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Synthesis of arylboronates via Cp*RuCl-catalyzed cycloaddition of alkynylboronates

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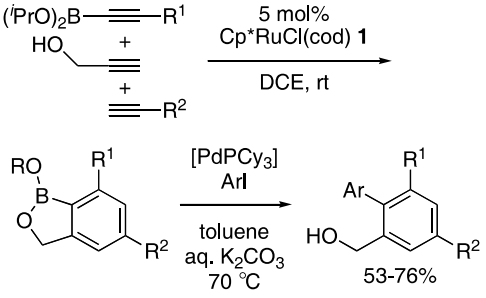
Abstract—In the presence of 5–10 mol% Cp*RuCl(cod), 1,6- and 1,7-diynes were allowed to react with an ethynylboronate at ambient temperature to give rise to bicyclic arylboronates in 64–93% isolated yields. 1,6-Diynes bearing a boronate terminal also underwent cycloaddition with monoalkynes to give the corresponding bicyclic arylboronates.

1. Introduction

Arylboronic acids and their congeners have become indispensable reagents in modern organic synthesis. In fact, they are now used for a wide variety of significant organic transformations including Suzuki–Miyaura cross coupling,[1] homo coupling,[2] rhodium-catalyzed asymmetric 1,2- and 1,4-additions to carbonyl compounds,[3,4] Heck-type reaction,[5] Petasis–Mannich condensation,[6,7] and others.[8] Arylboronic acid derivatives have been conventionally prepared by the reactions of arylmagnesium or -lithium reagents with trialkylborates, although reactive functional groups are incompatible with this method.[9] To address this issue, transition-metal-catalyzed couplings of arylhalides, -triflates, or -diazoniums with tetraalkoxydiboranes or dialkoxyboranes have been developed by several research groups.[10] Furthermore, transition-metal-catalyzed direct borylation of aromatic C–H bonds has emerged as an environmentally benign process.[11] In addition to these methods utilizing aromatic precursors, benzannulation or cycloaddition involving unsaturated organoboron reagents realized the assembly of highly substituted arylboronic acid frameworks, which are otherwise difficult to be prepared.[12,13] In this context, we recently developed the ruthenium-catalyzed cyclotrimerization of alkynylboronates, propargyl alcohol, and a terminal alkynes giving rise to arylboronates, which were subjected to one-pot Suzuki–Miyaura coupling to afford highly substituted biaryls as single regioisomers (Scheme 1).[14] As an extension of this study, we also explored the Cp*RuCl-catalyzed cycloaddition of α,ω-diynes with an ethynylboronate, yielding polycyclic arylboronates.[15] Herein, we wish to report the full details of our study on the catalytic partially intramolecular cycloaddition of alkynylboronates and diynylboronates.



Scheme 1.

2. Results and discussion

Aubert and co-workers recently reported the cycloaddition of the $Co_2(CO)_6$-complexed alkynylborates with α,ω-diynes bearing various tether lengths.[16] Although their protocol efficiently afforded various bicyclic arylboronates, the direct cycloaddition of diynes with alkynylboronates in the presence of appropriate catalyst is highly desirable in terms of atom economy.[17] Thus, our Cp*RuCl-catalyzed alkyne cyclotrimerization protocol would serve this purpose well.[14,18] In a recent work of Dixneuf and co-workers, Cp*RuCl(cod) also proved to be a competent precatalyst for [2+2] dimerization of an allenylboronate.[19]

Keywords: Ruthenium catalysis; Cyclotrimerization; Alkynylboronate; Arylboronate; Suzuki–Miyaura coupling.
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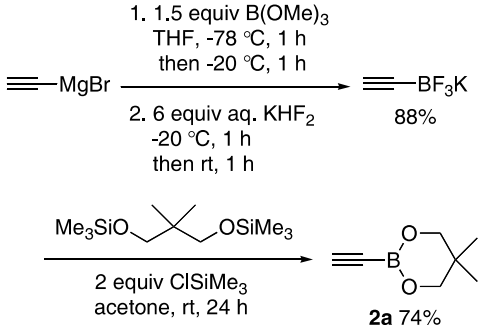
2.1. Preparation of ethynylboronate

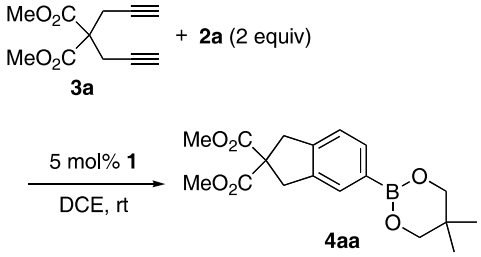
To realize an efficient catalytic protocol, we required an ethynylboronate because internal alkynes proved to be inefficient monoalkyne substrates for the ruthenium catalysis (vide infra).[18] The reaction of ethynylmagnesium bromide and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane with the standard procedures of Brown and co-workers,[20] however, led to the formation of an ethynylboronate in a moderate yield with rather low purity because of its low boiling point. Thus, we turned our attention to an alternative procedure to prepare alkynylboronates reported by Vaultier and co-workers.[21] Although this method gave the desired 2-ethynyl-5,5-dimethyl-1,3,2-dioxaborinane (**2a**), commercially unavailable chlorobis(diisopropylamino)borane is required as a boron source and diaminoborane intermediates are moisture sensitive. To overcome such disadvantages, a modified route was developed by taking advantage of the ligand exchange reaction of alkynyltrifluoroborates.[22] As outlined in Scheme 2, the established procedure was applied to the synthesis of ethynyltrifluoroborate,[23] which was then treated with 2,2-dimethylpropane-1,3-diol bis(trimethylsilyl) ether in the presence of chlorotrimethylsilane in acetone at room temperature to afford ethynylboronate **2a** in a reasonable yield with high purity.



Scheme 2.

2.2. Cp*RuCl-catalyzed cycloaddition of α,ω-diynes with ethynylboronate

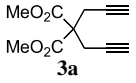
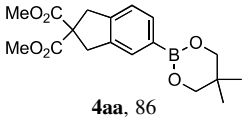
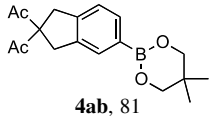
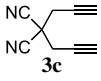
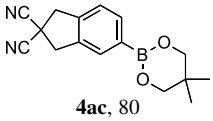
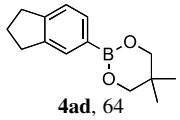
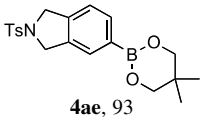
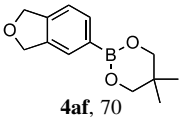
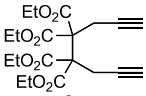
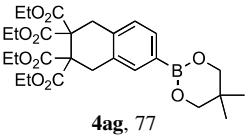
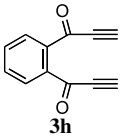
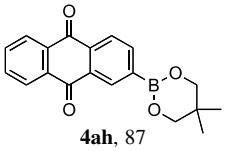
With ethynylboronate **2a** in hand, we next optimized its cycloaddition with dimethyl dipropargylmalonate (**3a**) in the presence of precatalyst Cp*RuCl(cod) (**1**) (Cp*=η^5-C_5Me_5, cod=1,5-cyclooctadiene) as shown in Scheme 3. To suppress diyne dimerization, a solution of **3a** in 1,2-dichloroethane (DCE) was added at room temperature via syringe pump over 1 h to the DCE solution of 5 mol% **1** and 2 equiv of **2a**. As a result, the desired cycloadduct **4aa** was isolated in 77% yield after purification with silica gel column chromatography. A similar yield was obtained with increased amounts of **2a** (4 equiv). On the other hand, the yield was improved to 86%, when the reaction mixture was stirred for 1 h after the syringe-pump addition of **3a**. The obtained product was characterized as bicyclic arylboronate **4aa** by ^{1}H and ^{13}C NMR, IR, mass, and elemental analyses. This structural assignment was also confirmed by X-ray crystallography.[15]



Scheme 3.

The generality of this protocol was well demonstrated by the results obtained with various diyne substrates (Table 1). The present method well tolerated functional groups including an ester, a ketone, and a nitrile, and as a consequence, arylboronates **4aa**–**4ac** were obtained in 80–86% yields (runs 1–3). The quaternary center of the tether is not essential for the cycloaddition. Although an increased

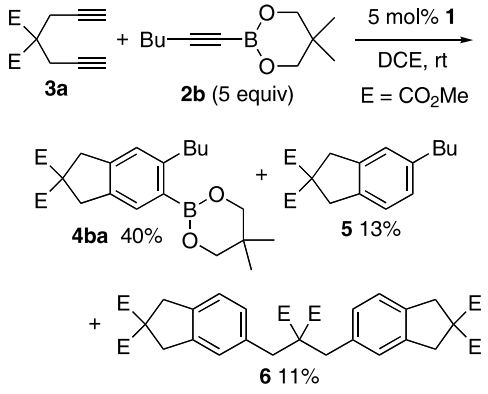
Table 1. Cycloaddition of diynes **3a**–**h** with ethynylboronate **2a**[a]

Run	Diyne	Product, yield (%)
1	 **3a**	 **4aa**, 86
2	 **3b**	 **4ab**, 81
3	 **3c**	 **4ac**, 80
4	 **3d**	 **4ad**, 64
5	 **3e**	 **4ae**, 93
6	 **3f**	 **4af**, 70
7	 **3g**	 **4ag**, 77
8	 **3h**	 **4ah**, 87

[a] A solution of **3** in DCE was added to a DCE solution of 5 mol% (10 mol% for runs 4, 6 and 7) Cp*RuCl(cod) **1** and 2 equiv of ethynyl boronate **2a** by syringe pump over 1 h, and the solution was stirred for 1 h at room temperature.

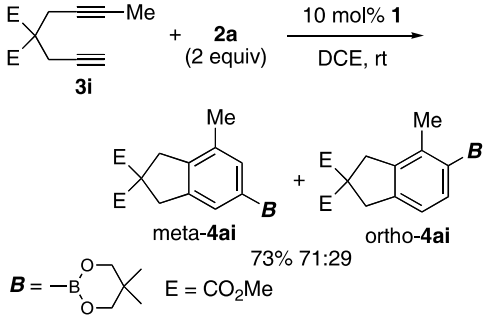
catalyst loading of 10 mol% was required, the parent 1,6-heptadiyne (**3d**) underwent cycloaddition with **2a** to furnish the corresponding product **4ad** in 64% yield (run 4). Similarly, *N*,*N*-dipropargyltosylamide (**3e**) and propargyl ether (**3f**) gave borylated heterocycles **4ae** and **4af** in 93 and 70% yields, respectively (runs 5 and 6). In addition to these 1,6-diynes, 1,7-diynes **3g** and **3h** were able to react with **2a** to give tetrahydronaphthalene derivative **4ag** and anthraquinone derivative **4ah** in 77 and 87% yields, respectively (runs 7 and 8).

As anticipated, internal alkynylboronate **2b** turned out to be less efficient than terminal **2a**. The reaction with diyne **3a** in a similar manner afforded the desired arylboronate **4ba** in a lower yield of 40% (Scheme 4). In this case, two additional by-products, protodeboration product **5** and diyne dimer **6** are formed even with the increased loading of the alkynylboronate (5 equiv).



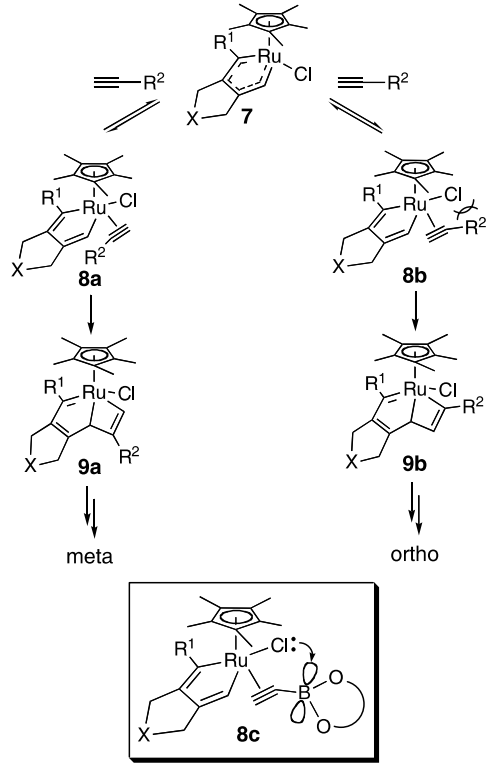
Scheme 4.

We next examined the influence of the terminal substituent on the diyne substrates. In our previous study, it was found that unsymmetrical diynes possessing a terminal substituent on one of the two alkyne moieties reacted with monoalkynes to afford *meta* isomers with excellent regioselectivity as high as *meta*:*ortho*=95:5.[18] On the other hand, the reaction of unsymmetrical diyne **3i** with **2a** was carried out in the presence of 10 mol% **1** to afford a regioisomer mixture of cycloadduct **4ai** in 73% combined yield with a diminished selectivity of *meta*:*ortho*=71:29 (Scheme 5).



Scheme 5.

The plausible regioselection mechanism is outlined in Scheme 6. The catalytic reaction starts with the oxidative cyclization of a diyne on the Cp*RuCl fragment, leading to a ruthenabicycle **7**. On the basis of density functional theory calculations, we and others have proposed the novel alkyne cyclotrimerization mechanism, in which the intermediacy of an unprecedented ruthenatricycle **9** was proposed for the conversion of a ruthenabicycle–alkyne complex **8** to a seven-membered ruthenacycle intermediate.[18,24] The coordinated alkyne is considered to react predominantly with the less substituted Ru–C bond as a consequence of the steric influence of the substituent R^1. In addition, the steric repulsion between the chloro ligand and the substituent R^2 on the coordinated monoalkyne might destabilize ruthenabicycle–alkyne complex **8b**. Therefore, the preferential pathway via alternative complex **8a** leads to the predominant formation of a *meta*-substituted product. In the case for an alkynylboronate, however, the attractive interaction between the non-bonding electron pair on the chlorine ligand and the vacant orbital on the boron center might render intermediate **8c** somewhat favorable, resulting in the decrease of regioselectivity.

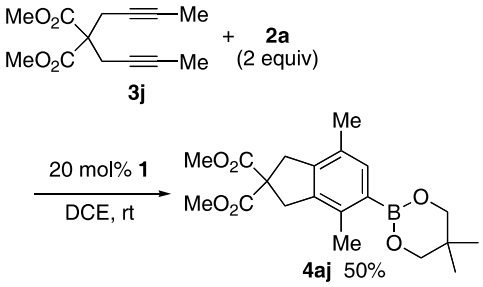


Scheme 6.

The cycloaddition of diyne **3j** bearing methyl substituents on both the alkyne termini suffered from severe steric repulsion between the terminal substituents and the boronate moiety of **2a** (Scheme 7). Consequently, the cycloaddition was carried out overnight with a 20 mol% catalyst loading, but the yield of the desired penta-substituted benzene was not higher than 50%.

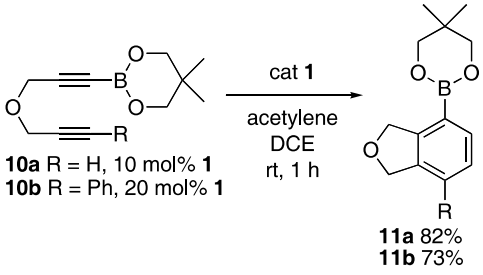
2.3. Cp*RuCl-catalyzed cycloaddition of diynylboronates with monoalkynes

We further explored an alternative partially intramolecular cyclotrimerization assembling bicyclic arylboronates from a diynylboronate and monoalkynes. Diynylboronate **10a**



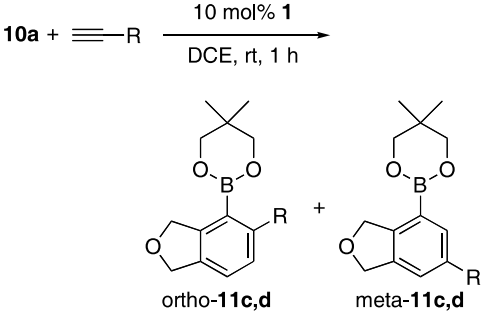
Scheme 7.

derived from dipropargyl ether was treated with 10 mol% **1** in DCE under acetylene atmosphere at room temperature for 1 h to give rise to borylated phthalan **11a** in 82% yield (Scheme 8). It is noteworthy that phthalan boronate isomers **4ah** and **11a** were selectively synthesized by the judicious choice of the precursors in our catalytic cyclotrimerization approach. In a similar manner with a 20 mol% catalyst loading, biphenyl derivative **11b** was obtained in 73% yield from **10b** possessing a phenyl terminal.



Scheme 8.

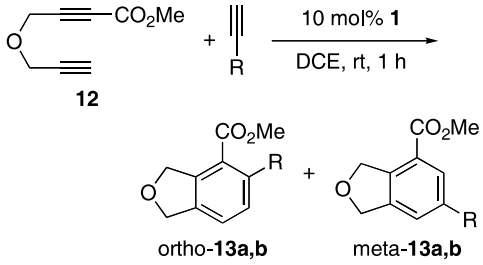
Encouraged by this result, we then examined the regioselectivity of the cycloaddition of **10a** with terminal alkynes (Scheme 9). Thus, **10a** was allowed to react with 4 equiv of 1-hexyne in the same manner. In striking contrast to our expectation of the selective formation of the *meta* isomer, cycloadduct **11c** was obtained as an approximately 1:1 regioisomer mixture in a combined yield of 70%. The total loss of regioselectivity in this system is probably attributed to the electron-withdrawing ability of the boronate terminal of **10a**. To confirm the generality of such an electronic influence, diynylester **12** was subjected to the same reaction conditions as shown in Scheme 10. Consequently, the complete loss of regioselectivity was again observed for



c: R = Bu, 70% yield, ortho:meta = 55:45
d: R = CH_2OMe, 58% yield, ortho:meta = 70:30

Scheme 9.

the formation of benzoate **13**. On the other hand, the moderate *ortho* selectivity was observed for the reaction of **10a** with methyl propargyl ether (5 equiv) resulting in a regioisomer ratio of *ortho*-**11d**:*meta*-**11d** = 70:30 (Scheme 9). The attractive interaction of the ether lone pair with the vacant orbital on the boron center might be a cause of the *ortho* selectivity as depicted in Figure 1 (vide infra). Without such an interaction of the methyl ether terminal, the cycloaddition of ester **12** with 5 equiv methyl propargyl ether under the same conditions lead to the almost complete loss of regioselectivity (Scheme 10).



a: R = Bu, 46% yield, ortho:meta = 51:49
b: R = CH_2OMe, 74% yield, ortho:meta = 55:45

Scheme 10.

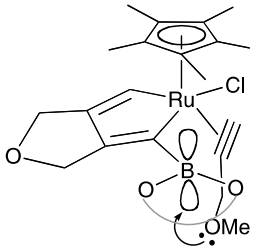
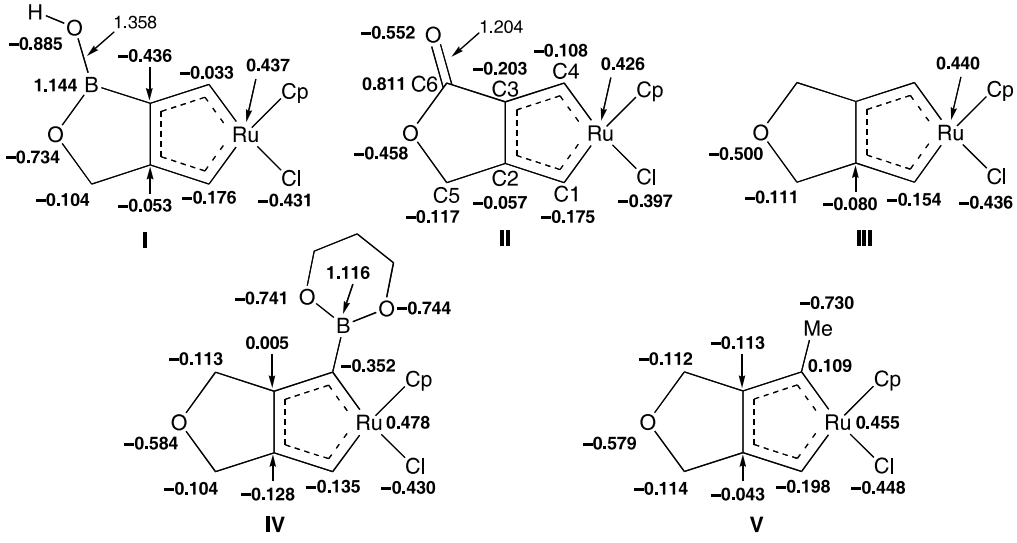


Figure 1. Possible intermediate of cycloaddition of **10** and methyl propargyl ether.

2.4. Density functional calculations of ruthenacycle intermediates

As mentioned above, an electron-withdrawing terminal on a diyne substrate exerted a deteriorative effect on the cycloaddition regioselectivity (Schemes 9 and 10). This is in striking contrast to the fact that internal electron-withdrawing group made favorable contribution to the regioselective cycloadditions.[25,26] To obtain insight into the role of the electron-withdrawing terminal, we carried out density functional theory (DFT) calculations of model ruthenacycle intermediates. Previous DFT calculations revealed that boraruthenacycle **I** and lactone-fused ruthenacycle **II** is electronically unsymmetrical compared to parent **III** as evidenced by the natural charge destributions, although the ruthenacyclopentatriene moieties are almost symmetrical in terms of the bond lengths and angles (Fig. 2).[25,26] Thus, the alkyne insertion was considered to take place at the more negatively charged α carbon anti to the electron-withdrawing boronate and carbonyl groups. With these facts in mind, we further examined ruthenacycles relevant to the present study. At the outset, methyl-substituted ruthenacycle **V** was optimized at the B3LYP/LACVP* level of theory to reveal that its



Typical bond lengths (Å) of model ruthenacycles **I-V.**

	Ru-Cl	Ru-C1	Ru-C4	C1-C2	C2-C3	C3-C4	C2-C5	C5-O	O-C6	C6-C3	O-B	B-C3
I	2.364	1.950	1.954	1.396	1.408	1.397	1.509	1.439	-	-	1.386	1.559
II	2.350	1.963	1.964	1.389	1.398	1.387	1.504	1.444	1.385	1.482	-	-
III	2.366	1.959	-	1.391	1.400	-	1.504	1.437	-	-	-	-
IV	2.364	1.969	1.994	1.381	1.403	1.397	1.505	1.435	1.438	1.505	-	-
V	2.374	1.938	1.989	1.399	1.394	1.397	1.503	1.434	1.437	1.507	-	-

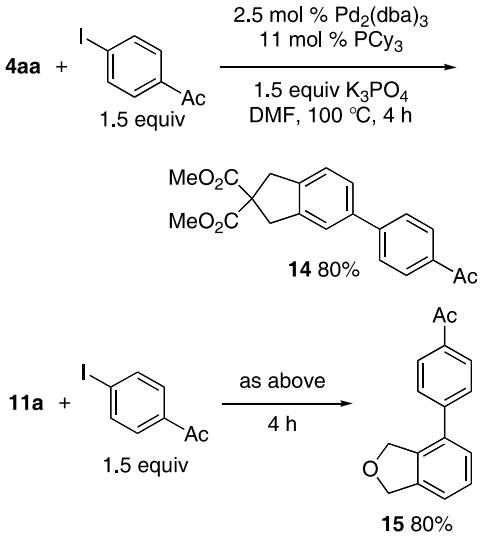
Figure 2. DFT-optimized geometries of model ruthenacycles **I–V** at the B3LYP/LACVP* level (bold numbers indicate natural charges).

ruthenacyclopentatriene moiety is remarkably unsymmetrical. The distance between the ruthenium center and the more substituted α carbon (Ru–C4) is 0.051 Å longer than that of Ru–C1 bond. On the other hand, the C3–C4 bond length is slightly shorter than that for C1–C2 (0.014 Å). Similar trends were observed for boronate-substituted ruthenacycle **IV**, although the difference in the ruthenium–carbon bonds are smaller (0.025 Å).

Further calculations of natural charges were carried out at the same level of theory and the obtained data were shown in Figure 2. The ruthenacyclopentatriene ring of **V** is unsymmetrical in terms of the natural charges compared to parent **III**. The less substituted α carbon C1 is more electronegative so that the alkyne insertion selectively takes place into the Ru–C1 bond as a consequence of the synergistic effect of both the steric and electronic directing effect. On the other hand, the α carbon connected to the boronate group is considerably electronegative (C4: −0.352) compared to the other a carbon (C1: −0.135) in **IV**. On the basis of these results, it is considered that the interference of both electronical and geometrical desymmetrizations of the ruthenacycle ring confuses the cycloaddition regiochemistry.

2.5. Transformations of arylboronates

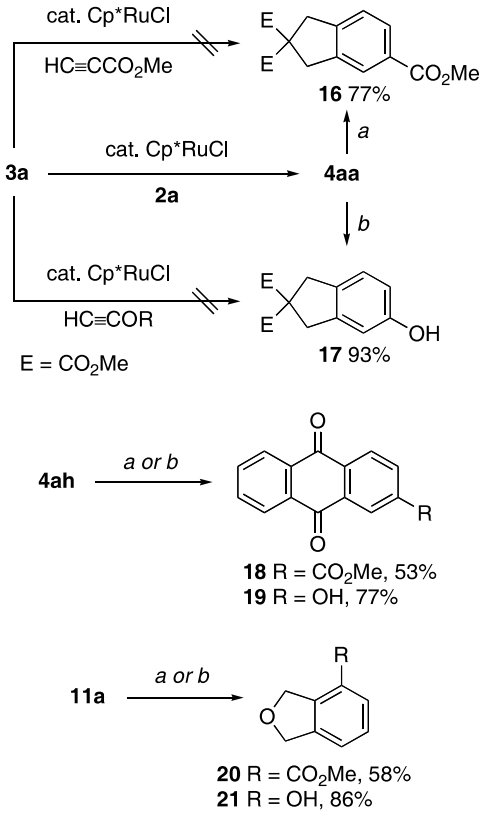
Finally, we demonstrated the synthetic utility of the present method by carrying out the transformations of the obtained arylboronates. The Suzuki–Miyaura couplings of **4aa** and **11a** with *p*-iodoacetophenone were carried out in the presence of 2.5 mol% $Pd_2(dba)_3$ (dba = dibenzylideneacetone), 11 mol% PCy_3, and 1.5 equiv of K_3PO_4 in DMF at 100 °C to give biaryls **14** and **15** in 80% yields (Scheme 11).



Scheme 11.

Electron-deficient monoalkynes such as acetylenedicarboxylates or propiolates are very reactive substrates for the Cp*RuCl-catalyzed cyclotrimerization.[18] Consequently, the cycloaddition of α,ω-diynes with those alkynes has never been accomplished under ruthenium-catalyzed conditions. To obtain the cycloadduct of **3a** and methyl propiolate

indirectly, the catalytic methoxycarbonylation of **4aa** was examined as shown in Scheme 12. The catalytic alkoxycarbonylation of arylboronates, however, has remained almost unexplored,[27] and we recently developed the new protocol to synthesize phthalides by the catalytic carbonylation of boraphthalides.[26] According to our own report, **4aa** was treated with 5 mol% $Pd(OAc)_2$, 11 mol% PPh_3, and 1 equiv of *p*-benzoquinone in MeOH under CO atmosphere at room temperature. The starting material was completely consumed within 2 h to afford the desired benzoate **16** in 77% yield. Electron-rich alkoxyacetylenes are also incompatible monoalkyne substrates for the ruthenium catalysis, although their cycloadducts are valuable pehenol derivatives. In this context, the cycloaddition of **2a** and **3a** followed by oxidation of resultant **4aa** gave bicyclic phenol **17** in a good yield. These methods were further applied to anthraquinone boronate **4ah** to deliver naturally occurring anthraquinone derivatives **18** and **19**.[28,29] Similarly, phthalan derivatives **20** and **21** were obtained from **11a** in 58 and 86% yields, respectively.



Scheme 12. Conditions. (a) 5 mol% $Pd(OAc)_2$, 11 mol% PPh_3, 1 equiv *p*-benzoquinone, 1 atm CO, MeOH, rt, 1.5–2 h; (b) H_2O_2, aq NaOH, THF, rt, 15 min.

3. Conclusion

We successfully developed a novel protocol to prepare bi- or tricyclic arylboronates via Cp*RuCl-catalyzed cycloaddition of 2-ethynyl-5,5-dimethyl-1,3,2-dioxaborinane with various 1,6- and 1,7-diynes. The present protocol tolerates reactive functional groups including an ester, a ketone, a nitrile, and a sulfonamide. Moreover, the Cp*RuCl-catalyzed cycloadditions of diynylboronate with monoalkynes successfully gave rise to similar bicyclic arylboronates albeit with a low regioselectivity. The obtained arylboronate products were further transformed into valuable compounds such as biphenyl, benzoate, and phenol derivatives by means of established procedures.

4. Experimental

4.1. General

Flash chromatography was performed with a silica gel column (Cica silica gel 60 N) eluted with mixed solvents [hexane/AcOEt]. ^1H and ^{13}C NMR spectra were obtained for samples in $CDCl_3$ solution at 25 °C on a Varian Mercury 300 spectrometer. ^1H NMR chemical shifts are reported in δ units, in ppm relative to the singlet at 7.26 ppm for chloroform. Coupling constants are reported in Hz. Infrared spectra were recorded for $CHCl_3$ sample solutions in 0.2 mm path length sodium chloride cavity cells on a JASCO FT/IR-230 spectrometer. Mass spectra were recorded on a JEOL JMS700 mass spectrometer. Elemental analyses were performed by the Instrumental Analysis Facility of Nagoya University. Melting points were obtained on a Büchi B-540 apparatus. 1,2-Dichloroethane and DMF were distilled from CaH_2, and degassed before use. MeOH was distilled from Mg. Cp*RuCl(cod) and $Pd_2(dba)_3 \cdot CHCl_3$ were prepared according to the established procedure.[30,31]

4.1.1. Synthesis of alkynylboronates.

4.1.1.1. 2-Ethynyl-5,5-dimethyl-1,3,2-dioxaborinane 2a. To a solution of ethynylmagnesium bromide in THF (0.5 M THF solution 20 mL, 10.0 mmol + THF 10 mL), trimethylborate (1.59 g, 15.3 mmol) was added at −78 °C. The solution was stirred for 1 h at this temperature, and then stirring was continued for 1 h at −20 °C. To the resultant white suspension, a solution of KHF_2 (4.71 g, 60.3 mmol) in distilled water (15 mL) was added at −20 °C and the solution was stirred at this temperature for 1 h, and at room temperature for 1 h. The obtained reaction mixture was concentrated and dried under reduced pressure over 3 h. The crude product was dissolved in hot acetone and the residue was removed by filtration. The filtrate was concentrated to afford potassium ethynyltrifluoroborate (1.15 g, 87%) as colorless solids (mp 211.2–212.0 °C decomp.).

To a solution of the potassium ethynyltrifluoroborate (1.32 g, 10.0 mmol) and 2,2-dimethyl-1,3-propanediol bis(trimethylsilyl) ether (2.49 g, 10.0 mmol) in dry acetone (10 mL) was added chlorotrimethylsilane (2.17 g, 20.0 mmol) at room temperature, and the solution was stirred overnight. The precipitates were removed by filtration under N_2 atmosphere, and the filtrate was concentrated in vacuo. The crude oil was purified by bulb-to-bulb distillation (80–95 °C/22 mmHg) to give **2a** (1.53 g, 74%) as colorless oil. The spectral data was in good agreement with those reported in the literature.[21] Alkynylboronate **2b**[21] was synthesized in a similar manner.

4.1.1.2. Diynylboronate 10. To a solution of dipropargyl ether (2.83 g, 30.1 mmol) in THF (30 mL), *n*-BuLi (1.6 M solution in hexane, 9.40 mL, 15.0 mmol) was added at −78 °C. The solution was stirred at −78 °C for 30 min, and then at 0 °C for 30 min. To the resultant orange suspension, $B(OMe)_3$ (2.34 g, 22.5 mmol) was added at −78 °C, and the reaction mixture was stirred at −78 °C for 1 h, and then at 0 °C for 1 h. To the reaction mixture, a solution of KHF_2 (7.03 g, 90.0 mmol) in distilled water (16 mL) was added at 0 °C and the reaction mixture was stirred at this temperature for 1 h, and at room temperature for 1 h. The obtained reaction mixture was concentrated and dried under reduced pressure over 4 h. The crude product was dissolved in hot acetone and the residue was removed by filtration. The filtrate was concentrated to afford a potassium diynyltrifluoroborate (1.66 g, 55%) as colorless solids, which was submitted to the following procedure without further purification.

To a solution of the potassium diynyltrifluoroborate (1.60 g, 8.0 mmol) and 2,2-dimethyl-1,3-propanediol bis(trimethylsilyl) ether (1.99 g, 8.0 mmol) in dry acetone (16 mL) was added chlorotrimethylsilane (1.76 g, 16.2 mmol) at room temperature, and the solution was stirred overnight. The precipitates were removed by filtration under N_2 atmosphere, and the filtrate was concentrated in vacuo. The crude oil was purified by bulb-to-bulb distillation (120–130 °C/1.0 mmHg) to give **10a** (1.34 g, 81%) as colorless oil: IR (neat) 3285 (C≡CH), 2213 (C≡C) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.98 (s, 6H), 3.64 (s, 4H), 4.26 (d, J=2.1 Hz, 2H), 4.29 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.8, 31.8, 56.4, 56.8, 72.6, 72.9, 78.8; MS (EI): *m/z* (%): 205 (1) [M^+-H], 176 (100) [M^+-H_2CO], 151 (28) [$M^+-OCH_2C{\equiv}CH$]; EA calcd (%) for $C_{11}H_{15}BO_3$ (206.05): C 64.12, H 7.34; found: C 63.93, H 7.47.

Dinynylboronate **10b** was synthesized similarly: mp 43.1–44.3 °C; IR (neat) 2214 (C≡C) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.98 (s, 6H), 2.43 (t, J=2.1 Hz, 1H), 3.65 (s, 4H), 4.35 (s, 2H), 4.49 (s, 2H), 7.27–7.33 (m, 3H), 7.41–7.46 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.8, 31.8, 56.9, 57.3, 72.6, 84.1, 86.7, 122.3, 128.1, 128.4, 131.6; MS (EI): *m/z* (%): 282 (33) [M^+], 252 (87) [M^+-H_2CO], 166 (100) [$M^+-H-CH_2C{\equiv}CPh$]; EA calcd (%) for $C_{17}H_{19}BO_3{\cdot}H_2O$ (300.16): C 68.02, H 7.05; found: C 68.07, H 6.95.

4.1.2. Cycloaddition of α,ω-diyne with alkynylboronate: synthesis of arylboronate 4aa from ethynylboronate 2a and dipropargylmalonate 3a. To a solution of Cp*RuCl(cod) (**1**) (17.1 mg, 0.045 mmol) and ethynylboronate **2a** (248.2 mg, 1.80 mmol) in dry degassed 1,2-dichloroethane (4.5 mL) was added a solution of diyne **3a** (187.4 mg, 0.90 mmol) in dry degassed 1,2-dichloroethane (6 mL) over 1 h via syringe pump at room temperature under Ar atmosphere. The solution was stirred at room temperature under Ar atmosphere for 1 h, and then, the solvent was removed under reduced pressure. The residue was purified by silica gel flash column chromatography (hexane/AcOEt 15:1) to give **4aa** (266.5 mg, 86%) as colorless solids (mp 133.6–133.7 °C): IR (neat) 1732 (CO_2Me) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.01 (s, 6H), 3.59 (s, 2H), 3.60 (s, 2H), 3.73 (s, 6H), 3.75 (s, 4H), 7.19 (d, J=7.5 Hz, 1H), 7.62 (d, J=7.5 Hz, 1H), 7.64 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.9, 31.9, 40.4, 40.7, 52.9, 60.2, 72.2, 123.3, 129.4, 132.5, 138.9, 142.5, 171.8; MS (EI): *m/z* (%): 346 (29) [M^+], 286 (100) [M^+-H-CO_2Me], 227 (13) [$M^+-H-2CO_2Me$]; EA calcd (%) for $C_{18}H_{23}BO_6$ (346.18): C 62.45, H 6.70; found: C 62.41, H 6.69.

4.1.2.1. Compound 4ab. Mp 116.8–116.9 °C; IR ($CHCl_3$) 1699 (COMe) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.01 (s, 6H), 2.16 (s, 6H), 3.49 (s, 2H), 3.51 (s, 2H), 3.76 (s, 4H), 7.19 (d, J=7.5 Hz, 1H), 7.62 (d, J=7.5 Hz, 1H), 7.64 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.9, 26.6, 31.9, 37.5, 37.8, 72.2, 74.5, 123.6, 129.7, 132.7, 138.8, 142.4, 204.7; MS (EI): *m/z* (%): no molecular ion peak 271 (100) [M^+-COMe], 256 (41) [$M^+-Me-COMe$], 228 (18) [$M^+-2COMe$]; EA calcd (%) for $C_{18}H_{23}BO_4$ (314.18): C 68.81, H 7.38; found: C 68.85, H 7.46.

4.1.2.2. Compound 4ac. Mp 169.1–169.3 °C; IR ($CHCl_3$) 2967 (CN) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.03 (s, 6H), 3.72 (s, 2H), 3.73 (s, 2H), 3.77 (s, 4H), 7.28 (d, J=7.5 Hz, 1H), 7.73 (s, 1H), 7.75 (d, J=7.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.9, 31.8, 33.6, 44.6, 44.8, 72.3, 116.3, 123.9, 123.0, 134.04, 135.4, 138.5; MS (EI): *m/z* (%): 280 (100) [M^+], 237 (18) [$M^+-MeCHMe$]; EA calcd (%) for $C_{16}H_{17}BN_2O_2$ (280.13): C 68.60, H 6.12, N 10.00; found: C 68.32, H 6.20, N 9.98.

4.1.2.3. Compound 4ad. Mp 111.4–111.5 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 1.02 (s, 6H), 2.06 (quint, J=7.5 Hz, 2H), 2.92 (t, J=7.5 Hz, 4H), 3.77 (s, 4H), 7.24 (d, J=7.5 Hz, 1H), 7.60 (d, J=7.5 Hz, 1H), 7.69 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.0, 25.3, 31.9, 32.6, 33.1, 72.2, 123.6, 129.6, 131.7, 143.3, 147.0; MS (EI): *m/z* (%): 230 (100) [M^+], 187 (35) [$M^+-MeCHMe$]; EA calcd (%) for $C_{14}H_{19}BO_2$ (230.11): C 73.07, H 8.32; found: C 73.00, H 8.47.

4.1.2.4. Compound 4ae. Mp 195.8–196.1 °C; IR ($CHCl_3$) 1320, 1163 (NTs) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.00 (s, 6H), 2.39 (s, 3H), 3.74 (s, 4H), 4.62 (s, 4H), 7.15 (d, J=7.5 Hz, 1H), 7.30 (d, J=8.1 Hz, 1H), 7.60 (s, 1H), 7.66 (d, J=7.5 Hz, 1H), 7.76 (d, J=8.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6, 21.9, 32.0, 53.6, 53.9, 72.3, 121.7, 127.5, 127.9, 129.7, 133.2, 133.6, 135.3, 138.5, 143.5; MS (EI): *m/z* (%): 385 (91) [M^+], 330 (100) [M^+-NTs]; EA calcd (%) for $C_{20}H_{24}BNO_4S$ (385.28): C 62.35, H 6.28, N 3.64; found: C 62.28, H 6.34, N 3.56.

4.1.2.5. Compound 4af. ^1H NMR (300 MHz, $CDCl_3$): δ 1.03 (s, 6H), 3.78 (s, 4H), 5.11 (s, 4H), 7.23 (d, J=7.5 Hz, 1H), 7.68 (s, 1H), 7.71 (d, J=7.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.0, 32.0, 72.3, 73.5, 73.6, 120.1, 126.2, 132.9, 138.3, 141.6; MS (EI): *m/z* (%): 232 (100) [M^+], 217 (22) [M^+-Me], 204 (93) [M^+-CO]; EA calcd (%) for $C_{13}H_{17}BO_3$ (232.08): C 67.28, H 7.38; found: C 67.09, H 7.57.

4.1.2.6. Compound 4ag. Mp 116.7–116.8 °C; IR ($CHCl_3$) 1732 (CO_2Et) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.01 (s, 6H), 1.20 (t, J=7.2 Hz, 12H), 3.52

(s, 2H), 3.54 (s, 2H), 3.75 (s, 4H), 4.12–4.23 (m, 8H), 7.07 (d, J=7.5 Hz, 1H), 7.52 (s, 1H), 7.53 (d, J=7.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 22.0, 31.9, 34.6, 34.9, 57.5, 61.7, 72.3, 127.4, 131.4, 131.7, 133.8, 135.3, 169.7, 169.8; MS (EI): *m/z* (%): 532 (42) [M^+], 487 (32) [M^+-OEt], 459 (31) [M^+-CO_2Et], 413 (70) [$M^+-HOEt-CO_2Et$], 385 (50) [$M^+-H-2CO_2Et$], 339 (100) [$M^+-H-HOEt-2CO_2Et$]; EA calcd (%) for $C_{27}H_{37}BO_{10}$ (532.39): C 60.91, H 7.01; found: C 61.11, H 7.25.

4.1.2.7. Compound 4ah. Mp 192.6–193.0 °C; IR ($CHCl_3$) 1673 (quinone) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.05 (s, 6H), 3.83 (s, 4H), 7.78–7.82 (m, 2H), 8.20 (dd, J=7.8, 1.2 Hz, 1H), 8.28 (dd, J=7.8, 0.3 Hz, 1H), 8.30–8.35 (m, 2H), 8.75 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.9, 32.0, 72.4, 125.9, 126.93, 127.0, 132.2, 132.7, 133.4, 133.4, 133.7, 133.9, 134.5, 139.1, 183.0, 183.2; MS (EI): *m/z* (%): 320 (100) [M^+], 280 (85) [$M^+-C_3H_4$], 235 (95) [$M^+-CH_2C(Me)_2CHO$]; EA calcd (%) for $C_{19}H_{17}BO_4$ (320.15): C 71.28, H 5.35; found: C 71.05, H 5.53.

4.1.2.8. Compound 4ba. Mp 38.0–40.8 °C; IR (neat) 1738 (CO_2Me) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.91 (t, J=7.2 Hz, 3H), 1.03 (s, 6H), 1.35 (sext, J=7.2 Hz, 2H), 1.46–1.57 (m, 2H), 2.81 (t, J=7.8 Hz, 2H), 3.55 (s, 4H), 3.73 (s, 6H), 3.75 (s, 4H), 6.99 (s, 1H), 7.55 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 21.9, 22.9, 31.6, 35.5, 35.7, 40.2, 40.7, 52.9, 60.4, 72.2, 125.0, 130.3, 136.1, 141.9, 148.2, 172.0; MS (EI): *m/z* (%): 402 (44) [M^+], 342 (100) [M^+-H-CO_2Me], 299 (24) [M^+-H-CO_2Me-Pr]; EA calcd (%) for $C_{22}H_{31}BO_6\cdot H_2O$ (420.30): C 62.87, H 7.91; found: C 62.79, H 7.98.

4.1.2.9. Compound 4ai. Mp 160.1–160.5 °C; IR ($CHCl_3$) 1732 (CO_2Me) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): *meta*-**4ai** δ 1.01 (s, 6H), 2.26 (s, 3H), 3.54 (s, 2H), 3.60 (s, 2H), 3.74 (s, 6H), 3.75 (s, 4H), 7.43 (s, 1H), 7.47 (s, 1H); *ortho*-**4ai** δ 1.02 (s, 6H), 2.42 (s, 3H), 3.55 (s, 2H), 3.60 (s, 2H), 3.74 (s, 6H), 3.76 (s, 4H), 7.01 (d, J=7.5 Hz, 1H), 7.57 (d, J=7.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): *meta*-**4ai** δ 18.9, 21.9, 31.9, 39.6, 40.6, 52.9, 59.8, 72.2, 120.5, 126.8, 133.3, 138.8, 141.5, 172.0; *ortho*-**4ai** δ 18.5, 21.9, 31.6, 39.9, 41.0, 52.9, 59.5, 72.2, 132.7, 134.0, 138.7, 139.5, 141.4, 172.1; MS (EI): *m/z* (%): 360 (31) [M^+], 300 (100) [M^+-H-CO_2Me]; EA calcd (%) for $C_{19}H_{25}BO_6$ (360.21): C 63.35, H 7.00; found: C 63.27, H 7.01.

4.1.2.10. Compound 4aj. Mp 116.1–116.2 °C; IR (neat) 1721 (CO_2Me) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.02 (s, 6H), 2.21 (s, 3H), 2.39 (s, 3H), 3.54 (s, 2H), 3.56 (s, 2H), 3.75 (s, 6H), 3.76 (s, 4H), 7.39 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.3, 18.6, 21.9, 31.7, 39.9, 40.2, 53.0, 59.3, 72.2, 129.6, 134.7, 136.6, 138.6, 140.4, 172.2; MS (EI): *m/z* (%): 374 (45) [M^+], 314 (100) [M^+-H-CO_2Me]; EA calcd (%) for $C_{20}H_{27}BO_6$ (374.24): C 64.19, H 7.27; found: C 64.13, H 7.54.

4.1.2.11. Compound 11a. Mp 95.3–95.4 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.02 (s, 6H), 3.76 (s, 4H), 5.09–5.11 (m, 2H), 5.25 (t, J=2.1 Hz, 2H), 7.23–7.32 (m, 2H), 7.69–7.72 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.9, 31.9, 72.2, 73.0, 75.0, 122.9, 126.3, 133.0, 138.0, 145.3; MS (EI): *m/z* (%): 231 (72) [M^+-H], 204 (100) [M^+-CO], 145 (49) [$M^+-OCH_2C(CH_3)_3$]; EA calcd (%) for $C_{13}H_{17}BO_3$ (232.08): C 67.28, H 7.38; found: C 67.26, H 7.40.

4.1.2.12. Compound 11b. Mp 101.6–102.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.04 (s, 6H), 3.79 (s, 4H), 5.21 (t, J=2.1 Hz, 2H), 5.32 (t, J=2.1 Hz, 2H), 7.34 (d, J=7.5 Hz, 1H), 7.36–7.46 (m, 5H), 7.82 (d, J=7.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.9, 31.9, 72.2, 72.9, 75.1, 126.5, 127.4, 127.7, 128.5, 133.9, 136.0, 137.9, 140.1, 146.3; MS (EI): *m/z* (%): 308 (89) [M^+], 280 (100) [M^+-CO]; EA calcd (%) for $C_{19}H_{21}BO_3$ (308.18): C 74.05, H 6.87; found: C 74.07, H 6.98.

4.1.2.13. Compound 11c. Mp 86.3–86.5 °C; ca. 1:1 mixture of *ortho* and *meta* isomers: ^{1}H NMR (300 MHz, $CDCl_3$): *ortho*-**11b** δ 0.95 (t, J=7.2 Hz, 3H), 1.05 (s, 6H), 1.31–1.45 (m, 2H), 1.51–1.67 (m, 2H), 2.87 (t, J=7.8 Hz, 2H), 3.77 (s, 3H), 5.07–5.09 (m, 2H), 5.20–5.23 (m, 2H), 7.08 (d, J=7.8 Hz, 1H), 7.15 (d, J=7.8 Hz, 1H); *meta*-**11b** δ 0.94 (t, J=7.2 Hz, 3H), 1.02 (s, 6H), 1.31–1.45 (m, 2H), 1.51–1.67 (m, 2H), 2.64 (t, J=7.8 Hz, 2H), 3.76 (s, 3H), 5.07–5.09 (m, 2H), 5.20–5.23 (m, 2H), 7.12 (s, 1H), 7.54 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.04 and 14.07, 21.90 and 21.91, 22.5 and 22.8, 31.6 and 31.8, 34.1 and 35.9, 35.47 and 35.51, 72.0 and 72.1, 72.9 and 73.1, 74.9 and 75.1, 121.8 and 122.9, 128.3 and 133.2, 135.2 and 138.3, 141.0 and 142.7, 145.3 and 148.1; MS (EI): *m/z* (%): 286 (31) [M^+], 243 (25) [$M^+-CH_2CH_2CH_3$]; EA calcd (%) for $C_{17}H_{25}BO_3$ (288.19): C 70.85, H 8.74; found: C 70.85, H 8.73.

4.1.2.14. Compound 11d. Mp 65.8–66.2 °C; ca. 7:3 mixture of *ortho* and *meta* isomers: IR (neat) 1720 (CO_2Me) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): *ortho*-**11c** δ 1.04 (s, 6H), 3.38 (s, 3H), 3.75 (s, 4H), 4.65 (s, 2H), 5.06 (s, 2H), 5.19 (t, J=1.8 Hz, 2H), 7.19 (d, J=7.5 Hz, 1H), 7.25 (d, J=7.5 Hz, 1H); *meta*-**11c** δ 1.01 (s, 6H), 3.38 (s, 3H), 3.75 (s, 4H), 4.46 (s, 2H), 5.08 (s, 2H), 5.22 (t, J=1.8 Hz, 2H), 7.29 (s, 1H), 7.65 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): *ortho*-**11c** δ 21.9, 31.7, 58.1, 72.1, 73.0, 74.3, 74.8, 121.7, 126.7, 137.3, 142.5, 145.1; *meta*-**11c** δ 21.9, 31.9, 58.1, 72.2, 72.9, 74.6, 74.9, 122.5, 132.9, 136.4, 138.6, 145.0; MS (EI): *m/z* (%): 279 (100) [M^+], 248 (28) [M^+-HOMe]; EA calcd (%) for $C_{15}H_{21}BO_4$ (276.14): C 65.24, H 7.67; found: C 65.35, H 7.56.

4.1.2.15. Compound 13a. Oil; ca. 1:1 mixture of *ortho* and *meta* isomers: ^{1}H NMR (300 MHz, $CDCl_3$): *ortho*-**13a** δ 0.92 (t, J=7.2 Hz, 3H), 1.36 (sept, J=7.2 Hz, 2H), 1.50–1.65 (m, 2H), 2.92 (t, J=7.8 Hz, 2H), 3.88 (s, 3H), 5.08 (s, 2H), 5.24 (t, J=1.8 Hz, 2H), 7.17 (d, J=7.8 Hz, 1H), 7.24 (d, J=7.8 Hz, 1H); *meta*-**13a** δ 0.92 (t, J=7.2 Hz, 3H), 1.02 (s, 6H), 1.36 (sept, J=7.2 Hz, 2H), 1.50–1.65 (m, 2H), 2.66 (t, J=7.8 Hz, 2H), 3.90 (s, 3H), 5.09 (s, 2H), 5.34 (t, J=1.8 Hz, 2H), 7.23 (s, 1H), 7.74 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.98 and 14.03, 22.3 and 22.8, 33.7 and 35.3, 34.0 and 34.3, 51.7 and 52.0, 72.9 and 73.1, 74.8 and 74.9, 123.7 and 125.3, 123.9 and 124.0, 128.7 and 130.3, 137.5 and 138.9, 140.6 and 141.2, 142.7 and 143.6, 166.4 and 167.4; MS (EI): *m/z* (%): 234 (100) [M^+], 217 (93) [M^+-H-Me], 206 (42) [M^+-CO], 189 (64)

[$M^+-2H-CH_2CH_2CH_3$]; EA calcd (%) for $C_{14}H_{18}O_3$ (234.29): C 71.77, H 7.74; found: C 71.67, H 7.79.

4.1.2.16. Compound 13b. Analyses other than ^1H NMR were omitted because **13b** was obtained as a mixture with the cyclotrimers of methyl propargyl ether. The yield and regioisomer ratio were determined by ^1H NMR analysis. ^1H NMR (300 MHz, $CDCl_3$): *ortho*-**13b** δ 3.45 (s, 3H), 3.90 (s, 3H), 4.82 (s, 2H), 5.12 (s, 2H), 5.28 (t, $J=1.8$ Hz, 2H), 7.26 (dd, $J=7.8$, 1.8 Hz, 1H), 7.55 (d, $J=7.8$ Hz, 1H); *meta*-**13b** δ 3.41 (s, 3H), 3.91 (s, 3H), 4.50 (s, 2H), 5.12 (s, 2H), 5.38 (t, $J=1.8$ Hz, 2H), 7.42 (s, 1H), 7.89 (s, 1H).

4.1.3. Suzuki–Miyaura coupling of arylboronates. To a solution of arylboronate **4aa** (104.0 mg, 0.30 mmol) and *p*-iodoacetophenone (111.8 mg, 0.45 mmol) in dry DMF (2 mL) was added $Pd_2(dba)_3\cdot CHCl_3$ (8.0 mg, 0.0077 mmol), PCy_3 (8.7 mg, 0.041 mmol), and K_3PO_4 (99.2 mg, 0.47 mmol). The mixture was degassed at −78 °C, and stirred at 100 °C under Ar atmosphere for 4 h. The reaction mixture was diluted with distilled water (10 mL) and extracted with AcOEt (5 mL×3). The organic layer was washed with brine (5 mL), dried with $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/AcOEt 20:1) to give **14** (82.9 mg, 80%) as colorless solids (mp 98.8–99.4 °C): IR ($CHCl_3$) 1733 (CO_2Me), 1680 (COMe) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.63 (s, 3H), 3.65 (s, 2H), 3.67 (s, 2H), 3.77 (s, 6H), 7.29 (d, $J=8.1$ Hz, 1H), 7.44 (d, $J=8.1$ Hz, 1H), 7.45 (s, 1H), 7.65 (d, $J=8.4$ Hz, 2H), 8.01 (d, $J=8.4$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.7, 40.4, 40.6, 53.1, 60.5, 123.0, 124.6, 126.2, 127.1, 127.3, 128.8, 135.6, 138.9, 140.1, 140.7, 145.7, 171.8, 197.5; MS (EI): *m/z* (%): 352 (79) [M^+], 292 (100) [M^+-H-CO_2Me], 277 (22) [M^+-H-CO_2Me-Me]; EA calcd (%) for $C_{21}H_{20}O_5$ (352.38): C 71.58, H 5.72; found: C 71.68, H 5.60.

The Suzuki–Miyaura coupling of **11a** with *p*-iodoacetophenone was carried out in the same manner to give **15**: mp 109.8–110.1 °C; IR ($CHCl_3$) 1681 (COMe) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.64 (s, 3H), 5.18–5.19 (m, 4H), 7.27–7.42 (m, 3H), 7.47–7.52 (m, 2H), 8.01–8.05 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.7, 73.3, 73.6, 120.6, 127.2, 127.9, 128.0, 128.6, 134.7, 135.9, 137.0, 140.1, 144.7, 197.3; MS (EI): *m/z* (%): 238 (100) [M^+], 223 (42) [M^+-Me], 209 (38) [M^+-H-CO], 195 (75) [M^+-COMe]; EA calcd (%) for $C_{16}H_{14}O_2$ (238.28): C 80.65, H 5.92; found: C 80.52, H 5.91.

4.1.4. Methoxycarbonylation of arylboronates. To a solution of arylboronate **4aa** (104.4 mg, 0.30 mmol) in dry MeOH (3 mL) was added $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), PPh_3 (9.3 mg, 0.035 mmol), and *p*-benzoquinone (32.6 mg, 0.30 mmol). The mixture was stirred at room temperature under CO atmosphere for 2 h. The reaction mixture was concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/AcOEt 15:1) to give **16** (68.4 mg, 77%) as colorless solids (mp 90.1–90.3 °C): IR ($CHCl_3$) 1735 (CO_2Me) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.63 (s, 4H), 3.75 (s, 6H), 3.89 (s, 3H), 7.26 (d, $J=8.1$ Hz, 1H), 7.86–7.88 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 40.2, 40.6, 52.0, 53.1, 60.3, 124.0, 125.3, 128.6, 129.0, 140.1, 145.2, 166.8, 171.5; MS (EI): *m/z* (%): 292 (39) [M^+], 261 (23) [M^+-OMe], 232 (100) [M^+-H-CO_2Me], 201 (43) [$M^+-HOMe-CO_2Me$], 173 (51) [$M^+-H-2CO_2Me$]; EA calcd (%) for $C_{15}H_{15}O_6$ (292.28): C 61.64, H 5.52; found: C 61.50, H 5.62.

The methoxycarbonylation of **4ah** and **11a** were carried out in a similar manner. The spectral data for **18** was in good agreement with those reported previously.[28]

Compound **20** mp 61.1–61.3 °C; IR ($CHCl_3$) 1717 (COMe) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.91 (s, 4H), 5.12–5.15 (m, 2H), 5.39 (t, $J=2.1$ Hz, 2H), 7.33–7.44 (m, 2H), 7.91–7.95 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.0, 72.9, 74.8, 124.3, 125.2, 127.4, 128.6, 140.4, 141.5, 166.2; MS (EI): *m/z* (%): 178 (2) [M^+], 149 (100) [M^+-H-CO]; EA calcd (%) for $C_{10}H_{10}O_3$ (178.18): C 67.41, H 5.66; found: C 67.17, H 5.72.

4.1.5. Oxidation of arylboronates. To a solution of arylboronate **4aa** (104.0 mg, 0.30 mmol) in THF (3.5 mL) was added a basic solution of H_2O_2 (30% aq H_2O_2 0.5 mL + 1 N NaOH 1 mL) at room temperature. The mixture was stirred at room temperature for 15 min. The reaction mixture was diluted with satd NH_4Cl (5 mL) and extracted with AcOEt (5 mL×3). The organic layer was washed with brine (5 mL), dried with $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography (hexane/AcOEt 10:1) to give **17** (69.5 mg, 93%) as colorless oil: IR (neat) 2449 (OH), 1723 (CO_2Me) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.51 (s, 2H), 3.54 (s, 2H), 3.74 (s, 6H), 4.57 (br s, 1H), 6.63 (dd, $J=8.4$, 2.7 Hz, 1H), 6.67 (m, 1H), 7.03 (d, $J=8.4$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 39.8, 40.6, 53.1, 60.8, 111.1, 114.1, 124.8, 131.4, 141.3, 155.0, 172.1; MS (EI): *m/z* (%): 250 (35) [M^+], 190 (100) [M^+-H-CO_2Me], 131 (55) [$M^+-H-2CO_2Me$]; EA calcd (%) for $C_{13}H_{14}O_5$ (250.25): C 62.39, H 5.64; found: C 62.37, H 5.67.

The oxidation of **4ah** and **11a** were carried out in a similar manner. The spectral data for **19** and **21** were in good agreement with those reported previously.[29,32]

4.2. Computational methods

The Q-chem 2.0 program[33] in Spartan'02 software package[34] was used for geometry optimizations, and atomic charges for the optimized geometries were obtained with the Gaussian 98 program package.[35] The geometries of ruthenacycles **I–VI** were fully optimized by means of the Becke's three-parameter hybrid density functional method (B3LYP)[36] with the LACVP* basis set, which uses a double-ζ basis set with the relativistic effective core potential of Hay and Wadt (LanL2 ECP)[37] for Ru and the 6-31G(d)[38] basis sets for other elements. Natural charges were computed at the B3LYP/LACVP* level using the natural population analysis method as implemented in Gaussian 98.[39]

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