A stereoselective synthesis of (E)- or (Z)-β-arylvinyl halides via borylative coupling/halodeborylation protocol

Jakub Szyling,a,b Adrian Franczyk,a Piotr Pawluć,b Bogdan Marciniec*a,b and Jędrzej Walkowiak*a

aCentre for Advanced Technologies, Adam Mickiewicz University in Poznan, Umultowska 89c, 61-614 Poznan
bFaculty of Chemistry, Adam Mickiewicz University in Poznan, Umultowska 89b, 61-614 Poznan

e-mail: jedrzejw@amu.edu.pl

1. General information

The chemicals were obtained from the following sources: toluene, hexane, diethyl ether, dichloromethane (DCM), acetonitrile, pentane, hexane, 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane, styrene, all substituted styrenes, bromine, iodine, N-iodosuccinimide (NIS), N-bromosuccinimide (NBS), sodium methoxide, deuterated chloroform CDCl₃, and acetone-d₆ were purchased from Sigma Aldrich or abcr. Sodium hydroxide, magnesium sulfate (MgSO₄), potassium hydroxide (KOH), sodium thiosulfate (Na₂S₂O₃) and RuCl₃·3H₂O were obtained from P.O.Ch., Gliwice. Toluene, hexane and diethyl ether were purified by an mBraun MB SPS 800 purification system and stored over molecular sieves type 4 Å. The reagents were used as delivered without any preliminary purification steps. The ruthenium catalysts [Ru(CO)Cl(H)(PPh₃)₃]¹ and [Ru(CO)Cl(H)(PCy₃)₂]² were prepared according to literature procedures. Borylative coupling reactions were carried out under argon atmosphere, while halodeborylation processes were proceeded in air.

Nuclear magnetic resonance (NMR) spectroscopy: ¹H NMR (300, 400 MHz), were recorded on a Bruker Ascend 400 MHz NANOBAY, Bruker UltraShield 300 MHz or Varian VNMR-S 400 MHz spectrometers in CDCl₃ solution. Chemical shifts were reported in δ (ppm) with reference to the residue solvent (¹H δH = 7.26 ppm, for CDCl₃). Analytical gas chromatographic (GC) analyses were performed on a Varian Star 3400CX with a DB-5 fused silica capillary column (30 m × 0.15 mm) and TCD. The mass spectra of the substrates and products were obtained by GC-MS analysis (Varian Saturn 2100T, equipped with a CP-SLI 6CB capillary column (30 m × 0.25 mm) and an ion trap detector). The halodeborylation products were isolated using column chromatography filled with silica 60 carried out using flash chromatography – Flash Chromatograph Biotage Isolera One.
2. Characterization of representative products of borylative coupling of styrenes with 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane

*(E)-1-(4',4',5',5'-Tetramethyl)—1'3',2'-dioxaboranyl-2-phenylethene* was synthesized according to the above described procedure. The reaction yield was 100 % and isolated yield of the product was 94 % (calculated according to the theoretical yield).

$^1$H NMR (400 MHz, CDCl$_3$, 25 $^\circ$C): $\delta = 1.22$ (s, 12H, CH$_3$), 6.09 (d, 1H, J$_{H-H}$ = 18.4 Hz, HC=), 7.15-7.47 (m, 6H, Ar, HC=) ppm.

$^{13}$C NMR (75 MHz, CDCl$_3$, 25$^\circ$C): 24.9 (CCH$_3$), 83.4 (CCH$_3$), 127.1, 128.6, 128.9, 137.5, 149.6 ppm.

MS m/z (rel. int., %): 230(M$^+$, 15), 215(29), 187(12), 173(13), 157(12), 144(100), 131(46), 105(23), 77(24), 51(11).
(E)-1-(4',4',5',5'-Tetramethyl)—1',3',2'-dioxaboronaryl-2-(4''-bromophenyl)ethene was synthesized according to the above described procedure. The reaction yield was 100 % and isolated yield of the product was 92 % (calculated according to the theoretical yield).

$^1$H NMR (400 MHz, acetone-d$_6$, 25 °C): $\delta$ = 1.23 (s, 12H, CH$_3$), 6.14 (d, 1H, $J_{H-H}$ = 18.4 Hz, HC=), 7.26 (d, 1H, $J_{H-H}$=18.4 Hz, HC=), 7.46-7.53 (4H, m, Ar) ppm.

$^{13}$C NMR (75 MHz, acetone-d$_6$, 25°C): 23.5 (CCH$_3$), 84.2 (CCH$_3$), 123.4, 129.9, 132.8, 137.8, 148.8 ppm.

MS m/z (rel. int., %): 308(M$^+$, 58), 293(24), 264(11), 251(13), 224(80), 209(7), 143(100), 77(5).
(E)-1-(4',4',5',5'-Tetramethyl)—1',3',2'-dioxaboronalyl-2-(2''-naphtalen-1''-ylo)ethane was synthesized according to the above described procedure. The reaction yield was 83% and isolated yield of the product was 54% (calculated according to the theoretical yield).

$^1$H NMR (400 MHz, CDCl$_3$, 25°C): $\delta$ 1.22 (s, 12H, CH$_3$), 6.17 (d, 1H, $J_{H-H}$ = 18.1 Hz, HC=), 7.30-7.41 (m, 3H, napht. and =CH), 7.61-7.71 (m, 3H, napht.), 8.09-8.15 (m, 2H, napht.) ppm.

$^{13}$C NMR (75 MHz, CDCl$_3$, 25°C): 24.96(CCH$_3$), 83.5 (CCH$_3$), 123.8, 124.2, 125.7, 125.9, 126.3, 128.62, 129.2, 131.2, 133.8, 135.4, 146.6 ppm.

MS m/z (rel. int., %): 280(M$^+$, 81), 265(12), 223(14), 193(10), 179(94), 163(30), 153(56), 127(6), 84(100).
3. $^1$H NMR spectra of (E)-β-aryl vinyl bromides

(E)-β-Bromostyrene (1a)
(E)-β-Bromo(4-methylstyrene) (2a)
(E)-β-Bromo(4-methoxystyrene) (3a)
(E)-β-Bromo(4-bromostyrene) (4a)

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PROTON

Br

Br

H

\( f_1 \) (ppm)

-20 0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400

7.34 7.04 6.93 6.67 3.34 1.94 1.00 1.00 1.00
(E)-β-Bromo(3-bromostyrene) (Sa)
(E)-β-Bromo(4-chlorostyrene) (6a)
(E)-\(\beta\)-Bromo(2-chlorostyrene) (7a)
4. $^1$H NMR spectra of (E)-$\beta$-arylvinyl iodides

(E)-$\beta$-Iodostyrene (1b)
(E)-β-Iodo(4-methylstyrene) (2b)

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(E)-β-Iodo(4-methoxystyrene) (3b)
(E)-β-Iodo(4-bromostyrene) (4b)

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-50 0 50 100 150 200 250 300 350 400 450 500 550 600 650 700

f1 (ppm)

1.00 2.04 1.00 2.02 6.70 A (d) 6.72 B (d) 7.20 B (d) 6.99 C (d) 7.29 D (d) 6.67 6.72 6.98 7.01 7.18 7.23 7.27 7.30 I B r
(E)-β-Iodo(3-bromostyrene) (5b)
(E)-β-Iodo(4-chlorostyrene) (6b)
(E)-β-Iodo(2-chlorostyrene) (7b)
(E)-1-ido-2-naphtylethene (8b)
5. $^1$H NMR spectra of (Z)-β-arylvinyl bromides

(Z)-β-Bromostyrene (9)
(Z)-β-Bromo(4-methylstyrene) (10)
(Z)-β-Bromo(4-methoxystyrene) (11)
(Z)-β-Bromo(4-chlorostyrene) (12)
(Z)-β-Bromo(4-bromostyrene) (13)
Literature