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Photocatalytic Polyene Cyclization to Cyclopentyl Thioethers with Consecutive Quaternary Centers in Fluorinated Alcohols

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Abstract: The synthesis of carbocycles bearing consecutive all-carbon quaternary centers remains a formidable challenge in organic chemistry due to their steric congestion and synthetic inaccessibility. Herein, an efficient and sustainable photocatalytic strategy for the cyclization of polyenes to cyclopentane thioethers using 2,4,6-triphenylpyrylium tetrafluoroborate (TPT^+) as a photocatalyst in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) is reported. The transformation proceeds via a thiyl radical-initiated mechanism, forming multiple C_{sp^3}–C_{sp^3} bonds and quaternary centers in a single step under mild conditions. The method tolerates a broad range of aliphatic and functionalized thiols and exhibits high yields and good diastereoselectivities, the latter strongly depending on the addressed mechanism of the transformation. Mechanistic investigations support a radical pathway initiated by thiol oxidation. This work highlights the potential of combining photocatalysis with microstructured solvent systems to facilitate polyene cyclizations. Overall, it provides a versatile platform for synthesizing sterically congested, biologically relevant carbocyclic frameworks.

Keywords: 1,1,1,3,3,3-hexafluoroisopropanol, photoredox catalysis, polyene cyclization, quaternary center, thioethers

1. Introduction

The synthesis of highly substituted carbocyclic scaffolds with consecutive all-carbon quaternary centers is a pivotal area of research in organic chemistry due to the structural complexity and biological significance of these molecules.[1–3] The challenge in synthesizing these congested skeletons arises from their inherent ring strain and severe steric hindrance. It is particularly demanding when simultaneously introducing several quaternary carbon centers next to each other.[4] Therefore, straightforward and flexible strategies for synthesizing these sterically dense structures are highly desirable. Among such molecules, terpenes, like, e.g., presilphiperfolan-8-ol, cortisone, conidiogenone, and camphor (**Figure 1**a), stand out prominently. These natural products feature intricate polycyclic carbon skeletons, most commonly as saturated or unsaturated cyclopentanes and -hexanes, as well as combinations thereof. Notably, they are rare in reactive functional groups like carbonyls, alkenes, and alcohols. Yet, they are rich in all-carbon quaternary centers. These structural features make them challenging to access synthetically.

Such compounds are generated in nature by ring-closing cascades triggered by functionalizations of the head or tail of the linear polyene substrate, simultaneously forging multiple rings, including (quaternary) stereocenters (see Figure 1b). Our group recently reported on polyene cyclizations by harnessing catalytic, supramolecular F-alcohol-Lewis base networks as enzyme mimics. Using this concept, the selective and efficient consecutive formation of C_{sp3}–C_{sp3} carbon

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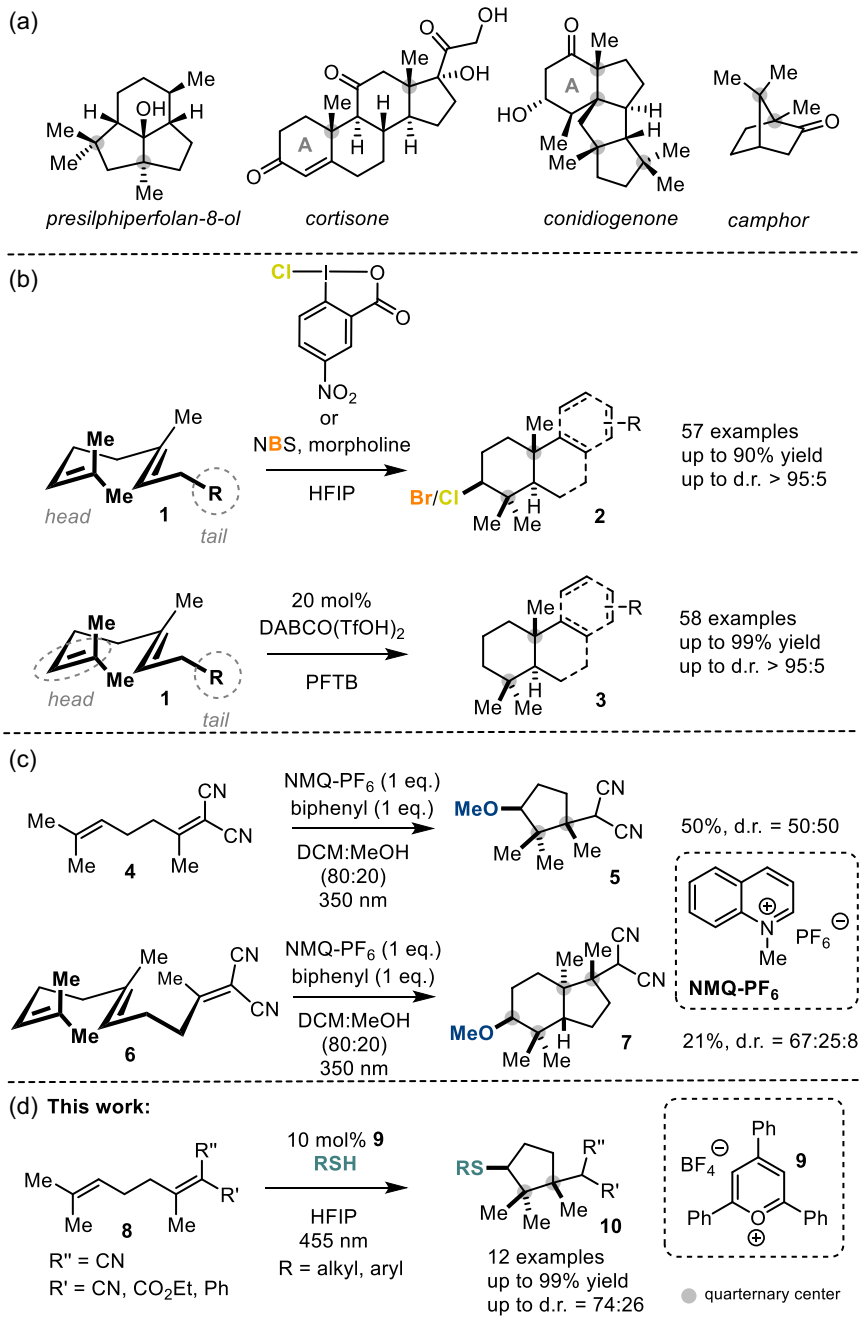

Figure 1. a) Examples of polycyclic terpenes exhibiting quaternary centers, b) electrophilic cation-π polyene cyclizations in F-alcohols,[2,3,11] and c) photoinduced polyene cyclizations by Demuth et al.[11] d) photocatalytic formations of 5-membered terpenoid-thioethers 10 with consecutive all-carbon quaternary centers.

bonds simultaneously building multiple quaternary centers upon either halogenation[5] or protonation[6] of the terminal alkene in **1** was achieved (Figure 1b). While the commonly addressed ionic carbocation-π ring closure gives rise mainly to six-membered rings,[4,7,8] radical cyclizations offer an interesting alternative as they easily forge five-membered carbocycles[9] In the late 1990s, Demuth and coworkers[10–14] demonstrated that terpenoids like **5** and **7** could be furnished by radical polyene cyclizations under irradiation with UV light using equimolar amounts of electron acceptor couples, such as *N*-methyl quinolinium salt (NMQ-PF_6) /biphenyl[11] (Figure 1c). Besides forming the cyclopentanyl moiety, a functional group, such as an alcohol or ether functionality, was simultaneously introduced. However, the yields, diastereoselectivities, and the addressable substrate scope were not satisfactory.[12,13]

In our continued effort to explore catalysis in confined space to target C_{sp3}-rich, cyclic molecular scaffolds, we set out to implement photocatalysis in terpene cyclizations

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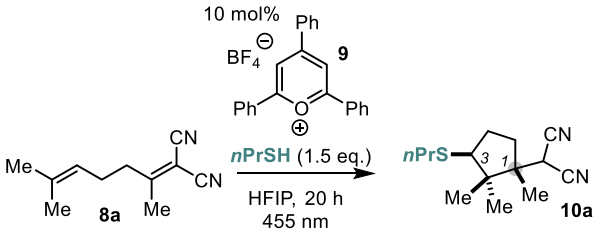
employing our microstructured *F*-alcohol-containing environments to expand our concept to cyclopentane scaffolds. Hereby, we started our investigations by using thiols as nucleophiles, giving access to the corresponding thioether products **10**. Sulfur-containing compounds are particularly interesting for pharmaceutical sciences, accounting for around 25% of the active pharmaceutical ingredients (APIs).[15–19] Thioethers often act as "prodrugs" to enhance membrane permeability, reduce toxicity, and facilitate site-specific targeting.[19] In addition, they are also common precursors for sulfone or sulfoxide pharmacophors. Given the versatility of thioethers, numerous methods for thioetherifications have been reported in the literature.[20–26] Still, these methods are unsuitable for accessing such sterically congested carbocycles **10** or involve complicated multistep endeavors. The cascade reactions reported here are a good way to improve the step economy for synthesizing such target structures.

2. Results and Discussion

Starting with Demuth's conditions using substrates **8a** and *n*PrSH as nucleophile, we drastically reduced the amount of photosensitizer NMQ^+/biphenyl (10 mol %/50 mol%) when conducting the reaction in HFIP (see Supporting Information (SI)). At the same time, the diastereoselectivity was slightly enhanced to 58:42 in favor of the *trans*-diastereomer **10a**. Encouraged by these results, we started screening different reaction conditions. First, we tested various photocatalysts in HFIP (see **Table 1**, entries 1–7) and irradiated the reaction mixture at different wavelengths depending on the absorption of the photocatalyst. The best results were obtained when 10 mol% 2,4,6-triphenylpyrylium tetrafluoroborate (TPT^+, **9**) was used with 1.5 eq. thiol. Product **10a** was obtained in almost quantitative yield and a diastereomeric ratio of 70:30, favoring the thermodynamically preferred *trans*-diastereomer (*C1*,*C3*). Changing the solvent to the nonfluorinated alcohol *i*-PrOH gave the thioether only in 24% yield and a d.r. = 64:36 (Table 1, entry 10). Interestingly, the corresponding *i*-Pr-ether was only observed in traces. While 2,2,2-trifluoroethanol (TFE) afforded **10a** in unsatisfying 81% yield and a d.r. = 65:35 (Table 1, entry 8), the perfluorinated *t*-butanol (PFTB) slightly increased the diastereoselectivity of **10a** (d.r. = 74:26, Table 1, entry 9), but extending the substrate scope was difficult using PFTB. In principle, other polar solvents, such as DCM or MeCN, also succeeded in cyclizing the polyene **8a**. However, these solvents were less effective in yield and/or diastereoselectivity for our model substrate **8a** (Table 1, entries 11 and 12), and severe problems arose during substrate scope extension. For example, no bicyclic product **10l** was obtained in DCM (cf. **Scheme 1**).

Table 1. Optimization of the photocatalytic cyclization of dicyano polyene 8a in the presence of *n*-propylthiol.



Entry[a]	Changes made to standard conditions	Yield [%][b]	d.r.[c]
1	None	99	70:30
2	Mes-Acr-Me^+	84	71:29
3	EY	77	66:34
4	XO	10	60:40
5	TXO	12	57:43
6	BP	22	55:45
7	DCN	20	55:45
8	TFE	81	65:35
9	PFTB	97	74:26
10	*i*PrOH	24	64:36
11	MeCN	78	64:36
12	DCM	81	70:30
13	No light	0	–
14	No catalyst	0	–
15	No thiol	0	–

[a] The reaction was performed with **8a** (100 µmol), 1-propanethiol (150 µmol), and TPT^+ (**9**, 10 mol%) in 1.00 mL HFIP at rt and irradiation with blue light (455 nm) overnight.

[b] Yields were determined by ^{1}H-NMR spectroscopy of the crude reaction mixture using 1,3,5-trimethoxybenzene as internal standard.

[c] The diastereomeric ratio (d.r.) was determined by ^{1}H-NMR spectroscopy of the crude reaction mixture. The given d.r.s refer to the configuration at the *C1* (highlighted in grey). Mes-Acr-Me^+ = 9-Mesityl-10-methylacridinium perchlorate; EY = eosin Y, XO = xanthone, TXO = thioxanthone, BP = benzophenone, DCN = naphthalene-1,4-dicarbonitrile.

Control experiments without light, thiol, or TPT^+ (**9**) yielded no **10a** (Table 1, entries 13–15).

With the optimum conditions in hand, we started to investigate the substrate scope of this transformation, first varying the structure of the mercaptans. Alkanethiols, such as *n*-PrSH, *i*-PrSH, *n*-BuSH, and even the sterically demanding adamantyl-SH, were all suitable for the photocatalytic polyene cyclization delivering the cyclopentanes **10a**–**10d** in almost quantitative yields (94–99%). The diastereomeric ratio of products **10a**–**10d** was not significantly affected by the bulkiness of the thiol rest and ranged between 64:36 and 73:27. Applying aromatic thiols was possible but gave the cyclopentanes **10e–10g** in slightly lower isolated yields and diastereomeric ratios. Surprisingly, only thiols equipped with slightly basic nitrogen atoms worked well under our reaction conditions. Using thiophenols

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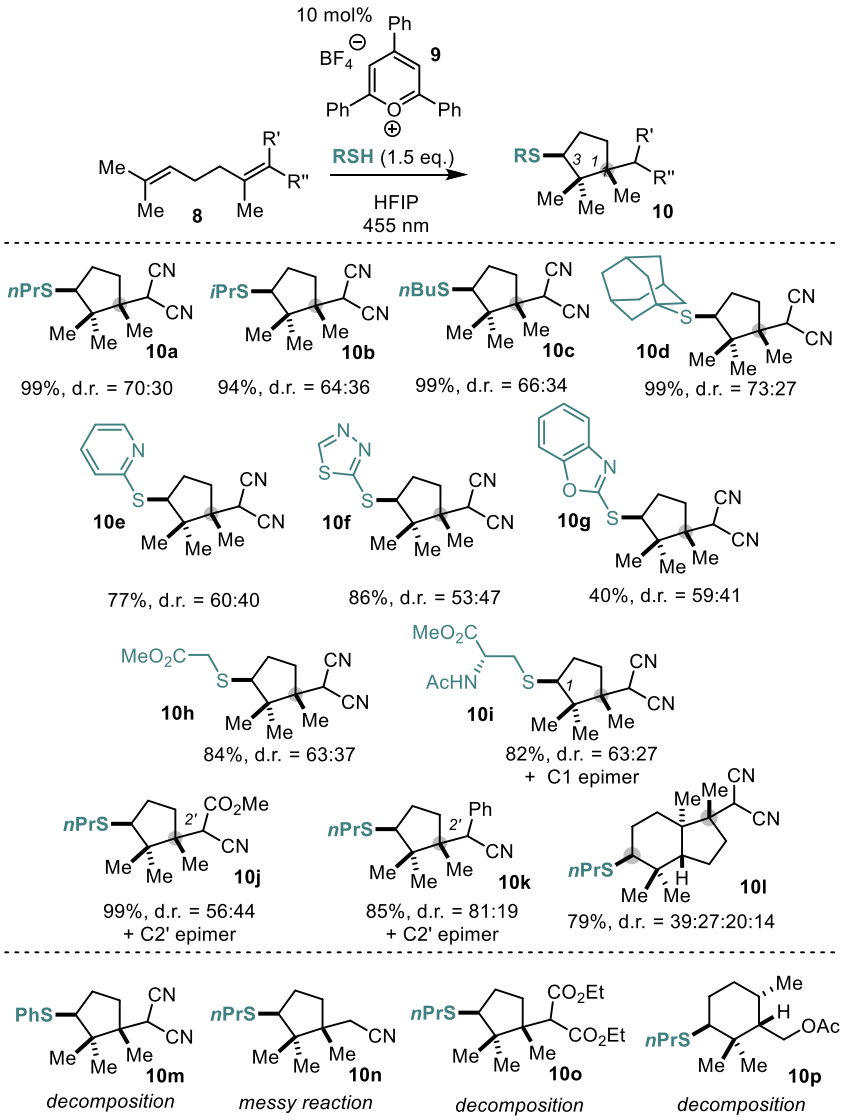

Scheme 1. Substrate scope for the photochemical terpenoid synthesis. All reactions were performed with **8** (100 µmol), thiol (150 µmol), and TPT^+ (10 mol%) in 1.00 mL HFIP at rt and irradiation with blue light (455 nm) overnight. The diastereomeric ratio (d.r.) was determined by ^{1}H-NMR spectroscopy of the crude reaction mixture. The given d.r.s refer to the *trans:cis* ration of *C1*:*C3* (highlighted in grey). All yields refer to isolated material.

(cf. Supporting Information), decomposition was observed with only traces of products, such as **10 m**, detectable by GC-MS. In the thiol moiety, functional groups, such as esters and amides, were tolerated under our optimized conditions (**10h** and **10i**). The reaction was susceptible to the substituents at the electron-poor alkene in **8**. Here, only disubstituted double bonds with at least one nitrile substituent present showed productive conversion (**10j** and **10k**; for more details, see Supporting Information). To our surprise, replacing one nitrile group with a phenyl substituent significantly impacts the diastereoselectivity of the cyclization, giving product **10k** with an increased d.r. of 81:19. Only decomposition was observed for the mononitrile substrate (→**10n**) and the malonic esters (→**10o**). These results were surprising as, at least for the diester substrates, a similar stabilization of the radical intermediate should occur as in the corresponding dicyano compounds. Extending the polyene chain was likewise possible, furnishing the 6,5-bicyclic products **10l** in 79%. Cyclohexyl derivatives, such as **10p**, were not accessible when applying our photocatalytic conditions, further hinting at a radical rather than an ionic cyclization pathway. This finding was corroborated by adding radical scavengers, such as 2,6-di-*tert*-butyl-4-methylphenol (BHT) or (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO). There, no product **10a** was formed.

With this straightforward access to cyclopentenyl thioethers **10** available, we next probed their synthetic utility. Therefore, an initial survey of subsequent reactions was exemplarily undertaken for substrate **10a**

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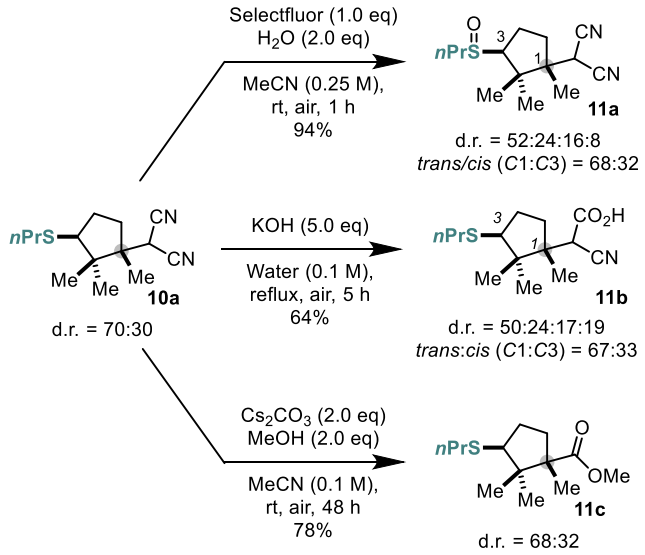
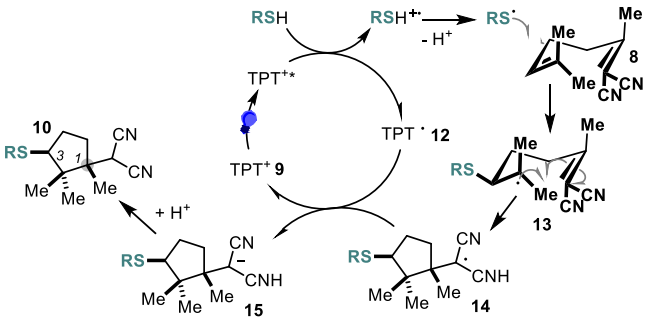


Scheme 2. Derivatization of sterically congested malononitrile **10a**.

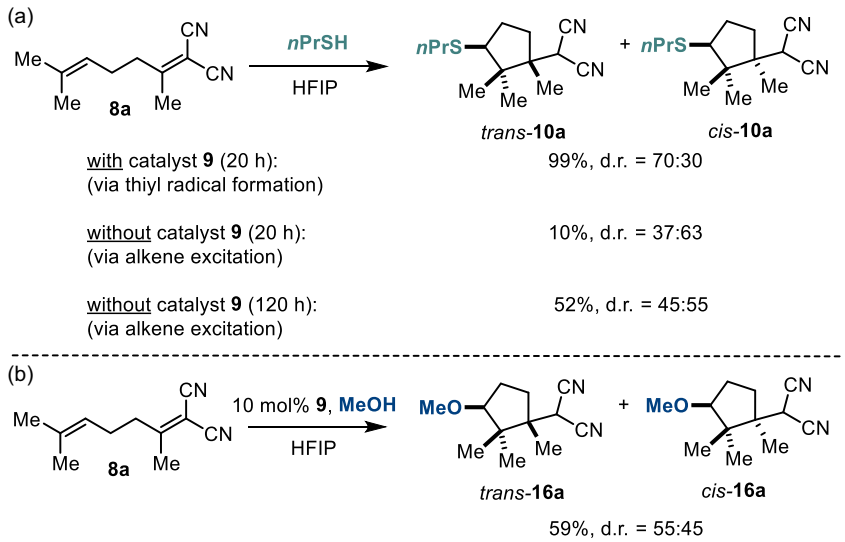


Scheme 3. Proposed mechanism of the photocatalytic polyene cyclization.

(**Scheme 2**). Oxidation of the thioether to the corresponding sulfoxide **11a** (94% yield) and hydrolysis of one nitrile moiety giving the cyano acid **11b** (64%) occurred smoothly. Under oxidative conditions,[27] the difficult-to-synthesize sterically congested methyl ester **11c** was formed in 78% yield. The reaction proceeds via an in situ-generated acyl cyanide that was converted to the methyl ester in the presence of methanol.

To elucidate the interplay of TPT^+ (**9**) and substrate **10a** with HFIP, respectively, NMR and UV/Vis experiments were conducted (cf. Supporting Information chapters 7 and 8). Thereby, a significant downfield shift of the OH proton in HFIP (2.89 ppm to 3.37 ppm), presenting as a doublet in the presence of **9**, was observed. In parallel, the protons of the pyrylium ring in **9** were shifted upfield. These findings hint at a strong H-bonding interaction between photocatalyst **9** and the F-alcohol. At the same time, substrate **10a** only weakly interacts with HFIP as the chemical shifts of the Michael system in **10a** only slightly deviated in the ^{13}C-NMR spectra measured upon the addition of HFIP.

Light-on/off experiments and a quantum yield of $\phi(455\ nm) = 0.04$ clearly identified the carbon cyclization as a light-dependent process disfavoring a radical chain mechanism. The excited state of TPT^+ **9** was quenched by both reaction partners, the alkene **8a** and *n*-PrSH (see Supporting Information). However, the Stern–Volmer fluorescence quenching studies[28,29] showed a faster reaction of the excited state $\mathbf{9}^*$ with the thiol than **8a** (see Supporting Information, chapter 9). Although TPT^+ **9a**[30,31] can oxidize the alkene **8a** and *n*-PrSH, thiol oxidation ($E_{1/2} = +1.21$ V vs. Fc/Fc^+ in HFIP) should be preferred over alkene **8a** oxidation ($E_{1/2} = +1.90$ V vs. Fc/Fc^+ in HFIP, see Supporting Information, chapter



Scheme 4. Impact of the reaction mechanism on the diastereoselectivity: a) direct excitation of **8a** versus photooxidation of *n*-PrSH and b) using MeOH as a nucleophile.

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9) due to their significant differences in their redox potentials.[32] These results suggest that in our case, the oxidation of the thiol by the photoexcited catalyst **9** is the reaction-initiating step (**Scheme 3**) rather than the PET process occurring at the *C*,*C*-double bond in **8a** as observed by Demuth et al. for their photochemically induced polyene cyclizations.[14,33–36] The thiyl radical then adds to the terminal double bond of substrate **8,** initiating a radical cyclization cascade that forges the carbocyclic framework **14**. Subsequent SET from the reduced $TPT^{\bullet}$ **12** to **14** simultaneously regenerates photocatalyst TPT^{+} (**9**) and the anion **15,** which delivers product **10** upon protonation.

To further prove this hypothesis, we conducted the reaction by irradiating the mixture at 365 nm without a photocatalyst. Only a direct excitation of the alkene **8a** in HFIP can occur at this wavelength as *n*-PrSH does not absorb according to the UV-Vis spectra. The transformation occurred slowly, giving rise to **10a** in 10% isolated yield employing our standard conditions (see Supporting Information, chapter 8). To our surprise, the diastereoselectivity of the thioetherification product **10a** was reversed entirely, with the kinetically favored *cis*-**10a** being now the major product after 20 h (d.r. = 37:63). This emphasizes that the mechanism of these transformations plays a vital role for diastereoselection. Extending the reaction, however, to 120 h resulted in an increased yield of **10a** (52%) but reduced diastereoselectivity of 45:55 (**Scheme 4**). These observations hint at a reversible process being operative when substrate **8a** is directly excited, leading to the enrichment of the thermodynamically favored product *trans*-**8a** over time. A similar behavior was observed when MeOH was used as the nucleophile. Here, only a PET from the excited TPT^{+} (**9**) to the polyene **10a** can occur under photocatalytic conditions. The corresponding methyl ether product **16a** was likewise isolated in low diastereoselectivities. In contrast, the thiyl radical-initiated photocatalytic polyene cyclization did not show any change in the diastereomeric ratio over time.

3. Conclusion and Outlook

We have developed a robust and efficient photocatalytic strategy for cyclizing linear polyenes **8** to access cyclopentane thioethers **10** bearing consecutive all-carbon quaternary centers. Utilizing 2,4,6-triphenylpyrylium tetrafluoroborate (TPT^{+}, **9**) as a photocatalyst in fluorinated alcohols, particularly HFIP, enabled high-yielding and diastereoselective transformations under mild conditions. The reaction proceeds via a thiyl radical-initiated mechanism, as evidenced by mechanistic studies, and thus contrasts with previously reported photoinduced electron transfer processes and offers improved control over product selectivity and substrate scope. Interestingly, the diastereoselectivity strongly depends on the mechanism of the radical cyclization. Furthermore, the synthetic utility of the resulting thioether products **10** was demonstrated through diverse downstream derivatizations.

This work is a step to broadening the chemical space by offering a green and versatile method to sterically congested 5-membered ring structures. Harnessing this methodology by including more diverse polyene architectures and nucleophiles may provide access to even more complex molecular frameworks with a high step economy. Overall, this study underscores the power of combining photocatalysis with microstructured solvent systems to mimic enzymatic environments, offering a promising platform for synthesizing architecturally sophisticated and biologically relevant molecules.

4. Experimental Section

General Procedure for the Cyclization of Linear Polyenes with Thiols: 3.95 mg (10 mol%, 10.0 µmol) TPT^{+} **9** was dissolved in 1.00 mL of HFIP. The corresponding linear polyene substrate **8** (100 µmol, 1.0 eq) and the thiol (150 µmol, 1.5 eq) were added at rt, and the mixture was irradiated with blue light (455 nm). The reaction was stirred until completion, monitored by TLC. Then, the solvent was removed under reduced pressure. The crude mixture was purified by column chromatography to obtain the corresponding product.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

All data relevent for this manuscript is reported in the Supporting Information.

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