Photocatalysis Hot Paper

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1,3,2-Diazaphospholene-Catalyzed Reductive Cyclizations of Organohalides**

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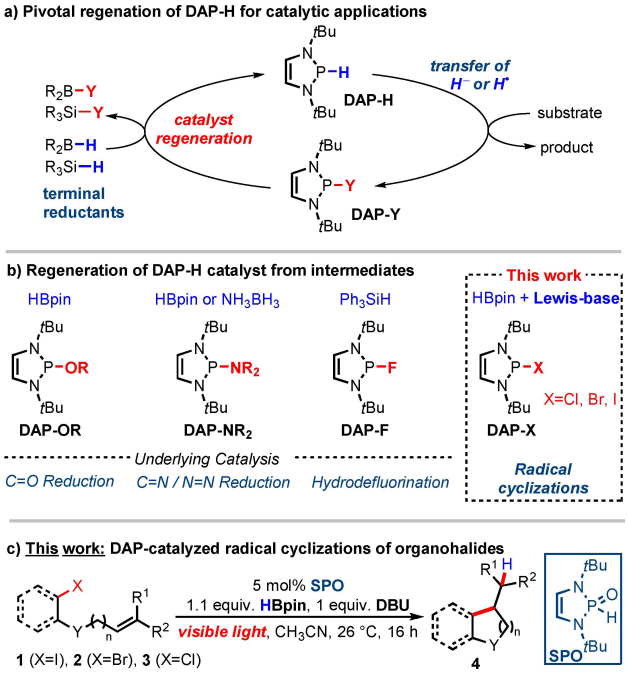
Abstract: 1,3,2-diazaphospholenes hydrides (DAP-Hs) are highly nucleophilic organic hydrides serving as main-group catalysts for a range of attractive transformations. DAP hydrides can act as stoichiometric hydrogen atom transfer agents in radical reactions. Herein, we report a DAP-catalyzed reductive radical cyclization of a broad range of aryl and alkyl halides under mild conditions. The pivotal DAP catalyst turnover was achieved by a DBU-assisted σ-bond metathesis between the formed DAP halide and HBpin, which rapidly regenerates DAP-H. The transformation is significantly accelerated by irradiation with visible light. Mechanistic investigations indicate that visible light irradiation leads to the formation of DAP dimers, which are in equilibrium with DAP radicals and accelerate the cyclization. The direct use of $(DAP)_2$ enabled a catalytic protocol in the absence of light.

Discovered in the 1980s, 1,3,2-diazaphospholenes (**DAPs**)[1] represent a class of electron-rich heterocycles with a great application potential as versatile main-group catalysts.[2] For, instance, diazaphospholene hydrides (**DAP-Hs**) are powerful nucleophiles and weakly basic organic hydride donors.[3] They efficiently reduce carbonyls[4] and, in conjugate fashion, α,β-unsaturated amides,[5] esters,[5b,6] ketones,[5] and acids (Scheme 1).[7] A σ-bond metathesis between the alkoxy-substituted **DAPs** and pinacol borane (HBpin) regenerating **DAP-H** rendered these processes catalytic.[4] Reports by Kinjo and Speed exploited σ-bond metathesis between the P–N and B–H bonds of ammonia borane and HBpin, respectively to enable catalytic reductions of azobenzenes[8] and imines.[5b,9] Cheng demonstrated the cleavage of the P–F bond in **DAP** fluorides by employing phenylsilane. This enables hydrodefluorination of trifluoromethylalkenes[10] and polyfluoroarenes.[11] The reactivity of **DAP-Hs** is not limited to the two-electron transfer processes.[12] Reductions of alkyl and aryl halides[13] and α-carboxy ketones[14] via radical pathways have been reported. Radical processes, where **DAPs** are involved catalytically are scarce. Only a single methodology describing a **DAP**-catalyzed deoxygenation of α-carboxy ketones is reported.[14] It capitalizes on the σ-bond metathesis between the P–O and B–H bonds for the catalyst's regeneration. In contrast to the **DAP-F**, the related halide bearing **DAP-X** (X = I, Br, Cl) does not undergo a σ-bond metathesis with borane or silane reagents. This reactivity gap hampers the closure of catalytic cycles. To exploit the full potential of **DAPs** in radical chemistry with organohalides, it is essential to render the transformations catalytic.

Radical cyclizations of organohalides across olefins are highly useful transformations to access diverse cyclic skeletons.[15] Typically, the reductive cyclization of organohalides operating through a radical mechanism requires stoichiometric amounts of toxic organostannanes[16] and



Scheme 1. a) **DAPs** in catalysis: Regeneration of **DAP-H** to close catalytic cycles. b) Landscape of reduction options for **DAP-Y** into **DAP-H** and the underlying catalytic processes c) **DAP**-catalyzed reductive radical cyclization of organohalides.

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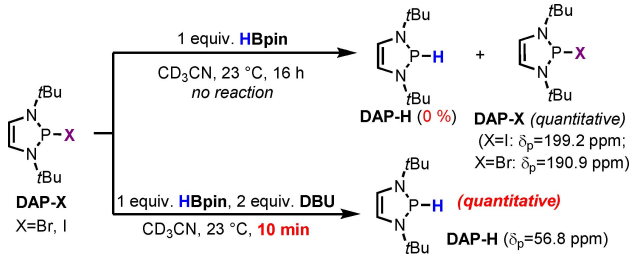
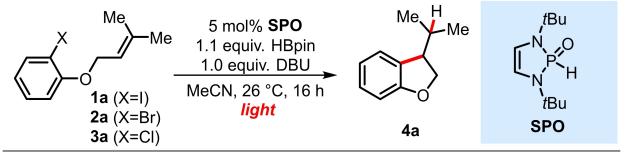
radical initiators such as AIBN[17] or Et_3B/O_2.[18] Advances in photochemical methods provided some sustainable alternatives including the use of metal- and organic photocatalysts[19] as well as electron-donor reagents.[20] The high affinity of **DAPs** towards organohalides makes them very attractive for activating this broad class of compounds.[21] Speed demonstrated the functionalization of organo- iodides and bromides.[22] However, catalytic variants of these processes remain so far elusive. The rapid and efficient regeneration of the **DAP-H** from **DAP-X** under mild conditions would be an essential gateway to catalytic transformations with organohalides. Herein, we report an efficient Lewis base-promoted regeneration of **DAP-H** from **DAP-X** and its application in the catalytic reductive radical cyclization of aryl and alkyl halides.

To close the catalytic cycle, we first investigated the regeneration of the pivotal **DAP-H** from the formed **DAP-I** of the stoichiometric process. Mixing **DAP-I** and HBpin in CD_3CN does not generate **DAP-H** after 16 h (Scheme 2). We hypothesized that the activation of the borane by a suitable Lewis base[23] could facilitate the σ-bond metathesis between **DAP-I** and HBpin. To our delight, adding DBU to the **DAP-I**/HBpin mixture in CD_3CN triggered a fast and quantitative conversion to **DAP-H**. The same reactivity was maintained with **DAP-Br**.



Scheme 2. Fast regeneration of **DAP-H** with the DBU/HBpin system.

Table 1: Optimization of the **DAP**-catalyzed cyclization of **1**–**2a**.[a]

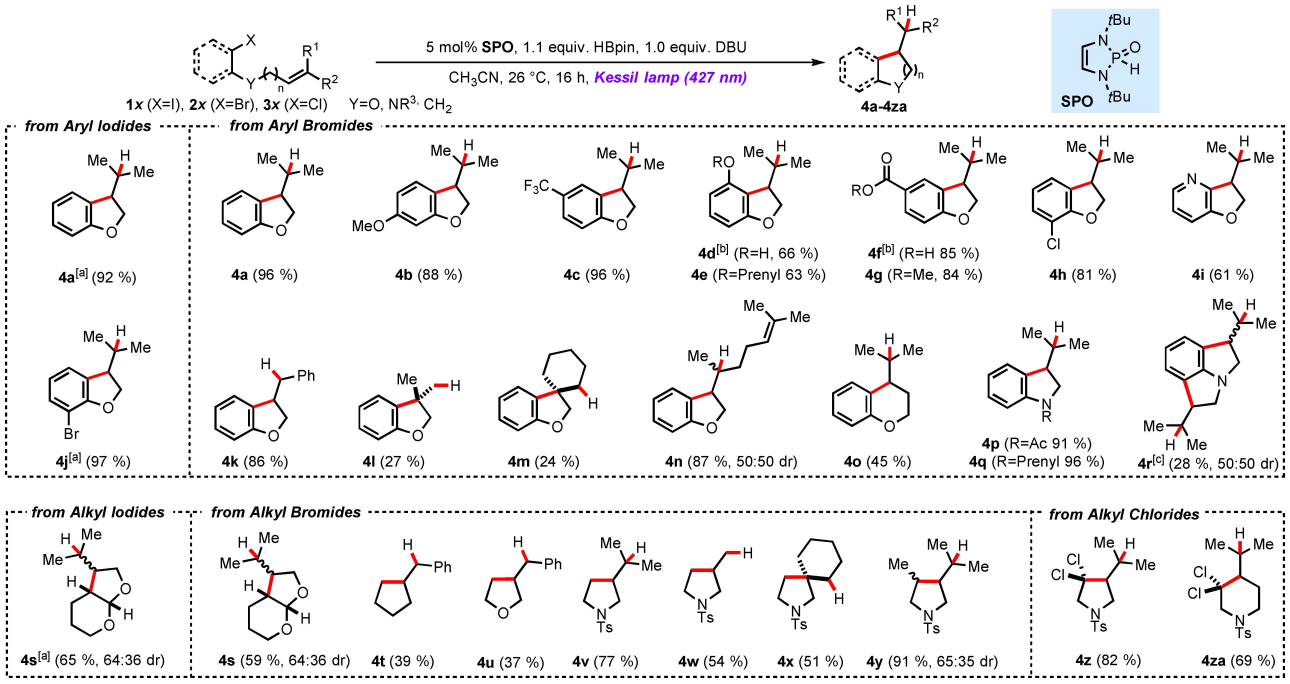


entry	substrate	variation	yield [%][b]
1	**1a**	ambient light	23
2	**1a**	*exclusion of light*	19
3	**1a**	white LEDs	89
4	**2a**	*exclusion of light*	0
5	**2a**	white LEDs	12
6	**2a**	Kessil lamp (427 nm)	91
7	**2a**	Kessil lamp (427 nm), no **SPO**	0
8	**2a**	Kessil lamp (427 nm), no DBU	5
9	**2a**	Kessil lamp (427 nm), no HBpin	0
10	**3a**	Kessil lamp (427 nm)	0

[a] Conditions: 0.1 mmol **1a**, 5 µmol **SPO**, 0.11 mmol HBpin, 0.1 mmol DBU, 0.1 M (0.8 M for **2a** and **3a**) in MeCN at 26 °C for 16 h, [b] Yields determined by ^{1}H NMR with an internal standard.

With the rapid regeneration of **DAP-H** from **DAP-X**, enabled by the DBU/HBpin system, we turned our efforts towards a fully catalytic transformation for the cyclization of aryl iodide **1a** and aryl bromide **2a** (Table 1). Employing 5 mol% of the robust and conveniently usable secondary phosphine oxide **SPO**[24] as the pre-catalyst with HBpin/DBU in MeCN, **1a** afforded **4a** in 23 % yield (entry 1). We noticed that the reaction rate and progress are highly sensitive to light. While still taking place under the exclusion of light (entry 2), the yield of **4a** almost quadrupled when irradiating the reaction with white LEDs (entry 3). This effect was even more pronounced with aryl bromide **2a**. However, no reaction took place in the absence of light (entry 4). The use of white LEDs restored some reactivity giving **4a** in 12 % yield (entry 5). Switching to a more powerful Kessil lamp (427 nm) increased the yield of **4a** to 91 % (entry 6). Elevated temperatures also promoted the cyclization to **4a**, albeit in low efficiency (27 % yield, see Supporting Information). Control experiments omitting **SPO**, DBU and HBpin showed their indispensable role (entries 7–9). Aryl chloride **3a** did not cyclize (entry 10).

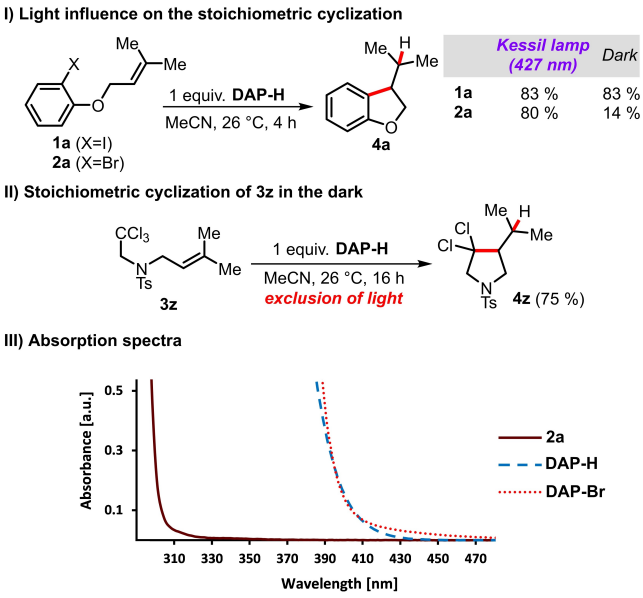
Next, we evaluated the scope of the **DAP**-catalyzed reductive cyclization for a broad set of substituted aryl halides (Scheme 3). Dihydrobenzofurane **4a** was isolated in excellent yields (92 % from **1a** and 96 % from **2a**). The transformation is tolerant to potentially reactive functional groups like methyl esters, free phenols, and carboxylic acids and reliably delivered products **4b**–**4g**. Notably, a switch from the Kessil lamp to white LEDs allowed for a selective cyclization originating from the aryl iodide moiety of **1j** *in the presence* of the adjacent bromide substituent, in 97 % yield. Along the same lines, the reaction of aryl bromide **2h** cleanly proceeded under standard conditions in the presence of an adjacent chloride moiety. The reaction of the bromopyridine **2i** cyclized to product **4i** without **DAP**-catalyzed reduction of its pyridine core.[25] Aryl bromides bearing different alkenyl tethers reacted well. For instance, styrene **2k** underwent cyclization in 86 % yield. The nature of the olefin acceptor portion was as well modifiable (**4l**–**4n**). Substrates, that pass through 1° or 2° alkyl radical intermediates, reacted in reduced yields (**4l** and **4m**). Besides the formation of the five-membered rings, the process enabled the 6-*exo*-trig cyclizations as demonstrated for 4-isopropylchromane **4o**. Aniline substrates were readily converted into functionalized indolines **4p**–**4r**. Next, we explored the potency of alkyl halide substrates to undergo cyclization. In this respect, iodo- **1s** and bromo-acetals **2s** smoothly reacted to bicyclic product **4s**. Primary alkyl bromides **2t** and **2u** cyclized to the corresponding cyclopentane **4t** and tetrahydrofuran **4u** in moderate yields. The cyclization of substituted alkenyl amines led to pyrrolidines **4v**–**4w** in good yield. A secondary alkyl bromide analogue formed disubstituted pyrrolidine **4y** in 91 % yield and 65:35 *dr*. Noteworthy, substrates bearing a trichloroalkyl group engaged in the



Scheme 3. Scope of the **DAP**-catalyzed cyclization of organohalides. Conditions: 0.20 mmol **1*x*–3*x***, 10 µmol **SPO**, 0.22 mmol HBpin, 0.20 mmol DBU in MeCN (**1*x*** = 0.2 M, **2*x*–3*x*** = 0.8 M) in MeCN at 26 °C for 16 h. [a] white LEDs instead of the Kessil lamp (427 nm). [b] 2.5 equiv HBpin. [c] 10 mol % **SPO**, 2.2 equiv. HBpin and 2.0 equiv. DBU.

transformation providing dichloro-substituted pyrrolidine **4z** and piperidine **4za** in 82 % and 69 % yield, respectively.

Mechanistic investigations were conducted to better understand the effect of light in this transformation. The stoichiometric reactions indicate that the cyclizations of **1a** and **2a** take place in the dark as well. However, irradiation by the Kessil lamp accelerates the transformation (Scheme 4). In contrast, the catalytic reaction with substrate **2a** occurs only under irradiation. Under catalytic conditions, aryl iodide **1a** still cyclized to **4a** in the dark, albeit with poor efficiency. The direct reaction of **DAP-H** and CCl_4 does not require activation by light affording **DAP-Cl** and a mixture of chloromethanes CH_mCl_{4-m} (m = 0–3).[21b] This P–H/C–Cl bond metathesis proceeds eventually through a radical mechanism. Substrate **3z** was exposed to one equivalent of **DAP-H** under the exclusion of light yielding 75 % of **4z**.[26] To gain mechanistic insight into the light-enhanced reaction, we first identified which species absorb light in the visible spectrum. The absorption spectra of **DAPs** and **2a** indicate that only **DAP-H** and **DAP-Br** absorb light at wavelengths above 400 nm, an emission tail of the Kessil lamp (427 nm). No ground state associations between the **DAPs** and **2a** were found (see Supporting Information). Based on this information, two scenarios in which visible light accelerates the cyclization of **2a** are plausible. In the scenario **I**, a photoexcitation of **DAP-H** triggers a SET from the excited **DAP-H*** to **2a**. Scenario **II** involves a photoexcitation of **DAP-H** leading to a **DAP** radical (**DAP•**). Based on electrochemical and spectroscopic measurements, we estimated the redox potential of the excited **DAP-H*** is −3.14 V (vs. Fc^+/Fc in



Scheme 4. Evaluation of the light influence on the cyclization efficiency and absorption spectra of the reaction components.

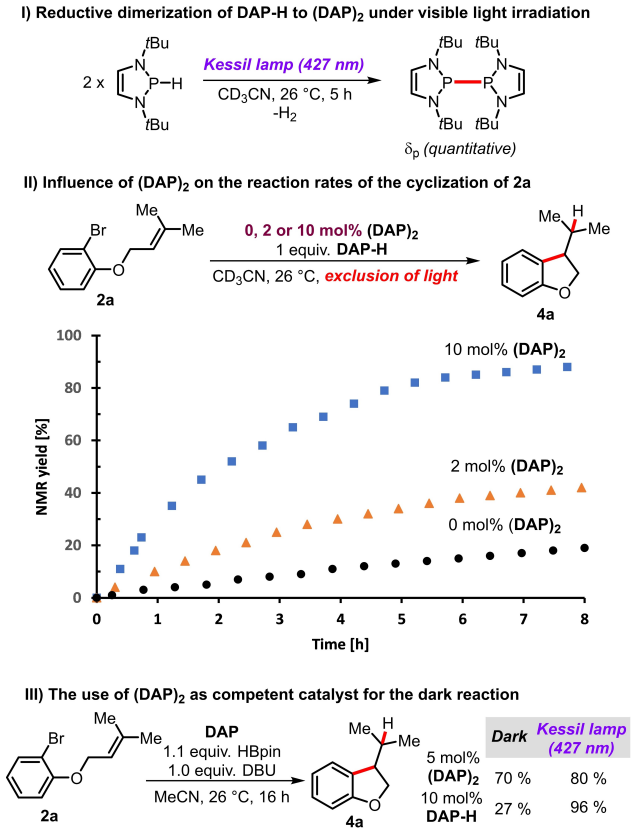
MeCN), indicating that a SET between **DAP-H*** and **2a** (E_{red} **2a**/**2a**$^{\bullet-}$ = −3.36 V) is endergonic (see Supporting Information). Then, we examined the generation of **DAP•** radical species by excitation of **DAP-H**. We hypothesized that visible light from the Kessil lamp could trigger a reductive dimerization of **DAP-H**. This was reported by Gudat using UV light.[27] The resulting **$(DAP)_2$** species, described as a weakly σ-bonded dimer, would dissociate in

solution to give the persistent radical **DAP•**.[28] Indeed, ^{31}P NMR analysis confirmed the formation of **$(DAP)_2$** from **DAP-H** upon irradiation by the Kessil lamp (Scheme 5). This evidence supports the proposed initiation of a radical chain process through **$(DAP)_2$**.

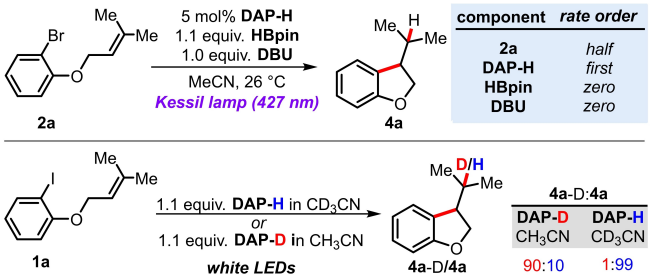
Next, we tested the influence of **$(DAP)_2$** on the cyclization reaction rate of **2a** with one equivalent of **DAP-H** in the dark. Notably, already 2 mol% of **$(DAP)_2$** remarkably accelerates the cyclization. This observation supports the outlined scenario II. Both findings led to the hypothesis that an exchange of the **SPO** catalyst by **$(DAP)_2$** would enable a *catalytic* process *without* visible light-promoted activation. Remarkably, 5 mol% **$(DAP)_2$** promoted a catalytic reaction in the absence of light forming **4a** in 70 % yield. Under irradiation, equimolar amounts of **DAP-H** afforded the cyclized product **4a** in comparably high yield. Under the exclusion of light, 10 mol% **DAP-H** was capable to generate **4a** in 27 % yield. Since the formation of **$(DAP)_2$** is not observed under these conditions,[29] the involvement of an alternative ionic pathway can be conceived. The conversion of **1a** to **4a** with stoichiometric amounts of **DAP-H** in the dark eventually supports this.

Initial-rate kinetic studies inferred a first-order dependence for **DAP-H** and a half order for substrate **2a**, supporting a radical chain mechanism (Scheme 6, see Supporting Information for details). The zeroth-order dependence of HBpin and DBU indicates that the regeneration of the **DAP-H** is not a turnover-limiting step. The reaction rates increase with the light intensity (see Supporting Information). Deuterium labelling studies with **1a** using **DAP-D** in CH_3CN or **DAP-H** in CD_3CN confirmed the origin of the hydrogen atom of **4a** from the catalyst.

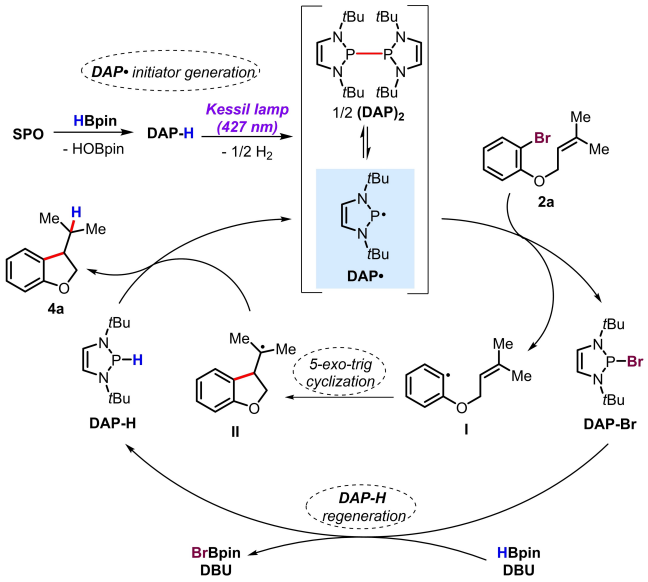
Taking all mechanistic experiments into account, we propose the following catalytic cycle (Scheme 7). With **SPO** as the pre-catalyst, the process is initiated by the reduction with HBpin forming **DAP-H**. Visible light irradiation converts **DAP-H** to **$(DAP)_2$**. The dissociation equilibrium of **$(DAP)_2$** into two molecules of **DAP•** initiates a radical chain process by bromine atom abstraction from **2a**.[30] The resulting aryl radical **I** adds across the C=C bond in a 5-*exo*-trig fashion forming radical species **II**. In turn, **II** abstracts the hydrogen atom from **DAP-H** delivering product **4a** and **DAP•**. Enabled by DBU, **DAP-Br** is converted back to **DAP-H** with HBpin. The use of **$(DAP)_2$** as catalyst allows entering the catalytic cycle bypassing the light activation step. However, the reduced yield of the **$(DAP)_2$**-catalyzed reaction in the dark indicates



Scheme 5. Illustration of the role of **$(DAP)_2$** in the **DAP**-catalyzed cyclizations.



Scheme 6. Initial-rate kinetics for the **DAP**-catalyzed cyclization and deuterium labelling studies.



Scheme 7. Proposed mechanism of the **DAP**-catalyzed cyclization of organohalides.

that light can heal the catalytic cycle by regenerating **DAP•** after radical chain terminations.

In summary, we developed a **DAP**-catalyzed reductive radical cyclization of organohalides. The **DAP** catalyst turnover was achieved by a DBU-assisted σ-bond metathesis between **DAP-X** (X = I, Br, Cl) and HBpin, which provided a fast regeneration of **DAP-H**. The transformation is significantly accelerated by the irradiation with visible light. The developed process allowed the efficient reductive cyclizations of a broad range of aryl and alkyl halides under mild and convenient conditions. Detailed mechanistic investigations revealed that visible light leads to the formation of **$(DAP)_2$** which is in equilibrium with **DAP•** and accelerates the cyclization. The direct use of **$(DAP)_2$** enabled a catalytic protocol in the absence of light. These findings will serve as blueprint and accelerator for the further developments of **DAP**-catalyzed radical processes.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: Cyclizations · Diazaphospholenes · Homogeneous Catalysis · Photocatalysis · Radical Reactions

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[29] We cannot completely exclude that the employed **DAP-H** contains very small amounts of **$(DAP)_2$**.
[30] An alternative mechanism involving SET from **DAP$^\bullet$** (E_{red} **DAP$^+$/DAP$^\bullet$** $= -1.76$ V) to **2a** (E_{red} **2a/2a$^{\bullet-}$** $= -3.36$ V) is thermodynamically prohibited (see Supporting Information).

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