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Tetrahedron 62 (2006) 4800–4806
Tetrahedron

Synthesis of functionalized *p*-dihydrobenzoquinones and *p*-benzoquinones based on [3+3] cyclizations of 1,3-bis-silyl enol ethers

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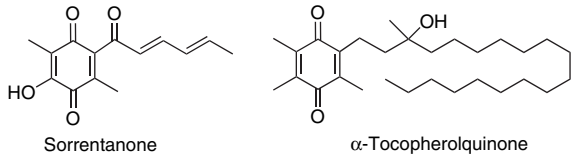
Received 14 February 2006; accepted 6 March 2006
Available online 29 March 2006

Abstract—Functionalized mono-protected *p*-dihydrobenzoquinones were prepared by [3+3] cyclization of 1,3-bis-silyl enol ethers with 2-acyloxy-3-(silyloxy)alk-2-en-1-ones. Deprotection and oxidation of the products afforded the corresponding *p*-benzoquinones.

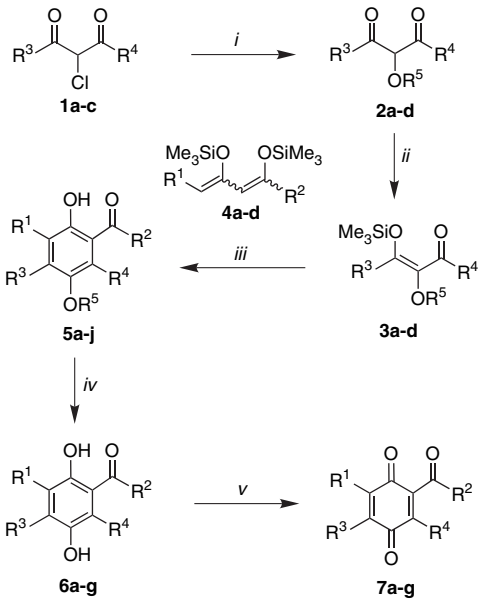
1. Introduction

p-Dihydrobenzoquinones[1,2] and *p*-benzoquinones[1,3,4] occur in a number of natural products, such as sorrentanone and α-tocopherolquinone (Scheme 1). They have found many technical and medicinal applications and represent important synthetic building blocks. Some years ago, Chan and co-workers reported an elegant approach to salicylates based on [3+3] cyclizations[5,6] of 1,3-bis-silyl enol ethers.[7] Recently, we reported the [3+3] cyclization of 1,3-bis-silyl enol ethers with 2-acyloxy-3-(silyloxy)alk-2-en-1-ones to give *p*-dihydrobenzoquinones.[8] Herein, we report full details of these studies. With regard to our preliminary communication,[8] we extended the methodology to the synthesis of *p*-benzoquinones. The transformations reported offer a convenient approach to functionalized mono-protected 1,4-dihydrobenzoquinones and to *p*-benzoquinones.



Scheme 1. *p*-Benzoquinones in natural products.

2-Chloro-1,3-diketones **1a–c** are readily available by reaction of 1,3-diketones with *N*-chlorosuccinimide (NCS).[9] The reaction of **1a–c** with sodium acetate and sodium benzoate afforded, according to a known procedure,[10] the 2-(acyloxy)alk-2-ene-1,3-diones **2a–d**. The reaction of **2a–d** with Me_3SiCl/NEt_3 gave the 2-acyloxy-3-(silyloxy)alk-2-en-1-ones **3a–d** (Scheme 2, Table 1). The $TiCl_4$ mediated [3+3] cyclization of **3a–d** with 1,3-bis-silyl enol ethers **4a–d** afforded the mono-protected *p*-dihydrobenzoquinones **5a–j**. Product **5f** contains one free and two orthogonally



Scheme 2. Synthesis of *p*-dihydrobenzoquinones **5a–j** and of *p*-benzoquinones **7a–g**; (i) NaOAc or NaOBz, DMSO, 3 h, 20 °C; (ii) Me_3SiCl, NEt_3, C_6H_6, 20 °C, 3 d; (iii) $TiCl_4$, CH_2Cl_2, −78→20 °C, 20 h; (iv) H_2SO_4 (5.0 M), THF, reflux, 36 h; (v) DDQ, C_6H_6, 3 h, 20 °C.

Keywords: Cyclization; Dihydroquinones; Oxidation; Quinones; Silyl enol ethers.
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doi:10.1016/j.tet.2006.03.019

Table 1. Products and yields

5,**6**,**7**	R^1	R^2	R^3	R^4	R^5	% (**5**)[a]	% (**6**)[a]	% (**7**)[a]
a	H	OMe	Me	Me	Ac	52	99[b]	90
b	H	OMe	Me	Ph	Ac	43	97[b]	84
c	Me	OEt	Me	Me	Ac	55	79	86
d	Et	OEt	Me	Me	Ac	54	91[b]	82
e	Et	OEt	Me	Ph	Ac	37	97[b]	82
f	OMe	OMe	Me	Me	Ac	50	83	86
g	H	OMe	Et	Et	Ac	51	98[b]	73
h	Me	OEt	Et	Et	Ac	39	—[c]	
i	H	OMe	Me	Me	Bz	55	—[c]	
j	Et	OEt	Me	Me	Bz	46	—[c]	

[a] Yields of isolated products.
[b] Used in crude form for the following step.
[c] Experiment not carried out.

protected hydroxyl groups. Treatment of a THF solution of **5a**–**g** with H_2SO_4 (5.0 M) resulted in clean deprotection to give **6a**–**g**; oxidation of the latter by DDQ afforded the *p*-benzoquinones **7a**–**g**.

The structure of all products was proved by spectroscopic methods. The structure of **5j** was independently confirmed by X-ray crystal structure analyses (Fig. 1).[11]

A great advantage of the methodology reported lies in the fact that mono-protected 1,4-dihydrobenzoquinones could be prepared without the need of regioselective protective group manipulations. The free hydroxyl group was successfully functionalized. For example, benzoate protected dihydroquinone **5i** was transformed into the corresponding enol triflate **8**. The Suzuki reaction of **8** with phenylboronic acid afforded the biaryl **9** (Scheme 3).

In conclusion, we have reported the synthesis of functionalized mono-protected *p*-dihydrobenzoquinones prepared by [3+3] cyclization of 1,3-bis-silyl enol ethers with 2-acyloxy-3-(silyloxy)alk-2-en-1-ones. Deprotection and oxidation of the products afforded the corresponding *p*-benzoquinones.

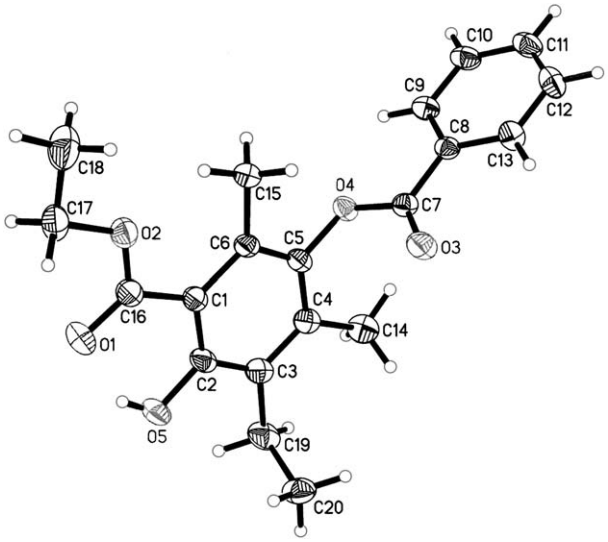
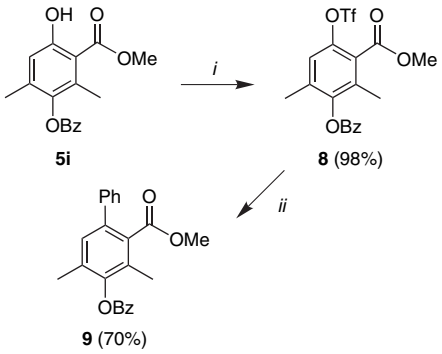


Figure 1. ORTEP plot of **5j** (non-hydrogen atoms are represented as thermal ellipsoids at the 30% probability level).



Scheme 3. (i) Tf_2O, pyridine, −78→−10 °C; (ii) phenylboronic acid, $Pd(PPh_3)_4$ (3 mol %), K_3PO_4 (1.5 equiv), dioxane, reflux.

2. Experimental

2.1. General comments

All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. For ^1H and ^{13}C NMR spectra the indicated deuterated solvents were used. Mass spectrometric data (MS) were obtained by electron ionization (EI, 70 eV), chemical ionization (CI, H_2O) or electrospray ionization (ESI). For preparative scale chromatography, silica gel (60–200 mesh) was used. Melting points are uncorrected.

2.2. General procedure for the synthesis of 2-acyloxy-1,3-diones (2b,g)

The 2-chloro-1,3-dione (1.0 mmol) was treated with sodium acetate (2.0 mmol) in anhydrous DMSO (2.60 mL/mmol) for 3 h at room temperature. After addition of water (50 mL), the organic layer was extracted with diethyl ether (3×). The combined organic layers were filtered, dried (Na_2SO_4) and concentrated. The residue was purified by chromatography (silica gel, 20% ethylacetate/heptane) to give the product.

2.2.1. Compound 2b. Starting with 2-chlorobenzoylacetone **1b** (3.00 g, 15.3 mmol), sodium acetate (2.50 g, 30.5 mmol) and DMSO (40 mL), **2b** was isolated as a colourless oil (2.40 g, 72%); ^1H NMR (300 MHz, $CDCl_3$): δ=2.22 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 6.25 (s, 1H, CH), 7.44–8.00 (m, 5H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=20.4, 26.8 (CH_3), 82.1 (CH), 128.0 (C), 128.7 (2C), 129.4 (2C), 134.2 (CH), 169.2, 190.8, 199.4 (C); IR (KBr): ν=3064 (w), 2934 (w), 1737 (s), 1693 (s), 1597 (m), 1449 (m), 1373 (m), 1228 (s), 1091 (m), 693 (m) cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 220.1 (M^+, 1), 178.1 (38), 136.0 (60), 105.0 (100), 77.0 (92); HRMS (EI): calcd for $C_{12}H_{12}O_4$ $[M]^+$: 220.0730; found: 220.0726.

2.2.2. Compound 2g. Starting with 4-chloro-3,5-heptanedione **1g** (3.0 g, 18.4 mmol), sodium acetate (3.00 g, 36.8 mmol) and DMSO (48 mL), **2g** was isolated as a colourless oil (2.50 g, 73%); ^1H NMR (300 MHz, $CDCl_3$): δ=1.01 (t, 6H, J=7.2 Hz, CH_3), 2.18 (s, 3H, CH_3), 2.50–2.74 (m, 4H, CH_2), 5.46 (s, 1H, CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=6.8 (2C), 20.4 (CH_3), 84.3 (CH), 169.3, 202.0 (2C, C);

IR (KBr): ν=2982 (w), 2943 (w), 1754 (s), 1737 (s), 1717 (s), 1374 (w), 1233 (s), 1091 (w) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 186.0 (M^+, 1), 144.0 (20), 130.0 (20), 88.0 (94), 57.0 (100), 43.0 (95); elemental analysis: calcd (%) for $C_9H_{14}O_4$ (186.20): C 58.05, H 7.57; found: C 58.45, H 7.50.

2.3. General procedure for the synthesis of alkyl 3-acyloxy-6-hydroxy salicylates (5a–j)

To a stirred CH_2Cl_2 solution (2 mL/mmol) of 1,3-bis-silyl enol ether (1.0 mmol) and silyl enol ether (1.0 mmol) was added $TiCl_4$ (1.0 mmol) at −78 °C under argon atmosphere. The temperature of the reaction mixture was allowed to rise to 20 °C during 20 h and saturated aqueous solution of $NaHCO_3$ (10 mL) was added. The organic layer was separated and extracted with diethyl ether (3×30 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated in vacuo. The residue was purified by column chromatography using 20% ethylacetate/heptane as eluent.

2.3.1. Compound 5a. Starting with 1,3-bis-silyl enol ether **4b** (1.00 g, 3.8 mmol), silyl enol ether **3a** (885 mg, 3.8 mmol) and $TiCl_4$ (0.42 ml, 3.8 mmol), **5a** was isolated as a colourless solid (470 mg, 52%), mp 79 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.12 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 3.93 (s, 3H, OCH_3), 6.73 (s, 1H, ArH), 11.07 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=15.3, 17.1, 20.3, 52.1 (CH_3), 110.7 (C), 117.1 (CH), 132.1, 138.2, 141.0, 160.1, 169.1, 171.6 (C); IR (KBr): ν=3490 (w), 2990 (w), 2961 (m), 1759 (s), 1664 (s), 1621 (m), 1476 (m), 1439 (m), 1362 (m),1319 (m), 1194 (s), 1072 (m), 802 (m) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 238 (M^+, 12), 196 (44), 164 (100); HRMS (EI): calcd for $C_{12}H_{14}O_5$ $[M]^+$: 238.0836; found: 238.0837.

2.3.2. Compound 5b. Starting with 1,3-bis-silyl enol ether **4b** (755 mg, 2.8 mmol), silyl enol ether **3b** (847 mg, 2.8 mmol) and $TiCl_4$ (0.31 ml, 2.8 mmol), **5b** was isolated as a colourless solid (366 mg, 43%), mp 97 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.80 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 3.39 (s, 3H, OCH_3), 6.91 (s, 1H, ArH), 7.08–7.33 (m, 5H, ArH), 10.89 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=17.0, 19.9, 51.7 (CH_3), 110.4 (C), 118.9, 126.8, 127.3 (2C), 128.2 (2C, CH), 136.4, 137.6, 138.8, 140.2, 159.5, 169.3, 170.7 (C); IR (KBr): ν=3526 (w), 3422 (w), 3055 (w), 3032 (w), 2954 (w), 1754 (s), 1670 (s), 1438 (m), 1358 (m), 1328 (m), 1237 (m), 1217 (s), 1205 (s), 1193 (s), 1072 (m), 705 (m) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 300.1 (M^+, 3), 258.1 (35), 226.0 (100); elemental analysis: calcd (%) for $C_{17}H_{16}O_5$ (300.31): C 67.99, H 5.37; found: C 67.93, H 5.69.

2.3.3. Compound 5c. Starting with 1,3-bis-silyl enol ether **4c** (808 mg, 2.8 mmol), silyl enol ether **3a** (645 mg, 2.8 mmol) and $TiCl_4$ (0.30 ml, 2.8 mmol), **5c** was isolated as a colourless solid (410 mg, 55%), mp 96 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.40 (t, 3H, J=8.4 Hz, CH_3), 2.09 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 4.41 (q, 2H, J=7.0 Hz, OCH_2), 11.51 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=9.7, 11.9, 12.2, 13.4, 18.5 (CH_3), 59.7 (CH_2), 108.2, 121.8, 126.8, 134.3, 138.7, 156.4, 167.5, 169.8 (C); IR (KBr): ν=3413 (w), 2989 (w), 2970 (w), 2904 (w), 1753 (s), 1653 (s), 1404 (m), 1369 (m), 1312 (m), 1262 (m),1215 (s), 1197 (s), 1035 (w), 801 (m) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%): 266.1 (M^+, 4), 224.1 (18), 178.0 (100), 150.1 (15), 43.1 (72); HRMS (EI): calcd for $C_{14}H_{18}O_5$ $[M]^+$: 266.1149; found: 266.1147.

2.3.4. Compound 5d. Starting with 1,3-bis-silyl enol ether **4d** (615 mg, 2.0 mmol), silyl enol ether **3a** (472 mg, 2.0 mmol) and $TiCl_4$ (0.22 ml, 2.0 mmol), **5d** was isolated as a colourless solid (304 mg, 54%), mp 62 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.10 (t, 3H, J=7.3 Hz, CH_3), 1.40 (t, 3H, J=7.0 Hz, CH_3), 2.11 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.65–2.75 (m, 2H, CH_2), 4.41 (q, 2H, J=7.0 Hz, OCH_2), 11.46 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.0, 13.1, 14.1, 15.3 (CH_3), 19.6 (CH_2), 20.3 (CH_3), 61.5 (CH_2), 110.2, 128.8, 129.6, 135.6, 140.7, 158.2, 169.3, 171.7 (C); IR (KBr): ν=3431 (w), 2979 (s), 2936 (m), 1757 (s), 1651 (s), 1465 (m), 1445 (m), 1395 (s), 1377 (s), 1367 (s), 1320 (s), 1278 (s), 1219 (s), 1042 (m), 806 (m) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%): 280.1 (M^+, 7), 238.1 (16), 192.1 (100), 164.0 (26), 43.0 (90); HRMS (EI): calcd for $C_{15}H_{20}O_5$ $[M]^+$: 280.1305; found: 280.1308.

2.3.5. Compound 5e. Starting with 1,3-bis-silyl enol ether **4d** (700 mg, 2.3 mmol), silyl enol ether **3b** (676 mg, 2.3 mmol) and $TiCl_4$ (0.25 ml, 2.3 mmol), **5e** was isolated as a colourless solid (290 mg, 37%), mp 79 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.65 (t, 3H, J=7.1 Hz, CH_3), 1.17 (t, 3H, J=7.5 Hz, CH_3), 1.79 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 2.78 (b, 2H, CH_2), 3.89 (q, 2H, J=7.1 Hz, OCH_2), 7.08–7.30 (m, 5H, ArH), 11.34 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=12.8, 13.0, 13.1 (CH_3), 19.9 (CH_2), 20.0 (CH_3), 60.8 (CH_2), 109.8 (C), 126.5, 127.3 (2C), 128.5 (2C, CH), 131.6, 133.3, 136.1, 138.3, 140.0, 157.7, 169.6, 170.9 (C); IR (KBr): ν=3444 (w), 2987 (m), 2937 (w), 1758 (s), 1655 (s), 1397 (m), 1376 (m), 1328 (m), 1279 (m), 1211 (s), 1117 (m), 1009 (w), 811 (w) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%): 342 (M^+, 4), 300 (38), 254 (95), 236 (28), 129 (57), 43 (100); elemental analysis: calcd (%) for $C_{20}H_{22}O_5$ (342.39): C 70.16, H 6.48; found: C 69.99, H 6.80.

2.3.6. Compound 5f. Starting with 1,3-bis-silyl enol ether **4f** (600 mg, 2.0 mmol), silyl enol ether **3a** (476 mg, 2.0 mmol) and $TiCl_4$ (0.22 ml, 2.0 mmol), **5f** was isolated as a colourless solid (263 mg, 50%), mp 68–72 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.10 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 3.83 (s, 3H, OCH_3), 3.94 (s, 3H, OCH_3), 11.16 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=10.8, 15.4, 20.7, 52.7, 60.6 (CH_3), 111.6, 127.2, 131.5, 140.8, 145.3, 154.4, 169.5, 172.1 (C); IR (KBr): ν=3501 (w), 3009 (w), 2960 (w), 2937 (w), 1753 (s), 1660 (s), 1440 (s), 1352 (s), 1214 (s), 1071 (m), 1041 (m), 806 (m) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%): 268 (M^+, 10), 226 (17), 194 (100), 165 (38), 67 (46); HRMS (EI): calcd for $C_{13}H_{16}O_6$ $[M]^+$: 268.0941; found: 268.0942.

2.3.7. Compound 5g. Starting with 1,3-bis-silyl enol ether **4b** (500 mg, 1.9 mmol), silyl enol ether **3g** (496 mg, 1.9 mmol) and $TiCl_4$ (0.21 ml, 1.9 mmol), **5g** was isolated as a colourless oil (258 mg, 51%); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.14 (t, 3H, J=7.4 Hz, CH_3), 1.25 (t, 3H,

J=7.5 Hz, CH_3), 2.32 (s, 3H, CH_3), 2.40–2.89 (m, 4H, CH_2), 3.95 (s, 3H, OCH_3), 6.78 (s, 1H, ArH), 11.16 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=12.9, 14.5, 20.5 (CH_3), 22.3, 23.6 (CH_2), 52.3 (CH_3), 110.2 (C), 115.6 (CH), 138.0, 140.3, 143.9, 160.4, 171.4 (C); IR (KBr): ν=2975 (m), 2879 (w), 1762 (s), 1665 (s), 1436 (m), 1369 (m), 1322 (m), 1232 (s), 1195 (s), 1079 (m), 808 (w) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%): 266 (M^+, 6), 235 (9), 224 (44), 192 (100), 149 (25); HRMS (EI): calcd for $C_{14}H_{18}O_5$ $[M]^+$: 266.1144; found: 266.1149.

2.3.8. Compound 5h. Starting with 1,3-bis-silyl enol ether **4c** (400 mg, 1.3 mmol), silyl enol ether **3g** (359 mg, 1.3 mmol) and $TiCl_4$ (0.15 ml, 1.3 mmol), **5h** was isolated as a colourless solid (155 mg, 39%), mp 40 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.09 (t, 3H, J=7.6 Hz, CH_3), 1.13 (t, 3H, J=7.6 Hz, CH_3), 1.14 (t, 3H, J=7.3 Hz, CH_3), 2.21 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 2.40–2.98 (m, 4H, CH_2), 4.42 (q, 2H, J=7.0 Hz, OCH_2), 11.43 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=11.5, 13.1, 13.9, 14.7, 20.6 (CH_3), 21.7, 22.3, 61.7 (CH_2), 109.8, 123.6, 134.9, 140.1, 141.9, 158.7, 170.3, 171.5 (C); IR (KBr): ν=3430 (w), 2971 (m), 2937 (m), 1755 (s), 1651 (s), 1407 (m), 1370 (m), 1314 (m), 1274 (m), 1219 (s), 1197 (s), 1022 (m), 807 (m) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 294.2 (M^+, 27), 252.2 (75), 206.1 (100), 163.1 (19); HRMS (EI): calcd for $C_{16}H_{22}O_5$ $[M]^+$: 294.1462; found: 294.1466.

2.3.9. Compound 5i. Starting with 1,3-bis-silyl enol ether **4b** (1.00 g, 3.8 mmol), silyl enol ether **3i** (1.12 g, 3.8 mmol) and $TiCl_4$ (0.42 ml, 3.8 mmol), **5i** was isolated as a colourless solid (625 mg, 55%), mp 80 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.17 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 3.95 (s, 3H, OCH_3), 6.78 (s, 1H, ArH), 7.51–8.26 (m, 5H, ArH), 11.16 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=15.5, 17.3, 52.2 (CH_3), 110.9 (C), 117.2, 128.7 (2C, CH), 128.9 (C), 130.2 (2C, CH), 132.5 (C), 133.8 (CH), 138.6, 141.1, 160.2, 164.7, 171.7 (C); IR (KBr): ν=3431 (w), 3034 (w), 2985 (w), 2958 (w), 1732 (s), 1661 (s), 1622 (m), 1443 (m), 1360 (m), 1323 (m), 1262 (s), 1236 (s), 1202 (s), 1153 (m), 1085 (s), 1062 (s), 1023 (m), 803 (m), 705 (s) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 300.1 (M^+, 39), 269.1 (9), 105.0 (100), 77.0 (71); HRMS (EI): calcd for $C_{17}H_{16}O_5$ $[M]^+$: 300.0992; found: 300.0990.

2.3.10. Compound 5j. Starting with 1,3-bis-silyl enol ether **4d** (800 mg, 2.6 mmol), silyl enol ether **3i** (773 mg, 2.6 mmol) and $TiCl_4$ (0.29 ml, 2.6 mmol), **5j** was isolated as a colourless solid (410 mg, 46%), mp 89 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.13 (t, 3H, J=7.5 Hz, CH_3), 1.40 (t, 3H, J=7.2 Hz, CH_3), 2.16 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 2.74 (q, 2H, J=3.5 Hz, CH_2), 4.42 (q, 2H, J=7.0 Hz, OCH_2), 7.51–8.27 (m, 5H, ArH), 11.50 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=13.2, 13.3, 14.2, 15.6 (CH_3), 19.8, 61.7 (CH_2), 128.7 (2C, CH), 129.1, 129.2, 129.8 (C), 130.2 (2C), 133.7 (CH), 135.9, 140.9, 158.4, 164.9, 171.9 (C); IR (KBr): ν=3437 (m), 2975 (m), 2933 (m), 2874 (w), 1731 (s), 1650 (s), 1611 (m), 1451 (m), 1394 (m), 1373 (m), 1321 (m), 1252 (s), 1205 (s), 1104 (s), 1066 (m), 1039 (m), 1026 (m), 807 (m), 715 (s) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 342.2 (M^+, 67), 296.1 (50), 191.1 (23), 105.0 (100); elemental analysis: calcd (%) for $C_{20}H_{22}O_5$ (342.39): C 70.16, H 6.48; found: C 70.14, H 6.78.

2.4. General procedure for the synthesis of *p*-dihydrobenzoquinones (6a–g)

H_2SO_4 (5 M, 8 mL/mmol) was added to a solution of starting material (1.0 mmol) in THF (50 mL/mmol) and refluxed for 36 h. The reaction mixture was concentrated on rotary, taken up in dichloromethane (20 mL) and washed with water (50 mL). The organic layer was dried (Na_2SO_4) and concentrated. The residue was purified by chromatography (silica gel, 20% ethylacetate/heptane) to give the product

2.4.1. Compound 6a. Starting with **5a** (265 mg, 1.1 mmol), 5 M H_2SO_4 (9 mL) and THF (50 mL), **6a** was isolated as a colourless solid (215 mg, 99%), mp 120 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.25 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 3.95 (s, 3H, OCH_3), 6.66 (s, 1H, ArH), 10.60 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.5, 16.9, 52.0 (CH_3), 110.8 (C), 116.6 (CH), 124.5, 132.5, 145.1, 156.0, 171.8 (C); IR (KBr): ν=3505 (s), 3086 (m), 2944 (m), 2862 (w), 1654 (s), 1621 (m), 1481 (s), 1442 (s), 1333 (s), 1237 (b), 1076 (m), 1050 (s), 967 (m), 796 (s), 719 (m) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 196.0 (M^+, 63), 163.9 (100), 135.9 (40), 107.0 (18), 79.0 (16); HRMS (EI): calcd for $C_{10}H_{12}O_4$ $[M]^+$: 196.0725; found: 196.0730.

2.4.2. Compound 6b. Starting with **5b** (264 mg, 0.8 mmol), 5 M H_2SO_4 (8 mL) and THF (40 mL), **6b** was isolated as a colourless solid (220 mg, 97%), mp 138 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.28 (s, 3H, CH_3), 3.39 (s, 3H, OCH_3), 6.85 (s, 1H, ArH), 7.18–7.49 (m, 5H, ArH), 10.56 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=16.9, 51.5 (CH_3), 109.0 (C), 119.1 (CH), 126.5 (C), 127.9, 128.9 (2C), 129.2 (2C, CH), 133.7, 136.4, 144.2, 155.5, 170.9 (C); IR (KBr): ν=3530 (s), 3421 (b), 2945 (m), 2867 (w), 1670 (s), 1455 (s), 1434 (s), 1331 (s), 1184 (b), 1076 (m), 760 (m), 705 (m) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 258.0 (M^+, 53), 226.0 (100), 197.9 (29), 141.0 (25), 115.0 (15); HRMS (EI): calcd for $C_{15}H_{14}O_4$ $[M]^+$: 258.0887; found: 258.0881.

2.4.3. Compound 6c. Starting with **5c** (70 mg, 0.2 mmol), 5 M H_2SO_4 (2 mL) and THF (14 mL), **6c** was isolated as a colourless solid (46 mg, 79%), mp 105 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.41 (t, 3H, J=5.3 Hz, CH_3), 2.17 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 4.30 (s, 1H, OH), 4.41 (q, 2H, J=7.1 Hz, OCH_2), 10.97 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=11.9, 13.2, 14.2, 14.6 (CH_3), 61.5 (CH_2), 110.1, 121.1, 123.0, 131.1, 144.6, 154.4, 171.9 (C); IR (KBr): ν=3382 (b), 2983 (m), 2940 (w), 1655 (s), 1616 (m), 1468 (m), 1439 (m), 1394 (m), 1376 (m), 1223 (m), 1268 (s), 1213 (s), 1049 (m), 1034 (m), 799 (m), 746 (m) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 224.0 (M^+, 26), 177.9 (100), 15.0 (61); HRMS (EI): calcd for $C_{12}H_{16}O_4$ $[M]^+$: 224.1042; found: 224.1043.

2.4.4. Compound 6d. Starting with **5d** (84 mg, 0.3 mmol), 5 M H_2SO_4 (3 mL) and THF (15 mL), **6d** was isolated as a colourless solid (65 mg, 91%), mp 98 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.11 (t, 3H, J=7.5 Hz, CH_3), 1.43 (t, 3H, J=7.1 Hz, CH_3), 2.26 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 2.72 (q, 2H, J=7.5 Hz, CH_2), 4.43 (q, 2H, J=7.1 Hz, OCH_2), 10.92 (s, 1H, OH); ^{13}C NMR (75 MHz,

$CDCl_3$): δ=12.5, 13.5, 14.2, 14.6 (CH_3), 19.6, 61.4 (CH_2), 110.2, 121.2, 129.1, 130.5, 144.8, 154.2, 171.9 (C); IR (KBr): ν=3450 (s), 1979 (s), 2936 (m), 2873 (m), 1655 (s), 1614 (m), 1465 (m), 1393 (m), 1375 (s), 1323 (m), 1276 (s), 1212 (s), 1109 (m), 1096 (m), 1047 (m), 802 (m), 764 (m) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 238.1 (M^+, 48), 192.1 (100), 177.1 (20), 164.1 (95), 149.1 (20), 121.1 (12), 91.1 (17); HRMS (EI): calcd for $C_{13}H_{18}O_4$ $[M]^+$: 238.1200; found: 238.1202.

2.4.5. Compound 6e. Starting with **5e** (166 mg, 0.4 mmol), 5 M H_2SO_4 (4 mL) and THF (25 mL), **6e** was isolated as a colourless solid (140 mg, 97%), mp 68 °C; ^1H NMR (300 MHz, $CDCl_3$): δ=0.65 (t, 3H, *J*=7.1 Hz, CH_3), 1.17 (t, 3H, *J*=7.5 Hz, CH_3), 2.34 (s, 3H, CH_3), 2.78 (q, 2H, *J*=7.5 Hz, CH_2), 3.89 (q, 2H, *J*=7.1 Hz, OCH_2), 7.18–7.47 (m, 5H, ArH), 11.01 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=12.4, 12.9, 13.3 (CH_3), 19.7, 60.6 (CH_2), 108.4 (C), 127.7 (CH), 128.5 (C), 128.9 (2C), 129.6 (2C, CH), 131.2, 131.9, 137.1, 143.8, 153.9, 171.1 (C); IR (KBr): ν=3531 (s), 2977 (m), 2934 (m), 2872 (w), 1653 (s), 1444 (m), 1398 (s), 1373 (s), 1330 (s), 1293 (m), 1249 (m), 1209 (s), 1080 (m), 1059 (m), 763 (m), 699 (m) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 300.1 (M^+, 38), 254.1 (100), 139. (61), 221.0 (46), 183.1 (14), 129.0 (65); HRMS (EI): calcd for $C_{18}H_{20}O_4$ $[M]^+$: 300.1356; found: 300.1358.

2.4.6. Compound 6f. Starting with **5f** (106 mg, 0.3 mmol), 5 M H_2SO_4 (3 mL) and THF (20 mL), **6f** was isolated as a colourless solid (73 mg, 83%), mp 81 °C; ^1H NMR (300 MHz, $CDCl_3$): δ=2.22 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 3.82 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 4.44 (s, 1H, OH), 10.52 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=9.7, 14.1, 52.1, 60.3 (CH_3), 111.3, 119.2, 125.3, 144.6, 144.7, 149.6, 171.8 (C); IR (KBr): ν=3523 (s), 3152 (w), 3004 (w), 2964 (m), 2854 (w), 1642 (s), 1480 (m), 1441 (s), 1421 (s), 1371 (m), 1329 (s), 1274 (s), 1229 (s), 1122 (m), 1070 (m), 1048 (s), 1032 (m), 967 (m), 800 (s), 759 (m) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 226.0 (M^+, 37), 194.0 (100), 165.0 (80), 151.0 (41), 95.1 (28), 83.0 (40); HRMS (EI): calcd for $C_{11}H_{14}O_4$ $[M]^+$: 226.0836; found: 226.0837.

2.4.7. Compound 6g. Starting with **5g** (170 mg, 0.4 mmol), 5 M H_2SO_4 (5 mL) and THF (30 mL), **6g** was isolated as a colourless oil (140 mg, 98%); ^1H NMR (400 MHz, $CDCl_3$): δ=1.19 (t, 3H, *J*=7.5 Hz, CH_3), 1.23 (t, 3H, *J*=7.5 Hz, CH_3), 2.61 (q, 2H, *J*=7.5 Hz, CH_2), 2.92 (q, 2H, *J*=7.5 Hz, CH_2), 3.95 (s, 3H, OCH_3), 6.69 (s, 1H, ArH), 10.58 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=12.9, 14.5 (CH_3), 20.9, 22.3 (CH_2), 52.2 (CH_3), 110.1 (C), 115.6 (CH), 130.5, 138.4, 143.9, 156.1, 171.6 (C); IR (KBr): ν=3442 (m), 2966 (m), 2875 (m), 1662 (s), 1437 (s), 1325 (m), 1252 (m), 1213 (m), 1081 (m), 806 (w) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%): 224.1 (M^+, 18), 192.1 (100), 149.1 (38), 91.1 (10); HRMS (EI): calcd for $C_{12}H_{16}O_4$ $[M]^+$: 224.1043; found: 224.1041.

2.5. General procedure for the synthesis of *p*-benzoquinones (7a–g)

A solution of dihydroquinones (**6a–g**) (1.0 mmol) and DDQ (1.0 mmol) in benzene (20 mL/mmol) was stirred at room temperature for 2 h. The reaction mixture was filtered, dried (Na_2SO_4) and concentrated. The residue was purified by chromatography (silica gel, 30% ethylacetate/heptane) to give the product.

2.5.1. Compound 7a. Starting with **6a** (107 mg, 0.5 mmol), DDQ (124 mg, 0.5 mmol) and benzene (11 mL), **7a** was isolated as a yellow solid (95 mg, 90%), mp 48 °C; ^1H NMR (300 MHz, $CDCl_3$): δ=2.02 (s, 3H, CH_3), 2.05 (d, 3H, *J*=1.5 Hz, CH_3), 3.88 (s, 3H, OCH_3), 6.57 (d, 1H, *J*=1.5 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.5, 16.0, 52.7 (CH_3), 132.6 (CH), 137.0, 142.0, 146.0, 164.4, 183.5, 187.3 (C); IR (KBr): ν=3455 (w), 2955 (w), 1737 (s), 1658 (s), 1622 (m), 1440 (m), 1331 (s), 1238 (s), 1179 (m), 1043 (m), 898 (w) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 222.0 (M^+, 82), 193.9 (83), 175.9 (100), 147.9 (93), 119.9 (36), 91.0 (61); HRMS (EI): calcd for $C_{10}H_{10}O_4$ $[M]^+$: 194.0573; found: 194.0574.

2.5.2. Compound 7b. Starting with **6b** (125 mg, 0.4 mmol), DDQ (110 mg, 0.4 mmol) and benzene (10 mL), **7b** was isolated as a yellow solid (105 mg, 84%), mp 128 °C; ^1H NMR (300 MHz, $CDCl_3$): δ=2.12 (s, 3H, CH_3), 3.64 (s, 3H, OCH_3), 6.71 (d, 1H, *J*=1.5 Hz, ArH), 7.25–7.29 (m, 5H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=16.2, 52.5 (CH_3), 128.1 (2C), 129.1 (2C), 129.8 (C, CH), 130.9 (C), 132.7 (CH), 136.8, 142.4, 146.1, 164.1, 183.8, 186.5 (C); IR (KBr): ν=3447 (w), 2950 (w), 1736 (s), 1653 (s), 1634 (m), 1432 (m), 1324 (m), 1237 (s), 1113 (m), 1036 (m), 755 (m), 698 (m) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%): 256.0 (M^+, 29), 224.0 (100), 196.0 (36), 168.0 (28), 139.0 (60); elemental analysis: calcd (%) for $C_{15}H_{12}O_4$ (256.25): C 70.31, H 4.72; found: C 70.08, H 4.85.

2.5.3. Compound 7c. Starting with **6c** (50 mg, 0.2 mmol), DDQ (51 mg, 0.2 mmol) and benzene (5 mL), **7c** was isolated as a yellow solid (42 mg, 86%), mp 46 °C; ^1H NMR (300 MHz, $CDCl_3$): δ=1.35 (t, 3H, *J*=7.1 Hz, CH_3), 2.02 (s, 9H, CH_3), 4.36 (q, 2H, *J*=7.1 Hz, OCH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ=12.1, 12.4, 13.3, 14.1 (CH_3), 61.9 (CH_2), 137.0, 140.3, 141.11, 141.16, 164.4, 183.8, 186.9 (C); IR (KBr): ν=3452 (w), 2993 (w), 2930 (w), 1739 (s), 1648 (s), 1625 (m), 1374 (m), 1292 (s), 1216 (s), 1061 (m), 1023 (m), 713 (w) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 222.0 (M^+, 82), 193.9 (83), 175.9 (100), 147.9 (93), 119.9 (36), 91.0 (61); HRMS (EI): calcd for $C_{12}H_{14}O_4$ $[M]^+$: 222.0882; found: 222.0887.

2.5.4. Compound 7d. Starting with **6d** (64 mg, 0.2 mmol), DDQ (61 mg, 0.2 mmol) and benzene (6 mL), **7d** was isolated as a yellow solid (50 mg, 82%), mp 43 °C; ^1H NMR (300 MHz, $CDCl_3$): δ=1.02 (t, 3H, *J*=7.5 Hz, CH_3), 1.34 (t, 3H, *J*=7.1 Hz, CH_3), 2.00 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 2.47 (q, 2H, *J*=7.5 Hz, CH_2), 4.36 (q, 2H, *J*=7.1 Hz, OCH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ=11.8, 12.7, 13.2, 14.1 (CH_3), 19.6, 61.9 (CH_2), 137.1, 140.5, 140.9, 145.4, 164.4, 183.4, 187.3 (C); IR (KBr): ν=3531 (s), 2977 (m), 2934 (m), 2872 (w), 1653 (s), 1444 (m), 1398 (s), 1373 (s), 1330 (s), 1293 (m), 1249 (m), 1209 (s), 1080 (m), 1059 (m), 763 (m), 699 (m) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 236.1 (M^+, 68), 190.1 (99), 162.1 (100), 134.1 (18), 105.1 (11), 91.1 (43), 67.1 (70); HRMS (EI): calcd for $C_{13}H_{16}O_4$ $[M]^+$: 236.1043; found: 236.1036.

2.5.5. Compound 7e. Starting with **6e** (92 mg, 0.3 mmol), DDQ (70 mg, 0.3 mmol) and benzene (7 mL), **7e** was isolated as a yellow solid (73 mg, 82%), mp 43 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.02 (t, 3H, J=7.1 Hz, CH_3), 1.06 (t, 3H, J=7.5 Hz, CH_3), 2.10 (s, 3H, CH_3), 2.56 (q, 2H, J=7.5 Hz, CH_2), 4.12 (q, 2H, J=7.1 Hz, OCH_2), 7.25–7.40 (m, 5H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=12.1, 12.8, 13.7 (CH_3), 19.8, 61.8 (CH_2), 128.0 (2C), 129.2 (2C), 129.6 (C, CH), 131.2, 136.9, 140.6, 141.8, 145.7, 164.0, 183.8, 186.6 (C); IR (KBr): ν=3442 (m), 2974 (m), 2937 (w), 2875 (w), 1736 (s), 1651 (s), 1615 (m), 1445 (m), 1373 (m), 1286 (s), 1221 (s), 1152 (m), 1021 (m), 699 (m) cm^{-1}; GC–MS (EI, 70 eV): m/z (%): 298.1 (M^+, 3), 252.0 (100), 237.0 (38), 224.1 (98), 129.0 (50); elemental analysis: calcd (%) for $C_{18}H_{18}O_4$ (298.33): C 72.47, H 6.08; found: C 72.28, H 5.83.

2.5.6. Compound 7f. Starting with **6f** (45 mg, 0.2 mmol), DDQ (46 mg, 0.2 mmol) and benzene (4 mL), **7f** was isolated as a yellow solid (38 mg, 86%), mp 40 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.95 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 3.90 (s, 3H, OCH_3), 4.02 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=8.9, 13.5, 52.7, 61.0 (CH_3), 128.9, 135.4, 142.2, 154.7, 164.6, 180.0, 187.2 (C); IR (KBr): ν=3430 (s), 2956 (w), 1740 (m), 1655 (s), 1616 (m), 1289 (m), 1225 (m), 1152 (w), 1056 (w), 950 (w), 728 (w) cm^{-1}; GC–MS (EI, 70 eV): m/z (%): 224 (M^+, 22), 192 (65), 164 (64), 149 (19), 135 (16), 83 (66), 67 (100); HRMS (EI): calcd for $C_{11}H_{12}O_5$ $[M]^+$: 224.0679; found: 224.0678.

2.5.7. Compound 7g. Starting with **6g** (109 mg, 0.5 mmol), DDQ (110 mg, 0.5 mmol) and benzene (10 mL), **7g** was isolated as a yellow oil (80 mg, 73%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.10 (t, 3H, J=7.5 Hz, CH_3), 1.13 (t, 3H, J=7.5 Hz, CH_3), 2.42 (q, 2H, J=7.5 Hz, CH_2), 2.78 (dq, 2H, J=7.4 Hz, 1.7 Hz, CH_2), 3.89 (s, 3H, OCH_3), 6.52 (t, 1H, J=1.6 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=11.5, 13.6 (CH_3), 21.6, 22.2 (CH_2), 52.6 (CH_3), 130.8 (CH), 136.3, 146.8, 151.1, 164.5, 184.2, 186.7 (C); IR (KBr): ν=2976 (m), 2941 (m), 1741 (s), 1653 (s), 1457 (w), 1338 (w), 1278 (m), 1223 (m), 1046 (m), 796 (w) cm^{-1}; GC–MS (EI, 70 eV): m/z (%): 222.1 (M^+, 2), 190.1 (100), 147.1 (13), 91.1 (28); HRMS (EI): calcd for $C_{12}H_{14}O_4$ $[M]^+$: 222.0887; found: 222.0886.

2.6. General procedure for the synthesis of triflate (8)

The reaction was carried out analogously by a known procedure. To a dichloromethane solution (10 mL/mmol) of **5i** (1.0 mmol) and triflic anhydride (1.2 mmol) was added pyridine (2.0 mmol) at −78 °C. The solution was allowed to warm to −10 °C within 4 h. The product was isolated by rapid chromatography (silica gel, dichloromethane) of the reaction mixture as a colourless solid.

2.6.1. Compound 8. Starting with **5i** (442 mg, 1.4 mmol), Tf_2O (0.29 mL, 1.7 mmol), pyridine (0.23 mL, 2.9 mmol) and dichloromethane (15 mL), **8** was isolated as a colourless solid (628 mg, 98%), mp 74 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.24 (s, 6H, CH_3), 3.95 (s, 3H, OCH_3), 7.10 (s, 1H, ArH), 7.52–8.24 (m, 5H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.1, 16.9, 52.7 (CH_3), 118.5 (q, J=318.2 Hz, CF_3), 121.3 (CH), 125.9, 128.2 (C), 128.8 (2C), 130.3 (2C, CH), 132.5 (C), 134.2 (CH), 135.3, 143.8, 147.9, 163.7, 164.7 (C); IR (KBr): ν=3435 (w), 3069 (w), 3006 (w), 2956 (w), 1745 (s), 1725 (s), 1454 (m), 1417 (s), 1282 (m), 1259 (s), 1245 (s), 1217 (s), 1190 (m), 1137 (m), 1079 (m), 1065 (m), 1015 (m), 827 (m), 707 (m) cm^{-1}; MS (EI, 70 eV): m/z (%): 432.1 (M^+, 1), 401.0 (6), 105.0 (100); HRMS (EI): calcd for $C_{18}H_{15}O_7SF_3$ $[M]^+$: 432.0485; found: 432.0480.

2.7. General procedure for Suzuki coupling (9)

A dioxane solution (5 mL per 1.0 mmol of triflate) of **8** (1.0 mmol), phenylboronic acid (1.3 mmol), K_3PO_4 (1.6 mmol) and $Pd(PPh_3)_4$ (0.03 mmol) was refluxed for 4 h. A saturated aqueous solution of ammonium chloride was added. The organic and the aqueous layer was separated and the latter was extracted (3×) with 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, 20% ethylacetate/heptane) to give the product.

2.7.1. Compound 9. Starting with **8** (255 mg, 0.5 mmol), Phenylboronic acid (86 mg, 0.7 mmol), K_3PO_4 (188 mg, 0.8 mmol), Pd catalyst (21 mg, 0.017 mmol) and dioxane (4 mL), **9** was isolated as a colourless solid (145 mg, 70%), mp 62 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.21 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 3.55 (s, 3H, OCH_3), 7.14 (s, 1H, ArH), 7.24–8.27 (m, 10H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.6, 16.6, 51.8 (CH_3), 127.3, 128.23 (2C), 128.26 (2C, CH), 128.3 (C), 128.7 (2C, CH), 128.9 (C), 129.9, 130.2 (2C, CH), 132.0, 132.4 (C), 133.8 (CH), 137.9, 140.5, 147.6, 164.2, 169.5 (C); IR (KBr): ν=3437 (m), 3061 (w), 3030 (w), 2949 (w), 1734 (s), 1451 (m), 1253 (s), 1235 (s), 1160 (s), 1082 (s), 1065 (s), 1024 (m), 709 (m) cm^{-1}; GC–MS (EI, 70 eV): m/z (%): 360.1 (M^+, 2), 329.1 (1), 223.0 (2), 165.1 (5), 152.0 (6), 105.0 (100); HRMS (EI): calcd for $C_{23}H_{20}O_4$ $[M]^+$: 360.1356; found: 360.1347.

Acknowledgements

Financial support by the state of Mecklenburg-Vorpommern (scholarship for Z.A. and Landesforschungsschwerpunkt 'Neue Wirkstoffe und Screeningverfahren') is gratefully acknowledged.

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11. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-299670. Copies of this data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(1223)336033 or e-mail: deposit@ccdc.cam.ac.uk) or via http://www.ccdc.cam.ac.uk/conts/retrieving.html.