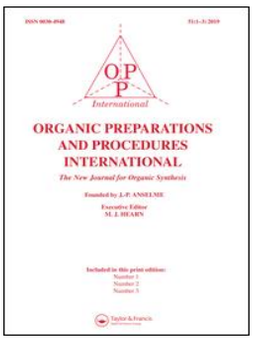

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EXPERIMENTAL PAPER

General Method for the Synthesis of Substituted Cyclopentenones via α-Borylzirconacyclopentene Intermediates

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The substituted cyclopentenone unit is a common scaffold in numerous natural products and pharmaceuticals.[1] As well, the cyclopentene moiety is also an important functional group in the prostaglandins (PGs).[2] For example, prostaglandin analogs (PGAs) have long been known to be involved in the control of renal function, hormone regulation, and vaso- and broncho-dilatation.[3] Moreover, these scaffolds are useful as agricultural chemicals, perfumes and as general intermediates in organic synthesis.[4] The α,β-unsaturated carbonyl structure is crucial in such varied biological processes as the inhibition of tumors, viruses and inflammation.[5,6]

Several methodologies for the synthesis of substituted cyclopentenones have thus been reported;[7,8] these have included the Nazarov cyclization,[9] the Pauson-Khand reaction[10] and the use of metal-carbonyl complexes.[11,12] However, given their significance, there is still considerable room for improvement in the preparation of these compounds. As background, we noted that using the reagent Cp_2ZrCl_2/2EtMgBr together with 1-alkynylboronates[13] leads to the regioselective formation of zirconacyclopentene boronate intermediates of Type **3** (Scheme 1).[14,15]

Syntheses of cyclopentenone boronates are yet to be reported, but these structures would be highly valued intermediates in organic synthesis and could be useful partners in such cross-coupling reactions as the Suzuki- Miyaura coupling.[16–20]

Herein we report for the first time the synthesis of cyclopentenone boronic acids under mild conditions using a simple work-up. The present method gives excellent results and offers a direct method for the synthesis of functionalized cyclopentenones. A number of zirconacyclopentenylboronates were treated with oxalyl chloride in THF at 0 °C to yield the corresponding cyclopentenone boronic acids (Table 1, Table 2).

Thus, alkyne boronate **2a** prepared by borylation of 1-heptyne (Table 1)[13] was chosen as a model to test our hypothesis. The zirconacyclopentenylboronate Type **3** intermediate was prepared by reacting two equivalents of the Cp_2ZrCl_2/2EtMgBr reagent with the 1-alkynylboronate. We found an efficient system for the desired transformation to **4a** could be made from the combination of CuCl catalyst in the presence of N,N'-

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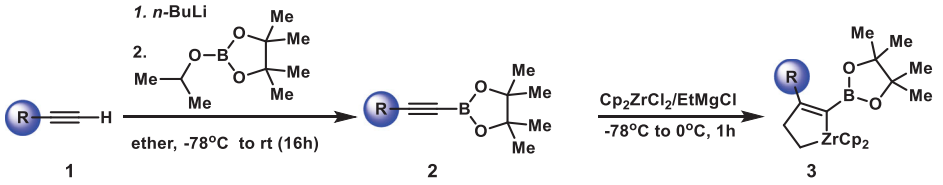
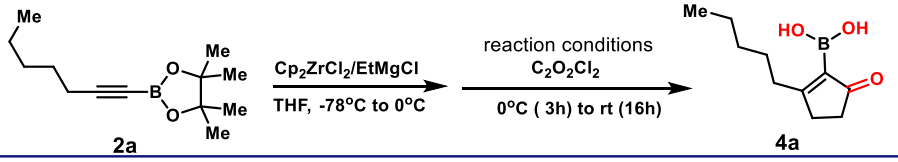


Scheme 1. Synthesis of zirconacyclopentenylboronates.

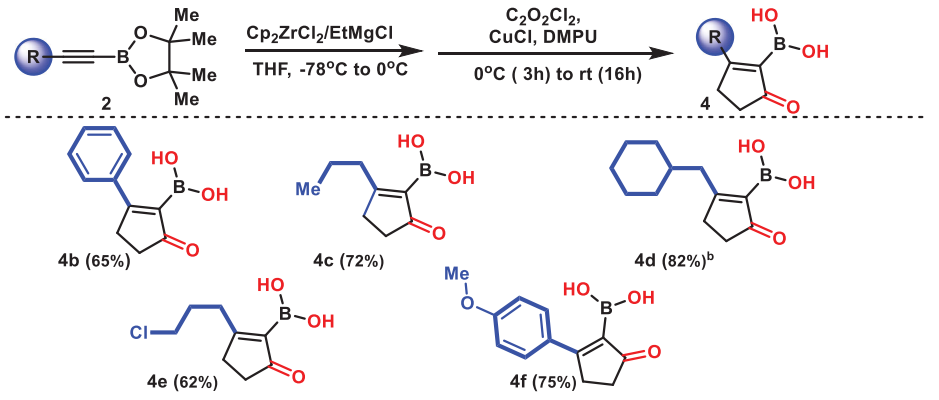
Table 1. Conditions for carbonylation of α-zirconacyclopentene boronates.[a]



Entry	Catalyst (10%)	Additive	% yield[b]
1	–	–	0
2	CuCl	–	15
3	CuI	–	Traces
4	CuI	DMPU	25
5	CuCl	DMPU	84 (75)[c]
6	CuCl (50 mol%)	DMPU	60[d]
7	$CuBr.S(CH_3)_2$	DMPU	Traces
8	$ZnCl_2$	DMPU	0
9	$CoCl_2$	DMPU	0
10	$CrCl_3$	DMPU	0

[a]All reactions were performed with 0.2 mmol of the substrate.
[b]GC yield.
[c]Isolated yield.
[d]Reduction of ethylated product was obtained as side-product.

Table 2. Access to substituted cyclopentenone boronic acids.[a]



[a]Isolated yields, 0.5 mmol scale.
[b]The molecular structure of 2-(cyclohexylmethyl)-5-oxocyclopent-1-enylboronic acid was determined by X-ray.

dimethyl-N,N'-trimethyleneurea (DMPU). In the absence of any catalyst and additive, no product **4a** was detected, and only the reduction of ethylated product was obtained (Entry 1, Table 1).

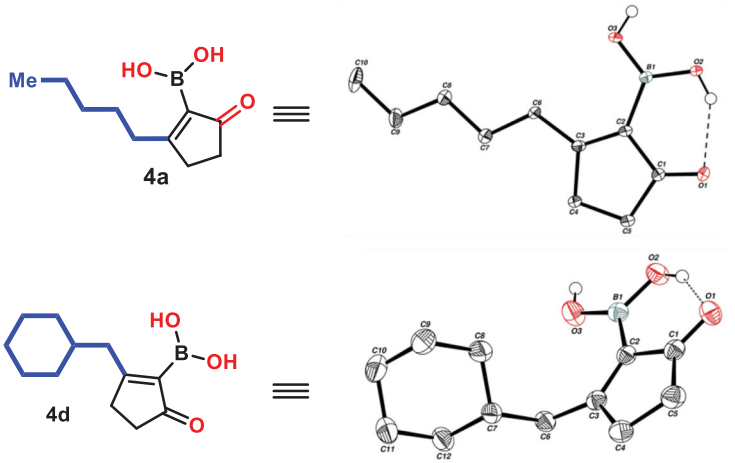


Figure 1. View of molecular structures of **4a** and **4d**.

When the α-zirconacyclopentene boronate intermediate was treated with oxalyl dichloride in the presence of freshly prepared CuCl catalyst it gave 15% of product **4a**. With a catalytic amount of CuI catalyst, the **α**-borylcyclopentenone product **4a** was only detected in trace amounts. When the α-zirconacyclopentene boronate intermediate was treated with oxalyl dichloride in the presence of a catalytic amount (10 mol%) of CuI and DMPU, the yield of α-borylcyclopentenone product **4a** was 25% (Entry 4). Fuller conversion occurred in the presence of 10 mol% CuCl catalyst (Entry 5). Other metal chloride catalysts did not show any conversion to **4a** (Entries 7-10).

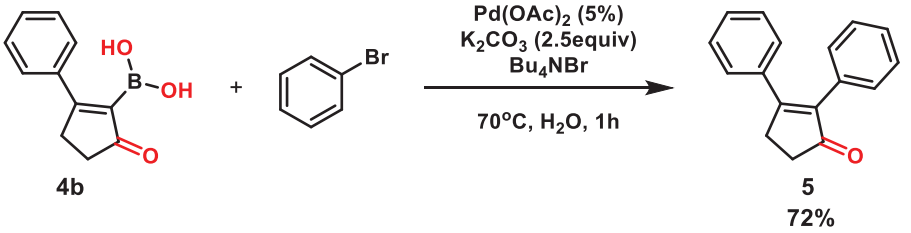
Our procedure was applied to several other alkyneboronates of Type **2** (Scheme 1). The designed precursors were then subjected to the carbonylation conditions to provide the corresponding α-borylcyclopentenone products in a regioselective manner and in good yields (Table 2). Under these conditions, acyclic, cyclic, aromatic and halogenated substituents were tolerated.

All the prepared compounds were characterized by ^{1}H NMR, ^{13}C NMR, ^{11}B NMR and HRMS. X-ray crystal structures were recorded using single crystal X-ray analysis for compounds **4a** and **4d** (Figure 1). The ^{11}B NMR chemical shift observed in the region (26.04-29.10 ppm) is expected for vinylboronate compounds.

The mechanism of this reaction is proposed to follow Cu(I)-catalyzed or -mediated reactions of organozirconium compounds as described by Xi's group.[20,21] The α-borylzirconacyclopentene intermediate undergoes transmetallation with CuCl followed by coordination of a carbonyl oxygen from oxalyl chloride to form a seven membered transition state. The cyclopentenone boronate moiety is generated upon intramolecular nucleophilic attack and elimination of CuCl, CO gas and zirconocene dichloride. Finally, using aqueous HCl during the workup gives the cyclopentenone product.

As an illustration of the preparation of a substituted cyclopentenone, cyclopentenone boronic acid **4b** was reacted with bromobenzene in the presence of $Pd(OAc)_2$ catalyst,[22] affording the corresponding coupling product **5** (Scheme 2) in good yield.

In conclusion, we have developed a method for the preparation of functionalized cyclopentenone derivatives which can be obtained from readily available starting



Scheme 2. Coupling of cyclopentenone boronic acid with bromobenzene.

materials. The introduction of the boronic acid functional group at the α-position of an α,β-unsaturated carbonyl moiety would be very useful for further functionalization of these scaffolds. We hope that this work will find direct application in the synthesis of bioactive natural products and their structural analogues.

Experimental section

Proton, carbon and boron NMR spectra were recorded on a Varian Mercury 300 MHz spectrometer in deuterated solvent. Proton chemical shifts are reported in ppm (δ) relative to tetramethylsilane with the solvent resonance employed as the internal standard ($CDCl_3$, δ 7.26 ppm). ^{13}C chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ 77.0 ppm). ^{11}B chemical shifts are reported in ppm. X-ray crystallographic data were recorded using single crystal X-ray analysis on X-ray diffractometer system (Bruker SMART APEX CCD). X-ray crystal structures were recorded using single crystal X-ray analysis for compounds **4a** and **4d**; and the complete data are available from the corresponding author upon request.

Synthesis of boronates

Following a literature procedure,[13] 2-isopropyloxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was prepared by the borylation reaction of pinacol with triisopropylborate. The borate ester reacted with 1-alkynyllithium to produce, after treatment with anhydrous hydrogen chloride, the corresponding 1-alkynylpinacolatoborane. Compounds **2a**, **2b**, **2f**[23], **2c**[24], **2d**[25] and **2e**[26] were previously described.

Typical procedure for the synthesis of α-borylcyclopentenone

To zirconocene dichloride (0.75 mmol, 1.5 equiv.) dissolved in 5 mL of dry THF at −78 °C was added 0.75 mL of 2 M EtMgCl (1.5 mmol, 3 equiv.) dropwise in a 25 mL round-bottom flask. After being stirred for 1 h at −78 °C, (0.5 mmol, 1 equiv.) of the corresponding alkyne boronate was added. The reaction was gradually warmed to 0 °C, stirred for 3 h. Then 0.005 g (0.05 mmol, 0.1 equiv.) of CuCl, 0.12 mL (2 mmol, 4 equiv.) of DMPU and 0.065 mL (0.75 mmol, 1.5 equiv.) oxalyl chloride were added to the reaction mixture and stirred for 1h at 0 °C. The reaction was warmed to room temperature and allowed to stir for 2h. The reaction mixture was quenched with dilute HCl solution and extracted with ethyl acetate. The organic layer was dried (Na_2SO_4), filtered and

concentrated *in vacuo*. The crude product was purified by flash chromatography (SiO_2, 30% EtOAc/hexanes).

5-Oxo-2-pentylcyclopent-1-enylboronic acid (4a)

The above procedure was applied by using zirconocene dichloride (0.44 g, 0.75 mmol), 2 M EtMgCl (0.75 mL, 1.5 mmol), 2-(hept-1-ynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (112 mg, 0.5 mmol), CuCl (5 mg, 0.05 mmol), DMPU (0.12 mL, 2 mmol) and oxalyl chloride (0.065 mL, 0. 75 mmol) in dry THF. The crude product was purified by flash chromatography (SiO_2, 30% EtOAc/hexanes) to yield 5-oxo-2-pentylcyclopent-1-enylboronic acid (82 mg, 75%, white solid). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 6.54 (s, 1H), 2.82 (t, 2H), 2.69-264 (m, 2H), 2.49-2.43 (m, 2H), 1.69-1.58 (m, 6H), 0.98 (t, $J = 7.4$ Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 218.32, 197.20, 133.70, 35,55, 35,50,35.40, 34.75,34.70, 34.60, 34.10, 21.43, 15.10. **^{11}B NMR** (96.24 MHZ): δ 26.97. **GC-MS** (EI, *m/z*): 197 (M^+). **HRMS** ($[M + Na]^+$): Calcd for $C_{10}H_{17}BO_3Na$, m/z 219.1168. Found, m/z 219.1164.

(5-Oxo-2-phenylcyclopent-1-en-1-yl)boronic acid (4b)

The above procedure was applied by using zirconocene dichloride (0.44 g, 0.75 mmol), 2 M EtMgCl (0.75 mL, 1.5 mmol), 4,4,5,5-tetramethyl-2-(phenylethynyl)-1,3,2-dioxaborolane (114 mg, 0.5 mmol), CuCl (5 mg, 0.05 mmol), DMPU (0.12 mL, 2 mmol) and oxalyl chloride (0.065 mL, 0. 75 mmol) in dry THF. The crude product was purified by flash chromatography (SiO_2, 30% EtOAc/hexanes) to yield (5-oxo-2-phenylcyclopent-1-en-1-yl)boronic acid (65 mg, 65%, white solid). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.36-7.20 (m, 5H), 2.98-2.91 (m, 2H), 2.72-2.69 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 218.60, 198.20, 138.16, 132,30, 131.36, 129.15, 128.50, 127.72, 35.62, 26.12. **^{11}B NMR** (96.24 MHZ): δ 27.86. **HRMS** ($[M + Na]^+$): Calcd for $C_{11}H_{11}BO_3Na$, m/z 225.0699. Found, m/z 225.0694.

(5-Oxo-2-propylcyclopent-1-en-1-yl)boronic acid (4c)

The above procedure was applied by using zirconocene dichloride (0.44 g, 0.75 mmol), 2 M EtMgCl (0.75 mL, 1.5 mmol), 4,4,5,5-tetramethyl-2-(pent-1-yn-1-yl)-1,3,2-dioxaborolane (97 mg, 0.5 mmol), CuCl (5 mg, 0.05 mmol), DMPU (0.12 mL, 2 mmol) and oxalyl chloride (0.065 mL, 0. 75 mmol) in dry THF. The crude product was purified by flash chromatography (SiO_2, 30% EtOAc/hexanes) to yield (5-oxo-2-propylcyclopent-1-en-1-yl)boronic acid (60 mg, 72%, white solid). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 6.64 (s, 2H), 2.79 (t, $J = 7.5$, 2H), 2.73 – 2.56 (m, 2H), 2.54 – 2.39 (m, 2H), 1.68 – 1.60 (m, 2H), 0.99 (t, $J = 7.4$ Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 218.92, 198.83, 133.91, 36.63, 36.49, 33.51, 22.64, 15.10. **^{11}B NMR** (96.24 MHZ): δ 26.04. **HRMS** ($[M + Na]^+$): Calcd for $C_8H_{13}BO_3Na$, m/z 191.0855. Found, m/z 191.0853.

(2-(Cyclohexylmethyl)-5-oxocyclopent-1-en-1-yl)boronic acid (4d)

The above procedure was applied by using zirconocene dichloride (0.44 g, 0.75 mmol), 2 M EtMgCl (0.75 mL, 1.5 mmol), 2-(3-cyclohexylprop-1-yn-1-yl)-4,4,5,5-tetramethyl-1,3,2-

dioxaborolane (124 mg, 0.5 mmol), CuCl (5 mg, 0.05 mmol), DMPU (0.12 mL, 2 mmol) and oxalyl chloride (0.065 mL, 0. 75 mmol) in dry THF. The crude product was purified by flash chromatography (SiO_2, 30% EtOAc/hexanes) to yield (2-(cyclohexylmethyl)-5-oxocyclopent-1-en-1-yl)boronic acid (91 mg, 82%, white solid). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 6.36 (s, 2H), 2.77 (d, $J = 9$, 2H), 2.68 – 2.63 (m, 2H), 2.50 – 2.45 (m, 2H), 1.75 – 58 (m, 6H), 1.32 – 1.12 (m, 4H), 1.12-1.00 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 218.40, 197.47. 131.87, 41.64, 37.20, 35.34, 33.58, 26.50, 26.30 (3peaks inside $CDCl_3$ peak). **^{11}B NMR** (96.24 MHZ): δ 29.10. **HRMS** ($[M + Na]^+$): Calcd for $C_{12}H_{19}BO_3Na$ m/z, 245.1325. Found, m/z 245.1322.

(2-(3-Chloropropyl)-5-oxocyclopent-1-en-1-yl)boronic acid (4e)

The above procedure was applied by using zirconocene dichloride (0.44 g, 0.75 mmol), 2 M EtMgCl (0.75 mL, 1.5 mmol), 2-(5-chloropent-1-yn-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (114 mg, 0.5 mmol), CuCl (5 mg, 0.05 mmol), DMPU (0.12 mL, 2 mmol) and oxalyl chloride (0.065 mL, 0. 75 mmol) in dry THF. The crude product was purified by flash chromatography (SiO_2, 30% EtOAc/hexanes) to yield (2-(3-chloropropyl)-5-oxocyclopent-1-en-1-yl)boronic acid (62 mg, 62%, white solid). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 6.22 (s, 2H), 3.64 (t, $J = 7.5$, 2H), 2.98 – 2.93 (m, 2H), 2.21 – 2.17 (m, 2H), 2.09 – 2.05 (m, 6H), 1.63 – 1.59 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 218.70, 196.87. 132.10, 44.64, 37.80, 32.30, 31.58, 27.60. **^{11}B NMR** (96.24 MHZ): δ 27.22. **HRMS** ($[M + Na]^+$): Calcd for $C_8H_{12}BClO_3Na$, m/z 225.0466. Found, m/z 225.0462.

(2-(4-Methoxyphenyl)-5-oxocyclopent-1-en-1-yl)boronic acid (4f)

The above procedure was applied by using zirconocene dichloride (0.44 g, 0.75 mmol), 2 M EtMgCl (0.75 mL, 1.5 mmol), 2-((4-methoxyphenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (130 mg, 0.5 mmol), CuCl (5 mg, 0.05 mmol), DMPU (0.12 mL, 2 mmol) and oxalyl chloride (0.065 mL, 0. 75 mmol) in dry THF. The crude product was purified by flash chromatography (SiO_2, 30% EtOAc/hexanes) to yield (2-(4-methoxyphenyl)-5-oxocyclopent-1-en-1-yl)boronic acid (87 mg, 75%, white solid). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.38 (d, 2H), 6.96 (d, 2H), 2.98-2.91 (m, 2H), 2.72-2.69 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 218.45, 198.30, 158.72, 138.21, 132,43, 131.27, 129.23, 127.81, 55.43, 35.57, 26.47. **^{11}B NMR** (96.24 MHZ): δ 28.76. **HRMS** ($[M + Na]^+$): Calcd for $C_{12}H_{13}BO_4Na$, m/z 255.0805. Found, m/z 255.0802.

Coupling reaction; Preparation of 2,3-Diphenylcyclopent-2-en-1-one (5)

Following a literature procedure,[22] to a 10 mL flask were added a stir-bar, 314 mg (2 mmol) of bromobenzene, 444 mg (2.2 mmol) of (5-oxo-2-phenylcyclopent-1-en-1-yl)boronic acid, 4.5 mg (1 mol %) of $Pd(OAc)_2$, 690 mg (5 mmol) of powdered K_2CO_3, and 645 mg (2 mmol) of Bu_4NBr. The flask was equipped with a rubber septum and flushed with nitrogen. Water (2.5 mL) was added with a syringe to the flask, and the resulting suspension was stirred and degassed to remove oxygen. The mixture was stirred and heated for 1 h at 70 °C. The reaction mixture was then cooled to room

temperature, diluted with water, and extracted with EtOAc. The organic layer was dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude product was purified by flash chromatography (SiO_2, 3% EtOAc/hexanes) to yield 2,3-diphenylcyclopent-2-en-1-one (337 mg, 72%, yellow oil). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.38-7.18 (m, 10H), 3.09-3.03 (m, 2H), 2.73-2.68 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 207.60, 168.10, 140.10, 135.20, 132.74, 130.10, 129.72, 128.84, 128. 62, 127.84, 127.60, 34.52, 29.6. **GC-MS** (EI, *m/z*): 235 (M^+). This compound has been described previously, and these spectral data are in agreement with the published ones.[27]

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