Formal [4 + 4]-, [4 + 3]-, and [4 + 2]-cycloaddition reactions of donor–acceptor cyclobutenes, cyclopropenes and siloxyalkynes induced by Brønsted acid catalysis†

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Brønsted acid catalyzed formal [4 + 4]-, [4 + 3]-, and [4 + 2]-cycloadditions of donor–acceptor cyclobutenes, cyclopropenes, and siloxyalkynes with benzopyrylium ions are reported. [4 + 2]-cyclization/deMayo-type ring-extension cascade processes produce highly functionalized benzocyclooctatrienes, benzocycloheptatrienes, and 2-naphthols in good to excellent yields and selectivities. Moreover, the optical purity of reactant donor–acceptor cyclobutenes is fully retained during the cascade. The 1,3-dicarbonyl product framework of the reaction products provides opportunities for salen-type ligand syntheses and the construction of fused pyrazoles and isoxazoles that reveal a novel rotamer-diastereoisomerism.

Medium-sized rings are the core skeletons of many natural products and bioactive molecules, and a growing number of strategies have been developed for their synthesis. Because of their enthalpic and entropic advantages, ring expansion is a highly efficient methodology for these constructions. For example, Sun and co-workers have developed acid promoted ring extensions of oxetanium and azetidinium species formed from siloxyalkynes with cyclic acetals and hemiaminals (Scheme 1a). Takasu and co-workers have reported an elegant ring expansion with a palladium(II) catalyzed 4π-electrocyclic ring-opening/Heck arylation cascade with fused cyclobutenes (Scheme 1b). Each transformation is initiated by the formation of fused bicyclic units followed by ring expansion or rearrangement to give medium-sized rings.

Strategies for the formation of fused bicyclic compounds rely on cycloaddition of dienes or dipoles with unsaturated cyclic compounds and, if the reactant cyclic compound is strained and chiral, the resulting bicyclic compound is activated toward ring opening that results in retention of chirality. We have recently reported access to donor–acceptor cycloalkenes by [3 + n] cycloaddition that have the prerequisites of unsaturated cyclic compounds suitable for cycloaddition. Donor–acceptor (D–A) cyclopropenes and cyclobutenes have sufficient strain in the resulting bicyclic compounds to undergo ring opening. We envision that the selection of a diene or dipolar reactant and suitable reaction conditions could realize cycloaddition and subsequent ring expansion. Benzopyrylium species, which are generated by metal or acid catalysis, have attracted our attention. We anticipated that their high reactivity would overcome the conventional unfavorable kinetic and/or

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Scheme 1 Cycloaddition/ring expansion background and this work.
thermodynamic factors that typically impede medium-sized ring formation. From a mechanistic perspective, benzopyrylium species are often formed by transition metal catalyzed reactions with 2-alkynylbenzaldehydes. Recently, the reaction between 1H-isochromene acetal and Bronsted acid catalyst forms the 2-benzopyrylium salts that could react with functional alkenes to give same cycloaddition products. Consequently, we believed that the [4 + 2]-cyclization between benzopyrylium species and donor–acceptor cyclobutenes, cyclopropenes, or siloxalkynes would give bridged oxetenium constructions.

Here we report bis(trifluoromethanesulfonylimide) (HNTf₂) catalyzed formal [4 + 4], [4 + 3] and [4 + 2]-cycloaddition reactions of D-A cyclobutenes, cyclopropenes, and siloxalkynes with benzopyrylium salts. Polysubstituted benzo-cyclooctatetraenes, benzo[cycloheptatrienes] and 2-naphthols, are produced in good to excellent yields and selectivities. Complete decomposition of 2-alkynylbenzaldehyde (Fig. 1-iv) or donor–acceptor functional groups facilitates deMayo-type ring-opening of the cyclobutane or cyclopropane skeletons (Scheme 1c).

Initially, we conducted transition metal catalyzed reactions with 2-alkynylbenzaldehyde intending to produce the corresponding benzopyrylium ion and explore the possibility of cycloaddition/ring opening with donor–acceptor cyclobutene 2a. Use of Ph₃PdCl/AgSbF₆, Pd(OAc)₂ and Cu(OTf)₂, which were efficient catalysts in previous transformations, gave only a trace amount of cycloaddition product (Fig. 1). Spectral analysis showed that mostly starting material remained (Fig. 1-i and ii). Increasing the reaction temperature led only to decomposition of 2-alkynylbenzaldehyde (Fig. 1-iv) or donor–acceptor cyclobutene 2a (Fig. 1-iv).

From these disappointments we turned our attention to 1H-isochromene acetal 1a as the benzopyrylium ion precursor. Various Lewis acid catalysts were employed with limited success, but we were pleased to observe the formation of the desired formal [4 + 4]-cycloaddition benzo[cyclooctatetraene] product 3aa, albeit in low yields (Table 1, entries 1–6). Selection of the Bronsted super acid HNTf₂ (ref. 14) proved to be the most promising, producing 3aa in 40% yield (Table 1, entry 7). Increasing the amount of D-A cyclobutene 2a by 30% gave a much higher yield of 3aa (Table 1, entry 8 vs. 7). Optimization of the stoichiometric reaction between 1a and 2a by increasing the reaction temperature from rt to 35 °C led to the formation of the desired product in 76% isolated yield (Table 1, entry 9 vs. 8). However, a further increase in the reaction temperature (Table 1, entry 10) or reducing the catalyst loading to 5 mol% did not improve the yield of 3aa (Table 1, entry 11).

With optimized conditions using 1a in hand, we examined the scope of the formal [4 + 4]-cycloaddition reactions of D-A cyclobutenes 2 with a diverse set of acetal compounds 1. As shown in Scheme 2, a wide range of acetal substrates (1a–1i) with different substituents at different positions all reacted

![Fig. 1 Reaction of 2-alkynylbenzaldehyde with donor–acceptor cyclobutene 2a.](image)

**Table 1** Optimization of reaction conditions

| Entry | Cat (10 mol%) | Temp. (°C) | Yieldb |
|-------|---------------|------------|---------|
| 1     | Sc(OTf)₂      | rt         | 23      |
| 2     | Yb(OTf)₂      | rt         | Trace   |
| 3     | In(OTf)₂      | rt         | 16      |
| 4     | TiCl₄         | rt         | Trace   |
| 5     | BF₃·OEt₂      | rt         | 20      |
| 6     | TMSOTf        | rt         | 17      |
| 7     | HNTf₂         | rt         | 40      |
| 8c    | HNTf₂         | 35         | 67      |
| 9d    | HNTf₂         | 35         | 78(76)d |
| 10f   | HNTf₂         | 60         | 62      |
| 11f   | HNTf₂         | 35         | 50      |

a Reactions were performed by adding the catalyst (10 mol%) to 1a (0.1 mmol) and 2a (0.1 mmol) in CH₂Cl₂ (2 mL) at the corresponding temperature for 24 h. Yields were determined by 1H NMR spectroscopic analysis with CH₂Br₂ as the internal standard. b 1.3 equiv. 2a was used. c Isolated yield. d Reaction performed at 60 °C for 12 h. e 5 mol% catalyst loading.

**Scheme 2** Scope of the [4 + 4]-cycloaddition reaction of D–A cyclobutenes and 1H-isochromene acetals. Reactions were performed by adding HNTf₂ (10 mol%) to 1 (0.1 mmol) and 2 (0.13 mmol) in CH₂Cl₂ (2 mL) at 35 °C for 24 h. Isolated yields are reported.
smoothly with D-A cyclobutene 2a to form the corresponding benzocyclooctatriene products 3 in good to excellent yields. Structural variations in the acetal produced only modest changes in product yields which ranged from 55 to 87%. Similarly, both electron-withdrawing and electron-donating substituents at the 4-position of the cyclobutene phenyl ring produced the corresponding products (3db-3dd) in good yields, and 2-naphthyl (2e) and 2-thiophenyl (2f) substituted cyclobutenes were suitable substrates (85% and 51% product yields, respectively). trans-1,2,3,4-Tetrasubstituted (R² = CH₃) 2-siloxy-cyclobutenecarboxylate 2g also underwent [4 + 4]-cycloaddition with 1d in good yield and fully retained its diastereoselectivity. The structure of 3fa was confirmed by X-ray diffraction (Scheme 2).

Chiral donor–acceptor cyclobutenes with high enantiomeric excess and diastereoselectivity are conveniently obtained by catalytic [3 + 1]-cycloaddition of enoldiazoacetates with acyl ylides of sulfur. To determine if optical purity is retained, chiral D-A cyclobutene 2a (80% ee) was reacted with 1d under the optimized conditions, and the corresponding benzocyclooctatriene product 3da was obtained in good yield with complete retention of configuration (Scheme 3, eqn (1)). With trans-disubstituted 2g and 2h that have higher optical purity, however, 3dg and 3dh were obtained in moderate yields with full retention of diastereo- and enantioselectivities, but addition products 8dg and 8dh were formed competitively (Scheme 3, eqn (2)). These compounds resulted from initial addition then desilylation, indicating that the [4 + 2]-cycloaddition is a stepwise reaction. Attempts to suppress the competing pathway by changing solvents or using the isopropyl acetal substrate to stabilize the incipient benzopyrylium ion gave higher selectivity (Scheme 3, eqn (3)).

To further expand the generality of this strategy, we investigated its use with donor–acceptor cyclopropenes 4. The desired formal [4 + 3]-cycloaddition products 5 were obtained in good to excellent yields (Scheme 4). Optimized conditions used 20 mol% HNTf₂ catalyst with 4 Å molecular sieves at room temperature for 2 h. The scope of this [4 + 3]-cycloaddition reaction with cyclopropenes 4 showed that acetals bearing both electron-donating and electron-withdrawing substituents on the aromatic ring were tolerated. However, as with [4 + 4]-cycloaddition reactions, the [4 + 3] reactions of 1 with R¹ = alkyl or H did not produce any of the desired products. Furthermore, 3-substituted cyclopropenes 4b–4d participated in this reaction, and their products (5ab–5ad) were obtained in 63%–81% yields.

Siloxyalkynes 6, as electron-rich alkenes, have been widely used in diverse cyclization reactions. We expected that 6 could also participate in [4 + 2]-cyclization/ring-expansion cascade processes, giving substituted 2-naphthol products. Interestingly, substituent controlled diverse products were obtained in good to excellent reactivity and selectivity (Scheme 5). Aryl (R¹) substituted acetals (1a-1d, 1f, 1h, 1i) reacted with siloxyalkynes 6a–6d, giving 2-naphthols (7aa–7ad and 7ba–7ia) in 35%–96% yields. With electron-donating group (EDG) substituents (7ba and 7ca) on the aromatic ring, higher reactivity was observed relative to those with electron-withdrawing groups (7da–7ia). In addition, the acetal with R¹ = H (1m) reacted with siloxyalkynes 6 to form the 2-naphthol-1-carboxaldehyde derivative in good yield, and the structure of 7ma was confirmed by X-ray diffraction (Scheme 5b).

Intriguingly, the n-buty1 (R¹) substituted acetal 1n reacted with siloxyalkynes via a [4 + 2]-cyclization with loss of methyl pentanoate (BuCO₂CH₃), affording siloxy naphthalenes 7na–7nd that are important precursors to the widely used axially chiral 2,2′-binol. The substrate scope of siloxyalkynes 6 for their formal [4 + 2]-cycloaddition reaction with n-butyl substituted acetal 1n was also explored (Scheme 5c). In all cases methyl pentanoate was eliminated to form 2,3-disubstituted naphthalene products (7na–7nd). Alkyl substituted siloxyalkynes (6a–6c) showed higher reactivity compared with phenyl substituted siloxyalkynes 6d. It should be mentioned that, recently, a similar transformation using BF₃·OEt₂ as catalyst or in excess (2 equiv.) with 2,4,6-collidine (1 equiv.) was reported.
and HNTf₂ was stated to be much less effective. To clarify this discrepancy, we carefully repeated these transformations (7ma and 7na) and found that all starting materials are completely consumed in less than 10 min to deliver [4 + 2]-cycloaddition products in good yields. Prolonging the reaction time to 12 hours, which was the reaction time used by the authors, results in their decomposition to a complex mixture of materials.

To illustrate the utility of this process, a large scale catalytic [4 + 4] cycloaddition was performed, and adduct 3da was obtained in 87% yield. Further transformations were conducted for the synthesis of pyrazole and isoxazole structures based on its 1,3-dicarbonyl skeleton (Fig. 2a). Compound 3da reacted with hydrazine and hydroxylamine in refluxed ethanol, affording pyrazole 14da and isoxazole 15da in 89% yield or 66% yield, respectively. The structure of 15da was confirmed by X-ray diffraction. Interestingly, two NMR distinguishable interconvertible diastereoisomers were detected for each of these eight-membered cyclic products (2.5 : 1 and 5 : 1 dr for 14da and 15da, respectively, in CDCl₃). These diastereoisomers are rotamers (for details, see ESI†) that exist at equilibrium with each other in solution but form one crystalline product (X-ray structure of 15da). In addition, the cycloaddition product 7ma reacted with chiral 1,2-cyclohexanediamine and 1,2-diphenylethylenediamine to give salen-type ligands L₁ and L₂ in 53% yield and 74% yield, respectively, which provides new opportunities for ligand screening (Fig. 2b).

Fig. 2 Large scale reaction, further transformations, and ligands synthesis.

In the mechanistic possibility considered for these HNTf₂ catalyzed cycloaddition reactions (Fig. 3), protonation of acetal 1 with HNTf₂ gives the corresponding highly reactive benzo-pyrylium intermediate int-I, which reacts with donor–acceptor cyclobutenes 2, cyclopropenes 4, or siloxylalkynes 6 affording addition intermediates int-II that undergo ring closure to int-III. Ring expansion then occurs to deliver 3, 5 and 7 in good to excellent yields with fully retained stereoselectivities. Furthermore, the formed TIPSNTf₂ ([4 + 4]- and [4 + 3]-cycloaddition) or HNTf₂ ([4 + 2] cycloaddition) are active acid catalysts for the conversion of 1 to benzopyrylium intermediate int-I that continues the catalytic cycle. With sterically larger D–A cyclobutenes or when a less ring-strained benzocyclopentene 12 is employed (for details, see ESI†), the competing direct desilylation of int-II occurs, delivering addition byproducts 8 or 13.

Compounds 7na–7nd arise from the analog to int-III from which ketene formation or methanol displacement effects 1,4-elimination.

Conclusions

In summary, we have realized formal [4 + 4], [4 + 3], and [4 + 2]-cycloaddition reactions of D–A cyclobutenes, cyclopropenes,
and silyloxyalkynes via Brønsted acid catalysis that are not feasible via the alternative metal catalysed process. The success of these transformations is attributed to the design of the [4 + 2]-cyclization/deMayo-type ring-expansion cascade processes in which various benzo[cyclo]octatetraenes, benzo[cyclo]heptatrienes and 2-naphthols are obtained in good to excellent yields and selectivities. In addition, the optical purity of the reactant donor–acceptor cyclobutenes is fully retained. The cycladdition products provide additional opportunities in salen-type ligand synthesis and heterocyclic synthesis exemplified by the formation of pyrazole and isoxazole products.

Conflicts of interest
There are no conflicts to declare.

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