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## Graphical Abstract

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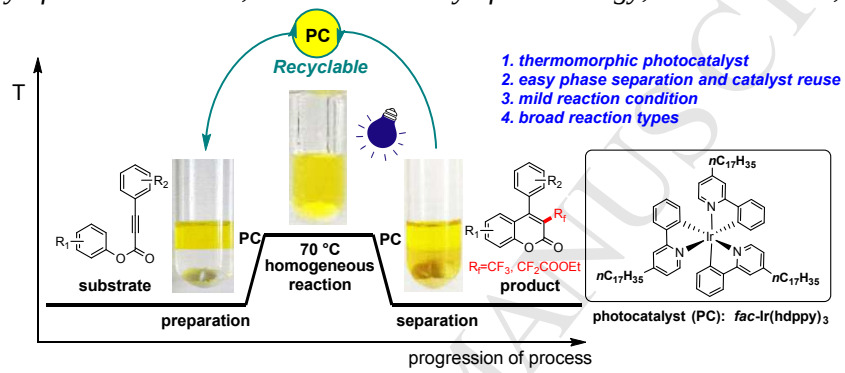
*State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116024, China*



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# Recyclable alkylated *fac*-Ir(ppy)$_3$ complex as a visible-light photoredox catalyst for the synthesis of 3-trifluoromethylated and 3-difluoroacetylated coumarins

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*State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116024, China*

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ABSTRACT

A recyclable *fac-tris*(heptadecanyl-2-phenylpyridine) iridium [*fac*-Ir(hdppy)$_3$] photocatalyst was synthesized. The hexane-phase-selective solubility of *fac*-Ir(hdppy)$_3$ in a thermomorphic multicomponent solvent (TMS) allowed its easy recycling by automatic liquid/liquid separation at room temperature. The excellent catalytic and recoverable activities of *fac*-Ir(hdppy)$_3$ were demonstrated via trifuoromethylation and difluoroacetylation reactions of phenyl 3-phenylpropiolate under visible-light irradiation in a TMS system.



## 1. Introduction

Photocatalysts (PCs) based on Ru and Ir complexes have been commonly used as efficient catalysts for organic transformations driven by visible light[1]. However, despite their emergence as efficient catalysts for a wide application, the relative high cost still limits their practical uses in large scale[2]. In addition, organometallic PCs have a notable impact on the environment because of slow degradation and tendency to act as fluorescent pollutants.

Recycling and reuse of PCs are receiving new attention as critical components of emerging chemical technologies due to both environmental concerns and economic benefits[3]. The present academic and industrial chemical processes are favoring heterogeneous catalysts, which leads to efficient recycling and reuse[4]. However, most heterogeneous catalysts not only require multiple synthetic steps in catalyst preparation, but also need an additional filtration or a workup of the final reaction mixture to recovery the catalyst[2,5]. In most instances, homogeneous catalysts have more advantages in terms of reaction activity, selectivity, and ease of handing for recycling over heterogeneous catalysts[6].

One way of realizing the desired homogenous catalysis involves use of a thermomorphic multicomponent solvent (TMS)[7]. In this TMS system, the catalyst is soluble in one solvent, while the reactants/products are soluble in the other solvent that is immiscible with the catalyst solvent[8]. The solvents comprising these thermomorphic systems form a homogeneous one-phasic mixture in a heating reactor, and the mixture can be separated into two liquid phases at lower temperatures after the reaction. Specifically, in 2016, Reiser[9] developed a hexa (PIB-polymer-tagged) *fac*-Ir(ppy)$_3$ complex PC, which catalyzed deiodation, deiodation/cyclization, and *E/Z* isomerization; the catalyst showed high activity due to its homogeneous nature in solution, while the installed tether allowed for its convenient separation from the reaction products through a TMS system. However, since the molecular weight distribution of (PIB-polymer-tagged) *fac*-Ir(ppy)$_3$, there are still solubility limitations and catalyst leaching problems. We aimed to develop a recyclable and homogeneous Ir complex PC with an accurate structure. Our initial strategy was to design a long alkyl-chain-bound 2-phenylpyridine Ir complex as a phase-selectively soluble homogeneous PC that could be applied in a TMS system.

With particular interest in photochemistry and fluorine chemistry, we describe herein an alkyl-bound 2-phenylprydine Ir complex PC, which serves as a homogeneous, recoverable PC, and is compatible with TMS such that the alkyl support is soluble in a nonpolar solvent while the products remain in a polar solvent. This PC shows good catalytic activity and can be easily recovered and reused for the trifluoromethylation and difluoroacetylation of phenyl 3-phenylpropiolates.

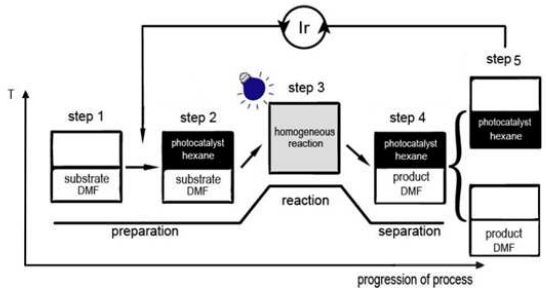
## 2. Results and discussion

As shown in Scheme 1, the substrates for the photochemical reaction were first dissolved in DMF (Scheme 1, step 1). Hexane containing the *fac*-Ir(hdppy)$_3$ PC and DMF containing the substrates were immiscible at room temperature (step 2). When heated to 70 °C in hot water bath, the two immiscible solvents

* Corresponding author. Tel./fax: +86 411 84986295;

E-mail address: ymli@dlut.edu.cn (Y. Li); cyduan@dlut.edu.cn (C. Duan).

hexane and DMF formed homogeneous phase (step 3). After completion of the reaction, the reaction tube was inserted in an ice bath. After sufficient cooling, the mixed solvent automatically separated into hexane and DMF phases again (step 4). Hexane which contained *fac*-Ir(hdppy)$_3$ was conveniently recovered and used for the next reaction, while purification of the DMF layer gave the desired product by silica gel column chromatography.



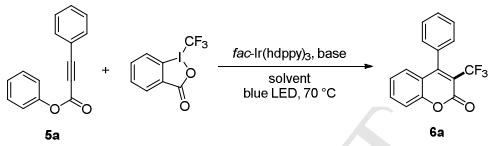

**Scheme 1.** Recoverable alkyl-bound Ir complexes PC and recovery progress.

Based on this strategy, we synthesized *fac*-Ir(hdppy)$_3$ for application to the TMS system as a homogeneous PC (Scheme 2). Initially, we synthesized *fac*-Ir(mppy)$_3$ using 2-phenyl-4-methyl pyridine instead of 2-phenyl pyridine, based on the reported synthetic method for *fac*-Ir(ppy)$_3$[10]. Then, *fac*-Ir(mppy)$_3$ reacted with 1-bromohexadecane and was converted into hexadecane-bound *fac*-Ir(heptadecanyl-ppy)$_3$ [abbreviated to *fac*-Ir(hdppy)$_3$]. Finally, purified *fac*-Ir(hdppy)$_3$ was obtained by silica gel column chromatography (for detailed synthetic procedures, see the Experimental Section and Supporting Information).

**Scheme 2.** Synthesis of the *fac*-Ir(hdppy)$_3$

Our group have long focused on the development in the new synthetic method for the trifluoromethylation of aromatic and heterocyclic compounds[11]. To test the catalytic activity and recyclability of *fac*-Ir(hdppy)$_3$, it was used to catalyze the trifluoromethylation of phenyl 3-phenylpropiolate under visible light as a model reaction, based on a similar reaction that a copper catalyzed cyclization and direct trifluoromethylation of internal phenyl 3-phenylpropiolate with Togni's reagent reported by Ding[12]. The reaction conditions were optimized for trifluoromethylation with Togni's reagent, $K_2HPO_4$, and 1 mol% of *fac*-Ir(hdppy)$_3$ under irradiation by a blue LED for 12h. First, $CH_3CN$ and DMF which are commonly used in reaction catalyzed by visible light were mixed with hexane; the DMF/hexane mixed solvents was found to be suitable for this reaction (Table 1, entries 1 and 2). The DMF and hexane layers could not merge into a homogeneous phase at 25°C, leading to a poor yield of 15% (entry 3). The reaction proceeded in the dark, confirming that blue light was necessary in this case (entry 4). Screening of organic and inorganic bases revealed that $K_2HPO_4$ was the most efficient base for this reaction (entries 5−8). Finally, even after increasing the reaction time to 24 h, the product yield remained at approximately 54% (entry 9).

**Table 1.** Optimization for the trifluoromethylation condition of phenyl 3-phenylpropiolate[a]

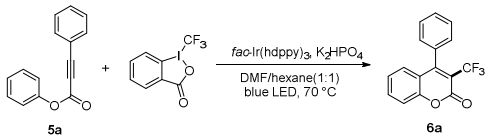



| Entry | Base | Solvent | Temp. | Time | Yield |
|---|---|---|---|---|---|
| 1 | $K_2HPO_4$ | $CH_3CN$/hexane | 70°C | 12h | 11% |
| 2 | $K_2HPO_4$ | DMF/hexane | 70°C | 12h | 53% |
| 3 | $K_2HPO_4$ | DMF/hexane | 25°C | 12h | 15% |
| 4[b] | $K_2HPO_4$ | DMF/hexane | 70°C | 12h | 9% |
| 5 | $K_3PO_4$ | DMF/hexane | 70°C | 12h | 35% |
| 6 | $K_2CO_3$ | DMF/hexane | 70°C | 12h | 29% |
| 7 | $Cs_2CO_3$ | DMF/hexane | 70°C | 12h | 37% |
| 8 | *i*Pr$_2$NEt | DMF/hexane | 70°C | 12h | 15% |
| 9 | $K_2HPO_4$ | DMF/hexane | 70°C | 24h | 54% |

[a]Reaction conditions: phenyl 3-phenylpropiolate (0.2 mmol), *fac*-Ir(hdppy)$_3$ (1 mol%), Togni's reagent (0.4 mmol), base (0.4 mmol), DMF (1 mL), $CH_3CN$ (1 mL) or hexane (1 mL), irradiation with 15 W blue LED at 70°C in hot water bath; isolated yields. [b]dark.

With the optimized conditions catalyzed by the recyclable *fac*-Ir(hdppy)$_3$ in hand, the recyclability and catalytic activity were then evaluated. The PC *fac*-Ir(hdppy)$_3$ recovered from the 1st run was reused without any treatment in the subsequent recycling run, and a new trifluoromethylation reaction (2nd run) was then performed with fresh reactants under the same conditions. As shown in Table 2, the recycled *fac*-Ir(hdppy)$_3$ was collected and reused without significant loss of catalytic activity (product yield 53%). Even after the 5th run, no significant decrease in the yield (51%) of **6a** was observed. In addition, the recovered upper layer of the Ir species from the initial catalyst into the reaction medium was investigated. After the 1st run and 5th run, the yields of the recovered *fac*-Ir(hdppy)$_3$ PC were 95% and 76%, respectively (measured by UV-vis spectroscopy). Inductively coupled plasma mass spectrometry (ICP-MS) analysis showed that the recovered yield of the Ir species was 79% after the 5th run.

**Table 2.** Recyclability studies of the [*fac*-Ir(hdppy)$_3$] catalyzed cyclization to 3-trifluoromethyl-4-phenyl-coumarin[a]

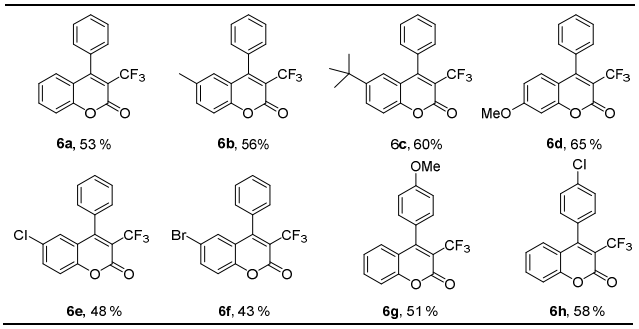



| Run | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Yield (%) | 53 | 53 | 54 | 51 | 51 |

[a]Reaction conditions: phenyl 3-phenylpropiolate (0.2 mmol), *fac*-Ir(hdppy)$_3$ (1 mol%), Togni's reagent (0.4 mmol), $K_2HPO_4$ (0.4 mmol), DMF (1 mL) and hexane (1 mL), irradiation with 15 W blue LED at 70°C in hot water bath; isolated yields.

Encouraged by the good recyclability and catalytic activity of *fac*-Ir(hdppy)$_3$ in the photoredox trifluoromethylation of phenyl 3-phenylpropiolate, we further investigated the substrates scope of this reaction. The electron-donating group substituted substrates afforded the corresponding products in moderate to good yields (Table 3, **6b**-**6d**). However, substrates bearing chlorine or bromine atom on the aromatic ring resulted in slightly lower yields (**6e** and **6f**). Additionally, a *para*-methyl and a *para*-chlorine substituted phenyl linked to the alkynyl moiety could also be used to construct 3-trifluoromethyl-4-phenyl-coumarin derivatives in moderate yields (**6g** and **6h**).

**Table 3.** Substrate scope of 3-trifluoromethyl-4-phenyl coumarin[a]




[a]Reaction conditions: phenyl 3-phenylpropiolate (0.2 mmol), *fac*-Ir(hdppy)$_3$ (1 mol%), Togni's reagent (0.4 mmol), $K_2HPO_4$ (0.4 mmol), DMF (1 mL) and hexane (1 mL), irradiation with 15 W blue LED at 70°C in hot water bath; isolated yields.

The difluoromethylene group ($CF_2$) is also an intriguing structural motif, similar to the trifluoromethyl group ($CF_3$) that has drawn the attention of many chemists. Fu[13] reported a mild and efficient method for the synthesis of 3-difluoroacetylated coumarins through visible-light promoted difluoroacetylation of phenyl 3-phenylpropiolate with $BrCF_2COOEt$, which also followed a radical procedure, similar to the trifluoromethylation reaction reported by Ding[12]. Therefore, we further investigated the recyclability and catalytic feasibility of *fac*-Ir(hdppy)$_3$ by using it to catalyze this difluoroacetylation at 70 °C, without changing the other condition reported by Fu[13]. This reaction gave the difluoroacetylated product in similar yield as the observed with *fac*-Ir(ppy)$_3$ at room temperature. In addtion, *fac*-Ir(hdppy)$_3$ could be still recovered in high yield of 97% from the upper layer. Until the 5$^{th}$ run, the recovered yield of *fac*-Ir(hdppy)$_3$ was 83%, and the products remained at 68% yield (Table 4).

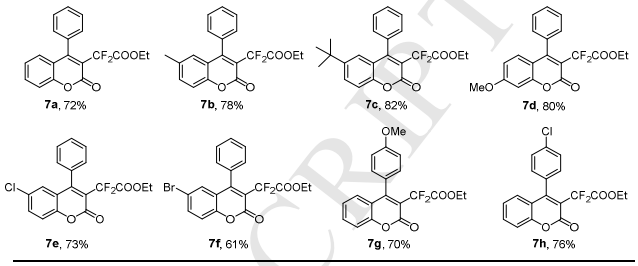
**Table 4.** Recyclability studies of the [*fac*-Ir(hdppy)$_3$] catalyzed cyclization to 3-difluoroacetyl-4-phenyl coumarin[a]


| Run | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Yield(%) | 72 | 70 | 70 | 71 | 68 |

[a]Reaction conditions: phenyl 3-phenylpropiolate (0.2 mmol), *fac*-Ir(hdppy)$_3$ (1 mol%), $BrCF_2COOEt$ (0.4 mmol), $K_2CO_3$ (0.4 mmol), DMF (1 mL) and hexane (1 mL), irradiation with 15 W blue LED at 70°C in hot water bath; isolated yields.

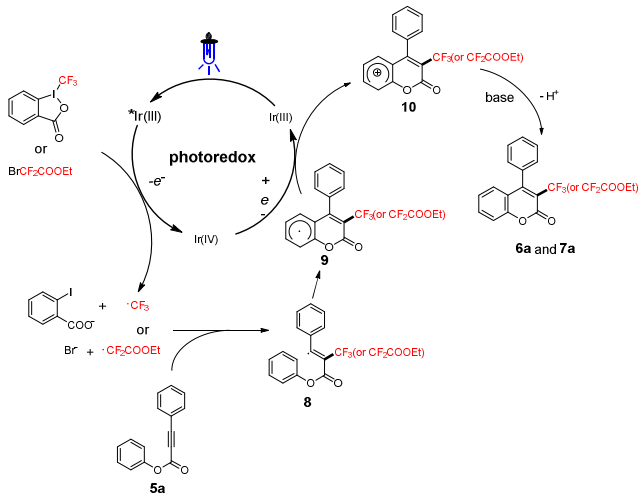
With the test results for the recyclability and catalytic activities in hand, we proceeded to explore the substrate scope of the *fac*-Ir(hdppy)$_3$-catalyzed difluoroacetylation. As shown in Table 5, both moderately electron-withdrawing groups and electron-donating groups located on the phenyl ring linked to the propiolate or alkynyl proceeded well to afford the desired coumarins (**7a-7e**) in good yields. The exception was the substrate bearing bromine at the *para* position of phenyl propiolate, which gave the product in a moderate yield of 61% (**7f**).

**Table 5.** Substrate scope of 3-difluoroacetyl-4-phenyl coumarin[a]




[a]Reaction conditions: phenyl 3-phenylpropiolate (0.2 mmol), *fac*-Ir(hdppy)$_3$ (1 mol%), $BrCF_2COOEt$ (0.4 mmol), $K_2CO_3$ (0.4 mmol), DMF (1 mL) and hexane (1 mL), irradiation with 15 W blue LED at 70°C in hot water bath; isolated yields.

On the basis of the experimental results and reported literatures[12-14], a plausible mechanism is proposed in Scheme 3. Initially, Ir(III) is excited to *Ir(III) under irradiation by a blue LED. Then, *Ir(III) is oxidatively quenched by Togni's reagent or $BrCF_2COOEt$ to generate a $CF_3$ or $CF_2COOEt$ radical, along with the generation of Ir(IV). Subsequently, the $CF_3$ or $CF_2COOEt$ radical attacks phenyl 3-phenylpropiolate (**5a**) and undergoes selective radical addition of the triple bond, leading to radical intermediate **8**. Compound **8** further undergoes intramolecular homolytic aromatic substitution to give the radical intermediate **9**. Intermediate **9** is then oxidized by Ir(IV) to form phenyl cation **10** via a single electron transfer, and Ir(III) is regenerated. Ultimately, 3-trifluoromethylated or 3-difluoroacetylated product **6a** or **7a** is produced in a progress of deprotonation of **10** assisted by base, respectively.




**Scheme 3.** Proposed reaction mechanism

## 3. Conclusion

In summary, *fac*-Ir(hdppy)$_3$, a recoverable *n*-heptadecanyl-bound *fac*-Ir(ppy)$_3$ PC is successfully synthesized. This catalyst shows excellent catalytic performance as well as recyclability for trifluoromethylation or difluoroacetylation of phenyl 3-phenylpropiolate to generate 3-trifluoromethylated and 3-difluoroacetylated coumarins under visible light, and could be easily separated from reaction products through a thermomorphic solvent (TMS) system based on the high phase-selective solubility of the long alkyl chain bound species. The PC could be reused up to five times without significant loss of activity. These features suggest this recyclable *fac*-Ir(hdppy)$_3$ would be generally useful for other photoredox reaction.

## 4. Experiment

### 4.1. General information

All reagents unless otherwise noted were obtained from commercial sources and used without further purification. $BrCF_2COOEt$ (>99.0%) were used without any purification. All these reactions were monitored by TLC with silica gel $GF_{254}$ precoated plates. The products were isolated by column chromatography on silica gel (200–300 mesh size). $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra were recorded on INOVA 500 instruments with operating frequencies of 500, 126 and 377 MHz, respectively. Chemical shifts for $^1$H NMR were reported in ppm relative to TMS. All $^{13}$C NMR spectra were reported in ppm relative to deuterated chloroform (77.00 ppm). The following abbreviations are used to set multiplicities: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, q = quartet, tq = triplet of quartets, qt = quartet of triplets, and m = multiplet. Coupling constants (J) were reported in Hertz (Hz). GC-MS data were also recorded. High-resolution mass spectrometry data were recorded on a high-resolution mass spectrometer in the ESI mode.

### 4.2. Synthesis of *fac*-Ir(hdppy)$_3$ complex

The synthetic method of *fac*-Ir(mppy)$_3$ was based on the report by K.R. Mann[10] in 2007. The detailed method could be found in SI.

A round-bottomed flask was charged with *fac*-Ir(mppy)$_3$ (348 mg, 0.5 mmol) and 40 mL of anhydrous tetrahydrofuran (THF) and cooled to -78 °C in a liquid nitrogen/ethyl acetate bath for 10 min. A solution of LDA, prepared *in situ* by treating a solution of 182 mg of *i*Pr$_2$NH (1.8 mmol, 1.2 equiv.) in 10 mL of THF with *n*BuLi 660 μL (1.65 mmol, 1.1 equiv.), was added dropwise to the flask by means of a syringe. The solution was stirred for 30 min at -78 °C during which time it turned brown in colour. A solution of 1-bromoheptadacane (460 μL, 1.5 mmol) in 5 mL of THF was added dropwise using a syringe, and the solution was allowed to warm to room temperature, followed by stirring for 2 h. After the completion of the reaction, THF was removed under reduced pressure. The obtained yellow residue was dissolved in ethyl acetate and concentrated under vacuum. Then, the residue was purified by column chromatography on silica with EtOAc/petroleum ether (1/100) as the eluent to give the desired product *fac*-Ir(hdppy)$_3$ (362 mg, 0.265 mmol, 53%). $^1$H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 5.1 Hz, 1H), 7.66 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.53 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.41 (s, 1H), 7.38 (td, *J* = 7.5, 1.0 Hz, 1H), 7.23 (td, *J* = 7.8, 1.7 Hz, 1H), 7.10 (dd, *J* = 5.1, 1.3 Hz, 1H), 2.64 (t, *J* = 7.7 Hz, 2H), 1.71 – 1.60 (m, 2H), 1.26 (s, 28H), 0.88 (t, *J* = 6.9 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 158.15 (s), 151.56 (s), 149.20 (s), 141.50 (s), 133.23 (s), 131.45 (s), 129.51 (s), 127.43 (s), 124.90 (s), 122.68 (s), 121.85 (s), 35.33 (s), 31.95 (s), 30.28 (s), 29.18-29.73 (m), 22.71 (s), 14.14 (s). HRMS (ESI) m/z: $[M]^+$ Calcd. For $C_{84}H_{126}IrN_3$ 1369.9591; found 1369.9601.

### 4.3. Procedure for trifluoromethylation and difluoroacetylation catalyzed by *fac*-Ir(hdppy)$_3$

A flame-dried reaction vessel with a magnetic stirring bar was sequentially charged with phenyl 3-phenylpropiolate (0.2 mmol), PC (0.002 mmol), Togni's reagent (0.4 mmol, 124 mg), $K_2HPO_4$ (0.4 mmol, 89 mg), DMF (1 mL) and hexane (1 mL). The mixture was stirred and heated in the 70°C hot water bath with irradiation by a blue LED, whereupon the two solvent phases merged into a homogeneous solvent. After the reaction was completed, the reaction vessel was placed in an ice-water bath for 30 min, and hexane and DMF separated into two phases again. Hexane, which contained *fac*-Ir(hdppy)$_3$ was suctioned gently for use in the next reaction. The DMF layer containing the product was charged with 10 mL of water and extracted with ethyl acetate (5×3 mL). The combined ethyl acetate layer was dried over $Na_2SO_4$ and concentrated under vacuum. After evaporation, the obtained residue was purified by column chromatography on silica gel with EtOAc/petroleum ether as the eluent to give the desired product.

**4-Phenyl-3-(trifluoromethyl)-2*H*-chromen-2-one (6a, CAS: 1562426-68-9)**[12,15]**.** White solid (31.3 mg, 53%). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.63 (t, *J* = 7.7 Hz, 1H), 7.53 (s, 3H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.26 (s, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 156.86 (q, *J* = 2.0 Hz), 156.32 (s), 153.46 (s), 134.09 (s), 132.86 (s), 129.31 (s), 129.26 (s), 128.49 (s), 127.30 (d, *J* = 1.5 Hz), 124.77 (s), 121.87 (q, *J* = 275.4 Hz), 119.49 (s), 116.84 (s), 114.98 (q, *J* = 30.3 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) δ -57.90 (s). GC–MS (EI, m/z): 290.23.

**6-Methyl-4-phenyl-3-(trifluoromethyl)-2*H*-chromen-2-one (6b, CAS: 1621190-85-9)**[12]**.** White solid (34.8 mg, 56%). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.49 (m, 3H), 7.43 (q, *J* =1.7 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.25 (dd, *J* = 6.5, 2.9 Hz, 2H), 6.75 (s, 1H), 2.27 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 156.84 (d, *J* = 2.0 Hz), 156.55 (s), 151.64 (s), 135.19 (s), 134.63 (s), 132.98 (s), 129.24 (s), 128.78 (s), 128.46 (s), 127.29 (d, *J* = 1.6 Hz), 121.95 (q, *J* = 275.1 Hz), 119.15 (s), 116.61 (s), 114.92 (q, *J* = 29.9 Hz), 20.91 (s). $^{19}$F NMR (377 MHz, $CDCl_3$) δ -57.82 (s). GC–MS (EI, m/z): 304.07.

**6-(tert-Butyl)-4-phenyl-3-(trifluoromethyl)-2*H*-chromen-2-one (6c, CAS: 2242965-74-6)** [11(e)]**.** White solid (42.6 mg, 60%). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 3H), 7.40 (d, *J* = 1.3 Hz, 1H), 7.26 – 7.21 (m, 3H), 6.93 (d, *J* = 8.5 Hz, 1H), 1.34 (s, 9H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 159.11 (s), 156.74 (s), 153.53 (s), 133.12 (s), 129.17 (s), 128.79 (s), 128.40 (s), 127.27 (d, *J* = 1.6 Hz), 122.40 (s), 122.04 (q, *J* = 274.9 Hz), 118.65 (s), 116.99 (s), 114.02 (q, *J* = 29.9 Hz), 113.59 (s), 35.43 (s), 30.87 (s).$^{19}$F NMR (377 MHz, $CDCl_3$) δ -57.77 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd. For $C_{20}H_{17}F_3O_2Na$ 369.1078; found 369.1086.

**7-Methoxy-4-(4-methoxyphenyl)-3-(trifluoromethyl)-2*H*-chromen-2-one (6d).** White solid (44.4 mg, 65%). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.49 (m, 3H), 7.33 (d, *J* = 9.1 Hz, 1H), 7.26 (dd, *J* = 6.7, 2.8 Hz, 2H), 7.20 (dd, *J* = 9.1, 3.0 Hz, 1H), 6.41 (d, *J* = 2.9 Hz, 1H), 3.64 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 156.58 (s), 156.50 (s), 156.16 (s), 147.87 (s), 132.91 (s), 129.36 (s), 128.52 (s), 127.21 (d, *J* = 1.6 Hz), 121.93 (q, *J* = 275.2 Hz), 121.40 (s), 119.93 (s), 117.81 (s), 115.25 (q, *J* = 30.1 Hz), 111.77 (s), 55.67 (s). $^{19}$F NMR (377 MHz, $CDCl_3$) δ -57.90 (s). IR ($cm^{-1}$): ν 2929, 1723, 1618, 1397, 1090. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. For $C_{17}H_{11}F_3O_3Na$ 343.0558; found 343.0547.

**6-Chloro-4-phenyl-3-(trifluoromethyl)-2*H*-chromen-2-one (6e, CAS: 2242965-75-7)**[11(e)]**.** White solid (33.0 mg, 48%). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.51 (m, 1H), 7.41 (d, *J* = 1.9 Hz, 1H), 7.24 (dd, *J* = 6.5, 2.9 Hz, 1H), 7.17 (dd, *J* = 8.7, 1.9 Hz, 1H), 6.95 (d, *J* = 8.7 Hz, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 156.27 (d, *J* = 2.0 Hz), 155.71 (s), 153.61 (s), 140.38 (s), 132.44 (s), 130.22 (s), 129.56 (s), 128.66 (s), 127.21 (d, *J* = 1.5 Hz), 125.47 (s), 121.71 (q, *J* = 275.3 Hz), 118.14 (s), 117.06 (s), 114.93 (q, *J* = 30.4 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) δ -57.95 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd. For $C_{16}H_8ClF_3O_2Na$ 347.0063; found 347.0056.

**6-Bromo-4-phenyl-3-(trifluoromethyl)-2*H*-chromen-2-one (6f, CAS: 2242965-76-8)**[11(e)]**.** White solid (33.8 mg, 43%). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.56 (dd, *J* = 4.9, 1.8 Hz, 3H), 7.30 (d, *J* = 8.8 Hz, 1H), 7.25 (dd, *J* = 6.4, 3.1 Hz, 2H), 7.10 (d, *J* = 2.2 Hz, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 155.75 (d, *J* = 2.2 Hz), 155.61 (s), 152.30 (s), 136.91 (s), 132.04 (s), 131.40 (s), 129.72 (s), 128.76 (s), 127.22 (s), 121.57 (q, *J* = 276.1 Hz), 121.08 (s), 118.63 (s), 117.65 (s), 116.04 (q, *J* = 30.8 Hz). $^{19}$F NMR (377 MHz, $CDCl_3$) δ -58.08 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd. For $C_{16}H_8BrF_3O_2Na$ 390.9557; found 390.9563.

**4-(4-Methoxyphenyl)-3-(trifluoromethyl)-2*H*-chromen-2-one (6g, CAS: 1621190-90-6)**[12,15]**.** White solid (34.4 mg, 51%). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.65 – 7.55 (m, 1H), 7.39 (dd, *J* = 8.3, 0.6 Hz, 1H), 7.23 – 7.16 (m, 3H), 7.11 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.05 (d, *J* = 8.7 Hz, 2H), 3.90 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 160.38 (s), 157.04 (d, *J* = 2.1 Hz), 156.47 (s), 153.43 (s), 133.98 (s), 129.29 (s), 128.89 (s), 124.79 (s), 124.70 (s), 121.97 (q, *J* = 275.2 Hz), 119.79 (s), 116.83 (s), 115.14 (q, *J* = 30.7 Hz), 113.98 (s), 55.38 (s).$^{19}$F NMR (377 MHz, $CDCl_3$) δ -57.79 (s). GC–MS (EI, m/z): 320.07.

**4-(4-Chlorophenyl)-3-(trifluoromethyl)-2*H*-chromen-2-one (6h, CAS: 1621190-89-3)**[12,15]**.** White solid (39.0 mg, 58%). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.68 – 7.61 (m, 1H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.42 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.25 – 7.19 (m, 3H), 7.00 (dd, *J* = 8.1, 1.4 Hz, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 156.02 (s), 155.62 (d, *J* = 2.0 Hz), 153.47 (s), 135.67 (s), 134.34 (s), 131.20 (s), 128.95 (s), 128.77 (s), 128.76 (s), 124.91 (s), 121.75 (q, *J* = 275.3 Hz), 119.13 (s), 117.00 (s), 115.38 (q, *J* = 30.1 Hz).$^{19}$F NMR (377 MHz, $CDCl_3$) δ -57.82 (s). GC–MS (EI, m/z): 324.02.

**Ethyl 2,2-difluoro-2-(2-oxo-4-phenyl-2*H*-chromen-3-yl)acetate (7a, CAS: 1699735-60-8)**[13]**.** White solid (51.0 mg, 72%). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.61 (t, *J* = 7.8 Hz, 1H), 7.54 – 7.48 (m, 3H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.32 (dd, *J* = 6.4, 2.7 Hz, 2H), 7.21 (t, *J* = 7.7 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 162.73 (t, *J* = 32.2 Hz), 158.98 (t, *J* = 4.4 Hz), 156.09 (s), 153.15 (s), 133.46 (s), 132.88 (s), 129.05 (s), 128.79 (s), 128.27 (s), 127.62 (t, *J* = 2.3 Hz), 124.81 (s), 120.20 (s), 118.05 (t, *J* = 22.9 Hz), 116.90 (s), 111.81 (t, *J* = 253.2 Hz), 63.24 (s), 13.82 (s). $^{19}$F NMR (377 MHz, $CDCl_3$) δ -98.34 (s). GC–MS (EI, m/z): 344.09.

**Ethyl 2,2-difluoro-2-(6-methyl-2-oxo-4-phenyl-2*H*-chromen-3-yl)acetate (7b, CAS:1699735-61-9)**[13]**.** White solid (58.1 mg, 78%). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.48 (m, 3H), 7.31 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.21 (s, 1H), 7.02 (dd, *J* = 8.2, 0.7 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 2.46 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 162.85 (t, *J* = 32.3 Hz), 159.26 (t, *J* = 4.5 Hz), 156.19 (s), 153.24 (s), 145.23 (s), 133.09 (s), 128.96 (s), 128.48 (s), 128.20 (s), 127.61 (t, *J* = 2.2 Hz), 126.06 (s), 117.80 (s), 116.98 (s), 116.83 (t, *J* = 22.9 Hz), 111.93 (t, *J* = 252.8 Hz), 63.17 (s), 21.72 (s), 13.81 (s). $^{19}$F NMR (377 MHz, $CDCl_3$) δ -98.04 (s). GC–MS (EI, m/z): 358.10.

**Ethyl 2-(6-tert-butyl-2-oxo-4-phenyl-2*H*-chromen-3-yl)-2,2-difluoroacetate (7c, CAS: 1699735-62-0)**[13]**.** White solid (68.1 mg, 82%). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 3H), 7.41 (d, *J* = 1.8 Hz, 1H), 7.31 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.25 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.34 (s, 9H), 1.33 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 162.81 (t, *J* = 32.3 Hz), 159.36 (t, *J* = 4.5 Hz), 158.38 (s), 156.01 (s), 153.22 (s), 133.12 (s), 128.95 (s), 128.41 (s), 128.19 (s), 127.59 (t, *J* = 2.2 Hz), 122.43 (s), 117.71 (s), 117.04 (t, *J* = 23.0 Hz), 113.65 (s), 111.93 (t, *J* = 252.7 Hz), 63.15 (s), 35.37 (s), 30.91 (s), 13.82 (s). $^{19}$F NMR (377 MHz, $CDCl_3$) δ -98.12 (s). GC–MS (EI, m/z): 400.15.

**Ethyl 2,2-difluoro-2-(7-methoxy-2-oxo-4-phenyl-2*H*-chromen-3-yl)acetate (7d).** White solid (60.8 mg, 80%).$^1$H NMR (500 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 5.0, 1.7 Hz, 3H), 7.35 (d, *J* = 9.0 Hz, 1H), 7.32 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.18 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.47 (d, *J* = 2.9 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.65 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 162.77 (t, *J* = 32.2 Hz), 159.15 (t, *J* = 4.5 Hz), 156.21 (s), 155.79 (s), 147.58 (s), 132.90 (s), 129.10 (s), 128.30 (s), 127.53 (t, *J* = 2.3 Hz), 120.70 (s), 120.65 (s), 118.30 (t, *J* = 22.9 Hz), 117.87 (s), 111.83 (t, *J* = 253.1 Hz), 111.42 (s), 63.23 (s), 55.69 (s), 13.82 (s). IR ($cm^{-1}$): ν 2937, 1793, 1741, 1627, 1371, 1160, 1090. $^{19}$F NMR (377 MHz, $CDCl_3$) δ -98.36 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd. For $C_{20}H_{19}F_2O_5Na$ 397.0863; found 397.0876.

**Ethyl 2-(6-chloro-2-oxo-4-phenyl-2*H*-chromen-3-yl)-2,2-difluoro-acetate (7e, CAS: 1699735-64-2)**[13]**.** White solid (57.1 mg, 73%).$^1$H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 1.9 Hz, 1H), 7.30 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.18 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.00 (d, *J* = 8.7 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 162.58 (t, *J* = 31.1 Hz), 158.40 (t, *J* = 4.5 Hz), 155.48 (s), 153.32 (s), 139.65 (s), 132.48 (s), 129.73 (s), 129.28 (s), 128.41 (s), 127.53 (s), 125.44 (s), 118.87 (s), 117.99 (t, *J* = 23.1 Hz), 117.14 (s), 111.68 (t, *J* = 253.8 Hz), 63.33 (s), 13.80 (s).$^{19}$F NMR (377 MHz, $CDCl_3$) δ -98.38 (s). GC–MS (EI, m/z): 378.05.

**Ethyl 2-(6-bromo-2-oxo-4-phenyl-2H-chromen-3-yl)-2,2-difluoroacetate (7f, CAS: 1699735-65-3)**[13]**.** (54.5 mg, 61%). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 1.7 Hz, 1H), 7.54 – 7.48 (m, 3H), 7.33 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.30 (dd, *J* = 6.5, 2.8 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 162.55 (t, *J* = 32.1 Hz), 158.30 (t, *J* = 4.4 Hz), 155.56 (s), 153.19 (s), 132.42 (s), 129.80 (s), 129.29 (s), 128.42 (s), 128.31 (s), 127.79 (s), 127.54 (t, *J* = 2.2 Hz), 120.10 (s), 119.24 (s), 118.19 (t, *J* = 23.0 Hz), 111.69 (t, *J* = 253.7 Hz), 63.33 (s), 13.81 (s). $^{19}$F NMR (377 MHz, $CDCl_3$) δ -98.42 (s). GC–MS (EI, m/z): 421.99, 423.99.

**Ethyl 2,2-difluoro-2-(4-(4-methoxyphenyl)-6-methyl-2-oxo-2*H*-chromen-3-yl)acetate (7g).** White solid (54.8 mg, 70%). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.60 (t, *J* = 8.5 Hz, 1H), 7.40 (dd, *J* = 8.3, 0.7 Hz, 1H), 7.25 (d, *J* = 8.8 Hz, 2H), 7.24 – 7.20 (m, 1H), 7.16 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.03 (d, *J* = 8.7 Hz, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 162.83 (t, *J* = 32.2 Hz), 160.24 (s), 159.12 (t, *J* = 4.3 Hz), 156.28 (s), 153.15 (s), 133.34 (s), 129.22 (s), 128.82 (s), 124.82 (s), 124.73 (s), 120.48 (s), 118.08 (t, *J* = 22.6 Hz), 116.90 (s), 113.75 (s), 111.86 (t, *J* = 253.1 Hz), 63.20 (s), 55.35 (s), 13.82 (s). $^{19}$F NMR (377 MHz, $CDCl_3$) δ -98.13 (s). IR

($cm^{-1}$): ν 2933, 1791, 1744, 1624, 1163, 1072. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. For $C_{20}H_{16}F_2O_5Na$ 397.0863; found 397.0857.

**Ethyl 2,2-difluoro-2-(4-(4-chlorophenyl)-6-methyl-2-oxo-2*H*-chromen-3-yl)acetate (7h).** White solid (62.0 mg, 76%). $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.63 (t, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.24 (t, *J* = 7.7 Hz, 1H), 7.05 (dd, *J* = 8.1, 1.3 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 162.59 (t, *J* = 32.1 Hz), 158.71 (t, *J* = 4.5 Hz), 154.84 (s), 153.15 (s), 135.35 (s), 133.69 (s), 131.25 (s), 129.10 (s), 128.70 (s), 128.46 (s), 124.95 (s), 119.83 (s), 118.40 (t, *J* = 22.9 Hz), 117.05 (s), 111.74 (t, *J* = 253.4 Hz), 63.35 (s), 13.81 (s).$^{19}F$ NMR (377 MHz, $CDCl_3$) δ -98.21 (s). IR ($cm^{-1}$): ν 2927, 1791, 1740, 1625, 1090, 1054. HRMS (ESI) m/z: $[M+Na]^+$ Calcd. For $C_{19}H_{13}ClF_2O_4Na$ 401.0368; found 401.0362.

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