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Graphical Abstract

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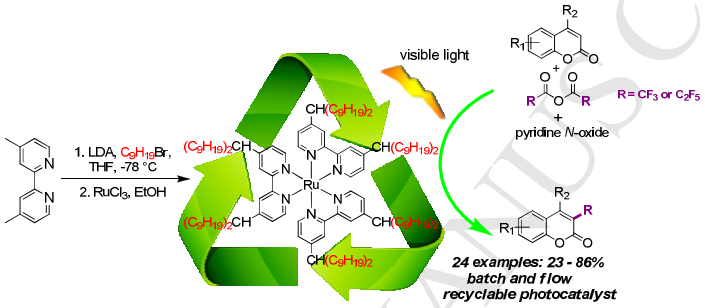

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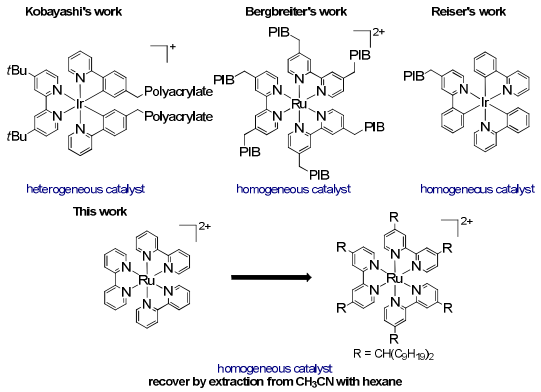
ABSTRACT

A recyclable Ruthenium *tris* [4,4'-*bis* (dinonylmethyl)-2,2'-bipyridine] ($Ru[(DNM)_2bpy]_3^{2+}$) photocatalyst (PC) was synthesized. Hexane-phase-selective solubility allowed its simple and efficient separation from reaction products via solvent extraction. The excellent catalytic activity and recoverability were demonstrated in batch and flow perfluoroalkylation reactions of coumarin under visible-light irradiation. High reaction rates and easy reusability of the catalyst make this approach attractive for large-scale applications.

1. Introduction

Visible light can serve as an attractive, sustainable, non-toxic, easy to use and universally available energy source. Photocatalysis involving visible light to trigger reactions is an alternative type of catalysis and a variety of photoredox catalysts have been used for a broad range of synthetic transformations including trifluoromethylation of arenes and heteroarenes, which are the fundamental building blocks of many top-selling pharmaceuticals and agrochemicals[1]. MacMillan reported on a strategy for the direct trifluoromethylation of unactivated arenes and heteroarenes using a Ru complex photocatalyst (PC) and a household light bulb[2-4]. Following this report, more intensive research on visible light photocatalyzed trifluoromethylation has been pursued in recent years. In 2015, Stephenson[5] reported a strategy for the use of trifluoroacetic anhydride in a scalable and operationally simple trifluoromethylation reaction using pyridine *N*-oxide, via photoredox catalysis, to realize facile decarboxylation to the CF_3 radical.

Several transition-metal complexes such as $[Ru(phen)]_3^{2+}$, $[Ru(bpy)_3]^{2+}$, Ir(I) complexes, $[Ir(ppy)_2(dtbpy)]^+$, and neutral *fac*-$Ir(ppy)_3$ are the most versatile PC for a broad range of reactions owing to their long excited state lifetime and good chemical stability[6]. Unfortunately, large-scale applications in industrial area with these Ru or Ir complexes PCs are currently limited[7]. Issues including catalyst cost, catalyst toxicity or contamination, make catalyst recycling desirable. Hence, chemists have focused on the modification of PC ligands (**Scheme 1**). In 2014, Kobayashi[8] reported an Ir-based heterogeneous complex immobilized by polyacrylate, which was used to catalyze the aerobic phosphonylation of *N*-aryl tetrahydroisoquinolines under visible light. Bergbreiter separately carried out the polymeric reaction, oxidative C-C bond cleavage of aldehydes and [2+2] cycloaddition of *bis*(enone)s in 2013[9a] and 2016[9b] catalyzed by polyisobutylene (PIB)-polymer-tagged Ru complexes, which could be recycled by extraction with heptane.



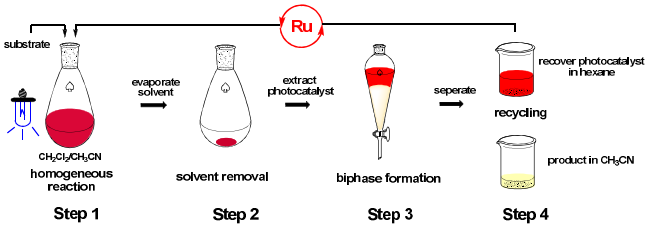
Scheme 1. Reported recoverable Ru and Ir complex PCs immobilized by polymers

A common problem encountered with the mentioned heterogeneous catalysts is poor mass transport. Moreover, heterogeneous supported PCs were impenetrable by visible light, which greatly reduces the quantum yield for a given reaction. In 2016, Reiser[7] developed a (PIB-polymer-tagged)

fac-Ir(ppy)$_3$ PC, which catalyzed deiodination, deiodination/cyclization, and *E/Z* isomerization, and showed high activity due to its homogeneous nature in solution. However, since the molecular weight distribution of (PIB-polymer-tagged) *fac*-Ir(ppy)$_3$, solubility limitations (activity) and catalyst leaching problems occured. We aimed to develop a recyclable and homogeneous Ru complex PC with an accurate structure. Our initial strategy was to design a long alkyl-chain-bound bipyridine Ru complex as a phase-selectively soluble homogeneous PC that could be extracted by hexane and reused.

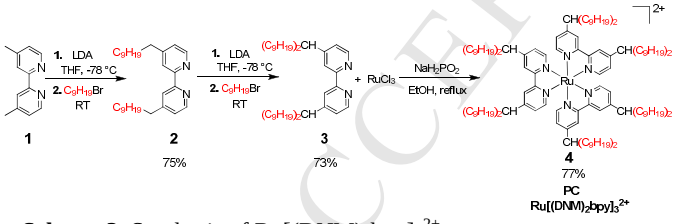
With particular interest in photochemistry and fluorine chemistry, we describe herein an alkyl-bound bipyridine Ru complex, which serves as a recoverable, reusable and hexane-soluble PC. This PC showed good catalytic activity for the perfluoroalkylation of coumarin under visible light, in the presence of trifluoroacetic and pentafluoropropionic anhydride as the CF_3 and C_2F_5 sources, respectively. The reaction proceeded on a range of substrates and had been demonstrated on a significant scale in both batch and flow reactor.

2. Results and discussion



Scheme 2. Recoverable alkyl-bound Ru complex photocatalyst and recovery process.

As shown in **Scheme 2**, the substrate for the photochemical reaction and the Ru[(DNM)$_2$bpy]$_3^{2+}$ PC were dissolved in an CH_3CN/CH_2Cl_2 mixed solvent to form a homogeneous solution (**step 1**). After the completion of reaction, the solvent was removed by vacuum evaporation (**step 2**). Then, two immiscible solvents, hexane and CH_3CN, were added to dissolve the residue, leading to organic biphasic formation. The less polar PC was extracted by hexane based on the huge solubility gap between the nonpolar and polar solvents (**step 3**). The recovered PC in hexane could be separated and reused for use in the next reaction (**step 4**).

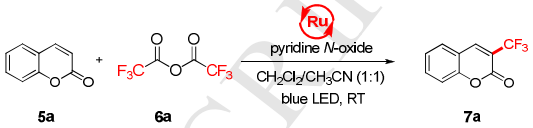


Scheme 3. Synthesis of Ru[(DNM)$_2$bpy]$_3^{2+}$

The synthesis of the Ru[(DNM)$_2$bpy]$_3^{2+}$ PC is shown in **Scheme 3**. Commercially available 4,4'-dimethyl-2,2'-dipyridine (**1**) first reacted with 1-bromononane and converted to the alkyl-bound bipyridine ligand, 4,4'-bis (dinonylmethyl)-2,2'-bipyridine, which was then allowed to react with $RuCl_3$ to generate the alkyl-bound bipyridine Ru complex (**4**) (for detailed synthetic procedures, see experimental section and supplementary information).

To demonstrate the feasibility of the phase-selectively soluble homogeneous PC, trifluoromethylation of coumarin catalyzed by Ru[(DNM)$_2$bpy]$_3^{2+}$ (**4**) was applied as the model reaction (**Table 1**). The reaction conditions were optimized for the trifluoromethylation of coumarin with trifluoroacetic anhydride/pyridine *N*-oxide under irradiation from a blue light emitting diode (LED) for 12 h. When using 1 mol% traditional Ru(bpy)$_3$Cl$_2$ PC and CH_3CN solvent, 3-trifluoromethyl coumarin (**7a**) was obtained in 63% yield (**entry 1**). Next Ru[(DNM)$_2$bpy]$_3^{2+}$ (**4**) was used as PC. Considering the poor solubility of Ru[(DNM)$_2$bpy]$_3^{2+}$ in CH_3CN, we chose a CH_3CN/CH_2Cl_2 mixed solvent system. After 12 h irradiation, **7a** was obtained in a slightly low yield of 55% (**entry 2**). Increasing the reaction time to 24 h increased the yield of **7a** to 66% (**entry 3**), which was comparable to that obtained when using the Ru(bpy)$_3$Cl$_2$ PC. Upon further extension of the reaction time to 36 h, the product yield remained unchanged. Finally, when reducing the amount of catalyst to 0.5 mol%, the yield of **7a** decreased to 48% (**entry 5**).

Table 1 Optimization of the trifluoromethylation reaction conditions[a]



Entry	Photocatalyst (PC)	Solvent	Time	Yield(%)
1	Ru(bpy)$_3$Cl$_2$	CH_3CN	12	63
2	Ru[(DNM)$_2$bpy]$_3^{2+}$	CH_2Cl_2/CH_3CN (5/5)	12	55
3	Ru[(DNM)$_2$bpy]$_3^{2+}$	CH_2Cl_2/CH_3CN (5/5)	24	66
4	Ru[(DNM)$_2$bpy]$_3^{2+}$	CH_2Cl_2/CH_3CN (5/5)	36	64
5[b]	Ru[(DNM)$_2$bpy]$_3^{2+}$	CH_2Cl_2/CH_3CN (5/5)	24	48

[a]Reaction conditions: coumarin (0.4 mmol), PC (1 mol %), pyridine *N*-oxide (0.82 mmol), trifluoroacetic anhydride (0.8 mmol), and solvent (1 mL), irradiation with 15 W blue LED at room temperature; isolated yields.
[b] PC (0.5mol %)

A recyclability test on the Ru[(DNM)$_2$bpy]$_3^{2+}$ PC in the trifluoromethylation of coumarin was further investigated **(Table 2)**. After completion of the 1st run reaction, the CH_3CN/CH_2Cl_2 mixed solvent was evaporated under reduced pressure, and the residue was redissolved in CH_3CN. The recycled Ru[(DNM)$_2$bpy]$_3^{2+}$ was extracted 5 times with hexane and collected for the next run. The product 3-trifluoromethyl coumarin (**7a**) remained in the CH_3CN phase, which was desolventized by rotary evaporation and purified by silica gel column chromatography.

As shown in **Table 2**, a new trifluoromethyl reaction (2nd run) was then performed using fresh reactants under the same conditions. The recycled Ru[(DNM)$_2$bpy]$_3^{2+}$ was collected and reused without significant loss of catalytic activity (yield 64%). After the 6th run, only a slight decrease in the yield (51%) of 3-trifluoromethyl coumarin (**7a**) was observed. The approximate yield (0.3%) of the residual **7a** in the hexane phase was determined by ^{19}F-NMR using trifluoromethyl phenyl sulfide as an internal standard. In addition, leaching of the Ru species from the initial catalyst into the polar phase during the recycling process was investigated. After the 1st and 6th runs, the amount of the recovered Ru[(DNM)$_2$bpy]$_3^{2+}$ PC were 93% and 53% respectively, corresponding to the initial amount of Ru PC used (measured by UV-vis spectroscopy). Inductively coupled plasma mass spectroscopy (ICP-MS) analysis revealed that the amount of the recovered Ru species was 57% after the 6th run. Thus, Ru[(DNM)$_2$bpy]$_3^{2+}$ (**4**) showed excellent catalytic activity in the photocatalyzed trifluoromethylation of coumarin, and could be successfully recovered and reused for 6 cycles with no significant loss of activity.

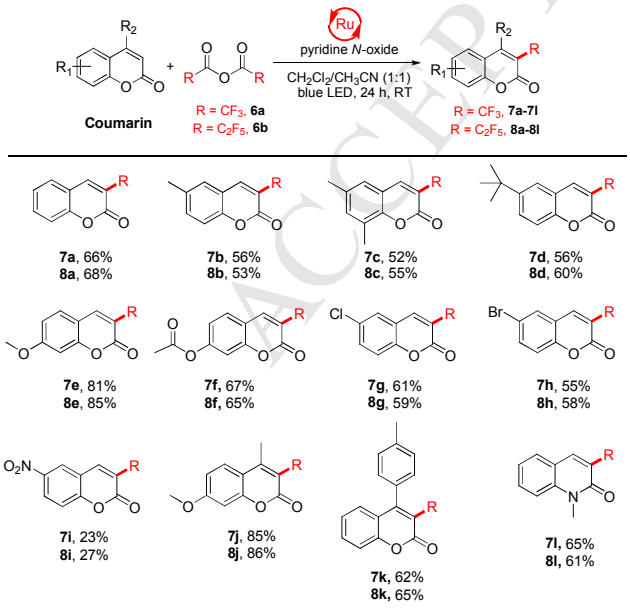
Table 2 Yields of 3-trifluoromethyl coumarin (**7a**) obtained using the $Ru[(DNM)_2bpy]_3^{2+}$ [a]

Run	1	2	3	4	5	6
Yield (%)	66	64	64	61	57	51

[a]Reaction conditions: coumarin (0.4 mmol), pyridine *N*-oxidie (0.82 mmol), trifluoroacetic anhydride (0.8 mmol), and CH_3CN (0.5 mL), CH_2Cl_2 (0.5 mL), irradiation with 15 W blue LED at room temperature; isolated yields.

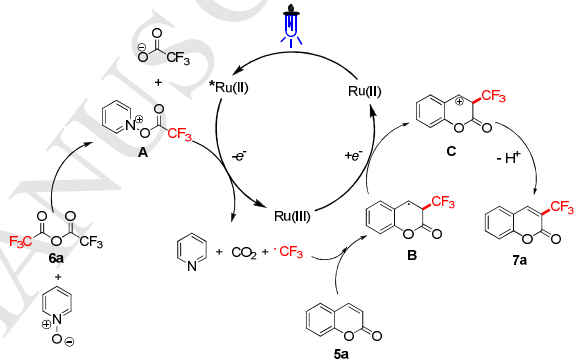
Having encouraged by the efficiency and recyclability of the $Ru[(DNM)_2bpy]_3^{2+}$ photocatalyzed trifluoromethylation of coumarin, we further investigated the substrates scope for both trifluoromethylation and pentafluoroethylation, since the latter has rarely been explored[10]. Pentafluoroethylation of coumarin was implemented under the same photocatalytic conditions using pentafluoropropionic anhydride, which is cheap and commercially available, instead of trifluoroacetic anhydride. As expected, the visible light-mediated trifluoromethylation and pentafluoroethylation of coumarins bearing electron-donating and electron-withdrawing groups proceeded smoothly to afford the desired products in moderate to good yields (**Table 3**). Both trifluoromethyl and pentafluoroethyl coumarins were obtained in 66% and 68% yields, respectively (**7a**, **8a**). Coumarins bearing alkyl groups gave the corresponding trifluoromethyl and pentafluoroethyl products in moderate yields (**7b-7d**, **8b-8d**), for example, 6-*t*-butyl coumarin gave **7d** and **8d** in 56% and 60% yields, respectively. Notably, coumarins with 7-methoxy or acetoxy groups were transformed into the desired products in satisfactory yields (**7e-7f, 8e-8f**). Coumarins with a halogen (Cl- or Br-) group were also tolerated under the reaction conditions, and products **7g**, **7h**, **8g**, **8h** were isolated in good yields. Unfortunately, when a coumarin bearing a strong electron-withdrawing group ($-NO_2$) at the 6-position was used, poor yields of the corresponding trifluoromethyl and pentafluoroethyl products (**7i** and **8i**) were obtained, i.e., 23% and 27%, respectively. Satisfactorily, trifluoromethylation and pentafluoroethylation of 4-methyl-7-methoxy coumarin afforded the products in high yields of 85% and 86%, respectively (**7j, 8j**). As family members of coumarin derivatives, 4-phenyl-coumarins are widely distributed in natural products and used in biological studies. The potentially valuable products **7k** and **8k** were obtained in good yields of 64% and 71%, respectively. Finally, we extended this method to a nitrogen-containing heterocycle, *N*-methyl quinolinone. As expected, the trifluoromethyl and pentafluoroethyl *N*-methyl quinolinones were obtained in 65% and 61% yields, respectively (**7l, 8l**).

Table 3 Substrate scope of coumarin[a]



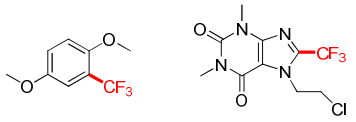
[a]Reaction conditions: coumarin (0.4 mmol), PC (1 mol %), pyridine *N*-oxidie (0.82 mmol), anhydride (0.8 mmol), and CH_3CN (0.5 mL), CH_2Cl_2 (0.5 mL), irradiation with 15 W blue LED at room temperature; isolated yields.

On the basis of the experimental results and reported literatures[11], a plausible mechanism was proposed in **Scheme 4**. Initially trifluoroacetic anhydride (TFAA, **6a**) was coupled by the electron-poor auxiliary pyridine *N*-oxidant to form TFAA adduct (**A**). The **Ru(II)** PC was irradiated by a blue LED to the excited state **[Ru(II)]***, which was oxidatively quenched by **A** with the generation of **Ru(III)**. The **A** was reduced by the excited **[Ru(II)]*** and underwent decarboxylation to produce CF_3 radical, CO_2, and pyridine. The CF_3 radical attacked the 3-position of coumarin (**5a**) to produce intermediate **B**. Afterwards the intermediate **B** was oxidized by **Ru(III)** to form carbocation intermediate **C** and **Ru(II)**. Finally 3-trifluoromethyl coumarin (**7a**) was produced in a process of deprotonation assisted by pyridine.



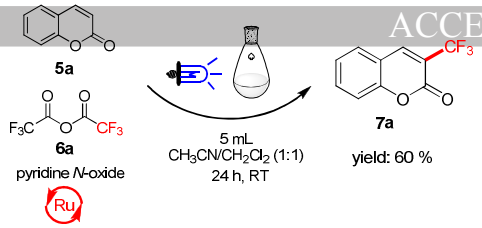
Scheme 4. Proposed reaction mechanism

To further demonstrate the generality and practicability of trifluoromethylation catalyzed by the recyclable $Ru[(DNM)_2bpy]_3^{2+}$, the electron-rich arene and xanthine derivative were investigated under the given conditions (**Scheme 5**). The *p*-dimethoxybenzene and 7-(2-Chloroethyl)theophylline afforded the corresponding trifluoromethylated products (**9** and **10**) in 40% and 32% yield, respectively.



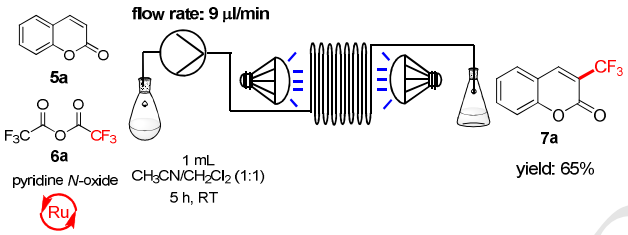
Scheme 5. Trifluoromethylation for *p*-dimethoxybenzene and 7-(2-Chloroethyl)theophylline by the $Ru[(DNM)_2bpy]_3^{2+}$.

Owing to the recyclable nature of PC and low cost of the fluorine sources, a up-scaled procedure of the trifluoromethylation reaction was carried out (**Scheme 6**). 3 mmol of the coumarin was used, and the concentration was 1.5-fold (0.6 M) of that under the optimized condition (0.4 M). The reaction afforded 3-trifluoromethyl coumarin in 60% yield (385mg).



Scheme 6. Up-scaled trifluoromethylation reaction of coumarin.

Recently, the use of continuous flow micro-reactors for photochemical applications has received much attention as it helps to overcome the issues associated with batch photochemistry. The narrow channel of a typical micro-reactor facilitates a uniform irradiation of the entire reaction mixture. Consequently, photochemical reactions can be accelerated substantially, and lower PC loadings are often feasible. Furthermore, scale-up of photochemical reactions is facilitated in continuous flow reactors[12]. Herein, we present a general protocol for visible light-induced trifluoromethylation of coumarin with trifluoroacetic anhydride/pyridine *N*-oxide in a continuous flow reactor (**Scheme 7**). The starting material solution was pumped continuously into a fluorinated ethylene propylene (FEP) tube reactor, which was irradiated by a blue LED. The reaction afforded 3-trifluoromethyl coumarin (**7a**) in 65 % yield for a residence time of 5 h, thus demonstrating a much shorter reaction time than that under the batch condition (24 h).



Scheme 7. Trifluoromethylation of coumarin in continuous system.

3. Conclusion

In summary, a recoverable alkyl-bound bipyridine Ru complex was successfully synthesized as a PC. $Ru[(DNM)_2bpy]_3^{2+}$ showed excellent catalytic performance as well as recyclability for both batch and flow reactions in a homogeneous solvent. Meanwhile the perfluoroalkyl reactions proceeded well for a wide range of coumarin substrates, and also gave good yields in a up-scale process. Moreover, the use of a continuous flow system for this reaction would significantly shorten the reaction time. The use of an alkyl-bound Ru complex would mitigate environment pollution as a recyclable environmentally friendly PC and made it possible for large-scale reaction catalyzed by visible light industrially beyond laboratory.

4. Experimental section

4.1 General information

All reagents unless otherwise noted were obtained from commercial sources and used without further purification. pyridine *N*-oxide (98.0%) and Trifluoroacetic anhydride (>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 470 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 Tof mass spectrometer in the ESI mode.

4.2 Preparation of ruthenium, *tris* (4,4'-*bis* (dinonylmethyl)-2,2'-bipyridine) ($Ru[(DNM)_2bpy]_3^{2+}$).

To a Schlenk flask was added 4,4'-*bis* (dinonylmethyl)-2,2'-bipyridine (619 mg, 0.9 mmol), $RuCl_3 \cdot 3H_2O$ (78 mg, 0.3 mmol), NaH_2PO_2 (10.6 mg, 0.1 mmol), and ethanol 30 mL to form a deep brown solution. The reaction mixture was stirred and refluxed at 90 °C under Ar for 12 h, whereupon the color changed to red-brown or dark orange. After cooling to room temperature, 100 mL of hexane and 100 mL of water were poured into the reaction solution, leading to organic biphasic formation. The upper hexane layer was separated and dried with Na_2SO_4, and then concentrated under vacuum. After evaporation, the residue was purified by column chromatography on silica with eluent EtOAc to give the orange-red $Ru[(DNM)_2bpy]_3^{2+}$ (514 mg, 77 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.60 (d, *J* = 5.8 Hz, 1H), 7.27 (d, *J* = 6.0 Hz, 2H), 2.93 – 2.75 (m, 1H), 1.85 – 1.54 (m, 4H), 1.39 – 1.07 (m, 28H), 0.90 – 0.81 (m,6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.96 (s), 156.85 (s), 150.54 (s), 126.92 (s), 124.46 (s), 45.67 (s), 35.55 (d, *J* = 9.8 Hz), 31.88 (s), 29.69 (s), 29.61 (s), 29.54 (d, *J* = 2.6 Hz), 29.30 (s), 27.59 (d, *J* = 3.5 Hz), 22.64 (s), 14.07 (s). HRMS (ESI) m/z: $[M-2Cl]^{2+}$ Calcd. For $C_{144}H_{252}N_6Ru$ 1083.9474; found 1083.9459.

4.3 General procedure for visible light-catalyzed coumarin trifluoromethylation, pentafluoroethylation and in a continuous reactor.

4.3.1 Procedure for the visible light-catalyzed reaction.

A flame-dried reaction vessel with a magnetic stirring bar was sequentially charged with coumarin or *p*-dimethoxybenzene or 7-(2-Chloroethyl)theophylline (0.4 mmol), PC (0.004 mmol), pyridine *N*-oxide (0.82 mmol, 78 mg), CH_2Cl_2 (0.5 mL) and CH_3CN (0.5 mL). Trifluoroacetic anhydride (0.8 mmol, 168 mg) was then added to the resulting homogeneous solution. The mixture was stirred at room temperature under irradiation from a blue LED. The solvent in the reaction mixture was removed under reduced pressure. The residue was redissolved in 2 mL of CH_3CN, and extracted 5 times with hexane (5 mL each time). The PC was extracted into the hexane layer and separated for use in the next reaction. The CH_3CN layer was dried with Na_2SO_4 and concentrated under vacuum. After separation and evaporation, the residue was purified by column chromatography on silica gel (200–300 mesh size) using petroleum ether/EtOAc as the eluent to give the trifluoromethyl coumarin.

4.3.2 Procedure for the visible light-catalyzed scale-up reaction.

A flame-dried flask with a magnetic stirring bar was sequentially charged with coumarin (3 mmol, 438 mg), PC (0.03 mmol), pyridine *N*-oxide (6.15 mmol, 584 mg), CH_2Cl_2 (2.5 mL) and CH_3CN (2.5 mL). Trifluoroacetic anhydride (6 mmol, 1260 mg) was then added to the resulting homogeneous solution. The mixture was stirred at room temperature under irradiation from a blue LED. The solvent in the reaction mixture was removed under reduced pressure. The residue was redissolved in 10 mL of

CH_3CN, and extracted with 30 mL of hexane. The PC was extracted into the hexane layer and separated. The CH_3CN layer was dried with Na_2SO_4 and then concentrated under vacuum. After separation and evaporation, the residue was purified by column chromatography on silica gel (200–300 mesh size) using petroleum ether/EtOAc as the eluent to give the trifluoromethyl coumarin.

4.3.3 Procedure for the visible light-catalyzed reaction in a continuous flow reactor.

A test tube was filled with a mixed solvent of CH_2Cl_2 (0.5 mL) and CH_3CN (0.5 mL), in which coumarin (0.4 mmol, 58.4 mg), PC (0.004 mmol), pyridine *N*-oxide (0.82 mmol, 78 mg), and trifluoroacetic anhydride (0.8 mmol, 168 mg) were dissolved. The solution was pumped into PTFE-FEP tube (1/32 inner diameter) using a pump (Syrris Ltd) at a flow rate of 9 μL min^{-1}. The solution stream flowed into a 2.7 mL convection flow coil (CFC) reactor (1/32 inner diameter), which was irradiated by two 15 W blue LEDs on both sides and maintained at room temperature (residence time: 5 h). The product stream exiting the reactor was collected in a test tube, and the solvent was removed under reduced pressure. The residue was redissolved in 2 mL of CH_3CN, and extracted 5 times with hexane (5 mL each time). The PC was extracted into the hexane layer. The CH_3CN layer was dried with Na_2SO_4 and then concentrated under vacuum. After separation and evaporation, the residue was purified by column chromatography on silica gel (200–300 mesh size) using petroleum ether/EtOAc as the eluent to give the trifluoromethyl coumarin.

3-(trifluoromethyl)-2H-1-Benzopyran-2-one (7a, CAS: 497959-34-9). A white solid (56.4 mg, 66%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.69 (t, *J* = 7.9 Hz, 1H), 7.64 (d, *J* = 6.7 Hz, 1H), 7.44 – 7.34 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.85 (s), 154.62 (s), 143.32 (q, *J* = 4.8 Hz), 134.42 (s), 129.47 (s), 125.26 (s), 121.33 (q, *J* = 272.0 Hz), 117.68 (q, *J* = 33.4 Hz), 116.96 (s), 116.76 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.18 (s). GC-MS (EI, m/z): 214(M^+, 100), 186(57), 136(52), 63(34).

***6-Methyl-3-(trifluoromethyl)-2H-1-Benzopyran-2-one* (7b, CAS: 1562426-71-4).** A white solid (52.1 mg, 56%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.48 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.40 (s, 1H), 7.29 (d, *J* = 8.5 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.12 (s), 152.83 (s), 143.26 (q, *J* = 4.9 Hz), 135.53 (s), 135.19 (s), 129.11 (s), 121.44 (q, *J* = 272.0 Hz), 117.58 (q, *J* = 33.1 Hz), 116.73 (s), 116.55 (s), 20.70 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.14 (s). GC–MS (EI, m/z): 228(M^+, 100), 200(48), 199(43), 131(43).

***6,8-Dimethyl-3-(trifluoromethyl)-2H-1-Benzopyran-2-one* (7c).** A white solid (47.7 mg, 52%); mp 126-127 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.34 (s, 1H), 7.22 (s, 1H), 2.43 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.30 (s), 151.22 (s), 143.60 (q, *J* = 4.8 Hz), 136.92 (s), 134.62 (s), 126.78 (s), 126.29 (s), 121.56 (q, *J* = 271.9 Hz), 117.14 (q, *J* = 33.0 Hz), 116.36 (s), 20.61 (s), 15.26 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.05 (s). HRMS (ESI) m/z: $[M + Na]^+$ Calcd For $C_{12}H_9F_3O_2Na$ 265.0452; found 265.0446.

***6-t-Butyl-3-(trifluoromethyl)-2H-1-Benzopyran-2-one* (7d).** A white solid (60.6 mg, 56%); mp 162-163 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.58 (s, 1H), 7.33 (d, *J* = 8.8 Hz, 1H), 1.37 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.24 (s), 152.72 (s), 148.61 (s), 143.81 (q, *J* = 4.9 Hz), 132.26 (s), 125.68 (s), 121.49 (q, *J* = 271.9 Hz), 117.38 (q, *J* = 33.3 Hz), 116.27 (s), 113.80 (s), 34.65 (s), 31.22 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.11 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd. For $C_{14}H_{13}F_3O_2Na$ 293.0765; found 293.0733.

***7-Methoxyl-3-(trifluoromethyl)-2H-1-Benzopyran-2-one* (7e, CAS:1562426-78-1).** A white solid (77.5 mg, 81%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.52 (d, *J* = 8.7 Hz, 1H), 6.93 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.84 (d, *J* = 2.3 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.01 (s), 156.84 (s), 156.38 (s), 143.26 (q, *J* = 4.8 Hz), 130.59 (s), 121.77 (q, *J* = 271.5 Hz), 113.77 (q, *J* = 33.3 Hz), 113.76 (s), 110.38 (s), 100.74 (s), 56.04 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ -65.68 (s). GC-MS (EI, m/z): 244(M^+, 78), 216(73), 201 (100), 69(40).

***7-Acetyloxy-3-(trifluoromethyl)-2H-1-Benzopyran-2-one* (7f, CAS:1562426-82-7).** A white solid (71.8 mg, 67%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.20 (d, *J* = 2.2 Hz, 1H), 7.16 (dd, *J* = 8.5, 2.2 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.30 (s), 155.51 (s), 155.39 (s), 155.22 (s), 142.72 (q, *J* = 4.9 Hz), 130.31 (s), 121.32 (q, *J* = 272.0 Hz), 119.36 (s), 117.04 (q, *J* = 33.4 Hz), 114.47 (s), 110.52 (s), 21.11 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.14 (s). GC-MS (EI, m/z): 230(M^+, 26), 202(27), 43(100), 32(38).

***6-Chloro-3-(trifluoromethyl)-2H-1-Benzopyran-2-one* (7g).** A white solid (62.3 mg, 61%); mp 160-161 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.63 (d, *J* = 11.8 Hz, 2H), 7.36 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.18 (s), 153.04 (s), 142.07 (q, *J* = 4.9 Hz), 134.36 (s), 130.68 (s), 128.54 (s), 121.06 (q, *J* = 272.4 Hz), 118.98 (q, *J* = 33.5 Hz), 118.53 (s), 117.75 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.35 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd. For $C_{10}H_4ClF_3O_2Na$ 270.9758; found 270.9750.

***6-Bromo-3-(trifluoromethyl)-2H-1-Benzopyran-2-one* (7h, CAS:1562426-73-6).** A white solid (63.8 mg, 55%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.76 (dd, *J* = 7.0, 2.2 Hz, 2H), 7.30 (d, *J* = 9.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.11 (s), 153.49 (s), 142.01 (q, *J* = 4.9 Hz), 137.16 (s), 131.63 (s), 121.04 (q, *J* = 272.4 Hz), 118.90 (q, *J* = 33.4 Hz), 118.75 (s), 118.25 (s), 117.84 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.34 (s). GC-MS (EI, m/z): 292(M^+, 71), 294(70), 157(89), 87(100).

***6-Nitro-3-(trifluoromethyl)-2H-1-Benzopyran-2-one* (7i, CAS: 500552-10-3).** A yellow solid (24.2 mg, 23%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (d, *J* = 2.0 Hz, 1H), 8.54 (dd, *J* = 9.1, 2.3 Hz, 1H), 8.25 (s, 1H), 7.56 (d, *J* = 9.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.85 (s), 154.11 (s), 144.50 (s), 142.02 (q, *J* = 5.0 Hz), 128.86 (s), 125.24 (s), δ 120.70 (q, *J* = 272.7 Hz), 120.14 (q, *J* = 34.1 Hz), 118.41 (s), 116.81 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.51 (s). GC-MS (EI, m/z): 256(M^+, 59), 157(100), 87(83), 62(55).

***7-Methoxy-4-Methyl-3-(trifluoromethyl)-2H-1-Benzopyran-2-one* (7j, CAS: 1562426-86-1).** A white solid (87.2 mg, 85%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 9.1 Hz, 1H), 6.92 (dd, *J* = 9.1, 2.5 Hz, 1H), 6.78 (d, *J* = 2.5 Hz, 1H), 3.91 (s, 3H), 2.63 (dd, *J* = 4.2, 2.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.40 (s), 156.32 (s), 155.13 (s), 155.10 (d, *J* = 1.2 Hz), 127.16 (s), 123.15 (q, *J* = 274.7 Hz), 113.37 (s), 112.47 (s), 112.00 (q, *J* = 30.3 Hz), 100.43 (s), 55.96 (s), 15.65 (q, *J* = 4.1 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -56.33 (q, *J* = 1.9 Hz). GC-MS (EI, m/z): 258(M^+, 68), 230(99), 215(100), 32(17).

***4-Methylphenyl-3-(trifluoromethyl)-2H-1-Benzopyran-2-one* (7k, CAS: 1621190-87-1).** A white solid (74.6 mg, 62%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (t, *J* = 7.7 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.33 (d, *J* = 7.7 Hz, 2H), 7.19 (t, *J* = 7.7 Hz, 1H), 7.14 (d, *J* = 7.7 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.21 (d, *J* = 2.0 Hz), 156.41 (s),153.43 (s), 139.38 (s), 133.98 (s), 129.87 (s), 129.32 (s), 129.14 (s), 127.28 (d, *J* = 1.5 Hz), 124.68 (s), 121.93 (q, *J*=275.2 Hz), 119.66 (s), 116.81 (s), 115.05 (q, *J* = 30.1 Hz), 21.39 (s); ^{19}F

NMR (470 MHz, $CDCl_3$) δ -57.39 (s). GC-MS (EI, m/z): 304(M^+, 100), 289(99), 276(64), 199(74).

1-Methyl-3-(trifluoromethyl)-2(1H)-Quinolinone **(7l, CAS: 1890080-20-2).** A white solid (60.5mg, 65%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.77 – 7.60 (m, 2H), 7.41 (d, *J* = 8.6 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 3.75 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.00 (s), 141.00 (s), 138.86 (q, *J* = 5.2 Hz), 133.15 (s), 130.44 (s), 122.92 (s), 122.40 (q, *J* = 271.7 Hz), 121.13 (q, *J* = 30.3 Hz), 118.06 (s), 114.40 (s), 29.52 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ -66.16 (s). GC-MS (EI, m/z): 227(M^+, 69), 179(78), 176(100), 121(68).

3-(pentafluoroethyl)-2H-1-Benzopyran-2-one **(8a).** A white solid (69.0 mg, 68%); mp 151-152 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.70 (t, *J* = 7.9 Hz, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.45 (t, *J* = 2.1 Hz), 154.86 (s), 146.13 (t, *J* = 7.8 Hz), 134.70 (s), 129.50 (s), 125.23 (s), 117.00 (s), 116.94 (s), 118.80 (qt, *J* = 287.2, *J* = 38.1 Hz), 116.29 (t, *J* = 24.0 Hz), 111.62 (tq, *J* = 256.7, *J* = 40.5 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -83.04 (s, 3F), -114.98 (s, 2F). HRMS (ESI) m/z: $[M+Na]^+$ Calcd. For $C_{11}H_5F_5O_2Na$ 287.0107; found 287.0102.

6-Methyl-3-(pentafluoroethyl)-2H-1-Benzopyran-2-one **(8b).** A white solid (60.0 mg, 53%); mp 153-154 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.42 (s, 1H), 7.28 (d, *J* = 8.4 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.70 (s), 153.01 (s), 146.13 (t, *J* = 7.7 Hz), 135.80 (s), 135.19 (s), 129.16 (s), 118.80 (qt, *J* = 287.2, *J* = 38.1 Hz), 116.74 (s), 116.58 (s), 115.99 (t, *J* = 24.9 Hz), 111.69 (tq, *J* = 256.6, *J* = 40.4 Hz), 20.63 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ -83.11 (s, 3F), -114.95 (s, 2F). HRMS (ESI) m/z: $[M+Na]^+$ Calcd. For $C_{12}H_7F_5O_2Na$ 301.0264; found 301.0253.

6,8-Dimethyl-3-(pentafluoroethyl)-2H-1-Benzopyran-2-one **(8c).** A white solid (62.3 mg, 55%); mp 156-157 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.35 (s, 1H), 7.23 (s, 1H), 2.43 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.87 (t, *J* = 2.0 Hz), 151.43 (s), 146.39 (t, *J* = 7.8 Hz), 137.14 (s), 134.59 (s), 126.79 (s), 126.21 (s), 118.87 (qt, *J* = 287.2, *J* = 38.0 Hz), 116.57 (s), 115.60 (t, *J* = 24.0 Hz), 111.77 (tq, *J* = 256.5, *J* = 40.4 Hz), 20.58 (s), 15.18 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ -83.13 (s, 3F), -114.90 (s, 2F). HRMS (ESI) m/z: $[M+Na]^+$ Calcd. For $C_{13}H_9F_5O_2Na$ 315.0425; found 315.0420.

6-t-Butyl-3-(pentafluoroethyl)-2H-1-Benzopyran-2-one **(8d).** A white solid (74.3 mg, 60%); mp 185-186 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.74 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.58 (d, *J* = 2.2 Hz, 1H), 7.34 (d, *J* = 8.8 Hz, 1H), 1.37 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.80 (t, *J* = 2.0 Hz), 152.95 (s), 148.58 (s), 146.58 (s), 132.55 (s), 125.66 (s), 118.86 (qt, *J* = 287.1 Hz, *J* = 38.2 Hz), 116.54 (s), 116.49 (s), 115.92 (t, *J* = 23.9 Hz), 111.73 (td, *J* = 256.7 Hz, *J* = 40.4 Hz), 34.68 (s), 31.24 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ -83.09 (s, 3F), -114.91 (s, 2F). HRMS (ESI) m/z: $[M+Na]^+$ Calcd. For $C_{15}H_{13}F_5O_2Na$ 343.0733; found 343.0724.

7-Methoxyl-3-(pentafluoroethyl)-2H-1-Benzopyran-2-one **(8e).** A white solid (103mg, 85%); mp 160-161 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.52 (d, *J* = 8.7 Hz, 1H), 6.93 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.84 (d, *J* = 2.4 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.24 (s), 157.13 (s), 155.92 (s), 145.86 (t, *J* = 7.6 Hz), 130.60 (s), 118.93 (qt, *J* = 287.1, *J* = 38.5 Hz), 113.80 (s), 112.03 (t, *J* = 24.2 Hz), 111.87 (tq, *J* = 256.3, *J* = 40.4 Hz), 110.72 (s), 100.57 (s), 56.05 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ -83.29 (s, 3F), -114.73 (s, 2F). HRMS (ESI) m/z: $[M+Na]^+$ Calcd. For $C_{12}H_7F_5O_3Na$ 317.0219; found 317.0213.

7-Acetyloxy-3-(pentafluoroethyl)-2H-1-Benzopyran-2-one **(8f).** A white solid (85.3 mg, 65%); mp 175-176 °C;. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.20 (d, *J* = 2.2 Hz, 1H), 7.16 (dd, *J* = 8.5, 2.2 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.27 (s), 155.62 (s), 155.43 (s), 155.07 (t, *J* = 2.0 Hz), 145.47 (t, *J* = 7.7 Hz), 130.34 (s), 119.33 (s), 118.95 (qt, *J* = 287.2, *J* = 38.1 Hz), 115.55 (t, *J* = 24.4 Hz), 114.70 (s), 111.58 (tq, *J* = 256.4, *J* = 40.1 Hz), 110.42 (s), 21.09 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ -83.04 (s, 3F), -114.98 (s, 2F). HRMS (ESI) m/z: $[M+Na]^+$ Calcd. For $C_{13}H_7F_5O_4Na$ 345.0162; found 345.0156.

6-Chloro-3-(pentafluoroethyl)-2H-1-Benzopyran-2-one **(8g).** A white solid (69.3 mg, 59%); mp 162-163 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.64 (d, *J* = 10.0 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.76 (t, *J* = 2.0 Hz), 153.22 (s), 144.89 (t, *J* = 7.9 Hz), 134.60 (s), 130.64 (s), 128.56 (s), 118.68 (qt, *J* = 287.3, *J* = 38.5 Hz), 118.45 (s), 117.90 (s), 117.62 (t, *J* = 24.1 Hz), 111.43 (tq, *J* = 256.4, *J* = 40.1 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -82.96 (s, 3F), -115.10 (s, 2F). HRMS (ESI) m/z: $[M+Na]^+$ Calcd. For $C_{11}H_4ClF_5O_2Na$ 320.9718; found 320.9708.

6-Bromo-3-(pentafluoroethyl)-2H-1-Benzopyran-2-one **(8h).** A white solid (78.4 mg, 58%) mp 166-167 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.83 – 7.67 (m, 2H), 7.29 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.69 (t, *J* = 2.0 Hz), 153.69 (s), 144.81 (t, *J* = 7.8 Hz), 137.39 (s), 131.65 (s), 118.68 (qt, *J* = 287.2, *J* = 38.2 Hz), 118.67 (s), 118.41 (s), 117.79 (s), 117.56 (t, *J* = 24.3 Hz), 111.41 (tq, *J* = 256.4, *J* = 40.6 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -82.97 (s, 3F), -115.09 (s, 2F). HRMS (ESI) m/z: $[M+Na]^+$ Calcd. For $C_{11}H_4BrF_5O_2Na$ 364.9205; found 364.9213.

6-Nitro-3-(pentafluoroethyl)-2H-1-Benzopyran-2-one **(8i).** A yellow solid (32.4 mg, 27%); mp 222-223 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, *J* = 2.2 Hz, 1H), 8.55 (dd, *J* = 9.1, 2.2 Hz, 1H), 8.26 (s, 1H), 7.56 (d, *J* = 9.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.03 (s), 153.70 (s), 144.89 (t, *J* = 7.9 Hz), 144.46 (s), 129.05 (s), 125.29 (s), 118.90 (t, *J* = 24.5 Hz), 118.56 (qt, *J* = 287.3, *J* = 38.2 Hz), 118.33 (s), 116.92 (s), 111.18 (tq, *J* = 256.3, *J* = 40.2 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -82.86 (s, 3F), -115.26 (s, 2F). HRMS (ESI) m/z: $[M+Na]^+$ Calcd. For $C_{11}H_4F_5NO_4Na$ 331.9958; found 331.9942.

7-Methoxy-4-Methyl-3-(pentafluoroethyl)-2H-1-Benzopyran-2-one **(8j).** A white solid (109.0 mg, 86%); mp 209-210 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 9.1 Hz, 1H), 6.92 (dd, *J* = 9.1, 2.5 Hz, 1H), 6.79 (d, *J* = 2.5 Hz, 1H), 3.91 (s, 3H), 2.62 (t, *J* = 2.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.48 (s), 157.35 (s), 156.25 (t, *J* = 1.9 Hz), 155.25 (s), 127.13 (s), 119.43 (qt, *J* = 287.6, *J* = 38.6 Hz), 119.42 (tq, *J* = 257.1, *J* = 40.8Hz), 113.38 (s), 112.78 (s), 110.40 (t, *J* = 22.1 Hz), 100.29 (s), 55.97 (s), 16.24 (td, *J* = 7.3, 1.4 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -83.43 (s), -106.67 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd. For $C_{13}H_9F_5O_3Na$ 331.0370; found 331.0376.

4-Methlylphenyl-3-(pentafluoroethyl)-2H-1-Benzopyran-2-one **(8k).** A white solid (89.2 mg, 65%); mp 159-160 °C;. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (t, *J* = 7.7 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.09 (d, *J* = 7.8 Hz, 2H), 6.89 (d, *J* = 8.1 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.21 (t, *J* = 2.2 Hz), 156.11 (t, *J* = 2.1 Hz), 153.45 (s), 138.88 (s), 134.21 (s), 130.04 (s), 129.44 (s), 128.73 (s), 127.16 (s), 124.63 (s), 120.35 (s), 118.89 (qt, *J* = 275.2 Hz, *J* = 37.5 Hz), 116.60 (s), 113.57 (t, *J* = 20.9 Hz), 112.71 (tq, *J* = 260.4 Hz, *J* = 40.7 Hz), 21.35 (s); ^{19}F NMR (470

MHz, $CDCl_3$) δ -81.80 (s, 3F), -106.22 (s, 2F). HRMS (ESI) m/z: $[M+Na]^+$ Calcd. For $C_{18}H_{11}F_5O_2Na$ 377.0577; found 377.0586.

1-Methyl-3-(pentafluoroethyl)-2(1H)-Quinolinone **(8l).** A white solid (66.6 mg, 61%); mp 153-154 °C;. ^1H NMR (500 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.75 – 7.66 (m, 2H), 7.41 (d, *J* = 8.6 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 3.75 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.90 (t, *J* = 1.9 Hz), 141.47 (t, *J* = 8.5 Hz), 141.20 (s), 133.36 (s), 130.48 (s), 122.85 (s), 119.82 (t, *J* = 22.4 Hz), 119.18 (qt, *J* = 282.2, *J* = 38.4 Hz), 118.23 (s), 114.35 (s), 112.69 (qt, *J* = 255.6, *J* = 40.2Hz), 29.63 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ -82.43 (s), -114.19 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd. For $C_{11}H_8F_5NONa$ 300.0418; found 300.0424.

1,4-Dimethoxy-2-(trifluoromethyl)-Benzene **(9, CAS: 84355-10-2)**. A colourless oil (33.4 mg, 40%); ^1H NMR (500 MHz, $CDCl_3$) δ 7.11 (d, *J* = 3.0 Hz, 1H), 7.01 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.94 (d, *J* = 9.0 Hz, 1H), 3.85 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.00 (s), 151.55 (s), 123.43 (q, *J* = 272.5 Hz), 119.44 (q, *J* = 31.0 Hz), 118.09 (s), 113.63 (s), 112.86 (q, *J* = 5.4 Hz), 56.55 (s), 55.86 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.41 (s). GC-MS (EI, m/z): 191(M^+, 100), 206(82), 129(33), 163(28).

1,3-Dimethyl-8-(trifluoromethyl)-7-(2-chloroethyl)-3,7-dihydro-1H-purine-2,6-dione **(10).** A white solid (39.1 mg, 32%); mp 96-97 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 4.78 (t, *J* = 6.4 Hz, 2H), 3.94 (t, *J* = 6.4 Hz, 2H), 3.61 (s, 3H), 3.43 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.13 (s), 151.19 (s), 147.10 (s), 139.26 (q, *J* = 40.1 Hz), 118.07 (q, *J* = 271.8 Hz), 108.95 (s), 47.91 (s), 41.66 (s), 29.96 (s), 28.30 (s); ^{19}F NMR (470 MHz, $CDCl_3$) δ -60.56 (s). HRMS (ESI) m/z: $[M+Na]^+$ Calcd. For $C_{10}H_{10}ClF_3N_4O_2Na$ 333.0342; found 333.0351.

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