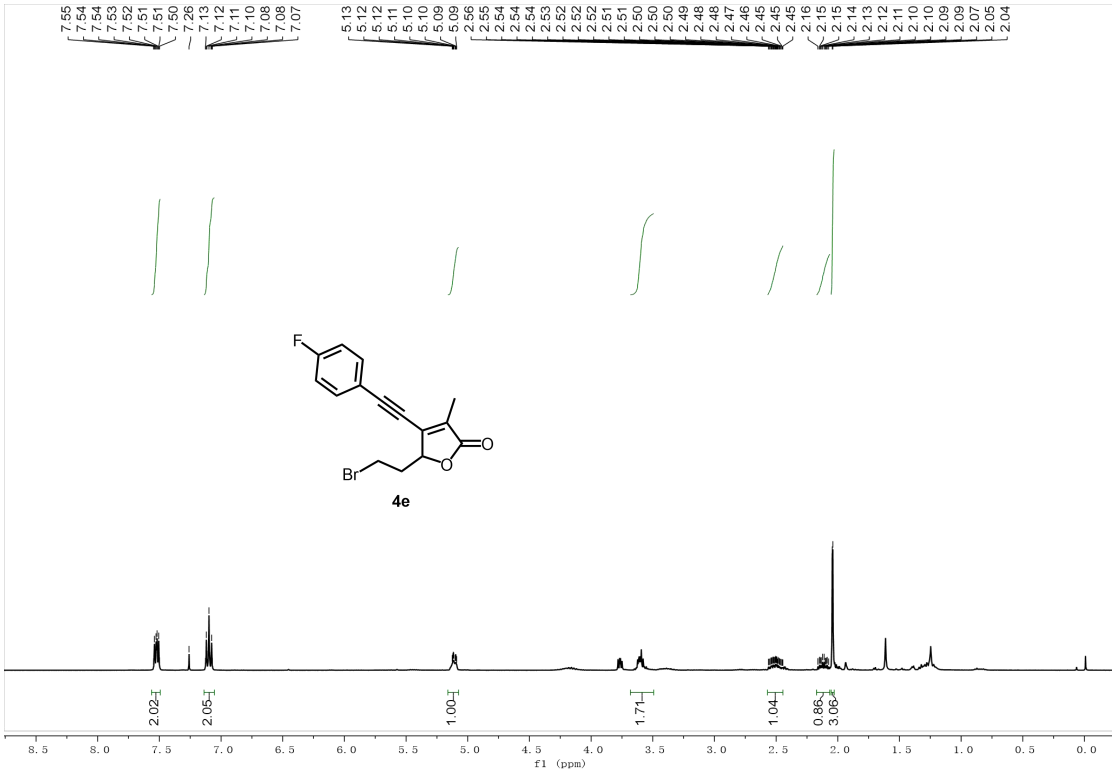
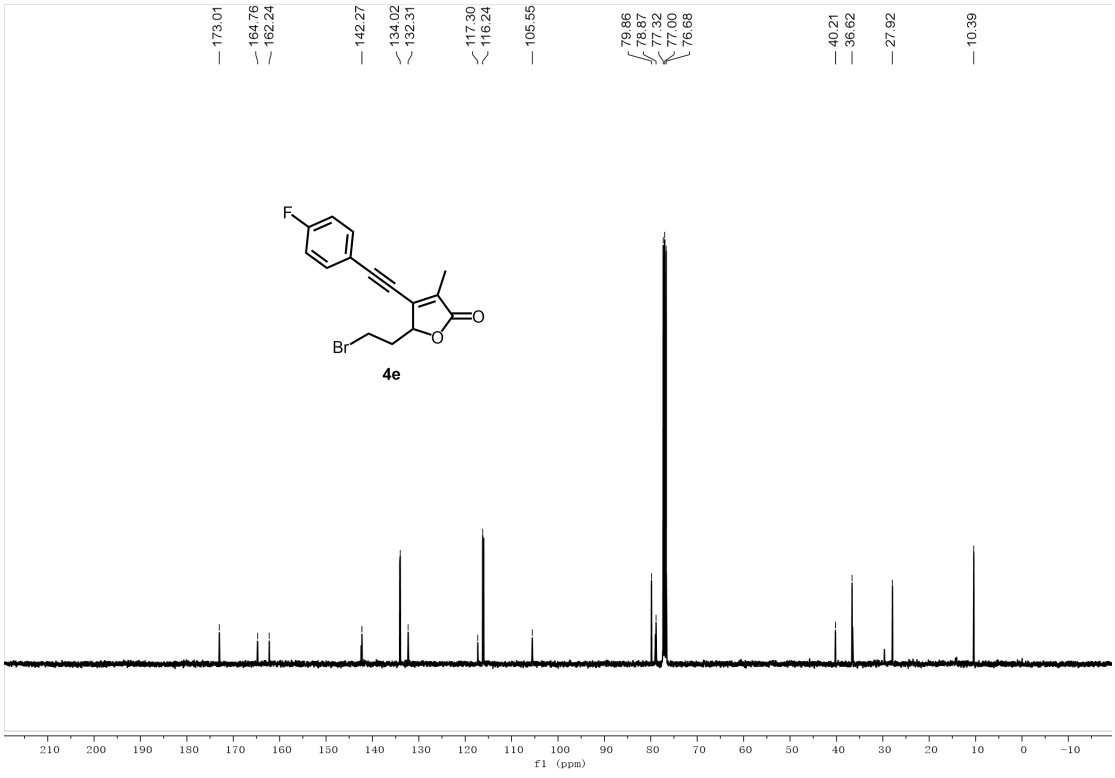
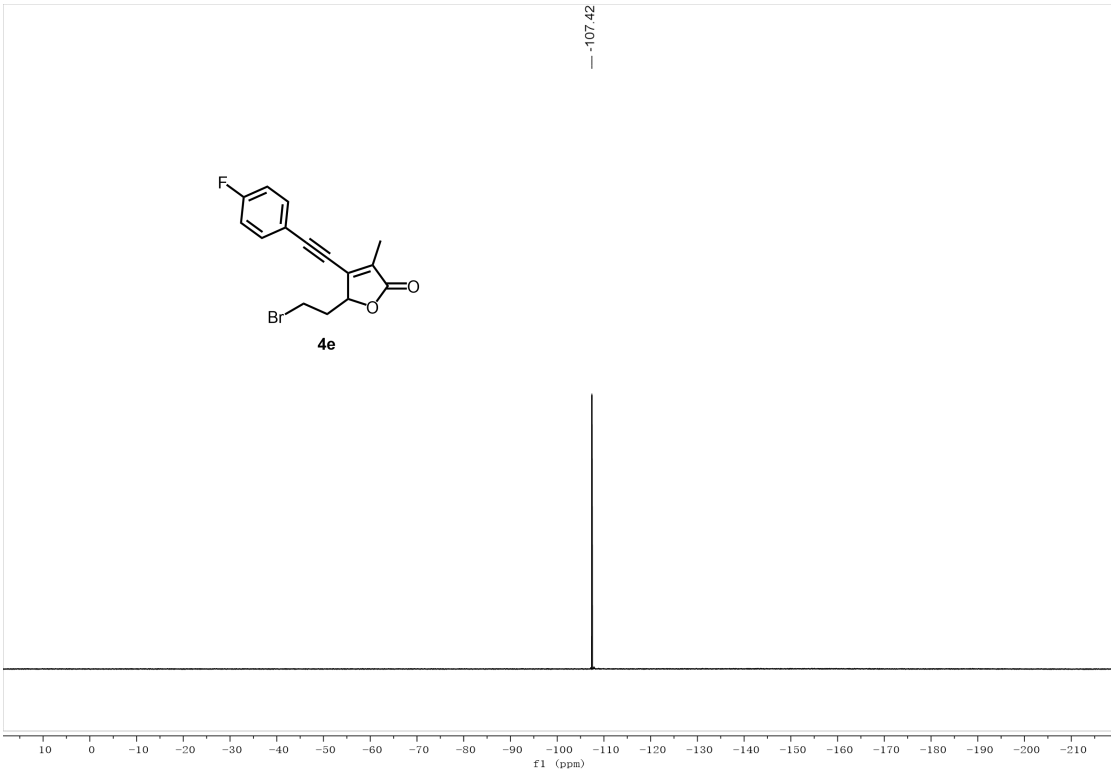
133.45
131.75
123.65
99.35
82.22
77.32
77.00
76.68
73.88
32.76
31.44
28.80
27.87
24.36
22.43
13.96
10.25
F
H3C
H3C
O
O
4d
f1 (ppm)


-107.93
F
H3C
H3C
O
O
4d
f1 (ppm)


7.55 7.54 7.54 7.53 7.52 7.51 7.51 7.50 7.26 7.13 7.12 7.11 7.10 7.08 7.08 7.07
5.13 5.12 5.12 5.11 5.10 5.10 5.09 5.09 2.56 2.55 2.54 2.54 2.54 2.53 2.52 2.52 2.52 2.51 2.51 2.50 2.50 2.50 2.49 2.48 2.48 2.47 2.46 2.45 2.45 2.45 2.16 2.15 2.15 2.14 2.13 2.12 2.11 2.10 2.10 2.09 2.09 2.07 2.05 2.04
F
O
O
Br
4e
2.02 2.05 1.00 1.71 1.04 0.86 3.06
f1 (ppm)


173.01 164.76 162.24 142.27 134.02 132.31 117.30 116.24 105.55 79.86 78.87 77.32 77.00 76.68 40.21 36.62 27.92 10.39
F
O
O
Br
4e
f1 (ppm)


-107.42
F
Br
O
O
4e
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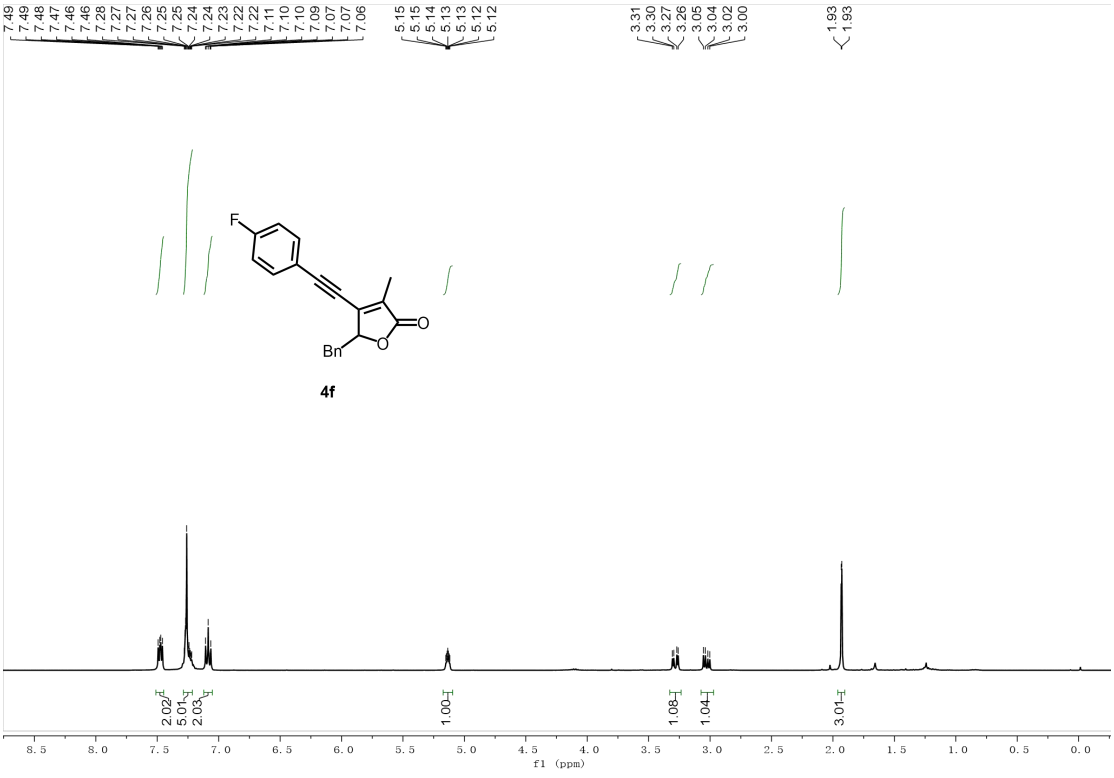
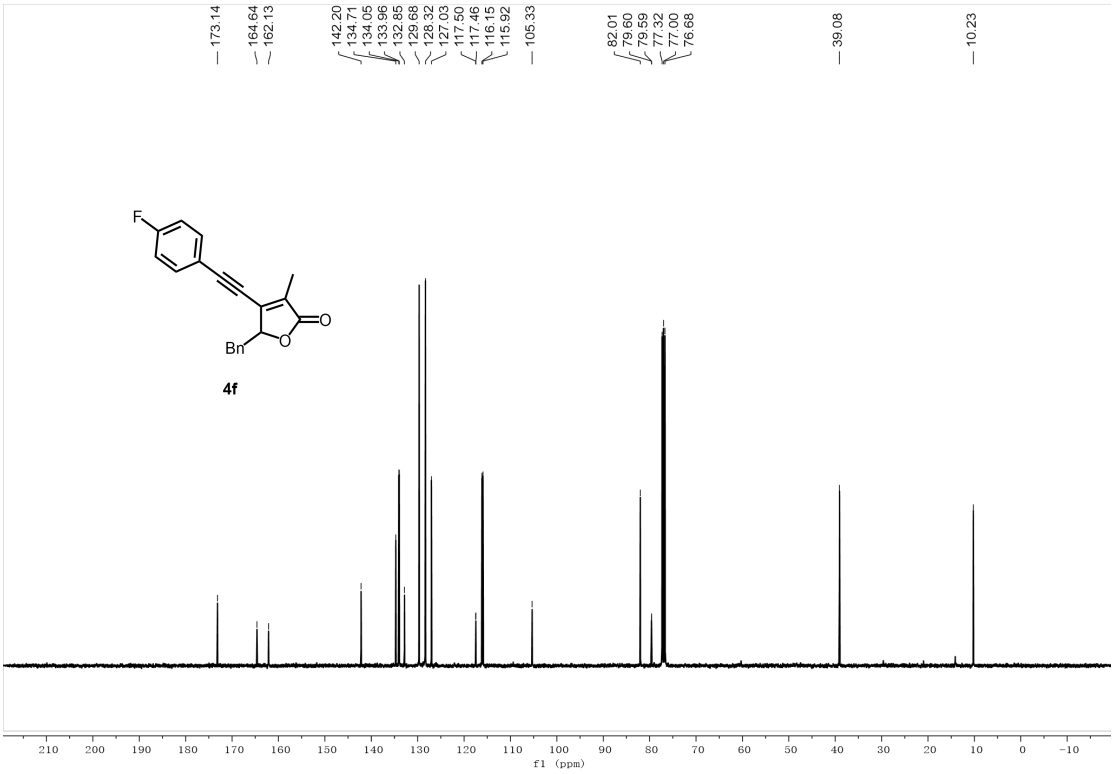
f1 (ppm)


7.49 7.49 7.48 7.47 7.46 7.46 7.28 7.27 7.27 7.26 7.25 7.25 7.24 7.24 7.23 7.22 7.22 7.11 7.10 7.10 7.09 7.07 7.07 7.06
5.15 5.15 5.14 5.13 5.13 5.12 5.12
3.31 3.30 3.27 3.26 3.05 3.04 3.02 3.00
1.93 1.93
F
Bn
O
O
4f
2.02 5.01 2.03 1.00 1.08 1.04 3.01
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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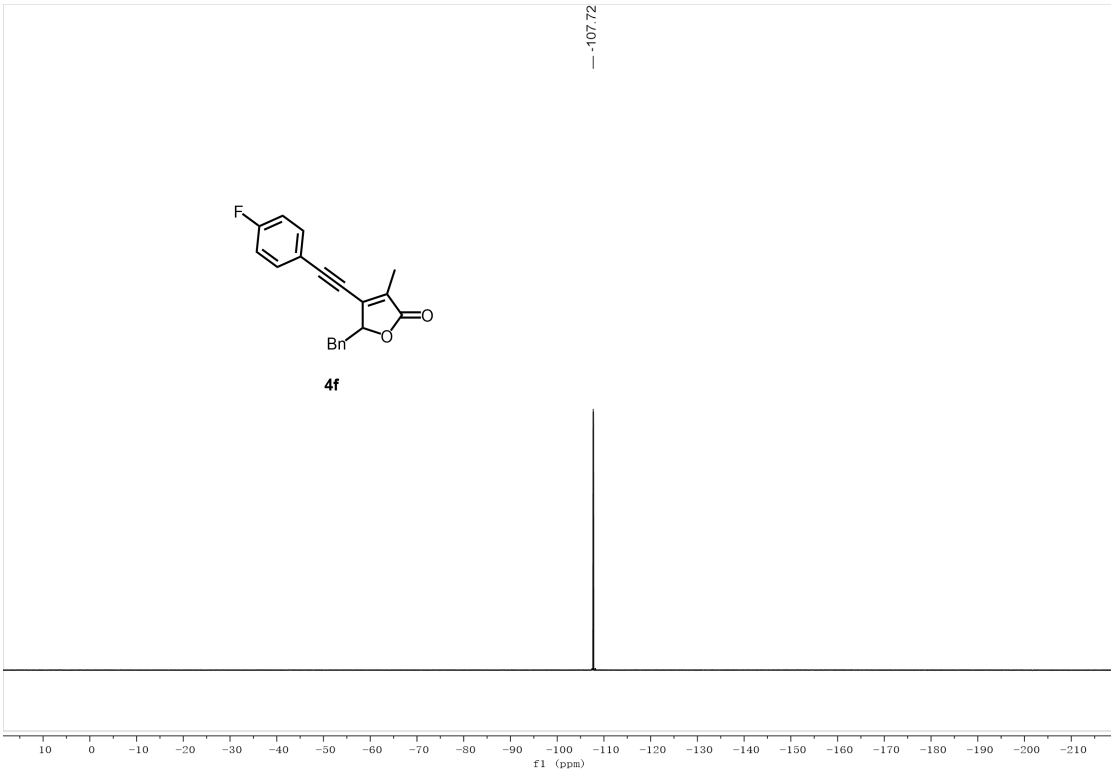
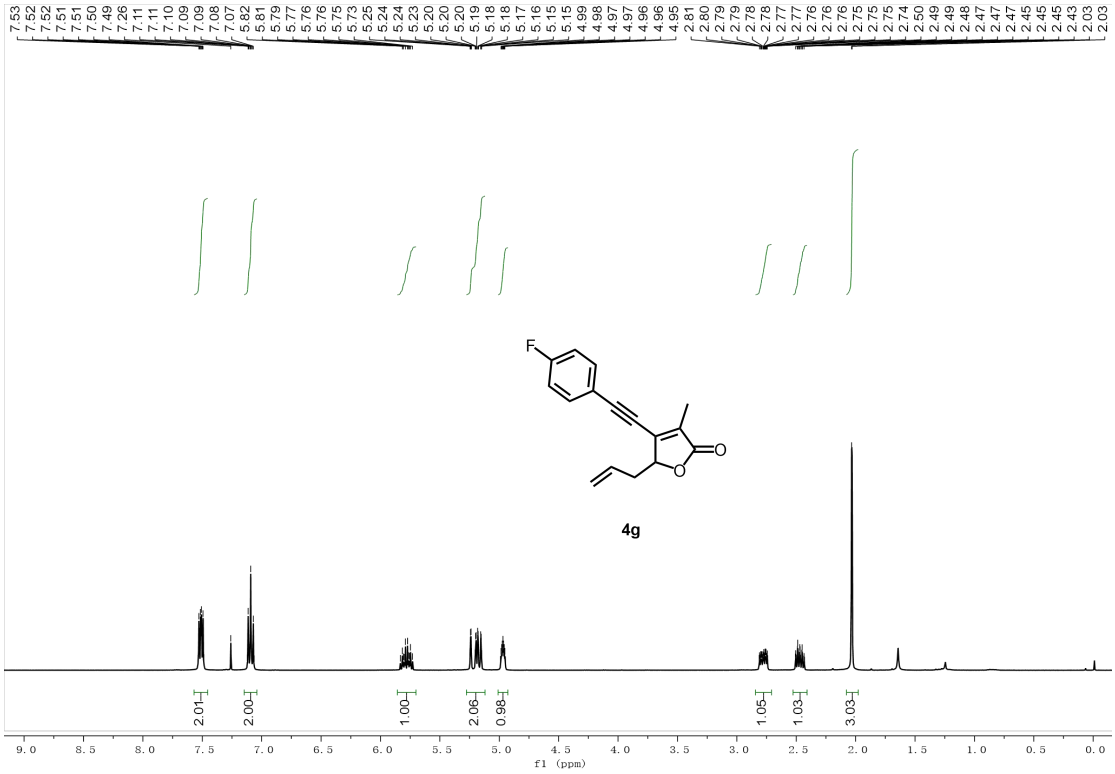
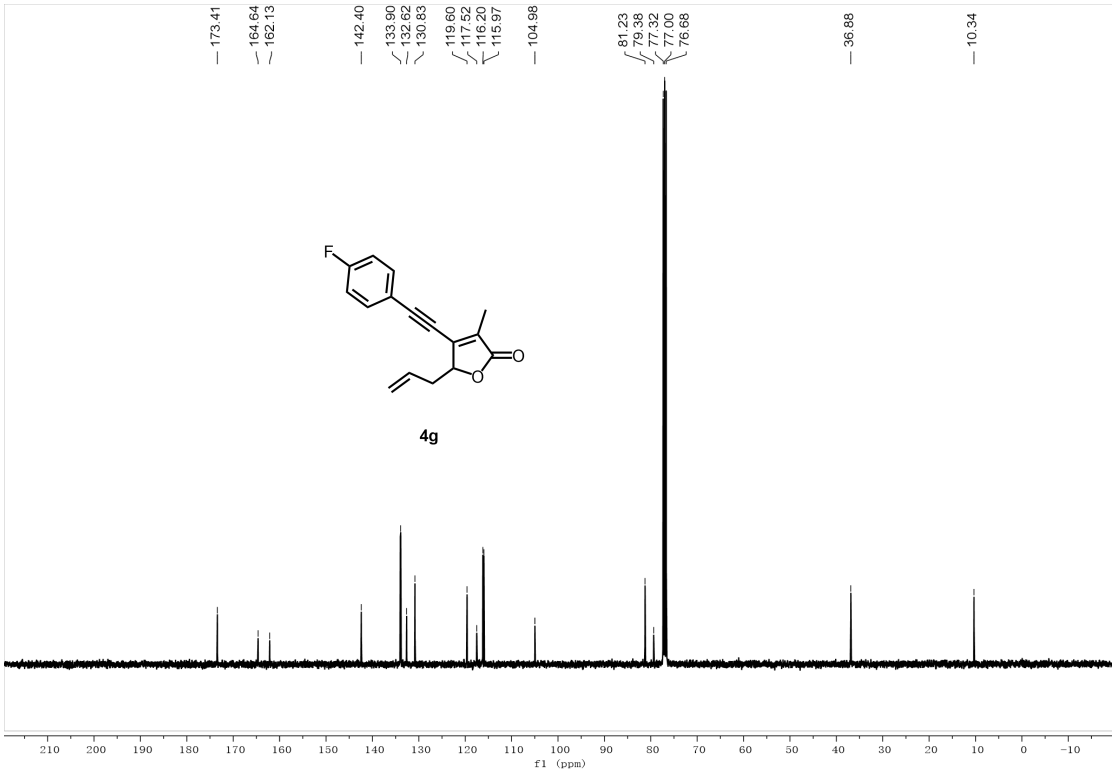
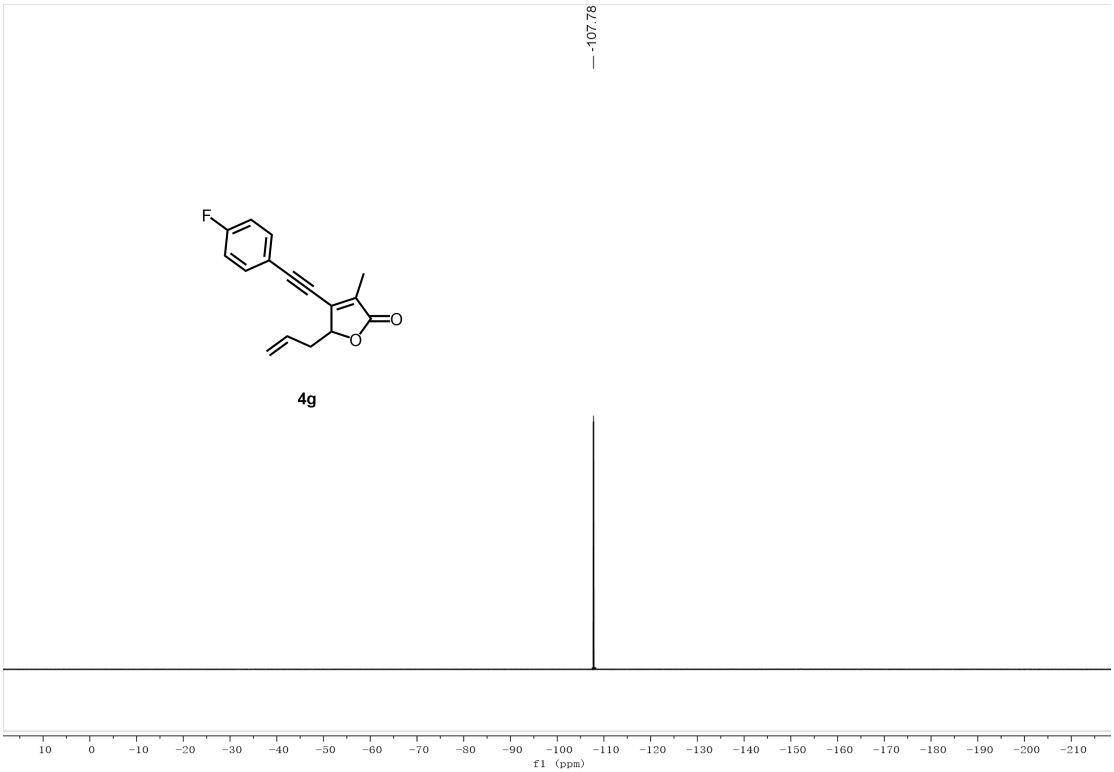
162.13
142.20
134.71
134.05
133.96
132.85
129.68
128.32
127.03
117.50
117.46
116.15
115.92
105.33
82.01
79.60
79.59
77.32
77.00
76.68
39.08
10.23
F
O
Bn
O
4f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


-107.72
F
O
Bn
O
4f
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)


7.53 7.52 7.52 7.51 7.51 7.50 7.49 7.26 7.11 7.11 7.10 7.09 7.09 7.08 7.07 5.82 5.81 5.79 5.77 5.76 5.76 5.75 5.73 5.25 5.24 5.24 5.23 5.20 5.20 5.19 5.18 5.17 5.16 5.15 5.15 4.99 4.98 4.97 4.97 4.96 4.96 4.95 2.81 2.80 2.79 2.79 2.78 2.78 2.77 2.77 2.76 2.76 2.76 2.75 2.75 2.74 2.50 2.49 2.49 2.48 2.47 2.47 2.47 2.45 2.45 2.43 2.03 2.03
F
O
O
4g
2.01 2.00 1.00 2.06 0.98 1.05 1.03 3.03
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)


173.41 164.64 162.13 142.40 133.90 132.62 130.83 119.60 117.52 116.20 115.97 104.98 81.23 79.38 77.32 77.00 76.68 36.88 10.34
F
O
O
4g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-107.78
F
O
O
4g
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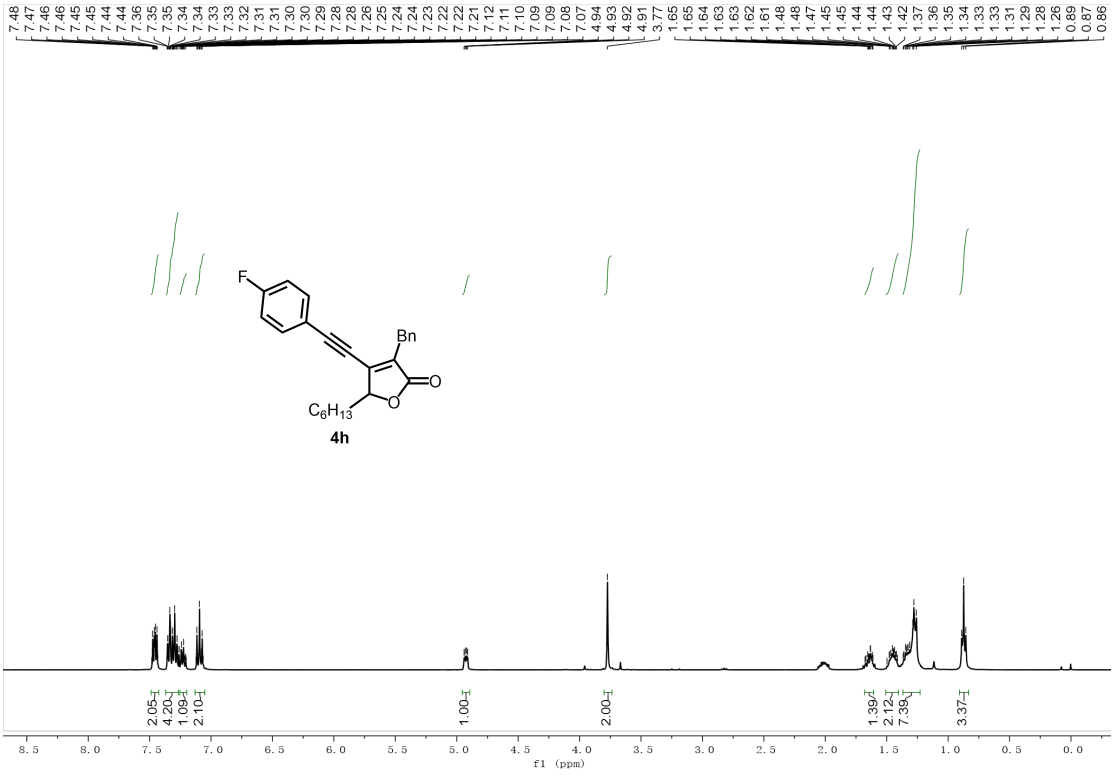
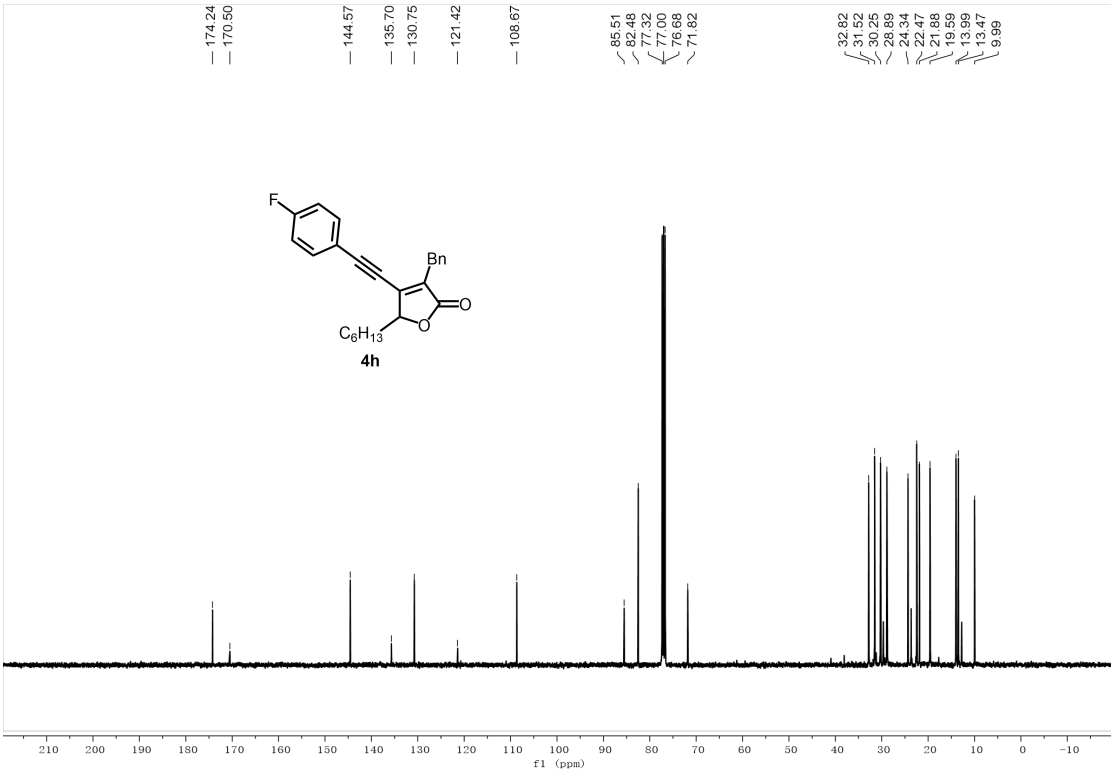
f1 (ppm)


F
Bn
O
O
C6H13
4h
2.05
4.20
1.09
2.10
1.00
2.00
1.39
2.12
7.39
3.37
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)


174.24
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144.57
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130.75
121.42
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82.48
77.32
77.00
76.68
71.82
32.82
31.52
30.25
28.89
24.34
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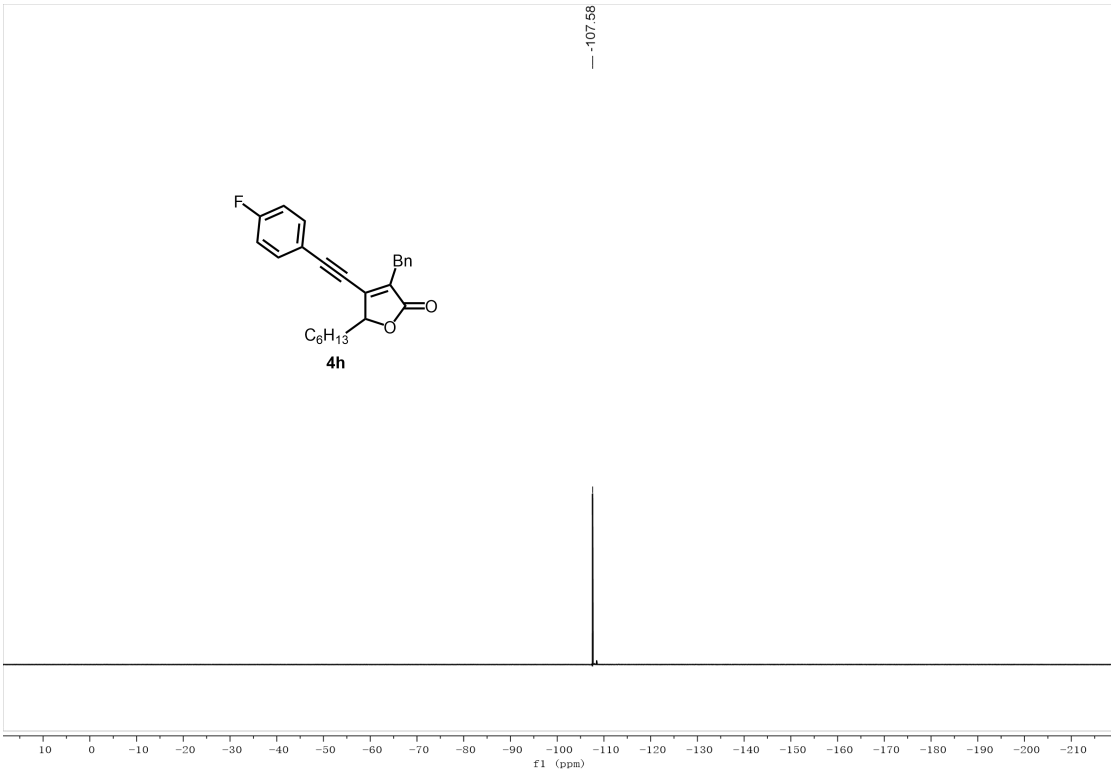
F
Bn
O
O
C6H13
4h
f1 (ppm)


-107.58
F
Bn
O
O
C6H13
4h
f1 (ppm)

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