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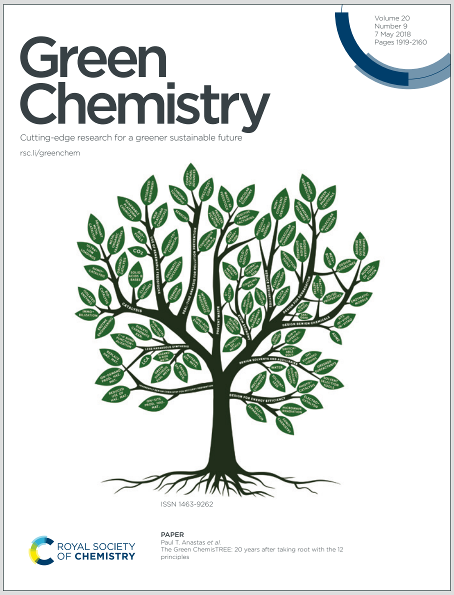

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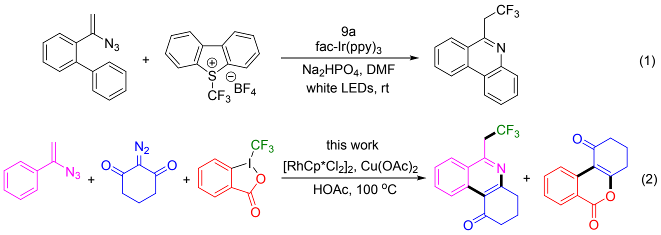
Two birds with one stone: One-pot simultaneous synthesis of 2,2,2-trifluoroethylphenanthridines and benzochromenones featuring with utilization of the byproduct of Togni's reagent

Cai Gao, Bin Li, Xueyang Geng, Qianting Zhou, Xinying Zhang*, and Xuesen Fan*

In this paper, a novel and efficient one-pot synthesis of 2,2,2-trifluoroethylphenanthridines (4) and benzochromenones (5) through the three-component reactions of vinyl azides (1) with cyclic α-diazo carbonyl compounds (2) and Togni's reagent (3) is presented. In these cascade reactions, 3 acted as not only the source of CF_3 radical to react with 1 and 2 to afford 4, but also the pool of *o*-iodobenzoic acid to couple with 2 to afford 5. To our knowledge, this is the first example in which 4 and 5 were obtained in a one-pot manner, and the byproduct of Togni's reagent, *o*-iodobenzoic acid, was trapped in situ by another substrate to give valuable product instead of being abandoned as a waste.

It is well known that phenanthridine derivatives present ubiquitously in natural products and man-made compounds possessing diverse pharmacological activities and unique functional properties.[1,2] Due to their importance, a number of methods for the preparation of functionalized phenanthridine derivatives have been developed based on different synthetic strategies.[3,4] While these elegant literature protocols are generally reliable, some of them still suffered from limitations such as necessitating the use of difficult-to-obtain *ortho*-functionalized biaryls as substrates and the production of halides or boronic acids as non reusable byproducts. In view of green and sustainable chemistry, there is an urgent need to develop novel approaches toward phenanthridine derivatives starting from easily accessible substrates and accomplished in a more sustainable and atom-economic manner.

The trifluoromethyl (CF_3) group is a valuable structural motif embedded in numerous pharmaceuticals, agrochemicals, and functional materials. Accordingly, extensive efforts have been made in developing reliable methods for the introduction of a CF_3 unit into the target molecules.[5,6] Meanwhile, vinyl azide is recently emerging as an important three-atom synthon for the construction of the synthetically and biologically valuable *N*-containing compounds (Scheme 1, (1)).[7-9] Under this background and as part of our continuing efforts in exploring α-diazo carbonyl compounds as an efficient coupling partner for Rh(III)-catalyzed inert C–H bond functionalizations,[10] we have studied the three-component reaction of (1-azidovinyl) benzene with 2-diazocyclohexane-1,3-dione and Togni's reagent. During this study, we serendipitously found that this reaction could not only provide a novel access toward the envisioned 2,2,2-trifluoroethylphenanthridine derivative, but also result in the formation of benzochromenone as an unexpected yet highly rewarding product through the in situ trapping of the decomposition product of Togni's reagent, *o*-iodobenzoic acid, with the cyclic α-diazo carbonyl substrate (Scheme 1, (2)). Herein, we would like to report the detailed results of our study in this regard.



Scheme 1 Syntheses of 2,2,2-trifluoroethyl phenanthridines from vinyl azide and trifluoromethylation reagent.

Results and discussion

Our study was initiated by treating a mixture of (1-azidovinyl)benzene (**1a**), 2-diazocyclohexane-1,3-dione (**2a**) and Togni's reagent (**3a**) with $[RhCp^*Cl_2]_2$ and AgOAc in CH_3CN at 80 °C for 3 h. From this reaction, 6-(2,2,2-trifluoroethyl)-3,4-

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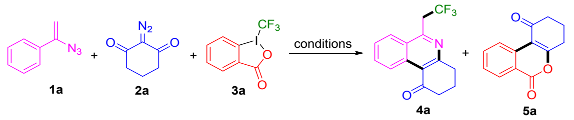
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x dihydrophenanthridin-1(2*H*)-one (**4a**) was obtained in a yield of 23%. Meanwhile, 3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione (**5a**) was obtained in 16% yield (Table 1, entry 1). We deduced that the unexpected formation of **5a** should involve the coupling of **2a** with *o*-iodobenzoic acid, generated in situ via the decomposition of **3a**. It occurred to us that the simultaneous formation of **4a** and **5a** is synthetically highly attractive due to the following reasons: 1) to the best of our knowledge, this is the first example in which the byproduct of Togni's reagent was trapped in situ to afford valuable product instead of being abandoned as a waste; 2) benzochromenone derivatives like **5a** have been found widely in nature, and many of them are highly effective antifungal and antiproliferation reagents, thus holding great potential in the development of new drugs.[11] To develop this novel reaction into an efficient and reliable one-pot synthesis of trifluoroethylphenanthridine and benzochromenone derivatives, and to make a better and greener use of Togni's reagent, various reaction conditions were then screened. It was firstly found that increasing the molar ratio of **2a** to **1a** and **3a** improved the yields of **4a** and **5a** obviously (entries 1-4). In specific, when 3 equiv of **2a** was used, **4a** and **5a** could be obtained in yields of 40% and 32%, respectively (entry 4). Following study on the effect of different solvents including DCE, CH_3OH, toluene and acetone revealed that acetone is the most effective medium for this reaction (entries 4-8). Next, $AgSbF_6$, CsOAc, $Cu(OAc)_2$, HOAc or PivOH was tried to replace AgOAc as the additive (entries 9-13). Among them, $Cu(OAc)_2$ was found to be the most effective (entry 11). In further screening on the effect of mixed additive, we were pleased to find that using a combination of $Cu(OAc)_2$ and HOAc as the additive improved the reaction efficiency significantly (entry 15). In addition, a slightly better result was obtained when the reaction was carried out at 100 °C compared with those run at 80 °C, 60 °C or 120 °C (entry 17 vs 15, 16 and 18). Finally, control experiments indicated that the presence of catalyst and additive is indispensable for the formation of **4a** and **5a** (entries 19-20).

With the establishment of the optimum conditions, the substrate scope of this novel reaction was explored, and the results are listed in Table 2. First, by using **2a** and **3a** as model substrates, the reaction of different vinyl azides **1** was studied. It turned out that phenyl substituted vinyl azides with either electron-donating groups (EDG) such as methyl, *tert*-butyl, methoxy and acetoxyl, or electron-withdrawing groups (EWG) such as fluoro, chloro and bromo attached on the phenyl ring took part in this reaction smoothly to give **4a**-**4i** in moderate to good yields. Notably, various functional groups were tolerated well under the reaction conditions. In the case of *meta*-substituted substrate, the reaction took place efficiently and regioselectively on the less hindered site to give **4i**. Furthermore, 2-naphthylvinyl azide reacted with **2a** and **3a** to give a benzo[*j*]phenanthridine derivative **4j** in a yield of 57%. Interestingly, vinyl azide **1** bearing a phenyl unit at the β-position could also participate in this reaction to give **4k**. Of particular interest was the successful synthesis of **4l** via this reaction as **4l** is structurally similar to Papaverine and might possess promising biological activities.[12] Meanwhile, **5a** was

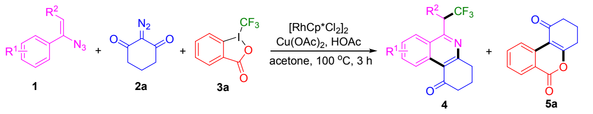
Table 1 Optimization studies for the formation of **4a** and **5a**[a]

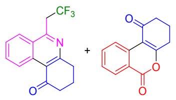


Entry	Solvent	Additive	T (°C)	Yield (%)[b]	
				4a	**5a**
1[c]	CH_3CN	AgOAc	80	23	16
2[d]	CH_3CN	AgOAc	80	29	17
3[e]	CH_3CN	AgOAc	80	35	27
4	CH_3CN	AgOAc	80	40	32
5	DCE	AgOAc	80	34	29
6	CH_3OH	AgOAc	80	45	32
7	toluene	AgOAc	80	18	20
8	acetone	AgOAc	80	48	35
9	acetone	$AgSbF_6$	80	ND	ND
10	acetone	CsOAc	80	trace	trace
11	acetone	$Cu(OAc)_2$	80	50	38
12	acetone	HOAc	80	trace	trace
13	acetone	PivOH	80	trace	trace
14[f]	acetone	$Cu(OAc)_2$	80	31	15
15[g]	acetone	$Cu(OAc)_2$	80	68	46
16[g]	acetone	$Cu(OAc)_2$	60	45	30
17[g]	acetone	$Cu(OAc)_2$	100	72	52
18[g]	acetone	$Cu(OAc)_2$	120	70	51
19[g,h]	acetone	$Cu(OAc)_2$	100	ND	ND
20	acetone	none	100	ND	ND

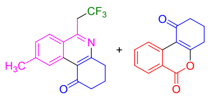
[a] Conditions: **1a** (0.3 mmol), **2a** (0.6 mmol), **3a** (0.2 mmol), $[RhCp^*Cl_2]_2$ (0.01 mmol), additive (0.4 mmol), solvent (2 mL), 3 h. [b] Isolated yield. [c] **1a** (0.3 mmol), **2a** (0.2 mmol), **3a** (0.2 mmol). [d] **1a** (0.3 mmol), **2a** (0.3 mmol), **3a** (0.2 mmol). [e] **1a** (0.3 mmol), **2a** (0.4 mmol), **3a** (0.2 mmol). [f] With 0.2 mmol of CsOAc. [g] With 0.2 mmol of HOAc. [h] Without $[RhCp^*Cl_2]_2$.

Table 2 Substrate scope for the synthesis of **4** and **5** (I)[a]

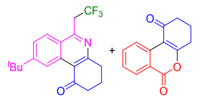




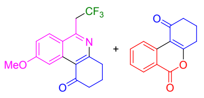
4a, 72%; **5a**, 52%



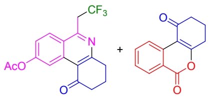
4b, 68%; **5a**, 50%



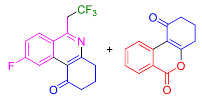
4c, 63%; **5a**, 50%



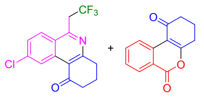
4d, 55%; **5a**, 48%



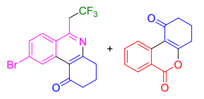
4e, 51%; **5a**, 45%



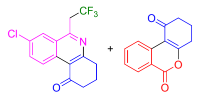
4f, 58%; **5a**, 48%



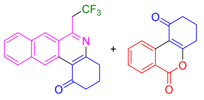
4g, 72%; **5a**, 56%



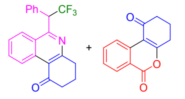
4h, 69%; **5a**, 51%



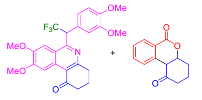
4i, 60%; **5a**, 49%



4j, 57%; **5a**, 50%



4k, 48%; **5a**, 46%



4l, 48%; **5a**, 46%

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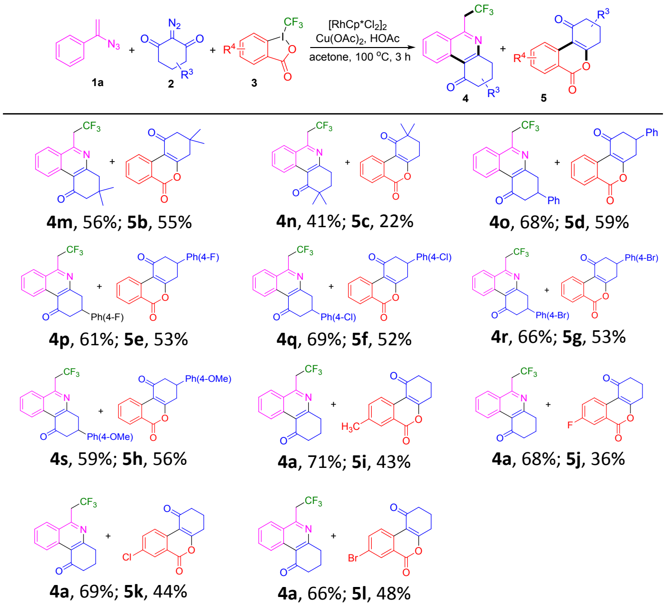
[a] Reaction conditions: **1** (0.3 mmol), **2a** (0.6 mmol), **3a** (0.2 mmol), $[RhCp^*Cl_2]_2$ (0.01 mmol), $Cu(OAc)_2$ (0.4 mmol), HOAc (0.2 mmol), acetone (2 mL), 100 °C, 3 h. [b] Isolated yield.

successfully obtained along with **4** in all these cases in yields ranging from 45-56%. Finally, it is worth to be noted that the structure of **4j** was unambiguously confirmed by its single crystal X-ray diffraction analysis.[13]

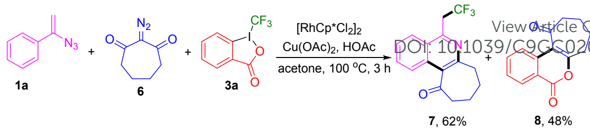
Next, the suitability of different diazo substrates **2** was studied. The results listed in Table 3 showed that in addition to **2a**, 2-diazo-5,5-dimethylcyclohexane-1,3-dione (**2b**) and 2-diazo-4,4-dimethylcyclohexane-1,3-dione (**2c**) were also suitable for this reaction to give the corresponding products **4m**, **4n** and **5b**, **5c** smoothly. Next, a series of 5-phenyl substituted 2-diazocyclohexane-1,3-diones with either EDG such as methoxy or EWGs such as fluoro, chloro or bromo attached on the phenyl ring were reacted with **1a** and **3a**. It turned out that these reactions took place effectively to give **4o**-**4s** and **5d**-**5h** in moderate to good yields without showing obvious electronic effect. Finally, functional group (R^4) variations (from H to methyl, fluoro, chloro or bromo) on the phenyl ring of Togni's reagent turned out to be equally successful to afford **4a** and **5i**-**5l**.

Table 3 Substrate scope for the synthesis of **4** and **5** (II)[a]



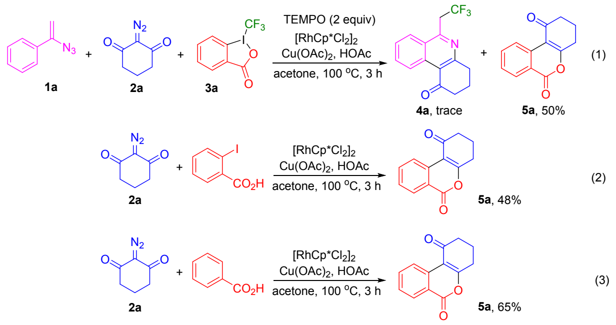
[a] Reaction conditions: **1a** (0.3 mmol), **2** (0.6 mmol), **3** (0.2 mmol), $[RhCp^*Cl_2]_2$ (0.01 mmol), $Cu(OAc)_2$ (0.4 mmol), HOAc (0.2 mmol), acetone (2 mL), 100 °C, 3 h. [b] Isolated yield.

Interestingly, 2-diazocycloheptane-1,3-dione (**6**) having a seven-membered ring was found to be also suitable for this reaction to give 5-(2,2,2-trifluoroethyl)-7,8,9,10-tetrahydro-11*H*-cyclohepta[*c*]-isoquinolin-11-one (**7**) and 7,8,9,10-tetrahydrocyclohepta[*c*]iso-chromene-5,11-dione (**8**) in moderate to good yields (Scheme 2).



Scheme 2 Reaction of **6** with **1a** and **3a** to give **7** and **8**.

To gain some insight into the mechanism of this reaction, several control experiments were conducted. First, 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO) as a radical scavenger was added to the reaction of **1a** with **2a** and **3a** under standard conditions. From this reaction, **4a** was formed only in trace amount. Meanwhile, **5a** was obtained in a yield of 50% (Scheme 3, (1)). These results showed that the formation of **4a** might involve a radical process, and the formation of **5a**, on the other hand, might be free of radical intermediate. Second, 2-iodobenzoic acid and **2a** was subjected to standard conditions for 3 h to afford **5a** in a yield of 48% (Scheme 3, (2)). Third, **2a** was treated with benzoic acid under standard conditions, from which **5a** was obtained in a yield of 65% (Scheme 3, (3)). These results indicated that either 2-iodobenzoic acid or benzoic acid might be an intermediate to react with **2a** to give **5a**.



Scheme 3 Control experiments.

Based on the above described experimental results and literature reports,[6,8,14] plausible mechanisms accounting for the formation of **4a** and **5a** from the reaction of **1a** with **2a** and **3a** were proposed in Scheme 4. Initially, decomposition of **3a** under the assistance of Cu(II) generates CF_3 radical and 2-iodobenzoic acid (**H**). Addition of the CF_3 radical onto **1a** gives **A**, which then undergoes a coordination with Cu(II) to give **B**. Metal transfer of Cu(III) with Rh(III) occurs with **B** followed by an *ortho*-C(sp^2)–H metallation to afford a five-membered rhodacyclic intermediate **C**. **C** then reacts with **2a** to give Rh-carbene species **D**. Next, migratory insertion of the carbene unit into the Rh–C bond in **D** affords **E**. Protonation of **E** gives **F** and releases the Rh(III) complex to start a new catalytic cycle. In the second stage of this cascade process, **F** undergoes an intramolecular *N*-nucleophilic addition to afford **G**, from which product **4a** is formed through an aromatization-driven elimination of water. As for the formation of **5a**, it should firstly involve the generation of a rhodacyclic species **I** through reaction of Rh(III) with benzoic acid, formed in situ through the deiodination of **H** under the reaction conditions.[15] Next, coordination of **I** with **2a** gives a Rh-carbene species **J** followed by migratory insertion of the carbene unit into the Rh–C bond in **J** to give intermediate **K**. Protonation of **K**

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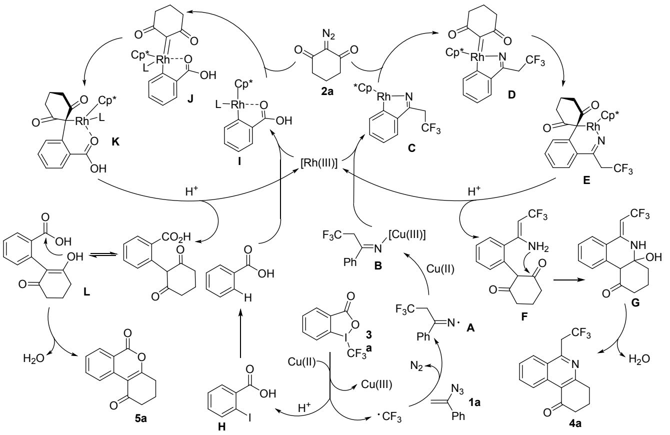
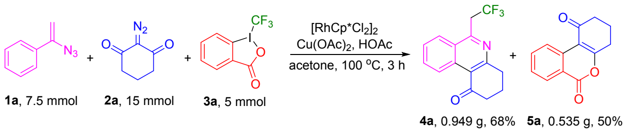
leads to the formation of **L** and releases the Rh(III) catalyst. Finally, **L** undergoes an intramolecular esterification to give **5a**. Meanwhile, it is worth to be noted that Li and Ribas have independently described the in situ generation of Ag(III) from Ag(I).[16] These precedent reports might explain our observation that with AgOAc as the additive, **4a** and **5a** could also be formed albeit in lower yields compared with that with Cu(OAc)$_2$ (Table 1, entries 1-8). In another example, Qing et al reported a hydrotrifluoromethylation of alkenes with CF$_3$ radical generated from the in situ formed AgCF$_3$ promoted by PhI(OAc)$_2$ working as an oxidant.[17] We thus deduced that the formation of **4a** in the presence of AgOAc might alternatively involve the in situ formation and spontaneously collapse of AgCF$_3$ to form CF$_3$ radical required for the trifluoromethylation process, in which Togni's reagent may serve as an oxidant. Further study is still required to elucidate the exact nature of this cascade reaction.



Scheme 4 Plausible reaction mechanisms accounting for the formation of **4a** and **5a**.

Finally, to see whether this newly developed synthesis of phenanthridine and benzochromenone derivatives is suitable for more practical applications, the reaction of **1a** with **2a** and **3a** was tried in an enlarged scale of 5 mmol. From this reaction, **4a** and **5a** were obtained in yields of 68% and 50%, respectively (Scheme 5).



Scheme 5 Gram-scale synthesis of **4a** and **5a**.

Conclusions

In summary, an unprecedented one pot synthesis of 2,2,2-trifluoroethylphenanthridines and benzochromenones from the cascade reactions of vinyl azides with cyclic α-diazo carbonyl compounds and Togni's reagent has been established. To the best of our knowledge, this is the first example in which Togni's reagent and its decomposition product were utilized simultaneously to afford two different kinds of highly valuable products in a one-pot manner. With notable features such as easily obtainable substrates, high efficiency, broad substrate scope, excellent functional group tolerance and high atom-economy, this new method is expected to find wide applications in related areas.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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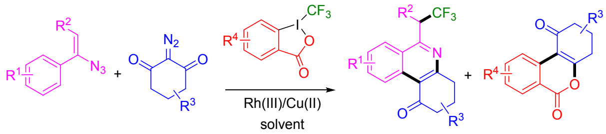

★ *Dual role of Togni's reagent & diazo carbonyl compounds with high efficiency*

★ *First reuse of the byproduct of Togni's reagent with remarkable sustainability*

A one-pot simultaneous synthesis of 2,2,2-trifluoroethylphenanthridines and benzochromenones featuring with utilization of the byproduct of Togni's reagent is presented.