**Supporting Information**

# Visible Light-Mediated Metal-Free Alkyl Suzuki-Miyaura Coupling of Alkyl Halides and Alkenylboronic Acids/Esters : A Green Method for the Synthesis Allyl Difluoride Derivatives

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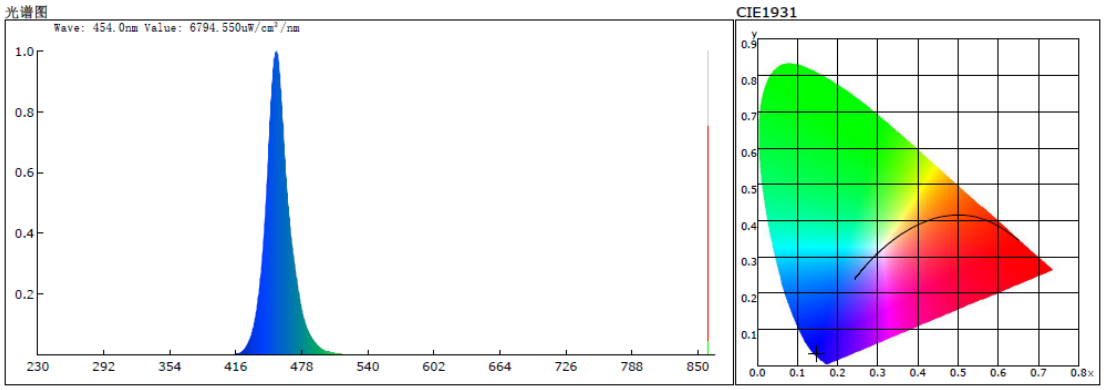
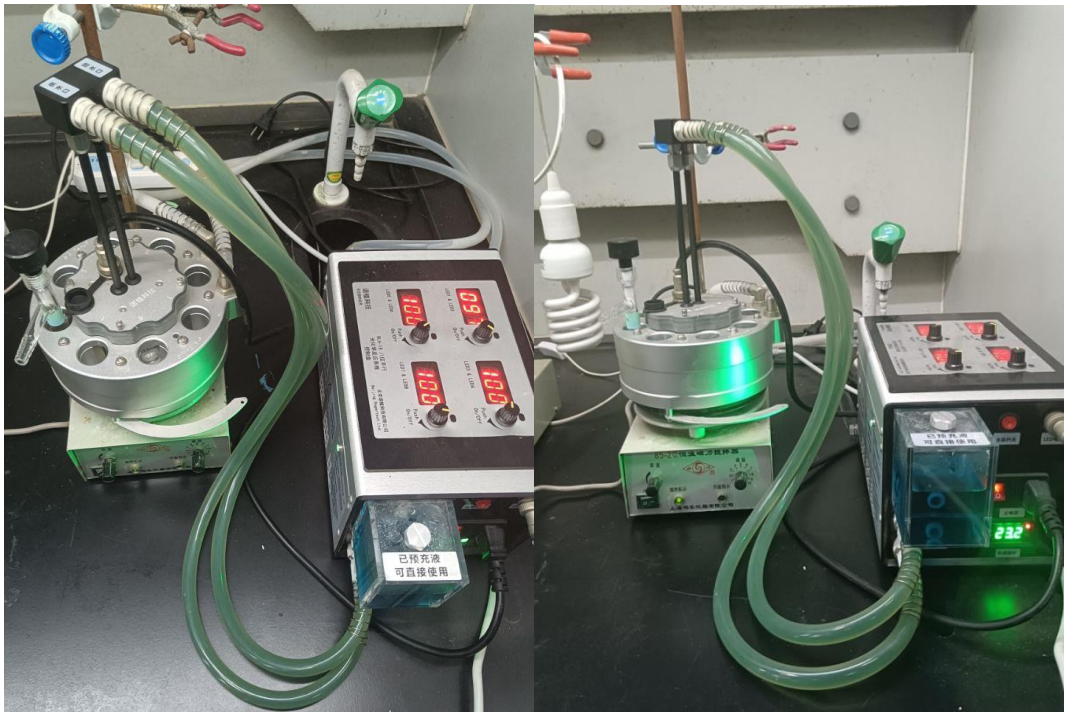
## General Information

$^{1}H$ NMR, $^{19}F$ NMR and $^{13}C$ NMR spectra were measured on 400 MHz spectrometer, using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts (δ) are given in ppm in relative to TMS, the coupling constants *J* are given in Hz. HRMS were obtained in the ESI mode. All reactions were carried out under Ar atmosphere unless otherwise noted. All solvents were obtained from commercial suppliers. α-Bromo difluoroacyl arenes[S1] **2a-2l** and α-Bromo difluoroacyl indole[S2] **2m** were prepared according to the literature. Reactions were monitored by TLC on silica gelplates (GF254), and the analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. Monochromatic light source device is a customized product.

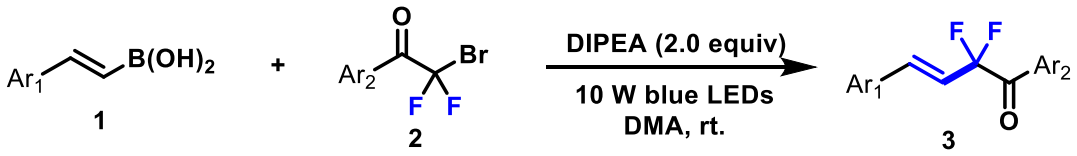
**454nm monochromatic light source is shown in the figure below**





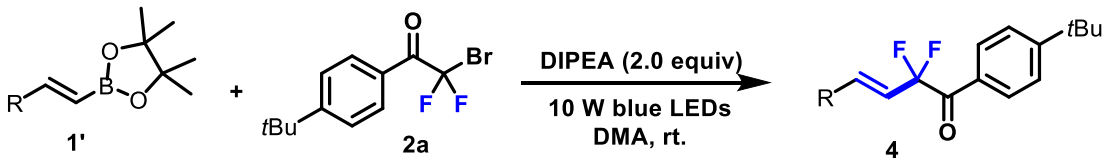
**photoreaction device with refrigeration circulating fluid**

## Experimental procedure for the metal-free difluoroalkylation of alkenylboronic acids



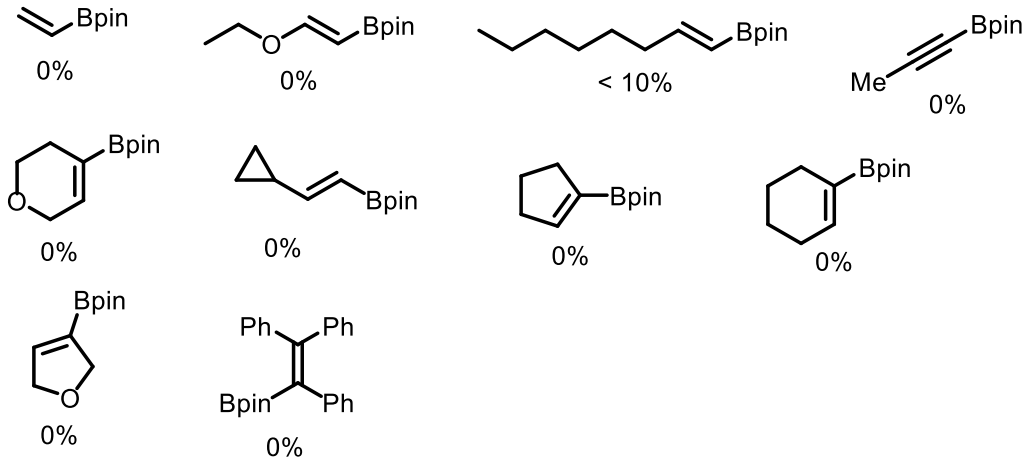

*N*,*N*-Diisopropylethylamine (70 μL, 0.4 mmol, 2.0 eq), alkenylboric acids **1** (0.2 mmol, 1.0 eq) and α-bromo difluoroacylarenes **2** (0.6mmol, 3 eq) were added to a flame-dried Schlenk flask containing a stirring bar and purged by evacuating the flask and backfilling with $N_2$ three times. In the absence of light, anhydrous *N*,*N*-dimethylacetamide (1 ml, 0.2 M) was added and the flask was sealed. The mixture was then stirred under irradiation from 10 W blue LEDs. After 48 h, the crude products were purified by column chromatography over silica gel using hexanes/EtOAc as eluent to yield **3**.

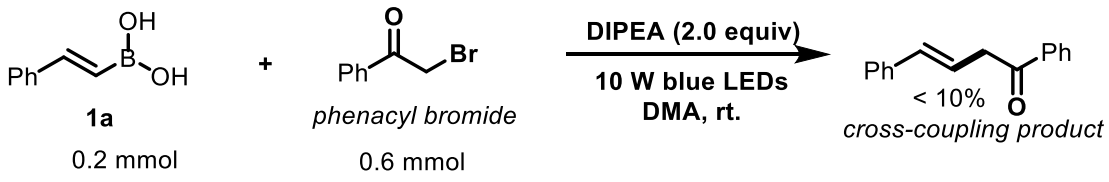
## Experimental procedure for the metal-free difluoroalkylation of alkenylboronic acid esters



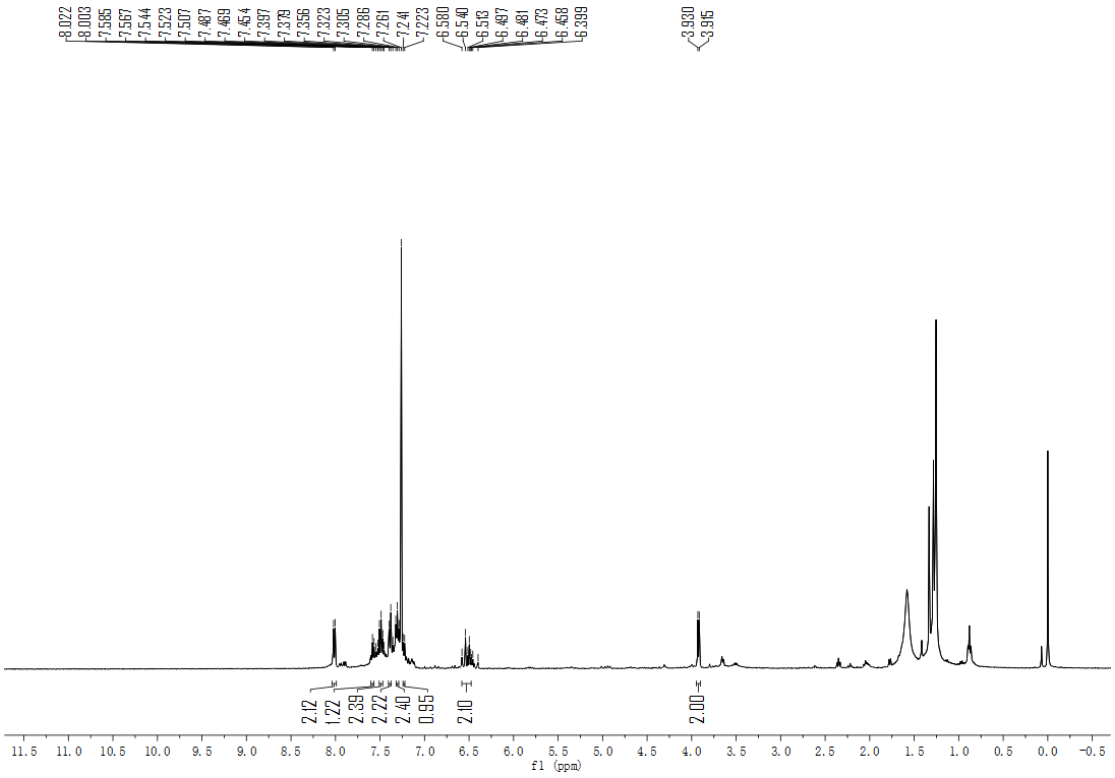

*N*,*N*-Diisopropylethylamine (70 µL, 0.4 mmol, 2.0 eq), alkenylboric acid esters **1'** (0.2 mmol, 1.0 eq) and α-bromo difluoroacylarene **2a** (97mg, 0.33 mmol, 1.65 eq) were added to a flame-dried Schlenk flask containing a stirring bar and purged by evacuating the flask and backfilling with $N_2$ three times. In the absence of light, anhydrous *N*,*N*-dimethylacetamide (1 ml, 0.2 M) was added and the flask was sealed. The mixture was then stirred under irradiation from 10 W blue LEDs. After 48 h, the crude products were purified by column chromatography over silica gel using hexanes/EtOAc as eluent to yield **4**.

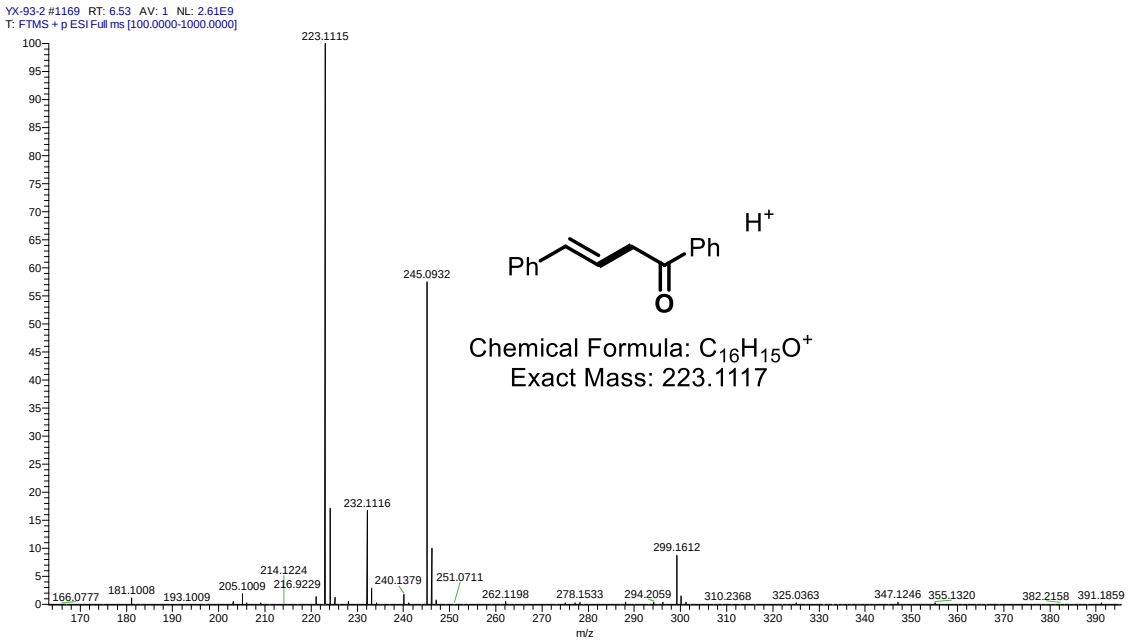
**Other unsuccessful substrates**



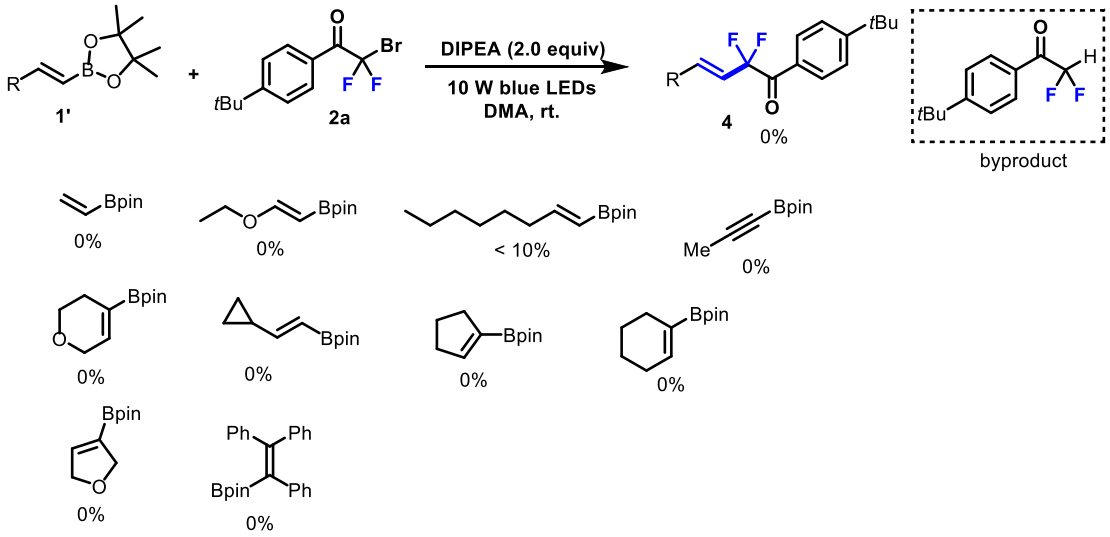
The amount of this cross-coupling **product** (3 mg, < 10% yield) is very small, and its spectrum is shown below.



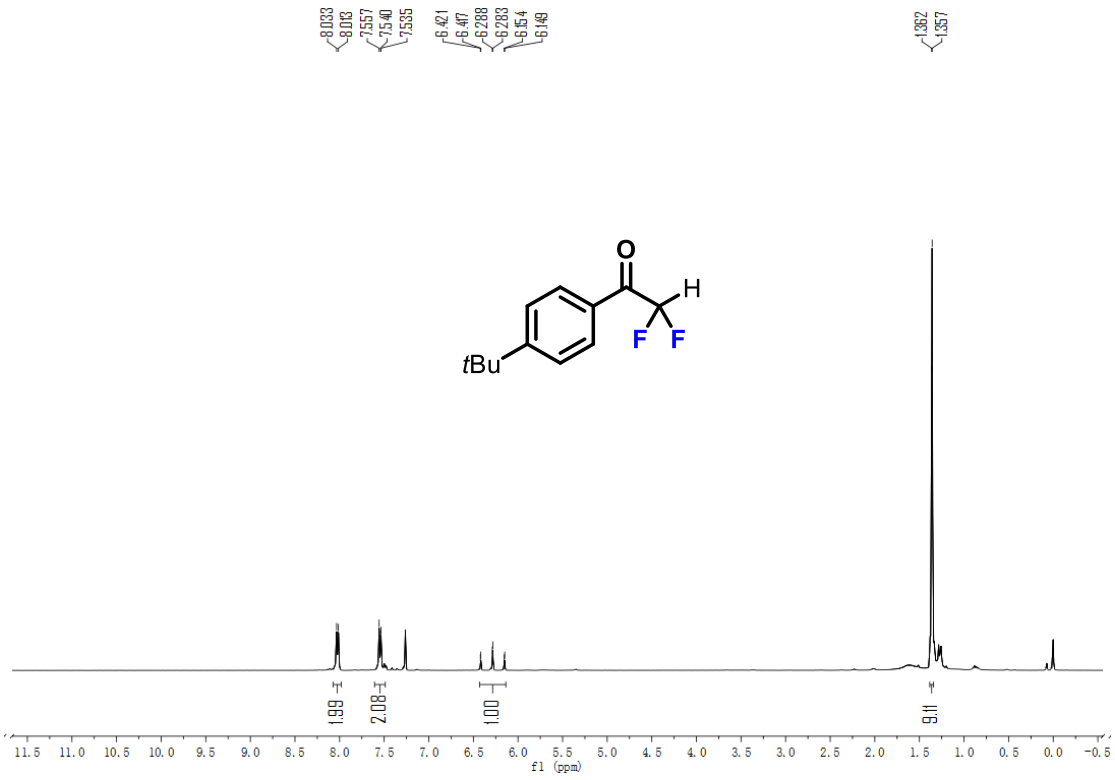




**By-product analysis**

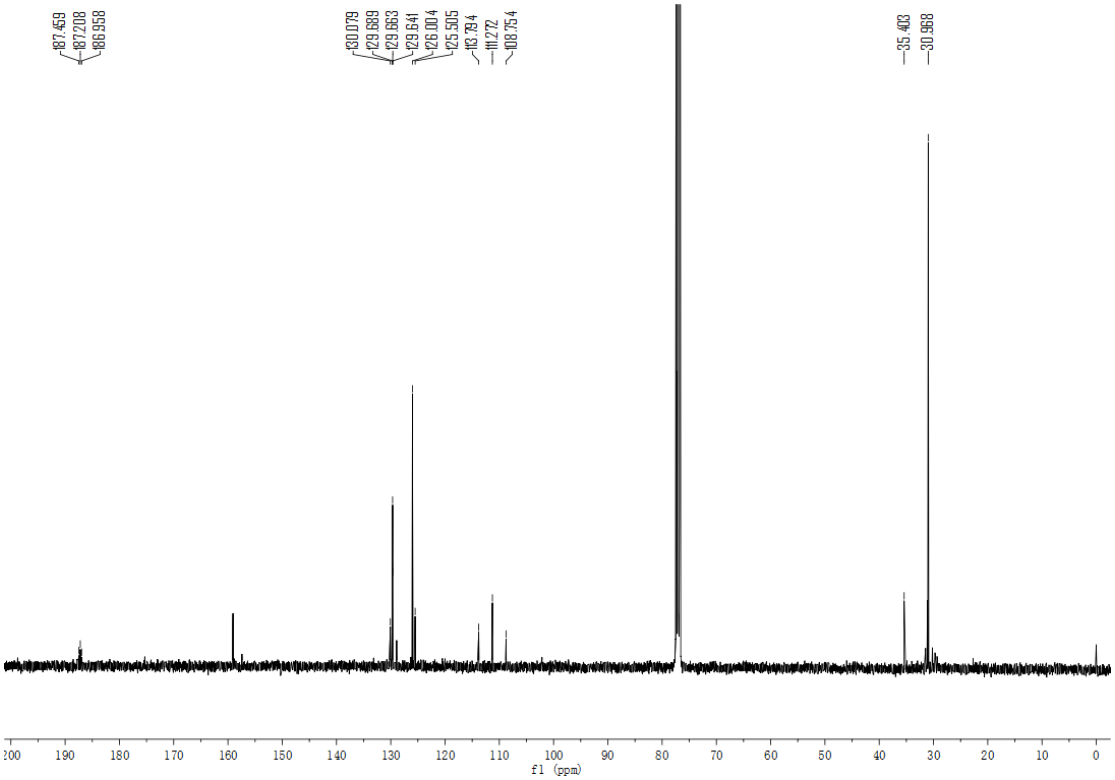
For the unreacted alkenyl boronic ester, we isolated new points that distinguish it from other than starting material **2a** and found the generation of hydrogenation by-products of **2a**, which may be due to hydrogen seizure by difluoroalkyl radicals, whose hydrogen source may be from DIPEA.



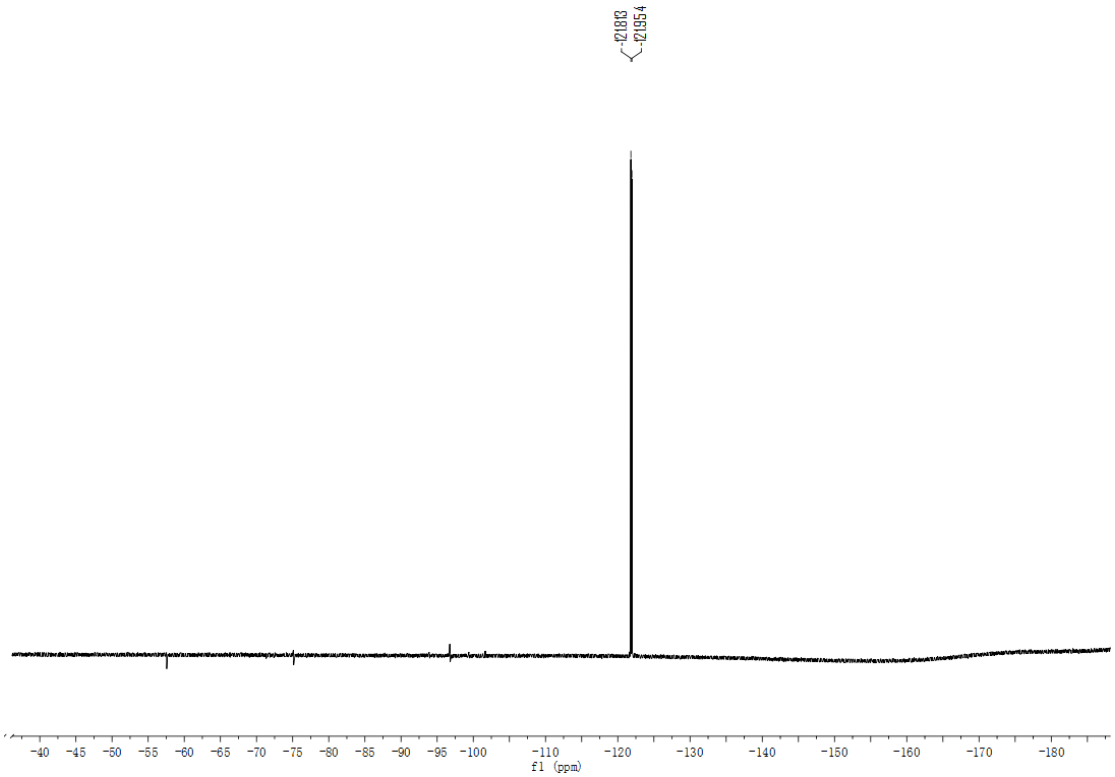

**$^{1}$H NMR (400 MHz)**



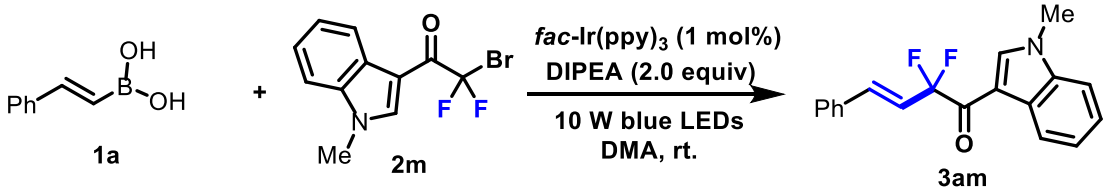

**$^{13}$C NMR (100 MHz)**




**$^{19}$F NMR (376 MHz)**

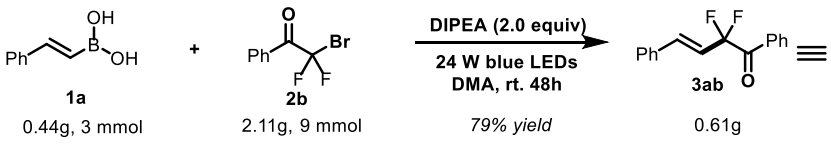


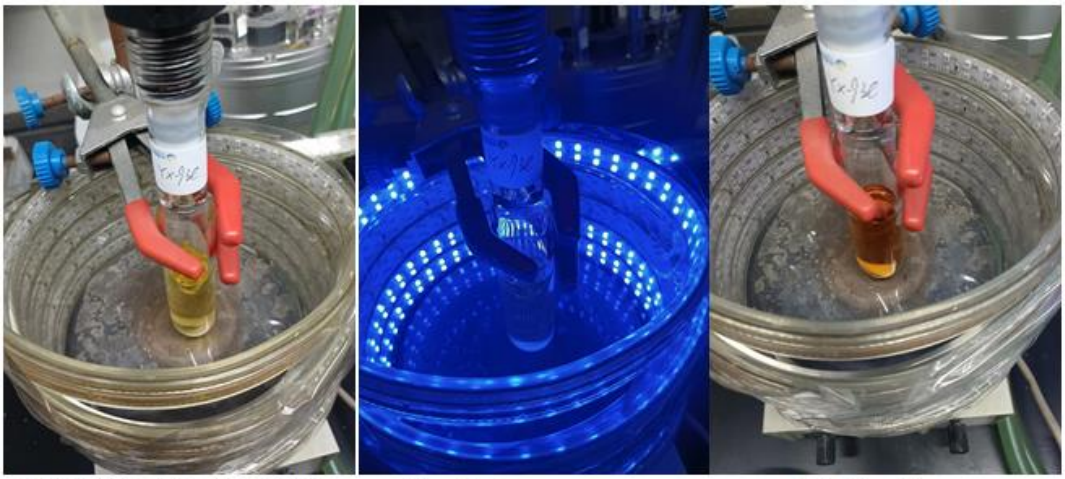
## Experimental procedure for the difluoroalkylation of alkenylboronic acid 1a with difluoroacylindole 2m




*N*,*N*-Diisopropylethylamine (70 μL, 0.4 mmol, 2.0 eq), alkenylboric acid **1a** (30 mg, 0.2 mmol, 1.0 eq), α-bromo difluoroacylindole **2m** (86mg, 0.3 mmol, 1.5 eq), and *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol, 1 mol%) were added to a flame-dried Schlenk flask containing a stirring bar and purged by evacuating the flask and backfilling with $N_2$ three times. In the absence of light, anhydrous *N*,*N*-dimethylacetamide (1 ml, 0.2 M) was added and the flask was sealed. The mixture was then stirred under irradiation from 10 W blue LEDs. After 24 h, the crude products were purified by column chromatography over silica gel using hexanes/EtOAc = 10% as eluent to yield **3am** 39 mg, 63% yield, yellow solid, E/Z = 3/1 .

## Gram-scale reaction of alkenylboronic acid 1a with α-bromodifluoroacylarene 2b



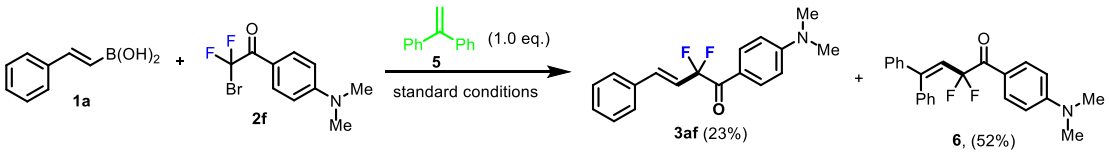




Alkenylboronic acid **1a** (0.44 g, 3 mmol, 1.0 eq) was added to a 25 mL flame-dried flask containing a stirring bar and purged by evacuating the flask and backfilling with $N_2$ three times. In the absence of light, DIPEA (1050 μL, 6 mmol, 2.0 eq), α-bromo difluoroacylarene **2b** (2.11 g, 9 mmol, 3.0 eq) and anhydrous DMA (15 ml, 0.2 M) were added and the flask was sealed. The mixture was then stirred under irradiation from 24 W blue LEDs (Home-made gram-scale photoreactors). After completion of the reaction, the reaction solution was extracted with ethyl acetate and water, and the organic phase was concentrated under reduced pressure. The residue was purified by column chromatography over silica gel using hexanes as elucent to yield **3ab** (0.61 g, 79%).

## Mechanistic consideration

### 1. HRMS Analysis

#### *1.1 Radical trapping experiment with 1,1-diphenylethylene or TEMPO*




**Scheme S1.** Trapping experiment in the standard reaction.

To a Schlenk tube charged with a magnetic stirring bar, substrate **1a** (0.2 mmol) was added and the Schlenk tube was purged with argon for three times. Subsequently, anhydrous DMA (1 ml), **2f**

(0.6 mmol, 167 mg) and 1,1-diphenylethylene (0.2 mmol, 35uL) were added in turn via syringes. The tightly sealed tube was then irradiated with a 10 W blue LEDs at room temperature for 48 h. The corresponding difluoroacetylated product **3af** was obtained in 23% yield （14 mg）after purification through flash column chromatography on silica gel. In the meanwhile, the $CF_2COAr$-trapped product **6** was isolated in 52% yield (39 mg, based on 1,1-diphenylethylene, Scheme S1), colorless oil, $R_f$ = 0.3 (Hexane/Ethyl acetate = 95/5),

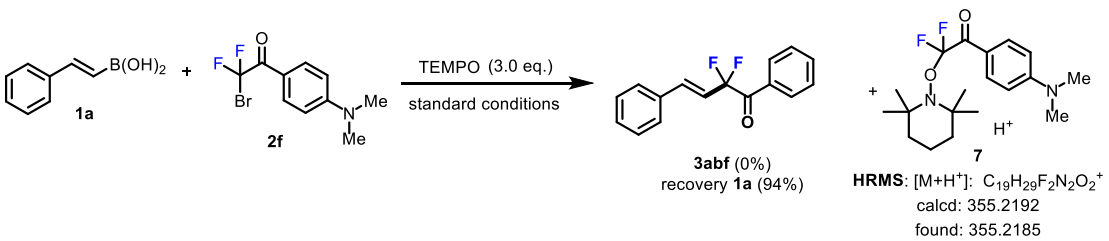
**$^1$HNMR** (400 MHz, $CDCl_3$): $\delta$ 7.76 (d, $J$ = 8.8 Hz, 2H), 7.24-7.17 (m, 8H), 6.93 (d, $J$ = 7.6 Hz, 2H), 6.78 (d, $J$ = 8.4 Hz, 2H), 6.41 (t, $J$ = 12.4 Hz, 1H), 2.98 (s, 6H) ppm;

**$^{13}$C NMR** (100 MHz, $CDCl_3$):

185.4 (t, $J$ = 29.2 Hz), 153.7, 150.2 (t, $J$ = 8.6 Hz), 141.1, 137.5, 132.3, 129.8, 128.8, 128.3, 128.2, 127.8, 127.7, 120.9 ( t, $J$ = 26.7 Hz), 119.6, 115.7 (t, $J$ = 245.9 Hz ), 40.0 ppm;

**$^{19}$F NMR** (376 MHz, $CDCl_3$): $\delta$ -87.5 (d, $J$ = 12.8 Hz) ppm.

The most common used for intermediate identification is adding an additional reagent to trap the species. The persistent free radical 2,2,6,6-tetramethylpiperdine 1-oxyl (TEMPO) is usually served as a trapping reagent of carbon-centered radicals, also for intramolecular radical cyclization. Based on above reasons, we applied this radical trapping agent in our reaction to examine its behavior. Under the standard reaction conditions, when 3.0 equivalent of TEMPO (with respect to **1a**) was added to the reactions, after long exposure to irradiation (48 h) products **3ab** could not be detected (Scheme S2, Figure S1), but the radical trapping product **7** was detected by HRMS analysis.




**Scheme S2.** Trapping experiment in the standard reaction.

This result may suggest the formation of the radical species involved in our reaction conditions, there is another plausible explanation that visible light induced the formation of difluoroacyl radical species .

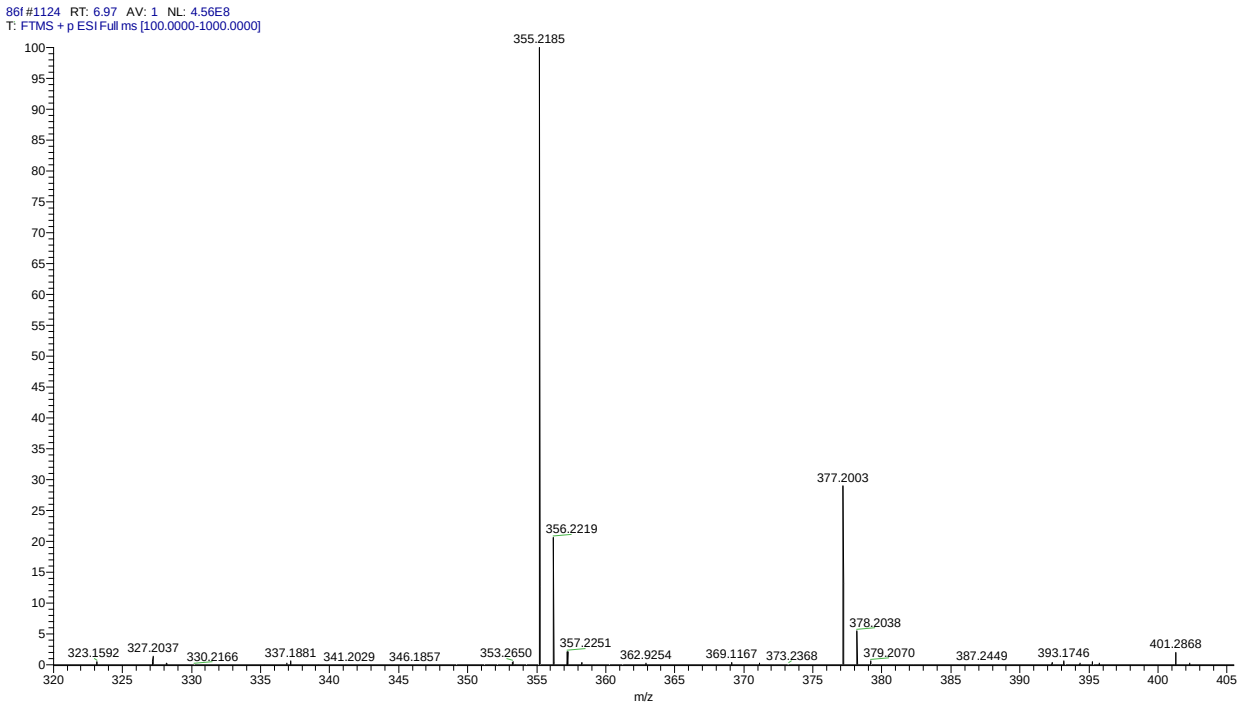
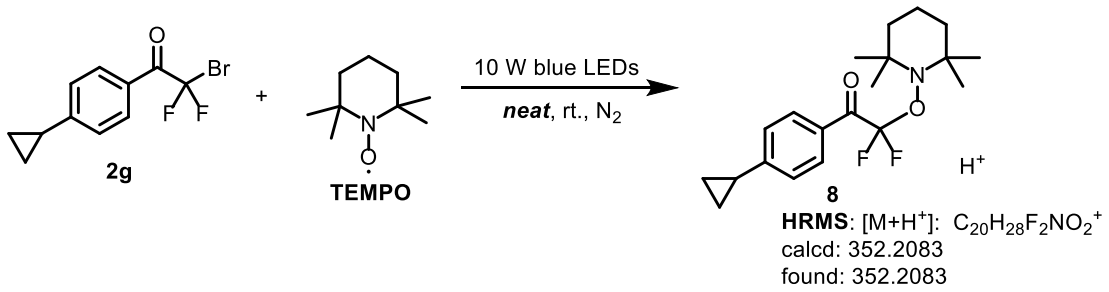


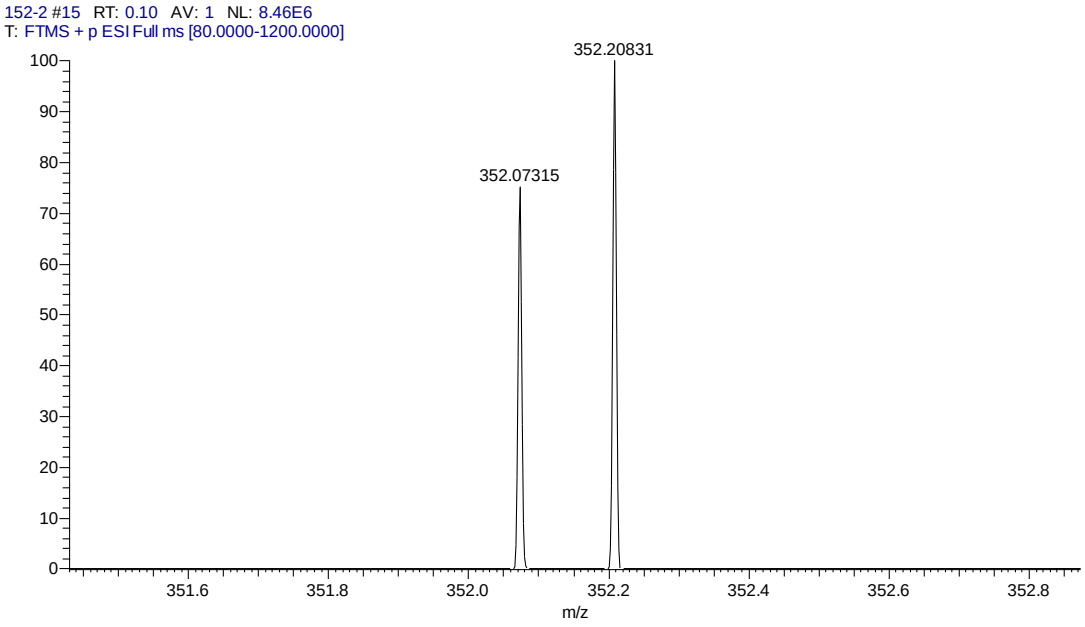

**Figure S1.** HRMS analysis of reaction mixture.

### *1.2 Trapping experiment with TEMPO free radical in different solvents*




**Scheme S3.** Trapping experiment under solvent- and base-free conditions.

Although we have previously proved that $ArCOCF_2Br$ can generate $ArCOCF_2$ radicals under light in the presence of no external base, considering that the heteroatoms in other reagents (e.g., solvent, substrate, or even water) may interact with $ArCOCF_2Br$ in halogen bonding and thus induce radical generation under visible light radiation. Based on this analysis, we tried to perform the radical trapping experiment again under solvent- and base-free conditions. Under solvent- and base-free conditions, when 3.0 equivalent of TEMPO (with respect to **2g**) was added to the reactions, after long exposure to irradiation (24 h), the radical trapping product **8** was detected by HRMS analysis, albeit in low abundance. Based on the promotion of radical generation by organic bases as well as by heteroatomic atoms in substrate molecules and solvents, we propose a new concept — halogen bonding induced $C_{sp}{}^3$-Br homolytic mechanism.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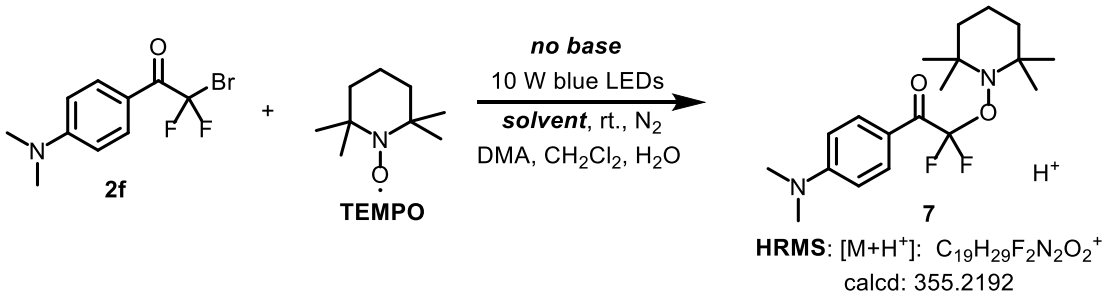
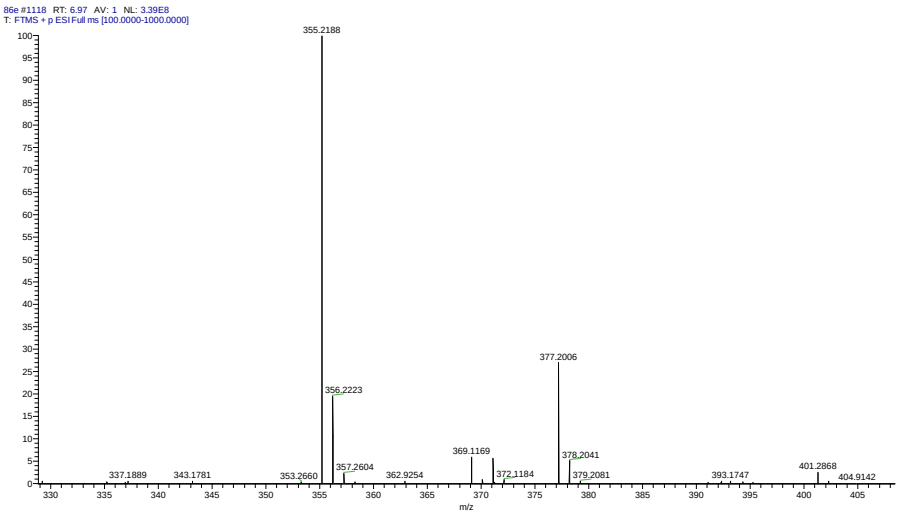
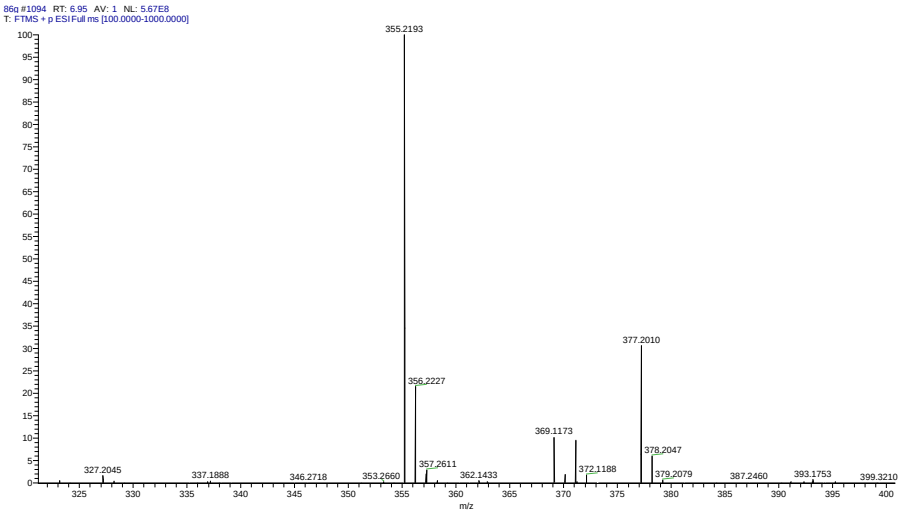
T: FTMS + p ESI Full ms [80.0000-1200.0000]
352.20831
352.07315
m/z


2f
TEMPO
no base
10 W blue LEDs
solvent, rt., N2
DMA, CH2Cl2, H2O
7
HRMS: [M+H+]: C19H29F2N2O2+
calcd: 355.2192

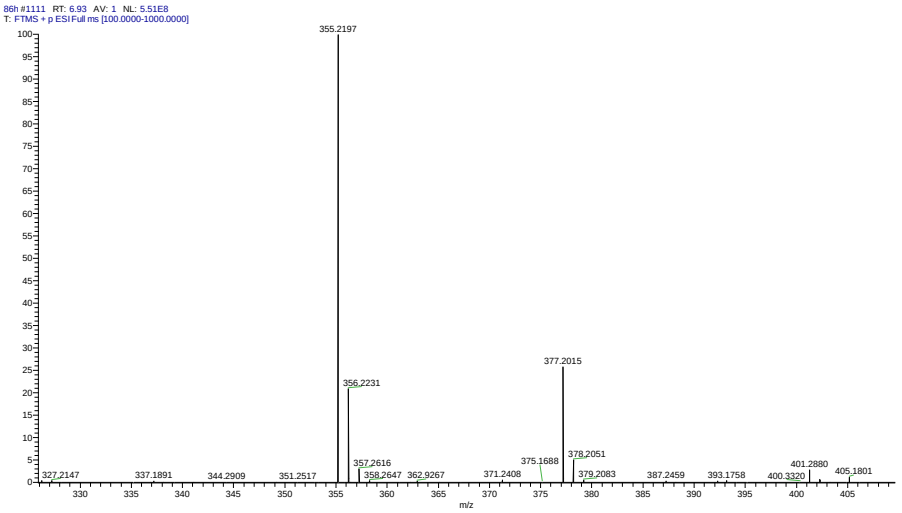
***DMA***


86e #1118 RT: 6.97 AV: 1 NL: 3.39E8
T: FTMS + p ESI Full ms [100.0000-1000.0000]
355.2188
356.2223
377.2006
m/z

***$CH_2Cl_2$***




***$H_2O$***




## 2. UV/Vis Plot

All the UV-vis absorption spectra were recorded in 1 cm path quartz cuvettes using a Persee TU-1950 UV-visible spectrophotometer.

A UV-vis absorbance experiment has been carried out for confirming the formation of halogen bond complexs as illustrated in Figure S1. Condition: measured with DMA as a solvent. **1a** (0.12 mmol), **2a** (0.36 mmol), DIPEA (0.24 mmol), and DMA (3 mL).

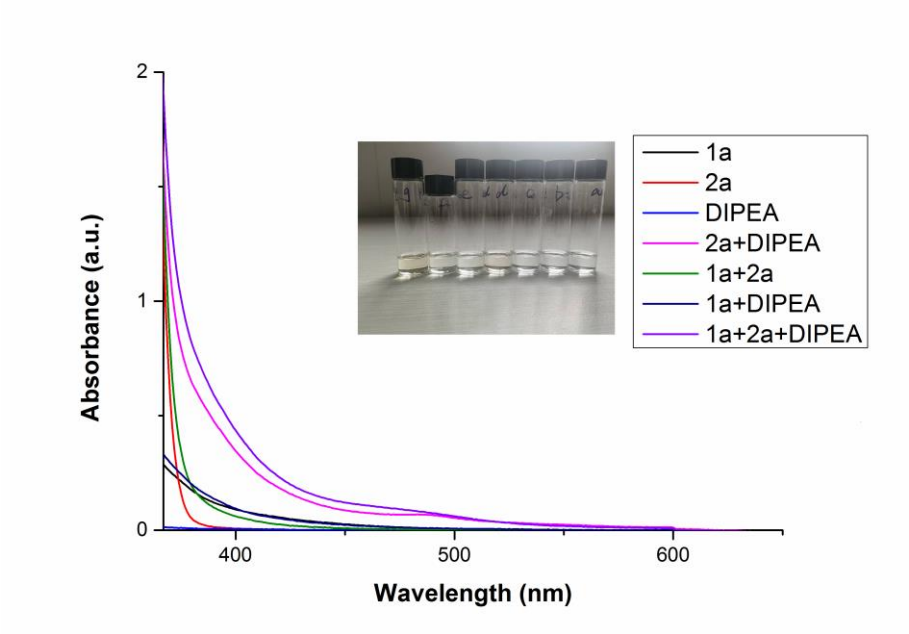



**Figure S2.** UV/vis absorption spectra of the starting materials in isolation and combined recorded in DMA as solvent. The numbers a,b,c,d,e,f,g on the bottles correspond to **1a**, **2a**, DIPEA, **2a**+DIPEA, **1a+2a**, **1a**+DIPEA,**1a**+**2a**+DIPEA respectively.

## 3. Luminescence quenching experiments

Stern–Volmer studies were carried out on an Agilent Cary Eclipse fluorescence spectrophotometer.

**Experimental procedures**: All the bromodifluoroacylarene 4-*t*BuPhCOCF$_2$Br **2a** (*in this manuscript*) solutions were excited at 371 nm and the emission intensity was collected at 380-650 nm. A screw-top quartz cuvette was charged with a solution of **2a** (0.1 mmol, 20 uL) in dry DMA (3.0 mL) and the initial emission was collected. Another series of samples, 33 mM (M = mol/L) **2a** in DMA with DIPEA as quencher in gradient concentrations, were tested and the emissions were collected.


**Figure S3.** Agilent Cary Eclipse fluorescence spectrophotometer

Quenching of **2a** was not observed for DIPEA, but fluorescence enhancement was observed. Stern-Volmer fluoresence quenching analysis showed that the excited state of *t*-BuPhCOCF$_2$Br **2a*** could not be quenched by DIPEA, with the emission of **2a***, upon excitation at 371 nm, being abnormally enhanced by DIPEA (Figure S4).This result may indicate that there is no electron transfer event between **2a** and DIPEA.[S3] The enhanced fluorescence may indicate that DIPEA promotes the generation of difluoroalkyl radicals (see Figure 8).

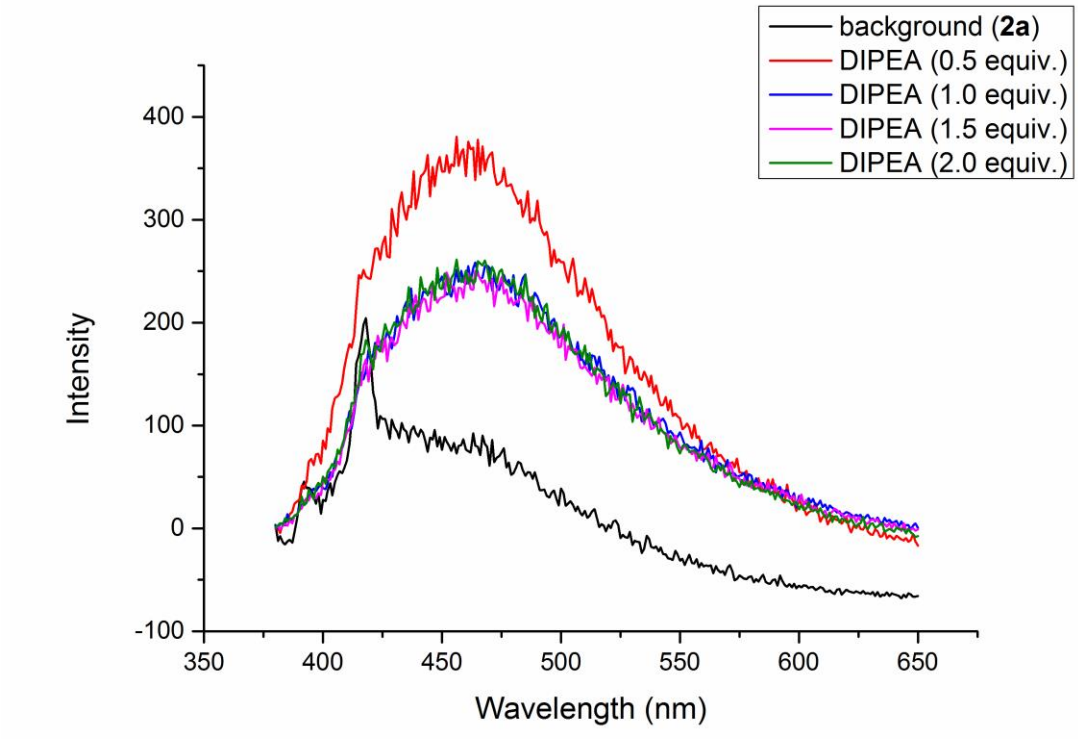
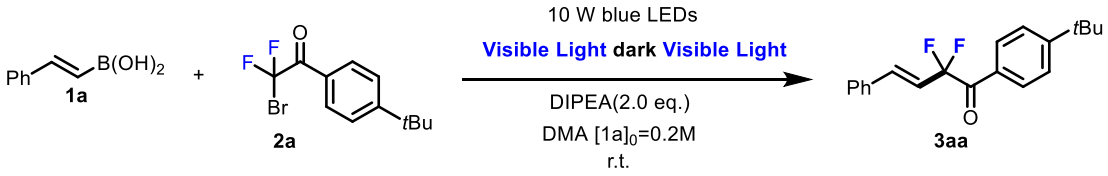
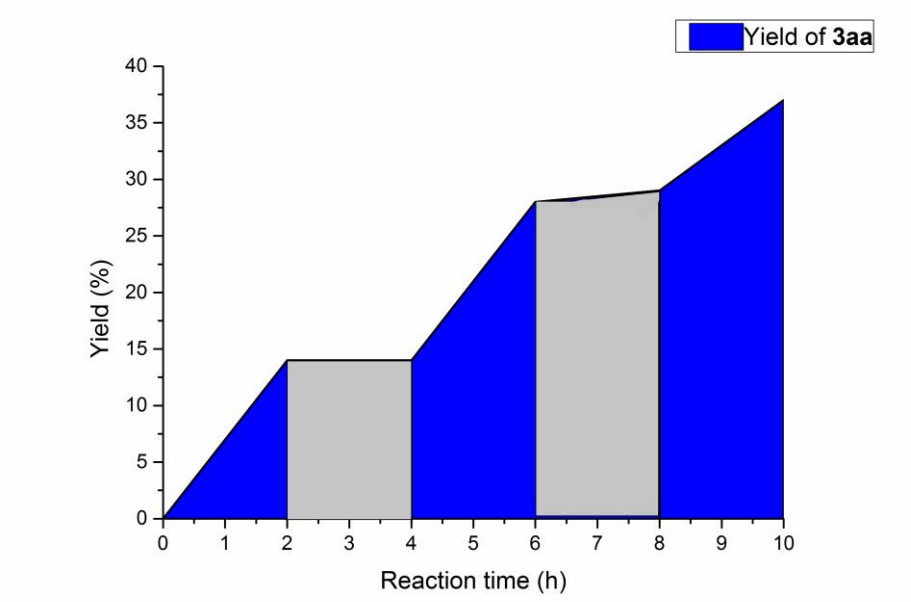


**Figure S4.** UV/vis absorption spectra of the starting materials in isolation and combined recorded in DMA as solvent.

## 4. Light turn on/off experiment




The reaction mixture was irradiated for 2 hours. An aliquot of 0.10 mL was taken from the reaction mixture and injected into a vial containing 0.50 mL of $CDCl_3$ containing 1-bromo-4-(trifluoromethyl)benzene (0.1 mmol, 14 uL) as the internal standard. The yield of product was determined by crude ***$^{19}$F NMR*** analysis. The reaction mixture was then sealed under $N_2$ atmosphere and re-subjected to 10 W blue LEDs. The yields later on were determined in the same way after some time light on or off.




## 5. Reaction quantum yield (Φ)measurment

According to the above experimental results, we plan to use a monochromatic light source with a wavelength of 454nm as the light source of the reaction quantum yield experiment.

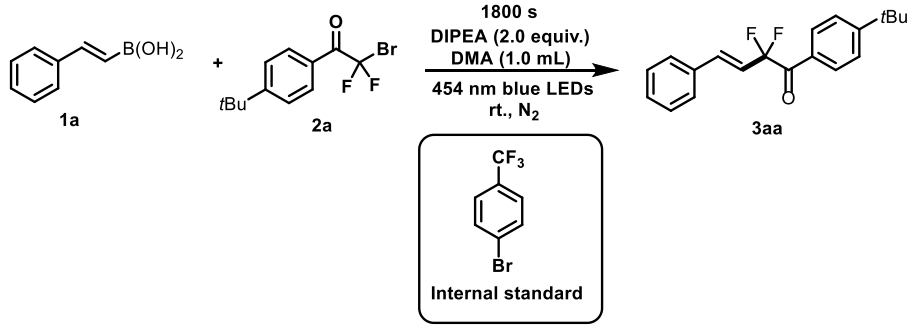
**Determination of the light intensity at 454 nm**

The quantum yield of the reaction was measured by chemical actinometry using 454 nm blue LEDs using potassium ferrioxalate following the procedure of E. E. Wegner (*J. Am. Chem. Soc.* **1966**, *88*, 394), J. N. Demas (*J. Phys. Chem.* **1981**, *85*, 2766), F. Glorius (*Org. Lett.* **2018**, *20*, 1546), R. Shang (*Science*, **2019**, *363*, 1429), J. Zhong (*Chem. Commun.* **2019**, *55*, 10848) and T. P. Yoon (*Chem. Sci.* **2015**, *6*, 5426). 0.737 g of potassium ferrioxalate trihydrate was dissolved in 10 mL $H_2SO_4$ (0.05 M) and stored in the dark. Then, a buffer solution was prepared by dissolving 2.5 g of sodium acetate and 0.5 mL of $H_2SO_4$ (95-98%) in 50 mL of distilled water.

Blue LED photoreactor (Irradiation at 454 nm), Φ of ferrioxalate at 454 nm estimated to be 0.95 (Hatchard, C. G.; Parker, C. A. *Proc. Roy. Soc. (London)* **1956**, *A235*, 518–536). Photon flux [S4] > 1.45 x $10^{-6}$ einstein $s^{-1}$

**Determination of the reaction quantum yield**

To obtain the quantum yield (Φ) of the difluoroalkylation of quinoxalinones. The number of moles of the product **3aa** were determined by ***$^{19}$F NMR*** analysis using 1-bromo-4-(trifluoromethyl)benzene as internal standard. As such, this reaction was performed under the set of optimized reaction conditions under visible light irradiation of 454 nm blue LEDs. After 1800 s of light irradiation, 4.5 x $10^{-6}$ moles of **3aa** were obtained.




The quantum yield of this reaction was calculated using the following equation:

$$\Phi = = \frac{mol\ of\ product\ formed}{photon\ flux \bullet t \bullet f}$$

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

*Where:*

A(454 nm) = is the absorbance at 454 nm of the reaction which was measured placing 1 mL of the solution in a cuvette of path length 1 cm by UV/Vis spectrophotometry. The absorbance of the

reaction mixture at 454 nm was measured to be 3.215, so the value of f is 0.999.

*t* = is the reaction time 1800 s

**The quantum yield (Φ) of the reaction is less than 0.055** ( see calculation below)

$$\Phi = = \frac{mol\ of\ product\ formed}{photon\ flux \bullet t \bullet f} < \frac{4.5 \times 10^{-6}\ mol}{1.45 \times 10^{-6}\ einstein\ s^{-1} \times 1800 \times 0.999} = 1.7X10^{-3}$$

## 6. Direct evidence of halogen bond interaction between bromodifluoroacylarenes and tertiary amines

### 6.1 Optimization of the reaction conditions

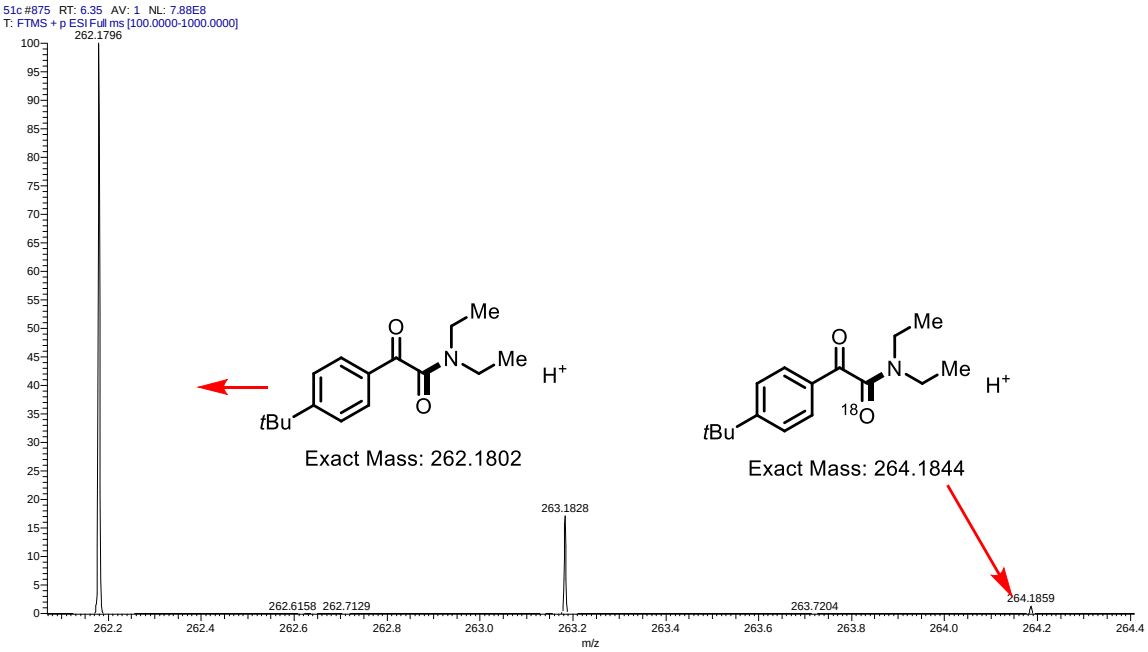
**Source of oxygen**


| Entry | $Et_3N$ | additive | Yield of **4a** (%) |
|---|---|---|---|
| 1 | Common $Et_3N$ | - | 63 |
| 2 | Common $Et_3N$ | 10eq $H_2O$ | 70 |
| 3 | Dry $Et_3N$ | 300 mg $Na_2SO_4$ | 54 |
| 4 | Dry $Et_3N$ | 10eq $H_2O^{18}$ | 72 |
| 5 | Common $Et_3N$ | 0.25mL $H_2O$ | 27 |

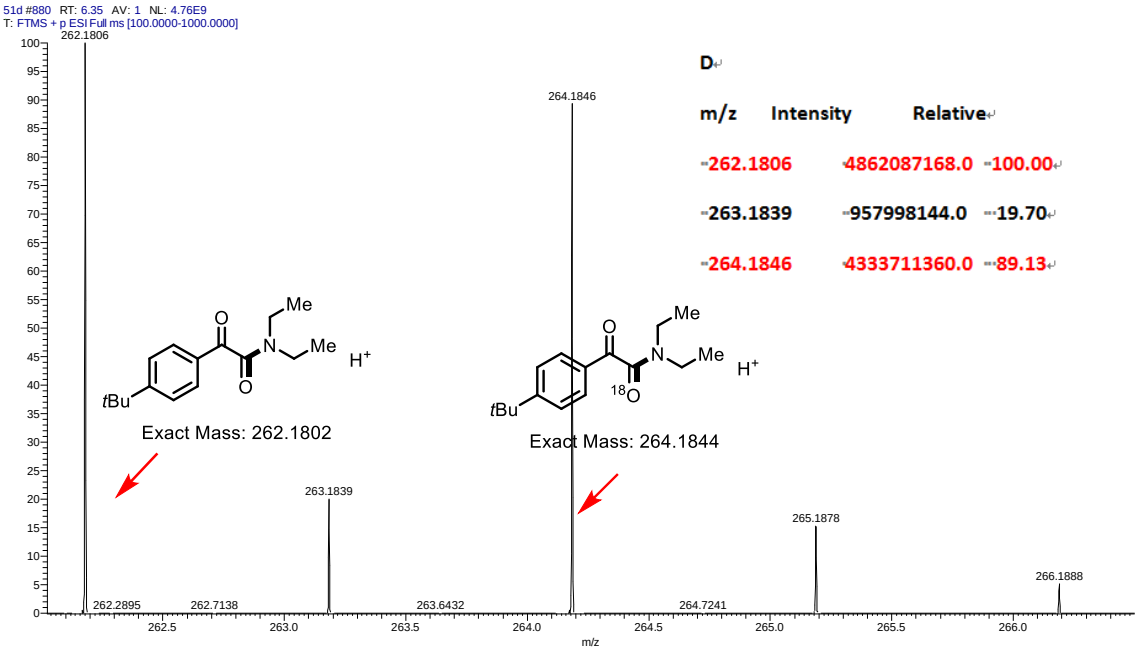
**HRMS analysis of entry 3**

C

| m/z | Intensity | Relative |
|---|---|---|
| 262.1796 | 798819136.0 | 100.00 |
| 263.1828 | 139347200.0 | 17.44 |
| 264.1859 | 11408897.0 | 1.43 |



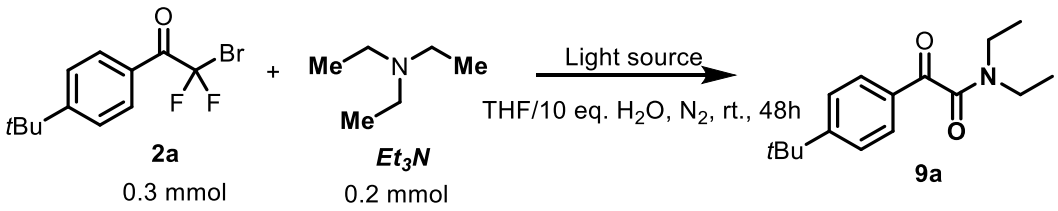

## HRMS analysis of entry 4




D

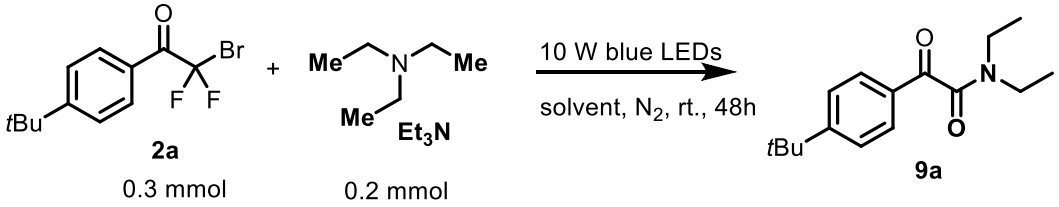
| m/z | Intensity | Relative |
|---|---|---|
| 262.1806 | 4862087168.0 | 100.00 |
| 263.1839 | 957998144.0 | 19.70 |
| 264.1846 | 4333711360.0 | 89.13 |

## Light source



| Entry | solvent | light source | Yield of **4a** (%) |
|---|---|---|---|
| 1 | THF (1 mL)/10eq $H_2O$ | 33 W CFL | 55 |
| **2** | **THF (1 mL)/10eq $H_2O$** | **10 W blue LEDs** | **70** |
| 3 | THF (1 mL)/10eq $H_2O$ | 10 W green LEDs | 51 |

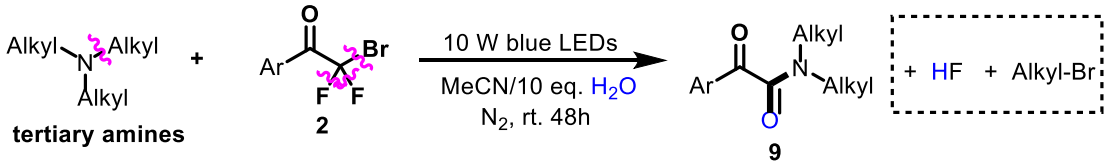
**Solvent**




| Entry | solvent | light source | Yield of **4a** (%) |
|---|---|---|---|
| 1 | THF/10eq $H_2O$ | 10 W blue LEDs | 70 |
| **2** | **MeCN/10eq $H_2O$** | **10 W blue LEDs** | **86** |
| 3 | DMF/10eq $H_2O$ | 10 W blue LEDs | 12 |
| 4 | MTBE/10eq $H_2O$ | 10 W blue LEDs | 73 |
| 5 | MeOH/10eq $H_2O$ | 10 W blue LEDs | 10 |
| 6 | $H_2O$/CTAB(1 ml/0.2 eq) | 10 W blue LEDs | - |
| 7 | $H_2O$/SDS (1 mL/0.2 eq) | 10 W blue LEDs | - |
| 8 | $H_2O$/Tween 80 (1 mL/80uL) | 10 W blue LEDs | - |
| 9 | $H_2O$/TBAB (1 mL/0.2 eq) | 10 W blue LEDs | - |

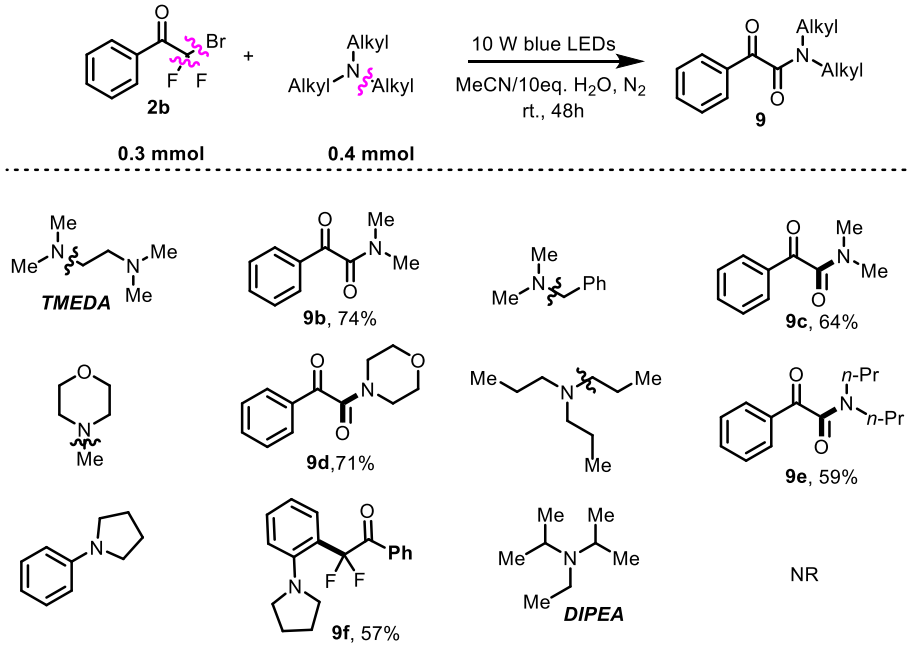
### 6.2 Other tertiary amines examination

**Experimental procedure for the metal-free reaction between tertiary amines and bromodifluoroacylarenes**




α-Bromo difluoroacylarenes **2** (0.3mmol, 1.5 eq.) were added to a flame-dried Schlenk flask containing a stirring bar and purged by evacuating the flask and backfilling with $N_2$ three times. In the absence of light, tertiary amines (0.2 mmol, 1.0 eq.), $H_2O$ (2 mmol, 10 eq.), and anhydrous MeCN (1 ml, 0.2 M) were added and the flask was sealed. The mixture was then stirred under

irradiation from 10 W blue LEDs. After 48 h, the crude products were purified by column chromatography over silica gel using hexanes/EtOAc as eluent to yield **9**.




**6.3 Possible mechanism (again proving the existence of bromine radicals):**

Based on the relevant literature reports[S5] and our understanding, we speculated on the mechanism of the reaction. Firstly, based on the tertiary amine radical-type dealkylation reported,[S5e] path B should be the more likely pathway, i.e., the tertiary amine radical cation is coupled with the difluoroalkyl radical to give the zwitterionic species **III**, followed by dealkylation to give the key intermediate **IV**. Subsequently, intermediate **IV** is stripped of two molecules of HF in the presence of water to give ketoamide **9a**, a process that has been reported in the literature (see Fig S5 gray dashed box).[S6,S5f] Furthermore, we confirmed by calculation that the real form of bromine radicals present in the system may be in the form of intermediate **I**. Due to the electron-deficient nature of the bromine radical, this intermediate has the potential to cause a significant increase in the polarization of the carbon-nitrogen bond of the tertiary amine, which in turn induces the breakage of the carbon-nitrogen bond of the tertiary amine to give nitrogen radical **IV**. Radical **IV** can also be coupled or added to the difluoroalkyl radical to give the key intermediate **IV**. Both of the above pathways we cannot completely exclude, and both could be present in this reaction system. In addition to the two possible dealkylation pathways mentioned above, the amine oxidation/hydrolysis pathway is also possible.[S5b-d] Considering the oxidative nature[S7] and the hydrogen atom transfer (HAT)[S8-10] properties of bromine radicals, and combined

with the reports in the relevant literature,[S5f-g] we speculate on this possible reaction pathway for path c. This pathway involves the electrophilicity[S10j] of the bromine radical and the nucleophilicity[S5g] of the α-amine alkyl radical. Firstly, in the presence of triethylamine/bromine radical complex **I**, the electron-rich α-amine alkyl radical **V** can be obtained by an intramolecular bromine radical-mediated HAT process.This radical can be easily combined with the electrophilic bromine radical to give intermediate **VI**, **VI** can be rapidly and irreversibly decomposed to give the thermodynamically stable imine bromine salt **VII**.[S5g] **VII** can be hydrolyzed to give diethylamine **VIII**. **VIII** can be reacted with difluorobromoaryl ketone in the presence of visible light to give the key intermediate **IV**. The interaction of **IV** with water gives the final product **9a**. This stage of the reaction has been confirmed by our control experiments (Figure S6) and similar literature.[S5f] *Therefore path c is more likely to be present in this reaction system*. In addition, the reaction for *N*-phenyltetrahydropyrrole can also be explained by halogen bonding.

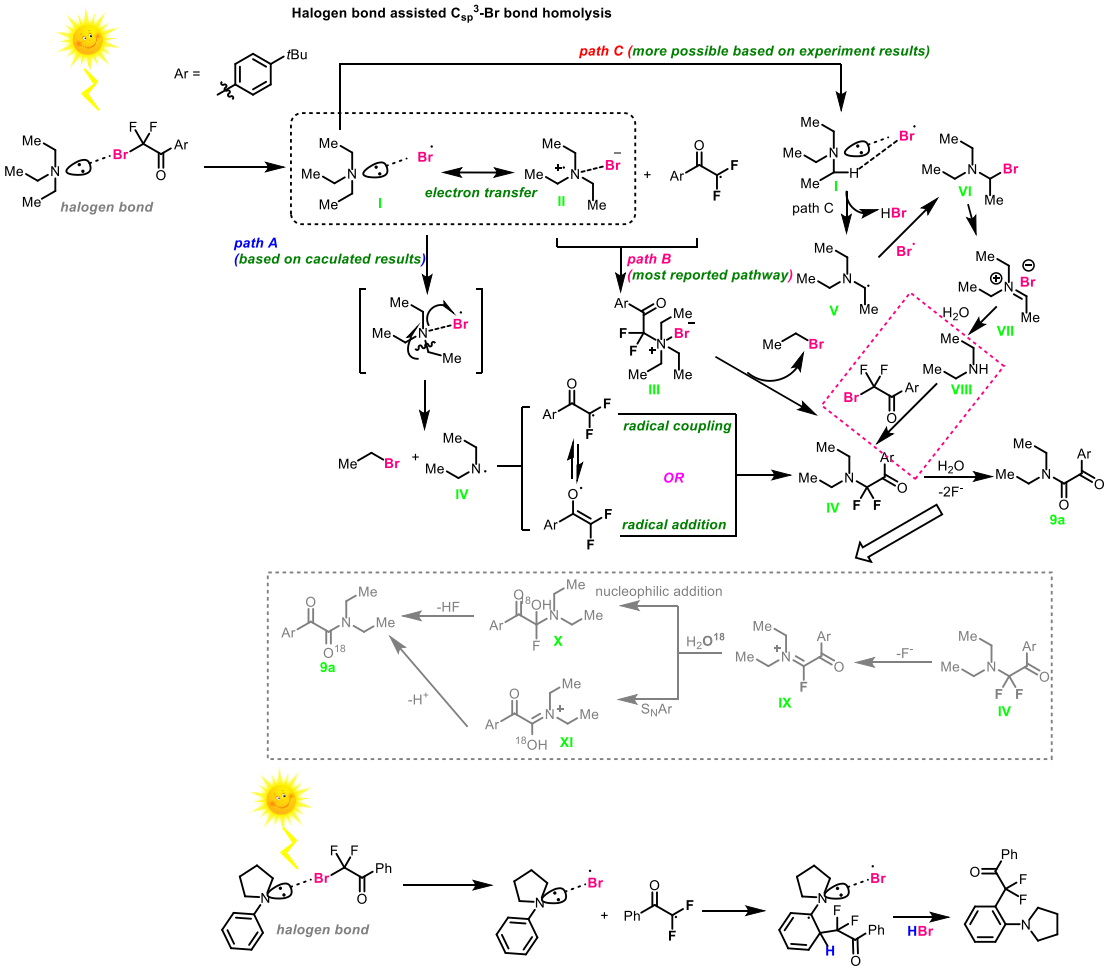
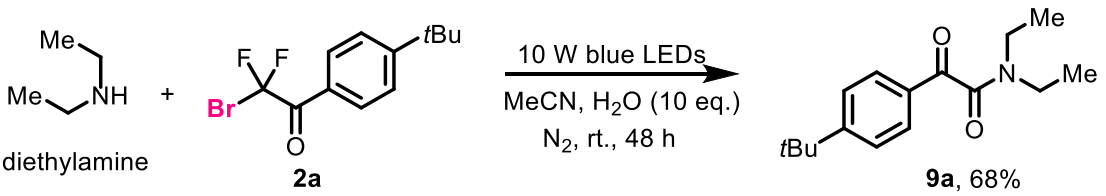



**Figure S5.**

**6.4 Control experiment:**




To a Schlenk tube charged with a magnetic stirring bar, substrate **2a** (0.3 mmol, 88 mg) was added and the Schlenk tube was purged with $N_2$ for three times. Subsequently, anhydrous MeCN (1 ml), diethylamine (0.4 mmol, 41 uL) and $H_2O$ (3 mmol,54 uL) were added in turn via syringes. The tightly sealed tube was then irradiated with a 10 W blue LEDs at room temperature for 48 h. The corresponding α-ketonamide **9a** was obtained in 68 % yield （53 mg）after purification through flash column chromatography on silica gel (Hexane/Ethyl acetate = 5/1).

This control experiment demonstrates that path c is the most likely mechanism:

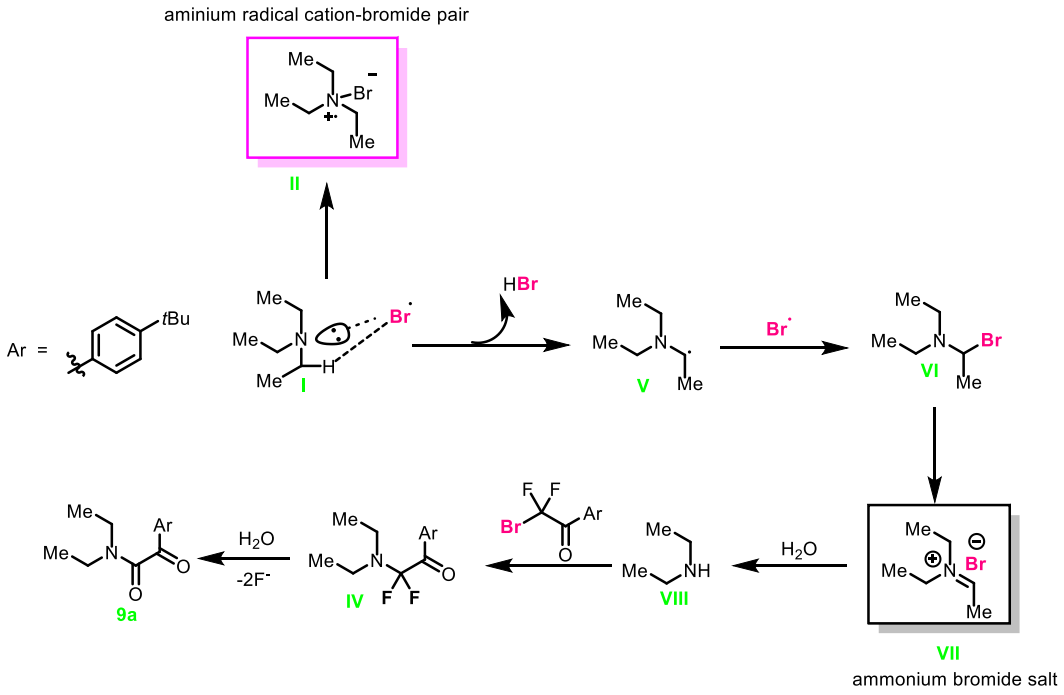
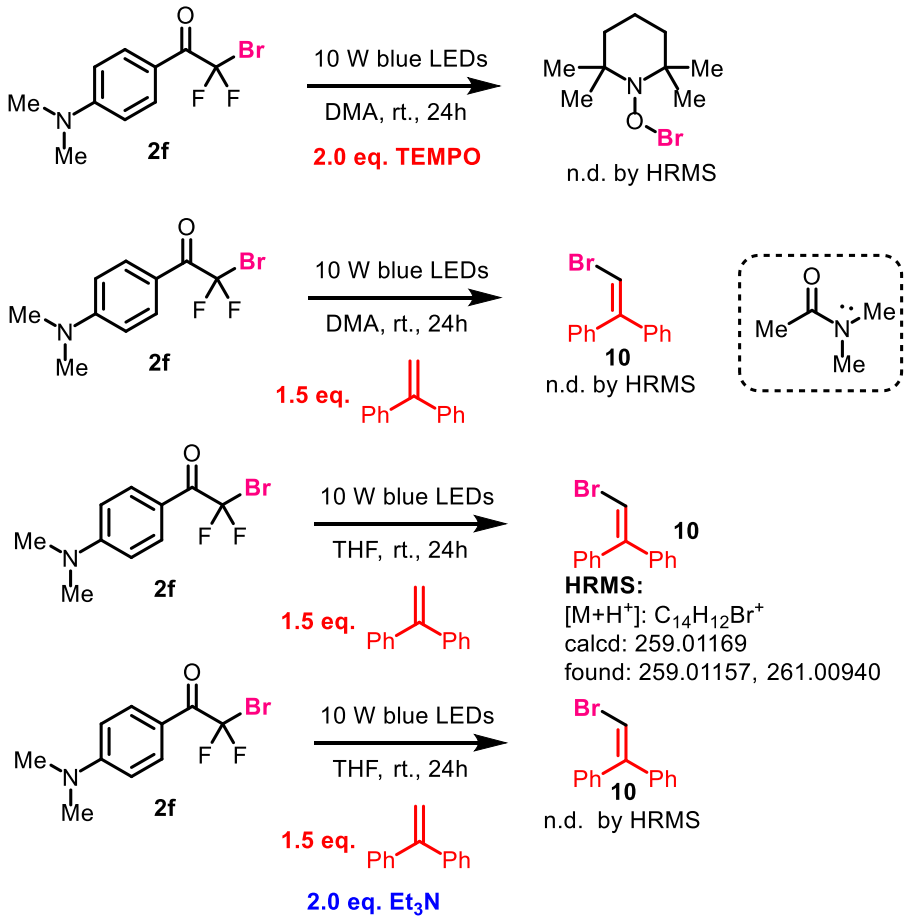


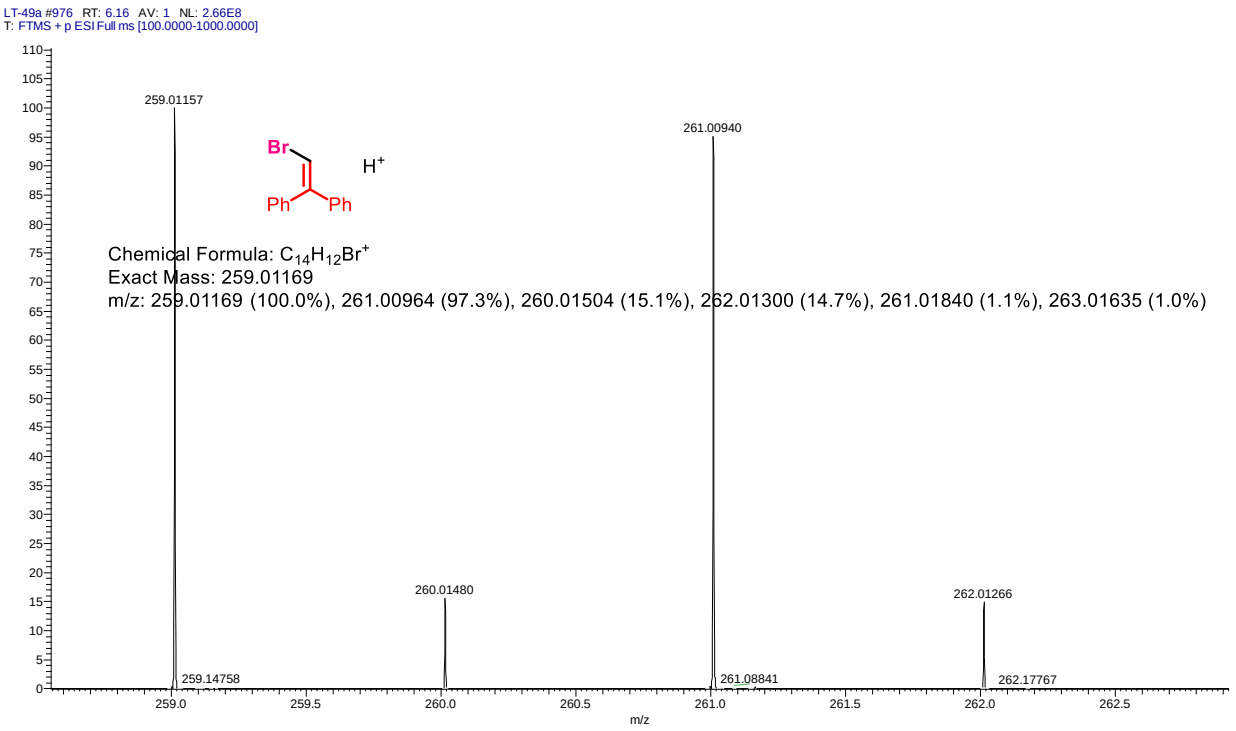

**Figure S6**

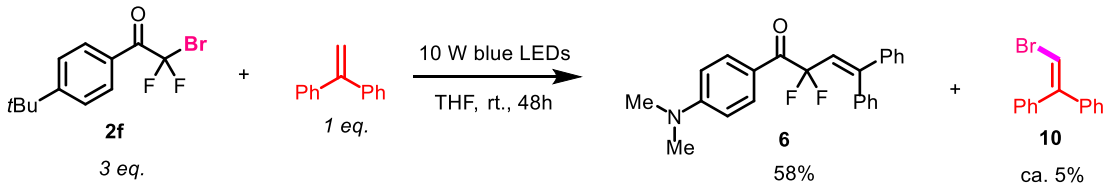
## 7.Bromine radical trapping experiments with 1,1-diphenylethylene or TEMPO

Unfortunately, the bromine radical–TEMPO adduct was not detected, which might be a result of stability issues. However, when the reaction was carried out in the presence of 1,1-diphenylethylene with THF as the solvent, bromine radical-trapping adduct **10** was produced, evidencing the contribution of visible light in the $C_{sp}^3$–Br bond homolysis of difluorobromoaryl ketones (there may be halogen bonding facilitation, such as oxygen in tetrahydrofuran and

nitrogen in difluorobromoaryl ketones). No bromine radical quencher **10** was observed by adding organic bases such as triethylamine. In addition, when the bromine radical trapping experiment is carried out in DMA, the bromine radical quencher **10** was also not observed. The above experimental results indicate that organic bases can quench bromine radicals, which has been proved by our above experiments (Figure S5, path c), similarly, it has been reported in the literature that DMA may also quench bromine radicals. [S11]






To a Schlenk tube charged with a magnetic stirring bar, **2f** (0.6 mmol, 167 mg) and 1,1-diphenylethylene (0.2 mmol, 35uL) were added and the Schlenk tube was purged with $N_2$ for three times. Subsequently, anhydrous THF (1 ml) was added. The tightly sealed tube was then irradiated with a 10 W blue LEDs at room temperature for 48 h. After purification through flash column chromatography on silica gel, the corresponding $CF_2COAr$-trapped product **6** and bromo-diphenylethylene **10** were obtained in 58% (44 mg) and 5% (2.6 mg) yield, respectively. The reaction was repeated 5 times and a total of 11 mg of compound **10** was collected, colorless oil, $R_f$ = 0.7 (Hexane),

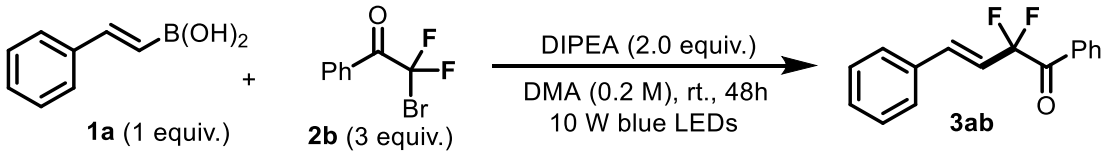
**$^1$HNMR** (400 MHz, $CDCl_3$): $\delta$ 7.44 – 7.34 (m, 3H), 7.30 (dd, $J$ = 7.9, 1.8 Hz, 5H), 7.24 – 7.16 (m, 2H), 6.77 (s, 1H) ppm;

**$^{13}$C NMR** (100 MHz, $CDCl_3$): 146.9, 140.7, 139.1, 129.7, 128.5, 128.3, 128.1, 128.0, 127.6, 105.2 ppm;

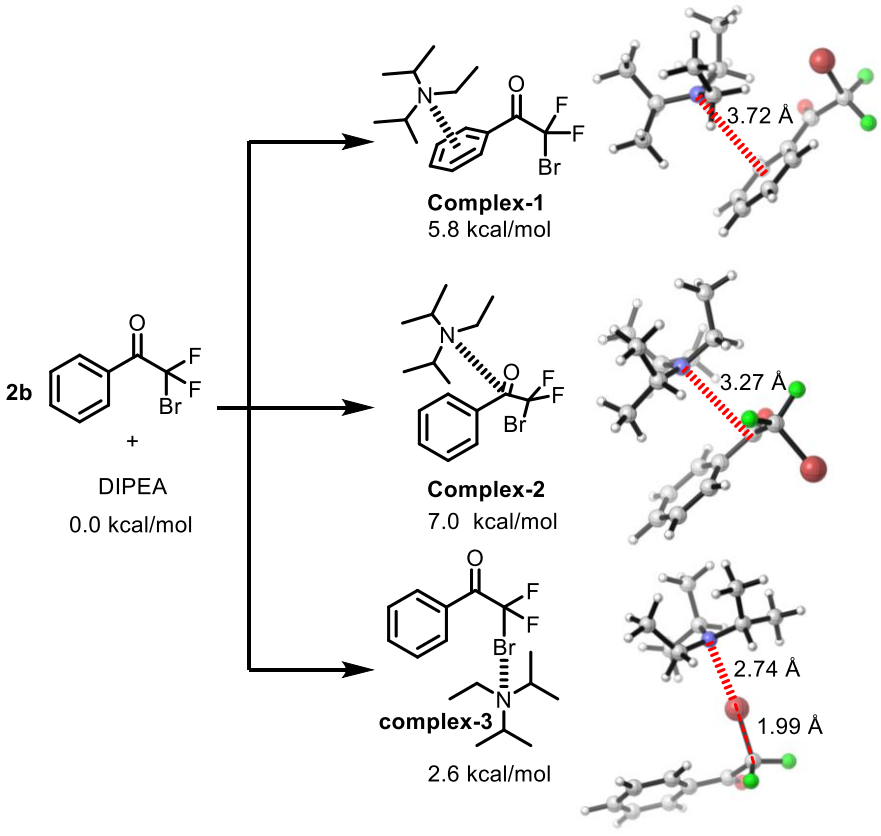
## 8. DFT calculation

**Computational details:** In this work, all DFT calculations were performed with Gaussian 16 program package.[S12] All geometries were optimized by using B3LYP-D3(BJ) functional with Grimme's dispersion correction[S13,S14] and 6-31G(d,p) basis set as well as vibrational frequency analysis at 298 K. The self-consistent reaction field (SCRF) and PCM[S15] solvation model in *N*,*N*-dimethylacetamide solvent were adopted to evaluate the effect of solvent.

### 8.1 Modeled reaction conditions




### 8.2 Radical initiation step



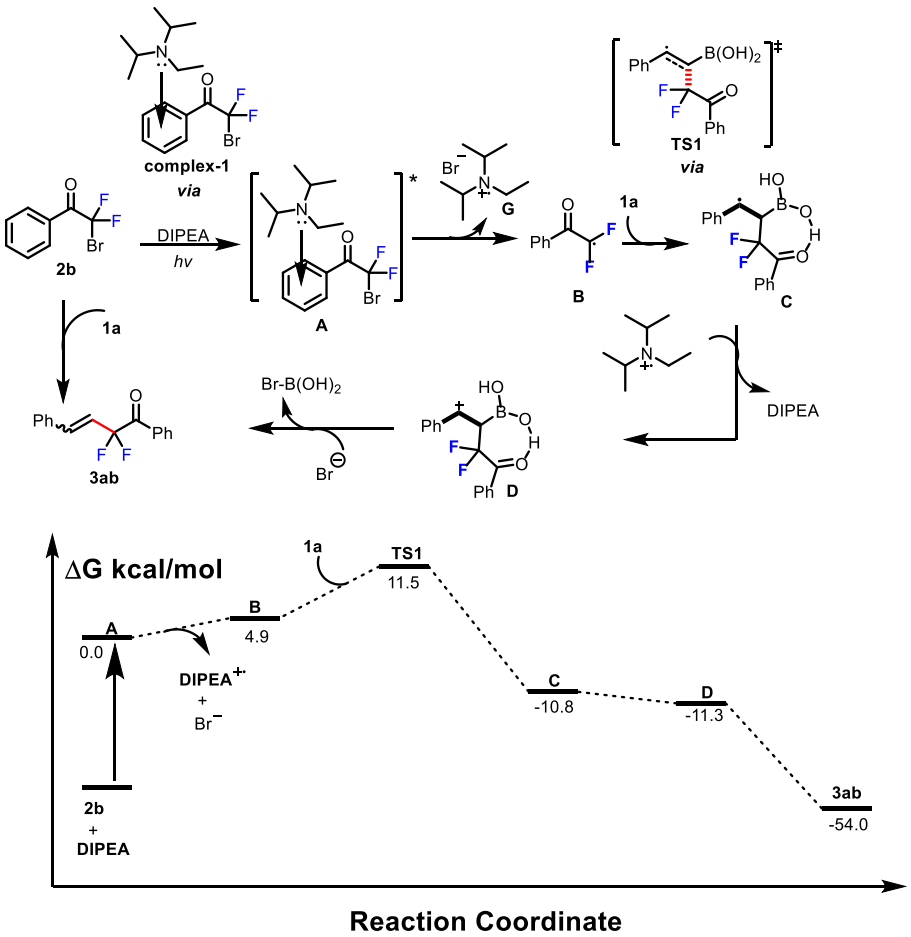

## Maxwell-Boltzmann distribution

| | | | |
|---|---|---|---|
| Temperature: | 298.15 | $Q_{(Relat)}$: | 1.012485 |

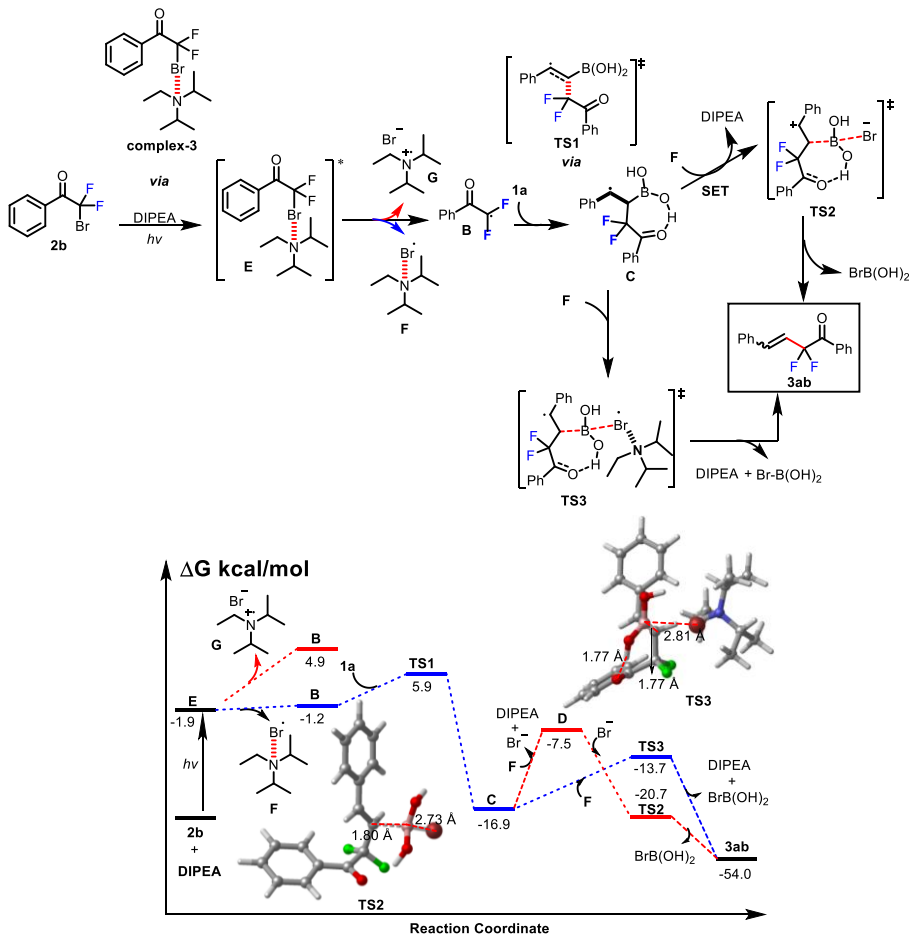
| Index | ΔG (kcal/mol) | $Q_{i(Relat)}$ | Percent |
|---|---|---|---|
| **2b**+DIPEA | 0 | 1.0000 | 98.77% |
| **complex-3** | 2.6 | 0.0124 | 1.23% |
| **complex-1** | 5.8 | 0.0001 | 0.01% |
| **complex-2** | 7 | 0.0000 | 0.00% |

***Both the EDAC pathway and the XB pathway are calibrated with the energy of intermediate A as the zero point to facilitate the comparison of the two pathways.***

### 8.3 Path A: EDAC process

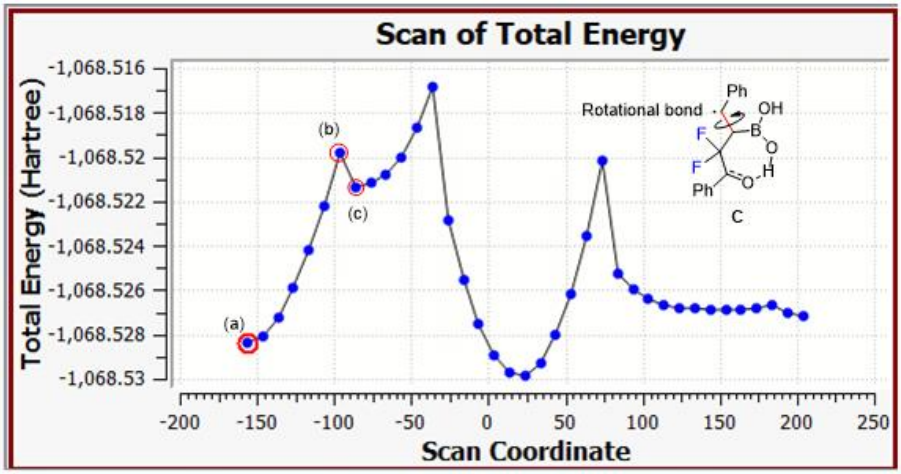


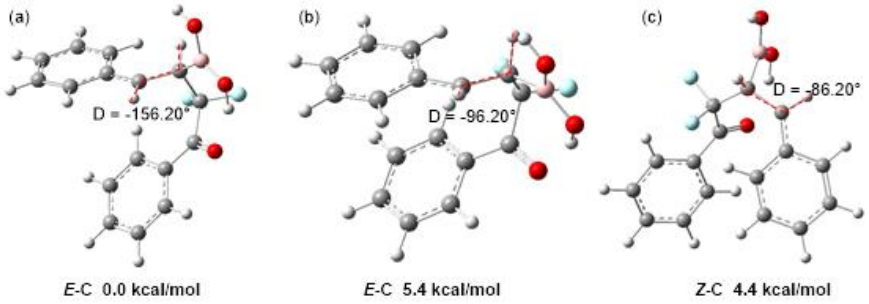

### 8.4 Path B: Halogen bond assisted $C_{sp}^{3}$-Br bond homolysis process




## 8.5 Energy of radical intermediate C in the E/Z configuration

Furthermore, we found from potential energy surface scans (shown below) that although the energy difference between E-C and Z-C is small, the process of flipping E-C to form Z-C is required to overcome an energy barrier. The energy required to overcome the flip results in a product E/Z conformation ratio.





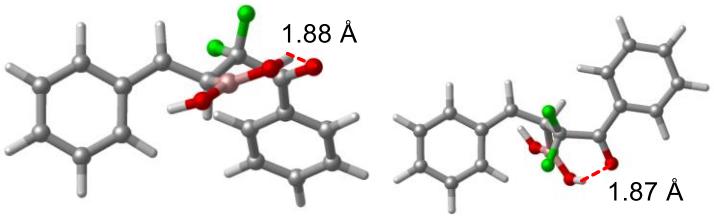
0.0 kca/mol

***E*-C**




1.3 kca/mol

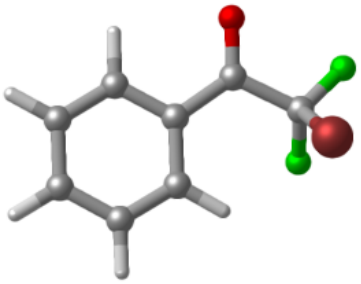
***Z*-C**




*E*-C *Z*-C

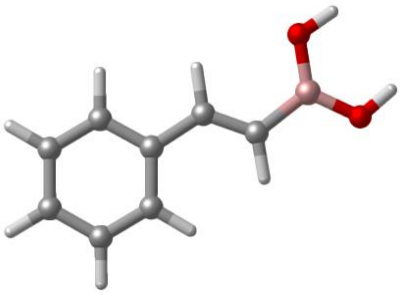
### 8.6 Coordination

### 2b



| | | | |
|---|---|---|---|
| Zero-point correction= | | | 0.112799 (Hartree/Particle) |
| Thermal correction to Energy= | | | 0.123214 |
| Thermal correction to Enthalpy= | | | 0.124158 |
| Thermal correction to Gibbs Free Energy= | | | 0.074722 |
| Sum of electronic and thermal Free Energies= | | | -3154.433320 |
| C | -2.86217900 | 0.84038900 | -1.18941200 |
| C | -1.84909600 | 0.80871600 | -0.23557300 |
| C | -1.22018400 | 2.00344000 | 0.15713000 |
| C | -1.62334900 | 3.22045000 | -0.42071200 |
| C | -2.63293900 | 3.24464200 | -1.37442200 |
| C | -3.25429300 | 2.05302400 | -1.76023300 |
| H | -3.34671500 | -0.08320900 | -1.48725900 |
| H | -1.56378000 | -0.13872900 | 0.20036800 |
| H | -1.13022100 | 4.13325800 | -0.10734000 |
| H | -2.93737500 | 4.18679600 | -1.81763700 |
| H | -4.04414200 | 2.07020900 | -2.50432400 |
| C | -0.13888400 | 2.07202800 | 1.16244900 |
| C | 0.41987500 | 0.75989200 | 1.77648200 |
| F | 0.68468500 | -0.17146200 | 0.83899600 |
| F | 1.54609300 | 1.00298300 | 2.45279700 |
| O | 0.36479900 | 3.10881900 | 1.55336400 |
| Br | -0.91464400 | 0.02463200 | 3.04559400 |

***E*-1a**

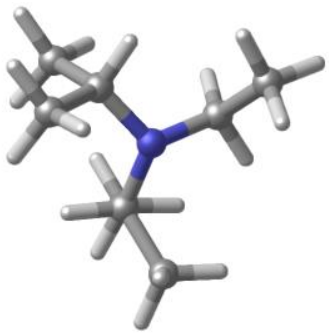


| | | | |
|---|---|---|---|
| Zero-point correction= | | | 0.158449 (Hartree/Particle) |
| Thermal correction to Energy= | | | 0.168622 |
| Thermal correction to Enthalpy= | | | 0.169566 |
| Thermal correction to Gibbs Free Energy= | | | 0.121626 |

Sum of electronic and thermal Free Energies= -485.607682

| | | | |
|---|---|---|---|
| C | 0.25520200 | -3.56464000 | -3.53183700 |
| C | 0.66504400 | -2.26282200 | -3.24893300 |
| C | 0.12270200 | -1.54909500 | -2.16569700 |
| C | -0.85101300 | -2.18439000 | -1.37209900 |
| C | -1.26154600 | -3.48327900 | -1.65407800 |
| C | -0.71063500 | -4.18030700 | -2.73469700 |
| H | 0.68862000 | -4.09691700 | -4.37292400 |
| H | 1.41698300 | -1.78520100 | -3.87109700 |
| H | -1.28999300 | -1.65707000 | -0.53158800 |
| H | -2.01456300 | -3.95640100 | -1.03122500 |
| H | -1.03367400 | -5.19367200 | -2.95156100 |
| C | 0.59296400 | -0.18156200 | -1.91378600 |
| C | 0.22807000 | 0.65105800 | -0.91902800 |
| H | 1.32842100 | 0.17964700 | -2.63247300 |
| H | -0.50176200 | 0.31003100 | -0.18511900 |
| B | 0.80840500 | 2.08543600 | -0.76237600 |
| O | 1.71261300 | 2.53329400 | -1.69521100 |
| H | 2.03601400 | 3.43021000 | -1.54522200 |
| O | 0.37890400 | 2.82735400 | 0.31112000 |
| H | 0.76886700 | 3.70898600 | 0.37168400 |

**DIPEA**

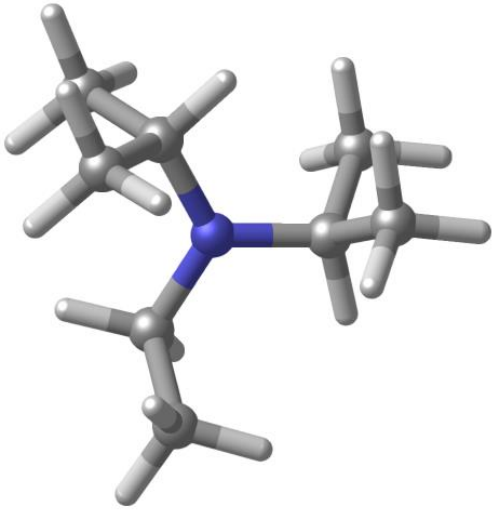


Zero-point correction= 0.262213 (Hartree/Particle)
Thermal correction to Energy= 0.274248
Thermal correction to Enthalpy= 0.275192
Thermal correction to Gibbs Free Energy= 0.225516
Sum of electronic and thermal Free Energies= -370.886353

| | | | |
|---|---|---|---|
| N | 2.66969100 | 0.15457900 | -0.51673200 |
| C | 2.55150400 | 1.48511900 | 0.10210100 |
| C | 3.69796700 | 1.73471900 | 1.08907800 |
| C | 1.18942200 | 1.79829300 | 0.74824600 |
| H | 2.68525300 | 2.19791600 | -0.71889500 |
| H | 4.66131300 | 1.54979600 | 0.60591800 |
| H | 3.67690300 | 2.76907100 | 1.44728500 |

| | | | |
|---|---|---|---|
| H | 3.62715700 | 1.08425000 | 1.96726500 |
| H | 1.14759500 | 2.84936400 | 1.05288200 |
| H | 0.36563700 | 1.61946000 | 0.05061500 |
| H | 1.02135600 | 1.18861800 | 1.64181100 |
| C | 2.39174100 | -1.00286900 | 0.35331900 |
| C | 3.36486400 | -2.14315700 | 0.02520600 |
| C | 0.93866700 | -1.51785700 | 0.34547200 |
| H | 2.61196100 | -0.67523200 | 1.37430100 |
| H | 4.39863600 | -1.79812800 | 0.11222700 |
| H | 3.21823700 | -2.99183800 | 0.70190500 |
| H | 3.21475200 | -2.50652800 | -0.99765500 |
| H | 0.22318200 | -0.72438000 | 0.56934600 |
| H | 0.67154300 | -1.95095300 | -0.62366900 |
| H | 0.81873000 | -2.30436400 | 1.09788000 |
| C | 2.10937700 | 0.07497000 | -1.86503500 |
| C | 3.01845700 | 0.71174400 | -2.91848500 |
| H | 1.10114800 | 0.52200700 | -1.92828700 |
| H | 1.98514400 | -0.98060300 | -2.12071800 |
| H | 2.57920400 | 0.60842900 | -3.91651900 |
| H | 3.17324100 | 1.77977000 | -2.73675600 |
| H | 3.99870300 | 0.22524500 | -2.91569800 |

**DIPEA$^{+\cdot}$**



Zero-point correction= 0.263161 (Hartree/Particle)
Thermal correction to Energy= 0.275402
Thermal correction to Enthalpy= 0.276346
Thermal correction to Gibbs Free Energy= 0.225574
Sum of electronic and thermal Free Energies= -370.706413

| | | | |
|---|---|---|---|
| N | 2.20191000 | 0.22885000 | -0.50072600 |

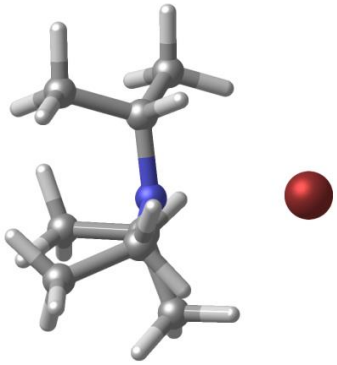
| | | | |
|---|---|---|---|
| C | 2.33535200 | 1.56535000 | 0.09111600 |
| C | 3.70286200 | 1.71620700 | 0.77803000 |
| C | 1.16147000 | 1.83578400 | 1.04856800 |
| H | 2.27544400 | 2.26662000 | -0.74312400 |
| H | 4.52055800 | 1.50655100 | 0.08598100 |
| H | 3.79098500 | 2.75100400 | 1.11656400 |
| H | 3.79482100 | 1.06536100 | 1.65014000 |
| H | 1.25120200 | 2.86649100 | 1.39908900 |
| H | 0.20249700 | 1.72503400 | 0.53865300 |
| H | 1.18679900 | 1.17661400 | 1.91891200 |
| C | 2.23031900 | -0.96948800 | 0.34417300 |
| C | 3.37645200 | -1.90060300 | -0.08272100 |
| C | 0.85965900 | -1.67079800 | 0.30732200 |
| H | 2.41690800 | -0.62146400 | 1.35988400 |
| H | 4.34046600 | -1.39070500 | -0.03597500 |
| H | 3.39603000 | -2.74289000 | 0.61245300 |
| H | 3.22567600 | -2.29588300 | -1.08966000 |
| H | 0.05701100 | -0.98818900 | 0.59153600 |
| H | 0.64365900 | -2.08739800 | -0.67861000 |
| H | 0.89041600 | -2.49210900 | 1.02681800 |
| C | 2.03743500 | 0.11742900 | -1.94092100 |
| C | 3.33258600 | 0.48319400 | -2.69137000 |
| H | 1.23490500 | 0.80676800 | -2.22637900 |
| H | 1.72801300 | -0.89793300 | -2.18161200 |
| H | 3.13345200 | 0.38678800 | -3.76062600 |
| H | 3.64036300 | 1.51086500 | -2.48981000 |
| H | 4.14413700 | -0.19400900 | -2.42129700 |

**Br-**

Zero-point correction= 0.000000 (Hartree/Particle)
Thermal correction to Energy= 0.001416
Thermal correction to Enthalpy= 0.002360
Thermal correction to Gibbs Free Energy= -0.016176
Sum of electronic and thermal Free Energies= -2571.886830

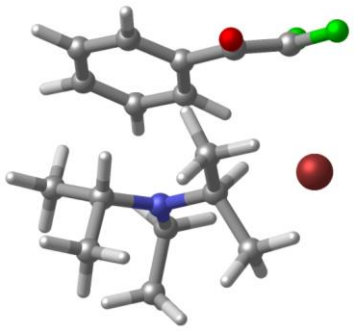
| | | | |
|---|---|---|---|
| Br | 1.57176200 | 0.50007600 | -1.51282400 |

**F**



| | | | |
|---|---|---|---|
| Zero-point correction= | | | 0.265444 (Hartree/Particle) |
| Thermal correction to Energy= | | | 0.279022 |
| Thermal correction to Enthalpy= | | | 0.279967 |
| Thermal correction to Gibbs Free Energy= | | | 0.225675 |
| Sum of electronic and thermal Free Energies= | | | -2942.602919 |
| N | -2.21586500 | -3.51252000 | -2.53501400 |
| C | -2.19435800 | -4.96103200 | -2.87018600 |
| C | -3.05582000 | -5.29865700 | -4.10141800 |
| C | -2.53364200 | -5.85082800 | -1.67771400 |
| H | -1.15111300 | -5.14998600 | -3.13569600 |
| H | -4.11199100 | -5.07219500 | -3.94407900 |
| H | -2.71263700 | -4.77374800 | -4.99429300 |
| H | -2.96336900 | -6.37108900 | -4.29347500 |
| H | -3.58247900 | -5.77816700 | -1.37955900 |
| H | -2.34394700 | -6.88852300 | -1.96346600 |
| H | -1.89144700 | -5.60314200 | -0.83033000 |
| C | -3.15305500 | -2.99624600 | -1.51270200 |
| C | -4.62564600 | -3.09045800 | -1.96063300 |
| C | -2.79464800 | -1.58156300 | -1.05941000 |
| H | -3.02492100 | -3.65616200 | -0.65405000 |
| H | -4.92506600 | -4.11711500 | -2.17428200 |
| H | -5.25189400 | -2.72432200 | -1.14240800 |
| H | -4.82512600 | -2.47896800 | -2.84184200 |
| H | -1.75177600 | -1.54562200 | -0.73995400 |
| H | -2.96498500 | -0.83322200 | -1.83696500 |
| H | -3.43145500 | -1.32436800 | -0.20923400 |
| C | -1.67064200 | -2.60307400 | -3.55400700 |
| C | -2.69678700 | -1.95764100 | -4.49628800 |
| H | -0.94501100 | -3.18327200 | -4.12622300 |
| H | -1.11320800 | -1.82454900 | -3.03411500 |
| H | -2.14470900 | -1.40625900 | -5.26293700 |
| H | -3.32990100 | -2.69211600 | -4.99534800 |
| H | -3.33898700 | -1.24562400 | -3.97560600 |
| Br | 0.09781400 | -3.59000900 | -1.00637000 |

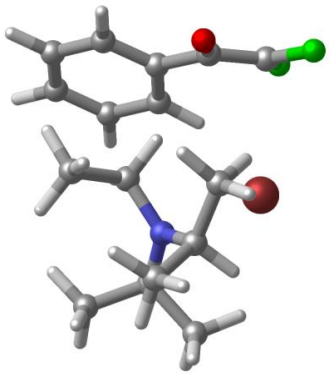
**A**



| | | | |
|---|---|---|---|
| Zero-point correction= | | | 0.375600 (Hartree/Particle) |
| Thermal correction to Energy= | | | 0.400705 |
| Thermal correction to Enthalpy= | | | 0.401649 |
| Thermal correction to Gibbs Free Energy= | | | 0.317320 |
| Sum of electronic and thermal Free Energies= | | | -3525.273347 |
| C | 2.03620300 | 2.01661700 | -0.90303600 |
| C | 1.67011900 | 0.68061800 | -1.06196800 |
| C | 1.51701700 | -0.13989500 | 0.06584300 |
| C | 1.71532300 | 0.39781500 | 1.34637400 |
| C | 2.09870400 | 1.72768400 | 1.49826800 |
| C | 2.26275600 | 2.54007300 | 0.37209700 |
| H | 2.14038100 | 2.65150500 | -1.77719300 |
| H | 1.44405600 | 0.28527700 | -2.04504900 |
| H | 1.57619600 | -0.24375200 | 2.20953400 |
| H | 2.26543400 | 2.13309100 | 2.49107300 |
| H | 2.55637600 | 3.57835700 | 0.48946500 |
| C | 1.12625900 | -1.57382400 | -0.02263400 |
| C | 1.51829700 | -2.32772700 | -1.16593900 |
| F | 2.44193400 | -1.95448900 | -2.02835300 |
| O | 0.47796400 | -2.14952900 | 0.88015000 |
| N | -2.14290300 | 0.87327300 | -0.04771200 |
| C | -2.44175300 | -0.54162100 | -0.24404000 |
| C | -3.66035100 | -0.71671600 | -1.17881500 |
| C | -2.56833900 | -1.35313100 | 1.03804700 |
| H | -1.58771100 | -0.92351700 | -0.83988800 |
| H | -4.56887900 | -0.30675200 | -0.73096800 |
| H | -3.48393500 | -0.25574600 | -2.15024300 |
| H | -3.79485400 | -1.78800500 | -1.34196000 |
| H | -3.43281400 | -1.06680700 | 1.64186900 |
| H | -2.69840600 | -2.39832300 | 0.74881700 |
| H | -1.65581200 | -1.29772200 | 1.63355000 |
| C | -2.31625600 | 1.52406900 | 1.25852900 |

| | | | |
|---|---|---|---|
| C | -3.81699800 | 1.82602800 | 1.48124000 |
| C | -1.45540500 | 2.77103700 | 1.43870300 |
| H | -2.01040600 | 0.78400300 | 2.00029300 |
| H | -4.43434400 | 0.93283900 | 1.37810000 |
| H | -3.93579800 | 2.21097100 | 2.49689900 |
| H | -4.17124800 | 2.58085500 | 0.77720700 |
| H | -1.57873600 | 3.11250400 | 2.46914800 |
| H | -0.39823700 | 2.55469800 | 1.28063500 |
| H | -1.75961200 | 3.58831900 | 0.78110800 |
| C | -1.71032100 | 1.63178400 | -1.21609200 |
| C | -2.78767300 | 2.57219200 | -1.78455100 |
| H | -1.39647400 | 0.90589100 | -1.97097800 |
| H | -0.83456200 | 2.21424100 | -0.92116400 |
| H | -2.38195600 | 3.03019900 | -2.68993600 |
| H | -3.69531100 | 2.02757400 | -2.04850100 |
| H | -3.04666800 | 3.37045400 | -1.08729600 |
| Br | -0.61551400 | -1.35818300 | -3.08783400 |
| F | 1.22795900 | -3.60443200 | -1.26889700 |

**E**

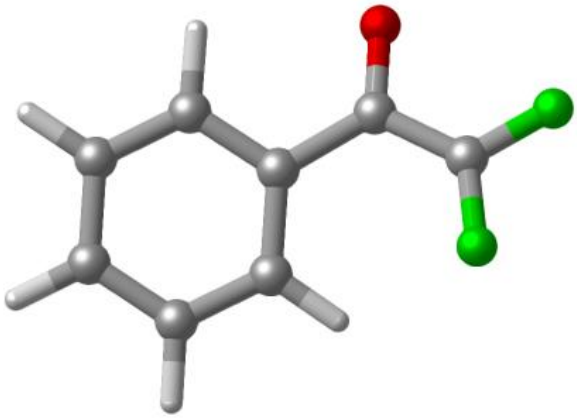


Zero-point correction= 0.376817 (Hartree/Particle)
Thermal correction to Energy= 0.401632
Thermal correction to Enthalpy= 0.402576
Thermal correction to Gibbs Free Energy= 0.319510
Sum of electronic and thermal Free Energies= -3525.276444

| | | | |
|---|---|---|---|
| C | 2.35034600 | -1.40756900 | -3.27681600 |
| C | 2.15179200 | -1.86674400 | -1.97581800 |
| C | 1.57537200 | -1.02033500 | -1.01636900 |
| C | 1.20346900 | 0.28246100 | -1.37998000 |
| C | 1.41298300 | 0.73965600 | -2.67771600 |
| C | 1.98583500 | -0.10675800 | -3.63100400 |
| H | 2.78063000 | -2.07206700 | -4.01930600 |
| H | 2.38105700 | -2.89376200 | -1.72676700 |
| H | 0.73848600 | 0.91760200 | -0.63446200 |

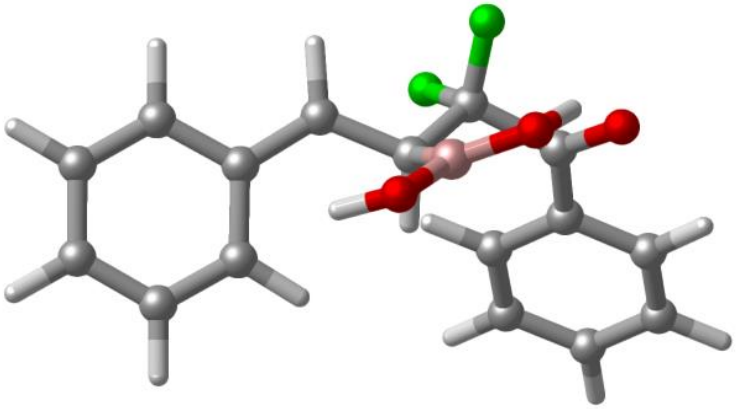
| | | | |
|---|---|---|---|
| H | 1.12612200 | 1.75080300 | -2.94828900 |
| H | 2.14206300 | 0.24428300 | -4.64617500 |
| C | 1.21700500 | -1.46412400 | 0.35919000 |
| C | 1.91646700 | -2.54386800 | 0.96636500 |
| F | 3.01761000 | -3.10020600 | 0.50752800 |
| O | 0.28529800 | -0.93160800 | 1.00369800 |
| N | -2.03795700 | -3.32331600 | -1.86996700 |
| C | -1.89437400 | -4.12670500 | -3.11082200 |
| C | -2.61870500 | -3.47926000 | -4.30581300 |
| C | -2.29250700 | -5.58790700 | -2.92823700 |
| H | -0.82070000 | -4.09604600 | -3.31426400 |
| H | -3.69485200 | -3.39775800 | -4.14009400 |
| H | -2.22063900 | -2.48969900 | -4.53463100 |
| H | -2.45559000 | -4.11270700 | -5.18175500 |
| H | -3.36649200 | -5.71786400 | -2.77362900 |
| H | -2.02314100 | -6.12770800 | -3.83949900 |
| H | -1.74320100 | -6.02743800 | -2.09362900 |
| C | -3.04691800 | -3.67264900 | -0.84884900 |
| C | -4.48226000 | -3.39953100 | -1.34292900 |
| C | -2.77015600 | -2.99189500 | 0.49080700 |
| H | -2.94258800 | -4.74802300 | -0.70203900 |
| H | -4.71659200 | -3.95732300 | -2.25050300 |
| H | -5.17570400 | -3.72333800 | -0.56209600 |
| H | -4.65155000 | -2.33837900 | -1.53179800 |
| H | -1.74370100 | -3.18961700 | 0.80438600 |
| H | -2.93753700 | -1.91286600 | 0.45721300 |
| H | -3.45431300 | -3.41075000 | 1.23309000 |
| C | -1.45547900 | -1.97774900 | -1.89153500 |
| C | -2.42507800 | -0.83250100 | -2.21914500 |
| H | -0.63937100 | -2.00117200 | -2.61333200 |
| H | -1.01811500 | -1.79255200 | -0.91400600 |
| H | -1.82850000 | 0.08055000 | -2.29903400 |
| H | -2.95417100 | -0.98000900 | -3.16119300 |
| H | -3.16068800 | -0.68162400 | -1.42742700 |
| Br | 0.17747400 | -4.57012200 | -0.62107400 |
| F | 1.59906900 | -2.98030700 | 2.16172500 |

**B**



| | | | |
|---|---|---|---|
| Zero-point correction= | | | 0.110378 (Hartree/Particle) |
| Thermal correction to Energy= | | | 0.119533 |
| Thermal correction to Enthalpy= | | | 0.120477 |
| Thermal correction to Gibbs Free Energy= | | | 0.074279 |
| Sum of electronic and thermal Free Energies= | | | -582.672312 |
| C | -0.79599500 | -1.33859600 | -3.89124700 |
| C | -0.20344600 | -0.87194100 | -2.71913600 |
| C | -0.91046200 | -0.92033300 | -1.50698200 |
| C | -2.21679400 | -1.43518100 | -1.49467000 |
| C | -2.80006600 | -1.90836400 | -2.66515800 |
| C | -2.08988400 | -1.86155500 | -3.86794700 |
| H | -0.24535700 | -1.28983800 | -4.82501200 |
| H | 0.79600100 | -0.45926000 | -2.76059400 |
| H | -2.75728200 | -1.45618000 | -0.55535100 |
| H | -3.80702600 | -2.31237500 | -2.64212400 |
| H | -2.54436700 | -2.22812100 | -4.78287800 |
| C | -0.38259700 | -0.41643000 | -0.20811800 |
| C | 1.02372300 | -0.25295600 | -0.00478100 |
| F | 1.97797700 | -0.57787200 | -0.85043400 |
| O | -1.12806500 | -0.14542700 | 0.75643400 |
| F | 1.49858200 | 0.20584900 | 1.12726900 |

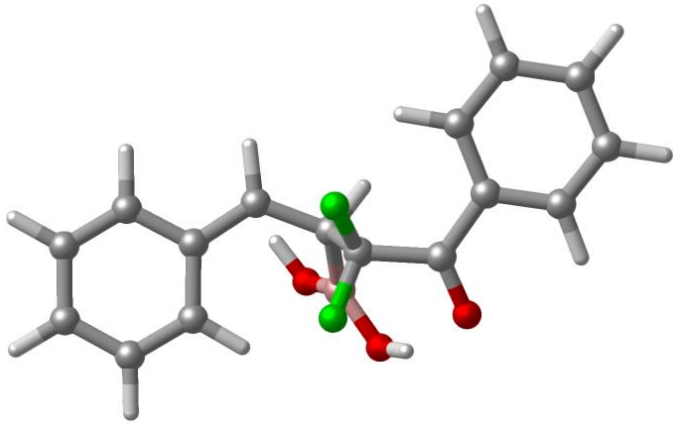
***E*-C**



| | | | |
|---|---|---|---|
| Zero-point correction= | | | 0.272509 (Hartree/Particle) |
| Thermal correction to Energy= | | | 0.291811 |
| Thermal correction to Enthalpy= | | | 0.292755 |
| Thermal correction to Gibbs Free Energy= | | | 0.221949 |
| Sum of electronic and thermal Free Energies= | | | -1068.305751 |
| C | -1.38362600 | -0.88214200 | 3.30289900 |
| C | -0.65375500 | -0.49637300 | 2.18191800 |
| C | 0.68439600 | -0.08365400 | 2.32408300 |
| C | 1.27067500 | -0.07179700 | 3.60413800 |
| C | 0.54077500 | -0.47043100 | 4.71567600 |
| C | -0.79002800 | -0.87451800 | 4.56646200 |
| H | -2.41644900 | -1.19311900 | 3.18866100 |
| H | -1.12432200 | -0.51931200 | 1.20910400 |
| H | 2.29913900 | 0.25556400 | 3.70125400 |
| H | 1.00142800 | -0.46357900 | 5.69775900 |
| H | -1.36323800 | -1.18159300 | 5.43535100 |
| C | 1.51771100 | 0.39416100 | 1.20373000 |
| C | 0.98405700 | 0.39652500 | -0.24956700 |
| F | 0.26258700 | -0.75427600 | -0.47924200 |
| O | 2.63537800 | 0.87411900 | 1.37459600 |
| F | 2.06864100 | 0.31789000 | -1.09110200 |
| C | -3.48458400 | 2.38639600 | -3.97002700 |
| C | -2.27114400 | 1.84222700 | -3.58606400 |
| C | -1.77120500 | 2.00864000 | -2.25977600 |
| C | -2.57628900 | 2.75720900 | -1.34926200 |
| C | -3.78932000 | 3.30160000 | -1.75009500 |
| C | -4.25509500 | 3.12398500 | -3.05800000 |
| H | -3.83988300 | 2.24298800 | -4.98588500 |
| H | -1.67734600 | 1.27641800 | -4.29785400 |
| H | -2.25024300 | 2.89766400 | -0.32396500 |
| H | -4.38155700 | 3.86650100 | -1.03683300 |
| H | -5.20408300 | 3.55170800 | -3.36359700 |
| C | -0.51921600 | 1.45354300 | -1.91212500 |
| C | 0.16541000 | 1.63519300 | -0.59165200 |

| | | | |
|---|---|---|---|
| H | 0.03150600 | 0.91864200 | -2.67945600 |
| H | -0.57760100 | 1.75815800 | 0.20726600 |
| B | 1.03556800 | 3.00871800 | -0.62581000 |
| O | 0.45450700 | 4.15447700 | -1.08875600 |
| H | -0.44171100 | 4.02465700 | -1.42567500 |
| O | 2.32549500 | 3.12356900 | -0.22152500 |
| H | 2.70161100 | 2.30954700 | 0.15659700 |

**_Z_-C**

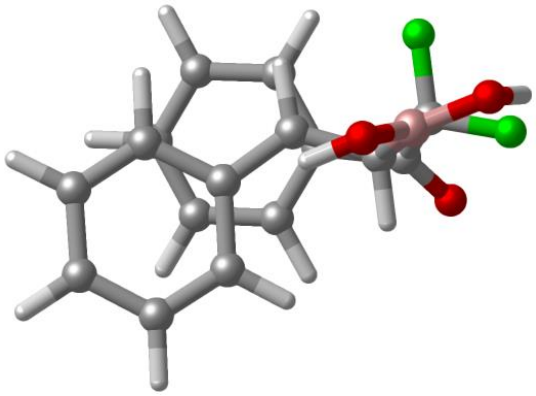


Zero-point correction= 0.272755 (Hartree/Particle)
Thermal correction to Energy= 0.291960
Thermal correction to Enthalpy= 0.292904
Thermal correction to Gibbs Free Energy= 0.222693
Sum of electronic and thermal Free Energies= -1068.303680

| | | | |
|---|---|---|---|
| C | 4.88586500 | 2.52381500 | 0.80182900 |
| C | 3.49849900 | 2.62840700 | 0.74998000 |
| C | 2.74922700 | 2.61969900 | 1.94122400 |
| C | 3.41742800 | 2.50970000 | 3.17571100 |
| C | 4.80207500 | 2.42018600 | 3.22048800 |
| C | 5.53905300 | 2.42487100 | 2.03160200 |
| H | 5.45791300 | 2.52375100 | -0.11974300 |
| H | 3.00833600 | 2.71461300 | -0.20939200 |
| H | 2.82887600 | 2.49614800 | 4.08551100 |
| H | 5.30958900 | 2.34222200 | 4.17607300 |
| H | 6.62123100 | 2.34995200 | 2.06508000 |
| C | 1.27465100 | 2.67187400 | 1.98249900 |
| C | 0.43522800 | 2.85324900 | 0.69482200 |
| F | 1.06500100 | 3.73110500 | -0.15667200 |
| O | 0.64329900 | 2.50281500 | 3.02322100 |
| F | -0.73277100 | 3.47960100 | 1.06189300 |
| C | -2.97556100 | 2.56612300 | -3.85255300 |
| C | -1.73967900 | 2.21608500 | -3.33425400 |

| | | | |
|---|---|---|---|
| C | -1.52934900 | 2.10717600 | -1.92770000 |
| C | -2.64062800 | 2.38297000 | -1.07837400 |
| C | -3.87361700 | 2.72952300 | -1.60973500 |
| C | -4.05539700 | 2.82335100 | -2.99588700 |
| H | -3.10720900 | 2.63998400 | -4.92769500 |
| H | -0.90703400 | 2.01344300 | -4.00163500 |
| H | -2.51863700 | 2.34504600 | -0.00316600 |
| H | -4.70416100 | 2.93439000 | -0.94117600 |
| H | -5.02354900 | 3.09607900 | -3.40287300 |
| C | -0.25404000 | 1.71802400 | -1.45182900 |
| C | 0.13293800 | 1.52180100 | -0.00897900 |
| H | 0.52354400 | 1.57025300 | -2.19477900 |
| H | 1.08351000 | 0.97072700 | -0.00935000 |
| B | -0.90240300 | 0.57287800 | 0.79437400 |
| O | -1.42763700 | -0.51907600 | 0.16245000 |
| H | -1.17249200 | -0.55768000 | -0.76811800 |
| O | -1.29184400 | 0.75510900 | 2.08207400 |
| H | -0.86446200 | 1.51150100 | 2.52200700 |

**D**

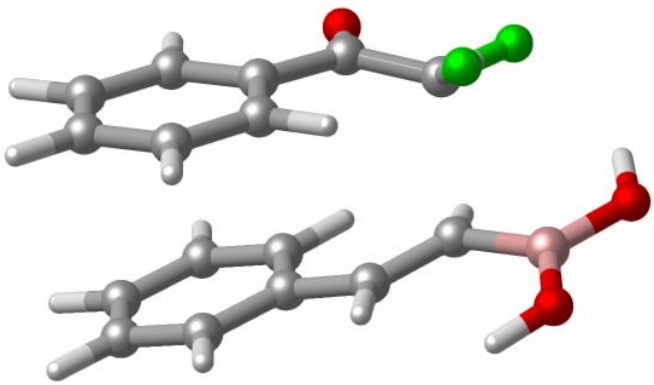


Zero-point correction= 0.274796 (Hartree/Particle)
Thermal correction to Energy= 0.294010
Thermal correction to Enthalpy= 0.294954
Thermal correction to Gibbs Free Energy= 0.226874
Sum of electronic and thermal Free Energies= -1068.125901

| | | | |
|---|---|---|---|
| C | -1.13128800 | -1.20952800 | -3.95117800 |
| C | -0.16029800 | -1.10260100 | -2.95765200 |
| C | -0.53884900 | -1.16559600 | -1.60293800 |
| C | -1.88710800 | -1.36032100 | -1.25830700 |
| C | -2.85278000 | -1.41865000 | -2.25484800 |
| C | -2.47587800 | -1.33621300 | -3.60234200 |
| H | -0.83895800 | -1.17227500 | -4.99454100 |

| | | | |
|---|---|---|---|
| H | 0.88131000 | -0.98294800 | -3.22671900 |
| H | -2.16474000 | -1.41486100 | -0.21181600 |
| H | -3.89836100 | -1.52786600 | -1.98929200 |
| H | -3.23384800 | -1.38075800 | -4.37683900 |
| C | 0.41670800 | -0.94493000 | -0.48528000 |
| C | 1.29254400 | 0.33871200 | -0.59419800 |
| F | 2.10622000 | 0.28302600 | -1.69549400 |
| O | 0.42166600 | -1.57471300 | 0.55009100 |
| F | 2.10642300 | 0.40271400 | 0.49965400 |
| C | -3.51368900 | 2.34467000 | -3.69379200 |
| C | -2.18824500 | 2.03965400 | -3.45018200 |
| C | -1.70769400 | 1.93263500 | -2.10846900 |
| C | -2.62222800 | 2.11129900 | -1.02560700 |
| C | -3.94138600 | 2.41518900 | -1.28466600 |
| C | -4.38487800 | 2.53546600 | -2.61399600 |
| H | -3.87797200 | 2.43162600 | -4.71019600 |
| H | -1.49550500 | 1.88788900 | -4.26987300 |
| H | -2.28610100 | 1.99995000 | -0.00235400 |
| H | -4.63972100 | 2.55313000 | -0.46802900 |
| H | -5.42634700 | 2.77172300 | -2.80506500 |
| C | -0.35967100 | 1.61325400 | -1.92372300 |
| C | 0.39091500 | 1.58145200 | -0.66399700 |
| H | 0.23201100 | 1.47702500 | -2.82414100 |
| H | -0.26601800 | 1.55803200 | 0.21211500 |
| B | 1.22840600 | 3.00552600 | -0.53611300 |
| O | 0.66367000 | 4.17746900 | -0.90810800 |
| H | -0.23170600 | 4.13750900 | -1.26268400 |
| O | 2.47525100 | 3.05023800 | -0.02544800 |
| H | 2.81534600 | 2.20158400 | 0.28604300 |

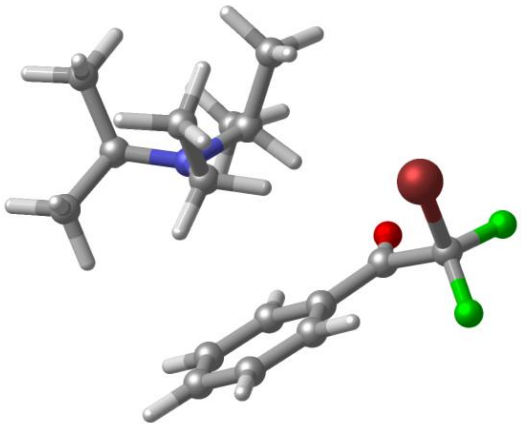
**TS1**



Zero-point correction= 0.269987 (Hartree/Particle)
Thermal correction to Energy= 0.289824
Thermal correction to Enthalpy= 0.290768

| | | | |
|---|---|---|---|
| Thermal correction to Gibbs Free Energy= | | | 0.219732 |
| Sum of electronic and thermal Free Energies= | | | -1068.268745 |
| C | -0.77730700 | -1.40186500 | -3.87614200 |
| C | -0.16091000 | -1.01533200 | -2.68773100 |
| C | -0.88492700 | -1.02925200 | -1.48381900 |
| C | -2.22644800 | -1.44694300 | -1.49569100 |
| C | -2.83570300 | -1.83223900 | -2.68200800 |
| C | -2.11230300 | -1.80653300 | -3.87832800 |
| H | -0.21337100 | -1.38059100 | -4.80295400 |
| H | 0.86999200 | -0.69249300 | -2.70952700 |
| H | -2.77721000 | -1.43527200 | -0.56316900 |
| H | -3.87590300 | -2.14091100 | -2.68101500 |
| H | -2.58975300 | -2.09850700 | -4.80838300 |
| C | -0.35070300 | -0.55565400 | -0.18336900 |
| C | 0.97198000 | 0.08558400 | -0.11904600 |
| F | 1.98900000 | -0.34346300 | -0.87939300 |
| O | -1.03466900 | -0.53031900 | 0.84737600 |
| F | 1.42318000 | 0.35521200 | 1.11246900 |
| C | -3.82214200 | 1.68601200 | -3.20663000 |
| C | -2.44348300 | 1.85644400 | -3.16826600 |
| C | -1.76552100 | 2.01978000 | -1.94235100 |
| C | -2.52608500 | 2.02063800 | -0.75322600 |
| C | -3.90410600 | 1.85131000 | -0.79510700 |
| C | -4.55903200 | 1.68097400 | -2.01953300 |
| H | -4.32345800 | 1.54996800 | -4.15956700 |
| H | -1.86847700 | 1.84197100 | -4.08910300 |
| H | -2.03334200 | 2.13344800 | 0.20542100 |
| H | -4.47318800 | 1.84745500 | 0.12919700 |
| H | -5.63534500 | 1.54385200 | -2.04647200 |
| C | -0.32159800 | 2.13870400 | -1.95356000 |
| C | 0.52351400 | 2.19321100 | -0.86362400 |
| H | 0.11799400 | 2.09900200 | -2.94975100 |
| H | 0.06171500 | 2.34056900 | 0.11168500 |
| B | 2.04911000 | 2.55660800 | -1.00391000 |
| O | 2.64989000 | 2.84852600 | -2.19821300 |
| H | 2.03524500 | 2.88051200 | -2.93969800 |
| O | 2.88379900 | 2.59797300 | 0.07904000 |
| H | 2.45106300 | 2.30051800 | 0.88799800 |

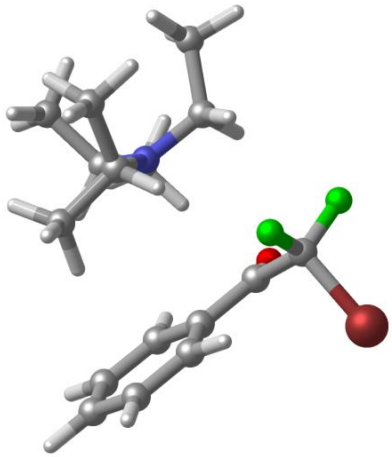
**complex-1**



| | | | |
|---|---|---|---|
| Zero-point correction= | | | 0.376748 (Hartree/Particle) |
| Thermal correction to Energy= | | | 0.401006 |
| Thermal correction to Enthalpy= | | | 0.401950 |
| Thermal correction to Gibbs Free Energy= | | | 0.321194 |
| Sum of electronic and thermal Free Energies= | | | -3525.310502 |
| C | 2.04678500 | 1.84152600 | -0.64597200 |
| C | 1.75413100 | 0.55998300 | -1.10223500 |
| C | 1.48856600 | -0.46710400 | -0.18056900 |
| C | 1.52405000 | -0.18829800 | 1.19689500 |
| C | 1.82031400 | 1.09192000 | 1.64642800 |
| C | 2.08066400 | 2.11019500 | 0.72398100 |
| H | 2.24390500 | 2.63280400 | -1.36101000 |
| H | 1.71587700 | 0.37281100 | -2.16645900 |
| H | 1.31758800 | -0.99072500 | 1.89500800 |
| H | 1.84712700 | 1.30016600 | 2.71060900 |
| H | 2.30934300 | 3.11192900 | 1.07324800 |
| C | 1.14466700 | -1.84901200 | -0.57101900 |
| C | 1.21243000 | -2.26126900 | -2.06761700 |
| F | 2.35432600 | -1.85215900 | -2.65512300 |
| O | 0.80755400 | -2.71713000 | 0.21337400 |
| N | -1.92049100 | 1.11547800 | 0.13940400 |
| C | -2.12712100 | -0.33428300 | 0.07442100 |
| C | -3.34643500 | -0.81408400 | -0.73926800 |
| C | -2.10380800 | -0.99278200 | 1.45548400 |
| H | -1.25511500 | -0.72371000 | -0.46141000 |
| H | -4.29037300 | -0.46196100 | -0.31374200 |
| H | -3.28728900 | -0.46766400 | -1.77428900 |
| H | -3.37071900 | -1.90956800 | -0.76369500 |
| H | -3.00489800 | -0.77577000 | 2.03811200 |
| H | -2.04128000 | -2.07776600 | 1.33391300 |
| H | -1.23222100 | -0.66556300 | 2.02868600 |
| C | -2.50699100 | 1.88964900 | 1.23291400 |

| | | | |
|---|---|---|---|
| C | -4.04385300 | 2.03903200 | 1.21629300 |
| C | -1.82947800 | 3.26003000 | 1.36041700 |
| H | -2.26334900 | 1.34967500 | 2.15455000 |
| H | -4.53415300 | 1.06234100 | 1.22100600 |
| H | -4.37907000 | 2.58281300 | 2.10736100 |
| H | -4.39105900 | 2.58653700 | 0.33667200 |
| H | -2.15980300 | 3.74964200 | 2.28135400 |
| H | -0.74194800 | 3.14956700 | 1.39818100 |
| H | -2.07875600 | 3.92525700 | 0.52808500 |
| C | -1.64823000 | 1.76931100 | -1.13367000 |
| C | -2.82254400 | 2.38835700 | -1.91487400 |
| H | -1.16562100 | 1.02217500 | -1.77014600 |
| H | -0.89488600 | 2.55236000 | -0.98198700 |
| H | -2.47230800 | 2.72603200 | -2.89749400 |
| H | -3.63409600 | 1.67338200 | -2.07083000 |
| H | -3.23771600 | 3.25902400 | -1.40017100 |
| Br | -0.32191700 | -1.46228200 | -3.04118600 |
| F | 1.13190400 | -3.58906600 | -2.18972800 |

**complex-2**

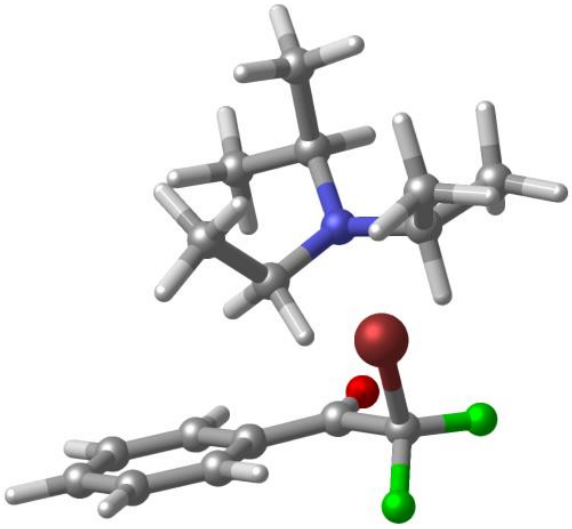


Zero-point correction= 0.377617 (Hartree/Particle)
Thermal correction to Energy= 0.401428
Thermal correction to Enthalpy= 0.402372
Thermal correction to Gibbs Free Energy= 0.324107
Sum of electronic and thermal Free Energies= -3525.308495

| | | | |
|---|---|---|---|
| C | 3.92573000 | 0.61989600 | -1.39854800 |
| C | 3.05184900 | -0.30126300 | -0.82739100 |
| C | 2.93298800 | -0.37999200 | 0.57047500 |
| C | 3.70559900 | 0.47081000 | 1.37994100 |
| C | 4.56724200 | 1.39558000 | 0.80365500 |
| C | 4.67921600 | 1.47123500 | -0.58850000 |

| | | | |
|---|---|---|---|
| H | 4.01538200 | 0.67498000 | -2.47809100 |
| H | 2.47875600 | -0.95424200 | -1.47080700 |
| H | 3.61032900 | 0.39514100 | 2.45616800 |
| H | 5.15251400 | 2.05630200 | 1.43429700 |
| H | 5.35366500 | 2.19177300 | -1.03970400 |
| C | 2.04748600 | -1.33786800 | 1.26137000 |
| C | 1.06696800 | -2.21194200 | 0.43421900 |
| F | 0.42313200 | -1.53294400 | -0.53717200 |
| O | 2.05681900 | -1.54097200 | 2.46219600 |
| N | -0.01460300 | 1.17696800 | 1.55324300 |
| C | -0.19291100 | 1.66833100 | 0.17463500 |
| C | 0.94528900 | 2.59231700 | -0.26986100 |
| C | -1.55545600 | 2.31833500 | -0.14518700 |
| H | -0.12777800 | 0.77342200 | -0.45696600 |
| H | 0.88832200 | 3.57705900 | 0.20368100 |
| H | 1.92179600 | 2.15989300 | -0.05363900 |
| H | 0.87610800 | 2.74566600 | -1.35079300 |
| H | -1.73689700 | 3.21014800 | 0.46061400 |
| H | -1.58275500 | 2.61485500 | -1.19982200 |
| H | -2.38052500 | 1.62109100 | 0.01865500 |
| C | 0.57231500 | 2.07690700 | 2.55534400 |
| C | 0.93728900 | 1.32223400 | 3.83978000 |
| C | -0.24072100 | 3.34379500 | 2.89830300 |
| H | 1.52147100 | 2.42023500 | 2.12861200 |
| H | 1.50635800 | 0.41795400 | 3.61907900 |
| H | 1.54686800 | 1.97039500 | 4.47667100 |
| H | 0.05256800 | 1.03780200 | 4.41744400 |
| H | 0.31639200 | 3.95673600 | 3.61631700 |
| H | -0.42421900 | 3.95846100 | 2.01449400 |
| H | -1.20708000 | 3.09795400 | 3.34500600 |
| C | -0.99690900 | 0.18870200 | 1.99160500 |
| C | -2.27773500 | 0.66455000 | 2.70214000 |
| H | -0.49878100 | -0.53245700 | 2.65010300 |
| H | -1.28412300 | -0.37737900 | 1.09974200 |
| H | -2.94661400 | -0.19070500 | 2.85321600 |
| H | -2.06111500 | 1.08583200 | 3.68692300 |
| H | -2.81752800 | 1.41953000 | 2.12690800 |
| F | 0.14751800 | -2.76539900 | 1.23020000 |
| Br | 2.10556800 | -3.67432400 | -0.41848300 |

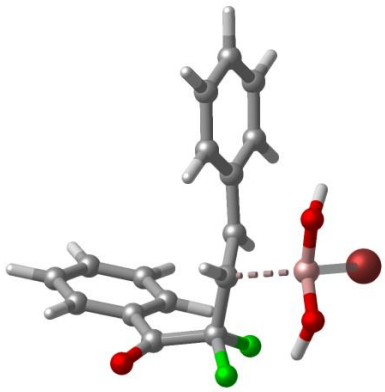
**complex-3**



| | | | |
|---|---|---|---|
| Zero-point correction= | | | 0.377686 (Hartree/Particle) |
| Thermal correction to Energy= | | | 0.401543 |
| Thermal correction to Enthalpy= | | | 0.402487 |
| Thermal correction to Gibbs Free Energy= | | | 0.321895 |
| Sum of electronic and thermal Free Energies= | | | -3525.315572 |
| C | 2.07081400 | 0.60391200 | -1.85918800 |
| C | 2.00898500 | -0.67868400 | -1.32156400 |
| C | 2.04756500 | -0.85694400 | 0.07261400 |
| C | 2.15027600 | 0.26729800 | 0.90958200 |
| C | 2.21523900 | 1.54508100 | 0.36716200 |
| C | 2.17463500 | 1.71517600 | -1.01988300 |
| H | 2.03672100 | 0.73595800 | -2.93540800 |
| H | 1.91930100 | -1.52728500 | -1.98520800 |
| H | 2.17668300 | 0.11457200 | 1.98234900 |
| H | 2.29594000 | 2.40777500 | 1.02007100 |
| H | 2.22273600 | 2.71245000 | -1.44541200 |
| C | 1.97277800 | -2.18127900 | 0.73396700 |
| C | 1.92514100 | -3.45464500 | -0.13404100 |
| F | 2.90166400 | -3.45612900 | -1.07732300 |
| O | 1.92624900 | -2.32704400 | 1.94380800 |
| N | -2.16654400 | -3.51532000 | -2.49164400 |
| C | -2.19378200 | -4.94353800 | -2.87755100 |
| C | -3.08217200 | -5.30776200 | -4.08150400 |
| C | -2.49869100 | -5.85270600 | -1.68324800 |
| H | -1.16017800 | -5.16502500 | -3.17885300 |
| H | -4.13675800 | -5.08808200 | -3.89908600 |
| H | -2.77214600 | -4.77505600 | -4.98314900 |
| H | -2.99183300 | -6.37967400 | -4.28796100 |
| H | -3.54132300 | -5.78170200 | -1.36029700 |
| H | -2.31340900 | -6.89171600 | -1.96940100 |

| | | | |
|---|---|---|---|
| H | -1.85171400 | -5.61192200 | -0.83613600 |
| C | -3.16584200 | -3.01260900 | -1.52856200 |
| C | -4.63608400 | -3.06630100 | -1.98604500 |
| C | -2.80249500 | -1.60526200 | -1.03826700 |
| H | -3.08587600 | -3.66594700 | -0.65350100 |
| H | -4.95221400 | -4.08797700 | -2.20626600 |
| H | -5.28097400 | -2.68806500 | -1.18525300 |
| H | -4.81148700 | -2.45740900 | -2.87550100 |
| H | -1.76912400 | -1.57514600 | -0.68762200 |
| H | -2.93017400 | -0.84630500 | -1.81506200 |
| H | -3.45719400 | -1.33611600 | -0.20472700 |
| C | -1.67613800 | -2.60461500 | -3.53042600 |
| C | -2.68302800 | -1.96483700 | -4.49919500 |
| H | -0.93821600 | -3.17220800 | -4.10748700 |
| H | -1.11287400 | -1.79901800 | -3.04531600 |
| H | -2.13513100 | -1.41565400 | -5.27292700 |
| H | -3.31628400 | -2.70416500 | -4.99317200 |
| H | -3.33476000 | -1.24941500 | -3.99201400 |
| Br | 0.14977300 | -3.54692600 | -1.03743200 |
| F | 2.09214300 | -4.54823600 | 0.63008000 |

**TS2**

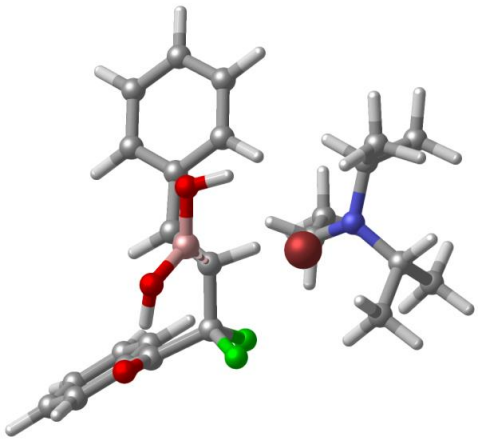


Zero-point correction= 0.271776 (Hartree/Particle)
Thermal correction to Energy= 0.293627
Thermal correction to Enthalpy= 0.294571
Thermal correction to Gibbs Free Energy= 0.217335
Sum of electronic and thermal Free Energies= -3640.030903

| | | | |
|---|---|---|---|
| C | -0.91450200 | -1.78092000 | -4.05921600 |
| C | -0.07506100 | -1.35004500 | -3.03446500 |
| C | -0.49769100 | -1.44285300 | -1.69636900 |
| C | -1.76138600 | -1.98664300 | -1.40660800 |
| C | -2.60072500 | -2.39828400 | -2.43520100 |
| C | -2.17912400 | -2.29315200 | -3.76388000 |
| H | -0.57996400 | -1.71472000 | -5.08887400 |

| | | | |
|---|---|---|---|
| H | 0.90612100 | -0.96254400 | -3.27250000 |
| H | -2.07375300 | -2.05985000 | -0.37113800 |
| H | -3.58249800 | -2.79824900 | -2.20498900 |
| H | -2.83465300 | -2.61341400 | -4.56716100 |
| C | 0.30933900 | -0.98580100 | -0.53411800 |
| C | 1.17464700 | 0.29886900 | -0.67047600 |
| F | 1.98219200 | 0.24957100 | -1.77992000 |
| O | 0.19707300 | -1.47036500 | 0.57734200 |
| F | 2.01466100 | 0.34788300 | 0.41238000 |
| C | -3.62290300 | 2.73230400 | -3.54895000 |
| C | -2.36431200 | 2.19174700 | -3.34836200 |
| C | -1.76181900 | 2.23632800 | -2.06531800 |
| C | -2.45876700 | 2.84403600 | -0.99038400 |
| C | -3.71159900 | 3.39484400 | -1.20491500 |
| C | -4.29365500 | 3.33670000 | -2.47818100 |
| H | -4.08546400 | 2.69221400 | -4.52841200 |
| H | -1.82582400 | 1.72571000 | -4.16674000 |
| H | -2.00632600 | 2.89167700 | -0.00820100 |
| H | -4.24515300 | 3.86436400 | -0.38643500 |
| H | -5.27861700 | 3.76382400 | -2.63567000 |
| C | -0.48823100 | 1.63089000 | -1.91124800 |
| C | 0.28130800 | 1.53467400 | -0.70291600 |
| H | -0.06684600 | 1.18632000 | -2.80238100 |
| H | -0.31990100 | 1.55759600 | 0.20848600 |
| B | 1.12651800 | 3.06962800 | -0.58067300 |
| O | 0.28917800 | 4.13486200 | -0.27632100 |
| H | -0.19247000 | 4.44923600 | -1.05000700 |
| O | 2.31601500 | 3.02828100 | 0.10145500 |
| H | 2.72569200 | 2.15664900 | 0.13421500 |
| Br | 1.52193600 | 3.43175200 | -2.91511300 |

**TS3**



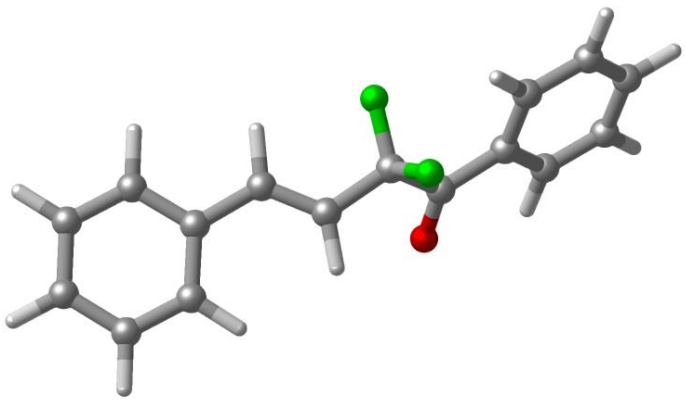
Zero-point correction= 0.537010 (Hartree/Particle)

Thermal correction to Energy= 0.571004
Thermal correction to Enthalpy= 0.571948
Thermal correction to Gibbs Free Energy= 0.469377
Sum of electronic and thermal Free Energies= -4010.895555

| | | | |
|---|---|---|---|
| C | -0.08497100 | -3.24335900 | -2.30751000 |
| C | -0.02002600 | -2.35687700 | -1.23677300 |
| C | -1.13342200 | -2.19789500 | -0.38776600 |
| C | -2.30090000 | -2.94866900 | -0.63403100 |
| C | -2.35107000 | -3.84256700 | -1.69388400 |
| C | -1.24266300 | -3.98948300 | -2.53479200 |
| H | 0.77229700 | -3.35441300 | -2.96234600 |
| H | 0.88787600 | -1.79528200 | -1.07275800 |
| H | -3.15417600 | -2.81320800 | 0.01974000 |
| H | -3.25068400 | -4.42165400 | -1.87188400 |
| H | -1.28356500 | -4.68403600 | -3.36756000 |
| C | -1.19033100 | -1.23856300 | 0.72778900 |
| C | 0.05016900 | -0.43211400 | 1.21123800 |
| F | 1.19992200 | -1.14962200 | 0.96820700 |
| O | -2.23619200 | -0.99319400 | 1.32578600 |
| F | -0.04771900 | -0.34631600 | 2.56916300 |
| C | 0.38397500 | 3.12000800 | -3.84016800 |
| C | -0.03906700 | 2.12752100 | -2.97326300 |
| C | 0.41469900 | 2.11183500 | -1.62674100 |
| C | 1.30738800 | 3.12377700 | -1.18150800 |
| C | 1.71911400 | 4.11327600 | -2.05356500 |
| C | 1.25969600 | 4.11160900 | -3.37953600 |
| H | 0.04004100 | 3.13238700 | -4.86775600 |
| H | -0.72056500 | 1.35385200 | -3.31110500 |
| H | 1.67412900 | 3.10971500 | -0.16493700 |
| H | 2.40114700 | 4.88545300 | -1.71671400 |
| H | 1.59215200 | 4.88884900 | -4.05973900 |
| C | -0.04842800 | 1.08697200 | -0.77558600 |
| C | 0.19608000 | 0.96803000 | 0.62168200 |
| H | -0.72999100 | 0.37608200 | -1.23919200 |
| H | 1.13819300 | 1.39925900 | 0.97170100 |
| B | -0.94721100 | 2.13195500 | 1.32121800 |
| O | -2.08081700 | 1.65273100 | 1.85288200 |
| H | -2.17052800 | 0.67969200 | 1.91372500 |
| O | -0.83039900 | 3.42638400 | 0.90471400 |
| H | -0.09492200 | 3.83722000 | 1.39215200 |
| N | 4.05499700 | 1.24915400 | 0.61602600 |
| C | 4.50294600 | 2.57393000 | 0.16161900 |
| C | 6.01460000 | 2.71853100 | -0.10546900 |
| C | 4.05196500 | 3.67813200 | 1.13188200 |

| | | | |
|---|---|---|---|
| H | 3.98654200 | 2.73704400 | -0.79107100 |
| H | 6.58765900 | 2.60116700 | 0.81983700 |
| H | 6.37842700 | 1.98506600 | -0.82684900 |
| H | 6.22963400 | 3.71830100 | -0.49832400 |
| H | 4.68098500 | 3.69615800 | 2.02881500 |
| H | 4.14119200 | 4.66123900 | 0.65733400 |
| H | 3.02391900 | 3.52909900 | 1.47081200 |
| C | 4.69900100 | 0.70997400 | 1.82659400 |
| C | 5.87190400 | -0.25565800 | 1.57321100 |
| C | 3.66711200 | 0.06205800 | 2.75979600 |
| H | 5.10387200 | 1.57822600 | 2.35617700 |
| H | 6.63900800 | 0.19230300 | 0.93781800 |
| H | 6.33779000 | -0.53380900 | 2.52451000 |
| H | 5.52749400 | -1.17894500 | 1.09597700 |
| H | 2.87599600 | 0.77224400 | 3.01160700 |
| H | 3.20375800 | -0.81266500 | 2.29572400 |
| H | 4.15128000 | -0.27137000 | 3.68473200 |
| C | 3.68366100 | 0.29829400 | -0.42744700 |
| C | 4.68946500 | 0.00226400 | -1.55324100 |
| H | 2.76142600 | 0.65408500 | -0.90604200 |
| H | 3.41451000 | -0.63819000 | 0.06508900 |
| H | 4.26185800 | -0.74746000 | -2.22870600 |
| H | 4.89952700 | 0.89527600 | -2.14875800 |
| H | 5.63723700 | -0.38517800 | -1.17307300 |
| Br | 0.90617500 | 2.78987900 | 3.32599100 |

**3ab**



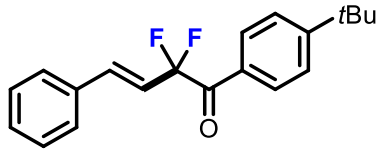
Zero-point correction= 0.237348 (Hartree/Particle)
Thermal correction to Energy= 0.253421
Thermal correction to Enthalpy= 0.254365
Thermal correction to Gibbs Free Energy= 0.190714

Sum of electronic and thermal Free Energies= -891.714113

| | | | |
|---|---|---|---|
| C | 4.14867500 | -3.31081600 | 0.20831200 |
| C | 3.33097000 | -2.19520400 | 0.04596800 |
| C | 2.18921300 | -2.04000300 | 0.85103500 |
| C | 1.88596200 | -3.01724400 | 1.81501800 |
| C | 2.70406500 | -4.12933600 | 1.97137100 |
| C | 3.83818100 | -4.27755900 | 1.16673100 |
| H | 5.02998900 | -3.42567800 | -0.41393000 |
| H | 3.58358100 | -1.45146100 | -0.69684600 |
| H | 1.00253300 | -2.88297300 | 2.42870400 |
| H | 2.46241200 | -4.88040400 | 2.71620500 |
| H | 4.47857000 | -5.14557600 | 1.28750100 |
| C | 1.26705800 | -0.88261100 | 0.74473000 |
| C | 1.51270500 | 0.18462900 | -0.35586200 |
| F | 2.77479200 | 0.71591600 | -0.12738100 |
| O | 0.31228800 | -0.72665900 | 1.49060100 |
| F | 1.57986300 | -0.45755700 | -1.57020200 |
| C | -2.90593600 | 3.73980600 | -2.96133400 |
| C | -1.94420600 | 2.74647900 | -2.78496400 |
| C | -1.25114900 | 2.61829600 | -1.56936300 |
| C | -1.55153300 | 3.51748000 | -0.52977900 |
| C | -2.51127100 | 4.50884100 | -0.70570700 |
| C | -3.19273800 | 4.62492300 | -1.92171600 |
| H | -3.42979300 | 3.82183100 | -3.90842700 |
| H | -1.72209500 | 2.05825800 | -3.59557900 |
| H | -1.03385000 | 3.44228700 | 0.42071500 |
| H | -2.73069000 | 5.19424300 | 0.10693100 |
| H | -3.94103400 | 5.39978900 | -2.05471800 |
| C | -0.24941100 | 1.55455600 | -1.44435900 |
| C | 0.50982400 | 1.28713800 | -0.37521100 |
| H | -0.12705700 | 0.92732000 | -2.32353000 |
| H | 0.44505800 | 1.84716000 | 0.55063300 |

**Characterization data of compounds**

**(*E*)-1-(4-(tert-butyl)phenyl)-2,2-difluoro-4-phenylbut-3-en-1-one (3aa)**




54 mg, 86% yield, colorless oil, *E*/*Z* = 5.3/1, $R_f$ = 0.3 (hexane = 5%);

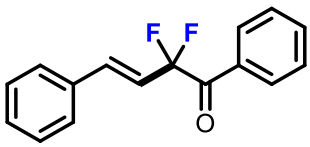
**$^1$H NMR** (400 MHz, $CDCl_3$):$\delta$ 8.07 (d, *J* = 8.2 Hz, 2H), 7.85 (d, *J* = 8.2 Hz, 0.38H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.43 (t, *J* = 9.3 Hz, 3H), 7.35 (d, *J* = 6.7 Hz, 2.57H), 7.25 (s, 0.37H), 7.09 (d, ***J* = 16.4 Hz**, 1H), 6.94 (d, *J* = 12.8 Hz, 0.22H), 6.48 (dt, ***J* = 16.4**, 11.2 Hz, 1H), 6.05 (dd, *J* = 26.8, 14.0 Hz, 0.19H), 1.34-1.32 (m, 10.7 H) ppm;

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 188.5 (t, *J* = 30.6 Hz), 158.4, 158.1, 138.8 (t, *J* = 8 Hz), 136.9 (t, *J* = 9.5 Hz), 134.4, 130.2, 130.2, 130.0, 129.6, 129.5, 129.2, 128.8, 128.6, 128.0, 127.4, 126.0, 125.8, 125.4, 122.4 (t, *J* = 26.2 Hz), 120.0 (t, *J* = 24.5 Hz), 116.3 (t, *J* = 248.9 Hz), 35.3, 31.0 ppm;

**$^{19}$F NMR** (376 MHz, $CDCl_3$): δ -90.9 (d, *J* = 16.3 Hz), -97.3 (d, *J* = 15.0 Hz) ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{20}H_{21}F_2O^+$) requires *m/z* 315.1555, found *m/z* 315.1553.

**(*E*)-2,2-difluoro-1,4-diphenylbut-3-en-1-one (3ab)**




42 mg, 81% yield, colorless oil, *E/Z* = 4.3/1, $R_f$ = 0.3 (hexane);

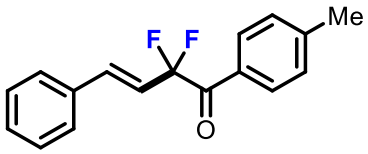
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.12 (d, *J* = 7.9 Hz, 2H), 7.87 (d, *J* = 7.9 Hz, 0.47H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.51 (dd, *J* = 14.9, 7.3 Hz, 2H), 7.47–7.42 (m, 1.78H), 7.37 (dd, *J* = 12.8, 4.0 Hz, 3H), 7.25 (t, *J* = 5.0 Hz, 1.36H), 7.10 (dd, ***J* = 16.3**, 2.3 Hz, 1H), 6.95 (d, *J* = 12.6 Hz, 0.22H), 6.48 (dt, ***J* = 16.3**, 11.3 Hz, 1H), 6.08 (dd, *J* = 26.7, 13.4 Hz, 0.23H) ppm;

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 189.0 (t, *J* = 31.4 Hz), , 139.0 (t, *J* = 8.1 Hz), 137.1 (t, *J* = 9.5 Hz), 134.3, 134.0, 132.2, 130.2, 130.2, 130.2, 129.9, 129.6, 129.1, 128.8, 128.7, 128.7 128.4, 128.1, 127.4, 122.4 (t, *J* = 26.6 Hz), 119.8 (t, *J* = 23.9 Hz), 116.3 (t, *J* = 249 Hz) ppm;

**$^{19}$F NMR** (376 MHz, $CDCl_3$): $\delta$ -90.4 (d, *J* = 13.6 Hz), -97.3 (d, *J* = 11.6 Hz) ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{16}H_{13}F_2O^+$) requires *m/z* 259.0929, found *m/z* 259.0933.

**(*E*)-2,2-difluoro-4-phenyl-1-(p-tolyl)but-3-en-1-one (3ac)**




46 mg, 84% yield, yellow solid, *E/Z* = 2.7/1, $R_f$ = 0.3 (hexane);

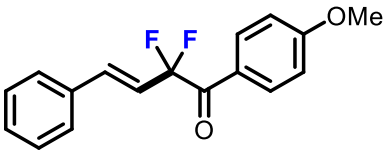
**$^1$H NMR** (400 MHz, $CDCl_3$): *δ* 8.02 (d, *J* = 7.9 Hz, 2H), 7.80 (d, *J* = 7.9 Hz, 0.74H), 7.48–7.41 (m, 2H), 7.35 (d, *J* = 6.2 Hz, 3H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 0.74H), 7.08 (d, ***J* = 16.3 Hz**, 1H), 6.93 (d, *J* = 12.7 Hz, 0.35H), 6.48 (dt, ***J* = 16.3**, 11.3 Hz, 1H), 6.06 (dd, *J* = 27.0, 13.8 Hz, 0.37H), 2.43 (s, 3H), 2.39 (s, 1.15H) ppm;

**$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 188.5 (t, *J* = 30.5 Hz), 187.6 (t, *J* = 29.8 Hz), 145.6, 145.2, 138.9 (t, *J* = 8.0 Hz), 136.9 (t, J = 9.5 Hz), 134.3, 130.4 (t, J = 2.9 Hz), 130.1 (t, J = 2.5 Hz), 129.6, 129.5, 129.2, 129.2, 128.8, 128.7, 128.1, 127.4, 122.5 (t, J = 26.2 Hz), 120.0 (t, J = 24.7 Hz), 116.4 (t, J = 249.0 Hz), 21.8, 21.8 ppm;

**$^{19}$F NMR** (376 MHz, $CDCl_3$): *δ* -90.6 (d, *J* = 16.4 Hz), -95.4--100.4 (m) ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{17}H_{15}F_2O^+$) requires *m/z* 273.1085, found *m/z* 273.1085.

**(*E*)-2,2-difluoro-1-(4-methoxyphenyl)-4-phenylbut-3-en-1-one (3ad)**




51 mg, 89% yield, white solid, 6.2/1, $R_f$ = 0.2 (ethyl acetate /hexane = 5%);

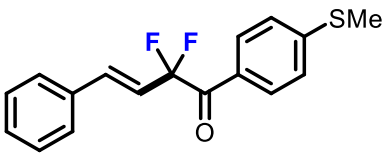
**$^1$H NMR** (400 MHz, $CDCl_3$): *δ* 8.12 (d, *J* = 8.8 Hz, 2H), 7.90 (d, *J* = 8.8 Hz, 0.3H), 7.48–7.39 (m, 2H), 7.39–7.31 (m, 3H), 7.08 (dt, ***J* = 16.3**, 2.4 Hz, 1H), 6.96 (d, *J* = 8.9 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 0.28H), 6.48 (dt, ***J* = 16.3**, 11.2 Hz, 1H), 6.05 (dd, *J* = 27.0, 13.9 Hz, 0.16H), 3.88 (s, 3H), 3.86 (s, 0.52H) ppm;

**$^{13}$C NMR** (100 MHz, $CDCl_3$): *δ* 187.3 (t, J = 30.6 Hz), 164.5, 164.3, 138.7 (t, J = 8.1 Hz), 136.7 (t, J = 9.5 Hz), 134.4, 132.8 (t, J = 3.3 Hz), 132.5 (t, J = 2.6 Hz), 129.56, 129.2 (t, J = 2.9 Hz), 128.8, 128.6, 128.0, 127.4, 125.0, 122.5 (t, J = 26.6 Hz), 120.1 (t, J = 24.8 Hz), 116.4 (t, J = 248.6 Hz), 114.1, 113.7, 55.6, 55.5 ppm;

**$^{19}$F NMR** (376 MHz, $CDCl_3$): *δ* -90.5 (d, *J* = 16.3 Hz), -96.9 (dd, J = 11.6, 2.7 Hz) ppm;

**HRMS (ESI)**: exact mass calculated for $[M+H]^+$ ($C_{17}H_{15}F_2O_2^+$) requires *m/z* 289.1035, found *m/z* 289.1031.

**(*E*)-2,2-difluoro-1-(4-(methylthio)phenyl)-4-phenylbut-3-en-1-one (3ae)**




50 mg, 82% yield, colorless oil, *E/Z* = 5/1, $R_f$ = 0.3 (ethyl acetate /hexane = 5%);

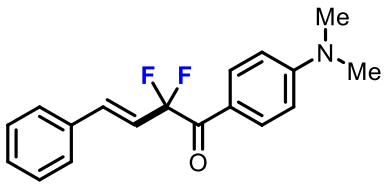
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.02 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.2 Hz, 0.45H), 7.47–7.41 (m, 2H), 7.35 (td, *J* = 4.7, 2.5 Hz, 3H), 7.29 (s, 1H), 7.25 (s, 0.17H), 7.18 (d, *J* = 8.6 Hz, 0.43H), 7.08 (dd, ***J* = 16.3**, 2.5 Hz, 1H), 6.94 (d, *J* = 12.7 Hz, 0.19H), 6.47 (dt, ***J* = 16.3**, 11.3 Hz, 1H), 6.13–5.98 (m, 0.19H), 2.51 (s, 3H), 2.49 (s, 0.6H) ppm;

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 187.8 (t, *J* = 30.9 Hz), 186.9 (t, *J* = 30.3 Hz), 148.2, 147.7, 138.9 (t, J = 8.0 Hz), 136.9 (t, J = 9.9 Hz), 134.3, 130.6, 130.6, 130.5, 130.3, 129.9, 129.6, 129.2, 128.8, 128.7, 128.1, 128.1, 127.5, 125.0, 124.8, 124.6, 122.4 (t, J = 26.6 Hz), 119.9 (t, J = 24.4 Hz), 116.4 (t, J = 248.7 Hz), 115.4 (t, J = 247.4 Hz), 14.6 ppm;

**$^{19}$F NMR** (376 MHz, $CDCl_3$): $\delta$ -90.5 (d, J = 16.3 Hz), -97.1 (dd, J = 11.9, 3.1 Hz) ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{17}H_{15}F_2OS^+$) requires *m/z* 305.0806, found *m/z* 305.0810.

***(E)*-1-(4-(dimethylamino)phenyl)-2,2-difluoro-4-phenylbut-3-en-1-one (3af)**




44 mg, 74% yield, colorless oil, *E/Z* > 20/1, $R_f$ = 0.3 (ethyl acetate /hexane = 10%);

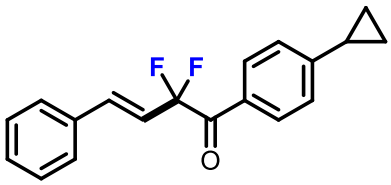
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 7.96 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 6.8 Hz, 2H), 7.31–7.23 (m, 3H), 6.99 (d, *J* = 16.3 Hz, 1H), 6.58 (d, *J* = 8.7 Hz, 2H), 6.42 (dt, ***J* = 16.3**, 11.1 Hz, 1H), 3.01 (d, *J* = 0.7 Hz, 6H) ppm;

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 186.4 (t, *J* = 29.7 Hz), 154.0, 136.1, 134.6, 132.7 (t, *J* = 3.1 Hz), 129.3, 128.7, 127.4, 120.94 (t, *J* = 25.1 Hz), 119.6, 116.7 (t, *J* = 249.8 Hz), 110.7, 40.0 ppm;

**$^{19}$F NMR** (376 MHz, $CDCl_3$): $\delta$ -96.54 (dd, $J$ = 11.6Hz) ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{18}H_{18}F_2NO^+$) requires *m/z* 302.1351, found *m/z* 302.1353.

**(*E*)-1-(4-cyclopropylphenyl)-2,2-difluoro-4-phenylbut-3-en-1-one (3ag)**




46 mg, 78% yield, white solid, *E/Z* = 6.2/1, $R_f$ = 0.3 (hexane);

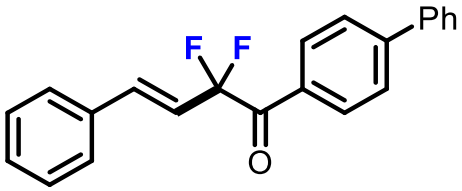
**$^{1}$H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.01 (d, $J$ = 8.2 Hz, 2H), 7.79 (d, $J$ = 8.2 Hz, 0.31H), 7.51–7.40 (m, 2H), 7.38–7.30 (m, 3H), 7.13 (d, $J$ = 8.2 Hz, 2H), 7.07 (d, ***J* = 16.4 Hz**, 1H), 6.92 (d, $J$ = 12.7 Hz, 0.17H), 6.47 (dt, ***J* = 16.4**, 11.3 Hz, 1H), 6.04 (dd, $J$ = 27.0, 13.8 Hz, 0.16H), 1.94 (ddd, $J$ = 13.1, 8.5, 5.0 Hz, 1H), 1.12–1.03 (m, 2.27H), 0.84–0.74 (m, 2.28H) ppm;

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 188.3 (t, $J$ = 30.6 Hz), 152.2, 151.9, 138.8 (t, $J$ = 8.0 Hz), 136.9 (t, $J$ = 9.5 Hz), 134.3, 130.5 (t, $J$ =2.9 Hz), 130.2 (t, $J$ = 2.5 Hz), 129.6, 129.3, 129.2 (t, $J$ = 3.1 Hz), 128.8, 128.7, 128.1, 127.4, 125.6, 125.3, 122.4 (t, $J$ = 26.6 Hz), 120.0 (t, $J$ = 24.8 Hz), 116.4 (t, $J$ = 248.9 Hz), 16.0, 15.9, 10.8, 10.7 ppm;

**$^{19}$F NMR** (376 MHz, $CDCl_3$): $\delta$ -90.7 (d, J = 13.6 Hz), -97.2 (d, J = 11.6 Hz) ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{19}H_{17}F_2O^+$) requires *m/z* 299.1242, found *m/z* 299.1245.

**(*E*)-1-([1,1'-biphenyl]-4-yl)-2,2-difluoro-4-phenylbut-3-en-1-one (3ah)**




58 mg, 87% yield, white solid, *E/Z* = 2.4/1, $R_f$ = 0.2 (hexane);

**$^{1}$H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.10 (dd, $J$ = 18.5, 8.5 Hz, 2H), 7.88 (d, $J$ = 8.4 Hz, 1H), 7.70–7.61 (m, 2H), 7.60–7.51 (m, 4H), 7.44–7.33 (m, 6H), 7.31–7.26 (m, 2H), 7.20 (d, $J$ = 2.3 Hz,

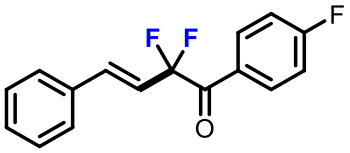
1H), 7.05 (dt, *J* = 16.3, 2.6 Hz, 1H), 6.90 (dt, *J* = 12.6, 1.9 Hz, 0.41H), 6.44 (dt, *J* = 16.3, 11.4 Hz, 1H), 6.04 (dt, *J* = 26.7, 13.3 Hz, 0.42H) ppm;

**$^{13}$C NMR** (100 MHz, $CDCl_3$): *δ* 188.5 (t, *J* = 31.2 Hz), 147.1, 139.5, 137.1 (t, *J* = 9.5 Hz), 134.3, 130.9 (t, *J* = 3.1 Hz), 130.8, 130.6, 130.3, 129.7, 129.2–129.0 (m), 128.9, 128.7, 128.6, 128.6, 128.1, 127.6, 127.5, 127.4, 127.3, 127.3, 127.0, 119.8 (t, *J* = 24.8 Hz), 116.4 (t, *J* = 250.3 Hz) ppm;

**$^{19}$F NMR** (376 MHz, $CDCl_3$): *δ* -90.48 (d, *J* = 14.3 Hz), -97.25 (dd, *J* = 11.2, 2.4 Hz) ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{22}H_{17}F_2O^+$) requires *m/z* 335.1242, found *m/z* 335.1250.

**(*E*)-2,2-difluoro-1-(4-fluorophenyl)-4-phenylbut-3-en-1-one (3ai)**




46 mg, 83% yield, light yellow oil, *E/Z* = 2.7/1, $R_f$ = 0.3 (hexane);

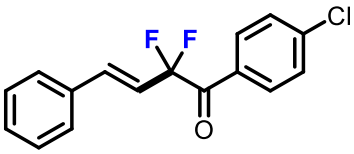
**$^{1}$H NMR** (400 MHz, $CDCl_3$): *δ* 8.17 (dd, *J* = 8.3, 5.5 Hz, 2H), 7.89 (dd, *J* = 8.4, 5.6 Hz, 0.61H), 7.45 (d, *J* = 5.6 Hz, 2H), 7.39–7.33 (m, 3H), 7.28–7.24 (m, 1H), 7.17 (t, *J* = 8.6 Hz, 2H), 7.09 (dd, ***J* = 16.4**, 2.2 Hz, 1H), 7.04 (d, *J* = 8.7 Hz, 0.46H), 6.96 (d, *J* = 12.6 Hz, 0.3H), 6.47 (dt, ***J* = 16.4**, 11.4 Hz, 1H), 6.07 (q, *J* = 13.4 Hz, 0.3H) ppm;

**$^{13}$C NMR** (100 MHz, $CDCl_3$): *δ* 187.4 (t, J = 31.7 Hz), 186.4 (t, J = 30.1 Hz), 167.7, 167.4, 165.2, 164.9, 139.2 (t, J = 8.0 Hz), 137.1 (t, J = 9.4 Hz), 134.2, 133.1 (dt, *J* = 9.5, 3.3 Hz), 132.7 (dt, *J* = 9.5, 2.8 Hz), 129.7, 129.1 (t, *J* = 2.9 Hz), 128.9, 128.8, 128.5, 128.1, 127.5, 122.3 (t, *J* = 27.0 Hz), 119.4 (t, *J* = 24.6 Hz), 116.2 (t, *J* = 248.9 Hz), 116.1 (d, *J* = 22.0 Hz), 115.7 (d, *J* = 22.0 Hz), 115.2 (t, J = 247.1 Hz) ppm;

**$^{19}$F NMR** (376 MHz, $CDCl_3$): *δ* -90.1 (d, *J* = 15.7 Hz), -96.5–-97.4 (m), -102.1 (ddd, *J* = 14.3, 8.5, 5.8 Hz), -102.5 –-102.9 (m) ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{16}H_{12}F_3O^+$) requires *m/z* 277.0835, found *m/z* 277.0841.

**(*E*)-1-(4-chlorophenyl)-2,2-difluoro-4-phenylbut-3-en-1-one (3aj)**




48 mg, 82% yield, yellow oil, *E/Z* = 1.7/1, $R_f$ = 0.2 (hexane);

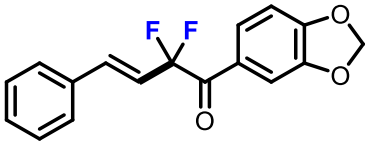
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.06 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.6 Hz, 1.13H), 7.52–7.42 (m, 4H), 7.41–7.32 (m, 4H), 7.29–7.23 (m, 1.77H), 7.21 (d, *J* = 7.0 Hz, 1H), 7.09 (dt, ***J* = 16.4**, 2.5 Hz, 1H), 6.97 (d, *J* = 12.6 Hz, 0.59H), 6.46 (dt, ***J* = 16.4**, 11.4 Hz, 1H), 6.06 (q, *J* = 13.4 Hz, 0.60H) ppm;

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 187.9 (t, *J* = 31.7 Hz), 186.9 (t, *J* = 30.2 Hz), 141.1, 140.7, 139.3 (t, *J* = 8.4 Hz), 137.3 (t, *J* = 9.5 Hz), 134.1, 131.6 (t, *J* = 3.3 Hz), 131.2 (t, *J* = 2.9 Hz), 130.4, 129.8, 129.2 129.1, 129.1, 129.1, 128.9, 128.8, 128.8, 128.1, 127.5, 122.2 (t, *J* = 26.9 Hz), 119.3 (t, *J* = 24.0 Hz), 116.2 (t, *J* = 248.9 Hz), 115.2 (t, *J* = 247.1 Hz) ppm;

**$^{19}$F NMR** (376 MHz, $CDCl_3$): $\delta$ -90.1 (d, *J* = 13.6 Hz), -97.2 (d, *J* = 10.9 Hz) ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{16}H_{12}ClF_2O^+$) requires *m/z* 293.0539, found *m/z* 293.0539.

**(*E*)-1-(benzo[d][1,3]dioxol-5-yl)-2,2-difluoro-4-phenylbut-3-en-1-one (3ak)**




45 mg, 75% yield, light yellow oil, *E/Z* = 14/1, $R_f$ = 0.3 (ethyl acetate /hexane = 5%);

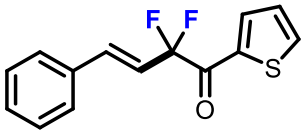
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 7.69 (d, *J* = 8.3 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 0.09H), 7.46 (s, 1H), 7.39 (s, 0.07H), 7.35 (d, *J* = 6.4 Hz, 2H), 7.26 (d, *J* = 6.6 Hz, 3H), 7.18-7.16 (m, 0.5H), 6.98 (d, ***J* = 16.4 Hz**, 1H), 6.79 (d, *J* = 8.3 Hz, 1H), 6.69 (d, *J* = 8.3 Hz, 0.08H), 6.37 (dt, ***J* = 16.4**, 11.2 Hz, 1H), 5.96 (s, 2H) ppm;

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 186.9 (t, *J* = 31.0 Hz), 152.9, 148.2, 136.8 (t, *J* = 9.5 Hz), 134.3, 129.6, 128.8, 128.1, 127.4, 127.4, 127.3, 126.5, 122.5 (t, *J* = 26.8 Hz), 120.0 (t, *J* = 24.8 Hz), 116.4 (t, *J* = 250.3 Hz), 109.7, 108.3, 102.2 ppm;

**$^{19}$F NMR** (376 MHz, $CDCl_3$): $\delta$ -90.0 (d, *J* = 13.6 Hz), -96.3--96.7 (m) ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{17}H_{13}F_2O_3^+$) requires *m/z* 303.0827, found *m/z* 303.0834.

**(*E*)-2,2-difluoro-4-phenyl-1-(thiophen-2-yl)but-3-en-1-one (3al)**




38 mg, 73% yield, yellow oil, *E/Z* = 3.3/1, $R_f$ = 0.2 (hexane);

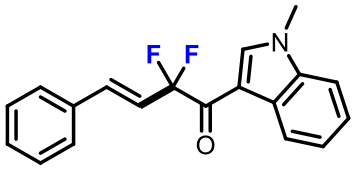
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.01 (d, *J* = 14.5 Hz, 1H), 7.84 (s, 0.27H), 7.76 (dd, *J* = 17.9, 4.8 Hz, 1H), 7.71 (d, *J* = 4.9 Hz, 0.29H), 7.47–7.38 (m, 2H), 7.35 – 7.28 (m, 4H), 7.21 – 7.07 (m, 2.34H), 7.00 (d, *J* = 12.6 Hz, 0.27H), 6.41 (ddd, *J* = 18.5, 13.8, 9.2 Hz, 1H), 6.00 (dt, *J* = 18.1, 9.1 Hz, 0.29H);

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 182.2 (t, *J* = 32.8 Hz), 139.4 (t, *J* = 7.6 Hz), 138.3, 138.2, 137.2 (t, *J* = 9.5 Hz), 136.5, 136.1, 135.9 (t, *J* = 4.7 Hz), 135.6 (t, *J* = 4.0 Hz), 134.3, 134.2, 129.7, 129.1 (t, *J* = 2.9 Hz), 128.9, 128.8, 128.7, 128.5, 128.1, 127.5, 121.7 (t, *J* = 26.2 Hz), 119.3 (t, *J* = 24.8 Hz), 116.0 (t, *J* = 249.3 Hz), 115.2 (t, *J* = 248.2 Hz);

**$^{19}$F NMR** (376 MHz, $CDCl_3$): $\delta$ -91.9 (d, *J* = 14.3 Hz), -98.9 (d, *J* = 11.6 Hz);

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{14}H_{11}F_2OS^+$) requires *m/z* 265.0493, found *m/z* 265.0492.

**(*E*)-2,2-difluoro-1-(1-methyl-1H-indol-3-yl)-4-phenylbut-3-en-1-one (3am)**




39 mg, 63% yield, yellow solid, *E/Z* = 3/1, $R_f$ = 0.3 (ethyl acetate /hexane = 5%);

**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.46 (dd, *J* = 6.2, 3.0 Hz, 0.87H), 8.43–8.37 (m, 0.58H), 8.00 (d, *J* = 5.6 Hz, 1H), 7.76 (s, 0.38H), 7.43 (t, *J* = 6.8 Hz, 2.74H), 7.37 (d, *J* = 2.3 Hz, 2.76H), 7.33 (d, *J* = 8.2 Hz, 2.77H), 7.30 (d, *J* = 7.1 Hz, 0.86H), 7.11 (dd, ***J* = 16.4**, 2.3 Hz, 1H), 6.95 (d, *J* = 12.7 Hz, 0.33H), 6.51 (dt, ***J* = 16.4**, 11.4 Hz, 1H), 6.04 (dd, *J* = 15.2, 2.4 Hz, 0.31H), 3.88 (s, 3H), 3.80 (s, 0.82H) ppm;

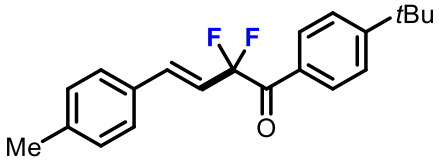
**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 183.8 (t, *J* = 30.9 Hz), 138.2 (t, *J* = 8.7 Hz), 137.9 (t, *J* = 7.0 Hz), 137.1 (t, *J* = 11.4 Hz), 136.1 (t, *J* = 9.4 Hz), 134.6, 129.4, 129.2 (t, *J* = 3.1 Hz), 128.8, 128.3,

128.0, 127.5, 127.4, 124.3, 124.1, 124.0, 123.6, 123.5, 123.4, 122.8, 122.7, 122.6, 122.4, 120.7 (t, *J* = 25.2 Hz), 116.5 (t, *J* = 247.8 Hz), 112.2 (t, *J* = 252.6 Hz), 110.7, 109.8 (t, *J* = 9.1 Hz), 33.9, 33.7, 29.7, 29.4 ppm;

**$^{19}$F NMR** (376 MHz, $CDCl_3$): $\delta$ -92.5 (d, J = 15.7 Hz), -97.7--99.1 (m) ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{19}H_{16}F_2NO^+$) requires *m/z* 312.1194, found *m/z* 312.1198.

**(*E*)-1-(4-(tert-butyl)phenyl)-2,2-difluoro-4-(p-tolyl)but-3-en-1-one (3ba)**




56 mg, 86% yield, white solid, *E/Z* = 2.1/1, $R_f$ = 0.2 (hexane);

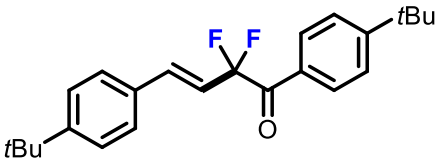
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.06 (d, *J* = 8.3 Hz, 2H), 7.87 (d, *J* = 8.2 Hz, 0.85H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 0.94H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 0.93H), 7.16 (d, *J* = 7.8 Hz, 1.92H), 7.08 (d, *J* = 7.5 Hz, 1H), 7.03 (s, 0.47H), 6.88 (d, *J* = 12.7 Hz, 0.45H), 6.42 (dt, ***J* = 16.4**, 11.4 Hz, 1H), 5.98 (dd, *J* = 27.3, 14.2 Hz, 0.47H), 2.35 (s, 3H), 2.33 (s, 1.29H), 1.34 (s, 9H), 1.32 (s, 4H) ppm;

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 188.6 (t, *J* = 31 Hz), 187.6 (t, *J* = 30.3 Hz), 158.3, 158.0, 139.8, 138.9 (t, *J* = 7.6 Hz), 138.8, 136.8 (t, *J* = 9.5 Hz), 131.6, 131.4, 130.3 (t, *J* = 2.9 Hz), 130.0 (t, *J* = 2.6 Hz), 129.5, (129.3 (t, *J* = 2.9 Hz), 128.8, 127.4, 126.0, 125.8, 125.4, 121.4 (t, *J* = 26.6 Hz), 118.9 (t, *J* = 24.8 Hz), 116.5 (t, *J* = 248.6 Hz), 115.6 (t, *J* = 247.4 Hz), 35.3, 35.2, 31.2, 31.0, 21.4, 21.3 ppm;

**$^{19}$F NMR** (376 MHz, $CDCl_3$): $\delta$ -91.0 (d, *J* = 16.4 Hz), -97.11 (d, *J* = 15.0 Hz) ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{21}H_{23}F_2O^+$) requires *m/z* 329.1711, found *m/z* 329.1710.

**(*E*)-1,4-bis(4-(tert-butyl)phenyl)-2,2-difluorobut-3-en-1-one (3ca)**




57 mg, 77% yield, white solid, *E*/*Z* = 2.2/1, $R_f$ = 0.3 (hexane);

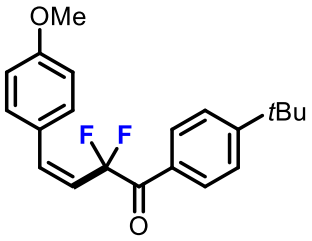
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.05 (d, *J* = 8.3 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 0.93H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.41 (s, 0.68H), 7.38 (s, 4H), 7.26 (d, *J* = 4.0 Hz, 0.92H), 7.21 (d, *J* = 8.3 Hz, 0.89H), 7.06 (dt, ***J* = 16.4**, 2.4 Hz, 1H), 6.88 (d, *J* = 12.7 Hz, 0.46H), 6.44 (dt, ***J* = 16.4**, 11.2 Hz, 1H), 6.00 (dd, *J* = 27.0, 14.1 Hz, 0.46H), 1.34 (s, 9H), 1.32 (s, 4.7H), 1.31 (s, 9H), 1.30 (s, 4.2H) ppm;

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 188.6 (t, *J* = 30.6 Hz), 187.6 (t, *J* = 29.9 Hz), 158.3, 157.9, 153.0, 151.9, 138.7 (t, *J* = 8.0 Hz), 136.7 (t, *J* = 9.5 Hz), 131.6, 131.4, 130.3 (t, *J* = 2.9 Hz), 129.9 (t, *J* = 2.2 Hz), 129.5, 129.3, 129.1 (t, *J* = 2.9 Hz), 127.2, 125.8, 125.7, 125.4, 125.0, 121.6 (t, *J* = 27.0 Hz), 119.2 (t, *J* = 24.8 Hz), 116.4 (t, *J* = 248.3 Hz), 115.4 (t, *J* = 247.2 Hz), 35.3, 35.2, 34.9, 34.7, 31.2, 31.2, 31.0 ppm;

**$^{19}$F NMR** (376 MHz, $CDCl_3$): $\delta$ -90.9 (d, *J* = 16.3 Hz), -97.2 (d, *J* = 11.9, 3.1 Hz) ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{24}H_{29}F_2O^+$) requires *m/z* 371.2181, found *m/z* 371.2181.

**(*Z*)-1-(4-(tert-butyl)phenyl)-2,2-difluoro-4-(4-methoxyphenyl)but-3-en-1-one (3da)**




54 mg, 79% yield, white solid; *E*/*Z* = 1/1.5, $R_f$ = 0.3 (ethyl acetate /hexane = 5%);

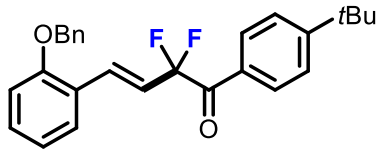
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 7.98 (d, *J* = 8.2 Hz, 1.27H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 0.27H), 7.48–7.41 (m, 1.21H), 7.38–7.33 (m, 2H), 7.31 (d, *J* = 8.2 Hz, 1.6H), 7.19 (dd, *J* = 10.5, 4.8 Hz, 2.68H), 6.95 (d, ***J* = 16.4 Hz**, 0.64H), 6.84–6.76 (m, 2H), 6.75–6.69 (m, 2.63H), 6.26 (dt, ***J* = 16.4**, 11.2 Hz, 0.67H), 5.85 (dd, *J* = 28.0, 13.7 Hz, 1H), 3.78–3.62 (m, 5.43H), 1.29–1.26 (m, 5.99H), 1.25 (d, *J* = 1.2 Hz, 9H) ppm;

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 188.7 (t, *J* = 30.8 Hz), 187.6 (t, *J* = 29.8 Hz), 160.7, 160.0, 158.3, 158.0, 138.5 (t, *J* = 8.0 Hz), 136.4 (t, *J* = 9.5 Hz), 131.1 (t, *J* = 3.3 Hz), 130.3 (t, *J* = 3.0 Hz), 130.0 (*J* = 2.4 Hz), 129.6, 129.4, 129.3, 128.9, 127.3, 127.1, 126.7, 125.7, 125.5, 125.4, 120.2 (t, *J* = 26.6 Hz), 117.5 (t, *J* = 24.8 Hz), 115.6 (t, *J* = 247.3 Hz), 114.3, 114.2, 113.5, 55.4, 55.3, 35.3, 35.2, 31.1, 31.0 ppm;

**$^{19}$F NMR** (376 MHz, $CDCl_3$): $\delta$ -91.0 (t, J = 14.0 Hz), -96.8 (d, J = 12.9 Hz) ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{21}H_{23}F_2O_2^+$) requires *m/z* 345.1661, found *m/z* 345.1663.

**(*E*)-4-(2-(benzyloxy)phenyl)-1-(4-(tert-butyl)phenyl)-2,2-difluorobut-3-en-1-one (3ea)**




62 mg, 74% yield, white solid, *E/Z* = 2.7/1, $R_f$ = 0.4 (ethyl acetate /hexane = 5%);

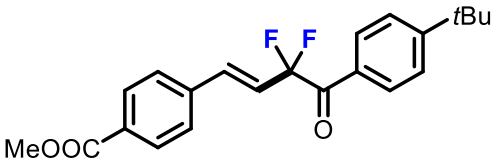
**$^{1}$H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.02 (d, *J* = 7.5 Hz, 2H), 7.77 (d, *J* = 7.5 Hz, 0.77H), 7.53–7.41 (m, 4H), 7.41–7.20 (m, 9.78H), 7.13 (d, *J* = 11.6 Hz, 0.43H), 6.94 (dd, *J* = 13.0, 5.2 Hz, 2.33H), 6.70 (d, *J* = 7.8 Hz, 0.36H), 6.61 (dtd, *J* = 13.9, 11.6, 2.3 Hz, 1H), 6.13 (tt, *J* = 12.3, 6.4 Hz, 0.40H), 5.10 (t, *J* = 5.1 Hz, 2H), 4.78 (t, *J* = 4.8 Hz, 0.76H), 1.32 (t, *J* = 5.0 Hz, 9H), 1.24 (t, *J* = 5.0 Hz, 3.9H) ppm;

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 188.6 (t, *J* = 30.6 Hz), 158.2, 157.7, 156.9, 156.0, 136.8, 136.6, 135.3 (t, *J* = 8.8 Hz), 132.4 (t, *J* = 10.2 Hz), 130.7, 130.4, 130.3, 130.3, 129.8, 129.6, 128.7, 128.5, 128.0, 127.8, 127.2, 126.9, 125.7, 125.2, 123.9, 123.7, 123.2 (t, *J* = 26.7 Hz), 121.1, 121.1, 120.9, 120.7, 120.4, 116.6 (t, *J* = 248.5 Hz), 112.7, 111.3, 70.4, 69.8, 35.3, 35.1, 31.0, 30.9 ppm;

**$^{19}$F NMR** (376 MHz, $CDCl_3$): $\delta$ -90.2 (d, *J* = 13.6 Hz), -94.8--100.0 (m) ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{27}H_{27}F_2O_2^+$) requires *m/z* 421.1974, found *m/z* 421.1977.

**methyl (*E*)-4-(4-(4-(tert-butyl)phenyl)-3,3-difluoro-4-oxobut-1-en-1-yl)benzoate （3fa)**




50 mg, 67% yield, white solid, *E*/*Z* = 3/1, $R_f$ = 0.3 (ethyl acetate /hexane = 5%);

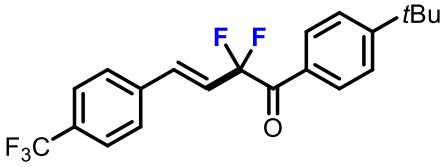
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.05 (dd, *J* = 16.3, 8.3 Hz, 4H), 7.95 (d, *J* = 8.2 Hz, 0.64H), 7.87 (d, *J* = 8.2 Hz, 0.58H), 7.52 (dd, *J* = 8.3, 4.0 Hz, 4H), 7.44 (d, *J* = 8.6 Hz, 0.69H), 7.34 (d, *J* = 8.2 Hz, 0.63H), 7.13 (d, ***J* = 16.4 Hz**, 1H), 6.97 (d, *J* = 12.8 Hz, 0.3H), 6.59 (dt, *J* = 16.4, 11.3 Hz, 1H), 6.14 (dd, *J* = 27.1, 13.9 Hz, 0.33H), 3.92-3.91 (m, 4H), 1.35-1.33 (m, 12H) ppm;

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 188.2 (t, *J* = 30.6 Hz), 166.7, 166.5, 158.6, 158.4, 139.0, 138.6, 137.7 (t, *J* = 7.5 Hz), 135.6 (t, *J* = 9.5 Hz), 130.8, 130.3, 130.1, 129.3, 129.0, 127.4, 125.8, 125.6, 124.0 (t, *J* = 26.5 Hz), 122.4 (t, *J* = 24.8 Hz), 116.0 (t, *J* = 249.6 Hz), 52.3, 52.3, 35.3, 31.0 ppm;

**$^{19}$F NMR** (376 MHz, $CDCl_3$): $\delta$ -91.1 (d, *J* = 13.6 Hz), -97.6 (d, *J* =10.9 Hz) ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{22}H_{23}F_2O_3^+$) requires *m/z* 373.1610, found *m/z* 373.1611.

**(*E*)-1-(4-(tert-butyl)phenyl)-2,2-difluoro-4-(4-(trifluoromethyl)phenyl)but-3-en-1-one (3ga)**




53 mg, 69% yield, white solid, *E*/*Z* = 5.8/1, $R_f$ = 0.3 (hexane);

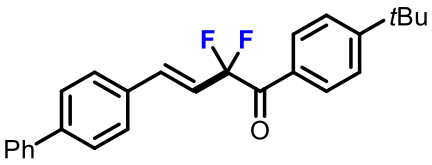
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.07 (d, *J* = 8.3 Hz, 2H), 7.87 (d, *J* = 8.3 Hz, 0.33H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.58–7.51 (m, 4H), 7.44 (d, *J* = 8.4 Hz, 0.32H), 7.38 (d, *J* = 8.2 Hz, 0.31H), 7.13 (d, ***J* = 16.4 Hz**, 1H), 6.97 (d, *J* = 12.7 Hz, 0.16H), 6.59 (dt, *J* = 16.4, 11.3 Hz, 1H), 6.16 (dd, *J* = 27.0, 13.9 Hz, 0.17H), 1.35 (s, 9H), 1.33 (s, 1.8H) ppm;

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 188.2 (t, *J* = 31.4 Hz), 158.7, 137.8, 135.2 (t, *J* = 9.4 Hz), 131.3 (q, *J* = 32.5 Hz), 130.3, 130.3, 130.1, 129.3, 127.7, 125.9, 125.8, 125.6, 122.6 (t, *J* = 24.4 Hz), 115.9 (t, *J* = 249.6 Hz), 35.3, 31.0 ppm;

**$^{19}$F NMR** (376 MHz, $CDCl_3$): $\delta$ -62.8 (d, *J* = 6.1 Hz), -91.2 (s), -97.7 (s) ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{21}H_{20}F_5O^+$) requires *m/z* 383.1429, found *m/z* 383.1426.

**(*E*)-4-([1,1'-biphenyl]-4-yl)-1-(4-(tert-butyl)phenyl)-2,2-difluorobut-3-en-1-one (3ha)**




62 mg, 80% yield, white solid, *E/Z* = 1.6/1, $R_f$ = 0.3 (hexane);

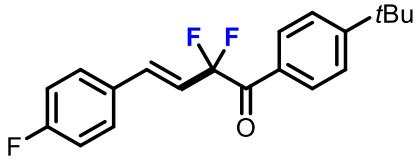
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.08 (d, *J* = 8.3 Hz, 2H), 7.88 (d, *J* = 8.3 Hz, 1.21H), 7.62–7.56 (m, 5.5H), 7.54 – 7.49 (m, 5.28H), 7.43 (dd, *J* = 11.8, 5.1 Hz, 4.5H), 7.36 (dd, *J* = 9.5, 5.1 Hz, 2.6H), 7.13 (d, ***J* = 16.4 Hz**, 1H), 6.95 (d, *J* = 12.7 Hz, 0.63H), 6.52 (dt, *J* = 16.4, 11.2 Hz, 1H), 6.06 (dd, *J* = 27.1, 14.2 Hz, 0.61H), 1.35 (s, 9H), 1.32 (s, 5H) ppm;

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 188.5 (t, *J* = 30.4 Hz), 158.4, 158.1, 142.4, 141.4, 140.4, 140.2, 138.4, 136.5, 136.4, 136.3, 133.3, 130.3, 130.0, 129.8, 128.9, 128.8, 127.9, 127.8, 127.6, 127.5, 127.0, 126.7, 125.8, 125.5, 122.2 (t, *J* = 26.2 Hz), 119.9 (t, *J* = 24.8 Hz), 116.4 (t, *J* = 248.8 Hz), 35.3, 31.0 ppm;

**$^{19}$F NMR** (376 MHz, $CDCl_3$): $\delta$ -90.90 (d, *J* = 14.3 Hz), -97.21 (d, *J* = 10.2 Hz) ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{26}H_{25}F_2O^+$) requires *m/z* 391.1868, found *m/z* 391.1870.

**(*E*)-1-(4-(tert-butyl)phenyl)-2,2-difluoro-4-(4-fluorophenyl)but-3-en-1-one (3ia)**




53 mg, 80% yield, white solid, *E/Z* = 2.5/1, $R_f$ = 0.3 (hexane);

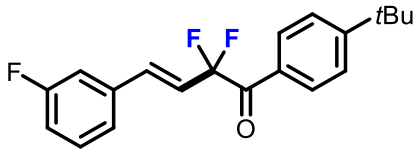
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.06 (d, *J* = 8.2 Hz, 2H), 7.87 (d, *J* = 8.3 Hz, 0.83H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.47–7.38 (m, 2.8H), 7.28 (dd, *J* = 9.0, 6.7 Hz, 1H), 7.04 (dd, *J* = 10.6, 6.2 Hz, 2.89H), 6.96 (t, *J* = 8.6 Hz, 0.8H), 6.88 (d, *J* = 12.6 Hz, 0.41H), 6.41 (dt, ***J* = 16.4**, 11.2 Hz, 1H), 6.04 (dd, *J* = 27.1, 13.9 Hz, 0.42H), 1.35 (s, 9H), 1.33 (s, 3.6H) ppm;

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 188.4 (t, *J* = 31.0 Hz), 187.4 (t, *J* = 30.0 Hz), 164.7, 164.1, 162.2, 161.6, 158.5, 158.3, 137.7 (t, *J* = 7.6 Hz), 135.6 (t, *J* = 9.8 Hz), 131.2 (dt, *J* = 8.1, 3.0 Hz), 130.6, 130.2 (t, *J* = 2.9 Hz), 130.0 (t, *J* = 2.4 Hz), 129.4, 129.3, 129.2, 129.1, 125.8, 125.5, 122.3 (t, *J* = 26.7 Hz), 119.7 (td, *J* = 24.8, 2.2 Hz), 116.2 (t, *J* = 249.0 Hz), 116.0, 115.8, 115.2, 115.0, 35.3, 35.3, 31.0 ppm;

**$^{19}$F NMR** (376 MHz, $CDCl_3$): $\delta$ -91.1 (dd, *J* = 25.5, 15.3 Hz), -97.3 (dd, *J* = 25.5, 12.6 Hz), -110.99 (s), -112.24 (s) ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{20}H_{20}F_3O^+$) requires *m/z* 333.1461, found *m/z* 333.1460.

**(*E*)-1-(4-(tert-butyl)phenyl)-2,2-difluoro-4-(3-fluorophenyl)but-3-en-1-one (3ja)**




49 mg, 74% yield, colorless oil, *E*/*Z* = 4.2/1, $R_f$ = 0.3 (hexane);

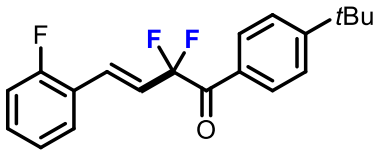
**$^{1}$H NMR** (400 MHz, $CDCl_3$): $\delta$ 7.99 (d, *J* = 8.8 Hz, 2H), 7.95 (d, *J* = 8.8 Hz, 1H), 7.80 (d, *J* = 8.8 Hz, 0.48H), 7.46 (t, *J* = 8.1 Hz, 3H), 7.37 (d, *J* = 8.8 Hz, 0.5H), 7.26 (td, *J* = 7.9, 5.9 Hz, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 7.10–7.06 (m, 1H), 7.02–6.80 (m, 3H), 6.42 (dt, ***J* = 16.4**, 11.3 Hz, 1H), 6.03 (dd, *J* = 26.7, 14.0 Hz, 0.24H), 1.28 (s, 9H), 1.26 (s, 2.2H) ppm;

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 188.3 (t, J = 30.6 Hz), 164.2, 161.8, 159.0, 158.6, 158.3, 136.6, 135.6 (t, J = 9.4 Hz), 130.4, 130.3, 130.3, 130.2, 130.2, 130.0, 129.7, 129.3, 126.0, 125.8, 125.5, 123.4, 121.4 (t, J = 24.4 Hz), 116.5, 116.3, 116.0 (t, J = 249.4 Hz), 114.0, 113.9, 111.3 (t, J = 249.8 Hz), 35.3, 31.0 ppm;

**$^{19}$F NMR** (376 MHz, $CDCl_3$): $\delta$ -91.1 (d, *J* = 16.3 Hz), -97.6 (d, *J* = 14.3 Hz), -112.2–-112.9 (m), -113.2--113.2 (m) ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{20}H_{20}F_3O^+$) requires *m/z* 333.1461, found *m/z* 333.1459.

**(*E*)-1-(4-(tert-butyl)phenyl)-2,2-difluoro-4-(2-fluorophenyl)but-3-en-1-one (3ka)**




51 mg, 77% yield, colorless oil, *E/Z* = 4.5/1, $R_f$ = 0.3 (hexane);

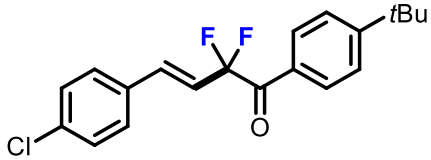
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.07 (d, *J* = 8.2 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 0.39H), 7.58–7.41 (m, 3.68H), 7.39–7.27 (m, 1.52H), 7.23-7.22 (m, 0.53H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.074 (t, *J* = 8.8 Hz), 7.02 – 6.86 (m, 0.39H), 6.61 (dt, *J* = 16.4, 11.4 Hz, 1H), 6.17 (dd, *J* = 26.7, 13.4 Hz, 0.22H), 1.35 (s, 9H), 1.33 (s, 1.96H) ppm;

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 188.4 (t, *J* = 30.9 Hz), 162.2, 159.7, 158.5, 158.2, 131.1, 131.0, 130.6, 130.5, 130.3 (t, *J* = 3.0 Hz), 129.9 (t, *J* = 2.7 Hz), 129.7 (d, *J* = 3.2 Hz), 129.6 (d, *J* = 3.3 Hz), 129.5 (d, *J* = 3.1 Hz), 129.4 (t, *J* = 1.9 Hz), 128.6 (d, *J* = 2.8 Hz), 125.8, 125.5, 124.4 (d, *J* = 3.3 Hz), 123.7 (d, *J* = 3.7 Hz), 122.8 (d, *J* = 6.5 Hz), 122.5 (d, *J* = 6.5 Hz), 122.3, 116.1 (t, *J* = 249.4 Hz), 116.2, 116.0, 115.1, 114.9, 35.3, 35.3, 31.2, 31.0 ppm;

**$^{19}$F NMR** (376 MHz, $CDCl_3$): $\delta$ -92.24 (d, *J* = 14.3 Hz), -97.92 (d, *J* = 14.3 Hz), -113.95 (dd, *J* = 17.7, 7.5 Hz), -115.18–-116.34 (m) ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{20}H_{20}F_3O^+$) requires *m/z* 333.1461, found *m/z* 333.1463.

**(*E*)-1-(4-(tert-butyl)phenyl)-4-(4-chlorophenyl)-2,2-difluorobut-3-en-1-one (3la)**




52 mg, 75% yield, white solid, *E/Z* = 4/1, $R_f$ = 0.3 (hexane);

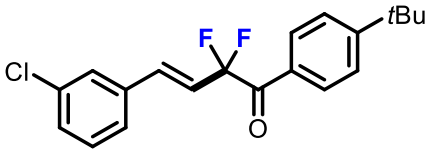
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.06 (d, *J* = 8.3 Hz, 2H), 7.88 (d, *J* = 8.3 Hz, 0.42H), 7.52 (d, *J* = 8.7 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 0.48H), 7.36 (dd, *J* = 21.1, 8.5 Hz, 4H), 7.24 (d, *J* = 1.8 Hz, 0.65H), 7.05 (d, ***J* = 16.4 Hz**, 1H), 6.87 (d, *J* = 12.7 Hz, 0.22H), 6.46 (dt, ***J* = 16.4**, 11.3 Hz, 1H), 6.06 (dd, *J* = 27.0, 14.2 Hz, 0.23H), 1.35 (s, 9H), 1.33 (s, 2.6H) ppm;

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 188.3 (t, J = 31.0 Hz), 158.5, 158.3, 137.5 (t, J = 7.6 Hz), 135.6-135.4 (m), 132.8, 132.7, 130.5 (t, J = 3.3 Hz), 130.2 (t, J = 2.9 Hz), 130.1 (t, J = 2.4 Hz), 129.4, 129.1, 128.7, 128.3, 125.8, 125.6, 122.9 (t, J = 26.2 Hz), 120.6 (t, J = 24.4 Hz), 116.1 (t, J = 249.2 Hz), 35.3, 31.0 ppm;

**$^{19}$F NMR** (376 MHz, $CDCl_3$): $\delta$ -91.1 (d, J = 14.3 Hz), 97.4 (d, J = 10.9 Hz) ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{20}H_{20}ClF_2O^+$) requires *m/z* 349.1165, found *m/z* 349.1169.

**(*E*)-1-(4-(tert-butyl)phenyl)-4-(3-chlorophenyl)-2,2-difluorobut-3-en-1-one (3ma)**




55 mg, 79% yield, white solid, *E/Z* = 5.9/1, $R_f$ = 0.3 (hexane);

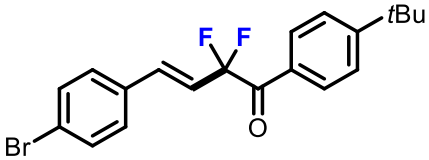
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 7.99 (d, *J* = 8.1 Hz, 2H), 7.77 (d, *J* = 7.9 Hz, 0.32H), 7.45 (dd, *J* = 5.2, 3.4 Hz, 2H), 7.37 (s, 1.17H), 7.26–7.21 (m, 2.53H), 7.19-7.10 (m, 1.75H), 6.97 (dd, ***J* = 16.4**, 2.4 Hz, 1H), 6.80 (d, *J* = 13.4 Hz, 0.18H), 6.50–6.36 (m, 1H), 6.04 (dd, *J* = 26.5, 13.7 Hz, 0.17H), 1.28 (s, 9H), 1.19 (s, 1.78H) ppm;

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 188.2 (t, *J* = 30.6 Hz), 158.6, 136.2, 135.4 (t, *J* = 9.8 Hz), 134.9, 130.2 (t, *J* = 2.9 Hz), 130.1, 129.9, 129.5, 129.3, 128.9, 128.6, 127.3, 125.8, 125.7, 125.5, 121.5 (t, *J* = 24.4 Hz), 116.0 (t, *J* = 249.3 Hz), 35.3, 31.0 ppm;

**$^{19}$F NMR** (376 MHz, $CDCl_3$): $\delta$ -90.99 (d, *J* = 13.6 Hz), -97.59 (d, *J* = 10.9 Hz) ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{20}H_{20}ClF_2O^+$) requires *m/z* 349.1165, found *m/z* 349.1164.

**(*E*)-4-(4-bromophenyl)-1-(4-(tert-butyl)phenyl)-2,2-difluorobut-3-en-1-one (3na)**




64 mg, 81% yield, white solid, *E/Z* = 5.9/1, $R_f$ = 0.3 (hexane);

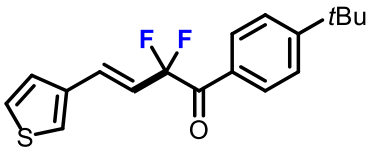
**$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 7.99 (d, *J* = 8.4 Hz, 2H), 7.80 (d, *J* = 8.6 Hz, 0.3H), 7.43 (dd, *J* = 11.9, 8.6 Hz, 4H), 7.35 (dd, *J* = 16.0, 8.5 Hz, 0.71H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 0.28H), 6.96 (dt, ***J* = 16.4**, 2.4 Hz, 1H), 6.78 (d, *J* = 12.6 Hz, 0.16H), 6.41 (dt, ***J* = 16.4**, 11.3 Hz, 1H), 6.00 (dd, *J* = 27.0, 14.2 Hz, 0.17H), 1.28 (s, 9H), 1.26 (s, 1.55H) ppm;

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 188.3 (t, $J$ = 31.0 Hz), 158.5,135.6 (t, $J$ = 9.5 Hz), 133.3, 132.0, 131.3, 130.7, 130.2 (t, $J$ = 2.9 Hz),130.1, 129.4, 128.9, 126.0, 125.8, 125.6, 123.7, 120.7 (t, $J$ = 24.5 Hz), 116.1 (t, $J$ = 249.3 Hz), 35.3, 31.0 ppm;

**$^{19}$F NMR** (376 MHz, $CDCl_3$): $\delta$ -91.1 (d, $J$ = 16.3 Hz), -97.4 (d, $J$ = 14.3 Hz) ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{20}H_{20}BrF_2O^+$) requires *m/z* 393.0660, found *m/z* 393.0663.

**(*E*)-1-(4-(tert-butyl)phenyl)-2,2-difluoro-4-(thiophen-3-yl)but-3-en-1-one (3oa)**




51 mg, 80% yield, white solid, *E/Z* = 13/1, $R_f$ = 0.3 (hexane);

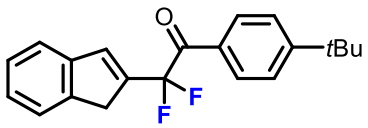
**$^{1}$H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.05 (d, $J$ = 8.4 Hz, 2H), 7.51 (d, $J$ = 8.6 Hz, 2H), 7.36 (s, 1H), 7.33–7.29 (m, 1H), 7.26 (s, 1H), 7.08 (dt, ***J* = 16.1**, 2.5 Hz, 1H), 6.39–6.17 (m, 1H), 1.35 (s, 9H) ppm;

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 188.5 (t, $J$ = 31.0 Hz), 158.4, 137.2, 130.7 (t, $J$ = 9.9 Hz), 130.3 (t, $J$ = 2.9 Hz), 129.5, 126.8, 126.3, 125.8, 124.9, 119.6 (t, $J$ = 24.8 Hz), 116.3 (t, $J$ = 250.2 Hz), 35.3, 31.0 ppm;

**$^{19}$F NMR** (376 MHz, $CDCl_3$): $\delta$ -92.45 (d, $J$ = 15.0 Hz), -97.26 (d, $J$ = 10.9 Hz) ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{18}H_{19}F_2OS^+$) requires *m/z* 321.1119, found *m/z* 321.1121.

**1-(4-(tert-butyl)phenyl)-2,2-difluoro-2-(1H-inden-2-yl)ethan-1-one (4a)**




48 mg, 74% yield, colorless oil, $R_f$ = 0.4 (hexane);

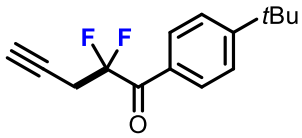
**$^{1}$H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.05 (d, $J$ = 8.3 Hz, 2H), 7.49 (d, $J$ = 8.6 Hz, 3H), 7.43 (d, $J$ = 6.4 Hz, 1H), 7.30 (t, $J$ = 5.7 Hz, 2H), 7.19 (s, 1H), 3.66 (s, 2H), 1.33 (s, 9H) ppm;

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 188.4 (t, $J$ = 30.4 Hz), 158.4, 143.5, 142.5, 139.0 (t, $J$ = 26.4 Hz), 134.5 (t, $J$ = 7.7 Hz), 130.3 (t, $J$ = 2.9 Hz), 129.6, 126.9, 126.6, 125.7, 124.1, 122.6, 116.3 (t, $J$ = 274.3 Hz), 37.5, 35.3, 31.0 ppm;

**$^{19}$F NMR** (376 MHz, $CDCl_3$): $\delta$ -96.28 (s) ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{21}H_{21}F_2O^+$) requires *m/z* 327.1555, found *m/z* 327.1560.

**1-(4-(tert-butyl)phenyl)-2,2-difluoropent-4-yn-1-one (4b)**




33 mg, 66% yield, colorless oil, $R_f$ = 0.4 (hexane);

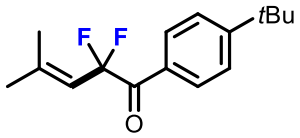
**$^{1}$H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.01 (d, $J$ = 8.4 Hz, 2H), 7.46 (d, $J$ = 8.6 Hz, 2H), 3.10 (td, $J$ = 15.6, 2.6 Hz, 2H), 2.07 (t, $J$ = 2.6 Hz, 1H), 1.28 (s, 9H) ppm;

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 187.4 (t, $J$ = 30.5 Hz), 130.31 (t, $J$ = 3.3 Hz), 128.82 (t, $J$ = 3.0 Hz), 126.00, 125.80, 117.09 (t, $J$ = 257.3 Hz), 74.55, 72.45, 35.35, 30.97, 25.48 (t, $J$ = 26.8 Hz) ppm;

**$^{19}$F NMR** (376 MHz, $CDCl_3$): $\delta$ -98.63 (t, $J$ = 15.7 Hz) ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{15}H_{17}F_2O^+$) requires *m/z* 251.1242, found *m/z* 251.1243.

**1-(4-(tert-butyl)phenyl)-2,2-difluoro-4-methylpent-3-en-1-one (4c)**




37 mg, 70% yield, colorless oil, $R_f$ = 0.4 (hexane);

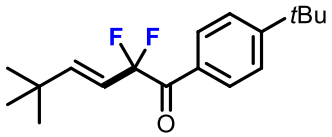
**$^{1}$H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.00 (d, $J$ = 8.6 Hz, 2H), 7.50 (d, $J$ = 8.7 Hz, 2H), 5.73–5.54 (m, 1H), 2.06–1.76 (m, 6H), 1.35 (s, 9H) ppm;

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 188.4 (t, $J$ = 31.4 Hz), 158.07, 147.0 (t, $J$ = 7.3 Hz), 130.2 (t, $J$ = 2.8 Hz) 129.3, 126.0, 125.6, 117.86 (t, $J$ = 26.2 Hz), 116.03 (t, $J$ = 247.8 Hz), 35.26, 30.99, 26.72, 19.38 ppm;

**$^{19}$F NMR** (376 MHz, $CDCl_3$): $\delta$ -92.93 (d, $J$ = 12.9 Hz) ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{16}H_{21}F_2O^+$) requires *m/z* 267.1555, found *m/z* 267.1552.

**(*E*)-1-(4-(tert-butyl)phenyl)-2,2-difluoro-5,5-dimethylhex-3-en-1-one (4d)**




39 mg, 67% yield, colorless oil, E/Z > 20/1, $R_f$ = 0.4 (hexane);

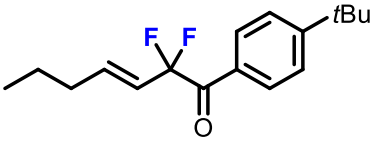
**$^{1}$H NMR** (400 MHz, $CDCl_3$): $\delta$ 7.93 (d, $J$ = 8.4 Hz, 2H), 7.43 (d, J = 8.6 Hz, 2H), 6.21 (dt, $J$ = 16.1, 2.6 Hz, 1H), 5.67 (dt, ***J* = 16.1**, 10.9 Hz, 1H), 1.28 (s, 9H), 0.98 (s, 9H) ppm;

**$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 189.0, 158.1, 150.0 (t, $J$ = 8.7 Hz), 130.2 (t, $J$ = 2.9 Hz), 125.6, 125.5, 117.6 (t, $J$ = 24.8 Hz), 116.3 (t, $J$ = 247.8 Hz), 35.3, 33.5, 31.0, 28.7 ppm;

**$^{19}$F NMR** (376 MHz, $CDCl_3$): $\delta$ -97.05 (d, $J$ = 14.3 Hz), -101.70 (d, $J$ = 44.3 Hz) ppm;

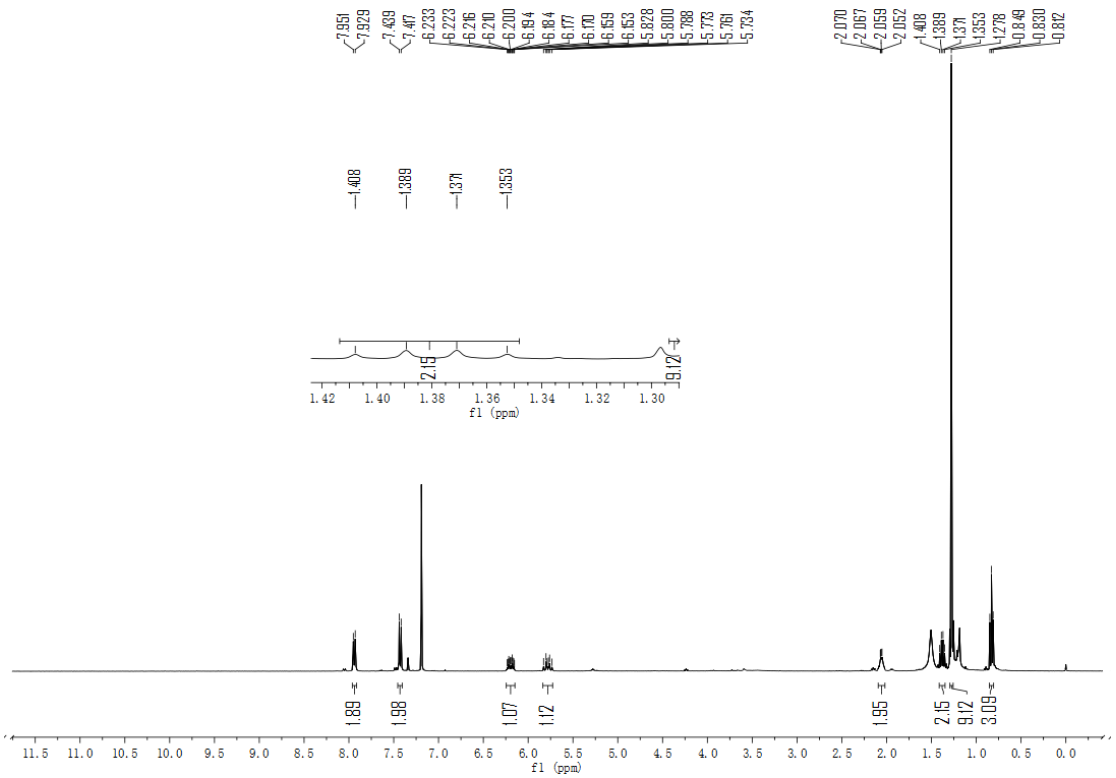
**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{18}H_{25}F_2O^+$) requires *m/z* 295.1868, found *m/z* 295.1865.

**(*E*)-1-(4-(tert-butyl)phenyl)-2,2-difluorohept-3-en-1-one (4e)**

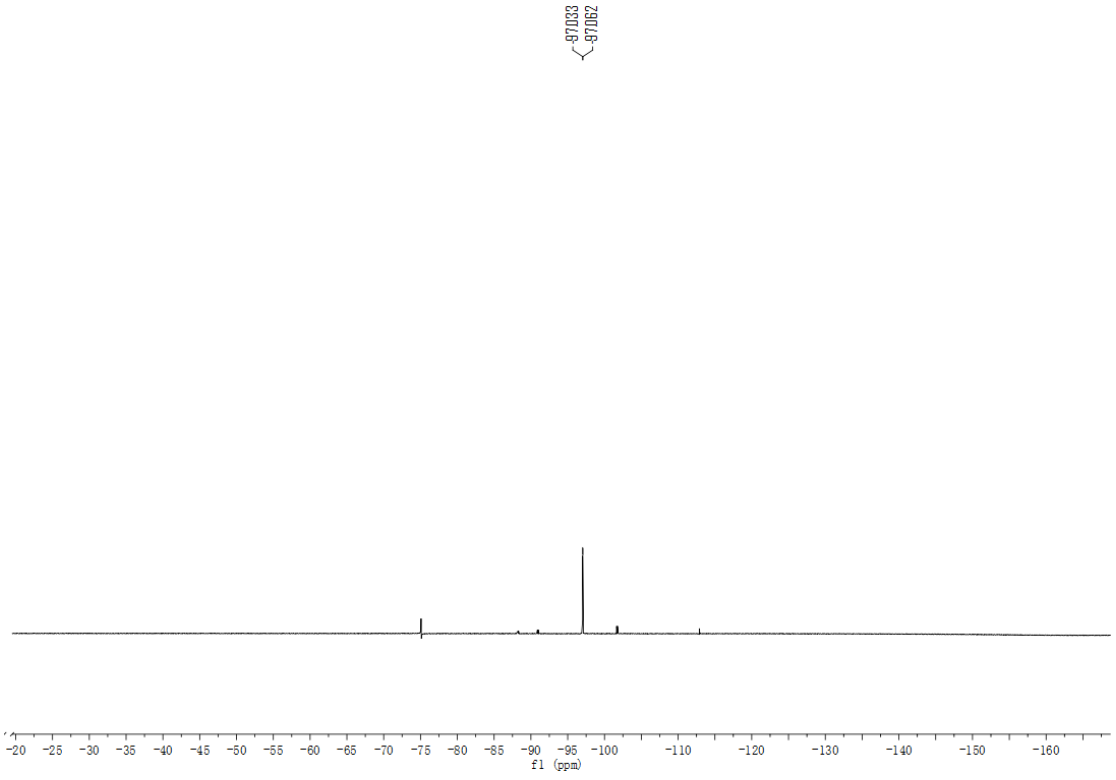



The amount of **4e** (3 mg, < 20% yield) is very small, and its spectrum is shown below, with some peaks of the carbon spectrum not appearing. These spectral data cannot be used, but only as a reference.

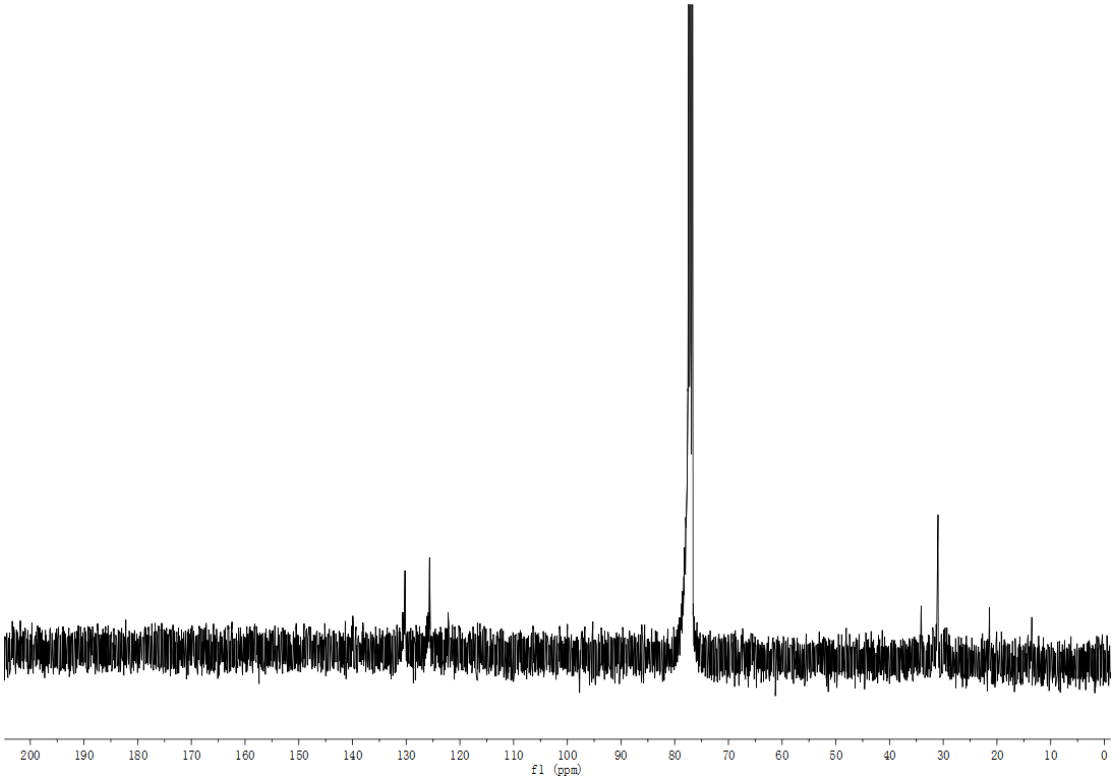
**$^{1}$H NMR (400 MHz, $CDCl_3$):**



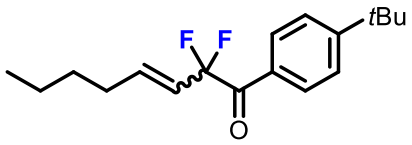
**$^{19}$F NMR** (376 MHz, $CDCl_3$)



**$^{13}$C NMR** (100 MHz, $CDCl_3$):

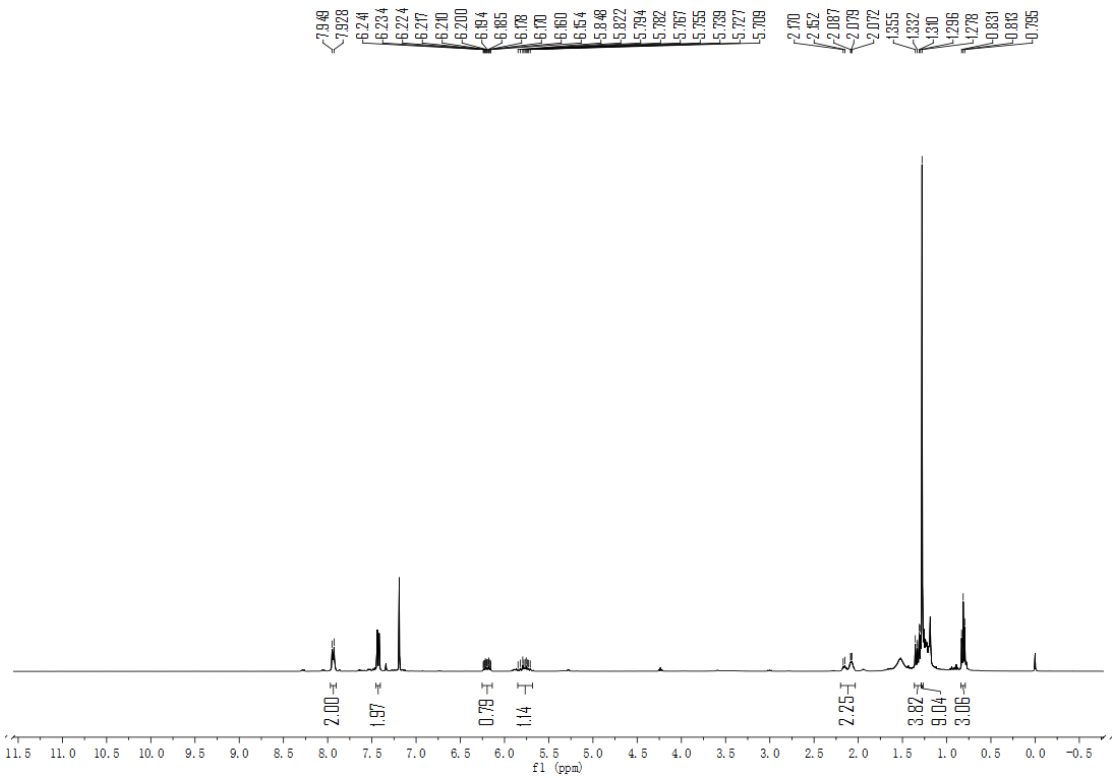



**(*E*)-1-(4-(tert-butyl)phenyl)-2,2-difluorooct-3-en-1-one (4f)**

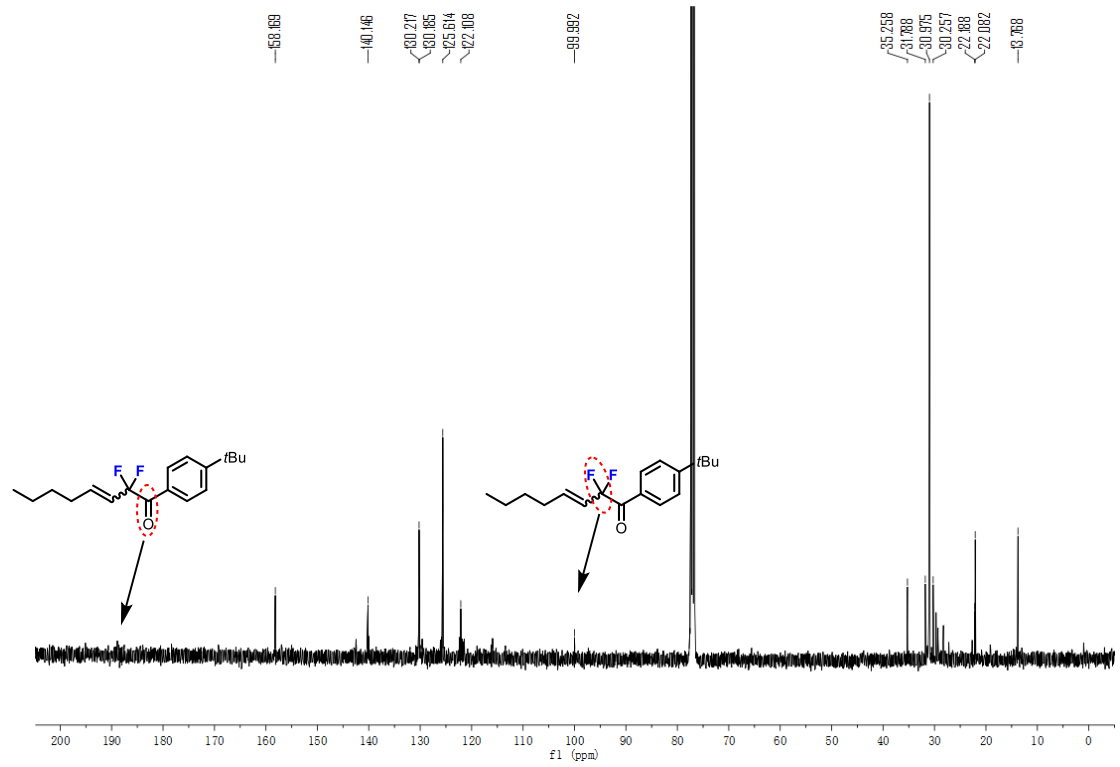



The amount of **4f** (5 mg, < 20% yield) is very small, and its spectrum is shown below, with some peaks of the carbon spectrum not appearing. These spectral data cannot be used, but only as a reference.

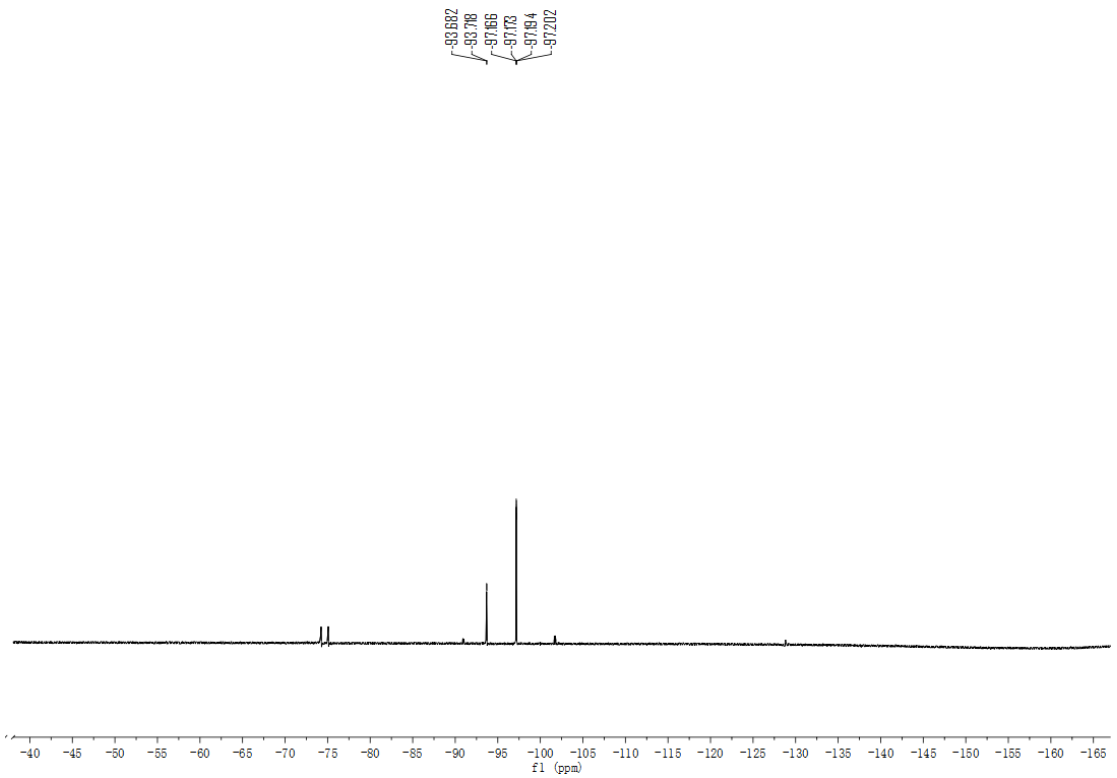
**$^{1}$H NMR (400 MHz, $CDCl_3$):**



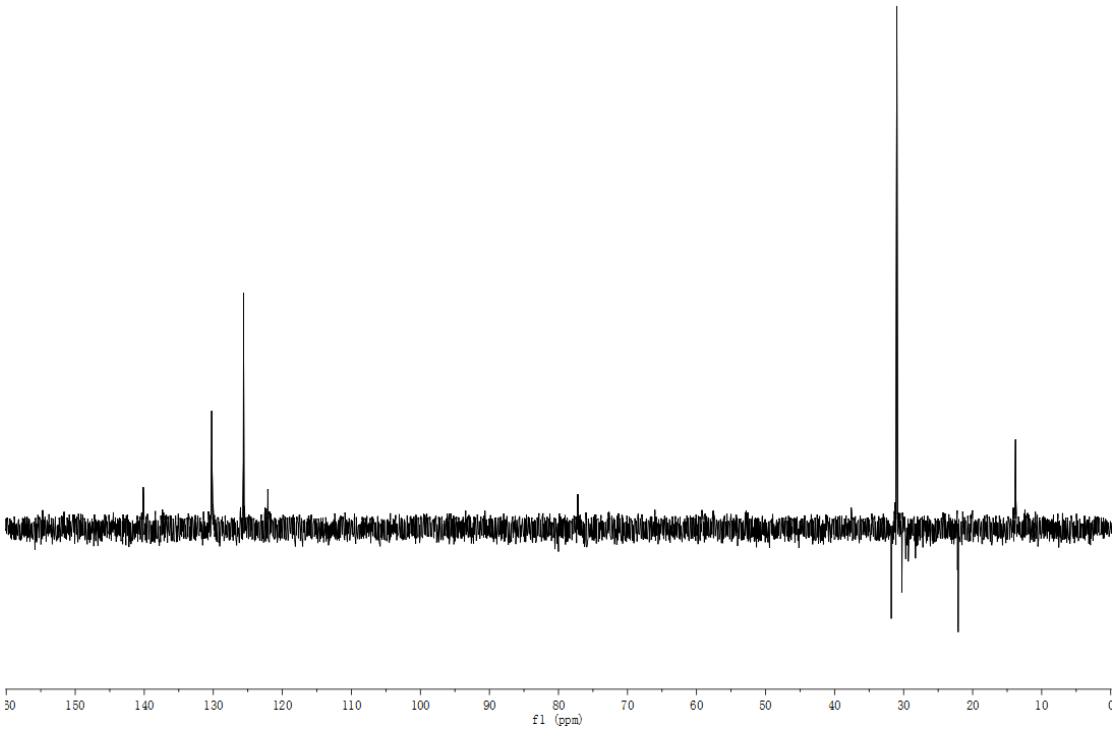
**$^{13}$C NMR** (100 MHz, $CDCl_3$):



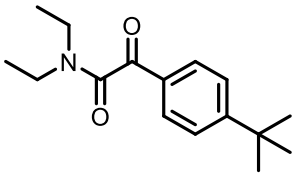
**$^{19}$F NMR** (376 MHz, $CDCl_3$)




**DEPT**




**2-(4-(tert-butyl)phenyl)-*N*,*N*-diethyl-2-oxoacetamide (9a)**



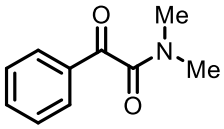
45 mg, 86% yield, colorless oil, Rf = 0.3 (25% EtOAc/hexane);

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 7.4 Hz, 2H), 3.58 (q, *J* = 8.0 Hz, 2H), 3.26 (q, *J* = 8.0 Hz, 2H), 1.36 (s, 9H), 1.31 (t, *J* = 8.0 Hz, 3H), 1.18 (t, *J* = 8.0 Hz, 3H) ppm;

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 191.4, 167.0, 158.6, 130.8, 129.6, 126.0, 42.1, 38.7, 35.4, 31.0, 14.1, 12.9 ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{16}H_{24}NO_2^+$) requires *m/z* 262.1802, found *m/z* 262.1806. This compound is known.[S16]

***N,N*-dimethyl-2-oxo-2-phenylacetamide (9b)**



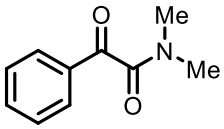
26 mg, 74% yield, colorless oil, Rf = 0.3 (25% EtOAc/hexane);

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.2 Hz, 2H), 7.65 (t, *J* = 9.2 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 2H), 3.13 (s, 3H), 2.97 (s, 3H) ppm;

**$^{13}$CNMR** (100 MHz, $CDCl_3$) δ 191.8, 167.1, 134.7, 133.1, 130.0, 129.7, 129.0, 128.5, 37.1, 34.0 ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{10}H_{12}NO_2^+$) requires *m/z* 178.0863, found *m/z* 178.0867. This compound is known.[S16]

***N,N*-dimethyl-2-oxo-2-phenylacetamide (9c)**



*The spectral data is the same as above.*

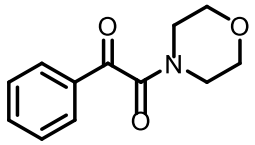
23 mg, 64% yield, colorless oil, Rf = 0.3 (25% EtOAc/hexane);

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.5 Hz, 2H), 7.65 (t, *J* = 9.0 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 3.13 (s, 3H), 2.97 (s, 3H) ppm;

**$^{13}$CNMR** (100 MHz, $CDCl_3$) δ 191.8, 167.1, 134.7, 133.1, 130.0, 129.7, 129.0, 128.5, 37.1, 34.0 ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{10}H_{12}NO_2^+$) requires *m/z* 178.0863, found *m/z* 178.0869. This compound is known.[S16]

**1- morpholino-2-phenylethane-1,2-dione (9d)**



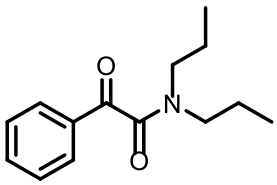
31 mg, 71% yield, colorless oil, Rf = 0.3 (25% EtOAc/hexane);

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 3.73 (s, 4H), 3.71–3.61 (m, 2H), 3.46–3.31 (m, 2H). ppm;

**$^{13}$CNMR** (100 MHz, CDCl3) δ 191.2, 165.5, 135.0, 133.0, 129.7, 129.1, 66.8, 66.7, 46.3, 41.6 ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{12}H_{14}NO_3^+$) requires *m/z* 220.0968, found *m/z* 220.0977. This compound is known.[S16]

**2- oxo-2-phenyl-N,N-dipropylacetamide (9e)**



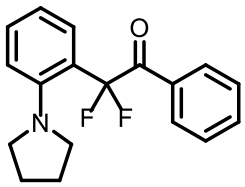
27 mg, 59% yield, colorless oil, Rf = 0.3 (25% EtOAc/hexane);

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 5.1, 3.3 Hz, 2H), 7.62 – 7.52 (m, 1H), 7.43 (dd, *J* = 10.6, 4.7 Hz, 2H), 3.45 – 3.35 (m, 2H), 3.16 – 2.99 (m, 2H), 1.72 – 1.60 (m, 2H), 1.57 – 1.47 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H), 0.72 (t, *J* = 7.5 Hz, 3H); ppm;

**$^{13}$CNMR** (100 MHz, $CDCl_3$) δ 191.6, 167.2, 134.5, 133.4, 129.6, 128.9, 49.3, 45.9, 21.8, 20.6, 11.4, 11.0 ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{14}H_{20}NO_2^+$) requires *m/z* 234.1489, found *m/z* 234.1494. This compound is known.[S16]

**2,2-difluoro-1-phenyl-2-(2-(pyrrolidin-1-yl)phenyl)ethan-1-one (9f)**




34 mg, 57% yield, colorless oil, Rf = 0.3 (25% EtOAc/hexane);

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.64 (d, *J* = 7.7 Hz, 2H), 7.38 (dd, *J* = 16.9, 7.9 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 1H), 2.51 (t, *J* = 6.1 Hz, 4H), 1.76 – 1.38 (m, 4H); ppm;

**$^{13}$CNMR** (100 MHz, $CDCl_3$) δ 183.0 (t, *J* = 27.4 Hz), 148.3, 133.2, 132.4, 132.0, 128.1, 128.1, 126.1 (t, *J* = 5.3 Hz), 125.6, 122.7, 114.5 (t, *J* = 245.1 Hz), 53.1, 24.1 ppm;

**$^{19}$F NMR** (376 MHz, $CDCl_3$): *δ* -93.0 (s) ppm;

**HRMS** (ESI): exact mass calculated for $[M+H]^+$ ($C_{18}H_{18}F_2NO^+$) requires *m/z* 302.1351, found *m/z* 302.1350.

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S9. (a) Z. Zhang, X. Hu, *ACS Catal.* **2020**, *10*, 777-782; (b) Z. Wang, Q. Liu, X. Ji, G. Deng, H. Huang, *ACS Catal.* **2020**, *10*, 154-159.

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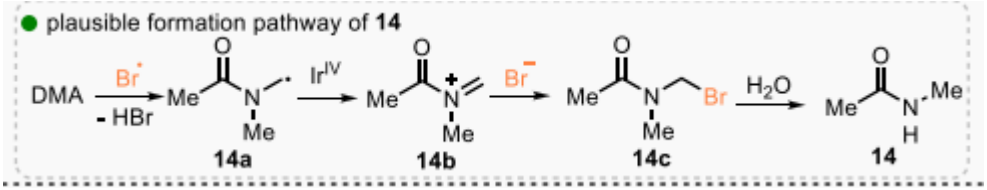
S11. P. Xu, C. G. Daniliuc, K. Bergander, C. Stein, A. Studer, *ACS Catal.* **2022**, *12*, 11934-11941.




S12. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian 2016; Gaussian, 2016.

S13. S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104-154119.

S14. S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456-1465.

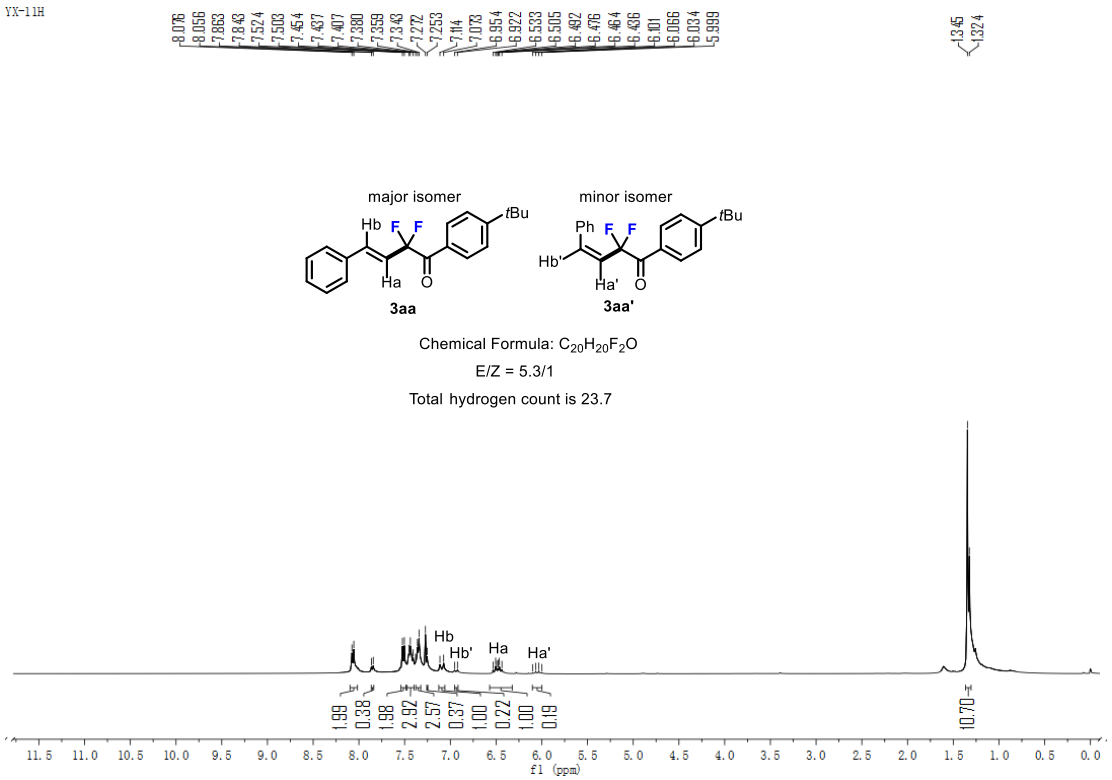
S15. J. Tomasi, B. Mennucci, E. Cances, *J. Mol. Struct.: THEOCHEM.* **1999**, *464*, 211−226.

S16. X.-B. Zhang, W.-C. Yang, L. Wang, *Org. Biomol. Chem.* **2013**, *11*, 3649-3654.

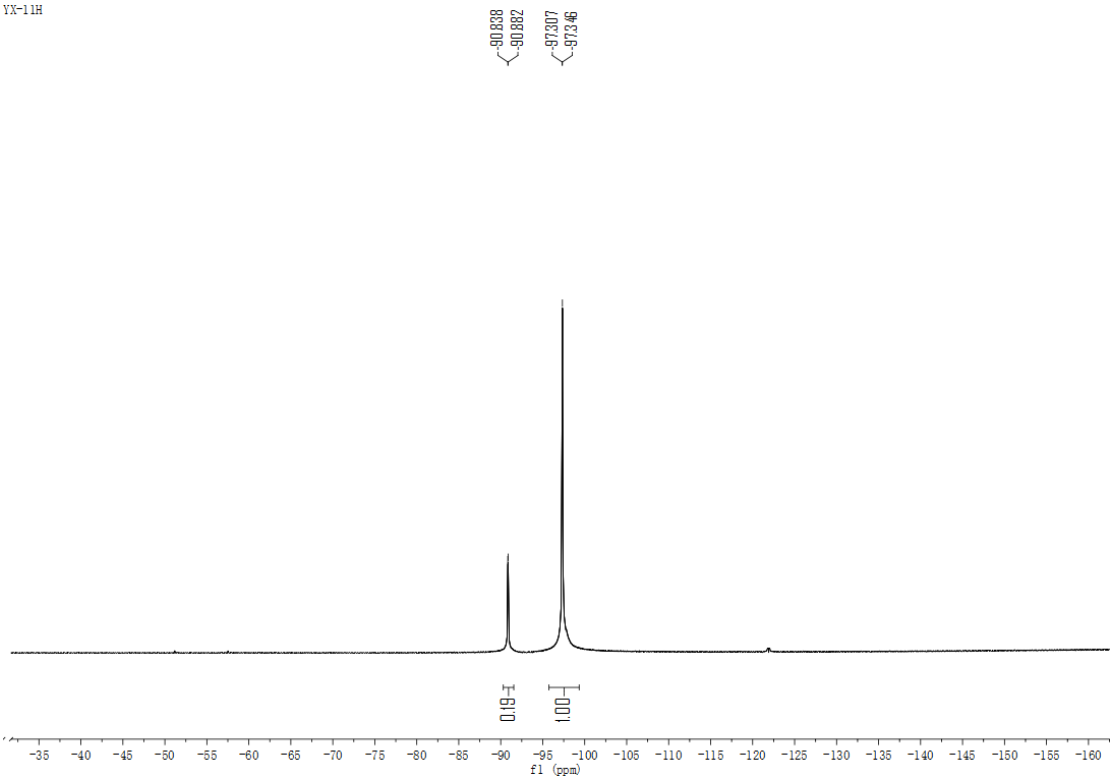
**Copies $^{1}$H NMR, $^{13}$C NMR, $^{19}$F NMR**

**(*E*)-1-(4-(tert-butyl)phenyl)-2,2-difluoro-4-phenylbut-3-en-1-one (3aa)**

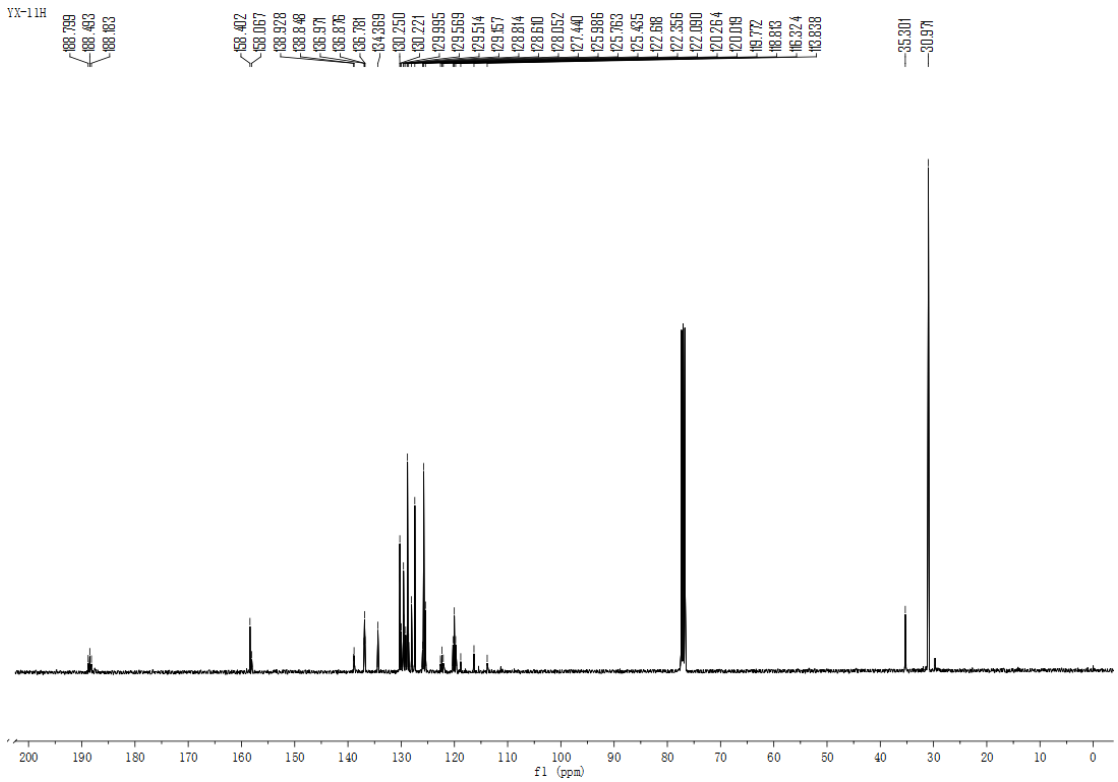
**$^{1}$H NMR (400 MHz, $CDCl_3$):**




## $^{19}$F NMR (376 MHz, $CDCl_3$):

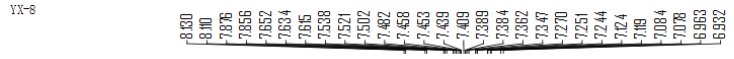



## $^{13}$C NMR (100 MHz, $CDCl_3$):

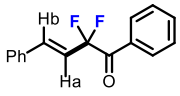



**(*E*)-2,2-difluoro-1,4-diphenylbut-3-en-1-one (3ab)**

**$^{1}$H NMR (400 MHz, $CDCl_3$):**

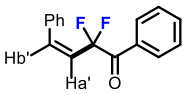



major isomer




**3ab**

minor isomer

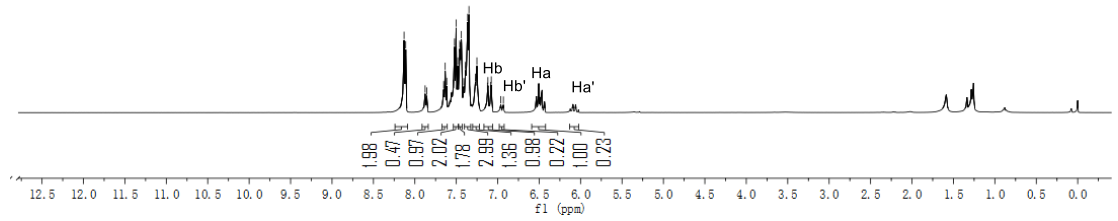



**3ab'**

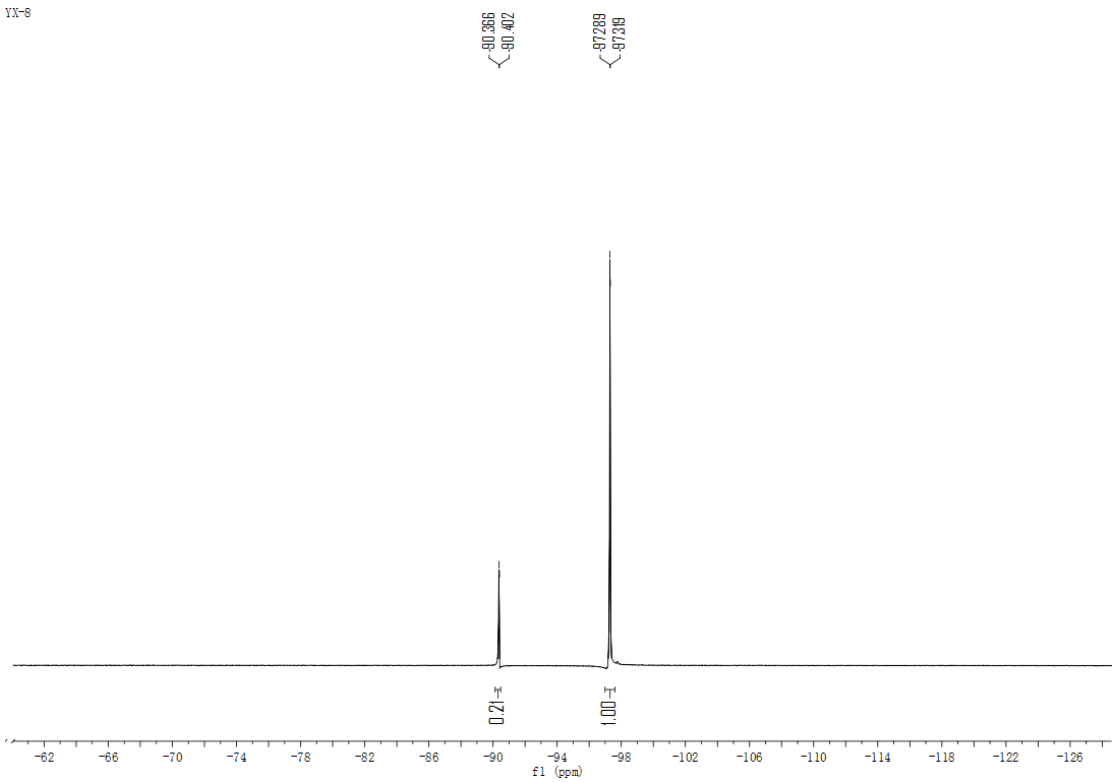
Chemical Formula: $C_{16}H_{12}F_2O$

E/Z = 4.3/1

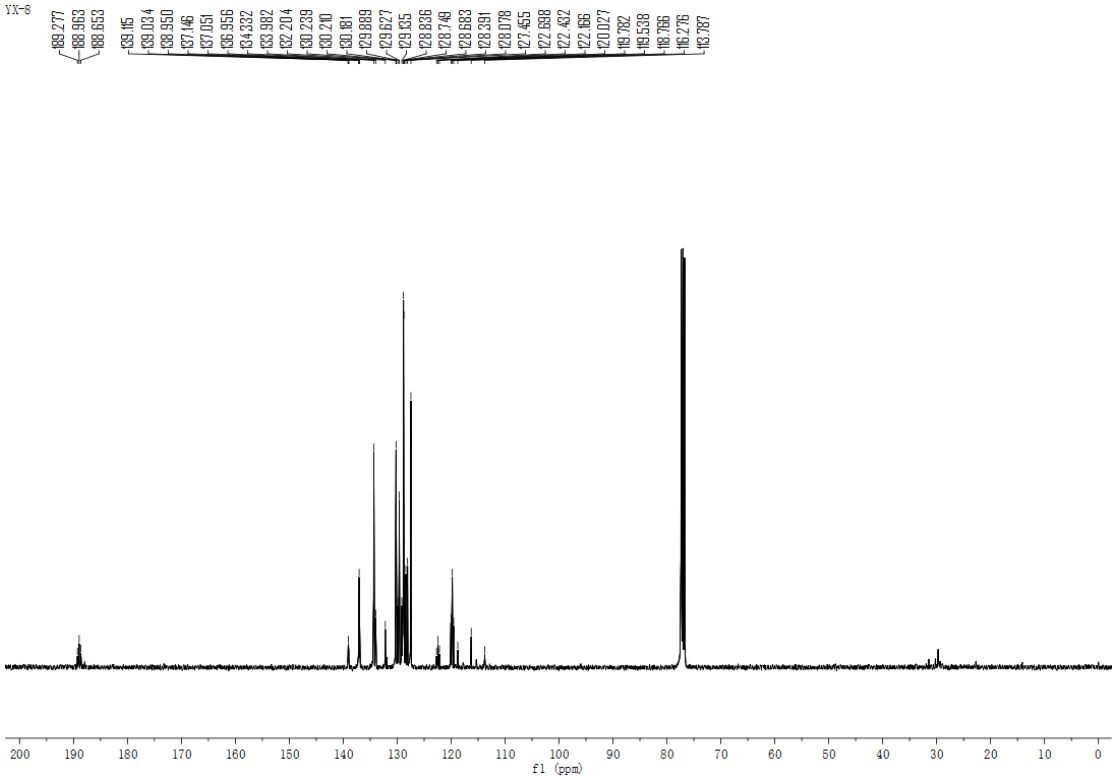
Total hydrogen count is 14.8




**$^{19}$F NMR (376 MHz, $CDCl_3$):**

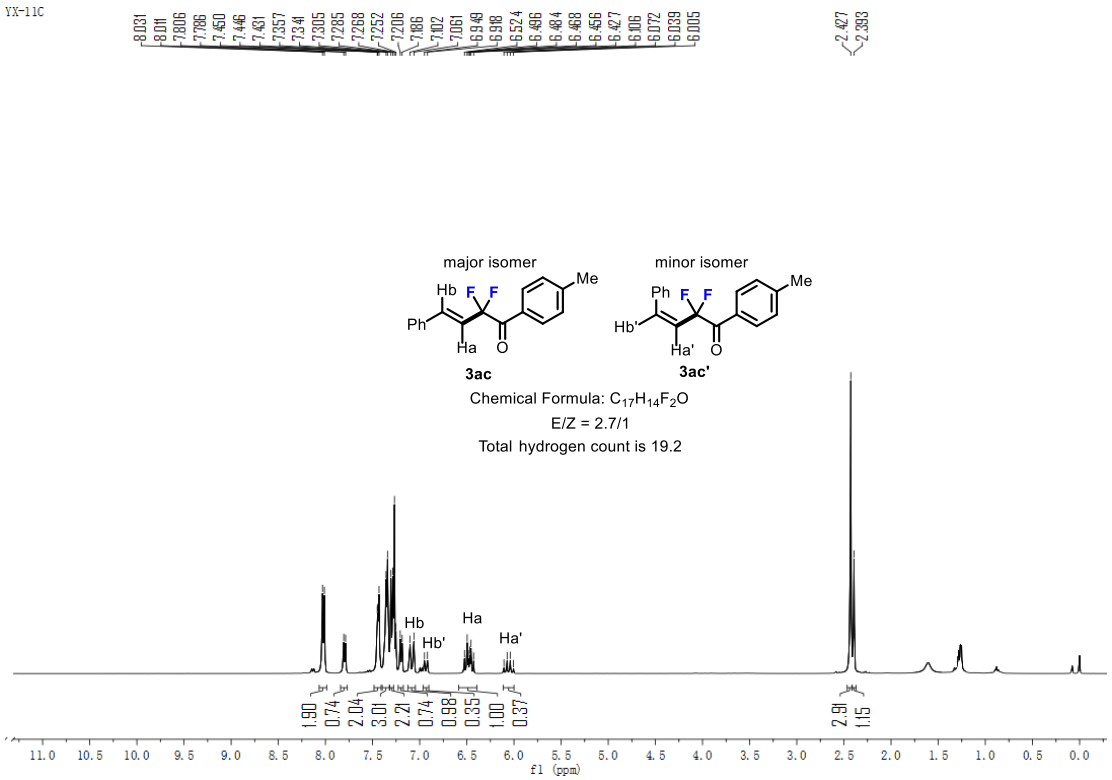



**$^{13}$C NMR (100 MHz, $CDCl_3$):**

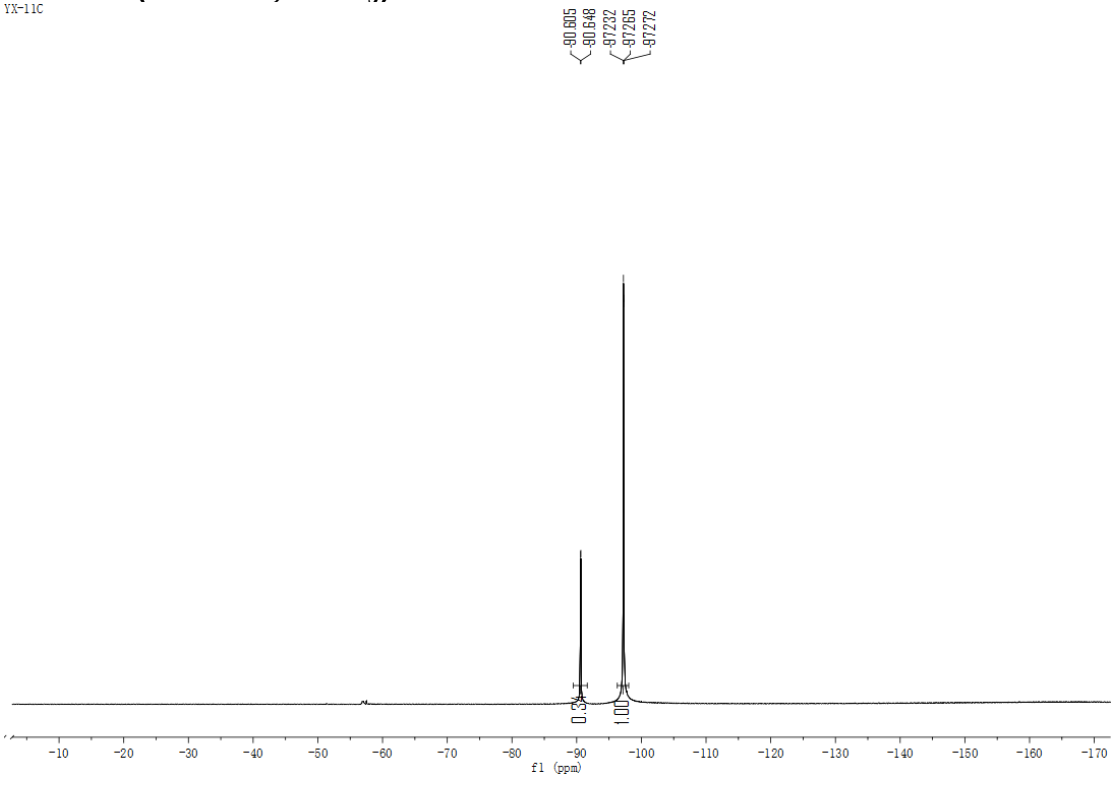



**(*E*)-2,2-difluoro-4-phenyl-1-(p-tolyl)but-3-en-1-one (3ac)**

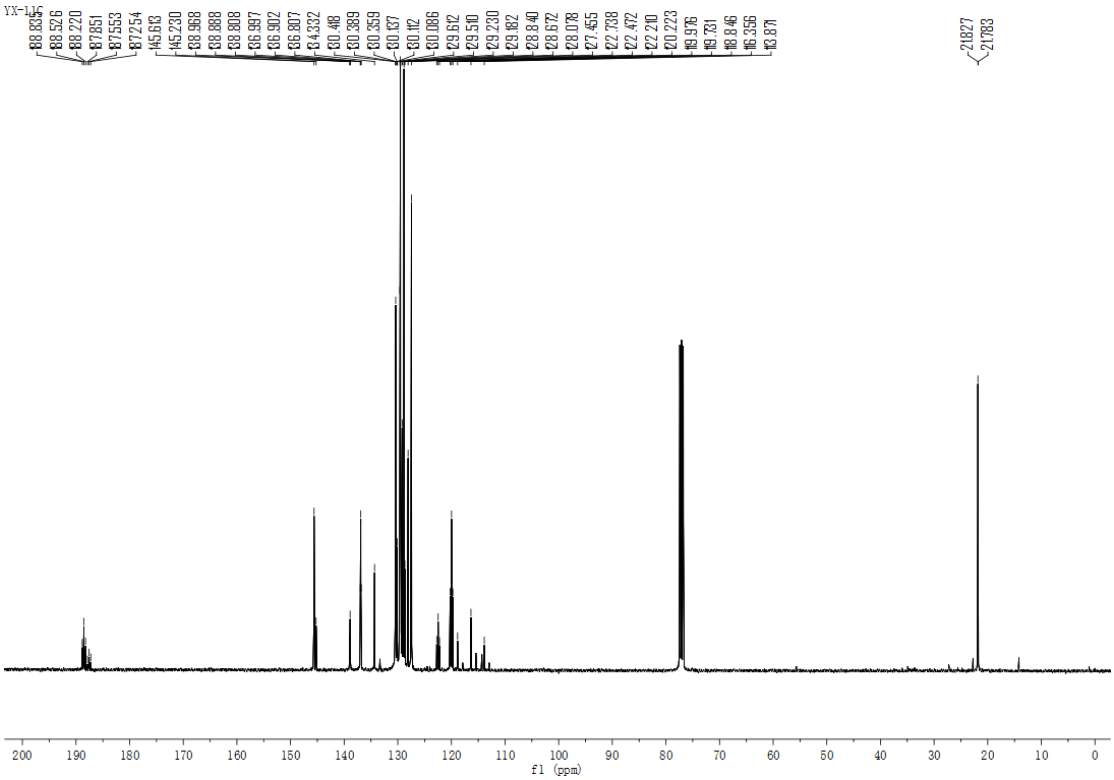
**$^{1}$H NMR (400 MHz, $CDCl_3$):**




## $^{19}$F NMR (376 MHz, $CDCl_3$):

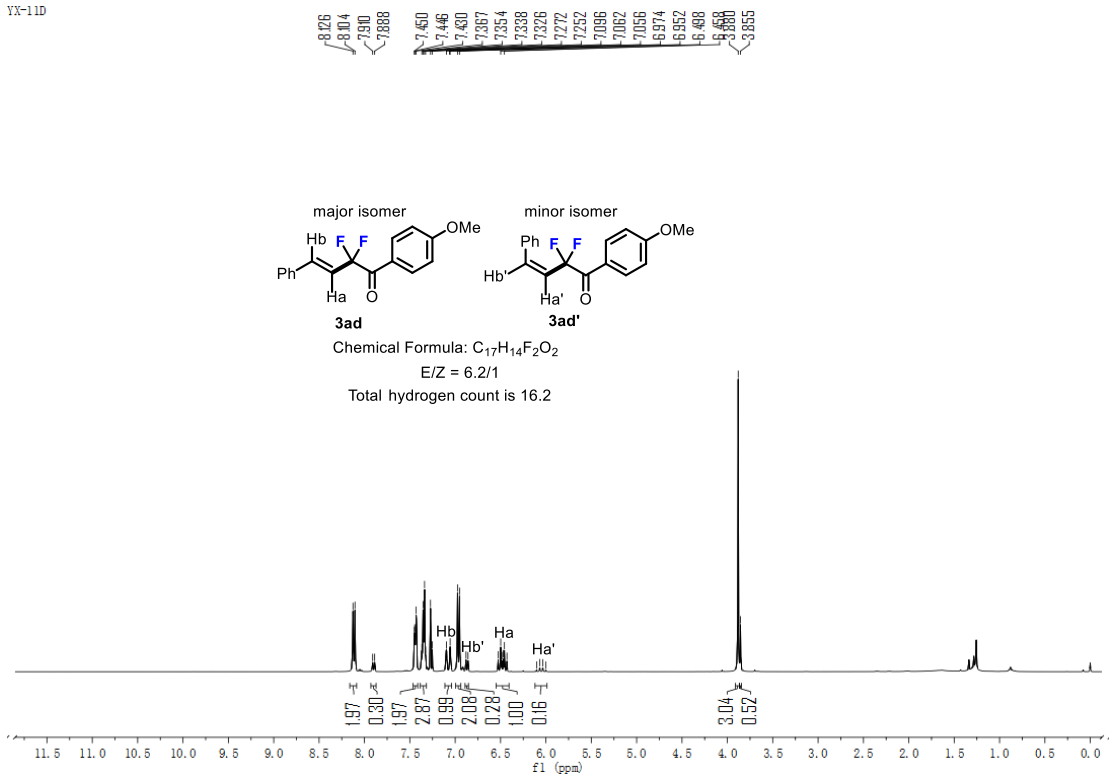



## $^{13}$C NMR (100 MHz, $CDCl_3$):

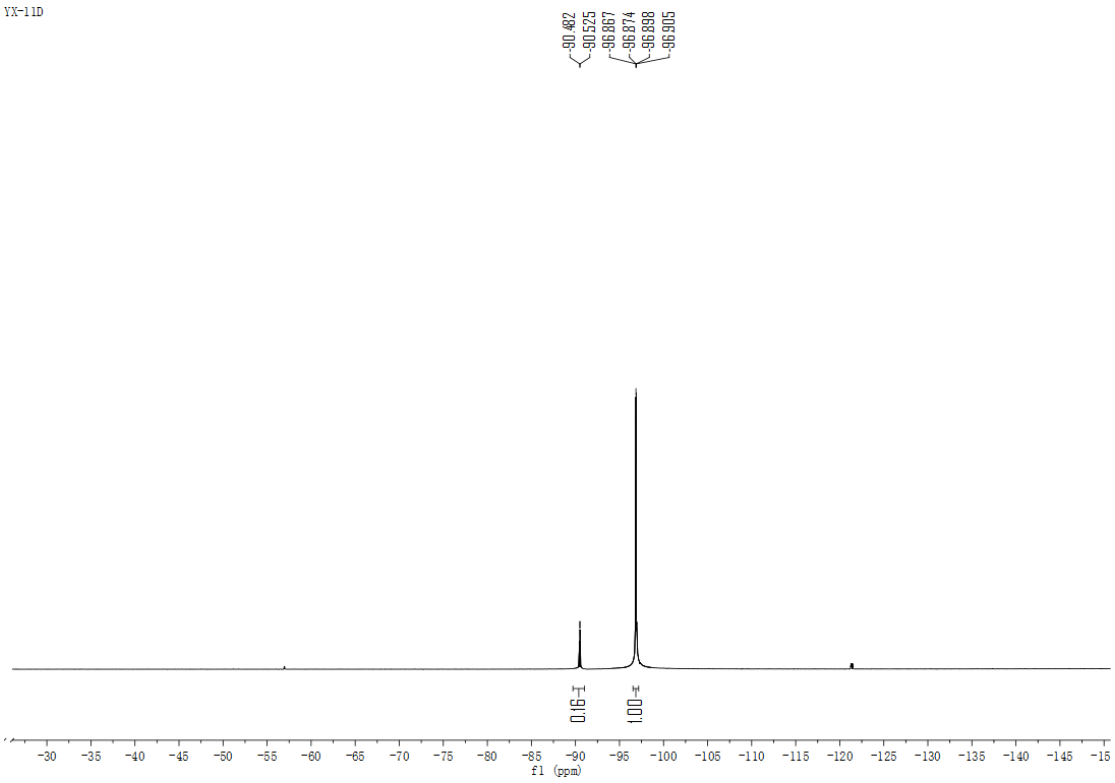


**(*E*)-2,2-difluoro-1-(4-methoxyphenyl)-4-phenylbut-3-en-1-one (3ad)**

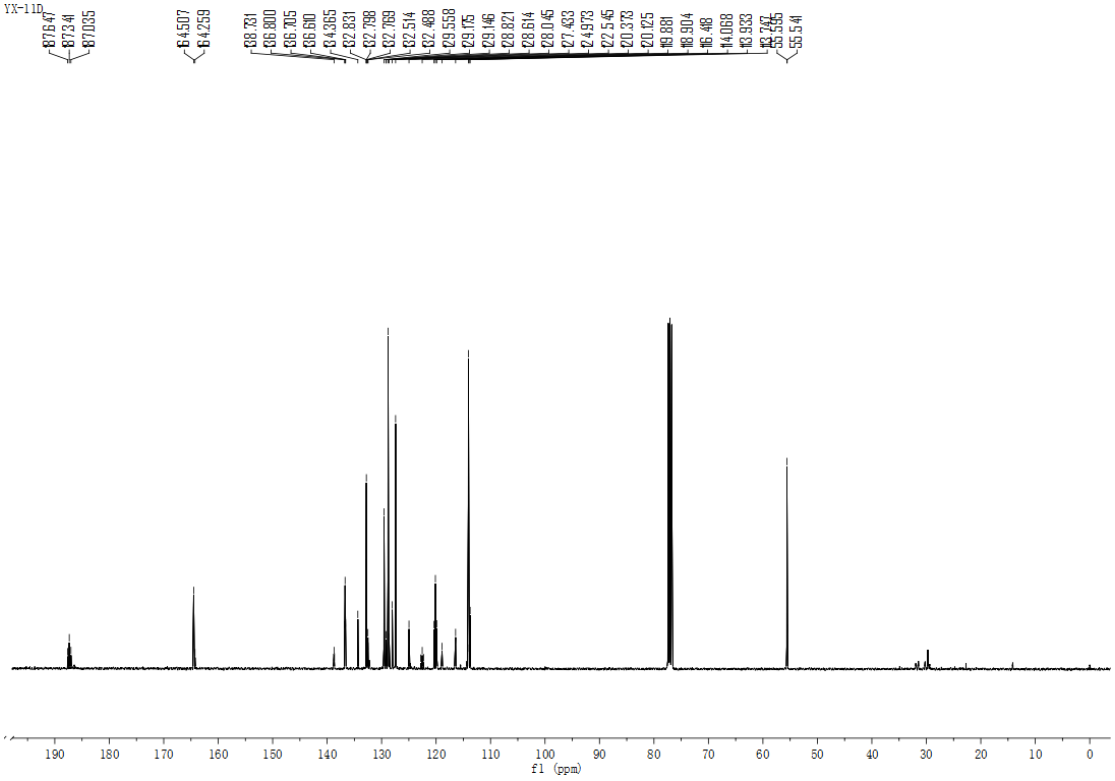
**$^{1}$H NMR (400 MHz, $CDCl_3$):**




**$^{19}$F NMR (376 MHz, $CDCl_3$):**

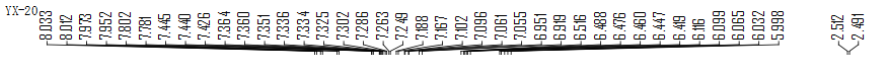


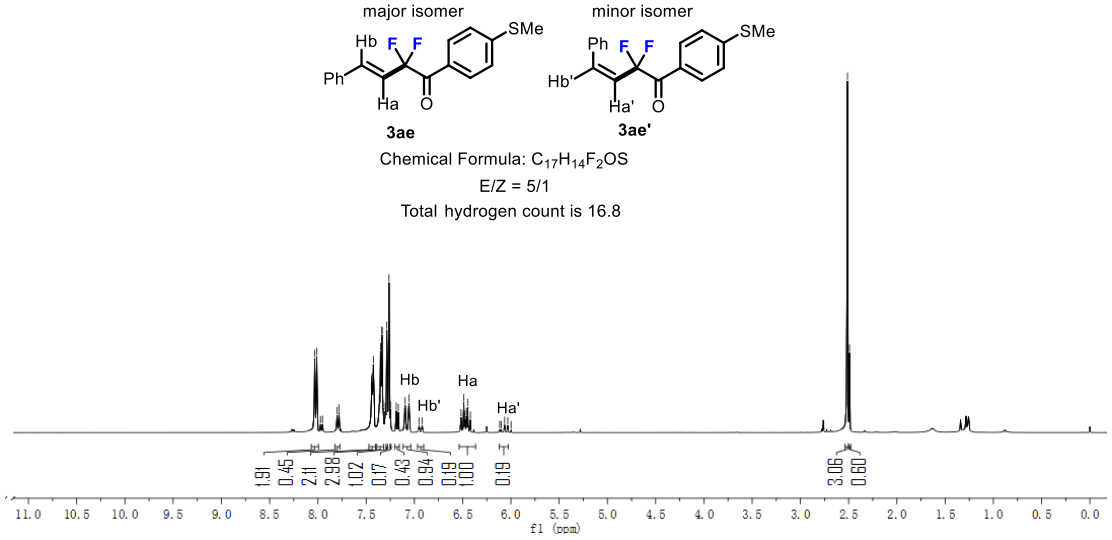

**$^{13}$C NMR (100 MHz, $CDCl_3$):**



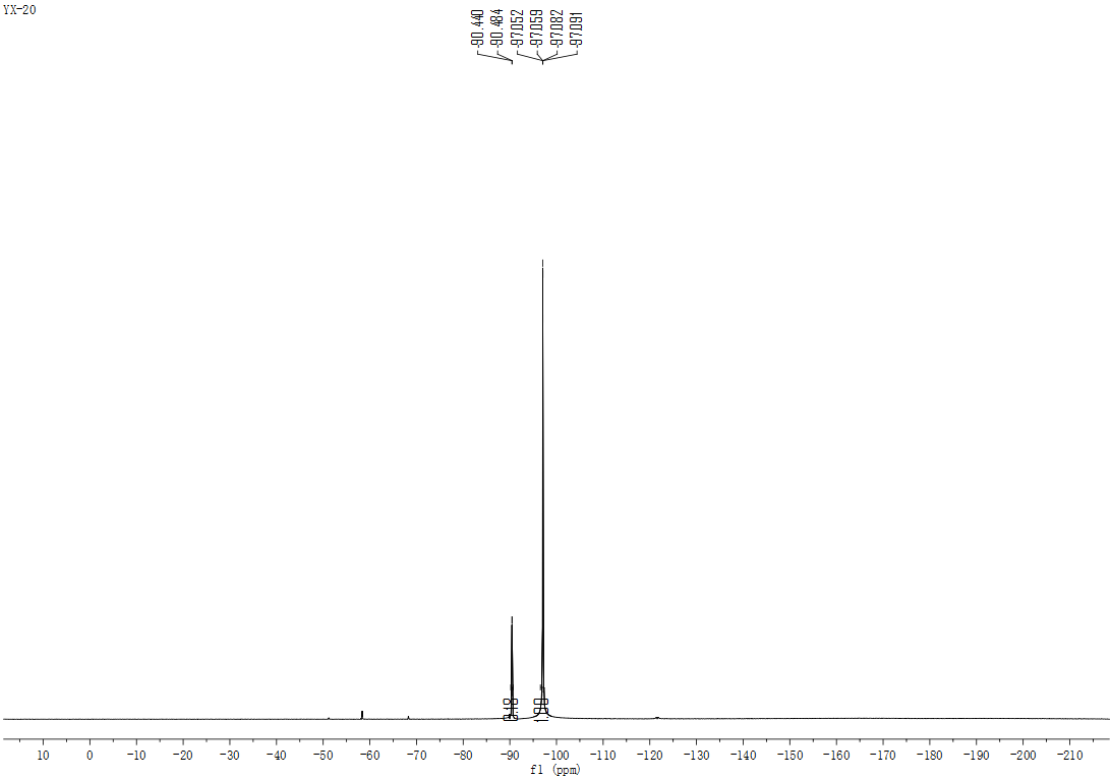

**(*E*)-2,2-difluoro-1-(4-(methylthio)phenyl)-4-phenylbut-3-en-1-one (3ae)**

**$^{1}$H NMR (400 MHz, $CDCl_3$):**

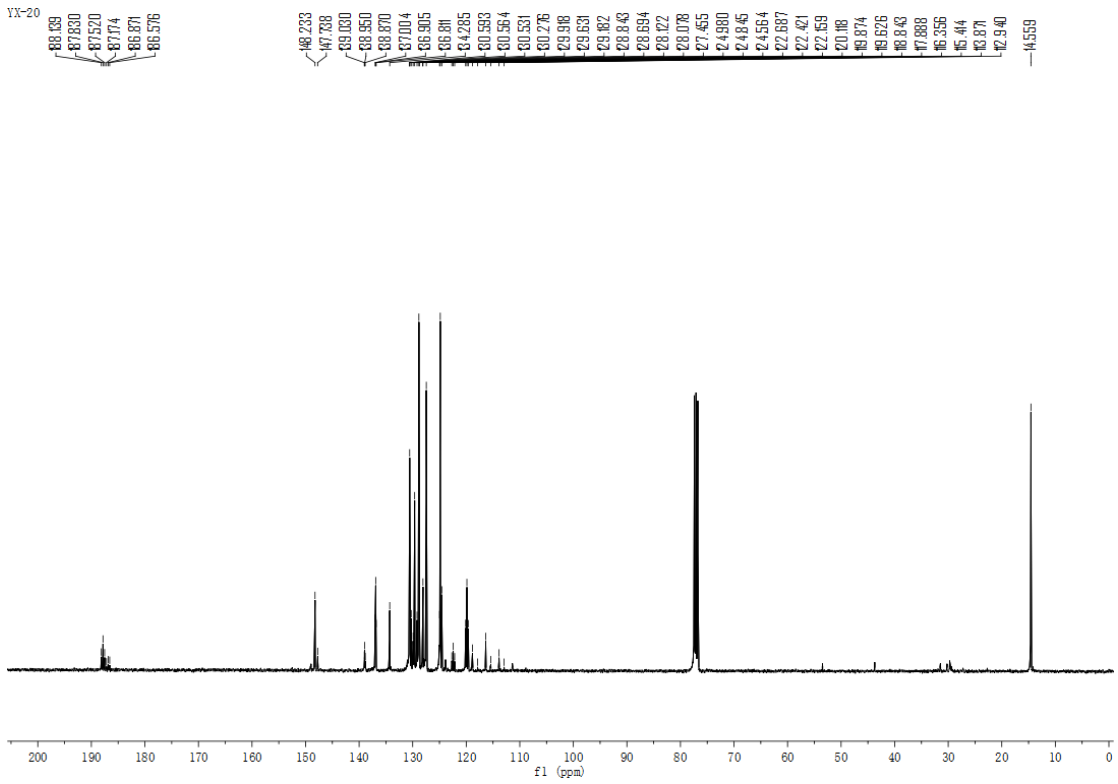





## $^{19}$F NMR (376 MHz, $CDCl_3$):

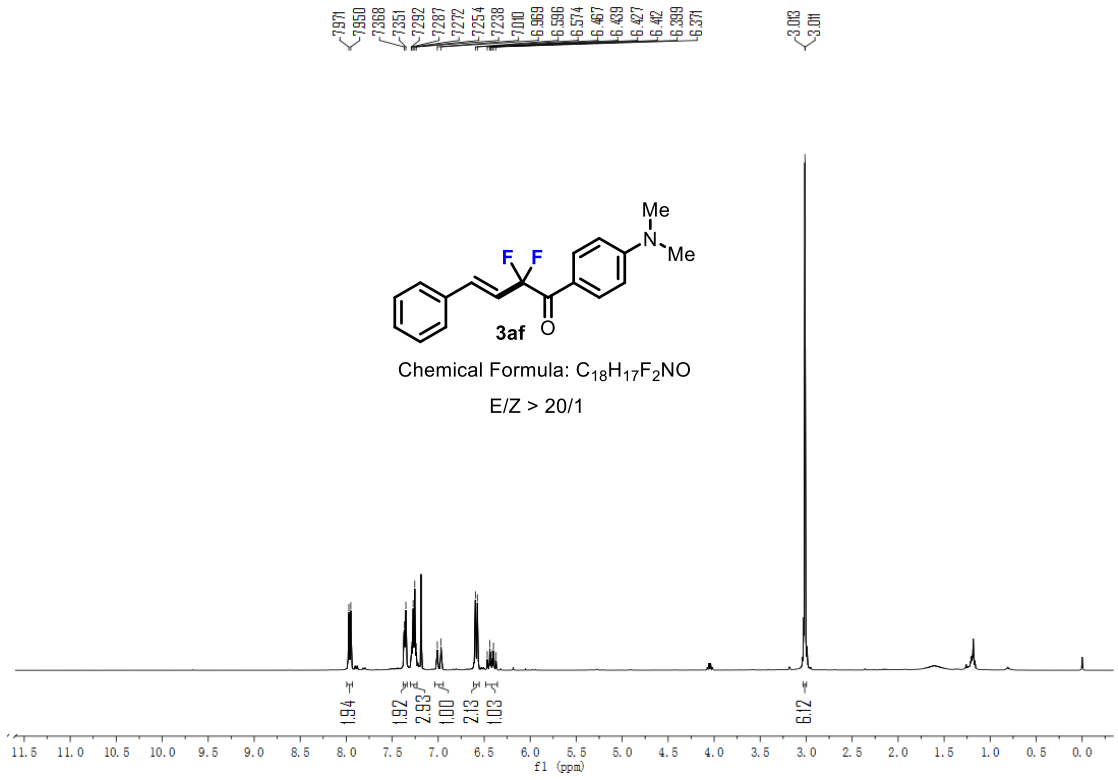



## $^{13}$C NMR (100 MHz, $CDCl_3$):

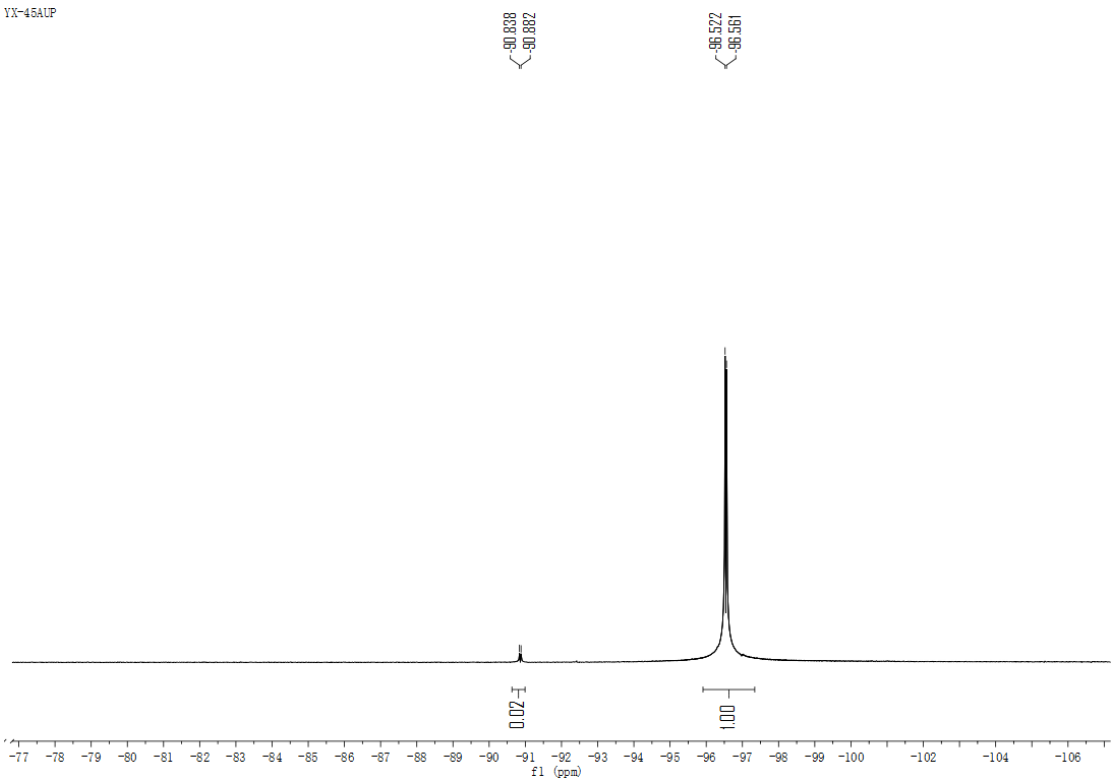


**(*E*)-1-(4-(dimethylamino)phenyl)-2,2-difluoro-4-phenylbut-3-en-1-one (3af)**

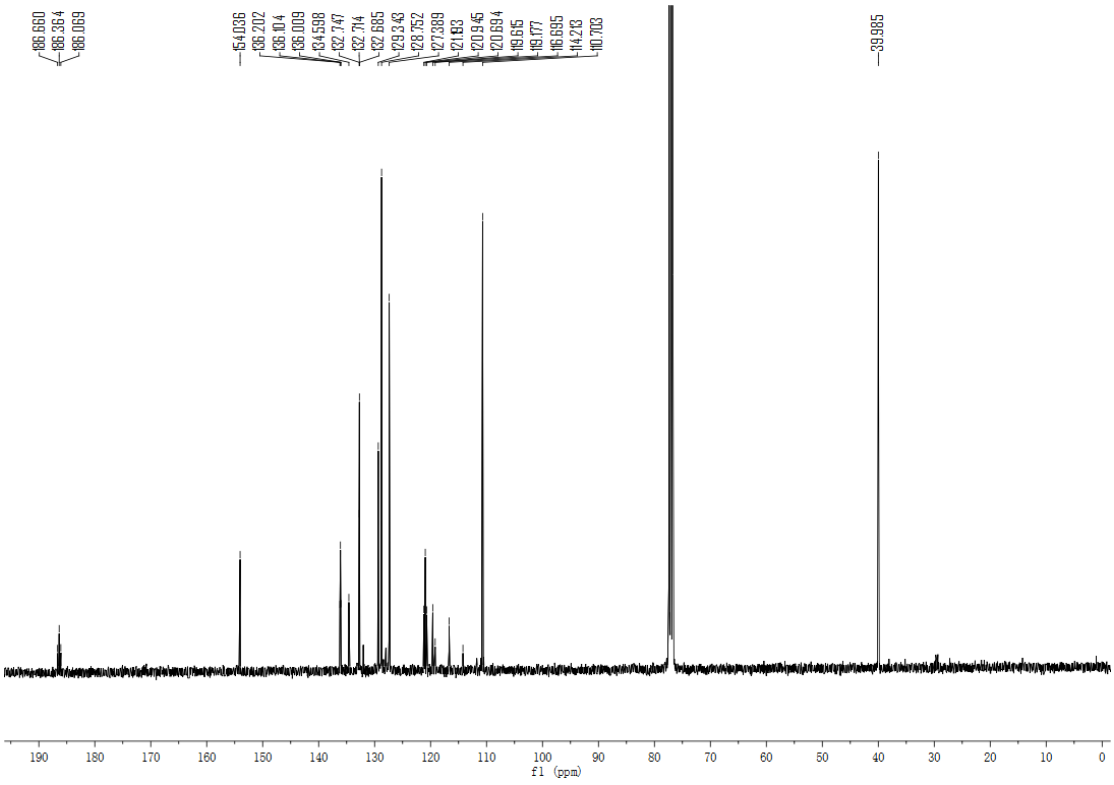
**$^{1}$H NMR (400 MHz, $CDCl_3$):**




**$^{19}$F NMR (376 MHz, $CDCl_3$):**

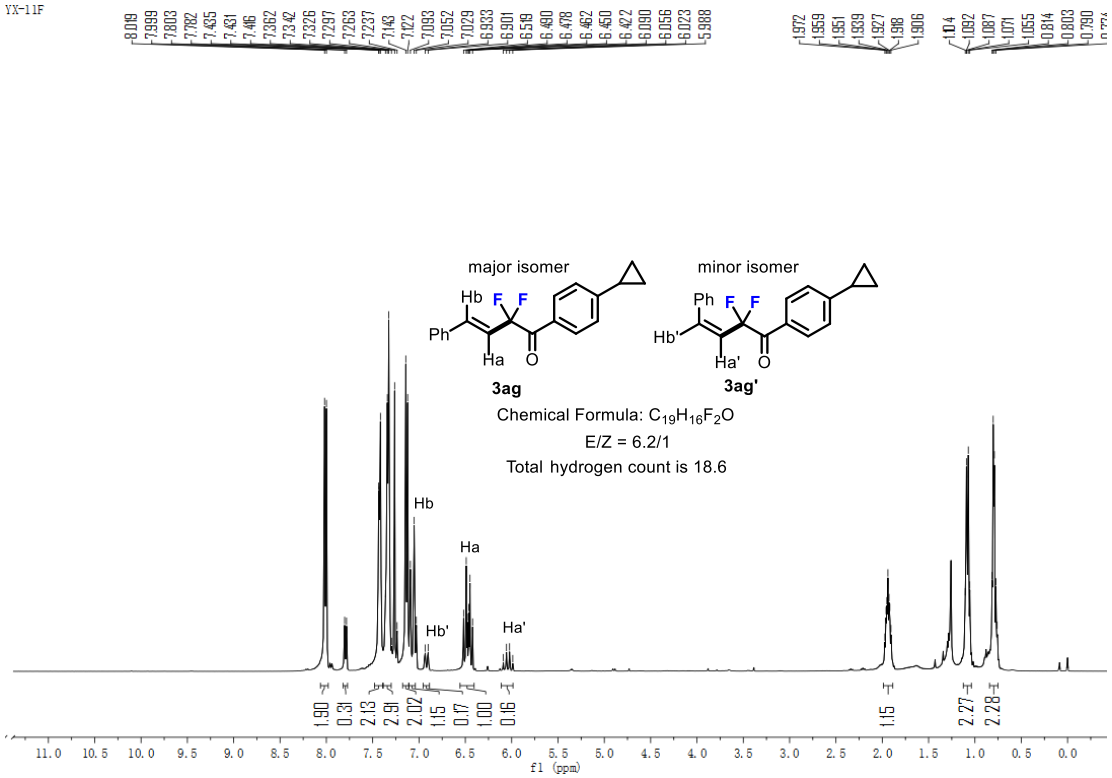



**$^{13}$C NMR (100 MHz, $CDCl_3$):**

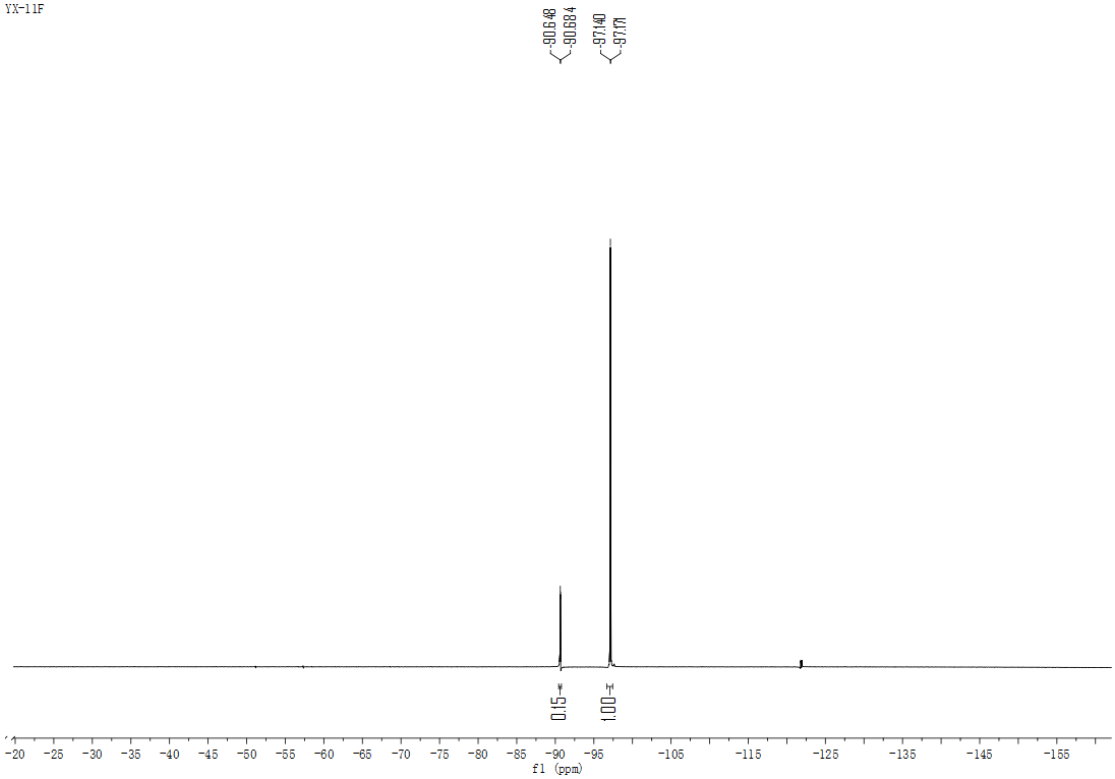



**(*E*)-1-(4-cyclopropylphenyl)-2,2-difluoro-4-phenylbut-3-en-1-one (3ag)**

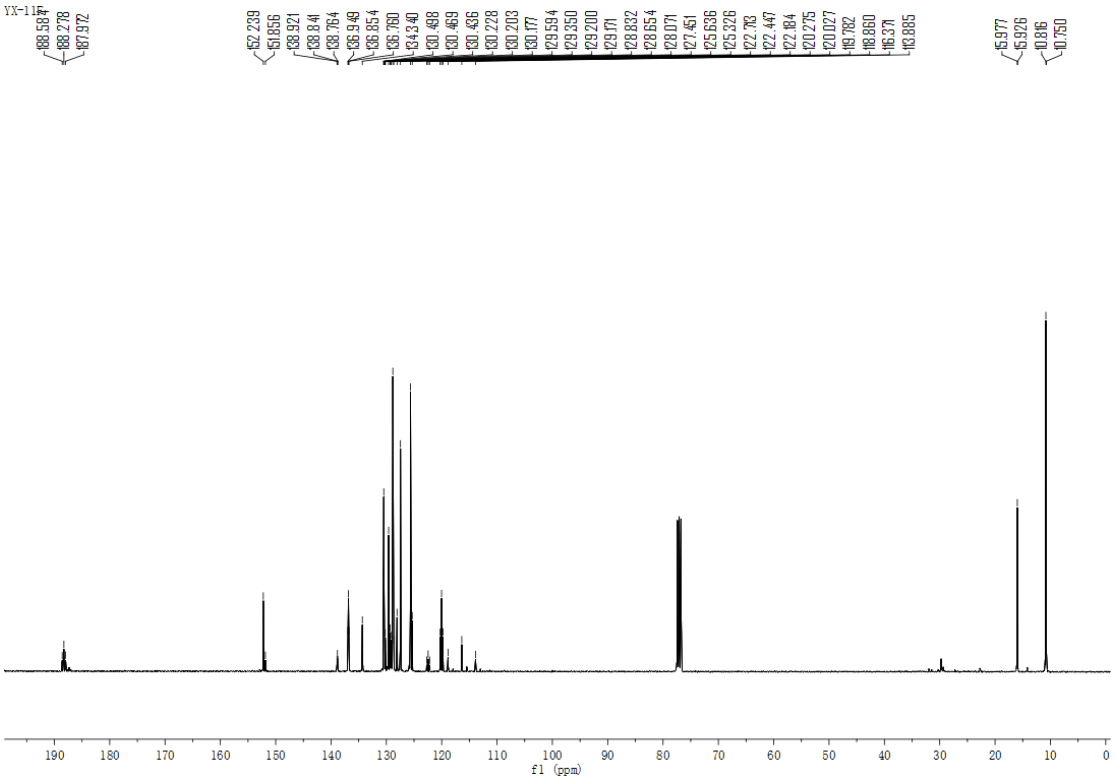
**$^{1}$H NMR (400 MHz, $CDCl_3$):**




## $^{19}$F NMR (376 MHz, $CDCl_3$):

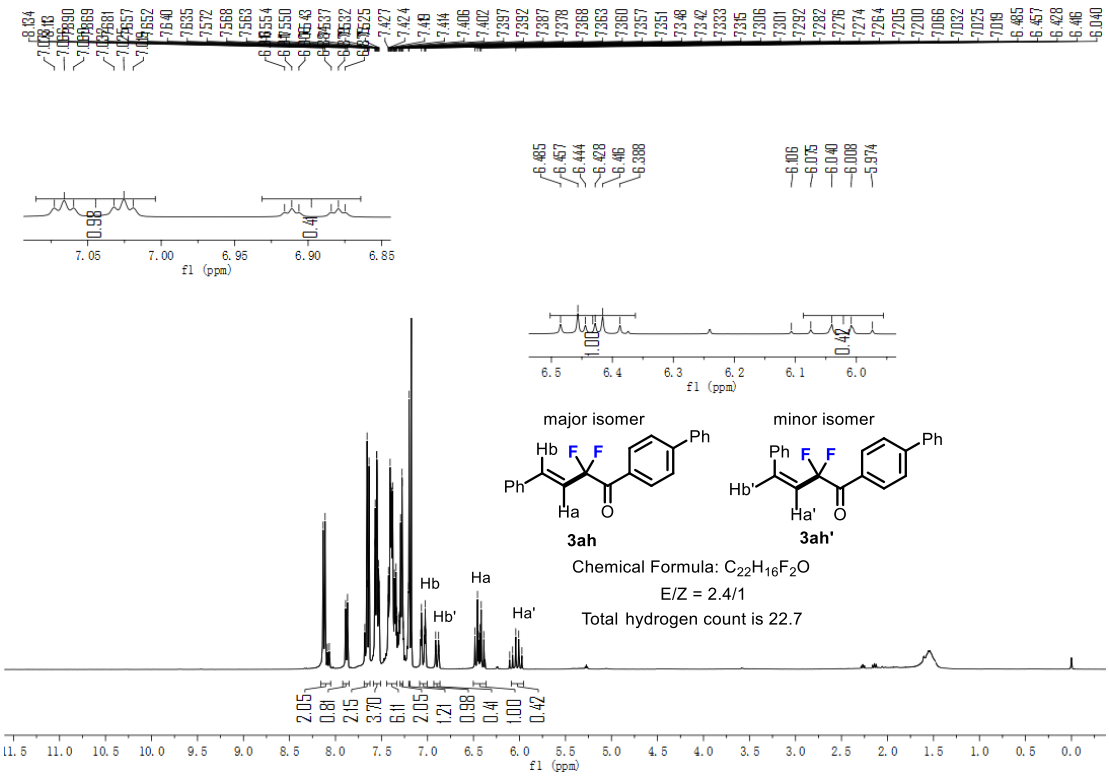



## $^{13}$C NMR (100 MHz, $CDCl_3$):

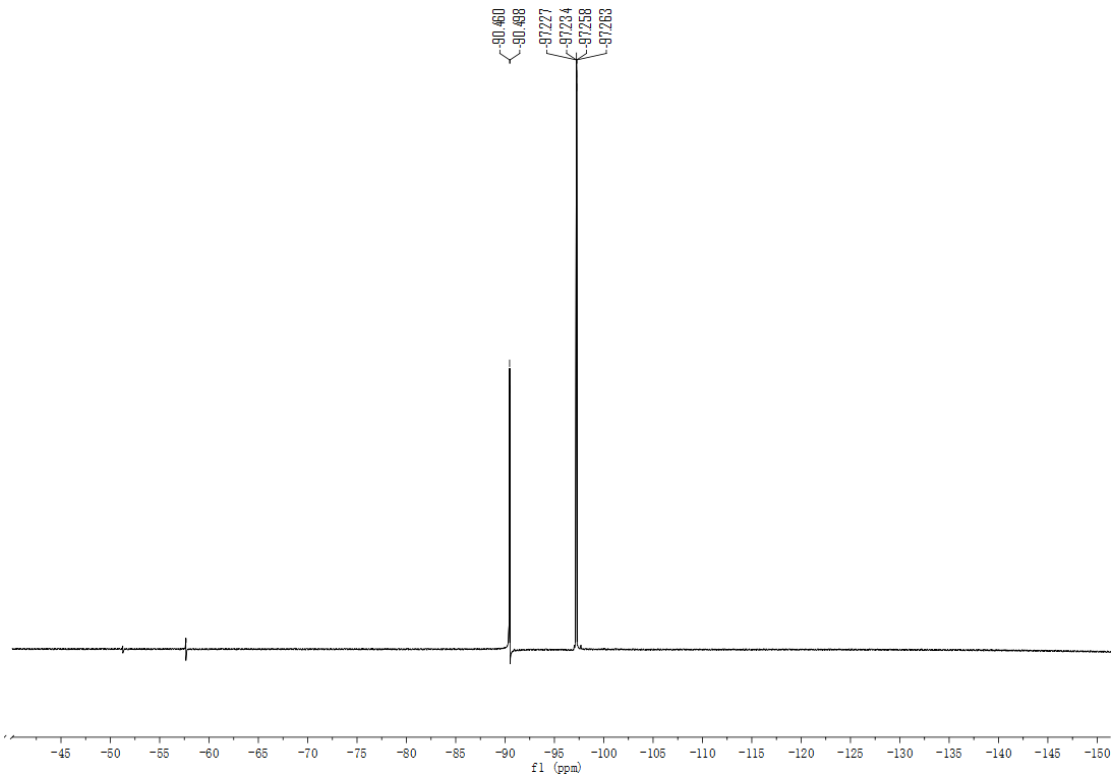


**(E)-1-([1,1'-biphenyl]-4-yl)-2,2-difluoro-4-phenylbut-3-en-1-one (3ah)**

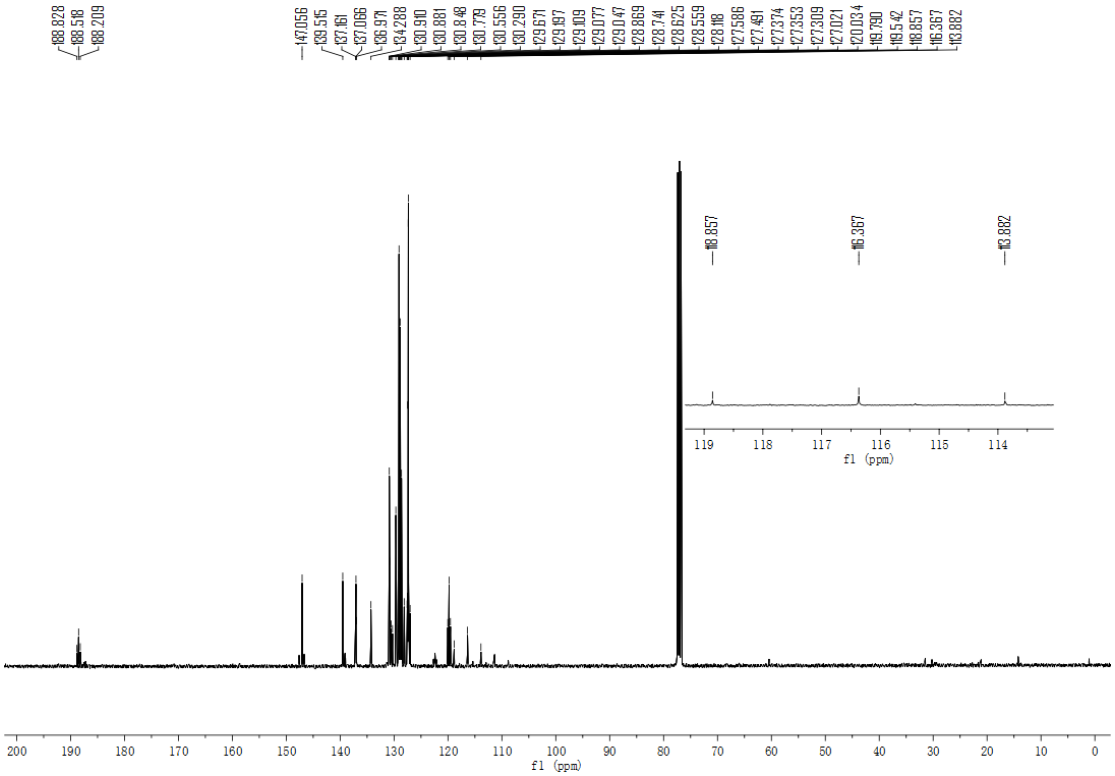
**$^{1}$H NMR (400 MHz, $CDCl_3$):**




**$^{19}$F NMR (376 MHz, $CDCl_3$):**

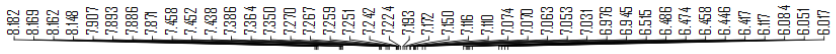


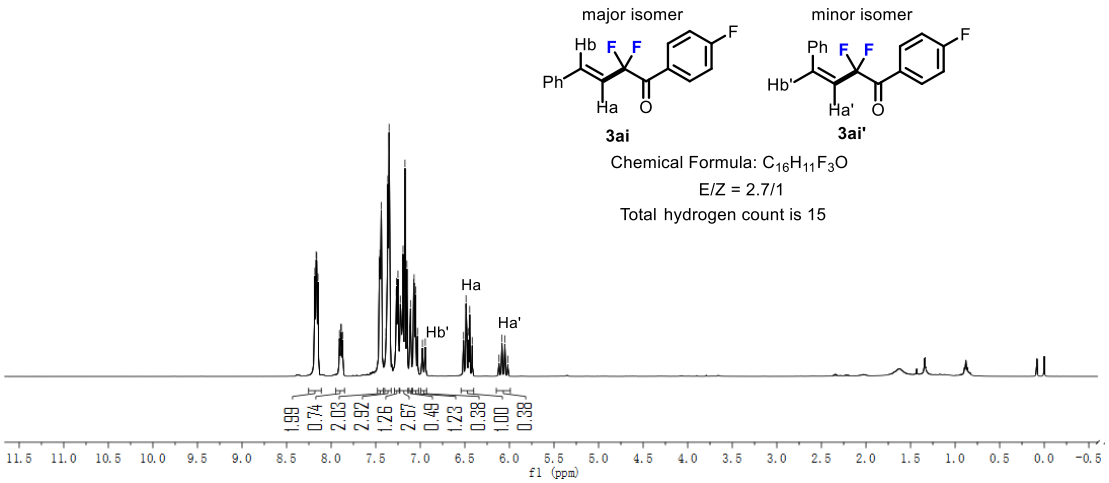

**$^{13}$C NMR (100 MHz, $CDCl_3$):**



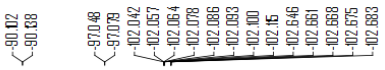

**(E)-2,2-difluoro-1-(4-fluorophenyl)-4-phenylbut-3-en-1-one (3ai)**

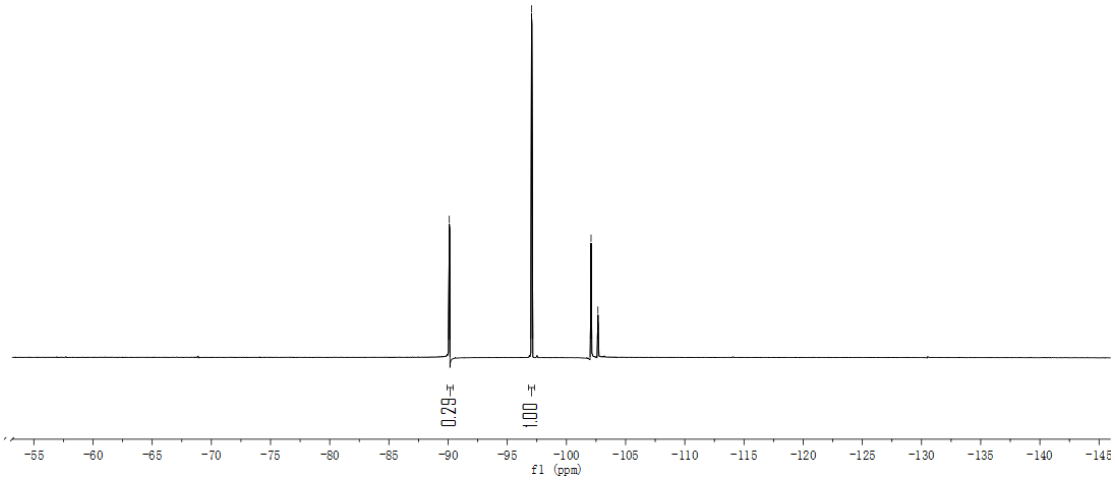
**$^{1}$H NMR (400 MHz, $CDCl_3$):**



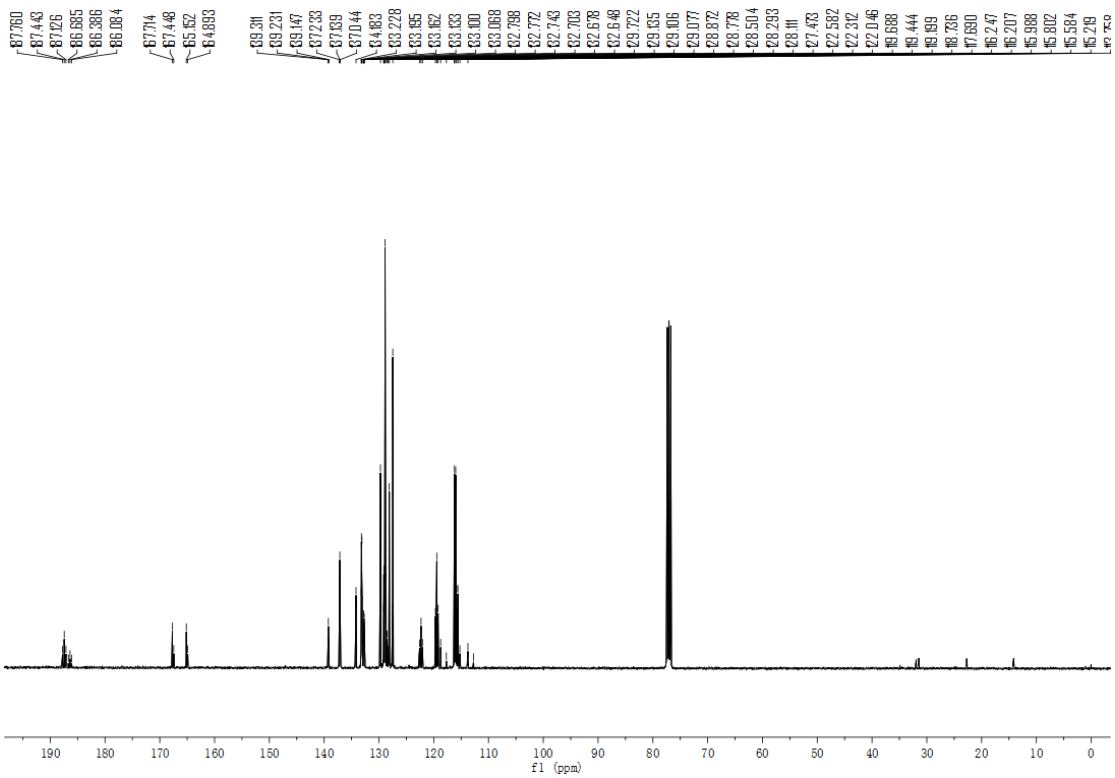



**$^{19}$F NMR (376 MHz, $CDCl_3$):**



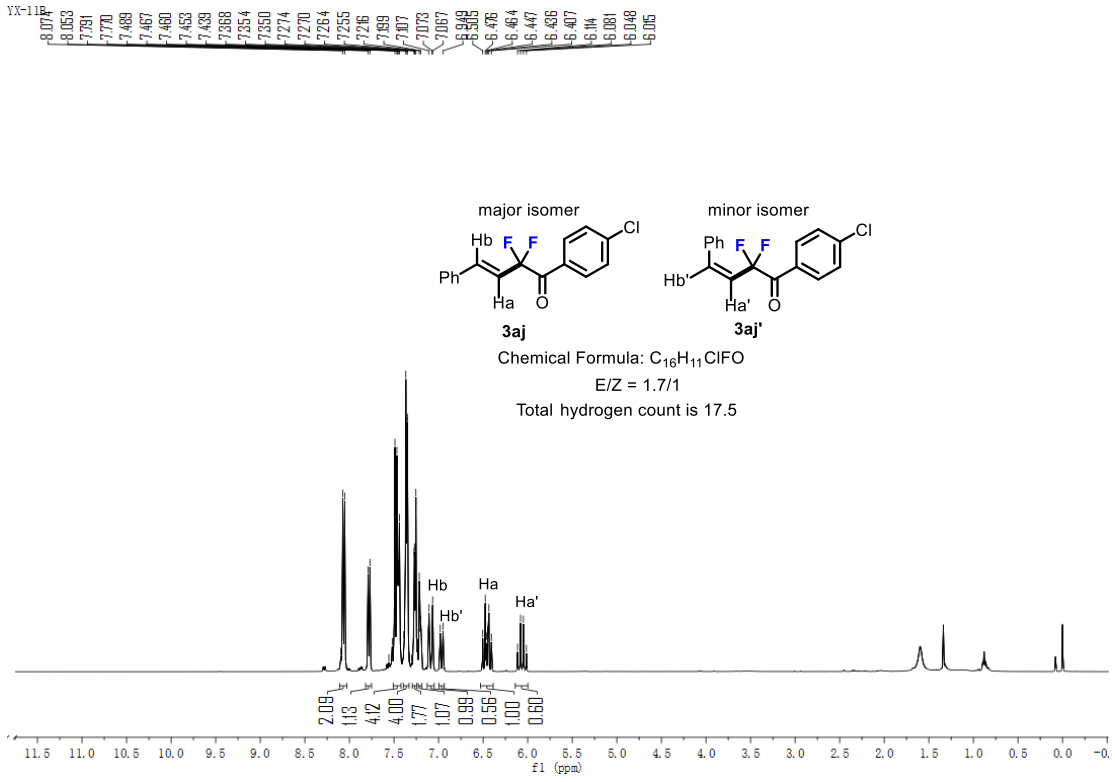



**$^{13}$C NMR (100 MHz, $CDCl_3$):**

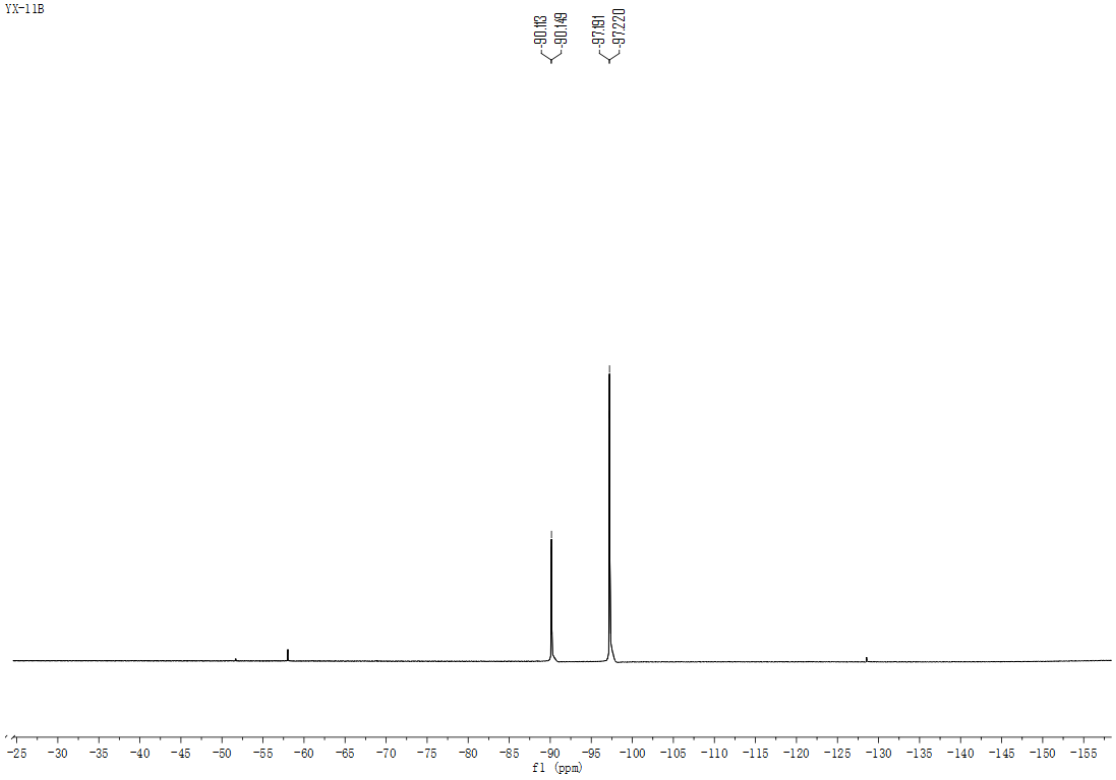


**(E)-1-(4-chlorophenyl)-2,2-difluoro-4-phenylbut-3-en-1-one (3aj)**

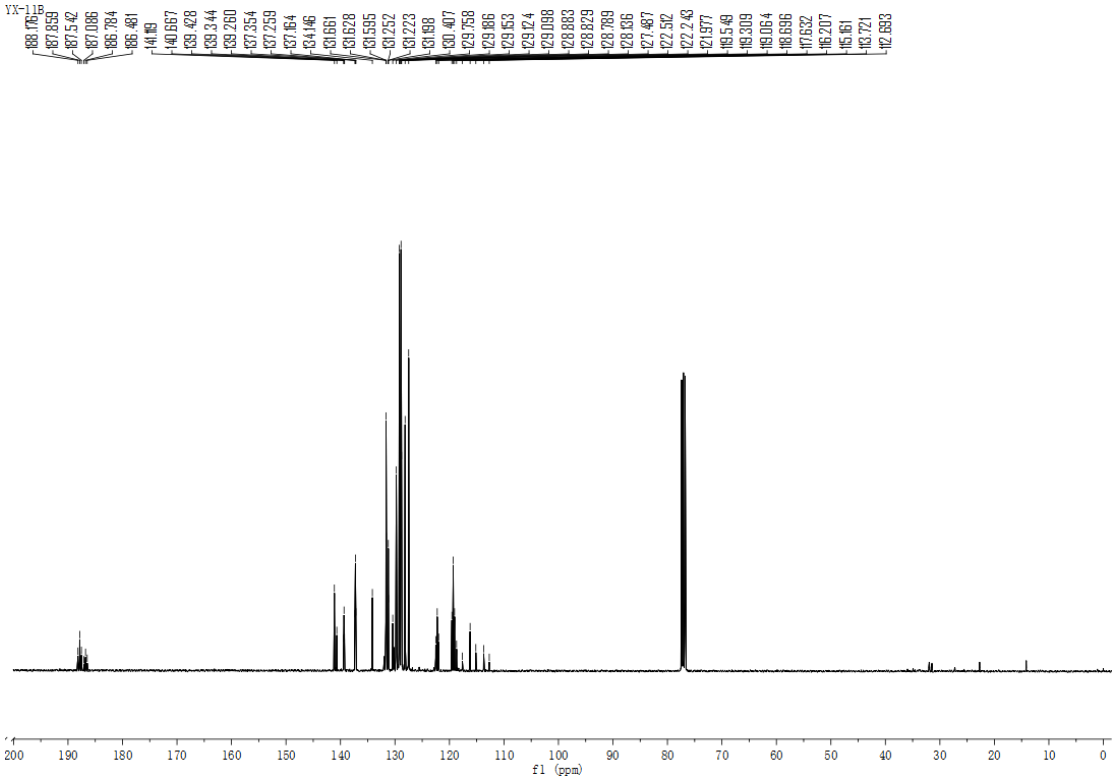
**$^{1}$H NMR (400 MHz, $CDCl_3$):**




**$^{19}$F NMR (376 MHz, $CDCl_3$):**

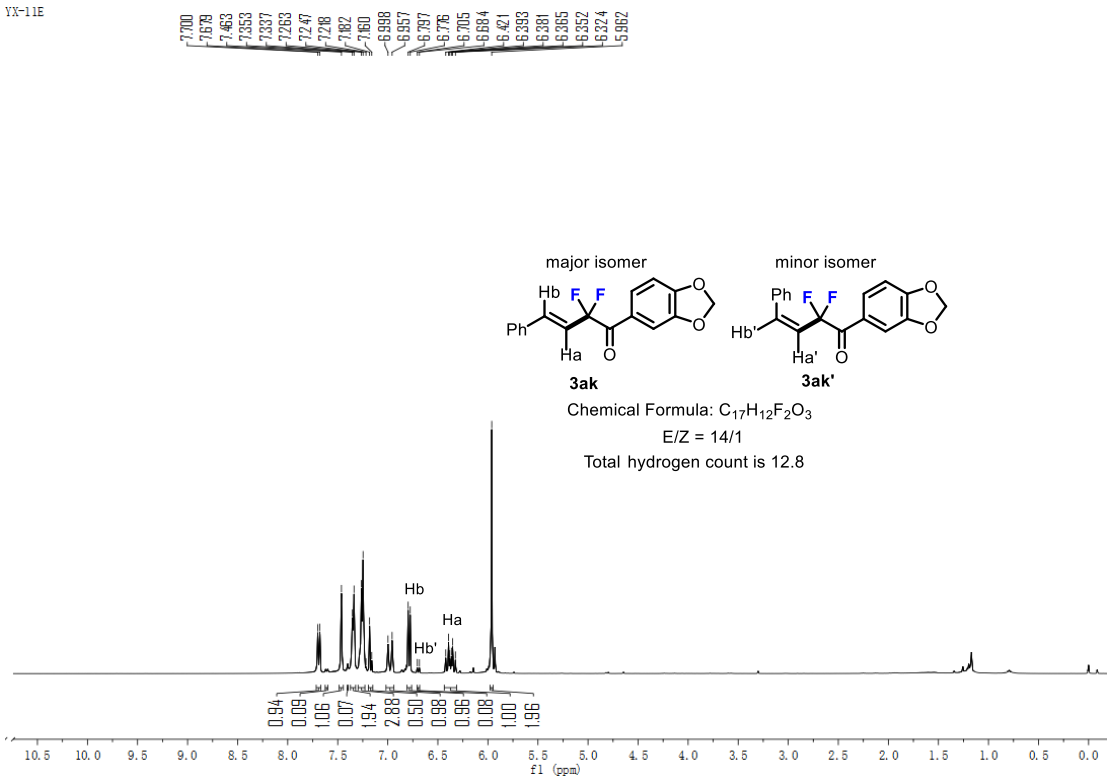



**$^{13}$C NMR (100 MHz, $CDCl_3$):**

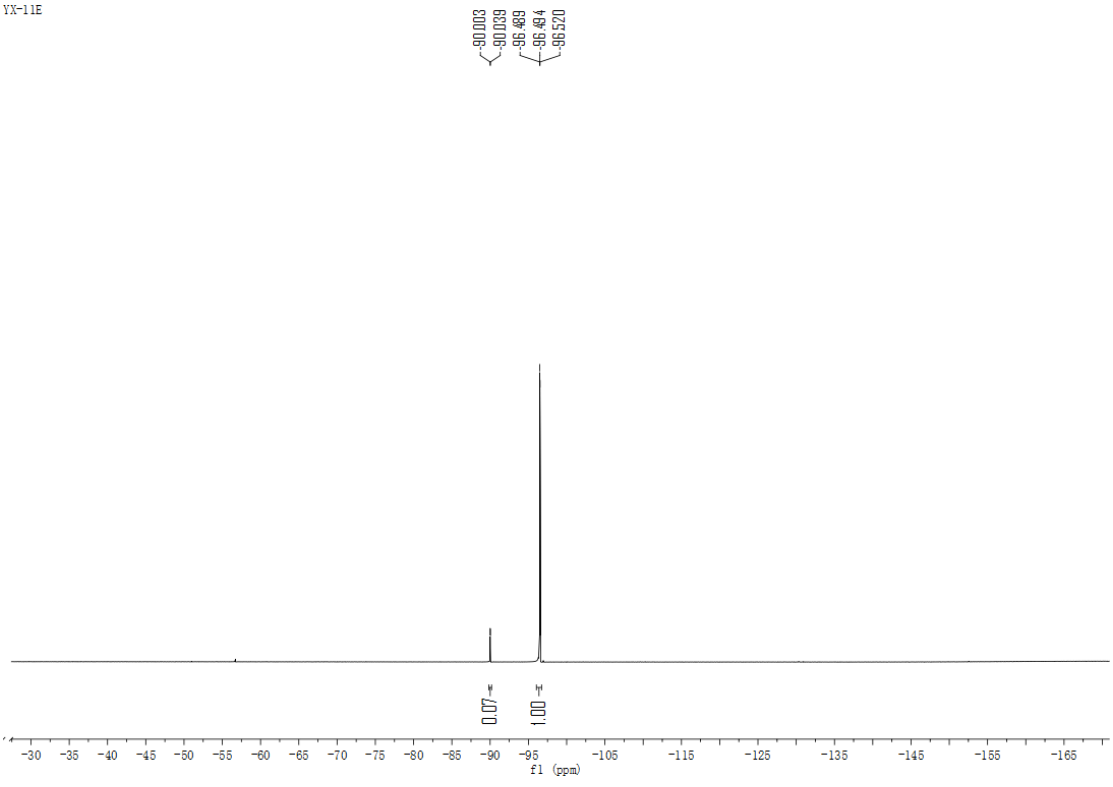



**(*E*)-1-(benzo[d][1,3]dioxol-5-yl)-2,2-difluoro-4-phenylbut-3-en-1-one (3ak)**

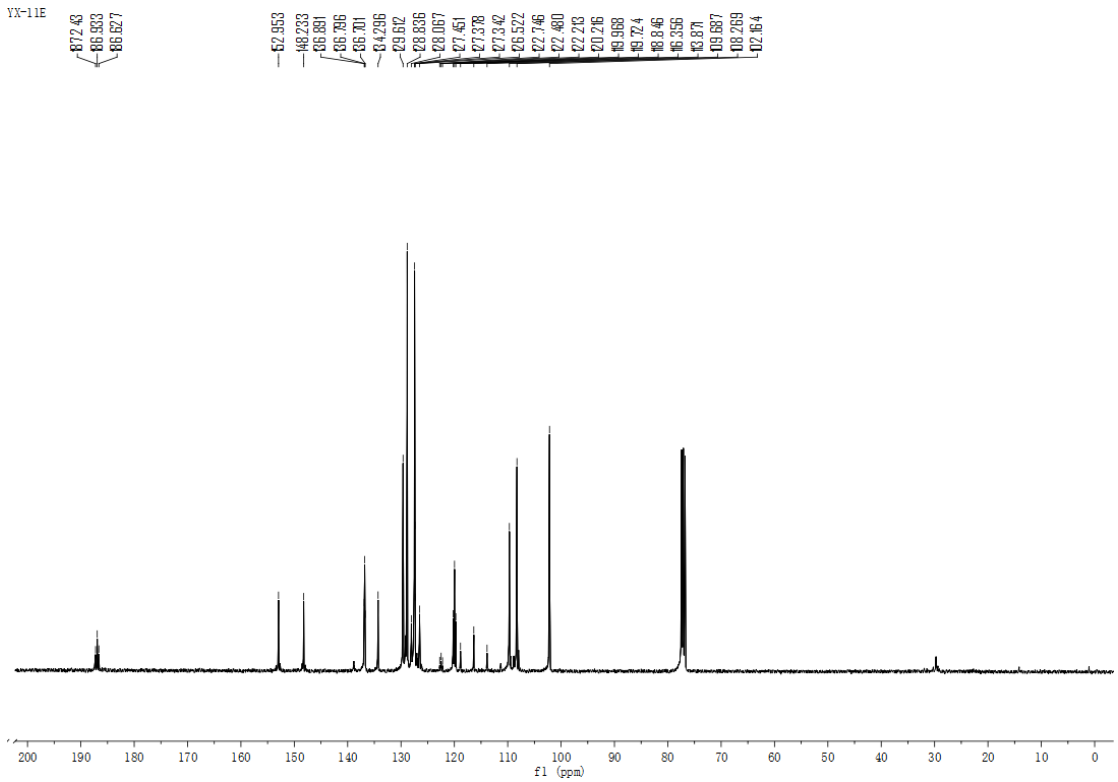
**$^{1}$H NMR (400 MHz, $CDCl_3$):**




## $^{19}$F NMR (376 MHz, $CDCl_3$):

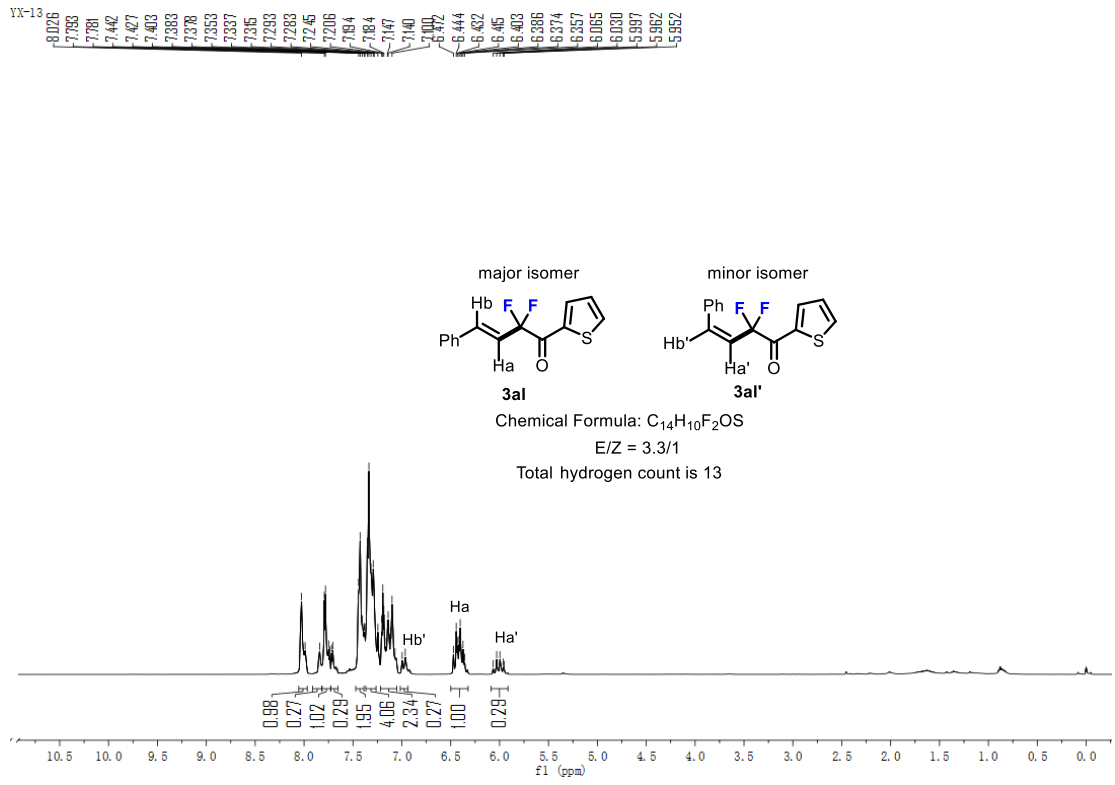



## $^{13}$C NMR (100 MHz, $CDCl_3$):

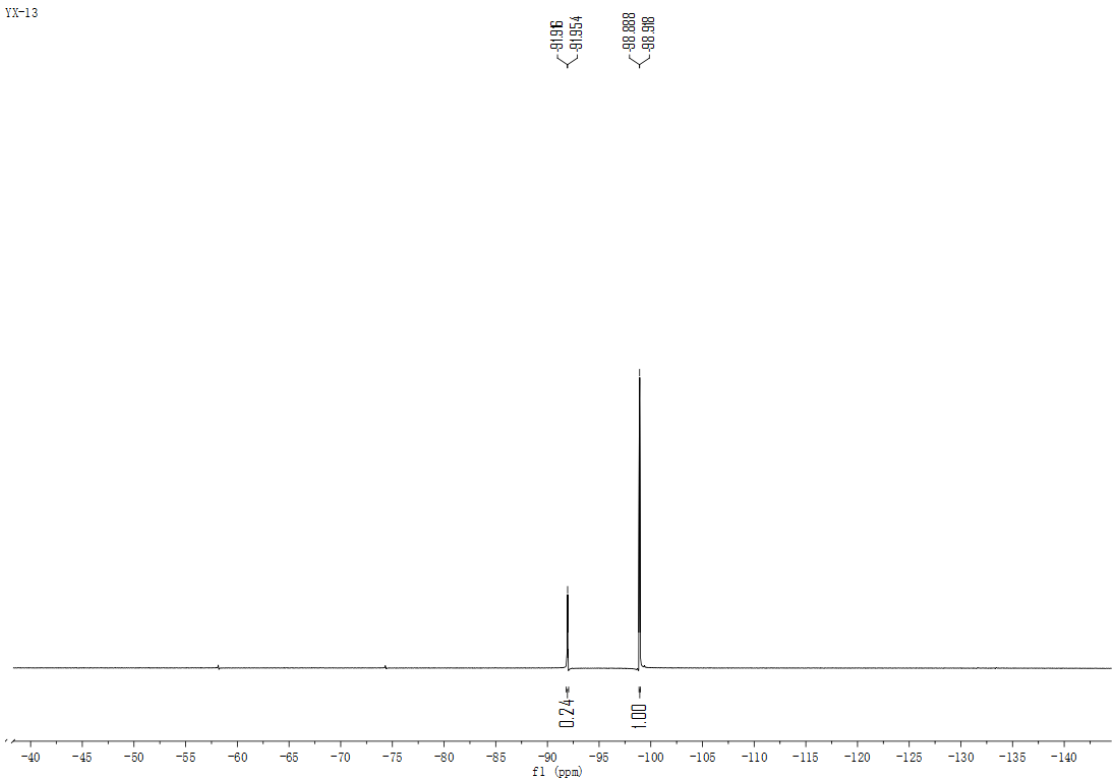



**(*E*)-2,2-difluoro-4-phenyl-1-(thiophen-2-yl)but-3-en-1-one (3al)**

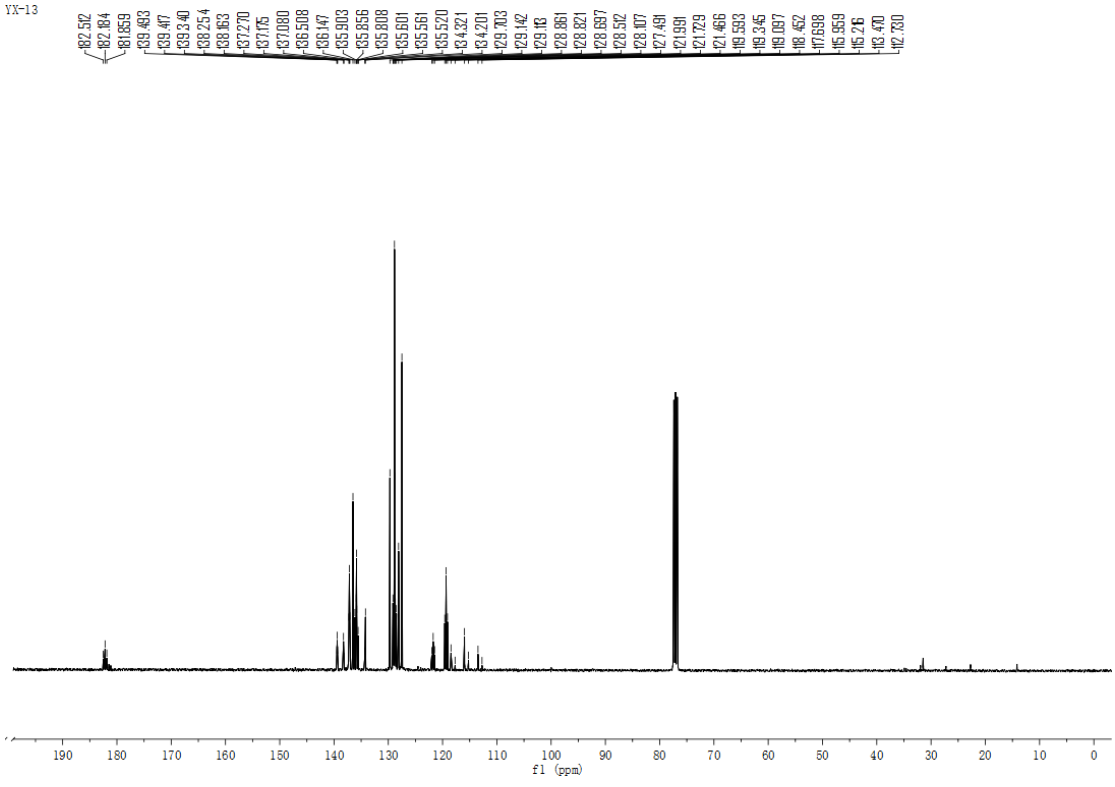
**$^{1}$H NMR (400 MHz, $CDCl_3$):**




**$^{19}$F NMR (376 MHz, $CDCl_3$):**

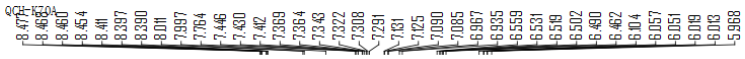



**$^{3}$C NMR (100 MHz, $CDCl_3$):**

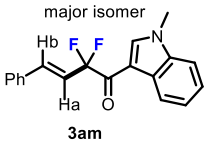



**(*E*)-2,2-difluoro-1-(1-methyl-1H-indol-3-yl)-4-phenylbut-3-en-1-one (3am)**

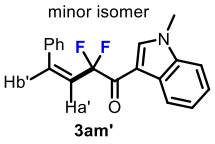
**$^{1}$H NMR (400 MHz, $CDCl_3$):**



major isomer




minor isomer

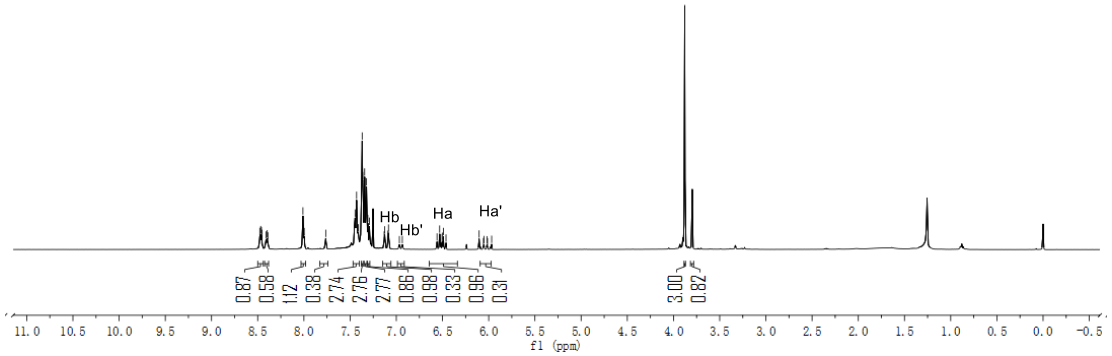



**3am** **3am'**

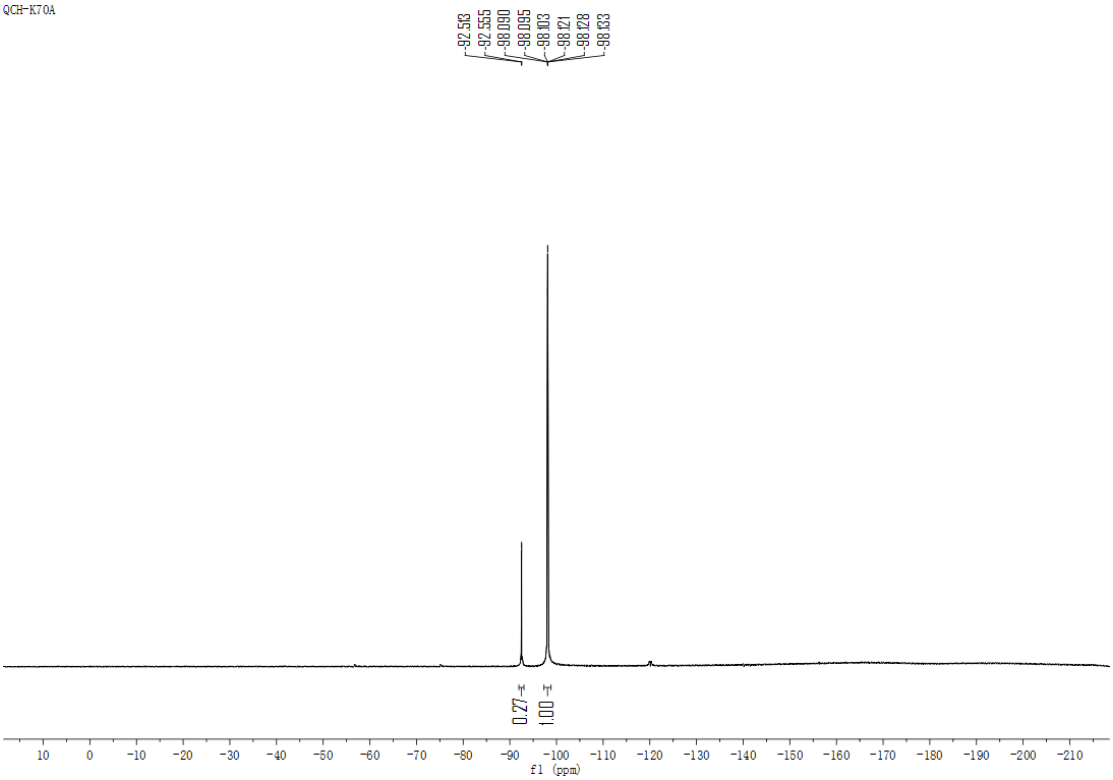
Chemical Formula: $C_{19}H_{15}F_2NO$

E/Z = 3/1

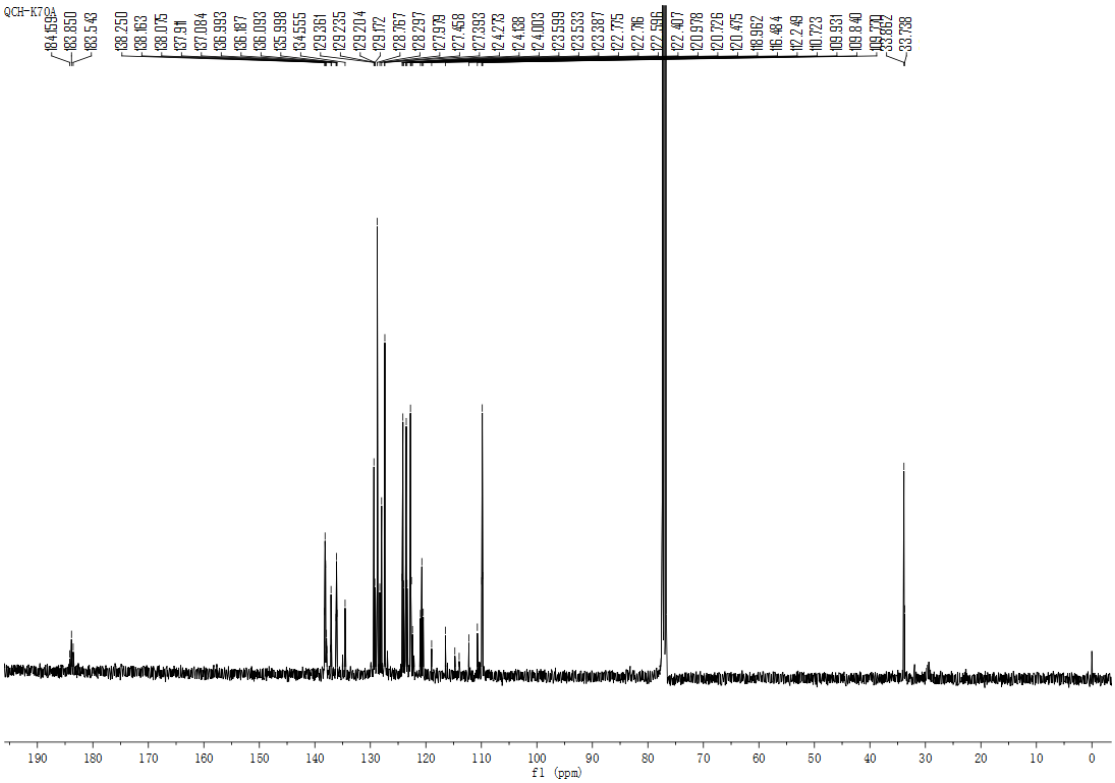
Total hydrogen count is 20




## $^{19}$F NMR (376 MHz, $CDCl_3$):

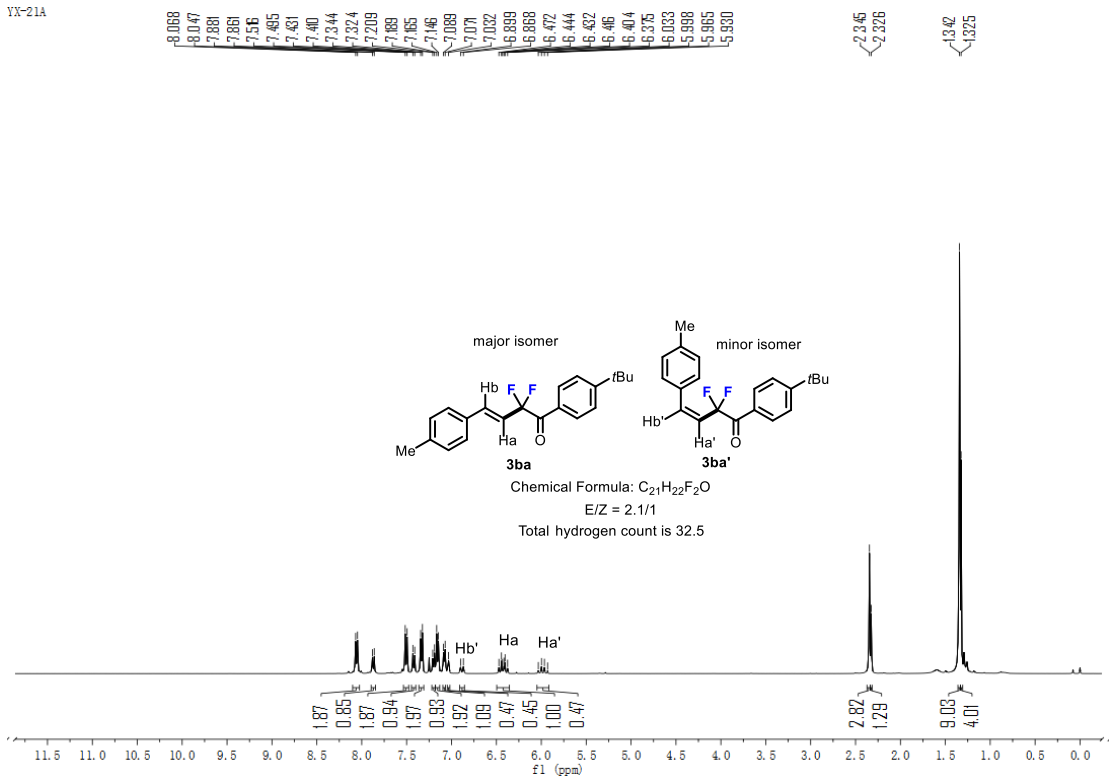



## $^{13}$C NMR (100 MHz, $CDCl_3$):

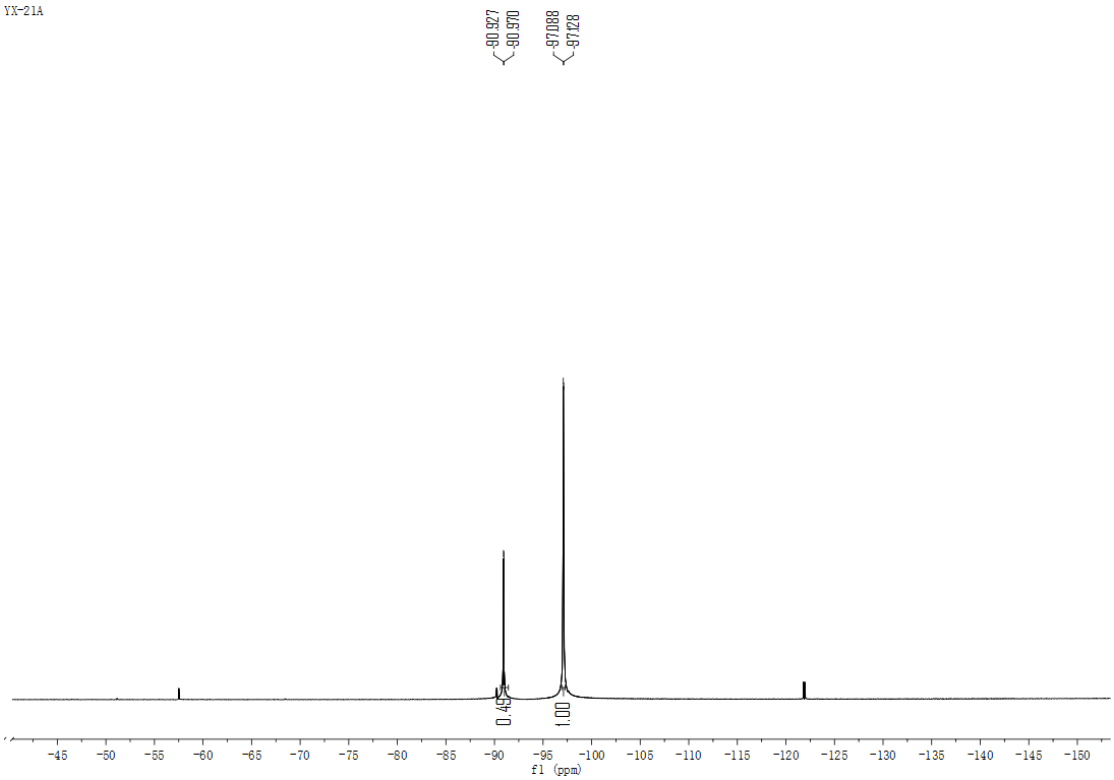



**(*E*)-1-(4-(tert-butyl)phenyl)-2,2-difluoro-4-(p-tolyl)but-3-en-1-one (3ba)**

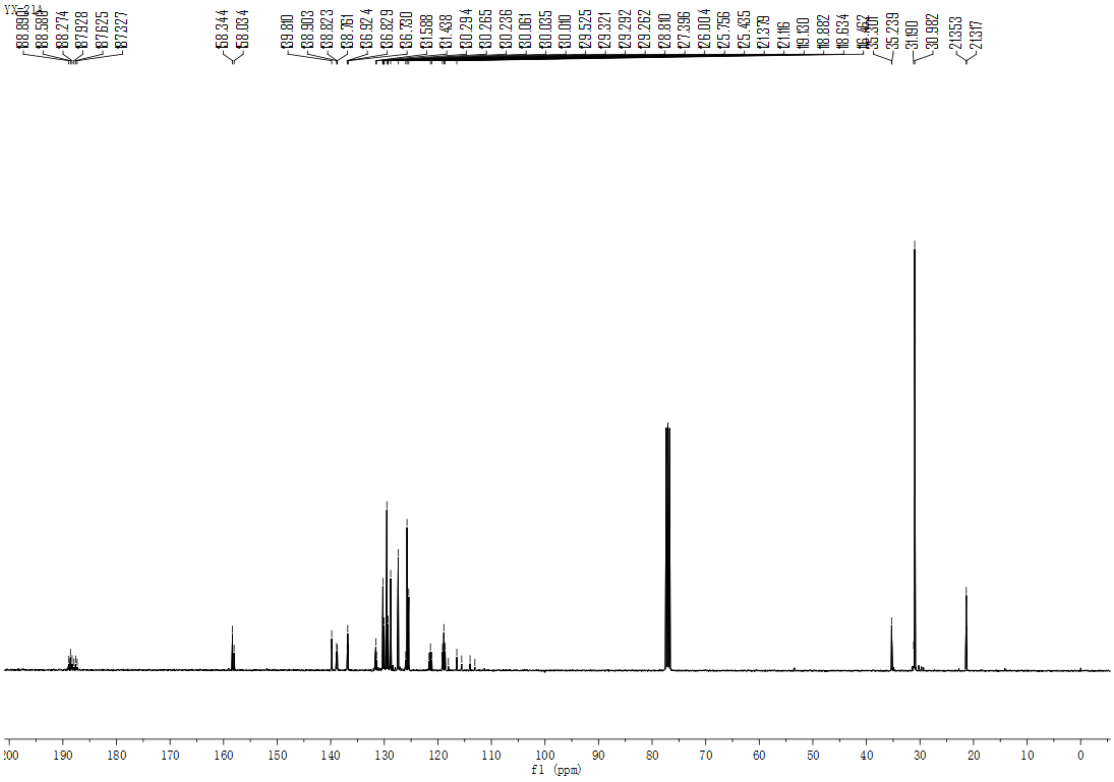
**$^{1}$H NMR (400 MHz, $CDCl_3$):**




**$^{19}$F NMR (376 MHz, $CDCl_3$):**

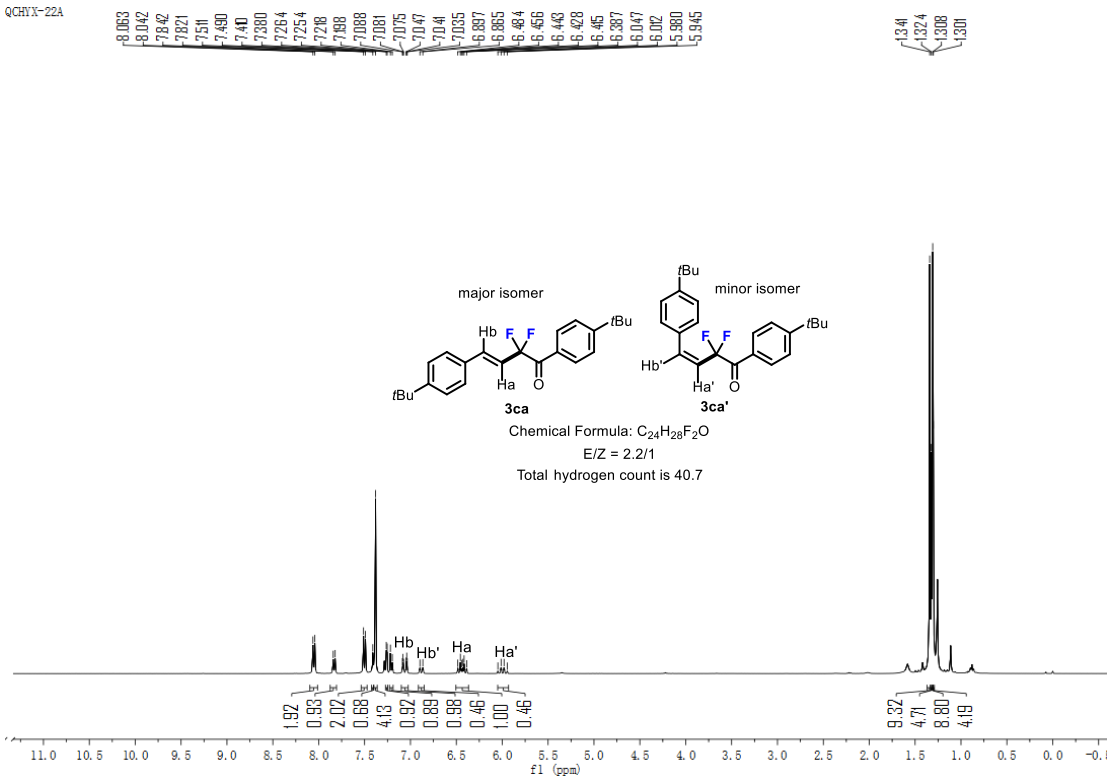



**$^{13}$C NMR (100 MHz, $CDCl_3$):**

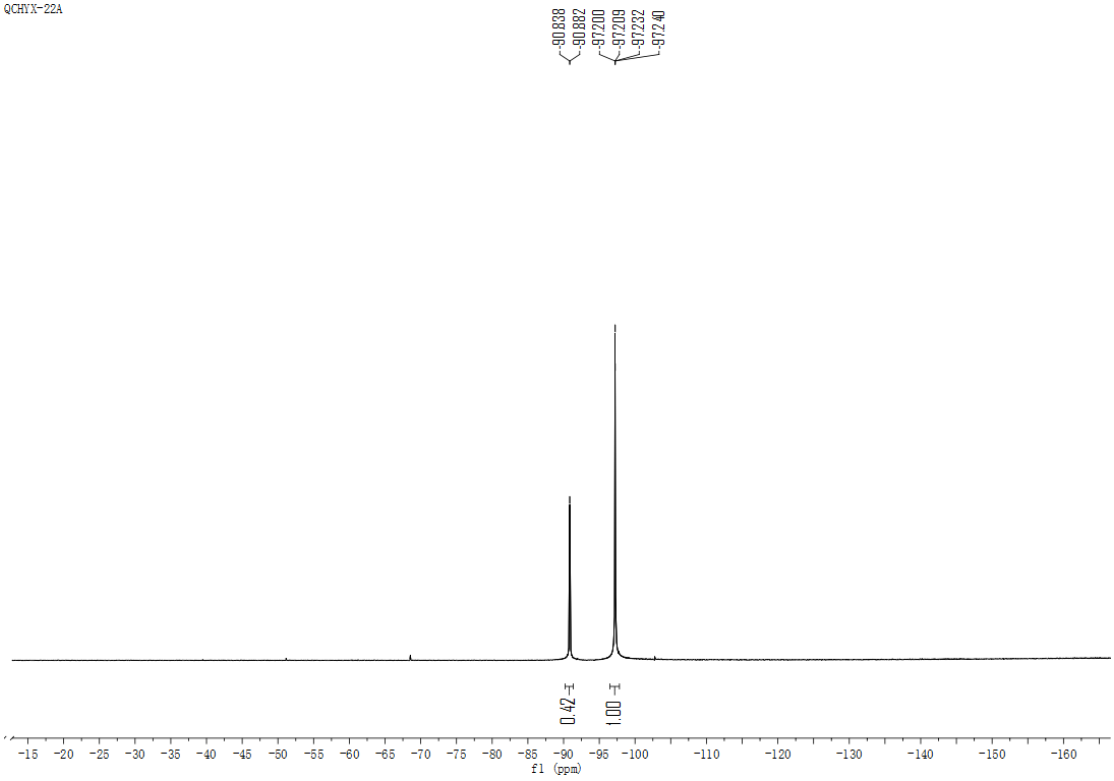



**(*E*)-1,4-bis(4-(tert-butyl)phenyl)-2,2-difluorobut-3-en-1-one (3ca)**

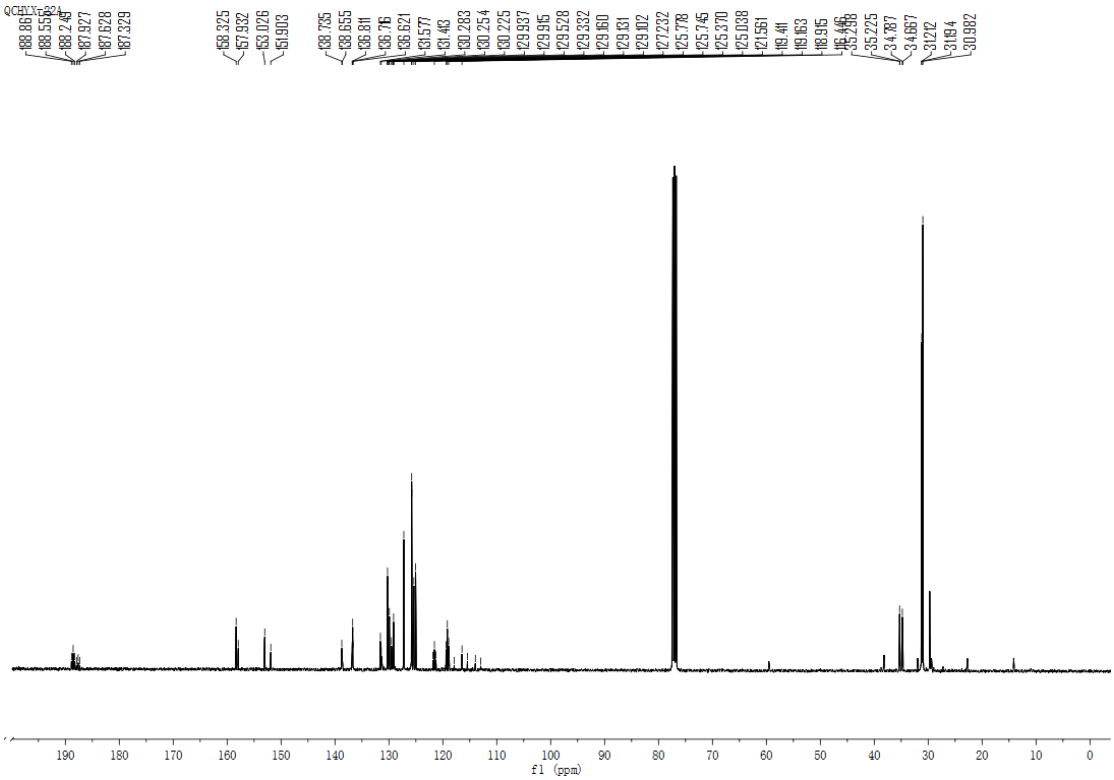
**$^{1}$H NMR (400 MHz, $CDCl_3$):**




## $^{19}$F NMR (376 MHz, $CDCl_3$):

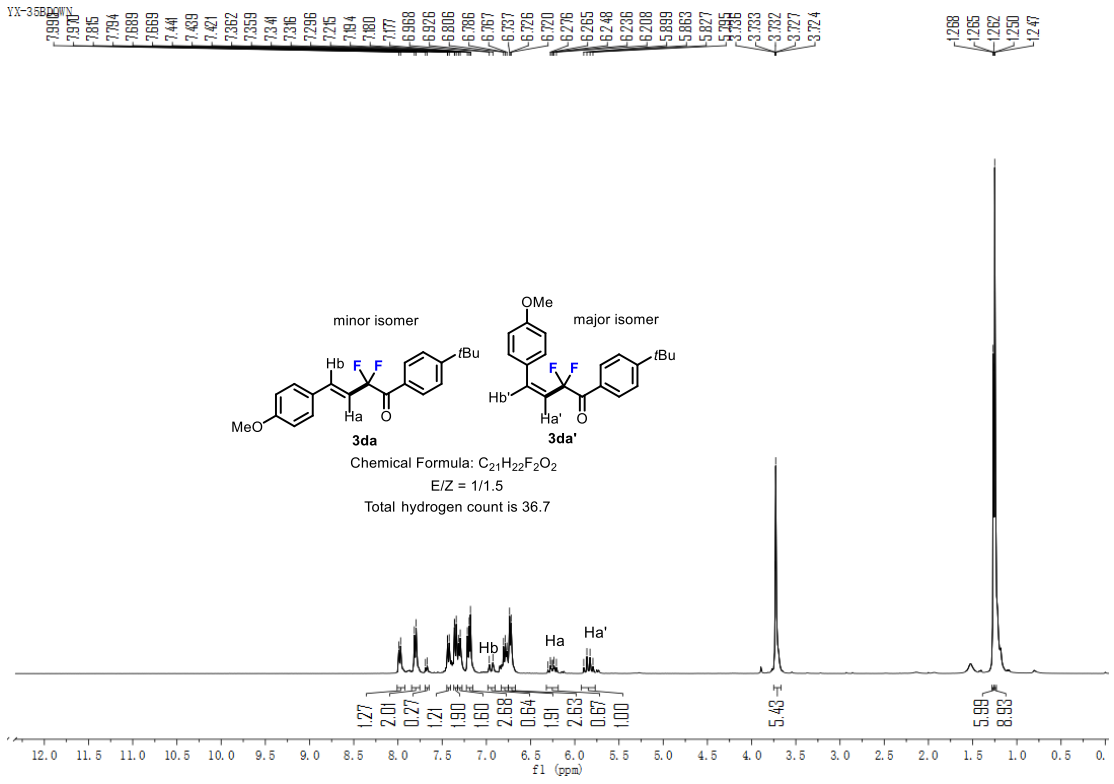



## $^{13}$C NMR (100 MHz, $CDCl_3$):

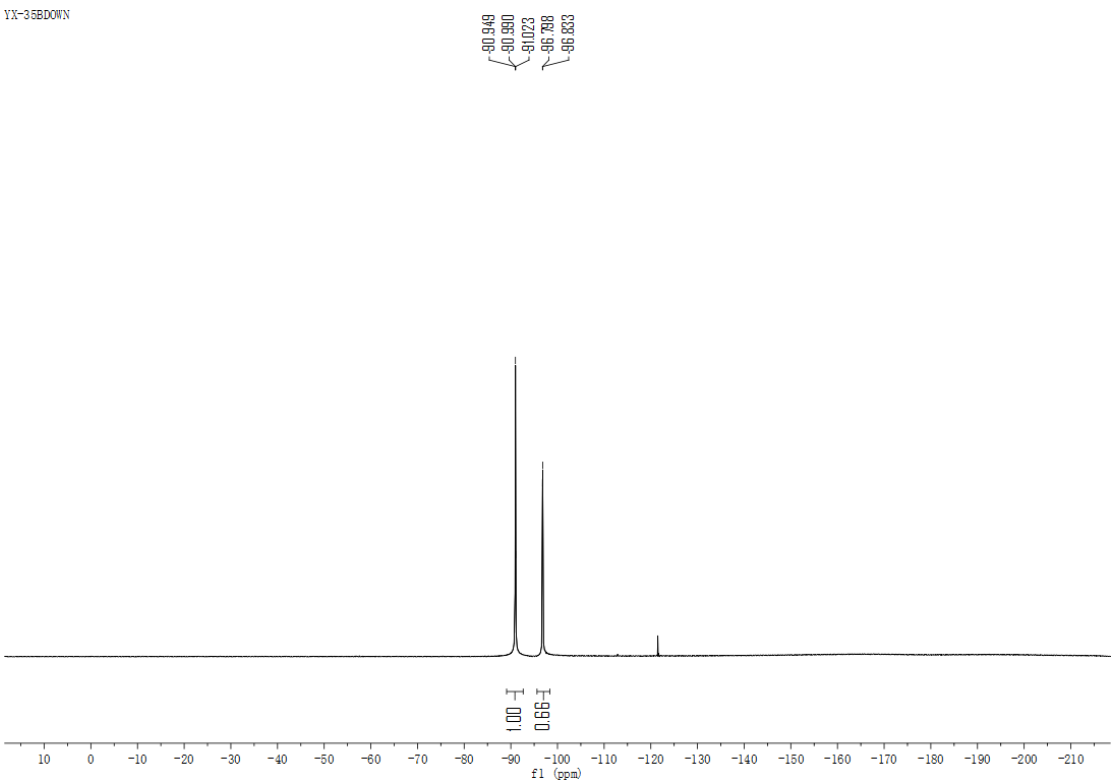


**(*Z*)-1-(4-(tert-butyl)phenyl)-2,2-difluoro-4-(4-methoxyphenyl)but-3-en-1-one (3da)**

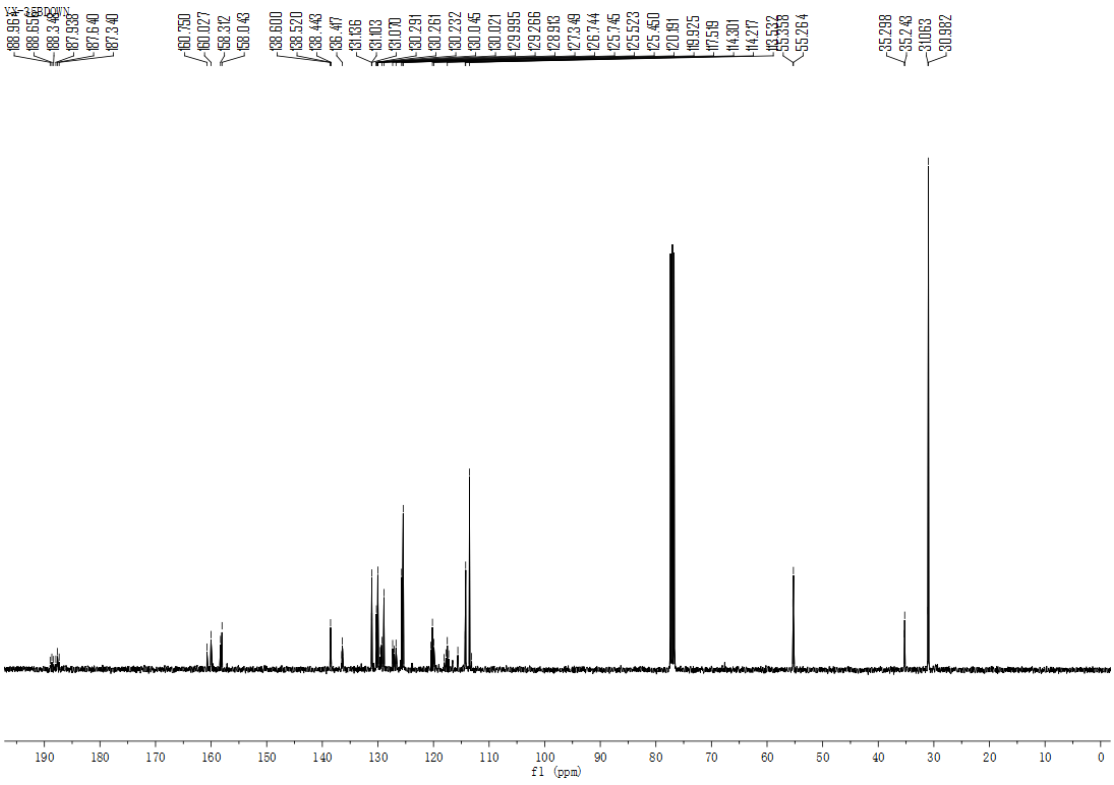
**$^{1}$H NMR (400 MHz, $CDCl_3$):**




**$^{19}$F NMR (376 MHz, $CDCl_3$):**

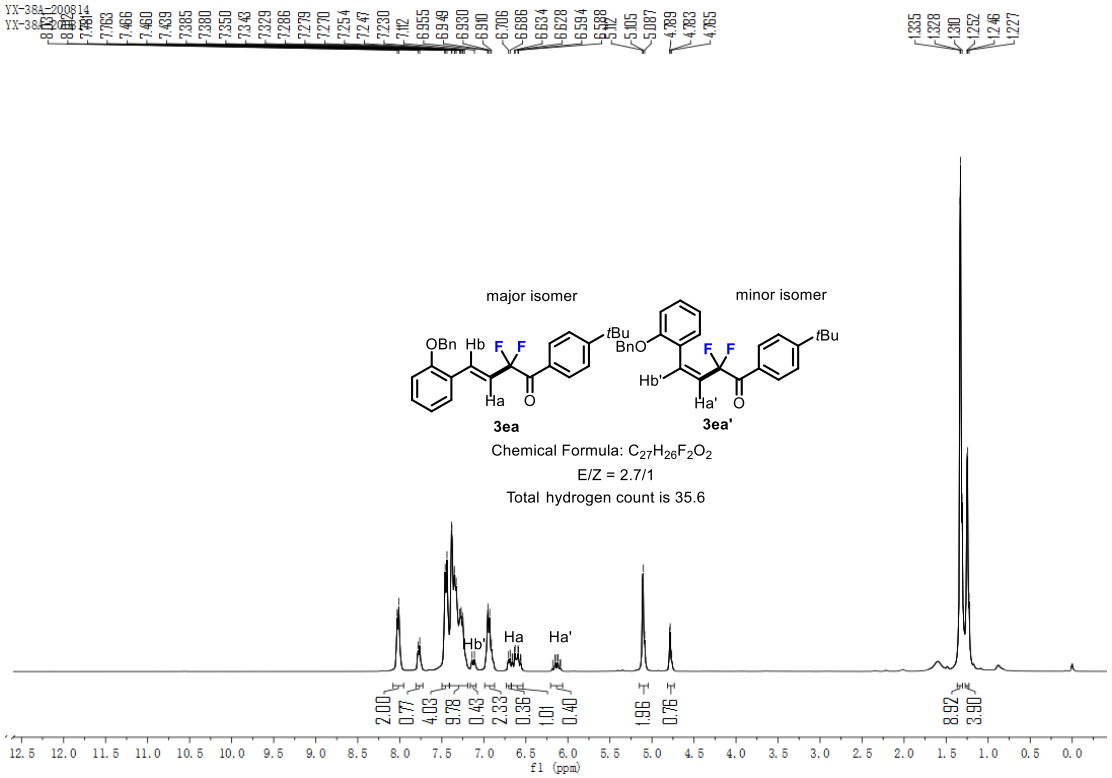



## $^{13}$C NMR (100 MHz, $CDCl_3$):

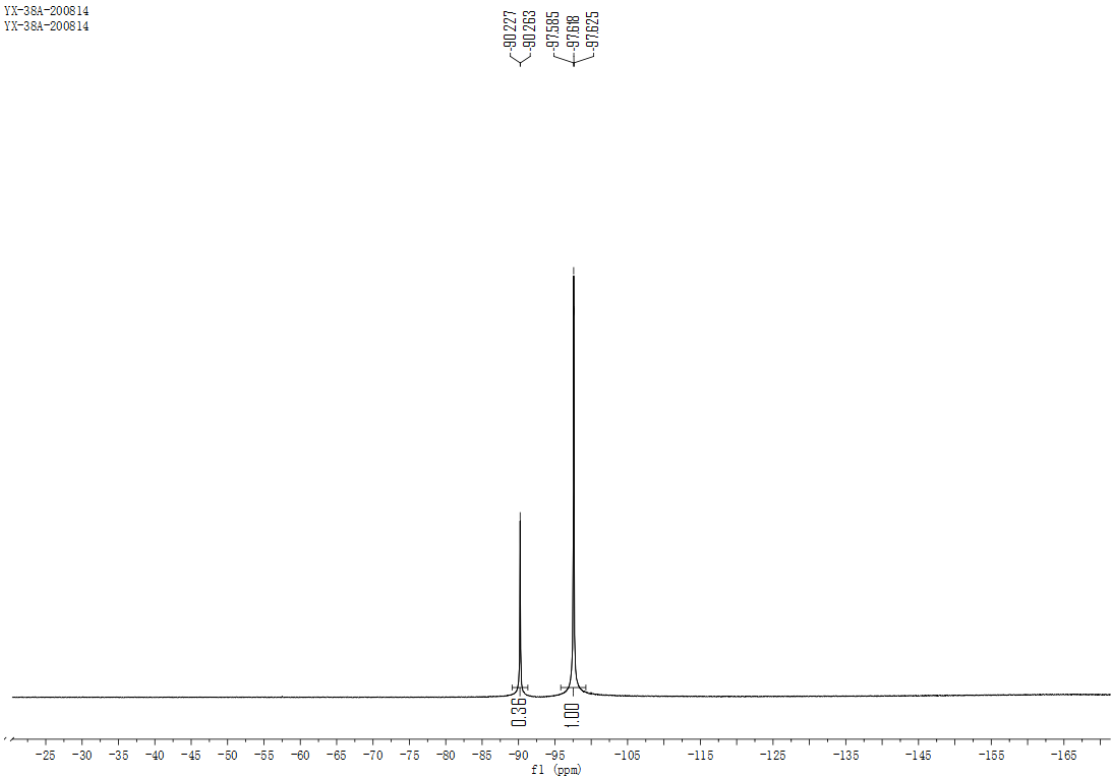



## (*E*)-4-(2-(benzyloxy)phenyl)-1-(4-(tert-butyl)phenyl)-2,2-difluorobut-3-en-1-one (3ea)

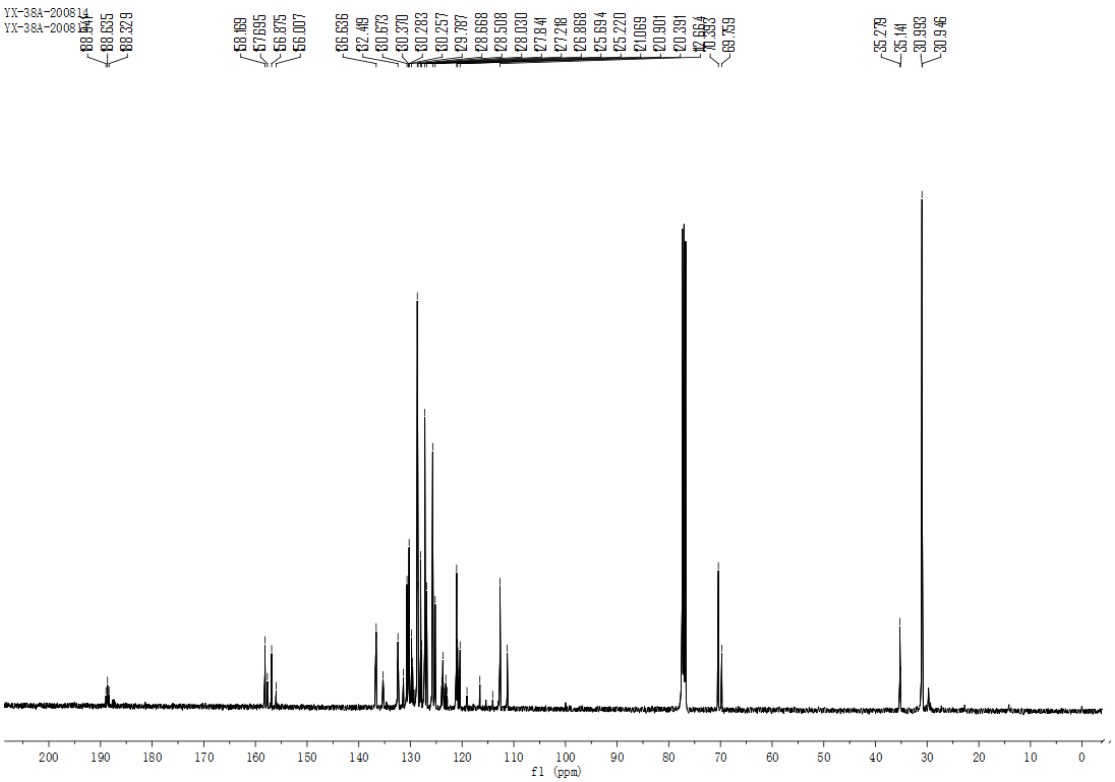
## $^{1}$H NMR (400 MHz, $CDCl_3$):




## $^{19}$F NMR (376 MHz, $CDCl_3$):

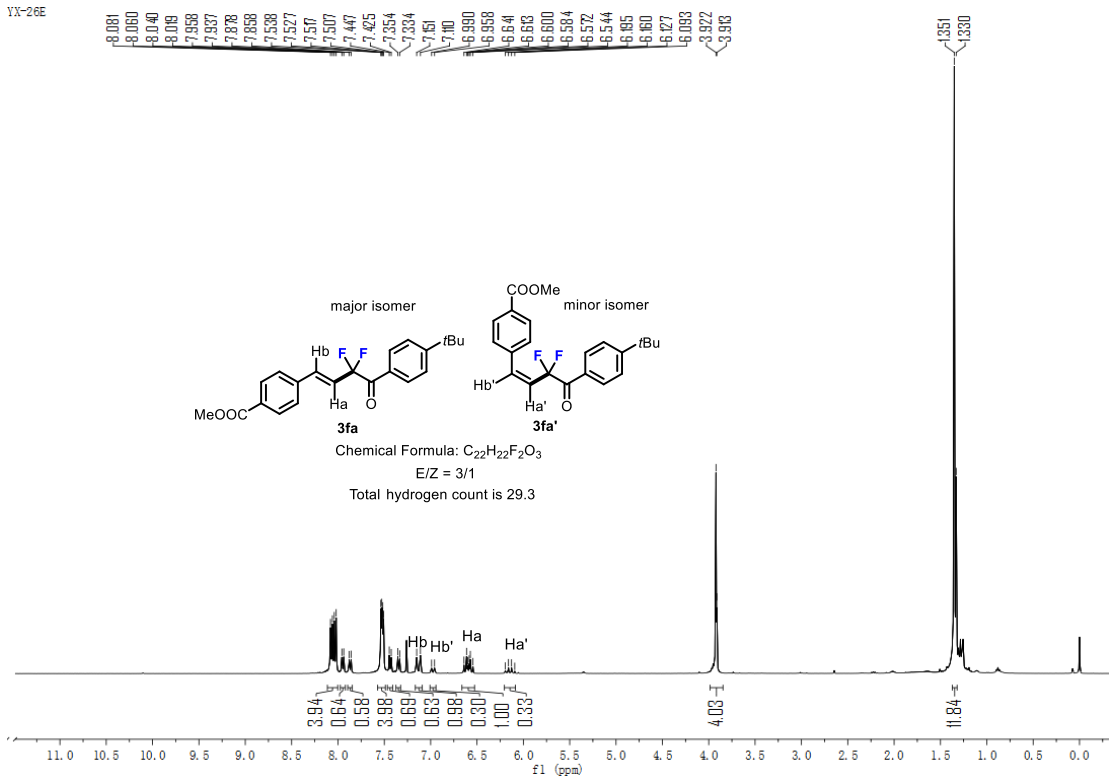



## $^{13}$C NMR (100 MHz, $CDCl_3$):

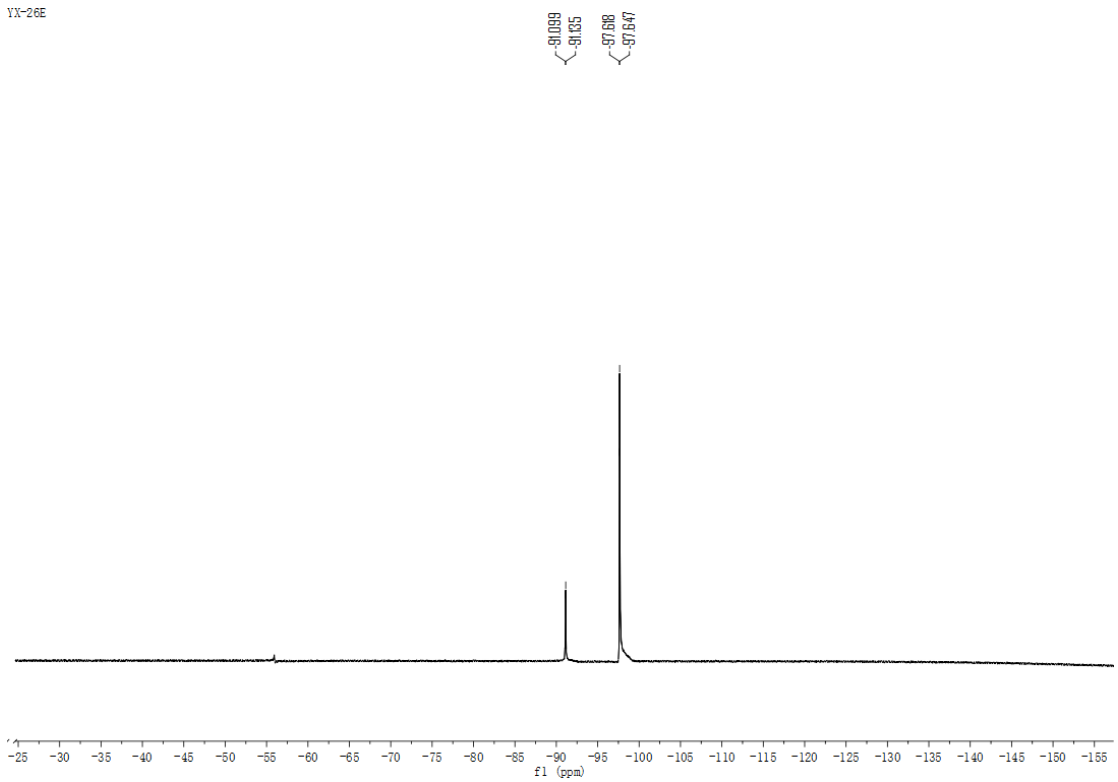


**methyl (*E*)-4-(4-(4-(tert-butyl)phenyl)-3,3-difluoro-4-oxobut-1-en-1-yl)benzoate (3fa)**

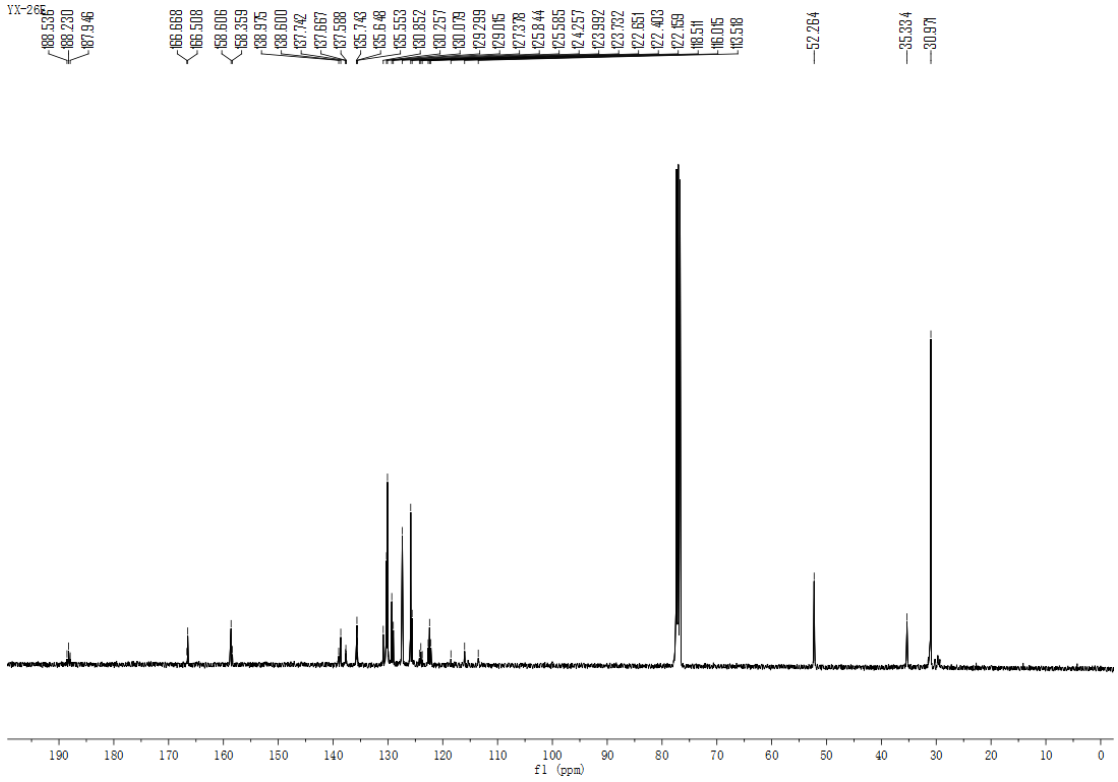
**$^{1}$H NMR (400 MHz, $CDCl_3$):**




**$^{19}$F NMR (376 MHz, $CDCl_3$):**

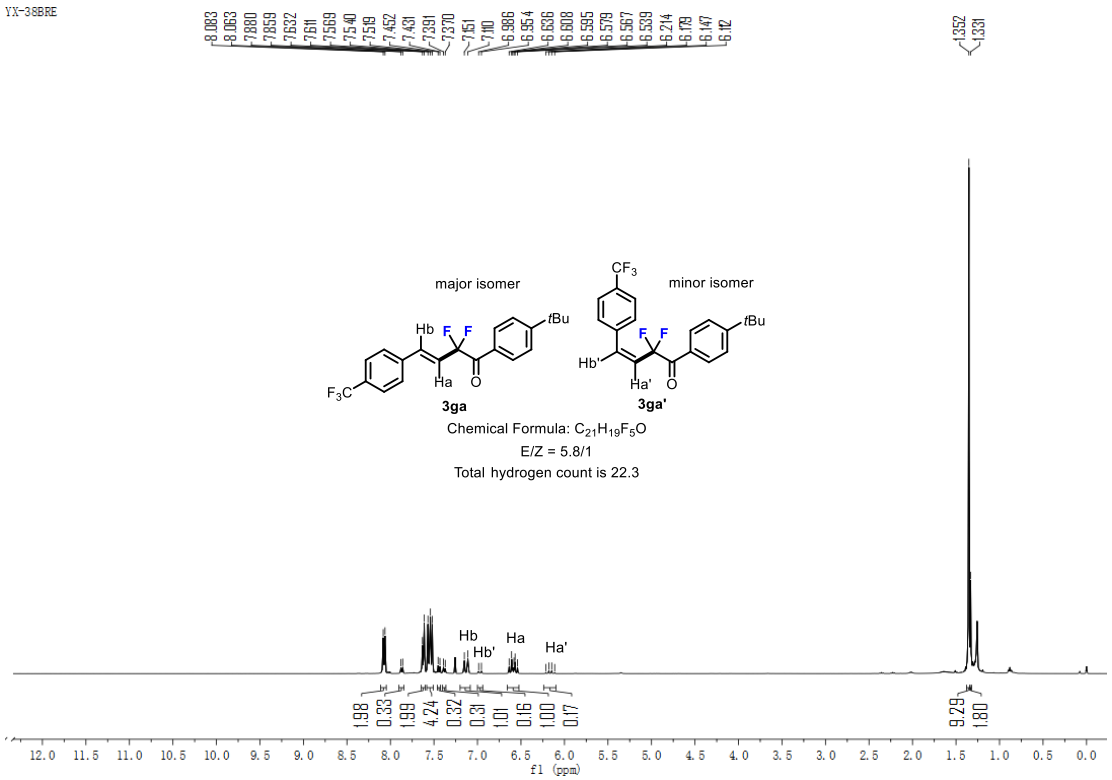



**$^{13}$C NMR (100 MHz, $CDCl_3$):**

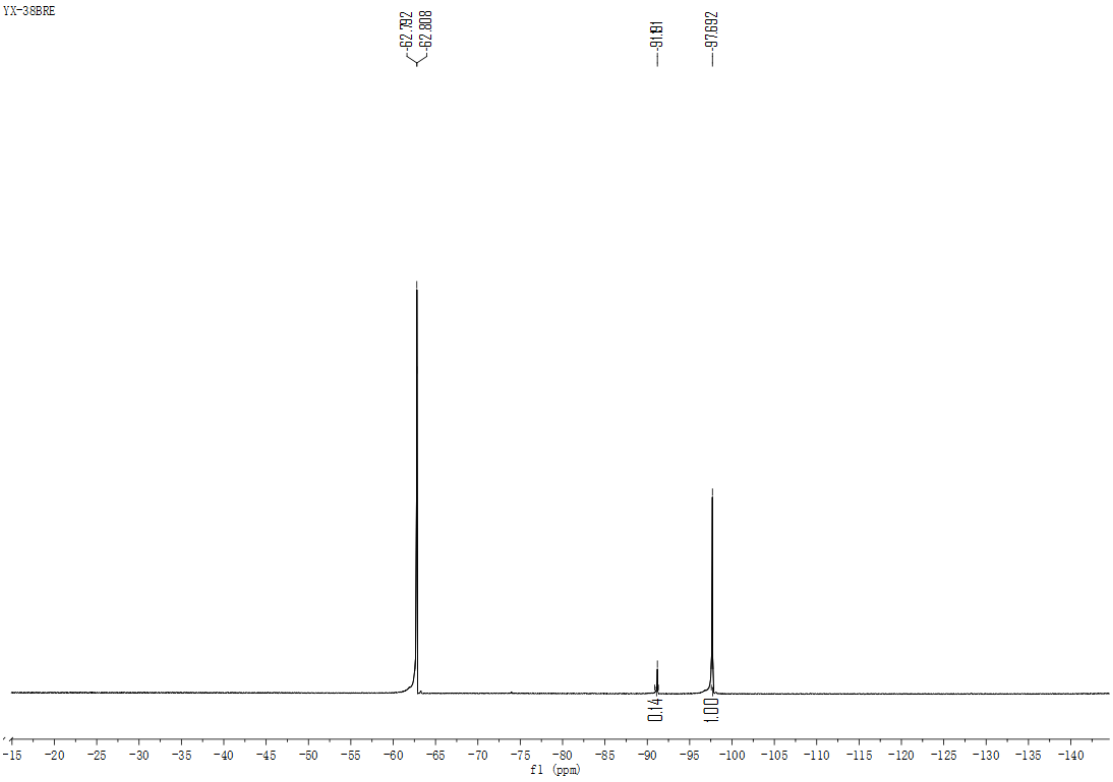



**(*E*)-1-(4-(tert-butyl)phenyl)-2,2-difluoro-4-(4-(trifluoromethyl)phenyl)but-3-en-1-one (3ga)**

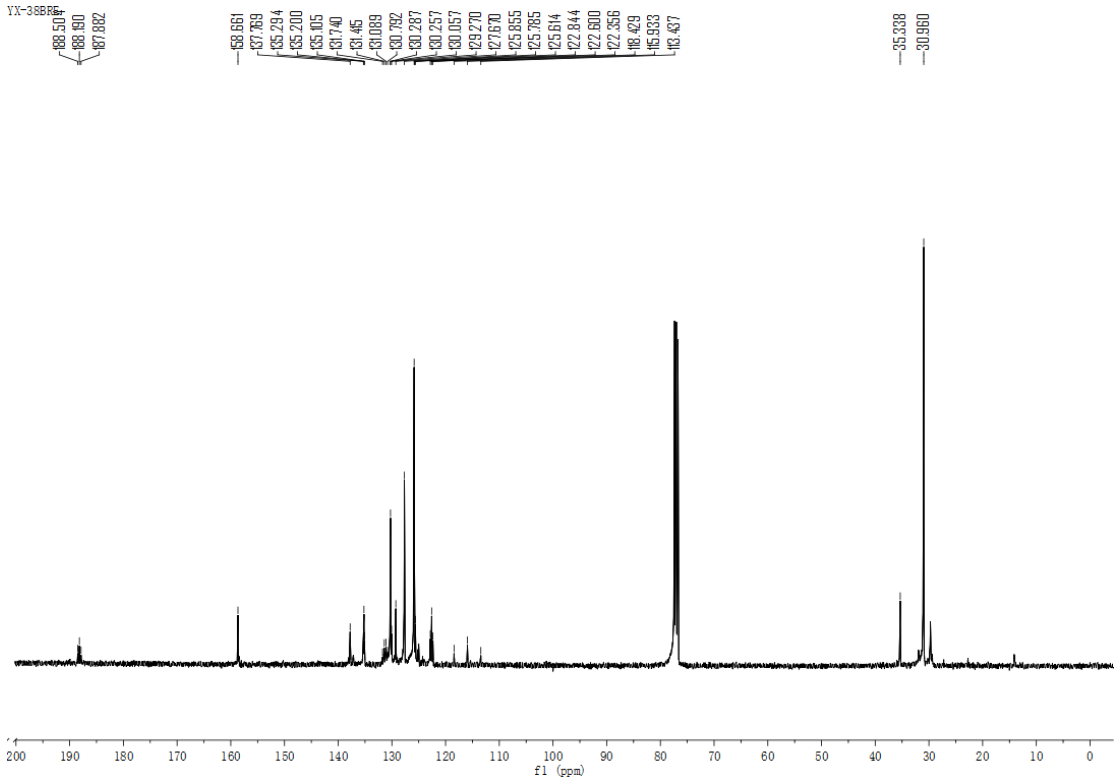
**$^{1}$H NMR (400 MHz, $CDCl_3$):**




## $^{19}$F NMR (376 MHz, $CDCl_3$):

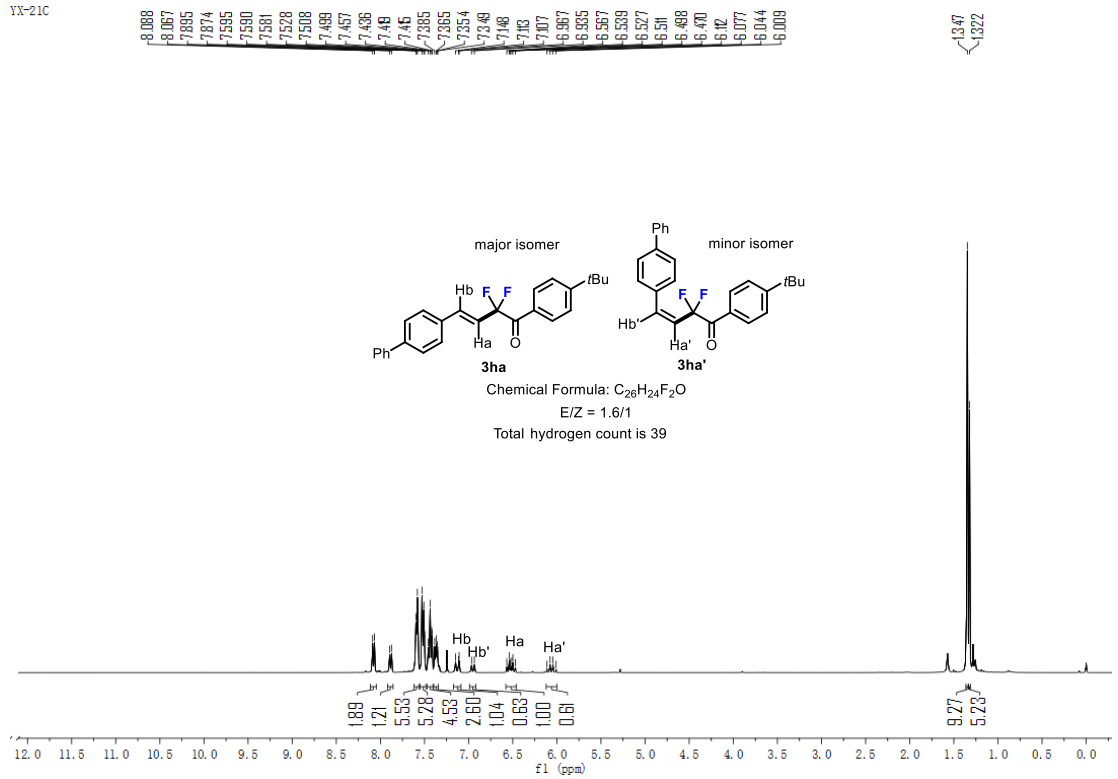



## $^{13}$C NMR (100 MHz, $CDCl_3$):

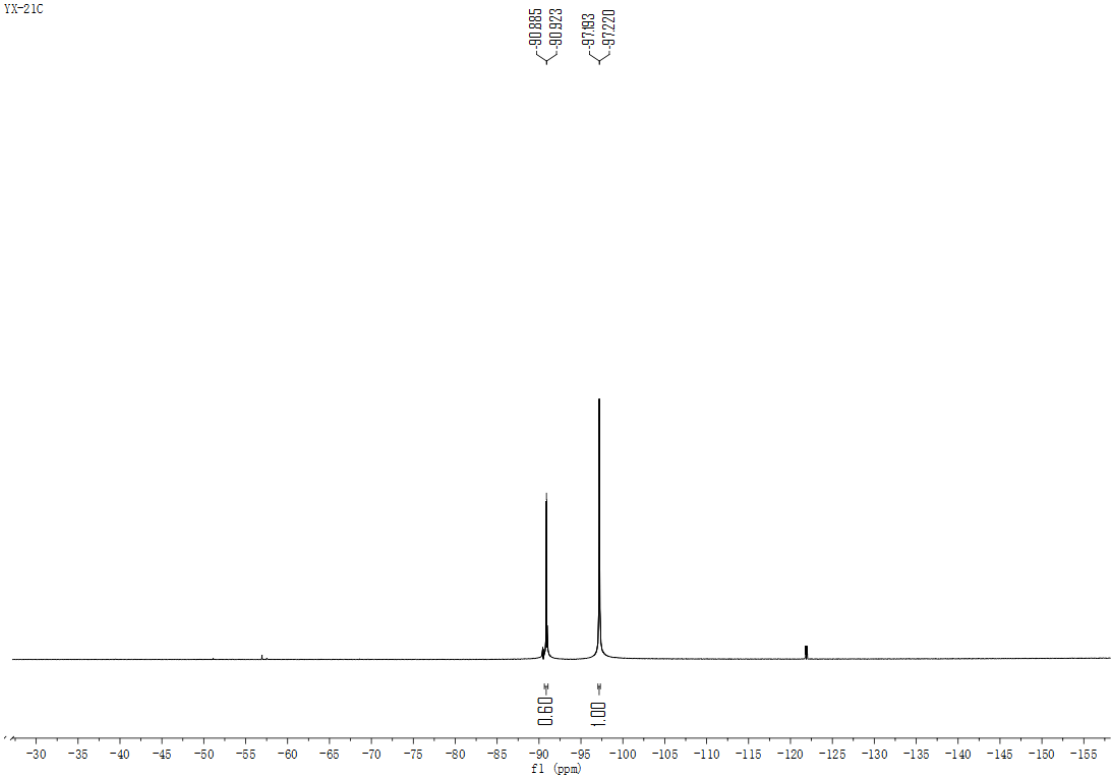


**(*E*)-4-([1,1'-biphenyl]-4-yl)-1-(4-(tert-butyl)phenyl)-2,2-difluorobut-3-en-1-one (3ha)**

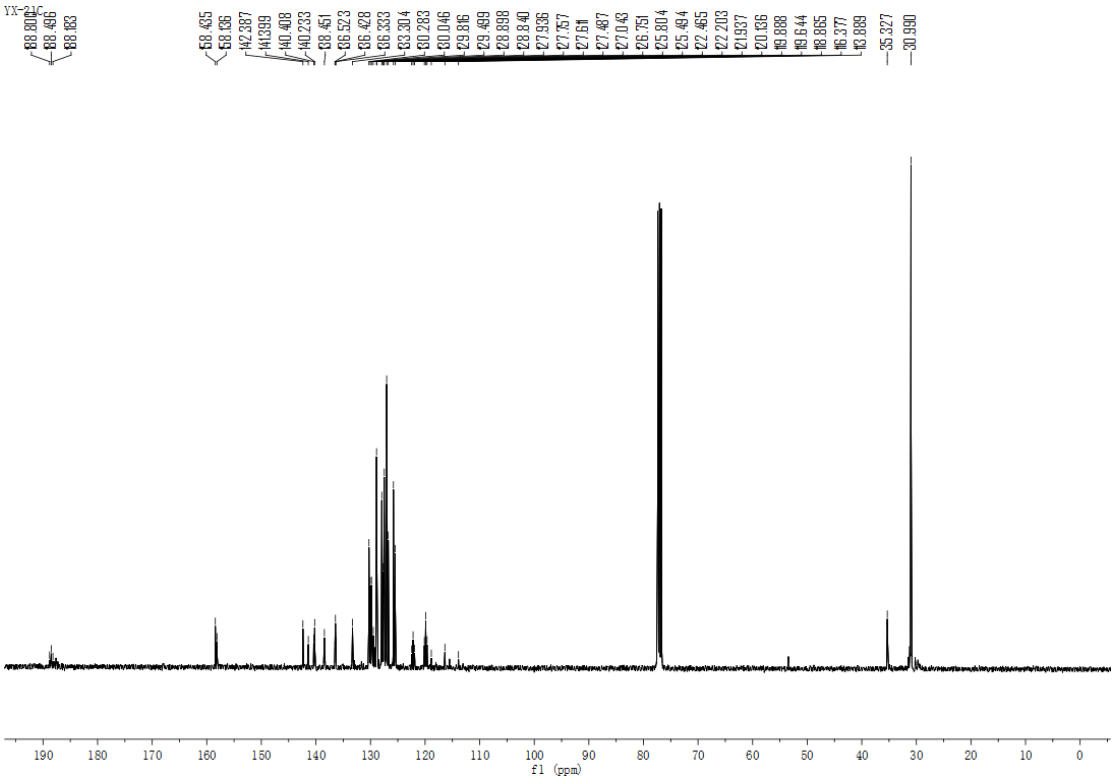
**$^{1}$H NMR (400 MHz, $CDCl_3$):**



**$^{19}$F NMR (376 MHz, $CDCl_3$):**

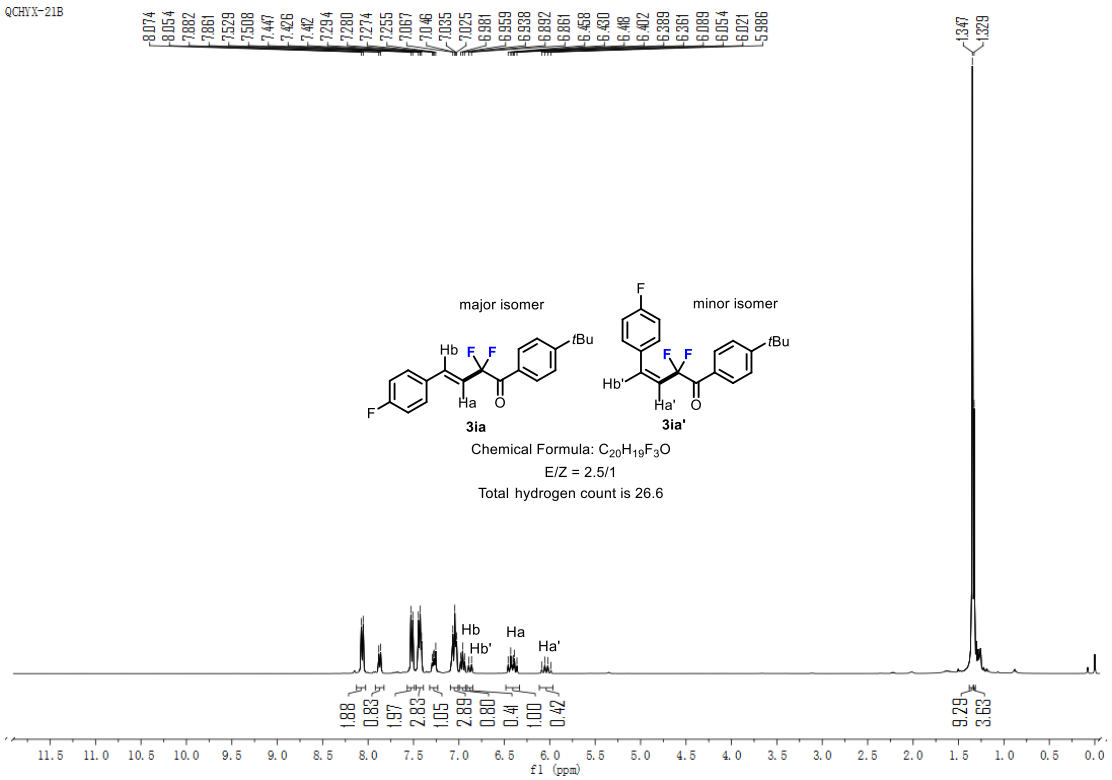



**$^{13}$C NMR (100 MHz, $CDCl_3$):**

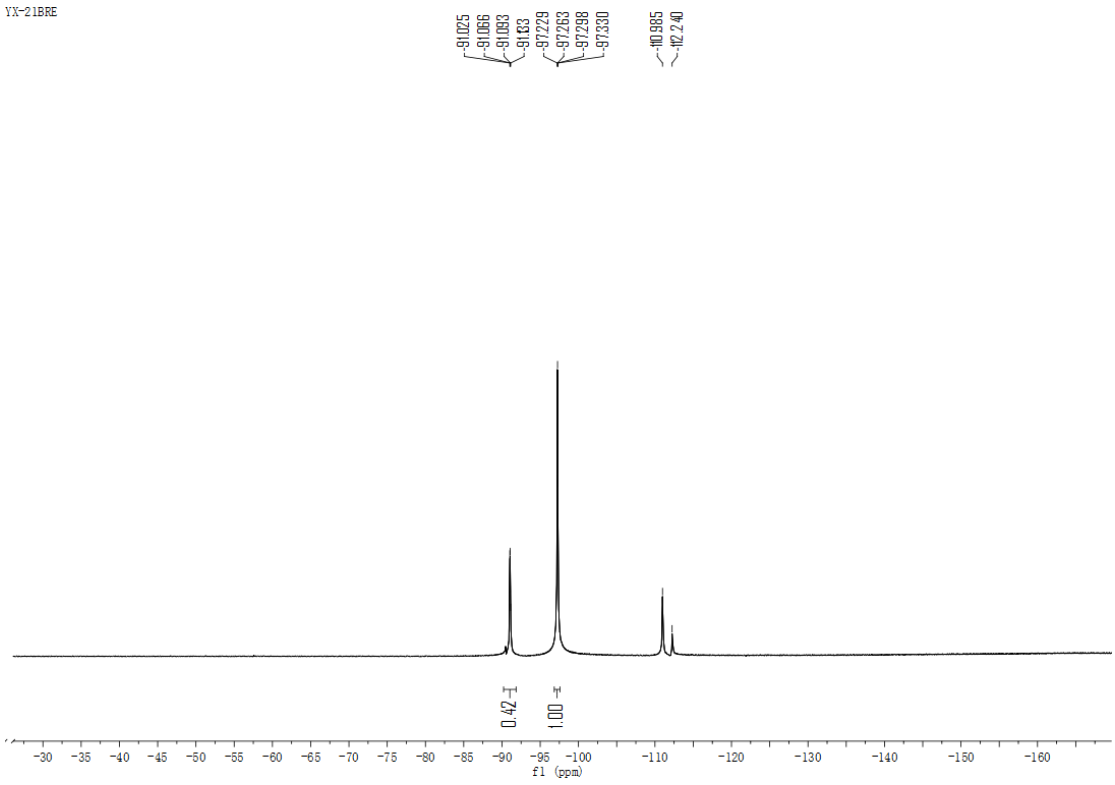



**(*E*)-1-(4-(tert-butyl)phenyl)-2,2-difluoro-4-(4-fluorophenyl)but-3-en-1-one (3ia)**

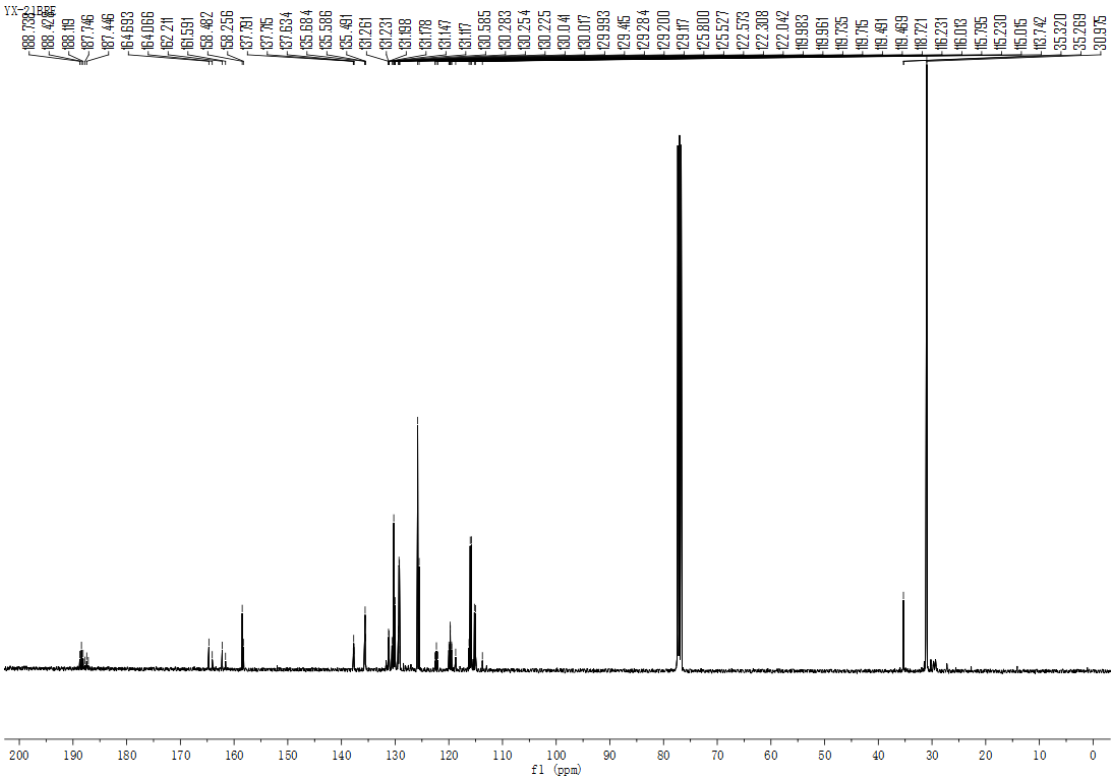
## $^{1}$H NMR (400 MHz, $CDCl_3$):



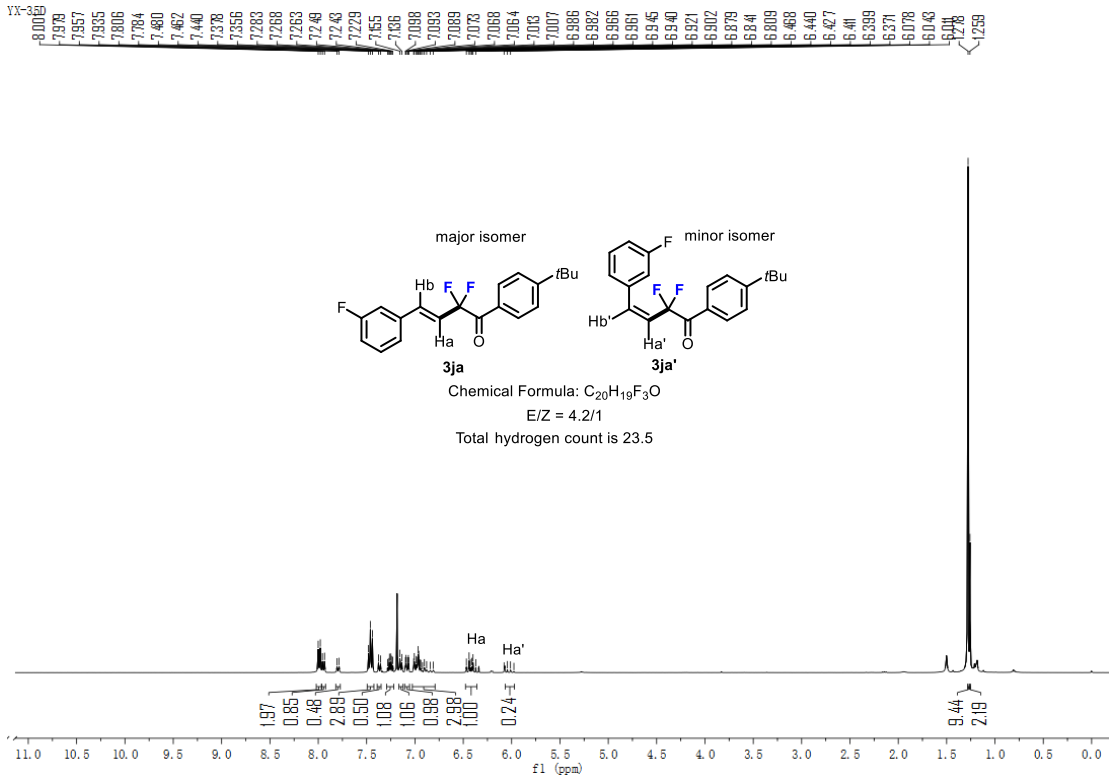

## $^{19}$F NMR(376 MHz, $CDCl_3$):



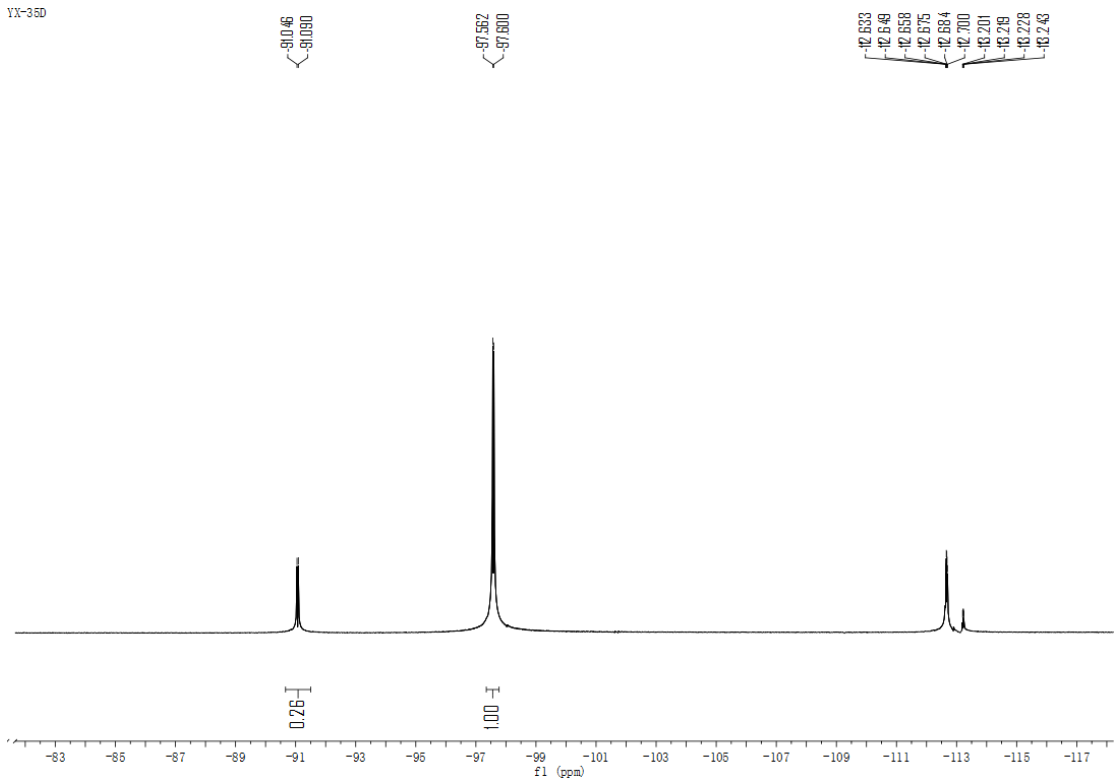

## $^{13}$C NMR (100 MHz, $CDCl_3$):



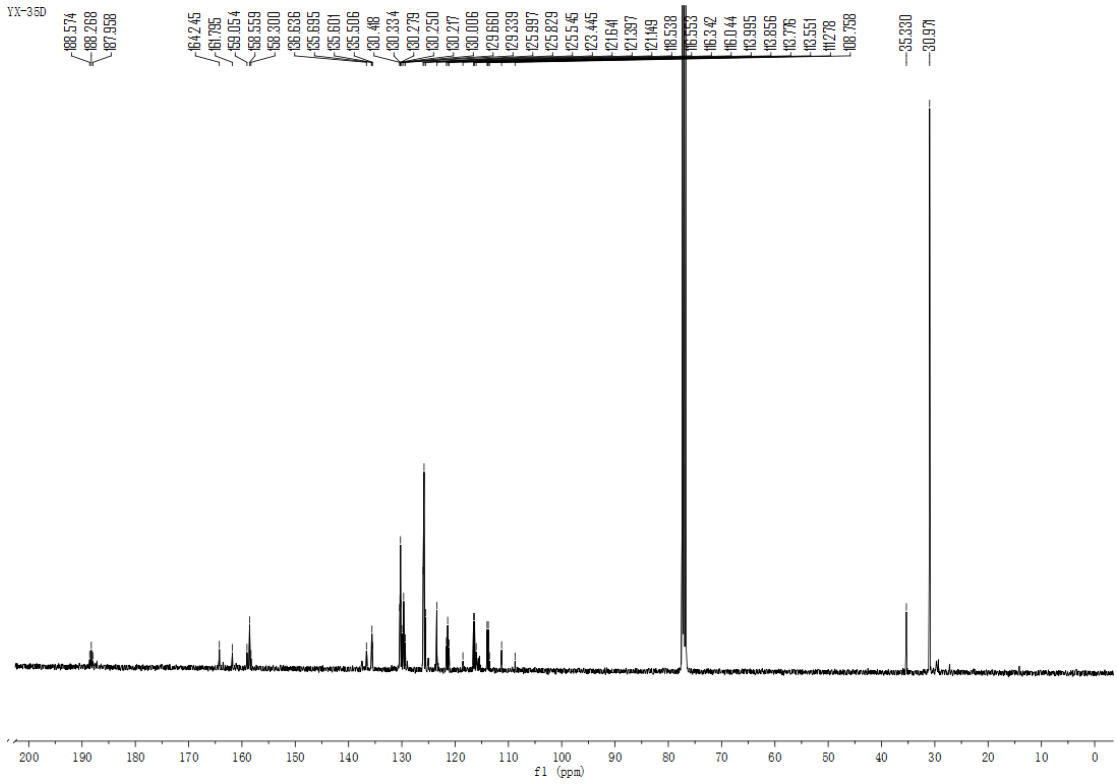
**(*E*)-1-(4-(tert-butyl)phenyl)-2,2-difluoro-4-(3-fluorophenyl)but-3-en-1-one (3ja)**
**$^{1}$H NMR (400 MHz, $CDCl_3$):**



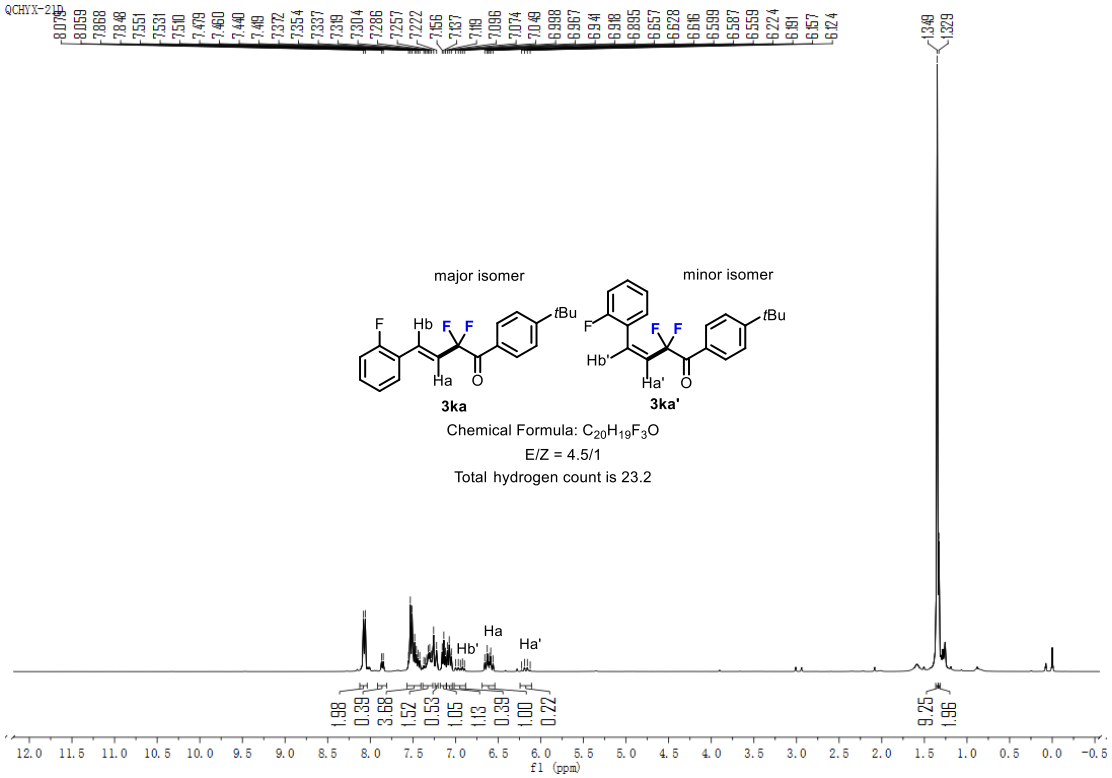

**$^{19}$F NMR (376 MHz, $CDCl_3$):**



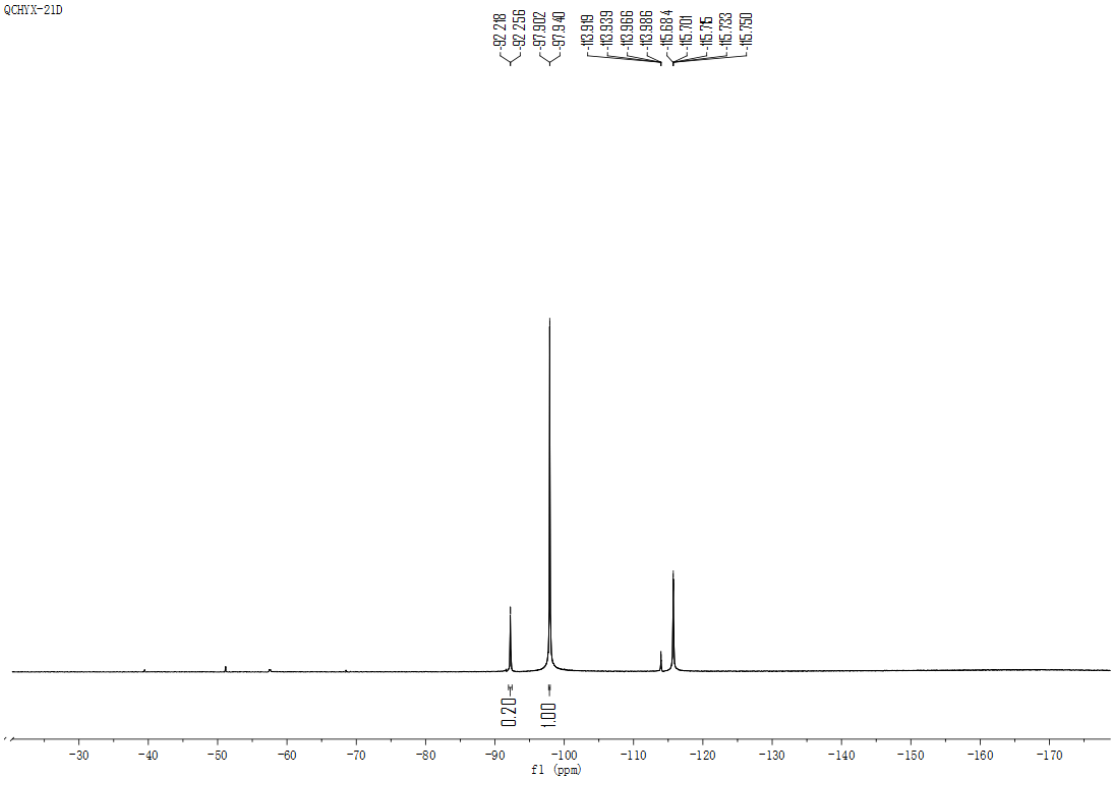

**$^{13}$C NMR (100 MHz, $CDCl_3$):**



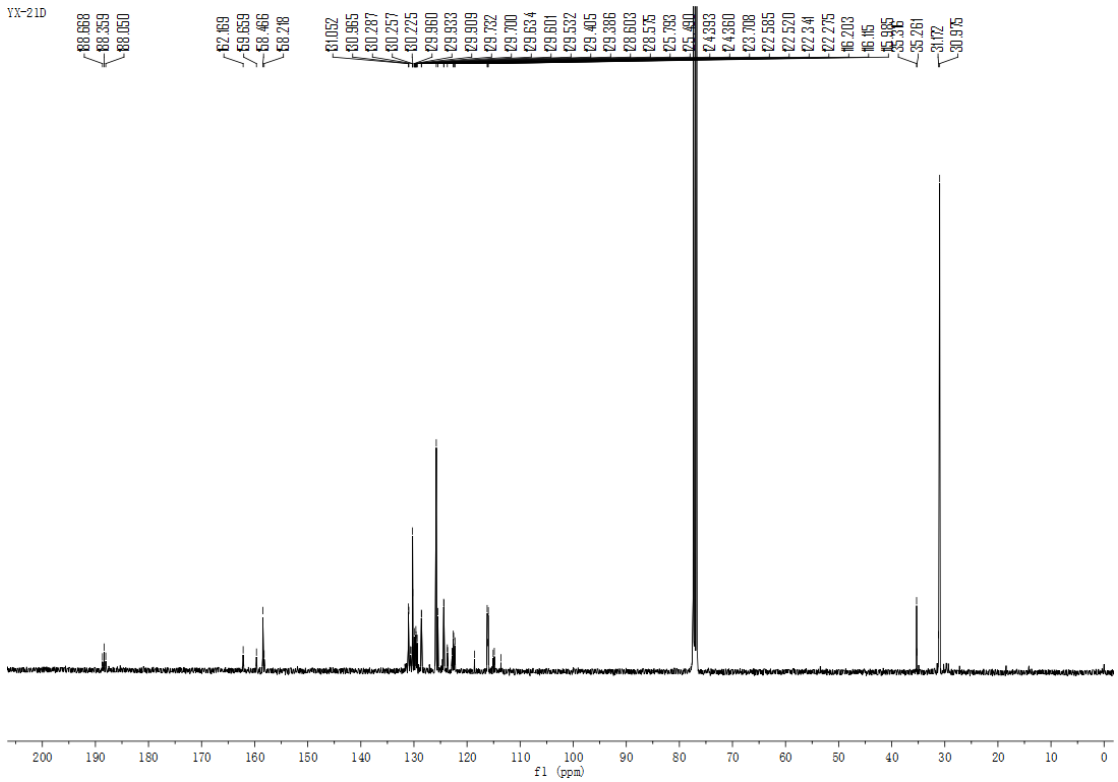

**(*E*)-1-(4-(tert-butyl)phenyl)-2,2-difluoro-4-(2-fluorophenyl)but-3-en-1-one (3ka)**
**$^{1}$H NMR (400 MHz, $CDCl_3$):**




## $^{19}$F NMR (376 MHz, $CDCl_3$):

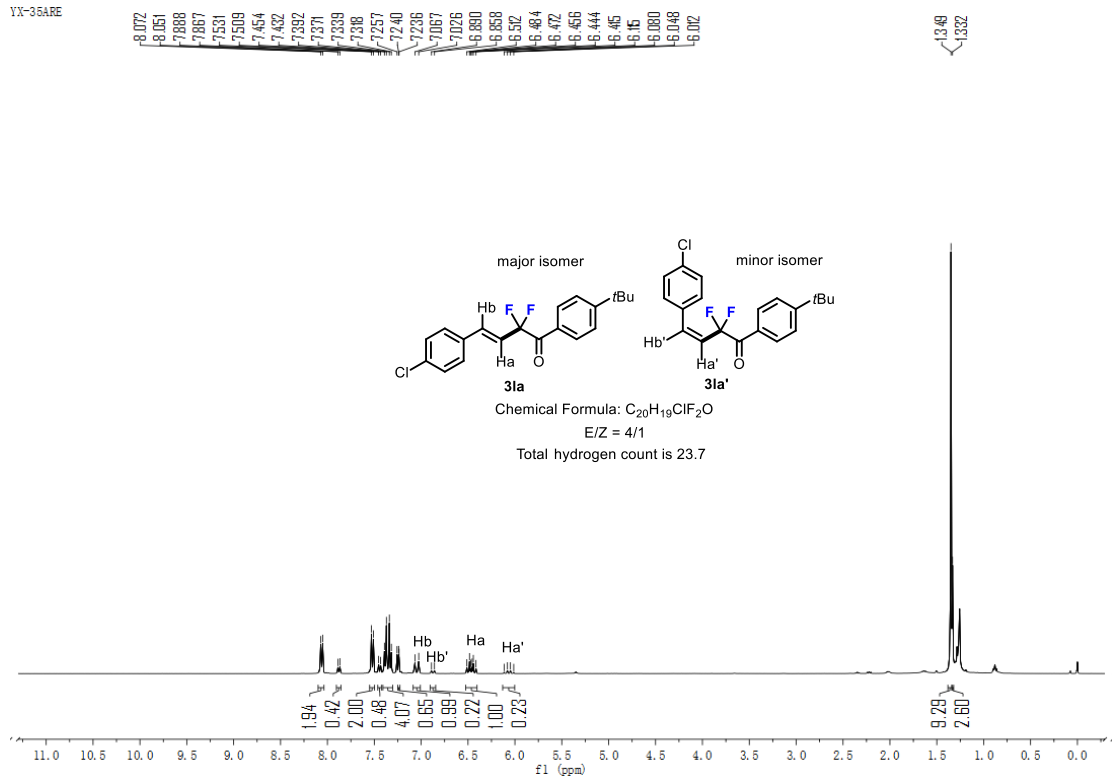



## $^{13}$C NMR (100 MHz, $CDCl_3$):

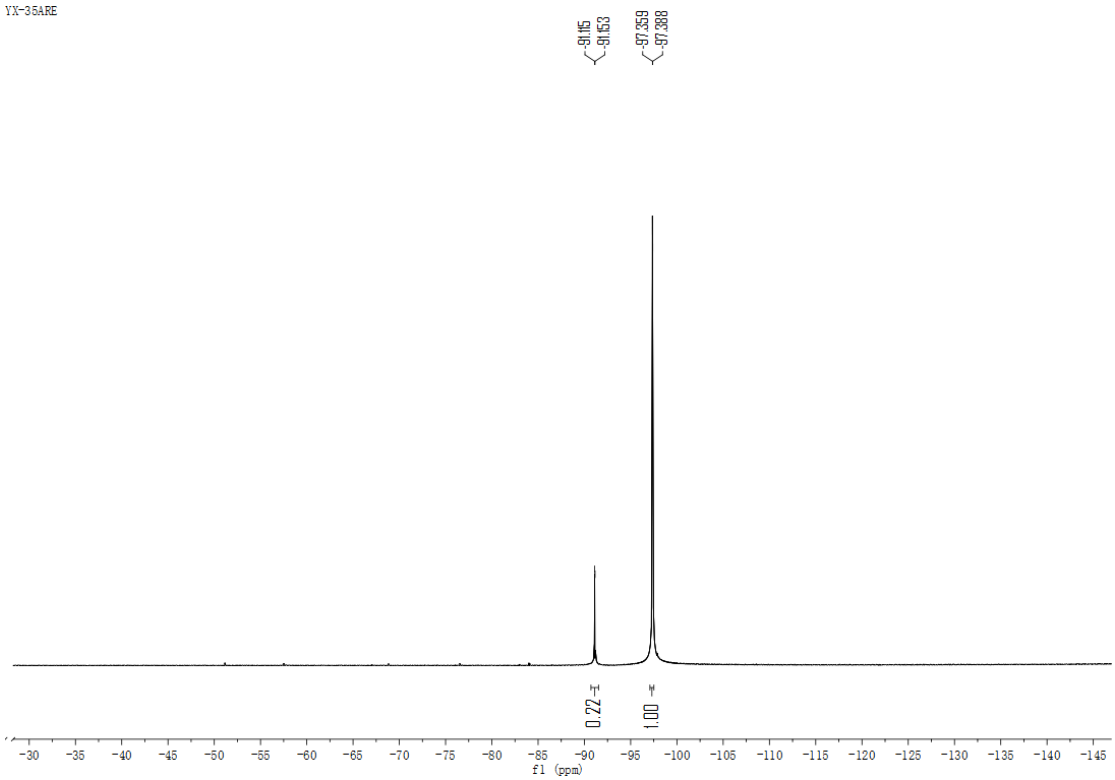



**(*E*)-1-(4-(tert-butyl)phenyl)-4-(4-chlorophenyl)-2,2-difluorobut-3-en-1-one (3la)**

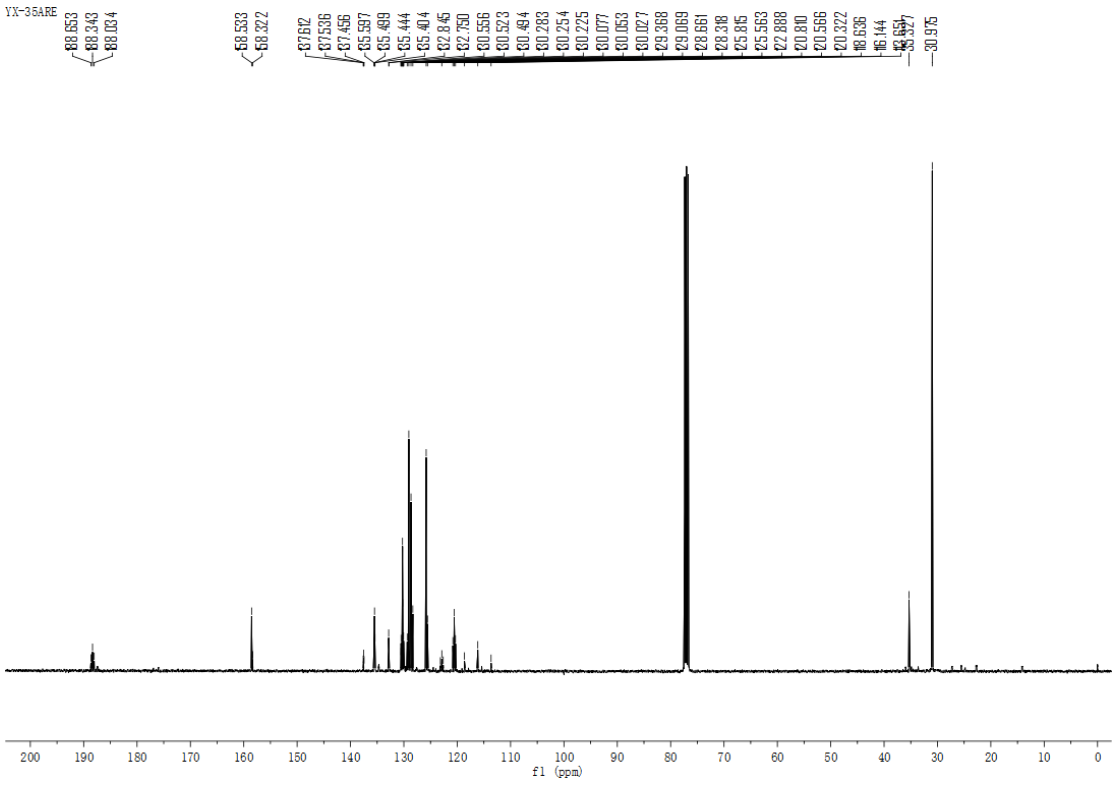
**$^{1}$H NMR (400 MHz, $CDCl_3$):**




**$^{19}$F NMR (376 MHz, $CDCl_3$):**

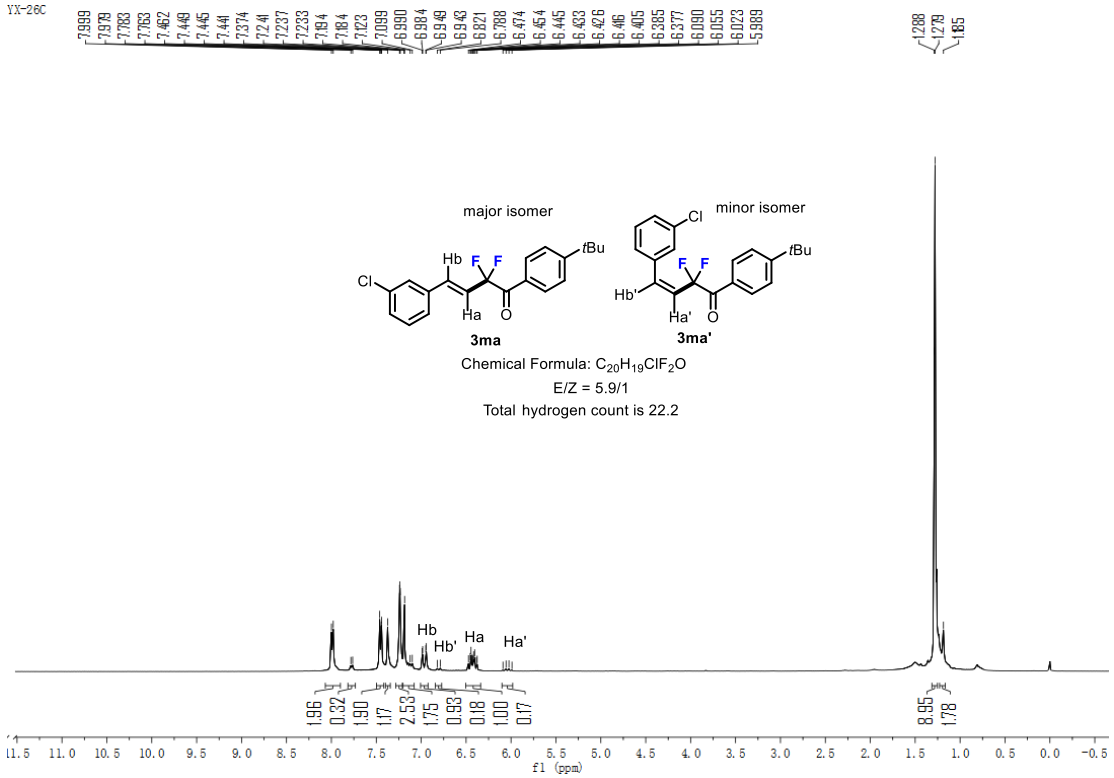



**$^{13}$C NMR (100 MHz, $CDCl_3$):**

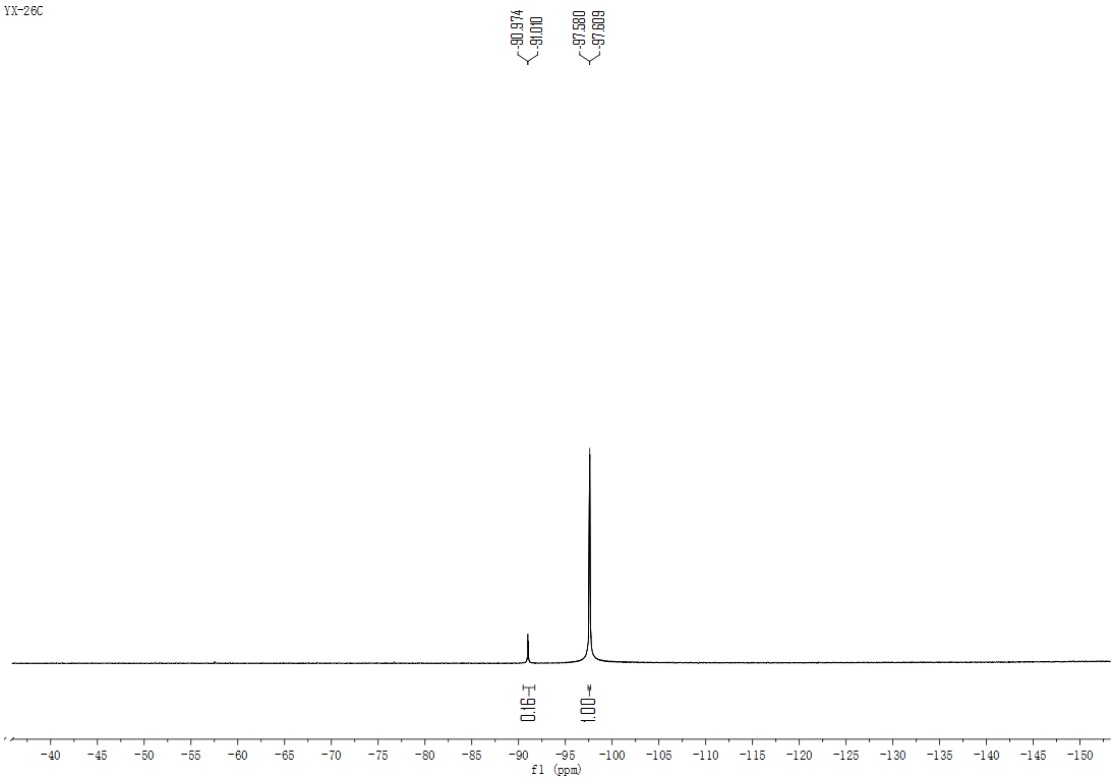



**(E)-1-(4-(tert-butyl)phenyl)-4-(3-chlorophenyl)-2,2-difluorobut-3-en-1-one (3ma)**

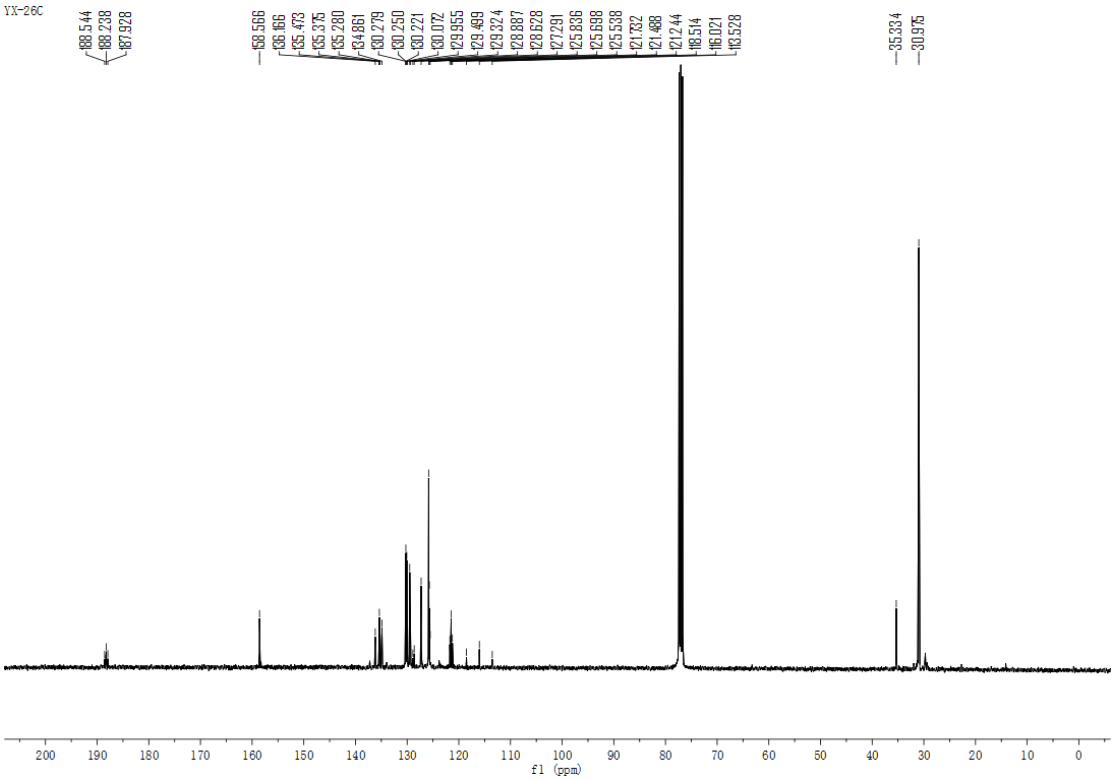
**$^{1}$H NMR (400 MHz, $CDCl_3$):**




## $^{19}$F NMR (376 MHz, $CDCl_3$):

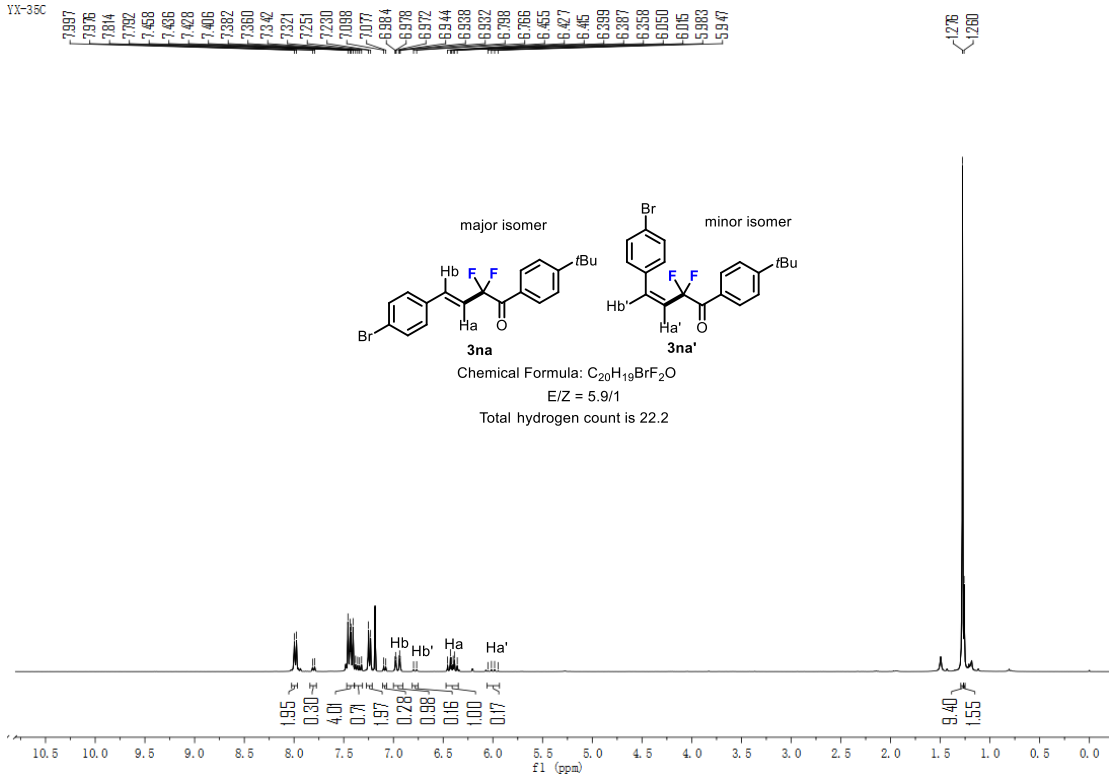



## $^{13}$C NMR (100 MHz, $CDCl_3$):

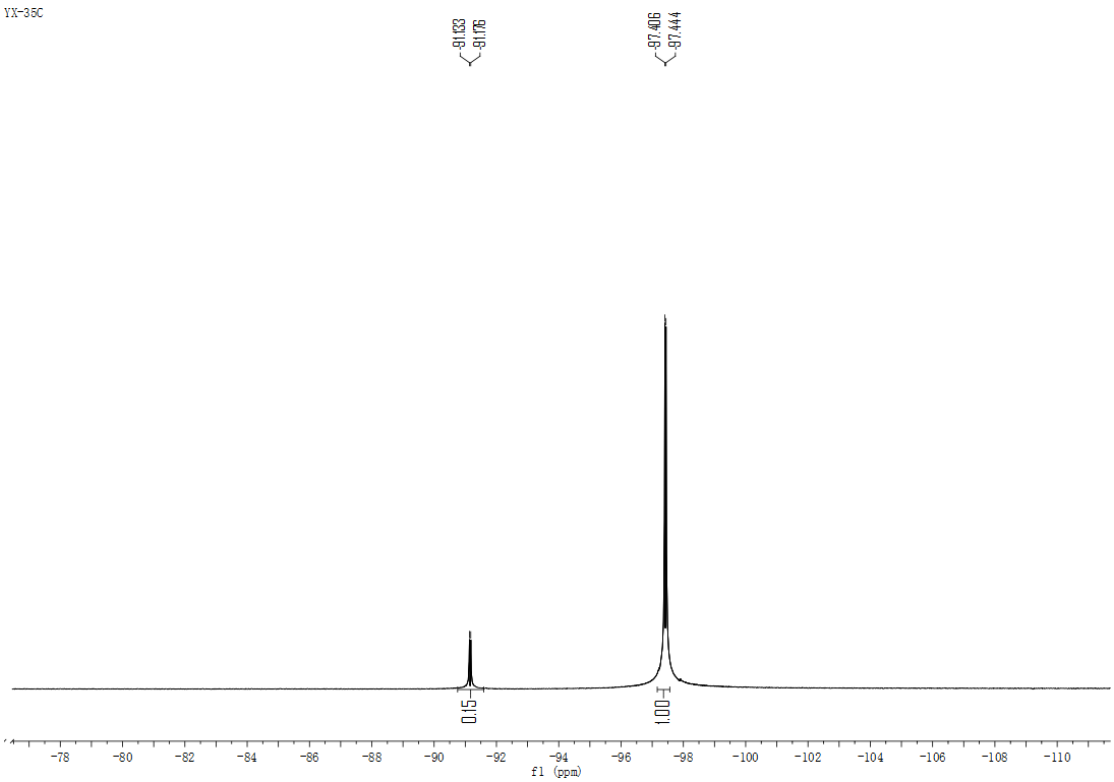



**(*E*)-4-(4-bromophenyl)-1-(4-(tert-butyl)phenyl-2,2-difluorobut-3-en-1-one (3na)**

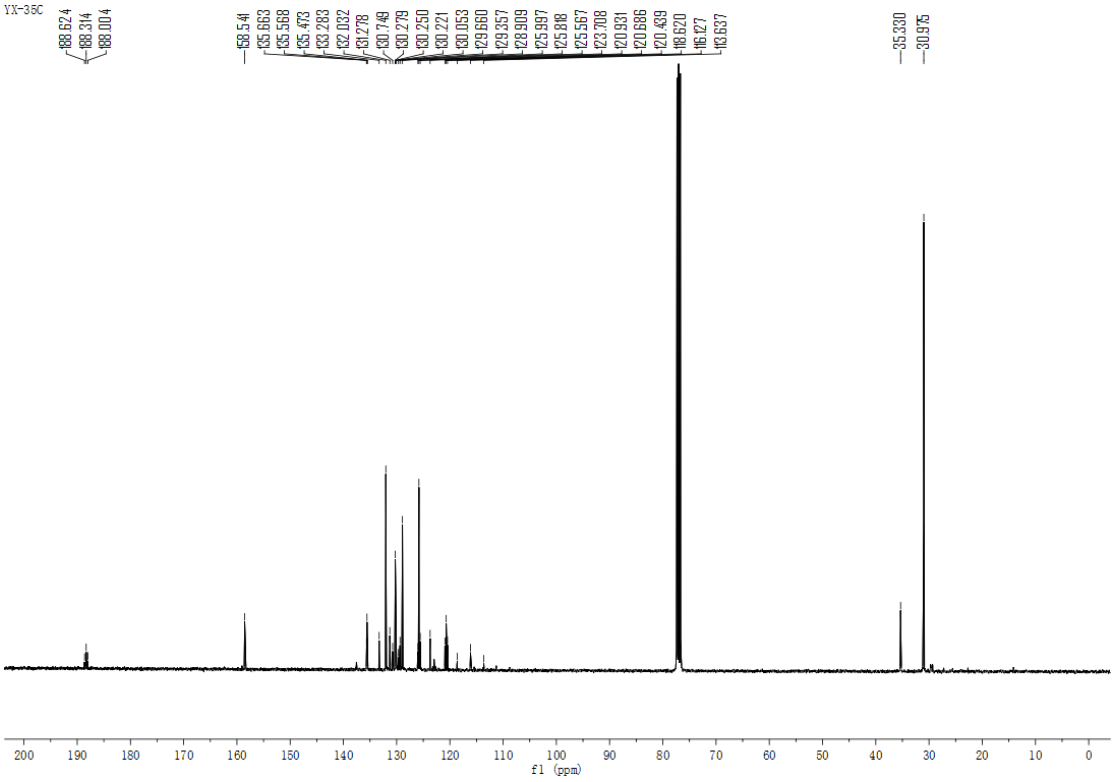
**$^{1}$H NMR (400 MHz, $CDCl_3$):**



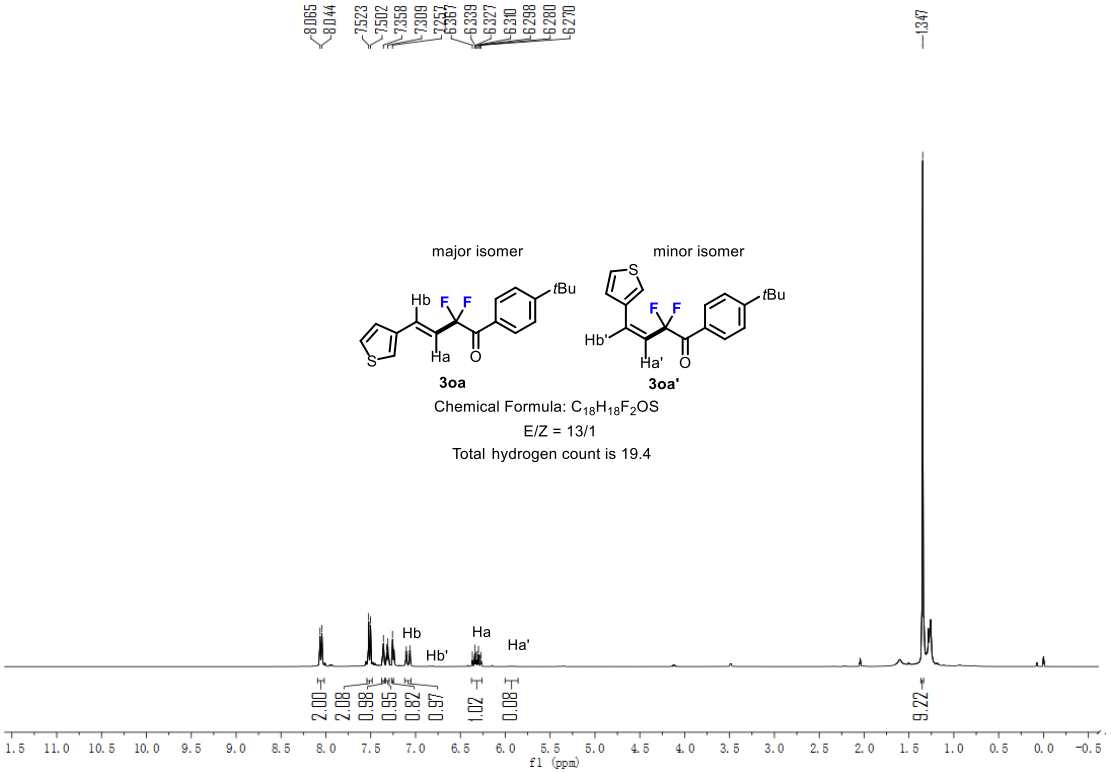

**$^{19}$F NMR (376 MHz, $CDCl_3$):**



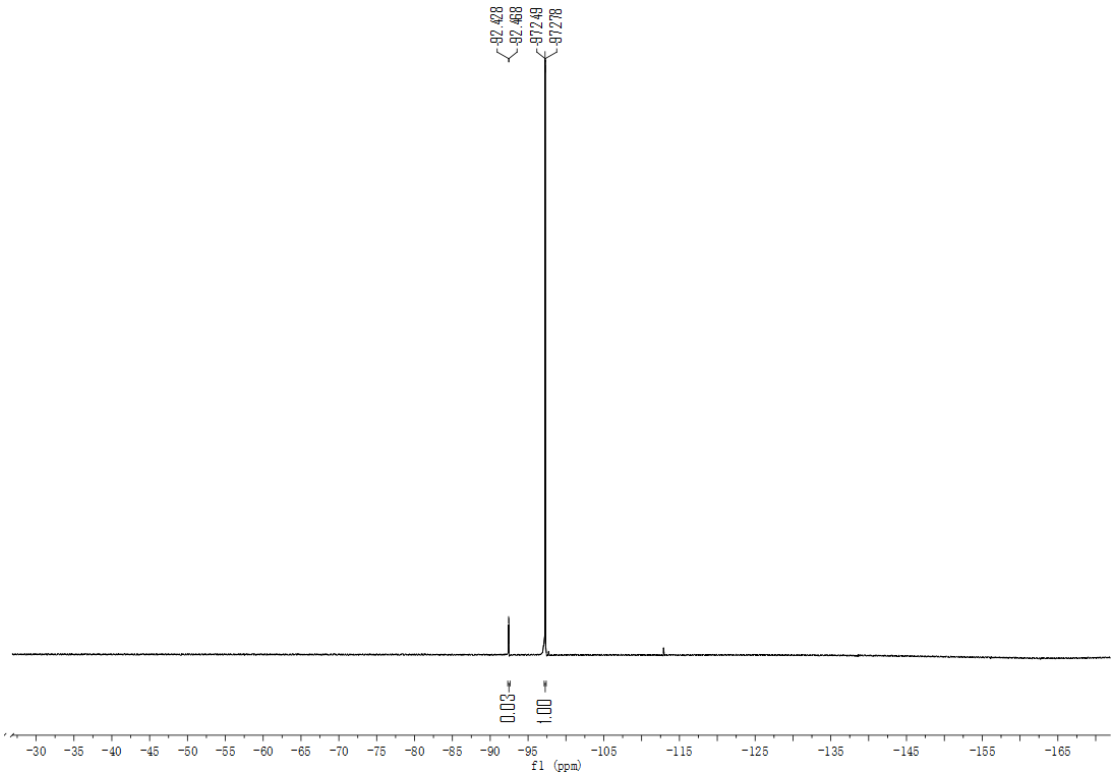

**$^{13}$C NMR (100 MHz, $CDCl_3$):**



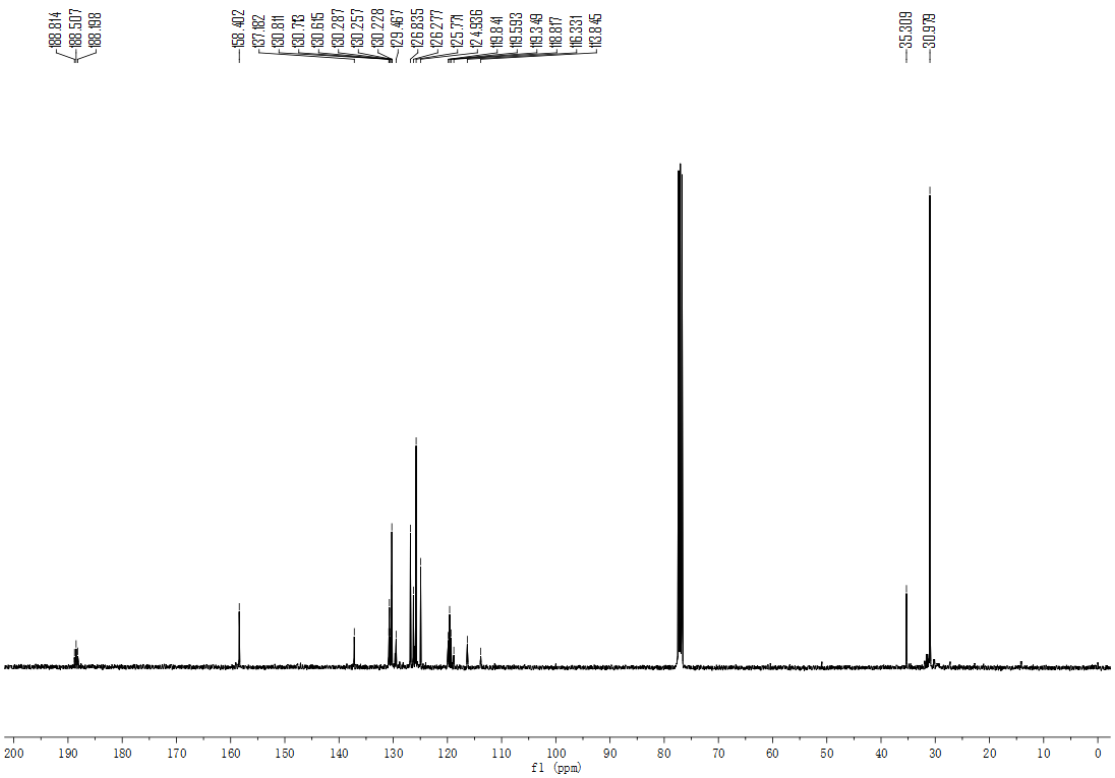

**(E)-1-(4-(tert-butyl)phenyl)-2,2-difluoro-4-(thiophen-3-yl)but-3-en-1-one (3oa)**
**$^{1}$H NMR (400 MHz, $CDCl_3$):**




**$^{19}$F NMR (376 MHz, $CDCl_3$):**

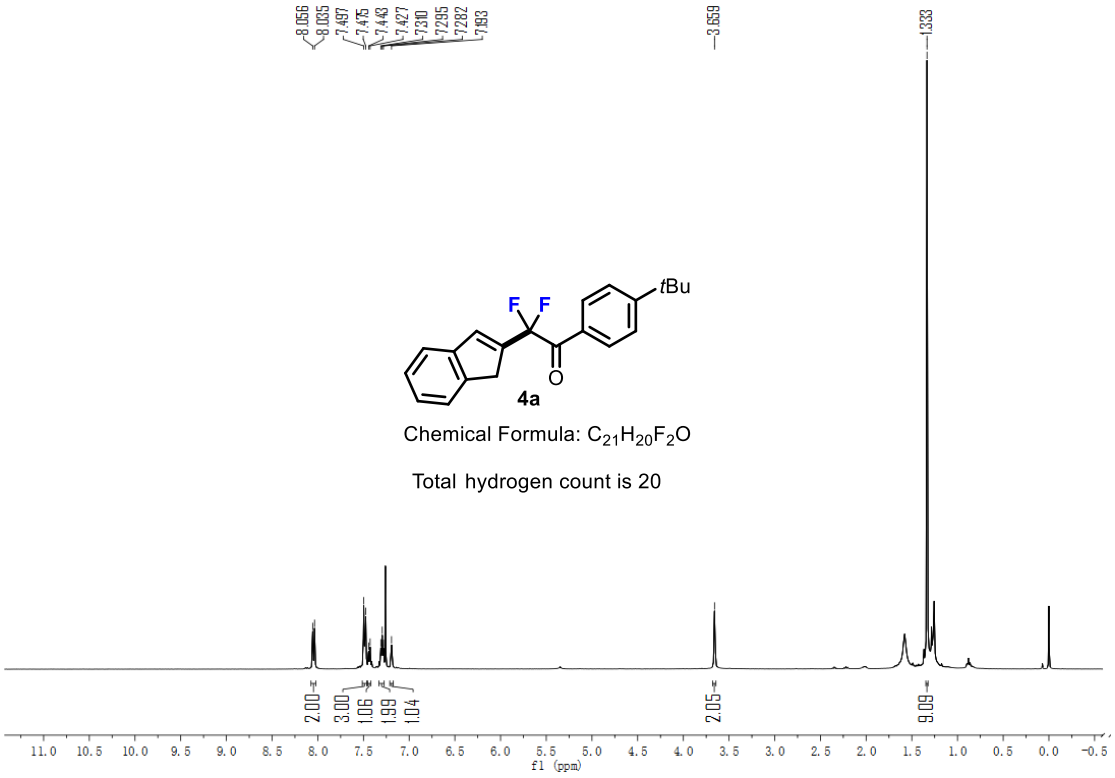



**$^{13}$C NMR (100 MHz, $CDCl_3$):**

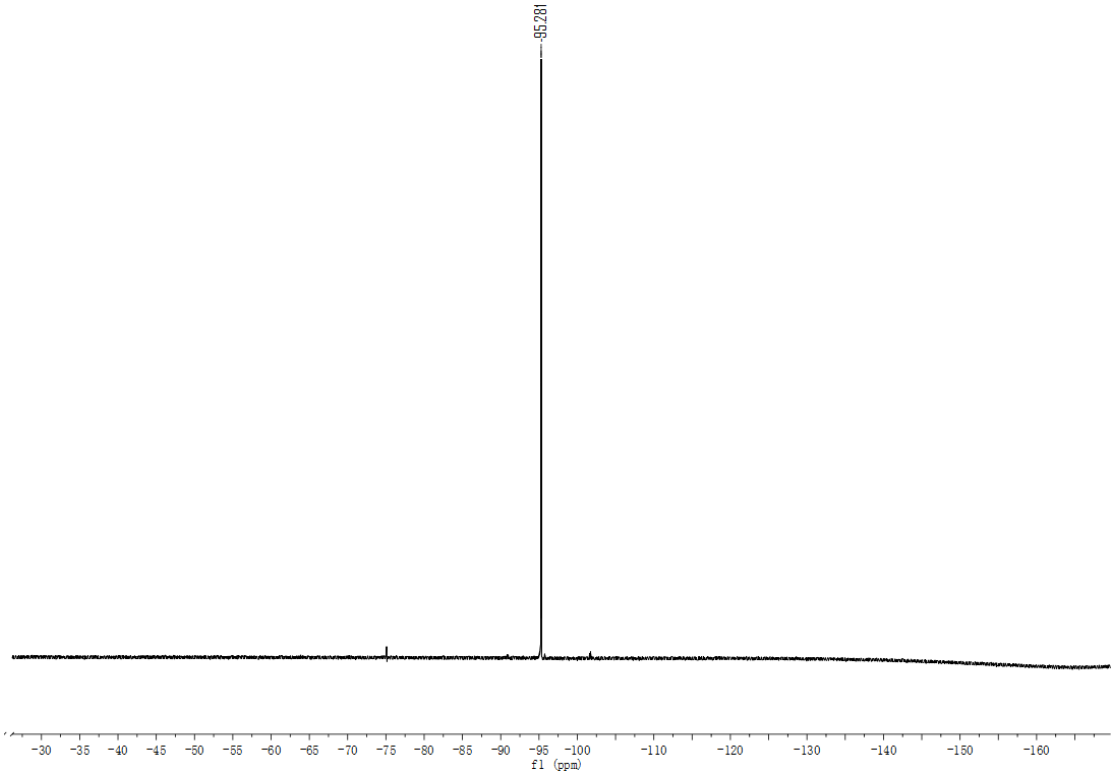



**1-(4-(tert-butyl)phenyl)-2,2-difluoro-2-(1H-inden-2-yl)ethan-1-one (4a)**

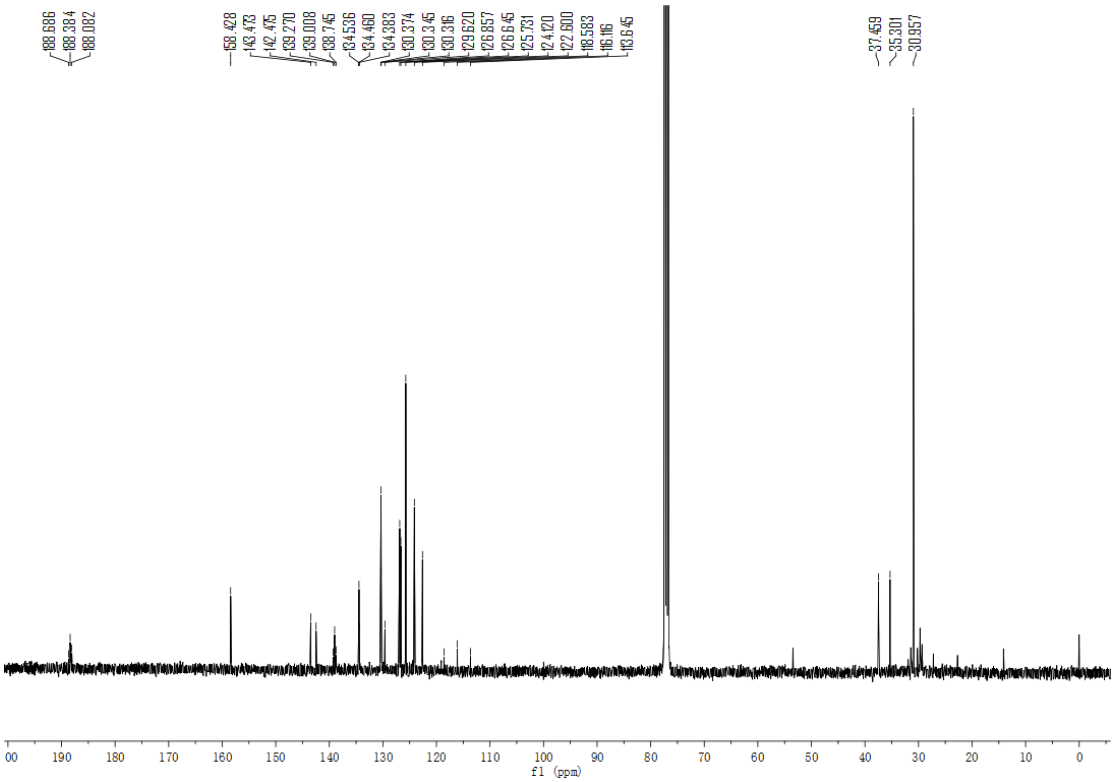
**$^{1}$H NMR (400 MHz, $CDCl_3$):**




**$^{19}$F NMR (376 MHz, $CDCl_3$):**

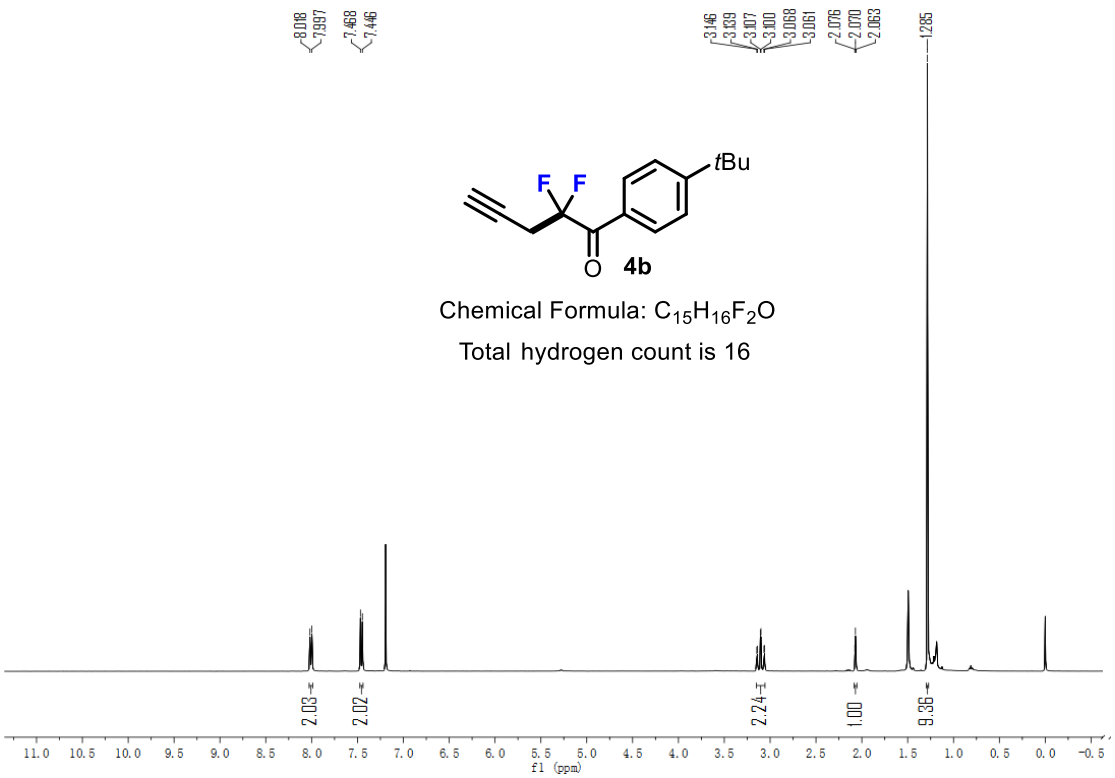



**$^{13}$C NMR (100 MHz, $CDCl_3$):**

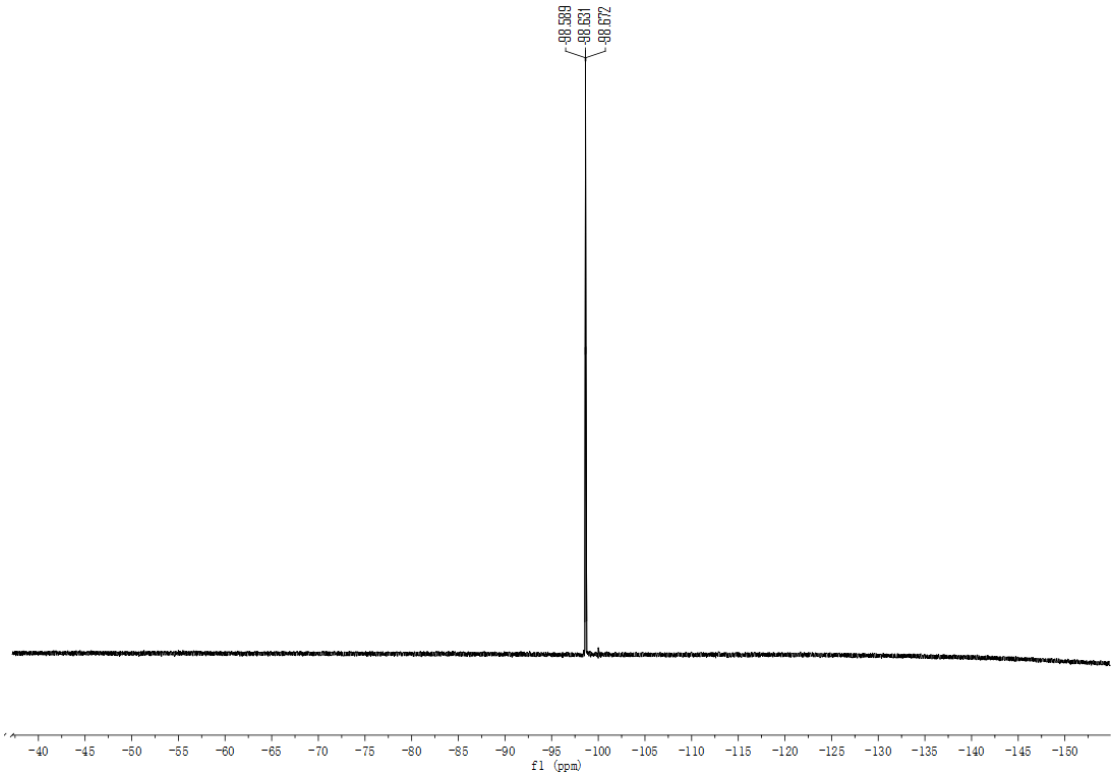



**1-(4-(tert-butyl)phenyl)-2,2-difluoropent-4-yn-1-one (4b)**

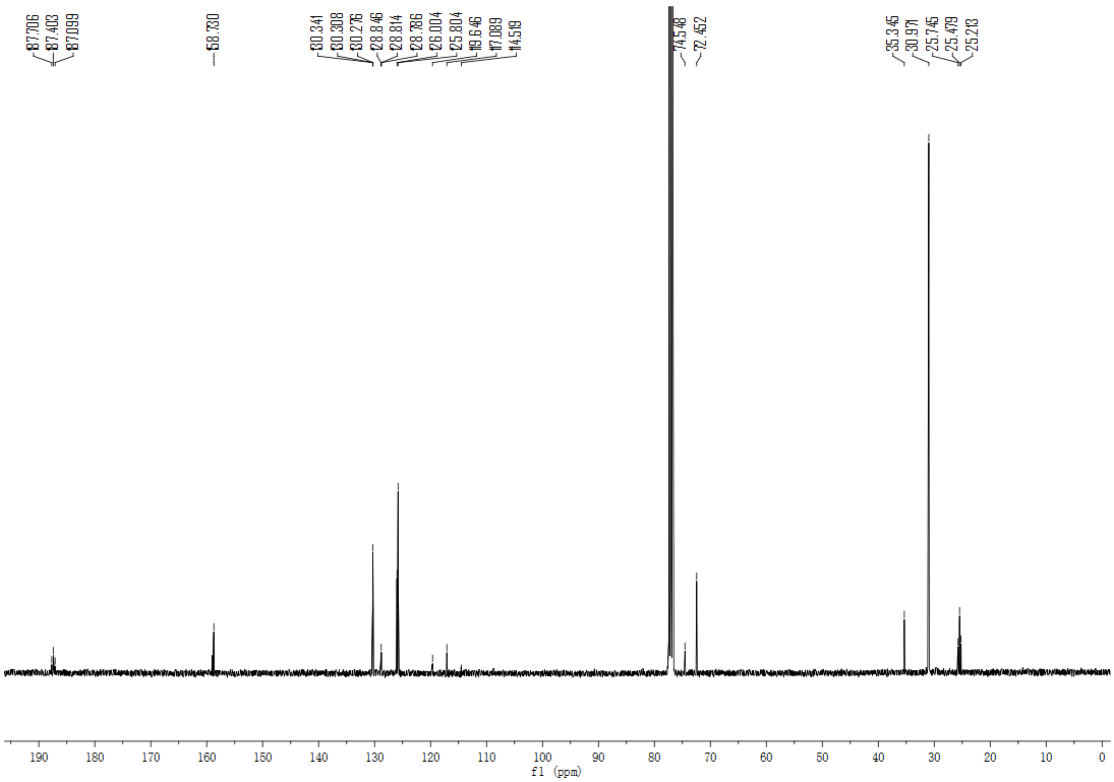
**$^{1}$H NMR (400 MHz, $CDCl_3$):**




**$^{19}$F NMR (376 MHz, $CDCl_3$):**

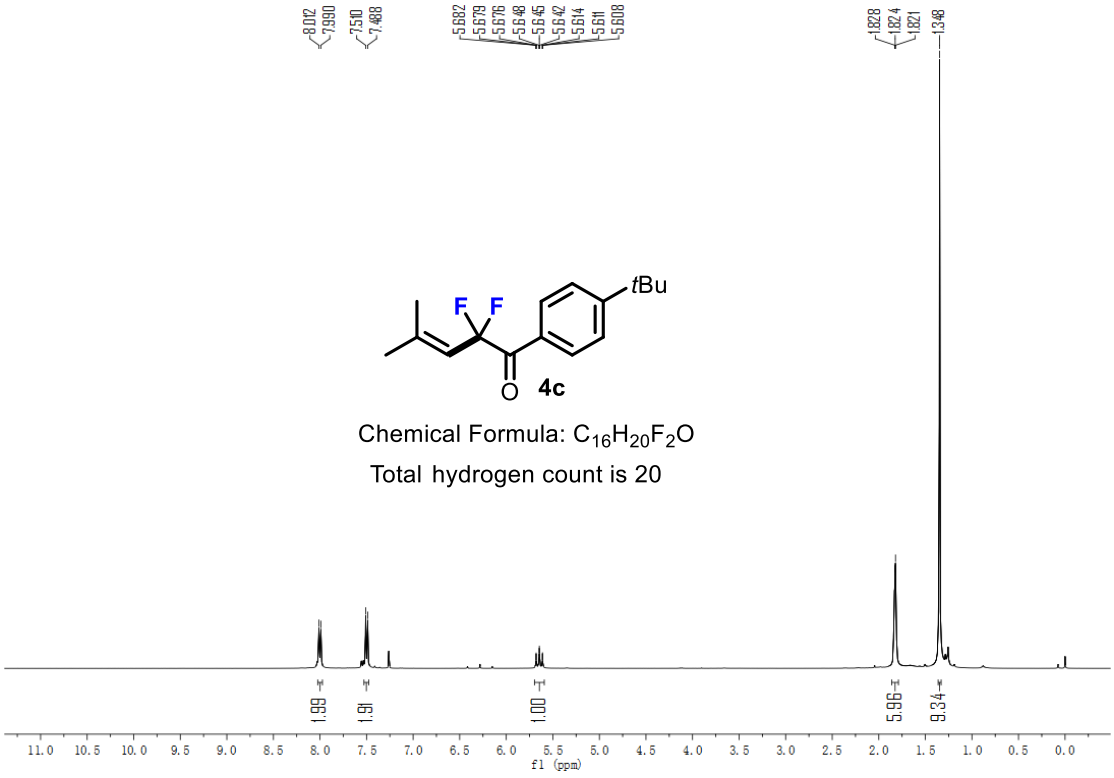



**$^{13}$C NMR (100 MHz, $CDCl_3$):**

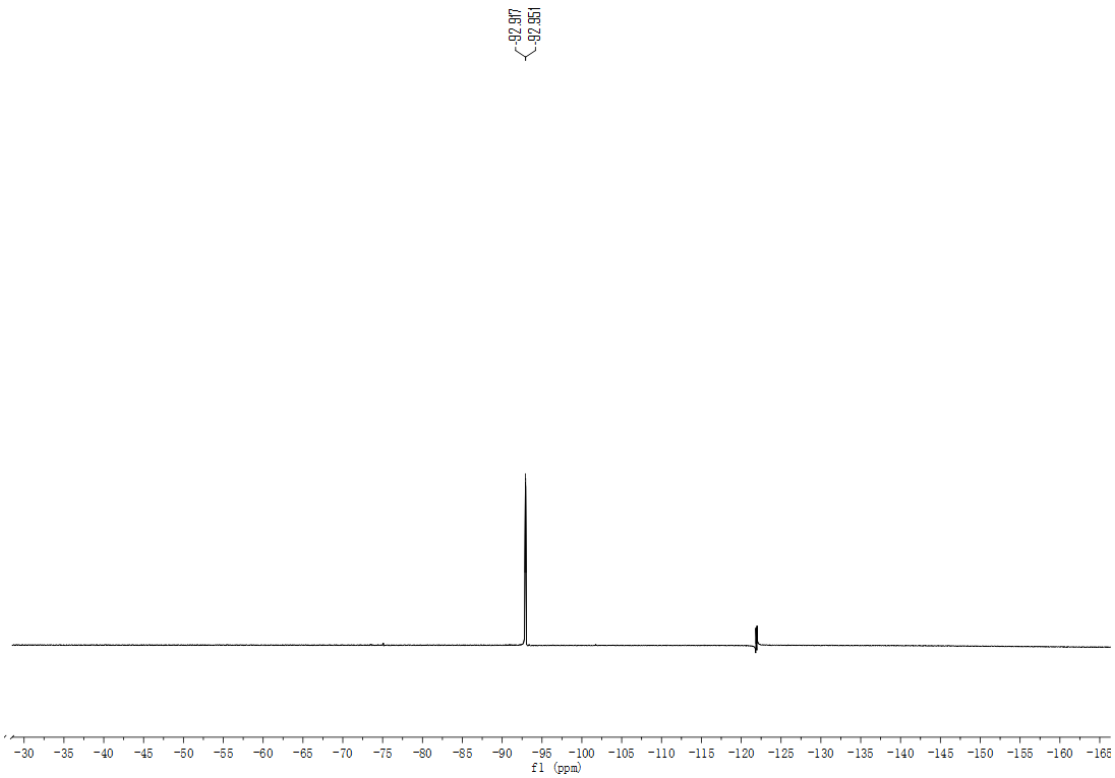



**1-(4-(tert-butyl)phenyl)-2,2-difluoro-4-methylpent-3-en-1-one (4c)**

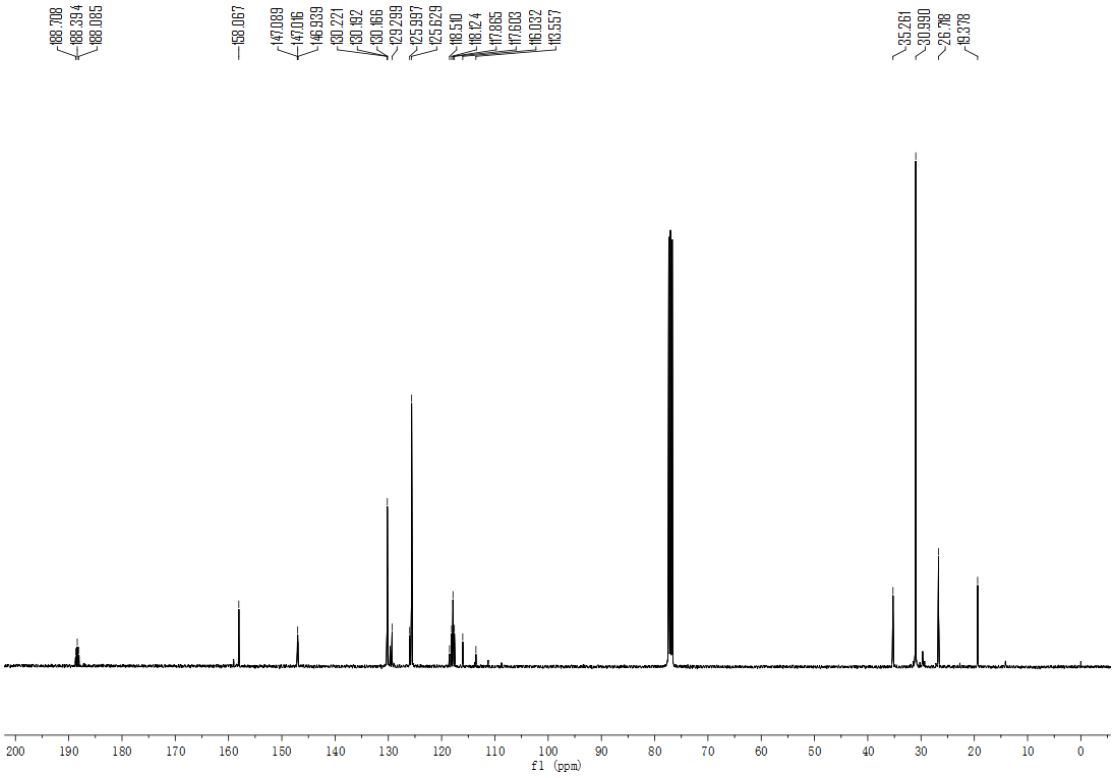
**$^{1}$H NMR (400 MHz, $CDCl_3$):**




**$^{19}$F NMR (376 MHz, $CDCl_3$):**

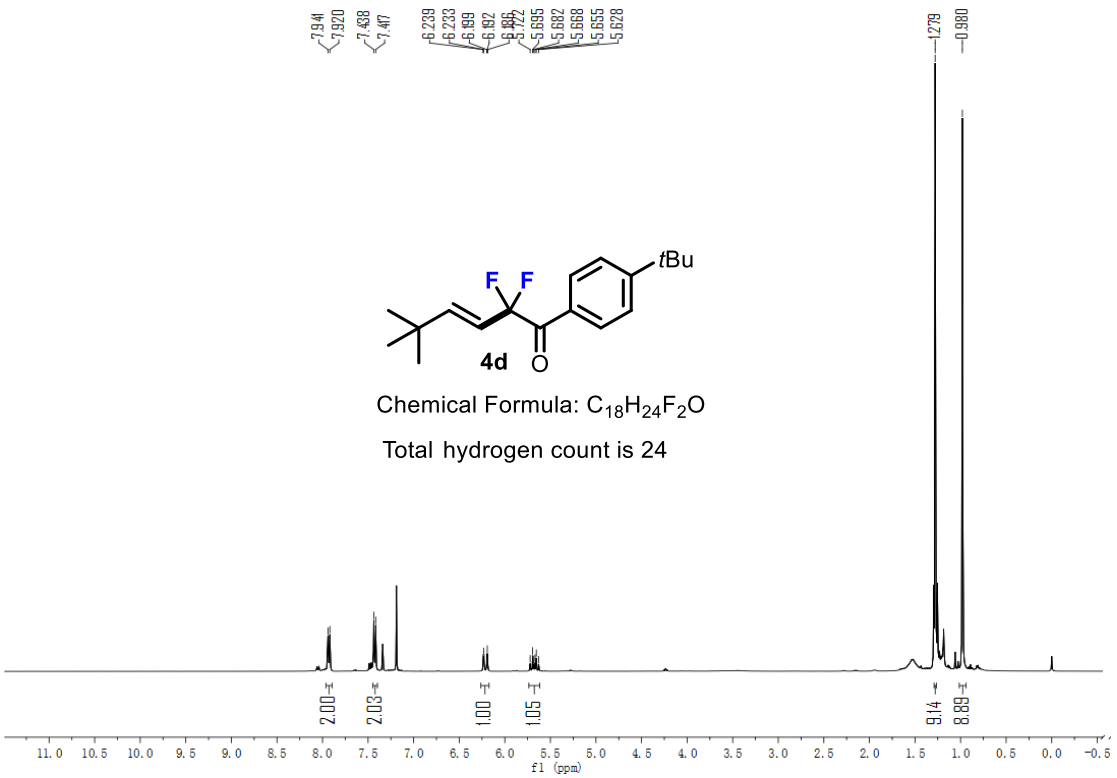



**$^{13}$C NMR (100 MHz, $CDCl_3$):**

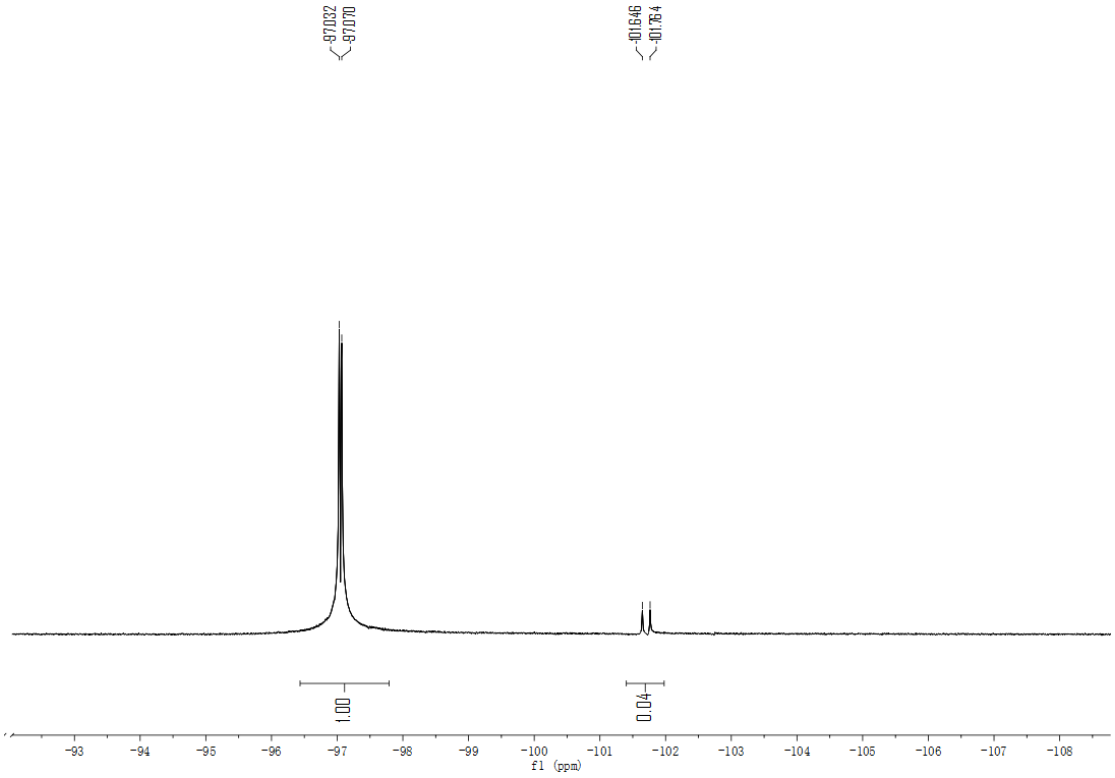



**(E)-1-(4-(tert-butyl)phenyl)-2,2-difluoro-5,5-dimethylhex-3-en-1-one (4d)**

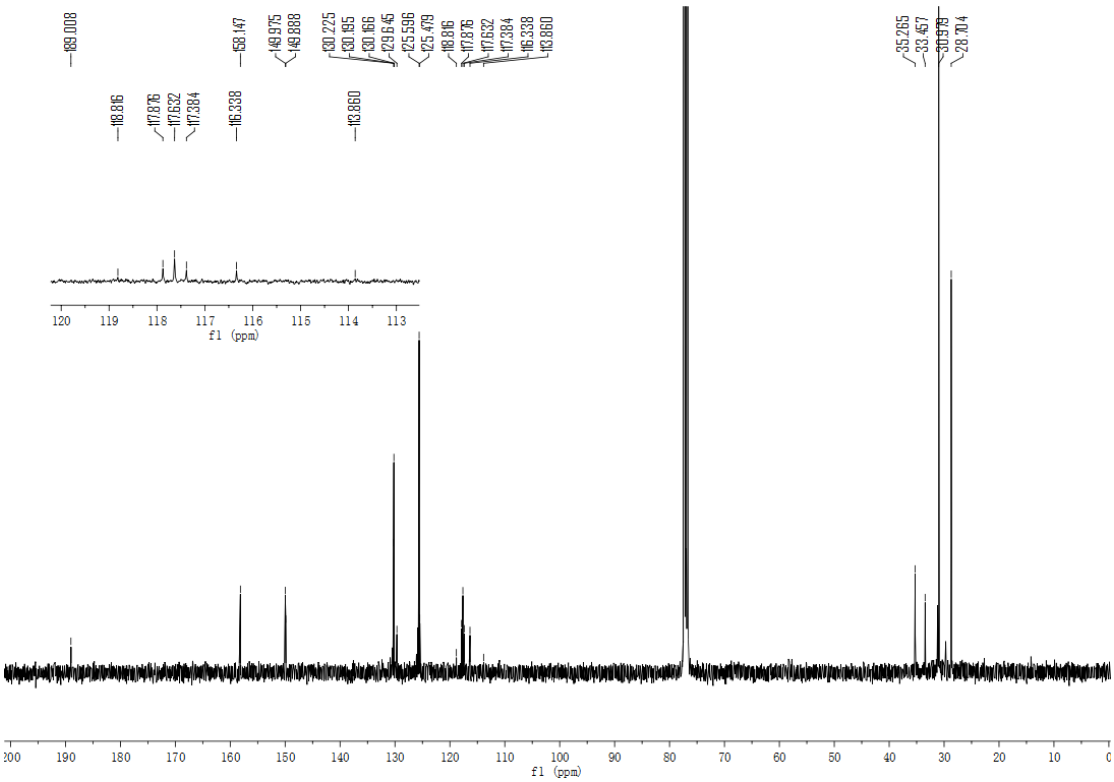
**$^{1}$H NMR (400 MHz, $CDCl_3$):**




**$^{19}$F NMR (376 MHz, $CDCl_3$):**

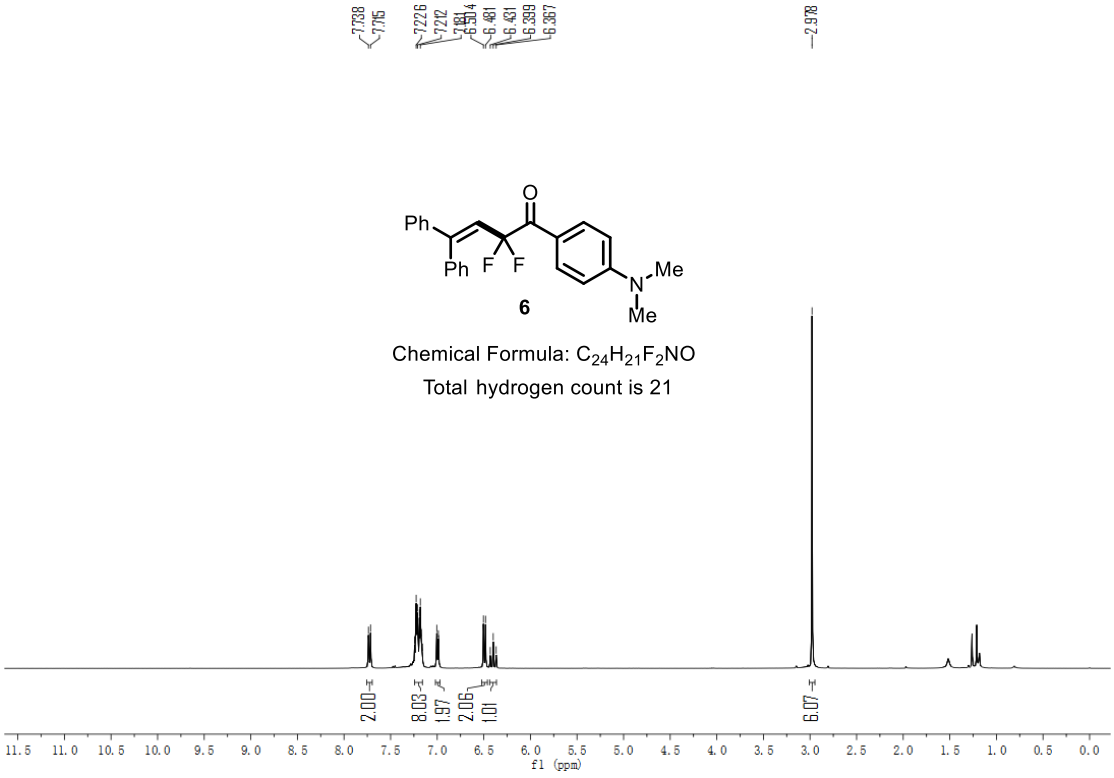



**$^{13}$C NMR (100 MHz, $CDCl_3$):**

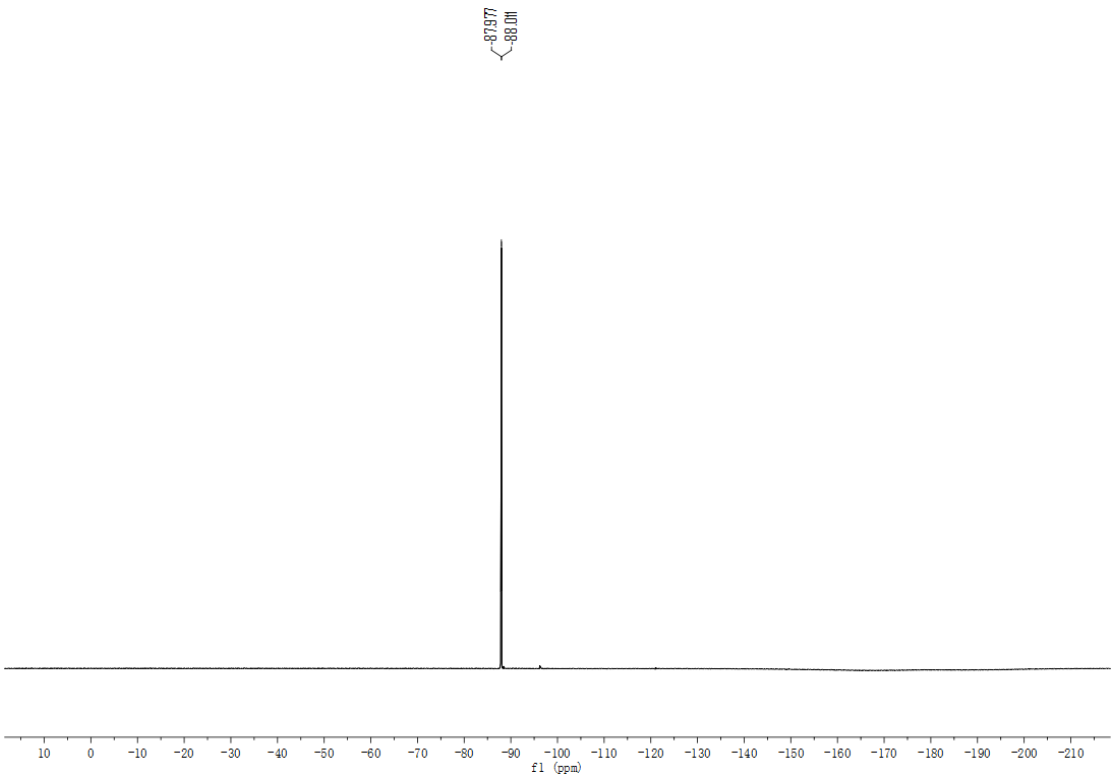



**1-(4-(dimethylamino)phenyl)-2,2-difluoro-4,4-diphenylbut-3-en-1-one (6)**

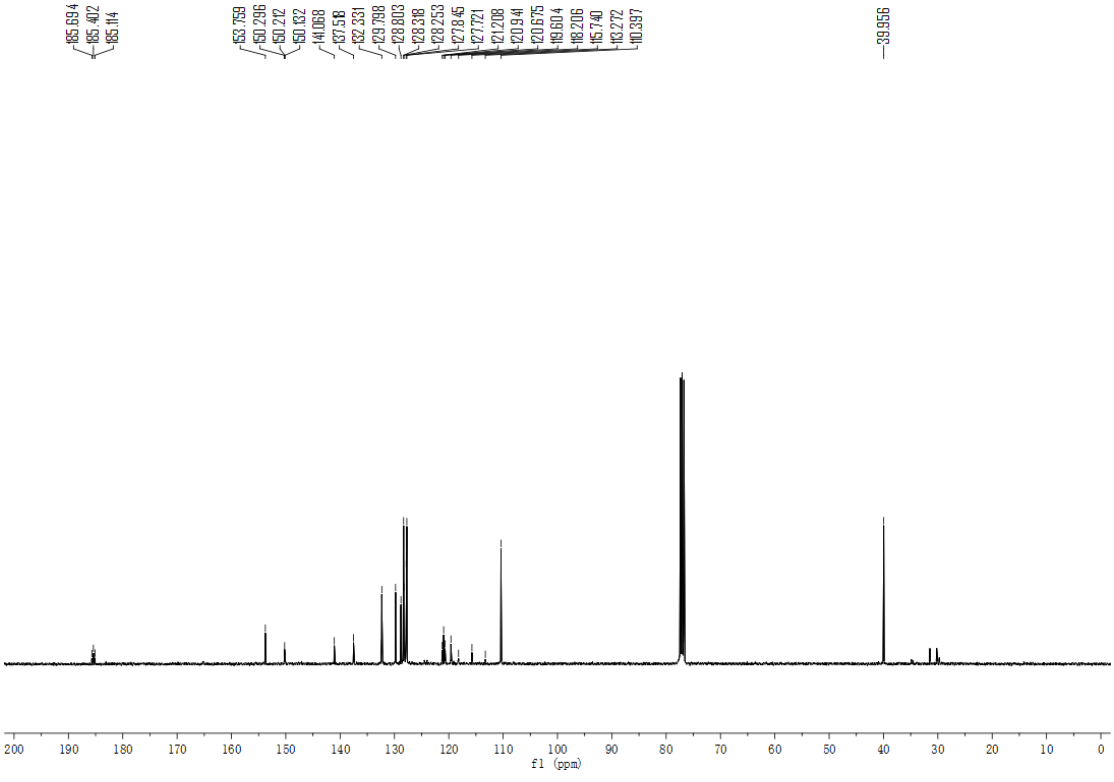
**$^{1}$H NMR (400 MHz, $CDCl_3$):**




**$^{19}$F NMR (376 MHz, $CDCl_3$):**

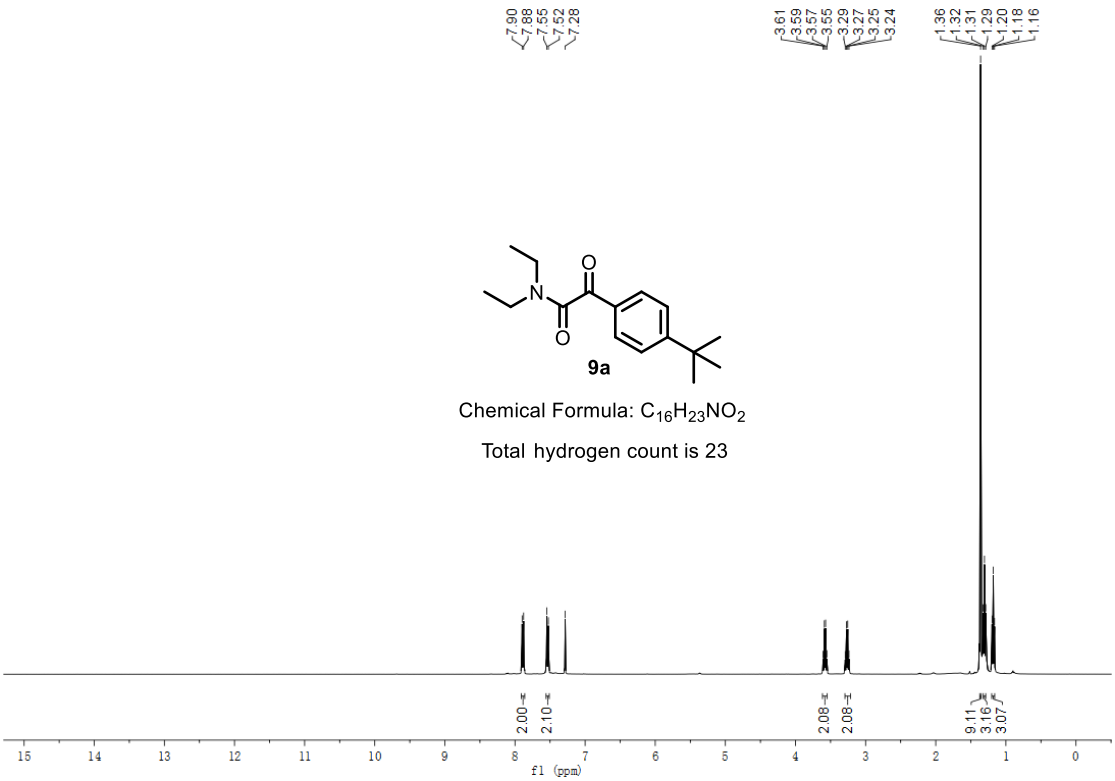



**$^{13}$C NMR (100 MHz, $CDCl_3$):**

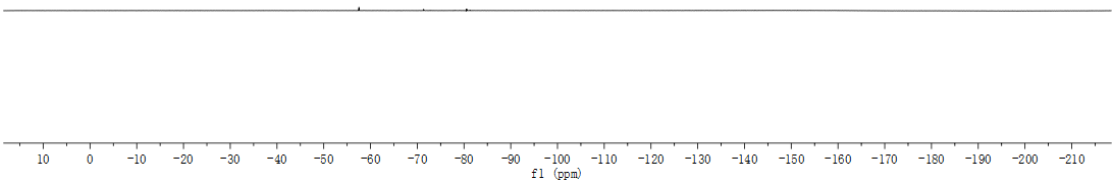



**2-(4-(tert-butyl)phenyl)-N,N-diethyl-2-oxoacetamide (9a)**

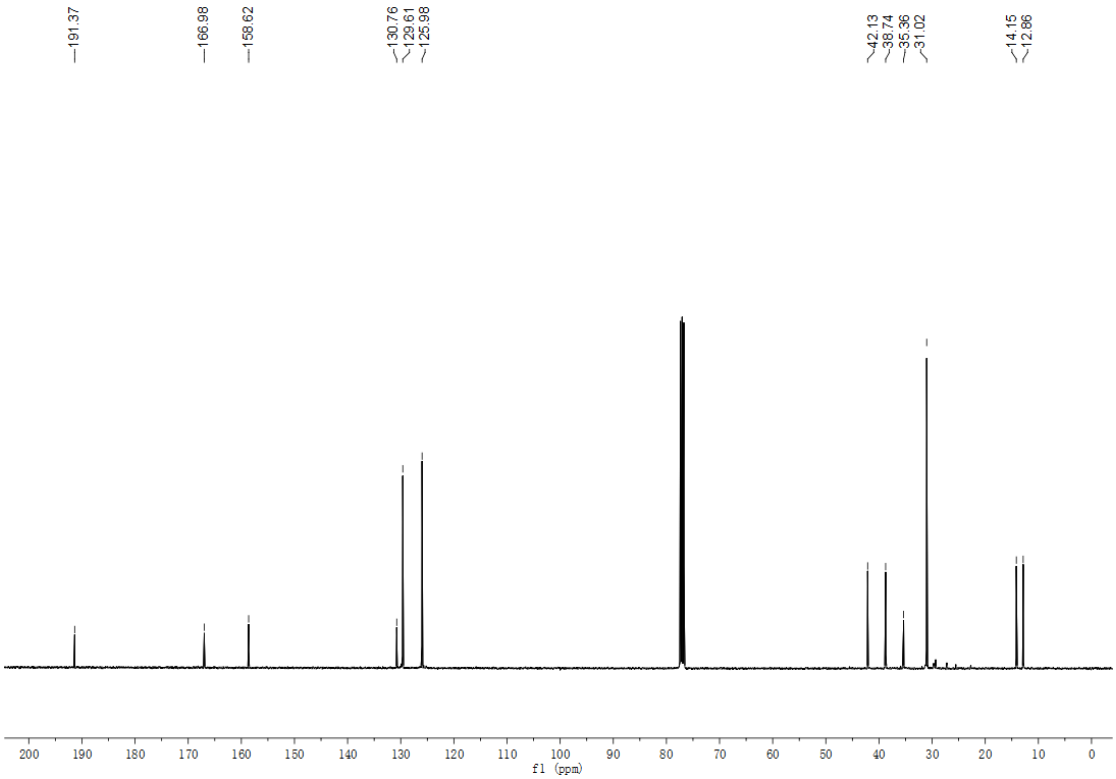
**$^{1}$H NMR (400 MHz, $CDCl_3$):**



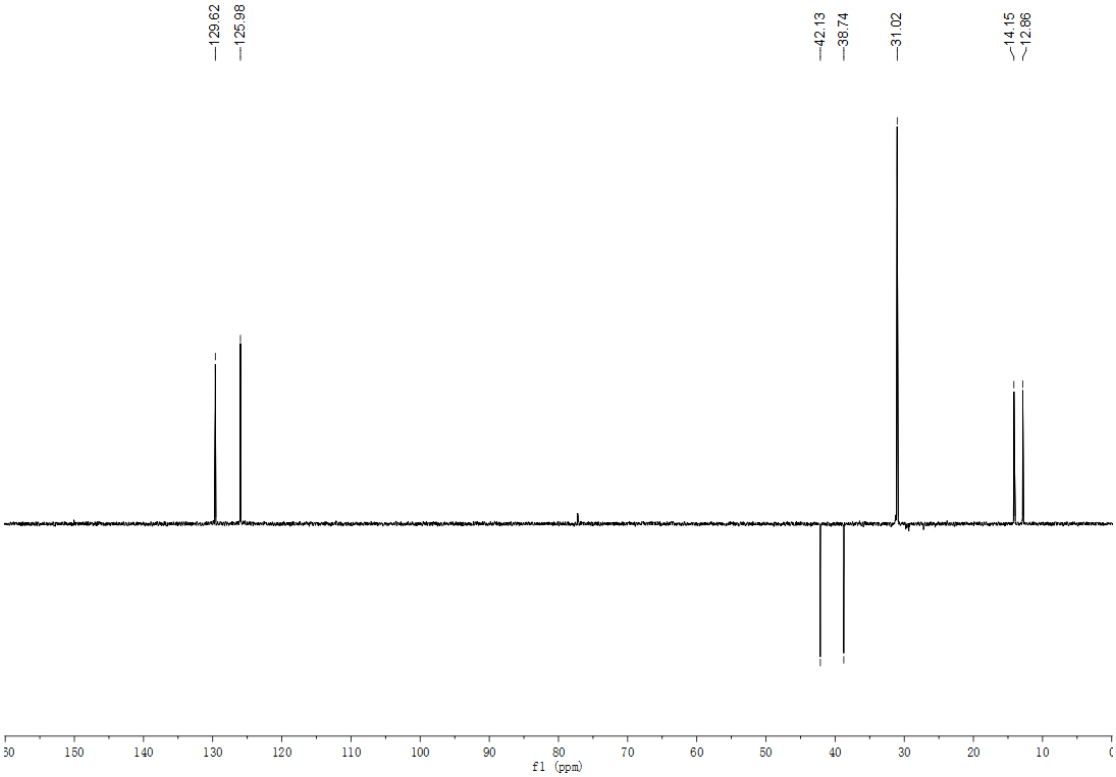

**$^{19}$F NMR (376 MHz, $CDCl_3$):**



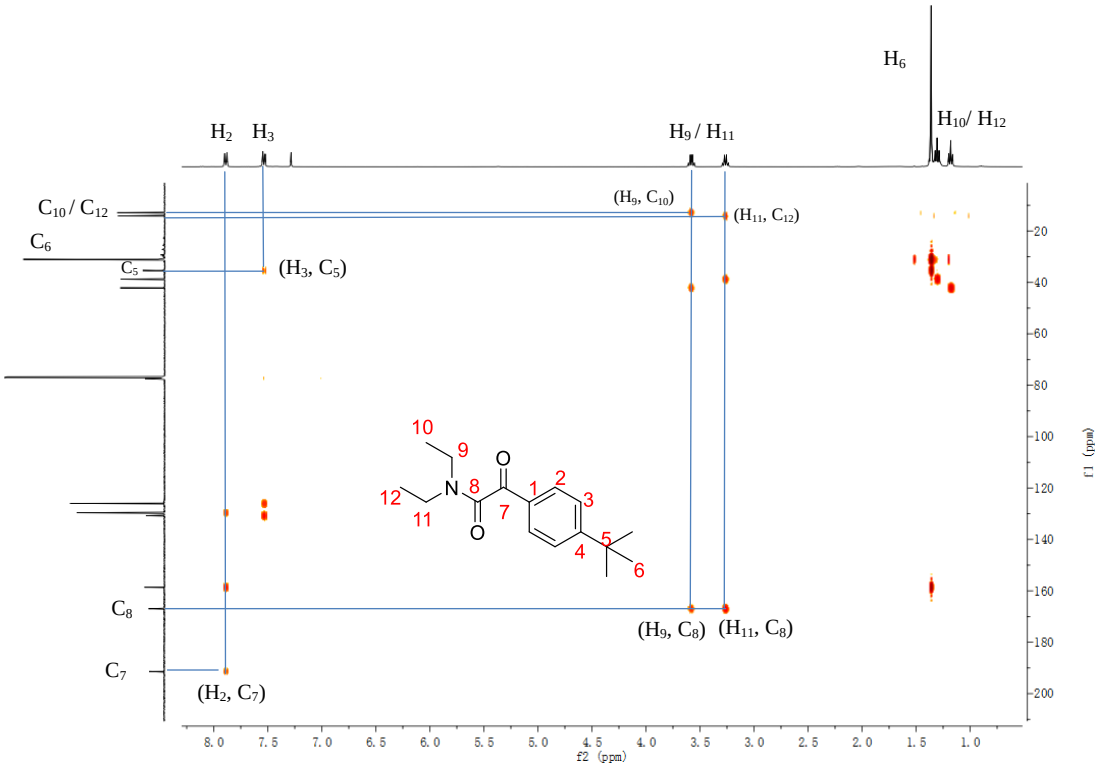

**$^{13}$C NMR (100 MHz, $CDCl_3$):**



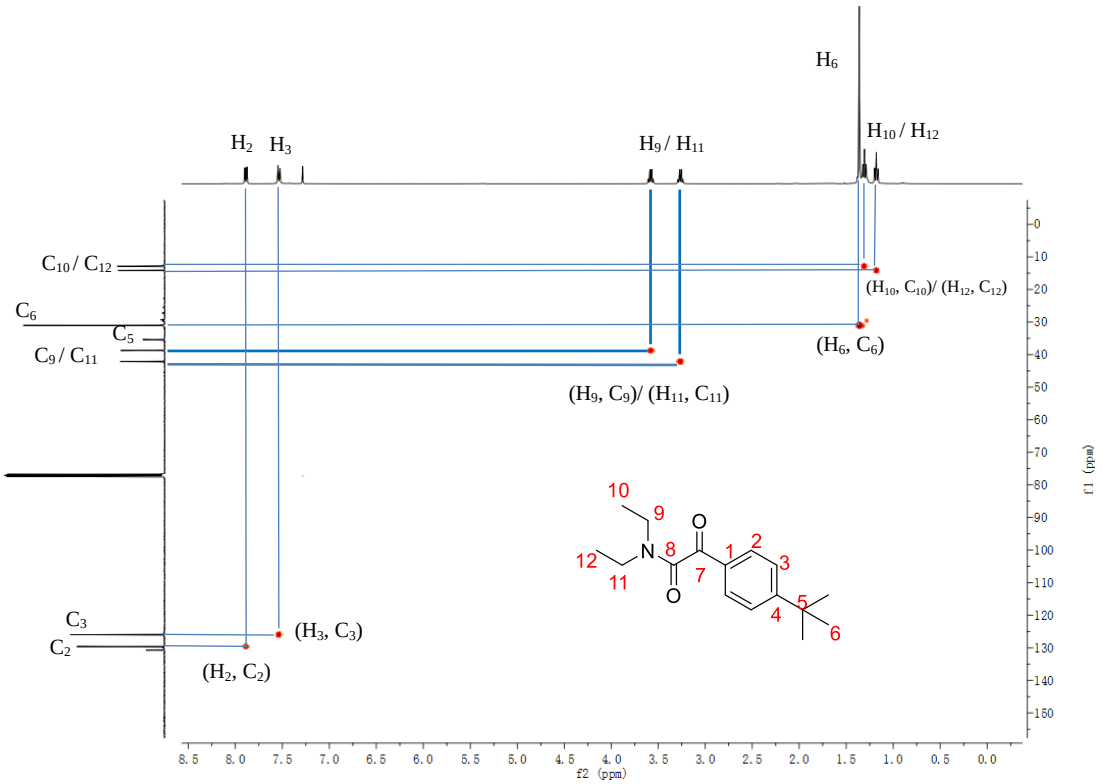

**DEPT 135 (100 MHz, $CDCl_3$):**




**HMBC：**

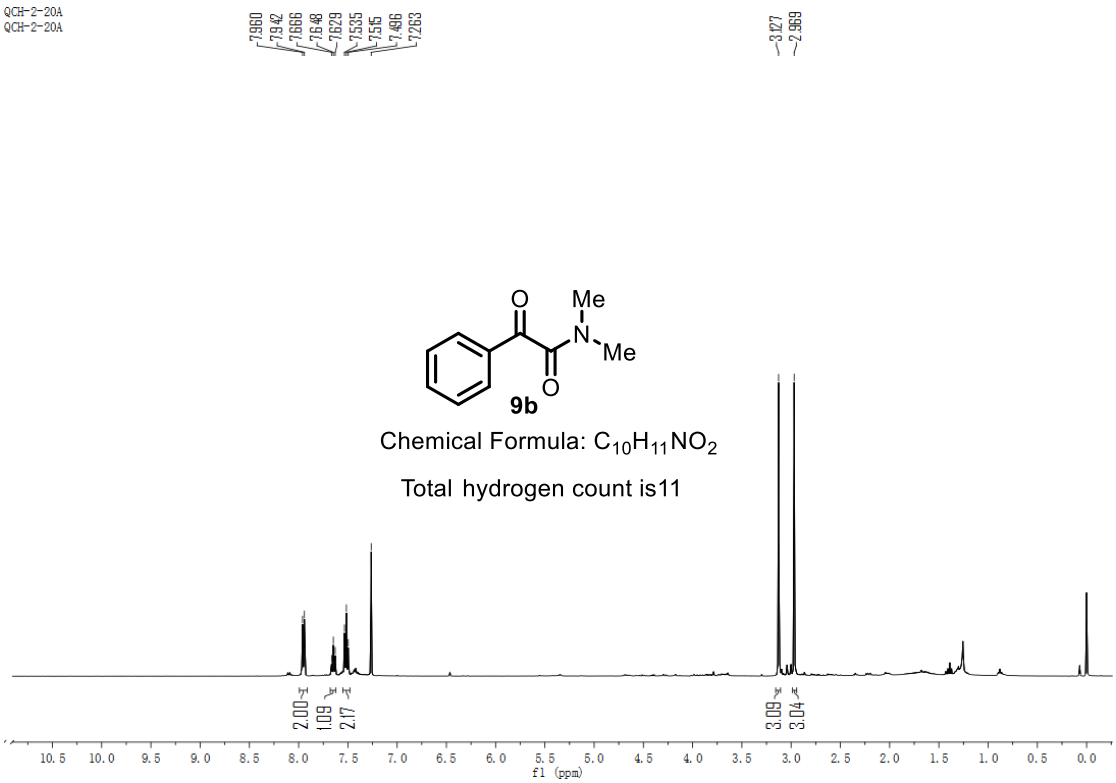



**HSQC**

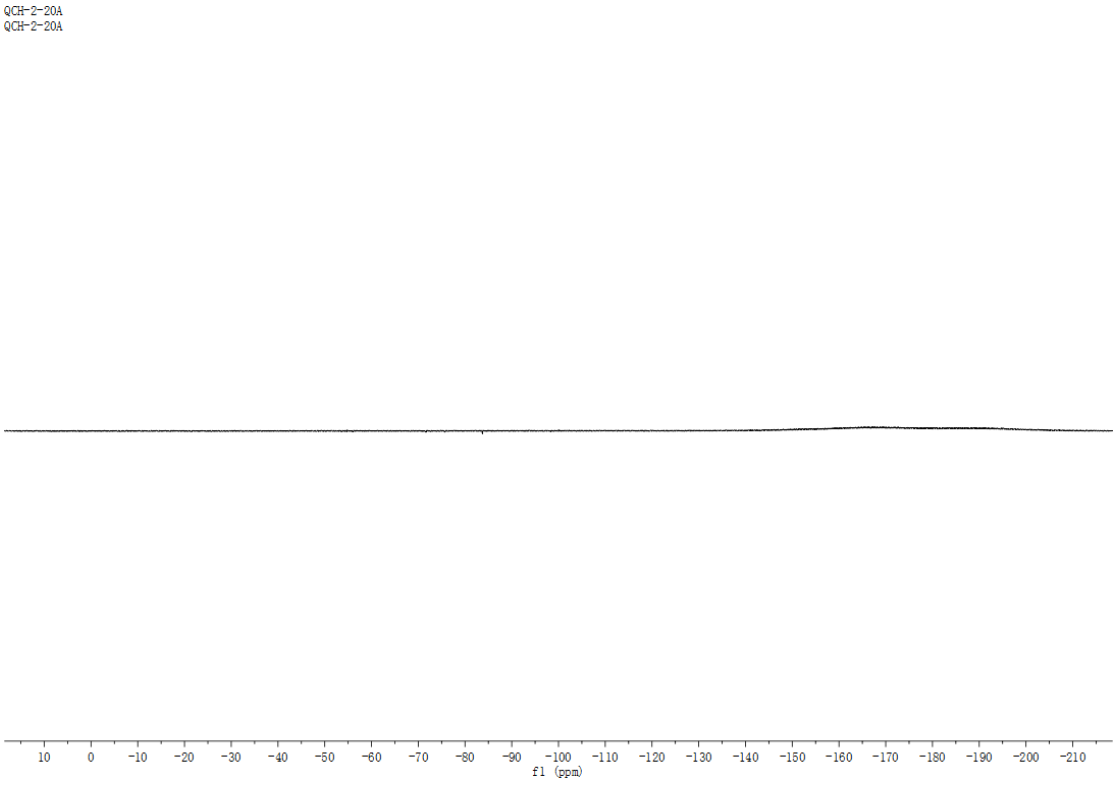



**N,N-dimethyl-2-oxo-2-phenylacetamide (9b)**

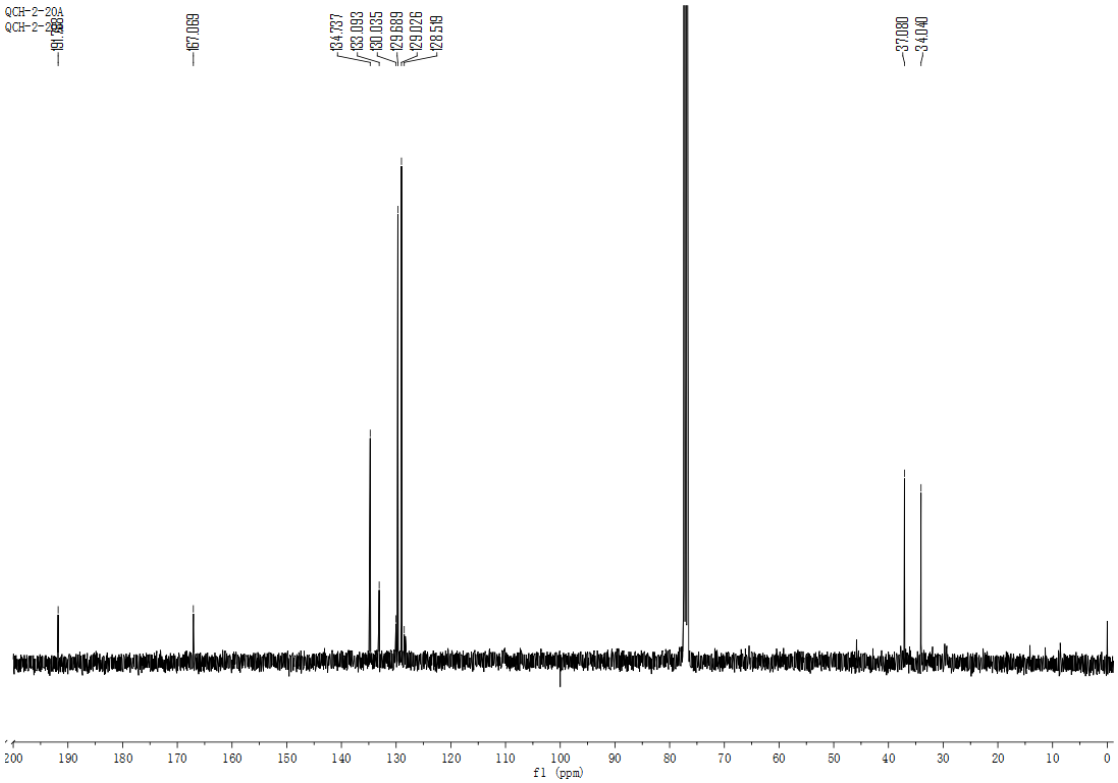
**$^1$H NMR (400 MHz, $CDCl_3$):**




**$^{19}$F NMR (376 MHz, $CDCl_3$):**

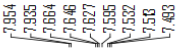



**$^{13}$C NMR (100 MHz, $CDCl_3$):**

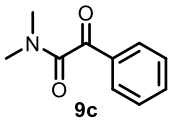



**N,N-dimethyl-2-oxo-2-phenylacetamide (9c)**

**$^{1}$H NMR (400 MHz, $CDCl_3$):**

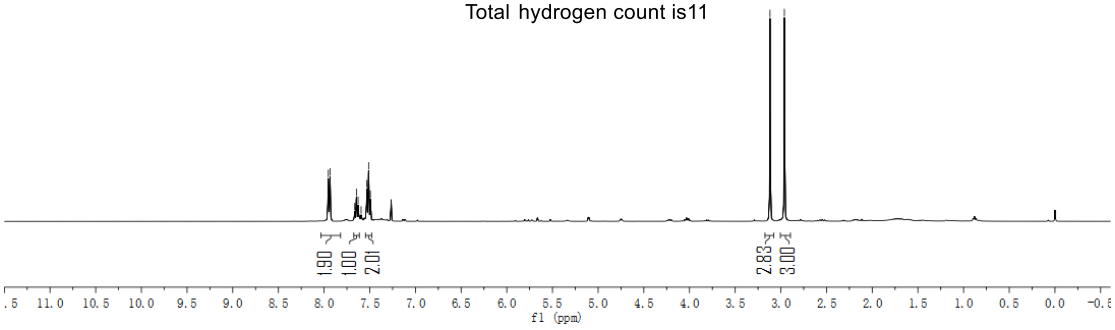




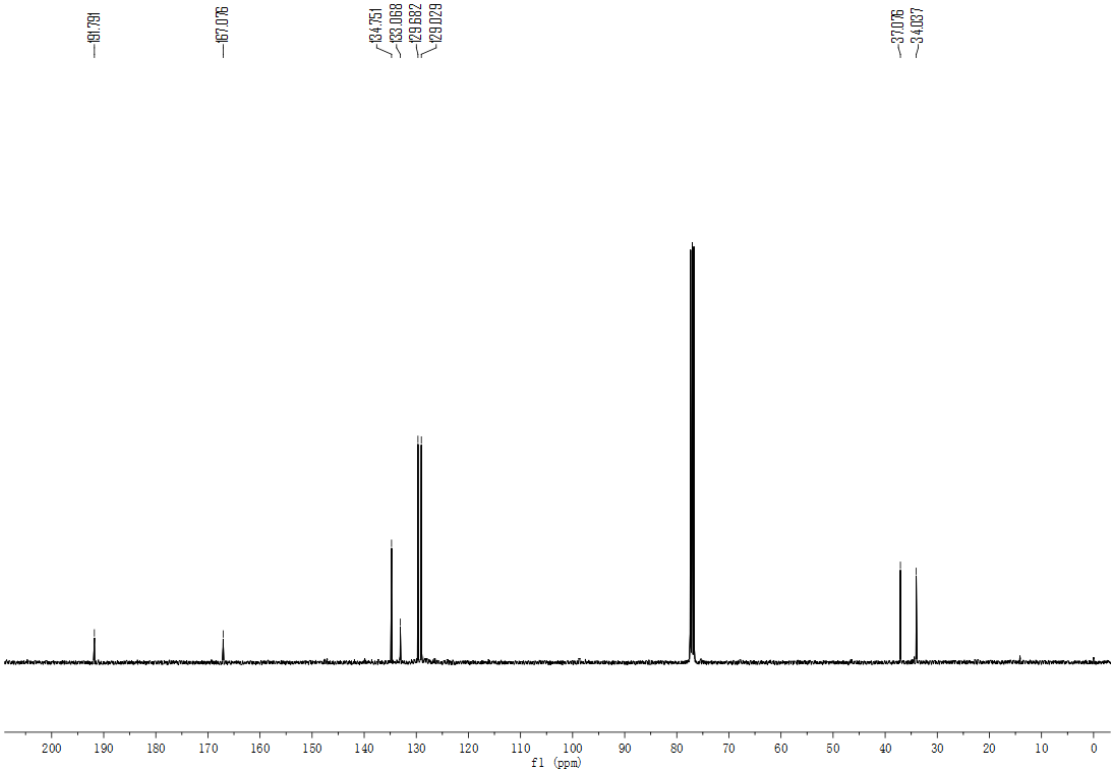



Chemical Formula:
$C_{10}H_{11}NO_2$

Total hydrogen count is11

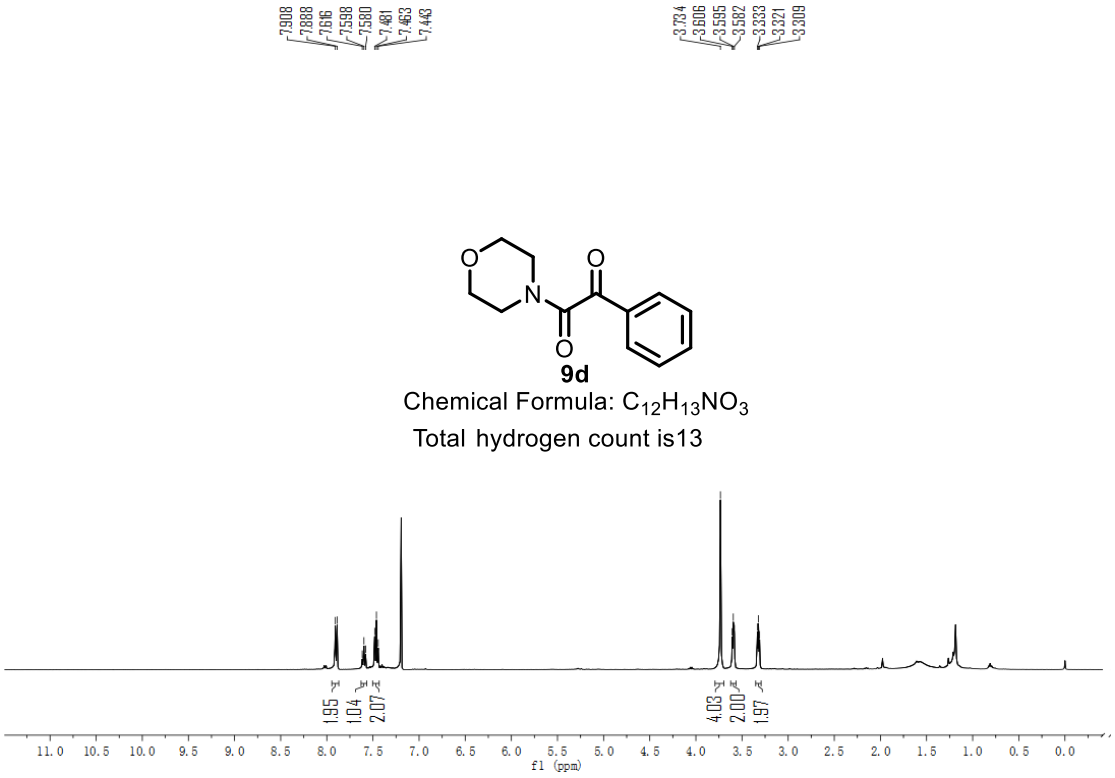



**$^{13}$C NMR (100 MHz, $CDCl_3$):+**

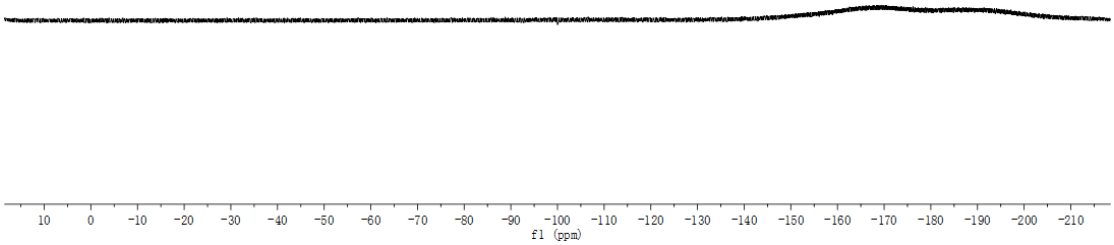



**1- morpholino-2-phenylethane-1,2-dione (9d)**

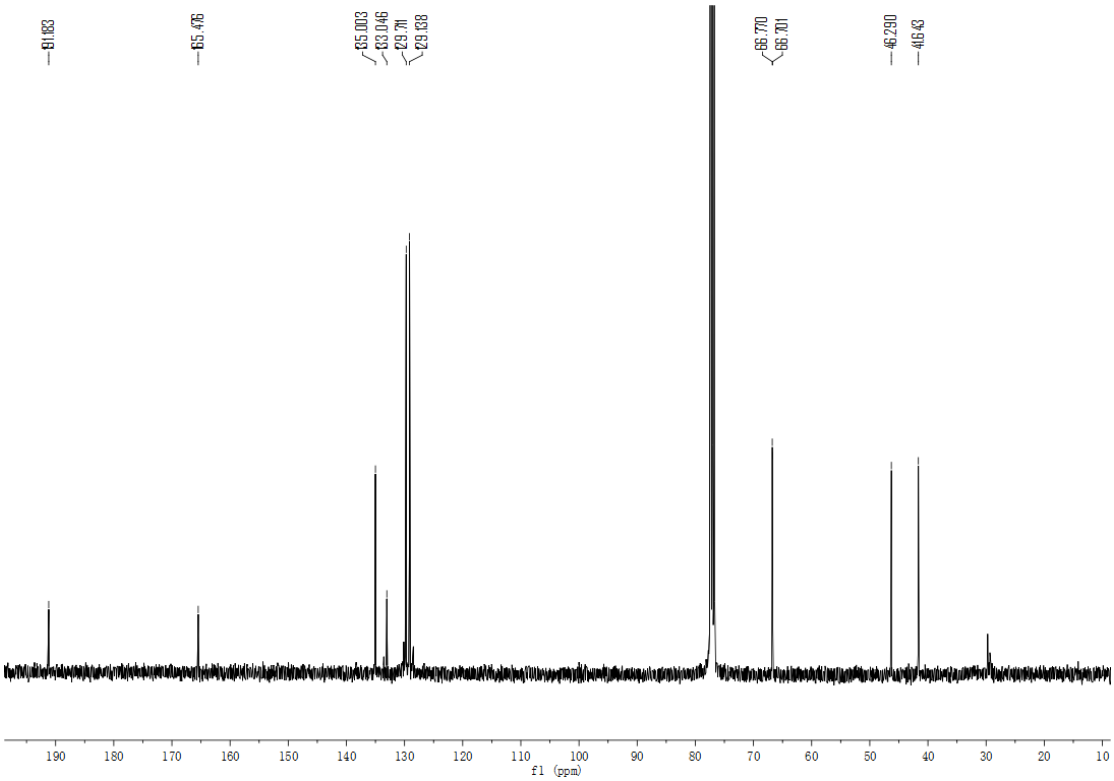
**1H NMR (400 MHz, CDCl3):**



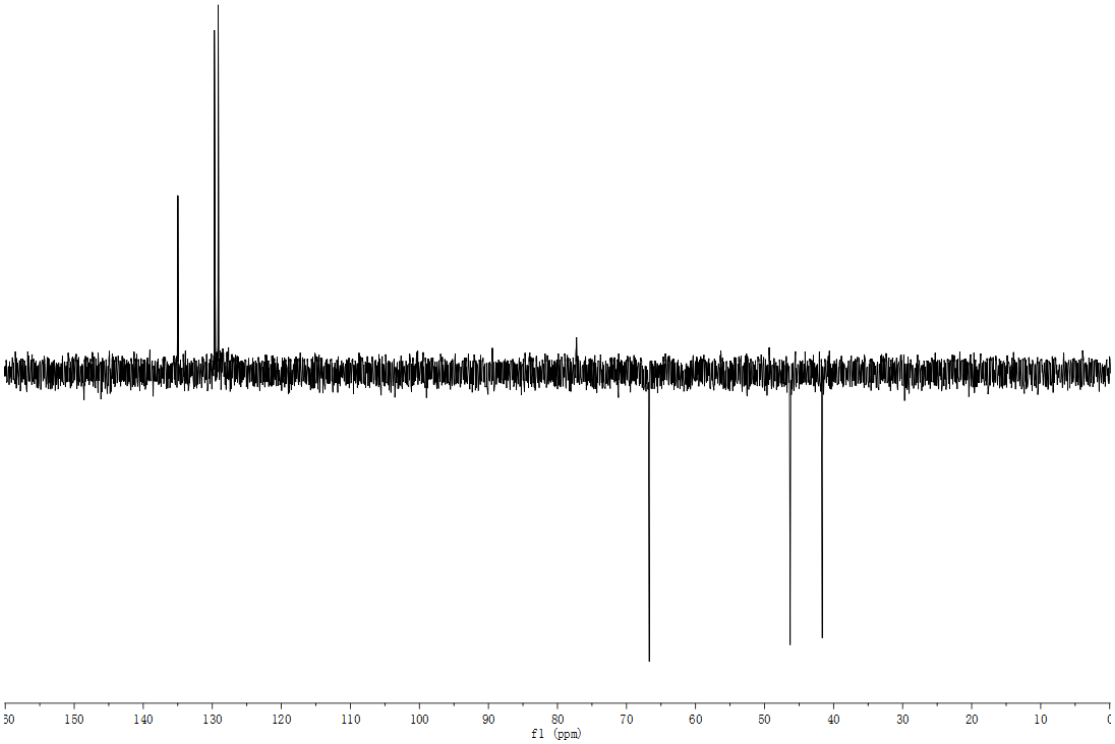

**$^{19}$F NMR (376 MHz, $CDCl_3$):**




**$^{13}$C NMR (100 MHz, $CDCl_3$):**

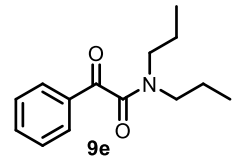



**DEPT**




**2- oxo-2-phenyl-N,N-dipropylacetamide (9e)**

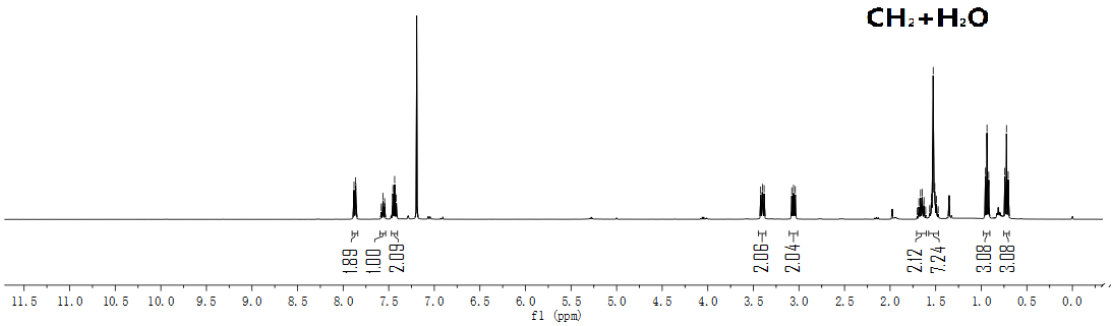
**$^{1}$H NMR (400 MHz, $CDCl_3$):**

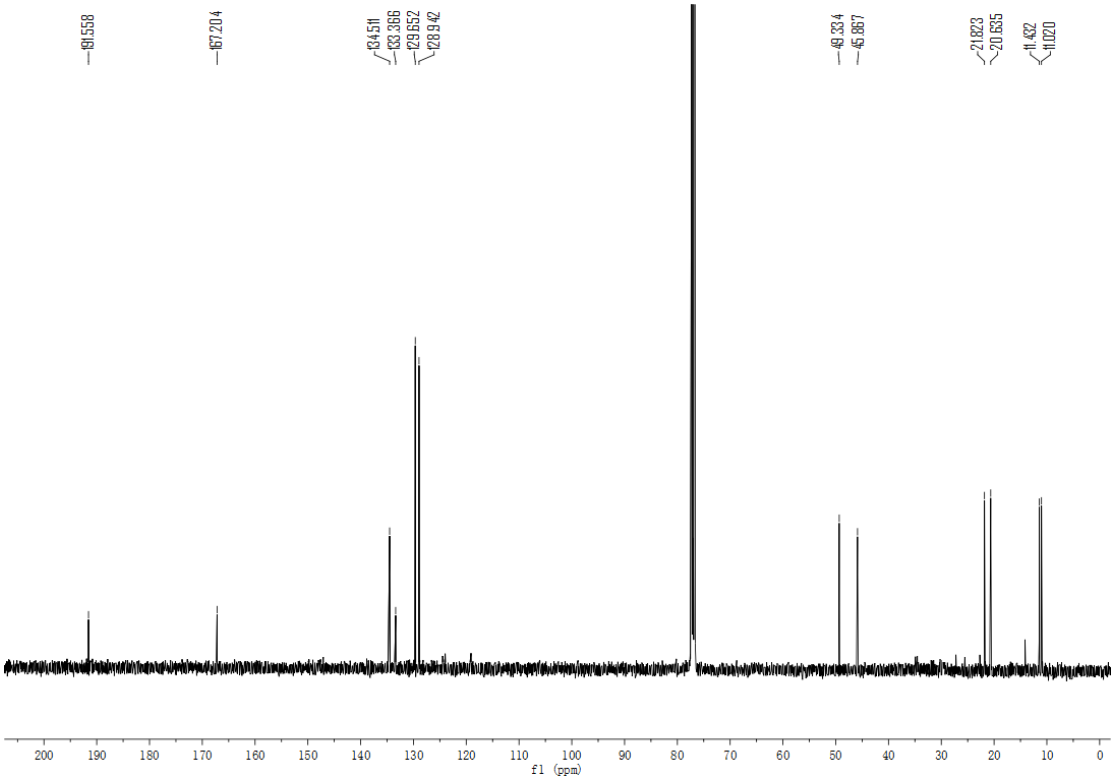
**9e**

Chemical Formula: $C_{14}H_{19}NO_2$

Total hydrogen count is19

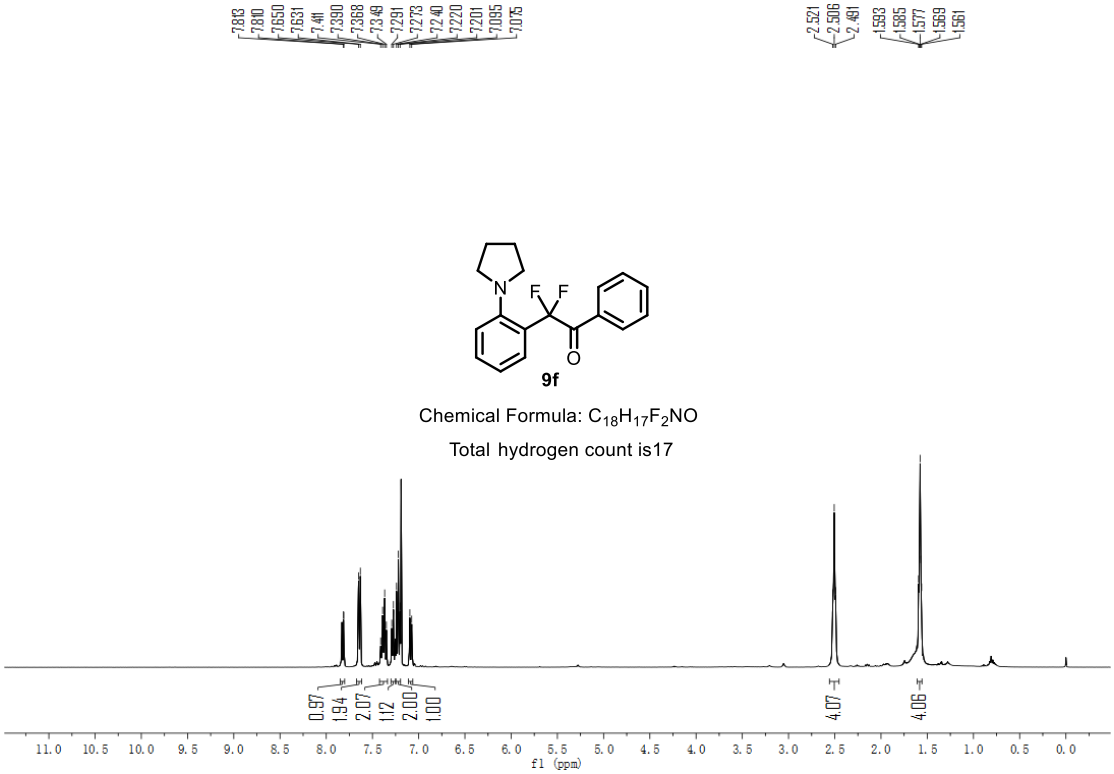



**$^{13}$C NMR (100 MHz, $CDCl_3$):**

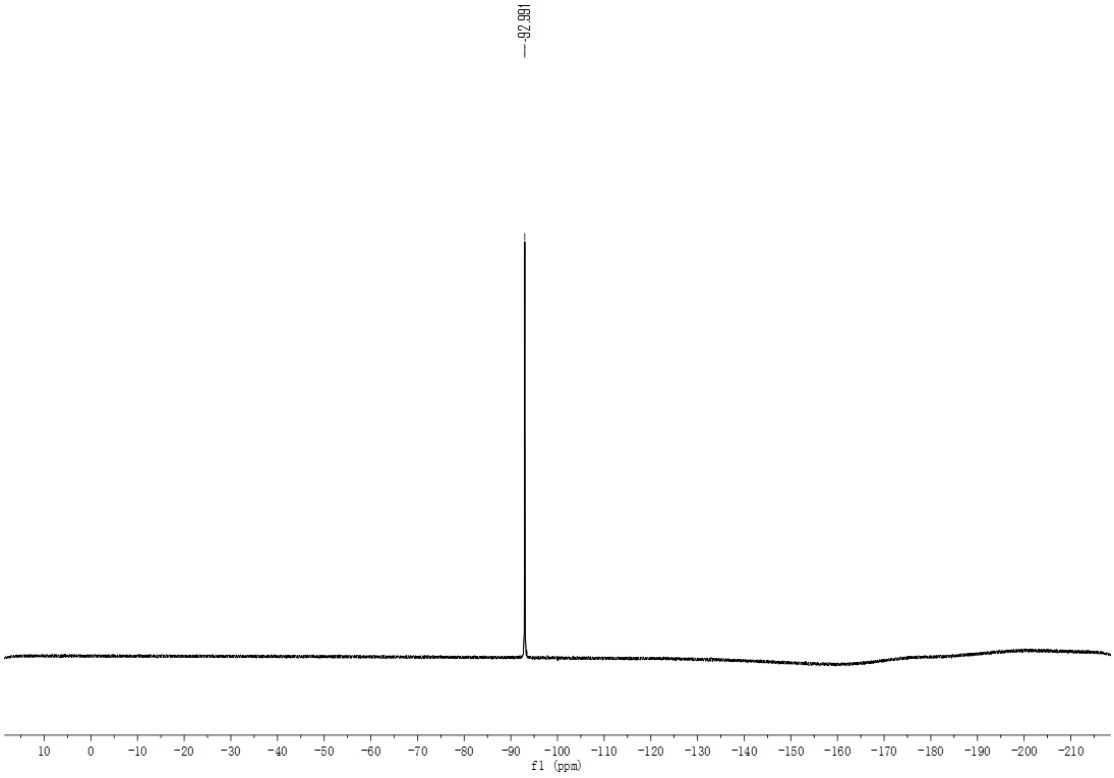



**2,2-difluoro-1-phenyl-2-(2-(pyrrolidin-1-yl)phenyl)ethan-1-one (9f)**

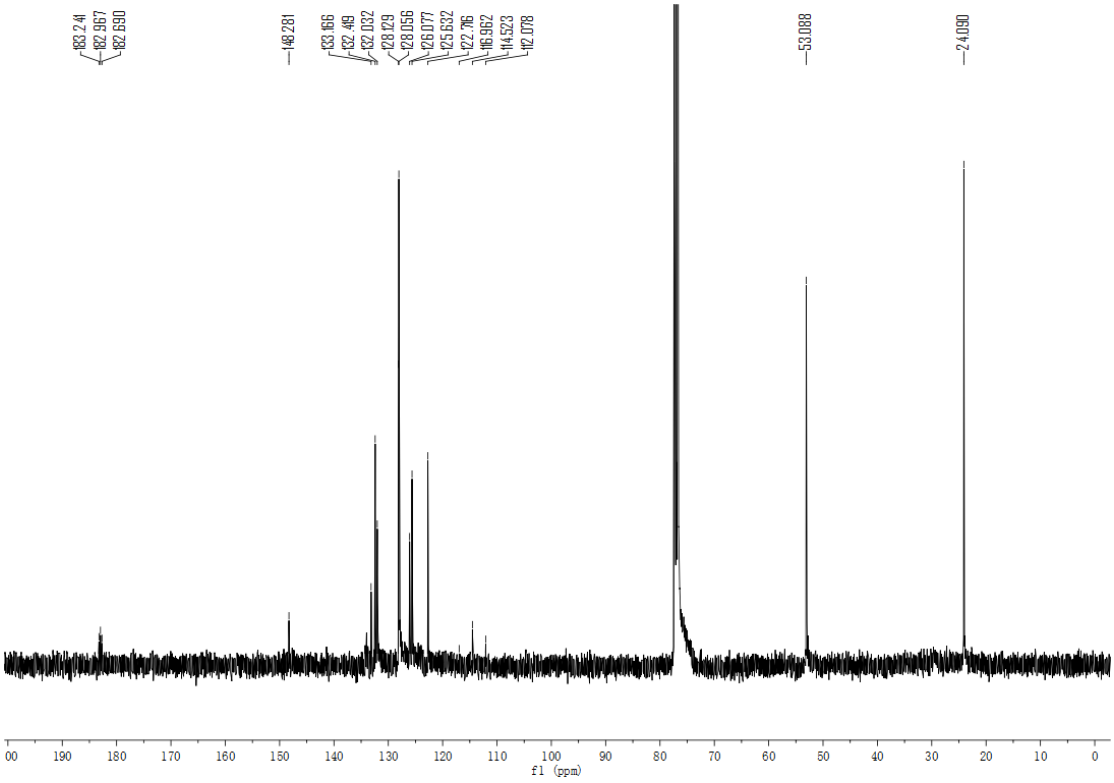
**$^{1}$H NMR (400 MHz, $CDCl_3$):**




**$^{19}$F NMR (376 MHz, $CDCl_3$):**

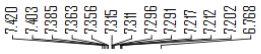


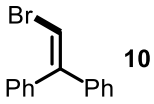

**$^{13}$C NMR (100 MHz, $CDCl_3$):**




(2-bromoethene-1,1-diyl)dibenzene (**10**)

**$^{1}$H NMR (400 MHz, $CDCl_3$):**

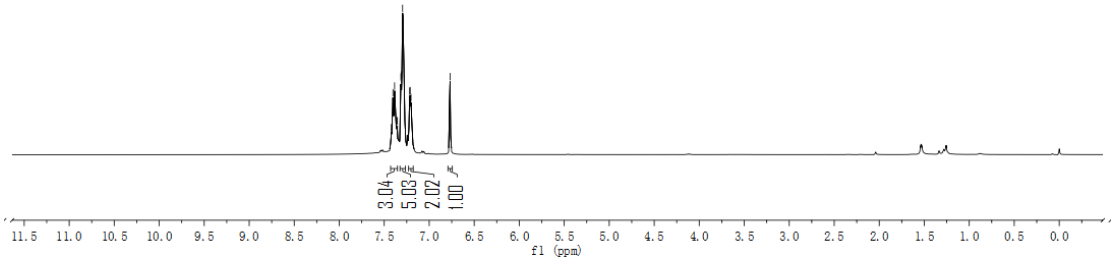


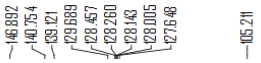

**10**

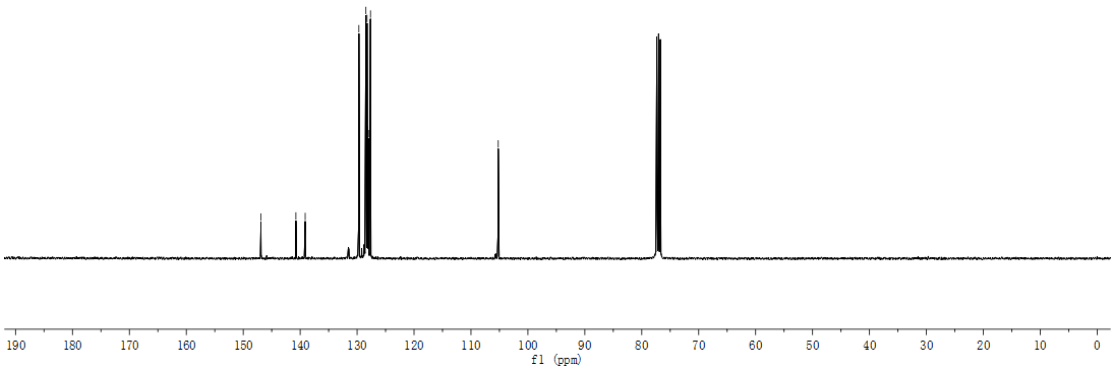
Chemical Formula: $C_{14}H_{11}Br$

Total hydrogen count is11

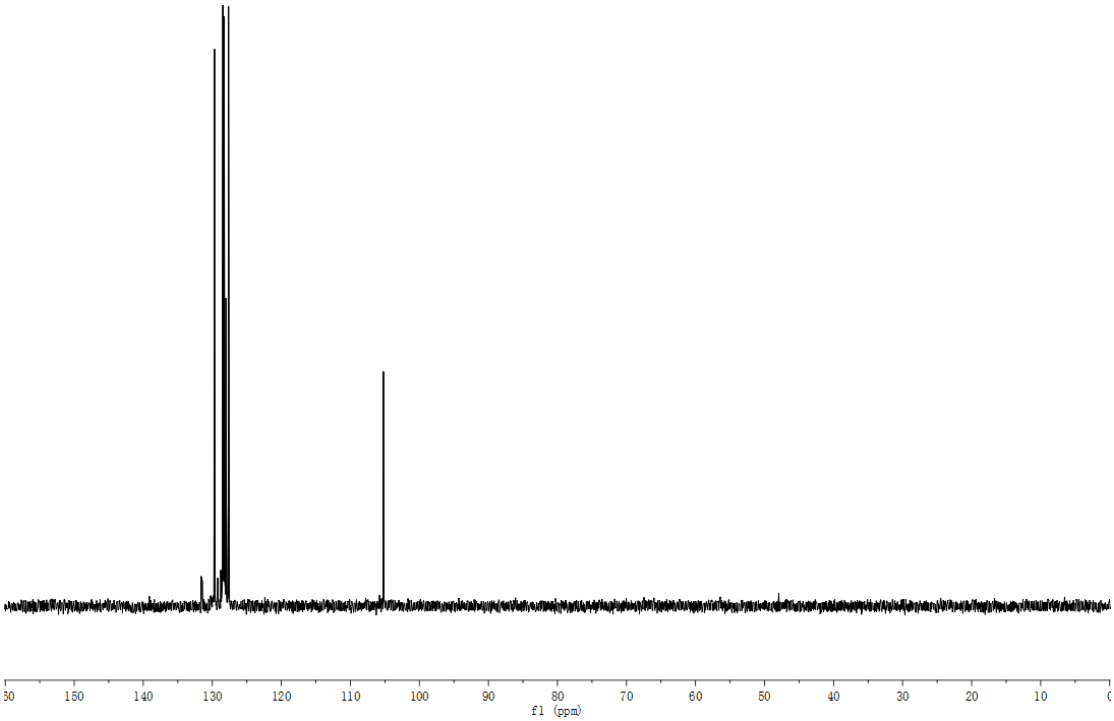



**$^{13}$C NMR (100 MHz, $CDCl_3$):**




DEPT


160
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10
f1 (ppm)