

Defunctionalization of γ -Alkylidene- α -hydroxybutenolides by Palladium(0)-Catalyzed Reaction of Enol Triflates with Hexylboronic Acid

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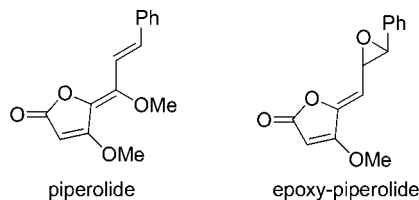
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The Suzuki reaction of hexylboronic acid with enol triflates derived from γ -alkylidene- α -hydroxybutenolides resulted in reductive formation of α -unsubstituted γ -alkylidenebutenolides. The formation of the products can be explained based

on an "oxidative addition/transmetalation/ β -hydride elimination/reductive elimination" mechanism.

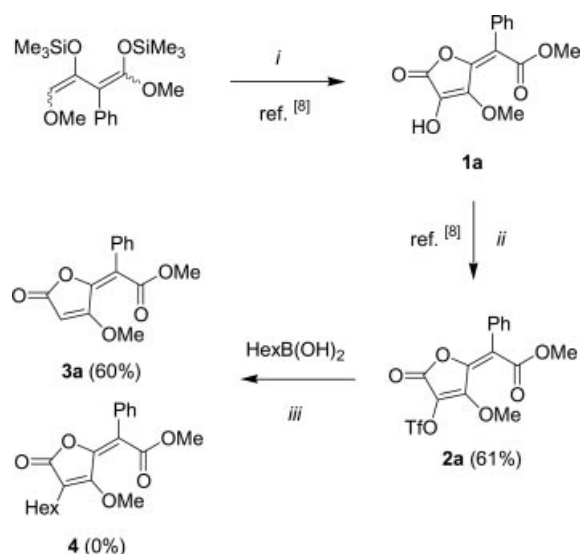
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γ -Alkylidenebutenolides are present in a variety of pharmacologically relevant natural products and natural product analogues.^[1] A number of natural products, such as piperolide, contain a hydrogen atom located at the α -position and a methoxy group located at the β -position of the butenolide.^[2] γ -Alkylidene- α -hydroxybutenolides are available by cyclization of 1,3-bis(silyl enol ethers)^[3,4] with oxalyl chloride;^[5] the hydroxy group has been functionalized by Stille^[6] and Suzuki^[7] cross coupling reactions of the corresponding enol triflates. This approach has been successfully applied to the synthesis of a number of natural products, such as pulvinic acids^[8] or linderone and lucidone;^[9] in addition, an analog of norbadione A has been recently prepared.^[10] During a synthetic project, there was the need to replace the α -hydroxy group of the butenolide by a hydrogen atom. Brückner et al. reported Stille reactions of butenolide-derived enol triflates with Bu_3SnH using catalytic amounts of palladium catalysts or $\text{NiCl}_2(\text{PPh}_3)_2$.^[11] However, these conditions proved to be unsuccessful for our substrates. Herein, we report an unexpected solution of this problem based on the reaction of enol triflates with hexylboronic acid; these transformations allow a convenient defunctionalization of the butenolide based on an "oxidative addition/transmetalation/ β -hydride elimination/reductive elimination" mechanism.



Results and Discussion

Our starting point was the reaction of triflate **2a**, readily available from butenolide **1a**,^[8] with alkylboronic acids. Notably, the reaction of **2a** with hexylboronic acid afforded the defunctionalized γ -alkylidenebutenolide **3a** rather than the expected coupling product **4** (Scheme 1). Optimal yields were obtained by application of standard reaction conditions [3 mol-% $\text{Pd}(\text{PPh}_3)_4$, 1.5 equiv. K_3PO_4 , dioxane, reflux]. All attempts to prepare **3a** by palladium(0)-catalyzed reactions using Bu_3SnH or formic acid proved to be unsuccessful. Unexpectedly, the use of butyl- rather than hexylboronic acid also proved to be unsuccessful.

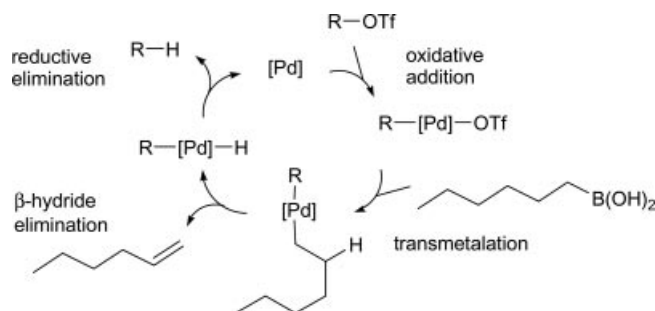


Scheme 1. Reductive cleavage of **2**. *i*: $(\text{COCl})_2$, Me_3SiOTf (0.3 equiv.), CH_2Cl_2 ; *ii*: TF_2O , pyridine, $-78 \rightarrow -10^\circ\text{C}$; *iii*: $\text{Pd}(\text{PPh}_3)_4$ (3 mol-%), K_3PO_4 (1.5 equiv.), dioxane, reflux.

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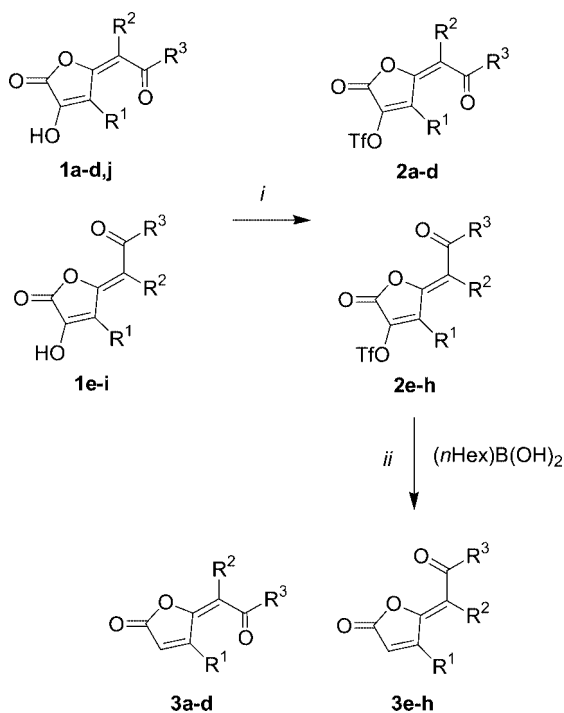
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The formation of **3a** can be explained by oxidative addition, transmetalation, β -hydride elimination and subsequent reductive elimination (Scheme 2). It is known that alkylboranes sometimes undergo a fast β -hydride elimination using $\text{Pd}(\text{PPh}_3)_4$ as a catalyst.^[12]



Scheme 2. Possible mechanism for the formation of **3a**.

The reaction of triflates **2b–d**, prepared from **1b–d**, with $\text{HexB}(\text{OH})_2$ afforded the defunctionalized γ -alkyldienebutenolides **3b–d** containing a methoxy-substituted butenolide moiety and an aryl group located at the exocyclic double bond (Scheme 3, Table 1). The high diastereomeric purity [$(E)/(Z) > 98:2$] of the exocyclic double bond was not reduced during the reaction, due to the higher thermodynamic stability of the (*E*)- compared to the (*Z*)-configured isomer. Butenolide **3e** was prepared by reaction of **2e** with hexylboronic acid. The high diastereomeric purity [$(E)/(Z) < 2:98$] was again not reduced during the reaction, due to the steric effect of the methoxy group and the absence of an additional substituent located at the exocyclic double bond. Likewise, the (*Z*)-configured γ -alkyldienebut-



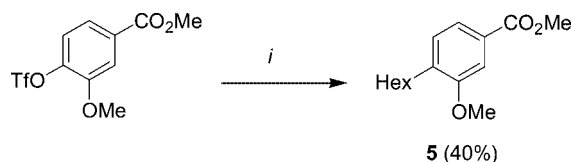
Scheme 3. Reductive cleavage of **2**. *i*: Tf_2O , pyridine, $-78 \rightarrow -10^\circ\text{C}$; *ii*: $\text{Pd}(\text{PPh}_3)_4$ (3 mol-%), K_3PO_4 (1.5 equiv.), dioxane, reflux.

enolides **3f** and **3g**, containing an ethoxy and a benzyloxy group located at the butenolide moiety, were prepared. Starting with **2h**, the (*Z*)-configured butenolide **3h**, containing an acetyl rather than an alkoxy carbonyl group located at the exocyclic double bond, was prepared. The reaction of hexylboronic acid with triflates **2i** and **2j**, containing an ethyl group or a hydrogen atom located at the butenolide moiety, respectively, failed to give the corresponding defunctionalized butenolides. In contrast, the corresponding butenolides **1i** and **1j** were recovered. This result can be explained based on electronic or neighbouring-group effects exerted by the alkoxy group located at carbon atom C-4. Notably, the reaction of hexylboronic acid with 2-methoxy-4-(methoxycarbonyl)phenyl triflate resulted, under identical conditions, in the formation of the expected methyl 4-hexyl-3-methoxybenzoate (**5**) (Scheme 4).

Table 1. Products and yields.

2,3	R ¹	R ²	R ³	2 [%] ^[a]	3 [%] ^[a]	(<i>E</i>)/(<i>Z</i>) ^[b]
a	OMe	Ph	OMe	61 ^[c]	60	> 98:2
b	OMe	4-(MeO)C ₆ H ₄	OMe	77 ^[c]	55	> 98:2
c	OMe	3,4-(MeO) ₂ C ₆ H ₃	OMe	66 ^[c]	54	> 98:2
d	OMe	3,4,5-(MeO) ₃ C ₆ H ₂	OMe	74 ^[c]	47	> 98:2
e	OMe	H	OMe	61 ^[d]	70	< 2:98
f	OEt	H	OEt	89	62	< 2:98
g	OBn	H	OEt	83 ^[d]	45	< 2:98
h	OMe	H	Me	46	67	< 2:98
i	Et	H	OEt	76 ^[e]	0	< 2:98
j	H	H	OMe	52 ^[e]	0	> 98:2

[a] Yields of isolated products. [b] Configuration of the exocyclic double bond (by ¹H NMR). [c] Known compound.^[8] [d] Known compound.^[6] [e] Known compound.^[7]



Scheme 4. *i*: $n\text{HexB}(\text{OH})_2$, $\text{Pd}(\text{PPh}_3)_4$ (3 mol-%), K_3PO_4 (1.5 equiv.), dioxane, reflux.

Conclusion

In summary, we have reported the defunctionalization of γ -alkyldiene- α -hydroxybutenolides based on palladium(0)-catalyzed reactions of enol triflates with hexylboronic acid.

Experimental Section

General Comments: All solvents were dried by standard methods and all reactions were carried out under an inert gas. For the ¹H and ¹³C NMR spectra the deuterated solvents indicated were used. MS data were obtained using the electron ionization (70 eV) or the chemical ionization technique (CI; H₂O). For preparative-scale chromatography silica gel (60–200 mesh) was used. Melting points are uncorrected.

General Procedure for the Preparation of Triflates 2: To a dichloromethane (10 mL per 1 mmol of starting material) solution of butenolide **1** (1.0 equiv.) triflic anhydride (1.2 equiv.) and pyridine (2.0 equiv.) were added at -78°C . The solution was warmed to -10°C within 4 h. The product was isolated by rapid chromatography (silica gel; dichloromethane) of the reaction mixture.

2f: Starting with **1f** (311 mg, 1.36 mmol), pyridine (0.22 mL, 2.72 mmol) and triflic anhydride (0.27 mL, 1.63 mmol), **2f** was isolated as a yellow solid (433 mg, 89%), m.p. $60\text{--}62^{\circ}\text{C}$. ^1H NMR (300 MHz, CDCl_3): δ = 1.33 (t, 3 H, J = 7.2 Hz, CH_3), 1.51 (t, 3 H, J = 6.9 Hz, CH_3), 4.28 (q, 2 H, J = 7.2 Hz, OCH_2), 4.61 (q, 2 H, J = 6.9 Hz, OCH_2), 5.83 (s, 1 H, =CH) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 14.09, 14.88 (CH_3), 61.43, 70.14 (CH_2), 100.41 (CH), 113.85 (C), 118.30 (q, J = 319.5, CF_3), 148.23, 154.41, 159.89, 162.16 (C) ppm. IR (KBr): $\tilde{\nu}$ = 2990 (s), 1813 (s), 1722 (s), 1664 (s), 1430 (s), 1328 (s), 1236 (s), 1133 (m), 1032 (m), 944 (m), 814 (m) cm^{-1} . MS (EI; 70 eV): m/z (%) = 359.9 (2) [M^+], 314.9 (2), 198.9 (33), 114.3 (49), 69.9 (100). $\text{C}_{11}\text{H}_{11}\text{O}_8\text{SF}_3$ (360.26): calcd. C 36.67, H 3.07; found C 36.77, H 3.48.

2h: Starting with **1h** (700 mg, 3.80 mmol), pyridine (0.61 mL, 7.60 mmol) and triflic anhydride (0.77 mL, 4.56 mmol), **2h** was isolated as a yellow solid (550 mg, 46%), m.p. $51\text{--}52^{\circ}\text{C}$. ^1H NMR (300 MHz, CDCl_3): δ = 2.51 (s, 3 H, CH_3), 4.33 (s, 3 H, OCH_3), 5.90 (s, 1 H, =CH) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 31.83, 60.70 (CH_3), 108.46 (CH), 113.66 (C), 118.40 (q, J = 319.50 Hz, CF_3), 146.75, 155.71, 159.32, 194.80 (C) ppm. IR (KBr): $\tilde{\nu}$ = 1804 (s), 1674 (s), 1428 (s), 1362 (m), 1325 (m), 1237 (s), 1217 (s), 1135 (s), 1073 (s), 956 (m), 828 (m) cm^{-1} . MS (EI; 70 eV): m/z (%) = 316.6 (7) [M^+], 300.6 (21), 167.8 (27), 126.9 (48), 69.9 (61). $\text{C}_9\text{H}_7\text{O}_7\text{SF}_3$ (316.21): calcd. C 34.18, H 2.23; found C 34.51, H 2.44.

General Procedure for the Synthesis of Butenolides 3 by Suzuki Reactions: A dioxane (5 mL per 1 mmol of starting material) solution of triflate **2** (1.0 equiv.), hexylboronic acid (1.3 equiv.), K_3PO_4 (1.5 equiv.) and $\text{Pd}(\text{PPh}_3)_4$ (3 mol-%) was refluxed for 4 h. A saturated aqueous solution (10 mL) of ammonium chloride was added. The organic and the aqueous layer were separated and the latter was extracted (3 $\times$) with diethyl ether. The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated in vacuo. The residue was purified by chromatography (silica gel; EtOAc/hexane).

3a: Starting with **2a** (100 mg, 0.24 mmol), hexylboronic acid (42 mg, 0.31 mmol), K_3PO_4 (84 mg, 0.39 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (10 mg, 0.008 mmol), **3a** was isolated as a yellow solid (38 mg, 60%), m.p. $137\text{--}138^{\circ}\text{C}$. ^1H NMR (300 MHz, CDCl_3): δ = 3.88 (s, 3 H, OCH_3), 3.97 (s, 3 H, OCH_3), 5.37 (s, 1 H, =CH), 7.26–7.66 (m, 5 H, ArH) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 53.02, 60.27 (CH_3), 90.50 (CH), 116.62 (C), 128.94 (2 C), 129.31 (2 C), 129.68 (CH), 130.96, 141.22, 166.76, 167.40, 170.09 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3433 (w), 2954 (w), 1766 (s), 1730 (s), 1607 (s), 1440 (m), 1366 (m), 1300 (m), 1207 (m), 1043 (m), 974 (m), 872 (m), 793 (m) cm^{-1} . MS (EI; 70 eV): m/z (%) = 260.1 (77) [M^+], 201.0 (12), 144.8 (26), 118.0 (49), 69.9 (59). $\text{C}_{14}\text{H}_{12}\text{O}_5$ (260.24): calcd. C 64.61, H 4.64; found C 64.10, H 4.85.

3b: Starting with **2b** (100 mg, 0.22 mmol), hexylboronic acid (39 mg, 0.29 mmol), K_3PO_4 (112 mg, 0.34 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (8 mg, 0.006 mmol), **3b** was isolated as a yellow solid (35 mg, 55%), m.p. $141\text{--}142^{\circ}\text{C}$. ^1H NMR (300 MHz, CDCl_3): δ = 3.83 (s, 3 H, OCH_3), 3.88 (s, 3 H, OCH_3), 3.95 (s, 3 H, OCH_3), 5.33 (s, 1 H, =CH), 6.92 (dd, 2 H, J = 2.1, 6.9 Hz, ArH), 7.61 (dd, 2 H, J = 2.1 Hz, 6.9 Hz, ArH) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 52.83, 55.38, 60.02 (CH_3), 89.73 (CH), 114.31 (2 C, CH), 116.40, 123.21

(C), 130.91 (2 C, CH), 139.59, 160.53, 166.88, 167.50, 170.01 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3215 (w), 2926 (w), 1779 (s), 1732 (s), 1605 (s), 1514 (m), 1289 (m), 1258 (m), 1185 (m), 1043 (m), 873 (m) cm^{-1} . MS (EI; 70 eV): m/z (%) = 290.0 (100) [M^+], 231.0 (81), 175.0 (19), 147.4 (19), 83.1 (44). $\text{C}_{15}\text{H}_{14}\text{O}_6$ (290.27): calcd. C 62.06, H 4.86; found C 61.80, H 5.03.

3c: Starting with **2c** (196 mg, 0.41 mmol), hexylboronic acid (71 mg, 0.54 mmol), K_3PO_4 (142 mg, 0.66 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (15 mg, 0.01 mmol), **3c** was isolated as a yellow solid (71 mg, 54%), m.p. $155\text{--}156^{\circ}\text{C}$. ^1H NMR (300 MHz, CDCl_3): δ = 3.88 (s, 3 H, OCH_3), 3.90 (s, 6 H, OCH_3), 3.96 (s, 3 H, OCH_3), 5.34 (s, 1 H, =CH), 6.87 (d, 1 H, J = 8.5 Hz, ArH), 7.16 (dd, 1 H, J = 2.2 Hz, 8.5 Hz, ArH), 7.30 (d, 1 H, J = 2.1 Hz, ArH) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 52.76, 55.86, 55.93, 59.99 (CH_3), 89.69, 110.95, 112.09 (CH), 116.33 (C), 122.61 (CH), 123.34, 139.66, 148.88, 150.24, 166.69, 167.26, 169.90 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3115 (w), 2948 (w), 1769 (s), 1733 (s), 1604 (s), 1522 (s), 1448 (m), 1366 (m), 1262 (s), 1155 (m), 873 (m) cm^{-1} . MS (EI; 70 eV): m/z (%) = 320.0 (100) [M^+], 261.1 (76), 205.1 (14), 143.1 (9), 69.9 (17). $\text{C}_{16}\text{H}_{16}\text{O}_7$ (320.29): calcd. C 59.99, H 5.03; found C 59.66, H 5.28.

3d: Starting with **2d** (245 mg, 0.49 mmol), hexylboronic acid (83 mg, 0.64 mmol), K_3PO_4 (256 mg, 0.78 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (18 mg, 0.014 mmol), **3d** was isolated as a yellow solid (80 mg, 47%), m.p. $149\text{--}150^{\circ}\text{C}$. ^1H NMR (300 MHz, CDCl_3): δ = 3.87 (s, 12 H, OCH_3), 3.97 (s, 3 H, OCH_3), 5.37 (s, 1 H, =CH), 6.87 (s, 2 H, ArH) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 52.82, 56.21 (2 C), 60.05, 60.84 (CH_3), 90.09, 106.62 (2 C, CH), 116.17, 125.86, 139.39, 140.59, 153.13 (2 C), 166.45, 167.01, 169.75 (C) ppm. IR (KBr): $\tilde{\nu}$ = 2943 (w), 1778 (s), 1740 (s), 1607 (s), 1510 (m), 1336 (m), 1275 (m), 1249 (m), 1160 (m), 1127 (s), 1057 (m), 866 (m) cm^{-1} . MS (EI; 70 eV): m/z (%) = 349.7 (3) [M^+], 290.7 (3), 238.8 (3), 180.9 (5), 57.3 (7), 28.0 (100). $\text{C}_{17}\text{H}_{18}\text{O}_8$ (350.32): calcd. C 58.28, H 5.17; found C 58.68, H 5.10.

3e: Starting with **2e** (400 mg, 1.20 mmol), hexylboronic acid (203 mg, 1.56 mmol), K_3PO_4 (383 mg, 1.80 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (42 mg, 0.03 mmol), **3e** was isolated as a yellow solid (154 mg, 70%), m.p. $120\text{--}121^{\circ}\text{C}$. ^1H NMR (300 MHz, CDCl_3): δ = 3.81 (s, 3 H, OCH_3), 3.98 (s, 3 H, OCH_3), 5.38 (s, 1 H, =CH), 5.64 (s, 1 H, =CH) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 53.01, 59.69 (CH_3), 90.96, 95.98 (CH), 151.60, 163.61, 166.68, 170.16 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3395 (w), 3224 (m), 3133 (m), 1796 (s), 1729 (s), 1674 (m), 1625 (s), 1440 (m), 1353 (m), 1238 (m), 1149 (m), 853 (m), 745 (w) cm^{-1} . MS (EI; 70 eV): m/z (%) = 183.9 (28) [M^+], 152.4 (41), 125.0 (8), 69.9 (100). $\text{C}_8\text{H}_8\text{O}_5$ (184.14): calcd. C 52.18, H 4.37; found C 52.22, H 4.50.

3f: Starting with **2f** (360 mg, 0.99 mmol), hexylboronic acid (169 mg, 1.30 mmol), K_3PO_4 (340 mg, 1.60 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (35 mg, 0.03 mmol), **3f** was isolated as a yellow solid (130 mg, 62%), m.p. $129\text{--}130^{\circ}\text{C}$. ^1H NMR (300 MHz, CDCl_3): δ = 1.32 (t, 3 H, J = 7.2 Hz, CH_3), 1.47 (t, 3 H, J = 6.9 Hz, CH_3), 4.18 (q, 2 H, J = 6.9 Hz, OCH_2), 4.26 (q, 2 H, J = 7.2 Hz, OCH_2), 5.33 (s, 1 H, =CH), 5.66 (s, 1 H, =CH) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 13.89, 14.11 (CH_3), 60.96, 69.07 (CH_2), 90.80, 96.24 (CH), 151.80, 163.21, 167.10, 169.16 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3423 (w), 3123 (m), 1807 (s), 1723 (s), 1676 (s), 1620 (s), 1332 (s), 1238 (s), 1148 (s), 1025 (m), 835 (m) cm^{-1} . MS (EI; 70 eV): m/z (%) = 211.8 (7) [M^+], 183.8 (21), 166.8 (27), 138.9 (19), 86.8 (26). $\text{C}_{10}\text{H}_{12}\text{O}_5$ (212.20): calcd. C 56.60, H 5.70; found C 56.70, H 5.84.

3g: Starting with **2g** (200 mg, 0.51 mmol), hexylboronic acid (86 mg, 0.66 mmol), K_3PO_4 (174 mg, 0.81 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (20 mg, 0.01 mmol), **3g** was isolated as a yellow solid (63 mg, 45%), m.p. $120\text{--}121^{\circ}\text{C}$. ^1H NMR (300 MHz, CDCl_3): δ = 1.31 (t, 3 H, J

= 6.9 Hz, CH₃), 4.26 (q, 2 H, *J* = 6.9 Hz, OCH₂), 5.14 (s, 2 H, OCH₂), 5.41 (s, 1 H, =CH), 5.69 (s, 1 H, =CH), 7.35–7.44 (m, 5 H, ArH) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 14.12 (CH₃), 61.03, 74.69 (CH₂), 91.91, 96.56, 127.91 (2 C), 128.93 (2 C), 129.30 (CH), 133.19, 151.70, 163.16, 166.89, 168.75 (C) ppm. IR (KBr): ν̄ = 3425 (m), 3102 (w), 1794 (s), 1701 (s), 1615 (s), 1324 (m), 1285 (m), 949 (m), 855 (m) cm⁻¹. MS (EI; 70 eV): *m/z* (%) = 274.1 (5) [M⁺], 246.0 (6), 229.0 (4), 205.0 (4), 159.0 (7), 91.0 (100). C₁₅H₁₄O₅ (274.27): calcd. C 65.68, H 5.14; found C 65.41, H 5.41.

3h: Starting with **2h** (320 mg, 1.01 mmol), hexylboronic acid (170 mg, 1.30 mmol), K₃PO₄ (343 mg, 1.61 mmol) and Pd(PPh₃)₄ (35 mg, 0.03 mmol), **3h** was isolated as a yellow solid (114 mg, 67%), m.p. 112–114 °C. ¹H NMR (300 MHz, CDCl₃): δ = 2.52 (s, 3 H, CH₃), 4.01 (s, 3 H, OCH₃), 5.42 (s, 1 H, =CH), 5.73 (s, 1 H, =CH) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 31.09, 59.76 (CH₃), 90.69, 104.90 (CH), 150.35, 166.26, 170.85, 196.13 (C) ppm. IR (KBr): ν̄ = 3105 (m), 1797 (s), 1769 (m), 1657 (s), 1616 (s), 1359 (m), 1332 (m), 1257 (s), 1182 (m), 976 (s), 849 (s) cm⁻¹. MS (EI; 70 eV): *m/z* (%) = 167.8 (17) [M⁺], 152.3 (47), 136.8 (34), 110.0 (10), 69.8 (100). C₈H₈O₄ (168.14): calcd. C 57.14, H 4.79; found C 57.48, H 5.36.

5: Starting with triflate (315 mg, 1.00 mmol), hexylboronic acid (169 mg, 1.30 mmol), K₃PO₄ (340 mg, 1.60 mmol) and Pd(PPh₃)₄ (35 mg, 0.03 mmol), **5** was isolated as a colorless oil (100 mg, 40%). ¹H NMR (250 MHz, CDCl₃): δ = 0.87 (t, 3 H, *J* = 1.5 Hz, CH₃), 1.29–1.60 (m, 8 H, CH₂), 2.63 (t, 2 H, *J* = 7.6 Hz, CH₂), 3.86 (s, 3 H, OCH₃), 3.89 (s, 3 H, OCH₃), 7.16 (d, 1 H, *J* = 7.6 Hz, ArH), 7.49 (d, 1 H, *J* = 1.5 Hz, ArH), 7.57 (dd, 1 H, *J* = 1.8 Hz, 7.6 Hz, ArH) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 14.11 (CH₃), 22.65, 29.24, 29.47, 30.31, 31.97 (CH₂), 52.00, 55.42 (CH₃), 111.09, 122.18 (CH), 129.38 (C), 129.54 (CH), 137.13, 157.32, 167.23 (C) ppm. IR (neat): ν̄ = 3054 (m), 2928 (m), 2858 (m), 1722 (s), 1460 (m), 1291 (m), 1106 (w), 761 (w) cm⁻¹. MS (EI; 70 eV): *m/z* (%) = 249.8 (50) [M⁺], 218.8 (8), 178.8 (100), 148.1 (17), 120.8 (14). C₁₅H₂₂O₃ (250.33): calcd. C 71.97, H 8.86; found C 72.03, H 9.07.

Acknowledgments

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