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A 2-pyrone cycloaddition route to functionalised aromatic boronic esters

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Abstract

A [4+2] cycloaddition/retro-cycloaddition route to functionalised aromatic boronic esters is outlined. A range of electron deficient dienes (2-pyrones) and dienophiles (alkynylboronates) were found to participate in the reaction. Furthermore, high levels of regiocontrol could be obtained in this process and a consistent mode of alkyne insertion has been uncovered.

1. Introduction

Organoboron reagents are among the most attractive synthetic intermediates in modern organic chemistry.[1] These compounds show good stability and their versatility provides the opportunity to construct new compounds through various carbon–carbon bond forming processes and functional group interconversion reactions. Aromatic boronic acids and esters have emerged as an important sub-class of these reagents. The rich chemistry of organoboron compounds allows the incorporation of these aromatic motifs into a diverse range of carbon-skeleta. Classically, these compounds have been prepared from main group organometallics (usually Grignard or organolithium reagents),[2] or more recently via milder Pd-catalysed C–B bond forming processes.[3] A powerful alternative strategy exploits metal-catalysed C–H bond activation processes.[4] Whilst both of these routes deliver a diverse range of benzenoid and heterocyclic boronates, they require an appropriately functionalised aromatic precursor. A complementary strategy, therefore, would be the benzannulation of an appropriate substrate bearing a boronate moiety, whereby ring formation and instalment of the boronate were accomplished in a single operation. This concept has been put into practise via cycloaddition reactions of alkynylboronates.[5] To date, metal-mediated[6] and metal-catalysed reactions[7] have been developed, as well as techniques based on dipolar cycloaddition[8] and [4+2] cycloaddition[9] processes.

Our preliminary work in this area showed that hydroquinone and quinone boronic esters could be prepared in good yield and with excellent regiocontrol through the employment of a Dötz benzannulation reaction.[6a,b] Whilst this process allows highly functionalised aromatic derivatives to be generated in a single operation, it requires one equivalent of a chromium Fischer carbene complex. Accordingly, in an effort to avoid the need for stoichiometric quantities of transition metal complex, we subsequently investigated a 'metal free' strategy that involved a [4+2] cycloaddition of cyclopentadienones with alkynylboronates followed by chelotropic extrusion of CO.[9a] Whilst this process also delivered functionalised boronic esters in good overall yield, the products were limited to heavily substituted polyaromatic compounds. Therefore, our more recent efforts have focused on the development of a more general protocol. In this context, we considered an alternative approach via the [4+2] cycloaddition/retro-cycloaddition of 2-pyrones as outlined in Figure 1.

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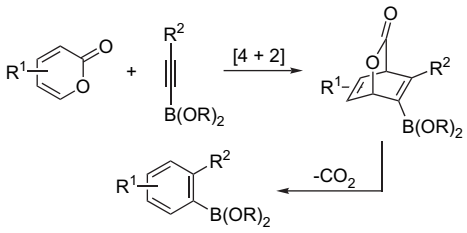


Figure 1. 2-Pyrone cycloaddition of alkynylboronates.

We report herein the development of this concept into an efficient method for generating functionalised aromatic boronic esters.[10,11]

2. Results and discussion

Our initial goal was to establish some preliminary data on the reaction scope and regioselectivity, and so we opted to investigate the cycloaddition of a series of alkynylboronates with isomeric 2-pyrones **1**–**4**. We were particularly drawn to these substrates because they were readily available,[12] and they provided a straightforward method for establishing the effect that an electron withdrawing ester group had on reaction efficiency and regiocontrol, given that **1**/**2** and **3**/**4** provided identical pairs of regioisomeric cycloadducts (Fig. 2).

Our investigations began with the cycloaddition reactions of 2-pyrones **1** and **2**, and our results are summarised in Table 1. Disappointingly, diene **1** was found to react sluggishly with alkynes **5a**,**b** providing the corresponding benzene boronic esters in poor yield. Furthermore, the isomeric 2-pyrone **2** failed to undergo cycloaddition with these compounds and starting material was recovered, even after prolonged reaction times.

We next turned our attention to the cycloaddition of methyl coumalate **3** and, as outlined in Table 2, were pleased to find that this pyrone performed significantly better in these cycloaddition reactions. Heating a neat mixture of **3** and **5a** at high temperature afforded the desired aromatic product in good yield but with no regiocontrol (entry 1). Examination of the crude reaction mixtures suggested that exposing the neat

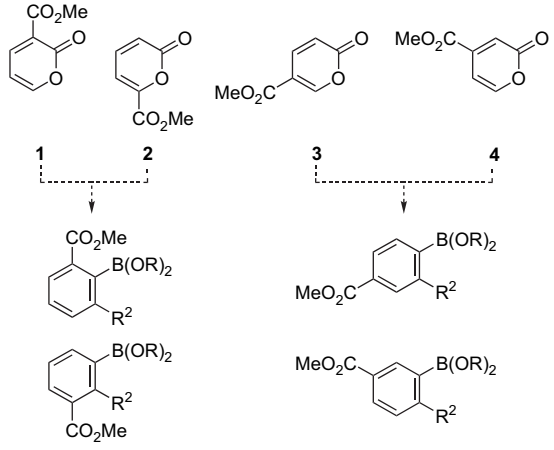
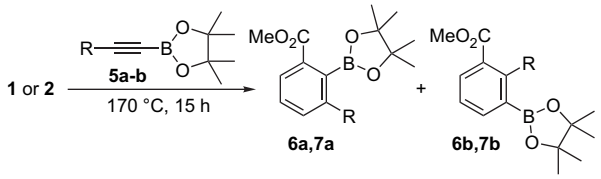


Figure 2. Cycloadditions of isomeric 2-pyrones.

Table 1
Cycloaddition of 2-pyrones **1** and **2**



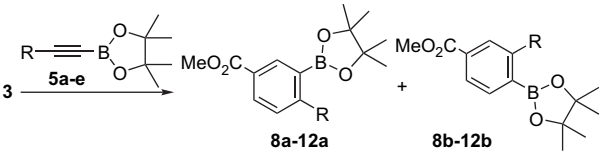
Entry[a]	2-Pyrone	R	Solvent	Yield (%) (**a**:**b**)
1	**1**	Me_3Si; **5a**	Neat	**6**; 19 (1:1)
2	**1**	H; **5b**	Ph_2O	**7**; 21 (1:5)
3	**2**	Me_3Si; **5a**	Neat	**6**; 0
4	**2**	H; **5b**	Ph_2O	**7**; 0

[a] Reactions run with 1–3 equiv of alkyne.

reaction mixture to such high temperatures was resulting in compound decomposition. Therefore, we screened a number of solvents and found *o*-dichlorobenzene (DCB) to be optimal. To our delight, the reaction of **3** and **5a** proceeded in quantitative yield when carried out at a similar temperature, albeit again with no regiocontrol (entry 2). Cycloaddition of phenylacetylene boronic ester **5c** proceeded in high yield and with excellent levels of regiocontrol (entries 3 and 4), whilst alkyne **5d** showed modest levels of regioselectivity, albeit with an analogous insertion pattern. Protected propargyl alcohol derived alkynylboronate **5e** underwent cycloaddition with poor regiocontrol (entries 7 and 8) whereas terminal alkyne **5b** provided **12** in high yield and with good selectivity for regioisomer **12b**.[13]

The final class of ester substituted 2-pyrone **4** was examined next, our results are summarised in Table 3. Cycloaddition of alkyne **5a** was found to proceed efficiently with 2-pyrone **4** to provide aromatic product **8** in high yield when the reaction was heated as a neat mixture or in DCB. Moreover, and in contrast to the cycloaddition with diene **3**, we were pleased to find that this cycloaddition exhibited some regiocontrol, providing modest selectivity for **8b** (entries 1 and 2).

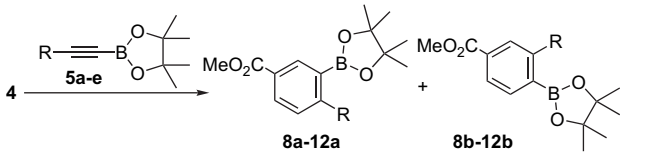
Table 2
Cycloaddition of methyl coumalate **3**



Entry	R	Conditions[a]	Yield (%) (**a**:**b**)
1	Me_3Si; **5a**	A	**8**; 85 (1:1)
2	Me_3Si; **5a**	B	**8**; 100 (1:1)
3	Ph; **5c**	A	**9**; 57 (14:1)
4	Ph; **5c**	B	**9**; 75 (14:1)
5	*n*-Bu; **5d**	A	**10**; 59 (3:1)
6	*n*-Bu; **5d**	B	**10**; 80 (3:1)
7	$BnOCH_2$; **5e**	A	**11**; 31 (1:1)
8	$BnOCH_2$; **5e**	B	**11**; 60 (1:1)
9	H; **5b**	Ph_2O, 170 °C	**12**; 77 (1:5)[b]

[a] A: neat, 170 °C, 15 h. B: *o*-dichlorobenzene, 180 °C, 18 h.
[b] Regioisomer **a** is identical to **7b**.

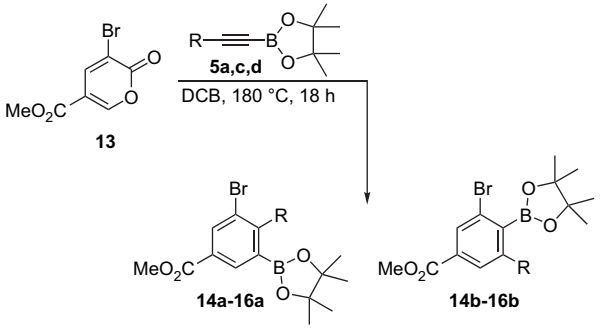
Table 3
Cycloaddition of 2-pyrone **4**



Entry	R	Conditions[a]	Yield (%) (**a**:**b**)
1	Me_3Si; **5a**	A	**8**; 70 (1:3)
2	Me_3Si; **5a**	B	**8**; 97 (1:3)
3	Ph; **5c**	A	**9**; 42 (1:1)
4	Ph; **5c**	B	**9**; 67 (1:1)
5	*n*-Bu; **5d**	A	**10**; 24 (1:10)
6	*n*-Bu; **5d**	B	**10**; 54 (1:10)
7	H; **5b**	B	**12**; 72 (2:3)[b,c]

[a] A: neat, 170 °C, 15 h. B: *o*-dichlorobenzene, 180 °C, 18 h.
[b] Regioisomer **a** is identical to **7b**.
[c] For this cycloaddition, 3.5 equiv of alkyne is used.

Table 4
Cycloaddition of 2-pyrone **13**



Entry	R	Yield (%) (**a**:**b**)
1	Me_3Si; **5a**	**14**; 77 (3:2)
2	Ph; **5c**	**15**; 77 (>95:<5)
3	*n*-Bu; **5d**	**16**; 82 (10:1)

Alkyne **5c** produced an equal mixture of boronic esters **9a** and **9b** in good yield when the reaction was conducted in DCB (entries 3 and 4), whereas 1-hexyne derived alkynylboronate **5d** was highly selective for the formation of **10b** (entries 5 and 6). Finally, the terminal alkyne **5b** provided the corresponding cycloadduct in good yield but with poor regiocontrol in this case (entry 7).

These preliminary studies suggested that 2-pyrones with substituents in the 3- and 6-positions would be sluggish towards cycloaddition (cf. dienes **1**, **2** vs **3**, **4**), presumably because of steric hinderance. Moreover, conjugation of the electron withdrawing group with the enol ester moiety of the 2-pyrone appeared to provide enhanced reactivity (cf. **1** vs **2**, **3** vs **4**). In the context of regiochemistry, these investigations also highlighted an interesting trend whereby those cycloadditions that were selective, followed a consistent pattern of alkyne insertion irrespective of the position of the ester group. Specifically, substituted alkynylboronates underwent cycloaddition with the regiochemistry highlighted in Figure 3. Finally, the observation that 2-pyrone **3** generally favoured formation of regioisomer **a**, whereas pyrone **4** was more generally selective for **b** demonstrates that this strategy offers access to different product regioisomers by judicious choice of diene component.[14]

The apparent increased reactivity of 2-pyrones bearing an ester group in the 5-position suggested that smaller substituents might be incorporated at C-3 or C-6 without significantly affecting the cycloaddition efficiency. In an effort to test this idea, we prepared pyrone **13**[15] and examined its reactivity with our alkynylboronate substrates. As outlined in Table 4, silylalkyne **5a** underwent smooth cycloaddition to provide **14**, unfortunately however, with poor levels of regiocontrol (entry 1). More promising was the reaction of **5c** with **13**, which provided the corresponding boronic ester **15** as a single regioisomer in 77% yield (entry 2). Finally, butyl-substituted boronate **5d** was also found to undergo efficient and selective cycloaddition, moreover, with an identical regiochemical insertion pattern to that of the Ph-substituted alkyne predominating (entry 3).[16]

Having explored the cycloaddition efficiency with regard to the diene component, we decided to briefly explore the effects of changing the boronic ester moiety of the dienophile. As shown in Figure 4, we envisaged that the electronic nature of the boronate unit would be affected by the ability of the flanking O-atoms to donate electron density to the vacant p-orbital on boron. Specifically, the angle strain imposed by having contiguous O–B–O sp^2-centres may be better accommodated in a six-membered ring than in a five-membered ring. Given that recent studies in our labs have suggested that alkynylboronates act as electron rich dieneophiles in [4+2] cycloadditions,[17] the donor/acceptor ability of the boronate could have an effect on reactivity as well as regioselectivity.

In order to gather evidence for this effect, we prepared alkynes **17**–**18** (Fig. 5). Compounds **5c** and **17** were found to be crystalline solids and so we undertook X-ray crystallographic

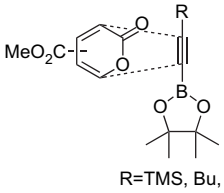


Figure 3. Cycloaddition regiochemistry.

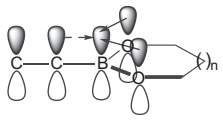


Figure 4. Boronate donor ability.

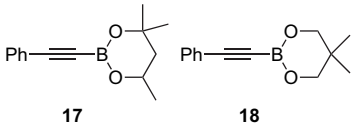


Figure 5. Six-membered ring boronates.

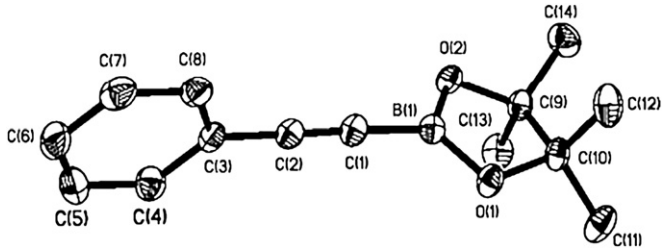


Figure 6. ORTEP diagram of **5c**. Selected bond distances [Å] and angles [°]: C(1)–C(2) 1.201(3), C(1)–B(1) 1.535(3), B(1)–O(1) 1.358(2), B(1)–O(2) 1.362(2); O(1)–B(1)–O(2) 114.84(17).

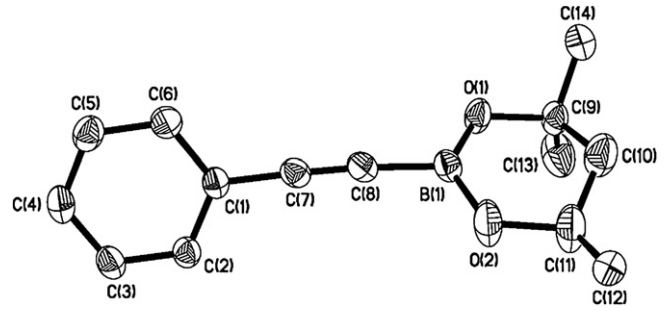
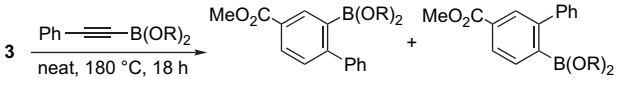


Figure 7. ORTEP diagram of **17**. Selected bond distances [Å] and angles [°]: C(7)–C(8) 1.205(5), C(8)–B(1) 1.541(6), B(1)–O(1) 1.339(5), B(1)–O(2) 1.364(5); O(1)–B(1)–O(2) 124.3(4).

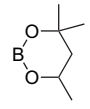
analysis of these alkynes to compare the relative bond lengths and angles around the boronate unit in each case, selected data are provided in Figures 6 and 7.[18] A striking difference in these structures was that **17** showed two quite different B–O bond lengths whereas those of **5c** are equal (within experimental error). The generally shorter B–O bonds in **17** appear to suggest greater donation from O→B with increased O–B–O bond angle and increased alkyne C–B bond length relative to **5c**.

In the context of cycloadditions, the reaction of alkynes **17** and **18** with methyl coumalate was performed in the absence of solvent and our results are highlighted in Table 5 (the results for the cycloaddition of **5c** are included for direct comparison). In general, we found the six-membered boronic esters to be quite prone to protodeboronation at high temperature; moreover, they were relatively sluggish towards cycloaddition. Nonethless, the corresponding aromatic products **19** and **20** could be obtained in acceptable yields. Interestingly, however, an increase in product regioselectivity was obtained in these reactions by comparison to the cycloaddition of compound **5c**. Whilst we have insufficient data to make general conclusions at this stage, it would appear that the cycloaddition of alkynylboronates bearing various boronic ester moieties may provide a further means by which the regioselectivity of these reactions can be optimised. Studies towards this end are currently underway and will be reported in due course.

Table 5
Cycloaddition of methyl coumalate **3**



9a, 19a, 20a **9b, 19b, 20b**

Entry	$B(OR)_2$	Yield (%) (**a**:**b**)
1	 **17**	**19**; 58 (20:1)
2	 **18**	**20**; 64 (20:1)
3	 **5c**	**9**; 57 (14:1)[a]

[a] Reaction runs at 170 °C, 15 h.

3. Conclusion

The [4+2] cycloaddition of 2-pyrones with alkynylboronates provides an efficient route to functionalised boronic esters with good to excellent levels of regiocontrol in many cases. Moreover, reaction regioselectivity was found to vary according to the position of electron withdrawing groups on the diene substrate. This observation suggests therefore that cycloaddition regiochemistry can, to some extent, be controlled by judicious positioning of electron deficient substituents on the 2-pyrone substrate. Finally, alternative boronic ester moieties were also found to participate in the cycloaddition process and may provide a further means to controlling reaction regioselectivity.

4. Experimental

4.1. General

Alkynylboronates **5** were prepared from the corresponding terminal alkynes by the method of Brown.[19] Alkynes **17**[20] and **18** were prepared from the corresponding alkynyltrifluoroborate salts by the method of Vaultier[21] and Yamamoto.[7g] Pyranones **1**,[12] **4**[12] and **13**[15] were prepared according to literature procedures.

4.2. General procedure for the [4+2] cycloaddition reaction of pyranone with alkynylboronates

*4.2.1. Methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trimethylsilyl)benzoate (**6a**) and methyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trimethylsilyl)benzoate (**6b**)*

A mixture of pyranone (**1**) (0.173 g, 1.12 mmol) and 4,4,5,5-tetramethyl-2-trimethylsilanylethynyl-1,3,2-dioxaborolane (**5a**) (0.755 g, 3.37 mmol) was heated at 170 °C and stirred for 15 h under N_2. The resulting brown solution was cooled to room temperature and purified by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 50:1 ratio) to give the title compounds (**6a**) and (**6b**) (1:1 ratio)

as a colourless solid, 0.071 g, 19%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.25 (9H, s, Si(CH_3)$_3$), 0.39 (9H, s, Si(CH_3)$_3$), 1.33 (12H, s, 4×CH_3), 1.49 (12H, s, 4×CH_3), 3.85 (3H, s, CO_2CH_3), 3.89 (3H, s, CO_2CH_3), 7.31–7.35 (2H, m, Ar-*H*), 7.67–7.71 (2H, m, Ar-*H*), 7.81 (1H, dd, *J*=7.5, 1.0 Hz, Ar-*H*), 7.91 (1H, dd, *J*=7.5, 1.5 Hz, Ar-*H*); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 0.4, 1.7, 25.2, 26.3, 52.1, 52.2, 84.2 (×2), 127.3 (×2), 127.5 (×2), 129.0 (×2), 130.1 (×2), 137.0, 137.8, 167.4, 167.5. FTIR: ν_{max}/$CHCl_3$, 2977 (m), 2953 (m), 2900 (w), 1577 (w), 1558 (w) cm^{-1}. HRMS (ES$^+$) calcd for $C_{17}H_{27}O_4BSiNa$: 357.1669. Found: 357.1657.

4.2.2. Methyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (*7b*)

A solution of pyranone (**1**) (0.100 g, 0.65 mmol) and 2-ethynyl-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (**5b**) (0.09 g, 0.65 mmol) in diphenylether (1 ml) was heated at 170 °C and stirred for 15 h under N_2. The resulting brown solution was cooled to room temperature and purified by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 50:1 ratio) to give the title compounds (**7a**) and (**7b**) (1:5 ratio) as a colourless solid, 0.036 g, 21%. Compound (**7b**): ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.28 (12H, s, 4×CH_3), 3.84 (3H, s, CO_2CH_3), 7.38 (1H, dd, *J*=8.0, 8.0 Hz, Ar-*H*), 7.90 (1H, ddd, *J*=8.0, 1.0, 1.0 Hz, Ar-*H*), 8.00 (1H, ddd, *J*=8.0, 1.0, 1.0 Hz, Ar-*H*), 8.05 (1H, br, Ar-*H*); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 24.9, 52.0, 84.1, 127.8, 129.6, 132.3, 135.8, 139.2, 167.2. FTIR: ν_{max}/$CHCl_3$, 2976 (w), 1718 (s) cm^{-1}. HRMS (EI$^+$) calcd for $C_{14}H_{19}BO_4$: 262.1376. Found: 262.1384.

4.2.3. Methyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(trimethylsilyl)benzoate (*8a*) and methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trimethylsilyl)benzoate (*8b*)

A mixture of (**3**) (0.1 g, 0.65 mmol) and (**5a**) (0.291 g, 1.3 mmol) in *o*-dichlorobenzene (0.65 ml) was heated at 180 °C for 18 h under N_2. The product was purified by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 25:1 ratio) to give the separated title compounds (**8a**) as a colourless oil, 0.108 g, 50% and (**8b**) as a colourless oil, 0.109 g, 50%. Compound (**8a**): ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.36 (9H, s, $SiMe_3$), 1.35 (12H, s, CH_3), 3.91 (3H, s, CO_2CH_3), 7.96 (2H, m, Ar-*H*), 8.24 (1H, d, *J*=1.5 Hz, Ar-*H*); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 0.4, 25.0, 52.1, 84.2, 128.5, 130.5, 134.8, 135.9, 147.3, 167.5. FTIR: ν_{max}/$CHCl_3$, 2979 (m), 2952 (w), 1726 (s), 1595 (w), 1548 (w) cm^{-1}. HRMS (EI$^+$) calcd for $C_{17}H_{27}O_4BSi$: 335.1850. Found: 335.1839. Compound (**8b**): ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.29 (9H, s, $SiMe_3$), 1.29 (12H, s, CH_3), 3.86 (3H, s, CO_2CH_3), 7.62 (1H, d, *J*=8.0 Hz, Ar-*H*), 7.93 (1H, dd, *J*=8.0, 1.5 Hz, Ar-*H*), 8.43 (1H, d, *J*=1.5 Hz, Ar-*H*); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 0.8, 25.0, 52.0, 84.1, 129.7, 130.2, 134.4, 136.4, 153.3, 167.4. FTIR: ν_{max}/$CHCl_3$, 2979 (m), 2951 (w), 2901 (w), 1726 (s), 1593 (w), 1551 (w) cm^{-1}. HRMS (EI$^+$) calcd for $C_{17}H_{27}O_4BSi$: 335.1850. Found: 335.1857.

4.2.4. Methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl-4-carboxylate (*9a*) and methyl 6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl-3-carboxylate (*9b*)

A mixture of (**3**) (0.1 g, 0.649 mmol) and (**5c**) (0.296 g, 1.298 mmol) in *o*-dichlorobenzene (0.649 ml) was heated at 180 °C for 18 h under N_2. The product was purified by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 25:1 ratio) to give compounds (**9a**) and (**9b**) (14:1 ratio) as an inseparable mixture of regioisomers as a colourless oil, 0.164 g, 75%. Compound (**9a**): ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.21 (12H, s, 4×CH_3), 3.92 (3H, s, CO_2CH_3), 7.35–7.48 (5H, m, Ar-*H*), 7.56 (1H, d, *J*=8.0 Hz, Ar-*H*), 7.98 (1H, dd, *J*=8.0, 1.5 Hz, Ar-*H*), 8.04 (1H, dd, *J*=1.0, 0.5 Hz, Ar-*H*); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 24.7, 52.2, 84.1, 127.0, 127.2, 127.5, 128.0, 129.0, 129.1, 135.7, 142.0, 147.9, 167.0. FTIR: ν_{max}/$CHCl_3$, 2991 (w), 2979 (w), 2940 (w), 1723 (s), 1600 (w) cm^{-1}. HRMS (EI$^+$) calcd for $C_{20}H_{23}O_4B$: 338.1689. Found: 338.1687. Compound (**9b**): ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.23 (12H, s, 4×CH_3), 3.95 (3H, s, CO_2CH_3), 7.35–7.48 (6H, m, Ar-*H*), 8.12 (1H, dd, *J*=8.0, 2.0 Hz, Ar-*H*), 8.38 (1H, dd, *J*=2.0, 0.5 Hz, Ar-*H*); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 24.6, 52.1, 84.0, 127.0, 127.5, 127.9, 128.9, 129.0, 130.0, 135.6, 142.1, 151.9, 167.0.

4.2.5. Methyl 4-butyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (*10a*) and methyl 3-butyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzoate (*10b*)

A mixture of (**3**) (0.1 g, 0.649 mmol) and (**5d**) (0.270 g, 1.298 mmol) in *o*-dichlorobenzene (0.65 ml) was heated at 180 °C for 18 h under N_2. The product was purified by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 25:1 ratio) to give compounds (**10a**) and (**10b**) (3:1 ratio) as an inseparable mixture of regioisomers as a colourless oil, 0.172 g, 80%. Compound (**10a**): ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.85 (3H, t, *J*=7.5 Hz, CH_2CH_3), 1.28 (12H, s, 4×CH_3), 1.22–1.37 (2H, m, CH_2CH_3), 1.38–1.56 (2H, m, $CH_2CH_2CH_3$), 2.85 (2H, app t, *J*=8.0 Hz, C=CCH_2), 3.89 (3H, s, CO_2CH_3), 7.79 (2H, s, Ar-*H*), 7.81 (1H, s, Ar-*H*); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 13.9, 22.7, 24.8, 35.2, 35.4, 52.0, 83.8, 125.6, 129.9, 131.8, 135.8, 150.2, 167.3. FTIR: ν_{max}/$CHCl_3$, 2977 (m), 2956 (m), 2931 (m), 2870 (m), 1723 (s) cm^{-1}. HRMS (EI$^+$) calcd for $C_{18}H_{27}O_4B$: 318.2002. Found: 318.2012. Compound (**10b**): ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.85 (3H, t, *J*=7.5 Hz, CH_2CH_3), 1.28 (12H, s, 4×CH_3), 1.22–1.37 (2H, m, CH_2CH_3), 1.38–1.56 (2H, m, $CH_2CH_2CH_3$), 2.85 (2H, app t, *J*=8.0 Hz, C=CCH_2), 3.88 (3H, s, CO_2CH_3), 7.16 (1H, d, *J*=8.0 Hz, Ar-*H*), 7.92 (1H, dd, *J*=8.0, 2.0 Hz, Ar-*H*), 8.34 (1H, d, *J*=2.0 Hz, Ar-*H*); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 13.9, 22.7, 24.8, 35.3, 35.6, 51.9, 83.7, 126.8, 129.3, 131.8, 137.2, 155.5, 167.3.

*4.2.6. Methyl 4-(benzyloxymethyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (**11a**) and methyl 3-(benzyloxymethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (**11b**)*

A mixture of (**3**) (0.1 g, 0.649 mmol) and (**5e**) (0.353 g, 1.298 mmol) in *o*-dichlorobenzene (0.65 ml) was heated at 180 °C for 18 h under N_2. The product was purified by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 25:1 ratio) to give compounds (**11a**) and (**11b**) (1:1 ratio) as a clear oil, 0.149 g, 60%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.25 (24H, s, CH_3), 3.93 (6H, s, CO_2CH_3), 4.61 (4H, m, ArCH_2O), 4.84 (2H, s, ArCH_2O), 4.89 (2H, s, ArCH_2O), 7.29–7.43 (10H, m, Ar-*H*), 7.64 (1H, d, *J*=8.0 Hz, Ar-*H*), 7.85 (1H, d, *J*=8.0 Hz, Ar-*H*), 7.90 (1H, dd, *J*=8.0, 2.0 Hz, Ar-*H*), 8.11 (1H, dd, *J*=8.0, 1.5 Hz), 8.46–8.47 (1H, m, Ar-*H*), 8.46 (1H, d, *J*=2.0 Hz, Ar-*H*); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 24.8×2, 51.9, 52.1, 71.3×2, 72.6×2, 83.9, 84.0, 127.2×2, 127.5, 127.6×2, 127.8, 127.9×2, 128.3, 128.4×2, 128.6, 132.0, 132.1, 135.5, 136.7, 144.7, 144.9, 167.1, 167.2. FTIR: ν_{max}/$CHCl_3$, 2993 (w), 2972 (w), 1725 (s), 1640 (w) cm^{-1}. HRMS (EI$^+$) calcd for $C_{22}H_{27}BO_5$: 382.1952. Found: 382.1949.

*4.2.7. Methyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (**7b**) and methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (**12b**)[3a]*

A mixture of (**3**) (0.1 g, 0.649 mmol), (**5b**) (0.09 g, 0.649 mmol) and diphenylether (1 ml) was heated at 170 °C with stirring, for 15 h under a nitrogen atmosphere. The product was purified by flash column chromatography (eluting solvent petroleum ether/EtOAc 100:1) to give compounds (**12b**) and (**7b**) (5:1 ratio) as a colourless crystalline solid, 0.130 g, 77%. Compound (**12b**):[3a] ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.28 (12H, s, CH_3), 3.84 (3H, s, CH_3OCO), 7.79 (2H, d, *J*=8.5 Hz, Ar-*H*), 7.96 (2H, d, *J*=8.5 Hz, Ar-*H*); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 24.8, 52.1, 84.1, 127.8, 135.8, 134.6, 167.1.

*4.2.8. Methyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(trimethylsilyl)benzoate (**8a**) and methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trimethylsilyl)benzoate (**8b**)*

A mixture of (**4**) (0.05 g, 0.325 mmol) and (**5a**) (0.145 g, 0.649 mmol) in *o*-dichlorobenzene (0.325 ml) was heated at 180 °C for 15 h under N_2. The product was purified by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 25:1 ratio) to give (**6a**) and (**6b**) (1:3 ratio) as colourless oils, 0.107 g, 97%.

*4.2.9. Methyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl-4-carboxylate (**9a**) and methyl 6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl-3-carboxylate (**9b**)*

A mixture of (**4**) (0.05 g, 0.324 mmol) and (**2a**) (0.148 g, 0.649 mmol) in *o*-dichlorobenzene (0.325 ml) was heated at 180 °C for 36 h under N_2. The product was purified by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 25:1 ratio) to give (**9a**) and (**9b**) (1:1 ratio) as a clear oil, 0.074 g, 67%.

*4.2.10. Methyl 4-butyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (**10a**) and methyl 3-butyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (**10b**)*

A mixture of (**4**) (0.050 g, 0.325 mmol) and (**5c**) (0.135 g, 0.649 mmol) in *o*-dichlorobenzene (0.65 ml) was heated at 180 °C for 36 h under N_2. The product was purified by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 25:1 ratio) to give compounds (**8a**) and (**8b**) (1:10 ratio) as a clear oil, 0.056 g, 54%.

*4.2.11. Methyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (**7b**) and methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (**12b**)[3a]*

A mixture of (**4**) (0.050 g, 0.325 mmol) and (**5b**) (0.172 g, 1.136 mmol) in *o*-dichlorobenzene (0.325 ml) was heated at 180 °C for 18 h under N_2. The product was purified by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 25:1 ratio) to give compounds (**7b**) and (**12b**)[3a] (2:3 ratio) as a colourless crystalline solid, 0.061 g, 72%.

*4.2.12. Methyl 3-bromo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-trimethylsilyl benzoate (**14** major) and methyl 3-bromo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trimethylsilyl)benzoate (**14** minor)*

A mixture of (**13**) (0.05 g, 0.215 mmol) and (**5a**) (0.096 g, 0.429 mmol) in *o*-dichlorobenzene (0.215 ml) was heated at 180 °C for 18 h under N_2. The product was purified by flash column chromatography containing a plug of 10% $AgNO_3$ impregnated silica (eluting solvent petroleum ether/ethyl acetate 25:1 ratio) to give compounds (**14a**) and (**14b**) (3:2 ratio) as a colourless crystalline solid, 0.068 g, 77%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.36 (5.4H, s, SiCH_3), 0.47 (3.6H, s, SiCH_3), 1.37 (4.8H, s, CCH_3), 1.46 (7.2H, s, CCH_3), 3.90 (3H, s, COCH_3), 8.08–8.16 (2H, m, Ar-*H*); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 0.0, 1.7, 25.3, 25.9, 25.3×2, 84.5, 85.1, 127.8, 130.8, 131.0, 131.5, 132.5, 132.7, 132.8, 134.6, 147.5, 149.8, 166.1×2. FTIR: ν_{max}/$CHCl_3$, 2952 (w), 1729 (s), 1338 (m) cm^{-1}. HRMS (ES$^+$) calcd for $C_{17}H_{27}BBrO_4Si$: 413.0955. Found: 413.0974.

*4.2.13. Methyl 2-bromo-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl-4-carboxylate (**15**)*

A mixture of (**13**) (0.05 g, 0.215 mmol) and (**5c**) (0.098 g, 0.429 mmol) in *o*-dichlorobenzene (0.215 ml) was heated at 180 °C for 18 h under N_2. The product was purified by flash column chromatography containing a plug of 10% $AgNO_3$ impregnated silica (eluting solvent petroleum ether/ethyl acetate 25:1 ratio) to give compound (**15**) as a colourless crystalline solid, 0.069 g, 77%. Mp 109–111 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.01 (12H, s, CH_3), 3.85 (3H, s, CH_3OCO), 7.30 (2H, m, Ar-*H*), 7.71 (3H, m, Ar-*H*), 8.17 (1H, d, *J*=2.0 Hz, Ar-*H*), 8.28 (1H, d, *J*=2.0 Hz, Ar-*H*); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 24.9, 52.6, 82.1, 122.9, 128.5, 128.8, 129.5, 130.9, 131.6, 134.7, 140.6, 147.4, 166.1. FTIR: ν_{max}/$CHCl_3$, 2978 (w), 1727 (s) cm^{-1}. HRMS (EI$^+$) calcd for $C_{20}H_{22}BBrO_4$: 417.0873. Found: 417.0886.

*4.2.14. Methyl 3-bromo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-butyl benzoate (**16**)*

A mixture of (**13**) (0.05 g, 0.215 mmol) and (**5d**) (0.089 g, 0.429 mmol) in *o*-dichlorobenzene (0.215 ml) was heated at 180 °C for 18 h under N_2. The product was purified by flash column chromatography containing a plug of 10% $AgNO_3$ impregnated silica (eluting solvent petroleum ether/ethyl acetate 25:1 ratio) to give compound (**16**) (10:1 ratio) as a clear oil, 0.070 g, 82%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.90–0.95 (3H, t, J=8.0 Hz, CH_2CH_3), 1.23 (12H, s, CCH_3), 1.25–1.38 (4H, m, $CH_2CH_2CH_3$), 3.04 (2H, t, J=8.0 Hz, $ArCH_2CH_2$), 3.88 (3H, s, CO_2CH_3), 8.18 (1H, d, J=2 Hz, Ar-*H*), 8.28 (1H, d, J=2 Hz, Ar-*H*); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 13.9, 23.0, 24.8, 33.2, 35.1, 52.2, 84.0, 125.4, 128.4, 136.0, 136.2, 153.7, 166.0. FTIR: $\nu_{max}/CHCl_3$, 2956 (w), 1728 (s), 1596 (m), 1338 (m) cm^{-1}. HRMS (ES$^+$) calcd for $C_{18}H_{27}BBrO_4$: 397.1186. Found: 397.1178.

*4.2.15. 2-(4,4,6-Trimethyl-1,3,2-dioxaborinan-2-yl)-biphenyl-4-carboxylic acid methyl ester (**19**)*

A mixture of **3** (0.15 g, 0.974 mmol) and **17** (0.444 g, 1.948 mmol) was heated at 180 °C for 18 h. The resulting brown solution was cooled to room temperature and purification by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 25:1 ratio) gave (**19a**) and (**19b**) (20:1 ratio) as a yellow oil, 0.191 g, 58%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.82–0.95 (9H, m, CH_3), 1.10–1.2 (2H, m, CCH_2CH), 3.86 (3H, s, CO_2CH_3), 4.20–4.35 (1H, m, CH_2CHCH_3), 7.30–7.42 (6H, m, Ar-*H*), 8.04 (1H, dd, J=8.0, 2.0 Hz, Ar-*H*), 8.30 (1H, d, J=2.0 Hz, Ar-*H*); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 22.8, 27.8, 30.7, 45.7, 52.0, 65.3, 71.5, 127.1, 127.9, 128.7, 128.9, 130.2, 134.8, 143.2, 151.1, 167.4. FTIR: $\nu_{max}/CHCl_3$, 2974 (m), 1721 (s), 1598 (m), 1384 (m) cm^{-1}. HRMS (EI$^+$) calcd for $C_{20}H_{23}BO_4$: 338.2052. Found: 338.2054.

*4.2.16. 2-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)-biphenyl-4-carboxylic acid methyl ester (**20a**)*

A mixture of **3** (0.2 g, 1.298 mmol) and **18** (566 mg, 2.6 mmol) was heated at 180 °C for 18 h. The resulting brown solution was cooled to room temperature and purification by flash column chromatography (eluting solvent petroleum ether/ethyl acetate 25:1 ratio) to give compounds (**20a**) and (**20b**) (20:1 ratio) as a brown oil, 0.269 g, 64%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.96 (6H, s, 2×CH_3), 3.57 (4H, s, CH_2), 3.92 (3H, s, CH_3), 7.30–7.43 (5H, m, Ar-*H*), 8.05 (1H, d, J=2.0 Hz, Ar-*H*), 8.10 (1H, d, J=2.0 Hz, Ar-*H*), 8.37 (1H, d, J=1.0 Hz, Ar-*H*); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 26.5, 32.2, 52.1, 70.6, 127.0, 127.3, 128.1, 128.9, 129.5, 130.1, 131.0, 149.6, 153.7, 167.6. FTIR: $\nu_{max}/CHCl_3$, 2900 (w), 1720 (m), 1439 (w), 1290 (m) cm^{-1}. HRMS (EI$^+$) calcd for $C_{19}H_{21}BO_4$: 324.1786. Found: 324.1789.

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13. The regiochemistry of compounds **8–10** was established by NOE studies,[10] whilst the regiochemistry of compound **12** was made on the basis of ^{1}H–^{1}H coupling patterns. Compound **11** was not prepared with regiocontrol and therefore regioisomer elucidation was not carried out in this case.
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16. The regiochemistry of compound **15** was confirmed by X-ray crystallography.[10] The regiochemistry of compound **16** was made on the basis of ^{1}H NOE spectroscopy.
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18. CCDC 650935 and CCDC 650936 contain the supplementary crystallographic data for compounds **5c** and **17**, respectively. This data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: (+44) 1223 336 033; or request@ccdc.cam.ac.uk).
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20. To a solution of 2-methyl-2,4-bis-trimethylsilanyloxy-pentane (13.126 g, 50 mmol) and potassium(phenylethynyl)trifluoroborate (10.401 g, 50 mmol) in acetone (50 ml) was added chlorotrimethyl silane (10.864 g, 100 mmol). The reaction mixture was allowed to stir at room temperature for 18 h. The reaction mixture was filtered and washed with acetone and then the solvent was removed in vacuo to give compound **17** as a colourless crystalline solid, 11.064 g, 97%. Mp 63–65 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.31 (3H, d, J=6.0 Hz, $C(CH_3)_2CH_2CH_3$), 1.35 (6H, s, $C(CH_3)_2CH_2CH_3$), 1.50–1.60 (1H, m, $C(CH_3)_2CH_2CH_3$), 1.83 (1H, dd, J=14.0, 3.0 Hz, $C(CH_3)_2CH_2CH_3$), 4.25–4.34 (1H, m, $CHCH_3$), 7.26–7.33 (3H, m, Ar-*H*), 7.50–7.54 (2H, m, Ar-*H*); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 22.9, 28.2, 31.0, 46.0, 66.8, 85.9, 90.7, 122.2, 128.0, 129.0, 132.4. FTIR 2975 (m), 2192 (m), 1490 (m), 1397 (s), 1294 (s), 1199 (s) cm^{-1}. HRMS (EI^+) calcd for $C_{14}H_{17}BO_2$: 228.1322. Found: 228.1328.
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