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Consecutive π-Lewis acidic metal-catalysed cyclisation/photochemical radical addition promoted by *in situ* generated 2-benzopyrylium as the photoredox catalyst†

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A π-Lewis acidic metal-catalysed cyclisation/photochemical radical addition sequence was developed, which utilises *in situ* generated 2-benzopyrylium cation intermediates as photoredox catalysts and electrophilic substrates to form 1*H*-isochromene derivatives in good yields in most cases. The key 2-benzopyrylium intermediates were generated through the activation of the alkyne moiety of *ortho*-carbonyl alkynylbenzene derivatives by such π-Lewis acidic metal catalysts as $AgNTf_2$ and $Cu(NTf_2)_2$, and the subsequent intramolecular cyclisation and proto-demetalation using trifluoroacetic acid. Further photo-excitation of the 2-benzopyrylium intermediates facilitated single-electron transfer from a benzyltrimethylsilane derivative as a donor molecule to promote the radical addition of arylmethyl radicals to the 2-benzopyrylium intermediates.

Introduction

Photo-excited compounds exhibit redox properties and high reactivity by transitioning from the ground state to the excited state after absorbing light energy, resulting in a large redox potential. Light-absorbing molecules for the photo-oxidation reaction are primarily divided into metal cations and organic cations. Organic cations are good electron acceptors and thus the excited ones have a larger oxidation potential and a shorter lifetime than excited metal cations, making them potentially applicable to substrates that cannot be oxidized by metal cations.[1] Among organic cations, iminium salts have long been used in photoreactions.[2,3] Meanwhile photochemical radical reactions initiated by organic cations as catalysts have been actively developed during the past decade and are based on two methods: one is the use of organic cations as photocatalysts, and the other is the catalytic generation of cationic species *in situ* for use as photo-oxidation agents. Several candidates for organic cations[1c,4] are used as photocatalysts, with acridinium[5] and pyrylium[6] salts as representative examples.

On the other hand, examples of methods for catalytically generating organic cations and using them as photo-excitation species include secondary amine catalysis for the formation of iminium cations[7] and acid catalysis for the formation of benzopyrylium cations[8] (Scheme 1). In 2017, Melchiorre and co-workers reported an enantioselective benzylation that used toluene derivatives, which involved the photo-excitation of an iminium cation intermediate generated *in situ* from a chiral secondary amine catalyst and α,β-unsaturated aldehydes (Scheme 1a).[7a] In 2021, we reported a method for activating the benzylic C–H bond of toluene derivatives by photo-excitation of a 1-benzopyrylium cation intermediate generated *in situ* from a chromenol derivative using a Brønsted acid catalyst (Scheme 1b).[8] In this work, we sought to develop an enantioselective variant using a chiral phosphoric acid (CPA) catalyst. However, the catalytic generation of organic cations used as oxidants by photo-excitation is mainly limited to the above two methods. The scope of organic cations generated under catalytic conditions is still narrow even though cationic species are readily available through various methods.[9] Therefore, it would be a more attractive approach if the catalytically generated organic cations could be used to broaden the range of cationic species applicable to photochemical reactions.

The intramolecular cyclisation reaction of alkynylbenzene derivatives having a carbonyl or related functional group at the *ortho*-position, which is initiated by the activation of the alkyne moiety using a π-Lewis acidic metal catalyst ([M]X), is a typical method for constructing heterocyclic skeletons (Scheme 2a).[10] The cationic intermediates produced in this cyclisation reaction are trapped by nucleophiles, enabling the construction of functionalised heterocycles in a single step. Based on this background, we envisioned the use of 2-benzopyrylium cation

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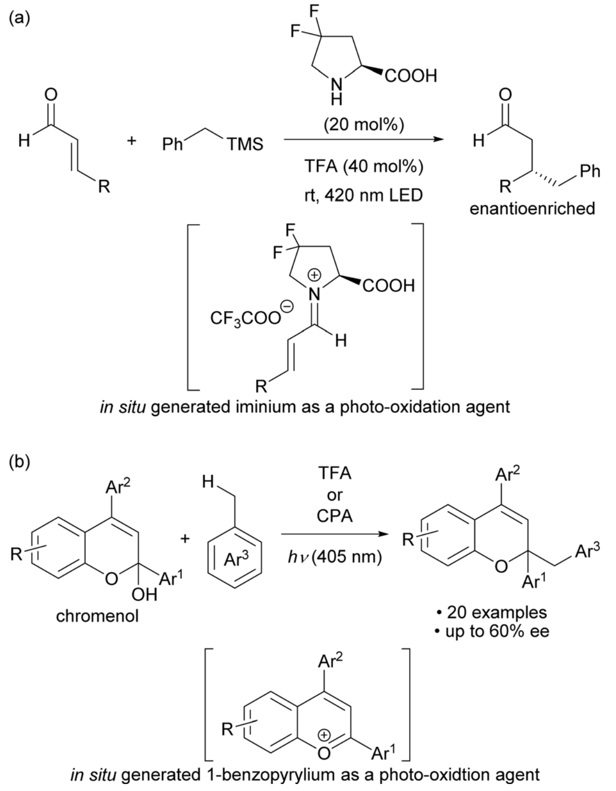
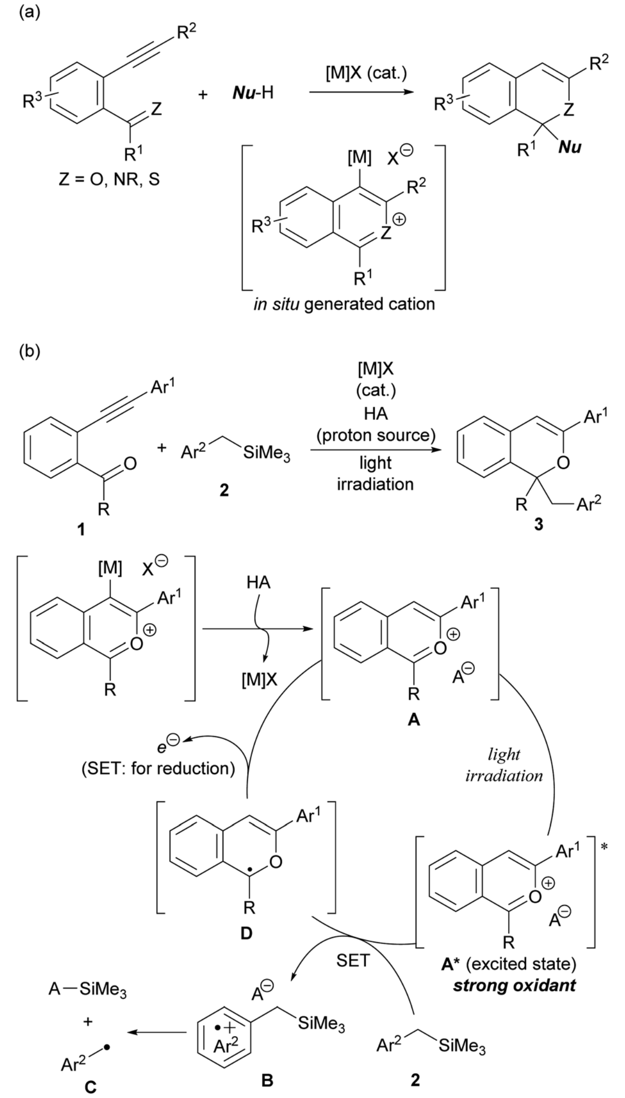


Scheme 1 (a) Photochemical enantioselective benzylation of an iminium cation intermediate generated *in situ* from a chiral secondary amine catalyst and an α,β-unsaturated aldehyde. (b) Photochemical reaction of 1-benzopyrylium cations generated *in situ* from a chromenol derivative using a Brønsted acid catalyst.



Scheme 2 (a) π-Lewis acidic metal-catalysed cyclisation of alkynylbenzene derivatives having a C = Z functional group at the *ortho*-position. (b) Consecutive π-Lewis acidic metal-catalysed cyclisation/photochemical radical addition promoted by *in situ* generated 2-benzopyrylium intermediates **A** as photoredox catalysts.

intermediates **A** as new photo-oxidation agents, which are generated *in situ* through the activation of the alkyne moiety of *ortho*-carbonyl alkynylbenzene derivatives **1** by [M]X and subsequent intramolecular cyclisation and proto-demetalation by HA (proton source) (Scheme 2b). Herein we report a π-Lewis acidic metal-catalysed cyclisation/photochemical radical addition sequence using **1** as the cation precursor. The use of benzyltrimethylsilane derivatives **2** as the donor molecules[11] for the single-electron transfer (SET) to catalytically generated 2-benzopyrylium intermediates **A** under light irradiation results in the formation of radical cations **B** for further transformations. The nucleophilic nature of radicals **C**, which are generated by desilylation from corresponding radical cations **B**, facilitates radical addition to 2-benzopyrylium intermediates **A**, giving rise to corresponding 1*H*-isochromene derivatives **3**[12] through further reduction by SET from radical intermediates **D**. Meanwhile the SET oxidises **D** to regenerate 2-benzopyrylium intermediates **A** that function not only as electrophilic substrates but also as photoredox catalysts.

Results and discussion

At the outset of our studies to verify the intended consecutive transformation, $AgNTf_2$ was used as the π-Lewis acidic metal catalyst for promoting the cyclisation of *ortho*-alkynyl acetophenone **1a**, and subsequent proto-demetalation was performed using trifluoroacetic acid (TFA) to generate the 2-benzopyrylium intermediate. The initial screening was conducted using 10 μmol (10 mol%) of $AgNTf_2$, 0.1 mmol of **1a**, 0.25 mmol (2.5 equiv.) of benzyltrimethylsilane (**2a**) as the donor molecule, and 0.25 mmol (2.5 equiv.) of TFA under light irradiation (blue LED: $\lambda_{max} = 448$ nm) at 0 °C for 1 h in 1 mL of dichloromethane. As shown in Table 1, entry 1, the reaction conducted in the absence of a phosphine ligand afforded corresponding product **3a** in low yield, and significant deposition of silver was observed during the reaction. In order to suppress the deposition, we added a phosphine ligand to stabilize the silver salt (entries 2–4), and the yield of **3a** was slightly improved even though it was dependent on the electronic properties of the phosphine ligand. Further screening of reaction conditions

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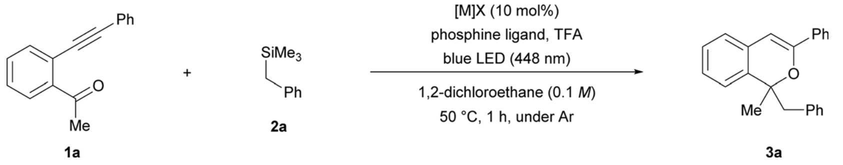
Table 1 Screening of reaction conditions[a]



Entry	[M]X	Phosphine ligand (mol%)	Equiv. of TFA	Equiv. of **2a**	Yield[b] (%)
1[c]	$AgNTf_2$	—	2.5	2.5	28
2[c]	$AgNTf_2$	PPh_3 (20)	2.5	2.5	37
3[c]	$AgNTf_2$	$P(C_6F_5)_3$ (20)	2.5	2.5	23
4[c]	$AgNTf_2$	$P(4\text{-}CF_3C_6H_4)_3$ (20)	2.5	2.5	43
5	$AgNTf_2$	$P(4\text{-}CF_3C_6H_4)_3$ (20)	2.5	2.5	50
6	$AgNTf_2$	$P(4\text{-}CF_3C_6H_4)_3$ (20)	2.5	10	65
7	**$AgNTf_2$**	**$P(4\text{-}CF_3C_6H_4)_3$ (20)**	**5**	**10**	**76 (81)**
8	$AgNTf_2$	$P(4\text{-}CF_3C_6H_4)_3$ (20)	10	10	64
9	AgOTf	$P(4\text{-}CF_3C_6H_4)_3$ (20)	5	10	71
10	**$Cu(NTf_2)_2$**	**$P(4\text{-}CF_3C_6H_4)_3$ (20)**	**5**	**10**	**78**
11	$Cu(OTf)_2$	$P(4\text{-}CF_3C_6H_4)_3$ (20)	5	10	31
12	$CuOTf \cdot C_6H_6$	$P(4\text{-}CF_3C_6H_4)_3$ (20)	5	10	34
13	$AuNTf_2$	$P(4\text{-}CF_3C_6H_4)_3$ (10)	2.5	10	38
14[d]	$AgNTf_2$	$P(4\text{-}CF_3C_6H_4)_3$ (20)	5	10	17

[a] Unless otherwise specified, all reactions were carried out using 0.1 mmol of **1a**, the indicated amount of **2a**, 10 μmol (10 mol%) of metal catalyst [M]X, 20 μmol (20 mol%) of the phosphine ligand, and TFA in 1,2-dichloroethane (1 mL: 0.1 M of **1a**) at 50 °C for 1 h. [b] Yield was calculated by NMR analysis using 1,1,2,2-tetrabromoethane as the internal standard. Isolated yield is indicated in parentheses. [c] In dichloromethane at 0 °C. [d] Purple LED ($\lambda_{max} = 405$ nm) was used.

using 20 mol% of $P(4\text{-}CF_3C_6H_4)_3$ as the ligand was conducted by elevating the reaction temperature to 50 °C (see ESI† for screening details) and increasing the amounts of TFA or **2a** (entries 5–8). Increasing the amounts of TFA and **2a** significantly improved the chemical yield of **3a** (entry 7),§ although a further increase in the amount of TFA lowered the yield (entry 8). When $AgNTf_2$ was replaced by other π-Lewis acidic metal catalysts such as copper and gold complexes (entries 9–13), $Cu(NTf_2)_2$ exhibited a comparable result to $AgNTf_2$ (entry 7 *vs.* 10), affording corresponding product **3a** in good yield.§ When the light source was changed from $\lambda_{max} = 448$ nm to 405 nm, a marked reduction in chemical yield was observed (entry 14).

As shown in Table 1 entries 7 and 10, $AgNTf_2$ and $Cu(NTf_2)_2$ catalysts were effective for the present consecutive transformation. Next, the scope of substrates in which various substituents were introduced to the terminal phenyl group was investigated in the presence of the $AgNTf_2$ or $Cu(NTf_2)_2$ catalyst under the optimal reaction conditions shown in Table 1 (entries 7 and 10). As shown in Table 2, the use of the $AgNTf_2$ or $Cu(NTf_2)_2$ catalyst resulted in the formation of product **3** in low to fairly good yields (see ESI† for details). When substrate **1b**, which has an electron-donating methoxy group at the *para*-position (entry 1), was used, the reaction temperature had to be lowered to 0 °C and the reaction time had to be extended to 6 h to obtain product **3b** in moderate yield (44%). In the case of substrates **1c** having a methyl substituent (a weak electron-donating group) and **1d** having a bromo substituent (a weak electron-withdrawing group) at the *para*-position, the $Cu(NTf_2)_2$ catalyst accelerated the reaction efficiently, affording **3c** and **3d**, respectively, in moderate to good yields (entries 2 and 3). In contrast, for substrate **1e** having a strong electron-withdrawing CF_3 group, the $AgNTf_2$ catalyst promoted the formation of **3e** in good yield (entry 4). Substrates having a methyl, bromo, or trifluoromethyl group at the *meta*-position gave products **3** in acceptable yields using the suitable metal catalyst for each reaction (entries 6–8), although, in the reaction of **1f** having a methoxy group at the *meta*-position, **3f** was formed in moderate yield using the $AgNTf_2$ catalyst (entry 5). The reaction of **1j** having a methyl group at the *ortho*-position afforded **3j** in good yield (entry 9).

Subsequently, the substituent at the carbonyl moiety was investigated (Scheme 3). Phenyl ketone **1k** was not fully consumed when the $Cu(NTf_2)_2$ catalyst was used. The use of $AgNTf_2$ resulted in a slight increase in yield, but the yield remained low. The optimal reaction conditions were not suitable for aldehyde **1l**. Nevertheless, the yield of product **3l** was improved to 65% by decreasing the amount of TFA to 2.5 equiv. and the concentration of **1l** to 0.05 M and prolonging the reaction to 2 h when the $AgNTf_2$ catalyst was used. The modified reaction conditions were applied to aldehyde **1m** having a 4-bromophenyl group at the alkynyl terminus, however **3m** was obtained in low yield even by using either $AgNTf_2$ or $Cu(NTf_2)_2$.

The scope of donor molecules **2b–e** was further investigated (Table 3). The reactions of **2b** and **2c**, in which an electron-withdrawing CF_3 group and an electron-donating MeO group[13] were introduced to the *para*-position of benzyltrimethylsilane, respectively, were conducted using the $AgNTf_2$ catalyst (entries 1 and 2). Product **3n** and **3o** were formed in low (18%) and

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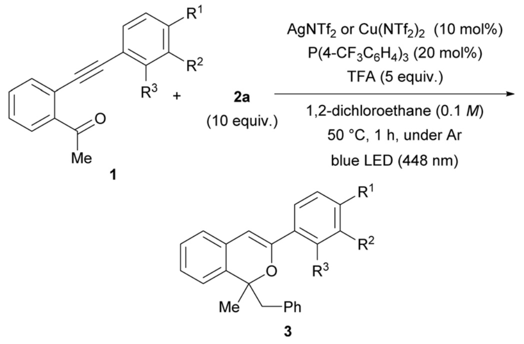
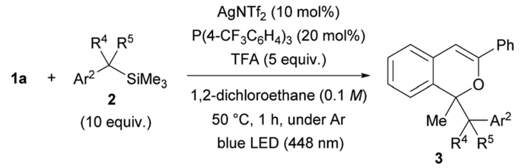
Table 2 Scope of substrates[a]



Entry	1	R^1	R^2	R^3	3	[M]X	Yield of 3[b] (%)
1[c]	**1b**	MeO	H	H	**3b**	$Cu(NTf_2)_2$	44
2	**1c**	Me	H	H	**3c**	$Cu(NTf_2)_2$	47
3	**1d**	Br	H	H	**3d**	$Cu(NTf_2)_2$	77
4	**1e**	CF_3	H	H	**3e**	$AgNTf_2$	72
5	**1f**	H	MeO	H	**3f**	$AgNTf_2$	39
6	**1g**	H	Me	H	**3g**	$Cu(NTf_2)_2$	58
7	**1h**	H	Br	H	**3h**	$AgNTf_2$	59
8	**1i**	H	CF_3	H	**3i**	$Cu(NTf_2)_2$	63
9	**1j**	H	H	Me	**3j**	$AgNTf_2$	74

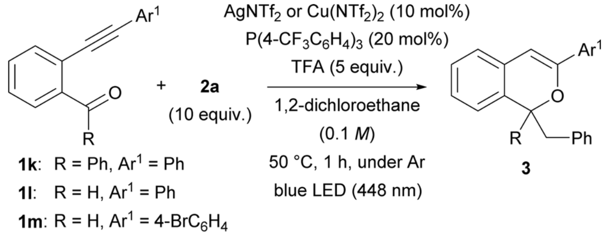
[a] Unless otherwise specified, all reactions were carried out using 0.1 mmol of **1**, 1.0 mmol (10 equiv.) of **2a**, 10 μmol (10 mol%) of $AgNTf_2$ or $Cu(NTf_2)_2$, 20 μmol (20 mol%) of $P(4\text{-}CF_3C_6H_4)_3$, and 5 equiv. of TFA in 1,2-dichloroethane (1 mL: 0.1 M of **1**) at 50 °C for 1 h. [b] Isolated yield. [c] At 0 °C for 6 h.

Table 3 Scope of donor molecules **2**[a]



Entry	2	Ar^2	R^4	R^5	3	Yield of 3[b] (%)
1[c]	**2b**	$4\text{-}CF_3C_6H_4$	H	H	**3n**	18 (21)[c]
2	**2c**	$4\text{-}BrC_6H_4$	H	H	**3o**	54 (50)[c]
3	**2d**	Ph	Me	H	**3p**	62
4	**2e**	Ph	Me	Me	**3q**	NR[d]

[a] Unless otherwise specified, all reactions were carried out using 0.1 mmol of **1**, 1.0 mmol (10 equiv.) of **2**, 10 μmol (10 mol%) of $AgNTf_2$, 20 μmol (20 mol%) of $P(4\text{-}CF_3C_6H_4)_3$, and 5 equiv. of TFA in 1,2-dichloroethane (1 mL: 0.1 M of **1**) at 50 °C for 1 h. [b] Isolated yield. [c] The reaction was conducted for 2 h. [d] NR: no reaction.



yield of **3** (%)	$AgNTf_2$	$Cu(NTf_2)_2$
3k: R = Ph, Ar^1 = Ph	30	10
3l: R = H, Ar^1 = Ph	65[a] (26)[b]	50[a] (26)[b]
3m: R = H, Ar^1 = $4\text{-}BrC_6H_4$	34[a]	23[a]

[a] The reaction was performed for 2 h using 0.05 *M* of **1** and 2.5 equiv. of TFA.
[b] Under the optimal reaction conditions.

Scheme 3 Consecutive transformation of phenyl ketone **1k** and aldehydes **1l** and **m**.

moderate (54%) yields, respectively, under the optimal reaction conditions. In each case, extending the reaction time from 1 hour to 2 hours did little improve the yield. Donor molecule **2d** having a methyl substituent at the benzylic position underwent the reaction smoothly, affording a diastereomeric mixture (65 : 35) of **3p** in 62% yield (entry 3). However, introduction of a dimethyl substituent at the benzylic position, *i.e.*, sterically congested **2e**, completely suppressed the formation of **3q** (entry 4).

Finally, in order to investigate whether cationic intermediates **A** function as photo-oxidation agents, we conducted several control experiments, UV-Vis measurements, and Stern–Volmer luminescence quenching experiments. First, in the control experiments (see ESI† for details), no product was formed when the reaction was performed without the metal catalyst or light irradiation. In the absence of TFA, the product was obtained, although the yield remained quite low (13% with $Cu(NTf_2)_2$ catalyst). These results indicate that the present consecutive transformation is a photochemical reaction and 2-benzopyrylium intermediate **A** is the key component. The formation of 2-benzopyrylium intermediate **A** was further confirmed by UV-Vis measurement.[14] As shown in Fig. 1, no absorption was observed in the visible region for substrate **1a** alone (dark blue line) and substrate **1a**/TFA mixture (gray line). On the other hand, when the substrate and $AgNTf_2$ were mixed, a small absorption peak appeared in the visible region (orange line). When TFA was added to this mixture, a large absorption peak was observed around 430 nm (light blue line). In addition, we performed Stern–Volmer luminescence quenching experiments using a 2-benzopyrylium cation and donor molecule **2** to confirm quenching of the photo-excited 2-benzopyrylium cation by **2** (see ESI† for details). As a result, the emission intensity of the 2-benzopyrylium cation derived from **1b** decreased as the amount of **2a** increased. From this observation, SET from **2** to the photo-excited 2-benzopyrylium cation was verified. These results indicate that cationic intermediate **A** excited by irradiation at $\lambda_{max} = 448$ nm, which is close to the maximum absorption wavelength, functioned as a photo-oxidation agent. However, as shown in Table 1, entry 14, when the light source was changed to purple LED ($\lambda_{max} = 405$ nm) which is also close to the maximum absorption wavelength, product **3a** was obtained in low yield presumably because of product degradation under the reaction conditions.

The plausible catalytic cycles are depicted in Fig. 2. The whole process is composed of three catalytic cycles, namely,

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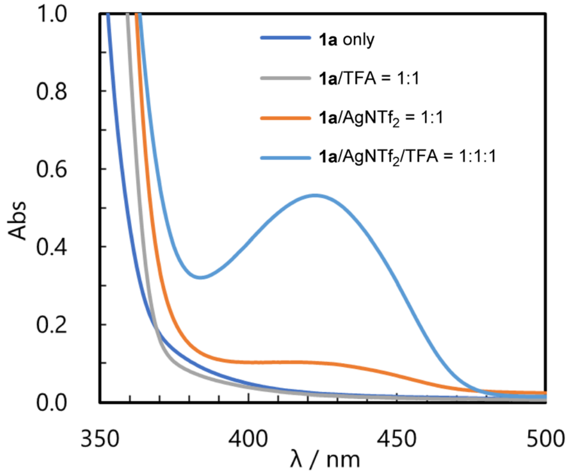

Fig. 1 UV-Vis spectra of related species in dichloromethane (5.0×10^{-4} M of **1a**).

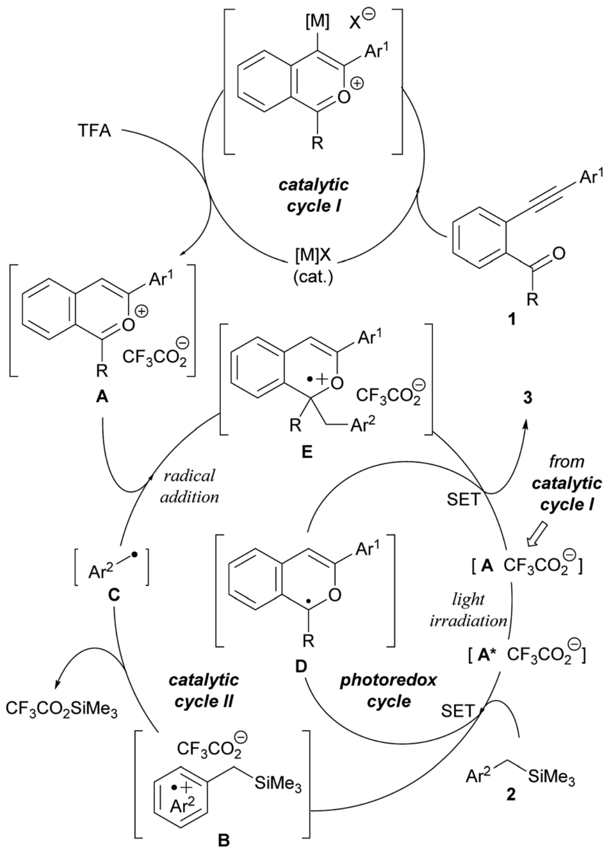

Fig. 2 Plausible catalytic cycles.

catalytic cycles I and II and a photoredox cycle of the photocatalyst. Catalytic cycle I generates key 2-benzopyrylium intermediates **A** from substrates **1** using π-Lewis acidic metal ([M]X) as the catalyst for the intramolecular cyclisation and TFA as the proto-demetalation agent. Subsequently, in catalytic cycle II, generated cationic intermediates **A** function not only as photocatalysts but also as electrophiles for the radical addition reaction with nucleophilic radicals **C**, which are generated by SET from donor molecules **2** to photo-excited cationic intermediates **A*** followed by the desilylation of radical cations **B** (see Scheme 2b). The radical addition of **C** to **A** produces radical cations **E**, which, in turn, are reduced by SET from radical intermediates **D**, a reduced form of photoredox catalyst **A**, affording corresponding 1*H*-isochromene derivatives **3**. The photoredox cycle is also completed by regenerating cation intermediates **A** from radical intermediates **D** by SET. In the carbon–carbon bond forming event, the radical coupling of radicals **C** with radical intermediates **D** is also assumed. However, on the basis of our previous study on the reaction of 1-benzopyrylium derivatives with the same benzyl radical (see Scheme 1b),[8] it is considered that the radical addition of **C** to **A** is more energetically favorable than the radical coupling.

Conclusions

We have developed a π-Lewis acidic metal-catalysed cyclisation/photochemical radical addition sequence that affords 1*H*-isochromene derivatives in good yields in most cases. In the present consecutive transformation, *ortho*-carbonyl alkynylbenzene derivatives were used as precursors for the formation of 2-benzopyrylium intermediates generated *in situ* through the activation of the alkyne moiety of the precursor by a π-Lewis acidic metal catalyst ([M]X) and the subsequent intramolecular cyclisation followed by proto-demetalation by TFA. Further photo-excitation of 2-benzopyrylium intermediates facilitated SET from benzyltrimethylsilane derivatives as donor molecules to initiate the radical addition of arylmethyl radicals to 2-benzopyrylium intermediates. The most distinctive feature of this consecutive transformation is that the *in situ* generated 2-benzopyrylium intermediates were used not only as electrophilic substrates but also as new photo-oxidation agents. On the basis of the present method, it can be considered that *in situ* generated organic cations other than 2-benzopyrylium will be used as photoredox catalysts, and hence other methodologies that can expand the possibilities of photoredox catalysis are expected. In addition, a flow photoreaction system is also applicable to enhance the reaction efficiency and scale-up the present consecutive transformation. Further studies of the development of other photoredox reactions, particularly those utilizing a variety of organic cations generated *in situ*, and these applications to flow photoreactions are in progress in our laboratory.

Data availability

The exploratory investigation, experimental procedures, and characterization data are available.

Author contributions

M. T. contributed conceptualization, project administration, writing – original draft & editing, supervision, and funding acquisition. R. Y., R. O., and Z. I. contributed experimental studies, data curation, and formal analysis. S. U. contributed

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formal analysis and writing – review & editing. J. K. contributed conceptualization, design of the work, and writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

§ Benzyltrimethylsilane (**2a**), which was not consumed in the corresponding radical reaction, was almost completely recovered in either catalytic reaction.

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