



rearrangement that follows the initial *ortho* photocycloaddition. Although mechanistically complex, the predictable creation of three-dimensional structures from arene precursors in these cascade reactions is a concise and attractive pathway to achieve structural product diversity.

Despite their obvious utility, enantioselective versions of cascades that include a photochemical step have remained rare.<sup>7</sup> In this contribution, we describe a new photochemical cascade reaction which we successfully developed into an enantioselective transformation employing a chiral Lewis acid for chromophore activation.<sup>8</sup> The study was triggered by a serendipitous discovery which was made when examining intramolecular *ortho* photocycloaddition reactions to naphthalene and benzene. Since the reacting aldehydes displayed a binding site for chiral 1,3,2-oxazaborolidine Lewis acids, the latter catalyst class was chosen for the enantioselective variant.

## Results and discussion

In initial experiments, we examined the reactivity of 1-naphthaldehyde **7a** in the presence of Lewis acidic catalysts under visible light irradiation ( $\lambda = 457$  nm) at  $-78$  °C in  $\text{CH}_2\text{Cl}_2$  as the solvent of choice.<sup>8d,e</sup> While there was no reaction in the absence of acid, a new product was formed when  $\text{AlBr}_3$  was added, and benzoisochromene *rac-8a* with a rearranged carbon skeleton was isolated in a yield of 42% (Scheme 1, bottom). The outcome was unexpected and surprising. The formyl group had moved to the terminal position of the olefin whereas the alkoxyethyl group had migrated to the former C-1 carbon atom of the naphthalene. To understand the photophysical fundamentals of the reaction, the UV/vis spectrum of 1-naphthaldehyde **7a** (Fig. 1) was recorded in the absence and presence of a Lewis acid.

The spectrum revealed a strong absorption at  $\lambda = 248$  nm ( $\epsilon = 21\,100$  L mol<sup>-1</sup> cm<sup>-1</sup>), which is assigned to a  $\pi\pi^*$  transition. A weaker but broad absorption band was observed at longer wavelength with a maximum at  $\lambda = 321$  nm ( $\epsilon = 7100$  L mol<sup>-1</sup> cm<sup>-1</sup>). The band tails into the longer wavelength region of the spectrum (up to  $\lambda = 390$  nm) and is assigned to additional arene  $\pi\pi^*$  transitions ( $L_a$  and  $L_b$  band) overlapping with the  $n\pi^*$  transition of the carbonyl group.<sup>9,10</sup> Upon successive addition of  $\text{EtAlCl}_2$ , two absorption bands became visible with

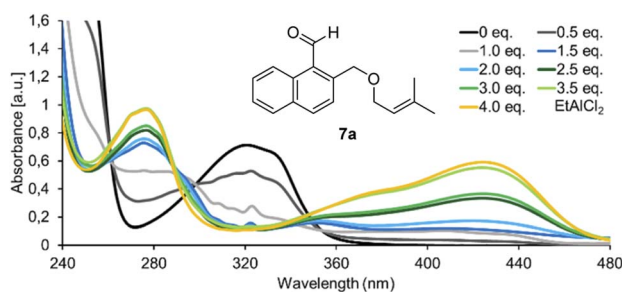
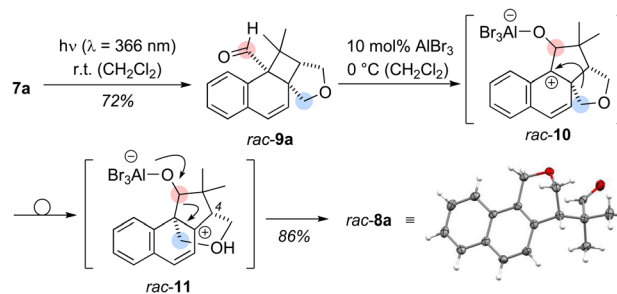


Fig. 1 UV/vis spectrum of 1-naphthaldehyde **7a** ( $c = 1.0$  mM in  $\text{CH}_2\text{Cl}_2$ , measured in a 1.0 mm quartz cuvette) in the presence of variable equivalents (eq.) of  $\text{EtAlCl}_2$ .



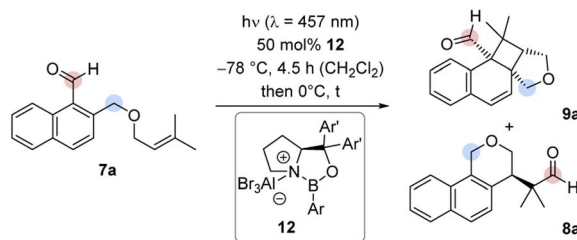
Scheme 2 *Ortho* photocycloaddition of 1-naphthaldehyde **7a** to cyclobutane *rac-9*, followed by the Lewis acid-catalysed rearrangement reaction to benzoisochromene *rac-8a*. The constitution of *rac-8a* was established by single crystal X-ray crystallography.

a maximum at  $\lambda = 277$  nm and  $\lambda = 424$  nm.<sup>11</sup> Upon addition of 4.0 eq. of  $\text{EtAlCl}_2$ , the absorption reached saturation indicating complete complexation of aldehyde **7a**. The extinction coefficients were determined as  $\epsilon = 9900$  L mol<sup>-1</sup> cm<sup>-1</sup> at  $\lambda = 277$  nm and  $\epsilon = 5800$  L mol<sup>-1</sup> cm<sup>-1</sup> at  $\lambda = 424$  nm. The latter absorption band seems responsible for the photochemical reactivity of **7a** observed in the presence of a Lewis acid because it overlaps with the emission spectrum of the light source.

Based on its UV/vis data, the reaction of aldehyde **7a** was examined at shorter wavelength without Lewis acid catalyst. Using an irradiation source with an emission maximum at  $\lambda = 366$  nm, full conversion of aldehyde **7a** was observed after five hours of irradiation at ambient temperature. Under these conditions, an exclusive *ortho* photocycloaddition<sup>12,13</sup> to the naphthalene C1/C2 bond occurred and cyclobutane *rac-9a* was formed in 72% yield (Scheme 2). A <sup>1</sup>H NMR spectrum of the crude product gave no indication for the formation of benzoisochromene *rac-8a*. However, the formation of product *rac-8a* from cyclobutane *rac-9a* was induced by the addition of either  $\text{AlBr}_3$  (10 mol%) or  $\text{EtAlCl}_2$  (10 mol%) yielding the rearranged product *rac-8a* in 86% or 81% yield. The structure of *rac-8a* was corroborated by single crystal X-ray crystallography.<sup>14</sup> Since benzoisochromene *rac-8a* was formed from cyclobutane *rac-9a* in a Lewis acid-catalysed rearrangement reaction, the sequence is likely initiated by Lewis acid coordination to the carbonyl oxygen atom of *rac-9a*. A 1,2-alkyl shift forms the benzylic cation *rac-10* which undergoes a second migration to cation *rac-11*.<sup>15</sup> Elimination of the Lewis acid and ring scission restores the aldehyde group and leads to re-aromatization in the final product of the cascade. All stereogenic centers are formed in the *ortho* photocycloaddition step and the stereogenic center at the C-4 carbon atom is preserved. It was therefore hypothesized that an enantioselective photocycloaddition step would lead to enantiomerically enriched rearrangement product and we envisioned 1-naphthaldehyde **7a** as a suitable substrate for chiral Lewis acid activation.<sup>16</sup>

Experiments with chiral  $\text{AlBr}_3$ -activated 1,3,2-oxazaborolidines<sup>8c,16,17</sup> commenced with the previously reported catalysts **12a** and **12b** in  $\text{CH}_2\text{Cl}_2$  under the conditions of the racemic reaction (Table 1, entries 1, 2). No conversion was observed. Catalyst **12c** bearing a 3-biphenyl group at the boron atom behaved similarly (entry 3). By switching the boron



**Table 1** Reaction optimisation for the catalytic, enantioselective cycloaddition/rearrangement cascade of 1-naphthaldehyde **7a** to benzoisochromene **8a**

Entry <sup>a</sup>	Lewis acid <b>12</b> <sup>b</sup>	<i>t</i> [h] at 0 °C	Yield <b>8a</b> + <b>9a</b> [%] (ratio) <sup>c</sup>	<i>ee</i> <b>8a</b> , ( <b>9a</b> ) [%] <sup>d</sup>
1	<b>12a</b>	— <sup>e</sup>	<10%	n.d.
2	<b>12b</b>	— <sup>e</sup>	<10%	n.d.
3	<b>12c</b>	— <sup>e</sup>	<10%	n.d.
4	<b>12d</b>	— <sup>e</sup>	88 (77 : 23)	89 (90)
5	<b>12e</b>	— <sup>e</sup>	90 (76 : 24)	37 (39)
6	<b>12f</b>	— <sup>e</sup>	87 (100 : 0)	54
7	<b>12g</b>	— <sup>e</sup>	86 (76 : 24)	65 (67)
8	<b>12d</b>	0.5	88 (100 : 0)	89

<sup>a</sup> The reactions were performed in CH<sub>2</sub>Cl<sub>2</sub> as the solvent with a substrate concentration of *c* = 20 mM. <sup>b</sup> **12a–12d**: Ar' = 3,5-dimethylphenyl; **12a**: Ar = 2,4,6-trifluorophenyl; **12b**: Ar = 2-(trifluoromethyl)phenyl; **12c**: Ar = 3-biphenyl; **12d**: Ar = 2,6-dimethylphenyl. **12e–12g**: Ar = 2,6-dimethylphenyl; **12e**: Ar' = 3',5'-dimethyl-2-biphenyl; **12f**: Ar' = 3,5-difluorophenyl; **12g**: Ar' = 2,3-dimethylphenyl. <sup>c</sup> Yield of isolated mixture **8a** and **9a**; the ratio was determined by <sup>1</sup>H NMR analysis of crude product. <sup>d</sup> The enantiomeric excess (*ee*) of **8a** and **9a** was determined by chiral-phase HPLC analysis. n.d. = not determined. <sup>e</sup> The reaction was quenched at –78 °C.

substituent to a 2,6-dimethylphenyl group (**12d**), full conversion was recorded after 4.5 h and the combined yield of products **8a** and **9a** was determined as 88% (entry 4). The enantiomeric excess (*ee*) of both products was high (89% and 90% *ee*). The influence of substituents Ar' at the prolinol was probed with catalysts **12e–12g** (entries 5–7). When catalyst **12e** with a bulky aryl group (Ar' = 3',5'-dimethyl-2-biphenyl) was applied, the starting material **7a** was fully converted and the yield of the products **8a** and **9a** was high (90%). However, the enantioface differentiation by the catalyst was poor (37% and 39% *ee*, entry 5). Likewise, catalysts **12f** (Ar' = 3,5-difluorophenyl) and **12g** (Ar' = 2,3-dimethylphenyl) gave a low enantioselectivity of 54% *ee* (entry 6) and 65% *ee* (67%, entry 7) but the yields were in both cases high. It appears as if the aromatic group Ar on the boron atom has a large influence on the reactivity while proper selection of Ar' is crucial for the enantioselectivity. Catalyst **12d** evolved from the screening experiments (for further information, see the ESI†) as the superior Lewis acid that promotes the reaction of **7a** to **8a/9a** with both high yield and enantioselectivity. Benzoisochromene **8a** could be obtained as a single product (88% yield, 89% *ee*), if the reaction mixture was warmed to 0 °C after irradiation and was subsequently stirred for 30 minutes at this temperature without irradiation (entry 8). Lower catalyst loadings led to a decrease in the enantioselectivity. With 25 mol% **12d**, the *ee* of product **8a** was only 83% *ee* and dropped to 73% *ee* at a catalyst loading of 10 mol%. It is likely that the high catalyst loading is required because the Lewis acid remains (partially) bound to the final product **8a** which also displays a Lewis-basic aldehyde functionality and

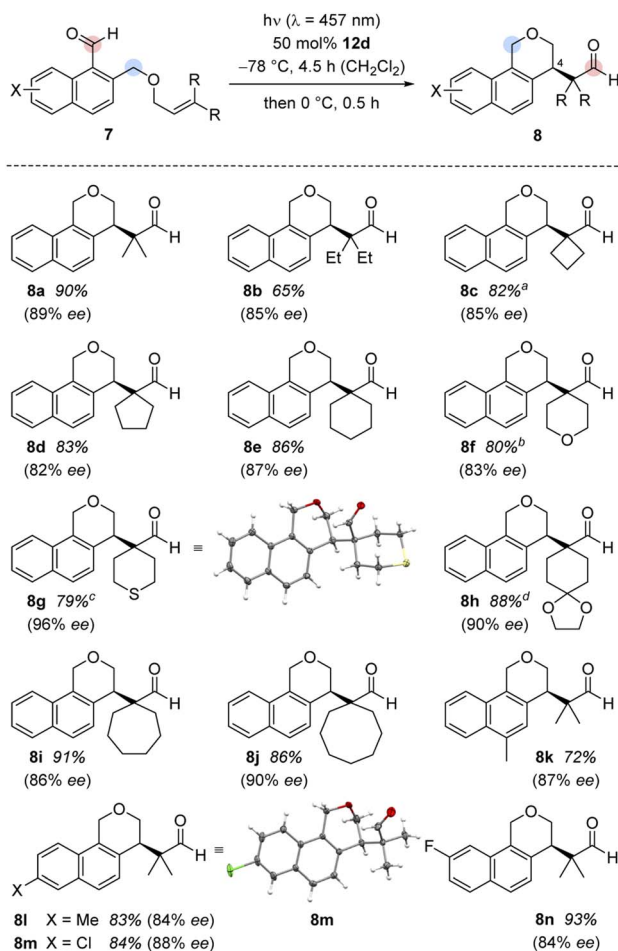
a tetrahydropyran ring. Dissociation of AlBr<sub>3</sub> may occur and initiate an unselective reaction.

It was possible to apply the method to a variety of substituted 1-naphthaldehydes **7** (Scheme 3). In a first set of experiments, 1-naphthaldehydes with different substituents on the terminal double bond were synthesized by a Williamson ether synthesis<sup>18</sup> between 1-bromo-2-(bromomethyl)naphthalene<sup>19</sup> and allylic alcohols followed by a formylation reaction<sup>20</sup> (see the ESI† for details). In addition to substrate **7a** with methyl groups at the terminal position, other alkyl groups in this position were tolerated and the cascade reaction proceeded smoothly with high enantioselectivity (products **8b–8e**).

Different heteroatoms within the cyclic substituents did not alter the consistently high enantioselectivity. Benzoisochromene with tetrahydro-2*H*-pyran, tetrahydro-2*H*-thiopyran, and 1,4-dioxaspiro[4.5]decane substituents (**8f–8h**) were isolated in high yields (79–88%) and excellent enantioselectivities (83–96% *ee*). The absolute configuration of benzoisochromene **8g** was determined by anomalous X-ray diffraction.<sup>21</sup> Substrates with larger alkyl rings (7- and 8-membered **7i** and **7j**) were converted to the respective products, again with high yield (91% and 86%) and in excellent optical purity (86% *ee* and 90% *ee*).

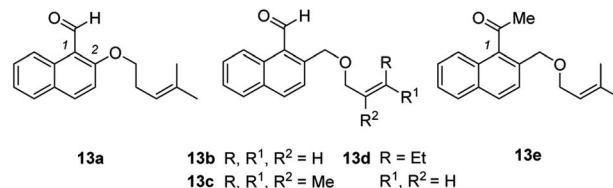
In a second set of experiments, the method was applied to 1-naphthaldehydes (**7k–7n**) with different substituents within the naphthalene core. The synthesis of these substrates started from 1-tetralones followed by a Vilsmeier-type  $\alpha$ -formylation reaction,<sup>22</sup> oxidative dehydrogenation,<sup>23</sup> reduction,<sup>24</sup> Williamson ether synthesis,<sup>18</sup> and aldehyde formation<sup>20</sup> (see the ESI† for details). While the substrates were not as





**Scheme 3** Enantioselective Lewis acid-catalysed cycloaddition/rearrangement cascade of 1-naphthaldehydes **7** to benzoisochromenes **8**. <sup>a</sup> The thermal rearrangement was performed at  $-78\text{ }^{\circ}\text{C}$  after irradiation. <sup>b</sup> The irradiation was performed for 16 hours at  $-78\text{ }^{\circ}\text{C}$ . <sup>c</sup> The irradiation was performed for 16 hours at  $-78\text{ }^{\circ}\text{C}$ . The reaction was stopped and the complete rearrangement was done by addition of  $\text{EtAlCl}_2$  (50 mol%) at  $0\text{ }^{\circ}\text{C}$  for 5 hours. <sup>d</sup> The irradiation was performed for twelve hours at  $-78\text{ }^{\circ}\text{C}$ .

straightforward to access, the enantioselectivities (84–88% *ee*) as well as the yields (72–93%) for their products **8k–8n** remained high. The chloro-substituted product **8m** gave suitable crystals for anomalous X-ray diffraction and the configuration at the newly formed stereogenic center could be assigned.<sup>25</sup> The absolute configuration was identical to the configuration previously established for **8g** and the configuration of the other major product enantiomers was based on analogy. Although the substrate scope is wide regarding substituents *R* (at the double bond) and *X* (at the arene), there are significant limitations. Fig. 2 summarizes substrates **13** which did not undergo the cascade reaction. The tether needs to be attached to the 2-position of the naphthalene *via* a  $\text{CH}_2\text{O}$  group. An O-alkyl tether (**13a**) was insufficient and the respective substrate did not undergo the reaction. Likewise, the intramolecular olefin component requires a specific substitution pattern. Only trisubstituted olefins underwent the reaction



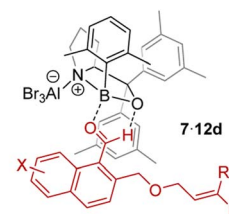
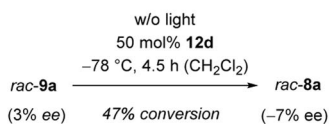
**Fig. 2** A selection of substrates (**13**) which did not show the desired reactivity under standard reaction conditions (see Scheme 3 and ESI†).

while mono- (**13b**), disubstituted (**13d**) or tetrasubstituted (**13c**) olefins did not react. Replacing the formyl group at C1 by an acetyl group led to a complex product mixture (**13e**).

In order to shed light on the reaction course, it was initially tested whether the chiral Lewis acid had any influence on the outcome of the rearrangement **9** → **8**. Although it was conceivable that a kinetic resolution<sup>26</sup> was partially responsible for the observed enantioselectivity, the rearrangement *rac-9a* → *rac-8a* performed in the presence of catalyst ruled out this option (Scheme 4). There was no enrichment of **8a** in the process. The reaction was stopped after several time periods and the substrate **9a** was always racemic (max. 3% *ee*). If at all, the Lewis acid led to a preferred formation of *ent-8a* with minimal *ee* (see the ESI† for details). After a conversion of 47% for example, there was an *ee* of 7%. Under the conditions of the reaction, *i.e.* after warming to  $0\text{ }^{\circ}\text{C}$ , the rearrangement went to completion and no *ee* was notable. It was thus clear that it is the *ortho* photocycloaddition which governs the enantioselectivity.

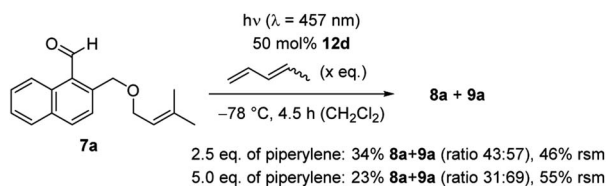
The explanation for the enantioface differentiation rests on the assumption that cationic oxazaborolidine-based Lewis acids bind to an aldehyde not only *via* the oxygen atom but that there is a second, non-classical hydrogen bond between the hydrogen atom of the aldehyde group and the oxygen atom of the 1,3,2-oxazaborolidine.<sup>17d,27</sup> For 1-naphthaldehydes **7**,<sup>28</sup> the respective complex **7·12d** is depicted in Scheme 4, whereby aldehyde **7** is in a locked conformation *via* a two-point interaction. One of the two enantiotopic faces of the arene is shielded by the 3,5-dimethylphenyl ring (in gray) of the proline-based backbone, which leads to a selective approach of the tethered olefin from the front face. The following rearrangement forms the

No kinetic resolution:



**Scheme 4** The *ortho* photocycloaddition step is responsible for the observed enantioselectivity in the reaction **7** → **8** as catalysed by Lewis acid **12d**: (Left) no kinetic resolution occurred in the Lewis acid-catalysed rearrangement of the *ortho* photocycloaddition product *rac-9a*. (Right) Model for association of Lewis acid **12d** to 1-naphthaldehydes **7** and for the enantioface differentiation in the *ortho* photocycloaddition step.





**Scheme 5** Qualitative triplet quenching experiments of the reaction **7a**  $\rightarrow$  **8a/9a** by addition of increasing amounts of piperylene. A qualitative decrease of yield is observed which suggests the intermediacy of triplet states (rsm = recovered starting material).

benzooisochromenes **8** with the depicted configuration at the future C-4 carbon atom (Scheme 2 and Table 1).

Further mechanistic studies to elucidate the pathway of the *ortho* photocycloaddition were conducted with 1-naphthaldehyde **7a** (Scheme 5). The enantioselective reaction was performed under optimized conditions without warming the reaction mixture. The reaction had previously led to complete conversion and products **8a/9a** were isolated in a yield of 88% (Table 1, entry 4). Upon addition of increasing amounts of the known triplet quencher piperylene,<sup>29</sup> the reaction slowed down notably. With 2.5 eq. of piperylene, the yield decreased to 34%, with 5.0 eq. of piperylene a further decrease to 23% was observed. Unreacted starting material **7a** was recovered in 46% and 55%, indicating that no side reactions occurred and that the reaction rate was reduced. In previous work, we had seen that piperylene does not affect photochemical reactions which are catalysed by  $\text{AlBr}_3$ -activated 1,3,2-oxazaborolidines and which occur on the singlet hypersurface.<sup>16f</sup> Against this background, the correlation between a higher quencher concentration with a lower reaction rate suggest that the *ortho* photocycloaddition occurs on the triplet hypersurface.

A triplet pathway is also in line with previous work performed on Lewis acid complexes of 1- and 2-naphthaldehyde.<sup>11c</sup> It had been found that olefins do not quench the fluorescent state of their 1 : 1 complexes with  $\text{EtAlCl}_2$  excluding a singlet reaction pathway from this state. Moreover, the  $\text{AlBr}_3$ -catalysed *ortho* photocycloaddition of 3-hexene to 2-naphthaldehyde had been shown to occur stereoconvergently, *i.e.* the same major cyclobutane diastereoisomer was formed irrespective of whether the (*E*)- or (*Z*)-isomer of 3-hexene was employed. The result rules out a concerted pathway on the singlet hypersurface which should be stereospecific and suggests a triplet reaction.

## Conclusions

In summary, we have discovered an enantioselective photocycloaddition/rearrangement cascade triggered by visible light and catalysed by chiral Lewis acid **12d**. The transformation enables the formation of structurally unique, polycyclic products and includes a photochemical de-aromatization followed by a thermal acid-catalysed rearrangement. Catalyst **12d** operates by a two-point interaction, whereupon the substrate is precisely oriented and fixed so that the attack can only occur from one of the two enantiotopic faces. The nature of this intermediate and its photophysical properties are currently

under investigation. Our results regarding an enantioselective, photochemically triggered cascade suggest the usefulness of this and related processes for synthetic applications and warrant further studies.

## Data availability

Original NMR datasets (FIDs) are available at Open Science Framework at <https://osf.io/mcvrm/>.

## Author contributions

S. S. and T. B. developed the project. Funding was acquired by T. B., S. S. designed and performed the synthetic experiments. C. J. performed the X-ray crystallographic analysis of compounds **8a**, **8g**, and **8m**. S. S. generated and validated the data. T. B. administered the project and supervised the research. S. S. and T. B. wrote, reviewed, and edited the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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