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Alkynyl triazenes enable divergent syntheses of 2-pyrones†

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The 2-pyrone motif occurs frequently in bioactive natural products and is appreciated as synthetic intermediates. However, only few methods allow for diversifying functional group modifications on this relevant heterocycle. The distinct properties of 1-alkynyl triazenes promote a smooth addition of propiolic acids across the triple bond. Addition of catalytic amounts of silver salt induces cyclization to 2-pyrones. Depending on the reaction temperature, either 6-triazenyl or 5-triazenyl 2-pyrones are selectively formed. The triazenyl unit is subsequently replaced by a variety of valuable groups in a one-pot process yielding for instance 2-fluoro pyrones. The substitution occurs with an intriguing 1,5-carbonyl transposition. Moreover, the triazenyl group serves as traceless activating group for subsequent Diels–Alder cycloadditions and as a constituting unit for rare fused aminopyrazole pyrone heterocycles.

Introduction

2-Pyrones represent a frequently encountered framework in diverse bioactive natural products, exhibiting a broad range of antifungal, antibiotic, cytotoxic and phytotoxic activities (Fig. 1).[1] These occurrences and properties sparked interests in the scaffold and motivated the development of 2-pyrone syntheses. To date, the repertoire of synthetic methods[2] to access 2-pyrones include cyclizations,[3] ring expansions,[4] cyclotrimerizations[5] and transition metal-catalyzed vinylic C–H annulations.[6] However, despite these diverse strategies, the reachable functional group variability on 2-pyrones remains relatively limited compared to that of the related benzannulated congeners, the isocoumarins. For instance, reported substituents at the 6-position are largely restricted to aryl or alkyl groups, while halo or other heteroatom substituents are scarce (Fig. 2a).[7–9] This might be attributed to tedious or non-viable routes to elaborate starting materials required for their construction. The limited substituent flexibility constitutes a bottleneck for medicinal chemistry studies involving these heterocycles.

Besides their bioactive properties, 2-pyrones are attractive dienes in Diels–Alder reactions delivering highly elaborate arenes after expulsion of CO_2.[10] However, installations of additional electron-donating substituents such as amino or methoxyphenyl groups are often required to enhance their reactivity (Fig. 2b).[11] Subsequent removal of these substituents, or difficulties in subjecting them to functional group manipulations, render the normal electron-demand Diels–Alder reaction of 2-pyrones far less adopted in total synthesis than its inverse electron-demand counterpart.[10a]

Over the past years, the use of alkynyl triazenes has gained momentum in organic synthesis.[12,13] They possess a unique ynamide-like reactivity,[14] and are compatible with transition metals[15] paired with versatile transformability into numerous functional groups. These values drew our interest to access triazenyl pyrones, which would in turn enable a divergent access to various functionalized pyrones. Inspired by Cui's synthesis of 2-pyrones from ynamides (Fig. 2c),[3a] we hereby report a smooth addition of propiolic acids to alkynyl triazenes, followed by a silver-catalyzed cyclization to triazenyl 2-pyrones (Fig. 2d). Divergent elaboration of the triazenyl groups into various valuable groups occurs under an unusual 1,5-carbonyl transposition delivering 3,4-substituted isomers. The triazene unit also serves as a traceless activating group for subsequent Diels–

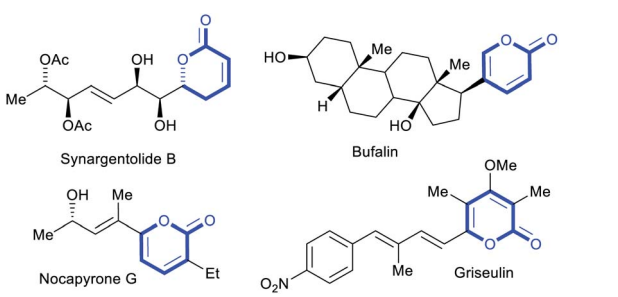

Fig. 1 Bioactive 2-pyrone containing natural products.

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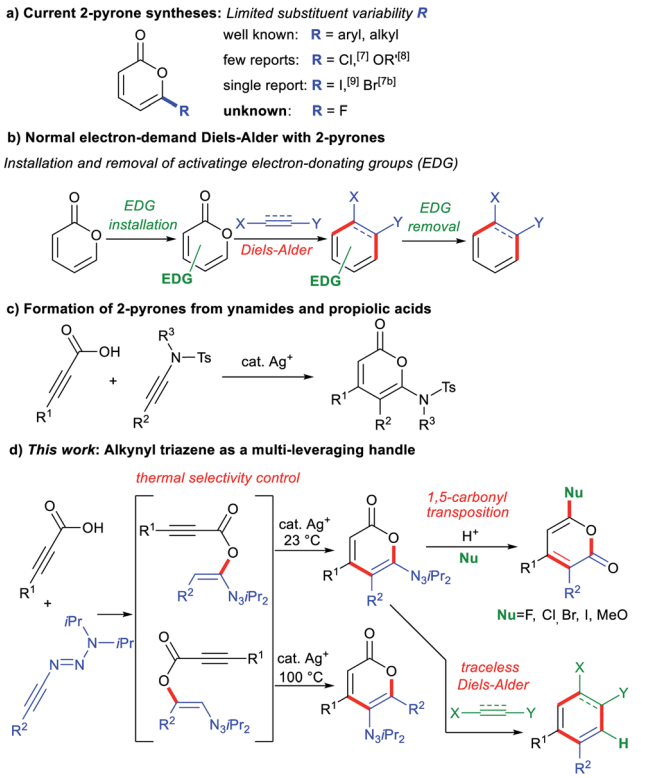


Fig. 2 Exploitation of the triazenyl group as a multi-leveraging reactivity and selectivity handle for the 2-pyrone synthesis and functionalization.

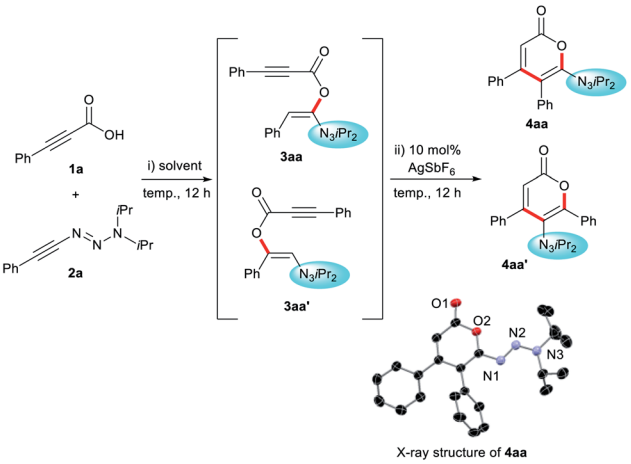
Alder cycloadditions and as a constituting unit for fused aminopyrazoles.

Results and discussion

Our studies were initiated by investigating the reaction between phenyl propiolic acid (**1a**) and alkynyl triazene **2a** (Table 1). At 60 °C in toluene, addition of **1a** to **2a** formed acyloxy alkene **3aa** in 95% yield and complete regioselectivity (entry 1). The sequential addition of catalytic $AgSbF_6$ initiated cyclization to 6-triazenyl pyrone **4aa** along with minor amounts of isomer **4aa′** (entry 2). The structure of **4aa** was confirmed by X-ray crystallography.[16] **4aa′** is presumably formed from the thermodynamic regioisomer **3aa′**. Indeed, a 1 : 1 mixture of **3aa** and **3aa′** was observed at 100 °C in the absence of $AgSbF_6$ (entry 3). Performing the process at ambient temperature in CH_2Cl_2 led to quantitative and exclusive formation of **4aa** (entries 4–6). The direct addition of $AgSbF_6$ at the start of reaction, or using a 5 mol% loading, resulted in lower yields (entries 7 and 8). Very notably, conducting the reaction at 100 °C strongly favored the formation of isomer **4aa′** in good yields (entries 10–12). In summary, this is a simple temperature switch of the reaction outcome.

Despite the highly-valued fluorine effect in heterocycles in drug discovery,[17] fluorinated 2-pyrones remain the rarest and least reported among functionalized 2-pyrones.[18] The complete lack of suitable methods to access 6-fluoro 2-pyrones

Table 1 Optimization studies of the triazenyl pyrone formation[a]

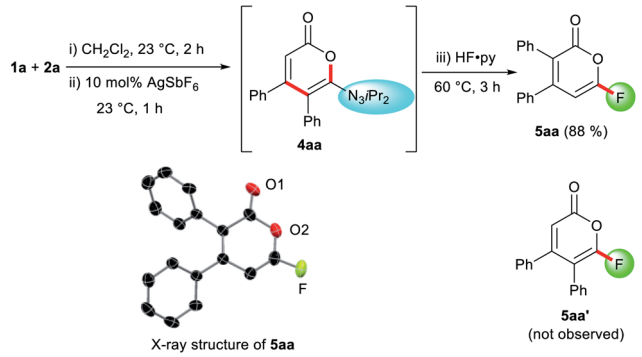


Entry	T (°C)	Solvent	% yield 3aa (3aa : 3aa′)	% yield 4aa	% yield 4aa′	4aa : 4aa′
1[b]	60	PhMe	95 (>20 : 1)[h]	Trace	—	—
2	60	PhMe	—	75	8	10 : 1
3[b]	100	PhMe	46 (1 : 1)[h]	—	—	—
4	23	PhMe	—	92	—	>20 : 1
5	23	CH_2Cl_2	—	99	—	>20 : 1
6[c]	**23**	**CH_2Cl_2**	**—**	**98**[h]	**—**	**>20 : 1**
7[d]	23	CH_2Cl_2	38 (>20 : 1)[h]	49	—	>20 : 1
8[e]	23	CH_2Cl_2	—	68	—	>20 : 1
9	100	PhMe	—	13	58	1 : 4.5
10[f]	100	PhMe	—	12	72[h]	1 : 6
11[g]	100	PhMe	—	13	65	1 : 5
12[f]	120	PhMe	—	13	70	1 : 5.4

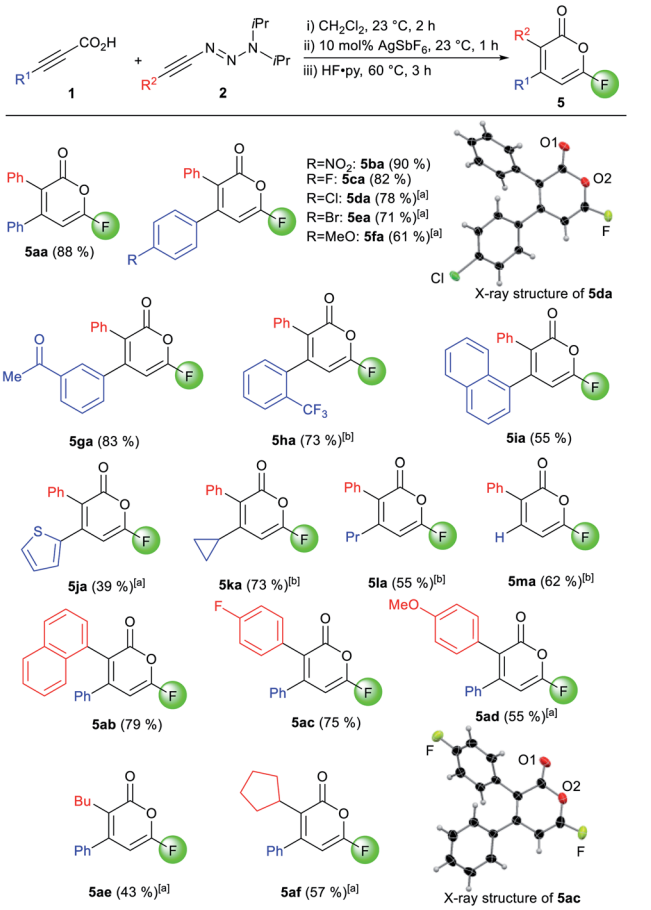
[a] Conditions: (i) 0.11 mmol **1a**, 0.10 mmol **2a**, 0.2 M in the indicated solvent and temperature for 12 h, (ii) 10 μmol $AgSbF_6$, 12 h, yield and ratio determined by ^{1}H-NMR with an internal standard. [b] 12 h for (ii), no $AgSbF_6$. [c] (i) 0.11 mmol **1a**, 0.10 mmol **2a** in CH_2Cl_2 for 2 h, (ii) 10 μmol $AgSbF_6$, 23 °C for 1 h. [d] 0.11 mmol **1a**, 0.10 mmol **2a**, 10 μmol $AgSbF_6$ in CH_2Cl_2 at 23 °C for 24 h. [e] 5 μmol $AgSbF_6$. [f] With 0.15 mmol **1a**. [g] With 0.18 mmol **1a**. [h] Isolated yields. Ortep structure of **4aa** with thermal ellipsoids are at 50% probability. Hydrogen atoms are omitted for clarity.

underscores the formidable challenges of regioselective fluorination of 2-pyrones. To address this gap in synthetic methodology, we opted to transform the triazene unit into a fluoride substituent by the Wallach reaction.[19] In a one-pot fashion, HF·py was added to the crude reaction mixture containing **4aa** (Scheme 1). Surprisingly, the expected 4,5-disubstituted pyrone **5aa′** was not detected. Instead, 3,4-disubstituted isomer **5aa** was isolated in 88% yield, confirmed by X-ray crystallography.[16] This unexpected phenomenon was attributed to a 1,5-carbonyl transposition (*vide infra*). Despite the facile acidic cleavage of **4aa**, its regioisomer **4aa′** was found to be unreactive or unproductive towards further transformations (see ESI† for details).

The scope for the one-pot 6-fluoropyrone formation was subsequently evaluated (Scheme 2). Both, electron-rich and electron-poor aryl groups R^1 were well tolerated, furnishing fluoropyrones **5ba–5ha** in good yields, with full regioselectivity



Scheme 1 1,5-Carbonyl transposition in the one-pot formation of fluoropyrone **5aa**. Ortep structure of **5aa** with thermal ellipsoids are at 50% probability. Hydrogen atoms are omitted for clarity.



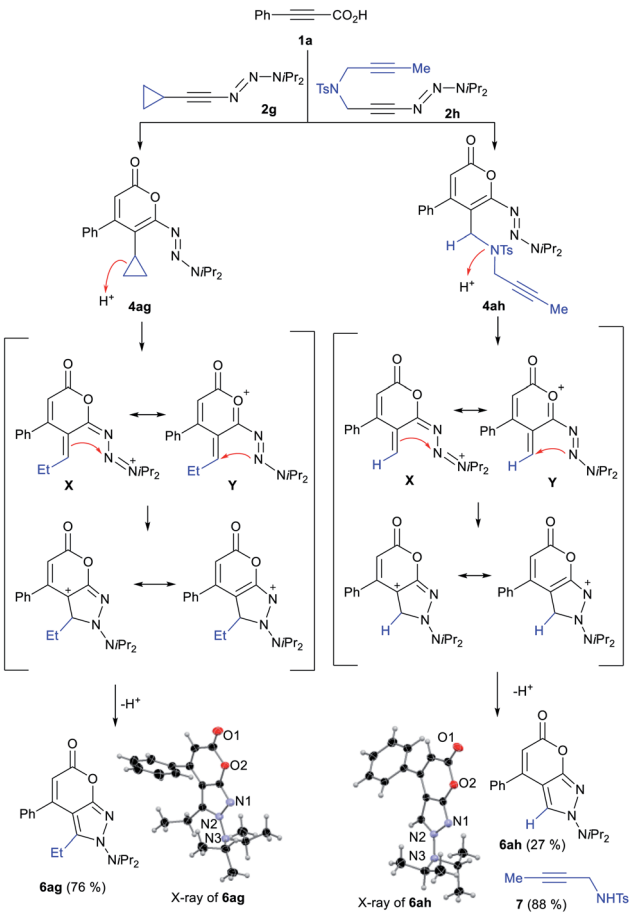
Scheme 2 Scope for fluoropyrone formation. Conditions: (i) 0.11 mmol **1a**, 0.10 mmol **2a** in CH_2Cl_2 (0.2 M) at 23 °C for 2 h, (ii) 10 μmol $AgSbF_6$ at 23 °C for 1 h, (iii) 1.0 mL HF·py at 60 °C for 3 h; [a] 0.5 mL HF·py at 23 °C for 48 h for step (iii); [b] 60 °C for 12 h for step (ii).

and complete 1,5-transposition. 1-Naphthyl- (**5ia**) and a thienyl-substituted products (**5ja**) were as well accessed. Alkyl groups like cyclopropyl (**5ka**) and propyl (**5la**) were well accepted. The use of parent propiolic acid **1m** provided 3-phenyl-6-fluoropyrone **5ma**. Concerning the alkynyl triazenes, various aryl and alkyl substituents consistently reacted well and afforded pyrones in good yields and full regioselectivity (**5ab–5af**). X-Ray crystallographic analysis of **5da** and **5ac** confirmed assignment of the substituent R^1 and R^2 on the pyrone core.[16]

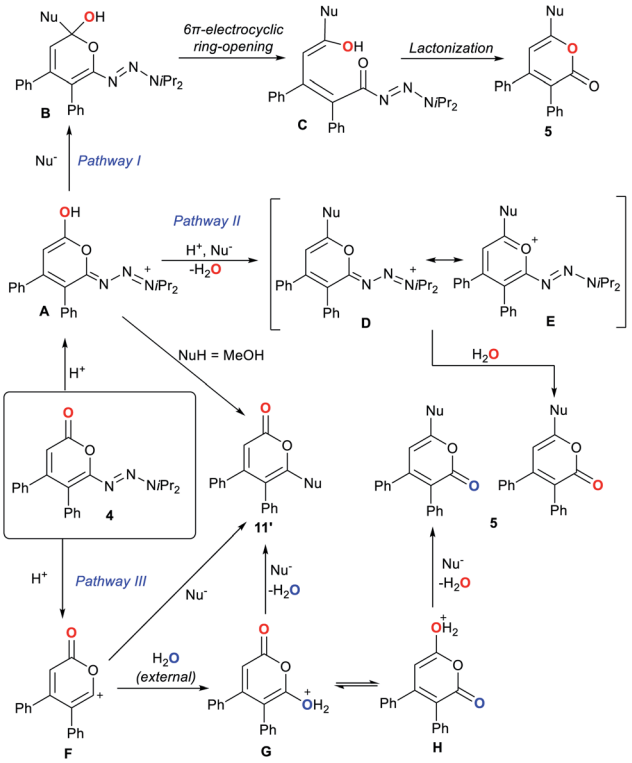
During our investigations, very notable reactivity profiles were encountered with specific alkynyl triazenes. In particular, cyclopropyl-substituted substrate **2g** provided pyrone-fused *N*-aminopyrazole **6ag** in 76% yield whereas the expected fluoropyrone was not observed at all (Scheme 3).[15g] This highly rare fused double heterocyclic system was as well obtained with tethered 1-diynyl triazene **2h**. The structures of **6ag** and **6ah** were unambiguously confirmed by single crystal X-ray diffraction[16] We reasoned that the *N*-aminopyrazoles arose from triazenyl pyrone intermediates **4ag** and **4ah** *via* the depicted mechanisms.[20] For **4ag**, a cyclopropane ring opening assisted by triazene or the conjugated oxygen leads to X and Y. An intramolecular cyclization and a subsequent rearomatization then give rise to **6ag**. In a similar fashion, displacement of the tosylamide group in **4ah** leads to **6ah**, further evidenced by the isolation of tosylamide **7**. These unique products underscore once again triazenes possess an untapped potential to forge novel and complex fused heterocyclic systems.

Next, we investigated further one-pot divergent functionalizations of the triazenyl pyrones (Scheme 4). For instance, performing the one-pot process with **1a** and **2a**, chloro- (**8**), bromo- (**9**) and iodo-pyrones (**10**) were efficiently prepared in high yields using the corresponding trimethylsilyl halides. Again, the 1,5-carbonyl transposition was observed for these products. The use of MeOH as the nucleophile gave a 4.4 : 1 mixture of transposed dimethoxy orthoester **11** and its non-transposed isomer **11′**. Notably, triazenyl pyrones engage in normal-electron demand Diels–Alder reactions. For instance, its reaction with acetylene dicarboxylate tetrasubstituted gave arene **12**. The triazenyl group was cleaved after the cycloaddition, presumably by a thermally-induced radical mechanism,[21] as evidenced by some amounts of triazenyl arene **13**. Anthraquinone **14** was furnished in 69% yield after two consecutive cycloadditions on *p*-quinone were engaged, followed by triazenyl elimination. The use of a larger excess *p*-quinone gave naphthoquinone **15**. Remarkably, the triazene was cleaved cleanly in all Diels–Alder examples. Contrasting to conventional strategies to activate pyrones for Diels–Alder cycloadditions, the triazenyl pyrones offer a highly efficient alternative to access densely substituted arenes leveraging the triazene moiety as a traceless activating group.

To the best of our knowledge, the observed pyrone 1,5-carbonyl transposition has not been reported to date. Three plausible pathway for this transposition can be envisioned (Scheme 5).[22–24] Initial protonation of the carbonyl oxygen atom would form pyranol **A**. For pathway **I**, a subsequent nucleophile addition leads to **B**.[22b,22c] In turn, **B** eventually undergoes a oxa 6π-electrocyclic ring opening[23] leading to δ-hydroxy unsaturated acyl triazene **C**. Lactonization of the activated acyl triazene unit[24] delivers transposed product **5**. For pathway **II**, the hydroxyl group of **A** alternatively might undergo a substitution by the nucleophile generating cationic intermediate **D** and a molecule of water. Species **D** may be stabilized by its pyrylium mesomer **E**. Both are capable of providing **5** upon triazene

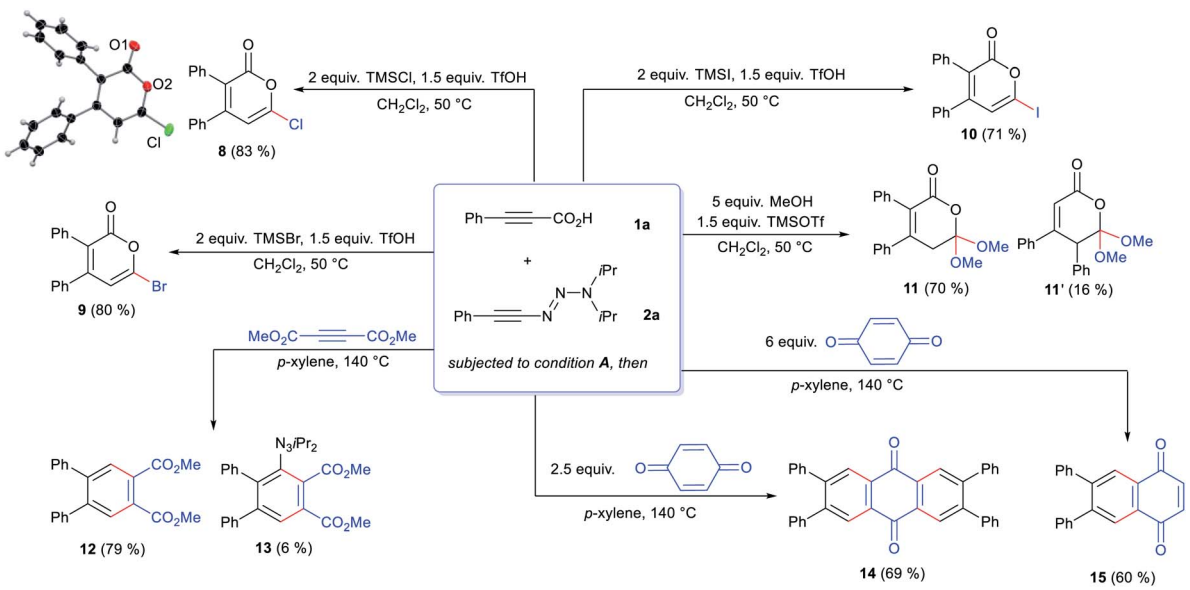


Scheme 3 *N*-Aminopyrazole formation from **2g** or **2h**. Condition: (i) 0.11 mmol **1a**, 0.10 mmol **2a** in CH_2Cl_2 (0.2 M) at 23 °C for 2 h, (ii) 10 μmol $AgSbF_6$ at 23 °C for 1 h, (iii) 1.0 mL HF·py at 60 °C for 3 h.

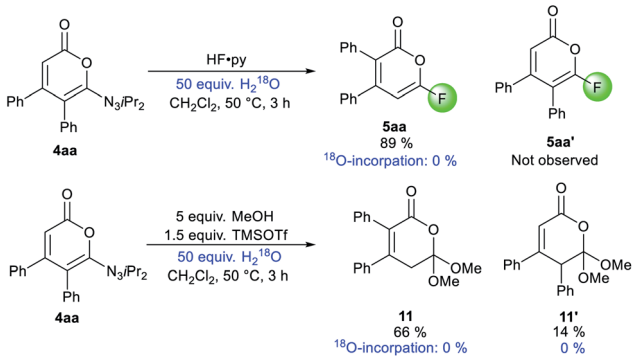


Scheme 5 Possible mechanism pathways for the 1,5-carbonyl transposition.

displacement by re-addition of the previously expelled water. A third pathway involves trapping of the putative cation **F** by an external water molecule to give isomeric hydroxy-pyrones **G** and **H**. However, the non-transposed isomer was not observed with any halide nucleophiles. The insufficient discrimination



Scheme 4 One-pot divergent formation of functionalized 2-pyrones and engagement in Diels–Alder cycloadditions. Condition **A**: 0.11 mmol **1a**, 0.10 mmol **2a**, 0.2 M CH_2Cl_2 at 23 °C for 2 h, then 10 μmol $AgSbF_6$ at 23 °C for 1 h.



Scheme 6 ^{18}O-Isotope labelling experiments of pyrone **4aa**.

between **G** and **H** reduces the likelihood of pathway **III**. Similarly, pathway **II** has a lower possibility as **A** should also be capable of generating the non-transposed isomer with halides.

Experimentally, isotope spiking experiments with 50 equivalents of $H_2{}^{18}O$ on the fluorination and methoxylation did not provide any incorporation of ^{18}O in **5aa** and **11** based on ^{13}C NMR and mass spectrometry (Scheme 6).[25] This is hinting towards an intramolecular mechanism. Therefore, illustrated pathway **I** might be the most plausible mechanism for the transposition. Minor isomer **11′** would be generated from **A** using methanol as a nucleophile.

Conclusions

In summary, we reported a one-pot divergent formation of a broad range of functionalized 2-pyrones by leveraging the reactivity of alkynyl triazenes on several instances. They first facilitate the addition of carboxylic acids across the alkyne triple bond. Secondly, it can be easily converted into a wide range of desirable functionalities. These comprise the synthesis of unreported 6-fluoropyrones, as well as pyrones with chloride, bromide, iodide and methoxy substituents at the 6-position. Notably, we have unraveled an unusual and mechanistically intriguing 1,5-carbonyl transposition, evidencing the non-innocent behavior of the triazenyl group. Furthermore, the triazenyl unit can be used to access rare pyrone-fused pyrazole heterocycles. Moreover, the triazene substituent acts as a traceless activating group facilitating normal electron-demand Diels–Alder cycloadditions, affording densely substituted arene products.

Data availability

The datasets supporting this article have been uploaded as part of the supplementary material. Crystallographic data for **4aa**, **5aa**, **5ca**, **5ac**, **6ag**, **6ah** and **8** has been deposited at the CCDC under 2075639 and 2075641-2075646 and can be obtained from www.ccdc.cam.ac.uk.

Author contributions

JFT, KS and NC conceived, designed and directed the project. JFT conducted the experiments. CTB synthesized the alkynyl triazenes. All authors wrote the manuscript.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

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16 Supplementary crystallographic data of the following compounds can be found from The Cambridge Crystallographic Data Centre: 2075639 (**4aa**), 2075641 (**5aa**), 2075642 (**5ca**), 2075643 (**5ac**), 2075644 (**6ag**), 2075645 (**6ah**) and 2075646 (**8**).†

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