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

Haifeng Zheng, Rui Wang, Kan Wang, Daniel Wherritt, Hadi Arman and Michael P. Doyle *

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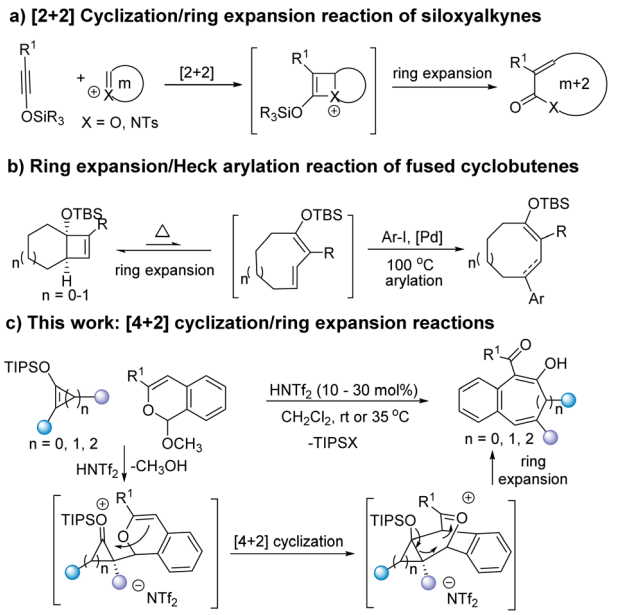
Brønsted acid catalyzed formal [4 + 4]-, [4 + 3]-, and [4 + 2]-cycloadditions of donor–acceptor cyclobutenes, cyclopropenes, and siloxyalkynes with benzopyrylium ions are reported. [4 + 2]-cyclization/deMayo-type ring-extension cascade processes produce highly functionalized benzocyclooctatrienes, benzocycloheptatrienes, 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,[1] and a growing number of strategies have been developed for their synthesis.[2] Because of their enthalpic and entropic advantages, ring expansion is a highly efficient methodology for these constructions.[3–6] For example, Sun and co-workers have developed acid promoted ring extensions of oxetenium and azetidinium species formed from siloxyalkynes with cyclic acetals and hemiaminals (Scheme 1a).[4] 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).[5] 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[7] 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.[8] Donor–acceptor (D–A) cyclopropenes[9] and cyclobutenes[10] 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,[11,12] 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



Scheme 1 Cycloaddition/ring expansion background and this work.

Department of Chemistry, The University of Texas at San Antonio, One UTSA Circle, San Antonio, TX 78249, USA. E-mail: michael.doyle@utsa.edu

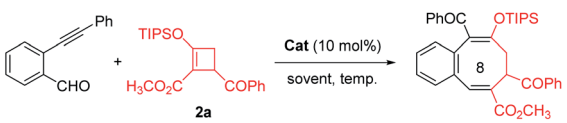
† Electronic supplementary information (ESI) available: General procedures, constraints for cycloaddition analytical and spectral characterizations, X-ray structures. CCDC 2009993 (**3fa**), 2024481 (**7ma**) and 2024482 (**15da**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1sc00158b

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.[11] Recently, the reaction between 1*H*-isochromene acetal and Brønsted acid catalyst forms the 2-benzopyrylium salts that could react with functional alkenes to give same cycloaddition products.[12] Consequently, we believed that the [4 + 2]-cyclization between benzopyrylium species and donor–acceptor cyclobutenes, cyclopropenes, or siloxyalkynes would give bridged oxetenium intermediates, which contain high strain energy that should provide the driving force for ring expansion. The "push and pull" electronic effect of donor–acceptor functional groups facilitates deMayo-type ring-opening of the cyclobutane or cyclopropane skeletons (Scheme 1c).[13]

Here we report bis(trifluoromethanesulfonyl)imide ($HNTf_2$) catalyzed formal [4 + 4]-, [4 + 3]- and [4 + 2]-cycloaddition reactions of D–A cyclobutenes, cyclopropenes, and siloxyalkynes with benzopyrylium salts. Polysubstituted benzocyclooctatrienes, benzocycloheptatrienes and 2-naphthols, are produced in good to excellent yields and selectivities. Complete retention of configuration occurs using chiral cyclobutenes, and opportunities for further functionalization are built into these constructions.

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 $Ph_3PAuCl/AgSbF_6$, $Pd(OAc)_2$ and $Cu(OTf)_2$, which were efficient catalysts in previous transformations,[11] 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).

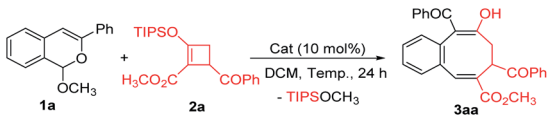
From these disappointments we turned our attention to 1*H*-isochromene acetal **1a** as the benzopyrylium ion precursor. Various Lewis acid catalysts were employed with limited success, but we were pleased to observe the formation of the desired formal [4 + 4]-cycloaddition benzocyclooctatriene product **3aa**, albeit in low yields (Table 1, entries 1–6). Selection of the Brønsted super acid $HNTf_2$ (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



(i) **Cat** = $Ph_3PAuCl/AgSbF_6$, CH_2Cl_2, rt, 48 h, <5% yield;
(ii) **Cat** = $Pd(OAc)_2$, CH_2Cl_2, rt, 48 h, <5% yield;
(iii) **Cat** = $Ph_3PAuCl/AgSbF_6$, THF, 80 °C, 12 h, <5% yield;
(iv) **Cat** = $Cu(OTf)_2$, THF, 80 °C, 12 h, <5% yield;

Fig. 1 Reaction of 2-alkynylbenzaldehyde with donor–acceptor cyclobutene **2a**.

Table 1 Optimization of reaction conditions[a]

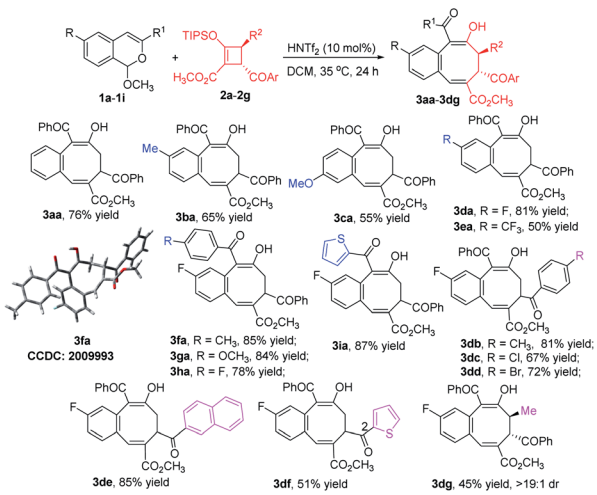


Entry	Cat (10 mol%)	Temp. (°C)	Yield[b]
1	$Sc(OTf)_3$	rt	23
2	$Yb(OTf)_3$	rt	Trace
3	$In(OTf)_3$	rt	16
4	$TiCl_4$	rt	Trace
5	$BF_3 \cdot OEt_2$	rt	20
6	TMSOTf	rt	17
7	$HNTf_2$	rt	40
8[c]	$HNTf_2$	rt	67
9[c]	$HNTf_2$	35	78(76)[d]
10[c,e]	$HNTf_2$	60	62
11[c,f]	$HNTf_2$	35	50

[a] Reactions were performed by adding the catalyst (10 mol%) to **1a** (0.1 mmol) and **2a** (0.1 mmol) in CH_2Cl_2 (2 mL) at the corresponding temperature for 24 h. [b] Yields were determined by ^1H NMR spectroscopic analysis with CH_2Br_2 as the internal standard. [c] 1.3 equiv. **2a** was used. [d] Isolated yield. [e] Reaction performed at 60 °C for 12 h. [f] 5 mol% catalyst loading.

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

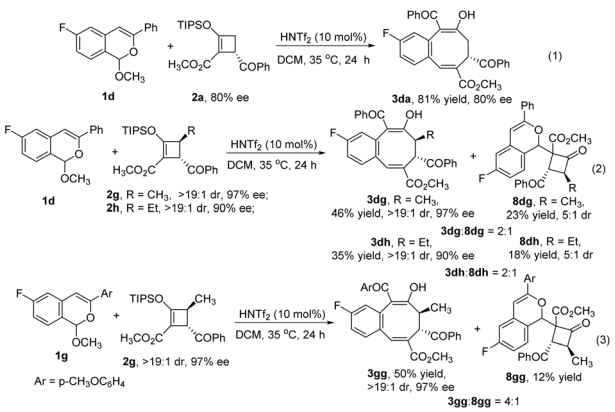


Scheme 2 Scope of the [4 + 4]-cycloaddition reaction of D–A cyclobutenes and 1*H*-isochromene acetals.[a] [a]Reactions were performed by adding $HNTf_2$ (10 mol%) to **1** (0.1 mmol) and **2** (0.13 mmol) in CH_2Cl_2 (2 mL) at 35 °C for 24 h. Isolated yields are reported.

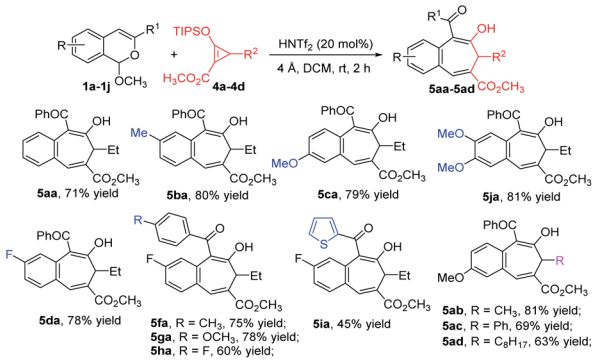
smoothly with D–A cyclobutene **2a** to form the corresponding benzocyclooctatriene products **3** in good to excellent yields. Structural variations in the acetals produced only modest changes in product yields which ranged from 55 to 87%. Similarly, both electron-withdrawing and electron-donating substituents at the 4-position of the cyclobutene phenyl ring produced the corresponding products (**3db–3dd**) in good yields, and 2-naphthyl (**2e**) and 2-thienyl (**2f**) substituted cyclobutenes were suitable substrates (85% and 51% product yields, respectively). *trans*-1,2,3,4-Tetrasubstituted ($R^2 = CH_3$) 2-siloxycyclobutenecarboxylate **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).[15]

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.[10] 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]-cyclization is a stepwise reaction. Attempts to suppress the competing pathway by changing solvents or using the isopropyl acetal substrate to form a bulky 2-propanol nucleophile (**1j**) failed (for details, see ESI†). However, *p*-methoxy (R^1) substituted **1g** that would stabilize the incipient benzopyrylium ion gave higher selectivity (4 : 1 *vs.* 2 : 1), and the desired [4 + 4] cycloaddition product **3gg** was isolated in 50% yield with 97% ee and >19 : 1 dr (Scheme 3, eqn (3)).

To further expand the generality of this strategy, we investigated its use with donor–acceptor cyclopropenes **4**. The desired



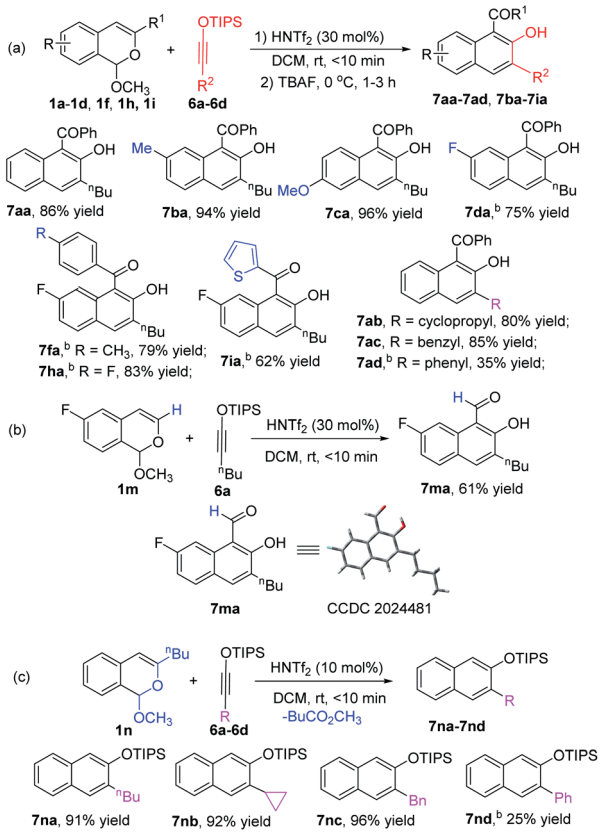
Scheme 3 Stereochemical features of the [4 + 4]-cycloaddition of D–A cyclobutenes and 1*H*-isochromene acetals.[a] [a]Reactions were performed by adding $HNTf_2$ (10 mol%) to **1** (0.1 mmol) and **2** (0.13 mmol) in CH_2Cl_2 (2 mL) at 35 °C for 24 h. Isolated yields are reported.



Scheme 4 Scope of the [4 + 3]-cycloaddition reaction of D–A cyclopropenes and 1*H*-isochromene acetals.[a] [a]Reactions were performed by adding $HNTf_2$ (20 mol%) to **1** (0.2 mmol), **4** (0.24 mmol) and 4 Å (50 mg) in CH_2Cl_2 (2 mL) at rt for 2 h. Isolated yields are reported.

formal [4 + 3]-cycloaddition products **5** were obtained in good to excellent yields (Scheme 4). Optimized conditions used 20 mol% $HNTf_2$ 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 R^1 = 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 alkynes, have been widely used in diverse cyclization reaction.[4,16] 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 (R^1) 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 R^1 = 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).[15] Intriguingly, the *n*-butyl (R^1) substituted acetal **1n** reacted with siloxyalkynes *via* a [4 + 2]-cyclization with loss of methyl pentanoate ($BuCO_2CH_3$), affording siloxy naphthalenes **7na–7nd** that are important precursors to the widely used axially chiral 2,2′-binols.[17] 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 $BF_3 \cdot OEt_2$ as catalyst or in excess (2 equiv.) with 2,4,6-collidine (1 equiv.) was reported,[18]



Scheme 5 Scope of the [4 + 2]-cycloaddition reaction of siloxyalkynes and 1*H*-isochromene acetals.[a] [a]Reactions were performed by adding $HNTf_2$ (10–30 mol%) to **1** (0.2 mmol) and **6** (0.3–0.4 mmol) in CH_2Cl_2 (2 mL) at rt for 10 min. Isolated yields are reported. [b]40 mol% $HNTf_2$ catalyst was used.

and $HNTf_2$ 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

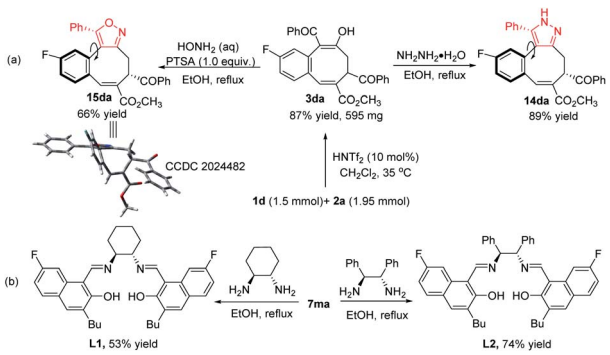


Fig. 2 Large scale reaction, further transformations, and ligands synthesis.

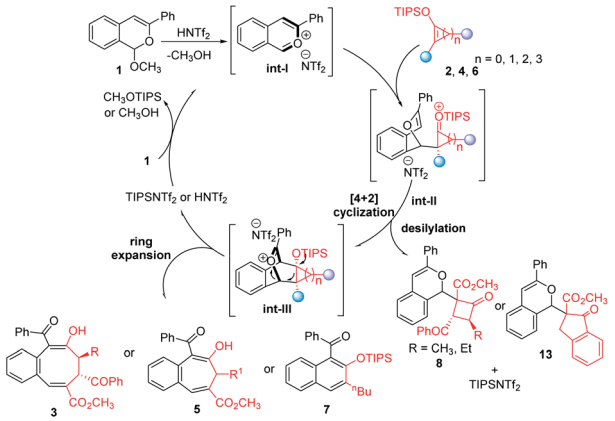


Fig. 3 Proposed mechanism.

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.[15] 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 $CDCl_3$). 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).[19]

In the mechanistic possibility considered for these $HNTf_2$ catalyzed cycloaddition reactions (Fig. 3), protonation of acetal **1** with $HNTf_2$ gives the corresponding highly reactive benzopyrylium intermediate **int-I**, which reacts with donor–acceptor cyclobutenes **2**, cyclopropenes **4**, or siloxyalkynes **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 $TIPSNTf_2$ ([4 + 4]- and [4 + 3]-cycloaddition) or $HNTf_2$ {[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 benzocyclooctatrienes, benzocycloheptatrienes 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 cycloaddition 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.

Acknowledgements

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