## PAPER

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# FeCl₃-catalyzed regioselective ring-opening of aryl oxirane with 4-hydroxycoumarin for the synthesis of furo[3,2-c]coumarins†‡

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The regioselective ring-opening of aryl oxiranes was investigated with various 4-hydroxycoumarins in dimethyl sulfoxide in the presence of 20 mol% FeCl₃ as a catalyst at 110 °C. This approach provided a short and concise synthetic route for the regioselective synthesis of 2-aryl-4*H*-furo[3,2-*c*] coumarin derivatives. Product formation occurred through regioselective ring-opening of the aryl oxirane at a less hindered site, followed by dehydration and concomitant cyclization. The salient features of our protocol were: cost-effectiveness; short reaction time; step- and atom economy; easy handling; broad scope of substrates; regioselectivity; good-to-excellent yields; non-requirement of dry solvents, co-catalysts, ligands, or any other additives; inert atmospheric conditions.

## Introduction

4-Hydroxycoumarin is an important coumarin derivative and an integral part of many naturally occurring compounds, for example, dicoumarol (**I**)[1a] and furocoumarins such as pterophyllin 2 (**II**), flemichapparin C (**III**), wedelolactone (**IV**), and neo-tanshinlactone (**V**).[1b] These derivatives exhibit interesting pharmacological activities.[1c] Some non-natural compounds derived from 4-hydroxycoumarin are also used as medicines due to their anticoagulant activity, such as warfarin.[1d] These compounds are shown in Fig. 1.

These derivatives display various biological activities: anticancer,[1e] anti-depressant,[2] antioxidant,[3] anticoagulant,[4] anti-inflammatory,[5] and antidiabetic.[6] They are also utilized as ingredients in cosmetics and perfumes and as additives in the food industry.[7] Due to their incredible fluorescent properties,[8] some of them are also used as fluorescent probes. Moreover, coumarins and furans are crucial heterocyclic scaffolds in many bioactive natural and non-natural products.[9,10] Combining coumarin with furan introduces some unique and valuable biological activities into the molecule.[11,12] An epoxide

ring–ring of styrene oxides[13] has been explored extensively in organic synthesis, and our research group has recently demonstrated the usefulness of aryl oxiranes (styrene oxides) in the synthesis of various new molecules.[14a–c] Taking cues from our earlier work, we envisioned that these aryl oxiranes could be explored further to synthesize furocoumarin derivatives on reaction with 4-hydroxycoumarins in the presence of FeCl₃ (which acts as a Lewis acid).[15a–d] In 2007, Hu and co-workers reported[16a] an elegant approach for the synthesis of furocoumarins from 3-(phenylethynyl)-4*H*-chromen-4-one through one-pot cascade addition–cyclization–oxidation, as shown in Scheme 1a. In 2010, Xu and co-workers demonstrated the synthesis of furocoumarins *via* a sequential Pd/Cu-catalyzed alkynylation and intramolecular hydroalk-oxylation, as depicted in Scheme 1b.[16b] In 2017, Li and colleagues and Wang *et al.*
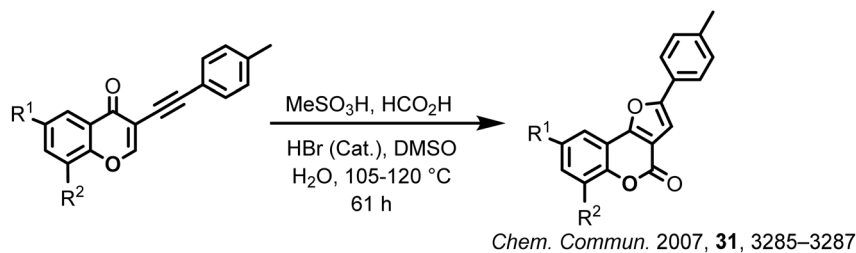
*Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati-781039, India. E-mail: atk@iitg.ac.in*
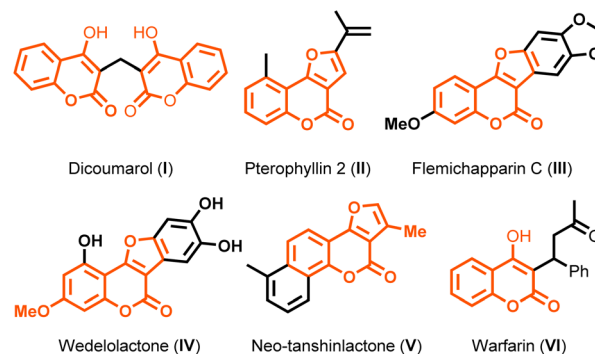
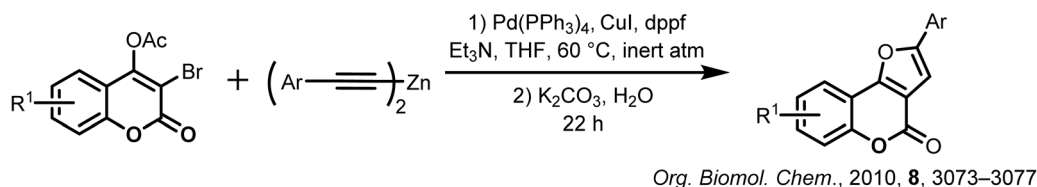Fig. 1 Some bioactive molecules containing a 4-hydroxycoumarin backbone.

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*Org. Biomol. Chem.*, 2024, **22**, 95–105 | 95

**Scheme 1a**



*Chem. Commun.* 2007, **31**, 3285–3287

**Scheme 1b**



*Org. Biomol. Chem.*, 2010, **8**, 3073–3077

**Scheme 1c**



*Adv. Synth. Catal.*, 2017, **359**, 467–475

**Scheme 1d**



*Org. Biomol. Chem.*, 2017, **15**, 8084–8090

**Scheme 1e**



**1a**: R = 6-CH$_3$
**1b**: R = H
**1c**: R = 7-OMe
**1d**: R = 6-Cl
**1e**: R = 6-F
**1f**: R = 7-OH

**2a**: Ar = Phenyl
**2b**: Ar = 4-Fluorophenyl
**2c**: Ar = 4-Chlorophenyl
**2d**: Ar = 4-Methylphenyl
**2e**: Ar = 3-Methylphenyl
**2f**: Ar = 2-Naphthyl

**3a-z & 4a-b**
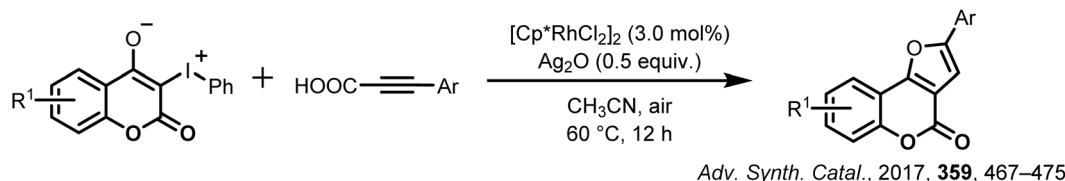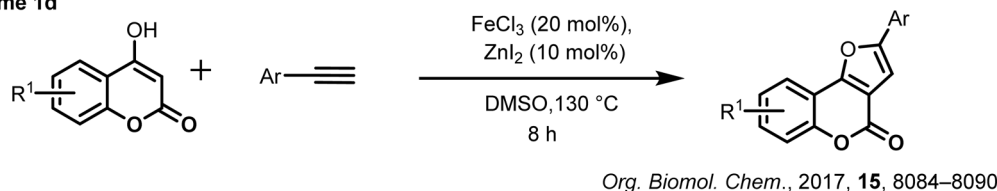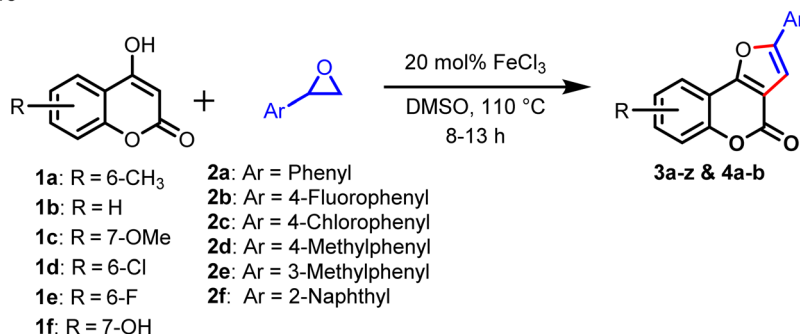
**Scheme 1** Previously reported methods and our synthetic strategy *via* regioselective ring-opening of aryl oxirane with 4-hydroxycoumarin.

showed[17] the tandem cyclization of hypervalent iodine reagent (HIR) derived from 4-hydroxycoumarin with propiolic acids *via* Rh-catalyzed decarboxylation along with Ag$_2$O as a co-catalyst for the synthesis of 4*H*-furo[3,2-*c*]chromen-4-one derivatives (Scheme 1c). In the same year, Hajra *et al.* reported the FeCl$_3$/ ZnI$_2$-catalyzed synthesis of furocoumarin derivatives by intermolecular coupling between 4-hydroxycoumarins and alkynes, in which ZnI$_2$ acted as an additive, as shown in Scheme 1d.[18a] Most of the earlier reported methods involved (directly or indirectly) aryl acetylenes or their derivatives to synthesize furocoumarin derivatives. Apart from aryl acetylenes, Chen *et al.* reported the synthesis of 2-aryl-3-allyl-furo[3,2-*c*]coumarins

using a ZnCl$_2$-mediated three-component reaction using a combination of 4-hydroxycoumarin, arylglyoxal monohydrate, and allyl trimethyl silane in toluene in addition to 2,3-diaryl-furo[3,2-*c*]coumarins by employing 20% mol% FeCl$_3$ as a catalyst. Recently, Choudhary *et al.* explored[18c] the synthesis of 2-aryl-furo[3,2-*c*]coumarins and 2-aryl-3-thioaryl-furo[3,2-*c*]coumarins derivatives depending upon reaction conditions from 4-hydroxycoumarin, arylglyoxal monohydrate, and thiophenol in toluene at 111 °C in the presence of 10 mol% Sc(OTf)$_3$. Due to unique structural features and biological activities, synthesizing these derivatives from the readily available starting materials is highly desirable. Though earlier approaches were

unique and elegant, some methods had certain demerits: the cumbersome procedure for the preparation of pre-functionalized and aryl acetylene is expensive as compared with that for styrene oxide;[16,17] requirement of additives;[18a] harsh and inert atmospheric reaction conditions; requirement of expensive transition-metal catalysts.[17] Consequently, there is scope to develop a new synthetic route, which should be efficient, convenient, reliable, step-economic, and straightforward to produce diverse furocoumarin derivatives. In addition, styrene oxide is a building block for the synthesis of organic molecules.[19]

We report a simple, high-atom-economical, straightforward, and inexpensive method for the synthesis of furocoumarin derivatives from 4-hydroxycoumarin and aryl oxirane *via* intermolecular regioselective ring-opening of an aryl oxirane followed by dehydration and cyclization using 20 mol% FeCl$_3$ as a Lewis-acid catalyst in DMSO (Scheme 1d). Moreover, the yield of the desired product from this protocol was higher than that achieved from earlier reported methods.
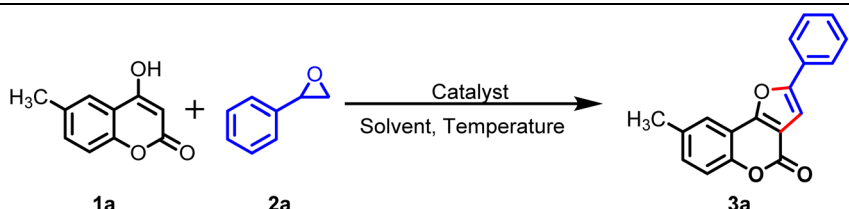
## Results and discussion

At the outset of the present study, model substrates were chosen (4-hydroxy-6-methylcoumarin (**1a**) and styrene oxide (**2a**)) to discover the most suitable reaction conditions. Initially, the reaction was carried out without a catalyst at room temperature and gradually increasing temperature up to 120 °C in DMSO as a solvent (Table 1, entry 1). No desired product was obtained. To ascertain the role of the catalyst, a similar reaction was carried out in the presence of 5 mol% FeCl$_3$ at room temperature for 24 h (Table 1, entry 2), but there was no progress in the reaction. Then, the same reaction mixture was placed in a pre-heated oil bath at 60 °C and was heated for 15 h (Table 1, entry 3): the desired product (**3a**) was isolated in 15% yield. The product **3a** was confirmed from spectra (IR, $^1$H, and $^{13}$C NMR) and HRMS. In the $^1$H NMR spectrum, the characteristic peak at $\delta$ 5.6 ppm for the H-3 group of compound **1a** and the peaks at $\delta$ 3.82, $\delta$ 3.09, and $\delta$ 2.76 for the protons in the epoxide disappeared, and a new peak at $\delta$ 7.18 appeared for the H-3 group of the desired product **3a**.

In the $^{13}$C-NMR spectrum, the peaks $\delta$ 51.9 and $\delta$ 50.8 for the epoxide carbon disappeared. In addition, the HRMS value of product **3a** gave 277.0859 instead of the expected value of 277.0860, further indicating the formation of the desired product **3a**. The role of temperature was also examined to improve the yield of the desired product. As we increased the temperature, the yield of (**3a**) increased significantly at 110 °C, and the desired product (**3a**) was obtained at 62% yield (Table 1, entries 4–7). Further increases in the temperature did not increase the yield of the desired product. The yield was reduced markedly above 140 °C and provided an inseparable mixture of products (which may have been due to decomposition). Next, the amount of catalyst required was examined, and the reaction was carried out using 10%, 20%, and 30 mol%, respectively (Table 1, entries 8–10). The screening result revealed that the reaction proceeded very well at

**Table 1** Optimization of reaction conditions[a,b]



| Entry | Catalyst | Mol% | Solvent | Time (h) | Temperature (°C) | Yield[b] (%) |
|---|---|---|---|---|---|---|
| 1[c] | — | — | DMSO | 24 | RT → 120 | ND |
| 2[c] | FeCl$_3$ | 5 | DMSO | 24 | RT | ND |
| 3 | FeCl$_3$ | 5 | DMSO | 15 | 60 | 15 |
| 4 | FeCl$_3$ | 5 | DMSO | 15 | 80 | 32 |
| 5 | FeCl$_3$ | 5 | DMSO | 13 | 100 | 45 |
| 6 | FeCl$_3$ | 5 | DMSO | 10 | 110 | 62 |
| 7 | FeCl$_3$ | 5 | DMSO | 10 | 120 | 59 |
| 8 | FeCl$_3$ | 10 | DMSO | 9 | 110 | 72 |
| **9** | **FeCl$_3$** | **20** | **DMSO** | **8** | **110** | **89** |
| 10 | FeCl$_3$ | 30 | DMSO | 8 | 110 | 88 |
| 11 | FeCl$_3$ | 20 | DMF | 8 | 110 | 56 |
| 12 | FeCl$_3$ | 20 | Toluene | 8 | 110 | 22 |
| 13 | FeCl$_3$ | 20 | Methanol | 8 | 110 | 18 |
| 14 | CoCl$_2$ | 20 | DMSO | 10 | 110 | 45 |
| 15 | CuCl$_2$ | 20 | DMSO | 10 | 110 | 23 |
| 16 | CSA(±) | 20 | DMSO | 10 | 110 | ND |

[a] Reaction conditions: all reactions were undertaken using 4-hydroxy-6-methylcoumarin (**1a**, 1.0 mmol) and styrene oxide (**2a**, 1.0 mmol). [b] Isolated yield. [c] Reaction carried out at room temperature. NR: no reaction; ND: no desired product.

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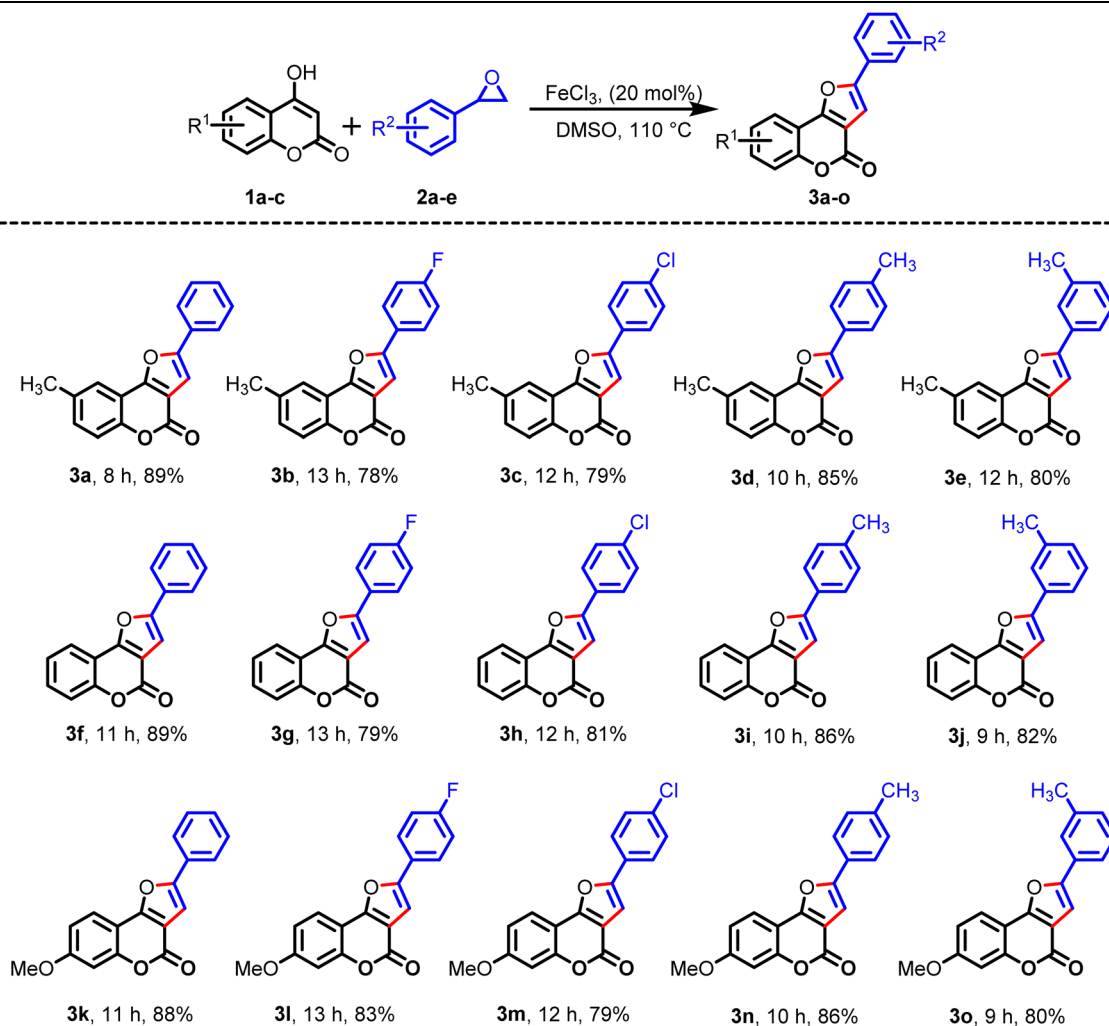*Org. Biomol. Chem.*, 2024, **22**, 95–105 | **97**

20 mol% of catalyst, and the desired product was isolated in 89% yield (Table 1, entry 9). To examine the suitability of other solvents, the reactions were carried out in DMF, toluene, and methanol (Table 1, entries 11–13). DMSO was the best solvent in terms of yield and reaction time. Motivated by this result, we carried out a reaction with other metal-chloride catalysts such as $CoCl_2$, and $CuCl_2$, and the yield obtained was 45% and 23%, respectively (Table 1, entries 14 and 15). However, no desired product (ND) was obtained in the presence of (±) CSA (Table 1, entry 16). After scrutinizing all the parameters, it was concluded that 20 mol% $FeCl_3$ was the most effective catalyst at 110 °C in DMSO for this particular transformation.

After optimizing the reaction conditions, the scope and practicability of the reaction procedure stated above were investigated with various substituted 4-hydroxycoumarins and styrene oxides, as shown in Table 2.
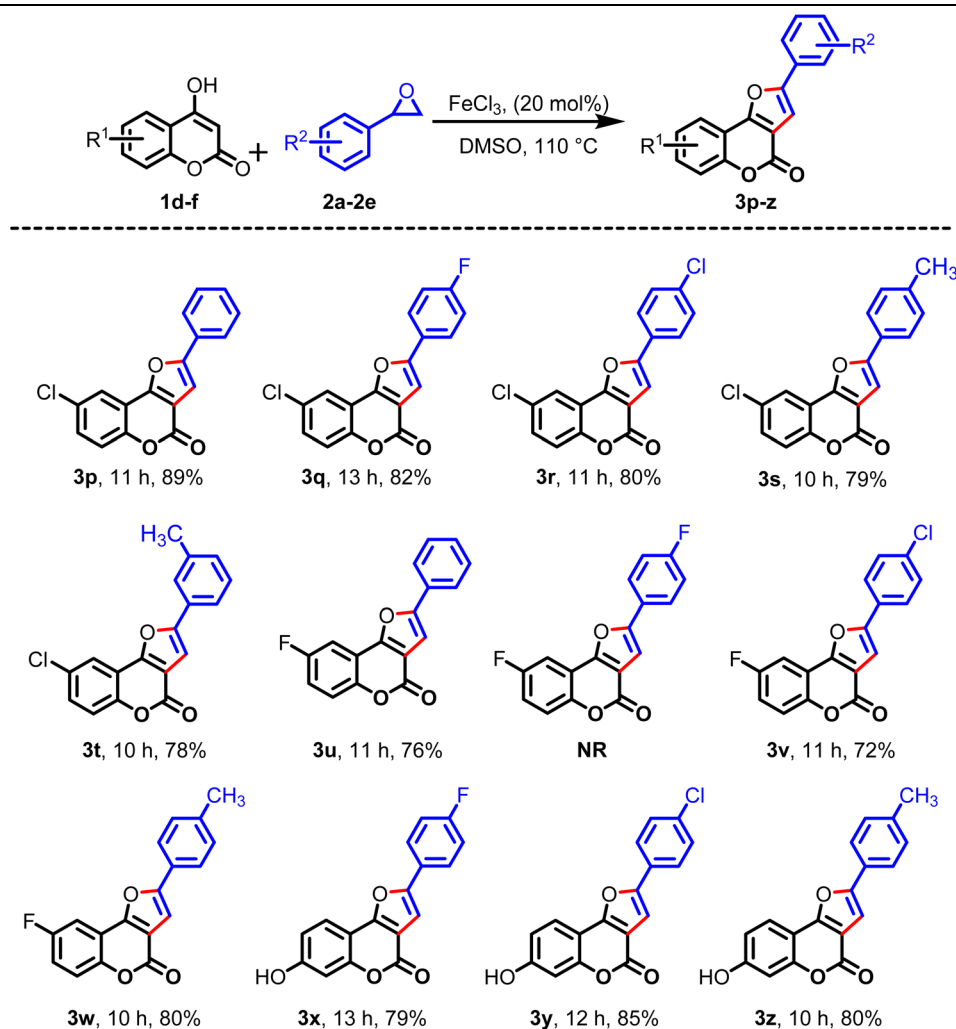
Then, the substrate scope of electron-rich 4-hydroxy-6-methylcoumarin (**1a**) was investigated with readily available 4-fluoro styrene oxide (**2b**) and 4-chloro styrene oxide (**2c**), and the expected products (**3b**) and (**3c**) were isolated in 78% and 79% yield, respectively. Subsequently, the reactions were examined with 4-hydroxy-6-methylcoumarin (**1a**) with the freshly prepared styrene oxides **2d** and **2e** under identical reaction conditions, and the desired products **3d** and **3e** were isolated in good yields. Notably, the styrene oxides having electron-withdrawing groups at the *para*-position, such as fluoro (**2b**) and chloro (**2c**), gave the cyclized products (**3b**) and (**3c**) in good-to-excellent yields. Similarly, the styrene oxide containing an electron-donating methyl group at the *para* (**2d**) and *ortho* (**2e**) positions provided the desired products **3d** and **3e** in good yields. To examine the generality of this protocol, similar reactions were examined with 4-hydroxy-coumarin (**1b**) with the five styrene oxides (**2a–e**) and afforded the desired products **3f–j** in 89–79% yields. Likewise, 4-hydroxy-7-methoxycoumarin (**1c**) proceeded well with the styrene oxides (**2a–e**) to furnish the corresponding expected products **3k–3o** in 79%–88% yields.

**Table 2** Substrate scope of furocoumarin scaffolds[a,b]



**3a**, 8 h, 89%    **3b**, 13 h, 78%    **3c**, 12 h, 79%    **3d**, 10 h, 85%    **3e**, 12 h, 80%

**3f**, 11 h, 89%    **3g**, 13 h, 79%    **3h**, 12 h, 81%    **3i**, 10 h, 86%    **3j**, 9 h, 82%

**3k**, 11 h, 88%    **3l**, 13 h, 83%    **3m**, 12 h, 79%    **3n**, 10 h, 86%    **3o**, 9 h, 80%

[a] Reaction conditions: all reactions were performed using 4-hydroxycoumarins (**1a–c**, 1.0 mmol) and styrene oxides (**2a–e**, 1.0 mmol) in the presence of $FeCl_3$ in 2 mL of DMSO at 110 °C. [b] Isolated yield.
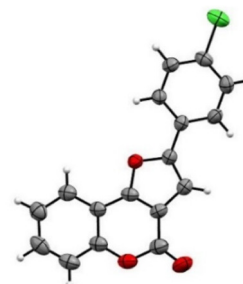
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**Table 3**  Substrate scope of furocoumarin scaffolds[a,b]



**3p**, 11 h, 89%    **3q**, 13 h, 82%    **3r**, 11 h, 80%    **3s**, 10 h, 79%

**3t**, 10 h, 78%    **3u**, 11 h, 76%    **NR**    **3v**, 11 h, 72%

**3w**, 10 h, 80%    **3x**, 13 h, 79%    **3y**, 12 h, 85%    **3z**, 10 h, 80%

[a] Reaction conditions: all reactions were performed using substituted 4-hydroxycoumarin (**1d–f**, 1.0 mmol) and substituted styrene oxide (**2a–e**, 1.0 mmol) in the presence of FeCl₃ in 2 mL of DMSO at 110 °C. [b] Isolated yield. NR: no reaction.

**Table 4**  Substrate scope of furocoumarin scaffolds[a,b]
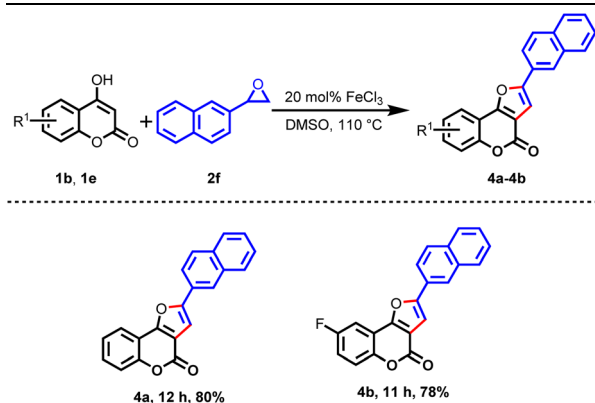


**4a, 12 h, 80%**    **4b, 11 h, 78%**

[a] Reaction conditions: all reactions were performed using substituted 4-hydroxycoumarin (**1b** and **1e**, 1.0 mmol) and 2-naphthyl oxirane (**2f**, 1.0 mmol) in the presence of FeCl₃ in 2 mL of DMSO at 110 °C. [b] Isolated yield.

Subsequently, the cyclization reaction was scrutinized with 4-hydoxycoumarin having an electron-withdrawing group at the sixth position, such as chloro (**1d**) and fluoro (**1e**), under similar reaction conditions. From these studies, the desired products **3p–3s** and **3t–3w** were obtained in fairly good yields,



**Fig. 2**  ORTEP diagram of product **3h**.

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as shown in Table 3. To enrich the diversity of products, the reactions were also examined with 4,7-dihydroxy coumarin (**1f**) and substituted styrene oxides **2b**, **2c**, and **2d**, and the desired products **3x**, **3y**, and **3z** were isolated in 79%, 85%, and 80% yields, respectively. To further check the practicability of the this procedure, the reaction was scrutinized with polyaromatic 2-naphthyl oxirane (**2f**) and 4-hydroxycoumarin (**1b**), and the

desired product **4a** was obtained in 80% yield. Likewise, the reaction between **2f** and 6-fluoro-4-hydroxycoumarin (**1e**) provided the desired product **4b** in 78% yield under identical reaction conditions, as depicted in Table 4.
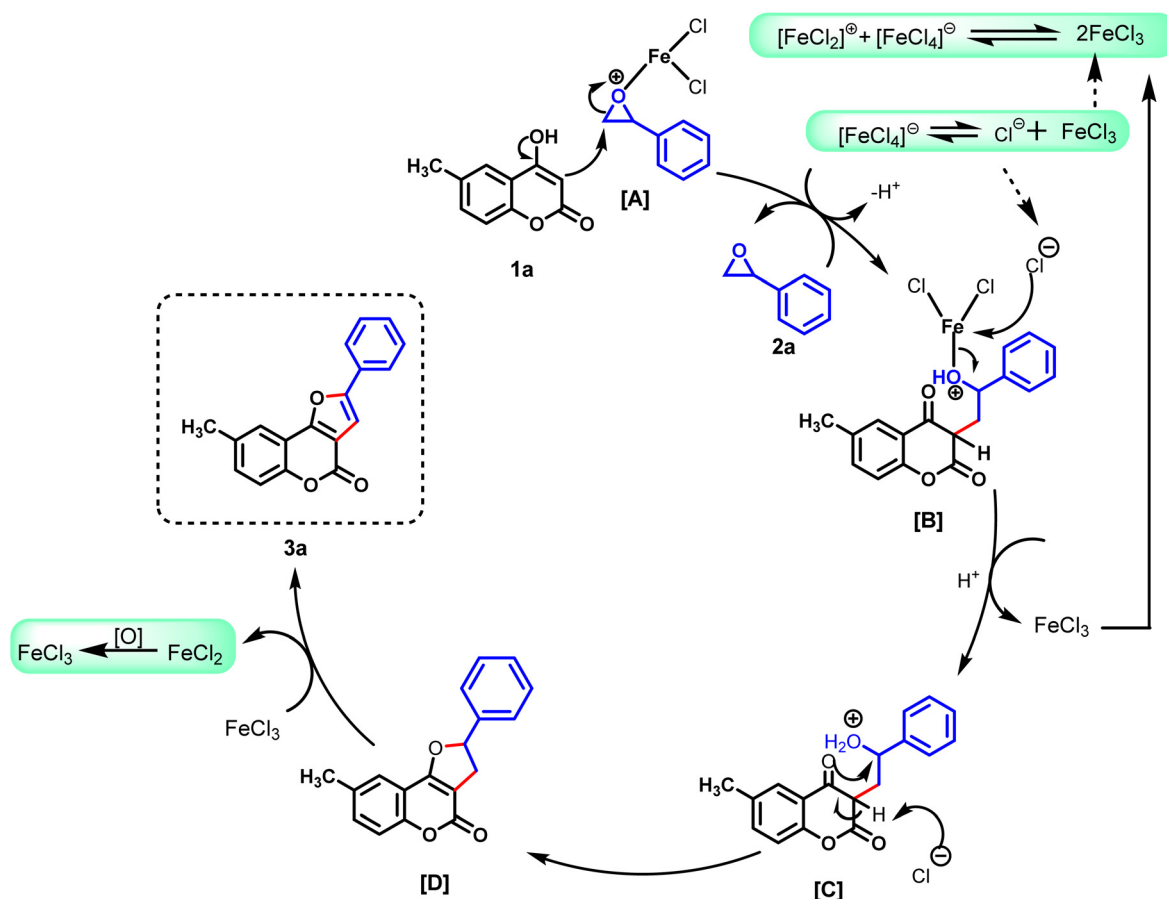
All products were characterized using spectroscopy (IR, $^1$H-NMR, and $^{13}$C-NMR) as well as HRMS. To ascertain the regioselective opening of the styrene oxide, the product **3h** was also confirmed with a single XRD datum. The ORTEP diagram of compound **3h** is depicted in Fig. 2.

To ascertain if the reaction was going through a radical pathway, a control experiment was performed with 6-methyl-4-hydroxycoumarin (**1a**) and styrene oxide (**2a**) in the presence of the radical inhibitor (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO, 1 equiv.), which is shown in Scheme 2. Experimental results revealed that the product **3a** was isolated in 62% yield. Next, we prepared substrate **5** by another route, and we examined the cyclization reaction under identical reaction conditions in the presence of the catalyst (20 mol% FeCl$_3$). However, we did not obtain the expected cyclized product **3g**. From these two observations, we concluded that the reaction did not go through a radical pathway or through intermediate **5**.

The formation of the product could be explained. In 1964, Swanson and Laurie reported that FeCl$_3$ could undergo a dis-
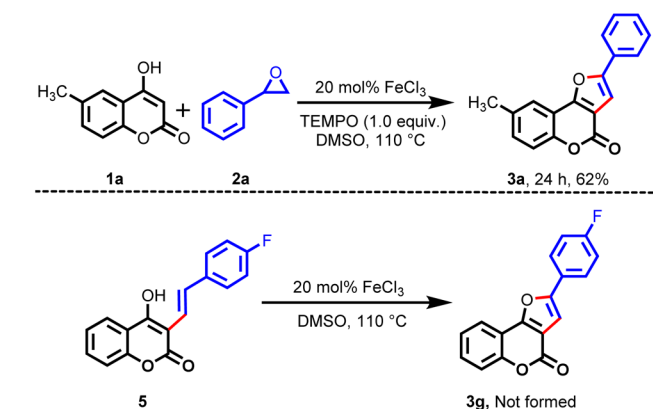


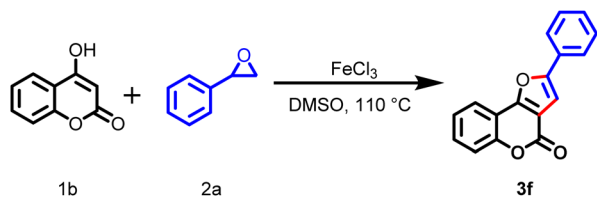Scheme 2 Control experiment.



Scheme 3 A plausible mechanism for the synthesis of furocoumarin derivatives.

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**Scheme 4** Large-scale reaction between 4-hydroxycoumarin (**1b**) with styrene oxide (**2a**).

proportionate reaction to give reactive Lewis-acid species $[FeCl_2]^+$ and $[FeCl_4]^-$ in polar solvents such as DMF, pyridine, and DMSO.[21] In 2018, Matsubara *et al.* demonstrated that FeCl_3 acted as an ion-pairing Lewis-acid catalyst for the aza-Diels–Alder reaction.[15d] Based on their observations, we postulated a mechanism for formation of the desired product, as shown in Scheme 3. Initially, styrene oxide reacts with the reactive species $[FeCl_2]^+$ to give the highly reactive intermediate **A**. Subsequently, intermediate **A** reacts with 4-hydroxy-6-methyl-coumarin (**1a**) to provide intermediate **B** by regioselective epoxide ring-opening at the less hindered site of styrene oxide (**2a**).[13–15] Then, the chloride anion (Cl$^-$), obtained from $[FeCl_4]^-$, assists in breaking of the Fe–O bond to provide the intermediate **C**. Next, Cl$^-$ removes the hydrogen atom from intermediate **C**, which generates the negatively charged oxygen atom, which facilitates the cyclization of intermediate **C** by eliminating one molecule of water to provide the cyclized intermediate **D**. Finally, the cyclized intermediate **D** undergoes oxidation by FeCl_3 to form the desired product **3a**. Simultaneously, the reduced FeCl_2 undergoes aerial oxidation to FeCl_3, and participates in the catalytic cycle. The unsuccessful result of the reaction between **1e** and **2c** may not occur. This is probably because of an electron-withdrawing group on both rings. Cyclization of the intermediate **C** is not facilitated if both rings contain a strong electron-withdrawing group because a lone pair of oxygen atoms is not readily available to attack the carbon atom to cyclize.

A large-scale reaction (0.810 g, 5 mmol) was examined with 4-hydroxycoumarin (**1a**) and styrene oxide (**2a**). The desired product **3f** was obtained at 1.012 g (97%) along with the recovery of 0.168 g of 4-hydroxycoumarin (**1a**). The yield was calculated based on recovery of the starting material (Scheme 4).

## Conclusions

We demonstrated that the regioselective ring-opening of aryl oxirane with 4-hydroxycoumarins was a useful reaction for synthesizing 2-Aryl-4*H*-furo[3,2-*c*]coumarin derivatives. The catalyst FeCl_3 had unique features: it acted as a Lewis acid and existed in an ion-pair form in the solvent. The product was created through formation of a *C–C* bond between the H-3 C of 4-hydroxycoumarin and the less hindered site of the styrene oxide, followed by concomitant cyclization with the elimination of water molecules. Product formation proceeded

through a cascade reaction, such as intermolecular coupling–dehydration–cyclization. The advantages of this protocol were: no need for derivatization of 4-hydroxycoumarin required for incorporation of arylacetylene at the *C*-3 position; non-requirement of any additive; easy handling; mild reaction conditions; high regioselectivity; no need for additives or ligands. Furthermore, diverse furocoumarins were developed using this protocol. This novel synthetic approach might attract attention from pharmaceutical and fine-chemical industries, and may be considered a "greener" approach compared with strategies reported previously.

### General procedure for the synthesis of aryl oxirane (2d–2f)[20]

In a 100 mL dry round-bottomed flask, the corresponding substituted styrene (5 mmol) was taken in 25 mL of dichloromethane. The reaction flask was placed in an ice bath at 0–5 °C. Then, *m*-chloroperbenzoic acid (*m*-CPBA) was added in portions for 30 min at the ice-bath temperature. After 2 h of stirring at 0–5 °C, the reaction was brought slowly to room temperature and stirred for an additional 6 h. The resulting mixture was passed through a filter paper. The solvent was concentrated using a rotatory evaporator. The crude residue was separated by column chromatography (silica gel at 60–120 mesh).

### General procedure for the synthesis of furocoumarin derivatives 3a–3z and 4a–4b

In a dry 25 mL round-bottomed flask, 4-hydroxycoumarin (1, 1.0 mmol) and styrene oxide (2, 1.0 mmol) were dissolved in 2 mL of DMSO. Then, the catalyst (20 mol% FeCl_3) was added to the reaction mixture and placed in a pre-heated oil bath at 110 °C with constant stirring under an air atmosphere. The progress of the reaction was monitored by checking TLC occasionally. After completion of the reaction, the reaction mixture became a Castleton Green color. Then, the reaction was brought to room temperature, and the resulting mixture was diluted with 10 mL of DCM. The organic layer was washed with brine solution (5 mL × 2). The organic extract was dried over anhydrous sodium sulfate, and the solvent was removed in a rotary evaporator. Finally, the crude residue was passed through a silica-gel column (mesh of 60–120) to obtain the pure and desired products.

### 8-Methyl-2-phenyl-4*H*-furo[3,2-*c*]chromen-4-one (3a)

White solid (245.70 mg, 89%) mp 185–186 °C (lit. mp. 187–188 °C).[18] $^1$H NMR (600 MHz, CDCl_3) $\delta$ 7.82 (d, *J* = 7.8 Hz, 2H), 7.75 (s, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.41–7.39 (m, 1H), 7.34 (q, *J* = 8.6 Hz, 2H), 7.18 (s, 1H), 2.49 (s, 3H); $^{13}$C NMR (150 MHz, CDCl3) $\delta$ 158.6, 157.1, 156.6, 151.0, 134.6, 131.8, 129.2, 129.1, 129.1, 124.7, 120.6, 117.2, 112.5, 112.5, 102.8, 21.1; IR (KBr) $\nu_{max}$/cm$^{-1}$ 1745 (C=O), 1622 (C=C), 1310 (C–O); HRMS (ESI) calcd for $C_{18}H_{13}O_3$ 277.0860 (M + H$^+$); found 277.0859.

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### 2-(4-Fluorophenyl)-8-methyl-4*H*-furo[3,2-*c*]chromen-4-one (3b)

White solid (229.37 mg, 78%) mp 215–216 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.79 (ddd, $J$ = 8.8, 5.0, 2.5 Hz, 2H), 7.72 (s, 1H), 7.33 (d, $J$ = 2.1 Hz, 2H), 7.17 (t, $J$ = 8.6 Hz, 2H), 7.10 (s, 1H), 2.48 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.2 ($J_{C-F}$ = 248 Hz), 162.0, 158.5, 157.1, 155.6, 150.9, 134.6, 131.9, 126.6 ($J_{C-F}$ = 8.2 Hz), 125.5 ($J_{C-F}$ = 3.37 Hz), 120.6, 117.3, 116.4, 116.2, 112.5 ($J_{C-F}$ = 8.9 Hz), 102.5 ($J_{C-F}$ = 1.4 Hz), 21.1; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ −111.12; IR (KBr) $\nu_{max}$/cm$^{-1}$ 1740 (C=O), 1620 (C=C), 1290 (C–O); HRMS (ESI) calcd for C$_{18}$H$_{12}$FO$_3$ 295.0765 (M + H$^+$); found 295.0765.

### 2-(4-Chlorophenyl)-8-methyl-4*H*-furo[3,2-*c*]chromen-4-one (3c)

White solid (244.93 mg, 79%) mp 210–212 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.74 (d, $J$ = 8.9 Hz, 3H), 7.45 (d, $J$ = 8.3 Hz, 2H), 7.36–7.33 (m, 2H), 7.16 (s, 1H), 2.48 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 158.4, 157.2, 155.4, 151.0, 135.1, 134.6, 132.0, 129.4, 127.6, 125.8, 120.6, 117.3, 112.5, 112.4, 103.3, 21.1; IR (KBr) $\nu_{max}$/cm$^{-1}$ 1740 (C=O), 1622 (C=C), 1290 (C–O); HRMS (ESI) calcd for C$_{18}$H$_{12}$ClO$_3$ 311.0470 (M + H$^+$); found 311.0465.

### 8-Methyl-2-(*p*-tolyl)-4*H*-furo[3,2-*c*]chromen-4-one (3d)

White solid (246.58 mg, 85%) mp 185–186 °C (lit. mp. 185–187 °C).[18] $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.75 (s, 1H), 7.71 (d, $J$ = 8.1 Hz, 2H), 7.35–7.31 (m, 2H), 7.28 (d, $J$ = 8.0 Hz, 2H), 7.11 (s, 1H), 2.48 (s, 3H), 2.42 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 158.7, 156.8, 156.8, 150.9, 139.4, 134.5, 131.6, 129.8, 126.4, 124.6, 120.6, 117.2, 112.6, 112.5, 102.0, 21.5, 21.1; IR (KBr) $\nu_{max}$/cm$^{-1}$ 1735 (C=O), 1600 (C=C), 1280 (C–O); HRMS (ESI) calcd for C$_{18}$H$_{13}$O$_3$ 291.1016 (M + H$^+$); found 291.1035.

### 8-Methyl-2-(*m*-tolyl)-4*H*-furo[3,2-*c*]chromen-4-one (3e)

White solid (232.07 mg, 80%) mp 238–240 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.77 (s, 1H), 7.64–7.62 (m, 2H), 7.38–7.33 (m, 3H), 7.21 (d, $J$ = 7.6 Hz, 1H), 7.16 (s, 1H), 2.49 (s, 3H), 2.45 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.3, 158.6, 157.0, 156.8, 151.0, 138.9, 134.5, 131.8, 130.0, 129.0, 125.2, 121.9, 120.7, 117.2, 112.6, 112.6, 102.7, 21.6, 21.1; IR (KBr) $\nu_{max}$/cm$^{-1}$ 1750 (C=O), 1580 (C=C), 1280 (C–O); HRMS (ESI) calcd for C$_{18}$H$_{13}$O$_3$ 291.1016 (M + H$^+$); found 291.1043.

### 2-Phenyl-4*H*-furo[3,2-*c*]chromen-4-one (3f)

White solid (233.23 mg, 89%) mp 184–185 °C (lit. mp. 186–187 °C).[18] $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.98 (dd, $J$ = 7.8, 1.4 Hz, 1H), 7.84–7.82 (m, 2H), 7.56–7.50 (m, 2H), 7.49–7.46 (m, 2H), 7.43–7.37 (m, 2H), 7.19 (s, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 158.4, 157.0, 156.8, 152.7, 130.7, 129.33, 129.2, 129.1, 124.7, 124.7, 120.9, 117.5, 112.9, 112.6, 102.8; IR (KBr) $\nu_{max}$/cm$^{-1}$ 1742 (C=O), 1622 (C=C), 1250 (C–O); HRMS (ESI) calcd for C$_{17}$H$_{11}$O$_3$ 263.0703 (M + H$^+$); found 263.0681.

### 2-(4-Fluorophenyl)-4*H*-furo[3,2-c]chromen-4-one (3g)

White solid (221.24 mg, 79%) mp 192–196 °C (lit. mp. 210–215 °C).[18] $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.95 (d, $J$ = 7.7 Hz, 1H), 7.80 (dd, $J$ = 8.6, 5.2 Hz, 2H), 7.55–7.52 (m, 1H), 7.47 (d, $J$ = 8.3 Hz, 1H), 7.39 (t, $J$ = 7.5 Hz, 1H), 7.18 (t, $J$ = 8.6 Hz, 2H), 7.13 (s, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 163.3 ($J_{C-F}$ = 248.7 Hz), 158.3, 157.0, 155.8, 152.7, 130.8, 126.7($J_{C-F}$ = 8.2 Hz), 125.4 ($J_{C-F}$ = 3.3 Hz), 124.7, 120.9, 117.6, 116.4 ($J_{C-F}$ = 22 Hz), 112.8, 112.6, 102.5 ($J_{C-F}$ = 1.0 Hz); $^{19}$F NMR (565 MHz, CDCl$_3$) $\delta$ −110.99; IR (KBr) $\nu_{max}$/cm$^{-1}$ 1750 (C=O), 1590 (C=C), 1280 (C–O); HRMS (ESI) calcd for C$_{17}$H$_{10}$FO$_3$ 281.0609 (M + H$^+$); found 281.0609.

### 2-(4-Chlorophenyl)-4*H*-furo[3,2-*c*]chromen-4-one (3h)

White solid (239.77 mg, 81%) mp 248–250 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.96 (d, $J$ = 7.8 Hz, 1H), 7.75 (d, $J$ = 8.4 Hz, 2H), 7.54 (t, $J$ = 7.8 Hz, 1H), 7.46 (t, $J$ = 7.6 Hz, 3H), 7.39 (t, $J$ = 7.5 Hz, 1H), 7.18 (s, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 158.2, 157.2, 155.6, 152.8, 135.2, 131.0, 129.5, 127.6, 125.9, 124.8, 120.9, 117.6, 112.8, 112.7, 103.3; IR (KBr) $\nu_{max}$/cm$^{-1}$ 1736 (C=O), 1620 (C=C), 1280 (C–O); HRMS (ESI) calcd for C$_{17}$H$_{10}$ClO$_3$ 297.0313 (M + H$^+$); found 297.0313.

### 2-(*p*-Tolyl)-4*H*-furo[3,2-*c*]chromen-4-one (3i)

White solid (237.42 mg, 86%) mp 186–188 °C (lit. mp. 190–192 °C).[18] $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.98–7.96 (m, 1H), 7.71 (d, $J$ = 8.2 Hz, 2H), 7.53 (ddd, $J$ = 8.6, 7.2, 1.5 Hz, 1H), 7.48–7.45 (m, 1H), 7.40–7.36 (m, 1H), 7.29 (d, $J$ = 8.0 Hz, 2H), 7.13 (s, 1H), 2.42 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.5, 157.0, 156.8, 156.4, 152.7, 139.5, 130.6, 129.8, 126.4, 124.7, 120.9, 117.5, 113.0, 112.6, 102.0, 21.5; IR (KBr) $\nu_{max}$/cm$^{-1}$ 1743 (C=O), 1585 (C=C), 1200 (C–O); HRMS (ESI) calcd for C$_{18}$H$_{13}$O$_3$ 277.0860 (M + H$^+$); found 277.0860.

### 2-(*m*-Tolyl)-4*H*-furo[3,2-*c*]chromen-4-one (3j)

White solid (226.38 mg, 82%) mp 168–169 °C (lit. mp. 168–170 °C).[18] $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.99 (dd, $J$ = 7.8, 1.4 Hz, 1H), 7.63 (d, $J$ = 8.2 Hz, 2H), 7.56–7.51 (m, 1H), 7.48–7.46 (m, 1H), 7.41–7.35 (m, 2H), 7.22 (d, $J$ = 7.3 Hz, 1H), 7.17 (s, 1H), 2.45 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 175.1, 152.7, 138.9, 130.7, 130.7, 130.1, 129.1, 129.0, 128.6, 125.3, 124.7, 121.9, 120.9, 117.5, 112.9, 112.6, 102.7, 21.6; IR (KBr) $\nu_{max}$/cm$^{-1}$ 1743 (C=O), 1585 (C=C), 1200 (C–O); HRMS (ESI) calcd for C$_{18}$H$_{13}$O$_3$ 277.0860 (M + H$^+$); found 277.0862.

### 7-Methoxy-2-phenyl-4*H*-furo[3,2-*c*]chromen-4-one (3k)

White solid (257.02 mg, 88%) mp 172–173 °C (lit.[16] mp. 170–172 °C). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.86 (d, $J$ = 9.3 Hz, 1H), 7.81–7.79 (m, 2H), 7.47 (t, $J$ = 7.7 Hz, 2H), 7.38 (t, $J$ = 7.4 Hz, 1H), 7.15 (s, 1H), 6.97 (dq, $J$ = 4.0, 2.3 Hz, 2H), 3.91 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 162.1, 158.7, 157.9, 157.8, 155.9, 154.6, 129.3, 129.1, 129.0, 124.5, 121.9, 113.0, 106.3, 102.6, 101.6, 55.9; IR (KBr) $\nu_{max}$/cm$^{-1}$ 1740 (C=O), 1622 (C=C), 1300 (C–O); HRMS (ESI) calcd for C$_{18}$H$_{13}$O$_4$ 293.0809 (M + H$^+$); found 293.0810.

### 2-(4-Fluorophenyl)-7-methoxy-4*H*-furo[3,2-*c*]chromen-4-one (3l)

White solid (257.35 mg, 83%) mp 220–221 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.84 (d, $J$ = 9.3 Hz, 1H), 7.79–7.76 (m, 2H),

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7.17 (t, $J$ = 8.7 Hz, 2H), 7.08 (s, 1H), 6.98–6.95 (m, 2H), 3.90 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.3, 162.1, 158.7, 157.7, 154.9, 154.5, 126.4 ($J_{C-F}$ = 8.26 Hz), 125.6 ($J_{C-F}$ = 1.58 Hz), 121.8, 116.3 ($J_{C-F}$ = 22.1 Hz), 113.1, 110.1, 106.2, 102.3 ($J_{C-F}$ = 1.29 Hz), 101.6, 55.9; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ −111.47. IR (KBr) $\nu_{max}$/cm$^{-1}$ 1735 (C=O), 1592 (C=C), 1285 (C–O); HRMS (ESI) calcd for C$_{18}$H$_{12}$FO$_4$ 311.0715 (M + H$^+$); found 311.0716.

### 2-(4-Chlorophenyl)-7-methoxy-4*H*-furo[3,2-*c*]chromen-4-one (3m)

White solid (257.56 mg, 79%) mp 218–220 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.86–7.84 (m, 1H), 7.74–7.71 (m, 2H), 7.46–7.43 (m, 2H), 7.14 (s, 1H), 6.97 (dd, $J$ = 6.3, 2.4 Hz, 2H), 3.91 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$, 162.3, 158.5, 157.9, 154.7, 154.6, 134.8, 129.4, 127.7, 125.7, 121.9, 113.1, 110.1, 106.1, 103.1, 101.6, 55.9; IR (KBr) $\nu_{max}$/cm$^{-1}$ 1735 (C=O), 1592 (C=C), 1285 (C–O); HRMS (ESI) calcd for C$_{18}$H$_{12}$ClO$_4$ 327.0419 (M + H$^+$); found 327.0419.

### 7-Methoxy-2-(*p*-tolyl)-4*H*-furo[3,2-*c*]chromen-4-one (3n)

White solid (263.23 mg, 86%) mp 225–226 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.86–7.85 (m, 1H), 7.68 (d, $J$ = 8.1 Hz, 2H), 7.28–7.26 (m, 2H), 7.08 (s, 1H), 6.96 (dq, $J$ = 4.4, 2.3 Hz, 2H), 3.90 (s, 3H), 2.41 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 162.0, 158.8, 157.5, 156.1, 154.4, 139.1, 129.8, 126.5, 124.5, 121.8, 113.0, 110.2, 106.4, 101.8, 101.6, 55.9, 21.5; IR (KBr) $\nu_{max}$/cm$^{-1}$ 1738 (C=O), 1622 (C=C), 1310 (C–O); HRMS (ESI) calcd for C$_{19}$H$_{15}$O$_4$ 307.0965 (M + H$^+$); found 307.0965.

### 7-Methoxy-2-(*m*-tolyl)-4*H*-furo[3,2-*c*]chromen-4-one (3o)

White solid (244.87 mg, 80%) mp 228–230 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.88–7.87 (m, 1H), 7.60 (d, $J$ = 11.5 Hz, 2H), 7.36 (t, $J$ = 7.6 Hz, 1H), 7.20 (d, $J$ = 7.6 Hz, 1H), 7.13 (s, 1H), 6.97 (dq, $J$ = 4.3, 2.3 Hz, 2H), 3.90 (s, 3H), 2.44 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 162.1, 158.8, 157.7, 156.0, 154.5, 138.8, 129.8, 129.2, 129.0, 125.1, 121.9, 121.78, 113.0, 110.1, 106.4, 102.5, 101.6, 55.9, 21.6; IR (KBr) $\nu_{max}$/cm$^{-1}$ 1738 (C=O), 1622 (C=C), 1310 (C–O); HRMS (ESI) calcd for C$_{19}$H$_{15}$O$_4$ 307.0965 (M + H$^+$); found 307.0965.

### 8-Chloro-2-phenyl-4*H*-furo[3,2-*c*]chromen-4-one (3p)

White solid (263.46 mg, 89%) mp 215–216 °C (lit. mp. 215–216 °C).[16] $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.94 (d, $J$ = 2.4 Hz, 1H), 7.83–7.81 (m, 2H), 7.50–7.46 (m, 3H), 7.43–7.40 (m, 2H), 7.19 (s, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 157.7, 157.4, 155.6, 151.0, 130.6, 130.3, 129.6, 129.2, 128.8, 124.8, 120.4, 118.9, 113.9, 113.4, 102.9; IR (KBr) $\nu_{max}$/cm$^{-1}$ 1745 (C=O), 1583 (C=C), 1296 (C–O); HRMS (ESI) calcd for C$_{17}$H$_{10}$ClO$_3$ 297.0313 (M + H$^+$); found 297.0313.

### 8-Chloro-2-(4-fluorophenyl)-4*H*-furo[3,2-*c*]chromen-4-one (3q)

White solid (257.49 mg, 82%) mp 234–235 °C (lit. mp. 234 °C).[18] $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.92 (d, $J$ = 2.4 Hz, 1H), 7.82–7.79 (m, 2H), 7.48 (dd, $J$ = 8.9, 2.4 Hz, 1H), 7.41 (d, $J$ = 8.9 Hz, 1H), 7.19 (t, $J$ = 8.7 Hz, 2H), 7.13 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.4 ($J_{C-F}$ = 249.09 Hz), 157.7, 156.5, 155.6, 151.0, 130.7, 130.3, 126.8 ($J_{C-F}$ = 8.34 Hz), 125.1 ($J_{C-F}$ = 3.37 Hz), 120.4, 119.0, 116.5 ($J_{C-F}$ = 33.12 Hz), 113.8, 113.4, 102.6 ($J_{C-F}$ = 1.44 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ −110.45; IR (KBr) $\nu_{max}$/cm$^{-1}$ 1732 (C=O), 1580 (C=C), 1256 (C–O); HRMS (ESI) calcd for C$_{17}$H$_9$ClFO$_3$ 315.0219 (M + H$^+$); found 315.0213.

### 8-Chloro-2-(4-chlorophenyl)-4*H*-furo[3,2-*c*]chromen-4-one (3r)

White solid (263.98 mg, 80%) mp 262–263 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.93 (d, $J$ = 2.4 Hz, 1H), 7.76–7.74 (m, 2H), 7.49–7.46 (m, 3H), 7.41 (d, $J$ = 8.8 Hz, 1H), 7.18 (s, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 157.6, 156.3, 155.8, 151.1, 135.5, 130.8, 130.4, 129.5, 127.3, 126.0, 120.5, 119.0, 113.8, 113.4, 103.3; IR (KBr) $\nu_{max}$/cm$^{-1}$ 1732 (C=O), 1582 (C=C), 1256 (C–O); HHRMS (ESI) calcd for C$_{17}$H$_9$Cl$_2$O$_3$ 330.9924 (M + H$^+$); found 331.0257.

### 8-Chloro-2-(*p*-tolyl)-4*H*-furo[3,2-*c*]chromen-4-one (3s)

White solid (244.93 mg, 79%) mp 212–213 °C. $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ 7.99 (dd, $J$ = 8.5, 3.0 Hz, 1H), 7.92–7.90 (m, 2H), 7.57 (d, $J$ = 3.2 Hz, 1H), 7.41 (d, $J$ = 7.9 Hz, 2H), 7.01 (d, $J$ = 8.6 Hz, 1H), 6.96 (s, 1H), 2.44 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 160.5, 157.7, 157.2, 155.0, 154.0, 138.6, 129.7, 126.1, 124.2, 122.2, 113.6, 108.8, 104.3, 103.0, 102.2, 21.0. IR (KBr) $\nu_{max}$/cm$^{-1}$ 1745 (C=O), 1622 (C=C), 1310 (C–O); HRMS (ESI) calcd for C$_{18}$H$_{12}$ClO$_3$ 311.0470 (M + H$^+$); found 311.0708.

### 8-Chloro-2-(*m*-tolyl)-4*H*-furo[3,2-*c*]chromen-4-one (3t)

White solid (241.83 mg, 78%) mp 212–213 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.95 (d, $J$ = 2.3 Hz, 1H), 7.64–7.62 (m, 2H), 7.47 (dd, $J$ = 8.8, 2.4 Hz, 1H), 7.41–7.36 (m, 2H), 7.24 (d, $J$ = 7.8 Hz, 1H), 7.17 (s, 1H), 2.45 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 159.6, 157.8, 157.6, 155.6, 151.0, 139.0, 130.6, 130.4, 130.3, 129.1, 128.7, 125.4, 122.0, 120.6, 120.4, 118.9, 102.7, 29.8; IR (KBr) $\nu_{max}$/cm$^{-1}$ 1745 (C=O), 1610 (C=C), 1265 (C–O); HRMS (ESI) calcd for C$_{18}$H$_{12}$ClO$_3$ 311.0470 (M + H$^+$); found 311.0595.

### 8-Fluoro-2-phenyl-4*H*-furo[3,2-*c*]chromen-4-one (3u)

White solid (212.84 mg, 76%) mp 179–180 °C (lit. mp. 178.3–179.1 °C).[17] $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.83–7.82 (m, 2H), 7.65–7.63 (m, 1H), 7.50 (t, $J$ = 7.6 Hz, 2H), 7.46–7.41 (m, 2H), 7.25–7.23 (m, 1H), 7.20 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.2 ($J_{C-F}$ = 243.91 Hz), 157.8, 156.3 ($J_{C-F}$ = 3.9 Hz), 156.2, 148.9, 135.5, 129.5, 127.3, 126.0, 119.3 ($J_{C-F}$ = 8.58 Hz), 118.3 ($J_{C-F}$ = 24.38 Hz), 113.4, 109.9, 106.8 ($J_{C-F}$ = 25.81) 103.4; $^{19}$F NMR (377 MHz, CDCl$_3$) $\delta$ −116.24; IR (KBr) $\nu_{max}$/cm$^{-1}$ 1732 (C=O), 1580 (C=C), 1260 (C–O); HRMS (ESI) calcd for C$_{17}$H$_{10}$FO$_3$ 281.0609 (M + H$^+$); found 281.0652.

### 2-(4-Chlorophenyl)-8-fluoro-4*H*-furo[3,2-*c*]chromen-4-one (3v)

White solid (226.09 mg, 72%) mp 181–183 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.76–7.74 (m, 2H), 7.62 (dd, $J$ = 7.7, 3.0 Hz, 1H), 7.48–7.46 (m, 2H), 7.45–7.44 (m, 1H), 7.25–7.23 (m, 1H), 7.19 (s, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 159.3 ($J_{C-F}$ = 243.72 Hz), 157.9, 156.3 ($J_{C-F}$ = 2.91 Hz), 156.3, 149.0, 135.6, 129.6,

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127.4, 126.1, 119.4 ($J_{C-F}$ = 8.55 Hz), 118.4 ($J_{C-F}$ = 24.42 Hz), 113.6, 113.5, 106.9 ($J_{C-F}$ = 25.69 Hz), 103.5; $^{19}$F NMR (377 MHz, CDCl$_3$) $\delta$ −116.08; IR (KBr) $\nu_{max}$/cm$^{-1}$ 1736 (C=O), 1595 (C=C), 1293 (C−O); HRMS (ESI) calcd for C$_{17}$H$_9$ClFO$_3$ 315.0219 (M + H$^+$); found 315.0213.

### 8-Fluoro-2-(*p*-tolyl)-4*H*-furo[3,2-*c*]chromen-4-one (3w)

White solid (235.25 mg, 80%) mp 185–186 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.71 (d, $J$ = 8.1 Hz, 2H), 7.62 (dd, $J$ = 7.7, 2.9 Hz, 1H), 7.44 (dd, $J$ = 9.1, 4.2 Hz, 1H), 7.29 (d, $J$ = 8.0 Hz, 2H), 7.23 (td, $J$ = 8.7, 2.9 Hz, 1H), 7.13 (s, 1H), 2.42 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 159.1 ($J_{C-F}$ = 243.48 Hz), 158.1, 157.6, 155.8 ($J_{C-F}$ = 2.76 Hz), 148.7 ($J_{C-F}$ = 2.05 Hz), 139.8, 129.9, 126.1, 124.7, 119.2 ($J_{C-F}$ = 8.62 Hz), 117.9 ($J_{C-F}$ = 24.48 Hz), 113.7 ($J_{C-F}$ = 9.87 Hz), 113.4, 106.7 ($J_{C-F}$ = 25.75 Hz), 102.1, 21.5; $^{19}$F NMR (565 MHz, CDCl$_3$) $\delta$ −116.33. IR (KBr) $\nu_{max}$/cm$^{-1}$ 1745 (C=O), 1622 (C=C), 1310 (C−O); HRMS (ESI) calcd for C$_{18}$H$_{12}$FO$_3$ 295.0765 (M + H$^+$); found 295.0765.

### 2-(4-Fluorophenyl)-7-hydroxy-4*H*-furo[3,2-*c*]chromen-4-one (3x)

White solid (233.87 mg, 79%); mp 198–199 °C. $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ 7.99–7.96 (m, 2H), 7.89 (d, $J$ = 8.3 Hz, 1H), 7.54 (s, 1H), 7.35 (t, $J$ = 9.0 Hz, 2H), 6.92 (dd, $J$ = 8.5, 2.0 Hz, 1H), 6.87 (d, $J$ = 2.3 Hz, 1H); $^{13}$C NMR (150 MHz, DMSO-$d_6$) $\delta$ 162.2 ($J_{C-F}$ = 246.06 Hz), 160.7, 157.6, 157.4, 154.0, 153.8, 126.5 ($J_{C-F}$ = 8.31 Hz), 125.4 ($J_{C-F}$ = 3.03 Hz), 122.3, 116.2 ($J_{C-F}$ = 21.96 Hz), 113.6, 108.8, 104.2, 103.0, 102.9; $^{19}$F NMR (565 MHz, DMSO-$d_6$) $\delta$ −112.06; IR (KBr) $\nu_{max}$/cm$^{-1}$ 3510 (O–H), 1732 (C=O), 1615 (C=C), 1265 (C−O); HRMS (ESI) calcd for C$_{17}$H$_{10}$FO$_4$ 297.0558 (M + H$^+$); found 297.0743.

### 2-(4-Chlorophenyl)-7-hydroxy-4*H*-furo[3,2-*c*]chromen-4-one (3y)

White solid (265.21 mg, 85%); mp 288–290 °C. $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ 7.96 (d, $J$ = 8.5 Hz, 2H), 7.91 (d, $J$ = 8.6 Hz, 1H), 7.65 (s, 1H), 7.58 (d, $J$ = 8.5 Hz, 2H), 6.92 (dd, $J$ = 8.6, 2.1 Hz, 1H), 6.88 (d, $J$ = 2.0 Hz, 1H); $^{13}$C NMR (150 MHz, DMSO-$d_6$) $\delta$ 160.7, 157.5, 157.5, 154.1, 153.5, 133.2, 129.1, 127.6, 125.8, 122.3, 113.6, 108.8, 104.1, 103.9, 103.0; IR (KBr) $\nu_{max}$/cm$^{-1}$ 3500 (O–H), 1730 (C=O), 1615 (C=C), 1250 (C−O); HRMS (ESI) calcd for C$_{17}$H$_{10}$ClO$_4$ 313.0263 (M + H$^+$); found 313.0261.

### 7-Hydroxy-2-(*p*-tolyl)-4*H*-furo[3,2-*c*]chromen-4-one (3z)

White solid (233.65 mg, 80%); mp 265–266 °C (lit. mp. >250 °C). $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$ 7.99 (dd, $J$ = 8.5, 3.0 Hz, 1H), 7.92–7.90 (m, 2H), 7.57 (d, $J$ = 3.2 Hz, 1H), 7.41 (d, $J$ = 7.9 Hz, 2H), 7.01 (d, $J$ = 8.6 Hz, 1H), 6.97–6.96 (s, 1H), 2.44 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 160.5, 157.7, 157.2, 155.0, 154.0, 138.6, 129.7, 126.1, 124.2, 122.2, 113.6, 108.8, 104.3, 103.0, 102.2, 21.0; IR (KBr) $\nu_{max}$/cm$^{-1}$ 3500 (O–H), 1740 (C=O), 1622 (C=C), 1280 (C−O); HRMS (ESI) calcd for C$_{18}$H$_{13}$O$_4$ 293.0809 (M + H$^+$); found 293.0810.

### 2-(Naphthalen-2-yl)-4*H*-furo[3,2-*c*]chromen-4-one (4a)

White solid (249.66 mg, 80%); mp 230–232 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.32 (s, 1H), 8.05 (dd, $J$ = 7.8, 1.4 Hz, 1H), 7.94 (dd, $J$ = 8.0, 5.0 Hz, 2H), 7.88–7.85 (m, 2H), 7.57–7.52 (m, 3H), 7.48 (d, $J$ = 8.2 Hz, 1H), 7.43–7.40 (m, 1H), 7.30 (s, 1H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 158.4, 157.2, 156.8, 152.8, 133.5, 133.4, 130.8, 129.1, 128.5, 128.0, 127.1, 127.0, 126.3, 124.7, 123.8, 122.3, 121.0, 117.6, 112.9, 112.7, 103.3. IR (KBr) $\nu_{max}$/cm$^{-1}$ 1745 (C=O), 1621 (C=C), 1282 (C−O); HRMS (ESI) calcd for C$_{21}$H$_{13}$O$_3$ 313.0860 (M + H$^+$); found 313.0870.

### 8-Fluoro-2-(naphthalen-2-yl)-4*H*-furo[3,2-*c*]chromen-4-one (4b)

White solid (257.45 mg, 78%); mp 238–239 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.32 (s, 1H), 7.94 (dd, $J$ = 8.0, 3.7 Hz, 2H), 7.87 (d, $J$ = 7.6 Hz, 1H), 7.85 (dd, $J$ = 8.6, 1.7 Hz, 1H), 7.71 (dd, $J$ = 7.7, 2.9 Hz, 1H), 7.55 (pd, $J$ = 6.8, 1.4 Hz, 2H), 7.46 (dd, $J$ = 9.1, 4.3 Hz, 1H), 7.31 (s, 1H), 7.27–7.24 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.4, 157.9 ($J_{C-F}$ = 0.93 Hz), 157.4, 156.2 ($J_{C-F}$ = 2.75 Hz), 148.9 ($J_{C-F}$ = 2.05 Hz), 133.6, 133.4, 129.1, 128.6, 128.0, 127.2, 127.2, 126.1, 124.0, 122.2, 119.2 ($J_{C-F}$ = 8.56 Hz), 118.2 ($J_{C-F}$ = 24.47 Hz), 113.6, ($J_{C-F}$ = 9.66 Hz), 113.5, 106.9 ($J_{C-F}$ = 25.64 Hz), 103.43. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ −116.22. IR (KBr) $\nu_{max}$/cm$^{-1}$ 1740 (C=O), 1615 (C=C), 1280 (C−O); HRMS (ESI) calcd for C$_{21}$H$_{12}$FO$_3$ 331.0765 (M + H$^+$); found 331.0765.

## Author contributions

## Conflicts of interest

There are no conflicts of interest to declare.

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