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FULL PAPER

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# Unexpected reactivity of pyridinium salts toward alkynyl Fischer complexes to produce *oxo*-heterocycles

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The unprecedented reaction of ketone-containing aromatic pyridinium salts **3a**-**e** and alkynyl Fischer complexes **1a**-**f** proceeds via a mild domino process to provide 4,6-disubstituted pyran-2-ones **5a**-**k** and 2,3,5-trisubstituted furans **6a**-**h** (45-97%). According of the results of isotopic labeling experiments, a mechanism involving an initial Michael addition appears to be the key step, obtaining a mesomeric structure responsible for the formation of both products.

**KEYWORDS**
Alkynyl Fischer carbene, disubstituted 2*H*-pyran-2-one, pyridine ylide, trisubstituted furan

## 1 | INTRODUCTION

Since their discovery in 1935, pyridinium ylides have been studied extensively.[1] These compounds have the advantage of being easily-prepared building blocks while also possessing a wide range of applications as nucleophiles. In particular, pyridines, quinolones, indolizines and other molecules have been prepared using the pyridinium ylide platform.[2] In this sense, these compounds are involved in a range of processes such as multicomponent reactions, 1,3-cycloadditions, Michael additions and cyclopropanations as the most representative,[3] depending on the electrophile used and sometimes related with p$K_a$ value of the associated ions (however, the latter is not always a trustworthy factor).[4]

On the other hand, particular attention has been paid to the use of Fischer carbenes to prepare a wide range of chemical scaffolds. Our research group alone has provided evidence for the synthesis of *ortho*- and *para*-quinones, phenols, 4-amino-1-azadienes, *N*-benzyl pyrroles, *N*H pyrroles, among others, when alkoxy alkynyl carbenes

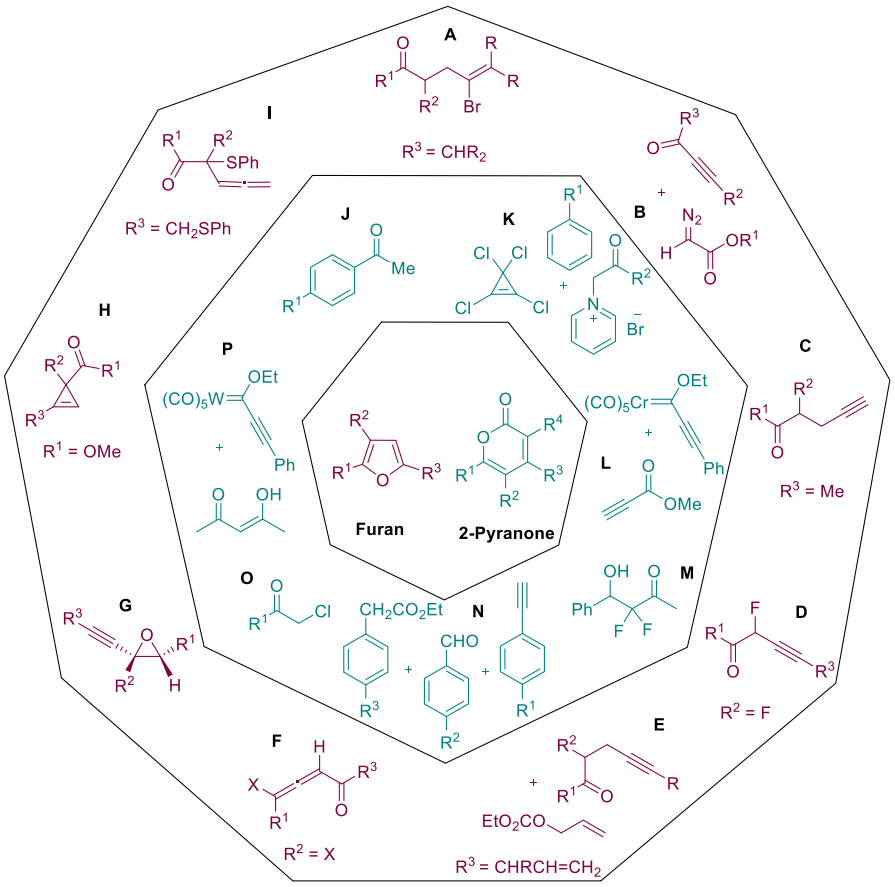
  

were employed. Thus, it can be said that these platforms are effective in the synthesis of a variety of heteroatom-containing compounds.[5]

Of the more than 20 million registered chemical compounds, about one half contain heterocycles and a large number of these have some biological activity.[6] This reason has motivated the development and increasing diversity of synthetic methodologies for preparing heterocycles. Indolizine and related groups are found in a wide range of natural products, as exemplified by the natural products swainsonine and monomorine I.[7] One interesting methodology used to construct this chemical skeleton involves the use of pyridinium ylides and electron-deficient ynamides.[8] However, beyond its frequent occurrence in nature, this structure commonly exhibits a range of biological activities, for instance against bacteria, viruses and parasites, regulating tumor genesis, diminishing inflammation, abating pain, preventing oxidation, and inhibiting enzymes, as well as further uses in materials science or industrial processes.[9]

Polysubstituted furans are other important class of five-membered heterocycles that can be found in many natural, pharmaceutical and agrochemical products.[10] Numerous routes to prepare this structure have been established, ranging from the traditional and simple cyclocondensations of 1,3- and 1,4-dicarbonyl compounds in the Feist-Bénary and Paal-Knorr methods, respectively, to more elegant alternatives using diverse carbonyl-containing substrates and metallic catalysts (Scheme 1) in routes involving copper (**A** and **B**), mercury (**C**), gold and silver (**D**), palladium (**E**), gold (**F**), indium (**G**), ruthenium (**H** and **I**), or employing Fischer carbene complexes.[11]

Pyranones, for their part, are valuable building blocks that have been used extensively in diversity-oriented synthesis.[12] In particular, pyran-2-ones are associated with divergent pharmacological activities such as cyclooxygenase-2 inhibition, immunosuppression of organisms, inhibition of HIV protease, or reduction of inflamed tissues, to mention just a few.[13] Among the reported methods of preparation, some are remarkable due to their flexibility in terms of substrates used to achieve the goal. In Scheme 1, several methods are depicted for obtaining a wide variety of substitution patterns on the heterocyclic ring, highlighting route **K**, which is based on the reactivity of pyridinium salts, as well as routes **L** and **P** where alkynyl Fischer carbenes were utilized. In particular, under the conditions employed therein, the organometallic fragment is preserved after the work up, unlike the route reported here. Methods **J**, **O**, **N** and **M** also provide access to this desired nucleus through simple protocols.[14]




**SCHEME 1** Highlighted syntheses of furan and pyran-2-one rings

Motivated by this background, we undertook investigations into the reactivity and scope of pyridinium ylides and α,β-unsaturated Fischer complexes, specifically targeting the construction of compounds with potential biological applications. The results of this study are presented herein.

## 2 | RESULTS AND DISCUSSION

With the aim of establishing a new path for the synthesis of a family of indolizidines, alkynyl carbene **1a** (1.2 mol equiv.) was treated with pyridinium salt **3a** (1.0 mol equiv.) under different chemical conditions. Attempts to use acetonitrile, toluene and THF as solvents at room temperature, and TEA or DIPEA as bases, found no success in the preparation of indolizine **4a**, although complete consumption of the reagents took place. Conversely, a mixture of 2*H*-pyran-2-one **5a**, furan **6a** and pentacarbonyl pyridine chromium complex **7a** was always obtained, with varying product ratios depending on the chosen conditions, but with THF being the best option as solvent (Scheme 2).

These results were surprising, especially given that we unambiguously established that **3a** undergoes a (3+2) cycloaddition when reacted with dimethylacetylene dicarboxylate ($K_2CO_3$, THF, rt, 4 h, 65%),[15a] an organic analogue of Fischer complexes **1**, affording indolizine **4b** (Figure 1)[15b] as the major product (Scheme 3). Moreover, this kind of cycloaddition has been reported in the reaction of alkenyl carbenes with 1,3-dipoles such as nitrilimines, where $\Delta^2$-pyrazolines were formed.[16]

It should be stated at this point that there is a clear difference in the reactivity of pyridinium salts with these groups of compounds (alkynyl ester *vs* alkynyl carbene), despite their structural similarities. For this reason, our investigations turned toward understanding the potential of the unexpected products **5** and **6**. Normally, unsaturated carbenes undergo 1,2-, 1,4- or 1,6-additions in the presence of carbon nucleophiles, depending on their hardness and steric bulk.[17] For this reason, a complete

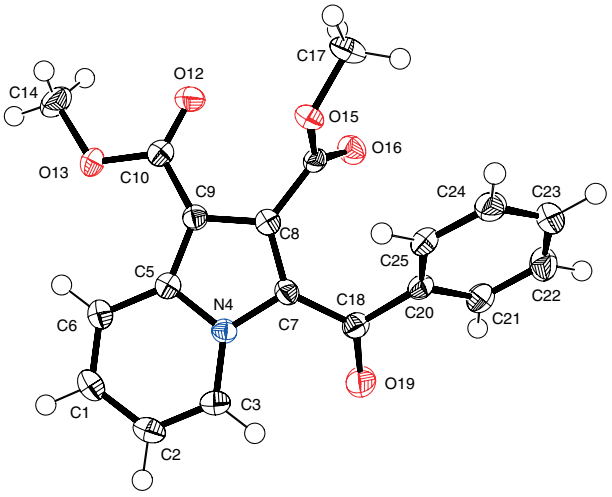
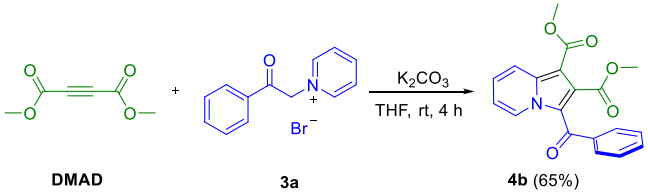
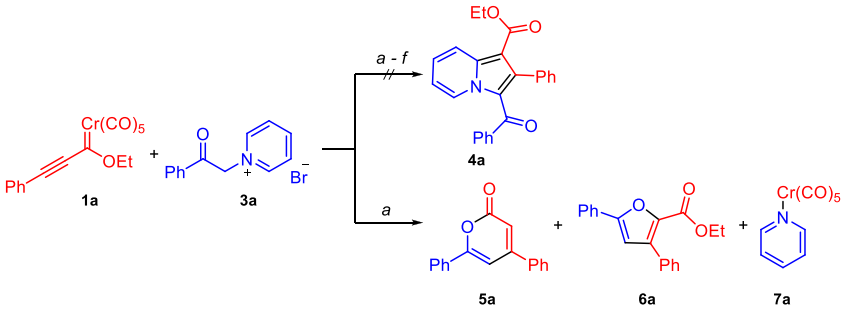



**FIGURE 1** ORTEP diagram of indolizine **4b**




**SCHEME 3** Dipolar cycloaddition of pyridinium ylide **3a** and DMAD

study was designed to fully unveil the reactivity of these particular nucleophiles (pyridinium ylides). Thus, during the optimization stage, several sets of conditions were evaluated to determine the best result. Reaction of carbene **1a** with salt **3a** in THF at reflux, with TEA as base, afforded pyranone **5a** in 30% yield and the oxidized alkynyl carbene as products; meanwhile, keeping the reactants constant but changing the base for a stronger one (LDA) at −78 °C furnished a mixture in which pyranone **5a** was formed in a similar yield (28%) but furan **6a** was also obtained in 15%. To determine which factor (temperature or base) played the decisive role in the final outcome, an additional experiment was performed with **1a** and **3a** using TEA at room temperature, leading to an




**SCHEME 2** Reaction between alkynyl Fischer carbene **1a** and pyridine salt **3a**. Reaction conditions: (a) TEA, THF, rt, 12 h, **5a** (45%), **6a** (29%), **7a** (26%). (b) TEA, $CH_3CN$, rt, 12 h, **5a** (40%), **6a** (24%), **7a** (36%). (c) TEA, PhMe, rt, 12 h, **5a** (32%), **6a** (23%), **7a** (45%). (d) DIPEA, THF, rt, 12 h, **5a** (41%), **6a** (24%), **7a** (35%). (e) DIPEA, $CH_3CN$, rt, 12 h, **5a** (38%), **6a** (21%), **7a** (41%). (f) DIPEA, PhMe, rt, 12 h, **5a** (28%), **6a** (20%), **7a** (52%)

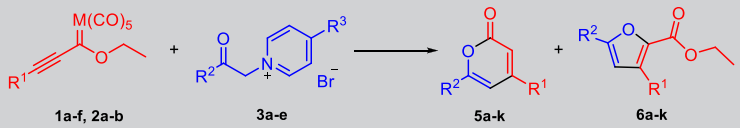
improvement of the yield (42% for **5a** and 30% for **6a**). The influence of microwave irradiation on the selectivity was also tested, finding that for short exposures (THF, 70 °C, 30 min, 150 W, closed system) the reaction was incomplete, with a 1:3 product ratio (**5a**:**6a**), but after 3.5 h the reaction was complete, with a ratio of 4:1. At this point the best results were achieved using THF and TEA at room temperature. However, to cover wider aspects of the synthesis, two experiments using either AgOAc or CuOAg as catalyst (20% mol) were carried out, leading to similar results for both cases: neither **5a** nor **6a** was formed as only a small quantity of salt **3a** reacted with **1a**. Nevertheless, the latter was found to be completely consumed. After these assays, the optimization process suggested that this combinatorial method could be applied in the synthesis of molecules with a variety of substituents. The scope of this reaction is summarized in Table 1.

According to the results displayed in Table 1, the reaction favors the formation of pyran-2-ones **5** over furans **6** in practically all cases. When comparing the variability of the groups on the alkynylcarbene **1**, a strong structural and electronic influence was clearly expressed, since no furans were formed when heteroaromatic or alkenyl groups were present in **1** and only pyran-2-ones were formed (Table 1, entries 13-15). Addressing the differences between the substitution patterns of carbenes **1** with aromatic scaffolds, electron-releasing groups increased the efficiency of the reaction compared with neutral or electro-withdrawing groups (Table 1, entries 1, 8 and 12). Moreover, a similar electronic effect seems to operate under the influence of salts **3** where $R^2$ was substituted with different groups (Table 1, entries 4 and 7), showing a preference for those salts bearing an electron-releasing group.

In addition, electronic activation of $R^2$ seems to play a non-determinant role for the final composition of the mixture (at least at the level of the influence exerted by $R^1$) since similar results in yield and selectivity were observed when reacting substrates such as heteroaromatic carbene **1e** (Table 1, entries 13 and 14). Similarly, substitution at the pyridinium ring did not affect the final yield (Table 1, entries 1 and 3), which was the reason we decided to work with the simplest structure.

Another remarkable difference was observed with the metallic fragment $[(CO)_5M]$ of the alkynyl carbene, as suggested by a number of studies wherein reactivity is

**TABLE 1** Divergent synthesis of pyranone (**5**) and furan (**6**) derivatives[a]




| Entry | Carbene | Salt | $R^1$ | $R^2$ | $R^3$ | 5 (%)[b] | 6 (%)[b] | Yield (%)[c] |
|---|---|---|---|---|---|---|---|---|
| 1 | **1a** | **3a** | Ph | Ph | H | **5a** (45) | **6a** (29) | 74 |
| 2 | **2a**[d] | **3a** | Ph | Ph | H | **5a** (56) | **6a** (39) | 95 |
| 3 | **1a** | **3b** | Ph | Ph | $NMe_2$ | **5a** (42) | **6a** (30) | 72 |
| 4 | **1a** | **3c** | Ph | 4-OMe-$C_6H_4$ | H | **5b** (58) | **6b** (24) | 82 |
| 5 | **1a** | **3d** | Ph | 4-Me-$C_6H_4$ | H | **5c** (57) | **6c** (24) | 81 |
| 6 | **2a**[d] | **3d** | Ph | 4-Me-$C_6H_4$ | H | **5c** (62) | **6c** (27) | 89 |
| 7 | **1a** | **3e** | Ph | 4-Cl-$C_6H_4$ | H | **5d** (55) | **6d** (30) | 85 |
| 8 | **1b** | **3a** | 4-Me-$C_6H_4$ | Ph | H | **5e** (49) | **6e** (33) | 82 |
| 9 | **2b**[d] | **3a** | 4-Me-$C_6H_4$ | Ph | H | **5e** (66) | **6e** (31) | 97 |
| 10 | **1b** | **3c** | 4-Me-$C_6H_4$ | 4-OMe-$C_6H_4$ | H | **5f** (31) | **6f** (14) | 45 |
| 11 | **1c** | **3d** | 3-Me-$C_6H_4$ | 4-Me-$C_6H_4$ | H | **5g** (53) | **6g** (18) | 71 |
| 12 | **1d** | **3a** | 3-$CF_3$-$C_6H_4$ | Ph | H | **5h** (36) | **6h** (20) | 56 |
| 13 | **1e** | **3a** | 3-thienyl | Ph | H | **5i** (58) | **6i** (0) | 58 |
| 14 | **1e** | **3d** | 3-thienyl | 4-Me-$C_6H_4$ | H | **5j** (59) | **6j** (0) | 59 |
| 15 | **1f** | **3a** | *c*-1-$C_6H_9$ | Ph | H | **5k** (48) | **6k** (0) | 48 |

[a]Reaction conditions: **1** or **2** (1.5 equiv.), **3** (1.0 equiv.), TEA (1.0 equiv.), THF, rt, 12 h.

[b]Isolated yields.

[c]Combined yield (**5** + **6**).

[d]M = W, reaction time = 48 h.

strongly influenced by this moiety.[18] For this particular case, the results indicated a preference for tungsten over chromium complexes when comparing yields of the molecular scaffolds (Table 1, entries 1 and 8, M = Cr *vs* 2 and 9, M = W). Similar observations have been established by other researchers interested in understanding the M-C bond, and the accepted explanation is based on the notion that a number of the chromium-containing intermediates are less stable than those derived from tungsten.[19] Despite the better results associated with tungsten complexes **2a**-**b** (Table 1, entries 2, 6 and 9), the time required for completion was practically four times that observed for chromium complex **1a**-**b**; for this reason the extended study was performed using only the second group of substrates.

On the other hand, this methodology showed limitations related to the structure of the pyridinium salt, perhaps due to steric effects, as evidenced by the lack of reactivity of the ylide derived from both neutral and electronically-activated coumarins **3f** and **3g** towards carbene **1a** under the previously optimized conditions, since only the oxidized ester derived from the alkyne could be recovered and no traces of **5l**-**m**/**6l**-**m** were detected (Scheme 4).

The structures of the formed pyran-2-ones, furans and pyridine chromium complexes were elucidated based on their $^{1}H$ and $^{13}C$ NMR spectroscopic data, as well as characteristic IR spectroscopic signals. In addition, the structures of products **5g**,[20] **6e**[21] and **7a**[22a] were unequivocally determined by X-ray diffraction crystallography (Figure 2). Although **7a** has been previously characterized and its crystal structure reported,[22b] an ORTEP diagram of the compound is presented here in order to support our mechanistic proposal discussed below. Concerning **5g**, there is a deviation of the torsion angle between the planes of the aryl rings and that of the oxygen-containing ring (12.6° (*m*-tolyl) and 12.3° (*p*-tolyl), respectively). Furan **6e** exhibits larger deviations in this metric (31.7° and 18.5°). In accordance with this **5g** displays a short contact of 2.49 Å between H-4 and O-2 of two molecules in the packing array, but this kind of interaction is practically nonexistent in **6e**.

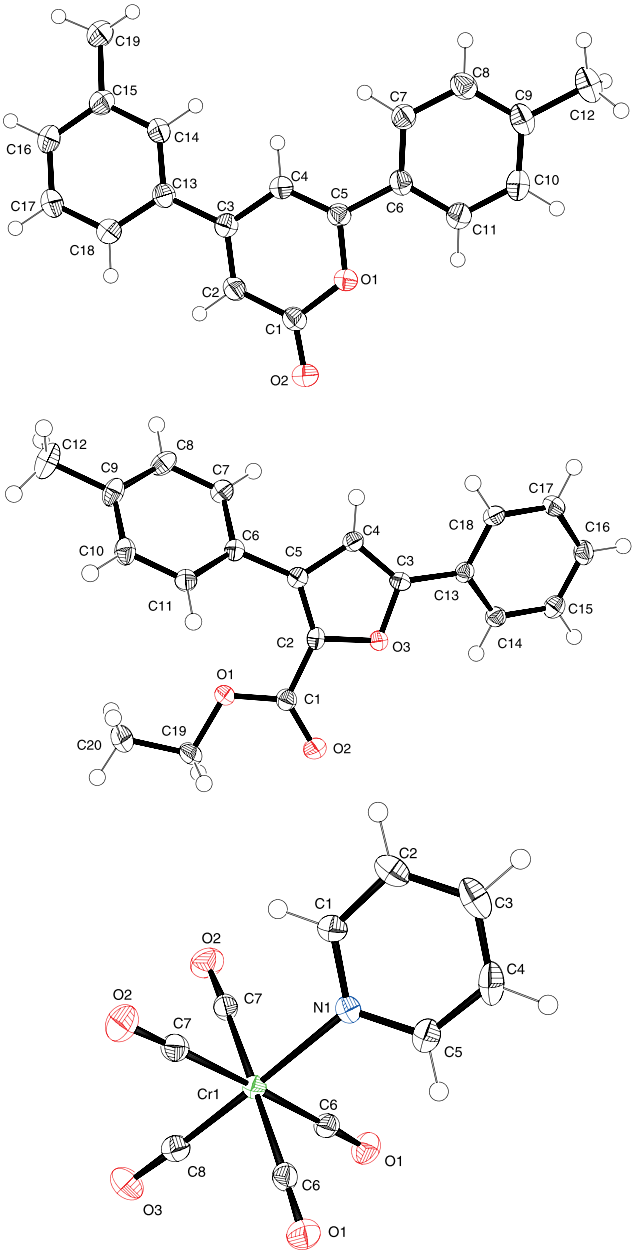
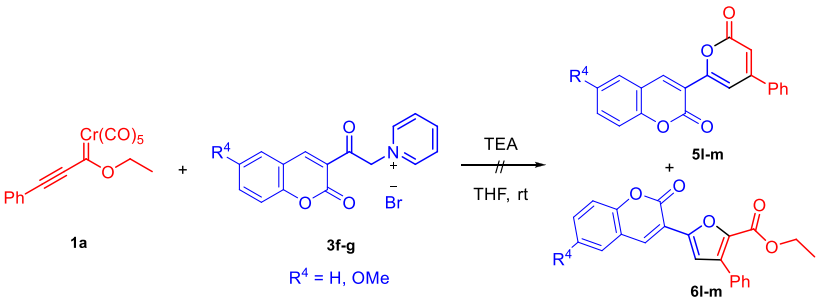
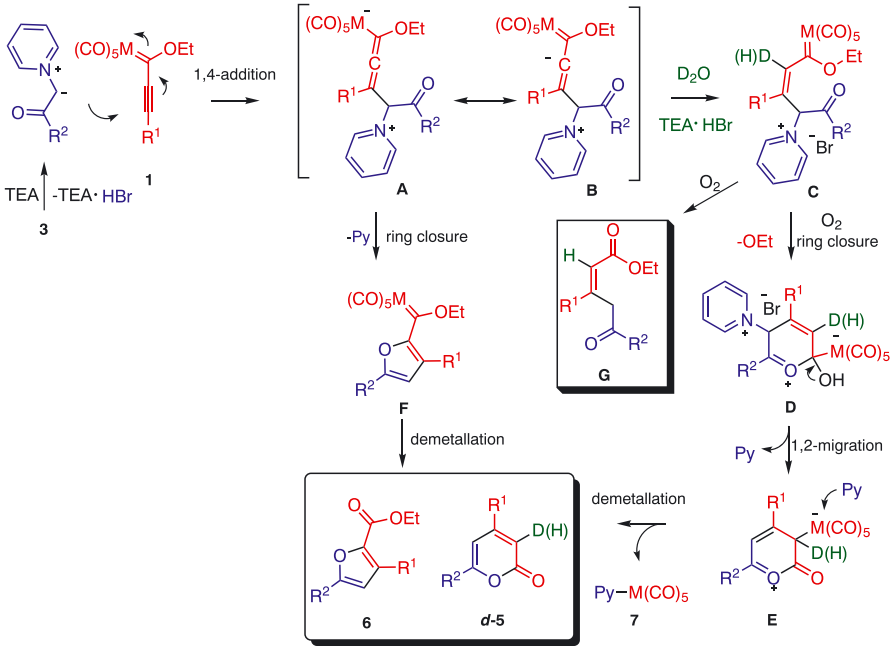



**FIGURE 2** ORTEP diagram of pyranone **5g**, furan **6e** and complex **7a**

A plausible mechanism to explain the formation of the obtained products is depicted in Scheme 5, featuring a domino process. The first step is proposed to be




**SCHEME 4** Non-viable ylides tested



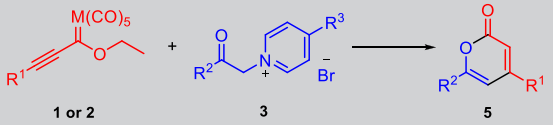

**SCHEME 5** Proposed mechanism for the formation of pyran-2-ones **5**, furans **6** and metal complexes **7**

the corresponding Michael addition of the pyridinium salt (derived from **3**) to the alkynyl carbene **1** (or **2**),[23] resulting in the species **A**, which has the alternative resonance structure **B** (metal allenes are well known to participate in carbene reactions).[24] In fact, a number of failed experiments using alkyl carbenes **1** ($R^1$ = *c*-propyl, *n*-propyl and trimethylsilyl) and salt **3a** ($R^2$ = Ph) afforded the 1,4-addition product in yields ranging from 5 to 15%, along with the oxidized ester derived from the respective carbene. This observation, and the presence of **G** (derived from reaction toward **5j**, Table 1, entry 14; Scheme 5), isolated and spectroscopically confirmed by HRMS (see Section 6 of the Supporting Information), would support the proposed initial step of the mechanism, which has also been proposed in previous reports where α,β-unsaturated Fischer carbenes are used in the synthesis of heterocycles.[5c] To obtain 2-pyranone **5**, **B** is protonated at the α position to afford **C** and then undergoes a *6-exo-trig* ring closure,[25] through a nucleophilic attack on the carbenic carbon by the ketone oxygen atom. This removes the ethoxy group,[26] and the carbene undergoes a subsequent oxidation process, as reported previously for loss of metal fragment,[5a] to afford the pyranylidene complex **D**.[27] Successively, **D** undergoes a 1,2-migration of the [$(CO)_5M$] fragment[28] to obtain the zwitterionic compound **E** with the consequent loss of pyridine. Addressing this step of the reaction, an experiment was performed in which **1a** was combined with **3a**, using pyridine instead of TEA as base, in order to prove the influence of external pyridine during this step. We observed that only **5a** was formed in a very low yield (12%) in this reaction. In the final step, the metal fragment undergoes attack by pyridine, causing delocalization of the electron density, directly yielding pyranone **5** and complex **7** as a byproduct. On the other hand, species **A** (which recalls the reactivity of the ketene complex involved in photochemical reactions of Fischer carbenes)[29] would lead to furan **6** through a *5-endo-dig* ring closure,[30] carried out at the *sp* carbon atom of the metallic allene by the ketone oxygen atom, affording species **F** after the loss of pyridine. This subsequently generates furan **6** by demetallation, explaining the results observed during the experiments.

A labeling experiment was performed to clarify the mechanistic steps of this process (Scheme 5). Carbene **1a** and salt **3a** were reacted under the conditions described above and then exposed to an equimolar amount of $D_2O$, producing pyranone ***d*-5a**, as evidenced by NMR and HRMS experiments.[31] This finding is consistent with the proposal of a Michael adduct **B** undergoing deuteration at the α carbon atom, and with the absence of furan ***d*-6a** in the mixture.

In a final attempt to achieve more selective results for this methodology, an additional experiment was performed using carbene complex **2a** to probe the effects of drastic temperatures on the optimized system. When a mixture of **2a** and **3a** was refluxed (PhMe, TEA, 110 °C, 4 h), the pyran-2-one **5a** was formed almost exclusively (94%). This fact indicates that pyran-2-ones show a preference to be formed under thermodynamic conditions (a previous experiment revealed that refluxing THF is not enough to ensure selectivity). With this evidence, some of the reactions of Table 1 were repeated to

**TABLE 2** Selective synthesis of pyran-2-ones (**5**) from alkynyl carbenes and pyridinium ylides[a]




| Entry | Carbene | Salt | $R^1$ | $R^2$ | $R^3$ | 5 (%)[b] |
|---|---|---|---|---|---|---|
| 1 | **2a** | **3a** | Ph | Ph | H | **5a** (94) |
| 2 | **2a**[c] | **3d** | Ph | 4-Me-$C_6H_4$ | H | **5c** (89) |
| 3 | **1a** | **3e** | Ph | 4-Me-$C_6H_4$ | H | **5d** (86) |
| 4 | **2b**[c] | **3a** | 4-Me-$C_6H_4$ | Ph | H | **5e** (95) |
| 5 | **1d** | **3a** | 3-$CF_3$-$C_6H_4$ | Ph | H | **5h** (79) |
| 6 | **1e** | **3a** | 3-thienyl | Ph | H | **5i** (77) |
| 7 | **1f** | **3a** | *c*-1-$C_6H_9$ | Ph | H | **5k** (73) |

[a]Reaction conditions: **1** or **2** (1.5 equiv), **3** (1.0 equiv), TEA (1.0 equiv), PhMe, 110 °C, 4 h.

[b]Isolated yields.

[c]M = W, reaction time = 6 h.

corroborate the reproducibility of the selectivity, and the results are depicted in Table 2.

Regardless of the existence of methodologies for the regioselective preparation of saturated structures similar to **5**,[32] in the method reported herein only one stage is required for completion, while the atom-economy and substituent tolerance are comparable with other routes. Furthermore, although the selectivity is diminished in its milder version, the reaction shows the advantage of generating products and byproducts with considerable potential in fields such as drug discovery.

## 3 | CONCLUSION

In summary, an unexpected reaction between chromium and tungsten alkynyl Fischer carbene complexes **1a-f** and **2a-c** and the pyridinium salts **3a-e** is reported, leading to highly functionalized pyran-2-ones **5a-k** and furans **6a-h** in moderate to good yields (45-97%), as well as excellent total conversion. In addition, the synthesis could be modulated to enhance selectivity toward compounds **5** (73-95%) by means of thermodynamic control, and the reaction proved to be effective for a wide variety of substituents, mainly aromatic groups. The substrates follow a probable reaction pathway consisting of a 1,4-addition/ring-closure/1,2-migration/demetallation cascade process for pyran-2-ones **5**, and another involving 1,4-addition/ring-closure/demetallation steps, concluding in the formation of furans **6**. This method represents a marked contrast from the conventional reactivity of pyridinium salts, leading to *oxo* compounds instead of the expected *aza* structures.

## 4 | EXPERIMENTAL SECTION

### 4.1 | General procedure for the synthesis of Alkynyl Fischer carbenes (1a-f and 2a-c)

The carbenes were prepared according to literature methods described in references 5a-c.

### 4.2 | General procedure for the synthesis of pyridinium salts (3a-g)

To an oven-dried 25 ml round-bottomed flask was added 3.7 mmol of the corresponding α-bromoketone, and this was dissolved in 5 ml of anhydrous $CH_3CN$. Slowly, 3.7 mmol of the selected pyridine was added dropwise and the mixture was stirred until a yellow solid precipitated. The product was then filtered and washed with acetone to remove colored impurities. Finally, a white solid was afforded in yields higher than 90% and stored at low temperature.

### 4.3 | General procedure for the synthesis of pyran-2-ones (5a-k) and trisubstituted furans (6a-k)

*A) Combinatorial method*: To a 50 ml oven-dried round-bottomed flask was added 0.85 mmol (1 equiv) of the corresponding pyridinium salt **3** and the container was deoxygenated by flushing with nitrogen for 5 min. Next, 10 ml of anhydrous THF was added to dissolve the solid, 0.85 mmol of TEA was slowly added, and the mixture was stirred for 40 min. To another dried flask was placed 0.86 mmol (1.2 equiv) of carbene **1**, and the flask was

deoxygenated as previously described. The contents of the first flask were then added to the second flask via cannula and the final mixture was stirred for 12 h. The reaction was monitored by TLC until completion, at which point the crude product was purified by column chromatography using hexanes as eluent. After complex **7** (yellow fraction) was separated, the polarity of the eluent was increased (Hex/AcOEt) and the corresponding pyran-2-one **5** and furan **6** were isolated and individually recovered after evaporation of the fractions under reduced pressure. *B) Selective method:* The quantities of the reagents were kept the same as in the combinatorial method, but THF is substituted by anhydrous PhMe and the mixture heated to reflux instead of room temperature for 4-6 h. After purification, pyran-2-ones **5** were recovered as the sole products.

### 4.3.1 | Dimethyl 3-benzoylindolizine-1,2-dicarboxylate (4b)

Yield: 65 % (yellow crystal mp = 165-166 °C). IR $\nu_{max}$ ($cm^{-1}$): 3105, 3008, 1741, 1699, 1623, 1211. $^{1}$HNMR (500 MHz, $CDCl_3$) δ (ppm): 9.65 (d, *J* = 9.0 Hz, 1H, H-9), 8.39 (d, *J* = 10.5 Hz, 1H, H-6), 7.69 (d, *J* = 8.5 Hz, 2H, H-12), 7.56 (t, *J* = 9.0 Hz, 1H, H-14), 7.50-7.43 (m, 3H, H-7, H-13), 7.12 (t, *J* = 8.5 Hz, 1H, H-8), 3.88 (s, 3H, H-16), 3.31 (s, 3H, H-18). $^{13}$C NMR (125 MHz, $CDCl_3$) δ (ppm): 52.0 (C-16), 52.6 (C-18), 104.3 (C-3), 116.4 (C-8), 120.3 (C-6), 121.2 (C-11), 128.4 (C-7), 128.5 (C-13), 128.9 (C-9), 129.0 (C-12), 132.0 (C-2), 132.2 (C-14), 138.6 (C-4), 139.9 (C-5), 163.7 (C-15), 165.6 (C-17), 187.2 (C-10). HRMS ($ESI^+$): m/z calcd for $C_{19}H_{15}NO_5^+$ $[M]^+$,337.0945; found, 337.0970.

### 4.3.2 | 4,6-diphenyl-2*H*-pyran-2-one (5a)

Yield method A: 56%; method B: 94% (white solid, mp = 140-141 °C). IR $\nu_{max}$ ($cm^{-1}$):1079 (C-O),1703 (C=O). $^{1}$H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.90 (d, *J* = 5.0 Hz, 2H, H-12), 7.65 (d, *J* = 5.0 Hz, 2H, H-8), 7.50 (m, 6H, H-9, H-10, H-13, H-14), 6.97 (s, 1H, H-5), 6.47 (s, 1H, H-3). $^{13}$C NMR (125 MHz, $CDCl_3$) δ (ppm): 162.6 (C-2), 160.3 (C-6), 155.5 (C-4), 136.0 (C-11), 131.4 (C-7), 130.8 (C-10), 130.6 (C-14), 129.2 (C-8), 128.9 (C-9), 126.6 (C-12), 125.7 (C-13), 109.2 (C-3), 101.3 (C-5). HRMS ($ESI^+$): m/z calcd for $C_{17}H_{13}O_2^+$ $[M+H]^+$ 249.0910; found, 249.0916.

### 4.3.3 | 4,6-diphenyl-2*H*-pyran-2-one-3-*d* (*d*-5a)

Yield method A: 45% (white solid, mp = 140-141 °C). IR $\nu_{max}$ ($cm^{-1}$):1079 (C-O),1703 (C=O). $^{1}$H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.90 (d, *J* = 5.0 Hz, 2H, H-12), 7.65 (d, *J* = 5.0 Hz, 2H, H-8), 7.55-7.48 (m, 6H, H-9, H-10, H-13, H-14), 6.97 (s, 1H, H-5), 6.48 (s, 0.65 Hz, H-3, ≈ 35% D).$^{13}$C NMR (125 MHz, $CDCl_3$) δ (ppm): 162.6 (C-2), 160.3 (C-6), 155.5 (C-4), 135.9 (C-11), 131.5 (C-7), 130.9 (C-10), 130.6 (C-14), 129.2 (C-8), 128.9 (C-9), 126.7 (C-12), 125.7 (C-13), 109.2 (C-3), 101.3 (C-5). HRMS ($ESI^+$): m/z calcd for $C_{17}H_{13}DO_2^+$ $[M+H]^+$, 250.0988; found 250.0975.

### 4.3.4 | 6-(4-Methoxyphenyl)-4-phenyl-2*H*-pyran-2-one (5b)

Yield method A: 58% (yellow solid, mp = 133-134 °C). IR $\nu_{max}$ ($cm^{-1}$):1181 (C-O), 1719 (C=O). $^{1}$H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.84 (d, *J* = 10.0 Hz, 2H, H-12), 7.64-7.62 (dd, $J_1$ = 5.0 Hz, $J_2$ = 10.0 Hz, 2H, H-8), 7.50-7.49 (m, 3H, H-9, H-10), 6.97 (d, *J* = 10.0 Hz, 2H, H-13), 6.84 (s, 1H, H-5), 6.39 (s, 1H, H-3), 3.86 (s, 3H, O*CH*$_3$). $^{13}$C NMR (125 MHz, $CDCl_3$) δ (ppm): 162.7 (C-6), 161.8 (C=O), 160.4 (C-4), 155.8 (C-7), 136.2 (C-11), 130.5 (C-10), 129.1 (C-9), 127.3 (C-12), 126.6 (C-8), 124.0 (C-14), 114.3 (C-13), 107.9 (C-3), 99.8 (C-5), 55.3 (O*C*H$_3$). HRMS ($ESI^+$): m/z calcd for $C_{18}H_{15}O_3^+$[M+H]$^+$, 279.1016; found, 279.0982.

### 4.3.5 | 4-Phenyl-6-(*p*-tolyl)-2*H*-pyran-2-one (5c)

Yield method A: 57%; method B: 89% (yellow solid, mp = 114-115 °C). IR $\nu_{max}$ ($cm^{-1}$):1081 (C-O), 1698 (C=O). $^{1}$H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.79 (d, *J* = 10.0 Hz, 2H, H-12), 7.65-7-63 (dd, $J_1$ = 5.0 Hz, $J_2$ = 10.0 Hz, 2H, H-13), 7.51 (d, *J* = 5.0 Hz, 3H, H- 9, H-10), 7.28 (d, *J* = 10.0 Hz, 2H, H-9), 6.92 (s, 1H, H-5), 6.44 (s, 1H, H-3), 2.41 (s, 3H, C*H*$_3$). $^{13}$C NMR (125 MHz, $CDCl_3$) δ (ppm): 162.7 (C=O), 160.6 (C-6), 155.6 (C-4), 141.4 (C-14), 136.1 (C-11), 130.5 (C-10), 129.6 (C-8), 129.1 (C-9), 128.7 (C-7), 126.6 (C-13), 125.6 (C-12), 108.7 (C-3), 100.6 (C-5), 21.4 (*C*H$_3$). HRMS ($ESI^+$): m/z calcd for $C_{18}H_{15}O_2^+$[M+H]$^+$, 263.1067; found, 263.1038.

### 4.3.6 | 6-(4-Chlorophenyl)-4-phenyl-2*H*-pyran-2-one (5d)

Yield method A: 55%; method B: 86% (yellow solid, mp = 175-176 °C). IR $\nu_{max}$ ($cm^{-1}$): 1090 (C-O), 1700 (C=O). $^{1}$H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.82 (d, *J* = 10.0 Hz, 2H, H-13), 7.64-7.62 (m, 2H, H-9), 7.52-7.51 (m, 3H, H-10, H-12), 7.44 (d, *J* = 10.0 Hz, 2H, H-8), 6.94 (s, 1H, H-5), 6.46 (s, 1H, H-3). $^{13}$C NMR (125 MHz, $CDCl_3$) δ (ppm): 162.1 (C-6), 159.1 (C=O), 155.3 (C-4), 137.0 (C-11), 135.8 (C-7), 130.7 (C-10), 129.9 (C-8), 129.2 (C-12), 126.9 (C-13), 126.6 (C-9), 109.4 (C-3), 101.4 (C-5). HRMS ($ESI^+$): m/z calcd for $C_{17}H_{12}ClO_2^+$ $[M+H]^+$, 283.0520; found, 283.0492.

### 4.3.7 | 6-Phenyl-4-(*p*-tolyl)-2*H*-pyran-2-one (5e)

Yield method A: 49%; method B: 95% (light brown solid, mp = 114-115 °C). IR $\nu_{max}$ ($cm^{-1}$): 1081 (C-O), 1698 (C=O). $^1H$ NMR (500 MHz, $CDCl_3$) δ (ppm): 7.79 (d, $J$ = 10.0 Hz, 2H, H-12), 7.65-7.63 (dd, $J_1$ = 5.0 Hz, $J_2$ = 10.0 Hz, 2H, H-13), 7.51 (d, $J$ = 10.0 Hz, 3H, H-8, H-14), 7.28 (d, $J$ = 5.0 Hz, 2H, H-9) 6.92 (s, 1H, H-5), 6.44 (s, 1H, H-3), 2.41 (s, 3H, C$H_3$). $^{13}C$ NMR (125 MHz, $CDCl_3$) (δ, ppm): 162.7 (C=O), 160.6 (C-6), 155.6 (C-4), 141.4 (C-10), 136.1 (C-11), 130.5 (C-7), 129.6 (C-8), 129.1 (C-9), 126.6 (C-13), 125.6 (C-12), 108.7 (C-3), 100.6 (C-5), 21.4 ($CH_3$). HRMS ($ESI^+$): m/z calcd for $C_{18}H_{15}O_2^+[M+H]^+$, 263.1067; found, 263.1046.

### 4.3.8 | 6-(4-Methoxyphenyl)-4-(*p*-tolyl)-2*H*-pyran-2-one (5f)

Yield method A: 31% (yellow solid, mp = 85-86 °C). IR $\nu_{max}$ ($cm^{-1}$):1184 (C-O), 1706 (C=O). $^1H$ NMR (500 MHz, $CDCl_3$) δ (ppm): 6.85 (d, $J$ = 5.0 Hz, 2H, H-8), 7.55 (d, $J$ = 10.0 Hz, 2H, H-9), 7.31 (d, $J$ = 10.0 Hz, 2H, H-12), 6.98 (d, $J$ = 10.0 Hz, 2H, H-13), 6.85 (s, 1H, H-5), 6.40 (s, 1H, H-3), 3.88 (s, 3H, OC$H_3$), 2.43 (s, 3H, C$H_3$). $^{13}C$ NMR (125 MHz, $CDCl_3$) δ (ppm): 163.0 (C-6), 161.7 (C=O), 160.3 (C-4), 141.0 (C-14), 133.3 (C-7), 129.9 (C-12), 127.4 (C-8), 126.6 (C-9), 124.1 (C-10), 114.3 (C-13), 107.4 (C-3), 99.8 (C-5), 55.4 (O$CH_3$), 21.4 ($CH_3$). HRMS ($ESI^+$): m/z calcd for $C_{19}H_{16}O_3^+[M+H]^+$, 293.1172; found, 293.1173.

### 4.3.9 | 4-(m-Tolyl)-6-(*p*-tolyl)-2*H*-pyran-2-one (5g)

Yield method A: 53% (pale yellow crystals, mp = 112-113 °C). IR $\nu_{max}$ ($cm^{-1}$):1081 (C-O), 1698 (C=O). $^1H$ NMR (500 MHz, $CDCl_3$) δ (ppm): 7.80 (d, $J$ = 10.0 Hz, 2H, H-14), 7.44-7.39 (m, 3H, H-12, H-15), 7.33-7.27 (m, 3H, H-8, H-9, H-10), 6.92 (s, 1H, H-5), 6.43 (s, 1H, H-3), 2.45 (s, 3H, C$H_3$), 2.42 (s, 3H, C$H_3$). $^{13}C$ NMR (125 MHz, $CDCl_3$) δ (ppm): 162.8 (C-2), 160.4 (C-6), 155.9 (C-4), 141.3 (C-7), 138.9 (C-11), 136.1 (C-16), 131.3 (C-9), 129.6 (C-15), 129.0 (C-10), 128.7 (C-13), 127.3 (C-12), 125.6 (C-14), 123.8 (C-8), 108.6 (C-3), 100.8 (C-5), 21.4 (both $CH_3$). HRMS ($ESI^+$): m/z calcd for $C_{19}H_{17}O_2^+[M+H]^+$, 277.1223; found, 277.1236.

### 4.3.10 | 6-Phenyl-4-(thiophen-3-yl)-2*H*-pyran-2-one (5i)

Yield method A: 58%; method B: 77% (brown solid, mp = 159-160 °C). IR $\nu_{max}$ ($cm^{-1}$): 1077 (C-O), 1691 (C=O). $^1H$ NMR (500 MHz, $CDCl_3$) δ (ppm): 7.91-7.89 (dd, $J_1$ = 5.0 Hz, $J_2$ = 10.0 Hz, 2H, H-8), 7.79 (m, 1H, H-9), 7.49 - 7.48 (dd, $J_1$ = 5.0 Hz, $J_2$ = 10.0 Hz, 4H, H-12, H-13), 7.44-7.43 (dd, $J_1$ = 5.0 Hz, $J_2$ = 10.0 Hz, 1H, H-10), 6.95 (s, 1H, H-5), 6.47 (s, 1H, H-3). $^{13}C$ NMR (125 MHz, $CDCl_3$) δ (ppm): 162.8 (C=O), 160.4 (C-2), 149.2 (C-6), 137.6 (C-12), 131.6 (C-7), 131.4 (C-4), 130.9 (C-15), 128.9 (C-14), 127.8 (C-11), 125.8 (C-8), 125.7 (C-13), 125.4 (C-10), 107.7 (C-3), 100.8 (C-5). HRMS ($ESI^+$): m/z calcd for $C_{15}H_{11}O_2S^+$ $[M+H]^+$, 255.0474; found, 255.0483.

### 4.3.11 | 4-(Thiophen-3-yl)-6-(*p*-tolyl)-2*H*-pyran-2-one (5j)

Yield method A: 59% (brown solid, mp = 186-187 °C). IR $\nu_{max}$ ($cm^{-1}$): 1076 (C-O), 1694 (C=O). $^1H$ NMR (500 MHz, $CDCl_3$) δ (ppm): 7.78 (d, $J$ = 10.0 Hz, 3H, H-9, H-12), 7.48-7.46 (dd, $J_1$ = 5.0 Hz, $J_2$ = 10.0 Hz, 1H, H-10), 7.43 (d, $J$ = 5.0 Hz, 1H, H-8), 7.28 (d, $J$ = 10.0 Hz, 2H, H-13), 6.90 (s, 1H, H-5), 6.43 (s, 1H, H-3), 2.41 (s, 3H, C$H_3$). $^{13}C$ NMR (125 MHz, $CDCl_3$) δ (ppm): 163.0 (C=O), 160.6 (C-6), 149.3 (C-4), 141.4 (C-14), 137.6 (C-7), 129.6 (C-12), 128.7 (C-11), 127.9 (C-10), 125.7 (C-13), 125.6 (C-8), 125.4 (C-9), 107.2 (C-3), 100.1 (C-5), 21.4 ($CH_3$). HRMS ($ESI^+$): m/z calcd for $C_{16}H_{13}O_2S^+$ $[M+H]^+$, 269.0631; found, 269.0614.

### 4.3.12 | 4-(Cyclohex-1-en-1-yl)-6-phenyl-2*H*-pyran-2-one (5k)

Yield method A: 48%; method B: 73% (dark brown solid, mp = 95-96 °C). IR $\nu_{max}$ ($cm^{-1}$):1074 (C-O), 1700 (C=O). $^1H$ NMR (500 MHz, $CDCl_3$) δ (ppm): 7.84 (dd, $J_1$ = 5.0 Hz, $J_2$ = 10.0 Hz, 2H, H-14), 7.45-7.44 (d, $J$ = 5.0 Hz, 3H, H-15, H-16), 6.82 (s, 1H, H-5), 6.58 (s, 1H, H-8), 6.16 (s, 1H, H-3), 2.31 (m, 4H, H-9, H-12), 1.81-1.78 (m, 2H, H-11), 1.70-1.66 (m, 2H, H-10). $^{13}C$ NMR (125 MHz, $CDCl_3$) δ (ppm): 166.4 (C=O), 158.8 (C-6), 155.3 (C-4), 133.3 (C-7), 132.8 (C-8), 131.9 (C-13), 130.5 (C-16), 128.8 (C-14), 125.6 (C-15), 106.6 (C-3), 99.2 (C-5), 26.2 (C-9), 25.6 (C-12), 22.3 (C-10), 21.5 (C-11). HRMS ($ESI^+$): m/z calcd for $C_{17}H_{17}O_2^+[M+H]^+$, 253.1223; found, 253.1195.

### 4.3.13 | Ethyl 3,5-diphenylfuran-2-carboxylate (6a)

Yield: 39% (pale yellow solid, mp = 92-93 °C). IR $\nu_{max}$ ($cm^{-1}$): 1189 (C-O), 1706 (C=O). $^1H$ NMR (500 MHz, $CDCl_3$) δ (ppm): 7.82 (d, $J$ = 10.0 Hz, 2H, H-11), 7.62 (d, $J$ = 10.0 Hz, 2H, H-7), 7.46-7.37 (m, 6H, H-8, H-9, H-12, H-13), 6.85 (s, 1H, H-4), 4.33 (q, $J$ = 10.0 Hz, 2H, O$CH_2$CH$_3$), 1.31 (t, $J$ = 5.0 Hz, 3H, OCH$_2$C$H_3$). $^{13}C$ NMR (125 MHz, $CDCl_3$) δ (ppm): 159.2 (C=O), 155.8 (C-5), 138.1 (C-2), 136.4 (C-6), 132.1 (C-3), 129.3 (C-8),

129.3 (C-12), 129.0 (C-9), 128.8 (C-13), 128.2 (C-10), 127.9 (C-7), 124.9 (C-11), 109.3 (C-4), 60.7 ($OCH_2CH_3$), 14.1 ($OCH_2CH_3$). HRMS ($ESI^+$): m/z calcd for $C_{19}H_{17}O_3^+$ $[M+H]^+$, 292.1172; found, 293.1176.

### 4.3.14 | Ethyl 5-(4-methoxyphenyl)-3-phenylfuran-2-carboxylate (6b)

Yield: 24% (yellow oil). IR $\nu_{max}$ ($cm^{-1}$): 1175 (C-O), 1710 (C=O). $^1H$ NMR (500 MHz, $CDCl_3$) δ (ppm): 7.76 (d, $J$ = 10.0 Hz, 2H, H-11), 7.61 (d, $J$ = 5.0 Hz, 2H, H-7), 7.43-7.37 (m, 3H, H-8, H-9), 6.97 (d, $J$ = 10.0 Hz, 2H, H-12), 6.72 (s, 1H, H-4), 4.32 (q, $J$ = 10.0 Hz, 2H, $OCH_2CH_3$), 3.86 (s, 3H, $OCH_3$), 1.30 (t, $J$ =10.0 Hz, 3H, $OCH_2CH_3$). $^{13}C$ NMR (125 MHz, $CDCl_3$) δ (ppm): 160.3 (C-13), 159.3 (C=O), 156.0 (C-5), 137.6 (C-2), 136.6 (C-6), 129.3 (C-7), 128.1 (C-9), 127.9 (C-8), 126.5 (C-11), 114.3 (C-12), 108.0 (C-4), 60.6 ($OCH_3$), 55.3 ($OCH_2CH_3$), 14.2 ($OCH_2CH_3$). HRMS ($ESI^+$): m/z calcd for $C_{20}H_{19}O_4^+$ $[M+H]^+$, 323.1278; found, 323.1280.

### 4.3.15 | Ethyl-3-phenyl-5-(*p*-tolyl) furan-2-carboxylate (6c)

Yield: 24% (pale yellow crystals, mp = 108-109 °C). IR $\nu_{max}$ ($cm^{-1}$): 1179 (C-O), 1709 (C=O). $^1H$ NMR (500 MHz, $CDCl_3$) δ (ppm): 7.72 (d, $J$ = 10.0 Hz, 2H, H-11), 7.61 (d, $J$ = 10.0 Hz, 2H, H-12), 7.41 (m, 3H, H-7, H-9), 7.25 (m, 3H, H-8, H-9), 6.80 (s, 1H, H-4), 4.33 (q, $J$ = 10.0 Hz, 2H, $OCH_2CH_3$), 2.40 (s, 3H, $CH_3$), 1.31 (t, $J$ = 10.0 Hz, 3H, $OCH_2CH_3$). $^{13}C$ NMR (125 MHz, $CDCl_3$) δ (ppm): 159.2 (C=O), 156.1 (C-5), 139.1 (C-2), 137.7 (C-6), 136.5 (C-13), 132.2 (C-9), 129.5 (C-12), 129.3 (C-8), 128.2 (C-10), 127.9 (C-7), 126.6 (C-9), 124.8 (C-11), 108.7 (C-4), 60.6 ($OCH_2CH_3$), 21.4 ($CH_3$), 14.2 ($OCH_2CH_3$). HRMS ($ESI^+$): m/z calcd for $C_{20}H_{19}O_3^+$ $[M+H]^+$, 307.1329; found, 307.1345.

### 4.3.16 | Ethyl 5-(4-chlorophenyl)-3-phenylfuran-2-carboxylate (6d)

Yield: 30% (light brown solid, mp = 91-92 °C). IR $\nu_{max}$ ($cm^{-1}$): 1170 (C-O), 1700 (C=O). $^1H$ NMR (500 MHz, $CDCl_3$) δ (ppm): 7.76 (d, $J$ = 5.0 Hz, 2H, H-11), 7.60 (d, $J$ = 5.0 Hz, 2H, H-12), 7.54 (d, $J$ = 5.0 Hz, 1H, H-9), 7.44-7.36 (m, 4H, H-7, H-8), 6.84 (s, 1H, H-4), 4.33 (q, $J$ = 10.0 Hz, 2H, $OCH_2CH_3$), 1.31 (t, $J$ = 10.0 Hz, 3H, $OCH_2CH_3$). $^{13}C$ NMR (125 MHz, $CDCl_3$) δ (ppm): 159.3 (C=O), 156.7 (C-5), 138.8 (C-2), 135.1 (C-3), 133.4 (C-13), 133.1 (C-6), 129.6 (C-10), 129.4 (C-8), 129.3 (C-7), 128.8 (C-12), 126.6 (C-9), 125.3 (C-11), 109.4 (C-4), 61.4, ($OCH_2CH_3$) 14.4 ($OCH_2CH_3$). HRMS ($ESI^+$): m/z calcd for $C_{17}H_{11}ClO_2$ ($[M+H]^+$-OEt), 282.0448; found, 282.2744.

### 4.3.17 | Ethyl 5-phenyl-3-(*p*-tolyl) furan-2-carboxylate (6e)

Yield: 33% (white solid, mp = 108-109 °C). IR $\nu_{max}$ ($cm^{-1}$): 1175 (C-O), 1702 (C=O). $^1H$ NMR (500 MHz, $CDCl_3$) δ (ppm): 7.82 (d, $J$ = 10.0 Hz, 2H, H-11), 7.53 (d, $J$ = 10.0 Hz, 2H, H-12), 7.49-7.36 (m, 3H, H-7, H-13), 7.24 (d, $J$ = 10.0 Hz, 2H, H-8), 6.84 (s, 1H, H-4), 4.32 (q, $J$ = 10.0 Hz, 2H, $OCH_2CH_3$), 2.40 (s, 3H, $CH_3$), 1.33 (t, $J$ = 10.0 Hz, 3H, $OCH_2CH_3$). $^{13}C$ NMR (125 MHz, $CDCl_3$) δ (ppm): 159.2 (C=O), 155.7 (C-5), 138.1 (C-2), 137.9 (C-6), 136.5 (C-3), 129.4 (C-12), 129.2 (C-13), 129.1 (C-9), 129.0 (C-10), 128.8 (C-7), 128.7 (C-8), 109.4 (C-11), 60.7 ($OCH_2CH_3$), 21.3 ($CH_3$), 14.2 ($OCH_2CH_3$). HRMS ($ESI^+$): m/z calcd for $C_{20}H_{19}O_3^+$ $[M+H]^+$, 307.1329; found, 307.1345.

### 4.3.18 | Ethyl 5-(4-methoxyphenyl)-3-(*p*-tolyl) furan-2-carboxylate (6f)

Yield: 14% (brown solid, mp = 98-99 °C). IR $\nu_{max}$ ($cm^{-1}$): 1172 (C-O), 1705 (C=O). $^1H$ NMR (500 MHz, $CDCl_3$) δ (ppm): 7.75 (d, $J$ = 10.0 Hz, 2H, H-11), 7.52 (d, $J$ = 5.0 Hz, 2H, H-7), 7.22 (d, $J$ = 5.0 Hz, 2H, H-8), 6.96 (d, $J$ = 10.0 Hz, 2H, H-12), 6.71 (s, 1H, H-4), 4.33 (q, $J$ = 10.0 Hz, 2H, $OCH_2CH_3$), 3.86 (s, 3H, $OCH_3$), 2.40 (s, 3H, $CH_3$), 1.32 (t, $J$ = 10.0 Hz, 3H, $OCH_2CH_3$).$^{13}C$ NMR (125 MHz, $CDCl_3$) δ (ppm): 160.3 (C-13), 159.3 (C=O), 155.9 (C-5), 138.1 (C-2), 137.4 (C-3), 136.7 (C-9), 129.3 (C-6), 129.2 (C-7), 128.6 (C-8), 126.4 (C-11), 122.4 (C-10), 114.2 (C-12), 108.0 (C-4), 60.5 ($OCH_2CH_3$), 55.3 ($OCH_3$), 21.2 ($CH_3$), 14.2 ($OCH_2CH_3$). HRMS ($ESI^+$): m/z calcd for $C_{21}H_{21}O_4^+$ $[M+H]^+$, 337.1434; found, 337.1440.

### 4.3.19 | Ethyl 5-phenyl-3-(3-(trifluoromethyl) phenyl) furan-2-carboxylate (6h)

Yield: 20% (brown solid, mp = 99-100 °C). IR $\nu_{max}$ ($cm^{-1}$):1180 (C-O), 1708 (C=O). $^1H$ NMR (500 MHz, $CDCl_3$) δ (ppm): 7.88 (s, 1H, H-7), 7.84-7.80 (m, 3H, H-9, H-15), 7.65 (d, $J$ = 5.0 Hz, 1H, H-11), 7.57-7.53 (dd, $J_1$ = 5.0 Hz, $J_2$ = 10.0 Hz, 2H, H-14), 7.46 (t, $J$ = 10.0 Hz, 2H, H-10), 7.40 (d, $J$ = 10.0 Hz, H-10), 4.33 (q, $J$ = 10.0 Hz, 2H, $OCH_2CH_3$), 1.30 (t, $J$ = 10.0 Hz, 3H, $OCH_2CH_3$). $^{13}C$ NMR (125 MHz, $CDCl_3$) δ (ppm): 158.9 (C=O), 156.3 (C-5), 138.5 (C-2), 134.7 (C-6), 133.0 (C-3), 132.6 (C-8), 129.2 (C-11), 128.9 (C-14), 128.4 (C-7), 126.3 ($CF_3$), 124.9 (C-13), 109.0 (C-4), 60.9 ($OCH_2CH_3$), 14.0 ($OCH_2CH_3$). $^{19}F$ NMR (500 MHz, $CDCl_3$) δ (ppm):-62.6 ($CF_3$). HRMS ($ESI^+$): m/z calcd for $C_{20}H_{16}F_3O_3^+[M+H]^+$, 361.1035; found 361.1004.

### 4.3.20 | Pentacarbonylpyridinylchromium(0) (7a)

Yield: 52% (yellow crystals, mp = 94-95 °C). IR $\nu_{max}$ ($cm^{-1}$): 439, 647, 655, 756, 1445, 1921, 2066, 2922, 3074, 3109. $^1H$ NMR (500 MHz, $CDCl_3$) δ (ppm):8.52 (bs, 2H, H-2), 7.64 (bs, 1H, H-4), 7.17 (bs, 2H, H-3).$^{13}C$ NMR (125 MHz, $CDCl_3$) δ (ppm): 220.7 ($CO_{trans}$), 214.4 ($CO_{cis}$), 155.4 (C-2), 137.2 (C-4), 124.9 (C-3). HRMS ($ESI^+$): m/z calcd for $Cr(CO)_4$ [$M^+$ - $C_5H_4NBr$ - CO], 163.9202; found 163.9783.

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