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VIP **Spirocycles** ***Very Important Paper***

Size-Programmable Matteson-Type Annulation: Construction of Spirocycles from Simple Cyclic Ketones

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Abstract: Despite the recent advancement, Matteson-type reactions are almost exclusively used to construct linear molecules. Herein we report an iterative boron-homologation approach to construct various carbocycles from a single precursor. This method utilizes an electron-withdrawing group (EWG) as a handle to enable intramolecular Matteson-type couplings, leading to diastereoselective and enantioselective ring formation. An intriguing role of the Lewis acid additive is identified. This approach proves to be general for preparing carbocycles with different ring sizes and multiple stereocenters. The annulation processes are also scalable, and the products can undergo various transformations to provide synthetically valuable structural motifs. In addition, this method can be extended to the preparation of diverse hard-to-make spirocyclic compounds from simple cyclic ketones. Moreover, an iterative approach to synthesize double spirocycles is also demonstrated.

Boron-based homologation, also known as the Matteson-type reaction, has been increasingly recognized as a promising tool for programmable organic synthesis.[1–8] The reaction involves addition of a carbenoid to a boronate substrate to form an ate complex, followed by 1,2-metallate rearrangement to furnish a net carbenoid insertion into the C─B bond (Scheme 1a).[9,10] Beyond the conventional Matteson reaction, the past two decades have witnessed enormous development of this field, including asymmetric homologation,[11,12] iterative insertion of heteroatoms,[13–15] and incorporation of sp^2 carbons,[16–19] etc. As a result, Matteson-type reactions have found impressive applications in programmable synthesis of linear compounds and linear fragments of complex molecules.[20–25] On the other hand, ring structures are ubiquitously found in functional organic molecules; thus, to realize the long-term goal of fully automated synthesis of diverse compounds,[26–28] the need to develop iterative annulation with retaining the boron moiety for further homologation is warranted (Scheme 1b).

The Matteson-type reaction has been rarely explored to construct rings. In 1999 Matteson reported a stereoselective cyclization to construct cyanocyclobutanes,[29] though later extension to cyclopropane formation encountered low diastereoselectivity.[30] To the best of our knowledge, using boron homologation to construct other sizes or other types of rings remained unachieved. We hypothesized that these limitations could be addressed through carefully choosing the coupling moieties and annulation strategies. Here we describe our initial attempt of a size-programmable and stereoselective Matteson-type annulation to construct carbocycles of different sizes from a simple common precursor, as well as a distinct approach to synthesize spirocycles from readily available cyclic ketones (Scheme 1c).

We proposed that a small boronate containing an EWG could be used as the starting piece. The following homologation should be compatible with the EWG owing to the presence of more electrophilic boron center, unless the EWG is too electrophilic. After a desired number of units are installed, a halo-substituted carbenoid is then inserted as a linking piece, which should promote the subsequent intramolecular Matteson reaction using the nucleophile generated from deprotonating the C─H bond adjacent to the EWG. The resulting carbocycle product should contain both the EWG and the boron moiety, serving as handles for further functionalization. We initiated our investigation using *tert*-butyl 3-propylboronic ester **1a** as the starting unit, readily synthesized from *tert*-butyl acrylate.[31] The *tert*-butyl ester or *tert*-butyloxy carbonyl (Boc) group was selected due to its versatility in subsequent transformations. Sequential one-carbon homologation with $LiCH_2Cl$ afforded **1b**, **1c**, and **1d** in high yields, each with an incremental increase in the carbon chain length. These alkyl boronates (**1**) were efficiently converted to the corresponding α-chloroboronic esters (**1-Cl**) in excellent yield by reacting with $LiCHCl_2$ (prepared from nBuLi and CH_2Cl_2),[32] setting the stage for the key cyclization step.

The Matteson annulation was optimized using **1c-Cl** as the model substrate (Table 1). LDA (lithium diisopropylamide) and LTMP (lithium 2,2,6,6-tetramethylpiperidide) were employed as the base, as they normally do not react with the α-chloroboronate moiety. Initial studies using LDA

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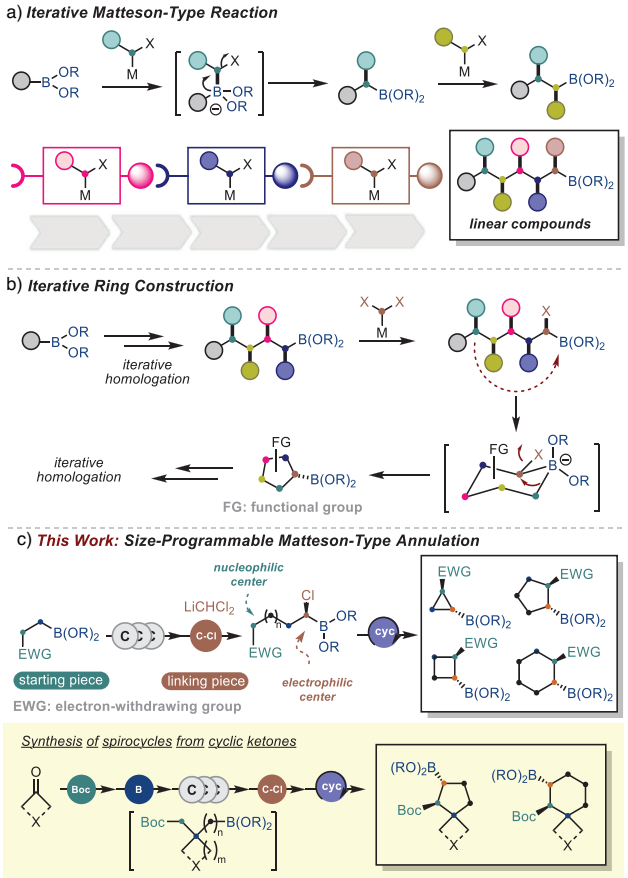
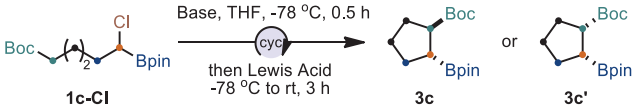
Additional supporting information can be found online in the Supporting Information section



Scheme 1. Matteson-type homologation and its use in ring construction scheme caption. a) Iterative Matteson-type reactions; b) Iterative ring construction; c) This work enables size-programmable Matteson-type annulation. Boc, *tert*-butyloxy carbonyl; cyc, cyclization. The legend in a cycle means installation of such a moiety in this operation.

(2.0 equiv) as base revealed that the presence of $MgBr_2$ (1.2 equiv) led to the selective formation of **3c** in 68% yield with excellent diastereoselectivity (>20:1 d.r., entry 1). The gradual reduction in $MgBr_2$ to 0.4 equiv preserved selectivity (>20:1 d.r., entry 2), whereas complete omission of the Lewis acid led to dramatic erosion in stereoselectivity (2.5:1 d.r., entry 3). Analogous stereochemical trends persisted upon reducing the LDA loading to 1.5 equiv (entries 4–6), although the absence of $MgBr_2$ only led to slightly compromised diastereoselectivity (11:1 d.r., entry 6). These results motivated us to examine the condition using 1.2 equiv of LDA without any Lewis acid additive, which showed excellent stereochemical control albeit slightly lower yield (entry 7). This is in sharp contrast with the prior Matteson system,[29] which was reported to not proceed without magnesium ions. On the other hand, employing LTMP as an alternative base gave the same trend but provided enhanced yields and/or diastereoselectivity (entries 8–14) compared to the corresponding LDA conditions. Further control experiments show that the cyclization product can be epimerized by LDA or LTMP alone, but not in the presence of $MgBr_2$ (Table S16). In addition, the same trend can also be observed when forming rings of different sizes or containing different EWGs (see Supporting Information

Table 1: Selected optimization studies for the five-membered cyclization[a]



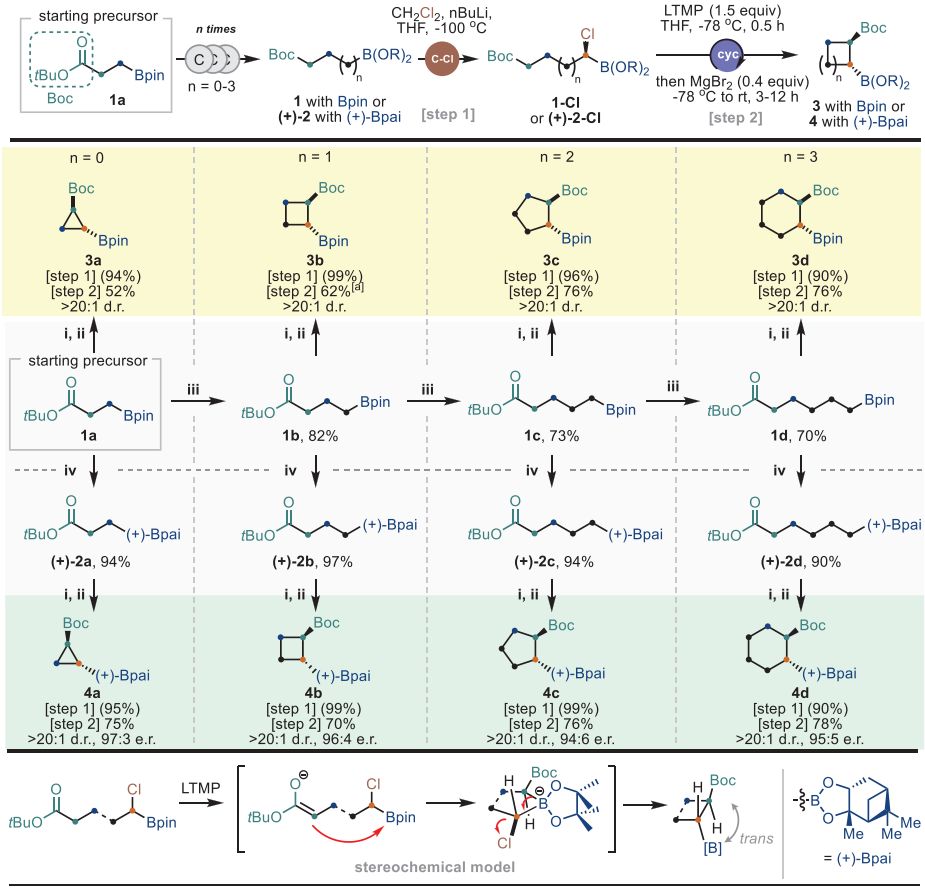
1c-Cl 3c 3c'

Entry	Base (equiv)	Additive (equiv)	Yield of 3c (%)[b]	Yield of 3c′ (%)[b]	d.r.[c]
1	LDA (2.0)	$MgBr_2$ (1.2)	68	<1	>20:1
2	LDA (2.0)	$MgBr_2$ (0.4)	68	<1	>20:1
3	LDA (2.0)	—	45	18	2.5:1
4	LDA (1.5)	$MgBr_2$ (1.2)	72	<1	>20:1
5	LDA (1.5)	$MgBr_2$ (0.4)	72	<1	>20:1
6	LDA (1.5)	—	66	6	11:1
7	LDA (1.2)	—	62	<1	>20:1
8	LTMP (2.0)	$MgBr_2$ (1.2)	80	<1	>20:1
9	LTMP (2.0)	$MgBr_2$ (0.4)	80	<1	>20:1
10	LTMP (2.0)	—	64	12	5.3:1
11	LTMP (1.5)	$MgBr_2$ (1.2)	80	<1	>20:1
12	**LTMP (1.5)**	**$MgBr_2$ (0.4)**	**80(76)**	**<1**	**>20:1**
13	LTMP (1.5)	—	66	5	13:1
14	LTMP (1.2)	—	68	<1	>20:1
15	LTMP (1.5)	$ZnCl_2$ (0.4)	72	<1	>20:1
16	LTMP (1.5)	$AlCl_3$ (0.4)	36	<1	>20:1

[a] Reaction conditions: **1c-Cl** (0.10 mmol), base, and THF (0.5 mL) at −78 °C for 0.5 h and then additive at rt for 3 h. Isolated yield is given in parentheses. [b] NMR yield was determined using dibromomethane as an internal standard. [c] The d.r. ratios were determined by the ^{1}H NMR analysis of the crude reaction mixture.

for details). Based on these observations, we hypothesized that the primary function of $MgBr_2$ is to attenuate residual base activity after the initial cyclization, thereby suppressing undesired post-reaction epimerization. This hypothesis is further supported by the comparable diastereoselectivity enhancement effect using other Lewis acids (entries 15 and 16), which represents another difference from the Matteson's system[29] that was described to not proceed using $ZnCl_2$ as the Lewis acid. Considering that slightly improved yield was observed when adding $MgBr_2$, a secondary role of the Lewis acid in promoting the 1,2-migration cannot be excluded (see Scheme S1).

Given that optimal yield was obtained using 1.5 equiv of LTMP and 0.4 equiv of $MgBr_2$ (entry 12, Table 1), this condition was employed to explore construction of rings with different sizes (Scheme 2). To our delight, cyclopropane formation gave excellent diastereoselectivity favoring the *trans* product, representing a notable advance over the prior work.[30] Forming cyclobutane **3b** requires a longer reaction time (12 h), implying a higher 1,2-migration barrier. The 6-membered ring formation proceeded smoothly, delivering the desired product **3d** in 76% yield. Attempts to realize both 7- and 8-membered ring formation were unsuccessful at this stage, despite complete consumption of starting materials. This is likely owing to the challenge of forming 8- and 9-membered ate complex intermediates. In addition, the high *trans* selectivity in the cyclized products is likely controlled by the configuration of the ate complex where the Boc and the Cl are *trans* to each other (Scheme 2 bottom), based on a model previously proposed by Matteson.[29]

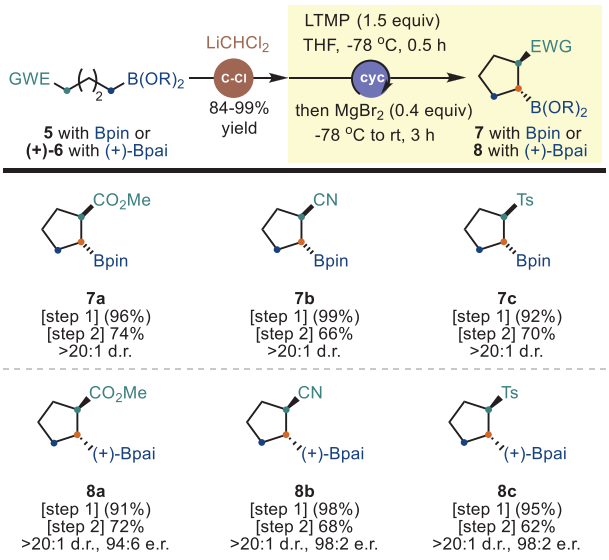


Scheme 2. Size-programmable diastereoselective and enantioselective synthesis of 3- to 6-membered carbocycles from a single precursor. Reaction conditions: i) CH_2Cl_2 (3.0 equiv), nBuLi (1.2 equiv) in THF, -100 °C, 30 min; then **1** or **(+)-2**, −78 °C, 15min; then $ZnCl_2$ (1.5 equiv) rt, 3 h. ii) **1-Cl** or **(+)-2-Cl** (0.20mmol), LTMP (1.5 equiv), and THF (1.0mL) at −78 °C for 0.5 h and then $MgBr_2$ (0.4 equiv) at rt for 3 h. iii) $LiCH_2Cl$ (2.5 equiv), THF, −78 °C to rt, 3 h. iv) (+)-pinanediol (1.0 equiv), Et_2O/H_2O, rt, 12 h. Yields of isolated products are given, and numbers in parentheses are NMR yields. d.r., diastereomeric ratio. Enantiomeric ratio (e.r.) of the product was determined after product derivatization using HPLC. a)The reaction was run for 12 h.

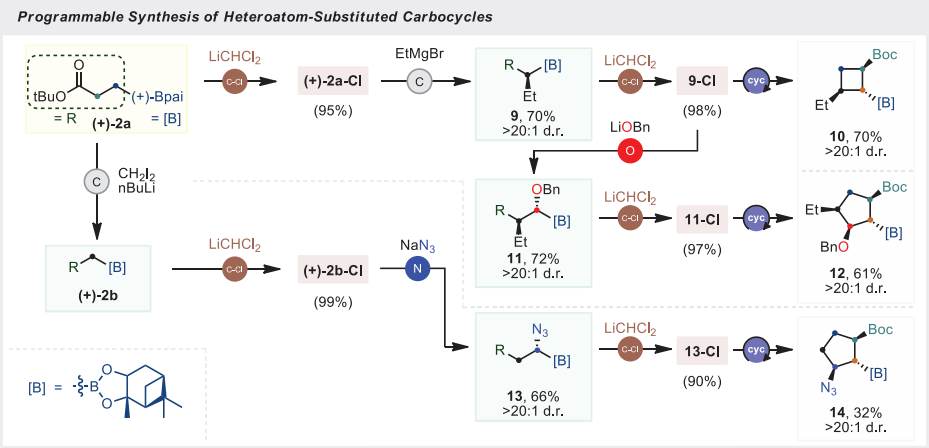
Besides preparing the racemic cyclized products, enantioenriched products can also be obtained using (+)-pinanediol as the chiral auxiliary.[5] Facile transesterification of pinacolboronic esters **1** to **(+)-2** proceeded in near-quantitative yield. Applying the optimized annulation protocol to the chiral substrates uneventfully afforded the enantioenriched cyclopropane (**4a**), cyclobutane (**4b**), cyclopentane (**4c**), and cyclohexane (**4d**) products in good yields (65–78%) with high diastereoselectivity (>20:1 d.r.) and excellent enantioselectivity (94:6–97:3 e.r. of the product derivatives). Unsurprisingly, the opposite enantiomer of the product can be obtained in comparable yield and enantioselectivity simply by employing the antipode (−)-pinanediol (see the Supporting Information).

In addition to the *tert*-butyl ester-mediated reactions, other EWGs were also competent for the Matteson-type annulation (Table 2). Under the optimized condition, good yields and nearly full diastereoselective control can be realized using methyl ester, nitrile, and sulfone as the handles (**7** and **8**). Again, excellent enantioselectivity was achieved using pinanediol as the chiral auxiliary.

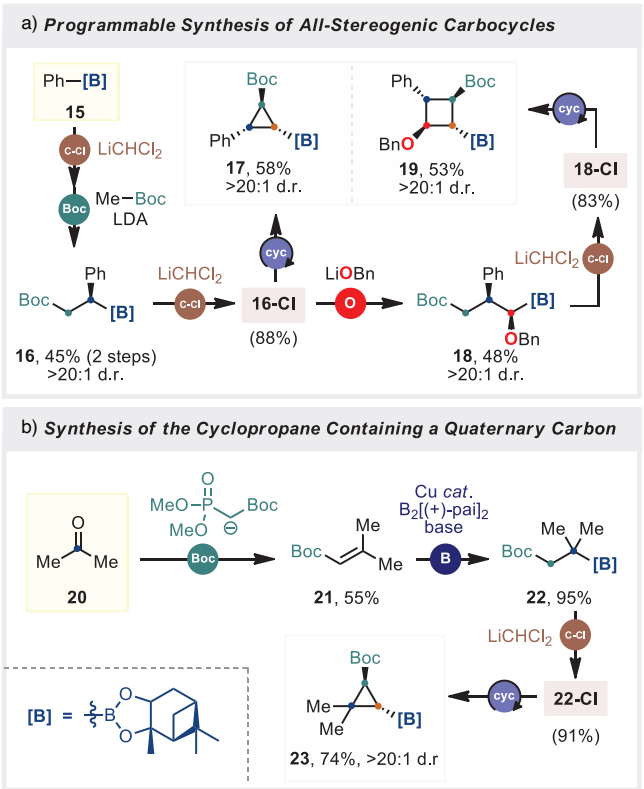
Table 2: Cyclization with other EWGs[a)]



a) Ts, *p*-toluenesulfonyl.



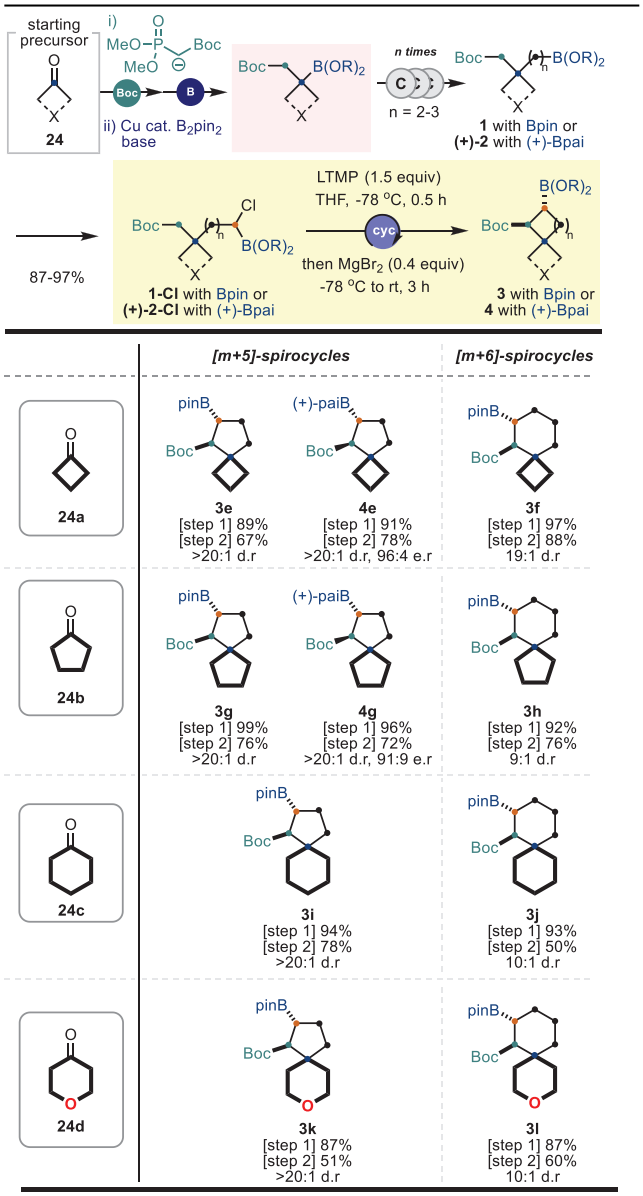
Scheme 3. Synthesis of highly functionalized carbocycles.

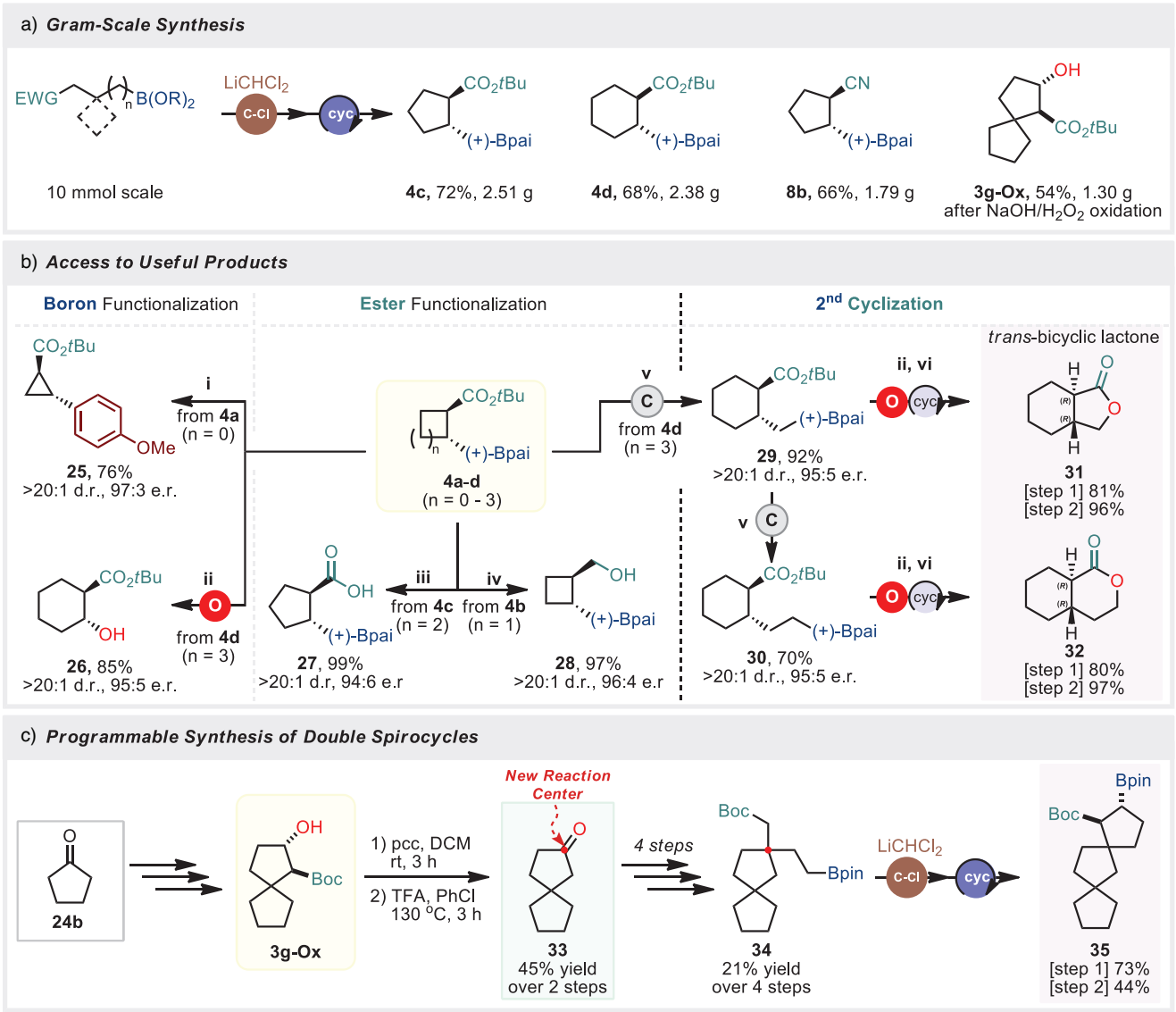


Scheme 4. Synthesis of fully substituted carbocycles. a) Programmable synthesis of all-stereogenic carbocycles; b) Synthesis of the cyclopropane containing a quaternary carbon.

Besides forming simple carbocycles, the advantage of this iterative strategy was then exploited to synthesize highly functionalized rings (Scheme 3a). Starting from **(+)-2a**, a typical Matteson reaction inserted an ethyl-substituted carbenoid in high efficiency to give intermediate **9**,[33–35] which then reacted with $LiCHCl_2$ to give the key common intermediate (α-chloroboronic ester **9-Cl**). Under the standard annulation conditions, **9-Cl** was smoothly converted to the trisubstituted cyclobutane **10** in good yield and excellent diastereoselectivity. Alternatively, treatment of **9-Cl** with benzyl alkoxide

Table 3: Programmable synthesis of spirocycles.





Scheme 5. Synthetic utilities of this annulation strategy. a) Gram-scale synthesis; b) Access to useful products; c) Programmable synthesis of double spirocycles. Reaction conditions: i) 4-bromoanisole, tris(dibenzylideneacetone)dipalladium, RuPhos, NaO^{t}Bu, toluene/H_2O, 80 °C, 24 h. ii) NaOH, H_2O_2, THF/H_2O, 0 °C to rt, 2 h. iii) Trifluoroacetic acid, DCM, rt, 2 h iv) $LiAlH_4$, THF, 0 °C to rt, 2 h. v) CH_2I_2, *n*BuLi, −78 °C, 0.5 h then rt, 3 h. vi) *p*-Toluenesulfonic acid, DCM, 50 °C, 2 h. Yields of Isolated products are given. d.r. was determined by ^{1}H-NMR; e.r. was determined by HPLC.

as the nucleophile installed an oxygen substituent,[33,36] and the resulting boronate (**11**) then underwent further homologation and cyclization to yield tetra-substituted cyclopentane **12** with nearly complete stereoselectivity. On the other hand, to introduce nitrogen-substituted carbocycles, intermediate **(+)-2b-Cl**, readily accessible from **(+)-2a**, was subjected to the chloromethylene homologation and then azide substitution.[36] The resulting boronate **13** was found to react under the standard homologation/annulation conditions to afford azido-substituted cyclopentane **14** in modest yield but excellent d.r.

Moreover, this programmable annulation approach can be extended to construct carbocycles containing substitution on each ring carbon (Scheme 4a). The syntheses were carried out using phenyl (+)-pinanediol boronic ester (**15**) as the starting material. The iterative insertion of chloromethylene, followed by reaction with the ester enolate and insertion of another chloromethylene, provided common intermediate **16-Cl**. The following annulation smoothly delivered cyclopropane **17** bearing three contiguous stereocenters. Likewise, the four-membered ring product bearing four different types of stereocenters (**19**) was furnished through installation of BnO-substituted methylene group from **16-Cl** followed by the standard homologative cyclization.

Next, we attempted the diastereoselective synthesis of cyclopropanes containing a congested quaternary carbon, which was problematic for stereocontrol in the prior Matteson's system (Scheme 4b).[30] An efficient approach was developed to access the tertiary boronate (**22**) via Horner−Wadsworth−Emmons (HWE) olefination with acetone, followed by Markovnikov 1,4-hydroborylation.[37] Upon chloromethylene insertion and annulation, this

protocol successfully delivered the desired cyclopropane **23** with nearly perfect diastereoselectivity. Altogether, these findings support the high versatility of this annulation method in constructing diverse and functionalized rings.

Next, we extended the application of this boron-mediated cyclization to the programmable synthesis of all-carbon spirocyclic compounds. Spirocycles feature two rings sharing a single quaternary carbon atom, representing a common structural motif in natural products and pharmaceuticals.[38,39] However, their synthesis poses substantial challenges, particularly for all-carbon spirocycles.[40–48] We conceived a general approach to access spirocycles with different ring sizes from simple cyclic ketones (**24**). Similar to the preparation of boronate **22**, our strategy started with sequential HWE olefination and 1,4-hydroboration[37] of the cyclic ketone to give the Boc-substituted boronate, which can then serve as the starting piece for the following programmable homologation and annulation (Table 3). Using this protocol, [4.5], [4.6], [5.5], [5.6], and [6.6]-spirocycles were all constructed in an efficient manner, by choosing the corresponding cyclic ketone precursors and homologation lengths. Notably, the oxygen-containing dihydro-*2H*-pyran-4(*3H*)-one (**24d**) proved compatible, affording heterospirocycles **3k** and **3l** in high yields and excellent diastereoselectivity. Moreover, the enantioselective control was showcased in the synthesis of [4.5]- (**4e**) and [5.5]-spirocycles (**4g**) with (+)-pinanediol as the chiral auxiliary.

To explore the synthetic utility of this method, this annulation reaction was first found to work well on gram-scale (Scheme 5a). Next, the ester and the boron moieties can serve as versatile synthetic handles for further transformations (Scheme 5b). Examples have been demonstrated on the stereoretentive Suzuki coupling of cyclopropane **4a**, boron oxidation to afford β-hydroxy-ester **26**, and ester hydrolysis and reduction to give carboxylic acid **27** and alcohol **28**, respectively, without touching the boronate moiety. On the other hand, sequential one- or two-carbon homologation of the boronate, followed by boron oxidation and acid-catalyzed lactonization, delivered *trans*-fused [6.5]- and [6.6]-bicyclic γ- and δ-lactones **31** and **32** in excellent yields. Finally, the spirocycle product (**3g-Ox**) obtained from cyclopentanone can be further converted back to a cyclic ketone (**33**) via a sequence of boron oxidation, alcohol oxidation, and decarboxylation (Scheme 5c). Ketone **33** then served as a new starting point to access alkylboronic ester **34** via the same protocol, which can undergo subsequent successful homologative cyclization to furnish double spirocycle **35**. Notably, such structures are challenging to prepare using conventional methods,[49] whereas our strategy offers a tunable and iterative approach to prepare poly-spirocycles.

In summary, we have developed a general size-programmable Matteson-type intramolecular cyclization, which can stereoselectively construct 3- to 6-membered multi-substituted carbocycles from a single precursor. Thus, it opens the door to prepare non-linear compounds via iterative boron homologation. In addition, this method also leads to an efficient and tunable protocol to prepare various hard-to-access spirocycles. It is anticipated that this study should not only offer an unconventional synthetic logic to access ring systems, but also lay the foundation towards programmable automated synthesis of complex cyclic molecules.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Annulation · Boronate · Homologation · Programmable synthesis · spirocycle

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