Regioselective Ortho Lithiation of 3-Aryl and 3- Styryl Furans

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Experimental Section

General procedure for the Suzuki coupling of 3-furanboronic acid (**1**) with *p*-substituted bromobenzenes (**2a-c**), benzyl bromides (**6a,b**) and vinyl bromide **10**:

To a solution of the bromide (2.72 mmol) in toluene (6.0 mL) under an argon atmosphere Pd(PPh₃)₄ (125 mg, 0.108 mmol) was added, followed by a 2 M aqueous solution of Na₂CO₃ (3.0 mL) and a solution of 3-furanboronic acid (365 mg, 3.26 mmol) in MeOH (1.5 mL). The reaction mixture was warmed to 80 °C for 2 – 6 h. After cooling, the mixture was partitioned between CH₂Cl₂ (5 mL) and 2 M aqueous Na₂CO₃ (5 mL). The layers were separated and the organic phase was dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, Hex:EtOAc = 50:1 → 5:1, to afford the desired 3-substituted furans **3a-c**, **7a,b** and **11** in 65 – 81 % yield.

3a: ¹H NMR (500 MHz, CDCl₃): δ = 7.66 (brs, 1 H), 7.46 (d, *J* = 1.6 Hz, 1 H), 7.42 (d, *J* = 8.7 Hz, 2 H), 6.92 (d, *J* = 8.7 Hz, 2 H), 6.66 (brs, 1 H), 3.83 (s, 3 H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ = 158.7, 143.5, 137.7, 128.7, 127.0 (2 C), 126.7, 114.2 (2 C), 108.8, 55.3 ppm; MS, *m/z* = 174 (M⁺, 100).

3b: ¹H NMR (500 MHz, CDCl₃): δ = 7.79 (brs, 1 H), 7.55 (d, *J* = 7.3 Hz, 2 H), 7.53 (t, *J* = 1.6 Hz, 1 H), 7.44 (t, *J* = 7.4 Hz, 2 H), 7.33 (t, *J* = 7.2 Hz, 1 H), 6.77 (d, *J* = 1.0 Hz, 1 H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ = 143.7, 138.5, 132.5, 128.9 (2 C), 127.0, 126.5, 125.9 (2 C), 108.9 ppm; MS, *m/z* = 144 (M⁺, 100).

3c: ¹H NMR (500 MHz, CDCl₃): δ = 7.71 (brs, 1 H), 7.50 (d, *J* = 1.6 Hz, 1 H), 7.47 (dd, *J*₁ = 8.7 Hz, *J*₂ = 5.2 Hz, 2 H), 7.10 (t, *J* = 8.7 Hz, 2 H), 6.68 (brs, 1 H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ = 161.9 (d, *J*_{C-F} = 244.4 Hz), 143.7, 138.2, 128.8, 127.4 (d, *J*_{C-F} = 7.9 Hz, 2 C), 125.7, 115.7 (d, *J*_{C-F} = 21.4 Hz, 2 C), 108.8 ppm; MS, *m/z* = 162 (M⁺, 95).

7a: ¹H NMR (500 MHz, CDCl₃): δ = 7.46 (brs, 1 H), 7.41 (t, *J* = 7.5 Hz, 2 H), 7.34 (m, 4 H), 6.35 (brs, 1 H), 3.88 (s, 2 H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ = 143.0, 140.3, 139.5, 128.5 (2 C), 128.4 (2 C), 126.1, 124.2, 111.2, 31.1 ppm; MS, *m/z* = 158 (M⁺, 100).

7b: ¹H NMR (500 MHz, CDCl₃): δ = 7.59 (d, *J* = 8.1 Hz, 2 H) 7.41 (t, *J* = 1.6 Hz, 1 H), 7.36 (d, *J* = 8.1 Hz, 2 H), 7.27 (brs, 1H), 6.27 (s, 1 H), 3.86 (s, 2H) ppm; ¹³C NMR (125

MHz, CDCl₃): δ = 144.4 (q, J_{C-F} = 1.4 Hz), 143.3, 139.7, 128.8, 128.6 (q, J_{C-F} = 32.0 Hz, 2 C), 128.4, 125.3 (q, J_{C-F} = 3.8 Hz, 2 C), 123.2 (q, J_{C-F} = 1.8 Hz), 111.0, 30.9 ppm; MS, m/z = 226 (M^+ , 100).

11: ¹H NMR (500 MHz, CDCl₃, *cis* isomer): δ = 7.44 (brs, 1 H), 7.40 (t, J = 1.4 Hz, 1 H), 6.47 (brs, 1 H), 6.15 (d, J = 11.4 Hz, 1 H), 5.59 (m, 1 H), 2.28 (dq, J_1 = 7.2 Hz, J_2 = 1.3 Hz, 2 H), 1.47 (m, 2 H), 1.30 (m, 12 H), 0.91 (t, J = 6.9 Hz, 3 H) ppm; ¹³C NMR (125 MHz, CDCl₃, *cis* isomer): δ = 142.5, 140.7, 132.2, 122.6, 118.5, 110.9, 31.8, 29.51, 29.49, 29.47, 29.36, 29.24, 29.18, 22.6, 14.0 ppm; MS, m/z = 220 (M^+ , 40). ¹H NMR (500 MHz, CDCl₃, *trans* isomer): δ = 7.34 (brs, 2 H), 6.52 (brs, 1 H), 6.24 (d, J = 15.7 Hz, 1 H), 5.96 (m, 1 H), 2.17 (brq, J = 6.8 Hz, 2 H), 1.47 (m, 2 H), 1.30 (m, 12 H), 0.91 (t, J = 6.9 Hz, 3 H) ppm; ¹³C NMR (125 MHz, CDCl₃, *trans* isomer): δ = 143.2, 139.2, 130.8, 124.5, 119.1, 107.5, 32.8, 29.51, 29.46, 29.36, 29.32, 29.26, 29.15, 22.6, 14.0 ppm; MS, m/z = 220 (M^+ , 20).

Preparation of 10, 17a, and 17b using standard a Wittig protocol: To a solution of BrCH₂PPh₃(⁺)Br(⁻) or **16a** or **16b** (1.19 mmol) in anhydrous THF (5 ml), at -78 °C, *t*-BuOK (133 mg, 1.19 mmol) was added. After 1 h at -78 °C, a solution of decanal or 3-furaldehyde (1.04 mmol) in anhydrous THF (1 mL) was added dropwise and the reaction mixture stirred for a further 1 h at -78 °C. The reaction was then warmed to room temperature over 1 h. Hexane (30 mL) was added to precipitate the by-product, PPh₃O, which was then removed by filtration. The solvent was evaporated in vacuo and the residue was purified by flash column chromatography (silica gel, Hexane:Et₂O = 30:1 → 15:1) to afford a mixture of **10** (*E:Z* = 1:3, 80 %) or **17a** (*E:Z* = 1:1, 78 %) or **17b** (*E:Z* = 1:1, 83 %) or **17c** (*E:Z* = 1:1, 87 %). It is important to note that complete separation of the geometrical isomers of **17a**, **17b** and **17c** was achieved.

10: ¹H NMR (500 MHz, CDCl₃, *cis* isomer): δ = 6.14 (d, J = 6.9 Hz, 1 H), 6.09 (m, 1 H), 2.20 (dq, J_1 = 6.9 Hz, J_2 = 0.8 Hz, 2 H), 1.42 (m, 2 H), 1.30 (m, 12 H), 0.89 (t, J = 6.9 Hz, 3 H) ppm; MS, m/z = 232 (M^+ , 5). ¹H NMR (500 MHz, CDCl₃, *trans* isomer): δ = 6.18 (m, 1 H), 6.01 (d, J = 13.5 Hz, 1 H), 2.04 (dq, J_1 = 7.0 Hz, J_2 = 0.8 Hz, 2 H), 1.42 (m, 2 H), 1.30 (m, 12 H), 0.89 (t, J = 6.9 Hz, 3 H) ppm; MS, m/z = 232 (M^+ , 5).

E-17a: ^1H NMR (500 MHz, CDCl_3): δ = 7.51 (brs, 1 H), 7.41 (brs, 1 H), 7.39, (d, J = 8.7 Hz, 2 H), 6.89, (d, J = 8.7 Hz, 2 H), 6.84 (d, J = 16.2 Hz, 1 H), 6.77 (d, J = 16.2 Hz, 1 H), 6.65, (d, J = 1.3 Hz, 1 H), 3.83 (s, 3 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ = 159.0, 143.5, 140.4, 130.1, 127.9, 127.2 (2 C), 124.7, 116.3, 114.0 (2 C), 107.3, 55.2 ppm; MS, m/z = 200 (M^+ , 100).

Z-17a: ^1H NMR (500 MHz, CDCl_3): δ = 7.41 (d, J = 1.4 Hz, 1 H), 7.29 (d, J = 8.7 Hz, 2 H), 7.27 (t, J = 1.4 Hz, 1 H), 6.87 (d, J = 8.7 Hz, 2 H), 6.50 (d, J = 11.9 Hz, 1 H), 6.33 (d, J = 11.9 Hz, 1 H), 6.20 (d, J = 1.4 Hz, 1 H), 3.83 (s, 3 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ = 158.7, 142.4, 141.8, 130.2, 129.9 (2 C), 129.1, 122.4, 118.9, 113.6 (2 C), 110.2, 55.2 ppm; MS, m/z = 200 (M^+ , 100).

E-17b: ^1H NMR (500 MHz, CDCl_3): δ = 7.60 (brs, 1 H), 7.53 (d, J = 7.5 Hz, 2 H), 7.48 (brs, 1 H), 7.41 (t, J = 7.5 Hz, 2 H), 7.32 (t, J = 7.3 Hz, 1 H), 7.05 (d, J = 16.2 Hz, 1 H), 6.90 (d, J = 16.2 Hz, 1 H), 6.73 (brs, 1 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ = 143.7, 140.9, 137.3, 128.6 (2 C), 128.4, 127.3, 126.1 (2 C), 124.5, 118.4, 107.4 ppm; MS, m/z = 170 (M^+ , 60).

Z-17b: ^1H NMR (500 MHz, CDCl_3): δ = 7.48 (brs, 1 H), 7.48 (d, J = 7.0 Hz, 2 H), 7.44 (t, J = 7.0 Hz, 2 H), 7.38 (t, J = 7.0 Hz, 1 H), 7.35 (d, J = 1.5 Hz, 1 H), 6.69 (d, J = 12.0 Hz, 1 H), 6.52 (d, J = 12.0 Hz, 1 H), 6.28 (brs, 1 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ = 142.5, 142.0, 137.9, 129.4, 128.6 (2 C), 128.2 (2 C), 127.1, 122.3, 120.1, 110.2 ppm; MS, m/z = 170 (M^+ , 55).

E-17c: ^1H NMR (500 MHz, CDCl_3): δ = 7.60 (d, J = 8.3 Hz, 2 H), 7.59 (brs, 1 H), 7.53, (d, J = 8.3 Hz, 2 H), 7.45 (brs, 1 H), 7.07 (d, J = 16.2 Hz, 1 H), 6.84 (d, J = 16.2 Hz, 1 H), 6.69, (brs, 1 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ = 143.9, 141.7, 140.8 (q, $J_{\text{C-F}}$ = 1.4 Hz), 126.8, 126.1 (2 C), 125.6 (q, $J_{\text{C-F}}$ = 3.8 Hz, 2 C), 125.4, 124.2, 123.2, 120.9, 107.2 ppm; MS, m/z = 238 (M^+ , 80).

Z-17c: ^1H NMR (500 MHz, CDCl_3): δ = 7.59 (d, J = 8.1 Hz, 2 H), 7.46 (d, J = 8.1 Hz, 2 H), 7.40 (brs, 1 H), 7.28 (brs, 1 H), 6.55 (d, J = 12.1 Hz, 1 H), 6.50 (d, J = 12.1 Hz, 1 H), 6.11 (brs, 1 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ = 142.9, 142.4, 141.6 (q, $J_{\text{C-F}}$ = 1.4 Hz), 129.3, 129.1, 129.0 (2 C), 127.8, 126.8, 125.2 (q, $J_{\text{C-F}}$ = 3.8 Hz, 2 C), 121.8, 109.9 ppm; MS, m/z = 238 (M^+ , 85).

Preparation of 13: To a solution of MeOCH₂PPh₃(⁺)Cl(⁻) (2.14 g, 6.24 mmol) in anhydrous THF (15 mL), at -10 °C, *n*-BuLi (4.16 ml of 1.5 M solution in Hexane, 6.24 mmol) was added dropwise and the reaction solution stirred for 1 h at room temperature. A solution of 3-furaldehyde (**12**, 0.087 mL, 1.04 mmol) in anhydrous THF (10 mL), at 0 °C, was then added dropwise and the reaction solution stirred for 30 min at room temperature. The mixture was then partitioned between of Et₂O (15 mL) and H₂O (15 mL). The layers were separated and the organic phase was dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, Hexane:EtOAc = 40:1 → 20:1) to afford **13** as a mixture of geometrical isomers (*E*:*Z* = 4:1, 75 %).

13: ¹H NMR (500 MHz, CDCl₃, *cis* isomer): δ = 7.70 (brs, 1 H), 7.40 (brs, 1 H), 6.63 (brs, 1 H), 6.13 (d, *J* = 6.4 Hz, 1 H), 5.22 (d, *J* = 6.4 Hz, 1 H), 3.79, (s, 3 H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ = 148.4, 142.2, 140.6, 137.4, 110.8, 96.4, 60.3 ppm. ¹H NMR (500 MHz, CDCl₃, *trans* isomer): δ = 7.40 (brs, 2 H), 6.92 (d, *J* = 12.9 Hz, 1 H), 6.45 (brs, 1 H), 5.72 (d, *J* = 12.9 Hz, 1 H), 3.68 (s, 3 H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ = 147.0, 143.3, 138.2, 137.3, 107.4, 95.0, 56.3 ppm.

Preparation of 21 by hydrogenation of 17b: A solution of **17b** (126 mg, 0.74 mmol) in MeOH:EtOAc (2:1, 5 ml) at room temperature had H₂ bubbled through it for 10 min. Pd (20 mg, 10 wt. % on activated carbon, 0.019 mmol) was then added and the reaction mixture stirred for a further 1 h under an H₂ atmosphere. After removal of the catalyst by filtration through a pad of celite, the filtrate was concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, Hexane:EtOAc = 50:1 → 30:1) to afford **21** in 65 % yield

21: ¹H NMR (500 MHz, CDCl₃): δ = 7.36 (brs, 1 H), 7.31 (t, *J* = 7.5 Hz, 2 H), 7.21 (m, 4 H), 6.27 (brs, 1 H), 2.89 (t, *J* = 8.4 Hz, 2 H), 2.76 (t, *J* = 8.4 Hz, 2 H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ = 142.7, 141.7, 139.0, 128.4 (2 C), 128.3 (2 C), 126.0, 124.5, 111.0, 36.4, 26.7 ppm; MS, *m/z* = 172 (M⁺, 40).

General procedure for ortho lithiation and subsequent silylation of 3-substituted furans 3a-c, 7a,b, 11, 13, *E*-17a,b and *Z*-17a,b: To a solution of 3-substituted furans

(0.39 mmol) in anhydrous THF (2 mL) at -25 °C, *n*-BuLi (0.49 mL, 1.6 M solution in hexane, 0.78 mmol) was added dropwise and the resulting solution was stirred for 30 min at -15 °C. TMSCl (85 mg, 0.78 mmol) was added at -15 °C and the resultant solution warmed to room temperature over 1 h. NH₄Cl (2 mL) was added, the layers were separated, and the organic phase was extracted with Et₂O (2 mL). The organic layer was washed with brine (2 mL), dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel Hex:EtOAc = 50:1 → 5:1) to afford the mixtures of 2- and 5-silylated products in 79 – 95 % total yield. The ratio of the two regioisomers were measured, in each case, before chromatographic purification of the crude reaction mixtures.

4a: ¹H NMR (500 MHz, CDCl₃): δ = 7.63 (d, *J* = 1.3 Hz, 1 H), 7.30 (d, *J* = 8.6 Hz, 2 H), 6.92 (d, *J* = 8.7 Hz, 2 H), 6.48 (d, *J* = 1.2 Hz, 1 H), 3.85 (s, 3 H), 0.22 (s, 9 H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ = 158.8, 154.7, 145.9, 136.9, 129.8 (2 C), 127.1, 113.5 (2 C), 111.8, 55.2, -0.9 ppm; MS, *m/z* = 246 (*M*⁺, 70).

4b: ¹H NMR (500 MHz, CDCl₃): δ = 7.67 (d, *J* = 1.0 Hz, 1 H), 7.34 (m, 5 H), 6.54 (d, *J* = 1.0 Hz, 1 H), 0.25 (s, 9 H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ = 159.5, 155.1, 146.0, 137.2, 128.7 (2 C), 128.0 (2 C), 127.0, 111.6, -1.0 ppm; MS, *m/z* = 216 (*M*⁺, 40).

4c: ¹H NMR (500 MHz, CDCl₃): δ = 7.64 (d, *J* = 1.6 Hz, 1 H), 7.32 (dd, *J*₁ = 8.5 Hz, *J*₂ = 5.6 Hz, 2 H), 7.06 (t, *J* = 8.6 Hz, 2 H), 6.46 (d, *J* = 1.6 Hz, 1 H), 0.20 (s, 9 H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ = 162.1 (*J*_{C-F} = 244.2 Hz), 155.1, 146.0, 136.1, 130.9, 130.2 (d, *J*_{C-F} = 7.9 Hz, 2 C), 114.9 (d, *J*_{C-F} = 21.3 Hz, 2 C), 111.6, -1.0 ppm; MS, *m/z* = 234 (*M*⁺, 100).

8a: ¹H NMR (500 MHz, CDCl₃): δ = 7.59 (d, *J* = 1.5 Hz, 1 H), 7.29 (m, 5 H), 6.22 (d, *J* = 1.5 Hz, 1 H), 3.93 (s, 2 H), 0.37 (s, 9 H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ = 155.0, 146.2, 140.9, 128.43 (2 C), 128.36 (2 C), 126.0, 124.1, 111.9, 31.7, -1.0 ppm; MS, *m/z* = 230 (*M*⁺, 40).

9a: ¹H NMR (500 MHz, CDCl₃): δ = 7.45 (s, 1 H), 7.29 (m, 5 H), 6.53 (s, 1 H), 3.82 (s, 2 H), 0.30 (s, 9 H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ = 160.9, 143.7, 140.6, 128.6 (2 C), 128.4 (2 C), 126.1, 121.2, 111.9, 31.0, -1.6 ppm; MS, *m/z* = 230 (*M*⁺, 35).

8b and 9b: ¹H NMR (500 MHz, CDCl₃): δ = 7.56 (d, *J* = 8.5 Hz, 4 H), 7.53 (brs, 1 H), 7.42 (brs, 1 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 7.28 (d, *J* = 8.1 Hz, 2 H), 6.44 (s, 1 H), 6.14 (d,

$J = 1.6$ Hz, 1 H), 3.93 (s, 2 H), 3.82 (s, 2H), 0.30 (s, 9 H), 0.25 (s, 9 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): $\delta = 161.3, 155.4, 146.5, 145.0$ (q, $J_{\text{C-F}} = 1.3$ Hz), 144.6 (q, $J_{\text{C-F}} = 1.4$ Hz), 143.8, 132.5, 128.8 (2 C), 128.6 (2 C), 128.4 (q, $J_{\text{C-F}} = 32.0$ Hz), 128.3 (q, $J_{\text{C-F}} = 32.1$ Hz), 125.3 (q, $J_{\text{C-F}} = 3.8$ Hz), 125.2 (q, $J_{\text{C-F}} = 3.8$ Hz), 123.16, 123.15, 123.1 (2 C), 120.8, 111.6 (2 C), 31.5, 30.8, -1.1, -1.8 ppm; MS, $m/z = 298$ (M^+ , 60).

14a: ^1H NMR (500 MHz, CDCl_3 , *cis* isomer): $\delta = 7.56$ (d, $J = 1.5$ Hz, 1H), 6.53 (d, $J = 1.5$ Hz, 1 H), 6.32 (d, $J = 11.4$ Hz, 1 H), 5.55 (m, 1 H), 2.28 (m, 2 H), 1.49 (m, 2 H), 1.28 (m, 12 H), 0.90 (t, $J = 6.8$ Hz, 3 H), 0.31 (s, 9 H) ppm; MS, $m/z = 292$ (M^+ , 10). ^1H NMR (500 MHz, CDCl_3 , *trans* isomer): $\delta = 7.51$ (d, $J = 1.5$ Hz, 1 H), 6.53 (d, $J = 1.5$ Hz, 1 H), 6.38 (d, $J = 15.7$ Hz, 1 H), 5.95 (m, 1 H), 2.17 (m, 2 H), 1.49 (m, 2 H), 1.28 (m, 12 H), 0.90 (t, $J = 6.8$ Hz, 3 H), 0.32 (s, 9 H) ppm; MS, $m/z = 292$ (M^+ , 10).

15a: ^1H NMR (500 MHz, CDCl_3 , *cis* isomer): $\delta = 7.63$ (s, 1 H), 6.66 (s, 1 H), 6.15 (d, $J = 11.4$ Hz, 1 H), 5.55 (m, 1 H), 2.28 (m, 2 H), 1.49 (m, 2 H), 1.28 (m, 12 H), 0.90 (t, $J = 6.8$ Hz, 3 H), 0.27 (s, 9 H) ppm; MS, $m/z = 292$ (M^+ , 10). ^1H NMR (500 MHz, CDCl_3 , *trans* isomer): $\delta = 7.53$ (s, 1 H), 6.74 (s, 1 H), 6.24 (d, $J = 15.7$ Hz, 1 H), 5.95 (m, 1 H), 2.17 (m, 2 H), 1.49 (m, 2 H), 1.28 (m, 12 H), 0.90 (t, $J = 6.8$ Hz, 3 H), 0.27 (s, 9 H) ppm; MS, $m/z = 292$ (M^+ , 10).

14b: ^1H NMR (500 MHz, CDCl_3 , *cis* isomer): $\delta = 7.53$ (brs, 1 H), 6.94 (d, $J = 1.5$ Hz, 1 H), 6.03 (d, $J = 6.4$ Hz, 1 H), 5.35 (d, $J = 6.4$ Hz, 1 H), 3.74 (s, 3 H), 0.34 (s, 9 H) ppm; MS, $m/z = 196$ (M^+ , 70). ^1H NMR (500 MHz, CDCl_3 , *trans* isomer): $\delta = 7.55$ (d, $J = 1.5$ Hz, 1 H), 6.87 (d, $J = 12.3$ Hz, 1 H), 6.41 (d, $J = 1.5$ Hz, 1 H), 5.85 (d, $J = 12.8$ Hz, 1 H), 3.67 (s, 3 H), 0.29 (s, 9 H) ppm; MS, $m/z = 196$ (M^+ , 70).

15b: ^1H NMR (500 MHz, CDCl_3 , *cis* isomer): $\delta = 7.82$ (s, 1 H), 6.82 (s, 1 H), 6.06 (d, $J = 6.4$ Hz, 1 H), 5.18 (d, $J = 6.4$ Hz, 1 H), 3.76 (s, 3 H), 0.35 (s, 9 H) ppm; MS, $m/z = 196$ (M^+ , 70). ^1H NMR (500 MHz, CDCl_3 , *trans* isomer): $\delta = 7.53$ (s, 1 H), 6.85 (d, $J = 12.6$ Hz, 1 H), 6.64 (s, 1 H), 5.68 (d, $J = 12.9$ Hz, 1 H), 3.64 (s, 3 H), 0.29 (s, 9 H) ppm; MS, $m/z = 196$ (M^+ , 70).

^{13}C NMR (125 MHz, CDCl_3 , mixture of **14b** and **15b**): $\delta = 161.1, 159.8, 148.3, 148.0, 146.9, 146.5, 144.6, 143.2, 142.2, 142.1, 140.4, 138.0, 137.2, 137.1, 128.6, 121.3, 121.1, 120.4, 119.9, 117.0, 110.6, 107.2, 96.3, 94.9, 60.19, 60.16, 56.29, 56.27, 1.9, 1.3, -1.7, -1.8$ ppm.

E-18a: ^1H NMR (500 MHz, CDCl_3): δ = 7.57 (d, J = 1.6 Hz, 1 H), 7.38 (d, J = 8.7 Hz, 2 H), 7.00 (d, J = 16.0 Hz, 1 H), 6.90 (d, J = 8.7 Hz, 2 H), 6.77 (d, J = 16.0 Hz, 1 H), 6.66 (d, J = 1.6 Hz, 1 H), 3.83 (s, 3 H), 0.37 (s, 9 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ = 159.0, 157.4, 146.6, 134.1, 130.4, 127.8, 127.2 (2 C), 117.7, 114.1 (2 C), 107.1, 55.3, -0.9 ppm; MS, m/z = 272 (M^+ , 70).

Z-18a: ^1H NMR (500 MHz, CDCl_3): δ = 7.45 (brs, 1 H), 7.25 (d, J = 8.6 Hz, 2 H), 6.83 (d, J = 8.6 Hz, 2 H), 6.50 (d, J = 11.8 Hz, 1 H), 6.47 (d, J = 11.7 Hz, 1 H), 6.16 (d, J = 1.2 Hz, 1 H), 3.82 (s, 3 H), 0.32 (s, 9 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ = 158.6, 157.9, 145.7, 132.3, 130.2 (2 C), 129.9, 129.4, 120.1, 113.4 (2 C), 110.4, 55.1, -1.3 ppm; MS, m/z = 272 (M^+ , 55).

E-18b: ^1H NMR (500 MHz, CDCl_3): δ = 7.59 (d, J = 1.6 Hz, 1 H), 7.46 (d, J = 7.7 Hz, 2 H), 7.36 (t, J = 7.7 Hz, 2 H), 7.25 (t, J = 7.1 Hz, 1 H), 7.15 (d, J = 16.2 Hz, 1 H), 6.83 (d, J = 16.1 Hz, 1 H), 6.69 (d, J = 1.6 Hz, 1 H), 0.39 (s, 9 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ = 158.2, 146.7, 137.6, 134.0, 128.7 (2 C), 128.3, 127.3, 126.1 (2 C), 119.8, 107.2, -0.9 ppm; MS, m/z = 242 (M^+ , 40).

Z-18b: ^1H NMR (500 MHz, CDCl_3): δ = 7.41 (d, J = 1.1 Hz, 1 H), 7.26 (m, 5 H), 6.54 (s, 2 H), 6.07 (d, J = 1.1 Hz, 1 H), 0.31 (s, 9 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ = 158.3, 145.6, 137.6, 132.1, 129.6, 128.9 (2 C), 128.0 (2 C), 127.0, 121.4, 110.3, -1.3 ppm; MS, m/z = 242 (M^+ , 30).

E-18c: ^1H NMR (500 MHz, CDCl_3): δ = 7.60 (m, 3 H), 7.53 (d, J = 8.2 Hz, 2 H), 7.23 (d, J = 16.1 Hz, 1 H), 6.83 (d, J = 16.1 Hz, 1 H), 6.69 (d, J = 1.6 Hz, 1 H), 0.39 (s, 9 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ = 159.3, 146.9, 141.1, 133.5, 129.0, 126.7, 126.1 (2 C), 125.6 (q, $J_{\text{C-F}}$ = 3.8 Hz, 2 C), 122.3, 119.6, 107.1, -0.9 ppm; MS, m/z = 310 (M^+ , 45).

Z-18c: ^1H NMR (500 MHz, CDCl_3): δ = 7.53 (d, J = 8.2 Hz, 2 H), 7.43 (d, J = 1.7 Hz, 1 H), 7.41 (d, J = 8.2 Hz, 2 H), 6.64 (d, J = 12.1 Hz, 1 H), 6.52 (d, J = 12.1 Hz, 1 H), 6.02 (d, J = 1.7 Hz, 1 H), 0.32 (s, 9 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ = 159.0, 146.0, 141.3, 131.4, 129.4, 129.2 (2 C), 129.1, 128.0, 125.0 (q, $J_{\text{C-F}}$ = 3.8 Hz, 2 C), 123.5, 110.1, -1.2 ppm; MS, m/z = 310 (M^+ , 30).

Silylation of 21: ^1H NMR (500 MHz, CDCl_3 , minor product): δ = 7.56 (d, J = 1.1 Hz, 1 H), 7.31 (m, 2 H), 7.22 (t, J = 7.4 Hz, 3 H), 6.29 (d, J = 1.1 Hz, 1 H), 2.82 (m, 4 H), 0.27

(s, 9 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ = 154.5, 146.0, 141.8, 128.5 (2 C), 128.4 (2 C), 126.0, 124.5, 111.2, 37.8, 27.9, -1.1 ppm; MS, m/z = 244 (M^+ , 30). ^1H NMR (500 MHz, CDCl_3 , major product): δ = 7.41 (s, 1 H), 7.31 (m, 2 H), 7.22 (t, J = 7.4 Hz, 3 H), 6.52 (s, 1 H), 2.82 (m, 4 H), 0.26 (s, 9 H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ = 160.5, 143.1, 141.9, 128.4 (2 C), 128.3 (2 C), 125.9, 121.0, 111.2, 36.6, 26.7, -1.6 ppm; MS, m/z = 244 (M^+ , 35).

3a

4c

7a

7b

7b

8a + 9a

8b + 9b

11

11

13

13

E-17b

E-17c

Z-18c

21

GC-MS SPECTRA

3a

3b

3c

4a

5a

4b

4c

7a

7b

8a+9a

8b+9b

E-10

Z-10

E-11

Z-11

14a+15a (E and Z isomers)

14b+15b (E and Z isomers)

28,181

25,537

25,565

E-17a+Z-17a

1,159,442

1,181,261

E-17b

Z-17b

E-17c+Z-17c

E-18a

E-19a

Z-18a

Z-19a

E-18b

E-19b

Z-18b

E-18c

E-19c

Z-18c

21

Silylation of 20 (major)