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Synthesis of 4-trifluoromethyl 2-pyrones and pyridones through the Brønsted base-catalyzed Pechmann-type reaction with cyclic 1,3-diones†

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An efficient method for the synthesis of 4-trifluoromethyl 2-pyrones through the Brønsted base-catalyzed Pechmann-type reaction of cyclic 1,3-diones with ethyl 4,4,4-trifluoroacetoacetate is described. In the presence of 2-dimethylamino pyridine (2-DMAP) as a catalyst, the resulting 4-trifluoromethyl 2-pyrones are formed in good to excellent yields. Additionally, the reaction also provides 4-trifluoromethyl 2-pyridones by using the easily available NH_4OAc as a source of NH_3.

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Introduction

The syntheses of 2-pyrones and their derivatives have been widely studied because of their intrinsic biological and pharmacological activities such as antifungal, antibiotic, cytotoxic, neurotoxic and phytotoxic activities (Fig. 1).[1,2] In addition, 2-pyrones also serve as versatile starting materials for the synthesis of key intermediates in synthetic organic chemistry as well as in medicinal chemistry.[3,4] As a consequence, significant progress has been made on the synthesis of 2-pyrones and their derivatives by the conventional approaches or by using a transition metal-catalysed reaction.[5–9]

The introduction of fluorine or fluorinated groups into biologically active molecules can modify the lipophilicity, metabolic profile and/or receptor-binding affinity of lead compounds.[10–13] The incorporation of the trifluoromethyl group ($-CF_3$) into pyrones to generate trifluoromethylated pyrones is expected to modify the biological activity of the parent pyrones due to the increased electrophilicity of the $-CF_3$ group. Therefore, significant effort has been focused on introducing the $-CF_3$ group into the pyrones.[14–19] Although the synthetic methods towards 3- or 6-trifluoromethylated 2-pyrones are highly documented, fewer examples focus on the regiocontrolled synthesis of their 4-trifluoromethylated isomers. Cao and co-workers reported the synthesis of 4-perfluoroalkyl-6-(α-furyl)-6-phyranones by hydrolysis of phosphoranes, starting from the reaction of (α-furoyl)methyltriphenylphosphonium bromide with methyl 2-perfluoroalkynoates (Scheme 1a).[20,21] Zanatta and co-workers reported a self-condensation reaction of 5-aryl-5-methoxy-3-(trifluoromethyl)penta-2,4-dienenitriles to afford 6-aryl-4-trifluoromethyl-2*H*-pyran-2-ones (Scheme 1b).[22] However, convenient and more efficient methods to construct 4-trifluoromethylated 2-pyrones by direct reactions with simple starting materials are extremely attractive.

The Pechmann reaction has emerged as a particularly popular and successful method for the synthesis of coumarins because of its preparative simplicity and requirement of inexpensive starting material.[23,24] The reaction is carried out by simply mixing the phenol with the β-keto ester in the presence of an acid as a catalyst and it is often highly efficient and easy to implement. The reaction mechanism involves three steps, *i.e.* electrophilic aromatic substitution, transesterification, and dehydration. This strategy has been widely applied to the syn-

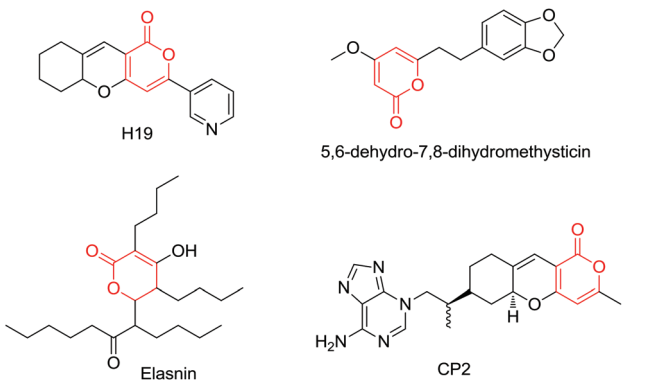

Fig. 1 Representative examples of bioactive 2-pyrone derivatives.

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†Electronic supplementary information (ESI) available: Copies of ^1H NMR, ^{13}C NMR, ^{19}F NMR of synthesized products. CCDC 1872006 and 1870545. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8ob02701c

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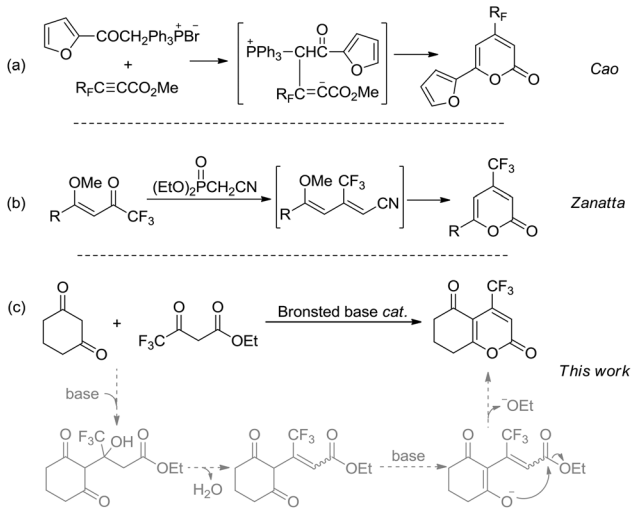


Scheme 1 Methods for the preparation of 4-trifluoromethyl 2-pyrone derivatives.

thesis of variously substituted coumarin derivatives, starting from phenols with β-keto esters.

1,3-Diketones are useful intermediates in organic synthesis, especially for the preparation of some biologically active compounds.[25,26] In view of the fact of the keto–enol tautomerism in 1,3-diketone compounds,[27,28] we envisioned that 1,3-diones may undergo the Pechmann-type reaction with ethyl 4,4,4-trifluoroacetoacetate to afford 4-trifluoromethyl 2-pyrone derivatives under Brønsted base-catalyzed conditions (Scheme 1c). With this understanding and our interest in the synthesis of perfluoroalkylated heteroaromatic molecules,[29–33] we herein report a general and practical procedure for the synthesis of 4-trifluoromethyl 2-pyrone and 2-pyridone derivatives.

Results and discussion

To test the feasibility of our envisioned method, the reaction of cyclohexane-1,3-dione (**1a**) with ethyl 4,4,4-trifluoroacetoacetate (**2**) was carried out under classic Pechmann-type reaction

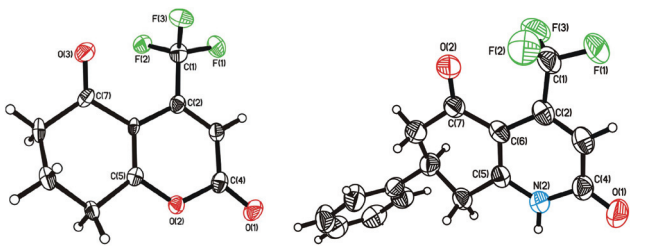
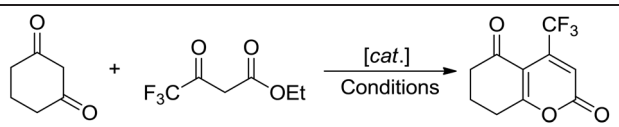


Fig. 2 ORTEP diagrams of **3a** (left) and **4e** (right) with thermal ellipsoids at the 40% probability level.

Table 1 Optimization of the synthesis of the 4-trifluoromethyl 2-pyrone derivative (**3a**)[a]



1a **2** **3a**

Entry	[cat.] (20 mol%)	Solvent	Temperature (°C)	Time (h)	Yield[b] (%)
1	H_2SO_4	Nitrobenzene	60	16	0
2	H_2SO_4	Nitrobenzene	120	24	<1
3	*p*-TsOH	Nitrobenzene	120	16	1
4	FeF_3	Nitrobenzene	120	16	12
5	$TiCl_4$	Nitrobenzene	120	16	3
6	$AlCl_3$	Nitrobenzene	120	16	5
7	NEt_3	Nitrobenzene	120	16	47
8	Pyridine	Nitrobenzene	120	16	69
9	2-DMAP	Nitrobenzene	120	16	73
10	4-DMAP	Nitrobenzene	120	16	38
11	2-DMAP	DMSO	120	16	27
12	2-DMAP	DMF	120	16	53
13	2-DMAP	DCE	120	16	99
14	2-DMAP	DMAc	120	16	0
15	2-DMAP	Diglyme	120	16	66
16	2-DMAP	NMP	120	16	39
17	2-DMAP	DCE	120	16	74[c]
18	2-DMAP	DCE	100	16	70
19	2-DMAP	DCE	80	16	35
20	2-DMAP	DCE	120	8	74

[a] Reaction conditions: **1a** (0.30 mmol), **2** (0.45 mmol, 1.5 equiv.), solvent (1.0 mL), N_2. [b] Yields were determined by ^{19}F NMR analysis of the crude reaction mixture with $PhOCF_3$ as an internal standard. *p*-TsOH = *p*-toluenesulfonic acid; 4-DMAP = 4-dimethylamino pyridine; 2-DMAP = 2-dimethylamino pyridine; DCE = 1,2-dichloroethane; DMAc = *N*,*N*-dimethylacetamide. [c] The reaction was conducted under an air atmosphere.

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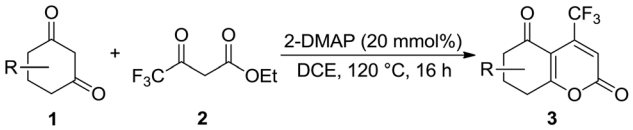
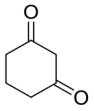
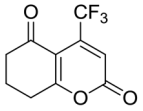
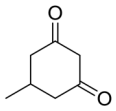
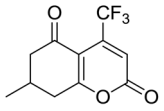
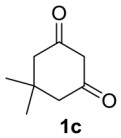
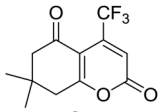
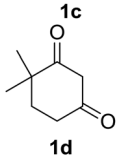
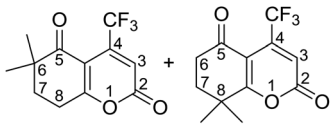
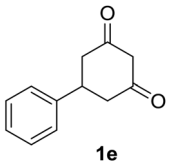
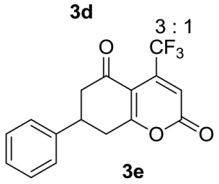
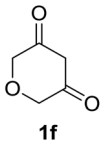
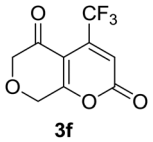
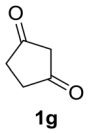
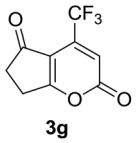
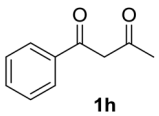
conditions [nitrobenzene, H_2SO_4 (20 mol%)][34] at 60 °C (Table 1). We observed that **2** remained unreacted (Table 1, entry 1), even at 120 °C after a reaction time of 24 h and even though these were the most efficient conditions for the Pechmann reaction of the phenol with the β-keto ester (Table 1, entry 2). Although *p*-TsOH was also reported as an efficient promoter of the Pechmann reaction,[35] under our conditions, only a trace amount of product **3a** could be monitored by ^{19}F NMR (Table 1, entry 3). Similarly, other Lewis acids, such as FeF_3, $TiCl_4$, and $AlCl_3$, provided product **3a** in a poor yield (Table 1, entries 4–6).

Interestingly, the further attempt produced a fruitful output, with the expected product **3a** being generated in 47% yield, when NEt_3 was used as the catalyst in nitrobenzene at 120 °C (Table 1, entry 7). Delighted by this result, we performed further optimization studies to establish the best reac-

Table 2 Synthesis of 4-trifluoromethyl 2-pyrones[a]



Entry	1,3-Dione substrates	Products	Yield[b] (%)
1	 **1a**	 **3a**	99
2	 **1b**	 **3b**	99
3	 **1c**	 **3c**	99
4	 **1d**	 **3d** **3d'**	99
5	 **1e**	 3 : 1 **3e**	99
6	 **1f**	 **3f**	43
7	 **1g**	 **3g**	84
8	 **1h**	No desired product	—

[a] Reaction conditions: **1** (0.30 mmol), **2** (0.45 mmol, 1.5 equiv.), 2-DMAP (0.060 mmol, 20 mmol%), DCE (1.0 mL), 120 °C, 16 h, N_2. [b] Isolated yields.

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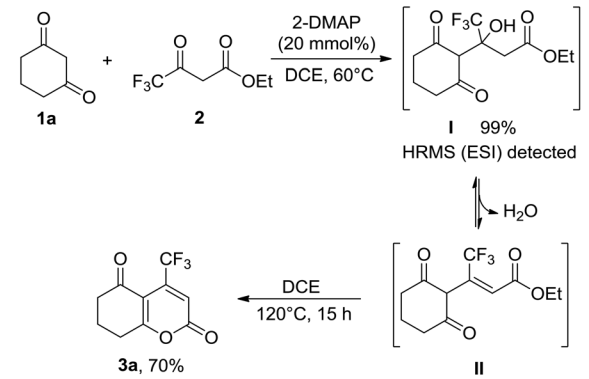
tion conditions. Other organic bases such as pyridine, 2-DMAP, and 4-DMAP were also found to be effective in driving this transformation, and afforded **3a** in 69, 73 and 38% yields, respectively (Table 1, entries 8–10). 2-DMAP was therefore established as the preferred catalyst for this transformation. In addition, the structure of **3a** was verified by X-ray crystallographic analysis (Fig. 2). After screening various common organic solvents, we found that the reaction proceeded most efficiently in DCE, which provided product **3a** in 99% yield (Table 1, entry 13). The reactions that were performed in DMSO, DMF, diglyme and NMP produced diminished product yields (Table 1, entries 11, 12, 15 and 16), whereas other solvents such as DMAc did not provide the desirable product for this reaction (Table 1, entry 14). Thus, DCE was selected as the preferred solvent for the subsequent experiments as a result of its efficiency in the reaction and ease of handling during the workup procedure. Notably, product **3a** was formed in a lower yield when the reaction was carried out under an air atmosphere (entry 17). Reactions performed at lower temperatures (100 or 80 °C) produced lower yields (70% and 35% yields, respectively; Table 1, entries 18 and 19). Furthermore, reducing the reaction time to 8 h resulted in incomplete conversion (74% yield; Table 1, entry 20).

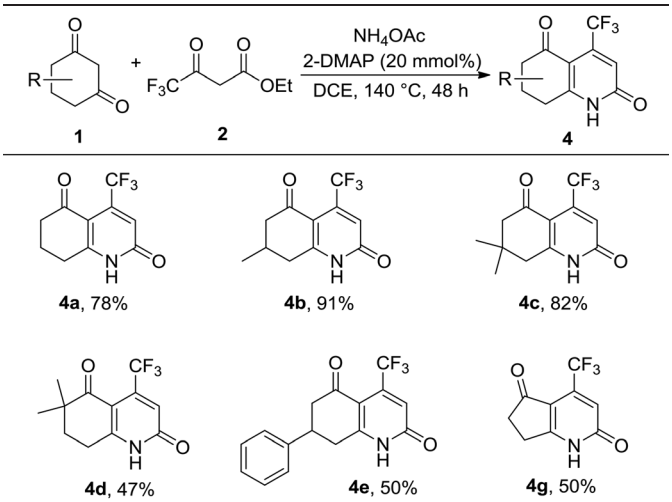
With the optimized reaction conditions in hand [*i.e.*, 2-DMAP (20 mol%) in 1,2-dichloroethane at 120 °C for 16 h], the Pechmann-type reaction of ethyl 4,4,4-trifluoroacetoacetate **2** with a variety of cyclic 1,3-diones **1** was examined (Table 2). Substituted 1,3-cyclohexanediones that contain a methyl (**1b**), dimethyl (**1c**), and phenyl group (**1e**) at the C-5 position took part in the reaction to effectively afford the desired 4-trifluoromethyl 2-pyrone products **3b**, **3c**, and **3e** all in nearly quantitative yields (Table 2, entries 2, 3, and 5). The reaction of 4,4-dimethylcyclohexane-1,3-dione (**1d**) with **2** led to the formation of a mixture containing two regioisomers **3d** and **3d′** in a 1 : 3 ratio with an overall yield of 99% (Table 2, entry 4). The triplet at δ 2.93 ppm in **3d**, corresponding to the resonance of C-8-*H* protons, appeared downfield compared to aliphatic hydrogen atoms because of the deshielding effect of the pyrone functionality. Importantly, heterocyclic derivatives of 1,3-diones such as pyran-3,5-dione **1f** smoothly underwent the reaction with **2** to give the desired product **3f** in 43% yield (Table 2, entry 6). In addition to 1,3-cyclohexanediones, 1,3-cyclopentanedione **1g** was also reactive under these reaction conditions and delivered the desired product **3g** in a good yield (84%; Table 2, entry 7). Unfortunately, the reaction of an acyclic 1,3-dione **1h** with **2** failed to provide any discernible pyrone products (Table 2, entry 8).

To examine whether any reactive species was involved in the cyclization, the progress of the reaction was monitored by ^{19}F NMR (see the ESI†). The results revealed that a nucleophilic addition product (**I**) is formed in 99% NMR yield during the reaction of **1** with **2** in the presence of 2-DMAP (20 mol%) at 60 °C (Scheme 2). Intermediate **I** underwent further reaction to afford the desired product **3a** in 70% NMR yield. These results provide support for the possible role of the nucleophilic addition species **I** as an intermediate in the reaction. Although



Scheme 2 Mechanistic experiments.

Table 3 Synthesis of 4-trifluoromethyl 2-pyridones[a,b]



[a] Reaction conditions: **1** (0.30 mmol), **2** (0.45 mmol, 1.5 equiv.), NH_4OAc (0.90–1.50 mmol), 2-DMAP (0.060 mmol, 20 mmol%), DCE (3.0 mL), 140 °C, 48 h, N_2. [b] Isolated yields.

other conceivable scenarios cannot be ruled out at this moment, we propose a mechanistic rationale of this reaction to be nucleophilic addition, dehydration, and enolization, followed by intramolecular nucleophilic substitution (Scheme 1c).

Encouraged by these results, we next explored the possibility for the synthesis of the pyridone analogues, a related class of compounds having wide applications from agriculture to medicine.[36–39] The reaction of the 1,3-dione substrates **1** with **2** and NH_4OAc (source of NH_3) in the presence of 20 mol% of 2-DMAP in DCE at 140 °C for 48 h resulted in the formation of the corresponding 4-trifluoromethyl 2-pyridines in moderate to excellent yields (Table 3). In contrast to its pyrone analogues, the pyridone product **4d** was obtained as a single regioisomer in 47% yield, implying that the reaction outcome is sensitive to the steric properties of the plausible pyrone intermediate **3d′**. The structure of **4e** was unambiguously assigned by X-ray crystallography (Fig. 2).

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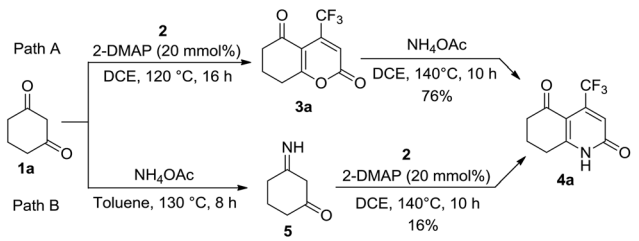
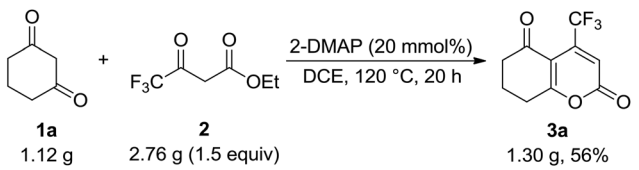
Two possible reaction pathways for the formation of pyridones were considered (Scheme 3); either a base-mediated Pechmann-type reaction of cyclic 1,3-dione **1a** with ethyl 4,4,4-trifluoroacetoacetate **2**, affording 2-pyrone **3a**, which, upon amination, led to the desired pyridone **4a** (path A), or, alternatively, 1,3-dione **1a** mono-aminated with NH_4OAc furnishing 3-iminocyclohexanone **5**, which, by reacting with **2**, resulted in the formation of **4a** (path B).

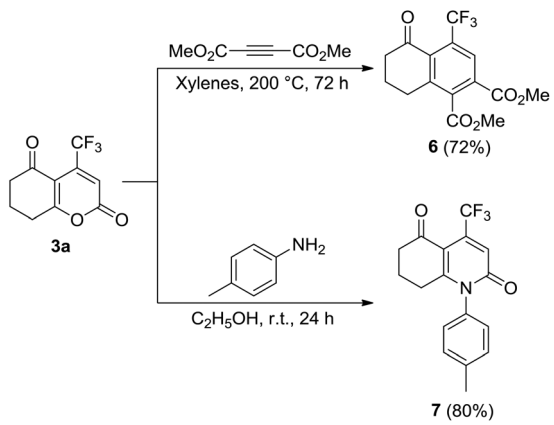
To distinguish these pathways, a series of experiments were rationally designed and performed. Firstly, the possible formation of 3-iminocyclohexanone **5** as an intermediate of path B was tested. Indeed, under the standard reaction conditions, the reaction of 3-iminocyclohexanone **5** with **2** led to the formation of **4a** in a low yield (16%). Path A, in contrast, was supported by the formation of **4a** (76% NMR yield) resulting from the amination of 2-pyrone **3a** with NH_4OAc. These results clearly demonstrate that path A involving the formation of 2-pyrone probably is favored during the aforementioned synthesis of pyridones although we could not rule out path B (Scheme 3).



Scheme 3 Proposed reaction pathways for the formation of **4a**.



Scheme 4 Scalability of the synthesis of **3a**.



Scheme 5 Derivatizations of **3a**.

To demonstrate the scalability and practicability of this procedure, 1.12 g of cyclohexane-1,3-dione (**1a**) was reacted with 2.76 g of ethyl 4,4,4-trifluoroacetoacetate (**2**) in DCE at 120 °C for 20 h (Scheme 4). The corresponding 4-trifluoromethyl 2-pyrone **3a** was isolated in 56% yield (1.30 g).

To demonstrate the high synthetic value of the obtained 4-trifluoromethyl 2-pyrones, we further investigated a variety of chemical transformations with compound **3a** as a model substrate (Scheme 5). Addition of dimethyl acetylenedicarboxylate (DMAD) to **3a** yielded the benzene derivative **6** in 72% yield. Treatment of **3a** with *p*-toluidine in ethanol led to the isolation of *N*-tolyl-substituted pyridin-2(1*H*)-one **7** in 80% yield.

Conclusions

In summary, we reported a Pechmann-type reaction of cyclic 1,3-diones with ethyl 4,4,4-trifluoroacetoacetate for the synthesis of 4-trifluoromethyl 2-pyrones. This Brønsted base-catalysed reaction proceeded well to furnish the desired 4-trifluoromethyl 2-pyrones in good to excellent yields. The method also gave access to a number of different 4-trifluoromethyl 2-pyridones by using the easily available NH_4OAc as a source of NH_3. We anticipate that this protocol will be useful for the synthesis of 4-trifluoromethyl 2-pyrones and pyridones that could find further applications as biologically active compounds.

Experimental

General remarks

^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded using a Bruker AVIII 400 spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts were reported in parts per million (ppm) downfield from tetramethylsilane and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as the external standard and low field is positive. Coupling constants (*J*) are reported in hertz (Hz). The residual solvent peak was used as an internal reference: ^{1}H NMR (chloroform δ 7.26) and ^{13}C NMR (chloroform δ 77.0). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. HRMS were obtained on a Thermo Exactive Plus LC-MS system. Reagents were obtained from commercial sources. Solvents were freshly dried and degassed according to the published procedures prior to use.

General procedure for the synthesis of 4-trifluoromethyl 2-pyrones

In a glove box filled with nitrogen, to an oven-dried 5 mL pressure tube equipped with a stir bar was added 1,3-diones **1** (0.30 mmol), ethyl 4,4,4-trifluoroacetoacetate **2** (0.45 mmol, 1.5 equiv.), 2-dimethylaminopyridine (0.060 mmol, 0.20 equiv.), and 1,2-dichloroethane (1.0 mL). The tube was sealed with a Teflon screw cap and the solution was stirred at 120 °C for

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16 h. The reaction mixture was cooled to room temperature, diluted with ethyl acetate, washed with saturated ammonium chloride solution (3 × 30 mL) and water (30 mL), dried over Mg_2SO_4, and filtered. The residue obtained was purified by flash column chromatography over silica gel with *n*-pentane/dichloromethane.

General procedure for the synthesis of 4-trifluoromethyl 2-pyridones

In a glove box filled with nitrogen, to an oven-dried 5 mL pressure tube equipped with a stir bar was added **1** (0.30 mmol), NH_4OAc (0.90–1.50 mmol, 3.0–5.0 equiv.), ethyl 4,4,4-trifluoroacetoacetate **2** (0.45 mmol, 1.5 equiv.), 2-dimethylaminopyridine (0.060 mmol, 0.20 equiv.), and 1,2-dichloroethane (3.0 mL). The tube was sealed with a Teflon screw cap and the solution was stirred at 140 °C for 48 h. The reaction mixture was cooled to room temperature, diluted with ethyl acetate, washed with saturated brine (3 × 30 mL) and water (30 mL), dried over Mg_2SO_4, and filtered. The residue obtained was purified by flash column chromatography over silica gel with *n*-pentane/ethyl acetate or dichloromethane/ethyl acetate.

Conflicts of interest

There are no conflicts to declare.

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