2,3-Functionalization of Furans, Benzofurans and Thiophenes via Magnesiation and Sulfoxide-Magnesium Exchange

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General:

All reactions were carried out under an argon atmosphere in flame-dried glassware. Syringes which were used to transfer anhydrous solvents or reagents were purged with argon prior to use. THF was continuously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen. 2-Methyl-THF was refluxed and distilled from sodium benzophenone ketyl under nitrogen. Yields refer to isolated yields of compounds estimated to be >95% pure as determined by ^{1}H-NMR (25 °C) and capillary GC. Column chromatography was performed using SiO_2 (0.040 – 0.063 mm, 230 – 400 mesh ASTM) from Merck. Purification via column chromatography was performed using Merck silica gel 60 (40 – 63 μm 230-400 mesh ASTM from Merck). All reagents were obtained from commercial sources. Liquid aldehydes and acid chlorides were distilled prior to use.

CuCN, $ZnCl_2$ and LiCl were obtained from Fluka. Melting points were measured using a Büchi B-540 apparatus and are uncorrected. NMR spectra were recorded in $CDCl_3$ or C_6D_6 and chemical shifts (δ) are reported in parts per million (ppm). Mass spectra and high resolution mass spectra (HRMS) were recorded using electrospray ionization (ESI) except where otherwise noted.

Preparation of $ZnCl_2$ solution:

$ZnCl_2$ solution (1.0 M in THF) was prepared by drying $ZnCl_2$ (136.3 g, 100 mmol) in a *Schlenk*-flask under vacuum at 140 °C for 5 h. After cooling, 100 mL dry THF was added and stirring was continued until all salts were dissolved.

Preparation of CuCN·2LiCl solution:

CuCN·2LiCl solution (1.0 M in THF) was prepared by drying CuCN (7.17 g, 80 mmol) and LiCl (6.77 g, 160 mmol) in a *Schlenk*-flask under vacuum at 140 °C for 5 h. After cooling, 80 mL dry THF was added and stirring was continued until all salts were dissolved.

Experimental procedures and analytical data

Typical procedure for preparation of sulfoxides 1a-c (TP1):

A dry and argon-flushed *Schlenk*-flask, equipped with a stirring bar and a septum, was charged with 2-heteroaryl(trimethyl)silane (15.0 mmol) in diethyl ether (45 mL). The reaction mixture was cooled to 0 °C and *n*BuLi (7.4 mL, 17.5 mmol in hexane) was added dropwise. The reaction mixture was allowed to warm to 25 °C and stirred for additional 10 min. In a second dry and argon-flushed *Schlenk*-flask, equipped with a stirring bar and a septum 4-methoxybenzene sulfinyl chloride (4.2 g, 22.0 mmol) was dissolved in THF (20 mL) and cooled to –50 °C. The lithiated heterocycle was added dropwise and the reaction mixture was allowed to warm to 25 °C and was then stirred for additional 30 min. The reaction mixture was quenched with sat. aq. NH_4Cl-solution (50 mL) and extracted three times with ethyl acetate (50 mL). The combined organic layers were dried ($MgSO_4$) and after filtration the solvent was removed under reduced pressure. Flash chromatographical purification yielded the products of type **1a-c**.

Typical procedure for *ortho*-metalation of sulfoxides and Negishi type cross-coupling leading to products 2a, d, e, g (TP2):

A dry and argon-flushed *Schlenk*-flask, equipped with a magnetic stirrer and a septum, was charged with a sulfoxide of type **1** (10.0 mmol) dissolved in THF (20 mL). The reaction mixture was cooled to –30 °C and TMPMgCl·LiCl (11.0 mmol, 1.20 M in THF) was added dropwise. After 20 min of stirring at –30 °C zinc chloride (10.0 mmol, 1.0 M in THF) was added, and the reaction mixture was allowed to warm to 25 °C. A palladium

catalyst and an electrophile were added and the reaction mixture was stirred at the given temperature until GC-analysis showed full conversion of the electrophile. The reaction mixture was quenched with sat. aq. NH_4Cl-solution (50 mL) and extracted three times with ethyl acetate (100 mL). The combined organic layers were dried ($MgSO_4$) and after filtration the solvent was removed under reduced pressure. Flash chromatographic purification yielded the products **2a, d, e, g**.

Typical procedure for *ortho*-metalation of sulfoxides and trapping with electrophiles leading to products 2c and 2f (TP3):

A dry and argon-flushed *Schlenk*-flask, equipped with a magnetic stirrer and a septum, was charged with a sulfoxide of type **1** (10.0 mmol) dissolved in THF (20 mL). The reaction mixture was cooled to –30 °C and TMPMgCl·LiCl (11.0 mmol, 1.20 M in THF) was added dropwise. After 20 min of stirring at –30 °C an electrophile (10.0 mmol, 1.0 M in THF) was added, the reaction mixture was allowed to warm to 25 ° and stirred at the given temperature until GC-analysis showed full conversion of the electrophile. The reaction mixture was quenched with sat. aq. NH_4Cl-solution (50 mL) and extracted three times with ethyl acetate (100 mL). The combined organic layers were dried ($MgSO_4$) and after filtration the solvent was removed under reduced pressure. Flash chromatographic purification yielded the products **2c** and **2f**.

Typical procedure for the sulfoxide-magnesium exchange and Negishi type cross-coupling leading to products 3a, b, c, e, f (TP4):

A dry and argon-flushed *Schlenk*-flask, equipped with a magnetic stirrer and a septum, was charged with a solution of sulfoxide of type **2** (1.0 mmol) in 2-Methyl-THF (2 mL). The reaction mixture was cooled to –50 °C and *i*PrMgCl·LiCl (1.1 mmol, 1.20 M in THF) was added dropwise. After stirring at –50 °C until GC-analysis showed full conversion of the sulfoxide zinc chloride (10.0 mmol, 1.0 M in THF) was added, and the reaction mixture was allowed to warm to 25 °C. A palladium catalyst and an electrophile were added and the reaction mixture was stirred at the given temperature until GC-analysis showed full conversion of the electrophile. The reaction mixture was quenched with sat. aq. NH_4Cl-solution (5 mL) and extracted three times with ethyl acetate (10 mL). The combined organic layers were dried ($MgSO_4$) and after filtration the solvent was removed under reduced pressure. Flash chromatographic purification yielded the products **3a, b, c, e, f**.

Typical procedure for the sulfoxide-magnesium exchange and trapping with electrophiles leading to products 3d and g (TP5):

A dry and argon-flushed *Schlenk*-flask, equipped with a magnetic stirrer and a septum, was charged with a solution of sulfoxide of type **2** (1.0 mmol) in 2-Methyl-THF (2 mL). The reaction mixture was cooled to –50 °C and *i*PrMgCl·LiCl (1.1 mmol, 1.20 M in THF) was added dropwise. After stirring at –50 °C until GC-analysis showed full conversion of the sulfoxide the desired electrophile (0.8 mmol) was added and the reaction mixture was stirred at the given temperature until GC-analysis showed full conversion of the electrophile. The reaction mixture was quenched with sat. aq. NH_4Cl-solution (5 mL) and extracted three times with ethyl acetate (10 mL). The combined organic layers were dried ($MgSO_4$) and after filtration the

solvent was removed under reduced pressure. Flash chromatographic purification yielded the products **3d** and **g**.

{5-[(4-Methoxyphenyl)sulfinyl]-2-furyl}(trimethyl)silane (1a)

According to **TP1** sulfoxide **1a** was prepared from 2-furyl(trimethyl)silane (2.10 g, 15.0 mmol), *n*BuLi (7.4 mL, 17.5 mmol in hexane) and 4-methoxybenzene sulfinyl chloride (4.2 g, 22.0 mmol) . Flash chromatographical purification (pentane / ethyl acetate = 2:1, silica gel) yielded **1a** as a yellow oil (3.43 g, 78%).

^{1}H-NMR ($CDCl_3$, 300 MHz, Me_4Si): δ (ppm) = 0.20 (s, 9 H), 3.82 (s, 3 H), 6.56–6.58 (m, 2 H), 6.96–7.01 (m, 2 H), 7.61–7.66 (m, 2 H).
^{13}C-NMR ($CDCl_3$, 75 MHz, Me_4Si): δ (ppm) = –1.9 (CH_3), 55.4 (CH_3), 114.5 (CH), 114.8 (CH), 120.2 (CH), 127.0 (CH), 132.8, 157.5, 162.0, 166.8.
IR (ATR): $\tilde{\nu}$ / cm^{-1} = 1716 (m), 1594 (m), 1578 (w), 1494 (m), 1462 (w), 1442 (w), 1410 (w), 1366 (w), 1304 (m), 1248 (s), 1182 (m), 1172 (m), 1140 (w), 1084 (s), 1050 (s), 1024 (m), 920 (m), 830 (vs), 794 (s), 756 (s), 712 (m), 702 (m), 652 (m), 630 (s).
MS (EI, 70 eV): *m/z* (%) = 248 (23), 247 (100), 246 (15), 232 (39), 231 (40), 182 (11), 165 (17), 157 (14), 155 (18), 139 (84), 115 (14), 73 (81).
HRMS (EI): calcd. for $C_{14}H_{18}O_3{}^{32}S^{28}Si$: 294.0766, found: 294.0735.

{5-[(4-Methoxyphenyl)sulfinyl]-2-thiophenyl}(trimethyl)silane (1b)

According to **TP1** sulfoxide **1b** was prepared from 2-thiophenyl(trimethyl)silane (7.10 g, 50.0 mmol), *n*BuLi (27.2

mL, 55.0 mmol in hexane) and 4-methoxybenzene sulfinyl chloride (14.3 g, 75.0 mmol). Flash chromatographical purification (pentane / diethyl ether = 6:4, silica gel) yielded **1b** as an orange oil (13.2 g, 85%).

^{1}H-NMR ($CDCl_3$, 300 MHz, Me_4Si): δ (ppm) = 0.24 (s, 9 H), 3.78 (s, 3 H), 6.93-6.98 (m, 2 H), 7.11 (d, J = 3.37 Hz, 1 H), 7.48 (d, J = 3.37 Hz, 1 H), 7.57-7.62 (m, 2 H).
^{13}C-NMR ($CDCl_3$, 75 MHz, Me_4Si): δ (ppm) = -0.5 (CH_3), 55.3 (CH), 114.5 (CH), 126.2 (CH), 131.4 (CH), 133.6 (CH), 136.0, 148.3, 152.5, 161.8.
IR (ATR): $\tilde{\nu}$ / cm^{-1} = 2956 (w), 1592 (m), 1578 (m), 1494 (s), 1462 (w), 1442 (w), 1408 (w), 1302 (m), 1248 (s), 1206 (m), 1180 (w), 1170 (m), 1086 (s), 1046 (s), 1026 (m), 1000 (s), 978 (m), 828 (vs), 796 (s), 756 (s), 740 (m), 698 (w), 624 (m).
MS (EI, 70 eV): m/z (%) = 295 (11), 264 (17), 263 (40), 262 (100), 249 (17), 248 (38), 247 (96), 139 (24), 123 (13), 73 (24).
HRMS (EI): calcd. for $C_{14}H_{18}O_2{}^{32}S_2{}^{28}Si$: 310.0517, found: 310.0528.

2-[(4-Methoxyphenyl)sulfinyl]-1-benzofuran (1c)

According to **TP1** sulfoxide **1c** was prepared from benzofuran (11.8 g, 100 mmol), *n*BuLi (54.5 mL, 110 mmol in hexane) and 4-methoxybenzene sulfinyl chloride (24.8 g, 130 mmol). Flash chromatographical purification (pentane / diethyl ether = 1:1, silica gel) yielded **1c** as a brown solid (12.7 g, 47%).

^{1}H-NMR ($CDCl_3$, 300 MHz, Me_4Si): δ (ppm) = 3.83 (s, 3 H), 7.00-7.04 (m, 2 H), 7.16 (s, 1 H), 7.22-7.28 (m, 1 H), 7.31-7.37 (m, 1 H), 7.43-7.46 (m, 1H), 7.58-7.61 (m, 1 H), 7.70-7.75 (m, 2 H).

^{13}C-NMR ($CDCl_3$, 75 MHz, Me_4Si): δ (ppm) = 55.5 (CH_3), 110.5 (CH), 112.0 (CH), 114.9 (CH), 122.2 (CH), 123.7 (CH), 126.5, 126.6 (CH), 127.3 (CH), 132.3, 156.3, 156.6, 162.5.

IR (ATR): $\tilde{\nu}$ / cm^{-1} = 3092 (w), 1594 (m), 1578 (m), 1532 (w), 1494 (s), 1462 (m), 1442 (m), 1408 (w), 1306 (m), 1254 (s), 1232 (s), 1170 (s), 1086 (s), 1072 (s), 1048 (vs), 1022 (s), 920 (m), 878 (m), 812 (m), 790 (s), 752 (vs), 634 (m).

MS (EI, 70 eV): *m/z* (%) = 256 (13), 225 (49), 224 (96), 210 (17), 209 (83), 181 (33), 152 (11), 139 (100), 112 (12), 77 (11).

HRMS (EI): calcd. for $C_{15}H_{12}O_3{}^{32}S$: 272.0507, found: 272.0510.

mp (°C): 52-54.

Ethyl 4-[2-[(4-methoxyphenyl)sulfinyl]-5-(trimethylsilyl)-3-furyl]benzoate (2a)

According to **TP2** sulfoxide **2a** was prepared from suloxide **1a** (5.89 g, 20.0 mmol), TMPMgCl·LiCl (19.8 mL, 22.0 mmol, 1.11 M in THF), $Pd(PPh_3)_4$ (462 mg, 0.40 mmol) and ethyl 4-iodobenzoate (6.63 g, 24.0 mmol) in 1 h at 25 °C. Flash chromatographical purification (pentane / diethyl ether = 1:1, silica gel) yielded **2a** as a yellow oil (6.52 g, 77%).

^{1}H-NMR ($CDCl_3$, 300 MHz, Me_4Si): δ (ppm) = 0.22 (s, 9 H), 1.41 (t, J = 7.14 Hz, 3 H), 3.83 (s, 3 H), 4.40 (q, J = 7.14 Hz, 2 H), 6.79 (s, 1 H), 6.94–7.01 (m, 2 H), 7.60–7.67 (m, 4 H), 8.07–8.13 (m, 2 H).

^{13}C-NMR ($CDCl_3$, 75 MHz, Me_4Si): δ (ppm) = –1.98 (CH_3), 14.3 (CH_3), 55.5 (CH_3), 61.1 (CH_2), 114.4 (CH), 121.0 (CH), 127.1 (CH), 128.6 (CH), 129.9 (CH), 130.1, 131.8, 132.2, 135.3, 151.8, 161.9, 161.1, 166.4.

IR (ATR): $\tilde{\nu}$ / cm^{-1} = 2958 (w), 1594 (m), 1578 (w), 1542 (vw), 1494 (m), 1462 (w), 1442 (w), 1408 (w), 1304 (m), 1248 (s), 1184 (m), 1172 (m), 1140 (w), 1106 (w), 1084 (s), 1050 (s),

1024 (s), 920 (m), 828 (vs), 794 (s), 756 (s), 712 (m), 702 (m), 652 (m), 630 (m).

MS (EI, 70 eV): *m/z* (%) = 428 (5), 427 (12), 426 (37), 397 (5), 396 (9), 395 (29), 394 (100), 291 (5), 275 (5), 139 (8), 73 (34).

HRMS (EI): calcd. for $C_{23}H_{27}O_5{}^{32}S^{28}Si$ (M+H): 443.1348, found: 443.1347.

[5-[(4-Methoxyphenyl)sulfinyl]-4-(phenylethynyl)-2-furyl](trimethyl)silane benzoate (2b)

A dry and argon-flushed *Schlenk*-flask, equipped with a stirring bar and a septum, was charged with the sulfoxide **1a** (2.94 g, 10.0 mmol) dissolved in THF (20 mL). The reaction mixture was cooled to –40 °C and TMPMgCl·LiCl (9.91 mL, 11.0 mmol, 1.11 M in THF) was added dropwise. After 20 min of stirring at –40 °C iodine (2.79 g, 11.0 mmol) was added and the reaction mixture was allowed to warm to 25 °C. In a second dry and argon-flushed *Schlenk*-flask, equipped with a stirring bar ethynylbenzene (1.53 g, 1.65 mL, 15.0 mmol) was added slowly to *i*PrMgCl·LiCl (9.43 mL, 15.0 mmol, 1.59 M in THF). After cessation of gas evolution the reaction mixture was heated to 60 °C for 5 min. After cooling to 25 °C a zinc chloride solution (7.5 mL, 7.5 mmol, 1.0 M in THF) was added slowly. The resulting zinc reagent was transferred to the previously prepared crude iodide. $Pd(PPh_3)_4$ (231 mg, 0.2 mmol), were added and the reaction mixture was stirred at 50 °C for 2 h. Then the reaction mixture was quenched with a sat. aq. NH_4Cl-solution (50 mL) and extracted three times with ethyl acetate (50 mL). The combined organic layers were dried ($MgSO_4$) and after filtration, the solvents were removed under reduced pressure. Flash chromatographical purification (pentane / ethyl acetate = 5:1, silica gel) yielded **2b** as a yellow oil (2.71 g, 69% yield).

^{1}H-NMR (C_6D_6, 300 MHz, Me_4Si): δ (ppm) = 0.00 (s, 9 H), 3.15 (s, 3 H), 6.50 (s, 1 H), 6.61–6.65 (m, 2 H), 7.03–7.06 (m, 3 H), 7.46–7.49 (m, 2 H), 7.69–7.73 (m, 2 H).
^{13}C-NMR (C_6D_6, 75 MHz, Me_4Si): δ (ppm) = –2.2 (CH_3), 54.9 (CH_3), 79.4, 96.2, 112.6, 114.9 (CH), 123.2 (CH), 123.7, 127.0 (CH), 128.7 (CH), 128.9 (CH), 131.9 (CH), 133.9, 160.2, 162.2, 165.9.
IR (ATR): $\tilde{\nu}$ / cm^{-1} = 3060 (w), 2959 (w), 1737 (w), 1592 (m), 1578 (m), 1493 (s), 1462 (m), 1442 (m), 1303 (m), 1249 (s), 1171 (s), 1140 (m), 1086 (s), 1058 (s), 1044 (s), 1025 (s), 926 (m), 839 (s), 826 (s), 689 (s), 636 (s), 583 (m), 565 (m).
MS (EI, 70 eV): *m/z* (%) = 348 (6), 347 (24), 346 (100), 139 (6), 73 (21).
HRMS (EI): calcd. for $C_{22}H_{22}O_3{}^{32}S^{28}Si$: 394.1059, found: 394.1050.

{4-[(4-Chlorophenyl)thio]-5-[(4-methoxyphenyl)sulfinyl]-2-furyl}(trimethyl)silane (2c)

According to **TP3** sulfoxide **2c** was prepared from sulfoxide **1b** (2.17 g, 7.00 mmol), TMPMgCl·LiCl (7.57 mL, 8.40 mmol, 1.11 M in THF), and *S*(4-chlorophenyl)benzene thiosulfonate (2.39 g, 8.40 mmol) in 1 h at 25 °C. Flash chromatographical purification (pentane / diethyl ether = 7:3, silica gel) yielded **2c** as an orange oil (2.46 g, 78%).

^{1}H-NMR ($CDCl_3$, 300 MHz, Me_4Si): δ (ppm) = 0.24 (s, 9 H), 3.77 (s, 3 H), 6.87-6.91 (m, 2 H), 6.97-7.01 (m, 3 H), 7.12-7.17 (m, 2 H), 7.59-7.64 (m, 2 H).
^{13}C-NMR ($CDCl_3$, 75 MHz, Me_4Si): δ (ppm) = -0.6 (CH_3), 55.3 (CH_3), 114.5 (CH), 126.7 (CH), 129.1 (CH), 129.7 (CH), 131.5 (CH), 132.4, 134.2, 135.4, 138.6, 147.5, 155.4, 162.0.
IR (ATR): $\tilde{\nu}$ / cm^{-1} = 2954 (w), 2360 (w), 1738 (w), 1592 (m), 1578 (m), 1494 (m), 1474 (m), 1440 (w), 1408 (w), 1390 (w), 1304 (w), 1248 (s), 1170 (m), 1084 (s), 1048 (s), 1024 (m),

1010 (m), 990 (s), 826 (vs), 796 (s), 756 (m), 732 (m), 700 (m), 624 (m).

MS (EI, 70 eV): *m/z* (%) = 452 (10), 436 (11), 407 (10), 406 (43), 405 (25), 404 (100), 391 (14), 390 (8), 389 (33), 73 (41).

HRMS (EI): calcd. for $C_{20}H_{21}{}^{35}ClO_2{}^{32}S_3{}^{28}Si$: 452.0161, found: 452.0156.

4-[2-[(4-Methoxyphenyl)sulfinyl]-5-(trimethylsilyl)-3-furyl]benzonitrile (2d)

According to **TP2** sulfoxide **2d** was prepared from sulfoxide **1b** (2.17 g, 7.00 mmol), TMPMgCl·LiCl (7.57 mL, 8.40 mmol, 1.11 M in THF), $Pd(PPh_3)_4$ (162 mg, 0.14 mmol) and 4-iodobenzonitrile (1.92 g, 8.40 mmol) in 1 h at 25 °C. Flash chromatographical purification (pentane / diethyl ether = 1:1, silica gel) yielded **2d** as a white solid (2.57 g, 89%).

^{1}H-NMR ($CDCl_3$, 300 MHz, Me_4Si): δ (ppm) = 0.28 (s, 9 H), 3.82 (s, 3 H), 6.94-6.99 (m, 2 H), 7.18 (s, 1 H), 7.52-7.57 (m, 2 H), 7.31-7.37 (m, 1 H), 7.67-7.74 (m, 3H).

^{13}C-NMR ($CDCl_3$, 75 MHz, Me_4Si): δ (ppm) = -0.5 (CH_3), 55.4 (CH_3), 111.8, 114.5 (CH), 118.5, 126.5 (CH), 129.9 (CH), 132.3 (CH), 134.9 (CH), 135.5, 138.7, 145.2, 148.3, 149.3, 162.0.

IR (ATR): $\tilde{\nu}$ / cm^{-1} = 2956 (w), 2224 (w), 1592 (m), 1578 (m), 1492 (m), 1462 (w), 1440 (w), 1406 (w), 1332 (vw), 1300 (w), 1248 (s), 1180 (w), 1170 (m), 1084 (m), 1048 (s), 992 (s), 830 (vs), 796 (s), 756 (s), 702 (w), 664 (w), 628 (m).

MS (EI, 70 eV): *m/z* (%) = 395 (10), 365 (9), 364 (24), 363 (100), 349 (14), 348 (53), 154 (8), 138 (14), 123 (8), 73 (18).

HRMS (EI): calcd. for $C_{21}H_{21}NO_2{}^{32}S_2{}^{28}Si$: 411.0783, found: 411.0769.

mp (°C): 152-154.

{4-(3-Methoxyphenyl)-5-[(4-methoxyphenyl)sulfinyl]-2-furyl}(trimethyl)silane (2e)

According to **TP2** sulfoxide **2e** was prepared from sulfoxide **1b** (6.20 g, 20.0 mmol), TMPMgCl·LiCl (21.6 mL, 24.0 mmol, 1.11 M in THF), $Pd(PPh_3)_4$ (462 mg, 0.40 mmol) and 3-iodoanisole (5.61 g, 24.0 mmol) in 1 h at 25 °C. Flash chromatographical purification (pentane / diethyl ether = 7:3, silica gel) yielded **2e** as an orange solid (7.28 g, 87%).

^{1}H-NMR (C_6D_6, 400 MHz, Me_4Si): δ (ppm) = -0.08 (s, 9 H), 3.08 (s, 3 H), 3.43 (s, 3 H), 6.54-6.58 (m, 2 H), 6.86 (ddd, J = 8.22 Hz, 2.55 Hz, 0.98 Hz, 1 H), 7.21 (s, 1 H), 7.32-7.35 (m, 1 H), 7.44-7.45 (m, 1 H), 7.59-7.63 (m, 1 H).
^{13}C-NMR (C_6D_6, 100 MHz, Me_4Si): δ (ppm) = -0.5 (CH_3), 54.8 (CH_3), 55.0 (CH_3), 114.7 (CH), 114.8 (CH), 115.2 (CH), 122.1 (CH), 126.7 (CH), 130.1 (CH), 136.4, 136.5 (CH), 137.4, 146.5, 147.8, 150.6, 160.4, 162.0.
IR (ATR): $\tilde{\nu}$ / cm^{-1} = 2952 (w), 1594 (m), 1490 (m), 1466 (m), 1344 (w), 1308 (w), 1244 (vs), 1202 (w), 1186 (w), 1086 (m), 1036 (s), 1018 (m), 1000 (s), 926 (m), 836 (vs), 818 (s), 798 (s), 782 (s), 752 (m), 700 (m), 680 (w), 630 (w).
MS (EI, 70 eV): *m/z* (%) = 416 (10), 401 (8), 400 (19), 370 (9), 369 (23), 368 (100), 354 (12), 353 (50), 249 (7), 73 (34).
HRMS (EI): calcd. for $C_{21}H_{24}O_3{}^{32}S_2{}^{28}Si$: 416.0936, found: 416.0941.
mp (°C): 107-108.

3-[(4-Chlorophenyl)thio]-2-[(4-methoxyphenyl)sulfinyl]-1-benzofuran (2f)

According to **TP3** sulfoxide **2f** was prepared from sulfoxide **1c** (1.90 g, 7.00 mmol), TMPMgCl·LiCl (7.85 mL, 8.40 mmol, 1.07 M in THF), and *S*(4-chlorophenyl)benzene thiosulfonate (2.39 g, 8.40 mmol) in 1 h at 25 °C. Flash chromatographical

purification (pentane / diethyl ether = 1:1, silica gel) yielded **2f** as an orange oil (2.56 g, 88%).

^{1}H-NMR ($CDCl_3$, 300 MHz, Me_4Si): δ (ppm) = 3.82 (s, 3 H), 6.95-7.00 (m, 2 H), 7.11-7.16 (m, 2 H), 7.17-7.21 (m, 2 H), 7.22-7.25 (m, 1 H), 7.35-7.42 (m, 2 H), 7.50-7.52 (m, 1 H), 7-67-7.71 (m, 2 H).
^{13}C-NMR ($CDCl_3$, 100 MHz, Me_4Si): δ (ppm) = 55.5 (CH_3), 112.7 (CH), 114.9 (CH), 115.2 (CH), 121.2 (CH), 124.3 (CH), 126.9, 127.6 (CH), 127.7 (CH), 129.4 (CH), 129.6, 132.1, 132.7, 132.8, 155.9, 157.6, 162.4.
IR (ATR): $\tilde{\nu}$ / cm^{-1} = 3064 (w), 2836 (w), 1590 (s), 1576 (m), 1492 (s), 1474 (s), 1440 (m), 1390 (w), 1304 (m), 1250 (vs), 1218 (m), 1170 (m), 1138 (m), 1084 (vs), 1052 (s), 1026 (s), 1010 (s), 882 (w), 826 (s), 806 (vs), 746 (vs), 712 (m), 660 (w), 648 (w).
MS (EI, 70 eV): *m/z* (%) = 398 (16), 369 (20), 368 (100), 367 (57), 366 (87), 275 (26), 255 (41), 227 (23), 224 (28), 139 (17).
HRMS (EI): calcd. for $C_{21}H_{15}{}^{35}ClO_3{}^{32}S_2$: 414.0151, found: 414.0152.

3-(4-Fluorophenyl)-2-[(4-methoxyphenyl)sulfinyl]-1-benzofuran (2g)

According to **TP2** sulfoxide **2g** was prepared from sulfoxide **1c** (1.90 g, 7.00 mmol), TMPMgCl·LiCl (7.85 mL, 8.40 mmol, 1.07 M in THF), $Pd(PPh_3)_4$ (162 mg, 0.14 mmol) and 1-fluoro-4-iodobenzene (1.86 g, 8.40 mmol) in 1 h at 25 °C. Flash chromatographical purification (pentane / diethyl ether = 1:1, silica gel) yielded **2g** as a white solid (2.04 g, 80%).

^{1}H-NMR ($CDCl_3$, 300 MHz, Me_4Si): δ (ppm) = 3.83 (s, 3 H), 6.99-7.04 (m, 2 H), 7.21-7.28 (m, 2 H), 7.29-7.33 (m, 1 H), 7.39-

7.45 (m, 1 H), 7.47-7.51 (m 1 H), 7.61-7.67 (m, 3 H), 7.68-7.72 (m, 2 H).

^{13}C-NMR ($CDCl_3$, 100 MHz, Me_4Si): δ (ppm) = 55.5 (CH_3), 112.5 (CH), 114.8 (CH), 116.2 (d, J = 21.91 Hz, CH), 121.4 (CH), 123.9 (CH), 125.4 (d, J = 3.35 Hz), 126.6, 126.7, 127.0 (CH), 127.7 (CH), 131.5 (d, J = 8.25 Hz, CH), 131.9, 150.4, 155.6, 162.1, 163.1 (d, J = 249.3 Hz, CF).

IR (ATR): $\tilde{\nu}$ / cm^{-1} = 3062 (w), 2952 (w), 1592 (s), 1576 (m), 1496 (vs), 1456 (m), 1442 (m), 1302 (m), 1250 (s), 1232 (s), 1216 (s), 1134 (s), 1102 (s), 1084 (s), 1044 (vs), 1018 (s), 966 (m), 828 (vs), 814 (s), 794 (s), 748 (vs), 718 (m), 660 (m), 642 (w), 632 (w).

MS (EI, 70 eV): m/z (%) = 350 (6), 334 (100), 319 (17), 317 (3), 316 (26), 231 (15), 184 (4), 172 (4), 171 (4), 139 (7).

HRMS (EI): calcd. for $C_{21}H_{15}{}^{19}FO_3{}^{32}S$: 366.4064, found: 366.4075.

mp (°C): 100-102.

Ethyl 4-[2-(4-chlorophenyl)-5-(trimethylsilyl)-3-furyl]benzoate (3a)

According to **TP4** sulfoxide **3a** was prepared from sulfoxide **2a** (6.20 g, 14.0 mmol), *i*PrMgCl·LiCl (9.5 mL, 15.4 mmol, 1.46 M in THF, -50 °C, 2 h), $Pd(PPh_3)_4$ (162 mg, 0.14 mmol) and 4-chloro-iodobenzene (2.67 g, 11.2 mmol) in 1 h at 25 °C. Flash chromatographical purification (pentane / diethyl ether = 25:1, silica gel) yielded **3a** as a colourless solid (3.05 g, 68%).

^{1}H-NMR (C_6D_6, 400 MHz, Me_4Si): δ (ppm) = −0.28 (s, 9 H), 1.04 (t, J = 7.04 Hz, 3 H), 4.16 (q, J = 7.24 Hz, 2 H), 6.64 (s, 1 H), 6.97–7.00 (m, 2 H), 7.27–7.30 (m, 2 H), 7.33–7.37 (m, 2 H), 8.14–.8.17 (m, 2 H).

^{13}C-NMR (C_6D_6, 100 MHz, Me_4Si): δ (ppm) = −2.0 (CH_3), 13.9 (CH_3), 60.5 (CH_2), 122.3, 123.6, 127.8 (CH), 128.4 (CH), 128.7 (CH),

129.5, 129.6 (CH), 130.0 (CH), 133.7, 138.9, 152.3, 159.7, 165.6.

IR (ATR): $\tilde{\nu}$ / cm^{-1} = 2990 (vw), 2974 (w), 2956 (w), 2900 (vw), 1710 (s), 1668 (w), 1652 (w), 1608 (m), 1588 (w), 1558 (w), 1510 (w), 1476 (m), 1446 (w), 1414 (w), 1402 (w), 1366 (w), 1312 (w), 1292 (m), 1274 (s), 1248 (s), 1180 (m), 1148 (m), 1126 (m), 1110 (s), 1100 (s), 1090 (s), 1050 (w), 1024 (m), 1014 (m), 982 (w), 972 (w), 954 (m), 940 (m), 876 (w), 828 (vs), 774 (s), 756 (s), 742 (m), 722 (m), 704 (s), 632 (m).

MS (EI, 70 eV): *m/z* (%) = 401 (10), 400 (36), 398 (100), 310 (17), 295 (15), 169 (7), 73 (7).

HRMS (EI): calcd. for $C_{22}H_{23}O_3{}^{35}Cl^{28}Si$: 398.1105, found: 398.1098.

mp (°C): 83–85.

Ethyl 4-[3-(phenylethynyl)-5-(trimethylsilyl)-2-furyl]benzoate (3b)

According to **TP4** sulfoxide **3b** was prepared from sulfoxide **2b** (395 mg, 1.00 mmol), *i*PrMgCl·LiCl (0.69 mL, 1.10 mmol, 1.59 M in THF, -50 °C, 15 min), $Pd(PPh_3)_4$ (23 mg, 0.02 mmol) and ethyl 4-iodobenzoate (221 mg, 0.80 mmol) in 1 h. Flash chromatographical purification (pentane / diethyl ether = 6:1, silica gel) yielded **3b** as a brown oil (212 mg, 68%).

^{1}H-NMR (C_6D_6, 400 MHz, Me_4Si): δ (ppm) = 0.19 (s, 9 H), 1.02 (t, J = 7.14 Hz, 3 H), 4.13 (q, J = 7.14 Hz, 2 H), 6.72 (s, 1 H), 6.99–7.07 (m, 3 H), 7.51–7.55 (m, 2 H), 8.23–8.26 (m, 2 H), 8.37–8.40 (m, 2 H).

^{13}C-NMR (C_6D_6, 100 MHz, Me_4Si): δ (ppm) = –1.9 (CH_3), 14.2 (CH_3), 60.8 (CH_2), 83.4, 95.3, 105.9, 123.9 (CH), 125.0 (CH), 125.4 (CH), 128.6 (CH), 128.8, 130.3, 130.4 (CH), 131.7 (CH), 134.8, 157.8, 160.7, 165.8.

IR (ATR): $\tilde{\nu}$ / cm^{-1} = 2322 (m), 17011 (m), 1608 (m), 1320 (m), 1281 (s), 1271 (m), 1193 (w), 1138 (w), 1103 (s), 1093 (w), 1040 (w), 1000 (w), 970 (m), 836 (s), 810 (vs), 780 (m), 753 (s), 640 (m).

MS (EI, 70 eV): *m/z* (%) = 388 (100), 345 (1), 344 (1), 300 (3), 285 (1).

HRMS (EI): calcd. for $C_{24}H_{24}O_3{}^{28}Si$: 388.1494, found: 388.1479.

.

Ethyl 5-[3-[(4-chlorophenyl)thio]-5-(trimethylsilyl)-2-thienyl]nicotinate (3c)

According to **TP4** sulfoxide **3c** was prepared from sulfoxide **2c** (453 mg, 1.00 mmol), *i*PrMgCl·LiCl (1.0 mL, 1.10 mmol, 1.11 M in THF, -50 °C, 1 h), $Pd(PPh_3)_4$ (23 mg, 0.02 mmol) and 5-bromonicotinic acid ethyl ester (184 mg, 0.80 mmol) in 6 h at 60 °C. Flash chromatographical purification (pentane / diethyl ether = 10:1, silica gel) yielded **3c** as a white solid (239 mg, 67%).

^{1}H-NMR (C_6D_6, 400 MHz, Me_4Si): δ (ppm) = 0.17 (s, 9 H), 0.92 (t, J = 7.23 Hz, 3 H), 4.00 (q, J = 7.23 Hz, 2 H), 6.72-6.81 (m, 4 H), 7.21 (s, 1 H), 8.60 (dd, J = 2.16 Hz, 2.14 Hz, 1 H) 9.15 (d, J = 2.14 Hz, 1 H), 9.37 (d, J = 2.16 Hz, 1 H).

^{13}C-NMR (C_6D_6, 100 MHz, Me_4Si): δ (ppm) = -0.5 (CH_3), 14.0 (CH_3), 61.2 (CH_2), 126.4, 127.5, 129.0 (CH), 129.4 (CH), 129.5, 132.1, 136.4, 136.8 (CH), 140.9 (CH), 142.1, 146.6, 150.6 (CH), 153.1 (CH), 164.6.

IR (ATR): $\tilde{\nu}$ / cm^{-1} = 2956 (w), 2360 (w), 1716 (s), 1574 (w), 1474 (m), 1392 (w), 1366 (w), 1292 (s), 1248 (s), 1222 (s), 1120 (m), 1108 (m), 1092 (m), 1022 (m), 1012 (m), 984 (s), 836 (vs), 816 (s), 764 (s), 704 (m), 652 (w), 624 (w).

MS (EI, 70 eV): *m/z* (%) = 450 (11), 449 (45), 448 (27), 447 (100), 435 (8), 434 (44), 433 (19), 432 (70), 165 (6), 73 (9).

HRMS (EI): calcd. for $C_{21}H_{22}{}^{35}ClNO_2{}^{32}S_2{}^{28}Si$: 447.0550, found: 447.0535.

mp (°C): 90-91.

4-[2-[(3,4-Dichlorophenyl)(hydroxy)methyl]-5-(trimethylsilyl)-3-thienyl]benzonitrile (3d)

According to **TP5** sulfoxide **3d** was prepared from sulfoxide **2d** (411 mg, 1.00 mmol), *i*PrMgCl·LiCl (1.0 mL, 1.10 mmol, 1.11 M in THF, -50 °C, 1 h) and 3,4-dichlorbenzaldehyde (140 mg, 0.80 mmol) in 1 h at 25 °C. Flash chromatographical purification (pentane / diethyl ether = 4:1, silica gel) yielded **3d** as a white solid (287 mg, 83%).

^{1}H-NMR (C_6D_6, 400 MHz, Me_4Si): δ (ppm) = 0.18 (s, 9 H), 1.61 (d, J = 4.20 Hz, 1 H), 5.48 (d, J = 4.20 Hz, 1 H), 6.74 (dd, J = 8.20 Hz, 2.15 Hz, 1 H), 6.93 (dd, J = 8.20 Hz, 0.39 Hz, 1 H), 6.97 (s, 1 H), 7.01-7.03 (m, 2 H), 7.06-7.08 (m, 2 H), 7.32 (dd, J = 2.15 Hz, 0.39 Hz, 1 H).

^{13}C-NMR (C_6D_6, 100 MHz, Me_4Si): δ (ppm) = -0.3 (CH_3), 69.0 (CH), 111.8, 118.7, 125.8 (CH), 128.4 (CH), 129.5 (CH), 130.6 (CH), 132.1, 132.3 (CH), 132.89, 135.7 (CH), 140.3, 140.4, 141.0, 143.9, 148.4.

IR (ATR): $\tilde{\nu}$ / cm^{-1} = 3468 (w), 2954 (w), 2234 (w), 1740 (w), 1604 (w), 1538 (w), 1498 (w), 1468 (w), 1384 (m), 1248 (m), 1144 (w), 1124 (w), 1028 (m), 1004 (m), 910 (w), 868 (m), 834 (vs), 820 (s), 758 (m), 738 (m), 712 (m), 676 (m), 626 (w).

MS (EI, 70 eV): *m/z* (%) = 431 (36), 418 (54), 417 (51), 416 (100), 415 (28), 402 (53), 400 (75), 73 (69), 44 (99), 43 (30).

HRMS (EI): calcd. for $C_{21}H_{19}{}^{35}Cl_2NO^{32}S^{28}Si$: 431.0334, found: 431.0323.

mp (°C): 145-146.

4-[3-(3-Methoxyphenyl)-5-(trimethylsilyl)-2-thienyl]benzonitrile (3e)

According to **TP4** sulfoxide **3e** was prepared from sulfoxide **2e** (6.67 g, 16.0 mmol), *i*PrMgCl·LiCl (18.5 mL, 17.6 mmol, 0.95 M in THF, -50 °C, 5 min), $Pd(PPh_3)_4$ (370 mg, 0.32 mmol) and 3-iodoanisole (2.93 g, 12.8 mmol) in 1 h at 25 °C. Flash chromatographical purification (pentane / diethyl ether = 20:1, silica gel) yielded **3e** as a white solid (3.97 mg, 85%).

^{1}H-NMR (C_6D_6, 400 MHz, Me_4Si): δ (ppm) = -0.28 (s, 9 H), 3.23 (s, 3 H), 6.72 (ddd, J = 8.22 Hz, 2.54 Hz, 0.98 Hz, 1 H), 6.79-6.82 (m, 3 H), 6.87-6.88 (m, 1 H), 7.04-7.07 (m, 3 H), 7.28 (s, 1 H).
^{13}C-NMR (C_6D_6, 100 MHz, Me_4Si): δ (ppm) = -0.2 (CH_3), 54.7 (CH_3), 111.4, 113.2 (CH), 115.1 (CH), 118.6, 121.8 (CH), 129.8 (CH), 130.0 (CH), 132.3 (CH), 137.9 (CH), 138.1, 138.8, 141.1, 141.6, 142.2, 160.4.
IR (ATR): $\tilde{\nu}$ / cm^{-1} = 2954 (w), 2226 (w), 1744 (w), 1602 (m), 1574 (m), 1448 (w), 1424 (w), 1334 (w), 1288 (w), 1242 (m), 1222 (m), 1208 (m), 1178 (m), 1052 (m), 1000 (s), 962 (m), 884 (w), 836 (vs), 778 (s), 754 (m), 702 (m), 684 (m), 628 (w).
MS (EI, 70 eV): *m/z* (%) = 365 (14), 364 (40), 363 (100), 350 (26), 349 (74), 348 (99), 332 (5), 215 (5), 174 (6), 115 (12).
HRMS (EI): calcd. for $C_{21}H_{21}NO^{32}S^{28}Si$: 363.1113, found: 363.1099.
mp (°C): 141-143.

4-{3-[(4-Chlorophenyl)thio]-1-benzofuran-2-yl}benzonitrile (3f)

According to **TP4** sulfoxide **3f** was prepared from sulfoxide **2f** (414 mg, 1.00 mmol), *i*PrMgCl·LiCl (1.16 mL, 1.10 mmol, 0.95 M in THF, -50 °C, 5 min), $Pd(PPh_3)_4$ (23 mg, 0.02 mmol) and 4-iodobenzonitrile (183 mg, 0.80 mmol) in 1 h at 25 °C. Flash

chromatographical purification (pentane / diethyl ether = 20:1, silica gel) yielded **3f** as a white solid (244 mg, 84%).

^{1}H-NMR (C_6D_6, 400 MHz, Me_4Si): δ (ppm) = 6.72-6.76 (m, 2 H), 6.79-6.82 (m, 2 H), 6.95-6.99 (m, 3 H), 7.03-7.08 (m, 1 H), 7.30-7.32 (m, 1 H), 7.37-7.40 (m, 1 H), 7.89-7.92 (m, 2 H).
^{13}C-NMR (C_6D_6, 100 MHz, Me_4Si): δ (ppm) = 107.8, 111.7 (CH), 113.2, 118.4, 120.9 (CH), 124.3 (CH), 126.7 (CH), 127.4 (CH), 128.2 (CH), 129.6 (CH), 130.5, 132.2 (CH), 132.3, 133.1, 134.0, 154.5, 155.2.
IR (ATR): $\tilde{\nu}$ / cm^{-1} = 2924 (w), 2224 (m), 1734 (w), 1610 (w), 1574 (w), 1492 (w), 1474 (s), 1450 (m), 1410 (m), 1390 (w), 1340 (w), 1250 (w), 1196 (m), 1084 (vs), 1008 (m), 890 (w), 836 (m), 818 (m), 802 (m), 750 (vs), 680 (w).
MS (EI, 70 eV): *m/z* (%) = 364 (9), 363 (38), 362 (24), 361 (100), 293 (13), 259 (17), 230 (13), 222 (10), 190 (19), 139 (8).
HRMS (EI): calcd. for $C_{21}H_{12}{}^{35}ClNO^{32}S$: 361.0328, found: 361.0323.
mp (°C): 190-192.

3-(4-Fluorophenyl)-1-benzofuran-2-carbaldehyde (3g)

According to **TP5** sulfoxide **3g** was prepared from sulfoxide **2g** (411 mg, 1.00 mmol), *i*PrMgCl·LiCl (1.0 mL, 1.10 mmol, 1.11 M in THF, -50 °C, 5 min) and DMF (58 mg, 0.80 mmol) in 1 h at 25 °C. Flash chromatographical purification (pentane / diethyl ether = 20:1, silica gel) yielded **3g** as a yellow solid (174 mg, 91%).

^{1}H-NMR (C_6D_6, 400 MHz, Me_4Si): δ (ppm) = 6.74-6.80 (m, 2 H), 6.90-6.06 (m, 3 H), 7.05-7.10 (m, 1 H), 7.24-7.29 (m, 2 H), 9.58 (s, 1 H).
^{13}C-NMR (C_6D_6, 100 MHz, Me_4Si): δ (ppm) = 112.8 (CH), 116.1 (d, J = 21.8 Hz, CH), 122.3 (CH), 124.1 (CH), 125.6 (d, J = 3.50

Hz), 127.4 (d, *J* = 0.78 Hz), 129.3 (CH), 131.4, 131.9 (d, *J* = 8.17 Hz, CH) 148.1, 155.5, 163.5 (d, *J* = 248.9 Hz, CF), 178.7 (CH).

IR (ATR): $\tilde{\nu}$ / cm^{-1} = 2876 (w), 1668 (s), 1608 (m), 1562 (m), 1506 (s), 1450 (m), 1394 (w), 1358 (m), 1332 (m), 1288 (m), 1274 (m), 1230 (m), 1210 (s), 1160 (s), 1100 (m), 1012 (m), 980 (m), 866 (s), 840 (s), 814 (m), 750 (vs), 648 (m), 638 (m).

MS (EI, 70 eV): *m/z* (%) = 241 (12), 240 (83), 239 (100), 184 (9), 183 (52), 182 (7), 181 (9), 120 (9), 92 (8), 57 (8).

HRMS (EI): calcd. for $C_{15}H_9{}^{19}FO_2$: 240.0587, found: 240.0582.

mp (°C): 145-146.

Ethyl 4-[2-(4-chlorophenyl)-5-iodo-3-furyl]benzoate

A dry and argon-flushed *Schlenk*-flask, equipped with a stirring bar and a septum, was charged with a solution of ethyl 4-[2-(4-chlorophenyl)-5-(trimethylsilyl)-3-furyl] (**3a**; 2.59 g, 6.50 mmol) in CH_3CN (33 mL). The reaction mixture was cooled to 0 °C and ICl (1.57 g, 9.75 mmol) was added dropwise. The reaction mixture was allowed to warm to 25 °C and stirred for additional 1 h. Then the reaction mixture was quenched with a sat. aq. NH_4Cl-solution (10 mL) and a sat. aq $Na_2S_2O_3$ (10 mL) and extracted three times with CH_2Cl_2 (50 mL). The combined organic layers were dried ($MgSO_4$) and after filtration, the solvent was removed under reduced pressure. Flash chromatographical purification (pentane / diethyl ether = 25:1, silica gel) yielded ethyl 4-[2-(4-chlorophenyl)-5-iodo-3-furyl]benzoate as a colourless solid (2.31 g, 79% yield).

^{1}H-NMR ($CDCl_3$, 300 MHz, Me_4Si): δ (ppm) = 1.40 (t, *J* = 7.15 Hz, 3 H), 4.39 (q, *J* = 7.15 Hz, 2 H), 6.70 (s, 1 H), 7.22–7.26 (m, 2 H), 7.35–7.42 (m, 4 H), 8.00–8.04 (m, 2 H).

^{13}C-NMR ($CDCl_3$, 75 MHz, Me_4Si): δ (ppm) = 14.3 (CH_3), 61.0 (CH_2), 88.4, 123.8 (CH), 124.5, 127.4 (CH), 128.1, 128.2 (CH), 128.7 (CH), 129.6, 130.0 (CH), 134.1, 137.2, 153.5, 166.1.
IR (ATR): $\tilde{\nu}$ / cm^{-1} = 3062 (w), 2986 (w), 2942 (w), 2908 (w), 1716 (vs), 1674 (w), 1652 (w), 1644 (w), 1634 (w), 1610 (s), 1568 (w), 1562 (w), 1504 (m), 1476 (m), 1446 (m), 1412 (m), 1392 (m), 1360 (m), 1310 (m), 1292 (s), 1272 (vs), 1252 (s), 1184 (m), 1156 (w), 1126 (s), 1104 (vs), 1094 (s), 1082 (s), 1038 (m), 1020 (s), 1010 (s), 966 (m), 950 (m), 924 (s), 868 (m), 850 (s), 836 (vs), 818 (s), 806 (s), 768 (vs), 740 (s), 718 (m), 704 (s), 684 (s), 638 (m), 630 (m), 614 (m).
MS (EI, 70 eV): *m/z* (%) = 454 (17), 453 (12), 452 (54), 297 (22), 269 (16), 189 (16), 174 (15), 140 (33), 139 (100), 111 (17), 43 (15).
HRMS (EI): calcd. for $C_{19}H_{14}O_3{}^{35}Cl^{127}I$: 451.9676, found: 451.9664.
mp (°C): 97–98.

Ethyl 5-(4-chlorophenyl)-4-[4-(ethoxycarbonyl)phenyl]-2-furoate (5)

A dry and argon-flushed *Schlenk*-flask, equipped with a stirring bar and a septum, was charged with a solution of ethyl 4-[2-(4-chlorophenyl)-5-iodo-3-furyl]benzoate (814 mg, 1.80 mmol) in THF (3 mL). The reaction mixture was cooled to -40 °C, *i*PrMgCl·LiCl (1.36 mL, 1.98 mmol, 1.46 M in THF) was added dropwise and the reaction mixture stirred at that temperature for 20 min. Then, ethyl cyanoformate (232 mg, 2.34 mmol,) was added and the reaction mixture was allowed to warm to 25 °C. Then the reaction mixture was quenched with a sat. aq. NH_4Cl-solution (20 mL) and extracted three times with ethyl acetate (30 mL). The combined organic layers were dried ($MgSO_4$) and after filtration, the solvent was removed under reduced pressure. Flash chromatographical purification (pentane /

diethyl ether = 2:1, silica gel) yielded **5** as a colourless solid (614 mg, 86% yield).

^{1}H-NMR ($CDCl_3$, 300 MHz, Me_4Si): δ (ppm) = 1.33–1.39 (m, 6 H), 4.32–4.39 (m, 4 H), 7.22–7.26 (m, 3 H), 7.38–7.48 (m, 4), 7.99–8.03 (m, 2 H).
^{13}C-NMR ($CDCl_3$, 75 MHz, Me_4Si): δ (ppm) = 14.3 (2 CH_3), 61.1 (2 CH_2), 120.7 (CH), 123.5, 127.9, 128.3 (CH), 128.4 (CH), 128.9 (CH), 130.1 (CH), 135.1, 137.2, 143.6, 151.4, 158.5, 166.1 (2 C_q).
IR (ATR): $\tilde{\nu}$ / cm^{-1} = 2986 (w), 2964 (w), 2942 (w), 2904 (w), 1712 (vs), 1614 (w), 1590 (w), 1562 (w), 1536 (w), 1524 (w), 1508 (w), 1474 (m), 1464 (m), 1446 (w), 1414 (w), 1402 (m), 1392 (m), 1366 (m), 1322 (s), 1304 (m), 1288 (m), 1268 (vs), 1252 (s), 1206 (s), 1174 (vs), 1124 (s), 1110 (vs), 1092 (vs), 1050 (m), 1016 (s), 1008 (s), 970 (m), 954 (m), 870 (m), 860 (m), 848 (m), 836 (s), 774 (s), 766 (s), 740 (m), 726 (s), 706 (s), 694 (s), 636 (m), 614 (m).
MS (EI, 70 eV): *m/z* (%) = 400 (38), 399 (28), 398 (100), 370 (18), 353 (27), 325 (15), 269 (16), 189 (29), 57 (12), 44 (37).
HRMS (EI): calcd. for $C_{22}H_{19}O_5{}^{35}Cl$: 398.0921, found: 398.0930.
mp (°C): 119–120.

Ethyl 5-(4-chlorophenyl)-3-(3,3-dimethylbutanoyl)-4-[4-(ethoxycarbonyl)phenyl]-2-furoate (6)

A dry and argon-flushed *Schlenk*-flask, equipped with a stirring bar and a septum, was charged with a solution of the furan **5** (359 mg, 0.90 mmol) in THF (2 mL). The reaction mixture was cooled to –40 °C and $TMP_2Mg\cdot LiCl$ (2.45 mL, 1.35 mmol, 0.55 M in THF) was added dropwise. The reaction mixture was stirred for 25 min and then $ZnCl_2$ (1.45 mL, 1.35 mmol, 1.0 M in THF) was added, followed by CuCN·2LiCl (1.35 mL, 1.35

mmol, 1.0 M in THF). Then 3,3-dimethylbutanoyl chloride (363 mg, 0.40 mL, 2.70 mmol,) was added dropwise and the reaction mixture was allowed to warm to 25 °C. Then the reaction mixture was quenched with a sat. aq. NH_4Cl-solution (10 mL) and extracted three times with diethylether (30 mL). The combined organic layers were dried ($MgSO_4$) and after filtration the solvent was removed under reduced pressure. Flash chromatographical purification (pentane / diethyl ether = 6:1, silica gel) yielded **6** as a colourless oil (414 mg, 93% yield).

^{1}H-NMR ($CDCl_3$, 600 MHz, Me_4Si): δ (ppm) = 0.86 (s, 9 H), 1.37 (t, J = 7.15 Hz, 3 H), 1.40 (t, J = 7.15 Hz, 3 H), 2.50 (s, 2 H), 4.38 (q, J = 7.15 Hz, 2 H), 4.39 (q, J = 7.15 Hz, 2 H), 7.23–7.25 (m, 2 H), 7.36–7.38 (m, 4 H), 8.05–8.06 (m, 2 H).
^{13}C-NMR ($CDCl_3$, 150 MHz, Me_4Si): δ (ppm) = 14.3 (CH_3), 14.3 (CH_3), 29.3 (CH_3), 30.7, 56.9 (CH_2), 61.2 (CH_2), 61.4 (CH_2), 121.6, 127.1, 128.1 (CH), 128.9 (CH), 129.9 (CH), 130.1 (CH), 130.6, 135.4, 135.5, 136.5, 138.6, 151.1, 157.9, 166.1, 199.4.
IR (ATR): $\tilde{\nu}$ / cm^{-1} = 1714 (vs), 1478 (m), 1404 (m), 1366 (s), 1324 (m), 1276 (s), 1222 (m), 1176 (s), 1154 (m), 1130 (s), 1110 (s), 1104 (s), 1092 (s), 1074 (m), 1014 (s), 958 (m), 866 (m), 842 (s), 824 (m), 794 (m), 782 (m), 772 (m), 744 (s), 732 (m), 714 (s), 700 (m), 654 (m).
MS (EI, 70 eV): *m/z* (%) = 498 (31), 497 (25), 496 (100), 451 (15), 440 (15), 439 (16), 427 (21), 425 (69), 367 (21), 321 (16), 307 (11), 138 (15).
HRMS (EI): calcd. for $C_{28}H_{29}O_6{}^{35}Cl$: 496.1653, found: 496.1645.

4-{3-(3-Methoxyphenyl)-5-[(trimethylsilyl)ethynyl]-2-thienyl}benzonitrile (7)

A dry and argon-flushed *Schlenk*-flask, equipped with a stirring bar and a septum, was charged with a solution of 4-[3-(3-methoxyphenyl)-5-(trimethylsilyl)-2-thienyl]benzonitrile

(**3e**; 3.27 g, 9.00 mmol) in CH_3CN (60 mL). The reaction mixture was cooled to 0 °C and ICl (2.19 g, 13.5 mmol) was added dropwise. The reaction mixture was allowed to warm to 25 °C and stirred for additional 1 h. Then the reaction mixture was quenched with a sat. aq. NH_4Cl-solution (20 mL) and a sat. aq $Na_2S_2O_3$ (20 mL) and extracted three times with ethyl acetate (50 mL). The combined organic layers were dried ($MgSO_4$) and after filtration, the solvent was removed under reduced pressure. The product was used for the next step without further purification.

A dry and argon-flushed *Schlenk*-flask, equipped with a stirring bar and a septum, was charged with a solution of 4-[5-iodo-3-(3-methoxyphenyl)-2-thienyl]benzonitrile (1.98 g, 4.50 mmol) in THF (6 mL). In a second dry and argon-flushed *Schlenk*-flask, equipped with a stirring bar, trimethylsilylacetylene (884 mg, 1.28 mL, 9.00 mmol) was added slowly to *i*PrMgCl·LiCl (5.66 mL, 9.00 mmol, 1.59 M in THF). After cessation of gas evolution the reaction mixture was heated to 60 °C for 5 min. After cooling to 25 °C a zinc chloride solution (9.0 mL, 9.00 mmol, 1.0 M in THF) was added slowly. The resulting zinc reagent was transferred to the crude iodide, $Pd(PPh_3)_4$ (208 mg, 0.18 mmol) was added and the reaction mixture was stirred at 50 °C for 2 h. Then the reaction mixture was quenched with a sat. aq. NH_4Cl-solution (30 mL) and extracted three times with ethyl acetate (50 mL). The combined organic layers were dried ($MgSO_4$) and after filtration, the solvent was removed under reduced pressure. Flash chromatographical purification (pentane / diethyl ether = 9:1, silica gel) yielded **7** as a colourless solid (1.53 g, 88% yield).

^{1}H-NMR (C_6D_6, 400 MHz, Me_4Si): δ (ppm) = 0.23 (s, 9 H), 3.19 (s, 3 H), 6.60-6.62 (m, 1 H), 6.64-6.66 (m, 2 H), 6.69-6.72 (m, 2 H), 6.82-6.85 (m, 2 H), 6.92-6.96 (m, 1 H), 7.19 (s, 1 H).

^{13}C-NMR (C_6D_6, 100 MHz, Me_4Si): δ (ppm) = -0.2 (CH_3), 54.7 (CH_3), 97.6, 101.2, 111.8, 113.7 (CH), 114.8 (CH), 118.4, 121.5 (CH), 123.8, 129.5 (CH), 129.9 (CH), 132.1 (CH), 136.5, 136.7 (CH), 137.6, 138.1, 139.9, 160.3.

IR (ATR): $\tilde{\nu}$ / cm^{-1} = 2956 (w), 2226 (w), 2142 (m), 1742 (m), 1602 (m), 1576 (m), 1482 (m), 1418 (m), 1374 (w), 1284 (w), 1236 (m), 1178 (w), 1148 (w), 1054 (w), 856 (s), 838 (vs), 792 (m), 774 (m), 696 (w), 630 (w).

MS (EI, 70 eV): *m/z* (%) = 389 (7), 388 (17), 387 (63), 374 (9), 373 (26), 372 (100), 356 (5), 328 (4), 186 (6), 185 (4).

HRMS (EI): calcd. for $C_{23}H_{21}NO^{32}S^{28}Si$: 387.1113, found: 387.1115.

mp (°C): 138-139.

4-{3-(3-Methoxyphenyl)-4-{4-[(triisopropylsilyl)oxy]phenyl}-5-[(trimethylsilyl)ethynyl]-2-thienyl}benzonitrile (8)

A dry and argon-flushed *Schlenk*-flask, equipped with a stirring bar and a septum, was charged with a solution of the thiophene **7** (387 mg, 1.00 mmol) in THF (2 mL). The reaction mixture was cooled to -20 °C and $TMP_2Mg\cdot LiCl$ (2.50 mL, 1.50 mmol, 0.60 M in THF) was added dropwise. The reaction mixture was stirred at this temperature for 12 h then $ZnCl_2$ (1.50 mL, 1.50 mmol, 1.0 M in THF) was added and the reaction mixture stirred at -20 °C for 30 minutes. (4-Iodo-phenoxy)-triisopropylsilane 541 mg, 1.50 mmol), and $Pd(PPh_3)_4$ (23 mg, 0.02 mmol) was added and the reaction stirred at 25 °C for 3 h. Then the reaction mixture was quenched with a sat. aq. NH_4Cl-solution (10 mL) and extracted three times with ethyl acetate (30 mL). The combined organic layers were dried ($MgSO_4$) and after filtration the solvent was removed under reduced pressure. Flash chromatographical purification (pentane / diethyl ether = 20:1, silica gel) yielded **8** as a yellow solid (476 mg, 75% yield).

^{1}H-NMR (C_6D_6, 400 MHz, Me_4Si): δ (ppm) = 0.24 (s, 9 H), 1.06-1.08 (m, 18 H), 1.11-1.18 (m, 3 H), 3.20 (s, 3 H), 6.66-6.70 (m, 2 H), 6.74-6.76 (m, 1 H), 6.86-6.90 (m, 3 H), 6.94-6.98 (m, 2 H), 7.22-7.26 (m, 4 H).

^{13}C-NMR (C_6D_6, 100 MHz, Me_4Si): δ (ppm) = -0.2 (CH_3), 12.9 (CH), 18.0 (CH_3), 54.7 (CH_3), 97.8, 101.2, 110.6, 113.7 (CH), 114.9 (CH), 118.6, 120.4 (CH), 121.7 (CH), 123.8, 130.0, 130.3 (CH), 130.9 (CH), 134.1 (CH), 136.4 (CH), 136.9, 137.7, 138.3, 140.1, 145.2, 157.2, 160.4.

IR (ATR): $\tilde{\nu}$ / cm^{-1} = 2944 (s), 2892 (m), 2866 (s), 2222 (m), 2146 (m), 1600 (s), 1512 (s), 1486 (s), 1462 (m), 1368 (w), 1266 (s), 1248 (s), 1174 (m), 1042 (w), 996 (w), 908 (m), 882 (m), 838 (vs), 786 (m), 740 (m), 674 (m).

MS (EI, 70 eV): *m/z* (%) = 635 (37), 594 (27), 593 (48), 592 (100), 564 (45), 536 (43), 262 (23), 261 (38), 260 (82), 253 (42).

HRMS (EI): calcd. for $C_{38}H_{45}NO_2{}^{32}S^{28}Si_2$: 635.2710, found: 635.2711.

mp (°C): 67-69.