Supporting Information
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SUPPORTING INFORMATION

Ruthenium(II) complex catalyzed O-borylation of alcohols with vinylboronates
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General methods:

$^1$H NMR (300 MHz), $^{13}$C NMR (75 MHz), $^{29}$SiNMR (79 MHz) and $^{11}$B NMR (96 MHz) spectra were recorded on Varian XL 300 MHz spectrometer in CDCl$_3$ or [D$_8$]toluene (C$_6$D$_5$CD$_3$) solution. Chemical shifts are reported in (ppm) with reference to the residue portion solvent (CH$_3$Cl) peak for $^1$H, $^{13}$C, to TMS for $^{29}$Si and to BF$_3$-Et$_2$O for $^{11}$B. Analytical gas chromatographic (GC) analyses were performed on a Varian Star 400CX with a DB-5 fused silica capillary column (30m · 0.15mm) and TCD. Mass spectra of the substrates and products were obtained by GC–MS analysis (VarianSaturn 2100T, equipped with a BD-5 capillary column (30m) and an ion trap detector). Elemental analyses were carried out by Vario EL III. Thin-layer chromatography (TLC) was made on plates coated with 250 µm thick silica gel (Aldrich and Merck) and the column chromatography was performed with silica gel 60 (70–230 mesh; Fluka). Toluene was dried by distillation from sodium and hexane from sodium hydride. Liquid substrates were also dried and degassed by bulb to bulb distillation. The reactions were carried out under dry argon atmosphere or in air depending on the catalyst. The chemicals were obtained from the following sources: toluene, dodecane and hexane were purchased from Fluka, ethyl acetate from POCH; CDCl$_3$ and C$_6$D$_5$CD$_3$ from Dr Glaser A.G. Basel. The alcohols were bought from Aldrich and Fluka. 2-vinyl-1,3-dioxaborinane was synthesized according to the literature procedure with some modifications [1-2]. The ruthenium complexes [RuHCl(CO)(PCy$_3$)$_2$] (I), [RuHCl(CO)(PPh$_3$)$_3$] (II), [Ru(BO$_2$C$_6$H$_4$)Cl(CO)(PCy$_3$)$_2$] (III) were prepared according to literature procedures [3-5].

Representative experimental procedure for O-borylation of alcohols by vinylboronates:

In a typical test, the ruthenium catalyst [Ru(CO)Cl(H(PPh$_3$)$_3$)] (II) (2 mol%) was dissolved in toluene and placed in a glass ampoule. The reagents and dodecane as internal standard (5% by volume all components), alcohol (0.5 mmol) and 2-vinyl-1,3,2-dioxaborinane (1 – 2.5 mmol)
were added. The ampoule was heated at 60-80°C and maintained at this temperature for 24h. Alcohol conversion was determined by GC and GC-MS. After the reaction, the solvent and excess of borane were removed under vacuum, and the crude product was purified by column chromatography (silica gel modified with HMDS) with hexane/ethyl acetate as eluent.

**Spectroscopic data of synthesized compounds**

2-butoxy-1,3-dioxaborinane: $^1$H NMR (300 MHz, CDCl$_3$); $\delta$ = 1.1 (t, 3H, CH$_3$), 1.78 (q, 2H, CH$_2$CH$_3$), 1.92 (qu, 2H, BOCH$_2$CH$_2$CH$_2$O, $J = 5.5$ Hz), 2.16 (CH$_2$CH$_2$CH$_3$), 3.85 (t, 2H, CH$_2$(CH)$_2$CH$_3$, $J = 4.6$ Hz), 4.03 (t, 4H, BOCH$_2$CH$_2$CH$_2$O $J = 5.5$ Hz) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$); $\delta$ = 15.8 (CH$_3$), 20.3 (CH$_2$CH$_3$), 27.2 (BOCH$_2$CH$_2$CH$_2$O), 33.2 (CH$_2$CH$_2$CH$_3$), 62.7 (BOCH$_2$CH$_2$CH$_3$), 64.7 (BOCH$_2$CH$_2$CH$_2$O) ppm; $^{11}$B NMR (96 MHz, CDCl$_3$); $\delta$ = 28.7 ppm; MS (EI): m/z (%): 143 (1) [M$^+$-15], 129 (2), 115 (100), 103 (29), 85 (22), 71 (11), 56 (14); elemental analysis calcd for (%): C$_7$H$_{15}$BO$_2$: C, 53.21; H, 9.57; found C, 53.01, H 9.44

2-(3’-methylbutoxy)-1,3-dioxaborinane: $^1$H NMR (300 MHz, CDCl$_3$); $\delta$ = 0.82 (d, 6H, CH$_2$CH(CH$_3$)$_2$), 1.37 (m, 1H CH$_2$CH(CH$_3$)$_2$), 1.81 (br, CH$_2$CH(CH$_3$)$_2$), 1.88 (qu, 2H, BOCH$_2$CH$_2$CH$_2$O), 3.74 (t, 2H, BOCH$_2$CH$_2$CH(CH$_3$)$_2$), 3.97 (BOCH$_2$CH$_2$CH$_2$O) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$); $\delta$ = 22.5 (CH$_2$CH(CH$_3$)$_2$), 24.5 (CH$_2$CH(CH$_3$)$_2$), 27.2 (BOCH$_2$CH$_2$CH$_2$O), 40.2 (CH$_2$CH(CH$_3$)$_2$), 61.4 (BOCH$_2$CH$_2$CH(CH$_3$)$_2$), 62.7 (BOCH$_2$CH$_2$CH$_2$O) ppm; $^{11}$B NMR (96 MHz, CDCl$_3$); $\delta$ = 28.7 ppm; MS (EI): m/z (%): 157 (1) [M$^+$-15], 143 (12), 115 (100), 103 (4), 85 (18), 71 (9), 57 (9), 45 (12); elemental analysis calcd for (%): C$_9$H$_{17}$BO$_2$: C, 55.85; H, 9.96; found C, 55.93, H 10.02

2-hepyloxy-1,3-dioxaborinane: $^1$H NMR (300 MHz, CDCl$_3$); $\delta$ = 0.87 (t, 3H, CH$_3$), 1.28 (br, 6H, CH$_2$CH$_2$CH$_2$H), 1.54 (qu, 2H, CH$_2$C$_2$H$_9$), 1.76 (br, 2H, CH$_2$C$_2$H$_9$), 1.93 (BOCH$_2$CH$_2$CH$_2$O) 3.84 (t, 2H, BOCH$_2$C$_2$H$_9$), 4.03 (BOCH$_2$CH$_2$CH$_2$O) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$); $\delta$ = 14.1 (CH$_3$), 22.6 (CH$_2$), 25.7 (CH$_2$), 27.1 (BOCH$_2$CH$_2$CH$_2$O), 29.6 (CH$_2$), 31.4 (CH$_2$), 32.8 (CH$_2$), 62.7 (BOCH$_2$CH$_2$CH$_2$O), 63.1 (OCH$_2$C$_2$H$_9$) ppm; $^{11}$B NMR (96 MHz, CDCl$_3$); $\delta$ = 28.7 ppm; MS (EI): m/z (%): 201 (1) [M$^+$+1], 187 (6), 115 (100), 103 (89), 85 (27), 75 (37), 70 (74), 55 (68), elemental analysis calcd for (%): C$_{10}$H$_{21}$BO$_2$: C, 60.03; H, 10.58; found C, 59.81, H 10.44

2-(pent-4’-enyloxy)-1,3,2-dioxaborinane: MS (EI): m/z (%): 170 (1) [M$^+$], 141 (5), 115 (100), 85 (37), 67 (36)
2-benzyloxy-1,3-dioxaborinane: $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 1.88 (qu, 2H, BOC$_2$CH$_3$), $J$ = 5.5 Hz), 4.25 (t, 4H, BOC$_2$CH$_2$, $J$ = 5.5 Hz), 4.86 (s, 2H, BOC$_2$Ph), 7.31-7.46 (br, 5H, C$_6$H$_5$) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 27.2 (BOC$_2$CH$_2$), 62.7 (BOC$_2$CH$_2$), 65.3 (BOC$_2$Ph), 126.8 (C$_6$H$_5$), 128.2 (C$_6$H$_5$), 128.5 (C$_6$H$_5$), 132.0 (C$_6$H$_5$) ppm. $^{11}$B NMR (96 MHz, CDCl$_3$): $\delta$ = 28.7 ppm; MS (EI): m/z (%): 164 (40) [M$^+$-28], 149 (79), 121 (100), 115 (7), 105 (7), 91 (19), 77 (15); elemental analysis calcd for (%) C$_{10}$H$_{13}$BO$_3$: C, 62.55; H, 6.82; found C, 62.31, H 7.04

2-(2'-phenyletoxy)-1,3,2-dioxaborinane: $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 1.90 (qu, 2H, BOC$_2$CH$_2$O, $J$ = 5.5 Hz), 2.78 (t, OCH$_2$CH$_2$Ph, $J$ = 5.7 Hz), 3.89 (t, 4H, BOC$_2$CH$_2$Ph, $J$ = 5.7 Hz), 4.03 (t, 4H, BOC$_2$CH$_2$CH$_2$O, $J$ = 5.5 Hz), 7.20-7.37 (br, 5H, C$_6$H$_5$) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 27.2 (BOC$_2$CH$_2$CH$_2$O), 38.0 (OCH$_2$CH$_2$Ph), 62.7 (BOC$_2$CH$_2$CH$_2$O), 63.9 (BOC$_2$CH$_2$Ph), 126.4 (C$_6$H$_5$), 128.2 (C$_6$H$_5$), 129.0 (C$_6$H$_5$), 138.8 (C$_6$H$_5$) ppm. $^{11}$B NMR (96 MHz, CDCl$_3$): $\delta$ = 28.7 ppm; MS (EI): m/z (%): 205 (1) [M$^+$-1], 115 (100), 104 (98), 91 (43), 85 (25), 77 (16), 65 (21); elemental analysis calcd for (%) C$_{13}$H$_{15}$BO$_3$: C, 64.12; H, 7.34; found C, 62.04, H 7.18

2-cyclohexyloxy-1,3,2-dioxaborinane: $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 1.26 (m, 4H, C$_6$H$_{11}$), 1.51 (m, 2H, C$_6$H$_{11}$), 1.76-1.92 (br, 4H, C$_6$H$_{11}$), 2H BOC$_2$CH$_2$CH$_2$O), 3.83 (1H, OC$_6$H$_{11}$), 4.02 (t, 4H BOC$_2$CH$_2$CH$_2$O, $J$ = 5.5 Hz) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 24.1 (C$_6$H$_{11}$), 25.4 (C$_6$H$_{11}$), 27.0 (BOC$_2$CH$_2$CH$_2$O), 34.3 (C$_6$H$_{11}$), 35.4 (C$_6$H$_{11}$), 62.7 (BOC$_2$CH$_2$CH$_2$O), 70.3 (C$_6$H$_{11}$) ppm. $^{11}$B NMR (96 MHz, CDCl$_3$): $\delta$ = 28.6 ppm; MS (EI): m/z (%): 184 (9) [M$^+$], 155 (27), 141 (100), 113 (38), 82 (37), 67 (36), 55 (14); elemental analysis calcd for (%) C$_{18}$H$_{27}$BO$_3$: C, 58.74; H, 9.31; found C, 58.58, H 9.13

3-(1',3'2'-dioxaborian-2'-yl)oxy)propanonitrile: $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 1.99 (qu, 2H, BOC$_2$CH$_2$CH$_2$O, $J$ = 5.5 Hz), 2.60 (t, 2H CH$_2$C≡N), 3.89 (t, 2H, CH$_2$C≡C≡N) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 26.3 (CH$_2$C≡N), 27.1 (BOC$_2$CH$_2$CH$_2$O), 57.9 (BOC$_2$CH$_2$ C≡N), 62.8 (BOC$_2$CH$_2$CH$_2$O), 117.6 (C≡N) ppm. $^{11}$B NMR (96 MHz, CDCl$_3$): $\delta$ = 28.7 ppm; MS (EI): m/z (%): 156 (6) [M$^+$+1], 140 (7), 125 (10), 115 (100), 98 (25), 85 (23), 71 (10), 54 (28); elemental analysis calcd for (%) C$_{6}$H$_{10}$BNO$_3$: C, 58.74; H, 9.31; N, 9.04 found C, 58.88, H 9.23, N, 9.18

2-((tetrahydrofuran-2'-yl)metoxy)-1,3,2-dioxaborinane: MS (EI): m/z (%): 186 (1) [M$^+$], 115 (10), 85 (18), 71 (100), 57 (7)
