Stereoselective Diels-Alder Reactions of *gem*-Diborylalkenes: Toward the Synthesis of *gem*-Diboron-Based Polymers via ROMP

Nadim Eghbarieh,[1#] Nicole Hanania,[1#] Alon Zamir,[1,2] Molhm Nassir,[1] Tamar Stain,[1,2]* and Ahmad Masarwa[1]*

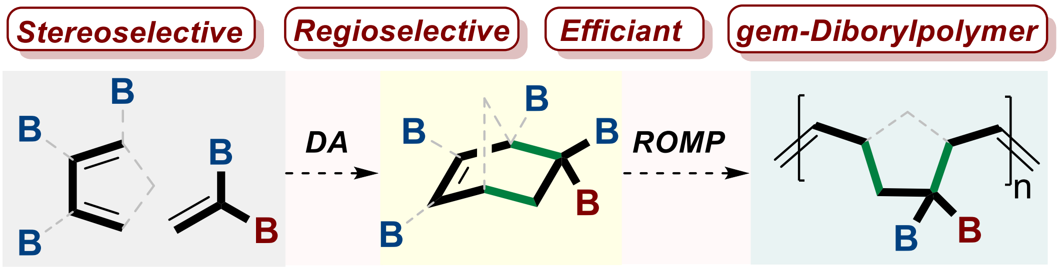
[1]Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 9190401 (Israel)

[2]Fritz Haber Center for Molecular Dynamics Research, Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 9190401 (Israel)

[#]These authors contributed equally to the work

*Corresponding authors: E-mail: tamar.stein@mail.huji.ac.il ; Ahmad.Masarwa1@mail.huji.ac.il

TOC:



Abstract:

Although *gem*-diborylalkenes are known to be among the most valuable reagents in modern organic synthesis, providing a rapid access to a wide array of transformations, including the construction of C−C and C-heteroatom bonds, their use as dienophile-reactive groups has been rare. Herein we report the Diels-Alder (DA) reaction of (unsymmetrical) *gem*-diborylalkenes. These reactions provide a general and efficient method for the stereoselective conversion of *gem*-diborylalkenes to rapidly access 1,1-bisborylcyclohexenes. Using the same DA reaction manifold with borylated-dienes and *gem*-diborylalkenes, we also developed a concise, highly regioselective synthesis of 1,1,2-tris- and 1,1,3,4-tetrakis(boronates)cyclohexenes, a family of compounds that currently lack efficient synthetic access. Furthermore, DFT calculations provided insight into the underlying factors that control the chemo-, regio, and stereoselectivity of these DA reactions. This method also provides stereodivergent syntheses of *gem*-diboryl-norbornenes. The utility of the *gem*-diboryl-norbornene building blocks was demonstrated by ring-opening metathesis polymerization (ROMP), providing a highly modular approach to the first synthesis of the *gem*-diboron-based polymers. Given its simplicity and versatility, we believe that this novel DA and ROMP approach holds great promise for organoboron synthesis as well as organoboron-based polymers and that it will result in more novel transformations in both academic and industrial research.

Over the years, generations of chemists have learned how to prepare new molecular structures, typically by the interconversion of functional groups. Since the end of the twentieth century, the scientific community has been witnessing the emergence of truly complementary trends in organic synthesis.[1] Driven by environmental and economic requirements, chemists have focused on the discovery and disclosure of new reactions that enable multi-direct derivations of organic molecules, for example, the new direct diversification of compounds containing the carbon–boron (C–B) bond, which has historically been considered as a fundamental tool in synthetic organic chemistry.[2]

Organoboron reagents have had an enormous impact on the development of new chemical reactions and have extended the scope of accessible complex molecular scaffolds.[3, 4] Organoboronate compounds are particularly attractive owing to their wide availability and air stability,[5] making them versatile reagents in organic synthesis.[6, 7]

Although many synthetic methods utilize transformations of C–B bonds,[2] the development of polyborylated reagents would enable greater structural diversity — an important objective.[8] Therefore, over the last decade, much effort has been expended to synthesize new functionalized classes of polyboronates, which have been shown to be excellent building blocks for the modular construction of new compounds.[9-12]

Among polyboron-containing structural motifs, (unsymmetrical)[13] *gem*-diboron derivatives (**2, 3'**) are a well-known emerging class with good potential for novel synthetic applications (Figure 1A).[14-17] The special properties and structures of bisnucleophile *gem*-diboryl compounds **2, 3'** (termed geminated organodimetallics)[18, 19] have attracted increasing attention from synthetic chemists, particularly in constructing C–C/ C–heteroatom bonds. In recent years, *gem*-diboryl compounds **2, 3'** have been widely adopted as coupling partners in synthetic chemistry.[11, 20]

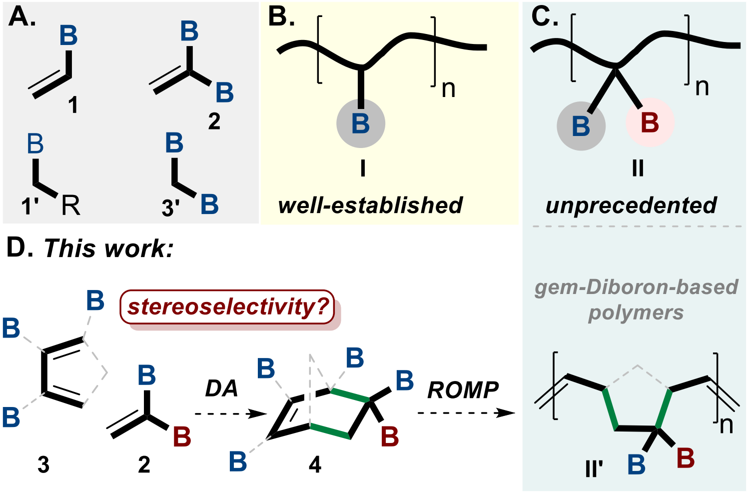


Figure 1 | General scheme of the work. A. Classifying of organoboron compounds. **B.** The well-known boron-based polymer **I**. **C.** The unprecedented *gem*-diboron based polymer **II**. **D.** General scheme of the Diels-Alder reaction of polyboronated compounds **3** with **2** and the application of their cycloaddition product **4** in the ROMP reaction to generate the *gem*-diborylpolymers **II'**. B = boron group.

Despite the fact that organoborons **1, 1'** (Figure 1A) have been applied in many fields including materials, polymers[21-24] **I** (Figure 1B), drugs, and in industry, *gem*-diboryl units **2**, **3'** have seldom been employed in these fields, e.g., polymer **II** (Figure 1C). To this end, we contend that a new paradigm of research is needed to complementarily propel this *gem*-diboryl class of compounds to reach the same application level as their mono-boron analogs.

As a part of a general program to investigate the reactivity and selectivity of *gem*-diboryl compounds in new synthetic applications, we sought to prepare variants bearing the *gem*-diboryl-norbornene group (**4**) because these strained compounds (~27 kcal/mol of inherent strain) might offer new opportunities toward the ROMP reaction[25] and lead to unprecedented *gem*-diboryl-based polymers **II'** (Figure 1D).

Results and discussions:

We posited that an efficient way to prepare *gem*-diboryl-norbornene structural motifs **4** would be through a [4+2] cycloaddition reaction of *gem*-diborylalkenes **2** with cyclopentadiene-CP **3**. Although the [4+2] cycloaddition reactions of vinylboranates,[26] e.g., **1**, are well documented in the literature (Figure 2A),[27-30] to the best of our knowledge, the use of *gem*-diboryllkenes (**2**) in these types of reactions is rare, despite the potential to provide new and efficient strategies to efficiently construct complex molecules (Figure 2B).[28, 30]

Recently, we reported a photoredox-mediated reaction of *gem*diborylalkenes[31] and showed that *gem*-diboryalkenes (**2**) are more electron deficient compared to vinyl-boron **1**;[31] hence, **2** should serve as a suitable dienophile for this type of cycloaddition reaction. However, key challenges include: (1) the steric repulsion introduced by the two groups of the bulky Bpin units in the TS of the cycloaddition reaction[32] (2) whether the regio- and stereoselectivity of the cycloaddition can be controlled when two unsymmetrical boron groups are placed on the geminated carbon of dienophile **2'**[13] (3) whether the reaction can proceed in a regioselective manner when borylated dienes react with **2** (Figure 2B)?[28]

To answer these questions, we first conducted computational studies on the DA reaction to predict whether *gem*-diborylalkenes (**2**) could be used as dienophile reactive partners for the DA reaction.[29, 33] According to our theoretical calculations of the energy profile of the cycloaddition reaction of diene-Cp **3e** with dienophiles **1**, **2** at room temperature-rt, the transition state of **gemBpinBpin-TS** is likely to be more energetically stabilized compared to vinyboronate TS's **Bpin-exo-TS** by 1.4 Kcal/mol.[30, 33, 34] This supports the fact that **2** is slightly more "dienophilic" toward the DA reaction than **1**, albeit more bulky (Figures 2C-D).

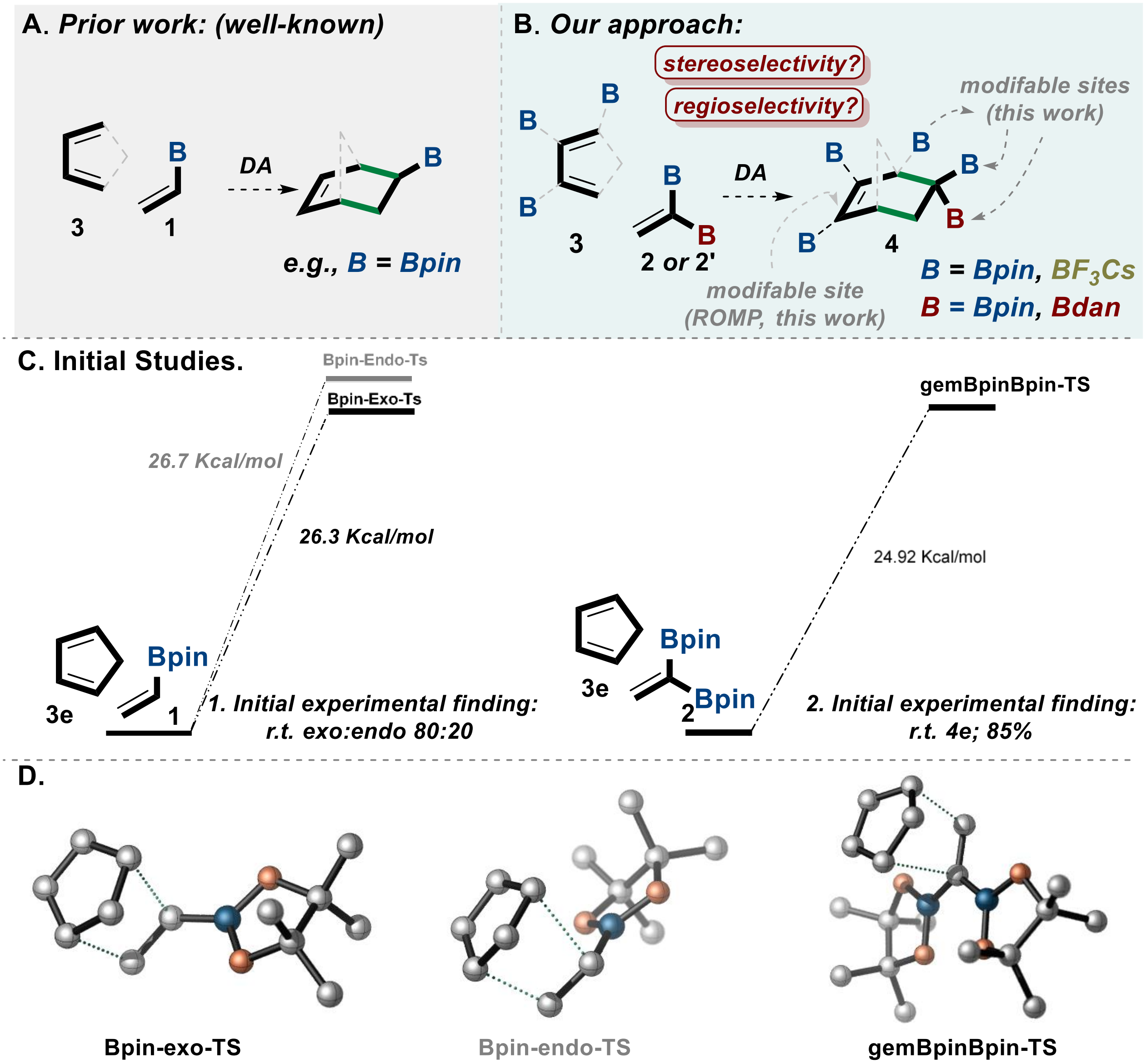


Figure 2 | Initial study and work plan. **A.** The well-known DA reaction using the vinylborantes **1** with diene **3. B.** A description of our DA reaction of polyboronated compounds**. C.** Theoretical investigations indicate that gem-diborylalkene **2** can undergo the DA reaction with diene **3e**. **D.** Cylview structures of the TSs of **Bpin-exo-TS**, **Bpin-endo-TS** and **gemBpinBpin-TS**, the calculations were performed with Gaussian 16 software using the M06-2X.[35] TS structures were visualized with: Legault, C. Y.CYLview.1.0b.[36] B = boron group, Bpin = pinacolato-boron, Bdan = B-1,8-diaminonaphthalene.

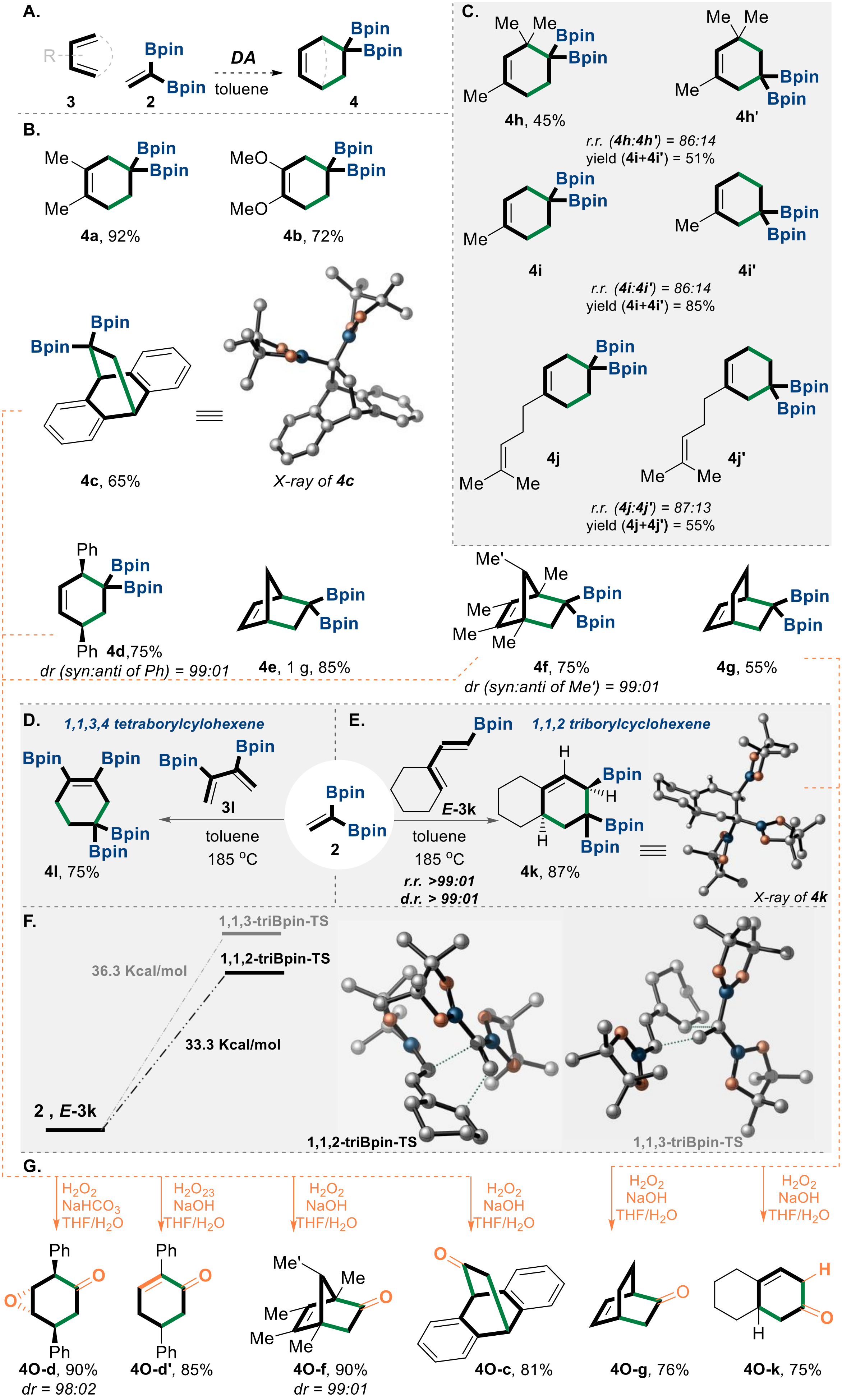
To investigate our proposed reaction, *gem*-diborylalkene (**2**), along with **3e**, was subjected to DA reaction conditions (Figures 2C-2, 3A-B). We obtained the desired *gem*-diborylated cycloaddition product **4e** in good yield at room temperature (rt) with toluene as solvent. Next, we investigated the scope of the DA using readily available *gem*-diborylalkene **2** and various diene substrates (**3**) bearing aliphatic, aromatic, and heteroatom substituents (Figure 3B). Generally, the products (**4a**–**g**) were isolated in good yields under the established optimal conditions. The reaction also proceeded in very good yield on a gram scale e.g., **4e**. The reaction works well with anthracene derivative **3c**, affording the *gem*-diborylcylic adduct **4c**, which was confirmed by X-ray crystallographic analysis (see the *CYLview* structure of **4c**, Figure 3B).

Using bulky dienes (i.e., pentamethylcyclopentadiene **3f**), along with adjusting the reaction temperature played a critical role in controlling diastereoselectivity (i.e., the *syn vs anti* outcomes on **4f**; Figure 3B). Whereas at a high temperature (185 ^{o}C) the reaction proceeds with moderate diastereoselectivity (d.r. = 83:17), at room temperature the reaction afforded the bis-borylated compound **4f** as the exclusive diastereoisomer (d.r. > 99:1).

The reaction also exhibits moderate regioselectivity when unsymmetrical dienes are used, giving the *para* adduct (**4h**–**4j**, Figure 3C). Notably, the constitutional isomers in **4(h, h')** and **4(i, i')** can be easily separated by column chromatography (Figure 3C, see SI).

Moreover, we examined the DA reaction of 1-boron-diene[28, 37] ***E*-3k** with *gem*-diborylalkene **2**, and surprisingly, the reaction generated the rare 1,1,2-triboryl cyclic adduct **4k** as the exclusive isomer with complete stereospecificity (Figure 3E).[12, 37, 38] We have obtained unambiguous support for the structures of **4k** using X-ray crystallographic analysis (see *CYLviews* in Figure 3E). Theoretical calculations indicate that the TS of the 1,1,2 triboryl constitutional isomer is favored by 3 Kcal/mol over the TS of 1,1,3 triboryl isomer (**1,1,2-triBpin-TS** *vs* **1,1,3 triBpin-Ts**; Figure 3F). Remarkably, the reaction of **2** with 3,4 diboryl diene **3l** can create the exceptional 1,1,3,4 tetraborylcyclohexene skeletal **4l** (Figure 3D).

Next, the polyborylated cycloadducts **4** were subjected to oxidation reactions using H_2O_2 (Figure 3G).[39] Oxygenated compounds **4O** were obtained in a chemoselective manner (Figure 3G). Thus, we have demonstrated that *gem*-diborylalkenes serve as ketene equivalents in [4+2] cycloadditions.[40] Of note, **4d** has been subjected to two oxidation reactions that lead chemoselectively to two different products **4O-d** and **4O-d'**. In **4O-d**, first the double bond was stereoselectively epoxidized and then the *gem*-di-Bpin unit underwent oxidization. However, in **4O-d'** the geminated-Bpin position first underwent oxidation and then the double bond isomerizes due to the deprotonation of the acidic benzylic, and allylic proton which is located α to the generated carbonyl (Figure 3G; see proposed mechanisms in SI). When triboryl compound **4k** was subjected to the oxidation conditions, ketone **4O-k** was selectively obtained, most likely resulting from oxidation of the *gem*-diboryl moiety to give a boron-enolate[41] which hydrolyzed in situ to finally give **4O-k** (Figure 3G; see proposed mechanisms in SI).


A.
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3
Bpin
Bpin
2
DA
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Bpin
Bpin
4
B.
Me
Me
Bpin
Bpin
4a, 92%
MeO
MeO
Bpin
Bpin
4b, 72%
Bpin
Bpin
4c, 65%
X-ray of 4c
Ph
Ph
Bpin
Bpin
4d,75%
dr (syn:anti of Ph) = 99:01
Bpin
Bpin
4e, 1 g, 85%
Me'
Me
Me
Me
Me
Bpin
Bpin
4f, 75%
dr (syn:anti of Me') = 99:01
Bpin
Bpin
4g, 55%
C.
Me Me
Me
Bpin
Bpin
4h, 45%
Me Me
Me
Bpin
Bpin
4h'
r.r. (4h:4h') = 86:14
yield (4i+4i') = 51%
Me
Bpin
Bpin
4i
Me
Bpin
Bpin
4i'
r.r. (4i:4i') = 86:14
yield (4i+4i') = 85%
Bpin
Bpin
Me
Me
4j
Bpin
Bpin
Me
Me
4j'
r.r. (4j:4j') = 87:13
yield (4j+4j') = 55%
D.
1,1,3,4 tetraborylcylohexene
Bpin
Bpin
Bpin
Bpin
4l, 75%
Bpin
Bpin
3l
toluene
185 °C
Bpin
Bpin
2
E.
Bpin
E-3k
toluene
185 °C
r.r. >99:01
d.r. > 99:01
1,1,2 triborylcyclohexene
H
H
H
Bpin
Bpin
Bpin
4k, 87%
X-ray of 4k
F.
1,1,3-triBpin-TS
1,1,2-triBpin-TS
36.3 Kcal/mol
33.3 Kcal/mol
2 , E-3k
1,1,2-triBpin-TS
1,1,3-triBpin-TS
G.
H_2O_2
$NaHCO_3$
THF/H_2O
H_2O_{23}
NaOH
THF/H_2O
H_2O_2
NaOH
THF/H_2O
H_2O_2
NaOH
THF/H_2O
H_2O_2
NaOH
THF/H_2O
H_2O_2
NaOH
THF/H_2O
Ph
O
O
Ph
4O-d, 90%
dr = 98:02
Ph
O
Ph
4O-d', 85%
Me'
Me
Me
Me
Me
O
4O-f, 90%
dr = 99:01
O
4O-c, 81%
O
4O-g, 76%
H
H
O
4O-k, 75%

Figure 3 | Diels-Alder reaction with 2. **A.** general reaction conditions of the DA with **2**. **B.** examples of the DA products as a result of reaction of **2** with symmetrical dienes. **C.** examples of the DA products as a result of a regioselective reaction of **2** with unsymmetrical dienes. **D.** preparation of the 1,1,3,4 tetraBpincyclohexene **4l** by the DA reaction of **2** with diene **3l**. **E.** regioselective preparation of the 1,1,2-triBpincyclohexene adduct **4k** by the stereospecific DA reaction of **2** with diene ***E*-3k**. **F.** Theoretical calculations for regionselective rational by the TSs of **1,1,2-triBpin-TS** and **1,1,3-triBpin-Ts**, the calculations were performed with guassian 16 software using the M06-2X.[35] **G.** examples of the utility of gem-diborylcyclohexenes **4** in the oxidation reactions that yields the ketone products **4O**. The relative structures of **4f** and **4O-d** have been confirmed by 2D-NMR NOESY. X-ray and TS structures were visualized with: Legault, C. Y. CYLview.1.0b.[36] *r.r. = regioisomeric ratio, dr = diastereomeric ratio, yields are isolated.* Bpin = pinacolato-boron.

Furthermore, we investigated the DA reaction using unsymmetrical 1,1bisdiboryalkenes (**2'** and **2-F**). It was anticipated that the cycloaddition might proceed with good stereoselectivity (Figure 4).[13] We were happy to discover that the reaction of 1,1 BpinBdan-ethene (**2'**) with dienes **3a**–**d** afforded the unsymmetrical *gem*-diborylalkane **5a**–**d** (confirmed by X-ray crystallographic analyses of **5a** and **5c**) in good yield (Figures 4A-B). High diastereoselectivity was observed in the reaction of **2'** with CP, affording cycloaddition product **5c** (*endo:exo* = 92:8). Our calculations indicate that the reaction favors the endo product **5c** with Ts-energies of **endo-BpinBdan-TS**, which is 2 Kcal /mol less than that of **exo-BpinBdan-TS** (Figure 4E).[21, 29, 33] This is in a good agreement with the fact that the aromatic-planar Bdan group is less bulky than the Bpin group.[13, 27, 32, 42] Therefore, it would appear that the diastereoselectivity in this case is driven primarily by sterics.

Moreover, the DA reaction of 1-boron-diene[28, 37] (***E*-3k**) with *gem*-diborylalkene **2'** generated regioselectively the separable diastereomers of 1,1,2-triboryl cyclic adduct with complete stereospecificity (**5k, 5k'**; Figure 4G).[37, 38] We have obtained unambiguous support for the structures of **5k'** using X-ray crystallographic analysis (see *CYLviews* in Figure 4G). Additionally, the reaction of **2'** with 3,4 diboryl diene **3l** yielded 1,1,3,4 tetraborylcyclohexene adduct **5l** (Figure 4F). These two different boron groups can provide the basis for selective C–B sequential functionalization, which in turn, reacts differently.[13, 43]

Unlike boronic-esters, for example, the Bpin and Bdan groups, mono-alkyl-trifluoroborate salts are known to be easily activated and to undergo rapid transmetalation with transition-metal complexes. In general, owing to their air, moisture, shelf, and thermal stability, as well as their occurrence as free-flowing crystalline solids, monotrifluoroborate salts have now become extremely popular reagents in synthesis. Thus, we attempted to use the *gem*-BpinBF$_3$K alkene **2-F** as a dienophile for the DA reaction. Unfortunately, the reaction did not afford the desired product (*gem*-diborylcyclohexen BF$_3$K containing **6**) and instead led to decomposition (Figure 4C). Alternatively, we sought to obtain product **6** using our recently reported conditions for late-stage trifluoroboration of *gem*-diborylalkenes by employing CsF (Figures 4C-D).[44] We were pleased to observe the desired mono-BF$_3$K products **6a-d** in a good yield (Figure 4D). Moreover, the reaction shows moderate diastereoselectivity in **6b** and **6d** when **4e** and **4f**, respectively, are used. The rationale of the diastereoselectivity is in good agreement with our reported mechanism that follows the likelihood that fluorination occurs from the less sterically encumbered face of norbornene **4e-f**, affording the *exo* disposed BF$_3$K group (**6b and 6d respectively**).[44]

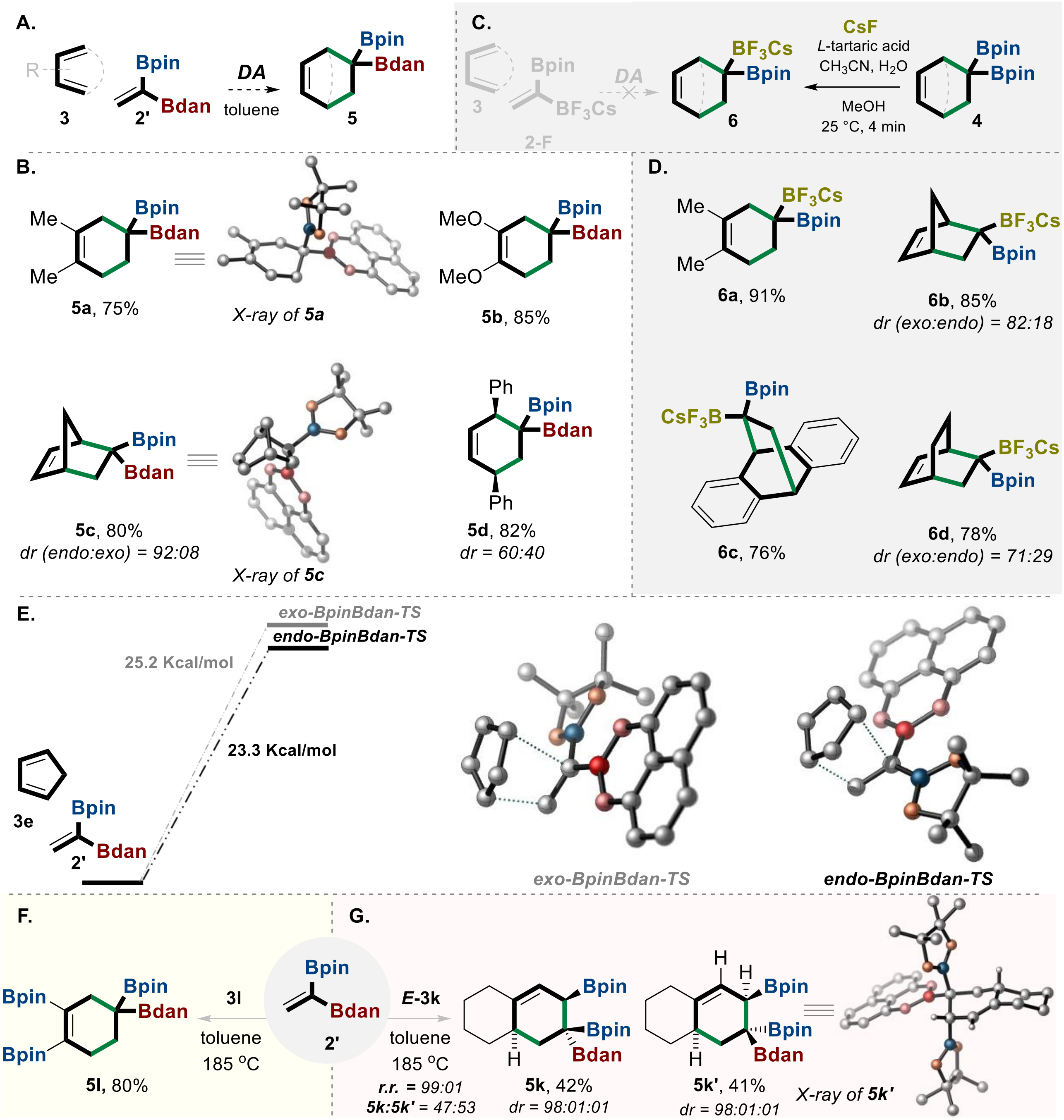


Figure 4 | Diels-Alder reaction with 2'. **A.** general reaction conditions of the DA with unsymmetrical *gem*-diborylalkene **2'**. **B.** examples of the DA products as a result of reaction of **2** with different dienes. **C.** general reaction conditions of the chemoselective trifluorination with *gem*diborylalkanes **4** as an alternative method for the unsuccessful direct DA of **2-F** with diene **3**. **D.** examples of the trifluorination products as a result of reaction of **2** with different dienes. **E.** Theoretical calculations of the TSs of ***exo-BpinBdanTS***, and ***endo-BpinBdan-Ts***, the calculations were performed with Gaussian 16 software using the M06-2X.[35] **F.** DA reaction of **2’** with diene **3l** leads to 1-Bdan-1,3,4 triBpin-cyclohexene **5l**. **G.** The stereospecific DA reaction of **2’** with diene ***E*-2K** leads regioselectively to diastereomers **5k** and **5k’**, the two 1,1,2-triboryl products were easily separated by column chromatography. The 1,2-regioselectivity manner has been determined by X-ray structure of **5k’**. The relative configuration of **6b**, **6d,** and **5k** has been confirmed by 2D-NMR NOESY. X-ray and TS structures were visualized with: Legault, C. Y.CYLview.1.0b.[36] *r.r. = regioisomeric ratio, dr = diastereomeric ratio, yields are isolated.* Bpin = pinacolato-boron, Bdan = B-1,8-diaminonaphthalene.

Next, we envisioned a stereodivergent synthesis of neroborene **5f** to involving controlling *exo* and *endo* norbornene structural motifs as illustrated in Figure 5. Toward this goal, cyclopentadienyl **3f** was reacted in two different scenarios. In path a (Figure 5): **3f** reacted with the unsymmetrical *gem*-diborylalkene **2’** to form only the cycloaddition product **5f-*endo*** (confirmed by an X-ray) in 85% yield. In path b (Figure 5): **3f** was first reacted with the symmetrical *gem*-BpinBpinalkene **2** to yield **4f** as a single diastereomer, which was then subjected to a diastereoselective trifluoroboration favoring the less sterically hindered face of the norbornene (denoted by arrows in **4f)** to afford **6f** in high diastereoselectivity (92:8; yellow box, Figure 5).[44] Finally, the BF_3Cs group was converted to the Bdan group to afford the **5f-*exo*** product (pink box, Figure 5).[44] Overall, our method serves as a powerful tool for the diastereocontrolled synthesis of norbornene motifs.

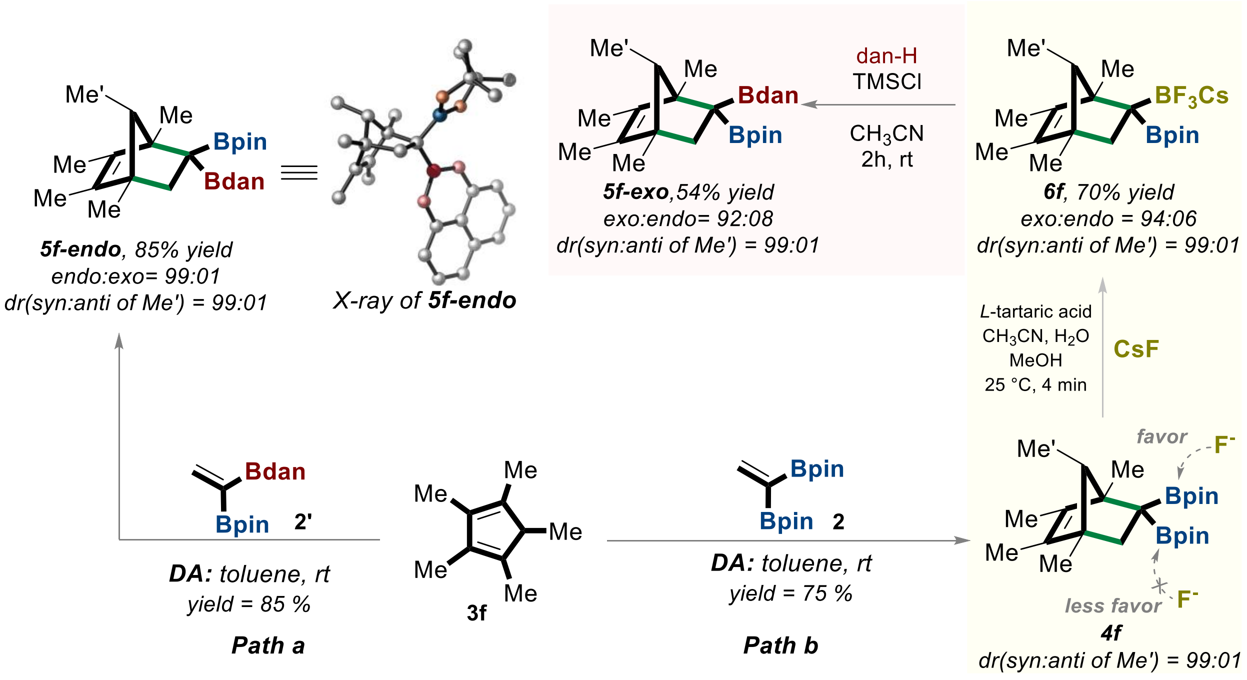


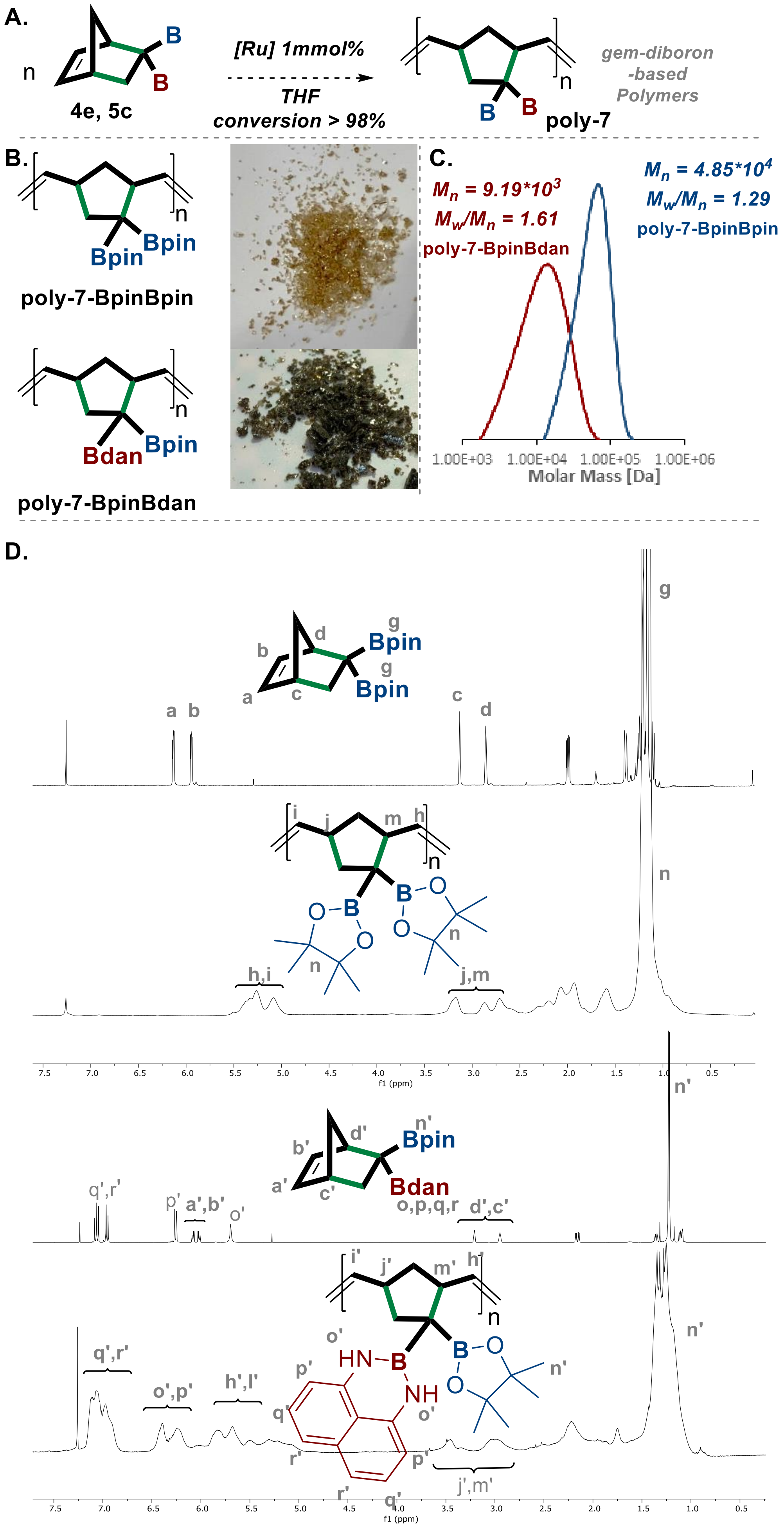
Figure 5 | Stereodivergent synthesis of norbornene-5f. **Path a:** Norbornene diastereomer **5f-endo** was stereoselectivity synthesized in one step from DA reaction of cyclopentadiene **3f** with the unsymmetrical *gem*-diborylalkene **2’**. The relative configuration of **5f-endo** was determined using x-ray crystallography (see Cylview structure of **5f-endo**). Path b: **5f-exo** was synthesized in three steps. Step 1: the diastereoselective DA reaction of **3f** with gem-diborolalkene **2** which leads to norbornene **4f**. Step 2 (yellow box): stereoselective triflourination of norbornene **4f** from the less hindered *si-face* leading to the exo product **6f**. Step 3 (pink box): the *gem*-diborylnorbornene-BF_3Cs **6f** was directly converted to unsymmetrical *gem*-Bpin Bdan-norbornene **5f-exo** in stereospecific manner. X-ray structures were visualized with: Legault, C. Y. CYLview.1.0b.[36] *dr = diastereomeric* *ratio, yields are isolated.* Bpin = pinacolato-boron, Bdan = B-1,8-diaminonaphthalene*.*

With these valuable *gem*-diborylcyclohexenes in hand, e.g., *gem*-diborylnoroborenes, we sought to demonstrate their synthetic utility in selective transformations of the double bond through the ROMP reaction, as depicted in Figure 6A to generate the novel *gem*-diborylalkene-based polymers (Figure 6).

Organoboron polymers have attracted widespread attention, since they provide unique properties for catalysis, sensing, luminescent materials, and biomedical applications.[23, 24] Among them, polymers with pendant boronic acids/esters account for the majority, since boronic acids/esters could serve as responsive sites of sensitive materials or dynamic crosslinking points of self-assembled polymers and self-healing materials.[23, 24]

Moreover, the presence of the boron moiety on the polymer offers a great opportunity for post-polymerization modifications to achieve new functional groups that are difficult to achieve in regular polymerizations.[21, 22] Although polymers which contain mono-boron units have been widely used,[24] their *gem*-diboryl analogs have not been investigated; thus, they can provide a new array of polymer properties to forge a wider diversity of *gem*-diboron-based polymers. Thus, *gem*-diborylnorbornenes hold great promise to serve as a monomer for ROMP[25] reactions that form polymers containing *gem*-diboryl units (Figure 6A).

We subjected norbornenes **4e** and **5c** to ROMP[25] polymerization reaction conditions using 1 mmol % of the [Ru] Grubbs' second-generation catalyst and THF as a solvent.[45] We were gratified to observe that *gem*-diborylnoroborenes **4e** and **5c** selectively polymerized to afford, for the first time, *gem*diboron-based polymers **poly-7-BpinBpin** and **poly-7-BpinBdan**, respectively, in high conversions (Figure 6B). This transformation was followed by ^{1}H-NMR spectroscopy of both monomers **4e** and **5c,** and their corresponding polymers **poly-7-BpinBpin** and **poly-7-BpinBdan**, respectively, as depicted in Figure 6D.[22] The resulting polymer, **poly-7-BpinBpin**, was observed as a light yellowish color; it has a high molecular weight (MW = $4.85*10^4$) and polydispersity indexes (PDI) of Mw/Mn = 1.29, based on gel permeation chromatography (GPC) (Figures 6B-C). Furthermore, the polymer **poly-7-BpinBdan** was dark-green and has a lower molecular weight (MW = $9.19*10^3$) and a higher PDI of Mw/Mn = 1.61 (Figures 6B-C).[21, 22, 25, 34]


A.
n
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4e, 5c
[Ru] 1mmol%
THF
conversion > 98%
n
B
B
poly-7
gem-diboron
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Polymers
B.
n
Bpin
Bpin
poly-7-BpinBpin
n
Bdan
Bpin
poly-7-BpinBdan
C.
Mn = 9.19*10^3
Mw/Mn = 1.61
poly-7-BpinBdan
Mn = 4.85*10^4
Mw/Mn = 1.29
poly-7-BpinBpin
1.00E+03
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Molar Mass [Da]
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7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
n'
b'
d'
n'
Bpin
a'
c'
Bdan
q',r'
p'
a',b'
o'
o,p,q,r
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q'
q',r'
o',p'
h',l'
j',m'
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

Figure 6 | Synthesis of *gem*-diboron-based polymers. **A.** a general scheme of the catalyzed Ru ROMP of norbornenes **4e** and **5c** to yield polymers **poly-7-BpinBpin** and **poly-7-BpinBdan** with > 98% conversion. **B.** The obtained polymers. **C.** Polydispersity indexes (PDI) gel permeation chromatography (GPC) of both polymers. **D.** HNMR spectra compression and characterization of the monomers **4e** and **5c** with polymers **poly-7-BpinBpin** and **poly-7-BpinBdan** respectively. [Ru] = Grubbs' second-generation catalyst. Bpin = pinacolato-boron, Bdan = B-1,8-diaminonaphthalene.

Summary

In conclusion, we have developed a method that addresses the long-standing challenge of regio- and stereoselective Diels-Alder cycloadditions with poly-alkenylboranes. This was achieved by introducing a new method that enables the use of (unsymmetrical) *gem*-diborylalkenes as a reasonable reactive dienophile for the DA reaction. The products of these reactions enable the formal synthesis of polyborylated-cycloadducts, particularly the 1,1,2 tri- and 1,1,3,4 tetraborylcyclic adduct, which would be difficult to accomplish with the existing strategies. In addition, the reaction offers the stereodivergent synthesis of norbornenes by using a diastereoselective trifluorination reaction. We demonstrate the use of the *gem*-diboryllkenes as ketene equivalents in [4+2] cycloadditions. We utilized *gem*-diborylnorbornene in the synthesis, for the first time, of *gem*-diboryl-based polymers through ROMP. Studies to achieve an enantioselective DA transformation using chiral *gem*-diborylalkenes[27] as well as new post-polymerization transformations of *gem*-diborylcycloalkene-based polymers are currently under investigation and will be reported in due course.

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Author contributions

A.M. had the idea for and directed the project, and wrote the manuscript with feedback from the co-authors. N.E., N.H., M.N., and A.M. planned, conducted, and analyzed experiments. N.E. and N.H. contributed equally to the work. T.S. and A.Z. conducted the theoretical calculations study. All authors contributed to discussions.

Additional information

Correspondence and requests for materials should be addressed to T.S. and A.M.

Competing financial interest

The authors declare no competing financial interest.