# Supporting Information

# Photocatalytic arylation/alkylation of olefins/alkynes *via* halogen-atom transfer mediated by NHC-BH<sub>3</sub>

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# 1. General information

Unless stated otherwise, all reactions were carried out under argon. Column chromatography was performed using silica gel (200-300 mesh) or thin layer chromatography was performed using silica gel (GF254). All catalytic experiments were performed under an atmosphere of argon by using Glove Box. <sup>1</sup>H NMR spectra were recorded using a Bruker 400 MHz instrument with tetramethylsilane (TMS) as an internal standard. Abbreviations used in the NMR follow-up experiments: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. <sup>13</sup>C{<sup>1</sup>H} NMR spectra were obtained at 101 MHz and referenced to the internal solvent signals. <sup>19</sup>F NMR spectra were obtained at 376 MHz. <sup>11</sup>B NMR spectra were obtained at 128 MHz. High resolution mass spectra (HRMS) were performed on an Agilent 6540 spectrometer with ESI ionization. Commercially available reagents were used without further purification unless indicated otherwise, all reagents and solvents were bought from Leyan Ltd, Energy Chemical Ltd, Bide Ltd and Sigma Aldrich as received. The light source was 30 W blue LED (447 nm, 1 W\*30, 30-50 cd/m<sup>2</sup>, made in Everlight Electronics., Ltd.); borosilicate glass Schlenk tube was used as the irradiation vessel; the distance from the light source to the irradiation vessel; 2-3 cm and no filter was used.

All the substrates used in the experiment have been reported and synthesized in the order described in the literature. <sup>[1]</sup>

# 2. General Procedure for Photoredox Reactions



To an oven dried 25 mL Schlenk-tube,  $\alpha$ -(trifluoromethyl)styrenes or *N*-arylacrylamides (0.2 mmol), iodides (0.44 mmol), Ir(ppy)<sub>3</sub> (1.0 mol%), NHC-BH<sub>3</sub> (0.30 mmol), KHCO<sub>3</sub> (0.40 mmol) and MeCN (2 mL) were added under argon atmosphere in glove box. The reaction mixture was stirred under the irradiation of 30 W 447 nm LED lamp at room temperature. After completion of the reaction, the crude reaction mixture was extracted with saturated sodium chloride and EtOAc (2 mL x 3) and the product was concentrated in vacuum. The extracts were combined, dried over sodium sulfate, and filtered, and the volatiles were removed under reduced pressure. The combined organic layers were filtered by silica gel and the filtrate was evaporated under reduced

pressure to obtain the desired product.

# 1.0 光谱三原色色比 R=2.1%,G=1.9%,B=96.0%,主波长: 447 nm 0.5 380 460 540 620 700 780 CIE1931 色度图

# 3. Emission Spectrum of blue LED Strip



# 4. Optimization of reaction condition



Entry <sup>[a]</sup>	РС	additive	Solvent	<b>B</b> Source	Yield (%) <sup>[b]</sup>
1	PC 1	KHCO <sub>3</sub>	MeCN	NHC-BH <sub>3</sub>	90
2	PC 2	KHCO <sub>3</sub>	MeCN	NHC-BH <sub>3</sub>	29
3	PC 3	KHCO <sub>3</sub>	MeCN	NHC-BH <sub>3</sub>	11
4	<b>PC 4</b>	KHCO <sub>3</sub>	MeCN	NHC-BH <sub>3</sub>	16
5	PC 5	KHCO <sub>3</sub>	MeCN	NHC-BH <sub>3</sub>	39
6	<b>PC 6</b>	KHCO <sub>3</sub>	MeCN	NHC-BH <sub>3</sub>	n.d.
7	PC 7	KHCO <sub>3</sub>	MeCN	NHC-BH <sub>3</sub>	n.d.
8	PC 8	KHCO <sub>3</sub>	MeCN	NHC-BH <sub>3</sub>	n.d.
9	PC 1	KHCO <sub>3</sub>	MeCN	DMAP-BH <sub>3</sub>	n.d.
10	<b>PC 1</b>	KHCO <sub>3</sub>	MeCN	Me <sub>3</sub> N-BH <sub>3</sub>	n.d.
11	PC 1	KHCO <sub>3</sub>	MeCN	Ph <sub>3</sub> P-BH <sub>3</sub>	n.d.
12	<b>PC 1</b>	KHCO <sub>3</sub>	MeCN	Pyridine-BH <sub>3</sub>	n.d.
13	PC 1	$K_2CO_3$	MeCN	NHC-BH <sub>3</sub>	65
14	PC 1	Na <sub>2</sub> CO <sub>3</sub>	MeCN	NHC-BH <sub>3</sub>	80
15	<b>PC 1</b>	Li <sub>2</sub> CO <sub>3</sub>	MeCN	NHC-BH <sub>3</sub>	57
16	<b>PC 1</b>	K <sub>2</sub> HPO <sub>4</sub>	MeCN	NHC-BH <sub>3</sub>	62
17	PC 1	PhCOOK	MeCN	NHC-BH <sub>3</sub>	68
18	<b>PC 1</b>	DABCO	MeCN	NHC-BH <sub>3</sub>	30
19	PC 1	2,6-lutidine	MeCN	NHC-BH <sub>3</sub>	38
20	<b>PC 1</b>	DBU	MeCN	NHC-BH <sub>3</sub>	24
21	<b>PC 1</b>	KHCO <sub>3</sub>	Acetone	NHC-BH <sub>3</sub>	36
22	PC 1	KHCO <sub>3</sub>	THF	NHC-BH <sub>3</sub>	n.d.
23	PC 1	KHCO <sub>3</sub>	DCE	NHC-BH <sub>3</sub>	18
24	PC 1	KHCO <sub>3</sub>	DCM	NHC-BH <sub>3</sub>	21
25	PC 1	KHCO <sub>3</sub>	Toluene	NHC-BH <sub>3</sub>	n.d.
26	PC 1	KHCO <sub>3</sub>	EtOAx	NHC-BH <sub>3</sub>	42
27	<b>PC</b> 1	KHCO <sub>3</sub>	DMF	NHC-BH <sub>3</sub>	n.d.

<sup>[a]</sup> Reaction conditions: Ir(ppy)<sub>3</sub> (1.0 mol%), **B 1** (1.5 eq.), KHCO<sub>3</sub> (2.0 eq.), iodobenzene 1 (2.2 eq.),  $\alpha$ -trifluoromethylstyrene 2 (1.0 eq.), MeCN (0.1 M), 30 W LED lamp ( $\lambda$  = 447 nm) at room temperature, Ar atmosphere. <sup>[b]</sup> Yield determined by <sup>1</sup>H NMR spectroscopy using 1,3-benzodioxole as an internal standard.

# 5. Control experiments

Controlled experiments were conducted to discern the essential components in the reaction system. The findings unequivocally demonstrated that the photocatalyst, light source, and NHC-BH<sub>3</sub> are all indispensable for the reaction to proceed.

+ 1, 2.2 eq.	CF <sub>3</sub> 2, 0.2 mmol <b>"standard conditions"</b> Ir(ppy) <sub>3</sub> (1 %mol) B 1 (1.5 eq.) KHCO <sub>3</sub> (2.0 eq.) MeCN (0.1 M) 30 W blue LED lamp	
Entry <sup>[a]</sup>	Variation from the standard condition	Yield (%) <sup>[b]</sup>
1	w/o light	0
2	w/o Ir(ppy) <sub>3</sub>	0
3	w/o <b>B 1</b>	0
4	Heating at 60 °C in dark	0
5	TEA instead of <b>B</b> 1	0
6	TTMSS instead of <b>B</b> 1	0

<sup>[a]</sup> Reaction conditions: Ir(ppy)<sub>3</sub> (1.0 mol%), **B 1** (1.5 eq.), KHCO<sub>3</sub> (2.0 eq.), iodobenzene **1** (2.2 eq.),  $\alpha$ -trifluoromethylstyrene **2** (1.0 eq.), MeCN (0.1 M), 30 W LED lamp ( $\lambda$  = 447 nm) at room temperature, Ar atmosphere. <sup>[b]</sup> Yield determined by <sup>1</sup>H NMR spectroscopy using 1,3-benzodioxole as an internal standard.

# 6. Gram-scale reaction



A) To an oven dried 100 mL Schlenk flask, iodides 1 (2.2 equiv.),  $\alpha$ -(trifluoromethyl)styrenes 2b (5.5 mmol, 1.023 g) or 2l (5.5 mmol, 1.100 g), Ir(ppy)<sub>3</sub> (1.0 mol%, 36.0 mg), NHC-BH<sub>3</sub> (1.5 equiv., 907.5 mg), KHCO<sub>3</sub> (11.0 mmol, 1100 mg, 2.0 equiv) and MeCN (55 mL, 0.1 M) were added under argon atmosphere. The reaction mixture was stirred under the irradiation of 30 W 447 nm LED lamp at room temperature for 28 to 32 h. After completion of the reaction, the crude reaction mixture was extracted with saturated sodium chloride and EtOAc (20 mL x 3) and the

product was concentrated in vacuum. The extracts were combined, dried over sodium sulfate, and filtered, and the volatiles were removed under reduced pressure. The combined organic layers were filtered by silica gel and the filtrate was evaporated under reduced pressure to obtain **47** (0.940 g, 70 % isolated yield) and **57** (1.310 g, 77 % isolated yield).

To an dried 100 mL Schlenk flask, iodides 1a (2.2)**B**) oven equiv.), N-methyl-N-phenylmethacrylamide **3** (6.0 mmol, 1.050 g),  $Ir(ppy)_3$  (1.0 mol%, 39.0 mg), NHC-BH3 (1.5 equiv., 990.0 mg), KHCO3 (12.0 mmol, 1200 mg, 2.0 equiv) and MeCN (60 mL, 0.1 M) were added under argon atmosphere. The reaction mixture was stirred under the irradiation of 30 W 447 nm LED lamp at room temperature for 24 h. After completion of the reaction, the crude reaction mixture was extracted with saturated sodium chloride and EtOAc (20 mL x 3) and the product was concentrated in vacuum. The extracts were combined, dried over sodium sulfate, and filtered, and the volatiles were removed under reduced pressure. The combined organic layers were filtered by silica gel and the filtrate was evaporated under reduced pressure to obtain 43 (1.374 g, 89 % isolated yield).

# 7. Mechanistic studies

#### 7.1 UV-Vis spectroscopic analysis

#### 7.1.1 Evidence for the absence of an EDA complex

Prompted by report on the radical silvldifluoromethylation of electron-deficient alkenes<sup>[16]</sup>, we decided to investigate ground state interactions between the reactants in our mixture. we started by recording an absorption spectrum of single components (**1a**, **2a**, **B1**) and that of a mixture of **1a** and **B1** to seek for the formation of, e.g., an EDA complex (Figure S2).



Figure S2 Absorption spectra of B1, 1a, 2a and a mixture of 1a and B1. All spectra were recorded 0.2 M in MeCN in quartz cuvettes (optical path: 1 cm). Scan rate: medium.

In our experiments we could not find any evidence for the formation of an EDA complex (447 nm,

Table S2).

Next, we recorded absorption spectra to see if **PC1** could form and EDA complex with **B1**(Figure S3).



Figure S3 Absorption spectra of B1, PC1 and a mixture of PC1 and B1. All spectra were recorded 1.0\*10<sup>-3</sup> M in MeCN in quartz cuvettes (optical path: 1 cm). Scan rate: medium.

**PC1** is the only light absorbing species when irradiating at 447 nm, these results prove that an EDA complex between electron-deficient **PC1** and electron-rich **B1** is not formed (Figure S3).

### 7.1.2 Photostability of the photocatalyst

Then, we recorded an absorption spectrum of an Ar-bubbled (60 s) solution of **PC1** ( $1*10^{-3}$  M in MeCN) before and after irradiation with a 30 W LED lamp (447 nm, full intensity, 5 cm away

from cuvette) to check the photostability of the photocatalyst alone (Figure S4).



Figure S4 Absorption spectra of an Ar-bubbled solution of PC1 (5\*10<sup>-3</sup> M in MeCN) before and after irradiation (60 s) with a LED lamp (full intensity, 5 cm away from cuvette).

No appreciable changes were observed after 60 s of continuous irradiation, which shows that **PC1** is stable under operating conditions (Figure S4).

#### 7.2 Stern-Volmer quenching experiments

**Formulation solution:** Iodobenzene (1, 224.4 mg) was dissolved in MeCN in a 5 mL volumetric flask to set the concentration to be 0.22 M. (3,3,3-trifluoroprop-1-en-2-yl)benzene (2, 86.0 mg) was dissolved in MeCN in a 5 mL volumetric flask to set the concentration to be 0.10 M. **B1** (82.5 mg) was dissolved in MeCN in a 5 mL volumetric flask to set the concentration to be 0.15 M. Photocatalyst **PC1** (1.7 mg) was dissolved in MeCN (25.0 mL) to set the concentration to be 0.1 mM.

**Experimental procedure:** The resulting 0.1 mM solution of **PC1** in MeCN (40  $\mu$ L) was added to cuvette to obtain different concentrations of catalyst solution. This solution was then diluted to a volume of 2.0 mL by adding MeCN to prepare a 2.0\*10<sup>-6</sup> M solution. The resulting mixture was sparged with argon for 3 minutes and then irradiated at 364 nm. Fluorescence emission spectra were recorded (3 trials per sample). Into this solution, 20.0  $\mu$ L of an iodobenzene (1) solution was successively added and uniformly stirred, and the resulting mixture was bubbled with argon for 3 minutes and irradiated at 364 nm. Fluorescence emission spectra of 0  $\mu$ L, 20.0  $\mu$ L, 40.0  $\mu$ L, 60.0  $\mu$ L, 80.0  $\mu$ L, 100  $\mu$ L fluorescence intensity. Follow this method and make changes to the amount



to obtain the Stern-Volmer relationship in turn. The results were shown in the following figures.

Figure S5 Emission quenching of PC1 with iodobenzene (1a) in MeCN



Figure S6 Emission quenching of PC1 with (3,3,3-trifluoroprop-1-en-2-yl)benzene (2a) in MeCN



Figure S7 Emission quenching of PC1 with borane (B1) in MeCN

# 7.3 Radical trapping experiments

According to general procedure 3, when TEMPO or BHT was added. After completion of the reaction, the crude residues were analyzed by GC-MS. Yield of **4** was reduced to no detected and the TEMPO-adduct and BHT-adduct products were detected by GC-MS (Figure S8).





Figure S8 Radical trapping experiments

# 7.4 <sup>11</sup>B NMR experiments

To an oven dried 25 mL Schlenk-tube, iodobenzene 1 (0.22 mmol),  $\alpha$ -(trifluoromethyl)styrene 2 (0.1 mmol), Ir(ppy)<sub>3</sub> (1.0% mol), NHC-BH<sub>3</sub> (0.15 mmol), KHCO<sub>3</sub> (0.20 mmol) and MeCN (0.1 M) were added under argon atmosphere. The reaction mixture was stirred under the irradiation of 30 W blue LEDs at room temperature. After completion of the reaction (indicated by TLC), the solution was concentrated in vacuum and the product was purified by flash column chromatography, and the product detected by <sup>11</sup>B NMR (Figure S9).



Figure S9 <sup>11</sup>B NMR spectroscopic figure of reaction mixture

# 7.5 Switch light experiments

Conducted the relationship of products with light on-off under standard conditions. Subsequent samples (each 10  $\mu$ L) taken at regular time intervals and determined by GC with tetradecane as the internal standard. The corresponding experimental results were constructed in Figure S10.



Figure S10 Plot of light on-off experiments

#### 7.6 Quantum yield measurements

The photon flux of blue LED was determined by standard ferrioxalate actinometry. In a dark room equipped with a red light, a 0.15 mol/L solution of ferrioxalate was prepared by dissolving 328 mg, 0.750 mmol of  $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$  in 5.0 mL of 0.20 mol/L  $H_2SO_4$ . A buffered solution of phenanthroline was prepared by dissolving 54.1 mg, 0.3 mmol of phenanthroline and 1.23 g, 15.0 mmol of NaOAc in 20 mL of 0.20 mol/L  $H_2SO_4$ .

The actinometry measurements were done as follows: To a reaction tube equipped with a stir bar was added 0.50 mL of the ferrioxalate solution. The reaction tube was sealed and placed 2 cm away from a 30 W blue LEDs. After irradiation for 5 seconds, 1.5 mL of the aqueous sulfuric acid and 2.0 mL of the buffered solution was added to the reaction tube. The solution was then allowed to rest for 1 hour to allow the resultant ferrous ions to react completely with 1,10-phenanthroline. 50  $\mu$ L of the resulting solution was taken as an aliquot and diluted with 3.0 mL of 0.20 mol/L aqueous sulfuric acid. The absorbance of the resulting solution in a cuvette (l = 1.0 cm) at 510 nm was measured by UV-Vis spectrometer. A non-irradiated sample was also prepared and the absorbance at 510 nm was measured. The amount of ferrous ion formed was calculated as follows:

mol Fe<sup>2+</sup> = 
$$\frac{V \times \Delta A}{l \times \varepsilon}$$

where V is the total volume (0.024 L) of the solution that was analyzed,  $\Delta A$  is the difference in absorbance at 510 nm between the irradiated and non-irradiated samples, l is the path length (1.00 cm), and  $\varepsilon$  is the molar absorptivity at 510 nm (11,100 L/(mol•cm)).

The photon flux was calculated as follows:

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

where  $\emptyset$  is the quantum yield for the ferrioxalate actinometer (approximated as 0.846, which was reported for a 0.15 mol/L solution at  $\lambda = 457.9$  nm), *t* is the irradiation time, and *f* is the fraction of light absorbed at 447 nm (0.2667).

The fraction of light absorbed was determined by the following equation:

$$f = 1.0000 - 10^{-A}$$

where A is the measured absorbance (0.1347) of the 0.15 mol/L solution of potassium ferrioxalate at 447 nm.

## The photo flux is $3.33 \times 10^{-7}$ Einstein/s.

where flux is the photon flux determined by ferrioxalate actinometry ( $3.33 \times 10^{-7}$  Einstein/s), *t* is the time, and *f* is the fraction of light absorbed by the irradiated reaction system at 447 nm, and the absorbance of the irradiated reaction system at 447 nm was 0.9664. The fraction of light absorbed at 447 nm was calculated:  $f = 1.0000 - 10^{-4} = 1.0000 - 10^{-0.9664} = 0.8920$ .

$$\emptyset = \frac{\text{mol product}}{flux \times t \times f}$$

Considering that the yield for compound 4 after 4 h in the same setup is 39.5% ( $3.95 \times 10^{-5}$  mol), the quantum yield was calculated:  $\emptyset = 0.01$ .

#### 7.7 Mechanism of functionalization

Figure S11 illustrates the mechanism of functionalization of the key carbon radical intermediate G within a photoredox catalytic cycle. Figure S11A elucidates the capture of carbon radical intermediate **D** by  $\alpha$ -trifluoromethylpropene substrate, forming intermediate **H**, which undergoes single electron reduction by a long-lived triplet excited state Ir photocatalyst to generate carbon-negative intermediate F. Subsequent  $\beta$ -F elimination yields the gem-difluoroolefins products. In Figure S11B, carbon radical intermediate **D** reacts with N-arylacrylamide to generate radical intermediate J, which then undergoes rapid intramolecular cyclization. Simultaneously, it is oxidized by the more oxidizing  $Ir^{IV}$  species to form carbon-positive intermediate **K**, followed by H-elimination to produce the 2-indolone products. Figure S11C illustrates the reaction between aryl/alkyl olefin and carbon-radical intermediate **D**. After the olefin captures intermediate **D**, carbon radical intermediate L is generated, which is then reduced by single-electron reduction of a long-lived triplet excited state Ir photocatalyst to produce carbon-negative intermediate M. Subsequently, it combines with a proton in the system to yield a hydrogen arylation products. When the proton transfer reagent is introduced, it undergoes hydrogen atom transfer (HAT) with NHC-BH<sub>3</sub> (B 1), leading to the generation of the hydroarylation product and NHC-BH<sub>2</sub> radical species (E). The mechanisms for aryl alkynes (Figure S11D) are analogous to those demonstrated in Figure S11C, with trans-olefin product N undergoing rapid energy transfer with the Ir photocatalyst to yield the cis-olefin products.

#### A: radical addtion and gem-difluoroallylation



B: radical addtion and cyclization to produce 2-indolinones





Figure S11 Possible functionalization mechanism.

## 8. Characterization data of all products

(3,3-difluoroprop-2-ene-1,2-diyl)dibenzene (4)<sup>[4]</sup>



Purified by silica gel chromatography (petroleum ether), the desired product **4** was obtained as a colorless oil, 42.3 mg, 90 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.24 – 7.05 (m, 10H), 3.65 (s, 2H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -90.37 (d, 1F, *J* = 40.0 Hz), -90.92 (d, 1F, *J* = 40.1 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  154.6 (dd, <sup>1</sup>*J*<sub>C-F</sub> = 291.9, 287.5 Hz), 138.7 (t, <sup>4</sup>*J*<sub>C-F</sub> = 3.0 Hz), 133.7 (t, <sup>3</sup>*J*<sub>C-F</sub> = 3.8 Hz), 128.7, 128.6, 128.5, 128.5 (d, <sup>4</sup>*J*<sub>C-F</sub> = 7.0 Hz), 127.5, 126.6, 91.9 (dd, <sup>2</sup>*J*<sub>C-F</sub> = 21.3, 13.6 Hz), 34.1 (t, <sup>3</sup>*J*<sub>C-F</sub> = 1.0 Hz).

#### 1-(3,3-difluoro-2-phenylallyl)-4-methylbenzene (5)<sup>[4]</sup>



Purified by silica gel chromatography (petroleum ether), the desired product **5** was obtained as a colorless oil, 46.8 mg, 96 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.36 – 7.19 (m, 5H), 7.08 (s, 4H), 3.72 (s, 2H), 2.31 (s, 3H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -90.52 (d, 1F, *J* = 40.5 Hz), -91.07 (d, 1F, *J* = 40.3 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  154.6 (dd, <sup>1</sup>*J*<sub>C-F</sub> = 292.9, 287.9 Hz), 136.1, 135.6 (t, <sup>3</sup>*J*<sub>C-F</sub> = 2.7 Hz), 133.8 (t, <sup>3</sup>*J*<sub>C-F</sub> = 3.8 Hz), 129.4, 128.5, 128.5 (t, <sup>4</sup>*J*<sub>C-F</sub> = 3.5 Hz), 128.3, 127.4, 92.0 (dd, <sup>2</sup>*J*<sub>C-F</sub> = 21.3, 13.2 Hz), 33.7 (t, <sup>3</sup>*J*<sub>C-F</sub> = 1.5 Hz), 21.2.

#### 1-(3,3-difluoro-2-phenylallyl)-4-methoxybenzene (6)<sup>[2]</sup>



Purified by silica gel chromatography (PE: EA/100: 1), the desired product **6** was obtained as a colorless oil, 47.8 mg, 92 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.37 – 7.22 (m, 5H), 7.14 – 7.08 (m, 2H), 6.86 – 6.79 (m, 2H), 3.80 (s, 3H), 3.71 (s, 2H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$ 

-90.87 (d, 1F, J = 40.9 Hz), -91.26 (d, 1F, J = 40.9 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  158.4, 154.5 (dd, <sup>1</sup> $J_{C-F} = 291.6$ , 287.3 Hz), 133.8 (t, <sup>3</sup> $J_{C-F} = 4.0$  Hz), 130.7 (t, <sup>4</sup> $J_{C-F} = 2.7$  Hz), 129.5, 128.5, 128.5 (t, <sup>4</sup> $J_{C-F} = 3.5$  Hz), 127.5, 114.1, 92.3 (dd, <sup>2</sup> $J_{C-F} = 21.1$ , 13.3 Hz), 55.4, 33.3 (t, <sup>3</sup> $J_{C-F} = 1.6$  Hz); HRMS (ESI) m/z calcd for C<sub>16</sub>H<sub>15</sub>F<sub>2</sub>O<sup>+</sup> (M+H)<sup>+</sup> 261.1086, found 261.1083.

#### 4-(3,3-difluoro-2-phenylallyl)-1,1'-biphenyl (7)<sup>[3]</sup>



Purified by silica gel chromatography (PE: EA/100: 1), the desired product 7 was obtained as a colorless oil, 50.8 mg, 83 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.55 – 7.48 (m, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.31 – 7.23 (m, 5H), 7.23 – 7.16 (m, 3H), 3.74 (t, *J* = 2.3 Hz, 2H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -90.08 (d, *J* = 39.7 Hz), -90.60 (d, *J* = 39.6 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  154.7 (dd, <sup>1</sup>*J*<sub>C-F</sub> = 292.0, 287.5 Hz), 141.0, 139.5, 137.8 (t, <sup>4</sup>*J*<sub>C-F</sub> = 2.8 Hz), 133.7 (t, <sup>3</sup>*J*<sub>C-F</sub> = 3.8 Hz), 128.9, 128.9, 128.6, 128.5 (t, <sup>4</sup>*J*<sub>C-F</sub> = 3.5 Hz), 127.5, 127.4, 127.3, 127.2, 91.9 (dd, <sup>2</sup>*J*<sub>C-F</sub> = 21.2, 13.6 Hz), 33.8 (d, <sup>3</sup>*J*<sub>C-F</sub> = 1.9 Hz).

#### 1-(3,3-difluoro-2-phenylallyl)-4-ethylbenzene (8)



Purified by silica gel chromatography (petroleum ether), the desired product **8** was obtained as a colorless oil, 43.3 mg, 84 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.31 (d, *J* = 4.4 Hz, 4H), 7.24 (tt, *J* = 5.5, 4.1 Hz, 1H), 7.10 (d, *J* = 1.4 Hz, 4H), 3.73 (s, 2H), 2.61 (q, *J* = 7.5 Hz, 2H), 1.22 (t, *J* = 7.9 Hz, 3H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -90.42 (d, *J* = 40.4 Hz), -91.03 (d, *J* = 40.4 Hz); <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  154.7 (dd, <sup>1</sup>*J*<sub>C-F</sub> = 291.8, 287.3 Hz), 142.5, 135.9 (t, <sup>4</sup>*J*<sub>C-F</sub> = 2.7 Hz), 133.9 (t, <sup>3</sup>*J*<sub>C-F</sub> = 3.8 Hz), 128.6, 128.5 (t, <sup>4</sup>*J*<sub>C-F</sub> = 3.5 Hz), 128.4, 128.2, 127.4, 92.0 (dd, <sup>2</sup>*J*<sub>C-F</sub> = 21.3, 13.2 Hz), 33.7 (d, <sup>3</sup>*J*<sub>C-F</sub> = 2.0 Hz), 28.6, 15.7; HRMS (ESI) m/z calcd for C<sub>17</sub>H<sub>17</sub>F<sub>2</sub><sup>+</sup> (M+H)<sup>+</sup> 259.1293, found 259.1290.

#### 1-(3,3-difluoro-2-phenylallyl)-4-isopropylbenzene (9)



Purified by silica gel chromatography (petroleum ether), the desired product **9** was obtained as a colorless oil, 47.3 mg, 87 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.33 – 7.28 (m, 4H), 7.27 – 7.20 (m, 1H), 7.12 (q, *J* = 4.4, 3.2 Hz, 4H), 3.72 (s, 2H), 2.87 (dddd, *J* = 15.1, 8.1, 6.7, 3.4 Hz, 1H), 1.23 (d, *J* = 3.6 Hz, 6H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -90.27 (d, *J* = 40.3 Hz), -90.99 (d, *J* = 40.2 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  154.7 (dd, <sup>1</sup>*J*<sub>C-F</sub> = 292.0, 287.4 Hz), 147.2, 136.0 (t, <sup>4</sup>*J*<sub>C-F</sub> = 2.7 Hz), 134.0 (t, <sup>3</sup>*J*<sub>C-F</sub> = 3.9 Hz), 128.6, 128.5 (t, <sup>4</sup>*J*<sub>C-F</sub> = 3.9 Hz), 128.4, 127.4, 126.8, 92.0 (dd, <sup>2</sup>*J*<sub>C-F</sub> = 21.3, 13.2 Hz), 33.9, 33.7 (d, <sup>3</sup>*J*<sub>C-F</sub> = 1.7 Hz), 24.2; HRMS (ESI) m/z calcd for C<sub>18</sub>H<sub>19</sub>F<sub>2</sub><sup>+</sup> (M+H)<sup>+</sup> 273.1449 found 273.1441.

#### 1-(tert-butyl)-4-(3,3-difluoro-2-phenylallyl)benzene (10)<sup>[5]</sup>



Purified by silica gel chromatography (petroleum ether), the desired product **10** was obtained as a colorless oil, 45.8 mg, 80 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.32 – 7.16 (m, 7H), 7.09 (d, *J* = 8.2 Hz, 2H), 3.70 (s, 2H), 1.28 (s, 9H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -90.12 (d, *J* = 40.1 Hz), -90.91 (d, *J* = 39.9 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  154.7 (dd, <sup>1</sup>*J*<sub>C-F</sub> = 292.1, 287.3 Hz), 149.4, 135.6 (t, <sup>4</sup>*J*<sub>C-F</sub> = 2.7 Hz), 134.0 (t, <sup>3</sup>*J*<sub>C-F</sub> = 3.9 Hz), 128.6, 128.5 (t, <sup>4</sup>*J*<sub>C-F</sub> = 3.5 Hz), 128.0, 127.4, 125.6, 91.8 (dd, <sup>2</sup>*J*<sub>C-F</sub> = 21.4, 13.0 Hz), 34.6, 33.5, 31.6.

1-(3,3-difluoro-2-phenylallyl)-4-fluorobenzene (11)<sup>[2]</sup>



Purified by silica gel chromatography (petroleum ether), the desired product **11** was obtained as a colorless oil, 42.7 mg, 86 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.33 – 7.19 (m, 5H), 7.19 – 7.06 (m, 2H), 6.97 – 6.87 (m, 2H), 3.70 (t, J = 2.3 Hz, 2H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -90.56 (d, J = 40.1 Hz), -90.89 (d, J = 40.2 Hz), -116.78; <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  161.8 (d, <sup>1</sup>*J*<sub>C-*F*</sub> = 244.4 Hz), 154.6 (dd, <sup>1</sup>*J*<sub>C-*F*</sub> = 291.8, 287.7 Hz), 134.3 (q, <sup>4</sup>*J*<sub>C-*F*</sub>, <sup>4</sup>*J*<sub>C-*F*</sub> = 2.9 Hz), 133.5 (t, <sup>3</sup>*J*<sub>C-*F*</sub> = 3.6 Hz), 130.0, 129.9, 128.6, 128.5 (t, <sup>4</sup>*J*<sub>C-*F*</sub> = 3.4 Hz), 127.6, 115.6, 115.4, 92.0 (dd, <sup>2</sup>*J*<sub>C-*F*</sub> = 21.1, 14.0 Hz), 33.4 (d, <sup>3</sup>*J*<sub>C-*F*</sub> = 1.8 Hz).

#### 1-(3,3-difluoro-2-phenylallyl)-4-methylbenzene (12)



Purified by silica gel chromatography (petroleum ether), the desired product **12** was obtained as a colorless oil, 39.1 mg, 74 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.33 – 7.16 (m, 7H), 7.07 (d, *J* = 8.0 Hz, 2H), 3.69 (s, 2H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -90.20 (d, 1F, *J* = 39.4 Hz), -90.57 (d, 1F, *J* = 39.1 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  154.6 (dd, <sup>1</sup>*J*<sub>*C*-*F*</sub> = 292.2, 287.8 Hz), 137.1 (t, <sup>4</sup>*J*<sub>*C*-*F*</sub> = 3.0 Hz), 133.3 (t, <sup>3</sup>*J*<sub>*C*-*F*</sub> = 3.7 Hz), 132.4, 129.8, 128.8, 128.7, 128.4 (t, <sup>4</sup>*J*<sub>*C*-*F*</sub> = 3.4 Hz), 127.7, 91.7 (dd, <sup>2</sup>*J*<sub>*C*-*F*</sub> = 21.1, 14.1 Hz), 33.5 (t, <sup>3</sup>*J*<sub>*C*-*F*</sub> = 2.0 Hz); HRMS (ESI) m/z calcd for C<sub>15</sub>H<sub>12</sub>ClF<sub>2</sub><sup>+</sup> (M+H)<sup>+</sup> 265.0590, found 265.0585.

#### 1-bromo-4-(3,3-difluoro-2-phenylallyl)benzene (13)<sup>[2]</sup>



Purified by silica gel chromatography (petroleum ether), the desired product **13** was obtained as a colorless oil, 45.1 mg, 73 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.33 – 7.27 (m, 2H), 7.26 – 7.21 (m, 2H), 7.21 – 7.11 (m, 3H), 6.97 (d, *J* = 8.2 Hz, 2H), 3.63 (s, 2H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -90.13 (d, 1F, *J* = 39.0 Hz), -90.51 (d, 1F, *J* = 39.5 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  154.6 (dd, <sup>1</sup>*J*<sub>C-F</sub> = 292.2, 287.8 Hz), 137.6 (t, <sup>4</sup>*J*<sub>C-F</sub> = 2.7 Hz), 133.3 (t, <sup>3</sup>*J*<sub>C-F</sub> = 3.7 Hz),

131.8, 130.2, 128.7, 128.4 (t,  ${}^{4}J_{C-F} = 3.4$  Hz), 127.7, 120.5, 91.6 (dd,  ${}^{2}J_{C-F} = 21.2$ , 14.1 Hz), 33.6 (t,  ${}^{3}J_{C-F} = 1.7$  Hz).

methyl 4-(3,3-difluoro-2-phenylallyl)benzoate (14)



Purified by silica gel chromatography (PE: EA/50: 1), the desired product **14** was obtained as a colorless oil, 66 % yield for methyl 4-iodobenzoate (19.0 mg) and 31 % yield for methyl 4-bromobenzoate (8.9 mg); <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.96 – 7.87 (m, 1H), 7.31 – 7.18 (m, 4H), 3.87 (s, 1H), 3.78 (t, *J* = 2.3 Hz, 1H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -89.91 (d, *J* = 38.9 Hz), -90.33 (d, *J* = 38.8 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  167.1, 154.7 (dd, <sup>1</sup>*J*<sub>C-F</sub> = 292.3, 287.9 Hz), 144.1 (t, <sup>4</sup>*J*<sub>C-F</sub> = 2.8 Hz), 133.3 (t, <sup>4</sup>*J*<sub>C-F</sub> = 3.7 Hz), 130.0, 128.7, 128.5, 128.4 (t, <sup>3</sup>*J*<sub>C-F</sub> = 3.4 Hz), 127.7, 91.5 (dd, <sup>2</sup>*J*<sub>C-F</sub> = 21.2, 14.4 Hz), 52.2, 34.2 (d, <sup>3</sup>*J*<sub>C-F</sub> = 1.8 Hz); HRMS (ESI) m/z calcd for C<sub>17</sub>H<sub>15</sub>F<sub>2</sub>O<sub>2</sub><sup>+</sup> (M+H)<sup>+</sup> 289.1035, found 289.1035.

#### 4-(3,3-difluoro-2-phenylallyl)benzonitrile (15)



Purified by silica gel chromatography (PE: EA/50: 1), the desired product **15** was obtained as a colorless oil, 60 % yield for 4-iodobenzonitrile (15.3 mg) and 36 % yield for 4-bromobenzonitrile (9.2 mg); <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.56 – 7.50 (m, 2H), 7.35 – 7.19 (m, 7H), 3.79 (s, 2H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -89.37 (d, *J* = 38.0 Hz), -89.76 (d, *J* = 37.7 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  154.7 (dd, <sup>1</sup>*J*<sub>C-F</sub> = 292.9, 288.2 Hz), 144.2 (d, <sup>4</sup>*J*<sub>C-F</sub> = 2.9 Hz), 132.9, 132.6, 129.3, 128.81, 128.3 (t, <sup>4</sup>*J*<sub>C-F</sub> = 3.5 Hz), 127.9, 119.0, 110.7, 91.0 (dd, <sup>2</sup>*J*<sub>C-F</sub> = 21.1, 14.9 Hz), 34.2 (d, <sup>3</sup>*J*<sub>C-F</sub> = 2.2 Hz); HRMS (ESI) m/z calcd for C<sub>16</sub>H<sub>12</sub>F<sub>2</sub>N<sup>+</sup> (M+H)<sup>+</sup> 256.0932, found 256.0929.

#### 1-(3,3-difluoro-2-phenylallyl)-4-phenoxybenzene (16)



Purified by silica gel chromatography (PE: EA/100: 1), the desired product **16** was obtained as a colorless oil, 48.9 mg, 76 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.37 – 7.21 (m, 7H), 7.16 – 7.05 (m, 3H), 6.98 (dt, J = 7.7, 1.2 Hz, 2H), 6.94 – 6.87 (m, 2H), 3.73 (s, 2H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -90.46 (d, 1F, J = 39.9 Hz), -90.90 (d, 1F, J = 40.2 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  157.5, 155.9, 154.6 (dd, <sup>1</sup>*J*<sub>C-F</sub> = 291.9, 287.5 Hz), 133.7 (t, <sup>3</sup>*J*<sub>C-F</sub> = 3.8 Hz), 133.5 (t, <sup>4</sup>*J*<sub>C-F</sub> = 2.7 Hz), 129.9, 129.7, 128.6, 128.5 (t, <sup>4</sup>*J*<sub>C-F</sub> = 3.5 Hz), 127.5, 123.3, 119.2, 118.9, 92.0 (dd, <sup>2</sup>*J*<sub>C-F</sub> = 21.2, 13.5 Hz), 33.4 (d, <sup>3</sup>*J*<sub>C-F</sub> = 2.0 Hz); HRMS (ESI) m/z calcd for C<sub>21</sub>H<sub>17</sub>F<sub>2</sub>O<sup>+</sup> (M+H)<sup>+</sup> 323.1242, found 323.1242.

#### 1-(benzyloxy)-4-(3,3-difluoro-2-phenylallyl)benzene (17)



Purified by silica gel chromatography (PE: EA/100: 1), the desired product **17** was obtained as a colorless oil, 54.4 mg, 81 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.41 – 7.14 (m, 10H), 7.07 – 7.00 (m, 2H), 6.87 – 6.79 (m, 2H), 4.97 (s, 2H), 3.64 (s, 2H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -90.77 (d, 1F, *J* = 40.8 Hz), -91.18 (d, 1F, *J* = 40.8 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  157.6, 154.5 (dd, <sup>1</sup>*J*<sub>C-F</sub> = 291.7, 287.2 Hz), 137.2, 133.8 (d, <sup>1</sup>*J*<sub>C-F</sub> = 3.7 Hz), 131.0 (t, <sup>4</sup>*J*<sub>C-F</sub> = 2.7 Hz), 129.5, 128.8, 128.6, 128.5 (t, <sup>4</sup>*J*<sub>C-F</sub> = 3.4 Hz), 128.2, 127.7, 127.5, 115.0, 92.2 (dd, <sup>2</sup>*J*<sub>C-F</sub> = 21.2, 13.2 Hz), 70.2, 33.3; HRMS (ESI) m/z calcd for C<sub>22</sub>H<sub>19</sub>F<sub>2</sub>O<sup>+</sup> (M+H)<sup>+</sup> 337.1399, found 337.1398.

#### 1-(3,3-difluoro-2-phenylallyl)-4-(trifluoromethoxy)benzene (18)



Purified by silica gel chromatography (petroleum ether), the desired product **18** was obtained as a colorless oil, 52.8 mg, 84 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.34 – 7.27 (m, 2H), 7.27 – 7.23 (m, 3H), 7.19 – 7.14 (m, 2H), 7.13 – 7.05 (m, 2H), 3.73 (t, *J* = 2.3 Hz, 2H); <sup>19</sup>F NMR (376 MHz,

Chloroform-*d*)  $\delta$  -57.93, -90.03 (d, *J* = 39.3 Hz), -90.48 (d, *J* = 39.5 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  154.6 (dd, <sup>1</sup>*J*<sub>*C*-*F*</sub> = 292.4, 287.9 Hz), 148.0 (d, <sup>2</sup>*J*<sub>*C*-*F*</sub> = 2.1 Hz), 137.4 (t, <sup>3</sup>*J*<sub>*C*-*F*</sub> = 2.8 Hz), 133.3 (t, <sup>4</sup>*J*<sub>*C*-*F*</sub> = 3.7 Hz), 129.7, 128.7, 128.4 (t, <sup>4</sup>*J*<sub>*C*-*F*</sub> = 3.5 Hz), 127.7, 121.8 (q, <sup>1</sup>*J*<sub>*C*-*F*</sub> = 262.6 Hz), 121.2, 91.6 (dd, <sup>3</sup>*J*<sub>*C*-*F*</sub> = 21.2, 14.0 Hz); HRMS (ESI) m/z calcd for C<sub>16</sub>H<sub>12</sub>F<sub>5</sub>O<sup>+</sup> (M+H)<sup>+</sup> 315.0803, found 315.0804.

#### 1-(3,3-difluoro-2-phenylallyl)-4-(difluoromethoxy)benzene (19)



Purified by silica gel chromatography (petroleum ether), the desired product **19** was obtained as a colorless oil, 47.4 mg, 80 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.34 – 7.19 (m, 5H), 7.17 – 7.05 (m, 2H), 7.02 – 6.95 (m, 2H), 6.44 (t, *J* = 74.1 Hz, 1H), 3.71 (t, *J* = 2.3 Hz, 2H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -80.61, -90.26 (d, *J* = 40.1 Hz), -90.67 (d, *J* = 39.6 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  154.6 (dd, <sup>1</sup>*J*<sub>C-F</sub> = 292.2, 287.7 Hz), 150.0 (t, <sup>2</sup>*J*<sub>C-F</sub>' = 2.8 Hz), 136.0 (t, <sup>3</sup>*J*<sub>C-F</sub> = 3.1 Hz), 133.5 (t, <sup>4</sup>*J*<sub>C-F</sub> = 3.7 Hz), 129.8, 128.7, 128.5 (t, <sup>4</sup>*J*<sub>C-F</sub> = 3.4 Hz), 127.7, 119.8, 116.2 (t, <sup>1</sup>*J*<sub>C-F</sub>' = 259.3 Hz), 91.8 (dd, <sup>2</sup>*J*<sub>C-F</sub> = 21.0, 13.9 Hz), 33.4 (t, <sup>3</sup>*J*<sub>C-F</sub> = 1.7 Hz); HRMS (ESI) m/z calcd for C<sub>16</sub>H<sub>13</sub>F<sub>4</sub>O<sup>+</sup> (M+H)<sup>+</sup> 297.0897, found 297.0904.

#### 1-(3,3-difluoro-2-phenylallyl)-3-fluorobenzene (20)



Purified by silica gel chromatography (petroleum ether), the desired product **20** was obtained as a colorless oil, 40.2 mg, 81 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.37 – 7.15 (m, 6H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.87 (tt, *J* = 7.0, 2.0 Hz, 2H), 3.73 (t, *J* = 2.3 Hz, 2H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -89.97 (d, *J* = 39.0 Hz), -90.42 (d, *J* = 39.1 Hz), -113.32; <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  163.0 (d, <sup>1</sup>*J*<sub>C-F</sub>' = 245.7 Hz), 154.5 (dd, <sup>1</sup>*J*<sub>C-F</sub> = 292.2, 287.7 Hz), 141.0 (d, <sup>4</sup>*J*<sub>C-F</sub>, <sup>3</sup>*J*<sub>C-F</sub>' = 7.0 Hz), 133.2, 129.9 (d, <sup>3</sup>*J*<sub>C-F</sub>' = 8.3 Hz), 128.5, 128.2 (t, <sup>4</sup>*J*<sub>C-F</sub> = 3.5 Hz), 127.5, 124.0 (d, <sup>4</sup>*J*<sub>C-F</sub>' = 2.9

Hz), 115.2 (d,  ${}^{2}J_{C-F}$ ' = 21.6 Hz), 113.4 (d,  ${}^{2}J_{C-F}$ ' = 21.2 Hz), 91.3 (dd,  ${}^{2}J_{C-F}$  = 21.1, 14.2 Hz), 33.7; HRMS (ESI) m/z calcd for C<sub>15</sub>H<sub>12</sub>F<sub>3</sub><sup>+</sup> (M+H)<sup>+</sup> 249.0886, found 249.0885.

#### 1-(3,3-difluoro-2-phenylallyl)-3-methylbenzene (21)<sup>[2]</sup>



Purified by silica gel chromatography (petroleum ether), the desired product **21** was obtained as a colorless oil, 40.1 mg, 76 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.36 – 7.27 (m, 2H), 7.27 – 7.20 (m, 3H), 7.19 – 7.12 (m, 3H), 7.03 (dq, *J* = 4.5, 3.0, 2.4 Hz, 1H), 3.70 (t, *J* = 2.3 Hz, 2H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -89.82 (d, *J* = 38.7 Hz), -90.25 (d, *J* = 38.8 Hz); <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  154.7 (dd, <sup>1</sup>*J*<sub>C-F</sub> = 292.4, 288.0 Hz), 140.7 (t, <sup>4</sup>*J*<sub>C-F</sub> = 3.0 Hz), 134.5, 133.3 (t, <sup>3</sup>*J*<sub>C-F</sub> = 3.7 Hz), 129.9, 128.7, 128.6, 128.4 (t, <sup>4</sup>*J*<sub>C-F</sub> = 3.5 Hz), 127.7, 126.9, 126.7, 91.5 (dd, <sup>2</sup>*J*<sub>C-F</sub> = 21.2, 14.3 Hz), 33.8 (d, <sup>3</sup>*J*<sub>C-F</sub> = 1.8 Hz).

#### 1-(3,3-difluoro-2-phenylallyl)-3-methylbenzene (22)



Purified by silica gel chromatography (petroleum ether), the desired product **22** was obtained as a colorless oil, 44.9 mg, 92 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.27 (d, *J* = 5.0 Hz, 4H), 7.23 – 7.16 (m, 1H), 7.12 (t, *J* = 7.8 Hz, 1H), 7.05 – 6.89 (m, 3H), 3.69 (s, 2H), 2.28 (s, 3H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -90.29 (d, 1F, *J* = 39.9 Hz), -90.87 (d, 1F, *J* = 40.2 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  154.6 (dd, <sup>1</sup>*J*<sub>C-F</sub> = 292.0, 287.3 Hz), 138.6 (t, <sup>4</sup>*J*<sub>C-F</sub> = 2.7 Hz), 138.3, 133.8 (t, <sup>3</sup>*J*<sub>C-F</sub> = 3.9 Hz), 129.2, 128.6, 128.5 (t, <sup>4</sup>*J*<sub>C-F</sub> = 3.5 Hz), 127.4, 127.4, 125.5, 91.8 (dd, <sup>2</sup>*J*<sub>C-F</sub> = 21.3, 13.3 Hz), 34.0 (d, <sup>3</sup>*J*<sub>C-F</sub> = 2.0 Hz), 21.6; HRMS (ESI) m/z calcd for C<sub>16</sub>H<sub>15</sub>F<sub>2</sub><sup>+</sup> (M+H)<sup>+</sup> 245.1136, found 245.1135.

#### 1-(3,3-difluoro-2-phenylallyl)-3-methoxybenzene (23)<sup>[4]</sup>



Purified by silica gel chromatography (PE: EA/100: 1), the desired product **23** was obtained as a colorless oil, 49.9 mg, 96 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.33 – 7.24 (m, 4H), 7.22 (ddd, J = 9.3, 5.3, 2.4 Hz, 1H), 7.15 (t, J = 7.7 Hz, 1H), 6.83 – 6.67 (m, 3H), 3.73 (s, 3H), 3.70 (t, J = 2.3 Hz, 2H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -90.29 (d, J = 40.0 Hz), -90.82 (d, J = 39.7 Hz); <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  159.9, 154.6 (dd, <sup>1</sup> $J_{C-F} = 291.8, 287.5$  Hz), 140.3 (t, <sup>4</sup> $J_{C-F} = 2.9$  Hz), 133.7, 129.7, 128.6, 128.4 (d, <sup>4</sup> $J_{C-F} = 3.5$  Hz), 127.5, 120.9, 114.3, 111.8, 91.8 (dd, <sup>3</sup> $J_{C-F} = 21.4, 13.7$  Hz), 55.3, 34.1.

### 1-(3,3-difluoro-2-phenylallyl)-2-methoxybenzene (24)



Purified by silica gel chromatography (PE: EA/100: 1), the desired product **24** was obtained as a colorless oil, 28.6 mg, 55 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.29 (d, *J* = 6.1 Hz, 3H), 7.25 – 7.14 (m, 3H), 7.12 – 7.05 (m, 1H), 6.83 (t, *J* = 7.4 Hz, 2H), 3.79 (s, 3H), 3.74 (s, 2H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -89.87 (d, 1F, *J* = 39.5 Hz), -90.29 (d, 1F, *J* = 39.7 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  157.5, 154.6 (dd, <sup>1</sup>*J*<sub>C-F</sub> = 291.3, 287.9 Hz), 134.0 (d, <sup>3</sup>*J*<sub>C-F</sub> = 3.9 Hz), 129.2, 128.6 – 128.3 (m), 128.4, 127.7, 127.3, 126.8 (t, <sup>4</sup>*J*<sub>C-F</sub> = 2.6 Hz), 120.6, 110.3, 91.0 (dd, <sup>2</sup>*J*<sub>C-F</sub> = 21.1, 13.5 Hz), 55.4, 27.9 (d, <sup>3</sup>*J*<sub>C-F</sub> = 2.0 Hz); HRMS (ESI) m/z calcd for C<sub>16</sub>H<sub>15</sub>F<sub>2</sub>O<sup>+</sup> (M+H)<sup>+</sup> 261.1086, found 261.1083.

#### 1-(3,3-difluoro-2-phenylallyl)-2,4-dimethylbenzene (25)



Purified by silica gel chromatography (petroleum ether), the desired product **25** was obtained as a colorless oil, 33.0 mg, 64 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.32 – 7.17 (m, 5H), 6.99 –

6.92 (m, 2H), 6.87 (dd, J = 7.9, 1.9 Hz, 1H), 3.65 (t, J = 2.4 Hz, 2H), 2.25 (s, 3H), 2.24 (s, 3H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -90.09 (d, J = 40.2 Hz), -90.56 (d, J = 40.2 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  154.4 (dd, <sup>1</sup> $J_{C-F} = 291.3$ , 287.8 Hz), 136.2, 136.1, 134.0 (t, <sup>4</sup> $J_{C-F} = 3.8$  Hz), 133.4 (t, <sup>3</sup> $J_{C-F} = 2.6$  Hz), 131.2, 128.5, 128.5 (t, <sup>4</sup> $J_{C-F} = 2.0$  Hz), 127.5, 126.9, 91.3 (dd, <sup>2</sup> $J_{C-F} = 21.1$ , 13.6 Hz), 31.2 (d, <sup>3</sup> $J_{C-F} = 1.9$  Hz), 21.1, 19.7; HRMS (ESI) m/z calcd for C<sub>17</sub>H<sub>17</sub>F<sub>2</sub><sup>+</sup> (M+H)<sup>+</sup> 259.1293, found 259.1294.

#### 4-(3,3-difluoro-2-phenylallyl)-1,2-dimethylbenzene (26)



Purified by silica gel chromatography (petroleum ether), the desired product **26** was obtained as a colorless oil, 36.1 mg, 70 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.30 (d, *J* = 4.4 Hz, 4H), 7.27 – 7.18 (m, 1H), 7.01 (d, *J* = 7.7 Hz, 1H), 6.96 (d, *J* = 2.0 Hz, 1H), 6.90 (dd, *J* = 7.6, 2.0 Hz, 1H), 3.68 (t, *J* = 2.3 Hz, 2H), 2.21 (s, 6H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -90.41 (d, *J* = 40.3 Hz), -91.04 (d, *J* = 40.4 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  154.6 (dd, <sup>1</sup>*JC*-*F* = 292.9, 288.9 Hz), 136.8, 136.0 (t, <sup>4</sup>*JC*-*F* = 2.7 Hz), 134.7, 134.0, 129.9, 129.7, 128.5, 128.5 (t, <sup>4</sup>*JC*-*F* = 3.5 Hz), 127.4, 125.8, 92.0 (dd, <sup>2</sup>*JC*-*F* = 21.3, 13.1 Hz), 33.6, 12.0, 19.5; HRMS (ESI) m/z calcd for C<sub>17</sub>H<sub>17</sub>F<sub>2</sub><sup>+</sup> (M+H)<sup>+</sup> 259.1293, found 259.1288.

#### 5-(3,3-difluoro-2-phenylallyl)benzo[d][1,3]dioxole (27)



Purified by silica gel chromatography (PE: EA/100: 1), the desired product **27** was obtained as a colorless oil, 50.4 mg, 92 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.39 – 7.21 (m, 5H), 6.76 – 6.59 (m, 3H), 5.93 (s, 2H), 3.70 – 3.65 (m, 2H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -90.69 (d, *J* = 41.3 Hz), -91.01 (d, *J* = 40.2 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  154.5 (dd, <sup>1</sup>*J*<sub>C-F</sub> = 291.8, 287.5 Hz), 147.9, 146.3, 133.6 (t, <sup>4</sup>*J*<sub>C-F</sub> = 3.7 Hz), 132.4 (t, <sup>3</sup>*J*<sub>C-F</sub> = 2.7 Hz), 128.6, 128.5 (t, <sup>4</sup>*J*<sub>C-F</sub> = 3.4

Hz), 127.5, 121.4, 108.9, 108.4, 101.1, 92.1 (dd,  ${}^{2}J_{C-F} = 21.0$ , 13.5 Hz), 33.8 (d,  ${}^{3}J_{C-F} = 1.9$  Hz); HRMS (ESI) m/z calcd for C<sub>16</sub>H<sub>13</sub>F<sub>2</sub>O<sub>2</sub><sup>+</sup> (M+H)<sup>+</sup> 275.0878, found 275.0880.

#### 3-(3,3-difluoro-2-phenylallyl)thiophene (28)



Purified by silica gel chromatography (PE), the desired product **28** was obtained as a colorless oil, 23.1 mg, 49 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.32 – 7.13 (m, 3H), 6.94 – 6.79 (m, 1H), 3.68 (d, *J* = 2.4 Hz, 1H); <sup>19</sup>F NMR (376 MHz, Chloroform-d)  $\delta$  -90.17 (d, *J* = 39.8 Hz), -90.99 (d, *J* = 40.2 Hz); <sup>13</sup>C NMR (101 MHz, Chloroform-d)  $\delta$  195.61 (d, <sup>1</sup>*J*<sub>C-F</sub> = 14.3 Hz), 168.48, 148.60, 137.36, 133.94, 132.67 (dd, <sup>4</sup>*J*<sub>C-F</sub> = 4.9, 2.9 Hz), 132.07 (d, <sup>3</sup>*J*<sub>C-F</sub> = 9.6 Hz), 131.58 (d, <sup>4</sup>*J*<sub>C-F</sub> = 9.1 Hz), 130.09, 128.87 (dd, <sup>2</sup>*J*<sub>C-F</sub> = 14.2, 12.1 Hz), 127.84, 123.19, 37.95 (d, <sup>3</sup>*J*<sub>C-F</sub> = 2.5 Hz).; HRMS (EI) m/z calcd for C<sub>13</sub>H<sub>11</sub>F<sub>2</sub>S<sup>+</sup> (M+H)<sup>+</sup> 237.0544, found 237.0538.

#### (6,6-difluorohex-5-ene-1,5-diyl)dibenzene (29)<sup>[7]</sup>



Purified by silica gel chromatography (petroleum ether), the desired product **29** was obtained as a colorless oil, 49.0 mg, 90 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.39 – 7.30 (m, 2H), 7.30 – 7.22 (m, 5H), 7.20 – 7.09 (m, 3H), 2.60 – 2.52 (m, 2H), 2.42 (tt, *J* = 7.5, 2.4 Hz, 2H), 1.68 – 1.56 (m, 2H), 1.41 (p, *J* = 7.6 Hz, 2H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -91.83; <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  153.8 (t, <sup>1</sup>*J*<sub>C-F</sub> = 288.2 Hz), 142.6, 134.0 (d, <sup>3</sup>*J*<sub>C-F</sub> = 1.6 Hz), 128.6, 128.6, 128.5, 128.5 (d, <sup>4</sup>*J*<sub>C-F</sub> = 6.5 Hz), 127.4, 125.9, 92.5 (dd, <sup>2</sup>*J*<sub>C-F</sub> = 18.4, 16.4 Hz), 35.7, 30.9, 27.6, 27.5 (t, <sup>3</sup>*J*<sub>C-F</sub> = 2.6 Hz).

#### (3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzene (30)<sup>[6]</sup>



Purified by silica gel chromatography (petroleum ether), the desired product **30** was obtained as a colorless oil, 45.3 mg, 96 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.39 – 7.21 (m, 5H), 2.27 (dt, J = 7.3, 2.5 Hz, 2H), 1.73 – 1.56 (m, 5H), 1.25 (dtq, J = 14.3, 7.0, 3.5 Hz, 1H), 1.11 (tq, J = 8.7, 3.3 Hz, 3H), 0.98 – 0.84 (m, 2H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -91.43 (d, J = 44.3 Hz), -91.88 (d, J = 44.5 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  154.2 (dd, <sup>1</sup> $J_{C-F} = 290.0, 285.9$  Hz), 134.4 (dd, <sup>3</sup> $J_{C-F} = 4.5, 3.0$  Hz), 128.6, 128.5 (t, <sup>4</sup> $J_{C-F} = 3.2$  Hz), 127.3, 91.3 (dd, <sup>2</sup> $J_{C-F} = 22.0, 12.7$  Hz), 35.9 (t, <sup>3</sup> $J_{C-F} = 2.4$  Hz), 35.5, 33.1, 26.6, 26.3.

#### 1-(3,3-difluoro-2-phenylallyl)adamantine (31)<sup>[7]</sup>



Purified by silica gel chromatography (petroleum ether), the desired product **31** was obtained as a colorless oil, 56.4 mg, 98 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.32 (d, *J* = 4.5 Hz, 4H), 7.27 – 7.17 (m, 1H), 2.20 (t, *J* = 2.6 Hz, 2H), 1.85 (q, *J* = 6.7, 5.0 Hz, 3H), 1.71 – 1.49 (m, 6H), 1.38 (d, *J* = 3.0 Hz, 6H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -89.10 (d, *J* = 40.7 Hz), -92.18 (d, *J* = 40.9 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  154.6 (dd, <sup>1</sup>*J*<sub>C-F</sub> = 290.5, 287.0 Hz), 136.2 (dd, <sup>3</sup>*J*<sub>C-F</sub> = 4.8, 2.9 Hz), 128.6 (t, <sup>4</sup>*J*<sub>C-F</sub> = 2.9 Hz), 128.4, 127.1, 90.0 (dd, <sup>2</sup>*J*<sub>C-F</sub> = 21.9, 12.6 Hz), 42.9, 40.6 (d, <sup>3</sup>*J*<sub>C-F</sub> = 4.4 Hz), 37.1, 34.9 (t, <sup>4</sup>*J*<sub>C-F</sub> = 2.5 Hz), 28.9.

#### 1-(3,3-difluoro-2-phenylallyl)-4-((1s,4r)-4-propylcyclohexyl)benzene (32)



Purified by silica gel chromatography (PE: EA/80: 1), the desired product **32** was obtained as a colorless oil, 53.8 mg, 76 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.28 (d, *J* = 4.7 Hz, 4H), 7.25 – 7.12 (m, 1H), 7.07 (s, 4H), 3.69 (t, *J* = 2.3 Hz, 2H), 2.40 (tt, *J* = 12.2, 3.2 Hz, 1H), 1.87 – 1.80 (m, 4H), 1.47 – 1.14 (m, 5H), 1.24 – 1.13 (m, 2H), 1.09 – 0.94 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -90.24 (d, *J* = 39.8 Hz), -90.96 (d, *J* = 39.8 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz,

Chloroform-*d*)  $\delta$  154.7 (dd, <sup>1</sup>*J*<sub>C-*F*</sub> = 292.0, 287.3 Hz), 146.2, 136.0 (t, <sup>4</sup>*J*<sub>C-*F*</sub> = 2.6 Hz), 134.0 (t, <sup>3</sup>*J*<sub>C-*F*</sub> = 3.9 Hz), 128.6, 128.5 (t, <sup>4</sup>*J*<sub>C-*F*</sub> = 3.5 Hz), 128.3, 127.4, 127.1, 91.9 (dd, <sup>2</sup>*J*<sub>C-*F*</sub> = 21.3, 13.2 Hz), 44.4, 39.9, 37.2, 34.5, 33.8, 33.6 (d, <sup>3</sup>*J*<sub>C-*F*</sub> = 1.9 Hz), 20.3, 14.6; HRMS (ESI) m/z calcd for C<sub>24</sub>H<sub>29</sub>F<sub>2</sub><sup>+</sup> (M+H)<sup>+</sup> 355.2332, found 355.2336.

#### 1-(3,3-difluoro-2-phenylallyl)-4-(3,3-dimethylbut-1-yn-1-yl)benzene (33)



Purified by silica gel chromatography (petroleum ether), the desired product **33** was obtained as a colorless oil, 27.4 mg, 42 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.37 – 7.31 (m, 2H), 7.28 – 7.24 (m, 2H), 7.21 (td, *J* = 6.3, 1.5 Hz, 3H), 7.08 (d, *J* = 8.0 Hz, 2H), 3.71 (t, *J* = 2.3 Hz, 2H), 0.23 (s, 9H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -90.42 (d, *J* = 39.6 Hz), -90.69 (d, *J* = 40.1 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  154.6 (dd, <sup>1</sup>*J*<sub>C-F</sub> = 292.9, 288.9 Hz), 139.3, 133.4, 132.3, 128.6, 128.5 (d, <sup>4</sup>*J*<sub>C-F</sub> = 6.8 Hz), 128.5, 127.6, 121.4, 94.2, 91.7 (dd, <sup>2</sup>*J*<sub>C-F</sub> = 20.9, 14.3 Hz), 34.1, 0.2; HRMS (ESI) m/z calcd for C<sub>20</sub>H<sub>21</sub>F<sub>2</sub>Si<sup>+</sup> (M+H)<sup>+</sup> 327.1375, found 327.1378.

#### 3-(4-fluorobenzyl)-1,3-dimethylindolin-2-one (34)<sup>[9]</sup>



Purified by silica gel chromatography (PE: EA/20: 1), the desired product **34** was obtained as a colorless oil, 38.7 mg, 72 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.23 – 7.12 (m, 2H), 7.04 (td, J = 7.5, 1.1 Hz, 1H), 6.78 (ddt, J = 8.3, 5.2, 2.5 Hz, 2H), 6.75 – 6.67 (m, 2H), 6.62 (dt, J = 7.8, 0.8 Hz, 1H), 3.11 (d, J = 13.1 Hz, 1H), 2.97 (s, 3H), 2.96 (d, J = 13.3 Hz, 1H), 1.46 (s, 3H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -116.57, <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  179.9, 161.8 (d, <sup>1</sup> $J_{C-F} = 244.4$  Hz), 143.3, 133.0, 132.1 (d, <sup>4</sup> $J_{C-F} = 3.3$  Hz), 131.4, 131.3, 128.1, 123.3, 122.4, 114.6, 114.4, 108.1, 50.2, 43.9, 26.1, 22.9.

3-(4-chlorobenzyl)-1,3-dimethylindolin-2-one (35)<sup>[9]</sup>



Purified by silica gel chromatography (PE: EA/20: 1), the desired product **35** was obtained as a colorless oil, 39.3 mg, 69 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.23 – 7.12 (m, 2H), 7.08 – 6.97 (m, 3H), 6.79 – 6.72 (m, 2H), 6.66 – 6.60 (m, 1H), 3.11 (d, *J* = 13.0 Hz, 1H), 2.99 (s, 2H), 2.96 (d, *J* = 13.1 Hz, 1H), 1.46 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  179.8, 143.3, 134.9, 132.8, 132.5, 131.2, 128.1, 127.8, 123.3, 122.4, 108.2, 50.1, 44.0, 26.1, 23.1.

#### 4-((1,3-dimethyl-2-oxoindolin-3-yl)methyl)benzonitrile (36)<sup>[11]</sup>



Purified by silica gel chromatography (PE: EA/10: 1), the desired product **36** was obtained as a colorless oil, 33.1 mg, 60 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.34 – 7.28 (m, 2H), 7.24 – 7.16 (m, 2H), 7.06 (td, *J* = 7.3, 1.0 Hz, 1H), 6.95 – 6.89 (m, 2H), 6.65 – 6.58 (m, 1H), 3.22 (d, *J* = 12.8 Hz, 1H), 3.04 (s, 1H), 2.96 (s, 3H), 1.49 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  179.3, 143.2, 142.1, 132.3, 131.5, 130.6, 128.5, 123.2, 122.6, 119.0, 110.6, 108.3, 50.1, 44.7, 26.1, 23.3.

#### methyl 4-((1,3-dimethyl-2-oxoindolin-3-yl)methyl)benzoate (37)<sup>[12]</sup>



Purified by silica gel chromatography (PE: EA/10: 1), the desired product **37** was obtained as a colorless oil, 40.8 mg, 66 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.74 – 7.67 (m, 2H), 7.17 (ddd, J = 8.7, 7.7, 1.3 Hz, 2H), 7.03 (td, J = 7.5, 1.0 Hz, 1H), 6.93 – 6.86 (m, 2H), 6.59 (dt, J = 7.5, 0.9 Hz, 1H), 3.83 (s, 3H), 3.19 (d, J = 12.8 Hz, 1H), 3.04 (d, J = 12.8 Hz, 1H), 2.96 (s, 3H), 1.48 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  179.7, 167.3, 143.2, 141.9, 132.7, 130.0, 129.0, 128.5, 128.2, 123.3, 122.4, 108.1, 52.1, 50.1, 44.6, 26.1, 23.2.

1,3-dimethyl-3-(4-methylbenzyl)indolin-2-one (38)<sup>[9]</sup>



Purified by silica gel chromatography (PE: EA/20: 1), the desired product **38** was obtained as a colorless oil, 35.5 mg, 67 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.19 (td, *J* = 7.7, 1.4 Hz, 1H), 7.11 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.03 (td, *J* = 7.5, 1.0 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 2H), 6.84 – 6.71 (m, 2H), 6.64 (dd, *J* = 7.8, 0.9 Hz, 1H), 3.07 (d, *J* = 13.1 Hz, 1H), 3.01 (s, 3H), 2.98 (d, *J* = 13.1 Hz, 1H), 2.21 (s, 3H), 1.46 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*) δ 180.3, 143.4, 136.0, 133.4, 133.3, 129.9, 128.4, 127.9, 123.5, 122.2, 107.9, 50.1, 44.2, 26.1, 22.9, 21.2.

#### 1,3-dimethyl-3-(3-methylbenzyl)indolin-2-one (39)<sup>[11]</sup>



Purified by silica gel chromatography (PE: EA/20: 1), the desired product **39** was obtained as a colorless oil, 35.0 mg, 66 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.18 (td, J = 7.6, 1.4 Hz, 1H), 7.10 (ddd, J = 7.3, 1.4, 0.6 Hz, 1H), 7.02 (td, J = 7.5, 1.0 Hz, 1H), 6.94 (t, J = 7.4 Hz, 1H), 6.91 – 6.85 (m, 1H), 6.69 – 6.59 (m, 3H), 3.06 (d, J = 13.0 Hz, 1H), 3.00 (s, 3H), 2.97 (d, J = 13.0 Hz, 1H), 2.16 (s, 3H), 1.46 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  180.3, 143.4, 137.2, 136.3, 133.3, 130.9, 127.9, 127.5, 127.3, 127.1, 123.6, 122.2, 107.9, 50.0, 44.7, 26.1, 22.8, 21.4.

#### 3-(3,4-dimethylbenzyl)-1,3-dimethylindolin-2-one (40)<sup>[13]</sup>



Purified by silica gel chromatography (PE: EA/20: 1), the desired product **40** was obtained as a colorless oil, 28.5 mg, 51 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.19 (td, *J* = 7.6, 1.4 Hz, 1H), 7.09 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.02 (td, *J* = 7.4, 1.0 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.69 – 6.62 (m,

2H), 6.58 (dd, *J* = 7.7, 1.9 Hz, 1H), 3.02 (s, 3H), 3.02 (d, *J* = 13.0 Hz, 1H), 2.96 (d, *J* = 13.0 Hz, 1H), 2.13 (s, 3H), 2.08 (s, 3H), 1.45 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*) δ 180.4, 143.4, 135.7, 134.6, 133.7, 133.5, 131.4, 128.9, 127.8, 127.5, 123.7, 122.1, 107.9, 49.9, 44.2, 26.1, 22.9, 19.7, 19.5.

#### 1,3-dimethyl-3-(thiophen-3-ylmethyl)indolin-2-one (41)



Purified by silica gel chromatography (PE: EA/20: 1), the desired product **41** was obtained as a colorless oil, 26.7 mg, 52 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.26 – 7.12 (m, 2H), 7.05 (td, J = 7.5, 1.0 Hz, 1H), 6.98 (dd, J = 4.9, 2.9 Hz, 1H), 6.69 – 6.63 (m, 2H), 6.51 (dd, J = 4.9, 1.3 Hz, 1H), 3.16 (d, J = 13.5 Hz, 1H), 3.04 (d, J = 13.5 Hz, 1H), 3.01 (s, 3H), 1.46 (s, 3H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  180.22, 143.51, 136.72, 133.60, 129.18, 128.07, 124.32, 123.14, 122.94, 122.40, 108.02, 49.81, 39.17, 26.14, 22.82; HRMS (ESI) m/z calcd for C<sub>15</sub>H<sub>15</sub>NOS<sup>+</sup> (M+H)<sup>+</sup> 258.0947, found 258.0943.

#### 1,3-dimethyl-3-nonylindolin-2-one (42)<sup>[15]</sup>



Purified by silica gel chromatography (PE: EA/30: 1), the desired product **42** was obtained as a colorless oil, 52.8 mg, 92 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.25 (td, *J* = 7.7, 1.3 Hz, 1H), 7.16 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.05 (td, *J* = 7.5, 1.0 Hz, 1H), 6.83 (dd, *J* = 7.7, 1.0 Hz, 1H), 3.20 (s, 3H), 1.87 (ddd, *J* = 13.3, 12.2, 4.7 Hz, 1H), 1.71 (ddd, *J* = 13.3, 12.2, 4.4 Hz, 1H), 1.34 (s, 3H), 1.30 – 1.09 (m, 12H), 0.97 (dtd, *J* = 12.3, 6.9, 3.2 Hz, 1H), 0.84 (t, *J* = 7.0 Hz, 3H), 0.88 – 0.75 (m, 1H); <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  181.1, 143.5, 134.5, 127.7, 122.6, 122.6, 108.0, 48.6, 38.7, 32.0, 29.9, 29.7, 29.48, 29.4, 26.3, 24.6, 24.0, 22.8, 14.3.

#### 1,3-dimethyl-3-(4-phenylbutyl)indolin-2-one (43)<sup>[14]</sup>



Purified by silica gel chromatography (PE: EA/20: 1), the desired product **43** was obtained as a colorless oil, 56.3 mg, 96 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.31 – 7.18 (m, 3H), 7.18 – 7.10 (m, 2H), 7.08 – 7.02 (m, 3H), 6.83 (dt, *J* = 7.8, 0.8 Hz, 1H), 3.20 (s, 3H), 2.46 (t, *J* = 8.0 Hz, 2H), 1.93 (ddd, *J* = 13.3, 12.0, 4.8 Hz, 1H), 1.77 (ddd, *J* = 13.3, 12.1, 4.5 Hz, 1H), 1.58 – 1.37 (m, 2H), 1.35 (s, 3H), 1.15 – 1.00 (m, 1H), 1.00 – 0.84 (m, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  181.0, 143.5, 142.7, 134.4, 128.4, 128.4, 127.8, 125.8, 122.7, 122.6, 108.1, 48.6, 38.4, 35.8, 31.8, 26.3, 24.5, 23.9.

#### 3-(cyclopentylmethyl)-1,3-dimethylindolin-2-one (44)<sup>[14]</sup>



Purified by silica gel chromatography (PE: EA/30: 1), the desired product **44** was obtained as a colorless oil, 45.7 mg, 94 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.26 (td, *J* = 7.7, 1.3 Hz, 1H), 7.19 – 7.13 (m, 1H), 7.06 (td, *J* = 7.5, 1.0 Hz, 1H), 6.84 (dt, *J* = 7.8, 0.8 Hz, 1H), 3.22 (s, 3H), 2.06 (dd, *J* = 13.7, 7.2 Hz, 1H), 1.89 (dd, *J* = 13.7, 6.0 Hz, 1H), 1.54 – 1.36 (m, 3H), 1.34 (s, 3H), 1.33 – 1.17 (m, 4H), 1.07 – 0.94 (m, 1H), 0.90 – 0.73 (m, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  181.3, 143.5, 134.6, 127.7, 123.0, 122.5, 108.0, 48.7, 44.7, 37.4, 34.0, 32.9, 26.4, 25.5, 25.1, 25.1.

#### 3-(cyclohexylmethyl)-1,3-dimethylindolin-2-one (45)<sup>[14]</sup>



Purified by silica gel chromatography (PE: EA/30: 1), the desired product **45** was obtained as a colorless oil, 95 % yield for iodocyclohexane (24.4 mg)and 42 % yield for bromocyclohexane (10.8 mg); <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.25 (td, *J* = 7.7, 1.3 Hz, 1H), 7.15 (dd, *J* = 7.3, 1.3 Hz, 1H),

7.05 (td, J = 7.5, 1.0 Hz, 1H), 6.83 (dt, J = 7.8, 0.7 Hz, 1H), 3.21 (s, 3H), 1.92 (dd, J = 14.0, 6.9 Hz, 1H), 1.72 (dd, J = 14.0, 5.2 Hz, 1H), 1.56 – 1.41 (m, 3H), 1.35 (dt, J = 3.5, 1.7 Hz, 1H), 1.30 (s, 3H), 1.20 (ddq, J = 10.1, 3.9, 2.1 Hz, 1H), 1.05 – 0.87 (m, 4H), 0.87 – 0.65 (m, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  181.3, 143.3, 134.6, 127.7, 122.9, 122.5, 108.1, 48.1, 45.6, 34.9, 34.7, 33.7, 26.4, 26.3, 26.3, 26.2.

#### 3-(adamantan-1-ylmethyl)-1,3-dimethylindolin-2-one (46)<sup>[14]</sup>



Purified by silica gel chromatography (PE: EA/30: 1), the desired product **46** was obtained as a colorless oil, 60.6 mg, 98 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.26 (tt, *J* = 7.8, 1.2 Hz, 1H), 7.19 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.03 (tt, *J* = 7.5, 1.0 Hz, 1H), 6.85 (dd, *J* = 7.8, 0.9 Hz, 1H), 3.23 (s, 3H), 2.00 (d, *J* = 14.5 Hz, 1H), 1.82 – 1.66 (m, 4H), 1.58 – 1.33 (m, 6H), 1.27 (s, 3H), 1.25 – 1.11 (m, 6H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*) δ 181.3, 142.8, 134.9, 127.6, 123.7, 122.2, 108.1, 52.2, 46.8, 43.5, 36.9, 34.0, 28.8, 28.7, 26.4.

#### 1-(1,1-difluoro-3-phenylprop-1-en-2-yl)-4-methylbenzene (47)<sup>[2]</sup>



Purified by silica gel chromatography (petroleum ether), the desired product **47** was obtained as a colorless oil, 40.0 mg, 82 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.32 – 6.96 (m, 9H), 3.71 (s, 2H), 2.29 (s, 3H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -90.84 (d, 1F, *J* = 41.0 Hz), -91.26 (d, 1F, *J* = 41.1 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  154.5 (dd, <sup>1</sup>*J*<sub>C-F</sub> = 288.9, 287.9 Hz), 138.8 (t, <sup>4</sup>*J*<sub>C-F</sub> = 2.6 Hz), 137.2, 130.7 (t, <sup>3</sup>*J*<sub>C-F</sub> = 3.8 Hz), 129.3, 128.7, 128.5, 128.3 (t, <sup>4</sup>*J*<sub>C-F</sub> = 3.5 Hz), 126.5, 91.6 (dd, <sup>2</sup>*J*<sub>C-F</sub> = 21.1, 13.7 Hz), 34.1 (d, <sup>3</sup>*J*<sub>C-F</sub> = 2.1 Hz), 21.3; HRMS (ESI) m/z calcd for C<sub>16</sub>H<sub>15</sub>F<sub>2</sub><sup>+</sup> (M+H)<sup>+</sup> 245.1136, found 245.1127.

#### 1-(1,1-difluoro-3-phenylprop-1-en-2-yl)-4-methoxybenzene (48)<sup>[2]</sup>



Purified by silica gel chromatography (PE: EA/100: 1), the desired product **48** was obtained as a colorless oil, 41.6 mg, 80 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.21 – 7.05 (m, 7H), 6.78 – 6.71 (m, 2H), 3.69 (s, 3H), 3.63 (s, 2H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -91.49 (d, 1F, *J* = 42.9 Hz), -91.90 (d, 1F, *J* = 42.8 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  158.9, 154.5 (dd, <sup>1</sup>*J*<sub>C-F</sub> = 290.7, 286.8 Hz), 138.8 (t, <sup>4</sup>*J*<sub>C-F</sub> = 2.7 Hz), 129.6 (t, <sup>4</sup>*J*<sub>C-F</sub> = 3.5 Hz), 128.7, 128.5, 126.6, 125.9 (t, <sup>3</sup>*J*<sub>C-F</sub> = 3.6 Hz), 114.0, 91.4 (dd, <sup>2</sup>*J*<sub>C-F</sub> = 21.3, 13.9 Hz), 55.4, 34.2 (d, <sup>3</sup>*J*<sub>C-F</sub> = 2.2 Hz).

#### (4-(1,1-difluoro-3-phenylprop-1-en-2-yl)phenyl)(methyl)sulfane (49)



Purified by silica gel chromatography (PE: EA/100: 1), the desired product **49** was obtained as a colorless oil, 42.0 mg, 76 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.39 – 6.75 (m, 9H), 3.71 (t, *J* = 2.3 Hz, 2H), 2.44 (s, 3H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -90.19 (d, *J* = 40.1 Hz), -90.58 (d, *J* = 40.1 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  154.6 (dd, <sup>1</sup>*J*<sub>*C*-*F*</sub> = 291.9, 287.7 Hz), 138.6 (t, <sup>4</sup>*J*<sub>*C*-*F*</sub> = 2.7 Hz), 137.8, 130.3 (t, <sup>3</sup>*J*<sub>*C*-*F*</sub> = 3.8 Hz), 128.8 (t, <sup>3</sup>*J*<sub>*C*-*F*</sub> = 3.6 Hz), 128.7, 128.5, 126.6, 126.5, 91.4 (dd, <sup>2</sup>*J*<sub>*C*-*F*</sub> = 21.6, 13.5 Hz), 34.0 (d, <sup>3</sup>*J*<sub>*C*-*F*</sub> = 2.0 Hz), 15.8; HRMS (ESI) m/z calcd for C<sub>16</sub>H<sub>15</sub>F<sub>2</sub>S<sup>+</sup> (M+H)<sup>+</sup> 277.0857, found 277.0859.

#### 1-(1,1-difluoro-3-phenylprop-1-en-2-yl)-4-ethylbenzene (50)



Purified by silica gel chromatography (petroleum ether), the desired product **50** was obtained as a colorless oil, 41.3 mg, 80 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.34 – 7.09 (m, 9H), 3.73 (s, 2H), 2.61 (q, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -90.66 (d,
1F, J = 40.9 Hz), -91.15 (d, 1F, J = 40.9 Hz); <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  154.7 (dd, <sup>1</sup> $J_{C-F} = 291.6, 287.1$  Hz), 143.5, 138.9 (t, <sup>4</sup> $J_{C-F} = 2.8$  Hz), 131.0 (t, <sup>3</sup> $J_{C-F} = 3.8$  Hz), 128.7, 128.5, 128.4 (t, <sup>4</sup> $J_{C-F} = 3.5$  Hz), 128.1, 126.6, 91.7 (dd, <sup>2</sup> $J_{C-F} = 21.0, 13.4$  Hz), 34.1 (d, <sup>3</sup> $J_{C-F} = 2.0$  Hz), 28.7, 15.5; HRMS (ESI) m/z calcd for C<sub>17</sub>H<sub>17</sub>F<sub>2</sub><sup>+</sup> (M+H)<sup>+</sup> 259.1293, found 259.1294.

#### 1-(1,1-difluoro-3-phenylprop-1-en-2-yl)-4-isopropylbenzene (51)<sup>[8]</sup>



Purified by silica gel chromatography (petroleum ether), the desired product **51** was obtained as a colorless oil, 44.6 mg, 82 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.22 – 7.03 (m, 9H), 3.65 (s, 2H), 2.78 (hept, J = 6.9 Hz, 1H), 1.14 (d, J = 6.9 Hz, 6H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -90.42 (d, 1F, J = 40.6 Hz), -90.97 (d, 1F, J = 40.7 Hz); <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  154.7 (dd, <sup>1</sup> $J_{C-F} = 291.8$ , 287.1 Hz), 148.1, 138.9 (t, <sup>4</sup> $J_{C-F} = 2.7$  Hz), 131.1 (t, <sup>3</sup> $J_{C-F} = 3.9$  Hz), 128.7, 128.5, 128.3 (t, <sup>4</sup> $J_{C-F} = 3.6$  Hz), 126.7, 126.6, 91.6 (dd, <sup>2</sup> $J_{C-F} = 21.1$ , 13.4 Hz), 34.1, 33.9, 24.1.

## 1-(tert-butyl)-4-(1,1-difluoro-3-phenylprop-1-en-2-yl)benzene (52)<sup>[2]</sup>



Purified by silica gel chromatography (petroleum ether), the desired product **52** was obtained as a colorless oil, 49.8 mg, 87 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.42 – 7.10 (m, 9H), 3.72 (s, 2H), 1.28 (s, 9H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -90.15 (d, 1F, *J* = 40.3 Hz), -90.75 (d, 1F, *J* = 40.4 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  154.8 (dd, <sup>1</sup>*J*<sub>C-F</sub> = 292.2, 287.1 Hz), 150.4, 138.9 (t, <sup>4</sup>*J*<sub>C-F</sub> = 2.7 Hz), 130.8 (t, <sup>3</sup>*J*<sub>C-F</sub> = 3.9 Hz), 128.7, 128.4, 128.0 (t, <sup>4</sup>*J*<sub>C-F</sub> = 3.7 Hz), 126.6, 125.5, 91.5 (dd, <sup>2</sup>*J*<sub>C-F</sub> = 21.1, 13.3 Hz), 34.7, 34.0 (d, <sup>3</sup>*J*<sub>C-F</sub> = 1.9 Hz), 31.5; HRMS (ESI) m/z calcd for C<sub>19</sub>H<sub>21</sub>F<sub>2</sub><sup>+</sup> (M+H)<sup>+</sup> 287.1606, found 287.1613.

#### 4-(1,1-difluoro-3-phenylprop-1-en-2-yl)-1,1'-biphenyl (53)<sup>[8]</sup>



Purified by silica gel chromatography (PE: EA/150: 1), the desired product **53** was obtained as a colorless oil, 36.7 mg, 60 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.57 (ddt, *J* = 14.8, 6.3, 1.6 Hz, 4H), 7.45 (td, *J* = 7.4, 1.4 Hz, 2H), 7.41 – 7.33 (m, 3H), 7.33 – 7.27 (m, 2H), 7.26 – 7.17 (m, 3H), 3.84 – 3.77 (m, 2H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -89.65 (d, *J* = 39.4 Hz), -90.19 (d, *J* = 38.9 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  154.8 (dd, <sup>1</sup>*J*<sub>C+F</sub> = 292.9, 292.9 Hz), 140.7, 140.2, 138.7, 132.7 (t, *J* = 3.8 Hz), 129.0, 128.8 (d, *J* = 3.6 Hz), 128.8, 128.5, 127.6, 127.3, 127.2, 91.6 (dd, *J* = 21.5, 12.9 Hz), 34.0 (d, *J* = 1.6 Hz).

#### (4-(1,1-difluoro-3-phenylprop-1-en-2-yl)phenyl)trimethylsilane (54)



Purified by silica gel chromatography (petroleum ether), the desired product **54** was obtained as a colorless oil, 48.9 mg, 81 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.47 – 7.40 (m, 2H), 7.30 – 7.22 (m, 4H), 7.18 (dt, *J* = 9.6, 3.1 Hz, 3H), 3.74 (t, *J* = 2.3 Hz, 2H), 0.23 (s, 9H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -89.60 (d, *J* = 38.9 Hz), -90.24 (d, *J* = 38.8 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  154.8 (dd, <sup>1</sup>*J*<sub>C-F</sub> = 292.7, 287.7 Hz), 139.7, 138.8 (t, <sup>4</sup>*J*<sub>C-F</sub> = 2.7 Hz), 134.2 (t, <sup>3</sup>*J*<sub>C-F</sub> = 4.0 Hz), 133.6, 128.7, 128.4, 127.6 (t, <sup>4</sup>*J*<sub>C-F</sub> = 3.5 Hz), 126.6, 91.8 (dd, <sup>2</sup>*J*<sub>C-F</sub> = 21.2, 13.1 Hz), 34.0 (d, <sup>3</sup>*J*<sub>C-F</sub> = 1.9 Hz), -1.0; HRMS (ESI) m/z calcd for C<sub>18</sub>H<sub>21</sub>F<sub>2</sub>Si<sup>+</sup> (M+H)<sup>+</sup> 303.1375, found 303.1368.

#### 1-(1,1-difluoro-3-phenylprop-1-en-2-yl)-4-fluorobenzene (55)<sup>[4]</sup>



Purified by silica gel chromatography (petroleum ether), the desired product **55** was obtained as a colorless oil, 40.7 mg, 82 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.29 – 7.17 (m, 5H), 7.16 – 7.10 (m, 2H), 7.01 – 6.91 (m, 2H), 3.70 (s, 2H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -90.72 (d, 1F, J

= 40.7 Hz), -91.15 (d, 1F, J = 40.8 Hz), -114.55 (s, 1F); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-d)  $\delta$ 163.3, 160.9, 154.6 (dd, <sup>1</sup> $J_{C-F}$  = 289.9, 286.2 Hz), 138.4 (t, <sup>4</sup> $J_{C-F}$  = 2.7 Hz), 130.2 (dt, <sup>4</sup> $J_{C-F}$ , <sup>3</sup> $J_{C-F}$ ' = 3.5, 3.4 Hz), 129.6 (q, <sup>3</sup> $J_{C-F}$ , <sup>4</sup> $J_{C-F}$ ' = 3.6 Hz), 128.8, 128.5, 126.7, 115.7, 115.5, 91.3 (dd, <sup>2</sup> $J_{C-F}$  = 21.9, 14.0 Hz), 34.3 (d, <sup>3</sup> $J_{C-F}$  = 1.9 Hz).

#### 1-chloro-4-(1,1-difluoro-3-phenylprop-1-en-2-yl)benzene (56)<sup>[8]</sup>



Purified by silica gel chromatography (petroleum ether), the desired product **56** was obtained as a colorless oil, 42.8 mg, 81 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.24 (dt, *J* = 7.2, 2.8 Hz, 4H), 7.18 (tq, *J* = 5.7, 2.3, 1.9 Hz, 3H), 7.13 (dd, *J* = 6.9, 1.9 Hz, 2H), 3.70 (s, 2H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -89.73 (d, *J* = 38.4 Hz), -90.13 (d, *J* = 38.8 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  154.6 (dd, <sup>1</sup>*J*<sub>C-F</sub> = 292.2, 288.1 Hz), 138.3 (t, <sup>4</sup>*J*<sub>C-F</sub> = 2.7 Hz), 133.4, 132.2 (t, <sup>3</sup>*J*<sub>C-F</sub> = 3.9 Hz), 129.8 (t, <sup>4</sup>*J*<sub>C-F</sub> = 3.5 Hz), 128.8, 128.8, 128.5, 126.8, 91.2 (dd, <sup>2</sup>*J*<sub>C-F</sub> = 21.9, 13.5 Hz), 34.0 (d, <sup>3</sup>*J*<sub>C-F</sub> = 1.6 Hz).

#### 1-bromo-4-(1,1-difluoro-3-phenylprop-1-en-2-yl)benzene (57)<sup>[4]</sup>



Purified by silica gel chromatography (petroleum ether), the desired product **57** was obtained as a colorless oil, 53.0 mg, 86 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.42 – 7.35 (m, 2H), 7.28 – 7.21 (m, 2H), 7.20 – 7.07 (m, 5H), 3.69 (t, J = 2.4 Hz, 2H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -89.51 (d, J = 38.2 Hz), -89.92 (d, J = 38.1 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  154.6 (dd, <sup>1</sup> $J_{C-F} = 292.3$ , 288.2 Hz), 138.2 (t, <sup>4</sup> $J_{C-F} = 2.6$  Hz), 132.7 (t, <sup>3</sup> $J_{C-F} = 3.9$  Hz), 131.77, 130.1 (t, <sup>4</sup> $J_{C-F} = 3.6$  Hz), 128.8, 128.5, 126.8, 121.5, 91.3 (dd, <sup>2</sup> $J_{C-F} = 22.0$ , 13.6 Hz), 33.9.

#### 1-(1,1-difluoro-3-phenylprop-1-en-2-yl)-4-phenoxybenzene (58)



Purified by silica gel chromatography (PE: EA/100: 1), the desired product **58** was obtained as a colorless oil, 51.5 mg, 80 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.36 – 7.29 (m, 2H), 7.29 – 7.14 (m, 7H), 7.13 – 7.07 (m, 1H), 7.03 – 6.96 (m, 2H), 6.94 – 6.86 (m, 2H), 3.71 (s, 2H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -90.69 (d, 1F, *J* = 41.0 Hz), -91.15 (d, 1F, *J* = 41.4 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  157.0, 156.8, 154.6 (dd, <sup>1</sup>*J*<sub>C-F</sub> = 291.4, 287.3 Hz), 138.6 (t, <sup>4</sup>*J*<sub>C-F</sub> = 2.7 Hz), 130.0, 129.8 (t, <sup>4</sup>*J*<sub>C-F</sub> = 3.6 Hz), 128.7, 128.5, 128.4 (d, <sup>3</sup>*J*<sub>C-F</sub> = 3.8 Hz), 126.7, 123.7, 119.4, 118.6, 91.3 (dd, <sup>2</sup>*J*<sub>C-F</sub> = 21.7, 13.8 Hz), 34.2. HRMS (ESI) m/z calcd for C<sub>21</sub>H<sub>17</sub>F<sub>2</sub>O<sup>+</sup> (M+H)<sup>+</sup> 323.1242, found 323.1242.

#### 1-(benzyloxy)-4-(1,1-difluoro-3-phenylprop-1-en-2-yl)benzene (59)



Purified by silica gel chromatography (PE: EA/100: 1), the desired product **59** was obtained as a colorless oil, 49.7 mg, 74 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.48 – 7.37 (m, 4H), 7.37 – 7.31 (m, 1H), 7.31 – 7.24 (m, 2H), 7.24 – 7.14 (m, 5H), 6.95 – 6.88 (m, 2H), 5.04 (s, 2H), 3.72 (s, 2H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -91.29 (d, 1F, *J* = 42.8 Hz), -91.72 (d, 1F, *J* = 42.4 Hz); <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  158.1, 154.5 (dd, <sup>1</sup>*J*<sub>C-F</sub> = 290.8, 287.0 Hz), 138.8 (t, <sup>4</sup>*J*<sub>C-F</sub> = 2.6 Hz), 137.1, 129.6 (t, <sup>4</sup>*J*<sub>C-F</sub> = 3.5 Hz), 128.8, 128.7, 128.5, 128.2, 127.7, 126.6, 126.2 (t, <sup>3</sup>*J*<sub>C-F</sub> = 3.7 Hz), 114.9, 91.4 (dd, <sup>2</sup>*J*<sub>C-F</sub> = 21.2, 13.8 Hz), 70.2, 34.2; HRMS (ESI) m/z calcd for C<sub>22</sub>H<sub>19</sub>F<sub>2</sub>O<sup>+</sup> (M+H)<sup>+</sup> 337.1399, found 337.1397.

#### 1-(1,1-difluoro-3-phenylprop-1-en-2-yl)-3-methylbenzene (60)



Purified by silica gel chromatography (petroleum ether), the desired product **60** was obtained as a colorless oil, 36.6 mg, 75 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.21 – 7.13 (m, 2H), 7.09 (t, *J* = 7.7 Hz, 4H), 6.97 (dd, *J* = 16.5, 8.9 Hz, 3H), 3.64 (s, 2H), 2.22 (s, 3H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -90.53 (d, *J* = 40.4 Hz), -91.01 (d, *J* = 40.6 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  154.6 (dd, <sup>1</sup>*J*<sub>C-*F*</sub> = 291.5, 287.3 Hz), 138.8 (t, <sup>4</sup>*J*<sub>C-*F*</sub> = 2.7 Hz), 138.1, 133.7 (t, <sup>3</sup>*J*<sub>C-*F*</sub> = 3.8 Hz), 129.2 (t, <sup>4</sup>*J*<sub>C-*F*</sub> = 3.4 Hz), 128.7, 128.5, 128.4, 128.3, 126.6, 125.6 (t, <sup>4</sup>*J*<sub>C-*F*</sub> = 3.3 Hz), 91.9 (dd, <sup>2</sup>*J*<sub>C-*F*</sub> = 21.0, 13.7 Hz), 34.2 (d, <sup>3</sup>*J*<sub>C-*F*</sub> = 2.1 Hz), 21.7; HRMS (ESI) m/z calcd for C<sub>16</sub>H<sub>15</sub>F<sub>2</sub><sup>+</sup> (M+H)<sup>+</sup> 245.1136, found 245.1129.

#### 1-(1,1-difluoro-3-phenylprop-1-en-2-yl)-3,5-dimethylbenzene (61)



Purified by silica gel chromatography (petroleum ether), the desired product **61** was obtained as a colorless oil, 38.7 mg, 75 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.56 – 6.97 (m, 5H), 6.79 (d, *J* = 6.7 Hz, 3H), 3.63 (s, 2H), 2.18 (s, 6H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -90.64 (d, 1F, *J* = 40.8 Hz), -91.06 (d, 1F, *J* = 40.8 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  154.6 (dd, <sup>1</sup>*J*<sub>*C*-*F*</sub> = 291.3, 287.1 Hz), 138.9 (t, <sup>4</sup>*J*<sub>*C*-*F*</sub> = 2.7 Hz), 138.0, 133.6 (t, <sup>3</sup>*J*<sub>*C*-*F*</sub> = 3.7 Hz), 129.3, 128.6, 128.5, 126.5, 126.3 (t, <sup>4</sup>*J*<sub>*C*-*F*</sub> = 3.4 Hz), 92.0 (dd, <sup>2</sup>*J*<sub>*C*-*F*</sub> = 20.8, 13.8 Hz), 34.2, 21.5; HRMS (ESI) m/z calcd for C<sub>17</sub>H<sub>17</sub>F<sub>2</sub><sup>+</sup> (M+H)<sup>+</sup> 259.1293, found 259.1294.

#### 5-(1,1-difluoro-3-phenylprop-1-en-2-yl)benzo[d][1,3]dioxole (62)



Purified by silica gel chromatography (PE: EA/100: 1), the desired product **62** was obtained as a colorless oil, 43.3 mg, 79 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.29 – 7.11 (m, 5H), 6.72 (d, *J* = 7.6 Hz, 3H), 5.91 (s, 2H), 3.66 (t, *J* = 2.4 Hz, 2H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -91.17 (d, *J* = 42.0 Hz), -91.26; <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  154.5 (dd, <sup>1</sup>*J*<sub>*C*-*F*</sub> = 290.2, 287.5 Hz), 147.8, 146.9, 138.6 (t, <sup>4</sup>*J*<sub>*C*-*F*</sub> = 2.7 Hz), 128.7, 128.5, 127.3 (t, <sup>3</sup>*J*<sub>*C*-*F*</sub> = 2.7 Hz), 126.6, 122.1 (t, <sup>4</sup>*J*<sub>*C*-*F*</sub> = 3.4 Hz), 109.0 (t, <sup>4</sup>*J*<sub>*C*-*F*</sub> = 3.6 Hz), 108.4, 101.3, 91.7 (dd, <sup>2</sup>*J*<sub>*C*-*F*</sub> = 20.8, 14.9 Hz), 34.4 (d, <sup>3</sup>*J*<sub>*C*-*F*</sup> = 1.6 Hz); HRMS (ESI) m/z calcd for C<sub>16</sub>H<sub>13</sub>F<sub>2</sub>O<sub>2</sub><sup>+</sup> (M+H)<sup>+</sup> 275.0878, found 275.0880.</sub>

#### 6-(1,1-difluoro-3-phenylprop-1-en-2-yl)-2,3-dihydrobenzo[b][1,4]dioxine (63)



Purified by silica gel chromatography (PE: EA/100: 1), the desired product **63** was obtained as a colorless oil, 49.5 mg, 86 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.24 (tt, *J* = 8.3, 1.5 Hz, 2H), 7.21 – 7.13 (m, 3H), 6.87 – 6.65 (m, 3H), 4.21 (s, 4H), 3.67 (t, *J* = 2.3 Hz, 2H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -90.92 (d, *J* = 41.5 Hz), -91.17 (d, *J* = 41.5 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  154.5 (dd, <sup>1</sup>*J*<sub>C-F</sub> = 291.2, 287.0 Hz), 143.4, 143.0, 138.7 (t, <sup>4</sup>*J*<sub>C-F</sub> = 2.6 Hz), 128.7, 128.4, 126.8 (t, <sup>3</sup>*J*<sub>C-F</sub> = 3.5 Hz), 126.6, 121.6 (t, <sup>4</sup>*J*<sub>C-F</sub> = 3.6 Hz), 117.4 (d, <sup>4</sup>*J*<sub>C-F</sub> = 3.7 Hz), 117.3, 91.2 (dd, <sup>2</sup>*J*<sub>C-F</sub> = 21.3, 13.8 Hz), 64.5, 64.5, 34.0 (d, <sup>3</sup>*J*<sub>C-F</sub> = 1.7 Hz); HRMS (ESI) m/z calcd for C<sub>17</sub>H<sub>15</sub>F<sub>2</sub>O<sub>2</sub><sup>+</sup> (M+H)<sup>+</sup> 289.1035, found 289.1036.

#### 4-(1,1-difluoro-3-phenylprop-1-en-2-yl)dibenzo[b,d]thiophene (64)



Purified by silica gel chromatography (PE: EA/100: 1), the desired product **64** was obtained as a colorless oil, 53.8 mg, 80 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.14 (ddt, *J* = 6.4, 4.1, 2.0 Hz, 1H), 8.08 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.91 – 7.81 (m, 1H), 7.55 – 7.43 (m, 2H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.24 – 7.16 (m, 3H), 7.11 (ddd, *J* = 14.5, 7.8, 1.5 Hz, 3H), 3.85 (t, *J* = 2.2 Hz, 2H); <sup>19</sup>F NMR (376 MHz,

Chloroform-*d*)  $\delta$  -87.19 (d, J = 36.8 Hz), -91.47 (d, J = 36.7 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  153.9 (t, <sup>1</sup>*J*<sub>*C-F*</sub> = 290.3 Hz), 140.0, 139.4, 138.3 (t, <sup>1</sup>*J*<sub>*C-F*</sub> = 2.6 Hz), 136.1, 135.9, 128.9, 128.6, 128.5 (d, <sup>3</sup>*J*<sub>*C-F*</sub> = 4.9 Hz), 128.1 (dd, <sup>4</sup>*J*<sub>*C-F*</sub> = 3.2, 1.6 Hz), 127.1, 126.8, 124.7, 124.6, 122.9, 121.9, 121.3, 91.7 (dd, <sup>2</sup>*J*<sub>*C-F*</sub> = 22.9, 16.6 Hz), 34.1 (d, <sup>3</sup>*J*<sub>*C-F*</sub> = 1.8 Hz); HRMS (ESI) m/z calcd for C<sub>21</sub>H<sub>15</sub>F<sub>2</sub>S<sup>+</sup> (M+H)<sup>+</sup> 337.0857, found 337.0858.

3-benzyl-1,3-dimethylindolin-2-one (65)<sup>[9]</sup>



Purified by silica gel chromatography (PE: EA/20: 1), the desired product **65** was obtained as a colorless oil, 34.1 mg, 68 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.18 (td, J = 7.7, 1.3 Hz, 1H), 7.15 – 7.10 (m, 1H), 7.08 – 7.00 (m, 4H), 6.93 – 6.79 (m, 2H), 6.61 (dt, J = 7.8, 0.8 Hz, 1H), 3.12 (d, J = 13.0 Hz, 1H), 3.01 (d, J = 13.0 Hz, 1H), 2.98 (s, 3H), 1.48 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  180.1, 143.3, 136.4, 133.2, 130.0, 127.9, 127.7, 126.6, 123.5, 122.2, 107.9, 50.1, 44.7, 26.1, 22.9.

#### 3-benzyl-1,3,5-trimethylindolin-2-one (66)<sup>[9]</sup>



Purified by silica gel chromatography (PE: EA/20: 1), the desired product **66** was obtained as a colorless oil, 37.1 mg, 70 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.06 (qd, J = 4.7, 1.5 Hz, 3H), 6.98 (dd, J = 7.8, 1.7 Hz, 1H), 6.94 (d, J = 1.7 Hz, 1H), 6.88 – 6.82 (m, 2H), 6.50 (d, J = 7.8 Hz, 1H), 3.10 (d, J = 12.9 Hz, 1H), 2.99 (d, J = 13.0 Hz, 1H), 2.96 (s, 3H), 2.34 (s, 3H), 1.46 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  180.1, 141.0, 136.5, 133.3, 131.7, 130.0, 128.1, 127.6, 126.6, 124.3, 107.6, 50.1, 44.7, 26.1, 23.0, 21.4.

#### 3-benzyl-5-methoxy-1,3-dimethylindolin-2-one (67)<sup>[9]</sup>



Purified by silica gel chromatography (PE: EA/15: 1), the desired product **67** was obtained as a colorless oil, 41.0 mg, 73 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.15 – 7.02 (m, 3H), 6.88 (dd, J = 6.5, 2.9 Hz, 2H), 6.74 – 6.67 (m, 2H), 6.55 – 6.48 (m, 1H), 3.77 (s, 3H), 3.09 (d, J = 13.0 Hz, 1H), 2.99 (d, J = 15.3 Hz, 1H), 2.96 (s, 3H), 1.45 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  179.81, 155.86, 136.93, 136.36, 134.59, 130.08, 127.70, 126.64, 112.14, 111.17, 108.16, 56.02, 50.45, 44.65, 26.15, 22.95.

#### 3-benzyl-5-fluoro-1,3-dimethylindolin-2-one (68)<sup>[9]</sup>



Purified by silica gel chromatography (PE: EA/20: 1), the desired product **68** was obtained as a colorless oil, 43.6 mg, 81 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.07 (qd, J = 4.1, 1.7 Hz, 3H), 6.87 (dddd, J = 9.1, 5.1, 3.4, 1.8 Hz, 4H), 6.55 – 6.47 (m, 1H), 3.13 (d, J = 13.1 Hz, 1H), 2.98 (d, J = 9.7 Hz, 4H), 1.46 (s, 3H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -121.08; <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  179.8, 159.2 (d, <sup>1</sup> $_{C-F} = 240.0$  Hz), 139.2 (d, <sup>4</sup> $_{C-F} = 1.9$  Hz), 136.0, 134.9 (d, <sup>3</sup> $_{C-F} = 7.9$  Hz), 129.9, 127.8, 126.8, 114.1 (d, <sup>2</sup> $_{C-F} = 23.5$  Hz), 111.6 (d, <sup>3</sup> $_{C-F} = 24.6$  Hz), 108.3 (d, <sup>2</sup> $_{C-F} = 8.1$  Hz), 50.6 (d, <sup>4</sup> $_{C-F} = 1.8$  Hz), 44.7, 26.2, 22.8.

#### 3-benzyl-5-chloro-1,3-dimethylindolin-2-one (69)<sup>[9]</sup>



Purified by silica gel chromatography (PE: EA/20: 1), the desired product **69** was obtained as a colorless oil, 45.6 mg, 80 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.21 – 7.01 (m, 5H), 6.88 – 6.81 (m, 2H), 6.51 (d, *J* = 8.2 Hz, 1H), 3.12 (d, *J* = 13.0 Hz, 1H), 2.98 (d, *J* = 13.1 Hz, 1H), 2.95 (s,

3H), 1.46 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*) δ 179.6, 141.9, 135.9, 135.0, 129.9, 127.9, 127.8, 127.6, 126.8, 124.0, 108.8, 50.4, 44.7, 26.2, 22.8.

#### 3-benzyl-5-bromo-1,3-dimethylindolin-2-one (70)<sup>[9]</sup>



Purified by silica gel chromatography (PE: EA/20: 1), the desired product **70** was obtained as a colorless oil, 52.8 mg, 80 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.29 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.24 (d, *J* = 2.0 Hz, 1H), 7.08 (dd, *J* = 4.9, 2.0 Hz, 3H), 6.91 – 6.79 (m, 2H), 6.47 (d, *J* = 8.2 Hz, 1H), 3.12 (d, *J* = 13.0 Hz, 1H), 2.97 (d, *J* = 13.1 Hz, 1H), 2.95 (s, 3H), 1.46 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  179.5, 142.4, 135.9, 135.4, 130.8, 129.9, 127.8, 126.8, 126.7, 114.9, 109.4, 50.4, 44.7, 26.1, 22.8.

#### 3-benzyl-1,3-dimethyl-2-oxoindoline-5-carbonitrile (71)<sup>[10]</sup>



Purified by silica gel chromatography (PE: EA/10: 1), the desired product **71** was obtained as a colorless oil, 35.9 mg, 65 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.50 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.37 (d, *J* = 1.6 Hz, 1H), 7.13 – 7.01 (m, 3H), 6.83 – 6.75 (m, 2H), 6.65 (d, *J* = 8.1 Hz, 1H), 3.15 (d, *J* = 13.1 Hz, 1H), 3.00 (s, 3H), 2.99 (d, *J* = 13.1 Hz, 1H), 1.49 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  179.8, 147.2, 135.4, 134.3, 133.4, 129.8, 128.0, 127.1, 126.8, 119.6, 108.4, 105.3, 50.1, 44.7, 26.3, 22.6.

#### methyl 3-benzyl-1,3-dimethyl-2-oxoindoline-5-carboxylate (72)



Purified by silica gel chromatography (PE: EA/10: 1), the desired product **72** was obtained as a colorless oil, 38.9 mg, 63 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.92 (dd, *J* = 8.2, 1.7 Hz, 1H),

7.87 (d, J = 1.6 Hz, 1H), 7.08 – 6.96 (m, 3H), 6.83 – 6.73 (m, 2H), 6.60 (d, J = 8.2 Hz, 1H), 3.92 (s, 3H), 3.17 (d, J = 13.0 Hz, 1H), 3.02 (d, J = 13.0 Hz, 1H), 2.97 (s, 3H), 1.50 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  180.3, 167.2, 147.5, 135.9, 133.2, 130.8, 129.8, 127.8, 126.8, 124.6, 124.2, 107.4, 52.2, 50.2, 44.8, 26.2, 22.9.

1-benzyl-1-methyl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinolin-2(1H)-one (73)<sup>[9]</sup>



Purified by silica gel chromatography (PE: EA/20: 1), the desired product **73** was obtained as a colorless oil, 33.2 mg, 60 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.14 – 6.97 (m, 3H), 6.98 – 6.90 (m, 3H), 6.87 (ddd, J = 7.7, 5.1, 2.5 Hz, 2H), 3.54 (ddd, J = 12.4, 8.0, 4.1 Hz, 1H), 3.41 (ddd, J = 12.9, 7.1, 4.2 Hz, 1H), 3.09 (d, J = 12.9 Hz, 1H), 2.99 (d, J = 12.9 Hz, 1H), 2.59 (qdd, J = 16.2, 7.4, 4.8 Hz, 2H), 1.84 (dtt, J = 13.9, 7.1, 4.5 Hz, 1H), 1.64 – 1.50 (m, 1H), 1.48 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  179.0, 139.1, 136.5, 131.8, 130.0, 127.6, 126.7, 126.5, 121.7, 121.3, 120.0, 51.4, 44.8, 38.7, 24.7, 22.4, 21.2.

#### 4-(1,1-difluoro-3-phenylprop-1-en-2-yl)phenyl adamantane-1-carboxylate (74)



Purified by silica gel chromatography (PE: EA/40: 1), the desired product **74** was obtained as a colorless oil, 68.5 mg, 84 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.23 (dd, J = 8.1, 6.4 Hz, 4H), 7.20 – 7.09 (m, 3H), 7.02 – 6.93 (m, 2H), 3.70 (t, J = 2.3 Hz, 2H), 2.06 (t, J = 3.5 Hz, 4H), 2.02 (d, J = 2.9 Hz, 5H), 1.75 (q, J = 3.3 Hz, 6H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -90.23 (d, J = 39.5 Hz), -90.62 (d, J = 40.0 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  176.2, 154.6 (dd, <sup>1</sup>*JC*-*F* = 292.0, 287.6 Hz), 150.3, 138.5 (t, <sup>4</sup>*JC*-*F* = 2.7 Hz), 131.0 (t, <sup>4</sup>*JC*-*F* = 3.8 Hz), 129.4 (t, <sup>3</sup>*JC*-*F* = 3.6 Hz), 128.7,

128.5, 126.7, 121.7, 91.3 (dd,  ${}^{2}J_{C-F} = 21.9$ , 13.7 Hz), 41.2, 38.9, 36.6, 34.1 (d,  ${}^{3}J_{C-F} = 1.8$  Hz), 28.1; HRMS (ESI) m/z calcd for C<sub>26</sub>H<sub>27</sub>F<sub>2</sub>O<sub>2</sub><sup>+</sup> (M+H)<sup>+</sup> 409.1974, found 409.1970.

4-(1,1-difluoro-3-phenylprop-1-en-2-yl)phenyl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate (75)



Purified by silica gel chromatography (PE: EA/40: 1), the desired product **75** was obtained as a colorless oil, 82.1 mg, 87 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.54 (dt, *J* = 8.1, 1.6 Hz, 2H), 7.47 – 7.39 (m, 3H), 7.38 – 7.32 (m, 1H), 7.28 – 7.07 (m, 9H), 6.99 – 6.92 (m, 2H), 3.95 (q, *J* = 7.1 Hz, 1H), 3.69 (t, *J* = 2.3 Hz, 2H), 1.62 (d, *J* = 7.1 Hz, 3H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -90.00 (d, *J* = 39.5 Hz), -90.42 (d, *J* = 39.6 Hz), -117.19; <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  172.5, 160.0 (d, <sup>1</sup>*J*<sub>C-F</sub>' = 248.7 Hz), 154.7 (dd, <sup>1</sup>*J*<sub>C-F</sub> = 292.2, 287.7 Hz), 149.9, 141.4 (d, <sup>3</sup>*J*<sub>C-F</sub>' = 7.7 Hz), 138.4 (t, <sup>4</sup>*J*<sub>C-F</sub> = 2.7 Hz), 135.6, 131.4 (t, <sup>4</sup>*J*<sub>C-F</sub> = 3.9 Hz), 131.2 (d, <sup>3</sup>*J*<sub>C-F</sub>' = 4.0 Hz), 129.5 (t, <sup>3</sup>*J*<sub>C-F</sub> = 3.5 Hz), 129.2 (d, <sup>2</sup>*J*<sub>C-F</sub>' = 3.0 Hz), 128.7, 128.7, 128.4, 127.9, 126.7, 123.8 (d, <sup>4</sup>*J*<sub>C-F</sub>' = 3.4 Hz), 121.5, 115.5 (d, <sup>2</sup>*J*<sub>C-F</sub>' = 23.8 Hz), 91.3 (dd, <sup>2</sup>*J*<sub>C-F</sub> = 21.9, 13.6 Hz), 45.3 (d, <sup>3</sup>*J*<sub>C-F</sub> = 1.5 Hz), 34.1, 18.5; HRMS (ESI) m/z calcd for C<sub>30</sub>H<sub>24</sub>F<sub>3</sub>O<sub>2</sub>+ (M+H)<sup>+</sup> 473.1723, found 473.1724.

#### 4-(1,1-difluoro-3-phenylprop-1-en-2-yl)phenyl 2-(6-methoxynaphthalen-2-yl)propanoate (76)



Purified by silica gel chromatography (PE: EA/30: 1), the desired product **76** was obtained as a colorless oil, 69.6 mg, 76 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.78 – 7.60 (m, 3H), 7.46 (dd, J = 8.5, 1.9 Hz, 1H), 7.27 – 7.04 (m, 9H), 6.95 – 6.84 (m, 2H), 4.06 (q, J = 7.1 Hz, 1H), 3.90 (s, 3H), 3.67 (t, J = 2.3 Hz, 2H), 1.66 (d, J = 7.2 Hz, 3H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -90.12 (d, J = 39.6 Hz), -90.53 (d, J = 39.6 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  173.2, 158.0, 154.6 (dd, <sup>1</sup> $J_{C-F} = 292.2, 287.6$  Hz), 150.1, 138.4 (t, <sup>4</sup> $J_{C-F} = 2.7$  Hz), 135.2, 134.1, 131.3 (t, <sup>4</sup> $J_{C-F} = 3.9$  Hz), 129.5,

129.4 (t,  ${}^{3}J_{C-F} = 3.5 \text{ Hz}$ ), 129.2, 128.7, 128.4, 127.6, 126.7, 126.3, 126.3, 121.5, 119.3, 105.8, 91.3 (dd,  ${}^{2}J_{C-F} = 21.8$ , 13.6 Hz), 55.5, 45.8, 34.1, 18.6; HRMS (ESI) m/z calcd for C<sub>29</sub>H<sub>25</sub>F<sub>2</sub>O<sub>3</sub><sup>+</sup> (M+H)<sup>+</sup> 459.1766, found 459.1767.

4-(1,1-difluoro-3-phenylprop-1-en-2-yl)phenyl 2-(4-isobutylphenyl)propanoate (77)



Purified by silica gel chromatography (PE: EA/40: 1), the desired product 77 was obtained as a colorless oil, 73.8 mg, 85 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.31 – 7.18 (m, 6H), 7.19 – 7.15 (m, 1H), 7.12 (d, *J* = 8.0 Hz, 4H), 6.95 – 6.88 (m, 2H), 3.90 (q, *J* = 7.2 Hz, 1H), 3.68 (d, *J* = 2.4 Hz, 2H), 2.45 (d, *J* = 7.2 Hz, 2H), 1.85 (dp, *J* = 13.5, 6.8 Hz, 1H), 1.57 (d, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 6H); <sup>19</sup>F NMR (376 MHz, Chloroform-*d*)  $\delta$  -90.13 (d, *J* = 39.5 Hz), -90.55 (d, *J* = 39.4 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  173.3, 154.6 (dd, <sup>1</sup>*J*<sub>C-F</sub> = 292.3, 287.5 Hz), 150.1, 141.0, 138.4 (t, <sup>4</sup>*J*<sub>C-F</sub> = 2.7 Hz), 137.3, 131.2 (t, <sup>3</sup>*J*<sub>C-F</sub> = 3.8 Hz), 129.7, 129.4 (t, <sup>4</sup>*J*<sub>C-F</sub> = 3.6 Hz), 128.7, 128.4, 127.4, 126.7, 121.5, 91.3 (dd, <sup>2</sup>*J*<sub>C-F</sub> = 21.9, 13.6 Hz), 45.5, 45.2, 34.1, 30.4, 22.6, 18.6; HRMS (ESI) m/z calcd for C<sub>28</sub>H<sub>29</sub>F<sub>2</sub>O<sub>2</sub><sup>+</sup> (M+H)<sup>+</sup> 435.2130, found 435.2129.

#### 1,2-diphenylethane (78)



Purified by silica gel chromatography (PE), the desired product **78** was obtained as a colorless oil, 14.6 mg, 40 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.39 – 7.03 (m, 10H), 2.94 – 2.88 (m, 4H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  142.0, 128.7, 128.5, 126.1, 38.2.

#### 1-methyl-4-phenethylbenzene (79)



Purified by silica gel chromatography (PE), the desired product **79** was obtained as a colorless oil, 22.3 mg, 57 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.45 – 7.32 (m, 2H), 7.35 – 7.21 (m, 3H), 7.19 (s, 4H), 3.00 (d, *J* = 1.9 Hz, 4H), 2.42 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  142.1, 138.9, 135.5, 129.2, 128.6, 128.5, 126.1, 38.3, 37.7, 21.2.

#### 1,3-diphenylpropane (80)



Purified by silica gel chromatography (PE), the desired product **80** was obtained as a colorless oil, 18.0 mg, 46 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.63 (td, *J* = 7.8, 3.7 Hz, 4H), 7.54 (q, *J* = 7.0, 5.7 Hz, 6H), 3.00 (td, *J* = 8.1, 3.6 Hz, 4H), 2.35 – 2.27 (m, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  142.4, 128.6, 128.4, 125.9, 35.6, 33.1.

#### 1-methoxy-4-(3-phenylpropyl)benzene (81)



Purified by silica gel chromatography (PE: EA/50: 1), the desired product **81** was obtained as a colorless oil, 24.0 mg, 53 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.43 – 7.35 (m, 2H), 7.29 (ddt, J = 7.0, 3.6, 1.6 Hz, 3H), 7.24 – 7.18 (m, 2H), 6.98 – 6.90 (m, 2H), 3.87 (s, 3H), 2.79 – 2.66 (m, 4H), 2.04 (dtdd, J = 9.5, 7.9, 6.0, 1.8 Hz, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  157.9, 142.5, 134.5, 129.5, 128.6, 128.5, 125.9, 113.9, 55.4, 35.5, 34.7, 33.4.

#### (*Z*)-1,2-diphenylethene (82)



Purified by silica gel chromatography (PE), the desired product **82** was obtained as a colorless oil, 15.1 mg, 42 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.32 – 7.13 (m, 10H), 6.59 (s, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  137.4, 130.4, 129.1, 128.4, 127.3.

### (Z)-1-chloro-3-styrylbenzene (83)



Purified by silica gel chromatography (PE), the desired product **83** was obtained as a colorless oil, 21.0 mg, 49 % yield; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.22 (s, 6H), 7.21 – 7.06 (m, 3H), 6.64 (d, *J* = 12.2 Hz, 1H), 6.51 (d, *J* = 12.2 Hz, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, Chloroform-*d*)  $\delta$  139.3, 136.8, 134.3, 131.8, 129.6, 129.0, 128.9, 128.5, 127.7, 127.3, 127.2.

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# 10. Copies of NMR spectra of all products

## <sup>1</sup>H NMR spectra of 4





# <sup>19</sup>F NMR spectra of

4



---90.31 ---90.42 ---90.87







<sup>1</sup>H NMR spectra of

6







~3.71













<sup>19</sup>F NMR spectra of







<sup>1</sup>H NMR spectra of















<sup>1</sup>H NMR spectra of

9

-3.72 -3.72 -2.92 -2.88 -2.28







<sup>1</sup>H NMR spectra of











---116.78













-3.69



12













<sup>1</sup>H NMR spectra of



















<sup>1</sup>H NMR spectra of

16

#### (1713) (1





# <sup>19</sup>F NMR spectra of








































-86 -87 -88 -89 -90 -91 -92 -93 -94 -95 -96 -97 -98 -99 -100 -101 -102 -103 -104 -105 -106 -107 -108 -109 -110 -111 -112 -113 -114 -115 -116 -11 fl (ppm)





## <sup>1</sup>H NMR spectra of

## 21







3.1 -88.3 -88.5 -88.7 -88.9 -89.1 -89.3 -89.5 -89.7 -89.9 -90.1 -90.3 -90.5 -90.7 -90.9 -91.1 -91.3 -91.5 -91.7 -91.9 -9. fl (ppm)

21

























24

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24









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25























**28** 





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---91.83





29



















<sup>19</sup>F NMR spectra of 31 ~-89.04 ~-89.15 ~-92.13 ~-92.24 79 -80 -81 -82 -83 -84 -85 -86 -87 -88 -89 -90 -91 -92 -93 -94 -95 -96 -97 -98 -99 -100 -101 -102 -103 -104 -10 fl (ppm) <sup>13</sup>C{<sup>1</sup>H} NMR spectra of 31 90.1 90.1 136.2 136.2 136.2 136.1 136.2 137.2 137. 100 90 80 fl (ppm) 70 90 60 50 40 20 -1( 180 170 160 150 140 130 120 110 30 10 0

## 32



---91.02

































































### <sup>1</sup>H NMR spectra of

#### 42











## <sup>1</sup>H NMR spectra of

#### 44


















**48** 





~3.69



**48** 











































<sup>1</sup>H NMR spectra of

### 53

77 200 77 200































56

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-3.70



















-87.0 -87.2 -87.4 -87.6 -87.8 -88.0 -88.2 -88.4 -88.6 -88.8 -89.0 -89.2 -89.4 -89.6 -89.8 -90.0 -90.2 -90.4 -90.6 -90.8 -91.0 -91.2 -91.4 -91.6 -91.8 -92.0 fl (ppm)





**58** 

77.7.25 77.





















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62

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# <sup>19</sup>F NMR spectra of

62



-91.12 -91.23 -91.26 --91.37









64

Partielle Partie





~87.14

-9142


























































<sup>13</sup>C{<sup>1</sup>H} NMR spectra of

74



<sup>1</sup>H NMR spectra of

















## <sup>19</sup>F NMR spectra of







<sup>13</sup>C{<sup>1</sup>H} NMR spectra of









**78** 





## <sup>13</sup>C{<sup>1</sup>H} NMR spectra of



























## 











