Empowering Visible Light Catalysis: Brominative Dearomatization of Biaryl Ynones

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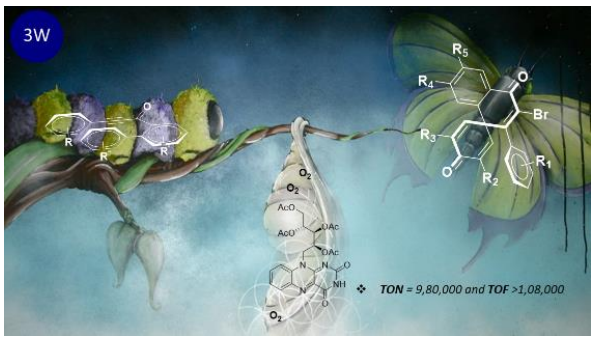
A step-economic photo-oxidative brominative carbannulation of biaryl ynones employing bromide source and riboflavin tetraacetate (RFTA) have been developed. The switchable reactivity between distal phenyl C-H activated *ortho*-annulation and dearomative *ipso*-annulation are well exemplified. The eminent features of the methodology include metal-free, external additive free, low-cost photocatalyst, use of simple precursor. Further, we elaborately discussed about the mechanistic investigation and the applicability of additional functional group incorporation.

KEYWORDS: Dearomatization, Biaryl Ynones, Bromination, RFTA, Photocatalysis



Dearomatization and installation of chemical functionalities in a complex molecular backbone with high degree of precision are still highly challenging and one of the most promising intrigues to solve molecular complexity at higher levels. In this aspect, dearomative cascade spiro-annulation of biaryl ynones deliver spiro[5.5]trienone skeleton, ubiquitous in many biologically active natural products[1, 2] and also prevalent as a template in diverse functionalisations in organic synthesis and medicinal chemistry.[3] For instance, the natural product laurencenone B, pulchelstyrene D as well as a potent inhibitor platencin with spiro[5.5]trieneone skeleton manifest antibiotic, antiviral activities. Similarly, C-H activated *ortho*-annulation of biaryl ynones flourish dibenzocycloheptenone framework containing a dibenzocycloheptane (6-7-6 carbocyclic) skeleton[4] that widely exists in many naturally occurring biologically active compounds[5] such as naturally occuring allocolchicine and related derivatives exhibiting anti-cancer activity.[6] Accordingly, a facile construction of these two pharmaceutically important core structures has gained the enormous interest of synthetic chemists.

In this context, traditional methods for the synthesis of spiro-compounds as well as dibenzocycloheptene-5-ones include oxidative dearomatization,[7] nucleophilic or electrophilic dearomatization,[8] transition-metal-mediated dearomatization,[9] and palladium-catalyzed domino homobiaryl coupling reaction,[10] sequential Suzuki-Miyaura coupling-aldol condensation synthesis[11]. For example, in 2013, Chen and co-workers first developed spiro[5.5]trieneones or dibenzocycloheptene-5-ones via intramolecular electrophilic cyclization of biaryl ynones.[12] In 2018, Zhang group reported copper- or silver-catalyzed cascade radical dearomative spiro-annulation of biaryl ynones with fluoroalkyl bromides or diethylphosphite.[13] Afterwards, in 2019, Liu and co-workers synthesized sulfonylated spiro[5.5]trieneones through Mn(III)-mediated radical oxidative *ipso*-annulation of biaryl ynones in presence of sodium sulfonates.[14] Recently, Duan group described alkylative dearomatization of biaryl ynones to get alkylated spiro[5.5]trieneones employing an unactivated nitro group as a leaving group.[15] Recently, Ackermann group and Reddy group have developed electrooxidative dearomatization of biaryl ynones to construct di- and tri- fluoromethylated spiro[5.5]trieneones and selenylated dibenzocycloheptenones and spiro[5.5]trieneones respectively.[16, 17] Though all of these methods elegantly provide diversely substituted spiro[5.5]trieneones, they necessitate the use of metal catalysts and/or external oxidants and thus produce hazardous byproducts and limit the functional group compatibility. Hence, the development of novel and sustainable annulation of biaryl ynones under benign conditions is highly desirable.

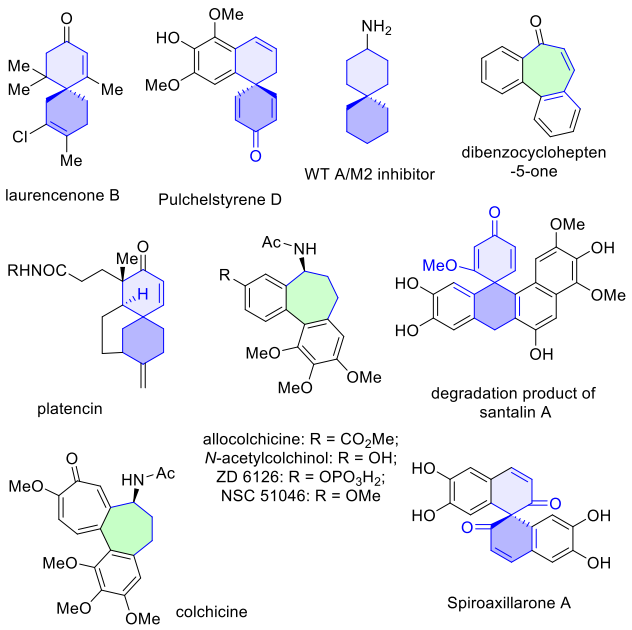
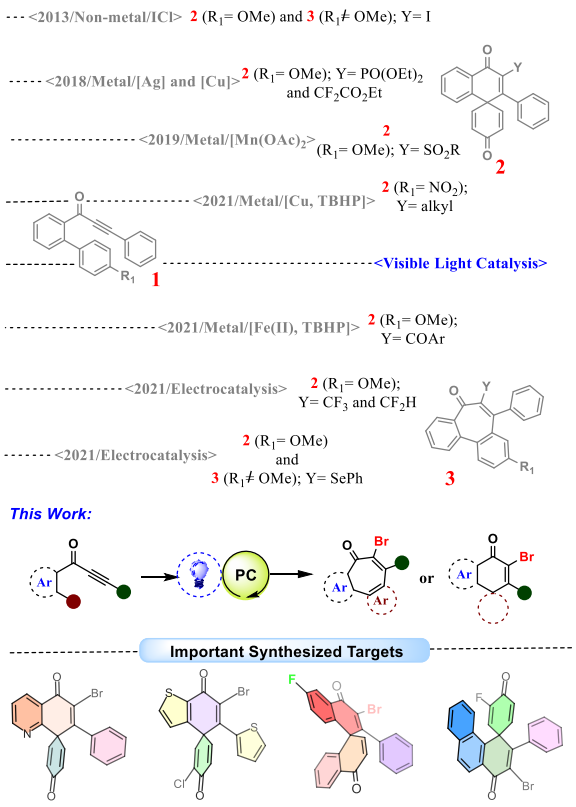


Figure 1. Biologically active natural products.



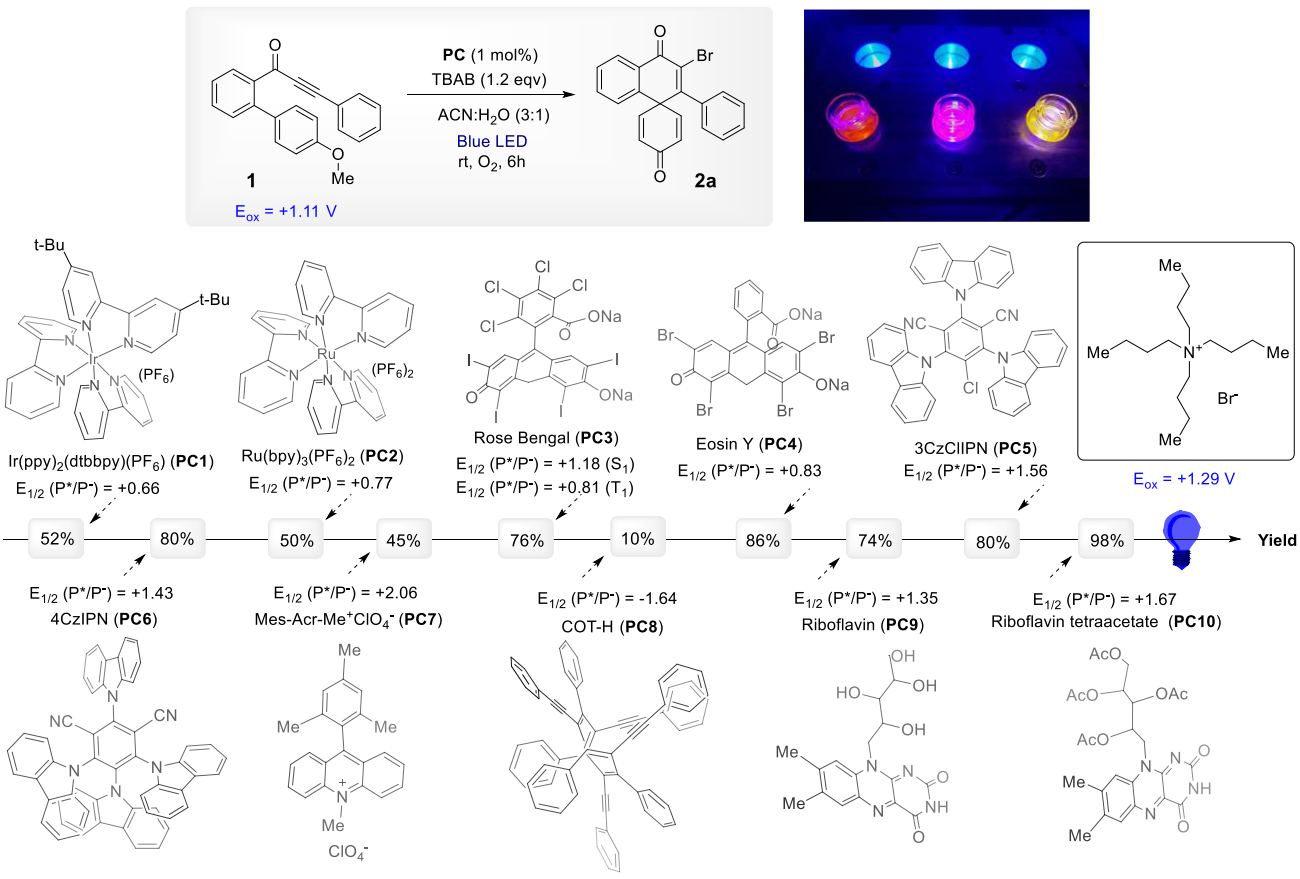
Scheme 1. Schematic illustration of prior art and importance of this perspective.

Over the past decade, visible light driven photoredox catalysis has gained colossal interest in the exploration of novel transformations employing photocatalyst to promote the reactions under external oxidant-free or reductant-free conditions.[18] Driven by our prolonged interest in dearomatisation chemistry[19] and newly gained interest in visible light promoted reaction, we explored the possibility of brominative carbannulation of biaryl ynones to form spiro[5.5]-trienones and bromo-dibenzocycloheptenones. Herein, we would like to introduce the application of Riboflavin tetraacetate (RFTA) as a metal-free photocatalyst[20] to facilitate the primary photoinduced events. To the best of our knowledge, this is the first example of applying RFTA as a photocatalyst to trigger dearomative *ipso*-annulation and *ortho*-annulation via an unprecedented photoredox-catalyzed electron transfer process.

Results and discussion:

Initially, we utilized 1-(4'-methoxy-[1,1'-biphenyl]-2-yl)-3-phenylprop-2-yn-1-one (**1a**) as the model substrate to optimize the reaction conditions and to investigate the efficiency of the photocatalyst RFTA in the visible-light driven radical cascade annulation of biaryl ynones and thereby, a model reaction condition was established as follows: **1a** (0.01 mmol), TBAB (1.2 equiv., 0.012mmol) and **PC10** (10 mol%) [$E_{1/2}(P^*/PC^{\bullet-})$ = +1.67 V] were mixed in 3 mL of

Scheme 2. Excited-State Reductive Potentials of Photocatalysts and Screening of PC1−10 for the Photosynthesis of 2a[a]



[a]The values of $E_{1/2}(P^*/P^{\bullet-})$ and E_{ox} (vs SCE in MeCN) were obtained from the reported literature.[21-25] Typical reaction conditions: **1** (0.01 mmol), **TBAB** (1.2 equiv), PC (1 mol %), were mixed in 3 mL of MeCN:H_2O (10:1) under irradiation of 3W single blue LED with O_2 protection at rt for 6 h, and the corresponding yields of 2a represent the isolated yields.

acetonitrile solvent under irradiation of single 3W blue LED (455 nm) with O_2 protection at rt for 4 h. To our delight, dearomative *ipso*-annulated product, 3'-bromo-2'-phenyl-4'H-spiro[cyclohexa[2,5]diene-1,1' naphthalene]-4,4'-dione (**2a**) was obtained with moderate yield, 74%. Thus, we first screened various photocatalysts (PCs) characterized by diverse redox and photochemical properties. Switching the photocatalyst RFTA with commercially available Riboflavin (**PC9**) led to **2a** in an inferior yield of 20% due to poor solubility. Using transition-metal photocatalysts like $Ir(ppy)_2(dtbbpy)(PF_6)_2$ (**PC1**) [$E_{1/2}(P^*/PC^{\bullet-})$ = +0.66 V] and $Ru(bpy)_3(PF6)_2$ (**PC2**) [$E_{1/2}(P^*/PC^{\bullet-})$ = +0.77 V] instead of RFTA displayed lower yields of 52% and 50% respectively. On the other hand, reactions with xanthene-based organic dyes Rose Bengal (**PC3**) [$E_{1/2}(P^*/PC^{\bullet-})$ = +0.81 V] (76%) and Eosin Y (**PC4**) [$E_{1/2}(P^*/PC^{\bullet-})$ = +0.83 V] (86%) as well as CDCB-based organic dyes 3CzClIPN (**PC5**) [$E_{1/2}(P^*/PC^{\bullet-})$ = +1.56 V] and 4CzIPN (**PC6**) [$E_{1/2}(P^*/PC^{\bullet-})$ = +1.43 V] also gave lower yields (with **PC5** and **PC6**, undesired catalyst side products were observed just above the product spot which makes difficulties in product isolation). Compared with RFTA, reaction with Mes-Acr-$Me^+ClO_4^-$ (**PC7**) [$E_{1/2}(P^*/PC^{\bullet-})$ = +2.06 V] also suffered decreased yield (45%). When the reaction was conducted in presence of COT-H (**PC8**) [$E_{1/2}(P^*/PC^{\bullet-})$ = +1.64 V], the expected product was obtained in only 10% yield. Notably, the relatively poor reactivity of **PC8** might be attributed to its inferior solubility. After extensive experimentation, RFTA was selected as the optimal photocatalyst to continue our follow-up study. Then, we investigated whether blue LED was necessary for the reaction. Changing the blue LED with other light sources did not deliver any product. When the reaction was carried out under sunlight as well as a dark environment it was found that the target product could not be observed. While the reaction mixture was irradiated using more powerful 35W blue LED to increase the yield of the reaction as well as decrease the reaction completion time, the result was not improved irradiating up to 10 h (**Fig. 2,** A). During optimization, biaryl ynone **1a** was used as the starting material to synthesize dearomative product **2a** using various brominating agents (**Fig. 2,** B). In presence of bromine and NBS we got only 62% and 86% yield respectively and when the reaction was performed using DBDMH, we got inferior result compared to TBAB (98% yield). We next assayed the impact of oxygen on the reaction which turned out to be unfavourable on changing the oxygen atmosphere to nitrogen or open-air condition as they led to decreased yield (**Fig. 2,** C). Furthermore, we focused to optimise the catalyst loading and it was found that 0.01 mol% RFTA gives maximum yield in optimum reaction completion time. It is interesting to note that, when the reaction was executed only in presence of oxygen atmosphere under blue light irradiation, the reaction proceeds and the product **2a** was found in 38% yield (**Fig. 2,** D).

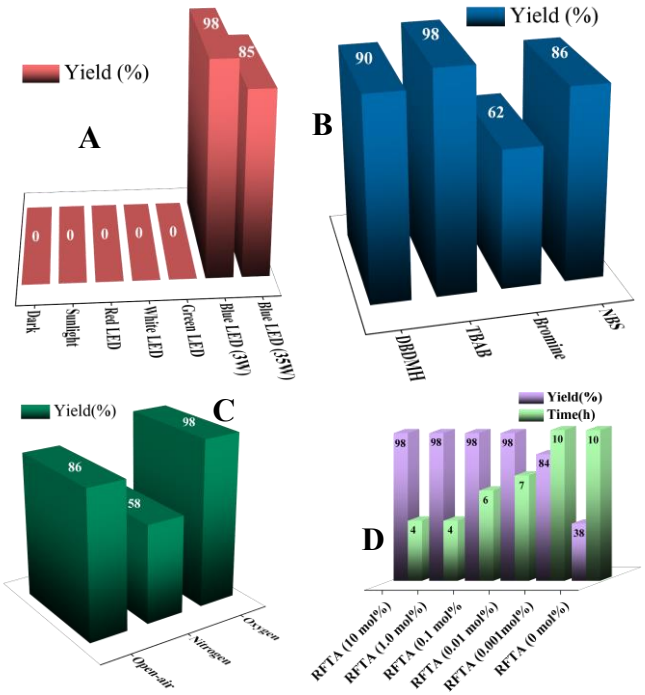
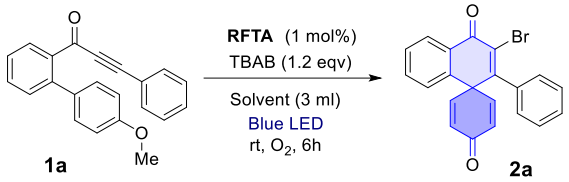


Figure 2. Deviation from the standard condition. (**A**) Schematic illustration of light dependence. Reaction conditions: **1** (0.01 mmol), **TBAB** (1.2 equiv), **PC10** (1 mol%) in 3 mL of MeCN:H_2O (10:1) under variable light irradiation with O_2 protection at rt for 8h. Isolated yields were given on the basis of substrate **1**. (**B**) Optimization of bromide source. Reaction conditions: **1** (0.01 mmol), **bromide source** (x equiv), **PC10** (1 mol%) in 3 mL of MeCN:H_2O (10:1) under irradiation of 3W single blue LED with O_2 protection at rt for 6h. Isolated yields were given on the basis of substrate **1**. (**C**) Dependence on the environment. Reaction conditions: **1** (0.01 mmol), **TBAB** (1.2 equiv), **PC10** (1 mol%) in 3 mL of MeCN:H_2O (10:1) under irradiation of 3W single blue LED in different environment at rt for 6h. Isolated yields were given on the basis of substrate **1**. (**D**) Schematic illustration of catalyst loading of reaction. **1** (0.01 mmol), **TBAB** (1.2 equiv), **PC10** (x mol%) in 3 mL of MeCN:H_2O (10:1) under irradiation of 3W single blue LED with O_2 protection at rt. Reaction was monitored by TCL analysis. Isolated yields were given on the basis of substrate **1**.

In the meantime, we surveyed a series of solvents for this transformation. When the reaction was performed using solvents having higher dielectric constant value, in general, we observed immaculate transformations. Replacement of CH_3CN with MeOH, Acetone, DCM, Toluene led to lower yields of **2a**. In presence of DMSO, the reaction took longer time for completion and notably, with H_2O we found 5% product formation, while a large amount of starting material was recovered, which might be attributed to the inferior solubility of organic substrate to the aqueous medium. This enthusiastic result further tempted us to check the effect of biphasic solvents employing on this transformation. Gratifyingly, the expected product **2a** was obtained in 98% yield in presence of ACN: H_2O (10:1) and changing the reaction solvent to other biphasic solvent led to lower yields of **2a**. Eventually, we came up with the optimized reaction conditions for this transformation: **1a** (0.1 mmol) and TBAB (1.2 equiv., 0.12 mmol) with RFTA (0.01 mol%) in ACN: H_20 (3.0 mL, 10:1) at room temperature under oxygen atmosphere for 7 h in presence of 3W single blue LED (455 nm) irradiation.

Table 1. Role of solvent in the course of the reaction[a]



Entry	Solvent (κ)	Conv. of 1a (%)[b]	Yield (%)[c]
1	Toluene (2.4)	20	12
2	DCM (8.9)	100	80
3	Acetone (20.7)	98	76
4	MeOH (32.7)	100	58
5	CH_3CN (37.5)	<100	74
6[d]	DMSO (46.6)	80 (94)[e]	78 (90)[e]
7	H_2O (80.1)	<10	5
8	Hexane (1.8) : H_2O	0	0
9	THF (7.6) : H_2O	40	0
10	DCE (10.4) : H_2O	96	86
11	EtOH (24.6) : H_2O	90	30
12	CH_3CN : H_2O	100	98
13	DMF (37.7) : H_2O	10	nd

[a]**1a** (0.01 mmol), TBAB (1.2 equiv, 0.012 mmol), RFTA (1 mol%) in variable solvent conditions under 3W single blue LED light irradiation with O_2 protection at rt for 6h. Isolated yields were given on the basis of substrate **1a.** [d]after 12 h. [e]after 18 h.

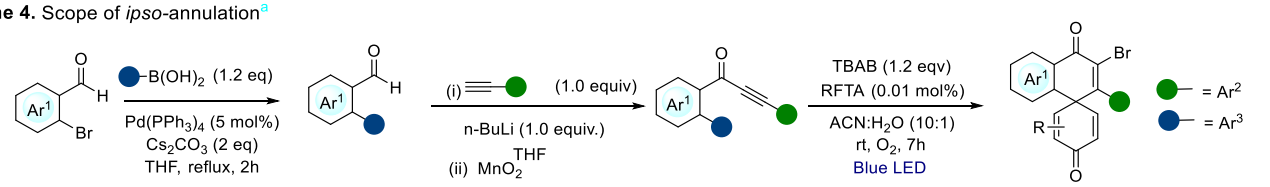
To investigate the generality of this new visible light-mediated method, we synthesized biaryl ynones **1** starting from 2-bromo benzaldehyde. With optimal reaction conditions in hand, we then set out to explore the substrate scope of this carbannulation reaction with respect to biaryl ynones. Although, the biaryls are challenging substrates as they performed efficiently in a range of radical reactions and their propensity to undergo the competiting reactions of C-H bonds on proximal phenyl ring (Ar^1) or the *ortho*- C-H bonds on distal phenyl ring (Ar^3) resulting in 5-exo-trig cyclization to indenones or 6-exo-trig *ortho*-dearomatization, thus presents a significant challenge to our desired reaction. Despite this challenge, our results outlined in **Scheme 4** show that the brominative dearomatization proved to be robust and general.

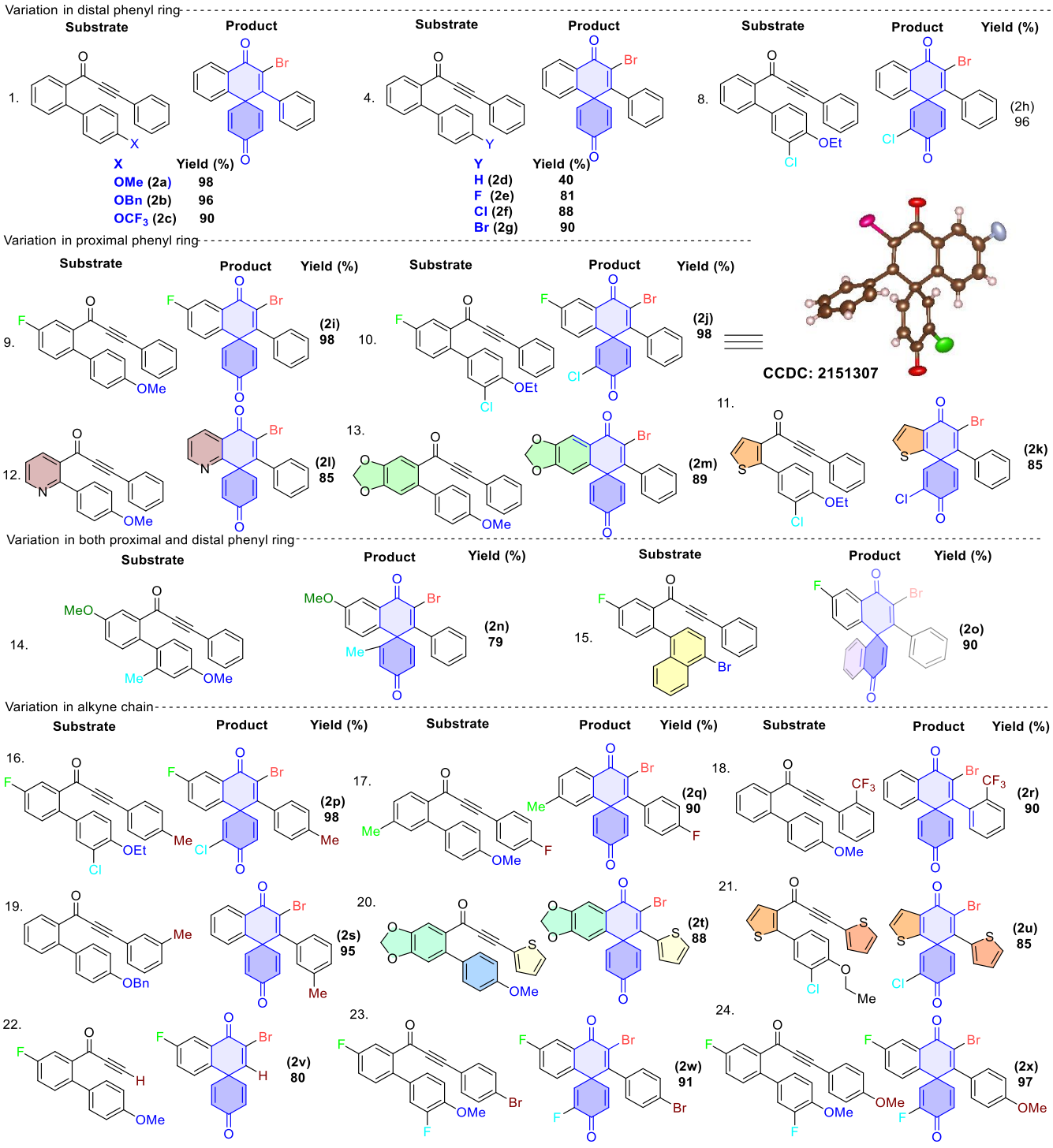
We first investigated the effect of mono-substitution at the *para*- position of the phenyl ring distal to the 1,1′-biphenyl bond, and the reaction was found to tolerate a wide range of functionalizations. For instance, both benzyloxy- and trifluoromethoxy-substituted substrates (**1b** and **1c**) led to the same spiro-conjugated compound (**2b** and **2c**) as the methoxy-substituted substrate **1a** (**Scheme 4**, entries 1−3). In presence of halogen groups (F, Cl and Br), the *ipso*-annulated products (**2e**-**2g**) were obtained in good yields (81% - 90%). Notably, when no substituent is present at the distal phenyl ring (**1d**), spiro compound (**2d**) is exclusively obtained (**Scheme 4**). Despite the reduced yield, the last case where in absence of any directing group, highlights the relatively benign and functional-group-tolerant nature of our visible light induced photocatalytic condition. In addition, the introduction of chlorine group in the *ortho*-position to the -OEt produced the spiro compound **2h** in 96% yield. Substitutions on the phenyl ring proximal to the 1,1′-biphenyl bond were next examined. Substrates bearing either mild electron-withdrawing groups (such as fluorine) or electron-donating groups (such as methoxy) on the proximal phenyl ring at the position *para*- to the 1,1′-biphenyl bond, did not alter the reaction outcome and the spiro compounds **2i**–**2j**, **2n** were efficiently obtained with excellent yields, 79% to 98%. Additionally, when the proximal phenyl ring bears a methyl group at the *meta*-position to the 1,1′- biphenyl bond, a 6-endo-dig cyclization takes place, leading exclusively to the *ipso*-annulated product **2q** in 90% yield. Subsequently, heteroaryl substituents (i.e. thiophenyl, pyridinayl, benzodioxolyl) were also compatible, and the expected spiro compounds were found in good yields (**2k** – **2m**). It is noteworthy that, in addition to the *para*-methoxy group, when a methyl group is introduced at the *ortho*- position of the distal phenyl ring, to our delight, the cyclization leads exclusively to the spiro compound **2n**, indicating that the groups on the distal phenyl ring induce a much stronger effect. Inspired by the preceding result, we then investigated the steric effects induced by the substituents on the distal phenyl ring. For instance, the incorporation of a bulkier backbone (naphthalenyl) was also found to be compatible for this methodology, resulting in the formation of *ipso*-annulated product (**2o**) in 90% yield.

The electronic effects of substituents of the alkynone triple bond were also explored. To our pleasure, various substituents such as methyl, fluoro, bromo, methoxy, and trifluoromethyl at the *para*- position of the phenyl ring tethered to alkyne were tolerated, affording the corresponding products **2p**-**2s**, **2w**, **2x** in good to excellent yields. Moreover, under our thus-far optimal conditions, the reaction also showed a high functional group tolerance: converting phenyl group to thiophene group of thiophenyl and benzodioxolyl phenome scaffold, which were usually sensitive to strong oxidative conditions, afforded the desired dearomatized product **2t**, **2u** with excellent yield. It was observed that with substituent of H− (**2v)** on the alkynone triple bond moiety also proceeded smoothly in this reaction underlining the general utility and expediency of our approach.

On removing the strongly electron-donating group from the *para*- position, generally a 7-endo-dig cyclization predominates, producing dibenzocycloheptene-5-ones whereas in our system we always ended up with spiro-annulated product via 6-endo-dig cyclization. We hence commence exploring the effect of polymethoxy substitution in distal phenyl rings in this methodology. For instance, incorporating two methoxy groups at the *meta*- positions of the distal phenyl ring, allowed formation of a mixture of spiro compound **2y** and dibenzocycloheptene-5-one **3a** in 8:1 ratio. However, in addition to the *para*-methoxy group, when two more weakly electron-donating methyl groups are introduced at the *meta*- positions of the distal phenyl ring, a mixture of **3b** and **2z** is obtained in a **1:12.5** ratio. On the other hand, when the proximal phenyl ring bears a methoxy group at the *para*- position to the 1,1′- biphenyl bond along with the *para*-methoxy group in distal phenyl ring, a mixture of spiro compound **3c** and dibenzocycloheptene-5-one **2za** is obtained in a 23.5:1 ratio (**Scheme 5**). It is worth mentioning

Scheme 4. Scope of *ipso*-annulation[a]

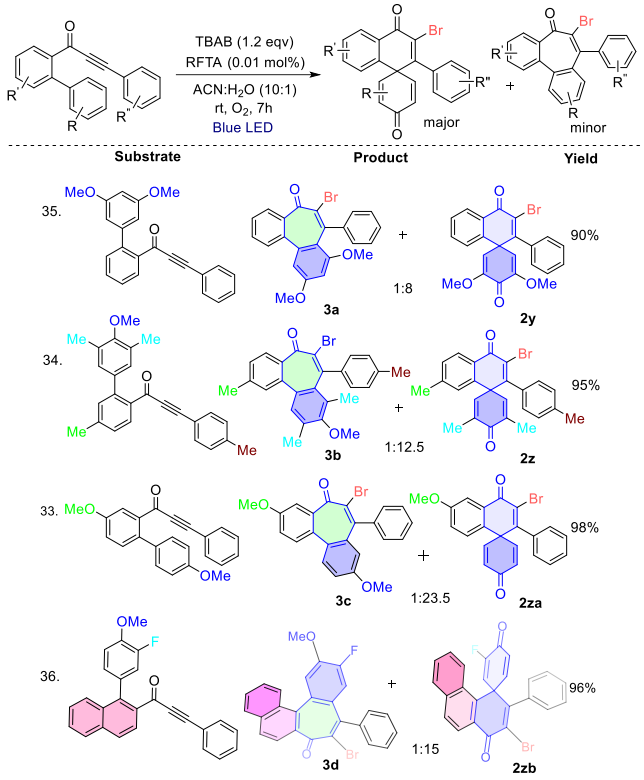




[a]1 (0.01 mmol), TBAB (1.2 equiv), RFTA (0.01 mol%) in 3 mL of MeCN : H2O (10:1) under 3W single blue LED light irradiation with O_2 protection at rt for 7h. Isolated yields were given on the basis of substrate 1.

that, in case of biaryl ynone having a fluorine at the *meta*-position and methoxy at the *para*- position of the distal phenyl ring (**Scheme 5**, entry **36**), the formation of a separable mixture of dibenzocyclohepten-5-one (**3d**) and the *ipso*-annulated spiro compound (**2zb**) is obtained.

Scheme 5. Multiple substitution effect on distal phenyl ring[a]

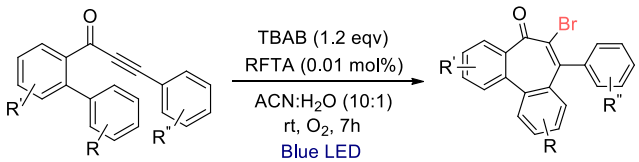


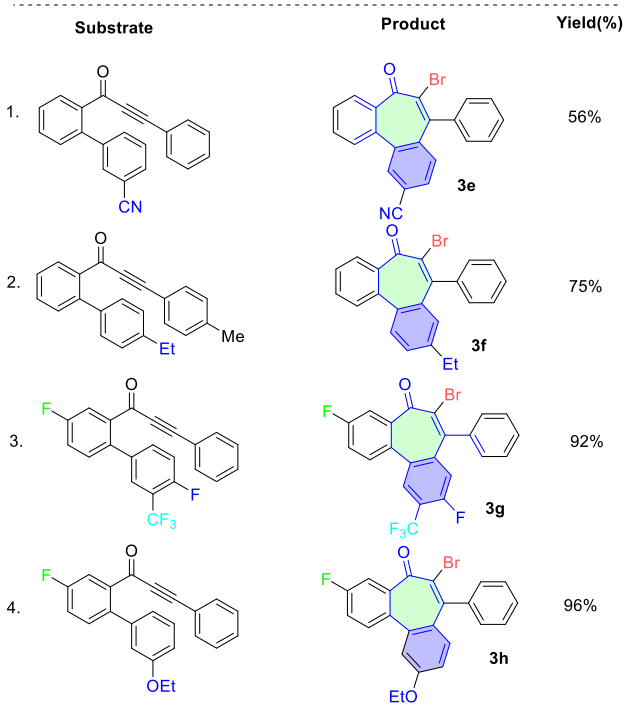
[a]**1** (0.01 mmol), TBAB (1.2 equiv), RFTA (0.01 mol%) in 3 mL of MeCN : H_2O (10:1) under 3W single blue LED light irradiation with O_2 protection at rt for 7h. Isolated yields were given on the basis of substrate **1**.

To showcase the utility of our method, we next sought to apply our protocol to the synthesis of dibenzocycloheptene-5-one via 7-endo-dig cyclization. Gratifyingly, the application of our optimized conditions to several biaryl ynones gave corresponding dibenzocycloheptene-5-ones in moderate to good yield **3e** to **3h** (**Scheme** 6).

To understand the mechanism of the present annulations, a couple of control experiments were performed. On the basis of our substrate scope exploration, the resulted regioselective cyclization substantially determined by the electron-density concentrated at the *ortho*- or *ipso*- position of the phenyl ring distal to the 1,1′-biphenyl bond, which again ensured by performing an electron-density experiment (**Fig. 3**).

Scheme 6. Scope of *ortho*- annulation[a]





[a]**1** (0.01 mmol), TBAB (1.2 equiv), RFTA (0.01 mol%) in 3 mL of MeCN : H_2O (10:1) under 3W single blue LED light irradiation with O_2 protection at rt for 7h. Isolated yields were given on the basis of substrate **1**.

In presence of a strong electron-donating substituent such as methoxy at either the *para*- or *ortho*- position of the distal phenyl ring, the electron density becomes more densed at the *ipso*- position and thus spiro annulation is preferred (**Figure 3,** a, c). Conversely, an *ortho*- electrophilic cyclization takes place when an electron-donating group is present at the *meta*- position of the distal phenyl ring or at the *para*- position of the proximal phenyl ring. Moreover, substitution on the distal phenyl ring persuaded much stronger substituent effect in comparison to the functionalization of the proximal phenyl ring probably due to their propinquity to the *ortho*- and *ipso*- positions (**Figure 3**, b). In case of multi-substituted biaryl ynones, the formation of the spiro[5.5] trieneones and bromo-dibenzocyclohepten-5-ones depend on the electronic effect of the substituents and their positions on the distal phenyl rings (e. g. **Scheme 5**). Additionally, the ratio of the mixture of these two annulated products is governed by the maximum electron density on the *ipso*- and *ortho*- positions as well as their vicinity to either the *ipso*- or the *ortho*- position of the distal phenyl ring.

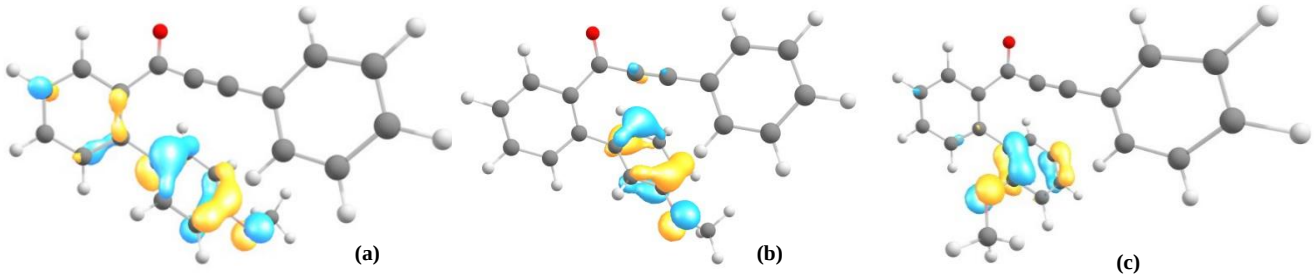
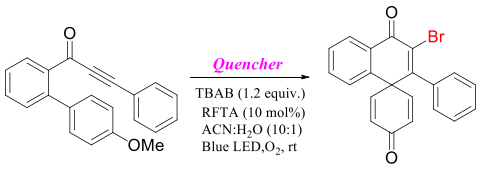


Figure 3. DFT-optimized structure of HOMO of (a) *p*-OMe, (b) *m*-OMe, (c) *o*-OMe substituted biaryl ynones illustrating the maximum electron density on *ipso*- and/or *ortho*- position depending on the methoxy group.

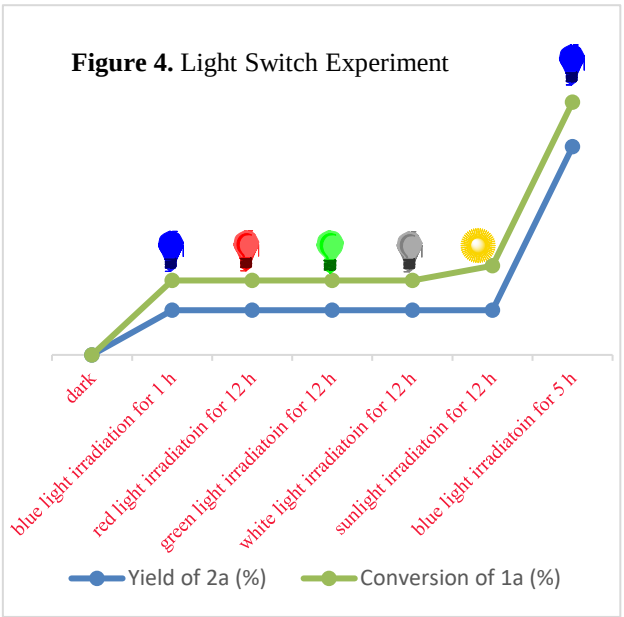
Scheme 7. Quenching Experiments[a]



Entry	Quencher (equiv.)	Purpose	Yield (%)[b]
1.	TEMPO (2)	Radical scavenger	10
2.	BHT (2)	Radical scavanger	60
3.	NaN_3 (1)	Singlet Oxygen scavenger	0
4.	DABCO (1)	Singlet Oxygen scavenger	30
5.	Benzoquinone (1)	Super oxide radical anion scavenger	52

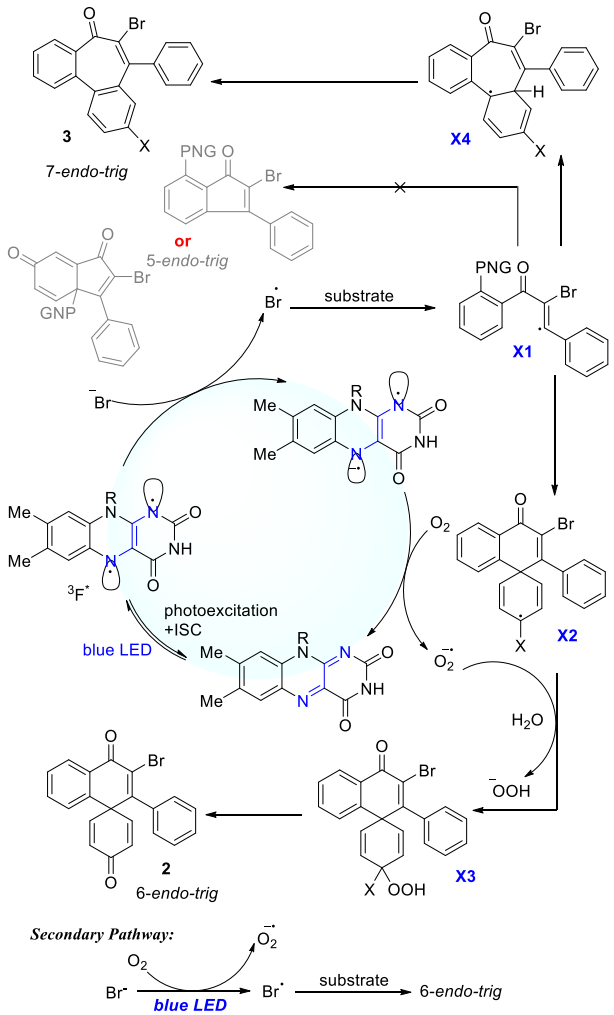
[a]Reaction Condition: **1a** (0.01 mmol), TBAB (0.012 mmol) and RFTA (10 mol%) in 3 mL ACN: H_2O (10:1) under O_2 atmosphere for 4 h using Blue LED. [b]Yield was determined by ^1H NMR using mesitylene as internal standard.

The radical trapping experiments helped us to understand that the reaction proceeded via radical pathway. Additionally, 3.0 equiv. TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) as radical scavenger to the standard reaction inhibited the dearomatization reaction and **2a** was isolated in 10% yield. On applying another radical scavenger BHT (Butylated hydroxytoluene) in the standard conditions, the dearomative product was obtained in 60% yield. Moreover, in the presence of both DABCO and Benzoquinone, decreased yield of the product was obtained. NaN_3 being a singlet oxygen quencher, completely suppressed the reaction further implying the radical pathway being operative



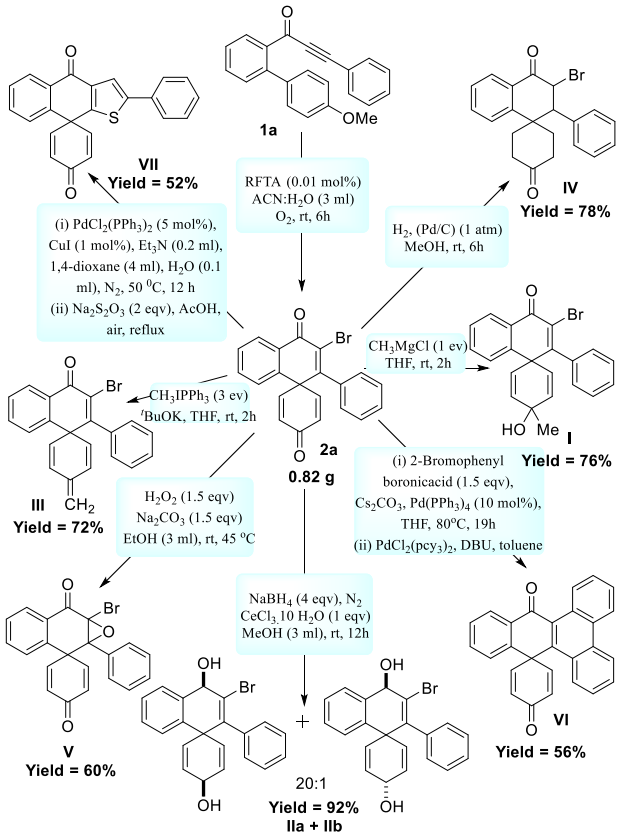
(**Scheme 7**). To verify whether the reaction was a radical chain reaction, a light switch experiment was carried out. It was found that the reaction could only proceed under 3W blue LED light irradiation conditions and did not occur in presence of other LED lights or without light.

Scheme 8. Plausible reaction pathway.



Mechanistically, we anticipated that, upon irradiation with blue LED light (455 nm) and after rapid intersystem crossing, the triplet-excited state of RFTA would be oxidant enough (E_{red} = 1.67 V vs SCE in MeCN) to undergo single electron oxidation of both TBAB (E_{ox} = 1.29 V vs SCE in MeCN) and model substrate **1a** (E_{ox} = 1.11 V vs SCE in

MeCN). On the basis of the aforesaid results, control experiments and reference related literature, we propose a plausible reaction mechanism in **Scheme 8**. Initial oxidation of bromide ion by the photoexcited RFTA generates the bromide radical, Br•. To support this reductive quenching step, Stern−Volmer luminescence quenching experiment is going on in our lab. The regioselective addition of the bromide radical to the alkyne **1** forms the vinyl radical intermediate **X1**, which proceeds to **X2** via 6-endo-trig cyclization (*ipso*-annulation). Subsequently, the superoxide radical anion in presence of H_2O accelerates the formation of dearomative *ipso*-annulated product **2** via the generation of intermediate **X3**. For the construction of bromo-dibenzocycloheptenones **3**, it is considered that vinyl radical **X1** undergoes 7-endo-dig cyclization (*ortho*-annulation) to **X4** which finally lead to the corresponding product **3** after dehydrogenation.



Scheme 9. Synthetic utility of spiro-trienone and gram-scale synthesis.

Further outline the utility of the methodology, several natural products were identified as synthetic targets having spiro-trienone moiety in their core structure (**Scheme 9**). Treatment of **2a** with MeMgCl at ice cold condition afforded the 1,2-carbonyl addition product **I** in 76% yield.[16] The selective reduction of **2a** under Luche conditions gave **II** in 92% yield. The 3'-bromo-2'-phenyl-4'H-spiro[cyclohexa[2,5]diene-1,1'-naphthalene]-4,4'-dione **2a** can be converted to 3'-bromo-4-methylene-2'-phenyl-4'H-spiro[cyclohexa[2,5]diene-1,1'-naphthalen]-4'-one moiety **III** by treatment with CH_3PPh_3Br (2.5 equiv.) and ^tBuOK in THF solvent.[16] A hexahydro spiro-cyclization product **IV** can be encountered followed by hydrogenation in presence of 10% Pd(C) and MeOH solvent in 1atm H_2 atmosphere. Epoxidation of **2a** to the *tetra*-substituted double bond have been performed using H_2O_2 and Na_2CO_3 in EtOH solvent at room temperature (**V**, 60%).[16] Next, to emphasize the presence of halo-group in spiro-product, the Suzuki-Miyaura cross coupling reaction of (**2a**) and 2- bromophenylboronic acid followed by the Pd-catalyzed *intra*-molecular cyclization, gave 14H-spiro[benzo[f]tetraphene-9,1'-cyclohexa[2,5]diene]-4',14-dione **VI** as a sole product (**Scheme 9**).[26] Finally, 2'-phenyl-4'H-spiro[cyclohexa[2,5]diene-1,9'-naphtho[2,3-b]thiophene]-4,4'-dione was synthesized from **2v** following the procedure mentioned in the ref. 27. The gram scale conversion of **1a** (1.0 g) → **2a** (0.82 g) under optimised condition justify the synthetic potential of our methodology.

In conclusion, we have achieved the first visible-light-driven, metal-free brominative dearomatization of biaryl ynones using inexpensive RFTA as a photocatalyst, which allows straightforward access to *ipso*-annulated spiro compounds as well as dibenzocycloheptene-5-ones, depending on the molecular architecture. The method is mild, operationally simple, tolerant of a number of functional groups and exhibit excellent scalability. We believe this methodology provides practitioners with an alternative tool that will permit the scrutiny of unexplored chemical space and find useful applications in organic synthesis.

CONFLICTS OF INTEREST

There are no conflicts to declare.

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